Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Facile Synthesis of Electrophilic Vinyl Boranes: Reactions of Alkynyl-borates and Diazonium Salts

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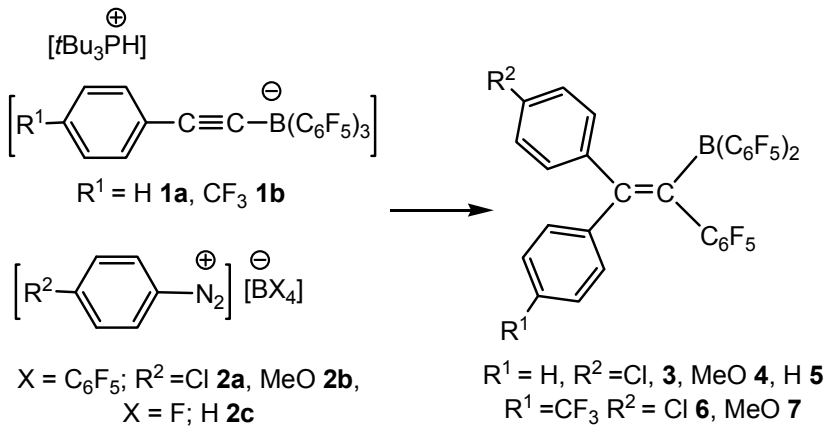
General Considerations. All manipulations were performed under an atmosphere of dry, oxygen-free N_2 by means of standard Schlenk or glovebox techniques (Innovative Technology glovebox equipped with a –38ºC freezer). Pentane, dichloromethane and toluene were dried using an Innovative Technologies solvent system and degassed prior to use. Dichloromethane-d^2 and Benzene-d^6 were purchased from Aldrich, dried on CaH_2 and was vacuum distilled onto 4Å molecular sieves prior to use. NMR spectra were obtained on a Bruker Avance 400 MHz or a Varian 400 MHz and spectra were referenced to residual solvent of C_6D_6 (^1H = 7.16 ppm for meta proton; ^{13}C = 128.06 ppm for carbon), and CD_2Cl_2 (^1H = 5.32 ppm; ^{13}C = 53.84 ppm). Chemical shifts (δ) listed are in ppm and absolute values of the coupling constants are in Hz. NMR assignments are supported by additional 2D experiments. Elemental analyses (C, N, H) and X-ray crystallography were performed in house. (tBu)$_3$P, HBF_4, $NaBF_4$, Aniline, 4-methoxyaniline, , 4-chloroaniline, phenylacetylene and 4-trifluoromethylphenylacetylene were purchased from Aldrich and used without further purification. $B(C_6F_5)_3$ was purchased from Boulder Scientific. Potassium tetrakis(pentafluorophenyl)borate was purchased from Bolder and used without further treatment.



The compounds **1**[1] and **2**[2] were prepared according to the references.

1. M. A. Dureen, C. C. Brown, D. W. Stephan, *Organometallics* **2010**, 29, 6594-6607.

2. C. Combellas, D. Jiang, F. Kanoufi, J. Pinson, F. I. Podvorica, *Langmuir* **2009**, 25, 286-293.

Synthesis of $(C_6H_4Cl)(Ph)CC(C_6F_5)(B(C_6F_5)_2)$ 3 (*E*-isomer): To a suspension of $[Cl(C_6H_4)N_2][B(C_6F_5)_4]$ (60 mg, 0.073 mmol) in CH_2Cl_2 (2.0 mL) was added a solution of $[HPtBu_3][PhCCB(C_6F_5)_3]$ (60 mg, 0.073 mmol) in CH_2Cl_2 (3.0 mL) at RT. The reaction mixture was stirred for 10 min-hours, during which time the all components dissolved and turned brownish. All volatiles were pumped off, pentane (10 mL) added, and the mixture stirred for 3 h. The yellow precipitate was filtered off through a plug of Celite. The green-brown filtrate was pumped down to 2 mL and kept at -35 ^oC to give yellow crystalline precipitate as the product. Yield: 31 mg, 58 %. Single crystals suitable for X-ray diffraction studies were obtained from a pentane solution.

Ratio of E-isomer : Z-isomer = somewhere between 94:6 and 80:20 by ^{19}F NMR. 31mg, 58 %.

^1H NMR (400 MHz, C_6D_6, 298 K): δ 6.97-6.86 (multiple multiplets, 5H, Ar), 6.71 (br, 4H, Ar). ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ -129.16 (dm, 4F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5, $B(C_6F_5)_2$), -139.03 (m, 2F, *o*-C_6F_5, $C=C(C_6F_5)$), -145.80 (br, 2F, *p*-C_6F_5, $B(C_6F_5)_2$), -153.51 (t, 1F, $^3J_{FF}$ = 22 Hz, *p*-C_6F_5, $C=C(C_6F_5)$), -160.84 (m, 4F, *m*-C_6F_5, $B(C_6F_5)_2$), -161.46 (m, 2F, *m*-C_6F_5, $C=C(C_6F_5)$). ^{11}B NMR (128 MHz, C_6D_6, 298 K): δ 57.9 (br). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K): δ 167.67 (s, =*C*(Ph)(C6H4Cl)), 147.95 (dm, $^1J_{CF}$ = 249 Hz, *o*-C_6F_5, $B(C_6F_5)_2$), 144.66 (dm, $^1J_{CF}$ = 247 Hz, *o*-C_6F_5, $C=C(C_6F_5)$), 143.75 (dm, $^1J_{CF}$ = 258 Hz, *p*-C_6F_5, $B(C_6F_5)_2$), 143.49 (s, Ar), 140.94 (dm, $^1J_{CF}$ = 248 Hz, *p*-C_6F_5, $C=C(C_6F_5)$), 140.40 (s, Ar), 138.33 (s, Ar), 137.96 (dm, $^1J_{CF}$ = 252 Hz, *m*-C_6F_5, $C=C(C_6F_5)$), 137.55 (dm, $^1J_{CF}$ = 254 Hz, *m*-C_6F_5, $B(C_6F_5)_2$), 132.27 (s, Ar), 130.76 (s, Ar), 130.57 (s, Ar), 128.71 (s, Ar), 128.68 (s, Ar). The signals for carbon atoms adjacent to B were not observed. Elem. Anal.: $C_{32}H_9BF_{15}Cl$, calc. C:53.04, H:1.25; found C: 53.59, H: 1.95.

