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Supporting Information

Exploiting Imine Photochemistry for Masked N-Centered Radical Reactivity**

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Supporting Information

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I. General Methods

Unless otherwise noted, all reactions were run under a nitrogen atmosphere in flame-dried glassware. Reactions were stirred using Teflon-coated magnetic stir bars. Reactions were monitored by thin layer chromatography (TLC) using glass-backed plates pre-coated with 230–400 mesh silica gel (250 μm thickness) with fluorescent indicator F254, available from EMD Millipore (cat. #: 1.05715.0001). Plates were visualized by treatment with UV, acidic *p*-anisaldehyde stain, $KMnO_4$ stain, or aqueous ceric ammonium molybdate (Hanessian's stain; CAM) with gentle heating. Products were purified by flash column chromatography using the solvent systems indicated. Silica gel was purchased from SiliCycle, specifically using SiliaFlash P60, 40-63 μm, 230-400 mesh (cat. #: R12030B). Basic alumina was purchased from Acros, basic, Brockmann I, 50-200 μm, 60 Å.

Organic solvents (acetonitrile, dichloromethane, diethyl ether, dimethylformamide, dimethyl sulfoxide, methanol, tetrahydrofuran, toluene) and amine bases (triethylamine, pyridine, N,N-diisopropylethylamine, and diisopropylamine) were purified prior to use by the method of Grubbs and co-workers[1] using a Phoenix Solvent Drying System (for organic solvents, available from JC-Meyer Solvent Systems) or PureSolv Micro amine drying columns (for amine bases, available from Innovative Technology/Inert) under positive argon pressure; all solvents were supplied by Fisher Scientific. Titanium isopropoxide was obtained from Oakwood Chemical, distilled immediately upon receipt, and stored in a clean sure-seal bottle under inert atmosphere. Unless otherwise noted, all other reagents were purchased from Sigma-Aldrich, stored as recommended by the supplier, and used without any additional purification.

NMR spectra were measured on a Varian INOVA 500 (^{1}H at 500 MHz), a Varian VNMR 500 (^{1}H at 500 MHz, ^{13}C at 126 MHz), or a Varian VNMR 700 MHz (^{1}H at 700 MHz, ^{13}C at 176 MHz) magnetic resonance spectrometer, as noted. ^{1}H chemical shifts are reported relative to the residual solvent peak (chloroform = 7.26 ppm; benzene = 7.16 ppm)[2] as follows: chemical shift (δ) (multiplicity [s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, hept = heptet, br = broad, *app.* = apparent], integration, coupling constant(s) in Hz, proton ID [when available, designated by carbon number]). Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. Proton assignments were made via 2D spectroscopy (COSY, HSQC, HMBC, and/or NOESY) and/or analogy to related systems. ^{13}C chemical shifts are reported relative to the residual deuterated solvent ^{13}C signals ($CDCl_3$ = 77.16 ppm, C_6D_6 = 128.1 ppm).[2] Infrared spectra were recorded on either a Perkin-Elmer Spectrum BX or a Nicolet iS50 FT-IR spectrophotometer using an ATR mount with a ZnSe crystal and are reported in wavenumbers (cm^{-1}). Optical rotation data were obtained using a JASCO P-2000 Polarimeter and are reported as $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\boldsymbol{T}}$ (*c* = grams/100 mL), where D indicates the sodium D line (589 nm) and T indicates temperature (all optical rotation values were obtained at ambient operating temperature, ca. 22-28 °C). High resolution mass spectra were obtained using a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer using electrospray ionization (ESI), positive ion mode, or electron impact ionization (EI); we thank Dr. James Windak and Dr. Paul Lennon at the University of Michigan Department of Chemistry instrumentation facility for conducting these experiments.

[1] Pangborn, A.; Giardello, M.; Grubbs, R.; Rosen, R.; Timmers, F. *Organometallics* **1996**, *15*, 1518-1520.
[2] Gottlieb, H.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512-7515.

II. Equipment for Batch and Flow Photochemistry

The following presents the specific equipment used to perform the methodology reported in the associated manuscript. Detailed procedures for the optimization of the photochemical methodology are provided in Section III.

II.A. Lighting and Safety Materials

The standard photochemical procedure utilizes a 390 nm LED lamp available from Kessil (PR160-390nm; http://www.kessil.com/photoredox/Products.php). Alternative wavelengths tested were chosen from the remaining Kessil PR160 series. The 300 nm trial was performed in a Luzchem LZC-ORG photoreactor operating Rayonet RPR-3000 light bulbs. Reactions were cooled with a standard fan (Westpointe, 4 inch personal fan). Reactions were performed behind plastic guards (provided by Ann Arbor Plastics) wrapped in orange film to provide eye protection during prolonged irradiation (film purchased from UV Process Supply, Amber UV filter film; http://www.uvps.com/product.asp?code=FILTER+++L); additional eye protection came in the form of orange safety googles from Honeywell (Uvex Skyper SCT-orange; https://www.uvex.us/en/products/general%20purpose%20eyewear/uvex-skyper).[3]

II.B. Batch Apparatus

Unless otherwise noted, all photochemical reactions were performed in batch in 2 dram vials. The apparatus used for each reaction in batch is shown in Figure S1. The PR160-390nm Kessil lamp was clamped such that the reaction mixture lies directly in the center of the beam path. The lamp was tilted at a 60° angle (with respect to the stir plate), positioning the center of the LED lamp 2 cm from the side of the vial. The cooling fan was suspended 5 cm above the top of the reaction vial, centered on the vial. After placing the orange-wrapped shield in front of the setup, the light was turned on, and the system was covered in aluminum foil.

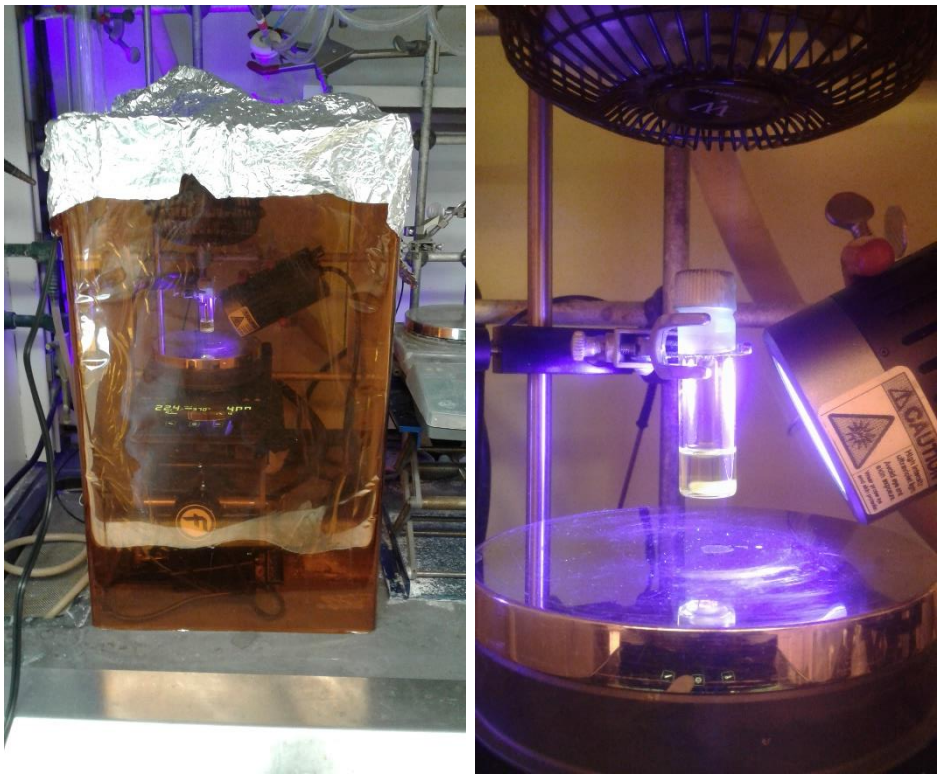


Figure S1. Batch Processing Equipment

Left: Full apparatus in use; Right: Zoom in on lamp orientation while in use (Kessil PR160-390nm pictured).

II.C. Flow Apparatus

The same 390 nm LED lamps were used for the flow photochemistry. In this setup, two lamps were placed on either side of the "reaction vessel," which consisted of Teflon PFA tubing (obtained from IDEX Health & Science, Part No.: 1514L). Tubing employed prior to the pump was 0.76 mm inner diameter and 0.91 mm outer diameter, while the reaction vessel itself consisted of 0.062" inner diameter, 0.125" outer diameter tubing. Material was pumped through the system with an IPC-04 Ismatec peristaltic pump (Model No.: ISM930C, 4 channel pump) with a range of 32.2 μL/min up to 3.2 mL/min. Calibration of the apparatus was achieved by flowing

[3] All web sources accessed on August 9th, 2018.

through a known volume of solvent; this also allows one to calculate the volume of the reaction vessel, based on the time needed for solvent to pass through the system as a given flow rate. Each calibration was repeated three times and averaged, and both the flow rate and reaction vessel volume calculations proved stable over time. The reaction vessel was determined to have a 3.8 mL capacity.

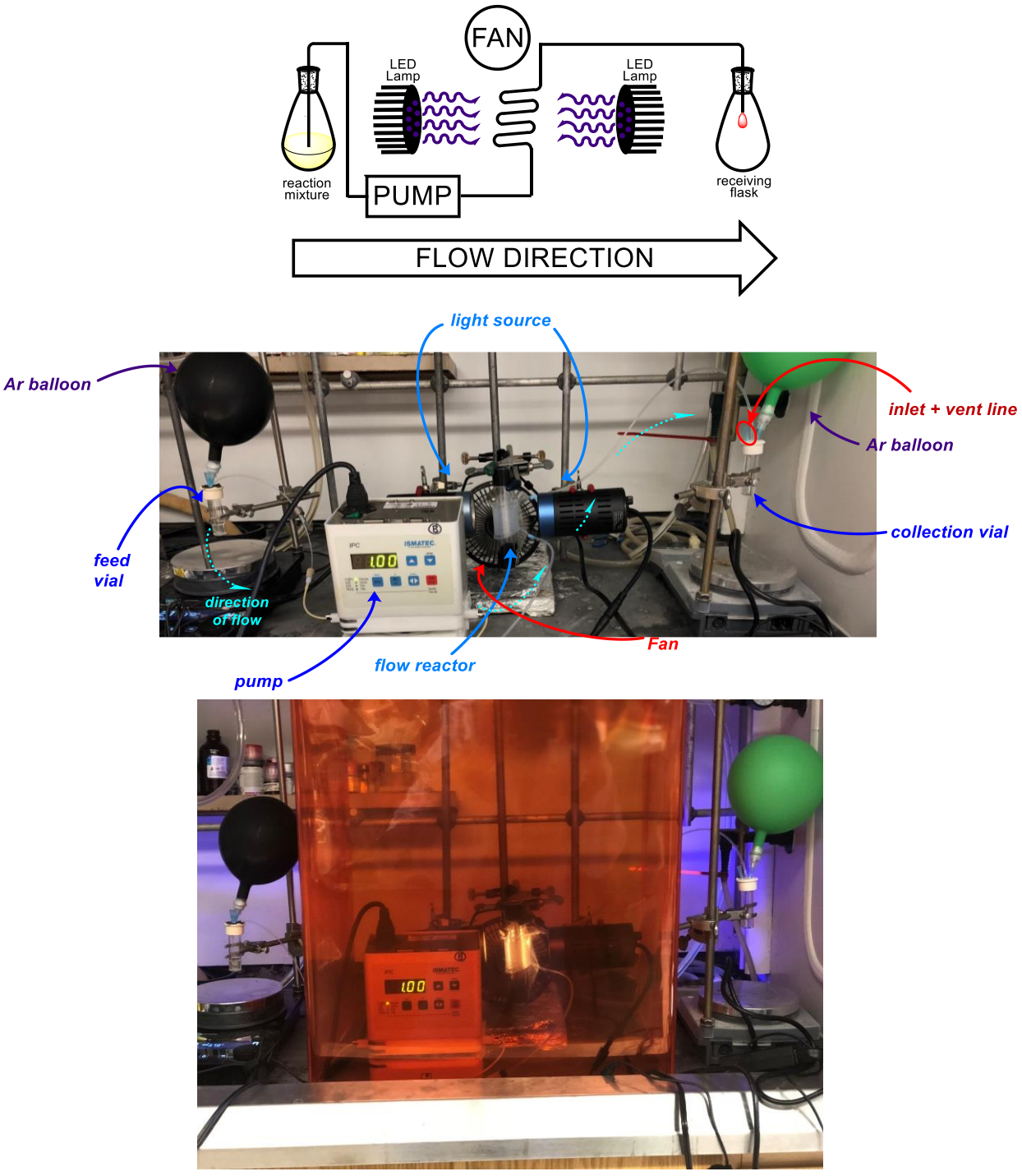


Figure S2. Full Apparatus
Top: Generic schematic of flow apparatus; Middle: Full apparatus with key parts labeled; Bottom: Apparatus in use (note: pump currently displaying 1.00 mL/min flow rate; reactions actually ran at 38.2 µL/min; calibration of this instrument determined that the 38.2 µL/min setting was equivalent to 47.5 µL/min).

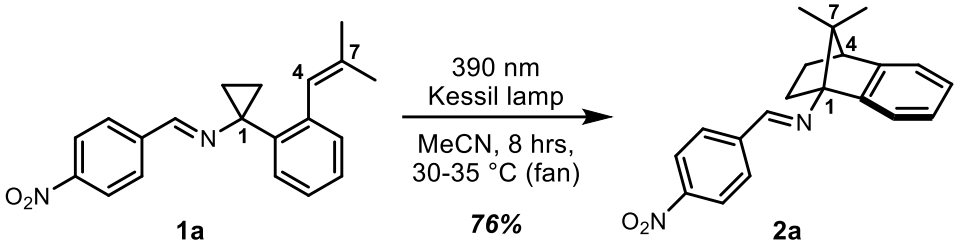
The starting material was drawn into the flow setup using tubing threaded through the center of a rubber septum (reaction mixtures were degassed via freeze-pump-thaw (3x), flushed with Ar, then the cap was rapidly replaced with tubing-threaded septum prior to re-flushing the headspace). Beyond the peristaltic pump, the tubing was wrapped around two 18 x 150 mm borosilicate test tubes and secured in place with tape. The reaction vessel itself was suspended vertically with the flow inlet at the bottom. Lamps were positioned

4 cm on either side of the reaction vessel. A fan was placed in between the two lamps 8 cm away from the vessel to cool the system. After the zone of irradiation, the end tubing was threaded through another rubber septum into a dry vial under inert atmosphere; this vial was under a balloon of Ar with a 25 gauge vent line in place to account for the pressure derived from the pump. The orange-wrapped shield was placed around the lamp/vessel portion of the apparatus; both the initial vial and the end vial were held outside the shield to prevent unwanted irradiation.

III. Reaction Optimization, Mechanistic Investigations, and Evaluation in Flow

III.A. Optimization of the Photochemical Conversion of Cyclopropylimines toward 1-Aminonorbornanes in Batch

The optimization of the title reaction was performed with benzo-fused, 7,7-dimethyl cyclopropylimine **1a** on ~200 μmol scale in the fashion described below. The results of these trials are summarized in Figure 2 in the text.



Procedure for 1-aminoNB 2a

The following procedure can be generalized to all formal [3+2] cycloadditions toward 1-aminoNBs:

In a dry vial under inert atmosphere, cyclopropylimine **1a** (65.3 mg, 204 μmol) was dissolved in 2.1 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 8 hrs, using the setup described in Section II.B (temperature maintained between 30-35 °C with a fan). Reaction mixture was dark red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (15% ethyl acetate:hexanes; loaded residue with PhMe). Obtained 49.8 mg (76.3% yield) of a light yellow solid.[4,5]

Additional Trials (entries from Figure 4)

300 nm light (entry 2)

Following the general procedure outlined above, 45.5 mg of aminoCP **1a** (151 μmol) in 1.6 mL dry MeCN was degassed and irradiated with Rayonet RPR-3000 light bulbs (as described above; max emission: 280-315 nm) for 12 hrs in a quartz tube. ^{1}H NMR analysis of the crude mixture revealed an estimated 1-2%[6] of 1-aminoNB **2a**. Isolation following above procedure afforded 44.7 mg of returned starting material (98.2% recovery).

370 nm light (entry 3)

Following the general procedure outlined above, 62.0 mg of aminoCP **1a** (194 μmol) in 2.1 mL dry MeCN was degassed and irradiated with a Kessil PR160-370nm LED lamp. ^{1}H NMR analysis of the crude mixture revealed a 0.48:1 mix of starting material to desired product. Isolation following above procedure afforded 50.6 mg of a mixture that consisted of 16.8 mg of recovered cyclopropylimine **1a** (27.1% recovery) and 31.3 mg of 1-aminoNB **2a** (50.5% yield) based on ^{1}H NMR analysis.

440 nm light (entry 4)

Following the general procedure outlined above, 64.0 mg of aminoCP **1a** (200 μmol) in 2.0 mL dry MeCN was degassed and irradiated with a Kessil PR160-440nm LED lamp. ^{1}H NMR analysis of the crude mixture revealed a 5.0:1 mix of starting material to desired product. Isolation following above procedure afforded a total of 48.1 mg of a mixture that consisted of 40.1 mg of recovered cyclopropylimine **1a** (62.7% recovery) and 8.0 mg of 1-aminoNB **2a** (12.5% yield) based on ^{1}H NMR analysis.

No light control (entry 5)

Following the general procedure outlined above, 76.0 mg of aminoCP **1a** (237 μmol) in 2.4 mL dry MeCN was degassed and the vial was wrapped entirely in black electrical tape before irradiating with a Kessil PR160-390nm LED lamp for 12 hrs using the standard

[4] 1-AminoNB **2a** could be re-crystallized from ether:hexanes to reveal a white solid (no discernable difference in NMR spectrum).

[5] Note: An analogous trial on 78.5 mg (245 μmol) cyclopropylimine **1a** yielded 62.4 mg of 1-aminoNB **2a** (79.5% yield) after 12 hrs of irradiation with 390 nm light. In general, altering the scale of the reaction does not have a large impact on performance as long as the time is adjusted accordingly and the reaction volume can be contained within a vial (one should assume the time will need to scaled exponentially, thus much larger scales will clearly suffer from exceptionally long reaction times, hence the evaluation in flow).

[6] This estimate is based on the C7-methyl peaks, as these are the most cleanly differentiated. In this sample, the desired product C7-Me's were only slightly resolved above baseline (the technically correct quantification would be <5% yield, but the 1-2% estimate was considered more instructive).

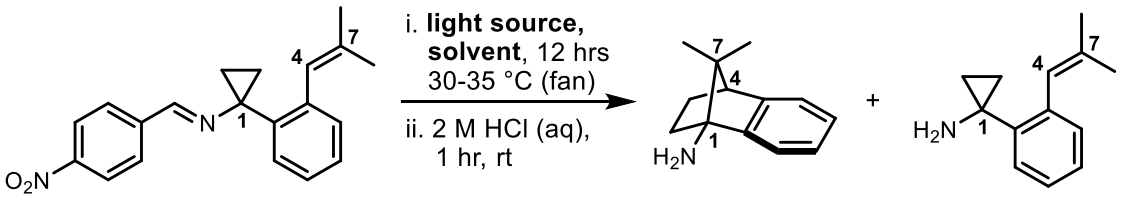
setup. Isolation following above procedure afforded 76 mg of recovered cyclopropylimine **1a** (>99% recovery).

Thermal reactivity control (entry 6)

Following the general procedure outlined above, 54.1 mg of aminoCP **1a** (160 μmol) in 1.6 mL dry MeCN was degassed and heated to 120 °C for 12 hrs (light excluded by placing aluminum foil around stir plate). Isolation following above procedure afforded a total of 50.7 mg of recovered cyclopropylimine **1a** (98.6% recovery).

One-pot Manipulations

The above trials optimized for the conversion of one Schiff base system (cyclopropylimine **1a**) to another (1-aminoNB **2a**). Alternative strategies that couple the condensation and/or hydrolysis of the imine with the photochemical step were also explored briefly. This work is summarized in Figures S3:



Trial	Light Source	Solvent	NMR Ratio[a] S1 : S2	Isolated Yield S1	Isolated Yield S2
1	violet LEDs (~410 nm)[b]	DCE	*79* : *21*	***26%***	***8%***
2	violet LEDs (~410 nm)	EtOAc	*49* : *51*	***17%***	***19%***
3	violet LEDs (~410 nm)	MeCN	*78* : *22*	***30%***	***22%***
4	**390 nm Kessil lamp**	MeCN	*100* : *0*	***41%***	**--**
5[c]	violet LEDs (~410 nm)	MeCN	*97* : *3*	**--**	**--**

Figure S3. Multi-step, one-pot variations on the photoauxiliary methodology

All trials were run on 200 μmol scale and isolated via analogous methods to those presented below. [a]Ratio of **S1**:**S2** determined based on C7-Me resonances; [b]Violet LED strips were obtained from Creative Lighting solutions (employed four 4.4 W strips for the allotted time); [c]Trial 5 was run starting with aminocyclopropane **S2** with the addition of 1.2 equivalents of 4-nitrobenzaldehyde (no isolation attempted).

These efforts clearly demonstrate the feasibility of performing the Schiff base manipulations with the photochemical strategy itself, while also serving as preliminary evaluations of solvent, time, and light source. As this program advances forward, further exploration of these multi-step procedures will be undertaken, especially as it pertains to continuous flow systems; these efforts will be reported in due course. Of note, aminocyclopropane **S2** was prepared via a separate route from cyclopropylimine **1a**, shown below in Figure S4. While this route provided sufficient material for initial studies, the length and irreproducibility of the Boc deprotection (decomposition via an unknown mechanism occasionally led to drastic yield losses) led us to pursue a separate route that ultimately was adopted for all the cyclopropylimine substrates (see pg. S15 for procedures en route to cyclopropylimine **1a**).

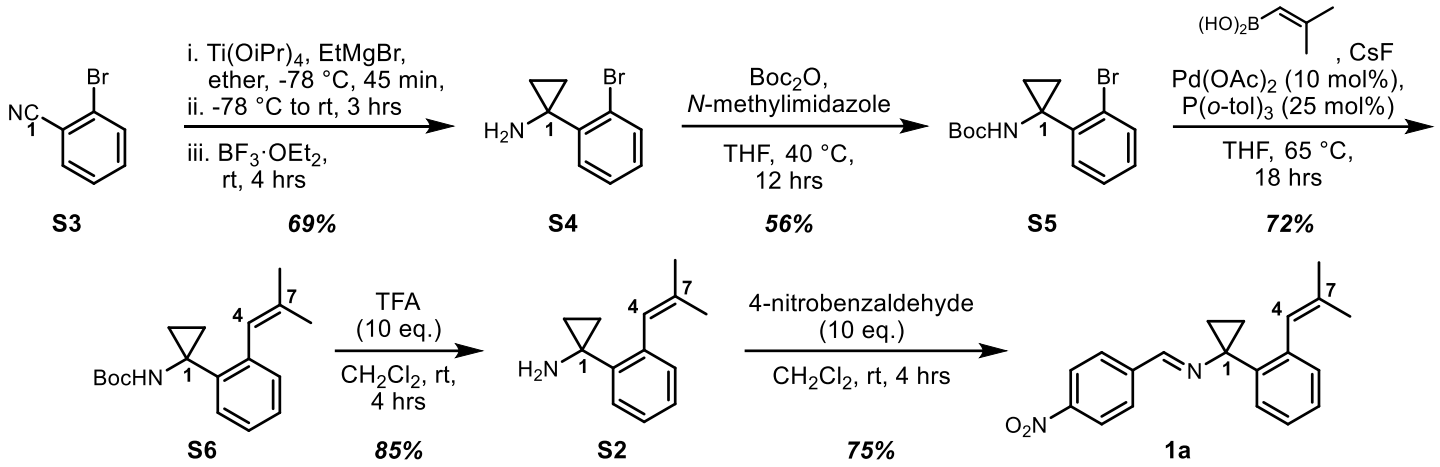
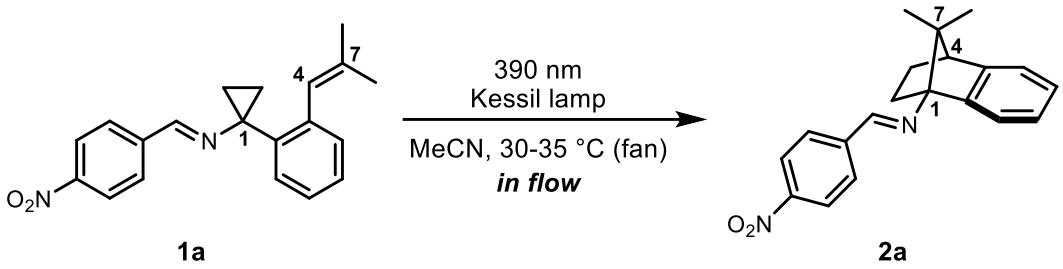


Figure S4. Original synthesis of cyclopropylimine **1a** and aminocyclopropane **S2**

III.B. Optimization and Execution of Photochemical Methodology in Continuous Flow

The title reaction was optimized for performance in continuous flow using the apparatus detailed in Section III.C. Multiple trials on ~20 mg-scale were run to identify the appropriate residence time, summarized below in Figure S5. The detrimental effect of prolonged irradiation is discussed below as it relates to batch reactivity (Section III.E), and it is anticipated that the same factors apply here.



Trial	Residence Time	NMR Ratio[a] 2a : 1a	Isolated Yield
1	31 min	*91* : *9*	***45%***
2	45 min	*93* : *7*	***69%***
3	145 min	*100* : *0*	***60%***
4	**79 min**	*100* : *0*	***72%***

Figure S5. Small-Scale Evaluations of Formal [3+2] Cycloadditions in Continuous Flow
[a]Ratio of **2a**:**1a** determined based on C7-Me resonances.

Procedure for small-scale continuous flow preparations of 1-aminoNB 2a

In a dry vial under nitrogen, cyclopropylimine **1a** was dissolved in dry MeCN, then degassed with three freeze-pump-thaw cycles. The reaction mixture was then flowed through the apparatus at the flow rate detailed above. Upon completion of the irradiation, the reaction mixture was quenched with 2 mL of 1:1 saturated $NaHCO_3$ (aq.):saturated $Na_2S_2O_3$ (aq.) and diluted with 2 mL ether. The phases were separated, then the aqueous phase was extracted with 2 mL portions of ether three times. The combined organics were dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The product was run through a plug of basic alumina, eluting with 15% ethyl acetate:pentane. Percent conversion was determined by ^{1}H NMR analysis. The product was isolated via chromatography over basic alumina (2 to 5 to 10% ethyl acetate:pentane).

Procedure for continuous flow preparation of 1-aminoNB 2a (entry 5, Figure 2)

In a dry vial under argon, cyclopropylimine **1a** (65.0 mg, 203 μmol) was dissolved in dry MeCN, then degassed with three freeze-pump-thaw cycles. The reaction mixture was then flowed through the apparatus at the flow rate detailed above (1.3 hr residence time). Upon completion of the irradiation, the reaction mixture was quenched with 2 mL of 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 2 mL ether. The phases were separated, then the aqueous phase was extracted with 2 mL portions of ether three times. The combined organics were dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The product was purified

via flash chromatography over basic alumina (15% ethyl acetate:pentane; loaded residue with PhMe). Collected 1-aminoNB **2a** as a white solid, 47 mg, 73% yield.

III.C. UV/Vis and Emission Data

As detailed in the main text, UV/Vis spectroscopy was used as a guide for selection of light source. The samples were collected using a Shimadzu UV-1601 UV/Vis Spectrophotometer, sweeping from 450-225 nm and using an MeCN blank for background subtraction. An initial 10 mM stock was made from ~10 mg of the given substrate in dry MeCN in a quartz cuvette, followed by serial dilutions to the concentration in question with additional dry MeCN. Each sample was sonicated for 60 seconds before acquisition. Graphical depictions and tabulated data are provided in the text. Molar absorptivities were estimated from the maximum absorbances using Beer's Law.

Emission spectra of the light sources listed in Figure 3 in the main text were collected on an Ocean Optics USB4000 Spectrometer, scanning from 180-885 nm. All light sources were set to the maximum intensity as they were during use in the photochemical methodology.

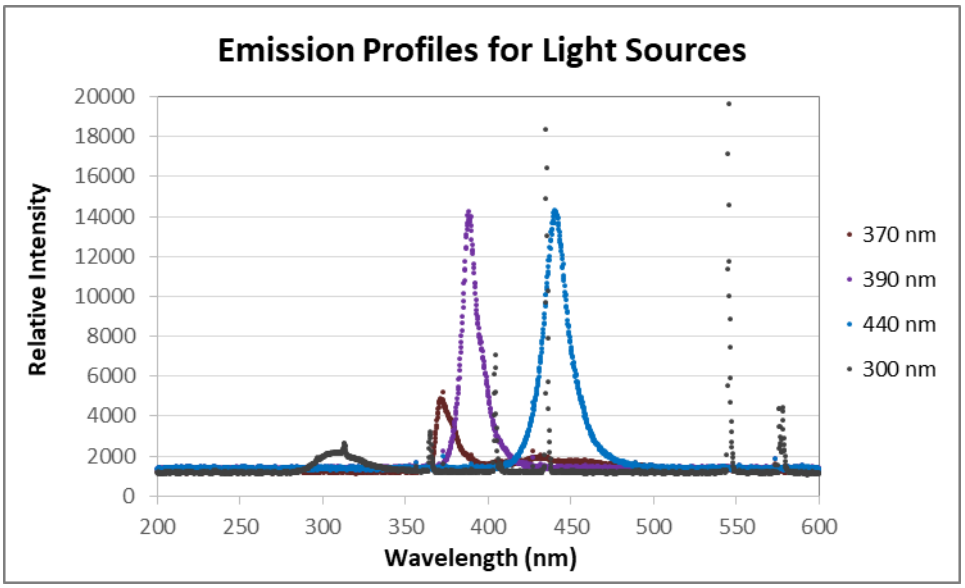


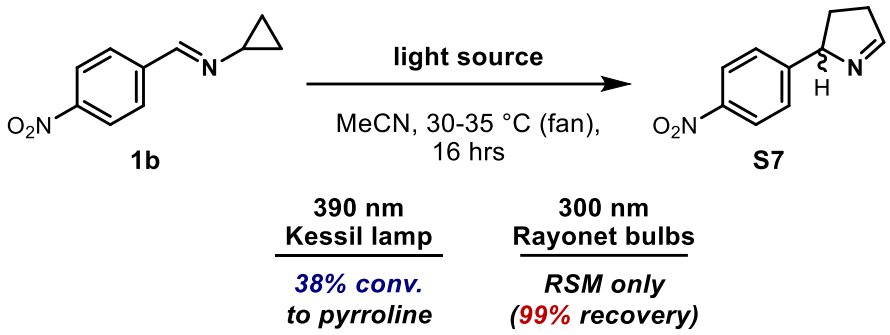
Figure S6. Emission spectra of light sources employed in Figure 3 of the main text
Of note, the Rayonet 300 nm lights show peak emission at ~308 nm, but also emit strongly at the spectral lines for Hg.

Importantly, this shows clear resolution between the emission of the optimal 390 nm light source and the π→π* transition absorbance highlighted in Figure 3A in the main text, thus supporting our mechanistic hypothesis that the fragmentation-cyclization sequence is initiated from the S_1(n,π*) excited state. Notably, there is a clear discrepancy in emission intensity between the 390 nm and 370 nm light source; though the former proved optimal (at 76% yield of **2a**), the latter produced 51% product despite emitting 69% fewer photons at the peak emission. However, the intersection of these emission intensity profiles occurs at 380 nm, just shy of the n→π* maximum absorbance measured for cyclopropylimine **1a**, thus it is not surprising that the two light sources led to similar productivity. As for the 440 nm light source (13% product formation), the hypsochromic tail of the emission does overlap with the bathochromic tail of the n→π* transition, indicating the potential for some population of the S_1(n,π*) excited state. Lastly, the minor amount of product formed with the Rayonet 300 nm lights is thought to be ascribable to the mercury H-line (405 nm; likely lying within the tail of the n→π* transition), rather than any S_2(π,π*) state-driven reactivity (i.e. via internal conversion).

Of note, while we are proposing that the desired reactivity is achieved by progressing directly from the S_1(n,π*) excited state, intersystem crossing to the T_2(π,π*) state is also possible, which would enable attack from the σ_{CC} bond into a π_N electrophile. However, it is unusual for this state to be lower in energy than the S_1(n,π*) state (benzophenone is the most closely related exception), suggesting that this intersystem crossing is likely to be thermodynamically-infeasible for our system.

III.D. Evaluation of Pyrroline Formation

While discussing mechanistic aspects of our transformations, the work of Sampedro et al.[7] studying the cyclopropylimine-pyrroline rearrangement also merits analysis. In this series of reports, the authors detail the rearrangement of cyclopropylimines with various substitution patterns to the corresponding pyrrolines; the authors also provide some computational data that they suggest supports an operative $S_2(\pi,\pi^*)$ state, achieved via excitation of absorbances at ~250 nm [note, the reactions were reported to be run through a Pyrex filter, theoretically preventing the involvement of UVA light; no additional experimental data was provided to clarify this issue]. Our work clearly supports direct n→π* excitation as the functional photochemical pathway for our transformation and likely any other process that proceeds via homolysis of C-C bonds vicinal to the imine nitrogen. Interestingly, pyrroline formation was not a major competing pathway relative to our designed radical cyclization sequence toward 1-aminoNBs. Baseline perturbations suspected to arise from trace pyrroline formation were noted in the crude ^{1}H NMR spectra for a handful of substrates, but not all (generally when employing electron-rich (hetero)aryl fused rings; the α-N methine at 5.0-5.5 ppm is a good diagnostic resonance); in fact, only 2,3-thiophene-fused system **S6** produced an isolable quantity of the pyrroline byproduct (see pg. S22; ~10% yield). To more directly evaluate the possibility of pyrroline formation, model cyclopropylimine **1b** was irradiated with both our standard conditions (390 nm light) and a UVB source designed to elicit π→π* transitions (300 nm light). Supportive of our n→π* transition proposal, the 390 nm light led to 38% conversion to the corresponding pyrroline, while the 300 nm trial returned only starting material.



Clearly a single substrate is not enough to refute the multiple reports from Sampedro and co-workers (it is hypothetically possible that an operative $S_1(n,\pi^*)$ is exclusive to 4-nitrobenzimines), but it does indicate that the mechanistic analysis of photochemical cyclopropylimine-pyrroline rearrangements is not yet complete. Additionally, thermal variations of the cyclopropylimine-pyrroline rearrangement are known (though generally occur at >300 °C),[8] and the mercury-arc lamps employed by Sampedro et al. are known to generate a great deal of heat (surface temp. = 500-600 °C as detailed by Hanovia[9]); a thermal control was run in the 2001 report,[7a] but this was performed in refluxing toluene rather than preparing a sample in an opaque reaction vessel and exposing to the standard conditions, thus it is unclear whether or not the heat from the light source influenced the previously reported chemistry.

It should also be noted that our 4-nitrobenzimine substrates are unique in that the n→π* vs π→π* transitions are separated by ~90 nm, thus it will not be as easy to deconvolute the importance of individual excited states for alternative cyclopropylimines. It is worth the effort, however, as the ever-increasing implementation of photochemistry within the industrial sector makes it imperative that academic photochemical methodology deliver comprehensive understanding of the transformations at hand if we are to maximize the real world impact of this genre of synthetic research.

III.E. NMR Time Course Study

To assess the rate of conversion for the photoauxiliary-enabled formal [3+2] cycloadditions, trials reactions were run in an NMR tube using d_3-MeCN. A setup analogous to that described in Section II.B was employed, positioning the NMR tube in place of the vial. Both cyclopropylimine **1a** and 1-aminoNB **2a** were evaluated in parallel.

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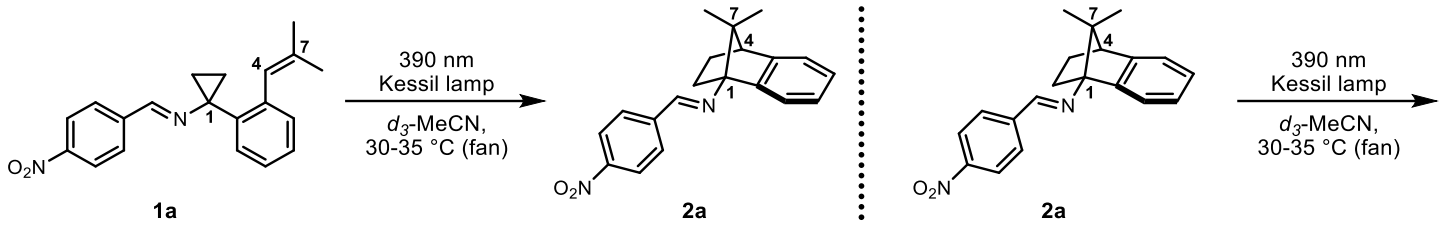
[7] a) Campos, P.; Soldevilla, A.; Sampedro, D.; Rodriguez, M. *Org. Lett.* **2001**, *3*, 4087-4089; b) Sampedro, D.; Soldevilla, A.; Rodriguez, M.; Campos, P.; Olivucci, M. *J. Am. Chem. Soc.* **2005**, *127*, 441-448; c) Sampedro, D.; Soldevilla, A.; Rodriguez, M.; Campos, P.; Olivucci, M. *J. Am. Chem. Soc.* **2005**, *127*, 441-448; d) Soldevilla, A.; Sampedro, D.; Campos, P.; Rodriguez, M. *J. Org. Chem.* **2005**, *70*, 6976-6979.

[8] Soldevilla, A.; Sampedro, D. Preparation and application of cyclopropylimines in organic synthesis. A review. *Org. Prep. Proced. Int.* **2007**, *39*, 561-590.

[9] https://www.hanovia-uv.com/photochemical-systems/; accessed 5-30-2019.



1a **2a** **2a**

Procedure for NMR Time Course Study

In separate dry vials under inert atmosphere, cyclopropylimine **1a** (15.1 mg, 47 μmol) was dissolved in 0.24 mL d_3-MeCN (all d_3-MeCN was degassed via three freeze-pump-thaw cycles prior to use), and 1-aminoNB **2a** (14.5 mg, 45 μmol) was dissolved in 0.23 mL d_3-MeCN. A stock of internal standard was prepared from trimethylphenylsilane (8.6 μL, 50 μmol) in 1.0 mL d_3-MeCN (50 mM stock). The 50 mM PhTMS stock was added to each vial (1:1 dilution), then 425 μL of each mixture was added to an NMR tube (oven-dried, capped, then flushed with N_2 to cool prior to transfer). The NMR samples were irradiated with 390 nm light as described above, collecting NMR data at the following time points: 0 min, 1 min, 2 min, 5 min, 10 min, 20 min, 30 min, 1 hr, 1.5 hrs, 2 hrs, 3 hrs, 4 hrs, 26 hrs. NMR tubes were transported in aluminum foil-wrapped Erlenmeyer flask to prevent unwanted irradiation. Quantification of starting material, product, and internal standard were based on the following resonances: cyclopropylimine **1a** [SM]: C7-Me at 1.75 ppm; 1-aminoNB **2a** [pdt]: C7-Me at 0.75 ppm; PhTMS [std]: TMS @ 0.25 ppm. Data is presented in tabular and graphical form below:

time elapsed (min)	integration results								
	SM trial						*Pdt trial*		
	std	SM	pdt	%SM	%pdt	SUM	std	pdt	%pdt
0	100.00	123.44	0.00	***100%***	***0%***	*100%*	100.00	130.11	***100%***
1	100.00	121.44	3.54	***98%***	***3%***	*101%*	100.00	129.07	***99%***
2	100.00	120.62	6.52	***98%***	***5%***	*103%*	100.00	129.57	***100%***
5	100.00	111.07	14.97	***90%***	***12%***	*102%*	100.00	130.54	***100%***
10	100.00	97.83	25.45	***79%***	***21%***	*100%*	100.00	129.40	***99%***
20	100.00	77.47	42.90	***63%***	***35%***	*98%*	100.00	128.96	***99%***
30	100.00	61.18	55.15	***50%***	***45%***	*94%*	100.00	126.25	***97%***
45	100.00	46.40	68.21	***38%***	***55%***	*93%*	100.00	125.39	***96%***
60	100.00	35.71	76.59	***29%***	***62%***	*91%*	100.00	124.30	***96%***
90	100.00	19.04	90.57	***15%***	***73%***	*89%*	100.00	123.13	***95%***
120	100.00	12.28	105.44	***10%***	***85%***	*95%*	100.00	127.21	***98%***
180	100.00	6.25	109.03	***5%***	***88%***	*93%*	100.00	125.28	***96%***
240	100.00	2.70	112.67	***2%***	***91%***	*93%*	100.00	124.26	***96%***
1560	100.00	0.00	104.94	***0%***	***85%***	*85%*	100.00	107.92	***83%***

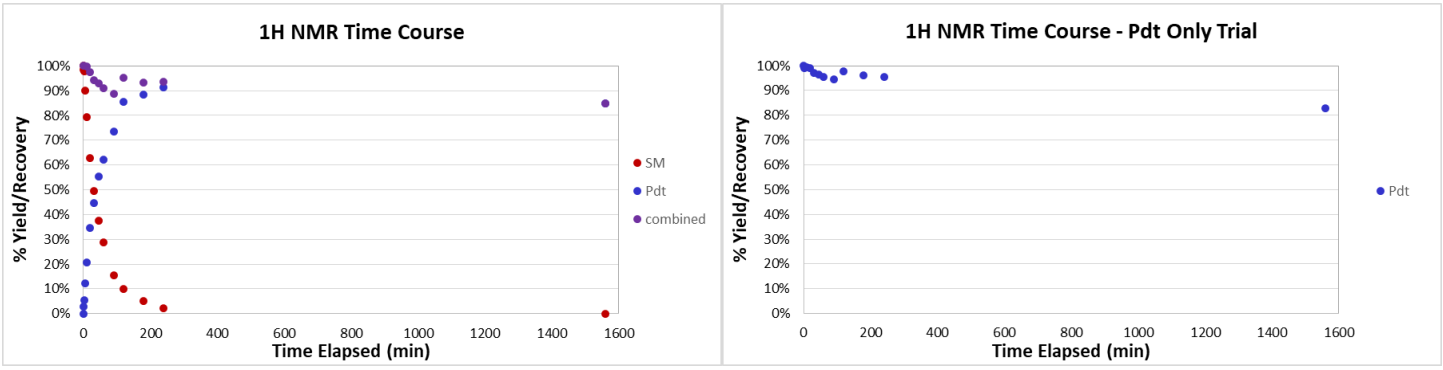


Figure S8. NMR Time Course Data

Top: Tabular data collected for NMR time course studies; Bottom Left: Cyclopropylimine **1a** [SM] trial; Bottom Right: 1-AminoNB **2a** [pdt] trial. Note: the slight discontinuity in both graphs arose due to brief sonication of the samples after the 90 min time point, which re-dissolved a small amount of precipitate suspected to be the product.

As the data in Figure S8 shows, the reaction proceeds quite cleanly and quickly to product, achieving over 80% conversion to product within 2 hrs on this scale. The remaining conversion progresses quite slowly, and it is clear that some amount of material is being consumed via unproductive pathways, though no specific byproducts were resolved from the baseline in the NMR spectra (these species have also eluded isolation and detection by MS methods). This does not appear to be entirely attributed to product instability, as the product decomposes more slowly than the overall loss in mass balance seen in the cyclopropylimine trial. Though not discussed in the main text, empirical observations demonstrate that the formation of colored impurities is much more prominent when irradiating the

starting material (see Figure S8), contributing to both the rapid reduction in reaction rate (by absorbing photons) and likely facilitating decomposition pathways. It is unclear what the identity of these colored impurities are at this time; the UV/Vis profile of a standard reaction mixture after irradiation (see Figure S9) does not show any specific new chromophore, but does show an increase in absorbance across the entirety of the spectrum (no additional absorbance bands were detected above 450 nm; data not shown).

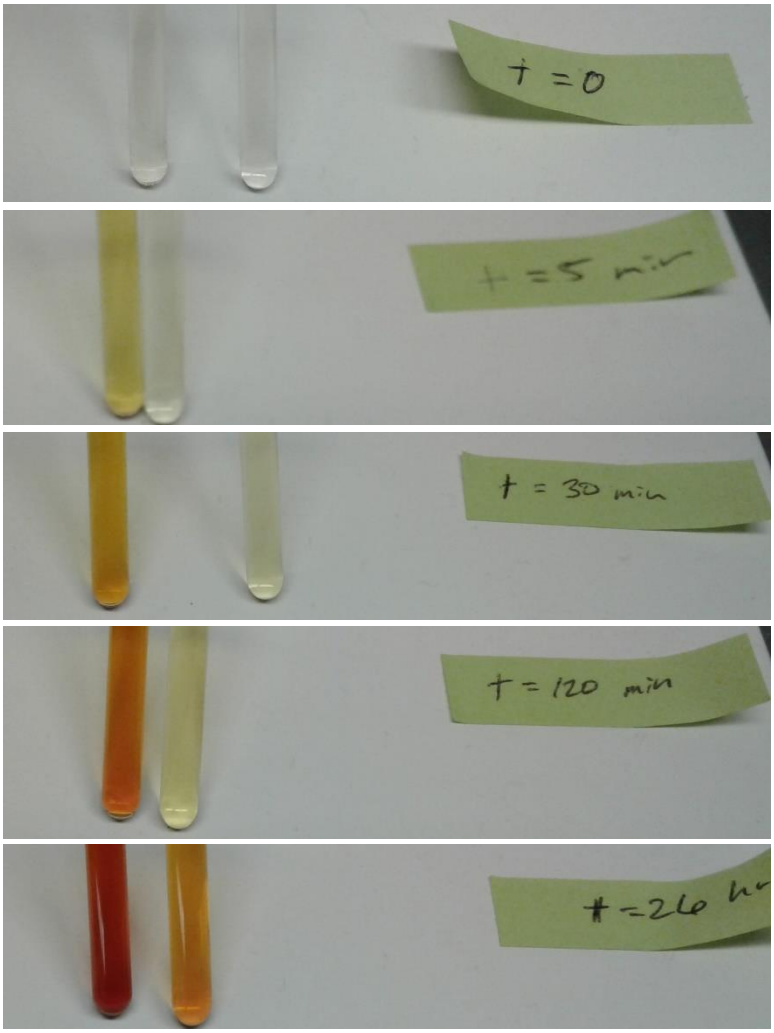


Figure S8. Darkening of Reaction Mixture observed during NMR Time course
Note: In all circumstances, the cyclopropylimine trial is on the left.

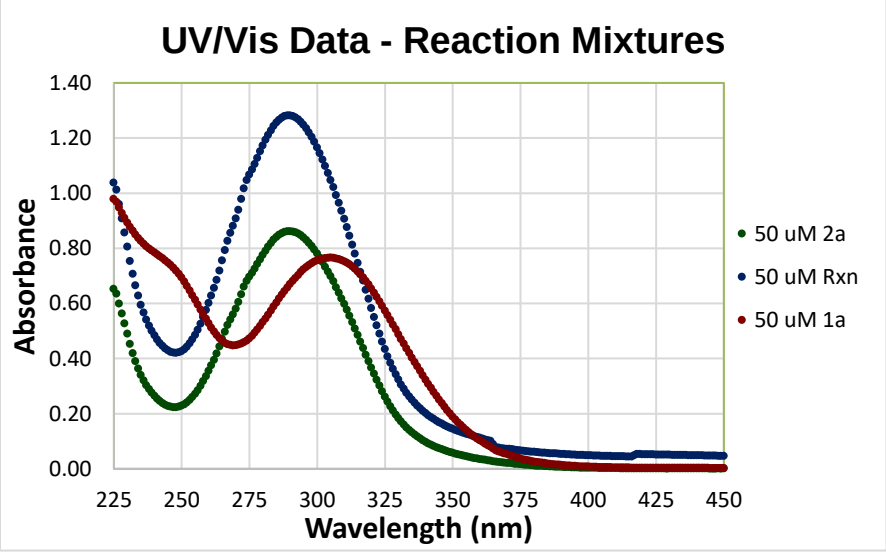


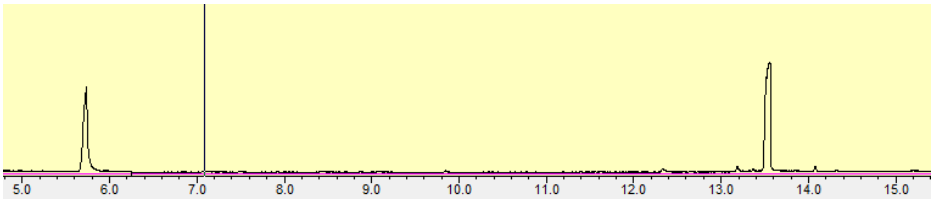
Figure S9. UV/Vis Spectrum of Reaction Mixture after Irradiation with 390 nm Light

III.F. Additive Trials

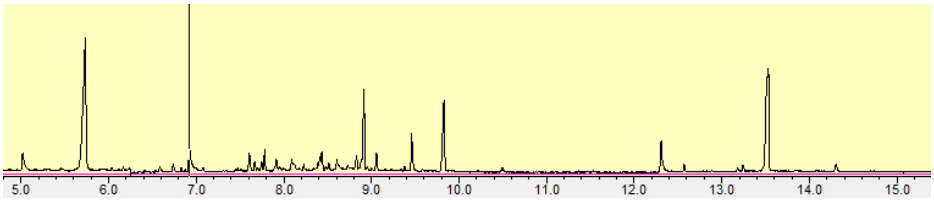
While the optimization detailed above in Section III.A focused on light source, the darkening of the reaction mixtures prompted initial investigation into additives that would serve to prevent the formation of this undesired and unidentified chromophore(s). Data from an illustrative study is provided below. Additives were chosen to evaluate a variety of H-atom and/or electron donors/acceptors.

A reaction mixture was prepared following the standard procedure and aliquoted into four portions containing 1.0 eq. of the following additives: 1) no additive; 2) BHT; 3) 2,2'-PyrSSPyr (aldrithiol); 4) Hantzsch ester (diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate). The GCMS traces of the reaction mixtures were collected with the inclusion of a dodecane standard, and yields were quantified as normalized to the no additive control. The traces are provided below:

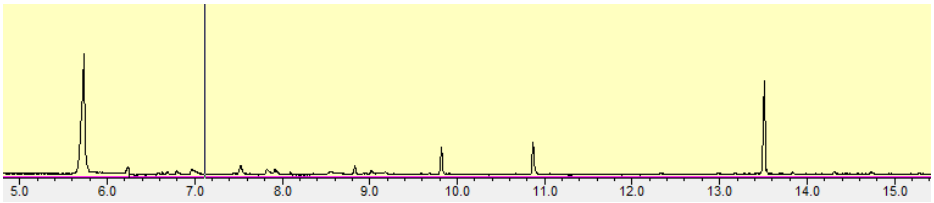
1) no additive (100% 2a)



2) BHT (56% 2a)



3) 2,2'-PyrSSPyr (33% 2a)



4) Hantzsch ester (58% 2a)

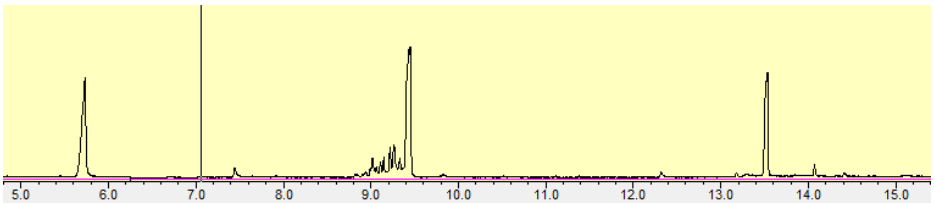
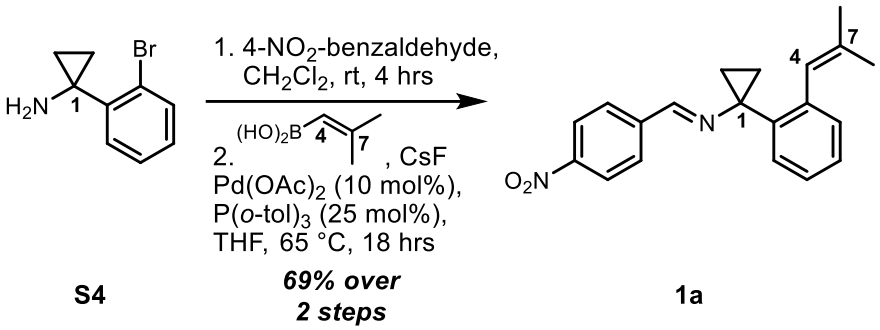


Figure S10. HPLC Traces of Additive Trials

Note: Quantification of product (**2a**) relative to the no additive trial is provided in parentheses after each additive name (product integrations first normalized to dodecane standard); retention times: dodecane = 5.75 min; 1-aminoNB **2a** = 13.56 min.

It is clear that the inclusion of additives has both a quantitative impact on the reaction performance as well as a qualitative effect on the cleanliness of the reaction profile. In all cases, multiple new byproducts are present that were undetectable in the no additive control. Additionally, the only additive that prevented the darkening of the reaction mixture was the aldrithiol, but this system also formed a grey precipitate that would be undesirable in continuous flow applications. For these reasons, additive-mediated prevention of reaction discoloration was not pursued further.



S4 — ***69% over 2 steps*** — **1a**

Procedure for cyclopropylimine 1a

In a dry flask under inert atmosphere, aminocyclopropane **S4**[10] (0.71 g, 3.3 mmol) dissolved in 24 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (1.26 g, 8.4 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (2 to 3 to 5 to 10 to 15% ethyl acetate:hexanes). Collected 1.05 g of the Schiff base intermediate (91.0%) as a slightly yellow oil. Partial characterization is provided below:

Partial Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.20 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.77 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.65 (d, 2H, *J* = 5.6 Hz, Ar), 7.62 (s, 1H, imine CH), 7.37 (*app*. d, 2H, *J* = 4.3 Hz, Ar, Ar), 7.27-7.22 (m, 1H, Ar), 1.72 (*app*. q, 2H, *J* = 4.6 Hz, CP), 1.46 (*app*. q, 2H, *J* = 4.5 Hz, CP) ppm
R_f = 0.25 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (2.29 g, 15.1 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2 and adding 4.0 mL dry, degassed THF (degassed by sparging with Ar through 22 gauge needle for 45 min prior to use, in separate dry flask). In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (68 mg, 301 µmol) and tris(o-tolyl)phosphine (229 mg, 753 µmol) were dissolved in 5.0 mL dry, degassed THF, then stirred for 20 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (1.04 g, 3.0 mmol) and (2,2-dimethyl)vinylboronic acid (452 mg, 4.5 mmol; purchased from Synthonix) were dissolved in 10 mL dry, degassed THF. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with three 3.0 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 20 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~50 mL ether. Concentrating mixture onto celite under vacuum (carefully), then added a 10 mL portion of pentane and re-concentrated two times. The celite mixture was loaded directly onto a column of basic alumina and the product was eluted (1 to 2 to 3 to 5 to 10% ethyl acetate:hexanes). Phosphine-derived impurities were mixed with a large portion of the desired product; clean fractions were set aside, while the mixed fractions were exposed to a second round of chromatography (same as above). Again, mixed fractions were collected a re-exposed to the chromatography conditions, finally affording product with any

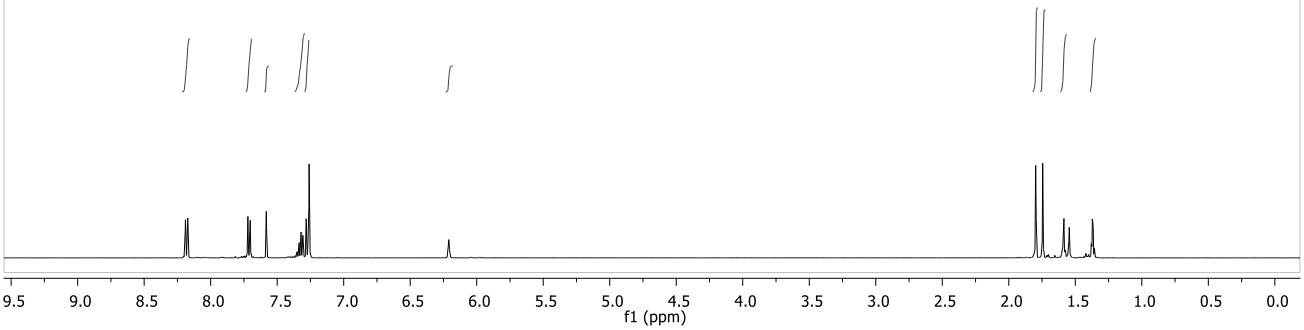
[10] The preparation of aminocyclopropane **S4** has previously been reported (Charette, B.; Boerneke, M.; Hermann, T. *ACS Chem. Biol.* **2016**, *11*, 3262-3267). Our protocol followed closely; briefly: 2-bromobenzonitrile (2.3 g, 13 mmol) was dissolved in 85 mL dry ether in a dry flask under inert atmosphere, and cooled to -78 °C. $Ti(OiPr)_4$ (4.1 mL, 14 mmol) was added in one portion, followed by addition of EtMgBr (3.0 M in ether, 9.2 mL, 28 mmol) dropwise over the course of 10 min. After 45 min at -78 °C, cold bath was removed, stirred while coming to room temp for 3 hrs. BF_3·etherate (3.1 mL, 25 mmol) was added dropwise over the course of 2 min, and the reaction mixture was stirred 4 hrs at room temp. The reaction was quenched by carefully pouring in 100 mL of a 3:1 mix of sat. Rochelle salt:1 M NaOH (aq), stirred vigorously for 30 min. Diluted with an 100 mL of the same aqueous mixture and 100 mL ether. Separated phases, extracted aqueous phase with three 100 mL portions of ether. Combined organics were washed with 100 mL brine + 1 mL 6 M NaOH (aq.), dried over anhydrous $MgSO_4$, filtered to remove solids, and concentrated under vacuum. Purified crude residue over silica (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; the silica was pre-neutralized with 8% ethyl acetate:hexanes + 1% NEt3; loaded residue with PhMe). Collected 1.84 g of aminocyclopropane **S4** (69.3% yield) as a slightly yellow oil.
Partial characterization: ^{1}H NMR ($CDCl_3$, 500 MHz): 7.55 (dd, 1H, *J* = 7.9, 1.1 Hz, Ar), 7.36 (dd, 1H, *J* = 7.6, 1.7 Hz, Ar), 7.25 (td, 1H, *J* = 7.5, 1.2 Hz, Ar), 7.10 (td, 1H, *J* = 7.7, 1.7 Hz, Ar), 2.11 (br s, 1H, NH_2), 1.08 (*app*. dd, 2H, *J* = 6.7, 4.6 Hz, CP), 0.91 (*app*. dd, 2H, *J* = 6.7, 4.6 Hz, CP) ppm. R_f = 0.30 (60% ethyl acetate:hexanes), one red spot, ninhydrin, UV.

phosphine-based contaminant. In total, the reaction yielded 736 mg of cyclopropylimine **1a** (76.2%; 69.3% over 2 steps) as a clear, colorless oil.

*Characterization Data for cyclopropylimine **1a**:*
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.18 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.71 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.58 (s, 1H, imine CH), 7.36-7.30 (m, 2H, Ar), 7.29-7.24 (m, 2H, Ar), 6.21 (s, 1H, C4), 1.80 (s, 3H, C7-Me), 1.74 (s, 3H, C7-Me), 1.59 (*app*. q, 2H, *J* = 4.3 Hz, CP), 1.37 (*app*. q, 2H, *J* = 4.3 Hz, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 154.8, 148.6, 142.6, 140.1, 137.0, 135.5, 131.3, 130.3, 128.2, 127.8, 126.8, 123.9, 123.8, 50.4, 26.5, 19.5, 18.4 ppm
IR (neat): 2910, 1599, 1519, 1446, 1343, 1207, 1111, 955, 943, 878, 849, 829, 763, 748, 691 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{20}H_{21}N_2O_2^+$: 321.1598, Found: 321.1600
R_f = 0.45 (20% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

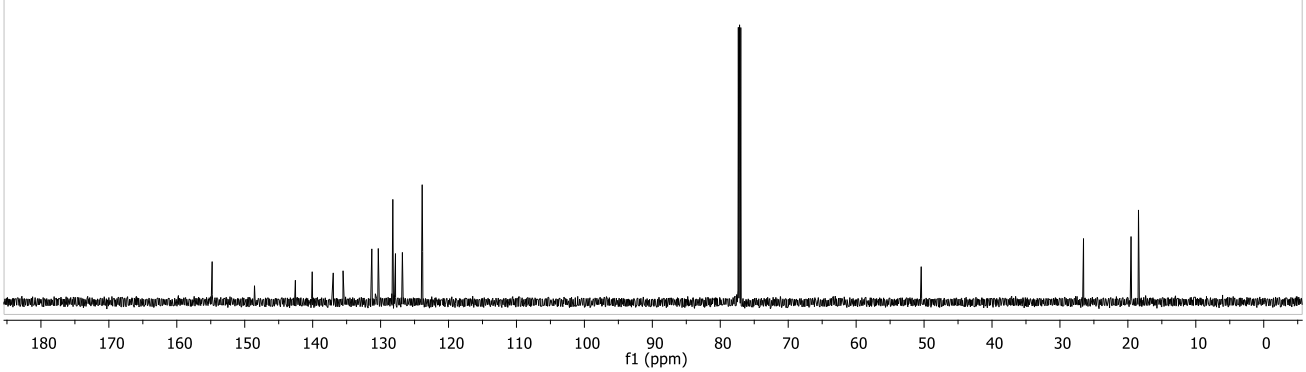
^{1}H NMR (500 MHz, $CDCl_3$) for 1a

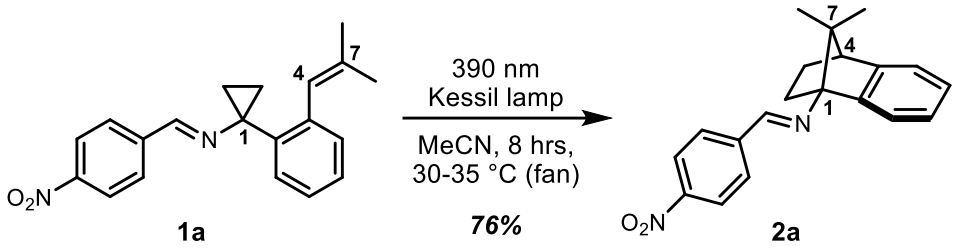
Parameter	Value
Title	DS.1814.1H.charB
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	52
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1006.8
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



^{13}C NMR (176 MHz, $CDCl_3$) for 1a

Parameter	Value
Title	JLC.0238.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2937.7
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for 1-aminoNB 2a

The detailed procedure for the preparation of 1-aminoNB **2a** is provided in Section III.A. The characterization data is provided below.

*Characterization Data for 1-aminoNB **2a***[11]*:*

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.63 (s, 1H, imine CH), 8.31 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.06 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 7.20 (d, 1H, *J* = 6.9 Hz, C8), 7.15 (td, 1H, *J* = 7.4, 1.0 Hz, C9/C10), 7.10 (dd, 1H, *J* = 7.4, 1.1 Hz, C9/C10), 6.87 (d, 1H, *J* = 7.1 Hz, C11), 2.97 (d, 1H, *J* = 3.7 Hz, C4), 2.31-2.21 (m, 2H, C3-eq, C2-eq), 1.50-1.45 (m, 1H, C2-ax), 1.37-1.31 (m, 1H, C3-ax), 0.99 (s, 3H, C7-Me), 0.80 (s, 3H, C7-Me) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 158.9, 149.4, 147.8, 147.1, 142.5, 129.0, 126.3, 125.6, 124.0, 121.8, 119.6, 80.3, 60.2, 51.8, 28.7, 26.8, 20.2, 19.4 ppm

IR (neat): 2958, 1642, 1602, 1521, 1458, 1344, 1285, 1108, 851, 840, 753, 691 cm^{-1}

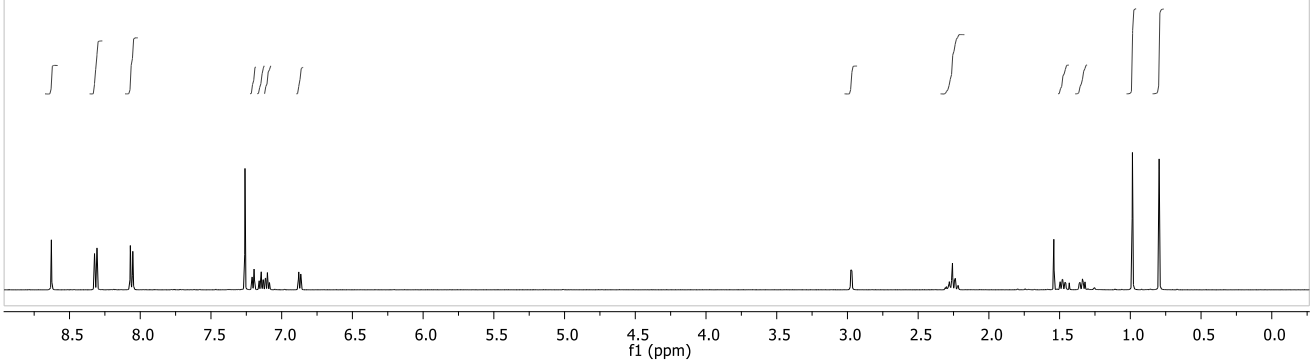
HRMS (ES+, *m/z)* calculated for $C_{20}H_{21}N_2O_2^+$: 321.1598, Found: 321.1602

R_f = 0.50 (10% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

[11] Assignments based on analogy to related scaffolds.

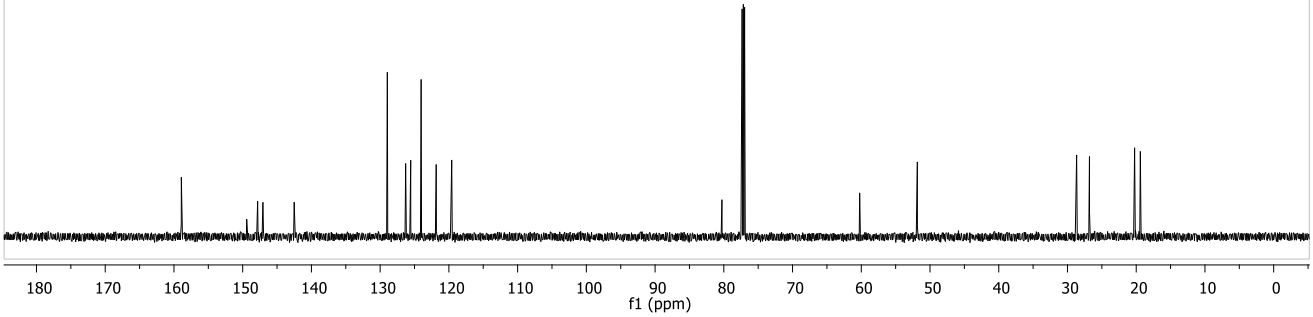
^{1}H NMR (500 MHz, $CDCl_3$) for 2a

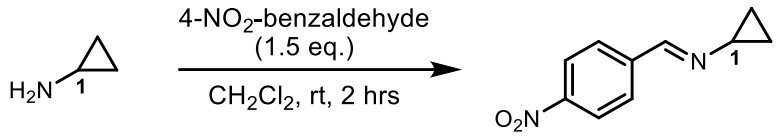
Parameter	Value
Title	DS.1865.1H.char3
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	54
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1007.3
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



^{13}C NMR (176 MHz, $CDCl_3$) for 2a

Parameter	Value
Title	DS.1865.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	50.0
Pulse Sequence	s2pul
Number of Scans	32
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2923.6
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S8 ***86%*** **1b**

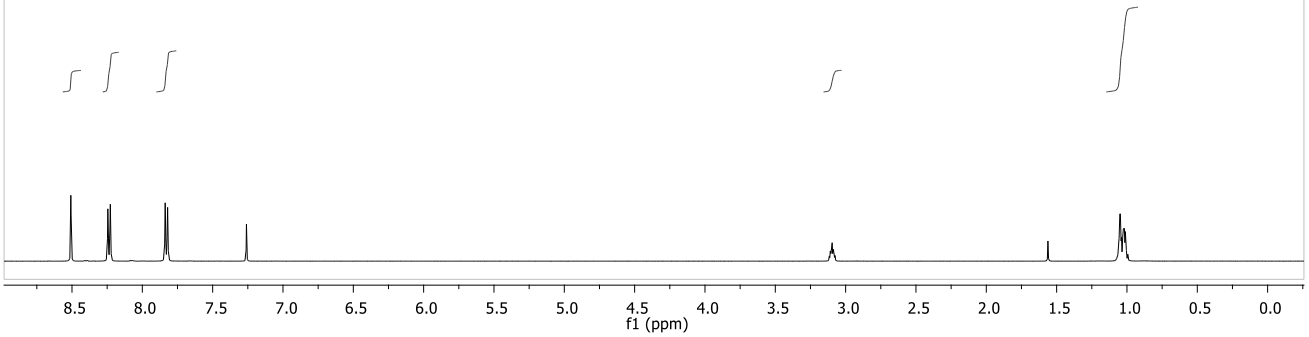
Procedure for cyclopropylimine 1b

Cyclopropylamine (**S8**; 646 mg, 11.3 mmol; purchased from Oakwood Chemical) was dissolved in 30 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (2.56 g, 17.0 mmol) in one portion. The reaction mixture was stirred at room temp for 2 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a silica column, and the product was eluted (5 to 25% ethyl acetate:hexanes, increasing in 5% increments; silica was pre-neutralized with 5% ethyl acetate:hexanes + 1% NEt_3). Collected a total 1.84 g of the desired cyclopropylimine **1b** (85.5% yield) as a white solid.

