

Supporting Information

**Functionalization of Styrenes by Copper-Catalyzed Borylation/
ortho-Cyanation and Silver-Catalyzed Annulation Processes**

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Supporting information

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I. General Information

Unless otherwise noted, all reactions were conducted in oven-dried vials with magnetic stirring under an atmosphere of dry nitrogen. Solvents were purified under nitrogen using a solvent purification system (Innovative Technology, inc., Model #SPS-400-3 and PS-400-3). IMesCuCl (Aldrich), all *N*-heterocyclic carbene salts (Aldrich), lithium *tert*-butoxide (Strem Chemicals, Inc.) were stored and weighed in an inert atmosphere glovebox. Analytical thin layer chromatography (TLC) was performed on SiliaPlate TLC 60Å F-254 (250 μm silica gel) and compounds were visualized with phosphomolybdic acid, ceric ammonium molybdate, or aqueous KMnO₄ stain. Flash column chromatography was performed using SiliaFlash® P60 (230-400 mesh) silica gel.

¹H-Nuclear Magnetic Resonance (¹H-NMR) and ¹³C Nuclear Magnetic Resonance (¹³C-NMR) spectra were recorded on Varian MR 400, Vnmrs 500, INOVA 500 and Vnmrs 700 MHz. NMR spectra were recorded in deuterated chloroform (CDCl₃) at rt unless otherwise stated. The NMR data were presented as follows: chemical shift in ppm with the proton signal of the residual of chloroform (δ 7.26 for ¹H-NMR) and (δ = 77.0 ppm for ¹³C-NMR) as internal standards, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet, br. = broad), coupling constant (*J*/Hz), integration. High resolution mass spectra were recorded on a VG 70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK) at the University of Michigan Mass Spectrometry Laboratory. IR spectra were collected on a Spectrum BX FTIR from Perkin-Elmer and reported in unit of cm⁻¹.

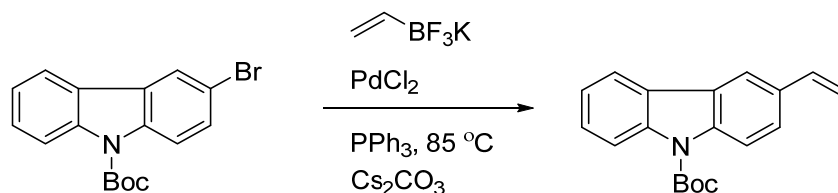
II. Preparation of Substrates

The following styrenes were purchased and used as received: **styrene**, **4-fluorostyrene**, **4-chlorostyrene**, **4-methylstyrene**, **4-*tert*-butylstyrene**, **4-phenylstyrene**, **3-methylstyrene**, **3-bromostyrene**, **3-vinylanisole**, **2-methylstyrene** and **2-vinylnaphthalene**.

The following styrenes were prepared by the literature procedure: ***tert*-butyldimethyl((4-vinylbenzyl)oxy)silane**,¹ **1-(diethoxymethyl)-4-vinylbenzene**,² **1-(prop-1-en-1-yl)-4-vinylbenzene**,³ ***tert*-butyldimethyl((3-vinylbenzyl)oxy)silane**,⁴ ***tert*-butyl 5-vinyl-1H-indole-1-carboxylate**,⁵ ***tert*-butyl 2-vinyl-1H-pyrrole-1-carboxylate**⁶ and **3-Vinylestrone**.⁷ All characterization data are in accordance with the literature.

N-cyano-4-methyl-*N*-phenylbenzenesulfonamide (NCTS, 1) was prepared according to the known procedure.⁸

tert-Butyl 3-vinyl-9H-carbazole-9-carboxylate⁵



In glove box, to an oven-dried 20-mL microwave tube was added potassium vinyltrifluoroborate (0.7 g, 5.0 mmol), PdCl₂ (17.7 mg, 0.1 mmol), PPh₃ (78.6 mg, 0.3 mmol), Cs₂CO₃ (4.9 g, 15.0 mmol) and *tert*-butyl 3-bromo-9H-carbazole-9-carboxylate (1.7 g, 5.0 mmol). The microwave tube was sealed with a cap and taken outside the glove box. Under N₂, THF/H₂O (9:1) (10 mL) were added. The resulting solution was stirred at 85 °C for 40 h, then cooled to rt and diluted with H₂O. The mixture was extracted with DCM, dried with Na₂SO₄, filtered, and concentrated, and the residue was chromatographed on

¹ P. J. M. Stals, T. N. T. Phan, D. Gignes, T. F. E. Paffen, E. W. Meijer, A. R. A. Palmans, *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 780.

² R. J. Mancini, J. Lee, H. D. Maynard, *J. Am. Chem. Soc.* **2012**, *134*, 8474-8479.

³ T. Bach, J. Löbel, *Synthesis* **2002**, 2521-2526.

⁴ S. W. Ryu, A. Hirao, *Macromolecules*, **2000**, *33*, 4765-4771.

⁵ G. A. Molander, A. R. Brown, *J. Org. Chem.* **2006**, *71*, 9681-9686.

⁶ J. Waser, B. Gaspar, H. Nambu, E. M. Carreira, *J. Am. Chem. Soc.* **2006**, *128*, 11693-11712.

⁷ Y. Yasu, T. Koike, M. Akita, *Org. Lett.* **2013**, *15*, 2136-2139.

⁸ T.-J. Gong, B. Xiao, W.-M. Cheng, W. Su, J. Xu, Z.-J. Liu, L. Liu, Y. Fu, *J. Am. Chem. Soc.* **2013**, *135*, 10630-10633.

silica gel (20:1 hexane/EtOAc), to afford 1.14 g (78%) of *tert*-butyl 3-vinyl-9*H*-carbazole-9-carboxylate as a colorless oil.

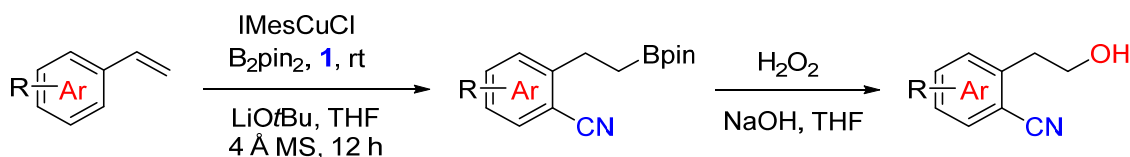
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.31 (d, $J = 8.4$ Hz, 1H), 8.26 (d, $J = 8.6$ Hz, 1H), 8.04 – 7.95 (m, 2H), 7.56 (dd, $J = 8.7, 1.8$ Hz, 1H), 7.48 (m, 1H), 7.37 (m, 1H), 6.89 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.85 (dd, $J = 17.6, 1.0$ Hz, 1H), 5.30 (dd, $J = 10.9, 0.9$ Hz, 1H), 1.78 (s, 9H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 151.0, 138.8, 138.1, 136.8, 132.7, 127.1, 126.0, 125.7, 125.3, 123.0, 119.6, 117.2, 116.3, 116.2, 112.9, 83.9, 28.4.

HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{19}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$: 316.1308, found: 316.1306.

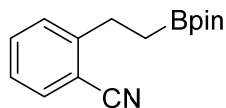
IR (neat, cm^{-1}): 2978, 1722, 1450, 1354, 1304, 1153, 748.

III. Copper-Catalyzed Borylation / *ortho*-Cyanation



General Procedure A. In glove box, to an oven-dried 10-mL vial was added IMesCuCl (12.1 mg, 0.03 mmol, 10 mol %), LiO-*t*-Bu (48.0 mg, 0.6 mmol, 2.0 eq), 4 Å molecular sieves (50.0 mg) and anhydrous THF (0.3 mL). The resulting solution was stirred for 15 min at rt. The B₂pin₂ (114.3 mg, 0.45 mmol, 1.5 eq) was then added. After stirring for 30 min at rt, the solution of styrene (0.3 mmol) and *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide **1** (NCTS, 163.2 mg, 0.6 mmol) in THF (0.5 mL) was then added by syringe (10 min). The resulting solution was stirred overnight and diluted with ethyl acetate, filtered through a silica gel pad, concentrated in vacuo, and the residue was purified by silica gel flash chromatography to afford cyanoborylated product.

General Procedure B. To a 10-mL vial was added the cyanoborylated product, NaOH (5.0 eq, 60.0 mg) and THF (1 mL). The resulting mixture was cooled to 0 °C followed by addition of 30% H₂O₂ (5.0 eq, 170.0 mg), dropwise. The reaction mixture was allowed to warm to rt and stir for 2 hours. The reaction mixture was then diluted with H₂O, extracted with ethyl acetate, dried with MgSO₄, filtered, and concentrated, and the residue was chromatographed on silica gel to afford the desired alcohol.



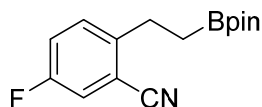
2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a colorless oil from styrene (31.2 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 64.8 mg, 84% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.60 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.50 (td, *J* = 7.7, 1.4 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.26 (dd, *J* = 7.6, 1.1 Hz, 1H), 2.98 (t, *J* = 10.0 Hz, 2H), 1.24 (m, 14H).

¹³C NMR (125 MHz, CDCl₃) δ 148.3, 132.7, 132.6, 128.9, 126.2, 118.1, 112.1, 83.3, 28.6, 24.8.

HRMS (EI) calculated for C₁₅H₂₀BNO₂ [M⁺]: 257.1587, found: 257.1594.

IR (neat, cm⁻¹): 2979, 2223, 1370, 1319, 1142, 848, 761.



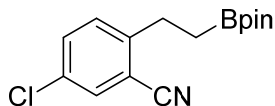
5-Fluoro-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a white solid from 4-fluorostyrene (36.6 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 66.8 mg, 81% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.35 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.27 (dd, *J* = 8.1, 2.7 Hz, 1H), 7.20 (td, *J* = 8.4, 2.7 Hz, 1H), 2.93 (t, *J* = 8.0 Hz, 2H), 1.21 (s, 12H), 1.21 – 1.15 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 160.2 (d, *J* = 246.3 Hz), 144.3 (d, *J* = 3.8 Hz), 130.80 (d, *J* = 7.5 Hz), 120.2 (d, *J* = 21.3 Hz), 119.1 (d, *J* = 23.8 Hz), 116.9 (d, *J* = 2.5 Hz), 113.2 (d, *J* = 8.6 Hz), 83.4, 27.9, 24.8.

HRMS (EI) calculated for C₁₅H₁₉BFNO₂ [M⁺]: 275.1493, found: 275.1496.

IR (neat, cm⁻¹): 2980, 2234, 1371, 1320, 1142, 840.



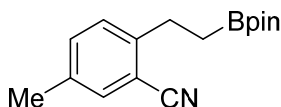
5-Chloro-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a white solid from 4-chlorostyrene (41.6 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 39.3 mg, 45%).

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 2.3 Hz, 1H), 7.45 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 2.93 (t, *J* = 8.1 Hz, 2H), 1.22 (s, 12H), 1.17 (t, *J* = 8.1 Hz, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 146.8, 132.9, 132.1, 130.4, 116.8, 113.6, 83.4, 28.1, 24.8.

HRMS (EI) calculated for C₁₅H₁₉BClNO₂ [M⁺]: 291.1197, found: 291.1203.

IR (neat, cm⁻¹): 2979, 2227, 1371, 1321, 1142, 848.



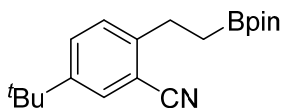
5-Methyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a white solid from 4-methylstyrene (35.5 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 65.9 mg, 81% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.36 (s, 1H), 7.29 – 7.20 (m, 2H), 2.89 (t, *J* = 8.1 Hz, 2H), 2.31 (s, 3H), 1.20 (s, 12H), 1.15 (m, *J* = 8.4 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 145.3, 135.9, 133.5, 132.9, 128.8, 118.3, 111.9, 83.2, 28.1, 24.8, 20.6.

HRMS (EI) calculated for C₁₅H₂₂BNO₂ [M⁺]: 271.1744, found: 271.1749.

IR (neat, cm⁻¹): 2976, 2224, 1371, 1318, 1142, 848.



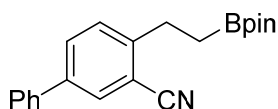
5-(*tert*-Butyl)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a colorless oil from 4-*tert*-butylstyrene (48.0 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 78.9 mg, 84% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 2.1 Hz, 1H), 7.48 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.29 – 7.23 (m, 1H), 2.90 (t, *J* = 8.1 Hz, 2H), 1.28 (s, 9H), 1.22 – 1.15 (m, 15H).

¹³C NMR (100 MHz, CDCl₃) δ 149.3, 145.2, 130.0, 129.5, 128.6, 118.6, 111.7, 83.3, 34.5, 31.1, 28.0, 24.8.

HRMS (ESI) calculated for C₁₉H₂₉BNO₂ [M+H]⁺: 314.2286, found: 314.2293.

IR (neat, cm⁻¹): 2973, 2222, 1371, 1320, 1142, 841, 737.



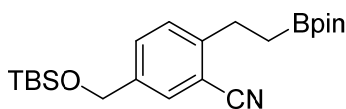
4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-[1,1'-biphenyl]-3-carbonitrile was prepared as a colorless oil from 4-phenylstyrene (54.0 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 78.9 mg, 79% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 1.9 Hz, 1H), 7.72 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.49 – 7.44 (m, 3H), 7.42 – 7.38 (m, 2H), 3.02 (m, 2H), 1.27 – 1.22 (m, 14H).

¹³C NMR (125 MHz, CDCl₃) δ 147.0, 139.4, 138.9, 131.3, 131.1, 129.4, 129.0, 128.0, 126.8, 117.9, 112.6, 83.3, 28.3, 24.8.

HRMS (EI) calculated for C₂₁H₂₄BNO₂ [M⁺]: 333.1900, found: 333.1908.

IR (neat, cm⁻¹): 2977, 2204, 1371, 1320, 1142, 762.



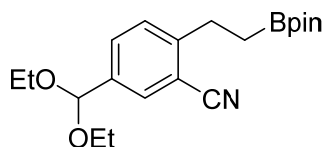
5-(((*tert*-Butyldimethylsilyl)oxy)methyl)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzotrile was prepared as colorless oil from *tert*-butyldimethyl((4-vinylbenzyl)oxy)silane (74.4 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 15:1 hexane/EtOAc, 86.6 mg, 72% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.55 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 4.71 (s, 2H), 2.95 (t, *J* = 8.2 Hz, 2H), 1.23 (s, 12H), 1.21 – 1.17 (m, 2H), 0.94 (s, 9H), 0.11 (s, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 146.8, 139.8, 130.3, 130.1, 128.8, 118.3, 111.9, 83.3, 63.8, 28.3, 25.9, 24.8, 18.3, -5.3.

HRMS (ESI) calculated for C₂₂H₃₆BNNaO₃Si [M+Na]⁺: 424.2450, found: 424.245.

IR (neat, cm⁻¹): 2930, 2225, 1371, 1320, 1143, 836.



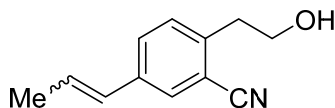
5-(Diethoxymethyl)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzotrile was prepared as a colorless oil from 1-(diethoxymethyl)-4-vinylbenzene (61.8 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 87.2 mg, 81% yield).

¹H NMR (500 MHz, C₆D₆) δ 7.64 (d, *J* = 1.7 Hz, 1H), 7.43 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 5.19 (s, 1H), 3.37 – 3.28 (m, 2H), 3.28 – 3.18 (m, 2H), 3.00 (t, *J* = 8.0 Hz, 2H), 1.24 (t, *J* = 8.0 Hz, 2H), 1.02 (t, *J* = 7.1 Hz, 6H), 0.97 (s, 12H).

¹³C NMR (125 MHz, C₆D₆) δ 148.0, 137.8, 131.0, 130.5, 128.6, 117.8, 112.5, 99.8, 82.8, 60.3, 28.5, 24.5, 14.9.

HRMS (ESI) calculated for C₂₀H₃₀BNNaO₄ [M+Na]⁺: 382.2160, found: 382.2163.

IR (neat, cm⁻¹): 2976, 2224, 1372, 1328, 1143, 1055, 848.



2-(2-Hydroxyethyl)-5-(prop-1-en-1-yl)benzonitrile was prepared as colorless oil from 1-(prop-1-en-1-yl)-4-vinylbenzene (*E/Z* = 1:1, 43.2 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg), NaOH (60.0 mg) and 30% H₂O₂ (170.0 mg) following the above general procedure A and B (eluent: 5:1 hexane/EtOAc, 36.5 mg, 65% yield for 2 steps, *E/Z* = 1/2).

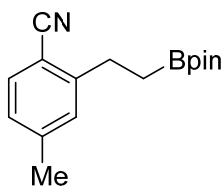
¹H NMR (500 MHz, CDCl₃, *E* isomer): δ 7.56 (d, *J* = 1.9 Hz, 1H), 7.47 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 6.39 – 6.31 (m, 1H), 6.27 (dq, *J* = 15.8, 6.2 Hz, 1H), 3.91 (d, *J* = 6.5 Hz, 2H), 3.05 (d, *J* = 6.5 Hz, 2H), 1.87 (d, *J* = 1.8 Hz, 3H).