The compounds **4-7** were prepared in a similar fashion: The diazonium salt **2** (0.05 mmol) was added in one portion to a solution of **1** (0.05 mmol) in CH_2Cl_2 (2 mL) at -35°C, the solution turned from light yellow to dark green or brown red (for **2**) after 10 min, and it was allowed to stir for another 30min. to several hours at R.T. Then CH_2Cl_2 was removed, the product was taken up by stirring in pentane (2 mL) for a few hours, after which the supernatant was filtered on celite, the green pentane solution was stored in freezer to precipite the residue byproduct then filtered again before evaporated pentane to give the crude product as a yellow green powder.

Crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from pentane at -35°C overnight.

$(C_6H_4MeO)(Ph)CC(C_6F_5)(B(C_6F_5)_2)$ 4:

Ratio of major isomer : minor isomer ~ about 1:0.2 by ^{19}F NMR. 21mg, yield 58%.^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ = 7.39 (tt, 1H, J_{HH} =7.4 Hz, *o*-Ph); 7.30 (tt, 2H, J_{HH} =7.8 Hz, *m*-Ph); 7.17 (dd, 2H, J_{HH} =8.0 Hz, *o*-PhOMe); 7.08 (d, 2H, J_{HH} =8.4 Hz, *o*-Ph); 6.71 (d, 2H, J_{HH} =8.8 Hz, *m*-PhOMe); 3.73 (s, 3H, C*H*$_3$O).^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) δ = -130.6 (d, 4F, J_{FF} =17.6 Hz, *o*-(C_6F_5)$_2$); -141.1 (s, 2F, *p*-(C_6F_5)$_2$); -150.1 (s, 2F, *o*-C_6F_5); -157.1 (t, 1F, J_{FF} =20.8 Hz, *p*-C_6F_5); -163.4 (s, br., 4F, *m*-(C_6F_5)$_2$); -163.9 (td, 2F, J_{FF} =21.1 Hz, *m*-C_6F_5) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) δ = 58.1 (s, br) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2, 298 K): δ 170.3 (s, =*C*(Ph)), 163.7(=*C*B), 148.9 (*o*-C_6F_5, B(C_6F_5)$_2$), 146.4 (C_q, =C(C_6F_5)), 145.8 (C_q, B(C_6F_5)$_2$), 144.5 (*o*-C_6F_5, C=C(C_6F_5)), 143.4 (*p*-C_6F_5, B(C_6F_5)$_2$), 142.0 (*p*-C_6F_5, C=C(C_6F_5)), 140.8 (t, C_q, Ph), 138.8 (*m*-C_6F_5, C=C(C_6F_5)), 138.3 (*C*-OCH_3), 136.3 (dm, *m*-C_6F_5, B(C_6F_5)$_2$), 134.3, 132.7, 132.1 (t, *p*-Ph), 131.4 (*o*-Ph), 130.5 (*o*-Ph), 129.8, 129.4 (*m*-Ph), 127.8 (*m*-Ph), 119.3, 115.0, 113.4, 58.1, 56.7 (*C*H_3O), 55.3. Elem. Anal.: $C_{33}H_8BF_{18}Cl$, calc. C:55.11, H:1.54, found C: 56.43, H: 1.77.

$(C_6H_4Ph)(Ph)CC(C_6F_5)(B(C_6F_5)_2)$ 5:

Phenyldiazonium tetrafluoroborane salt was used for the reaction without ion exchange. 14mg, yield 42%. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ = 7.39 (tt, 1H, J_{HH} =7.6 Hz, C*H*, Ph); 7.30 (t, 3H, J_{HH} =7.4 Hz, C*H*, Ph); 7.20 (t, 2H, J_{HH} =7.8 Hz, C*H*, Ph); 7.14 (m, 4H, C*H*, Ph). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) δ = -130.2 (dt, 4F, J_{FF} =20.3 Hz, *o*-B(C_6F_5)$_2$); -140.6 (d, 2F, J_{FF} =16.4 Hz, *o*-(C_6F_5)); -149.4 (s, 2F, *p*-B(C_6F_5)$_2$); -156.6 (t, 1F, J_{FF} =20.7 Hz, *p*-C_6F_5); -163.3 (s, br., 4F, *m*-B(C_6F_5)$_2$); -163.6 (td, 2F, J_{FF} =21.3 Hz, *m*-C_6F_5) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) δ = 58.8 (s, br.) ppm. ^{13}C NMR {^{1}H} (101 MHz, CD_2Cl_2, 298 K): δ 164.7 (s, =*C*(Ph)), 147.8 (dm, overlapped signals of *o*-C_6F_5), 145.3 (dm, *p*-C_6F_5), 145.2 (s, Ar), 142.8 (dm, *p*-C_6F_5), 140.9 (s, Ar), 137.5 (dm, *m*-C_6F_5), 132.0 (s, *C*H, Ph), 131.5 (s, *C*H, Ph), 131.1 (s, *C*H, Ph), 130.5 (s, *C*H, Ph), 128.8 (s, *C*H, Ph), 128.7 (s, *C*H, Ph), =*C*B was not observed. Elem. Anal.: $C_{32}H_8BF_{15}$, calc. C: 55.85, H:1.17; found C: 55.55, H: 1.32.

