Supporting information for:

Copper-Mediated Oxidative Trifluoromethylation of Boronic Acids

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General Information----------S1

General Procedure of Trifluoromethylation ----------S1

PDF file of Copies of ^{1}H NMR and ^{13}C NMR Spectra----------S8

General information: ^{1}H NMR and ^{19}F NMR spectra ($CFCl_3$ as outside standard and low field is positive) were recorded on a Bruker AM300 spectrometer. ^{13}C NMR was recorded on a Bruker AM400 spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

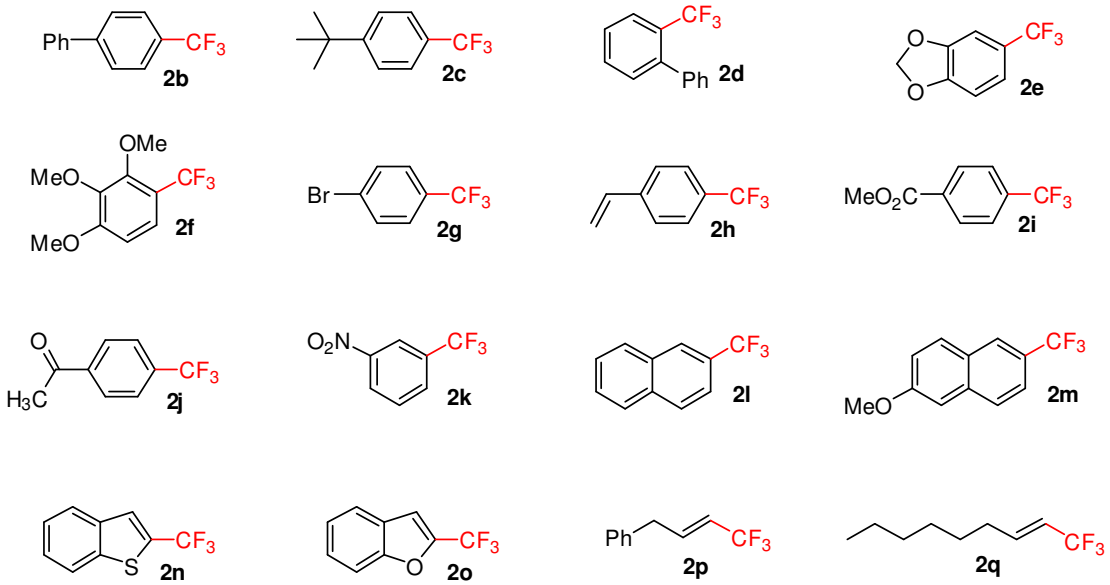
Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. DMF was distilled from $CaSO_4$. KF was

General Procedure for the Copper-Mediated Oxidative Trifluoromethylation of boronic acids with Me_3SiCF_3:

In a glove box, $[Cu(OTf)]_2 \cdot C_6H_6$ (0.12 mmol), phen (0.24 mmol), K_3PO_4 (0.6 mmol) and KF

(1.0 mmol) were added to a reaction tube that is equipped with a stirring bar. The tube was capped with a septum and taken out. $AgCO_3$ (0.2 mmol) and DMF (2.0 mL) was added. Next, Me_3SiCF_3 was added by springe and then the resulting mixture was heated to 45°C. A solution of boronic acid **1b** (0.2 mmol) in 2.0 mL DMF was added to the tube over 2 h by using a syringe pump under N_2 atmosphere (1 atom). After addition of **1b**/DMF solution, the reaction mixture was kept for another 2 h at 45°C. At the conclusion of the reaction, the mixture was allowed to cool to room temperature, and water was added to the mixture at 0°C. The resulting mixture was extracted by ethyl ether, and the combined organic phase was washed with a large amount of water for 3 times, with brine for once and then dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel with pentane to give **2b**.

Products:



Compounds **2b**,[1] **2c**,[2] **2d**,[3] **2g**,[4] **2h**,[5] **2i**,[6] **2j**,[7] **2k**,[8] **2l**,[9] **2m**, [10]**2n**,[11] **2o**[11] and **2q**[12] are known

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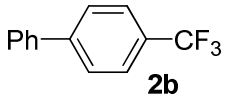
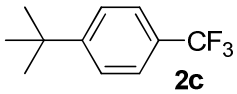
compounds.



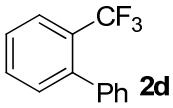
2b

4-(trifluoromethyl)biphenyl 2b: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.68 (s, 4H), 7.61-7.58 (m, 2H), 7.49-7.40 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -62.3 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 144.72 (q, *J* = 1.4 Hz), 139.76, 129.34 (q, *J* = 31.9 Hz), 128.97, 128.17, 127.41, 127.27, 125.69 (q, *J* = 3.9 Hz), 124.31 (q, *J* = 270.5 Hz). IR (ATR): ν_{max} 3081, 2927, 1616, 1405, 1265, 974, 844, 767, 602 cm^{-1}. MS (EI): *m/z* (%) 222 (100). HRMS: Calculated for $C_{13}H_9F_3$: 222.0656; Found: 222.0659.



2c

1-*tert*-butyl-4-(trifluoromethyl)benzene 2c: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.57 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 1.35 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -62.2 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 149.10, 127.74 (q, *J* = 31.7 Hz), 125.61, 124.97 (q, *J* = 4.1 Hz), 124.38 (q, *J* = 270.3 Hz), 34.91, 31.09. IR (ATR): ν_{max} 2965, 1778, 1618, 1328, 1015, 840 cm^{-1}. MS (EI): *m/z* (%) 202, 187 (100). HRMS: Calculated for $C_{11}H_{13}F_3$: 202.0969; Found: 202.0968.



2d

2-(trifluoromethyl)biphenyl 2d: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.76 (d, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.45-7.40 (m, 3H), 7.36-7.35 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -56.7 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 141.42 (q, *J* = 1.0 Hz), 139.84, 132.01, 131.25 (q, *J* = 0.8 Hz), 128.93 (q, *J* = 2.1 Hz), 128.45 (q, *J* = 30.2 Hz), 127.72, 127.59, 127.29, 126.02 (q, *J* = 10.6 Hz), 124.15 (q, *J* = 272.6

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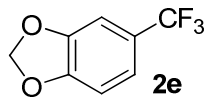
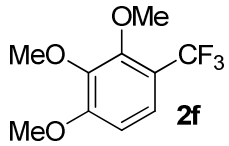
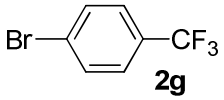
Hz). IR (ATR): ν_{max} 3065, 2926, 1483, 1316, 1171, 1072, 768, 654 cm^{-1}. MS (EI): *m/z* (%) 222 (100). HRMS: Calculated for $C_{13}H_9F_3$: 222.0656; Found: 222.0661.



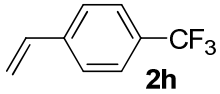
5-(trifluoromethyl)benzo[d][1,3]dioxole 2e: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.15 (d, *J* = 8.1 Hz, 1H), 7.04 (s, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.04 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -61.3 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 150.27 (q, *J* = 1.2 Hz), 147.93, 124.23 (q, *J* = 32.4 Hz), 124.03 (q, *J* = 270.4 Hz), 119.81 (q, *J* = 4.3 Hz), 108.16, 105.79 (q, *J* = 3.7 Hz), 101.84. IR (ATR): ν_{max} 2956, 1313, 1124, 895, 851 cm^{-1}. MS (EI): *m/z* (%) 190 (100). HRMS: Calculated for $C_8H_5O_2F_3$: 190.0242; Found: 190.0240.



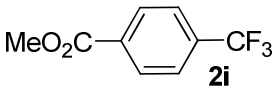
1,2,3-trimethoxy-4-(trifluoromethyl)benzene 2f: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.18 (d, *J* = 9.0 Hz, 1H), 6.61 (d, *J* = 9.0 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.81 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -60.6 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 156.74 (q, *J* = 0.9 Hz), 152.24 (q, *J* = 1.0 Hz), 124.88, 123.61 (q, *J* = 270.4 Hz), 121.47 (q, *J* = 4.9 Hz), 116.97 (q, *J* = 30.8 Hz), 106.32, 61.58, 60.78, 56.03. IR (ATR): ν_{max} 2942, 1602, 1474, 1326, 1119, 1014, 806, 693 cm^{-1}. MS (EI): *m/z* (%) 236 (100). HRMS: Calculated for $C_{10}H_{11}O_3F_3$: 236.0660; Found: 236.0661.



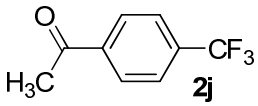
1-bromo-4-(trifluoromethyl)benzene 2g: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.64 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -62.6 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 132.05, 129.53 (q, *J* = 32.8 Hz), 126.86 (q, *J* = 4.1 Hz), 126.42 (q, *J* = 1.7 Hz), 123.83 (q, *J* = 270.8 Hz). IR (ATR): ν_{max} 2925, 1379, 1021, 804 cm^{-1}. MS (EI): *m/z* (%) 222 (100). HRMS: Calculated for $C_7H_4BrF_3$: 223.9448; Found: 223.9452.



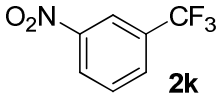
1-(trifluoromethyl)-4-vinylbenzene 2h: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.59 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 6.75 (dd, *J* = 10.8 Hz, *J* = 17.4 Hz, 1H), 5.85 (d, *J* = 17.1 Hz, 1H), 5.39 (d, *J* = 10.8 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -62.2 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 140.91 (q, *J* = 1.3 Hz), 135.60, 129.62 (q, *J* = 32.3 Hz), 126.36, 125.46 (q, *J* = 3.8 Hz), 124.15 (q, *J* = 270.4 Hz), 116.44. IR (ATR): v_{max} 2924, 1372, 1128, 803 cm^{-1}. GC-MS: 172 (M^+). HRMS: Calculated for $C_9H_7F_3$: 172.0500; Found: 172.0502.



