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Supporting Information

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Stereocontrolled Synthesis of Amino-Substituted Carbocycles via Pd-Catalyzed Alkene Carboamination Reactions

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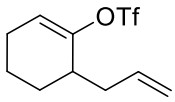
Supporting Information

General Considerations: All reactions were carried out under a nitrogen atmosphere using oven or flame-dried glassware. All palladium complexes, ligands, and reagents were obtained from commercial sources and used without further purification unless otherwise noted. All amines were distilled from CaH_2 prior to use in reactions. (*S*)-*t*ert-ButylPHOX,[1] 2-allylphenyl trifluoromethanesulfonate,[2] 2-allylnaphthalen-1-yl trifluoromethanesulfonate,[3] 2-allyl-4-fluorophenyl trifluoromethanesulfonate,[4] 2-allyl-4-methoxyphenyl trifluoromethanesulfonate,[4] 1-allyl-2-oxo-cyclopentanecarboxylic acid

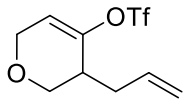
ethyl ester,[5] 2-allylcyclopentan-1-one,[6] 2-allylcyclohexan-1-one,[6] 2-cinnamylcyclopentan-1-one,[6] 3-allyltetrahydro-4H-pyran-4-one,[6,7] *tert*-butyl 3-allyl-4-oxopiperidine-1-carboxylate,[6] allyl 2-oxocylopentane-1-carboxylate,[8] allyl 2-oxocyclohexane-1-carboxylate,[8] allyl 1-methyl-2-oxocyclohexane-1-carboxylate,[9] 2-allyl-2-methylcyclohexan-1-one,[10] *N*-(2-pyridyl)triflimide,[11] *N*'-3,4-dihydro-*2H*-naphthalenylidene-*N,N*-dimethylhydrazine,[12] 2-allyl-2-methylcyclohexane-1,3-dione,[13] 3,3-dimethylhex-5-en-2-one,[14] methyl 2-phenylpent-4-enoate,[15] 2-methyl-2-phenylpent-4-enoic acid,[16] 3,3-diallylhex-5-en-2-one[17] were prepared according to published procedures. Alkenyl triflate compounds (**9a-e, 11, 13a-d, 17a-b, 19a-c, 22a-b**) were stored in a freezer under nitrogen due to observed decomposition of 5-allylcyclopent-1-en-1-yl trifluoromethanesulfonate (**13a**) when stored at ambient temperature for prolonged periods of time. Toluene, tetrahydrofuran, diethyl ether, diisopropylamine and dichloromethane were purified using a GlassContour solvent system. All yields refer to isolated compounds that are estimated to be ≥95% pure as judged by ^{1}H NMR analysis, unless noted otherwise. The diastereomeric ratios were determined by ^{1}H NMR analysis. The yields reported in the supporting information describe the result of a single experiment, whereas yields reported in Tables **1-5** and equations **1-4** are average yields of two or more experiments. Thus, the yields reported in the supporting information may differ from those shown in Tables **1-5** and equations **1-4**.

Preparation and Characterization of Substrates

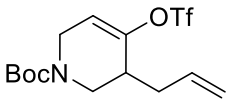


(±)-6-Allylcyclohex-1-en-1-yl trifluoromethanesulfonate (9a). Following a procedure reported by McMurry,[18] a solution of 2-allylcyclohexan-1-one[6] (824 mg, 5.96 mmol) in THF (12 mL) was added dropwise over 30 min to a solution of LDA (6.56 mmol) in THF (18 mL) at –78 °C and stirred for an additional 2 h. A solution of *N*-phenyl-bis(trifluoromethanesulfonimide) (2.28 g, 6.38 mmol) in THF (12 mL) was then added dropwise over 30 minutes at –78 °C. After addition, the mixture was warmed to 0 °C and

stirred until the starting material had been completely consumed as judged by TLC analysis. The solvent was removed *in vacuo* and the resultant yellow oil was purified by column chromatography to affording the title compound (1.29 g, 80%) as a volatile clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (td, *J* = 4.1, 1.4 Hz, 1H), 5.73 (dddd, *J* = 16.7, 10.4, 7.8, 6.5 Hz, 1H), 5.16 – 5.00 (m, 2H), 2.51 (dt, *J* = 8.5, 4.8 Hz, 1H), 2.45 (dddt, *J* = 13.3, 6.6, 3.2, 1.4 Hz, 1H), 2.19 - 2.10 (m, 3H), 1.87 - 1.81 (m, 1H), 1.72 – 1.46 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.90, 135.19, 119.53, 118.67 (q, *J* = 324.1 Hz) 117.65, 37.28, 35.98, 27.76, 24.49, 19.08; IR (film) 1201, 1413 cm^{-1}; MS (EI) 270.0543 (270.0538 calcd for $C_{10}H_{13}F_3O_3S$, M+).

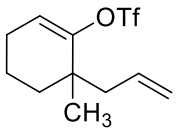


(±)-3-Allyl-3,6-dihydro-2*H*-pyran-4-yl trifluoromethanesulfonate (9b). The title compound was prepared using a procedure analogous to that described above for the preparation of (*E*)-5-cinnamylcyclopent-1-en-1-yl trifluoromethanesulfonate except 3-allyltetrahydro-4H-pyran-4-one[6,7] was employed as the starting material, and the reaction mixture was stirred -41 °C for 3 h. This procedure afforded the title compound (1.1 g, 78%) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (t, *J* = 2.9 Hz, 1H), 5.75 (dddd, *J* = 16.0, 10.1, 8.1, 5.9 Hz, 1H), 5.18 – 5.07 (m, 2H), 4.25 (q, *J* = 2.9 Hz, 2H), 3.78 (t, *J* = 3.4 Hz, 2H), 2.54 – 2.41 (m, 2H), 2.28 (dt, *J* = 14.1, 9.4 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 148.56, 134.41, 118.61 (q, *J* = 318.4 Hz), 118.28, 117.22, 67.86, 64.44, 37.99, 33.70; IR (film) 1206, 1140 cm^{-1}; MS (EI) 272.0322 (272.0330 calcd for $C_9H_{11}F_3O_4S$, M+).

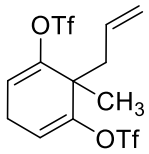


(±)-*N*-Boc-3-allyl-4-{[(trifluoromethyl)sulfonyl]oxy}-3,6-dihydropyridine (9c). The title compound was prepared using a procedure analogous to that described above for

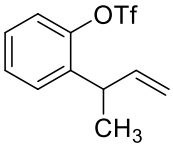
the preparation of (*E*)-5-cinnamylcyclopent-1-en-1-yl trifluoromethanesulfonate except *tert*-butyl 3-allyl-4-oxopiperidine-1-carboxylate[6,7] was employed as the substrate and the reaction mixture was stirred at –41 °C for 3h. This procedure afforded the title compound (974 mg, 34%) was afforded as a clear oil. ^{1}H NMR and ^{13}C NMR spectra were sufficiently broadened and complex due to rotamers. ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.85 – 5.67 (m, 2H), 5.18 - 5.09 (m, 2H), 4.42 – 3.19 (m, 5H), 2.60 - 2.35 (m, 1H), 2.14 (dt, *J* = 15.8, 8.9 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.63, 134.02, 119.50, 118.38, 117.68, 80.69, 44.19, 41.73, 34.08, 28.49; IR (film) 1700, 1140 cm^{-1}; MS (ESI) 394.0905 (394.0906 calcd for $C_{14}H_{20}F_3NO_5S$, M + Na^+).



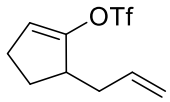
(±)-6-Allyl-6-methylcyclohex-1-en-1-yl trifluoromethanesulfonate (9d). The title compound was prepared according to a procedure reported by Cramer[19] except using 2-allyl-2-methylcyclohexan-1-one[10] as substrate and diethyl ether as the solvent for the aqueous extraction. This procedure afforded the title compound (913 mg, 81%) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.63 (m, 2H), 5.18 – 4.97 (m, 2H), 2.30 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.24 – 2.07 (m, 3H), 1.77 (ddd, *J* = 13.1, 9.6, 3.5 Hz, 1H), 1.71 – 1.55 (m, 2H), 1.55 – 1.42 (m, 1H), 1.14 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.04, 133.54, 118.67, 118.52 (q, *J* = 317.3 Hz), 117.22, 42.95, 38.27, 35.25, 24.91, 24.46, 18.31; IR (film) 1200, 1413 cm^{-1}; MS (EI) 284.0695 (284.0694 calcd for $C_{11}H_{15}F_3O_3S$, M+).



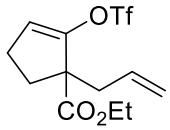
2-Allyl-2-methylcyclohexa-3,6-diene-1,3-diyl bis(trifluoromethanesulfonate) (9e). The title compound was prepared using a procedure analogous to that employed for the synthesis of 5,5-diallylcyclopent-1-en-1-yl trifluoromethanesulfonate except using 2-allyl-2-methylcyclohexane-1,3-dione[10] as the substrate. This procedure afforded the title compound (1.2 g, 41%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (t, *J* = 3.8 Hz, 2H), 5.65 (ddt, *J* = 17.1, 9.5, 7.4 Hz, 1H), 5.21 – 5.06 (m, 2H), 3.01 (q, *J* = 4.0 Hz, 2H), 2.35 (d, *J* = 7.3 Hz, 2H), 1.41 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 148.17, 131.71, 119.71, 118.44 (q, *J* = 317.6 Hz), 113.39, 44.14, 39.63, 24.62, 22.84; IR (film) 1211, 1140 cm^{-1}; MS (EI) 429.9962 (429.9980 calcd for $C_{12}H_{12}F_6O_6S_2$, M+).



(±)-2-(But-3-en-2-yl)phenyl trifluoromethanesulfonate (11). The title compound was prepared according to a procedure previously reported by our group[4] except using crotyl bromide in place of allyl bromide. This procedure afforded the title compound (1.1 g, 38% over 3 steps) as a clear oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.21 (m, 2H), 5.96 (dddd, *J* = 16.3, 10.4, 5.9, 0.9 Hz, 1H), 5.15 – 5.04 (m, 2H), 3.86 (qdd, *J* = 7.1, 5.8, 1.6 Hz, 1H), 1.37 (d, *J* = 7.0, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 147.36, 140.98, 138.33, 129.35, 128.67, 128.03, 121.43, 118.74 (q, *J* = 318.2 Hz), 114.68, 35.96, 20.09; IR (film) 1418, 1207, 1136 cm $^{-1}$; MS (EI) 280.0388 (280.0381 calcd for $C_{11}H_{11}F_3O_3S$, M+).

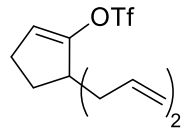


(±)-5-Allylcyclopent-1-en-1-yl trifluoromethanesulfonate (13a). The title compound was prepared using a procedure analogous to that employed for the synthesis of 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate except using 2-allylcyclopentan-1-one[6] as the substrate. This procedure afforded the title compound (959 mg, 48%) as a clear oil. The product was generated as an 8:1 mixture of regioisomers; data are for the major regioisomer shown. (Note: the enol triflate was stored under N_2 at -8 °C to prevent decomposition). ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.75 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.65 (app. q, *J* = 2.4 Hz, 1H), 5.15 – 5.03 (m, 2H), 2.99 – 2.84 (m, 1H), 2.44 – 2.29 (m, 3H), 2.22 – 2.07 (m, 2H), 1.78 – 1.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.53, 134.91, 118.71 (q, *J* = 319 Hz), 117.44, 117.35, 42.77, 36.64, 26.79, 26.73; IR (film) 1202, 1419 cm^{-1}; MS (EI) 256.0389 (256.0381 calcd for $C_9H_{11}F_3O_3S$, M+).



(±)-Ethyl 1-allyl-2-{[(trifluoromethyl)sulfonyl]oxy}cyclopent-2-ene-1-carboxylate (13b). Following a slight modification of a procedure reported by McMurry[20], a solution of 1-allyl-2-oxo-cyclopentanecarboxylic acid ethyl ester[5] (1.5 g, 7.64 mmol) in THF (15 mL) was added dropwise over 30 min to a solution of LDA (9.17 mmol) in THF (31 mL) at –78 °C. The solution was stirred at –78 °C for 2 h then a solution *N*-(2-pyridyl)triflimide[11] (3.28 g, 9.17 mmol) in THF (18 mL) was then added dropwise over 30 minutes at –78 °C. After the addition was complete, the reaction mixture was warmed to rt and stirred overnight. The crude mixture was then diluted with water (20 mL) and extracted with diethyl ether (3 x 20 mL). The combined organic layers was dried over anhydrous $MgSO_4$, filtered through a cotton plug, and concentrated *in vacuo*. The crude mixture was purified by column chromatography to afford the title compound (1.85 g, 74%) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (t, *J* = 2.5 Hz, 1H), 5.69 (dddd, *J*

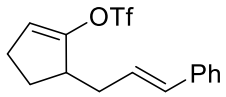
= 17.0, 10.2, 7.7, 6.8 Hz, 1H), 5.21 – 5.09 (m, 2H), 4.27 – 4.09 (m, 2H), 2.64 (ddt, *J* = 14.1, 7.8, 1.1 Hz, 1H), 2.53 – 2.41 (m, 3H), 2.41 – 2.27 (m, 1H), 2.08 – 1.96 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 172.65, 148.09, 132.33, 119.62, 118.55 (q, *J* = 316.7 Hz), 118.28, 61.74, 57.41, 38.95, 31.15, 26.32, 14.11; IR (film) 1734, 1210 cm^{-1}; MS (ESI) 329.0669 (329.0665 calcd for $C_{12}H_{15}F_3O_5S$, M + H^+) or 346.0933 (346.0931 calcd for $C_{12}H_{15}F_3O_5S$, M + NH_4^+).



5,5-Diallylcyclopent-1-en-1-yl trifluoromethanesulfonate (13c). Following a procedure reported by Tsuji[21], a 25 mL Schlenk flask was flame-dried under vacuum and cooled under a stream of N_2 (g). $Pd_2(dba)_3$ (104 mg, 2.5 mol %) and PPh_3 (210 mg, 20 mol %) were added and the tube was purged with N_2 (g). A solution of 2-oxocylopentane-1-carboxylate (673 mg, 4 mmol) in THF (12 mL) was added, followed by diallyl carbonate (1.15 mL, 8 mmol). The mixture was stirred at 65 °C until the starting material had been completely consumed as judged by ^{1}H NMR analysis (ca. 30 min). The solvent was removed *in vacuo* and the crude product was purified by column chromatography to afford 491 mg (75%) of 2,2-diallylcyclopentan-1-one as a clear oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.77 – 5.62 (m, 2H), 5.12 – 5.01 (m, 4H), 2.26 – 2.07 (m, 6H), 1.92 – 1.80 (m, 4H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 222.45, 133.83, 118.54, 51.80, 40.02, 38.62, 32.13, 18.87; IR (film) 3078, 1726 cm^{-1}.

Following a procedure reported by Cramer[19] that was slightly modified, solid KHMDS (716 mg, 3.59 mmol) was dissolved in THF (24 mL) in a flame-dried flask. The resulting solution was cooled to –78 °C then 2,2-diallylcyclopentan-1-one (491 mg, 2.99 mmol) in THF (6 mL) was added dropwise. The solution was allowed to stir for an additional 30 min at –78 °C and then *N*-phenyl-bis(trifluoromethanesulfonimide) (1.18g, 3.29 mmol) in THF (6.6 mL) was added and the mixture was stirred for 20 min at –78 °C. The mixture was then warmed to rt, stirred for 1 h, then was quenched with satd. NH_4Cl

(aq). The aqueous phase was extracted with EtOAc (30 mL x 3) and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by column chromatography to afford the title compound (708 mg, 80%) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 – 5.69 (m, 2H), 5.63 (t, *J* = 2.7 Hz, 1H), 5.13 – 5.08 (m, 4H), 2.34 – 2.09 (m, 6H), 1.93 – 1.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.84, 133.56, 118.70, 118.60 (q, *J* = 318.7 Hz) 114.43, 50.32, 41.96, 30.07, 26.19; IR (film) 1205, 1421 cm^{-1}; MS (EI) 296.0693 (296.0694 calcd for $C_{12}H_{15}F_3O_3S$, M+)



(±)-(*E*)-5-Cinnamylcyclopent-1-en-1-yl trifluoromethanesulfonate (13d). Following a slight modification of a procedure reported by McMurry[18], to a stirring solution of LDA (4.94 mmol) in THF (20 mL) at –78 °C was added a solution of 2-cinnamylcyclopentan-1-one[6] (825 mg, 4.12 mmol) in THF (21 mL) over 30 min. The resulting solution was stirred at –78 °C for an 2 h, then a solution of *N*-(2-pyridyl)triflimide[11] (1.77 g, 4.94 mmol) in THF (10 mL) was then added dropwise over 30 minutes at –78 °C. After the addition was complete, the mixture was warmed to –41 °C in CH_3CN/dry ice bath and stirred for 2.5 h. The reaction was quenched at –41 °C with satd. NH_4Cl (aq) and the resulting biphasic mixture was warmed to rt. The aqueous phase was extracted with EtOAc (30 mL x 3) then the organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by column chromatography to afford the title compound (1.18 g, 86%) as a clear oil. The product was afforded as a mixture of regioisomers (9:1); data are for the major regioisomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 4H), 7.23 (tt, *J* = 7.2, 1.7 Hz, 1H), 6.46 (dd, *J* = 15.8, 1.5 Hz, 1H), 6.15 (dt, *J* = 15.8, 7.2 Hz, 1H), 5.68 (app. q, *J* = 2.4 Hz, 1H), 3.10 – 2.94 (m, 1H), 2.55 (dddd, *J* = 14.2, 7.3, 4.3, 1.4 Hz, 1H), 2.44 – 2.12 (m, 4H), 1.78 (qd, *J* = 7.4, 5.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.43, 137.44, 132.70, 128.68,

127.38, 126.48, 126.22, 118.7 (q, *J* = 319.0 Hz) 117.60, 43.17, 35.82, 26.84, 26.78; IR (film) 1418, 1204, 1138 cm $^{-1}$; MS (EI) 332.0683 (332.0694 calcd for $C_{15}H_{15}F_3O_3S$, M+)

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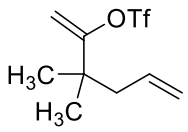
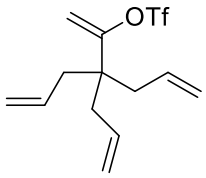
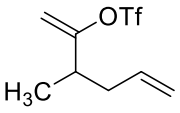


(±)-3,3-Dimethylhexa-1,5-dien-2-yl trifluoromethanesulfonate (17a). A flame-dried round bottom flask with a stir bar was cooled under a stream of N_2 and charged with solid KHMDS (503 mg, 2.5 mmol) and THF (16 mL). The solution was cooled to –78 °C with stirring, then a solution of 3,3-dimethylhex-5-en-2-one[14] (264 mg, 2.1 mmol) in THF (4 mL) was added dropwise. The mixture was stirred at –78 °C for 1 h, then a solution of *N*-phenyl-bis(trifluoromethanesulfonimide) (900 mg, 2.5 mmol) in THF (5 mL) was added dropwise and stirring was continued at –78 °C for 2 h. The cold solution was then poured over $NaHCO_3$ (aq) (20 mL) into a separatory funnel. The aqueous layer was extracted using pentanes (3 x 25 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated slowly on rotary evaporator (T = 22 °C at -750 mbar). The crude material was purified by column chromatography to afford the title compound (333 mg, 61%) as a clear, volatile oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.15 – 5.03 (m, 3H), 4.92 (d, *J* = 4.4 Hz, 1H), 2.19 (app d, *J* = 7.4 Hz, 2H), 1.15 (s, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.79, 133.37, 118.65, 118.51 (q, *J* = 317.7 Hz), 101.23, 43.81, 39.69, 25.37; IR (film) 1418, 1213 cm^{-1}; MS (EI) 217.0143 (217.0146 calcd for $C_6H_8F_3O_3S$, M^+ – ·$CH_2CH{=}CH_2$). Note: The molecular ion was not detected using EI or ESI techniques. The observed mass corresponds to loss of an allyl radical via fragmentation.



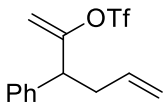
3,3-Diallylhexa-1,5-dien-2-yl trifluoromethanesulfonate (17b). The title compound was prepared using a procedure analogous to that employed for the synthesis of 5,5-diallylcyclopent-1-en-1-yl trifluoromethanesulfonate, except using 3,3-diallylhex-5-en-2-one[17] (1.1 g, 6.2 mmol) as the substrate. This procedure afforded 1.46 g (76%) of the title compound as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (ddt, *J* = 17.4, 10.4, 7.3 Hz, 3H), 5.28 (d, *J* = 4.7 Hz, 1H), 5.20 – 5.07 (m, 6H), 4.88 (d, *J* = 4.7 Hz, 1H), 2.21 (dt, *J* = 7.3, 1.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.40, 132.42, 119.26, 118.44 (q, *J* = 317 Hz), 103.26, 45.77, 38.07; IR (film) 1406, 1207, 1140, 915 cm $^{-1}$; MS (EI) 269.0463 (269.0459 calcd for $C_{10}H_{12}F_3O_3S$, M^+ – ·$CH_2CH{=}CH_2$). Note: The molecular ion was not detected using EI or ESI techniques. The observed mass corresponds to loss of an allyl radical via fragmentation.



(±)-3-Methylhexa-1,5-dien-2-yl trifluoromethanesulfonate (19a). To a cooled solution of ethyl 2-methylacetoacetate (2.8 mL, 20 mmol) in THF (20 mL) at 0 °C was added NaH (881 mg, 36.7 mmol of 60% in mineral oil) portion-wise. The resulting mixture was stirred at 0 °C for 30 min, then allyl bromide (1.9 mL, 22 mmol) was then added dropwise and the solution was heated to reflux overnight. The solution was then cooled to rt, quenched with H_2O (20 mL), and extracted with diethyl ether (3 x 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography to afford 3.34 g (91%) of ethyl 2-acetyl-2-methylpent-4-enoate. Characterization data matched that that previously reported in the literature.[22]

Decarboxylation of ethyl 2-acetyl-2-methylpent-4-enoate (1.5 g, 8.1 mmol) was accomplished using a general procedure reported by Šmit[23] for decarboxylation of β-ketoesters except using pentanes instead of diethyl ether for the extraction. This procedure afforded 547 mg (60%) of 3-methylhex-5-en-2-one as a volatile oil. Note: Slow evaporation of pentanes was necessary to avoid loss of product. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.11 – 4.98 (m, 2H), 2.59 (h, *J* = 7.0 Hz, 1H), 2.40 (dtt, *J* = 14.5, 6.6, 1.4 Hz, 1H), 2.18 – 2.06 (m, 4H), 1.10 (d, *J* = 7.0 Hz, 3H).

The title compound was prepared using a procedure analogous to that employed for the synthesis of 3-phenylhexa-1,5-dien-2-yl trifluoromethanesulfonate, except using 3-methylhex-5-en-2-one (1.49 g, 13.3 mmol) as substrate. This procedure afforded the title compound (1.99 g, 61%) as a volatile, clear oil. Note: Slow evaporation of the organic layer was necessary to avoid loss of product. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (ddt, *J* = 13.8, 9.9, 5.7 Hz, 1H), 5.17 – 5.04 (m, 3H), 4.92 (d, *J* = 3.9 Hz, 1H), 2.50 (sextet, *J* = 6.8 Hz, 1H), 2.34 (dt, *J* = 19.1, 1.3 Hz, 1H), 2.15 (dt, *J* = 14.1, 7.6 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.31, 134.68, 118.61 (q, *J* = 317.9 Hz), 117.81, 102.90, 38.27, 37.92, 17.32; IR (film) 1416, 1205, 1140, 924 cm $^{-1}$; MS (EI) 244.0374 (244.0381 calcd for $C_8H_{11}F_3O_3S$, M+).

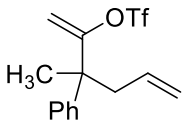


(±)-3-Phenylhexa-1,5-dien-2-yl trifluoromethanesulfonate (19b). To a stirred solution of methyl 2-phenylpent-4-enoate[15] (1.88 g, 9.87 mmol) in THF (49 mL) was added *N,O*-dimethylhydroxylamine hydrochloride (2.02 g, 20.7 mmol). The resulting mixture was cooled to 0 °C, then a solution of *i*-PrMgCl (19.8 mL, 29.5 mmol, 2M in THF) was added dropwise. The mixture was stirred at 0 °C for 1 h, then the reaction was quenched with satd. NH_4Cl (aq) (25 mL) and the resulting mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to afford 1.9 g (88%) of the *N*-methoxy-*N*-

methyl-2-phenylpent-4-enamide that was used without further purification. Characterization data matched that previously reported in the literature.[24]

A flame-dried round bottom flask equipped with a stir-bar was cooled under a stream of N_2 and charged with *N*-methoxy-*N*-methyl-2-phenylpent-4-enamide (1.9 g, 8.7 mmol) and THF (17 mL). The resulting solution was cooled to 0 °C in an ice-bath, then a solution of CH_3MgBr (10.4 mL, 10.4 mmol, 1M in THF) was added dropwise. The mixture was stirred at 0 °C for 1 h, then the reaction was quenched with satd. NH_4Cl (aq) and the mixture was extracted with EtOAc (3 x 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to afford 1.46 g (97%) of the 3-phenylhex-5-en-2-one product that was used without further purification. Characterization data matched that that previously reported in the literature.[25]

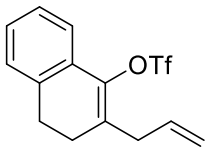
The title compound was prepared using a procedure analogous to that employed for the synthesis of 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate, except using 3-phenylhex-5-en-2-one (800 mg, 4.59 mmol) as the substrate and *N*-(2-pyridyl)triflimide[11] (1.97g, 5.51 mmol) as the triflylating reagent. The crude product was purified by column chromatography to afford the title compound (974 mg, 69%) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.1 Hz, 2H), 5.66 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.25 (d, *J* = 3.9 Hz, 1H), 5.11 – 5.00 (m, 3H), 3.60 (t, *J* = 7.6 Hz, 1H), 2.70 (dt, *J* = 14.1, 6.9 Hz, 1H), 2.55 (dt, *J* = 14.7, 7.5 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 158.22, 138.41, 134.65, 128.91, 128.21, 127.79, 118.51 (q, *J* = 318.3 Hz), 117.60, 104.55, 50.16, 37.29; IR (film) 1416, 1206, 1136 cm^{-1}; MS (EI) 306.0551 (306.0538 calcd for $C_{13}H_{13}F_3O_3S$, M+).



(±)-3-Methyl-3-phenylhexa-1,5-dien-2-yl trifluoromethanesulfonate (19c). A flame-dried round bottom flask equipped with a stir bar was cooled under a stream of nitrogen and charged with 2-methyl-2-phenylpent-4-enoic acid[16] (1.2 g, 6.3 mmol) and Et_2O (28

mL). The mixture was cooled to –78 °C and a solution of MeLi (15.8 mmol, 1.6M in Et_2O) was added dropwise. The resulting mixture was stirred for 1 h at –78 °C, then was heated to reflux for 1 h. The mixture was then cooled to 0 °C and quenched with H_2O (20 mL). The aqueous phase was extracted with Et_2O (3 x 20 mL), and the organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude mixture was purified by column chromatography to afford 773 mg (65%) of 3-methyl-3-phenylhex-5-en-2-one as a clear oil. Characterization data matched that previously reported in the literature.[26]

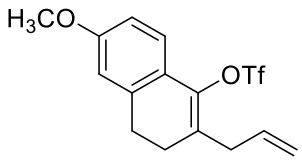
The title compound was prepared using a procedure analogous to that employed for the synthesis 3,3-dimethylhexa-1,5-dien-2-yl trifluoromethanesulfonate except using 3-methyl-3-phenylhex-5-en-2-one (773 mg, 4.1 mmol) as the substrate and *N*-(2-pyridyl)triflimide[11] (1.77 g, 4.9 mmol) as triflylating agent. This procedure afforded 562 mg (43%) of the title compound as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (q, J = 2.5 Hz, 4H), 7.29 – 7.24 (m, 1H), 5.56 (ddt, J = 17.1, 10.2, 7.1 Hz, 1H), 5.28 (d, J = 4.5 Hz, 1H), 5.16 – 5.03 (m, 3H), 2.67 (ddd, J = 7.3, 4.2, 1.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.57, 142.08, 133.09, 128.62, 127.29, 126.67, 119.15, 102.24, 47.06, 42.86, 23.87. The quartet associated with the CF_3 group was not fully resolved; IR (film) 1413, 1206 cm $^{-1}$; MS (EI) 320.0691 (320.0694 calcd for $C_{14}H_{15}F_3O_3S$, M+).



2-Allyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (22a). Following a modification of a procedure reported by Murphy *et. al.*[12], to a stirring solution of *n*-BuLi (2.5 M in Hexanes) (8.9 mL, 22 mmol) diluted with THF (70 mL) at 0 °C was added a solution of *N*'-3,4-dihydro-*2H*-naphthalenylidene-*N,N*-dimethylhydrazine[12] (3.8 g, 20 mmol) in THF (20 mL) dropwise. The resulting solution was stirred for 1 h at 0 °C, then a solution of allyl bromide (1.73 mL, 20 mmol) in THF (20 mL) was added dropwise at 0 °C. The reaction mixture was then warmed to rt and stirred for an additional 16 h. A

solution of 2N HCl (aq.) (110 mL) was then added and the resulting mixture was stirred vigorously for 48 h. The mixture was then extracted with EtOAc (30 mL x 3) and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by column chromatography to afford 3.1 g (82%) of 2-allyl-3,4-dihydronaphthalen-1(2*H*)-one as a clear oil. Characterization data matched data previously reported in the literature for this compound.[12]

The title compound was prepared following a procedure reported by Lin *et. al*.[27] for the synthesis of 2-methyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate except using 2-allyl-3,4-dihydronaphthalen-1(2*H*)-one in place of 2-methyl-1-tetralone as the substrate. This procedure afforded the title compound (1.32 g, 78%) as a clear oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.19 (m, 2H), 7.15 (d, *J* = 7.3 Hz, 1H), 5.79 (ddt, *J* = 16.9, 10.1, 6.8 Hz, 1H), 5.20 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.17 (dt, *J* = 10.1, 1.3 Hz, 1H), 3.13 (d, *J* = 6.7 Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.42 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 140.72, 135.75, 133.39, 131.22, 129.74, 128.49, 127.49, 126.86, 121.47, 118.70 (q, *J* = 318.4 Hz), 118.36, 35.54, 27.39, 27.36; IR (film) 1206, 1138 cm^{-1}; MS (EI) 318.0544 (318.0538 calcd for $C_{14}H_{13}F_3O_3S$, M+).



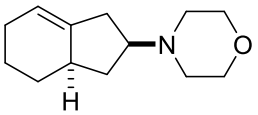
2-Allyl-6-methoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (22b). The title compound was prepared using a procedure analogous to that employed for the synthesis of 2-allyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate except using 6-methoxy-1-tetralone as the starting material. This procedure afforded the title compound (627 mg, 19% over 3 steps) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 6.79 – 6.62 (m, 2H), 5.76 (ddt, *J* = 16.8, 10.1, 6.7 Hz, 1H), 5.23 – 5.03 (m, 2H), 3.79 (s, 3H), 3.07 (app. d, *J* = 8 Hz, 2H), 2.77 (t, *J* = 7.9 Hz, 2H), 2.36 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.79, 140.60, 137.81, 133.67, 128.05, 122.92,

122.72, 120.29, 118.10, 113.94, 111.30, 55.45, 35.36, 27.82, 27.30. The quartet associated with the CF_3 group was not fully resolved; IR (film) 1404, 1205, 1138 cm^{-1}; MS (ESI) 349.0720 (349.0716 calcd for $C_{15}H_{15}F_3O_4S$, M + H^+).

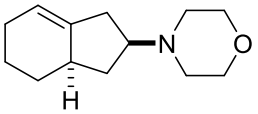
Preparation and Characterization of Products

General Procedure for Pd-Catalyzed Alkene Difunctionalization Reactions

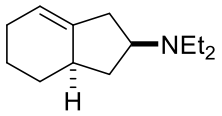
A flame-dried Schlenk tube equipped with a stir bar was cooled under a stream of N_2 and charged with $Pd(OAc)_2$ (4 mol %), BrettPhos (6 mol %), and lithium *tert*-butoxide (0.14 mmol, 1.4 equiv). The tube was purged with N_2 (g) and a solution of the appropriate enol triflate (0.1 mmol, 1.0 equiv) in toluene (0.5 mL) was added via syringe with stirring. The appropriate nucleophile (0.12 mmol, 1.2 equiv) was then added *neat* via micro-syringe followed by toluene (0.5 mL) to wash the inside of the Schlenk tube so all reagents were in solution. The resulting mixture was heated to 95 ^oC for 16 h at which time the starting material had been completely consumed as judged by ^1H NMR analysis of an aliquot removed from the reaction mixture. After cooling to room temperature, H_2O (3 mL) was added. The aqueous layer was extracted with EtOAc (3 mL x 3), the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was then purified by column chromatography on silica gel unless otherwise noted. In some instances, the product was protonated from silica gel chromatography. Thus, the neutral product was obtained by re-dissolving in DCM (5 mL) and washing with aqueous 1M NaOH (5 mL) in a separatory funnel. The organic layer was collected, dried with anhydrous Na_2SO_4, filtered through a cotton plug, and concentrated to afford the neutral desired product.



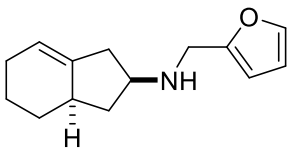
(±)-(2*S,3a*R**)-4-(2,3,3a,4,5,6-Hexahydro-1*H*-inden-2-yl)morpholine (10a).** The general procedure was used for the coupling of morpholine (10.4 µL, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (27.0 mg, 0.1 mmol), except the reaction was conducted at 70 ^{o}C and 10 mol % BrettPhos was used. The crude product was purified by flash chromatography on silica gel to afford 17.3 mg (80%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (t, *J* = 3.2 Hz, 1H), 3.72 (t, *J* = 4.7 Hz, 4H), 2.65 – 2.54 (m, 2H), 2.47 (app. br s, 4H), 2.19 – 2.06 (m, 3H), 2.02 – 1.91 (m, 3H), 1.80 – 1.73 (m, 1H), 1.42 (ttd, *J* = 13.8, 7.4, 4.1 Hz, 1H), 1.03 (dtd, *J* = 17.6, 11.3, 10.7 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 141.73, 118.30, 67.08, 64.95, 52.69, 39.90, 38.13, 35.38, 28.86, 25.34, 22.46; IR (film) 1118, 1671 cm^{-1}; MS (ESI) 208.1699 (208.1696 calcd for $C_{13}H_{21}NO$, M + H^+).



Gram scale: (±)-(2*S,3a*R**)-4-(2,3,3a,4,5,6-Hexahydro-1*H*-inden-2-yl)morpholine (10a).** The general procedure was used for the gram scale coupling of morpholine (388 µL, 4.44 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (1.0 g, 3.7 mmol) except the reaction was conducted at 70^{o} C for 17 h. This procedure afforded 594 mg (76%, >20:1 dr) of the title compound as a clear-yellow oil. Characterization data were identical to those reported above for the small (0.1 mmol) scale reaction.

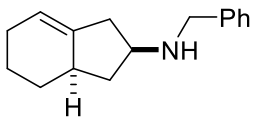


(±)-(2*S,3a*R**)-N,N-diethyl-2,3,3a,4,5,6-hexahydro-1H-inden-2-amine (10b).** The general procedure was used for the coupling of diethylamine (12.4 µL, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (26.5 mg, 0.1 mmol). The crude product was purified by flash chromatography on silica gel to afford 9.5 mg (50%, 2.7:1 dr) of the title compound as a yellow oil. Data are for a diastereomeric mixture as the diastereomers were not readily separable: ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.38 (app br s, 0.27H), 5.37 (app. br s, 0.74H), 3.20 – 3.03 (m, 1 H), 2.66 (q, *J* = 7 Hz, 4H), 2.57 (dd, *J* = 17.0, 9.2 Hz, 1 H), 2.43 (app. br s, 0.3H), 2.38 (dd, *J* = 13.7, 6.8 Hz, 0.3H), 2.30 (m, 0.32H), 2.25 – 2.14 (m, 1.62H), 2.09 (dt, *J* = 11.3, 6.1 Hz, 0.76H), 2.03 – 1.91 (m, 3.79H), 1.80 – 1.73 (m, 1.15H), 1.60 – 1.54 (m, 0.3H), 1.54 – 1.38 (m, 1.72H), 1.16 – 0.90 (m, 8.74H), 0.90 – 0.80 (m, 1.43H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 118.13, 117.53, 60.34, 60.28, 43.95, 43.83, 42.69, 39.89, 39.81, 38.08, 37.72, 37.26, 35.86, 35.29, 30.14, 29.85, 29.09, 28.81, 25.34, 25.05, 22.73, 22.49, 11.02; IR (film) 1445, 1368 cm^{-1}; MS (ESI) 194.1903 (194.1903 calcd for $C_{13}H_{24}N^{+}$, M + H^{+}).

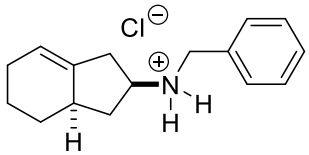


(±)-(2*S,3a*R**)-*N*-(Furan-2-ylmethyl)-2,3,3a,4,5,6-hexahydro-1H-inden-2-amine (10c).** The general procedure was used for the coupling of furfurylamine (10.6 µL, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (27.0 mg, 0.1 mmol), except 10 mol % BrettPhos was used. The crude product was purified by flash chromatography on silica gel to afford 14.8 mg (68%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (app. br s, 1H), 6.30 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.19 (d, *J* = 3.1 Hz, 1H), 5.38 (app. br s, 1H), 3.79 (s, 2H), 3.17 (tt, *J* = 9.2, 6.4 Hz, 1H), 2.65 (ddd, *J* = 15.2, 8.5, 3.0 Hz, 1H), 2.36 – 2.16 (m, 3H), 2.06 – 1.92 (m, 4H), 1.77

(dp, *J* = 10.9, 3.6 Hz, 1H), 1.43 (tdd, *J* = 13.2, 6.1, 2.9 Hz, 1H), 1.09 – 0.93 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 153.81, 142.24, 141.94, 118.29, 110.27, 107.07, 56.51, 44.92, 40.86, 39.81, 37.91, 29.09, 25.31, 22.55; IR (film) 1146, 1506 cm^{-1}; MS (ESI) 218.1544 (218.1539 calcd for $C_{14}H_{19}NO$, M + H^+).

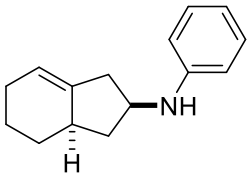


(±)-(2*S,3a*R**)-N-benzyl-2,3,3a,4,5,6-hexahydro-1H-inden-2-amine (10d).** The general procedure was used for the coupling of benzylamine (13.1 µL, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (27.0 mg, 0.1 mmol). The crude product was purified by flash chromatography on silica gel to afford 19.2 mg (76%, >20:1 dr) of the title compound as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 4.7 Hz, 4H), 7.28 – 7.21 (m, 1H), 5.39 (s, 1H), 3.78 (s, 2H), 3.20 (dt, *J* = 15.1, 7.6 Hz, 1H), 2.68 (dd, *J* = 14.6, 7.8 Hz, 1H), 2.27 - 2.14 (m, 2H), 2.10 – 1.90 (m, 5H), 1.78 (ddd, *J* = 13.0, 7.0, 3.8 Hz, 1H), 1.43 (dtt, *J* = 18.9, 9.0, 4.4 Hz, 1H), 1.11 – 0.93 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.51, 140.53, 128.53, 128.36, 127.06, 118.22, 56.80, 52.66, 41.15, 39.83, 38.19, 29.18, 25.35, 22.59; IR (film) 1456, 1240, 1030 cm^{-1}; MS (ESI) 228.1750 (228.1747 calcd for $C_{16}H_{21}N$, M + H^+).

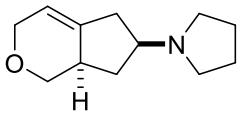


(±)-(2*S,3a*R**)-*N*-benzyl-2,3,3a,4,5,6-hexahydro-1H-inden-2-amine hydrochloride (10d•HCl).** In a vial charged with (±)-(2*S**,3a*R**)-N-benzyl-2,3,3a,4,5,6-hexahydro-1H-inden-2-amine (0.075 mmol, 17.2 mg) was added HCl (2N in Et_2O) (37.5 µL, 0.075 mmol). The oil immediately solidified to a pale yellow solid (m.p. = 218–220 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.3 Hz, 2H), 7.42 – 7.29 (m, 3H), 5.42 (s, 1H), 3.98 (d,

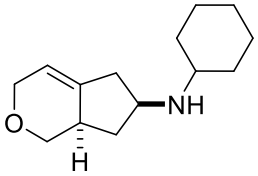
J = 13.5 Hz, 1H), 3.92 (d, J = 13.5 Hz, 1H), 3.22 (dt, *J* = 15.1, 7.6 Hz, 1H), 2.70 (dd, J = 15.9, 9.4 Hz, 1H), 2.55 (dd, J = 14.8, 8.7 Hz, 1H), 2.30 (dt, *J* = 11.8, 6.2 Hz, 1H), 2.17 – 1.86 (m, 5H), 1.77 (dt, *J* = 13.3, 4.0 Hz, 1H), 1.55 – 1.33 (m, 3H), 1.11 (q, *J* = 13.3, 12.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.60, 131.45, 130.37, 129.21, 129.13, 120.19, 55.14, 50.06, 39.57, 37.20, 34.12, 28.18, 25.11, 22.20.



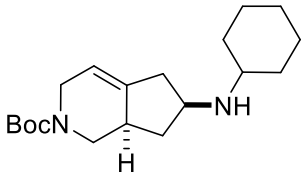
(±)-(2*S,3a*R**)-*N*-phenyl-2,3,3a,4,5,6-hexahydro-1H-inden-2-amine (10e)**. In a flame-dried 4 mL vial equipped with a stir bar and Teflon screw cap was added 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (106.3 mg, 0.39 mmol), followed by $Pd_2(dba)_3$ (3.7 mg, 1 mol %), 2-(2-(diphenylphosphanyl)phenyl)-4,5-dihydrooxazole (5.3 mg, 4 mol %), and lithium *tert*-butoxide (44.8 mg, 0.56 mmol). The mixture was pre-stirred for 5 minutes at rt before aniline (43.7 µL, 0.48 mmol) was added *neat*. The vial was sealed and heated to 95 ^{o}C for 6 hr. The vial was cooled to rt and the crude product (4:1 dr) was purified by column chromatography to afford 62.9 mg (75%, 6:1 dr) of the title compound as a slightly yellow-tinted solid (m.p. = 52 ^{o}C–54 ^{o}C). The reported ^{1}H and ^{13}C NMR data are for the major diastereomer only. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.7 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 2H), 5.46 (s, 1H), 3.88 (ddd, *J* = 14.7, 8.5, 6.0 Hz, 1H), 3.66 (br s, 1H), 2.99 – 2.83 (m, 1H), 2.45 (dt, *J* = 12.5, 6.8 Hz, 1H), 2.39 – 2.21 (m, 1H), 2.12 – 1.98 (m, 4H), 1.84 (dp, *J* = 13.0, 3.7 Hz, 1H), 1.49 (dtdd, *J* = 13.6, 11.2, 7.8, 2.6 Hz, 1H), 1.15 – 1.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.00, 142.22, 129.32, 118.61, 117.25, 113.45, 52.43, 41.13, 39.29, 39.06, 29.34, 25.27, 22.53; IR (film) 1600, 1501 cm $^{-1}$; MS (ESI) 214.1591 (214.1590 calcd for $C_{15}H_{19}N$, M + H^+).



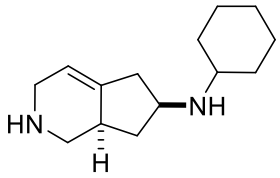
(±)-1-((6*S,7a*R**)-1,3,5,6,7,7a-Hexahydrocyclopenta[*c*]pyran-6-yl)pyrrolidine (10f).** The general procedure was used for the coupling of pyrrolidine (10 µL, 0.12 mmol) and 3-allyl-3,6-dihydro-2H-pyran-4-yl trifluoromethanesulfonate (27.2 mg, 0.1 mmol). The crude product was purified by flash chromatography on silica gel to afford 11.2 mg (58%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 (app. br s, 1H), 4.21 – 4.00 (m, 3H), 3.08 (t, *J* = 10.1 Hz, 1H), 2.69 – 2.60 (m, 2H), 2.53 (app. br s, 5H), 2.35 – 2.22 (m, 1H), 2.01 (dt, J = 11.4, 5.2 Hz, 1H), 1.79 (app. br s, 4H), 1.09 (q, J = 11.6 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 136.55, 119.00, 68.35, 65.13, 64.34, 52.95, 38.50, 33.54, 32.82, 23.59; IR (film) 1653, 1080 cm^{-1}; MS (ESI) 194.1538 (194.1539 calcd for $C_{12}H_{19}NO$, M + H^+).



(±)-(6*S,7a*R**)-*N*-Cyclohexyl-1,3,5,6,7,7a-hexahydrocyclopenta[c]pyran-6-amine (10g).** The general procedure was used for the coupling of cyclohexylamine (13.7 µL, 0.12 mmol) and 3-allyl-3,6-dihydro-2H-pyran-4-yl trifluoromethanesulfonate (27.1 mg, 0.1 mmol). The crude product was purified by flash chromatography on silica gel to afford 18.5 mg (84%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 (s, 1H), 4.22 – 4.01 (m, 3H), 3.41 (q, *J* = 7.8 Hz, 1H), 3.06 (t, *J* = 10.1 Hz, 1H), 2.77 – 2.67 (m, 1H), 2.55 – 2.42 (m, 2H), 2.11 (dt, *J* = 12.3, 6.4 Hz, 1H), 2.07 – 1.98 (m, 1H), 1.87 (app. br d, *J* = 12.4 Hz, 2H), 1.72 (app. br d, *J* = 9.6 Hz, 2H), 1.65 – 1.58 (m, 1H), 1.33 – 1.19 (m, 3H), 1.18 – 1.11 (m, 1H), 1.10 – 1.0 (m, 2H), 0.86 (br p, *J* = 10.4 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 140.17, 116.95, 69.34, 65.27, 55.52, 54.10, 38.70, 37.66, 36.51, 33.53, 26.08, 25.25; IR (film) 2926, 1456, 1120 cm^{-1}; MS (ESI) 222.1855 (222.1852 calcd for $C_{14}H_{23}NO$, M + H^+).

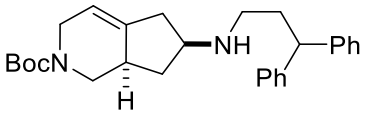


(±)-(6*S,7a*R**)-*tert*-Butyl 6-(cyclohexylamino)-1,3,5,6,7,7a-hexahydro-2*H*-cyclopenta[*c*]pyridine-2-carboxylate (10h).** The general procedure was used for the coupling of cyclohexylamine (13.8 µL, 0.12 mmol) and *N*-Boc-3-allyl-4-{[(trifluoromethyl)sulfonyl}oxy}-3,6-dihydropyridine (37.1 mg, 0.1 mmol). The crude product was purified by flash chromatography on silica gel to afford 22.5 mg (70%, >20:1 dr) of the title compound as a white solid (m.p. = 44 °C–50 °C). The diastereomeric ratio was determined after cleavage of the -Boc group due to compound **10h** existing as a mixture of carbonyl rotamers in solution. ^{1}H NMR and ^{13}C NMR spectra were sufficiently broadened and complex due to rotamers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.36 (d, *J* = 17.8 Hz, 1H), 4.47 – 4.02 (m, 2H), 3.57 – 3.45 (br m, 1H), 3.38 (p, *J* = 8.2 Hz, 1H), 2.70 (dd, *J* = 15.7, 7.5 Hz, 1H), 2.50 – 2.23 (m, 3H), 2.16 (dt, *J* = 12.0, 6.1 Hz, 1H), 2.02 (dd, *J* = 15.5, 5.8 Hz, 1H), 1.86 (d, *J* = 11.1 Hz, 2H), 1.72 (d, *J* = 13.0 Hz, 2H), 1.61 (d, *J* = 12.5 Hz, 1H), 1.45 (s, 9H), 1.29 – 1.19 (m, 3H), 1.14 (ddd, *J* = 15.4, 9.1, 2.8 Hz, 1H), 1.04 (q, *J* = 10.1, 9.6 Hz, 2H), 0.92 (q, *J* = 11.0 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 114.71, 110.13, 79.57, 55.27, 54.49, 46.78, 45.52, 43.71, 39.08, 38.21, 34.14, 28.63, 26.25, 25.30; IR (film) 1694, 1150 cm $^{-1}$; MS (ESI) 321.2539 (321.2537 calcd for $C_{19}H_{32}N_2O_2$, M + H^+).



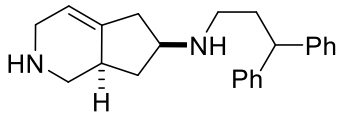
(±)-(6*S,7a*R**)-*N*-Cyclohexyl-2,3,5,6,7,7a-hexahydro-1H-cyclopenta[c]pyridin-6-amine (10h•H).** A 20 mL scintillation vial equipped with a stir bar was charged with (±)-(6*S**,7a*R**)-*tert*-butyl 6-(cyclohexylamino)-1,3,5,6,7,7a-hexahydro-2*H*-cyclopenta[*c*]pyridine-2-carboxylate (22.5 mg, 0.07 mmol) in DCM (5 mL) and cooled to

0 ^{o}C in an ice bath. Trifluoroacetic acid (100 µL) was added over 5 min and the solution was allowed to warm to rt. After completion as judged by TLC, the crude mixture was concentrated *in vacuo*. The residue was dissolved in DCM (5 mL) and aqueous NaOH (1M) (3 mL). The aqueous layer was extracted using DCM (5 mL x 3), dried over anhydrous Na_2SO_4, filtered over a pad of cotton, and concentrated *in vacuo* to afford essentially quantitative yield of the desired product. The diastereomeric ratio was determined to be >20:1 by ^{1}H NMR analysis of the sufficiently pure de-protected product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (s, 1H), 3.43 – 3.22 (m, 4H), 2.76 – 2.61 (m, 1H), 2.48 (tt, *J* = 10.6, 3.8 Hz, 1H), 2.40 – 2.24 (m, 2H), 2.14 (dt, *J* = 12.2, 6.2 Hz, 1H), 2.01 (ddt, *J* = 16.6, 7.3, 2.2 Hz, 1H), 1.92 – 1.81 (m, 3H), 1.71 (dt, *J* = 12.4, 3.9 Hz, 2H), 1.66 – 1.54 (m, 1H), 1.30 – 0.98 (m, 6H), 0.89 (tt, *J* = 11.4, 8.1 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 141.28, 116.67, 55.41, 54.42, 53.83, 48.25, 44.39, 39.19, 33.58, 28.64, 26.10, 25.25. IR (film) 3360, 1031 cm^{-1}; MS (ESI) 221.2014 (221.2012 calcd for $C_{14}H_{24}N_2$, M + H^{+}).

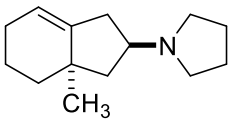


(±)-(6*S,7a*R**)-*tert*-Butyl 6-([3,3-diphenylpropyl]amino)-1,3,5,6,7,7a-hexahydro-2*H*-cyclopenta[*c*]pyridine-2-carboxylate (10i).** The general procedure was used for the coupling of 3,3-diphenylpropylamine (24.8 µL, 0.12 mmol) and *N*-Boc-3-allyl-4-{[(trifluoromethyl)sulfonyl]oxy}-3,6-dihydropyridine (37.2 mg, 0.1 mmol). The crude product was purified by flash chromatography on silica gel to afford 32.2 mg (74%, >20:1 dr) of the title compound as a yellow oil. The diastereomeric ratio was determined after deprotection of the -Boc group due to compound **10i** existing as a mixture of carbonyl rotamers in solution. ^{1}H NMR and ^{13}C NMR spectra were sufficiently broadened and complex due to rotamers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.10 (m, 10H), 5.33 (br s, 1H), 4.45 – 4.05 (m, 3H), 3.99 (t, *J* = 7.8 Hz, 1H), 3.49 (br d, *J* = 13.1 Hz, 1H), 3.16 (p, *J* = 9.0, 1H), 2.69 – 2.49 (m, 3H), 2.45 – 2.17 (m, 4H), 2.08 (dt, *J* = 12.4, 6.4 Hz, 1H), 1.98 (dd, *J* = 16.4, 7.0 Hz, 1H), 1.46 (s, 9H), 0.88 (q, *J* = 11.3 Hz,1H);

^{13}C NMR (175 MHz, $CDCl_3$) δ 144.84, 128.59, 127.88, 126.33, 115.22, 114.76, 79.57, 57.79, 49.33, 47.09, 46.77, 45.52, 43.67, 43.09, 38.96, 37.86, 37.60, 36.30, 28.62; IR (film) 1681, 1153 cm $^{-1}$; MS (ESI) 433.2860 (433.2850 calcd for $C_{28}H_{36}N_2O_2$, M + H^+).

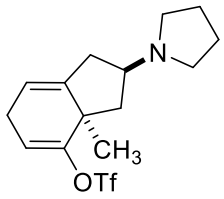


(±)-(6*S,7a*R**)-*N*-(3,3-Diphenylpropyl)-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridin-6-amine (10i•H).** Using the procedure for the synthesis of N-cyclohexyl-2,3,5,6,7,7a-hexahydro-1H-cyclopenta[c]pyridin-6-amine except using (±)-(6*S**,7a*R**)-*tert*-butyl 6-[(3,3-diphenylpropyl)amino]-1,3,5,6,7,7a-hexahydro-2*H*-cyclopenta[*c*]pyridine-2-carboxylate in place of (±)-(6*S**,7a*R**)-*tert*-butyl 6-(cyclohexylamino)-1,3,5,6,7,7a-hexahydro-2*H*-cyclopenta[*c*]pyridine-2-carboxylate, the title compound was afforded in essentially quantitative yield. The diastereomeric ratio was determined to be >20:1 by ^{1}H NMR analysis of the sufficiently pure de-protected product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 8H), 7.16 (tt, *J* = 6.8, 2.0 Hz, 2H), 5.36 (s, 1H), 3.99 (t, *J* = 7.8 Hz, 1H), 3.41 – 3.20 (m, 3H), 3.13 (tt, *J* = 8.9, 6.5 Hz, 1H), 2.70 – 2.44 (m, 3H), 2.35 – 2.19 (m, 4H), 2.06 (td, *J* = 11.1, 10.5, 5.1 Hz, 1H), 1.94 (dd, *J* = 16.3, 6.2 Hz, 1H), 1.89 – 1.68 (m, 2H), 0.82 (q, *J* = 10.7 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 144.68, 141.55, 128.63, 127.87, 126.38, 115.41, 57.14, 49.28, 47.62, 46.93, 43.65, 38.25, 37.64, 35.85, 28.62.; IR (film) 3390, 1450 cm $^{-1}$; MS (ESI) 333.2329 (333.2325 calcd for $C_{23}H_{28}N_2$, M + H^+).

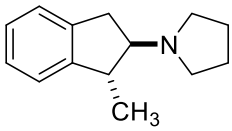


(±)-1-((2*S,3a*R**)-3a-Methyl-2,3,3a,4,5,6-hexahydro-1*H*-inden-2-yl)pyrrolidine (10j).** The general procedure was used for the coupling of pyrrolidine (10 µL, 0.12 mmol) and 6-allyl-6-methylcyclohex-1-en-1-yl trifluoromethanesulfonate (28.4 mg, 0.1 mmol). The

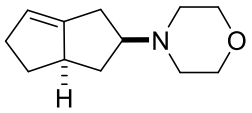
crude product was purified by flash chromatography on silica gel to afford 19.4 mg (94%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (tt, *J* = 3.7, 1.9 Hz, 1H), 2.78 (tt, *J* = 9.7, 6.1 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.47 (app. br s, 4H), 2.26 – 2.16 (m, 1H), 1.99 – 1.92 (m, 2H), 1.88 (dd, *J* = 11.7, 6.4 Hz, 1H), 1.77 (app. br p, *J* = 3.7 Hz, 4H), 1.70 (dt, *J* = 12.2, 3.4 Hz, 1H), 1.65 – 1.58 (m, 2H), 1.32 – 1.23 (m, 2H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.33, 117.92, 62.29, 53.25, 48.87, 40.83, 36.39, 36.19, 25.39, 25.10, 23.43, 18.78; IR (film) 2929, 1457 cm $^{-1}$**;** MS (ESI) 206.1906 (206.1903 calcd for $C_{14}H_{23}N$, M + H^+).



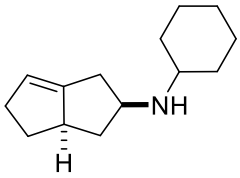
(±)-(2*R,3a*R**)-3a-Methyl-2-(pyrrolidin-1-yl)-2,3,3a,6-tetrahydro-1*H*-inden-4-yl trifluoromethanesulfonate (10k).** The general procedure was used for the coupling of pyrrolidine (20 µL, 0.24 mmol) and 2-allyl-2-methylcyclohexa-3,6-diene-1,3-diyl bis(trifluoromethanesulfonate) (86.1 mg, 0.2 mmol), except RuPhos (6 mol %) ligand and 1.1 equiv of LiO*t*Bu base were used and the reaction was conducted for 1 hr. The crude product was purified by flash chromatography on silica gel to afford 51.1 mg (73%, >20:1 dr) of the title compound as a red oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69 (dd, *J* = 5.0, 2.8 Hz, 1H), 5.34 (dd, *J* = 4.8, 2.2 Hz, 1H), 2.98 – 2.71 (m, 4H), 2.49 (br s, 4H), 2.38 (dd, J = 16.8, 5.0 Hz, 1H), 2.00 (dd, *J* = 11.8, 6.6 Hz, 1H), 1.78 (m, 5H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.07, 144.16, 114.36, 113.15, 61.23, 53.03, 44.83, 42.98, 35.00, 27.81, 24.22, 23.42; IR (film) 1413, 1210 cm $^{-1}$; MS (ESI) 352.1198 (352.1189 calcd for $C_{15}H_{20}F_3NO_3S$, M + H^+).



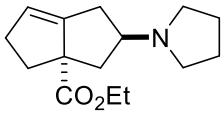
(±)-1-((1*R,2*R**)-1-Methyl-2,3-dihydro-1H-inden-2-yl)pyrrolidine (12).** The general procedure was used for the coupling of pyrrolidine (10 µL, 0.12 mmol) and 2-(but-3-en-2-yl)phenyl trifluoromethanesulfonate (28 mg, 0.1 mmol). The crude product was purified by flash chromatography on silica gel to afford 10.9 mg (54%, 10:1 dr) of the title compound as a viscous oil. Data are for the major diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 4H), 3.23 (p, J = 6.9 Hz, 1H), 3.11 (dd, *J* = 15.7, 7.7 Hz, 1H), 2.97 (dd, *J* = 15.7, 7.7 Hz, 1H), 2.84 (q, *J* = 7.5 Hz, 1H), 2.66 (br s, 4H), 1.82 (br s, 4H), 1.39 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 146.53, 140.34, 126.88, 126.86, 124.36, 123.61, 72.66, 52.35, 43.84, 36.69, 23.54, 20.21.; IR (film) 2962, 1148 cm^{-1}; MS (ESI) 202.1592 (202.1590 calcd for $C_{14}H_{19}N$, M + H^+).



(±)-(2*S,3a*R**)-4-(1,2,3,3a,4,5-Hexahydropentalen-2-yl)morpholine (14a).** The general procedure was used for the coupling of morpholine (10.5 µL, 0.12 mmol) and 5-allylcyclopent-1-en-1-yl trifluoromethanesulfonate (28.5 mg, 0.1 mmol), except 10 mol % BrettPhos was used. The crude product was purified by flash chromatography on silica gel to afford 14.5 mg (75%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.25 (s, 1H), 3.73 (t, *J* = 4.8 Hz, 4H), 2.98 (p, *J* = 10 Hz, 1H), 2.84 (app. br s, 1H), 2.61 – 2.38 (m, 7H), 2.17 – 2.03 (m, 3H), 1.42 (p, *J* = 10 Hz, 1H), 1.02 (q, *J* = 11.1 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 150.28, 119.10, 70.59, 66.89, 52.34, 50.30, 37.19, 36.89, 31.93, 29.04; IR (film) 1119, 1266 cm^{-1}; MS (ESI) 194.1542 (194.1539 calcd for $C_{12}H_{19}NO$, M + H^+).

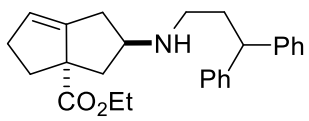


(±)-(2*S,3a*R**)-*N*-Cyclohexyl-1,2,3,3a,4,5-hexahydropentalen-2-amine (14b).** The general procedure was used for the coupling of cyclohexylamine (13.7 µL, 0.12 mmol) and 5-allylcyclopent-1-en-1-yl trifluoromethanesulfonate (28.5 mg, 0.1 mmol), except 10 mol % BrettPhos was used. The crude product was purified by flash chromatography on silica gel to afford 17.8 mg (87%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26 (app. br s, 1H), 3.64 (p, *J* = 9.4 Hz, 1H), 2.82 – 2.77 (m, 1H), 2.64 – 2.38 (m, 4H), 2.25 (dt, *J* = 12.2, 6.4 Hz, 1H), 2.07 (dt, *J* = 13.0, 6.9 Hz, 1H), 1.98 (app. br d, *J* = 15.6 Hz, 1H), 1.90 (app. br t, *J* = 12.2 Hz, 2H), 1.73 (br dt, *J* = 12.8, 3.9 Hz, 2H), 1.62 (br dt, *J* = 12.7, 3.5 Hz, 1H), 1.40 (dq, *J* = 12.0, 9.4 Hz, 1H), 1.31 – 1.05 (m, 6H), 0.99 – 0.80 (m, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 151.56, 118.68, 59.77, 55.11, 50.35, 41.42, 37.03, 34.26, 33.98, 33.02, 32.19, 26.31, 25.34, 25.31; IR (film) 1146, 1452 cm $^{-1}$; MS (ESI) 206.1908 (206.1903 calcd for $C_{14}H_{23}N$, M + H^+).

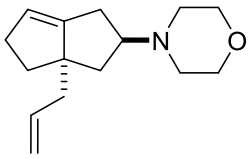


(±)-(2*R,3a*S**)-Ethyl 2-(pyrrolidin-1-yl)-2,3,4,5-tetrahydropentalene-3a(1*H*)-carboxylate (14c).** The general procedure was used for the coupling of pyrrolidine (10 µL, 0.12 mmol) and ethyl 1-allyl-2-{[(trifluoromethyl)sulfonyl]oxy}cyclopent-2-ene-1-carboxylate (32.8 mg, 0.1 mmol). The crude product was purified by flash chromatography on silica gel to afford 19.1 mg (76%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 (app br s, 1H), 4.19 – 4.09 (m, 2H), 3.15 (br p, *J* = 6.3 Hz, 1H), 2.85 – 2.77 (m, 1H), 2.57 – 2.44 (m, 7H), 2.39 (dd, *J* = 15.0, 10.0 Hz, 1H), 2.25 (br dd, *J* = 11.7, 4Hz, 1H), 1.82 (dt, *J* = 9.1, 6.8 Hz, 1H), 1.77 (app. br s, 4H), 1.39 (dd, *J* = 12.1, 9.7 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 176.26, 149.15, 123.26, 68.24, 65.42, 60.65, 52.92, 42.98, 37.69, 36.96,

30.25, 23.40, 14.35; IR (film) 1719, 1152 cm $^{-1}$; MS (ESI) 250.1808 (250.1802 calcd for $C_{15}H_{23}NO_2$, M + H^+).

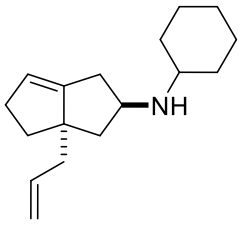


(±)-(2*R,3a*S**)-Ethyl 2-[(3,3-diphenylpropyl)amino]-2,3,4,5-tetrahydropentalene-3a(1*H*)-carboxylate (14d).** The general procedure was used for the coupling of 3,3-diphenylpropylamine (24.8 µL, 0.12 mmol) and ethyl 1-allyl-2-{[(trifluoromethyl)sulfonyl]oxy}cyclopent-2-ene-1-carboxylate (32.8 mg, 0.1 mmol). The crude product was purified by flash chromatography on silica gel to afford 22 mg (55%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 8H), 7.18 (tt, *J* = 7.0, 1.8 Hz, 2H), 5.47 (app. br s, 1H), 4.15 – 4.08 (m, 2H), 4.00 (t, *J* = 7.8 Hz, 1H), 3.57 (dp, *J* = 11.4, 3.8 Hz, 1H), 2.85 – 2.75 (m, 1H), 2.61 (dd, *J* = 11.8, 7.0 Hz, 1H), 2.57 – 2.49 (m, 4H), 2.44 (dd, *J* = 12.7, 6.8 Hz, 1H), 2.24 (qd, *J* = 7.9, 1.8 Hz, 2H), 1.95 (br dd, *J* = 17.5, 3.6 Hz, 1H), 1.77 (dt, *J* = 12.8, 9.3 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.10 (dd, *J* = 12.6, 8.1 Hz, 1H), 0.93 (app. br q, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.12, 149.34, 144.88, 144.84, 128.59, 127.91, 127.89, 126.32, 123.29, 65.05, 61.68, 60.64, 49.37, 46.93, 44.45, 37.91, 36.82, 36.24, 32.14, 14.33; IR (film) 1717, 697 cm $^{-1}$; MS (ESI) 390.2436 (390.2428 calcd for $C_{26}H_{31}NO_2$, M + H^+).

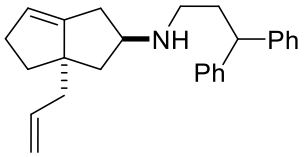


(±)-(2*S,3a*S**)-4-(3a-Allyl-1,2,3,3a,4,5-hexahydropentalen-2-yl)morpholine (14e).** The general procedure was used for the coupling of morpholine (10.5 µL, 0.12 mmol) and 5,5-diallylcyclopent-1-en-1-yl trifluoromethanesulfonate (29.6 mg, 0,1 mmol), except 10 mol % BrettPhos was used. The crude product was purified by flash chromatography

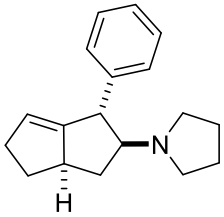
on silica gel to afford 21.7 mg (93%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.80 (dddd, *J* = 16.8, 10.1, 8.0, 6.4 Hz, 1H), 5.23 (app. br s, 1H), 5.10 – 4.96 (m, 2H), 3.71 (t, *J* = 4.7 Hz, 4H), 3.11 (tt, *J* = 9.8, 6.3 Hz, 1H), 2.61 – 2.55 (m, 1H), 2.53 – 2.33 (m, 6H), 2.18 (dd, *J* = 16.9, 5.5 Hz, 1H), 2.11 (dd, *J* = 13.9, 6.6 Hz, 1H), 2.02 (dt, *J* = 12.1, 8.2 Hz, 2H), 1.94 (dd, *J* = 12.4, 6.9 Hz, 1H), 1.60 (dt, *J* = 12.5, 9.5 Hz, 1H), 1.19 (dd, *J* = 11.8, 10.0 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 152.81, 136.17, 119.32, 116.79, 68.73, 67.06, 58.80, 52.34, 41.25, 40.41, 37.10, 35.82, 28.20; IR (film) 1636, 1266, 1118 cm^{-1}; MS (ESI) 234.1859 (234.1852 calcd for $C_{15}H_{23}NO$, M + H^+).