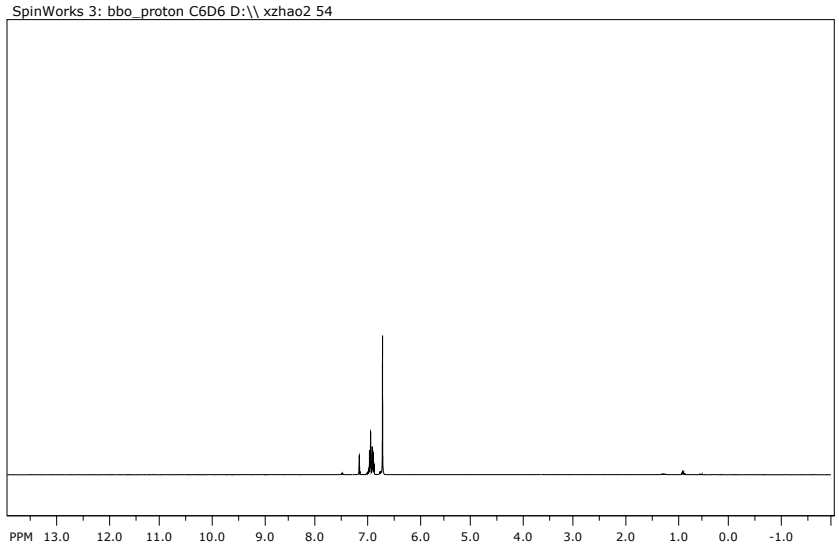
$(CF_3C_6H_4)(ClC_6F_4)CC(C_6F_5)(B(C_6F_5)_2)$ 6:

Ratio of major isomer : minor isomer ~ about 1:0.04 by ^{19}F NMR. 31mg, yield 78%. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ = 7.58 (d, 2H, $^{3}J_{HH}$ = 8.3 Hz, *m*-Ph-CF_3); 7.28 (d, 2H, $^{3}J_{HH}$ =8.0 Hz, *o*-Ph-CF_3); 7.21 (d, 2H, $^{3}J_{HH}$ =8.3 Hz, *m*-Ph-Cl); 7.03 (d, 2H, $^{3}J_{HH}$ = 8.3 Hz, *o*-Ph-Cl). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) δ = -63.3 (s, 3F, C*F*$_3$); -129.0 (dt, 4F, J_{FF} =20.2 Hz, *o*-B(C_6F_5)$_2$); -139.2 (d, 2F, J_{FF} =15.7 Hz, *o*-(C_6F_5)); -146.8 (s, 2F, *p*-B(C_6F_5)$_2$); -154.0 (t, 1F, J_{FF} =20.8 Hz, *p*-C_6F_5); -161.5 (td, 4F, J_{FF} =19.7 Hz, *m*-B(C_6F_5)$_2$); -161.7 (td, 2F, J_{FF} =21.1 Hz, *m*-C_6F_5) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) δ = 59.0 (s, br) ppm. ^{13}C NMR {^{1}H} (101 MHz, CD_2Cl_2, 298 K): δ 164.7 (s, =*C*(Ph)), 148.2 (dm, overlapped signals of *o*-C_6F_5), 144.5 (m, *p*-C_6F_5), 144.2 (m, *p*-C_6F_5), 144.1 (s, Ar), 143.0 (s, Ar), 138.8 (s, Ar), 138.2 (m, *m*-C_6F_5), 137.8 (m, *m*-C_6F_5), 132.5 (s, *C*H, *o*-Ph-Cl), 131.4 (s, *o*-Ph-CF_3), 129.4 (s, *C*H, *m*-Ph-Cl), 126.0 (q, $^{3}J_{CF}$ = 3.7 Hz, *m*-Ph-CF_3), 124.4 (q, $^{1}J_{CF}$ = 272 Hz, CF_3), =*C*B was not observed. Elem. Anal.: $C_{33}H_8BF_{18}Cl$, calc. C:50.0, H:1.02, found C: 50.87, H: 1.21.

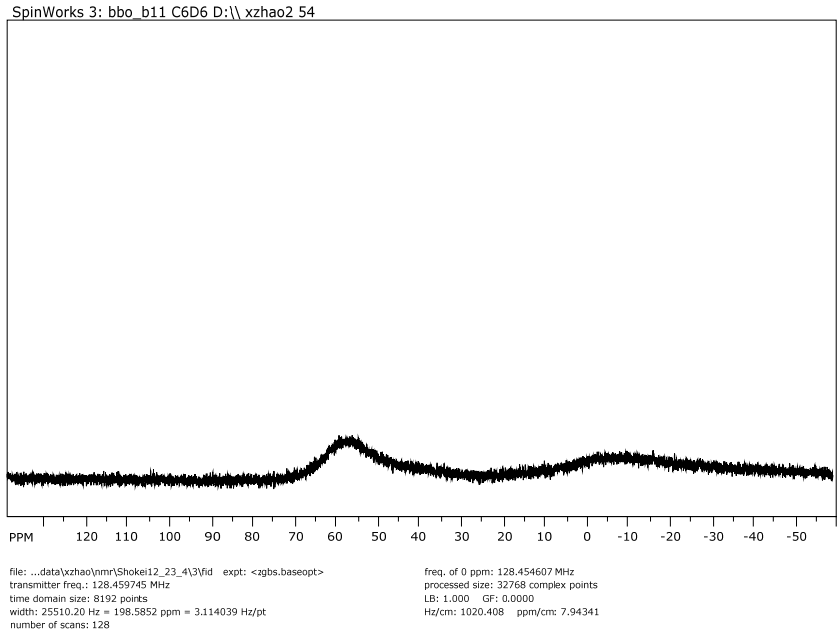
(CF$_3$C$_6$H$_4$)(MeOC$_6$F$_4$)CC(C$_6$F$_5$)(B(C$_6$F$_5$)$_2$) 7:

Ratio of *E*-isomer : *Z*- isomer ~ about 1:0.05 by ^{19}F NMR. **16** mg, yield 41%. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ = 7.57 (d, 2H, $^{3}J_{HH}$ = 8.2 Hz, *m*-Ph-CF_3); 7.32 (d, 2H, $^{3}J_{HH}$ =8.1 Hz, *o*-Ph-CF_3); 7.03 (d, 2H, $^{3}J_{HH}$ =8.3 Hz, *m*-Ph-OMe); 6.72 (d, 2H, $^{3}J_{HH}$ = 8.6 Hz, *o*-Ph-OMe), 3.75 (s, 3H, C*H*$_3$O). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) δ = -63.2 (s, 3F, C*F*$_3$); -129.3 (d, 4F, J_{FF} =19.9 Hz, *o*-B(C_6F_5)$_2$); -139.8 (s, 2F, *o*-(C_6F_5)); -148.2 (s, 2F, *p*-B(C_6F_5)$_2$); -154.9 (t, 1F, J_{FF} =20.8 Hz, *p*-C_6F_5); -162.1 (td, 6F, J_{FF} =21.2 Hz, *m*-B(C_6F_5)$_2$ and *m*-C_6F_5) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) δ = 62.0 (s, br) ppm. ^{13}C NMR {^{1}H} (101 MHz, CD_2Cl_2, 298 K): δ 163.8 (s, =*C*(Ph)), 147.9 (dm, overlapped signals of *o*-C_6F_5), 144.3 (s, Ar), 137.6 (s, Ar), 133.2 (s, *C*H, *o*-Ph-OMe), 131.5 (s, *o*-Ph-CF_3), 125.7 (q, $^{3}J_{CF}$ = 3.7 Hz, *m*-Ph-CF_3), 56.7 (s, *C*H$_3$O). Elem. Anal.: $C_{34}H_{11}BF_{18}O$, calc. C:51.81, H:1.41; found C: 51.32, H: 2.0.

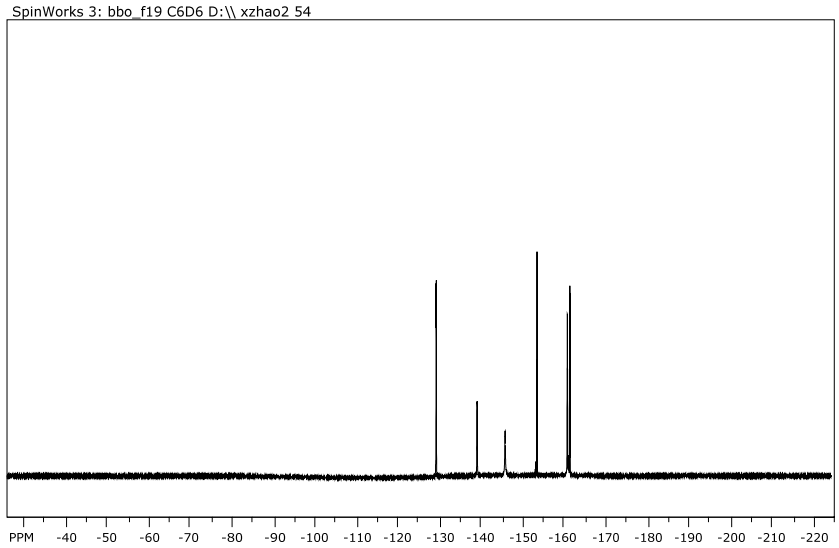
^{1}H NMR of **3**



^{11}B NMR of **3**



^{19}F NMR of **3**



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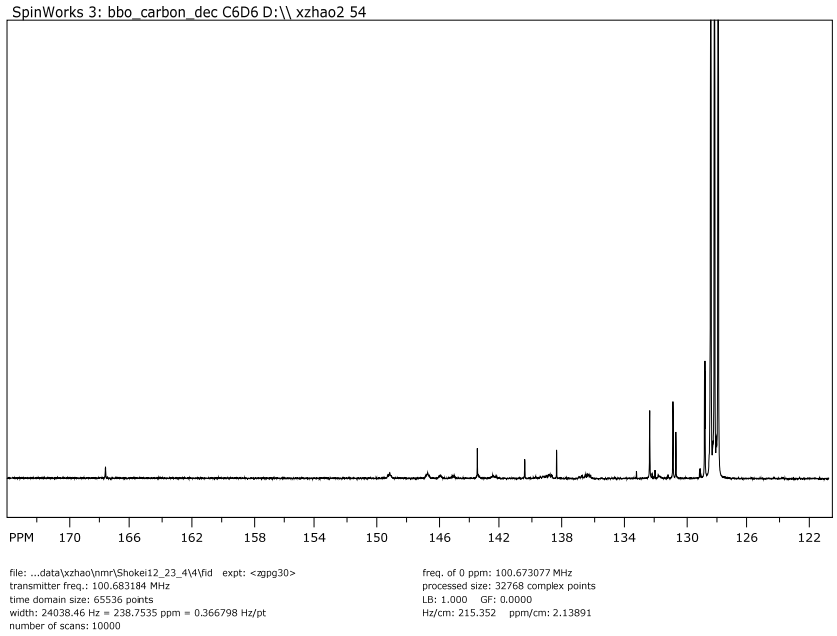
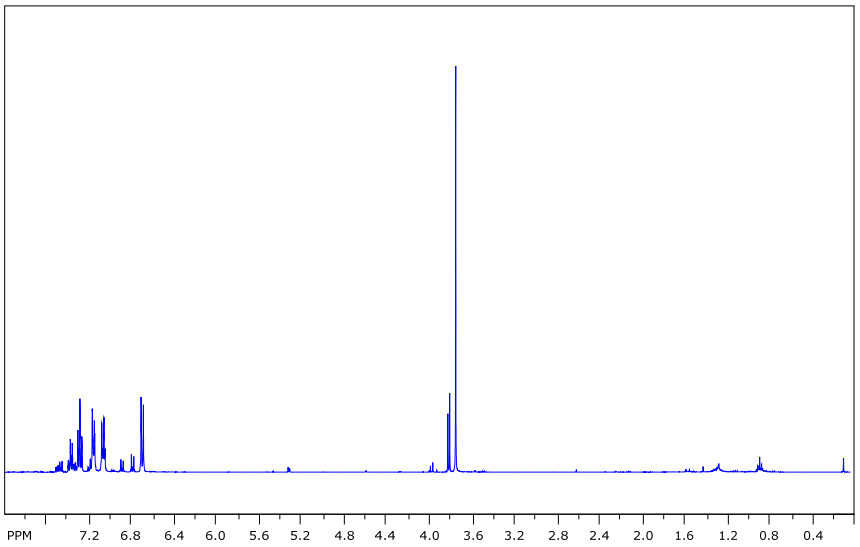


