

Copper(I)-Catalyzed Formal Methylboration of Alkynes: Synthesis of Tri- and Tetrasubstituted Vinylboronates

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Supporting Information

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General Experimental Details

Tetrahydrofuran and toluene were purified by passing through a Pure Solv™ column drying system from Innovative Technology, Inc. Piperidine was dried by distillation over calcium hydride. Unless indicated otherwise, all reactions were conducted under an atmosphere of argon using flame-dried glassware with standard vacuum-line techniques.

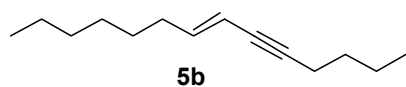
¹H NMR spectra were recorded on a Bruker 300 and 500 MHz spectrometers. The proton signal for residual non-deuterated solvent (δ 7.26 for CHCl₃) was used as an internal reference. ¹³C NMR spectra were recorded on a Bruker 300 MHz (75 MHz) spectrometer with complete proton decoupling. For ¹³C NMR spectra, chemical shifts are reported relative to the δ 77.0 resonance of CDCl₃. The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad).

Starting Materials and Reagents

(*E*)-1-iodo-1-octene, all commercial alkynes **2**, enynes **5c,d,e**, CuCl, NaOt-Bu (2.0 M in THF), xantphos, PPh₃, dppe and P(*p*-tolyl)₃ were purchased from Aldrich Chemical Co. and used as received. Bis(pinacolato)diboron was purchased from Strem Chemicals Inc. and dried under vacuum prior to use. Methyl iodide was purchased from Aldrich Chemical Co. and distilled prior to use. Alkynes **2k**,¹ **2m**,² **2p**³ and **2s**⁴ and enyne **5a**⁵ were prepared according to previously reported procedures.

Preparation of 1,3-enyne **5b**

(*E*)-Tetradec-7-en-5-yne, **5b**.



Pd(PPh₃)₄ (0.1 mmol) was added at room temperature to a solution of (*E*)-1-iodo-1-octene (1.0 mmol) in piperidine (10 mL) and stirred for 5 min. Then, a solution of 1-hexyne (1.0 mmol) was added, followed by the addition of CuI (0.1 mmol). After stirring at room temperature overnight, NH₄Cl (sat. aq. solution) and pentane were added to the reaction mixture. The phases were separated and the aqueous phase was extracted with pentane (x 2).

¹ Stepp, B. R.; Gibbs-Davis, J. M.; Koh, D. L. F.; Nguyen, S. T. *J. Am. Chem. Soc.* **2008**, *130*, 9628.

² Rodriguez, J. G.; Esquivias, J.; Lafuente, A.; Rubio, L. *Tetrahedron*, **2006**, *62*, 3112.

³ García Ruano, J. L.; Alemán, J.; Marzo, L.; Alvarado, C.; Tortosa, M.; Díaz-Tendero, S.; Fraile, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 2712.

⁴ Warger, C. E.; Shea, K. J. *Org. Lett.* **2004**, *6*, 313.

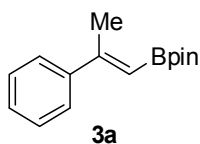
⁵ Braddock, D. C.; Bhuvu, R.; Pérez-Fuertes Y.; Pouwer, R.; Roberts, C. A.; Ruggiero, A.; Stokes, E. S. E.; White, A. J. P. *Chem. Commun.* **2008**, 1419.

The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated. The crude product was purified by column chromatography (pentane) affording compound **5b** (57% yield) as a colorless oil. ^1H NMR (300 MHz): δ 6.04 (dt, J = 6.0, 0.9 Hz, 1H), 5.42 (d, J = 18.6 Hz, 1H), 2.28 (t, J = 6.0 Hz, 2H), 2.03 (q, J = 6.0 Hz, 2H), 1.15-1.27 (m, 12H), 0.91 (t, J = 6.2 Hz, 3H), 0.87 (t, J = 6.2 Hz, 3H). ^{13}C (75 MHz): δ 143.3, 109.8, 88.6, 79.2, 32.7, 31.7, 30.9, 28.8, 28.7, 2.6, 21.9, 19.0, 14.1, 13.6. HRMS (EI $^+$): Calcd for $\text{C}_{14}\text{H}_{24} [\text{M}]^+$: 192.1878, Found: 192.1870.

General Procedure I for the Copper-Catalyzed Methylboration of Terminal Alkynes and Enynes.

An oven-dried vial was charged with CuCl (0.04 mmol, 3.95 mg), a phosphine (xantphos or PPh_3 , 0.04 mmol) and bis(pinacolato)diboron (0.44 mmol, 112 mg). After being sealed with a septum, the vial was connected to an argon-vacuum line and was evacuated and backfilled with argon (x 3). THF (0.1-0.6 M) was added and the mixture was stirred for 5 min at room temperature. Then, a 2.0 M NaOt-Bu solution in THF (0.22 mL) was added dropwise and the mixture got a dark brown color. After stirring for 5 min, the alkyne or enyne (0.4 mmol) was added (neat or dissolved in the minimal amount of THF if it is a solid) followed by MeI (1.6 mmol, 0.1 mL). The septum was sealed with parafilm and the mixture was stirred at room temperature for 16-24 hours. Et_2O and water were added and the layers were separated. The aqueous phase was extracted with Et_2O (x 2) and the combined organic layers were dried over Mg_2SO_4 and concentrated. The crude product was purified using a fluorisil column (100% pentanes) or a rapid-short SiO_2 column (2-5% EtOAc-hexanes). We found that most of the vinylboronates presented in this paper were partially volatil. Consequently, the rotary evaporator pressure was carefully controlled during the work-up and purification.

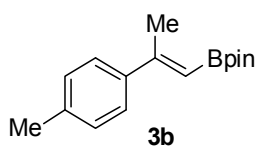
(*E*)-4,4,5,5-Tetramethyl-2-(2-phenylprop-1-enyl)-1,3,2-dioxaborolane, **3a**.



Following the general procedure I described above (with xantphos, 0.1 M in THF), compound **3a** was obtained in 74% yield as colorless oil. The spectral data for **3a** matched those previously described.⁶ When 5% mol of CuCl and 5% mol of xantphos were used, compound **3a** was obtained in 72% yield. The stereochemistry of the double bond was determined by nOe experiment (see NMR spectrum, below). ^1H NMR (300 MHz): δ 7.52-7.49 (m, 2H), 7.36-7.27 (m, 8H), 5.76 (q, J = 0.9 Hz, 1H), 2.42 (d, J = 0.9 Hz, 3H), 1.32 (s, 12H).

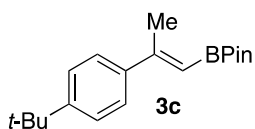
⁶ Coapes, R. B.; Souza, F. E. S.; Thomas, R. Ll.; Hall, J. J.; Marder, T. B. *Chem. Comm.* **2003**, 614.

(E)-4,4,5,5-Tetramethyl-2-(2-*p*-tolylprop-1-enyl)-1,3,2-dioxaborolane, 3b.



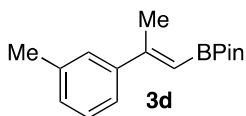
Following the general procedure I described above (with xantphos, 0.1 M in THF), compound **3b** was obtained in 68% yield as colorless oil. ¹H NMR (300 MHz): δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 5.77 (q, *J* = 1.0 Hz, 1H), 2.42 (d, *J* = 1.0 Hz, 3H), 2.36 (s, 3H), 1.33 (s, 12H). ¹³C (75 MHz): δ 157.6, 140.9, 137.7, 128.8 (2C), 125.7 (2C), 82.8 (2C), 24.9 (4C), 21.1, 20.0 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ¹¹B nucleus].⁷ HRMS (EI+): Calcd for C₁₆H₂₃BO₂ [M]⁺: 258.1791, Found: 258.1786.

(E)-2-(2-(4-*tert*-Butylphenyl)prop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3c.



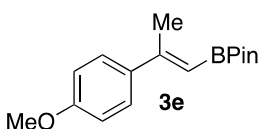
Following the general procedure I described above (with xantphos, 0.1 M in THF), compound **3c** was obtained in 83% yield as a colorless oil. ¹H NMR (300 MHz): δ 7.46 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 5.77 (q, *J* = 0.9 Hz, 1H), 2.41 (d, *J* = 0.9 Hz, 3H), 1.32 (s, 9H), 1.31 (s, 12H). ¹³C (75 MHz): δ 157.5, 150.9, 140.7, 125.5 (2C), 125.0 (2C), 82.8 (2C), 34.5, 31.3 (3C), 24.9 (4C), 19.9 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ¹¹B nucleus]. HRMS (EI+): Calcd for C₁₉H₂₉BO₂ [M]⁺: 300.2261, Found: 300.2266.

(E)-4,4,5,5-Tetramethyl-2-(2-*m*-tolylprop-1-enyl)-1,3,2-dioxaborolane, 3d.



Following the general procedure I described above (with xantphos, 0.1 M in THF), compound **3d** was obtained in 75% yield as a colorless oil. ¹H NMR (300 MHz): δ 7.33-7.50 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 5.76 (q, *J* = 0.9 Hz, 1H), 2.42 (d, *J* = 0.9 Hz, 3H), 2.36 (s, 3H), 1.33 (s, 12H). ¹³C (75 MHz): δ 158.0, 143.9, 137.6, 128.6, 128.0, 126.7, 122.9, 82.9 (2C), 24.8 (4C), 21.4, 20.1 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ¹¹B nucleus]. HRMS (EI+): Calcd for C₁₆H₂₃BO₂ [M]⁺: 258.1791, Found: 258.1801. Anal. Calcd for C₁₆H₂₃BO₂ C 74.44; H, 8.98; Found: C 75.14; H 9.03.

(E)-2-(2-(4-Methoxyphenyl)prop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3e.

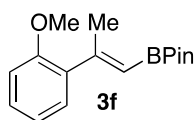


Following the general procedure I described above (with xantphos, 0.6 M in THF), compound **3e** was obtained in 76% yield as a colorless oil. ¹H NMR (300 MHz): δ 7.48, (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz,

⁷ (a) B. Wrackmeyer, *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *12*, 227. (b) N. F. Pelz, A. R. Woodward, H. E. Burks, J. D. Sieber, J. P. Morken, *J. Am. Chem. Soc.* **2004**, *126*, 16328.

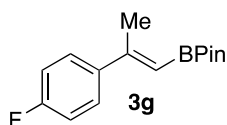
2H), 5.72 (s, 1H), 3.81 (s, 3H), 2.40 (s, 3H), 1.32 (s, 12H). ^{13}C (75 MHz): δ 159.5, 157.0, 136.1, 127.0 (2C), 113.4 (2C), 82.8 (2C), 55.2, 24.9 (4C), 19.9 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{16}\text{H}_{23}\text{BO}_3$ $[\text{M}]^+$: 274.1740, Found: 274.1735. Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{BO}_3$: C 70.09; H 8.46; Found: C 69.84; H 8.40.

(E)-2-(2-(2-Methoxyphenyl)prop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3f.



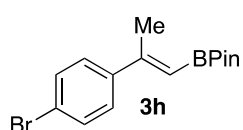
Following the general procedure I described above (with xantphos, 0.6 M in THF), compound **3f** was obtained in 80% yield as a colorless oil. ^1H NMR (300 MHz): δ 7.29-7.15 (m, 2H), 6.93-6.85 (m, 2H), 5.42 (s, 1H), 3.81 (s, 3H), 2.35 (s, 3H), 1.31 (s, 12H). ^{13}C (75 MHz): δ 159.6, 156.0, 136.0, 129.1, 128.4, 120.5, 110.8, 82.8 (2C), 55.4, 24.9 (4C), 21.8 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{16}\text{H}_{23}\text{BO}_3$ $[\text{M}]^+$: 274.1740, Found: 274.1728. Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{BO}_3$: C 70.09; H, 8.46; Found: C 69.93; H 8.43.

(E)-2-(2-(4-Fluorophenyl)prop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3g.



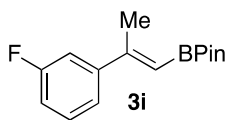
Following the general procedure I described above (with xantphos, 0.1 M in THF), compound **3g** was obtained in 72% yield as a colorless oil. ^1H NMR (300 MHz): δ 7.47 (dd, $J = 9.0, 5.4$ Hz, 2H), 7.0 (t, $J = 8.8$ Hz, 2H), 5.70 (s, 1H), 2.39 (s, 3H), 1.31 (s, 12H). ^{13}C (75 MHz): δ 162.6 (d, $J = 247.3$ Hz), 156.5, 127.5 (d, $J = 10.2$ Hz, 2C), 114.9 (d, $J = 21.3$ Hz, 2C), 83.0 (2C), 24.9 (4C), 20.1 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{15}\text{H}_{20}\text{BFO}_2$ $[\text{M}]^+$: 262.1540, Found: 262.1531. Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{BFO}_2$: C 68.73; H 7.69; Found: C 68.66; H 7.52.

(E)-2-(2-(4-Bromophenyl)prop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3h.



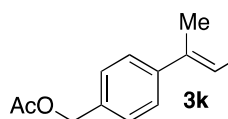
Following the general procedure I described above (with xantphos, 0.1 M in THF), compound **3h** was obtained in 72% yield as a colorless oil. ^1H NMR (300 MHz): δ 7.44 (d, $J = 8.8$ Hz, 2H), 7.35 (d, $J = 8.8$ Hz, 2H), 5.74 (q, $J = 1.0$ Hz, 1H), 2.38 (d, $J = 1.0$ Hz, 3H), 1.31 (s, 12H). ^{13}C (75 MHz): δ 156.4, 142.6, 131.2 (2C), 127.4 (2C), 122.0, 83.0 (2C), 24.9 (4C), 19.9 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{15}\text{H}_{20}\text{BBro}_2$ $[\text{M}]^+$: 322.0740, Found: 322.0730.

(E)-2-(2-(3-Fluorophenyl)prop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3i.



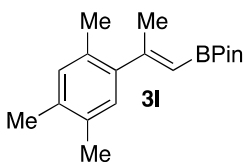
Following the general procedure I described above (with xantphos, 0.1 M in THF), compound **3i** was obtained in 66% yield as a colorless oil. ¹H NMR (300 MHz): δ 7.28-7.25 (m, 2H), 7.20-7.15 (m, 1H), 6.99-6.93 (m, 1H), 5.76 (q, *J* = 0.9 Hz, 1H), 2.38 (d, *J* = 0.9 Hz, 3H), 1.31 (s, 12H). ¹³C (75 MHz): δ 162.8 (d, *J* = 245 Hz), 156.2 (d, *J* = 2.15 Hz), 146.2 (d, *J* = 7.16 Hz), 129.5 (d, *J* = 8.3 Hz), 121.5 (d, *J* = 2.8 Hz), 114.6 (d, *J* = 21.2 Hz), 112.8 (d, *J* = 22.0 Hz), 83.1 (2C), 24.9 (4C), 20.0 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ¹¹B nucleus]. HRMS (EI+): Calcd for C₁₅H₂₀BF₂O₂ [M]⁺: 262.1540, Found: 262.1533.

(E)-4-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)benzyl acetate, 3k.



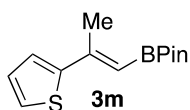
Following the general procedure I described above (with xantphos, 0.1 M in THF), compound **3k** was obtained in 70% yield as a colorless oil. ¹H NMR (300 MHz): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 5.75 (q, *J* = 1.0 Hz, 1H), 5.09 (s, 2H), 2.39 (d, *J* = 1.0 Hz, 3H), 2.09 (s, 3H), 1.31 (s, 12H). ¹³C (75 MHz): δ 170.8, 157.1, 143.8, 135.5, 128.0 (2C), 126.0 (2C), 82.9 (2C), 65.9, 24.8 (4C), 20.9, 20.0 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ¹¹B nucleus]. HRMS (EI+): Calcd for C₁₈H₂₅BO₄ [M]⁺: 316.1846, Found: 316.1852.

(E)-4,4,5,5-Tetramethyl-2-(2-(2,4,5-trimethylphenyl)prop-1-en-1-yl)-1,3,2-dioxaborolane, 3l.



Following the general procedure I described above (with xantphos, 0.6 M in THF), compound **3l** was obtained in 81% yield as colorless oil. ¹H NMR (300 MHz): δ 6.95 (s, 1H), 6.91 (s, 1H), 5.26 (q, *J* = 1.0 Hz, 1H), 2.29 (d, *J* = 1.0 Hz, 3H), 2.26 (s, 3H), 2.24 (s, 3H), 2.23 (s, 3H), 1.33 (s, 12H). ¹³C (75 MHz): δ 161.1, 144.3, 134.8, 133.3, 131.5, 130.7, 128.4, 82.8 (2C), 24.9 (4C), 23.1, 19.3, 19.2, 19.1 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ¹¹B nucleus]. HRMS (EI+): Calcd for C₁₈H₂₇BO₂ [M]⁺: 286.2104, Found: 286.2112.

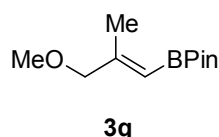
(E)-4,4,5,5-Tetramethyl-2-(2-(thiophen-2-yl)prop-1-enyl)-1,3,2-dioxaborolane, 3m.



Following the general procedure I described above (with xantphos, 0.6 M in THF), compound **3m** was obtained in 83% yield as a colorless oil. ¹H NMR (300 MHz): δ 7.21 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.15 (dd, *J* = 3.7, 1.1

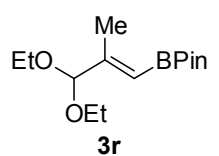
Hz, 1H), 6.98 (dd, $J = 5.1, 3.7$ Hz, 1H), 5.82 (q, $J = 0.9$ Hz, 1H), 2.42 (d, $J = 0.9$ Hz, 1H), 1.30 (s, 12H). ^{13}C (75 MHz): δ 150.4, 148.4, 127.5, 125.7, 124.6, 82.9 (2C), 24.8 (4C), 19.7 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{13}\text{H}_{19}\text{BO}_2\text{S}$ $[\text{M}]^+$: 250.1199, Found: 250.1207.

(E)-2-(3-Methoxy-2-methylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3q.



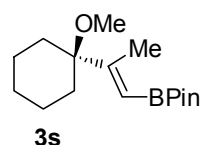
Following the general procedure I described above, compound **3q** was obtained in 59% yield as a colorless oil. ^1H NMR (300 MHz): δ 5.39 (s, 1H), 3.85 (s, 2H), 3.32 (s, 2H), 1.95 (s, 3H), 1.27 (s, 12H). ^{13}C (75 MHz): δ 157.4, 82.6, 78.5, 58.0, 24.8, 17.8 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{11}\text{H}_{21}\text{BO}_3$ $[\text{M}]^+$: 212.1584, Found: 212.1591.

(E)-2-(3,3-Diethoxy-2-methylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3r.



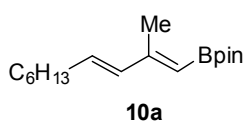
Following the general procedure I described above, compound **3r** was obtained in 56% yield as a colorless oil. ^1H NMR (300 MHz): δ 5.42 (s, 1H), 4.46 (s, 1H), 3.54-3.48 (m, 2H), 3.46-3.34 (m, 2H), 1.90 (s, 3H), 1.20 (s, 12H), 1.14 (t, $J = 9.0$ Hz, 6H). ^{13}C (75 MHz): δ 156.6, 105.7, 82.9, 61.8, 24.8, 15.7, 17.1 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. We observed the HRMS (EI+) peak for the deprotected aldehyde, due to the conditions used to run the experiment. HRMS (EI+): Calcd for $\text{C}_{10}\text{H}_{17}\text{BO}_3$ $[\text{M}]^+$: 196.1271, Found: 196.1264.

(E)-2-(2-(1-Methoxycyclohexyl)prop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3s.



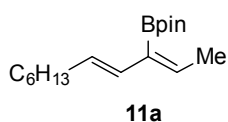
Following the general procedure I described above, compound **3s** was obtained in 57% yield as a colorless oil. ^1H NMR (300 MHz): δ 5.25 (s, 1H), 2.92 (s, 3H), 1.88 (s, 3H), 1.83-1.71 (m, 4H), 1.53-1.30 (m, 4H), 1.24-1.12 (m, 2H), 1.24 (s, 12H). ^{13}C (75 MHz): δ 164.2, 83.2, 79.5, 49.8, 36.9, 33.0, 26.3, 25.2, 22.3, 16.7 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{16}\text{H}_{29}\text{BO}_3$ $[\text{M}]^+$: 280.2210, Found: 280.2222.

4,4,5,5-Tetramethyl-2-((1*E*,3*E*)-2-methyldeca-1,3-dien-1-yl)-1,3,2-dioxaborolane, **10a**.



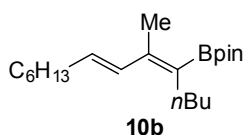
Following the general procedure I described above (0.6M in THF), a unseparable mixture 67:33 of the regioisomers **10a/11a** was obtained in 55% yield (PPh₃) and 68% yield (xantphos). Colorless oil. ¹H NMR (500 MHz): δ 6.20 (d, *J* = 12.0 Hz, 1H), 5.89 (dt, *J* = 6.0, 1.2 Hz, 1H), 5.26 (s, 1H), 2.18-2.13 (m, 2H), 2.13 (s, 3H), 1.45-1.35 (m, 2H), 1.37 (s, 6H), 1.32 (s, 12H), 0.91-0.89 (m, 3H). ¹³C (125 MHz): δ 156.0, 139.4, 136.3, 82.7 (2C), 32.9, 31.7, 29.5, 24.9 (4C), 22.6, 17.7, 14.1 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ¹¹B nucleus]. HRMS (EI⁺): Calcd for C₁₇H₃₁BO₂ [M]⁺: 278.2417, Found: 278.2417.

4,4,5,5-Tetramethyl-2-((2*E*,4*E*)-undeca-2,4-dien-3-yl)-1,3,2-dioxaborolane, **11a**.



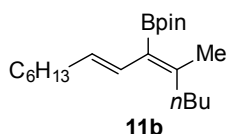
Following the general procedure I described above (0.6M in THF), a unseparable mixture 67:33 of the regioisomers **10a/11a** was obtained in 55% yield (PPh₃) and 68% yield (xantphos). ¹H NMR (500 MHz): δ 6.15 (d, *J* = 12.0 Hz, 1H), 6.10 (d, 12.0 Hz 1H), 5.76 (dt, *J* = 6.0, 1.4 Hz, 1H), 2.09 (q, *J* = 6.0 Hz, 2H), 1.92 (d, 10.0 Hz, 3H), 1.45-1.35 (m, 2H), 1.37 (s, 6H), 1.32 (s, 12H), 0.91-0.89 (m, 3H). ¹³C (125 MHz): δ 139.2, 135.4, 132.4, 82.9 (2C), 33.2, 31.9, 31.7, 29.5, 24.9 (4C), 17.4, 14.1 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ¹¹B nucleus]. HRMS (EI⁺): Calcd for C₁₇H₃₁BO₂ [M]⁺: 278.2417, Found: 278.2417.

4,4,5,5-Tetramethyl-2-((5*Z*,7*E*)-6-methyltetradeca-5,7-dien-5-yl)-1,3,2-dioxaborolane, **10b**.