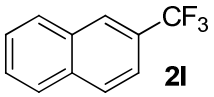
methyl 4-(trifluoromethyl)benzoate 2i: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.16 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 3.96 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -62.9 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 165.85, 134.41 (q, *J* = 32.6 Hz), 133.31 (q, *J* = 1.4 Hz), 129.95, 125.38 (q, *J* = 3.6 Hz), 123.60 (q, *J* = 271.3 Hz), 52.49. IR (ATR): v_{max} 2958, 1736, 1439, 1327, 1282, 1134, 1019, 863, 705 cm^{-1}. MS (EI): *m/z* (%) 204, 173 (100), 145. HRMS: Calculated for $C_9H_7O_2F_3$: 204.0398; Found: 204.0395.



1-(4-(trifluoromethyl)phenyl)ethanone 2j: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.04 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 2.63 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -63.0 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 196.88, 139.63 (q, *J* = 1.0 Hz), 134.32 (q, *J* = 32.6 Hz), 126.55, 125.59 (q, *J* = 3.6 Hz), 123.56 (q, *J* = 271.3 Hz), 26.65. IR (ATR): v_{max} 3067, 2956, 1694, 1410, 1328, 1132, 844, 719, 609 cm^{-1}. MS (EI): *m/z* (%) 188, 173 (100), 145. HRMS: Calculated for $C_9H_7OF_3$: 188.0449; Found: 188.0448.

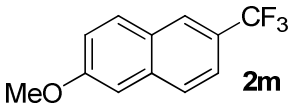


1-nitro-3-(trifluoromethyl)benzene 2k: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.50 (s, 1H), 8.43 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 8.1 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -62.9 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 132.31 (q, *J* = 68.3 Hz), 131.10 (q, *J* = 3.3 Hz), 130.31, 126.63 (q, *J* = 1.0 Hz), 122.81 (q, *J* = 271.5 Hz), 120.83 (q, *J* = 3.9 Hz). IR (ATR): v_{max} 2925, 1544, 1324, 811, 699 cm^{-1}. MS (EI): *m/z* (%) 191, 145(100). HRMS: Calculated for $C_7H_4NO_2F_3$: 191.0194; Found: 191.0193.



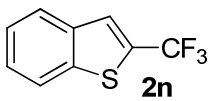
2l

2-(trifluoromethyl)naphthalene 2l: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.16 (s, 1H), 7.97-7.90 (m, 3H), 7.67-7.57 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -62.1 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 134.54 (q, *J* = 0.9 Hz), 132.17, 128.95, 128.79, 128.02, 127.85 (q, *J* = 30.0 Hz), 127.83, 127.13, 125.65 (q, *J* = 4.1 Hz), 124.39 (q, *J* = 271.0 Hz), 124.41 (q, *J* = 3.5 Hz). IR (ATR): v_{max} 2925, 1128, 1065, 825, 751 cm^{-1}. MS (EI): *m/z* (%) 196 (100). HRMS: Calculated for $C_{11}H_7F_3$: 196.0500; Found: 196.0502.



2m

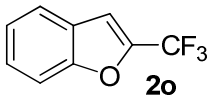
2-methoxy-6-(trifluoromethyl)naphthalene 2m: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.05 (s, 1H), 7.80 (d, *J* = 12.0 Hz, 2H), 7.59 (d, *J* = 11.6 Hz, 1H), 7.22 (dd, *J* = 3.2 Hz, *J* = 12.4 Hz,1H), 7.16 (s, 1H), 3.94 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -62.3 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 159.24, 136.08 (q, *J* = 1.4 Hz), 130.24, 127.58, 127.55, 125.63, 124.58 (q, *J* = 270.4 Hz), 125.37 (q, *J* = 4.3 Hz), 122.00 (q, *J* = 3.1 Hz), 120.10, 105.66, 55.36. IR (ATR): v_{max} 2978, 1492, 1321, 1113, 857, 683 cm^{-1}. MS (EI): *m/z* (%) 226 (100). HRMS: Calculated for $C_{12}H_9OF_3$: 226.0605; Found: 226.0609.



2n

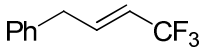
2-(trifluoromethyl)benzo[b]thiophene 2n: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.89-7.85 (m, 2H), 7.69 (s, 1H), 7.49-7.41 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -56.3 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 139.97, 137.58, 131.11 (q, *J* = 18.6 Hz),

126.38, 125.44 (q, J = 4.1 Hz), 125.04, 124.92, 122.45, 122.35 (q, J = 267.9 Hz). IR (ATR): ν_{max} 2925, 1296, 1136, 752 cm^{-1}. MS (EI): *m/z* (%) 202 (100). HRMS: Calculated for $C_9H_5SF_3$: 202.0064; Found: 202.0066.



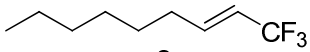
2o

2-(trifluoromethyl)benzofuran 2o: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.67 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 8.7 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.17 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -64.8 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 155.14, 143.48 (q, J = 41.4 Hz), 126.90, 125.99, 123.95, 122.46, 119.32 (q, J = 265.9 Hz), 112.08, 108.09 (q, J = 3.1 Hz). IR (ATR): ν_{max} 2925, 1459, 1176, 1143, 1024 cm^{-1}. MS (EI): *m/z* (%) 186 (100). HRMS: Calculated for $C_9H_5OF_3$: 186.0292; Found: 186.0293.



2p

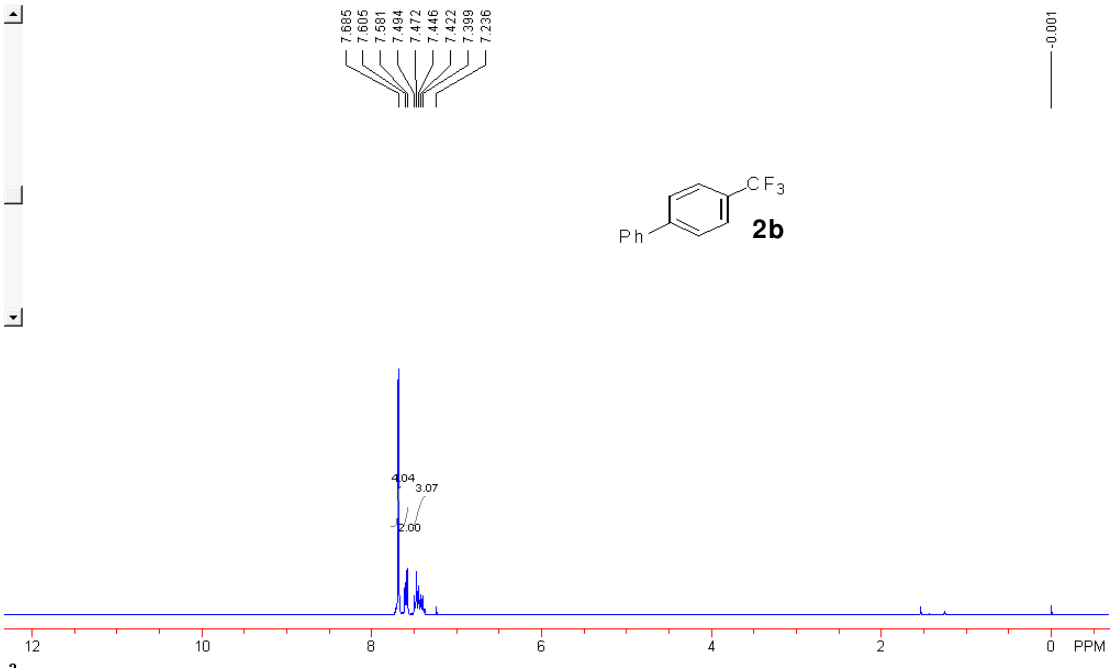
(E)-(4,4,4-trifluorobut-2-enyl)benzene 2p: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.36-7.24 (m, 3H), 7.17 (d, J = 7.2 Hz, 2H), 6.59-6.50 (m, 1H), 5.66-5.55 (m, 1H), 3.48-3.47 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -63.7 (s, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 139.32 (q, J = 5.9 Hz), 137.29 (q, J = 0.9 Hz), 128.76, 128.73, 126.84, 123.00 (q, J = 268.2 Hz), 119.53 (q, J = 33.3 Hz), 37.64. IR (ATR): ν_{max} 3074, 2926, 1685, 1285, 1124, 976, 749 cm^{-1}. MS (EI): *m/z* (%) 186, 117 (100). HRMS: Calculated for $C_{10}H_9F_3$: 186.0656; Found: 186.0654.