(±)-(2*S,3a*S**)-3a-Allyl-*N*-cyclohexyl-1,2,3,3a,4,5-hexahydropentalen-2-amine (14f).** The general procedure was used for the coupling of cyclohexylamine (13.7 µL, 0.12 mmol) and 5,5-diallylcyclopent-1-en-1-yl trifluoromethanesulfonate (29.6 mg, 0.1 mmol), except 10 mol % BrettPhos was used. The crude product was purified by flash chromatography on silica gel to afford 24.8 mg (>95%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.24 (app. br s, 1H), 5.07 – 4.98 (m, 2H), 3.72 (tdd, *J* = 8.9, 6.7, 4.9 Hz, 1H), 2.60 – 2.52 (m, 2H), 2.43 (tt, *J* = 10.7, 3.8 Hz, 1H), 2.36 (ddd, *J* = 13.1, 8.7, 3.1 Hz, 1H), 2.16 (dd, *J* = 12.2, 6.8 Hz, 1H), 2.07 (dd, *J* = 13.8, 6.7 Hz, 1H), 2.01 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.86 (app. br d, *J* = 12.3 Hz, 1H), 1.80 (app. br d, *J* = 12.4 Hz, 1H), 1.71 (app. br d, *J* = 13.2 Hz, 2H), 1.65 – 1.54 (m, 2H), 1.27 – 1.19 (m, 2H), 1.13 (qt, *J* = 12.7, 3.6 Hz, 1H), 1.08 – 0.97 (m, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 153.59, 136.37, 119.19, 116.62, 58.60, 57.66, 55.06, 45.91, 40.65, 37.26, 35.64, 34.29, 33.84, 32.20, 26.30, 25.36, 25.28; IR (film) 1448, 1636 cm $^{-1}$; MS (ESI) 246.2223 (246.2216 calcd for $C_{17}H_{27}N$, M + H^+).

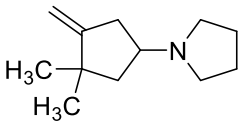


(±)-(2*S,3a*S**)-3a-Allyl-*N*-(3,3-diphenylpropyl)-1,2,3,3a,4,5-hexahydropentalen-2-amine (14g).** The general procedure was used for the coupling of 3,3-diphenylpropylamine (24.8 µL, 0.12 mmol) and 5,5-diallylcyclopent-1-en-1-yl trifluoromethanesulfonate (29.6 mg, 0.1 mmol). The crude product was purified by flash chromatography on silica gel to afford 26.4 mg (94%, >20:1 dr) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 8H), 7.19 (tt, *J* = 7.0, 1.8 Hz, 2H), 5.80 (dddd, *J* = 16.9, 10.2, 7.8, 6.7 Hz, 1H), 5.26 (app br s, 1H), 5.08 – 4.99 (m, 2H), 4.01 (t, *J* = 7.8 Hz, 1H), 3.50 (tdd, *J* = 8.6, 6.8, 4.6 Hz, 1H), 2.63 – 2.45 (m, 3H), 2.29 (ddt, *J* = 15.8, 8.7, 2.7 Hz, 1H), 2.25 (tdd, *J* = 10.0, 6.7, 3.0 Hz, 2H), 2.13 (dd, *J* = 12.4, 6.8 Hz, 1H), 2.07 (dd, *J* = 13.8, 6.7 Hz, 1H), 2.01 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.98 – 1.89 (m, 3H), 1.60 (dt, *J* = 12.4, 9.5 Hz, 1H), 1.08 (br s, 1 H), 1.00 (dd, *J* = 12.4, 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.45, 144.94, 144.89, 136.30, 128.58, 127.92, 127.89, 126.30, 119.32, 116.67, 61.14, 58.65, 49.40, 46.93, 45.36, 40.77, 37.34, 36.29, 35.65, 31.58; IR (film) 1450, 698 cm $^{-1}$; MS (ESI) 358.2530 (358.2529 calcd for $C_{26}H_{31}N$, M + H^+).

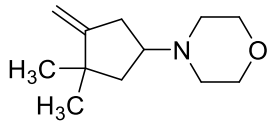


(±)-1-((1*R,2*S**,3a*R**)-1-Phenyl-1,2,3,3a,4,5-hexahydropentalen-2-yl)pyrrolidine (14h).** The general procedure was used for the coupling of pyrrolidine (33.4 µL, 0.4 mmol) and (*E*)-5-cinnamylcyclopent-1-en-1-yl trifluoromethanesulfonate (66.5 mg mg, 0.2 mmol), except XPhos (5.7 mg, 6 mol %) was used as ligand an the reaction was conducted using 200 µL toluene solvent in a 4 mL vial equipped with a Teflon cap. The crude product was purified by flash chromatography on silica gel to afford 19 mg (37%,

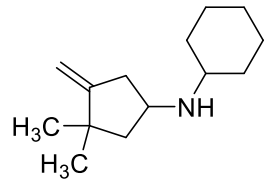
5:1 dr) of the title compound as a viscous liquid. The reported ^{1}H NMR data is for the major diastereomer only. The reported ^{13}C NMR data is for the mixture of diastereomers. ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.23 (d, J = 7.3 Hz, 2H), 7.17 (d, J = 7.5 Hz, 2H), 7.07 (app. br t, J = 7.1 Hz, 1H), 5.20 (app. br s, 1H), 3.72 (d, J = 5.8 Hz, 1H), 3.18 (ddd, J = 10.2, 7.2, 5.9 Hz, 1H), 3.05 (ddtt, J = 12.3, 9.3, 6.3, 3.2 Hz, 1H), 2.60 – 2.22 (m, 6H), 2.21 – 1.99 (m, 2H), 1.60 – 1.39 (m, 5H), 1.32 (q, J = 11.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.76, 146.50, 128.77, 128.44, 128.19, 127.82, 125.95, 120.39, 119.87, 78.64, 75.66, 53.36, 52.95, 51.35, 50.35, 50.16, 48.07, 39.66, 37.19, 37.03, 36.05, 34.59, 32.19, 29.85, 23.36, 23.31; IR (film) 1451, 700 cm $^{-1}$; MS (ESI) 254.1908 (254.1903 calcd for $C_{18}H_{23}N$, M + H^+).



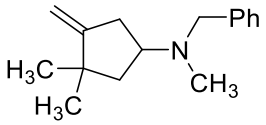
(±)-1-(3,3-Dimethyl-4-methylenecyclopentyl)pyrrolidine (18a). The general procedure was used for the coupling of pyrrolidine (10 µL, 0.12 mmol) and 3,3-dimethylhexa-1,5-dien-2-yl trifluoromethanesulfonate (25.8 mg, 0.1 mmol), except the reaction was conducted for 1 hour. After cooling to rt, Et_2O (5 mL) was added and the crude mixture was filtered through a cotton plug. The crude mixture was transferred into a separatory funnel and was extracted using aqueous 1M HCl (3 x 10 mL). The combined aqueous layers were placed back into a separatory funnel and treated with 4 M NaOH until pH > 13. The basic aqueous layer was then extracted using DCM (3 x 10 mL), the organic fractions were combined, dried over anhydrous Na_2SO_4, filtered through a cotton plug, and concentrated to afford 14.3 mg (80%) of the title compound as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.81 (s, 1H), 4.75 (s, 1H), 2.65 (ddd, J = 15.4, 6.9, 1.5 Hz,1H), 2.60 – 2.47 (m, 5H), 2.41 (ddt, J = 15.5, 10.0, 2.9 Hz, 1H), 1.85 – 1.74 (m, 5H), 1.56 (t, J = 11.3 Hz, 1H), 1.13 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 159.95, 104.13, 63.10, 53.45, 48.16, 41.41, 40.38, 30.73, 29.64, 23.50; IR (film) 1344, 878 cm $^{-1}$; MS (ESI) 180.1745 (180.1747 calcd for $C_{12}H_{21}N$, M + H^+).



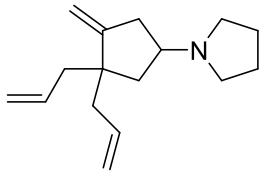
(±)-4-(3,3-Dimethyl-4-methylenecyclopentyl)morpholine (18b). The general procedure was used for the coupling of morpholine (31.5 µL, 0.36 mmol) and 3,3-dimethylhexa-1,5-dien-2-yl trifluoromethanesulfonate (77.8 mg, 0.3 mmol), except the reaction was conducted for 1 hour. The crude product was purified by liquid-liquid extraction as described for (±)-1-(3,3-dimethyl-4-methylenecyclopentyl)pyrrolidine to afford 33.8 mg (57%) of the title compound as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.82 (s, 1H), 4.76 (s, 1H), 3.73 (br t, *J* = 4.7 Hz, 4H), 2.69 (dd, *J* = 15.3, 6.7 Hz, 1H), 2.61 (app. p, *J* = 10.3 Hz, 1H), 2.48 (s, 4H), 2.40 – 2.29 (m, 1H), 1.83 (ddd, *J* = 11.9, 6.2, 1.7 Hz, 1H), 1.48 (br t, *J* = 11.3 Hz, 1H), 1.14 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 159.11, 104.44, 66.97, 63.68, 52.70, 46.17, 41.33, 38.50, 30.67, 29.41; IR (film) 1453, 1118 cm $^{-1}$; MS (ESI) 196.1695 (196.1696 calcd for $C_{12}H_{21}NO$, M + H^+).



(±)-*N*-(3,3-Dimethyl-4-methylenecyclopentyl)cyclohexanamine (18c). The general procedure was used for the coupling of cyclohexylamine (13.7 µL, 0.12 mmol) and 3,3-dimethylhexa-1,5-dien-2-yl trifluoromethanesulfonate (25.4 mg, 0.98 mmol), except the reaction was conducted for 6 h. The crude product was purified by column chromatography on silica gel to afford 12.3 mg (60%) of the title compound as a yellow-tinted, clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (app s, 1H), 4.75 (app s, 1H), 3.33 (tt, *J* = 9.7, 6.7 Hz, 1H), 2.75 (dd, *J* = 16.0, 7.2 Hz, 1H), 2.48 (tt, *J* = 10.6, 3.9 Hz, 1H), 2.16 (ddt, *J* = 15.3, 9.4, 2.6 Hz, 1H), 1.93 – 1.82 (m, 3H), 1.72 (dt, *J* = 12.8, 3.9 Hz, 2H), 1.67 – 1.55 (m, 2H), 1.39 – 1.00 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.01, 104.08, 55.34, 53.06, 49.57, 41.76, 41.19, 34.17, 34.01, 30.53, 29.57, 26.26, 25.34; IR (film) 1149, 880 cm $^{-1}$; MS (ESI) 208.2058 (208.206 calcd for $C_{14}H_{25}N$, M + H^+).

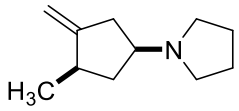


(±)-*N*-Benzyl-N,3,3-trimethyl-4-methylenecyclopentan-1-amine (18d). The general procedure was used for the coupling of *N*-benzylmethylamine (15.5 µL, 0.12 mmol) and 3,3-dimethylhexa-1,5-dien-2-yl trifluoromethanesulfonate (26 mg, 0.1 mmol), except tris(pentafluorophenyl)phosphine (3.2 mg, 6 mol %) was used as ligand and the reaction was conducted for 6 h. The crude product was purified by column chromatography on silica gel to afford 13.2 mg (57%) of the title compound as a clear oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.36 - 7.31 (m, 4H), 7.29 – 7.26 (m, 1H), 4.84 (s, 1H), 4.78 (s, 1H), 3.60 (br s, 2H), 2.93 (br s, 1H), 2.77 (dd, J = 16.0, 7.5 Hz, 1H), 2.55 (br s, 1H), 2.17 (s, 3H), 1.90 (dd, *J* = 12.1, 6.3 Hz, 1H), 1.68 (app. br s, 1H), 1.17 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.29, 129.58, 129.10, 128.48, 127.40, 104.33, 62.82, 60.37, 46.42, 41.49, 39.84, 38.75, 30.58, 29.36; IR (film) 1455, 697 cm $^{-1}$; MS (ESI) 230.1909 (230.1903 calcd for $C_{16}H_{23}N$, M + H^+).

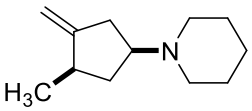


(±)-1-(3,3-Diallyl-4-methylenecyclopentyl)pyrrolidine (18e). The general procedure was used for the coupling of pyrrolidine (10 µL, 0.12 mmol) and 3,3-diallylhexa-1,5-dien-2-yl trifluoromethanesulfonate (30.9 mg, 0.1 mmol), except RuPhos (2.8 mg, 6 mol %) was used as ligand and the reaction was conducted for 1.5 h. The crude product was purified by liquid-liquid extraction as described for (±)-1-(3,3-dimethyl-4-methylenecyclopentyl)pyrrolidine to afford 22.4 mg (97%) of the title compound as a clear oil that was contaminated with ca 5% of an unidentified impurity as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 – 5.72 (m, 2H), 5.07 – 4.95 (m, 5H), 4.72 (d, *J* = 2.9 Hz, 1H), 2.59 (dd, *J* = 15.3, 6.6 Hz, 1H), 2.56 – 2.41 (m, 5H), 2.33 (ddt, *J* = 13.8, 10.4, 2.9 Hz, 1H), 2.25 – 2.05 (m, 4H), 1.82 (dd, *J* = 12.7, 6.5 Hz, 1H), 1.77 (s,

4H), 1.63 (dd, *J* = 12.5, 10.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.90, 135.58, 135.37, 117.64, 117.30, 106.17, 63.10, 53.42, 47.60, 45.06, 44.89, 42.16, 41.22, 23.47; IR (film) 3062, 909 cm $^{-1}$; MS (ESI) 232.2059 (232.206 calcd for $C_{16}H_{25}N$, M + H^+).

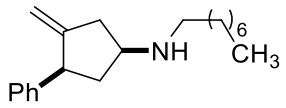


(±)-1-((1*S,3*R**)-3-Methyl-4-methylenecyclopentyl)pyrrolidine (20a).** The general procedure was used for the coupling of pyrrolidine (20 µL, 0.24 mmol) and 3-methylhexa-1,5-dien-2-yl trifluoromethanesulfonate (48.4 mg, 0.2 mmol), except CPhos (5.2 mg, 6 mol %) was used as ligand and the reaction was conducted for 1.5 h. The crude product was purified by liquid-liquid extraction as described for (±)-1-(3,3-dimethyl-4-methylenecyclopentyl)pyrrolidine to afford 29 mg (88%,12:1 dr) of the title compound as a slightly yellow-tinted, clear oil. Characterization data are for the major diastereomer. This material contained 6% of an impurity that was determined to be CPhos as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.84 (br s, 1H), 4.74 (br s, 1H), 2.60 (dd, *J* = 15.9, 7.1, 1H), 2.56 – 2.38 (m, 6H), 2.31 (m, 1H), 2.09 (dt, *J* = 11.6, 5.75 Hz, 1H), 1.77 (p, *J* = 3.4 Hz, 4H), 1.22 (q, J = 11.6 Hz, 1H), 1.09 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.58, 104.85, 64.30, 53.41, 41.84, 39.79, 37.55, 23.47, 18.81; IR (film) 1656, 1457 cm^{-1}; MS (ESI) 166.1588 (16.159 calcd for $C_{11}H_{19}N$, M + H^+).

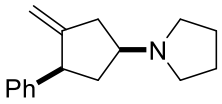


(±)-1-((1*S,3*R**)-3-Methyl-4-methylenecyclopentyl)piperidine (20b).** The general procedure was used for the coupling of piperidine (11.9 µL, 0.12 mmol) and 3-methylhexa-1,5-dien-2-yl trifluoromethanesulfonate (24.2 mg, 0.1 mmol), except CPhos (2.6 mg, 6 mol %) was used as ligand and the reaction was conducted for 1.5 h. The

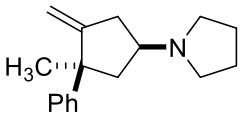
crude product was purified by liquid-liquid extraction as described for (±)-1-(3,3-dimethyl-4-methylenecyclopentyl)pyrrolidine to afford 14.9 mg (98%, 6:1 dr) of the title compound as a slightly yellow-tinted, clear oil. Characterization data are for the major diastereomer. This material contained 3.5% of an impurity that was determined to be CPhos as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.83 (br s, 1H), 4.75 (br s, 1H), 2.65 (ddd, *J* = 16.1, 7.4, 2.0 Hz, 1H), 2.53 – 2.35 (m, 5H), 2.28 (ddq, *J* = 15.2, 9.8, 2.6 Hz, 1H), 2.14 (dt, *J* = 11.6, 5.8 Hz, 1H), 1.59 (p, *J* = 6.0 Hz, 5H), 1.43 (m, *J* = 9.4, 5.8 Hz, 2H), 1.18 (q, *J* = 11.5 Hz, 1H), 1.09 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.31, 104.76, 65.09, 53.28, 40.04, 38.34, 37.48, 25.97, 24.53, 18.59; IR (film) 2929, 880, 732 cm $^{-1}$; MS (ESI) 180.1745 (180.1747 calcd for $C_{12}H_{21}N$, M + H^+).



(±)-(1*S,4*R**)-3-Methylene-*N*-octyl-4-phenylcyclopentan-1-amine (20c).** The general procedure was used for the coupling of octylamine (19.8 µL, 0.12 mmol) and and 3-phenylhexa-1,5-dien-2-yl trifluoromethanesulfonate (30.9 mg, 0.1 mmol), except RuPhos (2.8 mg, 6 mol %) was used as ligand and the reaction was conducted for 6 h. The crude product was purified by column chromatography on silica gel to afford 20.7 mg (72%, 4:1 dr) of the title compound as a yellow-tinted, oil. ^{1}H NMR data are for the major diastereomer and ^{13}C NMR data are for the mixture. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.16 (m, 3H), 4.96 (app. s, 1H), 4.55 (app. s, 1H), 3.58 (ddd, *J* = 12.5, 7.3, 2.8 Hz, 1H), 3.51 (ddd, *J* = 17.5, 10.4, 6.6 Hz, 1H), 3.00 (dd, *J* = 16.4, 7.7 Hz, 1H), 2.96 – 2.87 (m, 2H), 2.82 (m, 1H), 2.59 (dt, *J* = 12.6, 6.7 Hz, 1H), 2.15 (q, 1H), 1.81 – 1.73 (m, 2H), 1.34 – 1.17 (m, 10H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 150.13, 142.31, 128.67, 128.65, 128.45, 128.10, 126.86, 126.66, 110.73, 110.40, 57.43, 57.12, 49.36, 47.70, 47.65, 47.55, 39.34, 37.18, 31.82, 29.24, 29.23, 29.17, 29.16, 27.00, 26.95, 26.87, 22.73, 14.20; IR (film) 1236, 1028, 638 cm $^{-1}$; MS (ESI) 286.2536 (286.2529 calcd for $C_{20}H_{31}N$, M + H^+).



(±)-1-((1*S,4*R**)-3-Methylene-4-phenylcyclopentyl)pyrrolidine (20d).** The general procedure was used for the coupling of pyrrolidine (10 µL, 0.12 mmol) and 3-phenylhexa-1,5-dien-2-yl trifluoromethanesulfonate (30.9 mg, 0.1 mmol), except RuPhos (2.8 mg, 6 mol %) was used as ligand and the reaction was conducted for 1.5 h. The crude product was purified by liquid-liquid extraction as described for (±)-1-(3,3-dimethyl-4-methylenecyclopentyl)pyrrolidine to afford 22.6 mg (>98%, >20:1 dr) of the title compound as a yellow-tinted, clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.17 (m, 3H), 4.96 (s, 1H), 4.50 (s, 1H), 3.61 (ddt, *J* = 12.6, 7.1, 2.8 Hz, 1H), 2.79 (dd, *J* = 15.3, 2.0 Hz, 1H), 2.66 – 2.49 (m, 6H), 2.35 (p, *J* = 11.6 Hz, 1H), 1.89 – 1.75 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.25, 144.16, 128.52, 128.47, 126.34, 108.37, 64.51, 53.54, 50.13, 42.73, 40.42, 23.57, 23.52; IR (film) 2778, 697 cm $^{-1}$; MS (ESI) 228.1746 (228.1747 calcd for $C_{16}H_{21}N$, M + H^+).

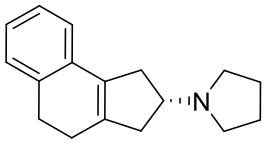


(±)-1-((1*R,3*R**)-3-Methyl-4-methylene-3-phenylcyclopentyl)pyrrolidine (20e).** The general procedure was used for the coupling of pyrrolidine (10 µL, 0.12 mmol) and 3-methyl-3-phenylhexa-1,5-dien-2-yl trifluoromethanesulfonate (32 mg, 0.1 mmol), except RuPhos (2.8 mg, 6 mol %) was used as ligand and the reaction was conducted for 1.5 h. The crude product was purified by column chromatography on silica gel to afford 19.4 mg (80%, >20:1 dr) of the title compound as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.27 (br t (incidental overlap with $CDCl_3$), *J* = 9.7, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 5.01 (s, 1H), 4.60 (s, 1H), 2.83 (dd, *J* = 14.7, 5.9 Hz, 1H), 2.74 - 2.64 (m, 1H), 2.64 – 2.47 (m, 5H), 2.17 – 2.02 (m, 2H), 1.79 (br s, 4H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.63, 149.82, 128.04, 126.72, 125.72, 108.08, 63.67, 53.55,

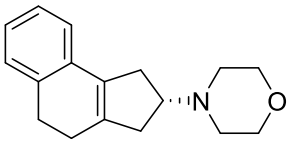
51.19, 49.62, 42.07, 29.01, 23.51; IR (film) 1344, 697 cm $^{-1}$; MS (ESI) 242.1903 (242.1903 calcd for $C_{17}H_{23}N$, M + H^+).

Asymmetric Pd-Catalyzed Alkene Carboamination Reactions

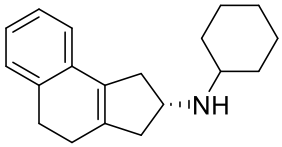
The absolute configuration was assigned based on analogy with our previous results[4] which utilized identical reagents ($Pd(OAc)_2$, (*S*)-^{t}BuPhox ligand, LiO^tBu base, toluene, pyrrolidine nucleophile, 95 °C), except the structurally similar starting material 2-allylnaphthalen-1-yl trifluoromethanesulfonate was used in place of 2-allyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate.



(+)-(*S*)-1-(2,3,4,5-Tetrahydro-1*H*-cyclopenta[*a*]naphthalen-2-yl)pyrrolidine (23a). The general procedure was used for the coupling of pyrrolidine (10 µL, 0.12 mmol) and 2-allyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (31.8 mg, 0.1 mmol), except (*S*)-^{t}BuPHOX was used as ligand. The crude product was purified by flash chromatography on silica gel to afford 18.2 mg (76%) of the title compound as crystalline yellow needles (m.p. = 80 °C - 83 °C). This material was judged to be 98:2 er by chiral HPLC analysis (Chiralcel OD-H, 0.46 cm x 15 cm, 1% IPA/Hexanes (+0.1% diethylamine), 0.5 mL/min, λ 275 nm, R_T = 7.6 min and 10.6 min, $[\alpha]_D^{26}$ +50.2 (*c* 1.03, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.05 (m, 3H), 7.00 (d, *J* = 7.4 Hz, 1H), 3.13 (p, *J* = 7.6 Hz, 1H), 2.91 – 2.76 (m, 3H), 2.68 – 2.49 (m, 7H), 2.30 (t, *J* = 8.0 Hz, 1H), 1.83 (app. br p, *J* = 3.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.02, 135.16, 133.71, 132.41, 127.41, 126.44, 126.20, 122.34, 64.20, 52.80, 41.87, 36.55, 28.62, 24.39, 23.64.; IR (film) 1653, 1341 cm^{-1}; MS (ESI) 240.1749 (240.1747 calcd for $C_{17}H_{21}N$, M + H^+).

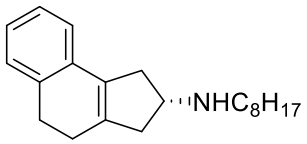


(+)-(*S*)-4-(2,3,4,5-Tetrahydro-1*H*-cyclopenta[*a*]naphthalen-2-yl)morpholine (23b). The general procedure was used for the coupling of morpholine (10.5 μL, 0.12 mmol) and 2-allyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (31.8 mg, 0.1 mmol), except (*S*)-^{t}BuPHOX was used as ligand. The crude product was purified by flash chromatography on silica gel to afford 19.1 mg (75%) of the title compound as an orange oil. This material was judged to be 94:6 er by chiral HPLC analysis (Chiralcel OD-H, 0.46 cm x 15 cm, 1% IPA/Hexanes (+0.1% diethylamine), 0.5 mL/min, λ 285 nm, R_T = 14.1 min and 26.3 min, $[\alpha]_D^{26}$ +23.2 (*c* 1.3, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.07 (m, 3H), 6.99 (d, *J* = 7.4 Hz, 1H), 3.77 (br t, *J* = 4.7 Hz, 4H), 3.23 (p, *J* = 7.5 Hz, 1H), 2.92 – 2.76 (m, 3H), 2.65 – 2.46 (m, 7H), 2.30 (br t, *J* = 7.6 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 137.61, 135.12, 133.35, 132.21, 127.49, 126.50, 126.41, 122.32, 66.83, 65.26, 51.53, 39.63, 34.50, 28.56, 24.28; IR (film) 1653, 1264, 1117 cm^{-1}; MS (ESI) 256.1700 (256.1696 calcd from $C_{17}H_{21}NO$, M + H^+).

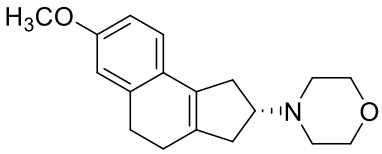


(+)-(*S*)-*N*-Cyclohexyl-2,3,4,5-tetrahydro-1*H*-cyclopenta[*a*]naphthalen-2-amine (23c). The general procedure was used for the coupling of cyclohexylamine (13.7 μL, 0.12 mmol) and 2-allyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (31.8 mg, 0.1 mmol), except (*S*)-^{t}BuPHOX was used as ligand. The crude product was purified by flash chromatography on silica gel to afford 11.7 mg (44%) of the title compound as an orange oil. This material was judged to be 98.5:1.5 er by chiral HPLC analysis (Chiralcel OD-H, 0.46 cm x 15 cm, 1% IPA/Hexanes (+0.1% diethylamine), 0.5 mL/min, λ 275 nm, R_T = 9.2 min and 10.3 min, $[\alpha]_D^{26}$ +17.4 (*c* 0.81, CH_2Cl_2). MS (ESI) 268.2059 (268.2060 calcd for $C_{19}H_{25}N$, M + H^+). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.05 (m, 3H), 6.98 (d, *J*

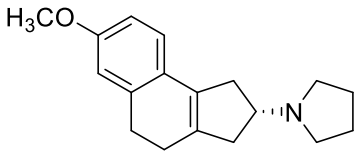
= 7.4 Hz, 1H), 3.80 (tt, *J* = 8.0, 5.6 Hz, 1H), 2.94 (dd, *J* = 15.4, 7.8 Hz, 1H), 2.87 (t, *J* = 8.2 Hz, 2H), 2.77 (dd, *J* = 16.9, 7.7 Hz, 1H), 2.58 (tt, *J* = 10.5, 3.6 Hz, 1H), 2.44 (dp, *J* = 15.4, 2.7 Hz, 1H), 2.37 – 2.25 (m, 3H), 1.99 – 1.87 (m, 2H), 1.76 (d, *J* = 12.6 Hz, 2H), 1.64 (d, *J* = 12.4 Hz, 1H), 1.36 – 1.05 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.90, 135.13, 133.82, 132.18, 127.38, 126.41, 126.16, 122.35, 55.03, 54.14, 44.33, 38.94, 34.04, 33.93, 28.59, 26.31, 25.37, 24.49; IR (film) 2922, 1448 cm^{-1}; MS (ESI) 268.2062 (268.2060 calcd for $C_{19}H_{25}N$, M + H^+).



(+)-(*S*)-*N*-Octyl-2,3,4,5-tetrahydro-1*H*-cyclopenta[*a*]naphthalen-2-amine (23d). The general procedure was used for the coupling of octylamine (19.8 µL, 0.12 mmol) and 2-allyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (31.8 mg, 0.1 mmol), except (*S*)-^{t}BuPHOX was used as ligand. The crude product was purified by flash chromatography on silica gel to afford 8.1 mg (28%) of the title compound as a yellow viscous oil. This material was judged to be 98.5:1.5 er by chiral HPLC analysis (Chiralcel OD-H, 0.46 cm x 15 cm, 1% IPA/Hexanes (+0.1% diethylamine), 0.5 mL/min, λ 275 nm, R_T = 9.9 min and 12.3 min, $[\alpha]_D^{26}$ +92.4 (*c* 0.62, CH_2Cl_2). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.20 – 7.06 (m, 3H), 6.98 (d, *J* = 7.5 Hz, 1H), 3.62 (ddd, *J* = 12.8, 7.6, 5.1 Hz, 1H), 2.93 (dd, *J* = 15.8, 7.7 Hz, 1H), 2.87 (t, *J* = 8.3 Hz, 2H), 2.77 (dd, *J* = 17.0, 7.7 Hz, 1H), 2.65 (tt, *J* = 11.3, 5.6 Hz, 2H), 2.46 (app. br d, *J* = 17.2 Hz, 1H), 2.37 - 2.26 (m, 3H), 1.52 (p, *J* = 7.3 Hz, 2H), 1.39 – 1.20 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 137.91, 135.17, 133.86, 132.21, 127.39, 126.42, 126.17, 122.37, 57.58, 48.45, 43.94, 38.59, 31.99, 30.56, 29.71, 29.43, 28.62, 27.69, 24.49, 22.82, 14.25; IR (film) 2923, 1457 cm^{-1}; MS (ESI) 298.2530 (298.2529 calcd for $C_{21}H_{31}N$, M + H^+).

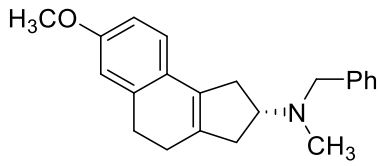


(+)-(*S*)-4-(7-Methoxy-2,3,4,5-tetrahydro-1*H*-cyclopenta[*a*]naphthalen-2-yl)morpholine (23e). The general procedure was used for the coupling of morpholine (10.5 μL, 0.12 mmol) and 2-allyl-6-methoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (34.8 mg, 0.1 mmol), except (*S*)-^{t}BuPHOX was used as ligand. The crude product was purified by flash chromatography on silica gel to afford 17.5 mg (61%) of the title compound as an orange viscous oil. This material was judged to be 93:7 er by chiral HPLC analysis (Chiralcel OD-H, 0.46 cm x 15 cm, 1% IPA/Hexanes (+0.1% diethylamine), 0.5 mL/min, λ 275 nm, R_T = 17.2 min and 21.9 min, $[\alpha]_D^{26}$ +20.4 (*c* 1.3, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (d, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 2.5 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.7 Hz, 1H), 3.79 (s, 3H), 3.76 (br t, *J* = 4.7 Hz, 4H), 3.22 (p, *J* = 7.4 Hz, 1H), 2.88 – 2.73 (m, 3H), 2.62 – 2.45 (m, 7H), 2.27 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.30, 136.98, 134.84, 131.74, 126.76, 123.24, 114.20, 110.70, 67.09, 65.28, 55.40, 51.69, 39.69, 34.78, 29.05, 24.21; IR (film) 1606, 1243, 1117 cm^{-1}; MS (ESI) 286.1803 (286.1802 calcd for $C_{18}H_{23}NO_2$, M + H^+).

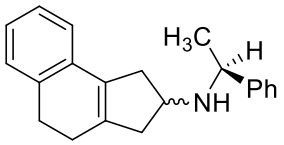


(+)-(*S*)-1-(7-Methoxy-2,3,4,5-tetrahydro-1*H*-cyclopenta[*a*]naphthalen-2-yl)pyrrolidine (23f). The general procedure was used for the coupling of pyrolidine (10 μL, 0.12 mmol) and 2-allyl-6-methoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (34.8 mg, 0.1 mmol), except (*S*)-^{t}BuPHOX was used as ligand. The crude product was purified by flash chromatography on silica gel to afford 16.8 mg (62%) of the title compound as an orange oil. This material was judged to be 98:2 er by chiral HPLC analysis (Chiralcel OD-H, 0.46 cm x 15 cm, 1% IPA/Hexanes (+0.1% diethylamine), 0.5 mL/min, λ 275 nm, R_T = 9.4 min and 10.4 min, $[\alpha]_D^{26}$ +30.1 (*c*

1.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (d, *J* = 8.2 Hz, 1H), 6.71 (br s, 1H), 6.68 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.78 (s, 3H), 3.16 (p, *J* = 7.4 Hz, 1H), 2.88 – 2.74 (m, 3H), 2.67 – 2.49 (m, 7H), 2.27 (br t, *J* = 8.1 Hz, 2H), 1.84 (br p, *J* = 3.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.20, 137.00, 135.15, 131.92, 127.03, 123.25, 114.14, 110.66, 64.27, 55.40, 52.81, 41.78, 36.72, 29.08, 24.29, 23.63; IR (film) 1500, 1244 cm^{-1}; MS (ESI) 270.1857 (270.1852 calcd for $C_{18}H_{23}NO$, M + H^+).

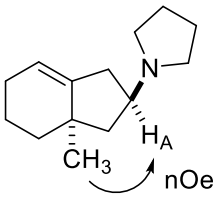


(+)-(*S*)-*N*-Benzyl-7-methoxy-N-methyl-2,3,4,5-tetrahydro-1H-cyclopenta[a]naphthalen-2-amine (23g). The general procedure was used for the coupling of *N*-benzylmethylamine (15.5 µL, 0.12 mmol) and 2-allyl-6-methoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (34.8 mg, 0.1 mmol), except (*S*)-^{t}BuPHOX was used as ligand. The crude product was purified by flash chromatography on silica gel to afford 15.7 mg (50%) of the title compound as an orange oil. This material was judged to be 85:15 er by chiral HPLC analysis (Chiralcel OD-H, 0.46 cm x 15 cm, 1% IPA/Hexanes (+0.1% diethylamine), 0.5 mL/min, λ 275 nm, R_T = 9.2 min and 10.4 min, $[\alpha]_D^{26}$ +12.0 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.27 (m (incidental overlap with $CDCl_3$), 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.72 (s, 1H), 6.70 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.80 (s, 3H), 3.62 – 3.51 (m, 3H), 2.89 – 2.76 (m, 3H), 2.75 – 2.56 (m, 3H), 2.30 (br s, 2H), 2.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.29, 136.99, 135.24, 131.99, 129.38, 129.28, 128.43, 127.21, 126.87, 123.33, 114.21, 110.71, 63.64, 59.30, 55.42, 39.59, 38.89, 34.47, 29.08, 24.25; IR (film) 1499, 1244 cm^{-1}; MS (ESI) 320.2013 (320.2009 calcd for $C_{22}H_{25}NO$, M + H^+).



(S)-*N*-(-1-Phenylethyl)-2,3,4,5-tetrahydro-1H-cyclopenta[a]naphthalen-2-amine (24). The general procedure was used for the coupling of (*S*)-(−)-α-methylbenzylamine (15.5 μL, 0.12 mmol) and 2-allyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (31.8 mg, 0.1 mmol) to afford 8.2 mg (29%) of the title product as an inseparable 1.2:1 mixture of diastereomers as a clear oil. This material was judged to be 99.2:0.8 er for the major diastereomer and 99.5:0.5 er for the minor diastereomer by chiral HPLC analysis (Chiralcel AD-H, 25 cm x 4.6 mm, 1% IPA/Hexanes (+0.1% diethylamine), 1.0 mL/min, λ 275 nm, R_T = 6.385 min and 9.491 min for the major diastereomer and 6.739 min and 8.943 min for the minor diastereomer). Characterization data are for the mixture of diastereomers: ^{1}H NMR (700 MHz, CD_3OD) δ 7.42 (t, *J* = 6.8 Hz, 2H), 7.38 (dt, *J* = 7.6, 4.0 Hz, 2H), 7.29 (td, *J* = 7.3, 4.5 Hz, 1H), 7.16 – 7.09 (m, 2H), 7.06 (q, *J* = 7.4 Hz, 1H), 7.00 (d, J = 7.4 Hz, 0.5H), 6.92 (d, *J* = 7.4 Hz, 0.5H), 3.97 (q, J = 6.7 Hz, 0.45H), 3.93 (q, *J* = 6.7 Hz, 0.53H), 3.42 (h, *J* = 6.5 Hz, 1H), 2.87 – 2.76 (m, 3H), 2.70 – 2.55 (m, 1.5H), 2.46 (td, *J* = 21.0, 20.3, 5.4 Hz, 1H), 2.36 – 2.24 (m, 2.5H), 1.45 (d, *J* = 2.5 Hz, 145H), 1.44 (d, *J* = 2.5 Hz, 1.55H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.78, 138.04, 137.78, 135.16, 135.12, 133.75, 132.26, 132.10, 128.60, 128.60, 128.59, 127.40, 127.37, 127.11, 126.90, 126.88, 126.42, 126.17, 122.34, 122.32, 56.51, 56.42, 55.03, 54.91, 44.36, 43.52, 39.03, 28.60, 24.71, 24.60, 24.55, 24.44; IR (film) 1490, 1127 cm^{-1}; MS (ESI) 290.1904 (290.1903 calcd for $C_{21}H_{23}N$, M + H^+).

Relative Stereochemistry: nOe



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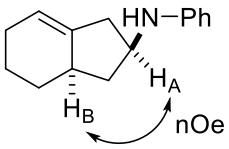
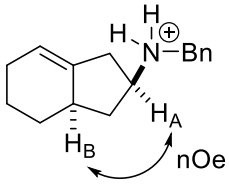
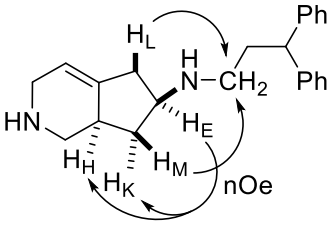


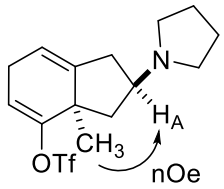
10e



10d·HCl



10i·H



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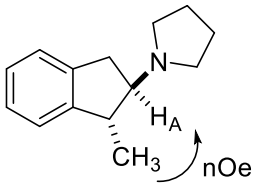
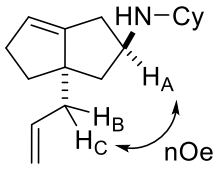
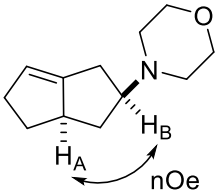


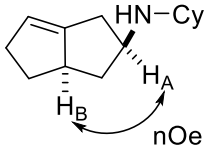
12



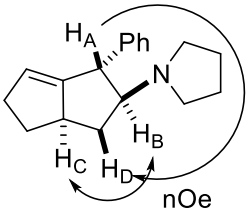
14f



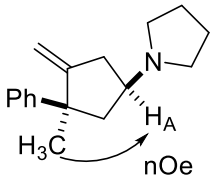
14a



14b



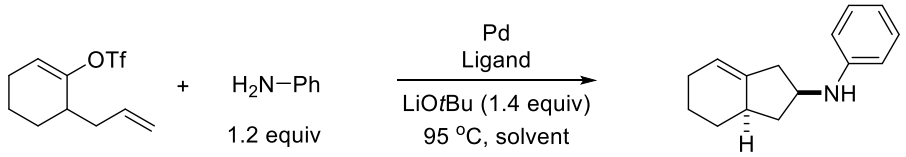
14h



20e

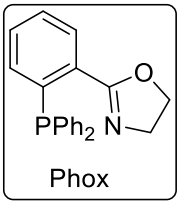
Aniline Nucleophile Optimization

The key findings during optimization studies are highlighted in red.

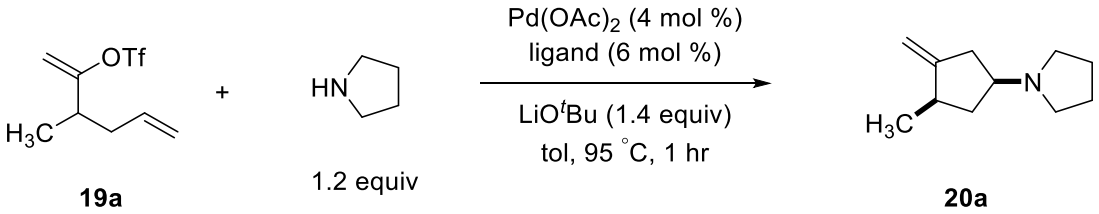


9a **10e**

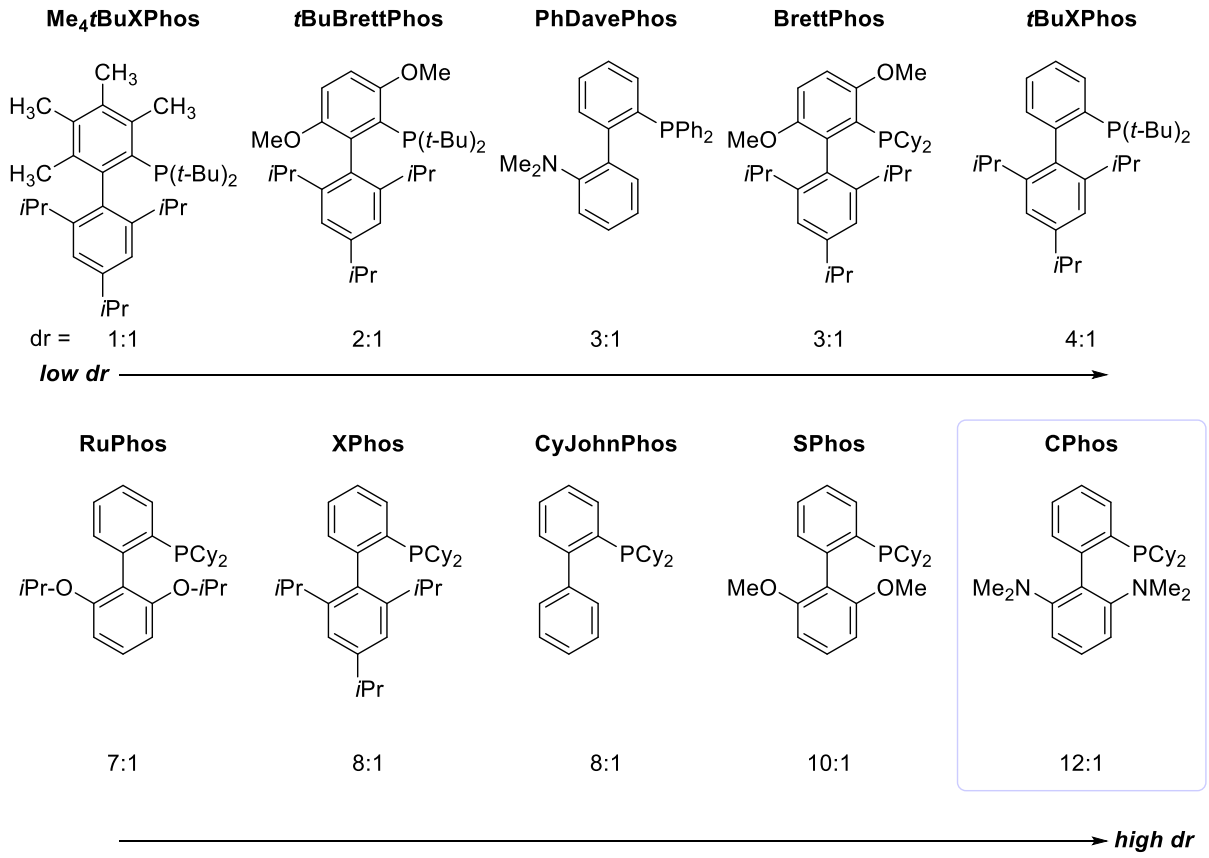
entry	Pd (mol %)	Ligand (mol %)	solvent (M)	time (h)	result (isolated %)
1	$Pd(OAc)_2$ (4)	DPEPhos (6)	*neat*	17	42% conv., 0% **10e**
2	$Pd(OAc)_2$ (4)	2,2'-bipyridyl (6)	toluene (0.33)	15	32% conv., 0% **10e**
3	$Pd(OAc)_2$ (4)	PPh_3 (6)	toluene (0.33)	15	67% conv., 0% **10e**
4	$Pd(OAc)_2$ (4)	BrettPhos (6)	toluene (0.1)	15	<10% conv., 2% **10e**
5	$Pd(OAc)_2$ (4)	RuPhos (6)	***neat***	14.25	100% conv., (16% **10e**, >20:1 dr)
6	$Pd(OAc)_2$ (4)	**(*S*)-^{t}BuPHOX (6)**	toluene (0.33)	15	(81% **10e**, 1.7:1 dr)
7	$Pd(OAc)_2$ (4)	(*R*)-*i*PrPHOX (6)	*neat*	14	(34% **10e**, 5:1 dr)
8	$Pd(OAc)_2$ (4)	**Phox (6)**	***neat***	22	**50 % conv., (35% 10e, 10:1 dr)**
9	$Pd(OAc)_2$ (4)	Phox (6)	toluene (0.5)	21	22% conv., <4% **10e**
10	$Pd(OAc)_2$ (4)	Phox (6)	DMF (0.5)	21	100% conv., trace **10e**
11	$Pd(OAc)_2$ (4)	Phox (6)	1,4-dioxane (0.5)	20	50% conv,, 22% **10e**
12	$Pd(OAc)_2$ (4)	Phox (6)	aniline (3 equiv)	15	13% conv., 14% **10e**
13	$Pd(OAc)_2$ (2)	Phox (3)	*neat*	6	<10% conv., <10% **10e**
14	**$Pd_2(dba)_3$ (1)**	Phox (3)	*neat*	6	**<50% conv., (40% 10e, 6:1 dr)**
15	$[Pd(allyl)Cl]_2$ (1)	Phox (3)	*neat*	6	67% conv, 35% **10e**, 2.5:1 dr
16	**$Pd_2(dba)_3$ (1)**	**Phox (4)**	*neat*	**6**	**90% conv., 84% 10e, 4.3:1 dr (75% 10e, 6:1 dr)**
17	$Pd_2(dba)_3$ (1)	Phox (6)	*neat*	6	100% conv., 50% **10e**, 6:1 dr



Ligand and Selectivity



19a **20a**



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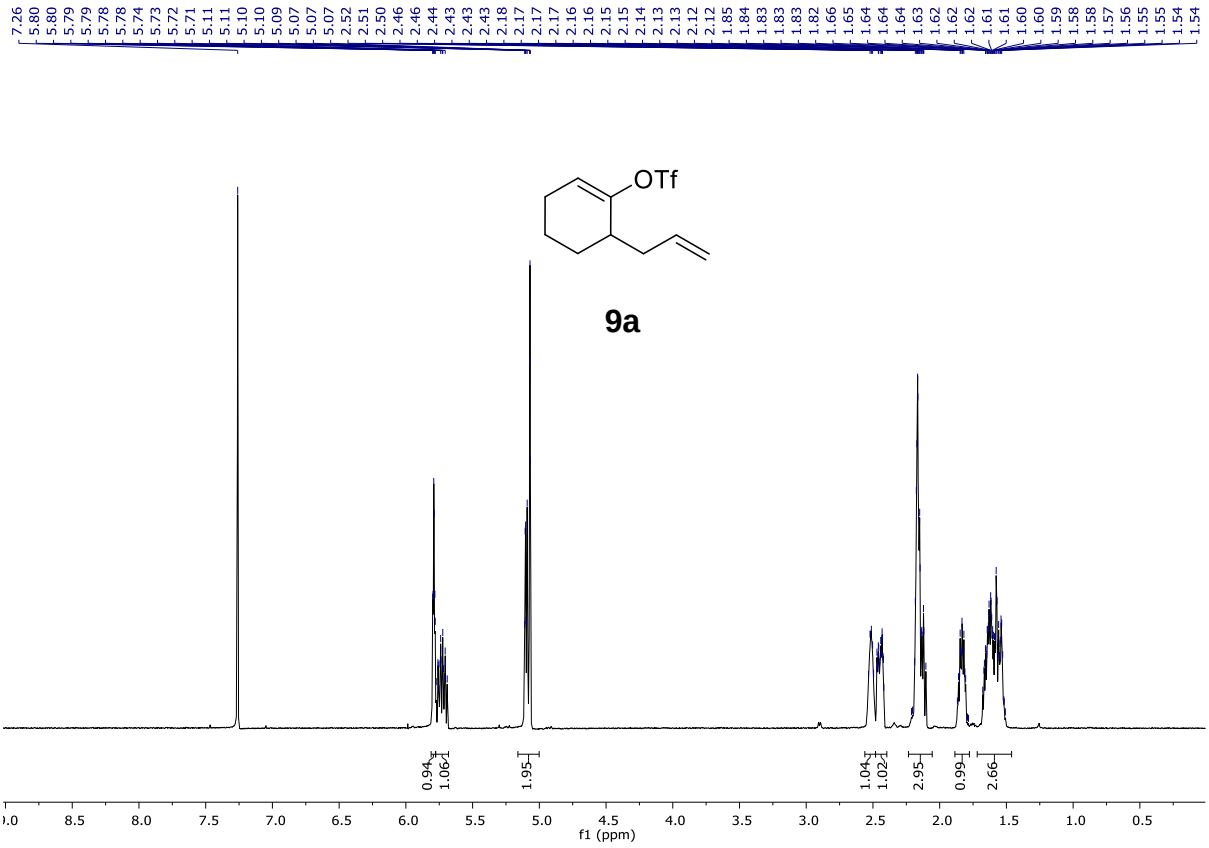
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9a
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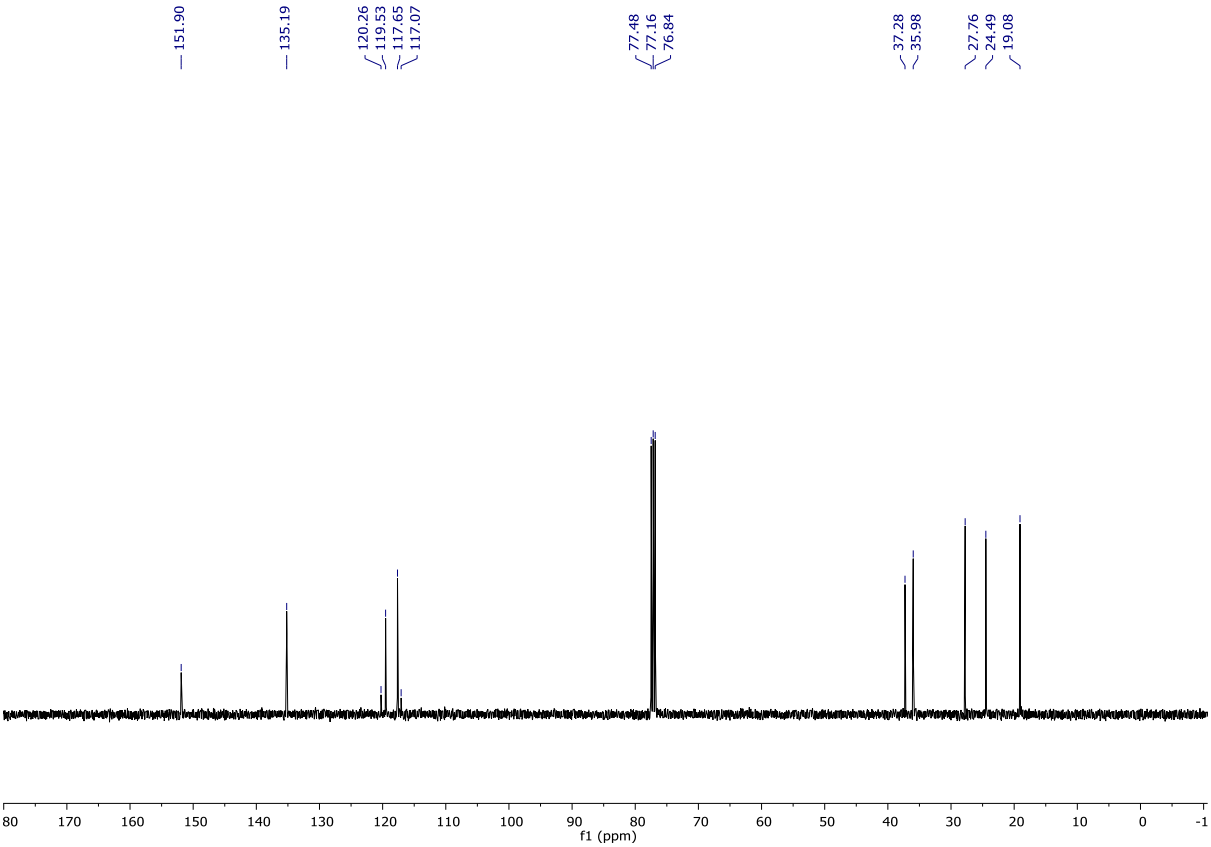
f1 (ppm)


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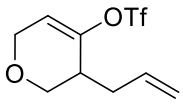
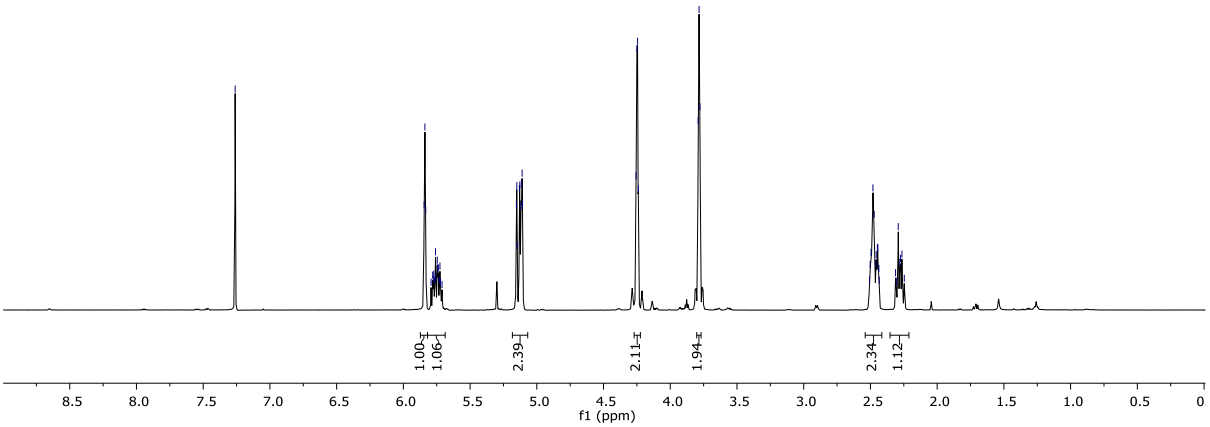
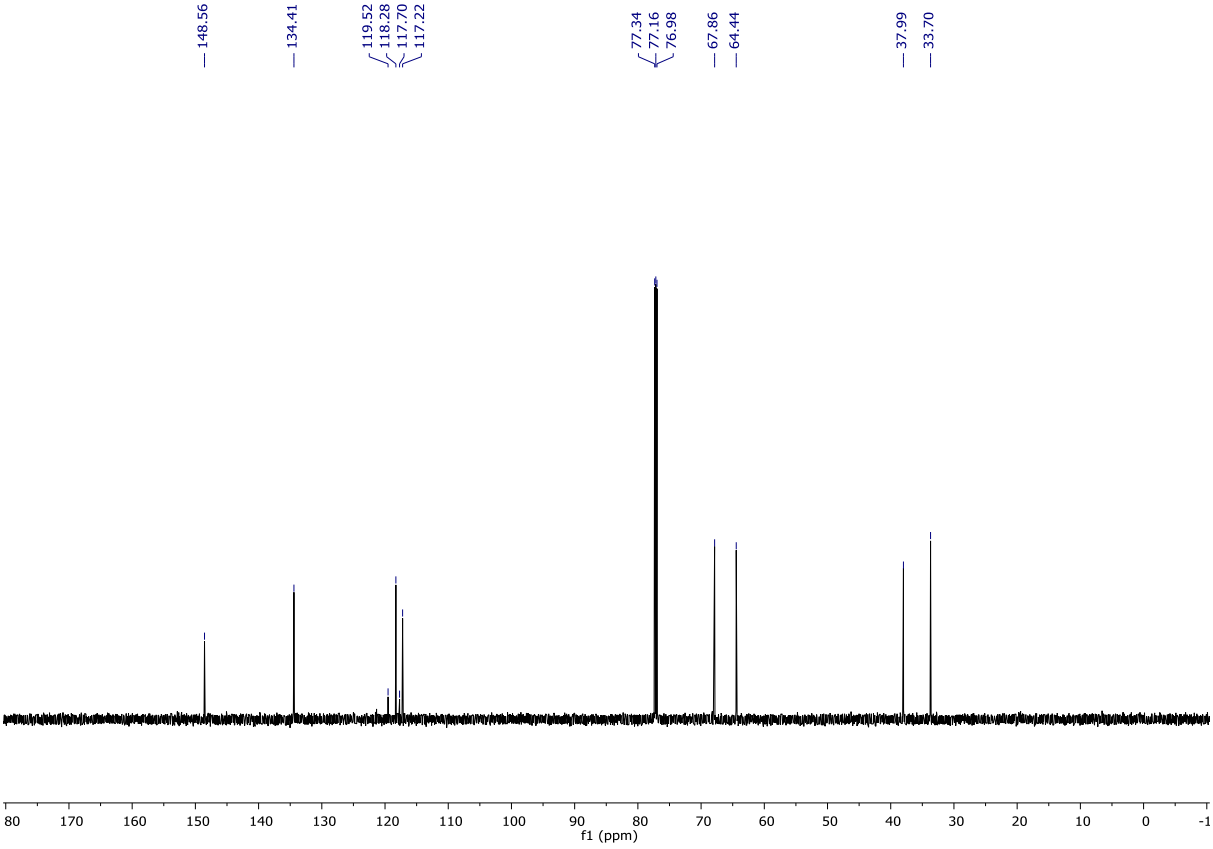
5.73
5.72
5.71
5.15
5.15
5.15
5.13
5.13
5.12
5.12
5.11
4.26
4.25
4.24
4.24
3.79
3.78
3.78
2.51
2.50
2.50
2.48
2.47
2.46
2.46
2.45
2.44
2.44
2.43
2.31
2.31
2.29
2.28
2.27
2.26
2.25


OTf
O

9b


1.00
1.06
2.39
2.11
1.94
2.34
1.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


148.56
134.41
119.52
118.28
117.70
117.22
77.34
77.16
76.98
67.86
64.44
37.99
33.70
80
170
160
150
140
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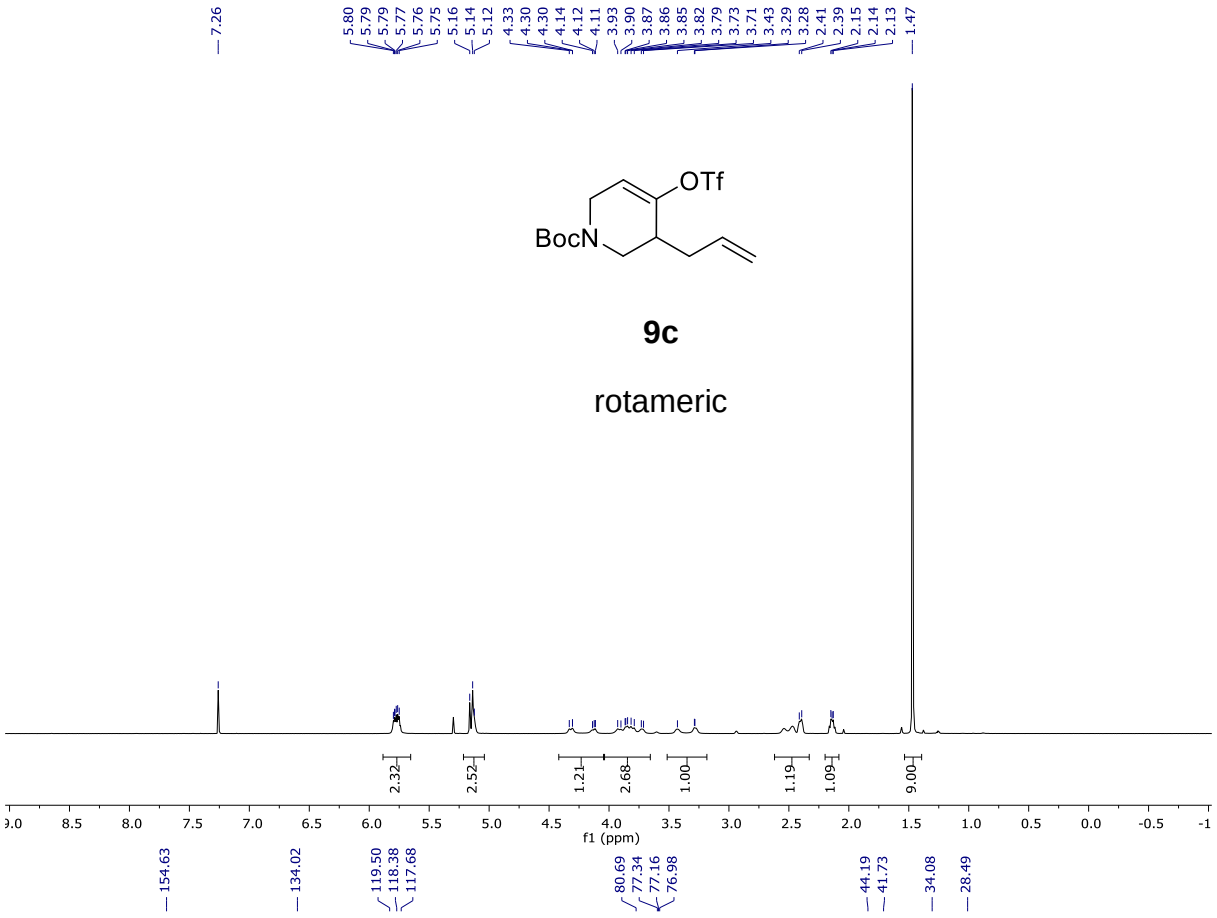
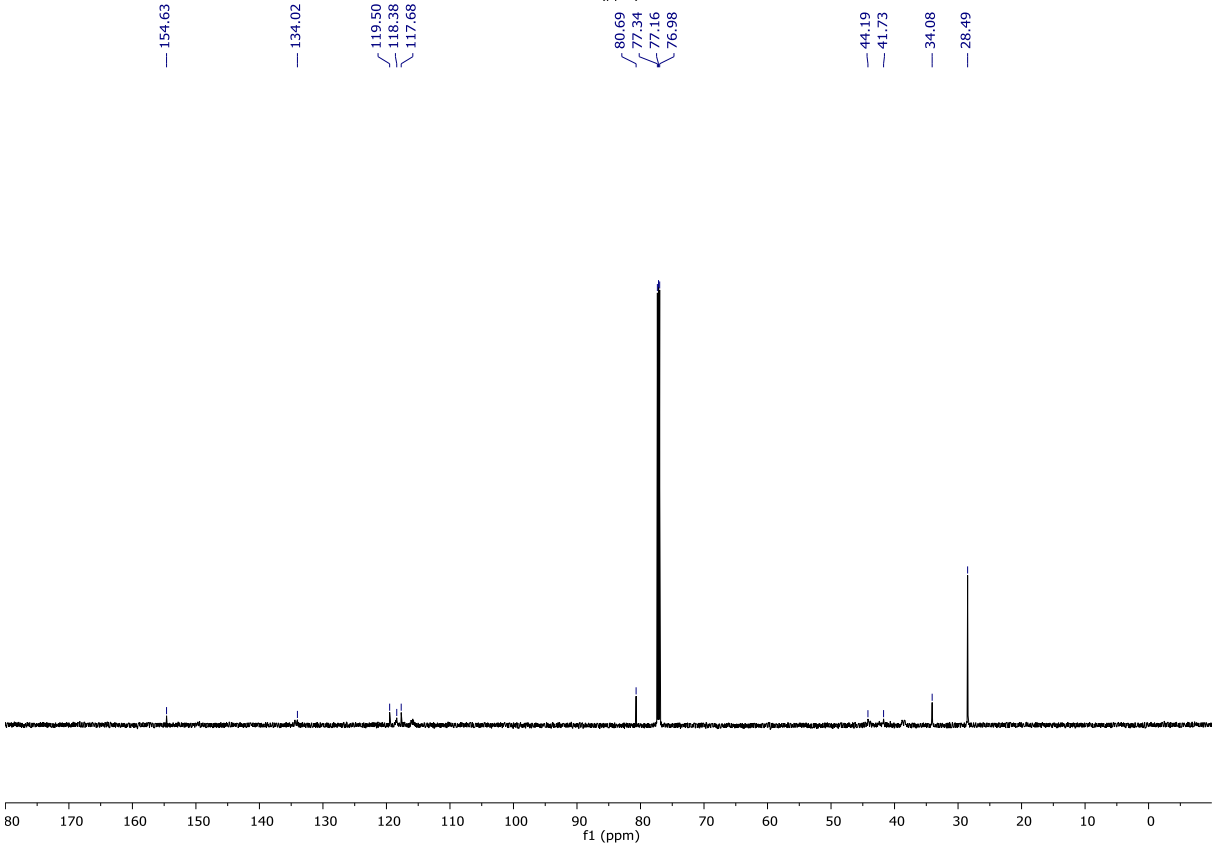
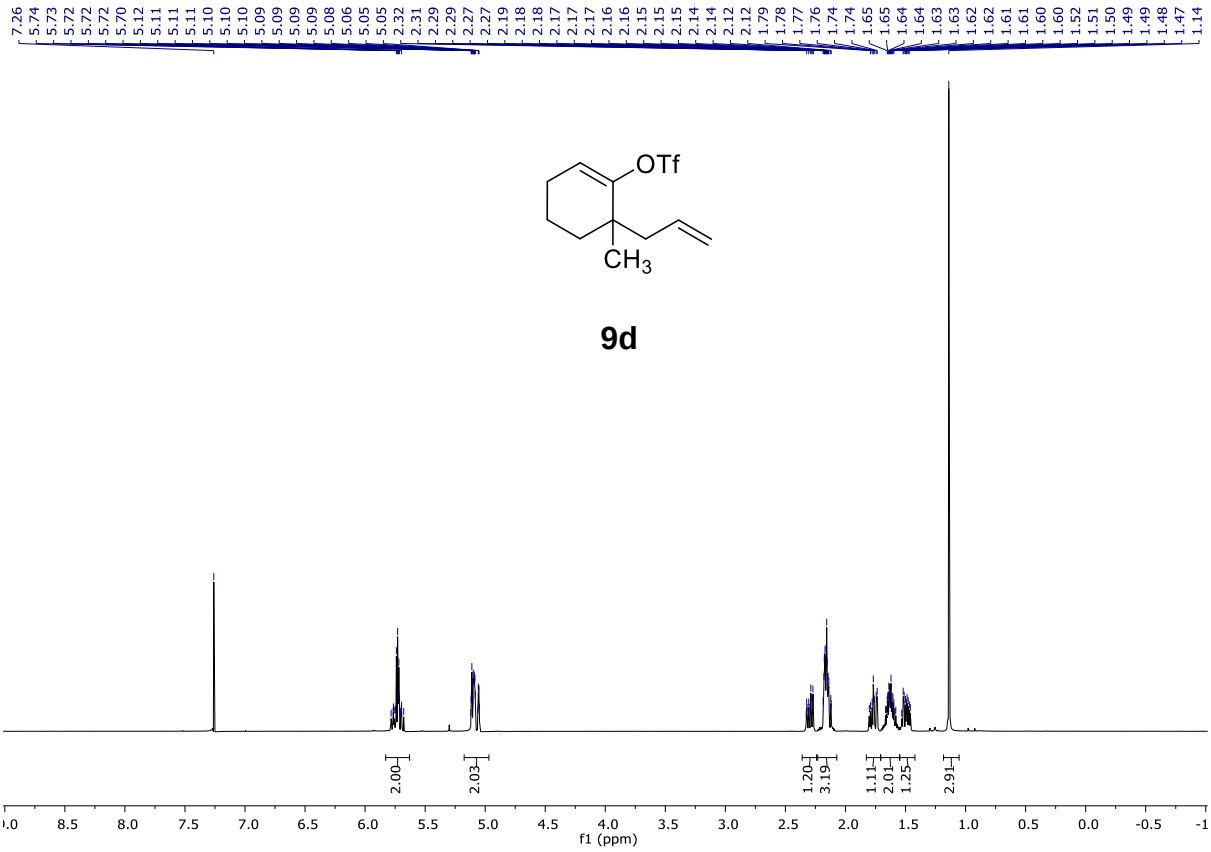
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