Following the general procedure I described above (0.6M in THF), a unseparable mixture 67:33 of the regioisomers **10b/11b** was obtained in 58% yield (PPh₃) and 52% yield (xantphos). ¹H NMR (500 MHz): δ 6.09 (dt, *J* = 10.1 Hz, 1H), 5.49 (dt, *J* = 10.0, 0.1 Hz, 1H), 2.33-2.32 (m, 2H), 2.12-2.10 (m, 2H), 2.07 (s, 3H), 1.37-1.21 (s, 12H), 1.32 (s, 12H), 0.94-0.90 (m, 6H). ¹³C (125 MHz): δ 143.4, 132.7, 128.7, 83.0 (2C), 32.9, 31.7, 29.5 29.8, 24.9 (4C), 22.7, 22.6, 20.7, 18.8, 14.1, 13.6, 11.6 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ¹¹B nucleus]. HRMS (EI⁺): Calcd for C₂₁H₃₉BO₂ [M]⁺: 334.3043, Found: 334.3052.

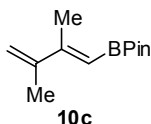
4,4,5,5-Tetramethyl-2-((5*Z*,7*E*)-5-methyltetradeca-5,7-dien-6-yl)-1,3,2-dioxaborolane, **11b**.



Following the general procedure I described above (0.6M in THF), an unseparable mixture 67:33 of the regioisomers **10b/11b** was obtained in 58% yield (PPh₃) and 52% yield (xantphos). ¹H NMR (300 MHz): δ 6.59 (dt, *J* = 15.1 Hz, 1H), 5.86 (dt, *J* = 10.0, 0.1 Hz, 1H), 2.42-2.39 (m, 2H), 2.32-2.13 (m, 2H),

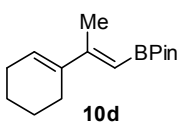
1.89 (s, 3H), 1.37-1.21 (s, 12H), 1.32 (s, 12H), 0.94-0.90 (m, 6H). ^{13}C (125 MHz): δ 143.3, 131.6, 129.4, 83.3 (2C), 34.7, 33.0, 29.9, 29.8, 24.8 (4C), 22.8, 22.6, 19.3, 18.7, 14.3, 14.1, 14.0 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{21}\text{H}_{39}\text{BO}_2$ $[\text{M}]^+$: 334.3043, Found: 334.3052.

(E)-2-(2,3-Dimethylbuta-1,3-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 10c.



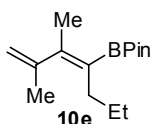
Following the general procedure I described above (with xantphos, 0.6M in THF), compound **10c** was obtained in 62% yield. ^1H NMR (300 MHz): δ 5.47 (m, 1H), 5.22 (m, 1H), 5.07 (m, 1H), 2.15 (s, 3H), 1.92 (s, 3H), 1.28 (s, 12H). ^{13}C (75 MHz): δ 156.7, 145.5, 114.9, 82.8 (2C), 24.9 (4C), 20.8, 18.2 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{12}\text{H}_{21}\text{BO}_2$ $[\text{M}]^+$: 208.1635, Found: 208.1640.

(E)-2-(2-(Cyclohex-1-en-1-yl)prop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 10d.



Following the general procedure I described above (with xantphos, 0.6M in THF), compound **10d** was obtained in 77% yield. ^1H NMR (300 MHz): δ 6.10-6.08 (m, 1H), 5.36 (s, 1H), 2.21-2.10 (m, 4H), 2.14 (s, 3H), 1.71-1.51 (m, 4H), 1.27 (s, 12H). ^{13}C (75 MHz): δ 157.8, 138.7, 127.4, 82.7 (2C), 26.2, 25.7, 24.8 (4C), 23.0, 22.1, 18.0 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{15}\text{H}_{25}\text{BO}_2$ $[\text{M}]^+$: 248.1948, Found: 248.1947.

(Z)-2-(4,5-Dimethylhexa-3,5-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 10e.



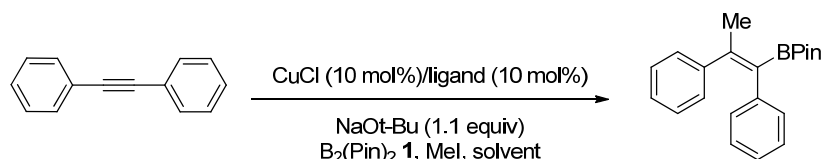
Following the general procedure I described above (with xantphos, 0.6M in THF), an unseparable mixture 88:12 of the regioisomers **10e/11e** was obtained in 65% conversion according to the ^1H NMR of the crude product. We could not calculate a real yield because we observed significant decomposition of **10e** during the purification process. ^1H NMR (300 MHz): δ 4.84-4.82 (m, 1H), 4.60-4.58 (m, 1H), 2.12 (q, J = 7.5 Hz, 2H), 1.97 (t, J = 0.8 Hz, 3H), 1.79 (dd, J = 1.5, 1.0 Hz, 3H), 1.30 (s, 12H), 0.92 (t, J = 7.5 Hz, 3H). ^{13}C (75 MHz): δ 151.1, 148.1, 110.6, 82.9 (2C), 25.4, 24.8 (4C), 22.2, 22.1, 15.5 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{14}\text{H}_{25}\text{BO}_2$ $[\text{M}]^+$: 236.1948, Found: 236.1944.

General Procedure II for the Copper-Catalyzed Methylboration of non-Terminal Alkynes

An oven-dried vial was charged with CuCl (0.04 mmol, 3.95 mg), P(*p*-tolyl)₃ (0.04 mmol, 12 mg) and bis(pinacolato)diboron (0.44 mmol, 112 mg). After being sealed with a septum, the vial was connected to an argon-vacuum line and was evacuated and backfilled with argon (x 3). Toluene (0.6 M) was added and the mixture was stirred for 5 min at room temperature. Then, a 2.0 M NaOt-Bu solution in THF (0.22 mL) was added dropwise and the mixture got a dark brown color. After stirring for 5 min, the alkyne (0.4 mmol) was added (neat or dissolved in the minimal amount of toluene if it is a solid) followed by MeI (1.6 mmol, 0.1 mL). The septum was sealed with parafilm and the mixture was stirred at 60 °C for 24 hours. Et₂O and water were added and the layers were separated. The aqueous phase was extracted with Et₂O (x 2) and the combined organic layers were dried over Mg₂SO₄ and concentrated. The crude product was purified using a fluorisil column (100% pentanes) or a rapid-short SiO₂ column (2-5% EtOAc-hexanes).

Optimization of experimental conditions for methylboration of non-Terminal Alkynes

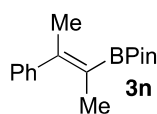
Table S1. Screening of conditions for disubstituted alkynes.^a



Entry	Ligand (10 %mol)	Solvent	T (°C)	Yield (%)
1 ^b	PPh ₃	THF	rt	20
2 ^b	PPh ₃	Toluene	60	34
3 ^c	PPh ₃	Toluene	60	39
4 ^c	P(<i>o</i> -CH ₃ C ₆ H ₄) ₃	THF	rt	---
5 ^c	P(<i>o</i> -CH ₃ C ₆ H ₄) ₃	Toluene	60	---
6 ^c	P(<i>p</i> -CH ₃ C ₆ H ₄) ₃	THF	rt	20
7 ^c	P(<i>p</i> -CH ₃ C ₆ H ₄) ₃	Toluene	60	43

^aAll reaction were performed with 0.4 mmol of an alkyne for 24 h. ^b 0.5 M in toluene. ^c 0.6 M in THF or toluene.

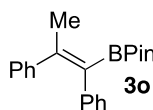
(Z)-4,4,5,5-Tetramethyl-2-(3-phenylbut-2-en-2-yl)-1,3,2-dioxaborolane, 3n.



Following the general procedure II described above, compound **3n** was obtained in 50% yield as a colorless oil. ¹H NMR (300 MHz): δ 7.36-7.30, (m, 2H), 7.22 (tt, *J* = 6.6, 1.6 Hz, 1H), 7.14-7.11 (m, 2H), 2.25 (q, *J* = 1.5 Hz, 3H), 1.60 (q, *J* = 1.5 Hz, 3H), 1.34 (s, 12H). ¹³C (75 MHz): δ 150.5, 144.8, 128.0, 127.4 (2C), 126.2, 83.1 (2C),

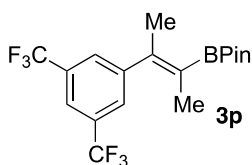
24.9 (4C), 24.6, 18.2 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{16}\text{H}_{23}\text{BO}_2$ $[\text{M}]^+$: 258.1791, Found: 258.1802.

(Z)-2-(1,2-Diphenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3o.



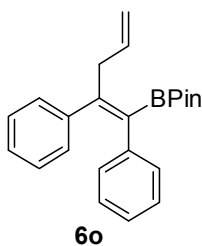
Following the general procedure II described above, compound **3o** was obtained in 50% yield as colorless oil. ^1H NMR (300 MHz): δ 7.08-7.02 (m, 4H), 7.01-6.95 (m, 4H), 6.92-6.89 (m, 2H), 2.35 (s, 3H), 1.31 (s, 12H). ^{13}C (75 MHz): δ 149.0, 143.6, 141.7, 129.6 (2C), 128.5 (2C), 127.6 (2C), 127.4 (2C), 126.2, 125.2, 83.6 (2C), 24.7 (4C) [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{21}\text{H}_{25}\text{BO}_2$ $[\text{M}]^+$: 320.1948, Found: 320.1942. Anal. Calcd for $\text{C}_{21}\text{H}_{25}\text{BO}_2$: C 78.76; H 7.87; Found: C 78.81; H 7.82.

(Z)-2-(3-(3,5-Bis(trifluoromethyl)phenyl)but-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3p.



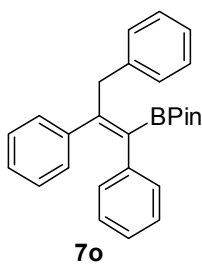
Following the general procedure II described above, compound **3p** was obtained in 70% yield as a colorless oil. ^1H NMR (300 MHz): δ 7.75 (m, 1H), 7.58 (m, 2H), 2.25 (q, J = 1.6 Hz, 3H), 1.57 (q, J = 1.6 Hz, 3H), 1.33 (s, 12H). ^{13}C (75 MHz): δ 146.9, 147.9, 131.5 (q, J = 33 Hz, 2C), 127.8 (m, 2C), 123.4 (q, J = 273 Hz, 2C), 120.3 (q, J = 4.1 Hz, 1C), 83.5 (2C), 24.9 (4C), 24.2, 18.3 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{18}\text{H}_{21}\text{BF}_6\text{O}_2$ $[\text{M}]^+$: 394.1539, Found: 394.1527.

(Z)-2-(1,2-Diphenylpenta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 6o.



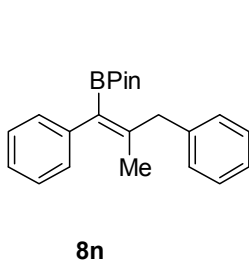
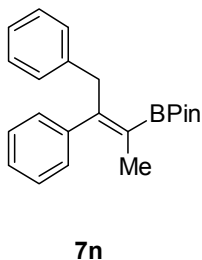
Following the general procedure I described above (in this case only 1.1 equiv. of allyl iodide was used), compound **6o** was obtained in 42% yield as a colorless oil. ^1H NMR (300 MHz): δ 7.10-6.92 (m, 10H), 5.89-5.75 (m, 1H), 5.05 (dd, J = 15.0, 3.0 Hz, 1H), 4.97 (d, J = 9.0 Hz, 1H), 3.50 (d, J = 9.0 Hz, 2H), 1.33 (s, 12H). ^{13}C (75 MHz): δ 158.9, 142.1, 141.5, 136.5, 129.6, 129.1, 127.5, 127.4, 126.3, 125.3, 115.8, 83.7, 42.8, 24.7 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{23}\text{H}_{27}\text{BO}_2$ $[\text{M}]^+$: 346.2104, Found: 346.2107.

(Z)-4,4,5,5-Tetramethyl-2-(1,2,3-triphenylprop-1-en-1-yl)-1,3,2-dioxaborolane, 7o.



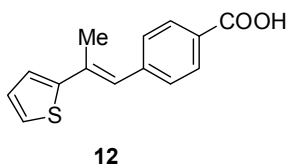
Following the general procedure I described above (in this case only 1.1 equiv. of benzyl bromide was used), compound **7o** was obtained in 60% yield as a colorless oil. ^1H NMR (300 MHz): δ 7.30-7.24 (m, 4H), 7.18-7.16 (m, 1H), 7.12-7.00 (m, 8H), 6.85-6.82 (m, 2H), 4.11 (s, 2H), 1.36 (s, 12H). ^{13}C (75 MHz): δ 151.6, 141.4, 139.6, 129.6, 129.1, 129.0, 128.0, 127.4, 127.3 (2C), 126.1, 125.8, 125.3, 83.7, 44.4, 24.7 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{27}\text{H}_{29}\text{BO}_2$ $[\text{M}]^+$: 396.2261, Found: 396.2264.

(Z)-2-(3,4-Diphenylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 7n and (E)-4,4,5,5-tetramethyl-2-(2-methyl-1,3-diphenylprop-1-en-1-yl)-1,3,2-dioxaborolane 8n.



Following the general procedure I described above (in this case only 1.1 equiv. of benzyl bromide was used), compound **7n** and **8n** were obtained as an inseparable mixture 75:25 in 55% yield as a colorless oil. *Major isomer*: ^1H NMR (300 MHz): δ 7.17-7.04 (m, 8H), 6.84 (d, J = 9.0 Hz, 2H), 3.99 (s, 2H), 1.60 (s, 3H), 1.33 (s, 12H). ^{13}C (75 MHz): δ 153.6, 142.8, 140.2, 129.1, 128.1, 127.9, 127.8, 126.2, 125.6, 83.3, 43.9, 24.9, 18.4 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. *Minor isomer*: ^1H NMR (300 MHz): δ 7.33-7.04 (m, 10H), 3.77 (s, 2H), 1.53 (s, 3H), 1.25 (s, 12H). ^{13}C (75 MHz): δ 149.8, 142.5, 140.5, 129.1, 129.0, 128.3, 127.8, 125.9, 125.2, 83.3, 44.3, 24.7, 20.0 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. HRMS (EI+): Calcd for $\text{C}_{22}\text{H}_{27}\text{BO}_2$ $[\text{M}]^+$: 334.2104, Found: 334.2096.

(E)-4-(2-(Thiophen-2-yl)prop-1-en-1-yl)benzoic acid, 12.



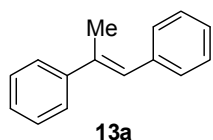
$\text{Pd}(\text{PPh}_3)_4$ (12 mg, 0.01 mmol) was added at room temperature to a solution of vinyl boronate **3m** (0.1 mmol), methyl *p*-iodobenzoate (0.1 mmol) and NaOH (0.3 mmol, 2.0 M in H_2O) in dioxane (1 mL). The reaction mixture was stirred at 100 $^\circ\text{C}$ for 3h. H_2O was added and the mixture was extracted with AcOEt (x 3). The solvent was removed under reduced pressure and the residue was purified by column chromatography (2:1 AcOEt/ *n*-hexane) affording compound **12** as a white solid (67% yield). The spectral data for **12** matched those

previously described.⁸ ¹H NMR (300 MHz): δ 8.03 (d, J = 9.0 Hz, 2H), 7.42 (d, J = 6.0 Hz, 1H), 7.37 (d, J = 9.0 Hz, 2H), 7.18-7.11 (m, 1H), 6.98-6.91 (m, 1H), 6.90 (s, 1H), 2.26 (s, 3H). ¹³C (75 MHz): δ 171.5, 147.4, 143.3, 133.4, 130.2, 129.2, 128.5, 127.3, 124.9, 124.7, 124.1, 17.6. HRMS (EI+): Calcd for C₁₄H₁₂O₂S [M]⁺: 244.0558, Found: 244.0571.

General Procedure for the *one pot* Methylboration-Suzuki Coupling

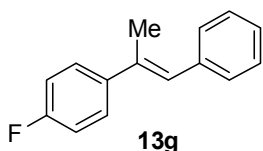
An oven-dried vial was charged with CuCl (0.04 mmol, 3.95 mg), a phosphine (xantphos or PPh₃, 0.04 mmol) and bis(pinacolato)diboron (0.44 mmol, 112 mg). After being sealed with a septum, the vial was connected to an argon-vacuum line and was evacuated and backfilled with argon (x 3). THF (0.1-0.6 M) was added and the mixture was stirred for 5 min at room temperature. Then, a 2.0 M NaOt-Bu solution in THF (0.22 mL) was added dropwise and the mixture got a dark brown color. After stirring for 5 min, the alkyne or enyne (0.4 mmol) was added (neat or dissolved in the minimal amount of THF if it is a solid) followed by MeI (1.6 mmol, 0.1 mL). The septum was sealed with parafilm and the mixture was stirred at room temperature for 16-24 hours. Then, the reaction mixture was transferred to a sealed tube using 1 mL of dry THF to rinse. To this solution, Pd(PPh₃)₄ (0.04 mmol), PhI (0.4 mmol) and NaOH (1.2 mmol, 2.0 M in H₂O) were sequentially added. After stirring at 70 °C overnight, H₂O was added to the reaction mixture and the mixture was extracted with Et₂O for three times. The combined organic layers were washed with sat. NH₄Cl/H₂O, brine, and dried over magnesium sulfate. The residue was concentrated and purified by column chromatography (pentane).

(*E*)-prop-1-ene-1,2-diylidibenzene, **13a**.



Following the general procedure described above, compound **13a** was obtained as a white solid (65%, 2 steps). The spectral data for **13a** matched those previously described.⁹ ¹H NMR (300 MHz): δ 7.59 (d, J = 9.1 Hz, 2H), 7.46-7.41 (m, 4H), 7.38-7.30 (m, 4H), 6.91 (s, 1H), 2.34 (d, J = 1.3 Hz, 3H).

(*E*)-1-Fluoro-4-(1-phenylprop-1-en-2-yl)benzene, **13g**.



Following the general procedure described above, compound **13g** was obtained as a white solid (58%, 2 steps). The spectral data for **13g** matched those previously described.¹⁰ ¹H NMR (300 MHz): δ 7.38 (dd,

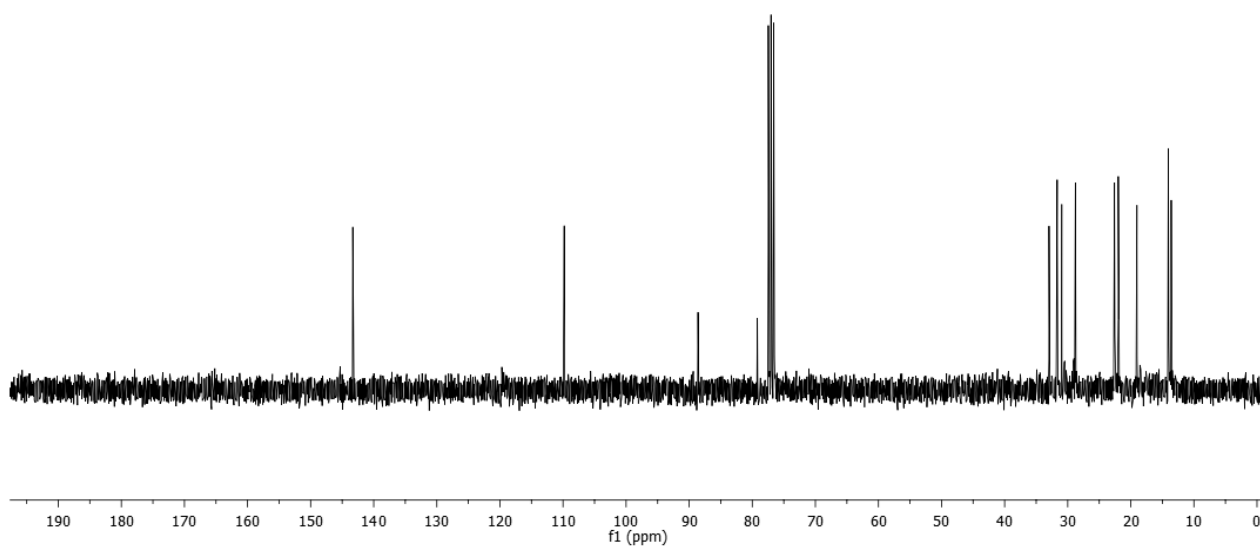
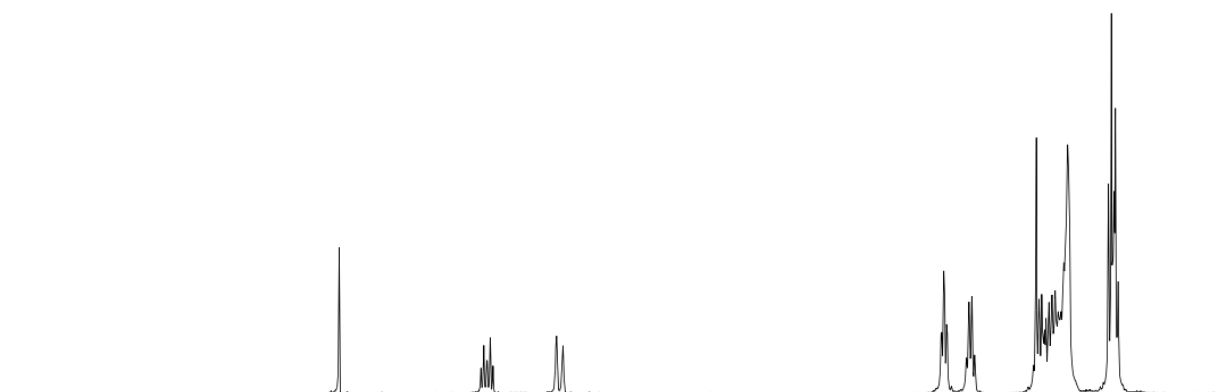
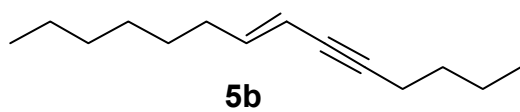
⁸ Manfredini, S.; Simoni, D.; Caminiti, G.; Vertuani, S.; Invidiata, F.; Moscato, B.; Hatse, S.; De Clercq, E.; Balzarini, J. *Med. Chem. Res.* **1998**, 8, 291

