Supporting Information

Highly Regio- and Stereoselective Synthesis of Alkenylboronic Esters by Copper-catalyzed Boron Additions to Disubstituted Alkynes

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Contents:

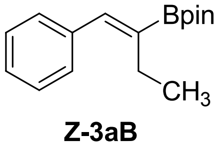
Experimental

General Methods. All reactions were performed in oven-dried Schlenk tubes under nitrogen. THF was distilled from sodium benzophenone ketyl under nitrogen. Cu(I)Cl, NaO*t*-Bu, bis(pinacolato)diboron and other commercial substrates were purchased and used as received. Flash chromatography was performed on silica gel from Fuji Silysia Chemical (75–200 mesh). All ^{1}H NMR spectra were obtained on Varian Mercury 300 systems and reported in parts per million (ppm) downfield from tetramethylsilane. ^{13}C NMR spectra were reported in ppm referenced to deuteriochloroform (77.16 ppm). GC analysis was performed on a Younglin Acme 9000 series. Infrared spectra (IR) were obtained on Nicolet 205 FTIR and are recorded in cm^{-1}. High resolution mass spectra (HRMS) were obtained at Korea Basic Science Institute Daegu, Korea and reported in the form of m/z (intensity relative to base peak = 100).

Commercially unavailable alkynes were synthesized via Pd-catalyzed Negishi cross coupling of aryl halides with propynylmetals or Sonogashira coupling of terminal alkynes with aryl halides by following published procedures.[1–3]

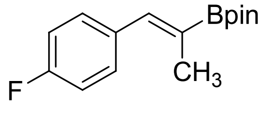
1. General procedure for the copper-catalyzed boron addition to disubstituted alkynes

To an oven dried schlenk tube equipped with a stir bar were added CuCl (2.5 mg, 0.025 mmol), NaO*t*-Bu (9.6 mg, 0.1 mmol), tri-*p*-tolylphosphine (9.3 mg, 0.05 mmol) and THF (0.4 mL) under nitrogen. After the mixture was stirred at room temperature for 30 min, bis(pinacolato)diboron (140 mg, 0.55 mmol) dissolved in THF (0.3 mL) was added. The reaction mixture was stirred for 10 min. Then, internal alkyne (0.5 mmol) was added followed by MeOH (0.04 mL, 1 mmol). The reaction was washed with THF (0.3 mL), sealed, and stirred until no starting material was detected by TLC. The reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography.



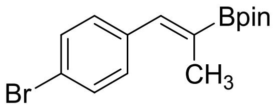
Z-3aB

(*Z*)-4,4,5,5-tetramethyl-2-(1-phenylbut-1-en-2-yl)-1,3,2-dioxaborolane (Table 1, entry 9): The title compound was isolated as a colorless oil in 90% yield (116.8 mg). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.367.22 (m, 5H), 7.21 (br s, 1H), 2.40 (q, *J* = 7.5 Hz, 2H), 1.31 (s, 12H), 1.10 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 141.5, 138.0, 129.1, 128.2, 127.2, 83.5, 25.0, 22.8, 14.8; IR (KBr) 2975, 1363, 1137 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{16}H_{23}BO_2$: 258.1791, found: 258.1790.



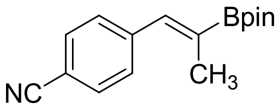
Z-3bB

(*Z*)-2-(1-(4-fluorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 1): The title compound was isolated as a colorless oil 90% yield (117.8 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (td, *J* = 8.7 Hz, 2.2 Hz, 2H), 7.19 (br s, 1H), 7.02 (tt, *J* = 8.7Hz, 2.2 Hz, 2H), 1.97 (d, *J* = 1.8 Hz, 3H), 1.31 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 160.2, 141.3, 134.2, 131.2, 131.1, 115.2, 115.0, 83.7, 25.0, 16.0; IR (KBr) 2983, 1357, 1227, 1132 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{15}H_{20}BFO_2$: 262.1540, found: 262.1541.



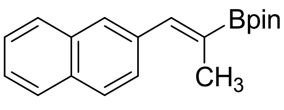
Z-3cB

(*Z*)-2-(1-(4-bomophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 2): The title compound was isolated as a white solid in 92% yield (147.6 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.15 (br s, 1H), 2.00 (d, *J* = 1.3 Hz, 3H), 1.30 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 136.8, 131.3, 131.0, 121.1, 83.7, 25.0, 16.0; IR (KBr) 2978, 1344, 1123 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{15}H_{20}BBrO_2$: 322.0740, found: 322.0742.



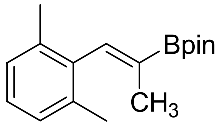
Z-3dB

(*Z*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-enyl)-benzonitrile (Table 2, entry 3): The title compound was isolated as a white solid in 93% yield (125.2 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.20 (br s, 1H), 1.98 (d, *J* = 1.8 Hz, 3H), 1.32 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 140.3, 132.0, 129.9, 119.1, 110.5, 84.0, 25.0, 16.1; IR (KBr) 2976, 2225, 1349, 1132 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{16}H_{20}BNO_2$: 269.1587, found: 269.1584.



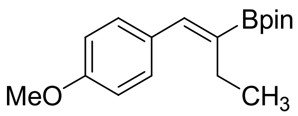
Z-3eB

(*Z*)-4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)prop-1-en-2-yl)-1,3,2-dioxaborolane (Table 2, entry 4): The title compound was isolated as a colorless oil in 92% yield (136.2 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (br s, 1H), 7.817.76 (m, 4H), 7.547.41 (m, 3H), 2.14 (d, *J* = 1.8 Hz, 3H), 1.31 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 135.6, 133.3, 132.5, 128.7, 128.3, 127.66, 127.63, 127.59, 126.12, 126.10, 83.6, 25.0, 16.2; IR (KBr) 2981, 1369, 1148 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{19}H_{23}BO_2$: 294.1791, found: 294.1794.



Z-3fB

(*Z*)-2-(1-(2,6-dimethylphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-di-oxaborolane (Table 2, entry 5): The title compound was isolated as a white solid in 89% yield (120.7 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (br s, 1H), 7.096.99 (m, 3H), 2.16 (s, 6H), 1.51 (d, *J* = 1.6 Hz, 3H), 1.32 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 137.7, 135.5, 127.0, 126.6, 83.5, 25.0, 20.3, 15.6; IR (KBr) 2981, 1712, 1371, 1121 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{17}H_{25}BO_2$: 272.1948, found: 272.1944.

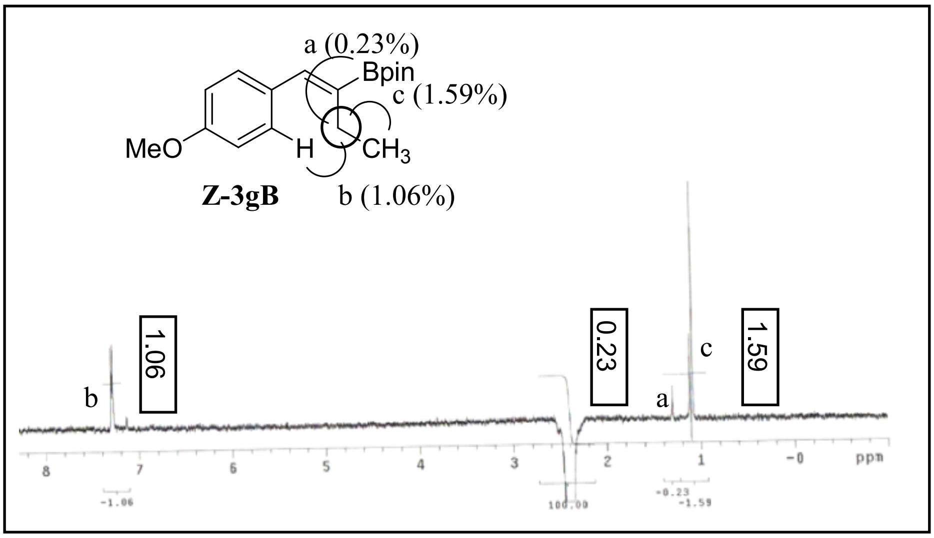


Z-3gB

(*Z*)-2-(1-(4-methoxyphenyl)but-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 6): The title compound was isolated as a colorless oil in 90% yield (129.6 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 7.15 (br s, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.42 (q, *J* = 7.5 Hz, 2H), 1.30 (s, 12H), 1.11 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 141.1, 134.5(C–B), 130.6, 130.5, 113.6, 83.4, 55.3, 24.9, 22.7, 14.7; IR (KBr) 2976, 1511, 1361, 1133 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{17}H_{25}BO_3$: 288.1897, found: 288.1898.

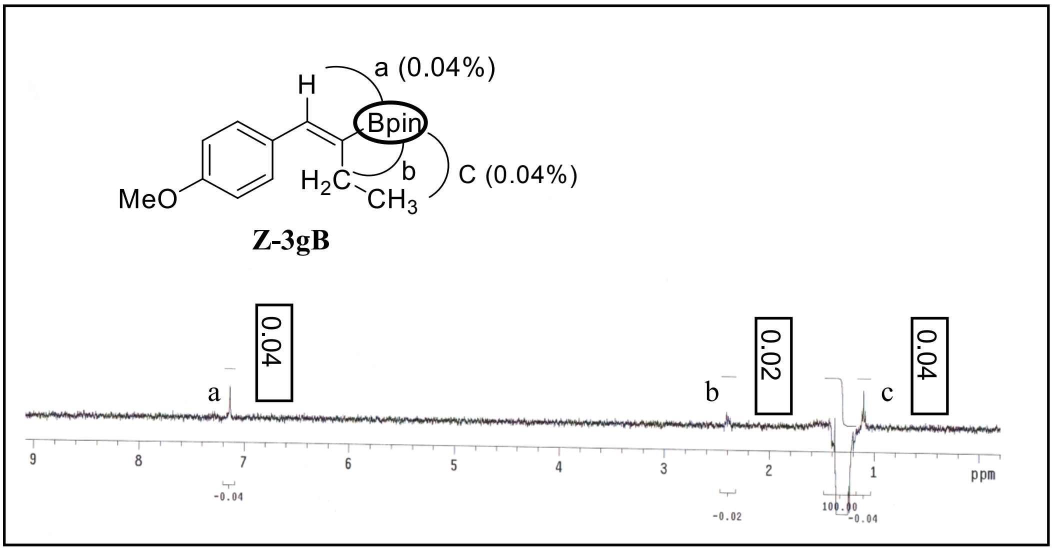
Irradiation of the allylic hydrogens at 2.42 ppm resulted in a 1.59% enhancement of the methyl hydrogens signal at 1.11 ppm, 0.23% enhancement of the boronic ester hydrogens signal at 1.30 ppm and 1.06% enhancement of the aryl proton signal at 7.15 ppm.

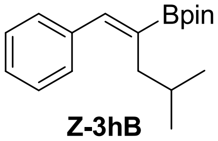
Figure 1-1. NOE spectrum of ***(Z)*- 3gB**



Irradiation of the boronic ester hydrogens at 1.30 ppm resulted in a 0.04% enhancement of the vinyl proton signal at 7.15 ppm, 0.02% enhancement of the allylic hydrogenes at 2.42 ppm and 0.04% enhancement of the methyl hydrogenes signal at 1.30 ppm.

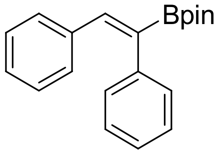
Figure 1-2. NOE spectrum of ***(Z)*- 3gB**





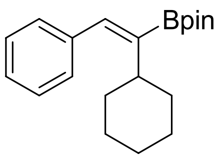
Z-3hB

(*Z*)-4,4,5,5-tetramethyl-2-(4-methyl-1-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (Table 2, entry 7): The title compound was isolated as a colorless oil in 90% yield (129.2 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.347.18 (m,5H), 7.27 (br s, 1H), 2.31 (br d, *J* = 7.2 Hz, 2H), 1.921.78 (m, 1H), 1.30 (s, 12H), 0.86 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 138.2, 134.8 (C–B), 129.2, 128.1, 127.0, 83.4, 38.1, 28.9, 24.8, 22.8; IR (KBr) 2963, 1366, 1138 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{18}H_{27}BO_2$: 286.2104, found: 286.2102.



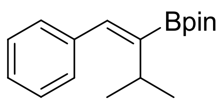
Z-3i

(*Z*)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 8): The title compound was isolated as a white solid in 91% yield (138.7 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.347.03 (m, 10H), 1.30 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 140.7, 137.2, 130.2, 129.1, 128.5, 128.1, 127.8, 126.5, 84.0, 25.0; IR (KBr) 2984, 1332, 1144 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{20}H_{23}BO_2$: 306.1791, found: 306.1792.

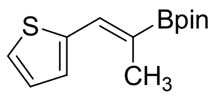


Z-3jB

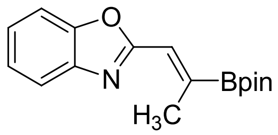
(*Z*)-2-(1-cyclohexyl-2-phenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 9): The crude reaction mixture contained a 86:14 ratio of **Z-3jB** and **Z-3jA** as measured by GC analysis. The isomers were inseparable and obtained in 88% yield (137.3 mg). (major isomer, **Z-3jB**) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.19 (m, 5H), 7.14 (br s, 1H), 2.70–2.63 (m, 1H), 1.72–1.46 (m, 10H), 1.29 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 138.4, 129.0, 128.1, 126.9, 83.1, 39.5, 32.1, 26.5, 26.2, 24.9; IR (KBr) 2928, 1355, 1139 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{20}H_{29}BO_2$: 312.2261, found: 312.2263.


Z-3kB

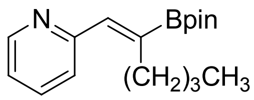
(*Z*)-4,4,5,5-tetramethyl-2-(3-methyl-1-phenylbut-1-en-2-yl)-1,3,2-dioxaborolane (Table 2, entry 10): The crude reaction mixture contained a 80:20 ratio of **Z-3kB** and **Z-3kA** as measured by GC analysis. The isomers were inseparable and obtained in 82% yield (111.7 mg). (major isomer, **Z-3kB**) ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.34–7.20 (m, 5H), 7.15 (s, 1H), 3.00 (sept, *J* = 6.8 Hz, 1H), 1.30 (s, 12H), 1.13 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 140.1, 138.4, 128.9, 128.1, 126.9. 83.1, 28.8, 24.9, 22.4; IR (KBr) 2973, 1366, 1143 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{17}H_{25}BO_2$: 272.1948, found: 272.1947.


Z-3lB

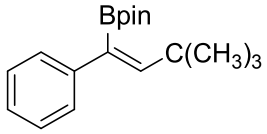
(*Z*)-4,4,5,5-tetramethyl-2-(1-(thiophen-2-yl)prop-1-en-2-yl)-1,3,2-dioxaborolane (Table 2, entry 11): The title compound was isolated as a light yellow oil in 93% yield (117 mg). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.42 (br s, 1H), 7.35 (d, *J* = 5.0 Hz, 1H), 7.15 (d, *J* = 3.2 Hz, 1H), 7.04 (dd, *J* = 5.0 Hz, 3.6 Hz, 1H), 2.05 (d, *J* = 1.5 Hz, 3H), 1.29 (s, 12H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 141.6, 135.1, 129.4, 127.2, 126.9, 83.6, 25.0, 16.4; IR (KBr) 2984, 1367, 1143 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{13}H_{19}BO_2S$: 250.1199, found: 250.1199.


Z-3mB

(*Z*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-enyl)-benzo[d]oxazole (Table 2, entry 12): The title compound was isolated as a light yellow soild in 90% yield (128.3 mg). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.80–7.72 (m, 1H), 7.55–7.48 (m, 1H), 7.34–7.30 (m, 2H), 7.14 (d, *J* = 1.6 Hz, 1H), 2.42 (d, *J* = 1.6 Hz, 3H), 1.31 (s, 12H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 162.4, 150.0, 142.0, 126.2, 125.3, 124.4, 120.3, 110.6, 84.2, 24.9, 17.3; IR (KBr) 2985, 1358, 1137 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{16}H_{20}BNO_3$: 285.1536, found: 285.1533.

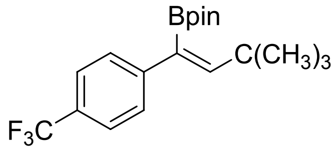

Z-3nB

(*Z*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-enyl)-pyridine (Table2, entry 13): The title compound was isolated as a colorless oil in 89% yield (127.8 mg). ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.61 (d, *J* = 3.9 Hz, 1H) 7.62 (td, *J* = 7.7 Hz, *J* = 1.8 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.22 (s, 1H), 7.10 (ddd, *J* = 7.5 Hz, *J* = 4.8 Hz, *J* = 1.0 Hz, 1H), 2.64 (t, *J* = 7.4 Hz, 2H), 1.60-1.32 (m, 4H), 1.30 (s, 12H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 157.0, 149.4, 140.4, 135.9, 124.4, 121.6, 83.6, 32.1, 29.1, 24.9, 22.9, 14.2; IR (KBr) 2973, 1350, 1140 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{17}H_{26}BNO_2$: 287.2057, found: 287.2056.



E-5aA

(*E*)-2-(3,3-dimethyl-1-phenylbut-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, entry 1): The title compound was isolated as a white solid in 91% yield (130.3 mg). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.347.04 (m, 5H), 6.48 (s, 1H), 1.22 (s, 12H), 0.91(s, 9H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 156.1, 141.8, 128.8, 127.4, 125.6, 83.5, 35.7, 31.1, 24.8; IR (KBr) 2971, 1329, 1146 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{18}H_{27}BO_2$: 286.2104, found: 286.2106.

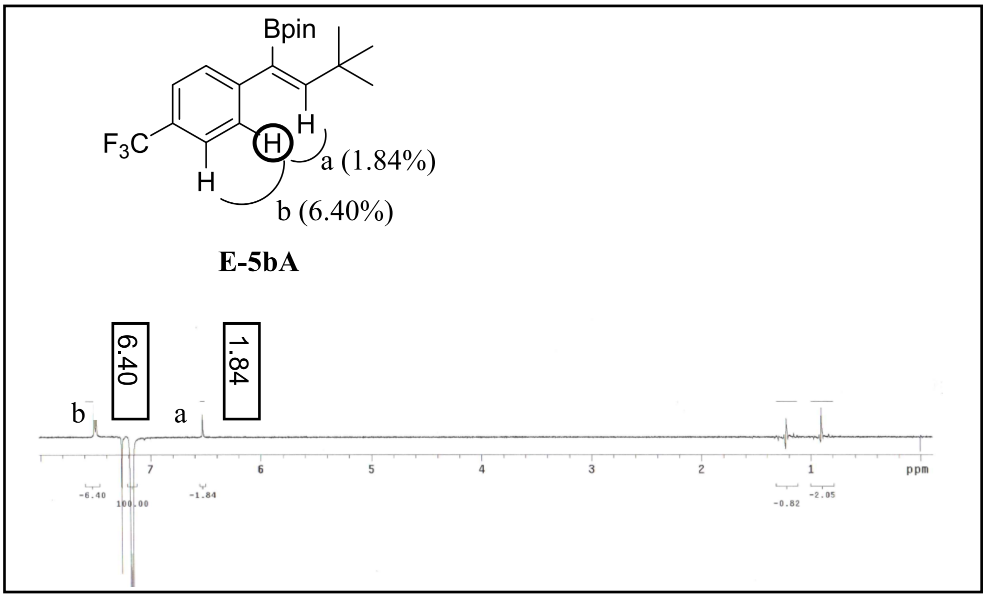


E-5bA

(*E*)-2-(3,3-dimethyl-1-(4-trifluoromethyl)phenyl)but-1-enyl)-4,4,5,5-tetra-methyl-1,3,2-dioxaborolane (Table 3, entry 2): The title compound was isolated as a white solid in 92% yield (163.1 mg). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.53 (s, 1H), 1.23 (s, 12H), 0.90 (s, 9H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 157.1, 146.0, 129.2, 127.9 (q, *J* = 32 Hz), 124.7 (q, *J* = 272 Hz), 124.4 (q, *J* = 3.9 Hz), 83.8, 35.9, 31.0, 24.8; IR (KBr) 2969, 1325, 1256, 1121 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{19}H_{26}BF_3O_2$: 354.1978, found: 354.1980.