*Characterization Data for cyclopropylimine **1b**:*
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.51 (s, 1H, imine C-H), 8.24 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 7.83 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 3.10 (*app*. dquart, 1H, *J* = 10.2, 3.5 Hz, C1), 1.07-0.99 (m, 4H, CP, CP) ppm
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 155.9, 148.7, 142.2, 128.2, 124.0, 42.6, 9.8 ppm
IR (neat): 2948, 2877, 1594, 1513, 1419, 1383, 1342, 1329, 1241, 1023, 953, 895, 849, 748, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{10}H_{11}N_2O_2^+$: 191.0815, Found: 191.0814
R_f = 0.45 (20% ethyl acetate:hexanes), one yellow spot, $KMnO_4$, UV

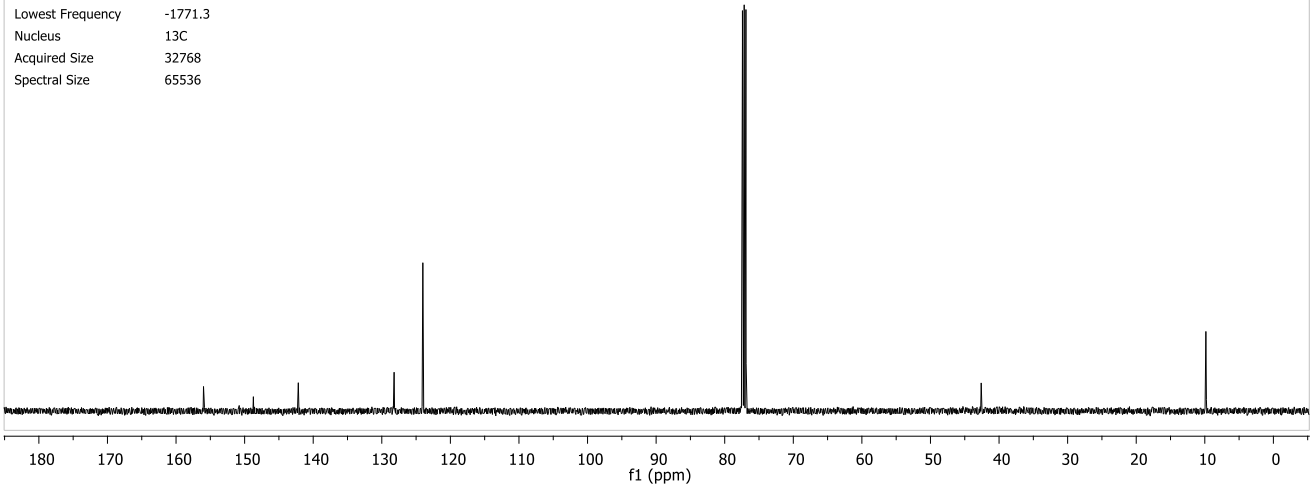
^{1}H NMR (500 MHz, $CDCl_3$) for 1b

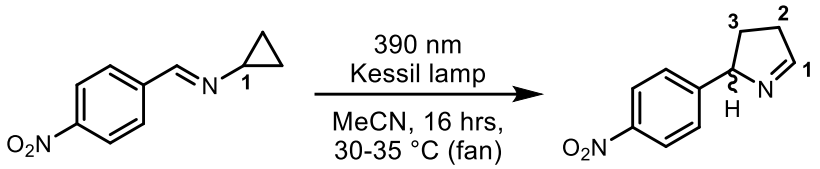
Parameter	Value
Title	DS.1863.1H.char
Comment	STANDARD FLUORINE PARAMETERS
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	46
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	500.08
Spectral Width	8012.8
Lowest Frequency	-1005.4
Nucleus	1H
Acquired Size	28045
Spectral Size	65536



^{13}C NMR (126 MHz, $CDCl_3$) for 1b

Parameter	Value
Title	DS.1863.13C.char
Comment	STANDARD 1H OBSERVE - profile
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	336
Receiver Gain	30
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.0486
Spectrometer Frequency	125.76
Spectral Width	31250.0
Lowest Frequency	-1771.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536





1b ***38%*** **[^{1}H NMR]** **S7**

Procedure for pyrroline S7

In a dry vial under inert atmosphere, cyclopropylimine **1b** (37.0 mg, 195 μmol) was dissolved in 2.0 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 16 hrs, using the setup described in Section II.B (temperature maintained between 30-35 °C with a fan). Reaction mixture was dark red. The mixture was poured into 10 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 5 mL ether. Phases were separated, and the aqueous phase was further extracted with 5 mL ether three times. Combined organics were washed with 5 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. Obtained 35.8 mg of an orange solid. Crude ^{1}H NMR analysis of the resultant residue revealed 39.1% conversion to pyrroline **S7** (1:1.56 ratio of pyrroline:RSM; NMR spectrum provided below; based on α-amino methine resonances) with no observable contaminants. This calculates to a 37.8% yield based on ^{1}H NMR.

Due to the extreme sensitivity of this product to chromatography conditions, characterization grade material was obtained from a mixture of multiple crude residues (parallel trials of the above conditions). The purification was executed via Biotage chromatography over silica (10%, 20%, 30%, 40%, then 70% ethyl acetate:hexanes; loaded residue with PhMe). The resulting white solid was used to collect the data shown below.

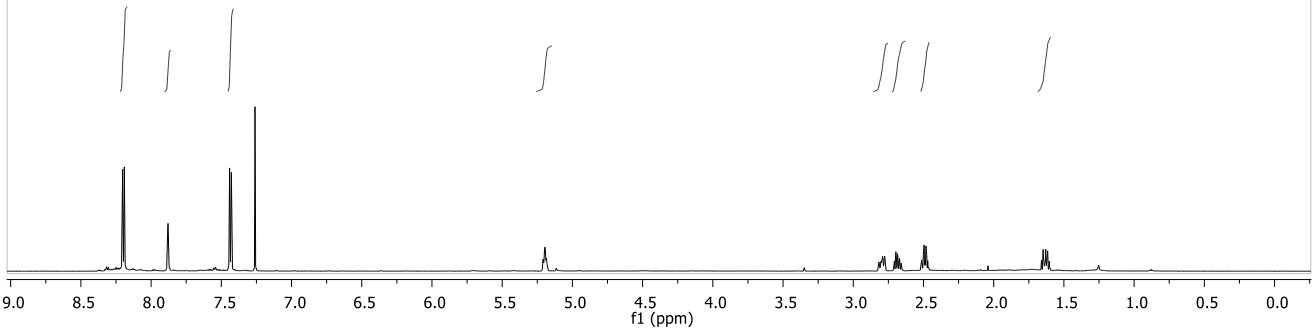
Additional Trial: 300 nm trial

Following the general procedure detailed above, 37.0 mg (195 μmol) of cyclopropylimine **1b** in 2.0 mL dry, degassed MeCN were irradiated at 300 nm for 24 hrs (as described in Section II.A). Crude ^{1}H NMR analysis revealed pure starting material (no detectable resonances for product or unidentified byproducts). Recovered yield was 36.6 mg (98.9% recovery) of cyclopropylimine **1b**.

*Characterization Data for pyrroline **S7**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ= 8.20 (d, *J* = 8.6 Hz, 1H, Ar), 7.88 (s, 1H, C1), 7.43 (d, *J* = 8.8 Hz, 1H, Ar), 5.20 (td, *J* = 8.2, 2.3 Hz, 1H, α-amino methine), 2.83-2.77 (m, 1H, C2), 2.67 (ddd, *J* = 17.9, 10.1, 2.2 Hz, 1H, C2), 2.49 (*app*. tdd, 1H, *J* = 12.9, 9.1, 3.7 Hz, C3), 1.63 (ddd, *J* = 18.0, 13.0, 8.2 Hz, 1H, C3) ppm.
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 169.0, 151.8, 147.2, 127.4, 124.0, 75.4, 37.8, 30.5 ppm.
IR (neat): 1597, 1516, 1344, 1285, 1227, 1108, 853, 754, 700 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{10}H_{11}N_2O_2^+$: 191.0815, Found: 191.0815
R_f = 0.20 (70% ethyl acetate:hexanes + 1% NH_4OH), UV active, $KMnO_4$

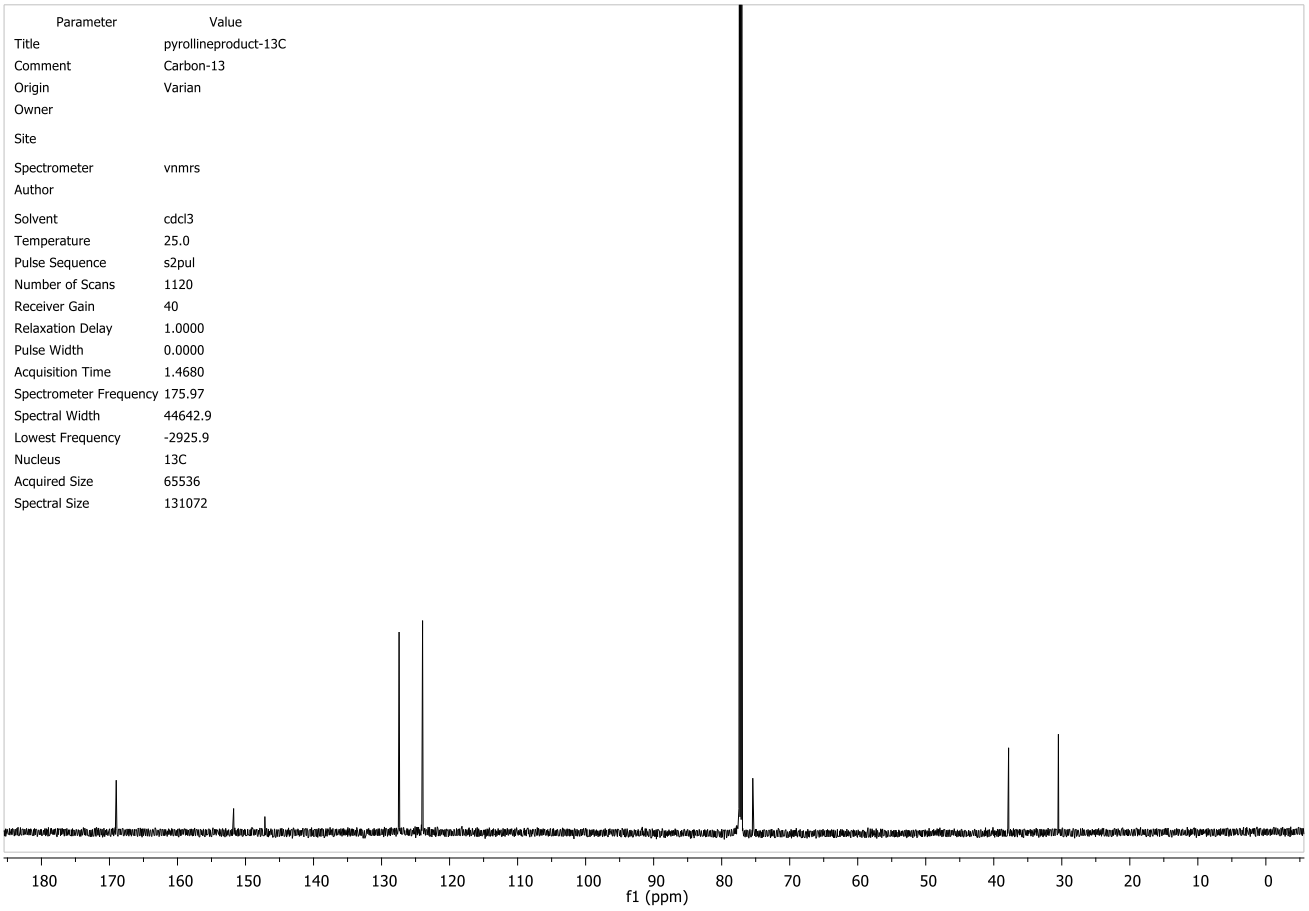
^{1}H NMR (700 MHz, $CDCl_3$) for S7

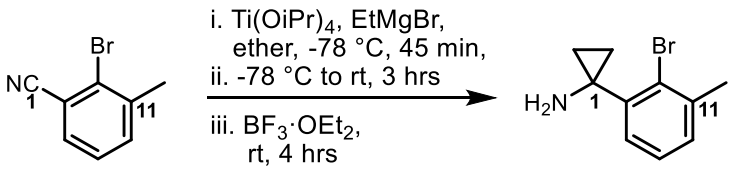
Parameter	Value
Title	pyrollineproduct-1H
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	54
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1380.5
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for S7

Parameter	Value
Title	pyrollineproduct-13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	1120
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2925.9
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S9 ***43%*** **S10**

Procedure for C11-methyl aminocyclopropane S10

2-Bromo-3-methyl-benzonitrile **S9** (2.00 g, 10.2 mmol; purchased from Sigma Aldrich) was dissolved in 88.7 mL dry ether in a dry flask under inert atmosphere, then cooled to -78 °C. Titanium isopropoxide (3.34 mL, 11.2 mmol; purchased from Oakwood Chemical) was added in one portion, followed by addition of ethylmagnesium bromide (3.0 M in ether, 7.48 mL, 22.4 mmol) via syringe, dropwise down the side of the vial over the course of 5 min. The dark brown-black reaction mixture (clear, colorless at outset of EtMgBr addition) was stirred at 45 min while coming to room temp, cold bath was removed, and the reaction was stirred an additional 3 hrs at room temp. BF3·etherate (2.52 mL, 20.5 mmol) was added dropwise over the course of 2 min, and the reaction mixture was stirred 4 hrs at room temp. The reaction was quenched by carefully pouring in 100 mL of a 3:1 mix of sat. Rochelle salt:1 M NaOH (aq), followed by 30 min of vigorous stirring at room temp. The biphasic mixture was diluted with an additional 100 mL of the same aqueous mixture and 200 mL ether. The phases were separated. The aqueous phase was extracted with three 100 mL portions of ether. The combined organics were then washed with 100 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under vacuum. The crude residue was purified via flash chromatography over silica (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; the silica was pre-neutralized with 8% ethyl acetate:hexanes + 1% NEt3; the residue was loaded with PhMe). Collected 998 mg of aminocyclopropane **S10** (43% yield) as a yellow oil.

*Characterization Data for C11-methyl aminocyclopropane **S10**:*

^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.20-7.17 (m, 1H, Ar), 7.16-7.11 (m, 2H, Ar), 2.43 (s, 3H, C11-Me), 2.11 (br s, 2H, NH_2), 1.09-1.06 (m, 2H, CP), 0.92-0.88 (m, 2H, CP) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 145.1, 139.1, 129.5, 128.2, 127.8, 127.2, 39.4, 23.8, 16.0 ppm

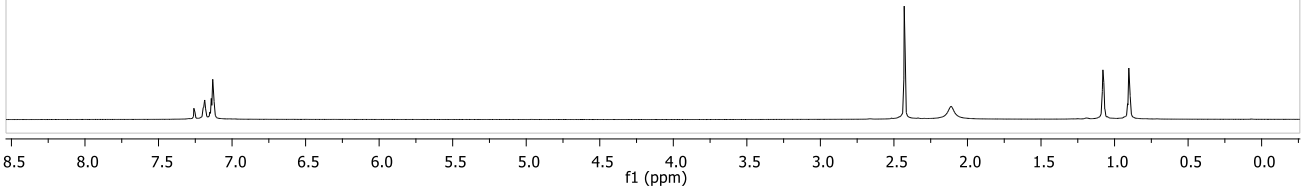
IR (neat): 3008, 1574, 1450, 1399, 1379, 1320, 1276, 1180, 1019, 907, 828, 785, 724, 713, 642 cm^{-1}

HRMS (ES+, *m/z)* calculated for $C_{10}H_{12}BrN^+$: 226.0226, Found: 226.0227

R_f = 0.55 (60% ethyl acetate:hexanes + 1% NH_4OH), one red spot, ninhydrin, UV

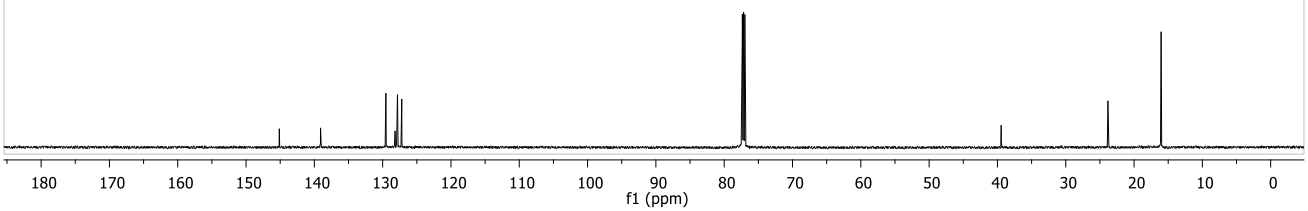
^{1}H NMR (700 MHz, $CDCl_3$) for S10

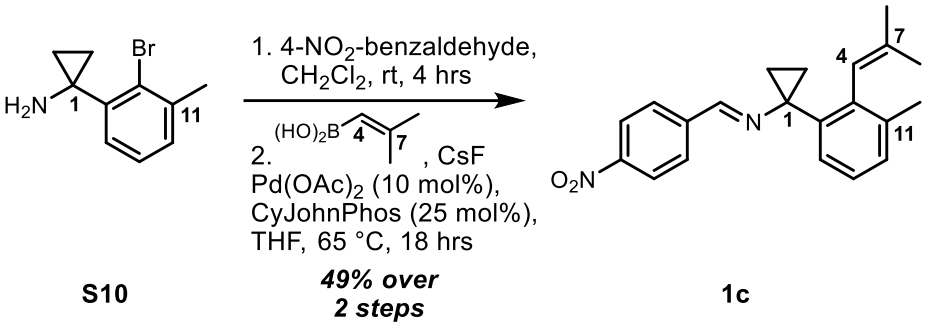
Parameter	Value
Title	JLC-0179product-1Hclean
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	44
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1381.2
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for S10

Parameter	Value
Title	JLC-0179product-13Cclean
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	784
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2938.6
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S10 ***49% over 2 steps*** **1c**

Procedure for C11-methyl cyclopropylimine 1c

Aminocyclopropane **S10** (200 mg, 0.885 mmol) was dissolved in 3.34 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (189 mg, 1.25 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (0 to 1 to 2 to 3 to 5 to 10% ethyl acetate:hexanes). Collected 265 mg of the Schiff base intermediate (83.4% yield) as a clear oil. Partial characterization is provided below.

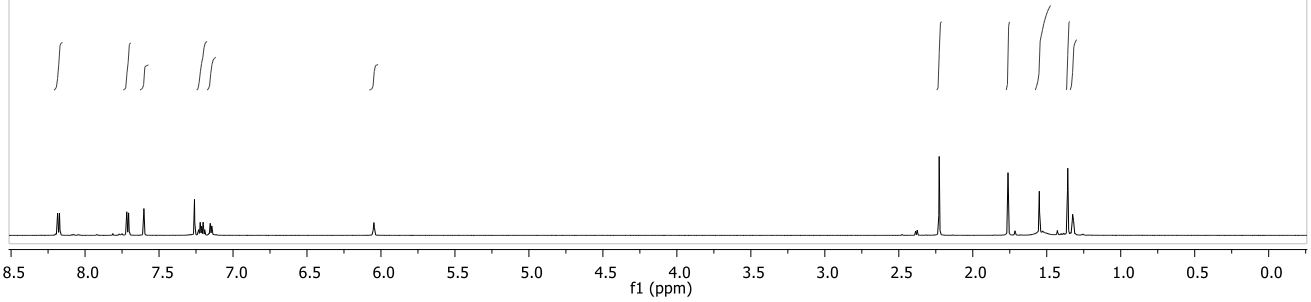
Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.18 (d, *J* = 8.6 Hz, 2H, 4-NO_2-Ar), 7.77 (d, *J* = 8.7 Hz, 2H, 4-NO_2-Ar), 7.63 (s, 1H, imine CH), 7.26 (d, *J* = 4.7 Hz, 2H, Ar), 7.22-7.18 (m, 1H, Ar), 2.47 (s, 3H, C11-Me), 1.78-1.69 (m, 2H, CP), 1.45 (*app.* d, *J* = 2.5 Hz, 2H, CP) ppm
R_f = 0.50 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (317 mg, 2.09 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2. In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (9.4 mg, 0.0418 mmol) and CyJohnPhos (25.4 mg, 0.0725 mmol) were dissolved in 2 mL dry, degassed THF(degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask), then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (150 mg, 0.418 mmol) was dissolved in 2 mL dry, degassed THF before adding (2,2-dimethyl)vinylboronic acid (62.6 mg, 0.626 mmol; purchased from Synthonix) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with two 0.5 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~100 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was dry loaded with celite). Obtained vinylated cyclopropylimine **1c** as a slighty orange oil, 83.0 mg (49% yield over 2 steps).

*Characterization Data for C11-methyl cyclopropylimine **1c**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.18 (d, 2H, *J* = 8.7 Hz, 4-NO_2Ar), 7.71 (d, 2H, *J* = 8.7 Hz, 4-NO_2Ar), 7.60 (s, 1H, imine-CH), 7.23 (d, 1H, *J* = 7.2 Hz, Ar), 7.20 (d, 1H, *J* = 7.4 Hz, Ar), 7.15 (d, 1H, *J* = 7.4 Hz, Ar), 6.07 (s, 1H, C4), 2.23 (s, 3H, C11-Me), 1.76 (s, 3H, C7-Me), 1.60-1.48 (br s, 2H, CP), 1.36 (s, 3H, C7-Me), 1.35-1.29 (m, 2H, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 154.5, 148.5, 142.6, 140.1, 137.7, 137.4, 135.5, 129.9, 128.8, 128.2, 126.8, 123. 9, 122.5, 51.0, 25.3, 20.2, 19.8, 18.6 ppm
IR (neat): 2925, 1599, 1519, 1444, 1376, 1343, 1207, 1107, 1051, 1024, 959, 846, 790, 748, 692 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{21}H_{22}N_2O_2^+$: 335.1754, Found: 335.1755
R_f = 0.75 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

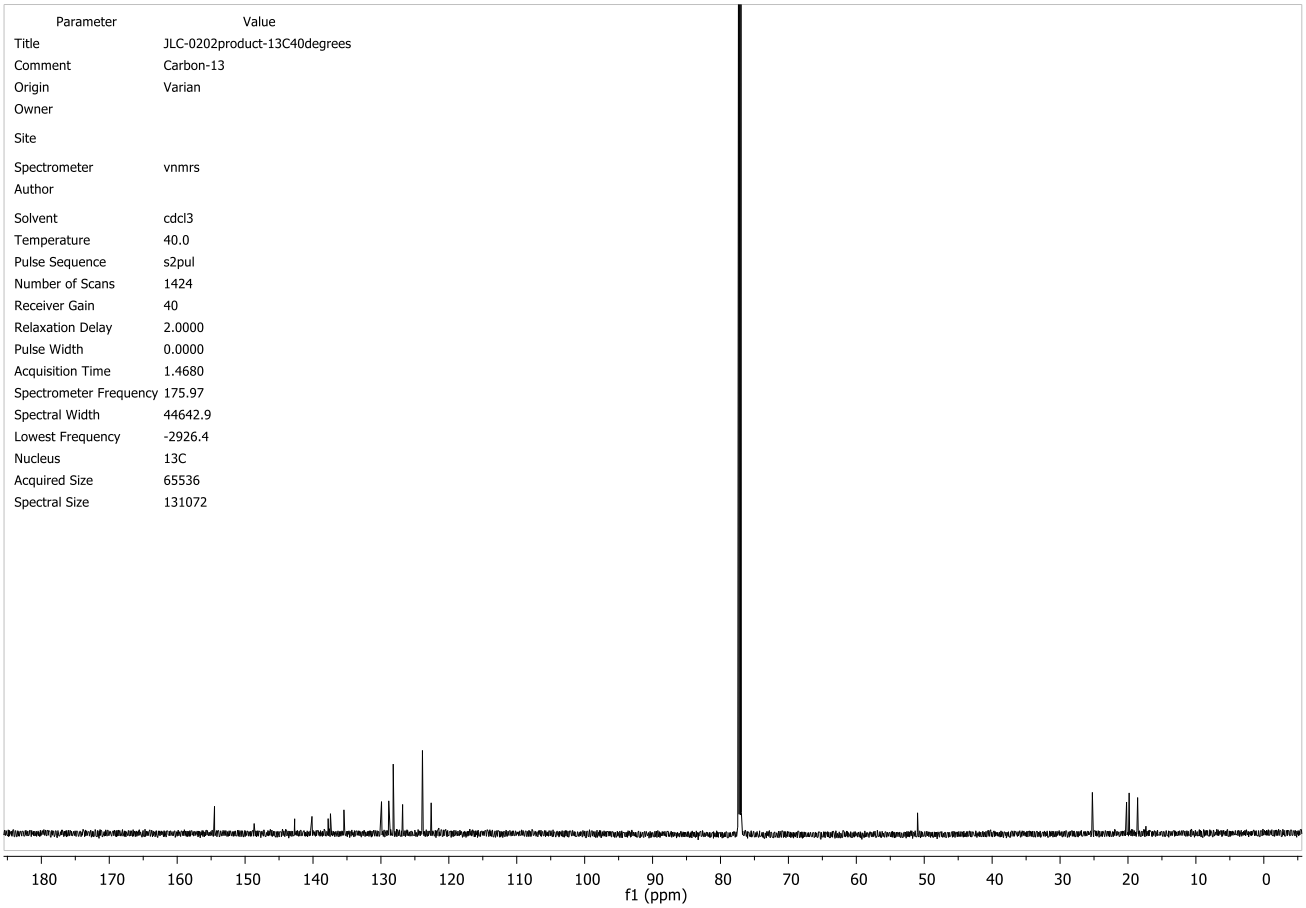
^{1}H NMR (700 MHz, $CDCl_3$) for 1c

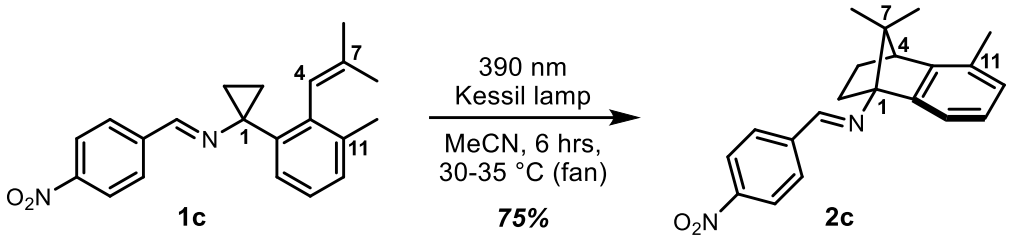
Parameter	Value
Title	JLC-0208product-1Hdry2
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	52
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$ @ 40 °C) for 1c

Parameter	Value
Title	JLC-0202product-13C40degrees
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	40.0
Pulse Sequence	s2pul
Number of Scans	1424
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2926.4
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for C11-methyl 1-aminoNB 2c

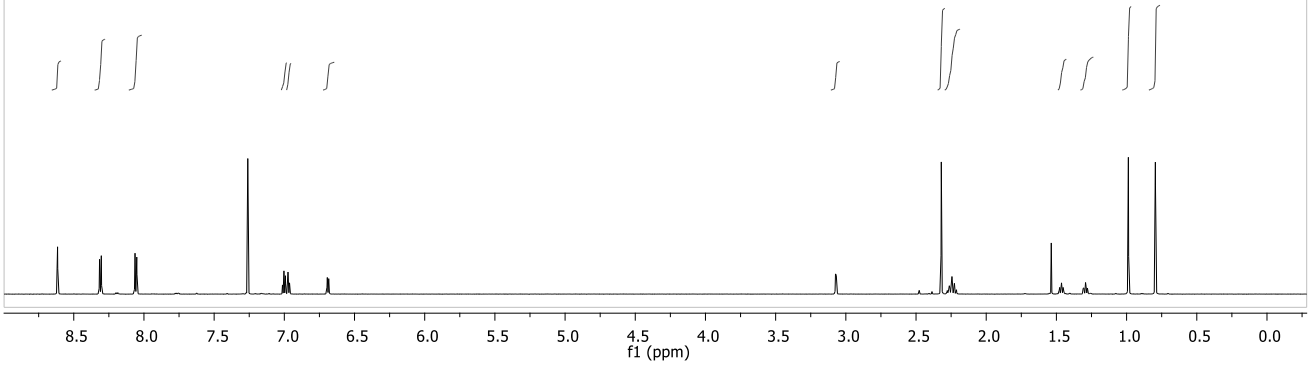
In a dry vial under inert atmosphere, cyclopropylimine **1c** (47.4 mg, 142 μmol) was dissolved in 1.5 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 6 hrs,[12] using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was clear and light red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (8% ethyl acetate:hexanes; loaded residue with PhMe). Obtained 35.5 mg of a light yellow solid, determined to be clean 1-aminoNB **2c** (74.9% yield).

*Characterization Data for C11-methyl 1-aminoNB **2c**[13]:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.62 (s, 1H, imine CH), 8.31 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.06 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 7.00 (*app.* t, 1H, *J* = 7.4 Hz, C9), 6.97 (d, 1H, *J* = 7.5 Hz, C8/C10), 6.69 (d, 1H, *J* = 7.1 Hz, C8/C10), 3.07 (d, 1H, *J* = 3.8 Hz, C4), 2.32 (s, 3H, C11-Me), 2.29-2.21 (m, 2H, C3-eq, C2-eq), 1.48-1.44 (m, 1H, C2-ax), 1.31-1.27 (m, 1H, C3-ax), 0.99 (s, 3H, C7-Me), 0.80 (s, 3H, C7-Me) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 158.9, 149.2, 147.5, 145.1, 142.4, 131.0, 129.0, 127.4, 125.4, 124.0, 116.9, 80.4, 59.7, 49.2, 28.5, 25.9, 20.2, 19.4, 18.2 ppm
IR (neat): 2961, 1639, 1599, 1517, 1476, 1381, 1341, 1288, 1184, 1105, 856, 770, 746, 691 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{21}H_{23}N_2O_2^+$: 335.1754, Found: 335.1757
R_f = 0.70 (20% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

[12] Time course adjusted to account for the smaller amount of starting material.
[13] Assignments based on analogy to related scaffolds.

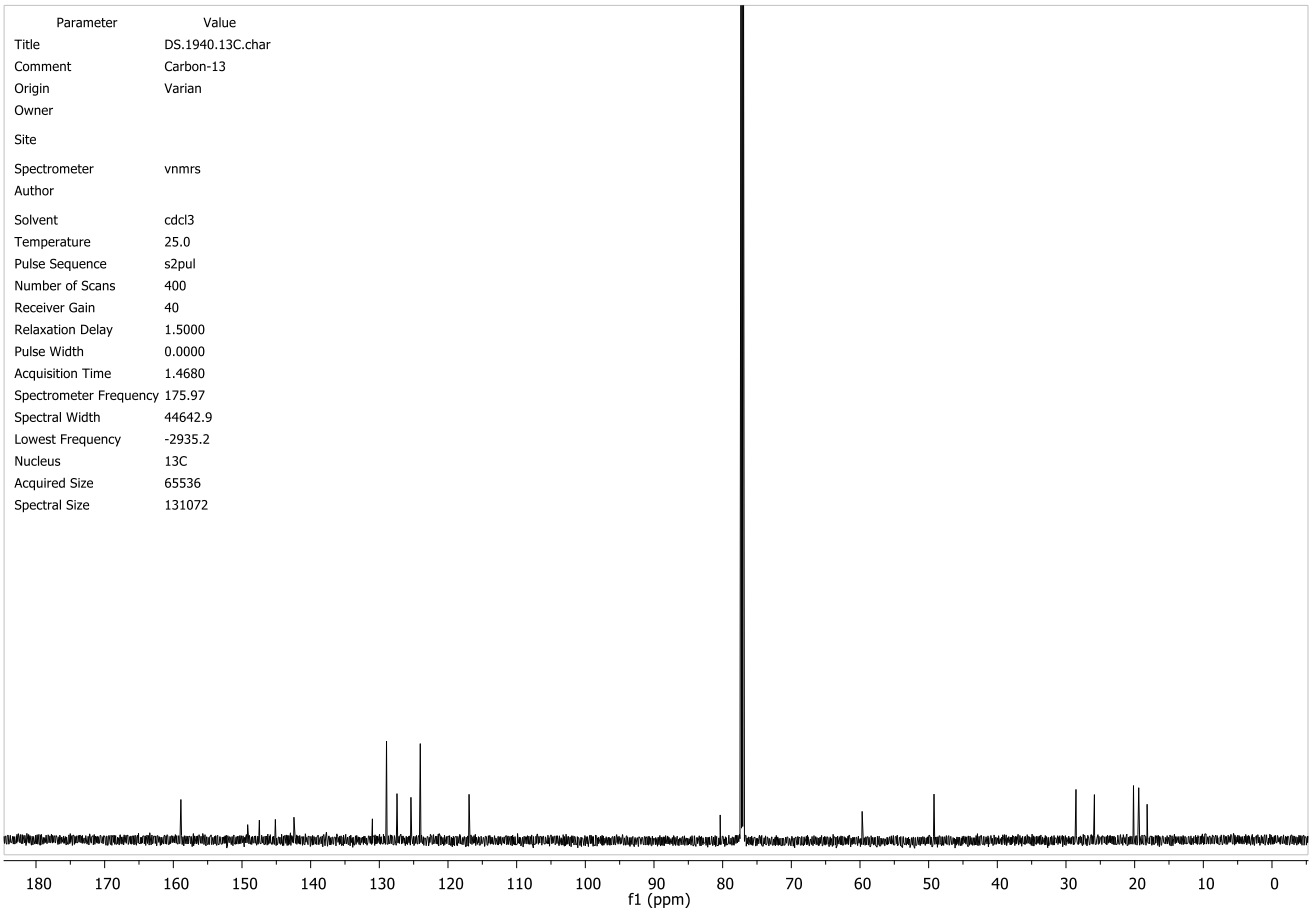
^{1}H NMR (700 MHz, $CDCl_3$) for 2c

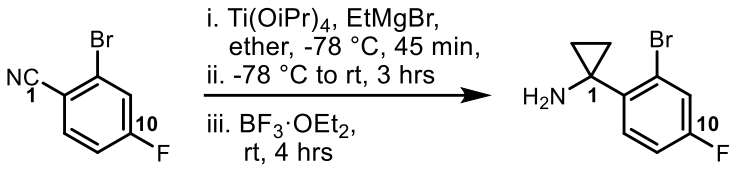
Parameter	Value
Title	DS.1940.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	56
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 2c

Parameter	Value
Title	DS.1940.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	400
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.2
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S11 ***59%*** **S12**

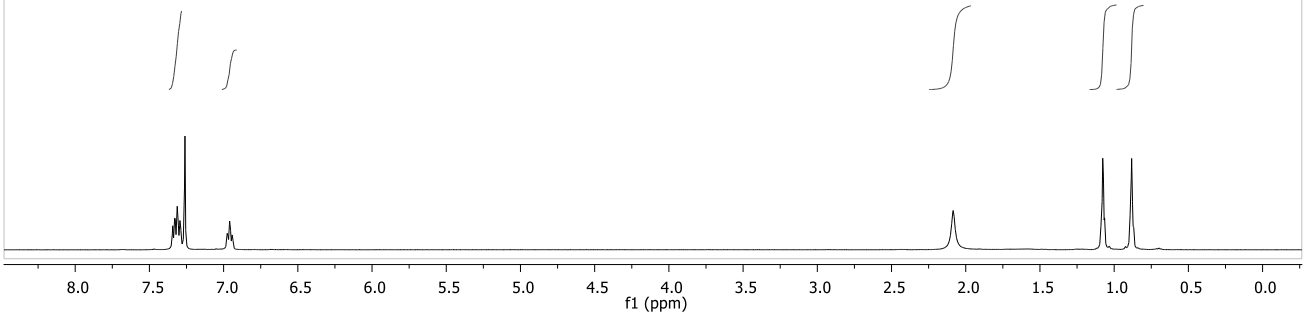
Procedure for C10-fluoro aminocyclopropane S12

2-Bromo-4-fluorobenzonitrile **S11** (3.0 g, 15 mmol; purchased from Matrix Scientific) was dissolved in 85 mL dry ether in a dry flask under inert atmosphere, then cooled to -78 °C. Titanium isopropoxide (4.91 mL, 16.5 mmol; purchased from Oakwood Chemical) was added in one portion, followed by addition of ethylmagnesium bromide (3.0 M in ether, 11 mL, 33 mmol) via syringe, dropwise down the side of the vial over the course of 10 min. The dark orange-brown reaction mixture (clear, colorless at outset of EtMgBr addition) was stirred at 1 hr while coming to room temp, cold bath was removed, and the reaction was stirred an additional 3 hrs at room temp turning a dark red-brown color during this time. BF_3·etherate (3.71 mL, 30.1 mmol) was added dropwise over the course of 2 min, and the reaction mixture was stirred 4 hrs at room temp. The reaction was quenched by carefully pouring in 100 mL of a 3:1 mix of sat. Rochelle salt:1 M NaOH (aq), followed by 15 min of vigorous stirring at room temp. The biphasic mixture was diluted with an additional 100 mL of the same aqueous mixture and 100 mL ether. The phases were separated. The aqueous phase was extracted with three 100 mL portions of ether. The combined organics were then washed with 100 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under vacuum. The crude residue was purified via flash chromatography over silica (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; the silica was pre-neutralized with 8% ethyl acetate:hexanes + 1% NEt_3; the residue was loaded with PhMe). Collected 2.04 g of aminocyclopropane **S12** (59.1% yield) as a yellow oil.

*Characterization Data for C10-fluoro aminocyclopropane **S12**:*
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.38-7.27 (m, 2H, Ar), 6.96 (td, 1H, *J* = 8.3, 2.3 Hz, Ar), 2.08 (bs, 2H, NH_2), 1.08 (*app.* t, 2H, *J* = 5.4 Hz, CP), 0.88 (*app.* t, 2H, *J* = 5.4 Hz, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 161.2 (d, *J* = 250.0 Hz), 140.8 (d, *J* = 3.5 Hz), 131.1 (d, *J* = 8.4 Hz), 125.4 (d, *J* = 9.7 Hz), 120.3 (d, *J* = 24.4 Hz), 114.4 (d, *J* = 20.7 Hz), 38.2, 15.7 ppm
IR (neat): 3089, 3010, 1598, 1584, 1482, 1387, 1257, 1203, 1107, 1030, 891, 817, 729 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_9H_{10}BrFN^+$: 229.9975, Found: 229.9979
R_f = 0.25 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

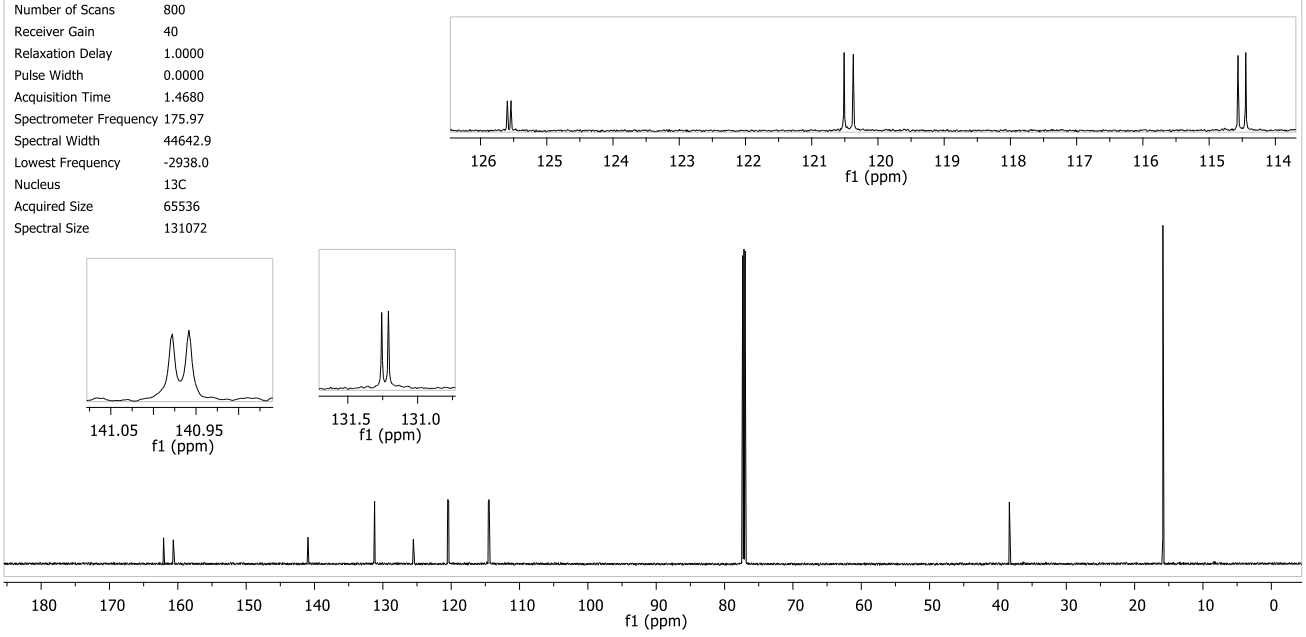
^{1}H NMR (500 MHz, $CDCl_3$) for S12

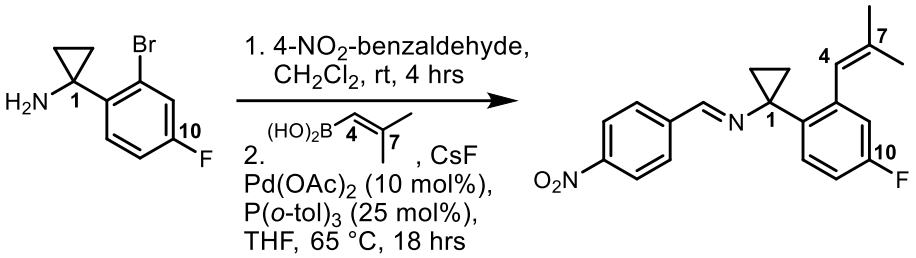
Parameter	Value
Title	RCM_574_B_PDT_HNMR_FINAL
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	50
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1006.8
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



^{13}C NMR (176 MHz, $CDCl_3$) for S12

Parameter	Value
Title	RCM_574_Pdt_CNMR_final
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	800
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2938.0
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for C10-fluoro cyclopropylimine 1d

Aminocyclopropane **S12** (1.5 g, 6.5 mmol) was dissolved in 40 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (2.46 g, 16.3 mmol) in one portion. The reaction mixture was stirred at room temp for 6 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (1 to 2 to 3 to 5 to 10 to 20% ethyl acetate:hexanes). Collected 1.90 g of the Schiff base intermediate (80.1% yield) as a yellow oil. Partial characterization is provided below.

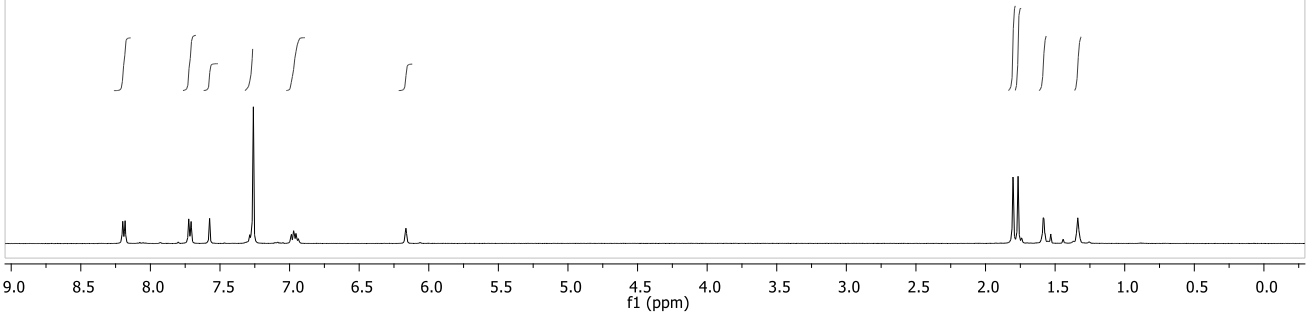
Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.20 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.77 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.61 (s, 1H, imine-CH), 7.40 (dd, 1H, *J* = 8.2, 1.8 Hz, Ar), 7.35 (dd, 1H, *J* = 7.9, 6.5 Hz, Ar), 7.09 (td, 1H, *J* = 8.3, 1.7 Hz, Ar), 1.74-1.69 (*app.* q, 2H, *J* = 4.9 Hz, CP), 1.43 (*app.* q, 2H, *J* = 4.9 Hz, CP) ppm
R_f = 0.80 (20% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (1.05 g, 6.88 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2 and adding 5 mL dry, degassed THF (degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask). In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (30.9 mg, 138 µmol) and tris(o-tolyl)phosphine (83.8 mg, 275 µmol) were dissolved in 5 mL dry, degassed THF, then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (500 mg, 1.38 mmol) was dissolved in 5 mL dry, degassed THF before adding (2,2-dimethyl)vinylboronic acid (206 mg, 2.07 mmol; purchased from Synthonix) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with three 3 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~50 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was loaded with PhMe). Obtained vinylated cyclopropylimine **1d** as a clear and colorless oil, 186 mg (32% yield over 2 steps).

*Characterization Data for C10-fluoro cyclopropylimine **1d**:*
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.19 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.72 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.57 (s, 1H, imine-CH), 7.30-7.26 (m, 1H, Ar), 7.01-6.91 (m, 2H, Ar), 6.16 (s, 1H, C4-H), 1.80 (s, 3H, C7-Me), 1.77 (s, 3H, C7-Me), 1.58 (*app.* q, 2H, *J* = 4.3 Hz, CP), 1.33 (*app.* q, 2H, *J* = 4.3 Hz, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 162.0 (d, *J* = 246.3 Hz), 154.5, 148.5, 142.2, 142.0 (d, *J* = 8.0 Hz), 136.7, 132.8 (d, *J* = 8.6 Hz), 132.7 (d, *J* = 3.1 Hz), 128.1, 123.8, 122.8, 116.8 (d, *J* = 21.3 Hz), 113.3 (d, *J* = 21.1 Hz), 49.5, 26.4, 19.4, 18.4 ppm
^{19}F NMR ($CDCl_3$, 376 MHz): δ = -114.5 (dd, *J* = 15.3, 8.8 Hz) ppm
IR (neat): 3081, 2978, 2913, 1596, 1576, 1512, 1447, 1345, 1314, 1163, 1110, 882, 830, 748, 688 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{20}H_{20}FN_2O_2^+$: 339.1503, Found: 339.1506
R_f = 0.35 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

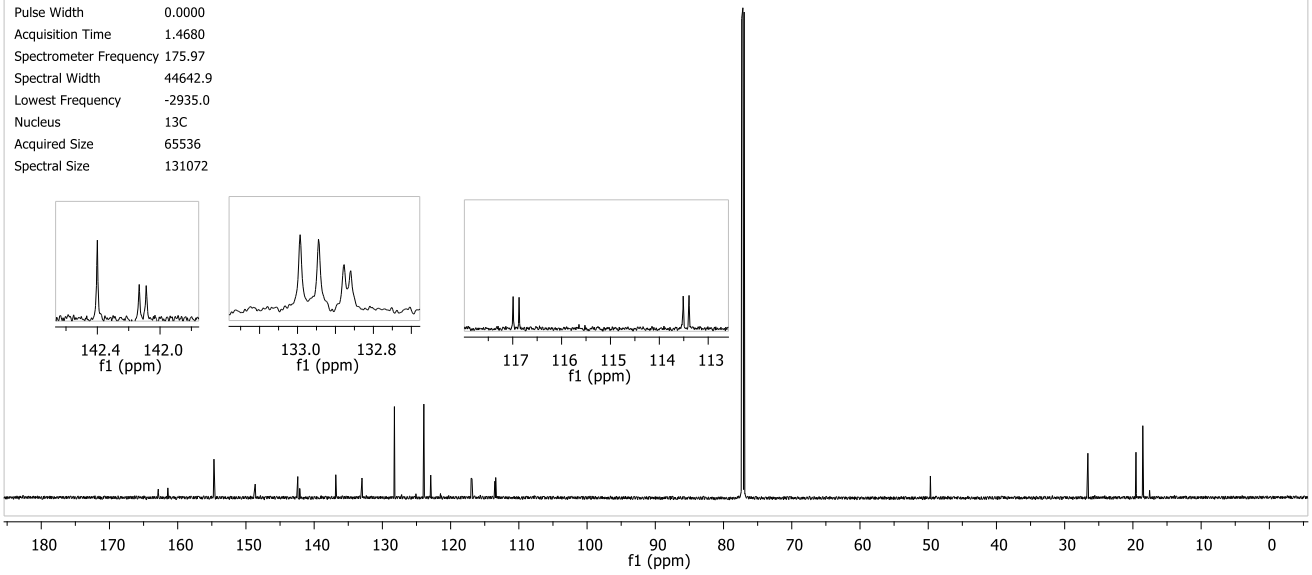
^{1}H NMR (500 MHz, $CDCl_3$) for 1d

Parameter	Value
Title	RCM_579_PDT_HNMR_FINAL_2
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	50
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1006.8
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



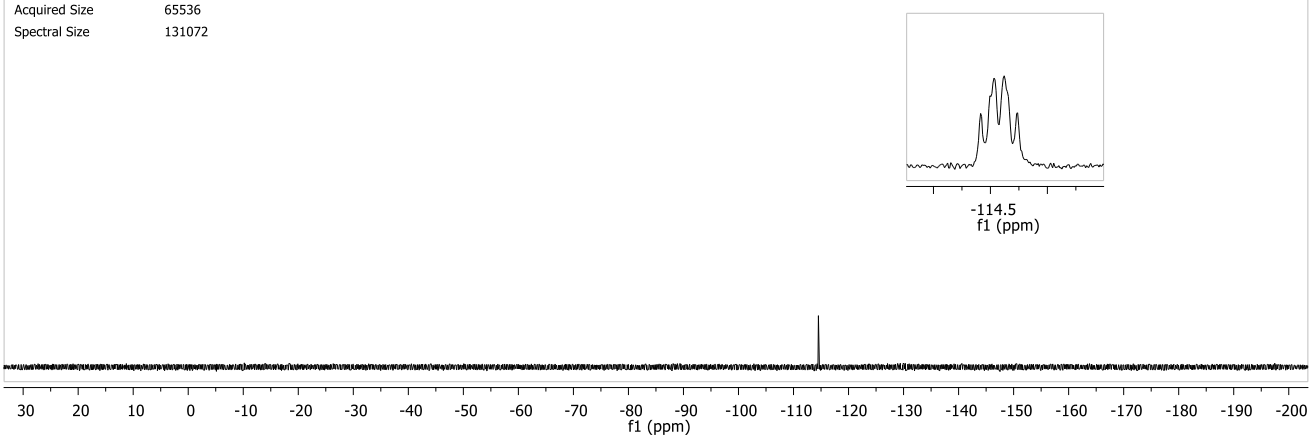
^{13}C NMR (176 MHz, $CDCl_3$) for 1d

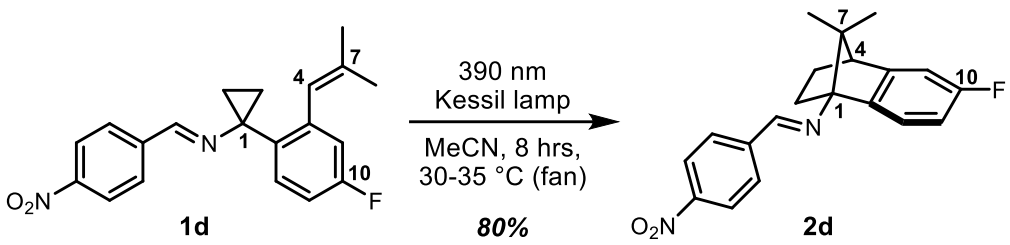
Parameter	Value
Title	RCM_579_Pdt_CNMR
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	1488
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.0
Nucleus	13C
Acquired Size	65536
Spectral Size	131072



^{19}F NMR (376 MHz, $CDCl_3$) for 1d

Parameter	Value
Title	RCM_579_pdt_FNMR_final
Comment	STANDARD FLUORINE PARAMETERS
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.7340
Spectrometer Frequency	376.83
Spectral Width	89285.7
Lowest Frequency	-76676.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072





Procedure for C10-fluoro 1-aminoNB 2d

In a dry vial under inert atmosphere, cyclopropylimine **1d** (69.5 mg, 205 μmol) was dissolved in 2.1 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 8 hrs, using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was clear and light red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (20 to 30 to 40% ethyl acetate:hexanes; loaded residue with PhMe). Obtained 55.6 mg of a light yellow solid, determined to be clean 1-aminoNB **2d** (80.0% yield).

*Characterization Data for C10-fluoro 1-aminoNB **2d**[14]:*

^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.61 (s, 1H, imine CH), 8.31 (d, 2H, J = 8.6 Hz, 4-NO_2-Ar), 8.05 (d, 2H, J = 8.6 Hz, 4-NO_2-Ar), 6.93 (dd, 1H, J = 8.4, 2.2 Hz, C11), 6.80 (dd, 1H, J = 8.0, 5.1 Hz, C8), 6.78-6.75 (m, 1H, C9), 2.97 (d, 1H, J = 3.8 Hz, C4), 2.30-2.22 (m, 2H, C3-eq, C2-eq), 1.48-1.43 (m, 1H, C2-ax), 1.36-1.30 (m, 1H, C3-ax), 0.97 (s, 3H, C7-Me), 0.81 (s, 3H, C7-Me) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 161.9 (J_{CF} = 243 Hz, C10), 159.1, 149.3, 148.9 (J_{CF} = 8.0 Hz), 143.3 (J_{CF} = 2.5 Hz), 142.2, 129.0, 124.1, 120.6 (J_{CF} = 8.7 Hz), 111.6 (J_{CF} = 22.2 Hz), 109.9 (J_{CF} = 23.0 Hz), 79.7, 60.4, 51.7, 28.3, 26.6, 20.1, 19.3 ppm

^{19}F NMR ($CDCl_3$, 376 MHz): δ = -116.7 (td, J = 8.9, 4.5 Hz) ppm

IR (neat): 2959, 1642, 1600, 1520, 1468, 1343, 1289, 1231, 1115, 930, 887, 862, 839, 746, 690 cm^{-1}

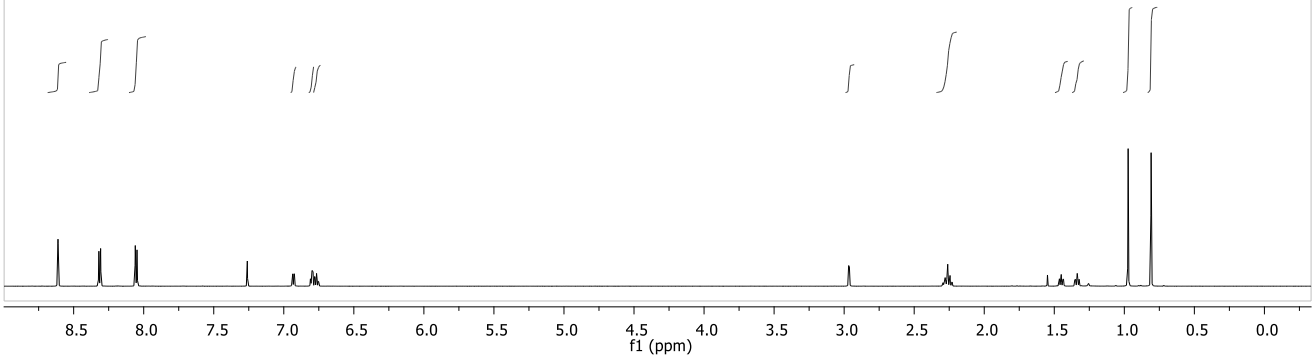
HRMS (ES+, *m/z)* calculated for $C_{20}H_{20}FN_2O_2^+$: 339.1503, Found: 339.1509

R_f = 0.45 (10% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

[14] Assignments based on analogy to related scaffolds.

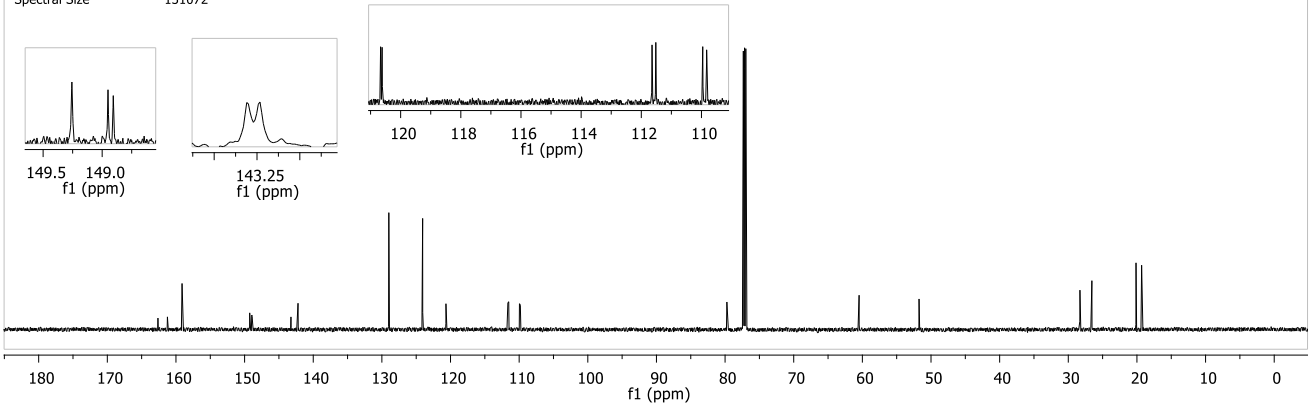
^{1}H NMR (700 MHz, $CDCl_3$) for 2d

Parameter	Value
Title	DS.1900.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	46
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



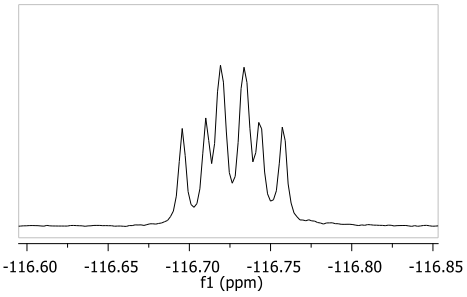
^{13}C NMR (176 MHz, $CDCl_3$) for 2d

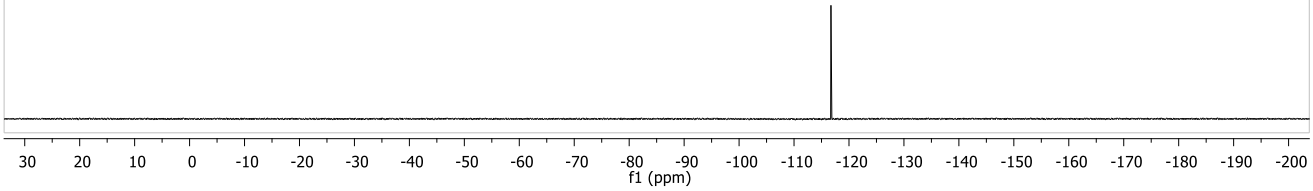
Parameter	Value
Title	DS.1900.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	176
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2936.3
Nucleus	13C
Acquired Size	65536
Spectral Size	131072

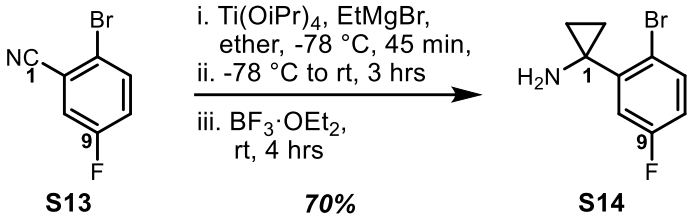


^{19}F NMR (376 MHz, $CDCl_3$) for 2d

Parameter	Value
Title	DS.1900.19F
Comment	Fluorine-19
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	24.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.7340
Spectrometer Frequency	375.91
Spectral Width	89285.7
Lowest Frequency	-76597.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072







S13 ***70%*** **S14**

Procedure for C9-fluoro aminocyclopropane S14

2-Bromo-5-fluorobenzonitrile **S13** (3.0 g, 15 mmol; purchased from Oakwood Chemical) was dissolved in 85 mL dry ether in a dry flask under inert atmosphere, then cooled to -78 °C. Titanium isopropoxide (4.91 mL, 16.5 mmol; purchased from Oakwood Chemical) was added in one portion, followed by addition of ethylmagnesium bromide (3.0 M in ether, 11 mL, 33 mmol) via syringe, dropwise down the side of the vial over the course of 10 min. The dark yellow-brown reaction mixture (clear, colorless at outset of EtMgBr addition) was stirred at 1 hr while coming to room temp, cold bath was removed, and the reaction was stirred an additional 3 hrs at room temp turning a dark red-brown color during this time. BF_3·etherate (3.71 mL, 30.1 mmol) was added dropwise over the course of 2 min, and the reaction mixture was stirred 4 hrs at room temp. The reaction was quenched by carefully pouring in 100 mL of a 3:1 mix of sat. Rochelle salt:1 M NaOH (aq), followed by 15 min of vigorous stirring at room temp. The biphasic mixture was diluted with an additional 100 mL of the same aqueous mixture and 100 mL ether. The phases were separated. The aqueous phase was extracted with three 100 mL portions of ether. The combined organics were then washed with 100 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under vacuum. The crude residue was purified via flash chromatography over silica (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; the silica was pre-neutralized with 8% ethyl acetate:hexanes + 1% NEt_3; the residue was loaded with PhMe). Collected 2.43 g of aminocyclopropane **S14** (70.4% yield) as a yellow oil.

*Characterization Data for C9-fluoro aminocyclopropane **S14**:*

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.50 (dd, 1H, *J* = 8.6, 5.3 Hz, Ar), 7.07 (dd, 1H, *J* = 9.1, 2.3 Hz, Ar), 6.84 (td, 1H, *J* = 8.0, 2.3 Hz, Ar), 2.11 (bs, 2H, NH_2), 1.09 (*app.* t, 2H, *J* = 5.3 Hz, CP), 0.90 (*app.* t, 2H, *J* = 5.3 Hz, CP) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 161.8 (d, *J* = 247.7 Hz), 146.7 (d, *J* = 6.7 Hz), 134.2 (d, *J* = 8.0 Hz), 119.3 (d, *J* = 3.2 Hz), 117.3 (d, *J* = 22.4 Hz), 115.4 (d, *J* = 22.4 Hz), 38.8 (d, *J* = 1.2 Hz), 15.5 ppm

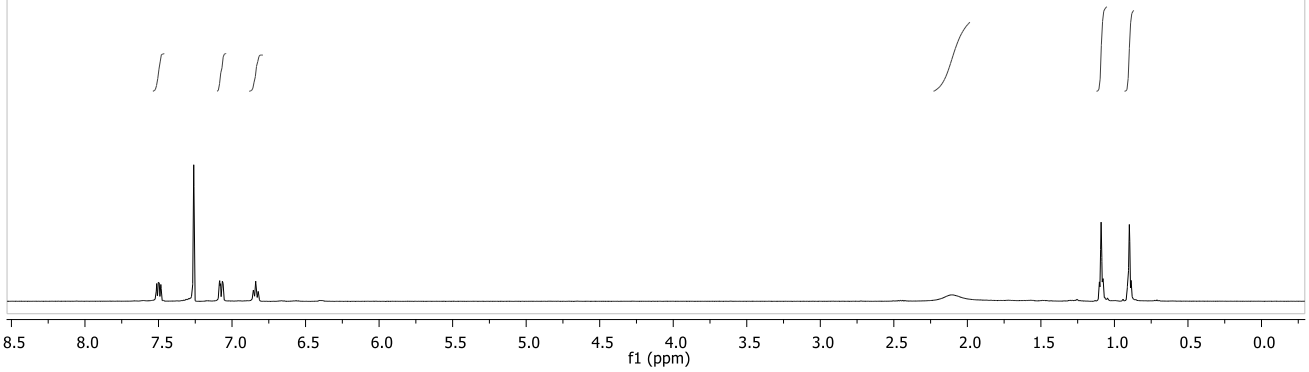
IR (neat): 3089, 3009, 2361, 2337, 1576, 1460, 1402, 1271, 1244, 1198, 1096, 1032 cm^{-1}

HRMS (ES+, *m/z)* calculated for $C_9H_{10}BrFN^+$: 229.9975, Found: 229.9977

R_f = 0.40 (50% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

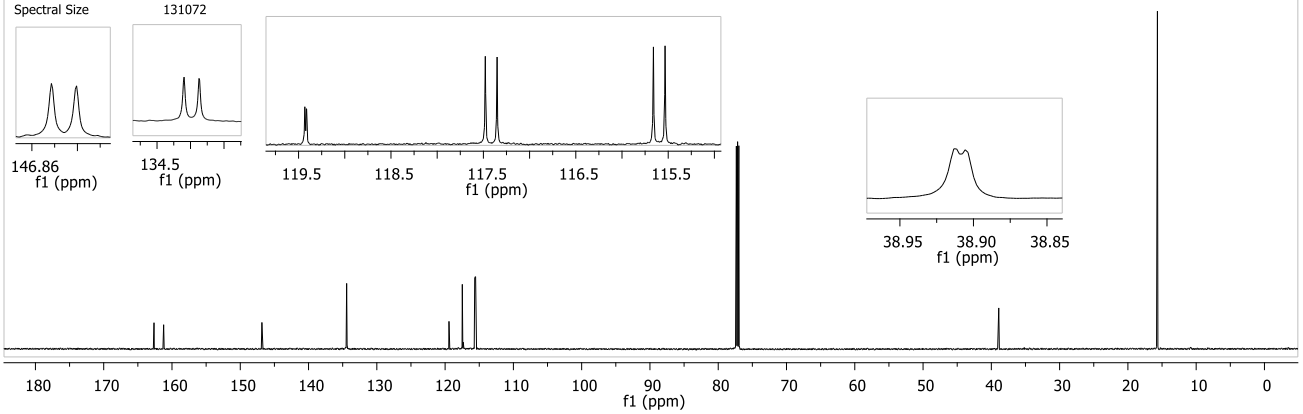
^{1}H NMR (500 MHz, $CDCl_3$) for S14

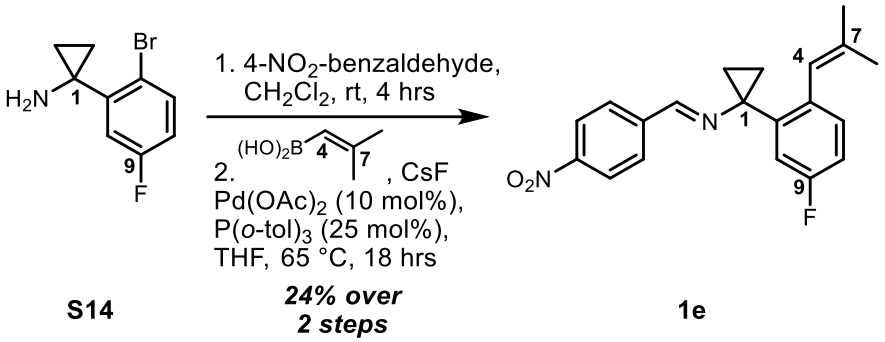
Parameter	Value
Title	RCM_565_Pdt_HNMR_final
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	50
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1006.8
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



^{13}C NMR (176 MHz, $CDCl_3$) for S14

Parameter	Value
Title	RCM_565_Pdt_CNMR_final
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	864
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2942.6
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S14 **1e**

Procedure for C9-fluoro cyclopropylimine 1e

Aminocyclopropane **S14** (1.0 g, 4.35 mmol) was dissolved in 30 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (1.64 g, 10.9 mmol) in one portion. The reaction mixture was stirred at room temp for 6 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (1 to 2 to 3 to 5 to 10 to 20% ethyl acetate:hexanes). Collected 1.50 g of the Schiff base intermediate (95.0% yield) as a clear oil. Partial characterization is provided below.

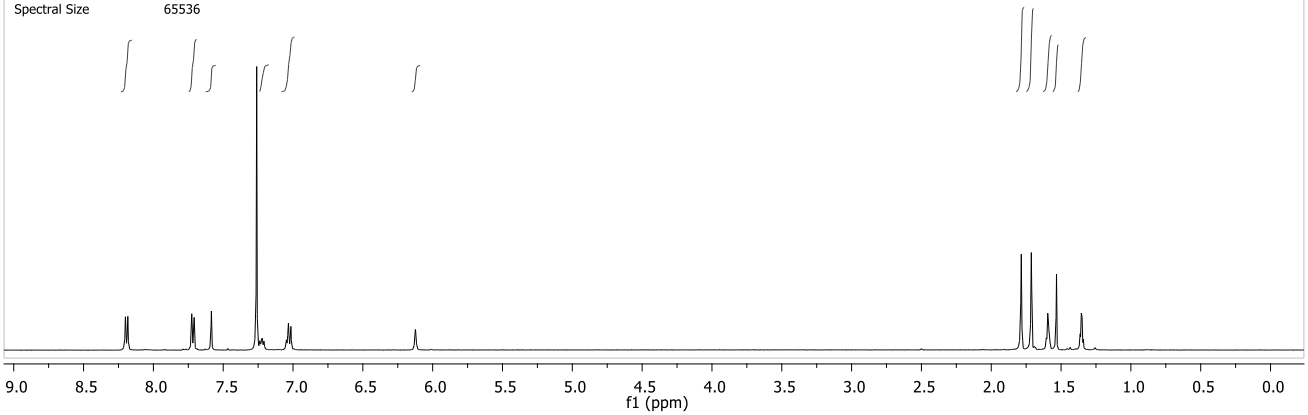
Characterization Data for C9-fluoro Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.20 (d, 2H, *J* = 8.3 Hz, 4-NO_2-Ar), 7.78 (d, 2H, *J* = 8.3 Hz, 4-NO_2-Ar), 7.63 (s, 1H, imine-CH), 7.61 (dd, 1H, *J* = 8.5, 5.4 Hz, Ar), 7.11 (dd, 1H, *J* = 8.7, 2.4 Hz, Ar), 6.99 (td, 1H, *J* = 8.1, 2.4 Hz, Ar), 1.73 (t, 2H, *J* = 5.7 Hz, C1-CH_2), 1.45 (t, 2H, *J* = 5.6 Hz, C1-CH_2) ppm
R_f = 0.80 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (1.05 g, 6.88 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2 and adding 5 mL dry, degassed THF (degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask). In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (30.9 mg, 138 µmol) and tris(o-tolyl)phosphine (83.8 mg, 275 µmol) were dissolved in 5 mL dry, degassed THF, then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (500 mg, 1.38 mmol) was dissolved in 5 mL dry, degassed THF before adding (2,2-dimethyl)vinylboronic acid (206 mg, 2.07 mmol; purchased from Synthonix) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with three 3 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~50 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was loaded with PhMe). Obtained vinylated cyclopropylimine **1e** as a clear and colorless oil, 115 mg (24% yield over 2 steps).

