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Supporting Information

A Carbene-Extended ATRA Reaction

Guojiao Wu, Jennifer Börger, and Axel Jacobi von Wangelin**

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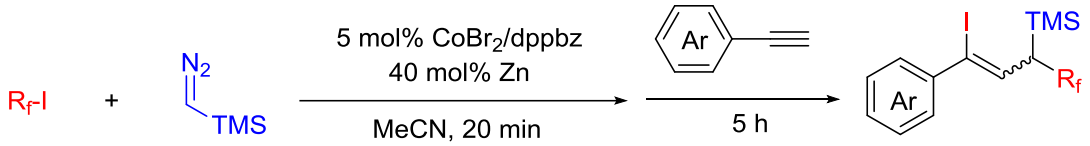
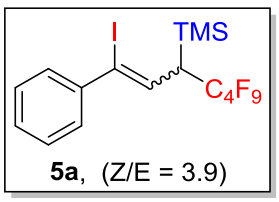
1. General experimental methods.

Reagents were purchased from commercial suppliers and used without further purification. THF, toluene, and hexane, ethyl ether were used after distillation with the sodium. Dry acetonitrile and dichloromethane were purchased from Acros Organics. Column chromatograph was performed on 35-70 mesh silica gel (Acros Organics). ^{1}H (300 Hz), ^{13}C (75 Hz), ^{19}F (125 Hz) spectra were recorded on a Bruker Avance Kryo spectrometer using $CDCl_3$ as solvent. Chemical shifts are reported in ppm and referenced to residual solvent signal ($CDCl_3$: ^{1}H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.0 ppm). High Resolution Mass Spectrometry (HRMS) were on Finnigan MAT 900s. GC-yields was obtained using dodecane as internal standard with gas chromatography with FID (GC-FID, HP6890 GC-System with injector 7683B and Agilent 7820A System, carried recorded gas: H_2). The *stereo* was determined by comparing with the similar CF_3 compound reported[1] and *Z*/*E* ratios herein were determined by ^{1}H NMR and

2. General Procedure and characterization data

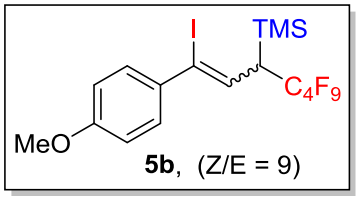


An oven-dried reaction tube was charged with $CoBr_2$ (2.1 mg, 0.01 mmol, 0.05 equiv), dppbz (4.5 mg, 0.01 mmol, 0.05 equiv) and Zn (5.12 mg, 0.08 mmol, 0.40 equiv). The tube was evacuated and backfilled with nitrogen for three times. Acetonitrile (0.8 mL) was added into the tube and stirred for 1 minutes. Trimethylsilyldiazomethane (0.34 mmol, 2 M in hexane, 1.7 equiv) was added into the system, followed with R_f-X (0.26 mmol, 1.3 equiv). The mixture was stirred at room temperature for 20 minutes until nearly no bubble came out. Then the alkyne (0.2 mmol) was added into the system (Note: if it is solid, dissolve it in 0.1-0.2 mL dichloromethane) and reacted for another 5 hours. The solvent was removed to leave a crude product, which was purified by column chromatography on silica gel to afford the product **5**. (Note: In SI, the Z/E were determined by ^{1}H NMR)

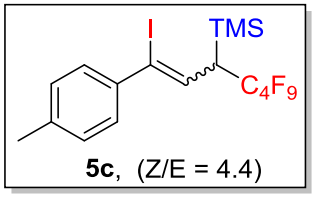


According to the general procedure, the product **5a** was purified with silica gel chromatography (Pe) as a pale yellow oil in 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.36-7.29 (m, 4.23H), 6.46 (d, *J* = 12.1 Hz, 0.25H), 5.83 (dd, *J* = 11.2, 1.7 Hz, 1H), 3.28 (dd, *J* = 35.7, 11.1 Hz, 1H), 2.88-2-70 (m, 0.25H), 0.30 (s, 9H), 0.15 (s, 2.25H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 141.1 (minor), 133.5 (d, *J* = 12.0 Hz) (minor), 130.3 (d, *J* = 13.8 Hz), 128.6, 128.5, 128.48 (minor), 128.44 (minor), 128.36, 106.8, 43.8 (dd, *J* = 33.3, 25.0 Hz), 38.0 (dd, *J* = 31.7, 25.7 Hz) (minor), -0.89 (d, *J* = 1.6 Hz), -1.11 (d, *J* = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, $CDCl_3$) δ -80.98 to -81.04 (m, 3F, *Z*+*E*), -101.1 to -102.1 (m, 1F, *Z*+*E*), -108.1

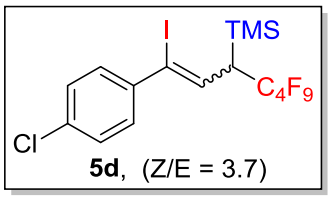
to -108.7 (m, 0.85F), -108.9 to -109.4 (m, *E*, 0.23F), -119.53 to -121.8 (m, 2F, *Z*+*E*), -124.6 to -125.4 (m, 1F, *Z*+*E*), -125.8 to -127.1 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): $[M\text{-}TMSF]^+$ calcd for $C_{13}H_7F_8I$: 441.9459, found: 441.9448.



According to the general procedure, the product **5b** was purified with silica gel chromatography (Pe/EA = 50 : 1) as a pale yellow oil in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 0.22H), 6.89-6.83 (m, 2.25H), 6.42 (d, *J* = 12.0 Hz, 0.11H), 5.73 (dd, *J* = 11.2, 1.1 Hz, 1H), 3.83 (s, 3.33H), 3.25 (dd, *J* = 35.7, 11.1 Hz, 1H), 2.88-2-70 (m, 0.25H), 0.29 (s, 9H), 0.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 159.4 (minor), 135.9, 129.7, 128.8 (d, *J* = 13.8 Hz), 113.8 (minor), 113.6, 106.8, 55.4, 55.2 (minor), 43.7 (dd, *J* = 33.2, 25.0 Hz), -0.92 (d, *J* = 1.6 Hz), -1.14 (d, *J* = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.02 to -81.06 (m, 3F), -101.6 to -102.1 (m, 1F), -108.1 to -108.6 (m, 1F), -120.7 to -121.8 (m, 2F), -124.6 to -125.2 (m, 1F), -126.5 to -127.1 (m, 1F); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{17}H_{18}F_9IOSi$: 564.0022, found: 564.0019.

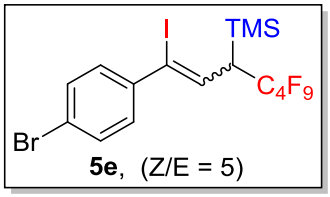


According to the general procedure, the product **5c** was purified with silica gel chromatography (Pe) as a pale yellow oil in 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.20-7-17 (m, 0.86H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 12.1 Hz, 0.22H), 5.79 (dd, *J* = 11.2, 1.3 Hz, 1H), 3.34-3.17 (m, 1H), 2.89-2.71 (m, 0.22H), 2.37 and 2.36 (s, overlap, 3.66 H), 0.29 (s, 9H), 0.15 (s, 1.98H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 138.6, 138.4 (minor), 138.3 (minor), 129.5 (d, *J* = 13.7 Hz), 129.2 (minor), 129.0, 128.4, 128.3 (minor), 107.0, 43.7 (dd, *J* = 33.4, 25.0 Hz), 21.2, 21.1 (minor), -0.90 (d, *J* = 1.5 Hz), -1.11 (d, *J* = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.04 to -81.08 (m, 3F), -101.6 to -102.1 (m, 1F), -108.1 to -108.7 (m, 1F), -120.7 to -121.8 (m, 2F), -124.6 to -125.2 (m, 1F), -126.5 to -127.1 (m, 1F); HRMS (EI) (*m/z*): $[M\text{-}TMSF]^+$ calcd for $C_{14}H_9F_8I$: 455.9616, found: 455.9609.



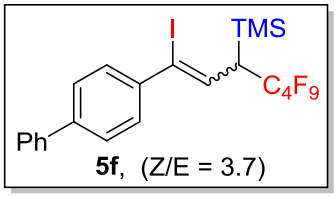
According to the general procedure, the product **5d** was purified with silica gel chromatography (Pe) as a colorless oil in 88% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.27 (m, 4.6H), 7.24-7.19 (m, 0.55H), 6.46 (d, *J* = 12.2 Hz, 0.27H), 5.81 (dd, *J* = 11.2, 1.4 Hz, 1H), 3.26 (dd, *J* = 35.5, 11.0 Hz, 1H), 2.76-2.59 (m, 0.24H), 0.29 (s, 9H), 0.14 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6, 139.6 (minor), 134.5, 134.4 (minor), 131.0 (d, *J* = 13.6 Hz), 129.8 (minor), 129.7, 128.8 (minor), 128.5, 105.0, 93.4 (minor), 43.8 (dd, *J* = 33.6, 25.0 Hz), 38.2 (dd, *J* = 32.1, 25.4 Hz) (minor), -0.91 (d, *J* = 1.5 Hz), -1.15 (d, *J* = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -81.0 to -81.1 (m, 3F, *Z*+*E*), -101.2 to -102.3 (m, 1F, *Z*+*E*),

-108.2 to -109.4 (m, 1F, *Z*+*E*), -119.6 to -121.9 (m, 2F, *Z*+*E*), -124.4 to -125.4 (m, 1F, *Z*+*E*), -126.2 to -127.1 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): [M-TMSF]$^+$ calcd for $C_{13}H_6ClF_8I$: 475.9069, found: 475.9064.



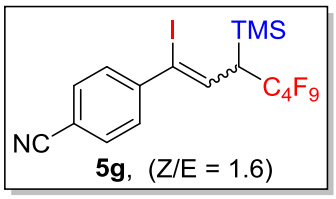
5e, (Z/E = 5)

According to the general procedure, the product **5e** was purified with silica gel chromatography (Pe) as a pale yellow oil in 79% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.48 (m, 0.37H), 7.47-7.43 (m, 2H), 7.31-7.26 (m, 2H), 7.17-7.13 (m, 0.36H), 6.46 (d, *J* = 12.3 Hz, 0.18H), 5.81 (dd, *J* = 11.2, 1.4 Hz, 1H), 3.31-3.15 (m, 1H), 2.80-2.63 (m, 0.17H), 0.28 (s, 9H), 0.14 (s, 1.56H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 140.1 (minor), 131.8 (minor), 131.5, 131.1 (d, *J* = 13.7 Hz), 130.0, 122.7, 122.6 (minor), 105.0, 93.4 (minor), 43.8 (dd, *J* = 33.6, 25.0 Hz), -0.89 (d, *J* = 1.6 Hz), -1.12 (d, *J* = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.02 to -81.05 (m, 3F), -101.7 to -102.2 (m, 1F), -108.1 to -108.7 (m, 1F), -120.7 to -121.9 (m, 2F), -124.6 to -125.2 (m, 1F), -126.5 to -127.1 (m, 1F); HRMS (EI) (*m/z*): [M-TMSF]$^+$ calcd for $C_{13}H_6BrF_8I$: 519.8564, found: 519.8566.



5f, (Z/E = 3.7)

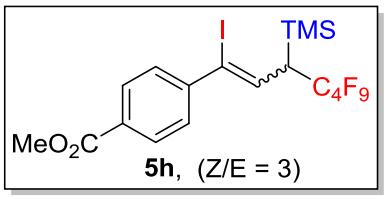
According to the general procedure, the product **5f** was purified with silica gel chromatography (Pe) as a pale yellow solid in 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.36 (m, 11.56), 6.50 (d, *J* = 12.2 Hz, 0.27H), 5.90 (dd, *J* = 11.2, 1.3 Hz, 1H), 3.31 (dd, *J* = 35.7, 11.1 Hz, 1H), 2.94-2.78 (m, 0.28H), 0.32 (s, 9H), 0.18 (s, 2.44H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 141.5, 141.2 (minor), 140.3, 140.1 (minor), 140.0 (minor), 130.3 (d, *J* = 14.1 Hz), 129.0, 128.9, 127.7 (minor), 127.6, 127.1, 127.0, 106.5, 95.1 (minor), 43.5 (dd, *J* = 33.2, 24.9 Hz), -0.86 (d, *J* = 1.5 Hz), -1.06 (d, *J* = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.9 to -81.0 (m, 3F, *Z*+*E*), -101.0 to -102.1 (m, 1F, *Z*+*E*), -108.0 to -109.3 (m, 1F, *Z*+*E*), -119.4 to -121.8 (m, 2F, *Z*+*E*), -124.5 to -125.3 (m, 1F, *Z*+*E*), -126.1 to -127.0 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): [M-TMSF]$^+$ calcd for $C_{19}H_{11}F_8I$: 517.9772, found: 517.9776.



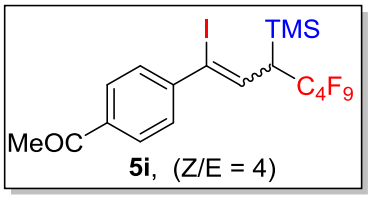
5g, (Z/E = 1.6)

According to the general procedure, the product **5g** was purified with silica gel chromatography (Pe/EA = 5 : 1) as a pale yellow oil in 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 1.32H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 1.30H), 6.51 (d, *J* = 12.3 Hz, 0.64H), 5.93 (d, *J* = 11.1, 1H), 3.25 (dd, *J* = 35.1, 11.2 Hz, 1H), 2.72-2.55 (m, 0.68H), 0.28 (s, 9H), 0.14 (s, 5.94H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 145.5 (minor), 135.3 (d, *J* = 11.1 Hz) (minor), 133.4 (d, *J* = 13.1 Hz), 132.3 (minor), 132.2, 129.2 (minor), 129.1, 118.3, 118.1 (minor), 112.3, 112.2 (minor), 103.6, 91.6 (minor), 44.0 (dd, *J* = 34.1, 25.3 Hz), 38.4 (dd, *J* = 32.7, 25.1 Hz), -0.88 (d, *J* = 1.6 Hz), -1.15 (d, *J*

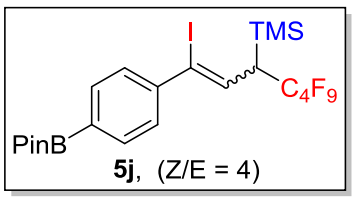
= 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -81.0 to -81.1 (m, 3F, *Z*+*E*), -101.2 to -102.4 (m, 1F, *Z*+*E*), -108.3 to -109.5 (m, 1F, *Z*+*E*), -119.5 to -121.9 (m, 2F, *Z*+*E*), -124.6 to -125.4 (m, 1F, *Z*+*E*), -126.1 to -127.0 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{17}H_{15}F_9INSi$: 558.9869, found: 558.9858.



According to the general procedure, the product **5h** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a colorless oil in 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 0.68H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 0.64H), 6.48 (d, *J* = 12.4 Hz, 0.32H), 5.91 (dd, *J* = 11.2, 1.2, 1H), 3.94 and 3.92 (s, overlap, 4H), 3.26 (dd, *J* = 35.5, 11.1 Hz, 1H), 2.79-2.61 (m, 0.33H), 0.28 (s, 9H), 0.12 (s, 2.93H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 166.3 (minor), 147.1, 145.5 (minor), 134.5 (d, *J* = 11.5 Hz) (minor), 132.2 (d, *J* = 13.4 Hz), 130.0 (minor), 129.8 (minor), 129.7, 105.1, 93.3 (minor), 52.3 (minor), 52.2, 43.9 (dd, *J* = 33.6, 25.0 Hz), 38.2 (dd, *J* = 32.1, 25.5 Hz) (minor), -0.87 (d, *J* = 1.6 Hz), -1.13 (d, *J* = 1.6 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -81.0 to -81.1 (m, 3F, *Z*+*E*), -101.2 to -102.3 (m, 1F, *Z*+*E*), -108.2 to -109.5 (m, 1F, *Z*+*E*), -118.6 to -121.9 (m, 2F, *Z*+*E*), -124.6 to -125.2 (m, 1F, *Z*+*E*), -126.5 to -127.1 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{18}H_{18}F_9IO_2Si$: 591.9972, found: 591.9967.

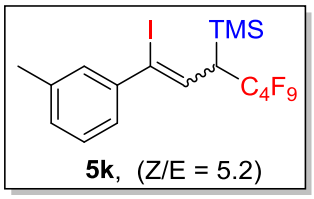


According to the general procedure, the product **5i** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a colorless oil in 62% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 0.5H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 0.5H), 6.49 (d, *J* = 11.6 Hz, 0.25H), 5.92 (dd, *J* = 11.2, 1.1, 1H), 3.27 (dd, *J* = 35.4, 11.2 Hz, 1H), 2.61 (s, 0.75H), 2.60 (s, 3H), 0.28 (s, 9H), 0.13 (s, 2.21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2 (minor), 197.1, 147.2, 145.6 (minor), 136.8, 136.7 (minor), 132.3 (d, *J* = 13.5 Hz), 128.7, 128.5 (minor), 128.4, 105.0, 44.0 (dd, *J* = 33.6, 25.0 Hz), 26.7, 26.6 (minor), -0.87 (d, *J* = 1.6 Hz), -1.13 (d, *J* = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) -81.0 to -81.1 (m, 3F, *Z*+*E*), -101.2 to -102.3 (m, 1F, *Z*+*E*), -108.2 to -109.5 (m, 1F, *Z*+*E*), -119.5 to -121.9 (m, 2F, *Z*+*E*), -124.6 to -125.3 (m, 1F, *Z*+*E*), -126.2 to -127.0 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{18}H_{18}F_9IOSi$: 576.0022, found: 576.0040.



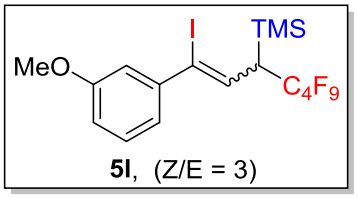
According to the general procedure, the product **5j** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a colorless oil in 45% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.85 (overlap, m, 2.54H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 0.51H), 6.44 (d, *J* = 12.2 Hz, 0.23H), 5.84 (dd, *J* = 11.2, 1.1, 1H), 3.26

(dd, J = 35.6, 11.2 Hz, 1H), 2.84-2.66 (m, 0.24H), 1.35 (s, 14.80H), 0.27 (s, 9H), 0.13 (s, 2.09H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 143.7 (minor), 134.8, 130.8 (d, J = 13.2 Hz), 127.8, 127.7 (minor), 106.7, 95.1 (minor), 84.0 (minor), 83.9, 43.8 (dd, J = 33.4, 25.1 Hz), 24.9 (minor), 24.8, -0.88 (d, J = 1.6 Hz), -1.11 (d, J = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) -80.98 to -81.03 (m, 3F, *Z*+*E*), -101.2 to -102.2 (m, 1F, *Z*+*E*), -108.1 to -109.5 (m, 1F, *Z*+*E*), -119.6 to -121.8 (m, 2F, *Z*+*E*), -124.6 to -125.4 (m, 1F, *Z*+*E*), -126.2 to -127.1 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{22}H_{27}BF_9IO_2Si$: 660.0769, found: 660.0766.



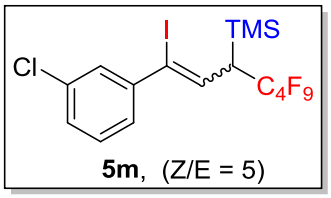
5k, (Z/E = 5.2)

According to the general procedure, the product **5k** was purified with silica gel chromatography (Pe) as a colorless oil in 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24-7.21 (m, 3.16H), 7.12-7.06 (m, 1.51H), 6.43 (d, J = 12.0 Hz, 0.17H), 5.80 (dd, J = 11.2, 1.3 Hz, 1H), 3.34-3.19 (m, 1H), 2.86-2.70 (m, 0.17H), 2.38 (s, 3H), 2.35 (s, 0.54H), 0.29 (s, 9H), 0.15 (s, 1.56H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 141.0 (minor), 138.2 (minor), 138.1, 130.0 (d, J = 13.6 Hz), 129.4, 129.2 (minor), 129.1, 128.9 (minor), 128.3 (minor), 128.2, 125.6, 125.4 (minor), 107.1, 43.7 (dd, J = 33.5, 24.9 Hz), 21.33, 21.30 (minor), -0.87 (d, J = 1.6 Hz), -1.09 (d, J = 1.6 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -81.00 to -81.05 (m, 3F), -101.6 to -102.1 (m, 1F), -108.1 to -108.7 (m, 1F), -120.7 to -121.8 (m, 2F), -124.6 to -125.1 (m, 1F), -126.5 to -127.1 (m, 1F); HRMS (EI) (*m/z*): $[M\text{-}TMSF]^+$ calcd for $C_{14}H_9F_8I$: 455.9619, found: 455.9611.



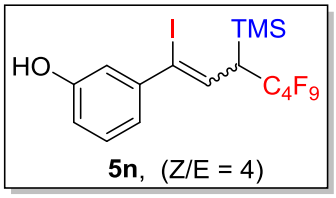
5l, (Z/E = 3)

According to the general procedure, the product **5l** was purified with silica gel chromatography (Pe/EA = 50 : 1) as a colorless oil in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.21 (m, 1.50H), 7.03-6.97 (m, 2H), 6.88-6.81 (m, 2H), 6.43 (d, J = 12.1 Hz, 0.31H), 5.84 (dd, J = 11.2, 1.3 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 0.95H), 3.26 (dd, J = 35.7, 11.2 Hz, 1H), 2.90-2.73 (m, 0.33H), 0.28 (s, 9H), 0.15 (s, 2.89H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 144.5, 142.3 (minor), 133.5 (d, J = 11.5 Hz) (minor), 130.5 (d, J = 13.5 Hz), 129.5 (minor), 129.3, 120.8, 120.7 (minor), 114.7, 114.5 (minor), 113.7, 113.5 (minor), 106.4, 95.0 (minor), 55.3, 55.2 (minor), 43.7 (dd, J = 33.4, 24.9 Hz), 38.0 (dd, J = 31.8, 25.5 Hz) (minor), -0.89 (d, J = 1.5 Hz), -1.09 (d, J = 1.4 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -81.0 to -81.1 (m, 3F, *Z*+*E*), -101.1 to -102.2 (m, 1F, *Z*+*E*), -108.1 to -109.4 (m, 1F, *Z*+*E*), -119.5 to -121.8 (m, 2F, *Z*+*E*), -124.6 to -125.4 (m, 1F, *Z*+*E*), -126.2 to -127.1 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{17}H_{18}F_9IOSi$: 564.0022, found: 564.0035.



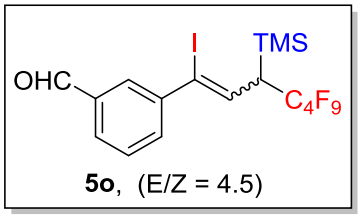
5m, (Z/E = 5)

According to the general procedure, the product **5m** was purified with silica gel chromatography (Pe) as a colorless oil in 74% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.34-7.27 (m, 3.65H), 7.20-7.17 (m, 0.21H), 6.49 (d, *J* = 12.2 Hz, 0.2H), 5.87 (dd, *J* = 11.2, 1.2 Hz, 1H), 3.26 (dd, *J* = 35.5, 11.2 Hz, 1H), 2.83-2.66 (m, 0.2H), 0.31 (s, 9H), 0.18 (s, 1.82H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 142.7 (minor), 134.3 (minor), 134.2, 131.7 (d, *J* = 13.6 Hz), 129.8 (minor), 129.6, 128.63 (minor), 128.6, 128.5, 126.7, 126.5 (minor), 104.4, 43.8 (dd, *J* = 33.7, 25.0 Hz), -0.87 (d, *J* = 1.6 Hz), -1.11 (d, *J* = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.99 to -81.04 (m, 3F, *Z*+*E*), -101.2 to -102.2 (m, 1F, *Z*+*E*), -108.2 to -109.5 (m, 1F, *Z*+*E*), -119.6 to -121.8 (m, 2F, *Z*+*E*), -124.6 to -125.3 (m, 1F, *Z*+*E*), -126.2 to -127.1 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): [M-TMSF]$^+$ calcd for $C_{13}H_6ClF_8I$: 475.9069, found: 475.9071.



5n, (Z/E = 4)

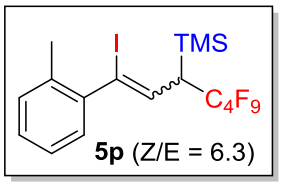
According to the general procedure, the product **5n** was purified with silica gel chromatography (Pe) as a pale yellow oil in 69% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.25-7.16 (m, 2.24H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.92-6.91 (m, 1H), 6.85 (d, *J* = 7.7 Hz, 0.25H), 6.78-6.75 (m, 1.44H), 6.42 (d, *J* = 12.1 Hz, 0.22H), 5.83 (dd, *J* = 11.2, 1.1 Hz, 1H), 5.07 (s, 1.20H), 3.24 (dd, *J* = 35.6, 11.1 Hz, 1H), 2.90-2.73 (m, 0.23H), 0.27 (s, 9H), 0.14 (s, 2.05); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3 (minor), 155.2, 144.7, 142.5 (minor), 133.7 (d, *J* = 11.1 Hz) (minor), 130.6 (d, *J* = 13.8 Hz), 129.8 (minor), 129.6, 121.1, 120.8 (minor), 115.7, 115.6 (minor), 115.6, 115.4 (minor), 105.9, 94.4 (minor), 43.7 (dd, *J* = 33.4, 25.0 Hz), -0.91 (d, *J* = 1.5 Hz), -1.10 (d, *J* = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.97 to -81.05 (m, 3F, *Z*+*E*), -101.1 to -102.2 (m, 1F, *Z*+*E*), -108.1 to -109.3 (m, 1F, *Z*+*E*), -119.6 to -121.8 (m, 2F, *Z*+*E*), -124.6 to -125.3 (m, 1F, *Z*+*E*), -126.1 to -127.1 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): [M]$^+$ calcd for $C_{16}H_{16}F_9IOSi$: 549.9866, found: 549.9860.



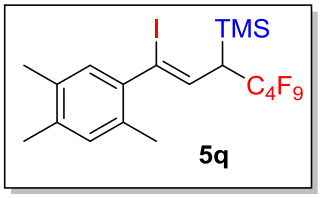
5o, (E/Z = 4.5)

According to the general procedure, the product **5o** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a colorless oil in 45% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.04 (s, 1H), 10.01 (s, 0.21), 7.90-7.89 (m, 1H), 7.82-7.77 (m, 1.44H), 7.69-7.65 (m, 1H), 7.55-7.47 (m, 1.45H), 6.51 (d, *J* = 12.2 Hz, 0.22H), 5.90 (dd, *J* = 11.2, 1.3 Hz, 1H), 3.32-3.15 (m, 1H), 2.80-2.63 (m, 0.27H), 0.28 (s, 9H), 0.14 (s, 2.44H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6, 191.3 (minor), 144.1, 142.1 (minor), 136.6 (minor), 136.5, 134.1, 132.1 (d, *J* = 13.8 Hz), 129.7, 129.5, 129.42 (minor), 129.39 (minor), 129.2, 104.5, 43.9 (dd, *J* = 33.7, 25.1 Hz), 21.2, 21.1 (minor), -0.84 (d, *J* = 1.6 Hz), -1.11 (d, *J* = 1.6 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.99-81.02 (m, 3F), -101.7 to -102.3 (m, 1F), -108.1 to -108.7 (m,

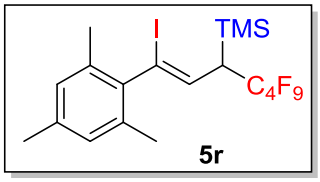
1F), -120.7 to -121.8 (m, 2F), -124.6 to -125.1 (m, 1F), -126.4 to -127.3 (m, 1F); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{17}H_{16}F_9IOSi$: 561.9866, found: 561.9853.



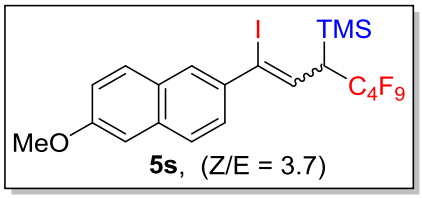
According to the general procedure, the product **5p** was purified with silica gel chromatography (Pe) as a pale yellow oil in 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22-7.15 (m, 3H), 7.11-7.08 (m, 1H), 5.58 (dd, *J* = 11.1, 1.1 Hz, 1H), 3.29-3.13 (m, 1H), 2.29 (s, 3H), 0.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 135.5, 131.3 (d, *J* = 12.5 Hz), 130.5, 126.7, 126.6, 125.8, 104.5, 42.8 (dd, *J* = 33.2, 25.2 Hz), 19.8, -0.82 (d, *J* = 1.8 Hz); ^{19}F NMR (564 MHz, CDCl3) δ -81.00-81.05 (m, 3F), -101.2-101-6 (m, 1F), -107.9 to -108.5 (m, 1F), 121.1 (d, *J* = 7.9 Hz, 2F), -124.5 to -125.1 (m, 1F), -126.4 to -127.0 (m, 1F); HRMS (EI) (*m/z*): $[M\text{-}TMSF]^+$ calcd for $C_{14}H_9F_8I$: 455.9619, found: 455.9612.



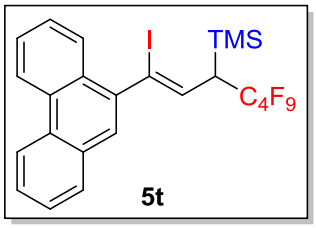
According to the general procedure, the product **5q** was purified with silica gel chromatography (Pe) as a pale yellow oil in 79% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.87 (s, 1H), 5.54 (dd, *J* = 11.1, 1.2 Hz, 1H), 3.28-3.13 (m, 1H), 2.26 (s, 3H), 2.24 (s, 6H), 0.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 137.2, 133.8, 132.6, 131.8, 130.9 (d, *J* = 13.2 Hz), 129.7, 105.1, 42.8 (dd, *J* = 33.1, 25.0 Hz), 19.7, 19.2, -0.83 (d, *J* = 1.8 Hz); ^{19}F NMR (564 MHz, CDCl3) δ -81.00-81.04 (m, 3F), -101.1 (d, J = 277.0 Hz, 1F), -107.9 to -108.5 (m, 1F), -120.7 to -120.9 (m, 2F), -124.5 to -125.1 (m, 1F), -126.4 to -127.0 (m, 1F); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{19}H_{22}F_9ISi$: 576.0386, found: 576.0376.



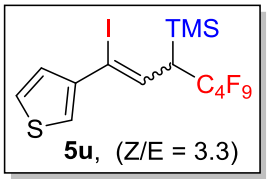
According to the general procedure, the product **5r** was purified with silica gel chromatography (Pe) as a colorless oil in 79% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (s, 2H), 5.51 (d, *J* = 10.9, 1H), 3.28-3.10 (m, 1H), 3.32 (s, 3H), 2.28 (s, 3H), 2.21 (s, 3H), 0.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 138.2, 136.1, 135.5, 131.0 (d, *J* = 12.7 Hz), 128.8, 128.4, 105.3, 43.1 (dd, *J* = 32.1, 25.9 Hz), 21.0, 20.8, 19.6 (dd, *J* = 3.6, 1.6 Hz), -0.62 (d, *J* = 2.5 Hz); ^{19}F NMR (564 MHz, CDCl3) δ -81.00-81.05 (m, 3F), -100.1 (dd, J = 277.5, 15.9 Hz, 1F), -106.7 to -107.3 (m, 1F), -120.3 to -120.9 (m, 1F), -121.2 to -121.7 (m, 1F), -124.4 to -125.0 (m, 1F), -126.7 to -127.3 (m, 1F); HRMS (EI) (*m/z*): $[M\text{-}I]^+$ calcd for $C_{19}H_{22}F_9Si$: 449.1342, found: 449.1330.



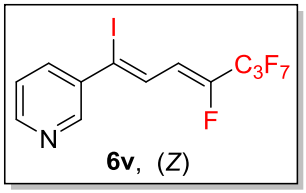
According to the general procedure, the product **5s** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a pale yellow oil in 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.67 (m, 4H), 7.54 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.37 (dd, *J* = 8.6, 1.7 Hz, 0.30H), 7.21-7.17 (m, 1.36H), 7.14-7.13 (m, 1.37H), 6.53 (d, *J* = 12.0 Hz, 0.28H), 5.92 (dd, *J* = 11.2, 1.2 Hz, 1H), 3.94 (s, 3.91H), 3.34 (dd, *J* = 35.7, 11.2 Hz, 1H), 2.97-2.79 (m, 0.28H), 0.33 (s, 9H), 0.16 (s, 2.56H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5 (minor), 158.3, 138.3, 136.1 (minor), 134.5, 134.2 (minor), 129.9 (d, *J* = 13.5 Hz), 129.7, 129.66 (minor) , 129.2 (d, *J* = 11.8 Hz) (minor), 128.3, 128.1 (minor), 127.6, 127.12 (minor), 127.1 (minor), 126.8, 126.6, 119.6 (minor), 119.5, 107.4, 105.7 (minor), 105.6, 96.1 (minor), 55.34 (minor), 55.29, 43.8 (dd, *J* = 33.4, 25.0 Hz), -0.85 (d, *J* = 1.6 Hz), -0.11 (d, *J* = 1.6 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.9 to -81.0 (m, 3F, *Z*+*E*), -101.0 to -102.1 (m, 1F, *Z*+*E*), -108.0 to -109.2 (m, 1F, *Z*+*E*), -119.4 to -121.7 (m, 2F, *Z*+*E*), -124.5 to -125.3 (m, 1F, *Z*+*E*), -126.1 to -127.1 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{21}H_{20}F_9IOSi$: 614.0179, found: 614.0177.



According to the general procedure, the product **5t** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a pale yellow oil in 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76-8.73 (m, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.15-8.11 (m, 1H), 7.93-7.90 (m, 1H), 7.72-7.60 (m, 5H), 5.92 (dd, *J* = 11.1, 1.1 Hz, 1H), 3.52-3.36 (m, 1H), 0.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1, 132.7 (d, *J* = 13.5 Hz), 131.1, 130.7, 130.4, 129.5, 128.9, 127.3, 127.2, 127.0, 126.6, 126.5, 126.4, 122.9, 122.6, 103.1, 42.9 (dd, *J* = 33.3, 25.3 Hz), -0.69 (d, *J* = 1.7 Hz); ^{19}F NMR (564 MHz, CDCl3) δ -80.9 (s, 3F), -101.4 (dd, *J* = 276.6, 15.9 Hz, 1F), -107.8 to -108.2 (m, 1F), -120.8 (s, 2F), -124.4 to -125.0 (m, 1F), -126.2 to -126.8 (m, 1F); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{24}H_{20}F_9ISi$: 634.0230, found: 634.0241.

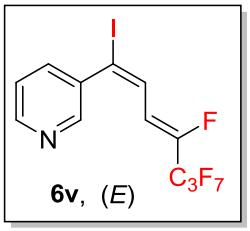


According to the general procedure, the product **5u** was purified with silica gel chromatography (Pe) as a pale yellow oil in 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2.27H), 7.24-7.22 (m, 1.29H), 7.07 (dd, *J* = 5.0, 1.1 Hz, 0.31H), 6.42 (dd, *J* = 12.0 Hz, 0.30H), 5.95 (dd, *J* = 11.2, 1.2 Hz, 1H), 3.32-3.16 (m, 1H), 3.03-2.86 (m, 0.31H), 0.27 (s, 9H), 0.14 (s, 2.78H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 141.1 (minor), 134.3 (d, *J* = 11.2 Hz) (minor), 128.5 (d, *J* = 14.4 Hz), 128.4 (minor), 126.2, 126.0, 125.9 (minor), 125.4, 123.6 (minor), 99.6, 43.3 (dd, *J* = 33.5, 25.1 Hz), -0.91 (d, *J* = 1.7 Hz), -1.29 (d, *J* = 1.6 Hz); ^{19}F NMR (564 MHz, CDCl3) δ -80.99 to -81.06 (m, 3F, *Z*+*E*), -101.2 to -102.1 (m, 1F, *Z*+*E*), -108.1 to -109.6 (m, 1F, *Z*+*E*), -119.6 to -121.8 (m, 2F, *Z*+*E*), -124.6 to -125.4 (m, 1F, *Z*+*E*), -126.2 to -127.1 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): $[M\text{-}TMSF]^+$ calcd for $C_{11}H_5F_8IS$: 447.9023, found: 447.9013.



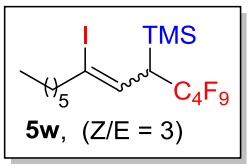
6v, (*Z*)

According to the general procedure, the product **6v** (*Z*) was purified with silica gel chromatography (Pe/EA = 5 : 1) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.56 (s, 1H), 7.84 (d, *J* = 8.0, 1H), 7.33-7.28 (m, 1H), 6.92 (d, *J* = 10.5, 1H), 6.51 (dd, *J* = 31.1, 10.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5, 148.8, 138.0, 136.6, 125.6 , 123.2, 117.4 (d, *J* = 4.3 Hz), 109.1; ^{19}F NMR (564 MHz, CDCl3) δ -80.7 (t, *J* = 8.7 Hz, 3F), 118.8 (td, *J* = 16.5, 8.2 Hz, 2F), -125.5 to -125.6 (m, 1F), -127.1 (d, *J* = 7.8 Hz, 2F); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{12}H_6F_8I$: 442.9412, found: 442.9402.



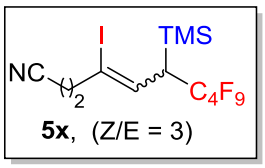
6v, (*E*)

According to the general procedure, the product **6v** (*E*) was purified with silica gel chromatography (Pe/EA = 5 : 1) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60-8.56 (m, 2H), 7.67-7.64 (m, 1H), 7.45 (d, *J* = 11.5, 1H), 7.38-7.33 (m, 1H), 5.94 (dd, *J* = 30.3, 11.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 148.9, 136.7, 131.4 (d, *J* = 3.4 Hz), 123.4, 110.5 (d, *J* = 5.4 Hz); ^{19}F NMR (564 MHz, CDCl3) δ -80.7 (t, *J* = 8.4 Hz, 3F), 118.6 (td, *J* = 16.4, 8.6 Hz, 2F), -121.4 to -121.5 (m, 1F), -127.1 (d, *J* = 7.8 Hz, 2F); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{12}H_6F_8I$: 442.9412, found: 442.9408.



5w, (Z/E = 3)

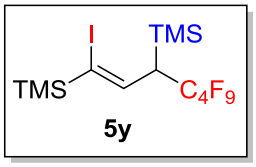
According to the general procedure using 0.8 equiv zinc and run the reaction at 60 °C after addition of alkyne, the product **5w** was purified with silica gel chromatography (Pe) as a pale yellow oil in 31% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.11 (d, *J* = 12.0 Hz, 0.30H), 5.95 (dd, *J* = 11.0, 0.9 Hz, 1H), 3.12-2.94 (m, 1H), 2.93-2.75 (m, 0.39H), 2.52 (t, *J* = 7.3 Hz, 2H), 2.31-2.21 (m, 0.69H), 1.58-1.46 (m, 3.37H, overlap with H_2O), 1.30-1.26 (m, 7.96H), 0.91-0.86 (m, 4.08H), 0.20 (s) with 0.18 (s) (12.41H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.3 (d, *J* = 13.3 Hz), 112.6, 45.5, 42.1 (dd, *J* = 32.8, 24.9 Hz), 38.3 (minor), 31.6 (minor), 31.5, 29.6 (minor), 29.5, 28.4 (minor), 27.9, 22.6, 22.5 (minor), 13.96, 13.93 (minor), -1.03 (d, *J* = 1.7 Hz), -1.42 (d, *J* = 1.6 Hz, minor); ^{19}F NMR (564 MHz, CDCl3) δ -81.0 to -81.1 (m, 3F, *Z*+*E*), -100.9 to -101.8 (m, 1F, *Z*+*E*), -108.1 to -108.7 (m, 0.83F, *Z*), -109.6 to -110.2 (m, 0.24F, *E*), -120.2 to -121.1 (m, 2F, *Z*+*E*), -124.4 to -125.1 (m, 1F, *Z*+*E*). -126.6 to -127.2 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): $[M\text{-}TMSF]^+$ calcd for $C_{13}H_{15}F_8I$: 450.0085, found: 450.0071.



5x, (Z/E = 3)

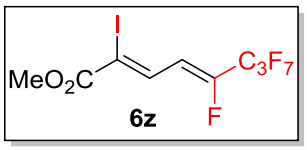
According to the general procedure using 0.8 equiv zinc and run the reaction at 60 °C after addition of alkyne, the product **5x** was purified with silica gel chromatography (Pe/EA = 10 : 1) as a pale yellow oil in 20% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.24 (d, *J* = 12.2 Hz, 0.32H),

5.95 (dd, J = 11.0, 0.9 Hz, 1H), 3.12-2.94 (m, 1H), 2.93-2.78 (m, 0.44H), 2.70 (t, J = 7.0 Hz, 2H), 2.56-2.44 (m, 0.55H), 2.39-2.69 (m, 2.76H), 1.99-1.85 (m, 2.76H), 0.21 (d, J = 0.54 Hz, 9H) with 0.19 (d, J = 0.54 Hz, 2.8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.3 (d, J = 13.3 Hz), 118.9, 108.4, 43.6, 42.2 (dd, J = 33.1, 24.9 Hz), 36.6 (minor), 25.6 (minor), 25.0, 16.1 (minor), 15.5, -1.03 (d, J = 1.7 Hz), -1.46 (d, J = 1.6 Hz, minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.97 to -81.03 (m, 3F, *Z*+*E*), -101.1 to -101.9 (m, 1F, *Z*+*E*), -108.1 to -108.7 (m, 0.78F, *Z*), -109.5 to -110.3 (m, 0.23F, *E*), -120.0 to -121.1 (m, 2F, *Z*+*E*), -124.6 to -125.2 (m, 1F, *Z*+*E*). -126.5 to -127.1 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): [M-TMSF]$^+$ calcd for $C_{11}H_8F_8IN$: 432.9568, found: 432.9560.



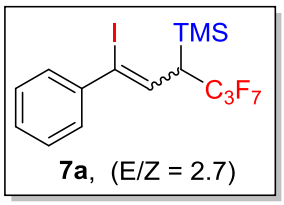
5y

According to the general procedure using 0.8 equiv zinc and run the reaction at 60 °C after addition of alkyne, the product **5x** was purified with silica gel chromatography (Pe) as a pale yellow oil in 39% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (dd, J = 10.7, 1.7 Hz, 1H), 3.44-3.26 (m, 1H), 0.21 (s, 9H), 0.19 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2 (d, J = 12.6 Hz), 115.7, 44.9 (dd, J = 32.2, 24.4 Hz), -1.01 (d, J = 1.4 Hz), -1.47; ^{19}F NMR (564 MHz, CDCl3) δ -81.0 to -81.1 (m, 3F), -101.5 to -102.1 (m, 1F), -108.2 to -108.8 (m, 1F), -121.4 to -121.5 (m, 2F), -124.6 to -125.2 (m, 1F), -126.5 to -127.1 (m, 1F); HRMS (EI) (*m/z*): [M-TMSF]$^+$ calcd for $C_{10}H_{11}F_8ISi$: 437.9541, found: 437.9552.



6z

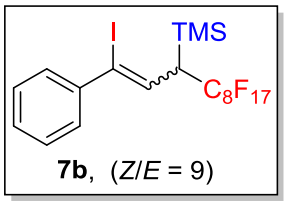
According to the general procedure using 0.8 equiv zinc and run the reaction at 60 °C after addition of alkyne, the product **5x** was purified with silica gel chromatography (Pe/EA = 40 : 1) as a colorless oil in 24% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 11.0, 0.8 Hz, 1H), 6.49 (dd, J = 30.5, 11.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2 (d, J = 12.6 Hz), 115.7, 44.9 (dd, J = 32.2, 24.4 Hz), -1.01 (d, J = 1.4 Hz), -1.47; ^{19}F NMR (564 MHz, CDCl3) δ -80.6 (t, J = 9.0 Hz, 3F), -114.8 (m, 1F), -118.9 (dq, J = 17.2, 8.5 Hz, 2F), -126.95 to -126.97 (m, 2F); HRMS (EI) (*m/z*): [M]$^+$ calcd for $C_9H_5F_8IO_2$: 423.9201, found: 423.9209.



7a, (E/Z = 2.7)

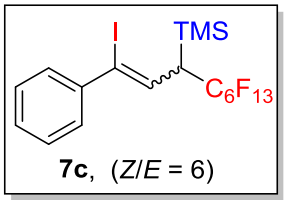
According to the general procedure, the product **7a** was purified with silica gel chromatography (Pe) as a pale yellow oil in 44% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.36-7.28 (m, 4.90H), 6.45 (d, J = 12.1 Hz, 0.37H), 5.81 (dd, J = 11.2, 1.1 Hz, 1H), 3.33-3.16 (m, 1H), 2.84-2.67 (m, 0.39H), 0.28 (s, 9H), 0.14 (s, 3.39H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 141.1 (minor), 133.5 (d, J = 9.6 Hz) (minor), 130.4 (d, J = 13.8 Hz), 128.54, 128.50, 128.48 (minor), 128.42 (minor), 128.3, 106.8, 95.4 (minor), 43.5 (dd, J = 33.5, 25.4 Hz), 37.4 (dd, J = 32.0, 26.1 Hz) (minor), -0.91 (d, J = 1.5 Hz), -1.11 (d, J = 1.6 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.26 (dd, J = 12.7, 10. 4 Hz, 1F, *E*), -80.31 (dd, J = 12.7, 9.2 Hz, 3F,

Z), -101.4 to -102.5 (m, 1.37F, *Z*+*E*), -109.0 to -109.6 (m, 1F, *Z*), -109.6 to -110.2 (m, 0.4F, *E*), -122.8 to -123.3 (m, 0.4F, *E*), -124.0 to -124.6 (m, 1F, *Z*), -124.7 to -125.3 (m, 1.33F, *Z*+*E*); HRMS (EI) (*m/z*): $[M\text{-}TMSF]^+$ calcd for $C_{12}H_7F_6I$: 391.9491, found: 391.9485.



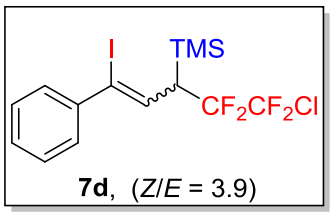
7b, (*Z*/*E* = 9)

According to the general procedure, the product **7b** was purified with silica gel chromatography (Pe) as a pale yellow oil in 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.36-7.28 (m, 3.55H), 6.46 (d, *J* = 12.0 Hz, 0.11H), 5.83 (d, *J* = 11.1 Hz, 1H), 3.36-3.19 (m, 1H), 2.87-2-71 (m, 0.12H), 0.29 (s, 9H), 0.15 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 141.1 (minor), 130.4 (d, *J* = 13.7 Hz), 128.6 (minor), 128.5, 128.48 (minor), 128.44 (minor), 128.36, 106.8, 43.8 (dd, *J* = 33.5, 24.8 Hz), -0.91 (d, *J* = 1.6 Hz), -1.14 (d, *J* = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.88 to -80.90 (m, 3F), -101.6 to -102.1 (m, 1F), -107.8 to -108.3 (m, 1F), -109.5 to -123.4 (m, 10F), -125.5 to -126.8 (m, 2F, *Z*); HRMS (EI) (*m/z*): $[M\text{-}TMSF]^+$ calcd for $C_{17}H_7F_{16}I$: 641.9331, found: 641.9345.



7c, (*Z*/*E* = 6)

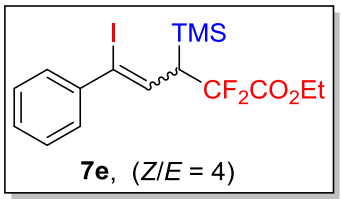
According to the general procedure, the product **7c** was purified with silica gel chromatography (Pe) as a pale yellow oil in 74% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.36-7.29 (m, 3.95H), 6.46 (d, *J* = 12.1 Hz, 0.19H), 5.83 (d, *J* = 11.1 Hz, 1H), 3.27 (ddt, *J* = 35.4, 11.2, 2.5 Hz, 1H), 2.87-2.60 (m, 0.20H), 0.29 (s, 9H), 0.14 (s, 1.78H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 141.1 (minor), 130.4 (d, *J* = 13.5 Hz), 128.6, 128.5 128.47 (minor), 128.44 (minor), 128.4, 106.8, 43.9 (dd, *J* = 33.3, 25.0 Hz), 37.4 (dd, *J* = 32.0, 26.1 Hz) (minor), -0.89 (d, *J* = 1.6 Hz), -1.11 (d, *J* = 1.6 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.9 (t, *J* = 9.5 Hz, 3F), -101.5 to -102.1 (m, 1F), -107.8 to -108.4 (m, 1F), -109.5 to -123.6 (m, 6F), -125.8 to -127.0 (m, 2F); HRMS (EI) (*m/z*): $[M\text{-}TMSF]^+$ calcd for $C_{15}H_7F_{12}I$: 541.9395, found: 541.9396.



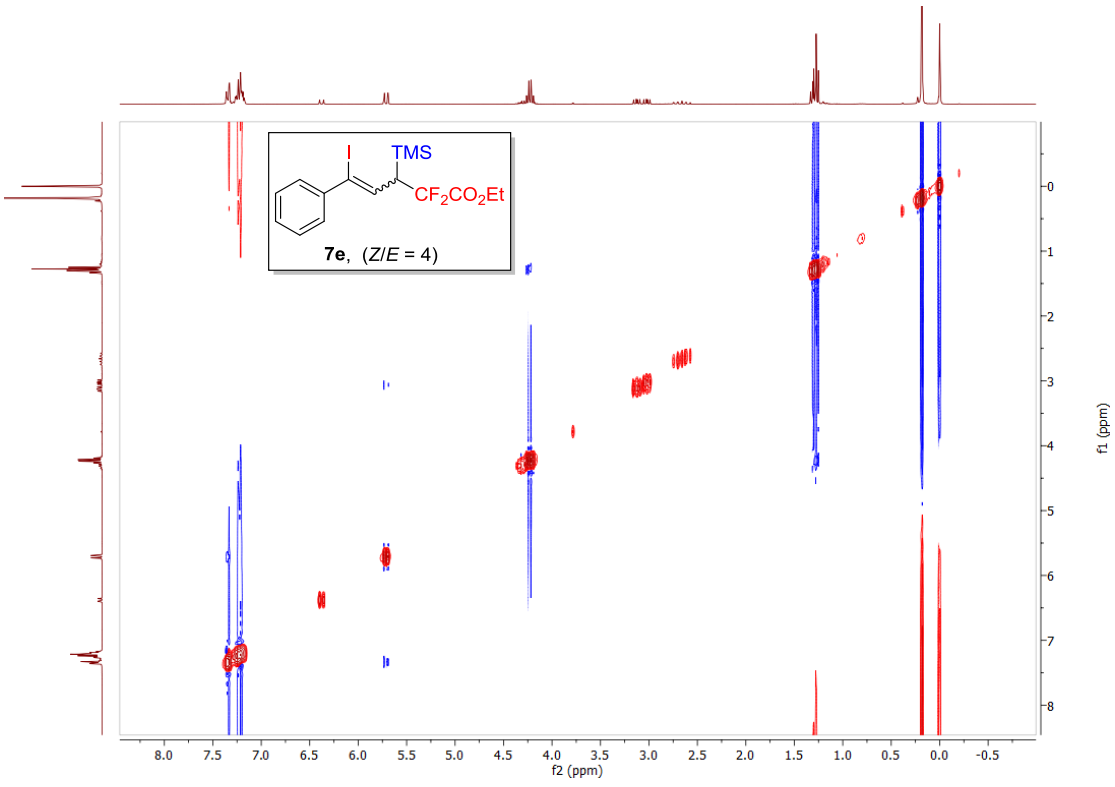
7d, (*Z*/*E* = 3.9)

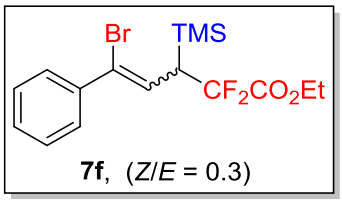
According to the general procedure, the product **7d** was purified with silica gel chromatography (Pe/EA = 10 : 1) as a pale yellow oil in 55% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.35-7.27 (m, 4.49H), 6.44 (d, *J* = 12.4 Hz, 0.26H), 5.80 (dd, *J* = 11.4, 1.0 Hz, 1H), 3.32-3.16 (m, 1H), 2.80-2.64 (m, 0.26H), 1.42-1.34 (m, overlap, 3.87H), 0.28 (s, 9H), 0.14 (s, 2.42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 141.1 (minor), 130.4 (d, *J* = 13.7 Hz), 128.6 (minor), 128.5, 128.48 (minor), 128.44 (minor), 128.36, 106.8, 43.8 (dd, *J* = 33.5, 24.8 Hz), -0.91 (d, *J* = 1.6 Hz), -1.12 (d, *J* = 1.5 Hz) (minor); ^{19}F NMR (564 MHz, CDCl3) δ -66.9 (dd, *J* = 174.2, 9.5 Hz, 0.26F, *E*), -68.1 to -68.4 (m, 0.26F, *E*), -68.3 (d, *J* = 173.7 Hz, 1F, *Z*), -68.7 (dd, *J* = 174.1, 9.3 Hz, 1F, *Z*), -98.9 (d, *J* = 265.1 Hz, 0.26F, *E*), -99.7 (d, *J*

= 263.2 Hz, 1F, *Z*), -109.8 to-110.4 (m, 0.26F, *E*), 110.3 (ddd, *J* = 262.9, 34.7, 9.4 Hz, 1F, *Z*);; HRMS (EI) (*m/z*): [M-TMSF]$^+$ calcd for $C_{11}H_7ClF_3I$: 357.9228, found: 357.9224.