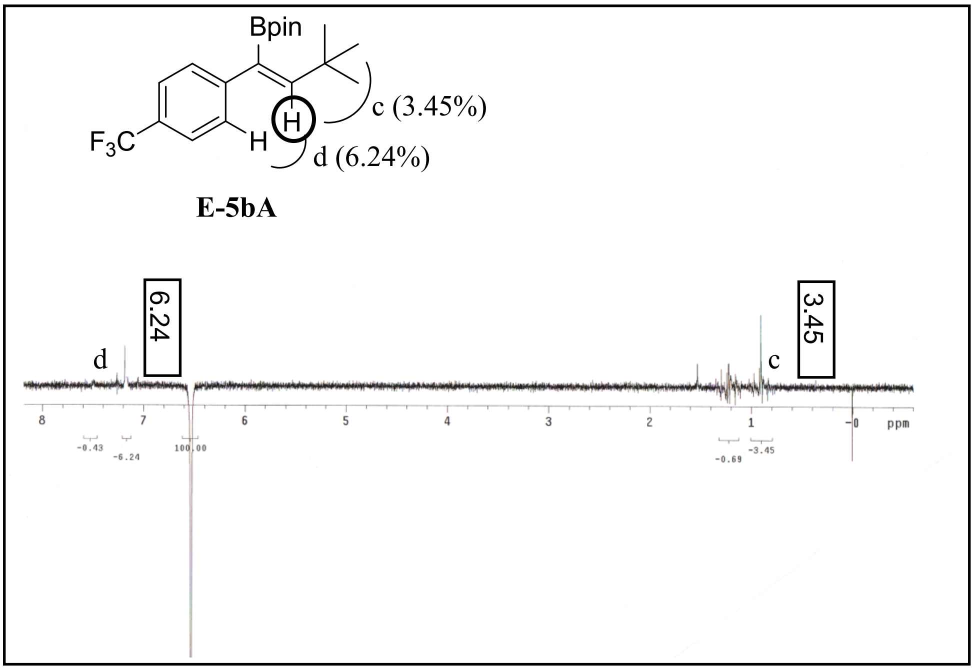
Irradiation of the aryl proton at 7.17 ppm resulted in a 6.40% enhancement of the aryl proton signal at 7.50 ppm and 1.84% enhancement of the vinyl proton signal at 6.53 ppm.

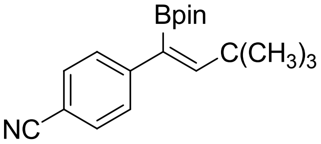
Figure 2-1. NOE spectrum of ***(E)*- 5bA**



Irradiation of the vinyl proton at 6.53 ppm resulted in a 6.24% enhancement of the aryl proton signal at 7.17 ppm and 3.45% enhancement of the tert-butyl signal at 0.90 ppm.

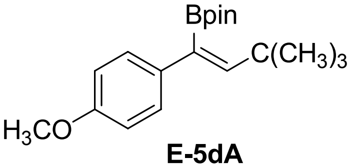
Figure 2-2. NOE spectrum of ***(E)*- 5bA**





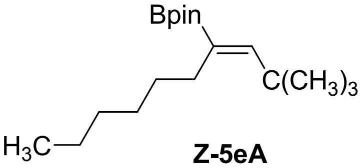
E-5cA

(*E*)-4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-but-1-enyl)benzonitrile (Table 3, entry3): The title compound was isolated as a white solid in 92% yield (143.2 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.53 (s, 1H), 1.22 (s, 12H), 0.90 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 147.5, 131.2, 129.5, 119.4, 109.4, 83.7, 35.8, 30.8, 24.7; IR (KBr) 2973, 2224, 1328, 1143 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{19}H_{26}BNO_2$: 311.2057, found: 311.2058.



E-5dA

(*E*)-2-(1-(4-methoxyphenyl)-3,3-dimethylbut-1-enyl)-4,4,5,5-tetra-methyl-1,3,2-dioxaborolane (Table 3, entry4): The title compound was isolated as a white solid in 62% yield (98.7 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.146.90 (m, 2H), 6.846.74 (m, 2H), 6.46 (s, 1H), 3.79 (s, 3H), 1.22 (s, 12H), 0.91 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 156.4, 133.9, 129.8, 112.9, 83.4, 55.2, 35.6, 31.1, 24.8; IR (KBr) 2957, 2113, 1337, 1145 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{19}H_{29}BO_3$: 316.2210, found: 316.2210.

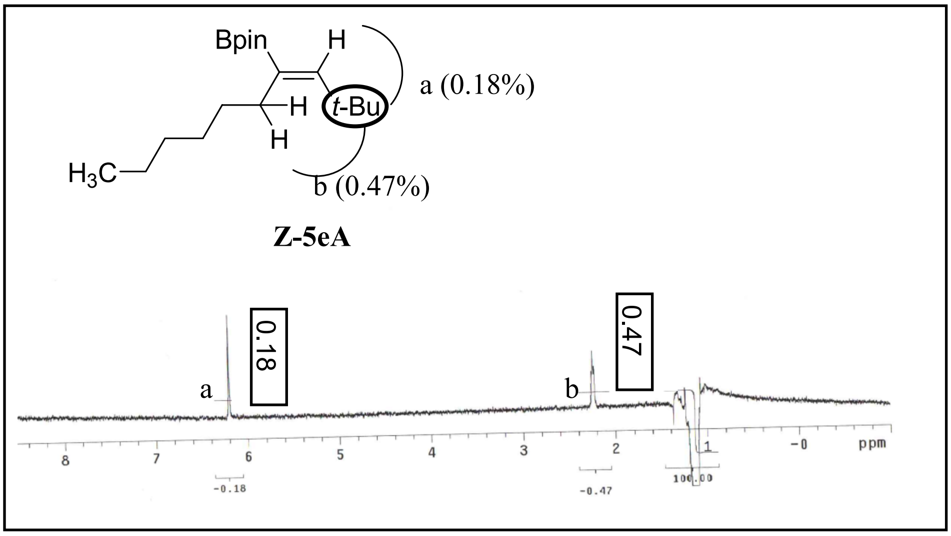


Z-5eA

(*Z*)-2-(2,2-dimethyldec-3-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-di-oxaborolane (Table 3, entry 5): The title compound was isolated as a colorless oil in 37% yield (55 mg). ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.21 (s, 1H), 2.24 (t, *J* = 6.3 Hz, 2H), 1.38–1.26 (m, 8H), 1.25 (s, 12H), 1.14 (s, 9H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 153.7, 83.1, 34.3, 32.0, 31.2, 30.8, 29.9, 29.7, 24.9, 22.8, 14.2; IR (KBr) 1353, 1142 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{18}H_{35}BO_2$: 294.2730, found: 294.2732.

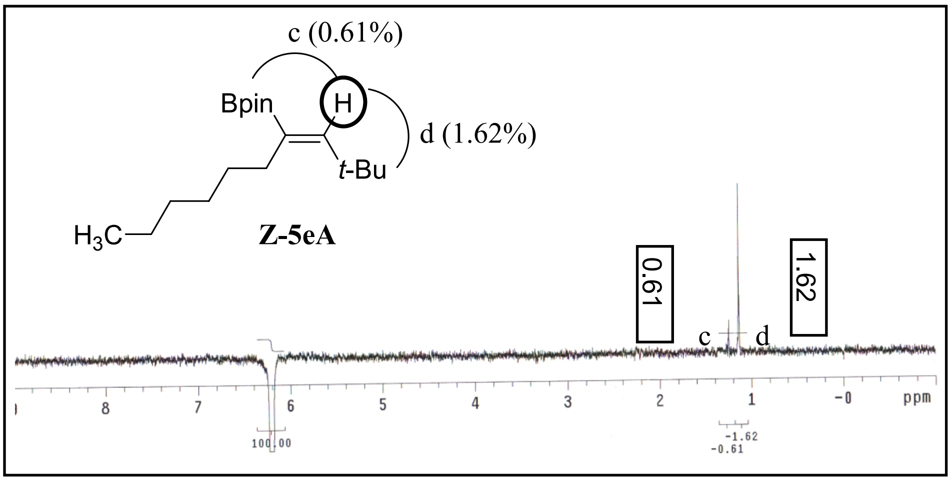
Irradiation of the *t*-butyl hydrogens at 1.14 ppm resulted in a 0.18% enhancement of the allylic hydrogens at 2.24 ppm and 0.47% enhancement of the vinyl proton signal at 6.21 ppm.

Figure 3-1. NOE spectrum of ***(Z)*- 5eA**

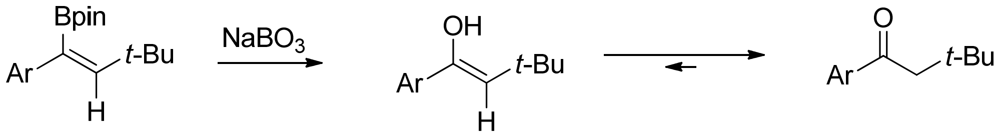


Irradiation of the vinyl proton at 6.21 ppm resulted in a 0.61% enhancement of the pinacol boronate signal at 1.25 ppm and 1.62% enhancement of the tert-butyl hydrogens signal at 1.14 ppm.

Figure 3-2. NOE spectrum of ***(Z)*- 5eA**

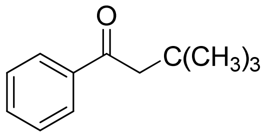


Oxidation of the –addition products (5aA-5dA) in Table 3 for the determination of regio-selectivity:

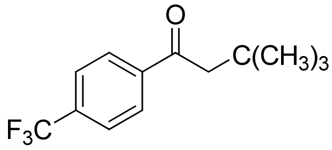


5A

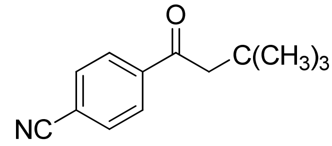
To the α-addition product (**5aA-5dA**) in THF (2.5 mL) and H_2O (2.5 mL) was added sodium perborate[4] (1.5 mmol, 102.3 mg). The reaction mixture was stirred vigorously for 0.5–1 h at room temperature. The reaction mixture was quenched with H_2O and then extracted with ethyl acetate (20 mL x 3). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The corresponding aryl ketone product was purified by silica gel chromatography.



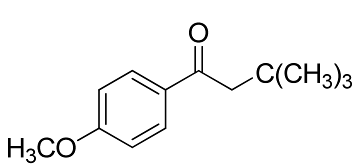
3,3-dimethyl-1-phenylbutan-1-one: The title compound was isolated as a colorless oil in 90% yield (47.4 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04–7.88 (m, 2H), 7.60–7.38 (m, 3H), 2.86 (s, 2H), 1.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 138.6, 132.8, 128.6, 128.3, 50.1, 31.5, 31.2.



3,3-dimethyl-1-(4-(trifluoromethyl)phenyl)butan-1-one: The title compound was isolated as a colorless oil in 88% yield (64.2 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 2.89 (s, 2H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 141.3, 128.6, 125.7 (q, J = 3.4 Hz), 50.5, 31.6, 31.0, 30.1, 26.4.

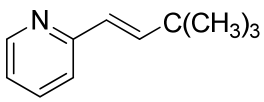


4-(3,3-dimethylbutanoyl)benzonitrile: The title compound was isolated as a colorless oil in 89% yield (53.7 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 8.7 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 2.88 (s, 2H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9, 141.4, 132.4, 128.6, 118.0, 116.0, 50.3, 31.5, 29.9

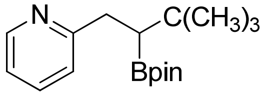


1-(4-methoxyphenyl)-3,3-dimethylbutan-1-one: The title compound was isolated as a colorless oil in 89% yield (55.0mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 2.80 (s, 2H), 1.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 163.3, 131.8, 130.7, 113.7, 55.6, 49.8, 31.6, 30.3.

2. Borylation of 2-(3,3-dimethylbut-1-ynyl)pyridine (eq. 1).



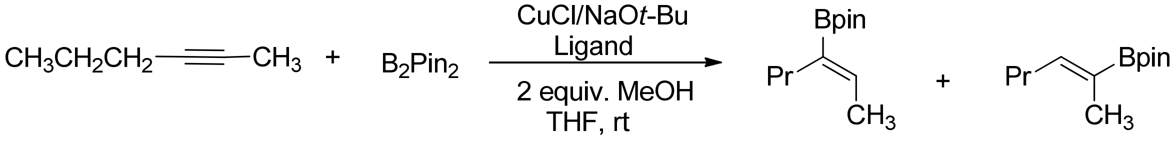
(*E*)-2-(3,3-dimethylbut-1-enyl)pyridine (6): The title compound was isolated as a colorless oil in 34% yield (27.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, *J* = 3.9 Hz, 1H), 7.57 (td, *J* = 7.7 Hz, *J* = 1.9 Hz, 1H), 7.26 (d, *J* = 6.0 Hz, 1H), 7.15–7.0 (m, 1H), 6.78 (d, *J* = 16 Hz, 1H), 6.41 (d, *J* = 16 Hz, 1H), 1.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 146.4, 136.5, 125.1, 121.6, 121.3, 113.6, 33.6, 29.5; HRMS(EI) *m/z* calcd for $C_{16}H_{15}N$: 161.1204, found: 161.1204.



2-(3,3-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-pyridine (7): The title compound was isolated as a colorless oil in 15% yield (21.3 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.3 Hz, 1H), 7.54 (td, *J* = 7.6 Hz, *J* = 1.8 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 5.0 Hz, *J* = 2.2 Hz, 1H), 2.99 (dd, *J* = 14.4 Hz, *J* = 5.0 Hz, 1H), 2.90 (dd, *J* = 14.4 Hz, *J* = 11.3 Hz, 1H), 1.40 (dd, *J* = 11.3 Hz, *J* = 5.0 Hz, 1H), 1.12 (s, 12H), 1.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 148.0, 136.2, 123.2, 120.8, 82.5, 36.8 (C–B), 35.5, 32.2, 29.7, 25.2; IR (KBr) 2962, 1369, 1145 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{17}H_{23}BNO_2$: 289.2213, found: 289.2214.

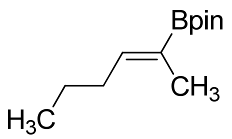
3. Copper-catalyzed boron addition to 2-Hexyne.

Scheme



Entry	Ligand	Time (h)	Convn (%)	Product ratio **Z-5gA**	Product ratio **Z-5gB**	Yield(%)
1	P(*p*-tolyl)$_3$	24	58	23	77	-
2[a]	P(OEt)$_3$	24	69	19	81	-
3[a,b]	P(OEt)$_3$	24	82	18	82	70

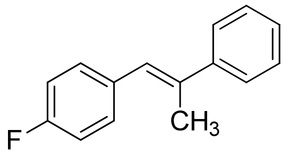
[a] Cu(I)Cl : Ligand : NaO*t*-Bu = 10 : 10 : 20 mol% [b] Reaction was conducted at 60 °C.



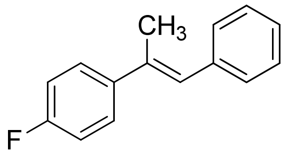
(*Z*)-2-(hex-2-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Z-5gB): The crude reaction mixture contained a 82:18 ratio of **Z-5gB** and **Z-5gA** as measured by GC analysis. The isomers were inseparable and obtained in 70% yield (73.5 mg). (major isomer, **Z-5gB**) ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (td, *J* = 7.0 Hz, 1.6 Hz, 1H), 2.10 (quartet, *J* = 7.1 Hz, 2H), 1.68 (d, *J* = 1.6 Hz, 3H), 1.50–1.32 (m 2H), 1.26 (s, 12H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4, 140.4, 83.1, 30.9, 25.0, 23.1, 14.1; IR (KBr)1360, 1141 cm^{-1}; HRMS(EI) *m/z* calcd for $C_{12}H_{23}BO_2$: 210.1791, found: 210.1791.

4. Synthetic application of the alkenyl boronate products (Scheme 2).

Suzuki-Miyaura coupling of alkenylbronate with aryl bromide[5]: To an oven dried schlenk tube equipped with a stir bar were added $Pd_2(dba)_3$ (13.8 mg, 0.015 mmol), PPh_3 (15.7 mg, 0.06 mmol), K_3PO_4 (191 mg, 0.9 mmol) and distilled DMF (1.5 mL) under nitrogen. After the mixture was stirred at room temperature for 10 min, alkenylboronate (0.3 mmol) and aryl bromide (0.42 mmol) were added. The reaction was washed with distilled DMF (0.3 mL), sealed. The reaction mixture was heated 80 °C for 10 h. The reaction mixture was cooled to room temperature, filtered through Celite, washed with Et_2O and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude material was purified via silica gel chromatography.

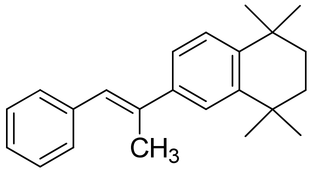


(*E*)-1-fluoro-4-(2-phenylprop-1-enyl)benzene (8)[6]: Compound **8** was synthesized from **(3bB)** and bromobenzene as a white solid in 90% yield by following the Suzuki-Miyaura coupling procedure; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.47 (m, 2H), 7.40–7.27 (m, 5H), 7.08–7.01 (m, 2H), 6.77 (br s, 1H), 2.23 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 160.0, 143.9, 137.5, 134.48, 134.43, 130.9, 130.8, 128.5, 127.4, 126.7, 126.1, 115.3, 115.0, 17.5.; HRMS(EI) *m/z* calcd for $C_{15}H_{13}F$: 212.1001, found: 212.1003.



(*E*)-1-fluoro-4-(1-phenylprop-1-en-2-yl)benzene (10): Compound **10** was synthesized from **(9)**[7] and 1-bromo-4-fluorobenzene as a white solid in 87% yield by following the Suzuki-Miyaura coupling procedure; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60–6.90 (m, 9H), 6.77 (br s, 1H), 2.24 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 160.7, 140.1, 138.3, 136.5, 129.2, 128.3, 127.76, 127.74, 127.72, 127.6, 126.7, 115.4, 115.1, 17.7; IR (KBr) 3049, 1332, 1235 cm^{-1}; HRMS(EI) *m/z* calcd for

$C_{15}H_{13}F$: 212.1001, found: 212.1002.



(*E*)-1,1,4,4-tetramethyl-6-(1-phenylprop-1-en-2-yl)-1,2,3,4-tetrahydronaphthalene (12)[9]: Compound **12** was synthesized from (**9**)[7] and 6-bromo-2,2,3,3,-tetrahydro-1,1,4,4,-tetramethylnaphthalene (**11**)[8] as a white solid in 86% yield by following the Suzuki-Miyaura coupling procedure; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.27 (m, 5H), 7.08 (s, 1H), 7.01 (m, 2H), 6.77 (br s, 1H), 2.05 (d, J = 1.8 Hz, 3H), 1.53 (s, 4H), 1.41 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 160.0, 143.9, 137.5, 134.48, 134.43, 130.9, 130.8, 128.5, 127.4, 126.7, 126.1, 115.3, 115.0, 33.0, 29.1, 17.5.; HRMS(EI) *m/z* calcd for $C_{23}H_{23}$: 304.2191, found: 304.2190.

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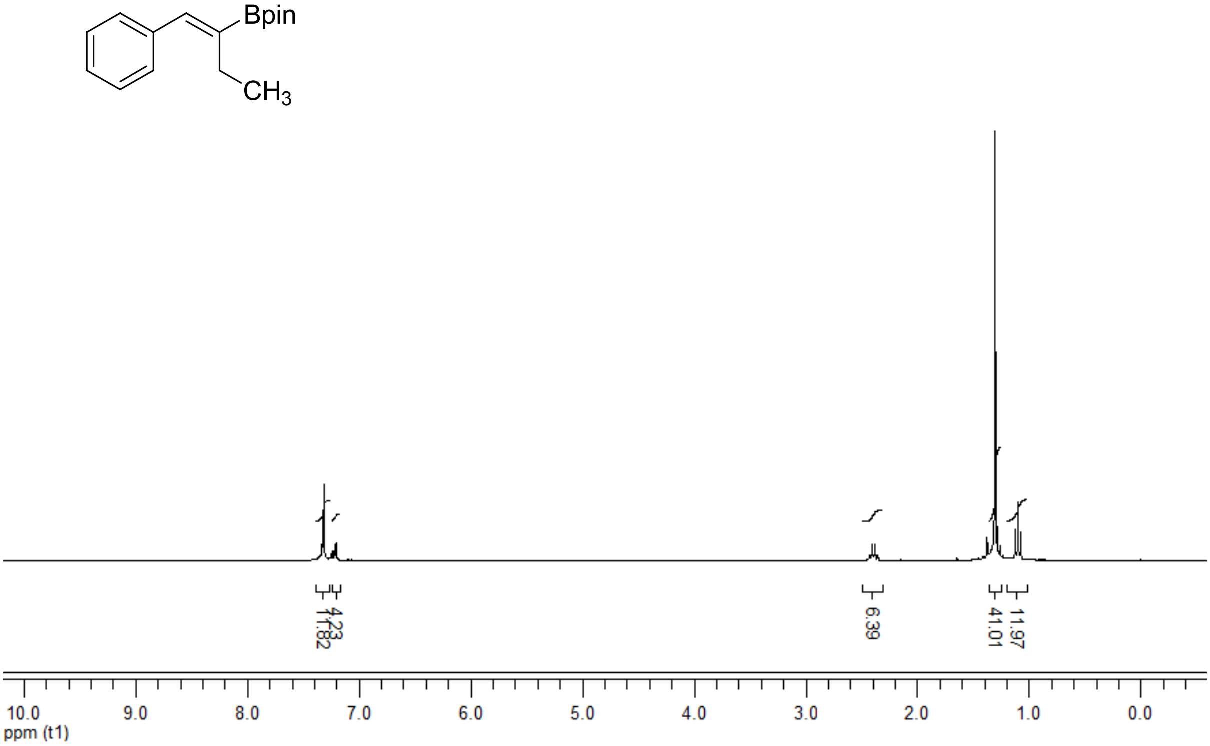
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2.0
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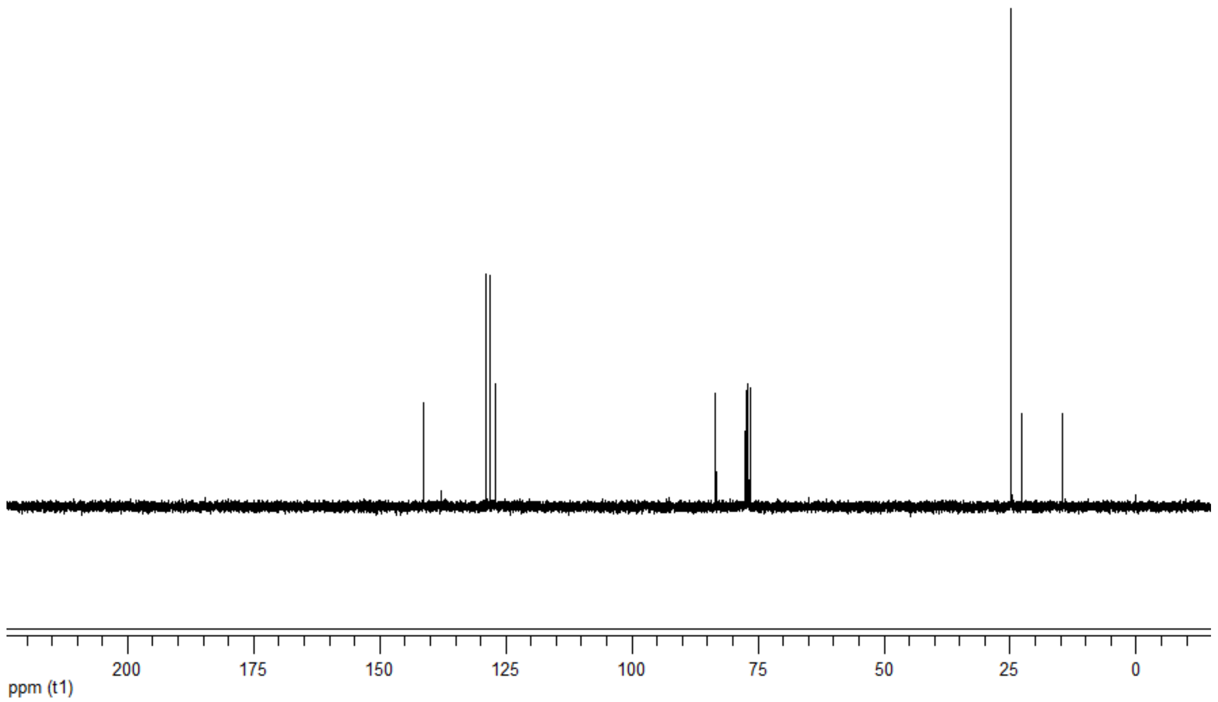
ppm (t1)