^{1}H NMR of **4**



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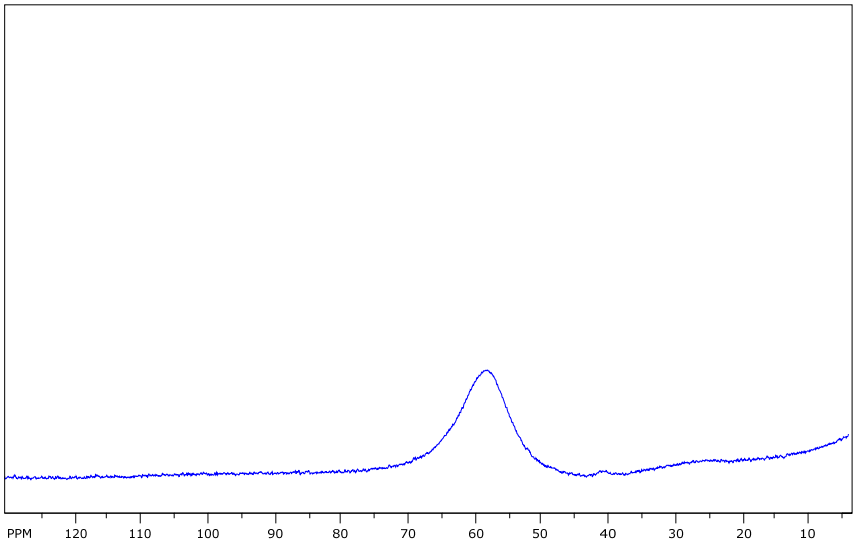

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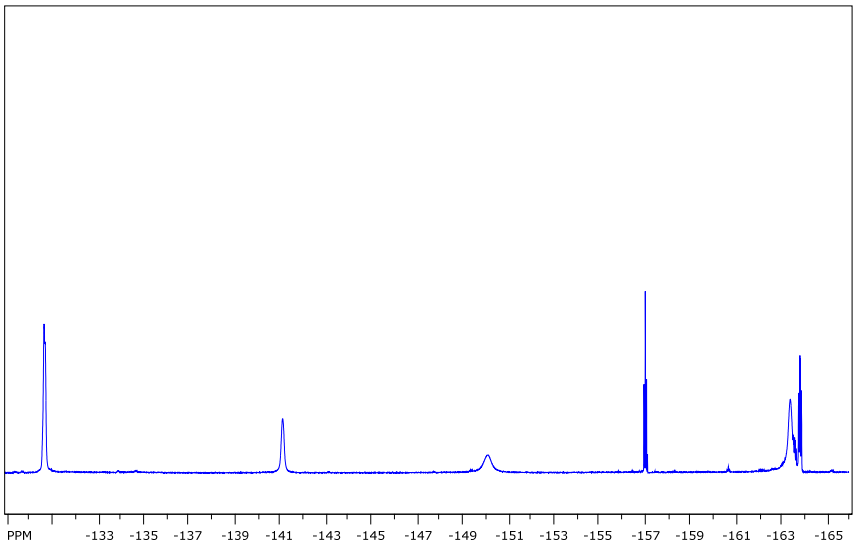
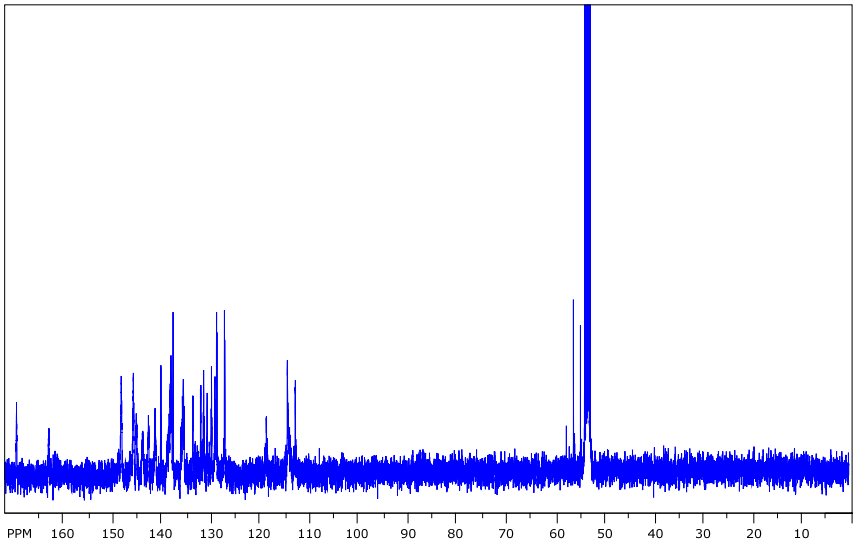
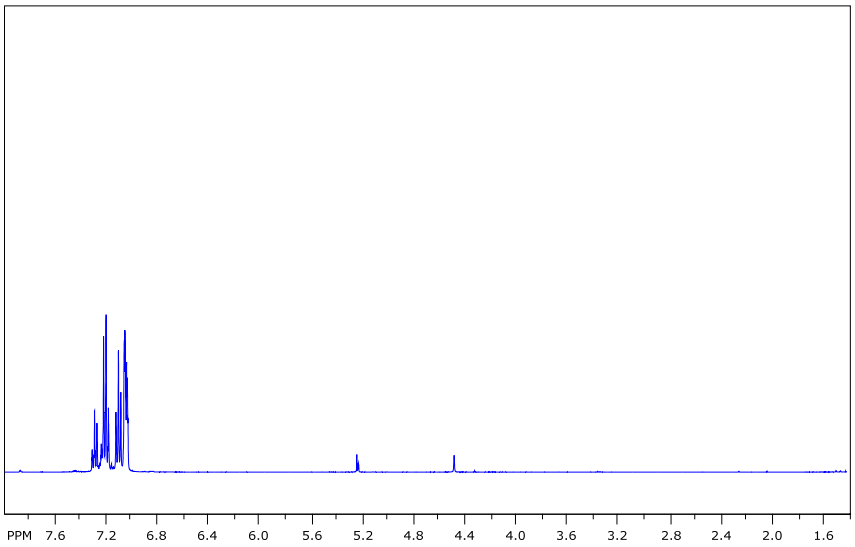