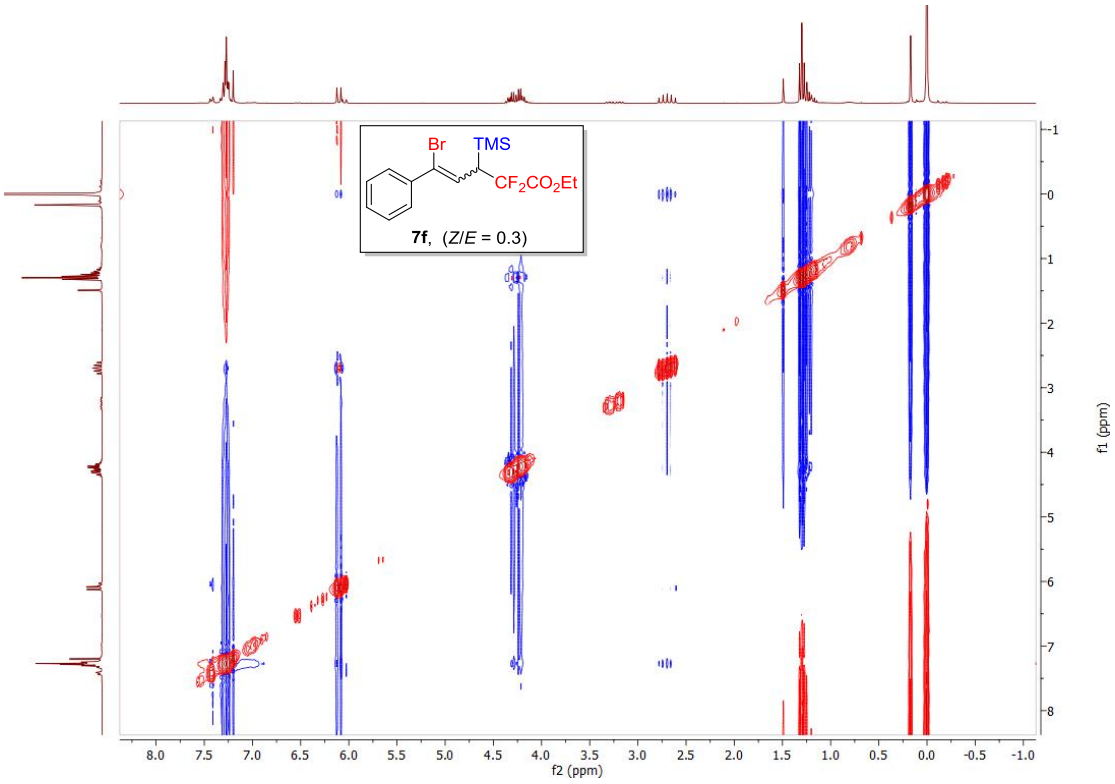


According to the general procedure, the product **7e** was purified with silica gel chromatography (Pe/EA = 10 : 1) as a pale yellow oil in 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.36-7.28 (m, 4.26H), 6.46 (d, *J* = 12.4 Hz, 0.25H), 5.79 (dd, *J* = 11.4, 1.0 Hz, 1H), 4.40-4.27 (m, overlap, 2.46H), 3.15 (ddd, *J* = 31.4, 11.4, 7.8 Hz, 1H), 2.74 (dt, *J* = 25.6, 12.4 Hz, 0.26H), 1.42-1.34 (m, overlap, 3.87H), 0.27 (s, 9H), 0.08 (s, 2.30H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2 (dd, *J* = 36.6, 33.8 Hz), 143.0, 141.0 (minor), 134.5 (dd, *J* = 8.9, 3.4 Hz), 131.5 (dd, *J* = 12.2, 1.4 Hz), 128.61 (minor), 128.57, 128.54, 128.41 (minor), 128.34 (minor), 128.29, 117.6 (t, *J* = 251.9 Hz), 108.0, 96.7 (minor), 62.9, 46.3 (dd, *J* = 31.7, 26.5 Hz), 40.7 (dd, *J* = 29.5, 25.9 Hz) (minor), 14.1, 14.0 (minor), -1.07, -1.61 (minor); ^{19}F NMR (564 MHz, CDCl3) δ -97.7 (dd, *J* = 250.6, 7.8 Hz, 1F, *Z*), -103.3 (dd, *J* = 251.5, 13.0 Hz, 0.25F, *E*), -101.0 (dd, *J* = 251.6, 25.6 Hz, 0.26F, *E*), -98.0 (dd, *J* = 250.6, 31.3 Hz, 1F, *Z*); HRMS (EI) (*m/z*): [M]$^+$ calcd for $C_{16}H_{21}F_2IO_2Si$: 438.0318, found: 438.0322.





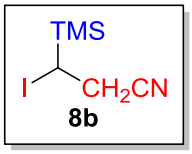
According to the general procedure, the product **7f** was purified with silica gel chromatography (Pe/EA = 10 : 1) as a pale yellow oil in 43% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.47 (m, 0.59H), 7.39-7.31 (m, 5.97H), 6.17 (d, *J* = 12.6 Hz, 1H), 6.11 (dd, *J* = 11.5, 1.1 Hz, 0.28H), 4.39-4.24 (m, overlap, 2.66H), 3.30 (ddd, *J* = 31.3, 11.5, 8.3 Hz, 0.3H), 2.76 (dt, *J* = 25.7, 12.9 Hz, 1H), 1.38-1.28 (m, overlap, 4.08H), 0.23 (s, 2.43), 0.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4 (t, *J* = 34.5 Hz), 139.7 (minor), 138.0 (minor), 128.9, 128.8, 128.5, 128.4 (minor), 127.6 (minor), 126.1 (dd, *J* = 9.2, 3.4 Hz), 124.2 (dd, *J* = 12.1, 1.5 Hz) (minor), 122.4 (d, *J* = 1.5), 117.2 (t, *J* = 251.9 Hz), 62.9, 41.5 (dd, *J* = 31.7, 26.8 Hz) (minor), 39.0 (dd, *J* = 29.7, 26.1 Hz), 14.0, -1.26 (minor), -1.63; ^{19}F NMR (564 MHz, CDCl3) δ -96.7 to -98.1 (m, 1.26F, *Z*+*E*), -101.2 (dd, *J* = 252.1, 25.7 Hz, 1F, *E*), -103.6 (dd, *J* = 250.9, 31.4 Hz, 0.26F, *Z*);; HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{16}H_{21}F_2BrO_2Si$: 390.0457, found: 390.0463.



1,1 addtion to $TMSCHN_2$

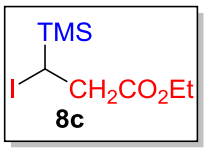
An oven-dried reaction tube was charged with $CoBr_2$ (4.2 mg, 0.02 mmol, 0.05 equiv), dppbz (8.9 mg, 0.02 mmol, 0.05 equiv), Zn (10.24 mg, 0.16 mmol, 0.40 equiv). The tube was evacuated and backfilled with nitrogen for three times. Acetonitrile (2 mL) was added into the tube and stirred for 1 minutes. Trimethylsilyldiazomethane (0.52 mmol, 2 M in hexane, 1.3 equiv) was added into the system, followed with R-X (0.4 mmol, 1.0 equiv). The mixture was stirred at room temperature for 10 hours. The solvent was removed to leave a crude product, which was purified by column

chromatography on silica gel to afford the product.



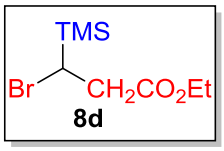
8b

According to the general procedure, the product **8b** was purified with silica gel chromatography (Pe/EA = 5 : 1) as a pale yellow oil in 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.19 (dd, *J* = 9.6, 4.9 Hz, 1H), 3.06 (dd, *J* = 17.5, 4.9 Hz, 1H), 2.86 (dd, *J* = 17.5, 9.6 Hz, 1H), 0.21 (s, 9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 118.8, 24.3, 8.0, -2.3; HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_6H_{12}INSi$: 252.9778, found: 252.9772.



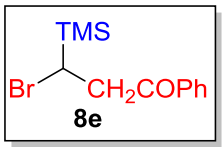
8c

According to the general procedure, the product **8c** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a pale yellow oil in 54% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.18 (q, *J* = 7.1 Hz, 2H), 3.45 (dd, *J* = 11.9, 3.8 Hz, 1H), 2.96 (dd, *J* = 16.4, 3.8 Hz, 1H), 2.74 (dd, *J* = 16.4, 11.9 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.15 (s, 9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 61.0, 39.7, 14.2, 11.7, -2.4; HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_8H_{17}IO_2Si$: 300.0037, found: 300.0029.



8d

According to the general procedure, the product **8d** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a pale yellow oil in 53% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20 (q, *J* = 7.1 Hz, 2H), 3.63 (dd, *J* = 11.7, 3.7 Hz, 1H), 2.87 (dd, *J* = 16.2, 3.7 Hz, 1H), 2.72 (dd, *J* = 16.2, 11.7 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.15 (s, 9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 61.0, 39.0, 36.1, 14.2, -3.2; HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_8H_{17}BrO_2Si$: 252.0176, found: 252.0181.

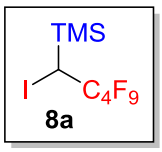


8e

According to the general procedure, the product **8e** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a pale yellow oil in 55% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.94 (m, 2H), 7.61-7.54 (m, 1H), 7.50-7.45 (m, 2H), 3.91 (dd, *J* = 10.7, 3.5 Hz, 1H), 3.63 (dd, *J* = 17.4, 10.7 Hz, 1H), 3.29 (dd, *J* = 17.4, 3.5Hz, 1H), 0.20 (s, 9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 136.8, 133.3, 128.6, 128. 1, 42.0, 34.8, -3.0; HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{12}H_{17}BrOSi$: 284.0227, found: 284.0221.

3. Gram scale experiments

Gram scale synthesis of ***8a***

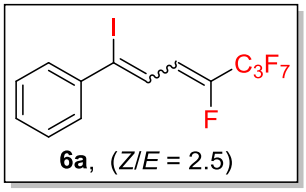


8a

An oven-dried reaction tube was charged with $CoBr_2$ (21.6 mg, 0.1 mmol, 0.05 equiv), dppbz (44.6 mg, 0.1 mmol, 0.05 equiv), Zn (21.6 mg, 0.4 mmol, 0.20 equiv). The tube was evacuated and backfilled with nitrogen for three times. Acetonitrile (15 mL) was added into the tube and stirred for 1 minutes.

Trimethylsilyldiazomethane (2.6 mmol, 2 M in hexane, 1.3 equiv) was added into the system, followed with C_4F_9I (2 mmol, 1.0 equiv). The mixture was stirred at room temperature for 1 hours. The solvent was removed to leave a crude product, which was purified by column chromatography on silica gel (Pe) to afford the product **8a** as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.49-3.37 (m, 1H), 0.32 (s, 9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 5.45 (t, *J* = 31.8 Hz), -0.32; ^{19}F NMR (564 MHz, CDCl3) δ -80.88 to -80.92 (m, 3F, *Z*+*E*), -96.1 to -97.3 (m, 2F), -115.6 to -116.2 (m, 1F), -119.6 to -120.3 (m, 1F), -124.5 to -125.1 (m, 1F), -126.4 to -127.0 (m, 1F, *Z*+*E*); HRMS (EI) (*m/z*): $[M\text{-}TMS]^+$ calcd for C_5HF_8I: 339.8990, found: 339.8981.

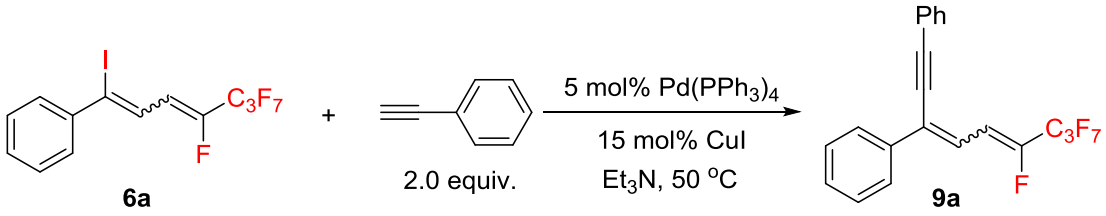
Gram scale synthesis of ***6a***

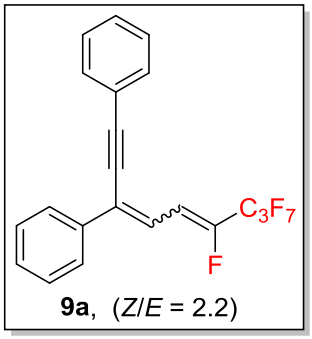


An oven-dried reaction tube was charged with $CoBr_2$ (21.6 mg, 0.1 mmol, 0.05 equiv), dppbz (44.6 mg, 0.1 mmol, 0.05 equiv), Zn (21.6 mg, 0.4 mmol, 0.20 equiv). The tube was evacuated and backfilled with nitrogen for three times. Acetonitrile (15 mL) was added into the tube and stirred for 1 minutes. Trimethylsilyldiazomethane (2.6 mmol, 2 M in hexane, 1.7 equiv) was added into the system, followed with C_4F_9I (2 mmol, 1.3 equiv). The mixture was stirred at room temperature for 1 hour minutes until nearly no bubble came out. Then phenyl acetylene (2.0 mmol) was added into the system and reacted for another 10 hours. Then CsF (0.6 mmol, 0.3 equiv) was added into the system and reacted for another 2 hours. The solvent was removed to leave a crude product, which was purified by column chromatography on silica gel (Pe) to afford the product **6a** as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.53 (m, 2H), 7.41-7.30 (m, 5.25H), 6.86 (dd, *J* = 10.6, 0.8 Hz, 1H), 6.54 (dd, *J* = 31.5, 10.6 Hz, 1H), 6.01 (dd, *J* = 31.2, 11.4 Hz, 0.4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 129.7, 129.5 (minor), 128.9 (minor), 128.8, 128.6 (minor), 128.5, 126.1, 117.9 (d, *J* = 4.1 Hz); ^{19}F NMR (564 MHz, CDCl3) δ -80.7 (t, *J* = 9.2 Hz, 3F), -80.8 (t, *J* = 9.1 Hz, 0.85H, *E*), -118.5 (dq, *J* = 16.4, 8.3 Hz, 2F), -118.75 (dq, *J* = 16.4, 8.2 Hz, 0.72F, *E*), -123.3 to -123.4 (m, 1F), -127.0 (d, *J* = 7.7 Hz, 2F), -127.2 (d, *J* = 7.3 Hz, 0.7F, *E*); HRMS (EI) (*m/z*): $[M\text{-}TMS]^+$ calcd for $C_{13}H_7F_8I$: 441.9459, found: 441.9450.

4. Fellow-up reactions

Palladium-catalyzed Sonogashira coupling

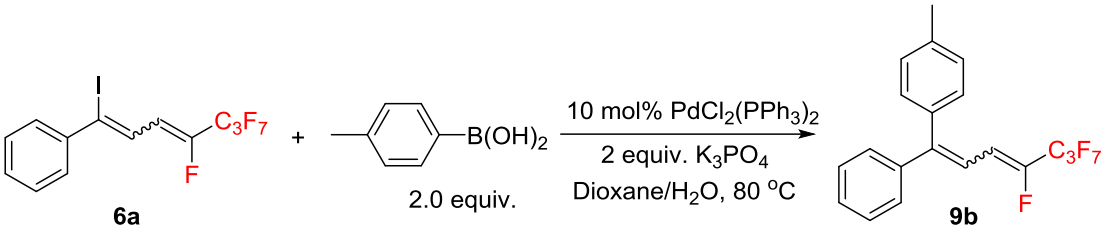


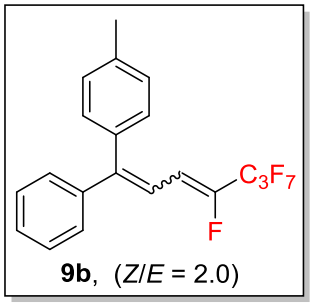


9a, (*Z*/*E* = 2.2)

To a 10 mL of Schlenk tube were added Pd $(PPh_3)_4$ (5 mol%, 0.01 mol, 11.5 mg), CuI (15 mol%, 0.03 mmol, 5.7 mg). The mixture was evacuated and backfilled with N_2 for 3 times. Et_3N (2.0 mL), **6a** (1.0 equiv, 0.2 mmol, 88.4 mg) and phenylacetylene (2.0 equiv, 0.4 mmol, 40.8 mg) were added subsequently. The mixture was stirred at 50 °C for 6 hours. After cooling to room temperature, the solvent was removed under vacuum and purified by flash column chromatography on silica gel (PE) to give the desired product **9a** with 82% yield (68.3 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.60-7.56 (m, 1.9H), 7.52-7.39 (m, 9H), 7.21 (dd, *J* = 11.5, 1.3 Hz, 1H), 7.02 (dd, *J* = 11.7, 1.3 Hz, 0.45H), 6.99 (dd, *J* = 32.0, 10.4 Hz, 1H), 6.45 (dd, *J* = 31.3, 11.8 Hz, 0.44H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.6, 136.3 (minor), 131.8 (minor), 131.7, 129.4 (minor), 129.2, 129.03, 128.99 (minor), 128.89 (minor), 128.71, 128.67(minor), 128.6, 128.4 (minor), 126.7, 123.5 (minor), 122.6 (minor), 122.4, 121.4, 113.29 (q, *J* = 5.1 Hz), 111.6 (q, *J* = 5.3 Hz) (minor), 100.2, 94. 1 (minor), 90.8 (minor), 85.3; ^{19}F NMR (564 MHz, CDCl3) δ -80.7 (t, *J* = 8.9 Hz, 3F), -80.8 (t, *J* = 8.8 Hz, 1.35F, *E*), -118.2 (dq, *J* = 17.1, 8.8 Hz, 2F), -118.4 (dq, *J* = 17.1, 9.0 Hz, 0.92F, *E*), -126.2 to -126.4 (m, 1.5F, *Z*+*E*), -127.0 (d, *J* = 8.1 Hz, 2F), -127.2 (d, *J* = 8.0 Hz, 0.9F, *E*); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{21}H_{12}F_{10}$: 416.0806, found: 416.8013.

Palladium-catalyzed Sonogashira coupling



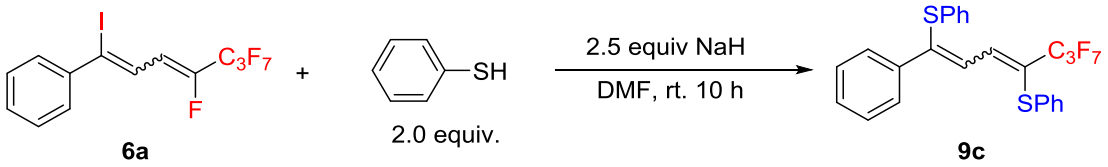


9b, (*Z*/*E* = 2.0)

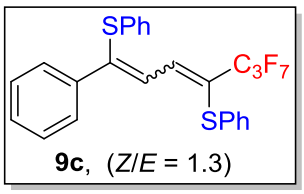
To a 10 mL of Schlenk tube were added 4-methylphenyl boronic acid (2.0 equiv, 0.4 mmol, 54.4 mg), $PdCl_2(PPh_3)_2$ (10 mol%, 0.02 mol, 14.0 mg), K_3PO_4 (2.0 equiv, 0.4 mmol, 84.8 mg). The mixture was evacuated and backfilled with N_2 for 3 times. 1,4-dioxane (2 mL), H_2O (100 uL) and **6a** (1.0 equiv, 0.2 mmol, 88.4 mg) were added subsequently. The mixture was stirred at 80 °C for 5 hours. After cooling to room temperature, the solvent was removed under vacuum and purified by flash column chromatography on silica gel (PE) to give the desired product **9b** with 73% yield (59.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.45 (m, 1H, *Z*+*E*), 7.36 (s, 3H), 7.29-7.12 (m, 5H), {6.95 (d, *J* = 11.4 Hz, *E*), 6.93 (d, *J* = 11.4 Hz, *Z*), 1H}, 6.37-6.16 (m, 1H, *Z*+*E*), 2.46 (s, 2H, *Z*), 2.40 (s, 1H, *E*) *J* = 31.2, 11.4 Hz, 0.4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 138.9,

138.5 (minor), 135.2, 130.2, 129.1 (minor), 128.7, 128.5, 128.4 (minor), 128.35, 128.2, 128.1 (minor), 115.2, 114.6 (minor), 113.0 (q, J = 5.1 Hz), 21.3, 21.2 (minor); ^{19}F NMR (564 MHz, CDCl3) δ -80.78 to -80.81 (m, 3F, *Z*+*E*), -80.8 (t, J = 9.1 Hz, 0.85H, *E*), 118.2 (dq, J = 18.1, 9.2 Hz, 2F, *Z*+*E*), -127.3 (d, J = 8.1 Hz, 2F), -130.6 to -130.7 (m, 0.7F, *Z*), -130.7 to -130.9 (m, 0.73, *E*); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{20}H_{14}F_8$: 406.0962, found: 406.0953.

Substitution with thiophenol



6a **9c**



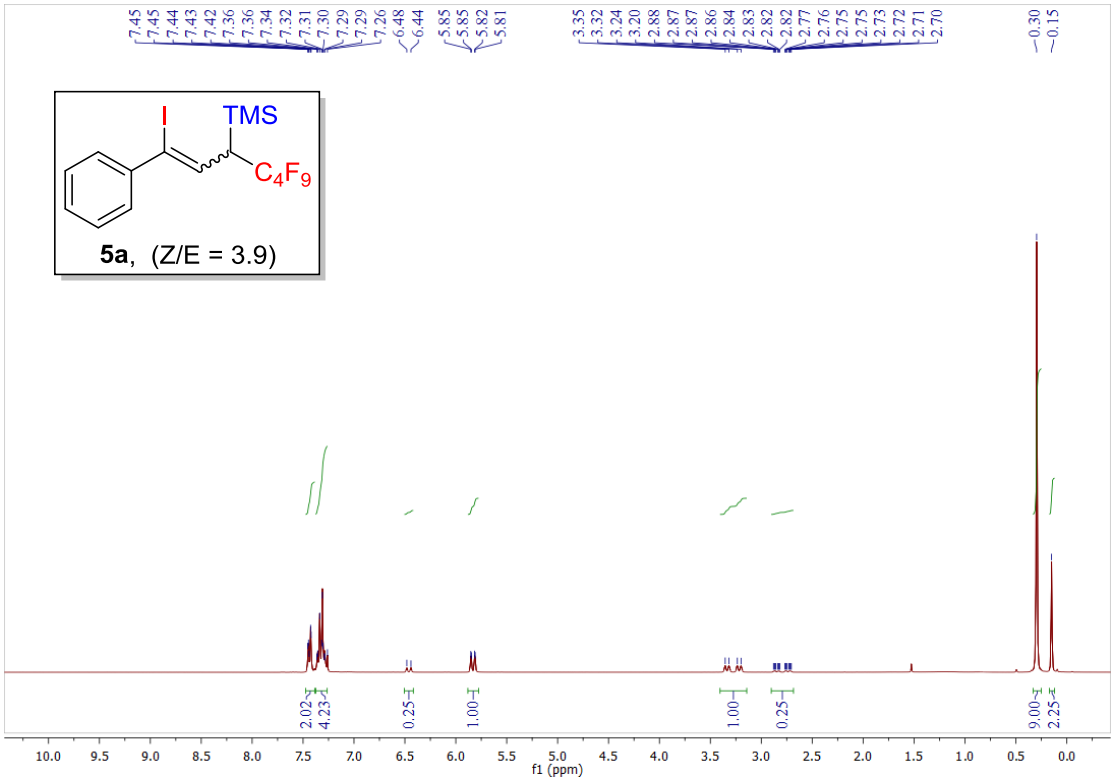
9c, (*Z*/*E* = 1.3)

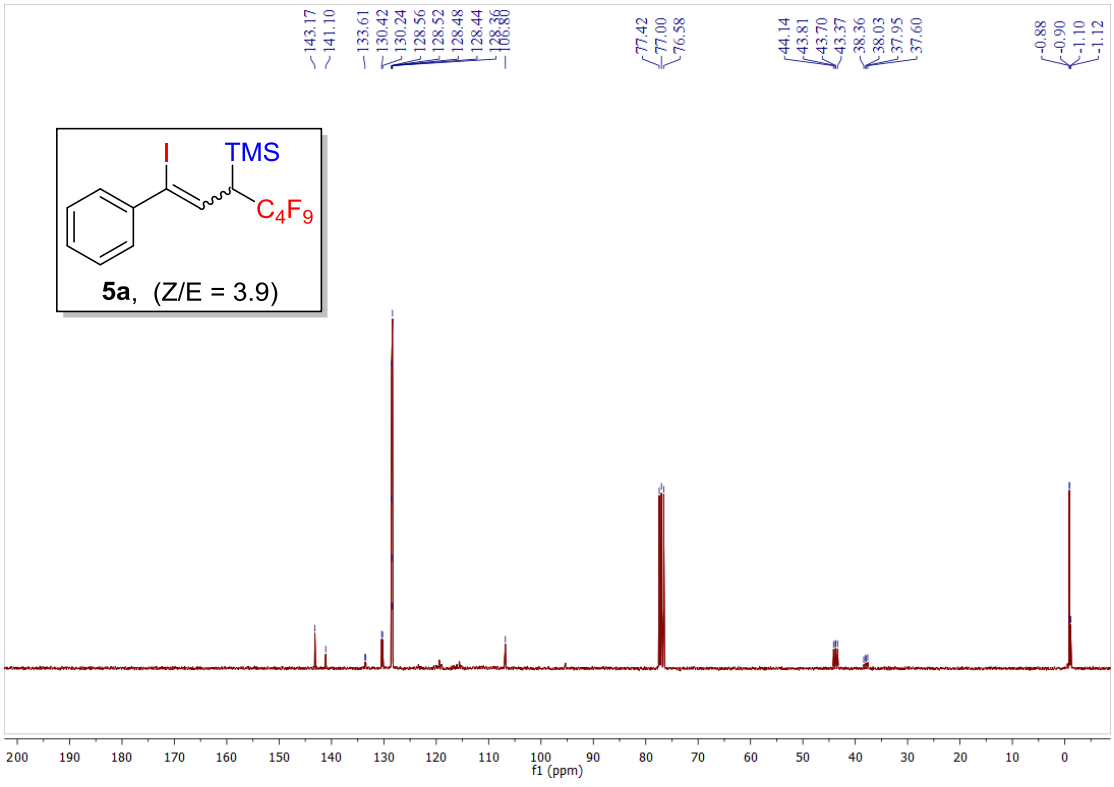
To a 10 mL of Schlenk tube was added NaH (3 equiv, 0.6 mmol, 14.4 mg). The tube was evacuated and backfilled with N_2 for 3 times. DMF (2 ml) and thiophenol (2 equiv, 0.4 mmol, 44.0 mg) were added at 0 °C and stirred for 10 minutes. Subsquently 3a' (1.0 equiv, 0.2 mmol, 88.4 mg) was added to the system and stirred for another 10 hours at room temperature. The system was quenced with NH_4Cl (aq) and extracted with dichloromethan (3 x 10 mL) and the combined organic layer was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (PE) to give the desired product **9c** with 62% yield (65.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, J = 10.6 Hz, 1H), 7.62-7.59 (m, 2H), 7.52 (s, 3.6H), 7.49-7.46 (m, 2H), 7.41-7.17 (m, 19.1H), 6. 60 (dt, J = 11.1, 1.3 Hz, 0.67H); Due to the isomers, the ^{13}C NMR is too complex, here just display all the carbon, ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 138.5, 136.2 (minor), 135.5 (minor), 135.1 (minor), 134.6, 133.9 (minor), 130.2, 129.7 (minor), 129.5, 129.4, 129.3 (minor), 129.2, 129.1, 128.9, 128.6 (minor), 128.55, 128.53, 128.4, 128.0, 127.6, 127.5, 127.2, 126.8, 126.6, 126.2, 119.6; ^{19}F NMR (564 MHz, CDCl3) δ -80.1 (t, J = 10.0 Hz, 3F), -80.2 (t, J = 10.1 Hz, 2.18F, *E*), -107.2 (q, J = 10.1 Hz, 2F), -107.4 (q, J = 10.1 Hz, 1.5F, *E*), -125.0 (s, 2F), -125.3 (s, 1.5F, *E*); HRMS (EI) (*m/z*): $[M]^+$ calcd for $C_{25}H_{17}F_7S_2$: 514.0654, found: 514.0653.

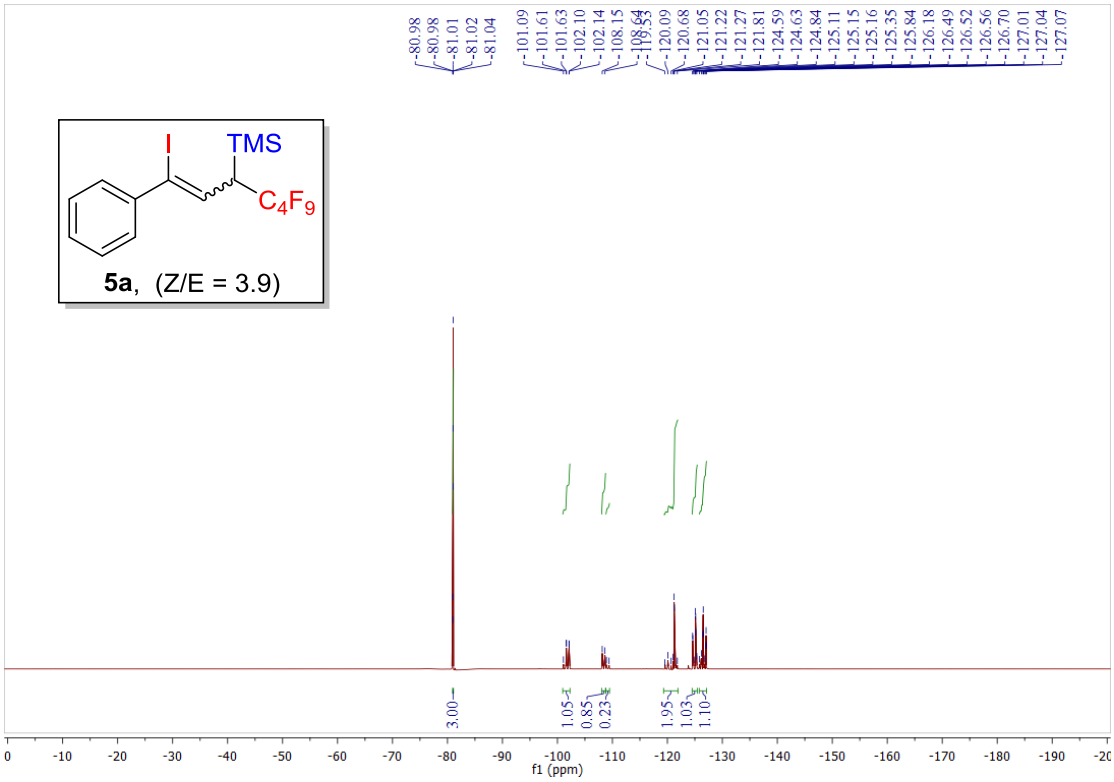
5. References

[1]. G.-B. Roh, N. Iqbal, E. J. Cho, *Chin. J. Chem*. **2016**, *34*, 459-464.

6. ^{1}H, ^{13}C and ^{19}F NMR spectra



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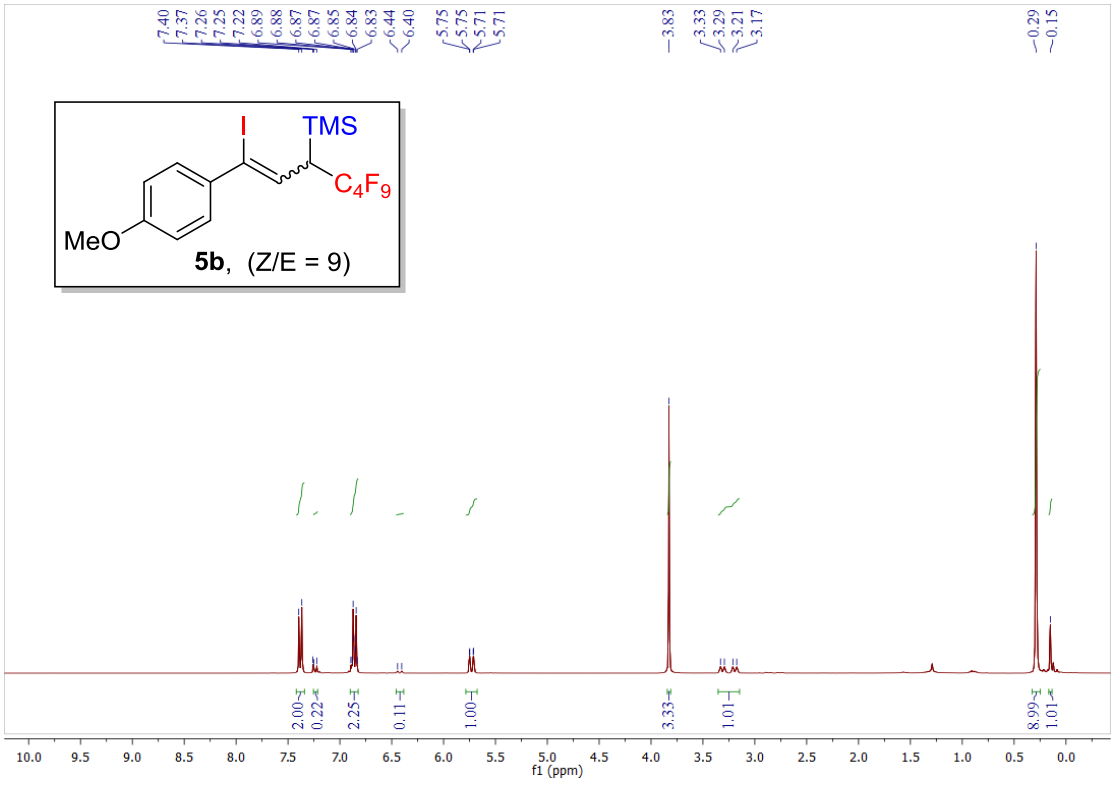
C_4F_9
5a, (Z/E = 3.9)
f1 (ppm)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MeO
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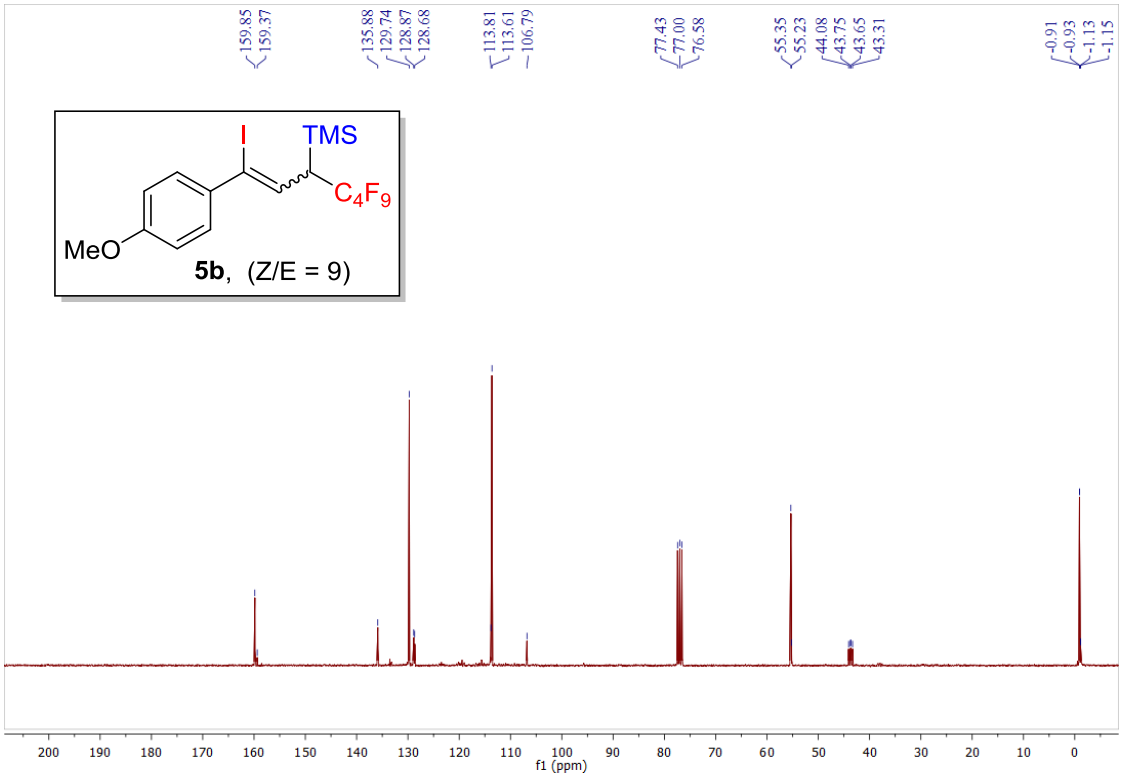
f1 (ppm)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113.81
113.61
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77.43
77.00
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55.23
44.08
43.75
43.65
43.31
-0.91
-0.93
-1.13
-1.15
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MeO
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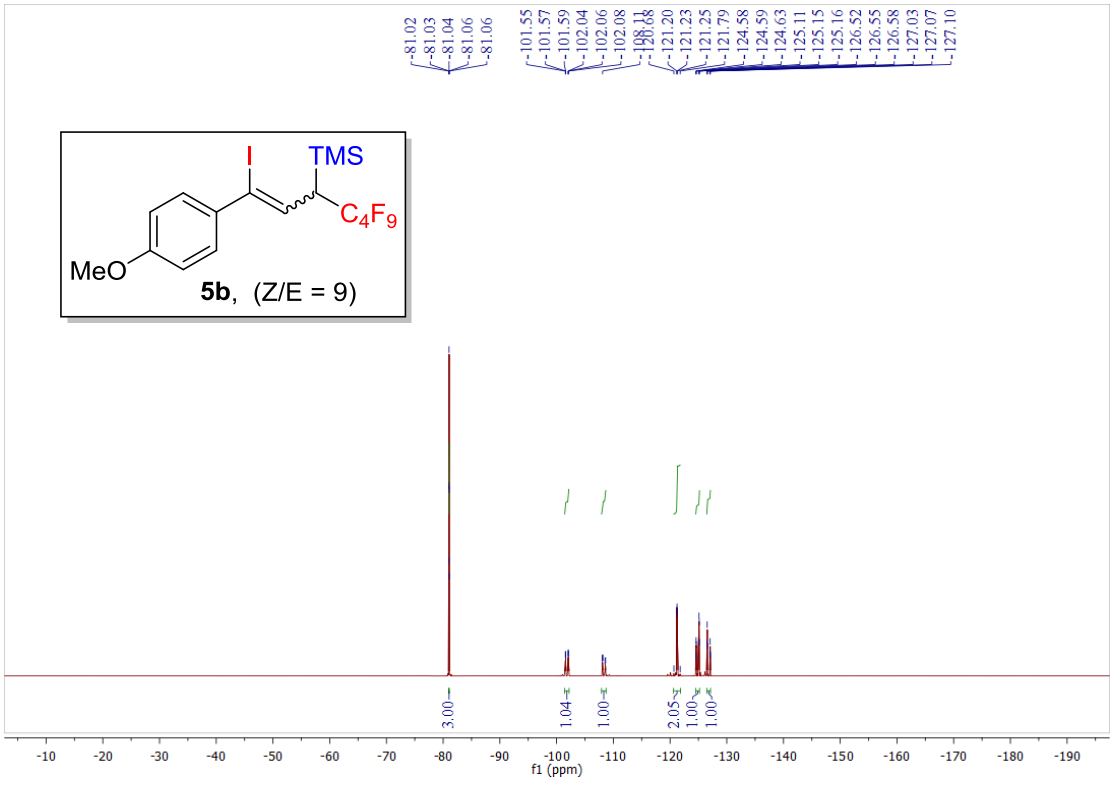
f1 (ppm)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-124.59
-124.63
-125.11
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-126.55
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-127.03
-127.07
-127.10
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TMS
C4F9
MeO
5b, (Z/E = 9)
3.00
1.04
1.00
2.05
1.00
1.00
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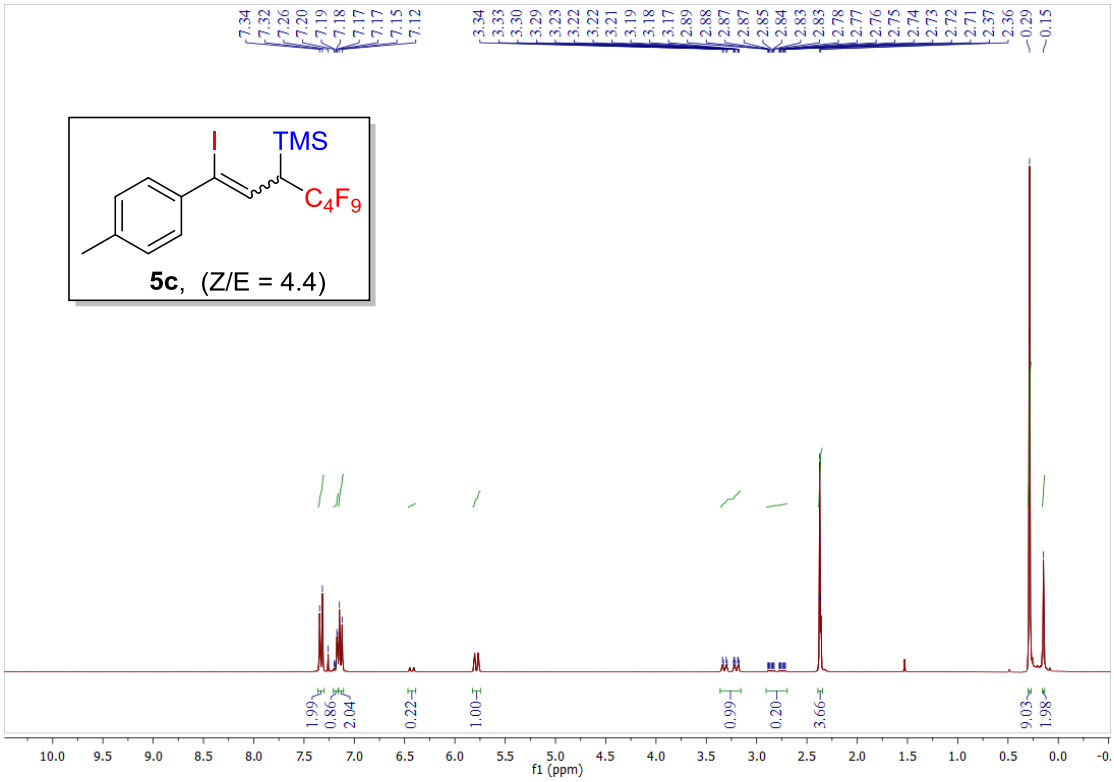
f1 (ppm)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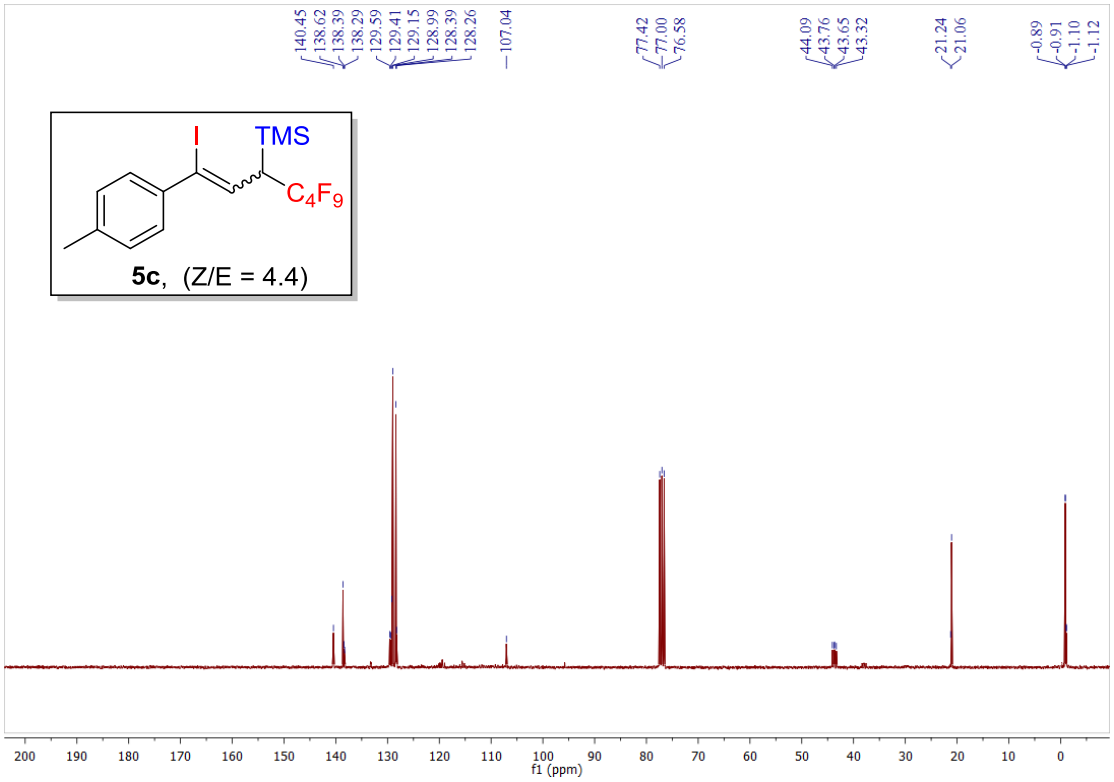
f1 (ppm)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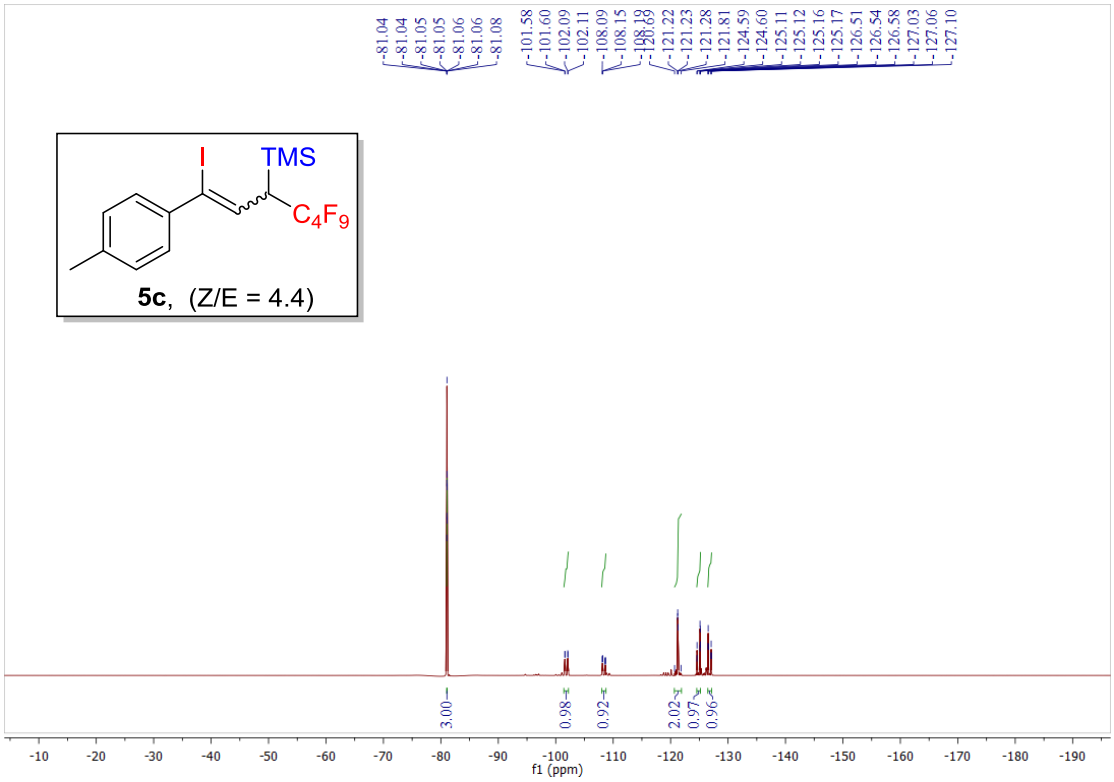
f1 (ppm)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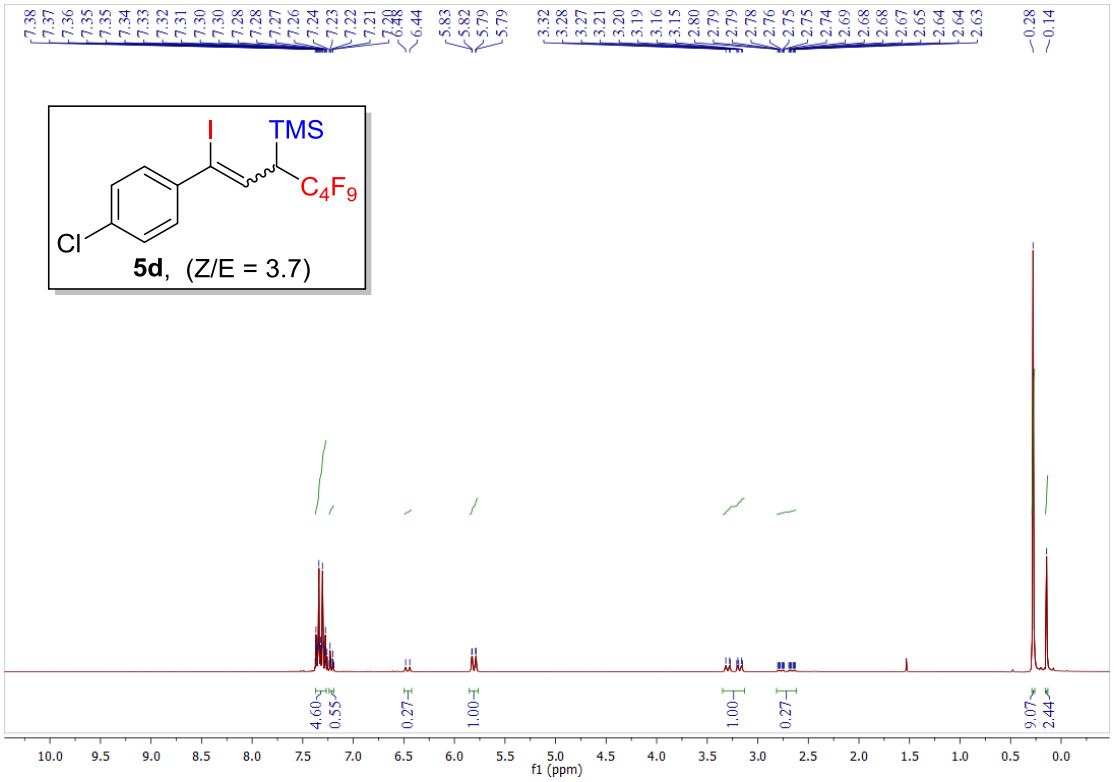
f1 (ppm)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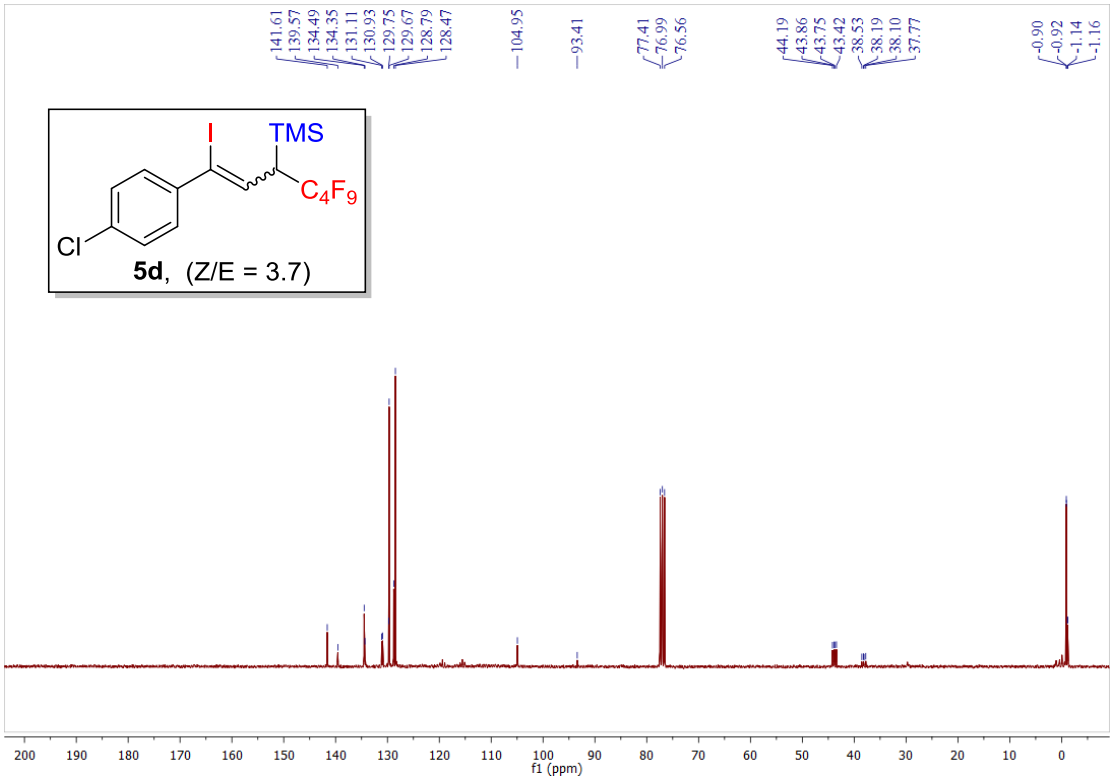
TMS
C_4F_9
Cl
5d, (Z/E = 3.7)
f1 (ppm)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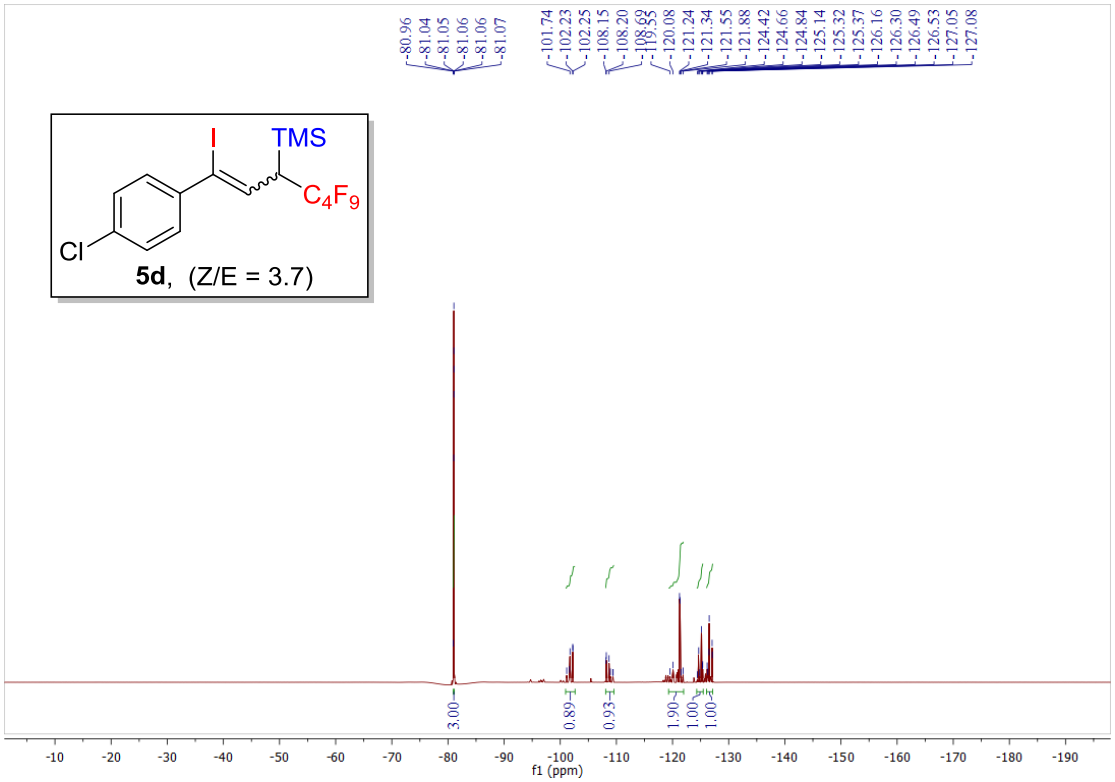
TMS
C_4F_9
Cl
5d, (Z/E = 3.7)
f1 (ppm)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TMS
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Cl
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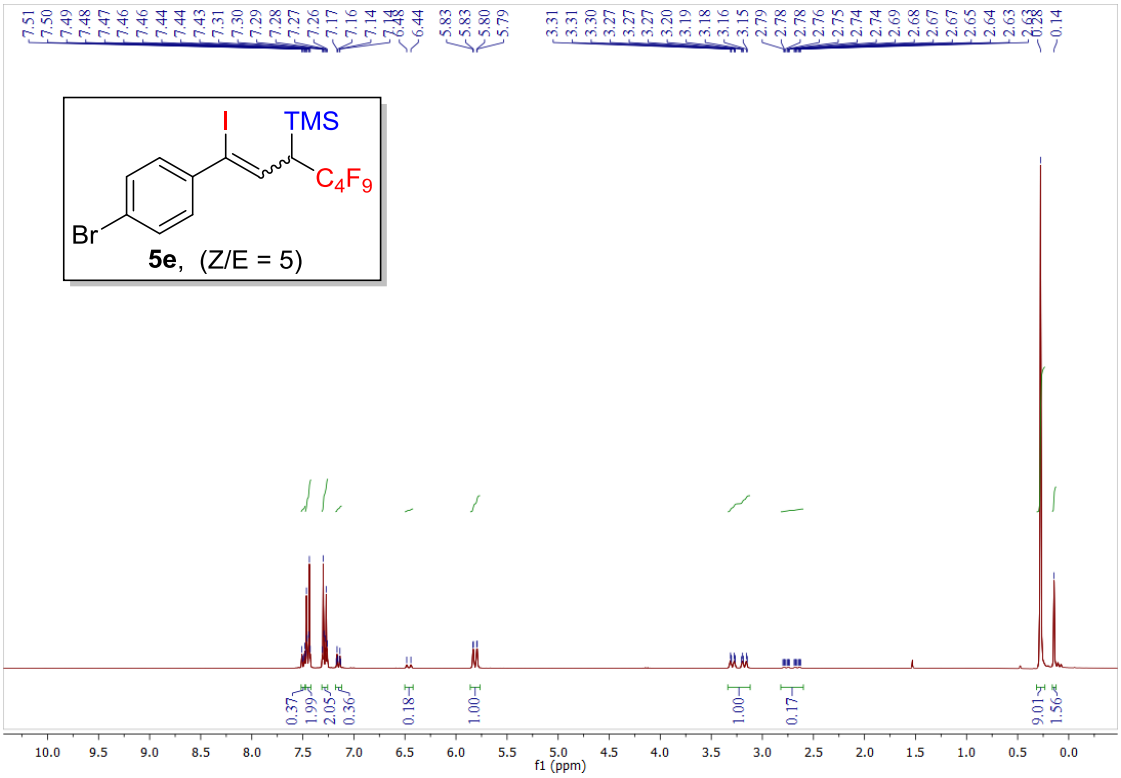
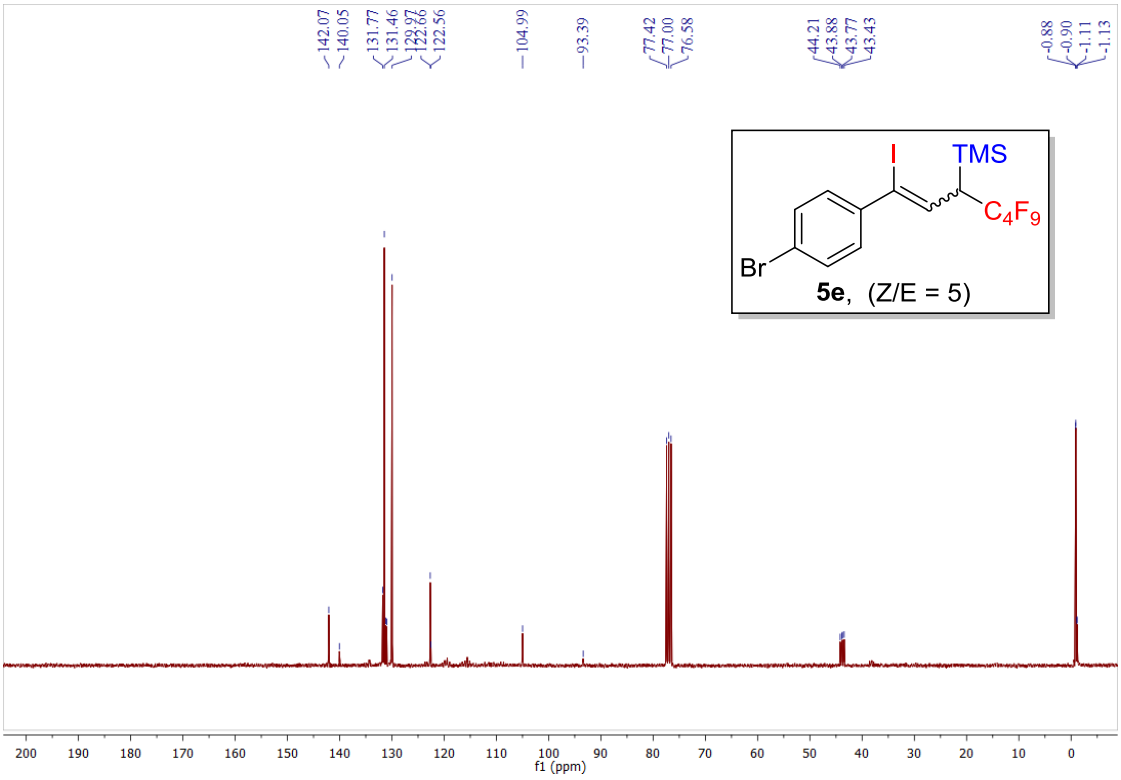
1.00
1.00
f1 (ppm)