9c

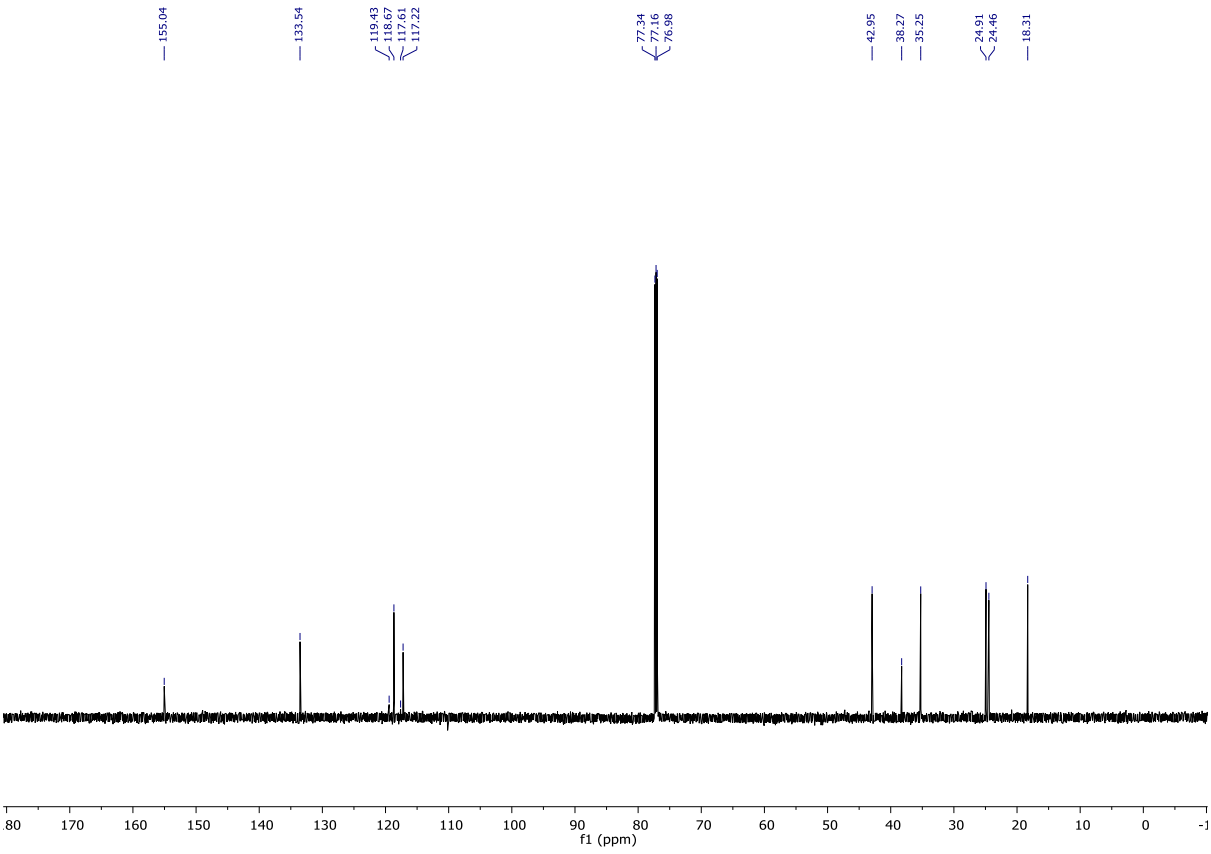
rotameric

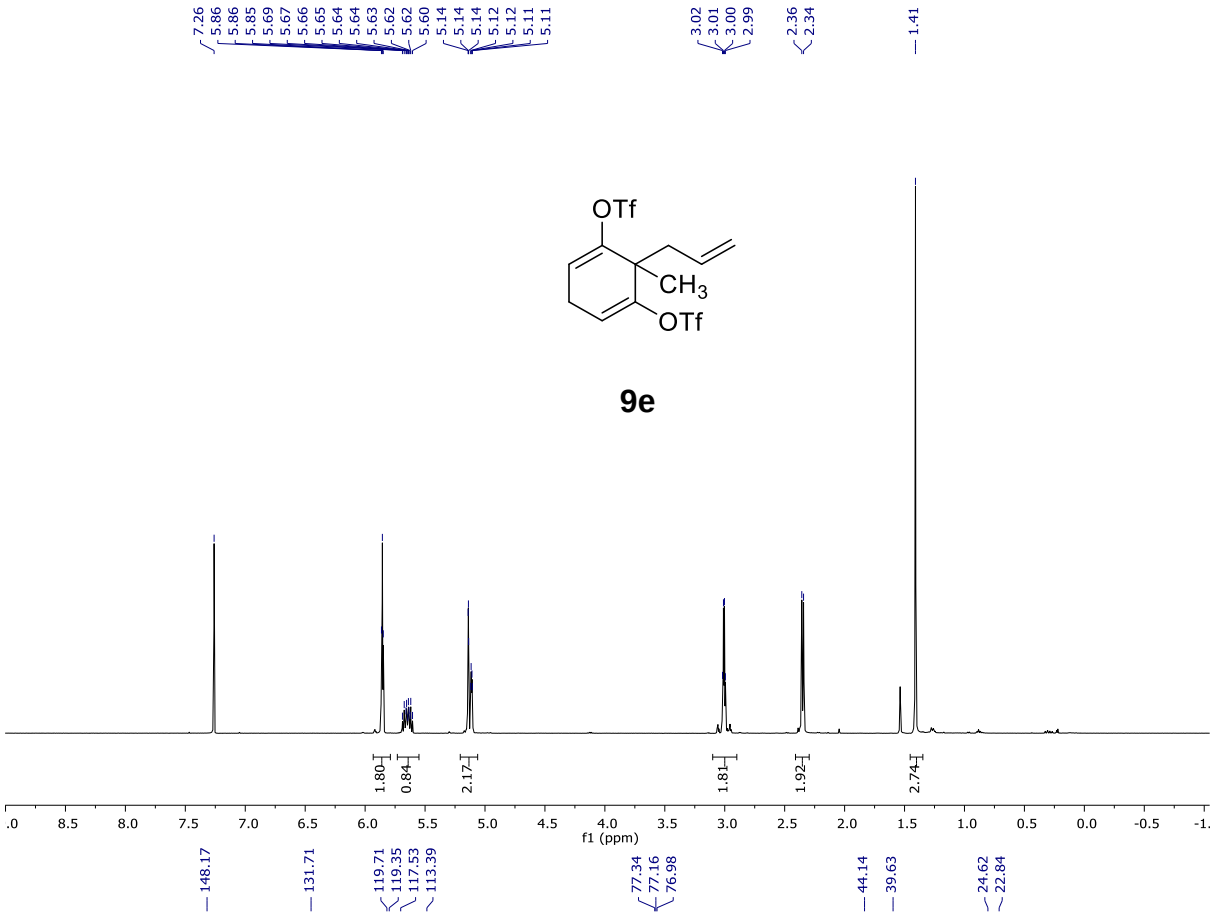



OTf
CH3

9d

7.26 5.74 5.73 5.72 5.72 5.72 5.70 5.12 5.11 5.11 5.11 5.10 5.10 5.10 5.09 5.09 5.09 5.09 5.08 5.06 5.05 5.05 2.32 2.31 2.29 2.29 2.27 2.27 2.19 2.18 2.18 2.17 2.17 2.17 2.16 2.16 2.15 2.15 2.15 2.14 2.14 2.12 2.12 1.79 1.78 1.77 1.76 1.74 1.74 1.65 1.65 1.64 1.64 1.63 1.63 1.62 1.62 1.61 1.61 1.60 1.60 1.52 1.51 1.50 1.49 1.49 1.48 1.47 1.14
2.00 2.03 1.20 3.19 1.11 2.01 1.25 2.91
f1 (ppm)


155.04 133.54 119.43 118.67 117.61 117.22 77.34 77.16 76.98 42.95 38.27 35.25 24.91 24.46 18.31
f1 (ppm)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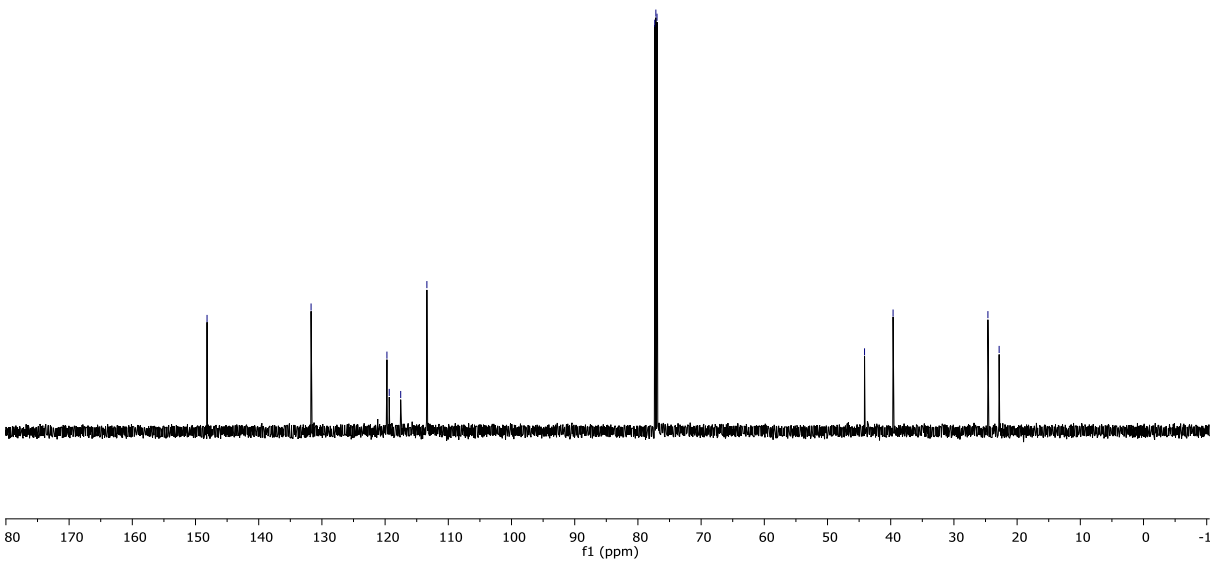
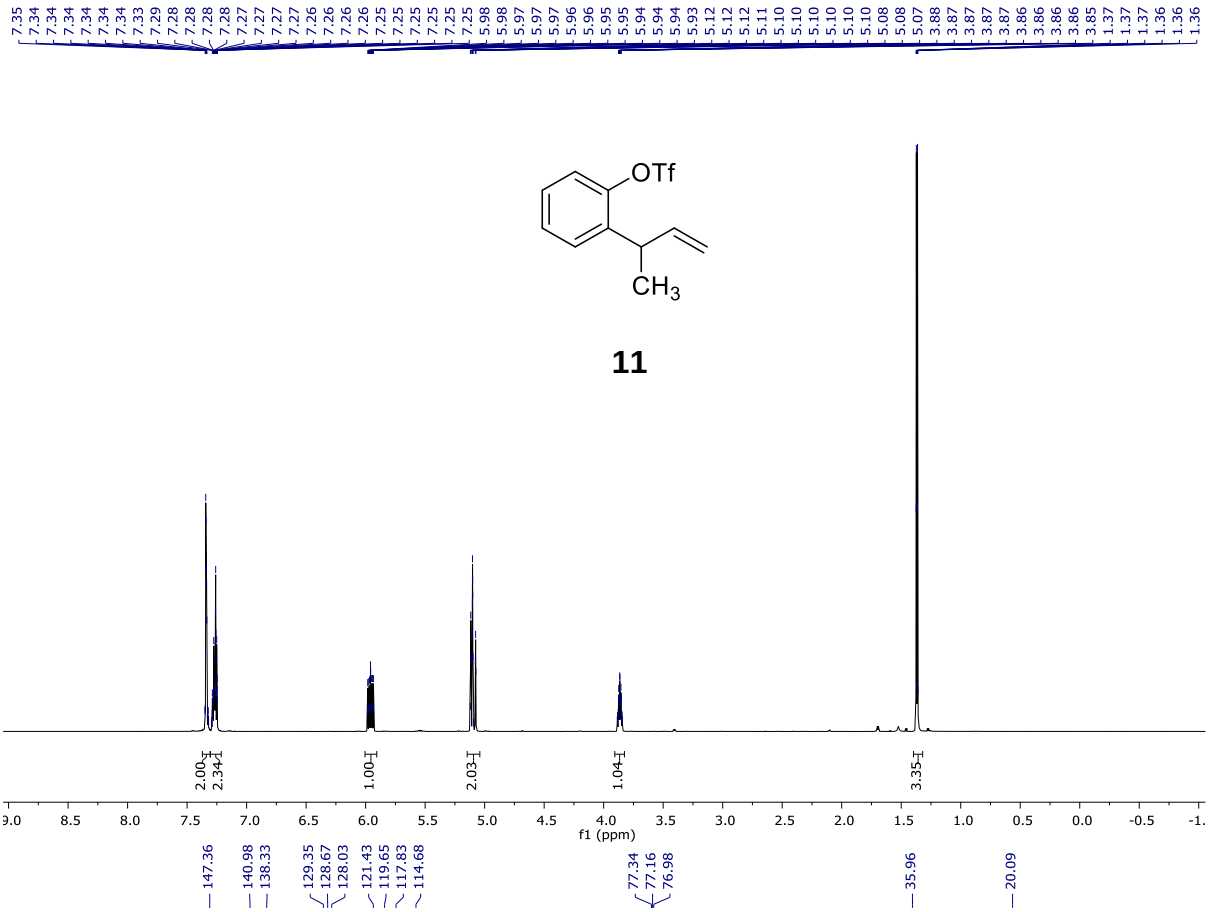
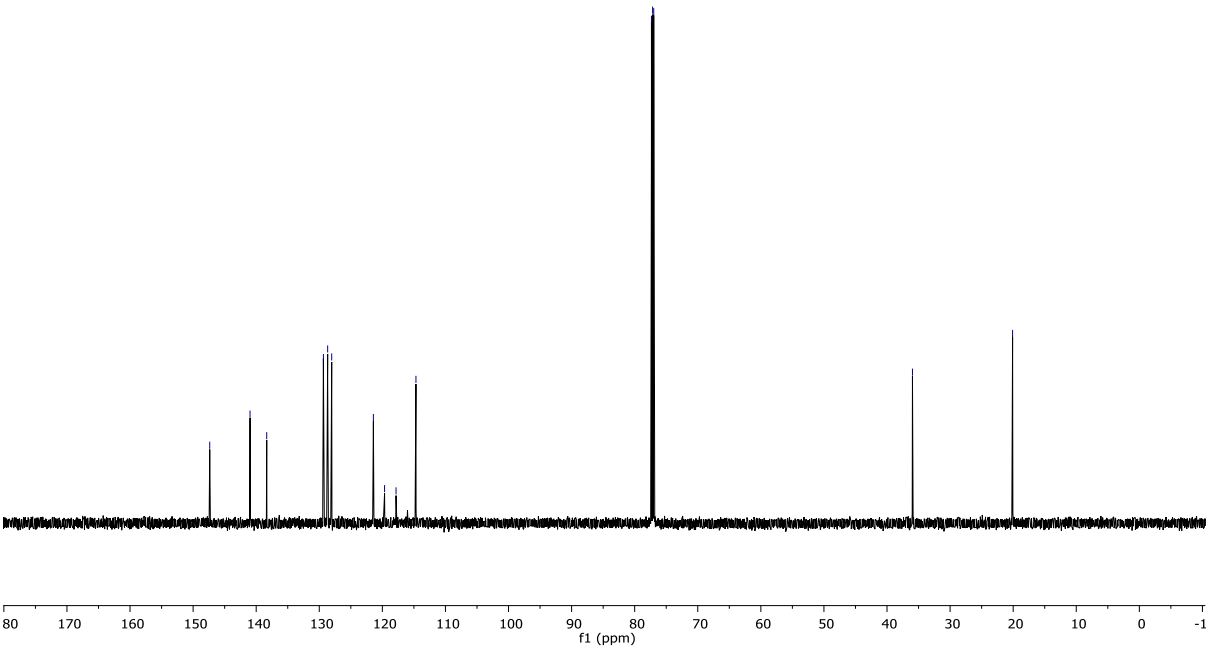
5.86
5.85
5.69
5.67
5.66
5.65
5.64
5.64
5.63
5.62
5.62
5.60
5.14
5.14
5.14
5.12
5.12
5.11
5.11
3.02
3.01
3.00
2.99
2.36
2.34
1.41
OTf
CH3
OTf
1.80
0.84
2.17
1.81
1.92
2.74
f1 (ppm)

9e


148.17
131.71
119.71
119.35
117.53
113.39
77.34
77.16
76.98
44.14
39.63
24.62
22.84
f1 (ppm)


OTf
CH3
11
f1 (ppm)


f1 (ppm)


7.26
5.77
5.75
5.74
5.73
5.66
5.65
5.65
5.65
5.11
5.11
5.11
5.09
5.09
5.08
5.08
5.08
5.08
5.08
5.07
5.07
5.07
5.07
5.06
2.92
2.92
2.40
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2.38
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2.37
2.37
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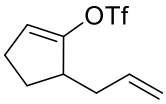
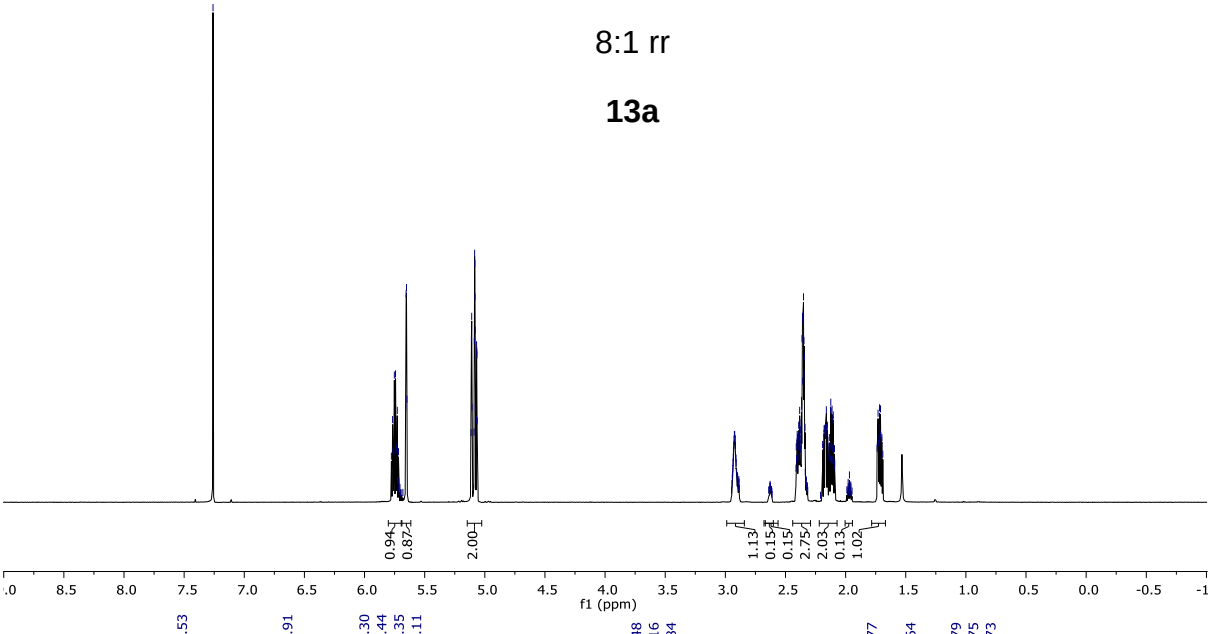
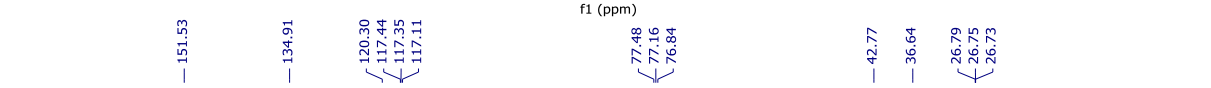
2.36
2.36
2.35
2.35
2.35
2.35
2.35
2.34
2.34
2.18
2.18
2.17
2.17
2.17
2.17
2.16
2.16
2.16
2.15
2.13
2.12
2.11
2.11
2.10
2.10
1.73
1.72
1.72
1.71
1.71
1.71

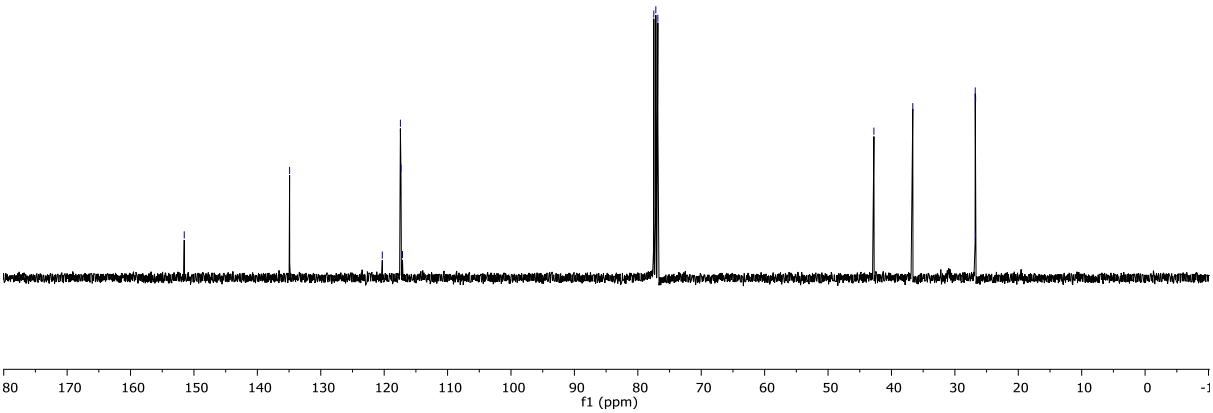

OTf

8:1 rr

13a


0.94
0.87
2.00
1.13
0.15
0.15
2.75
2.03
0.13
1.02
f1 (ppm)


151.53
134.91
120.30
117.44
117.35
117.11
77.48
77.16
76.84
42.77
36.64
26.79
26.75
26.73


f1 (ppm)


7.26
5.78
5.77
5.77
5.70
5.70
5.69
5.68
5.18
5.17
5.17
5.15
5.15
5.15
5.15
5.14
5.14
5.13
5.13
5.13
5.12
5.12
4.23
4.22
4.21
4.20
4.19
4.19
4.17
4.17
4.16
4.15
2.67
2.65
2.63
2.63
2.63
2.61
2.61
2.61
2.61
2.49
2.49
2.49
2.49
2.48
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2.47
2.47
2.46
2.45
2.45
2.45
2.44
2.44
2.44
2.42
2.37
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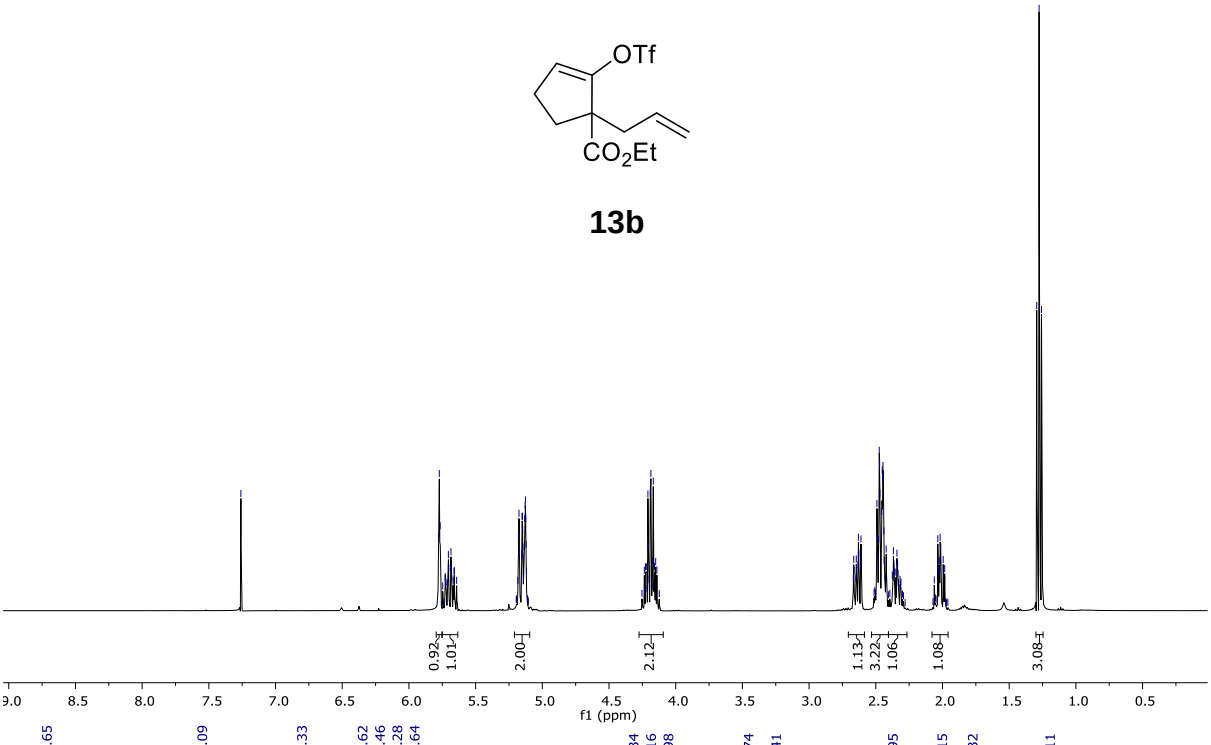
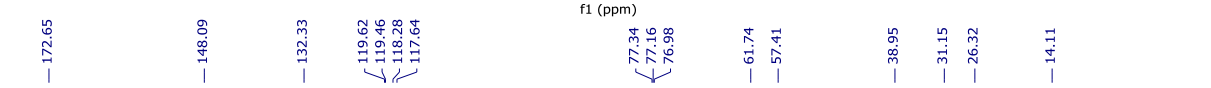
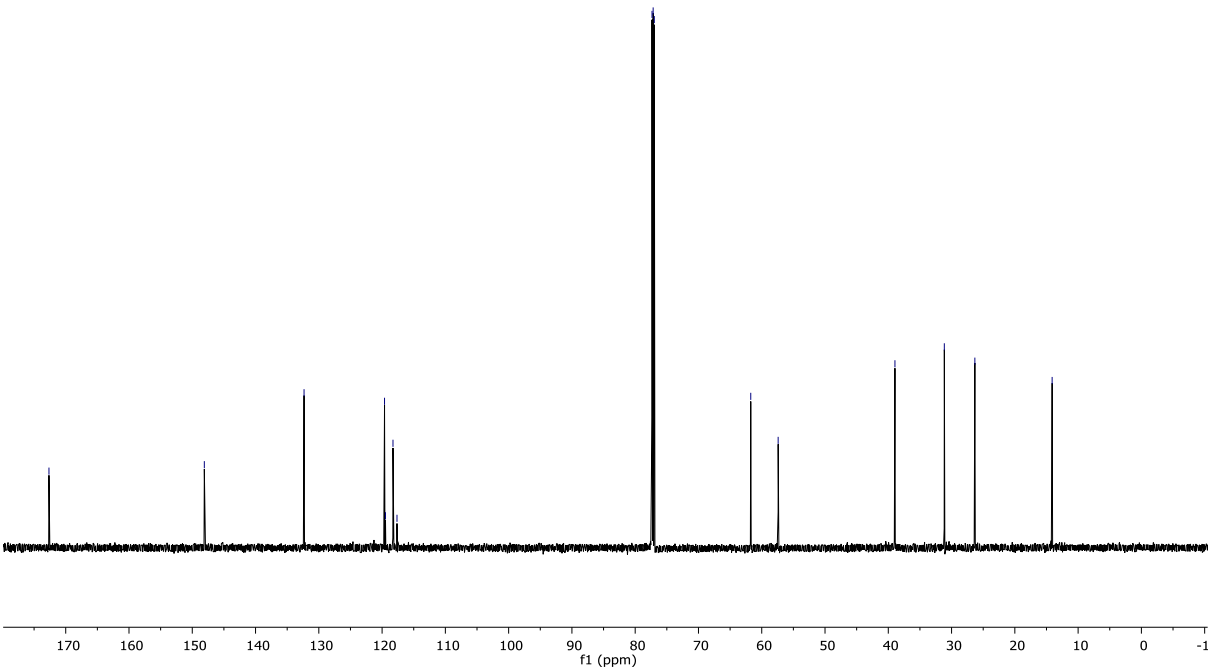
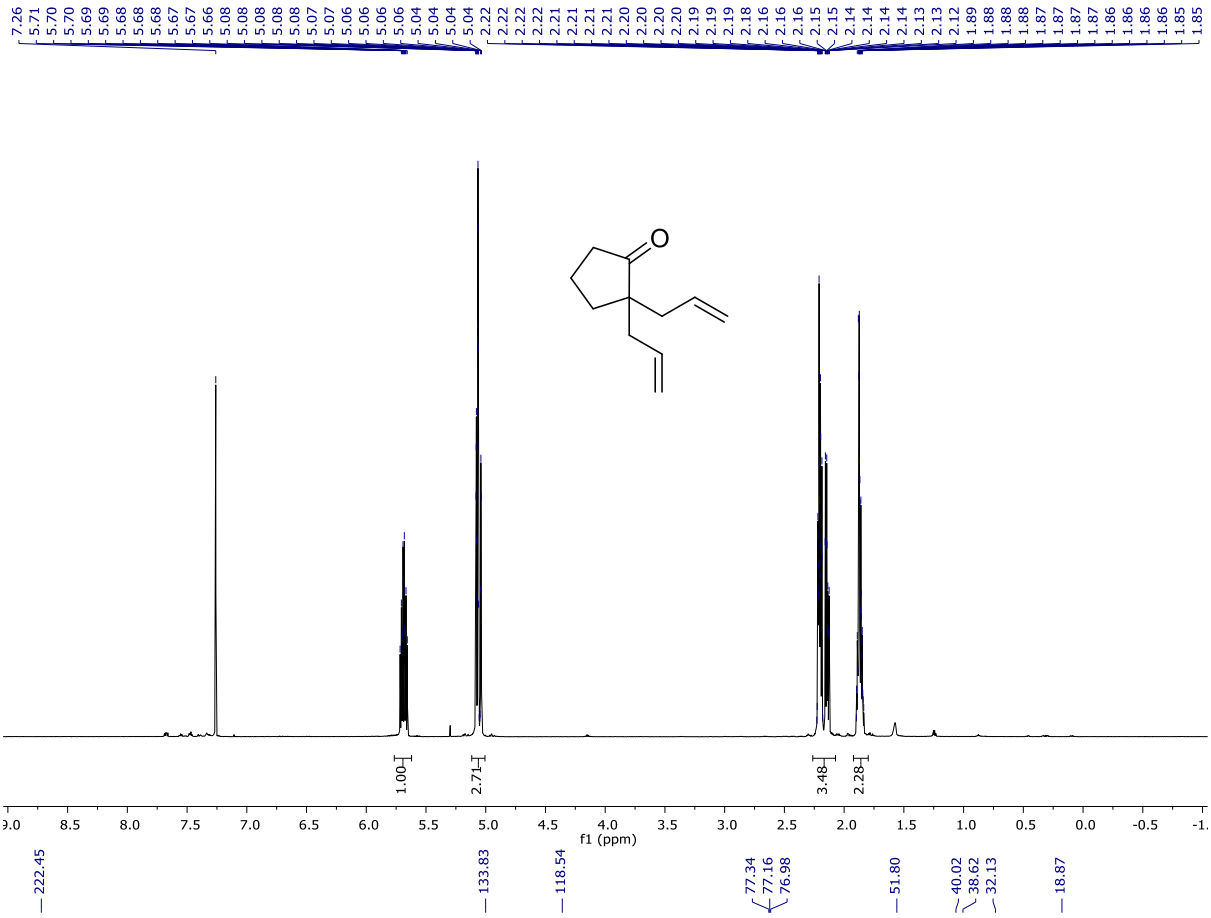
2.02
2.01
1.99
1.29
1.28
1.26

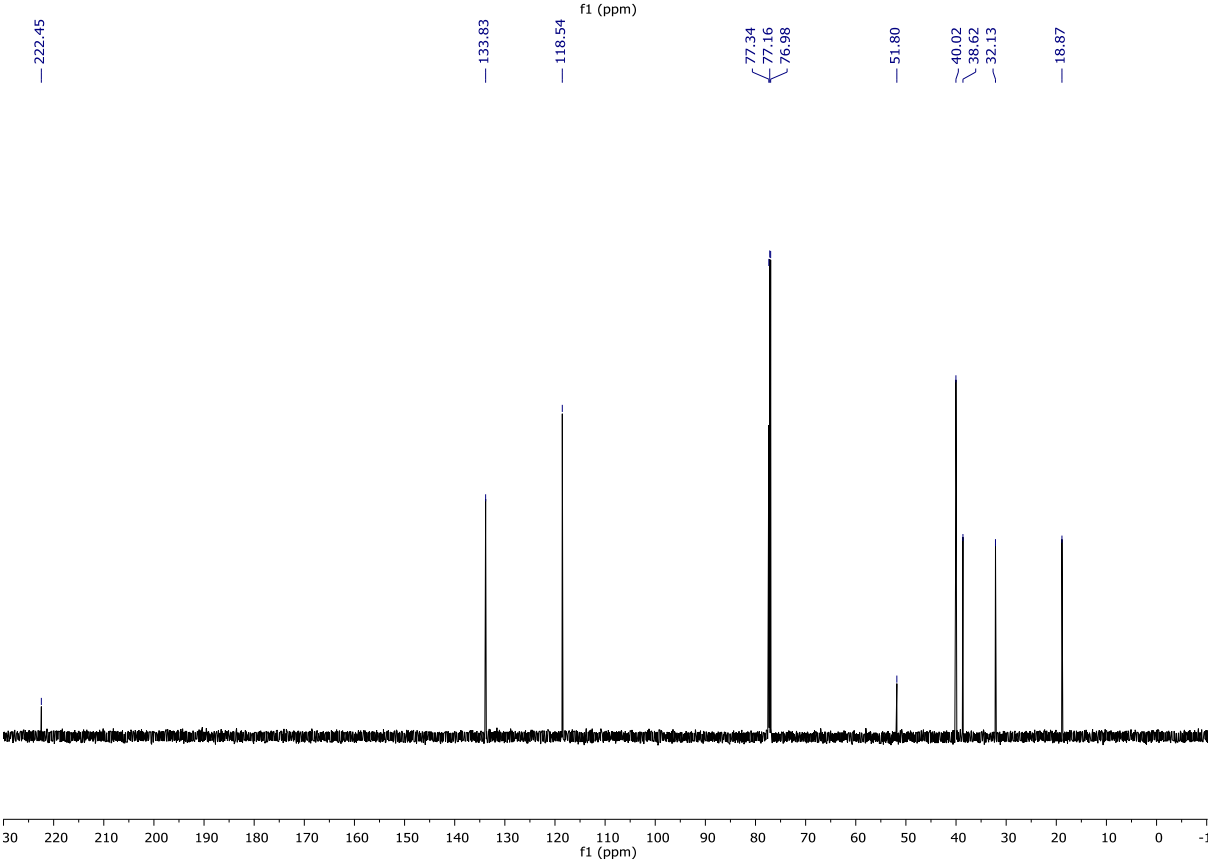

OTf
CO2Et
0.92
1.01
2.00
2.12
1.13
3.22
1.06
1.08
3.08
f1 (ppm)

13b


172.65
148.09
132.33
119.62
119.46
118.28
117.64
77.34
77.16
76.98
61.74
57.41
38.95
31.15
26.32
14.11


f1 (ppm)


7.26 5.71 5.70 5.70 5.69 5.69 5.68 5.68 5.68 5.67 5.67 5.66 5.08 5.08 5.08 5.08 5.07 5.07 5.06 5.06 5.06 5.06 5.04 5.04 5.04 5.04 2.22 2.22 2.22 2.22 2.21 2.21 2.21 2.21 2.20 2.20 2.20 2.20 2.19 2.19 2.19 2.18 2.16 2.16 2.16 2.15 2.15 2.14 2.14 2.14 2.14 2.13 2.13 2.12 1.89 1.88 1.88 1.88 1.87 1.87 1.87 1.87 1.86 1.86 1.86 1.85 1.85
O
1.00
2.71
3.48
2.28
f1 (ppm)


222.45
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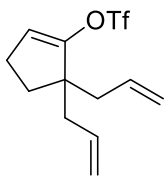
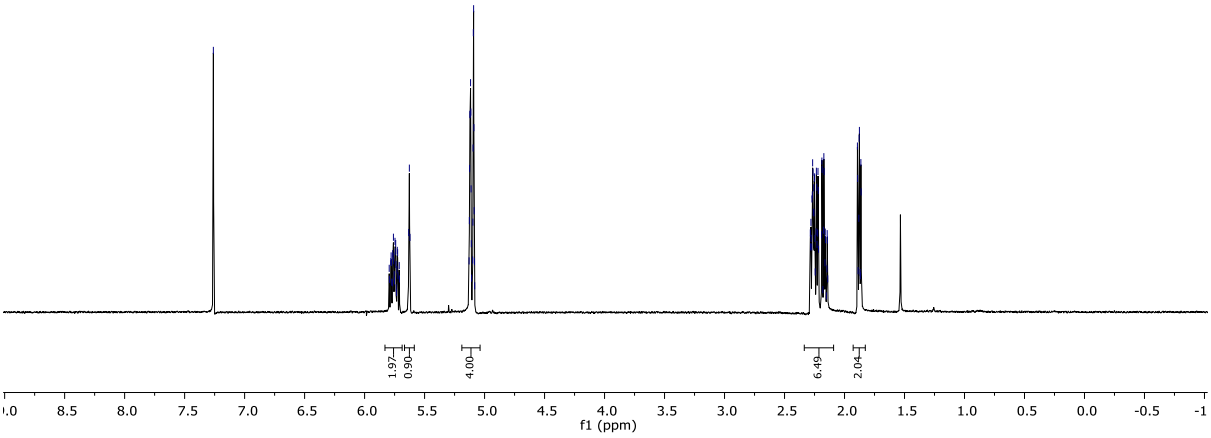
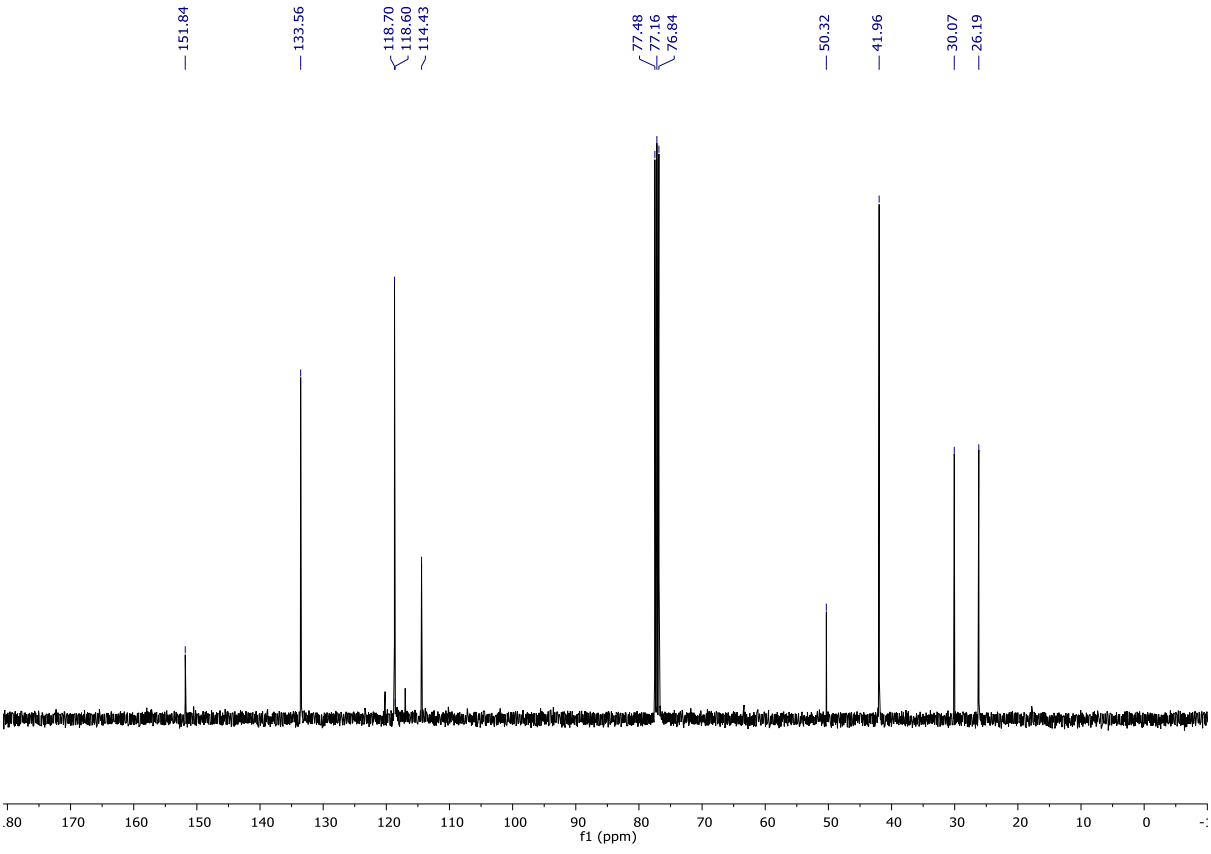
118.54
77.34
77.16
76.98
51.80
40.02
38.62
32.13
18.87
f1 (ppm)


OTf

13c


1.97
0.90
4.00
6.49
2.04
f1 (ppm)


151.84
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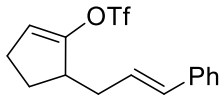
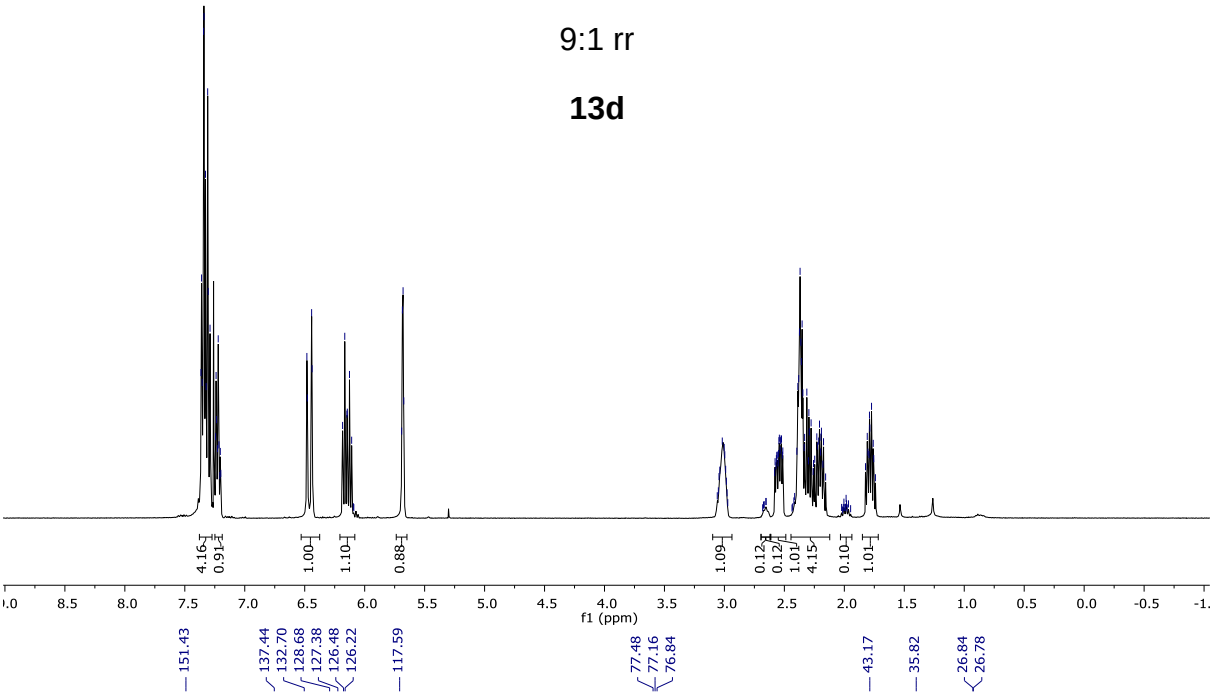
118.60
114.43
77.48
77.16
76.84
50.32
41.96
30.07
26.19
f1 (ppm)

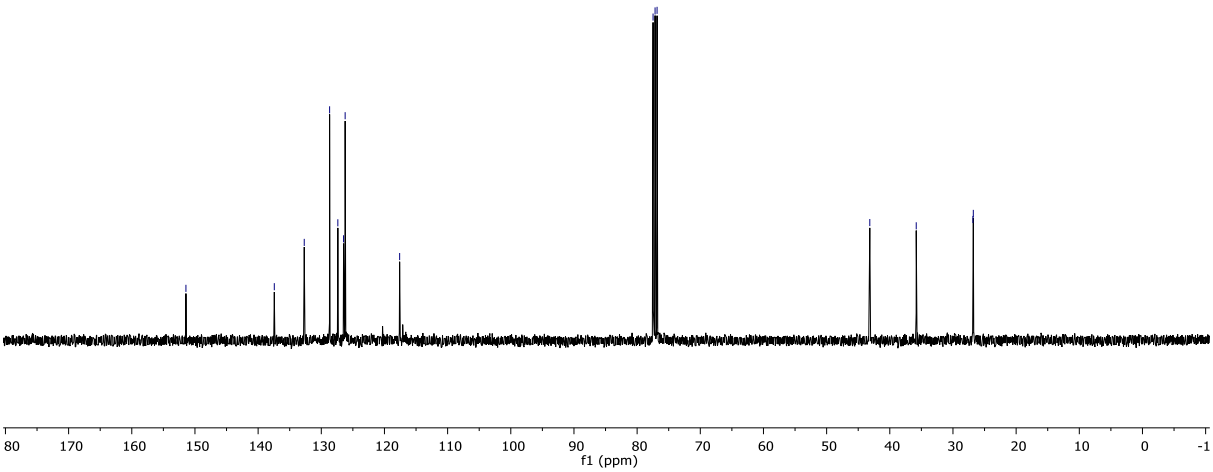

OTf
Ph

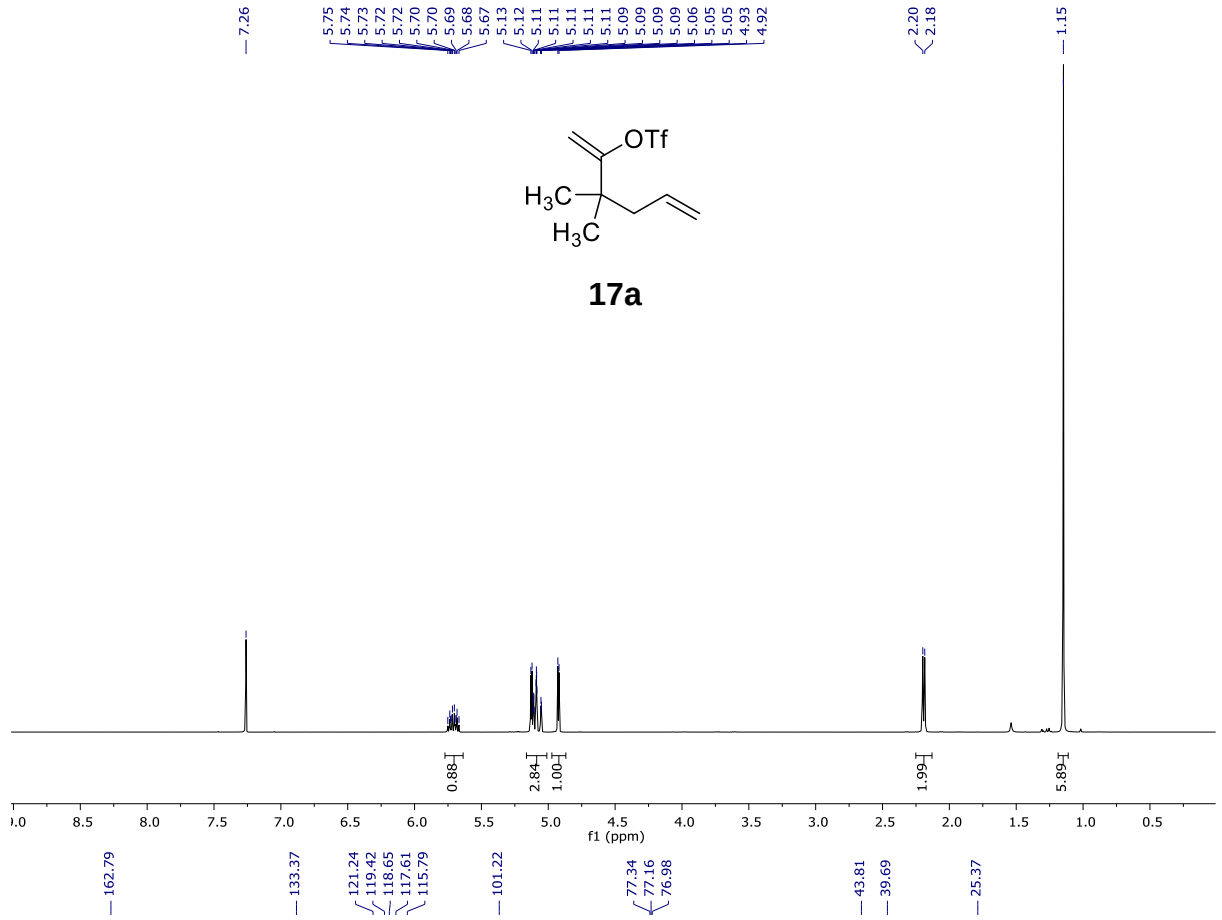
9:1 rr

13d

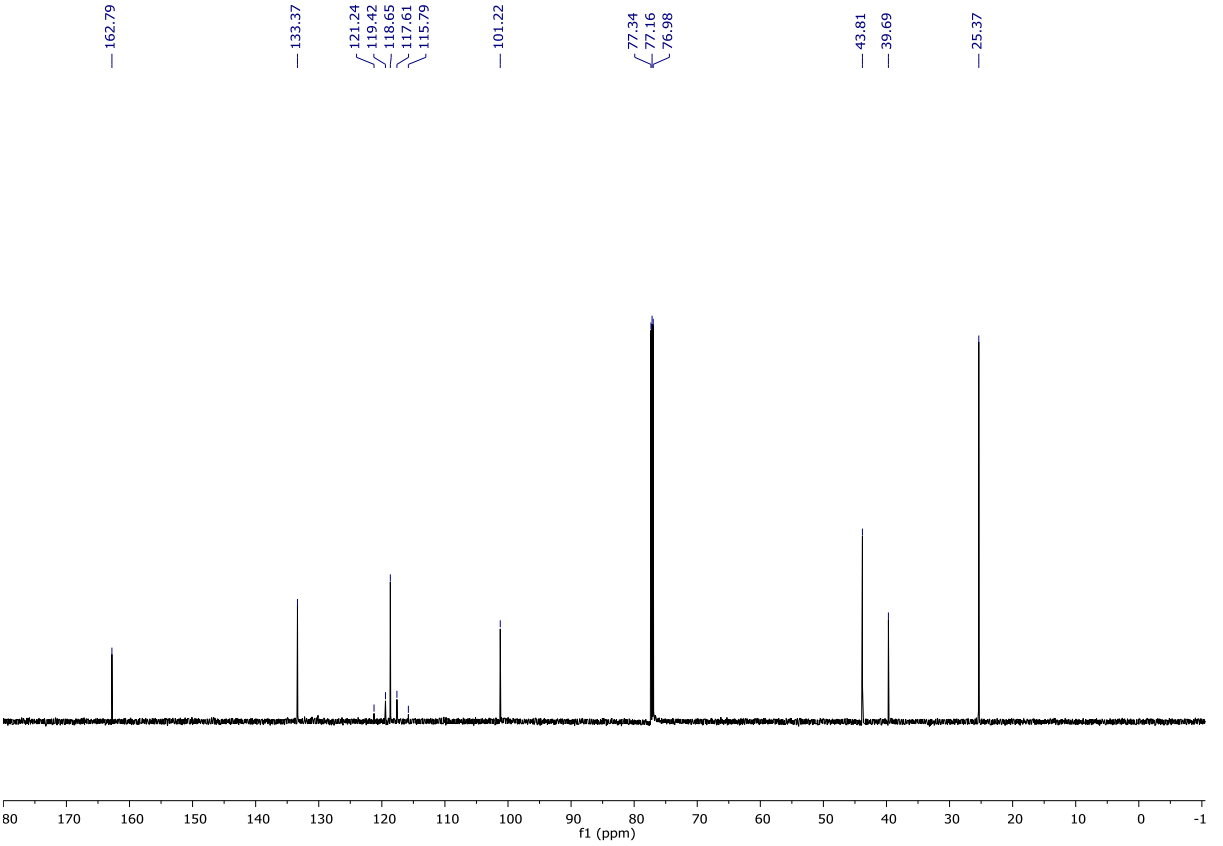

4.16
0.91
1.00
1.10
0.88
1.09
0.12
0.12
1.01
4.15
0.10
1.01
f1 (ppm)

151.43
137.44
132.70
128.68
127.38
126.48
126.22
117.59
77.48
77.16
76.84
43.17
35.82
26.84
26.78


f1 (ppm)


7.26
5.75
5.74
5.73
5.72
5.72
5.70
5.70
5.69
5.68
5.67
5.13
5.12
5.11
5.11
5.11
5.11
5.11
5.09
5.09
5.09
5.09
5.06
5.05
5.05
4.93
4.92
2.20
2.18
1.15
OTf
H3C
H3C
0.88
2.84
1.00
1.99
5.89
f1 (ppm)

17a


162.79
133.37
121.24
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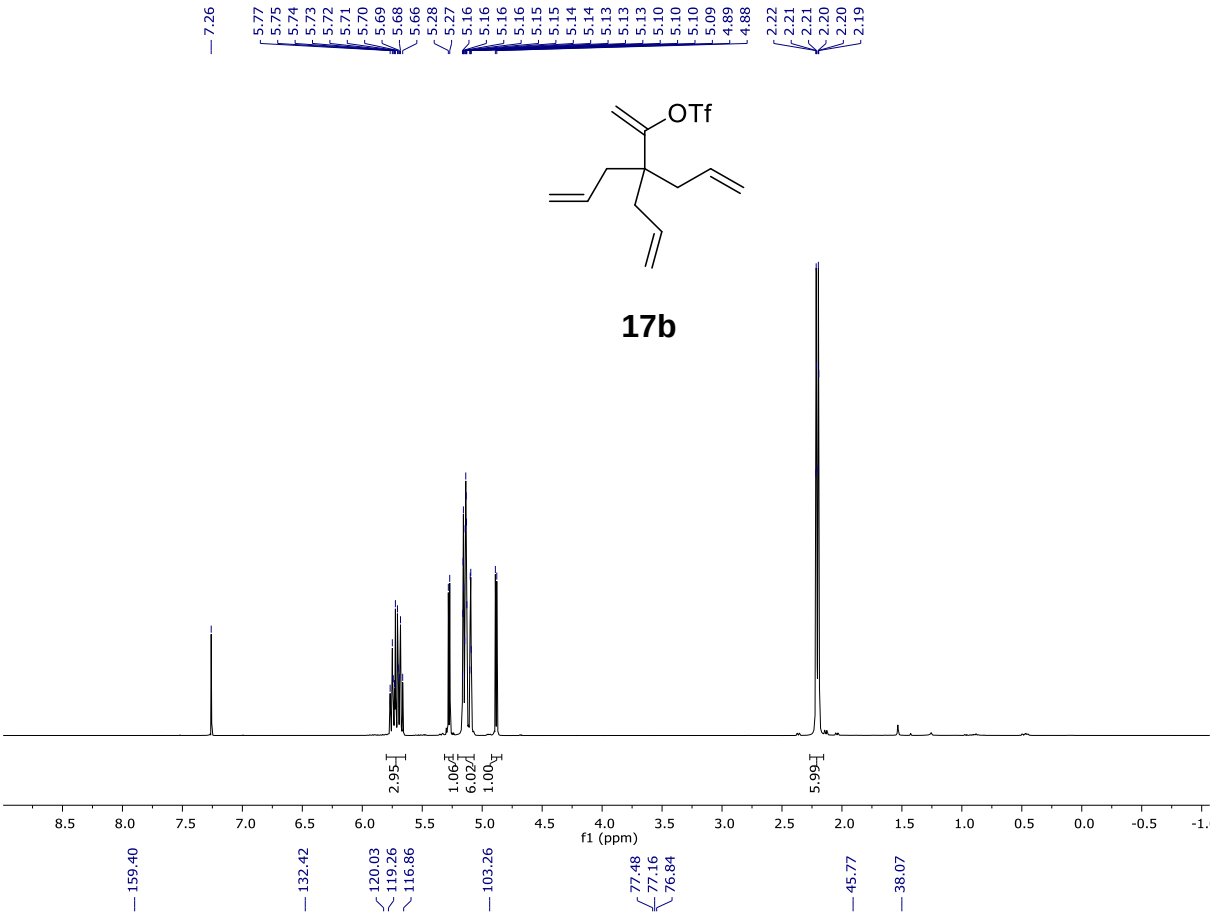
118.65
117.61
115.79
101.22
77.34
77.16
76.98
43.81
39.69
25.37
f1 (ppm)


7.26
5.77
5.75
5.74
5.73
5.72
5.71
5.70
5.69
5.68
5.66
5.28
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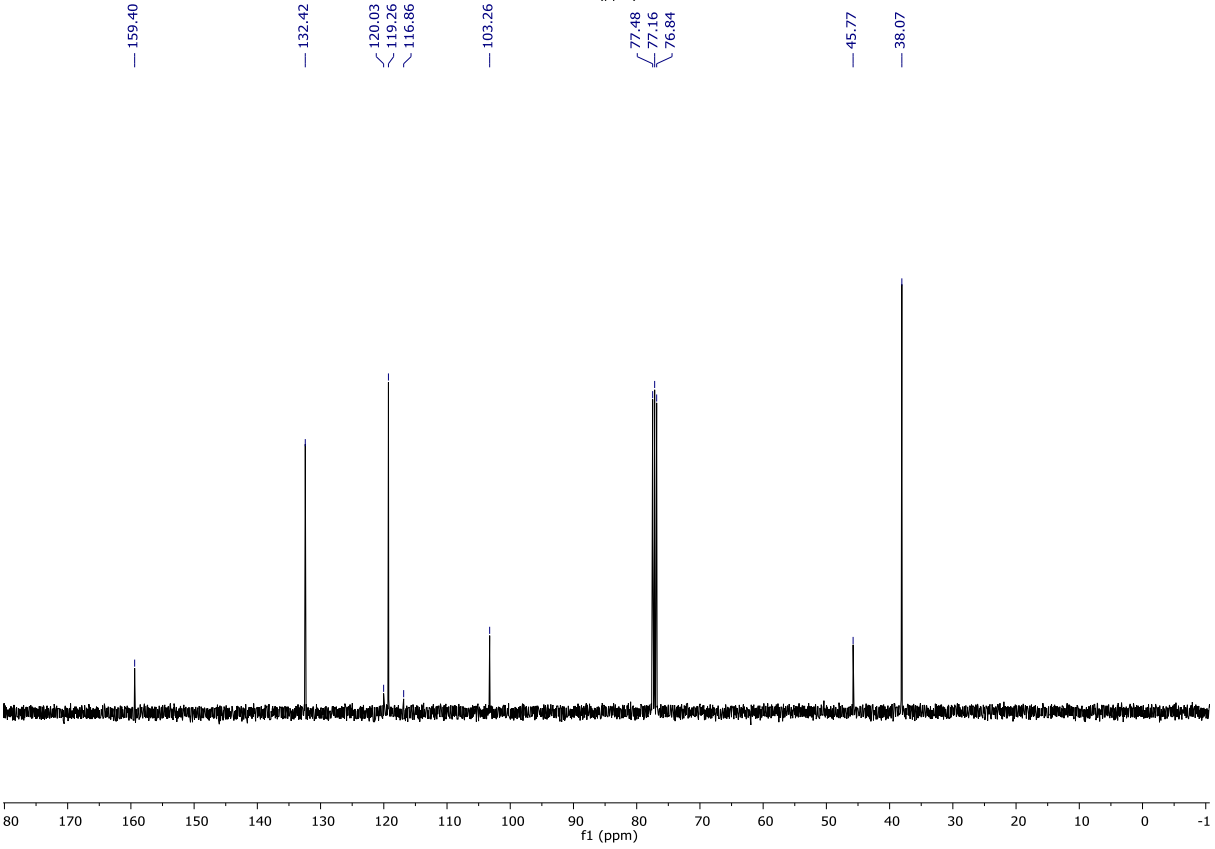
5.16
5.16
5.16
5.16
5.15
5.15
5.14
5.14
5.13
5.13
5.13
5.10
5.10
5.10
5.09
4.89
4.88
2.22
2.21
2.21
2.20
2.20
2.19
OTf
17b
2.95
1.06
6.02
1.00
5.99
f1 (ppm)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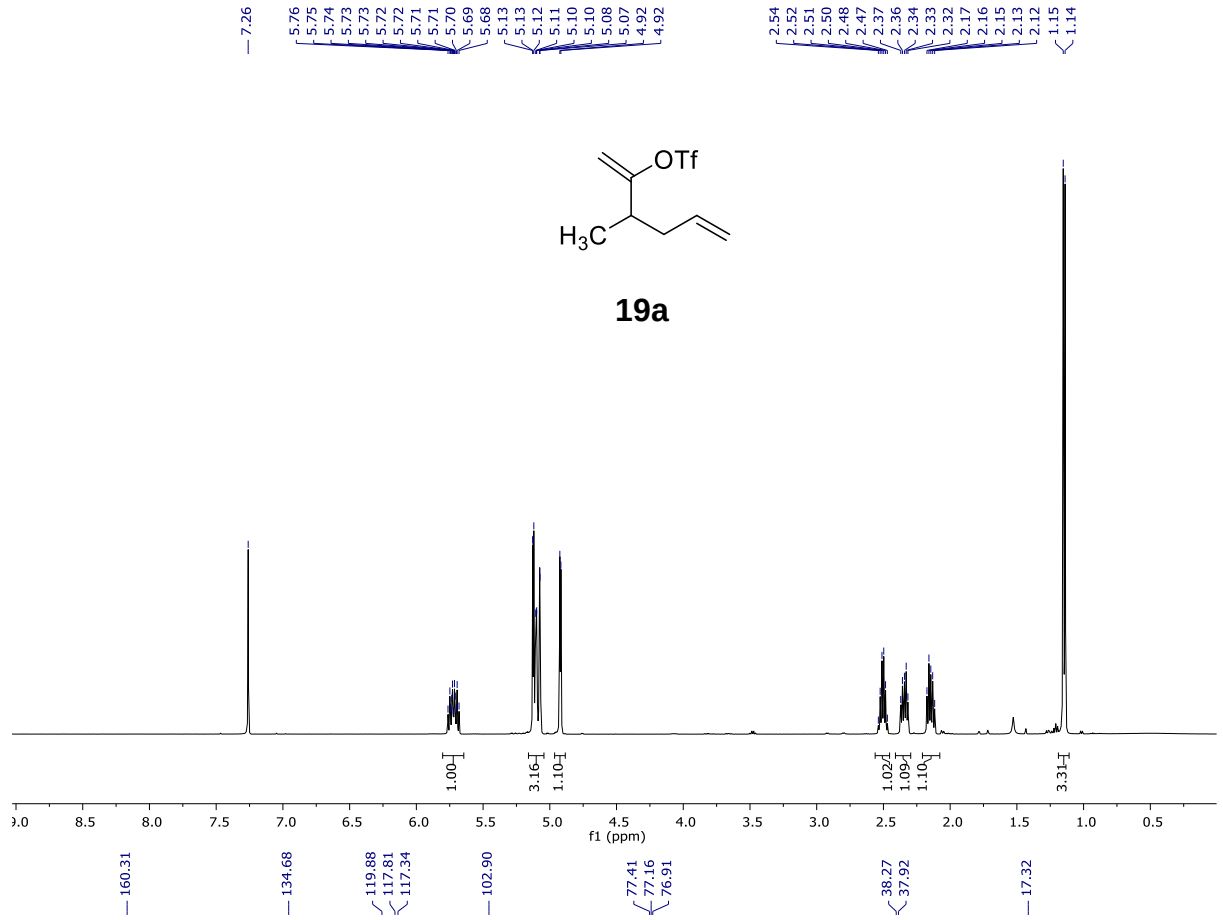
119.26
116.86
103.26
77.48
77.16
76.84
45.77
38.07
f1 (ppm)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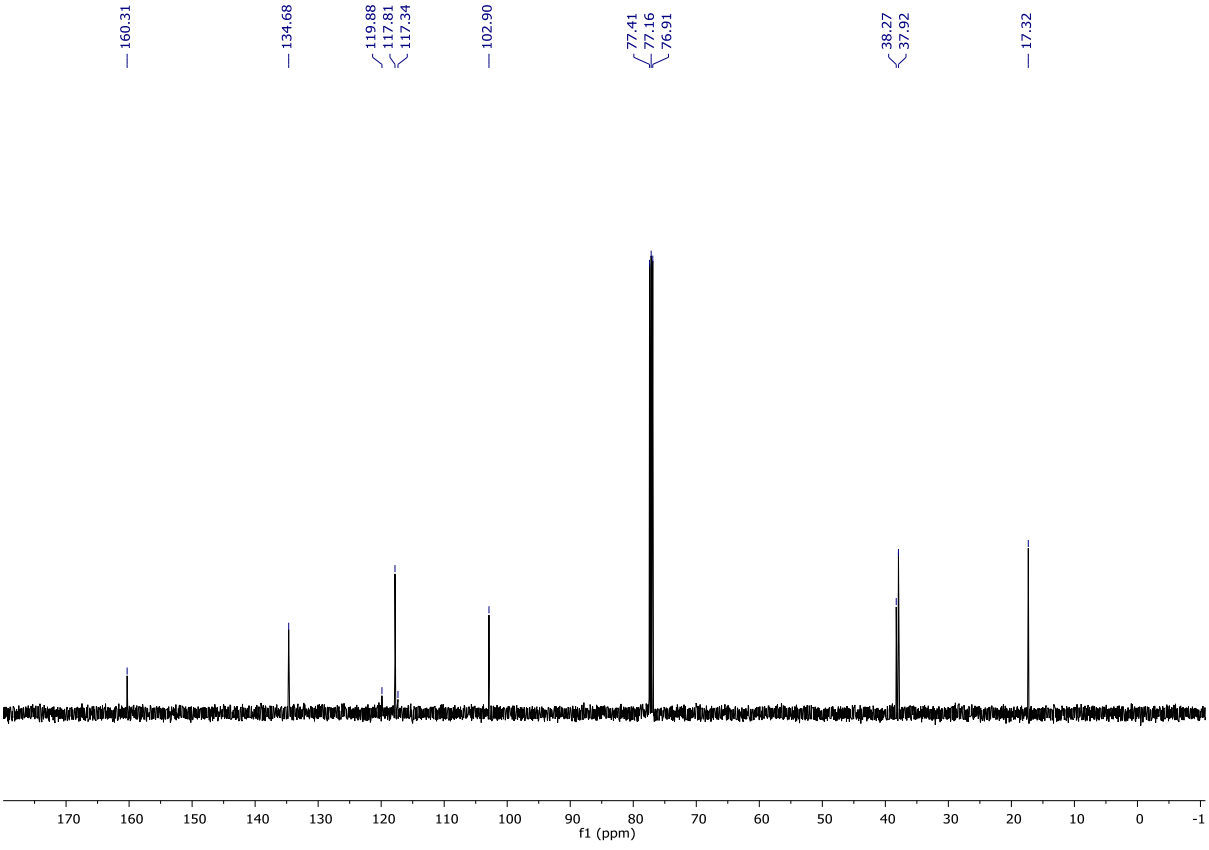
5.75
5.74
5.73
5.73
5.72
5.72
5.71
5.71
5.70
5.69
5.68
5.13
5.13
5.12
5.11
5.10
5.10
5.08
5.07
4.92
4.92
2.54
2.52
2.51
2.50
2.48
2.47
2.37
2.36
2.34
2.33
2.32
2.17
2.16
2.15
2.13
2.12
1.15
1.14
OTf
H3C
19a
1.00
3.16
1.10
1.02
1.09
1.10
3.31
f1 (ppm)


160.31
134.68
119.88
117.81
117.34
102.90
77.41
77.16
76.91
38.27
37.92
17.32
f1 (ppm)