*Characterization Data for C9-fluoro cyclopropylimine **1e**:*
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.19 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.72 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.58 (s, 1H, imine-CH), 7.24-7.20 (m, 1H, Ar), 7.03 (m, 2H, Ar), 6.12 (s, 1H, C4-H), 1.78 (s, 3H, C7-Me), 1.71 (s, 3H, C7-Me), 1.59 (*app.* q, 2H, *J* = 4.4 Hz, CP), 1.35 (*app.* q, 2H, *J* = 4.4 Hz, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 161.4 (d, *J* = 246.4 Hz), 154.7, 148.5, 142.2, 139.1 (d, *J* = 6.7 Hz), 135.8 (d, *J* = 3.3 Hz), 135.6, 131.7 (d, *J* = 7.7 Hz), 128.1, 123.8, 122.7, 117.8 (d, *J* = 20.8 Hz), 114.5 (d, *J* = 20.8 Hz), 50.0, 26.3, 19.3, 18.3 ppm
^{19}F NMR ($CDCl_3$, 376 MHz): δ = -115.8 (dd, *J* = 14.8, 8.3 Hz) ppm
IR (neat): 2974, 2910, 2362, 2337, 1599, 1519, 1481, 1343, 1221, 902, 848, 748 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{20}H_{20}FN_2O_2^+$: 339.1503, Found: 339.1513
R_f = 0.35 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

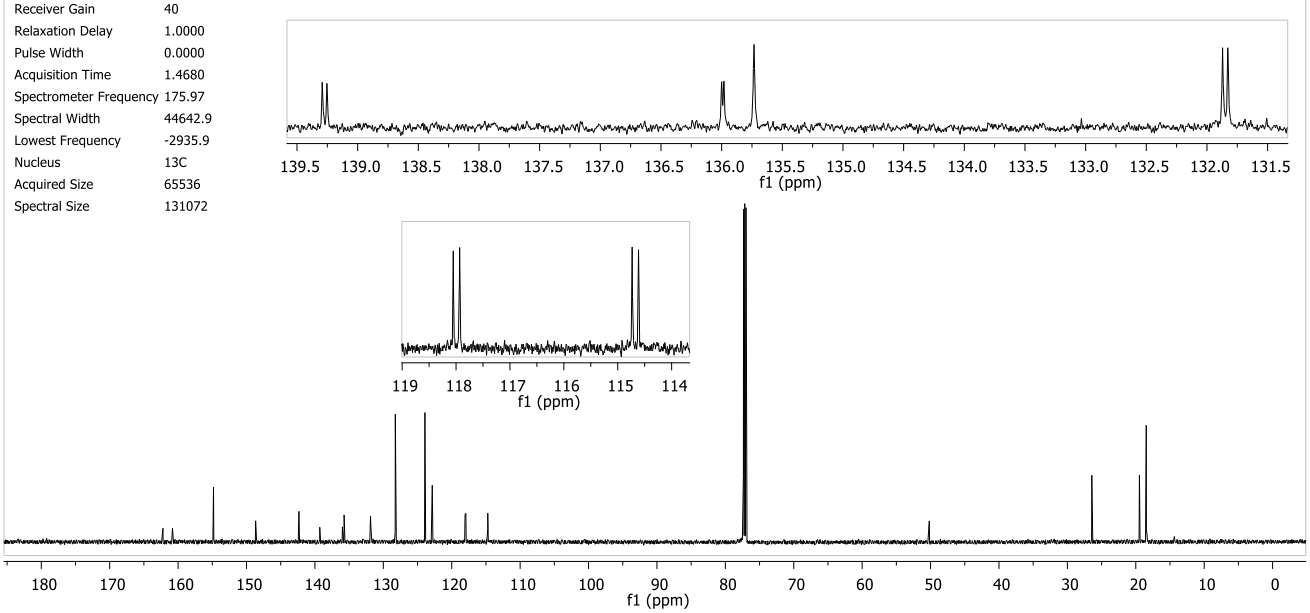
^{1}H NMR (500 MHz, $CDCl_3$) for 1e

Parameter	Value
Title	RCM_572_Pdt_HNMR_final
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	52
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1006.8
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



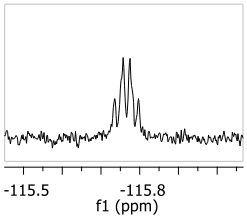
^{13}C NMR (176 MHz, $CDCl_3$) for 1e

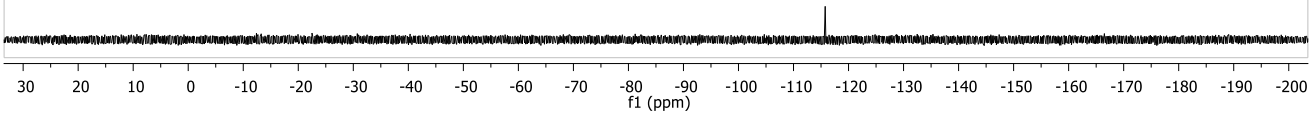
Parameter	Value
Title	RCM_572_Pdt_CNMR_final
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	704
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.9
Nucleus	13C
Acquired Size	65536
Spectral Size	131072



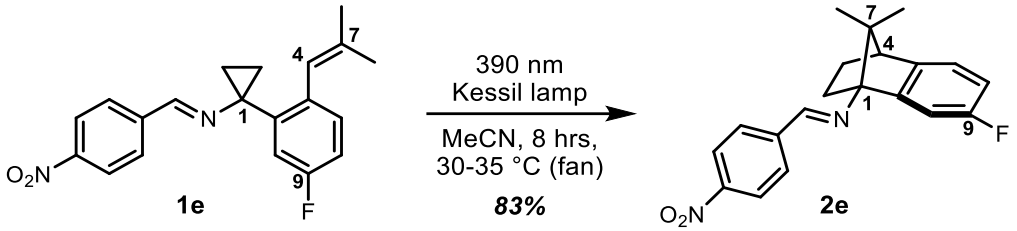
^{19}F NMR (376 MHz, $CDCl_3$) for 1e

Parameter	Value
Title	RCM_572_pdt_FNMR
Comment	STANDARD FLUORINE PARAMETERS
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	54
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.7340
Spectrometer Frequency	376.83
Spectral Width	89285.7
Lowest Frequency	-76676.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072





30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)



Procedure for C9-fluoro 1-aminoNB 2e

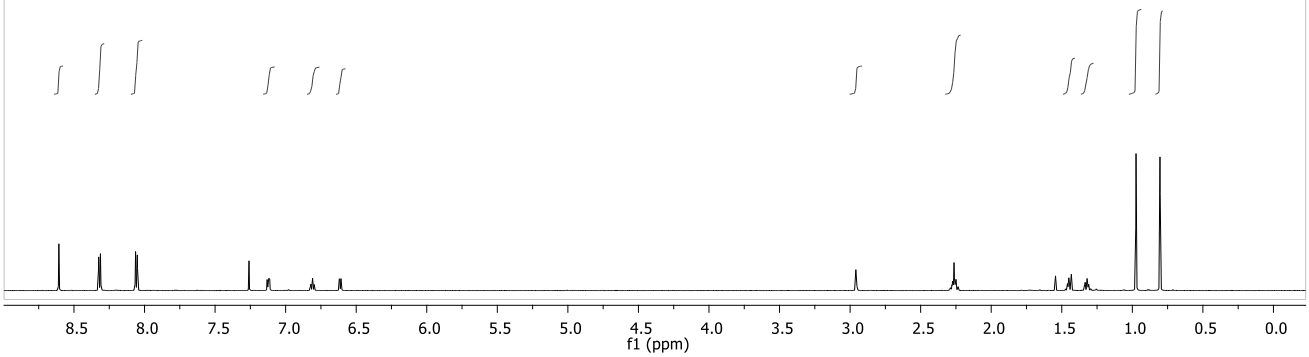
In a dry vial under inert atmosphere, cyclopropylimine **1e** (64.7 mg, 191 μmol) was dissolved in 2.0 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 8 hrs, using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was clear and light red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (10% ethyl acetate:hexanes; loaded residue with PhMe). Obtained 53.6 mg of a light yellow solid, determined to be clean 1-aminoNB **2e** (82.8% yield).

*Characterization Data for C9-fluoro 1-aminoNB **2e**[15]:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.61 (s, 1H, imine CH), 8.32 (d, 2H, *J* = 8.5 Hz, 4-NO_2-Ar), 8.06 (d, 2H, *J* = 8.5 Hz, 4-NO_2-Ar), 7.12 (dd, 1H, *J* = 7.9, 4.9 Hz, C11), 6.86-6.74 (m, 1H, C10), 6.61 (dd, 1H, *J* = 8.3, 2.2 Hz, C8), 2.96 (d, 1H, *J* = 3.4 Hz, C4), 2.30-2.23 (m, 2H, C3-eq, C2-eq), 1.48-1.42 (m, 1H, C2-ax), 1.34-1.29 (m, 1H, C3-ax), 0.97 (s, 3H, C7-Me), 0.80 (s, 3H, C7-Me) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 161.6 (J_{CF} = 243 Hz, C9), 159.2, 149.9 (J_{CF} = 7.3 Hz), 149.3, 142.3 (J_{CF} = 2.6 Hz), 142.1, 129.0, 124.1, 122.7 (J_{CF} = 8.1 Hz), 112.3 (J_{CF} = 22.1 Hz), 107.9 (J_{CF} = 23.5 Hz), 80.4, 60.7, 51.0, 28.1, 26.8, 20.1, 19.3 ppm
^{19}F NMR ($CDCl_3$, 376 MHz): δ = -116.9 (td, *J* = 9.2, 5.0 Hz) ppm
IR (neat): 2961, 1643, 1602, 1522, 1468, 1344, 1217, 1175, 859, 839, 823, 746, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated $C_{20}H_{20}FN_2O_2^+$: 339.1503, Found: 339.1509
R_f = 0.65 (20% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

[15] Assignments based on analogy to related scaffolds.

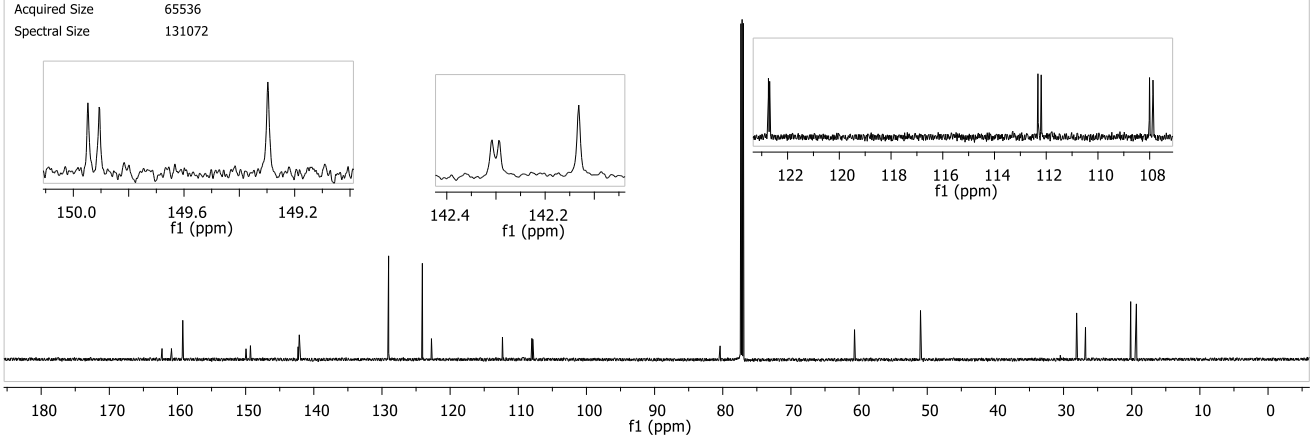
^{1}H NMR (700 MHz, $CDCl_3$) for 2e

Parameter	Value
Title	DS.1901.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	48
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1380.5
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



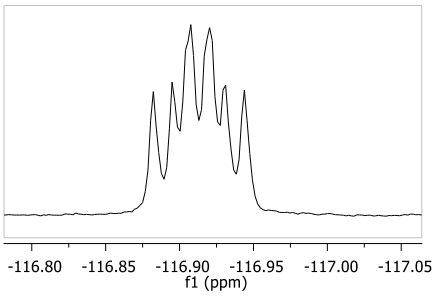
^{13}C NMR (176 MHz, $CDCl_3$) for 2e

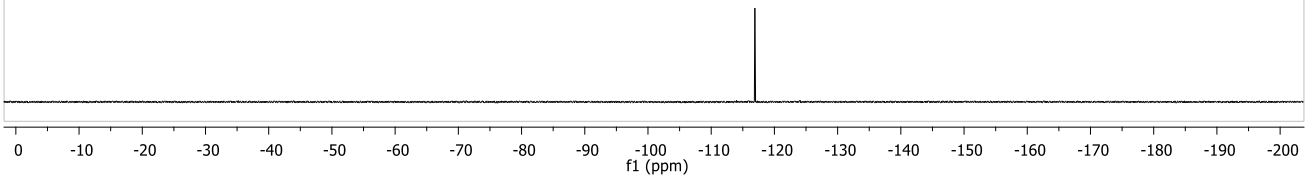
Parameter	Value
Title	DS.1901.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	368
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2936.3
Nucleus	13C
Acquired Size	65536
Spectral Size	131072

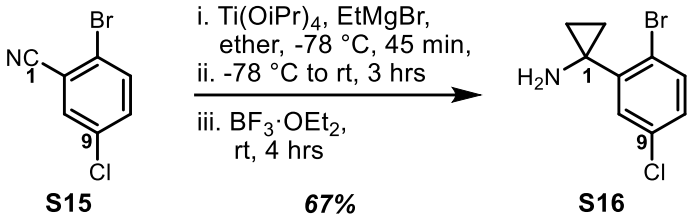


^{19}F NMR (376 MHz, $CDCl_3$) for 2e

Parameter	Value
Title	DS.1901.19F
Comment	Fluorine-19
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	24.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.7340
Spectrometer Frequency	375.91
Spectral Width	89285.7
Lowest Frequency	-76597.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072







S15 ***67%*** **S16**

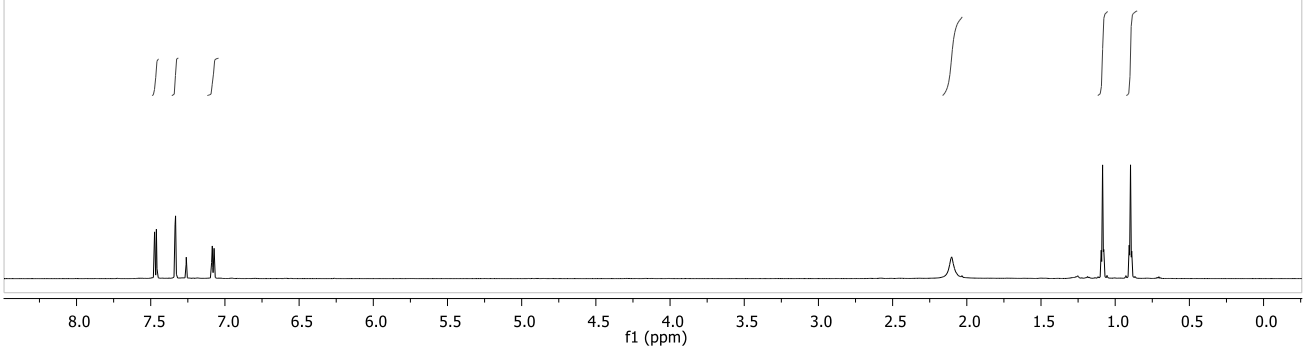
Procedure for C9-chloro aminocyclopropane S16

2-Bromo-5-chlorobenzonitrile **S15** (3.00 g, 13.9 mmol; purchased from Matrix Scientific) was dissolved in 112 mL dry ether in a dry flask under inert atmosphere, then cooled to -78 °C. Titanium isopropoxide (4.54 mL, 15.2 mmol; purchased from Oakwood Chemical) was added in one portion, followed by addition of ethylmagnesium bromide (3.0 M in ether, 10.2 mL, 30.5 mmol) via syringe, dropwise down the side of the vial over the course of 5 min. The dark brown-black reaction mixture (clear, colorless at outset of EtMgBr addition) was stirred at 45 min while coming to room temp, cold bath was removed, and the reaction was stirred an additional 3 hrs at room temp. BF3·etherate (3.43 mL, 27.8 mmol) was added dropwise over the course of 2 min, and the reaction mixture was stirred 4 hrs at room temp. The reaction was quenched by carefully pouring in 100 mL of a 3:1 mix of sat. Rochelle salt:1 M NaOH (aq), followed by 30 min of vigorous stirring at room temp. The biphasic mixture was diluted with an additional 100 mL of the same aqueous mixture and 200 mL ether. The phases were separated. The aqueous phase was extracted with three 100 mL portions of ether. The combined organics were then washed with 100 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under vacuum. The crude residue was purified via flash chromatography over silica (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; the silica was pre-neutralized with 8% ethyl acetate:hexanes + 1% NEt3; the residue was loaded with PhMe). Collected 2.30 g of aminocyclopropane **S16** (67.3% yield) as an orange oil.

*Characterization Data for C9-chloro aminocyclopropane **S16**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ= 7.47 (d, *J* = 8.4 Hz, 1H, Ar), 7.33 (d, *J* = 2.3 Hz, 1H, Ar), 7.08 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar), 2.10 (s, 2H, NH_2), 1.10-1.07 (m, 2H, C1-CH_2), 0.93-0.88 (m, 2H, C1-CH_2) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 146.3, 134.2, 133.3, 130.3, 128.4, 123.1, 38.7, 15.5 ppm
IR (neat): 1580, 1551, 1452, 1383, 1306, 1272, 1249, 1091, 1029, 1015, 993, 889, 811 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_9H_9BrClN^+$: 245.9680, Found: 245.9683
R_f = 0.40 (60% ethyl acetate:hexanes + 1% NH_4OH), one red spot, ninhydrin, UV

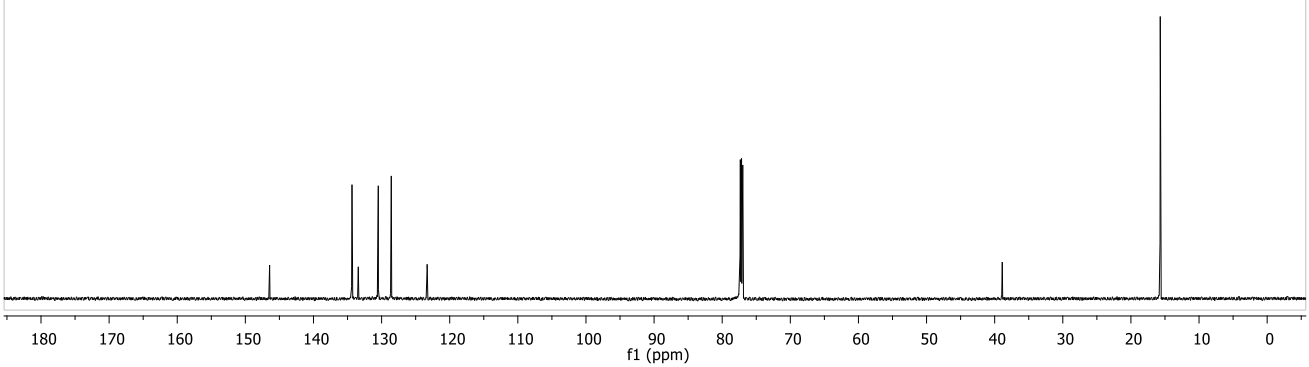
^{1}H NMR (700 MHz, $CDCl_3$) for S16

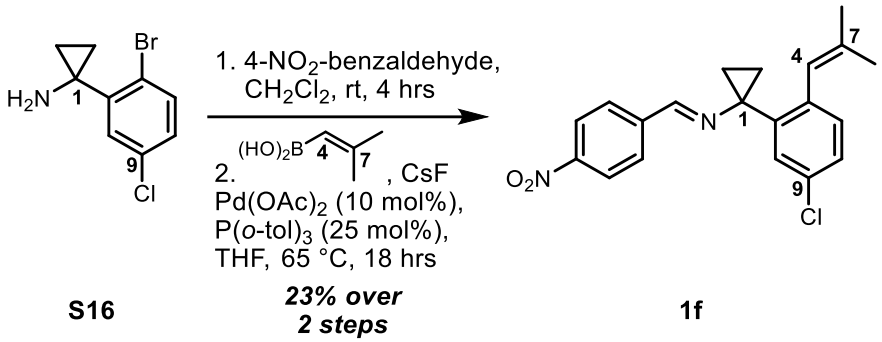
Parameter	Value
Title	JLC-0160product-1H
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	40
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for S16

Parameter	Value
Title	JLC-0160product-13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	784
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2939.4
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S16 **1f**

Procedure for C9-chloro cyclopropylimine 1f

Aminocyclopropane **S16** (200 mg, 0.811 mmol) was dissolved in 3.0 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (173 mg, 1.15 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (0 to 1 to 2 to 3 to 5 to 10% ethyl acetate:hexanes). Collected 211 mg of the Schiff base intermediate (68.5% yield) as an orange oil. Partial characterization is provided below.

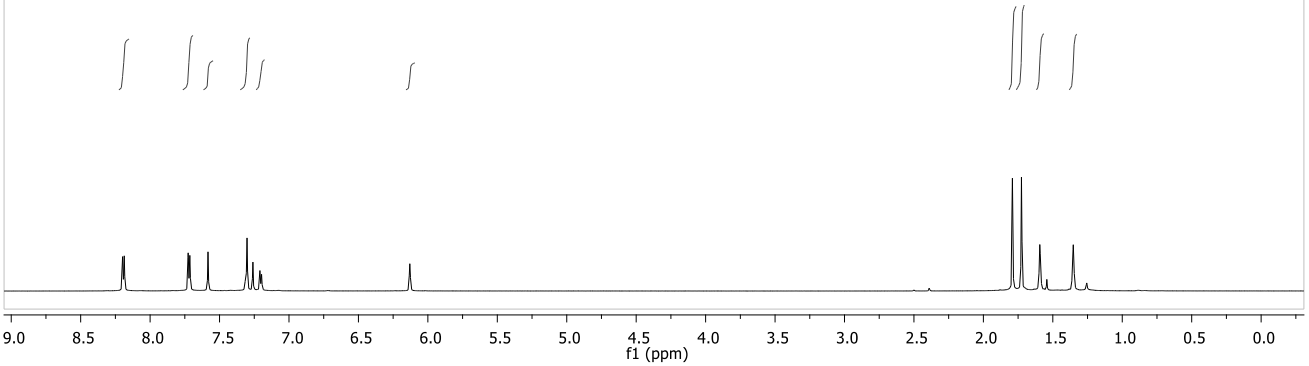
Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 401 MHz): δ = 8.19 (d, *J* = 8.7 Hz, 2H, 4-NO_2-Ar), 7.78 (d, *J* = 8.7 Hz, 2H, 4-NO_2-Ar), 7.63 (s, 1H, imine-CH), 7.57 (d, *J* = 8.5 Hz, 1H, Ar), 7.37 (d, *J* = 2.5 Hz, 1H, Ar), 7.23 (dd, *J* = 8.5, 2.5 Hz, 1H, Ar), 1.73 (*app.* q, *J* = 4.7 Hz, 2H, CP), 1.45 (*app.* q, *J* = 4.7 Hz, 2H, CP) ppm
R_f = 0.5 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (422 mg, 2.78 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2. In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (12.5 mg, 0.056 mmol) and tris(o-tolyl)phosphine (33.8 mg, 0.111 mmol) were dissolved in 4 mL dry, degassed THF(degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask), then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (211 mg, 0.56 mmol) was dissolved in 2 mL dry, degassed THF before adding (2,2-dimethyl)vinylboronic acid (83.3 mg, 0.834 mmol; purchased from Synthonix) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with two 0.5 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~100 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was loaded with PhMe. Obtained vinylated cyclopropylimine **1f** as a slighty yellow oil, 112 mg (21% yield over 2 steps).

*Characterization Data for C9-chloro cyclopropylimine **1f**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.19 (d, *J* = 8.3 Hz, 2H, 4-NO_2-Ar), 7.72 (d, *J* = 8.4 Hz, 2H, 4-NO_2-Ar), 7.58 (s, 1H, imine-CH), 7.31 (d, *J* = 6.8 Hz, 2H, Ar), 7.20 (d, *J* = 8.2 Hz, 1H, Ar), 6.13 (s, 1H, C4), 1.79 (s, 3H, C7-CH_3), 1.73 (s, 3H, C7-CH_3), 1.61-1.57 (m, 2H, CP), 1.36-1.33 (m, 2H, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 154.9, 148.7, 142.3, 139.0, 138.5, 136.4, 132.3, 131.6, 131.3, 128.3, 128.0, 123.9, 122.8, 50.1, 26.5, 19.5, 18.4 ppm
IR (neat): 2927, 2254, 1728, 1600, 1522, 1446, 1345, 1312, 1244, 1153, 1102, 905, 849, 832, 727 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{20}H_{19}ClN_2O_2^+$: 355.1208, Found: 355.1217
R_f = 0.60 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

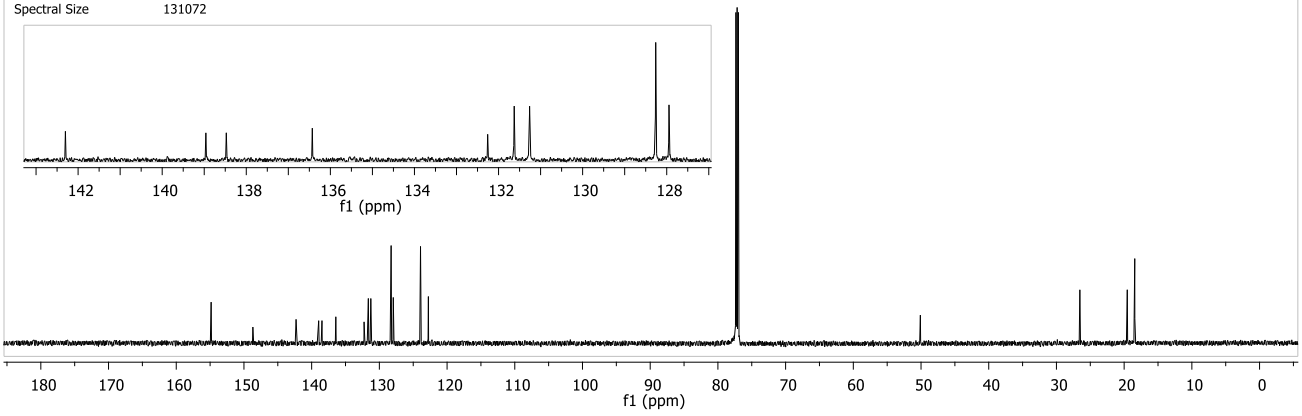
^{1}H NMR (700 MHz, $CDCl_3$) for 1f

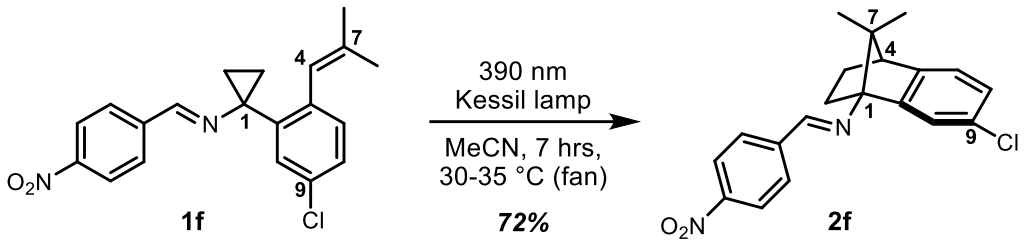
Parameter	Value
Title	JLC-0167product-1H
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	48
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 1f

Parameter	Value
Title	JLC-0167product-13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	416
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2936.3
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for C9-chloro 1-aminoNB 2f

In a dry vial under inert atmosphere, cyclopropylimine **1f** (59.9 mg, 169 μmol) was dissolved in 1.7 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 7 hrs,[16] using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was clear and light red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (2 to 5 to 10 to 15% ethyl acetate:hexanes; loaded residue with PhMe). Obtained 44.0 mg of a light yellow solid that was found to be 98.4 wt% pure (water contaminant), meaning that 43.3. mg of 1-aminoNB **2f** were produced (72.3% yield).

*Characterization Data for C9-chloro 1-aminoNB **2f**[17]:*

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.60 (s, 1H, imine CH), 8.32 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.06 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 7.14-7.10 (m, 2H, C10, C11), 6.86-6.74 (m, 1H, C10), 6.85 (s, 1H, C8), 2.96 (d, 1H, *J* = 3.5 Hz, C4), 2.31-2.21 (m, 2H, C3-eq, C2-eq), 1.50-1.42 (m, 1H, C2-ax), 1.34-1.27 (m, 1H, C3-ax), 0.97 (s, 3H, C7-Me), 0.81 (s, 3H, C7-Me) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 159.4, 149.8, 149.3, 145.3, 142.1, 131.2, 129.1, 126.2, 124.1, 123.0, 120.4, 80.2, 60.5, 51.1, 27.9, 26.6, 20.1, 19.3 ppm

IR (neat): 2960, 1642, 1601, 1520, 1452, 1413, 1343, 1285, 1266, 1205, 1156, 1130, 1065, 834, 744, 689 cm^{-1}

HRMS (ES+, *m/z)* calculated for $C_{20}H_{20}ClN_2O_2^+$: 355.1208, Found: 355.1208

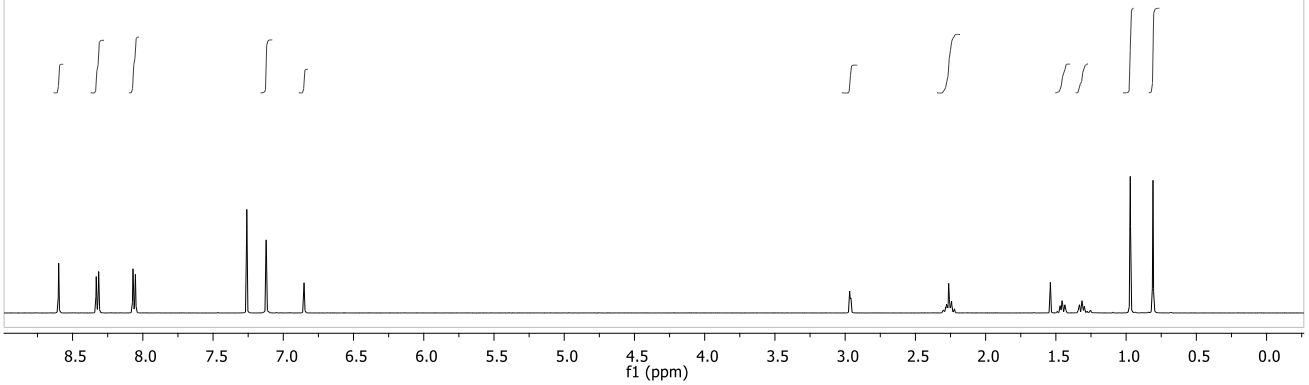
R_f = 0.55 (20% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

[16] Time course adjusted to account for the smaller amount of starting material.

[17] Assignments based on analogy to related scaffolds.

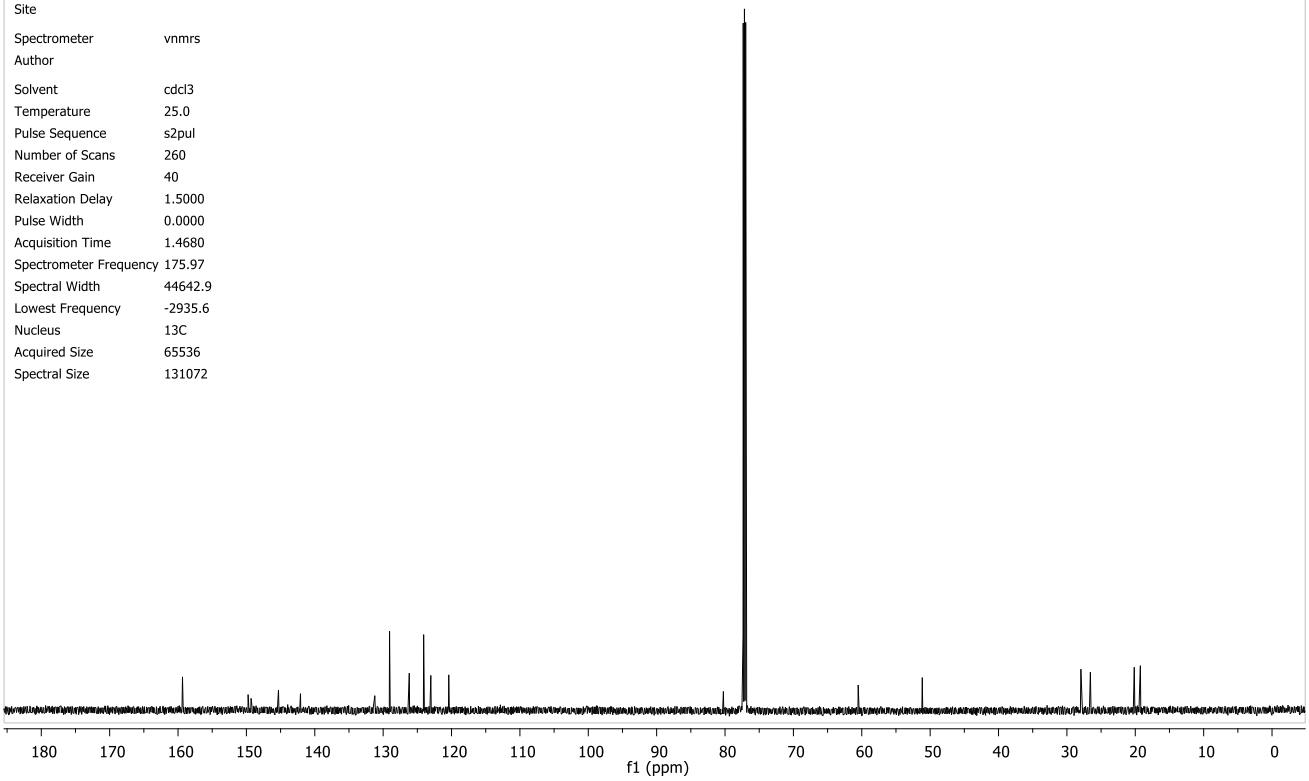
^{1}H NMR (500 MHz, $CDCl_3$) for 2f

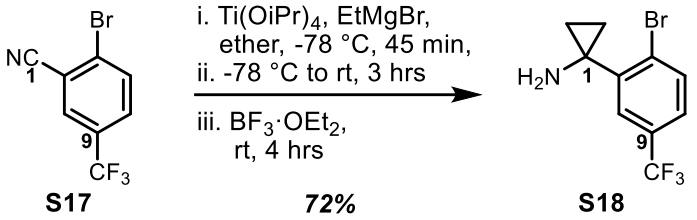
Parameter	Value
Title	DS.1939.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	58
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1007.2
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



^{13}C NMR (176 MHz, $CDCl_3$) for 2f

Parameter	Value
Title	DS.1939.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	260
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.6
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S17 ***72%*** **S18**

Procedure for C9-trifluoromethyl aminocyclopropane S18

2-Bromo-benzonitrile **S17** (3.00 g, 12.0 mmol; purchased from Matrix Scientific) was dissolved in 97 mL dry ether in a dry flask under inert atmosphere, then cooled to -78 °C. Titanium isopropoxide (3.93 mL, 13.2 mmol; purchased from Oakwood Chemical) was added in one portion, followed by addition of ethylmagnesium bromide (3.0 M in ether, 8.80 mL, 26.4 mmol) via syringe, dropwise down the side of the vial over the course of 5 min. The dark brown-black reaction mixture (clear, colorless at outset of EtMgBr addition) was stirred at 45 min while coming to room temp, cold bath was removed, and the reaction was stirred an additional 3 hrs at room temp. BF3·etherate (2.97 mL, 24.1 mmol) was added dropwise over the course of 2 min, and the reaction mixture was stirred 4 hrs at room temp. The reaction was quenched by carefully pouring in 100 mL of a 3:1 mix of sat. Rochelle salt:1 M NaOH (aq), followed by 30 min of vigorous stirring at room temp. The biphasic mixture was diluted with an additional 100 mL of the same aqueous mixture and 200 mL ether. The phases were separated. The aqueous phase was extracted with three 100 mL portions of ether. The combined organics were then washed with 100 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under vacuum. The crude residue was purified via flash chromatography over silica (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; the silica was pre-neutralized with 8% ethyl acetate:hexanes + 1% NEt3; the residue was loaded with PhMe). Collected 2.43 g of aminocyclopropane **S18** (72.3% yield) as an orange oil.

*Characterization Data for C9-trifluoromethyl cyclopropylimine **S18**:*

^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.67 (d, *J* = 8.2 Hz, 1H, Ar), 7.59 (s, 1H, Ar), 7.35 (d, *J* = 8.2 Hz, 1H, Ar), 2.13 (s, 2H, NH_2), 1.15-1.11 (m, 2H, CP), 0.96-0.90 (m, 2H, CP) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 145.8, 133.9, 130.2 (q, *J* = 32.6 Hz), 129.5, 127.1 (q, *J* = 3.7 Hz), 125.2 (q, *J* = 3.6 Hz), 123.9 (q, *J* = 272.4 Hz), 38.9, 15.8 ppm

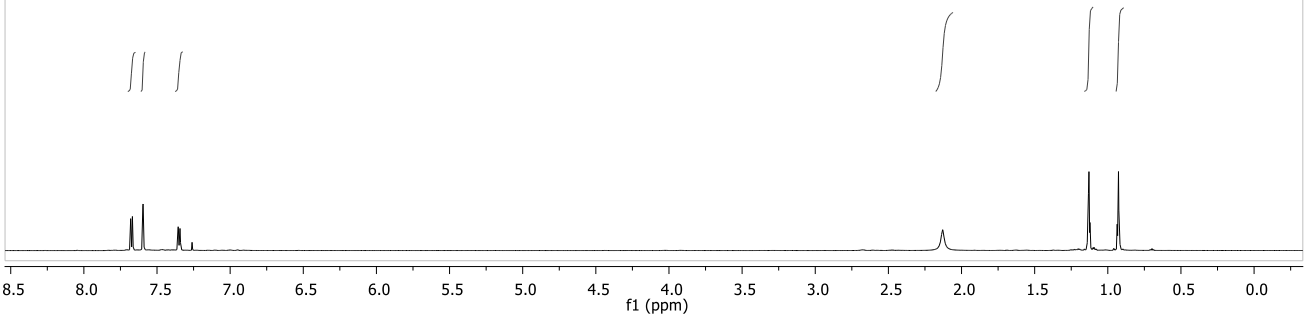
IR (neat): 3012, 1603, 1577, 1470, 1412, 1335, 1298, 1268, 1168, 1121, 1076, 1019, 823, 732, 712 cm^{-1}

HRMS (ES+, *m/z)* calculated for $C_{10}H_9BrF_3N^+$: 279.9943, Found: 279.9945

$\mathbf{R_f}$ = 0.70 (60% ethyl acetate:hexanes + 1% NH_4OH), one red spot, ninhydrin, UV

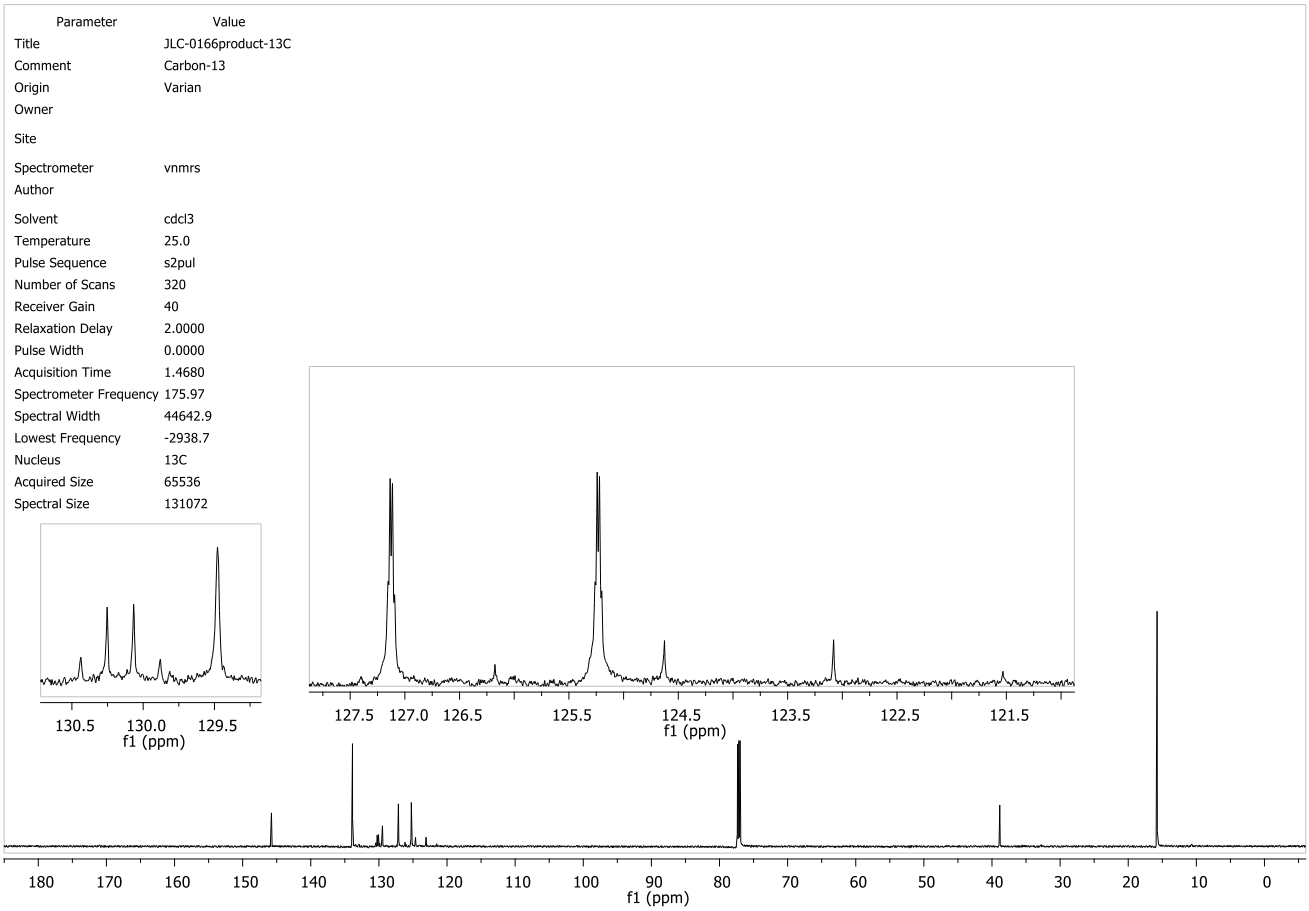
^{1}H NMR (700 MHz, $CDCl_3$) for S18

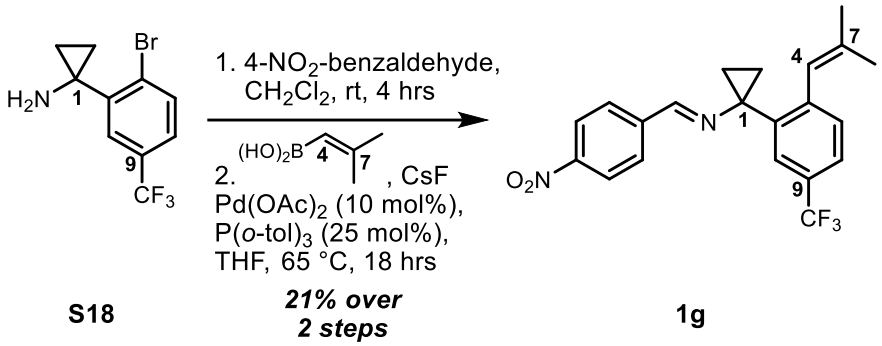
Parameter	Value
Title	JLC-0166product-1H
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	36
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for S18

Parameter	Value
Title	JLC-0166product-13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	320
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2938.7
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S18 **1g**

Procedure for C9-trifluoromethyl cyclopropylimine 1g

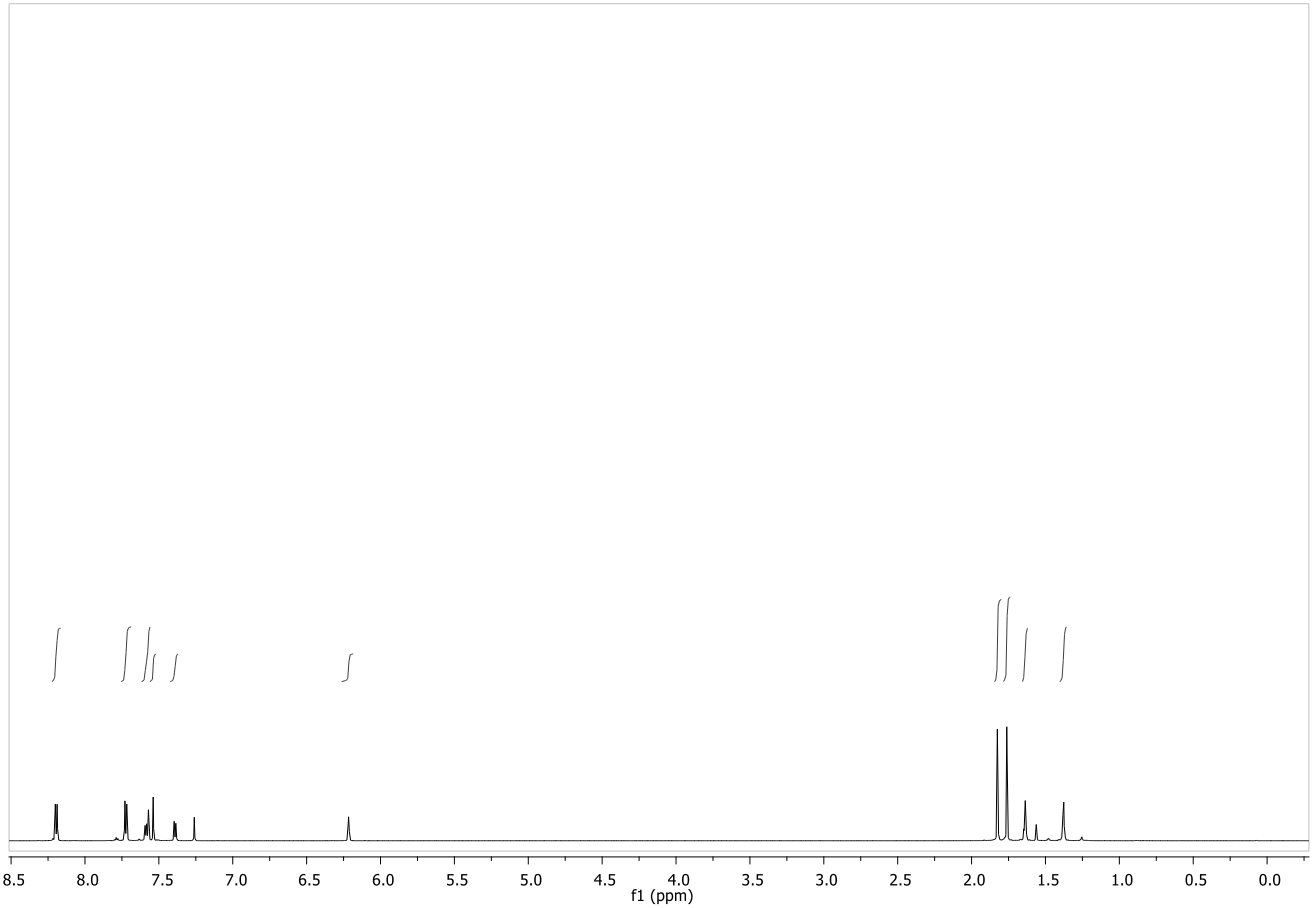
Aminocyclopropane **S18** (400 mg, 1.43 mmol) was dissolved in 5.4 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (305 mg, 2.02 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (0 to 1 to 2 to 3 to 5 to 10% ethyl acetate:hexanes). Collected 418 mg of the Schiff base intermediate (70.8% yield) as a yellow oil. Partial characterization is provided below.

Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 401 MHz): δ = 8.20 (d, *J* = 8.6 Hz, 2H, 4-NO_2-Ar), 7.82-7.75 (m, 3H, 4-NO_2-Ar, Ar), 7.64 (s, 1H, imine CH), 7.62-7.58 (m, 1H, Ar), 7.51 (d, *J* = 8.1 Hz, 1H, Ar), 1.78 (*app.* q, *J* = 4.7 Hz, 2H, CP), 1.48 (*app.* q, *J* = 4.7 Hz, 2H, CP) ppm
R_f = 0.40 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

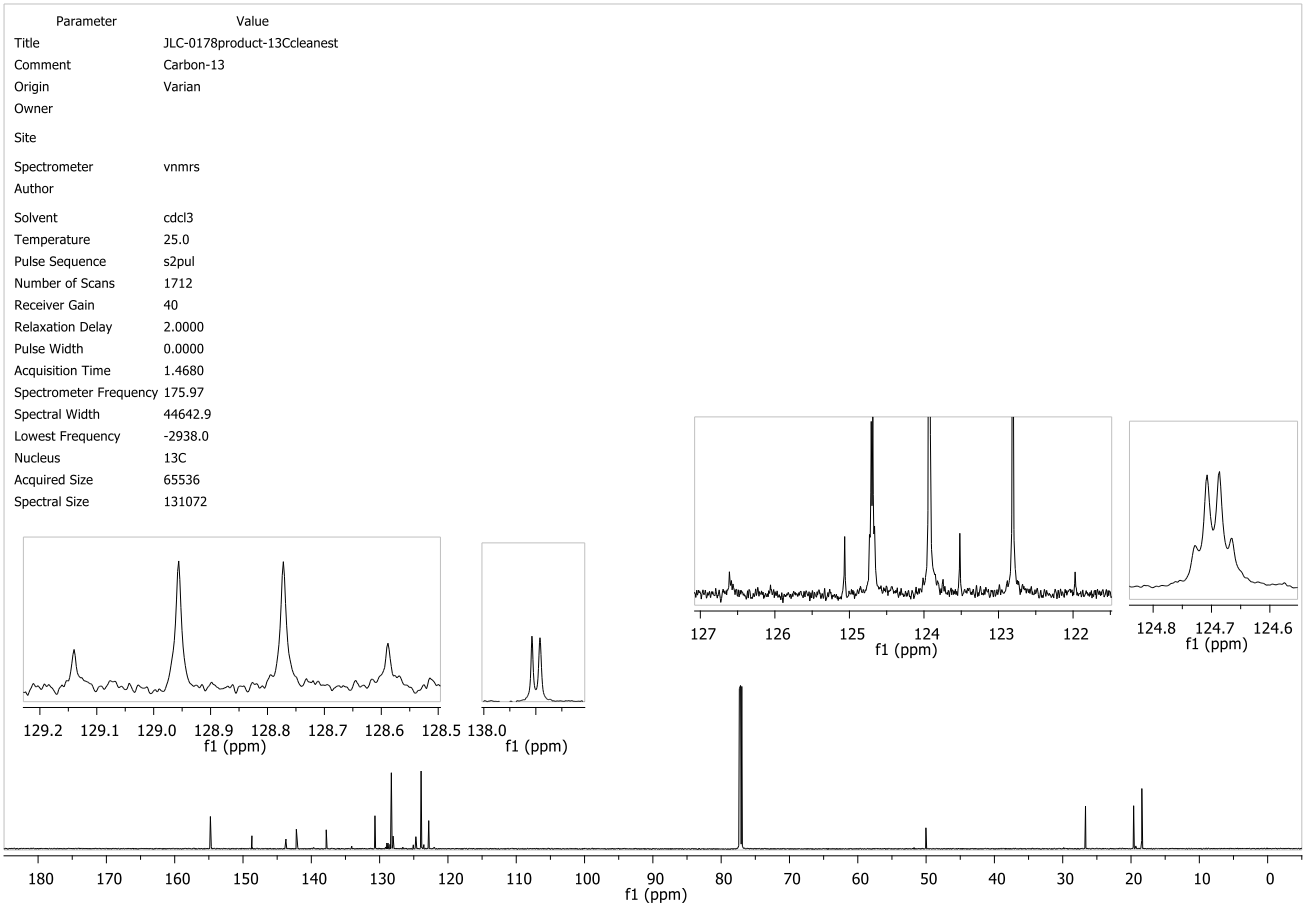
CsF (763 mg, 5.02 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2. In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (22.5 mg, 0.1 mmol) and tris(o-tolyl)phosphine (61.1 mg, 0.201 mmol) were dissolved in 6 mL dry, degassed THF(degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask), then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (415 mg, 1.00 mmol) was dissolved in 3 mL dry, degassed THF before adding (2,2-dimethyl)vinylboronic acid (151 mg, 1.51 mmol; purchased from Synthonix) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with three 1.00 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 °C for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~100 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was loaded with PhMe. Obtained vinylated cyclopropylimine **1g** as a clear colorless oil, 112 mg (21% yield over 2 steps).

*Characterization Data for C9-trifluoromethyl cyclopropylimine **1g**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.20 (d, 2H, *J* = 9.6 Hz, 4-NO_2Ar), 7.72 (d, 2H, *J* = 8.7 Hz, 4-NO_2Ar), 7.56 (m, 1H, Ar), 7.60-7.54 (s, 1H, imine-CH), 6.89 (d, 1H, *J* = 7.7 Hz, Ar), 7.39 (d, 1H, *J* = 8.0 Hz, Ar), 6.22 (s, 1H, C4), 1.83 (s, 3H, C7-Me), 1.77 (s, 3H, C7-Me), 1.65-1.62 (m, 2H, CP), 1.39-1.36 (m, 2H, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 154.8, 148.7, 143.7, 142.2, 137.8, 137.8, 130.7, 128.9 (J_{CF} = 32.3 Hz), 128.3, 128.0 (J_{CF} = 3.7 Hz), 124.7 (J_{CF} = 3.6 Hz), 124.3 (J_{CF} = 272.1 Hz), 123.9, 122.8, 50.0, 26.66, 19.6, 18.4 ppm
^{19}F NMR ($CDCl_3$, 376 MHz): δ = -62.3 ppm
IR (neat): 2916, 1597, 1515, 1342, 1301, 1273, 1185, 1117, 1077, 957, 881, 855, 831, 748, 692 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{21}H_{19}F_3N_2O_2^+$: 389.11471, Found: 389.1484
R_f = 0.50 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

^{1}H NMR (700 MHz, $CDCl_3$) for 1g



^{13}C NMR (176 MHz, $CDCl_3$) for 1g



Parameter	Value
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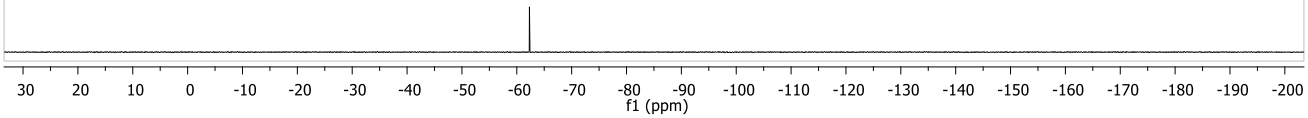
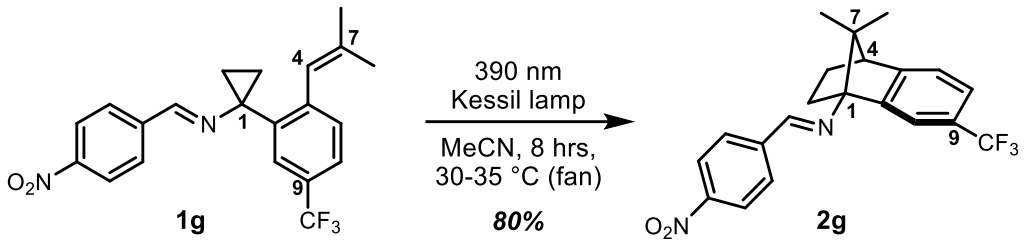
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	1712
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2938.0
Nucleus	13C
Acquired Size	65536
Spectral Size	131072

^{19}F NMR (376 MHz, $CDCl_3$) for 1g

Parameter	Value
Title	JLC-0178product-19F
Comment	STANDARD FLUORINE PARAMETERS
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	54
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.7340
Spectrometer Frequency	376.83
Spectral Width	89285.7
Lowest Frequency	-76676.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072





Procedure for C9-trifluoromethyl 1-aminoNB 2g

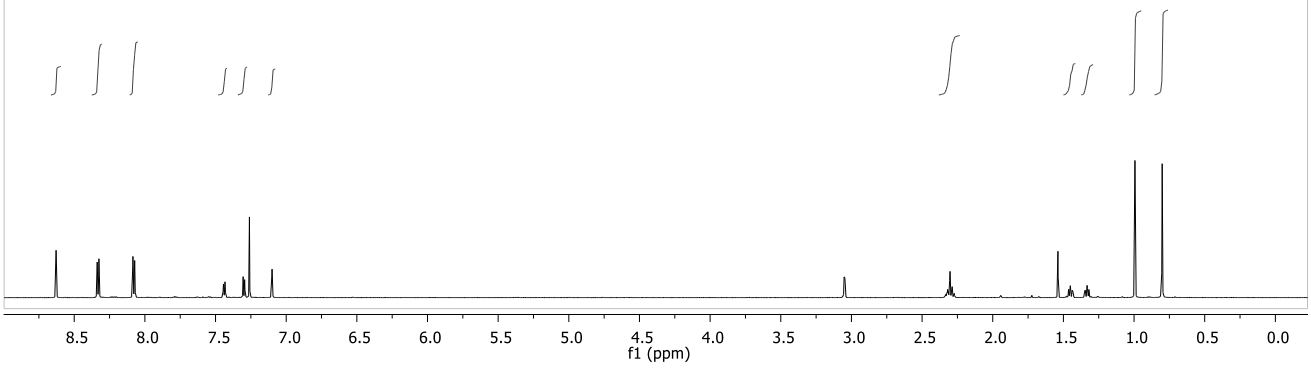
In a dry vial under inert atmosphere, cyclopropylimine **1g** (72.8 mg, 205 μmol) was dissolved in 2.2 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 8 hrs, using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was clear and light red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (5 to 15 to 25 to 35% ethyl acetate:hexanes; loaded residue with PhMe). Obtained 58.1 mg of a light yellow solid,[18] determined to be clean 1-aminoNB **2g** (79.8% yield).

*Characterization Data for C9-trifluoromethyl 1-aminoNB **2g**[19]:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.63 (s, 1H, imine CH), 8.33 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 8.08 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.44 (d, 1H, *J* = 7.6 Hz, C11), 7.30 (d, 1H, *J* = 7.6 Hz, C10), 7.10 (s, 1H, C8), 3.05 (d, 1H, *J* = 3.6 Hz, C4), 2.34-2.27 (m, 2H, C3-eq, C2-eq), 1.49-1.43 (m, 1H, C2-ax), 1.35-1.31 (m, 1H, C3-ax), 0.99 (s, 3H, C7-Me), 0.80 (s, 3H, C7-Me) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 159.5, 150.8, 149.4, 148.7, 142.0, 129.1, 128.1 (J_{CF} = 31.7 Hz, C9), 124.7 (J_{CF} = 270 Hz, CF_3), 124.1, 123.8 (J_{CF} = 4.0 Hz), 121.9, 116.6 (J_{CF} = 3.6 Hz), 80.1, 60.7, 51.6, 27.6, 26.3, 20.1, 19.2 ppm
^{19}F NMR ($CDCl_3$, 376 MHz): δ = -61.6 ppm
IR (neat): 2964, 1644, 1603, 1522, 1432, 1345, 1322, 1275, 1255, 1157, 1118, 1056, 838, 746, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{21}H_{20}F_3N_2O_2^+$: 389.1471, Found: 389.1471
R_f = 0.55 (20% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

[18] A subsequent round of chromatography revealed 1-aminoNB **2g** to be a white solid, though there was no discernable difference in the NMR spectra of the two samples.
[19] Assignments based on analogy to related scaffolds.

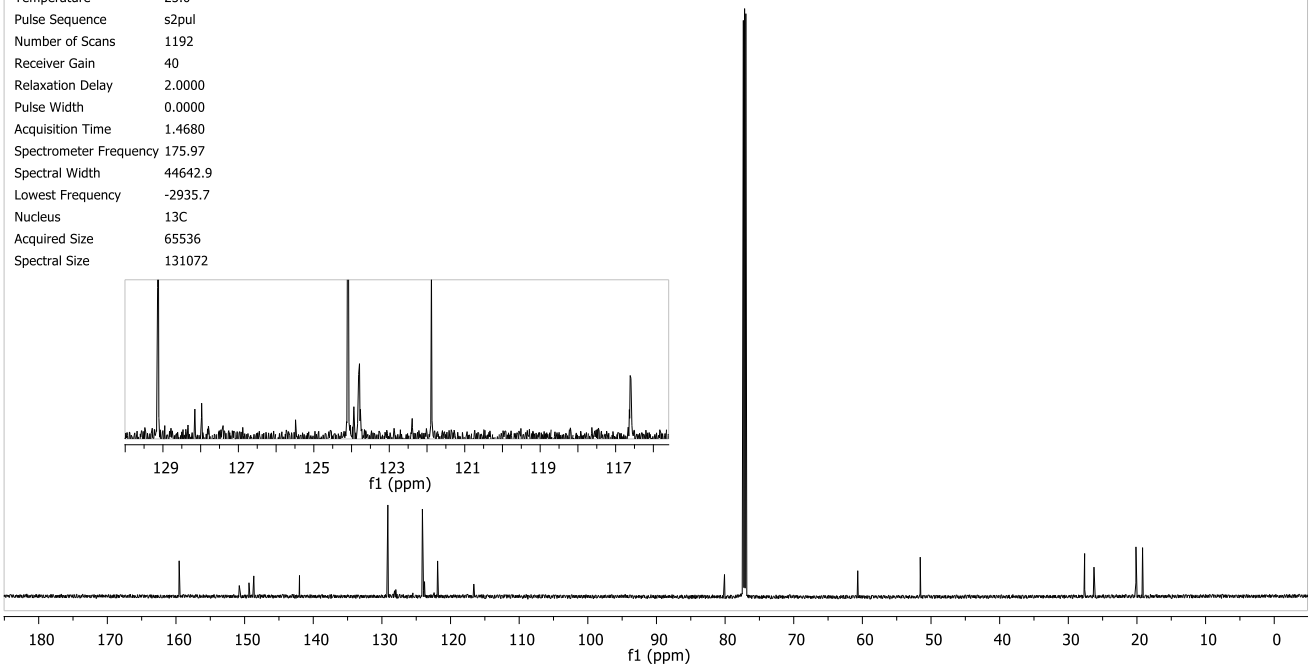
^{1}H NMR (700 MHz, $CDCl_3$) for 2g

Parameter	Value
Title	DS.1898.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	52
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



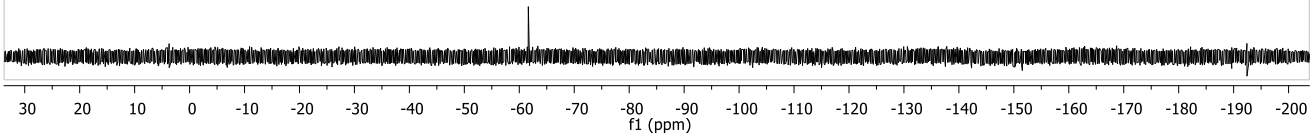
^{13}C NMR (176 MHz, $CDCl_3$) for 2g

Parameter	Value
Title	DS.1898.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	1192
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.7
Nucleus	13C
Acquired Size	65536
Spectral Size	131072



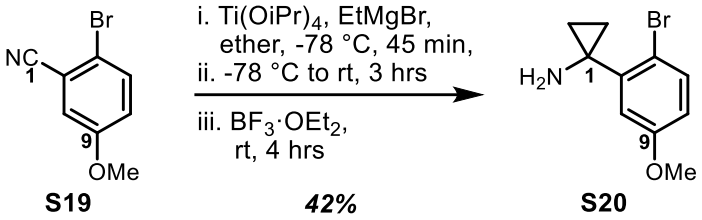
^{19}F NMR (376 MHz, $CDCl_3$) for 2g

Parameter	Value
Title	DS.1898.19F
Comment	Fluorine-19
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	24.0
Pulse Sequence	s2pul
Number of Scans	128
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.7340
Spectrometer Frequency	375.91
Spectral Width	89285.7
Lowest Frequency	-76597.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072



30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)



S19 ***42%*** **S20**

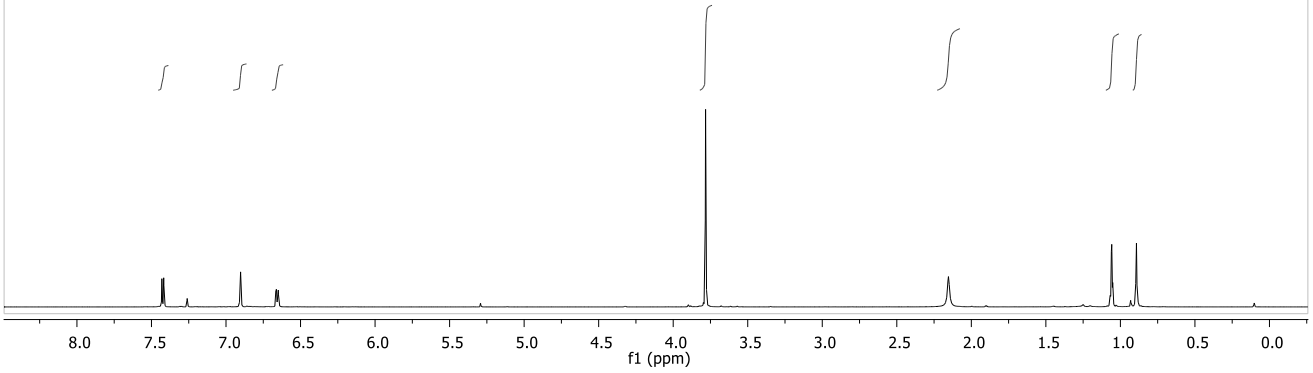
Procedure for C9-methoxy aminocyclopropane S20

2-Bromo-5-methoxy-benzonitrile **S19** (0.300 g, 1.41 mmol; purchased from Chem Cruz) was dissolved in 12.3 mL dry ether in a dry flask under inert atmosphere, then cooled to -78 °C. Titanium isopropoxide (0.463 mL, 1.56 mmol; purchased from Oakwood Chemical) was added in one portion, followed by addition of ethylmagnesium bromide (3.0 M in ether, 1.04 mL, 3.11 mmol) via syringe, dropwise down the side of the vial over the course of 5 min. The dark brown-black reaction mixture (clear, colorless at outset of EtMgBr addition) was stirred at 45 min while coming to room temp, cold bath was removed, and the reaction was stirred an additional 3 hrs at room temp. BF3·etherate (0.350 mL, 2.84 mmol) was added dropwise over the course of 2 min, and the reaction mixture was stirred 4 hrs at room temp. The reaction was quenched by carefully pouring in 50 mL of a 3:1 mix of sat. Rochelle salt:1 M NaOH (aq), followed by 30 min of vigorous stirring at room temp. The biphasic mixture was diluted with an additional 50 mL of the same aqueous mixture and 100 mL ether. The phases were separated. The aqueous phase was extracted with three 50 mL portions of ether. The combined organics were then washed with 50 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under vacuum. The crude residue was purified via flash chromatography over silica (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; the silica was pre-neutralized with 8% ethyl acetate:hexanes + 1% NEt3, followed by an ethyl acetate flush; the residue was loaded with PhMe). Collected 144 mg of aminocyclopropane **S20** (42% yield) as a yellow oil.