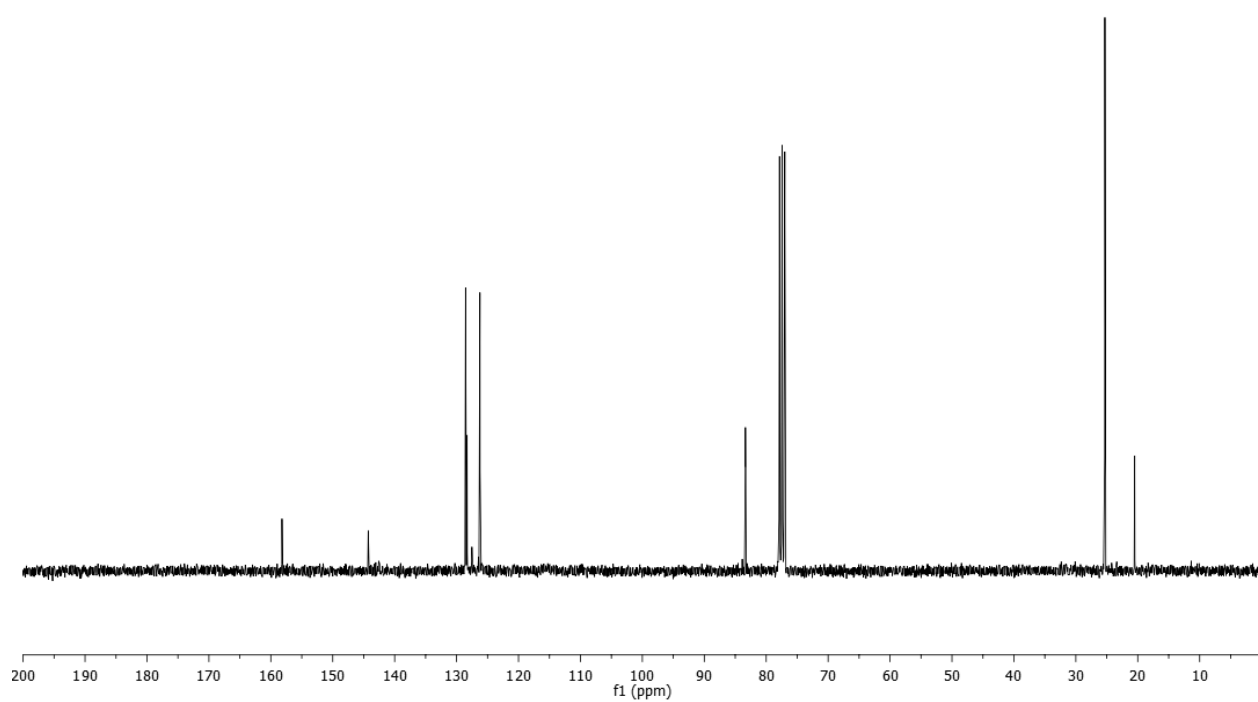
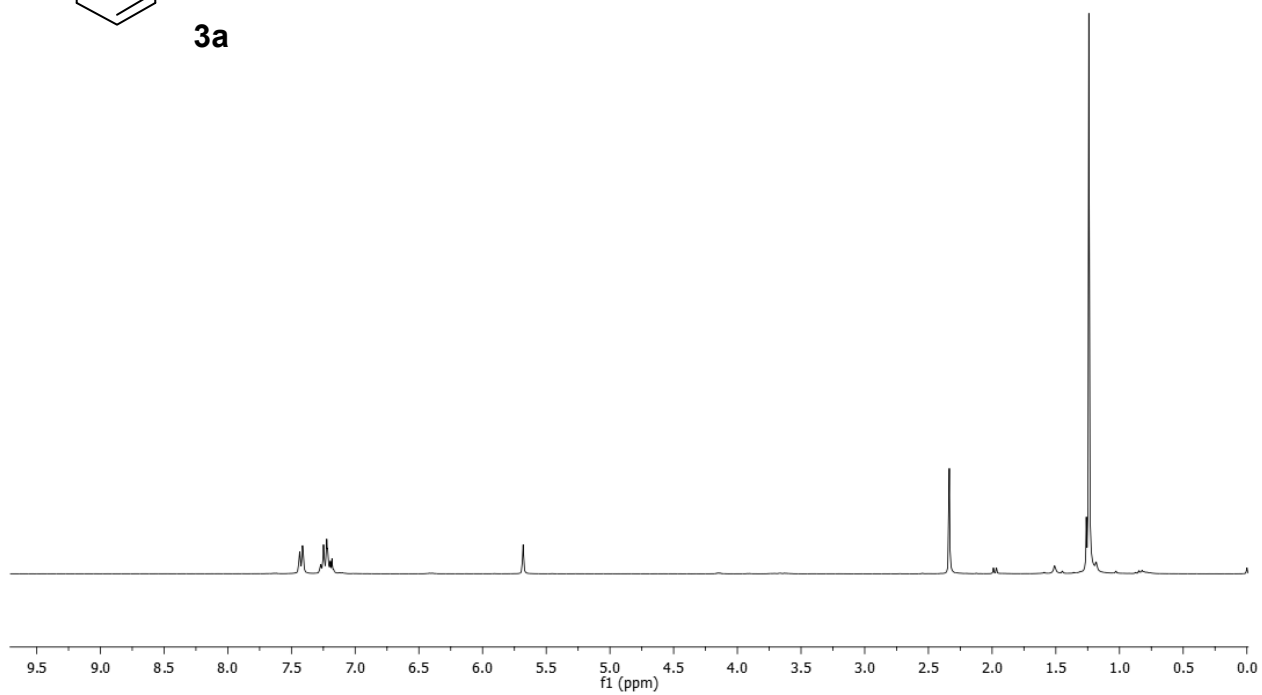
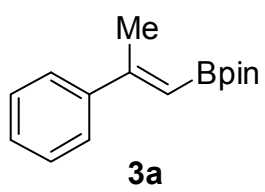
⁹ Liu, H.; Cao, L.; Sun, J.; Fossey, J. S.; Deng, W.-P. *Chem. Comm.* **2012**, 48, 2674.

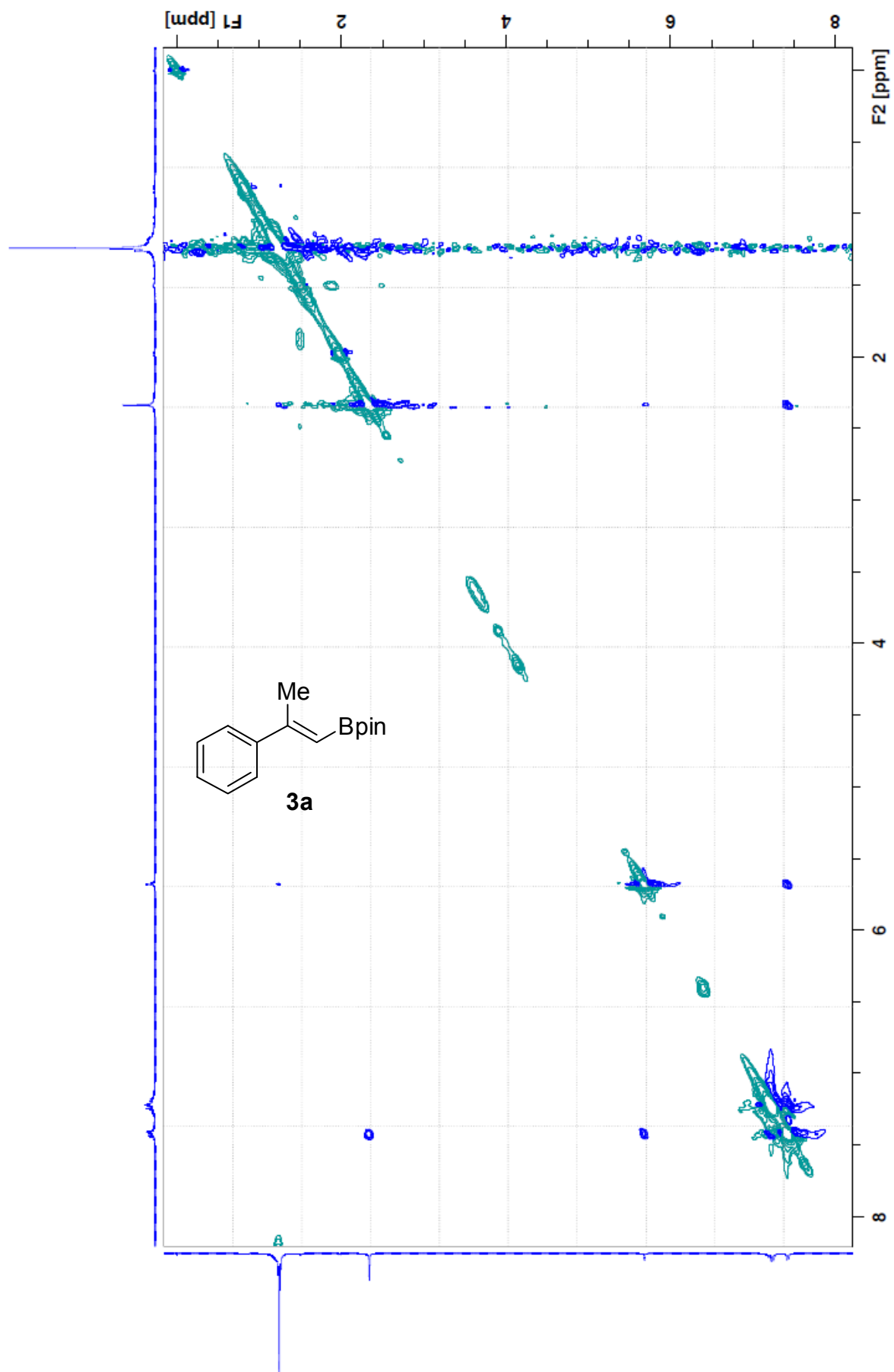
¹⁰ Kim, H. R.; Yun, J. *Chem. Comm.* **2011**, 47, 2943.

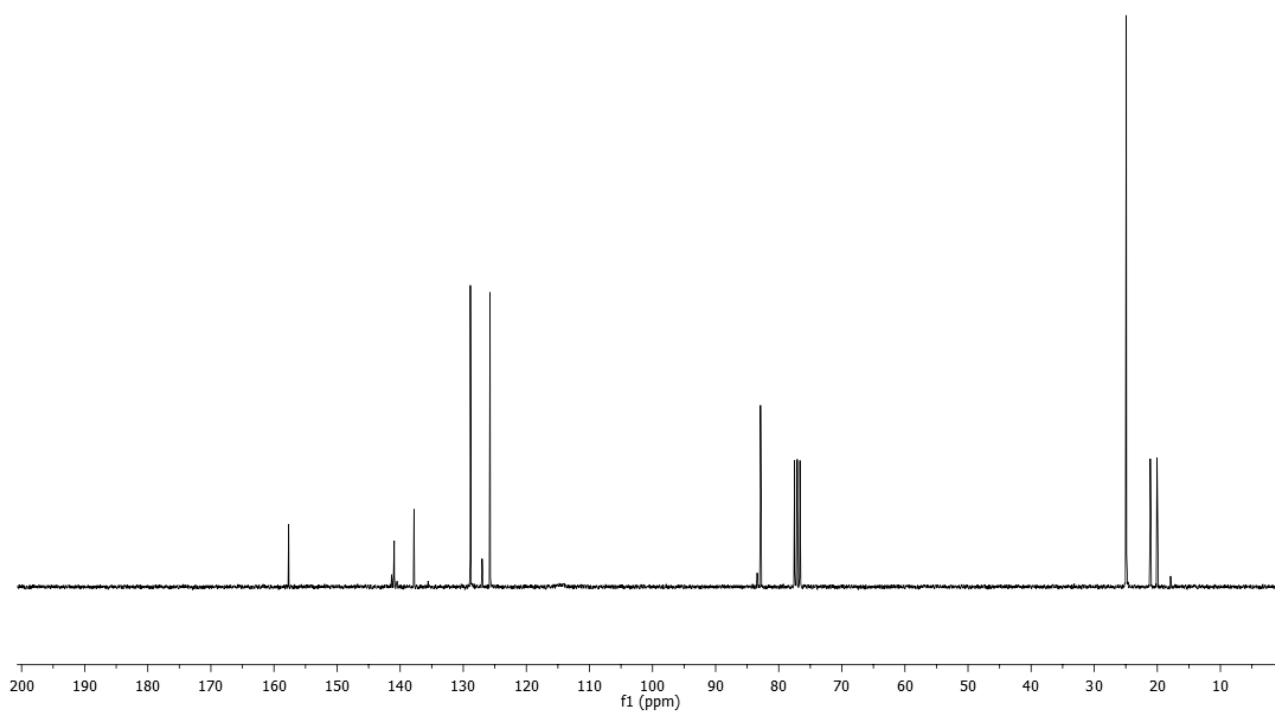
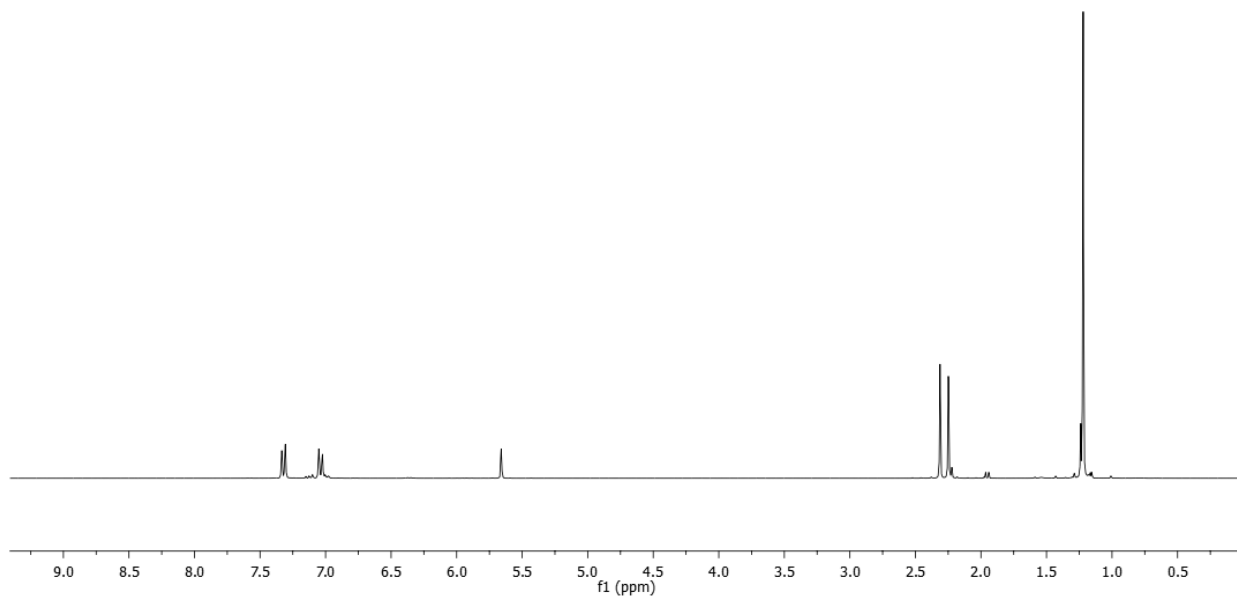
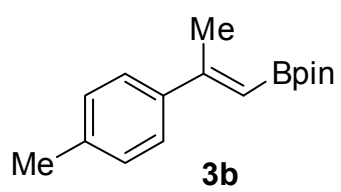
$J = 6.0, 3.1$ Hz, 2H), 7.28-7.25 (m, 3H), 7.18-7.13 (m, 1H), 6.95 (t, $J = 24.0$ Hz, 3H), 6.69 (s, 1H), 2.16 (d, $J = 1.3$ Hz, 3H).

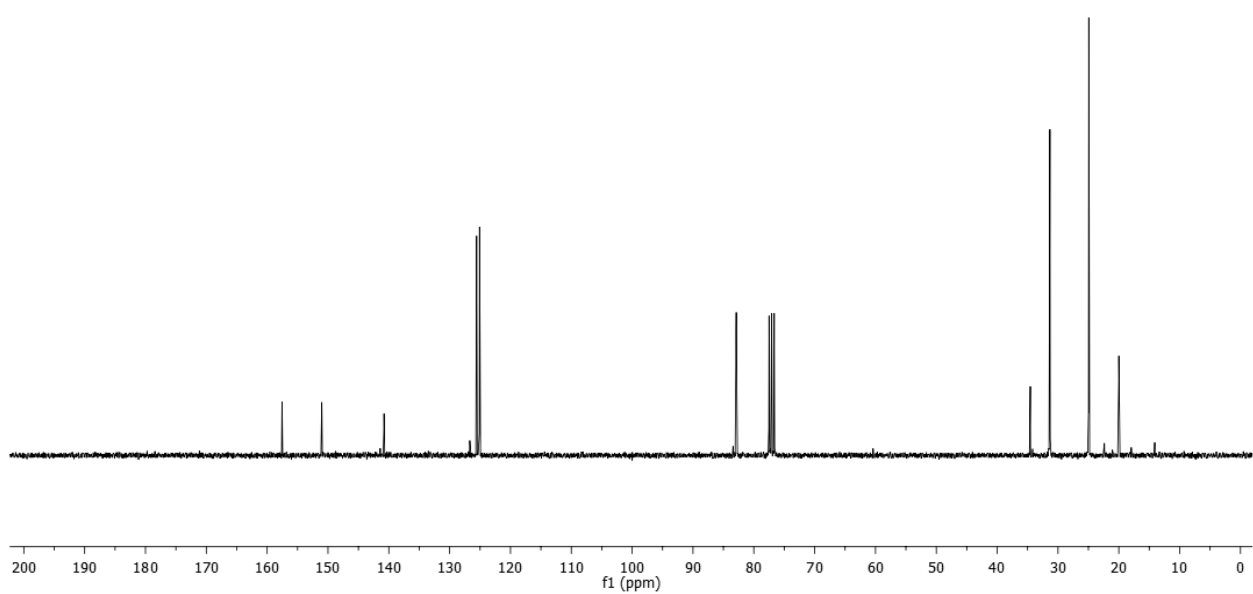
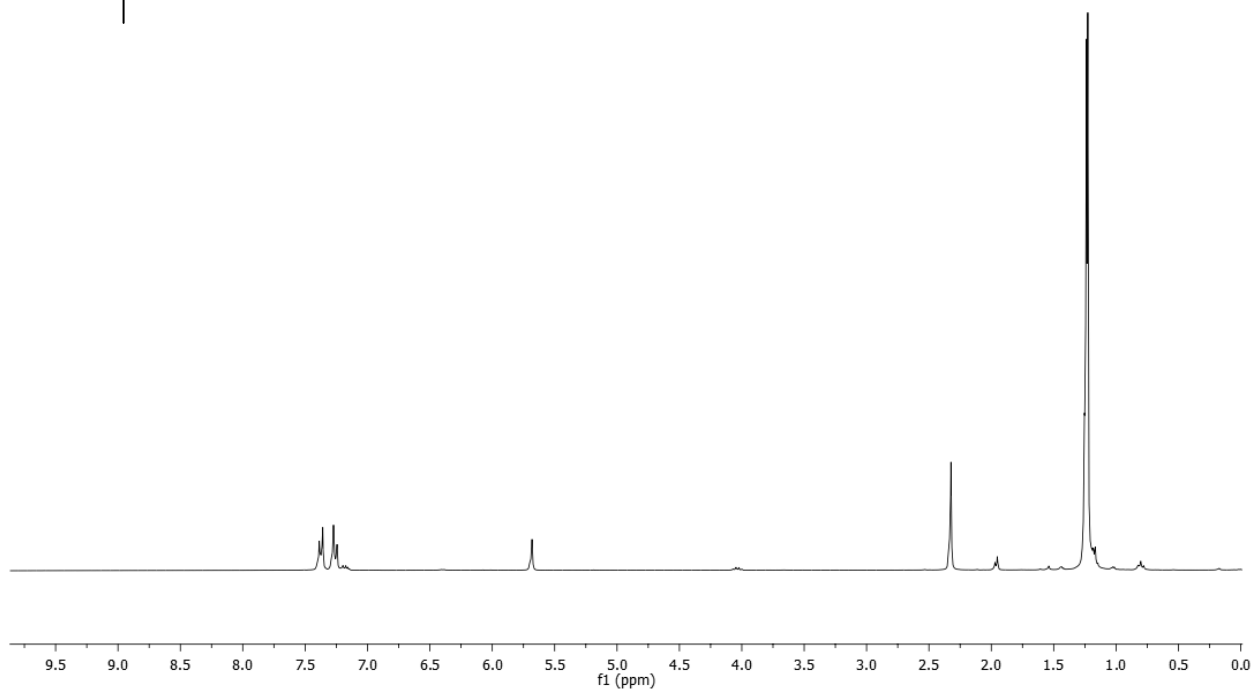
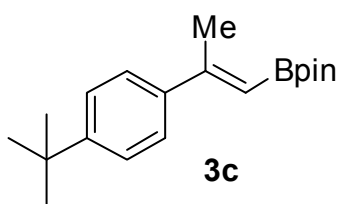
NMR spectra