7.36
7.35
7.33
7.30
7.29
7.27
7.26
7.23
7.22
5.70
5.68
5.68
5.67
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5.61
5.25
5.24
5.09
5.09
5.07
5.06
5.06
5.06
5.05
5.04
5.04
5.03
5.02
5.01
3.62
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2.71
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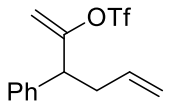
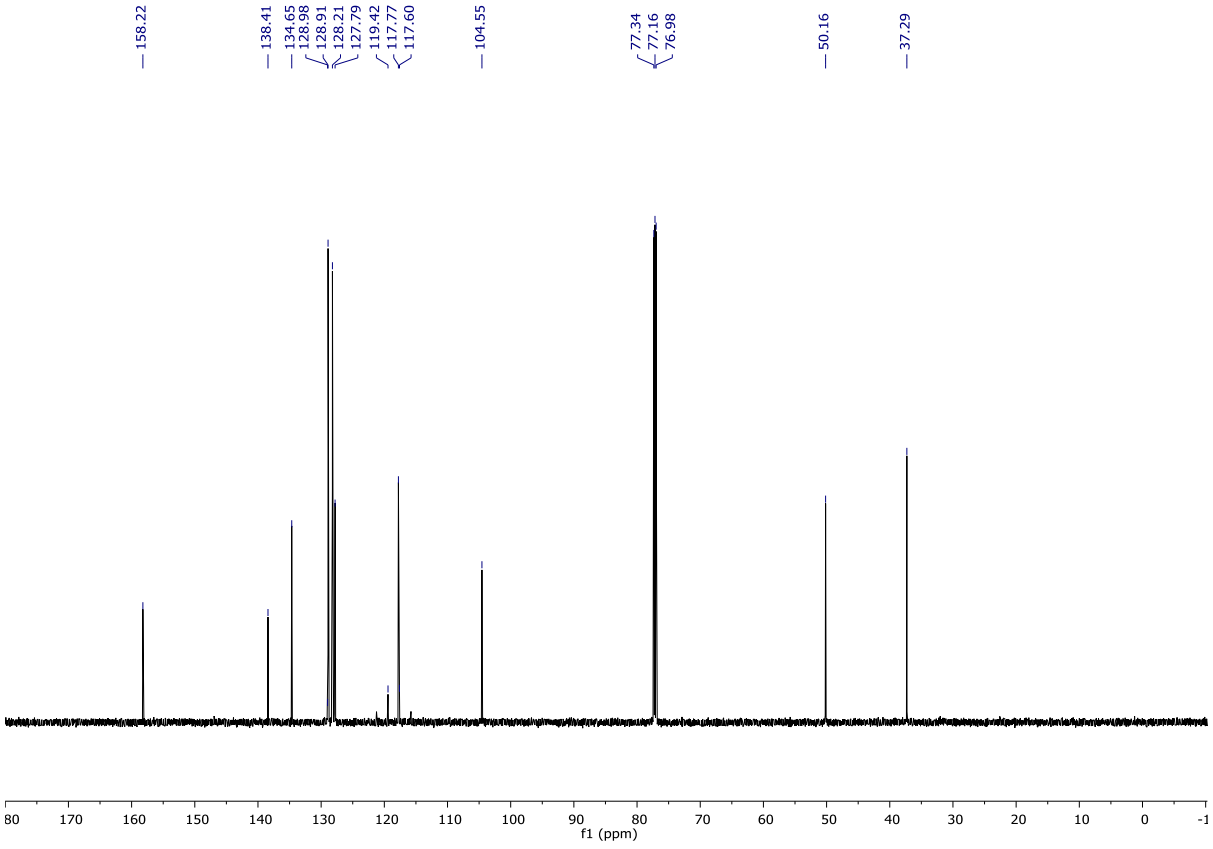
2.55
2.54
2.52


OTf
Ph

19b

2.07
1.07
2.04
1.00
1.11
3.28
1.07
1.15
1.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


158.22
138.41
134.65
128.98
128.91
128.21
127.79
119.42
117.77
117.60
104.55
77.34
77.16
76.98
50.16
37.29
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.26
7.26
7.25
7.25
5.61
5.60
5.59
5.58
5.57
5.55
5.55
5.54
5.53
5.51
5.28
5.27
5.14
5.13
5.13
5.13
5.12
5.11
5.10
5.10
5.10
5.09
5.09
5.09
5.08
5.08
5.08
5.07
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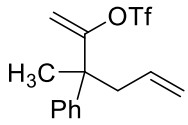
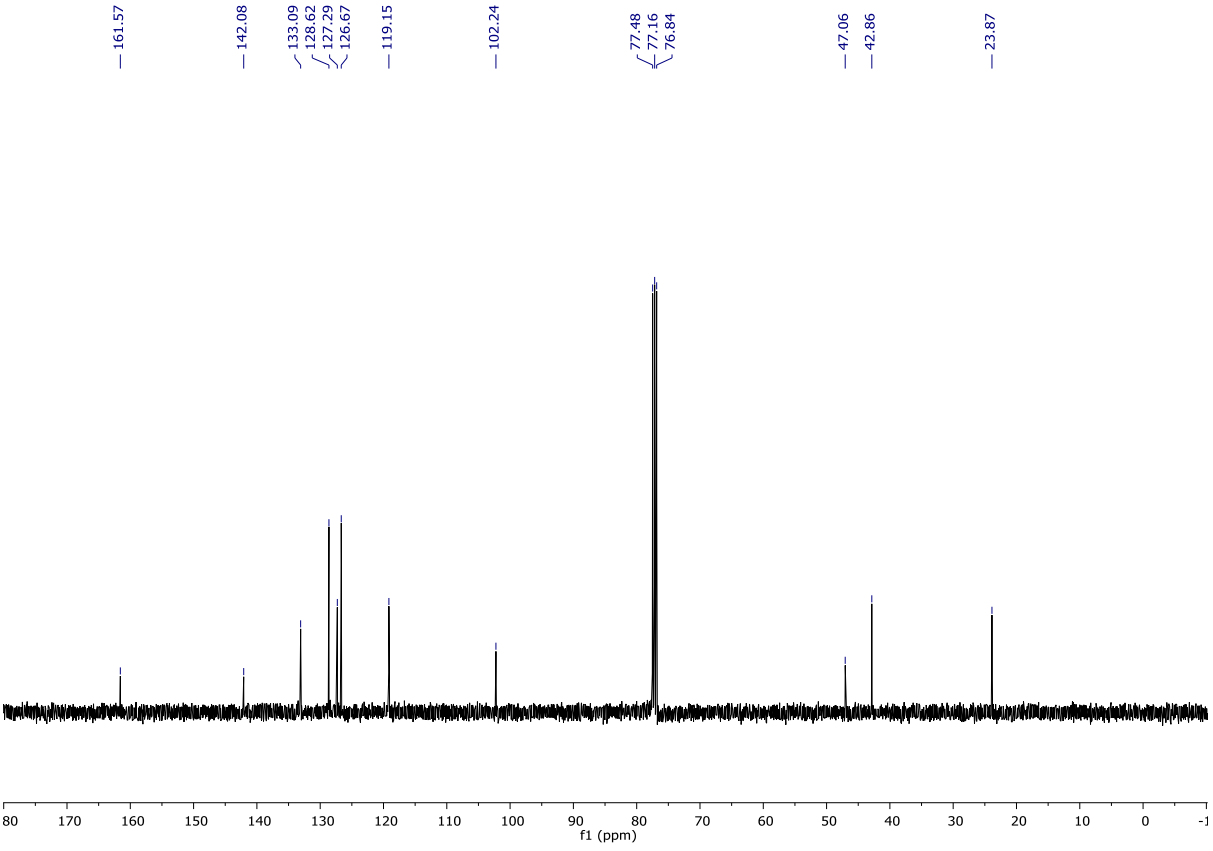
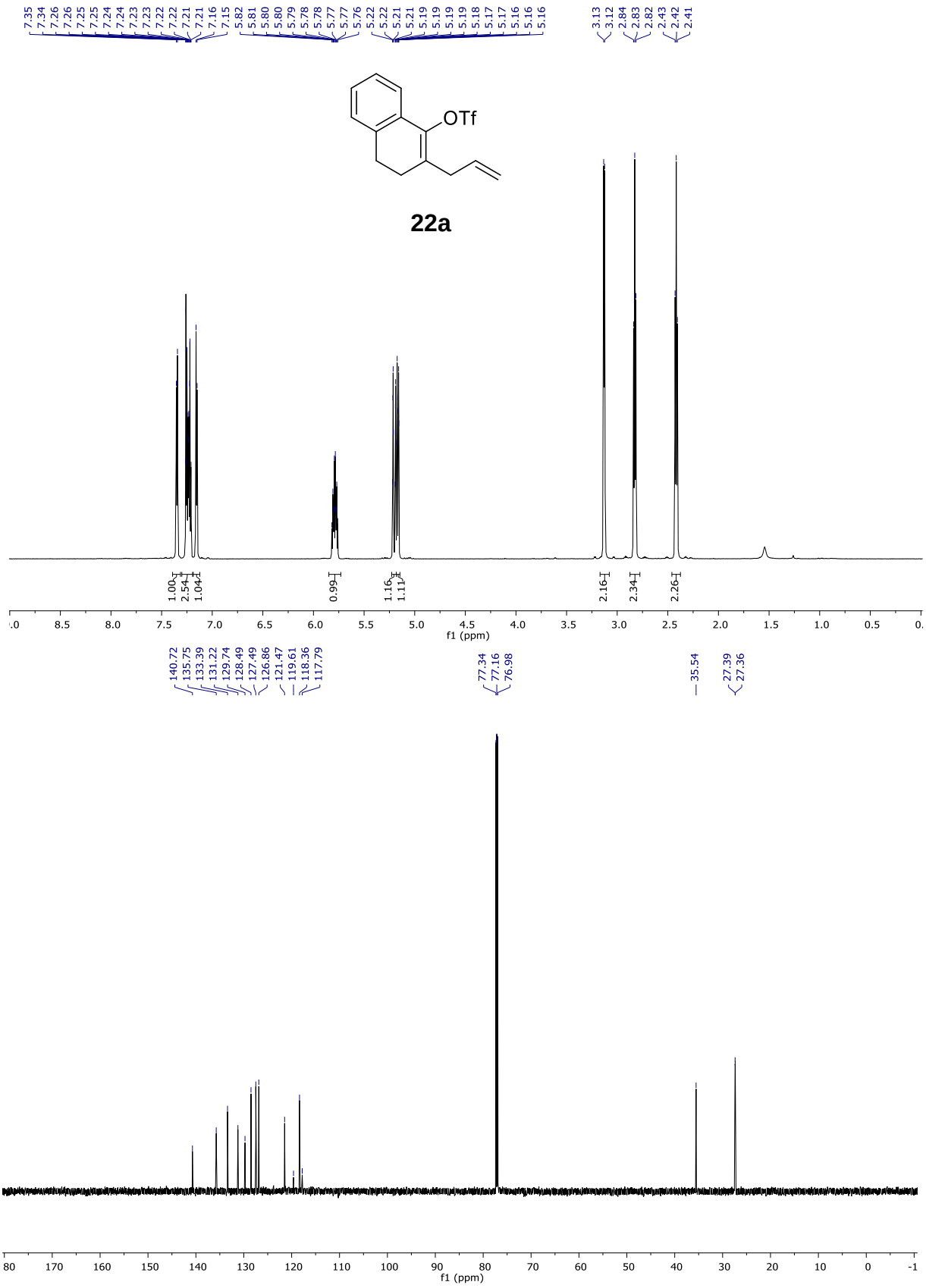
2.68
2.68
2.67
2.67
2.66
2.66
1.50


OTf
H3C
Ph

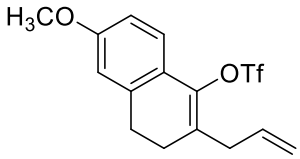
19c

4.09
1.45
1.00
1.17
3.29
1.96
3.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


161.57
142.08
133.09
128.62
127.29
126.67
119.15
102.24
77.48
77.16
76.84
47.06
42.86
23.87
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

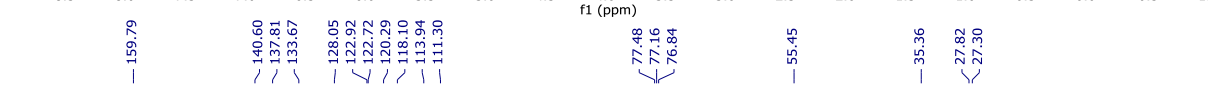

OTf
22a
f1 (ppm)
f1 (ppm)

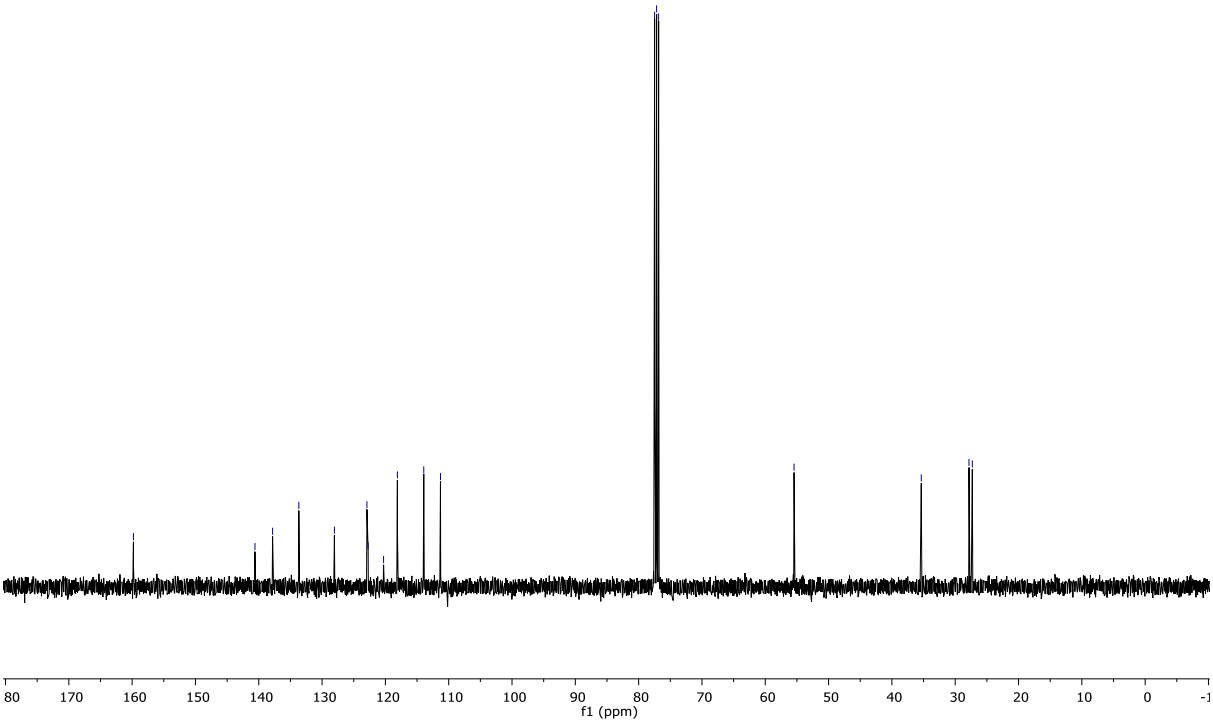

7.26
7.25
7.24
7.23
6.75
6.75
6.73
6.72
6.69
6.69
5.79
5.78
5.78
5.77
5.77
5.75
5.74
5.73
5.72
5.71
5.19
5.18
5.18
5.14
5.14
5.14
5.13
5.13
5.12
5.11
5.11
5.11
3.80
3.79
3.78
3.08
3.08
3.06
2.79
2.77
2.75
2.38
2.36
2.34


H3CO
OTf

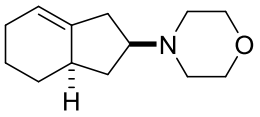
22b

1.11
2.05
0.84
1.89
2.75
2.01
2.08
2.10
f1 (ppm)

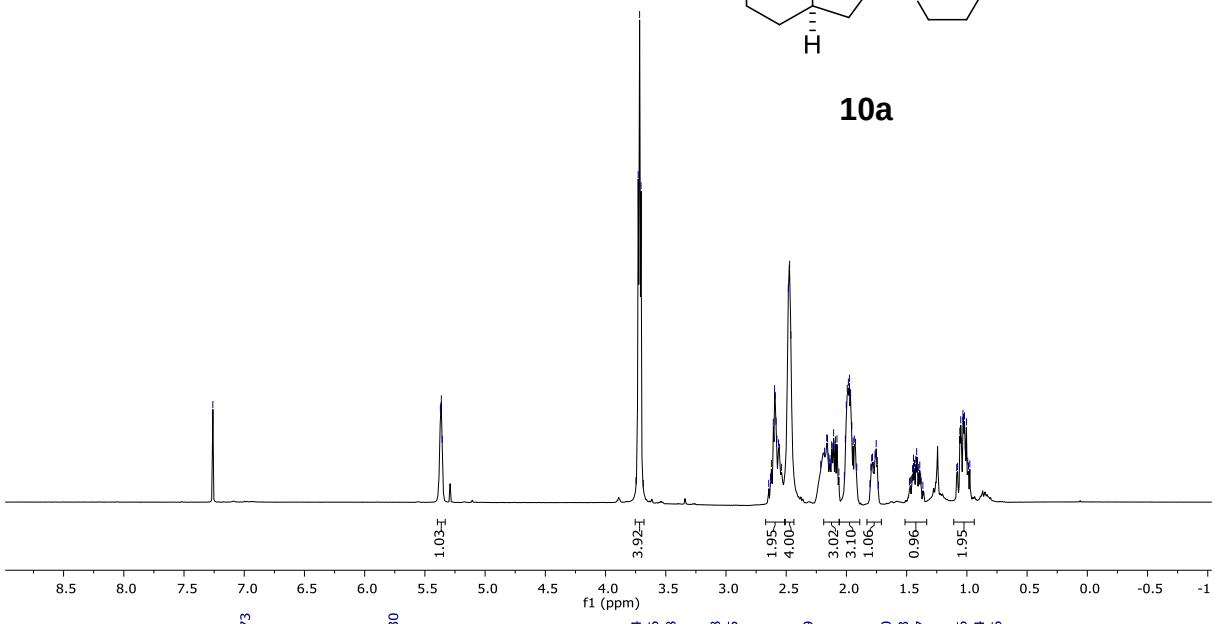

159.79
140.60
137.81
133.67
128.05
122.92
122.72
120.29
118.10
113.94
111.30
77.48
77.16
76.84
55.45
35.36
27.82
27.30

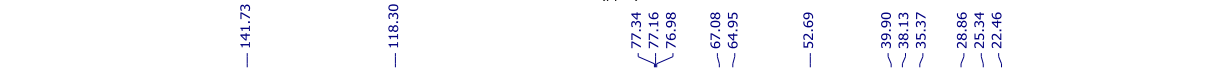

f1 (ppm)

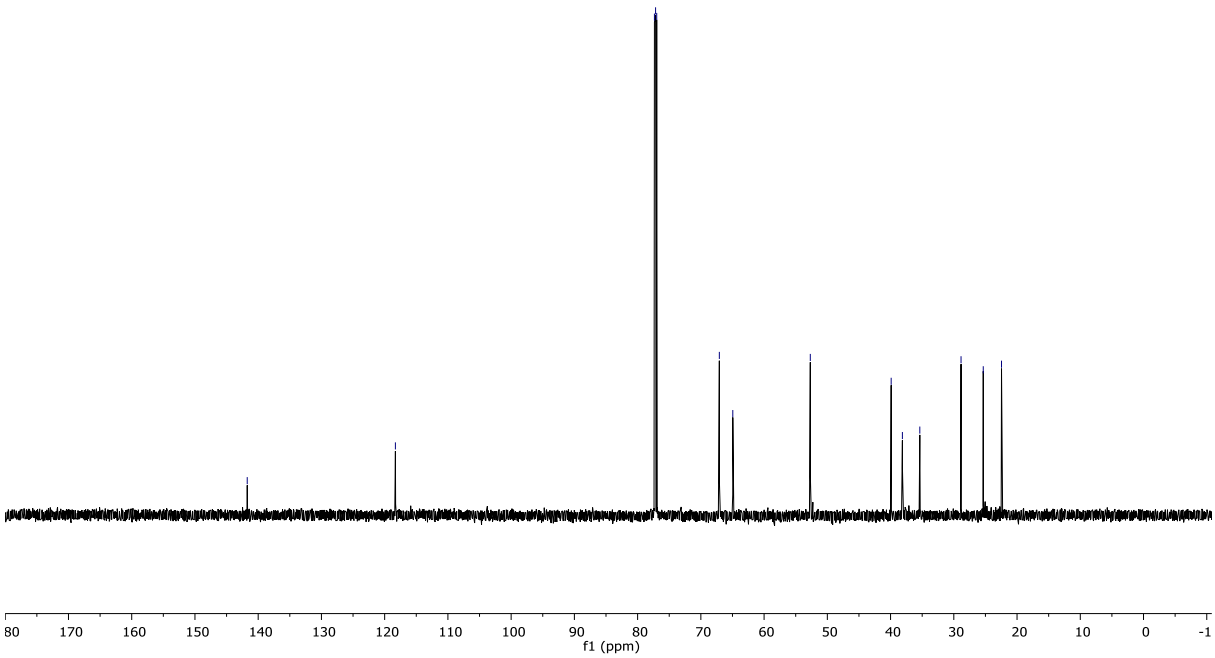

7.26
5.37
5.36
5.36
3.73
3.72
3.71
2.62
2.61
2.60
2.59
2.58
2.58
2.56
2.56
2.54
2.48
2.47
2.46
2.21
2.18
2.16
2.16
2.15
2.14
2.14
2.13
2.12
2.12
2.11
2.09
2.09
2.08
2.01
2.00
1.99
1.98
1.97
1.97
1.95
1.94
1.93
1.92
1.91
1.80
1.79
1.78
1.77
1.76
1.75
1.74
1.44
1.44
1.42
1.42
1.41
1.39
1.08
1.06
1.05
1.04
1.03
1.03
1.02
1.01
1.00
0.99
0.99
0.98

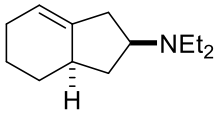

N
O
H

10a


1.03
3.92
1.95
4.00
3.02
3.10
1.06
0.96
1.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

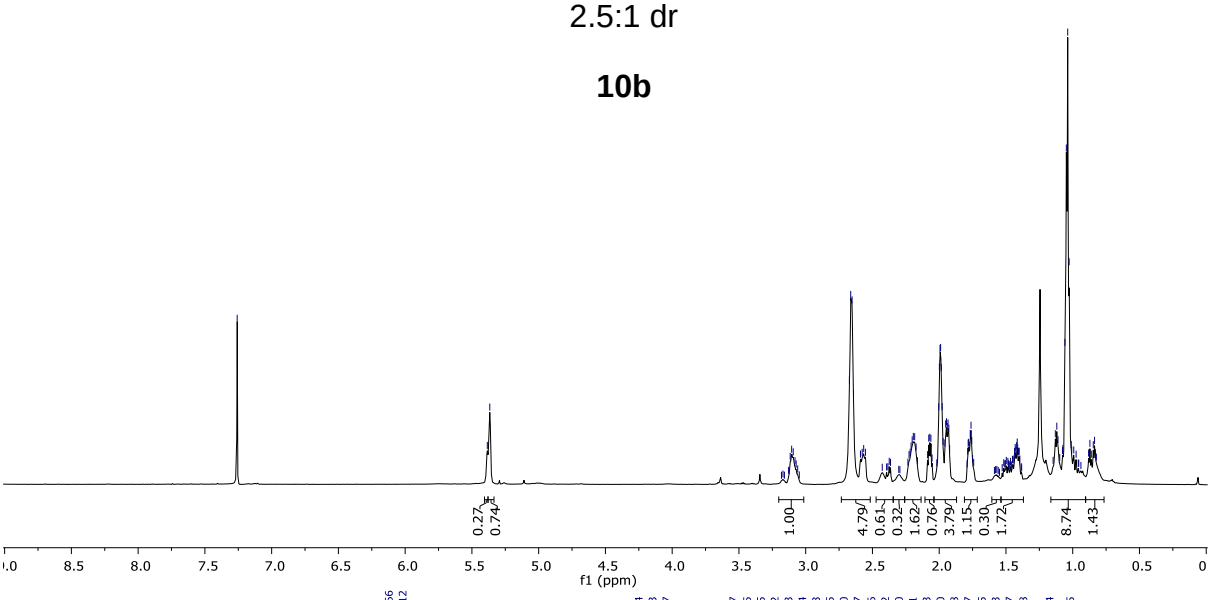

141.73
118.30
77.34
77.16
76.98
67.08
64.95
52.69
39.90
38.13
35.37
28.86
25.34
22.46

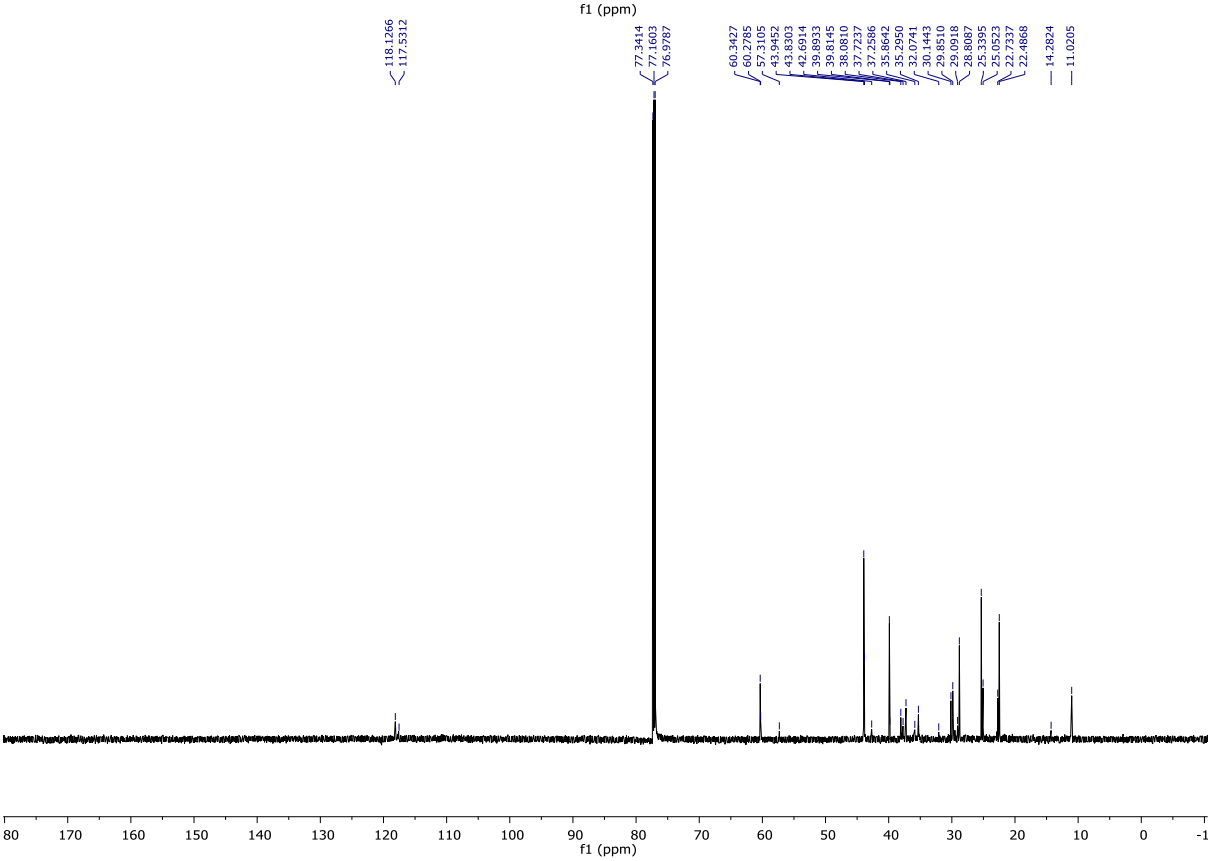

80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


NEt2
H

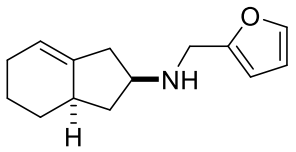
2.5:1 dr

10b

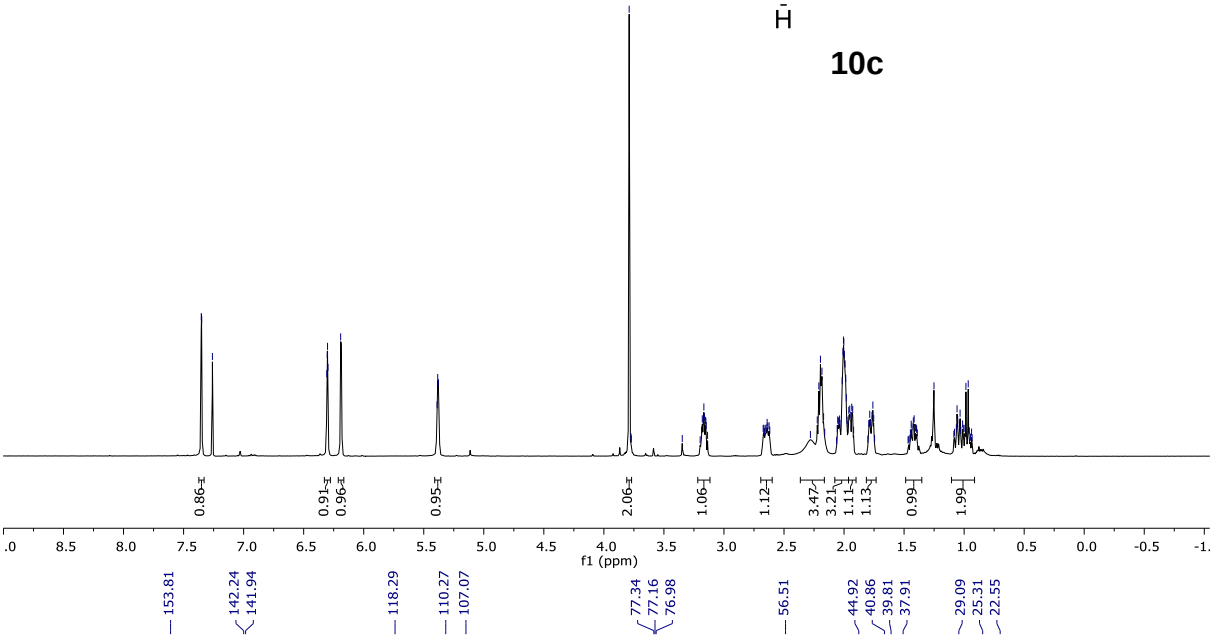

0.27
0.74
1.00
4.79
0.61
0.32
1.62
0.76
3.79
1.15
0.30
1.72
8.74
1.43
f1 (ppm)


f1 (ppm)

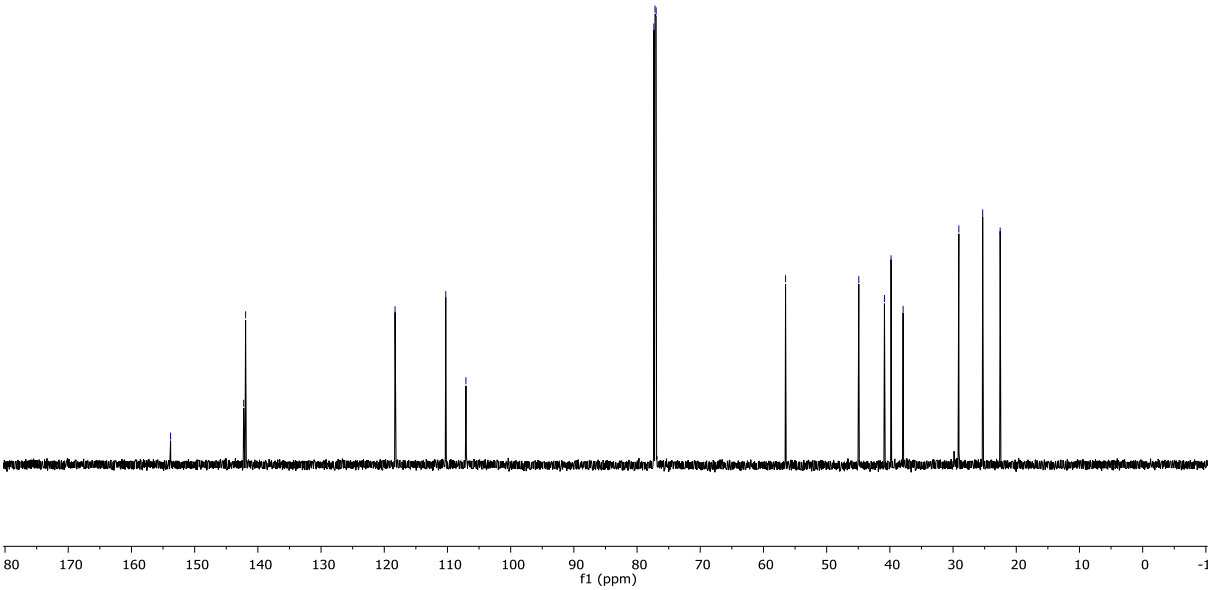

7.35 7.35 7.26 6.31 6.30 6.30 6.30 6.19 6.19 5.39 5.38 5.38 3.79 3.18 3.17 3.17 3.16 3.15 3.15 3.15 2.64 2.64 2.62 2.22 2.21 2.20 2.18 2.17 2.05 2.05 2.04 2.04 2.03 2.02 2.01 2.00 2.00 2.00 1.99 1.99 1.98 1.98 1.97 1.96 1.95 1.94 1.94 1.93 1.79 1.79 1.78 1.77 1.76 1.75 1.44 1.43 1.42 1.42 1.41 1.26 1.25 1.06 1.06 1.05 1.04 1.03 1.01 0.98 0.97


O
NH
H

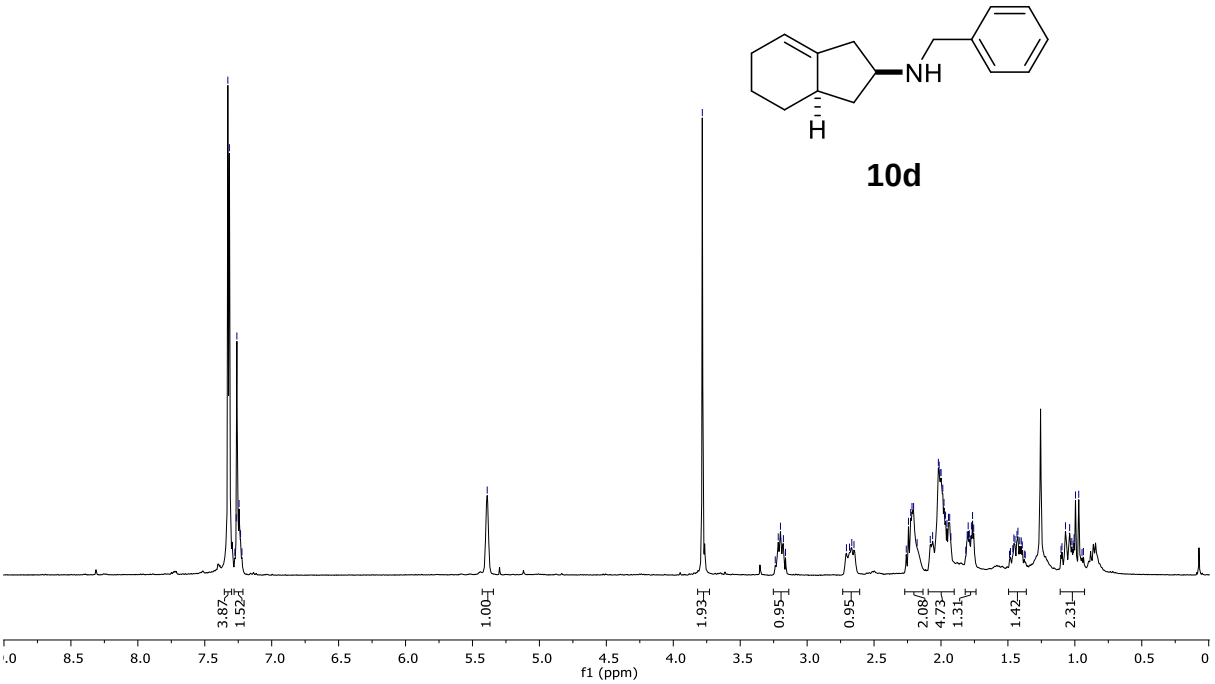
10c


0.86
0.91
0.96
0.95
2.06
1.06
1.12
3.47
3.21
1.11
1.13
0.99
1.99
f1 (ppm)

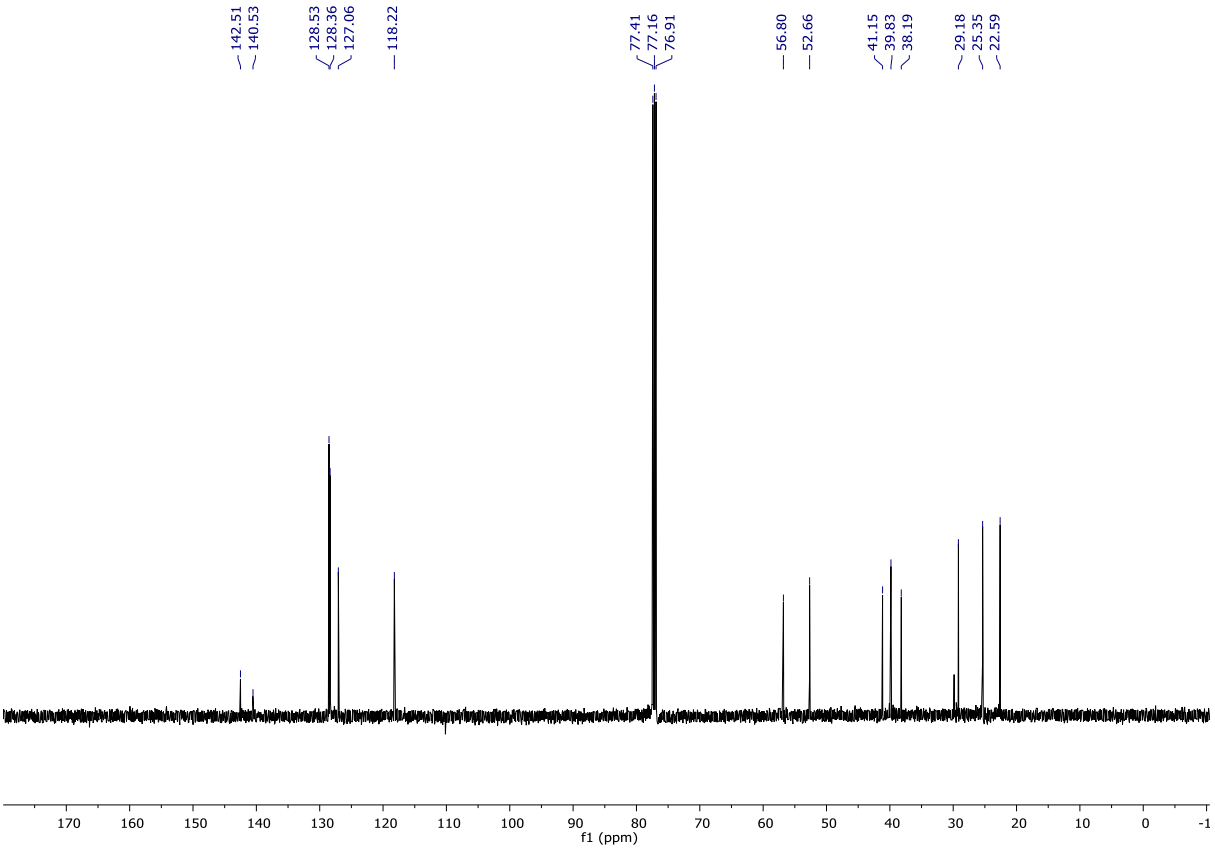
153.81
142.24
141.94
118.29
110.27
107.07
77.34
77.16
76.98
56.51
44.92
40.86
39.81
37.91
29.09
25.31
22.55

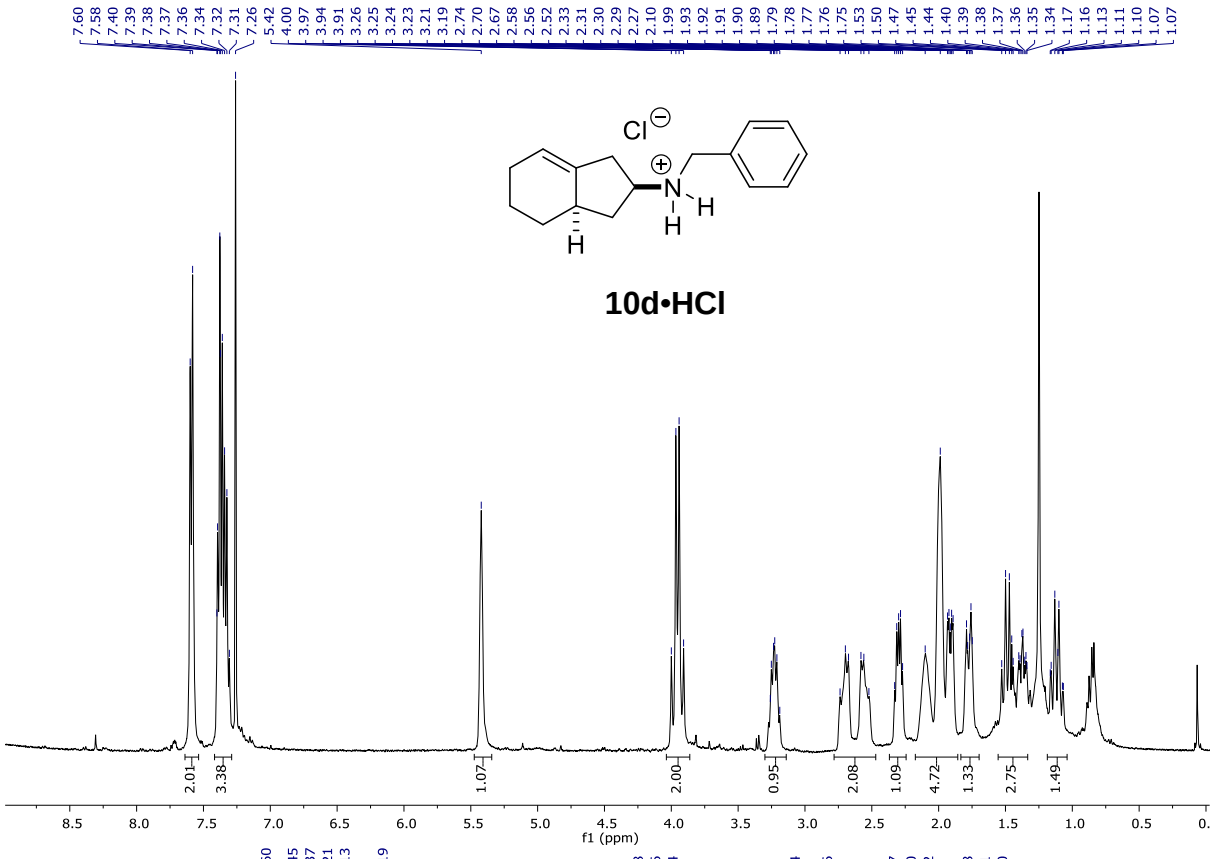

f1 (ppm)

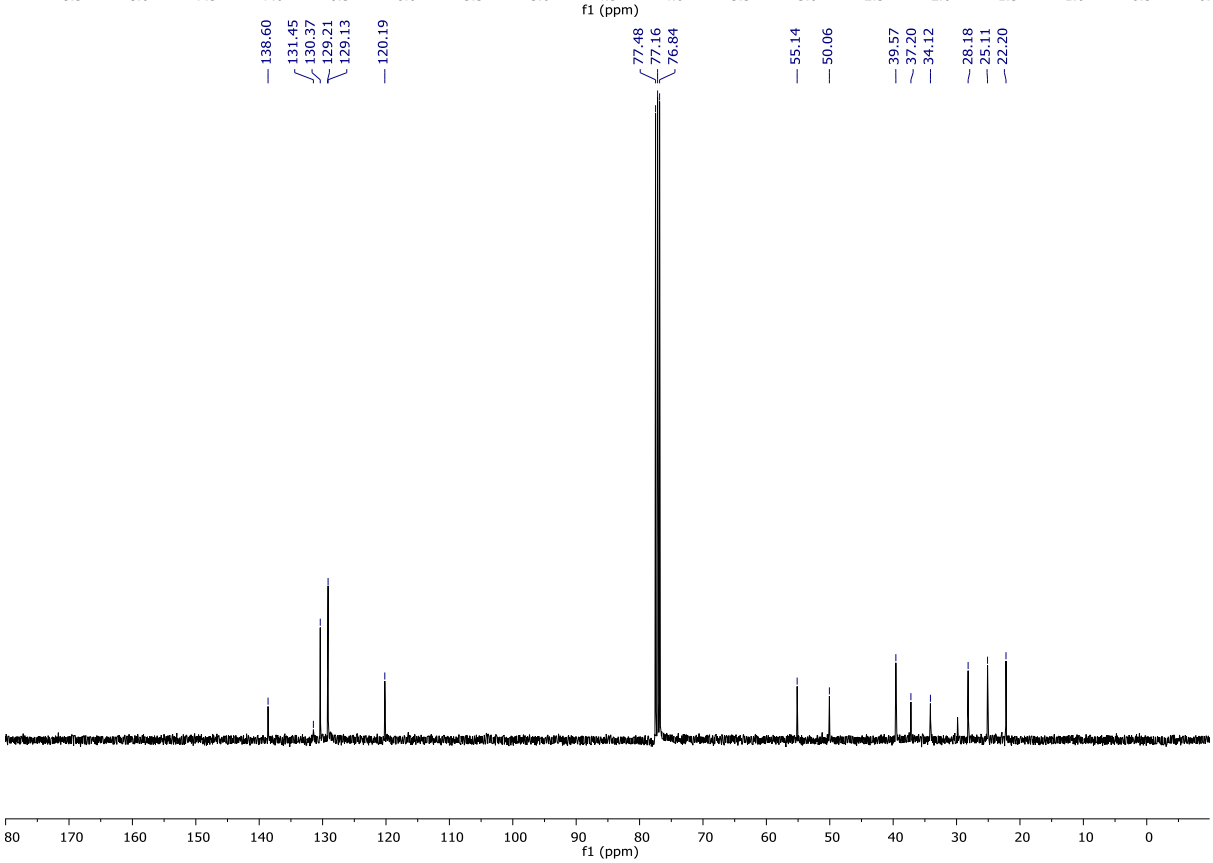

7.33
7.32
7.28
7.26
7.26
7.24
7.23
7.22
5.39
3.78
3.24
3.22
3.20
3.18
3.16
2.71
2.68
2.67
2.65
2.26
2.24
2.23
2.22
2.20
2.18
2.08
2.06
2.02
2.01
2.01
2.00
1.99
1.98
1.97
1.96
1.94
1.93
1.93
1.81
1.80
1.80
1.79
1.78
1.77
1.76
1.76
1.49
1.48
1.46
1.46
1.45
1.43
1.43
1.41
1.40
1.39
1.38
1.37
1.10
1.10
1.07
1.04
1.02
1.01
1.01
1.00
0.97
0.95
0.94

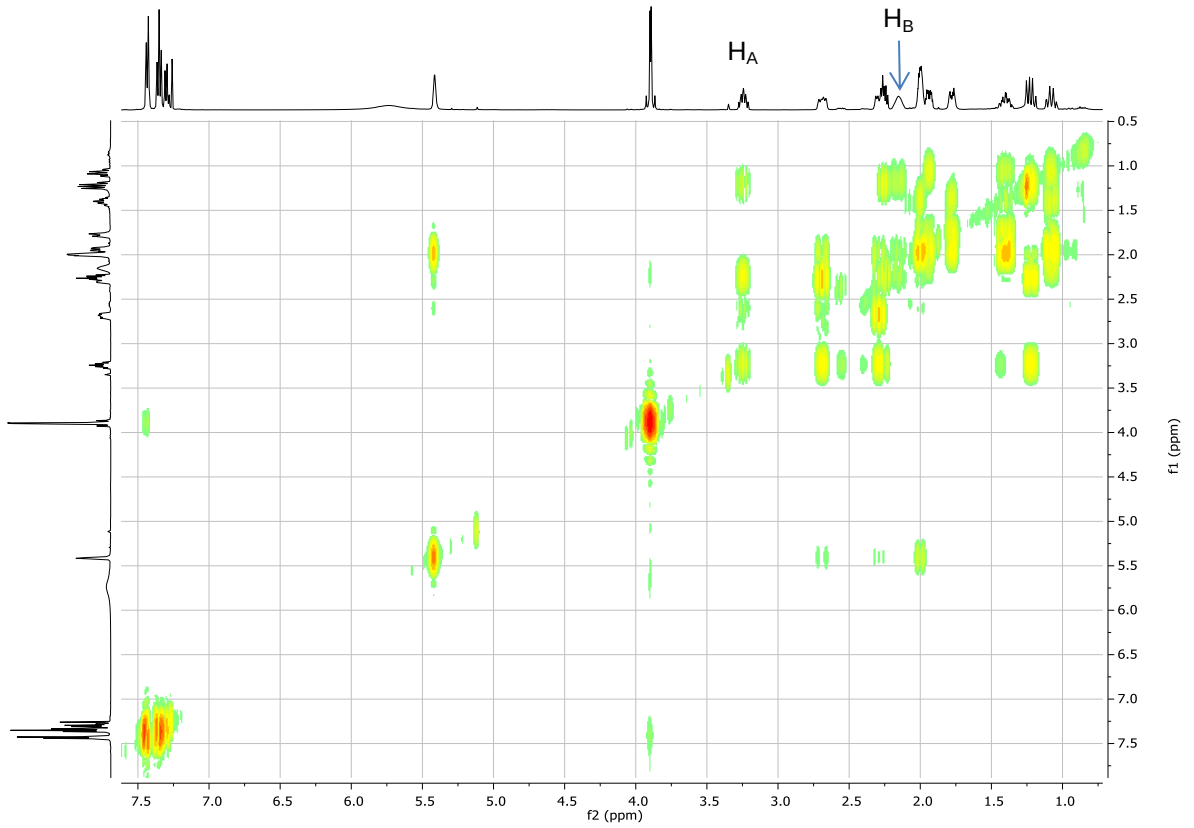

NH
H
3.87
1.52
1.00
1.93
0.95
0.95
2.08
4.73
1.31
1.42
2.31
f1 (ppm)

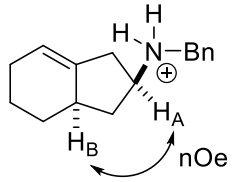
10d

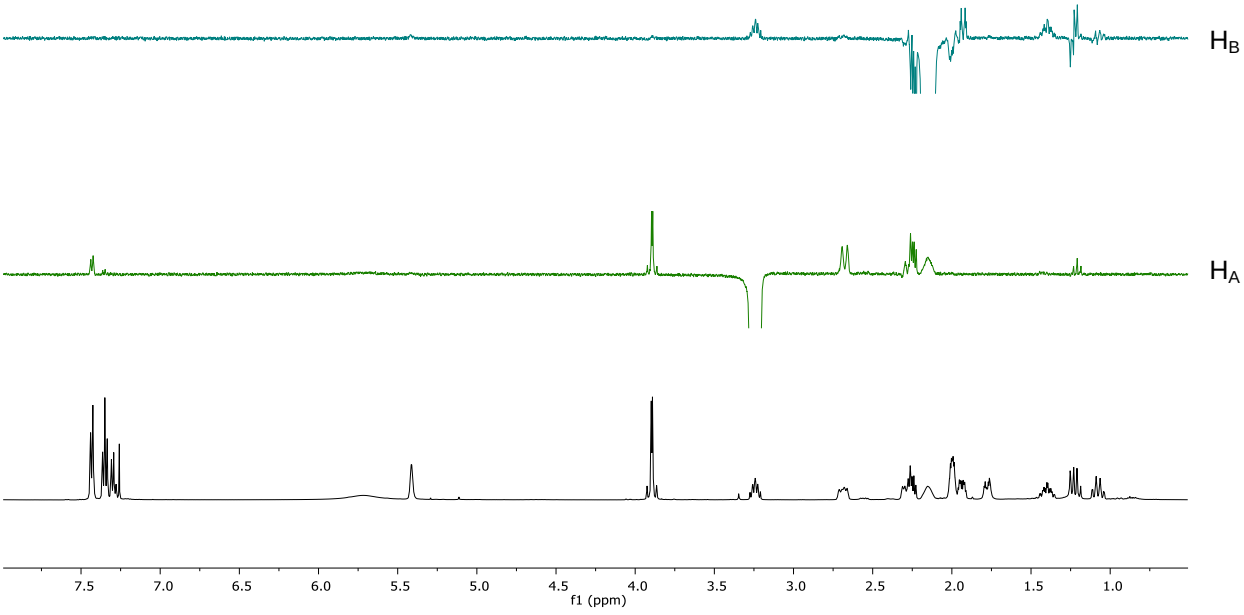

142.51
140.53
128.53
128.36
127.06
118.22
77.41
77.16
76.91
56.80
52.66
41.15
39.83
38.19
29.18
25.35
22.59
f1 (ppm)

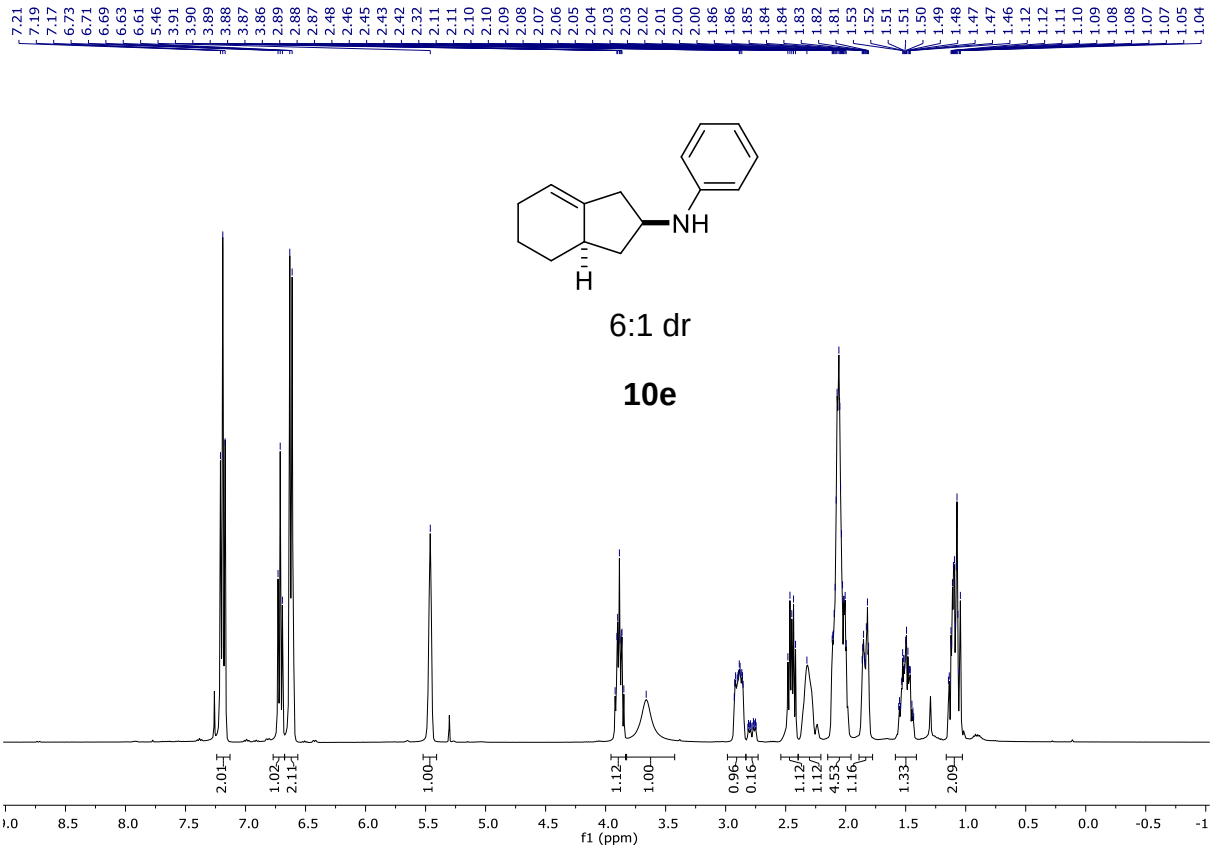

7.60 7.58 7.40 7.39 7.38 7.37 7.36 7.34 7.32 7.31 7.26 5.42 4.00 3.97 3.94 3.91 3.26 3.25 3.24 3.23 3.21 3.19 2.74 2.70 2.67 2.58 2.56 2.52 2.33 2.31 2.30 2.29 2.27 2.10 1.99 1.93 1.92 1.91 1.90 1.89 1.79 1.78 1.77 1.76 1.75 1.53 1.50 1.47 1.45 1.44 1.40 1.39 1.38 1.37 1.36 1.35 1.34 1.17 1.16 1.13 1.11 1.10 1.07 1.07
Cl
N
H
H
H
10d•HCl
2.01 3.38 1.07 2.00 0.95 2.08 1.09 4.72 1.33 2.75 1.49
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


138.60 131.45 130.37 129.21 129.13 120.19 77.48 77.16 76.84 55.14 50.06 39.57 37.20 34.12 28.18 25.11 22.20
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


H_A
H_B
f2 (ppm)
f1 (ppm)

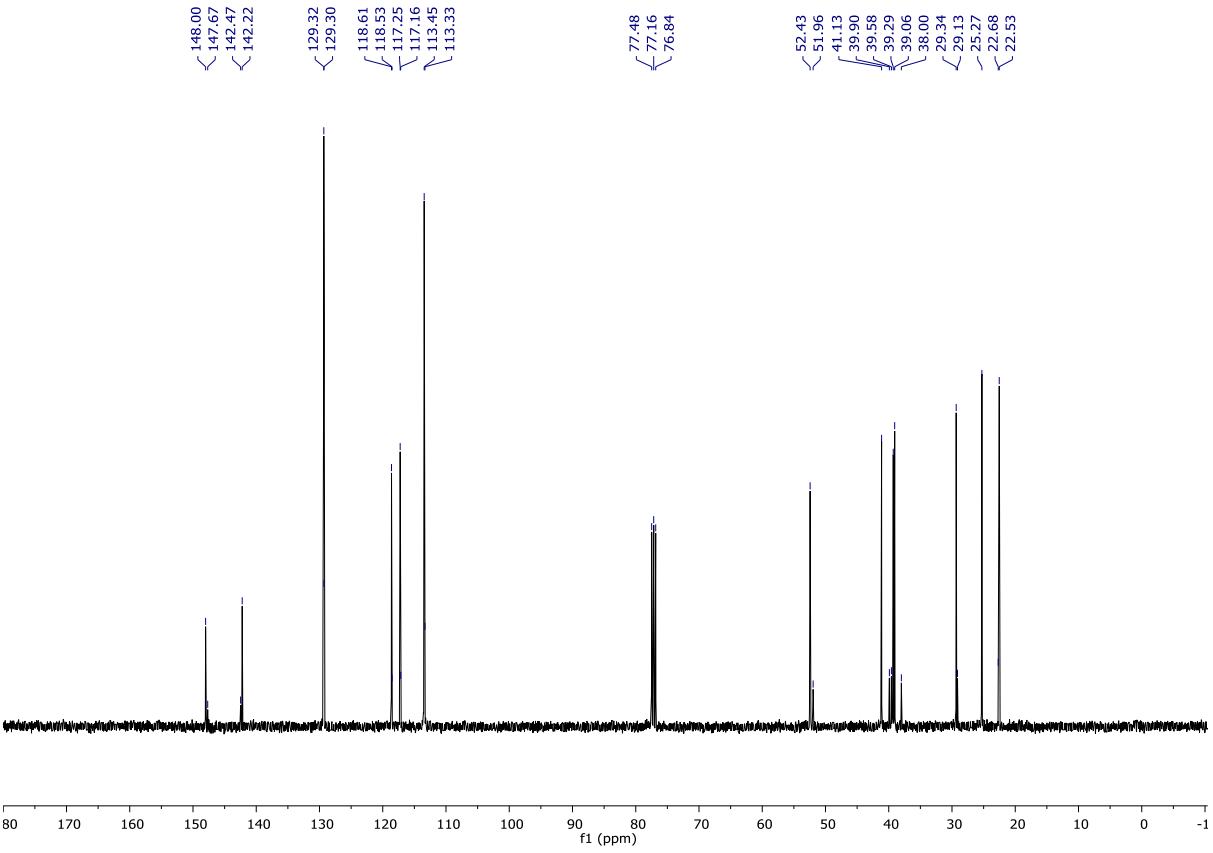

H
H
N–Bn
H_A
H_B
nOe

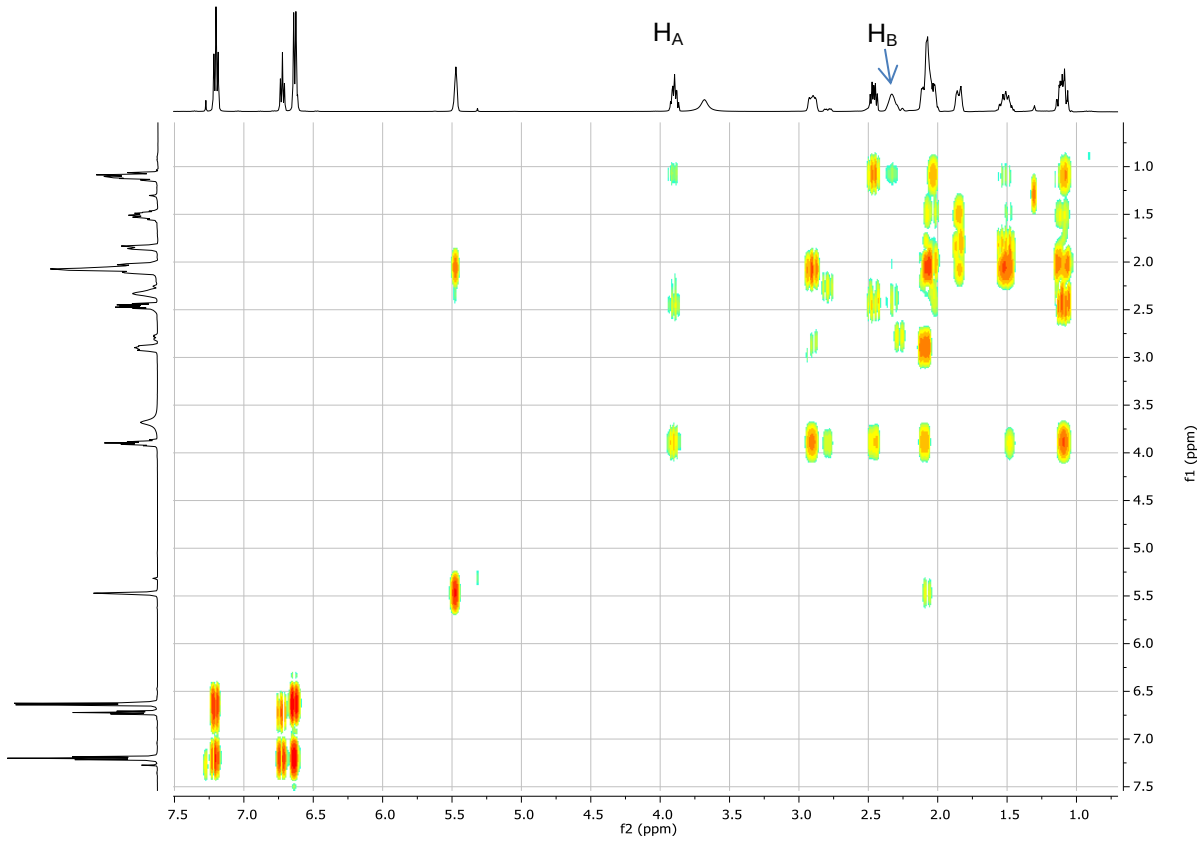

H_B
H_A
f1 (ppm)

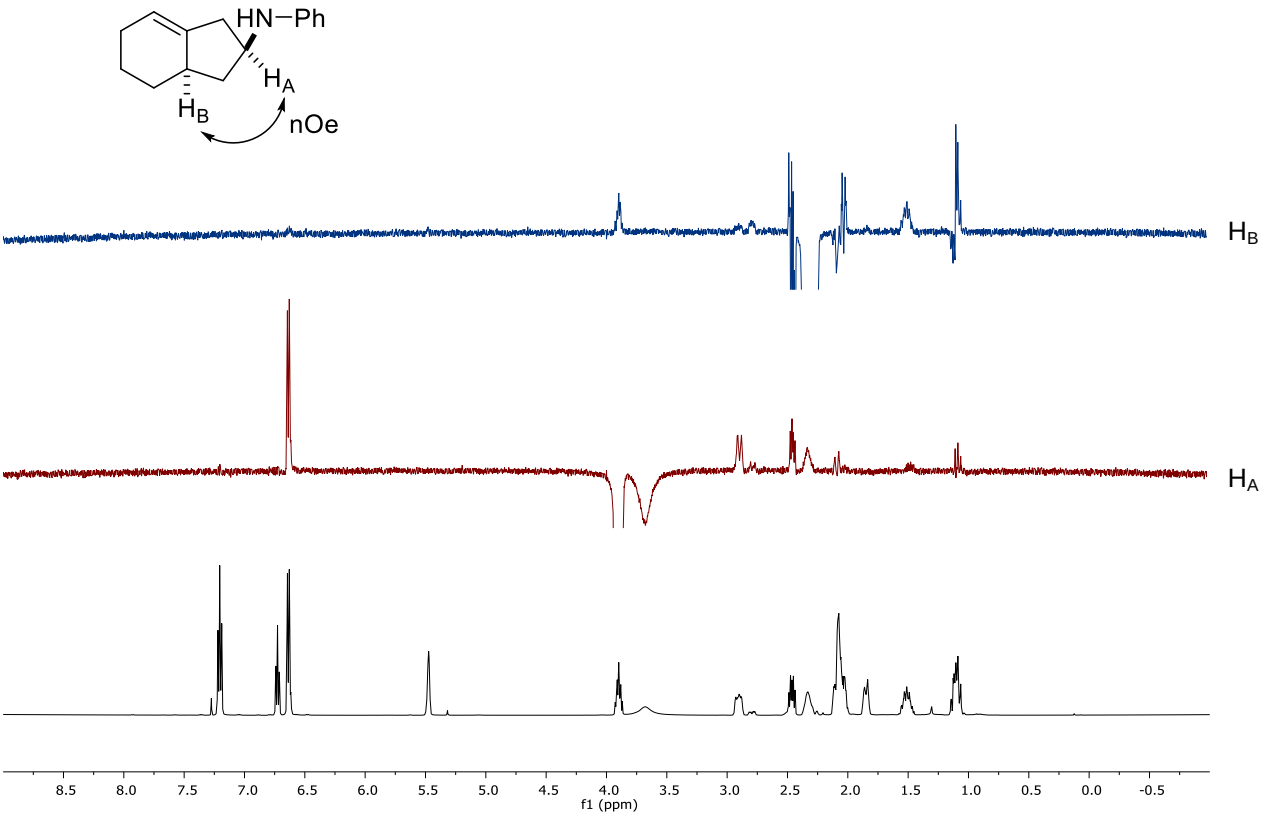


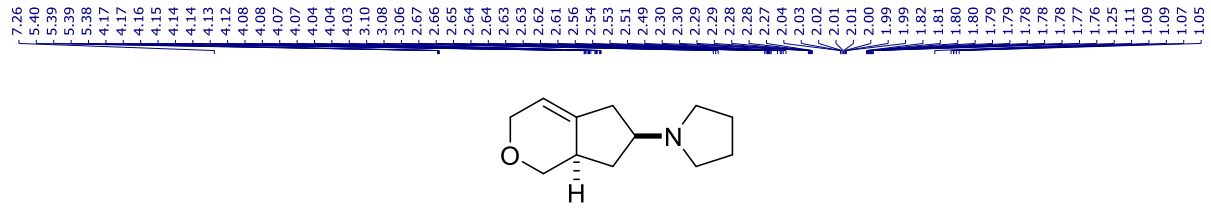
6:1 dr

10e

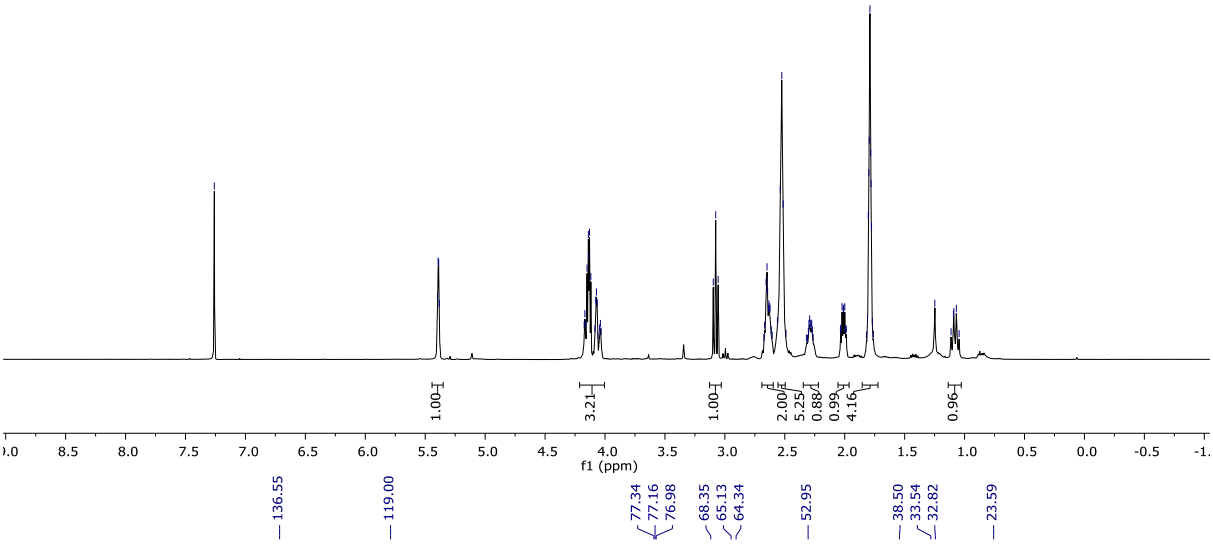


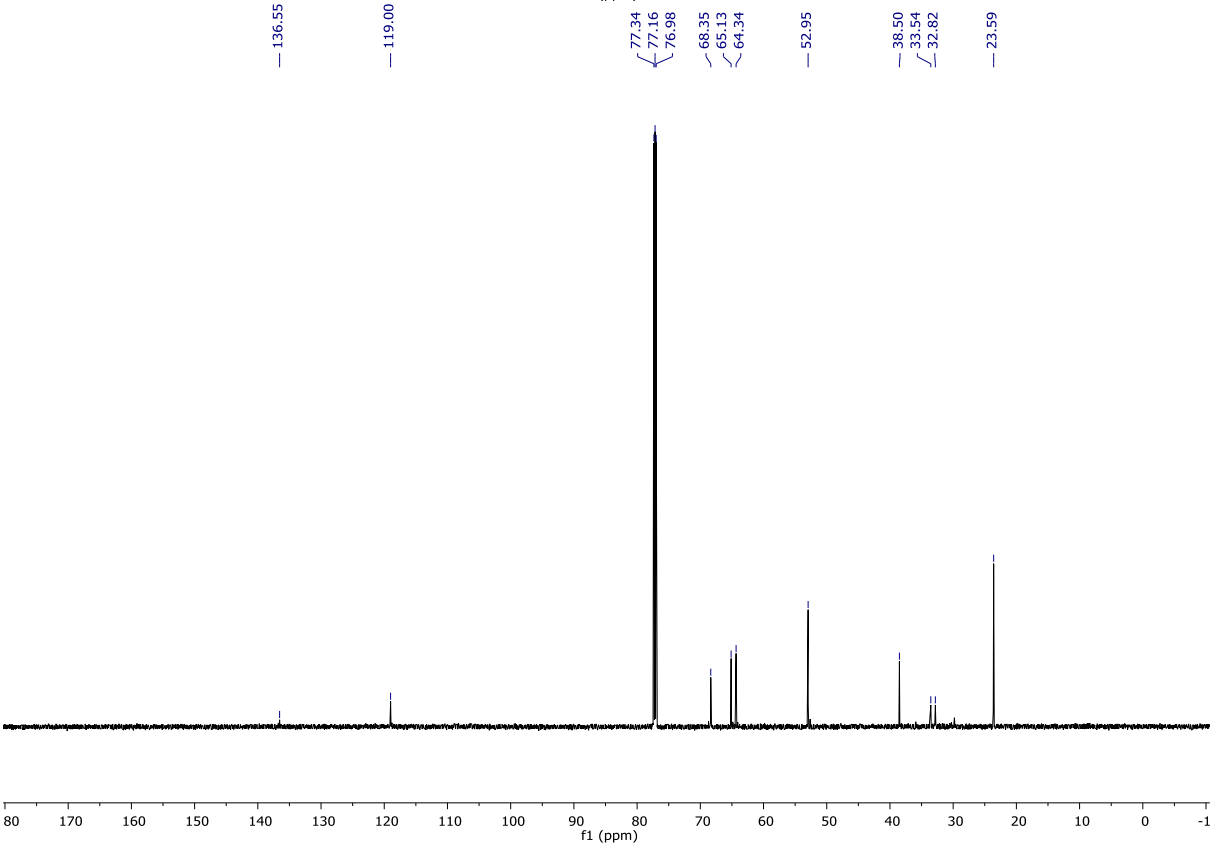

HA
HB
f2 (ppm)
f1 (ppm)