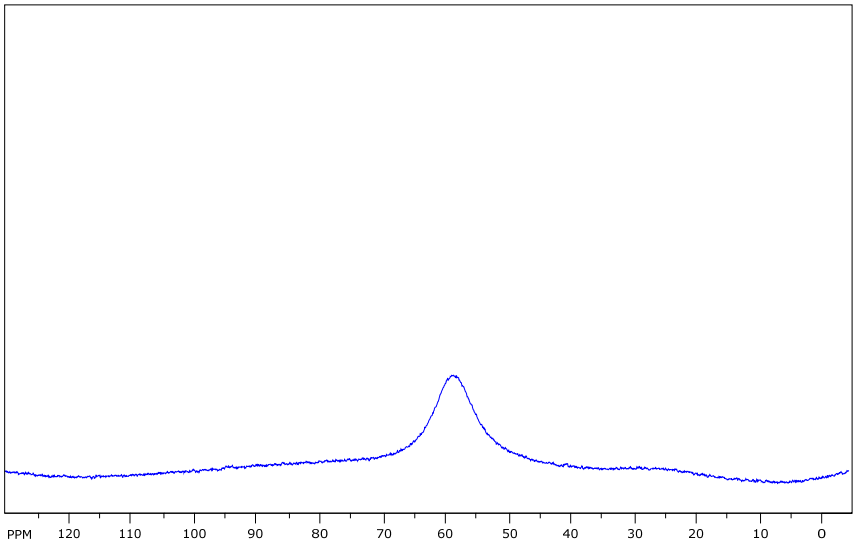
^{13}C NMR of **4**



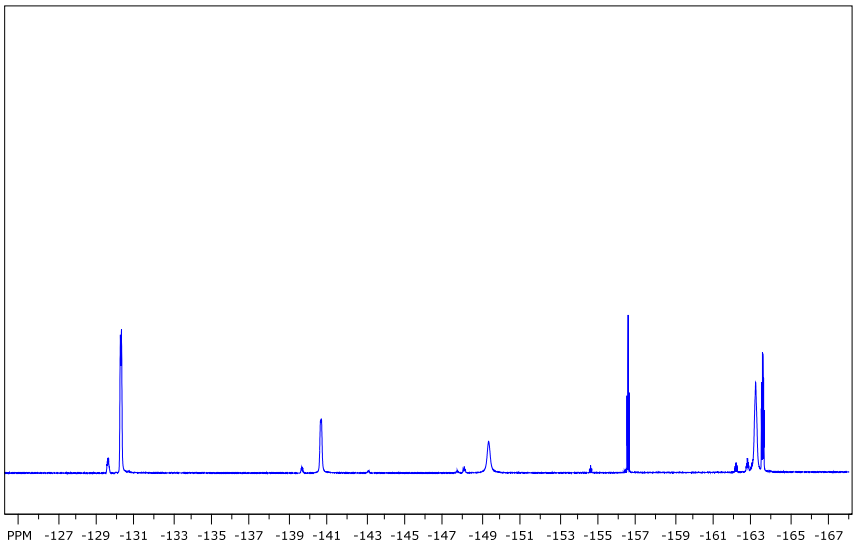
^{1}H NMR of **5**



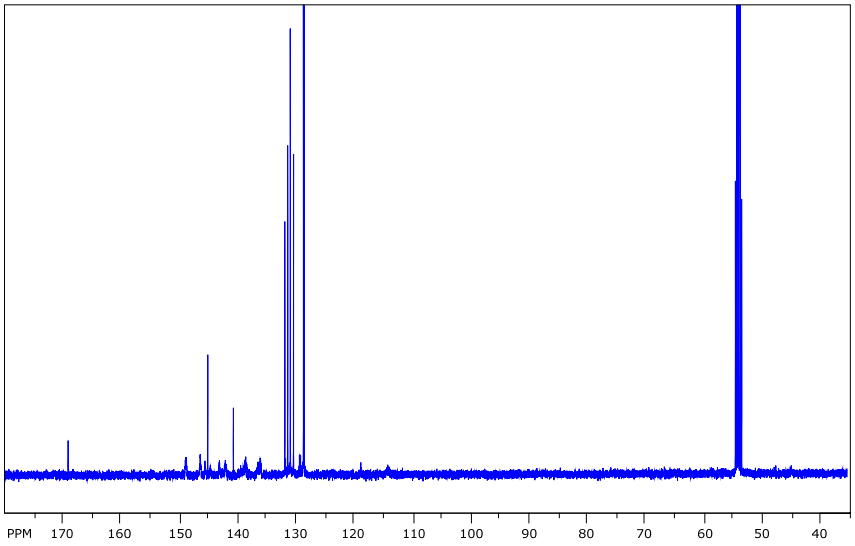
^{11}B NMR of **5**



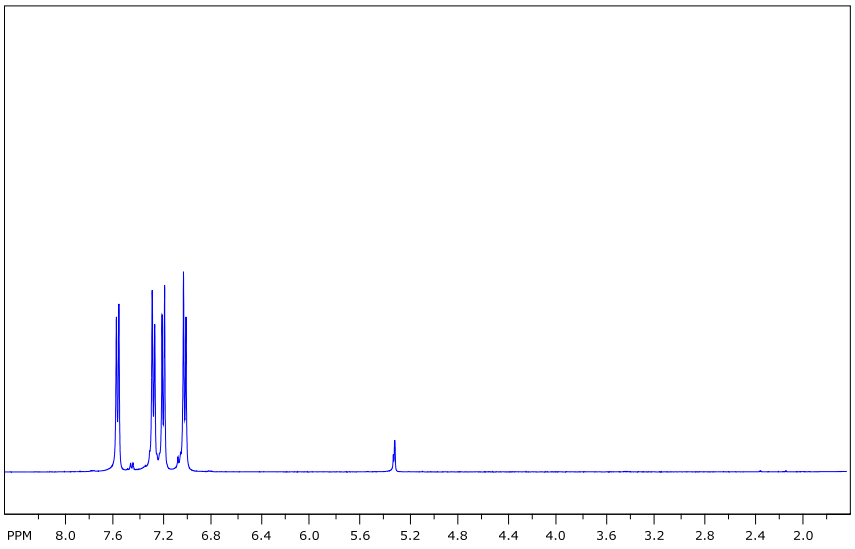
^{19}F NMR of **5**