¹H NMR (500 MHz, CDCl₃, *Z* isomer): 7.55 (d, *J* = 1.9 Hz, 1H), 7.44 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 6.39 – 6.31 (m, 1H), 5.88 (dq, *J* = 11.6, 7.2 Hz, 1H), 3.96 – 3.93 (m, 2H), 3.09 (t, *J* = 6.6 Hz, 2H), 1.89 (dd, *J* = 6.4, 1.5 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃, *E/Z* isomers) δ 140.6, 140.4, 137.2, 136.7, 133.1, 132.8, 130.5, 130.2, 129.98, 129.97, 129.0, 128.8, 128.1, 127.5, 118.2, 113.0, 112.7, 62.6, 37.4, 37.4, 18.5, 14.6.

HRMS (ESI) calculated for C₁₂H₁₃NNaO [M+Na]⁺: 210.0889, found: 210.0888.

IR (neat, cm⁻¹): 3416, 2942, 2225, 1495, 1044, 840.



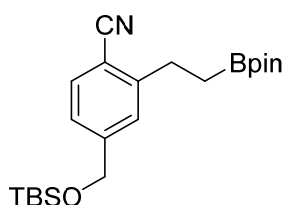
4-Methyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a colorless oil from 3-methylstyrene (35.5 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B₂pin₂ (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 52.8 mg, 65% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, *J* = 7.9 Hz, 1H), 7.17 (s, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 2.92 (t, 2 *J* = 8.0 Hz, H), 2.36 (s, 3H), 1.25 – 1.14 (m, 14H).

^{13}C NMR (125 MHz, CDCl_3) δ 148.2, 143.3, 132.6, 129.7, 127.0, 118.4, 109.1, 83.3, 28.5, 24.8, 21.8.

HRMS (EI) calculated for $\text{C}_{15}\text{H}_{22}\text{BNO}_2$ [M^+]: 271.1744, found: 271.1749.

IR (neat, cm^{-1}): 2977, 2222, 1370, 1316, 1142, 847, 731.



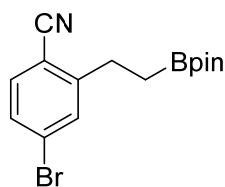
4-(((*tert*-Butyldimethylsilyl)oxy)methyl)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a colorless oil from *tert*-butyldimethyl((3-vinylbenzyl)oxy)silane (74.4 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_2pin_2 (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 15:1 hexane/EtOAc, 80.6 mg, 67% yield).

^1H NMR (500 MHz, CDCl_3) δ 7.54 (d, $J = 7.9$ Hz, 1H), 7.30 (s, 1H), 7.22 (d, $J = 7.9$ Hz, 1H), 4.73 (s, 2H), 2.95 (t, 2H), 1.24 – 1.16 (m, 14H), 0.93 (s, 9H), 0.09 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ 148.2, 146.7, 132.7, 126.1, 123.5, 118.3, 110.4, 83.3, 64.3, 28.6, 25.9, 24.8, -5.3.

HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{36}\text{BNNaO}_3\text{Si}$ [$\text{M}+\text{Na}$] $^+$: 424.2450, found: 424.2451.

IR (neat, cm^{-1}): 2930, 2223, 1371, 1319, 1143, 836.



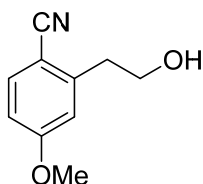
4-Bromo-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a white solid from 3-bromostyrene (54.3 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_2pin_2 (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 78.4 mg, 78% yield).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.57 (d, $J = 1.8$ Hz, 1H), 7.45 – 7.38 (m, 2H), 2.93 (t, $J = 7.9$ Hz, 2H), 1.22 (s, 12H), 1.20 – 1.15 (m, 2H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 150.1, 133.8, 132.5, 129.6, 127.6, 117.3, 111.1, 83.4, 28.5, 24.8.

HRMS (ESI) calculated for $\text{C}_{15}\text{H}_{20}\text{BrNO}_2$ $[\text{M}+\text{H}]^+$: 336.0765, found: 336.0767.

IR (neat, cm^{-1}): 2977, 2225, 1370, 1322, 1142, 846.



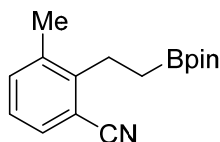
2-(2-Hydroxyethyl)-4-methoxybenzonitrile was prepared as a colorless oil from 3-vinylanisole (40.3 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_2pin_2 (114.3 mg, 0.45 mmol), $\text{LiO-}t\text{-Bu}$ (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg), NaOH (60.0 mg) and 30% H_2O_2 (170.0 mg) following the above general procedure A and B (eluent: 5:1 hexane/ EtOAc , 37.7 mg, 71% yield for 2 steps).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.57 (d, $J = 8.6$ Hz, 1H), 6.89 (d, $J = 2.3$ Hz, 1H), 6.83 (dd, $J = 8.6, 2.4$ Hz, 1H), 3.94 (t, $J = 6.5$ Hz, 2H), 3.85 (s, 3H), 3.06 (t, $J = 6.4$ Hz, 2H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 162.8, 144.8, 134.6, 116.0, 112.7, 109.1, 104.5, 62.5, 55.5, 37.9.

HRMS (ESI) calculated for $\text{C}_{10}\text{H}_{12}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 178.0863, found: 178.0862.

IR (neat, cm^{-1}): 3444, 2943, 2219, 1605, 1248, 1040, 820.



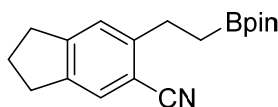
3-Methyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile was prepared as a white solid from 2-methylstyrene (35.5 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_2pin_2 (114.3 mg, 0.45 mmol), $\text{LiO-}t\text{-Bu}$ (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/ EtOAc , 54.5 mg, 67% yield).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.44 (d, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.14 (t, $J = 7.7$ Hz, 1H), 2.94 (t, $J = 8.5$ Hz, 2H), 2.37 (s, 3H), 1.25 (s, 15H), 1.08 (t, $J = 8.5$ Hz, 3H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 146.8, 137.0, 134.6, 130.7, 126.1, 118.6, 112.4, 83.3, 26.1, 24.8, 19.4.

HRMS (EI) calculated for $\text{C}_{15}\text{H}_{22}\text{BNO}_2$ [M^+]: 271.1744, found: 271.1745.

IR (neat, cm^{-1}): 2980, 2224, 1370, 1324, 1145, 850, 786.



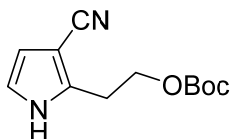
6-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2,3-dihydro-1H-indene-5-carbonitrile (5) was prepared as a colorless oil from 5-vinyl-2,3-dihydro-1H-indene (43.2 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_2pin_2 (114.3 mg, 0.45 mmol), $\text{LiO-}t\text{-Bu}$ (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 50.8 mg, 57% yield).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.41 (s, 1H), 7.21 (s, 1H), 2.93 – 2.87 (m, 6H), 2.07 (q, $J = 7.5$ Hz, 2H), 1.23 (s, 12H), 1.16 (t, $J = 8.5$ Hz, 2H).

$^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 150.1, 146.6, 142.3, 128.2, 124.9, 118.9, 109.4, 83.2, 33.2, 32.1, 28.5, 25.3, 24.8.

HRMS (ESI) calculated for $\text{C}_{18}\text{H}_{25}\text{BNO}_2$ [$\text{M}+\text{H}$] $^+$: 298.1973, found: 298.1979.

IR (neat, cm^{-1}): 2977, 2220, 1370, 1326, 1144, 968.



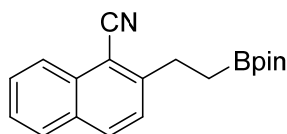
tert-Butyl (2-(3-cyano-1H-pyrrol-2-yl)ethyl) carbonate (6) was prepared as a pale yellow solid from *tert*-butyl 2-vinyl-1H-pyrrole-1-carboxylate (57.9 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_2pin_2 (114.3 mg, 0.45 mmol), $\text{LiO-}t\text{-Bu}$ (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg), NaOH (60.0 mg) and 30% H_2O_2 (170.0 mg) following the above general procedure A and B (eluent: 10:1 hexane/EtOAc, 53.1 mg, 75% yield for 2 steps).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.79 (s, 1H), 6.68 (t, $J = 2.8$ Hz, 1H), 6.38 (t, $J = 2.9$ Hz, 1H), 4.31 (t, $J = 5.9$ Hz, 2H), 3.12 (t, $J = 5.9$ Hz, 2H), 1.49 (s, 9H).

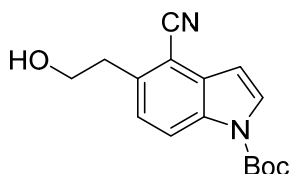
$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 153.0, 137.5, 118.3, 111.3, 91.9, 83.0, 65.5, 27.7, 26.2.

HRMS (ESI) calculated for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 259.1053, found: 259.1051.

IR (neat, cm^{-1}): 3308, 2981, 2220, 1741, 1279, 1162, 839.



2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-naphthonitrile (7) was prepared as a colorless oil from 2-vinylnaphthalene (45.2 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_2pin_2 (114.3 mg, 0.45 mmol), $\text{LiO-}t\text{-Bu}$ (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 76.4 mg, 83% yield). The data is in accordance with the literature.⁹



tert-Butyl 4-cyano-5-(2-hydroxyethyl)-1H-indole-1-carboxylate (8) was prepared as a colorless oil from *tert*-butyl 5-vinyl-1H-indole-1-carboxylate (72.9 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_2pin_2 (114.3 mg, 0.45 mmol), $\text{LiO-}t\text{-Bu}$ (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg), NaOH (60.0 mg) and 30% H_2O_2 (170.0 mg) following the above general procedure A and B (eluent: 3:1 hexane/EtOAc, 53.2 mg, 62% yield for 2 steps).

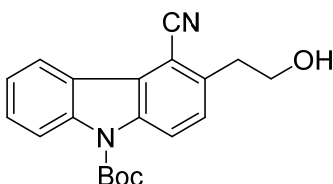
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.30 (d, $J = 8.5$ Hz, 1H), 7.72 (d, $J = 3.7$ Hz, 1H), 7.29 (d, $J = 8.6$ Hz, 1H), 6.77 – 6.72 (m, 1H), 3.96 (t, $J = 6.5$ Hz, 2H), 3.19 (t, $J = 6.5$ Hz, 2H), 1.67 (s, 9H), 1.62-1.55 (m, 1H).

⁹ Y. Yang, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2014**, *53*, 8677-8681.

^{13}C NMR (125 MHz, CDCl_3) δ 149.0, 137.8, 132.9, 128.5, 125.8, 119.5, 117.1, 110.0, 105.5, 103.8, 84.8, 63.1, 37.7, 28.1.

HRMS (ESI) calculated for $\text{C}_{16}\text{H}_{22}\text{N}_3\text{O}_3$ $[\text{M}+\text{NH}_4]^+$: 304.1656, found: 304.1655.

IR (neat, cm^{-1}): 3440, 2977, 2222, 1737, 1350, 1286, 1151, 1119, 1040, 767.



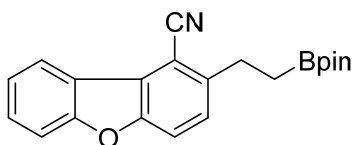
tert-Butyl 4-cyano-3-(2-hydroxyethyl)-9H-carbazole-9-carboxylate (9) was prepared as a white solid from *tert*-butyl 3-vinyl-9H-carbazole-9-carboxylate (87.9 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_2pin_2 (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol), 4 Å molecular sieves (50.0 mg), NaOH (60.0 mg) and 30% H_2O_2 (170.0 mg) following the above general procedure A (eluent: 3:1 hexane/EtOAc, 71.6 mg, 71% yield for 2 steps).

^1H NMR (500 MHz, CDCl_3) δ 8.60 (d, $J = 7.9$ Hz, 1H), 8.51 (d, $J = 8.6$ Hz, 1H), 8.30 (d, $J = 8.5$ Hz, 1H), 7.56 (t, $J = 7.9$ Hz, 1H), 7.45 (d, $J = 8.6$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 1H), 4.01 (t, $J = 6.5$ Hz, 2H), 3.25 (t, $J = 6.5$ Hz, 2H), 1.82 – 1.69 (m, 10H).

^{13}C NMR (125 MHz, CDCl_3) δ 150.5, 139.0, 138.2, 137.3, 128.8, 128.2, 126.7, 123.6, 123.1, 121.3, 120.4, 117.4, 116.1, 103.8, 84.9, 63.0, 37.4, 28.3.

HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{24}\text{N}_3\text{O}_3$ $[\text{M}+\text{NH}_4]^+$: 354.1812, found: 354.1812.

IR (neat, cm^{-1}): 3445, 2976, 2221, 1727, 1319, 1152, 746.



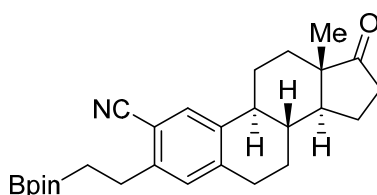
2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)dibenzo[b,d]furan-1-carbonitrile (10) was prepared as a white solid from 2-vinyldibenzo[b,d]furan (58.2 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_2pin_2 (114.3 mg, 0.45 mmol), LiO-*t*-Bu (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (eluent: 20:1 hexane/EtOAc, 73.9 mg, 71% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.43 (d, $J = 7.8$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.59 (d, $J = 8.1$ Hz, 1H), 7.55 (t, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 8.4$ Hz, 2H), 3.12 (t, $J = 8.0$ Hz, 2H), 1.31 – 1.25 (t, $J = 8.4$ Hz, 2H), 1.23 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.8, 154.0, 143.8, 128.7, 127.4, 125.8, 123.4, 122.1, 121.9, 116.7, 115.9, 111.8, 103.7, 83.3, 28.4, 24.8.

HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{22}\text{BNO}_3\text{K}$ $[\text{M}+\text{K}]^+$: 386.1324, found: 386.1329.

IR (neat, cm^{-1}): 2977, 2206, 1370, 1320, 1141, 848, 748.



Compound **11** was prepared as a white solid from 3-vinylestrone (84.0 mg, 0.3 mmol), NCTS (163.2 mg, 0.6 mmol), IMesCuCl (12.1 mg, 0.03 mmol), B_2pin_2 (114.3 mg, 0.45 mmol), $\text{LiO-}t\text{-Bu}$ (48.0 mg, 0.6 mmol) and 4 Å molecular sieves (50.0 mg) following the above general procedure A (elutnet: 15:1 hexane/EtOAc), 79.2 mg, 61% yield).

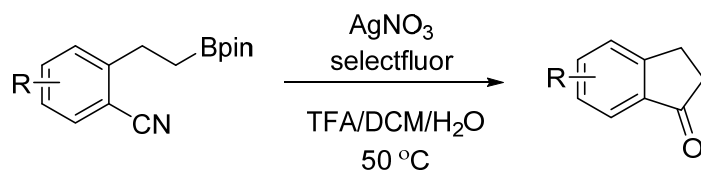
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.48 (s, 1H), 7.07 (s, 1H), 2.97 – 2.82 (m, 4H), 2.51 (dd, $J = 19.1, 8.7$ Hz, 1H), 2.37 (m, 1H), 2.25 (m, 1H), 2.15 (m, 1H), 2.08 – 1.95 (m, 3H), 1.66 – 1.43 (m, 6H), 1.23 (s, 12H), 1.16 (t, $J = 9.0$ Hz, 2H), 0.91 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 220.3, 145.3, 142.0, 138.2, 129.8, 129.4, 118.6, 109.3, 83.3, 50.3, 47.8, 43.7, 37.8, 35.8, 31.3, 29.5, 28.0, 26.1, 25.5, 24.8, 24.8, 21.5, 13.8.

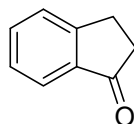
HRMS (ESI) calculated for $\text{C}_{27}\text{H}_{40}\text{BN}_2\text{O}_3$ $[\text{M}+\text{NH}_4]^+$: 451.3127, found: 451.3127.

IR (neat, cm^{-1}): 2930, 2221, 1739, 1372, 1145, 848.

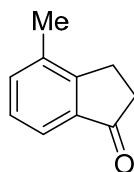
IV. Silver-mediated cyclization



General Procedure C: To a thick-walled tube was added AgNO₃ (17.0 mg, 0.1 mmol), cyanoborylated product (0.1 mmol), and Selectfluor (106.0 mg, 0.3 mmol). The tube was sealed with a cap, evacuated and filled with nitrogen. Dichloromethane (0.2 mL), water (0.5 mL), and TFA (0.3 mL) were added successively at rt. The resulting mixture was then stirred at 50 °C overnight, then cooled to rt and filtered through a silica gel pad. The mixture was washed with aqueous saturated NaHCO₃ solution and brine, dried with Na₂SO₄, filtered, and concentrated, and the residue was chromatographed on silica gel to afford cyclopentannulated product.