*Characterization Data for C9-methoxy aminocyclopropane **S20**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.42 (d, *J* = 8.7 Hz, 1H, Ar), 6.90 (d, *J* = 2.9 Hz, 1H, Ar), 6.66 (dd, *J* = 8.7, 2.9 Hz, 1H, Ar), 3.78 (s, 3H, -OMe), 2.15 (s, 2H, NH_2), 1.10-1.01 (m, 2H, CP), 0.93-0.85 (m, 2H, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 159.1, 145. 7, 133.8, 116.3, 115.7, 113.8, 55.6, 39.1, 15.6 ppm
IR (neat): 3364, 3087, 3006, 2936, 2835, 1590, 1568, 1464, 1409, 1397, 1289, 1221, 1180, 1106, 1013 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{10}H_{12}BrNO^+$: 242.0175, Found: 242.0177
R_f = 0.50 (60% ethyl acetate:hexanes + 1% NH_4OH), one red spot, ninhydrin, UV

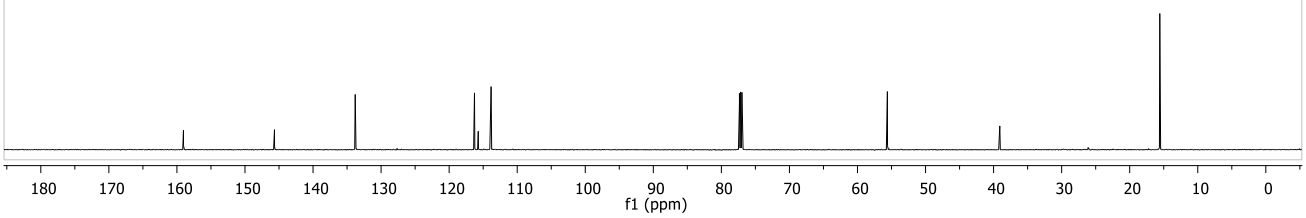
^{1}H NMR (500 MHz, $CDCl_3$) for S20

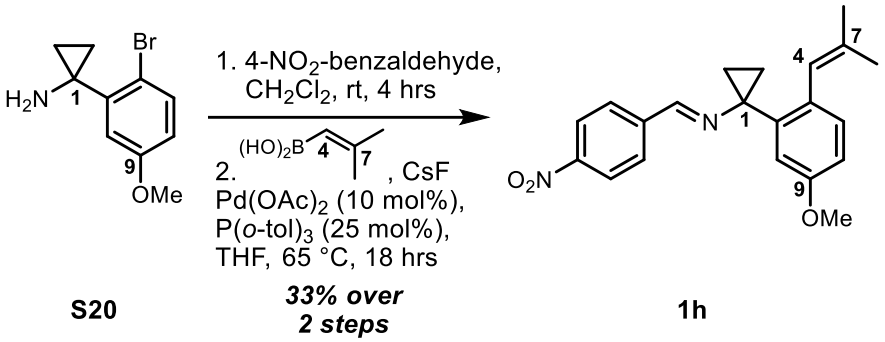
Parameter	Value
Title	JLC-0182product-1H
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	22.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	36
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (126 MHz, $CDCl_3$) for S20

Parameter	Value
Title	JLC-0182product-13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	22.0
Pulse Sequence	s2pul
Number of Scans	928
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2942.4
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S20 ***33% over 2 steps*** **1h**

Procedure for C9-methoxy cyclopropylimine 1h

Aminocyclopropane **S20** (120 mg, 0.496 mmol) was dissolved in 3.62 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (106 mg, 0.701 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (0 to 1 to 2 to 3 to 5 to 10% ethyl acetate:hexanes). Collected 134 mg of the Schiff base intermediate (72.1% yield) as a clear oil. Partial characterization is provided below.

Characterization Data for Schiff base intermediate:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.19 (d, *J* = 8.1 Hz, 2H, 4-NO_2-Ar), 7.78 (d, *J* = 8.1 Hz, 2H, 4-NO_2-Ar), 7.65 (s, 1H, imine-CH), 7.52 (d, *J* = 8.7 Hz, 1H, Ar), 6.92 (d, *J* = 2.3 Hz, 1H, Ar), 6.80 (dd, *J* = 8.7, 2.2 Hz, 1H, Ar), 3.82 (s, 3H, C9-CH_3), 1.86-1.57 (m, 2H, CP), 1.53-1.36 (m, 2H, CP) ppm

R_f = 0.15 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (271 mg, 1.79 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2. In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (8.02 mg, 0.0357 mmol) and tris(o-tolyl)phosphine (21.7 mg, 0.0714 mmol) were dissolved in 2 mL dry, degassed THF(degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask), then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (134 mg, 0.357 mmol) was dissolved in 2 mL dry, degassed THF before adding (2,2-dimethyl)vinylboronic acid (53.5 mg, 0.536 mmol; purchased from Synthonix) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with two 0.5 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~100 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was loaded with PhMe. Obtained vinylated cyclopropylimine **1h** as a slighty yellow oil, 112 mg (33% yield over 2 steps).

*Characterization Data for 9-methoxy cyclopropylimine **1h**:*

^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.18 (d, *J* = 7.8 Hz, 2H, 4-NO_2-Ar), 7.72 (d, *J* = 7.7 Hz, 2H, 4-NO_2-Ar), 7.61 (s, 1H, imine-CH), 7.20 (d, *J* = 8.3 Hz, 1H, Ar), 6.91-6.85 (m, 2H, Ar), 6.12 (s, 1H, C4-CH), 3.83 (s, 3H, C9-Methoxy), 1.77 (s, 3H, C7-CH_3), 1.73 (s, 3H, C7-CH_3), 1.62-1.57 (s, 2H, CP), 1.39-1.35 (s, 2H, CP) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 158.3, 154.9, 148.6, 142. 6, 138.4, 134.6, 132.5, 131.4, 128.2, 123.9, 123.3, 116.8, 112.9, 55.4, 50.6, 26.5, 19.5, 18.5 ppm

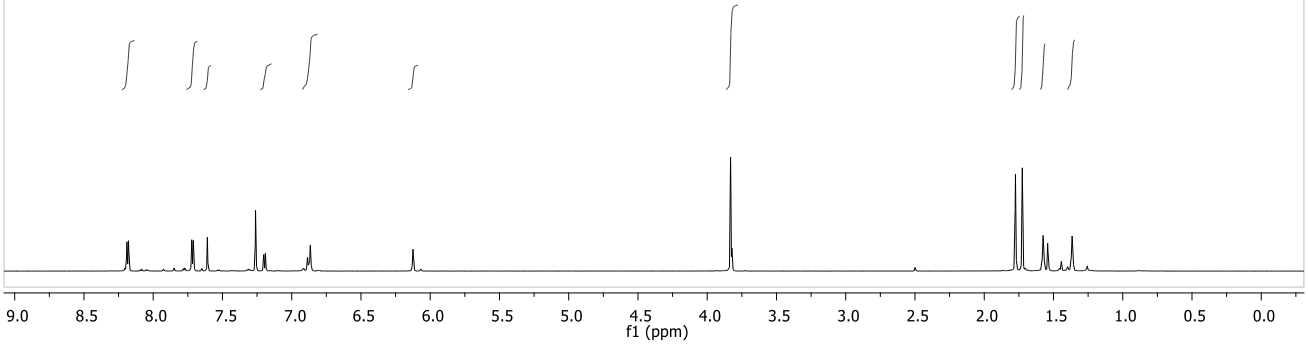
IR (neat): 2909, 1600, 1520, 1487, 1345, 1292, 1228, 1180, 1078, 1037, 957, 849, 749, 691 cm^{-1}

HRMS (ES+, *m/z)* calculated for $C_{21}H_{22}N_2O_3^+$: 351.1703, Found: 351.1714

R_f = 0.30 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

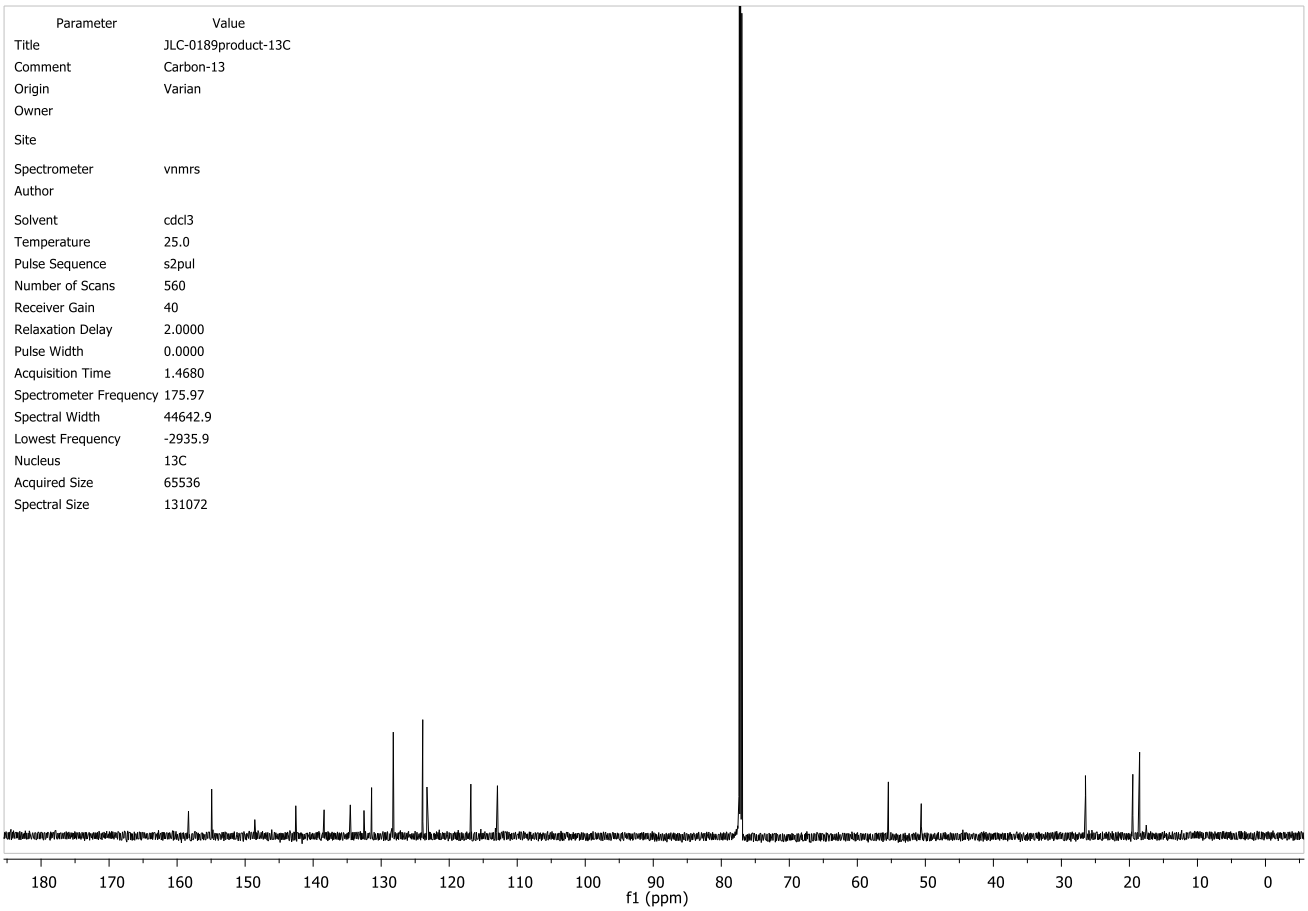
^{1}H NMR (700 MHz, $CDCl_3$) for 1h

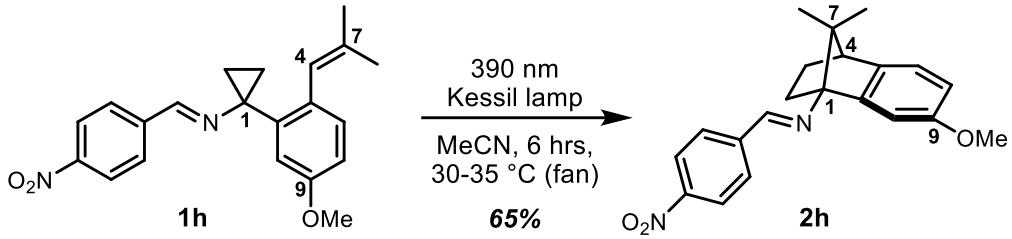
Parameter	Value
Title	JLC-0189product-1H
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	52
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 1h

Parameter	Value
Title	JLC-0189product-13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	560
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.9
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for C9-methoxy 1-aminoNB 2h

In a dry vial under inert atmosphere, cyclopropylimine **1h** (53.5 mg, 153 μmol) was dissolved in 1.6 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 6 hrs,[20] using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was clear and light red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (10% ethyl acetate:hexanes; loaded residue with PhMe). Obtained 40.6 mg of residue that proved to be 85.0 wt% product, 7.0 wt% starting material, and 8.0 wt% pentane, dictating that 2.8 mg were recovered cyclopropylimine **1h** (5.2% recovery) and 34.5 mg were desired product (64.5% yield).

To obtain characterization grade material, a portion of the isolated mixture (~10 mg), dissolved in a mixture of CH_2Cl_2 and $CDCl_3$, was irradiated for additional 30 min at 390 nm and re-purified, affording clean 1-aminoNB **2h** as a light yellow solid.

*Characterization Data for C9-methoxy 1-aminoNB **2h**[21]:*

^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.61 (s, 1H, imine CH), 8.31 (d, 2H, *J* = 8.4 Hz, 4-NO_2-Ar), 8.06 (d, 2H, *J* = 8.4 Hz, 4-NO_2-Ar), 7.10 (d, 1H, *J* = 7.9 Hz, C11), 6.65 (dd, 1H, *J* = 7.9, 2.2 Hz, C10), 6.47 (d, 1H, *J* = 2.1 Hz, C8), 3.75 (s, 3H, -OMe), 2.92 (d, 1H, *J* = 3.5 Hz, C4), 2.28-2.20 (m, 2H, C3-eq, C2-eq), 1.48-1.44 (m, 1H, C2-ax), 1.35-1.30 (m, 1H, C3-ax), 0.97 (s, 3H, C7-Me), 0.81 (s, 3H, C7-Me) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 159.0, 158.2, 149.4, 149.2, 142.3, 139.3, 129.0, 124.0, 122.3, 110.1, 107.2, 80.4, 60.2, 55.5, 50.9, 28.5, 27.1, 20.2, 19.4 ppm

IR (neat): 2955, 1641, 1601, 1520, 1472, 1343, 1290, 1280, 1217, 1177, 1098, 1041, 857, 838, 746, 690 cm^{-1}

HRMS (ES+, *m/z)* calculated for $C_{21}H_{23}N_2O_3^+$: 351.1703, Found: 351.1709

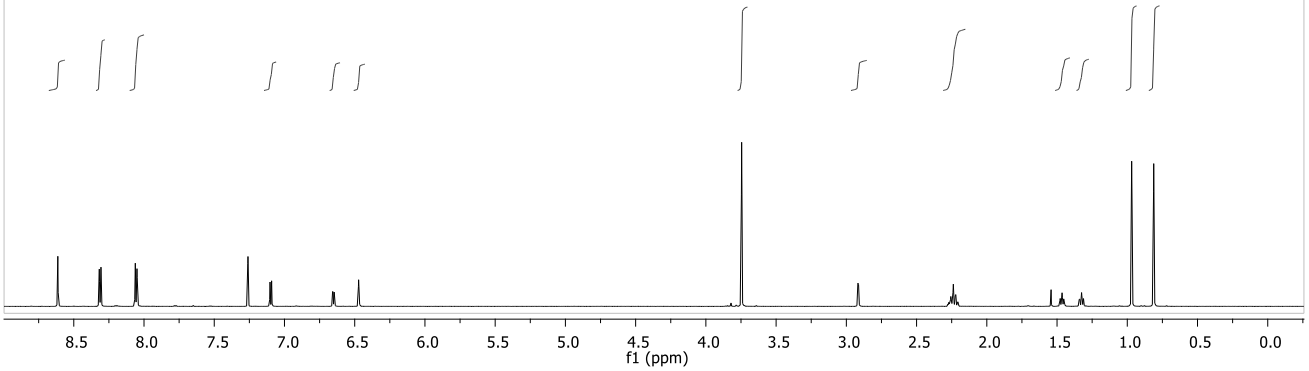
R_f = 0.50 (20% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

[20] Time course adjusted to account for the smaller amount of starting material.

[21] Assignments based on analogy to related scaffolds.

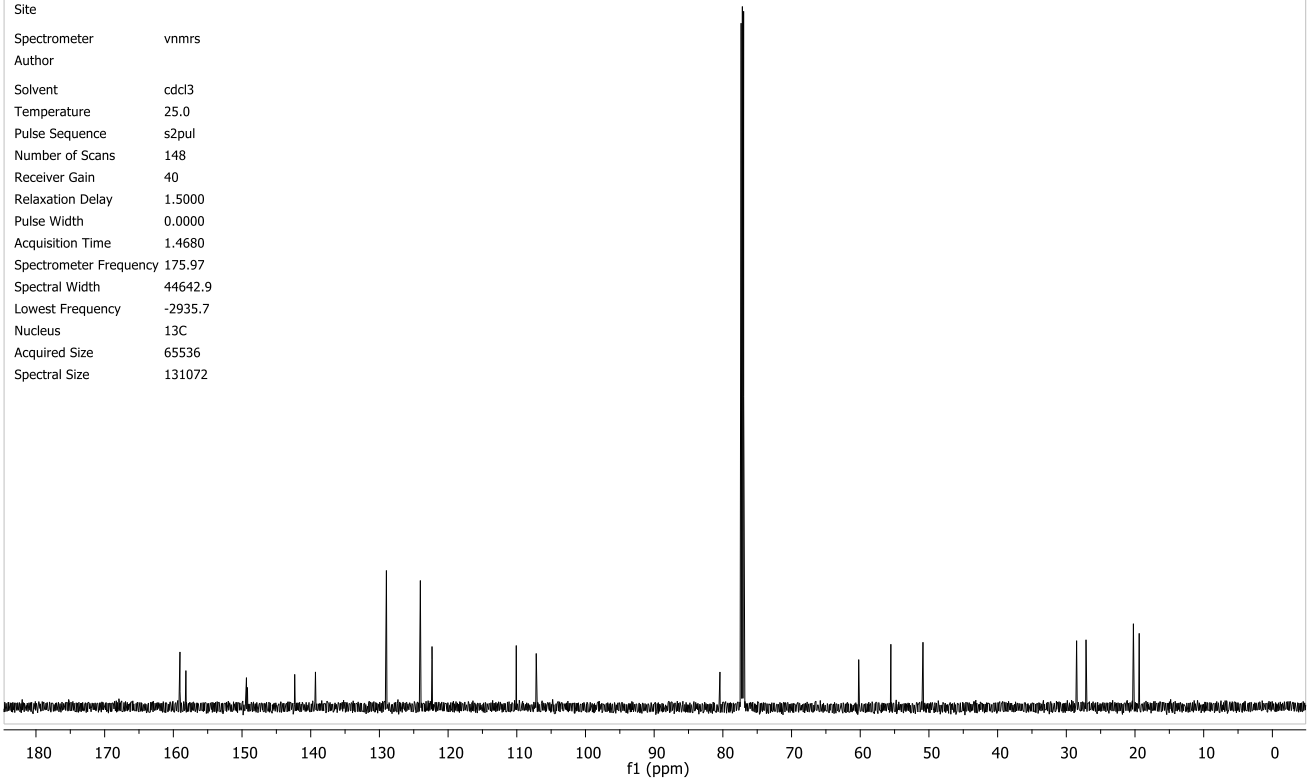
^{1}H NMR (700 MHz, $CDCl_3$) for 2h

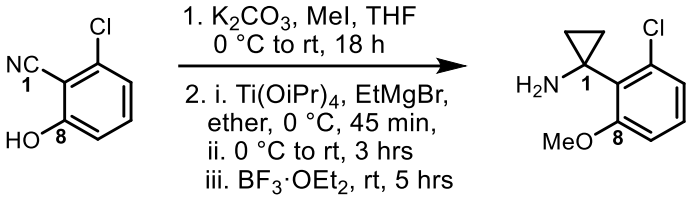
Parameter	Value
Title	DS.1906.1H.char1
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	50
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 2h

Parameter	Value
Title	DS.1906.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	148
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.7
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S21 ***37%*** **S22**

Procedure for C8-methoxy aminocyclopropane S22

To a flame dried flask equipped with a stir bar was added under inert atmosphere 2-chloro-6-hydroxy-benzonitrile **S21** (500 mg, 3.26 mmol), K_2CO_3 (540 mg, 3.91 mmol), and DMF (32 mL). The reaction was cooled to 0 °C followed by addition of CH_3I (223 µL, 3.58 mmol). The solution was warmed to room temp while stirring for 18 hrs before the reaction was diluted with aq sat NH_4Cl (25 mL). The phases were separated and the aqueous phase extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, rinsed with brine, dried over sodium sulfate, and filtered before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a silica column, and the product was eluted (0 to 40% ethyl acetate:hexanes). Collected 520 mg of the methylated benzonitrile intermediate (95.3% yield) as a white powder. Partial characterization is provided below.

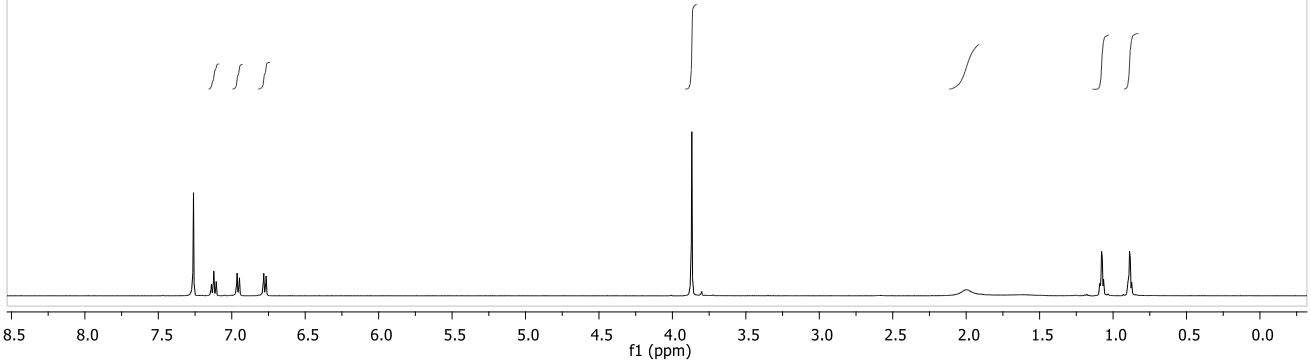
Partial Characterization Data for C8-methoxy benzonitrile intermediate:
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.45 (t, 1H, *J* = 8.4 Hz, Ar), 7.07 (d, 1H, *J* = 8.1 Hz, Ar), 6.88 (d, 1H, *J* = 8.6 Hz, Ar), 3.95 (s, 3H, OMe) ppm
R_f = 0.45 (30% ethyl acetate:hexanes), UV

2-Chloro-6-methoxybenzonitrile (520 mg, 3.1 mmol; prepared from above) was dissolved in 33 mL dry ether in a dry flask under inert atmosphere, then cooled to 0 °C. Titanium isopropoxide (1.02 mL, 3.41 mmol; purchased from Oakwood Chemical) was added in one portion, followed by addition of ethylmagnesium bromide (3.0 M in ether, 2.3 mL, 6.8 mmol) via syringe, dropwise down the side of the vial over the course of 10 min. The dark yellow-brown reaction mixture (clear, colorless at outset of EtMgBr addition) was stirred at 1 hr while coming to room temp, cold bath was removed, and the reaction was stirred an additional 3 hrs at room temp turning a dark red-brown color during this time. BF_3·etherate (768 µL, 6.22 mmol) was added dropwise over the course of 2 min, and the reaction mixture was stirred 5 hrs at room temp. The reaction was quenched by carefully pouring in 50 mL of a 3:1 mix of sat. Rochelle salt:1 M NaOH (aq), followed by 15 min of vigorous stirring at room temp. The biphasic mixture was diluted with an additional 50 mL of the same aqueous mixture and 100 mL ether. The phases were separated. The aqueous phase was extracted with three 50 mL portions of ether. The combined organics were then washed with 100 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under vacuum. The crude residue was purified via flash chromatography over silica (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; the silica was pre-neutralized with 8% ethyl acetate:hexanes + 1% NEt_3; the residue was loaded with PhMe). Collected 240 mg of aminocyclopropane **S22** (39.1% yield) as a yellow oil.

*Characterization Data for C8-methoxy aminocyclopropane **S22**:*
^{1}H NMR ($CDCl_3$, 500 MHz): 7.12 (t, 1H, *J* = 8.2 Hz, Ar), 6.96 (d, 1H, *J* = 8.0 Hz, Ar), 6.77 (d, 1H, *J* = 8.3 Hz, Ar), 3.87 (s, 3H, C8-OMe), 2.03 (bs, 2H, NH_2), 1.08 (*app.* q, 2H, *J* = 5.0 Hz, CP), 0.89 (*app.* q, 2H, *J* = 5.0 Hz, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 159.2, 135.9, 131.3, 128.2, 122.0, 109.3, 55.7, 31.6, 16.9 ppm
IR (neat): 3089, 3008, 2939, 2836, 1587, 1572, 1460, 1431, 1261, 1040, 1028, 845, 771 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{10}H_{13}ClNO^+$: 198.0680, Found: 198.0677
R_f = 0.50 (40% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

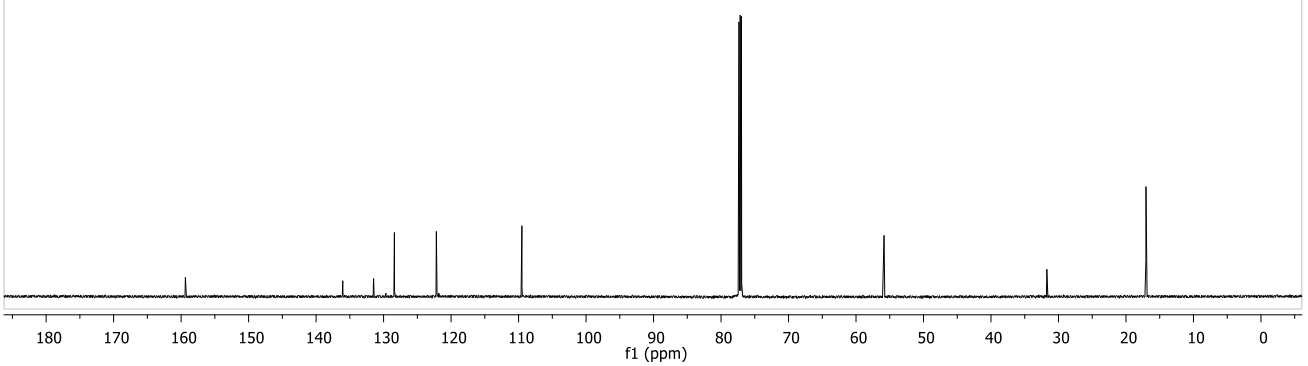
^{1}H NMR (500 MHz, $CDCl_3$) for S22

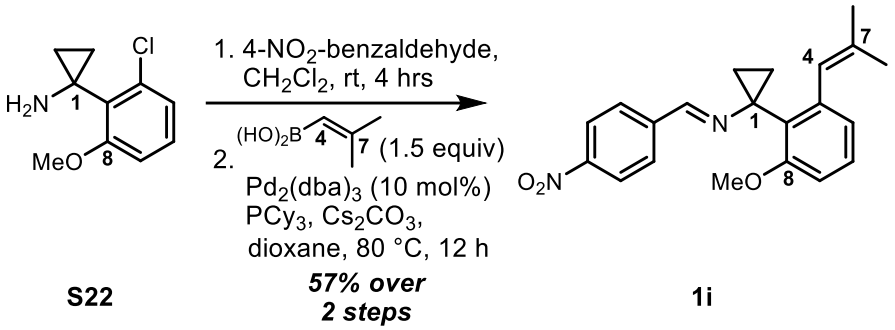
Parameter	Value
Title	RCM_619_PDT_HNMR_Final
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	50
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1006.8
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



^{13}C NMR (176 MHz, $CDCl_3$) for S22

Parameter	Value
Title	RCM_619_Pdt_CNMR_final
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	1152
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2936.4
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for 8-methoxy cyclopropylimine 1i

Aminocyclopropane **S22** (200 mg, 1.01 mmol) was dissolved in 10 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (382 mg, 2.53 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (1 to 2 to 3 to 5 to 10 to 15% ethyl acetate:hexanes). Collected 325 mg of the Schiff base intermediate (97.1% yield) as a light yellow powder. Partial characterization is provided below.

Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.18 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 7.78 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 7.63 (s, 1H, imine-CH), 7.29 (t, 1H, *J* = 8.2 Hz, Ar), 7.07 (d, 1H, *J* = 8.1 Hz, Ar), 6.87 (d, 1H, *J* = 8.3 Hz, Ar), 3.82 (s, 3H, -OMe), 1.78-1.70 (m, 2H, CP), 1.50-1.40 (m, 2H, CP) ppm
R_f = 0.30 (10% ethyl acetate:hexanes), one yellow spot, $KMnO_4$, UV

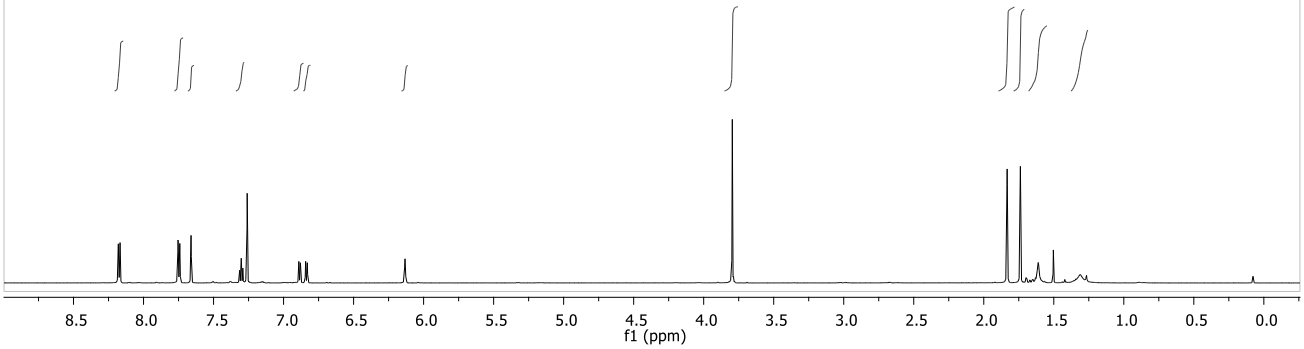
Cs_2CO_3 (985 mg, 3.02 mmol) was added to a flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2 and adding 2 mL dry, degassed 1,4-dioxane (degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask). In a separate dry vial under inert atmosphere, $Pd_2(dba)_3$ (27.7 mg, 302 µmol) and tris(cyclohexyl)phosphine (17.0 mg, 605 µmol) were dissolved in 2 mL dry, degassed THF, then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (200 mg, 0.605 mmol) was dissolved in 2 mL dry, degassed THF before adding (2,2-dimethyl)vinylboronic acid (90.6 mg, 0.907 mmol; purchased from Synthonix) in one portion. The starting material and boronic acid mixture was transferred into the Cs_2CO_3-containing flask via syringe, quantitating transfer with three 1 mL portions of dry, degassed 1,4-dioxane. Once the Pd^0-phosphine mixture (dark purple) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 80 ºC for 12 hrs, stirring vigorously to prevent Cs_2CO_3 from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~50 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over basic alumina (0 to 15% ethyl acetate:hexanes, increasing in 2% increments; residue was loaded with PhMe). Obtained vinylated cyclopropylimine **1i** as a light yellow oil, 122 mg (57% yield over 2 steps).

*Characterization Data for 8-methoxy cyclopropylimine **1i**:*
^{1}H NMR ($CDCl_3$, 700 MHz @ 40 °C[22]): δ = 8.17 (d, 2H, *J* = 8.7 Hz, 4-NO_2Ar), 7.75 (d, 2H, *J* = 8.7 Hz, 4-NO_2Ar), 7.66 (s, 1H, imine-CH), 7.30 (t, 1H, *J* = 8.0 Hz, Ar), 6.89 (d, 1H, *J* = 7.7 Hz, Ar), 6.84 (d, 1H, *J* = 8.3 Hz, Ar), 6.13 (s, 1H, C4), 3.80 (s, 3H, C8-OMe), 1.83 (s, 3H, C7-Me), 1.74 (s, 3H, C7-Me), 1.65-1.57 (m, 2H, CP), 1.37-1.24 (m, 2H, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz @ 40 °C): δ = 159.4, 153.4, 148.4, 142.7, 141.6, 134.9, 128.6, 128.2, 124.7, 124.4, 123.7, 122.9, 109.2, 55.5, 45.4, 26.3, 20.3, 19.5 ppm
IR (neat): 2911, 1598, 1570, 1518, 1466, 1342, 1266, 1088, 1048, 950, 830, 734, 691 cm^{-1}
HRMS (ESI+, *m/z)* calculated for $C_{21}H_{23}N_2O_3^+$: 351.1703, Found: 351.1705
R_f = 0.50 (20% ethyl acetate:hexanes), one yellow spot, $KMnO_4$, UV

[22] As noted in the main text, the need for increased temperature indicates slow rotation about the C1-Ar bond, suggesting that this substrate could be locked in a conformation unsuitable for the formal [3+2] cycloaddition which led to the low yield.

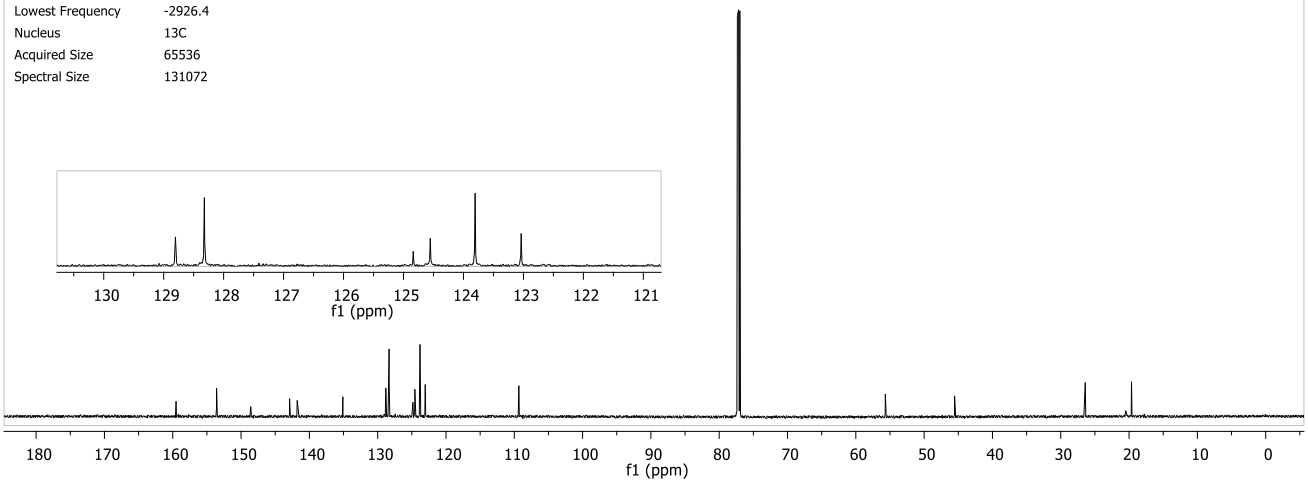
^{1}H NMR (700 MHz @40 °C, $CDCl_3$) for 1i

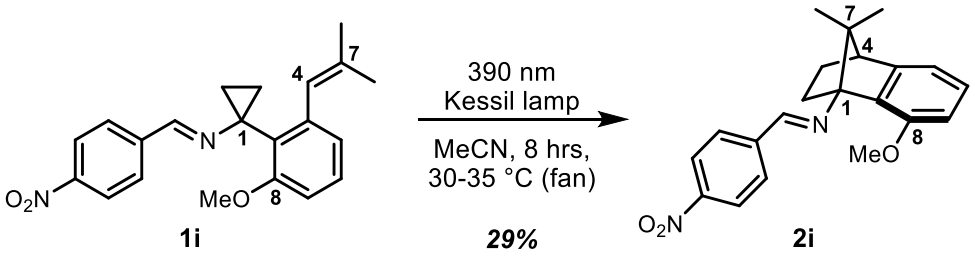
Parameter	Value
Title	RCM_626_PDT_HNMR_40degC
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	40.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	54
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz @40 °C, $CDCl_3$) for 1i

Parameter	Value
Title	RCM_626_PDT_CNMR_40degC
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	40.0
Pulse Sequence	s2pul
Number of Scans	2016
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2926.4
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for C8-methoxy 1-aminoNB 2i

In a dry vial under inert atmosphere, cyclopropylimine **1i** (68.7 mg, 196 μmol) was dissolved in 2.0 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 8 hrs, using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was clear and light red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (10 to 70% ethyl acetate:hexanes, increasing in 10% increments; loaded residue with PhMe). Obtained 41.4 mg of residue that proved to be 1.1:1 starting material to product;[23] this calculates to 21.7 mg of recovered cyclopropylimine **1i** (31.6% recovery) and 19.7 mg of 1-aminoNB **2i** (28.7% yield).

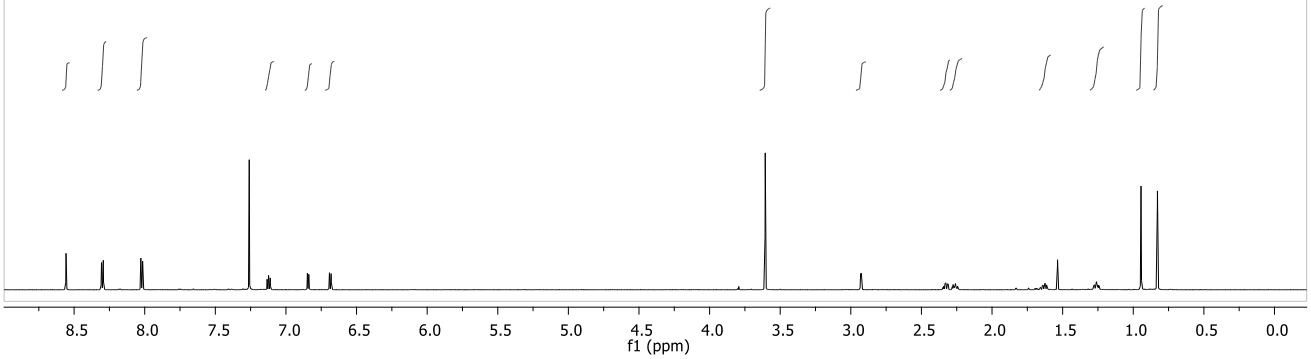
To obtain characterization grade material, the isolated mixture was exposed to two additional rounds of irradiation and purification (after 6 hrs, 0.14:1 starting material:product; after 4 additional hrs, product only) to obtain a pure sample of product. Ultimately collected 23.1 mg of 1-aminoNB **2i** as a white solid (33.6% yield over all exposures).

*Characterization Data for C8-methoxy 1-aminoNB **2i**[24]:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.56 (s, 1H, imine CH), 8.30 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.02 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 7.12 (dd, 1H, *J* = 8.1, 7.4 Hz, C10), 6.84 (d, 1H, *J* = 7.2 Hz, C9/C11), 6.69 (d, 1H, *J* = 8.3 Hz, C9/C11), 3.61 (s, 3H, -OMe), 2.93 (d, 1H, *J* = 4.0 Hz, C4), 2.33 (*app.* dd, 1H, *J* = 10.6, 3.6 Hz, C2-eq), 2.28-2.24 (m, 1H, C3-eq), 1.63 (ddd, 1H, *J* = 11.3, 9.4, 3.5, C2-ax), 1.26 (ddd, 1H, *J* = 11.8, 9.2, 3.5, C3-ax), 0.94 (s, 3H, C7-Me), 0.83 (s, 3H, C7-Me) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 159.5, 154.8, 149.9, 149.0, 142.9, 132.2, 128.9, 127.8, 124.0, 115.0, 110.1, 81.2, 60.2, 55.7, 51.7, 29.5, 27.3, 20.3, 19.1 ppm
IR (neat): 2957, 1645, 1601, 1588, 1521, 1480, 1344, 1288, 1260, 1108, 1083, 948, 857, 837, 689 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{21}H_{23}N_2O_3^+$: 351.1703, Found: 351.1702
R_f = 0.55 (20% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

[23] Also collected several mg of a residue of which the predominant constituent was believed to be the pyrroline byproduct.
[24] Assignments based on analogy to related scaffolds.

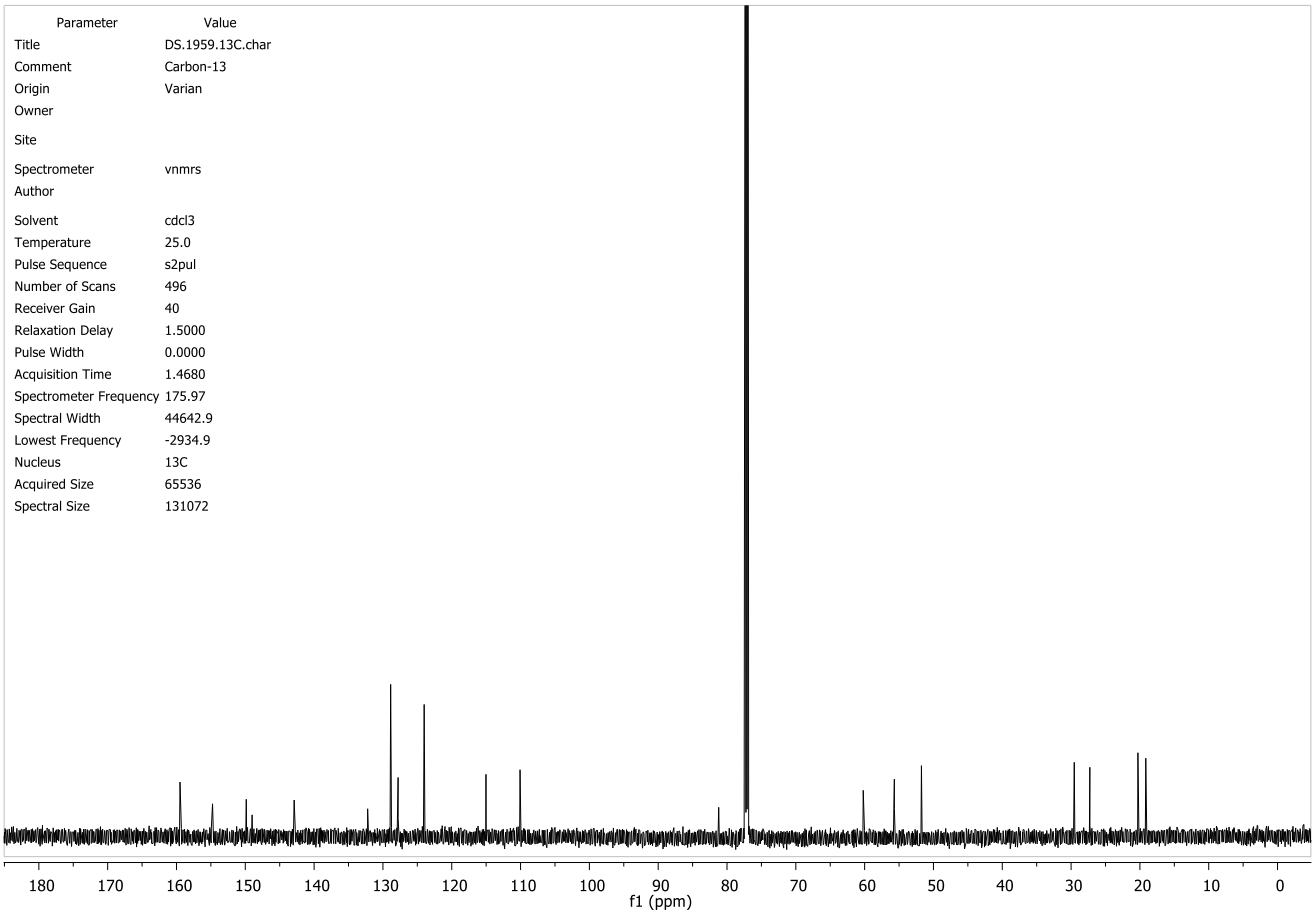
^{1}H NMR (700 MHz, $CDCl_3$) for 2i

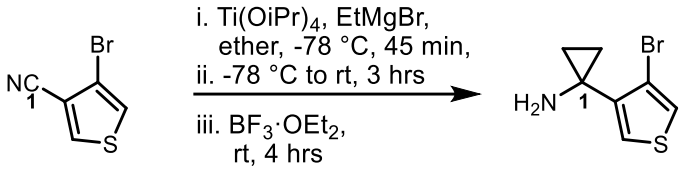
Parameter	Value
Title	DS.1959.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	56
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1380.1
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 2i

Parameter	Value
Title	DS.1959.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	496
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2934.9
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S23 ***60%*** **S24**

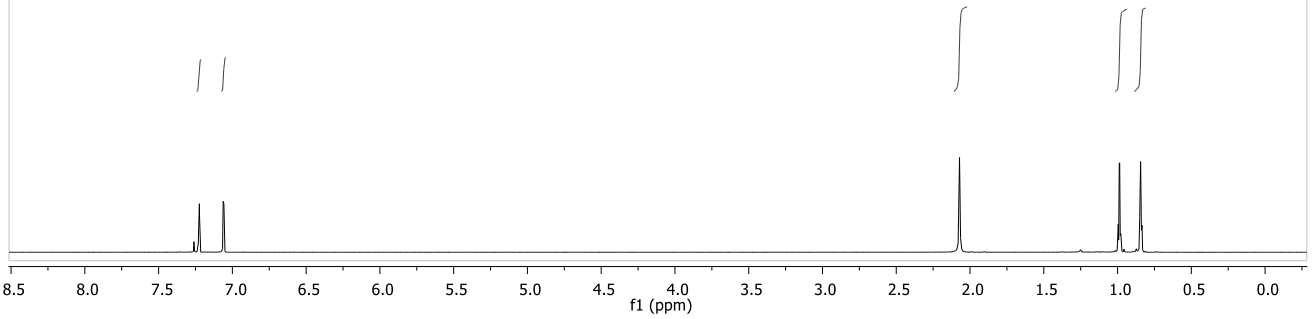
Procedure for 9-*thio* aminocyclopropane S24

3-Bromo-2-cyano-thiophene **S23** (300 mg, 1.60 mmol; purchased from Sigma Aldrich) was dissolved in 14.4 mL dry ether in a dry flask under inert atmosphere, then cooled to -78 °C. Titanium isopropoxide (0.52 mL, 1.75 mmol; purchased from Oakwood Chemical) was added in one portion, followed by addition of ethylmagnesium bromide (3.0 M in ether, 1.17 mL, 3.51 mmol) via syringe, dropwise down the side of the vial over the course of 5 min. The dark brown-black reaction mixture (clear, colorless at outset of EtMgBr addition) was stirred at 45 min while coming to room temp, cold bath was removed, and the reaction was stirred an additional 3 hrs at room temp. BF3·etherate (0.40 mL, 3.20 mmol) was added dropwise over the course of 2 min, and the reaction mixture was stirred 4 hrs at room temp. The reaction was quenched by carefully pouring in 100 mL of a 3:1 mix of sat. Rochelle salt:1 M NaOH (aq), followed by 15 min of vigorous stirring at room temp. The biphasic mixture was diluted with an additional 100 mL of the same aqueous mixture and 200 mL ether. The phases were separated. The aqueous phase was extracted with three 100 mL portions of ether. The combined organics were then washed with 100 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under vacuum. The crude residue was purified via flash chromatography over silica (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; the silica was pre-neutralized with 8% ethyl acetate:hexanes + 1% NEt3; the residue was loaded with PhMe). Collected 210 mg of aminocyclopropane **S24** (60% yield) as a yellow oil.

*Characterization Data for 9-thio aminocyclopropane **S24**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.23 (d, *J* = 3.4 Hz, 1H, Ar), 7.06 (d, *J* = 3.4 Hz, 1H, Ar), 2.07 (s, 2H, NH_2), 1.00-0.97 (m, 2H, CP), 0.86-0.82 (m, 2H, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 145.6, 124.0, 122.3, 112.6, 33.2, 14.5 ppm
IR (neat): 3091, 3009, 2204, 1583, 1516, 1446, 1411, 1350, 1282, 1256, 1020, 960, 849, 791, 727 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_7H_8BrNS^+$: 217.9634, Found: 217.9636
R_f = 0.40 (60% ethyl acetate:hexanes + 1% NH_4OH), one red spot, ninhydrin, UV

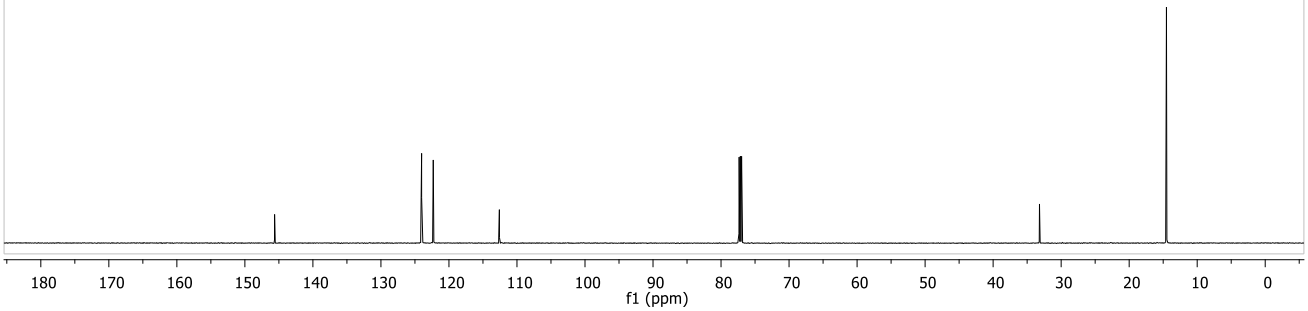
^{1}H NMR (700 MHz, $CDCl_3$) for S24

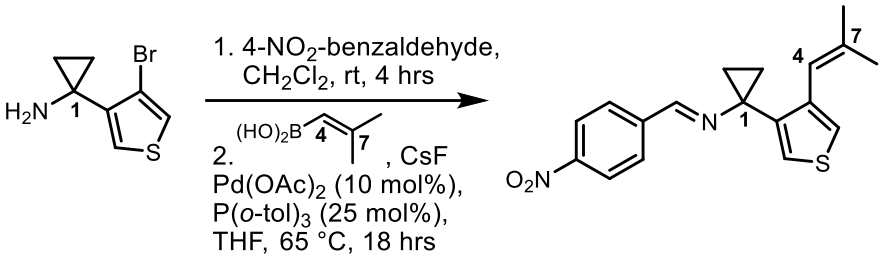
Parameter	Value
Title	JLC-0195product-1H
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	38
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for S24

Parameter	Value
Title	JLC-0195product-13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	672
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2942.4
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for 9-*thio* cyclopropylimine 1j

Aminocyclopropane **S24** (210 mg, 0.963 mmol) was dissolved in 7.00 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (206 mg, 1.36 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (0 to 1 to 2 to 3 to 5 to 10% ethyl acetate:hexanes). Collected 243 mg of the Schiff base intermediate (72% yield) as a yellow oil. Partial characterization is provided below.

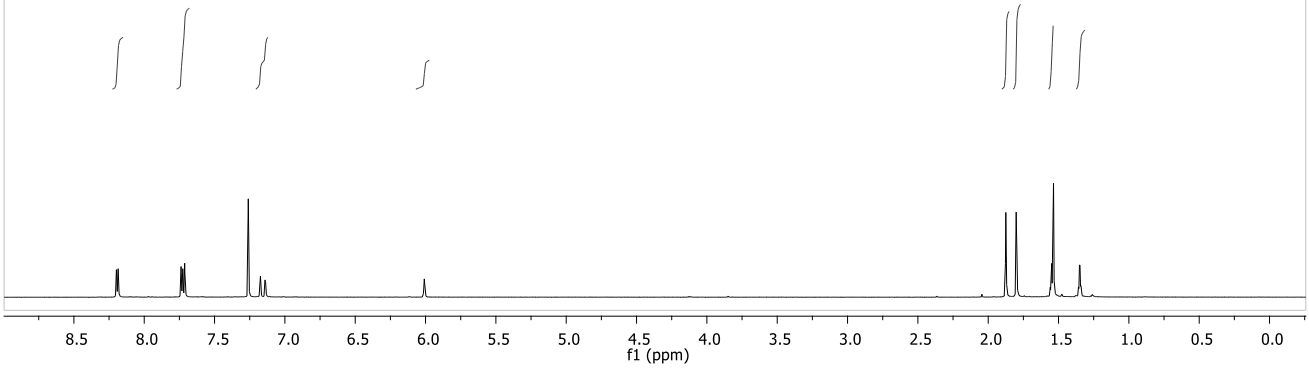
Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 401 MHz): δ = 8.20 (d, *J* = 8.6 Hz, 2H, 4-NO_2-Ar), 7.78 (d, *J* = 8.7 Hz, 2H, 4-NO_2-Ar), 7.74 (s, 1H, imine-CH), 7.36 (d, *J* = 3.4 Hz, 1H, Ar), 7.26 (d, *J* = 3.5 Hz, 1H, Ar), 1.64 (*app.* q, *J* = 4.4 Hz, 2H, CP), 1.44-1.34 (m, 2H, CP) ppm
R_f = 0.30 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (525 mg, 3.46 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2. In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (15.5 mg, 0.0692 mmol) and tris(o-tolyl)phosphine (42.1 mg, 0.138 mmol) were dissolved in 3 mL dry, degassed THF(degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask), then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (243 mg, 0.692 mmol) was dissolved in 2 mL dry, degassed THF before adding (2,2-dimethyl)vinylboronic acid (104 mg, 1.04 mmol; purchased from Synthonix) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with three 1 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~100 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was dry loaded with celite). Obtained vinylated cyclopropylimine **1j** as a slighty yellow oil, 137 mg (44% yield over 2 steps).

*Characterization Data for 9-thio cyclopropylimine **1j**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.19 (d, *J* = 8.6 Hz, 2H, 4-NO_2-Ar), 7.75-7.70 (m, 3H, 4-NO_2-Ar, imine-CH), 7.18 (d, *J* = 3.0 Hz, 1H, Ar), 7.14 (d, *J* = 2.9 Hz, 1H, Ar), 6.01 (s, 1H, C4), 1.88 (s, 3H, C7-CH_3), 1.80 (s, 3H, C7-CH_3), 1.57-1.54 (m, 2H, CP), 1.35 (d, *J* = 2.5 Hz, 2H, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 155.2, 148.6, 142.5, 140.1, 139.4, 136.4, 128.3, 125.3, 123. 9, 122.8, 118.5, 46.0, 26.9, 20.0, 17.6 ppm
IR (neat): 2913, 1719, 1599, 1520, 1454, 1344, 1296, 1208, 1107, 941, 858, 833, 800, 749, 691 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{18}H_{18}N_2O_2S^+$: 327.1162, Found: 327.1169
R_f = 0.50 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

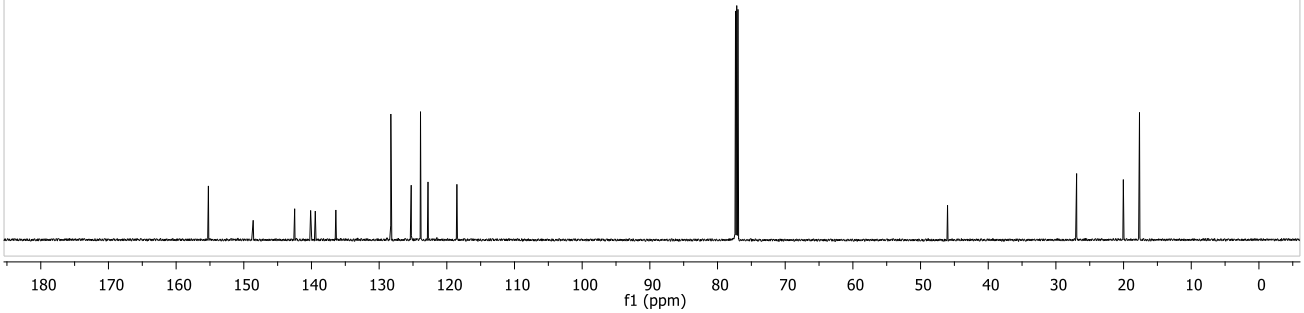
^{1}H NMR (700 MHz, $CDCl_3$) for 1j

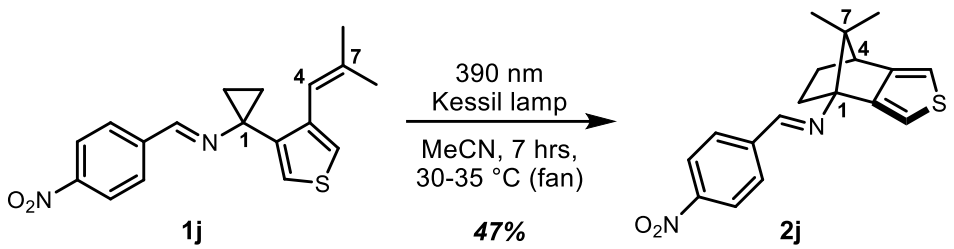
Parameter	Value
Title	JLC-0197product-1H4-17-18
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	28.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	56
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 1j

Parameter	Value
Title	JLC-0197product-13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	512
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2937.5
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for 9-*thio* 1-aminoNB 2j

In a dry vial under inert atmosphere, cyclopropylimine **1j** (50.0 mg, 153 μmol) was dissolved in 1.6 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 7 hrs,[25] using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was dark red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (1 to 3 to 5 to 10% ethyl acetate:hexanes; loaded residue with PhMe). Collected 29.2 mg of a yellow solid that proved to be a 0.25:1 mix of starting material to product, dictating that 5.9 mg were recovered cyclopropylimine **1j** (11.8% recovery) and 23.3 mg were the desired 1-aminoNB **2j** (46.5% yield).[26]

*Characterization Data for 9-thio 1-aminoNB **2j**[27]:*

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.78 (s, 1H, imine CH), 8.30 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.03 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 6.80 (d, 1H, *J* = 1.9 Hz, thiophene), 6.71 (d, 1H, *J* = 1.7 Hz, thiophene), 2.91 (d, 1H, *J* = 4.0 Hz, C4), 2.38 (td, 1H, *J* = 11.0, 3.7 Hz, C2-eq), 2.30 (*app.* tt, 1H, *J* = 11.0, 3.9 Hz, C3-eq), 1.66-1.60 (m, 1H, C2-ax), 1.44 (ddd, 1H, *J* = 12.5, 9.3, 3.6 Hz, C3-ax), 1.06 (s, 3H, C7-Me), 0.72 (s, 3H, C7-Me) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 158.5, 149.7, 149.5, 142.3, 128.9, 124.0, 113.1, 112.7, 79.4, 61.9, 48.8, 32.0, 27.7, 20.4, 19.5 ppm

IR (neat): 3103, 2961, 1641, 1601, 1519, 1471, 1342, 1293, 1186, 1107, 841, 784, 746, 688 cm^{-1}

HRMS (ES+, *m/z)* calculated for $C_{18}H_{19}N_2O_2S^+$: 327.1162, Found: 327.1168

R_f = 0.35 (10% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

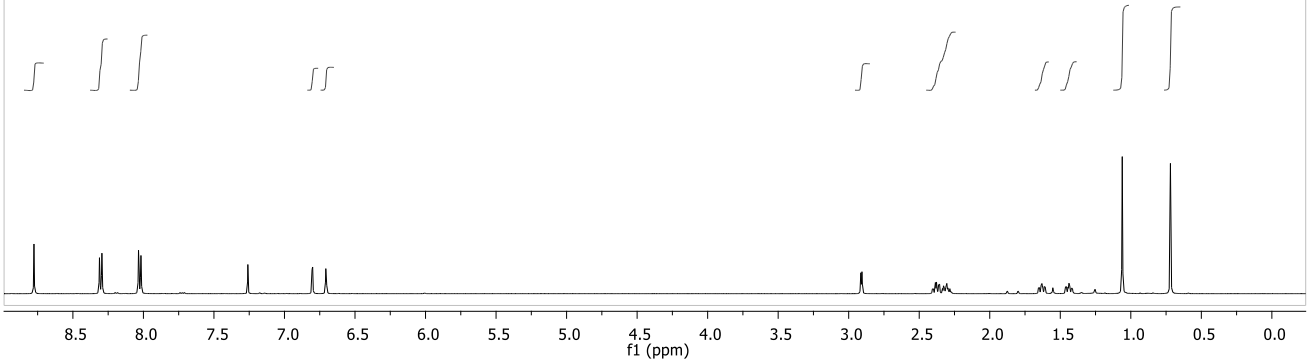
[25] Time course adjusted to account for reduced scale of reaction.

[26] A characterization-grade sample was obtained from a separate trial with cyclopropylimine **1j**, yielding 1-aminoNB **2j** as a light yellow solid.

[27] Assignments based on analogy to related scaffolds.

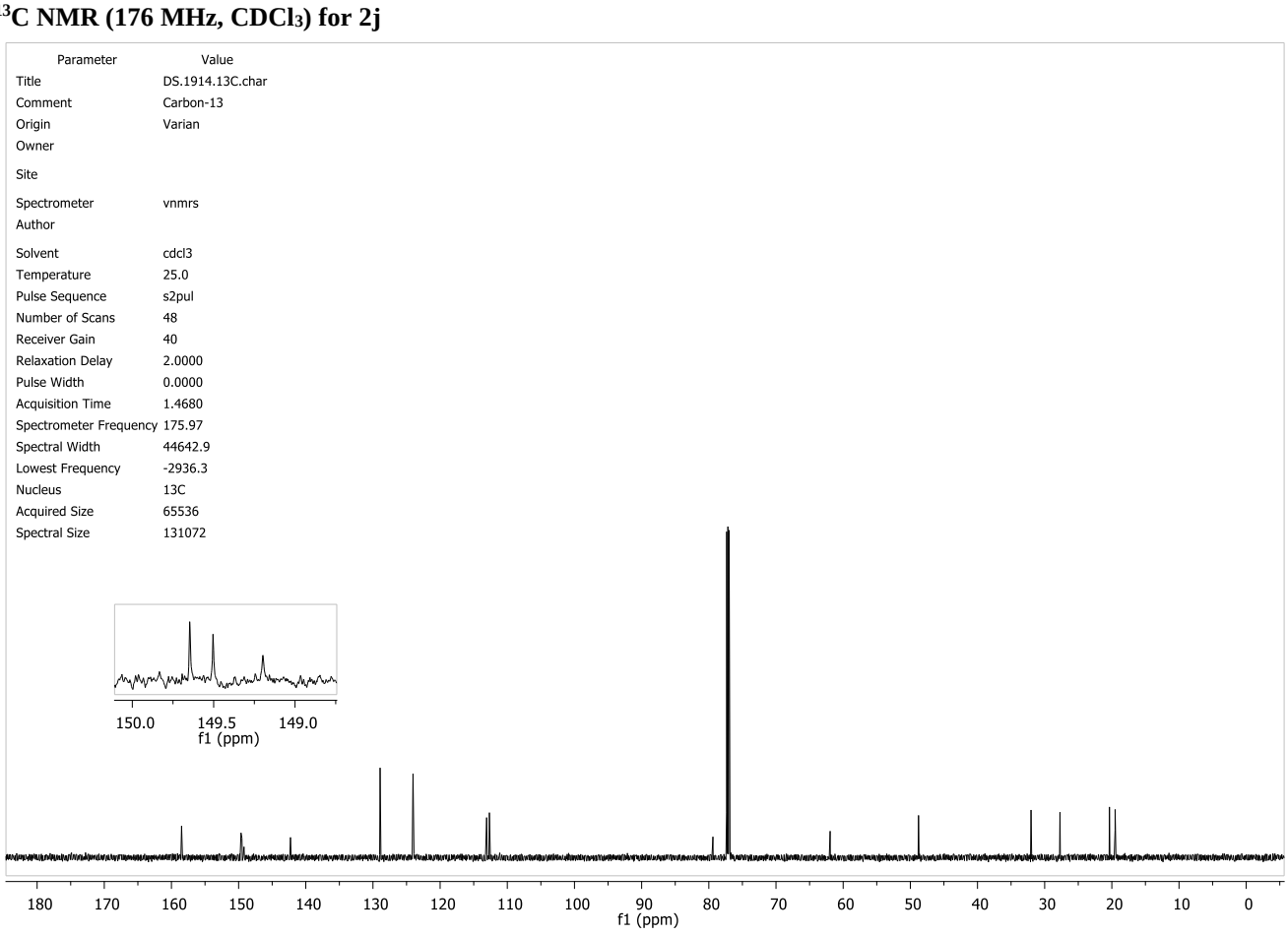
^{1}H NMR (500 MHz, $CDCl_3$) for 2j

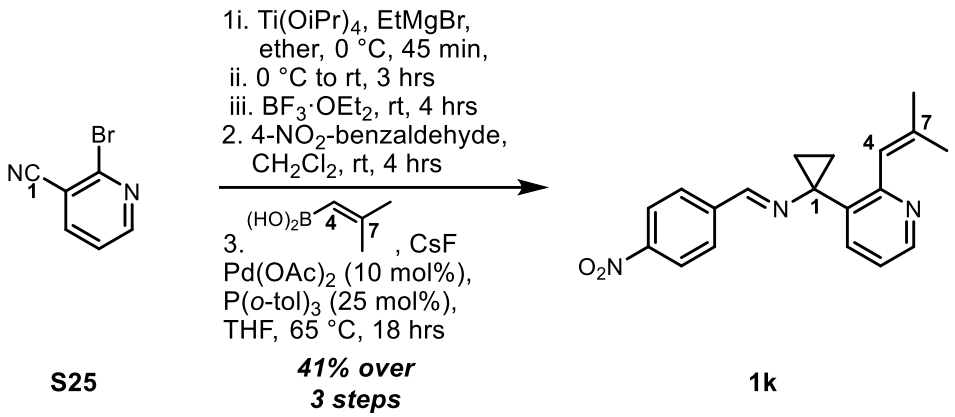
Parameter	Value
Title	DS.1914.c.pdtcenter
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	48
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1007.2
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



^{13}C NMR (176 MHz, $CDCl_3$) for 2j

Parameter	Value
Title	DS.1914.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	48
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2936.3
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for 11-*aza* cyclopropylimine 1k

2-Bromo-3-cyanopyridine **S25** (1.08 g, 5.9 mmol; purchased from AK Scientific) was dissolved in 120 mL dry ether in a dry flask under inert atmosphere, then cooled to 0 °C. Titanium isopropoxide (1.9 mL, 6.5 mmol; purchased from Oakwood Chemical) was added in one portion, followed by addition of ethylmagnesium bromide (3.0 M in ether; 4.3 mL, 13.0 mmol) via syringe, dropwise down the side of the vial over the course of 5 min. The dark brown-black reaction mixture (clear, colorless at outset of EtMgBr addition) was stirred at 4 hrs at 0 °C, before adding BF_3·etherate (1.5 mL, 11.8 mmol) dropwise over the course of 2 min. The reaction temperature was maintained at 0 °C for 1 hr, then the cold bath was removed followed by an additional 3 hrs of stirring while coming to room temp. The reaction was quenched by carefully pouring in 100 mL of a 1:1 mix of 1 M NaOAc (aq.):1 M NaOH (aq), followed by 30 min of vigorous stirring at room temp. The biphasic mixture was diluted with an additional 100 mL of the same aqueous mixture and 100 mL ether. The phases were separated. The aqueous phase was extracted with three 100 mL portions of ether. The combined organics were then washed with 100 mL brine + 1 mL 6 M NaOH (aq.), dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under vacuum. Collected 1.11 g of a yellow oil the desired aminocyclopropane mixed with some minor impurities.[28] This material was moved forward without further purification. Partial characterization is provided below:

Partial Characterization Data for aminocyclopropane intermediate:
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.25 (dd, 1H, *J* = 4.7, 1.9 Hz, pyr), 7.63 (dd, 1H, *J* = 7.5, 1.9 Hz, pyr), 7.21 (dd, 1H, *J* = 7.5, 4.7 Hz, pyr), 2.13 (br s, 2H, -NH_2), 1.13 (*app.* q, 2H, *J* = 4.8 Hz, CP), 1.61 (*app.* q, 2H, *J* = 4.8 Hz, CP) ppm
R_f = 0.15 (40% ethyl acetate:hexanes + 1% NH_4OH), one red spot, ninhydrin, UV

The crude aminocyclopropane from above (up to 5.9 mmol) was dissolved in 30 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (1.34 g, 8.9 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (10 to 50% ethyl acetate:hexanes, increasing in 10% increments). Collected 972 mg of the Schiff base intermediate (47.6% yield over 2 steps) as a clear, colorless oil. Partial characterization is provided below.