I
TMS
C_4F_9
Br
5e, (Z/E = 5)
f1 (ppm)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Br
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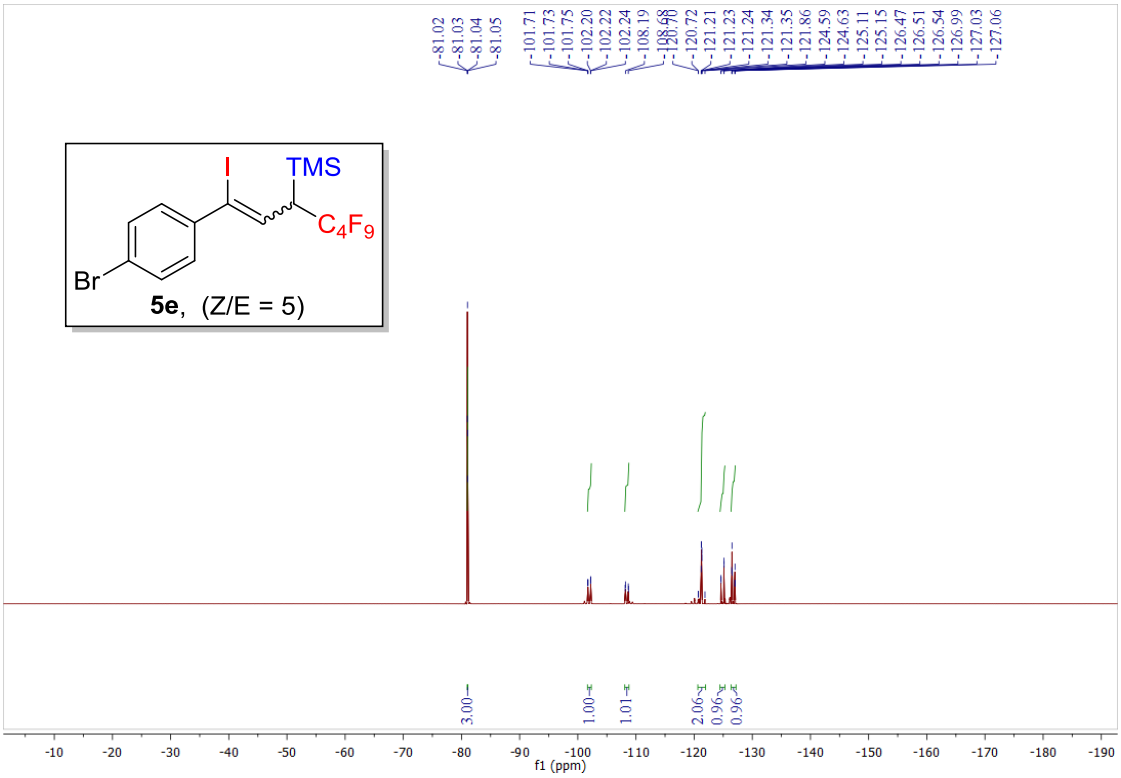
f1 (ppm)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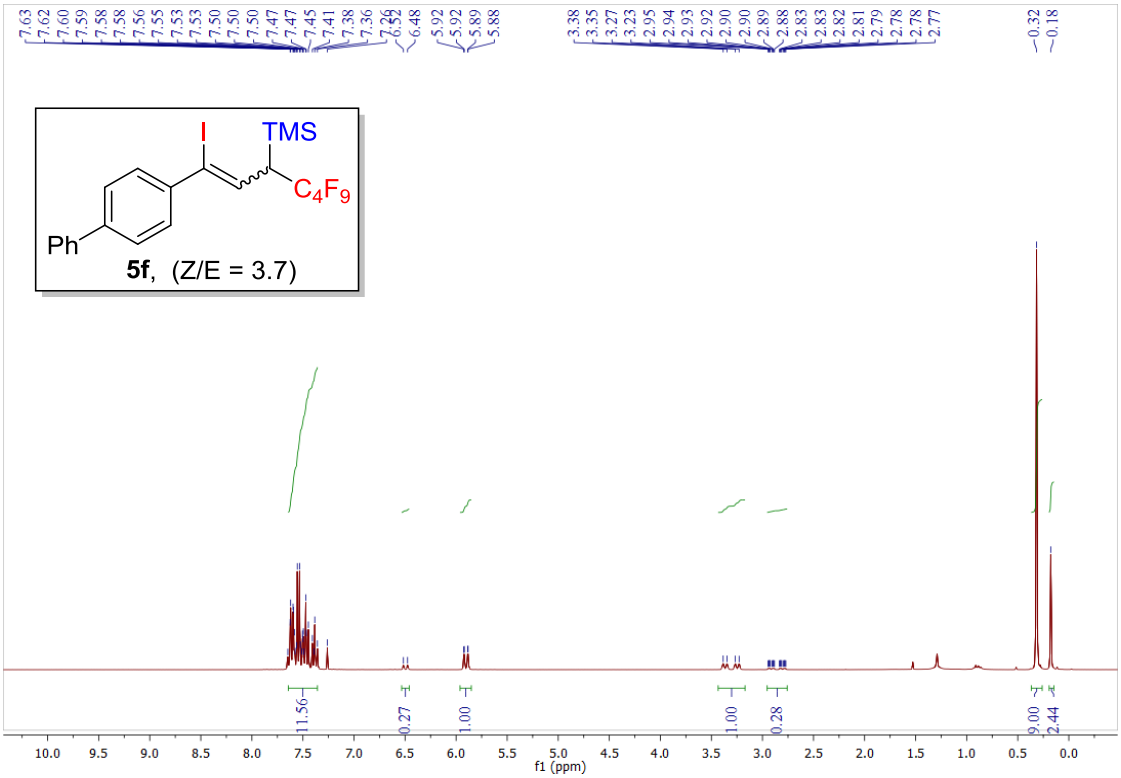
Br
5e, (Z/E = 5)
f1 (ppm)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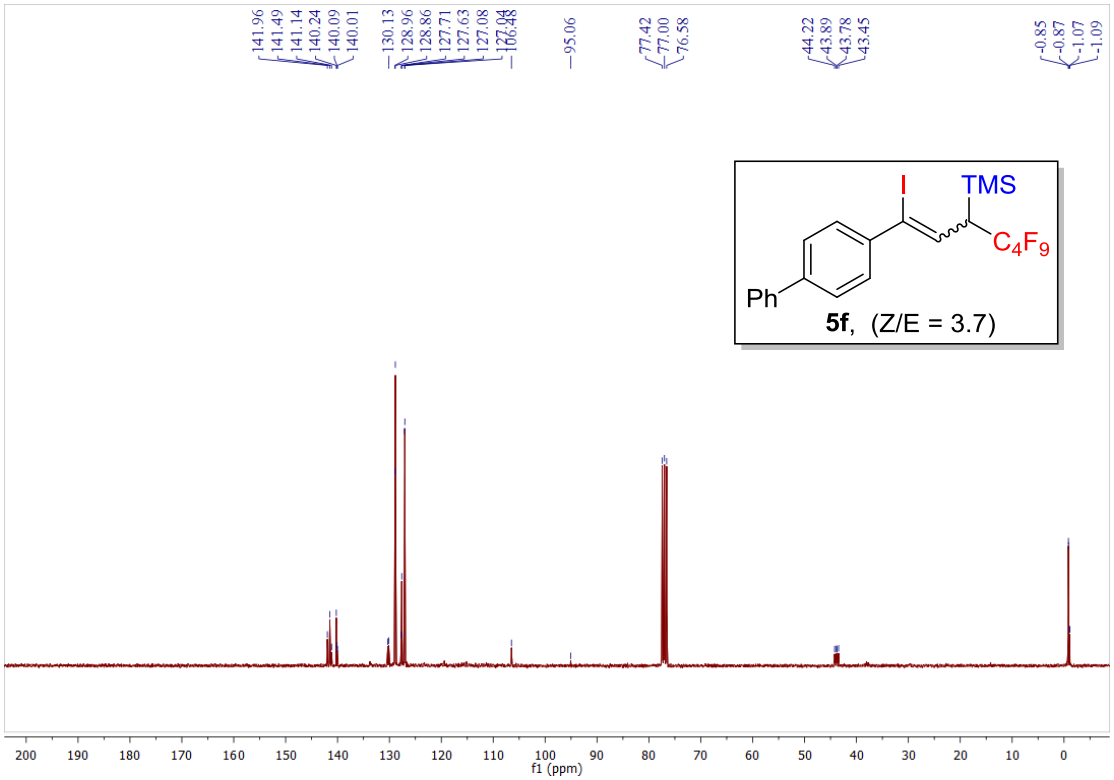
TMS
C_4F_9
Ph
5f, (Z/E = 3.7)
f1 (ppm)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140.09
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128.86
127.71
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127.04
126.48
95.06
77.42
77.00
76.58
44.22
43.89
43.78
43.45
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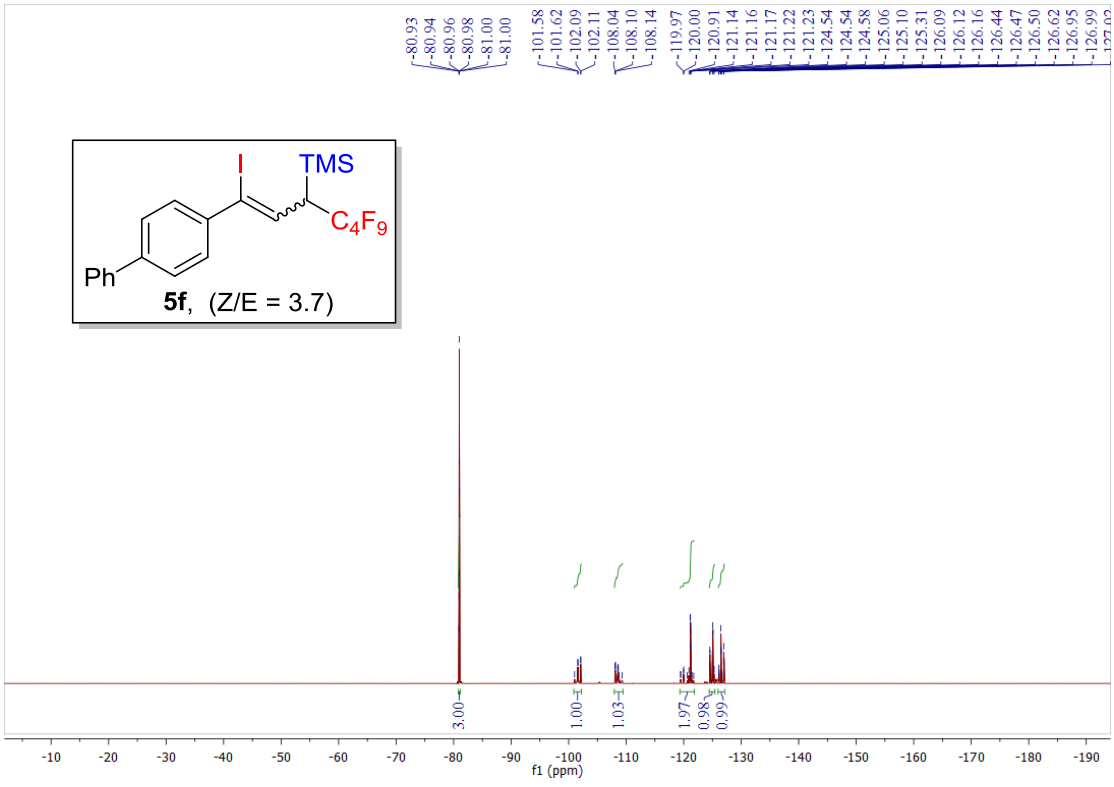
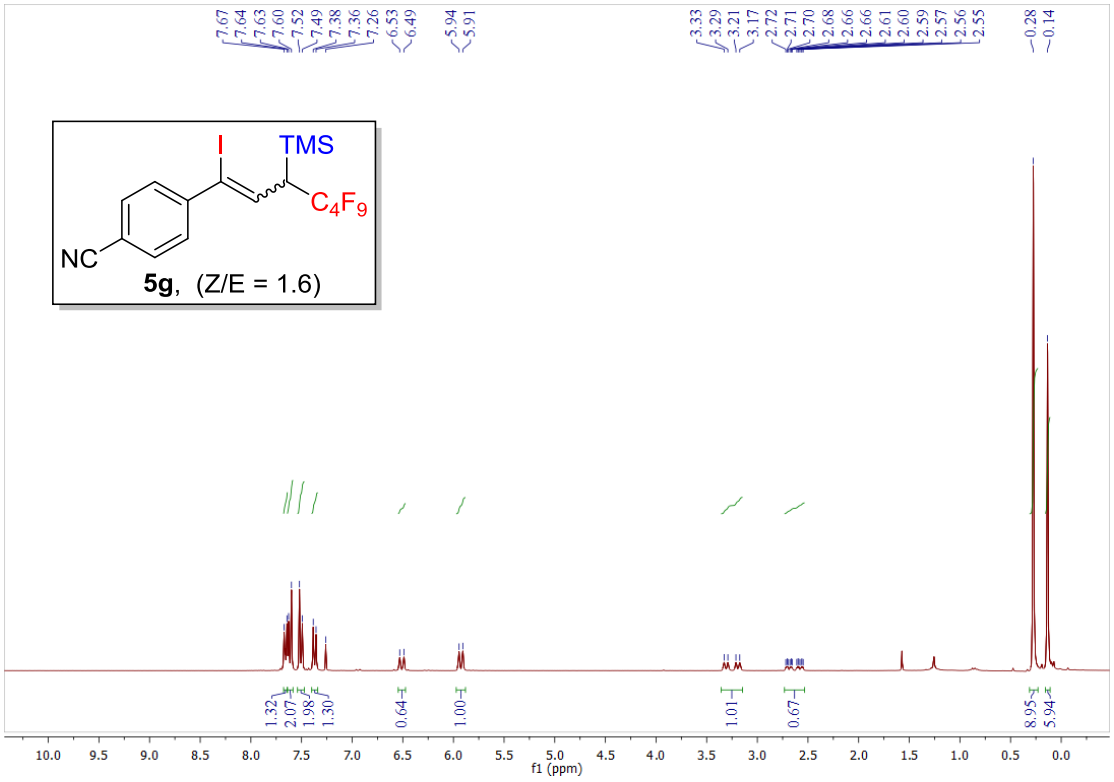
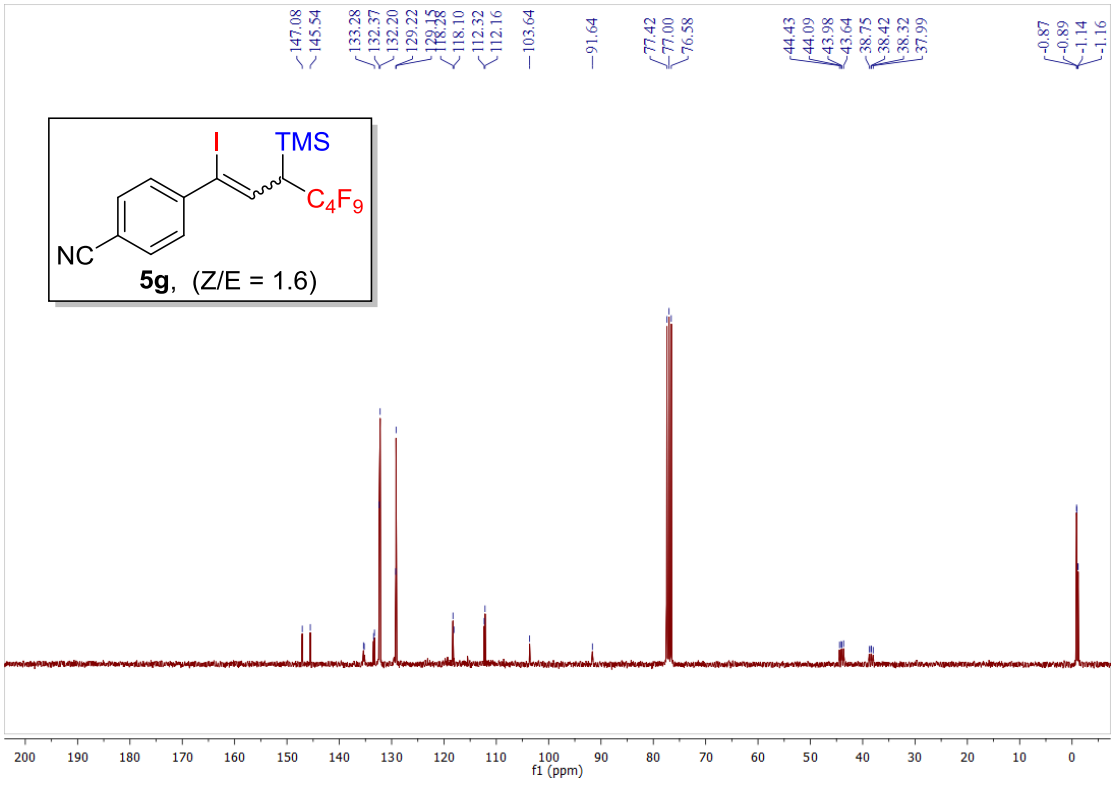
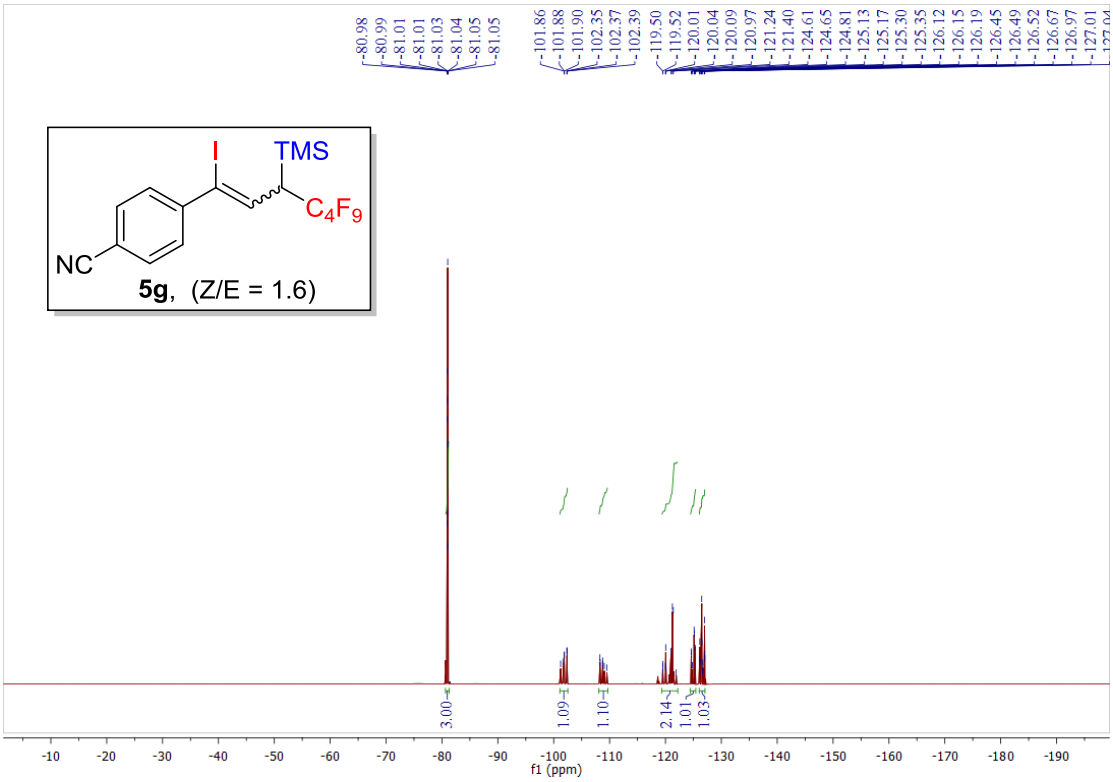
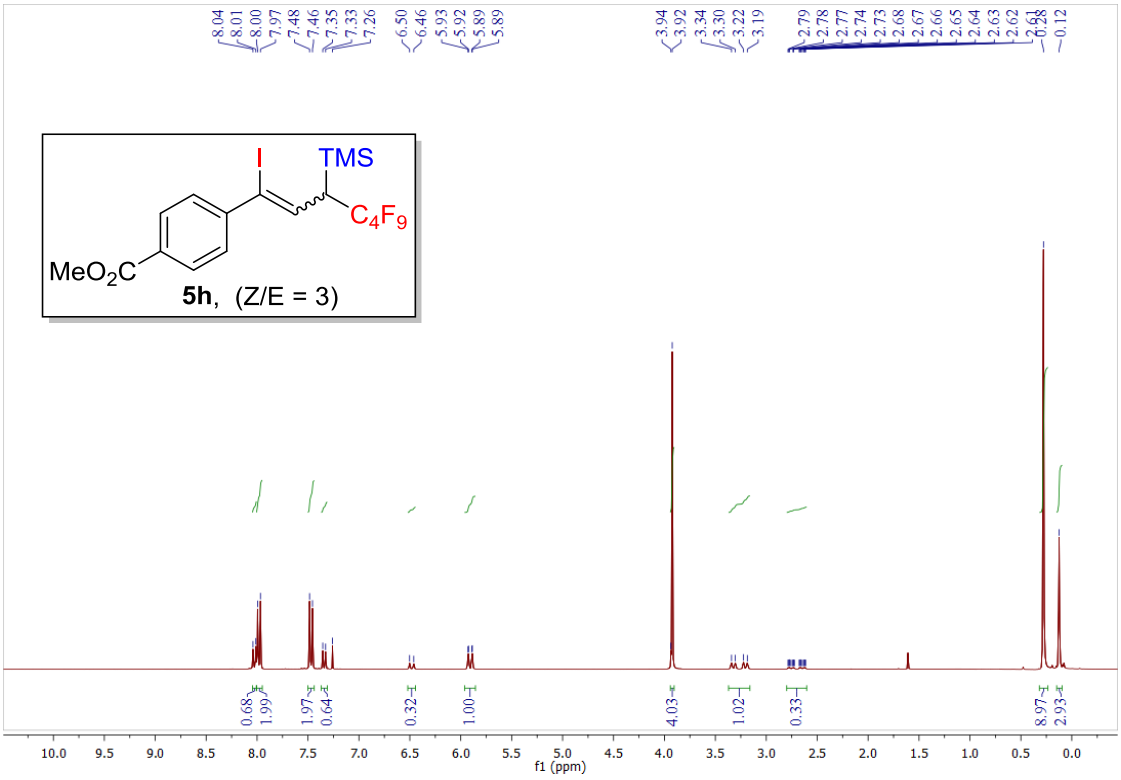
TMS
C4F9
Ph
5f, (Z/E = 3.7)
f1 (ppm)

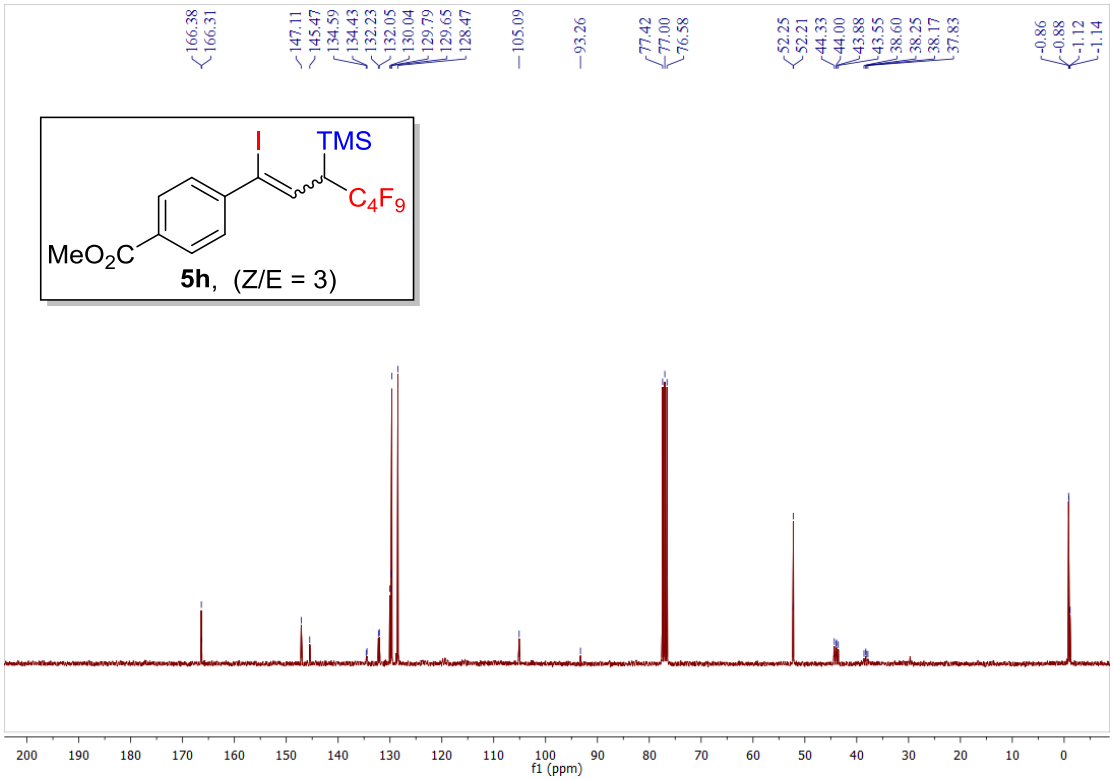

-80.93
-80.94
-80.96
-80.98
-81.00
-81.00
-101.58
-101.62
-102.09
-102.11
-108.04
-108.10
-108.14
-119.97
-120.00
-120.91
-121.14
-121.16
-121.17
-121.22
-121.23
-124.54
-124.54
-124.58
-125.06
-125.10
-125.31
-126.09
-126.12
-126.16
-126.44
-126.47
-126.50
-126.62
-126.95
-126.99
3.00
1.00
1.03
1.97
0.98
0.99
I
TMS
C4F9
Ph
5f, (Z/E = 3.7)
f1 (ppm)

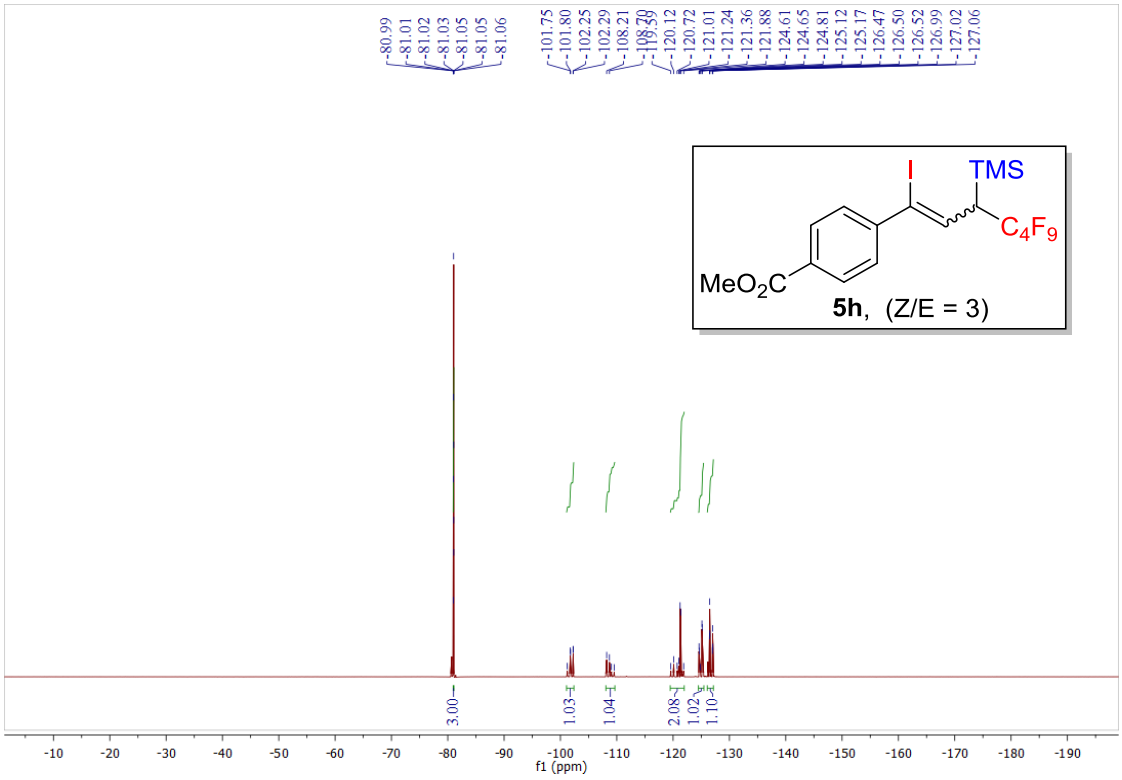

7.67
7.64
7.63
7.60
7.52
7.49
7.38
7.36
7.26
6.53
6.49
5.94
5.91
3.33
3.29
3.21
3.17
2.72
2.71
2.70
2.68
2.66
2.66
2.61
2.60
2.59
2.57
2.56
2.55
0.28
0.14
I
TMS
C4F9
NC
5g, (Z/E = 1.6)
1.32
2.07
1.98
1.30
0.64
1.00
1.01
0.67
8.95
5.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

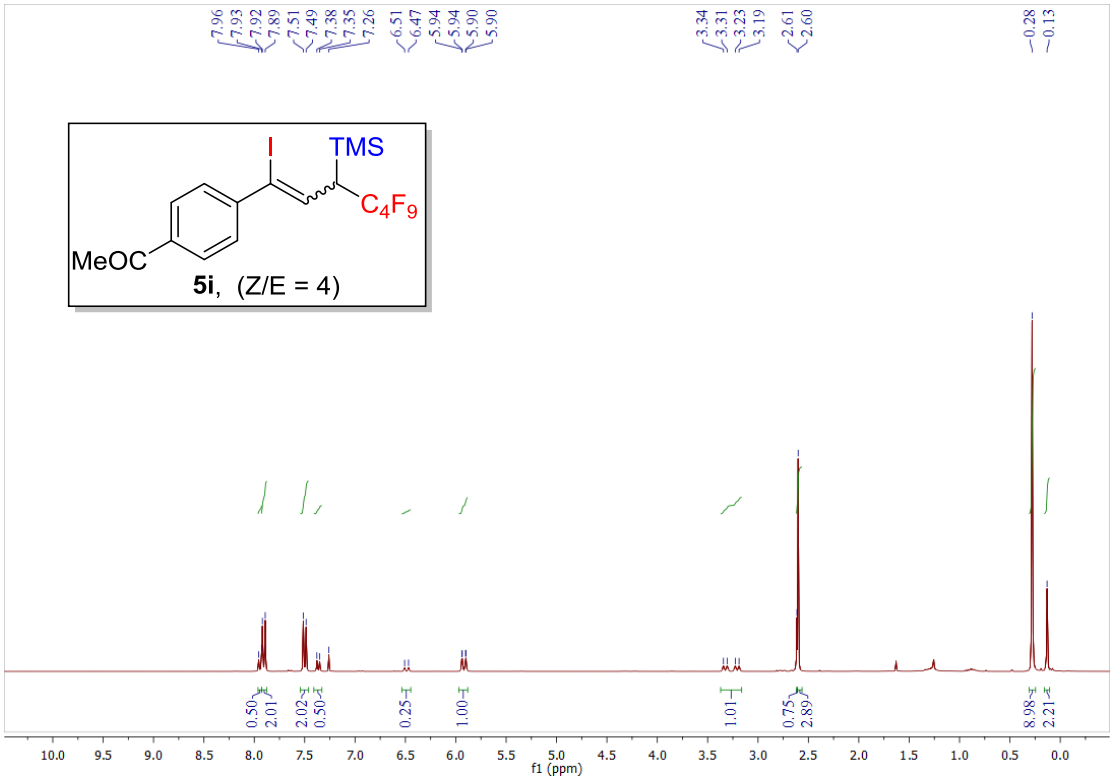

147.08
145.54
133.28
132.37
132.20
129.22
129.15
128.28
118.10
112.32
112.16
103.64
91.64
77.42
77.00
76.58
44.43
44.09
43.98
43.64
38.75
38.42
38.32
37.99
0.87
0.89
1.14
1.16
I
TMS
C4F9
NC
5g, (Z/E = 1.6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

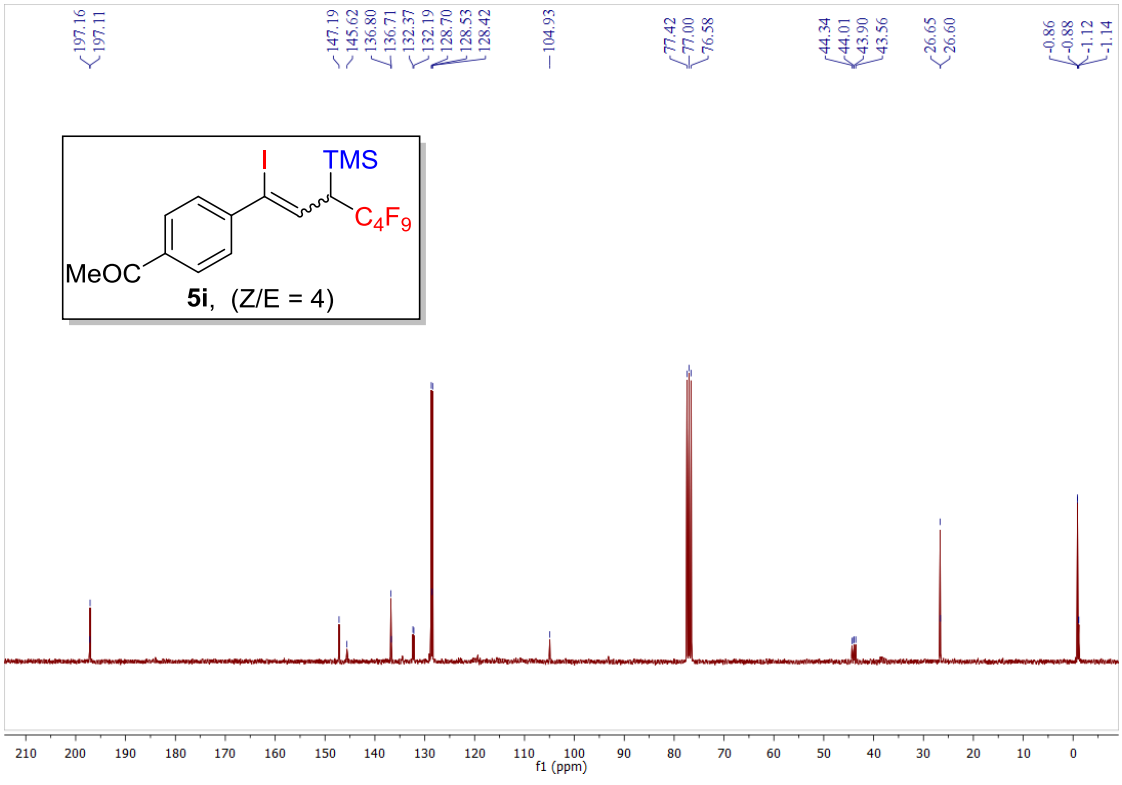

I
TMS
C_4F_9
NC
5g, (Z/E = 1.6)
f1 (ppm)

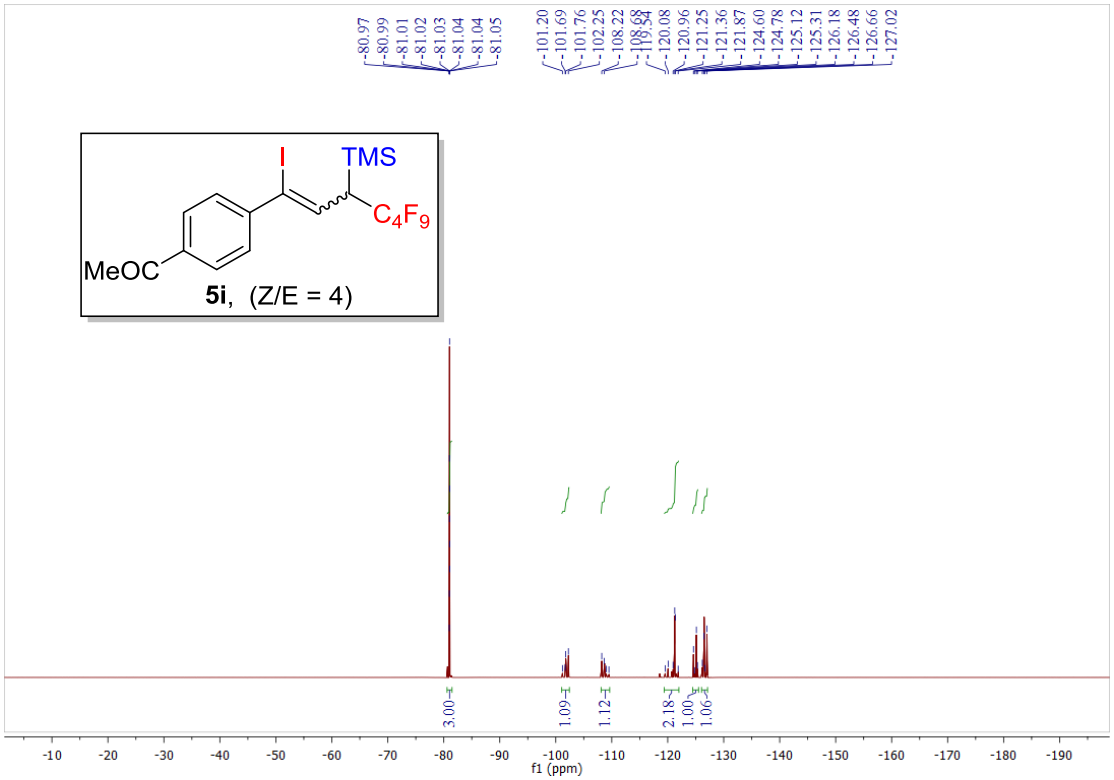

I
TMS
C_4F_9
MeO_2C
5h, (Z/E = 3)
f1 (ppm)

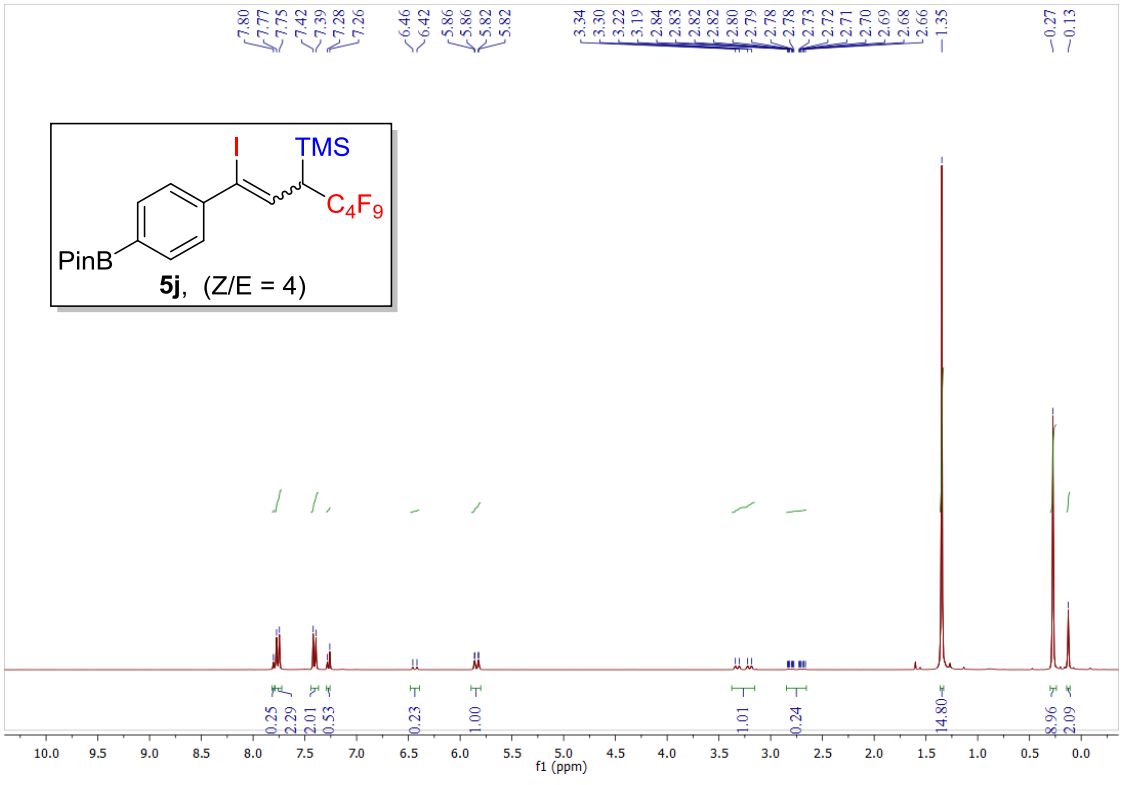

166.38
166.31
147.11
145.47
134.59
134.43
132.23
132.05
130.04
129.79
129.65
128.47
105.09
93.26
77.42
77.00
76.58
52.25
52.21
44.33
44.00
43.88
43.55
38.60
38.25
38.17
37.83
-0.86
-0.88
-1.12
-1.14
I
TMS
C4F9
MeO2C
5h, (Z/E = 3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

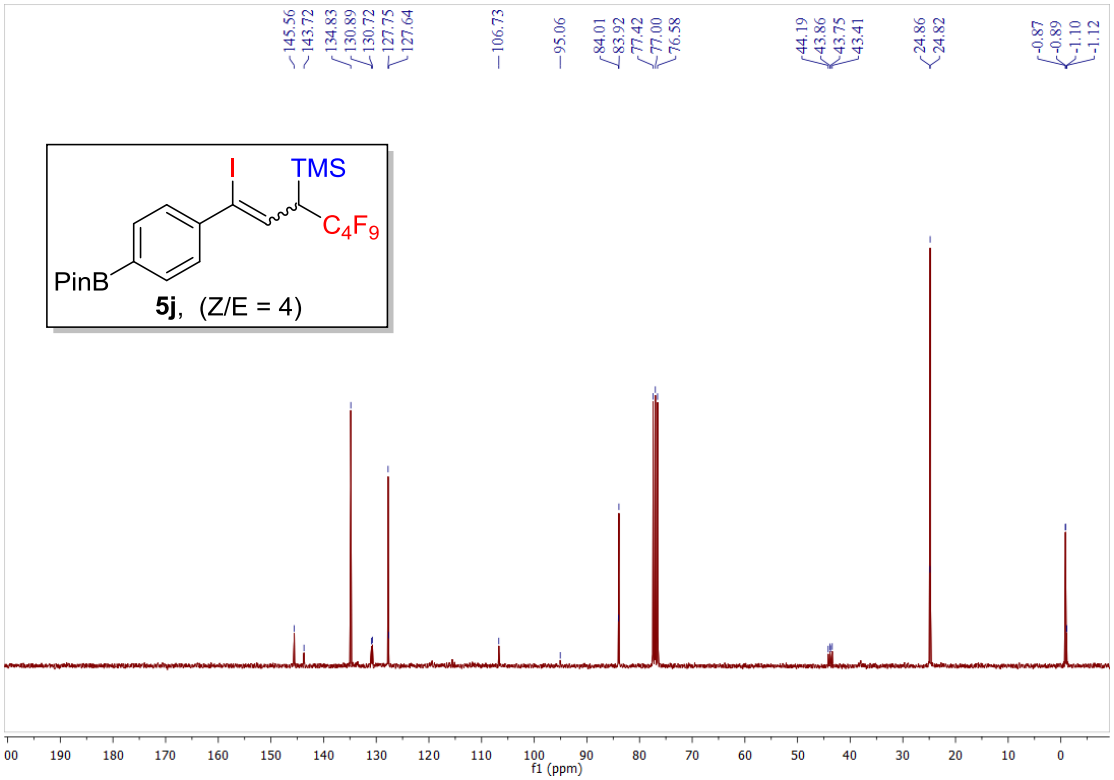

80.99
81.01
81.02
81.03
81.05
81.05
81.06
101.75
101.80
102.25
102.29
108.21
120.12
120.72
121.01
121.24
121.36
121.88
124.61
124.65
124.81
125.12
125.17
126.47
126.50
126.52
126.99
127.02
127.06
I
TMS
C4F9
MeO2C
5h, (Z/E = 3)
3.00
1.03
1.04
2.08
1.02
1.10
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

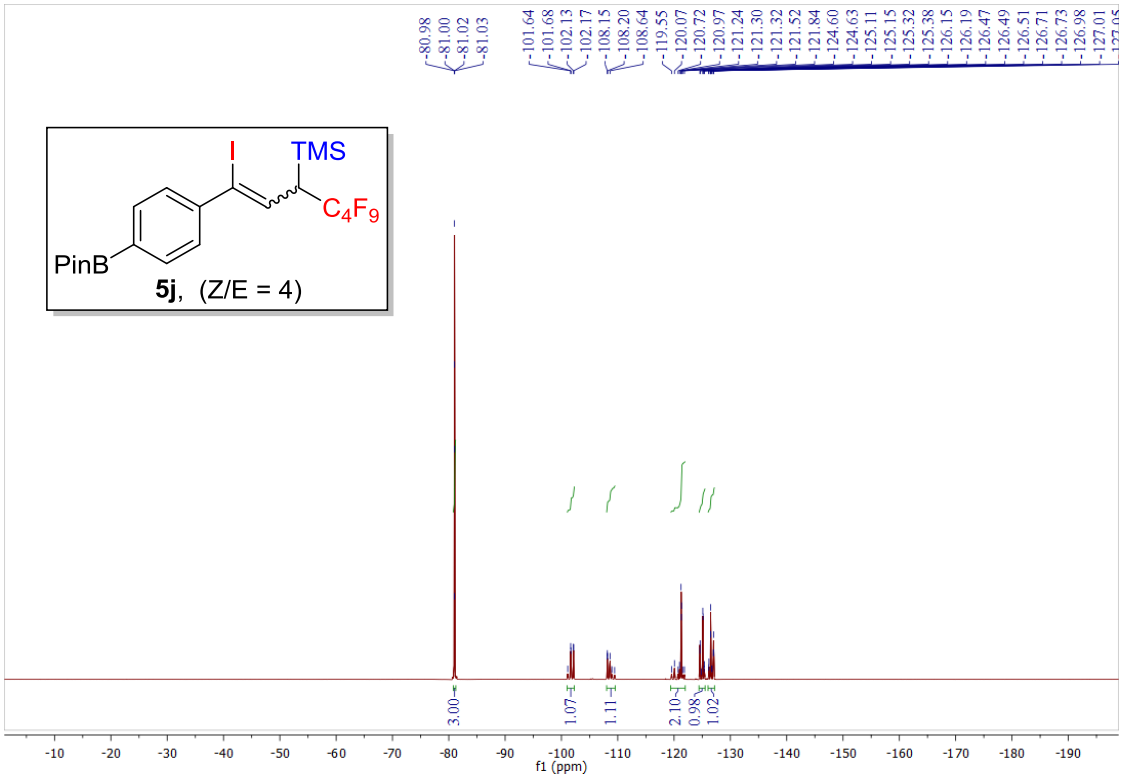

7.96
7.93
7.92
7.89
7.51
7.49
7.38
7.35
7.26
6.51
6.47
5.94
5.94
5.90
5.90
3.34
3.31
3.23
3.19
2.61
2.60
0.28
0.13
I
TMS
C4F9
MeOC
5i, (Z/E = 4)
0.50
2.01
2.02
0.50
0.25
1.00
1.01
0.75
2.89
8.98
2.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