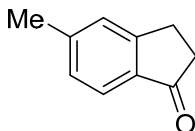
2,3-Dihydro-1H-inden-1-one (14) was prepared as a white solid from **2** (table 1, entry 1, 25.7 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 10:1 hexane/Et₂O, 9.8 mg, 74% yield). The characterization data is in accordance with the literature.¹⁰



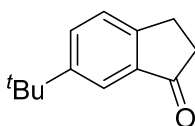
4-Methyl-2,3-dihydro-1H-inden-1-one (15) was prepared as a white solid from 3-methyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (table 1, entry 14, 27.1 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol)

¹⁰ A. L. García-Cabeza, R. Marín-Barrios, F. J. Moreno-Dorado, M. J. Ortega, G. M. Massanet, F. M. Guerra, *Org. Lett.* **2014**, *16*, 1598–1601.

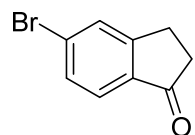
following the above general procedure C (eluent: 10:1 hexane/Et₂O, 9.8 mg, 67% yield). The characterization data is in accordance with the literature.¹¹



5-Methyl-2,3-dihydro-1H-inden-1-one (16) was prepared as a white solid from 4-methyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (table 1, entry 10, 27.1 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 10:1 hexane/Et₂O, 9.5 mg, 65% yield). The characterization data is in accordance with the literature.¹²



6-(tert-Butyl)-2,3-dihydro-1H-inden-1-one (17) was prepared as a white solid from 5-(tert-butyl)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (table 1, entry 5, 31.3 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 10:1 hexane/Et₂O, 13.2 mg, 70% yield). The characterization data is in accordance with the literature.¹³



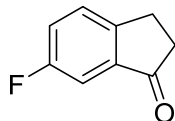
5-Bromo-2,3-dihydro-1H-inden-1-one (18) was prepared as a white solid from 4-bromo-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (table 1, entry 12, 33.6 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol)

¹¹ F. Romanov-Michailidis, L. Guénée, A. Alexakis, *Org. Lett.* **2013**, *15*, 5890-5893.

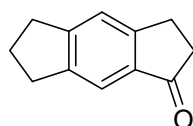
¹² N. R. Vautravers, D. D. Regent, B. Breit, *Chem. Commun.* **2011**, *47*, 6635-6637.

¹³ J. J. Matasi, J. P. Caldwell, J. Hao, B. Neustadt, L. Arik, C. J. Foster, J. Lachowicz, D. B. Tulshian, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1333-1336.

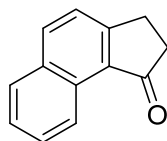
following the above general procedure C (eluent: 2:1 hexane/dichloromethane, 14.5 mg, 70% yield). The characterization data is in accordance with the literature.¹⁴



6-Fluoro-2,3-dihydro-1H-inden-1-one (19) was prepared as a pale yellow solid from 5-fluoro-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (table 1, entry 2, 27.5 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 2:1 hexane/dichloromethane, 5.6 mg, 37% yield). The characterization data is in accordance with the literature.¹²



3,5,6,7-Tetrahydro-s-indacen-1(2H)-one (20) was prepared as a white solid from 6-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2,3-dihydro-1H-indene-5-carbonitrile (table 2, 5, 27.5 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 10:1 hexane/ethyl acetate, 9.1 mg, 53% yield). The characterization data is in accordance with the literature.¹⁵

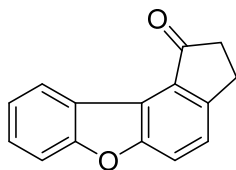


2,3-Dihydro-1H-cyclopenta[a]naphthalen-1-one (21) was prepared as a white solid from 2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-naphthonitrile (table 2, 5, 30.7 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol)

¹⁴ J.-I. Nishida, H. Deno, S. Ichimura, T. Nakagawa, Y. Yamashita, *J. Mater. Chem.* **2012**, *22*, 4483-4490.

¹⁵ M. E. Isabelle, R. H. Wightman, H. W. Avdovich, D. E. Laycock, *Canadian Journal of Chemistry*, **1980**, *58*, 1344-1349.

following the above general procedure C (eluent: 10:1 hexane/Et₂O, 11.3 mg, 62% yield). The characterization data is in accordance with the literature.¹⁶



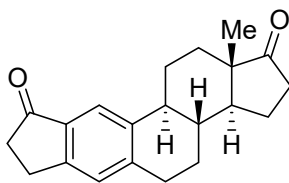
2,3-Dihydro-1H-indeno[5,4-b]benzofuran-1-one (22) was prepared as a pale yellow solid from **10** (34.7 mg, 0.1 mmol), AgNO₃ (17.0 mg, 0.1 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 2:1 hexane/dichloromethane, 13.5 mg, 61% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.92 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.54 (td, *J* = 8.3, 7.8, 1.3 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.39 (m, 1H), 3.31 (t, *J* = 5.5 Hz, 2H), 2.88 – 2.83 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 206.8, 157.1, 155.6, 151.3, 132.2, 128.5, 126.1, 124.2, 123.2, 123.1, 121.1, 117.7, 111.3, 37.01, 26.57.

HRMS (ESI) calculated for C₁₅H₁₁O₂ [M+H]⁺: 223.0754, found: 223.0753.

IR (neat, cm⁻¹): 2970, 1701, 1439, 1268, 1204, 756.



Compound **23** was prepared as a white solid from **9** (43.3 mg, 0.1 mmol), AgNO₃ (8.5 mg, 0.05 mmol) and Selectfluor (106.0 mg, 0.3 mmol) following the above general procedure C (eluent: 5:1 hexane/EtOAc, 12.9 mg, 42% yield).

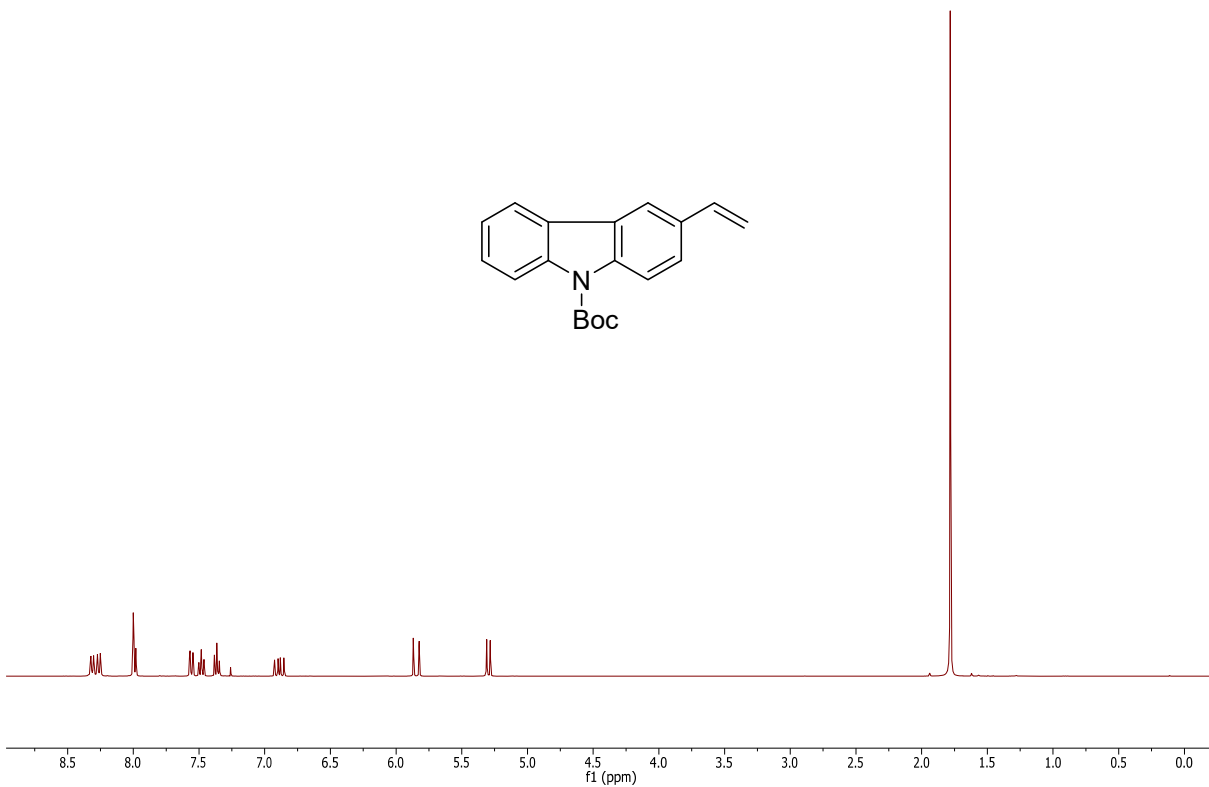
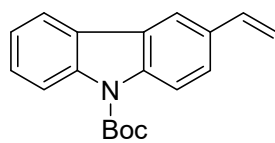
¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 1H), 7.21 (s, 1H), 3.12 – 2.95 (m, 4H), 2.72 – 2.63 (m, 2H), 2.56 – 2.46 (m, 2H), 2.39 – 2.27 (m, 1H), 2.20 – 1.97 (m, 4H), 1.65 – 1.47 (m, 6H), 0.91 (s, 3H).

¹⁶ A. S. Lubbe, N. Ruangsupapichat, G. Caroli, B. L. Feringa, *J. Org. Chem.* **2011**, *76*, 8599–8610.

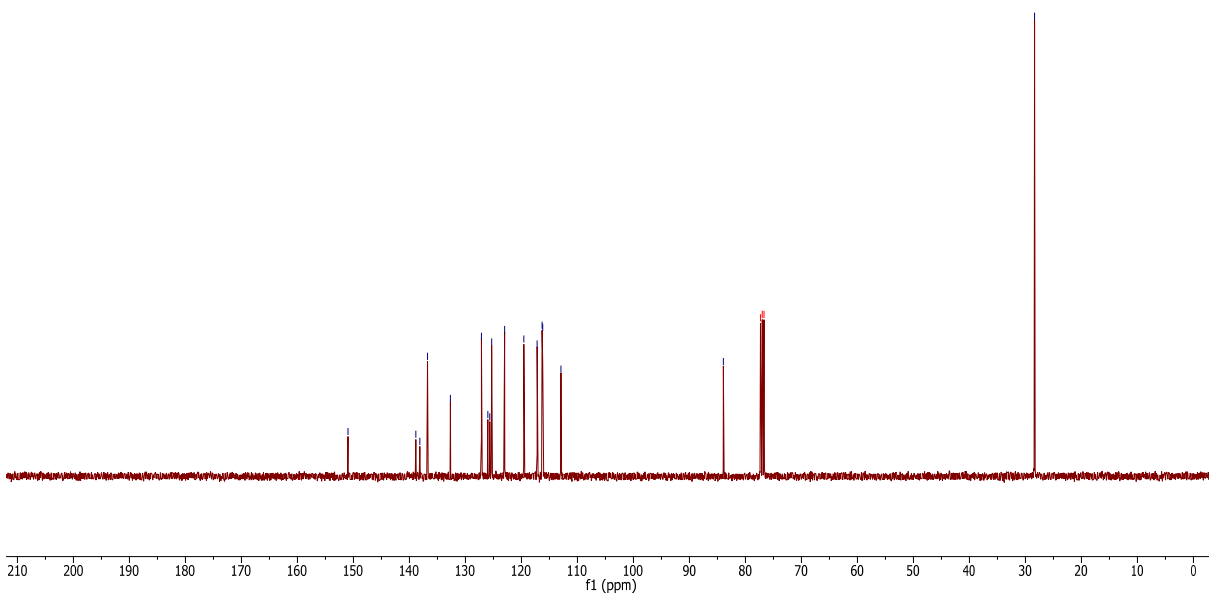
¹³C NMR (100 MHz, CDCl₃) δ 220.5, 206.9, 152.7, 144.8, 139.8, 135.1, 126.8, 120.3, 50.5, 47.9, 44.2, 37.9, 36.5, 35.8, 31.4, 30.1, 26.2, 25.7, 25.2, 21.6, 13.8.

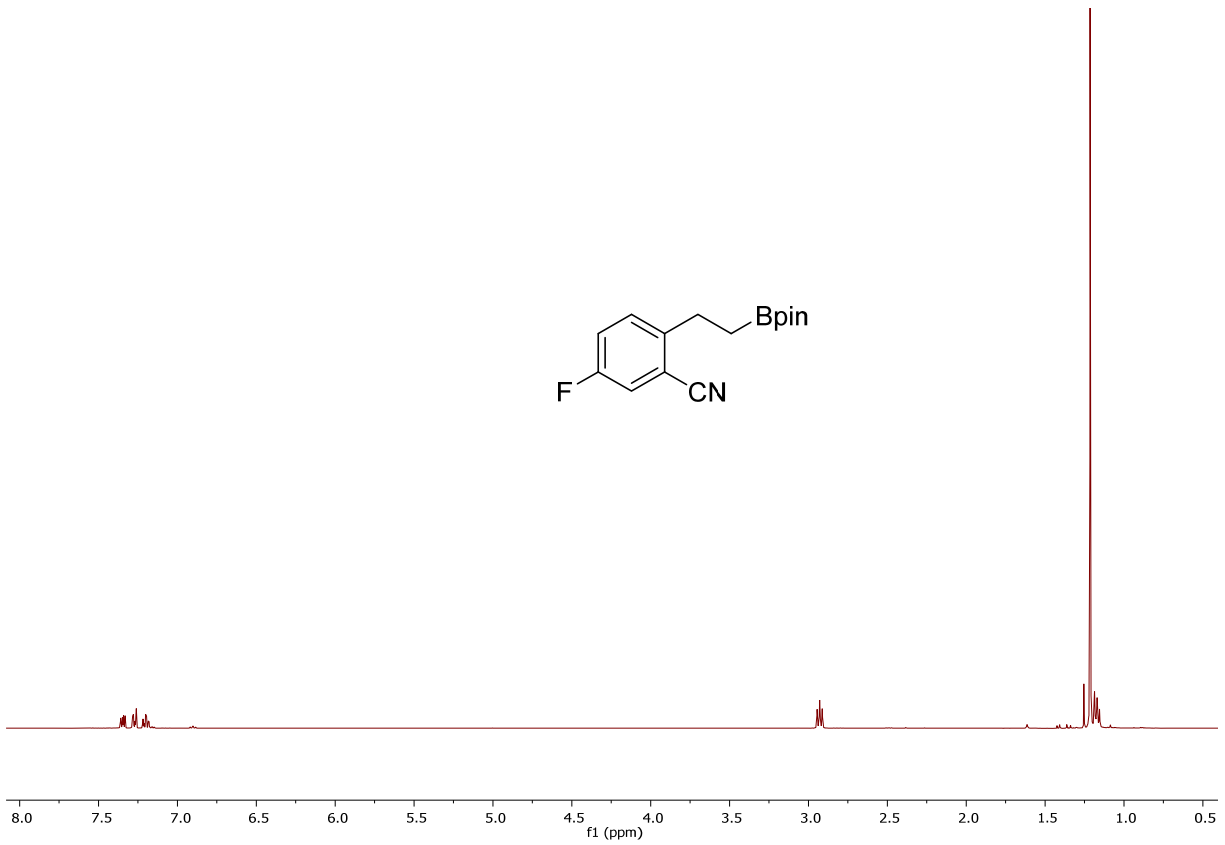
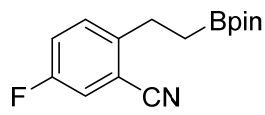
HRMS (ESI) calculated for C₂₁H₂₅O₂ [M+H]⁺: 309.1849, found: 309.1852.

IR (neat, cm⁻¹): 2925, 1737, 1702, 1250, 735.