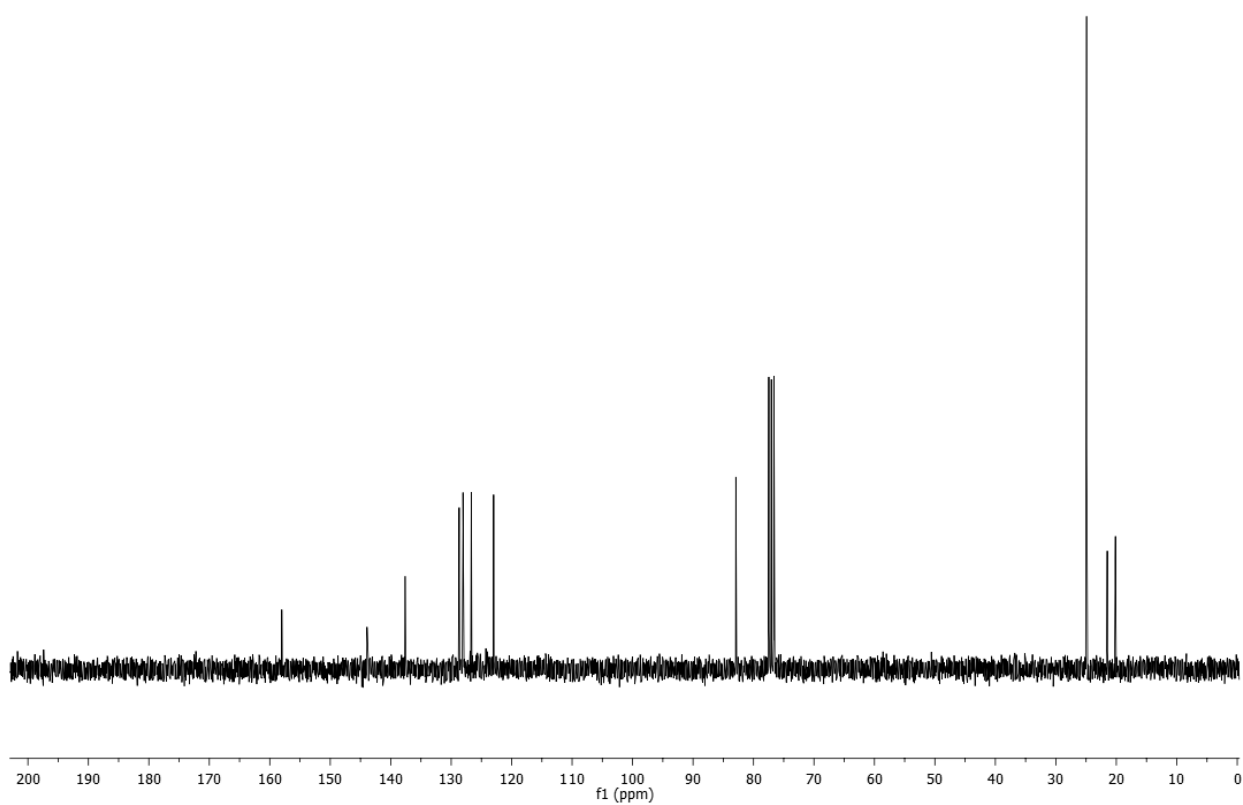
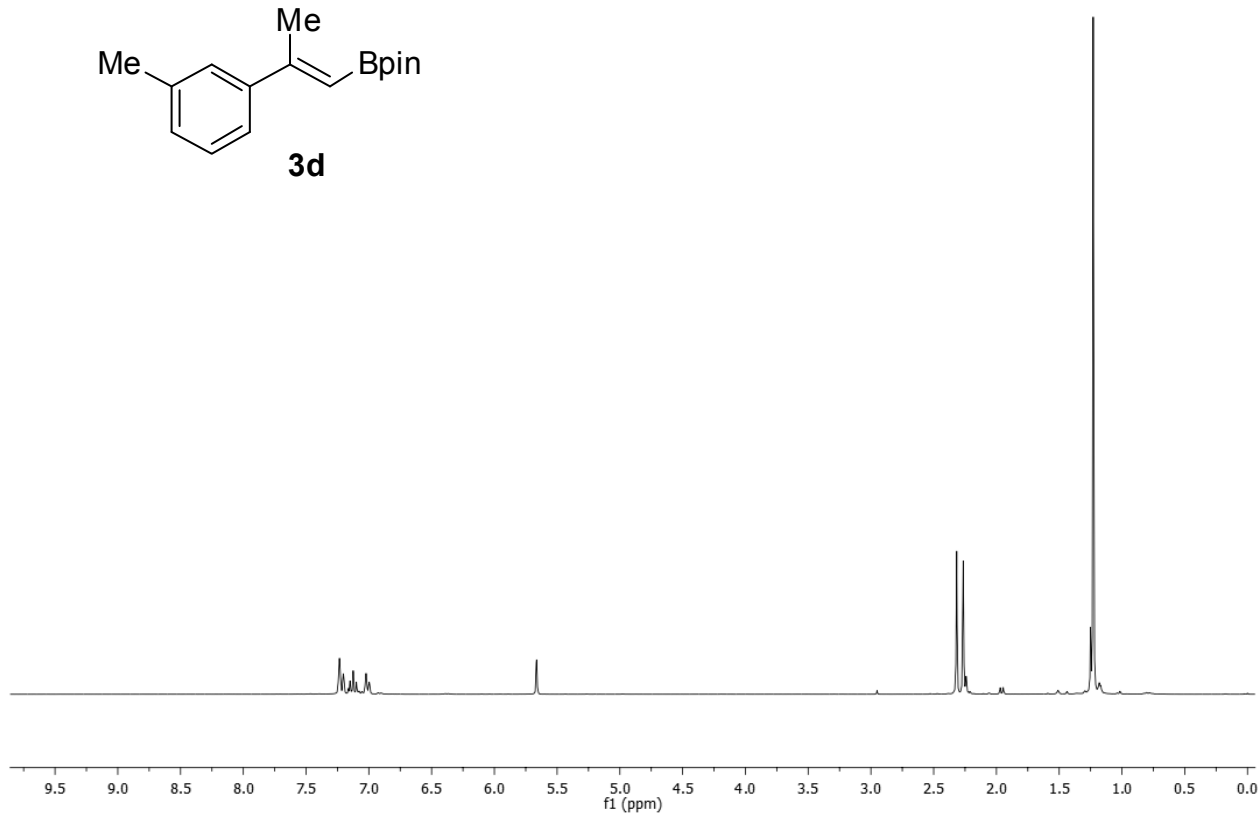
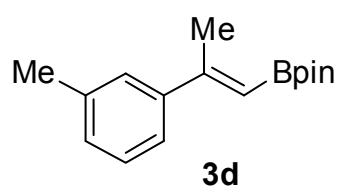


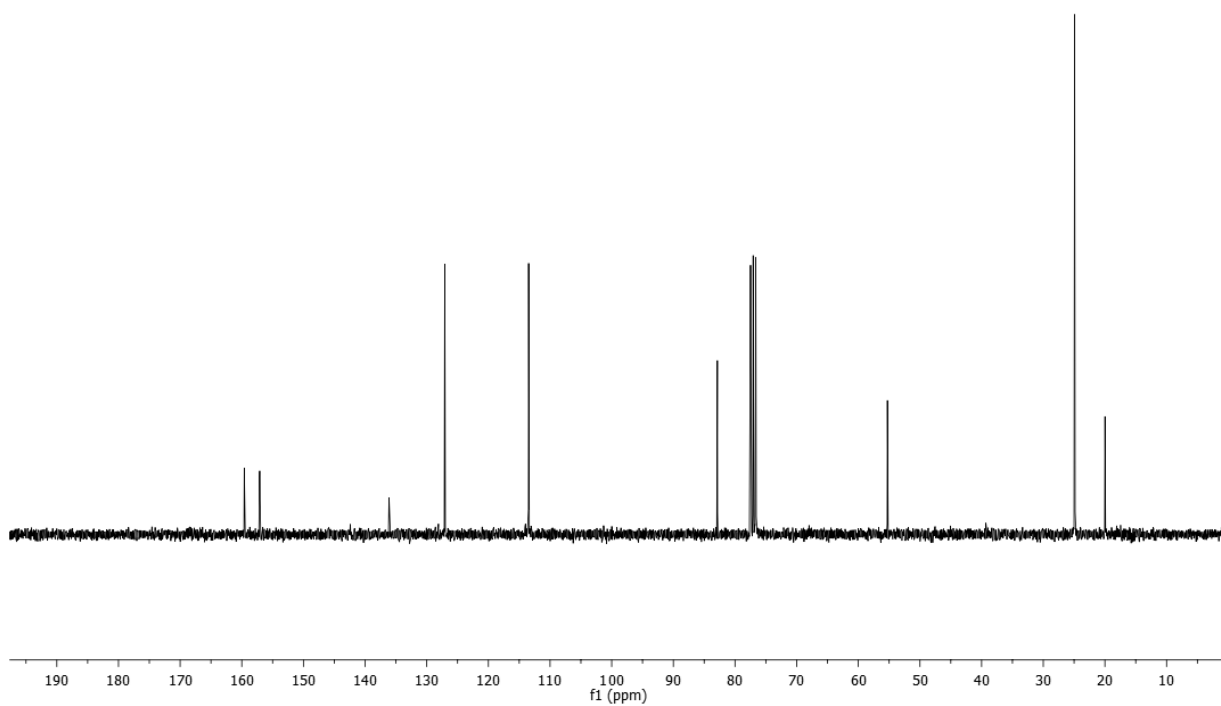
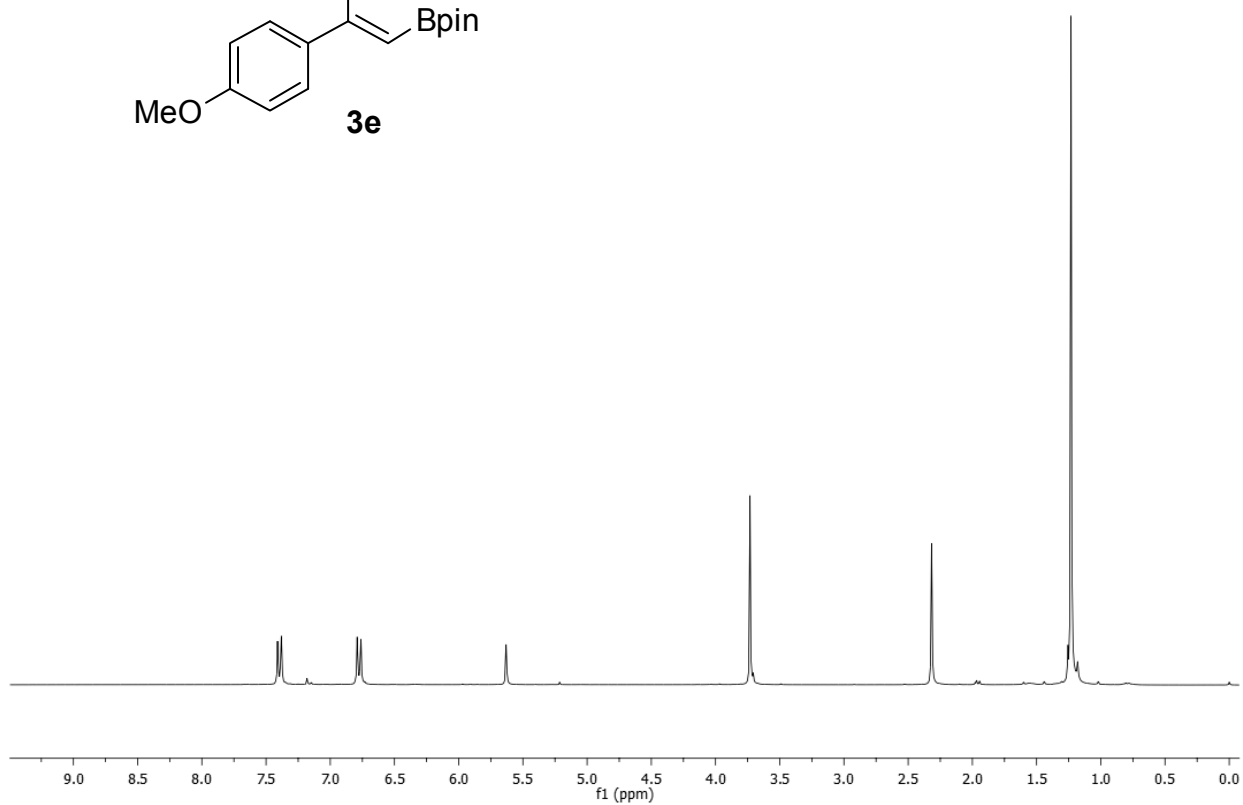
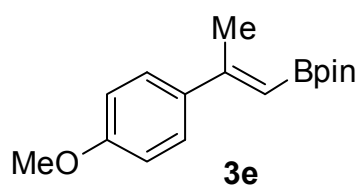


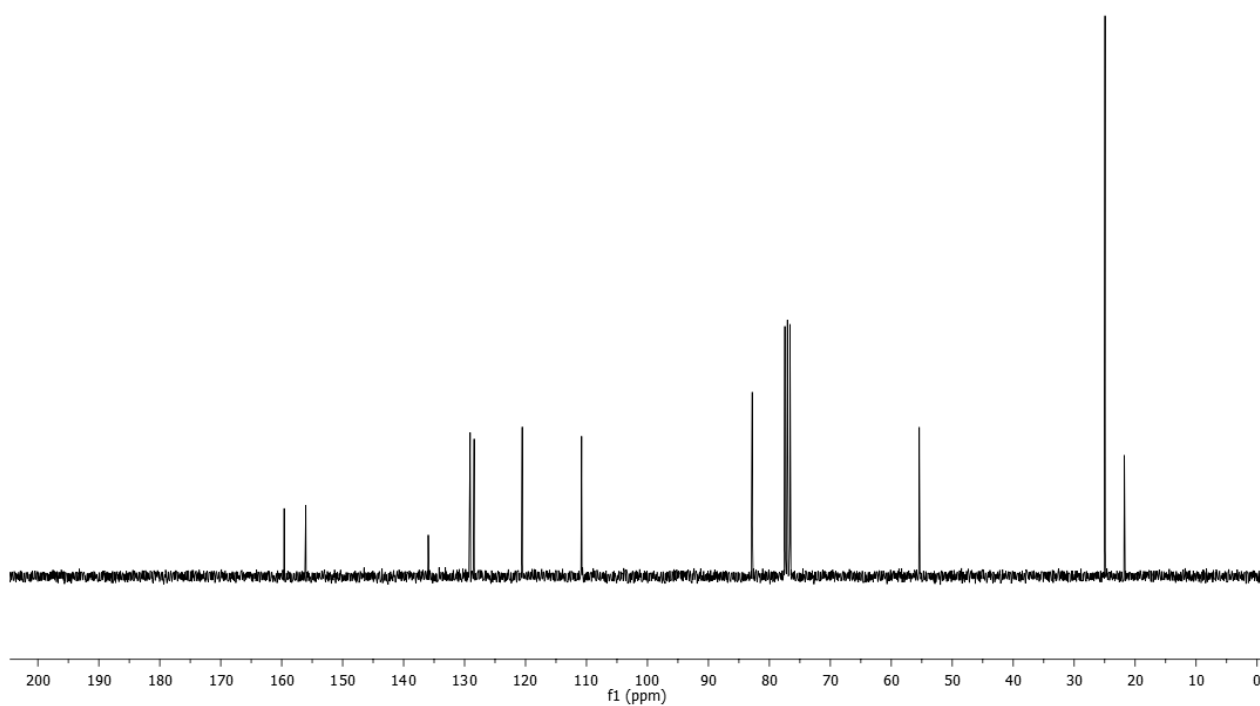
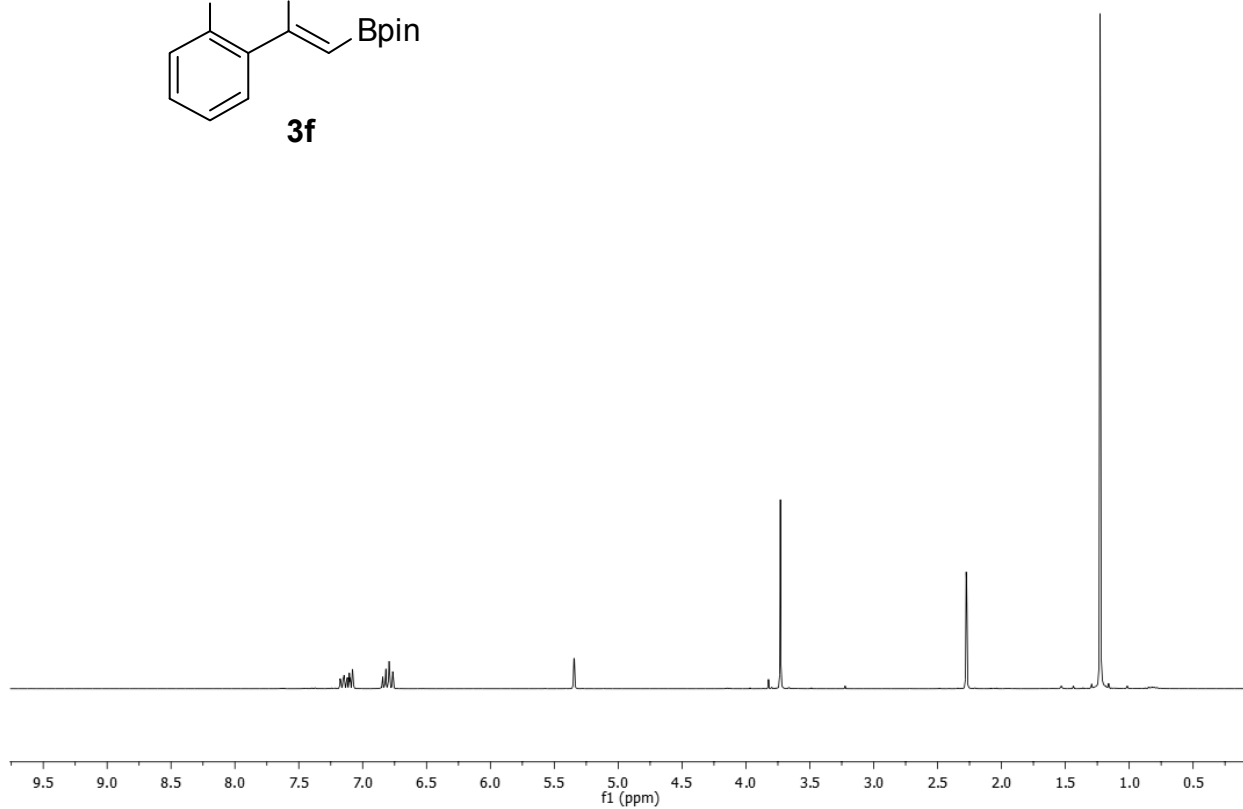
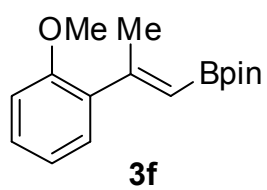


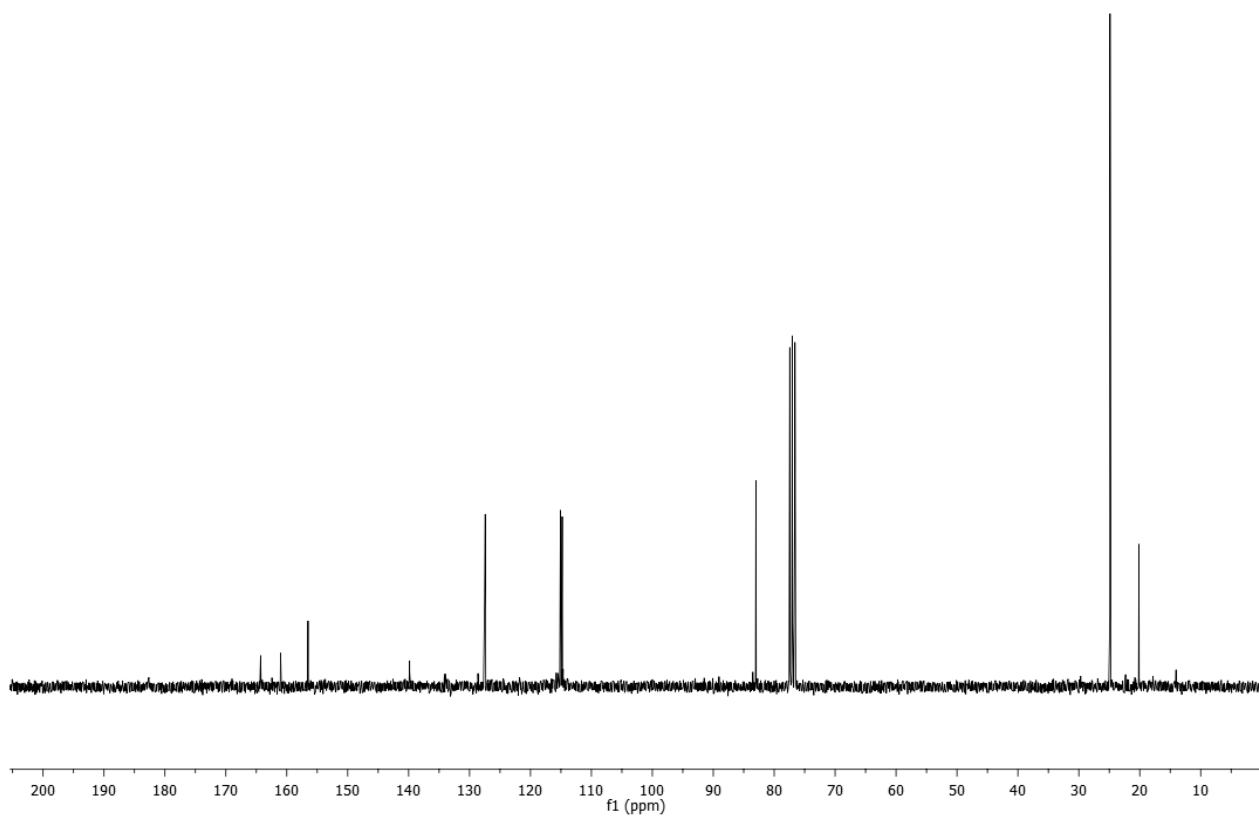
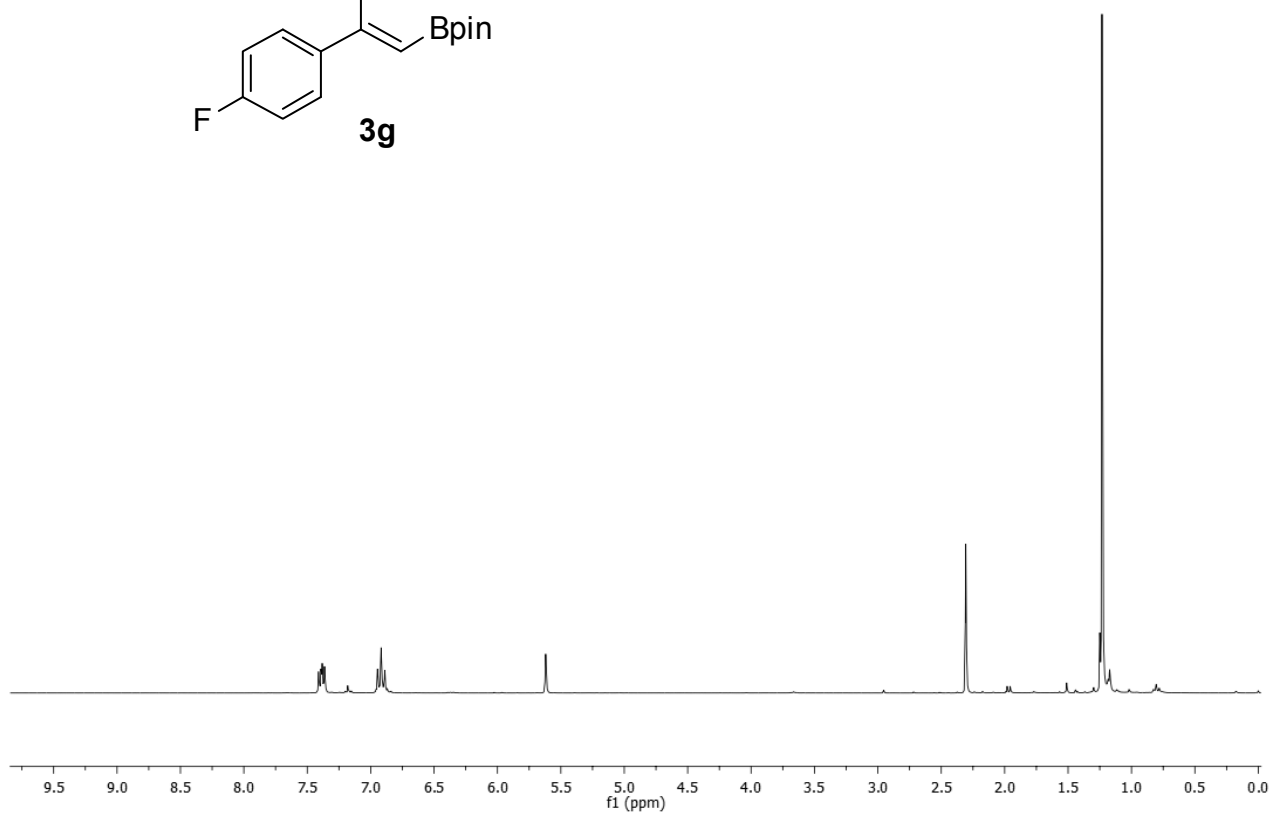
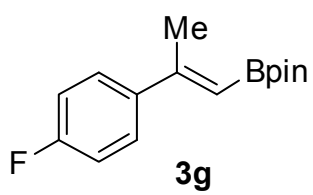