3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150
125
100
75
50
25
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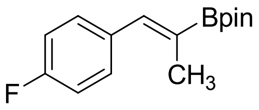
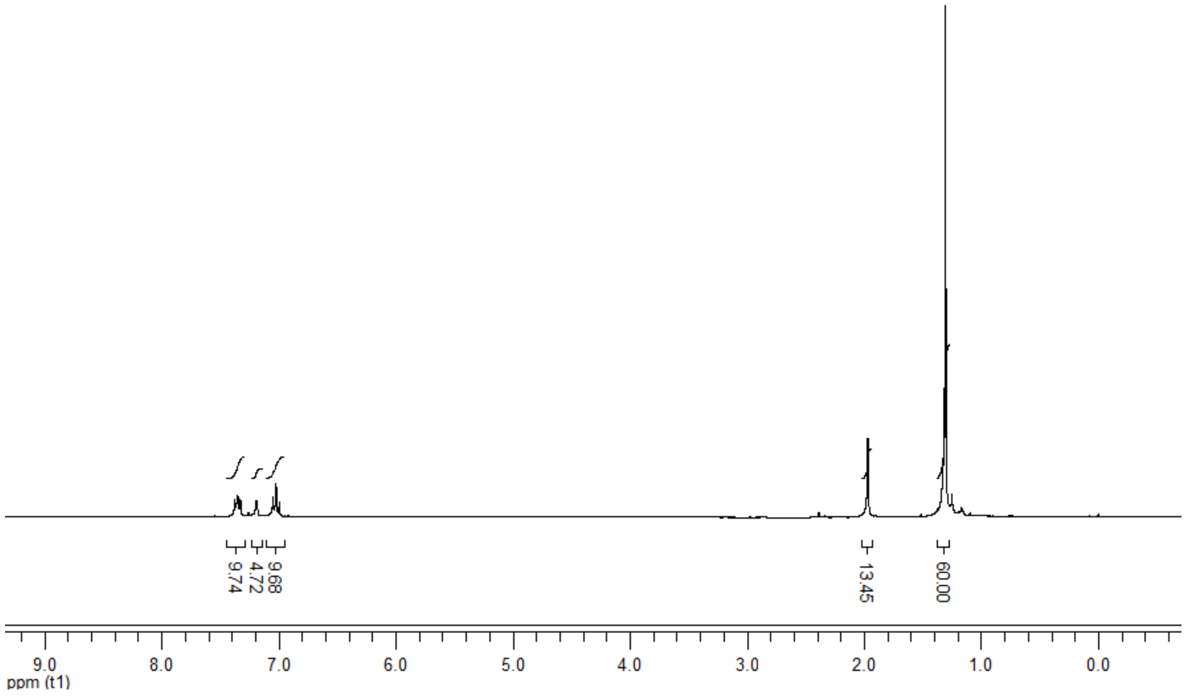
ppm (t1)


Bpin
CH3
F

3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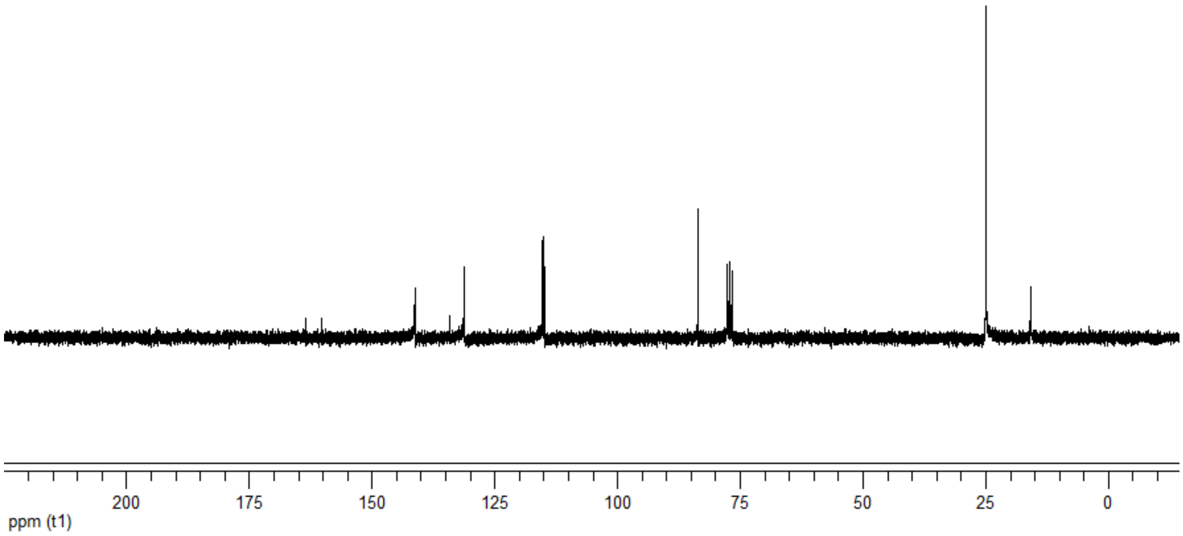
ppm (t1)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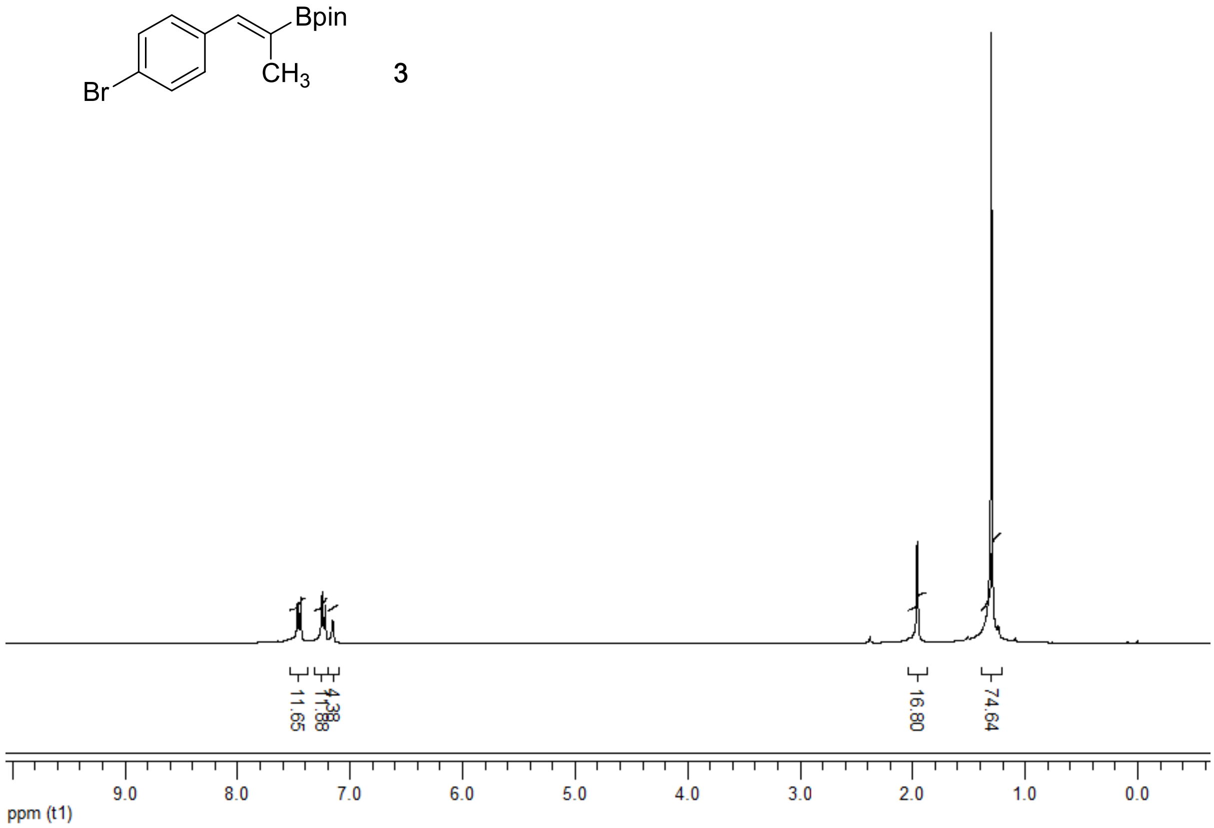
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3

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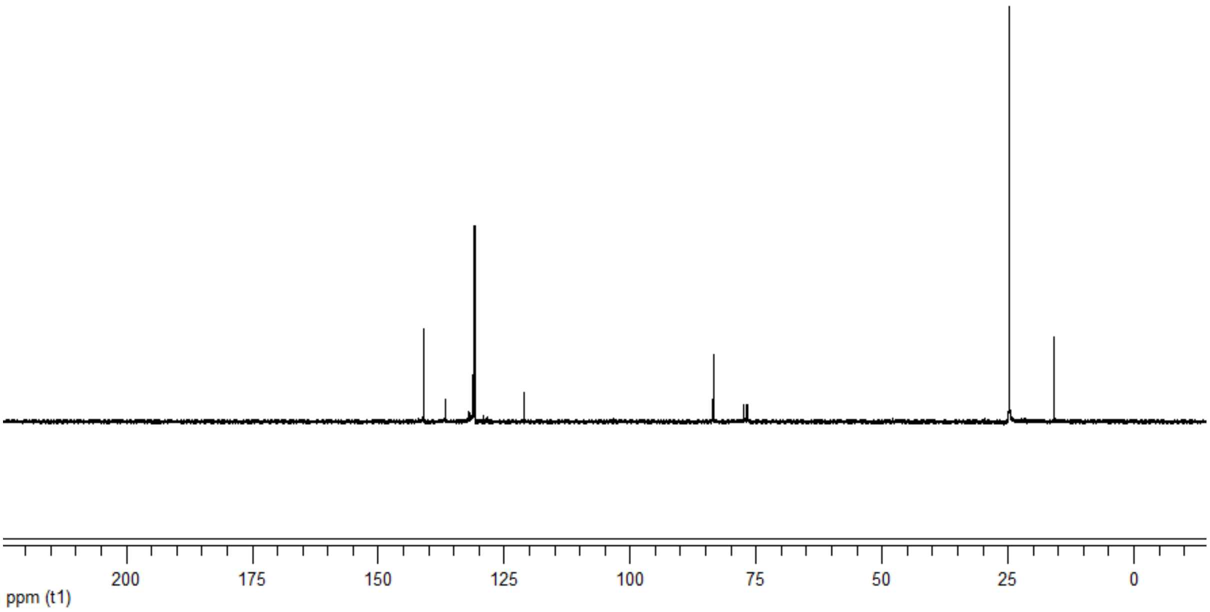
ppm (t1)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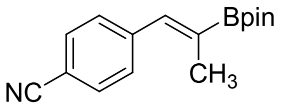
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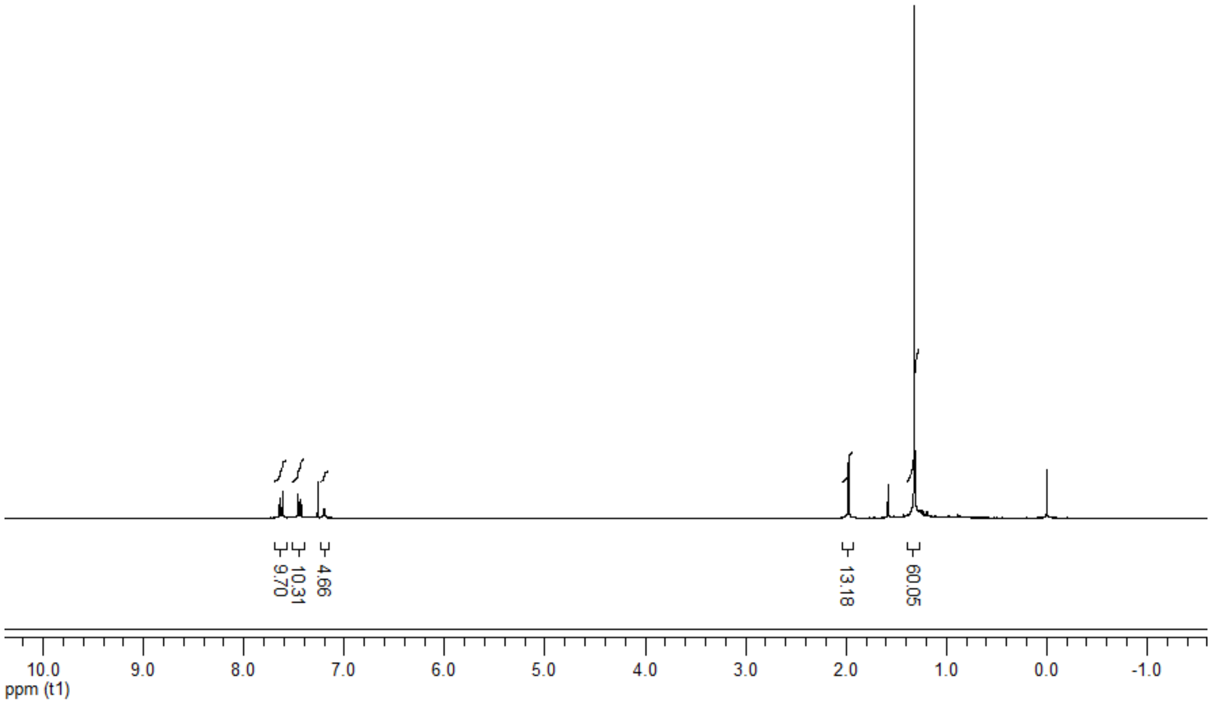
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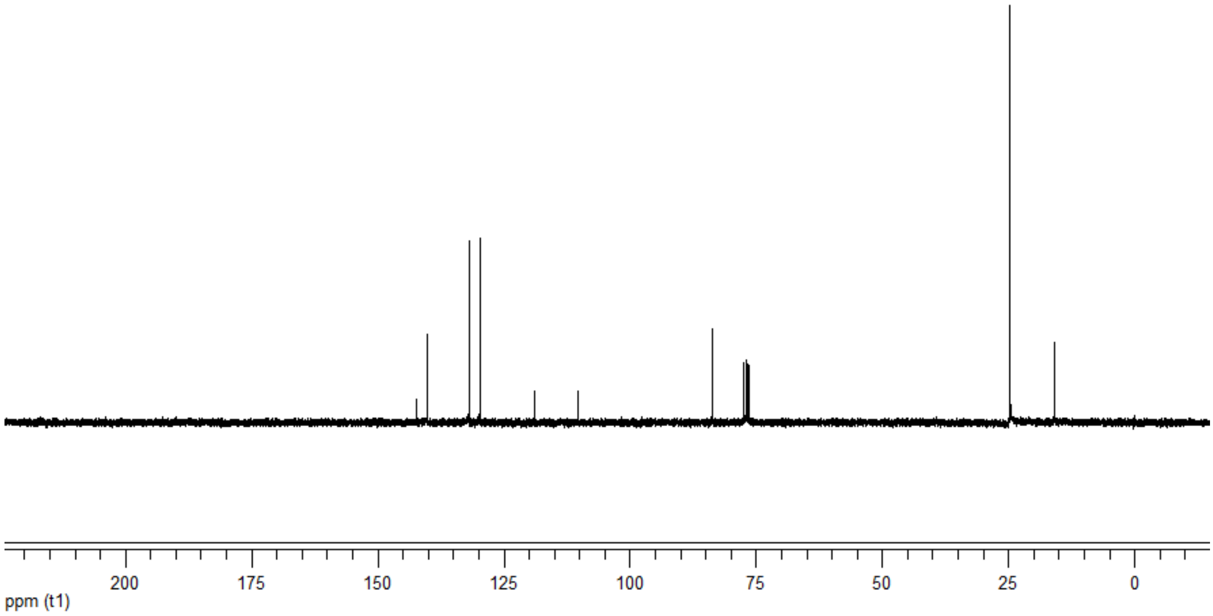
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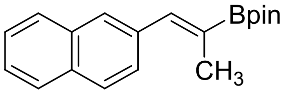
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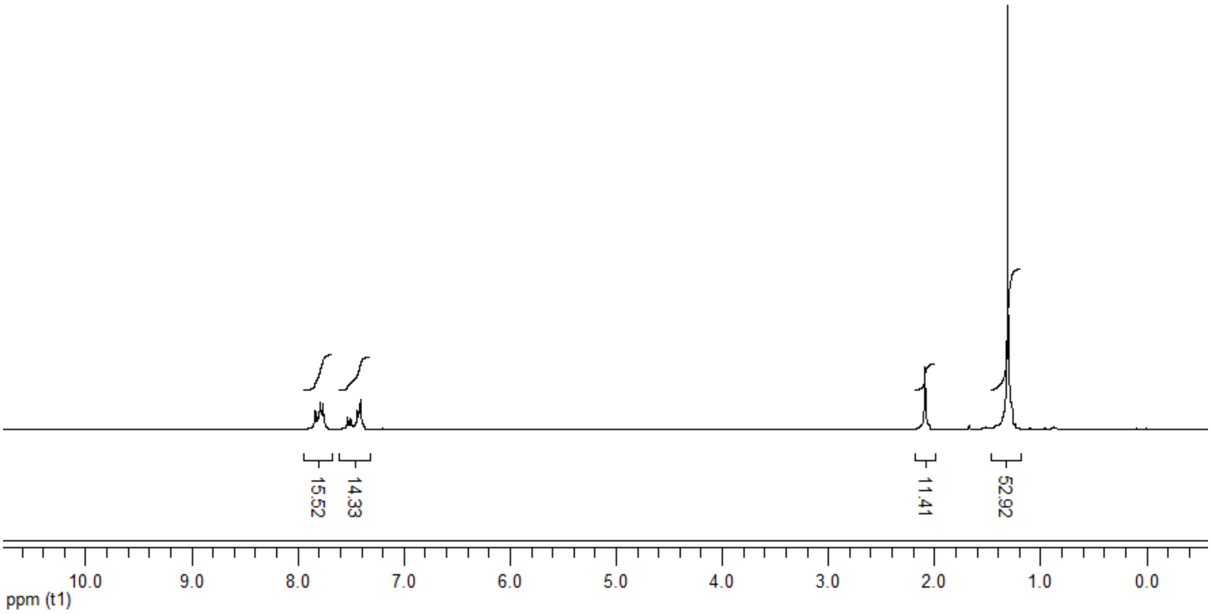
CH3