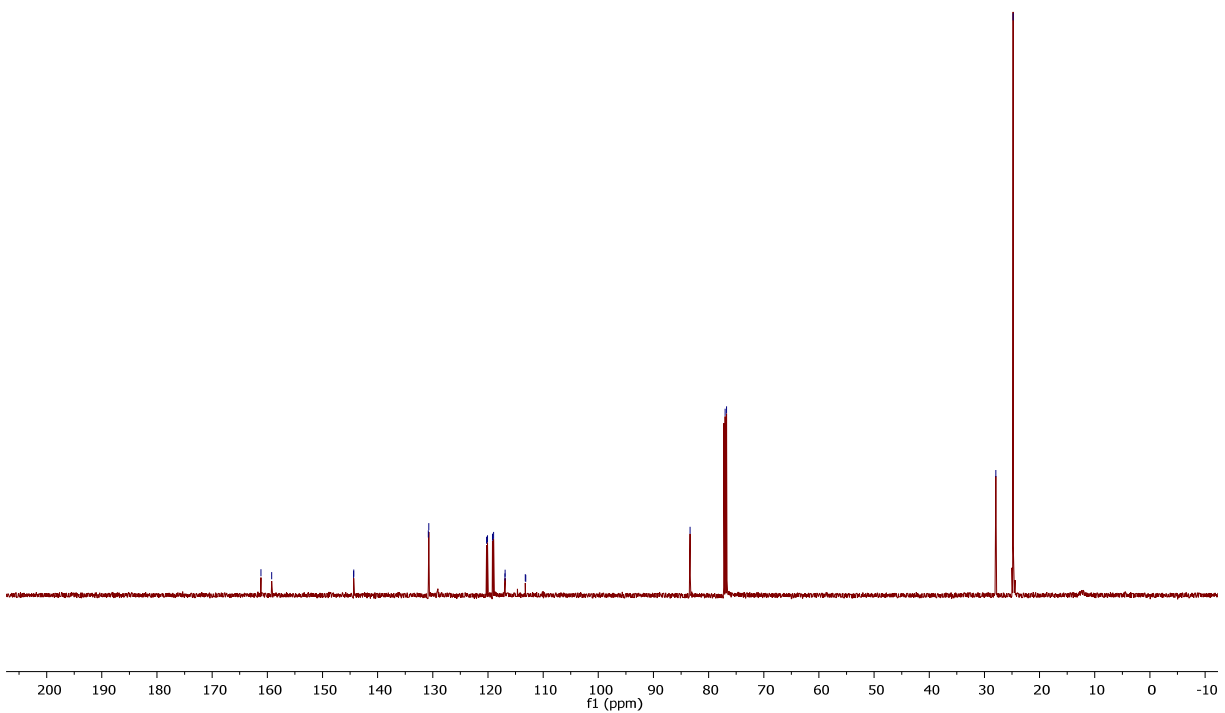


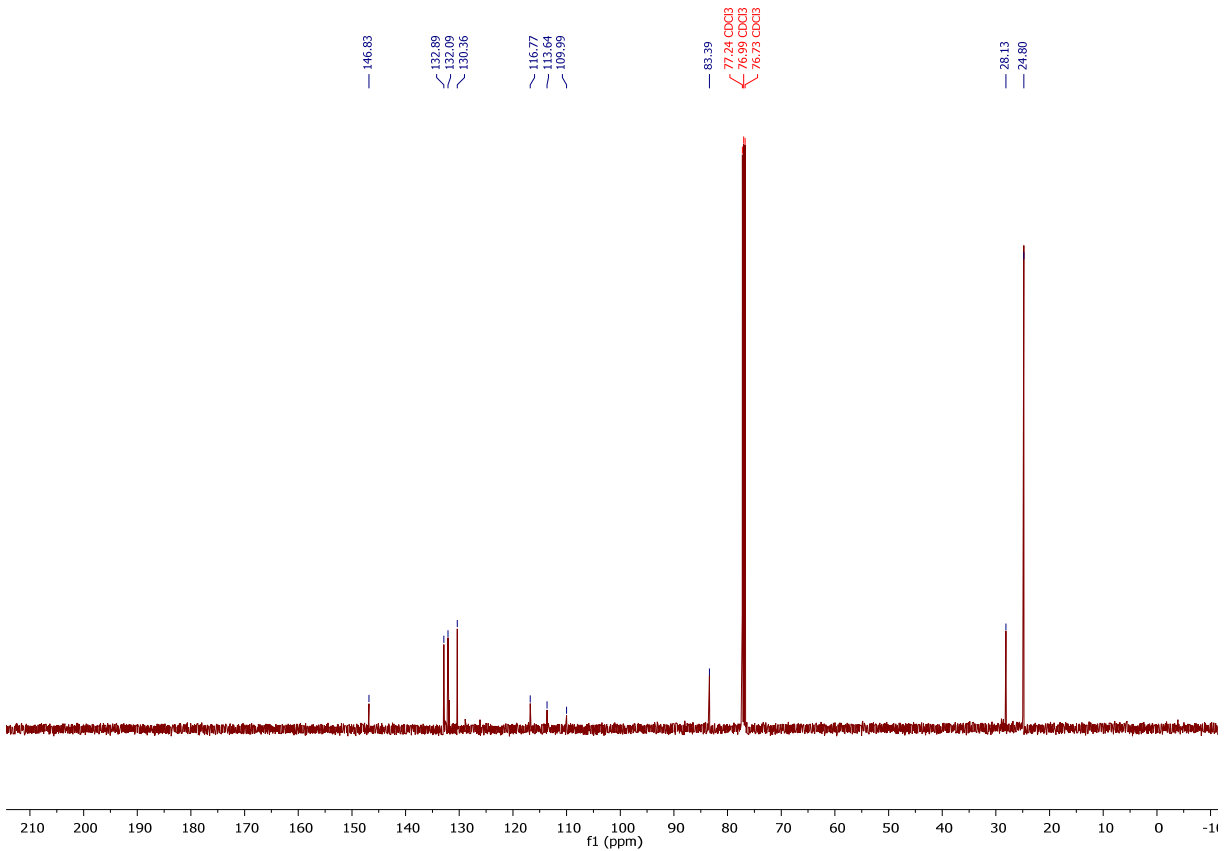
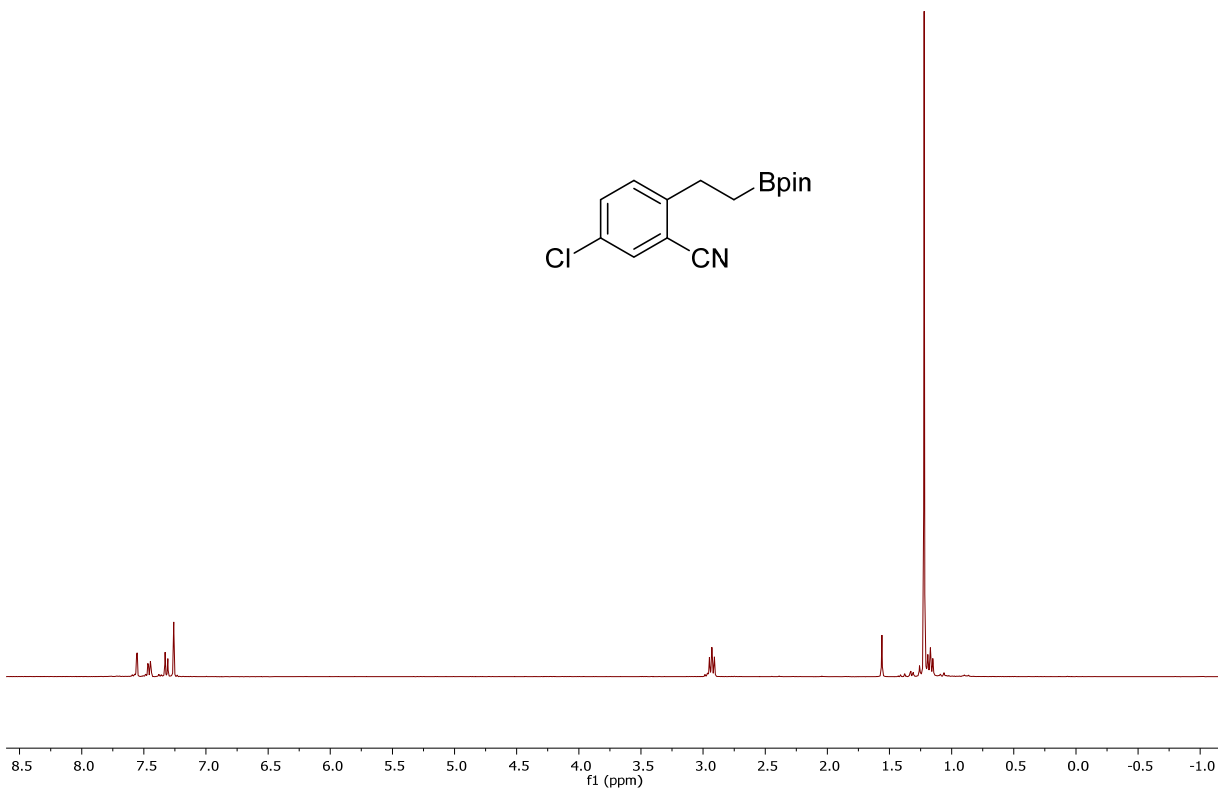
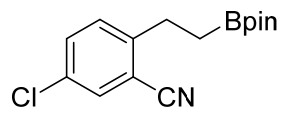
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136.74
132.77
132.68
127.13
125.98
125.65
125.29
123.00
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117.18
116.29
112.94
83.94
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
28.37

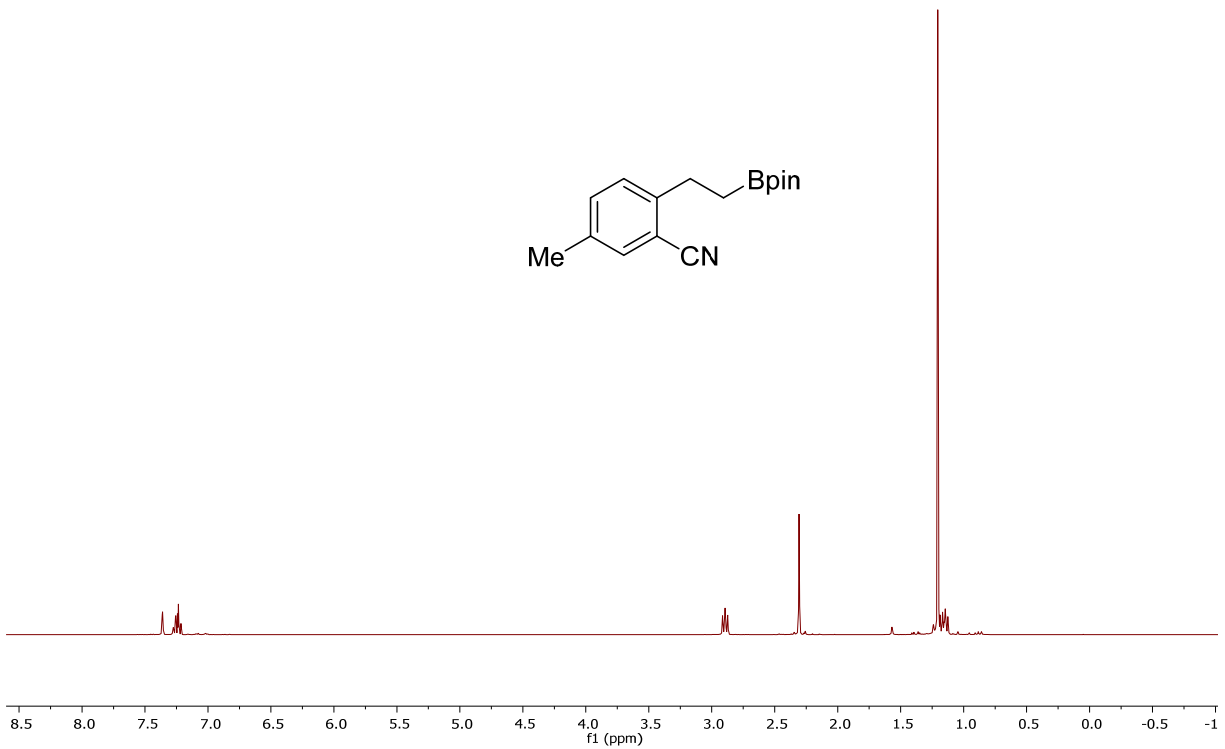
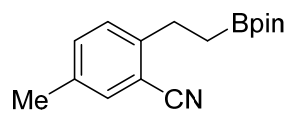




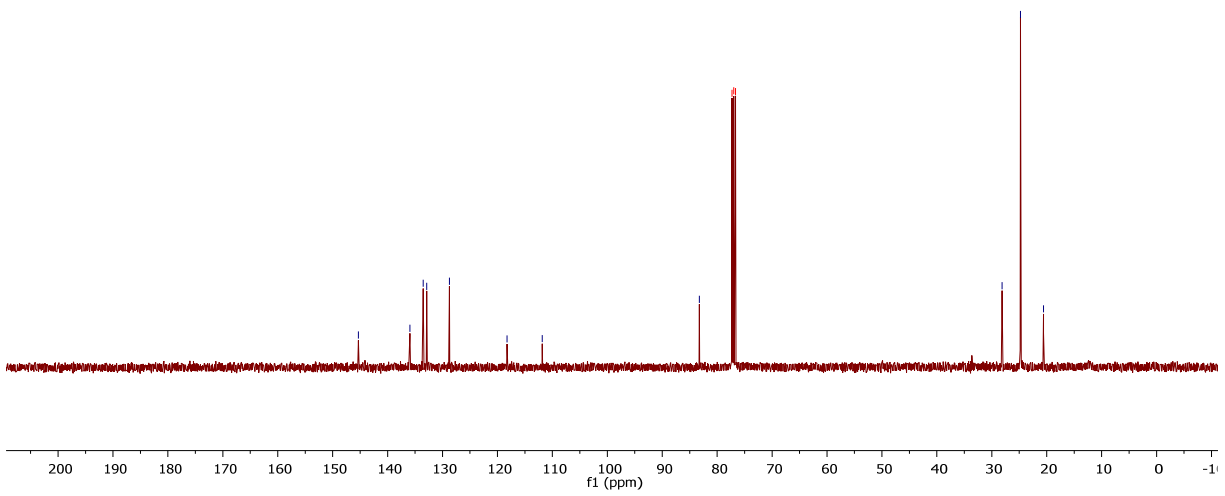
161.17
159.20
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144.32
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130.74
120.26
120.07
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118.98
116.92
116.90
113.22
113.15
83.35
77.00
76.75
27.93
24.79

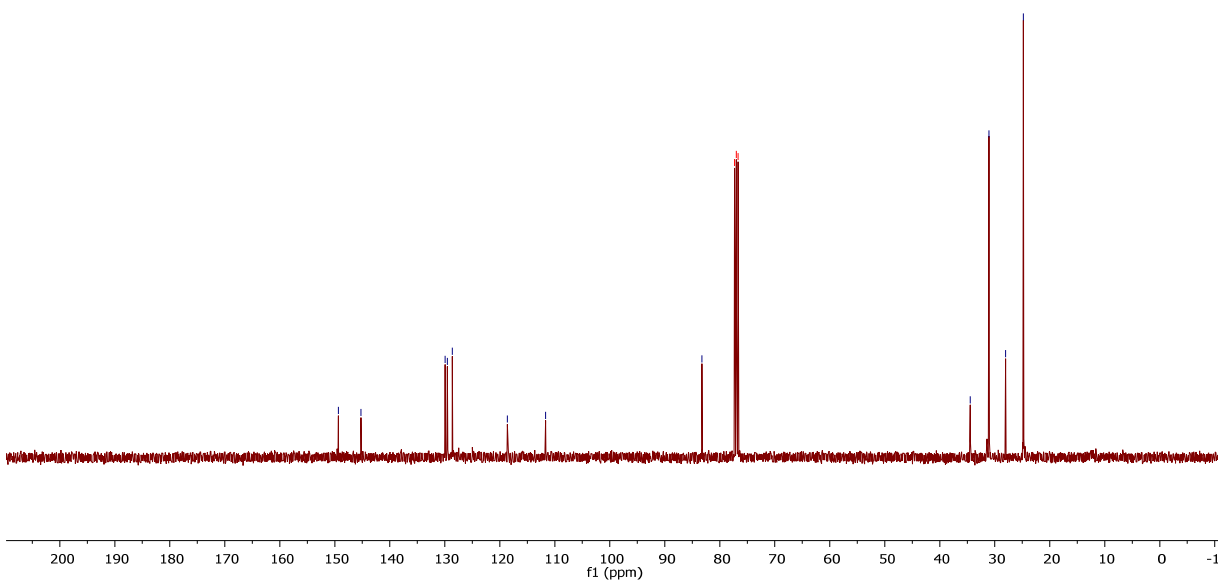
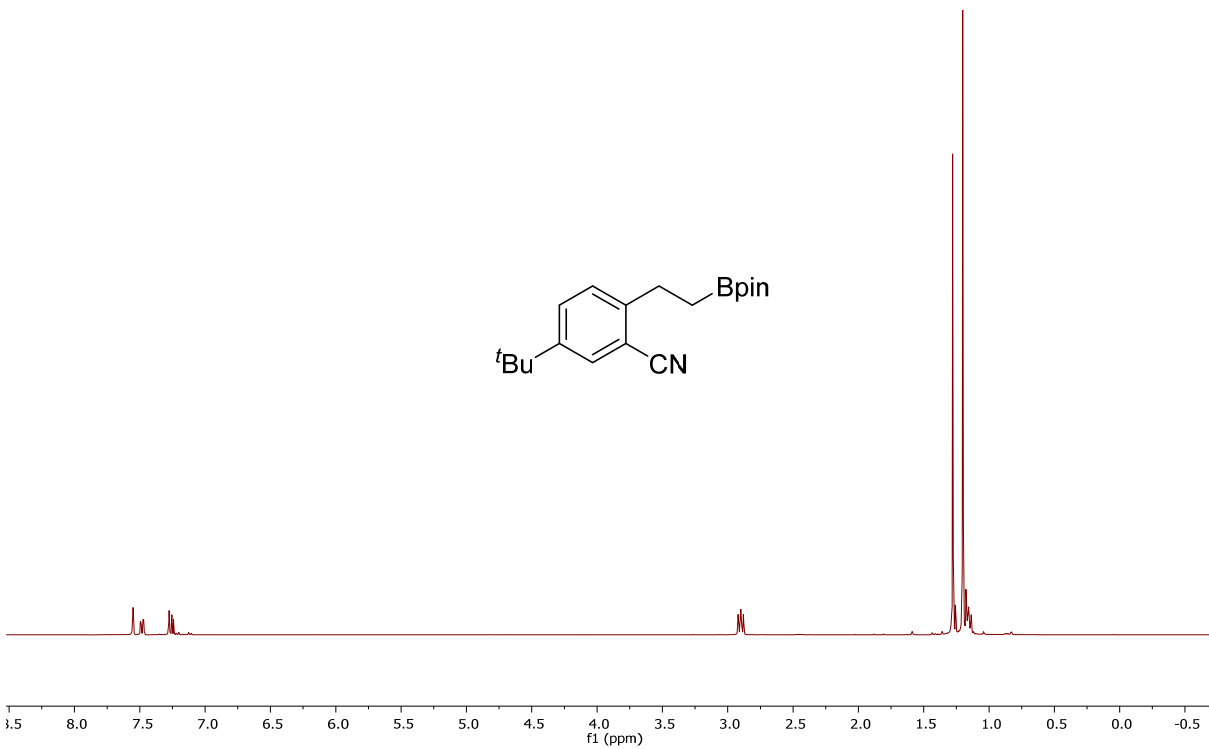
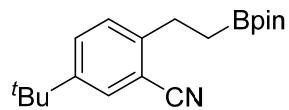