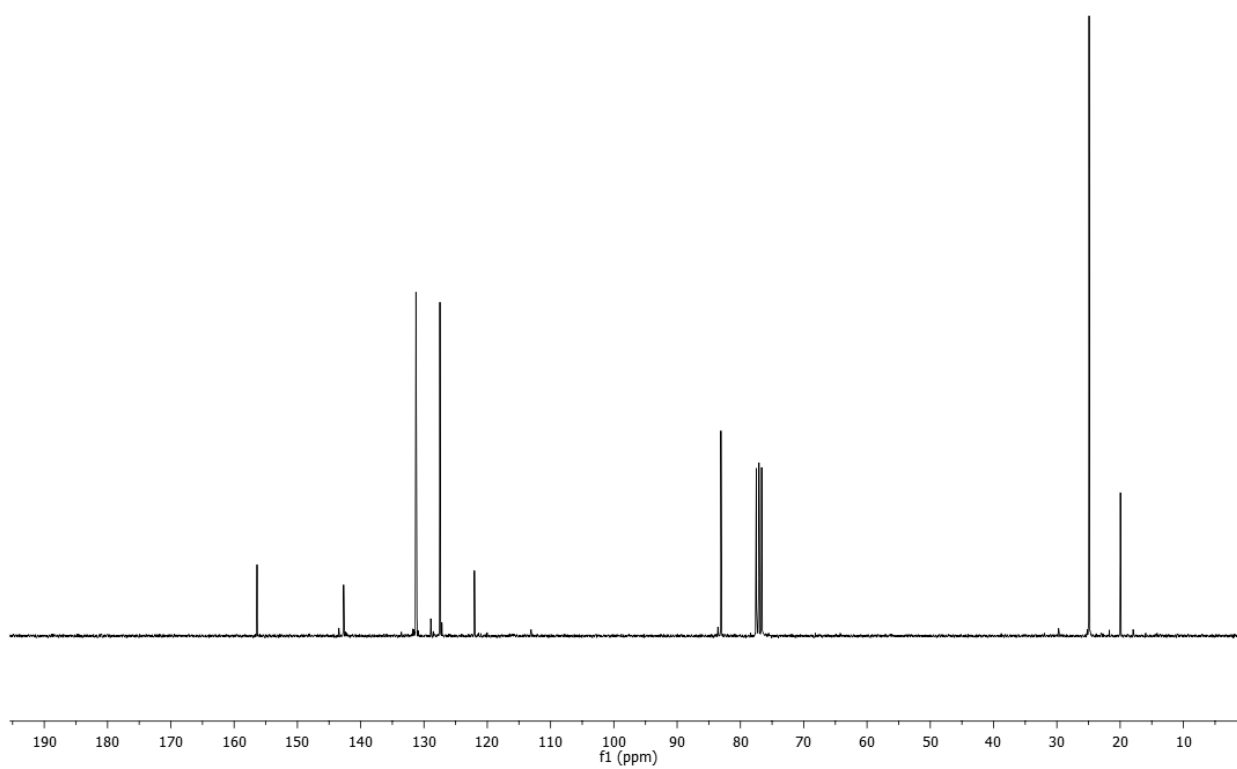
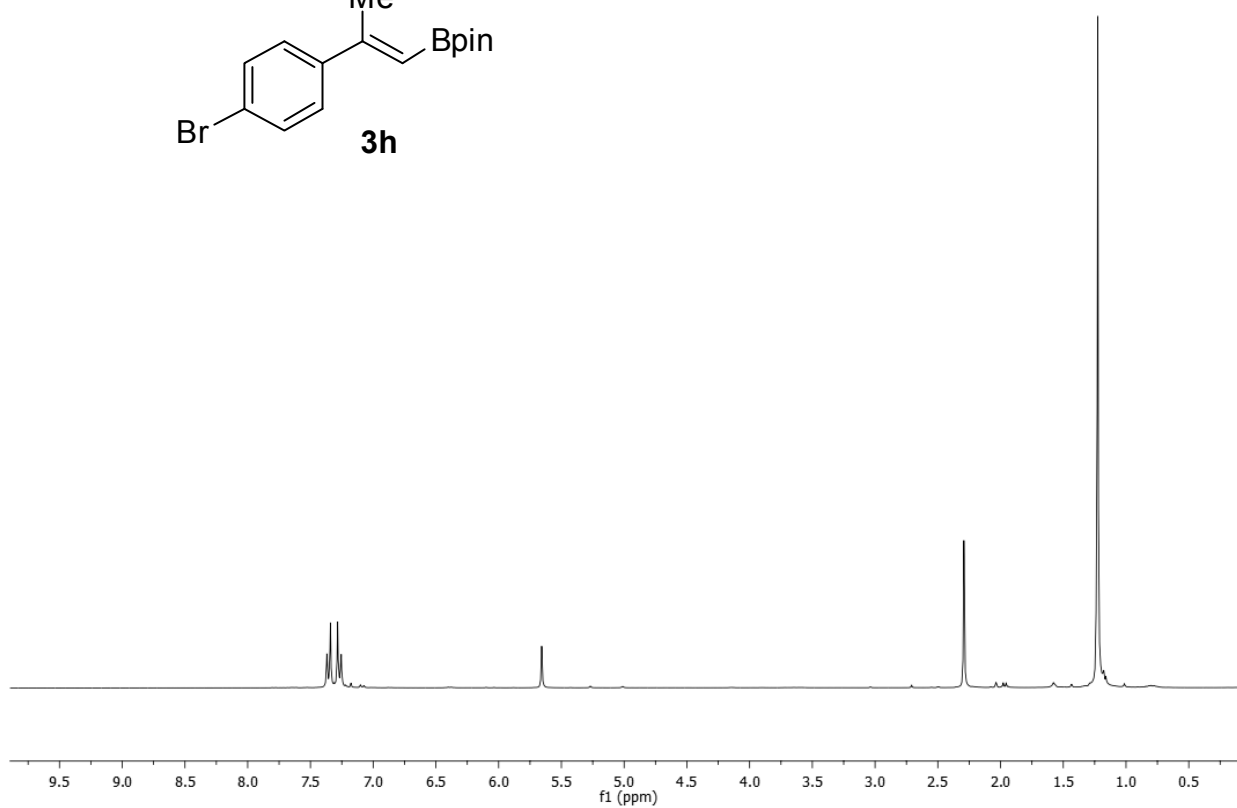
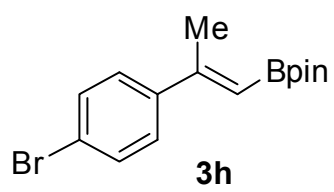


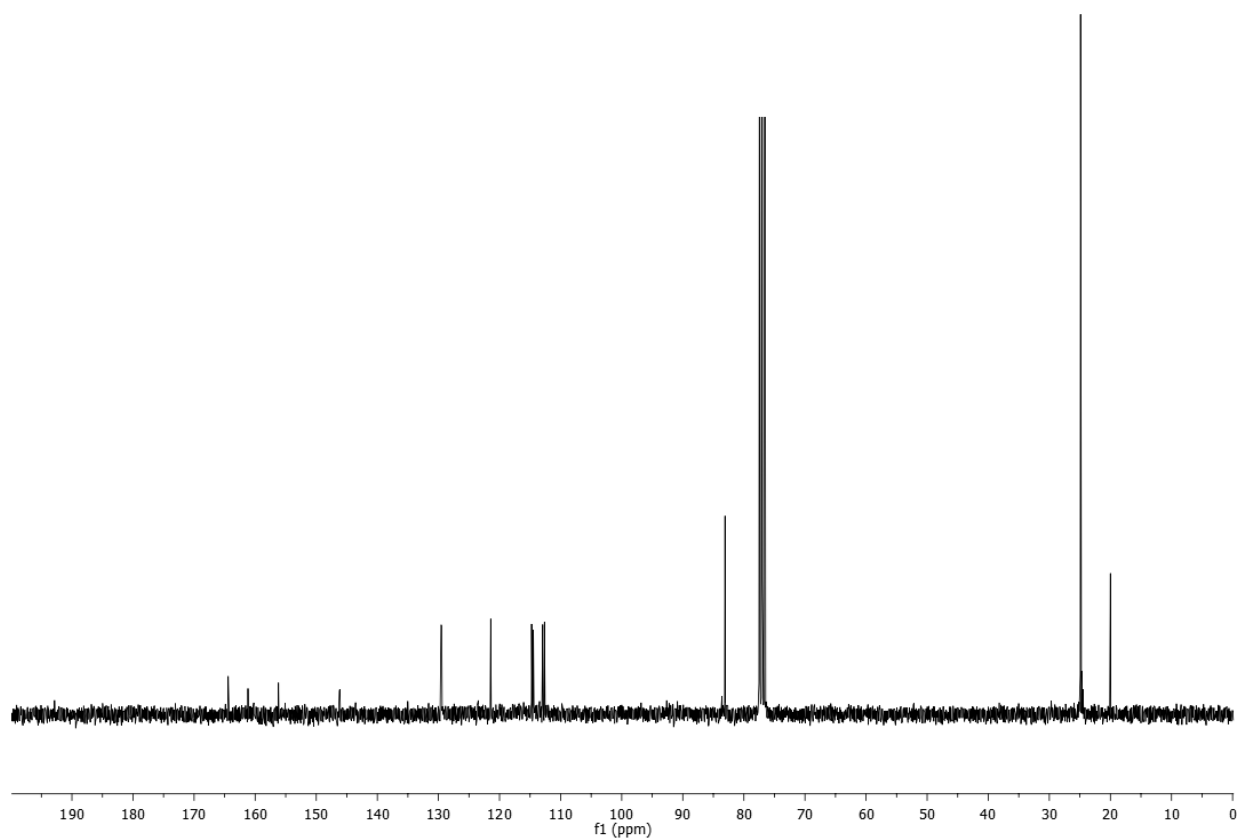
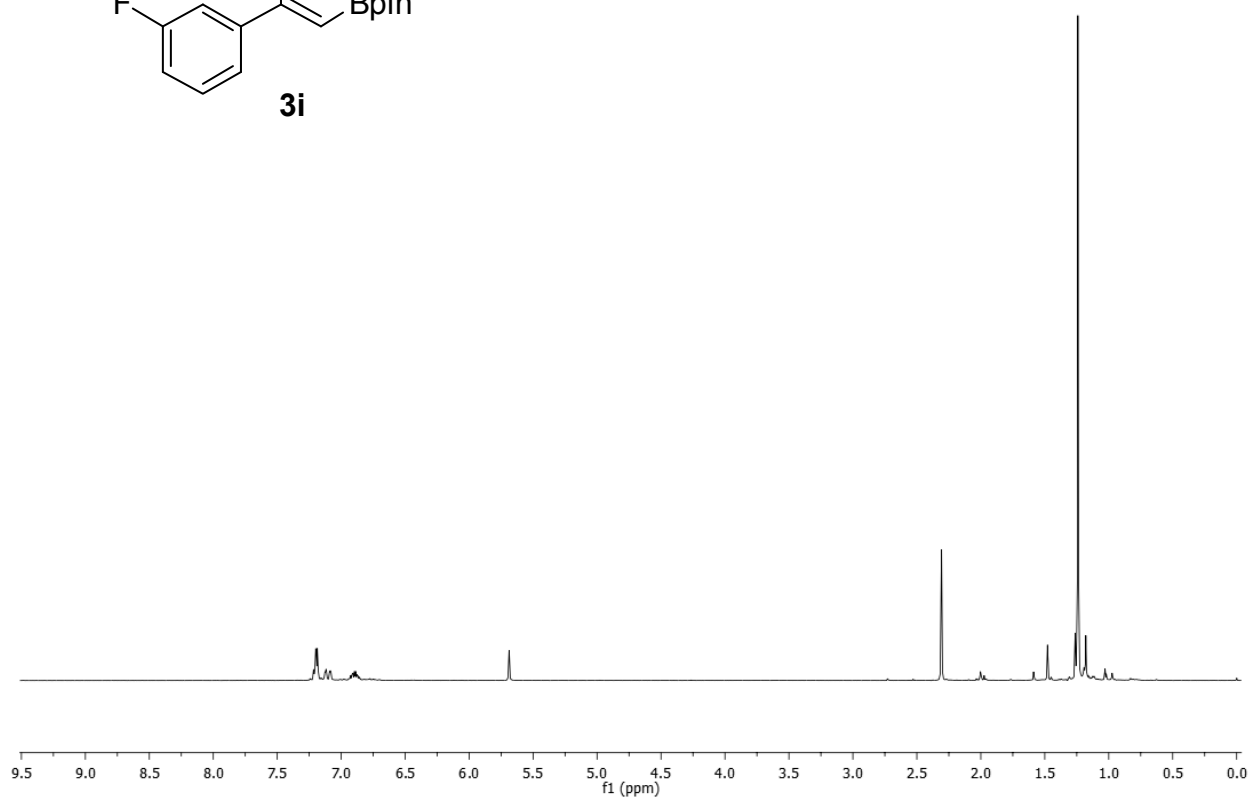
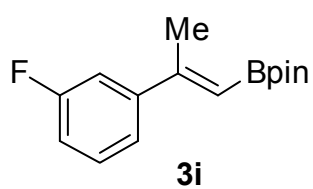


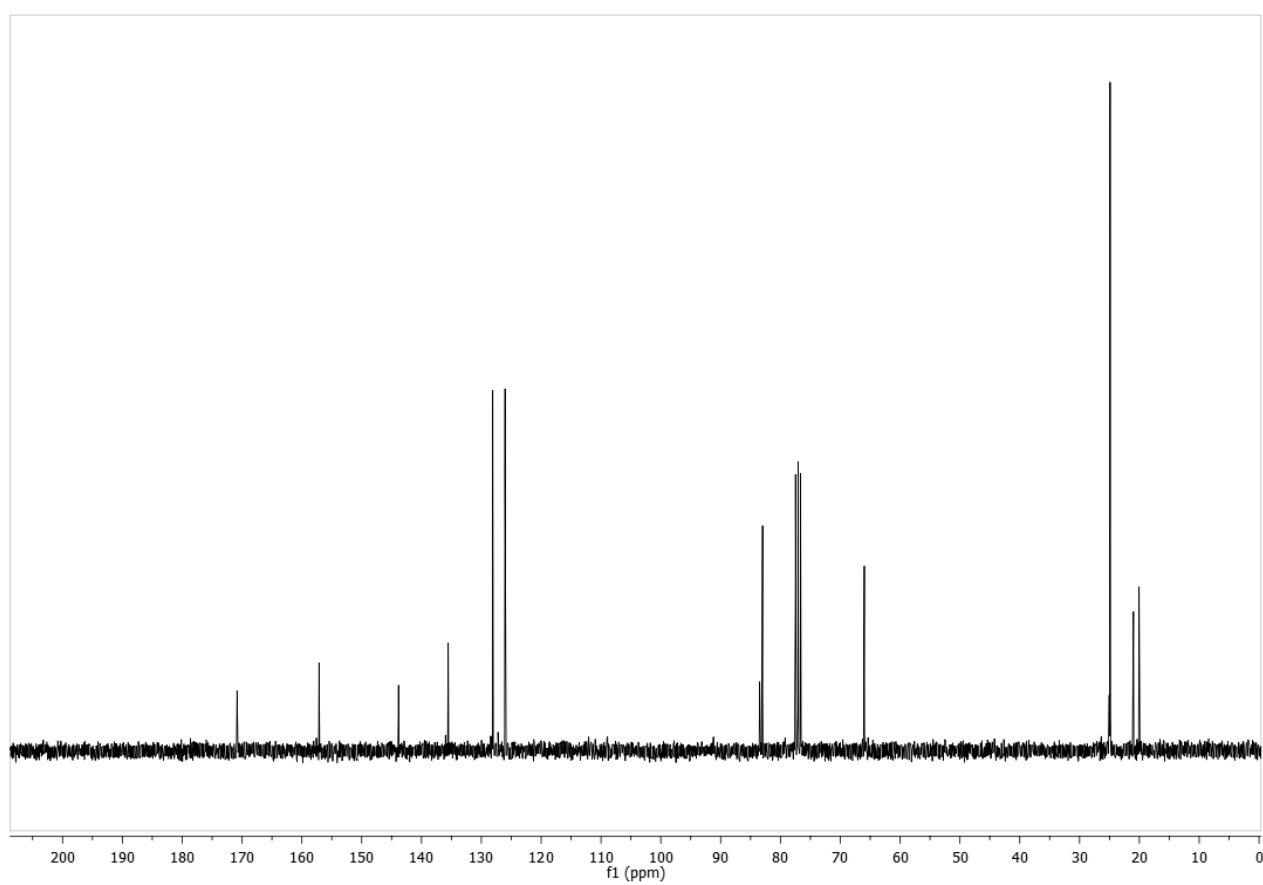
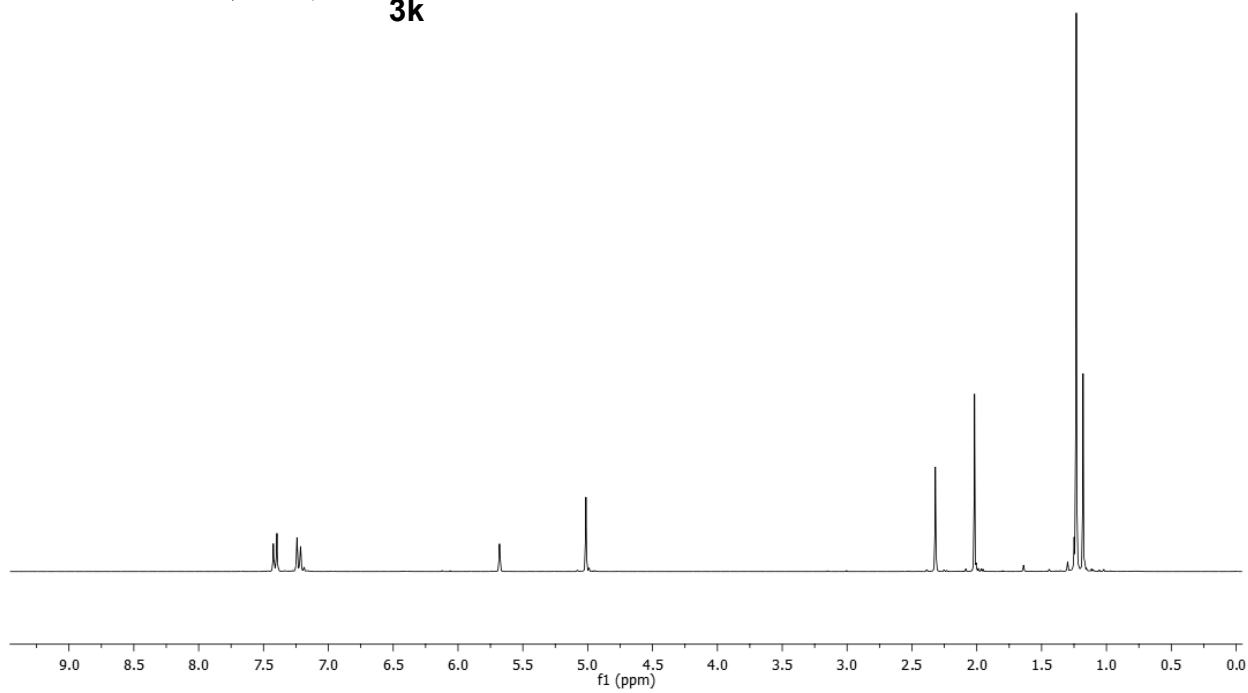
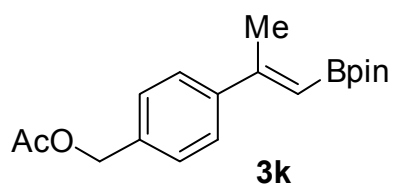


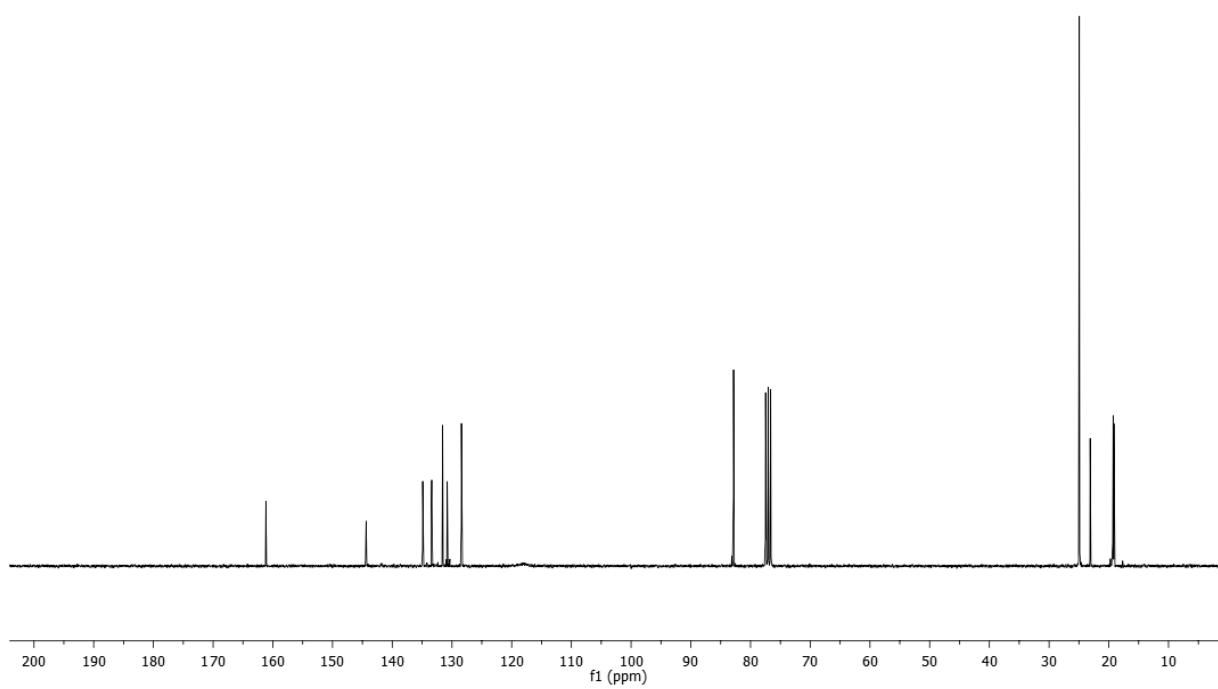
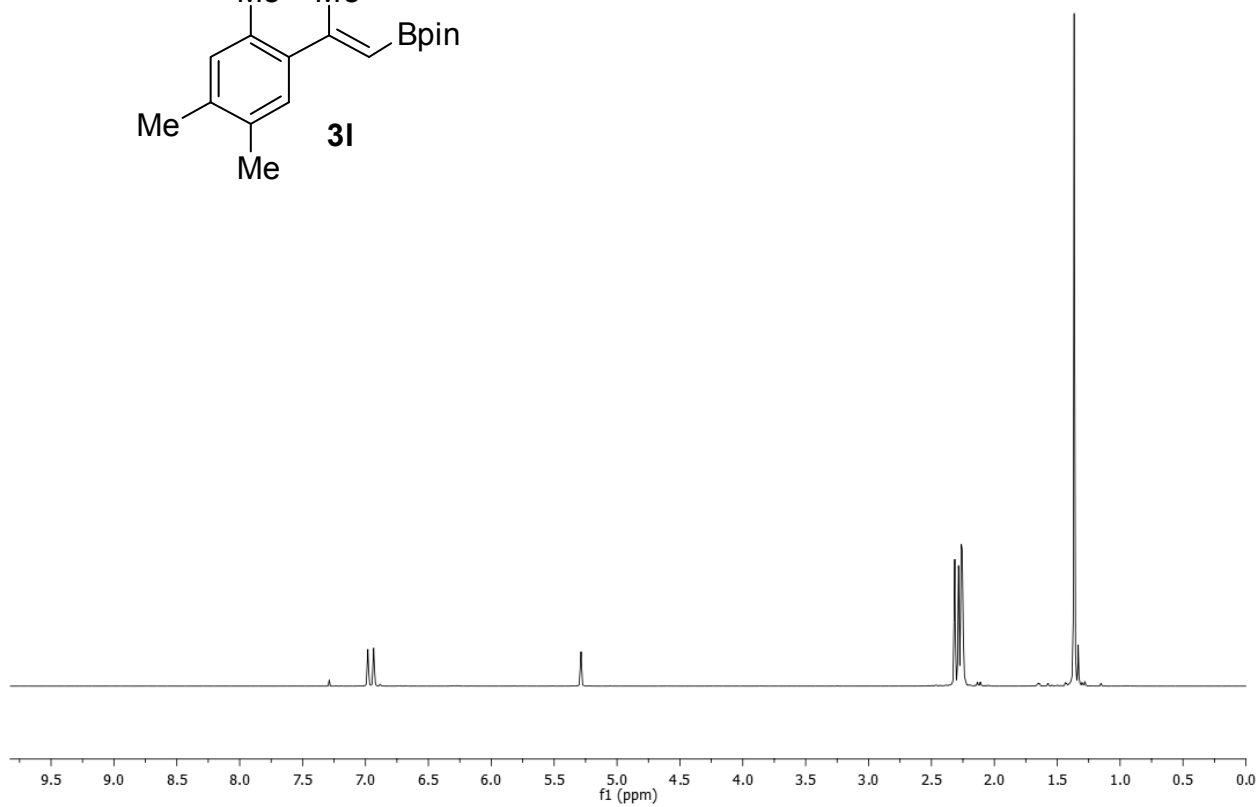