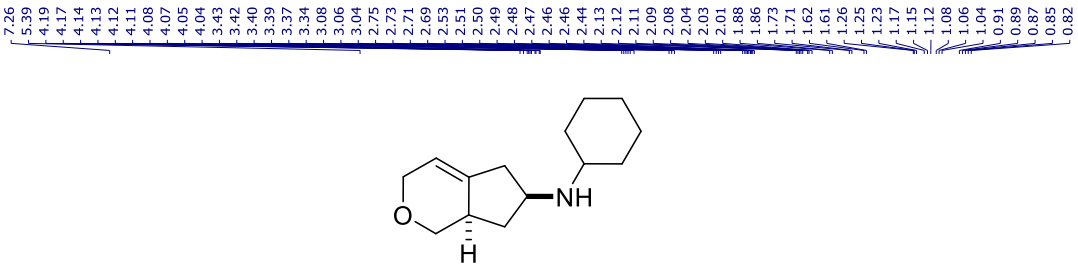

HN−Ph
HA
HB
nOe
HB
HA
f1 (ppm)


7.26 5.40 5.39 5.39 5.38 4.17 4.17 4.16 4.15 4.14 4.14 4.13 4.12 4.08 4.08 4.07 4.07 4.04 4.04 4.03 3.10 3.08 3.06 2.67 2.66 2.65 2.64 2.64 2.63 2.63 2.62 2.61 2.56 2.54 2.53 2.51 2.49 2.30 2.30 2.29 2.29 2.28 2.28 2.27 2.04 2.03 2.02 2.01 2.01 2.00 1.99 1.99 1.82 1.81 1.80 1.80 1.79 1.79 1.78 1.78 1.78 1.77 1.76 1.25 1.11 1.09 1.09 1.07 1.05
O
N
H

10f

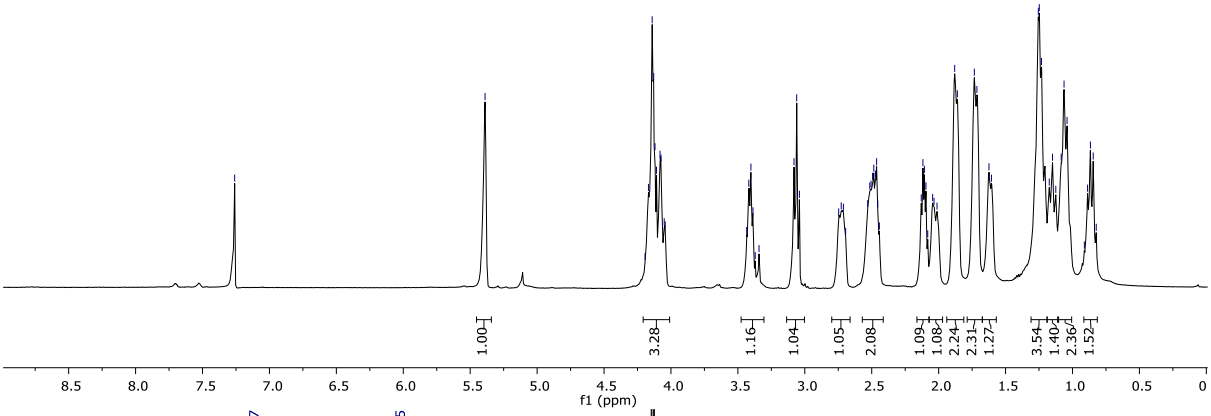

1.00
3.21
1.00
2.00
5.25
0.88
0.99
4.16
0.96
f1 (ppm)

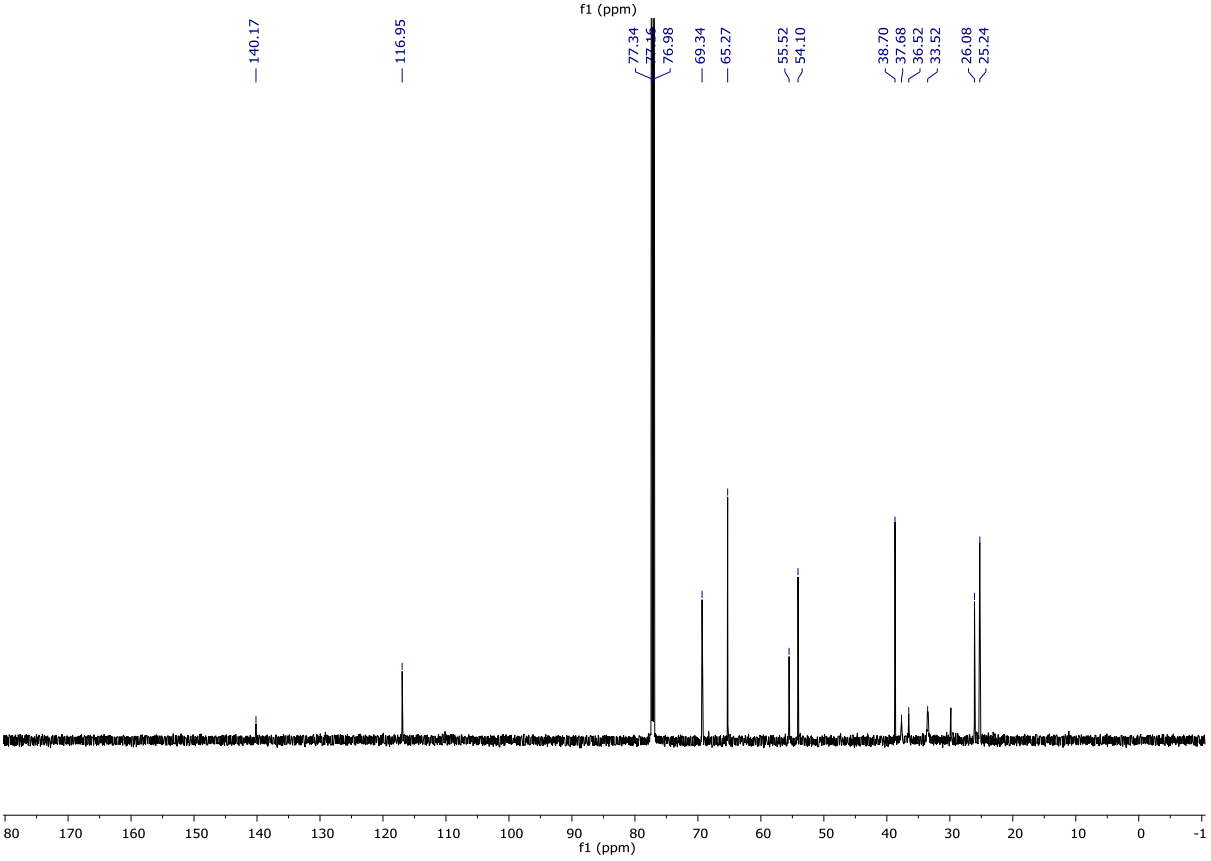

136.55
119.00
77.34
77.16
76.98
68.35
65.13
64.34
52.95
38.50
33.54
32.82
23.59
f1 (ppm)

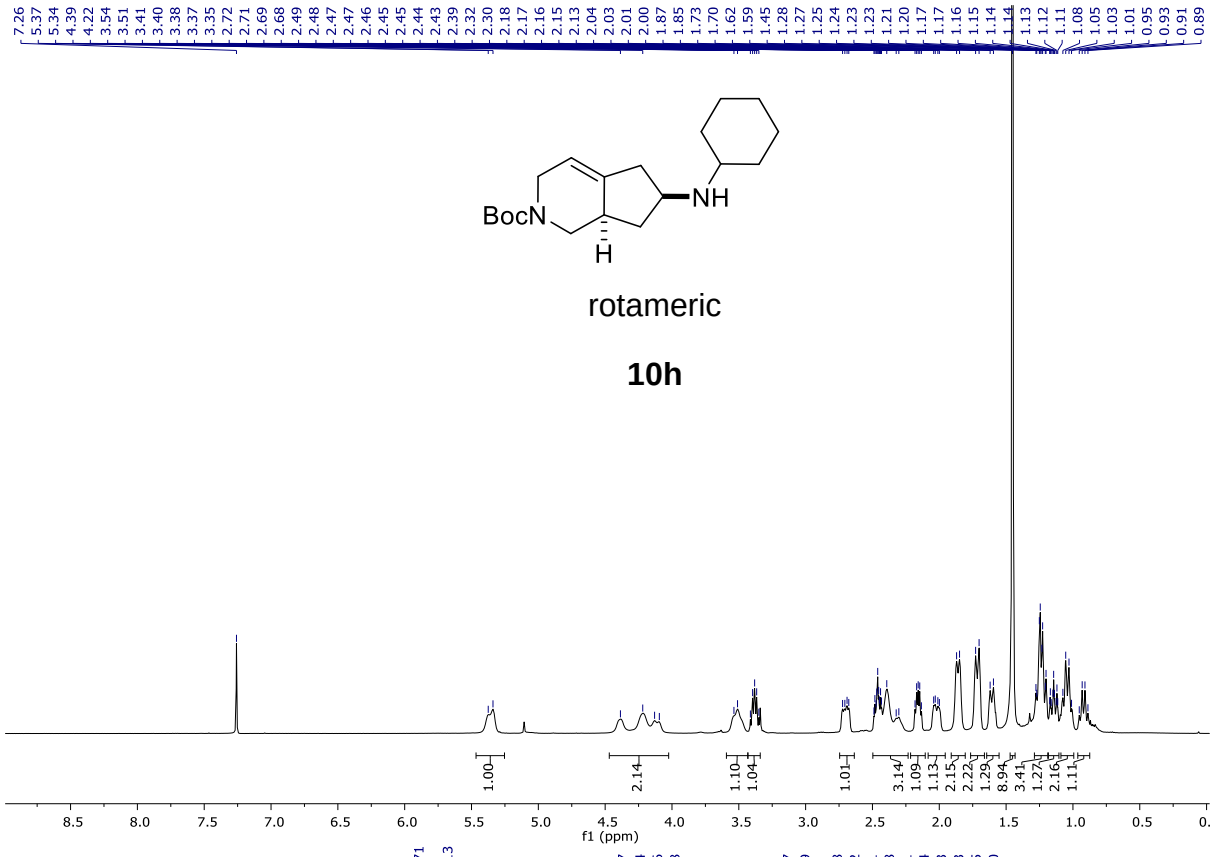

7.26
5.39
4.19
4.17
4.14
4.13
4.12
4.11
4.08
4.07
4.05
4.04
3.43
3.42
3.40
3.39
3.37
3.34
3.08
3.06
3.04
2.75
2.73
2.71
2.69
2.53
2.51
2.50
2.49
2.48
2.47
2.46
2.46
2.44
2.13
2.12
2.11
2.09
2.08
2.04
2.03
2.01
1.88
1.86
1.73
1.71
1.62
1.61
1.26
1.25
1.23
1.17
1.15
1.12
1.08
1.06
1.04
0.91
0.89
0.87
0.85
0.82

NH
O
H

10g

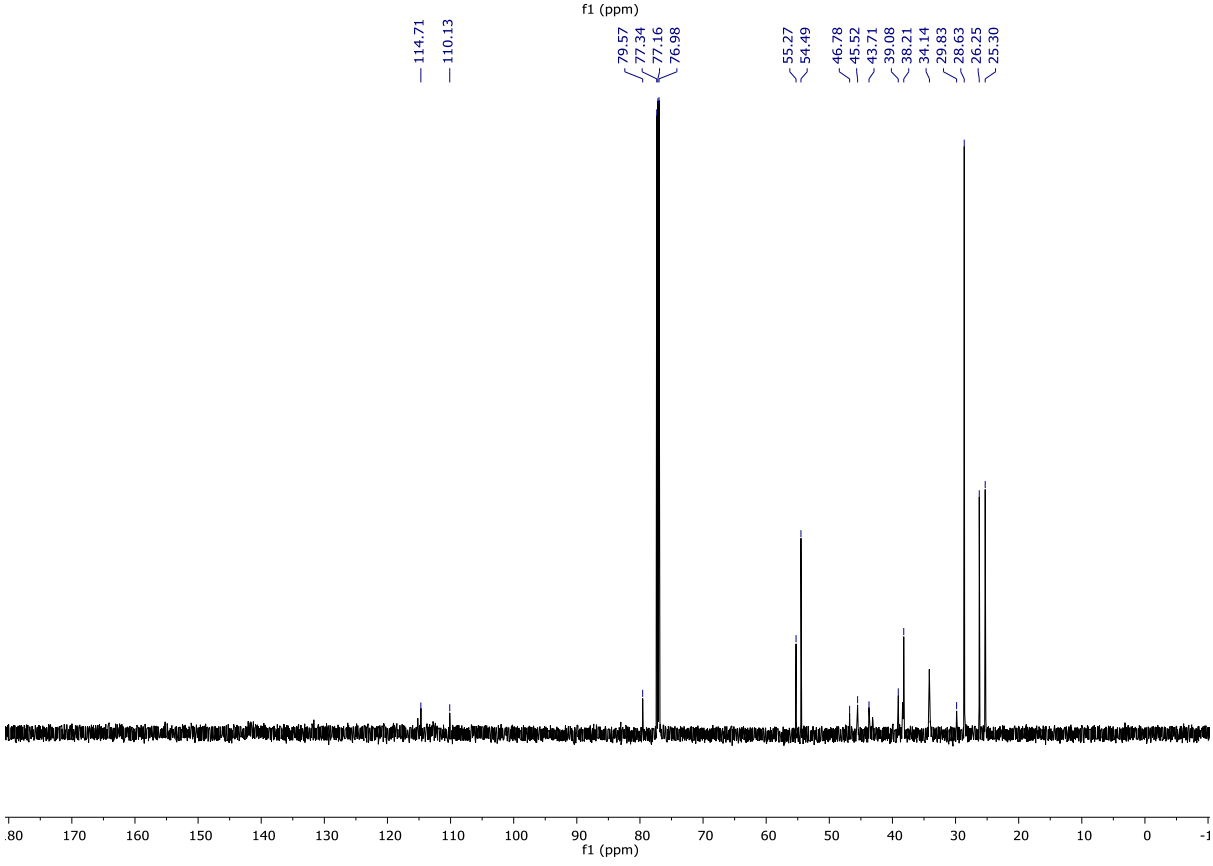

1.00
3.28
1.16
1.04
1.05
2.08
1.09
1.08
2.24
2.31
1.27
3.54
1.40
2.36
1.52
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

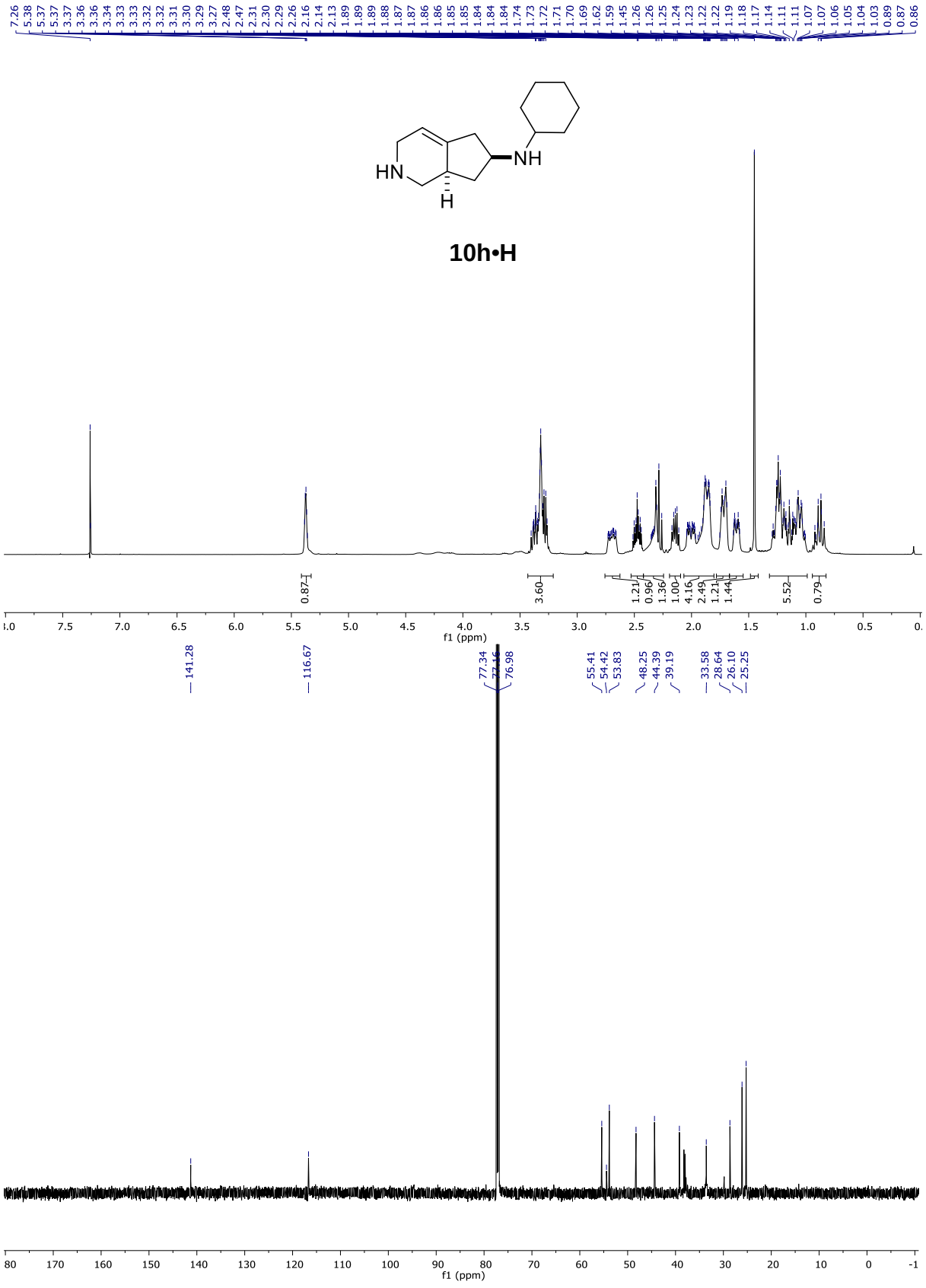

140.17
116.95
77.34
77.16
76.98
69.34
65.27
55.52
54.10
38.70
37.68
36.52
33.52
26.08
25.24
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

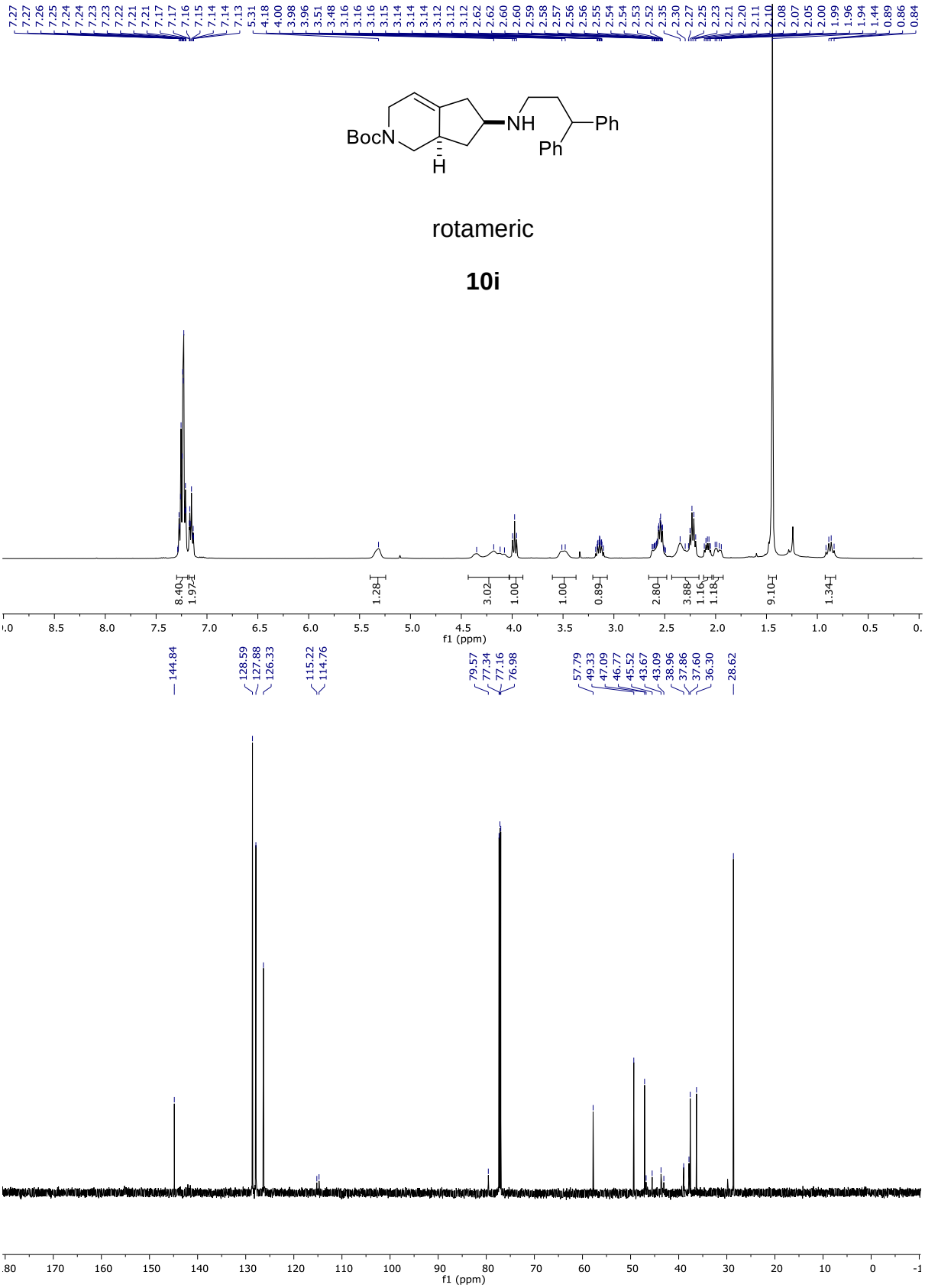


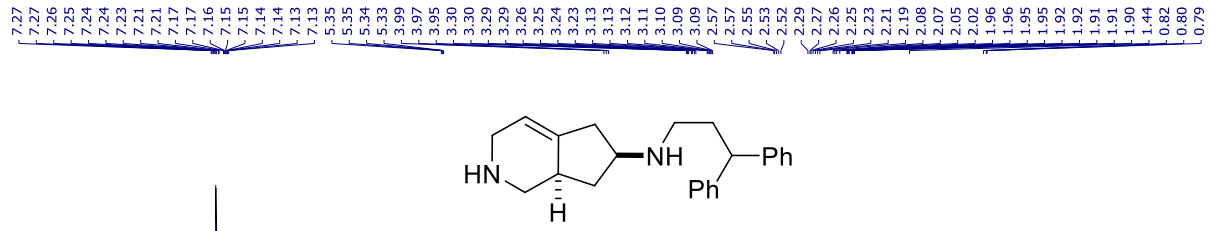
rotameric

10h



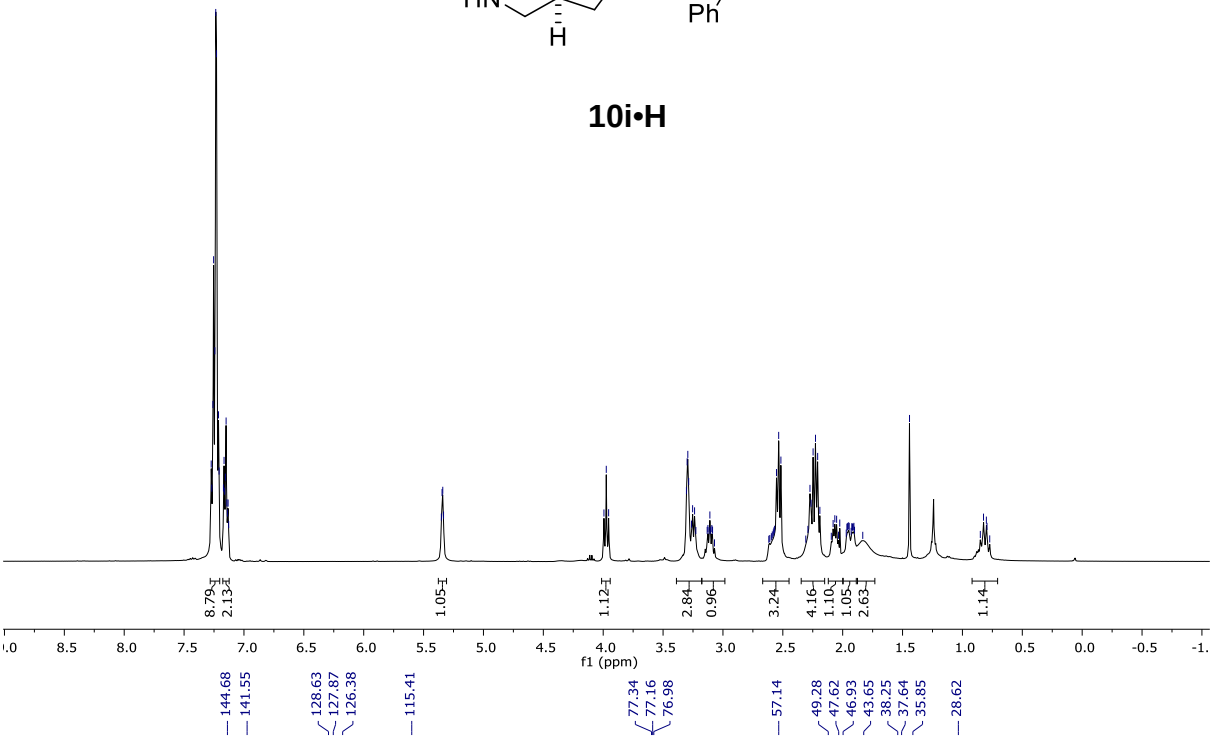

7.26 5.38 5.37 5.37 5.37 3.36 3.36 3.34 3.33 3.33 3.32 3.32 3.31 3.30 3.29 3.27 2.48 2.47 2.31 2.30 2.29 2.26 2.16 2.14 2.13 1.89 1.89 1.89 1.88 1.87 1.87 1.86 1.86 1.85 1.85 1.84 1.84 1.84 1.74 1.73 1.72 1.71 1.70 1.69 1.62 1.59 1.45 1.26 1.26 1.25 1.24 1.23 1.22 1.22 1.19 1.18 1.17 1.14 1.11 1.11 1.07 1.07 1.06 1.05 1.04 1.03 0.89 0.87 0.86
HN
NH
H
10h•H
0.87 3.60 1.21 0.96 1.36 1.00 4.16 2.49 1.21 1.44 5.52 0.79
f1 (ppm)
141.28 116.67 77.34 77.16 76.98 55.41 54.42 53.83 48.25 44.39 39.19 33.58 28.64 26.10 25.25
f1 (ppm)


BocN
NH
Ph
Ph
H
rotameric
10i
f1 (ppm)
f1 (ppm)

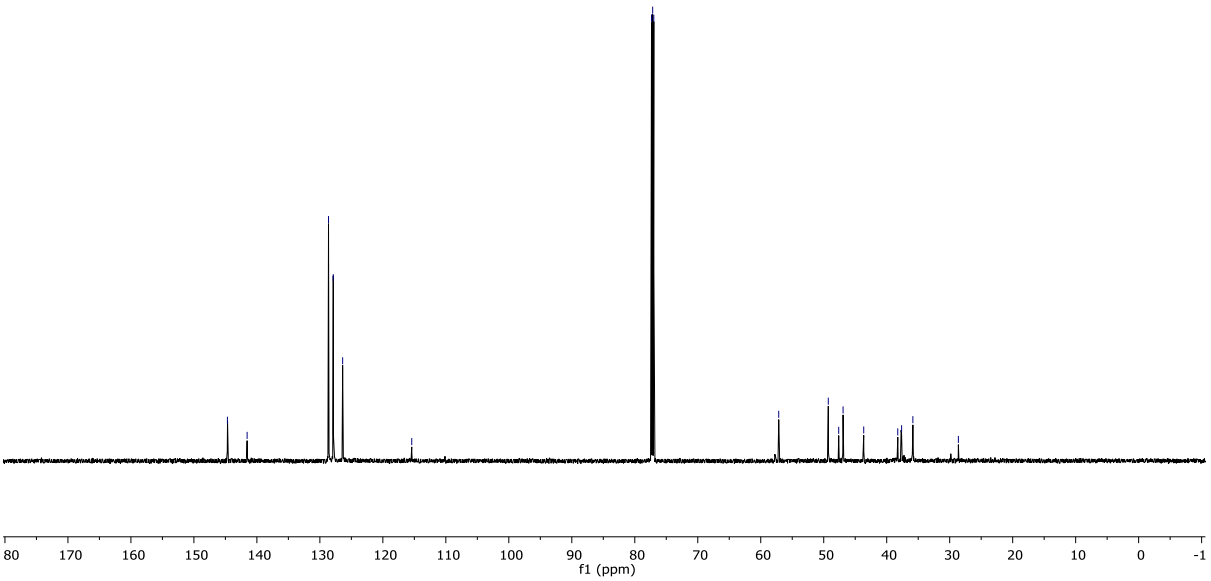


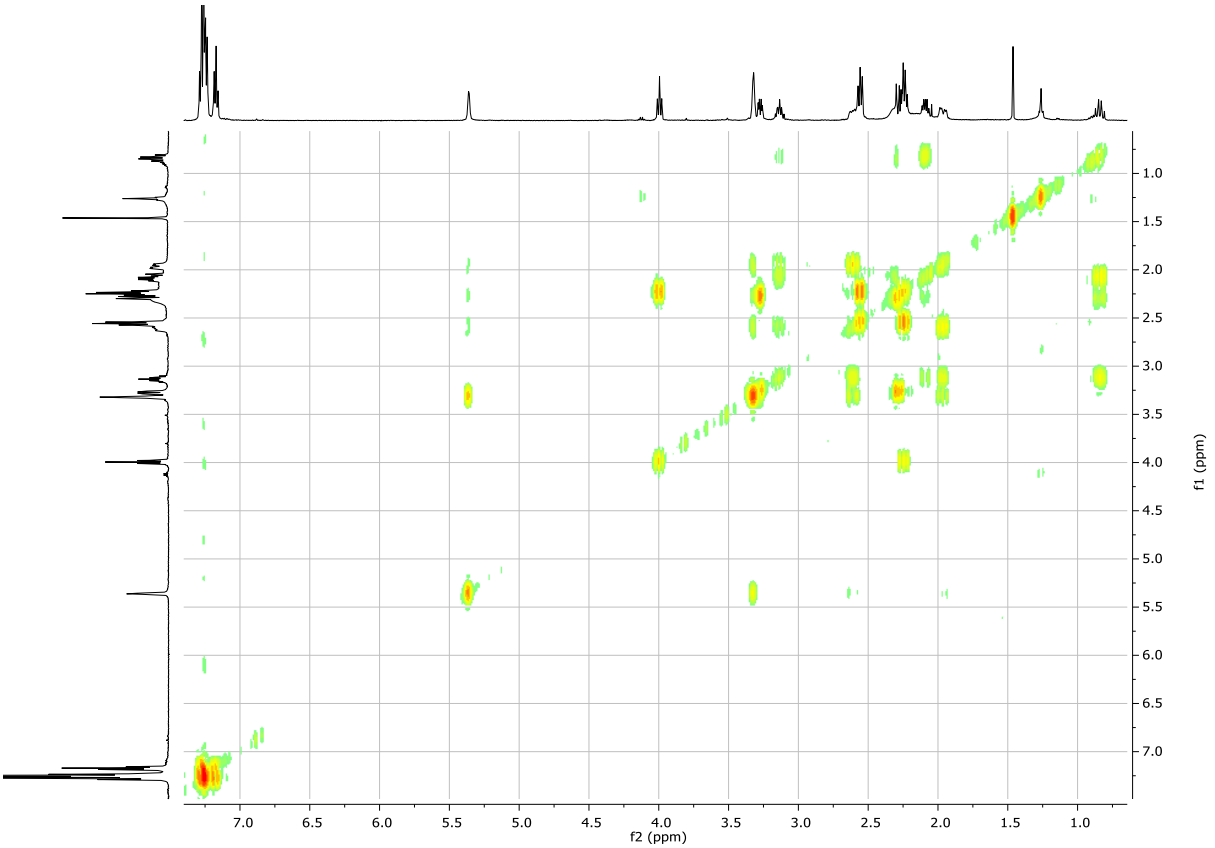
HN
NH
Ph
Ph
H

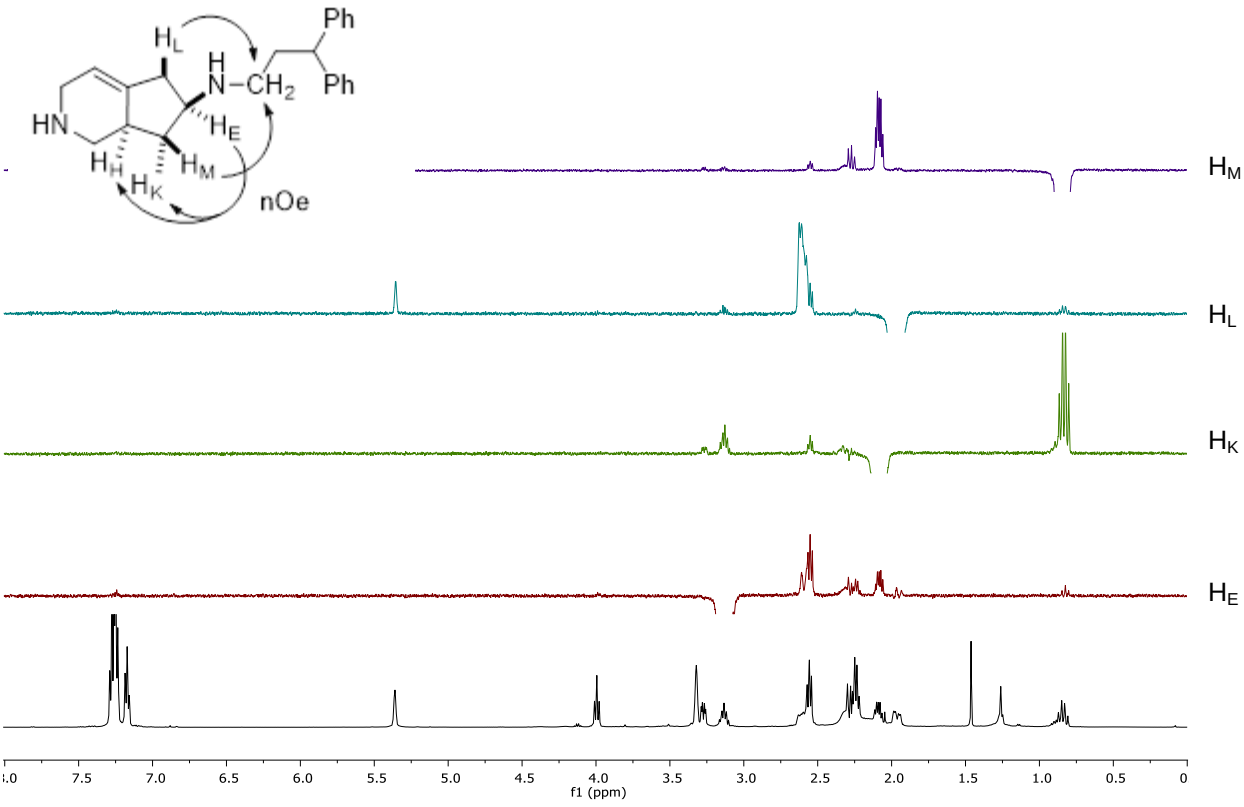
10i•H

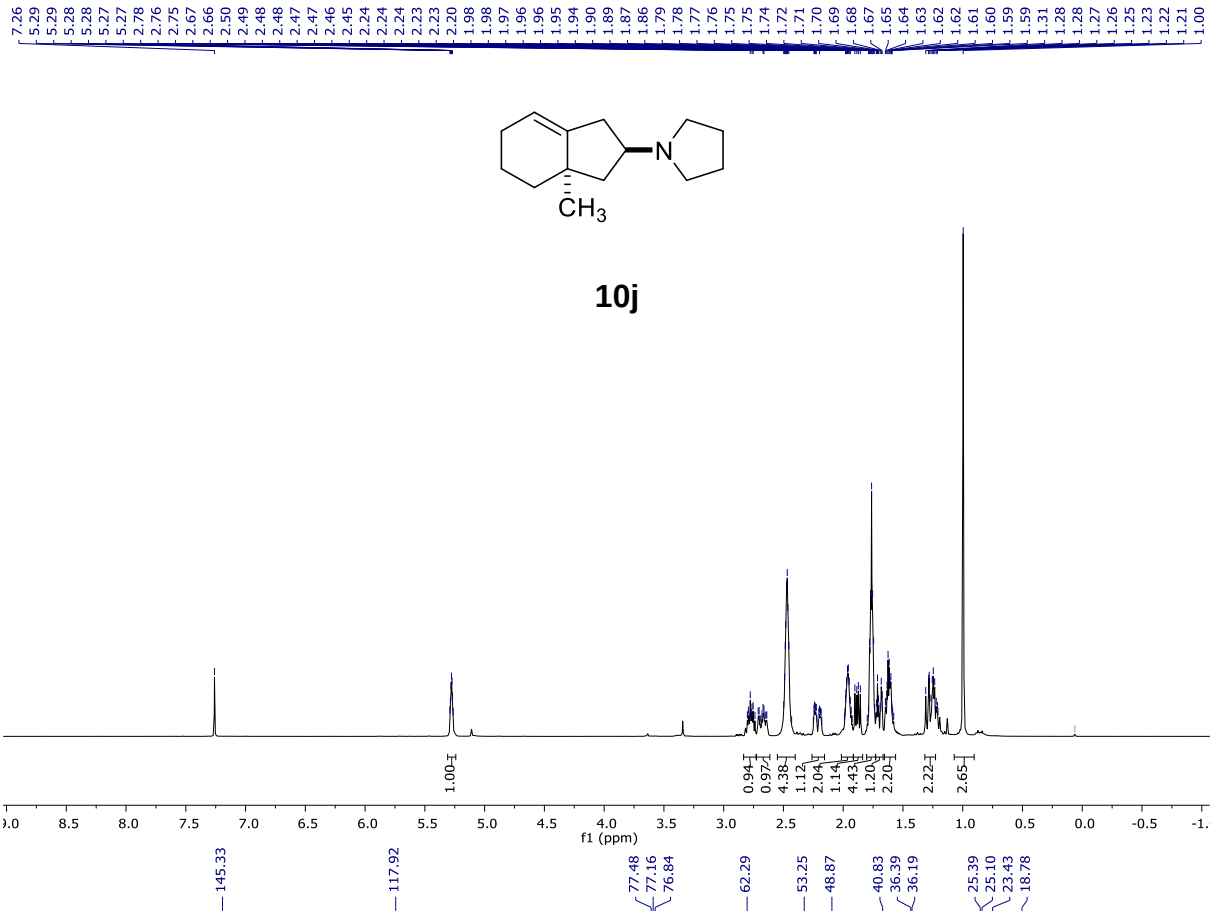

8.79
2.13
1.05
1.12
2.84
0.96
3.24
4.16
1.10
1.05
2.63
1.14
f1 (ppm)

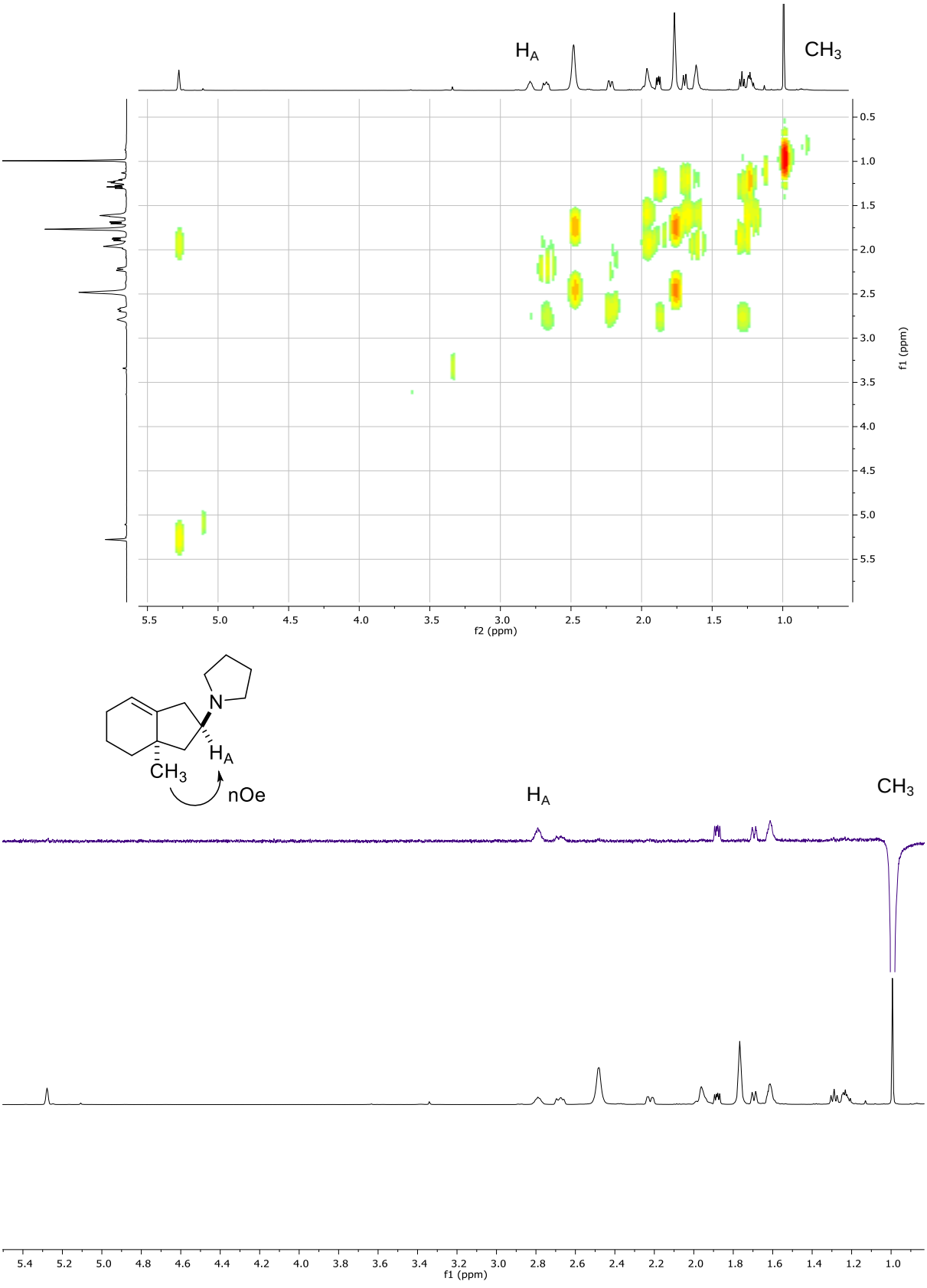
144.68
141.55
128.63
127.87
126.38
115.41
77.34
77.16
76.98
57.14
49.28
47.62
46.93
43.65
38.25
37.64
35.85
28.62

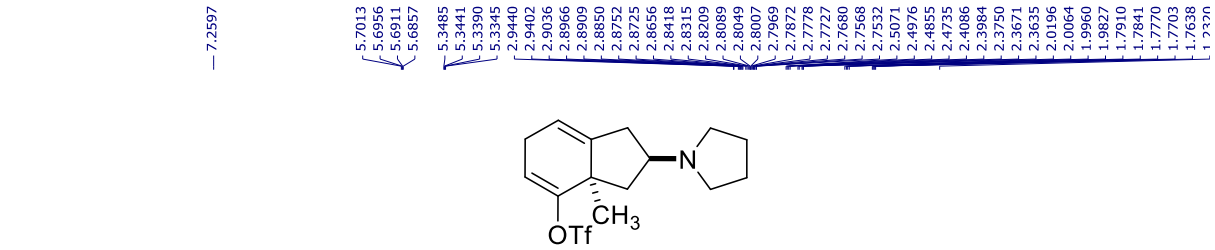

f1 (ppm)


f2 (ppm)
f1 (ppm)


HL
Ph
H
N–CH2
Ph
HN
HE
HH
HM
HK
nOe
HM
HL
HK
HE
f1 (ppm)

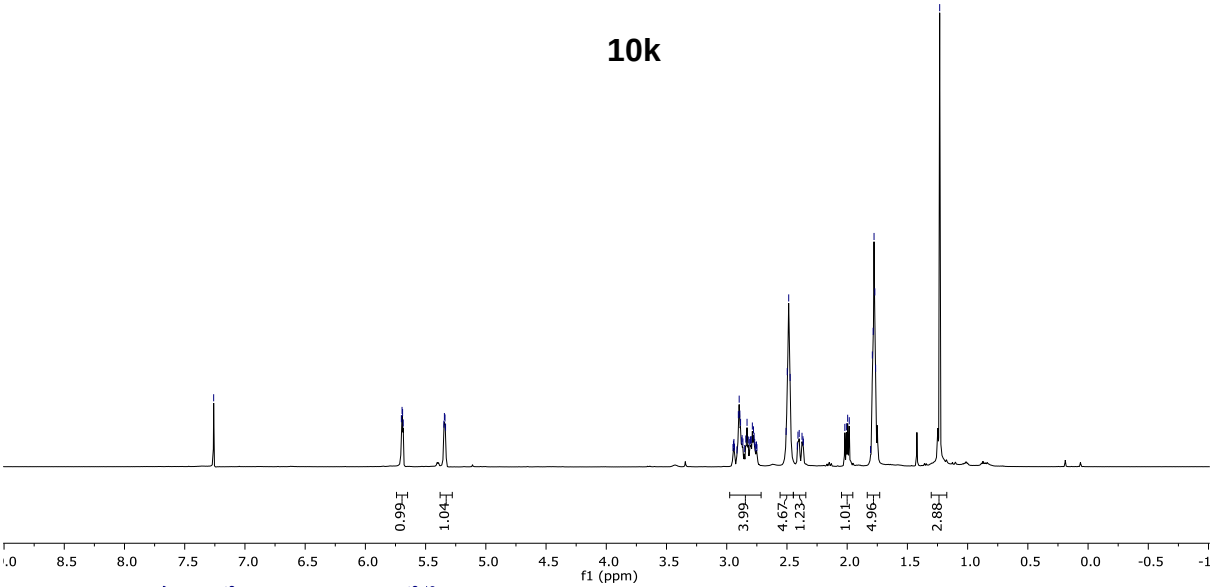

7.26 5.29 5.29 5.28 5.28 5.27 5.27 2.78 2.76 2.75 2.67 2.66 2.50 2.49 2.48 2.48 2.47 2.47 2.46 2.45 2.24 2.24 2.24 2.23 2.23 2.20 1.98 1.98 1.97 1.96 1.96 1.95 1.94 1.90 1.89 1.87 1.86 1.79 1.78 1.77 1.76 1.75 1.75 1.74 1.72 1.71 1.70 1.69 1.68 1.67 1.65 1.64 1.63 1.62 1.62 1.61 1.60 1.59 1.59 1.31 1.28 1.28 1.27 1.26 1.25 1.23 1.22 1.21 1.00
N
CH3
10j
1.00 0.94 0.97 4.38 1.12 2.04 1.14 4.43 1.20 2.20 2.22 2.65
f1 (ppm)
145.33 117.92 77.48 77.16 76.84 62.29 53.25 48.87 40.83 36.39 36.19 25.39 25.10 23.43 18.78
f1 (ppm)

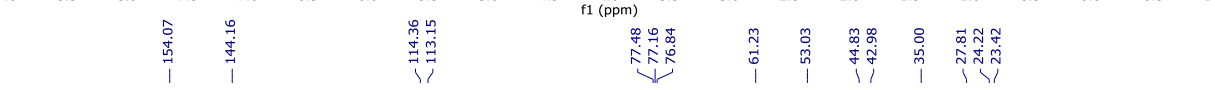

H_A
CH_3
f2 (ppm)
f1 (ppm)
N
H_A
CH_3
nOe
H_A
CH_3
f1 (ppm)

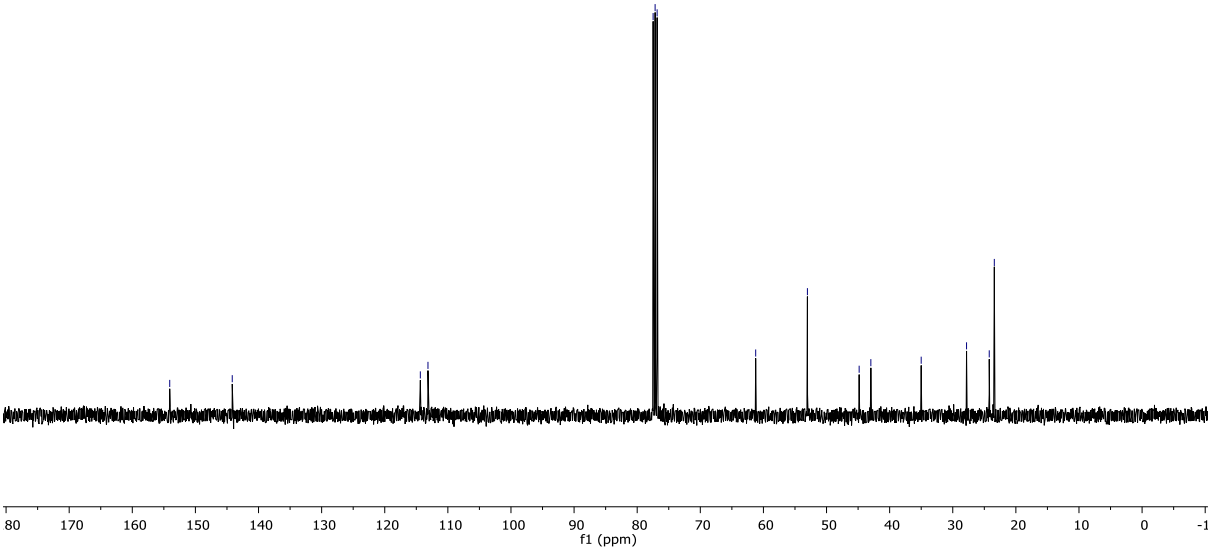

7.2597
5.7013
5.6956
5.6911
5.6857
5.3485
5.3441
5.3390
5.3345
2.9440
2.9402
2.9036
2.8966
2.8909
2.8850
2.8752
2.8725
2.8656
2.8418
2.8315
2.8209
2.8089
2.8049
2.8007
2.7969
2.7872
2.7778
2.7727
2.7680
2.7568
2.7532
2.5071
2.4976
2.4855
2.4735
2.4086
2.3984
2.3750
2.3671
2.3635
2.0196
2.0064
1.9960
1.9827
1.7910
1.7841
1.7770
1.7703
1.7638

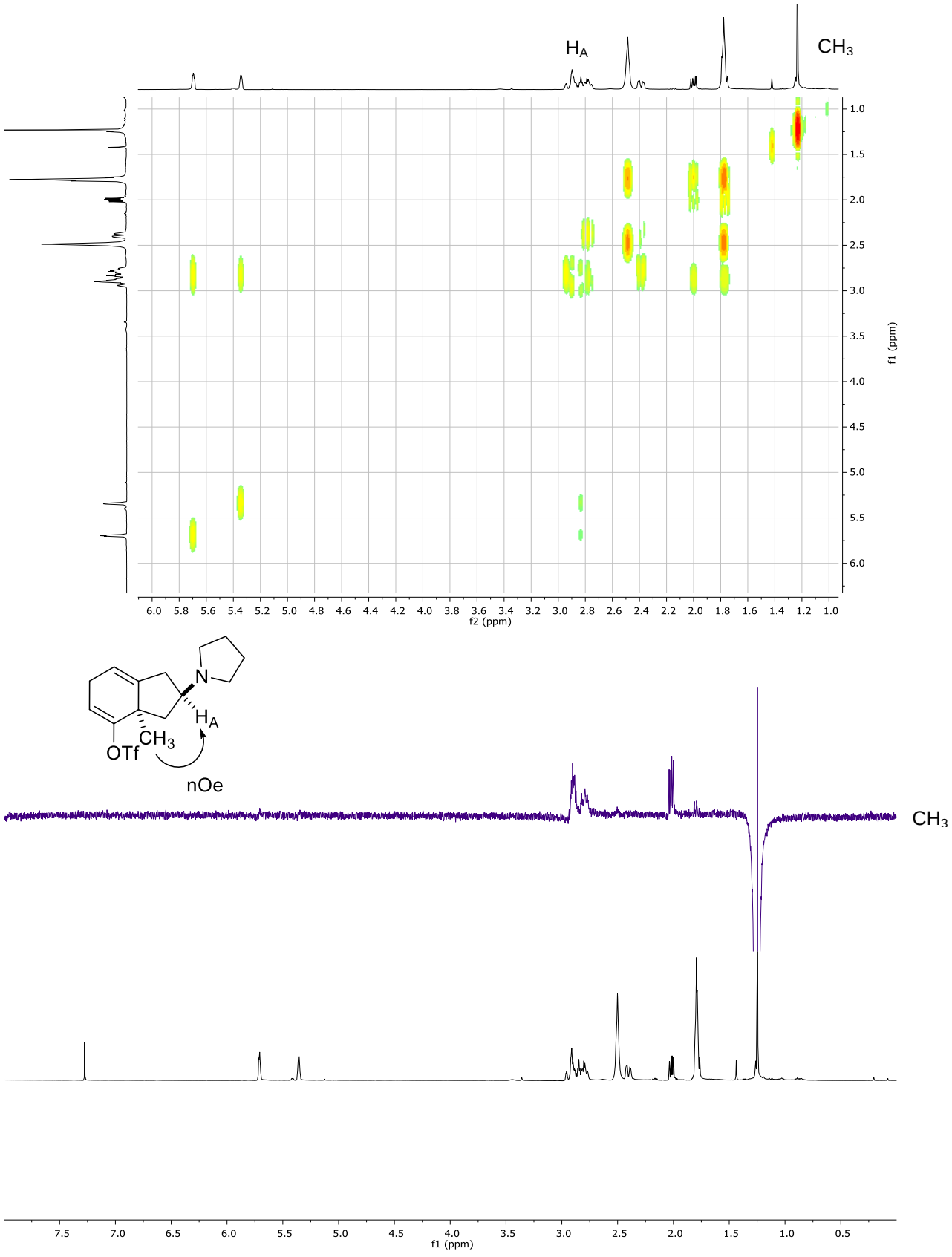
N
CH3
OTf

10k


0.99
1.04
3.99
4.67
1.23
1.01
4.96
2.88
f1 (ppm)


154.07
144.16
114.36
113.15
77.48
77.16
76.84
61.23
53.03
44.83
42.98
35.00
27.81
24.22
23.42


f1 (ppm)


H_A
CH_3
f2 (ppm)
f1 (ppm)
N
H_A
CH_3
OTf
nOe
CH_3
f1 (ppm)


7.26
7.19
7.18
7.17
7.16
7.15
7.15
7.15
7.14
7.13
7.12
7.12
3.26
3.24
3.23
3.22
3.20
3.14
3.12
3.11
3.09
2.99
2.97
2.96
2.94
2.86
2.85
2.84
2.83
2.82
2.81
2.68
2.67
2.66
1.86
1.85
1.84
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1.82
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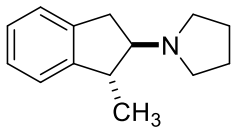
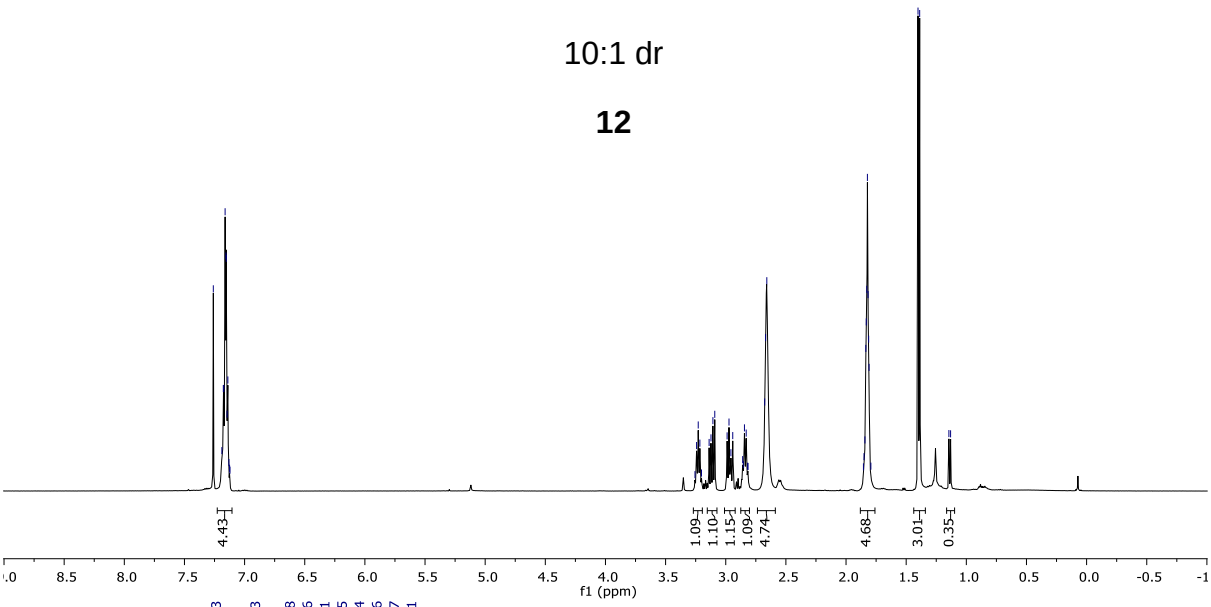
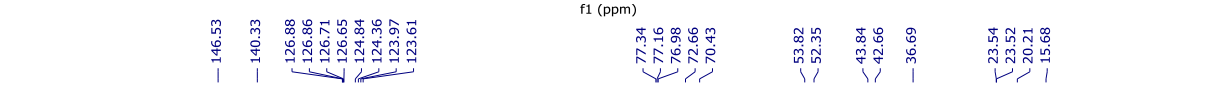
1.81
1.79
1.40
1.39
1.14
1.13

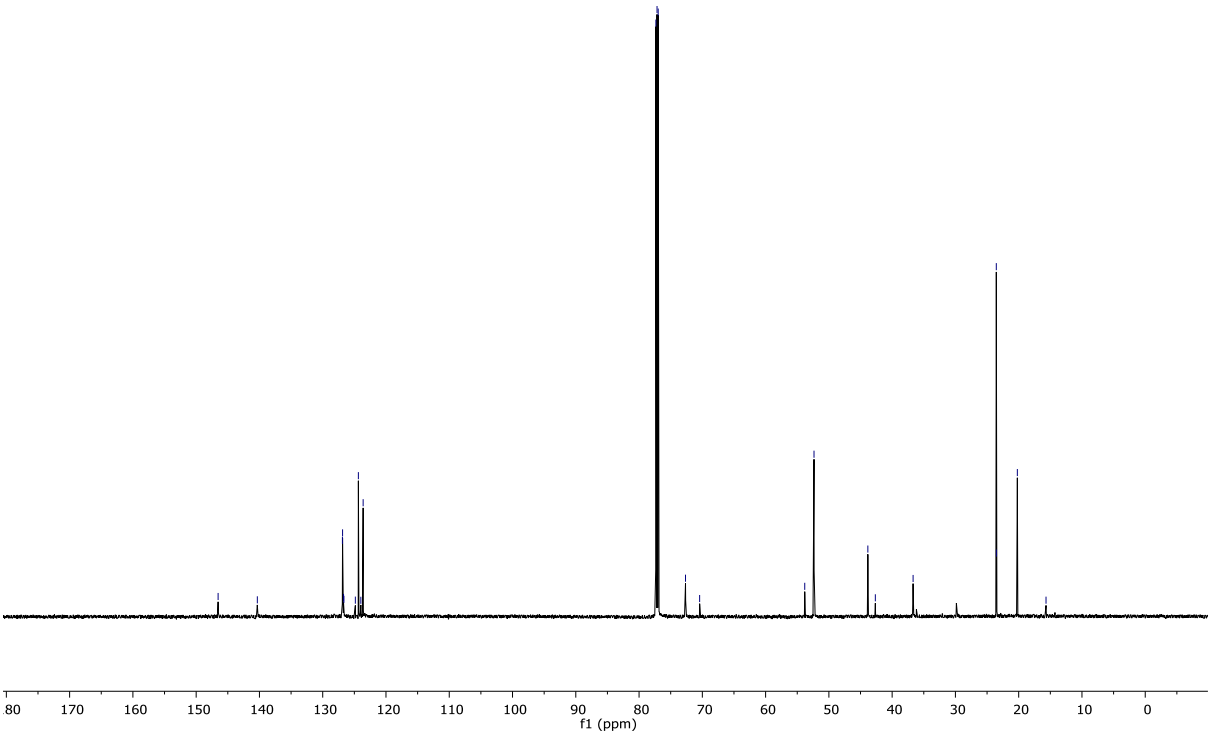

N
CH3

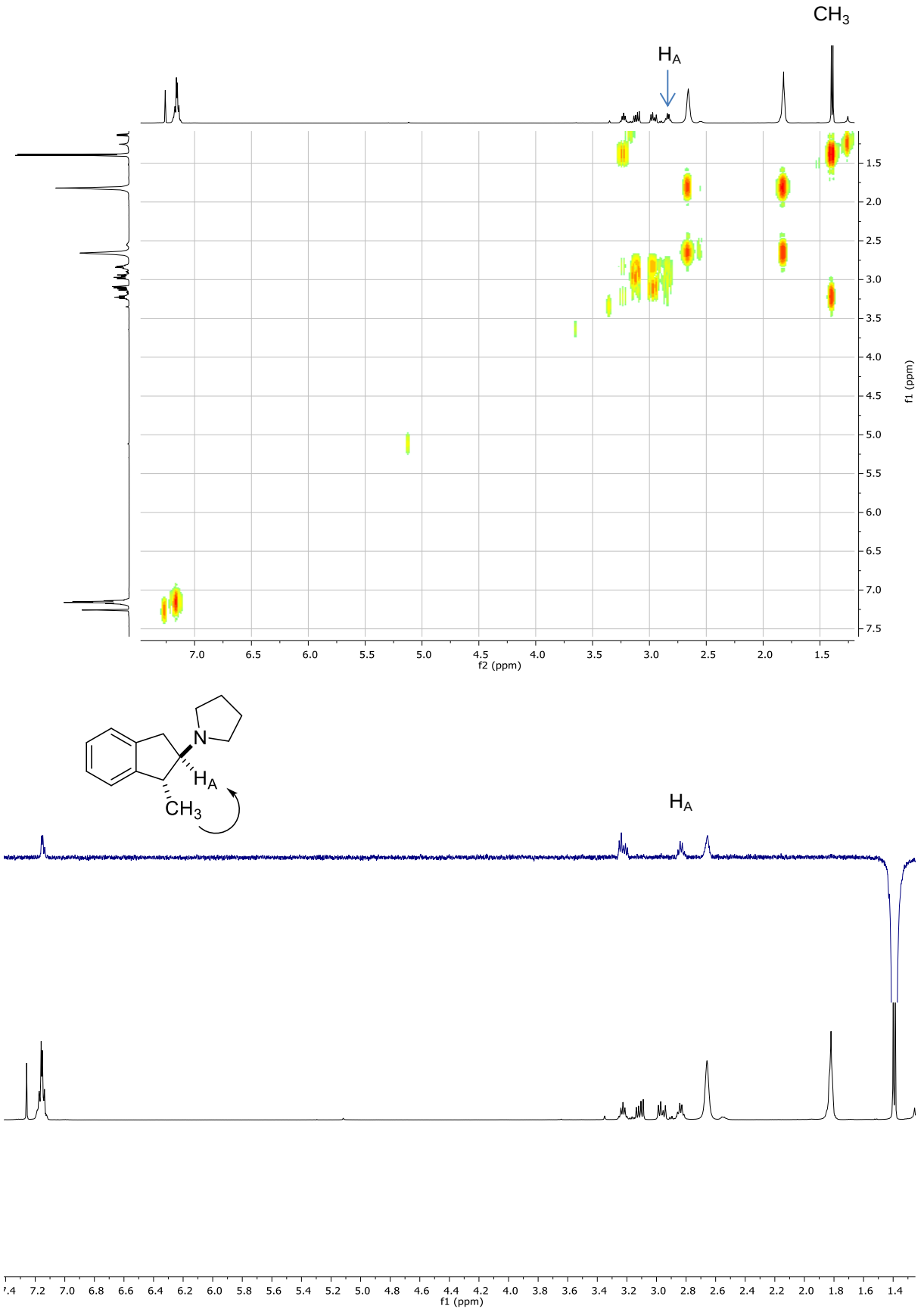
10:1 dr

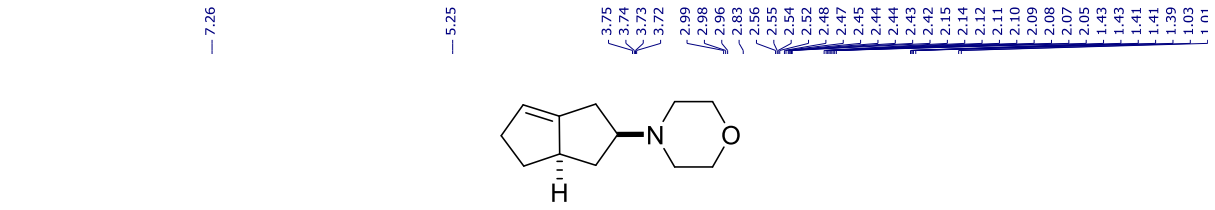
12


4.43
1.09
1.10
1.15
1.09
4.74
4.68
3.01
0.35
f1 (ppm)