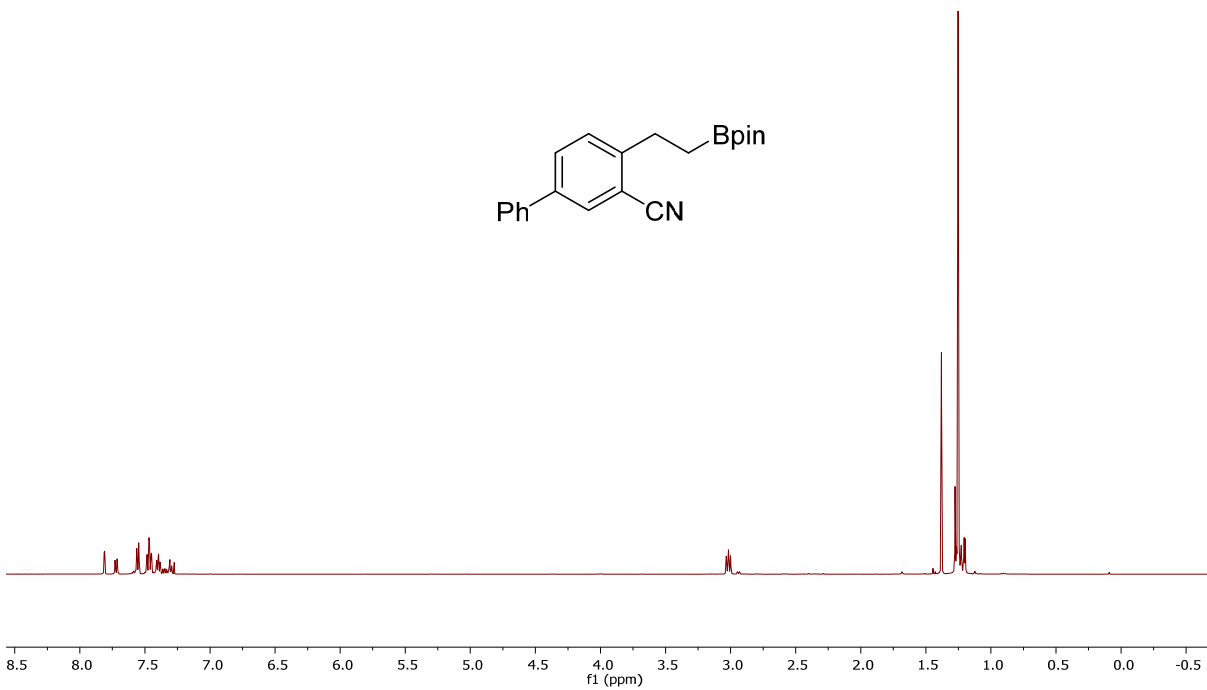
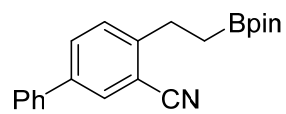




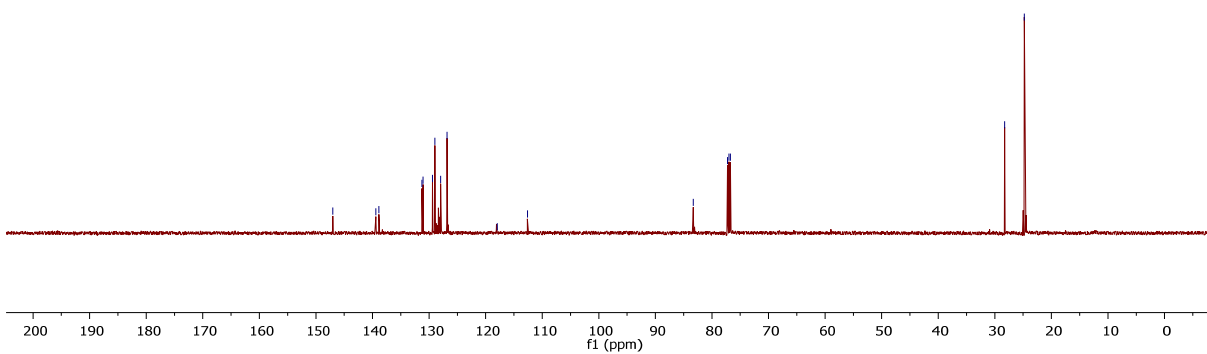
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118.25
111.85
83.24
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76.98 cdCl_3
76.66 cdCl_3
28.12
24.79
20.58

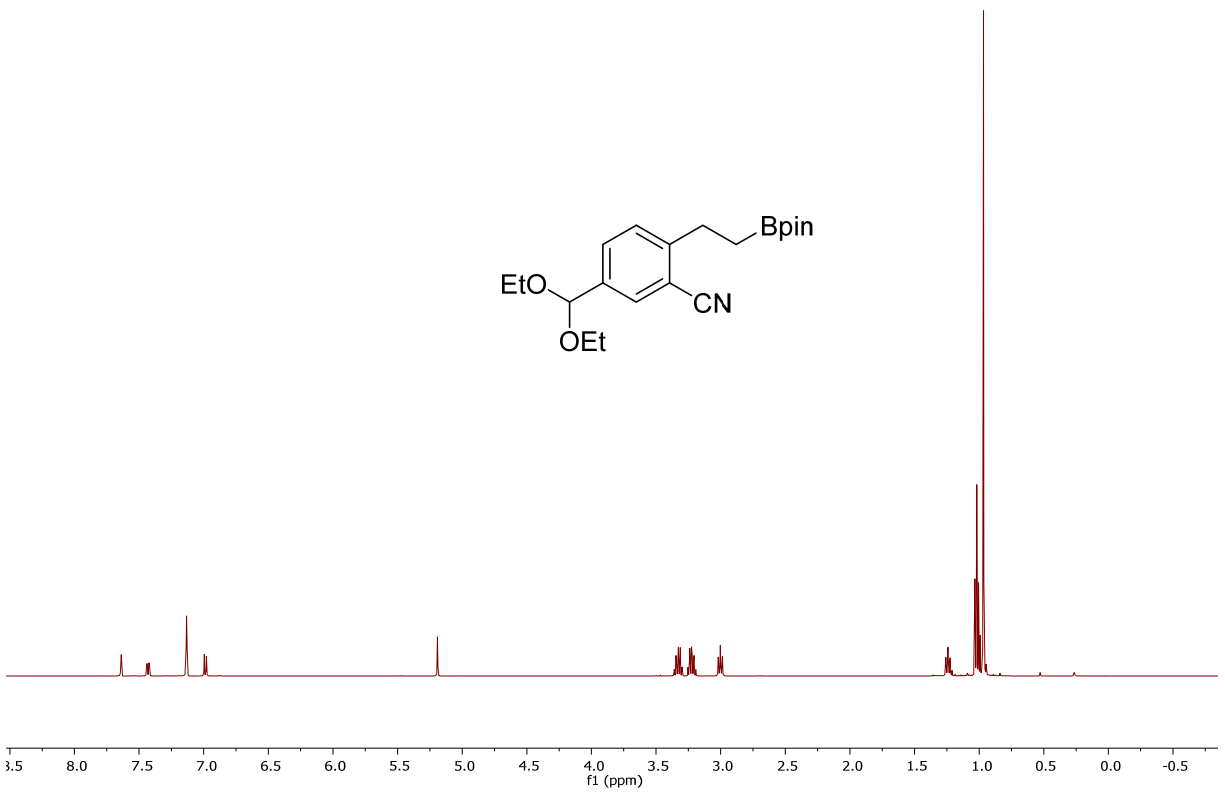
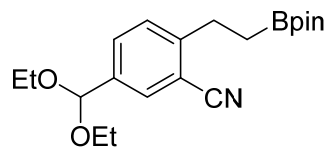


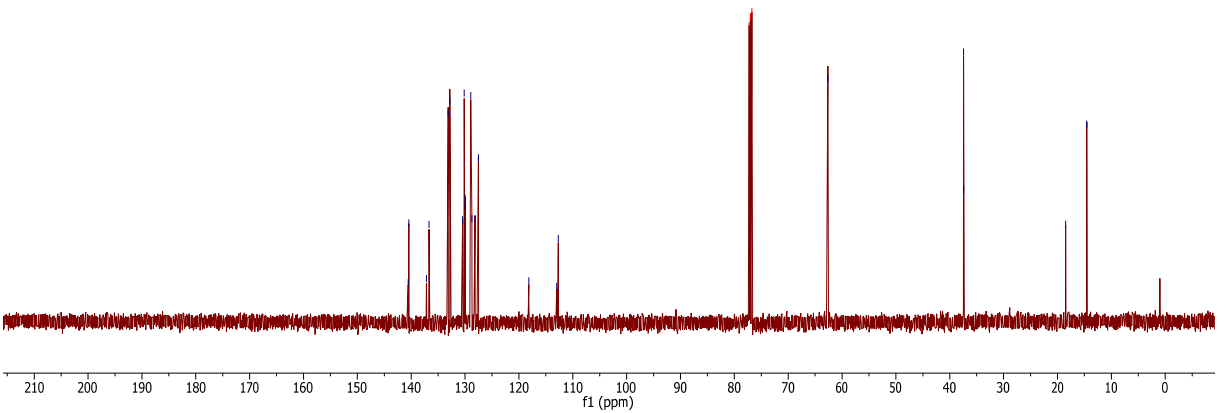
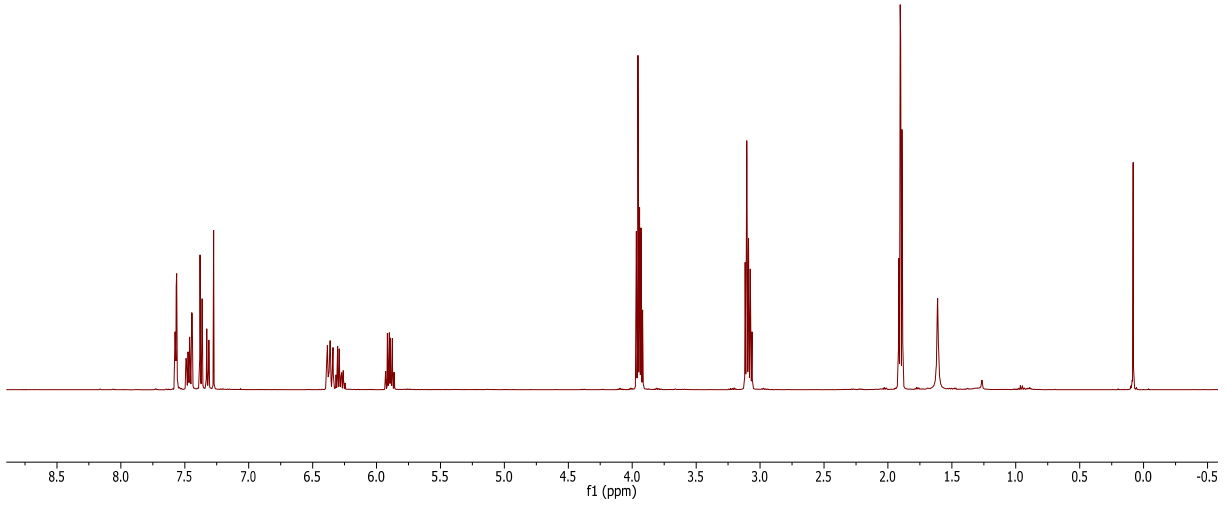
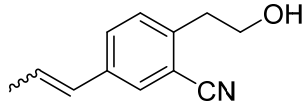


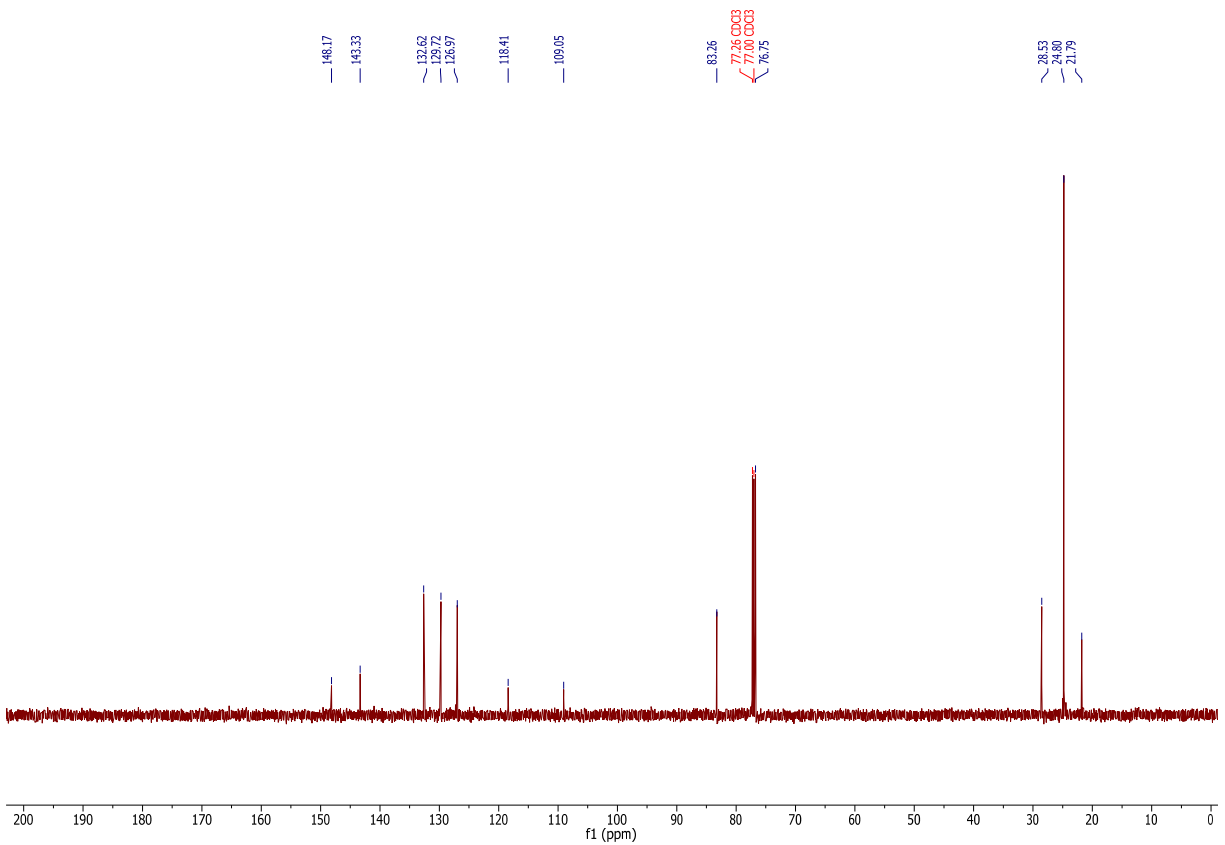
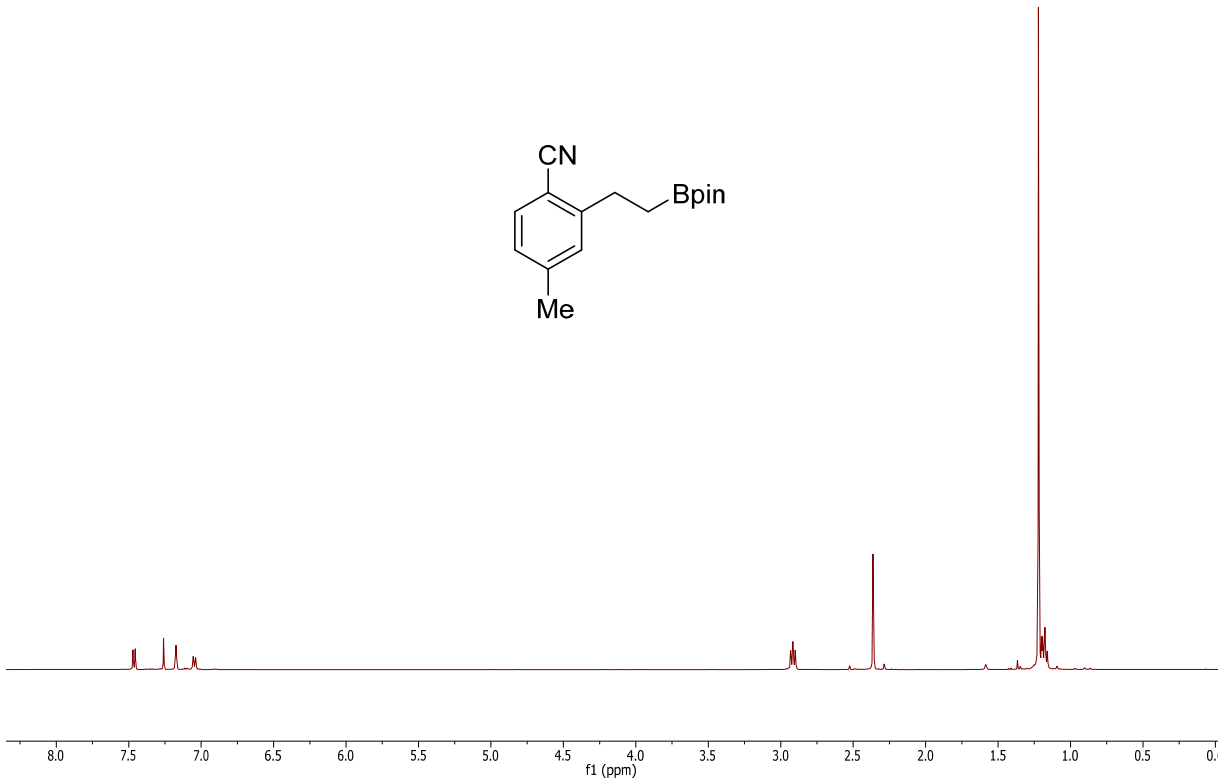
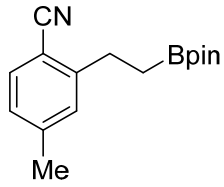