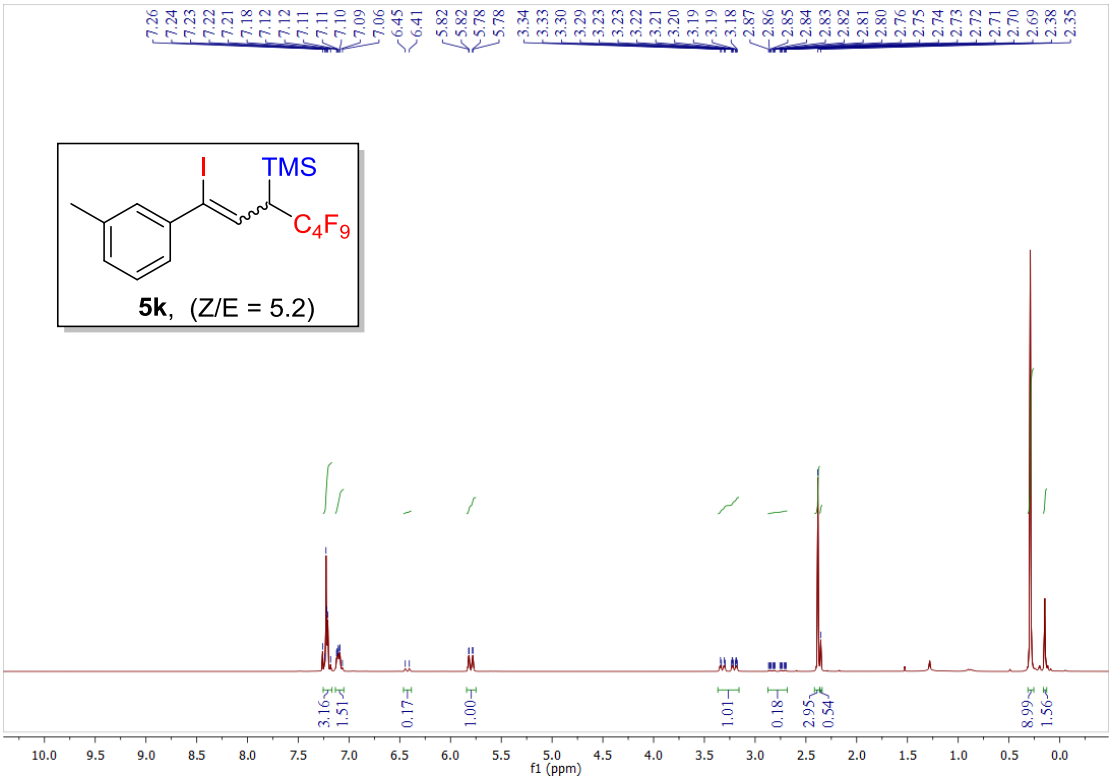

197.16
197.11
147.19
145.62
136.80
136.71
132.37
132.19
128.70
128.53
128.42
104.93
77.42
77.00
76.58
44.34
44.01
43.90
43.56
26.65
26.60
0.86
0.88
1.12
1.14
I
TMS
C4F9
MeOC
5i, (Z/E = 4)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

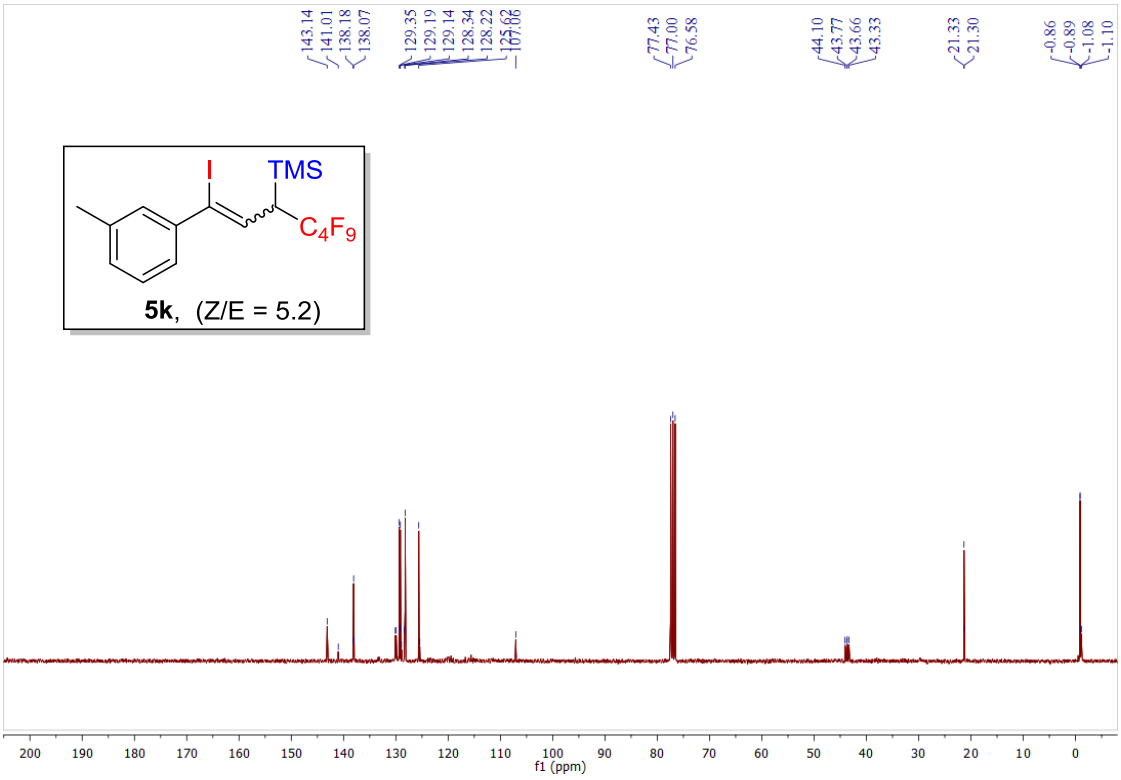

I
TMS
C_4F_9
MeOC
5i, (Z/E = 4)
f1 (ppm)

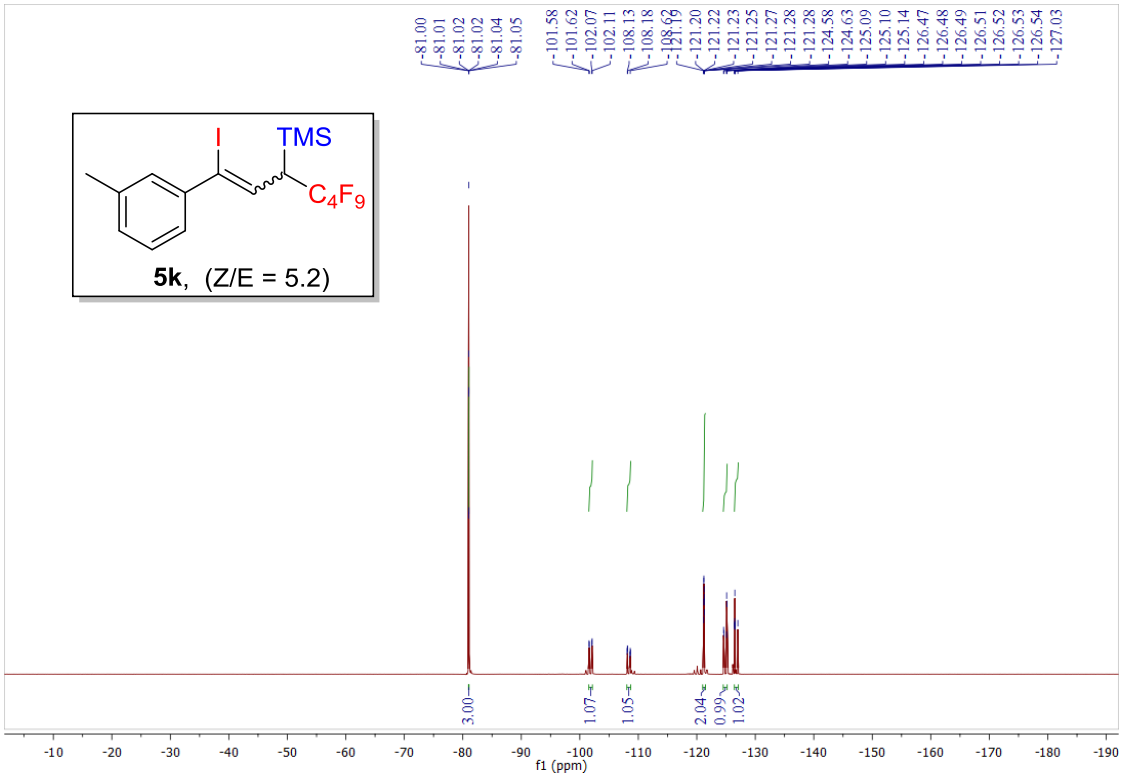

I
TMS
C_4F_9
PinB
5j, (Z/E = 4)
f1 (ppm)

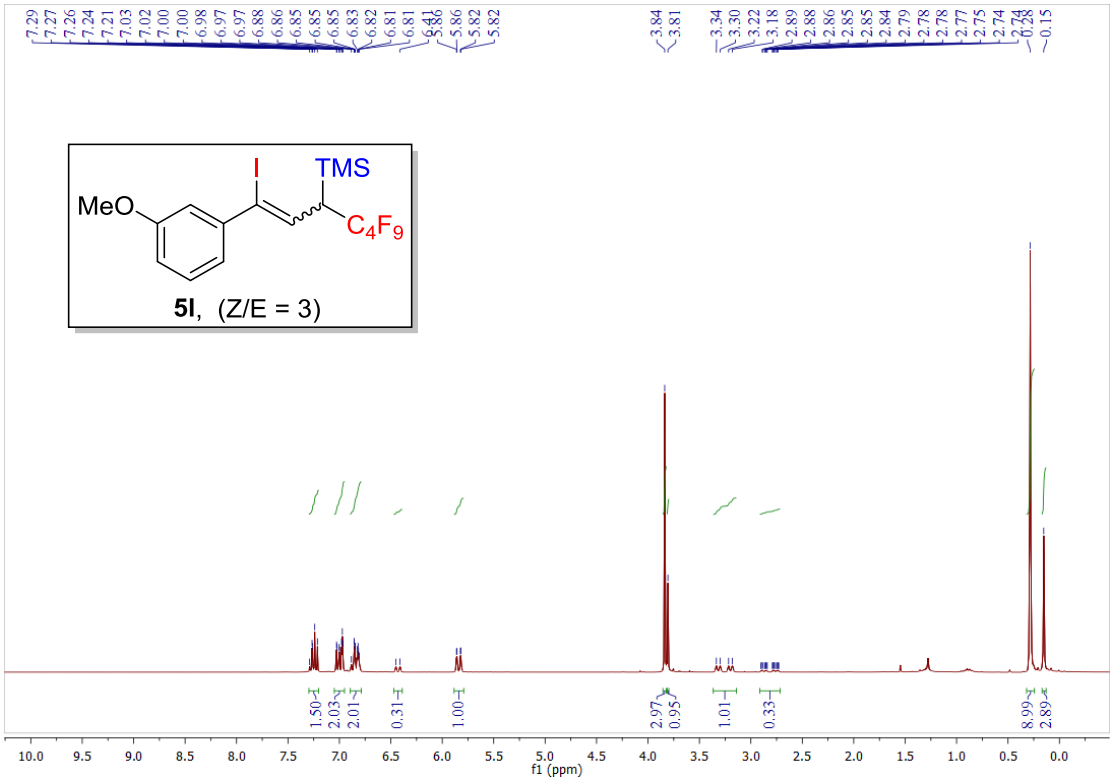

145.56
143.72
134.83
130.89
130.72
127.75
127.64
106.73
95.06
84.01
83.92
77.42
77.00
76.58
44.19
43.86
43.75
43.41
24.86
24.82
-0.87
-0.89
-1.10
-1.12
I
TMS
C4F9
PinB
5j, (Z/E = 4)
f1 (ppm)

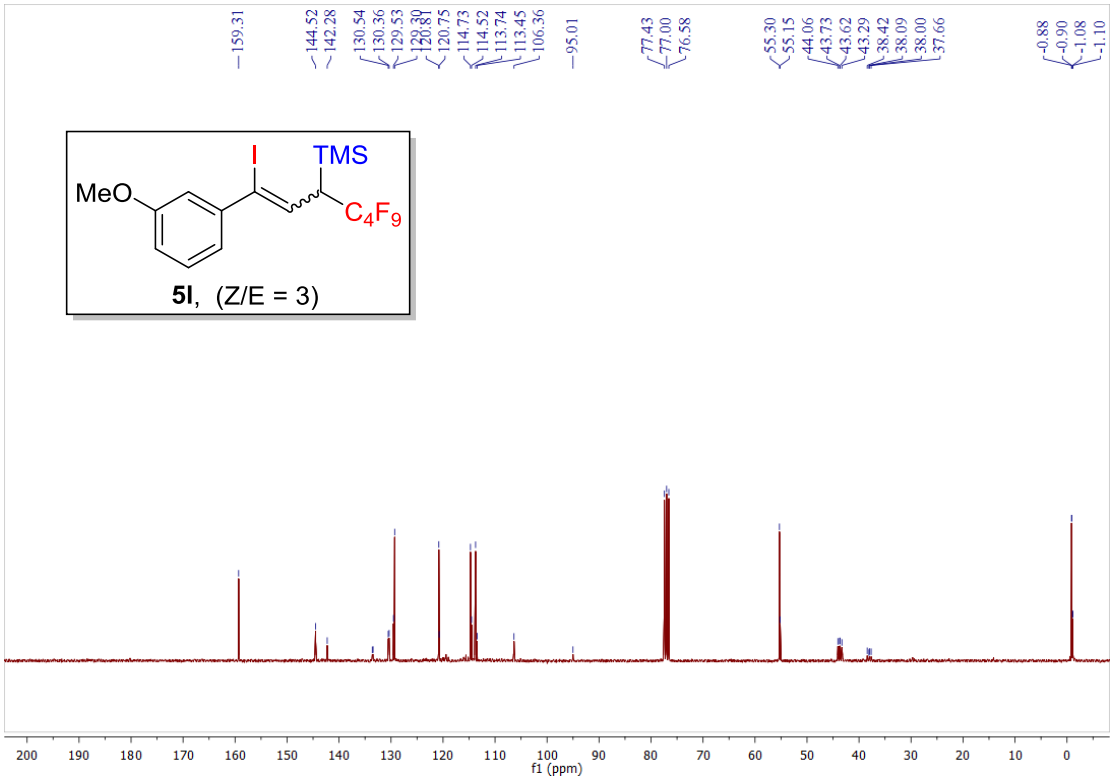

80.98
81.00
81.02
81.03
101.64
101.68
102.13
102.17
108.15
108.20
108.64
119.55
120.07
120.72
120.97
121.24
121.30
121.32
121.52
121.84
124.60
124.63
125.11
125.15
125.32
125.38
126.15
126.19
126.47
126.49
126.51
126.71
126.73
126.98
127.01
3.00
1.07
1.11
2.10
0.98
1.02
I
TMS
C4F9
PinB
5j, (Z/E = 4)
f1 (ppm)

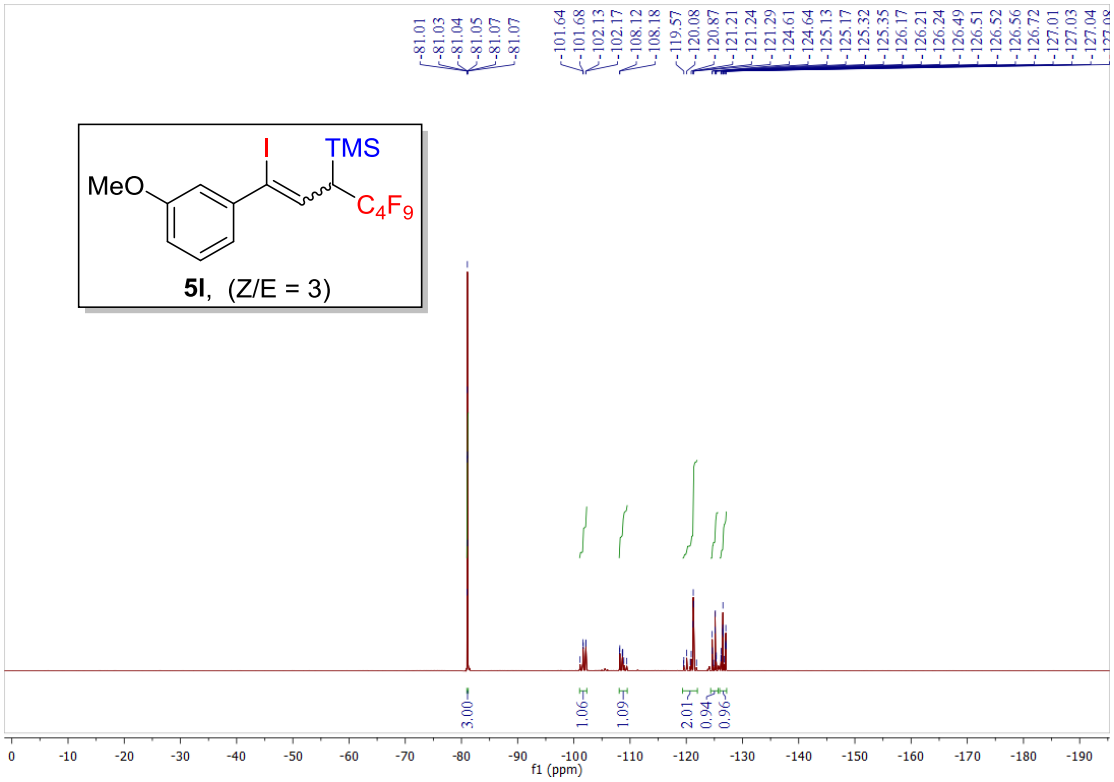

I
TMS
C_4F_9
5k, (Z/E = 5.2)
f1 (ppm)

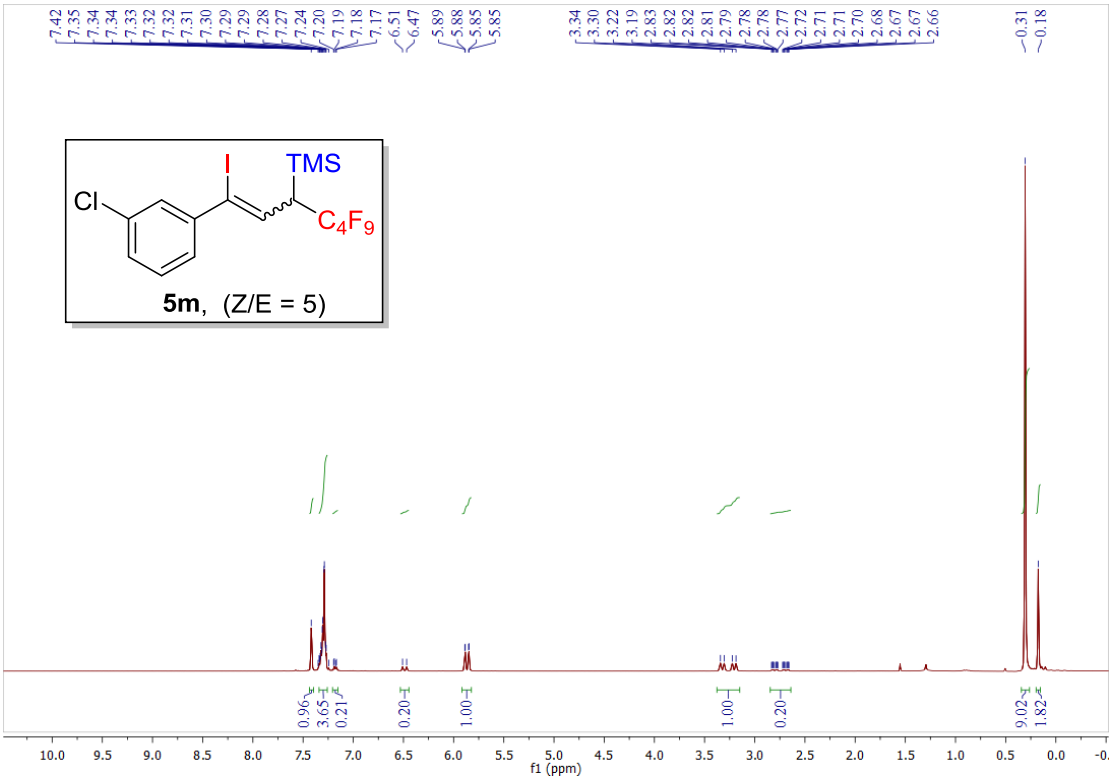

I
TMS
C_4F_9
5k, (Z/E = 5.2)
f1 (ppm)

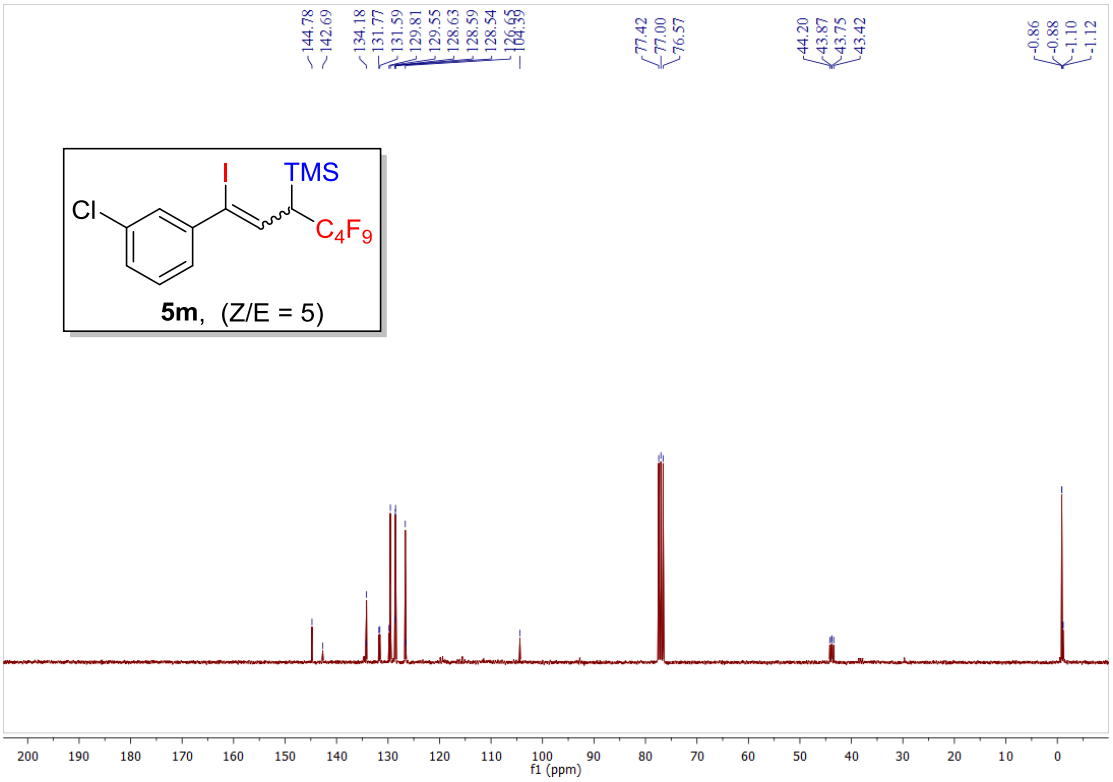

I
TMS
C_4F_9
5k, (Z/E = 5.2)
f1 (ppm)

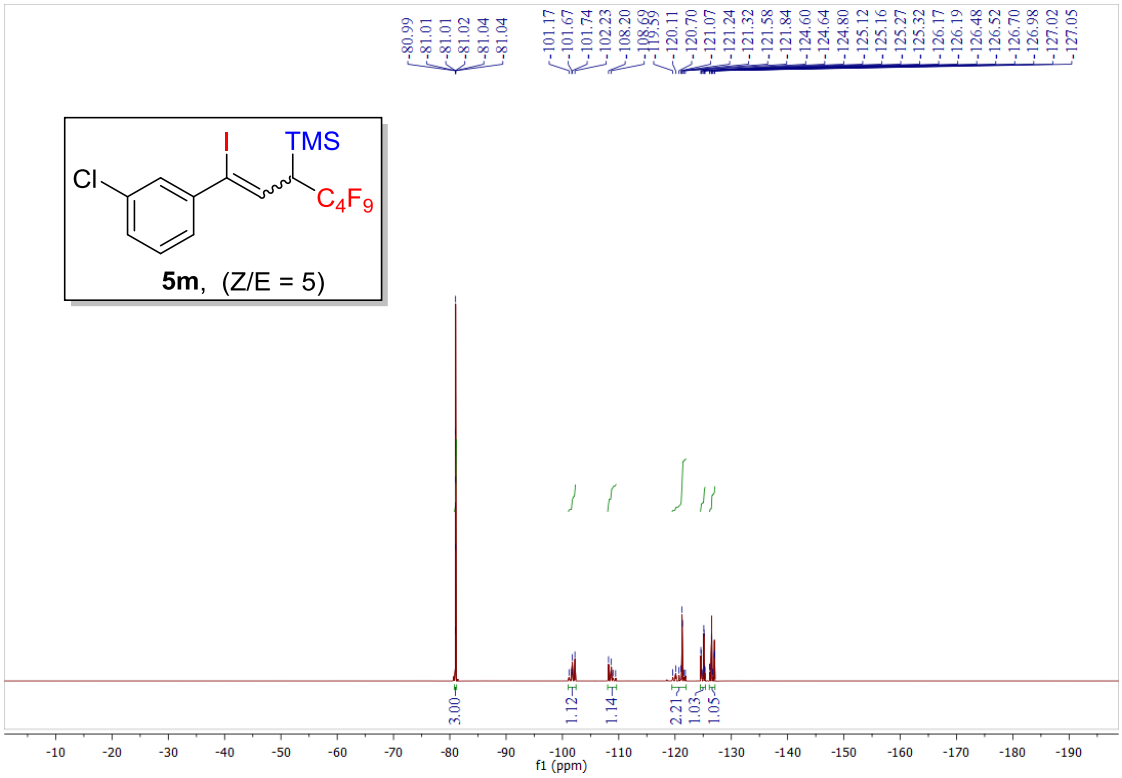

MeO
I
TMS
C_4F_9
5l, (Z/E = 3)
f1 (ppm)

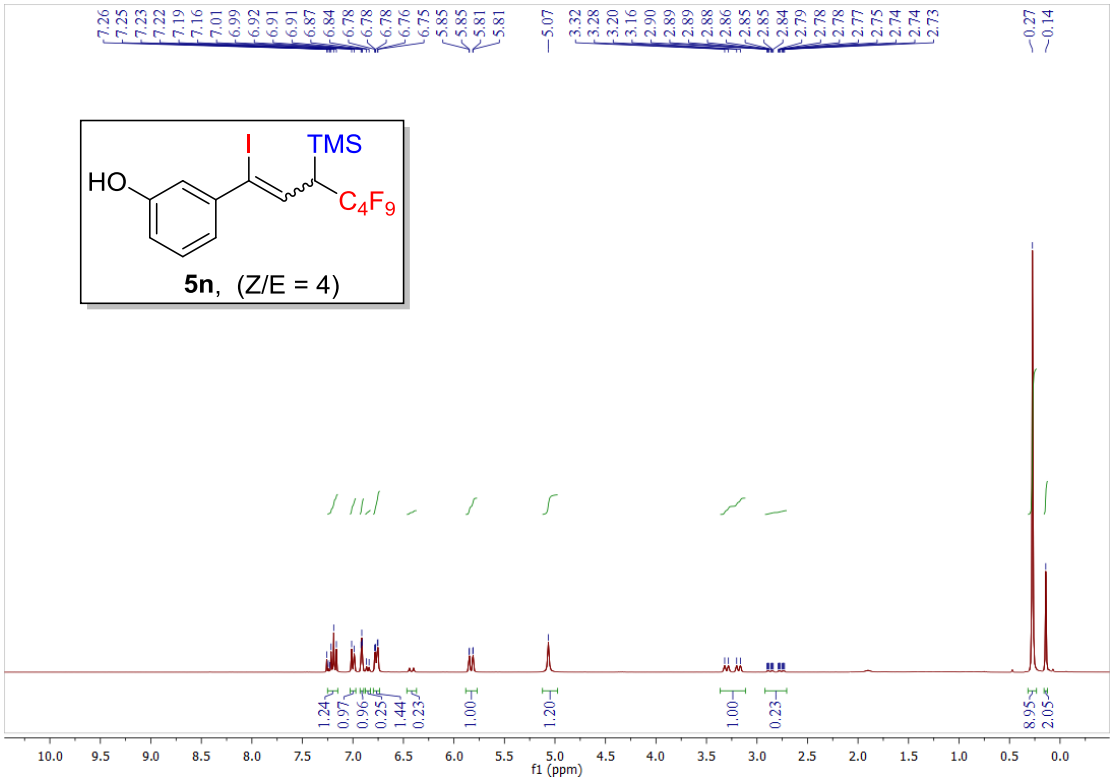

159.31
144.52
142.28
130.54
130.36
129.53
129.30
120.81
120.75
114.73
114.52
113.74
113.45
106.36
95.01
77.43
77.00
76.58
55.30
55.15
44.06
43.73
43.62
43.29
38.42
38.09
38.00
37.66
0.88
0.90
1.08
1.10
I
TMS
MeO
C4F9
5l, (Z/E = 3)
f1 (ppm)

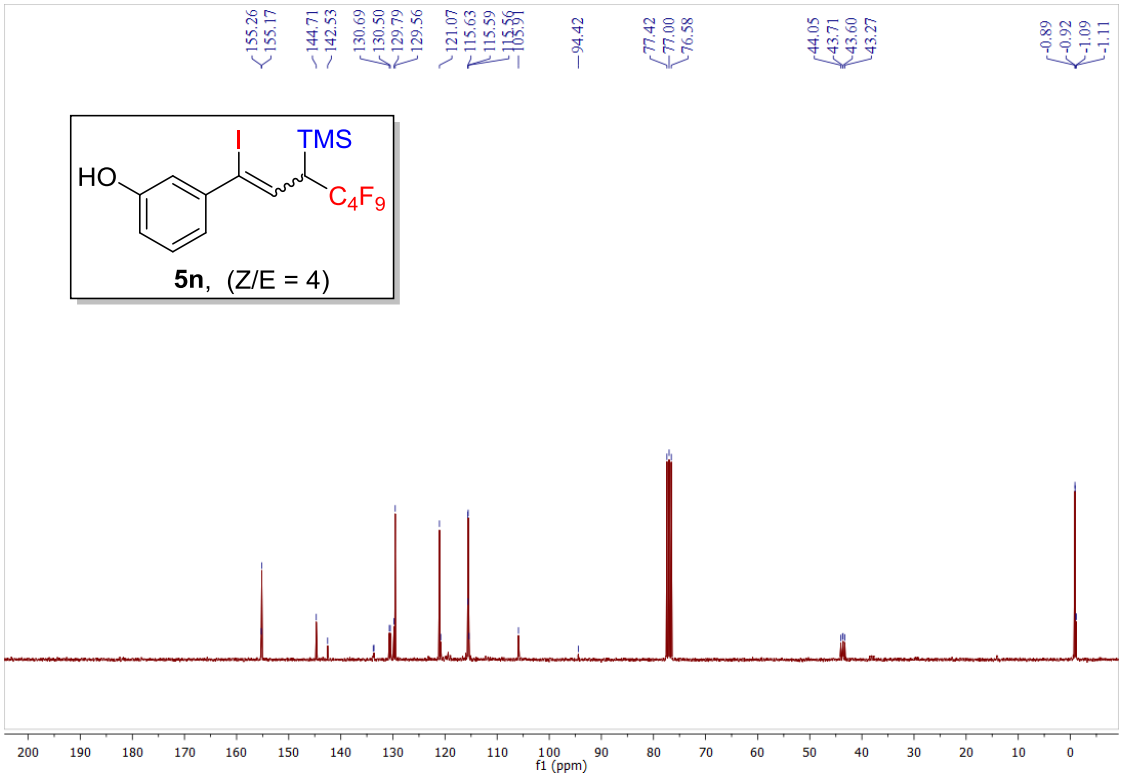

81.01
81.03
81.04
81.05
81.07
81.07
101.64
101.68
102.13
102.17
108.12
108.18
119.57
120.08
120.87
121.21
121.24
121.29
124.61
124.64
125.13
125.17
125.32
125.35
126.17
126.21
126.24
126.49
126.51
126.52
126.56
126.72
127.01
127.03
127.04
3.00
1.06
1.09
2.01
0.94
0.96
I
TMS
MeO
C4F9
5l, (Z/E = 3)
f1 (ppm)

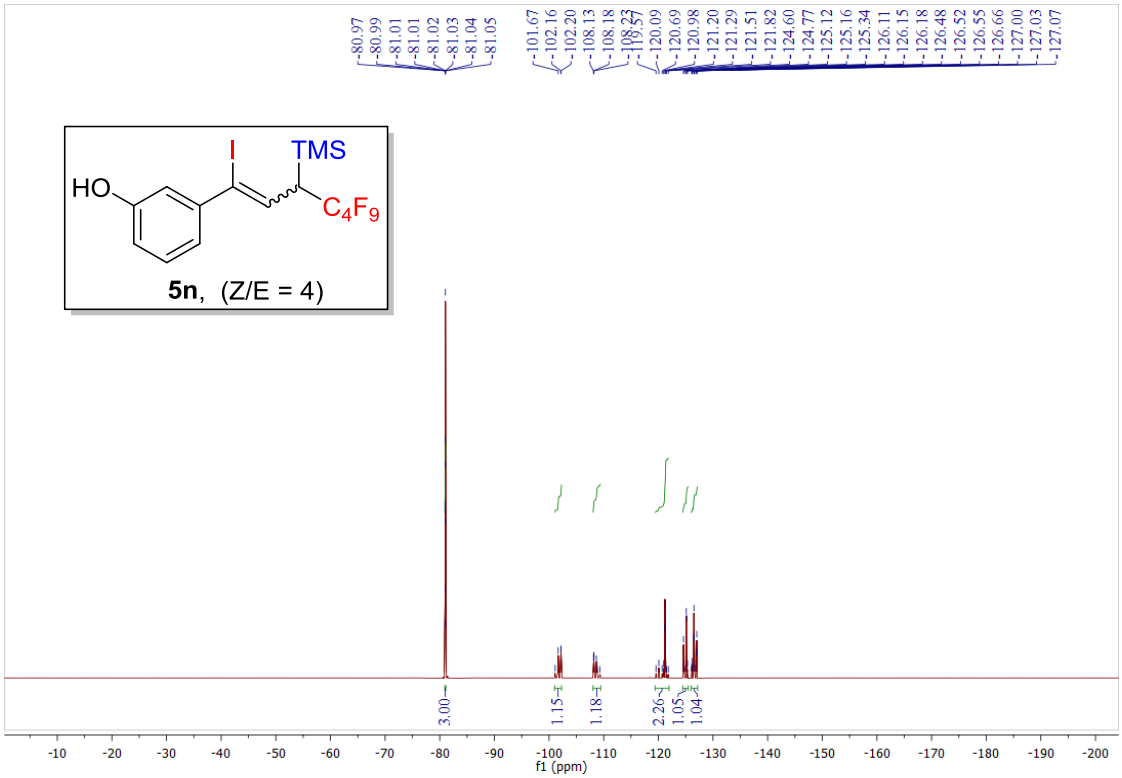

I
TMS
Cl
C_4F_9
5m, (Z/E = 5)
f1 (ppm)

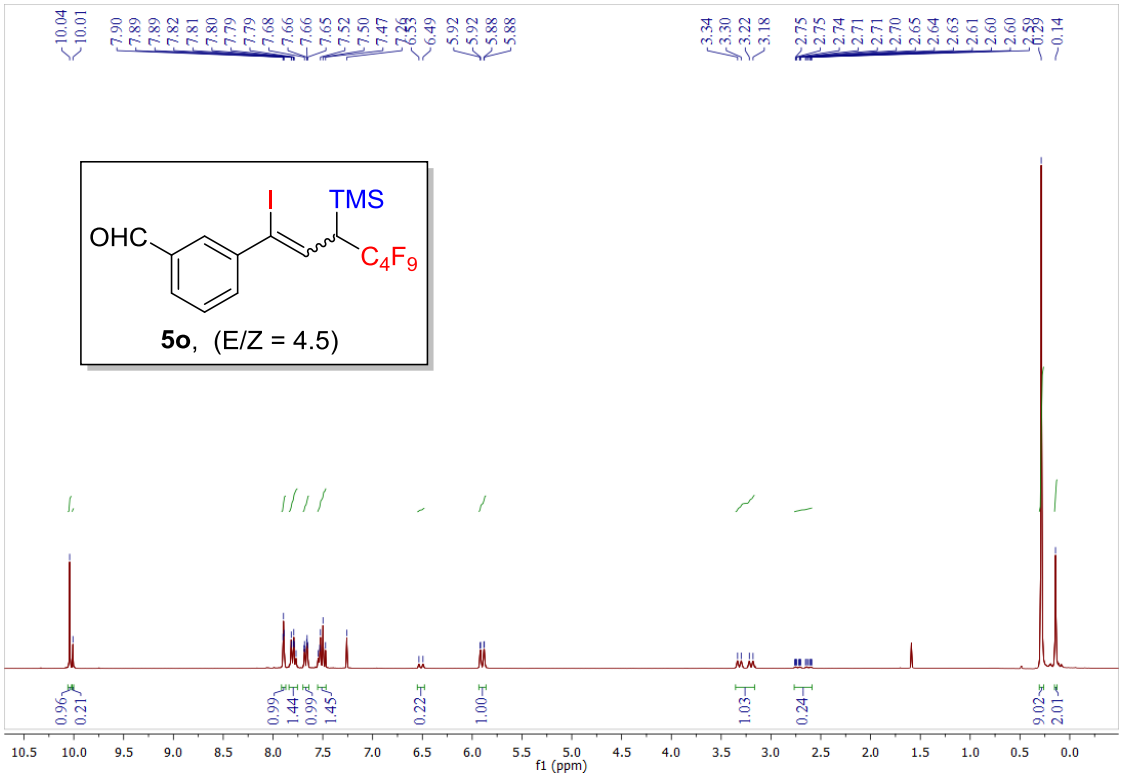

I
TMS
Cl
C_4F_9
5m, (Z/E = 5)
f1 (ppm)

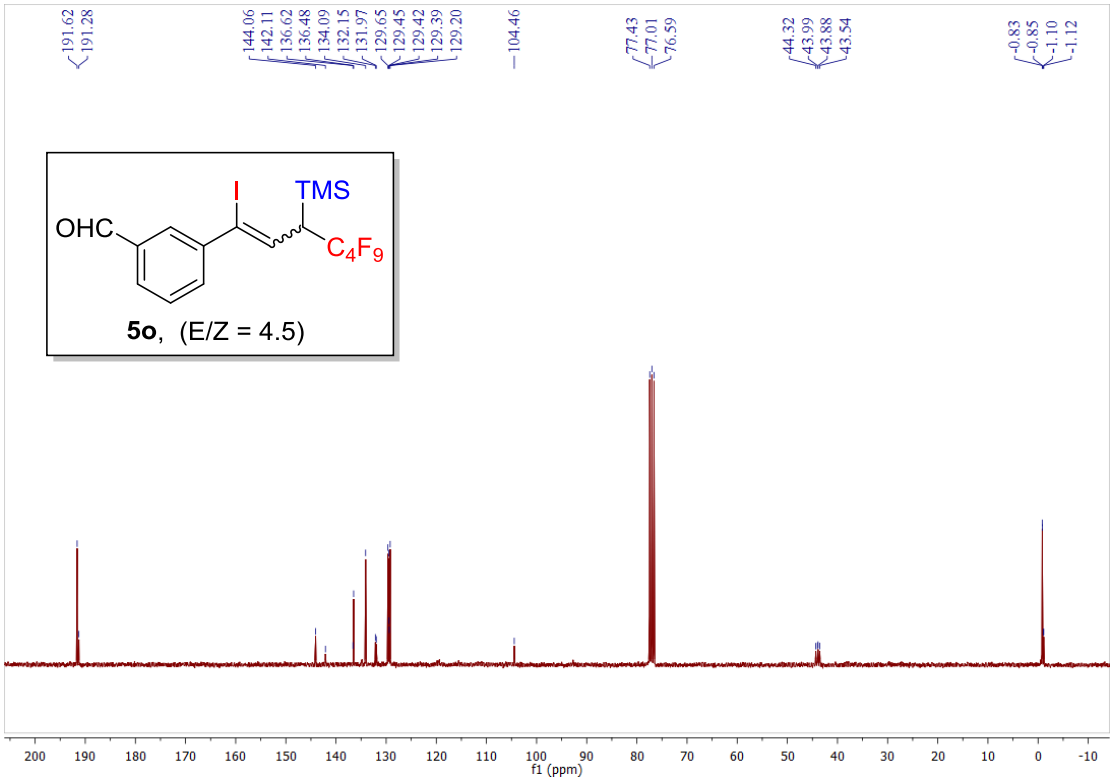

I
TMS
Cl
C_4F_9
5m, (Z/E = 5)
f1 (ppm)

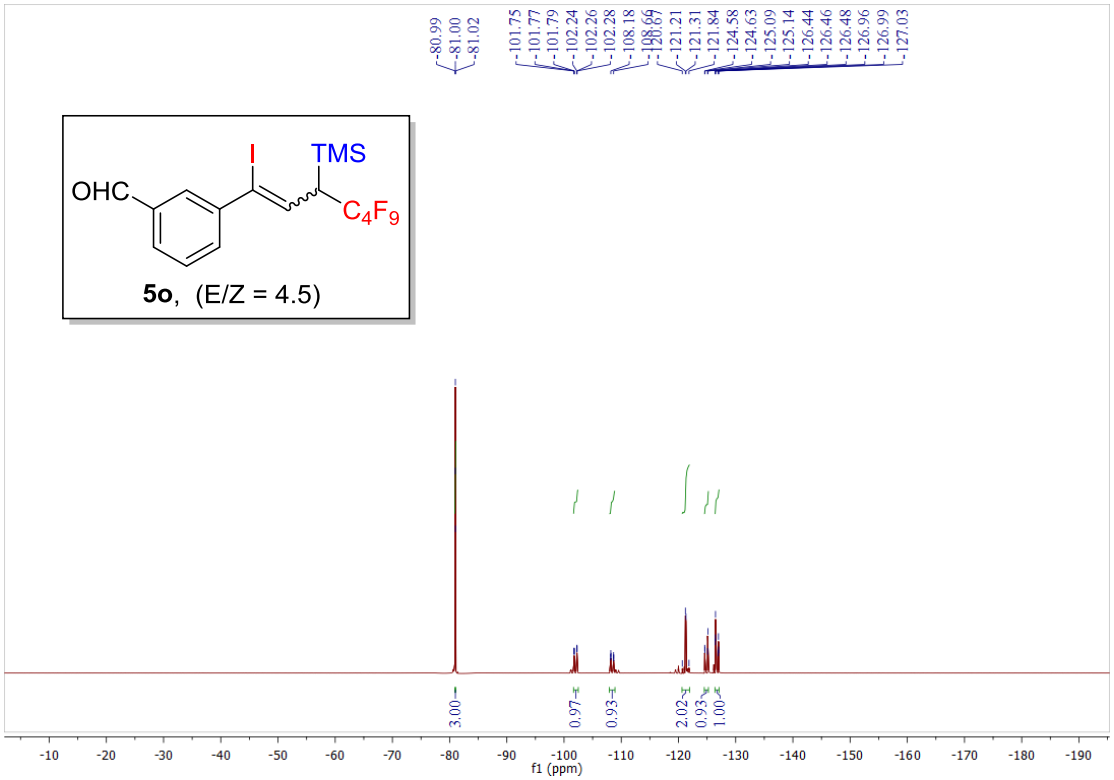

I
TMS
HO
C_4F_9
5n, (Z/E = 4)
f1 (ppm)

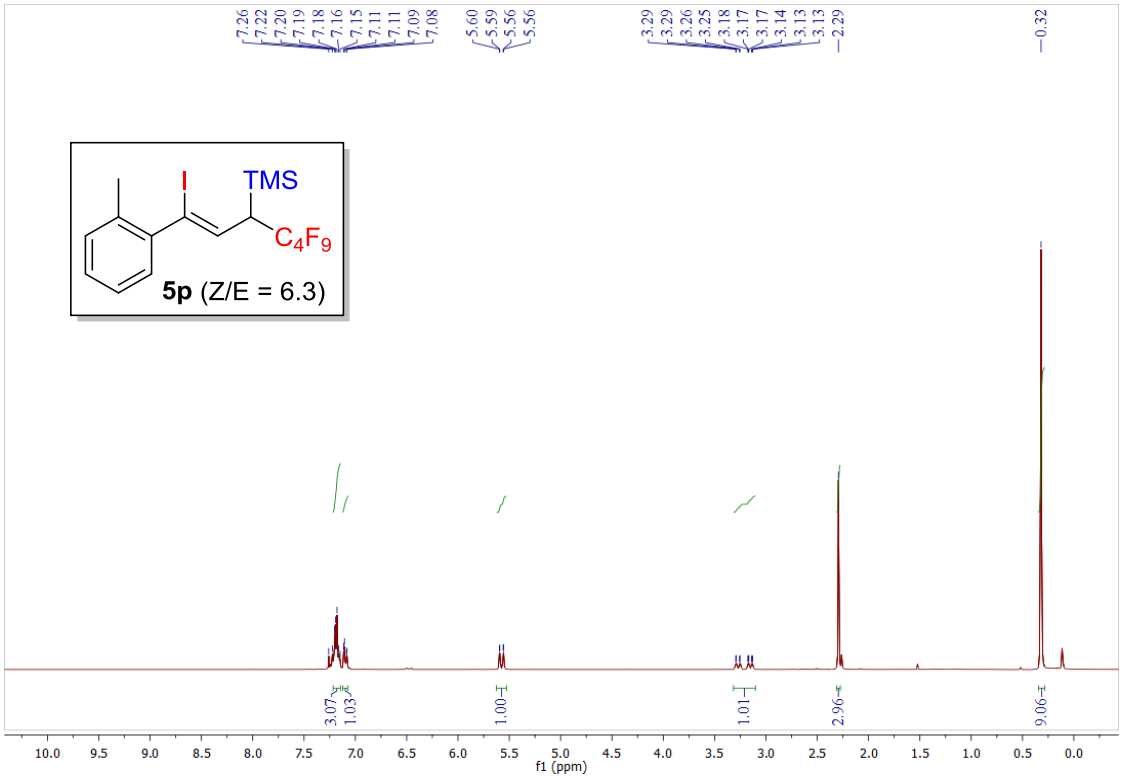

155.26
155.17
144.71
142.53
130.69
130.50
129.79
129.56
121.07
115.63
115.59
94.42
77.42
77.00
76.58
44.05
43.71
43.60
43.27
-0.89
-0.92
-1.09
-1.11
HO
I
TMS
C4F9
5n, (Z/E = 4)
f1 (ppm)

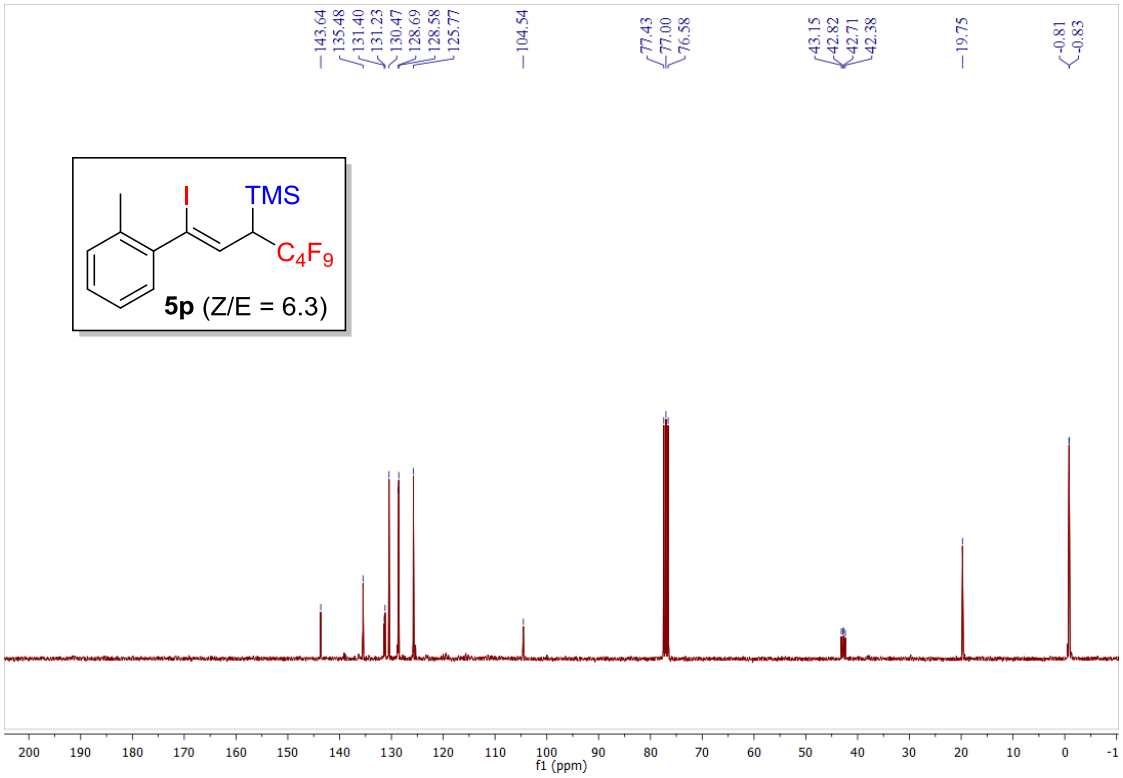

-80.97
-80.99
-81.01
-81.01
-81.02
-81.03
-81.04
-81.05
-101.67
-102.16
-102.20
-108.13
-108.18
-120.09
-120.69
-120.98
-121.20
-121.29
-121.51
-121.82
-124.60
-124.77
-125.12
-125.16
-125.34
-126.11
-126.15
-126.18
-126.48
-126.52
-126.55
-126.66
-127.00
-127.03
-127.07
HO
I
TMS
C4F9
5n, (Z/E = 4)
3.00
1.15
1.18
2.26
1.05
1.04
f1 (ppm)

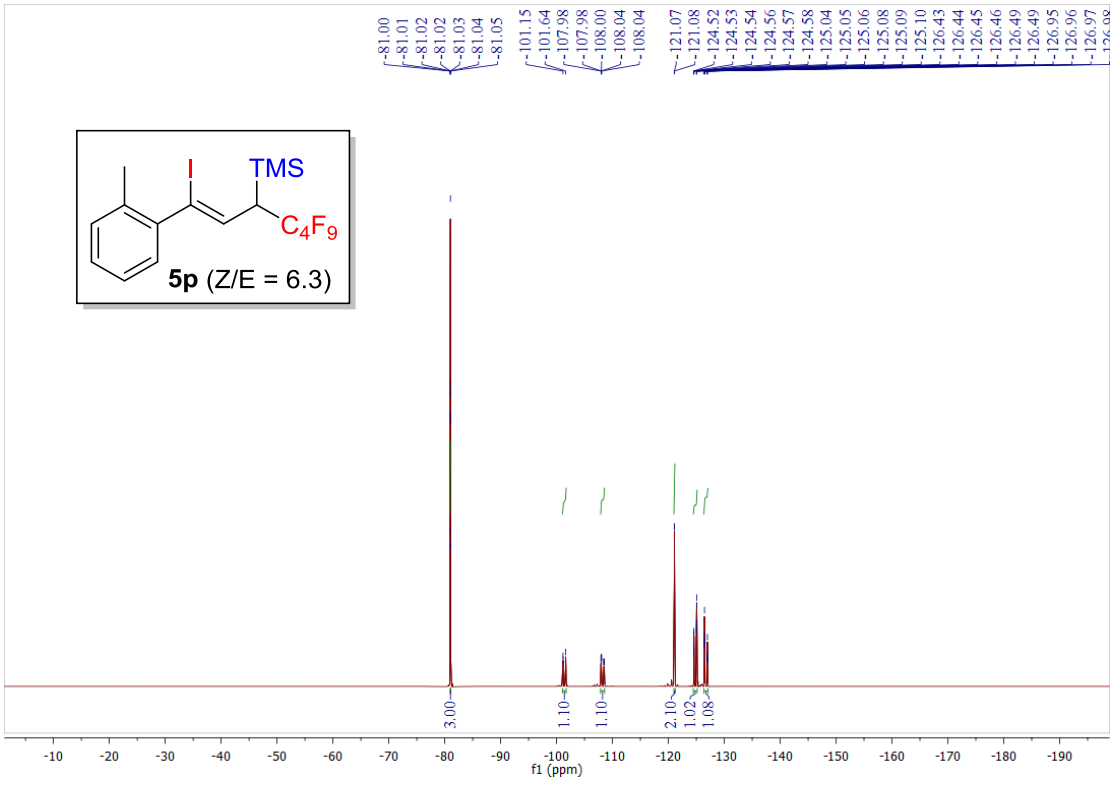

OHC
I
TMS
C4F9
5o, (E/Z = 4.5)
f1 (ppm)

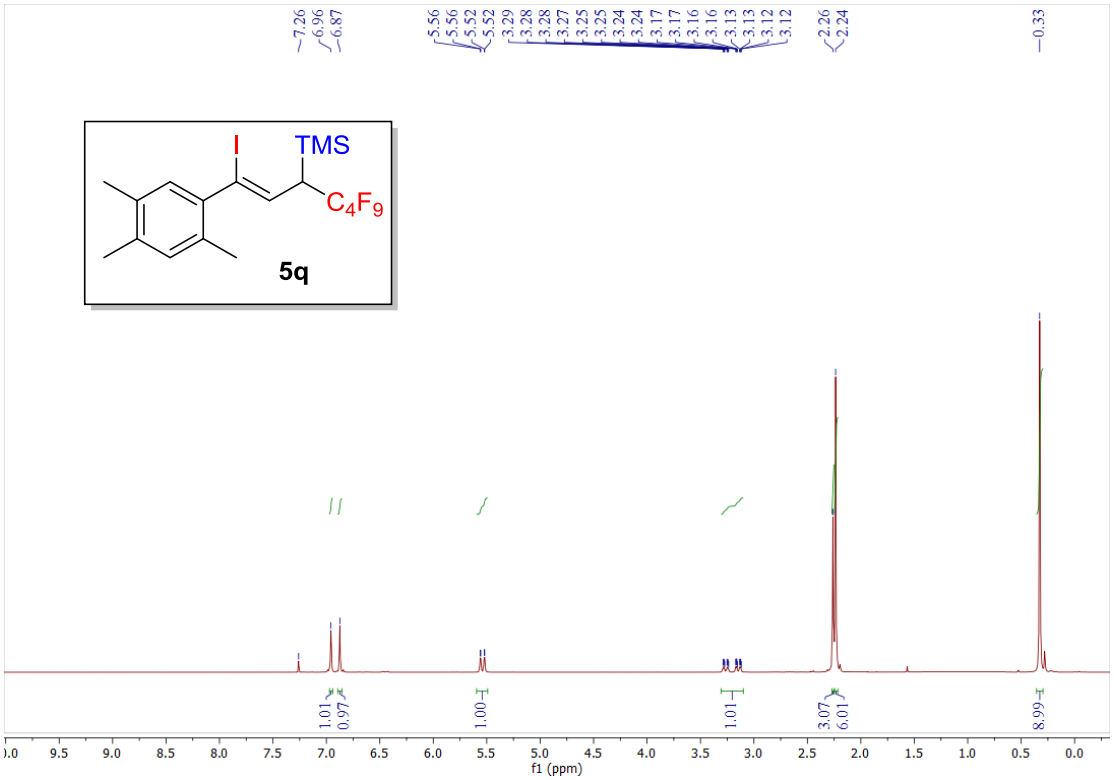

OHC
I
TMS
C4F9
5o, (E/Z = 4.5)
f1 (ppm)