Partial Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.41 (dd, 1H, *J* = 4.7, 2.0 Hz, pyr), 8.21 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.78 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.70 (dd, 1H, *J* = 7.5, 2.0 Hz, pyr), 7.66 (s, 1H, imine CH), 7.36 (dd, 1H, *J* = 7.5, 4.8 Hz, pyr), 1.78 (*app.* q, 2H, *J* = 4.8 Hz, CP), 1.61 (*app.* q, 2H, *J* = 4.8 Hz, CP) ppm
R_f = 0.45 (40% ethyl acetate:hexanes + 1% NH_4OH), one red spot, ninhydrin, UV

CsF (430 mg, 2.8 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2 and adding 0.5 mL dry, degassed dioxane (degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask). In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (13 mg, 57 µmol) and tris(o-tolyl)phosphine (50 mg, 142 µmol) were dissolved in 2 mL dry, degassed dioxane, then stirred for 20 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (197 mg, 0.57 mmol) and (2,2-dimethyl)vinylboronic acid (92 mg, 0.92 mmol; purchased from Synthonix) were dissolved in 1.5 mL dry, degassed dioxane. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with two 1 mL

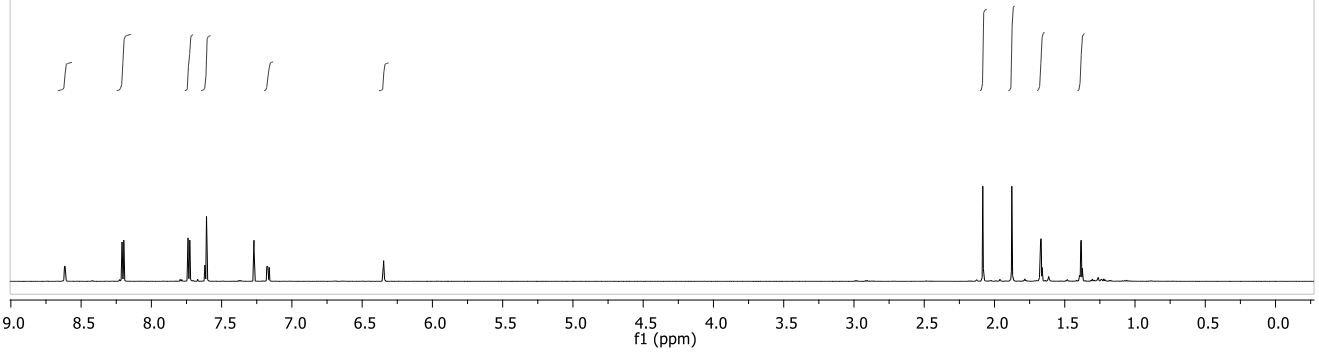
[28] The pyridine-based aminocyclopropane intermediates showed evidence of instability during chromatography, even upon neutralization of the silica or use of basic alumina; purification via chromatography was thus avoided.

portions of dry, degassed dioxane. Once the Pd^0-phosphine mixture (orange) had stirred for 20 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. The system was flushed with Ar, sealed, and the reaction was heated to 80 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~50 mL ether before concentrating under vacuum. The crude residue was purified via flash chromatography over basic alumina (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; residue was loaded with PhMe). Collected vinylated cyclopropylimine **1k** as a yellow oil in two portions, totaling 157 mg of the desired product (85.9% yield; 40.9% yield over 3 steps).

*Characterization Data for 11-aza cyclopropylimine **1k**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.62 (dd, 1H, *J* = 4.8, 1.7 Hz, pyr), 8.20 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.73 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.61 (dd, 1H, *J* = 7.4, 1.8 Hz, pyr), 7.64 (s, 1H, imine CH), 7.17 (dd, 1H, *J* = 7.6, 4.8 Hz, pyr), 6.35 (s, 1H, C4), 2.08 (s, 3H, C7-Me), 1.88 (s, 3H, C7-Me), 1.67 (*app.* q, 2H, *J* = 4.4 Hz, CP), 1.38 (*app.* q, 2H, *J* = 4.5 Hz, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 158.3, 155.1, 148.7, 148.6, 142.3, 142.2, 139.3, 132.2, 128.3, 123.9, 122.1, 121.2, 49.3, 27.6, 20.0, 18.5 ppm
IR (neat): 2910, 1651, 1600, 1580, 1557, 1520, 1446, 1419, 1344, 1208, 1126, 1051, 942, 850, 768 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{19}H_{20}N_3O_2^+$: 322.1550, Found: 322.1553
R_f = 0.55 (40% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

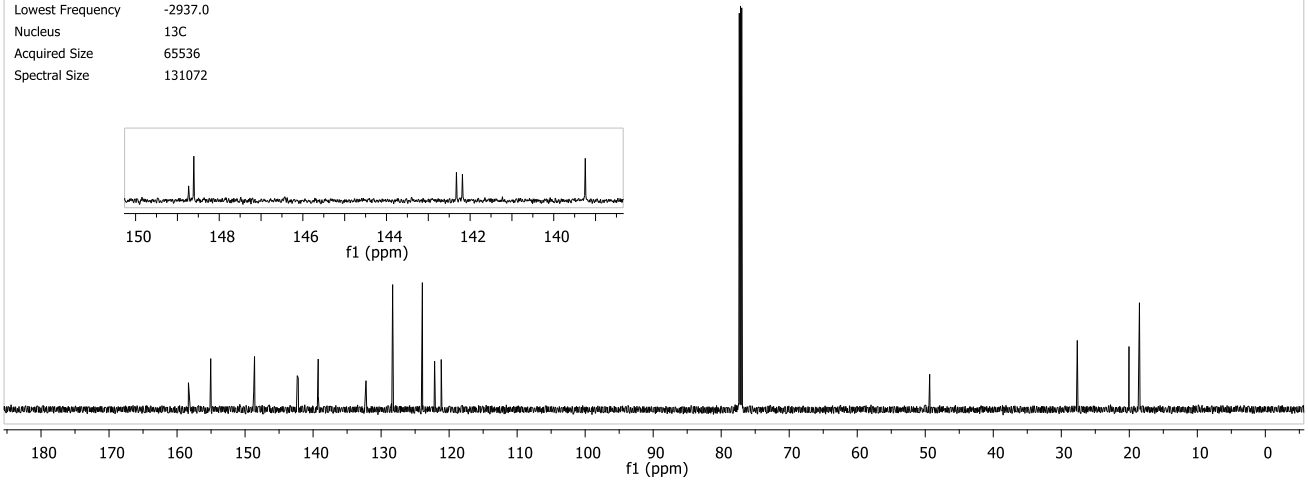
^{1}H NMR (700 MHz, $CDCl_3$) for 1k

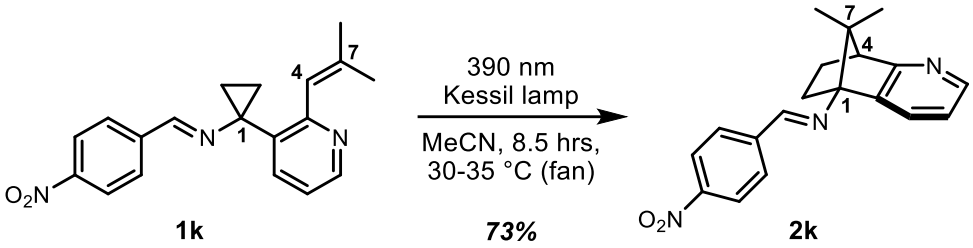
Parameter	Value
Title	DS.1952.1H.charattempt
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	44
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1373.5
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 1k

Parameter	Value
Title	DS.1952.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	96
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2937.0
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for 11-*aza* 1-aminoNB 2k

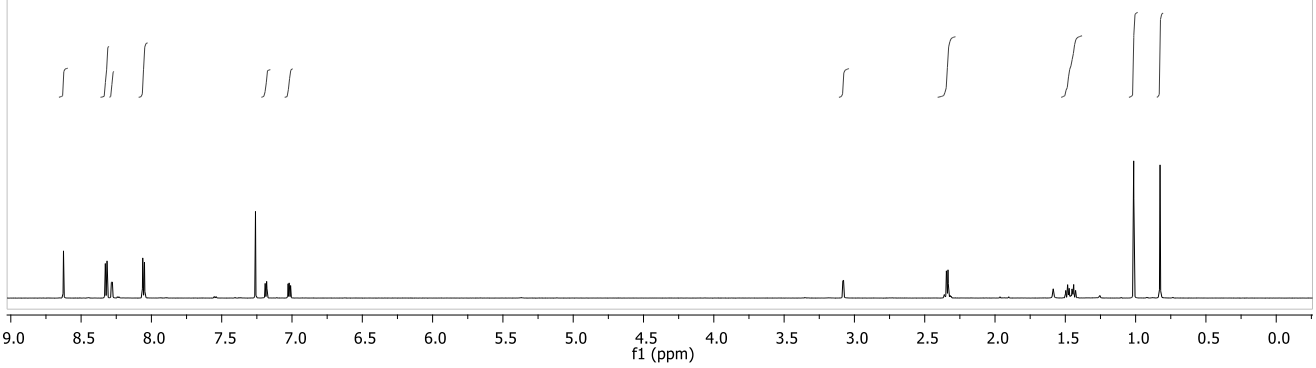
In a dry vial under inert atmosphere, cyclopropylimine **1k** (69.3 mg, 216 μmol) was dissolved in 2.2 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 8.5 hrs,[29] using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was clear and light red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (10 to 20 to 40 to 60 to 80 to 100% ethyl acetate:hexanes; loaded residue with PhMe). Collected 50.6 mg of a yellow solid that proved to be clean 1-aminoNB **2k** by ^{1}H NMR (73.0% yield).

*Characterization Data for 11-aza 1-aminoNB **2k**[30]:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.63 (s, 1H, imine CH), 8.32 (d, 2H, *J* = 8.5 Hz, 4-NO_2-Ar), 8.28 (*app.* d, 1H, *J* = 5.2 Hz, pyr), 8.06 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.19 (*app.* d, 1H, *J* = 7.3 Hz, pyr), 7.02 (dd, 1H, *J* = 7.3, 5.3 Hz, pyr), 3.08 (d, 1H, *J* = 3.4 Hz, C4), 2.37-2.31 (m, 2H, C2-eq, C3-eq), 1.51-1.42 (m, 2H, C2-ax, C3-ax), 1.01 (s, 3H, C7-Me), 0.83 (s, 3H, C7-Me) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 167.6, 159.4, 149.4, 146.6, 142.0, 141.3, 129.1, 127.1, 124.1, 121.0, 79.4, 59.6, 53.3, 28.2, 24.9, 20.0, 19.0 ppm
IR (neat): 2967, 1642, 1601, 1578, 1520, 1461, 1407, 1344, 1291, 1168, 1109, 1092, 1013, 840, 744, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{19}H_{20}N_3O_2^+$: 322.1550, Found: 322.1549
R_f = 0.25 (40% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

[29] Time course adjusted to account for the larger than normal amount of starting material.
[30] Assignments based on analogy to related scaffolds.

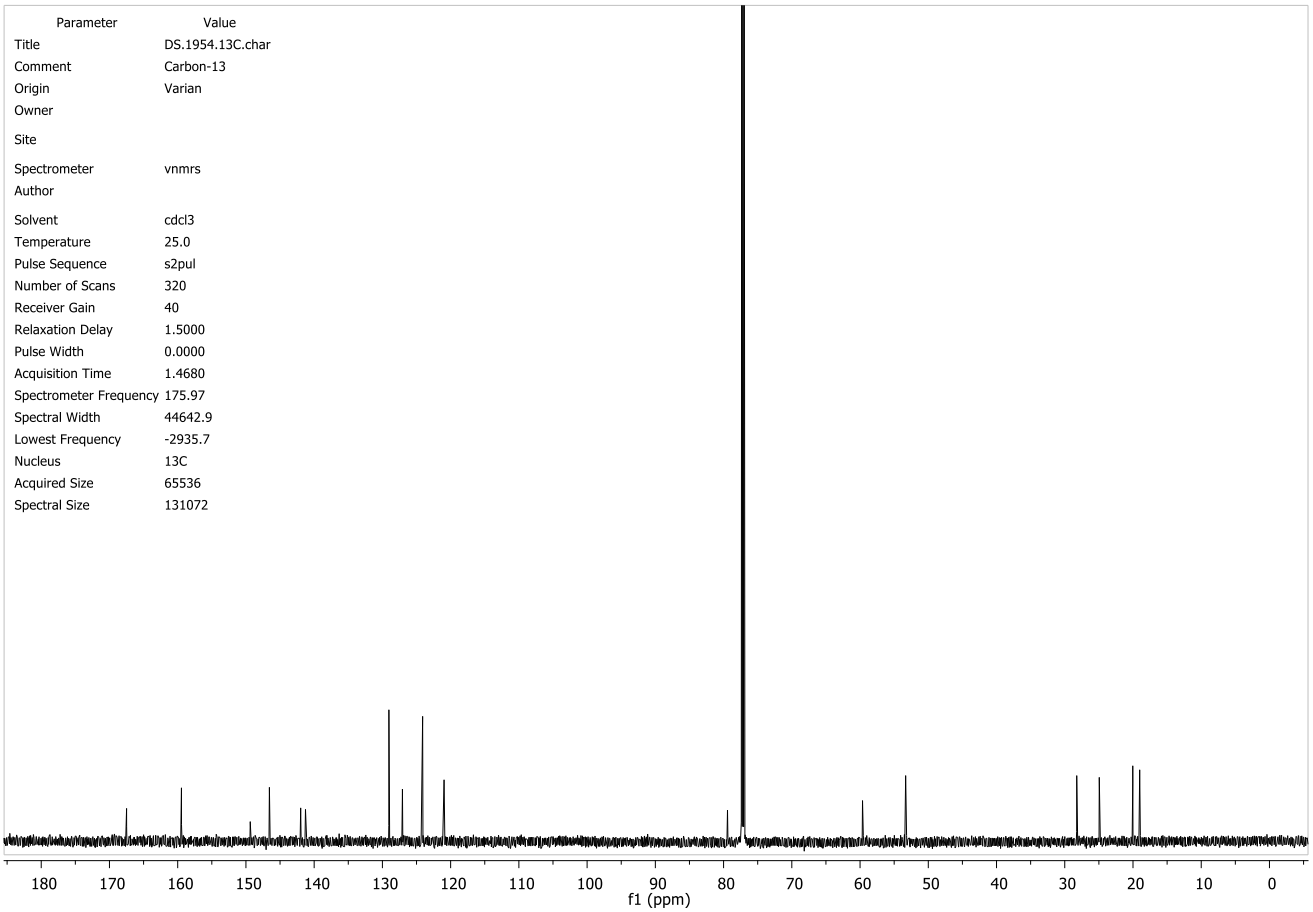
^{1}H NMR (700 MHz, $CDCl_3$) for 2k

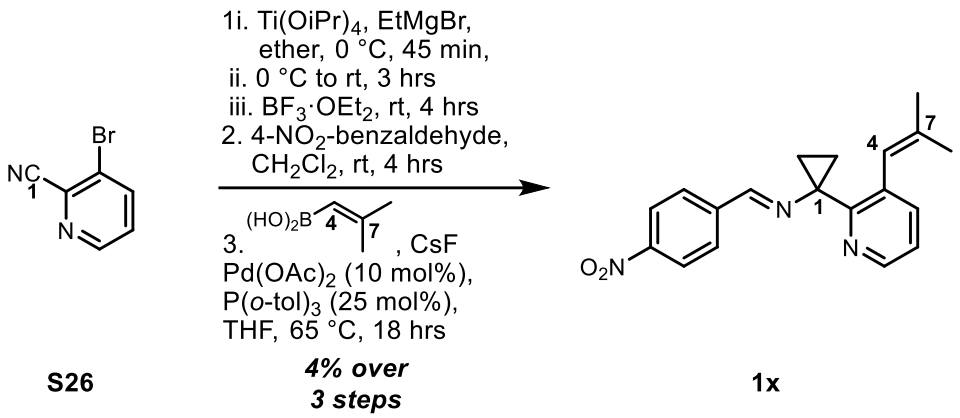
Parameter	Value
Title	DS.1954.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	54
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1380.0
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 2k

Parameter	Value
Title	DS.1954.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	320
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.7
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for 11-*aza* cyclopropylimine 1x

3-Bromo-2-cyanopyridine **S26** (1.03 g, 5.6 mmol; purchased from Matrix) was dissolved in 110 mL dry ether in a dry flask under inert atmosphere, then cooled to 0 °C. Titanium isopropoxide (1.8 mL, 6.2 mmol; purchased from Oakwood Chemical) was added in one portion, followed by addition of ethylmagnesium bromide (3.0 M in ether; 4.1 mL, 12.4 mmol) via syringe, dropwise down the side of the vial over the course of 5 min. The dark brown-black reaction mixture (clear, colorless at outset of EtMgBr addition) was stirred at 4 hrs at 0 °C, added 25 mL dry ether to account for evaporation, then added BF_3·etherate (1.4 mL, 11.3 mmol) dropwise over the course of 2 min. The reaction temperature was maintained at 0 °C for 1 hr, then the cold bath was removed followed by an additional 3 hrs of stirring while coming to room temp. The reaction was quenched by carefully pouring in 100 mL of a 1:1 mix of 1 M NaOAc (aq.):1 M NaOH (aq), followed by 30 min of vigorous stirring at room temp. The biphasic mixture was diluted with an additional 100 mL of the same aqueous mixture and 100 mL ether. The phases were separated. The aqueous phase was extracted with three 100 mL portions of ether. The combined organics were then washed with 100 mL brine + 1 mL 6 M NaOH (aq.), dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under vacuum. The crude residue was moved forward without further purification.[31]

The crude aminocyclopropane from above (up to 5.6 mmol) was dissolved in 30 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (1.27 g, 8.4 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (10 to 50% ethyl acetate:hexanes, increasing in 10% increments). Some of the impurities streaked through the column with the desired product, thus a second round of chromatography over basica alumina was implemented (5 to 10 to 15 to 20 to 30 to 40% ethyl acetate:hexanes). The desired product was collected as a mixture with a number of minor impurities, 210 mg of a red oily solid. This material was moved forward without further purification. Partial characterization is provided below.

Partial Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.63 (dd, 1H, *J* = 4.7, 1.5 Hz, pyr), 8.21 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.97 (dd, 1H, *J* = 8.0, 1.5 Hz, pyr), 7.78 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.69 (s, 1H, imine CH), 7.21 (dd, 1H, *J* = 8.0, 4.7 Hz, pyr), 1.76 (*app.* q, 2H, *J* = 4.7 Hz, CP), 1.61 (dd, 2H, *J* = 7.7, 4.8 Hz, CP) ppm
R_f = 0.80 (60% ethyl acetate:hexanes + 1% NH_4OH), one red spot, ninhydrin, UV

CsF (460 mg, 3.1 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2 and adding 0.5 mL dry, degassed dioxane (degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask). In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (14 mg, 62 µmol) and tris(o-tolyl)phosphine (53 mg, 151 µmol) were dissolved in 2 mL dry, degassed dioxane, then stirred for 20 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (0.6 mmol at most) and (2,2-dimethyl)vinylboronic acid (90 mg, 0.90 mmol; purchased from Synthonix) were dissolved in 1.5 mL dry, degassed dioxane. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with two 1 mL portions of dry, degassed dioxane. Once the Pd^0-phosphine mixture (orange) had stirred for 20 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. The system was flushed with Ar, sealed, and the reaction was heated to 80 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite,

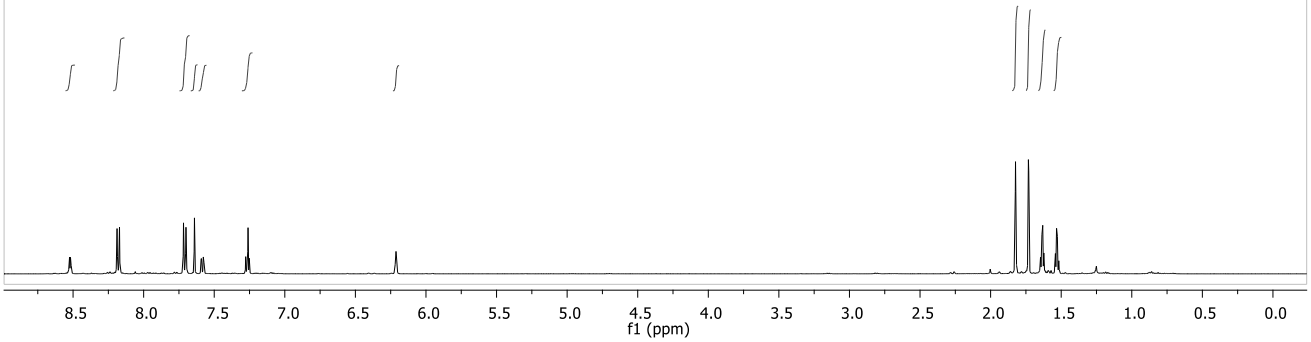
[31] The pyridine-based aminocyclopropane intermediates showed evidence of instability during chromatography, even upon neutralization of the silica or use of basic alumina; purification via chromatography was thus avoided.

eluting with ~50 mL ether before concentrating under vacuum. The crude residue was purified via flash chromatography over basic alumina (8 to 32% ethyl acetate:hexanes, increasing in 8% increments; residue was loaded with PhMe). Obtained 110 mg of the desired product still mixed with minor impurities. A second round of chromatography over basica alumina (4 to 6 to 10 to 15 to 20 to 25 to 35% ethyl acetate:hexanes) afforded 50.3 mg of clean cyclopropylimine **1x** and an additional 34.0 mg of mixed material. The mixed material was purified over basica alumina once more to provide an additional 14.5 mg of the desired product. Total recovery of cyclopropylimine **1x** equaled 65.1 mg (3.6% over 3 steps) as a red-orange oil.

*Characterization Data for 8-aza cyclopropylimine **1x**:*
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.52 (dd, 1H, *J* = 4.8, 1.6 Hz, pyr), 8.18 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.71 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.64 (s, 1H, imine CH), 7.58 (dd, 1H, *J* = 7.7, 1.3 Hz, pyr), 7.26 (dd, 1H, *J* = 8.0, 4.5 Hz, pyr), 6.21 (s, 1H, C4), 1.82 (s, 3H, C7-Me), 1.73 (s, 3H, C7-Me), 1.63 (dd, 2H, *J* = 7.4, 4.4 Hz, CP), 1.56-1.50 (m, 2H, CP) ppm
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 156.2, 154.6, 148.7, 147.5, 142.4, 137.9, 137.6, 135.3, 128.2, 123.9, 122.6, 121.7, 51.9, 26.6, 19.5, 17.9 ppm
IR (neat): 2969, 2928, 1599, 1518, 1424, 1342, 1209, 1170, 1095, 1013, 948, 885, 831, 793, 734, 691 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{19}H_{20}N_3O_2^+$: 322.1550, Found: 322.1552
R_f = 0.50 (40% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

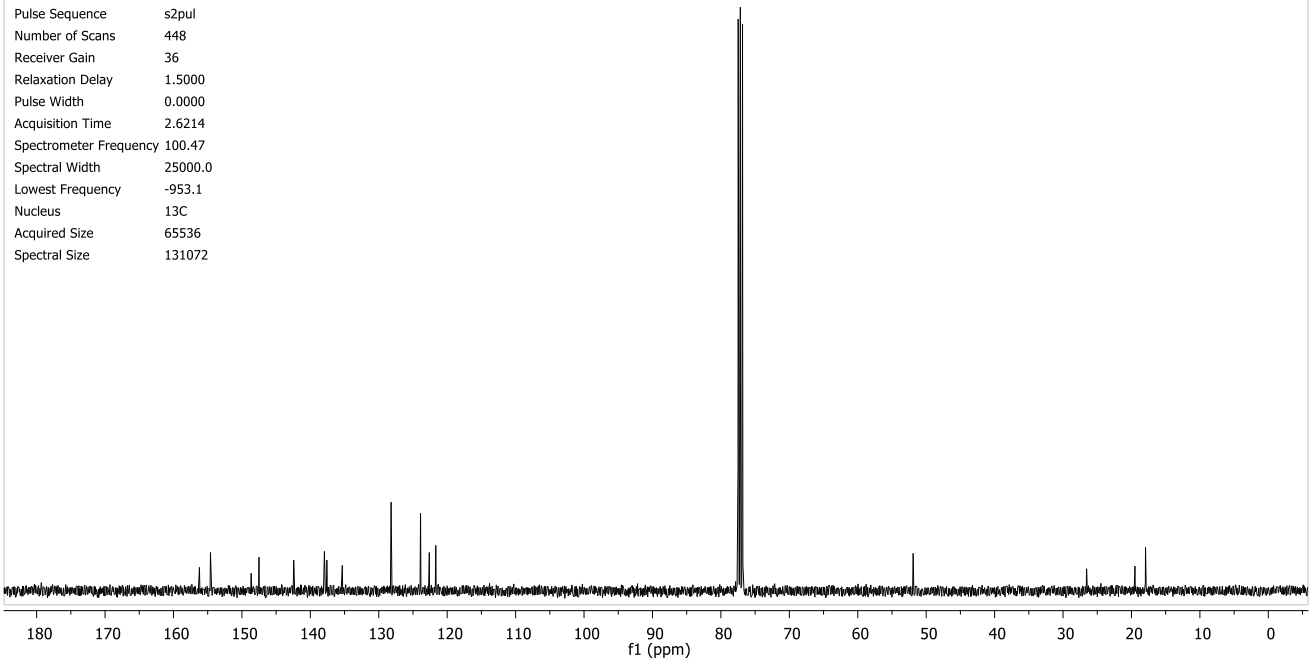
^{1}H NMR (500 MHz, $CDCl_3$) for 1x

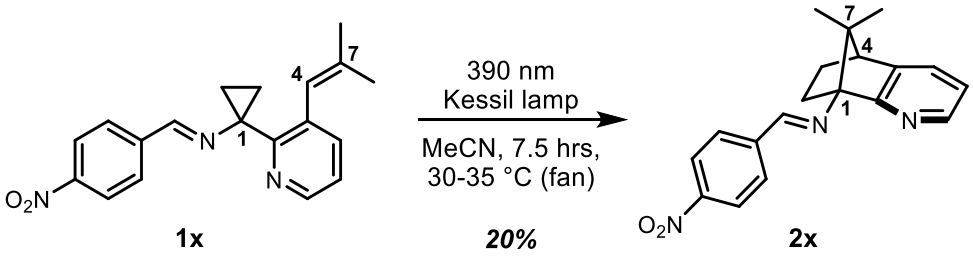
Parameter	Value
Title	DS.1949.c3.pdt
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	42
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1006.8
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



^{13}C NMR (100 MHz, $CDCl_3$) for 1x

Parameter	Value
Title	DS.1949.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	dmso
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	448
Receiver Gain	36
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	2.6214
Spectrometer Frequency	100.47
Spectral Width	25000.0
Lowest Frequency	-953.1
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for 8-*aza* 1-aminoNB 2x

In a dry vial under inert atmosphere, cyclopropylimine **1x** (58.0 mg, 180 μmol) was dissolved in 1.8 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 7.5 hrs,[32] using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was clear and light red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (30 to 50 to 75 to 100% ethyl acetate:hexanes; loaded residue with PhMe). Collected major UV active fractions, which proved to be a mixture of starting material, product, what is suspected to be the pyrroline byproduct, and a few other minor, unidentifiable byproducts. The residue was exposed to a second round of chromatography over basica alumina (5 o 10 to 15 to 20 to 25 to 35 to 45 to 55% ethyl acetate:hexanes). Obtained 19.8 mg of a 0.7:1 mix of starting material:product, indicating that 8.2 mg were recovered cyclopropylimine **1x** (14.1% recovery) and 11.6 mg were the desired 1-aminoNB (20.0% yield).

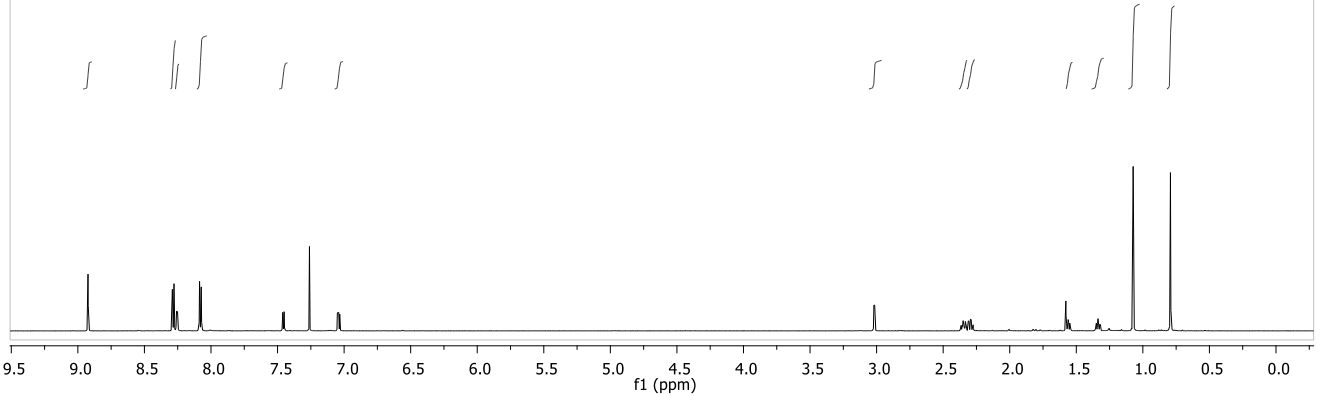
To obtain characterization grade material, the isolated mixture re-exposed to conditions and re-purified, ultimately yielding 16.4 mg of 1-aminoNB **2x** as an orange oil (28.3% yield following all manipulations).

*Characterization Data for 8-aza 1-aminoNB **2x**[33]:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.92 (s, 1H, imine CH), 8.28 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.28 (dd, 1H, *J* = 5.1, 1.3 Hz, pyr), 8.07 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.46 (dd, 1H, *J* = 7.3, 1.3 Hz, pyr), 7.04 (dd, 1H, *J* = 7.3, 5.2 Hz, pyr), 3.02 (d, 1H, *J* = 4.0 Hz, C4), 2.37-2.32 (m, 1H, C3-eq), 2.29 (*app*. td, 1H, *J* = 11.0, 3.7 Hz, C2-eq), 1.56 (ddd, 1H, *J* = 11.8, 7.4, 3.7 Hz, C2-ax) 1.34 (ddd, 1H, *J* = 12.0, 9.6, 3.6 Hz, C3-ax), 1.07 (s, 3H, C7-Me), 0.79 (s, 3H, C7-Me) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 166.6, 161.1, 149.2, 146.0, 142.5, 140.7, 129.2, 129.1, 123.9, 121.5, 79.6, 59.4, 49.8, 28.4, 26.9, 20.1, 19.3 ppm
IR (neat): 2961, 1641, 1600, 1518, 1474, 1460, 1405, 1342, 1290, 1160, 1108, 851, 788, 745, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{19}H_{20}N_3O_2^+$: 322.1550, Found: 322.1549
R_f = 0.55 (40% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

[32] Time course adjusted to account for the smaller amount of starting material.
[33] Assignments based on analogy to related scaffolds.

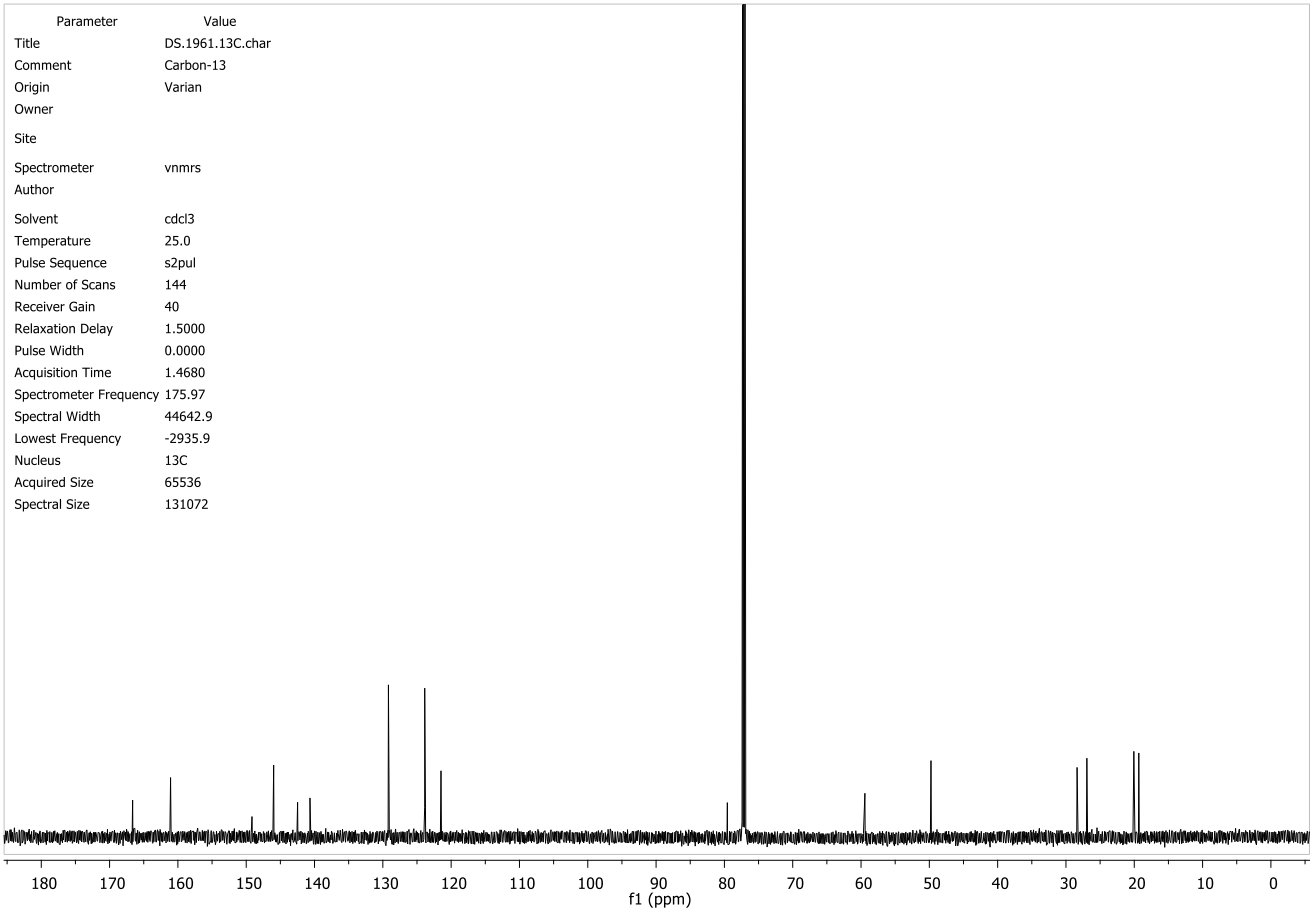
^{1}H NMR (700 MHz, $CDCl_3$) for 2x

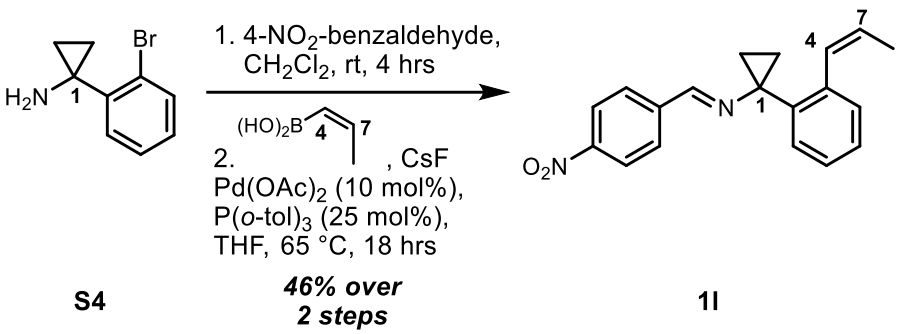
Parameter	Value
Title	DS.1961.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	52
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 2x

Parameter	Value
Title	DS.1961.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	144
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.9
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S4 **1l**

Procedure for C7-methyl cyclopropylimine 1l

Aminocyclopropane **S4** (580 mg, 2.73 mmol) was dissolved in 20 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (584 mg, 3.87 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (0 to 1 to 2 to 3 to 5 to 10% ethyl acetate:hexanes). Collected 831 mg of the Schiff base intermediate (88.0% yield) as a yellow oil. Partial characterization is provided below.

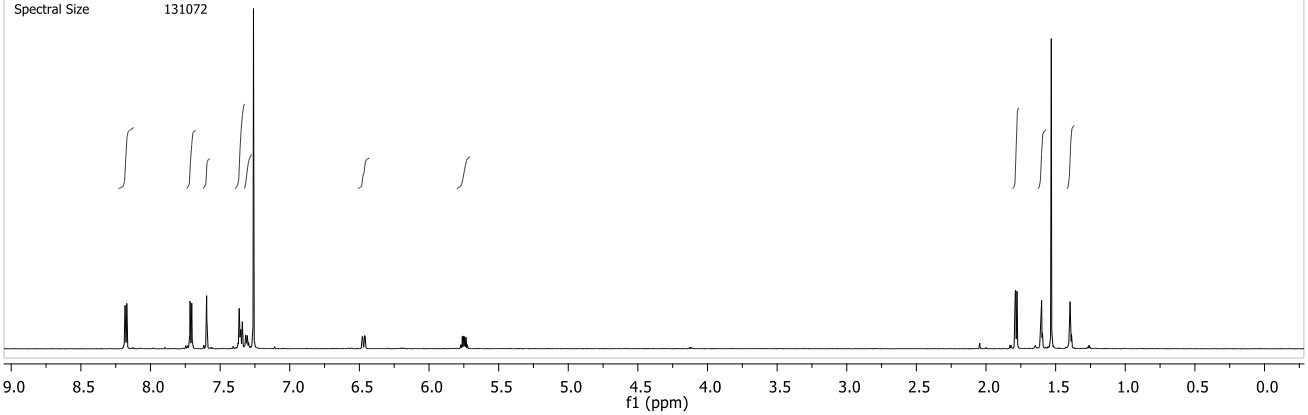
Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.19 (d, *J* = 8.8 Hz, 2H, 4-NO_2-Ar), 7.77 (d, *J* = 8.8 Hz, 2H, 4-NO_2-Ar), 7.65 (d, *J* = 8.0 Hz, 1H, Ar), 7.63 (s, 1H, imine-CH), 7.38 (d, *J* = 4.2 Hz, 2H, Ar), 7.25 (dt, *J* = 9.1, 4.5 Hz, 1H, Ar), 1.72 (*app.* q, *J* = 4.6 Hz, 2H, CP), 1.47 (*app.* q, *J* = 4.5 Hz, 2H, CP) ppm
R_f = 0.45 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (288 mg, 1.90 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2. In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (8.52 mg, 0.038 mmol) and tris(o-tolyl)phosphine (23.1 mg, 0.076 mmol) were dissolved in 2 mL dry, degassed THF(degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask), then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (131 mg, 0.38 mmol) was dissolved in 2 mL dry, degassed THF before adding cis-1-propen-1-yl boronic acid (49 mg, 0.57 mmol) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with two 0.5 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~100 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was dry loaded with celite). Obtained vinylated cyclopropylimine **1l** as a as a single olefin diastereomer (assigned as *Z* based on *J*-coupling value), slighty yellow oil, 60 mg (46% yield over 2 steps).

*Characterization Data for C7-methyl cyclopropylimine **1l**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.18 (d, *J* = 8.7 Hz, 2H, 4-NO_2-Ar), 7.71 (d, *J* = 8.7 Hz, 2H, 4-NO_2-Ar), 7.60 (s, 1H, imine-CH), 7.39-7.29 (m, 4H, Ar), 6.47 (d, *J* = 13.1 Hz, 1H, C4), 5.77-5.72 (m, 1H, C7), 1.78 (dd, *J* = 7.1, 1.7 Hz, 3H, C7-CH_3), 1.60 (*app.* q, *J* = 4.3 Hz, 2H, CP), 1.40 (*app.* q, *J* = 4.3 Hz, 2H, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 154.9, 148.6, 142.5, 138.8, 137.1, 131.5, 130.0, 128.6, 128.2, 127.8, 127.4, 127.2, 123.9, 50.3, 18.5, 14.6 ppm
IR (neat): 3021, 2917, 1599, 1518, 1446, 1412, 1343, 1207, 1106, 1025, 956, 832, 765, 748, 691 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{19}H_{18}N_2O_2^+$: 307.1441, Found: 307.1441
R_f = 0.30 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

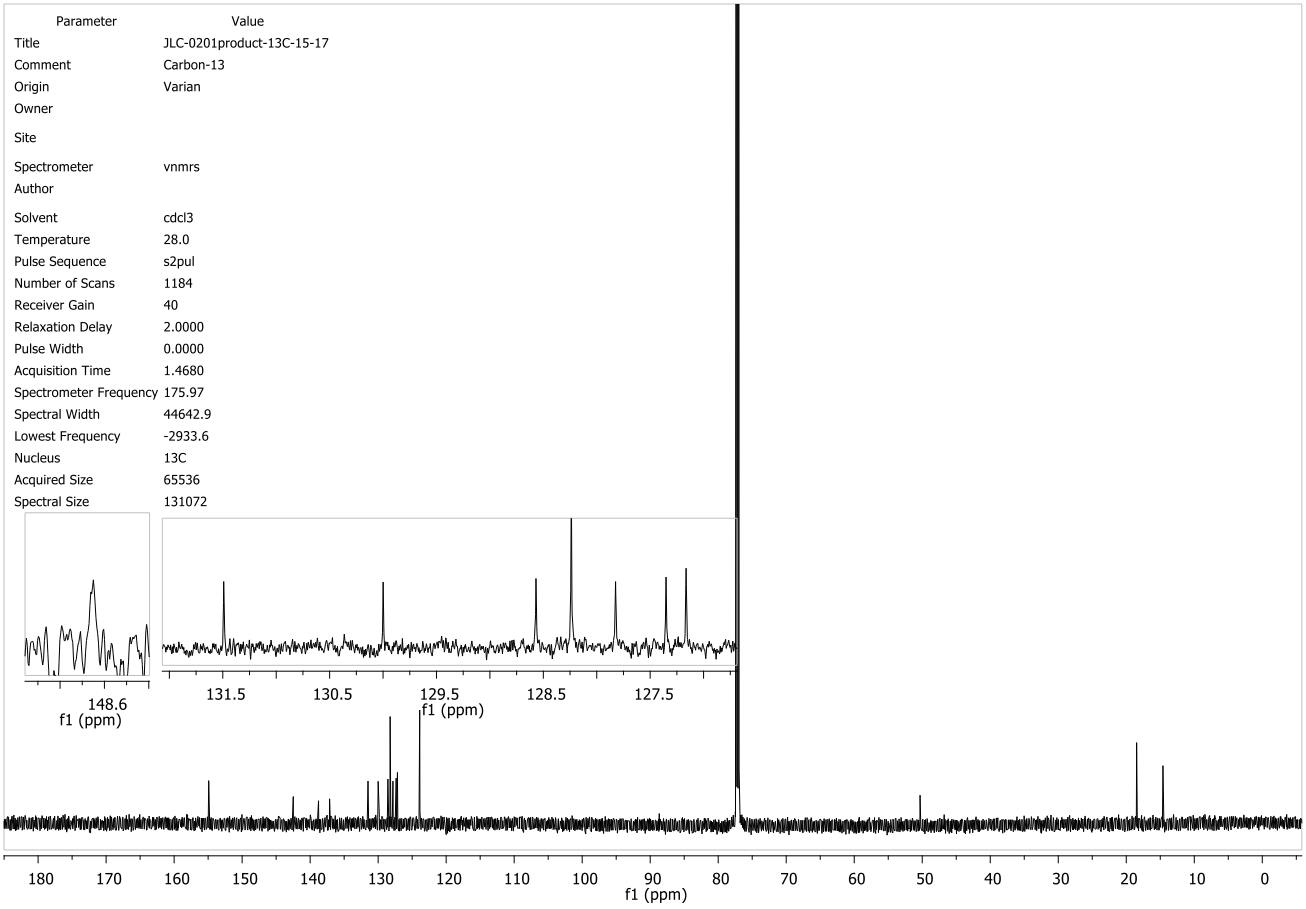
^{1}H NMR (700 MHz, $CDCl_3$) for 1l

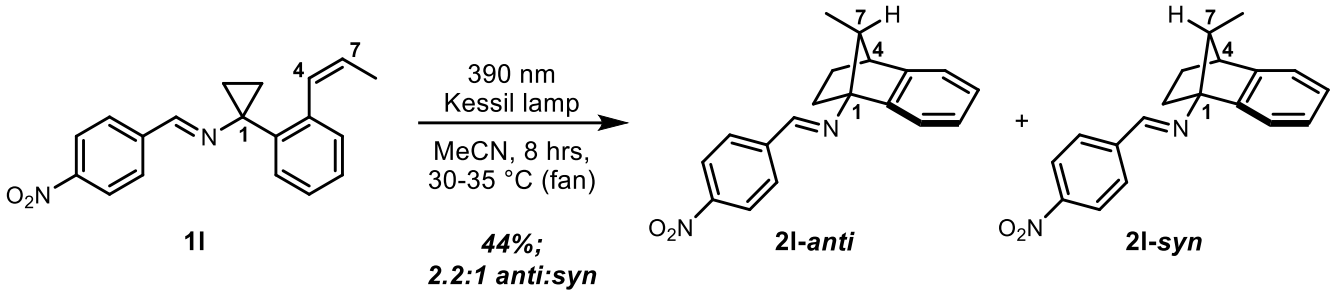
Parameter	Value
Title	JLC-0201product-1H4-15-17
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	28.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	58
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 1l

Parameter	Value
Title	JLC-0201product-13C-15-17
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	28.0
Pulse Sequence	s2pul
Number of Scans	1184
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2933.6
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for C7-methyl 1-aminoNBs 2l-anti and 2l-syn

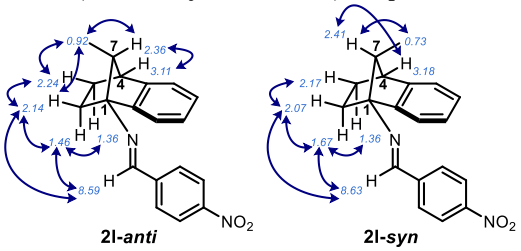
In a dry vial under inert atmosphere, cyclopropylimine **1l** (50.1 mg, 164 μmol) was dissolved in 1.7 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 7 hrs,[34] using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was dark red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (1 to 3 to 5 to 10 to 15% ethyl acetate:hexanes; loaded residue with PhMe). Obtained 29.2 mg of a yellow oil that ^{1}H NMR revealed to be a 1:1.05:2.37 mix of starting material to *syn* product to *anti* product, indicating the final yields were 6.6 mg of recovered cyclopropylimine **1l** (13.2% recovery) and 22.6 mg of 1-aminoNBs **2l-anti** and **2l-syn** as a 2.2:1 *anti*:*syn* ratio[35] (43.9% combined yield); characterization data was collected on the mixture (NMR data below is listed separately for clarity[36]).

*Characterization Data for C7-methyl 1-aminoNBs **2l-anti** and **2l-syn**:*
IR (neat): 2961, 2871, 1641, 1601, 1519, 1471, 1458, 1342, 1313, 1291, 1107, 1012, 839, 749, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{19}H_{19}N_2O_2^+$: 307.1441, Found: 307.1443
$\mathbf{R_f}$ = 0.75 (20% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

*NMR Data for anti-C7-methyl 1-aminoNB **2l-anti**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.59 (s, 1H, imine CH), 8.32 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.05 (d, 2H, *J* = 9.0 Hz, 4-NO_2-Ar), 7.22 (d, 1H, *J* = 7.2 Hz, Ar), 7.14 (td, 1H, *J* = 7.3, 1.0 Hz, Ar), 7.10 (td, 1H, *J* = 7.3, 1.0 Hz, Ar), 6.94 (d, 1H, *J* = 7.2 Hz, Ar), 3.13 (d, 1H, *J* = 3.9 Hz, C4), 2.37 (q, 1H, *J* = 6.7 Hz, C7), 2.27-2.22 (m, 1H, C3-eq), 2.15 (td, 1H, *J* = 10.7, 3.9 Hz, C2-eq), 1.49-1.45 (m, 1H, C2-ax), 1.41-1.36 (m, 1H, C3-ax), 0.93 (d, 3H, *J* = 6.8 Hz, C7-Me) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 159.3, 149.5, 149.3, 147.6, 145.5, 142.2, 129.0, 126.3, 125.7, 124.1, 120.9, 118.8, 79.3, 58.5, 46.2, 26.4, 26.2, 11.6 ppm

*NMR Data for syn-C7-methyl 1-aminoNB **2l-syn**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.63 (s, 1H, imine CH), 8.32 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.06 (d, 2H, *J* = 9.0 Hz, 4-NO_2-Ar), 7.24 (dd, 1H, *J* = 6.0, 1.9 Hz, Ar), 7.19-7.15 (m, 2H, Ar), 7.09-7.07 (m, 1H, Ar), 3.21 (d, 1H, *J* = 4.1 Hz, C4), 2.42 (qd, 1H, *J* = 6.5, 1.1 Hz, C7), 2.18 (tt, 1H, *J* = 10.9, 4.1 Hz, C3-eq), 2.07 (td, 1H, *J* = 10.9, 4.2 Hz, C2-eq), 1.67 (ddd, 1H, *J* = 11.0, 9.3, 4.0 Hz, C2-ax), 1.39-1.34 (m, 1H, C3-ax), 0.74 (d, 3H, *J* = 6.5 Hz, C7-Me) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 158.5, 149.2, 145.5, 145.1, 142.3, 129.0, 126.5, 126.0, 124.1, 122.6, 120.4, 79.7, 58.8, 48.1, 33.1, 28.2, 10.7 ppm

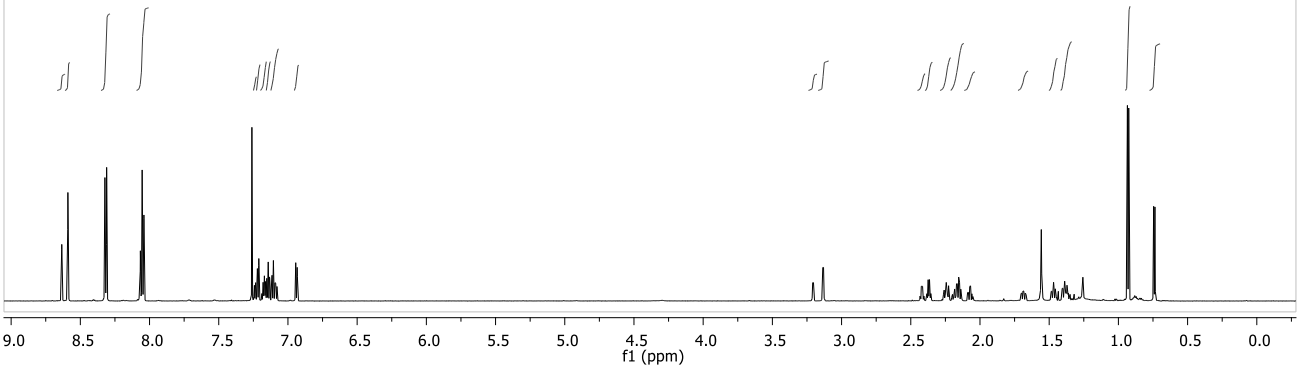
2D NMR Data
- COSY, HSQC, and NOESY experiments were employed to assign the various resonances to the two isomers and confirm the structure of the desired products. Key NOESY correlations (denoted by blue arrows) are provided for both 1-aminoNBs **2l-anti** and **2l-syn**.



[34] Time course adjusted to account for the smaller amount of starting material.
[35] The C4 resonances were employed to determine *anti*:*syn* ratio.
[36] The sample used for characterization was prepared after re-exposing the above sample to irradiation (in order to drive to completion), hence the altered isomeric ratio (now 1.9:1 *anti*:*syn*).

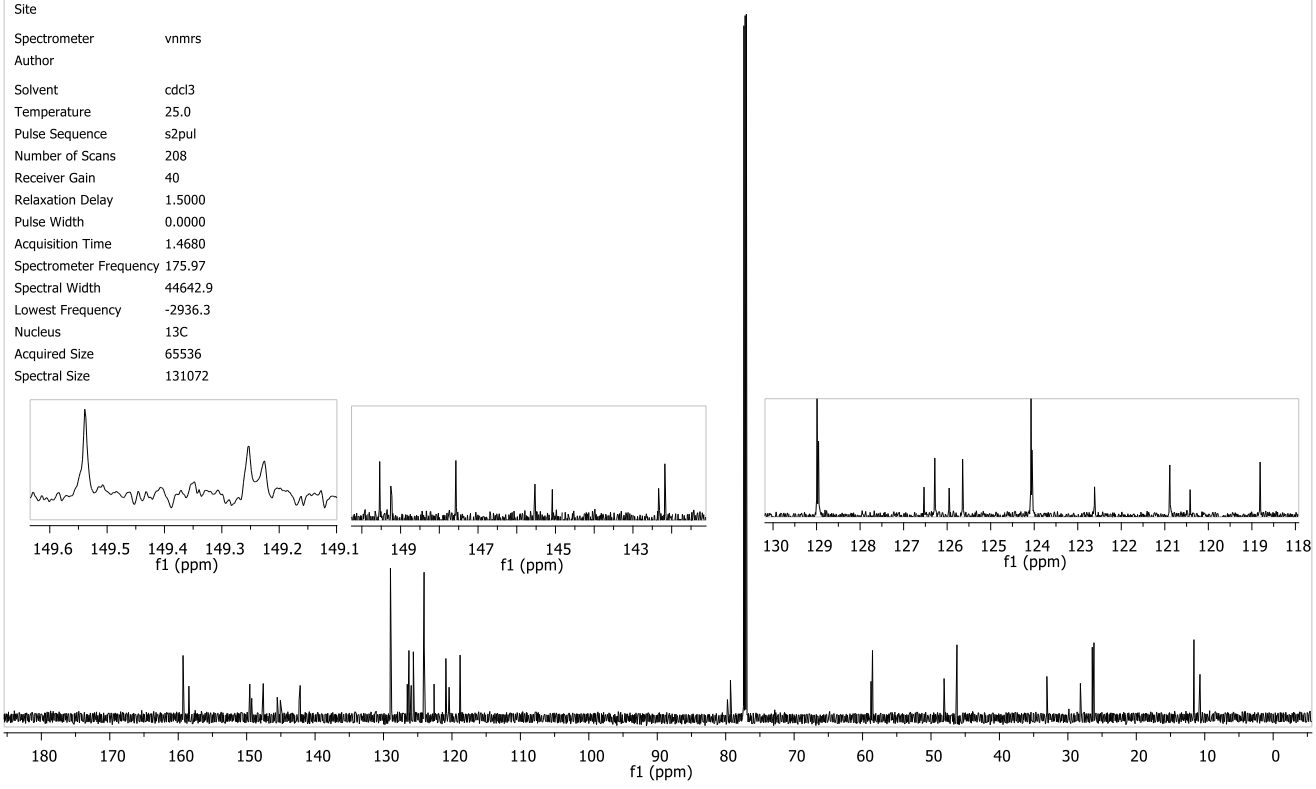
^{1}H NMR (700 MHz, $CDCl_3$) for 2l

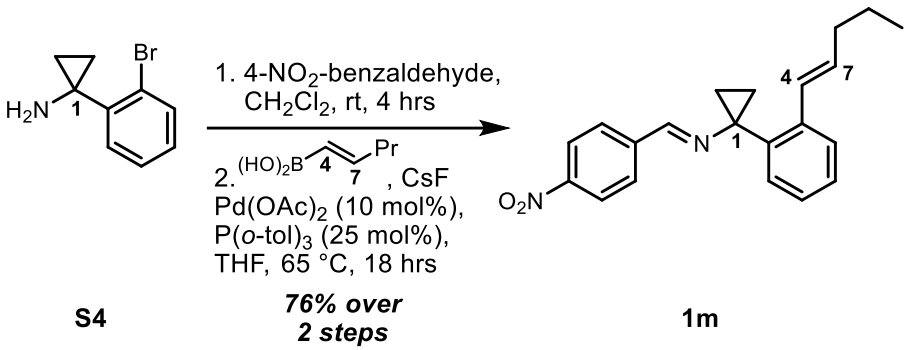
Parameter	Value
Title	DS.1982B.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	50
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 2l

Parameter	Value
Title	DS.1982B.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	208
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2936.3
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S4 ***76% over 2 steps*** **1m**

Procedure for C7-propyl cyclopropylimine 1m

Aminocyclopropane **S4** (580 mg, 2.73 mmol) was dissolved in 20 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (584 mg, 3.87 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (0 to 1 to 2 to 3 to 5 to 10% ethyl acetate:hexanes). Collected 831 mg of the Schiff base intermediate (88.0% yield) as a yellow oil. This material is equivalent to that employed to prepare cyclopropylimine **1a**.

CsF (330 mg, 2.17 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2. In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (9.76 mg, 0.044 mmol) and tris(o-tolyl)phosphine (26.5 mg, 0.087 mmol) were dissolved in 2 mL dry, degassed THF(degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask), then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (150 mg, 0.44 mmol) was dissolved in 2 mL dry, degassed THF before adding 1-penten-1-yl boronic acid (131 mg, 1.15 mmol) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with two 0.5 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~100 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was dry loaded with celite). Obtained vinylated cyclopropylimine **1m** as a white solid, 125 mg (76% yield over 2 steps).

*Characterization Data for 8-aza aminocyclopropane **1m**:*

^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.18 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.73 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.62 (s, 1H, imine-CH), 7.58 (d, 1H, *J* = 7.7 Hz, Ar), 7.35-7.23 (m, 3H, Ar), 6.55 (d, 1H, *J* = 15.8 Hz, C4), 6.16 (dt, 1H, *J* = 15.7, 7.0 Hz, C7), 2.12 (qd, 2H, *J* = 6.9, 1.3 Hz, C7-C*H*$_2$$CH_2CH_3$), 1.64 (q, 2H, *J* = 4.3 Hz, C7-CH_2C*H*$_2$$CH_3$), 1.44-1.33 (m, 4H, CP, CP), 0.83 (t, 3H, *J* = 7.4 Hz, C7-CH_2CH_2C*H*$_3$). ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 155.39, 148.60, 142.55, 139.08, 135.65, 133.02, 131.60, 128.42, 128.30, 127.68, 127.30, 125.52, 123.84, 50.04, 35.38, 22.63, 18.61, 13.71. ppm

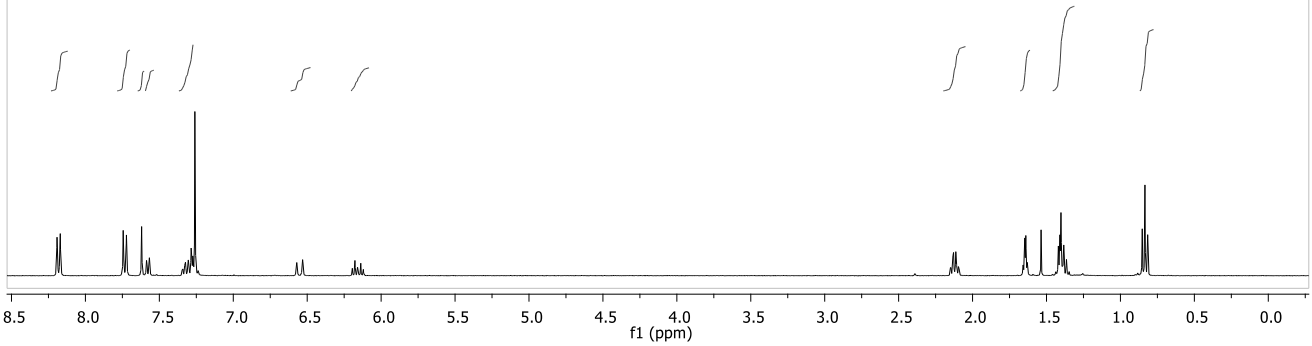
IR (neat): 2957, 2927, 1599, 1519, 1449, 1412, 1342, 1206, 1110, 1041, 967, 834, 748, 690 cm^{-1}

HRMS (ES+, *m/z)* calculated for $C_{19}H_{18}N_2O_2^+$: 335.1754, Found: 335.1764

R_f = 0.70 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

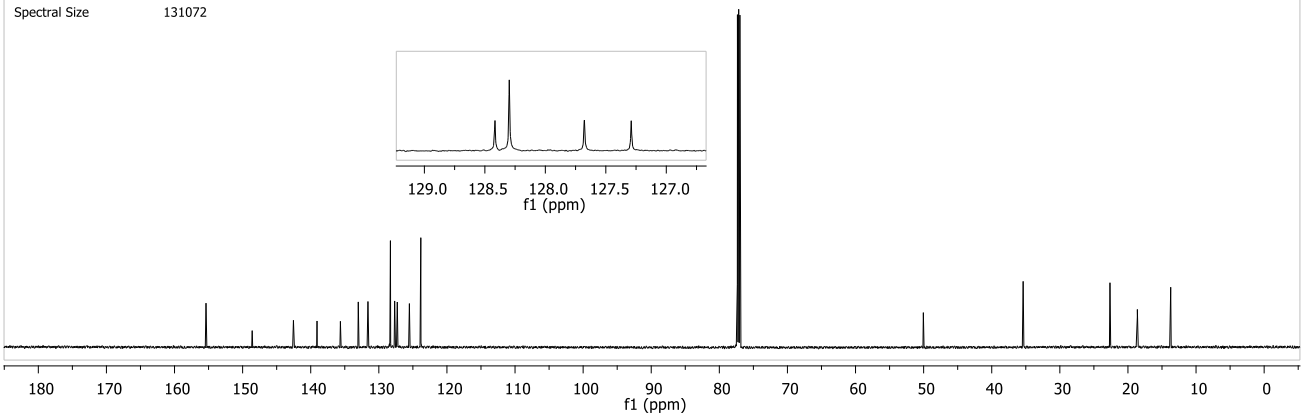
^{1}H NMR (700 MHz, $CDCl_3$) for 1m

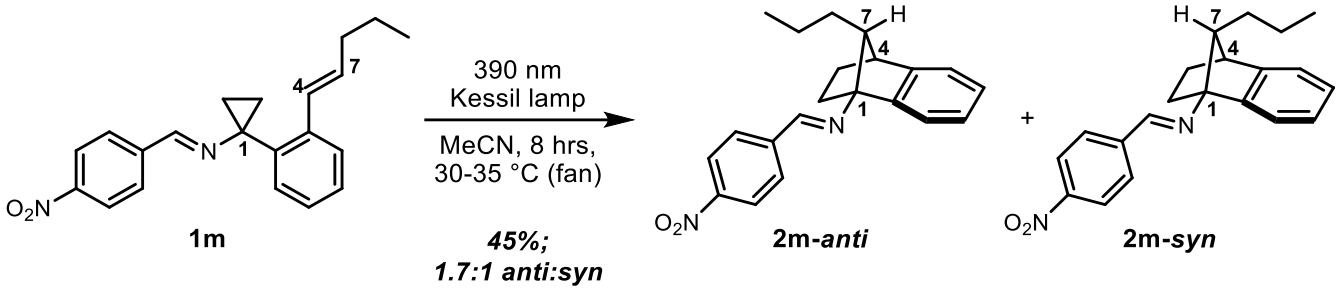
Parameter	Value
Title	DS.1840.c.pdt
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	24.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	58
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	399.54
Spectral Width	6377.6
Lowest Frequency	-784.8
Nucleus	1H
Acquired Size	22321
Spectral Size	65536



^{13}C NMR (176 MHz, $CDCl_3$) for 1m

Parameter	Value
Title	JLC-0199product-13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	608
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2936.6
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for C7-propyl 1-aminoNBs 2m-anti and 2m-syn

In a dry vial under inert atmosphere, cyclopropylimine **1m** (67.8 mg, 203 μmol) was dissolved in 2.0 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 8 hrs,[37] using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was red-orange. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (2 to 3 to 5 to 7 to 10 to 15 to 25 to 35% ethyl acetate:hexanes; loaded residue with PhMe). Collected starting material and product across two portions.

Portion 1: 39.1 mg of a yellow oil, revealed to be 16.5 mg of recovered cyclopropylimine **1m** (24.3% recovery) and 22.6 mg of 1-aminoNB mix as a 1.85:1 *anti*:*syn* ratio.[38]

Portion 2: 7.2 mg of a yellow oil, only desired 1-aminoNBs **2m-anti** and **2m-syn** in a 1.27:1 *anti*:*syn* ratio.

Combined yield of 1-aminoNBs **2m-anti** and **2m-syn** is thus 29.8 mg in a 1.7:1 *anti*:*syn* ratio (44.0% combined yield).

(characterization data was collected on the mixture; NMR data below is listed separately for clarity[39])

*Characterization Data for C7-propyl 1-aminoNBs **2m-anti** and **2m-syn**:*
IR (neat): 2956, 2928, 2871, 1641, 1601, 1520, 1458, 1343, 1292, 1108, 1012, 841, 749, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{21}H_{23}N_2O_2^+$: 335.1754, Found: 335.1754
$\mathbf{R_f}$ = 0.75 (20% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

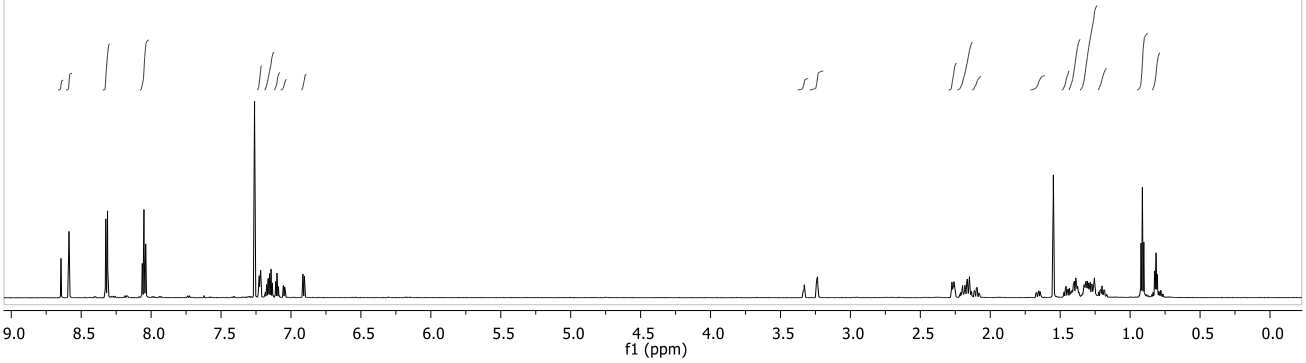
*NMR Data for anti-C7-propyl 1-aminoNB **2m-anti**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.59 (s, 1H, imine CH), 8.32 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.05 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.24-7.21 (m, 1H, Ar), 7.14 (td, 1H, *J* = 7.3, 1.0 Hz, Ar), 7.10 (td, 1H, *J* = 7.4, 1.0 Hz, Ar), 6.91 (d, 1H, *J* = 7.3 Hz, Ar), 3.24 (d, 1H, *J* = 3.9 Hz, C4), 2.28-2.24 (m, 1H, C7), 2.22-2.13 (m, 2H, C3-eq, C2-eq), 1.48-1.45 (m, 1H, C2-ax), 1.43-1.36 (m, 1H, C3-ax), 1.35-1.25 (m, 4H, C7-C*H*$_2$C*H*$_2$-), 0.91 (t, 3H, *J* = 7.2 Hz, C7-$CH_2CH_2CH_3$) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 159.3, 149.7, 149.3, 147.5, 142.2, 129.0, 126.3, 124.1, 120.9, 118.7, 79.4, 64.7, 44.2, 28.8, 27.7, 26.3, 21.2, 14.6 ppm

*NMR Data for syn-C7-propyl 1-aminoNB **2m-syn**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.64 (s, 1H, imine CH), 8.32 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.06 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.24-7.21 (m, 1H, Ar), 7.19-7.15 (m, 2H, Ar), 7.06-7.04 (m, 1H, Ar), 3.33 (d, 1H, *J* = 4.1 Hz, C4), 2.28-2.24 (m, 1H, C7), 2.18-2.14 (m, 1H, C3-eq), 2.10 (td, 1H, *J* = 10.8, 4.0 Hz, C2-eq), 1.66 (ddd, 1H, *J* = 11.0, 9.3, 4.0 Hz, C2-ax), 1.43-1.36 (m, 1H, C7-C*H*$_2$-), 1.35-1.25 (m, 2H, C3-ax), 1.23-1.16 (m, 2H, C7-CH_2C*H*$_2$-), 0.81 (t, 3H, *J* = 7.1 Hz, C7-$CH_2CH_2CH_3$) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 158.5, 149.1, 145.7, 145.4, 142.4, 129.0, 126.5, 125.9, 124.1, 122.5, 120.1, 79.7, 64.8, 45.8, 32.9, 28.3, 27.0, 21.8, 14.5 ppm

[37] Time course adjusted to account for the smaller amount of starting material.
[38] The C4 resonances were employed to determine *anti*:*syn* ratio.
[39] Assignments based on analogy to related systems. The sample used for characterization was prepared after re-exposing the above sample to irradiation (in order to drive to completion), hence the altered isomeric ratio (now 1.7:1 *anti*:*syn*.