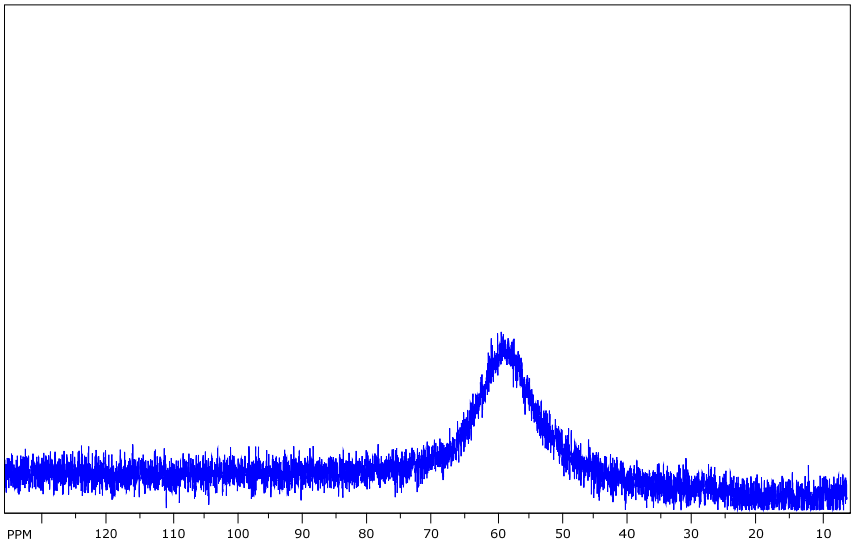
^{13}C NMR of **5**



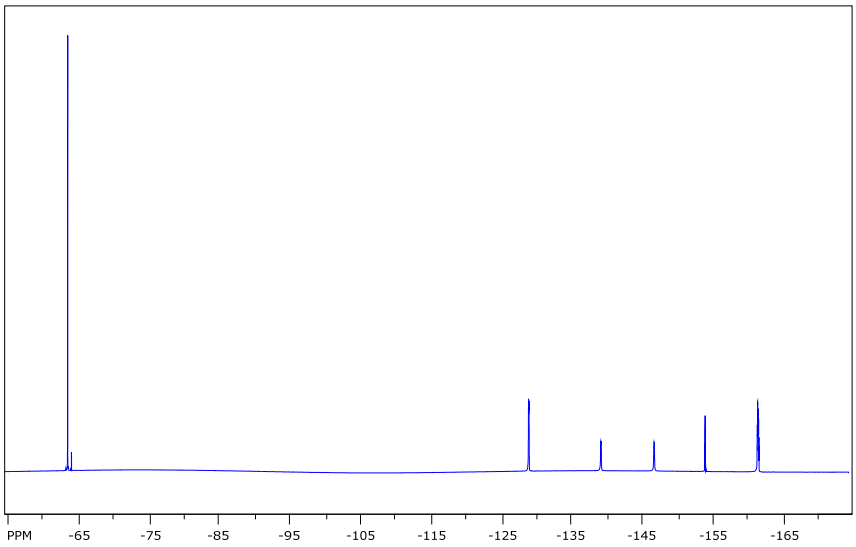
^{1}H NMR of **6**



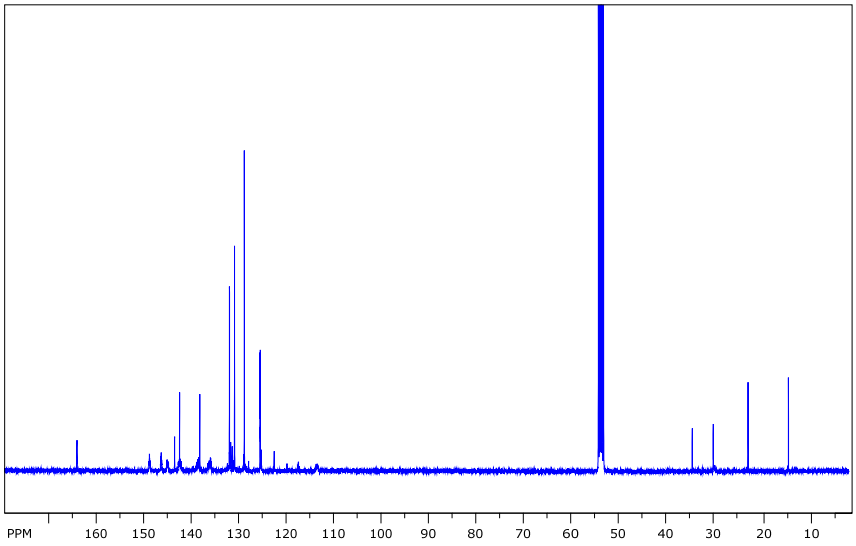
^{11}B NMR of **6**



^{19}F NMR of **6**



^{13}C NMR of **6**