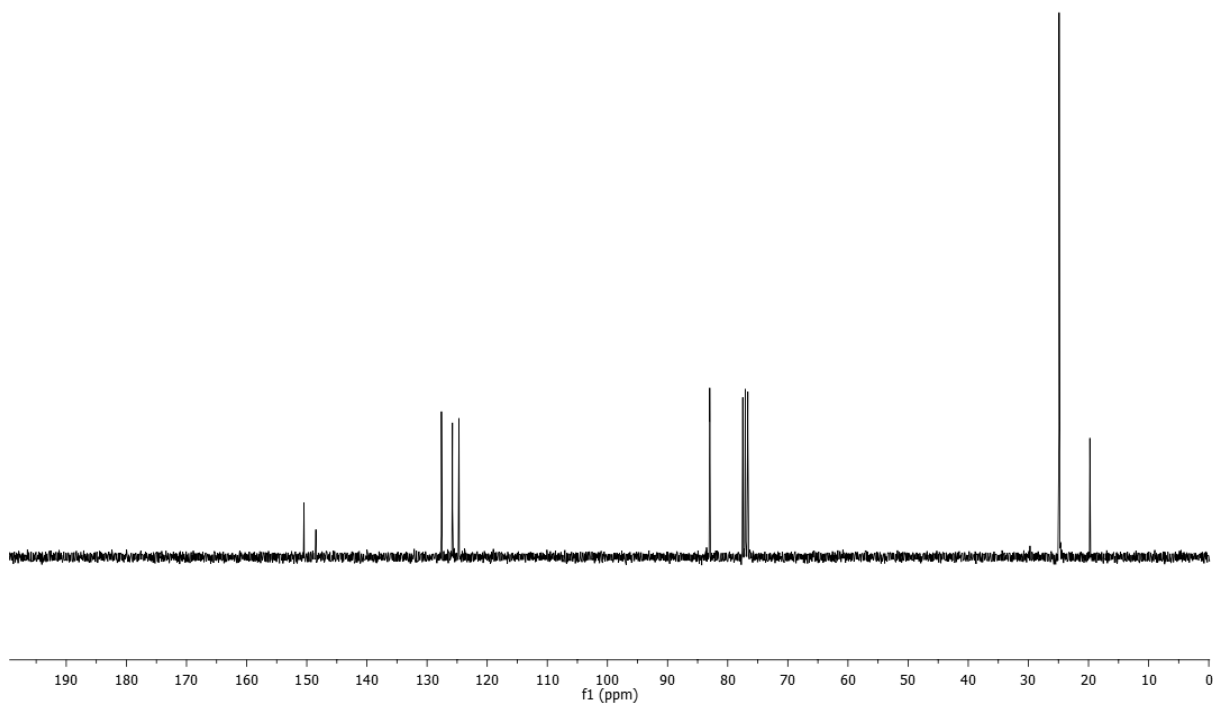
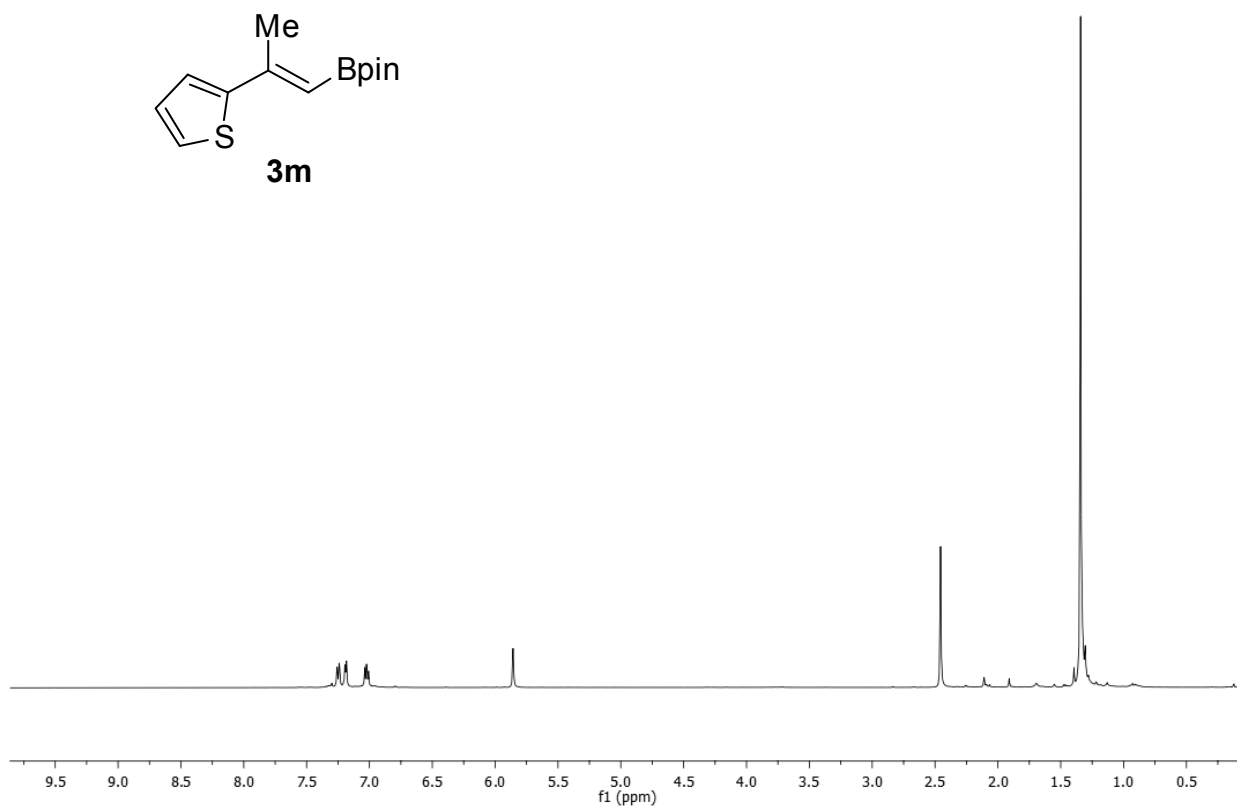
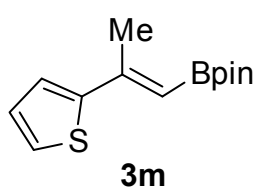


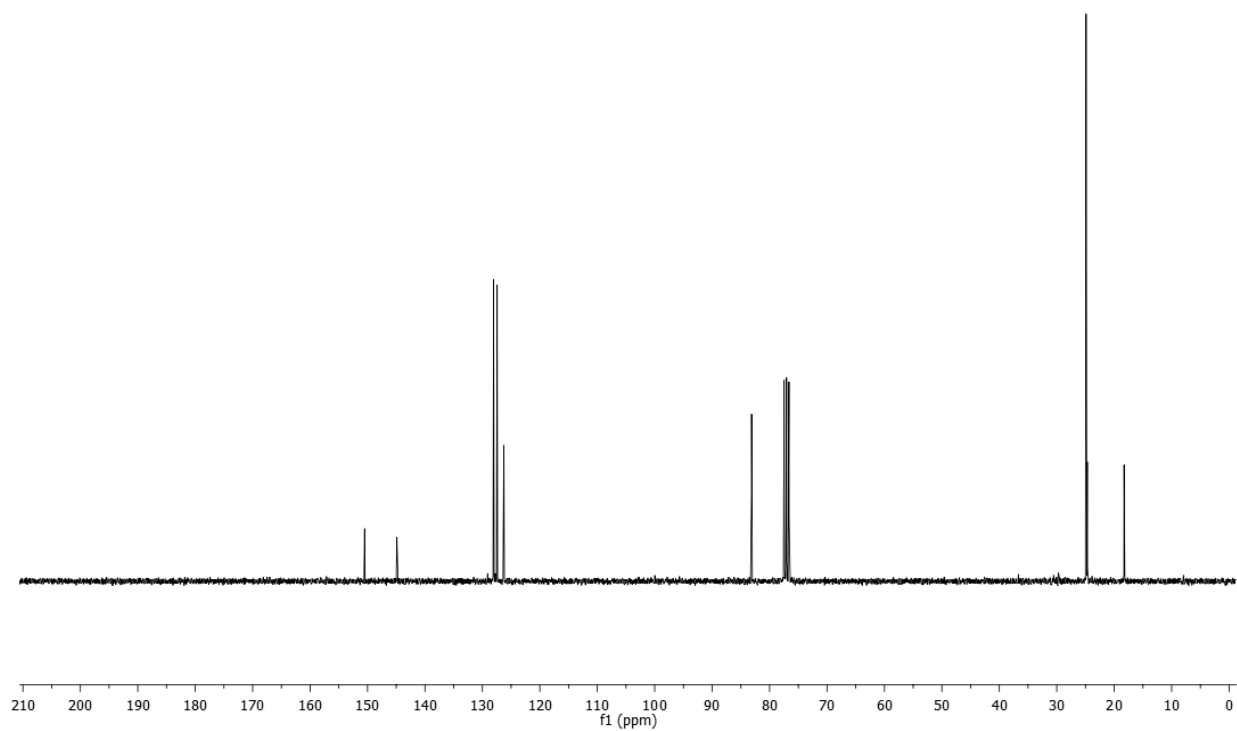
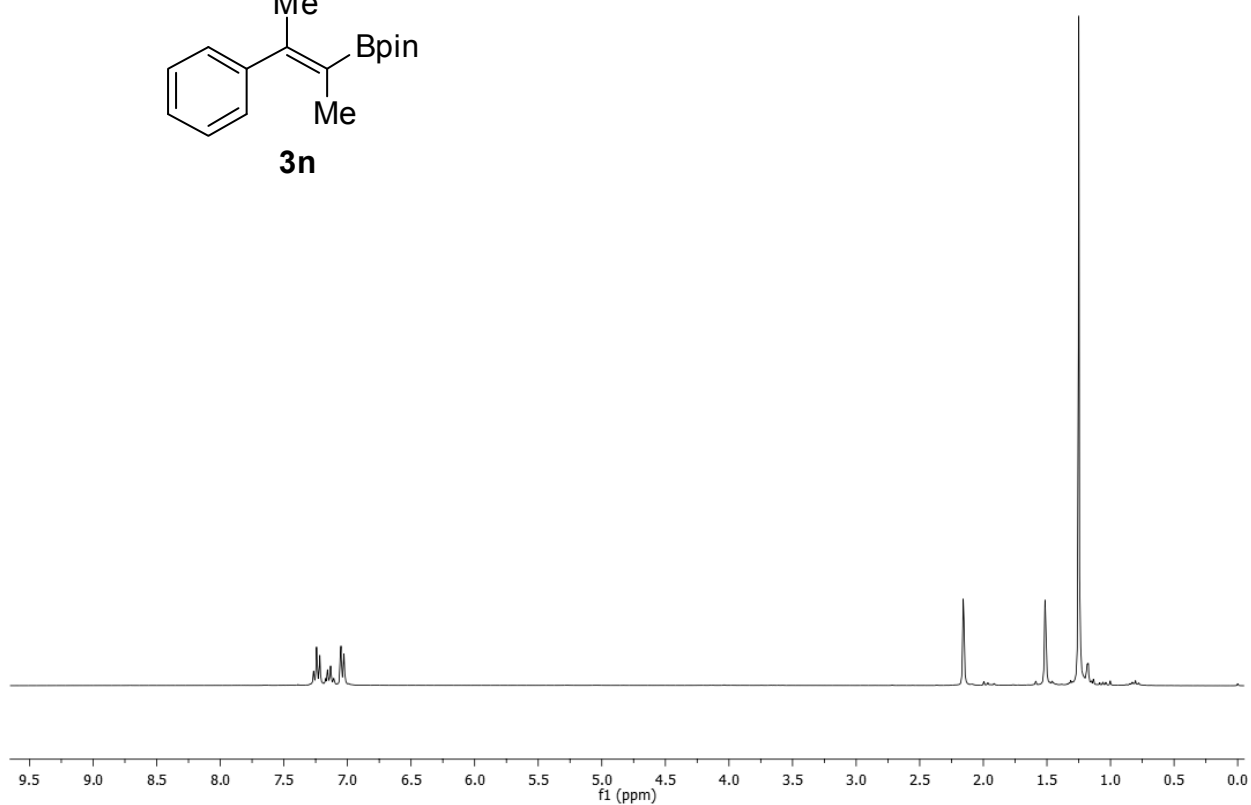
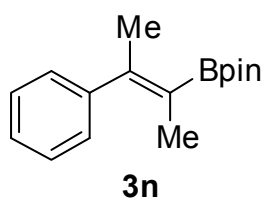


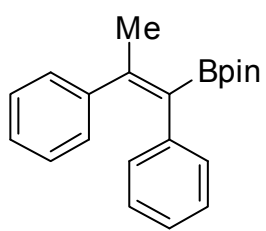




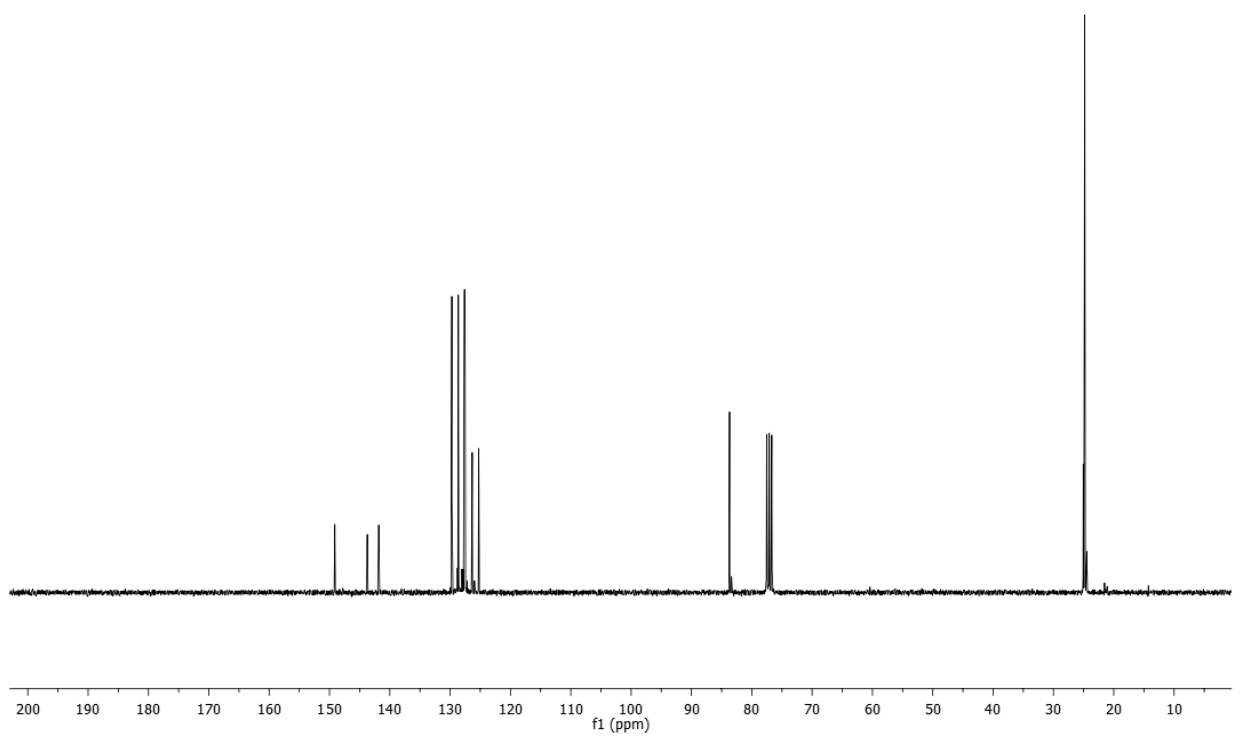
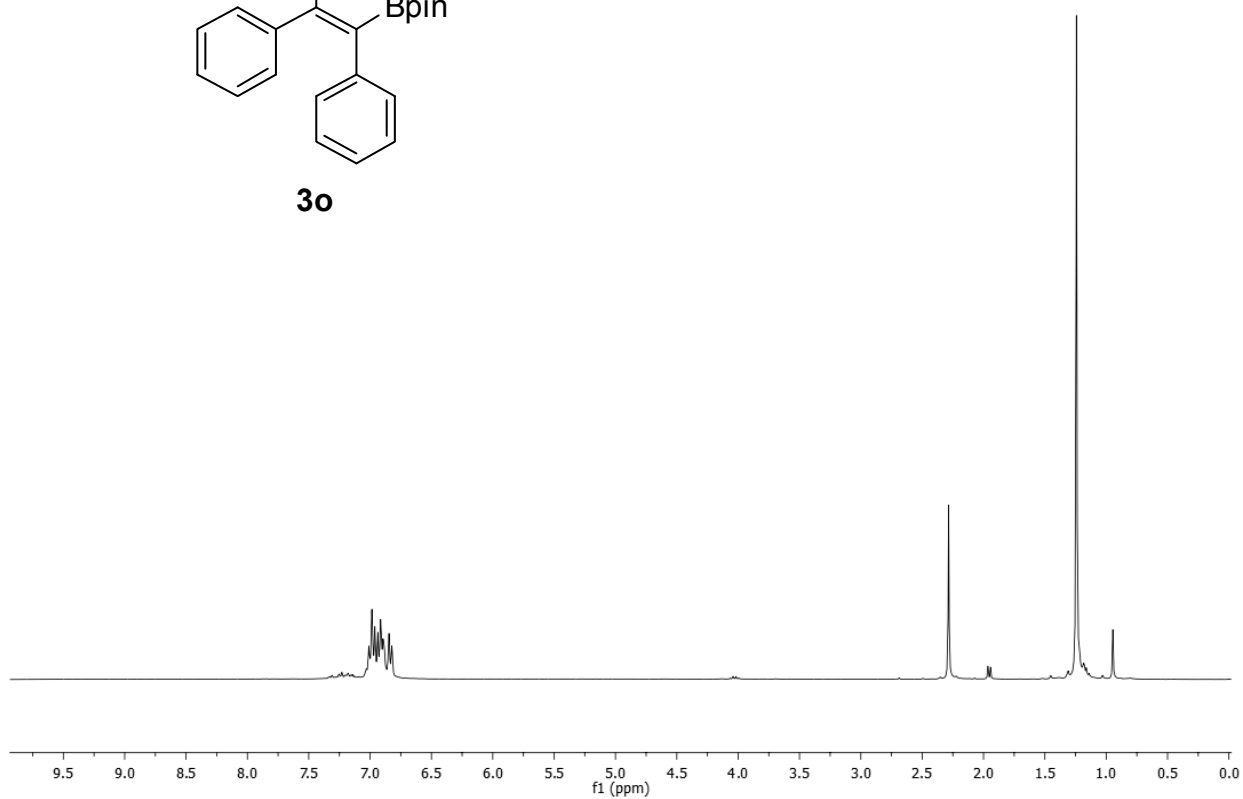