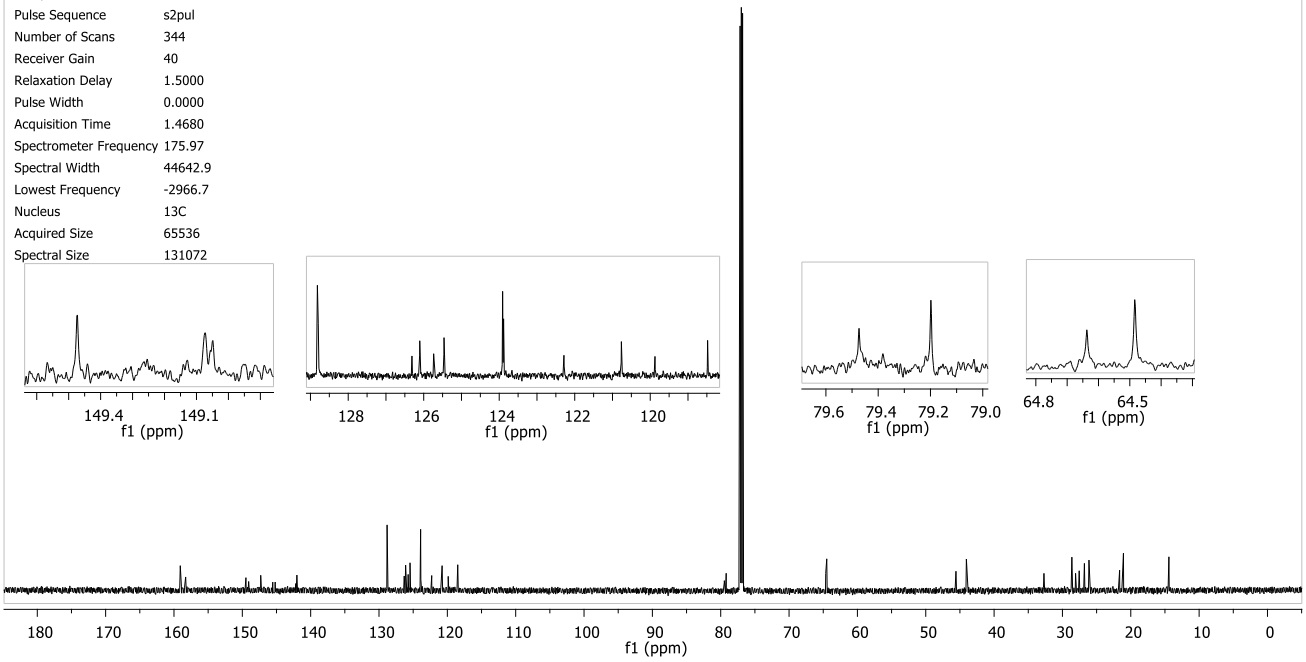
^{1}H NMR (700 MHz, $CDCl_3$) for 2m

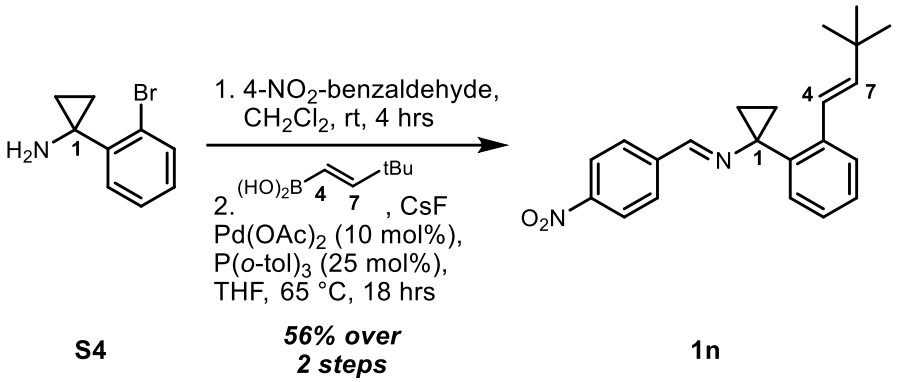
Parameter	Value
Title	DS.1982A.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	52
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 2m

Parameter	Value
Title	DS.1982A.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	344
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2966.7
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S4 ***56% over 2 steps*** **1n**

Procedure for C7-tert-butyl cyclopropylimine 1n

Aminocyclopropane **1n** (1.70 g, 8.02 mmol) was dissolved in 30 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (1.71 g, 11.3 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (0 to 1 to 2 to 3 to 5 to 10% ethyl acetate:hexanes). Collected 2.33 g of the Schiff base intermediate (84.2% yield) as a yellow oil. Partial characterization is provided below.

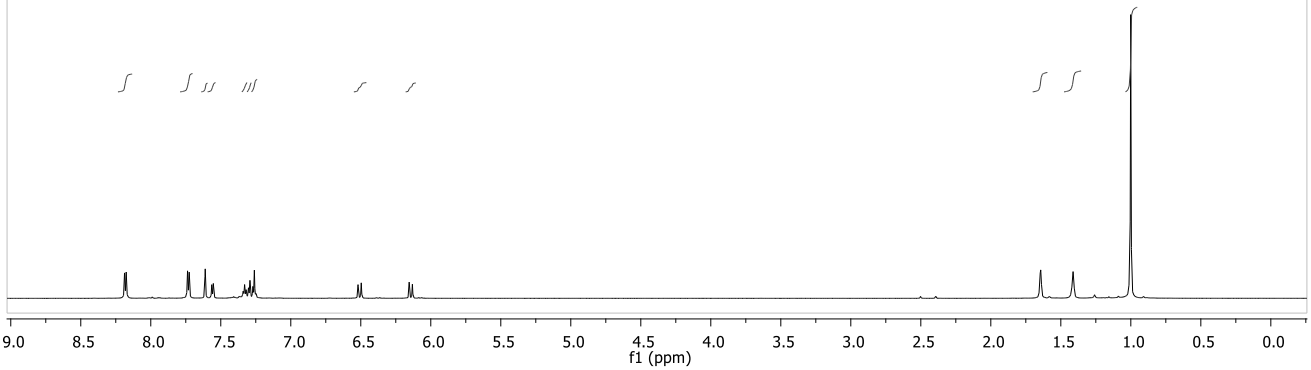
Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.19 (d, *J* = 8.8 Hz, 2H, 4-NO_2-Ar), 7.77 (d, *J* = 8.8 Hz, 2H, 4-NO_2-Ar), 7.65 (d, *J* = 8.0 Hz, 1H, Ar), 7.63 (s, 1H, imine-CH), 7.38 (d, *J* = 4.2 Hz, 2H, Ar), 7.25 (dt, *J* = 9.1, 4.5 Hz, 1H, Ar), 1.72 (*app.* q, *J* = 4.6 Hz, 2H, CP), 1.47 (*app.* q, *J* = 4.5 Hz, 2H, CP) ppm
R_f = 0.45 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (330 mg, 2.17 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2. In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (9.76 mg, 43.5 μmol) and tris(o-tolyl)phosphine (26.5 mg, 86.9 μmol) were dissolved in 3 mL dry, degassed THF (degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask), then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (150 mg, 0.435 mmol) was dissolved in 2 mL dry, degassed THF before adding 3,3-dimethyl-1-butenylboronic acid (83.4 mg, 0.652 mmol) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with two 0.5 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~100 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was loaded with toluene and pentane). Obtained vinylated cyclopropylimine **1n** as a slighty yellow oil, 101 mg (56.1% yield over 2 steps; 66.6% for cross-coupling).

*Characterization Data for C7-tert-butyl cyclopropylimine **1n**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.18 (d, *J* = 8.3 Hz, 2H, 4-NO_2-Ar), 7.73 (d, *J* = 8.3 Hz, 2H, 4-NO_2-Ar), 7.61 (s, 1H, imine-CH), 7.56 (d, *J* = 7.7 Hz, 1H, Ar), 7.33 (*app.* t, *J* = 7.4 Hz, 1H, Ar), 7.30 (dd, *J* = 7.2 Hz, 1H, Ar), 7.26 (*app.* t, *J* = 7.3 Hz, 1H, Ar), 6.51 (d, *J* = 16.1 Hz, 1H, C4), 6.14 (d, *J* = 16.1 Hz, 1H, C7), 1.64 (br s, 2H, CP), 1.41 (br s, 2H, CP), 1.00 (s, 9H, C7-tBu) ppm.
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 155.5, 148.6, 144.0, 142.6, 139.4, 135.9, 131.4, 128.4, 128.2, 127.2, 125.5, 123.9, 122.8, 50.0, 33.6, 29.7, 18.5 ppm
IR (neat): 2957, 2864, 1645, 1599, 1520, 1474, 1343, 1261, 1206, 1110, 1025, 973, 882, 828, 758, 691 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{22}H_{24}N_2O_2^+$: 349.1911, Found: 349.1914
R_f = 0.60 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

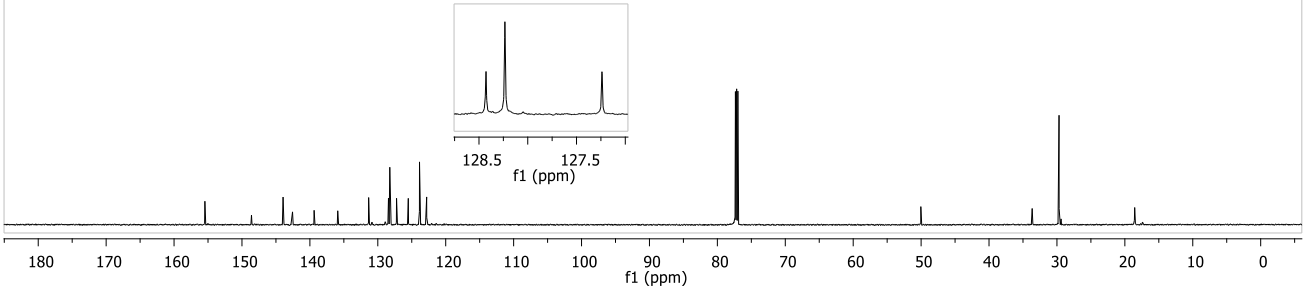
^{1}H NMR (700 MHz, $CDCl_3$) for 1n

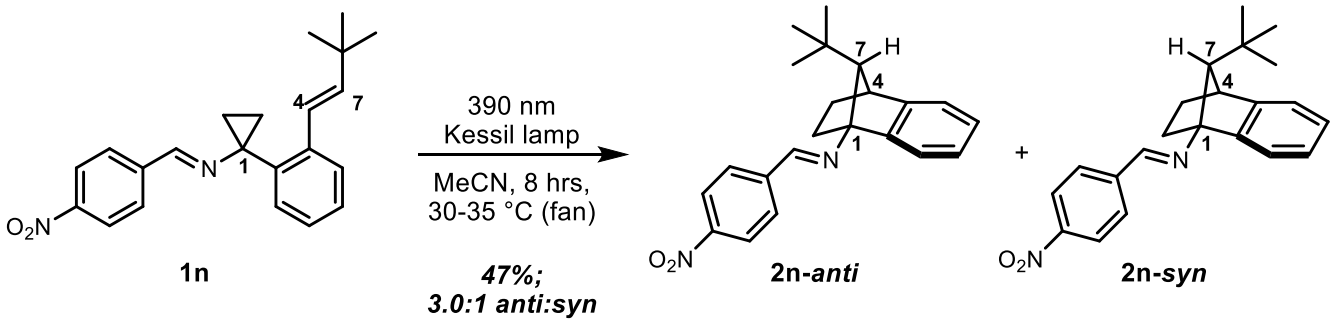
Parameter	Value
Title	JLC-0285product-1H-3
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	44
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 1n

Parameter	Value
Title	JLC-0285product-13C-3
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	816
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2937.0
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for C7-*tert*-butyl 1-aminoNB 2n

In a dry vial under inert atmosphere, cyclopropylimine **1n** (69.9 mg, 201 μmol) was dissolved in 2.0 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 8 hrs,[40] using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was red and slightly cloudy. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. Crude ^{1}H NMR revealed a 3.6:1 ratio of *anti*:*syn* isomers, as determined by the C4 resonances. The crude residue was purified via flash chromatography over basic alumina (5% ethyl acetate:hexanes; loaded residue with PhMe). Collected 56.0 mg of a yellow oil. ^{1}H NMR revealed a 3.0:1:2.8 mixture of **2n-*anti***:**2n-*syn***:recovered starting material. This calculates to 22.8 mg of starting material **1n** (32.7% recovery) and 33.1 mg of the 1-aminoNB mix (47.4% at 3.0:1 *anti*:*syn* dr). Of note, the characterization data was collected on the mixture; NMR line-listings are presented separately[41] for sake of clarity.

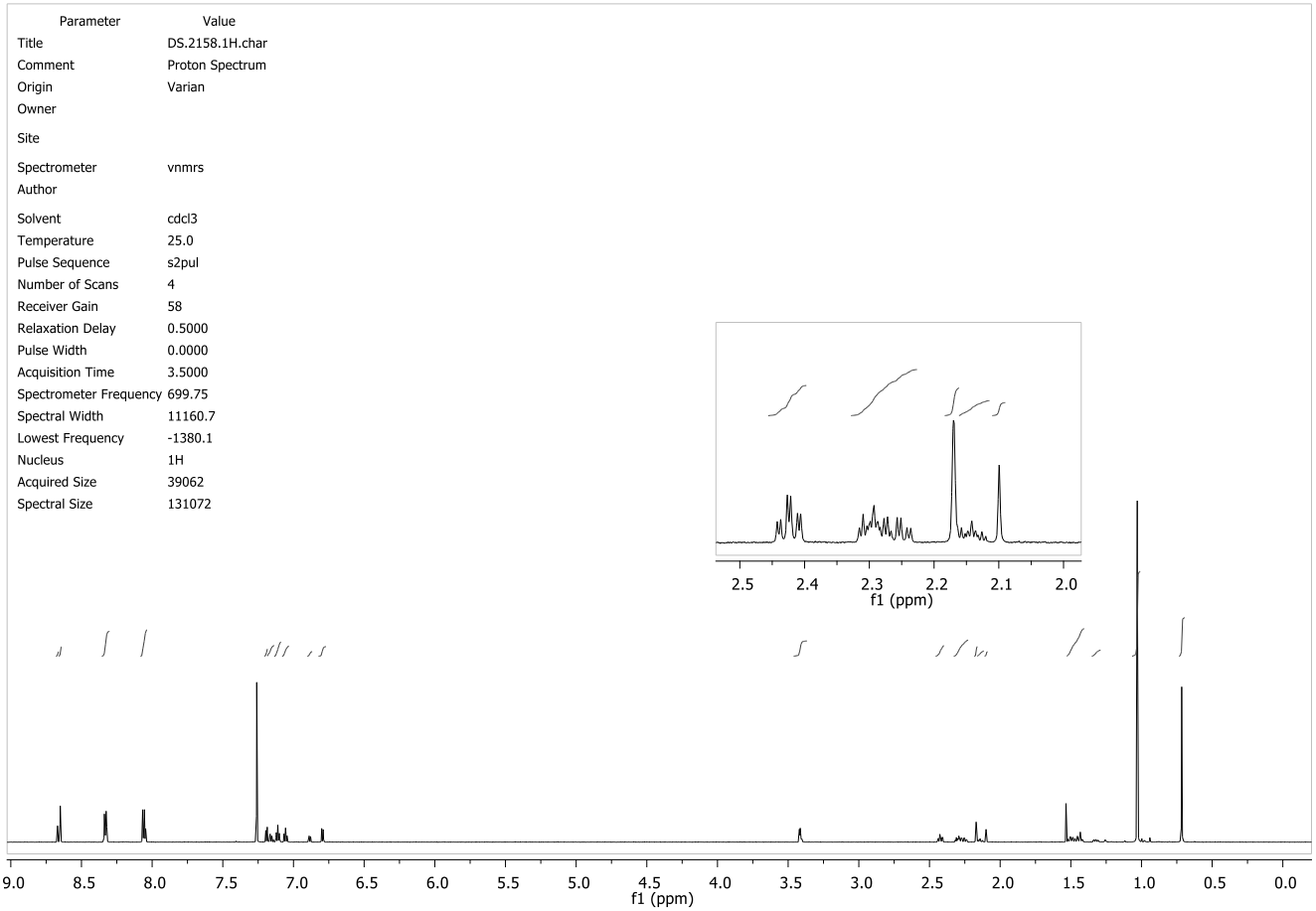
*Characterization Data for C7-tert-butyl 1-aminoNBs **2n-anti** and **2n-syn**:*
IR (neat): 2952, 1640, 1601, 1822, 1459, 1344, 1292, 1211, 1108, 1012, 842, 748, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{22}H_{25}N_2O_2^+$: 349.1911, Found: 349.1912
$\mathbf{R_f}$ = 0.50 (10% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

*NMR Data for anti-C7-tert-butyl 1-aminoNB **2n-anti**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.65 (s, 1H, imine CH), 8.33 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.06 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.19 (d, 1H, *J* = 7.2 Hz, Ar), 7.11 (*app.* t, 1H, *J* = 7.4 Hz, Ar), 7.06 (td, 1H, *J* = 7.5, 0.8 Hz, Ar), 6.79 (d, 1H, *J* = 7.2 Hz, Ar), 3.42 (d, 1H, *J* = 4.1 Hz, C4), 2.42 (*app.* td, 1H, *J* = 10.9, 3.5 Hz, C2-eq), 2.32-2.27 (m, 1H, C3-eq), 2.17 (s, 1H, C7), 1.52-1.48 (m, 1H, C2-ax), 1.48-1.43 (m, 1H, C3-ax), 1.03 (s, 9H, C7-tBu) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ =158.4, 151.4, 149.2, 148.2, 142.3, 129.0, 126.0, 125.3, 124.2, 120.8, 117.4, 80.4, 73.9, 44.8, 33.0, 30.4, 28.5, 27.9 ppm

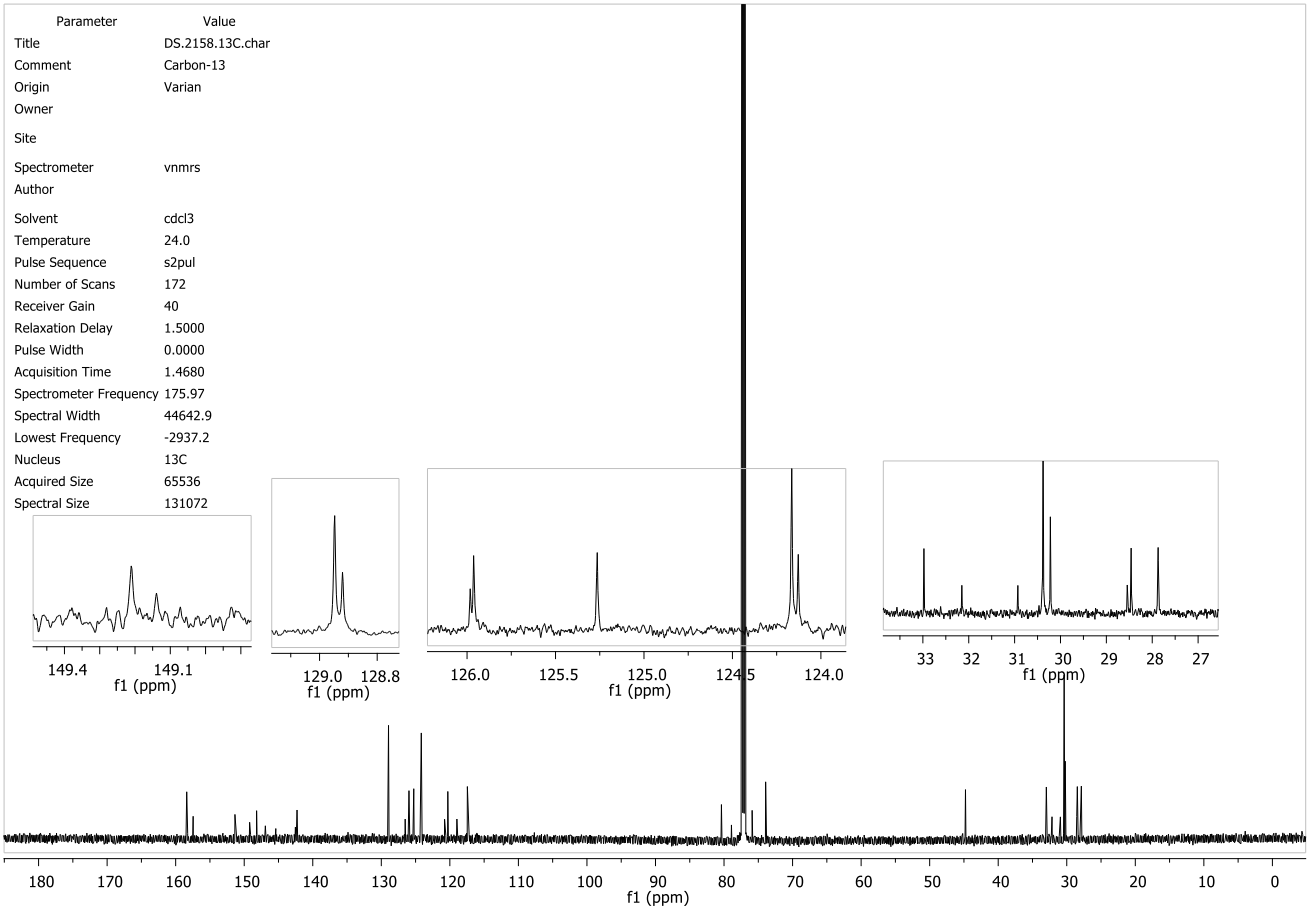
*NMR Data for syn-C7-tert-butyl 1-aminoNB **2n-syn**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.67 (s, 1H, imine CH), 8.33 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.05 (d, 2H, *J* = 8.5 Hz, 4-NO_2-Ar), 7.18-7.14 (m, 2H, Ar), 7.11 (*app.* t, 1H, *J* = 7.3 Hz, Ar), 6.88 (d, 1H, *J* = 7.2 Hz, Ar), 3.41 (d, 1H, *J* = 4.2 Hz, C4), 2.25 (*app.* td, 1H, *J* = 10.6, 4.1 Hz, C2-eq), 2.18 (*app.* tt, 1H, *J* = 10.9, 4.3 Hz, C3-eq), 2.10 (s, 1H, C7), 1.46-1.41 (m, 1H, C2-ax), 1.32 (ddd, 1H, *J* = 11.9, 9.6, 4.1 Hz, C3-ax), 0.72 (s, 9H, C7-tBu) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 157.4, 149.1, 146.9, 145.4, 142.5, 128.9, 126.5, 126.0, 124.1, 120.8, 119.0, 78.9, 75.9, 44.8, 32.1, 30.9, 30.2, 28.5 ppm

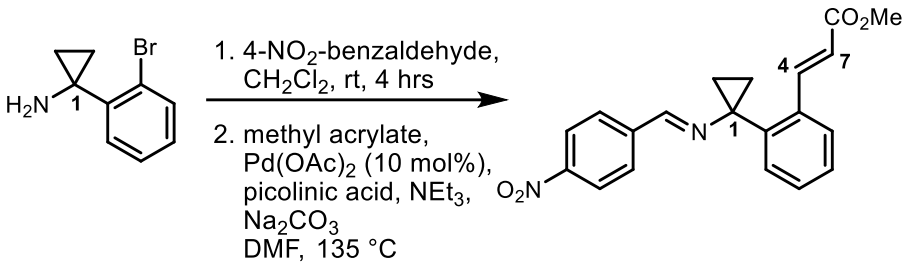
[40] Time course adjusted to account for amount of starting material.
[41] Assignments based on analogy to related scaffolds; of note, the anisotropic influence of the fused benzene ring is provides a simple diagnostic for assigning *syn* vs *anti*, as the C7 functionality of former will show a distinctive upfield shift relative to its *anti* counterpart (in this case >0.3 ppm difference [0.72 vs 1.03]).

^{1}H NMR (700 MHz, $CDCl_3$) for 2n



^{13}C NMR (176 MHz, $CDCl_3$) for 2n





Procedure for C7-CO_2Me cyclopropylimine 1o

Aminocyclopropane **S4** (1.20 g, 5.66 mmol) was dissolved in 21 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (1.21 g, 8.00 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 5 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (1 to 2 to 3 to 5 to 10% ethyl acetate:hexanes). Collected 1.70 g of the Schiff base intermediate (87.0% yield) as a light yellow oil. Partial characterization is provided below.

Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.19 (d, *J* = 8.8 Hz, 2H, 4-NO_2-Ar), 7.77 (d, *J* = 8.8 Hz, 2H, 4-NO_2-Ar), 7.65 (d, *J* = 8.0 Hz, 1H, Ar), 7.63 (s, 1H, imine-CH), 7.38 (d, *J* = 4.2 Hz, 2H, Ar), 7.25 (dt, *J* = 9.1, 4.5 Hz, 1H, Ar), 1.72 (*app.* q, *J* = 4.6 Hz, 2H, CP), 1.47 (*app.* q, *J* = 4.5 Hz, 2H, CP) ppm
R_f = 0.45 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

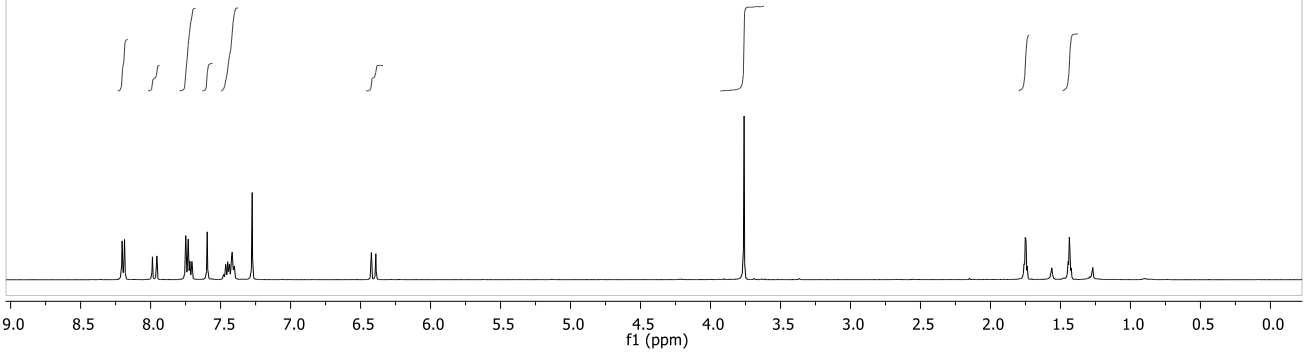
Schiff base intermediate from above (956 mg, 2.77 mmol) were dissolved in 7.5 mL of dry, degassed DMF (DMF was degassed by sparging with a balloon of Ar through a 22 gauge needle for 45 min prior to use). Na_2CO_3 (730 mg, 6.9 mmol), $Pd(OAc)_2$ (31 mg, 138 µmol), pyridine-2-carboxylic acid (34 mg, 276 µmol), and triethylamine (39 µL, 0.28 mmol) were added respectively in one portion each. Stirred 20 min at room temp; reaction mixture was cloudy orange. Added methyl acrylate (1.25 mL, 13.9 mmol) was added to the reaction solution, followed by an additional 2.0 mL of dry, degassed DMF to rinse down the sides of the flask. A reflux condenser was attached, the system was flushed with Ar, and the reaction mixture was refluxed at 135 °C for 14 hrs while stirring vigorously. Reaction mixture loses some color upon rising to temp, eventually darkens as time elapses. Upon cooling to room temp, the reaction mixture was poured into 100 mL of a 1:1 sat. $NaHCO_3$:water mixture, then diluted with 50 mL ether.[42] Extracted the aqueous phase with three portions of 50 mL ether. Combined organics were washed with 25 mL of 5% LiCl (aq.) then 25 mL brine (3 drops of 6 M NaOH (aq.) were added to each of the aqueous washes to ensure basicity). The organic phase was then dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (5 to 35% ethyl acetate:hexanes, increasing in 5% increments; residue was loaded with PhMe). Obtained vinylated cyclopropylimine **1o** in two portions. The end fractions afforded an orange solid,[43] 238 mg; revealed to be clean product by ^{1}H NMR. The early fractions provided 446 mg of a light yellow oil, which proved to be a 4.5:1:1 mix of starting material:product:pentane (78.8 wt% starting material; 17.9 wt% cyclopropylimine **1o**); this calculates to 352 mg of recovered starting material (36.8% recovery) and 80 mg of product. Total yield of cyclopropylimine **1o** = 338 mg (34.8% yield; 30.3% over 2 steps).

*Characterization Data for C7-CO_2Me cyclopropylimine **1o**:*
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.18 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 7.96 (d, 1H, *J* = 16.0 Hz, C4), 7.73 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 7.70 (d, 1H, *J* = 7.2 Hz, Ar), 7.58 (s, 1H, imine-CH), 7.49-7.34 (m, 3H, Ar), 6.39 (d, 1H, *J* = 16.0 Hz, C7), 3.75 (s, 3H, CO_2Me), 1.74 (*app.* q, 2H, *J* = 4.4 Hz, CP), 1.42 (*app.* q, 2H, *J* = 4.4 Hz, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 167.1, 155.3, 148.6, 142.0, 142.0, 138.5, 135.4, 132.1, 130.5, 128.6, 128.3, 126.6, 123.7, 119.6, 51.7, 49.5, 18.3 ppm
IR (neat): 2950, 1714, 1633, 1598, 1518, 1435, 1343, 1317, 1272, 1171, 826, 768 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{20}H_{19}N_2O_4^+$: 351.1339, Found: 351.1343
R_f = 0.50 (15% ethyl acetate:hexanes), one yellow spot, $KMnO_4$, UV

[42] Note: mixture forms an emulsion that took ~30 min to resolve. Filtering through a pad of celite prior to extraction is advisable if repeating this procedure.
[43] Cyclopropylimine **1o** tends to concentrate to an oil but will solidify with time. Storage at room temp is not recommended as this leads to discoloration and steady decomposition.

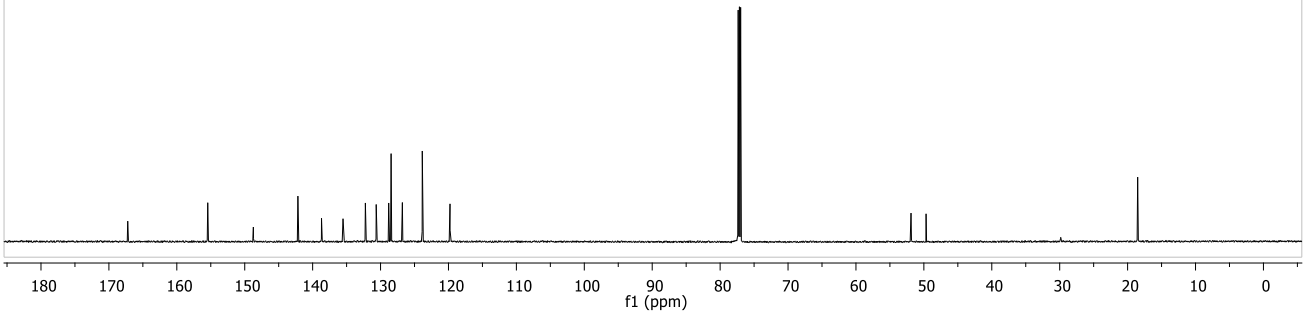
^{1}H NMR (500 MHz, $CDCl_3$) for 1o

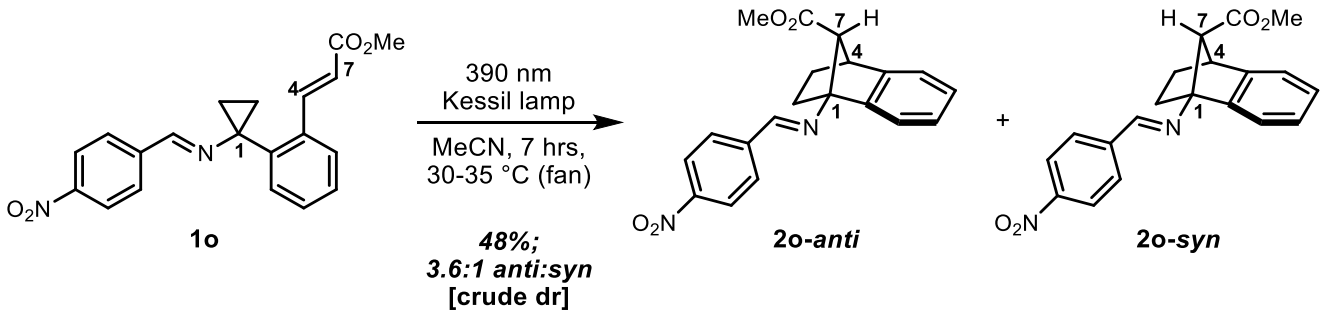
Parameter	Value
Title	RCM_647_pdt_HNMR
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	50
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-999.8
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



^{13}C NMR (176 MHz, $CDCl_3$) for 1o

Parameter	Value
Title	RCM_647_pdt_CNMR
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	2384
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.9
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





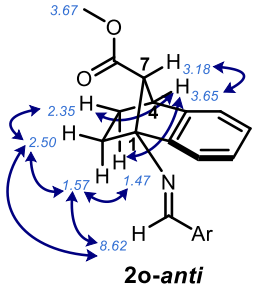
Procedure for C7-carbomethoxy 1-aminoNB 2o

In a dry vial under inert atmosphere, cyclopropylimine **1o** (58.5 mg, 167 μmol) was dissolved in 1.7 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 7 hrs,[44] using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was red and slightly cloudy. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine with 2 drops 6 M NaOH (aq.), dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. Crude ^{1}H NMR revealed a 3.6:1 ratio of *anti*:*syn* isomers, as determined by the C4 resonances. The crude residue was purified via flash chromatography over basic alumina (5 to 10 to 15 to 25 to 35% ethyl acetate:hexanes; loaded residue with 1:1 PhMe:pentane). Collected 28.0 mg of an off-white solid, which proved to be a 19:1 mix of **2o**-*anti*:**2o**-*syn* 1-aminoNBs (47.9% yield). Also obtained 8.2 mg of a yellow solid from the tail fractions that proved to be a 1:5 mix of **2o**-*anti*:**2o**-*syn* isomers, though this mixture was contaminated with other minor impurities.

*Characterization Data for C7-carbomethoxy 1-aminoNB **2o**-anti:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.62 (s, 1H, imine CH), 8.31 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 8.05 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.23 (d, 1H, *J* = 7.3 Hz, C11), 7.17 (t, 1H, *J* = 7.4 Hz, C9/C10), 7.14 (t, 1H, *J* = 7.4 Hz, C9/C10), 6.96 (d, 1H, *J* = 7.3 Hz, C7), 3.66 (s, 3H, -CO_2Me), 3.65 (d, 1H, *J* = 3.8 Hz, C4), 3.18 (s, 1H, C7), 2.49 (td, 1H, *J* = 10.8, 3.8 Hz, C2-eq), 2.36-2.31 (m, 1H, C3-eq), 1.58-1.53 (m, 1H, C2-ax), 1.49-1.44 (m, 1H, C3-ax) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 170.8, 159.3, 149.3, 148.1, 144.9, 142.1, 129.2, 126.9, 126.4, 124.1, 120.9, 118.9, 79.3, 64.7, 51.8, 44.8, 27.6, 27.5 ppm
IR (neat): cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{20}H_{19}N_2O_4^+$: 351.1339, Found: 351.1350
R_f = 0.50 (30% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

*Partial Characterization Data for C7-carbomethoxy 1-aminoNB **2o**-syn:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.69 (s, 1H, imine CH), 8.31 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 8.06 (d, 2H, *J* = 8.7 Hz, 4-NO_2-Ar), 7.29-7.19 (m, 4H, Ar), 3.75-3.71 (m, 1H, C7), 3.47 (s, 3H, -CO_2Me), 3.24 (d, 1H, *J* = 1.3 Hz, C4), 2.24 (*app.* td, 1H, *J* = 11.2, 4.3 Hz, C2-eq), 2.06 (*app.* td, 1H, *J* = 11.3, 4.1 Hz, C3-eq), 1.82 (ddd, 1H, *J* = 11.7, 9.2, 4.1 Hz, C2-ax), 1.40 (ddd, 1H, *J* = 12.3, 9.3, 4.1 Hz, C3-ax) ppm.
R_f = 0.50 (30% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

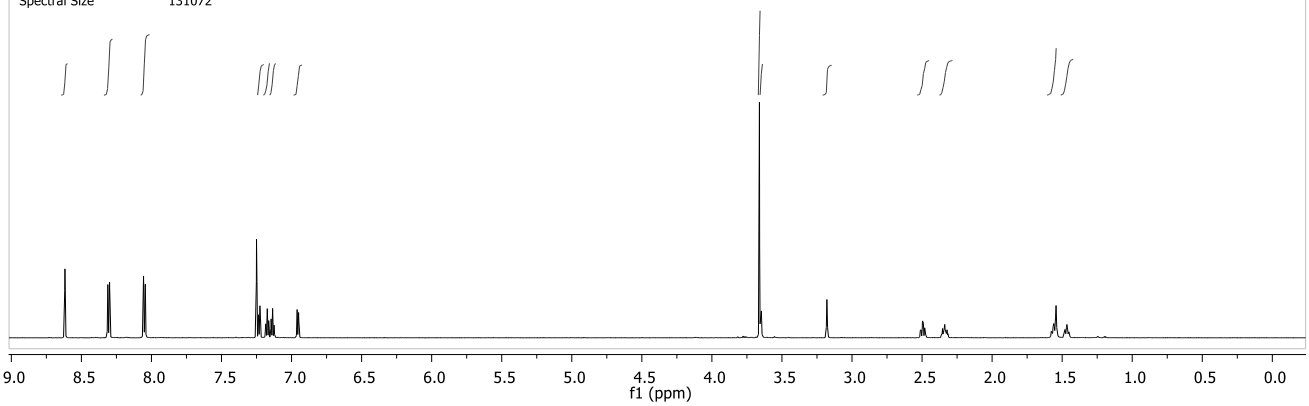
2D NMR Data
- COSY, HSQC, and NOESY experiments were employed to assign the various resonances and confirm the assignment as the *anti*-isomer. Key NOESY correlations (denoted by blue arrows) are provided below[45]:



[44] Time course adjusted to account for amount of starting material.
[45] While the *s*-trans conformation of the methyl ester motif prevents the detection of resonances via NOESY or other through-space methods, the deshielding anisotropic effect on the C2/C3-eq protons is considered indicative of the *anti*-configuration. Additionally, the pattern of the ^{13}C shifts is rather highly conserved across the C7-monosubstituted systems, and the above pattern aligns well with that of the various the *anti*-isomers. Additionally, NOESY correlations observed for the downstream C7-CO_2H intermediates (e.g. *syn*-C7-CO_2H system **2v**-***syn***) provide further evidence that this assignment is accurate.

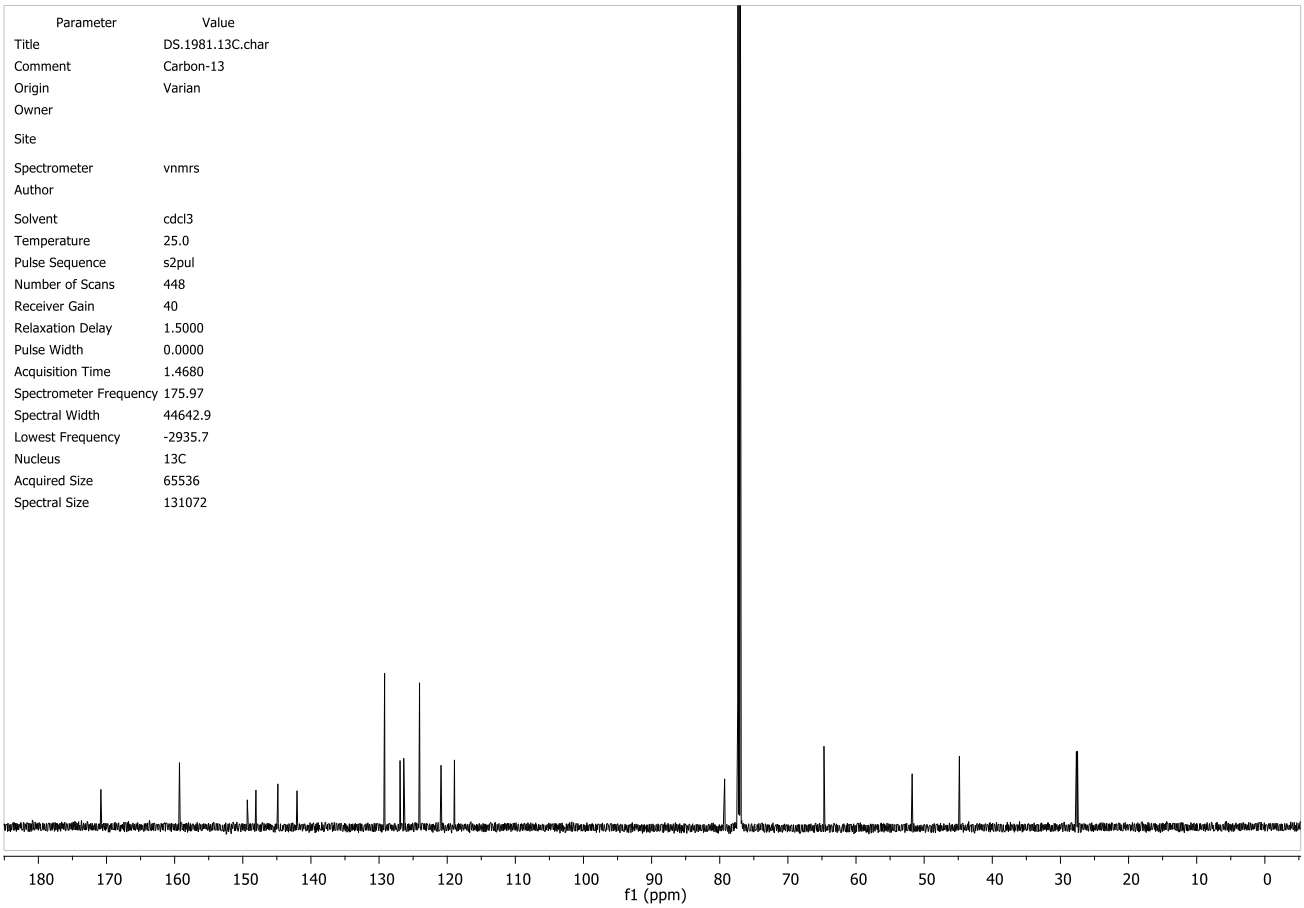
^{1}H NMR (700 MHz, $CDCl_3$) for 2o

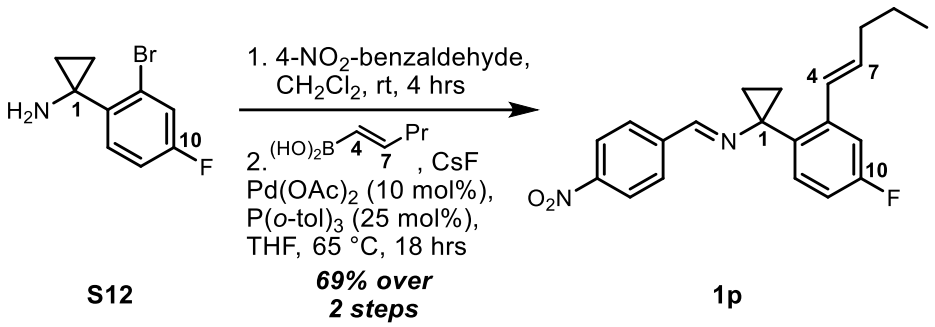
Parameter	Value
Title	DS.1981.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	54
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1386.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 2o

Parameter	Value
Title	DS.1981.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	448
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.7
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S12 **1p**

Procedure for C10-fluoro-C7-propyl cyclopropylimine 1p

Aminocyclopropane **S12** (1.5 g, 6.5 mmol) was dissolved in 40 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (2.46 g, 16.3 mmol) in one portion. The reaction mixture was stirred at room temp for 6 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (1 to 2 to 3 to 5 to 10 to 20% ethyl acetate:hexanes). Collected 1.90 g of the Schiff base intermediate (80.1% yield) as a yellow oil. Partial characterization is provided below.

Characterization Data for Schiff base intermediate:

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.20 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.77 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.61 (s, 1H, imine-CH), 7.40 (dd, 1H, *J* = 8.2, 1.8 Hz, Ar), 7.35 (dd, 1H, *J* = 7.9, 6.5 Hz, Ar), 7.09 (td, 1H, *J* = 8.3, 1.7 Hz, Ar), 1.72 (*app.* q, 2H, *J* = 4.9 Hz, CP), 1.43 (*app.* q, 2H, *J* = 4.9 Hz, CP) ppm

R_f = 0.80 (20% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (314 mg, 2.07 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2. In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (9.27 mg, 0.041 mmol) and tris(o-tolyl)phosphine (25.1 mg, 0.0826 mmol) were dissolved in 3 mL dry, degassed THF(degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask), then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (150 mg, 0.413 mmol) was dissolved in 2 mL dry, degassed THF before adding 1-penten-1-yl boronic acid (141 mg, 1.24 mmol) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with two 0.5 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~100 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was dry loaded with celite). Obtained vinylated cyclopropylimine **1p** as a single olefin diastereomer (assigned as *E* based on *J*-coupling value), slighty yellow oil, 106 mg (69% yield over 2 steps).

*Characterization Data for C10-fluoro-C7-propyl cyclopropylamine **1p**:*

^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.18 (d, *J* = 8.8 Hz, 2H, 4-NO_2-Ar), 7.73 (d, *J* = 8.8 Hz, 2H, 4-NO_2-Ar), 7.61 (s, 1H, imine-CH), 7.28-7.20 (m, 2H, Ar), 6.93 (td, *J* = 8.3, 2.7 Hz, 1H, Ar), 6.52 (d, *J* = 15.7 Hz, 1H, C4), 6.17 (dt, *J* = 15.6, 7.0 Hz, 1H, C7), 2.12 (q, *J* = 7.3 Hz, 2H, C7-propyl), 1.64 (q, *J* = 4.2 Hz, 2H, C7-propyl), 1.43-1.33 (m, 4H, CP, CP), 0.83 (t, *J* = 7.4 Hz, 3H, C7-propyl) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 162.8 (d, *J* = 246.1 Hz), 155.3, 148.7, 142.4, 141.3 (d, *J* = 7.9 Hz), 134.3, 133.4 (d, *J* = 8.5 Hz), 131.5, 128.3, 126.8 (d, *J* = 2.1 Hz), 123.9, 114.1 (d, *J* = 21.5 Hz), 111.9 (d, *J* = 22.0 Hz), 49.3, 35.3, 22.5, 18.7, 13.7 ppm

^{19}F NMR ($CDCl_3$, 376 MHz): δ = -114.1 (dd, *J* = 15.5, 7.5 Hz) ppm

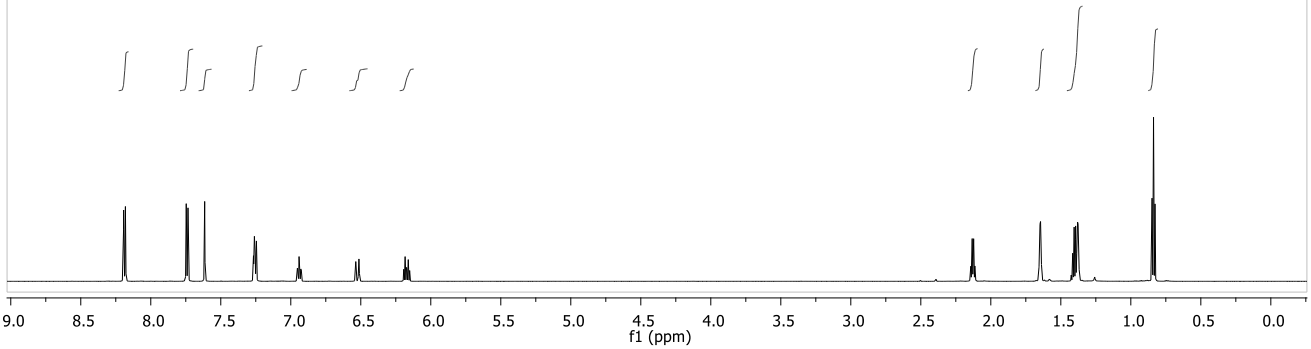
IR (neat): 2958, 2929, 1599, 1579, 1519, 1488, 1342, 1268, 1207, 1158, 1109, 966, 828, 748, 736 cm^{-1}

HRMS (ES+, *m/z)* calculated for $C_{21}H_{21}FN_2O_2^+$: 353.1660, Found: 353.1662

R_f = 0.40 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

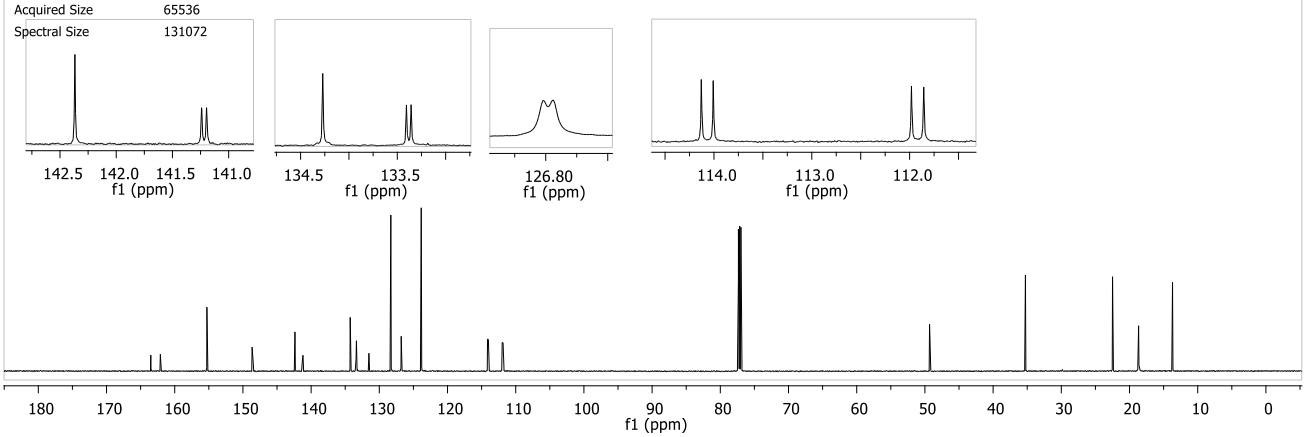
^{1}H NMR (700 MHz, $CDCl_3$) for 1p

Parameter	Value
Title	JLC-0214product-1H
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	36
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



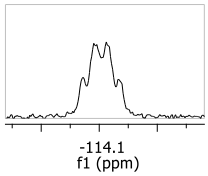
^{13}C NMR (176 MHz, $CDCl_3$) for 1p

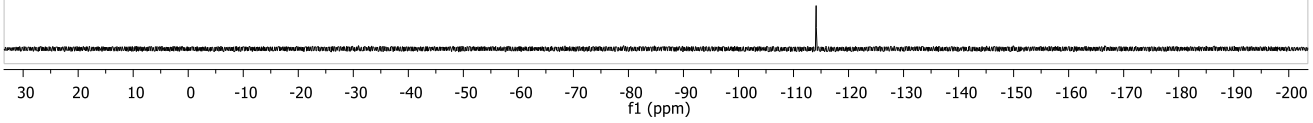
Parameter	Value
Title	JLC-0214product-13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	704
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2938.4
Nucleus	13C
Acquired Size	65536
Spectral Size	131072



^{19}F NMR (376 MHz, $CDCl_3$) for 1p

Parameter	Value
Title	JLC_0214_pdt_FNMR
Comment	STANDARD FLUORINE PARAMETERS
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.7340
Spectrometer Frequency	376.83
Spectral Width	89285.7
Lowest Frequency	-76676.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072





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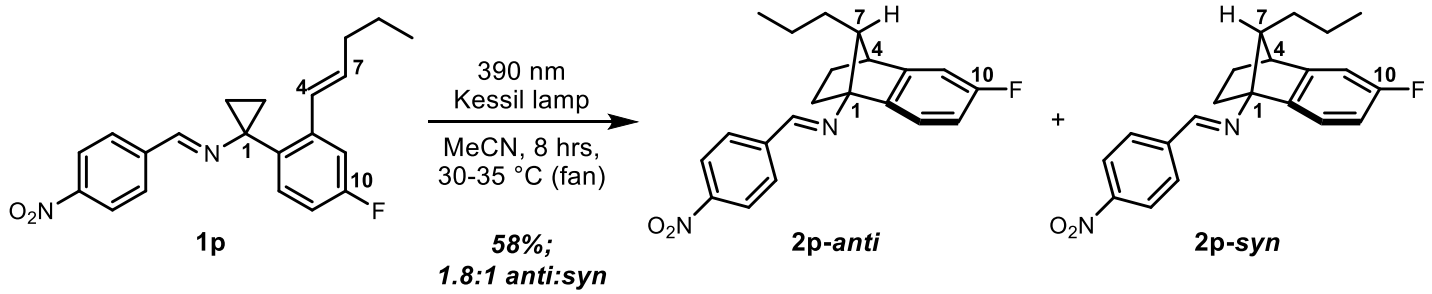
f1 (ppm)



Procedure for C7-propyl-C10-fluoro 1-aminoNBs 2p-anti and 2p-syn

In a dry vial under inert atmosphere, cyclopropylimine **1p** (68.8 mg, 195 μmol) was dissolved in 2.0 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 8 hrs, using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was dark red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; loaded residue with PhMe). Collected 51.7 mg of a 3.35:1 mix of the desired products to starting material, thus the final yields were 11.9 mg of recovered cyclopropylimine **1p** (17.3% recovery) and 39.8 mg of 1-aminoNBs **2p-anti** and **2p-syn** as a 1.8:1 *anti*:*syn* ratio[46] (57.8% combined yield).

(characterization data was collected on the mixture; NMR data below is listed separately for clarity[47])

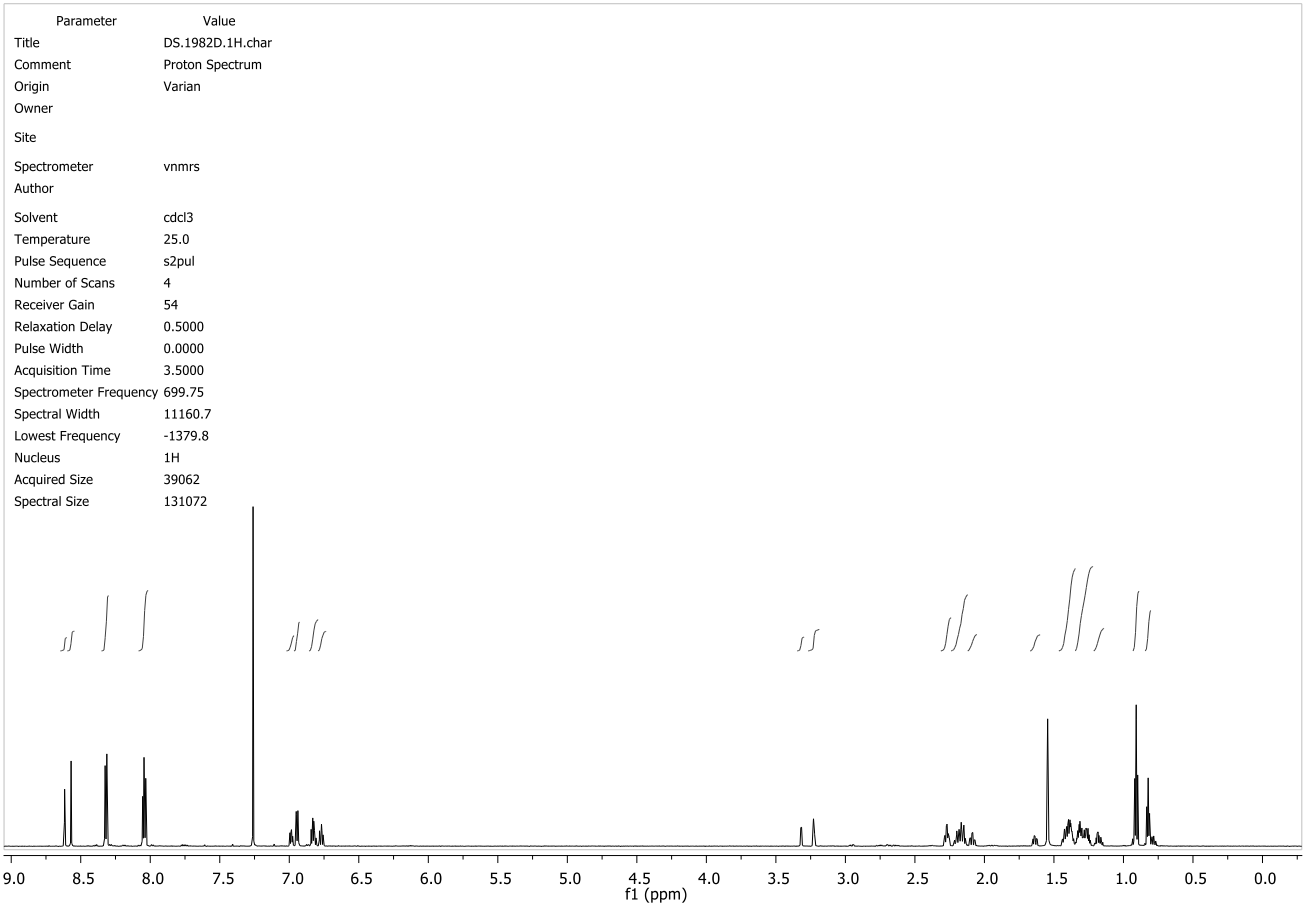
*Characterization Data for C7-propyl-C10-fluoro 1-aminoNBs **2p-anti** and **2p-syn**:*
IR (neat): 2956, 2872, 1642, 1601, 1521, 1474, 1344, 1291, 1225, 1109, 1012, 918, 859, 838, 749, 724, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{21}H_{22}FN_2O_2^+$: 353.1660, Found: 353.1660
$\mathbf{R_f}$ = 0.55 (10% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

*NMR Data for anti-C7-propyl-C10-fluoro 1-aminoNB **2p-anti**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.57 (s, 1H, imine CH), 8.32 (d, 2H, *J* = 8.5 Hz, 4-NO_2-Ar), 8.04 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 6.94 (dt, 1H, *J* = 8.4, 2.0 Hz, Ar), 6.85-6.80 (m, 1H, Ar), 6.77 (ddd, 1H, *J* = 10.3, 8.2, 2.4 Hz, Ar), 3.23 (d, 1H, *J* = 3.5 Hz, C4), 2.26 (dd, 1H, *J* = 9.3, 3.2 Hz, C7), 2.18-2.13 (m, 2H, C3-eq, C2-eq), 1.45-1.35 (m, 3H, C2-ax, C7-CH_2-), 1.34-1.23 (m, 2H, C7-CH_2CH_2CH_2-), 1.21-1.14 (m, 1H, C3-ax), 0.91 (t, 3H, *J* = 7.3 Hz, C7-$CH_2CH_2CH_2$CH_3) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 161.9 (J_{CF} = 243.0 Hz), 159.4, 149.4 (J_{CF} = 8.1 Hz), 149.3, 145.1 (J_{CF} = 2.4 Hz), 142.0, 129.0, 124.1, 119.8 (J_{CF} = 8.7 Hz), 111.8 (J_{CF} = 22.4 Hz), 108.9 (J_{CF} = 23.0 Hz), 78.9, 64.7, 44.4, 28.8, 26.8, 26.2, 21.2, 14.6 ppm
^{19}F NMR ($CDCl_3$, 376 MHz): δ = -116.6 (td, *J* = 9.2, 5.0 Hz)

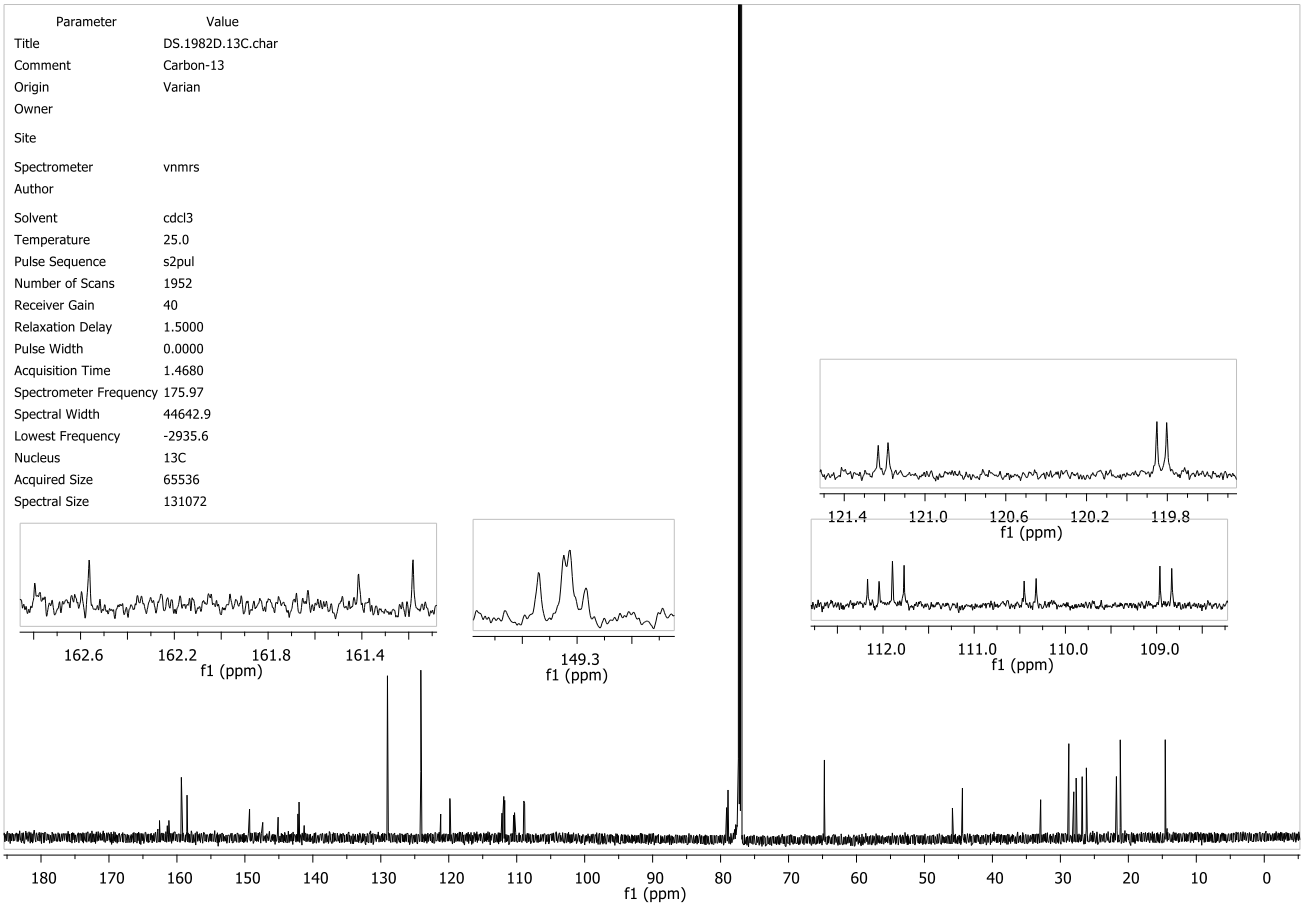
*NMR Data for syn-C7-propyl-C10-fluoro 1-aminoNB **2p-syn**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.62 (s, 1H, imine CH), 8.32 (d, 2H, *J* = 8.5 Hz, 4-NO_2-Ar), 8.05 (d, 2H, *J* = 8.4 Hz, 4-NO_2-Ar), 6.99 (dd, 1H, *J* = 8.0, 5.0 Hz, Ar), 6.85-6.80 (m, 2H, Ar, Ar), 3.32 (d, 1H, *J* = 3.9 Hz, C4), 2.28 (dd, 1H, *J* = 9.3, 3.2 Hz, C7), 2.20 (tt, 1H, *J*-= 10.3, 3.3 Hz, C3-eq), 2.09 (td, 1H, *J* = 10.8, 4.1 Hz, C2-eq), 1.64 (ddd, 1H, *J* = 11.0, 9.3, 3.9 Hz, C2-ax), 1.45-1.35 (m, 2H, C7-CH_2-), 1.34-1.23 (m, 3H, C3-ax, C7-CH_2CH_2-), 0.82 (t, 3H, *J* = 7.1 Hz, C7-CH_2CH_2CH_3) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 162.1 (J_{CF} = 243.0 Hz), 158.5, 149.3, 147.4 (J_{CF} = 7.9 Hz), 142.2, 141.3 (J_{CF} = 2.5 Hz), 129.0, 124.1, 121.2 (J_{CF} = 8.7 Hz), 112.1 (J_{CF} = 22.3 Hz), 110.4 (J_{CF} = 22.9 Hz), 79.1, 64.9, 45.9, 32.9, 28.0, 27.7, 21.7, 14.5 ppm
^{19}F NMR ($CDCl_3$, 376 MHz): δ = -116.6 (td, *J* = 9.1, 4.5 Hz)

[46] The C4 resonances were employed to determine *anti*:*syn* ratio.
[47] Assignments based on analogy to related systems. The sample used for characterization was prepared after re-exposing the above sample to irradiation (in order to drive to completion), hence the altered isomeric ratio (now 1.5:1 *anti*:*syn*).

^{1}H NMR (700 MHz, $CDCl_3$) for 2p

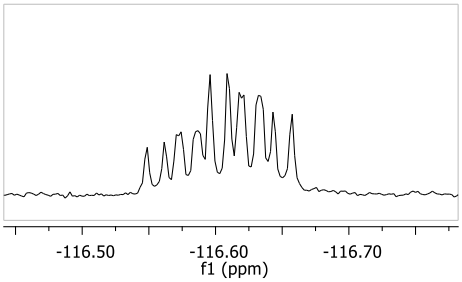


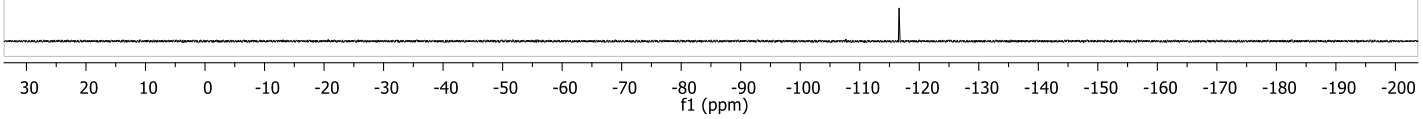
^{13}C NMR (176 MHz, $CDCl_3$) for 2p



^{19}F NMR (376 MHz, $CDCl_3$) for 2p

Parameter	Value
Title	DS.1982D.19F
Comment	Fluorine-19
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.7340
Spectrometer Frequency	375.91
Spectral Width	89285.7
Lowest Frequency	-76597.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072





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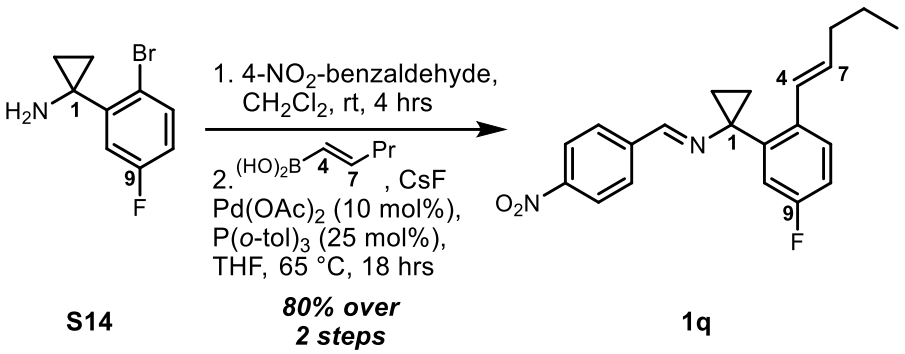
f1 (ppm)



S14 ***80% over 2 steps*** **1q**

Procedure for C9-fluoro-C7-propyl cyclopropylimine 1q

Aminocyclopropane **S14** (600 mg, 2.61 mmol) was dissolved in 10 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (557 mg, 3.69 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (0 to 1 to 2 to 3 to 5 to 10% ethyl acetate:hexanes). Collected 780 mg of the Schiff base intermediate (82.4% yield) as a yellow oil. Partial characterization is provided below.

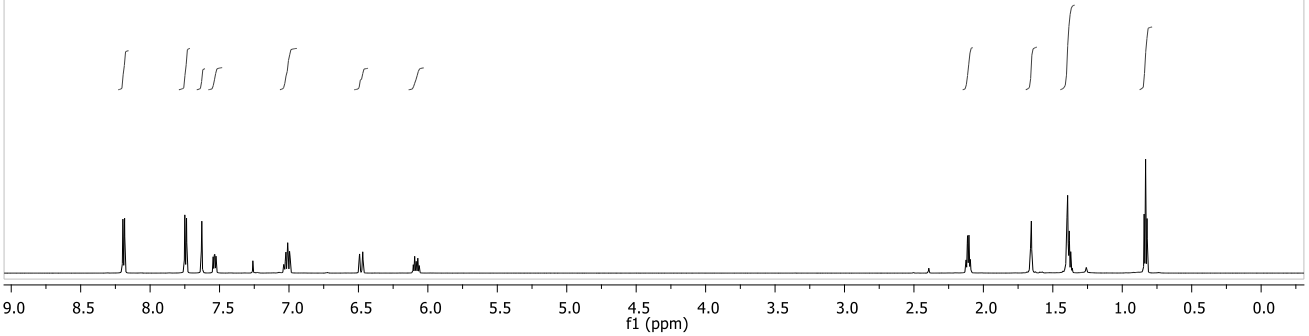
Characterization Data for Schiff base intermediate:
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.20 (d, *J* = 8.7 Hz, 2H, 4-NO_2-Ar), 7.77 (d, *J* = 8.7 Hz, 2H, 4-NO_2-Ar), 7.63 (s, 1H, imine-CH), 7.60 (dd, *J* = 8.8, 5.3 Hz, 1H, Ar), 7.11 (dd, *J* = 8.8, 3.0 Hz, 1H, Ar), 6.99 (td, *J* = 8.3, 3.0 Hz, 1H, Ar), 1.73 (*app.* q, *J* = 4.7 Hz, 2H, CP), 1.45 (*app.* q, *J* = 4.7 Hz, 2H, CP) ppm
R_f = 0.35 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (314 mg, 2.07 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2. In a separate dry vial under inert atmosphere, $Pd(OAc)_2$ (9.27 mg, 0.041 mmol) and tris(o-tolyl)phosphine (25.1 mg, 0.0826 mmol) were dissolved in 3 mL dry, degassed THF(degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask), then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (150 mg, 0.413 mmol) was dissolved in 2 mL dry, degassed THF before adding 1-penten-1-yl boronic acid (141 mg, 1.24 mmol) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with two 0.5 mL portions of dry, degassed THF. Once the Pd^0-phosphine mixture (orange) had stirred for 15 min, it was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~100 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (0 to 10% ethyl acetate:hexanes, increasing in 2% increments; residue was dry loaded with celite). Obtained vinylated cyclopropylimine **1q** as a single olefin diastereomer (assigned as *E* based on *J*-coupling value), slighty yellow oil, 142 mg (80% yield over 2 steps).