3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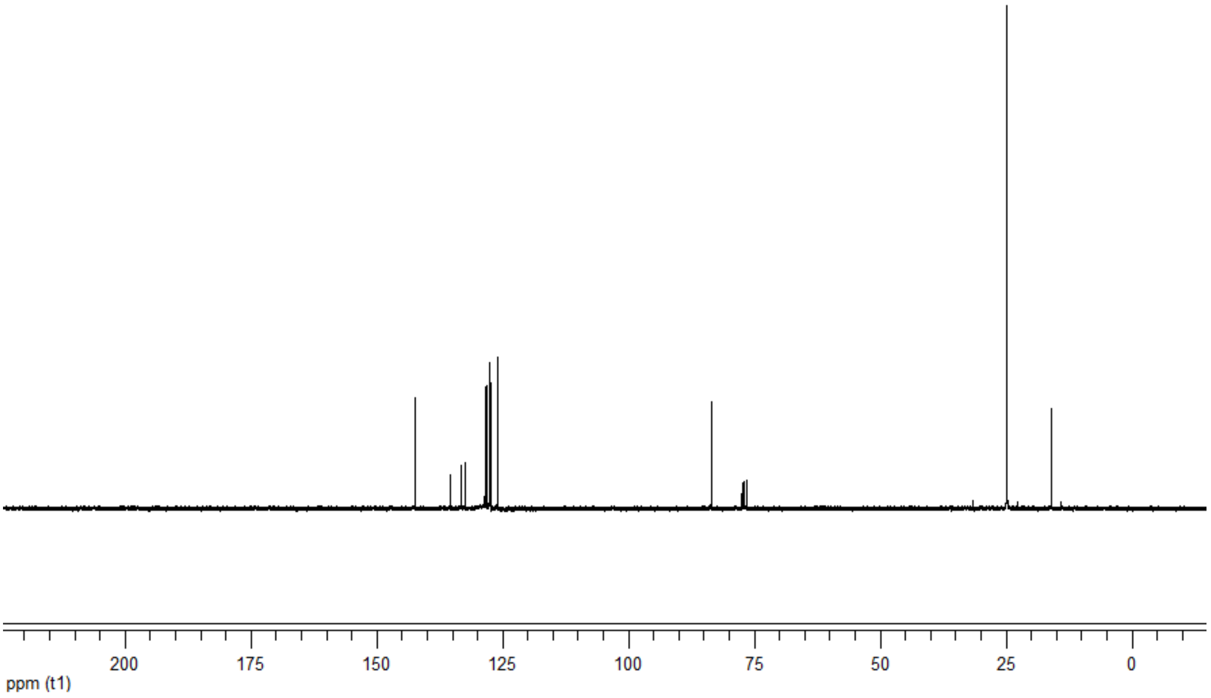
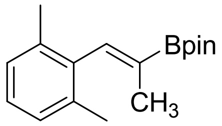
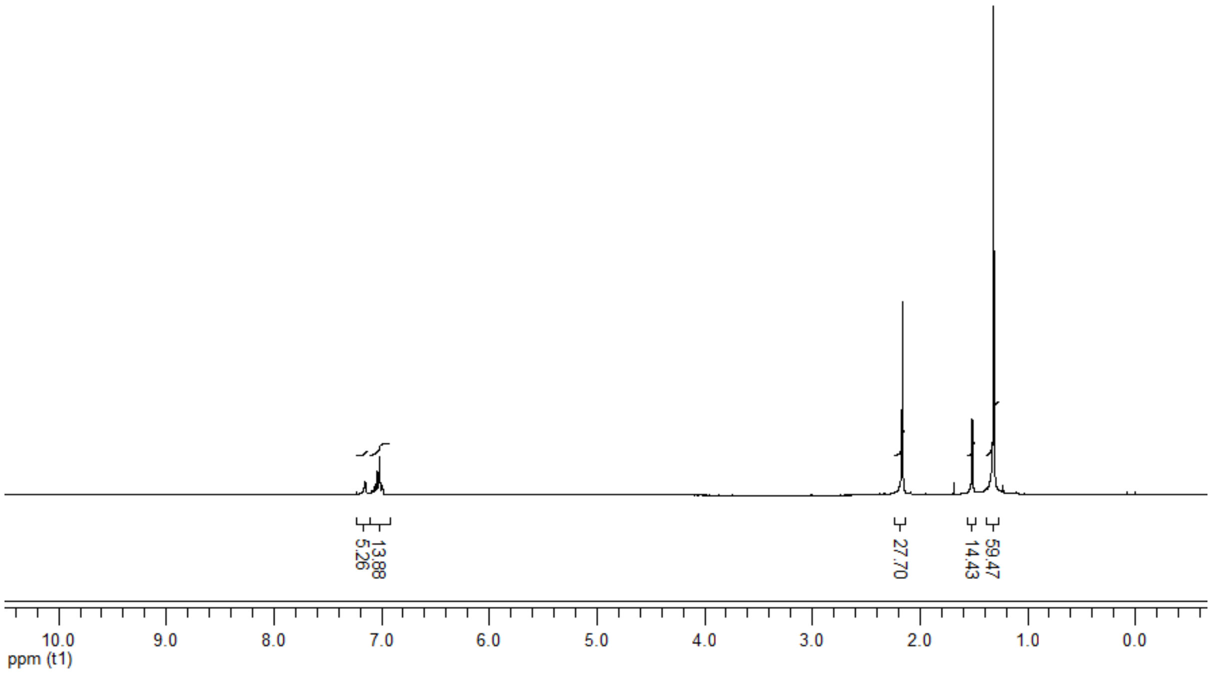
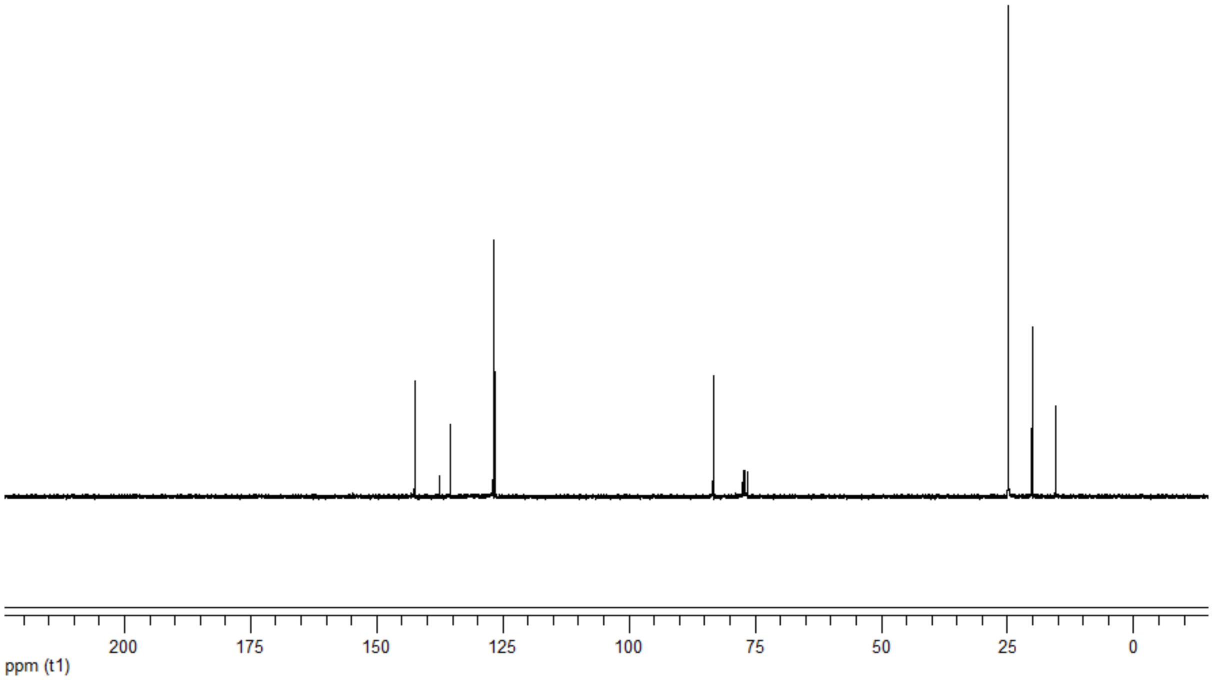
0.0
ppm (t1)

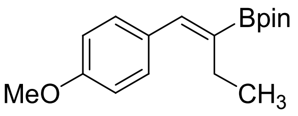

200
175
150
125
100
75
50
25
0
ppm (t1)


Bpin
CH3

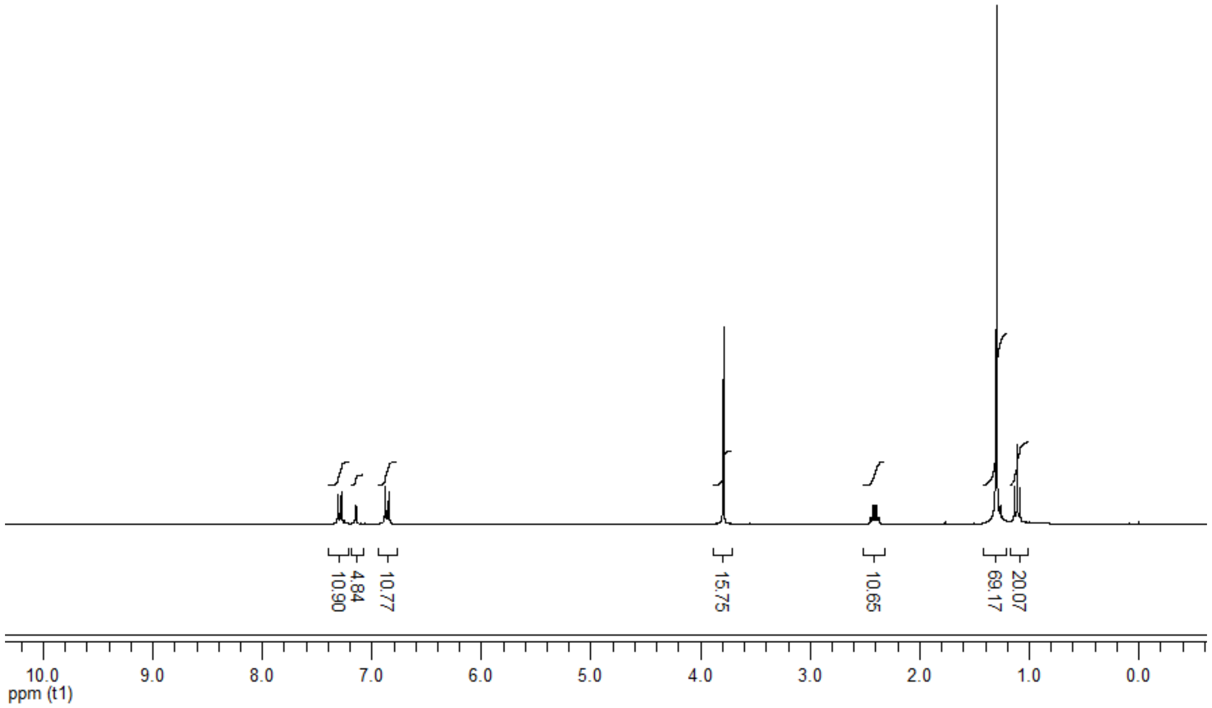
3

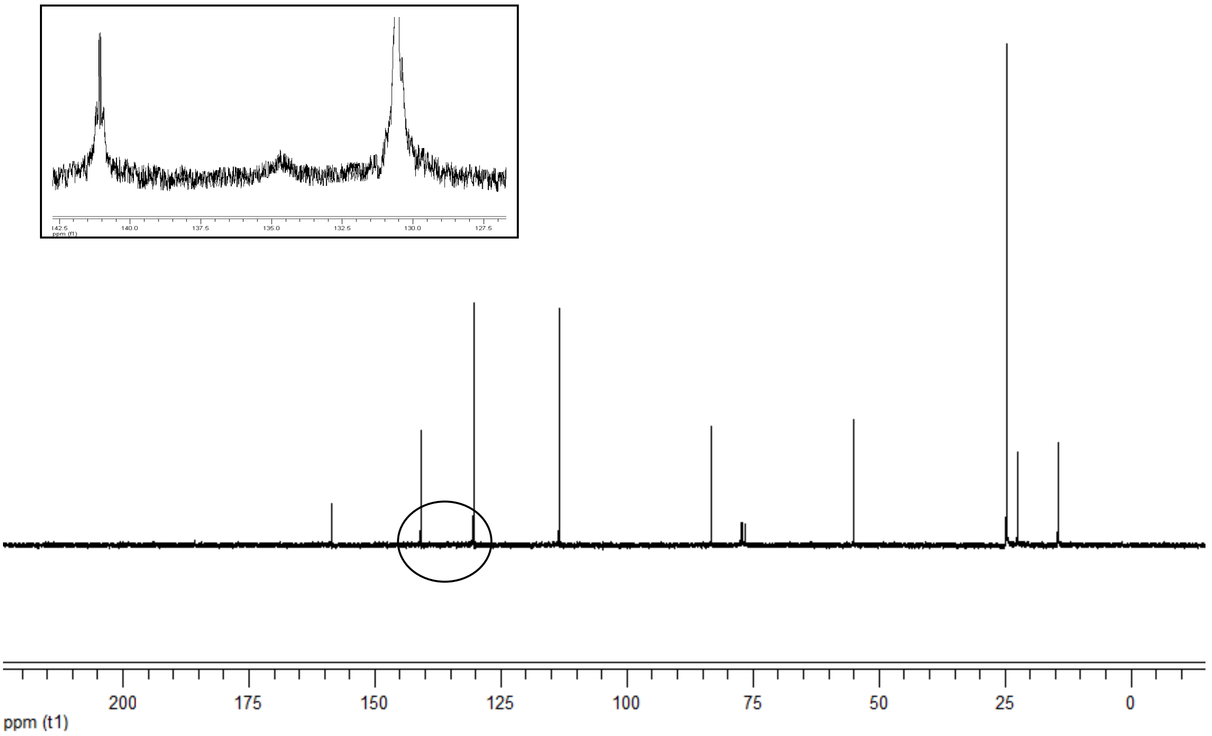

5.26
13.88
27.70
14.43
59.47
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

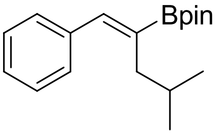

200
175
150
125
100
75
50
25
0
ppm (t1)


Bpin
MeO
CH3

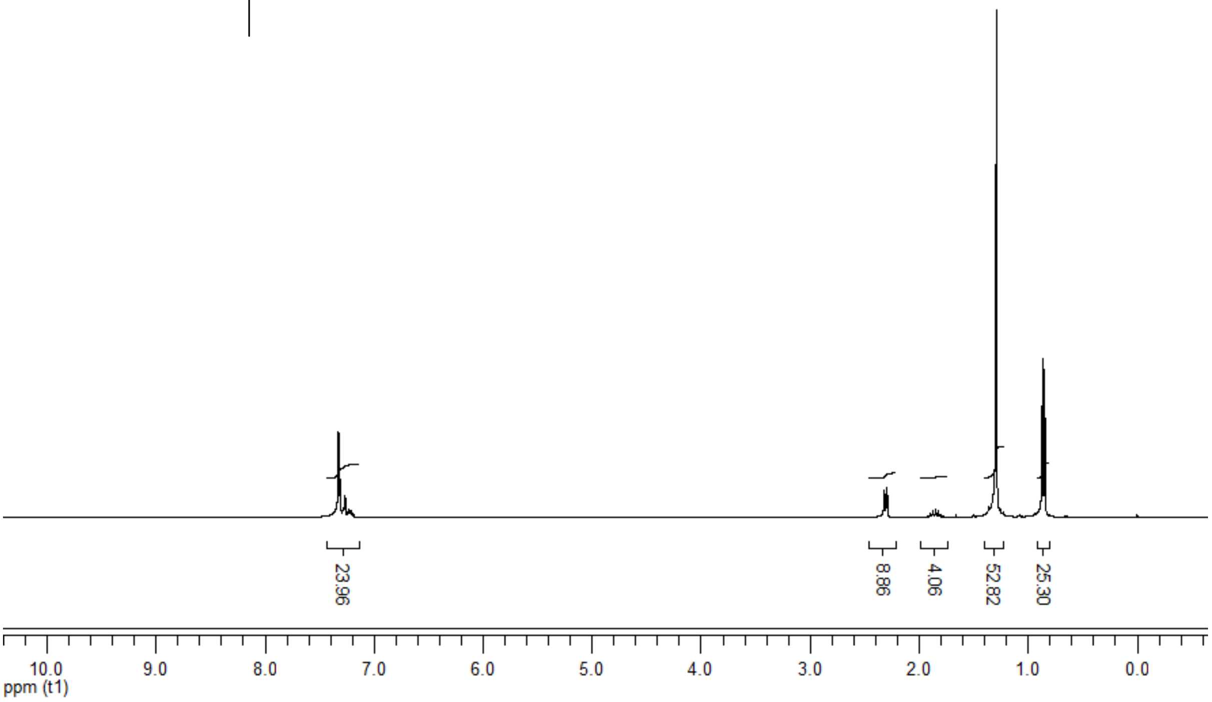
3

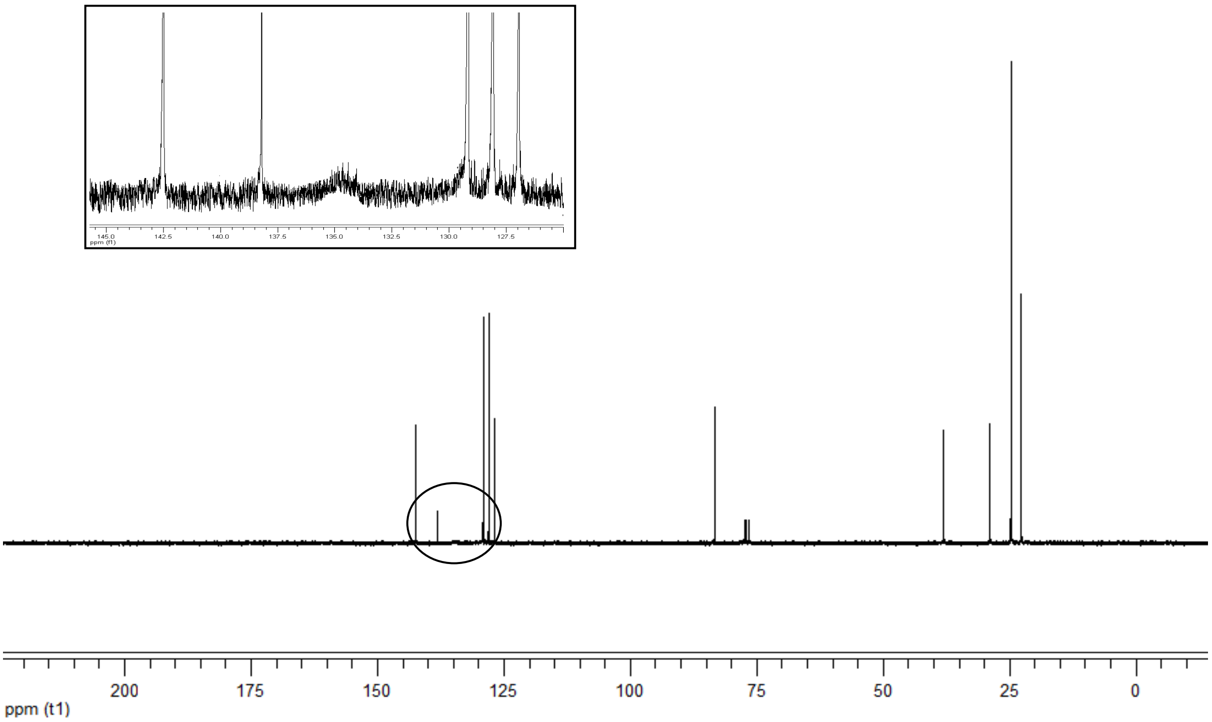

10.90
4.84
10.77
15.75
10.65
69.17
20.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

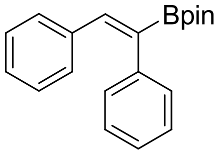

142.5
140.0
137.5
135.0
132.5
130.0
127.5
ppm (t1)
200
175
150
125
100
75
50
25
0
ppm (t1)