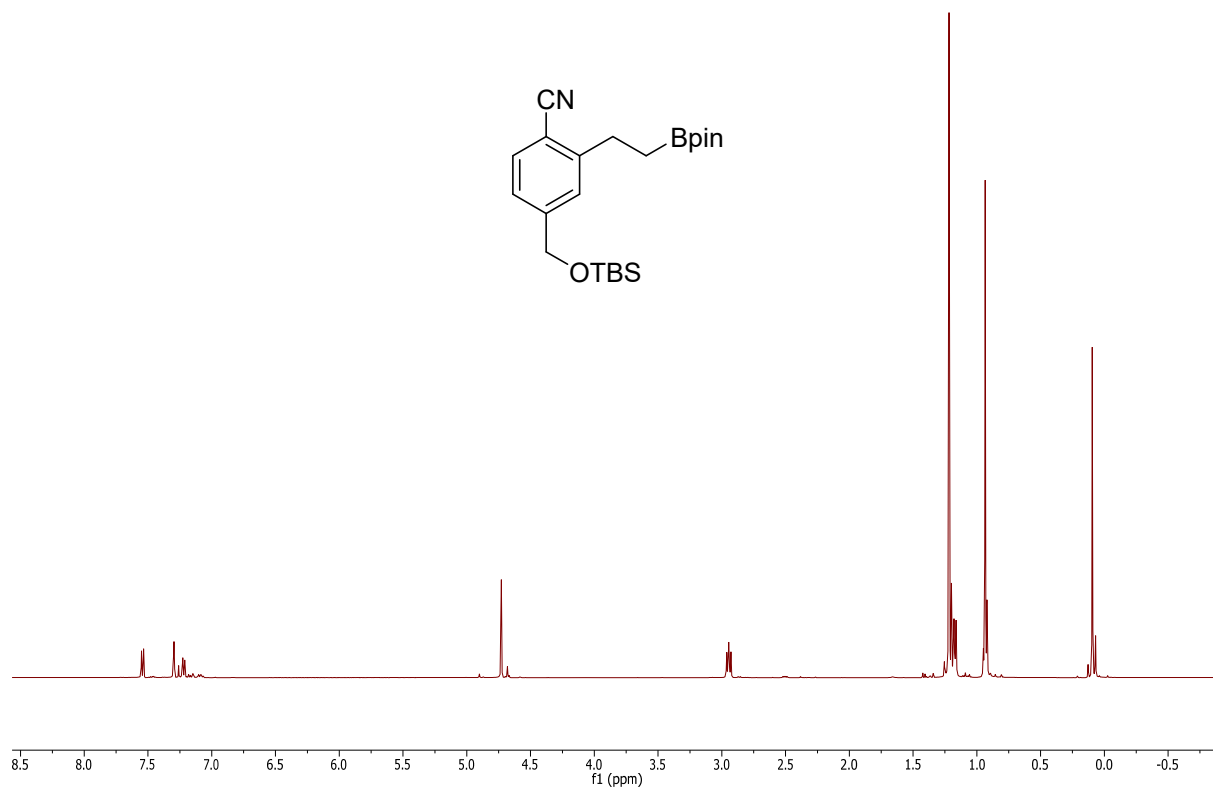
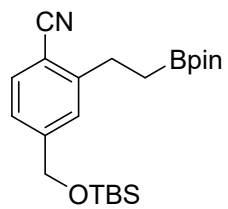
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112.61
83.31
77.25
77.00
76.75
28.26
24.80



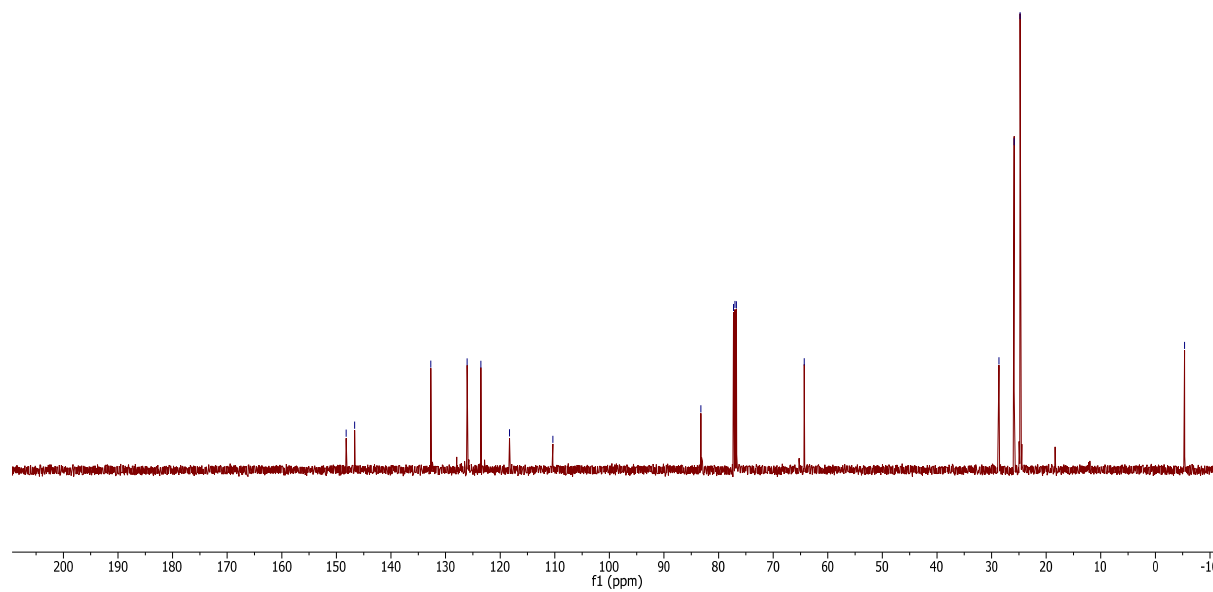


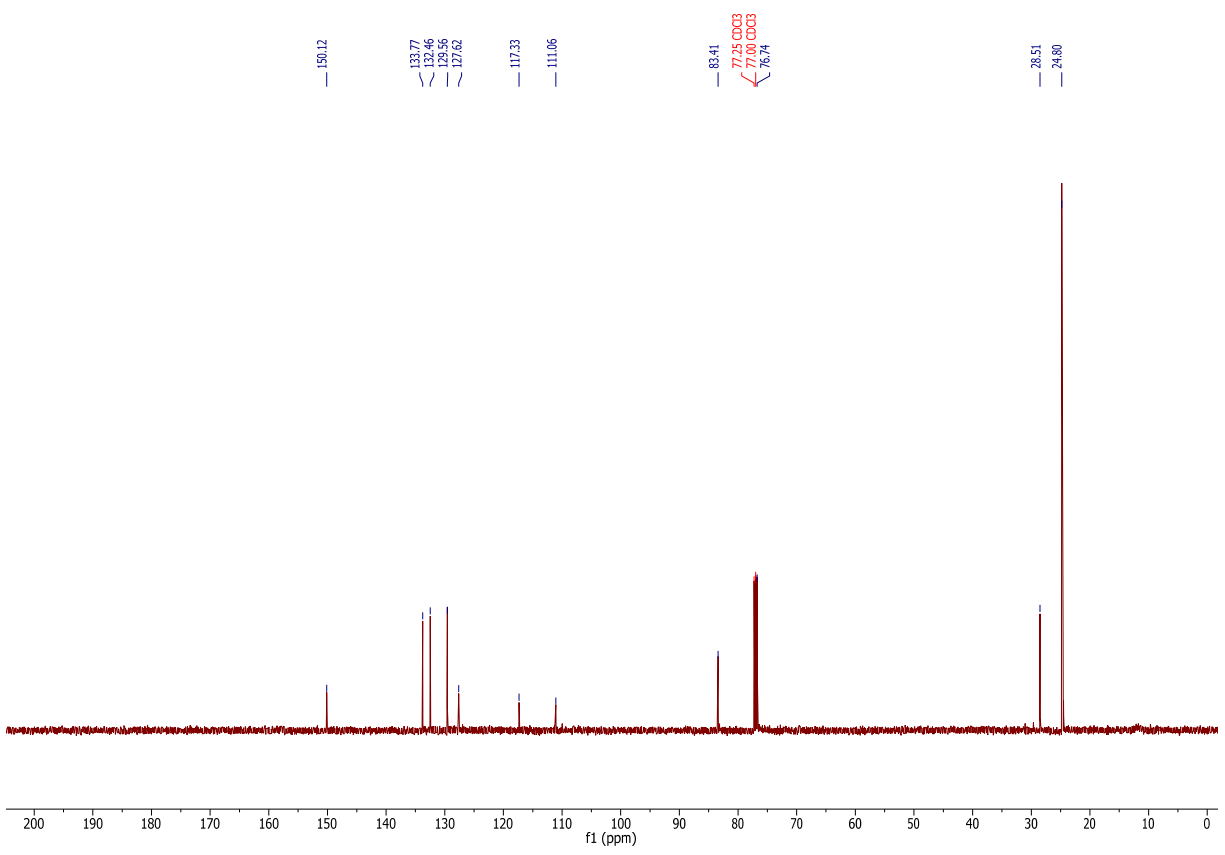
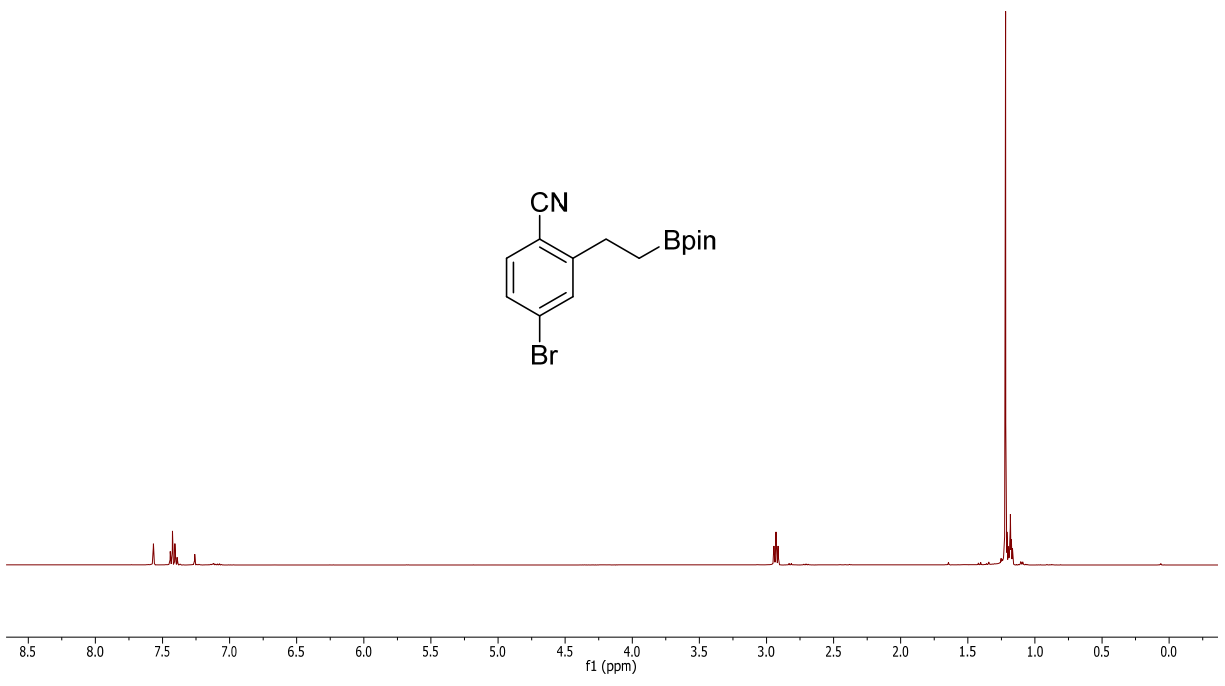


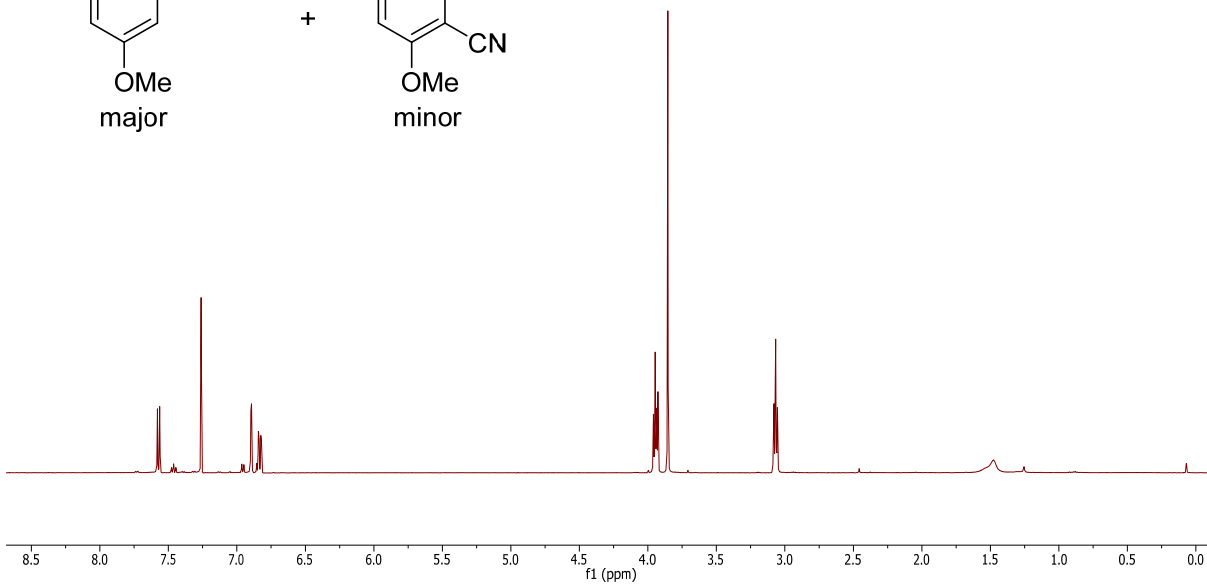
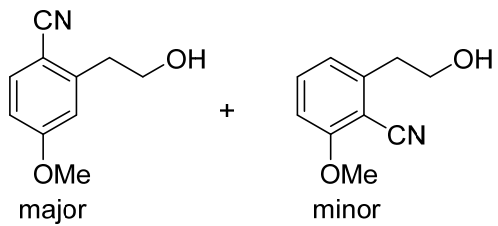