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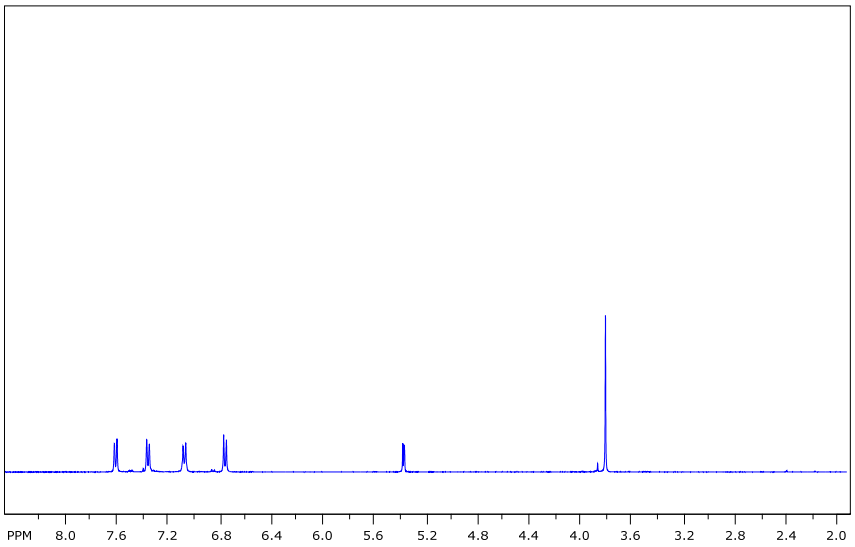
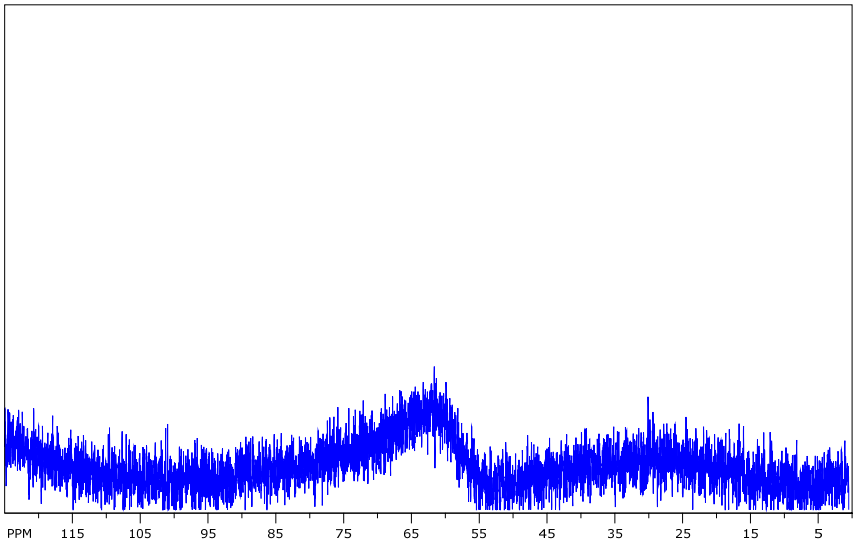
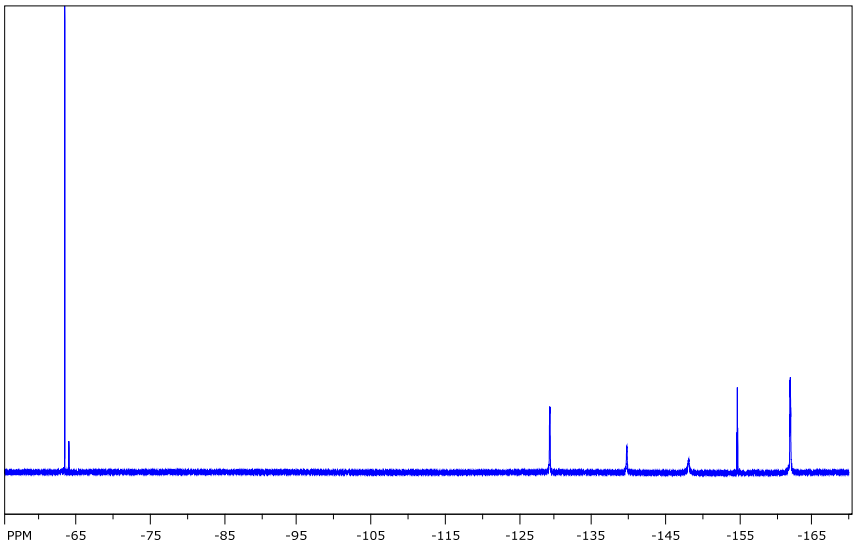


^{11}B NMR of **7**



^{19}F NMR of **7**



^{13}C NMR of **7**