Bpin

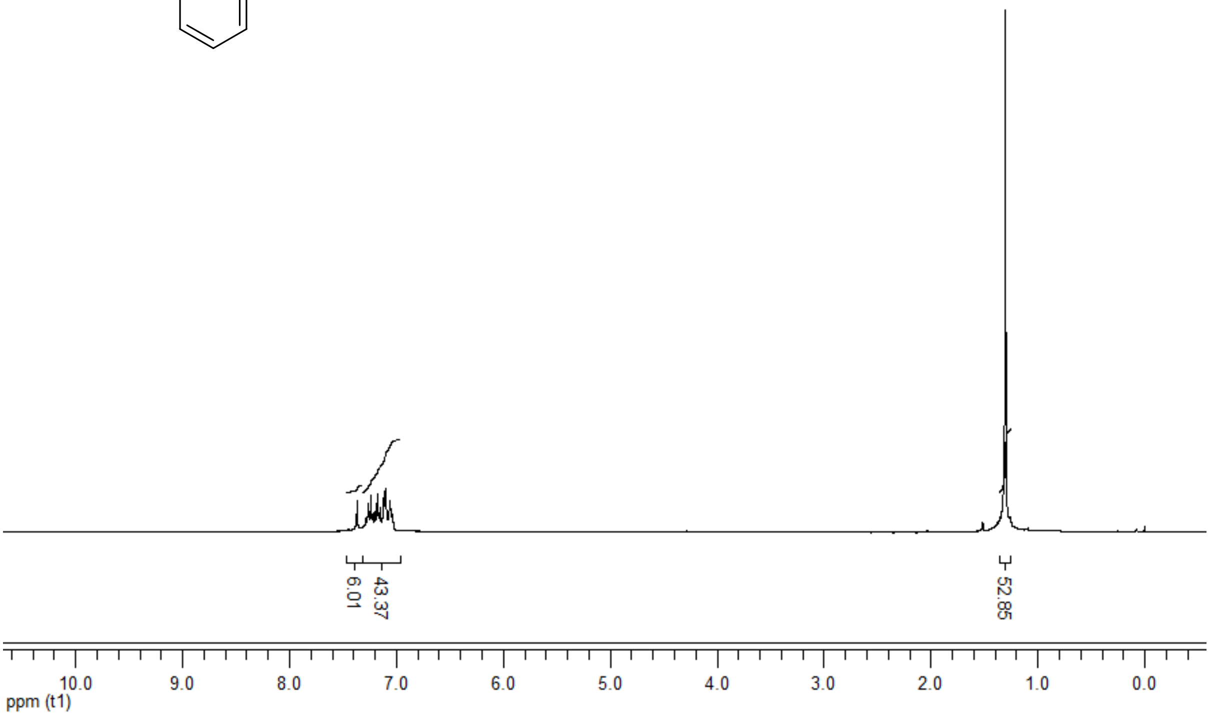
3

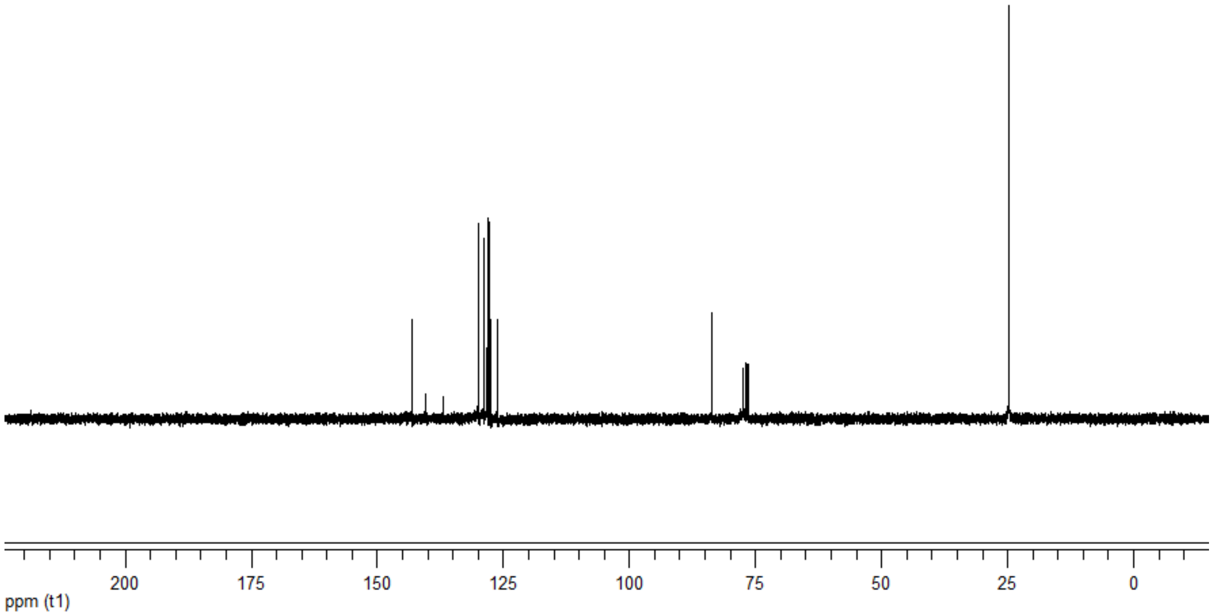

23.96
8.86
4.06
52.82
25.30
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

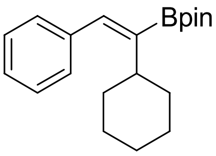

145.0
142.5
140.0
137.5
135.0
132.5
130.0
127.5
200
175
150
125
100
75
50
25
0
ppm (t1)


Bpin

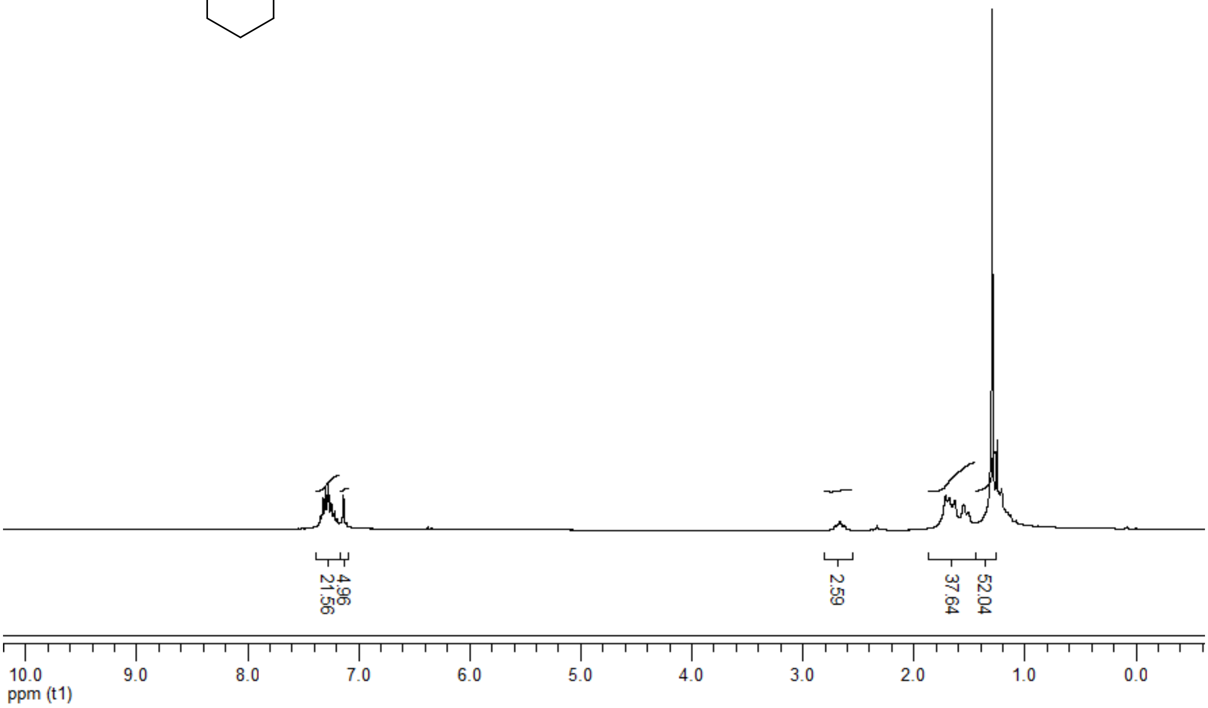
3

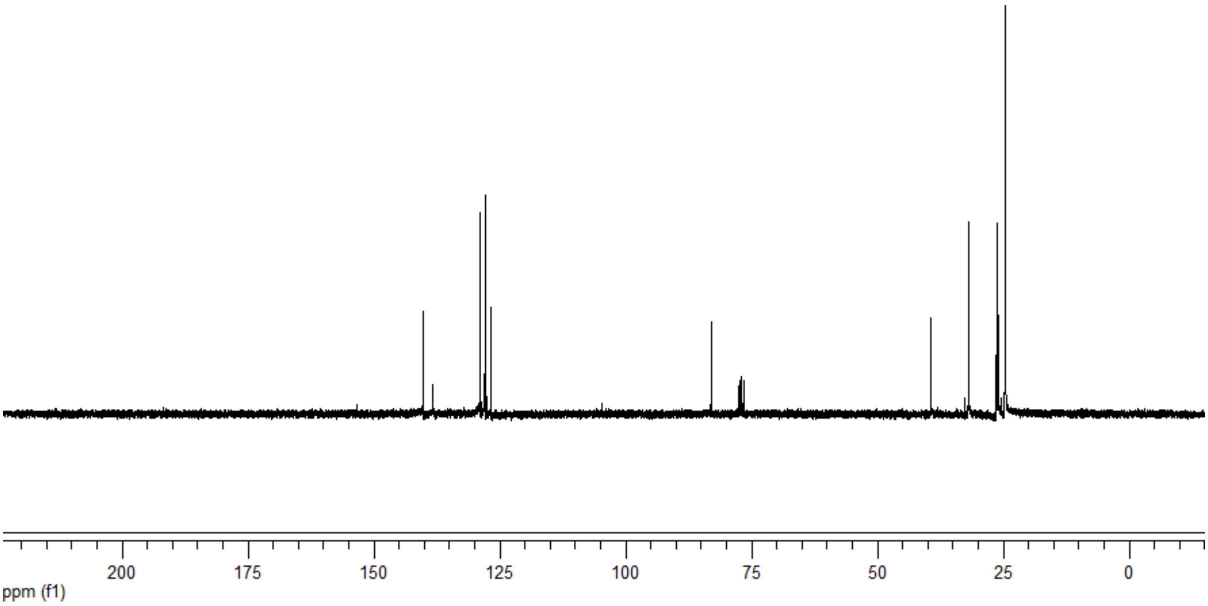

6.01
43.37
52.85
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

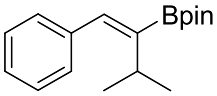

200
175
150
125
100
75
50
25
0
ppm (t1)


Bpin

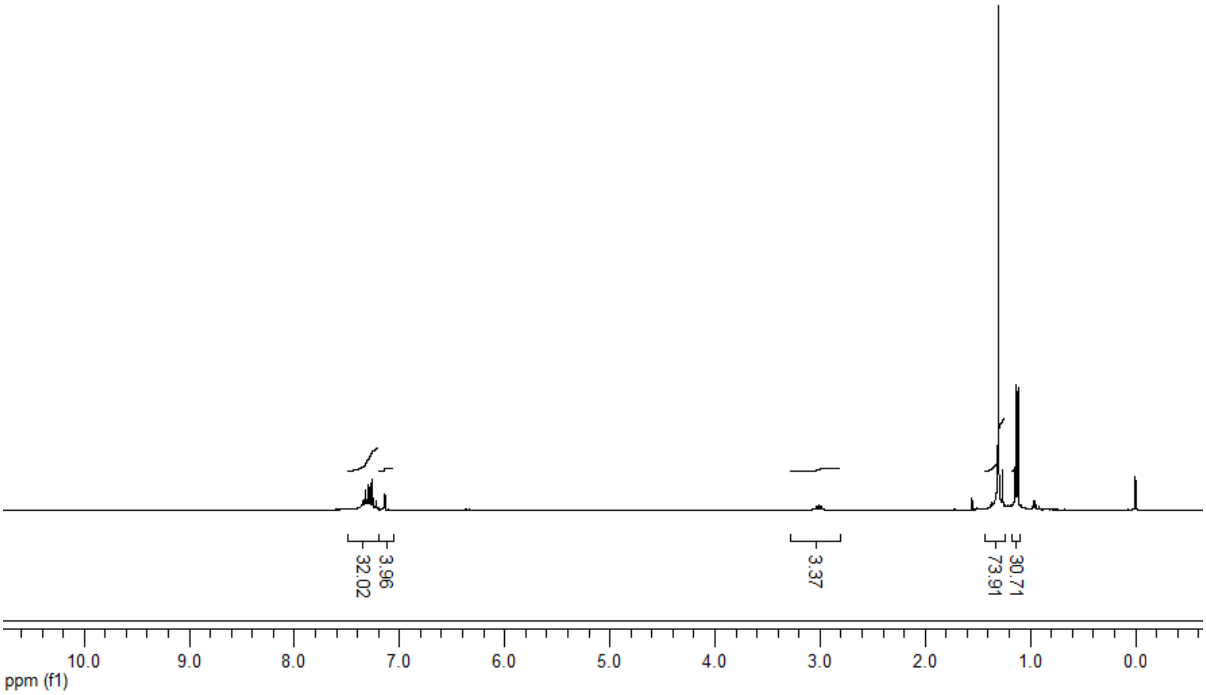
3

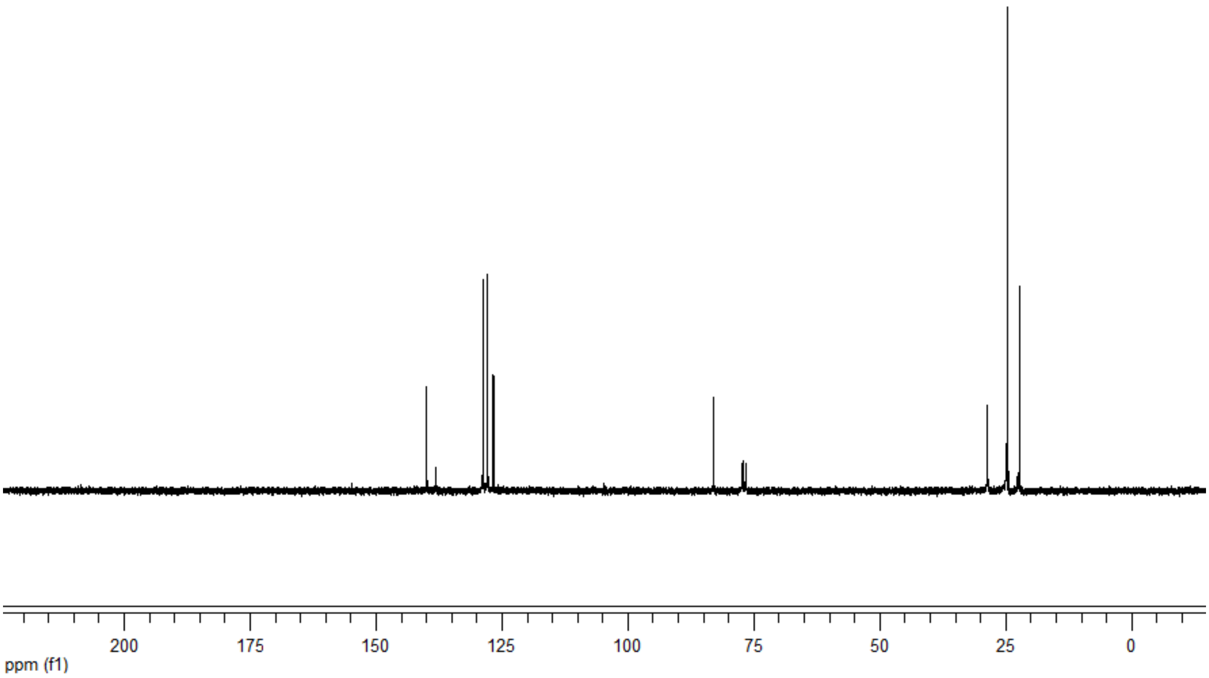

21.56
4.96
2.59
37.64
52.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

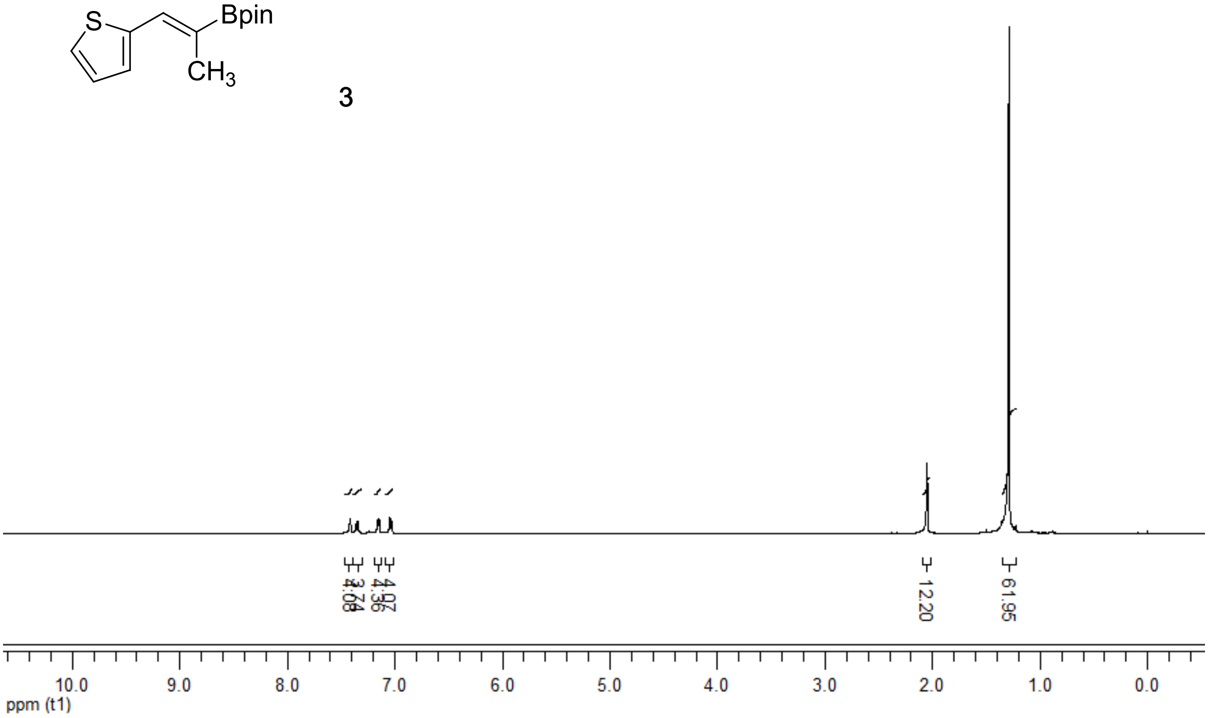

200
175
150
125
100
75
50
25
0
ppm (f1)


Bpin

3

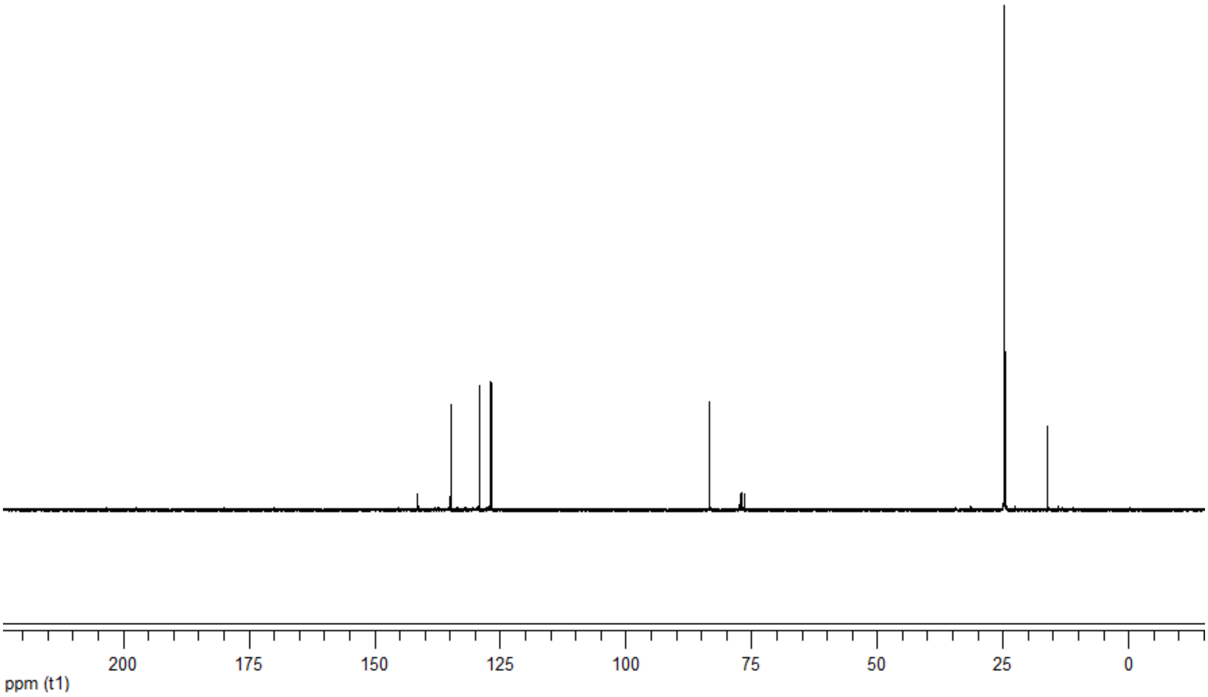

32.02
3.96
3.37
73.91
30.71
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


200
175
150
125
100
75
50
25
0
ppm (f1)