*Characterization Data for C9-fluoro-C7-propyl cyclopropylimine **1q**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.19 (d, *J* = 8.7 Hz, 2H, 4-NO_2-Ar), 7.74 (d, *J* = 8.7 Hz, 2H, 4-NO_2-Ar), 7.63 (s, 1H, imine-CH), 7.54 (dd, *J* = 8.5, 5.8 Hz, 1H, Ar), 7.01 (ddd, *J* = 15.4, 8.8, 4.2 Hz, 2H, Ar), 6.48 (dd, *J* = 15.7, 1.9 Hz, 1H, C4), 6.08 (dt, *J* = 15.2, 7.0 Hz, 1H, C7), 2.11 (q, *J* = 7.0 Hz, 2H, C7-propyl), 1.66 (q, *J* = 4.3 Hz, 2H, C7-propyl), 1.42 – 1.34 (m, 4H, CP, CP), 0.83 (t, *J* = 7.4 Hz, 3H, C7-propyl). ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 162.0 (d, *J* = 247.0 Hz), 155.4, 148.7, 142.3, 137.8 (d, *J* = 6.6 Hz), 135.2 (d, *J* = 3.2 Hz), 132.8, 128.3, 127.3 (d, *J* = 7.9 Hz), 126.7, 123.9, 118.0 (d, *J* = 20.8 Hz), 115.5 (d, *J* = 21.2 Hz), 49.8, 35.3, 22.6, 18.6, 13.7 ppm
^{19}F NMR ($CDCl_3$, 376 MHz): δ = -115.3 (dd, *J* = 14.7, 8.6 Hz) ppm
IR (neat): 2958, 2928, 1550, 1579, 1519, 1482, 1343, 1264, 1216, 1181, 1104, 965, 903, 827, 735 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{21}H_{21}FN_2O_2^+$: 353.1660, Found: 353.1665
R_f = 0.40 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

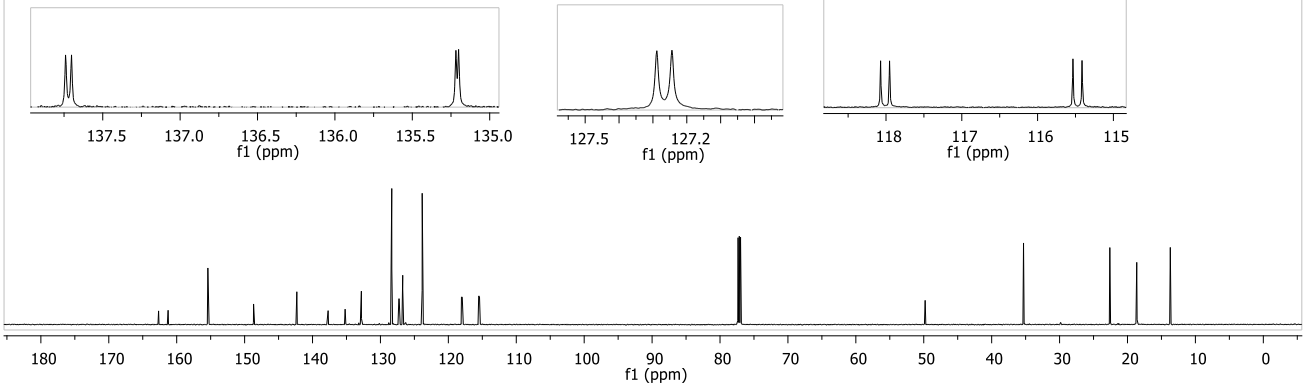
^{1}H NMR (700 MHz, $CDCl_3$) for 1q

Parameter	Value
Title	JLC-0212product-1H
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	34
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



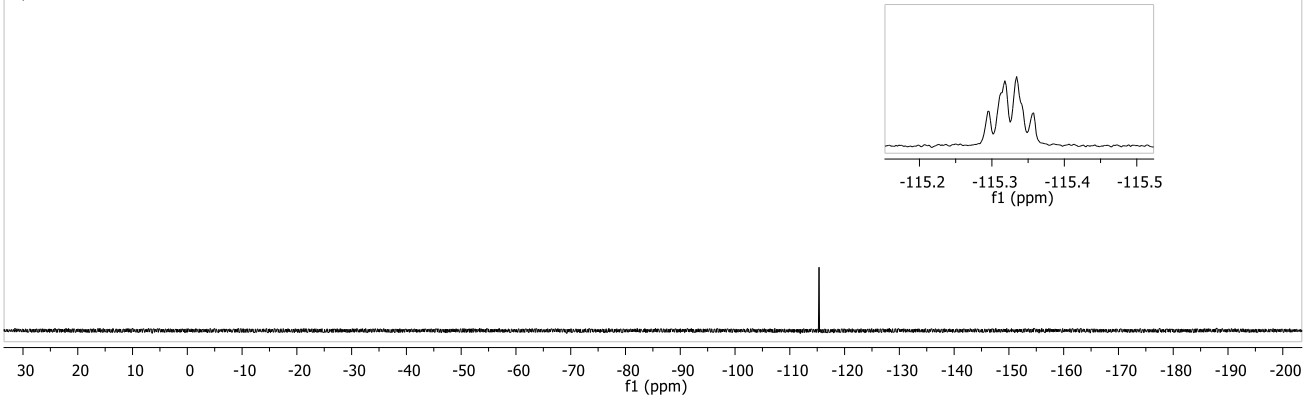
^{13}C NMR (176 MHz, $CDCl_3$) for 1q

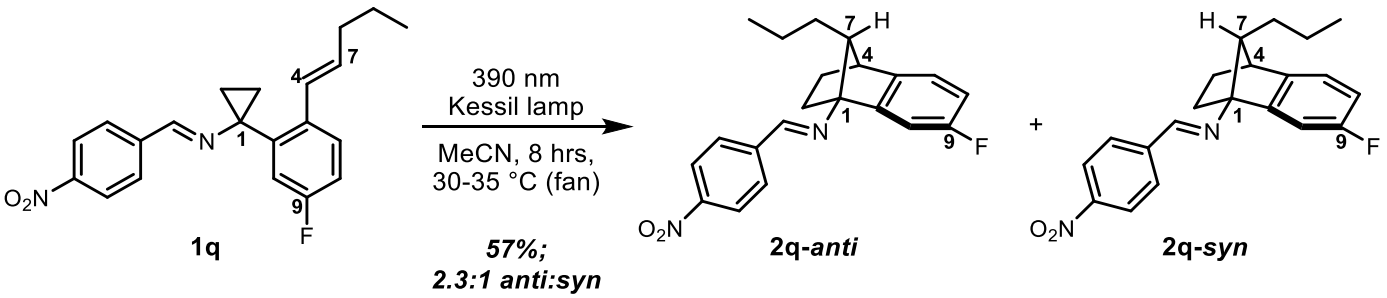
Parameter	Value
Title	JLC-0212product-13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	784
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2938.9
Nucleus	13C
Acquired Size	65536
Spectral Size	131072



^{19}F NMR (376 MHz, $CDCl_3$) for 1q

Parameter	Value
Title	JLC_0212_pdt_FNMR
Comment	STANDARD FLUORINE PARAMETERS
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.7340
Spectrometer Frequency	376.83
Spectral Width	89285.7
Lowest Frequency	-76676.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072





Procedure for C7-propyl-C9-fluoro 1-aminoNBs 2q-anti and 2q-syn

In a dry vial under inert atmosphere, cyclopropylimine **1q** (68.9 mg, 196 μmol) was dissolved in 2.0 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 8 hrs,[48] using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was dark red. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (8 to 40% ethyl acetate:hexanes, increasing in 8% increments; loaded residue with PhMe). Collected starting material and product across two portions.

Portion 1: 32.0 mg of a yellow oil, revealed to be 10.1 mg of recovered cyclopropylimine **1q** (14.7% recovery) and 21.9 mg of 1-aminoNB mix as a 3.06:1 *anti*:*syn* ratio.[49]

Portion 2: 17.6 mg of a slightly yellow solid, only desired 1-aminoNBs **2q-anti** and **2q-syn** in a 1.41:1 *anti*:*syn* ratio.

Combined yield of 1-aminoNBs **2q-anti** and **2q-syn** is thus 39.5 mg in a 2.3:1 *anti*:*syn* ratio (57.3% combined yield).

(characterization data was collected on the mixture; NMR data below is listed separately for clarity[50])

*Characterization Data for C7-propyl-C9-fluoro 1-aminoNBs **2q-anti** and **2q-syn**:*
IR (neat): 2957, 2872, 1641, 1601, 1522, 1466, 1345, 1293, 1268, 1182, 1107, 856, 839, 749, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{21}H_{22}FN_2O_2^+$: 353.1660, Found: 353.1660
$\mathbf{R_f}$ = 0.60 (10% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

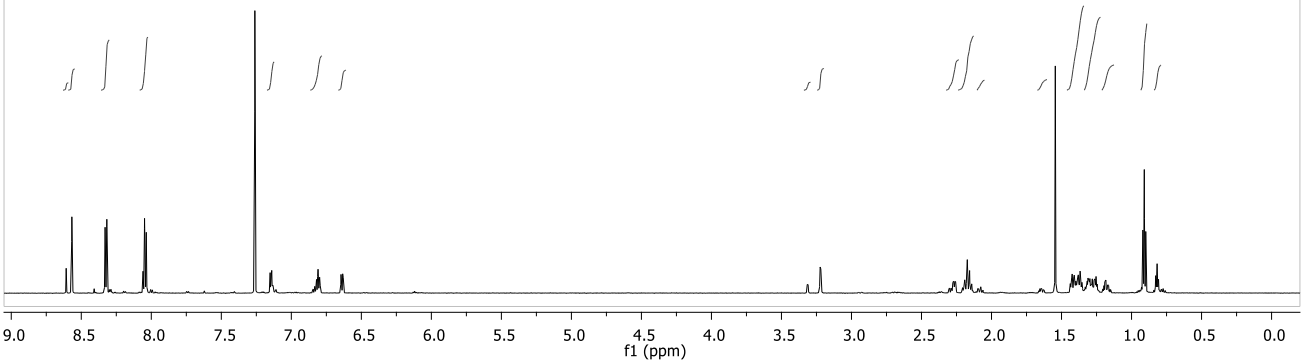
*NMR Data for anti-C7-propyl-C9-fluoro 1-aminoNB **2q-anti**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.57 (s, 1H, imine CH), 8.32 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 8.04 (d, 2H, *J* = 8.1 Hz, 4-NO_2-Ar), 7.14 (dd, 1H, *J* = 8.0, 4.9 Hz, Ar), 6.83-6.79 (m, 1H, Ar), 6.64 (dd, 1H, *J* = 8.3, 2.3 Hz, Ar), 3.22 (d, 1H, *J* = 2.9 Hz, C4), 2.27 (dd, 1H, *J* = 9.6, 4.0 Hz, C7), 2.18-2.13 (m, 2H, C3-eq, C2-eq), 1.44-1.35 (m, 3H, C2-ax, C7-C*H*$_2$-), 1.33-1.23 (m, 2H, C7-CH_2C*H*$_2$-), 1.21-1.15 (m, 1H, C3-ax), 0.91 (t, 3H, *J* = 7.2 Hz, C7-CH_2CH_2C*H*$_3$) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 161.5 (J_{CF} = 242.9 Hz), 159.5, 151.6 (J_{CF} = 7.3 Hz), 149.4, 142.9 (J_{CF} = 2.5 Hz), 142.0, 129.1, 124.1, 121.9 (J_{CF} = 8.2 Hz), 112.4 (J_{CF} = 22.2 Hz), 106.9 (J_{CF} = 23.5 Hz), 79.5 (J_{CF} = 1.9 Hz), 64.9, 43.6, 28.7, 26.6, 26.4, 21.2, 14.6 ppm
^{19}F NMR ($CDCl_3$, 376 MHz): δ = -116.7 (td, *J* = 9.2, 5.0 Hz)

*NMR Data for syn-C7-propyl-C9-fluoro 1-aminoNB **2q-syn**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.61 (s, 1H, imine CH), 8.32 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 8.05 (d, 2H, *J* = 8.1 Hz, 4-NO_2-Ar), 7.14 (dd, 1H, *J* = 8.0, 4.9 Hz, Ar), 6.85-6.82 (m, 1H, Ar), 6.83-6.79 (m, 1H, Ar), 3.31 (d, 1H, *J* = 4.0 Hz, C4), 2.29 (dd, 1H, *J* = 10.2, 2.3 Hz, C7), 2.19 (tt, 1H, *J* = 10.8, 4.0 Hz, C3-eq), 2.08 (td, 1H, *J* = 10.3, 3.4 Hz, C2-eq), 1.66-1.62 (m, 1H, C2-ax), 1.44-1.35 (m, 2H, C7-C*H*$_2$-), 1.33-1.23 (m, 3H, C3-ax, C7-CH_2C*H*$_2$-), 0.82 (t, 3H, *J* = 7.1 Hz, C7-CH_2CH_2C*H*$_3$) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 161.9 (J_{CF} = 242.8 Hz), 158.6, 149.3 (J_{CF} = 6.1 Hz), 148.1, 142.1, 141.0 (J_{CF} = 2.9 Hz), 129.0, 124.1, 123.4 (J_{CF} = 8.1 Hz), 112.6 (J_{CF} = 22.3 Hz), 108.4 (J_{CF} = 23.5 Hz), 79.7 (J_{CF} = 1.9 Hz), 65.0, 45.2, 32.9, 28.3, 27.7, 21.7, 14.5 ppm
^{19}F NMR ($CDCl_3$, 376 MHz): δ = -116.5 (td, *J* = 9.2, 4.9 Hz)

[48] Time course adjusted to account for the smaller amount of starting material.
[49] The C4 resonances were employed to determine *anti*:*syn* ratio.
[50] Assignments based on analogy to related systems. The sample used for characterization was prepared after re-exposing the above sample to irradiation (in order to drive to completion), hence the altered isomeric ratio (now 3.2:1 *anti*:*syn*).

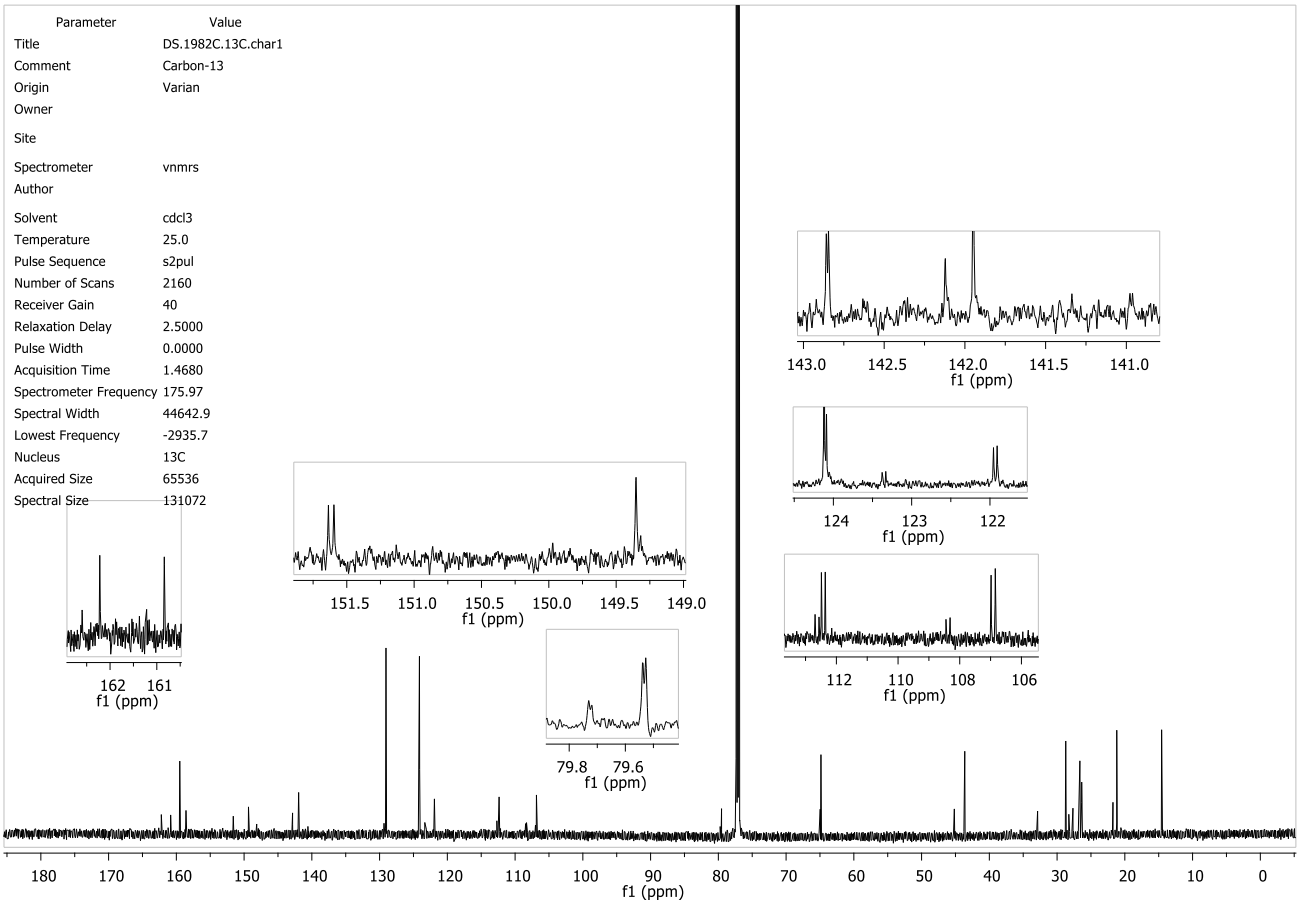
^{1}H NMR (700 MHz, $CDCl_3$) for 2q

Parameter	Value
Title	DS.1982C.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	56
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



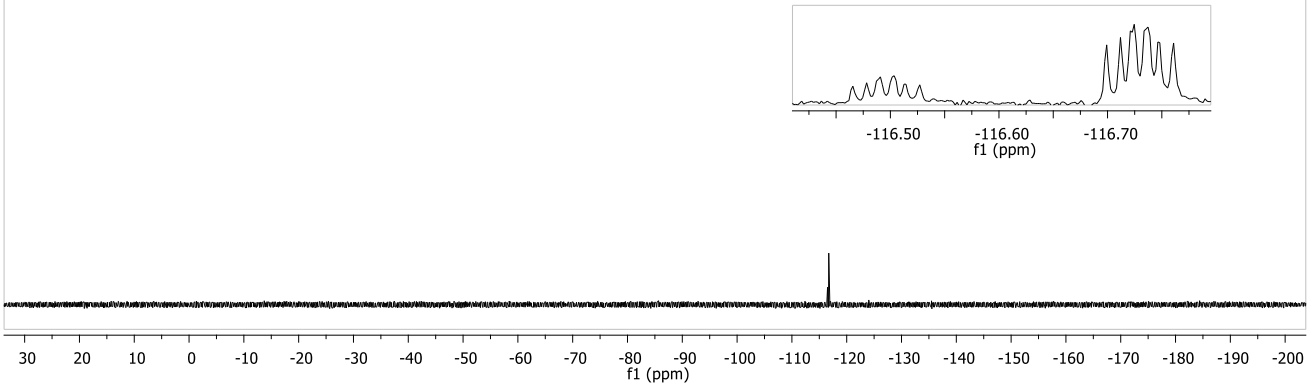
^{13}C NMR (176 MHz, $CDCl_3$) for 2q

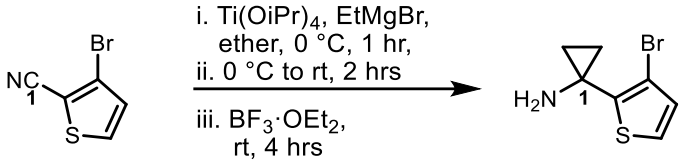
Parameter	Value
Title	DS.1982C.13C.char1
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	2160
Receiver Gain	40
Relaxation Delay	2.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.7
Nucleus	13C
Acquired Size	65536
Spectral Size	131072



^{19}F NMR (376 MHz, $CDCl_3$) for 2q

Parameter	Value
Title	DS.1982C.19F
Comment	Fluorine-19
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.7340
Spectrometer Frequency	375.91
Spectral Width	89285.7
Lowest Frequency	-76597.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072





S27 ***40%*** **S28**

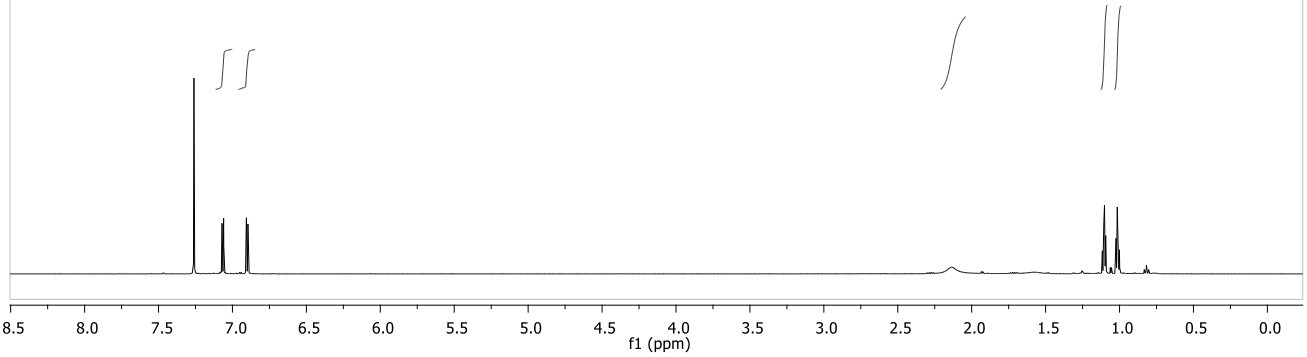
Procedure for 8-*thio* aminocyclopropane S28

3-Bromo-2-cyanothiophene **S27** (615 mg, 3.3 mmol; purchased from Aba ChemScene) was dissolved in 30 mL dry ether in a dry flask under inert atmosphere, then cooled to 0 °C. Titanium isopropoxide (1.07 mL, 3.6 mmol; purchased from Oakwood Chemical) was added in one portion, followed by addition of ethylmagnesium bromide (3.0 M in ether, 2.4 mL, 7.2 mmol) via syringe, dropwise down the side of the vial over the course of 5 min. The dark brown-black reaction mixture (clear, colorless at outset of EtMgBr addition) was stirred at 1 hr while coming to room temp, cold bath was removed, and the reaction was stirred an additional 2 hrs at room temp. BF3·etherate (0.81 mL, 6.5 mmol) was added dropwise over the course of 2 min, and the reaction mixture was stirred 4 hrs at room temp. The reaction was quenched by carefully pouring in 50 mL of a 3:1 mix of sat. Rochelle salt:1 M NaOH (aq), followed by 30 min of vigorous stirring at room temp. The biphasic mixture was diluted with an additional 50 mL of the same aqueous mixture and 100 mL ether. The phases were separated. The aqueous phase was extracted with three 50 mL portions of ether. The combined organics were then washed with 50 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under vacuum. The crude residue was purified via flash chromatography over silica (5 to 25% ethyl acetate:hexanes, increasing in 5% increments; the silica was pre-neutralized with 5% ethyl acetate:hexanes + 1% NEt3; the residue was loaded with PhMe). Collected 283 mg of aminocyclopropane **S28** (39.7% yield) as a yellow oil.

*Characterization Data for 8-thio aminocyclopropane **S28**:*
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.07 (d, 2H, *J* = 5.3 Hz, thiophene), 6.90 (d, 2H, *J* = 5.3 Hz, thiophene), 2.14 (br s, 2H, -NH_2), 1.10 (dd, 2H, *J* = 6.7, 4.5 Hz, CP), 1.01 (dd, 2H, *J* = 6.7, 4.5 Hz, CP) ppm
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 144.4, 130.8, 123.4, 109.7, 31.9, 16.5 ppm
IR (neat): 3365, 3089, 3009, 2965, 1587, 1514, 1436, 1413, 1345, 1268, 1149, 1044, 862, 821, 707 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_7H_9BrNS^+$: 217.9634, Found: 217.9630
R_f = 0.55 (40% ethyl acetate:hexanes + 1% NH_4OH), one red spot, ninhydrin, UV

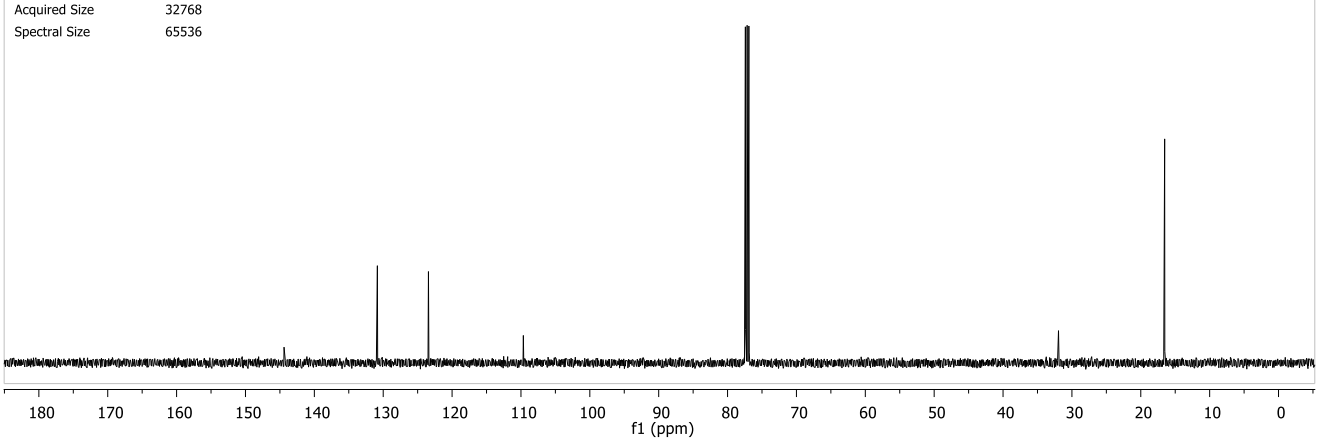
^{1}H NMR (500 MHz, $CDCl_3$) for S28

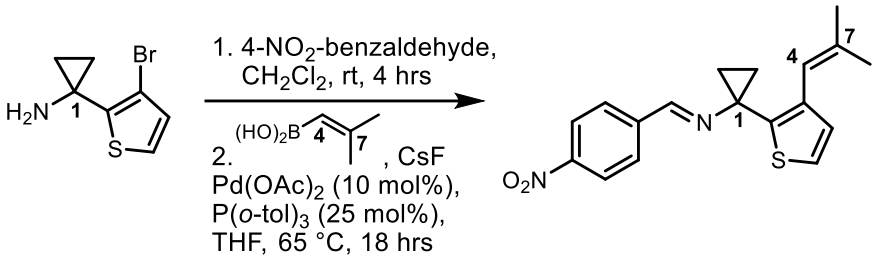
Parameter	Value
Title	DS.1860.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	58
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1006.8
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



^{13}C NMR (126 MHz, $CDCl_3$) for S28

Parameter	Value
Title	DS.1860.13C.char
Comment	STANDARD FLUORINE PARAMETERS
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	128
Receiver Gain	30
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.0486
Spectrometer Frequency	125.76
Spectral Width	31250.0
Lowest Frequency	-1775.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536





Procedure for 8-*aza* cyclopropylimine 1y

Aminocyclopropane **S28** (272 mg, 0.1.25 mmol) was dissolved in 7.0 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 4-nitrobenzaldehyde (0.47 g, 3.1 mmol) in one portion. The reaction mixture was stirred at room temp for 4 hrs before concentrating onto celite under vacuum; two 10 mL portions of pentane were added followed by re-concentration after each. The celite was loaded onto a basic alumina column, and the product was eluted (1 to 2 to 3 to 5 to 10 to 20% ethyl acetate:hexanes). Collected 362 mg of the Schiff base intermediate (82.7% yield) as a yellow oil. Partial characterization is provided below.

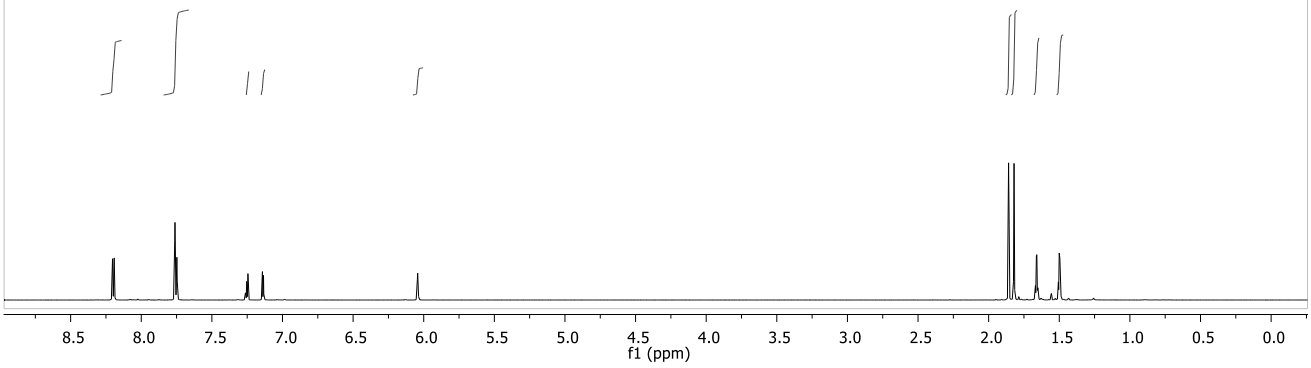
Characterization Data for Schiff Base Intermediate:
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.21 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.80 (d, 2H, *J* = 8.8 Hz, 4-NO_2-Ar), 7.76 (s, 1H, imine CH), 7.32 (d, 2H, *J* = 5.4 Hz, thiophene), 7.06 (d, 2H, *J* = 5.4 Hz, thiophene), 1.73 (td, 2H, *J* = 4.6, 2.9 Hz, CP), 1.55 (td, 2H, *J* = 4.2, 2.9 Hz, CP) ppm
R_f = 0.35 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

CsF (465 mg, 3.06 mmol) was added to flame-dried flask under Ar (with stir bar), the flask was sealed, then flame-dried under vacuum; this flask was stored under vacuum until cool, before purging with N_2 and adding 1.0 mL dry, degassed THF (degassed by sparging with Ar through 22 gauge needle for 30 min prior to use, in separate dry flask). In a separate dry vial under inert atmosphere, a stock of Pd^0 catalyst was prepared from $Pd(OAc)_2$ (62 mg, 276 µmol) and tris(o-tolyl)phosphine (215 mg, 706 µmol) in 4 mL dry, degassed THF, then stirred for 15 min at room temp. In separate dry vial under inert atmosphere, the Schiff base intermediate from above (215 mg, 0.61 mmol) was dissolved in 3 mL dry, degassed THF before adding (2,2-dimethyl)vinylboronic acid (92 mg, 0.92 mmol; purchased from Synthonix) in one portion. The starting material and boronic acid mixture was transferred into the CsF-containing flask via syringe, quantitating transfer with three 1 mL portions of dry, degassed THF. Once the Pd/phosphine mixture (orange) had stirred for 15 min, 1.8 mL (0.12 mmol Pd with 0.31 mmol ligand) was added to the reaction flask via syringe, adding dropwise over 30 seconds. A reflux condenser was attached, the system was flushed with Ar, and the reaction was heated to 65 ºC for 18 hrs, stirring vigorously to prevent CsF from settling. Upon cooling to room temp, the reaction mixture was filtered through a pad of celite, eluting with ~50 mL ethyl acetate before concentrating under vacuum. The crude residue was purified via flash chromatography over silica (1 to 2 to 3 to 5% ethyl acetate:hexanes; residue was loaded with PhMe). Obtained 158 mg of vinylated cyclopropylimine **1y** as a slighty yellow oil, still containing some residual ligand (also collected 88 mg of a mixture that was largely ligand along with some product and starting material; this was not further purified). After a second round of chromatography (identical to above), 150 mg of pure cyclopropylimine **1y** was obtained as a slightly yellow oil (75.0% yield; 62.0% yield over 2 steps).

*Characterization Data for 8-aza aminocyclopropane **1y**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.20 (d, 2H, *J* = 8.1 Hz, 4-NO_2-Ar), 7.76 (s, 1H, imine CH), 7.75 (d, 2H, *J* = 9.4 Hz, 4-NO_2-Ar), 7.25 (d, 2H, *J* = 5.3 Hz, thiophene), 7.14 (d, 2H, *J* = 5.3 Hz, thiophene), 1.86 (s, 3H, C7-Me), 1.82 (s, 3H, C7-Me), 1.66 (*app*. q, 2H, *J* = 4.5 Hz, CP), 1.50 (*app*. q, 2H, *J* = 4.5 Hz, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 155.2, 148.7, 142.4, 140.0, 136.7, 135.8, 129.1, 128.4, 124.3, 123.9, 118.5, 44.3, 27.0, 20.1, 19.8 ppm
IR (neat): 3099, 2973, 2911, 1599, 1518, 1442, 1380, 1342, 1298, 1206, 1106, 1051, 862, 748, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{18}H_{19}N_2O_2S^+$: 327.1162, Found: 327.1164
R_f = 0.40 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

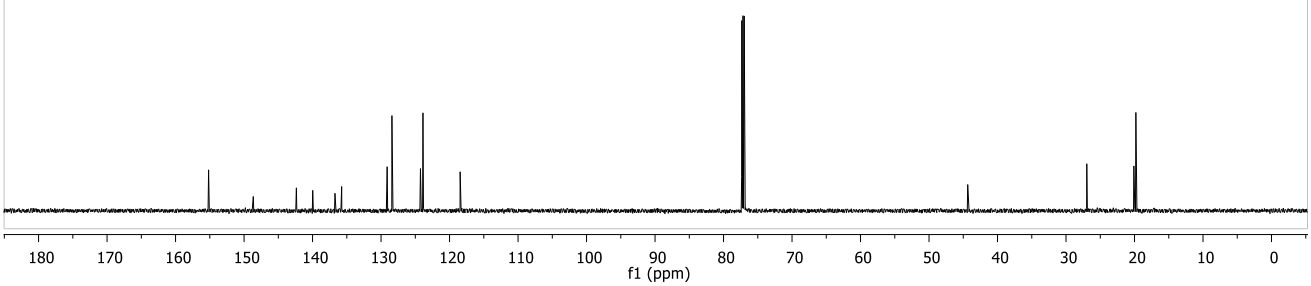
^{1}H NMR (700 MHz, $CDCl_3$) for 1y

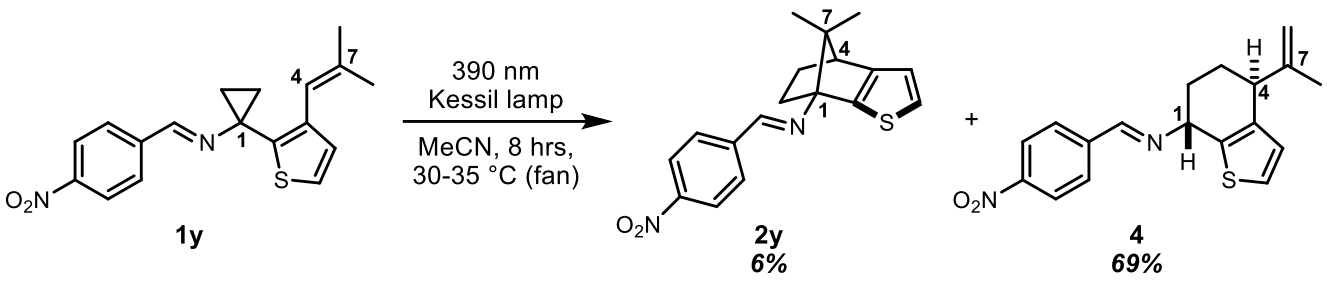
Parameter	Value
Title	DS.1878.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	42
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 1y

Parameter	Value
Title	DS.1878.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	68
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2937.0
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for 8-*thio* 1-aminoNB 2y

In a dry vial under inert atmosphere, cyclopropylimine **1y** (68.5 mg, 210 μmol) was dissolved in 2.1 mL dry MeCN. Reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction was irradiated with 390 nm light for 8 hrs, using the setup described in Section II.A (temperature maintained between 30-35 °C with a fan). Reaction mixture was dark red with minor amounts of a red precipitate. The mixture was poured into 20 mL 1:1 saturated $NaHCO_3$ (aq.):water and diluted with 10 mL ether. Phases were separated, and the aqueous phase was further extracted with 10 mL ether three times. Combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified via flash chromatography over basic alumina (2 to 4 to 6 to 10 to 15% ethyl acetate:hexanes; loaded residue with PhMe). Collected multiple portions of eluent:

Portion 1: 7.7 mg of a yellow oil that proved to be a 1.2:1 mix of starting material to product, dictating that 3.5 mg were recovered cyclopropylimine **1x** (5.1% recovery) and 4.2 mg were the desired 1-aminoNB **2y** (6.1% yield).

Portion 2: 47.5 mg of a yellow solid, identified as the cyclohexane byproduct **4** (69.3% yield).

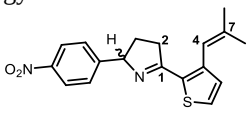
Portion 3: 7.0 mg of a yellow solid that is suspected to be the pyrroline byproduct (~10% yield).

*Partial Characterization Data for 8-thio 1-aminoNB **2y**[51]:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.83 (s, 1H, imine CH), 8.31 (d, 2H, *J* = 8.5 Hz, 4-NO_2-Ar), 8.04 (d, 2H, *J* = 8.5 Hz, 4-NO_2-Ar), 7.16 (d, 1H, *J* = 4.6 Hz, thiophene), 6.91 (d, 1H, *J* = 4.6 Hz, thiophene), 3.06 (d, 1H, *J* = 3.6 Hz, C4), 2.47-2.42 (m, 1H, C2-eq), 2.32-2.27 (m, 1H, C3-eq), 1.34-1.28 (m, 1H, C2-ax), 1.20-1.15 (m, 1H, C3-ax), 1.15 (s, 3H, C7-Me), 0.76 (s, 3H, C7-Me) ppm
R_f = 0.75 (20% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

Partial Characterization Data for 8-thio pyrroline[52]:
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.19 (d, 1H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.49 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.36 (d, 1H, *J* = 5.1 Hz, thiophene), 6.99 (d, 1H, *J* = 5.1 Hz, thiophene), 6.41 (s, 1H, C4), 5.32 (*app.* t, 1H, *J* = 8.0 Hz, C*H*-(4-NO_2-Ar)), 3.15-3.09 (m, 1H, C2), 3.03-2.95 (m, 1H, C2), 2.63 (*app*. tdd, 1H, 12.7, 9.0, 4.0 Hz, C3), 1.92 (s, 3H, C7-Me), 1.83-1.78 (m, 1H, C3), 1.77 (s, 3H, C7-Me) ppm
R_f = 0.25 (20% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

*Characterization Data for 8-thio cyclohexane byproduct **4**:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.50 (s, 1H, imine CH), 8.28 (d, 2H, *J* = 9.3 Hz, 4-NO_2-Ar), 7.96 (d, 2H, *J* = 8.6 Hz, 4-NO_2-Ar), 7.16 (d, 1H, *J* = 5.1 Hz, thiophene), 6.79 (d, 1H, *J* = 5.1 Hz, thiophene), 4.90 (s, 1H, C7-methylene), 4.75 (s, 1H, C7-methylene), 4.72 (t, 1H, *J* = 6.6 Hz, C1), 3.54 (*app*. t, 1H, *J* = 6.9 Hz, C4), 2.17 (ddd, 1H, *J* = 12.2, 8.6, 3.9 Hz, C2-pseudoequatorial), 2.12 (ddd, 1H, *J* = 12.8, 7.3, 2.5 Hz, C3-pseudoequatorial), 2.04 (ddd, 1H, *J* = 12.8, 10.8, 2.3 Hz, C2-pseudoaxial), 1.88-1.82 (m, 1H, C3-pseudoaxial), 1.69 (s, 3H, C7-Me) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 158.7, 149.3, 147.8, 141.7, 138.8, 137.7, 129.3, 128.0, 124.1, 124.0, 113.0, 66.4, 45.1, 30.7, 26.4, 19.8 ppm
IR (neat): 2937, 2858, 1640, 1601, 1520, 1448, 1374, 1344, 1314, 1286, 895, 853, 839, 749, 690 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{18}H_{19}N_2O_2S^+$: 327.1162, Found: 327.1162
R_f = 0.55 (20% ethyl acetate:hexanes + 1% NH_4OH), one UV-active spot

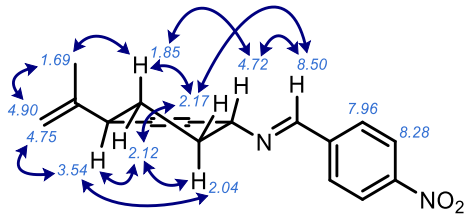
[51] Assignments based on analogy to related scaffolds, despite being unable to fully purify the material.
[52] Pyrroline byproduct **S31** was assigned based on analogy to other scaffolds:



S29

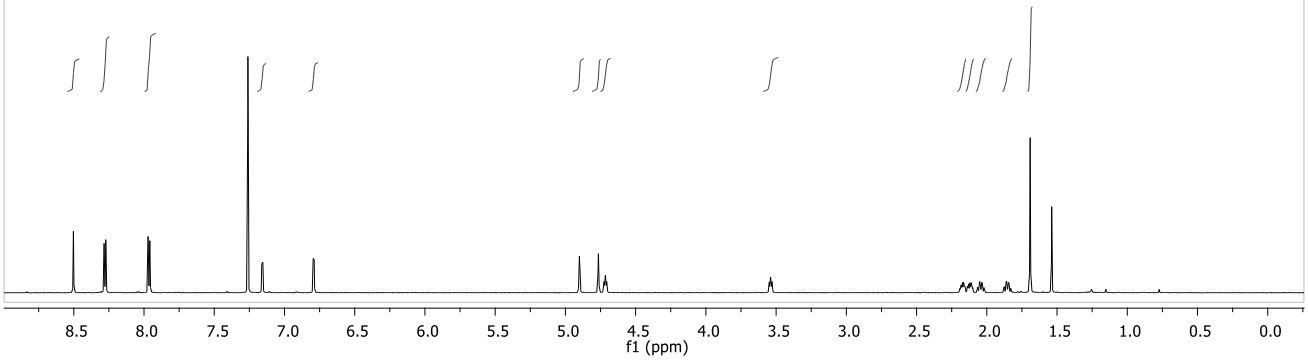
2D NMR Data

- COSY and NOESY experiments were employed to assign the connectivity and relative configuration of the cyclohexane byproduct **4**. isomer obtained, ultimately indicating the *anti*-isomer depicted above. Key NOESY correlations (denoted by blue arrows) are provided below:



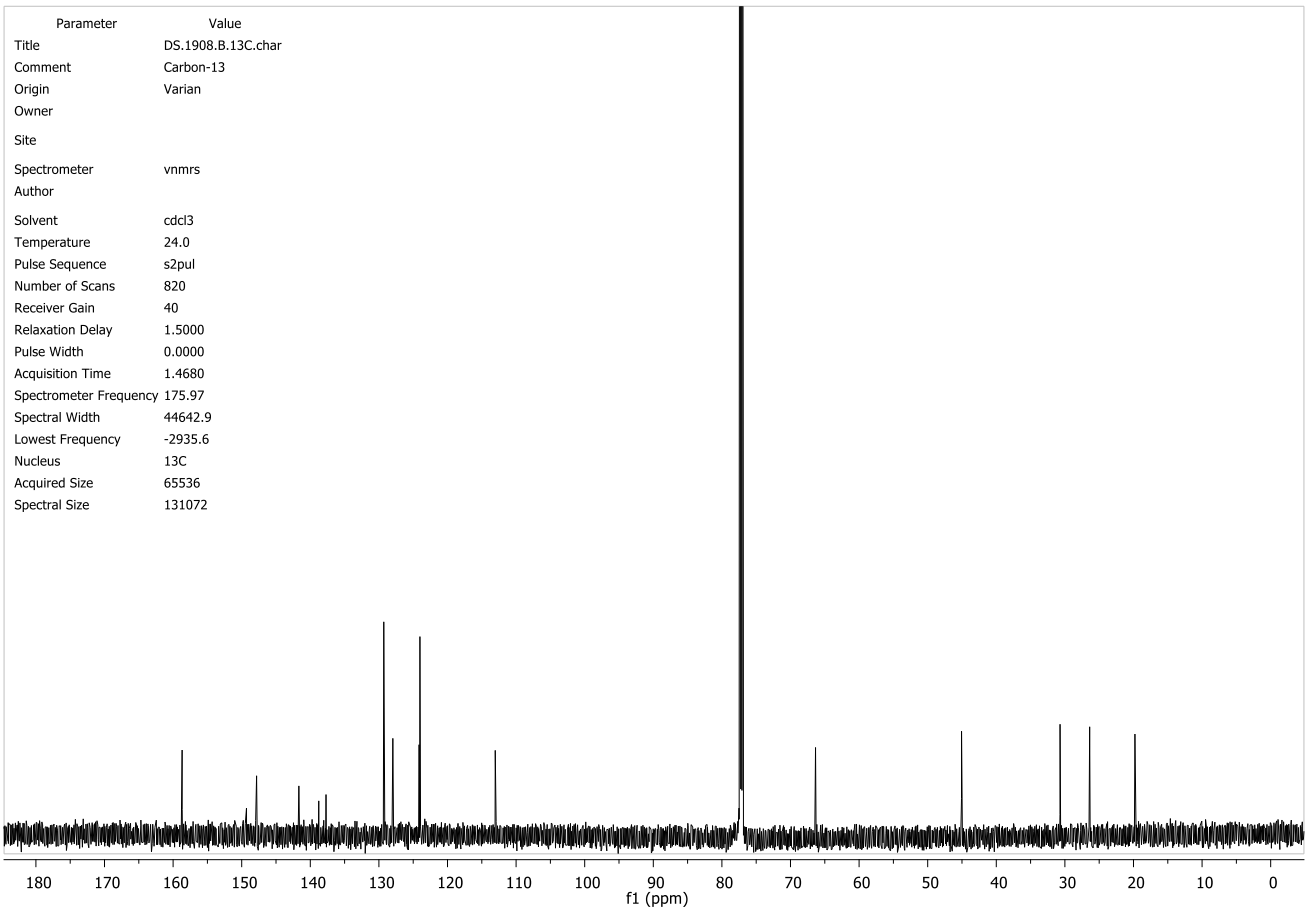
^{1}H NMR (700 MHz, $CDCl_3$) for cyclohexane 4

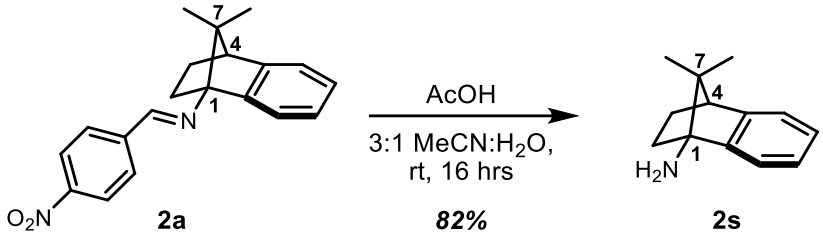
Parameter	Value
Title	DS.1908.B.1H.char1
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	24.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	58
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for cyclohexane 4

Parameter	Value
Title	DS.1908.B.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	24.0
Pulse Sequence	s2pul
Number of Scans	820
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.6
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





2a ***82%*** **2s**

Procedure for 1-aminoNB 2s

In a dry vial under inert atmosphere, Schiff base **2a** (95.0 mg, 0.30 mmol) was dissolved in 720 μL dry MeCN, followed by addition of 240 μL water and 240 μL acetic acid. Flushed with Ar, capped, and stirred at room temp for 16 hrs.[53] Diluted with 2 mL ether, then 2 mL 0.5 M HCl (aq.). Phases were separated, and the acidic aqueous phase was washed with 2 mL ether two times. Aqueous phase was then basified with 0.5 mL 6 M NaOH (aq.) and diluted with 2 mL ether. Phases were separated. Extracted basic aqueous phase with three additional portions of 2 mL ether. Combined organics were dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated carefully under a stream of nitrogen.[54] Collected 45.4 mg of 1-aminoNB **2s** (81.8% yield) as a clear, colorless liquid.

*Characterization Data for 1-aminoNB **2s**:*

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.19 (d, 1H, *J* = 7.2 Hz, Ar), 7.16-7.13 (m, 2H, Ar), 7.12-7.09 (m, 1H, Ar), 2.81 (d, 1H, *J* = 4.1 Hz, C4), 2.13-2.08 (m, 1H, C3-eq.), 1.87 (*app*. td, 1H, *J* = 11.1, 4.0 Hz, C2-eq), 1.43 (br s, 2H, -NH_2), 1.32 (ddd, 1H, *J* = 11.4, 9.6, 3.2 Hz, C2-ax), 1.16 (ddd, 1H, *J* = 12.2, 9.3, 4.0 Hz, C3-ax), 1.00 (s, 3H, C7-Me), 0.51 (s, 3H, C7-Me) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 149.1, 146.5, 125.8, 125.6, 121.4, 118.8, 69.5, 58.1, 51.0, 32.6, 26.1, 19.3, 18.5 ppm

IR (neat): 3370, 2951, 2870, 1605, 1475, 1458, 1367, 1314, 1238, 1219, 1161, 1126, 1012, 864, 822, 751 cm^{-1}

HRMS (ES+, *m/z)* calculated for $C_{13}H_{18}N^+$: 188.1434, Found: 188.1432

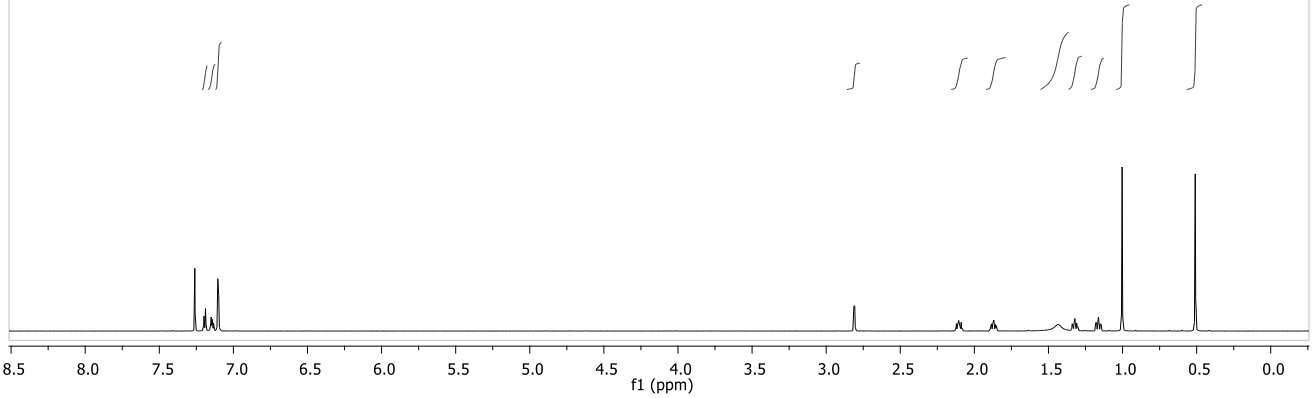
R_f = 0.15 (30% ethyl acetate:hexanes + 1% NH_4OH), one red spot, ninhydrin, UV

[53] Note: Starting material is not fully soluble in reaction mixture but will go into solution with time; best results were obtained upon periodically sonicating or swirling in order to suspend residual solid.

[54] The final product is relatively volatile; excessive concentration will lead to loss in yield.

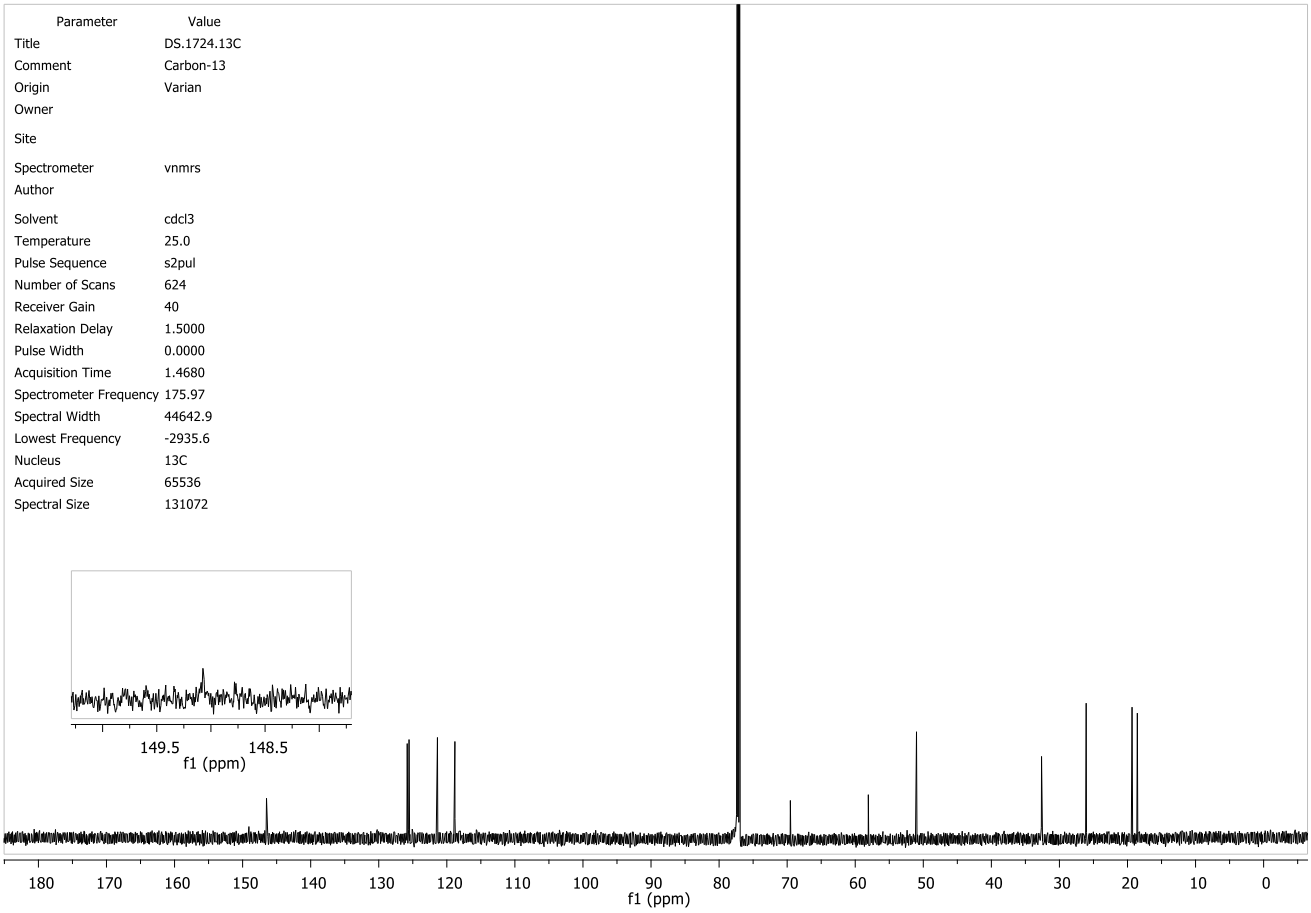
^{1}H NMR (500 MHz, $CDCl_3$) for 2s

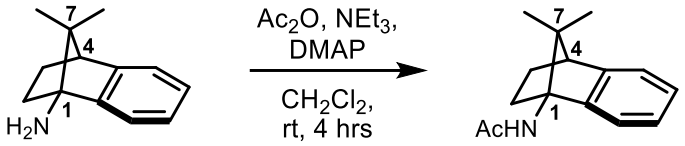
Parameter	Value
Title	DS.1724.1H.char2
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	54
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 2s

Parameter	Value
Title	DS.1724.13C
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	624
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.6
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





2s ***97%*** **2t**

Procedure for *N*-acetylated 1-aminoNB 2t

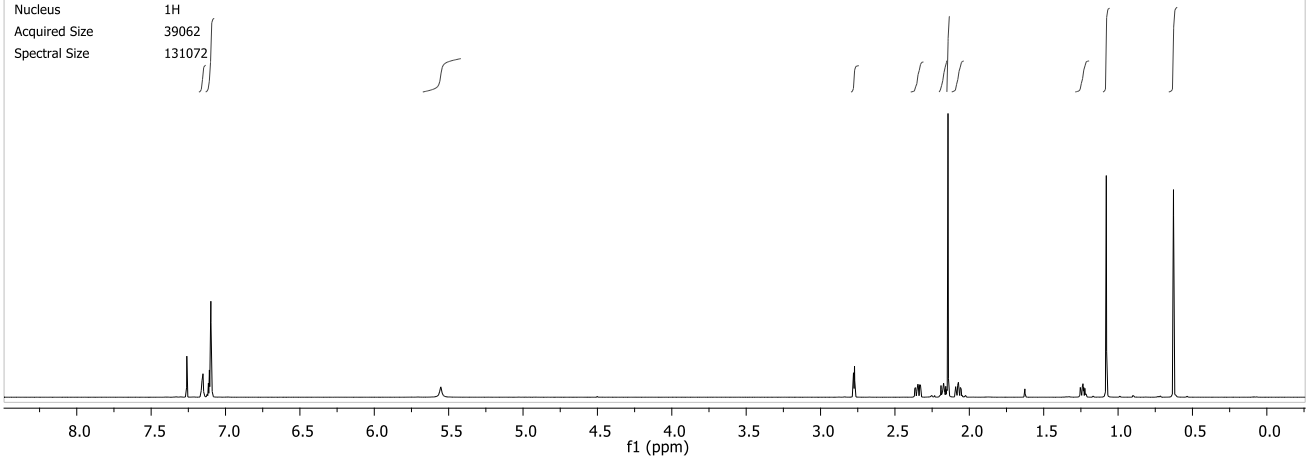
In a dry vial under inert atmosphere, 1-aminoNB **2s** (9.9 mg, 53 μmol) was dissolved in 550 μL dry CH_2Cl_2. Triethylamine (30 μL, 0.21 mmol), DMAP (3.0 mg, 26 μmol), and acetic anhydride (12.5 μL, 0.13 mmol) were added respectively in one portion each. Flushed with Ar, capped, and stirred at room temp for 4 hrs. Quenched reaction with 1 mL sat. $NaHCO_3$ (aq.), then diluted with 1 mL water and 2 mL ether. Phases were separated. Extracted aqueous phase with three additional portions of 2 mL ether. Combined organics were dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under a stream of nitrogen. Crude residue was purified via pipet chromatography over silica (40 to 60% ethyl acetate:hexanes). Obtained 11.7 mg of the acetylated 1-aminoNB **2t** (96.5% yield) as a white solid.

*Characterization Data for N-Ac 1-aminoNB **2t**[55]:*
^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.17-7.14 (m, 1H, Ar), 7.12-7.09 (m, 3H, Ar), 5.55 (br s, 1H, NH), 2.77 (d, 1H, *J* = 4.1 Hz, C4), 2.35 (ddd, 1H, *J* = 12.4, 10.3, 4.0 Hz, C2-eq), 2.17 (*app*. ddt, 1H, *J* = 12.2, 10.3, 4.1 Hz, C3-eq), 2.14 (s, 3H, NHAc), 2.07 (ddd, 1H, *J* = 12.4, 9.4, 4.1 Hz, C2-ax), 1.24 (ddd, 1H, *J* = 12.1, 9.6, 4.0 Hz, C3-ax), 1.08 (s, 3H, C7-Me), 0.63 (s, 3H, C7-Me) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 170.9, 146.3, 145.9, 126.2, 125.7, 121.4, 120.6, 70.4, 59.0, 50.6, 29.8, 26.5, 24.4, 20.1, 19.6 ppm
IR (neat): 3301, 3046, 2957, 2879, 1655, 1544, 1459, 1370, 1299, 1162, 1015, 751 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{15}H_{20}NO^+$: 230.1539, Found: 230.1538
R_f = 0.50 (80% ethyl acetate:hexanes), one yellow spot, $KMnO_4$ (weak), UV (weak)

[55] Assignments based on analogy to related scaffolds.

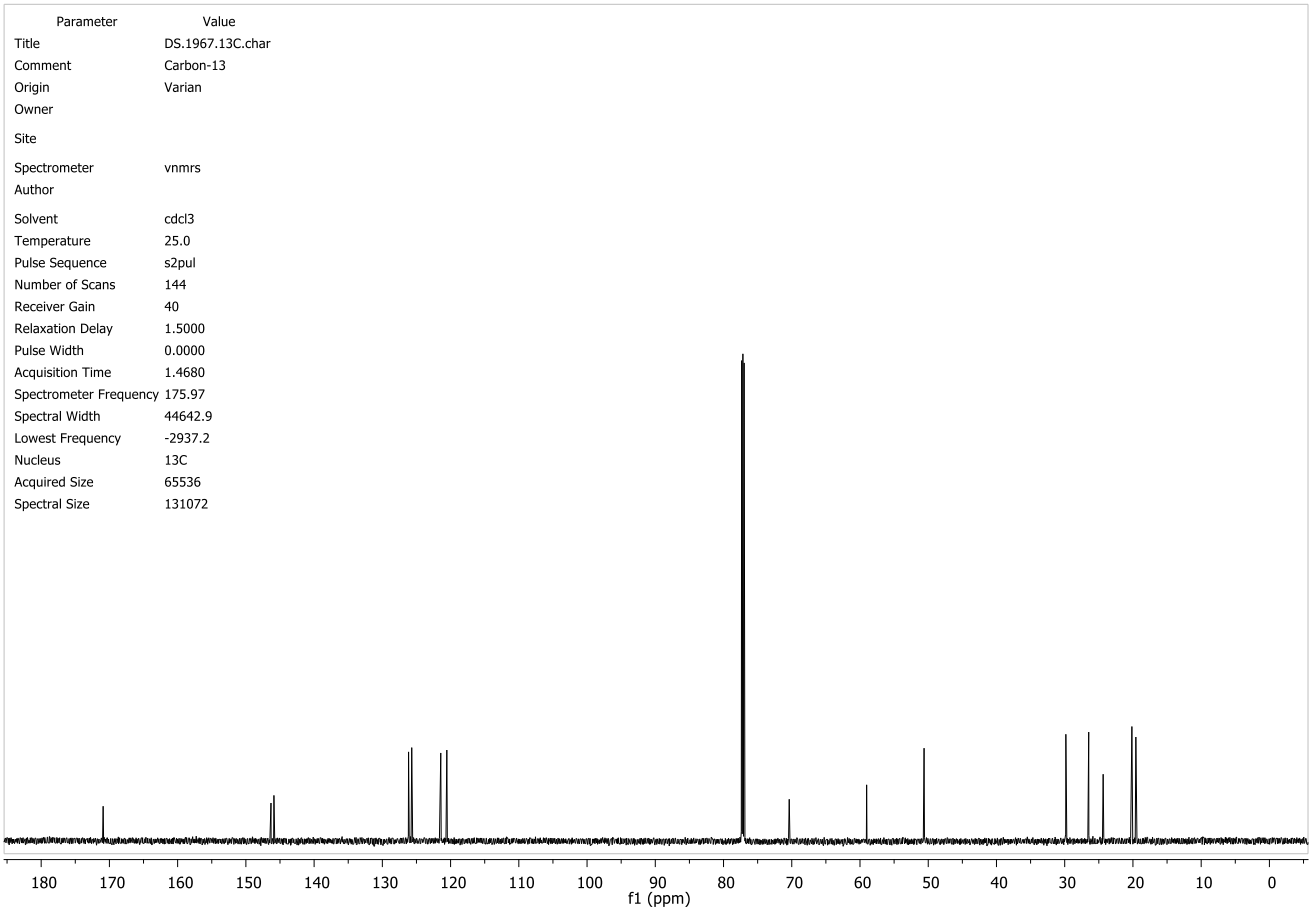
^{1}H NMR (700 MHz, $CDCl_3$) for 2t

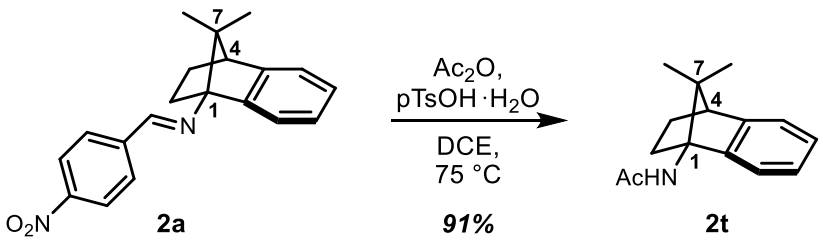
Parameter	Value
Title	DS.1967.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	44
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 2t

Parameter	Value
Title	DS.1967.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	144
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2937.2
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





One-Step Procedure for *N*-acetylated 1-aminoNB 2t

In a dry vial under inert atmosphere, Schiff base-protected 1-aminoNB **2a** (9.2 mg, 29 μmol) was dissolved in 600 μL dry CH_2Cl_2. Acetic anhydride (27 μL, 0.29 mmol) was added in one portion. Flushed vial with Ar, capped, and heated to 40 °C for 14 hrs. The reaction mixture was diluted with 1 mL water and 2 mL ethyl acetate before quenching with 1 mL sat. $NaHCO_3$ (aq.) and 5 drops of 6 M NaOH (aq.). Phases were separated. The aqueous phase was extracted with three portions of ethyl acetate, 2 mL each. The combined organics were dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under a stream of nitrogen. ^{1}H NMR analysis of the crude mixture revealed only ~5% conversion to the desired product (based on C7-methyl resonances).

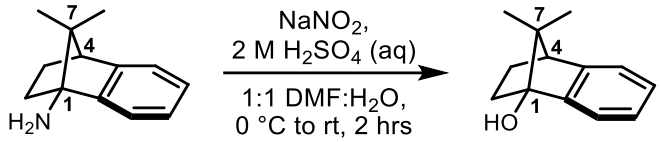
The crude residue was re-exposed to nearly the same conditions, but this round was supplemented with pTsOH monohydrate (0.6 mg, 3 μmol; acid was added in one portion prior to addition of Ac_2O). Heating to 40 °C for 14 hrs followed by the same workup procedure led to a 1.3:1 mixture of SM:pdt based on ^{1}H NMR analysis of the crude mixture.

A third exposure to conditions was applied, now supplementing with 1.1 mg (6 μmol) of pTsOH monohydrate and heating to 40 °C for 60 hrs followed by the same workup procedure. ^{1}H NMR analysis of the crude mixture revealed a 0.6:1 mixture of SM:pdt.

A fourth exposure retained the 0.2 eq. of pTsOH monohydrate but was run in dry DCE and was heated to 75 °C for 14 hrs following the Ar flush and capping. Following the same workup procedure, ^{1}H NMR analysis of the crude mixture revealed full consumption of the starting material. Purification of the crude residue was achieved via flash chromatography over silica (40 to 60 to 80% ethyl acetate:pentane). The desired acetamide **2t** was obtained as a white solid, 6.0 mg, 91.1% yield.

All spectroscopic data matched that obtained on the samples produced through the two-step procedure. The conversion data is tabulated below:

	eq. (Ac_2O/pTsOH)	solvent	temp (°C)	time (hrs)	SM:pdt
Exp. 1:	10/0	DCM	40	14	***~20:1***
Exp. 2:	10/0.1	DCM	40	14	***1.3:1***
Exp. 3:	10/0.2	DCM	40	60	***0.6:1***
Exp. 4:	10/0.2	DCE	75	14	**--**



2s ***74%*** **6**

Procedure for 1-hydroxyNB 6

In a dry vial under inert atmosphere, 1-aminoNB **2s** (21.3 mg, 114 μmol) was dissolved in 300 μL dry DMF, then cooled to 0 °C. Added 300 μL of 2 M H_2SO_4 (aq.). Prepared stock of $NaNO_2$ in HPLC-grade water to yield a stock concentration of 118 mg/600 μL (prepared 1.4 mL in total; 276 mg $NaNO_2$). The $NaNO_2$ stock was added (600 μL, 1.7 mmol) slowly down the side of the vial over the course of 3 min. The cold bath was removed, and the mixture was stirred at room temp for 2 hrs. Quenched by diluting with 2 mL ether then adding 2 mL of 3 M NaOH (aq.) slowly over 1 min followed by 500 μL sat. $Na_2S_2O_3$ (aq.). Phases were separated. Extracted aqueous phase with three additional portions of 2 mL ether. Combined organics were dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under a stream of nitrogen. Crude residue was purified via pipet chromatography over silica (5 to 10 to 20% ethyl acetate:pentane; loaded residue with PhMe). Obtained 16.4 mg of the 1-hydroxyNB **6** as a clear, colorless oil that was 96.5 wt% product mixed with CH_2Cl_2; true yield = 15.8 mg = 73.8% yield.