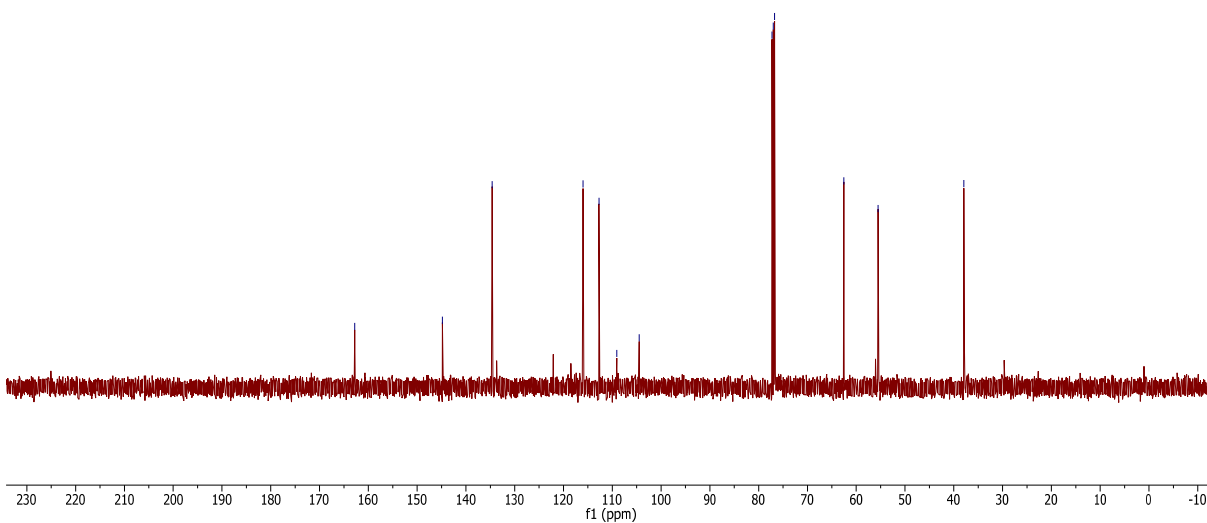
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76.75
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-5.34

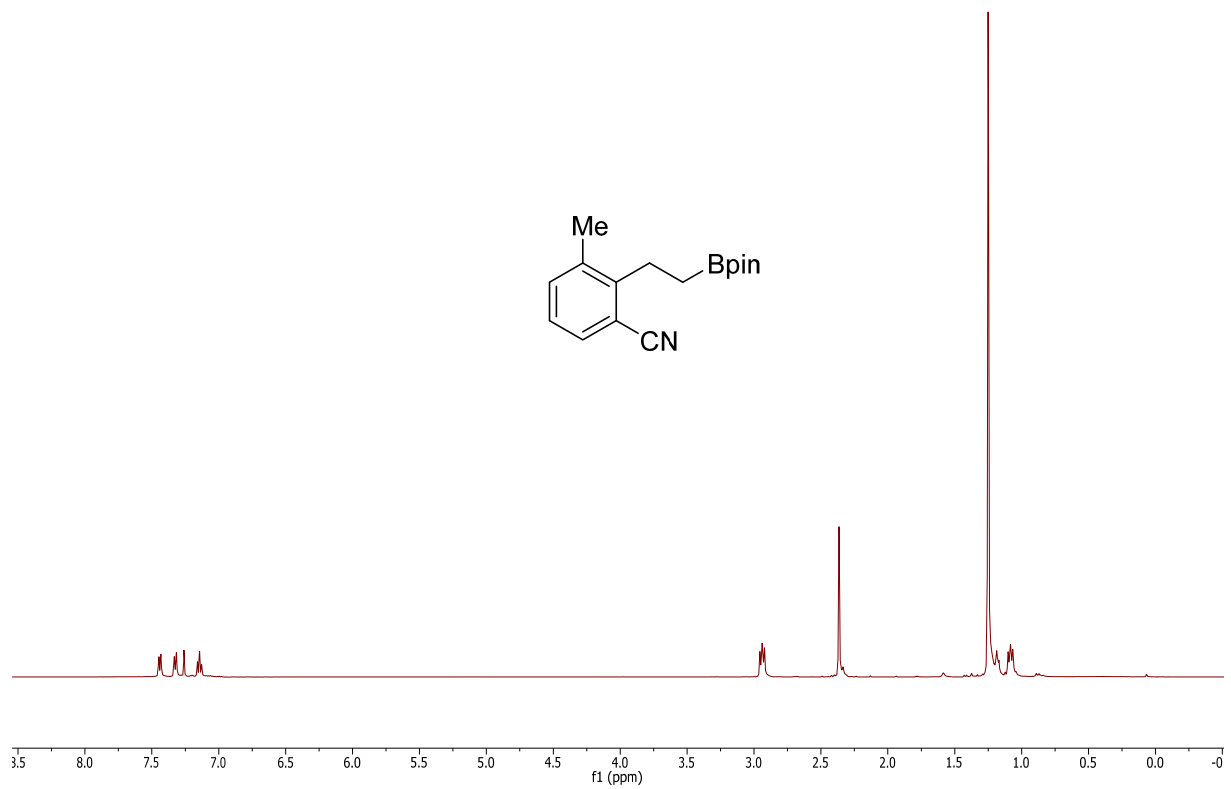
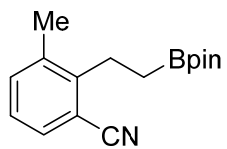






162.79 144.83 134.61 115.99 112.73 109.08 104.49 77.25 77.00 76.75 62.54 55.52 37.94





146.84

137.04

136.72

130.73

126.07

118.60

112.41

83.30

77.25 CDCl₃

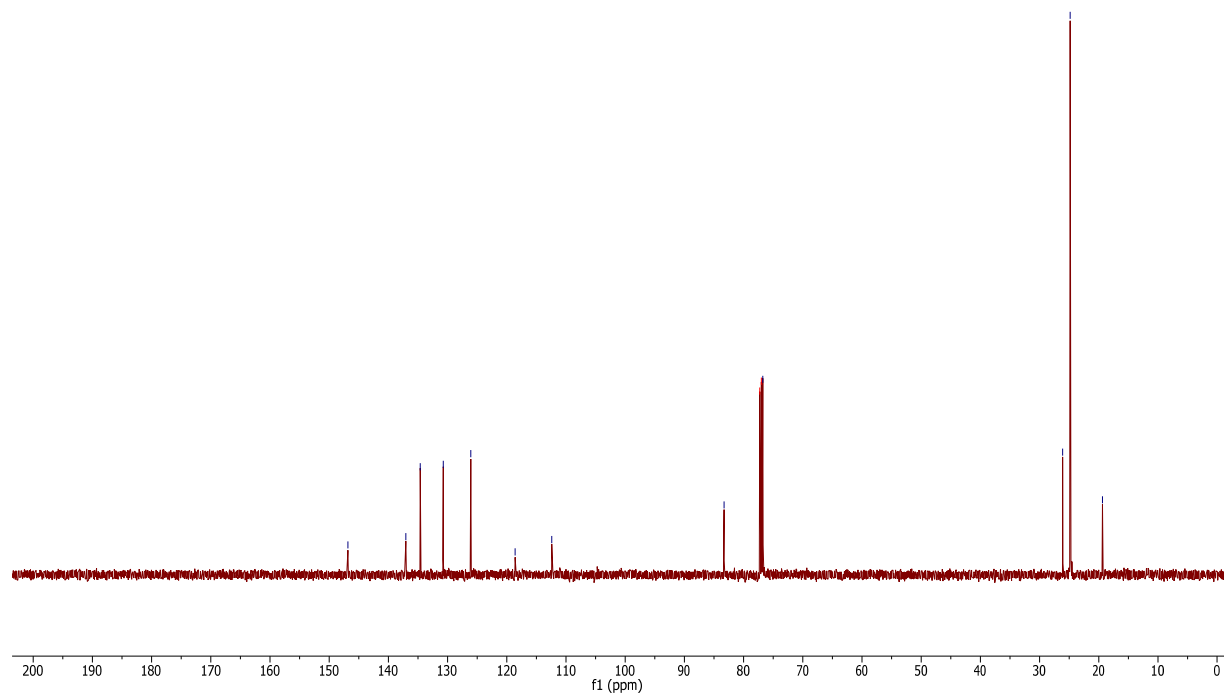
77.00 CDCl₃

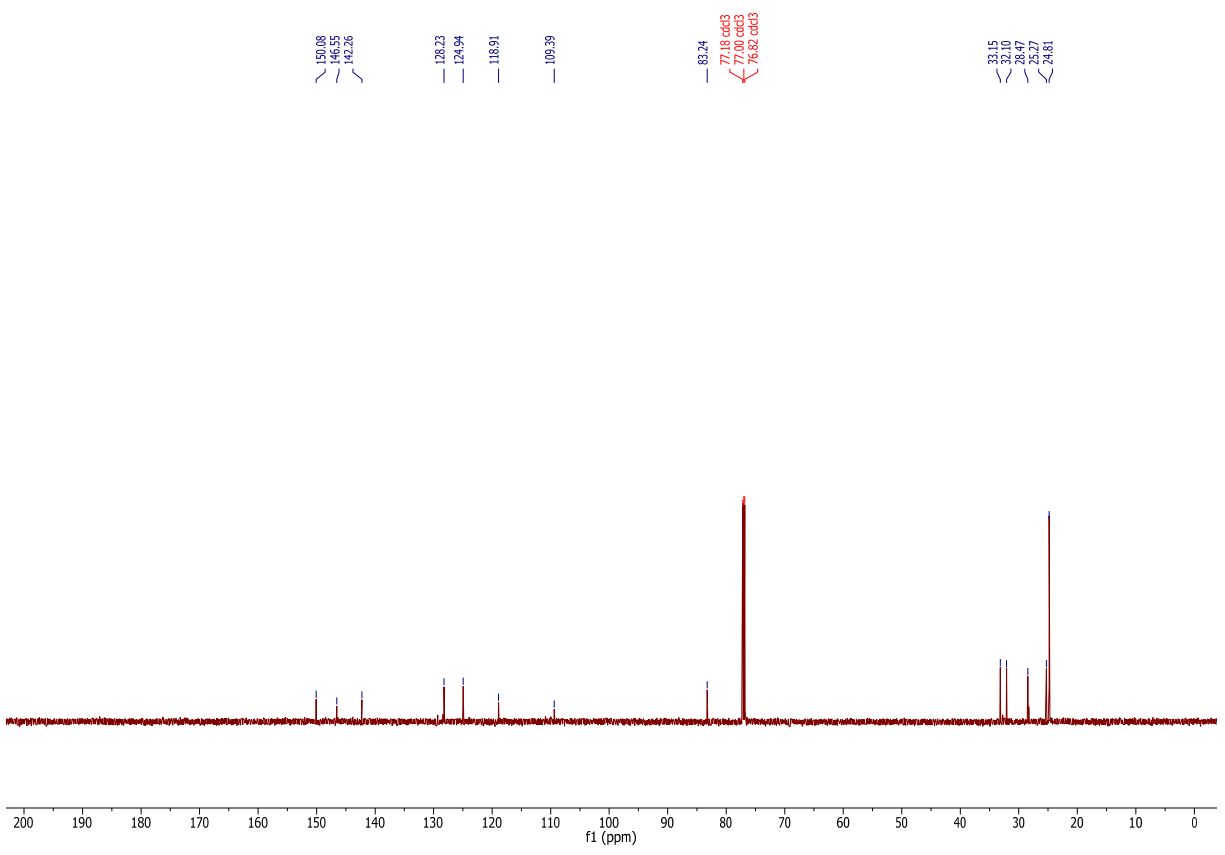
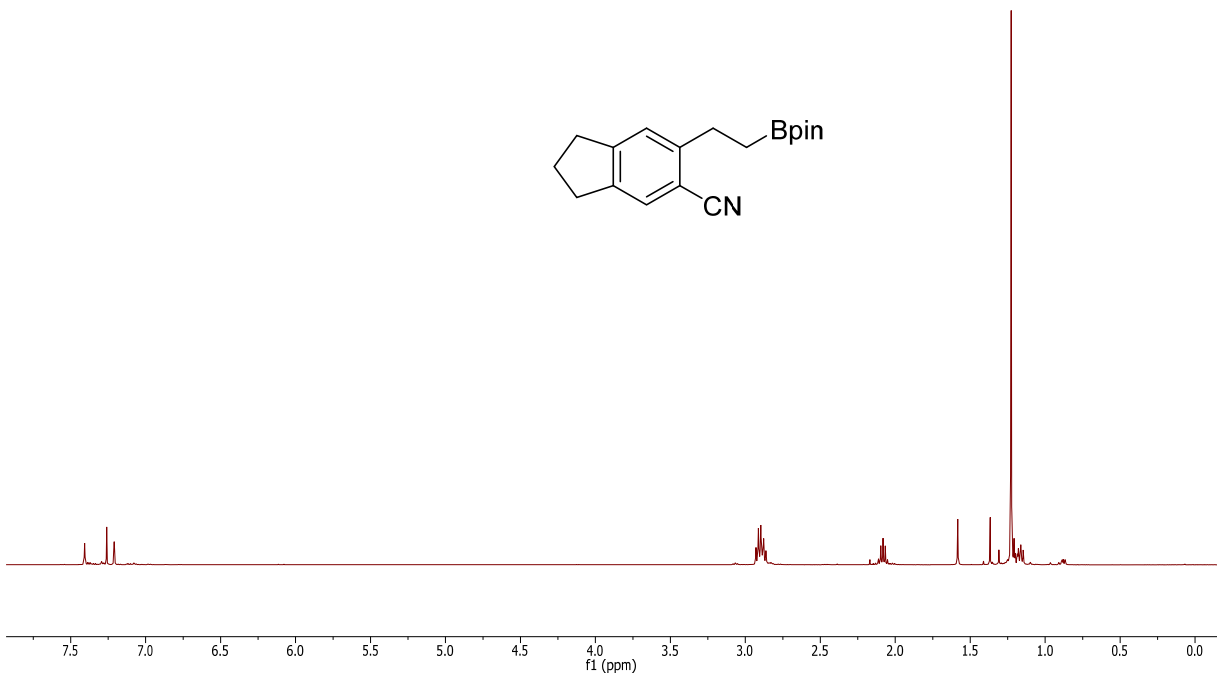
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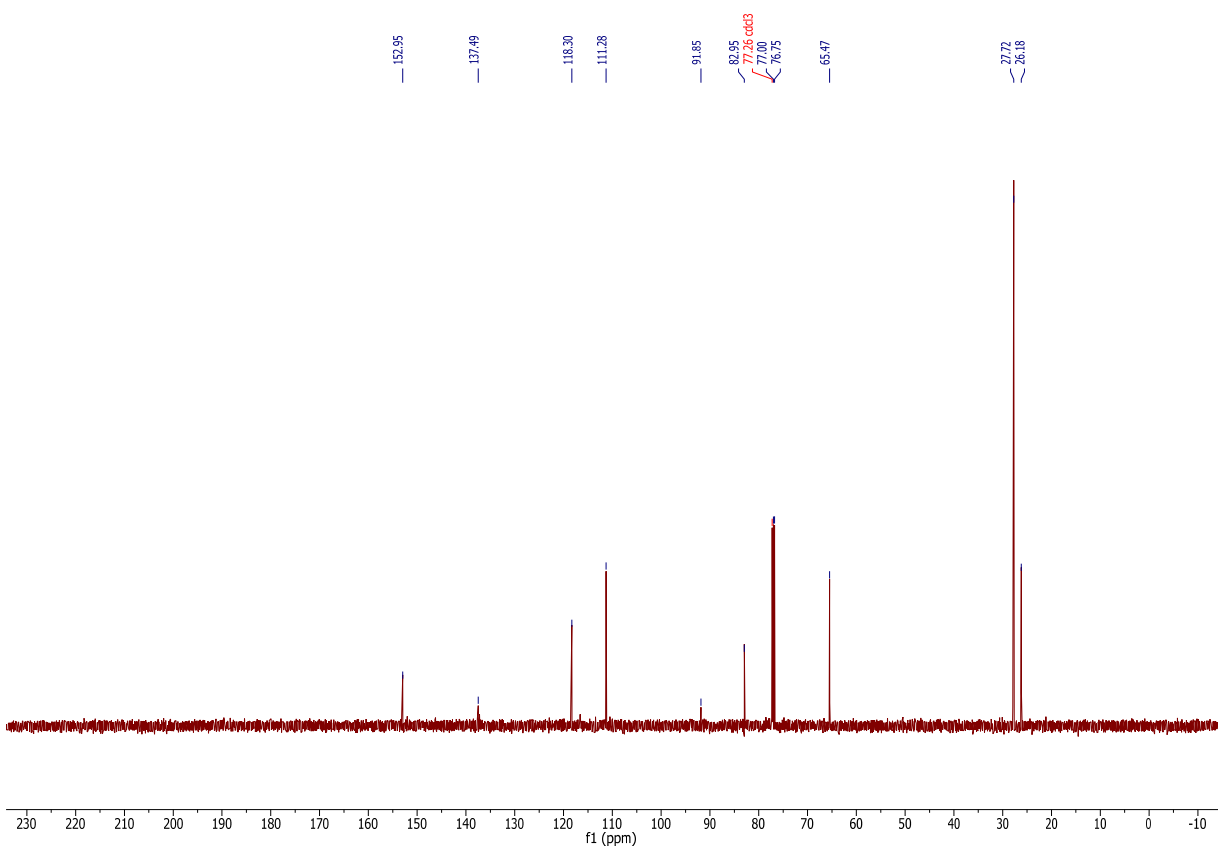
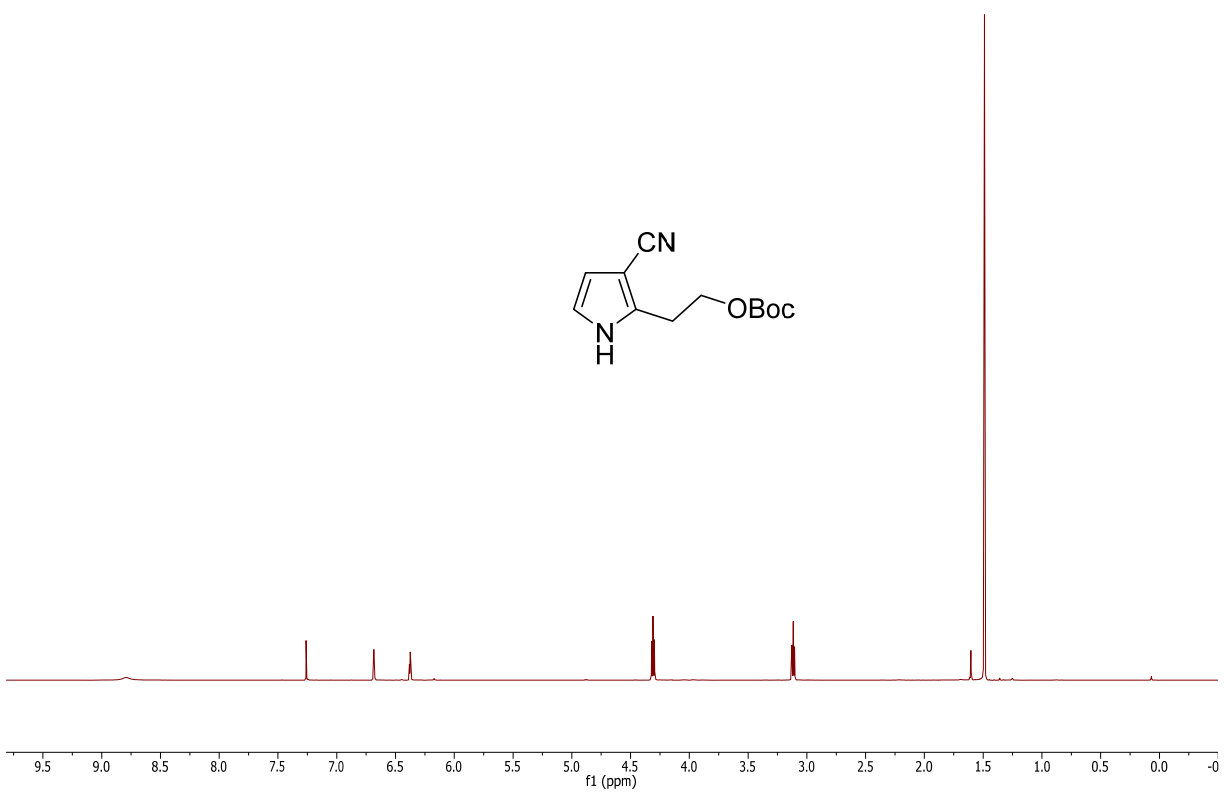
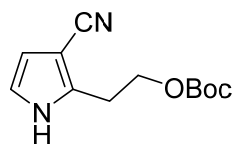
26.09