S
Bpin
CH3

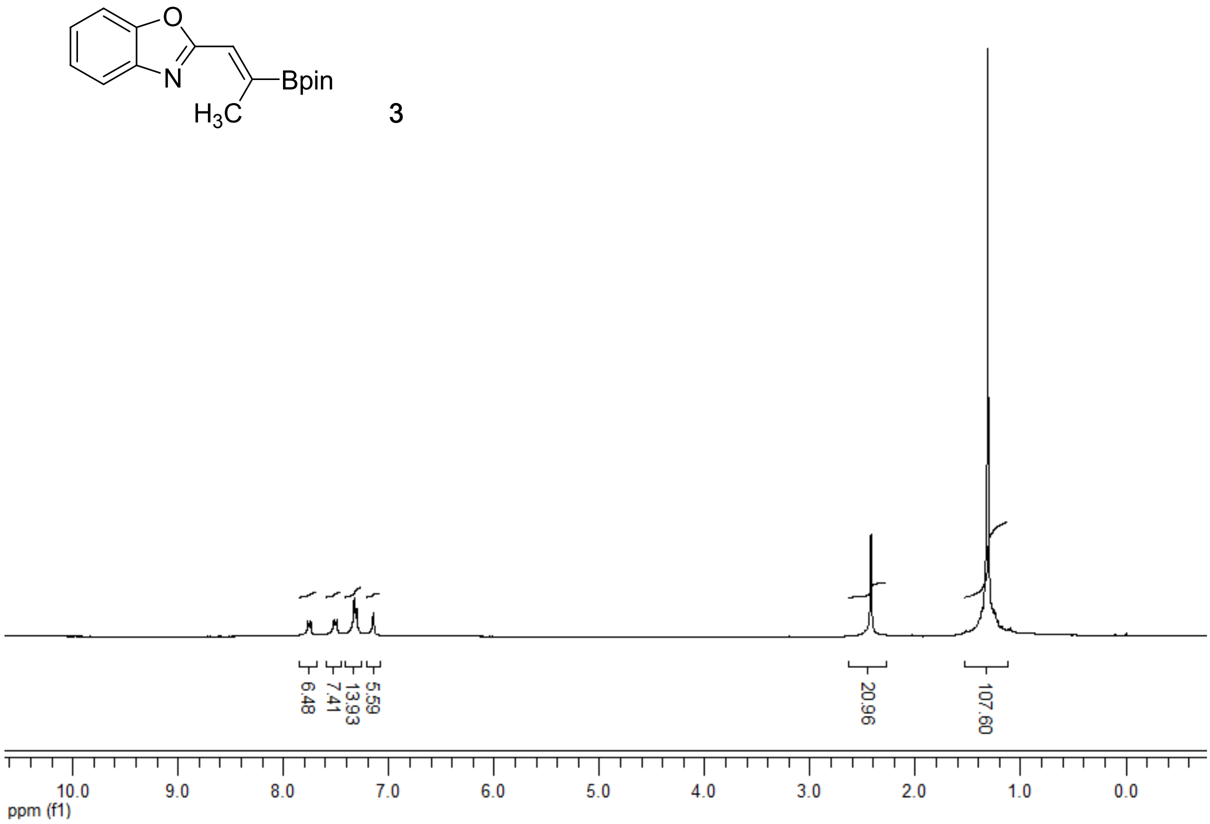
3

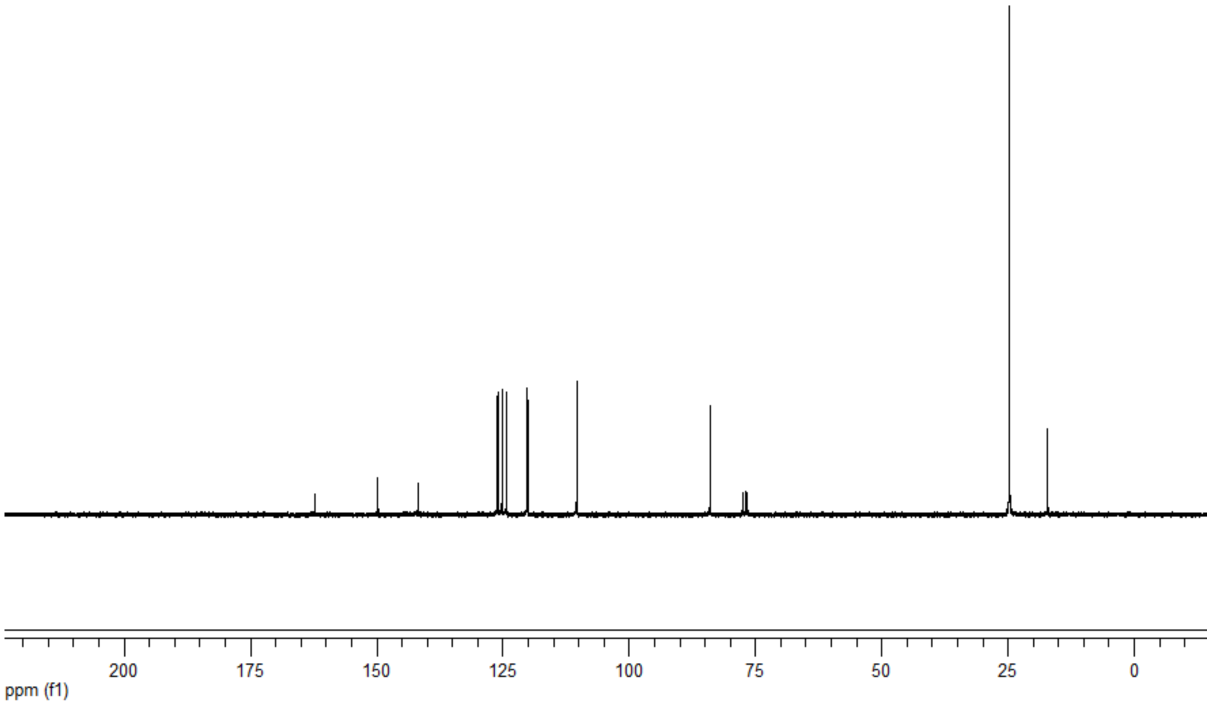
4.08
3.74
4.36
4.07
12.20
61.95
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

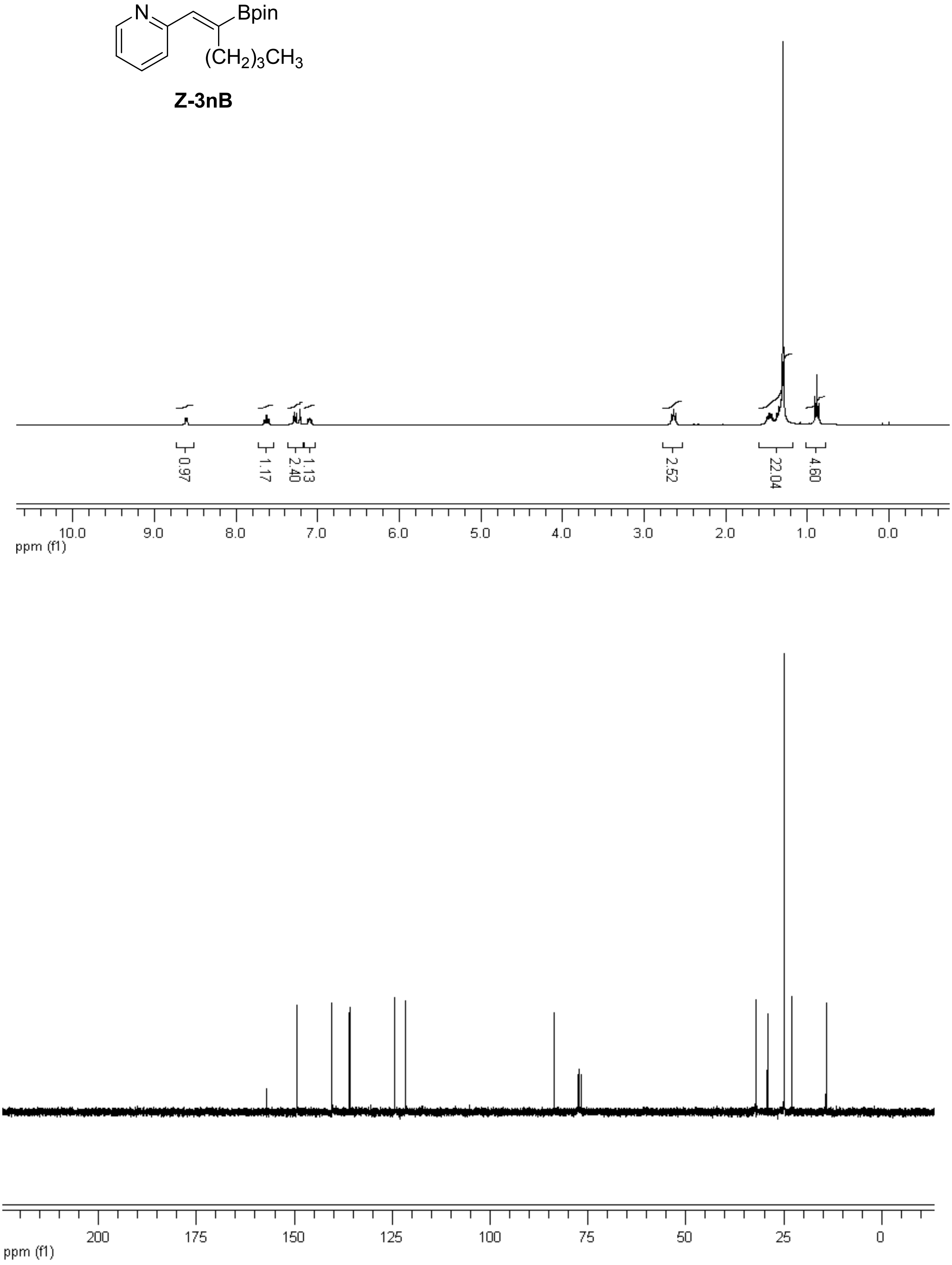

200
175
150
125
100
75
50
25
0
ppm (t1)

O
N
Bpin
H3C

3

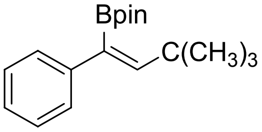

6.48
7.41
13.93
5.59
20.96
107.60
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


200
175
150
125
100
75
50
25
0
ppm (f1)

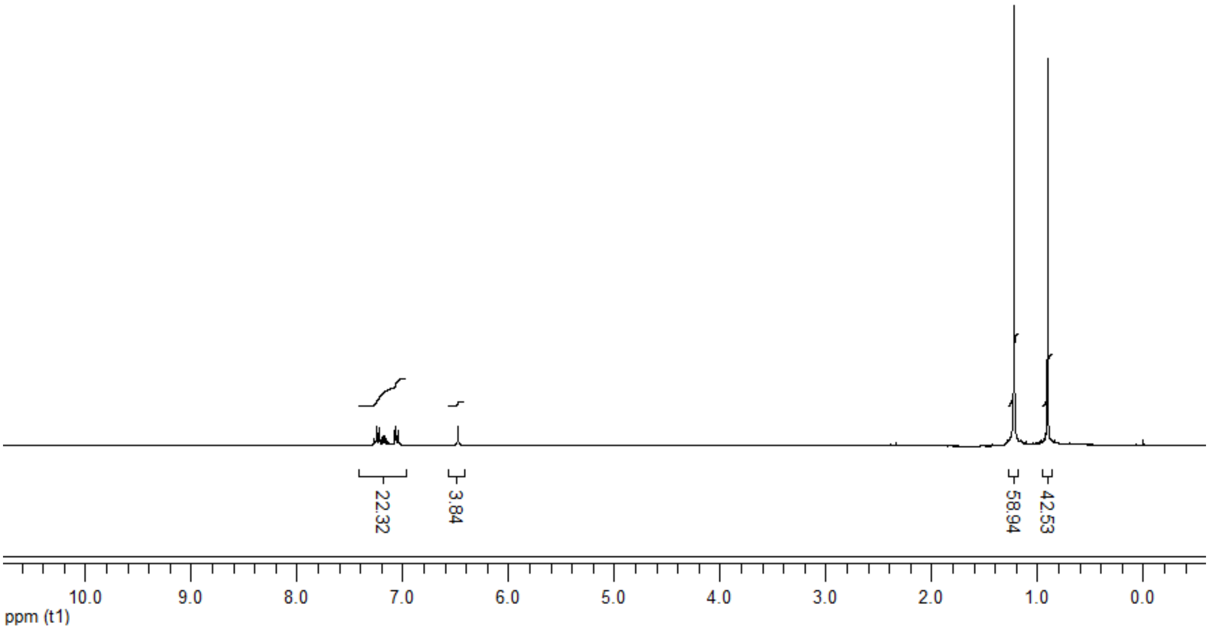


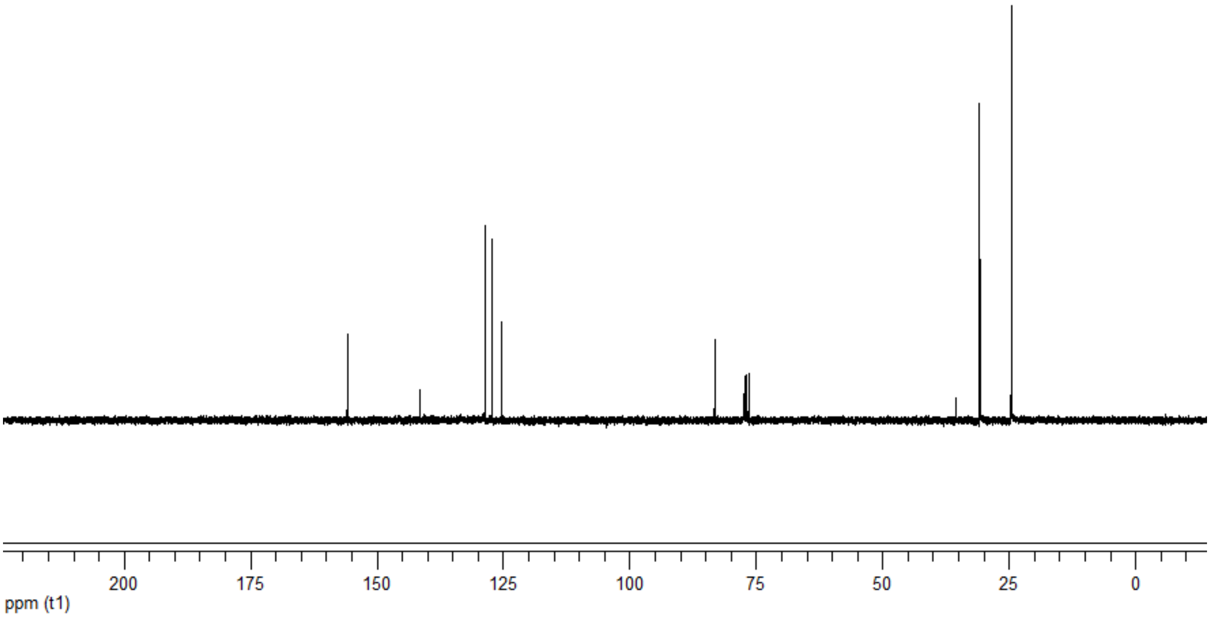
Z-3nB

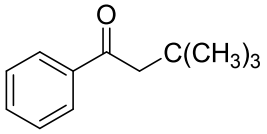
N
Bpin
(CH2)3CH3
0.97
1.17
2.40
1.13
2.52
22.04
4.60
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
200
175
150
125
100
75
50
25
0
ppm (f1)

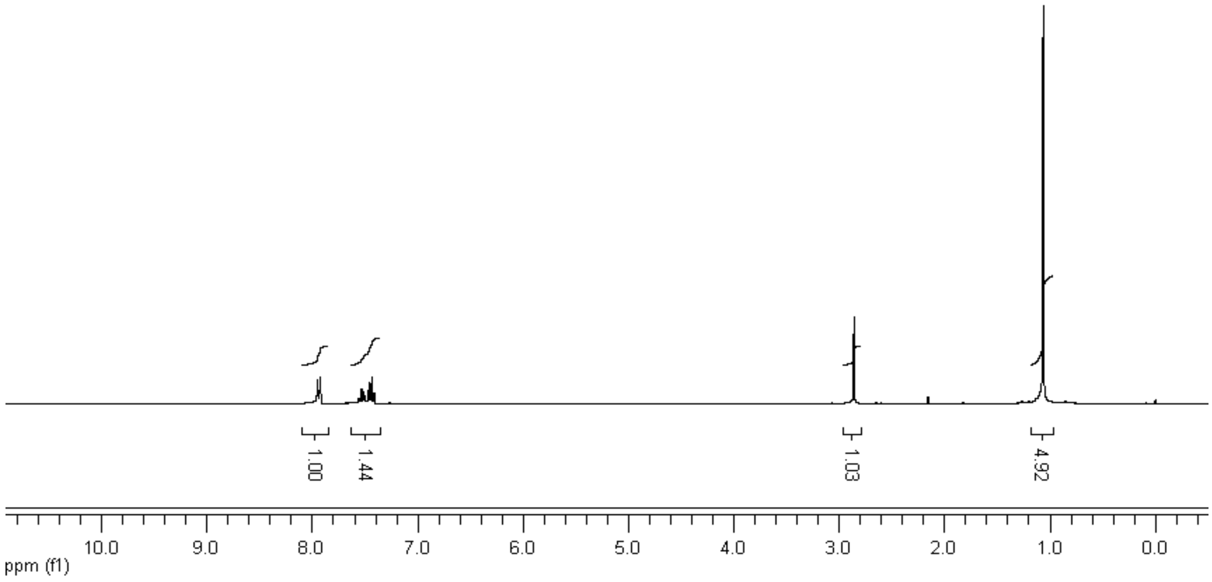

Bpin
C(CH3)3

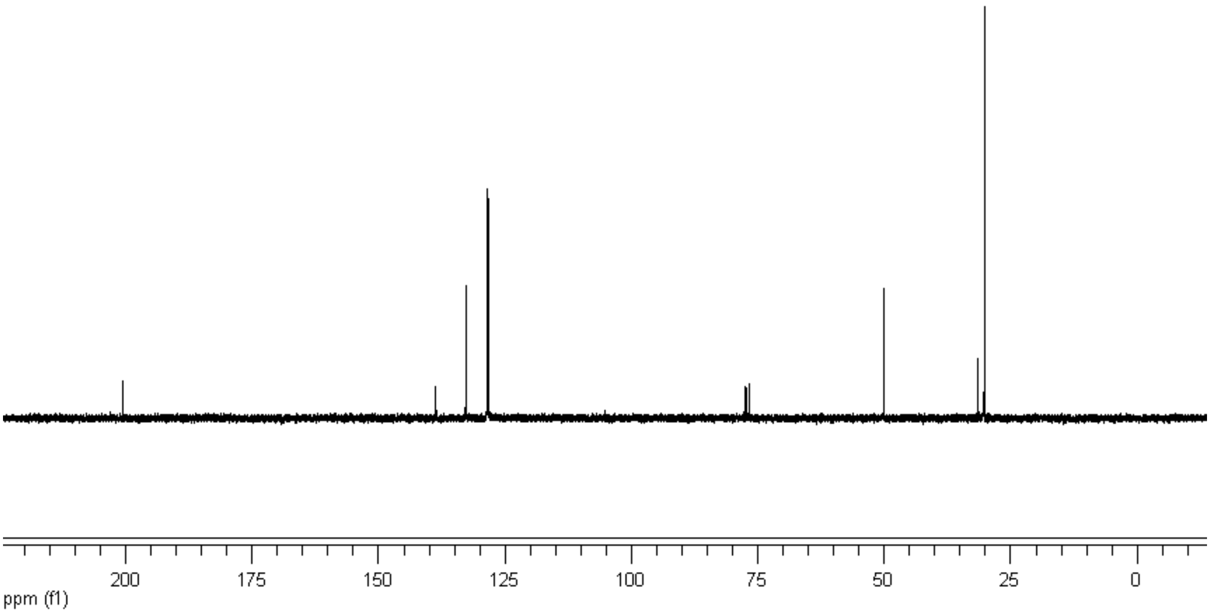
5

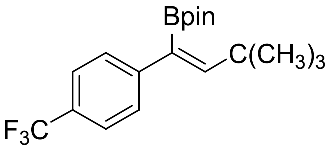

22.32
3.84
58.94
42.53
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


200
175
150
125
100
75
50
25
0
ppm (t1)