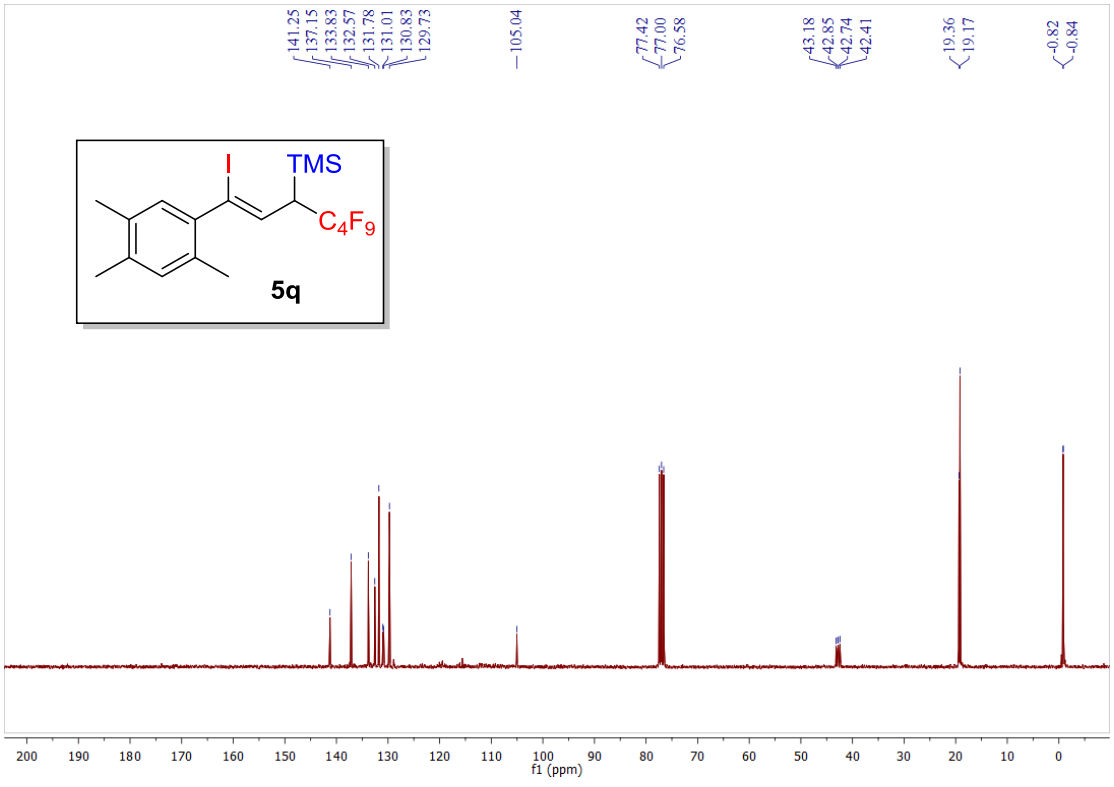

OHC
I
TMS
C_4F_9
5o, (E/Z = 4.5)
f1 (ppm)


I
TMS
C_4F_9
5p (Z/E = 6.3)
f1 (ppm)


143.64
135.48
131.40
131.23
130.47
128.69
128.58
125.77
104.54
77.43
77.00
76.58
43.15
42.82
42.71
42.38
19.75
0.81
0.83
I
TMS
C4F9
5p (Z/E = 6.3)
f1 (ppm)


81.00
81.01
81.02
81.02
81.03
81.04
81.05
101.15
101.64
107.98
107.98
108.00
108.04
108.04
121.07
121.08
124.52
124.53
124.54
124.56
124.57
124.58
125.04
125.05
125.06
125.08
125.09
125.10
126.43
126.44
126.45
126.46
126.49
126.49
126.95
126.96
126.97
I
TMS
C4F9
5p (Z/E = 6.3)
3.00
1.10
1.10
2.10
1.02
1.08
f1 (ppm)


7.26
6.96
6.87
5.56
5.56
5.52
5.52
3.29
3.28
3.28
3.27
3.25
3.25
3.24
3.24
3.17
3.17
3.16
3.16
3.13
3.13
3.12
3.12
2.26
2.24
0.33
I
TMS
C4F9
5q
1.01
0.97
1.00
1.01
3.07
6.01
8.99
f1 (ppm)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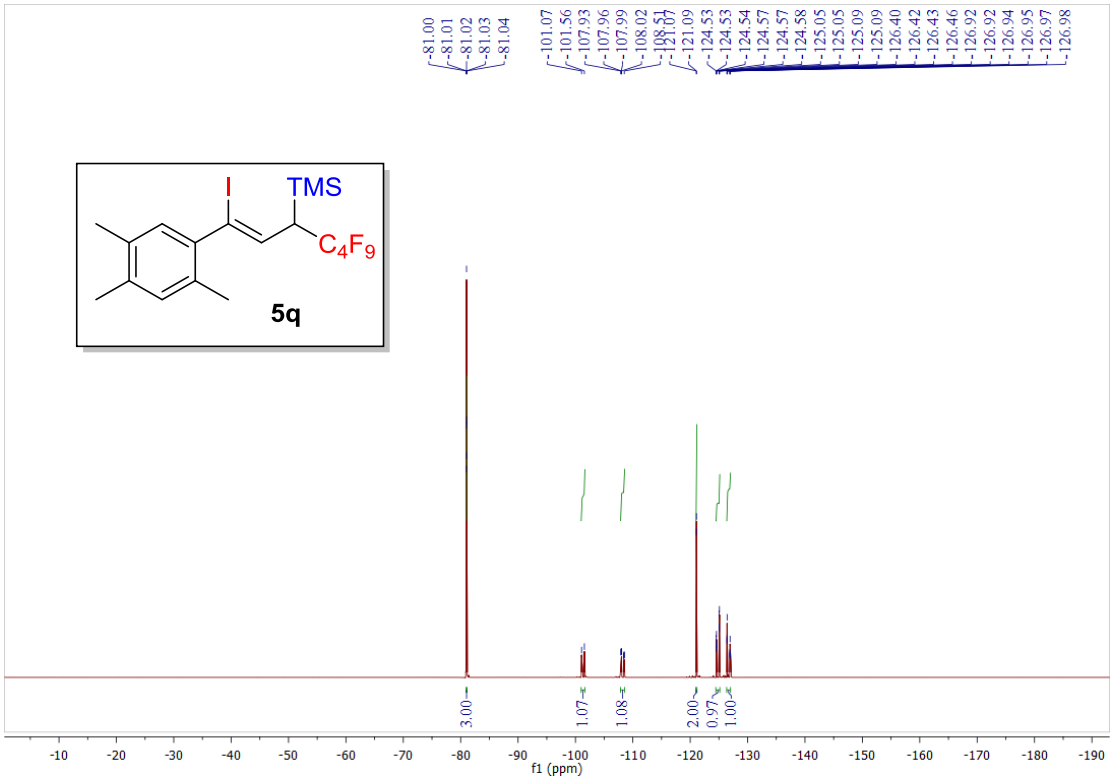
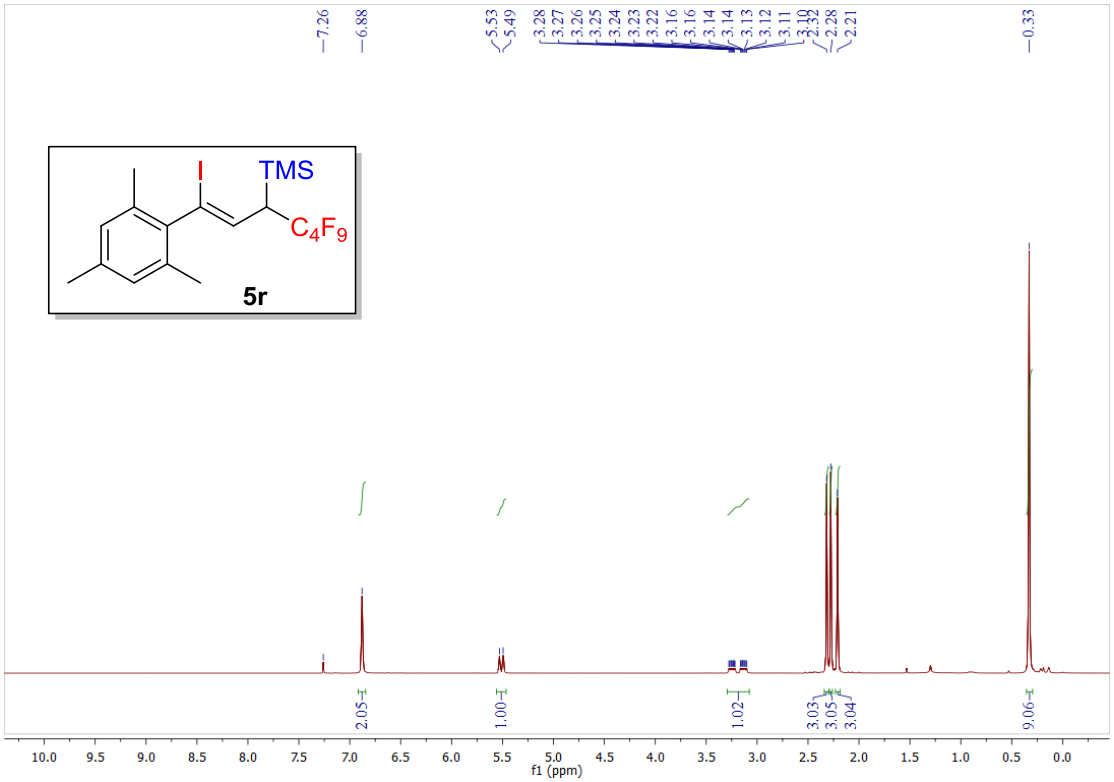
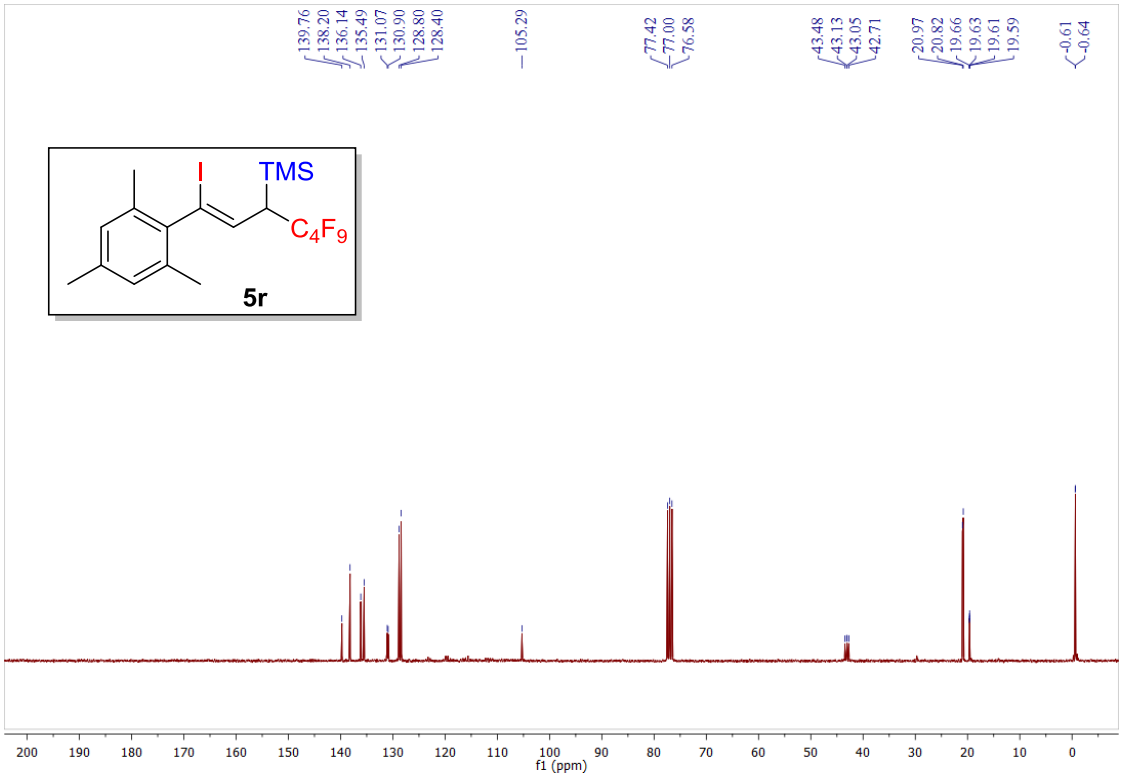
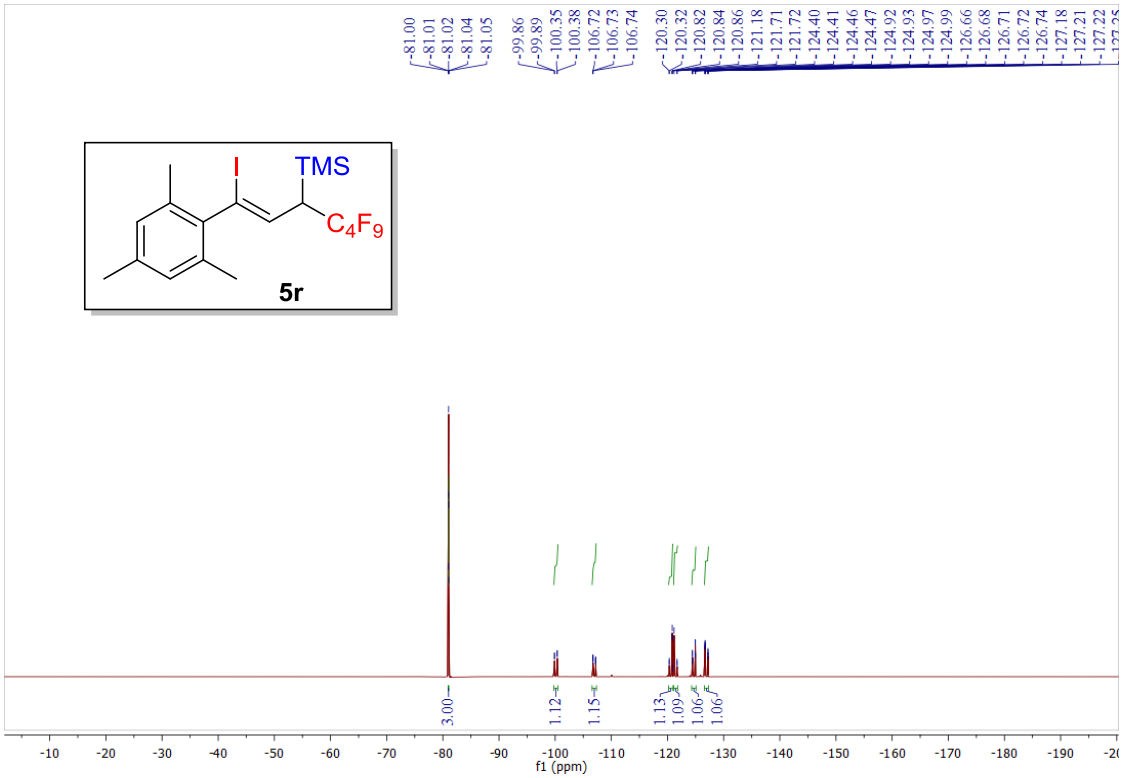
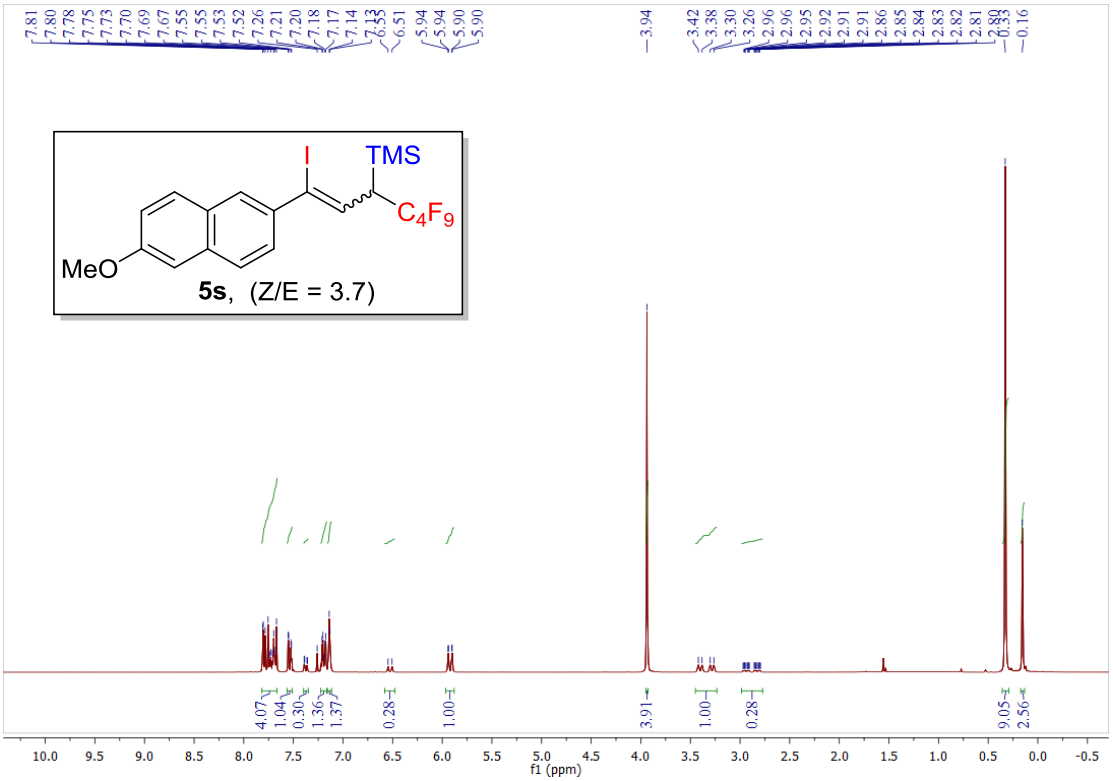
137.15
133.83
132.57
131.78
131.01
130.83
129.73
105.04
77.42
77.00
76.58
43.18
42.85
42.74
42.41
19.36
19.17
0.82
0.84
I
TMS
C4F9
5q
f1 (ppm)

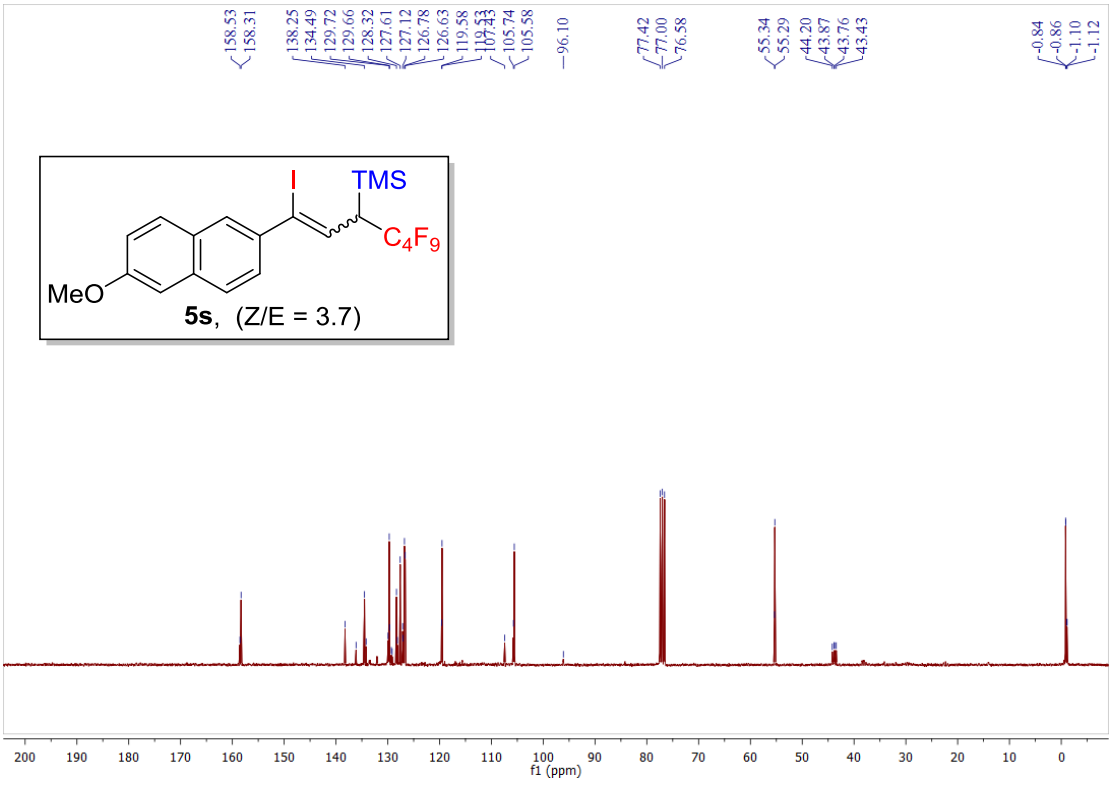

I
TMS
C_4F_9
5q
f1 (ppm)

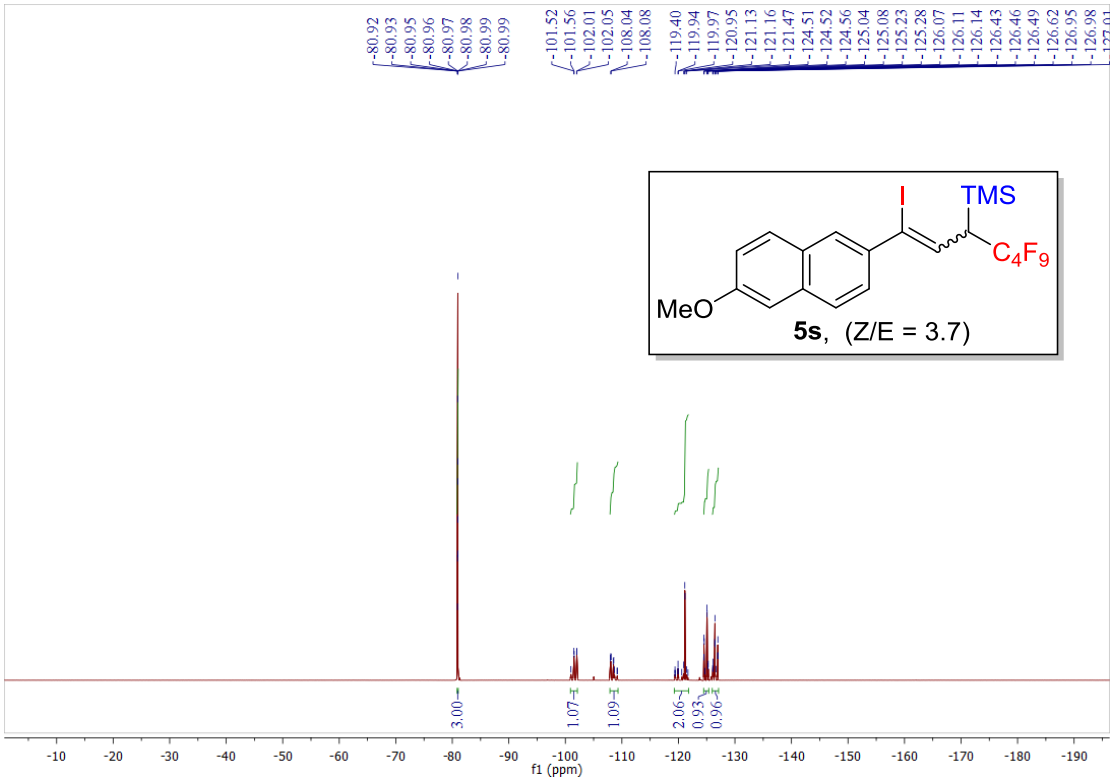

I
TMS
C_4F_9
5r
f1 (ppm)

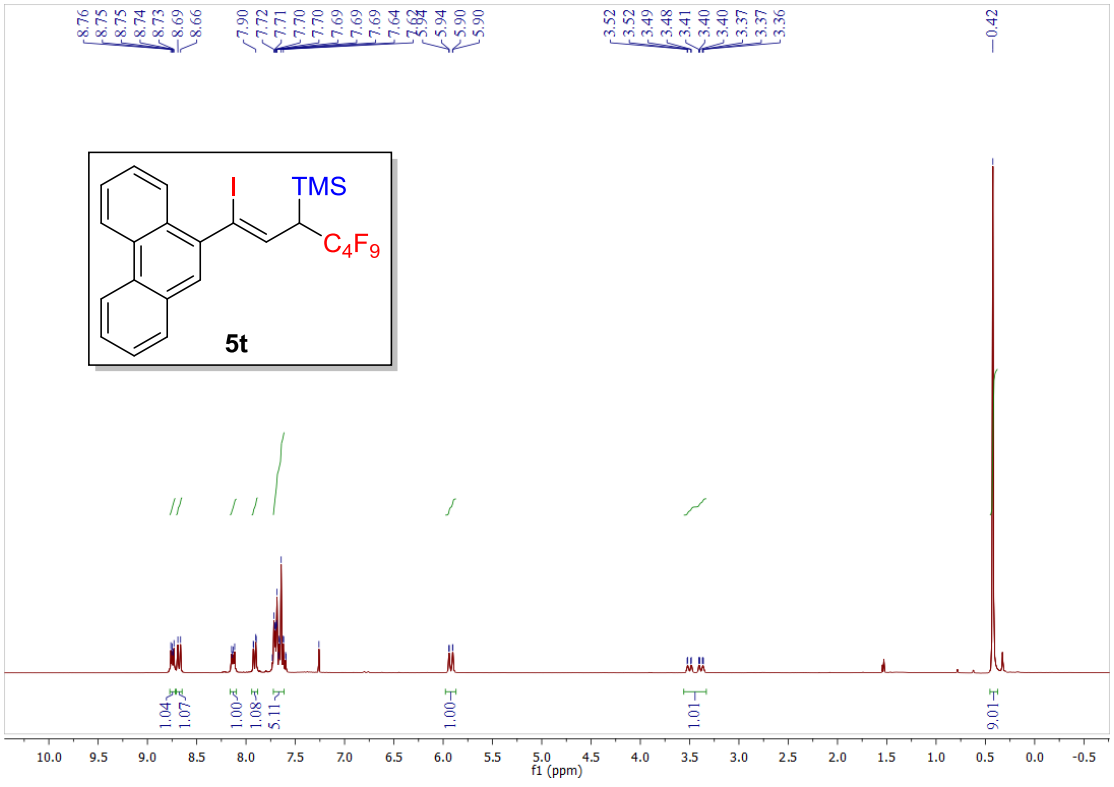

139.76
138.20
136.14
135.49
131.07
130.90
128.80
128.40
105.29
77.42
77.00
76.58
43.48
43.13
43.05
42.71
20.97
20.82
19.66
19.63
19.61
19.59
-0.61
-0.64
I
TMS
C4F9
5r
f1 (ppm)

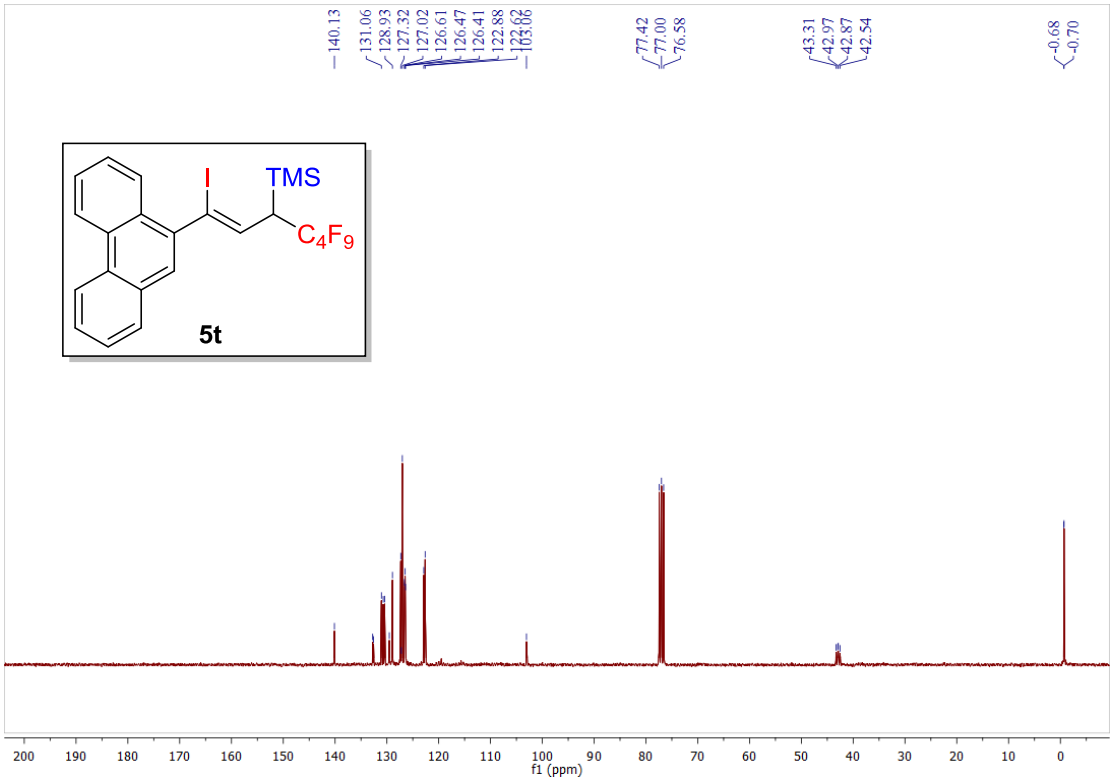

-81.00
-81.01
-81.02
-81.04
-81.05
-99.86
-99.89
-100.35
-100.38
-106.72
-106.73
-106.74
-120.30
-120.32
-120.82
-120.84
-120.86
-121.18
-121.71
-121.72
-124.40
-124.41
-124.46
-124.47
-124.92
-124.93
-124.97
-124.99
-126.66
-126.68
-126.71
-126.72
-126.74
-127.18
-127.21
-127.22
I
TMS
C4F9
5r
3.00
1.12
1.15
1.13
1.09
1.06
1.06
f1 (ppm)

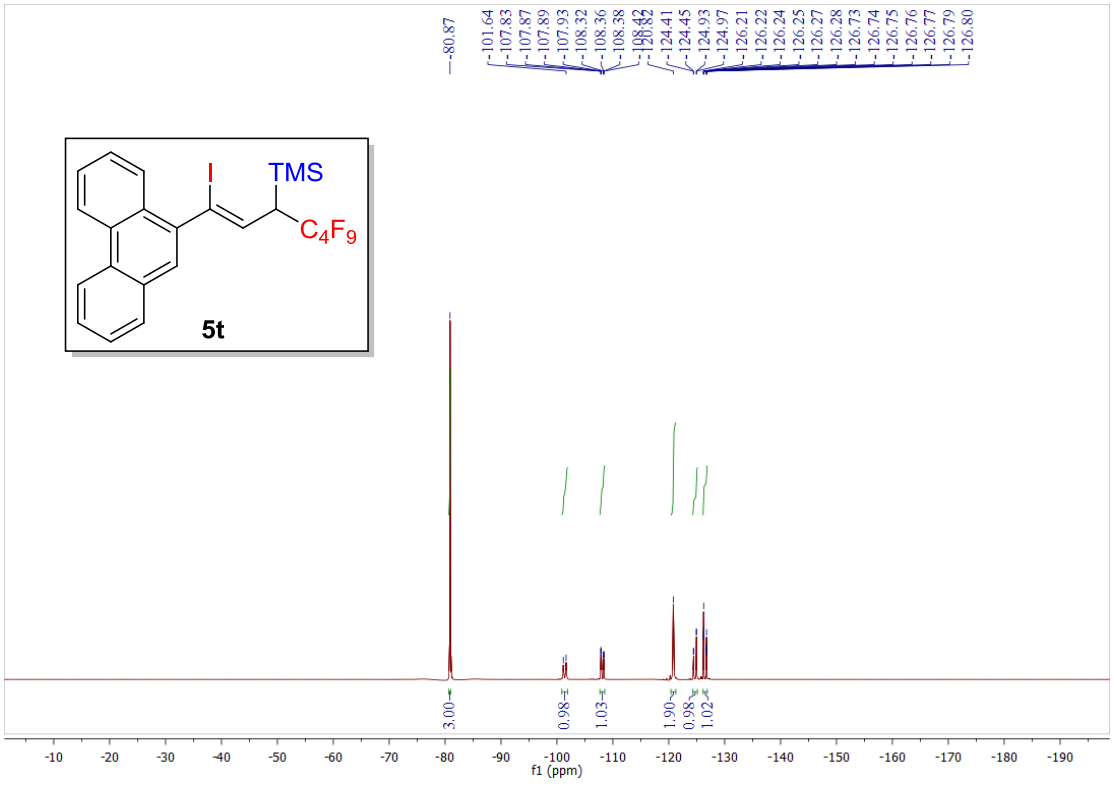

I
TMS
C_4F_9
MeO
5s, (Z/E = 3.7)
f1 (ppm)

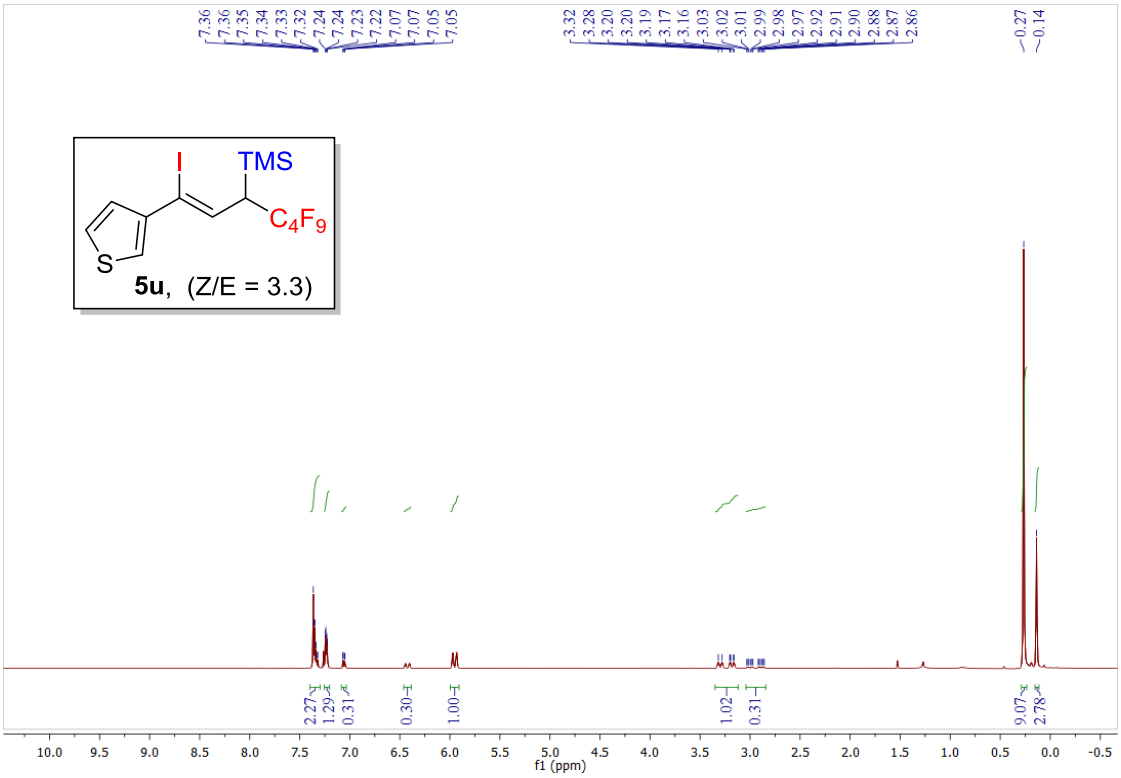

I
TMS
C_4F_9
MeO
5s, (Z/E = 3.7)
f1 (ppm)

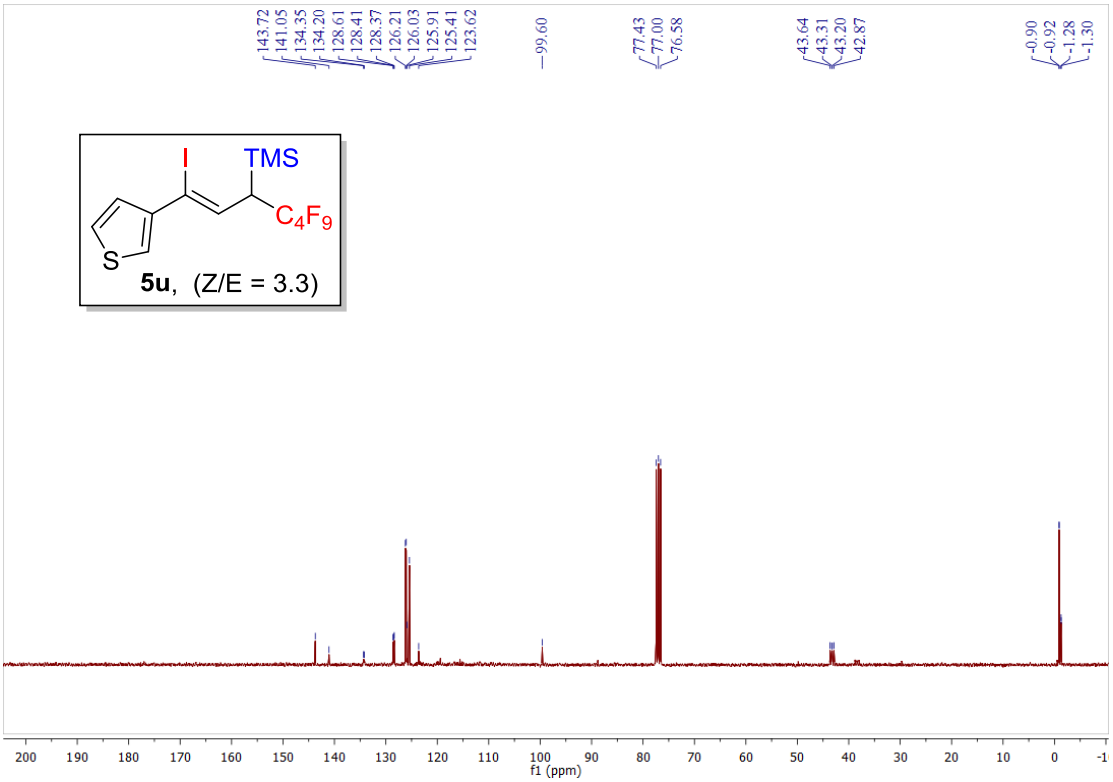

I
TMS
C_4F_9
MeO
5s, (Z/E = 3.7)
f1 (ppm)

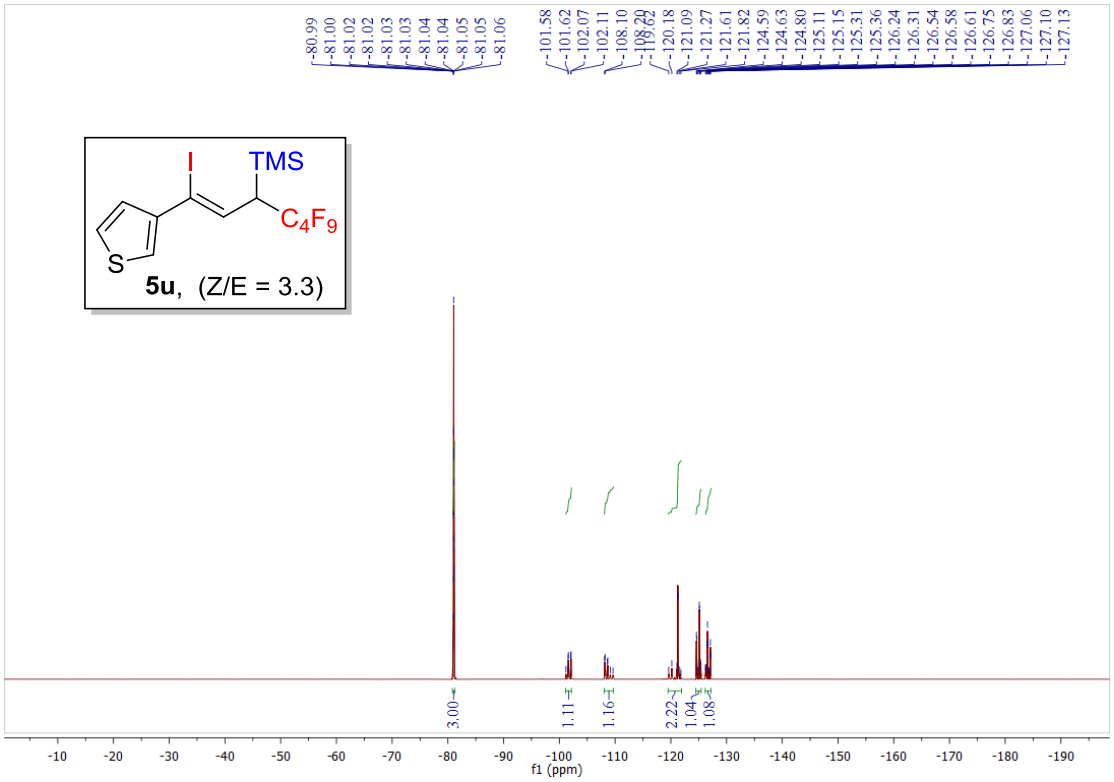

I
TMS
C_4F_9
5t
f1 (ppm)

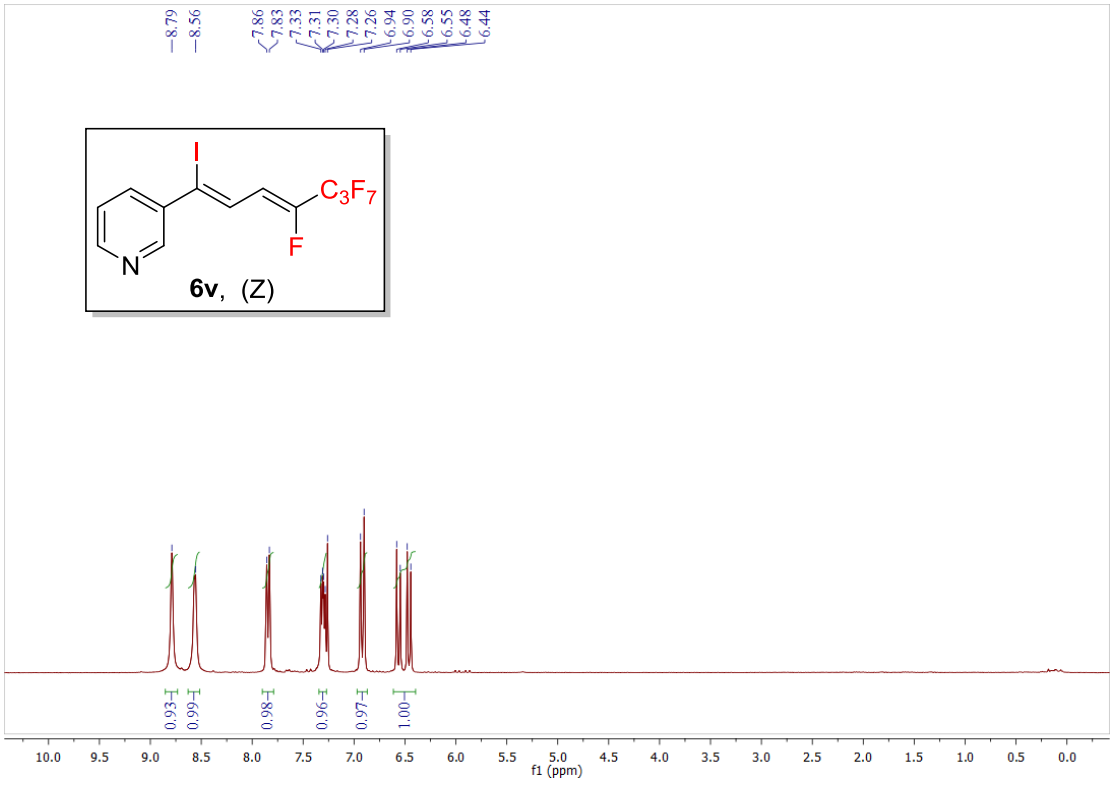

140.13
131.06
128.93
127.32
127.02
126.61
126.47
126.41
122.88
77.42
77.00
76.58
43.31
42.97
42.87
42.54
-0.68
-0.70
I
TMS
C4F9
5t
f1 (ppm)

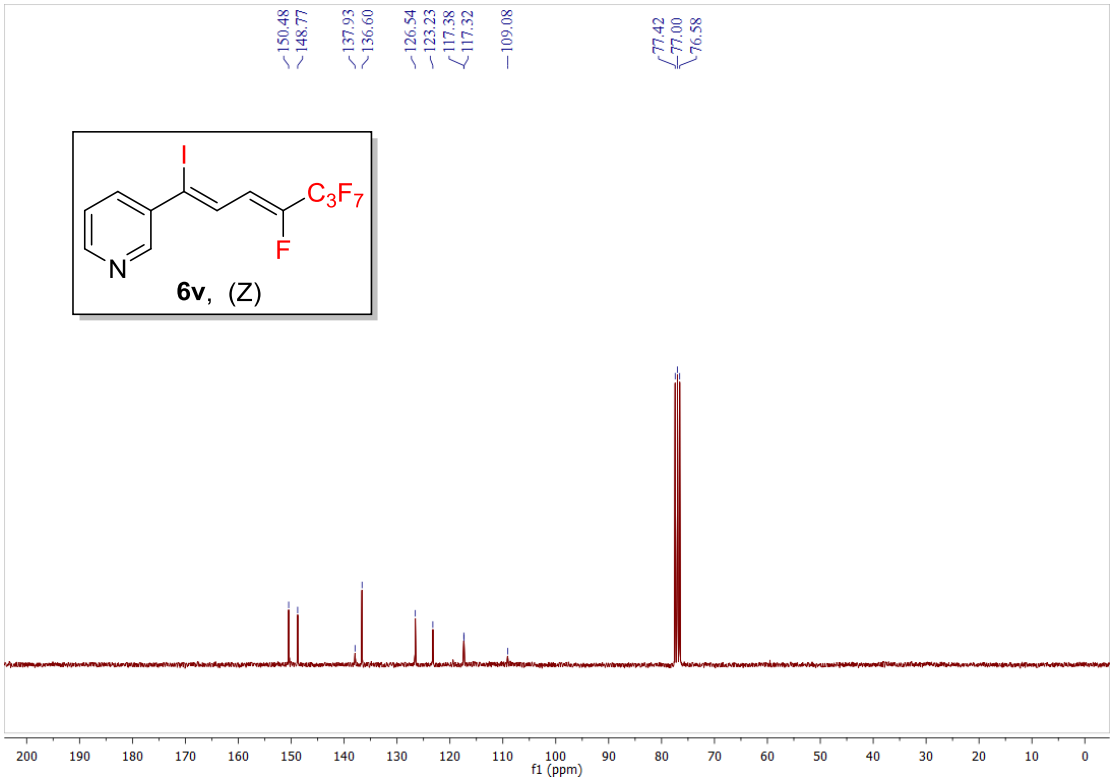

-80.87
-101.64
-107.83
-107.87
-107.89
-107.93
-108.32
-108.36
-108.38
-124.41
-124.45
-124.93
-124.97
-126.21
-126.22
-126.24
-126.25
-126.27
-126.28
-126.73
-126.74
-126.75
-126.76
-126.77
-126.79
-126.80
I
TMS
C4F9
5t
3.00
0.98
1.03
1.90
0.98
1.02
f1 (ppm)

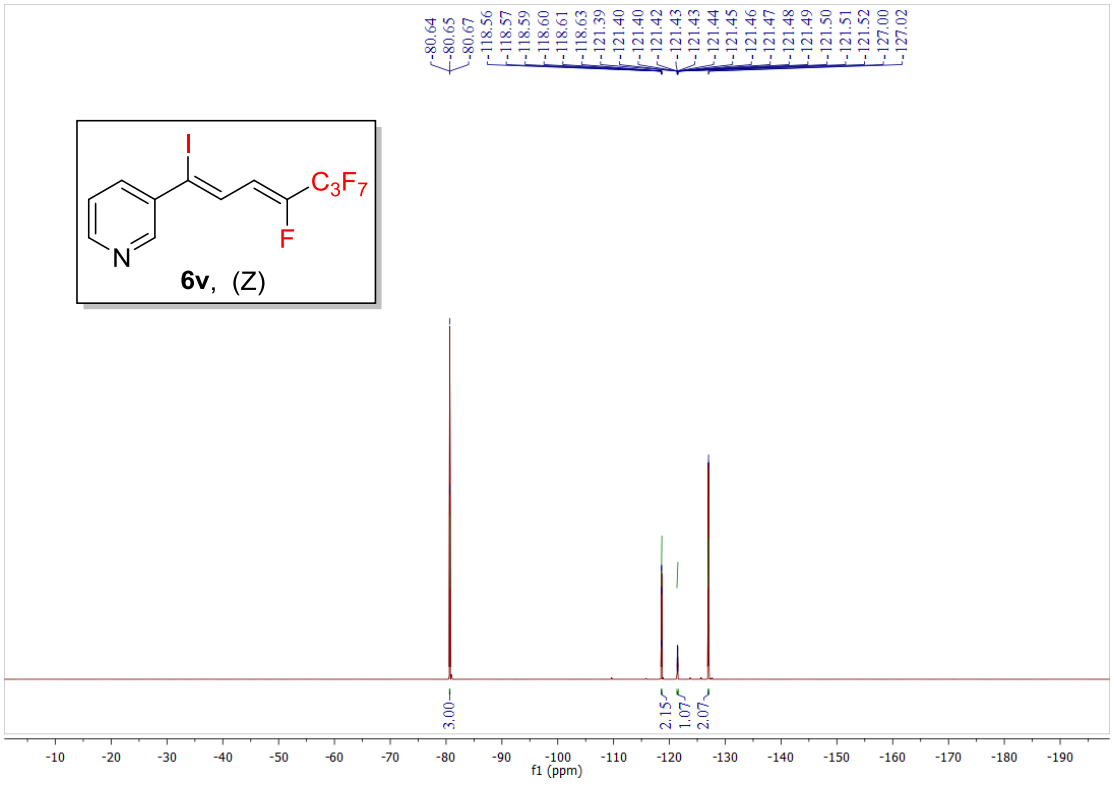

7.36
7.36
7.35
7.34
7.33
7.32
7.24
7.24
7.23
7.22
7.07
7.07
7.05
7.05
3.32
3.28
3.20
3.20
3.19
3.17
3.16
3.03
3.02
3.01
2.99
2.98
2.97
2.92
2.91
2.90
2.88
2.87
2.86
0.27
0.14
I
TMS
C4F9
S
5u, (Z/E = 3.3)
2.27
1.29
0.31
0.30
1.00
1.02
0.31
9.07
2.78
f1 (ppm)

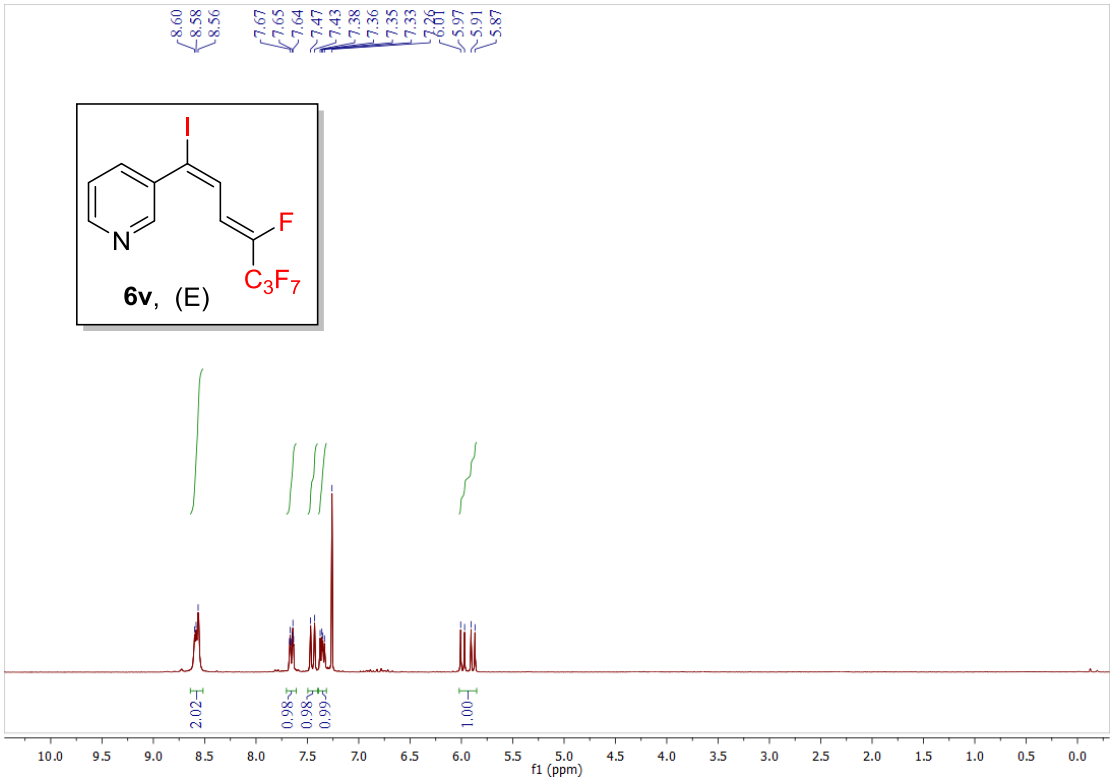

143.72
141.05
134.35
134.20
128.61
128.41
128.37
126.21
126.03
125.91
125.41
123.62
99.60
77.43
77.00
76.58
43.64
43.31
43.20
42.87
-0.90
-0.92
-1.28
-1.30
I
TMS
C4F9
S
5u, (Z/E = 3.3)
f1 (ppm)

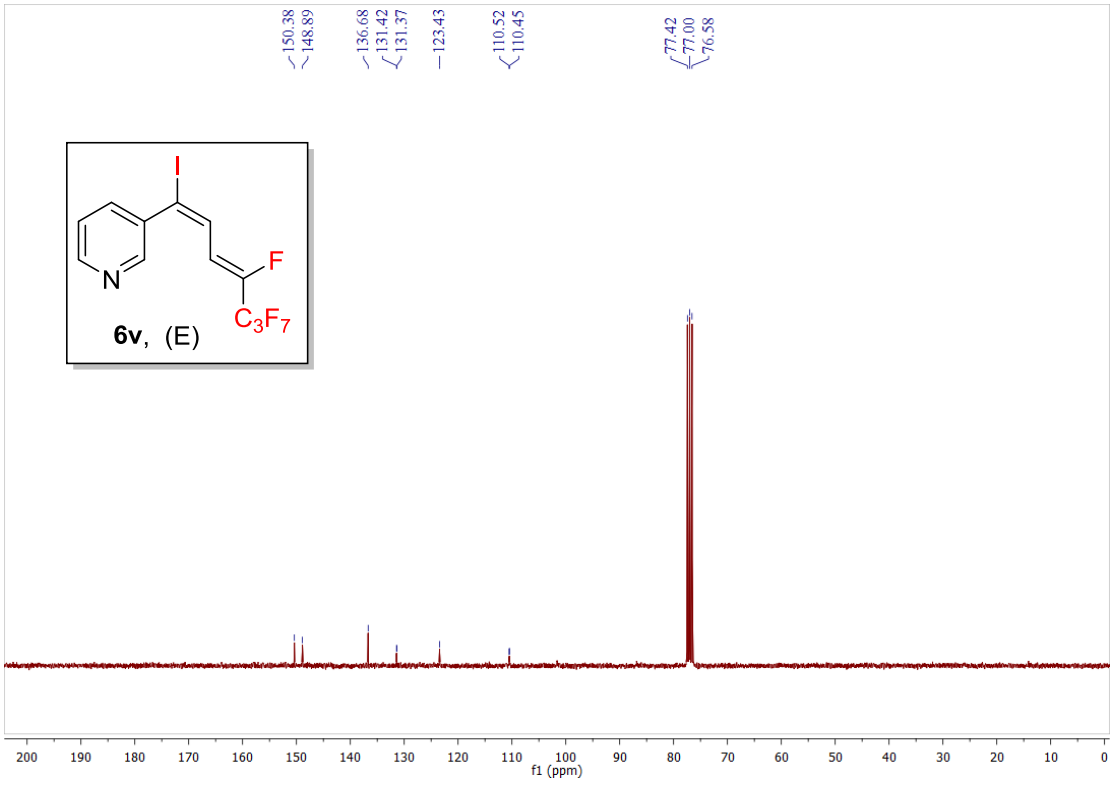

I
TMS
C_4F_9
S
5u, (Z/E = 3.3)
f1 (ppm)