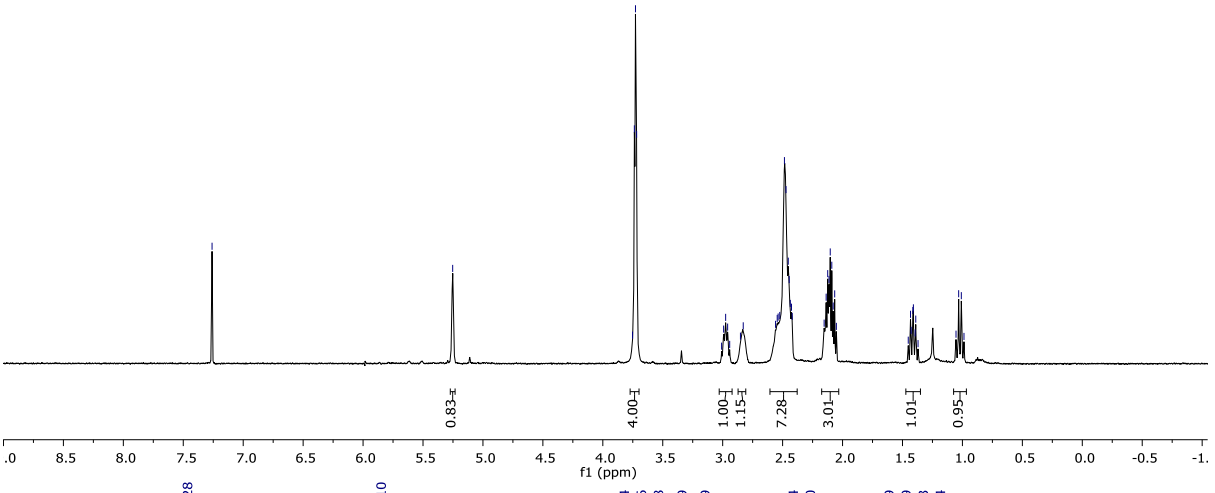

146.53
140.33
126.88
126.86
126.71
126.65
124.84
124.36
123.97
123.61
77.34
77.16
76.98
72.66
70.43
53.82
52.35
43.84
42.66
36.69
23.54
23.52
20.21
15.68

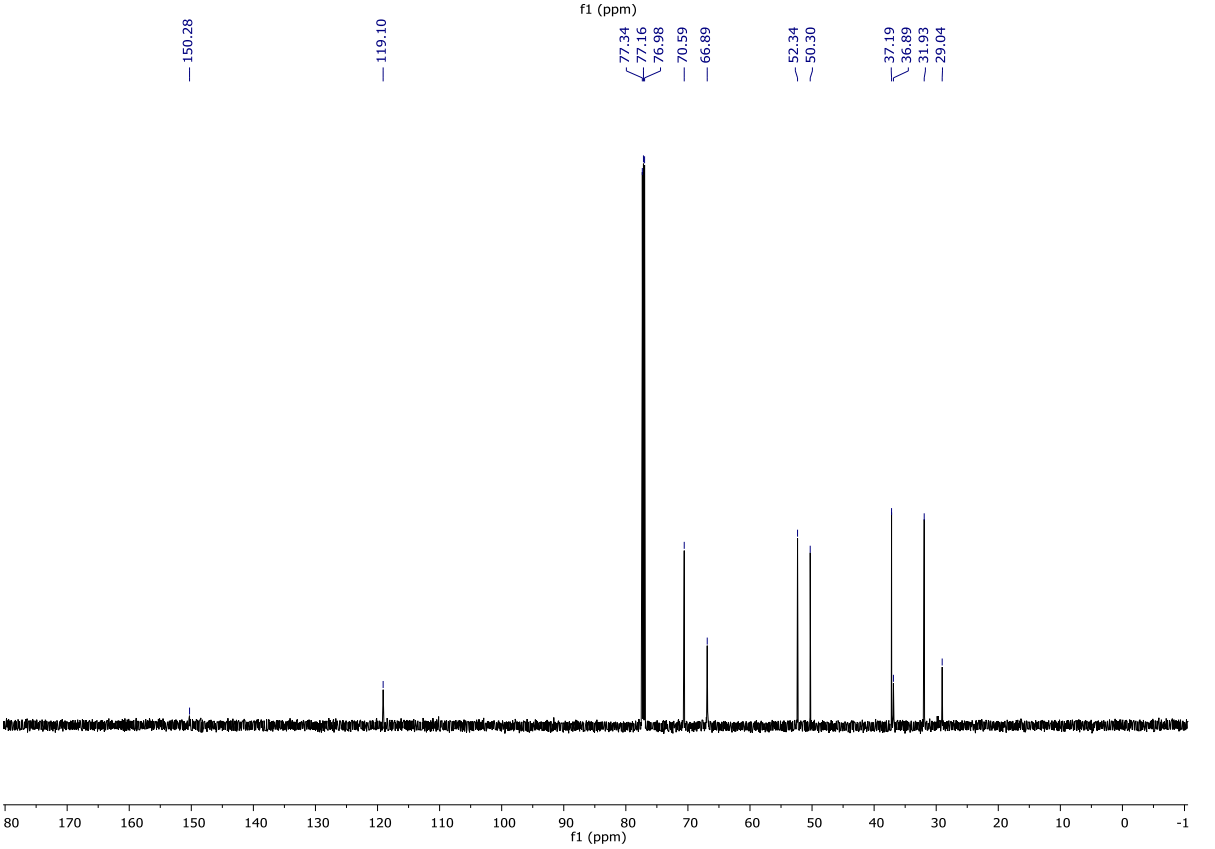

f1 (ppm)

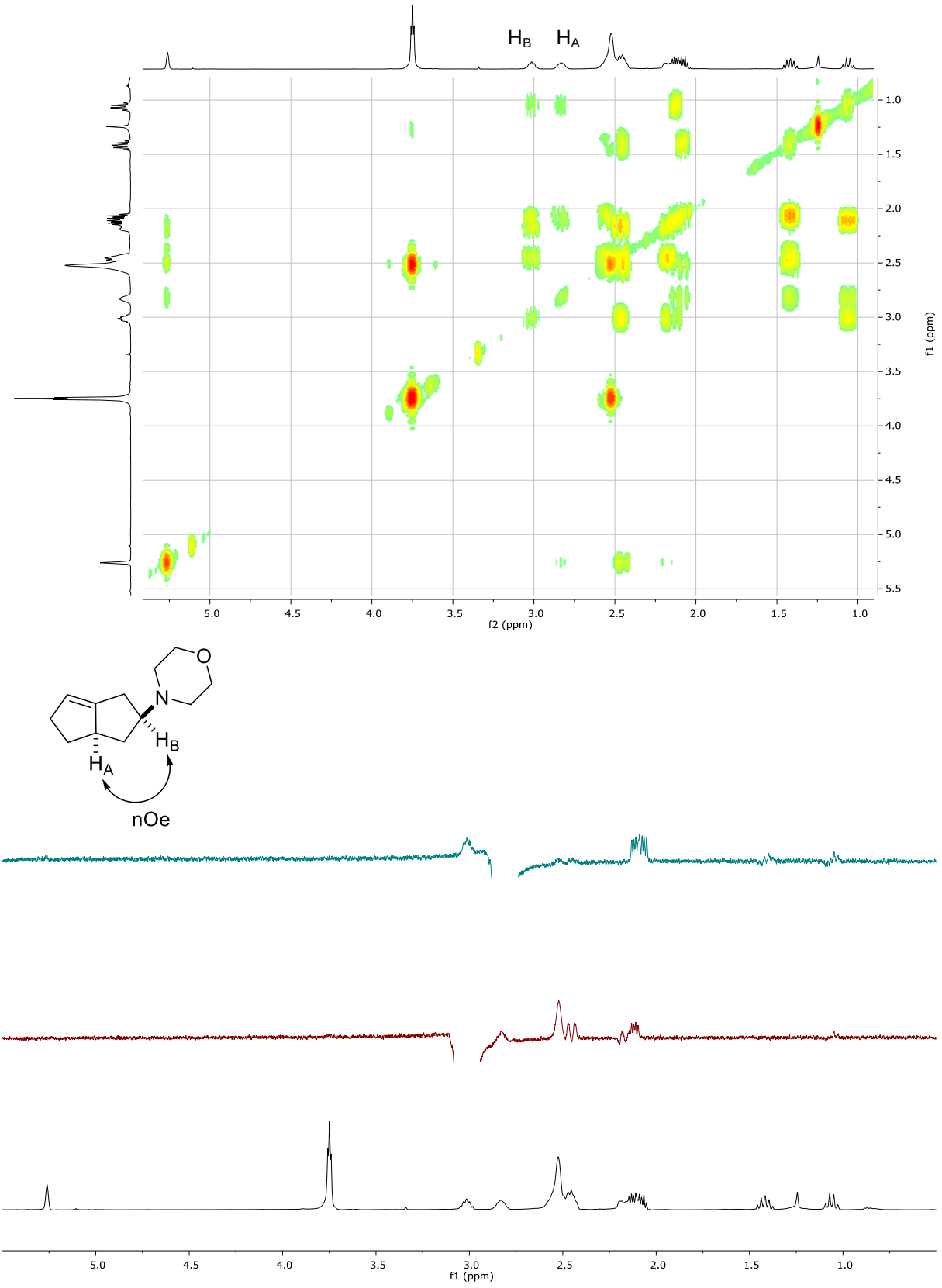

CH3
HA
f2 (ppm)
f1 (ppm)
N
HA
CH3
HA
CH3
f1 (ppm)


7.26
5.25
3.75
3.74
3.73
3.72
2.99
2.98
2.96
2.83
2.56
2.55
2.54
2.52
2.48
2.47
2.45
2.44
2.44
2.43
2.42
2.15
2.14
2.12
2.11
2.10
2.09
2.08
2.07
2.05
1.43
1.43
1.41
1.41
1.39
1.03
N
O
H

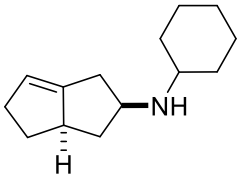
14a


0.83
4.00
1.00
1.15
7.28
3.01
1.01
0.95
f1 (ppm)

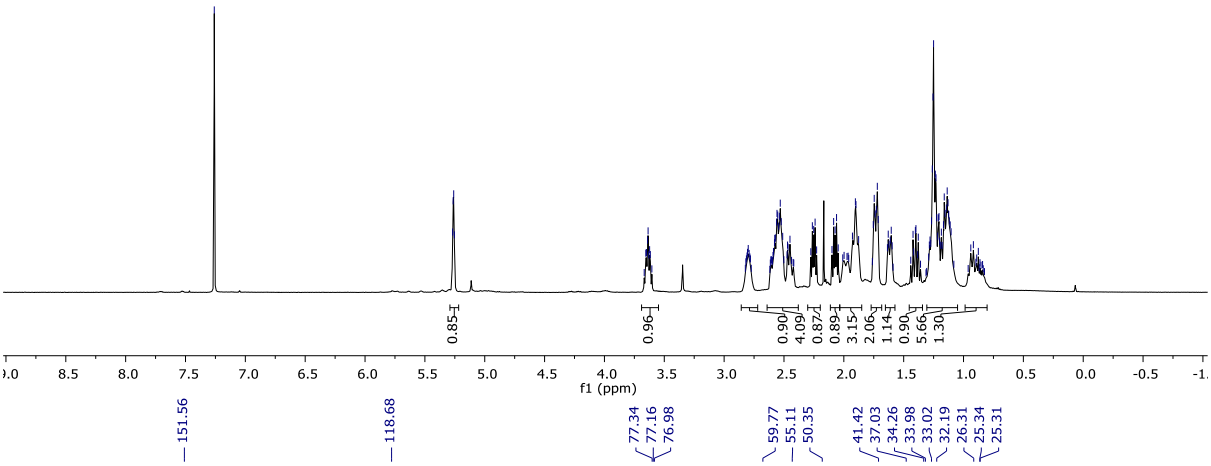

150.28
119.10
77.34
77.16
76.98
70.59
66.89
52.34
50.30
37.19
36.89
31.93
29.04
f1 (ppm)


H_B H_A
f2 (ppm)
f1 (ppm)
O
N
H_B
H_A
nOe
H_A
H_B
f1 (ppm)

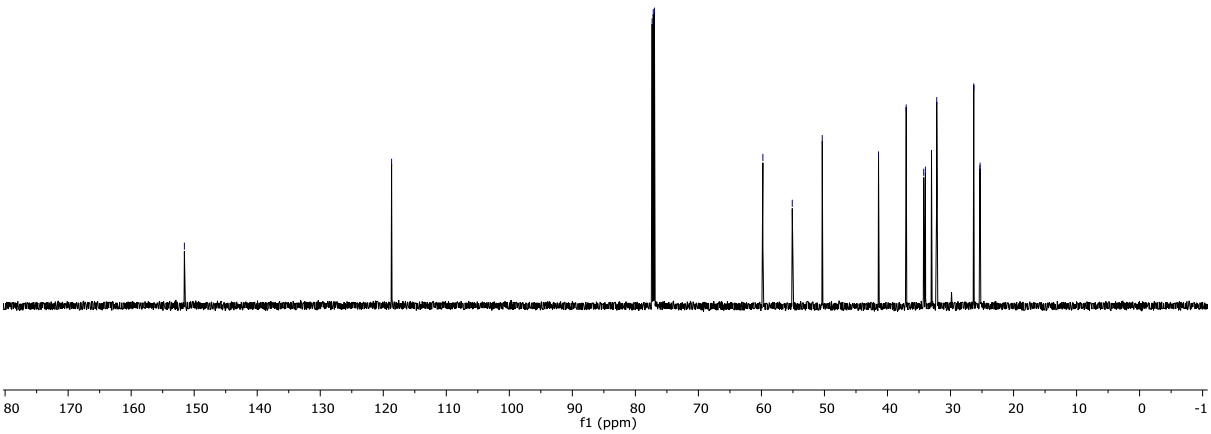

7.26
5.27
5.26
5.26
5.25
5.26
3.64
3.64
2.58
2.58
2.57
2.56
2.56
2.55
2.54
2.54
2.53
2.52
2.51
2.45
2.26
2.25
2.24
2.09
2.07
2.06
1.93
1.90
1.90
1.88
1.75
1.75
1.74
1.73
1.72
1.71
1.63
1.62
1.61
1.60
1.42
1.40
1.40
1.38
1.29
1.28
1.27
1.27
1.26
1.25
1.25
1.24
1.23
1.22
1.22
1.21
1.20
1.19
1.17
1.16
1.15
1.14
1.14
1.13
1.12
1.12
1.11
1.10
0.92

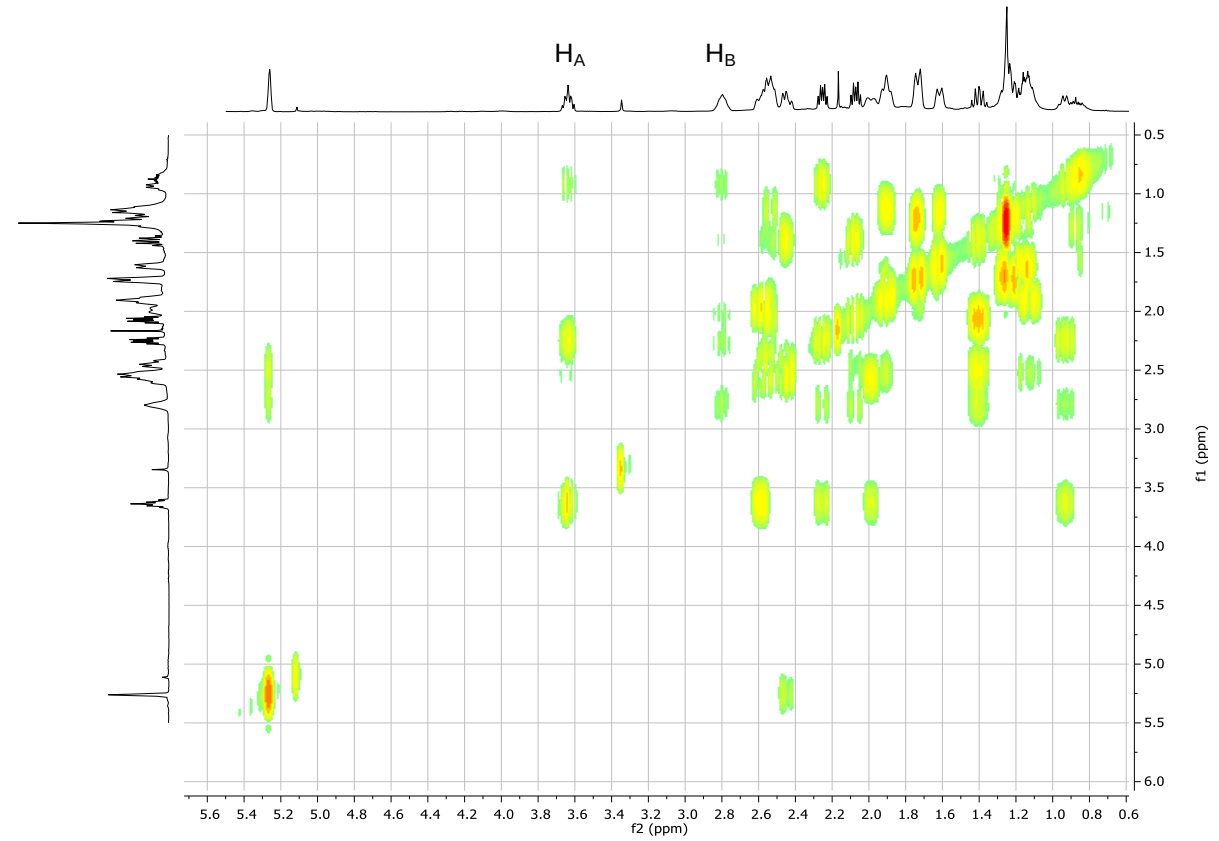

NH
H

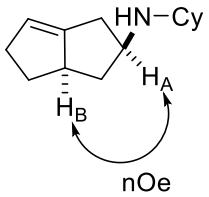
14b

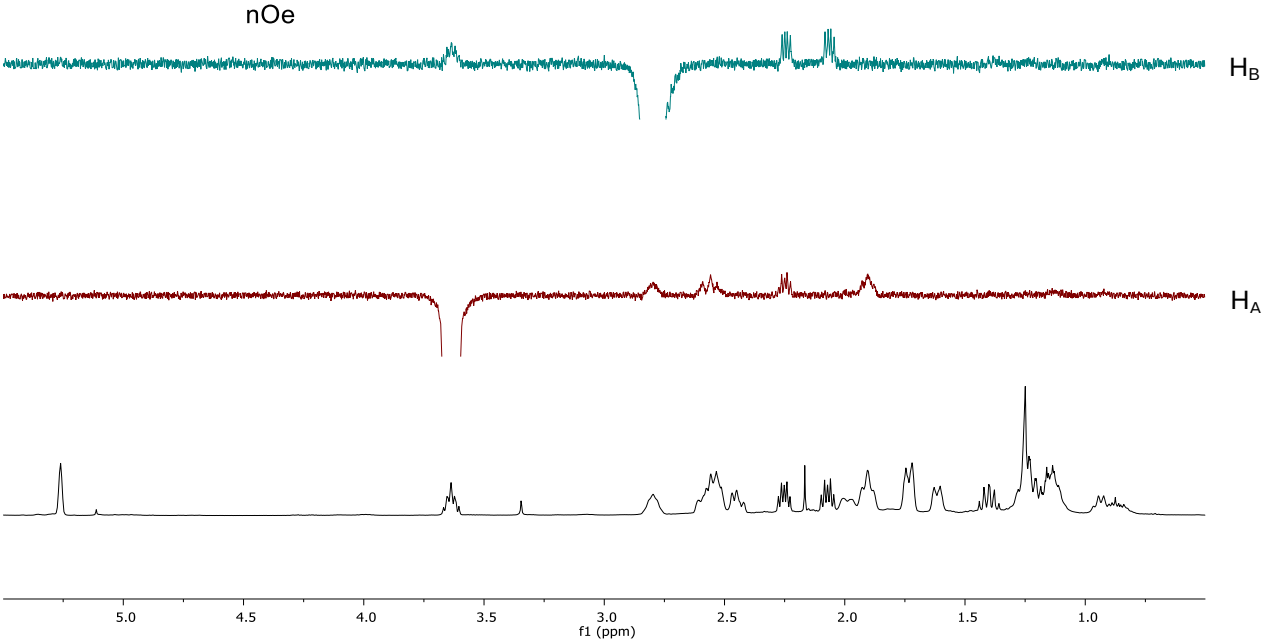

0.85
0.96
0.90
4.09
0.87
0.89
3.15
2.06
1.14
0.90
5.66
1.30
f1 (ppm)

151.56
118.68
77.34
77.16
76.98
59.77
55.11
50.35
41.42
37.03
34.26
33.98
33.02
32.19
26.31
25.34
25.31

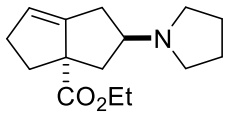

f1 (ppm)


H_A
H_B
f2 (ppm)
f1 (ppm)

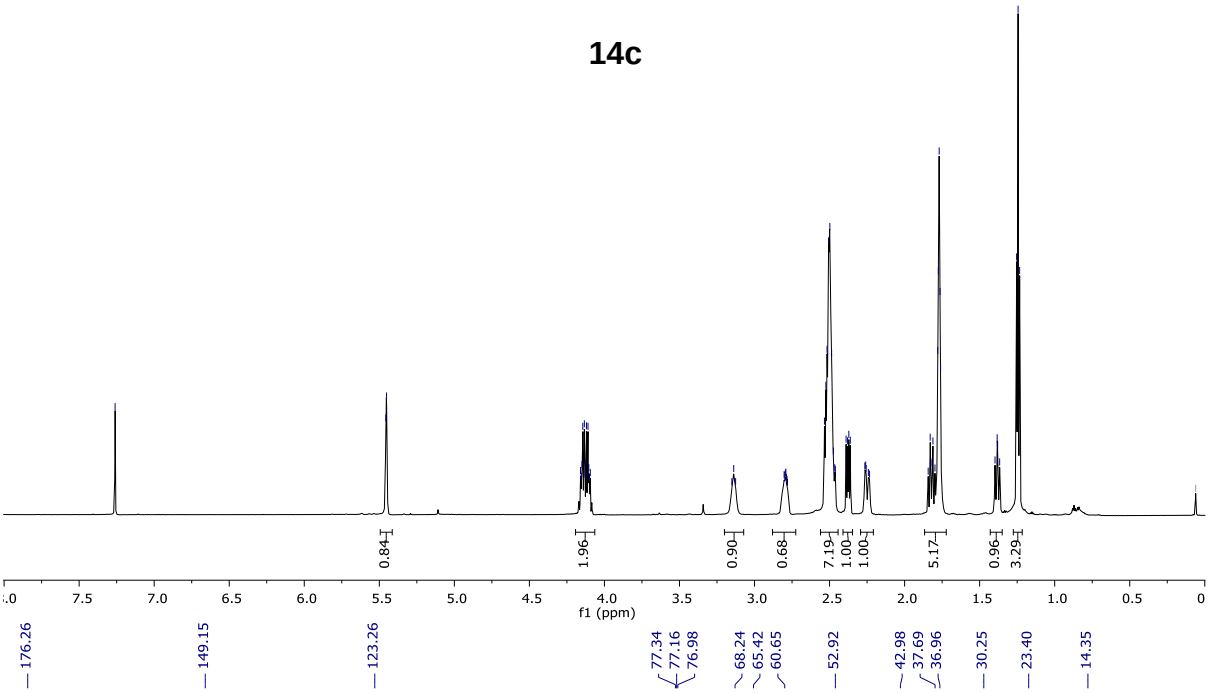

HN−Cy
H_A
H_B
nOe


H_B
H_A
f1 (ppm)

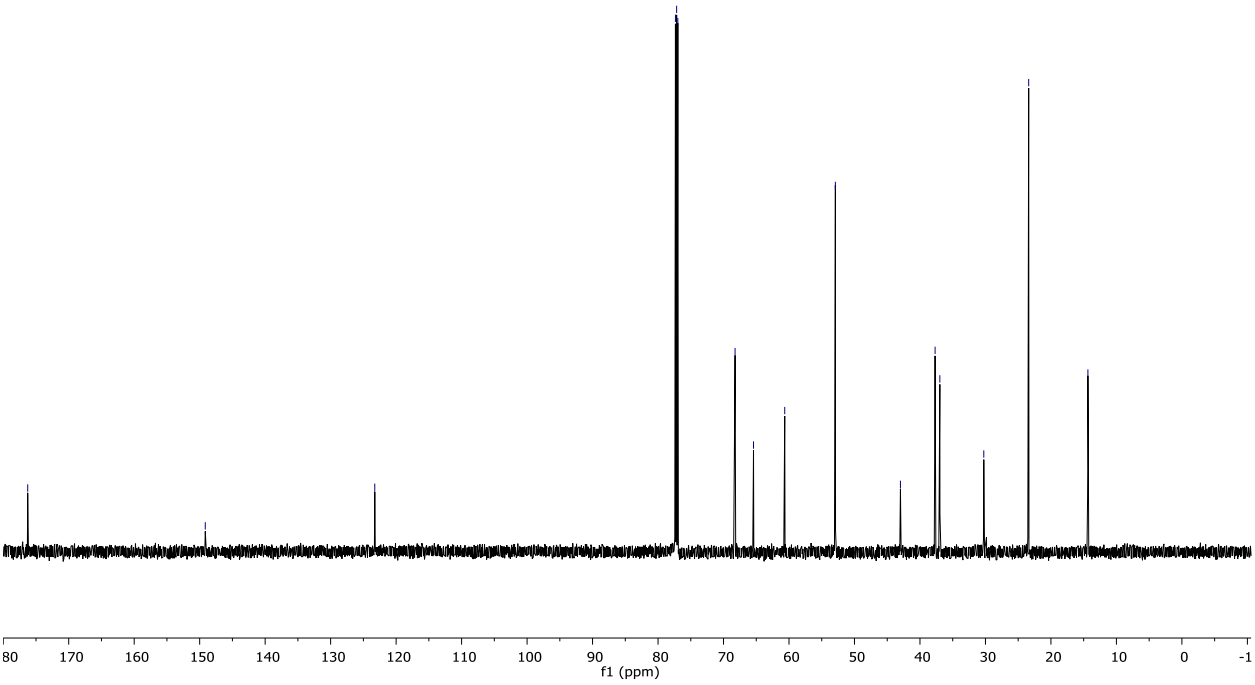

7.26
5.46
5.45
4.16
4.15
4.15
4.14
4.13
4.13
4.12
4.12
4.11
4.10
4.10
4.09
3.15
3.14
3.13
2.80
2.80
2.79
2.79
2.79
2.78
2.78
2.53
2.52
2.52
2.51
2.50
2.49
2.47
2.47
2.46
2.39
2.38
2.37
2.36
2.26
2.26
2.26
2.24
2.23
1.84
1.83
1.82
1.82
1.81
1.80
1.78
1.77
1.77
1.76
1.76
1.40
1.38
1.38
1.37
1.25
1.24
1.23
0.06

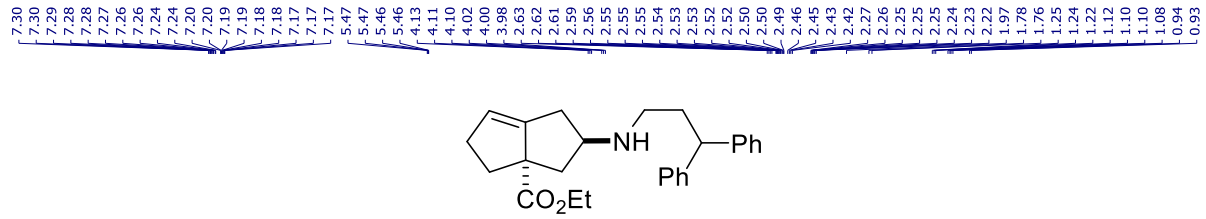

N
CO2Et

14c


0.84
1.96
0.90
0.68
7.19
1.00
1.00
5.17
0.96
3.29
f1 (ppm)

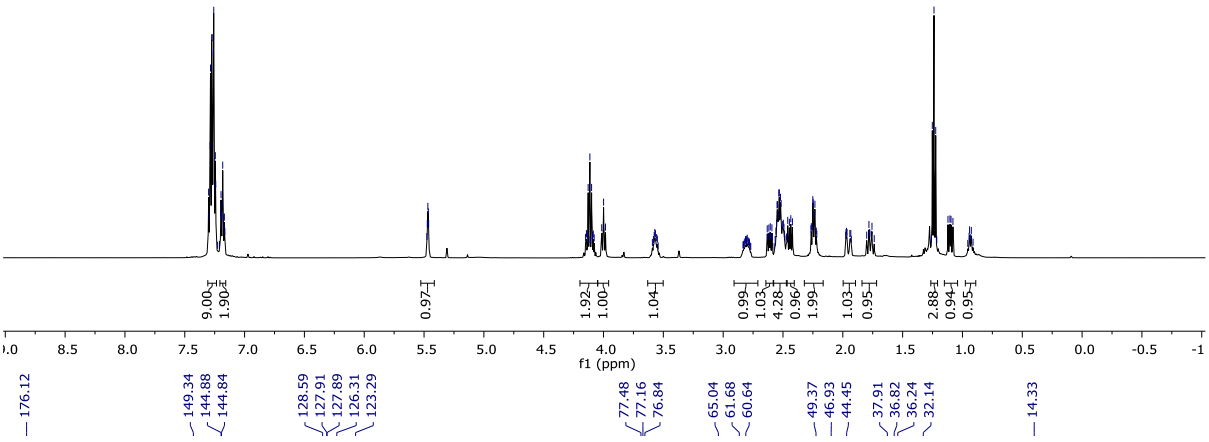
176.26
149.15
123.26
77.34
77.16
76.98
68.24
65.42
60.65
52.92
42.98
37.69
36.96
30.25
23.40
14.35


f1 (ppm)

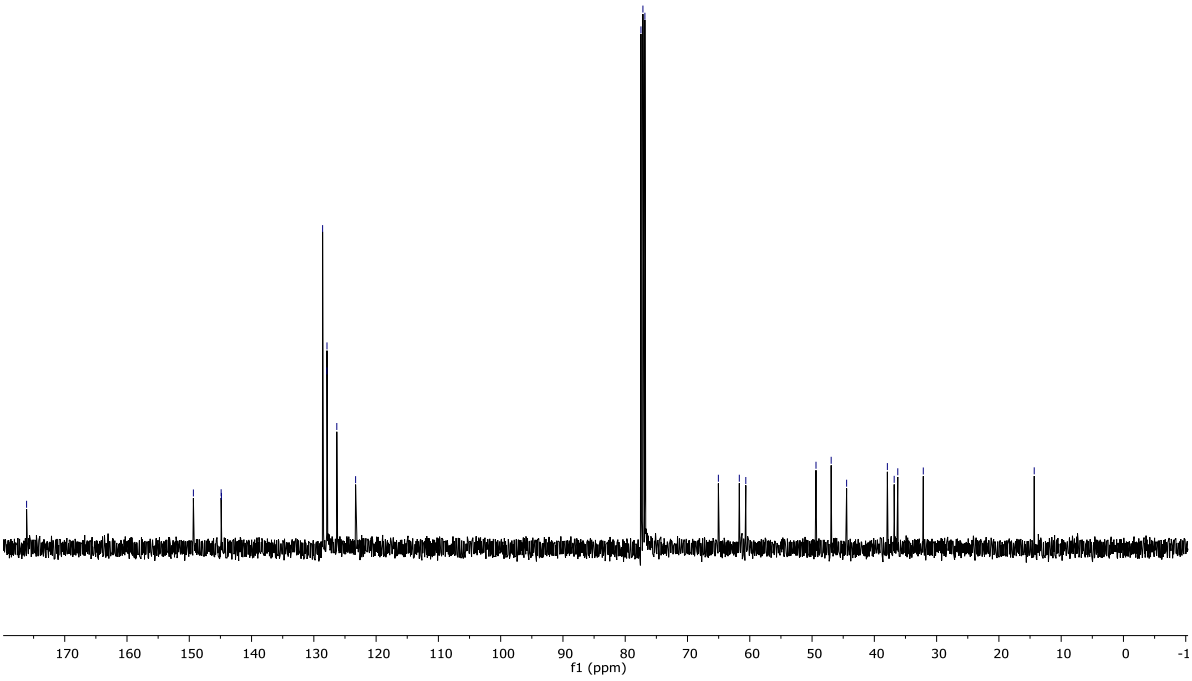

7.30 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.24 7.24 7.20 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.17 7.17
5.47 5.47 5.46 5.46 4.13 4.11 4.10 4.02 4.00 3.98 2.63 2.62 2.61 2.59 2.56 2.55 2.55 2.55 2.54 2.53 2.53 2.52 2.52 2.50 2.50 2.49 2.46 2.45 2.43 2.42 2.27 2.26 2.25 2.25 2.25 2.24 2.23 2.22 1.97 1.78 1.76 1.25 1.24 1.22 1.12 1.10 1.10 1.08 0.94 0.93

NH
Ph
Ph
CO2Et

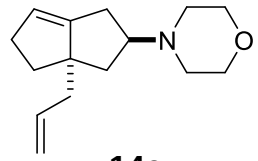
14d


9.00 1.90 0.97 1.92 1.00 1.04 0.99 1.03 4.28 0.96 1.99 1.03 0.95 2.88 0.94 0.95
f1 (ppm)

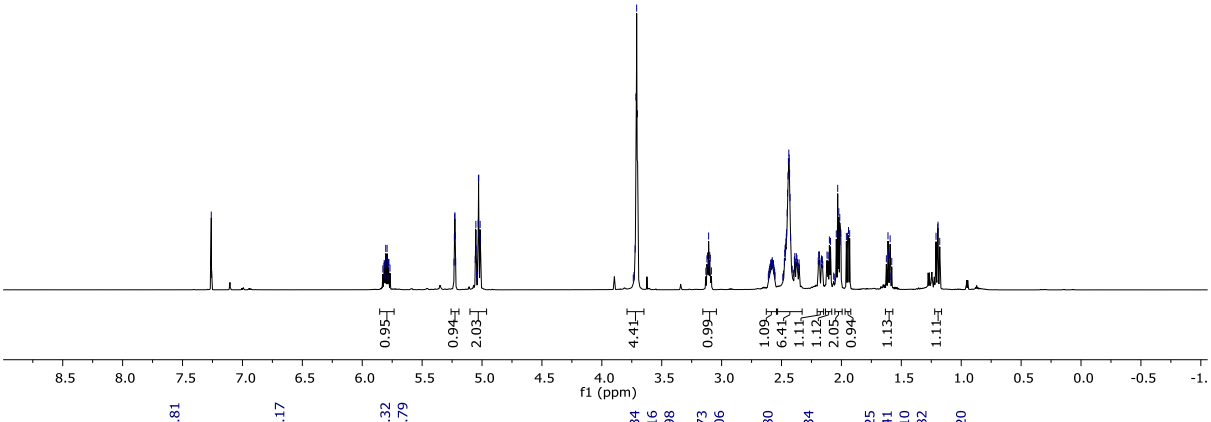
176.12
149.34 144.88 144.84
128.59 127.91 127.89 126.31 123.29
77.48 77.16 76.84
65.04 61.68 60.64
49.37 46.93 44.45
37.91 36.82 36.24 32.14
14.33

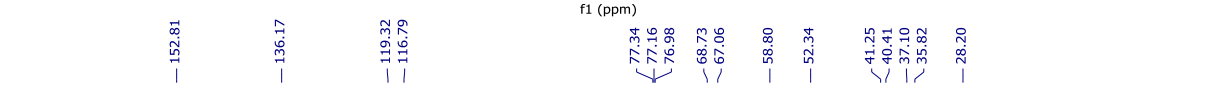

f1 (ppm)

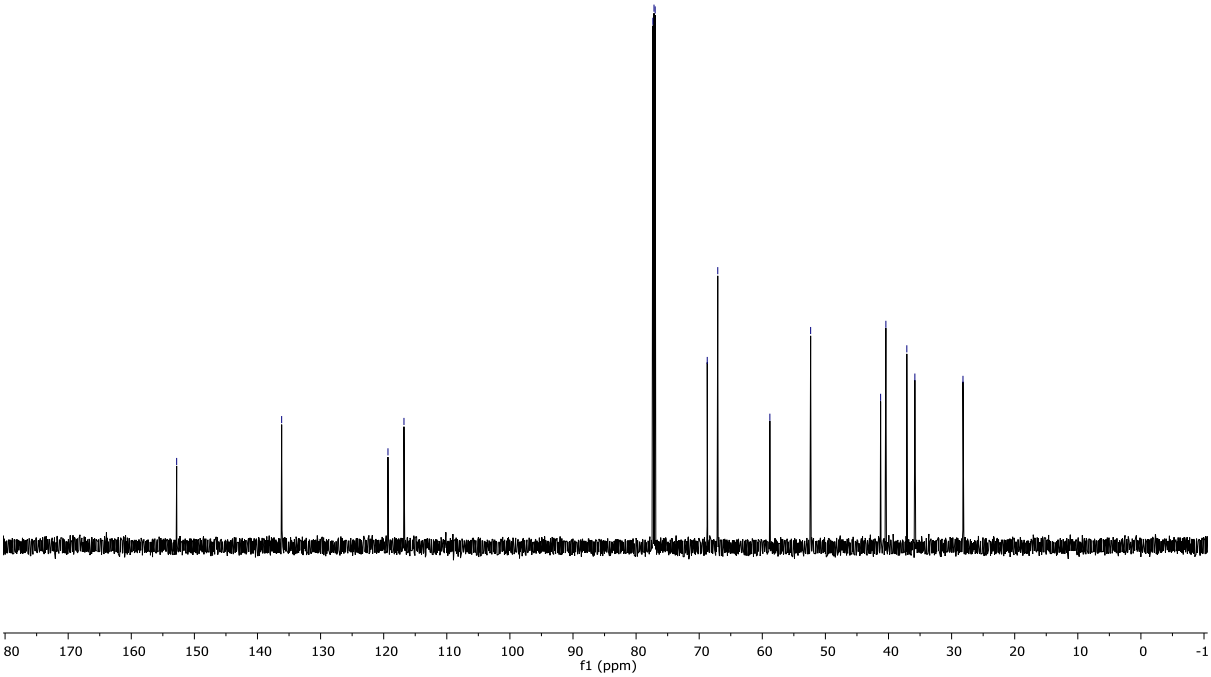

7.26
5.80
5.80
5.79
5.23
5.23
5.23
5.22
5.05
5.05
5.05
5.03
5.03
5.03
5.02
5.02
5.01
3.72
3.72
3.71
3.70
3.12
3.12
3.11
3.10
3.09
2.47
2.47
2.47
2.46
2.46
2.46
2.45
2.45
2.45
2.44
2.44
2.44
2.43
2.43
2.42
2.39
2.38
2.37
2.19
2.18
2.12
2.11
2.10
2.09
2.04
2.03
2.02
2.01
2.01
2.00
1.96
1.95
1.94
1.93
1.62
1.61
1.61
1.60
1.59
1.21
1.20
1.19
1.18

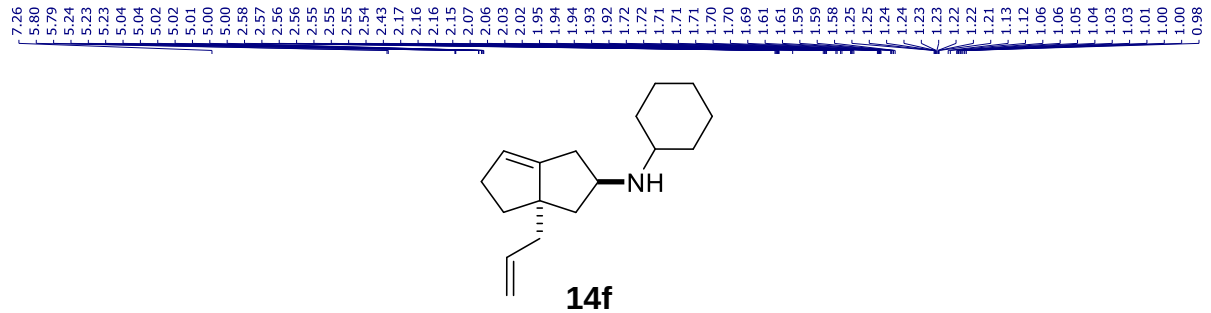

N
O

14e


0.95
0.94
2.03
4.41
0.99
1.09
6.41
1.11
1.12
2.05
0.94
1.13
1.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

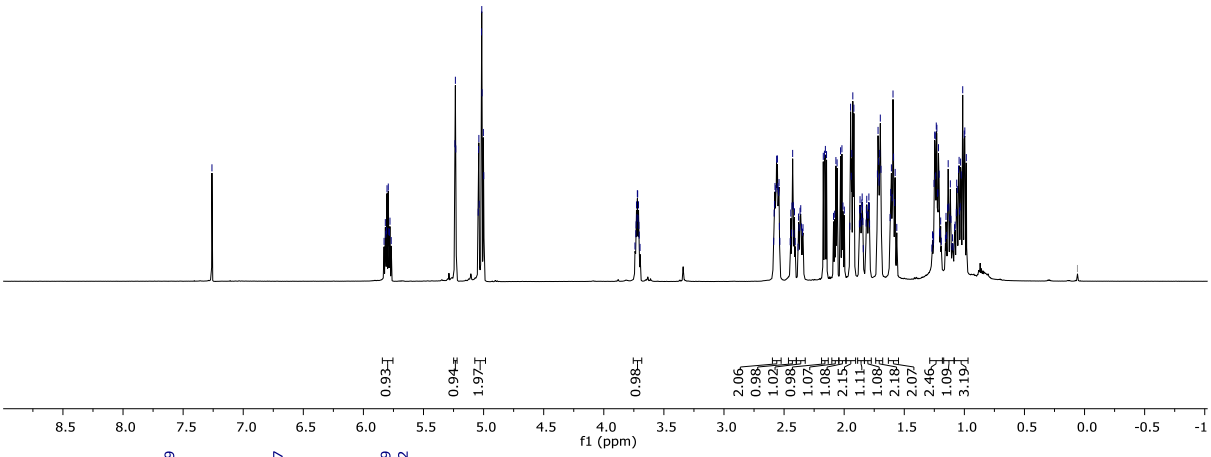

152.81
136.17
119.32
116.79
77.34
77.16
76.98
68.73
67.06
58.80
52.34
41.25
40.41
37.10
35.82
28.20

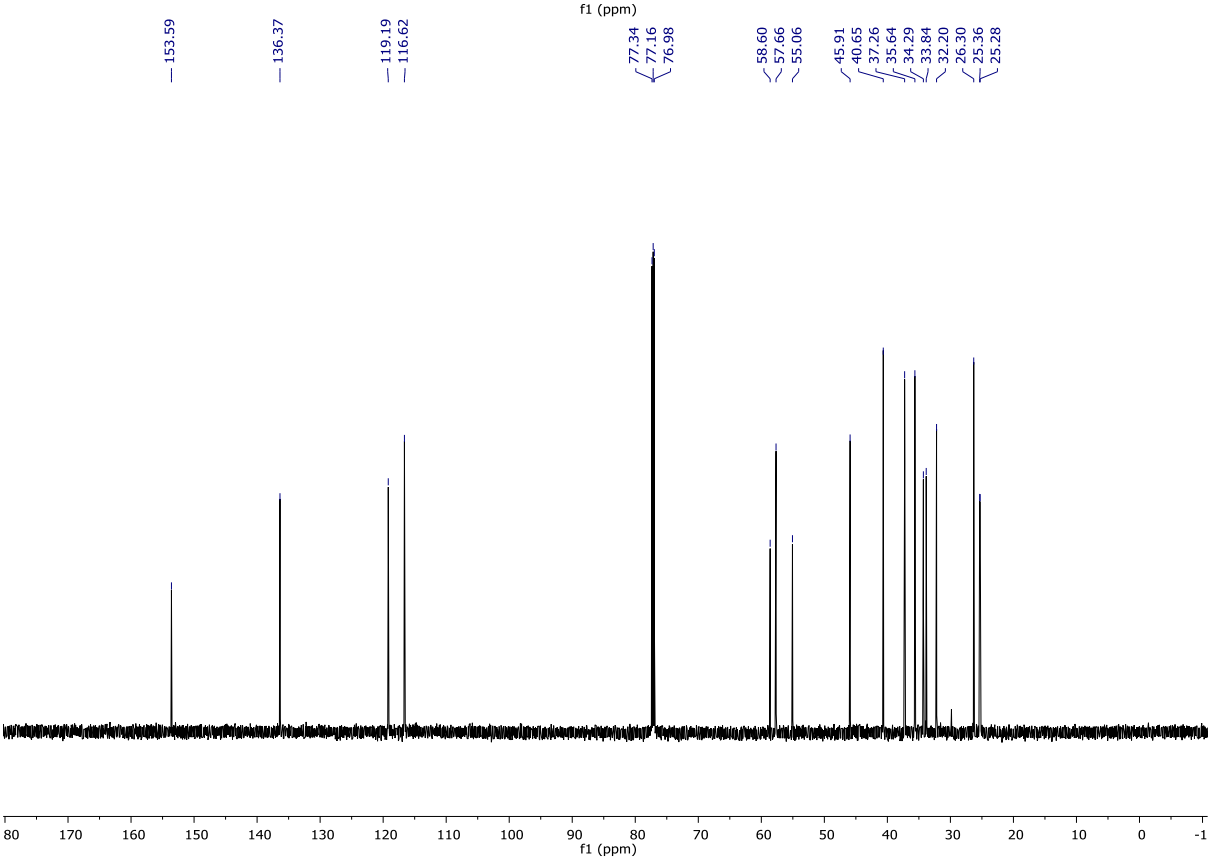

80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

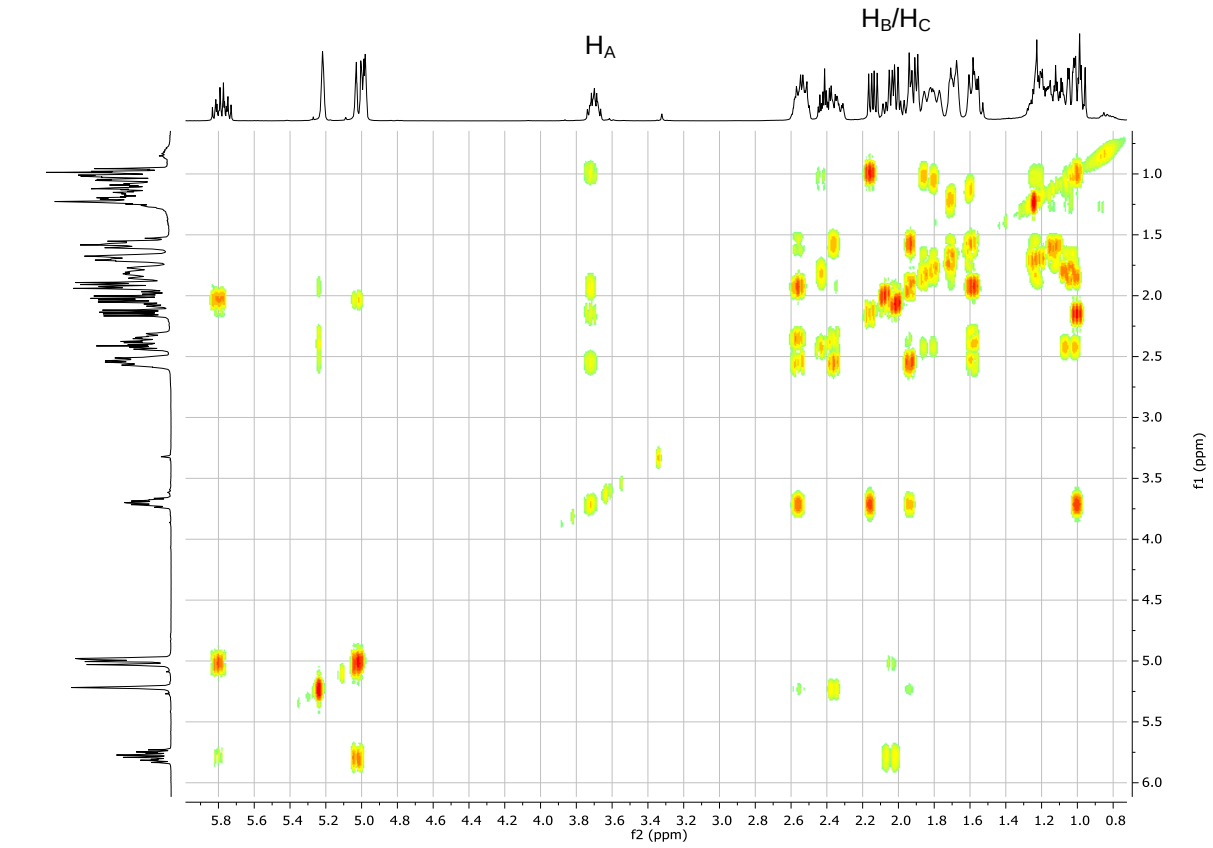

7.26 5.80 5.79 5.24 5.23 5.23 5.04 5.04 5.02 5.02 5.01 5.00 5.00 2.58 2.57 2.56 2.56 2.55 2.55 2.55 2.54 2.43 2.17 2.16 2.16 2.15 2.07 2.06 2.03 2.02 1.95 1.94 1.94 1.93 1.92 1.72 1.72 1.71 1.71 1.71 1.70 1.70 1.69 1.61 1.61 1.59 1.59 1.58 1.25 1.25 1.24 1.24 1.23 1.23 1.22 1.22 1.21 1.13 1.12 1.06 1.06 1.05 1.04 1.03 1.03 1.01 1.00 1.00 0.98

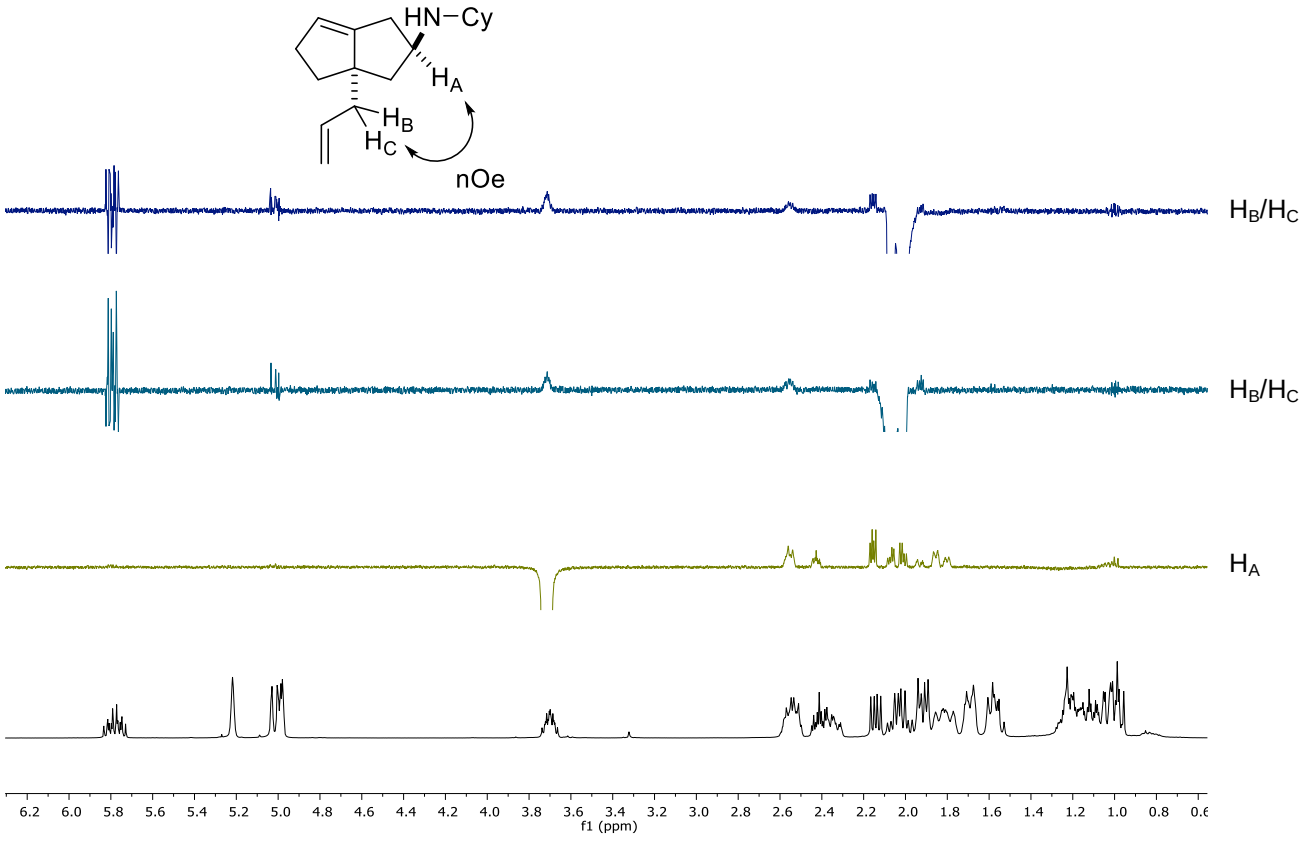
NH

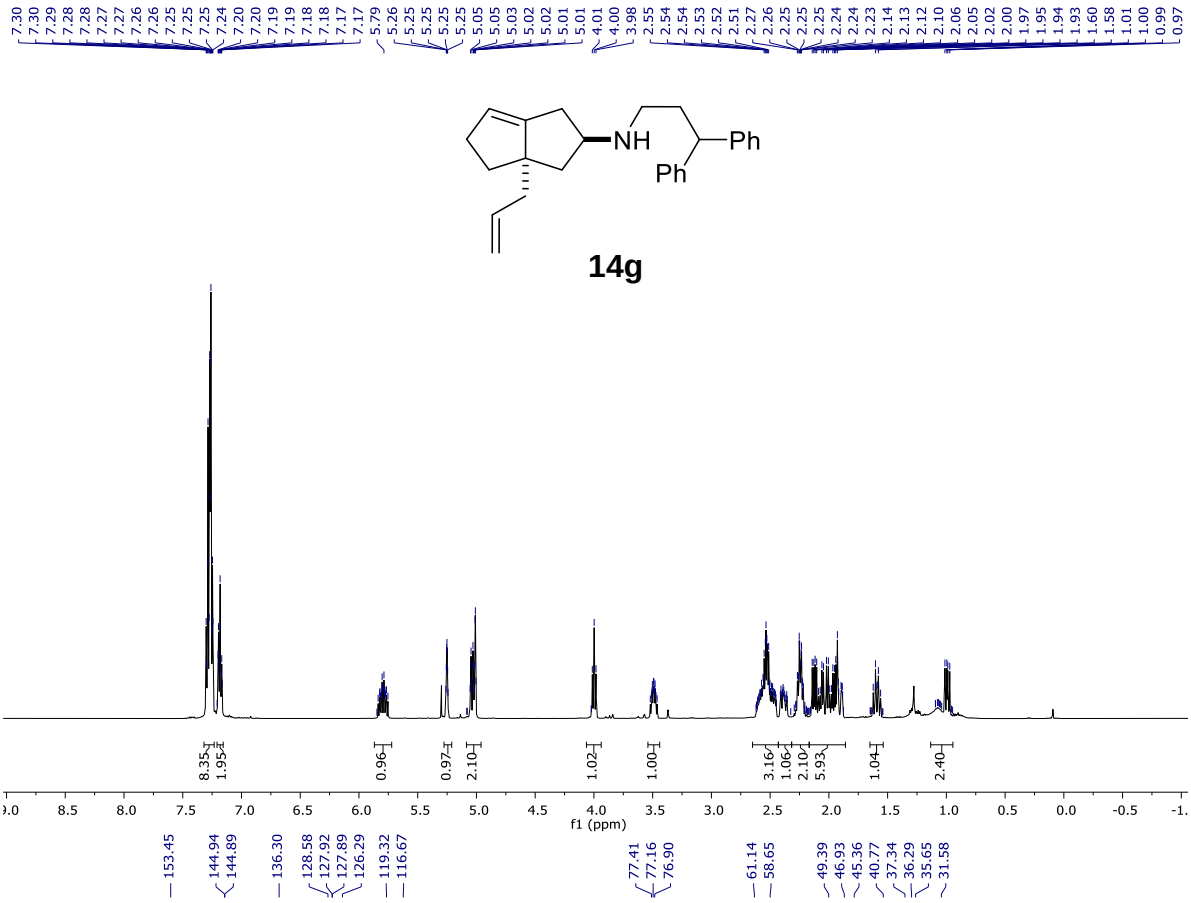
14f


0.93 0.94 1.97 0.98 2.06 0.98 1.02 0.98 1.07 1.08 2.15 1.11 1.08 2.18 2.07 2.46 1.09 3.19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

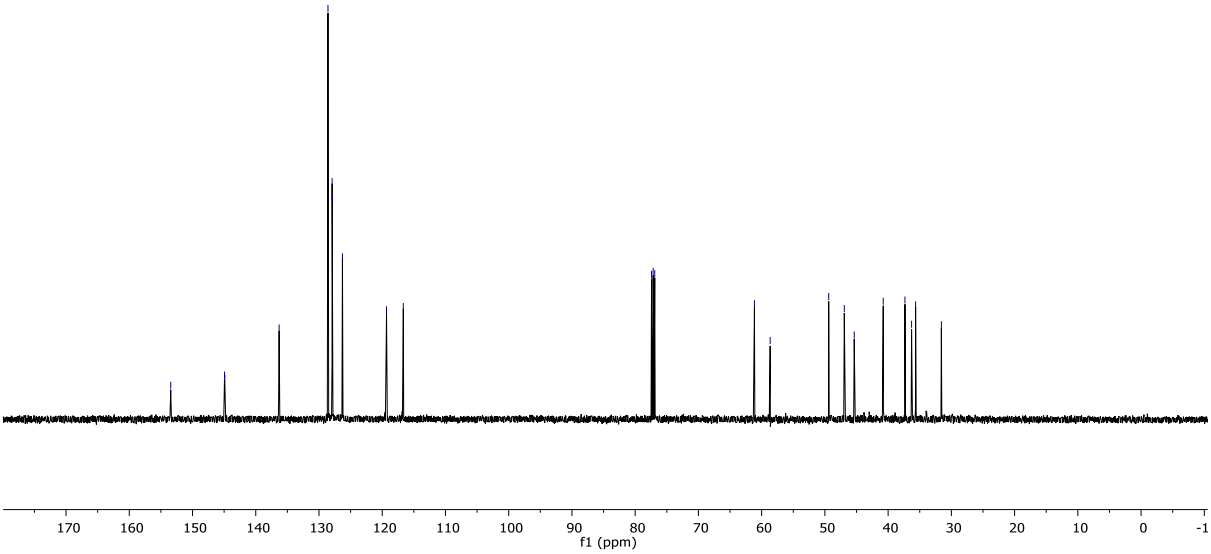

153.59 136.37 119.19 116.62 77.34 77.16 76.98 58.60 57.66 55.06 45.91 40.65 37.26 35.64 34.29 33.84 32.20 26.30 25.36 25.28
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

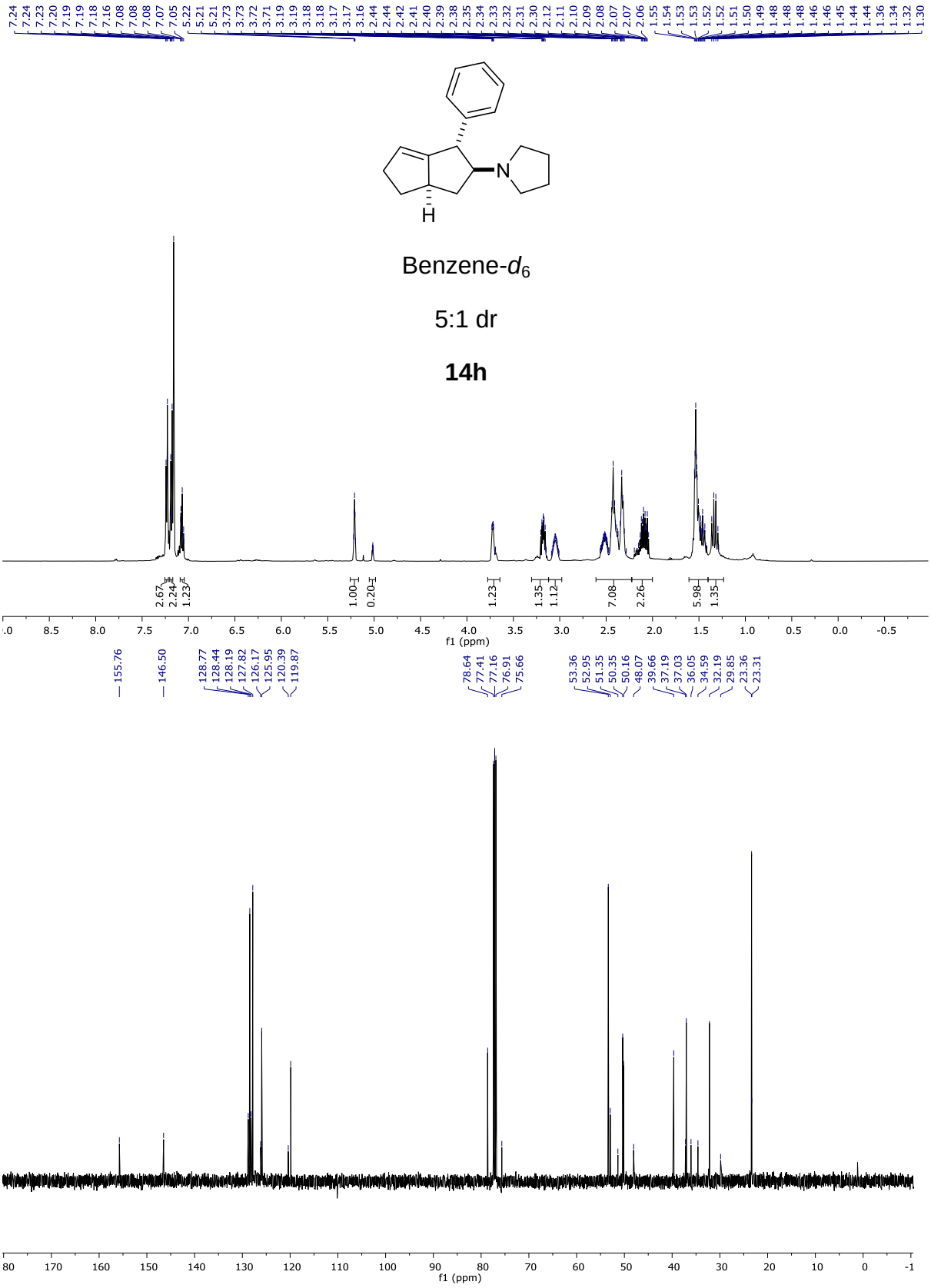

H_A
H_B/H_C
f2 (ppm)
f1 (ppm)

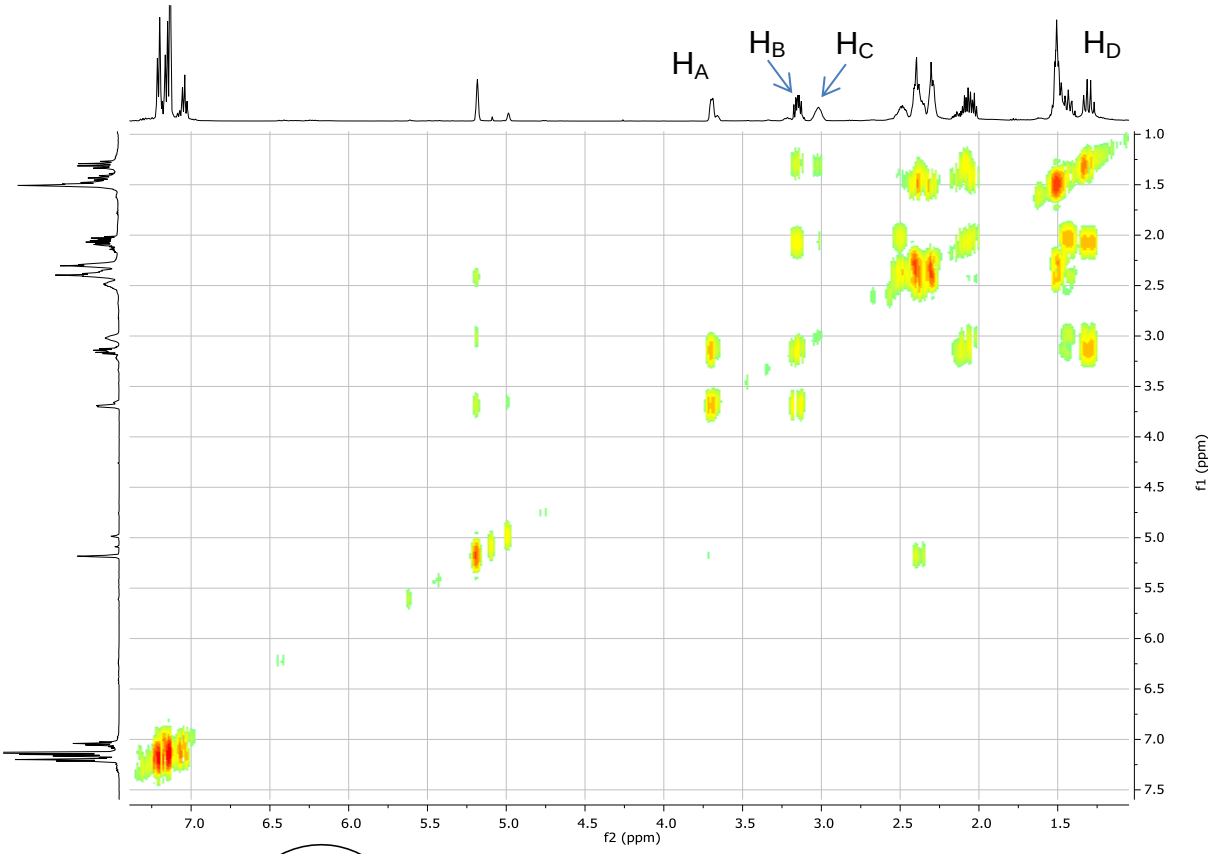

HN−Cy
H_A
H_B
H_C
nOe
H_B/H_C
H_B/H_C
H_A
f1 (ppm)