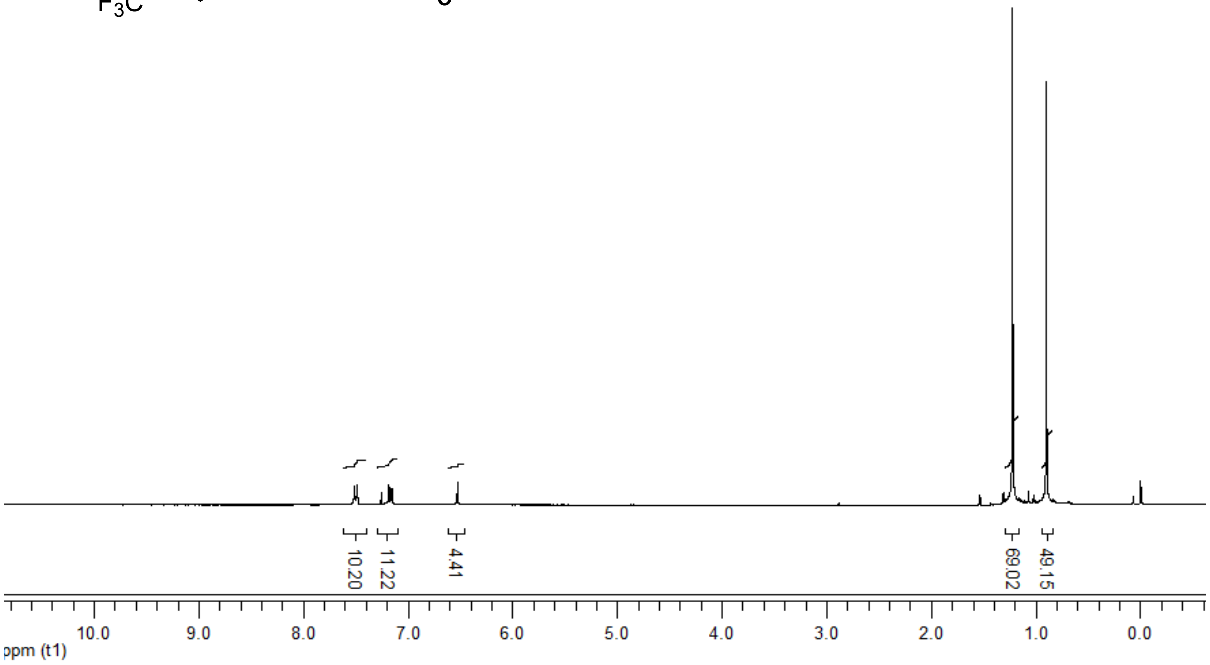

O
C(CH3)3

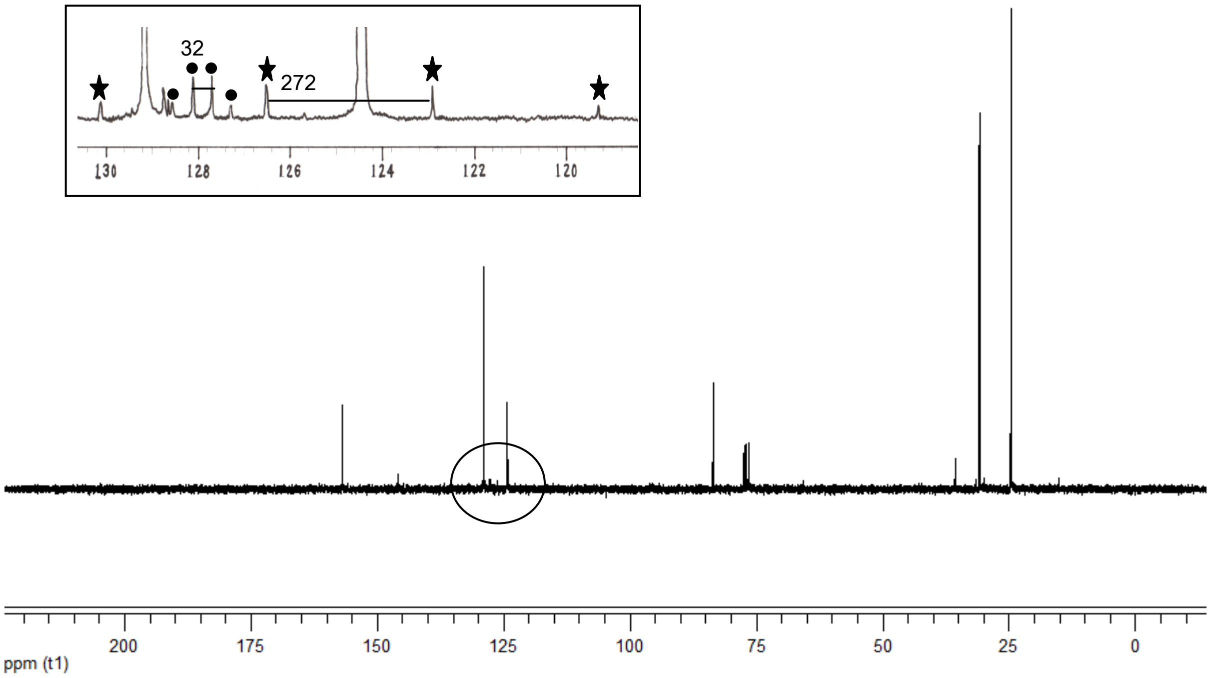

1.00
1.44
1.03
4.92
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

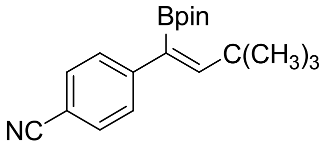

200
175
150
125
100
75
50
25
0
ppm (f1)


Bpin
C(CH3)3
F3C

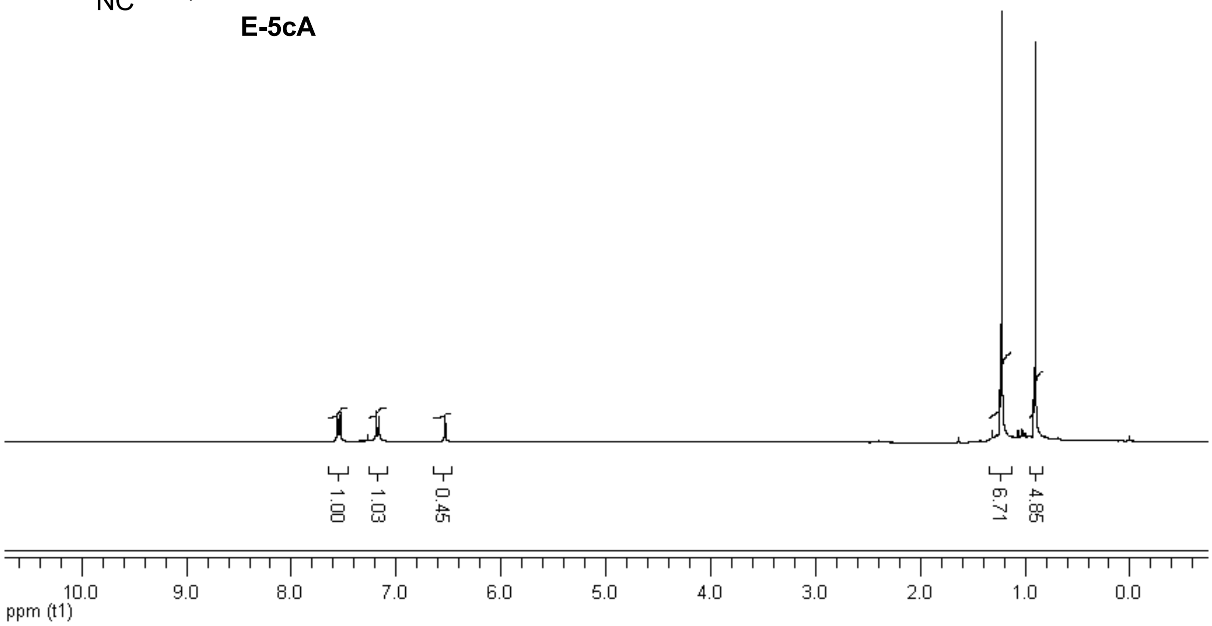
5

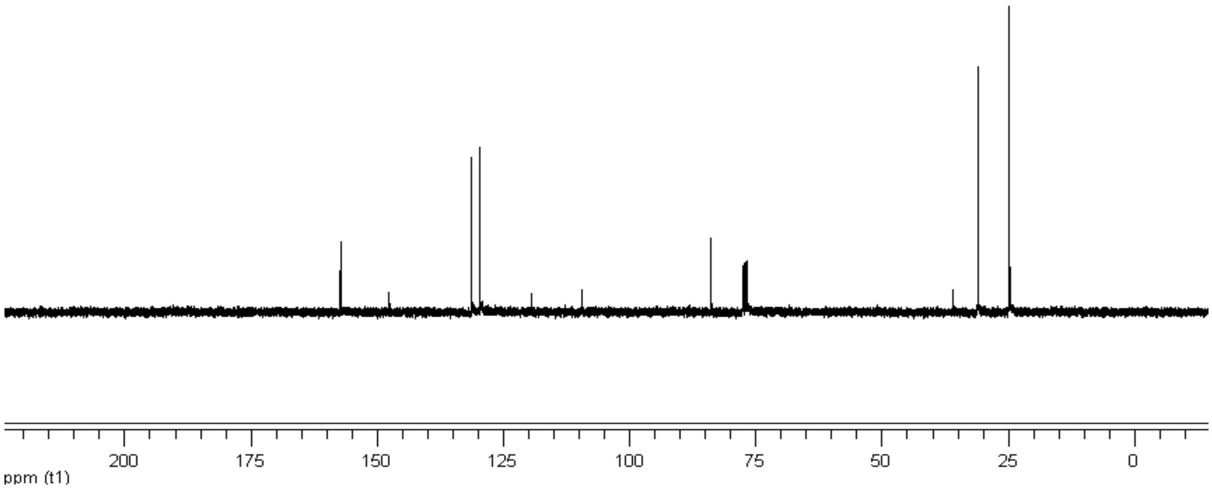

10.20
11.22
4.41
69.02
49.15
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

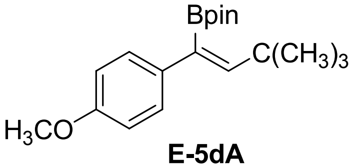

32
272
130
128
126
124
122
120
200
175
150
125
100
75
50
25
0
ppm (t1)


Bpin
C(CH3)3
NC

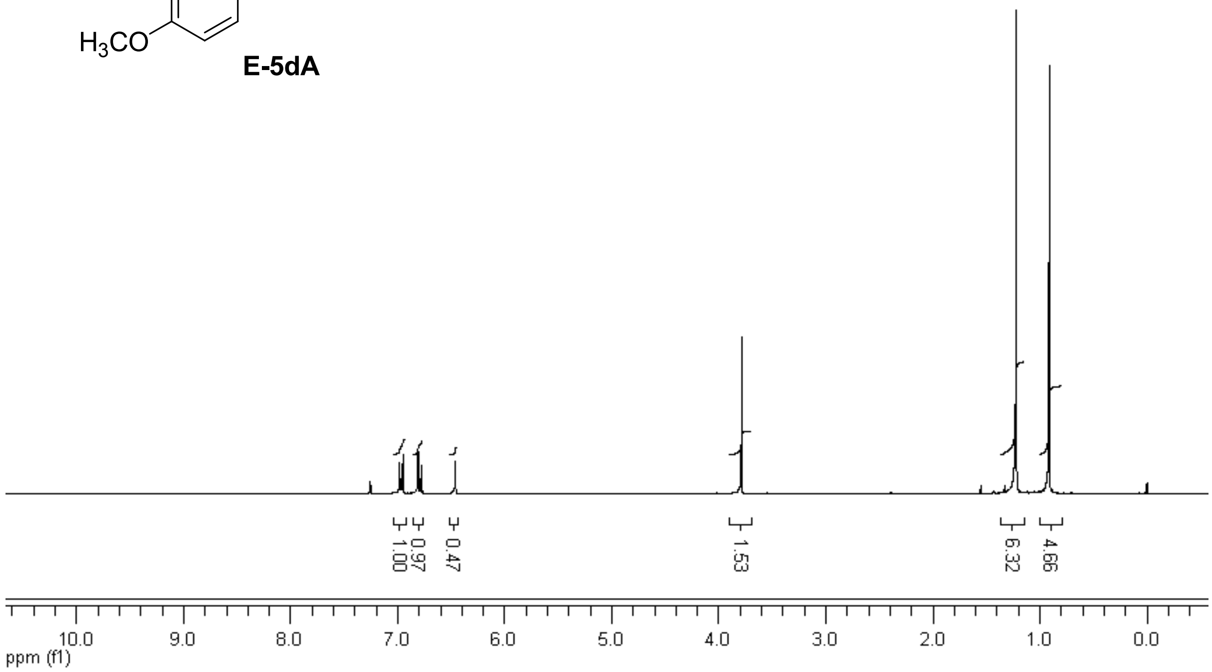
E-5cA

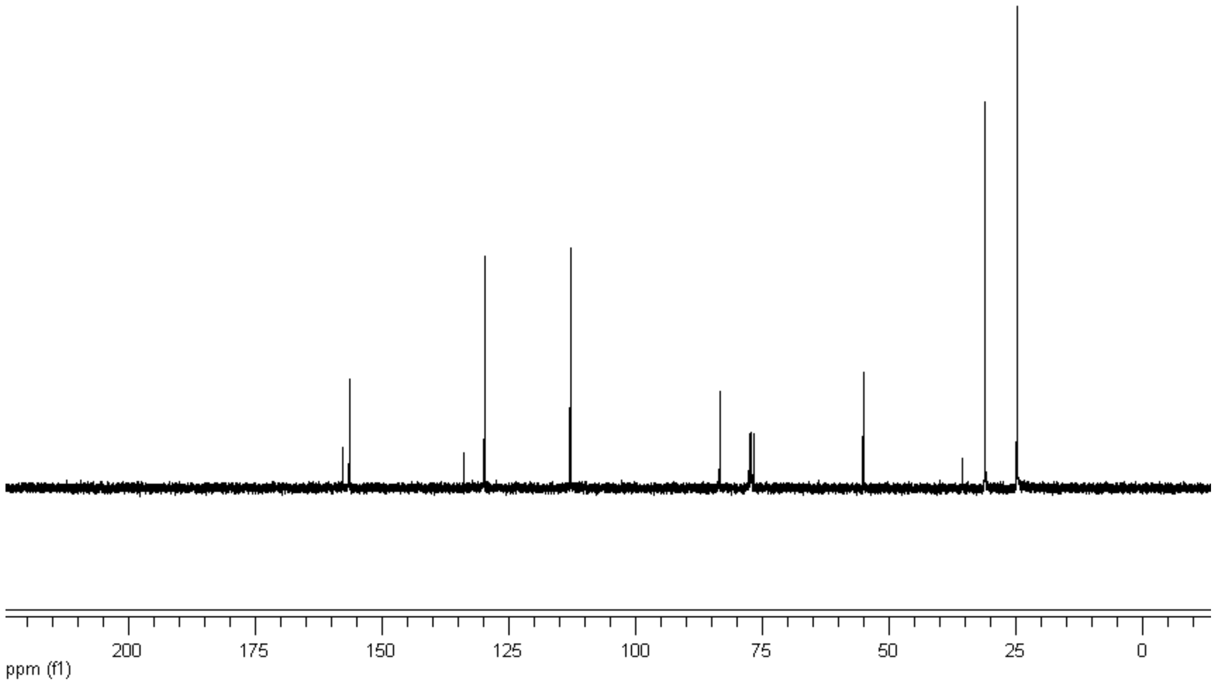

1.00
1.03
0.45
6.71
4.85
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

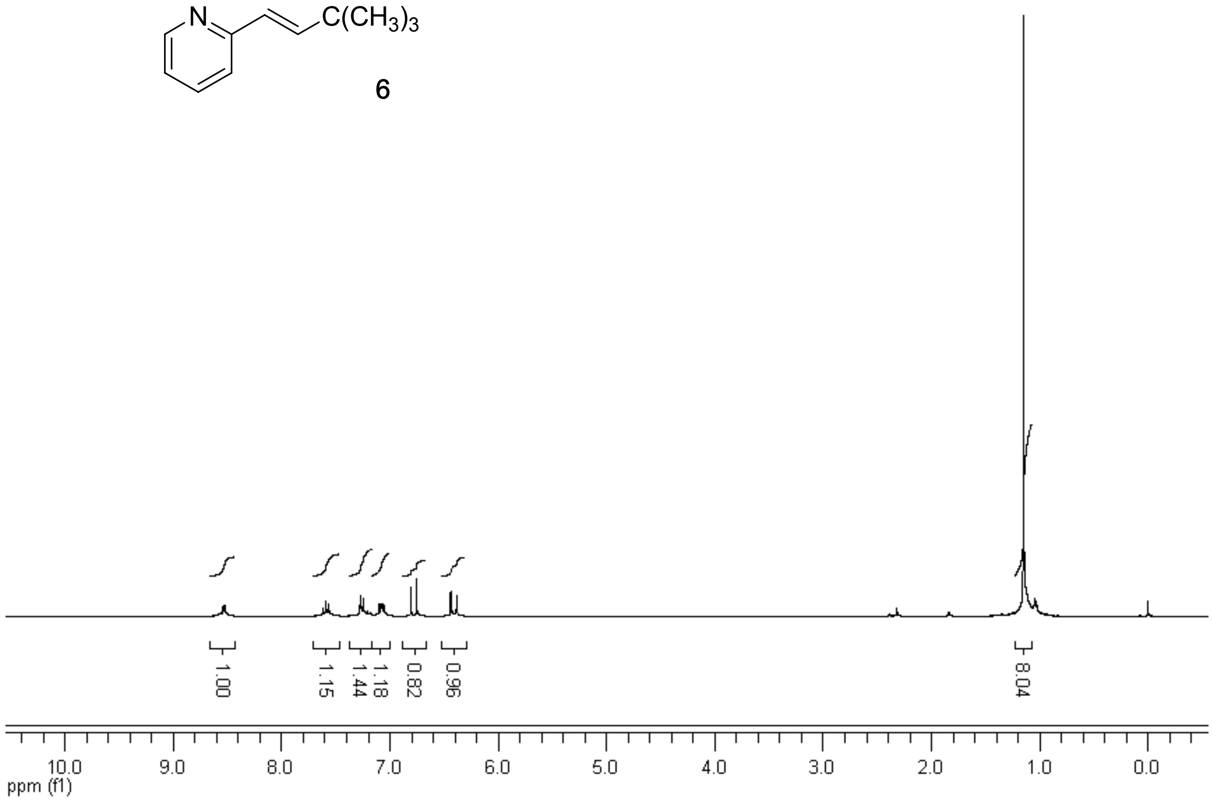

200
175
150
125
100
75
50
25
0
ppm (t1)


Bpin
C(CH3)3
H3CO

E-5dA

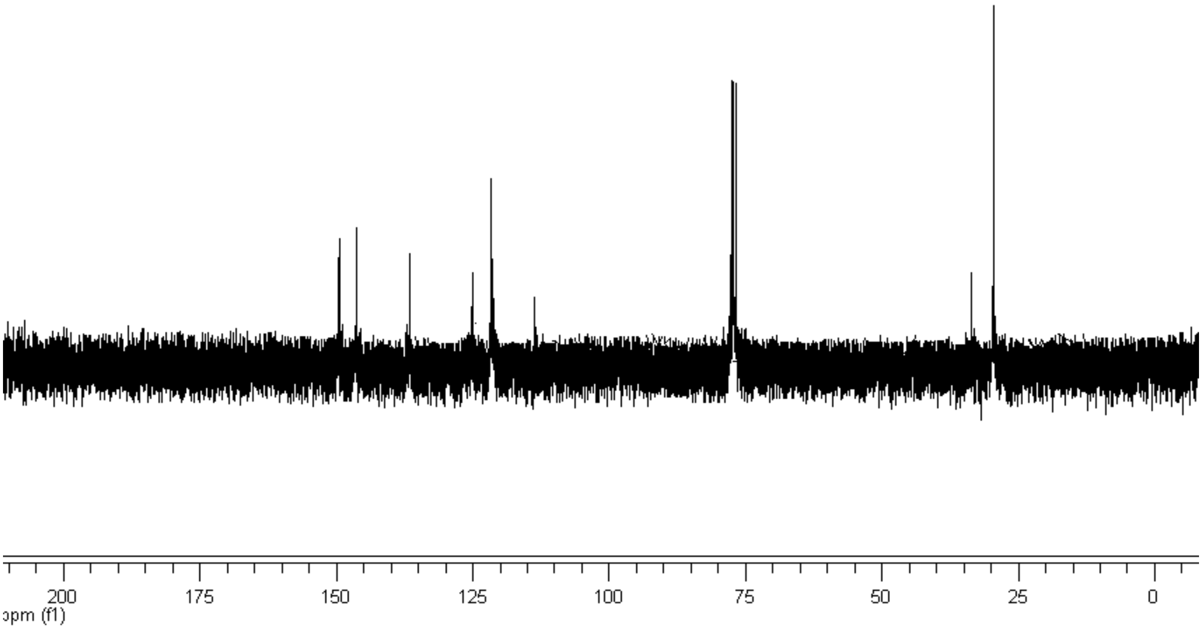

1.00
0.97
0.47
1.53
6.32
4.66
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


200
175
150
125
100
75
50
25
0
ppm (f1)