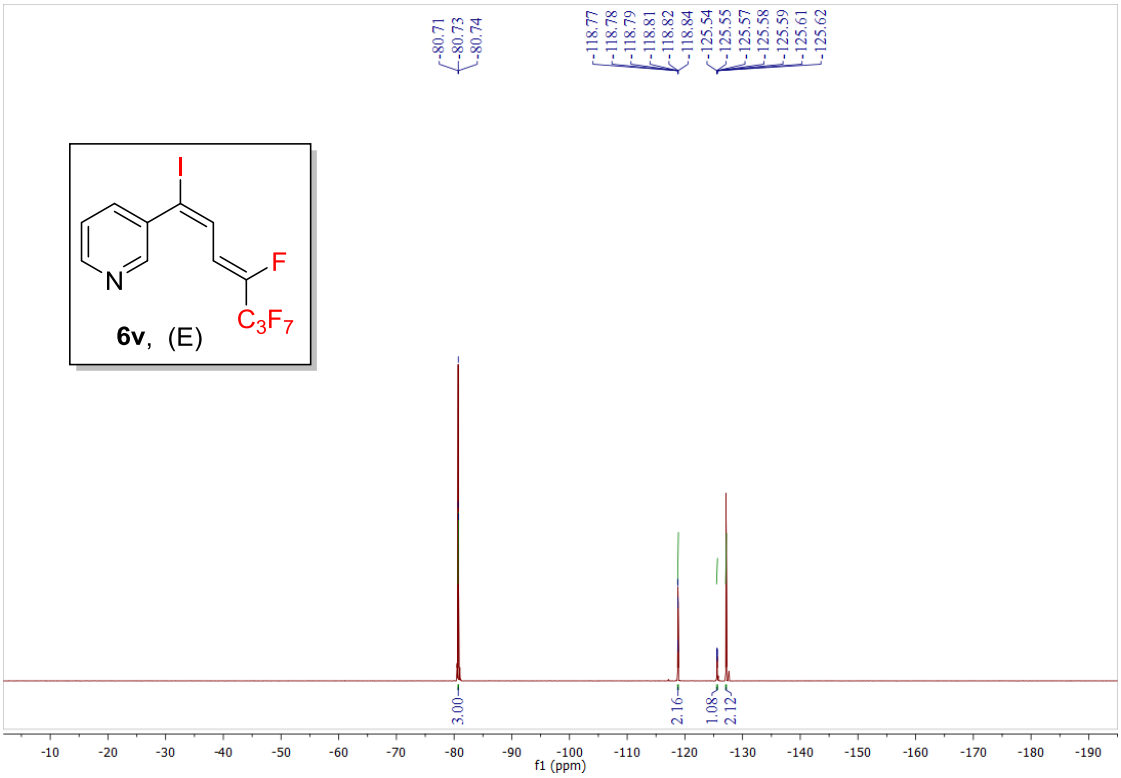

I
C_3F_7
F
N
6v, (Z)
f1 (ppm)

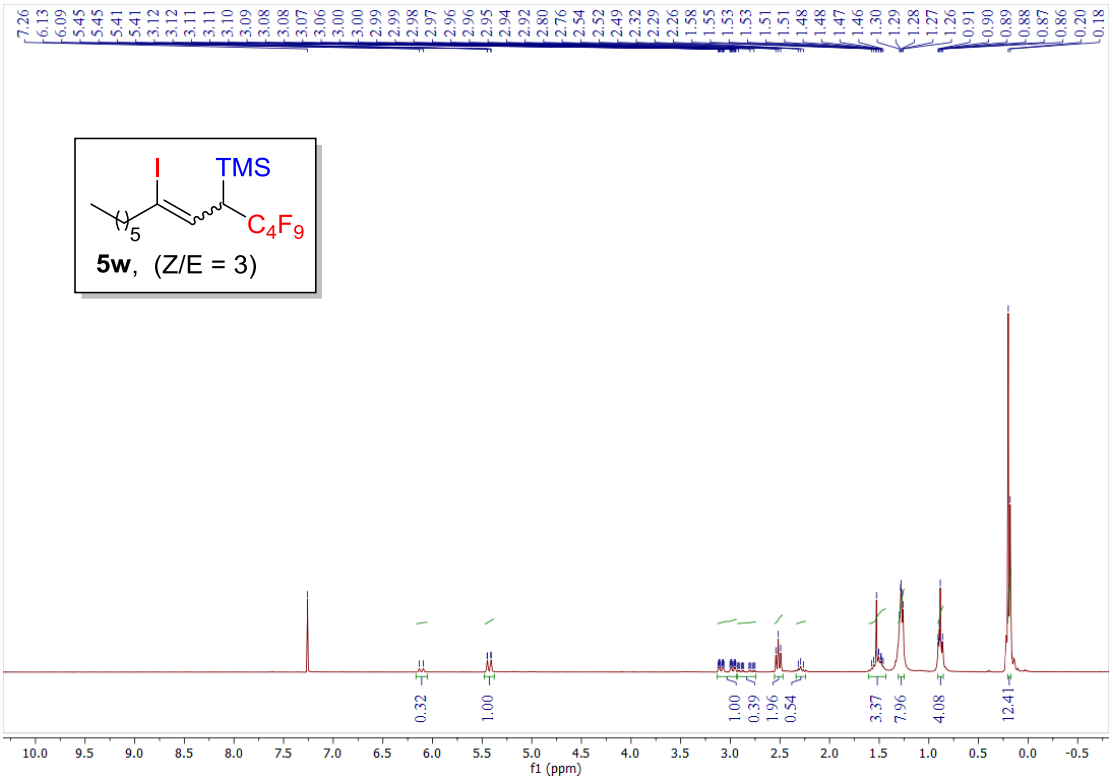

150.48
148.77
137.93
136.60
126.54
123.23
117.38
117.32
109.08
77.42
77.00
76.58
I
C_3F_7
F
N
6v, (Z)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

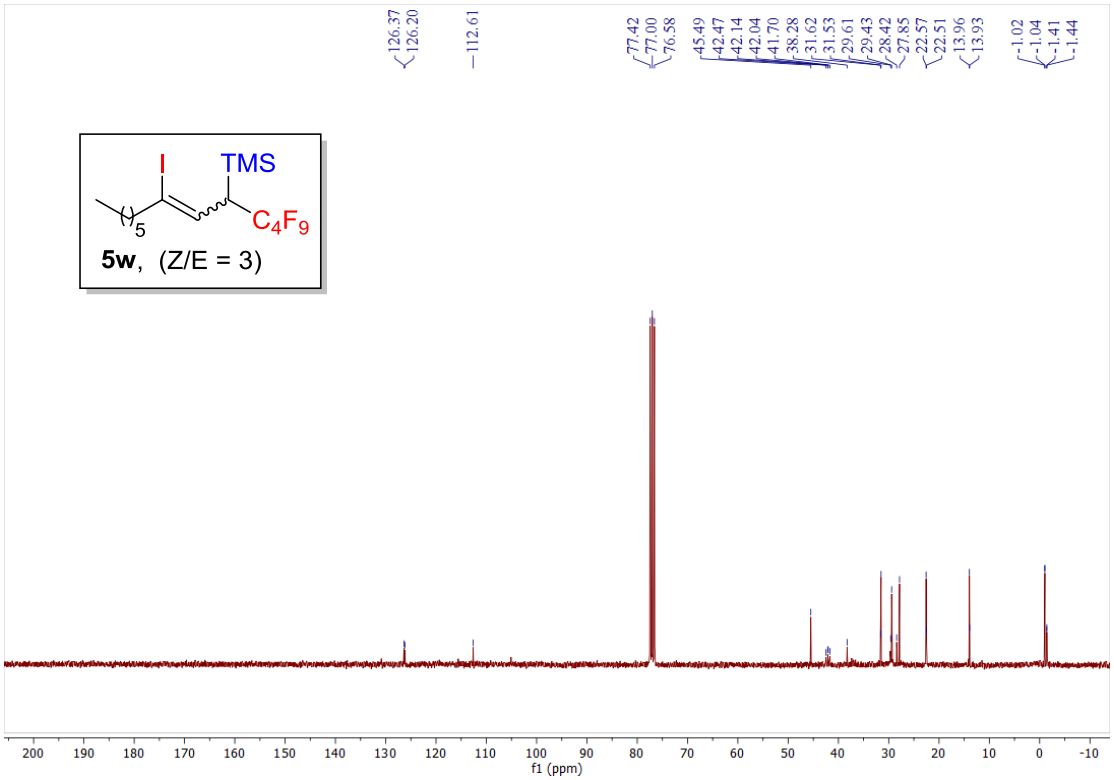

-80.64
-80.65
-80.67
-118.56
-118.57
-118.59
-118.60
-118.61
-118.63
-121.39
-121.40
-121.40
-121.42
-121.43
-121.43
-121.44
-121.45
-121.46
-121.47
-121.48
-121.49
-121.50
-121.51
-121.52
-127.00
-127.02
I
C_3F_7
F
N
6v, (Z)
3.00
2.15
1.07
2.07
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

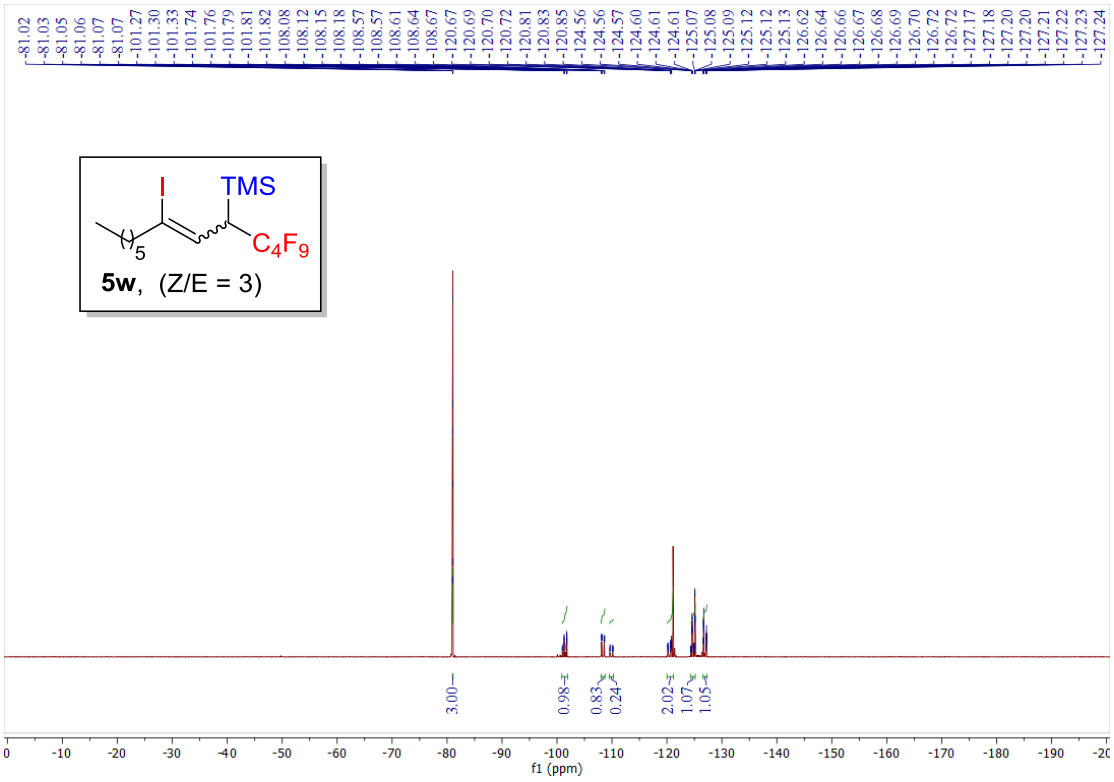

8.60
8.58
8.56
7.67
7.65
7.64
7.47
7.43
7.38
7.36
7.35
7.33
6.26
6.01
5.97
5.91
5.87
I
N
F
C_3F_7
6v, (E)
2.02
0.98
0.98
0.99
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

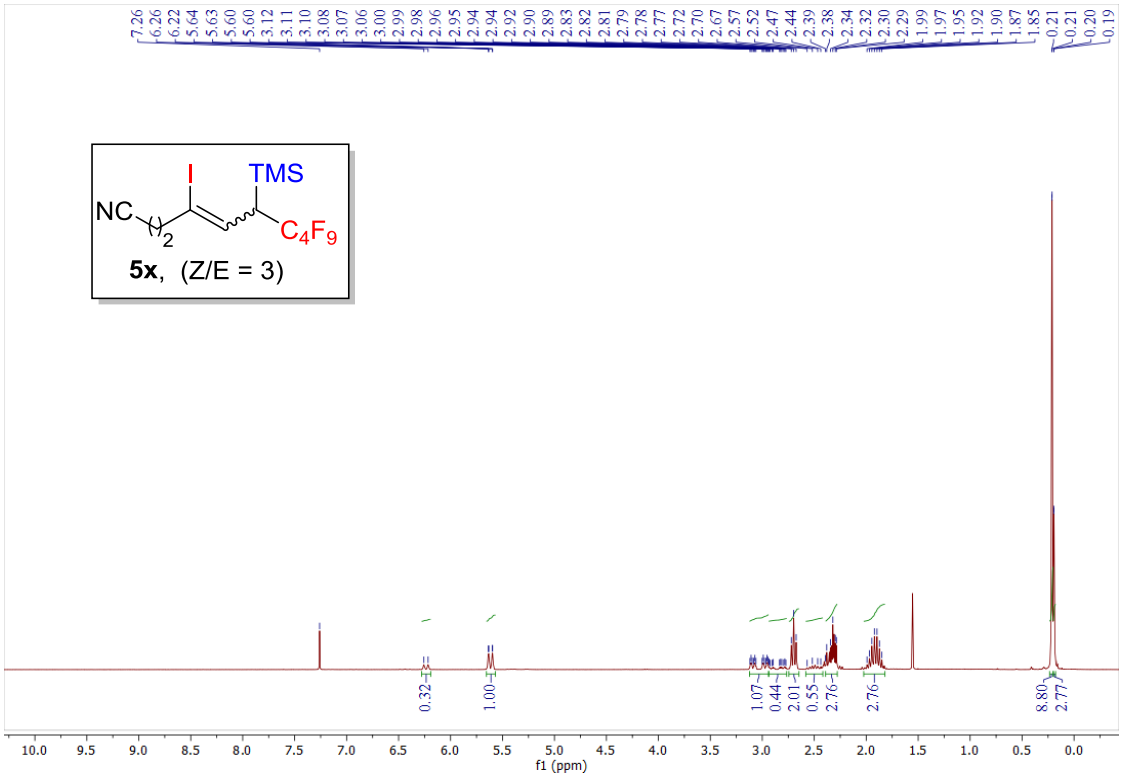

150.38
148.89
136.68
131.42
131.37
123.43
110.52
110.45
77.42
77.00
76.58
I
N
F
C_3F_7
6v, (E)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

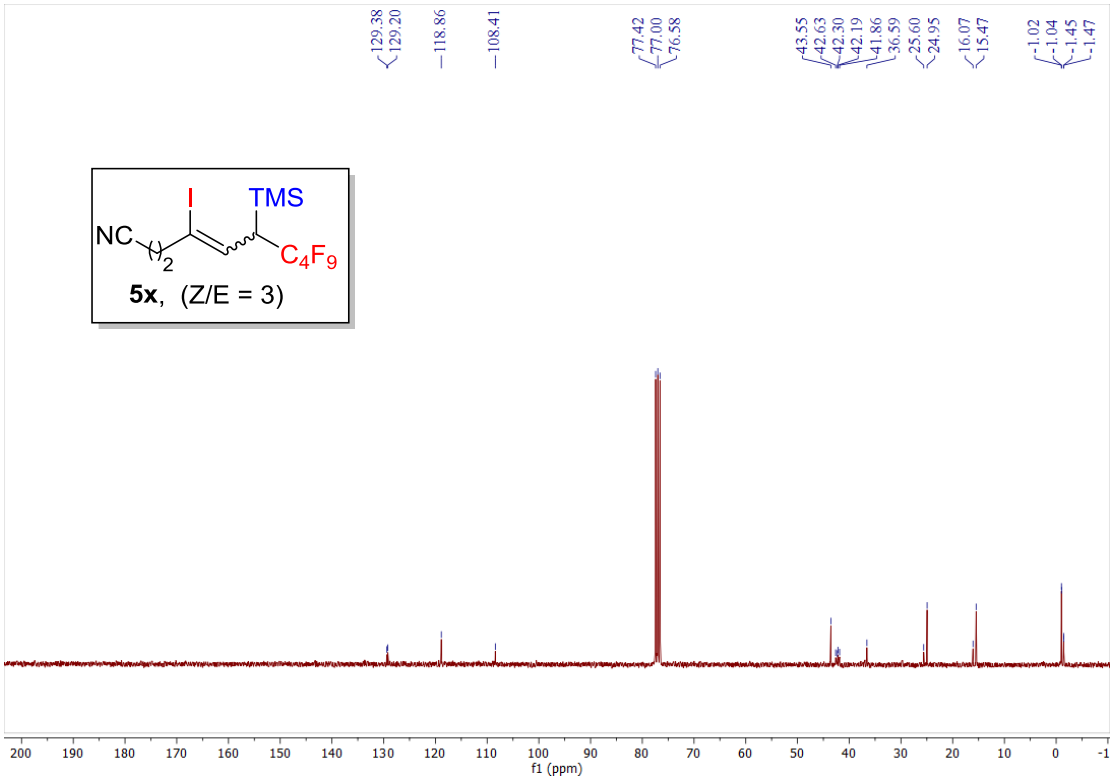

I
N
F
C3F7
6v, (E)
-80.71
-80.73
-80.74
-118.77
-118.78
-118.79
-118.81
-118.82
-118.84
-125.54
-125.55
-125.57
-125.58
-125.59
-125.61
-125.62
3.00
2.16
1.08
2.12
f1 (ppm)

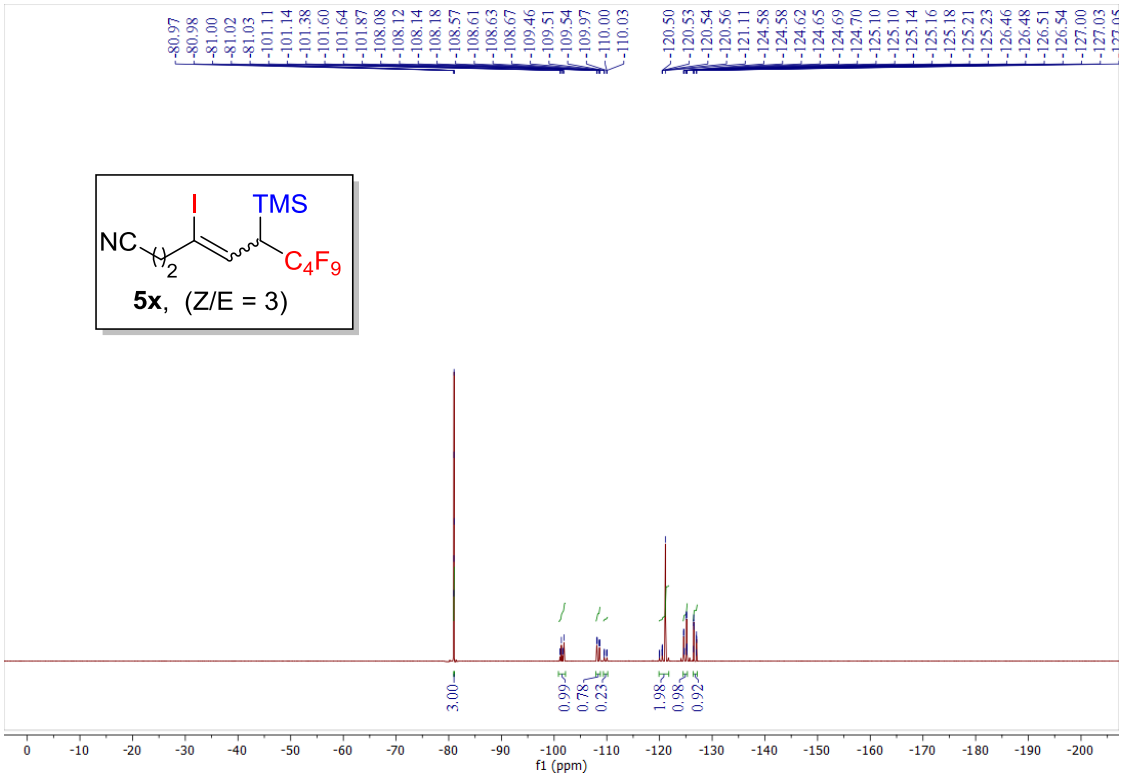

I
TMS
C4F9
5
5w, (Z/E = 3)
0.32
1.00
1.00
0.39
1.96
0.54
3.37
7.96
4.08
12.41
f1 (ppm)

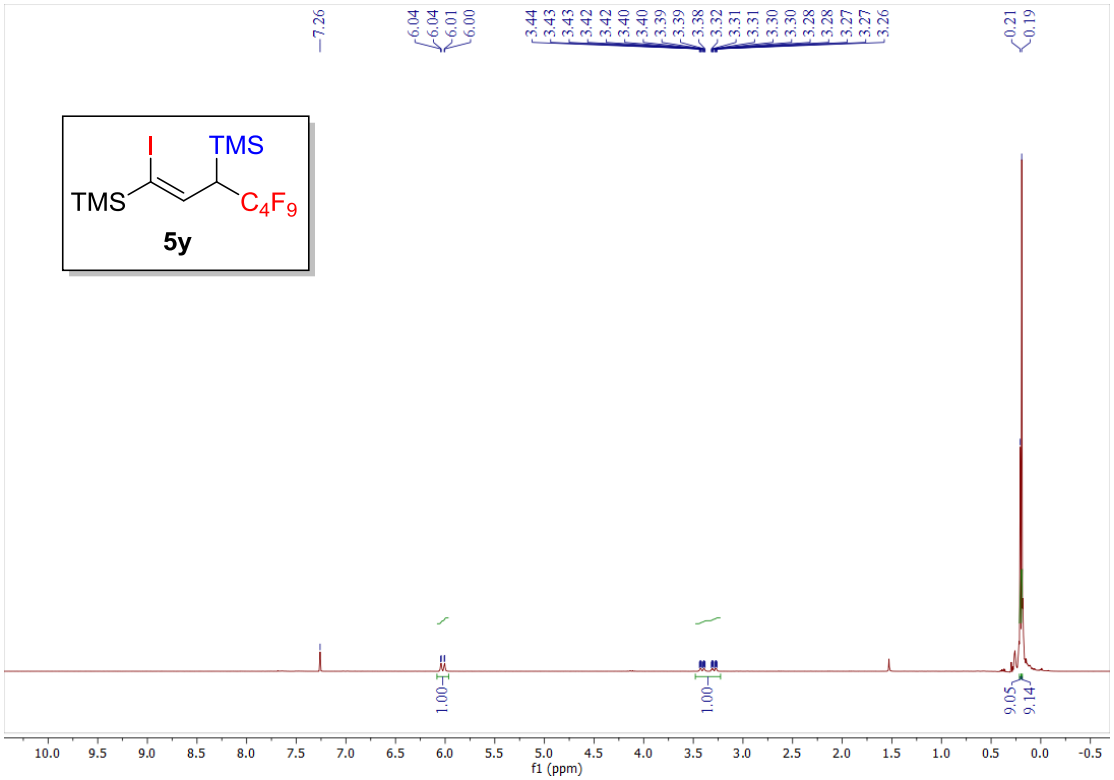

126.37
126.20
112.61
77.42
77.00
76.58
45.49
42.47
42.14
42.04
41.70
38.28
31.62
31.53
29.61
29.43
28.42
27.85
22.57
22.51
13.96
13.93
1.02
1.04
1.41
1.44
I
TMS
C4F9
5
5w, (Z/E = 3)
f1 (ppm)

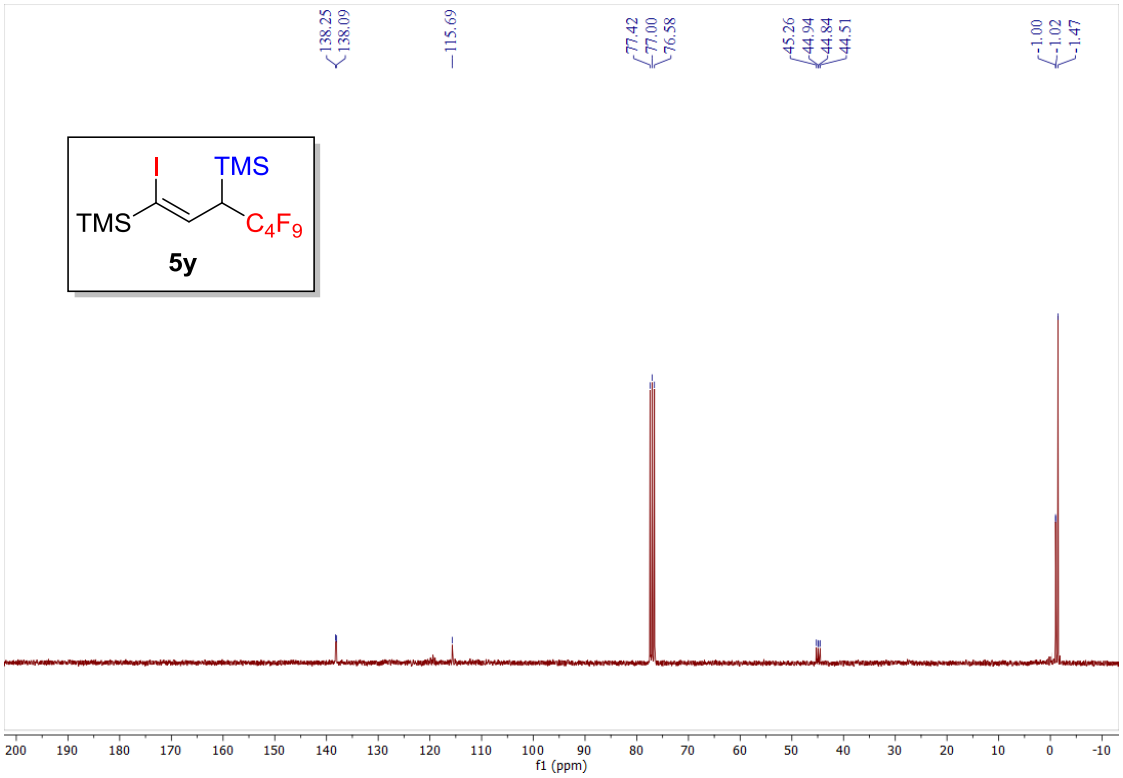

-81.02
-81.03
-81.05
-81.06
-81.07
-81.07
-101.27
-101.30
-101.33
-101.74
-101.76
-101.79
-101.81
-101.82
-108.08
-108.12
-108.15
-108.18
-108.57
-108.57
-108.61
-108.64
-108.67
-120.67
-120.69
-120.70
-120.72
-120.81
-120.83
-120.85
-124.56
-124.56
-124.57
-124.60
-124.61
-124.61
-125.07
-125.08
-125.09
-125.12
-125.12
-125.13
-126.62
-126.64
-126.66
-126.67
-126.68
-126.69
-126.70
-126.72
-126.72
-127.17
-127.18
-127.20
-127.20
-127.21
-127.22
-127.23
-127.24
I
TMS
C4F9
5
5w, (Z/E = 3)
3.00
0.98
0.83
0.24
2.02
1.07
1.05
f1 (ppm)

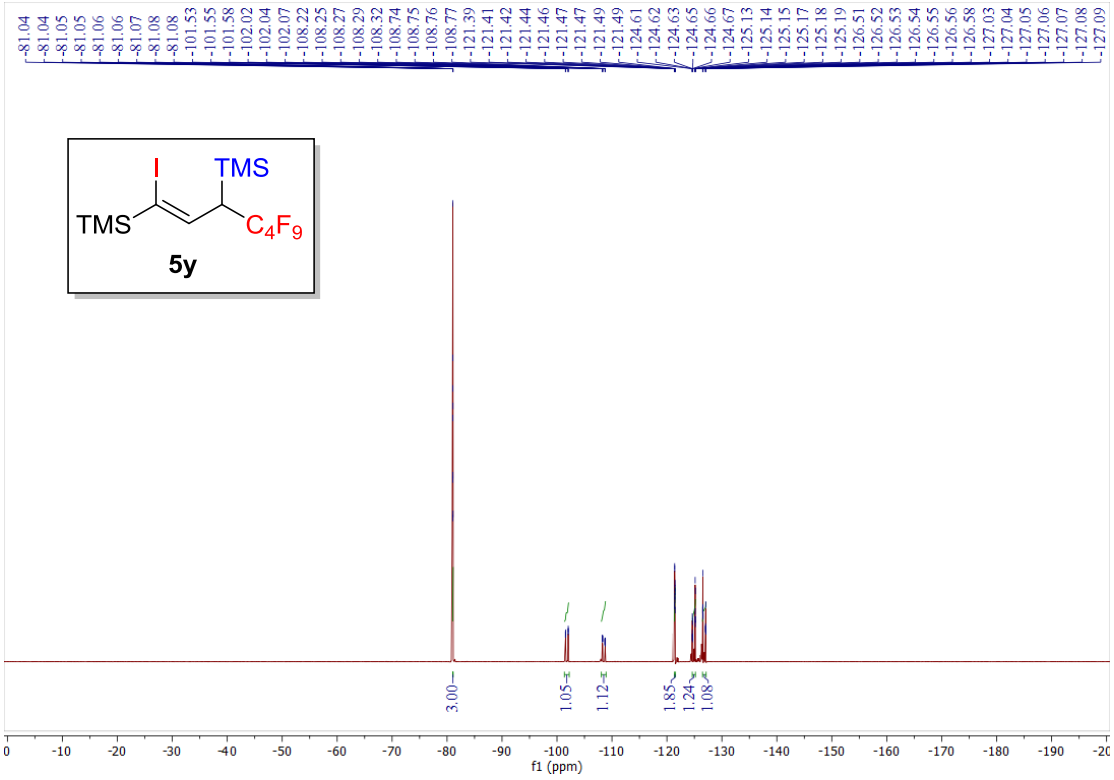

7.26
6.26
6.22
5.64
5.63
5.60
5.60
3.12
3.11
3.10
3.08
3.07
3.06
3.00
2.99
2.98
2.96
2.95
2.94
2.94
2.92
2.90
2.89
2.83
2.82
2.81
2.79
2.78
2.77
2.72
2.70
2.67
2.57
2.52
2.47
2.44
2.39
2.38
2.34
2.32
2.30
2.29
1.99
1.97
1.95
1.92
1.90
1.87
1.85
0.21
0.21
0.20
0.19
I
TMS
NC
2
C4F9
5x, (Z/E = 3)
0.32
1.00
1.07
0.44
2.01
0.55
2.76
2.76
8.80
2.77
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

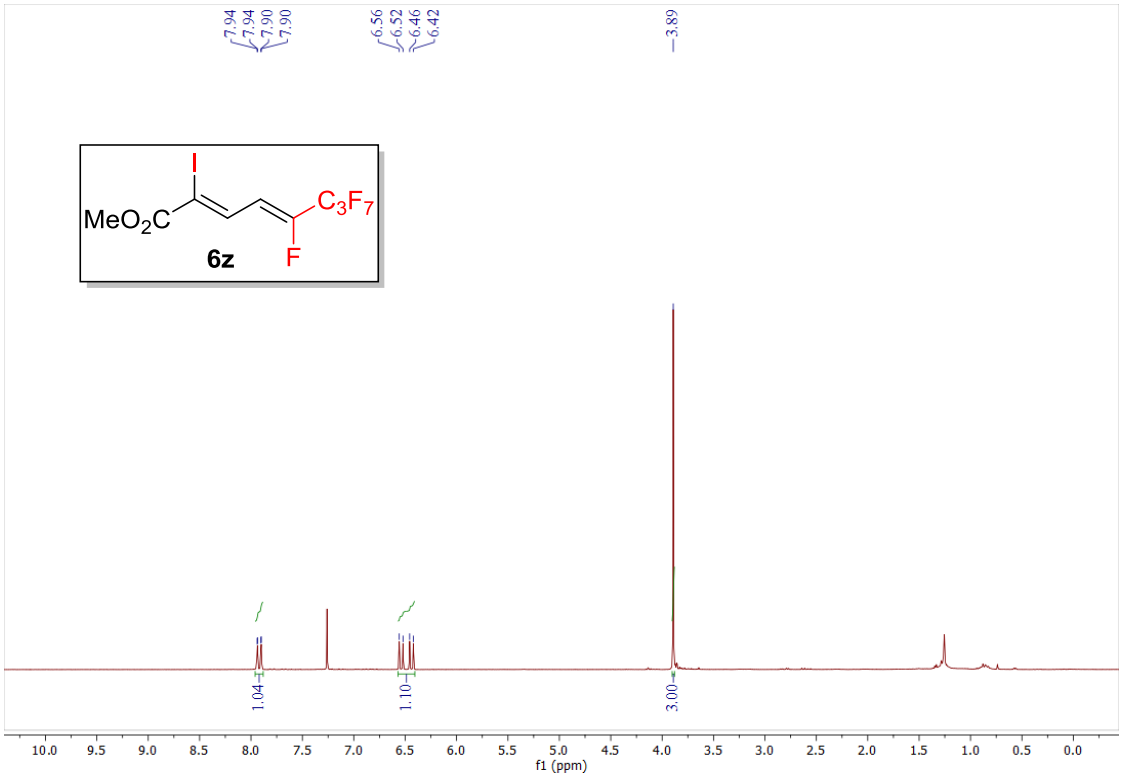

129.38
129.20
118.86
108.41
77.42
77.00
76.58
43.55
42.63
42.30
42.19
41.86
36.59
25.60
24.95
16.07
15.47
-1.02
-1.04
-1.45
-1.47
I
TMS
NC
2
C4F9
5x, (Z/E = 3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

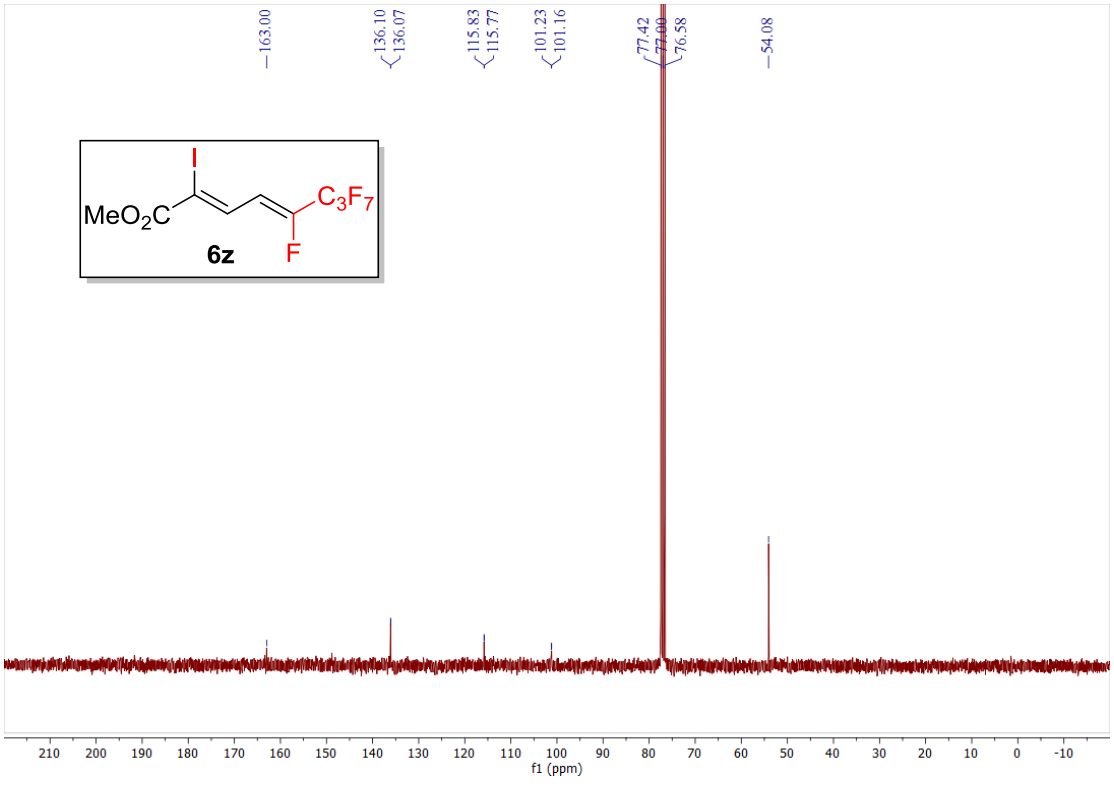

I
TMS
NC
2
C4F9
5x, (Z/E = 3)
f1 (ppm)

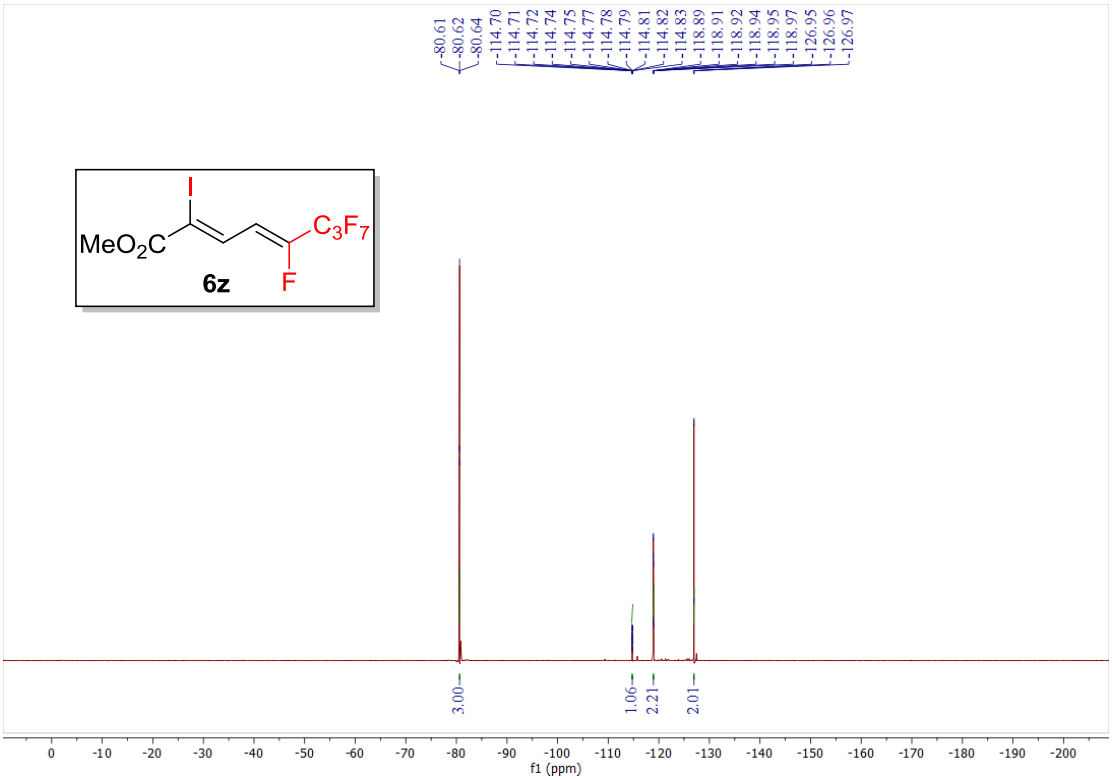

I
TMS
TMS
C4F9
5y
f1 (ppm)

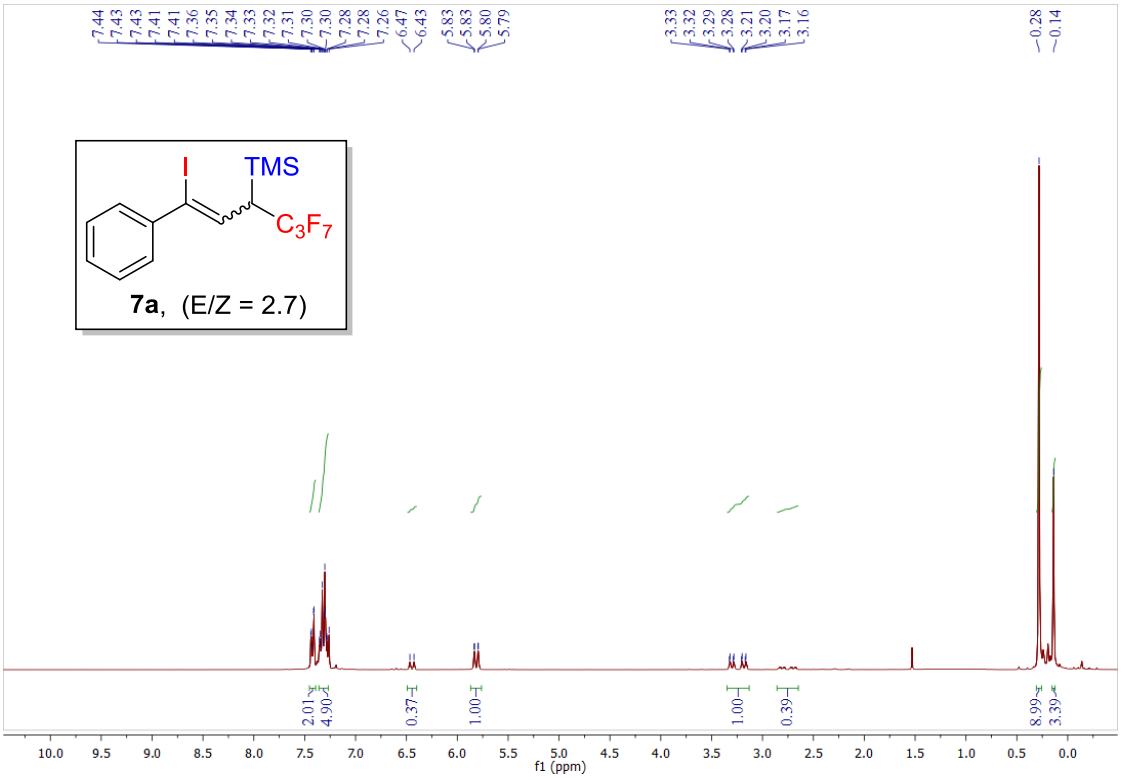

138.25
138.09
115.69
77.42
77.00
76.58
45.26
44.94
44.84
44.51
1.00
1.02
1.47
I
TMS
TMS
C_4F_9
5y
f1 (ppm)

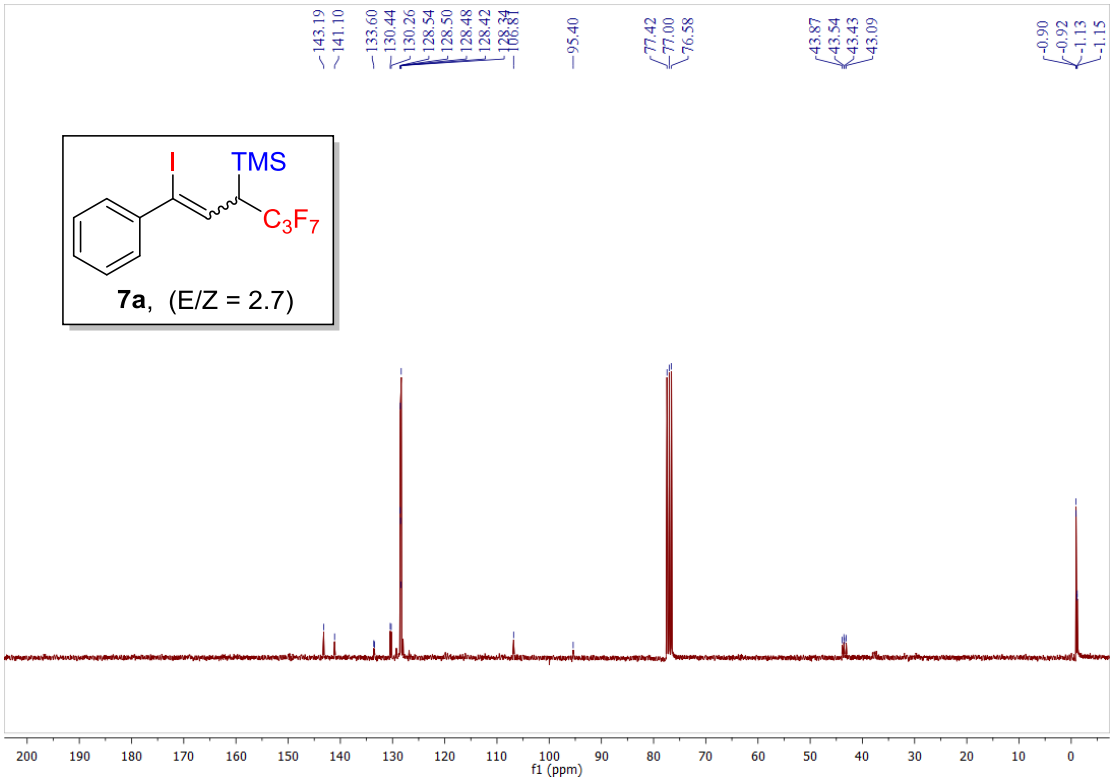

-81.04
-81.04
-81.05
-81.05
-81.06
-81.06
-81.07
-81.08
-81.08
-101.53
-101.55
-101.58
-102.02
-102.04
-102.07
-108.22
-108.25
-108.27
-108.29
-108.32
-108.74
-108.75
-108.76
-108.77
-121.39
-121.41
-121.42
-121.44
-121.46
-121.47
-121.47
-121.49
-121.49
-124.61
-124.62
-124.63
-124.65
-124.66
-124.67
-125.13
-125.14
-125.15
-125.17
-125.18
-125.19
-126.51
-126.52
-126.53
-126.54
-126.55
-126.56
-126.58
-127.03
-127.04
-127.05
-127.06
-127.07
-127.08
-127.09
I
TMS
TMS
C_4F_9
5y
3.00
1.05
1.12
1.85
1.24
1.08
f1 (ppm)

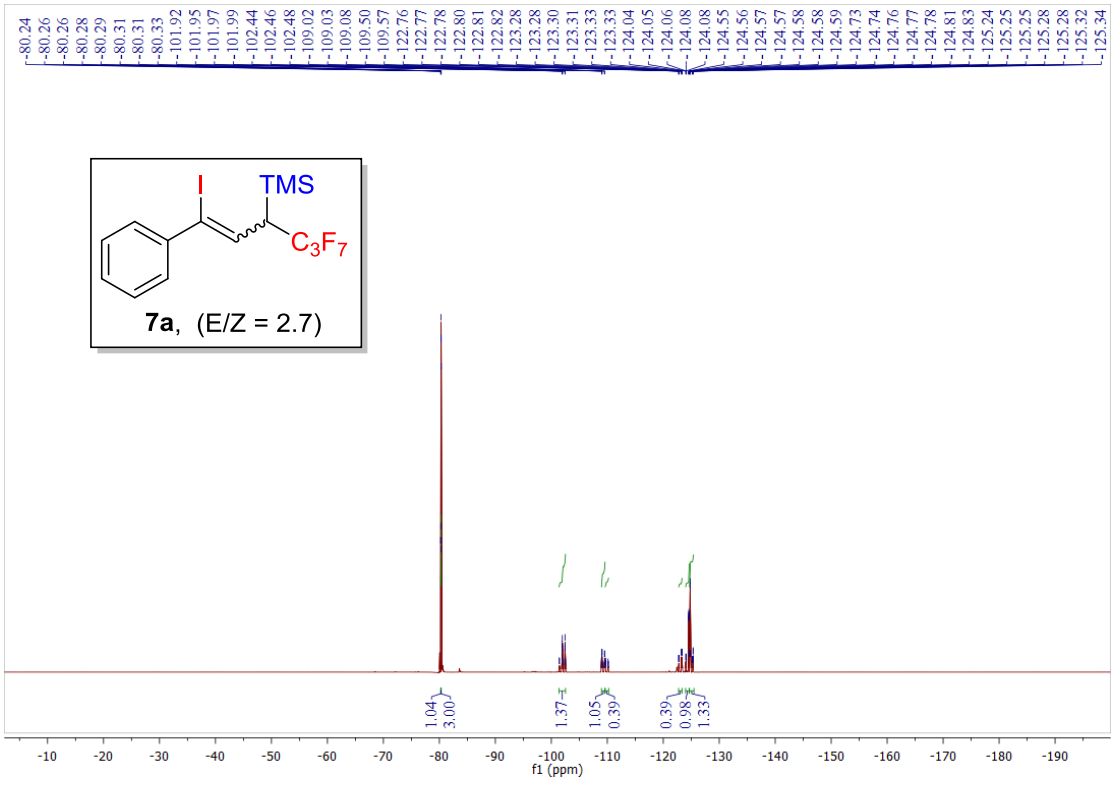

7.94
7.94
7.90
7.90
6.56
6.52
6.46
6.42
3.89
I
MeO2C
C3F7
F
6z
1.04
1.10
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

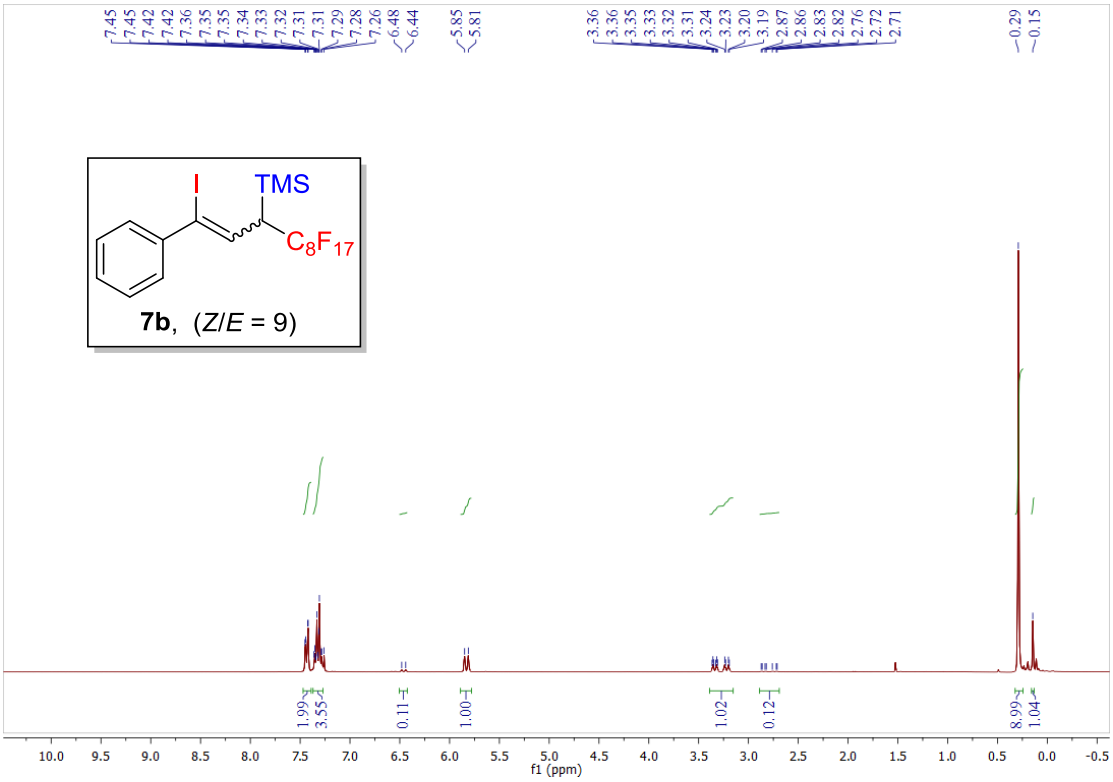

163.00
136.10
136.07
115.83
115.77
101.23
101.16
77.42
77.00
76.58
54.08
I
MeO2C
C3F7
F
6z
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

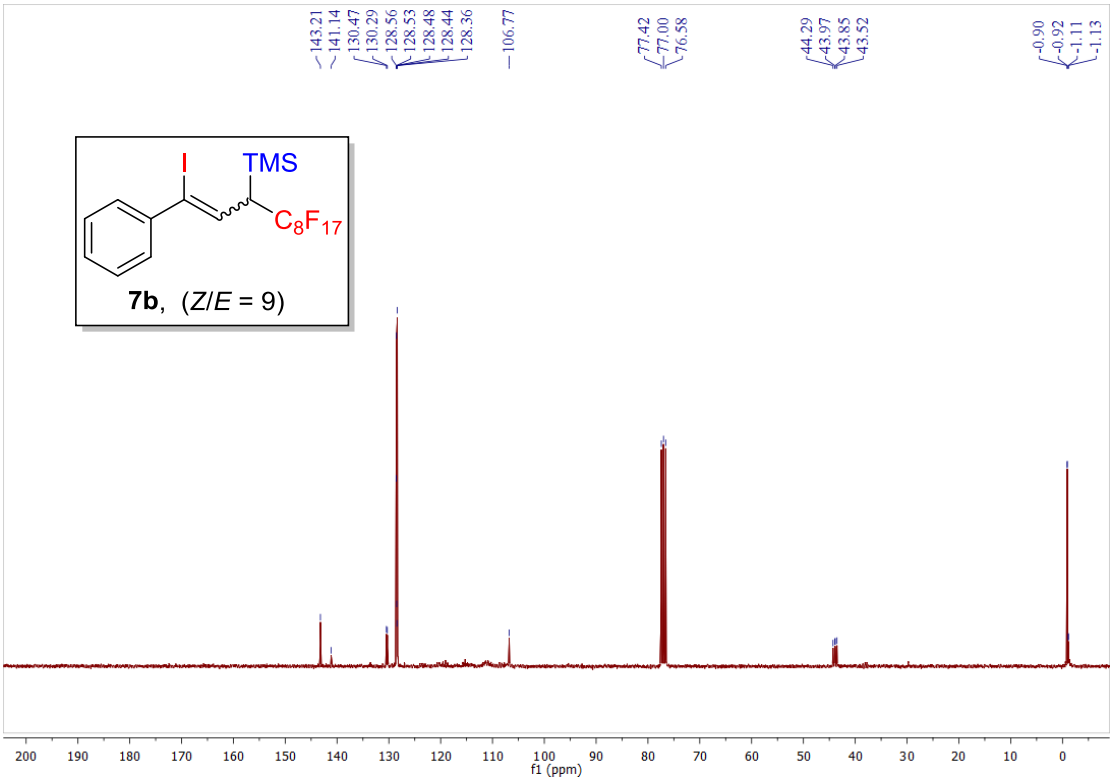

-80.61
-80.62
-80.64
-114.70
-114.71
-114.72
-114.74
-114.75
-114.77
-114.78
-114.79
-114.81
-114.82
-114.83
-118.89
-118.91
-118.92
-118.94
-118.95
-118.97
-126.95
-126.96
-126.97
I
MeO2C
C3F7
F
6z
3.00
1.06
2.21
2.01
f1 (ppm)