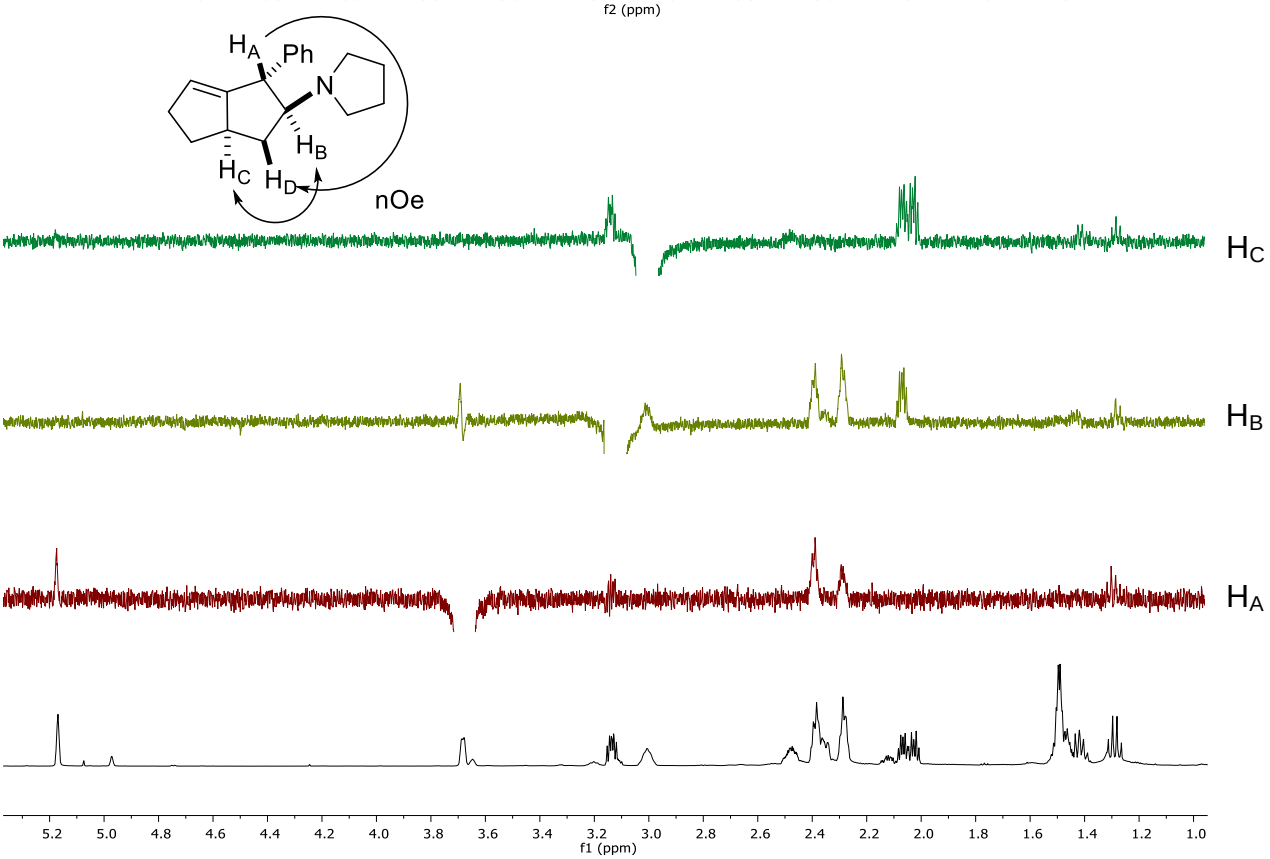


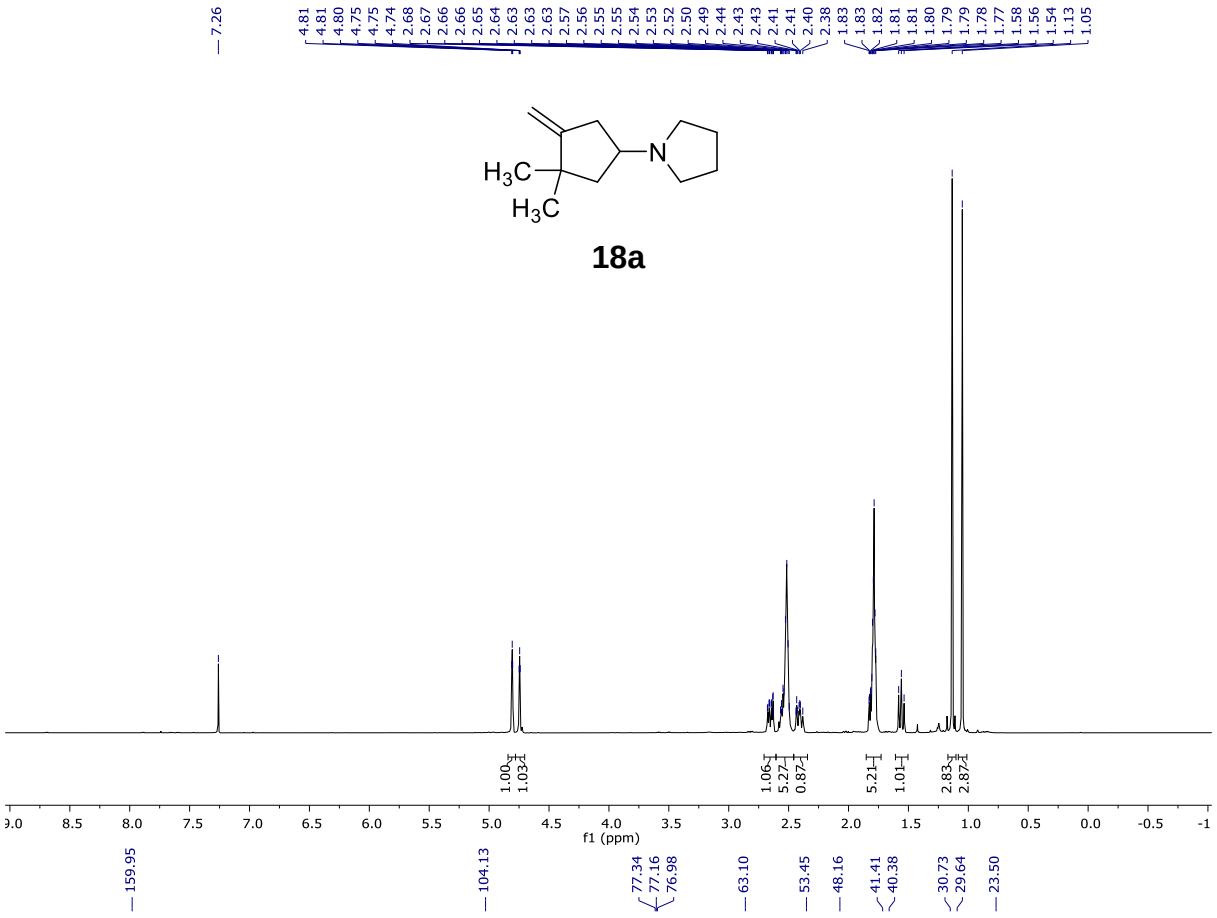
14g



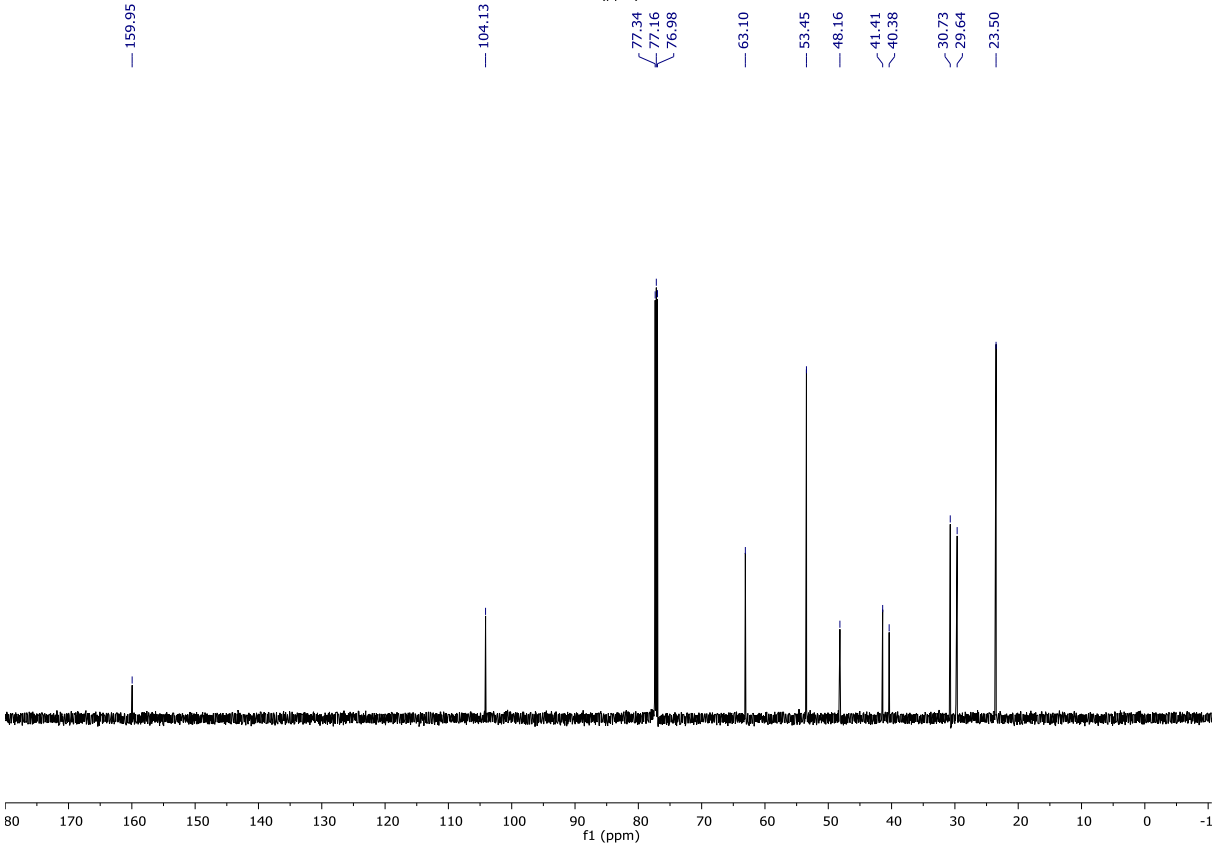

7.24 7.24 7.23 7.20 7.19 7.19 7.18 7.16 7.08 7.08 7.08 7.07 7.05 5.22 5.21 5.21 3.73 3.73 3.72 3.71 3.19 3.19 3.18 3.18 3.17 3.17 3.16 2.44 2.44 2.42 2.41 2.40 2.39 2.38 2.35 2.34 2.33 2.32 2.31 2.30 2.12 2.11 2.10 2.09 2.08 2.07 2.07 2.06 1.55 1.54 1.53 1.53 1.52 1.52 1.51 1.50 1.49 1.48 1.48 1.48 1.46 1.46 1.45 1.44 1.44 1.36 1.34 1.32 1.30
N
H
Benzene-d_6
5:1 dr
14h
2.67 2.24 1.23 1.00 0.20 1.23 1.35 1.12 7.08 2.26 5.98 1.35
f1 (ppm)
155.76 146.50 128.77 128.44 128.19 127.82 126.17 125.95 120.39 119.87 78.64 77.41 77.16 76.91 75.66 53.36 52.95 51.35 50.35 50.16 48.07 39.66 37.19 37.03 36.05 34.59 32.19 29.85 23.36 23.31
f1 (ppm)

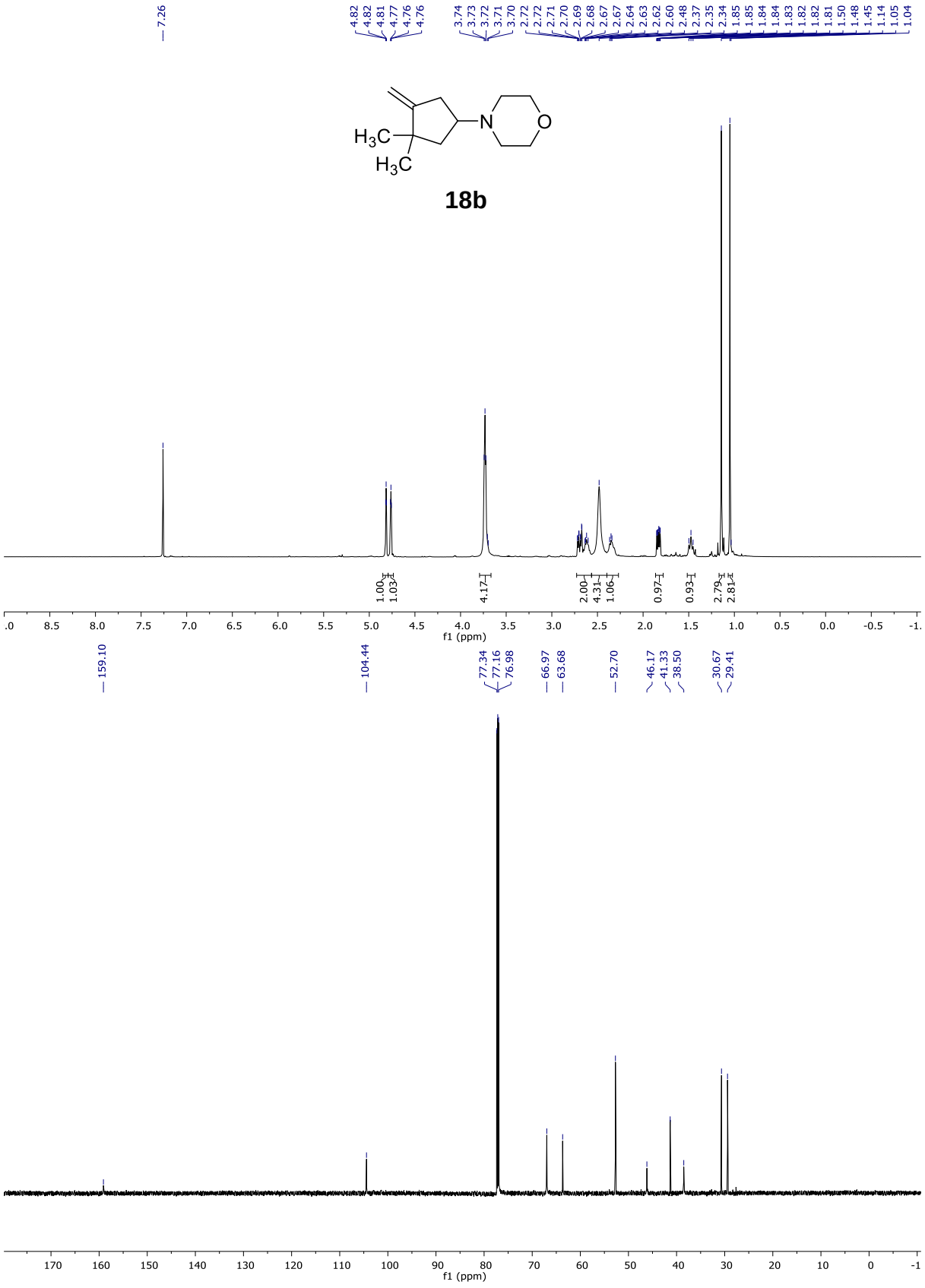

HA
HB
HC
HD
f2 (ppm)
f1 (ppm)


HA
Ph
N
HB
HC
HD
nOe
HC
HB
HA
f1 (ppm)

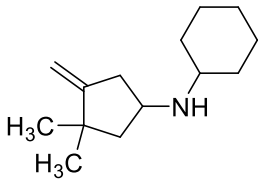

7.26
4.81
4.81
4.80
4.75
4.75
4.74
2.68
2.67
2.66
2.66
2.65
2.64
2.63
2.63
2.63
2.57
2.56
2.55
2.55
2.54
2.53
2.52
2.50
2.49
2.44
2.43
2.43
2.41
2.41
2.40
2.38
1.83
1.83
1.82
1.81
1.81
1.80
1.79
1.79
1.78
1.77
1.58
1.56
1.54
1.13
1.05
H3C
H3C
N
1.00
1.03
1.06
5.27
0.87
5.21
1.01
2.83
2.87
f1 (ppm)

18a


159.95
104.13
77.34
77.16
76.98
63.10
53.45
48.16
41.41
40.38
30.73
29.64
23.50
f1 (ppm)

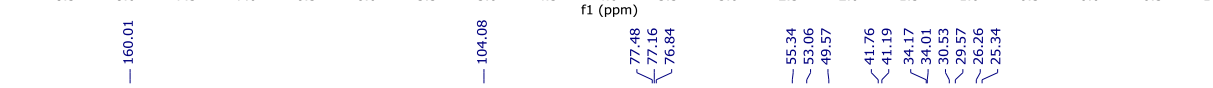

7.26
4.82
4.82
4.81
4.77
4.76
4.76
3.74
3.73
3.72
3.71
3.70
2.72
2.72
2.71
2.70
2.69
2.68
2.67
2.67
2.64
2.63
2.62
2.60
2.48
2.37
2.35
2.34
1.85
1.85
1.84
1.84
1.83
1.82
1.82
1.81
1.50
1.48
1.45
1.14
1.05
1.04
H3C
H3C
N
O
18b
1.00
1.03
4.17
2.00
4.31
1.06
0.97
0.93
2.79
2.81
f1 (ppm)
159.10
104.44
77.34
77.16
76.98
66.97
63.68
52.70
46.17
41.33
38.50
30.67
29.41
f1 (ppm)

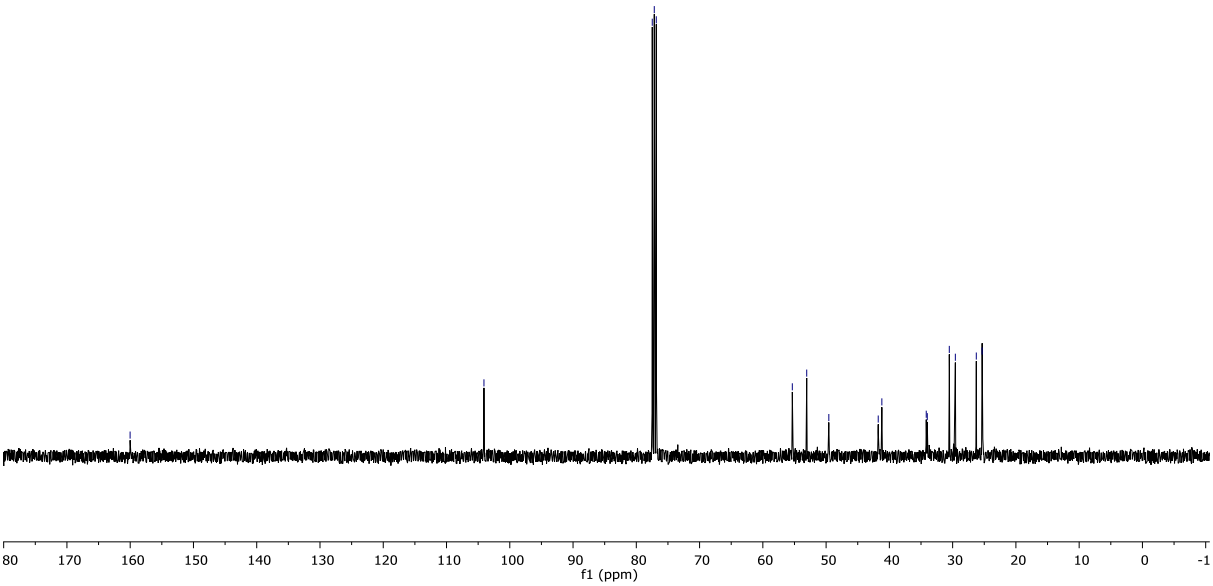

7.26
4.80
4.80
4.79
4.75
4.75
4.74
3.35
3.33
2.74
2.72
2.48
1.91
1.90
1.89
1.89
1.88
1.87
1.86
1.86
1.75
1.74
1.73
1.72
1.71
1.70
1.64
1.63
1.63
1.62
1.62
1.62
1.61
1.61
1.60
1.59
1.37
1.35
1.34
1.32
1.28
1.27
1.26
1.25
1.24
1.23
1.22
1.21
1.21
1.20
1.19
1.18
1.18
1.17
1.16
1.15
1.15
1.13
1.12
1.12
1.11
1.10
1.08
1.08
1.07
1.06
1.05
1.04
1.02

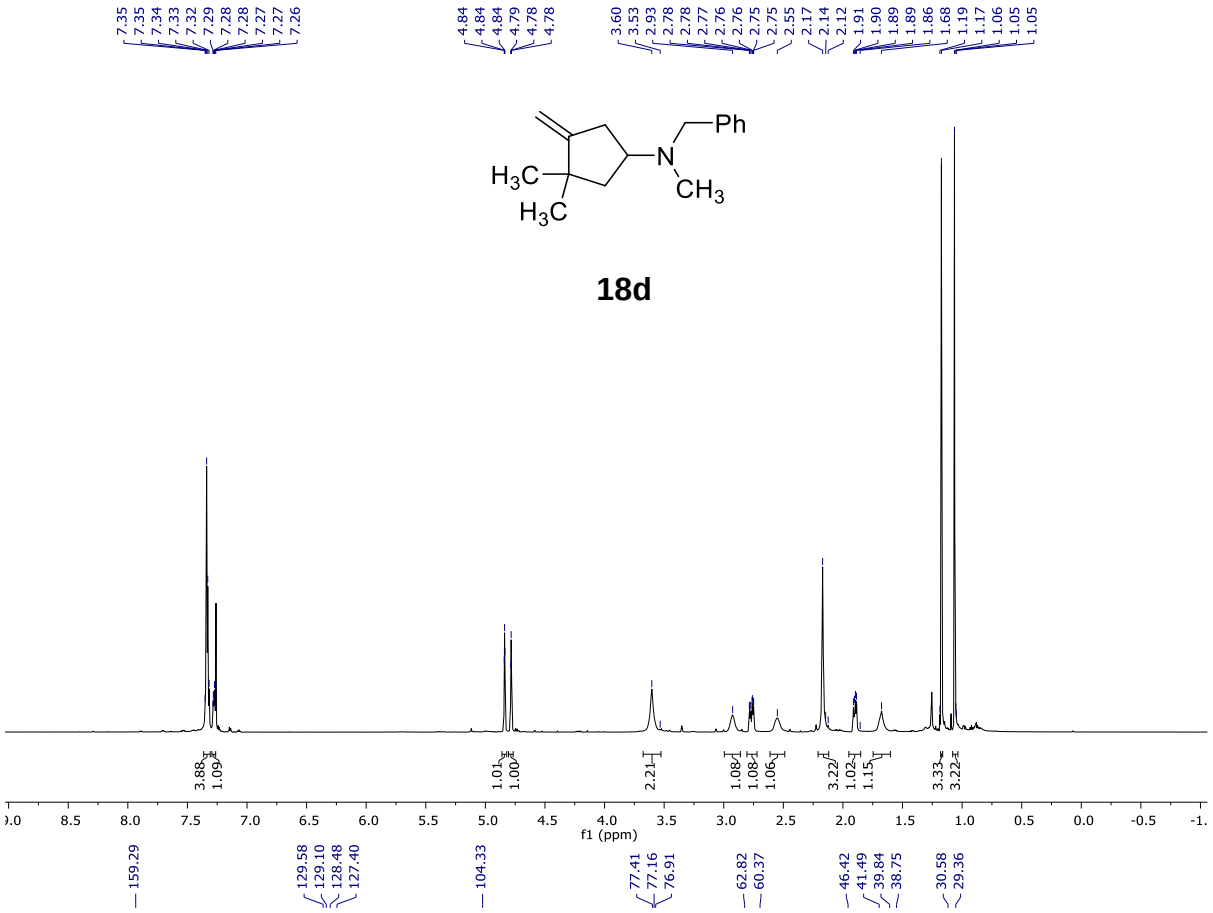

NH
H3C
H3C

18c

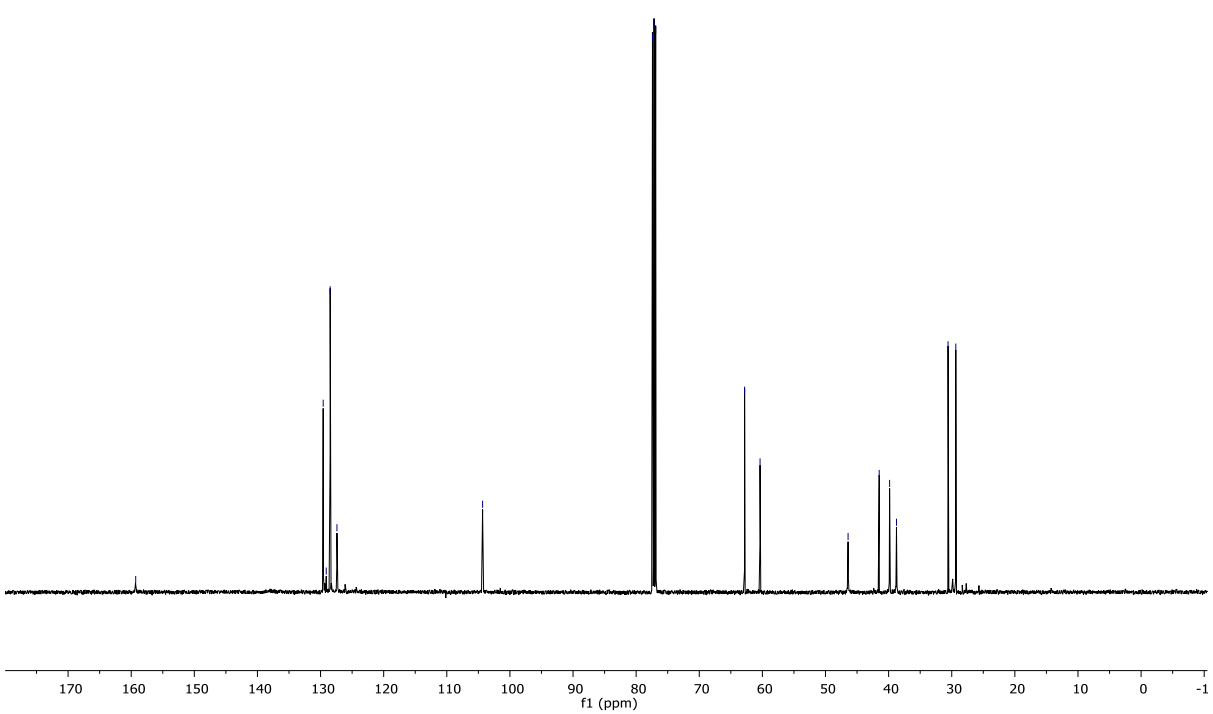
1.00
1.03
0.98
1.07
0.91
0.93
3.36
2.37
1.65
11.63
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


160.01
104.08
77.48
77.16
76.84
55.34
53.06
49.57
41.76
41.19
34.17
34.01
30.53
29.57
26.26
25.34

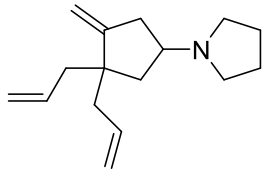

80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.35 7.35 7.34 7.33 7.32 7.29 7.28 7.28 7.27 7.27 7.26
4.84 4.84 4.84 4.79 4.78 4.78
3.60 3.53 2.93 2.78 2.78 2.77 2.76 2.76 2.75 2.75 2.55 2.17 2.14 2.12 1.91 1.90 1.89 1.89 1.86 1.68 1.19 1.17 1.06 1.05 1.05
Ph
N
CH3
H3C
H3C
3.88 1.09 1.01 1.00 2.21 1.08 1.08 1.06 3.22 1.02 1.15 3.33 3.22
f1 (ppm)

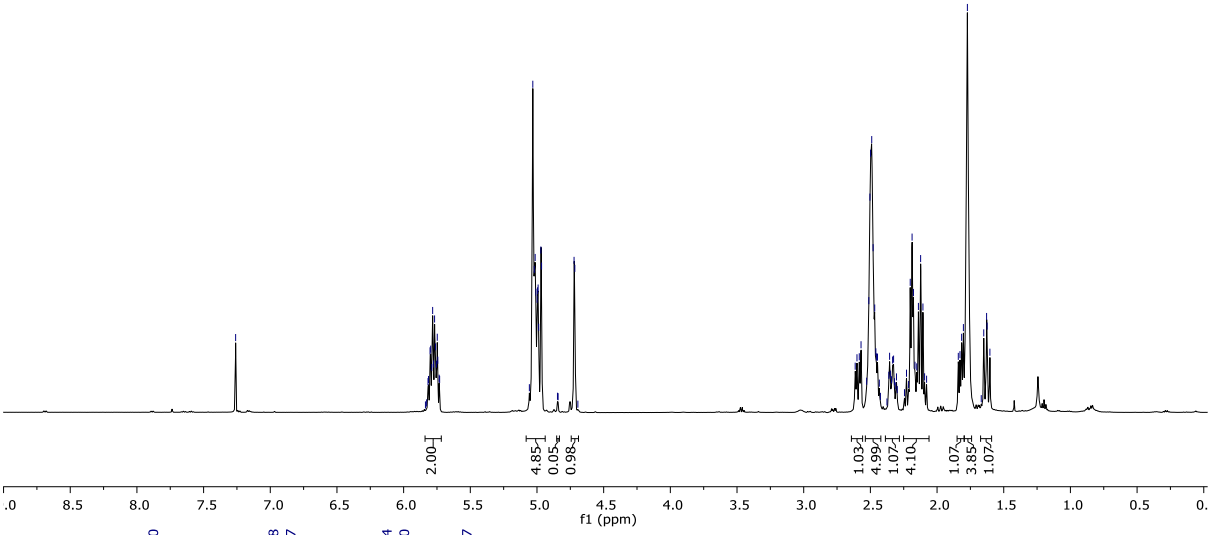
18d

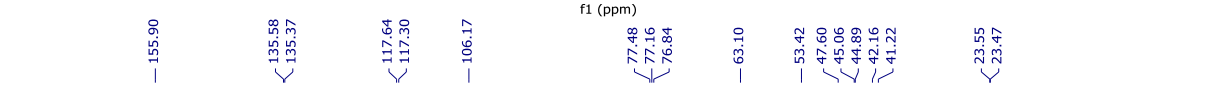

159.29
129.58 129.10 128.48 127.40
104.33
77.41 77.16 76.91
62.82 60.37
46.42 41.49 39.84 38.75
30.58 29.36
f1 (ppm)

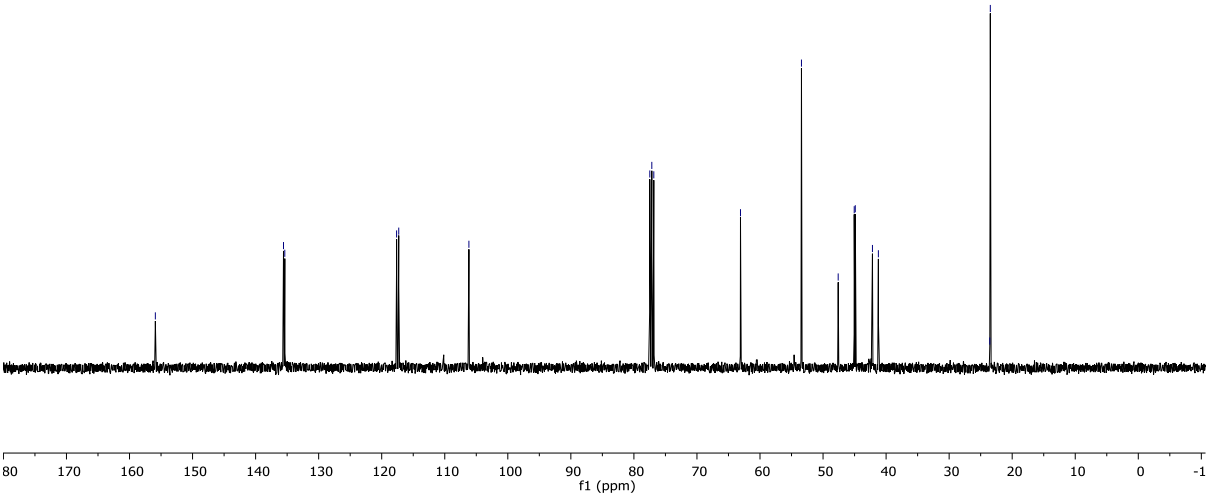

7.26
5.82
5.81
5.80
5.80
5.79
5.78
5.78
5.77
5.76
5.75
5.75
5.74
5.73
5.73
5.03
5.02
5.01
5.01
5.00
5.00
4.99
4.99
4.97
4.97
4.72
4.72
2.61
2.60
2.58
2.57
2.53
2.51
2.50
2.50
2.49
2.48
2.47
2.46
2.45
2.45
2.36
2.36
2.35
2.34
2.33
2.33
2.32
2.30
2.23
2.20
2.19
2.18
2.17
2.15
2.14
2.12
2.11
2.09
2.08
1.84
1.83
1.82
1.80
1.77
1.65
1.63
1.62
1.60

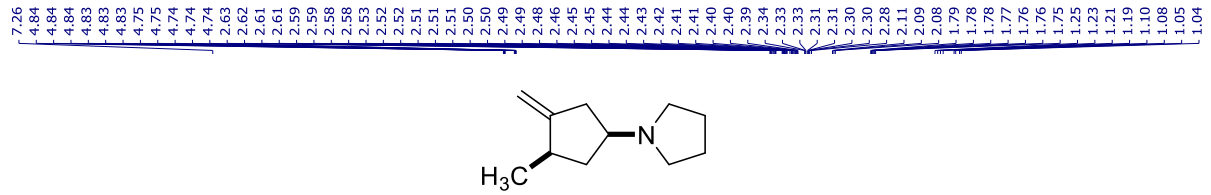

N

18e


2.00
4.85
0.05
0.98
1.03
4.99
1.07
4.10
1.07
3.85
1.07
f1 (ppm)


155.90
135.58
135.37
117.64
117.30
106.17
77.48
77.16
76.84
63.10
53.42
47.60
45.06
44.89
42.16
41.22
23.55
23.47

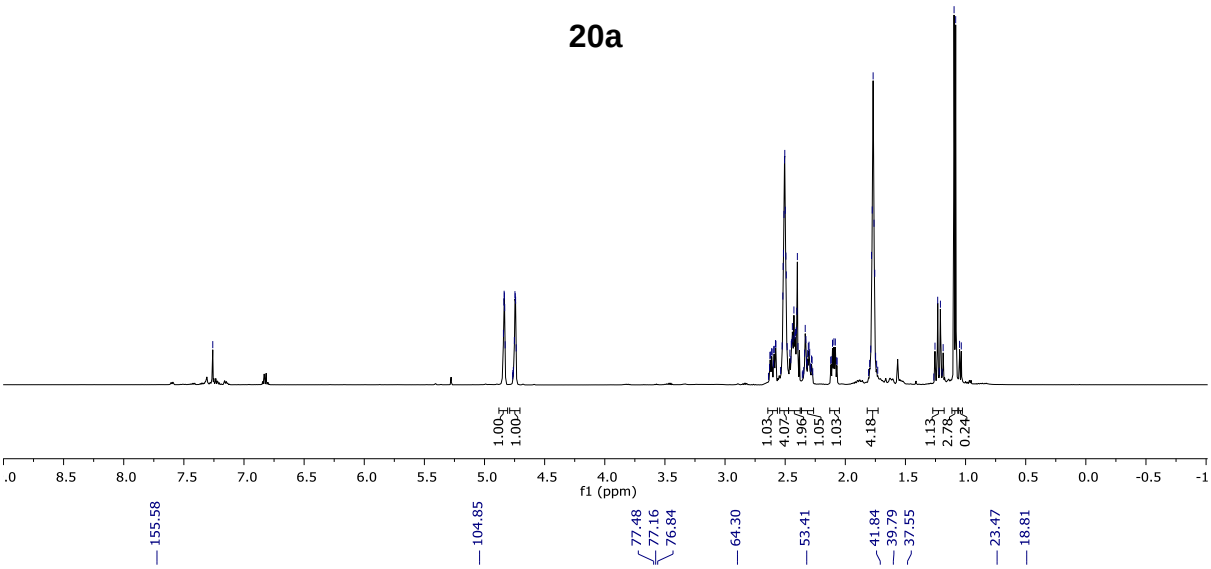

f1 (ppm)

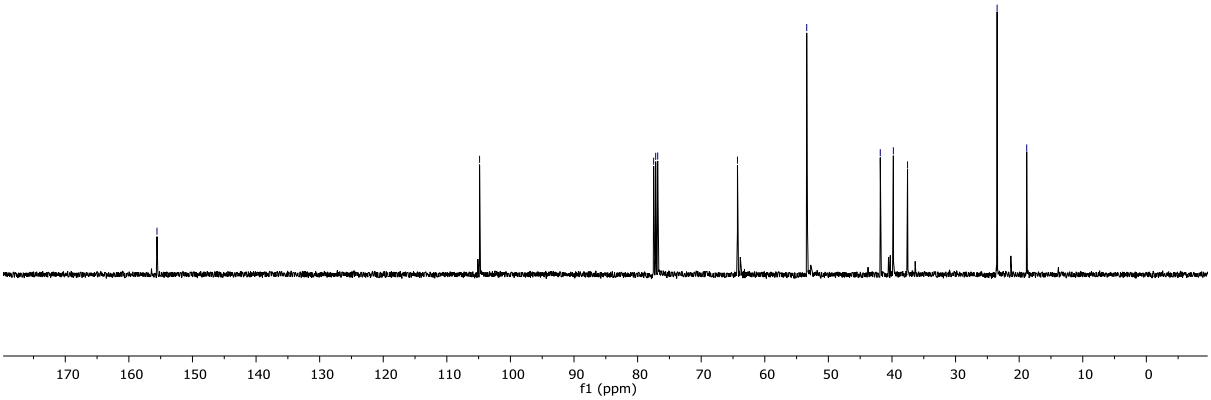


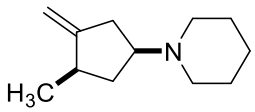
12:1 dr

(contains 6% CPhos impurity)

20a



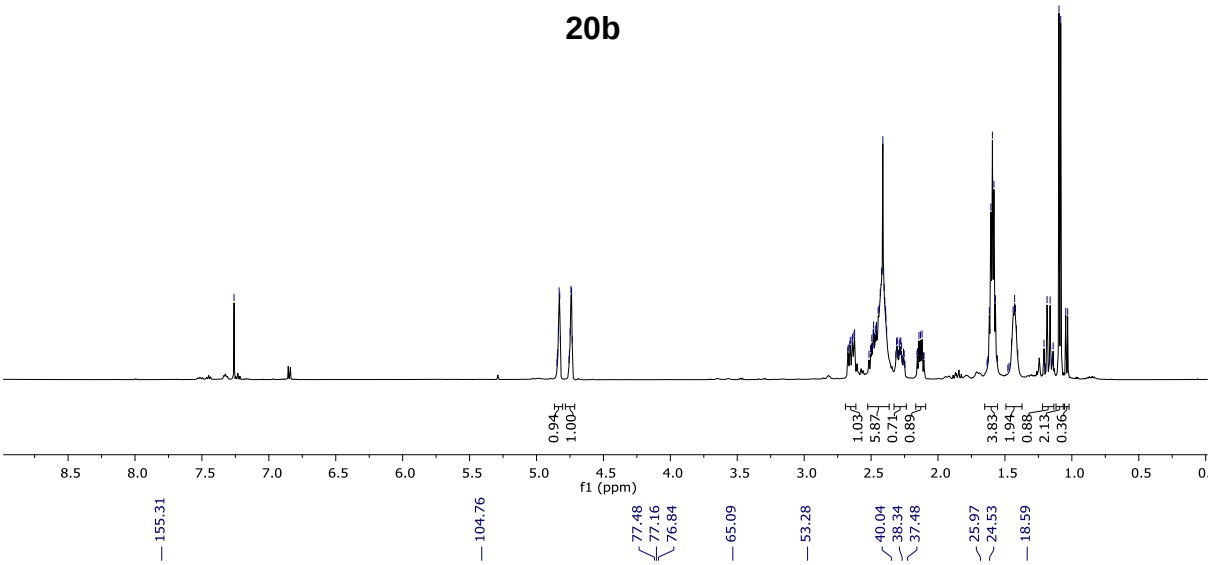


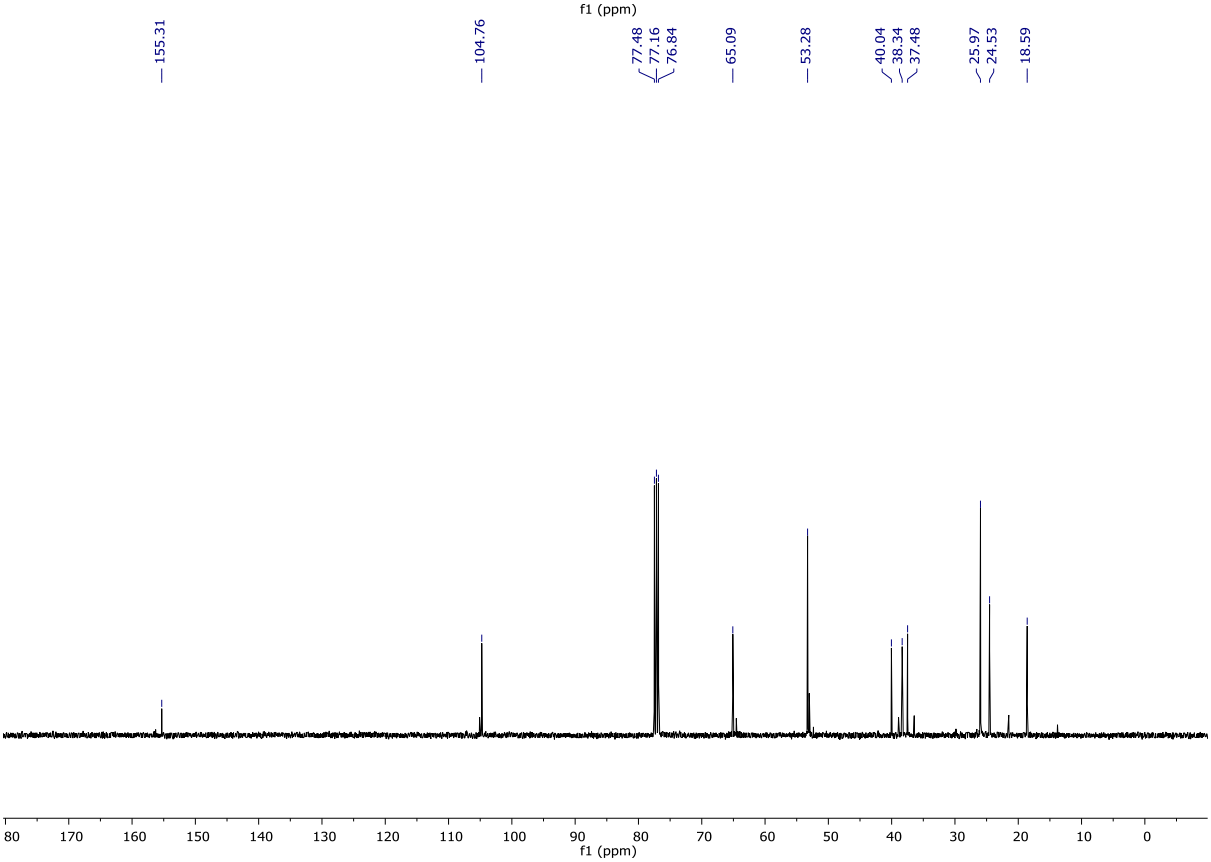


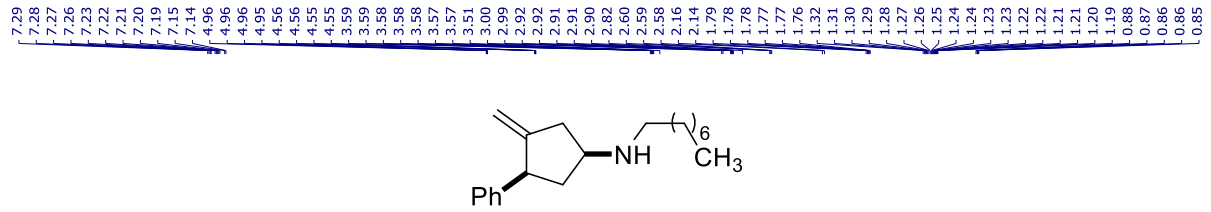
6:1 dr

(contains 3.5% CPhos impurity)

20b

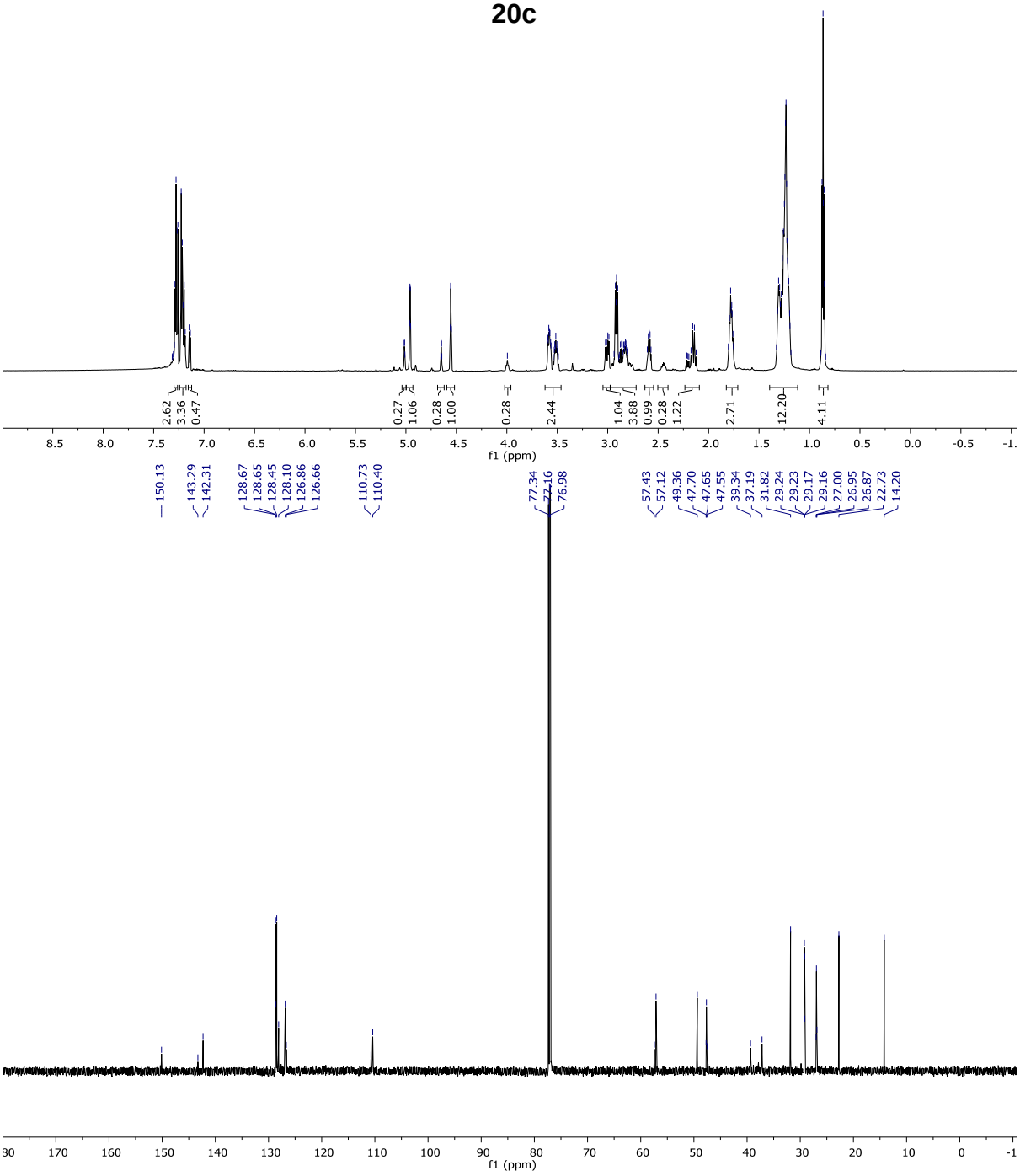


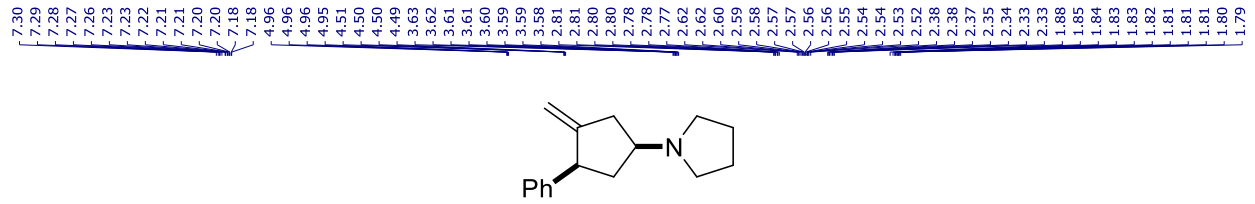




4:1 dr

20c

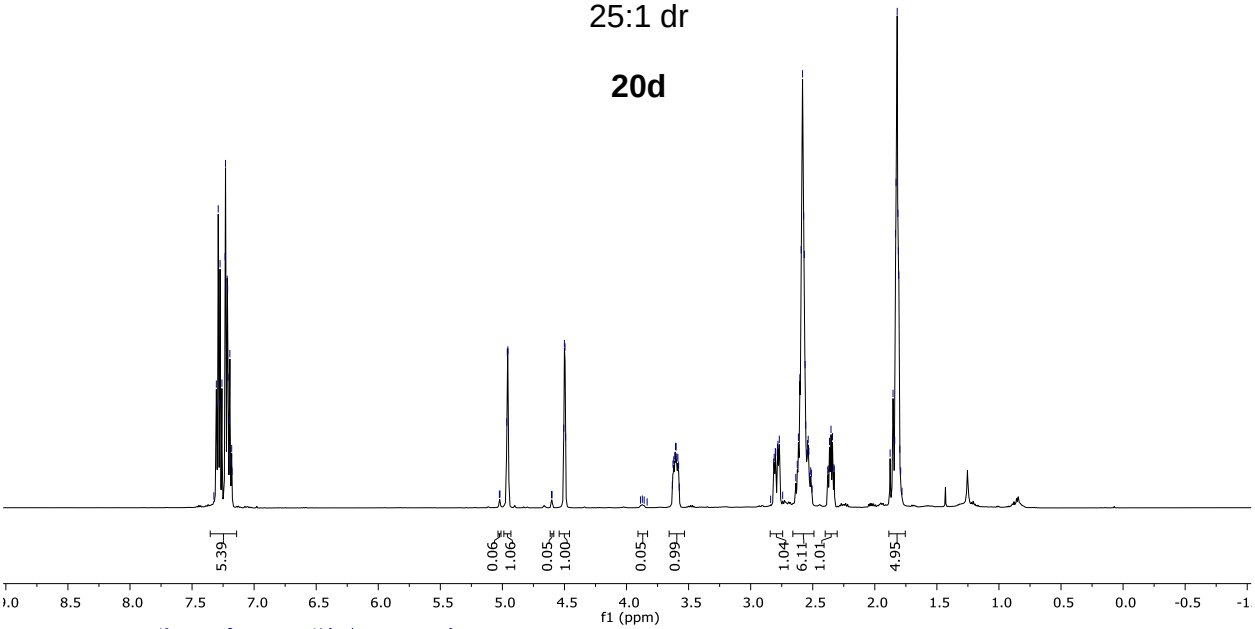


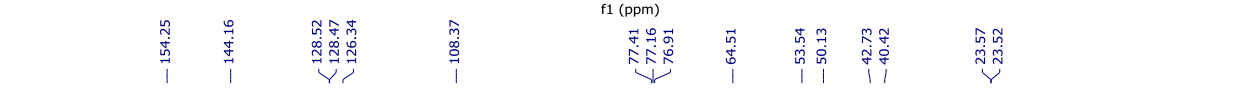


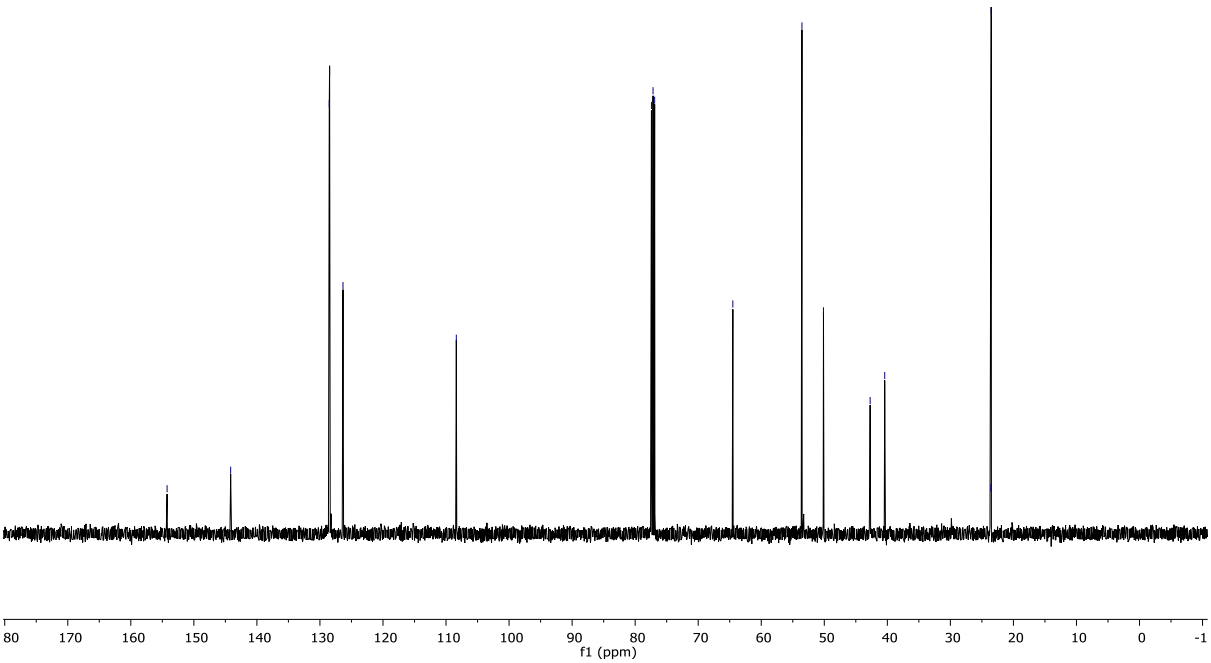
N
Ph

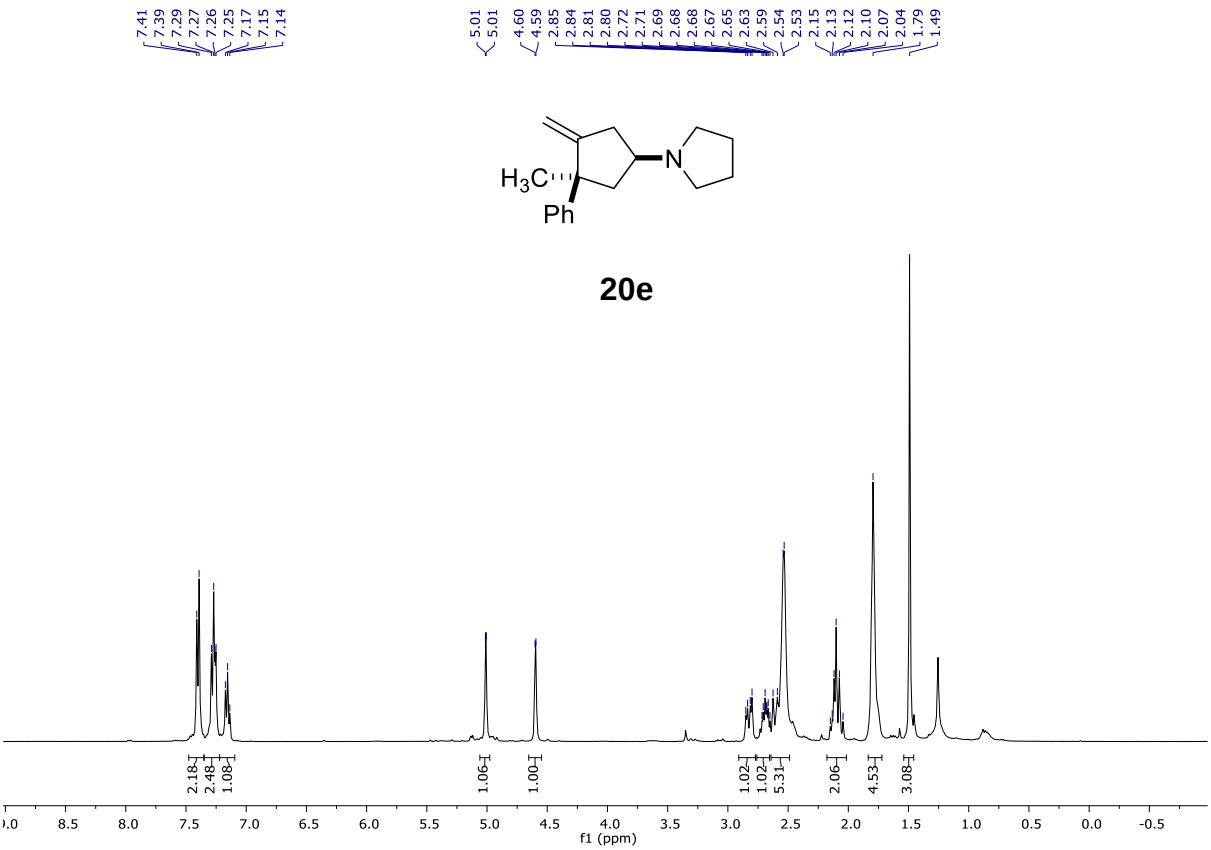
25:1 dr

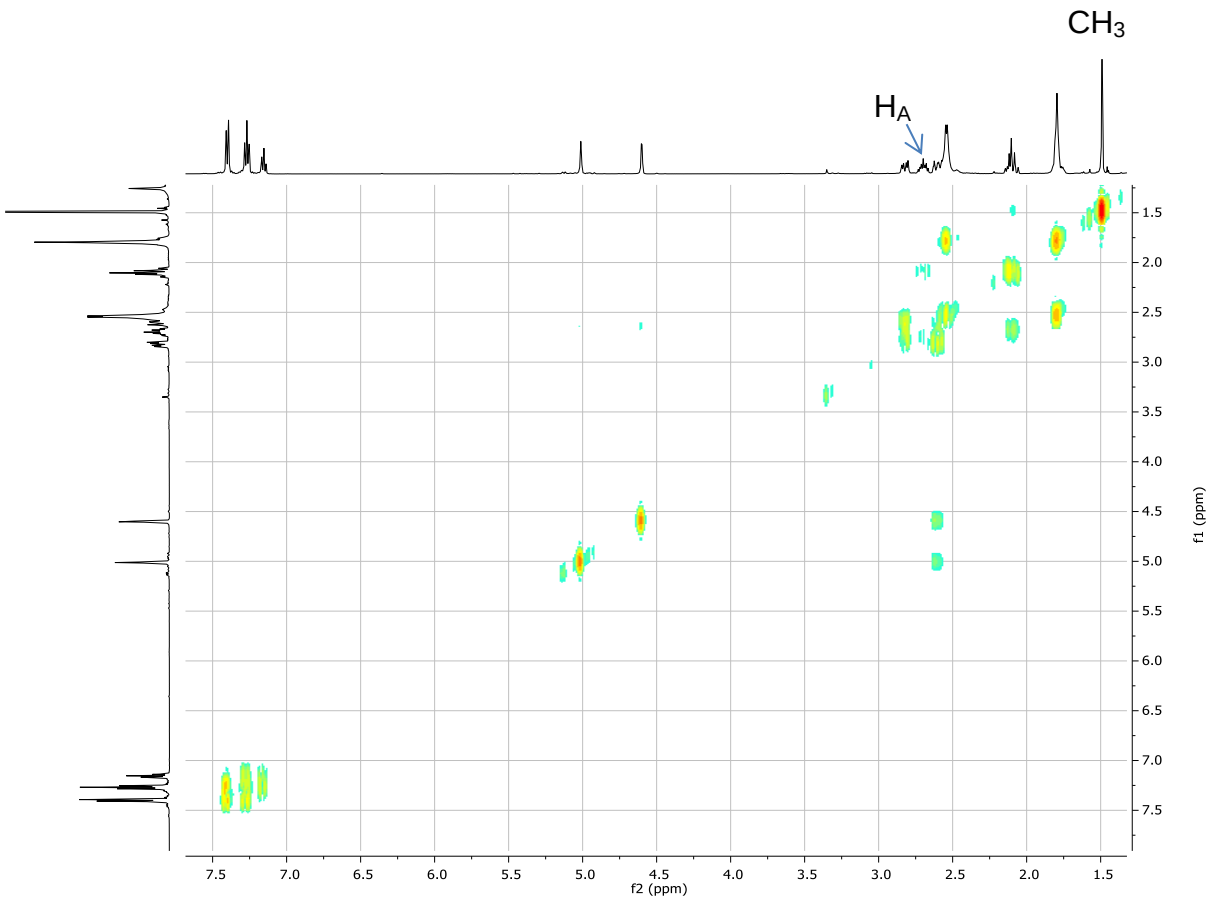
20d

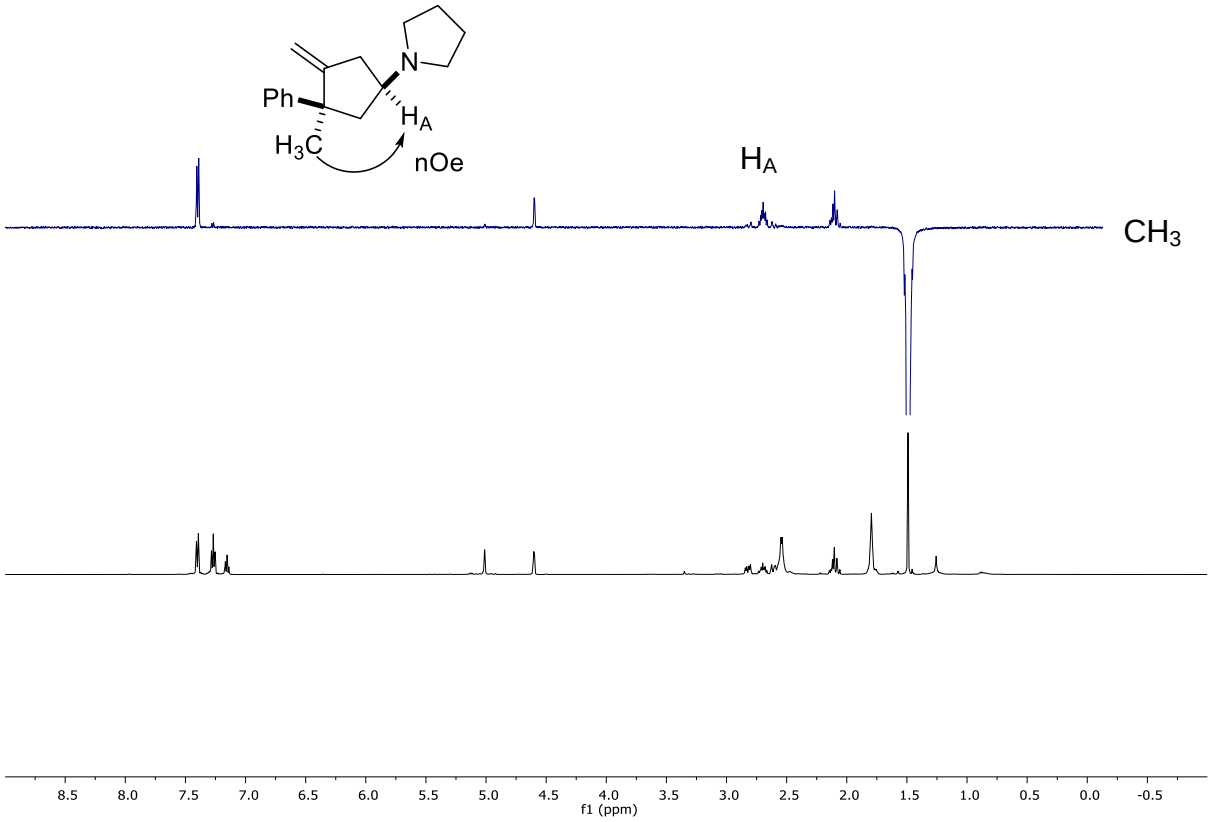

5.39
0.06
1.06
0.05
1.00
0.05
0.99
1.04
6.11
1.01
4.95
f1 (ppm)

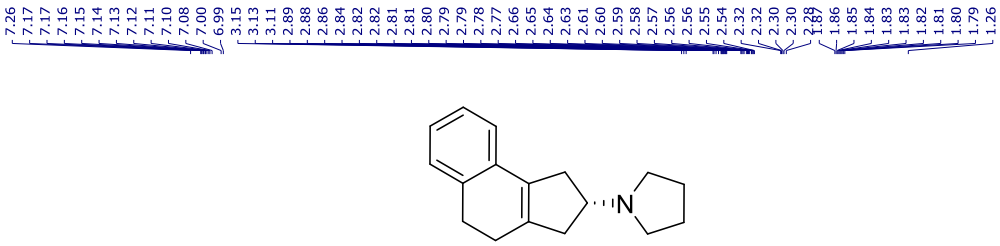

154.25
144.16
128.52
128.47
126.34
108.37
77.41
77.16
76.91
64.51
53.54
50.13
42.73
40.42
23.57
23.52


f1 (ppm)


7.41
7.39
7.29
7.27
7.26
7.25
7.17
7.15
7.14
5.01
5.01
4.60
4.59
2.85
2.84
2.81
2.80
2.72
2.71
2.69
2.68
2.68
2.67
2.65
2.63
2.59
2.54
2.53
2.15
2.13
2.12
2.10
2.07
2.04
1.79
1.49
H3C
Ph
N
20e
2.18
2.48
1.08
1.06
1.00
1.02
1.02
5.31
2.06
4.53
3.08
f1 (ppm)
159.63
149.82
128.04
126.72
125.72
108.08
77.48
77.16
76.84
63.67
53.55
51.19
49.62
42.07
29.01
23.51
f1 (ppm)

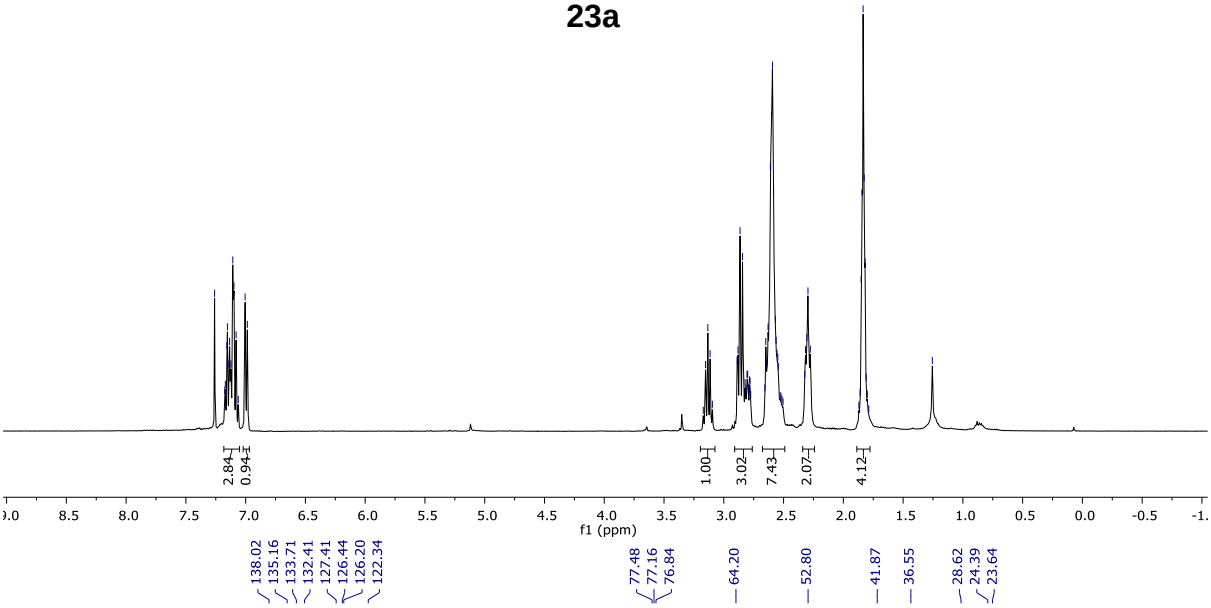

CH3
HA
f2 (ppm)
f1 (ppm)


N
Ph
HA
H3C
nOe
HA
CH3
f1 (ppm)