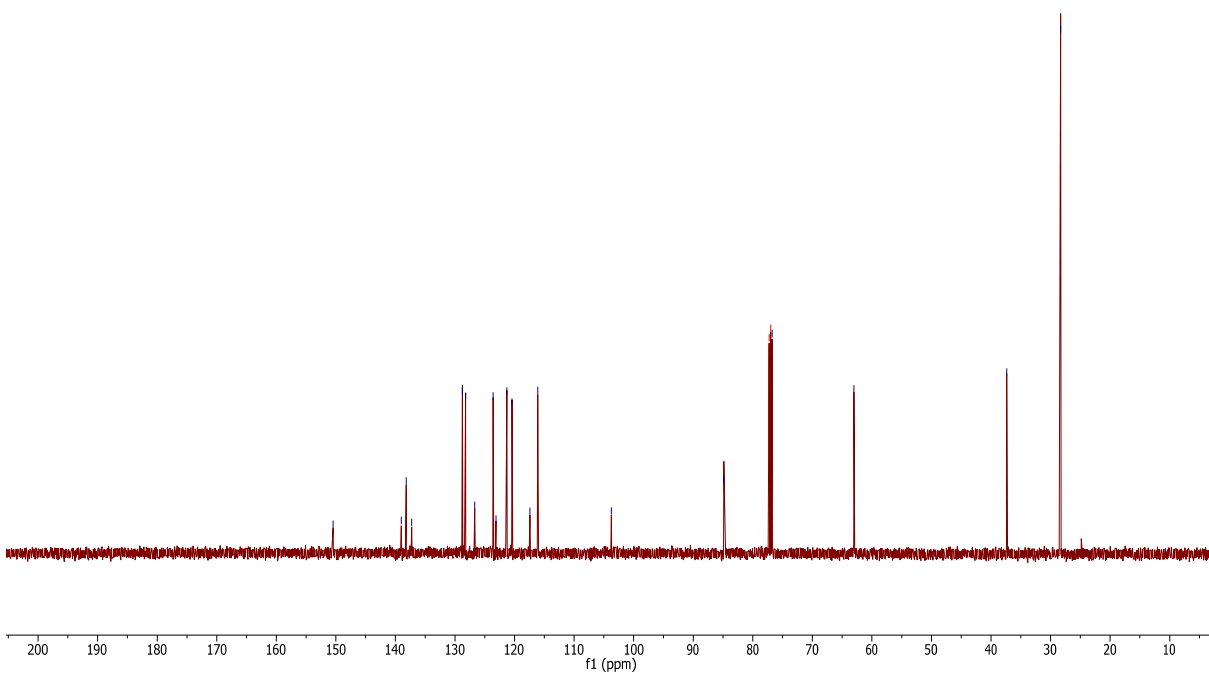
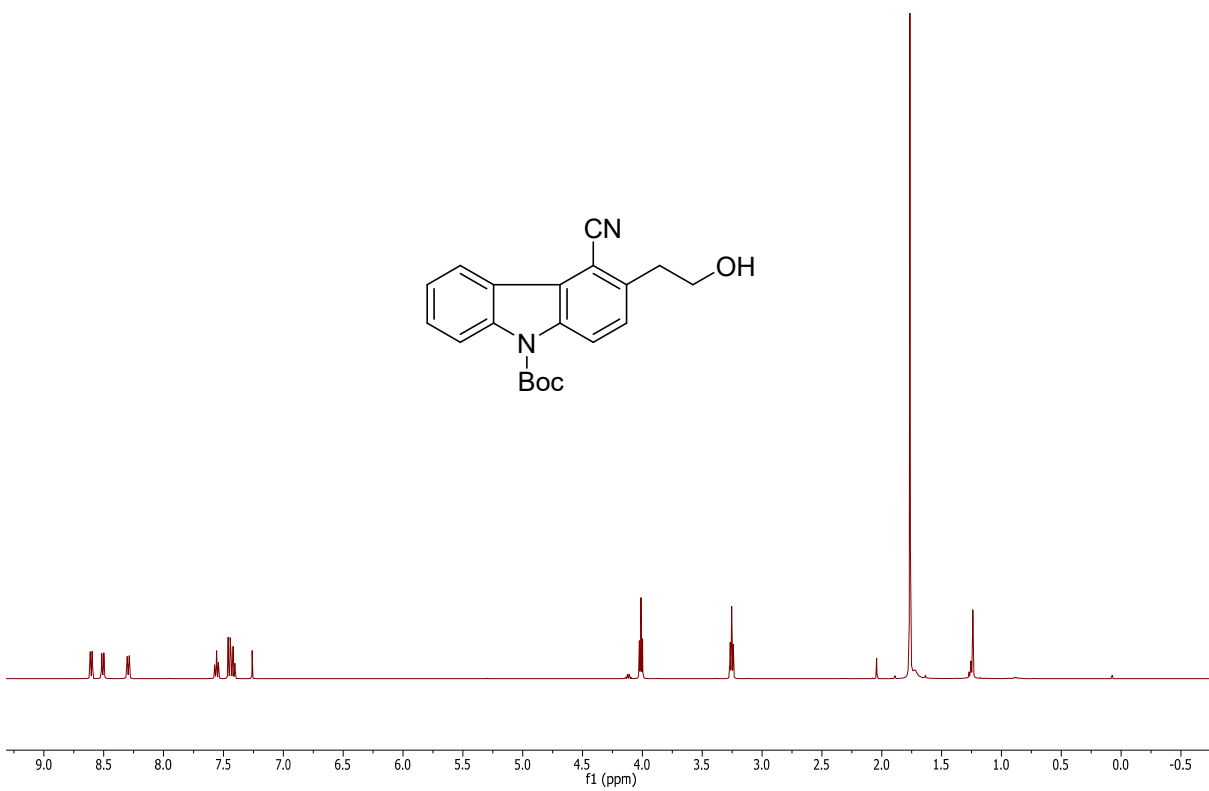
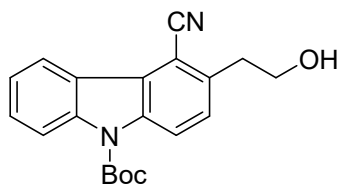
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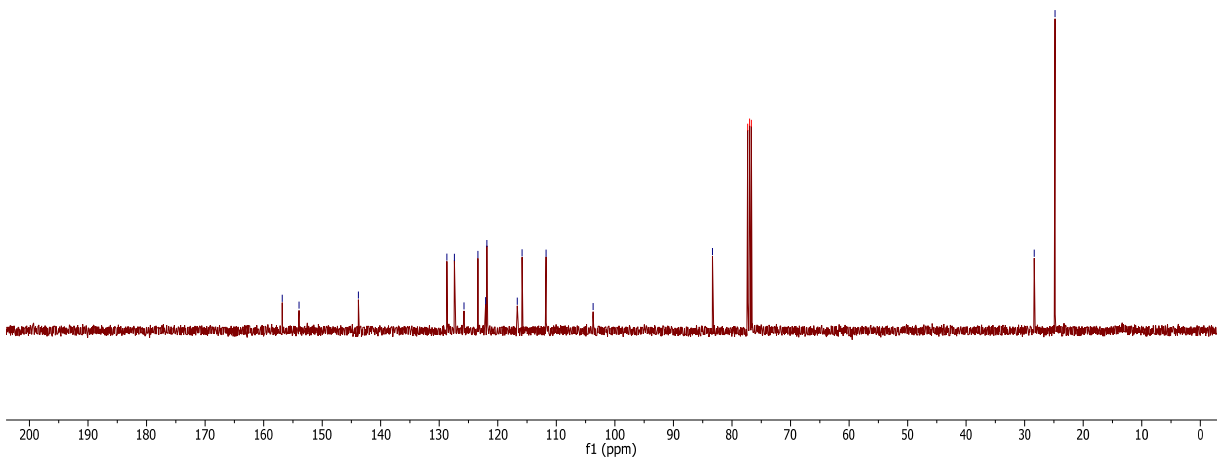
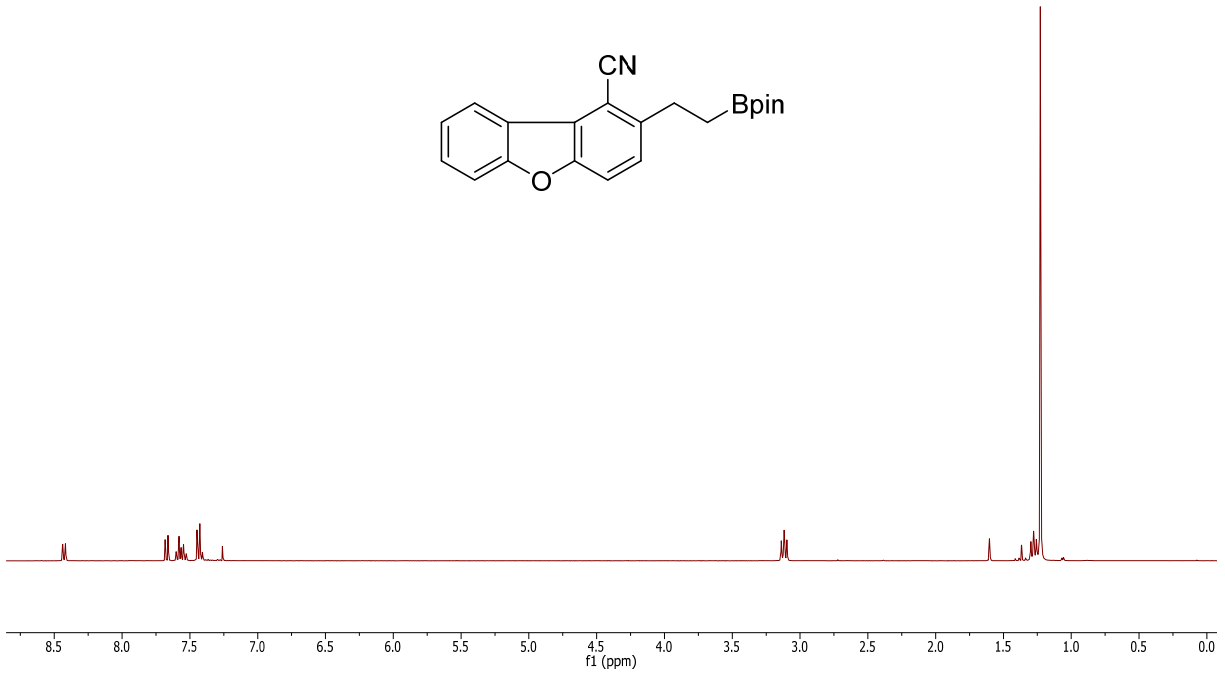
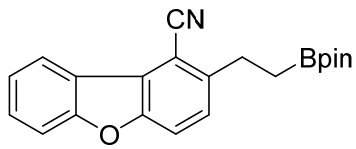
19.36

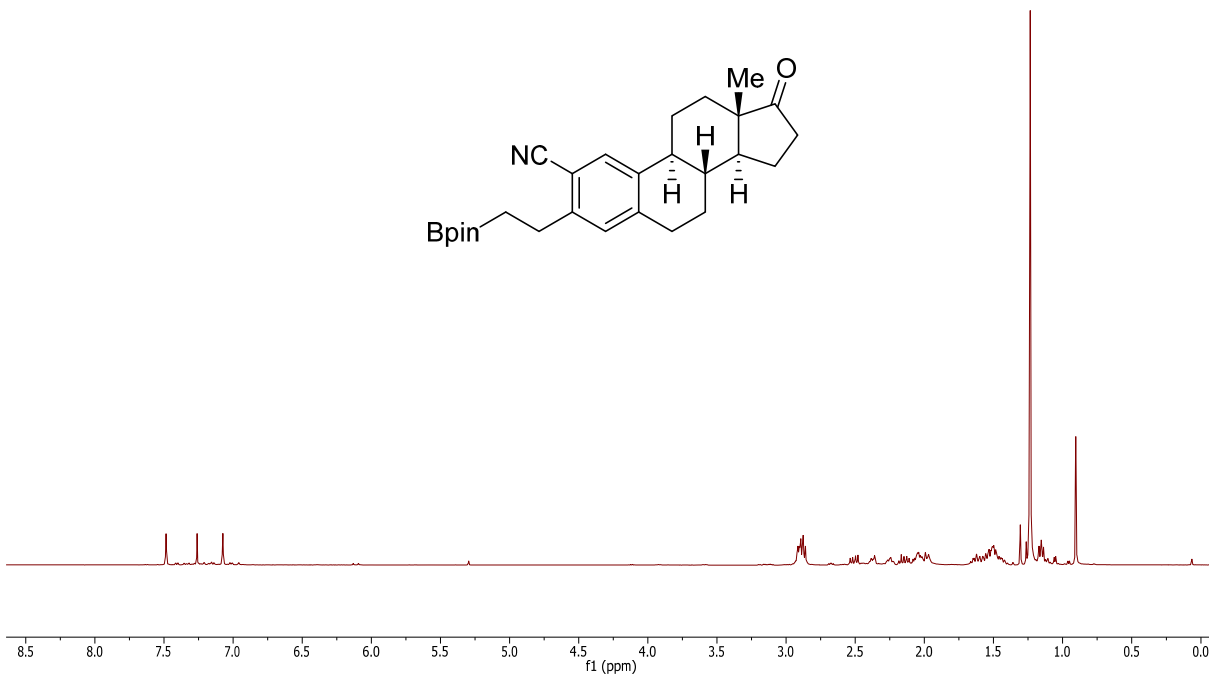
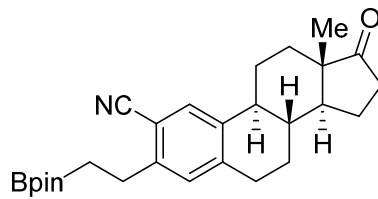












220.34

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76.68 cdd3

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