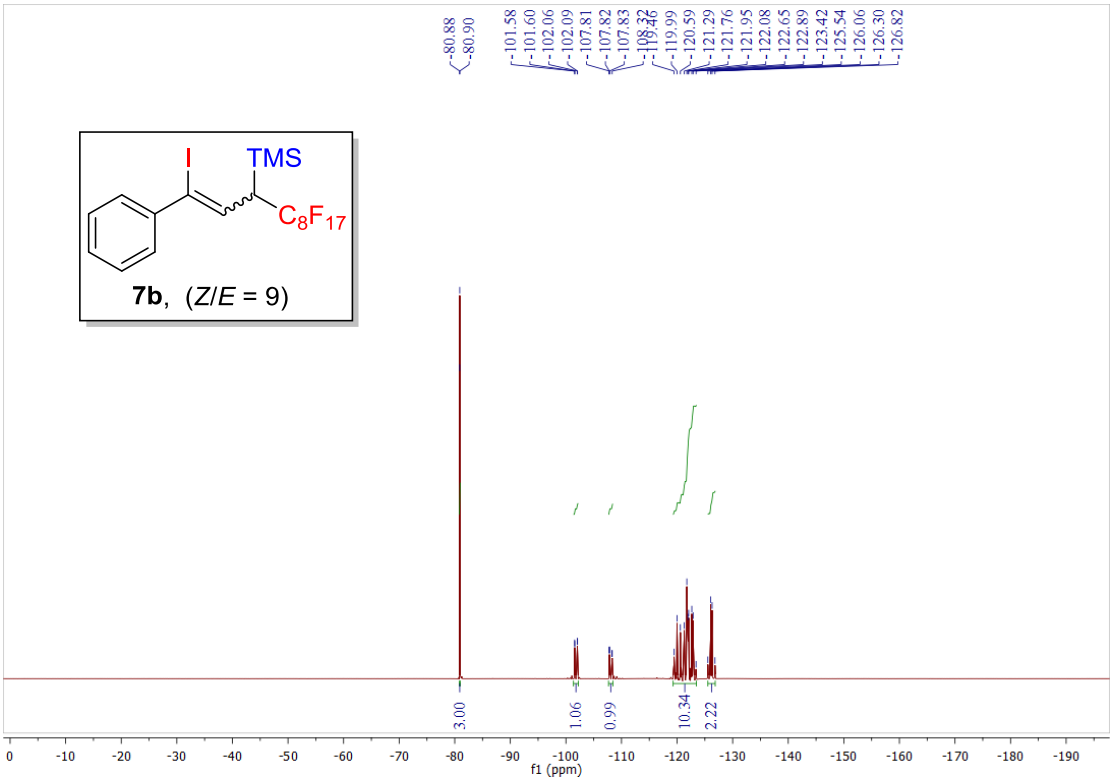

7.44
7.43
7.43
7.41
7.41
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.28
7.28
7.26
6.47
6.43
5.83
5.83
5.80
5.79
3.33
3.32
3.29
3.28
3.21
3.20
3.17
3.16
0.28
0.14
I
TMS
C3F7
7a, (E/Z = 2.7)
2.01
4.90
0.37
1.00
1.00
0.39
8.99
3.39
f1 (ppm)

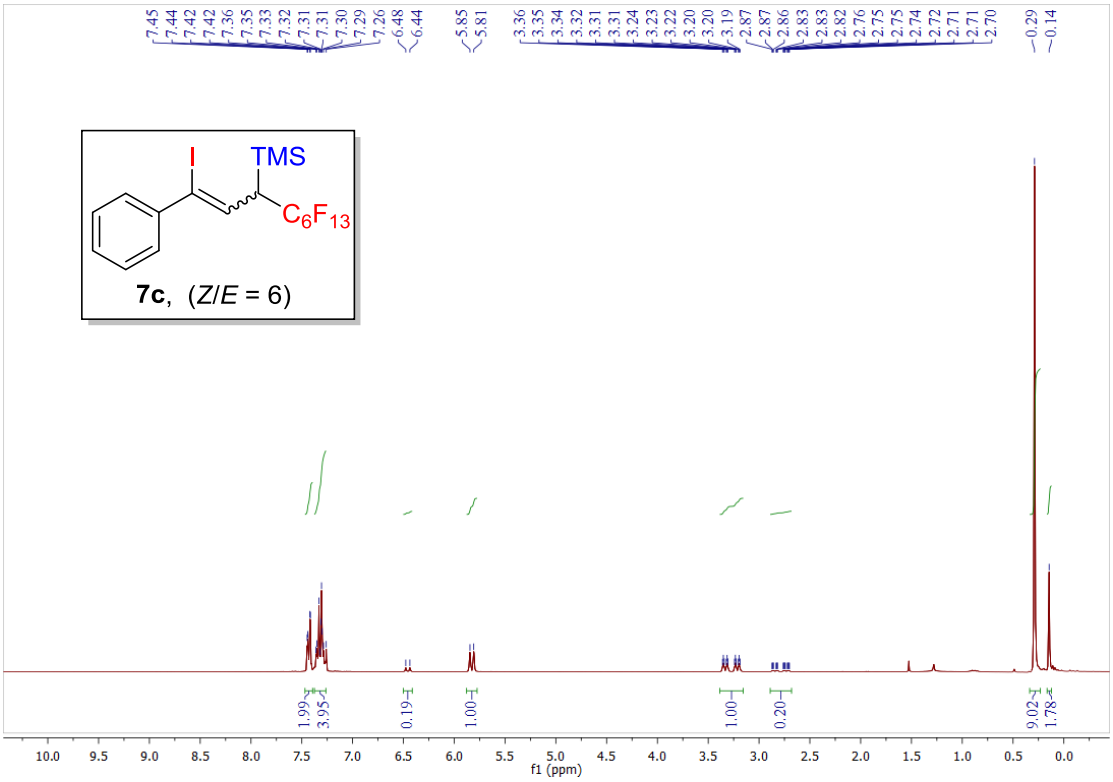

143.19
141.10
133.60
130.44
130.26
128.54
128.50
128.48
128.42
128.34
128.27
95.40
77.42
77.00
76.58
43.87
43.54
43.43
43.09
-0.90
-0.92
-1.13
-1.15
I
TMS
C3F7
7a, (E/Z = 2.7)
f1 (ppm)

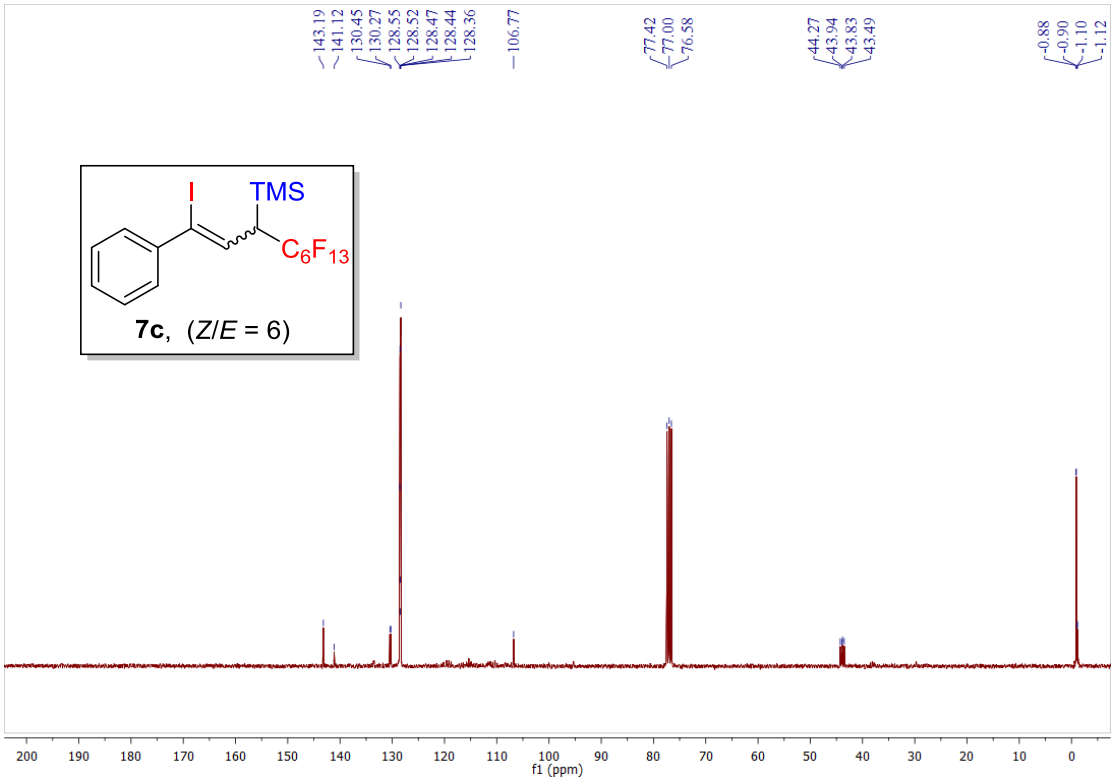

I
TMS
C3F7
7a, (E/Z = 2.7)
1.04
3.00
1.37
1.05
0.39
0.39
0.98
1.33
f1 (ppm)

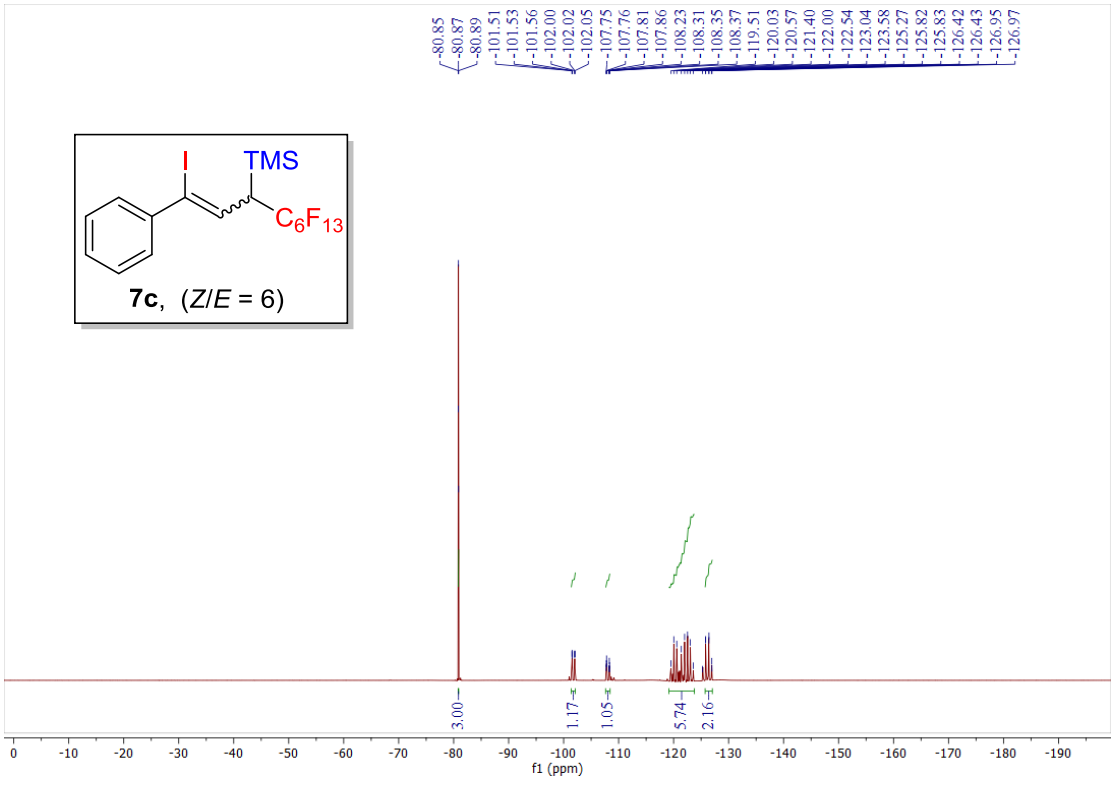

I
TMS
C_8F_{17}
7b, (Z/E = 9)
f1 (ppm)

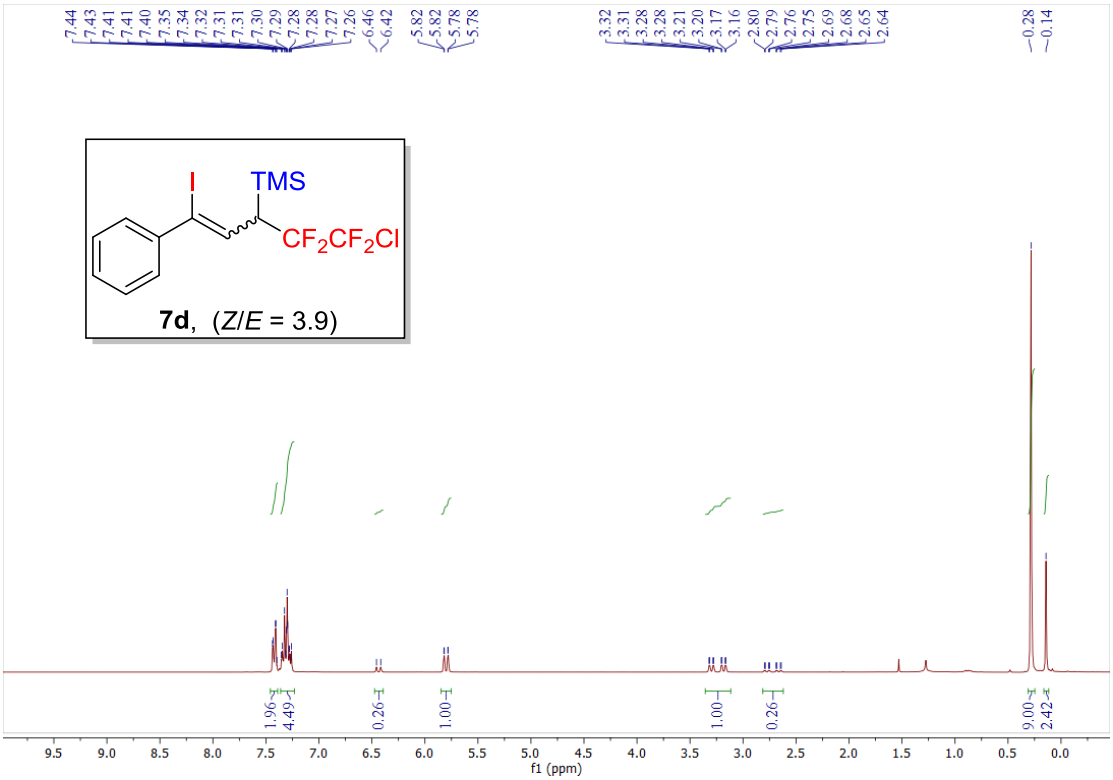

I
TMS
C_8F_{17}
7b, (Z/E = 9)
f1 (ppm)

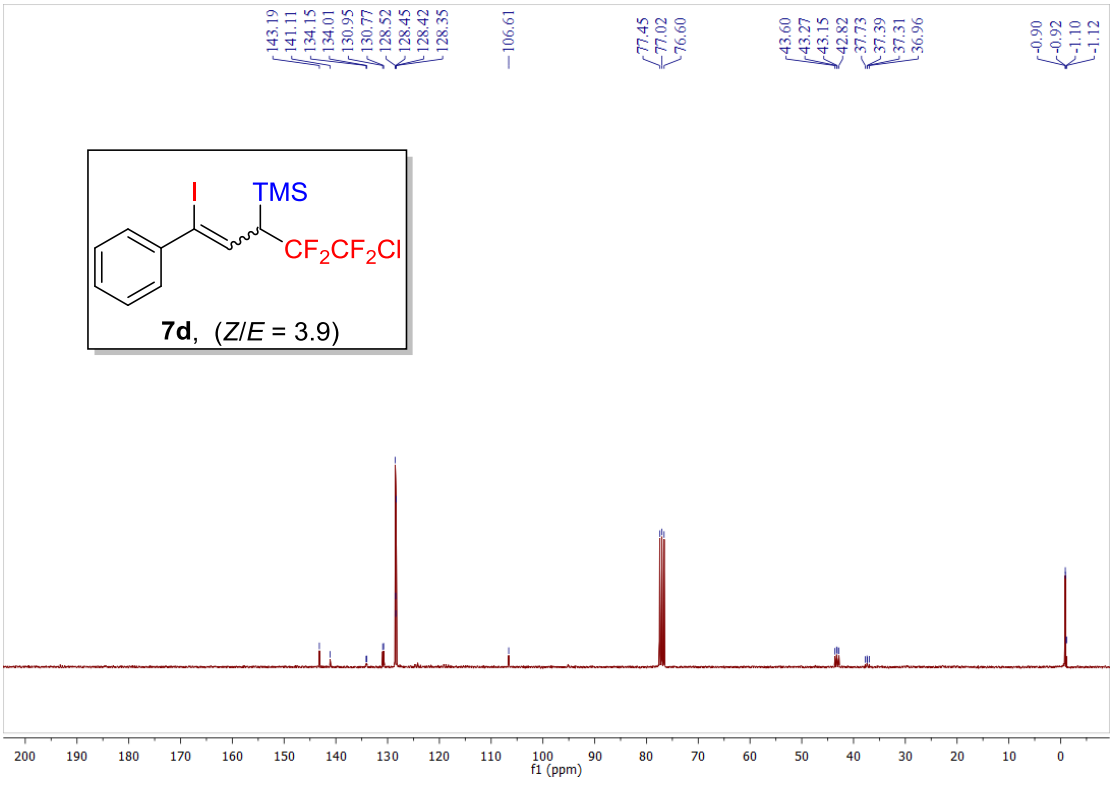

I
TMS
C_8F_{17}
7b, (Z/E = 9)
f1 (ppm)

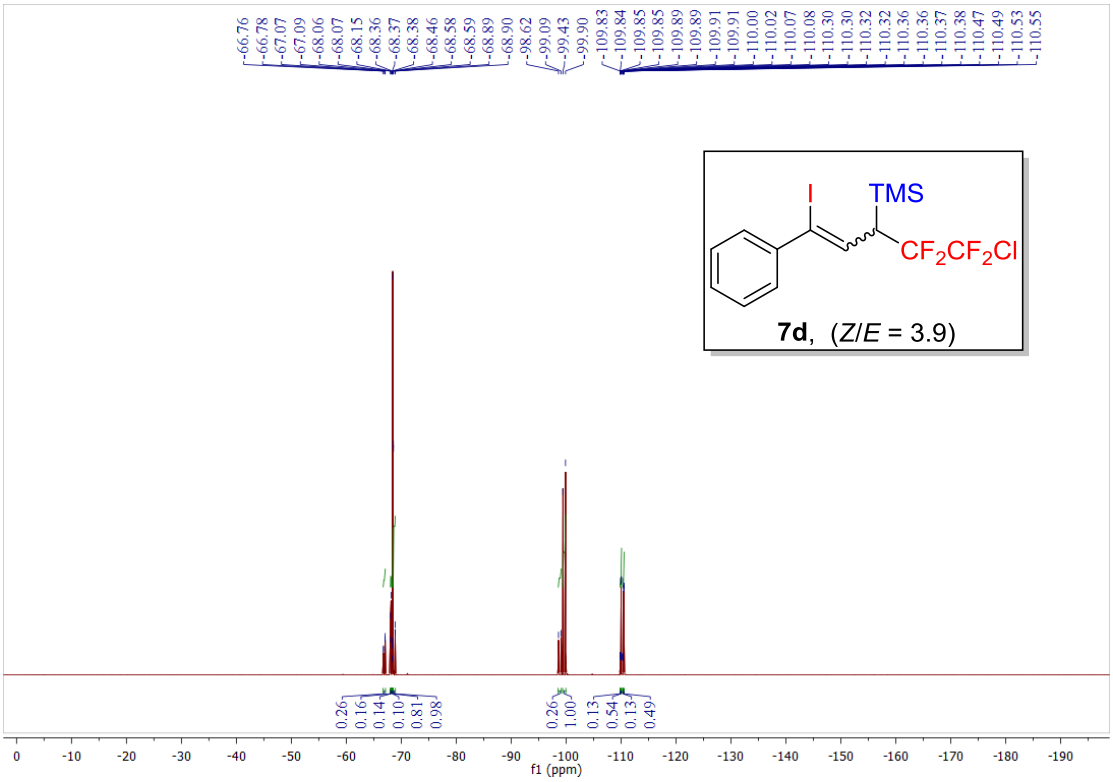

I
TMS
C_6F_{13}
7c, (Z/E = 6)
f1 (ppm)

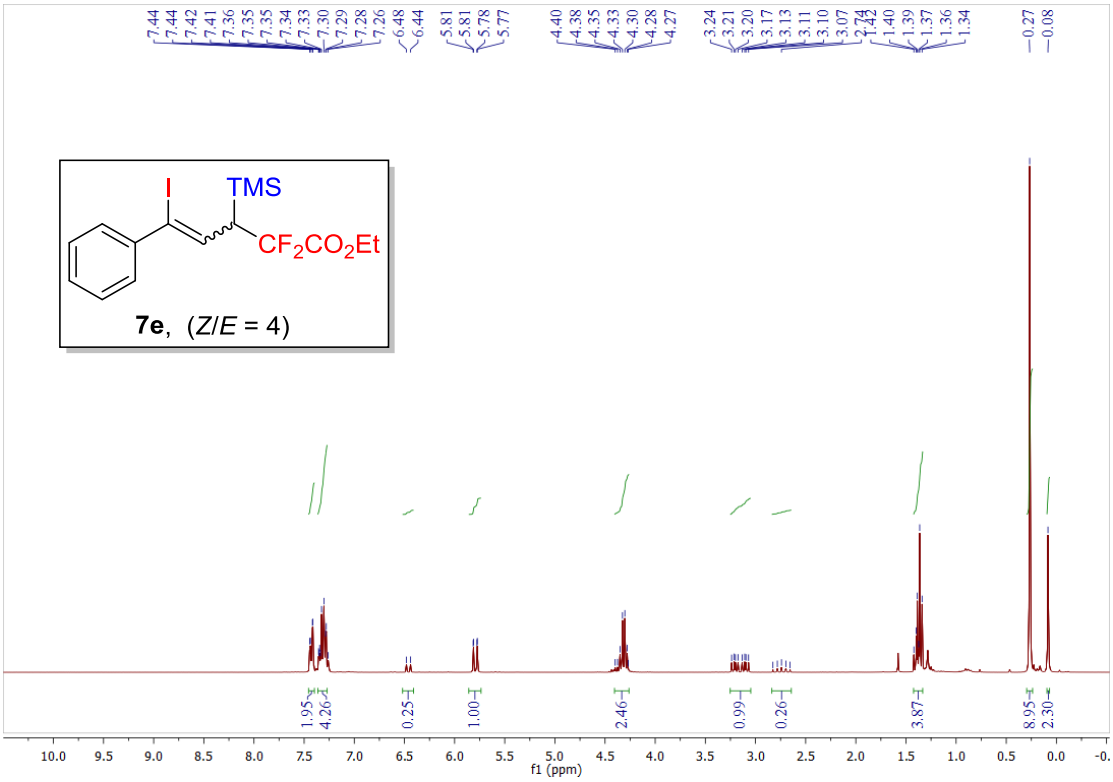

143.19
141.12
130.45
130.27
128.55
128.52
128.47
128.44
128.36
106.77
77.42
77.00
76.58
44.27
43.94
43.83
43.49
-0.88
-0.90
-1.10
-1.12
I
TMS
C6F13
7c, (Z/E = 6)
f1 (ppm)

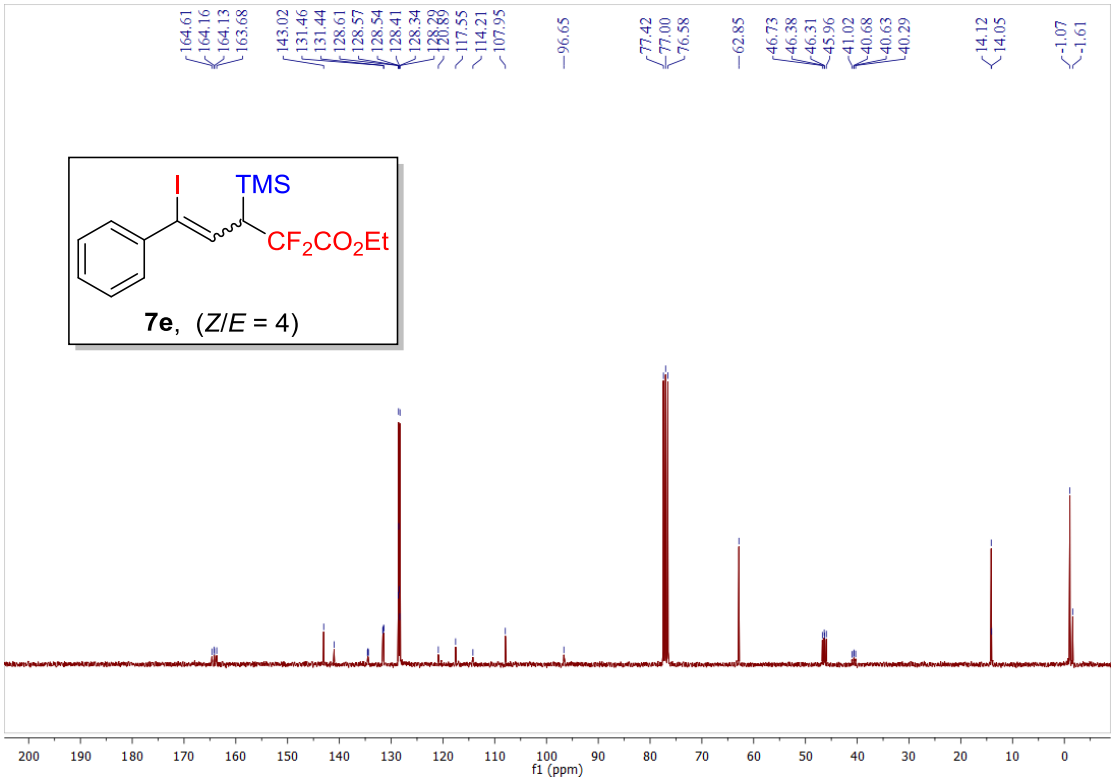

-80.85
-80.87
-80.89
-101.51
-101.53
-101.56
-102.00
-102.02
-102.05
-107.75
-107.76
-107.81
-107.86
-108.23
-108.31
-108.35
-108.37
-119.51
-120.03
-120.57
-121.40
-122.00
-122.54
-123.04
-123.58
-125.27
-125.82
-125.83
-126.42
-126.43
-126.95
-126.97
I
TMS
C6F13
7c, (Z/E = 6)
3.00
1.17
1.05
5.74
2.16
f1 (ppm)

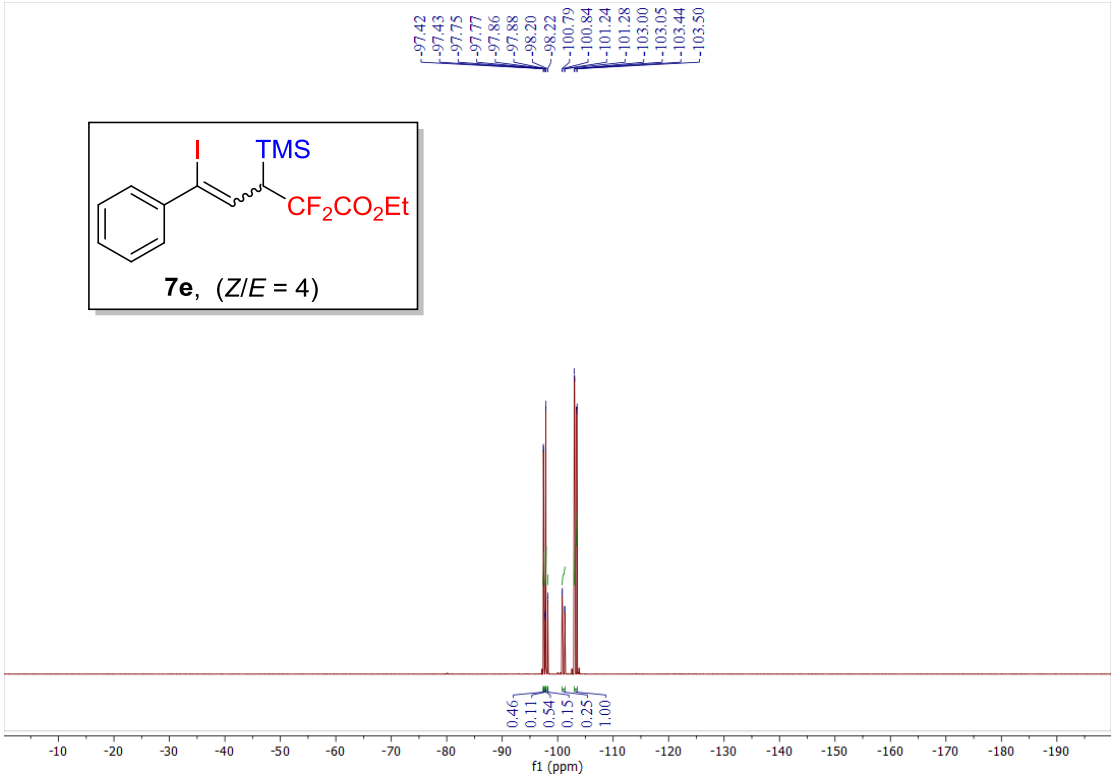

7.44
7.43
7.41
7.41
7.40
7.35
7.34
7.32
7.31
7.31
7.30
7.29
7.28
7.28
7.27
7.26
6.46
6.42
5.82
5.82
5.78
5.78
3.32
3.31
3.28
3.28
3.21
3.20
3.17
3.16
2.80
2.79
2.76
2.75
2.69
2.68
2.65
2.64
0.28
0.14
I
TMS
CF2CF2Cl
7d, (Z/E = 3.9)
1.96
4.49
0.26
1.00
1.00
0.26
9.00
2.42
f1 (ppm)

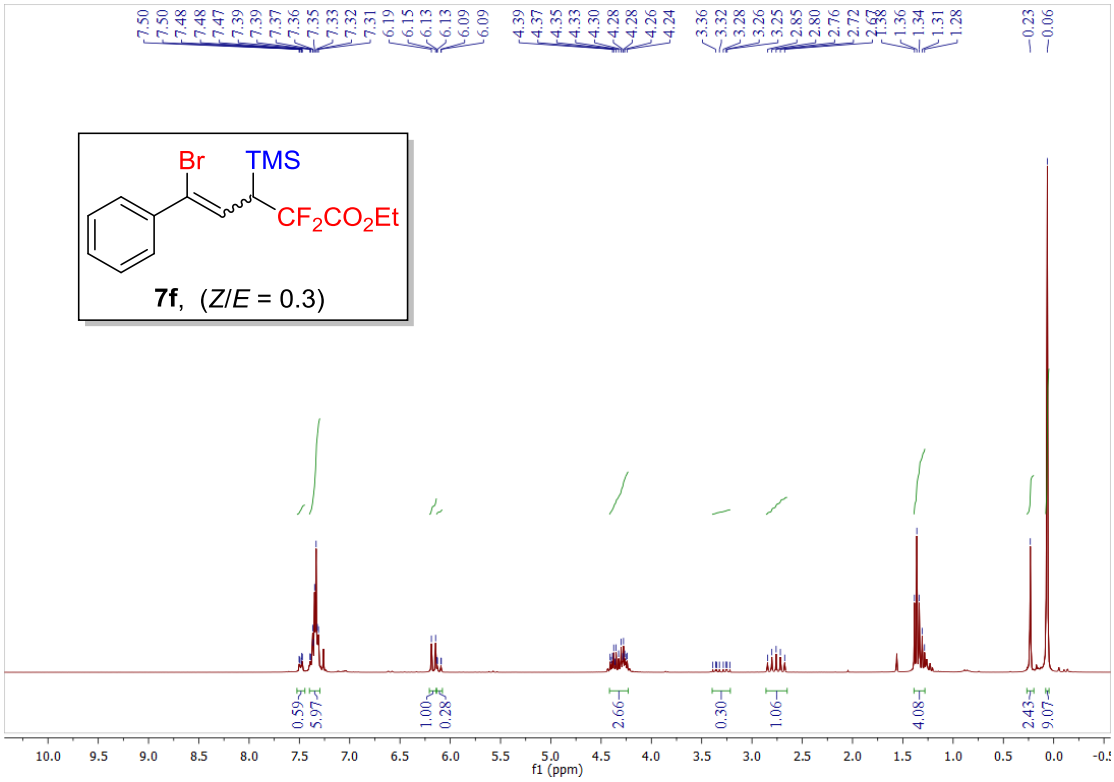

143.19
141.11
134.15
134.01
130.95
130.77
128.52
128.45
128.42
128.35
106.61
77.45
77.02
76.60
43.60
43.27
43.15
42.82
37.73
37.39
37.31
36.96
-0.90
-0.92
-1.10
-1.12
I
TMS
CF2CF2Cl
7d, (Z/E = 3.9)
f1 (ppm)

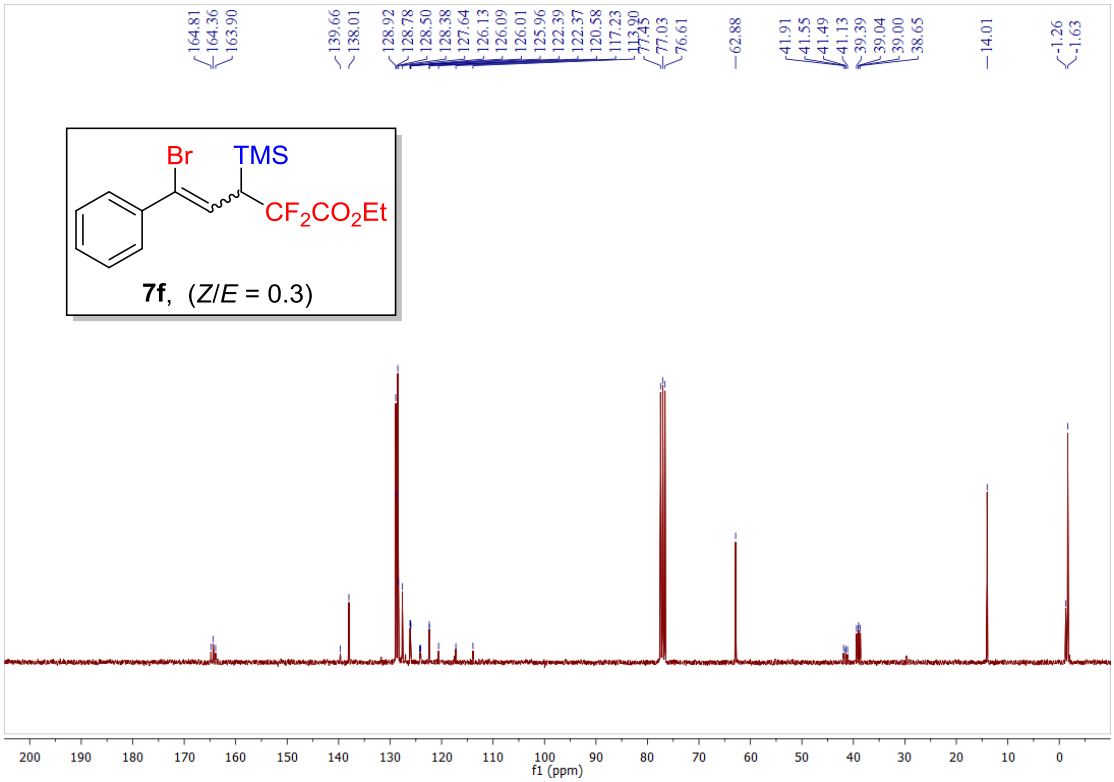

I
TMS
CF2CF2Cl
7d, (Z/E = 3.9)
f1 (ppm)

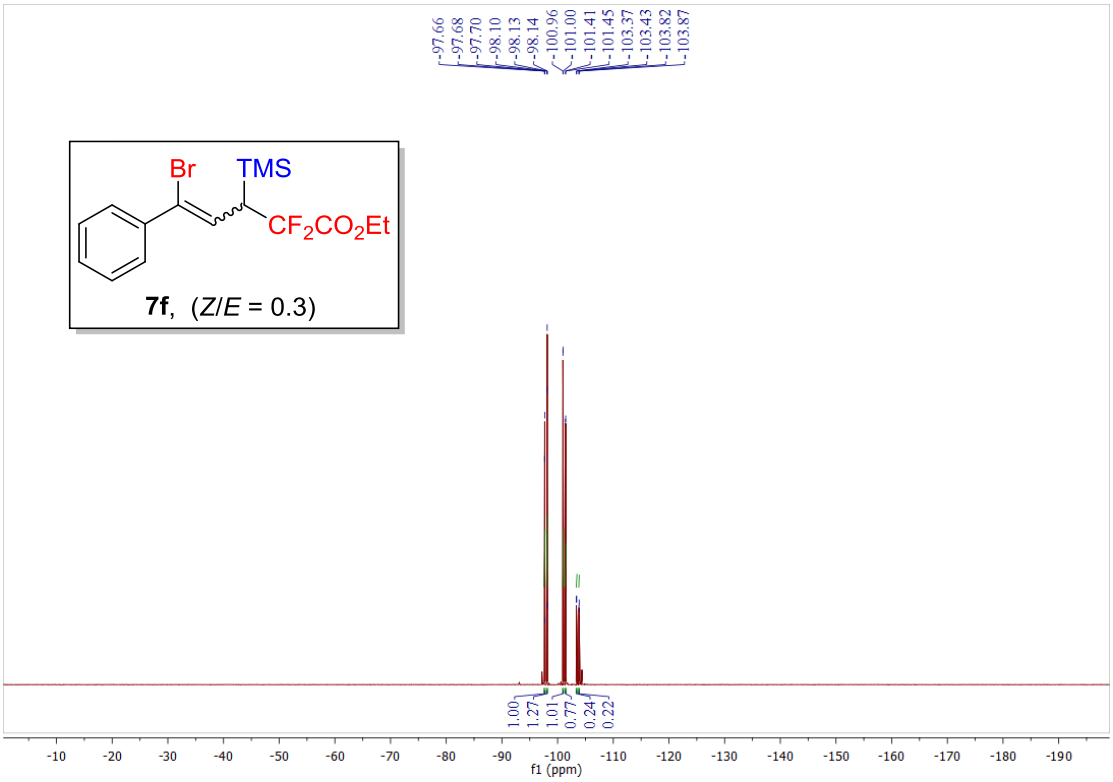

I
TMS
CF2CO2Et
7e, (Z/E = 4)
f1 (ppm)

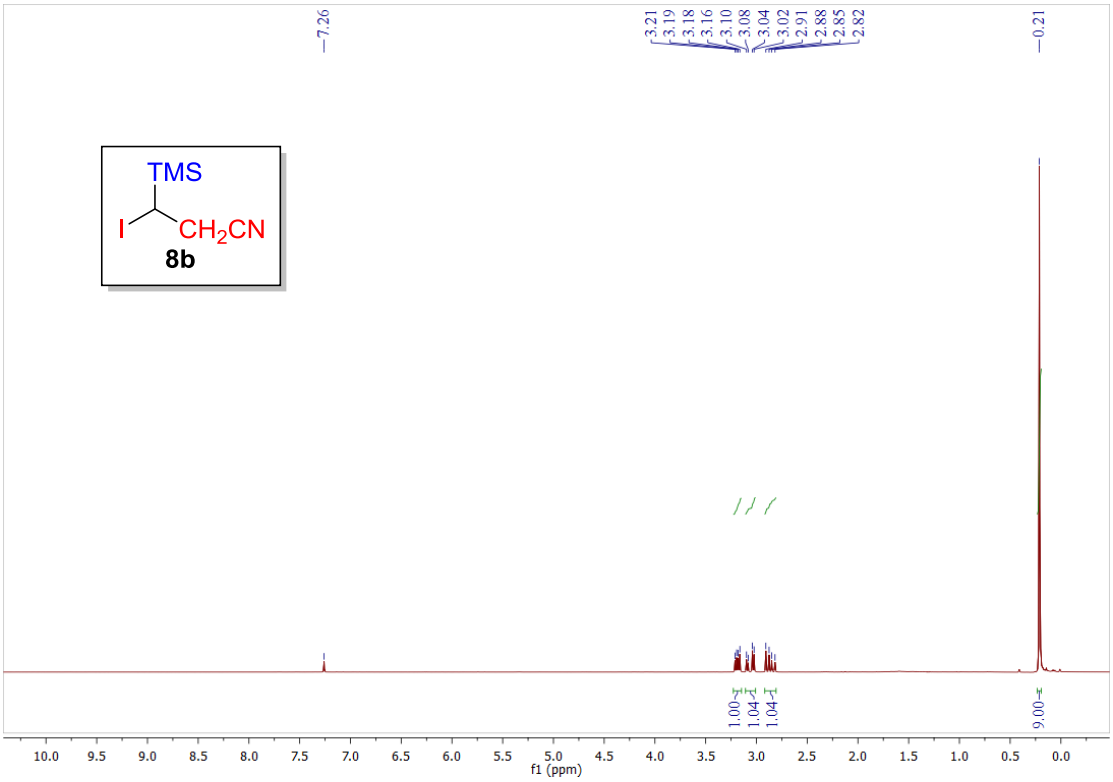

164.61
164.16
164.13
163.68
143.02
131.46
131.44
128.61
128.57
128.54
128.41
128.34
128.29
120.89
117.55
114.21
107.95
96.65
77.42
77.00
76.58
62.85
46.73
46.38
46.31
45.96
41.02
40.68
40.63
40.29
14.12
14.05
-1.07
-1.61
I
TMS
CF2CO2Et
7e, (Z/E = 4)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

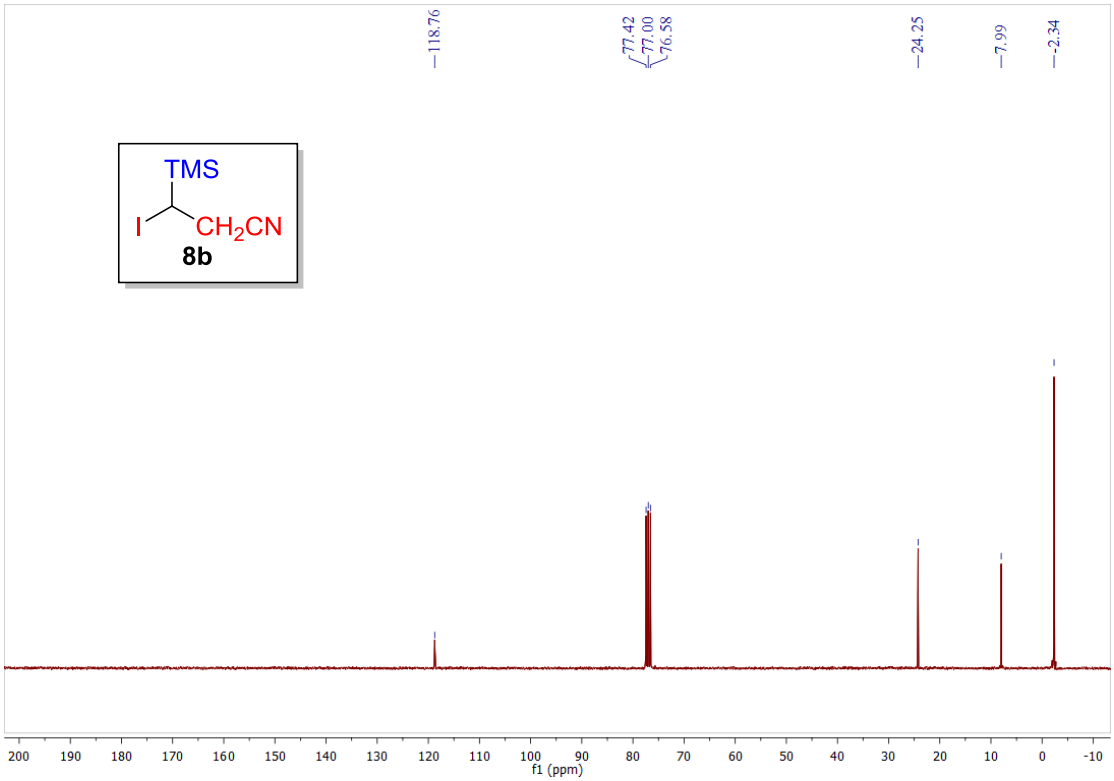

-97.42
-97.43
-97.75
-97.77
-97.86
-97.88
-98.20
-98.22
-100.79
-100.84
-101.24
-101.28
-103.00
-103.05
-103.44
-103.50
I
TMS
CF2CO2Et
7e, (Z/E = 4)
0.46
0.11
0.54
0.15
0.25
1.00
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

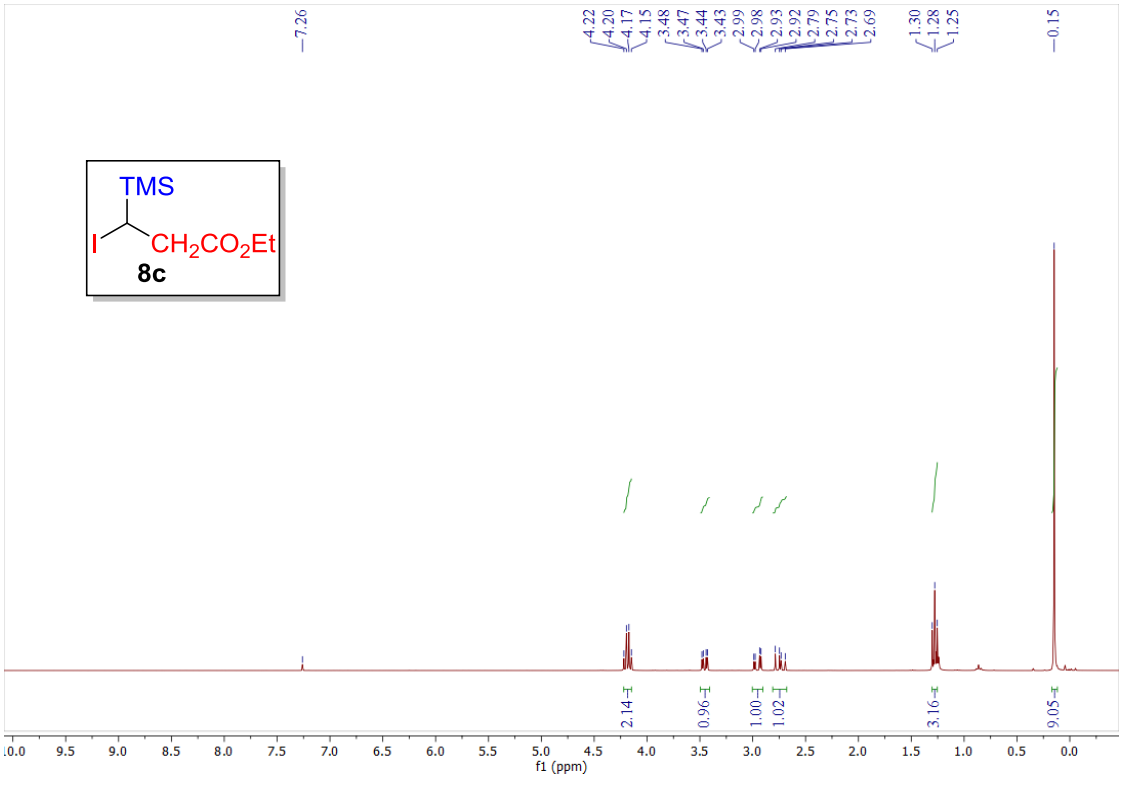

Br
TMS
CF2CO2Et
7f, (Z/E = 0.3)
f1 (ppm)

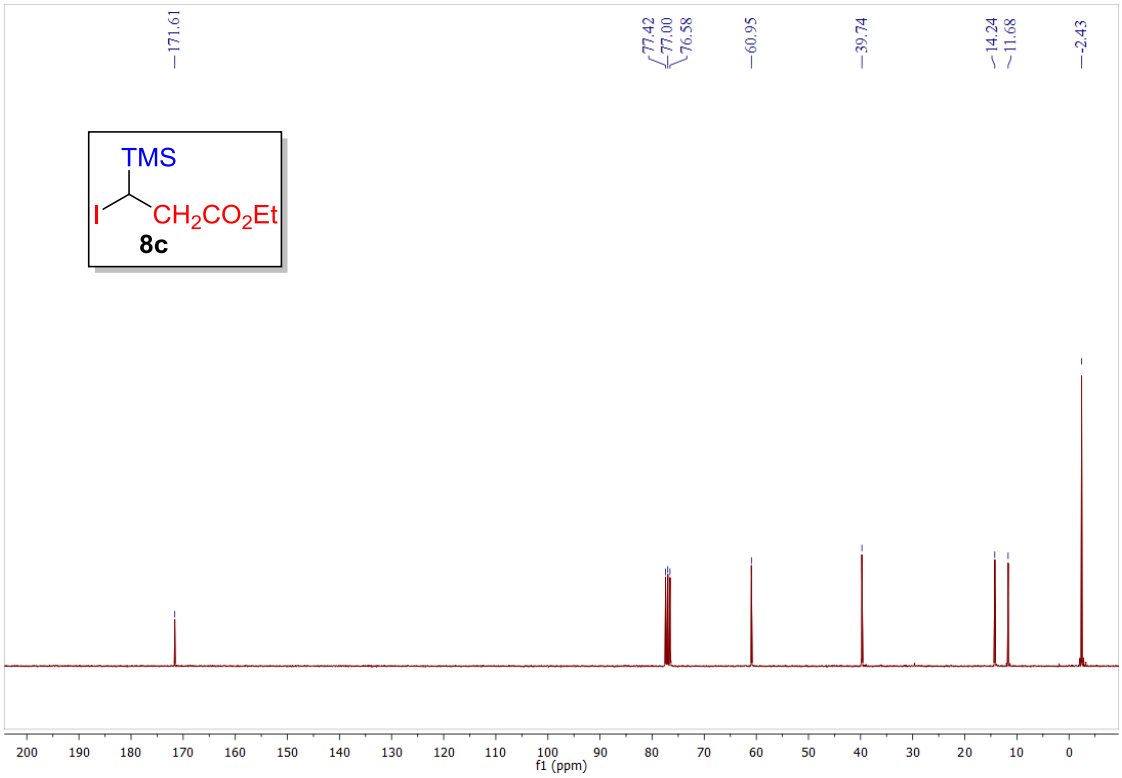

Br
TMS
CF2CO2Et
7f, (Z/E = 0.3)
f1 (ppm)

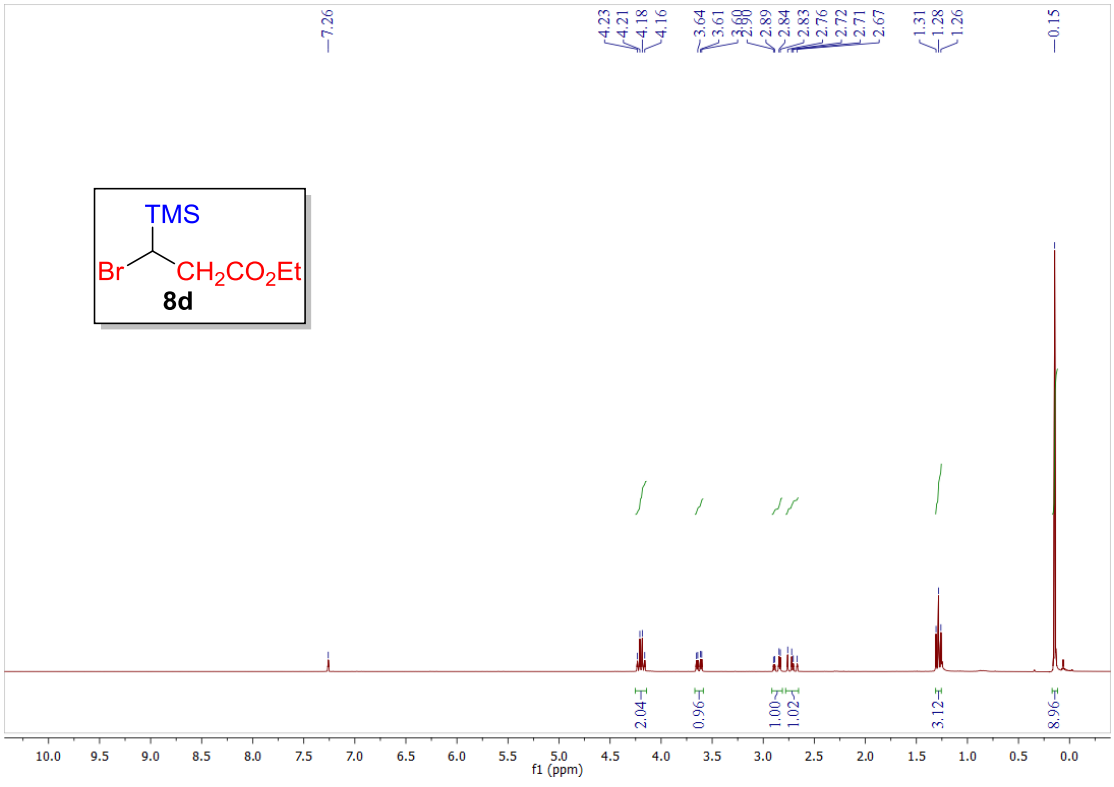

-97.66
-97.68
-97.70
-98.10
-98.13
-98.14
-100.96
-101.00
-101.41
-101.45
-103.37
-103.43
-103.82
-103.87
Br
TMS
CF2CO2Et
7f, (Z/E = 0.3)
1.00
1.27
1.01
0.77
0.24
0.22
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