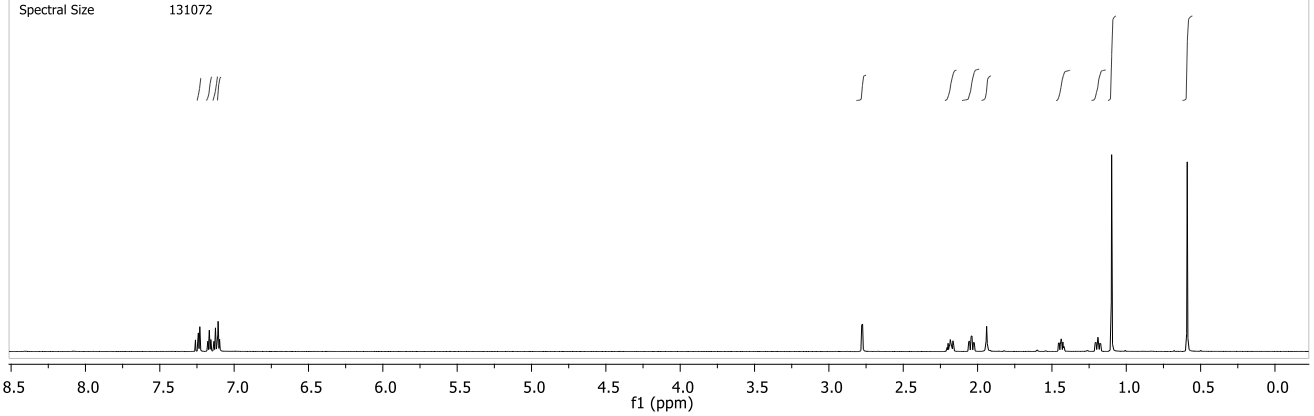
Characterization Data for 1-hydroxyNB ***6***[56]*:*

^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.24 (d, 1H, *J* = 7.1 Hz, Ar), 7.17 (t, 1H, *J* = 7.2 Hz, Ar), 7.13 (t, 1H, *J* = 7.2 Hz, Ar), 7.10 (d, 1H, *J* = 6.9 Hz, Ar), 2.78 (d, 1H, *J* = 4.2 Hz, C4), 2.21-2.15 (m, 1H, C3-eq.), 2.04 (*app*. td, 1H, *J* = 10.9, 4.1 Hz, C2-eq), 1.94 (s, 1H, -OH), 1.46-1.42 (m, 1H, C2-ax), 1.19 (ddd, 1H, *J* = 12.2, 9.4, 4.1 Hz, C3-ax), 1.10 (s, 3H, C7-Me), 0.59 (s, 3H, C7-Me) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 147.7, 145.5, 126.2, 125.7, 121.6, 118.6, 87.6, 58.0, 49.7, 31.2, 26.3, 19.3, 18.6 ppm
IR (neat): 3377, 2955, 2875, 1475, 1459, 1367, 1283, 1232, 1209, 1159, 1121, 1084, 1011, 900, 750, 668 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{13}H_{17}NaO^+$: 211.1093, Found: 211.1098
R_f = 0.40 (20% ethyl acetate:hexanes), one blue spot, CAM, UV (weak)

[56] Assignments based on analogy to related scaffolds.

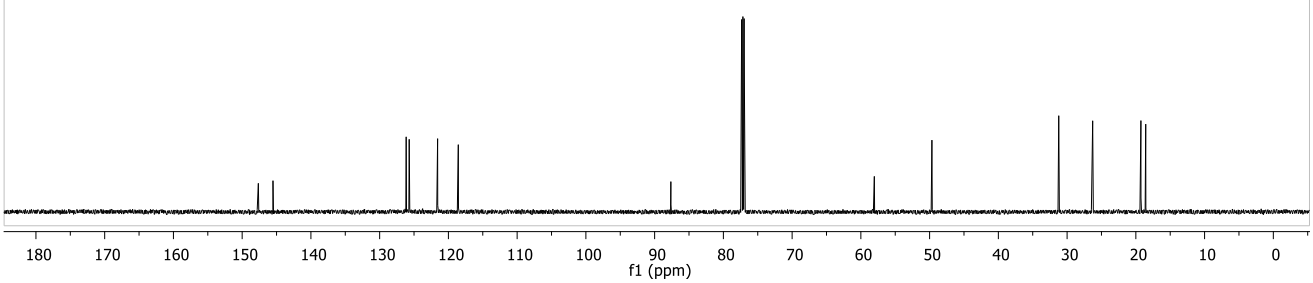
^{1}H NMR (700 MHz, $CDCl_3$) for 6

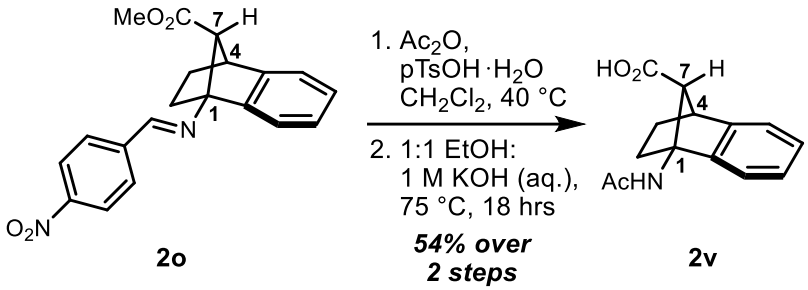
Parameter	Value
Title	DS.1925.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	12
Receiver Gain	40
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 6

Parameter	Value
Title	DS.1925.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	48
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2937.9
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for C7-CO_2H 1-aminoNB 2v

In a dry vial under inert atmosphere, Schiff base-protected 1-aminoNB **2o** (28 mg, 80 μmol) was dissolved in 800 μL dry CH_2Cl_2. Acetic anhydride (75 μL, 0.79 mmol) was added in one portion, followed by addition of pTsOH·H_2O (3.0 mg, 16 μmol). Flushed vial with Ar, capped, and heated to 40 °C for 72 hrs. The reaction mixture was quenched with 2 mL 1 M NaOH (aq.) and diluted with 2 mL ethyl acetate. Phases were separated. The aqueous phase was extracted with three portions of ethyl acetate, 2 mL each. The combined organics were dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated under a stream of nitrogen. ^{1}H NMR analysis of the crude mixture revealed a ~1:1 mixture of SM and the desired product. The crude residue was re-exposed to identical conditions for a 24 hr time course. Following the same workup procedure, ^{1}H NMR analysis of the crude mixture revealed full consumption of the starting material. Purification of the crude residue was achieved via flash chromatography over silica (5 to 10 to 20% acetone:dichloromethane). The desired acetamide **2v** was obtained as a white solid, 10.8 mg.

Partial Characterization Data for C7-CO_2Me C1-NHAc 1-aminoNB[57]*:*

^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.17-7.09 (m, 4H, Ar), 6.25 (br s, 1H, -NHAc), 3.70 (s, 3H, -CO_2Me), 3.54 (d, 1H, *J* = 2.7 Hz, C4), 3.49 (d, 1H, *J* = 1.2 Hz, C7), 2.22-2.15 (m, 1H, C3-eq), 2.13 (s, 3H, -NHAc), 2.15-2.08 (m, 1H, C2-eq), 1.67-1.61 (m, 1H, C2-ax), 1.31-1.25 (m, 1H, C3-ax) ppm

R_f = 0.25 (10% acetone:dichloromethane), one yellow spot, $KMnO_4$ (weak), UV (weak)

The acetamide obtained from the above procedure (assumed 42 μmol) was dissolved in 0.5 mL 200 proof ethanol before adding 0.5 mL of a freshly-prepared 1 M KOH solution in HPLC-grade water. The vial was flushed with Ar, capped, and heated to 75 °C for 18 hrs. The reaction was diluted with 4 mL water and 2 mL ether. The phases were separated. The basic aqueous phase was washed with 2 mL ether. The aqueous phase was then acidified to pH ~ 1 by addition of 1.5 mL 1 M HCl (aq.), then diluted with 2 mL ethyl acetate. The phases were separated. The aqueous phase was extracted with three portions of ethyl acetate, 2 mL each. The combined organics were dried over anhydrous sodium sulfate, filtered to remove solids, and concentrated under a stream of nitrogen. An orange residue seemed to cover a white solid. The orange residue could be rinsed away with 0.5 mL aliquots of ether, leaving 11.3 mg of a white solid that proved to be C7 carboxylic acid **2v-*anti*** mixed with residual solvent by ^{1}H NMR; integrations indicate the sample was 88.6 wt% product, thus 10.5 mg were obtained (>99% yield for saponification; 53.6% over two steps).

*Characterization Data for C7-CO_2H C1-NHAc 1-aminoNB **2v-anti**:*

^{1}H NMR (CD_3OD, 700 MHz): δ = 7.17-7.14 (m, 1H, Ar), 7.12-7.09 (m, 2H, Ar), 7.02-6.99 (m, 1H, Ar), 3.52 (d, 1H, *J* = 1.3 Hz, C4), 3.50-3.48 (m, 1H, C7), 2.27 (*app.* td, 1H, *J* = 10.6, 3.3 Hz, C2-eq), 2.24 (*app.* tt, 1H, *J* = 10.8, 3.6 Hz, C3-eq), 2.08 (s, 3H, -NHAc), 1.46-1.42 (m, 1H, C2-ax), 1.22-1.17 (m, 1H, C3-ax) ppm

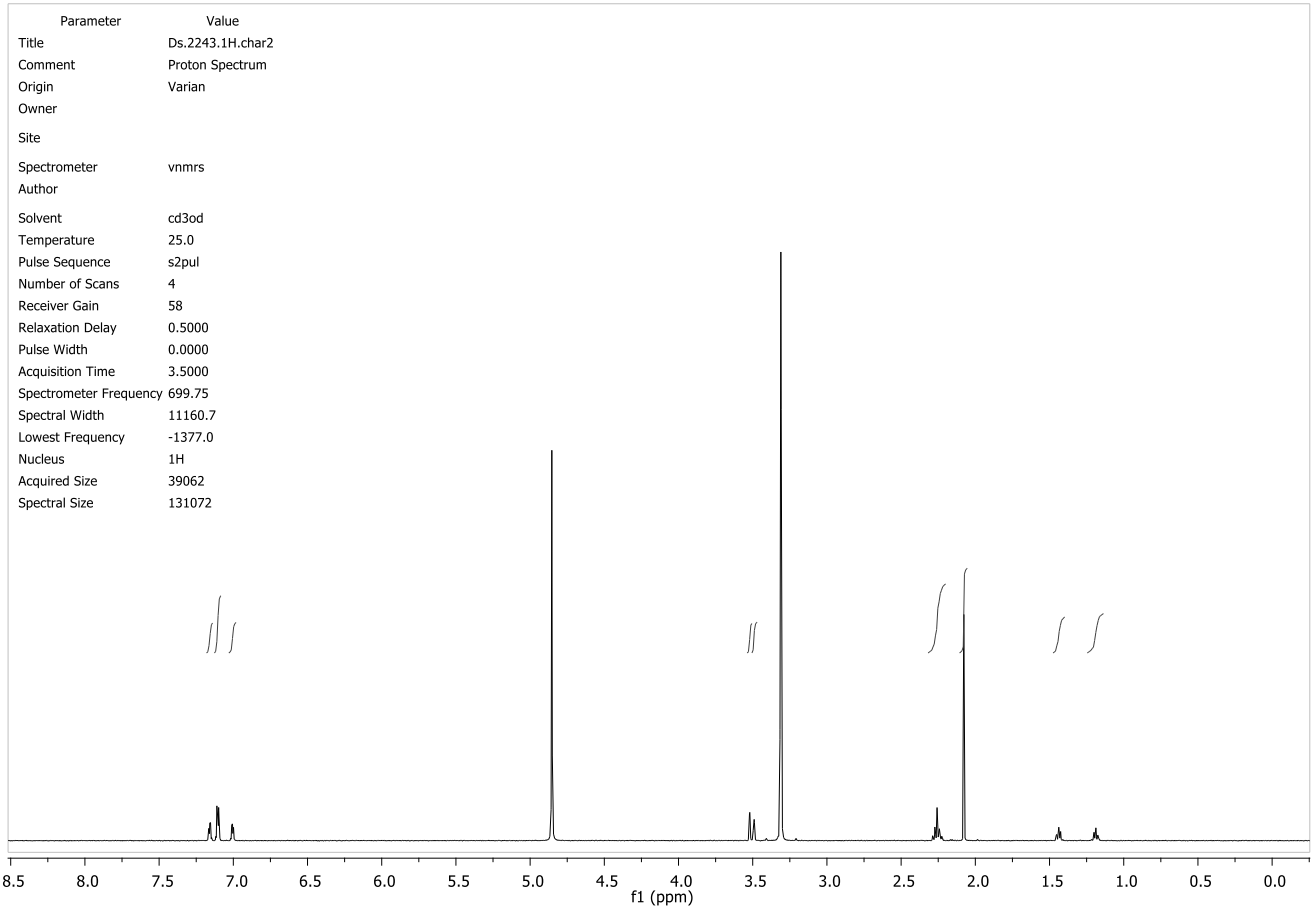
^{13}C NMR (CD_3OD, 176 MHz): δ = 173.7, 173.4, 147.4, 145.4, 127.4, 126.9, 121.7, 119.8, 68.2, 62.9, 45.3, 31.1, 26.8, 23.0 ppm.

HRMS (ES+, *m/z)* calculated for $C_{14}H_{16}NO_3^+$: 246.1125, Found: 246.1123

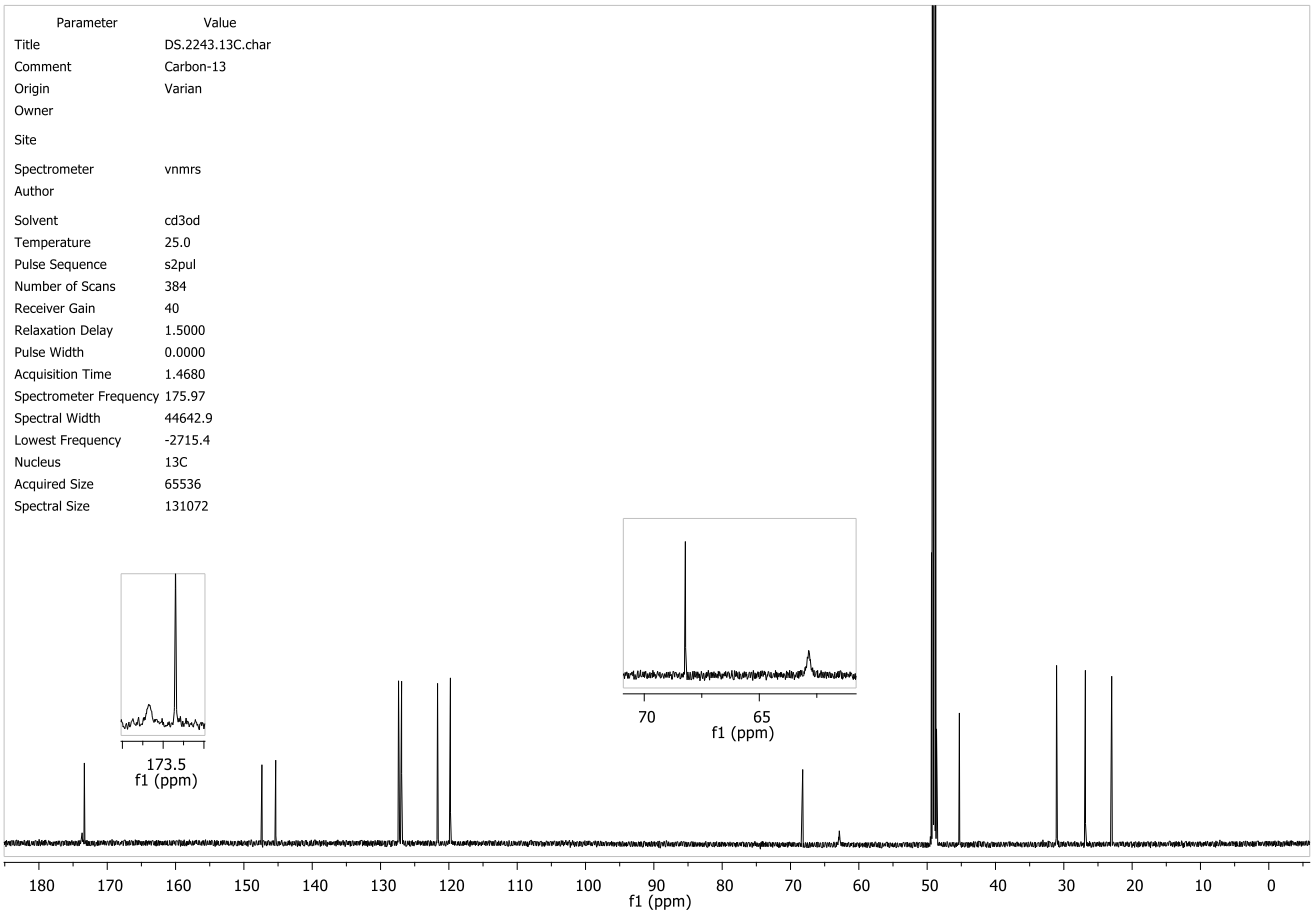
R_f = 0.20 (30% acetone:ethyl acetate + 0.2% AcOH), one blue spot, CAM (weak), UV (weak)

[57] All assignments based on analogy to related scaffolds.

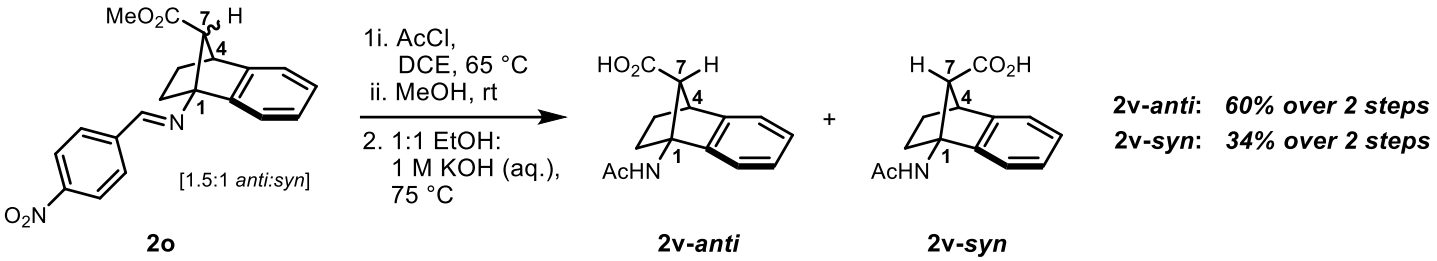
^{1}H NMR (700 MHz, CD_3OD) for 2v



^{13}C NMR (176 MHz, CD_3OD) for 2v



While the procedures listed above provide access to single C7-epimer by starting with isomerically-pure Schiff base-protected 1-aminoNB **2o-*anti***, alternative samples containing both C7-epimers could be pushed forward through analogous operations to afford the *syn* isomer. Of note, the separations to obtain clean *syn* isomer are quite laborious, regardless if one is separating a given intermediate or the final C7-CO_2H species itself.[58] It is recommended that one separate the isomers when protected as the Schiff base, as this proved to be the least demanding of the various separations (although these intermediates are the least stable to chromatography conditions, thus total mass recovery will usually be higher if one chooses to separate the isomers after converting to the acetamide). The characterization data for the C7-CO_2H 1-aminoNB **2v-*syn*** is provided below.



2o **2v-*anti*** **2v-*syn***

*Characterization Data for C7-CO_2H C1-NHAc 1-aminoNB **2v-syn**:*

^{1}H NMR (CD_3OD, 700 MHz): δ = 7.32-7.29 (m, 1H, Ar), 7.20-7.17 (m, 1H, Ar), 7.16-7.12 (m, 2H, Ar), 3.54 (d, 1H, *J* = 3.9 Hz, C4), 3.41 (d, 1H, *J* = 1.1 Hz, C7), 2.57 (*app.* td, 1H, *J* = 11.2, 4.1 Hz, C2-eq), 2.16 (*app.* tt, 1H, *J* = 11.3, 4.3 Hz, C3-eq), 2.11 (s, 3H, -NHAc), 1.59 (ddd, 1H, *J* = 11.7, 4.9, 4.4 Hz, C2-ax), 1.23-1.18 (m, 1H, C3-ax) ppm

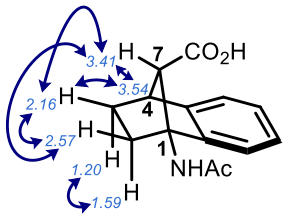
^{13}C NMR (CD_3OD, 176 MHz): δ = 174.6, 174.1, 145.2, 144.9, 128.0, 127.4, 122.6, 120.5, 69.3 (C1), 65.3 (C7), 45.9 (C4), 32.2 (C2), 28.2 (C3), 23.5 (-NHAc) ppm.

HRMS (ES+, *m/z)* calculated for $C_{14}H_{16}NO_3^+$: 246.1125, Found: 246.1123

R_f = 0.25 (30% acetone:ethyl acetate + 0.2% AcOH), one blue spot, CAM (weak), UV (weak)

2D NMR Data

- COSY, HSQC, and NOESY experiments were employed to assign the various resonances and confirm the assignment as the *syn*-isomer. Key NOESY correlations (denoted by blue arrows) are provided below:

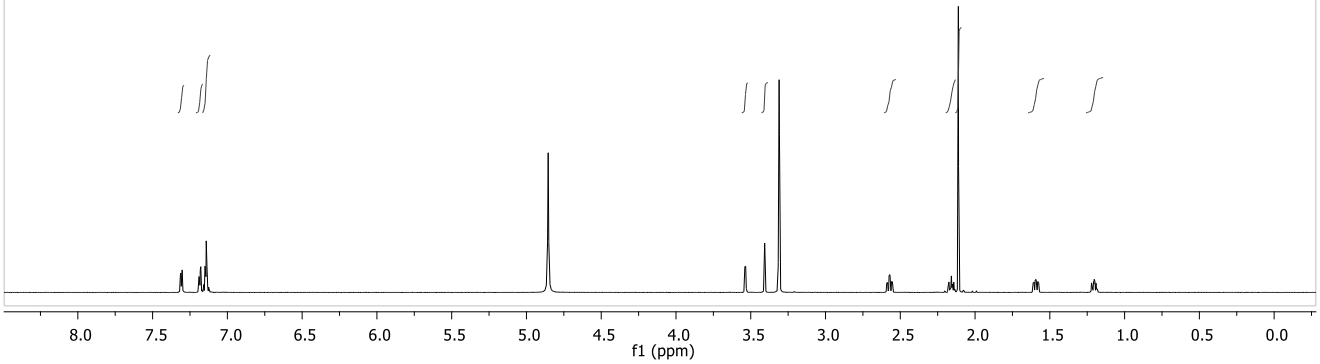


2v-*syn*

[58] Separation of the C7-CO_2H species was best achieved using the following chromatography conditions over silica (0 to 2 to 10% acetone:ethyl acetate + 0.2% AcOH).

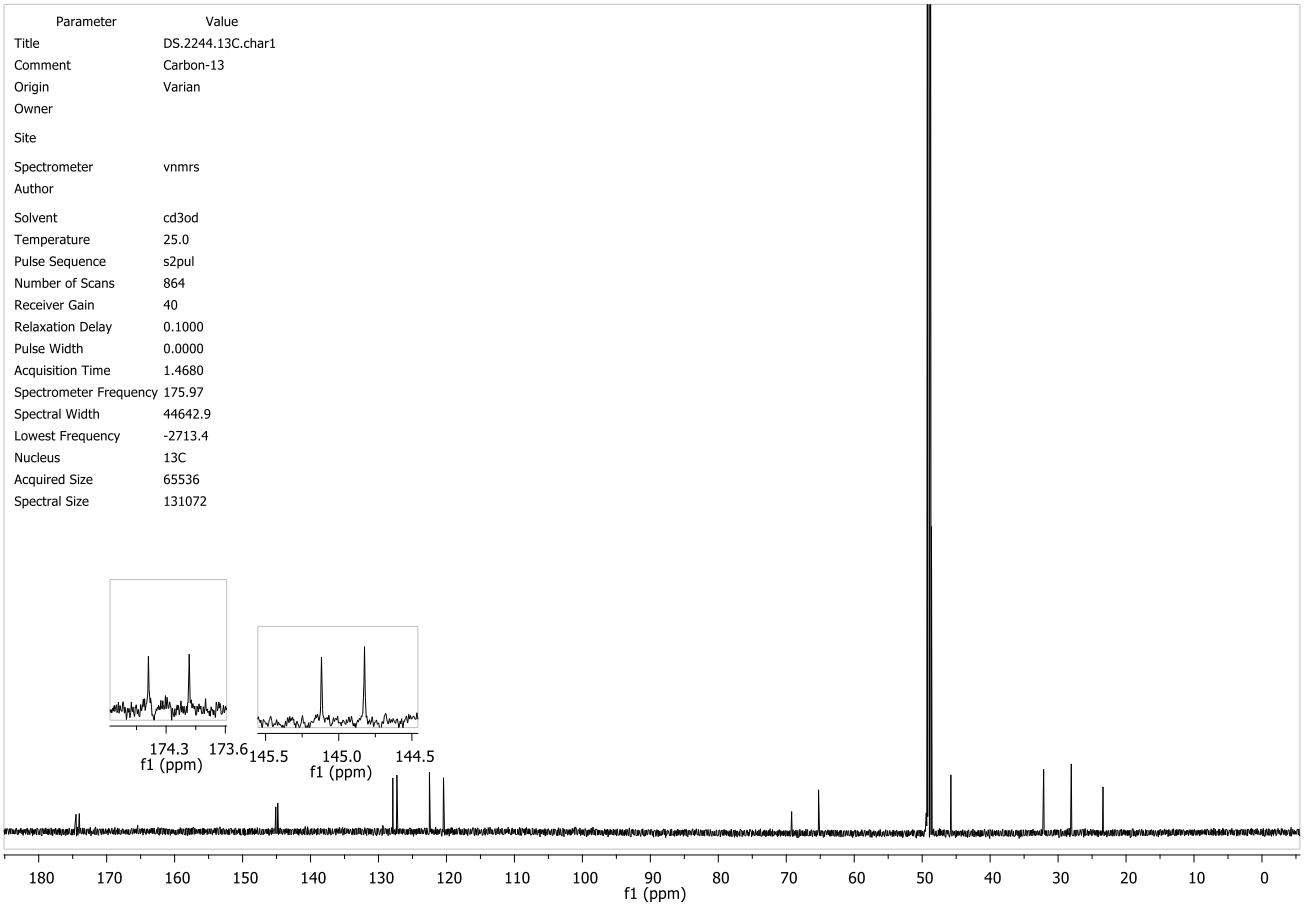
^{1}H NMR (700 MHz, CD_3OD) for 2v

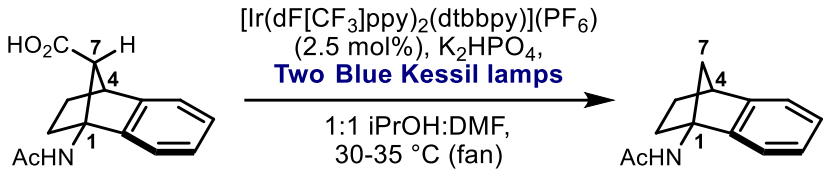
Parameter	Value
Title	DS.2244.1H.char700
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cd3od
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	54
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1377.0
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, CD_3OD) for 2v

Parameter	Value
Title	DS.2244.13C.char1
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cd3od
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	864
Receiver Gain	40
Relaxation Delay	0.1000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2713.4
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





2v ***48%*** **2u**

Procedure for C7-methylene 1-aminoNB 2u

Carboxylic acid **2v** (5.6 mg, 23 μmol) was dissolved in 250 μL dry DMF and 250 μL HPLC-grade isopropanol. Added the photocatalyst ([Ir(dF[CF_3]ppy)(dtbbpy)](PF_6), prepared in-house; 0.8 mg, 0.7 μmol) then anhydrous potassium phosphate dibasic (19.7 mg, 113 μmol). The sample was degassed via three freeze-pump-thaw cycles and sealed. The reaction mixture was irradiated with two Tuna blue Kessil lamps,[59] each positioned 5 cm from the vial at a 60° angle relative to the stir plate with the focal point of the light centered on the vial. A small fan (same model described in Section II.A) was placed 10 cm above the vial to maintain the temperature close to room temp (estimated 30-35 °C based on prior measurements in the lab). The sample was irradiated for a total of 18 hrs using this setup. Reaction mixture was still clear and bright yellow, though a visible portion of the K_2HPO_4 never went into solution. Reaction was diluted with 2 mL water, then added 3 drops 6 M NaOH (aq.) to basify. Diluted with 1 mL ethyl acetate. Phases were separated. Extracted aqueous phase with 1 mL ethyl acetate three times. Combined organics were then dried over magnesium sulfate, filtered to remove solids, and concentrated under a stream of nitrogen. ^{1}H NMR analysis of the crude sample revealed clean product only mixed with residual solvent, but the residue was an orange oil. Purified over a pipet column of silica (40 to 70 to 100% ethyl acetate:pentane), obtaining 2.2 mg of a white solid.[60] ^{1}H NMR analysis revealed pure C7-methylene 1-aminoNB **2u** as a white solid (47.9% yield; 67.1% BORSM [see below]).

To recover unreacted starting material, the basic aqueous phase was acidified by dropwise addition into 2 mL of 2 M HCl (aq.). Diluted with 1 mL ethyl acetate. Phases were separated. Extracted acidic aqueous phase with 1 mL ethyl acetate three times. Combined organics were then dried over sodium sulfate, filtered to remove solids, and concentrated under a stream of nitrogen. Collected 1.9 mg of carboxylic acid **2v** as a clear, colorless film that was 84.1 wt% **2v-*anti*** starting material mixed with solvent (28.6% recovery).

Additional Trial: DMF only[61]

Following the general procedure detailed above, 13.4 mg (54.6 μmol) of carboxylic acid **2v** were dissolved in 0.6 mL dry DMF. Ir(dF[CF_3]ppy)(dtbbpy)](PF_6) (1.6 mg, 1.4 μmol), KH_2PO_4 (18.5 mg, 136 μmol) and K_2HPO_4 (24.5 mg, 141 μmol) were added, the reaction mixture was degassed, and the reaction was irradiated for 48 hrs with a single Kessil PR-160 440 nm lamp. Following analogous purification procedures, 6.6 mg of carboxylic acid starting material was recovered (49.3% recovery), and 3.3 mg of 1-aminoNB **2u** were obtained as a white solid (30.0% yield [59.2% BORSM]).

*Characterization Data for C7-methylene 1-aminoNB **2u**:*

^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.17-7.10 (m, 4H, Ar), 6.04 (br s, 1H, -NHAc), 3.31 (d, 1H, *J* = 3.8 Hz, C4), 2.22 (td, 1H, *J* = 11.0, 4.2 Hz, C2-eq), 2.17 (*app.* ddd, 1H, *J* = 8.1, 4.2, 2.2 Hz, C7), 2.12 (s, 3H, -NHAc), 2.11 (*app.* tt, 1H, *J* = 11.1, 4.1 Hz, C3-eq), 1.99 (dd, 1H, *J* = 8.3, 1.3 Hz, C7), 1.59-1.54 (m, 1H, C2-ax), 1.31-1.26 (m, 1H, C3-ax) ppm

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 170.2, 146.3, 146.0, 126.4, 125.8, 121.1, 118.3, 67.1, 53.1, 41.6, 31.5, 28.5, 24.2 cm^{-1}

HRMS (ES+, *m/z)* calculated for $C_{13}H_{16}NO^+$: 202.1226, Found: 202.1227

R_f = 0.30 (70% ethyl acetate:hexanes), one yellow spot, $KMnO_4$ (weak), UV (weak)

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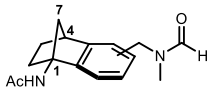
[59] It appears that this model is no longer available. The 440 nm or 456 nm PR-160 models are anticipated to be viable substitutes, as demonstrated in the additional trial.

[60] In some trials, the product was still be contaminated with a yellow film. This could be readily removed by rinsing with 1:1 ether:pentane or re-suspending in a small amount of ether followed by addition of pentane to precipitate the product.

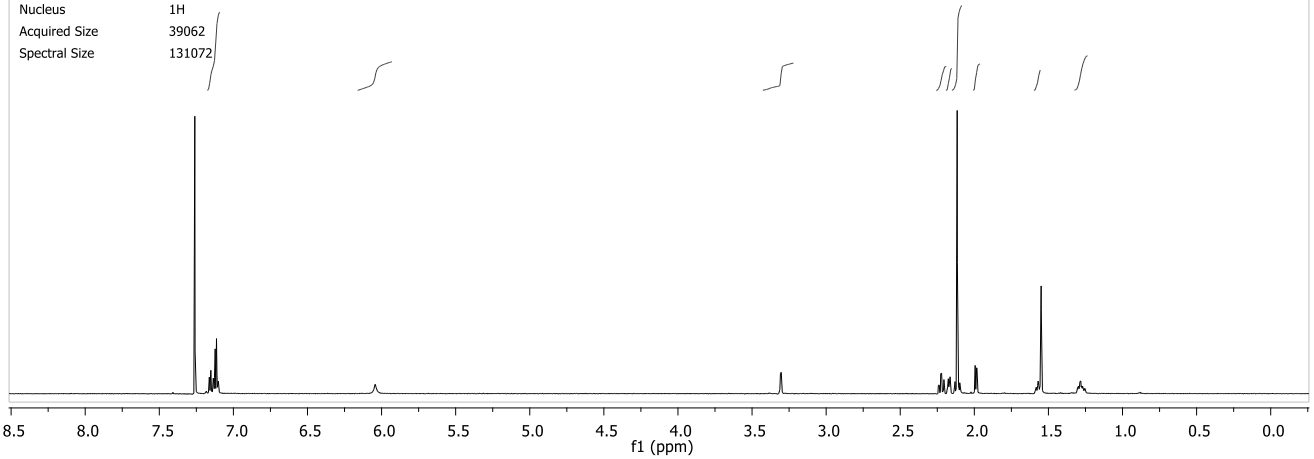
[61] More dilute trials with DMF as the only solvent would give rise to an additional byproduct, believed to be the result of DMF addition to the arene. The suspected identity of the DMF adduct byproduct (exact isomer is unknown) is represented by 1-aminoNB **S32**:



S30

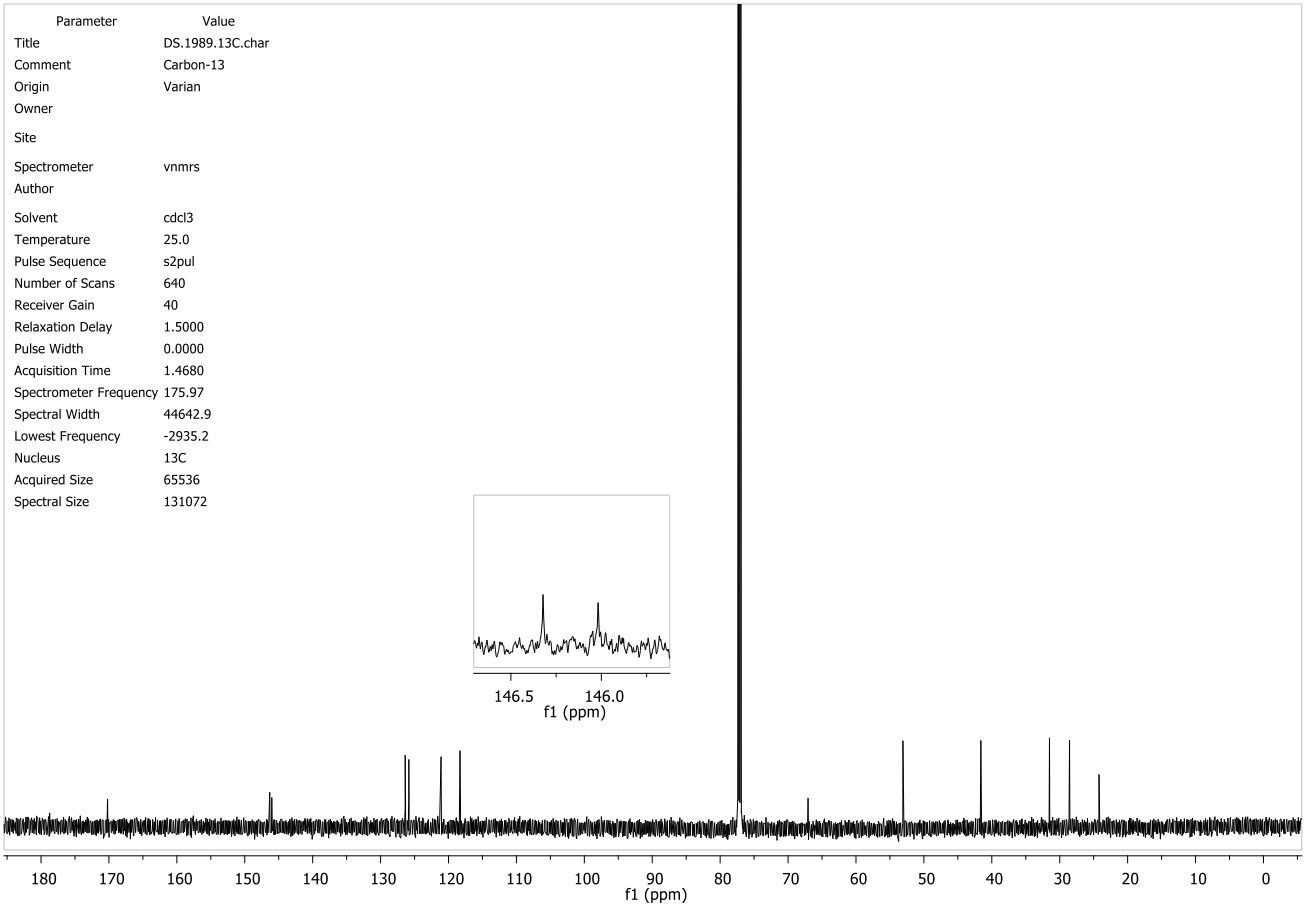
^{1}H NMR (700 MHz, $CDCl_3$) for 2u

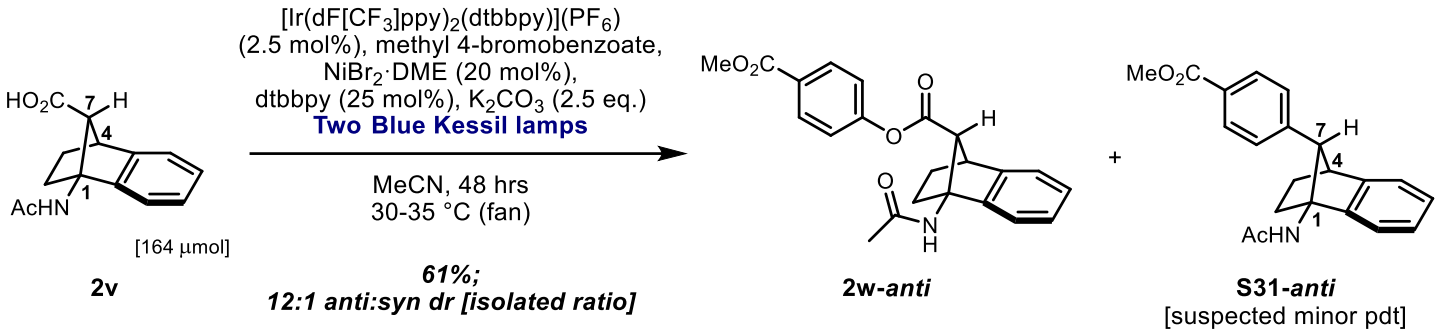
Parameter	Value
Title	DS.1989.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	58
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1379.8
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for 2u

Parameter	Value
Title	DS.1989.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	640
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.2
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for C7-aryl ester 1-aminoNBs 2w and S31

Carboxylic acid **2v** (40.3 mg, 164 μmol, 20:1 *anti*:*syn* dr) was dissolved in 1.7 mL dry, degassed MeCN (degassed 5 mL MeCN by sparging with balloon of Ar through 22 gauge needle of 45 min); solubility low. Added [Ir(dF[CF_3]ppy)(dtbbpy)](PF_6) (prepared in-house; 4.7 mg, 4.2 μmol), 4,4'-di-(tert-butyl)-2,2'-dipyridyl (11.3 mg, 42 μmol), $NiBr_2$·DME (10.4 mg, 34 μmol), methyl 4-bromobenzoate (88 mg, 0.41 mmol), and potassium carbonate (57 mg, 0.41 mmol) respectively, in one portion each. Addition of base greatly facilitates solubilization of starting material. Degassed reaction mixture with three freeze-pump-thaw cycles, then sealed. Sonicated for 1 min to dissolve any remaining starting material and suspend residual solids. Reaction mixture was yellow-green and slightly cloudy at this juncture. The reaction mixture was irradiated with two Tuna blue Kessil lamps,[62] each positioned 5 cm from the vial at a 60° angle relative to the stir plate with the focal point of the light centered on the vial. A small fan (same model described in Section II.A) was placed 10 cm above the vial to maintain the temperature close to room temp (estimated 30-35 °C based on prior measurements in the lab). The sample was irradiated for a total of 48 hrs using this setup. Reaction mixture was now slightly yellow-orange and milky in appearance. Reaction was quenched with 20 mL 1:1 sat. $NaHCO_3$ (aq.):water, then diluted with 10 mL ethyl acetate. Phases were separated. Extracted aqueous phase with 10 mL ethyl acetate three times. Combined organics were then dried over magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. ^{1}H NMR analysis of the crude sample revealed a 17:1 ratio of C7-arylated products **2w-*anti***:**2w-*syn***.[63] Crude residue was purified via flash chromatography over silica (10 to 20 to 30 to 40 to 60 to 80 to 100% EtOAc:hexanes; loaded residue with PhMe; silica was pre-neutralized with 20% EtOAc:hexanes + 1% NEt_3); pre-neutralization was found to be a mistake, as an aryl bromide-derived byproduct travels much slower through the silica if neutralized. The contaminated product mix was exposed to a second round of chromatography (5 to 10 to 15 to 30 to 50 to 70 to 100% EtOAc:hexanes; loaded residue with PhMe). Collected product in three portions:

1) 7.6 mg, white solid, 16.7:1 ratio of **2w-*anti***:**2w-*syn*** by ^{1}H NMR
2) 30.4 mg, white solid, 11.0:1 ratio of **2w-*anti***:**2w-*syn*** by ^{1}H NMR
3) 4.6 mg, yellow film, 6:1 ratio of **2w-*anti***:**2w-*syn*** by ^{1}H NMR, mixed with unidentified contaminants (one of which is suspected to be **S32**)

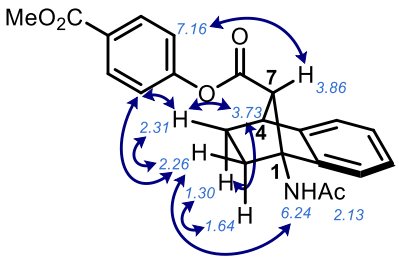
Fraction 3 was discarded, leaving a total yield of 38.0 mg at a 12.1:1 ratio of **2w-*anti***:**2w-*syn*** (61.1% yield). Subsequent rounds of chromatography yielded material for characterization. Partial characterization data for the *syn* isomer is provided below. No starting material was recovered upon acidification and extraction of aqueous phase.

*Characterization Data for anti-C7-arylated 1-aminoNB **2w-anti**:*
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.09 (d, 2H, *J* = 8.7 Hz, C7-Ar), 7.22-7.15 (m, 3H, Ar), 7.16 (d, 2H, *J* = 8.8 Hz, C7-Ar), 7.13-7.10 (m, 1H, Ar), 6.24 (br s, 1H, NH), 3.92 (s, 3H, -CO_2Me), 3.86 (d, 1H, *J* = 1.2 Hz, C7), 3.73 (d, 1H, *J* = 2.0 Hz, C4), 2.31 (*app.* tt, 1H, *J* = 10.5, 3.8 Hz, C3-eq), 2.26 (*app.* td, 1H, *J* = 10.6, 3.4 Hz, C2-eq), 2.13 (s, 3H, -NHAc), 1.64 (*app.* td, 1H, *J* = 10.3, 3.2 Hz, C2-ax), 1.43-1.36 (m, 1H, C3-eq) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 170.4, 168.7, 166.4, 154.1, 145.3, 143.2, 131.4, 128.0, 126.9, 126.6, 121.7, 121.1, 119.1, 67.5 (C1), 61.4 (C7), 52.4 (-CO_2Me), 44.4 (C4), 30.9 (C3), 26.3 (C2), 23.9 (-NHAc) ppm.
IR (neat): 3291, 1754, 1721, 1658, 1602, 1547, 1504, 1435, 1371, 1313, 1278, 1176, 1199, 1161, 1143, 1109, 1016, 980, 857, 753, 729, 690, 647 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{22}H_{22}NO_5^+$: 380.1492, Found: 380.1491
R_f = 0.45 (70% ethyl acetate:hexanes), one blue spot, CAM (weak), UV

[62] It appears that this model is no longer available. The 440 nm or 456 nm PR160 models are anticipated to be viable substitutes.
[63] While multiple resonances are diagnostic for assigning *anti* vs *syn*, the C4 and C7 resonance are the most readily integrated.

2D NMR Data

- COSY, HSQC, and NOESY experiments were employed to assign the various resonances and confirm the assignment as the *anti*-isomer. Key NOESY correlations (denoted by blue arrows) are provided below:

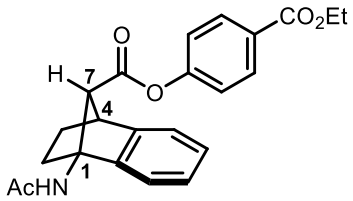


2w-*anti*

*Partial Characterization Data for anti-C7-arylated 1-aminoNB **2w-syn**:*

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.94 (d, 2H, *J* = 8.7 Hz, C7-Ar), 7.22 (d, 1H, *J* = 3.0 Hz, Ar), 7.24-7.13 (m, 3H, Ar), 6.75 (br s, 1H, NH), 6.72 (d, 2H, *J* = 8.8 Hz, C7-Ar), 3.93 (s, 3H, -CO_2Me), 3.76 (d, 1H, *J* = 3.0 Hz, C7), 3.51 (d, 1H, *J* = 2.0 Hz, C4), 2.66 (*app.* td, 1H, *J* = 11.5, 4.1 Hz, C2-eq), 2.27-2.20 (m, 1H, C3-eq), 2.14 (s, 3H, -NHAc), 1.96 (ddd, 1H, *J* = 12.1, 9.5, 4.3 Hz, C2-ax), 1.43-1.37 (m, 1H, C3-eq) ppm

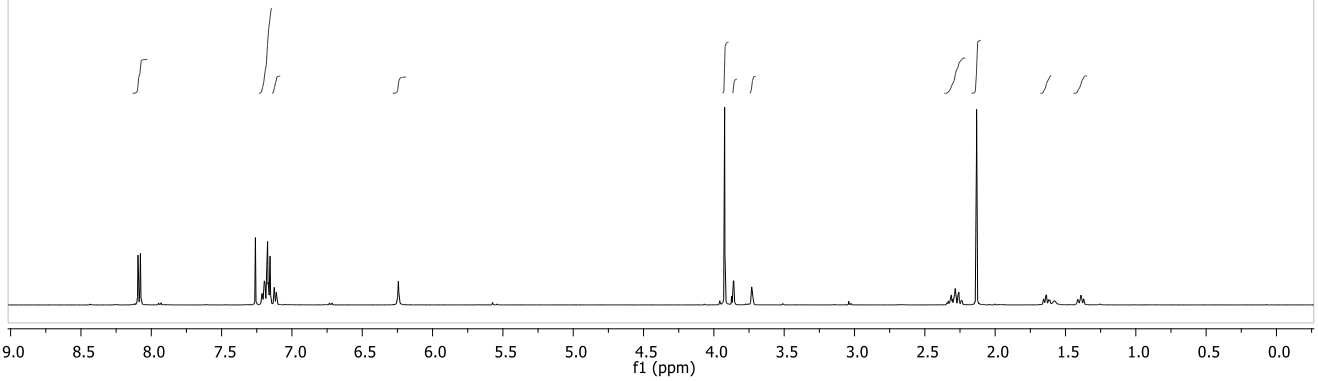
R_f = 0.45 (70% ethyl acetate:hexanes), one blue spot (overlapped with *anti*; *syn* elutes marginally more quickly in these conditions), CAM (weak), UV



2w-*syn*

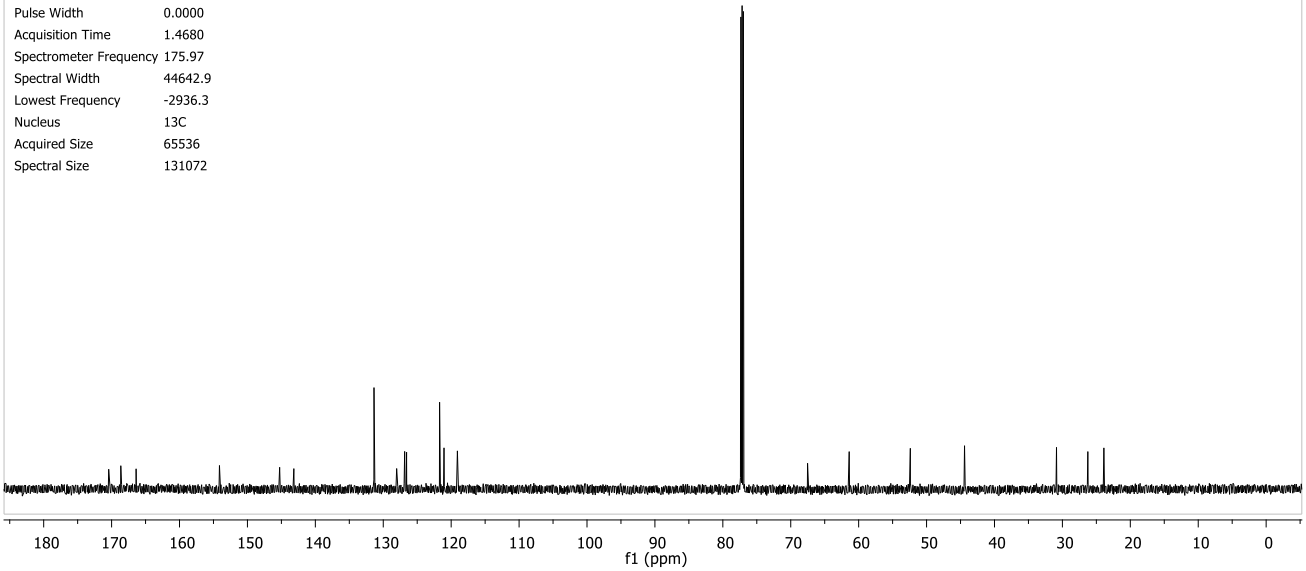
^{1}H NMR (500 MHz, $CDCl_3$) for 2w

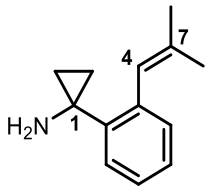
Parameter	Value
Title	DS.2254.c4.center
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	48
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.4999
Spectrometer Frequency	499.91
Spectral Width	7998.4
Lowest Frequency	-1007.3
Nucleus	1H
Acquired Size	27994
Spectral Size	65536



^{13}C NMR (176 MHz, $CDCl_3$) for 2w

Parameter	Value
Title	DS.2254.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	128
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2936.3
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





S2

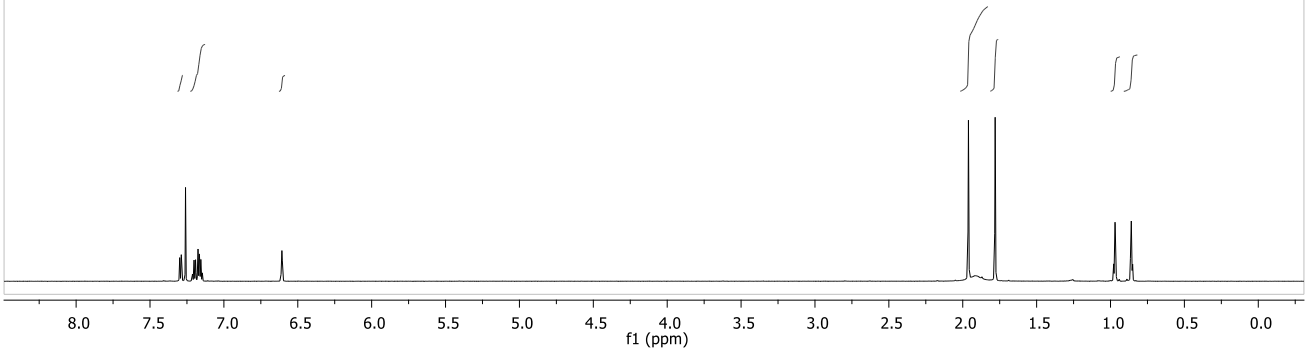
Aminocyclopropane S2

The route used for the preparation of aminocyclopropane **S2** is provided in Section III.A. The characterization data is provided below.

*Characterization Data for aminocyclopropane **S2**:*
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.29 (d, 1H, *J* = 7.4 Hz, Ar), 7.22-7.14 (m, 3H, Ar), 6.61 (s, 1H, C4), 1.96 (s, 3H, C7-Me), 1.91 (br s, 2H, -NH_2), 1.78 (s, 3H, C7-Me), 0.98-0.96 (m, 2H, CP), 0.87-0.84 (m, 2H, CP) ppm
^{13}C NMR ($CDCl_3$, 176 MHz): δ = 144.0, 138.2, 135.6, 130.3, 127.5, 126.4, 126.4, 123.8, 36.8, 26.4, 19.4, 14.6 ppm
IR (neat): 3017, 2910, 2854, 1478, 1446, 1376, 1262, 1180, 1052, 1018, 989, 853, 823, 784, 761, 743 cm^{-1}
HRMS (ES+, *m/z)* calculated for $C_{13}H_{18}N^+$: 188.1434, Found: 188.1431
R_f = 0.20 (30% ethyl acetate:hexanes + 1% NH_4OH), one red spot, ninhydrin, UV

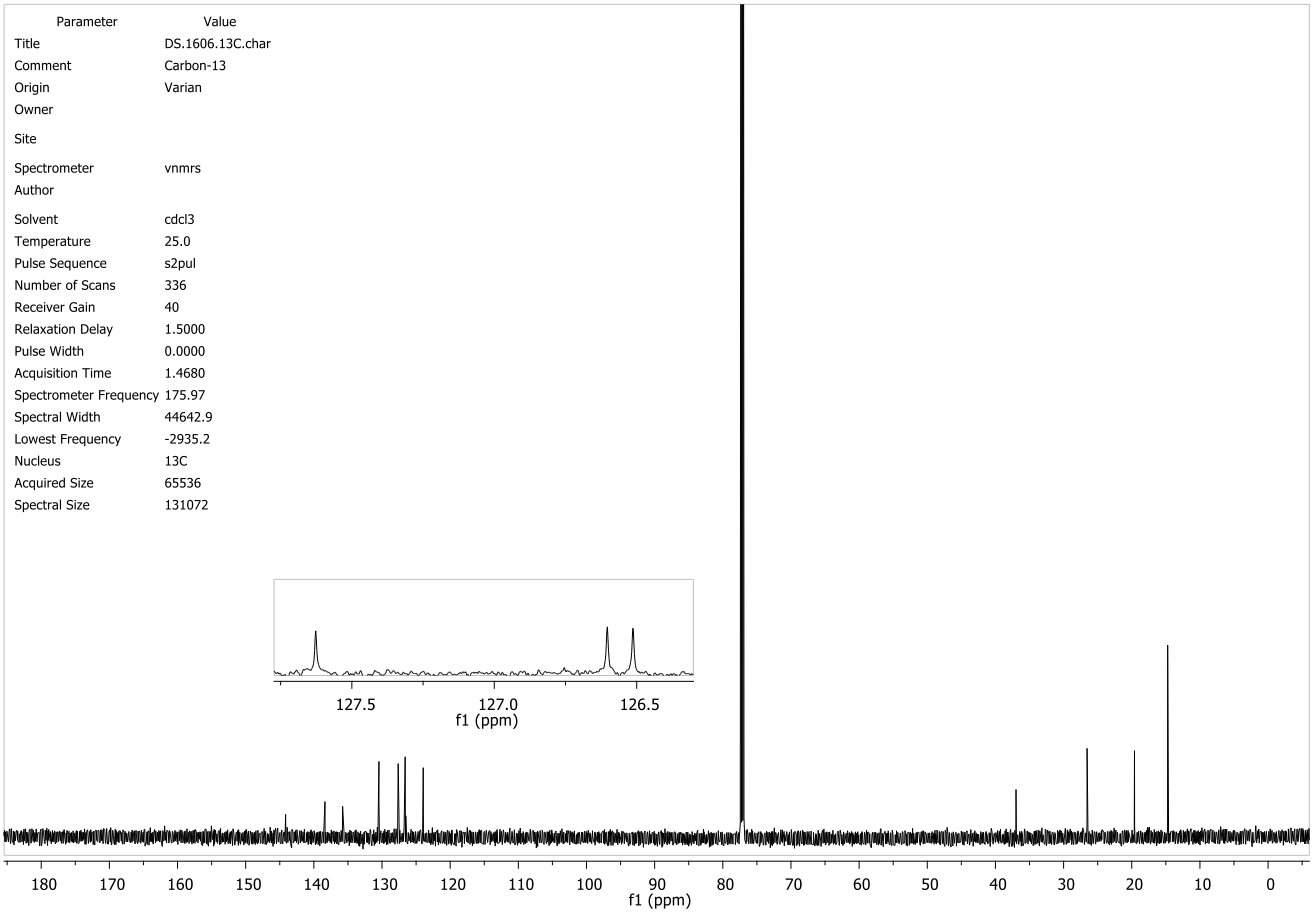
^{1}H NMR (500 MHz, $CDCl_3$) for S2

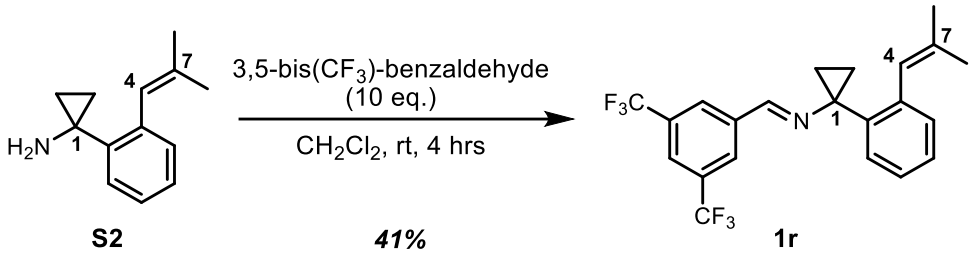
Parameter	Value
Title	DS.1606.1H.char
Comment	Proton Spectrum
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	54
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	3.5000
Spectrometer Frequency	699.75
Spectral Width	11160.7
Lowest Frequency	-1380.5
Nucleus	1H
Acquired Size	39062
Spectral Size	131072



^{13}C NMR (176 MHz, $CDCl_3$) for S2

Parameter	Value
Title	DS.1606.13C.char
Comment	Carbon-13
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	336
Receiver Gain	40
Relaxation Delay	1.5000
Pulse Width	0.0000
Acquisition Time	1.4680
Spectrometer Frequency	175.97
Spectral Width	44642.9
Lowest Frequency	-2935.2
Nucleus	13C
Acquired Size	65536
Spectral Size	131072





Procedure for bis(trifluoromethyl) cyclopropylimine 1r

Aminocyclopropane **S2** (54 mg, 0.29 mmol) was dissolved in 2.0 mL dry CH_2Cl_2 under inert atmosphere, followed by addition of 3,5-bis(trifluoromethyl)benzaldehyde (120 μL, 0.72 mmol) in one portion. The reaction mixture was stirred at room temp for 2 hrs. Quenched reaction by pouring into an aqueous mixture of 5 mL sat. $NaHCO_3$ and 5 mL 1 M NaOH, then diluted with 10 mL ether. The phases were separated. The aqueous phase was extracted with three 10 mL portions of ether. The combined organics were washed with 10 mL brine, dried over anhydrous magnesium sulfate, filtered to remove solids, and concentrated *in vacuo*. The crude residue was purified with flash chromatography over basic alumina (0.5 to 1 to 1.5 to 2.5 to 5% ethyl acetate:hexanes; residue was loaded with PhMe). Collected 48.6 mg of the Schiff base product **1r** as a clear, colorless oil (40.8% yield).

*Characterization Data for bis(trifluoromethyl) cyclopropylimine **1r**:*

^{1}H NMR ($CDCl_3$, 700 MHz): δ = 8.00 (s, 2H, 3,5-bis(CF_3)-Ar), 7.81 (s, 1H, 3,5-bis(CF_3)-Ar), 7.57 (s, 1H, imine-CH), 7.34 (*app*. t, 1H, *J* = 7.4 Hz, Ar), 7.32-7.26 (m, 3H, Ar), 6.20 (s, 1H, C4), 1.81 (s, 3H, C7-Me), 1.75 (s, 3H, C7-Me), 1.59 (*app.* q, *J* = 4.3 Hz, 2H, CP), 1.36 (*app.* q, *J* = 4.3 Hz, 2H, CP) ppm.

^{13}C NMR ($CDCl_3$, 176 MHz): δ = 153.9, 140.0, 138.9, 136.9, 135.6x, 132.0 (q, *J* = 33.5 Hz), 131.4, 130.4, 127.9, 127.5 (br s), 126.9, 123.8, 123.4 (q, *J* = 272.5 Hz), 123.2-123.0 (m), 50.1, 26.6, 19.6, 18.3 ppm

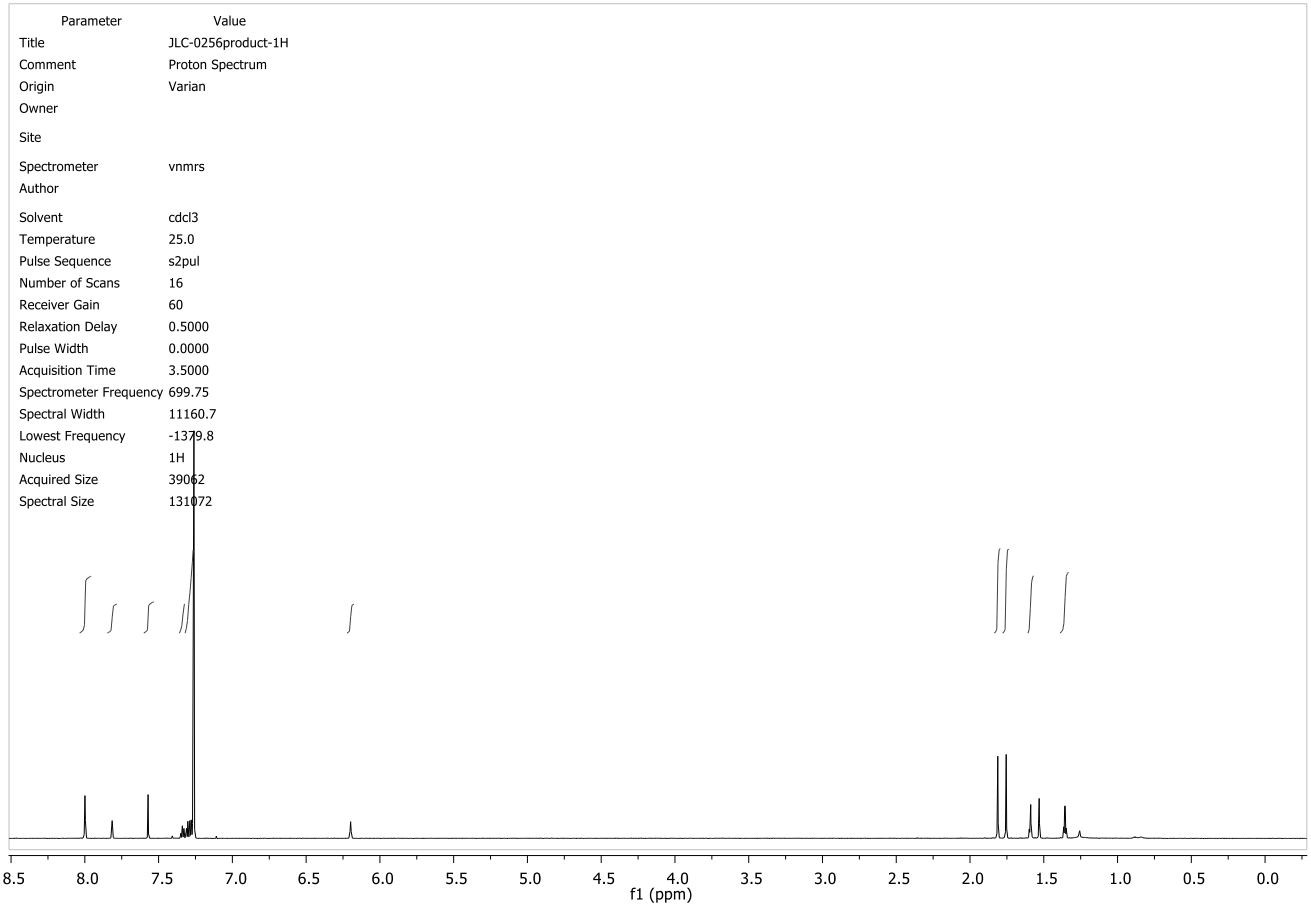
^{19}F NMR ($CDCl_3$, 376 MHz): δ = -62.9 (s) ppm

IR (neat): 2958, 2928, 1550, 1579, 1519, 1482, 1343, 1264, 1216, 1181, 1104, 965, 903, 827, 735 cm^{-1}

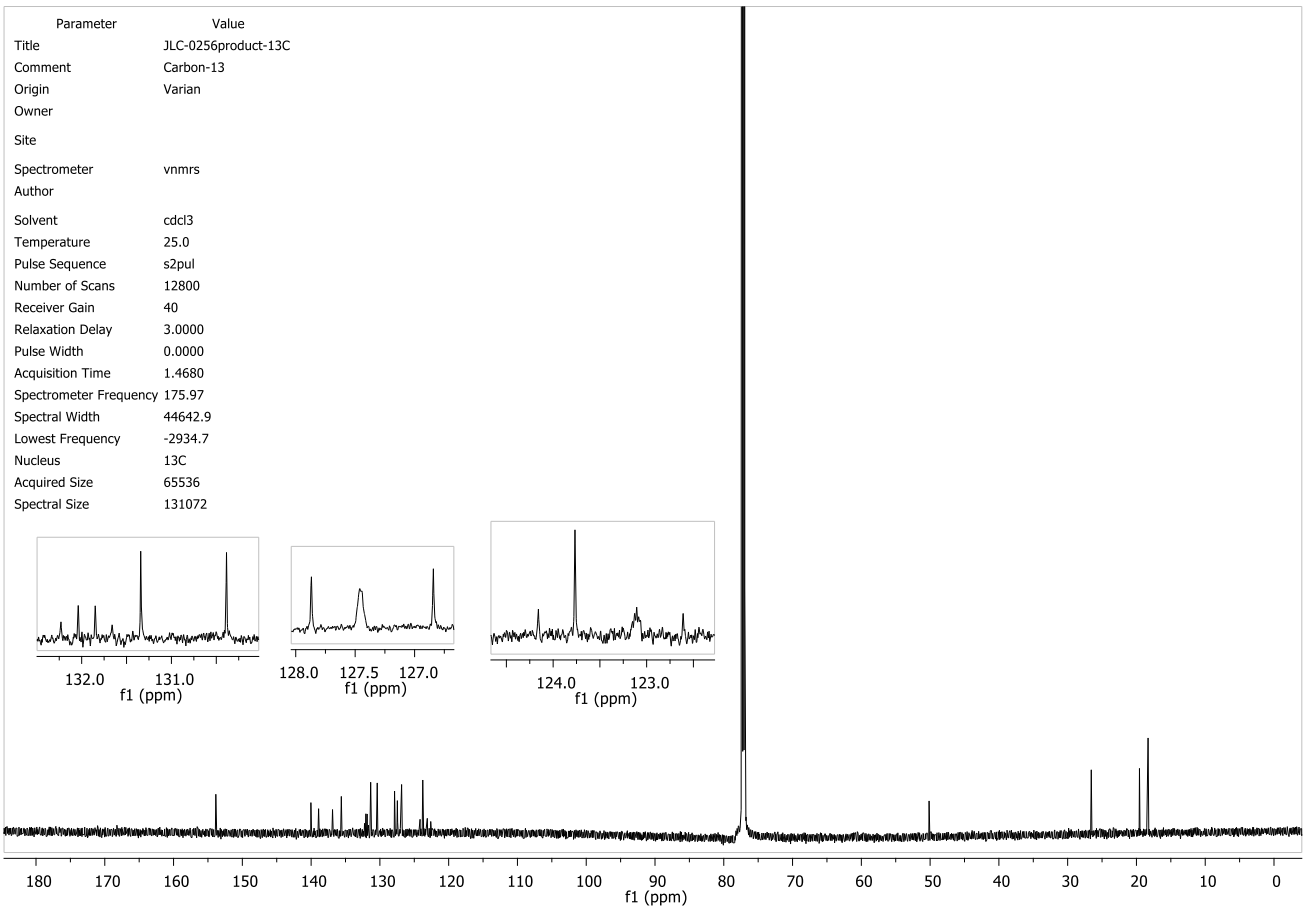
HRMS (ES+, *m/z)* calculated for $C_{22}H_{20}F_6N^+$: 412.1494, Found: 412.1500

R_f = 0.40 (10% ethyl acetate:hexanes + 1% NH_4OH), one yellow spot, $KMnO_4$, UV

^{1}H NMR (700 MHz, $CDCl_3$) for 1r



^{13}C NMR (176 MHz, $CDCl_3$) for 1r



^{19}F NMR (376 MHz, $CDCl_3$) for 1r

Parameter	Value
Title	JLC.0256.19F
Comment	Fluorine-19
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.7340
Spectrometer Frequency	375.91
Spectral Width	89285.7
Lowest Frequency	-76597.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072