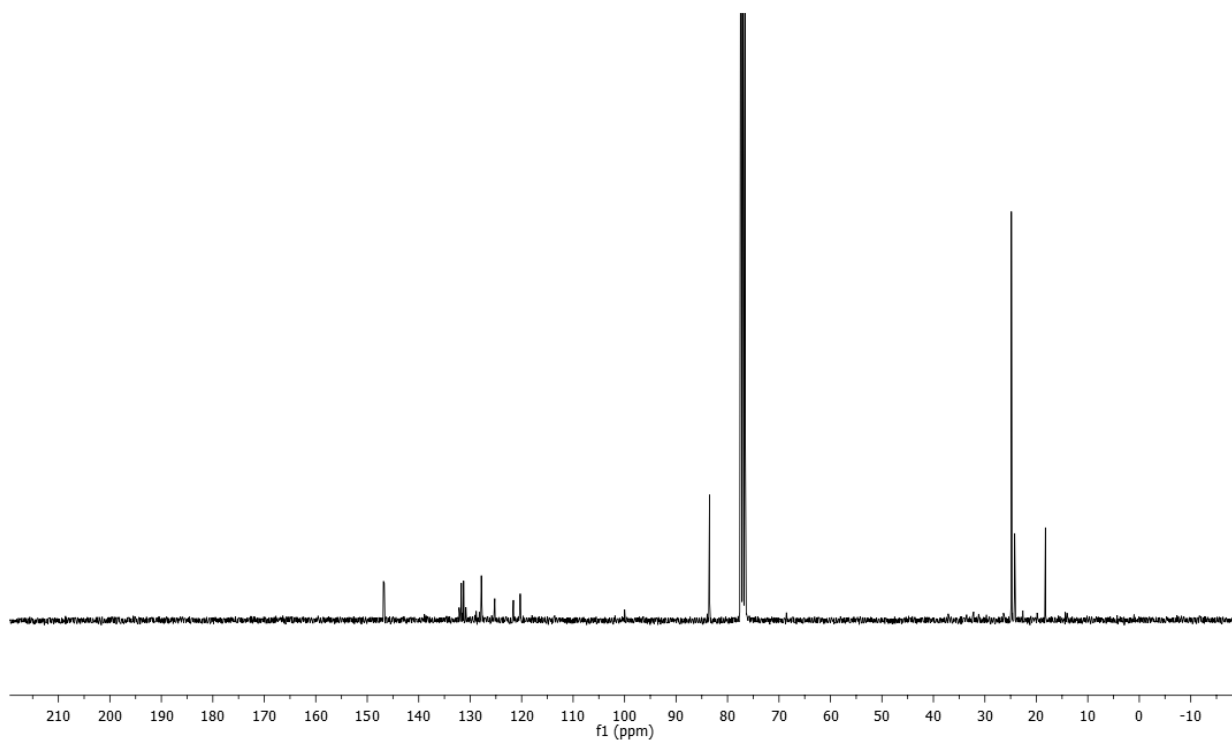
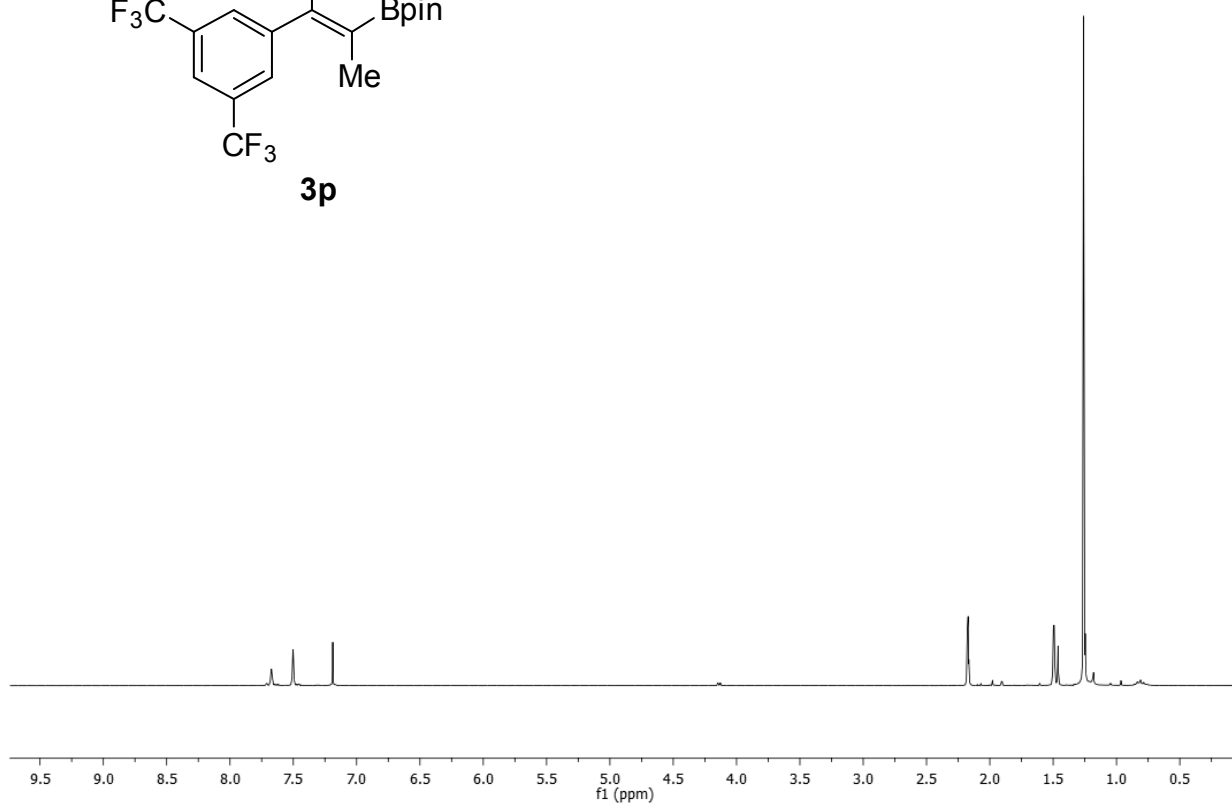
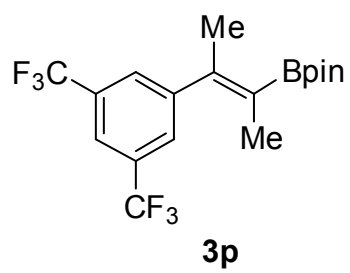


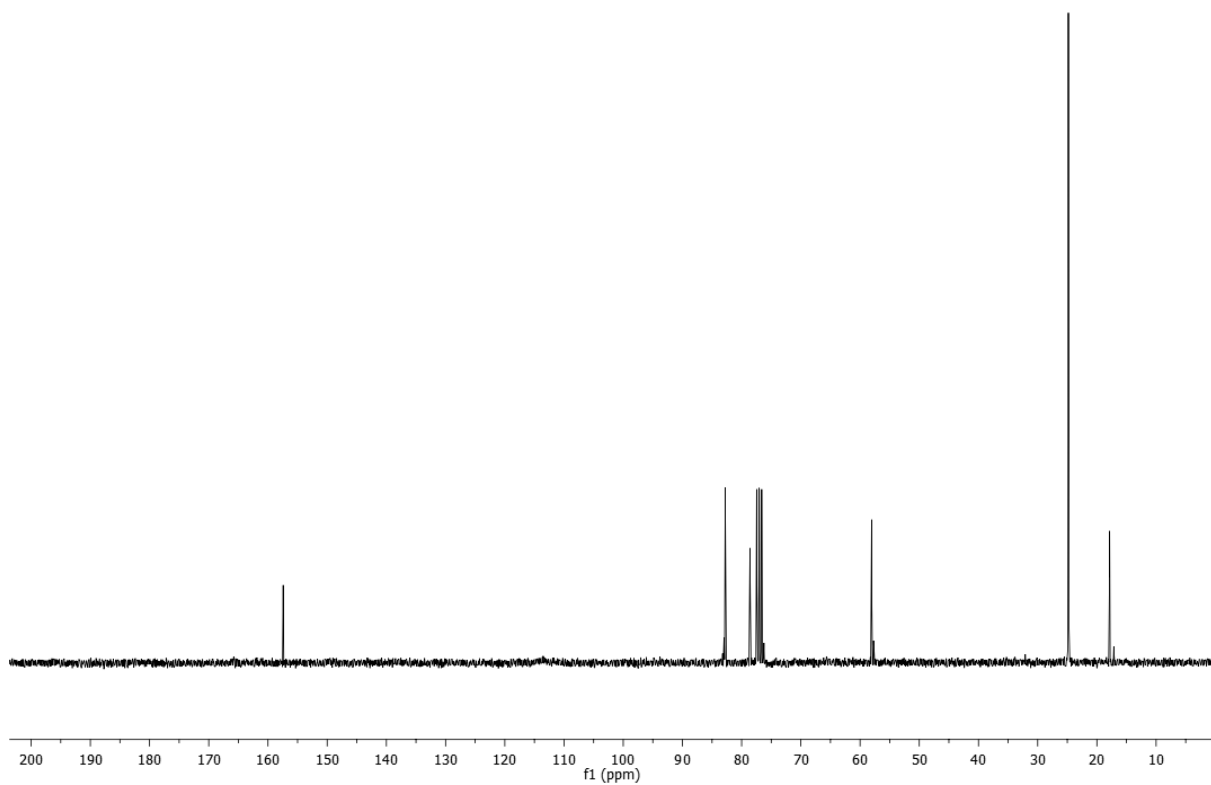
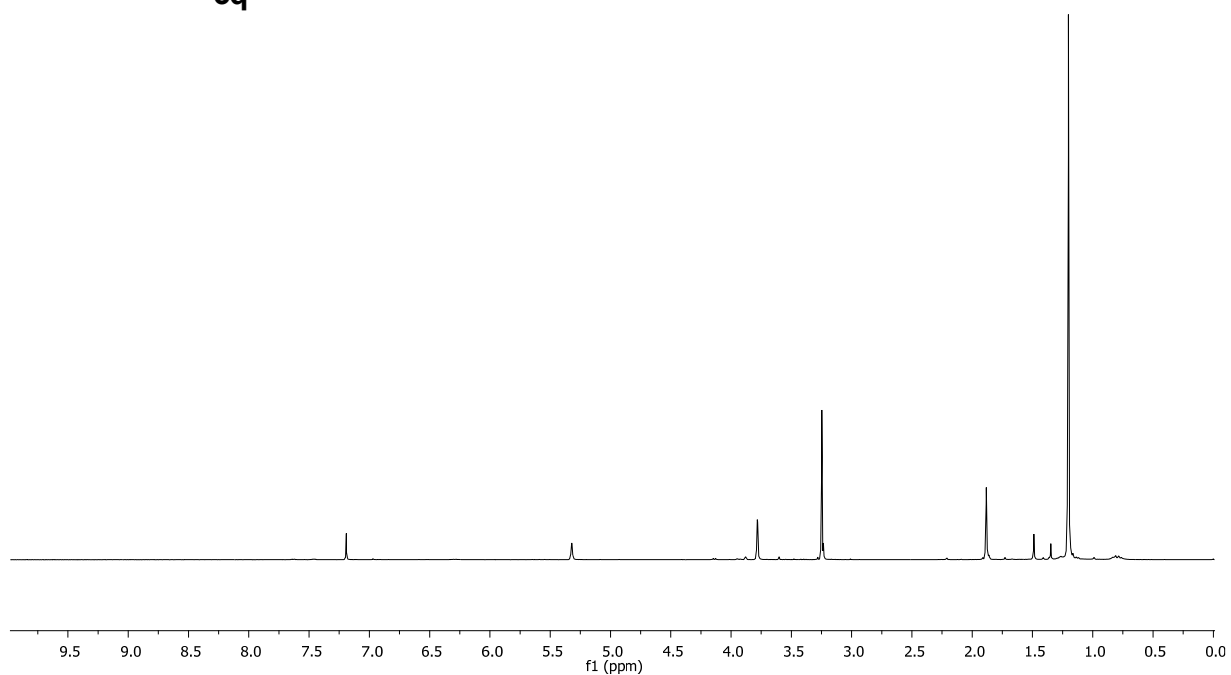
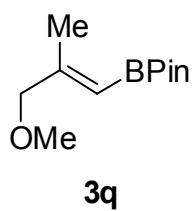


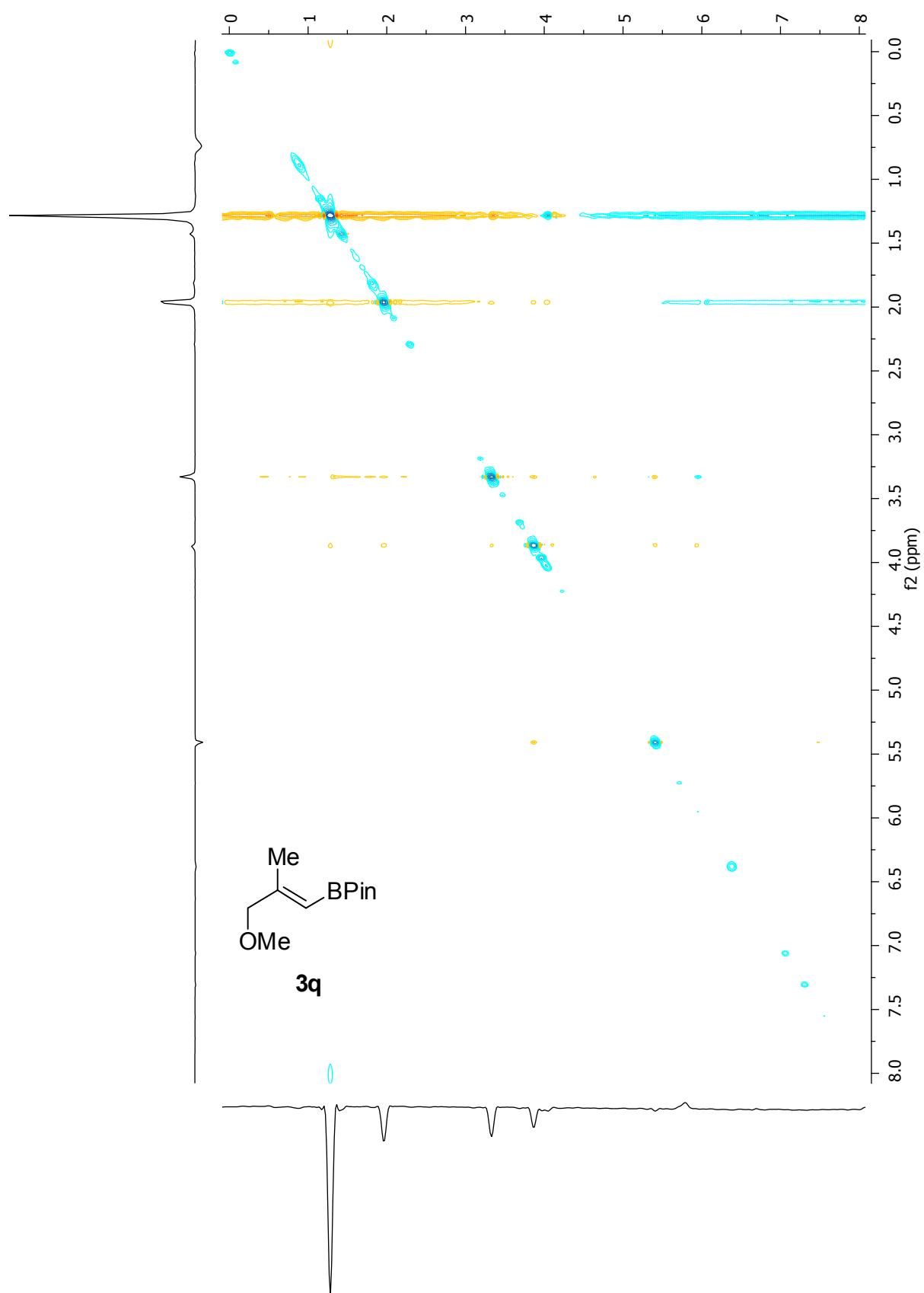


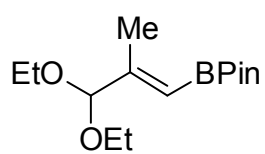
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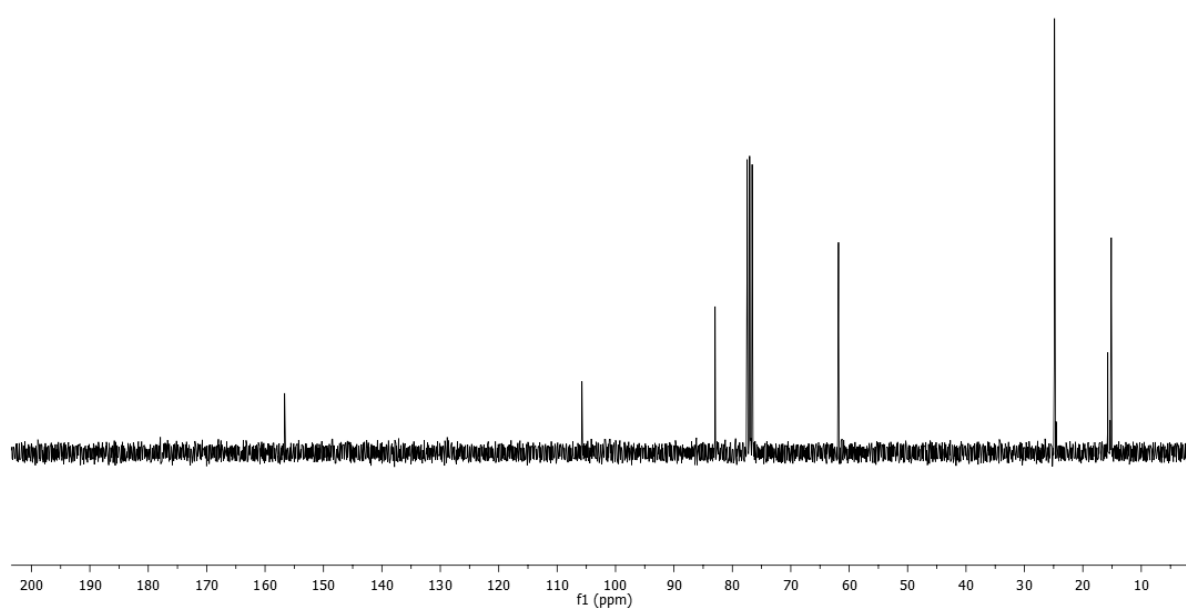
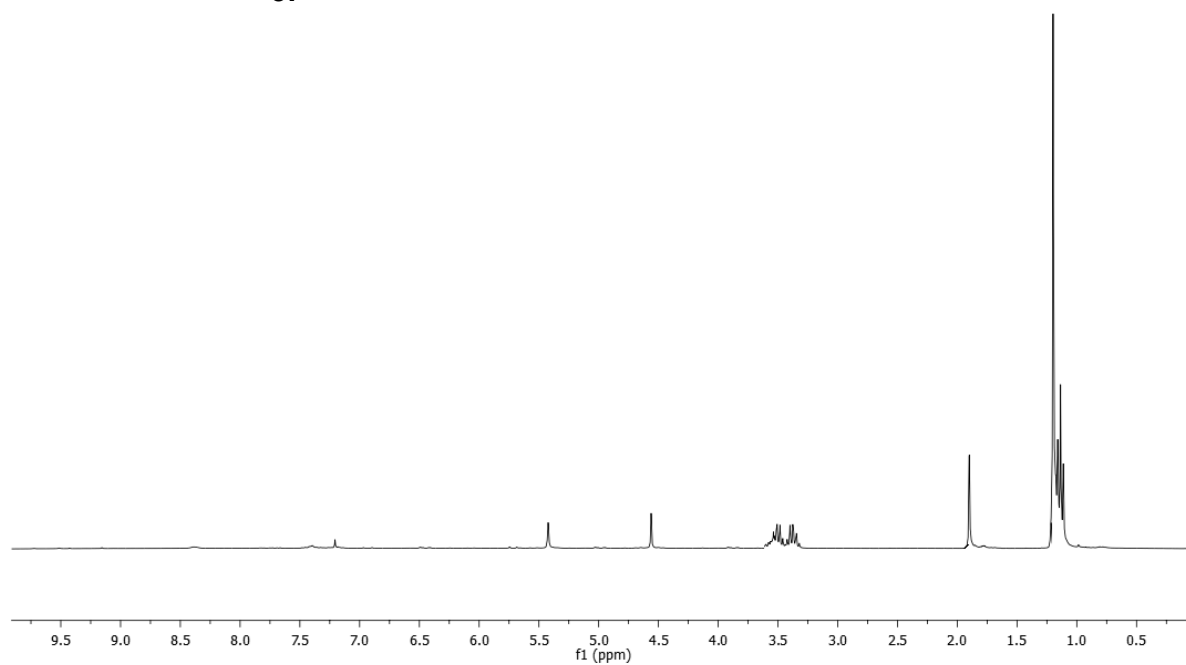


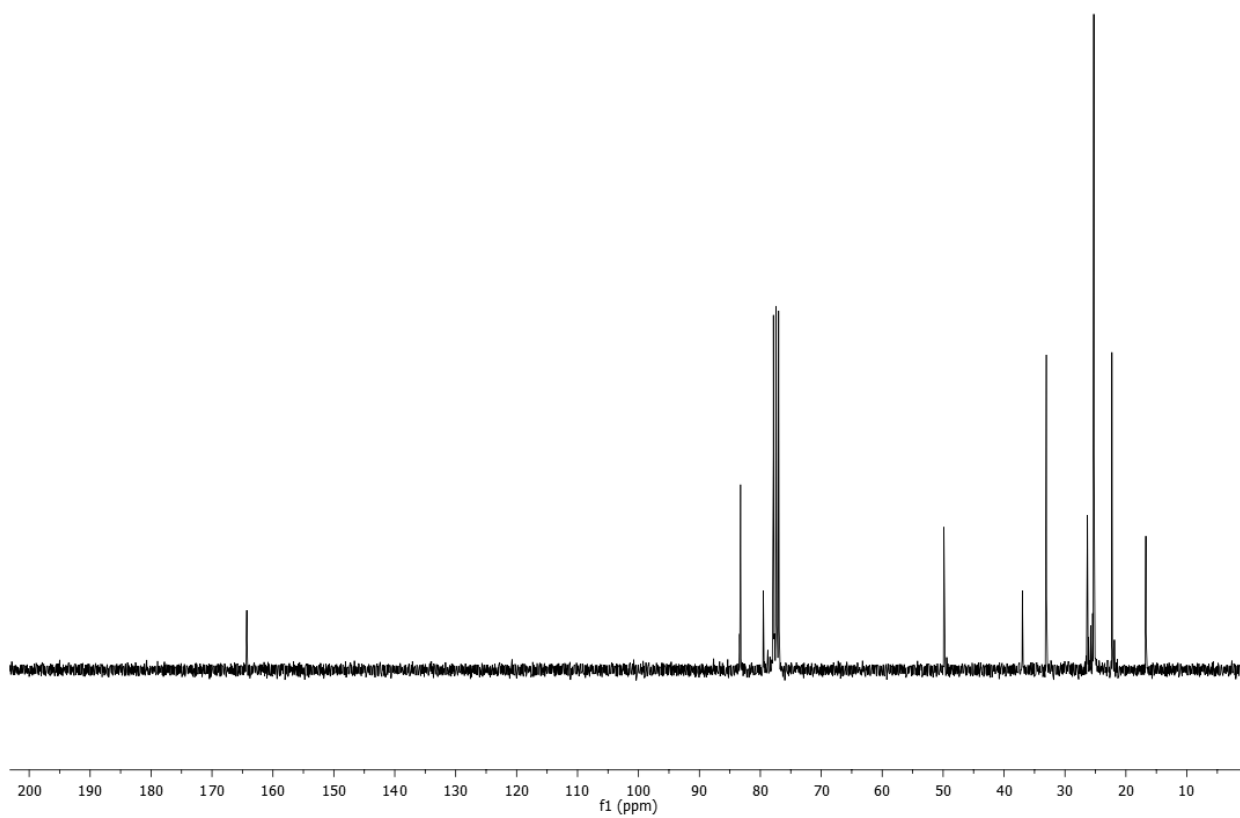
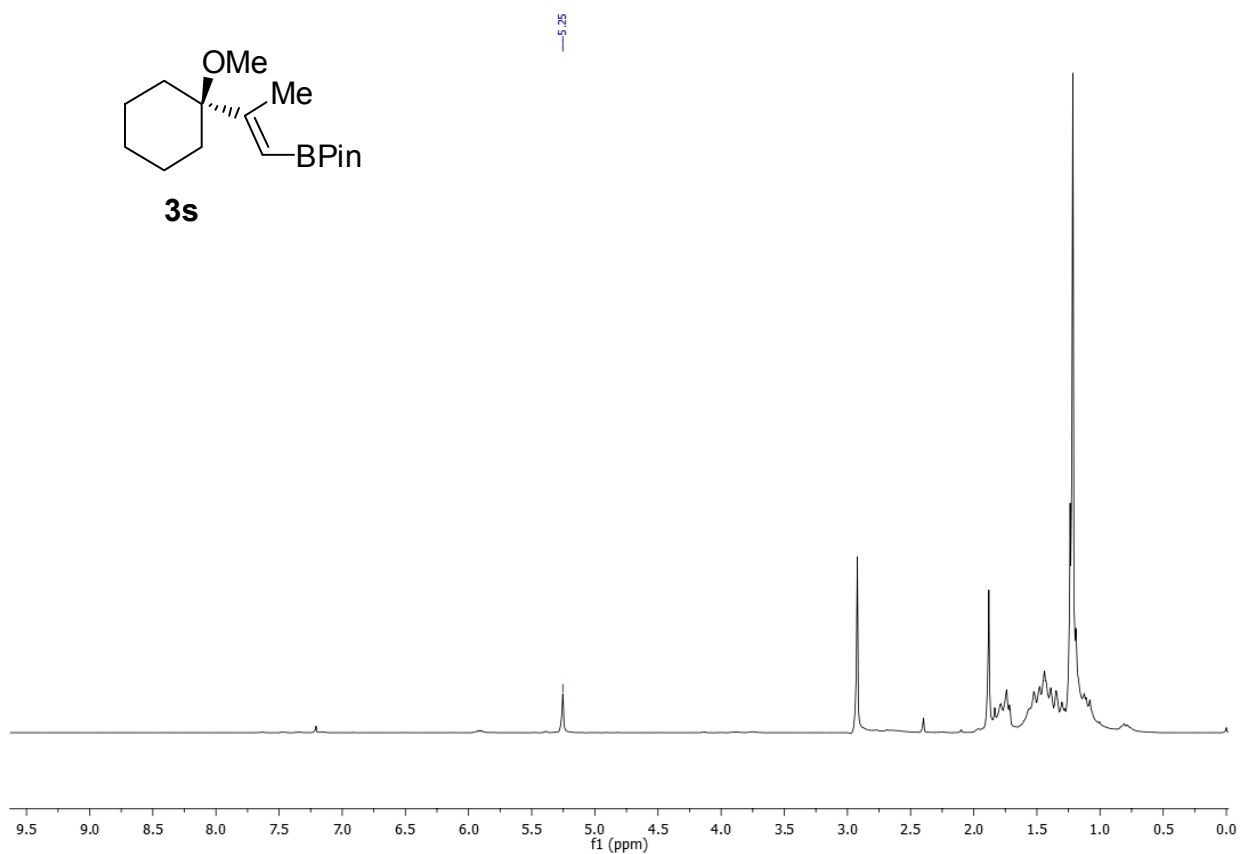
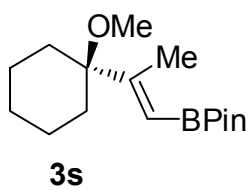