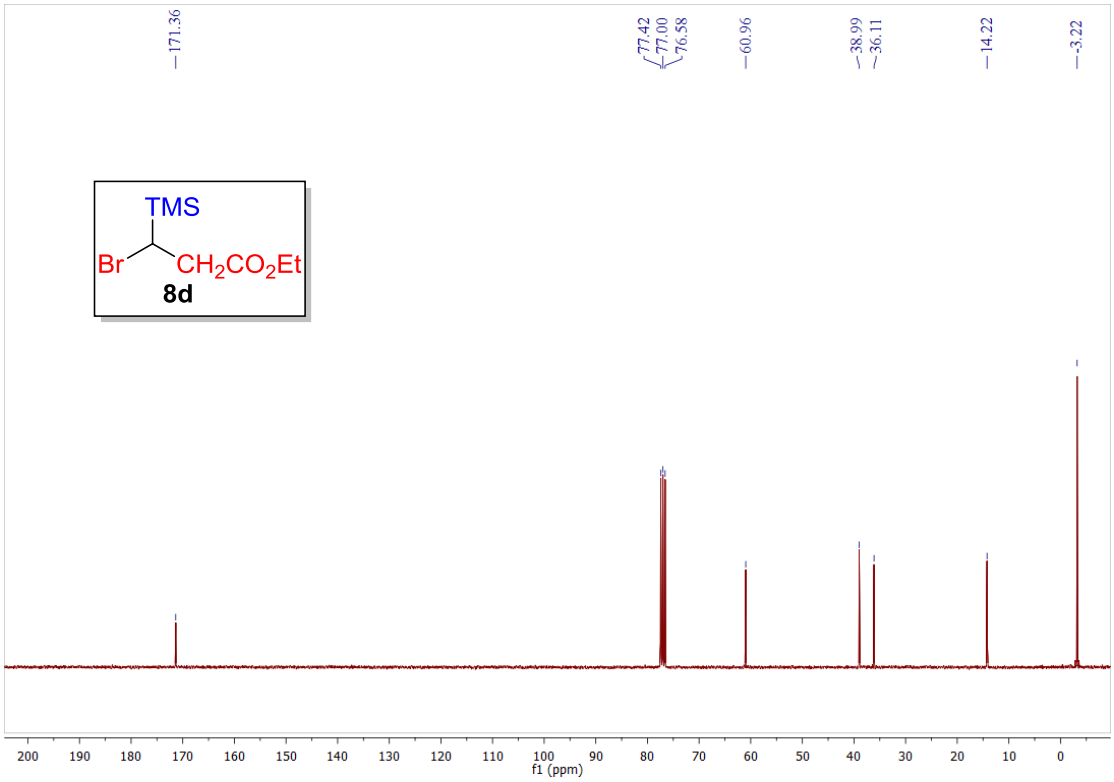

7.26
3.21
3.19
3.18
3.16
3.10
3.08
3.04
3.02
2.91
2.88
2.85
2.82
0.21
TMS
I
CH2CN
8b
1.00
1.04
1.04
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

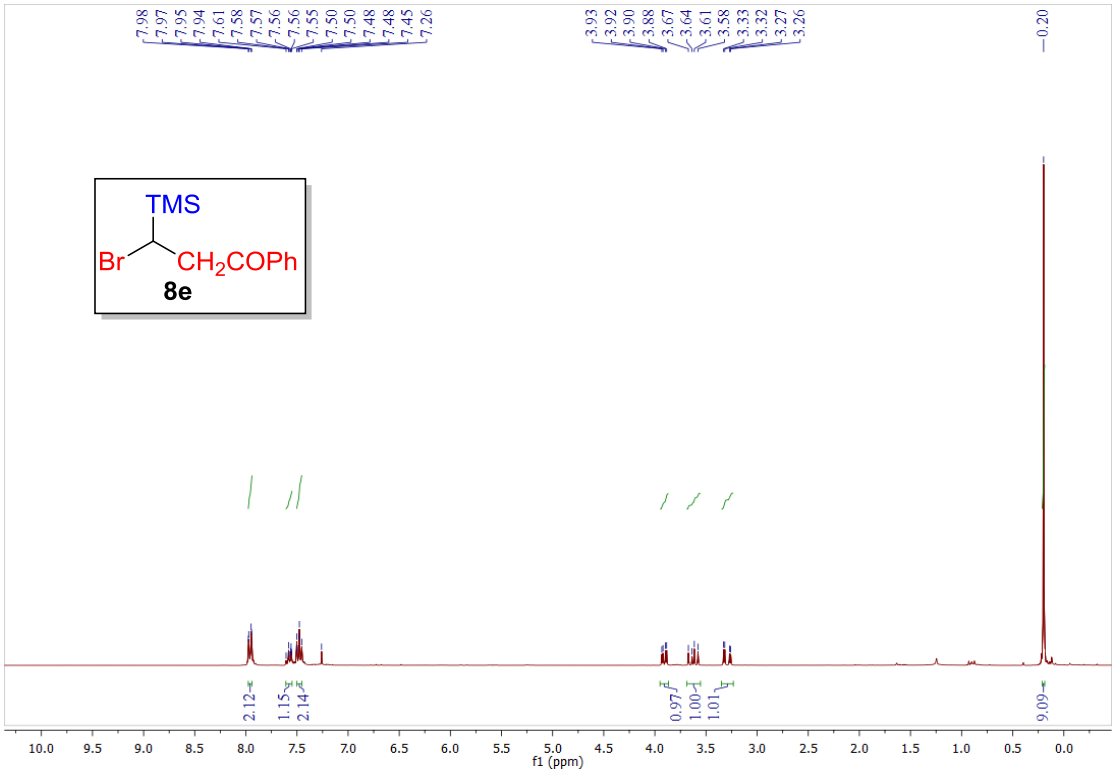

118.76
77.42
77.00
76.58
24.25
7.99
-2.34
TMS
I
CH2CN
8b
f1 (ppm)

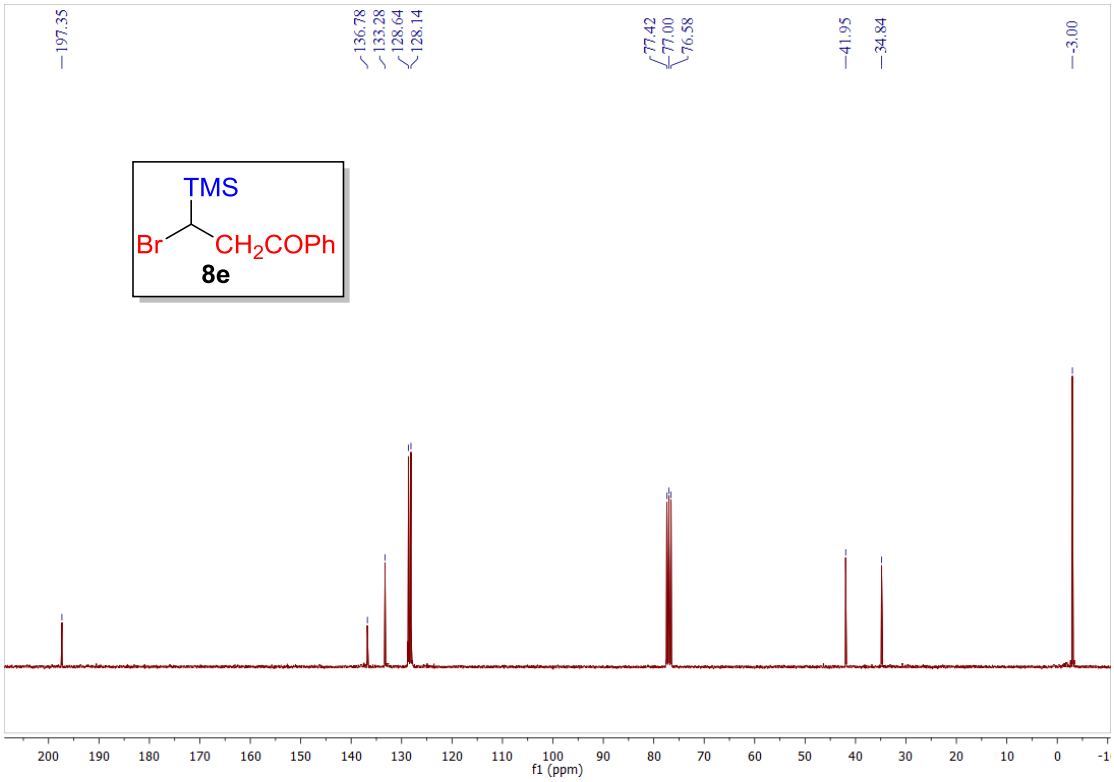

7.26
4.22
4.20
4.17
4.15
3.48
3.47
3.44
3.43
2.99
2.98
2.93
2.92
2.79
2.75
2.73
2.69
1.30
1.28
1.25
0.15
TMS
I
CH2CO2Et
8c
2.14
0.96
1.00
1.02
3.16
9.05
f1 (ppm)

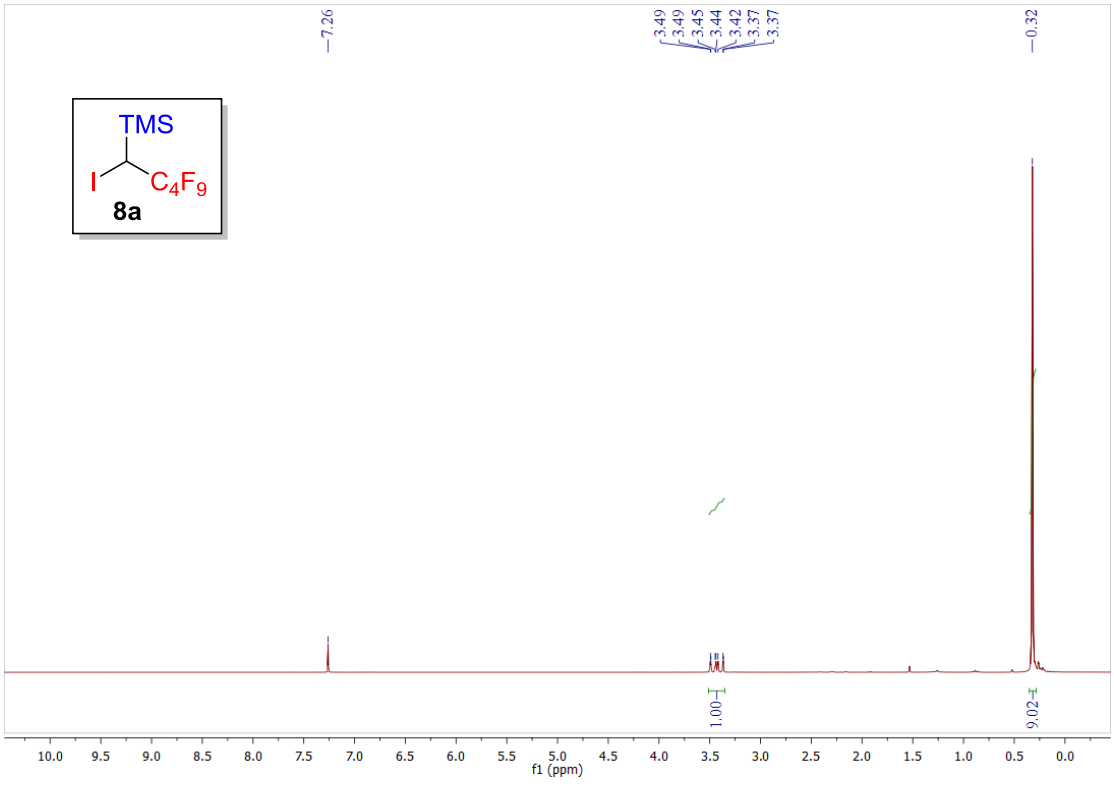

171.61
77.42
77.00
76.58
60.95
39.74
14.24
11.68
2.43
TMS
I
CH2CO2Et
8c
f1 (ppm)

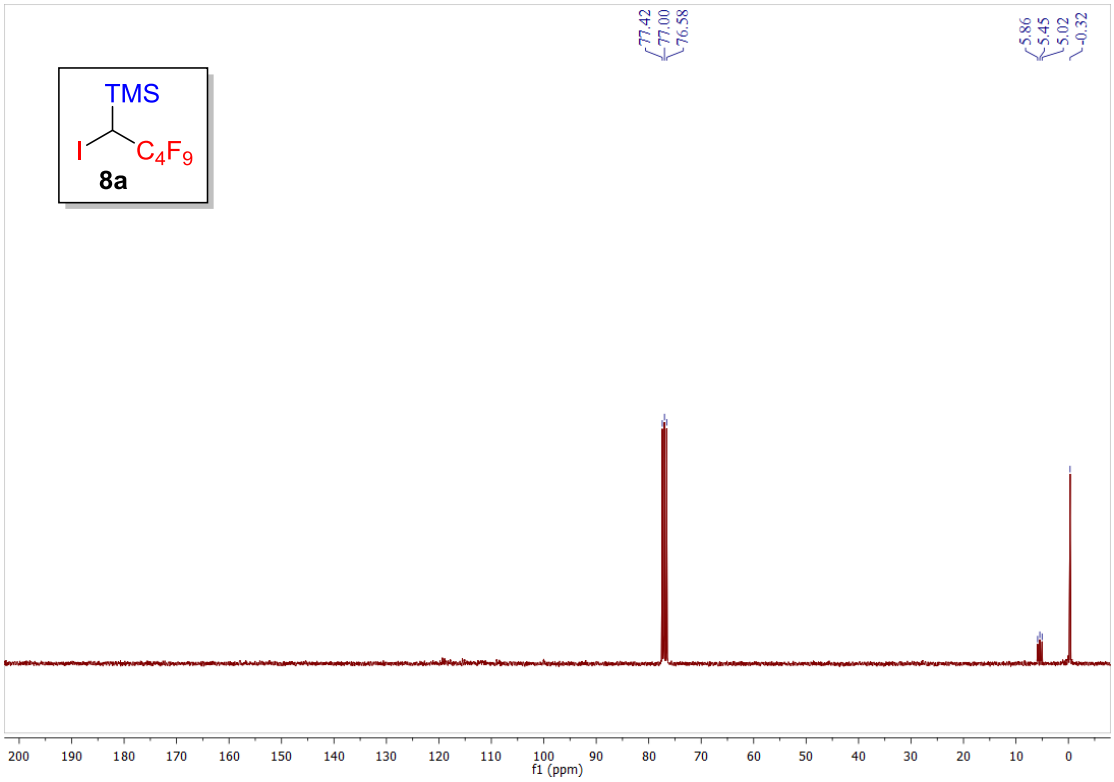

7.26
4.23
4.21
4.18
4.16
3.64
3.61
2.89
2.84
2.83
2.76
2.72
2.71
2.67
1.31
1.28
1.26
0.15
TMS
Br
CH2CO2Et
8d
2.04
0.96
1.00
1.02
3.12
8.96
f1 (ppm)

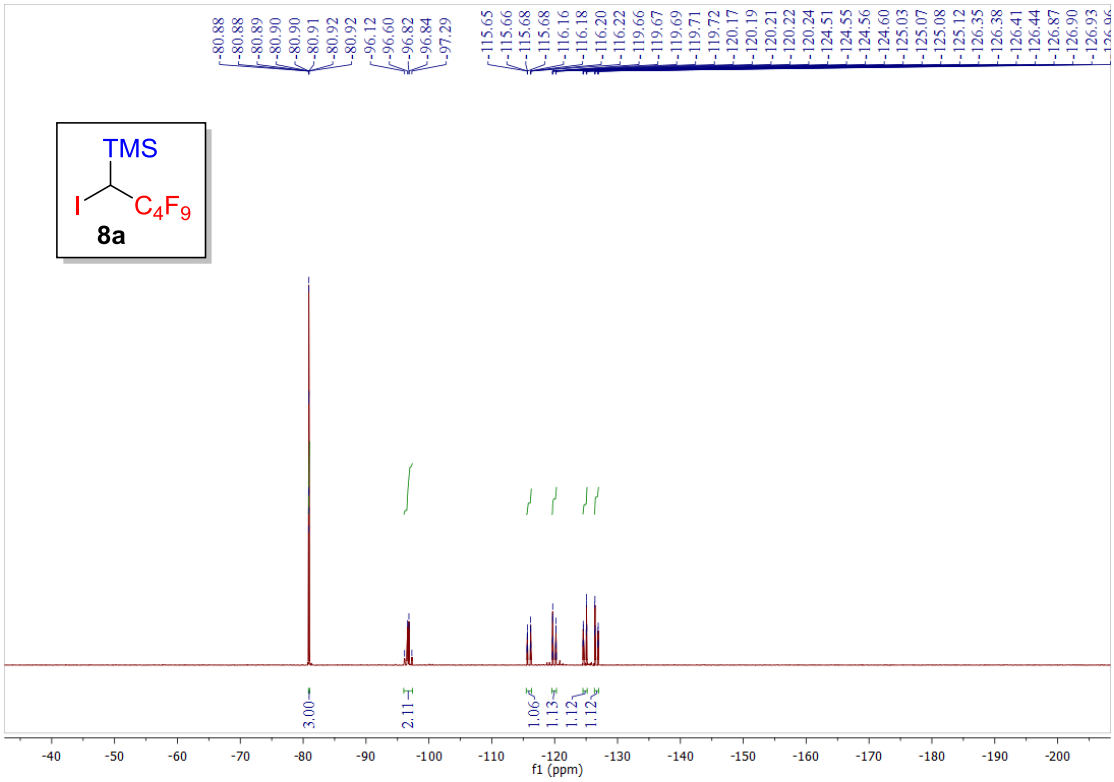

171.36
77.42
77.00
76.58
60.96
38.99
36.11
14.22
-3.22
TMS
Br
CH2CO2Et
8d
f1 (ppm)

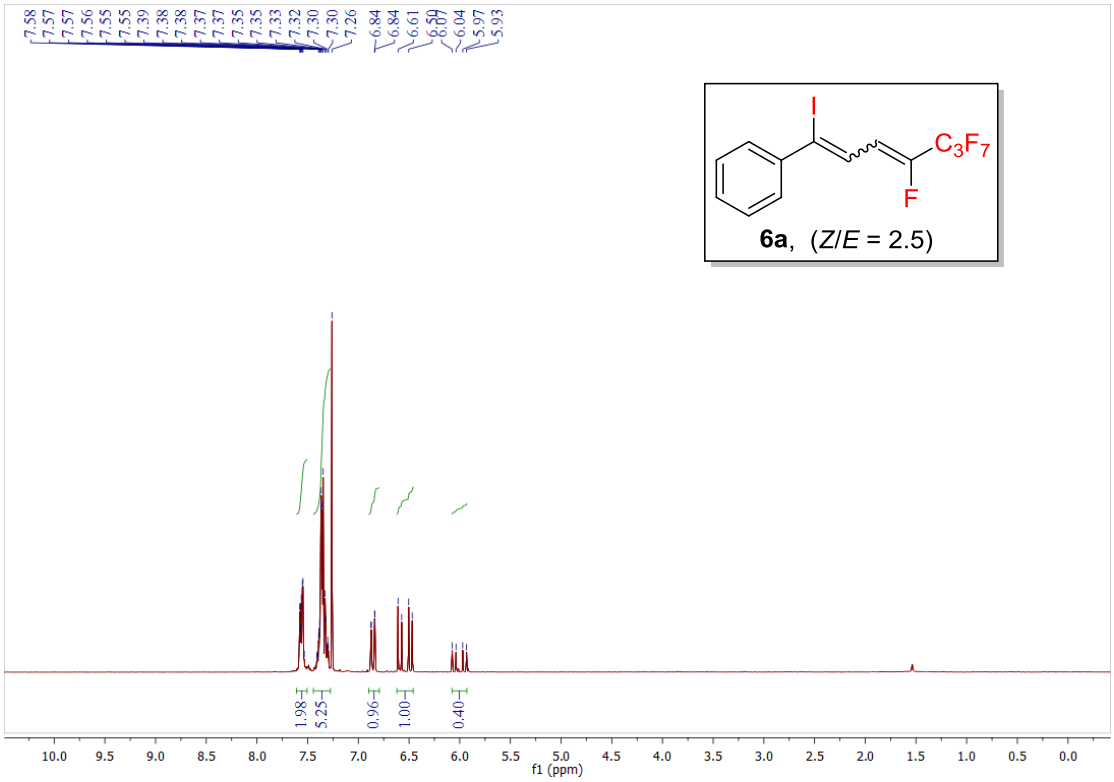

7.98
7.97
7.95
7.94
7.61
7.58
7.57
7.56
7.56
7.55
7.50
7.50
7.48
7.48
7.45
7.26
3.93
3.92
3.90
3.88
3.67
3.64
3.61
3.58
3.33
3.32
3.27
3.26
0.20
TMS
Br
CH2COPh
8e
2.12
1.15
2.14
0.97
1.00
1.01
9.09
f1 (ppm)

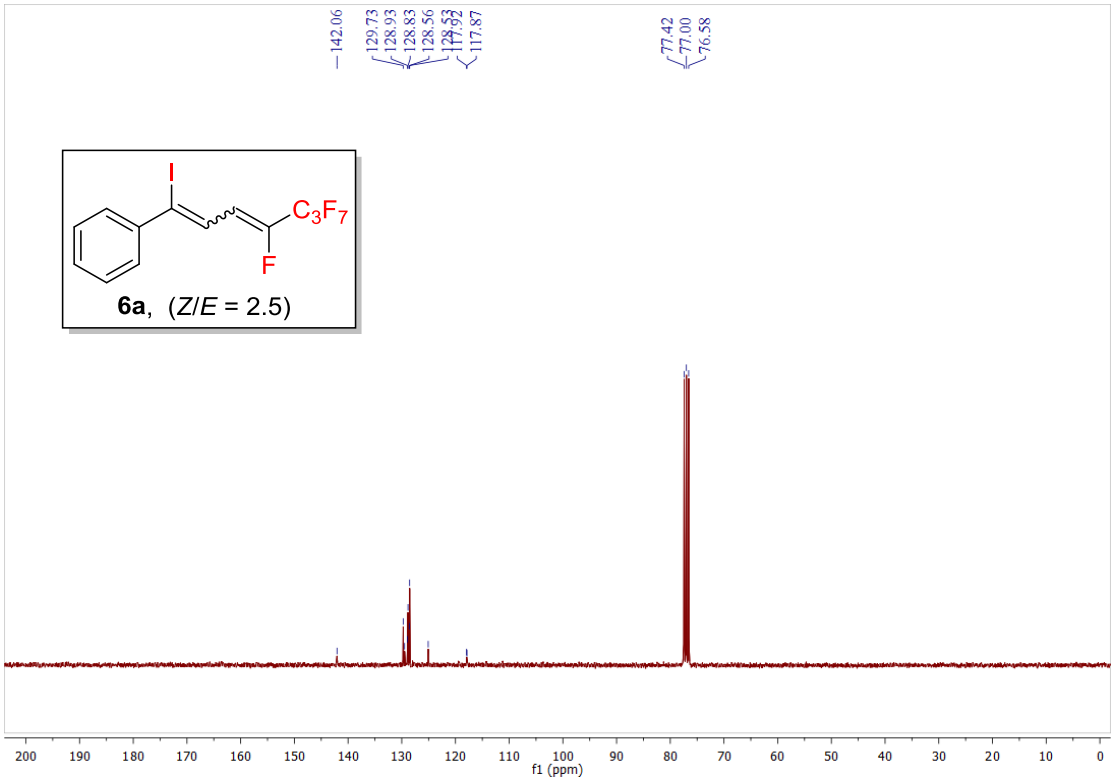

197.35
136.78
133.28
128.64
128.14
77.42
77.00
76.58
41.95
34.84
-3.00
TMS
Br
CH2COPh
8e
f1 (ppm)

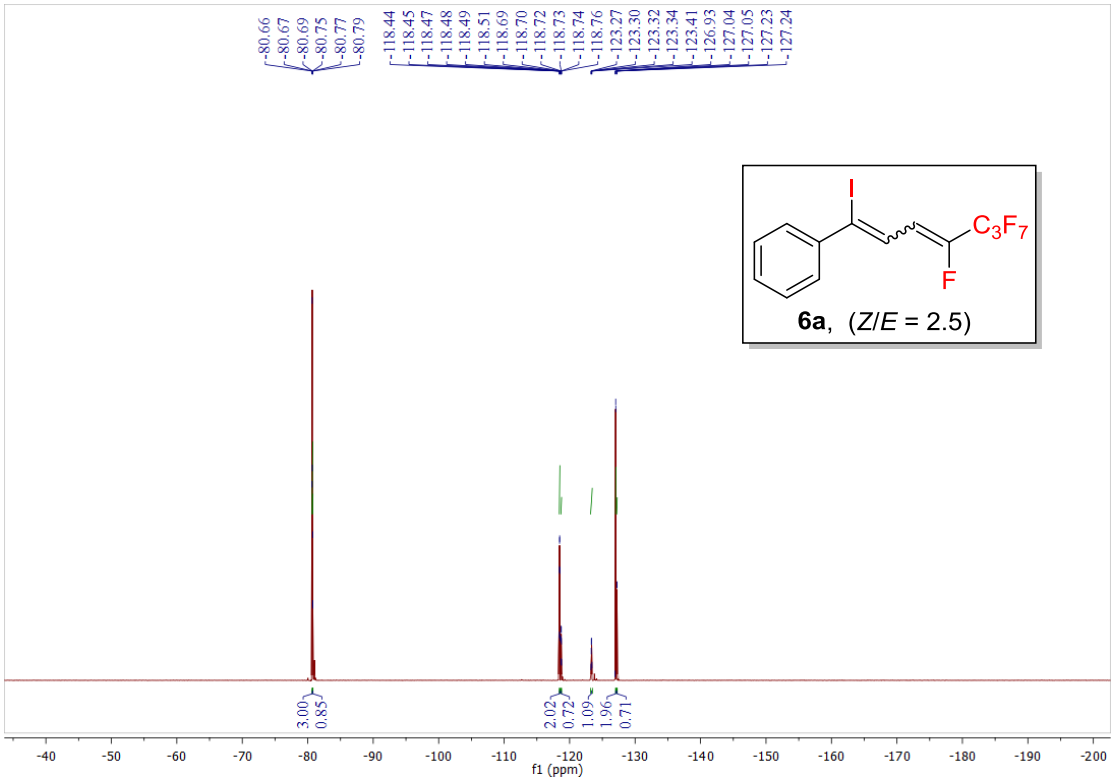

7.26
3.49
3.49
3.45
3.44
3.42
3.37
3.37
0.32
TMS
I
C4F9
8a
1.00
9.02
f1 (ppm)


TMS
I
C4F9
8a
77.42
77.00
76.58
5.86
5.45
5.02
-0.32
f1 (ppm)

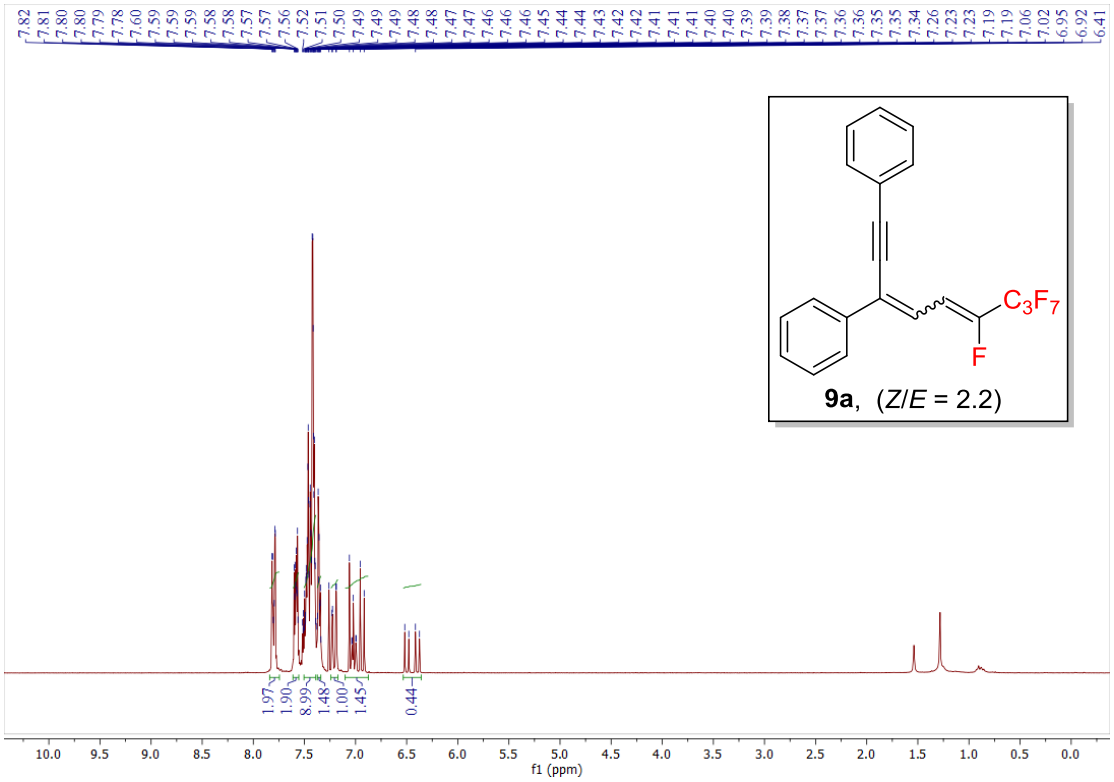

TMS
I
C4F9
8a
-80.88
-80.88
-80.89
-80.90
-80.90
-80.91
-80.92
-80.92
-96.12
-96.60
-96.82
-96.84
-97.29
-115.65
-115.66
-115.68
-115.68
-116.16
-116.18
-116.20
-116.22
-119.66
-119.67
-119.69
-119.71
-119.72
-120.17
-120.19
-120.21
-120.22
-120.24
-124.51
-124.55
-124.56
-124.60
-125.03
-125.07
-125.08
-125.12
-126.35
-126.38
-126.41
-126.44
-126.87
-126.90
-126.93
3.00
2.11
1.06
1.13
1.12
1.12
f1 (ppm)


7.58
7.57
7.57
7.56
7.55
7.55
7.39
7.38
7.38
7.37
7.37
7.35
7.35
7.33
7.32
7.30
7.30
7.26
6.84
6.84
6.61
6.59
6.07
6.04
5.97
5.93
I
C3F7
F
6a, (Z/E = 2.5)
1.98
5.25
0.96
1.00
0.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

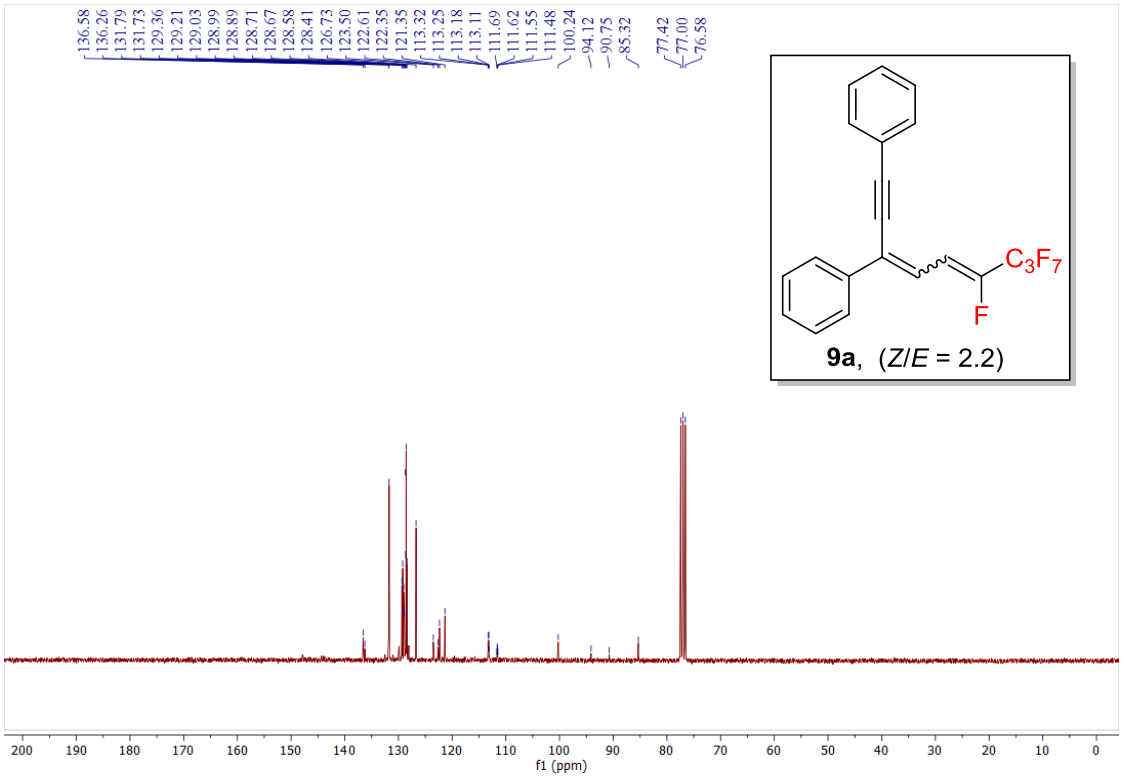

142.06
129.73
128.93
128.83
128.56
128.53
117.92
117.87
77.42
77.00
76.58
I
C3F7
F
6a, (Z/E = 2.5)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

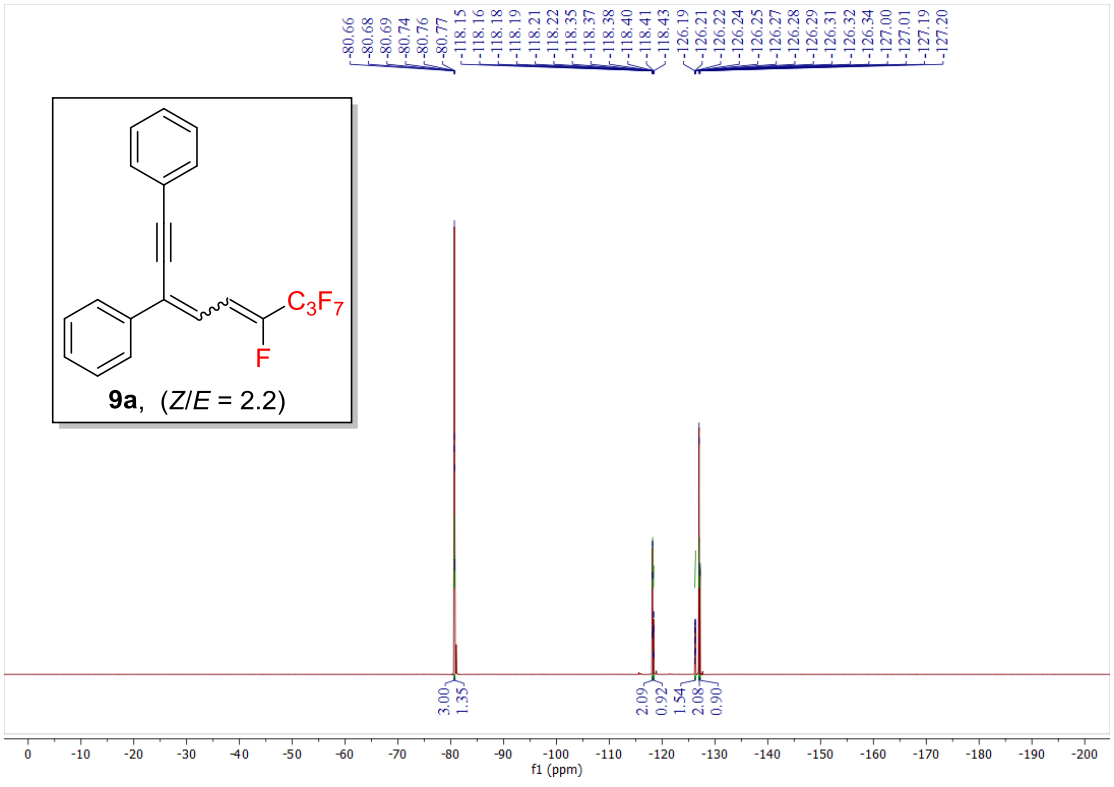


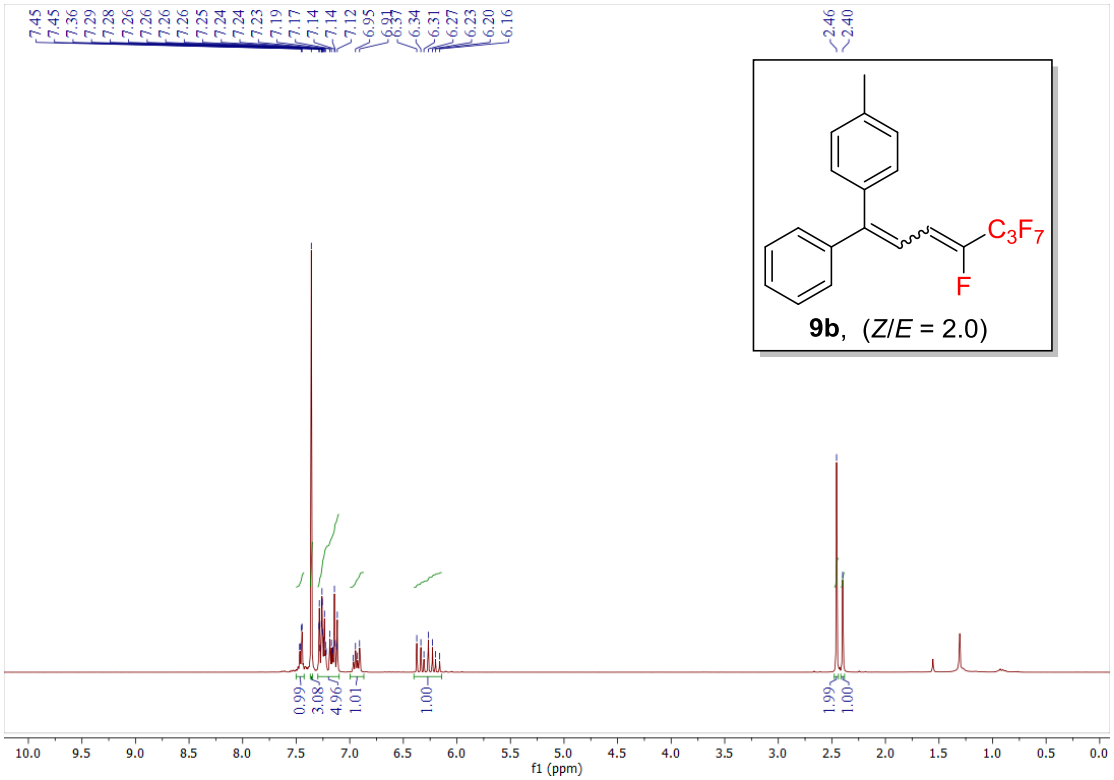
6a, (*Z*/*E* = 2.5)

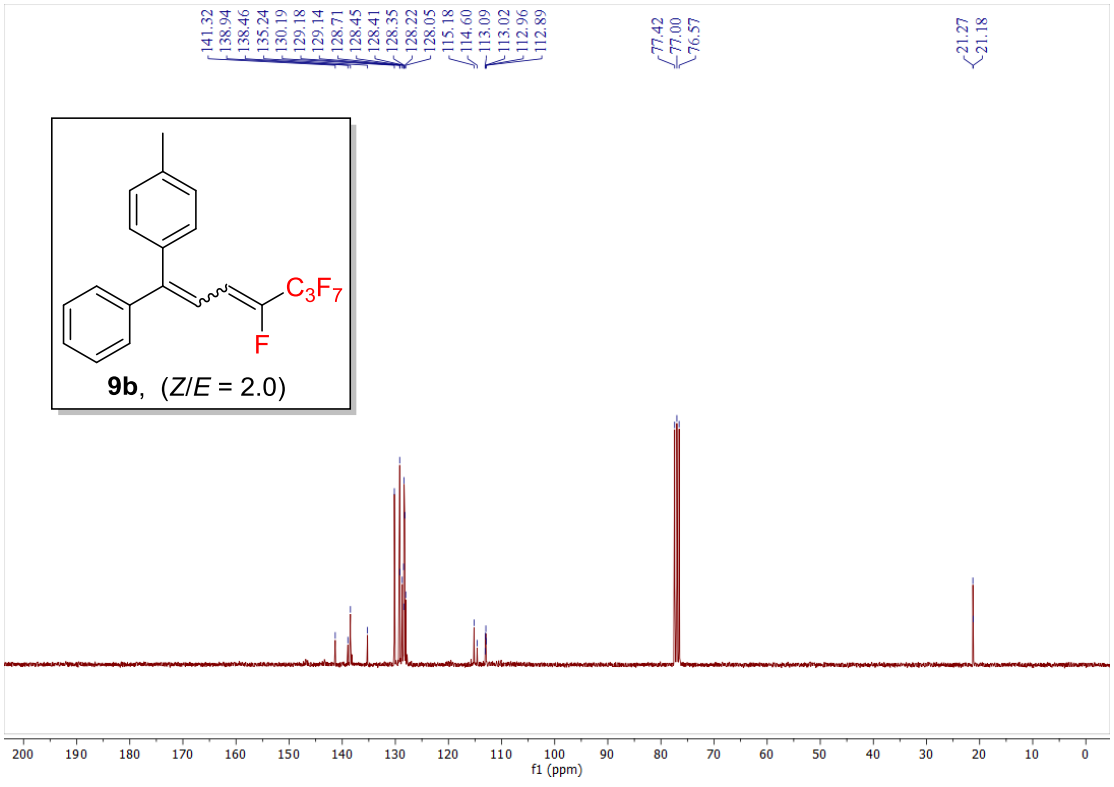


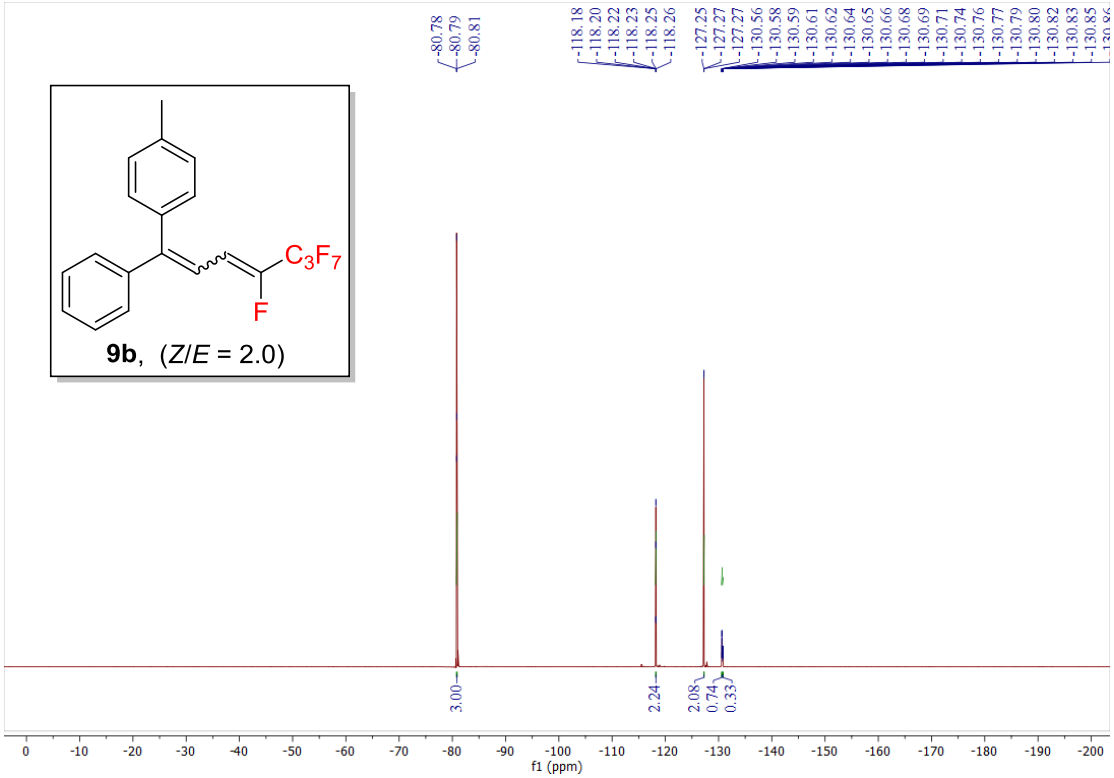
9a, (*Z*/*E* = 2.2)

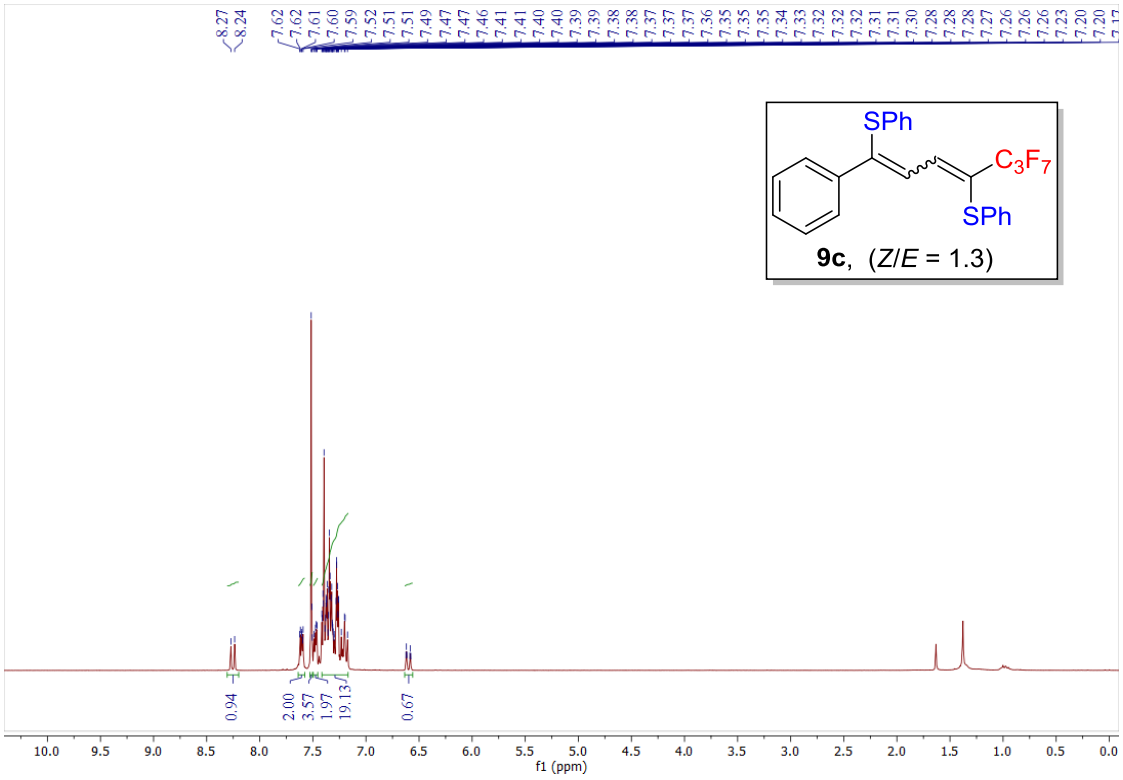

136.58
136.26
131.79
131.73
129.36
129.21
129.03
128.99
128.89
128.71
128.67
128.58
128.41
126.73
123.50
122.61
122.35
121.35
113.32
113.25
113.18
113.11
111.69
111.62
111.55
111.48
100.24
94.12
90.75
85.32
77.42
77.00
76.58
C3F7
F
9a, (Z/E = 2.2)
f1 (ppm)

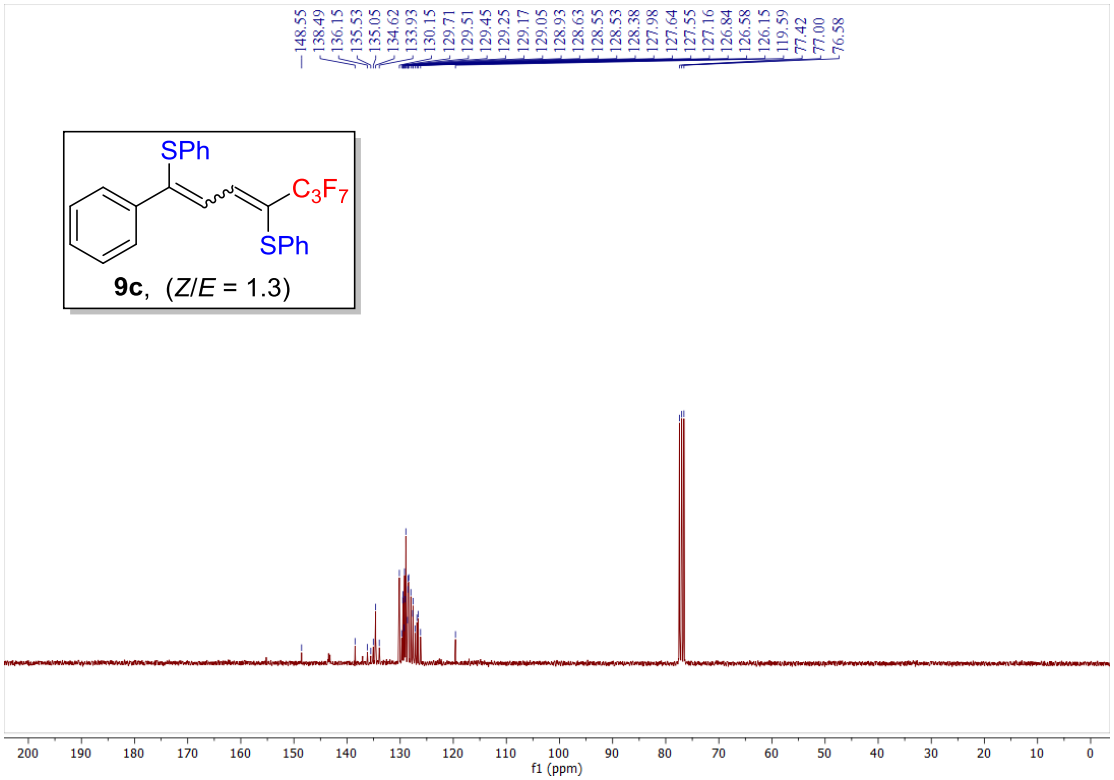

-80.66
-80.68
-80.69
-80.74
-80.76
-80.77
-118.15
-118.16
-118.18
-118.19
-118.21
-118.22
-118.35
-118.37
-118.38
-118.40
-118.41
-118.43
-126.19
-126.21
-126.22
-126.24
-126.25
-126.27
-126.28
-126.29
-126.31
-126.32
-126.34
-127.00
-127.01
-127.19
-127.20
C3F7
F
9a, (Z/E = 2.2)
3.00
1.35
2.09
0.92
1.54
2.08
0.90
f1 (ppm)

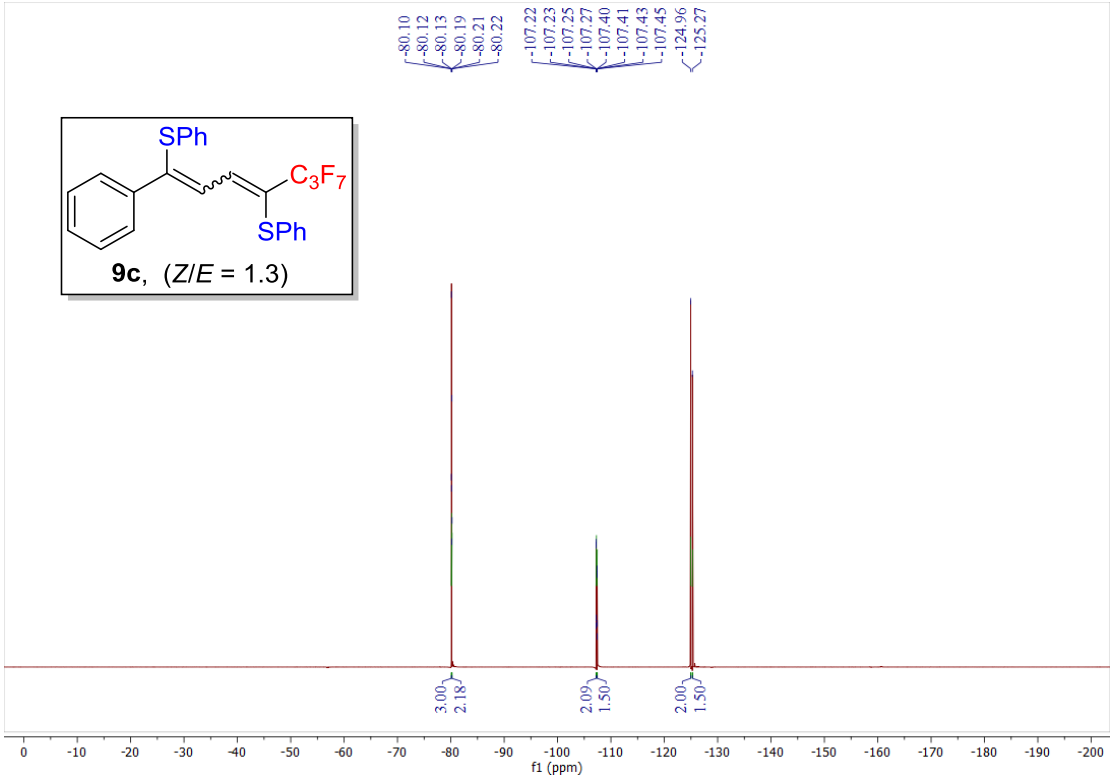

7.45
7.45
7.36
7.29
7.28
7.26
7.26
7.26
7.26
7.25
7.24
7.24
7.23
7.19
7.17
7.14
7.14
7.12
6.95
6.91
6.37
6.34
6.31
6.27
6.23
6.20
6.16
2.46
2.40
C_3F_7
F
9b, (Z/E = 2.0)
0.99
3.08
4.96
1.01
1.00
1.99
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


141.32
138.94
138.46
135.24
130.19
129.18
129.14
128.71
128.45
128.41
128.35
128.22
128.05
115.18
114.60
113.09
113.02
112.96
112.89
77.42
77.00
76.57
21.27
21.18
C_3F_7
F
9b, (Z/E = 2.0)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


C3F7
F
9b, (Z/E = 2.0)
f1 (ppm)


SPh
C3F7
SPh
9c, (Z/E = 1.3)
f1 (ppm)


148.55
138.49
136.15
135.53
135.05
134.62
133.93
130.15
129.71
129.51
129.45
129.25
129.17
129.05
128.93
128.63
128.55
128.53
128.38
127.98
127.64
127.55
127.16
126.84
126.58
126.15
119.59
77.42
77.00
76.58
SPh
C3F7
SPh
9c, (Z/E = 1.3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


80.10
80.12
80.13
80.19
80.21
80.22
107.22
107.23
107.25
107.27
107.40
107.41
107.43
107.45
124.96
125.27
SPh
C3F7
SPh
9c, (Z/E = 1.3)
3.00
2.18
2.09
1.50
2.00
1.50
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)