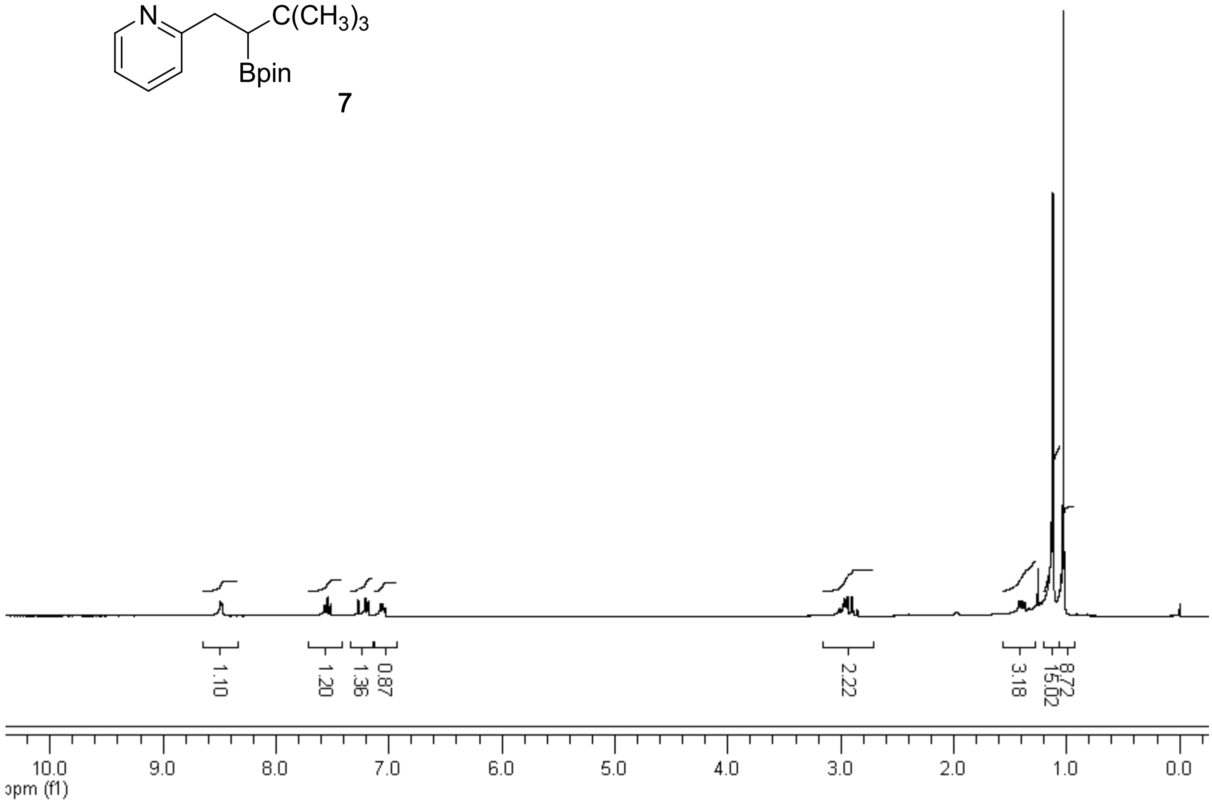


6

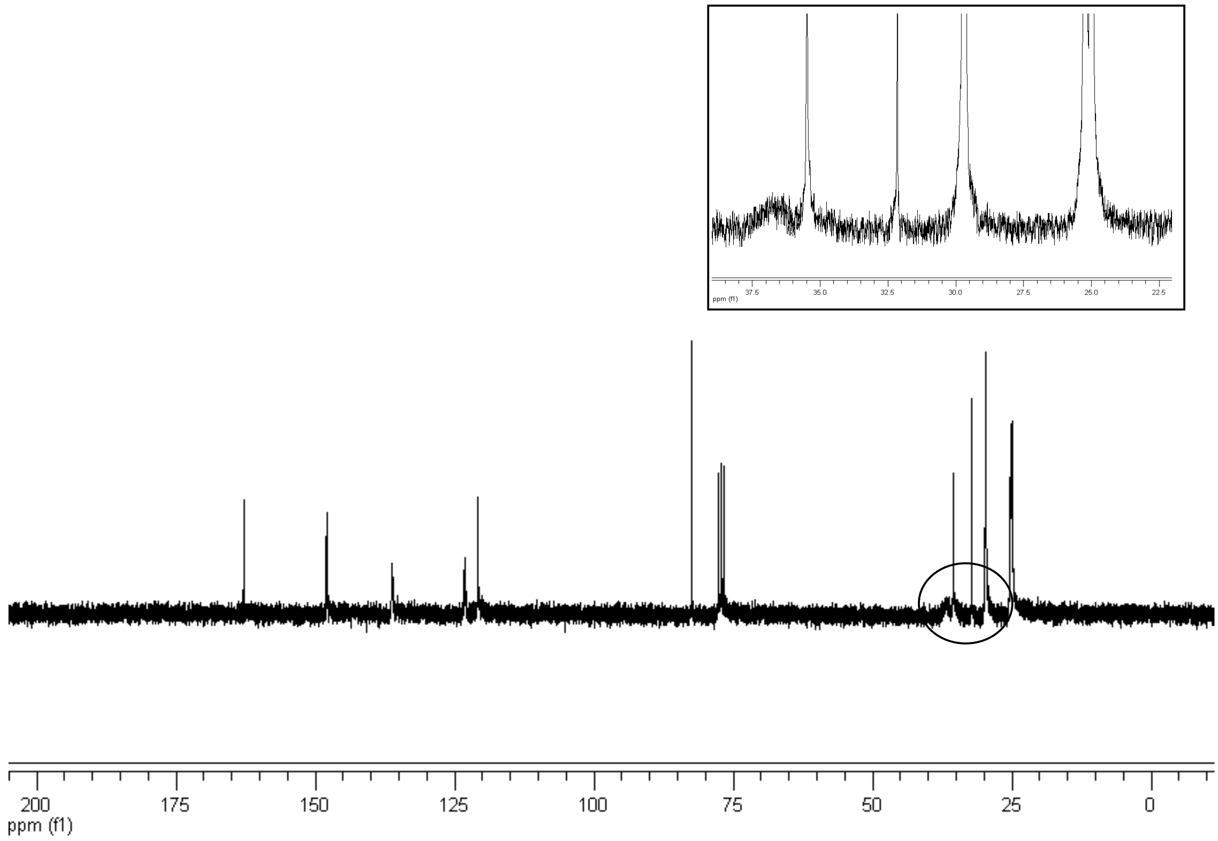
C(CH3)3
N
1.00
1.15
1.44
1.18
0.82
0.96
8.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

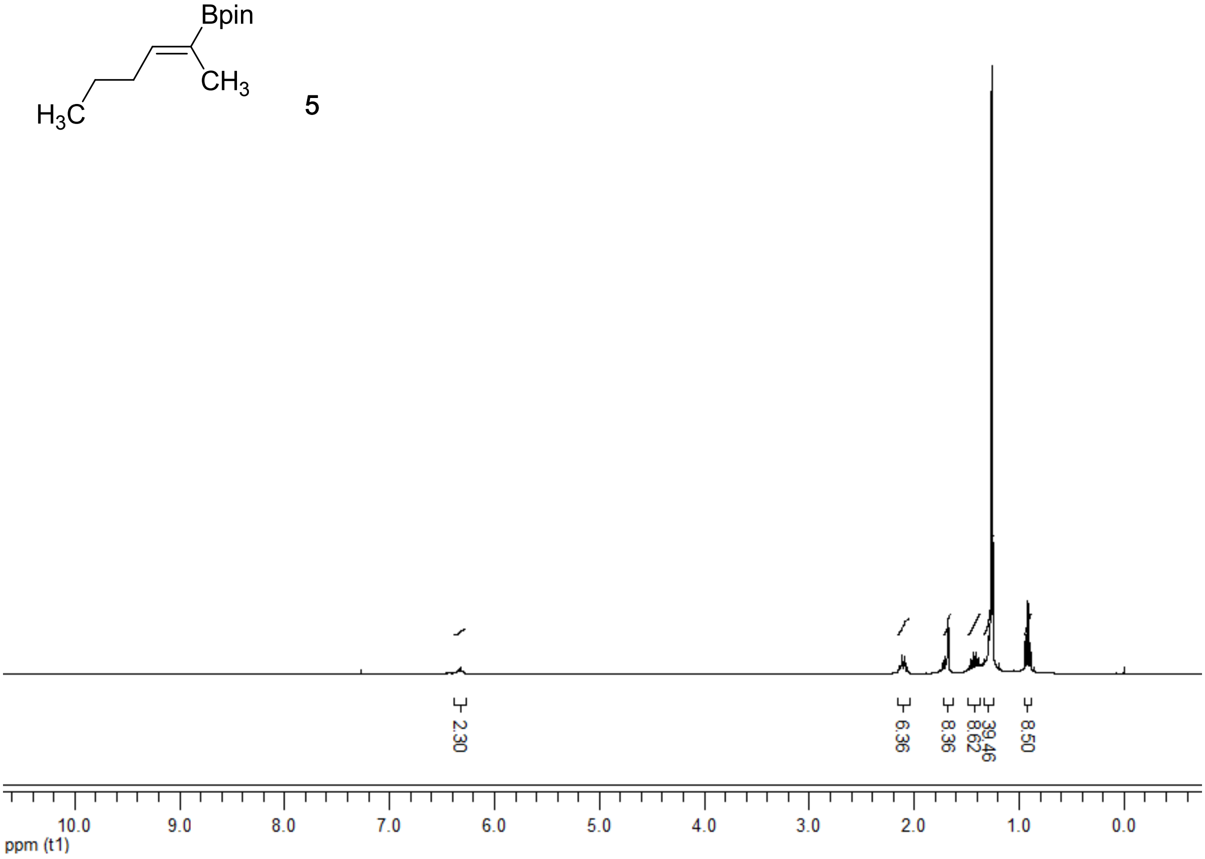


200
175
150
125
100
75
50
25
0
ppm (f1)

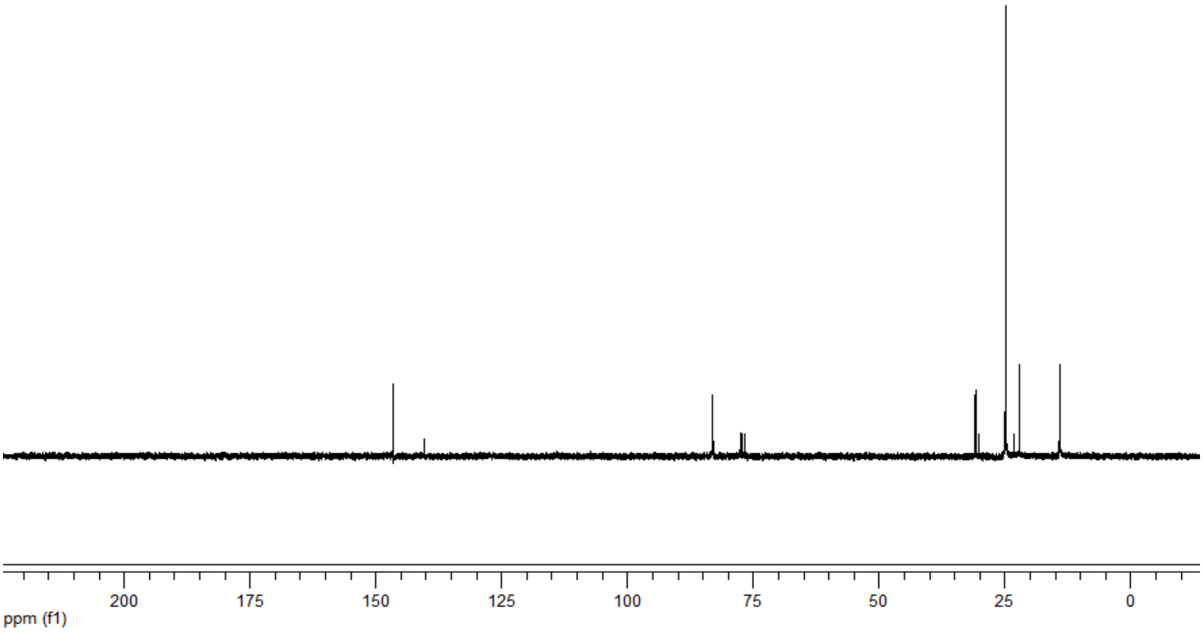

N
C(CH3)3
Bpin
1.10
1.20
1.36
0.87
2.22
3.18
15.02
8.72
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

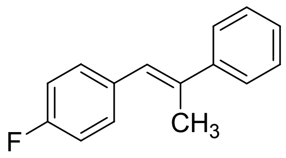
7


37.5
35.0
32.5
30.0
27.5
25.0
22.5
ppm (f1)
200
175
150
125
100
75
50
25
0
ppm (f1)

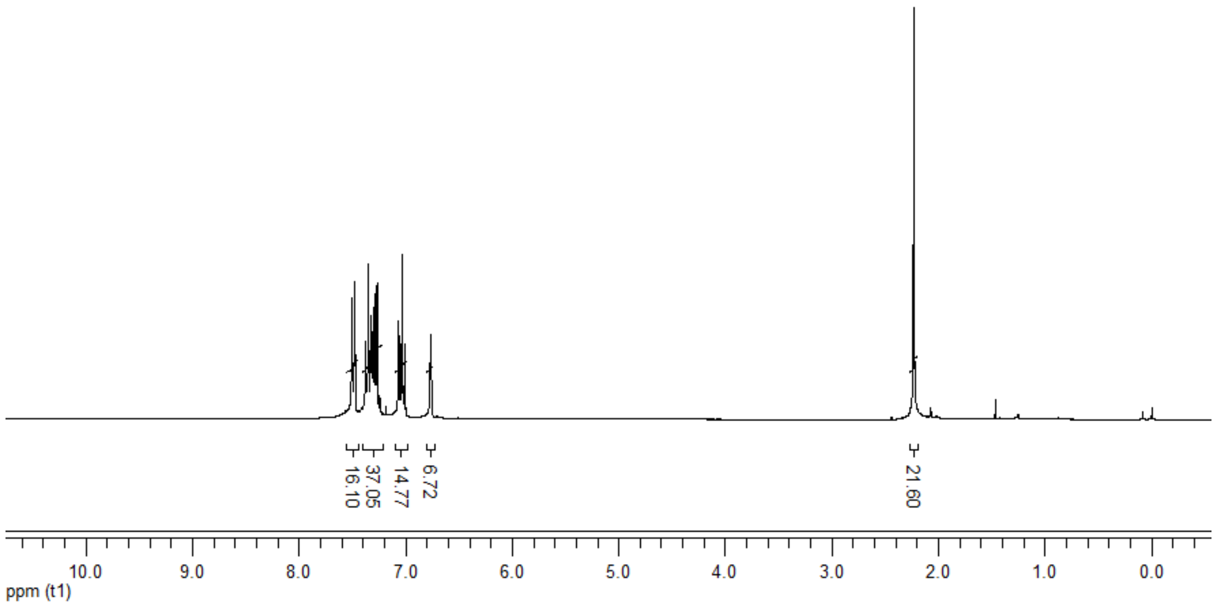

Bpin
CH3
H3C
2.30
6.36
8.36
8.62
39.46
8.50
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

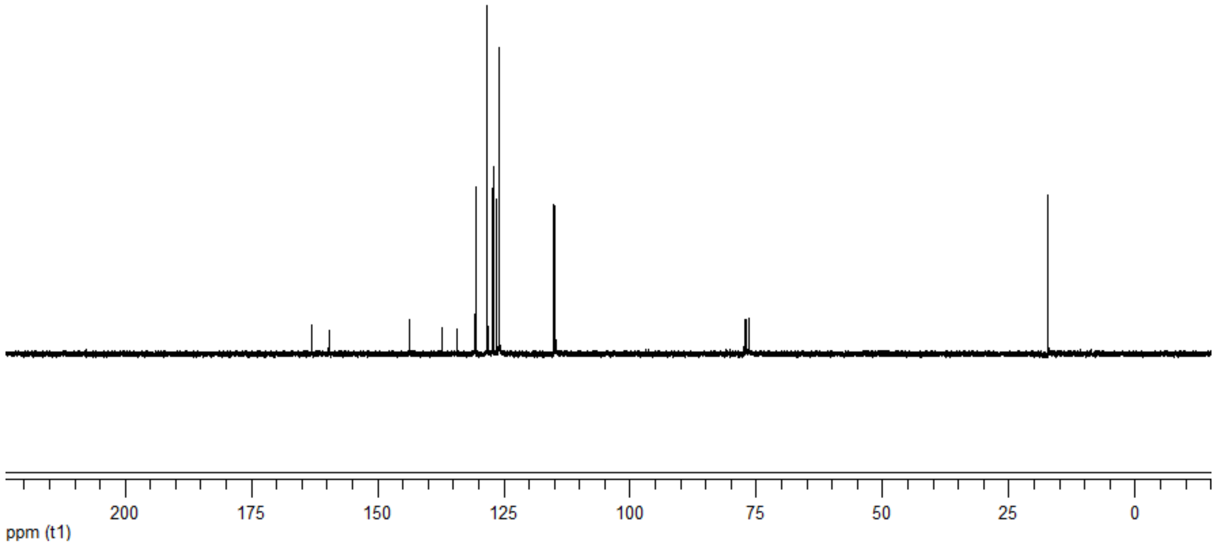
5

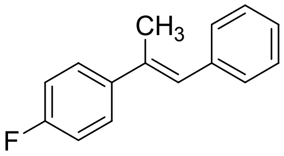

200
175
150
125
100
75
50
25
0
ppm (f1)


F
CH3

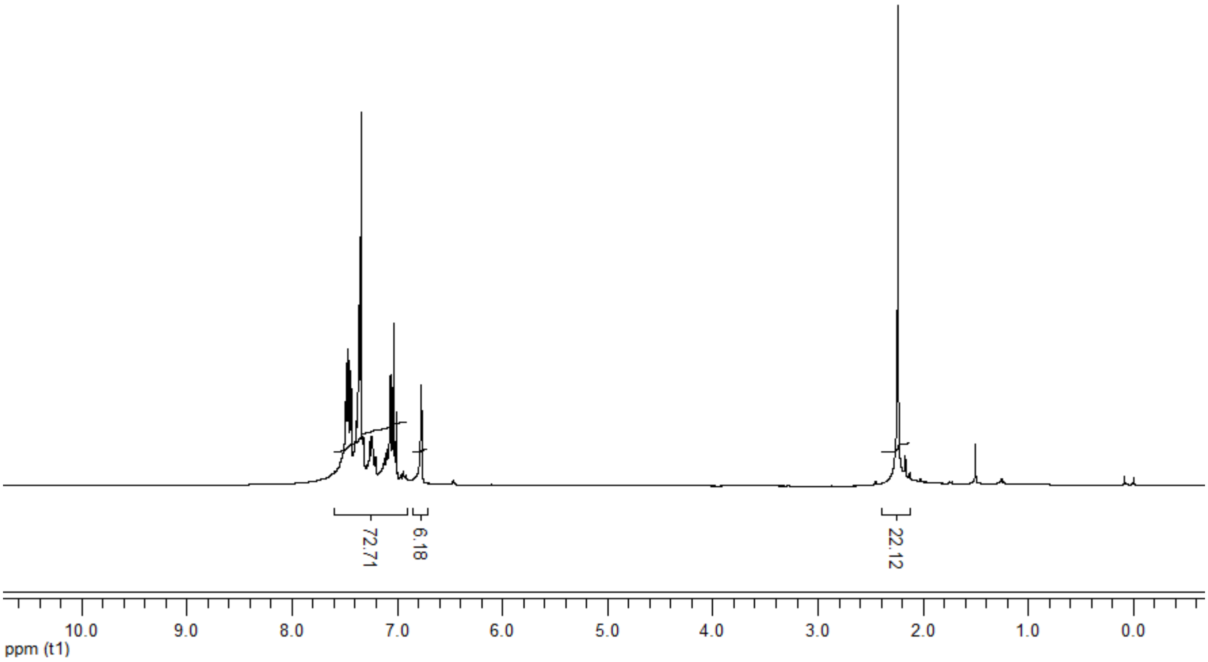
8

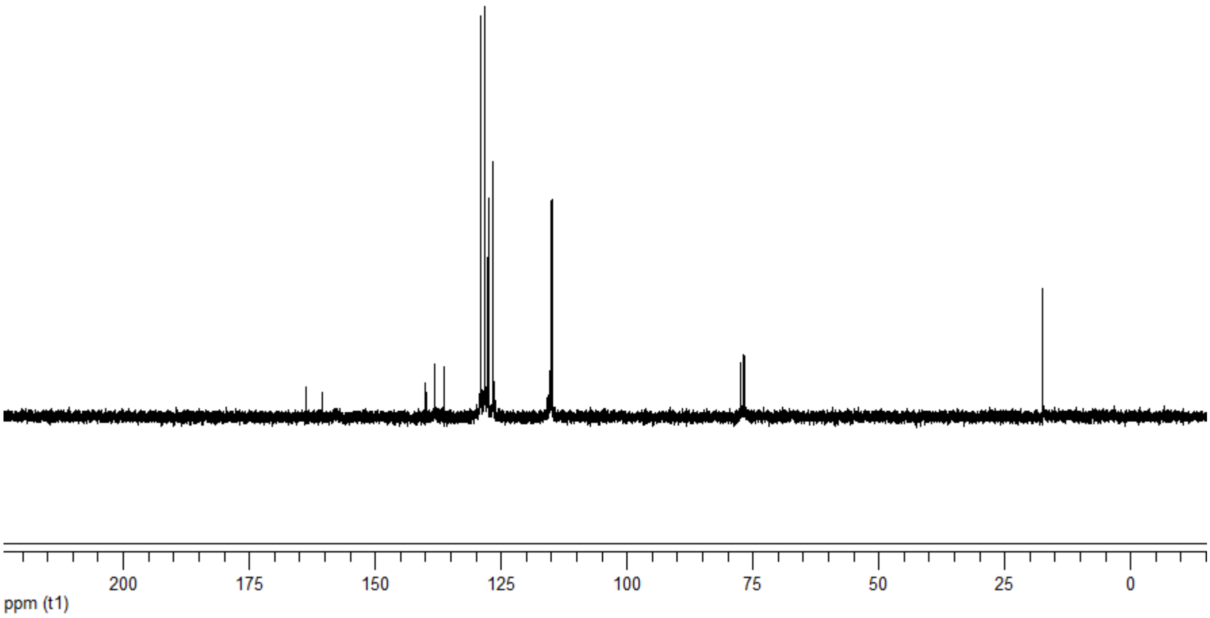

16.10
37.05
14.77
6.72
21.60
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


200
175
150
125
100
75
50
25
0
ppm (t1)


CH3
F

10


72.71
6.18
22.12
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


200
175
150
125
100
75
50
25
0
ppm (t1)