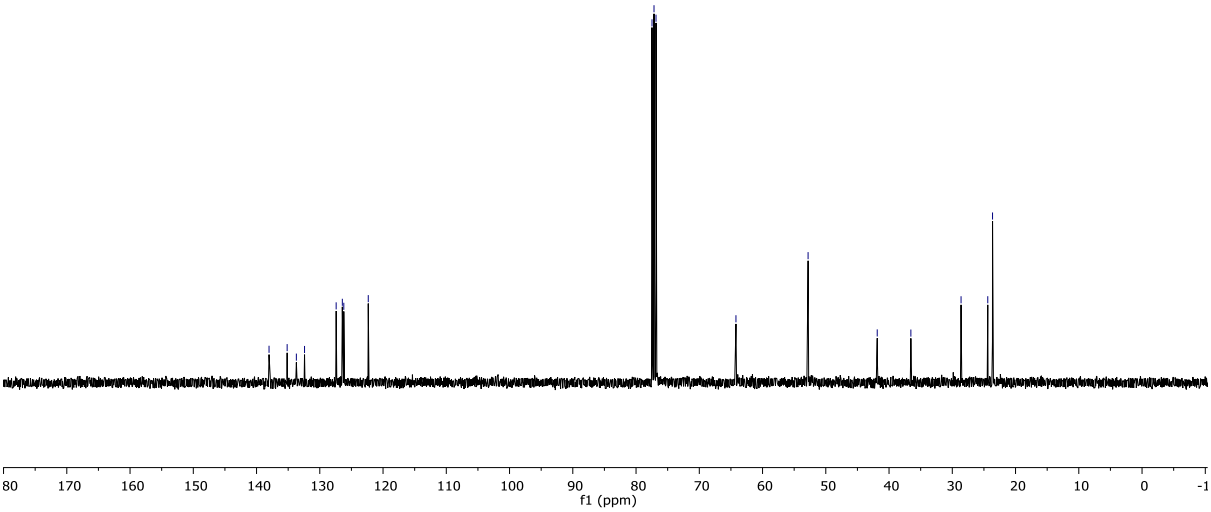

7.26
7.17
7.17
7.16
7.15
7.14
7.13
7.12
7.11
7.10
7.08
7.00
6.99
3.15
3.13
3.11
2.89
2.88
2.86
2.84
2.82
2.82
2.81
2.81
2.80
2.79
2.79
2.78
2.77
2.66
2.65
2.64
2.63
2.61
2.60
2.59
2.58
2.57
2.56
2.56
2.55
2.54
2.32
2.32
2.30
2.30
1.87
1.86
1.85
1.84
1.83
1.83
1.82
1.81
1.80
1.79
1.26

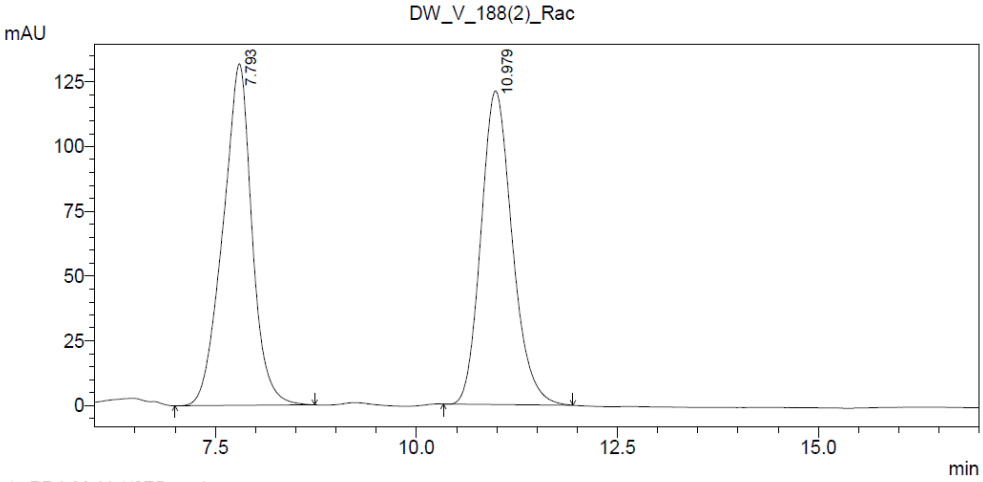
N

23a


2.84
0.94
1.00
3.02
7.43
2.07
4.12
f1 (ppm)

138.02
135.16
133.71
132.41
127.41
126.44
126.20
122.34
77.48
77.16
76.84
64.20
52.80
41.87
36.55
28.62
24.39
23.64


f1 (ppm)

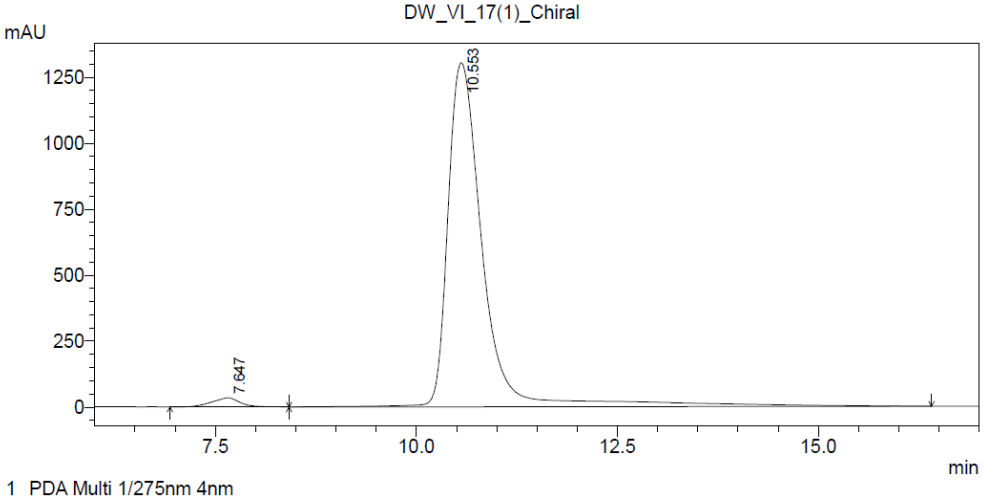


1 PDA Multi 1/275nm 4nm

PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.793	3325474	131989	50.354	52.141
2	10.979	3278780	121149	49.646	47.859
Total		6604254	253138	100.000	100.000

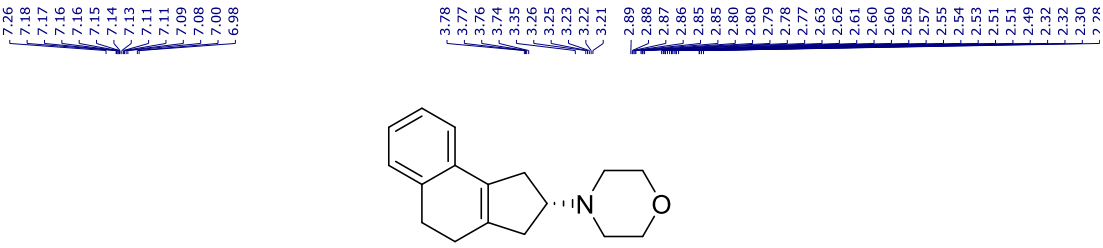


1 PDA Multi 1/275nm 4nm

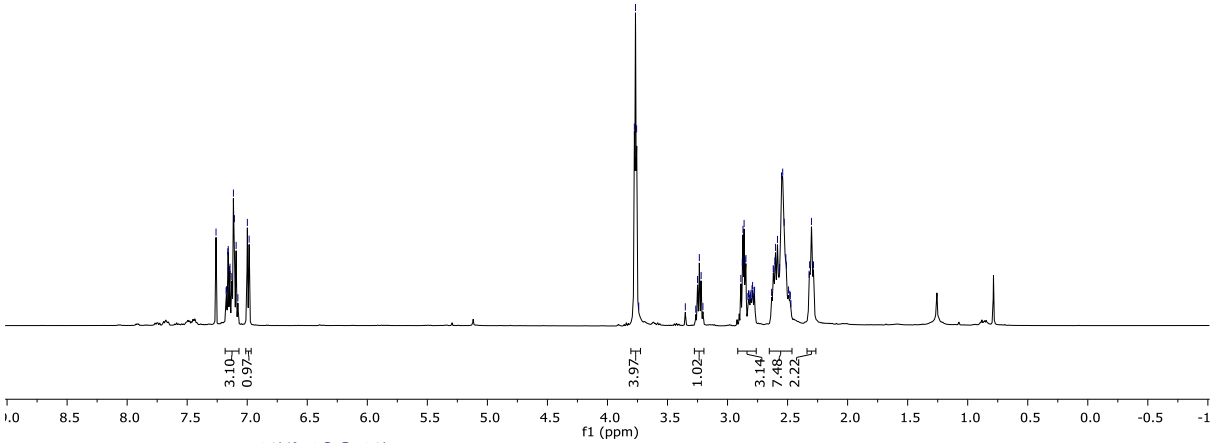
PeakTable

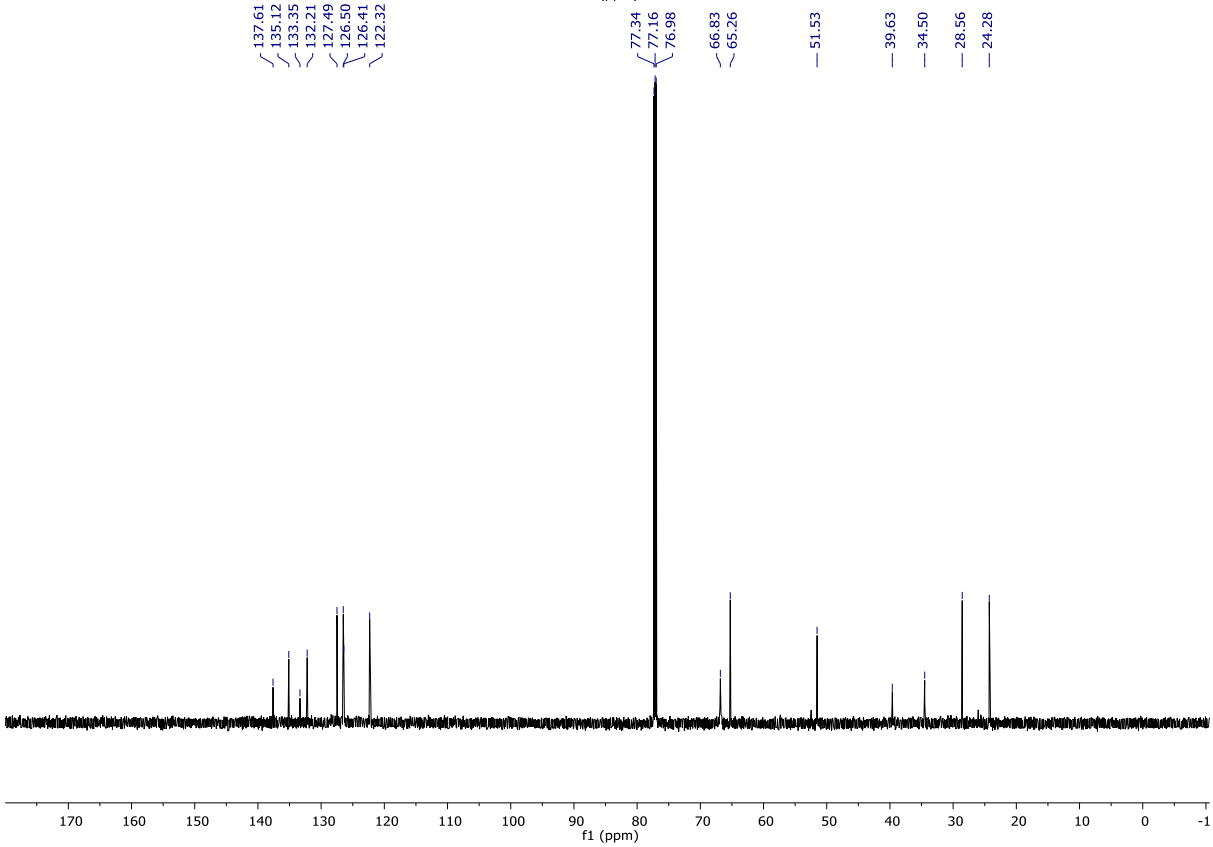
PDA Ch1 275nm 4nm

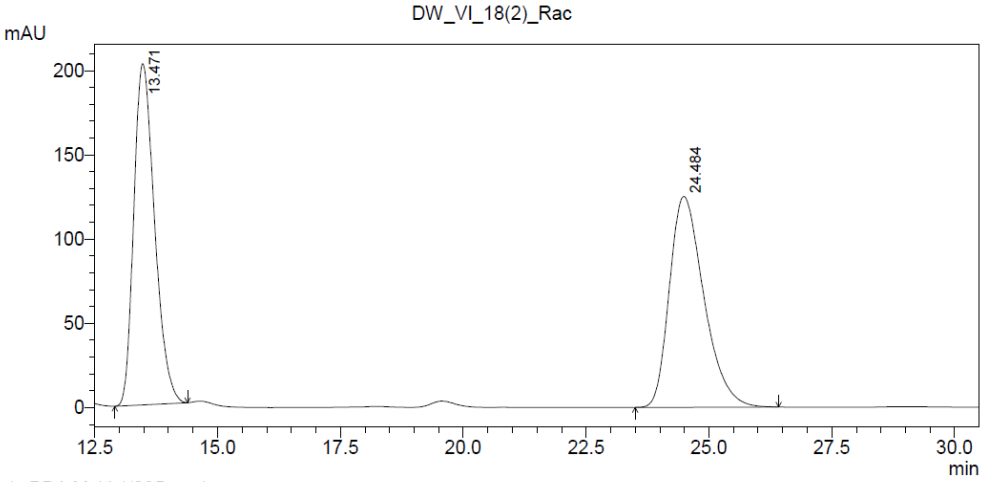
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.647	854712	34725	2.093	2.593
2	10.553	39991310	1304416	97.907	97.407
Total		40846022	1339141	100.000	100.000


7.26 7.18 7.17 7.16 7.16 7.15 7.14 7.13 7.11 7.11 7.09 7.08 7.00 6.98
3.78 3.77 3.76 3.74 3.35 3.26 3.25 3.23 3.22 3.21
2.89 2.88 2.87 2.86 2.85 2.85 2.80 2.80 2.79 2.78 2.77 2.63 2.62 2.61 2.60 2.60 2.58 2.57 2.55 2.54 2.53 2.51 2.51 2.49 2.32 2.32 2.30
N
O

23b


3.10
0.97
3.97
1.02
3.14
7.48
2.22
f1 (ppm)


137.61
135.12
133.35
132.21
127.49
126.50
126.41
122.32
77.34
77.16
76.98
66.83
65.26
51.53
39.63
34.50
28.56
24.28
f1 (ppm)

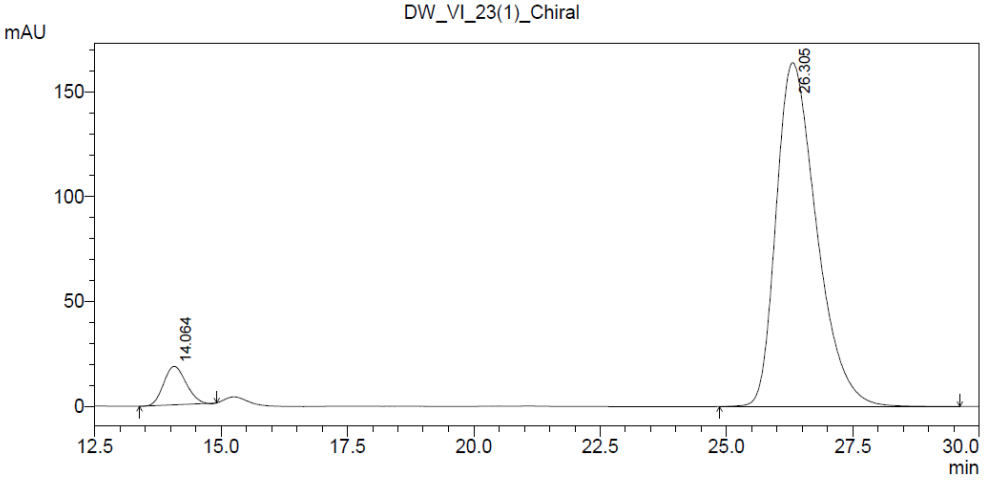


1 PDA Multi 1/285nm 4nm

PeakTable

PDA Ch1 285nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.471	5964134	202419	49.371	61.794
2	24.484	6116115	125151	50.629	38.206
Total		12080249	327569	100.000	100.000

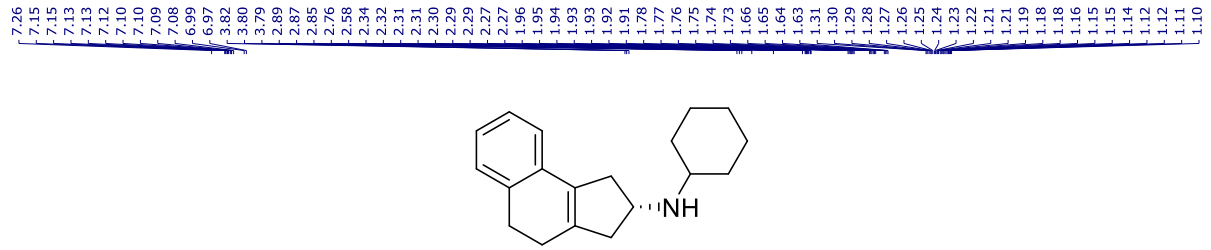


1 PDA Multi 1/285nm 4nm

PeakTable

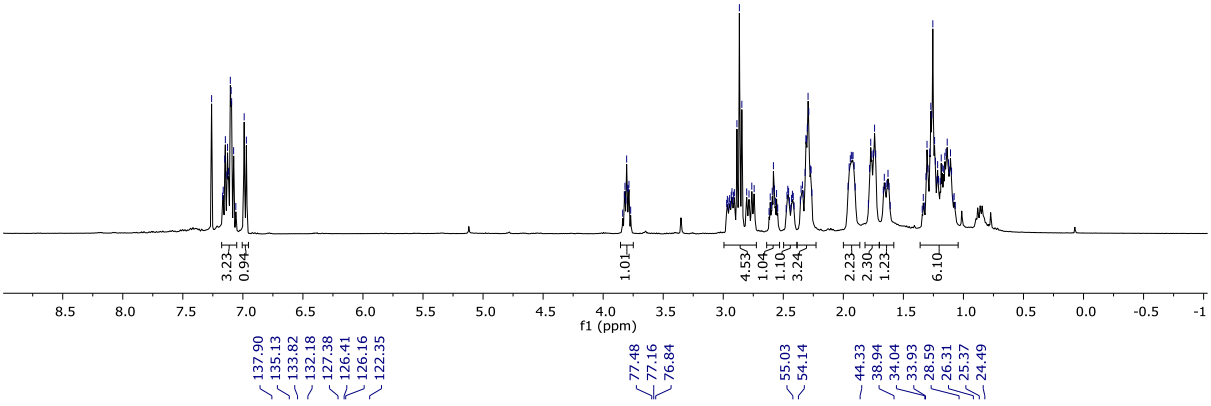
PDA Ch1 285nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.064	563734	18369	5.806	10.071
2	26.305	9146505	164033	94.194	89.929
Total		9710239	182402	100.000	100.000

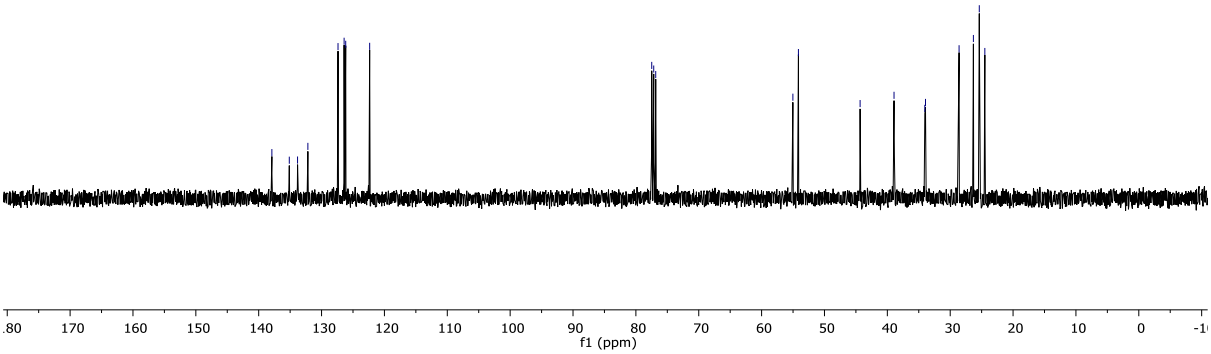

7.26 7.15 7.15 7.13 7.13 7.12 7.10 7.10 7.09 7.08 6.99 6.97 3.82 3.80 3.79 2.89 2.87 2.85 2.76 2.58 2.34 2.32 2.31 2.31 2.30 2.29 2.29 2.27 2.27 1.96 1.95 1.94 1.93 1.93 1.92 1.91 1.78 1.77 1.76 1.75 1.74 1.73 1.66 1.65 1.64 1.63 1.31 1.30 1.29 1.28 1.27 1.26 1.25 1.24 1.23 1.22 1.21 1.21 1.19 1.18 1.18 1.16 1.15 1.15 1.14 1.12 1.12 1.11 1.10

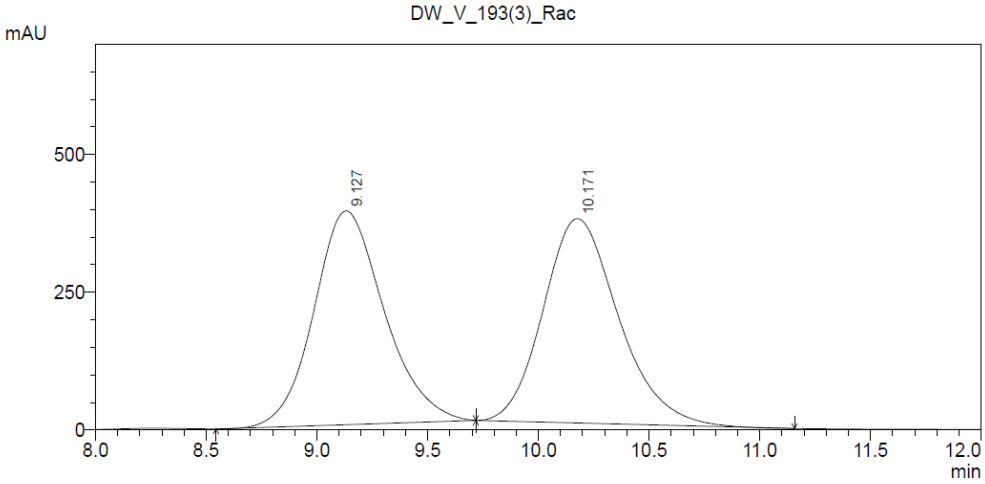
NH

23c


3.23
0.94
1.01
4.53
1.04
1.10
3.24
2.23
2.30
1.23
6.10
f1 (ppm)

137.90
135.13
133.82
132.18
127.38
126.41
126.16
122.35
77.48
77.16
76.84
55.03
54.14
44.33
38.94
34.04
33.93
28.59
26.31
25.37
24.49


f1 (ppm)

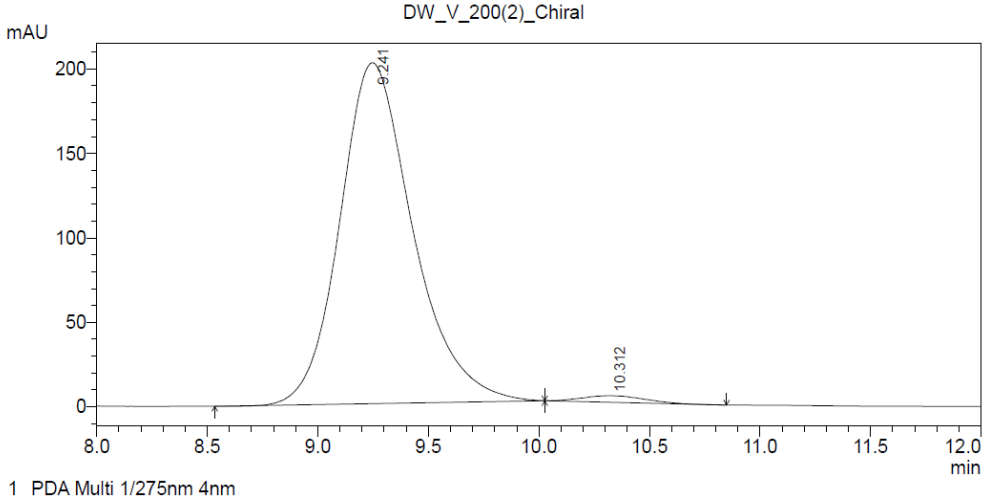


1 PDA Multi 1/275nm 4nm

PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.127	8572463	387999	49.421	51.126
2	10.171	8773277	370907	50.579	48.874
Total		17345740	758906	100.000	100.000



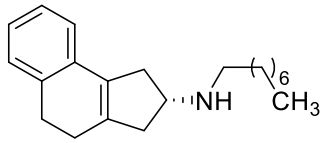
1 PDA Multi 1/275nm 4nm

PeakTable

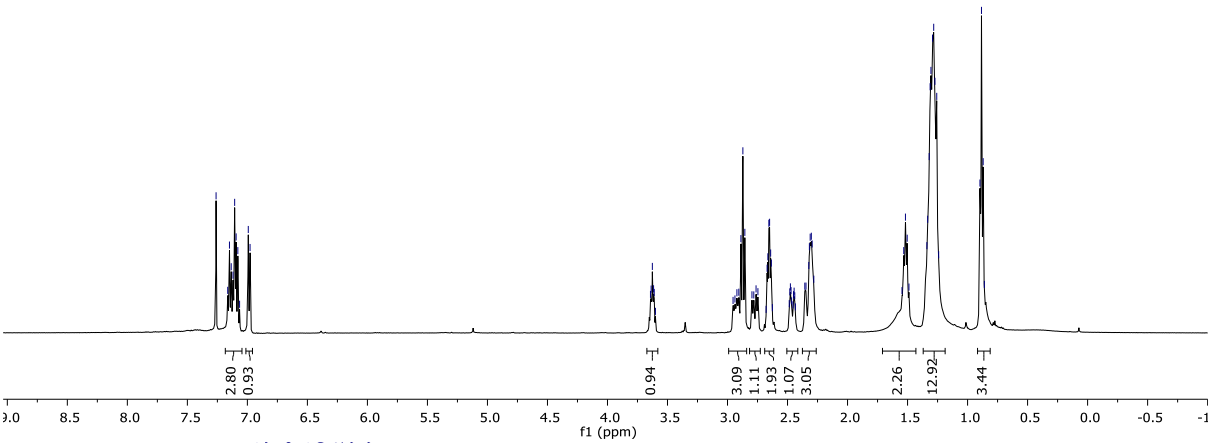
PDA Ch1 275nm 4nm

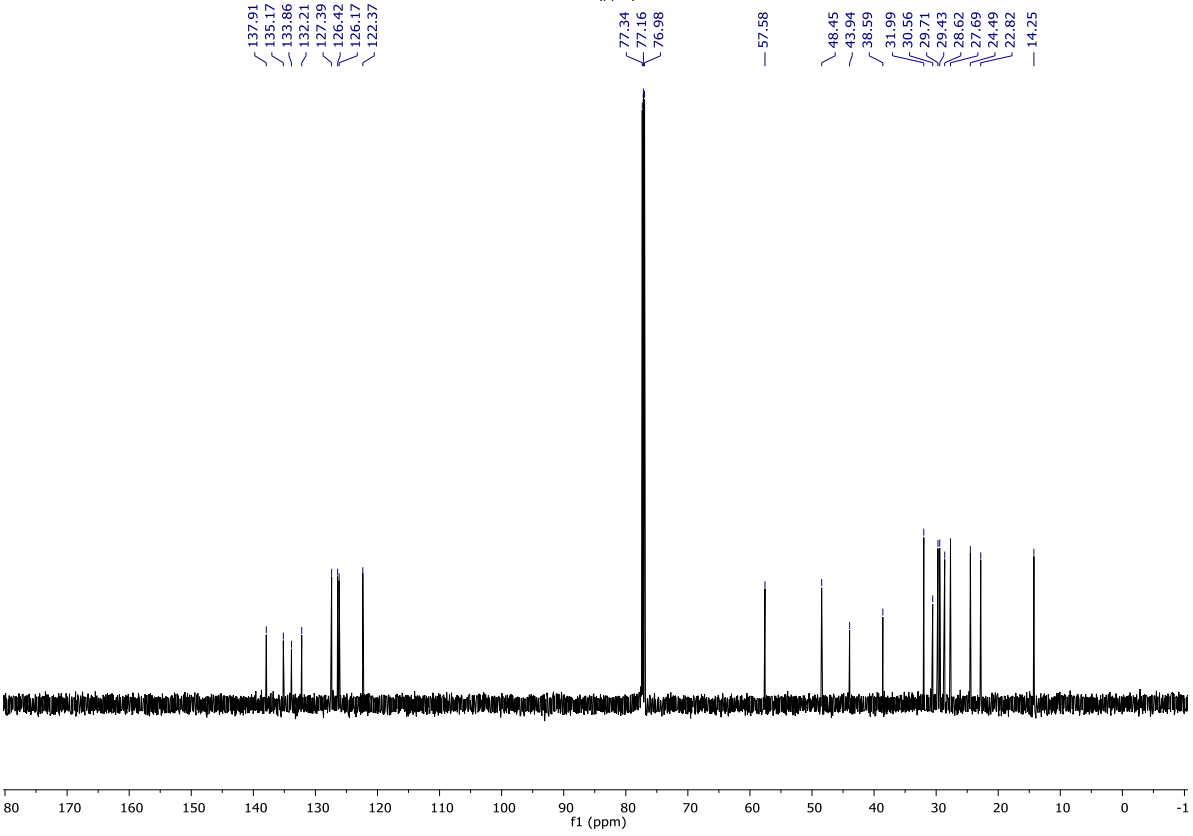
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.241	4633553	201731	98.450	98.148
2	10.312	72965	3806	1.550	1.852
Total		4706519	205537	100.000	100.000

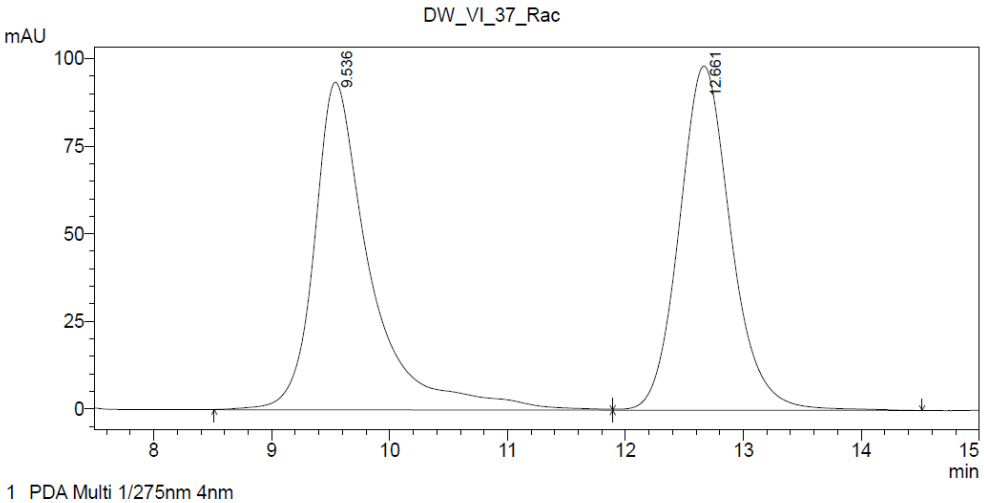

7.26
7.16
7.15
7.13
7.12
7.11
7.09
7.08
7.06
6.99
6.98
3.64
3.64
3.63
3.62
3.61
2.95
2.94
2.92
2.91
2.89
2.87
2.86
2.80
2.78
2.76
2.75
2.67
2.66
2.66
2.65
2.64
2.63
2.49
2.48
2.48
2.47
2.47
2.46
2.45
2.44
2.44
2.36
2.35
2.32
2.32
2.31
2.30
2.29
2.28
1.55
1.53
1.52
1.50
1.49
1.34
1.33
1.32
1.31
1.31
1.29
1.28
1.27
1.26
1.24
0.90
0.88
0.87
0.86


NH
6
CH3

23d


2.80
0.93
0.94
3.09
1.11
1.93
1.07
3.05
2.26
12.92
3.44
f1 (ppm)


137.91
135.17
133.86
132.21
127.39
126.42
126.17
122.37
77.34
77.16
76.98
57.58
48.45
43.94
38.59
31.99
30.56
29.71
29.43
28.62
27.69
24.49
22.82
14.25
f1 (ppm)

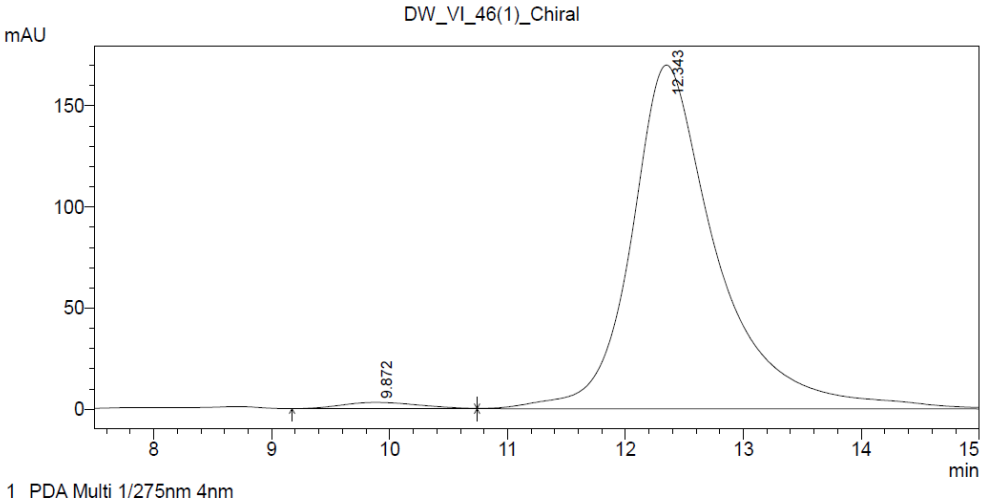


1 PDA Multi 1/275nm 4nm

PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.536	3094498	93526	50.801	48.765
2	12.661	2996899	98263	49.199	51.235
Total		6091397	191789	100.000	100.000

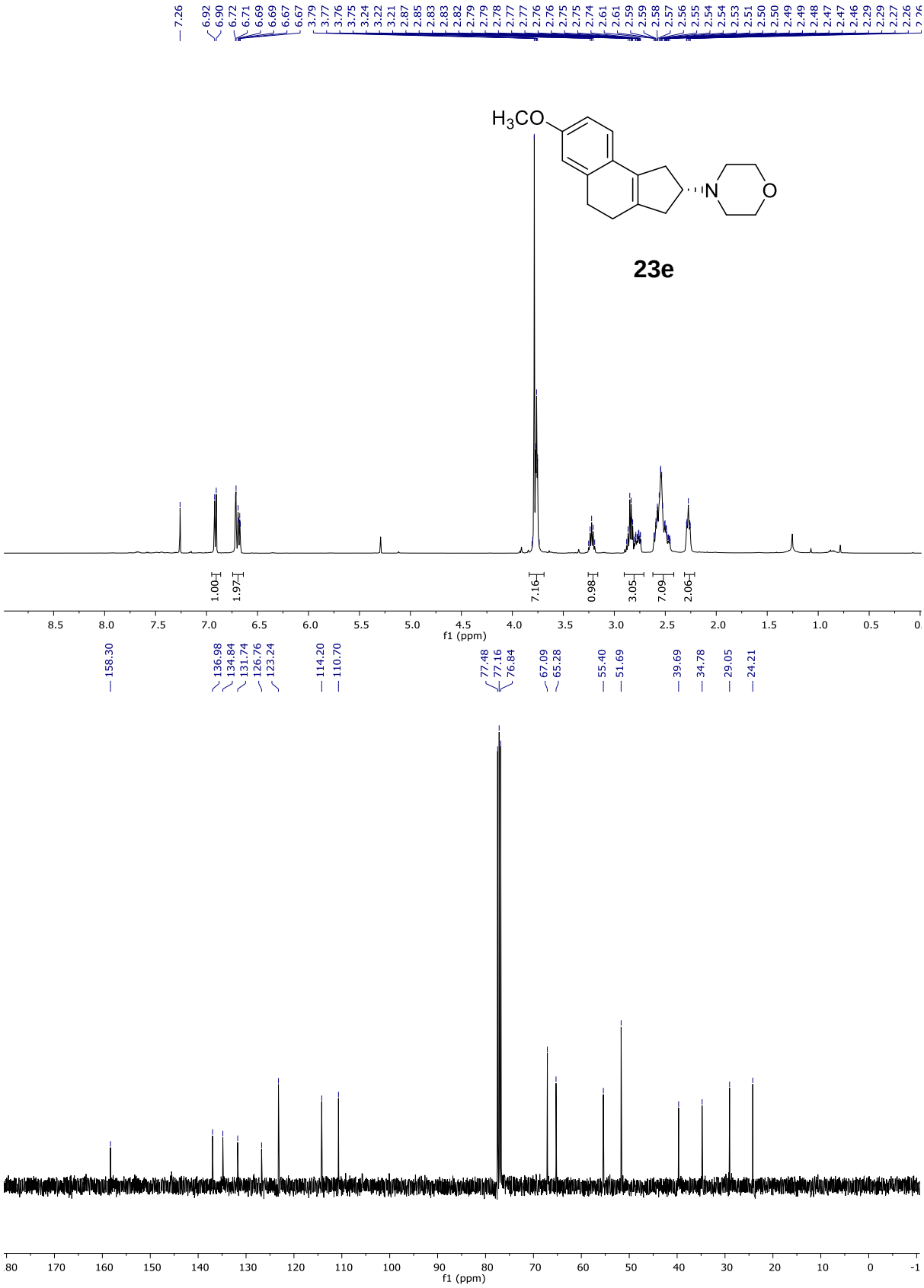


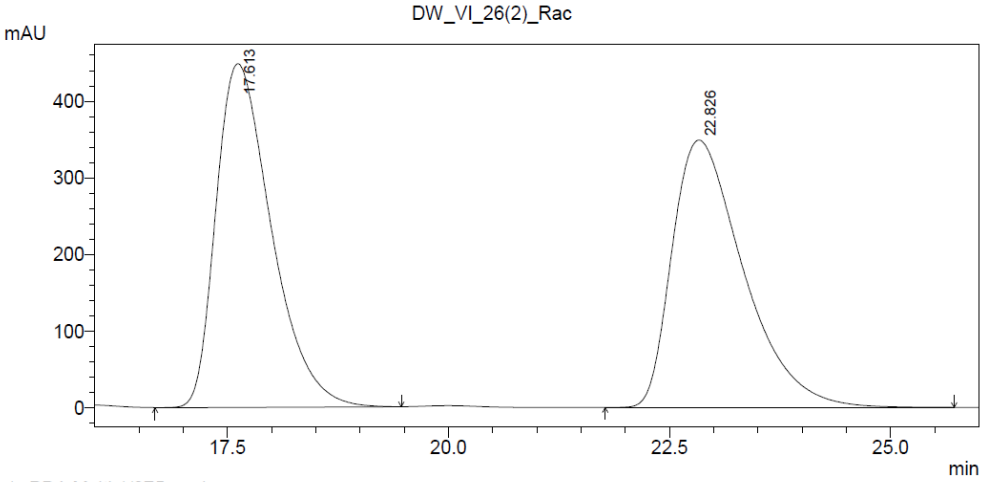
1 PDA Multi 1/275nm 4nm

PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.872	144874	3128	1.649	1.807
2	12.343	8640185	170011	98.351	98.193
Total		8785059	173139	100.000	100.000


7.26
6.92
6.90
6.72
6.71
6.69
6.69
6.67
6.67
3.79
3.77
3.76
3.75
3.24
3.22
3.21
2.87
2.85
2.83
2.83
2.82
2.79
2.79
2.78
2.77
2.77
2.76
2.76
2.75
2.75
2.74
2.61
2.61
2.59
2.59
2.58
2.57
2.56
2.55
2.54
2.54
2.53
2.51
2.50
2.50
2.49
2.49
2.48
2.47
2.47
2.46
2.29
2.29
2.27
2.26
H3CO
N
O
23e
1.00
1.97
7.16
0.98
3.05
7.09
2.06
f1 (ppm)
158.30
136.98
134.84
131.74
126.76
123.24
114.20
110.70
77.48
77.16
76.84
67.09
65.28
55.40
51.69
39.69
34.78
29.05
24.21
f1 (ppm)

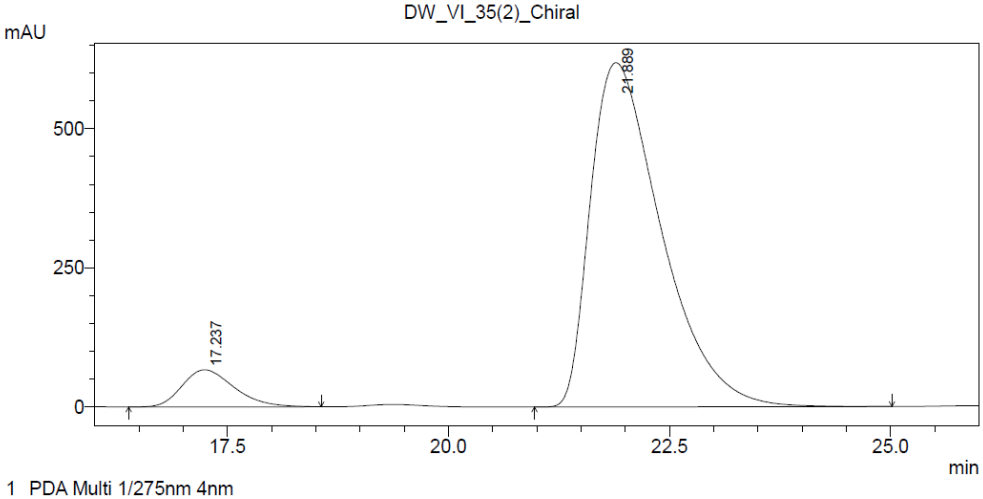


1 PDA Multi 1/275nm 4nm

PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.613	19548552	448355	49.948	56.239
2	22.826	19589423	348882	50.052	43.761
Total		39137975	797236	100.000	100.000

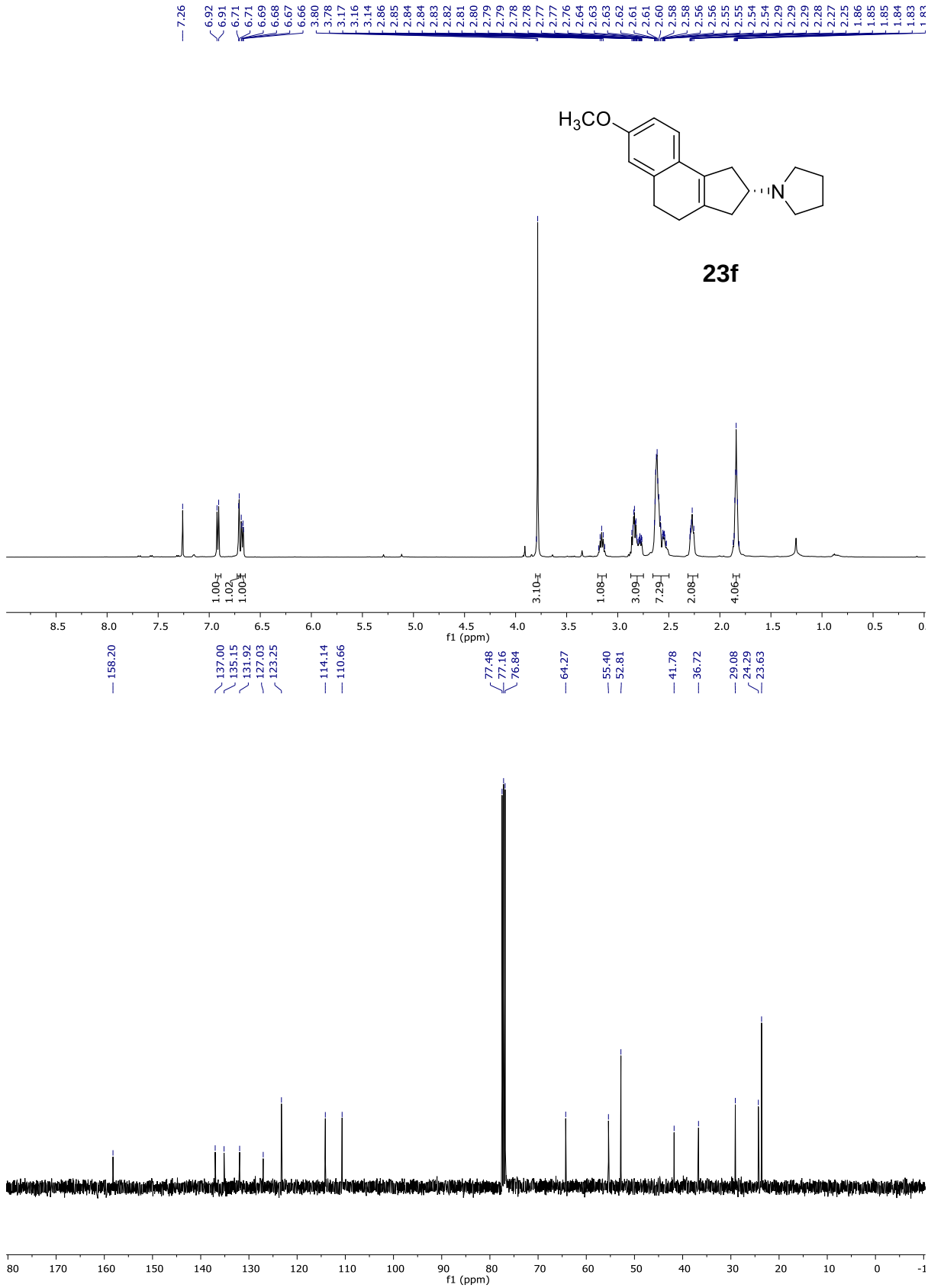


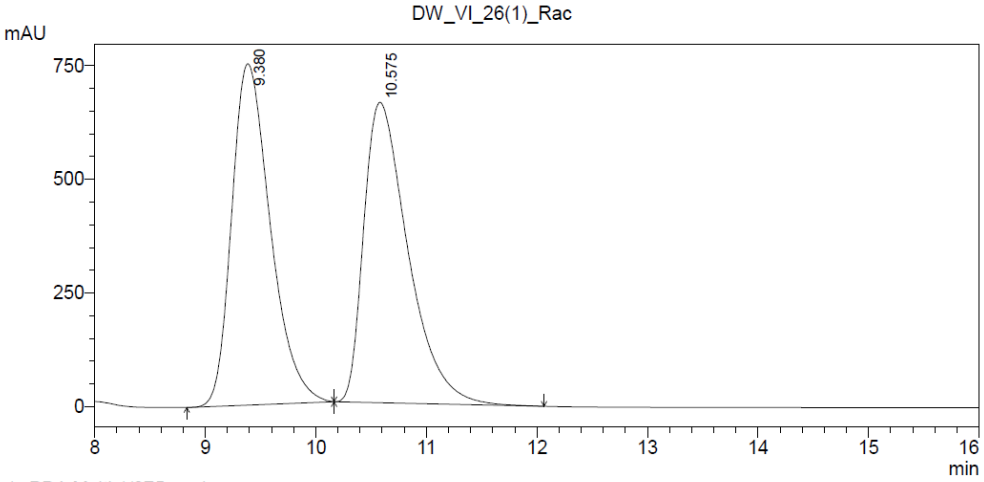
1 PDA Multi 1/275nm 4nm

PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.237	2735814	66672	7.346	9.731
2	21.889	34508118	618504	92.654	90.269
Total		37243932	685176	100.000	100.000


7.26
6.92
6.91
6.71
6.71
6.69
6.68
6.67
6.66
3.80
3.78
3.17
3.16
3.14
2.86
2.85
2.84
2.84
2.83
2.82
2.81
2.80
2.79
2.79
2.78
2.78
2.77
2.77
2.76
2.64
2.63
2.63
2.62
2.61
2.61
2.60
2.58
2.58
2.56
2.56
2.55
2.54
2.54
2.29
2.29
2.29
2.28
2.27
2.25
1.86
1.85
1.85
1.84
1.83
H3CO
N
23f
1.00
1.02
1.00
3.10
1.08
3.09
7.29
2.08
4.06
f1 (ppm)
158.20
137.00
135.15
131.92
127.03
123.25
114.14
110.66
77.48
77.16
76.84
64.27
55.40
52.81
41.78
36.72
29.08
24.29
23.63
f1 (ppm)

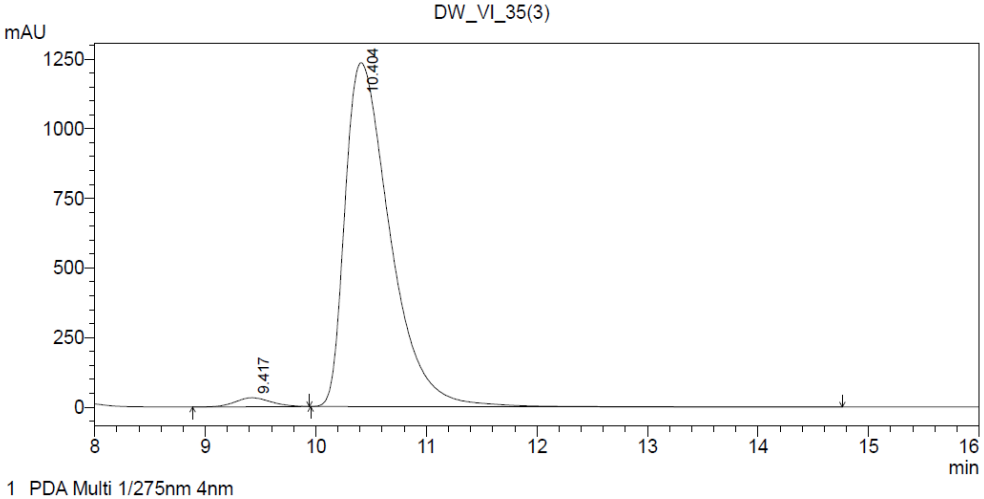


1 PDA Multi 1/275nm 4nm

PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.380	18254310	750797	49.841	53.198
2	10.575	18370984	660518	50.159	46.802
Total		36625294	1411315	100.000	100.000

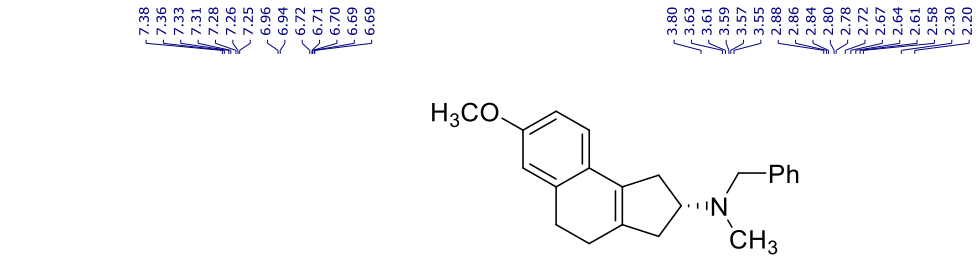


1 PDA Multi 1/275nm 4nm

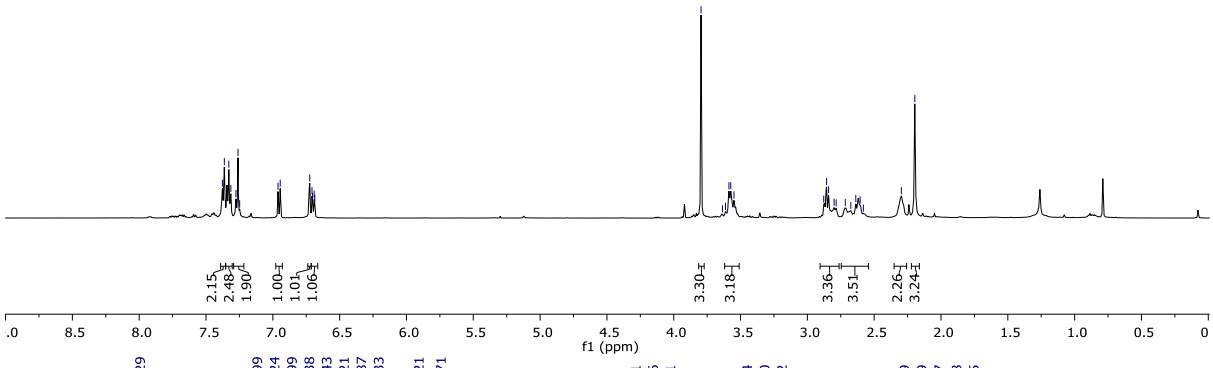
PeakTable

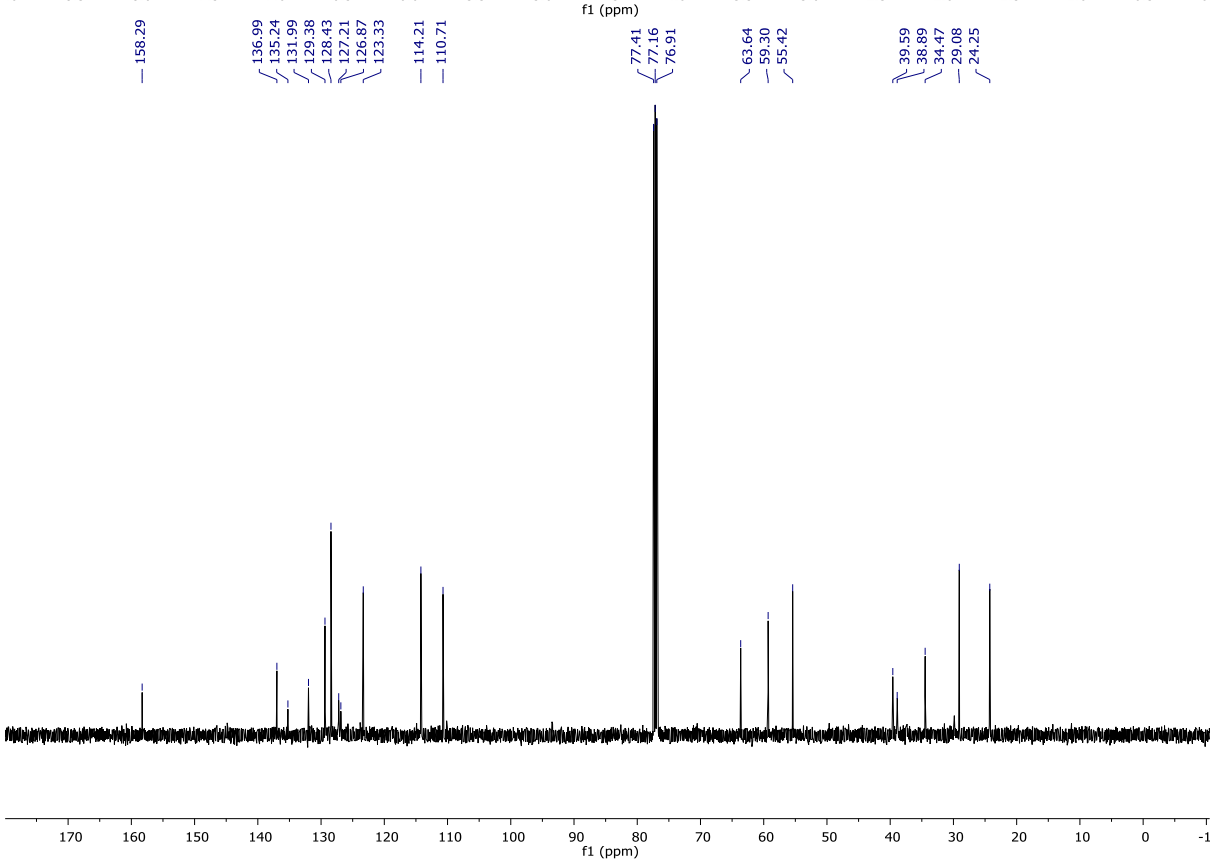
PDA Ch1 275nm 4nm

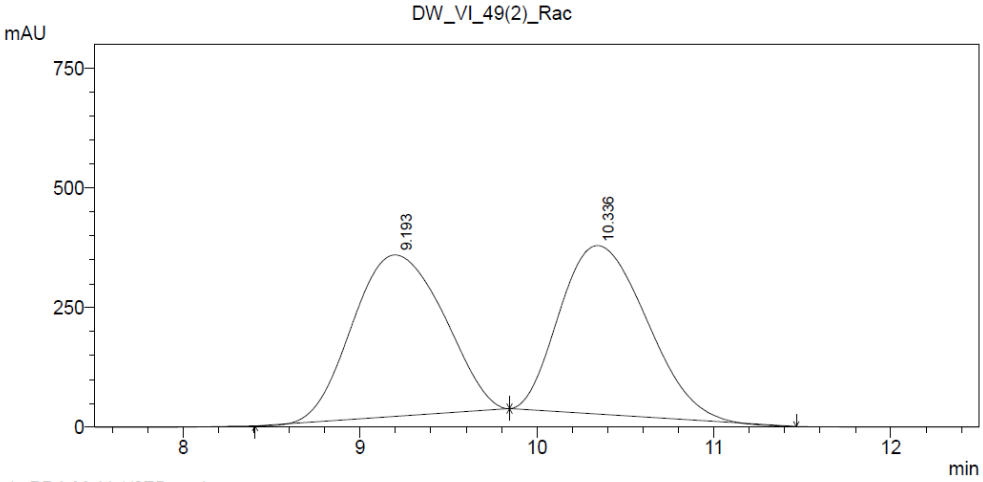
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.417	731463	32295	2.049	2.548
2	10.404	34964802	1234992	97.951	97.452
Total		35696265	1267287	100.000	100.000


7.38
7.36
7.33
7.31
7.28
7.26
7.25
6.96
6.94
6.72
6.71
6.70
6.69
6.69
3.80
3.63
3.61
3.59
3.57
3.55
2.88
2.86
2.84
2.80
2.78
2.72
2.67
2.64
2.61
2.58
2.30
2.20
H3CO
Ph
N
CH3

23g


2.15
2.48
1.90
1.00
1.01
1.06
3.30
3.18
3.36
3.51
2.26
3.24
f1 (ppm)


158.29
136.99
135.24
131.99
129.38
128.43
127.21
126.87
123.33
114.21
110.71
77.41
77.16
76.91
63.64
59.30
55.42
39.59
38.89
34.47
29.08
24.25
f1 (ppm)

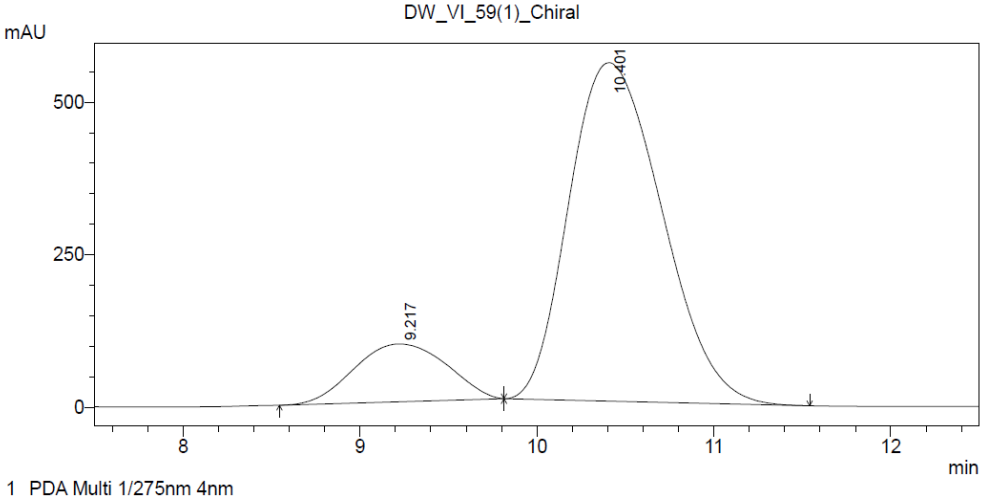


1 PDA Multi 1/275nm 4nm

PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.193	12101149	337663	50.153	48.956
2	10.336	12027313	352062	49.847	51.044
Total		24128462	689726	100.000	100.000

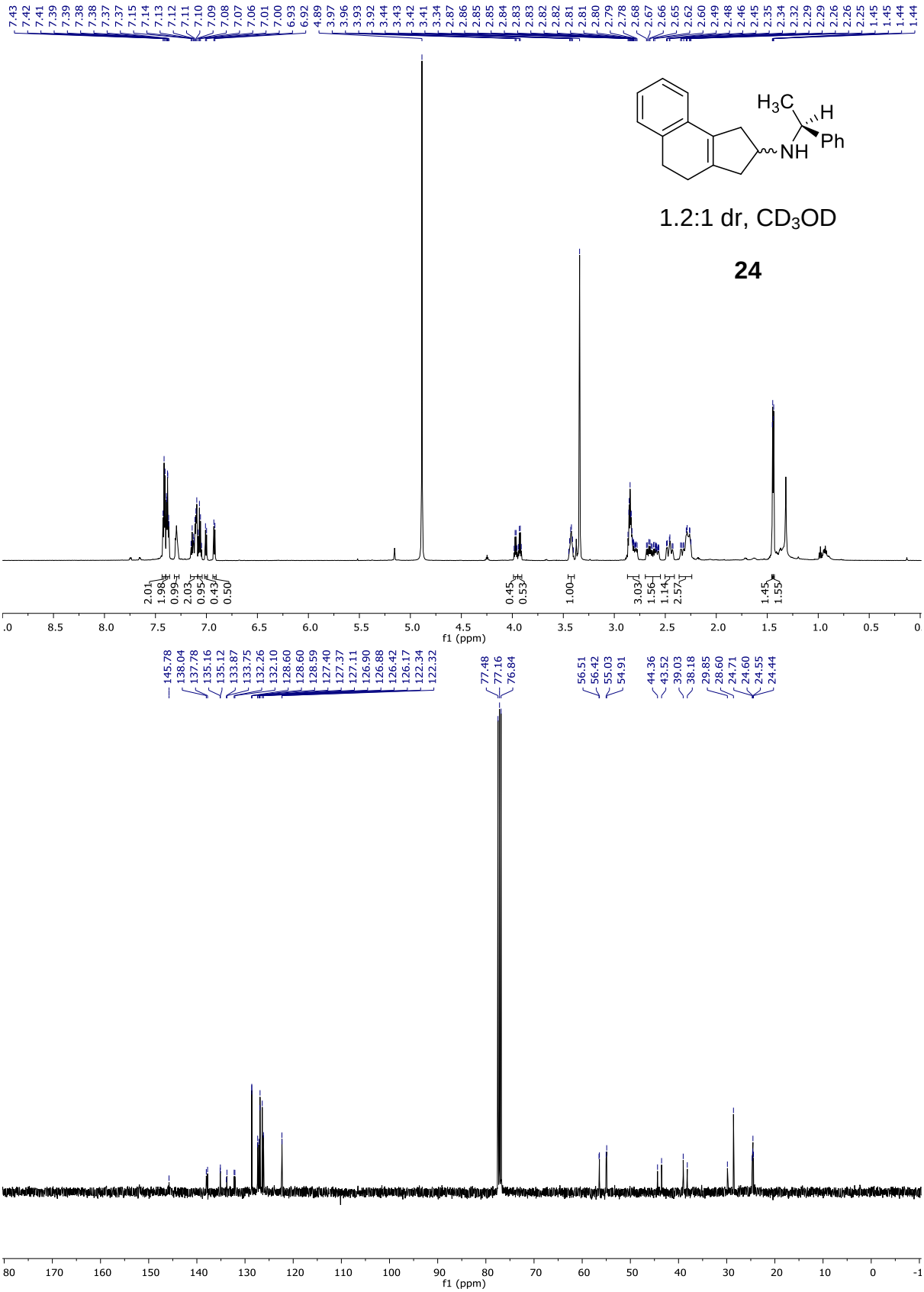


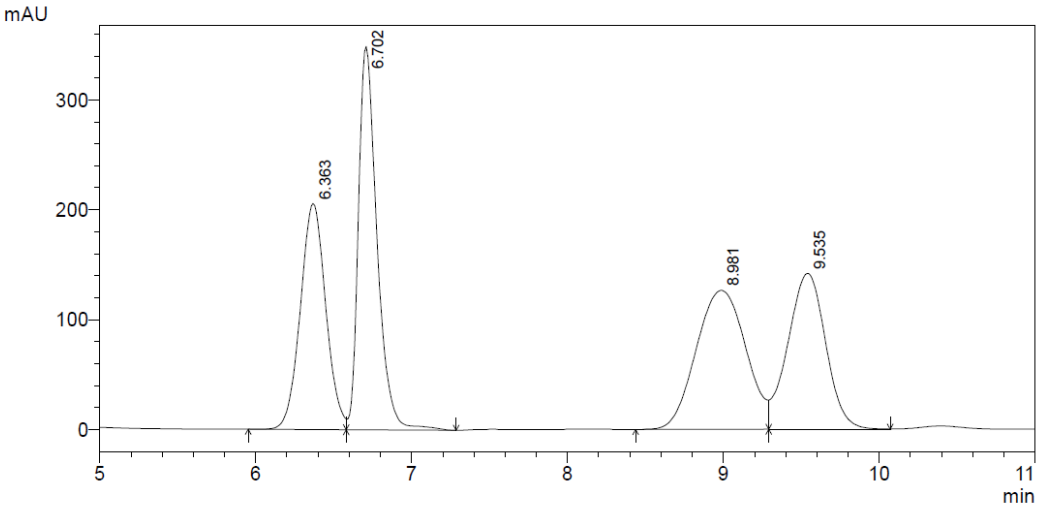
1 PDA Multi 1/275nm 4nm

PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.217	3440169	94740	14.513	14.585
2	10.401	20264634	554827	85.487	85.415
Total		23704802	649567	100.000	100.000


H3C
H
Ph
NH
1.2:1 dr, CD3OD
24
f1 (ppm)
f1 (ppm)

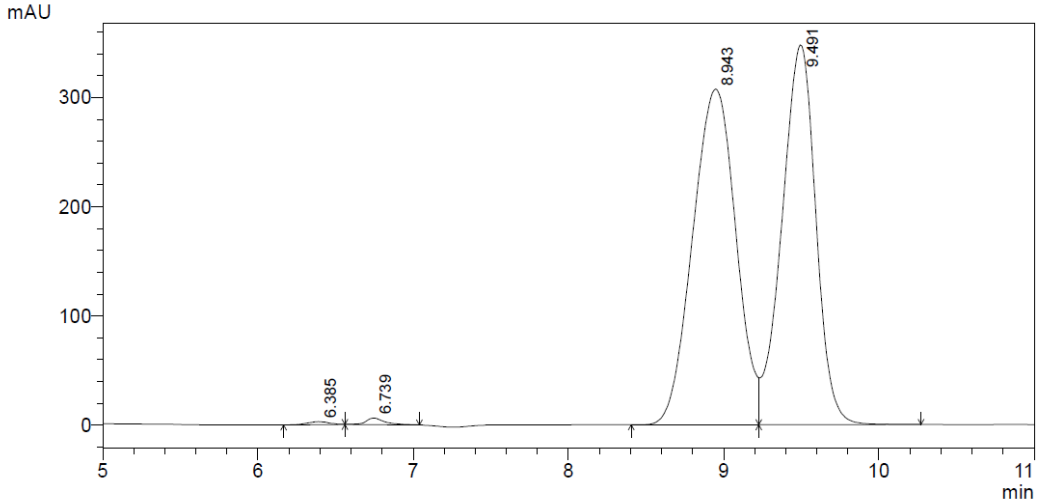


1 PDA Multi 1/275nm 4nm

PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.363	2336261	205796	22.442	25.013
2	6.702	2886412	348820	27.727	42.396
3	8.981	2807824	126394	26.972	15.362
4	9.535	2379665	141746	22.859	17.228
Total		10410161	822756	100.000	100.000



1 PDA Multi 1/275nm 4nm

PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.385	25802	2688	0.228	0.405
2	6.739	49061	5992	0.434	0.902
3	8.943	5963796	307510	52.700	46.314
4	9.491	5277891	347772	46.639	52.378
Total		11316550	663961	100.000	100.000