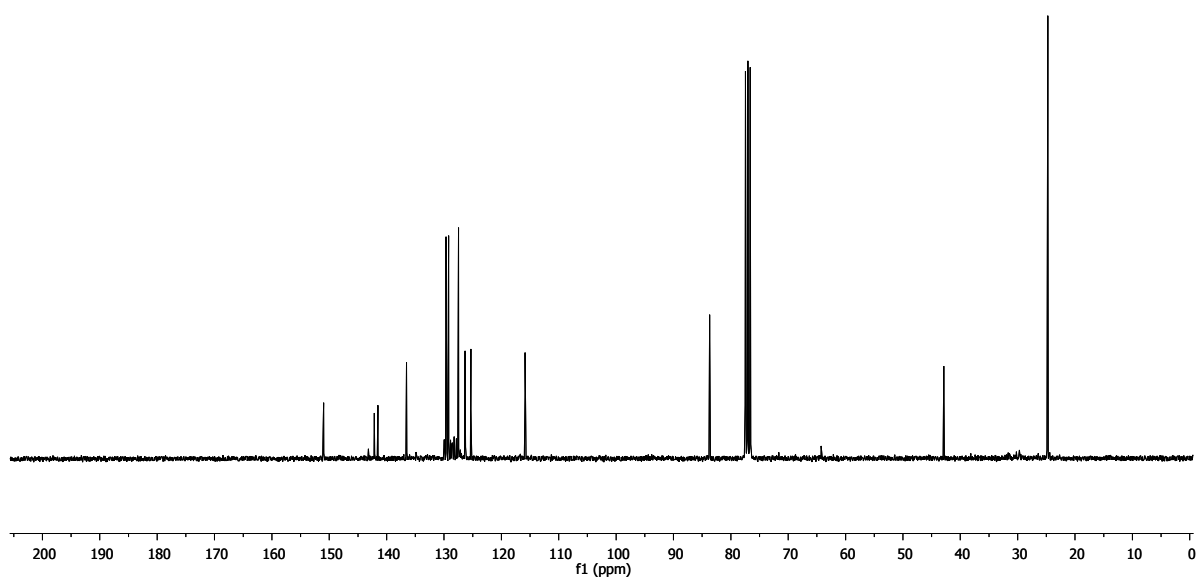
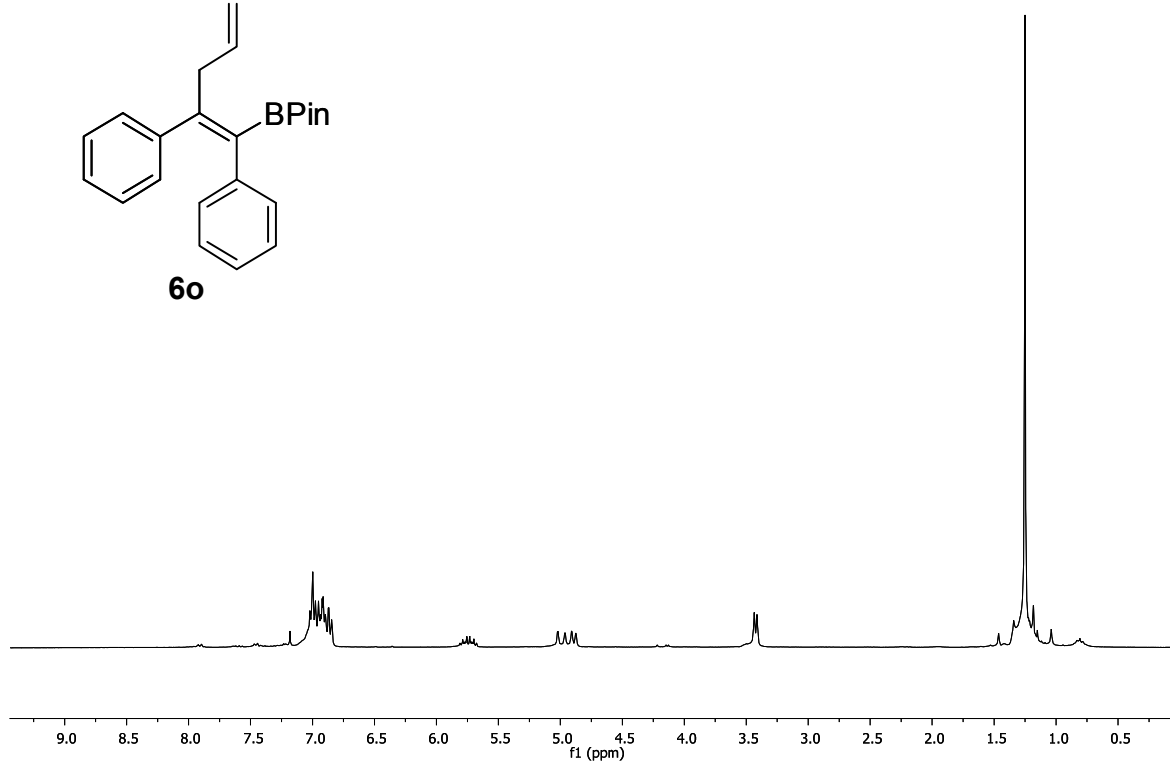
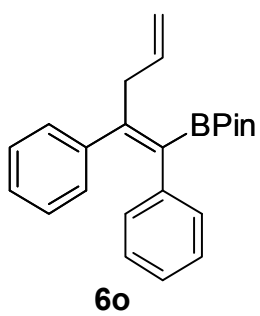


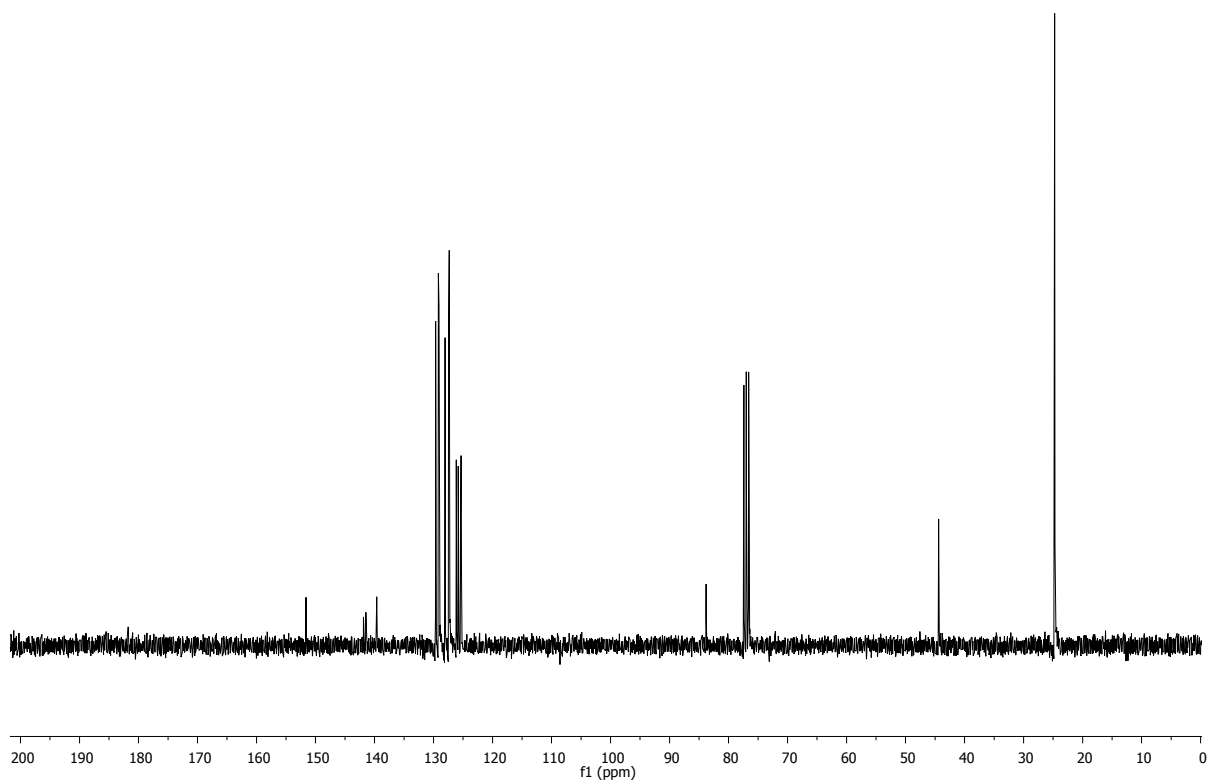
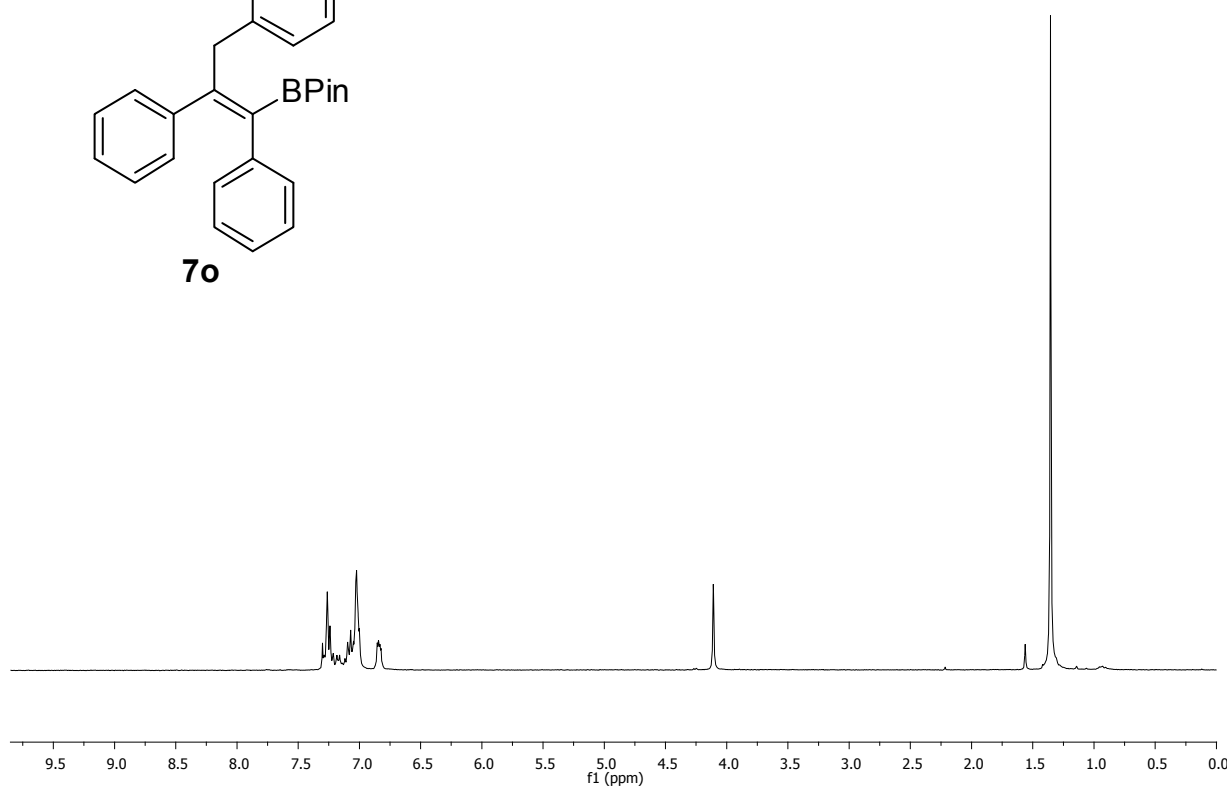
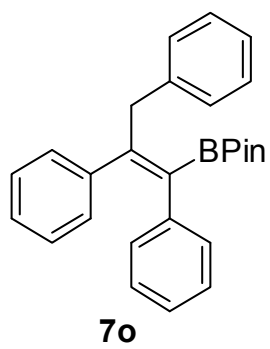


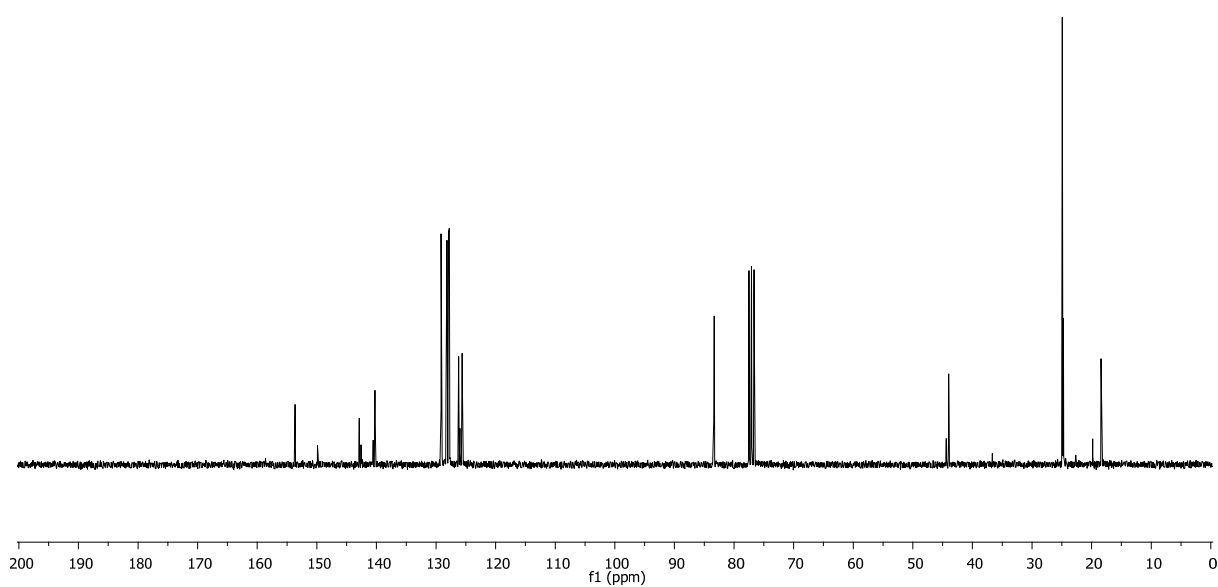
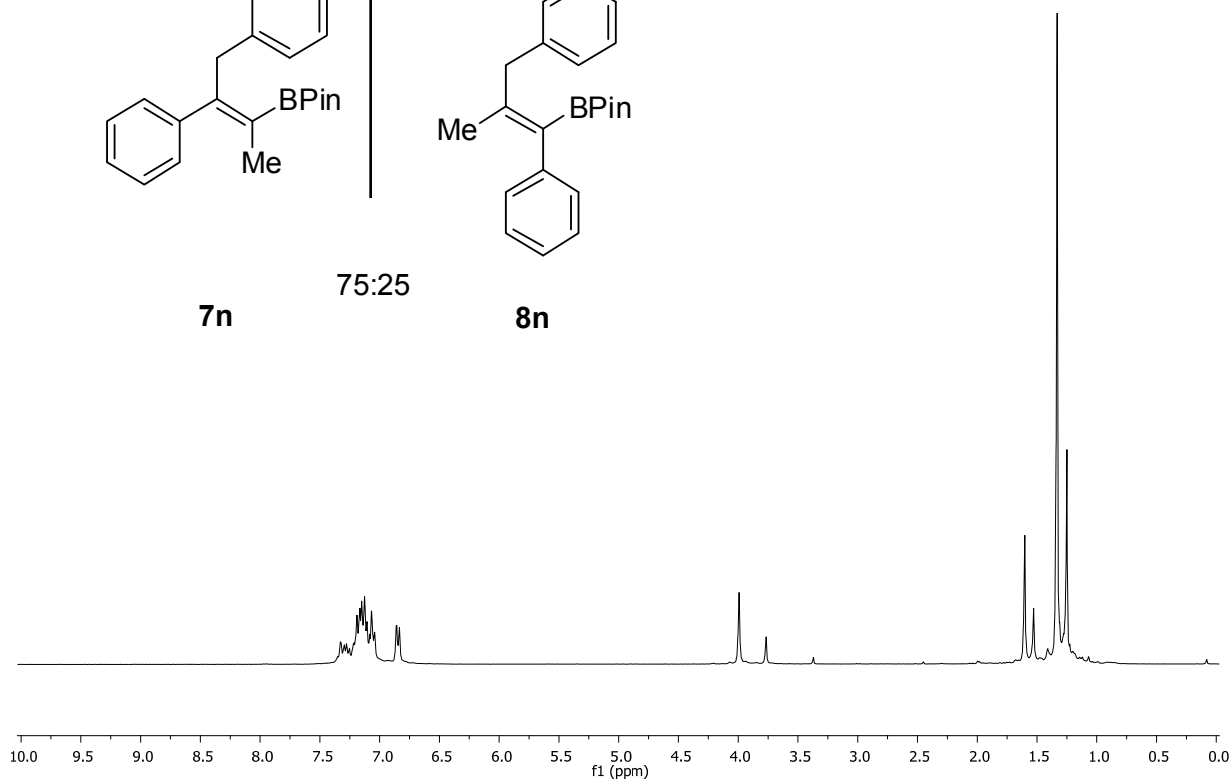
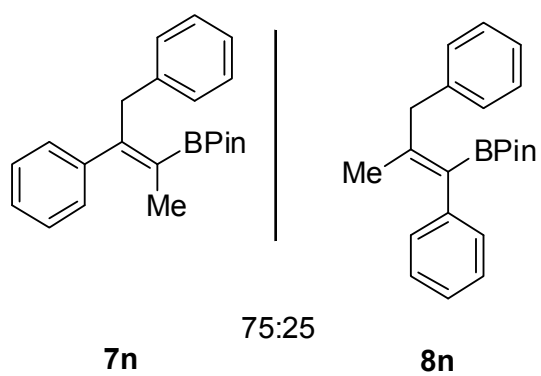
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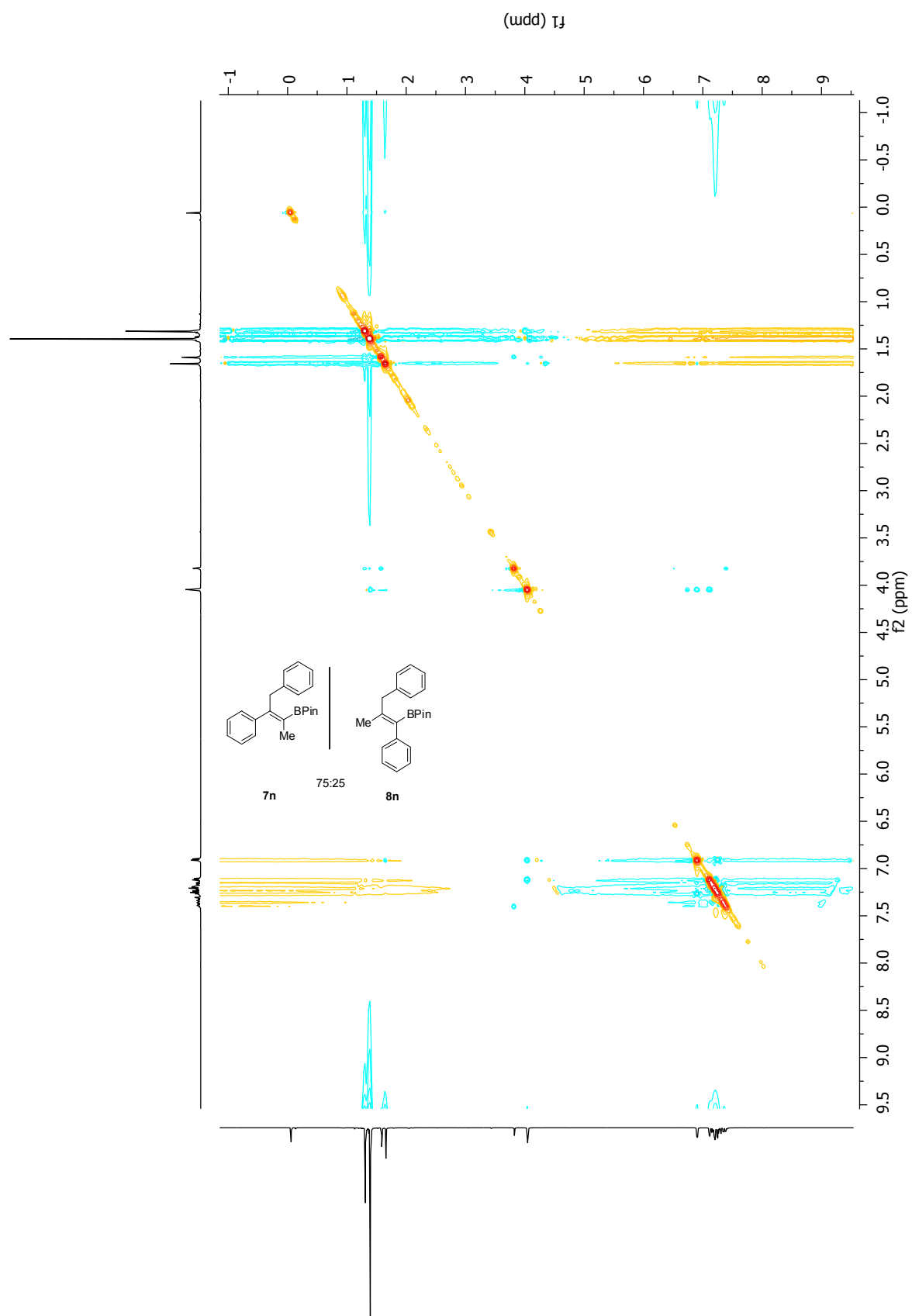


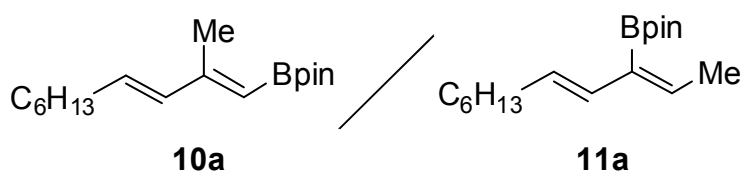












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