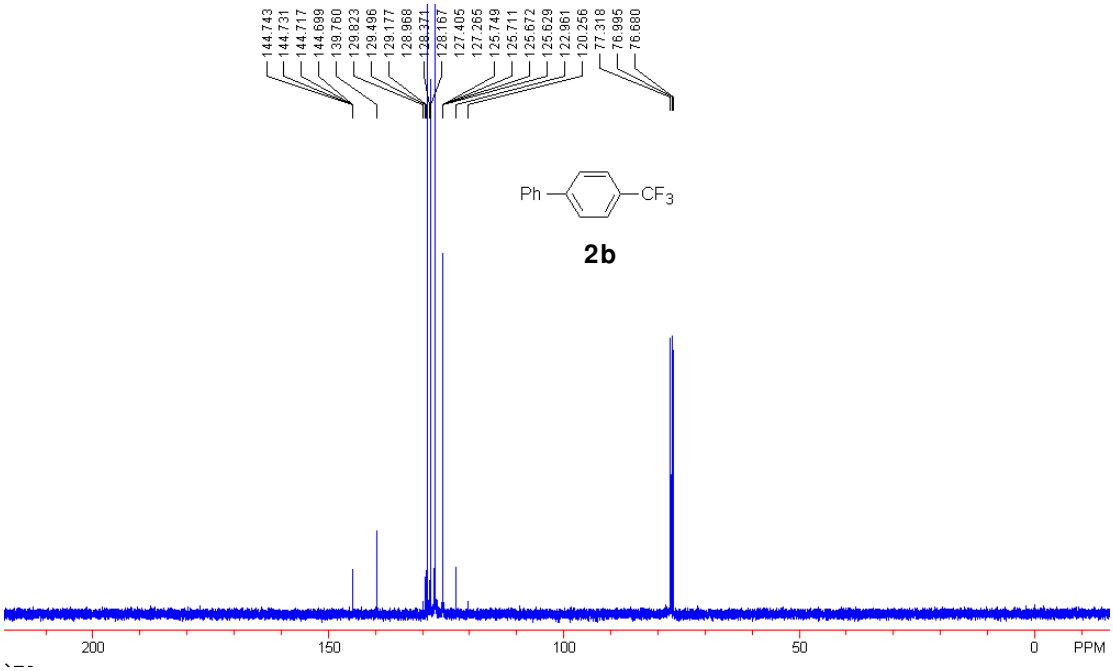


2q

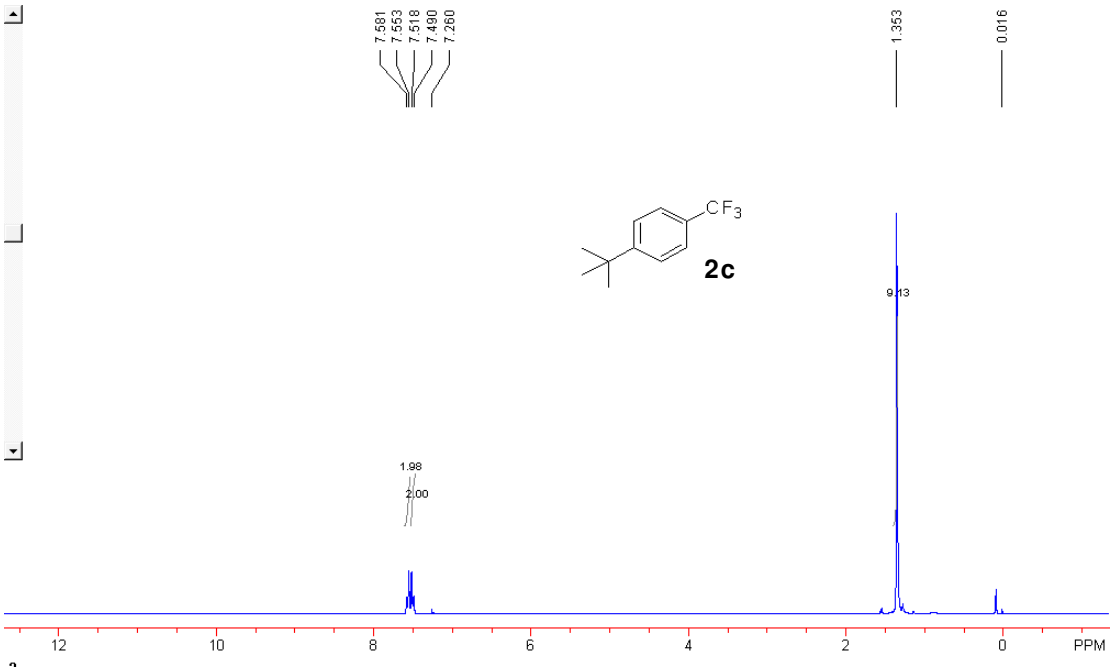
(E)-1,1,1-trifluoronon-2-ene 2q: ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 6.43-6.33 (m, 1H), 5.66-5.54 (m, 1H), 2.16-2.13 (m, 2H), 1.42 (q, J = 6.9 Hz, 2H), 1.29-1.26 (m, 6H), 0.89 (t, J = 6.9 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -63.8 (dd, J = 3.1 Hz, J = 6.8 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 140.79 (q, J = 6.5 Hz), 123.10 (q, J = 267.5 Hz), 118.24 (q, J = 32.7 Hz), 31.51, 31.41, 28.65, 27.89 (q, J = 1.3 Hz), 22.48, 13.97. IR (ATR): ν_{max} 2941, 913, 744 cm^{-1}. GC-MS: 180 (M^+). HRMS: Calculated for $C_9H_{15}F_3$: 180.1126; Found: 180.1125.

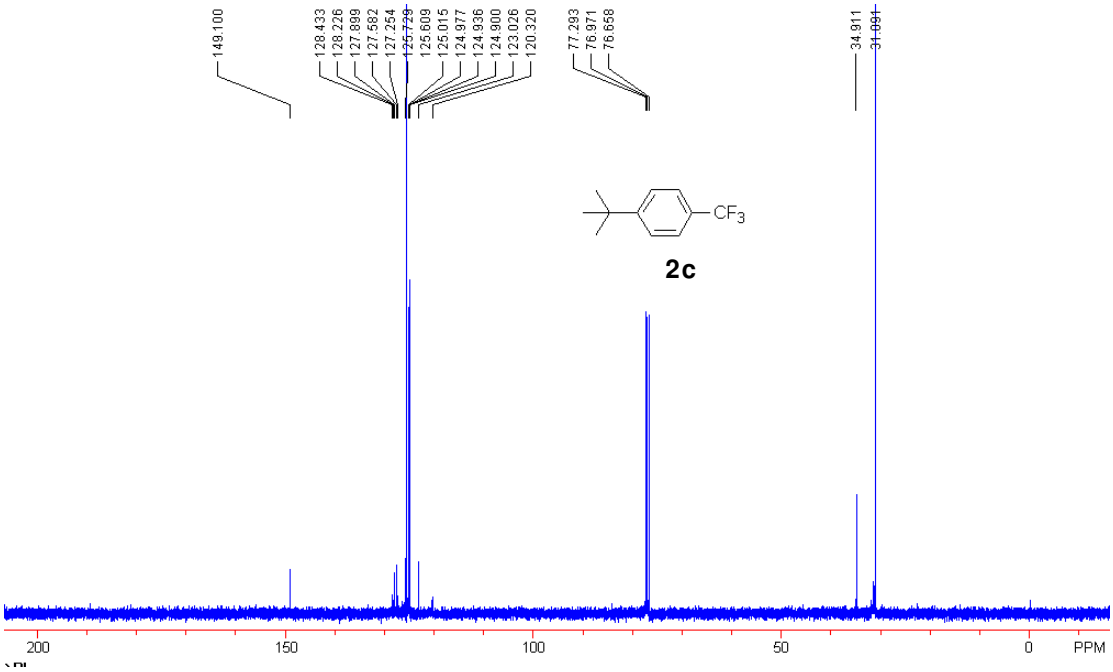
4-(trifluoromethyl)biphenyl 2b:



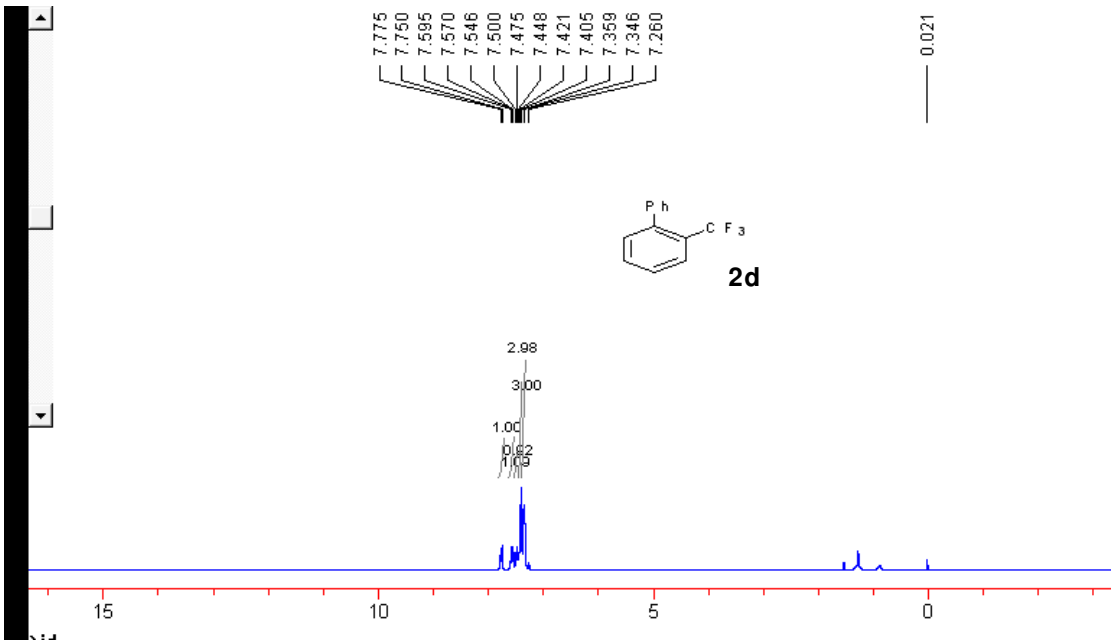


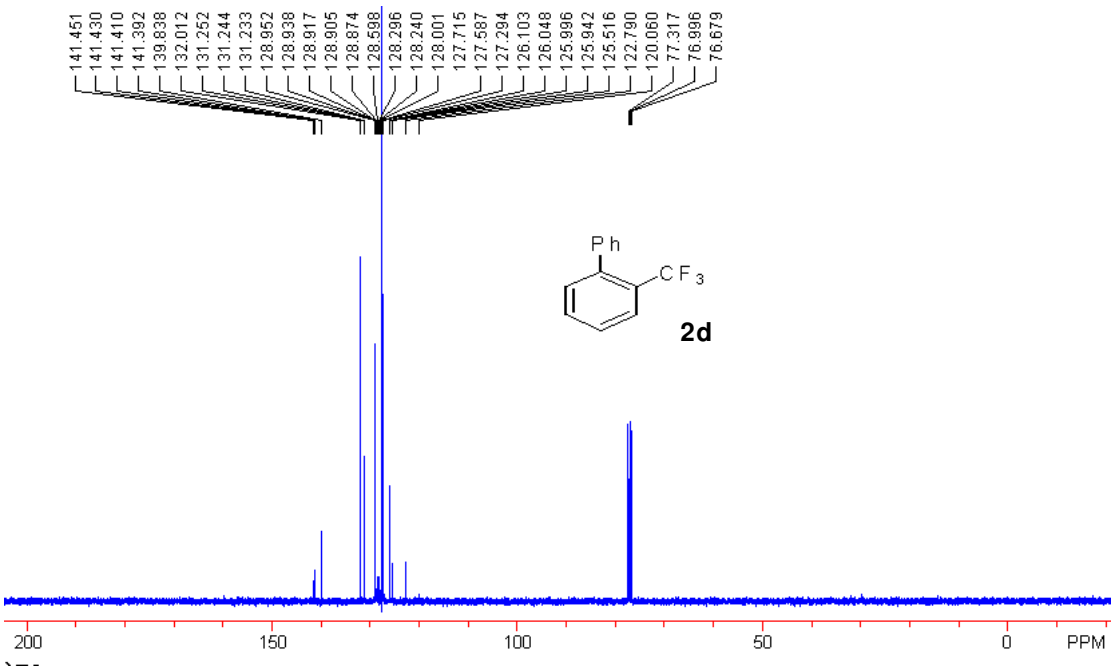
1-*tert*-butyl-4-(trifluoromethyl)benzene 2c:



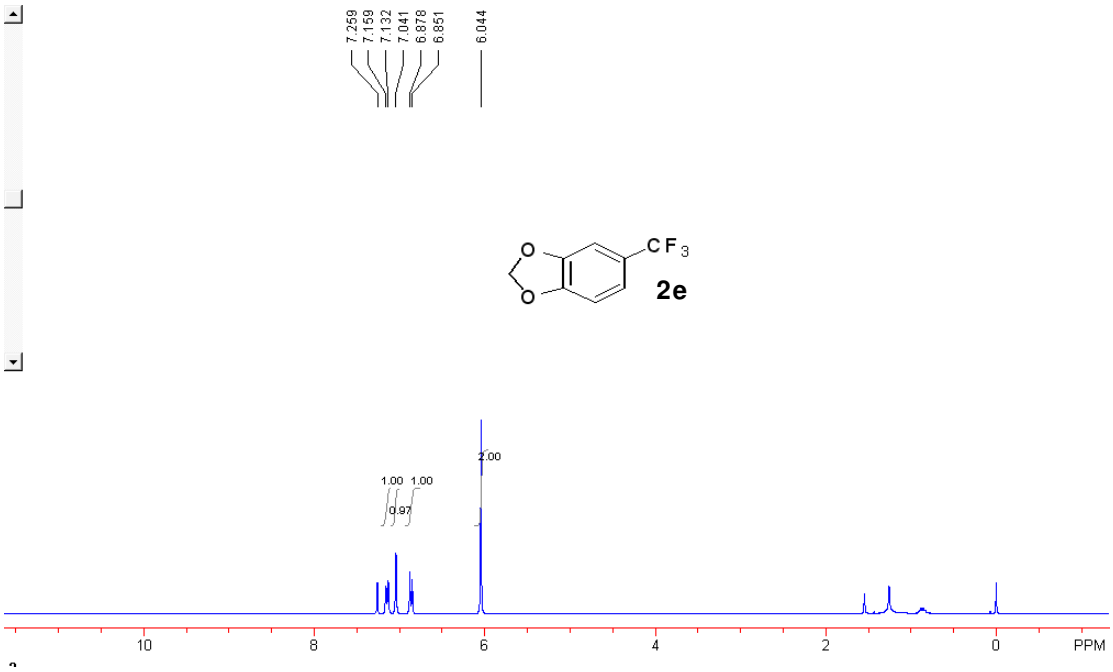


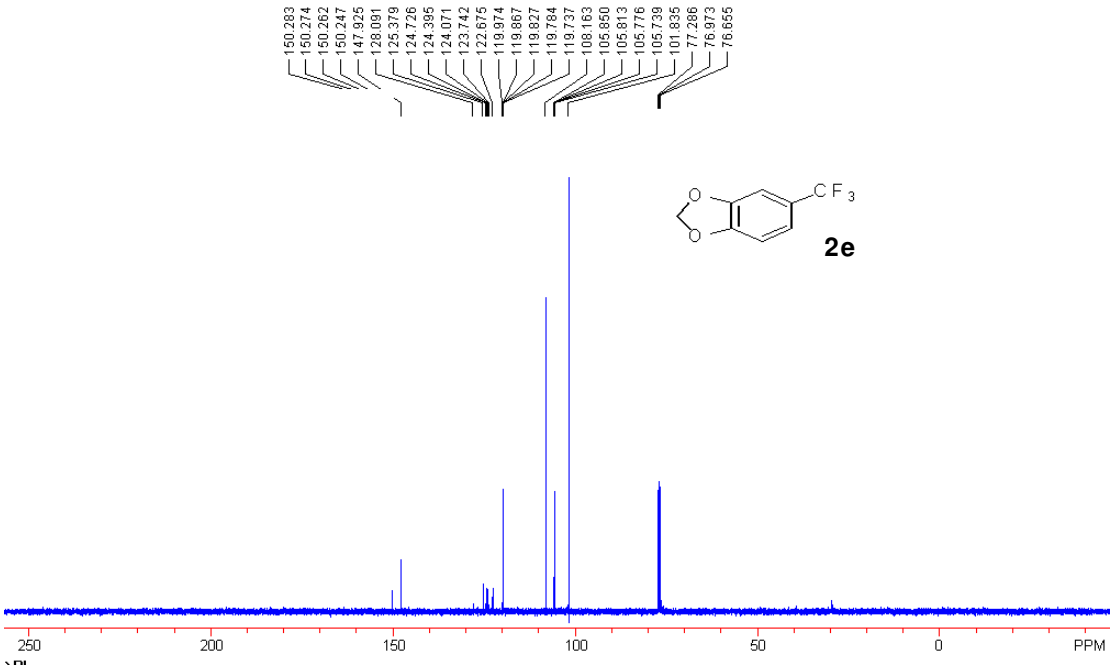
2-(trifluoromethyl)biphenyl 2d:



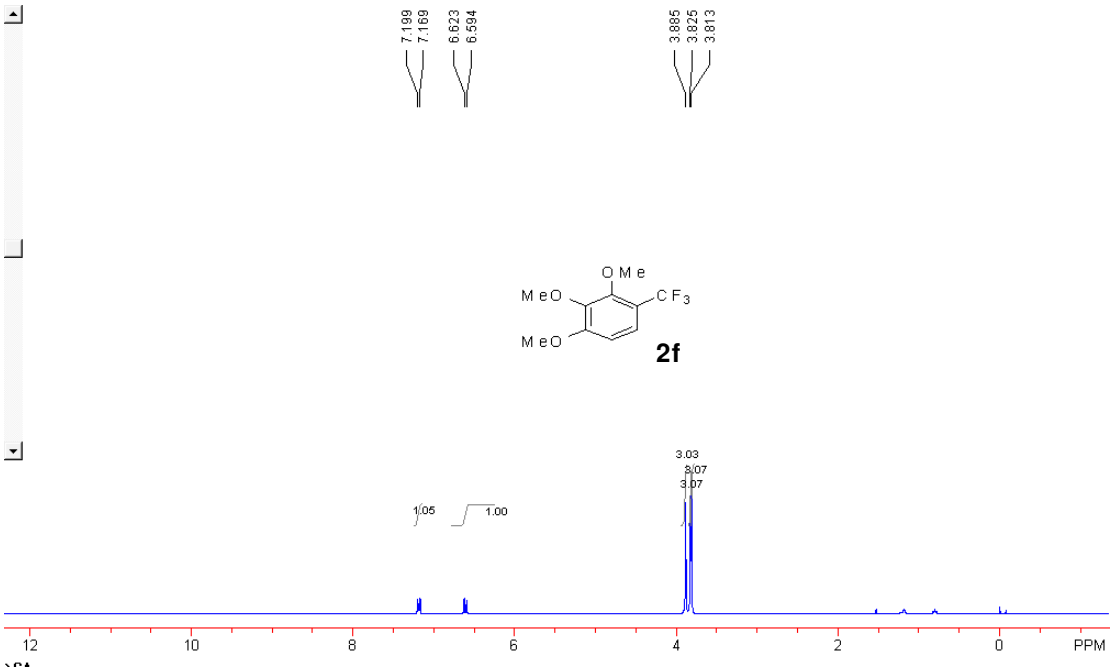


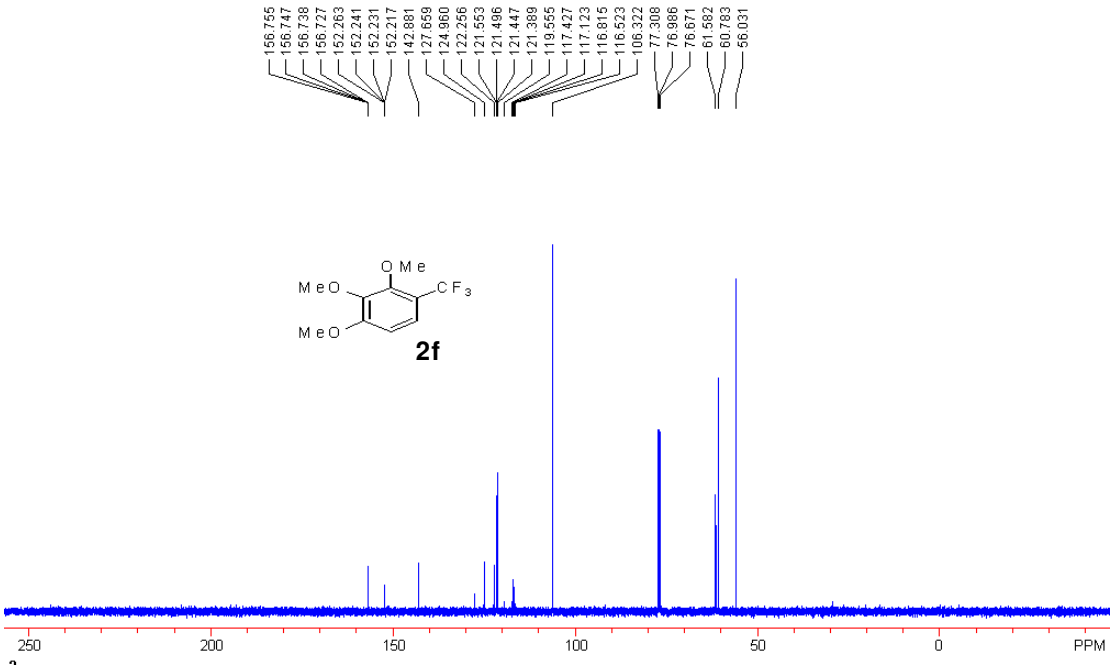
5-(trifluoromethyl)benzo[d][1,3]dioxole 2e:



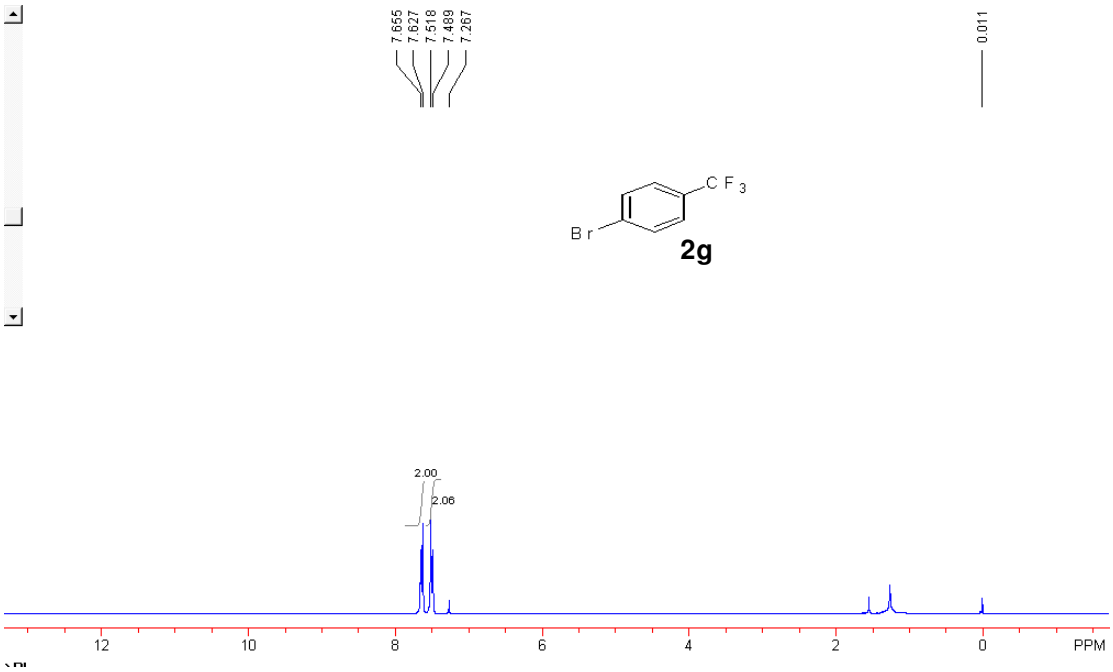


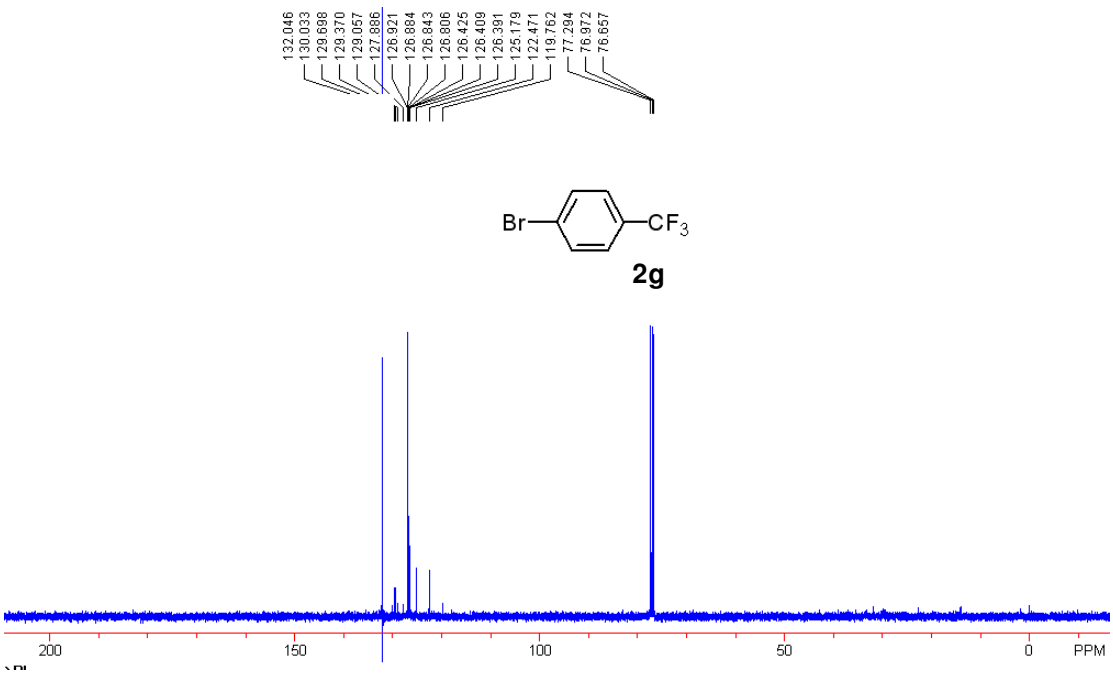
1,2,3-trimethoxy-4-(trifluoromethyl)benzene 2f:



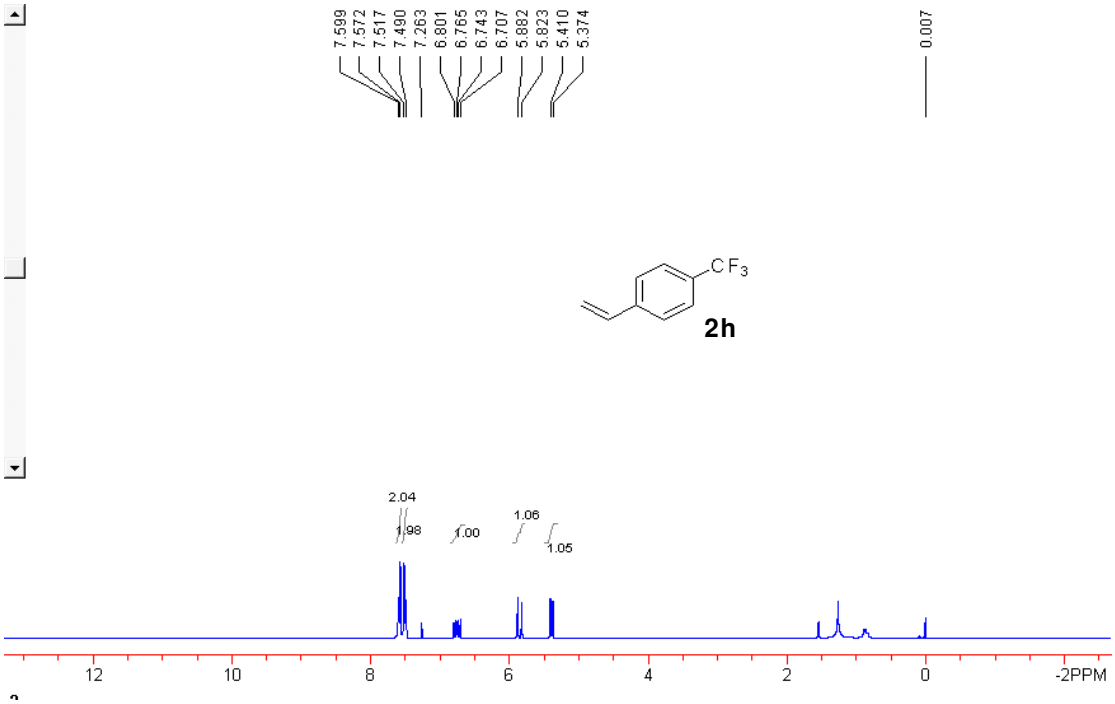


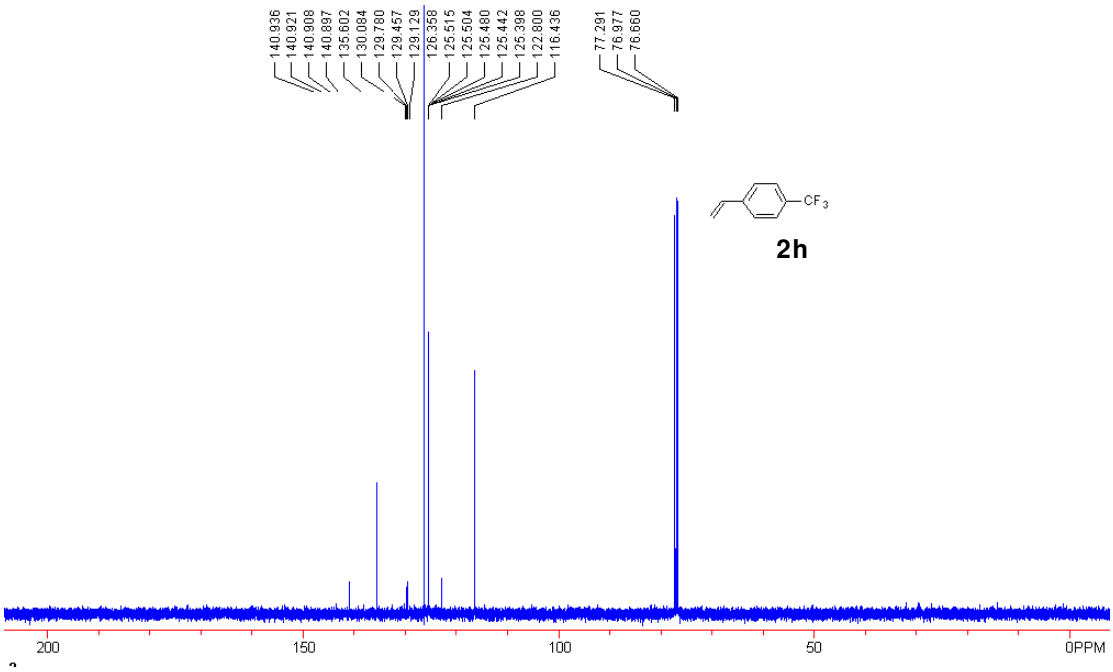
1-bromo-4-(trifluoromethyl)benzene 2g:



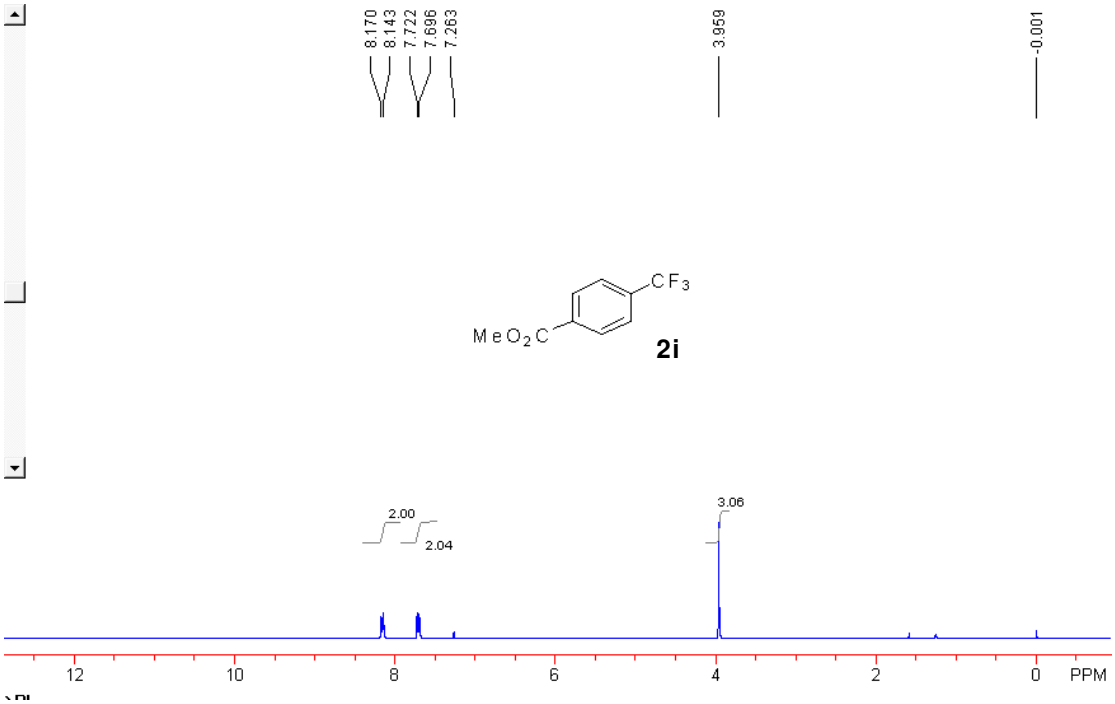


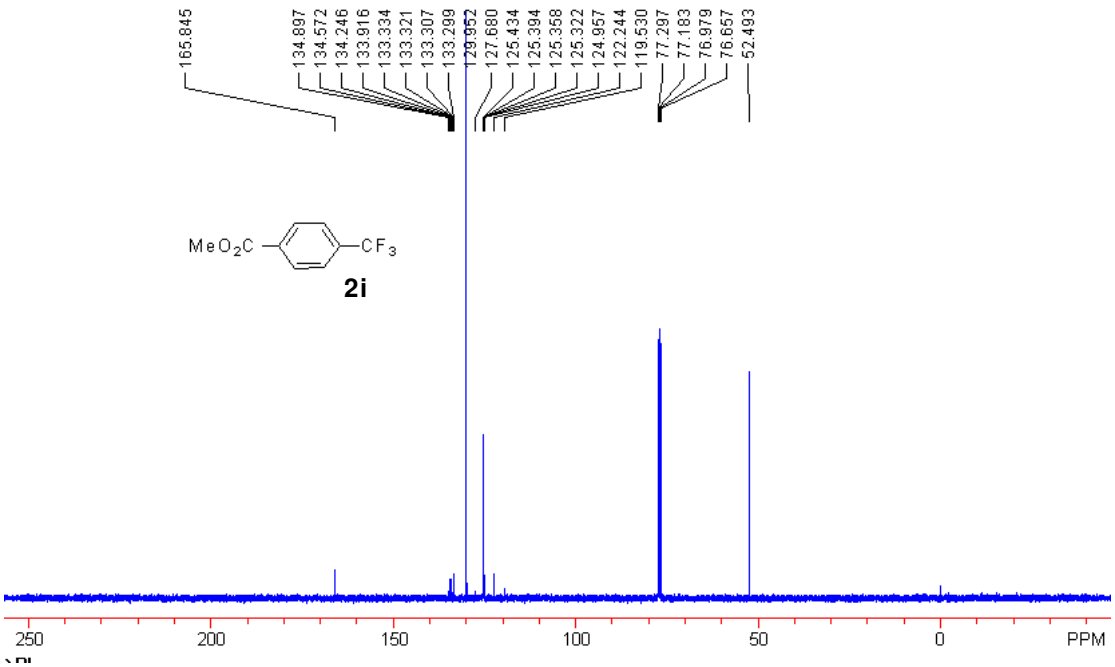
1-(trifluoromethyl)-4-vinylbenzene 2h:



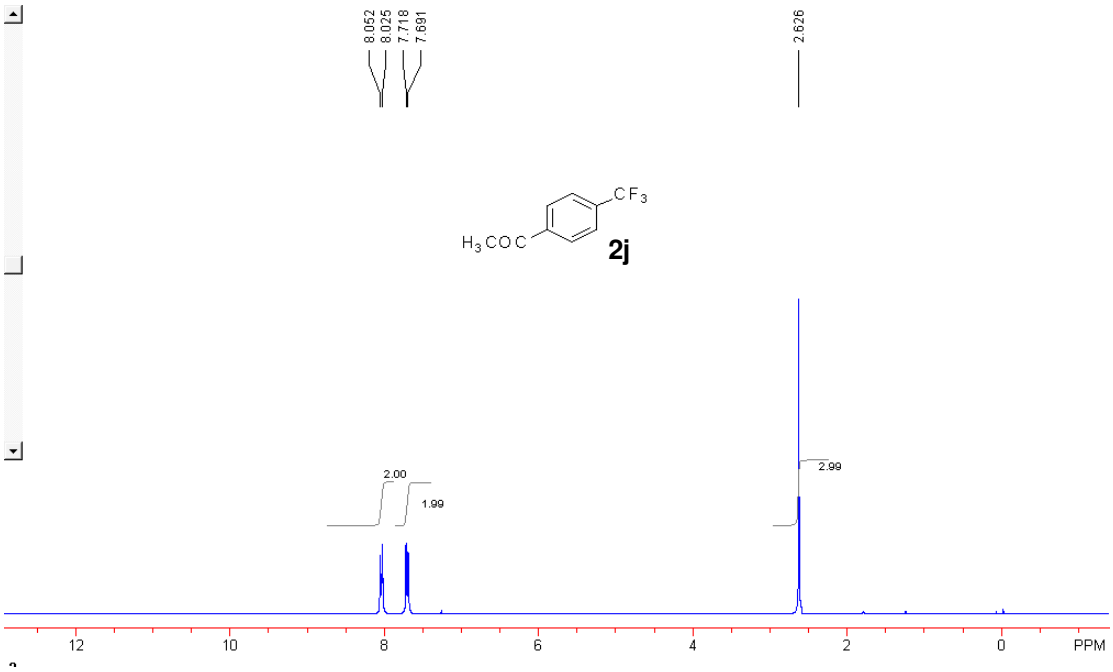


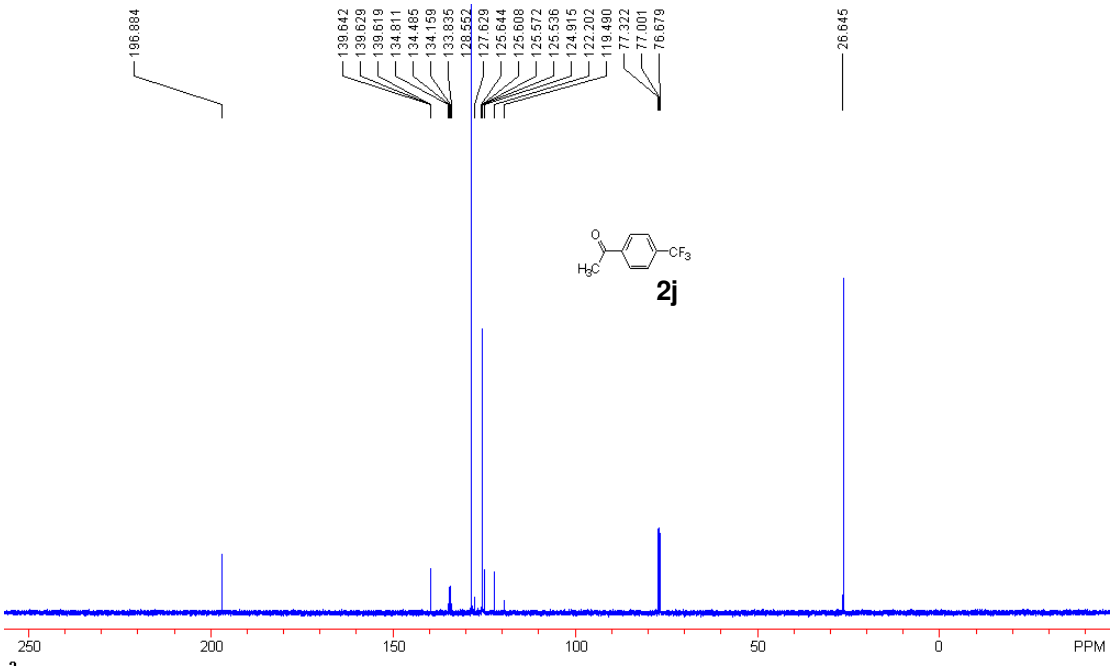
methyl 4-(trifluoromethyl)benzoate 2i:



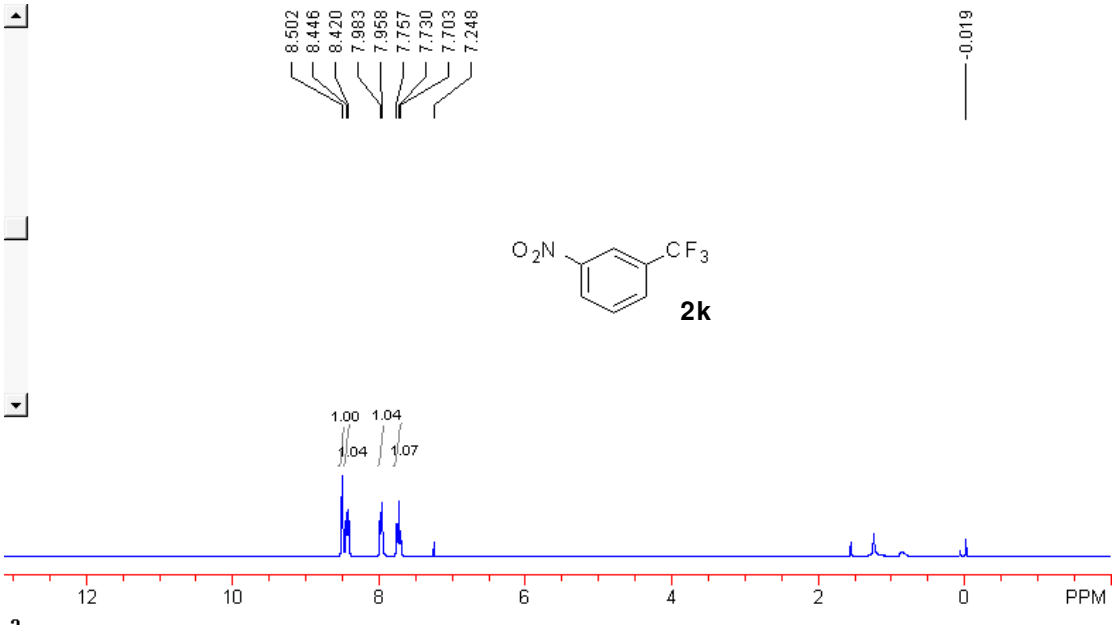


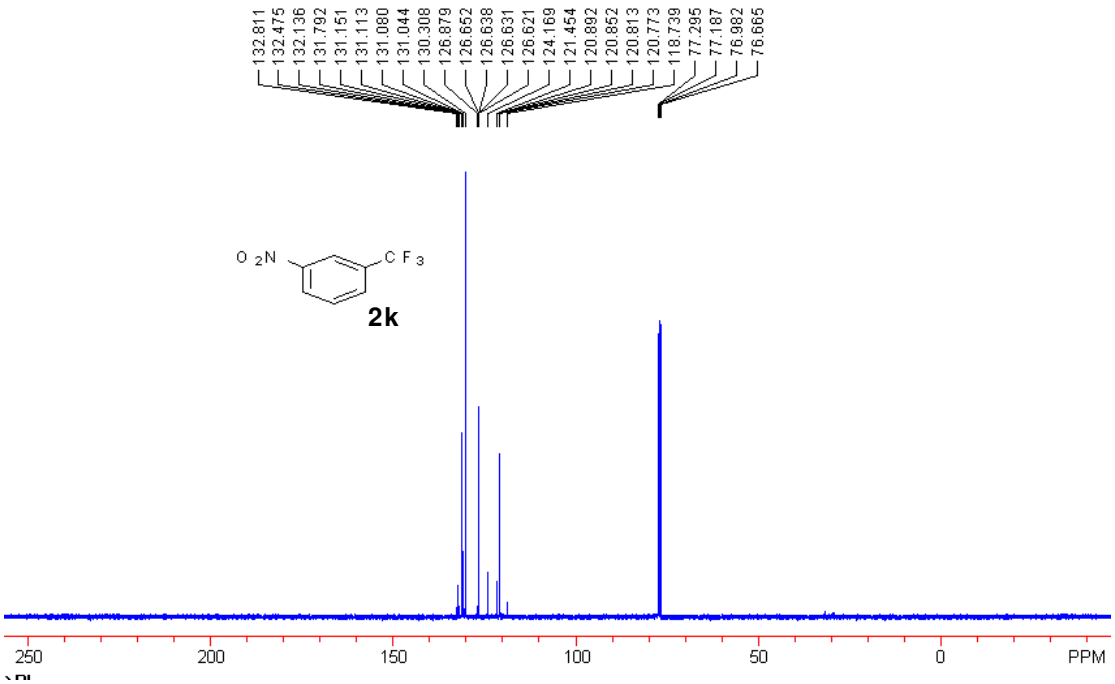
1-(4-(trifluoromethyl)phenyl)ethanone 2j:



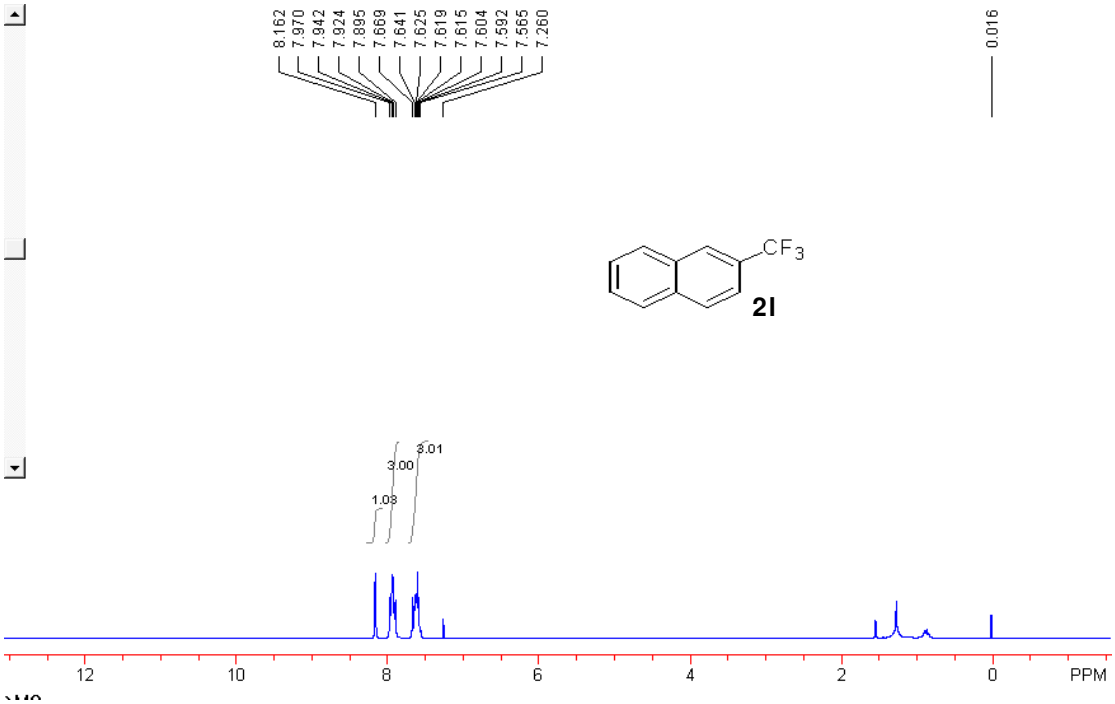


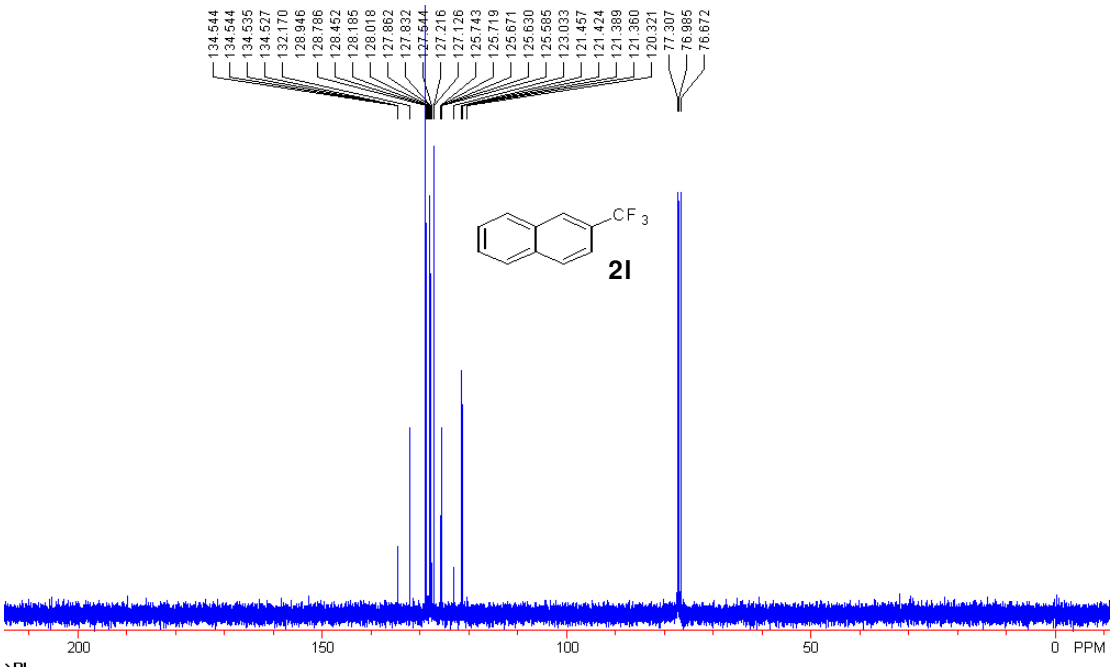
1-nitro-3-(trifluoromethyl)benzene 2k:



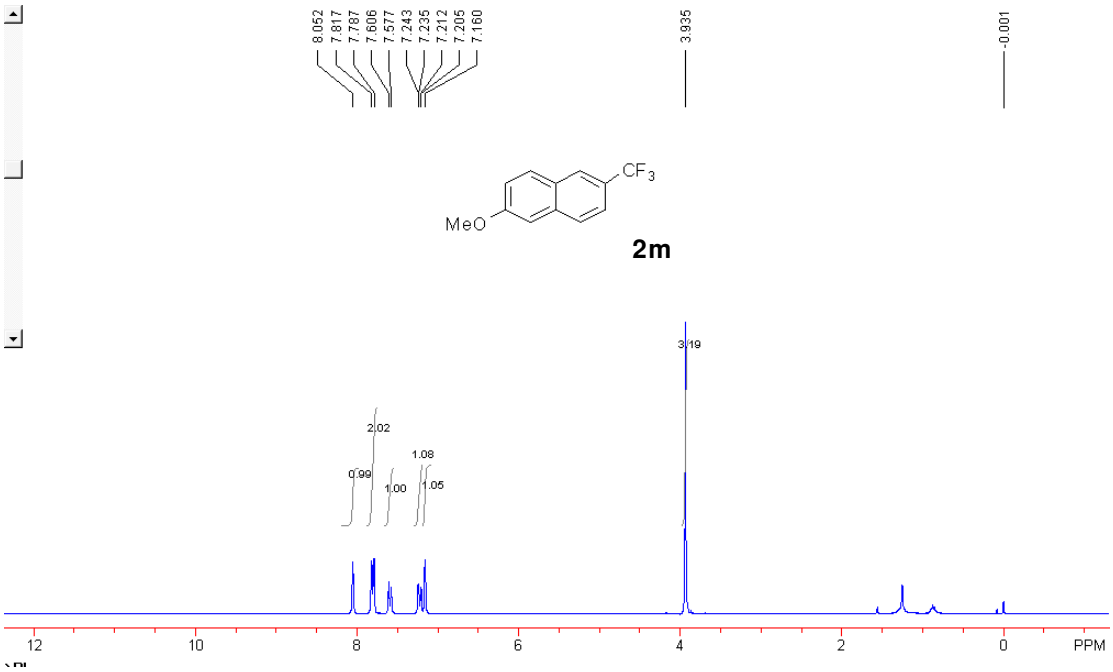


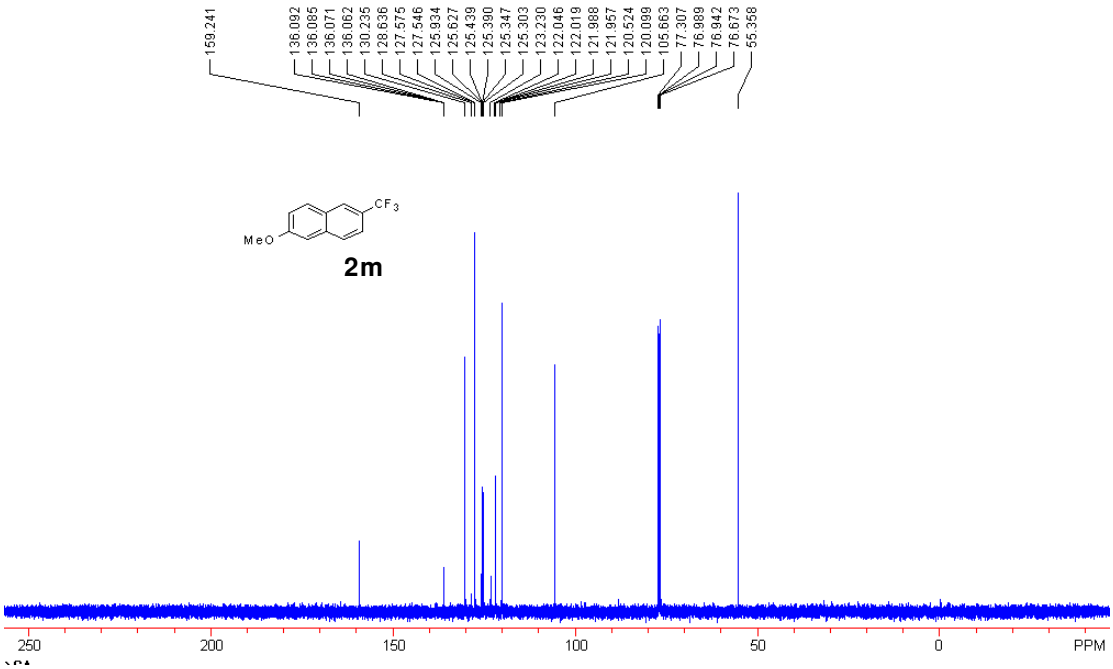
2-(trifluoromethyl)naphthalene 2l:



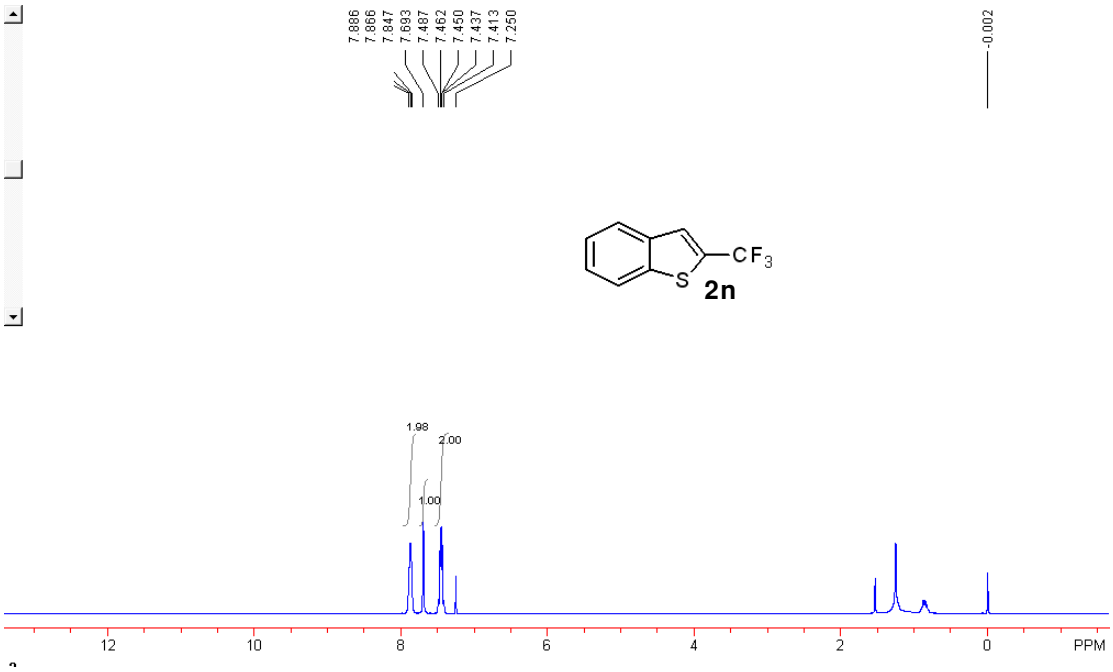


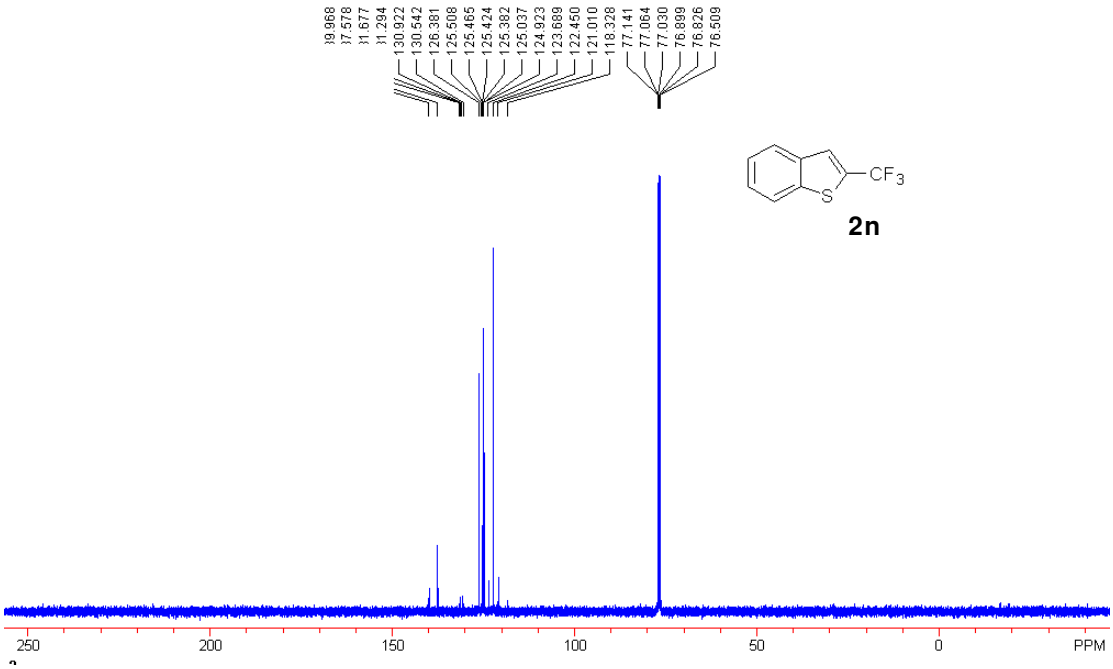
2-methoxy-6-(trifluoromethyl)naphthalene 2m:



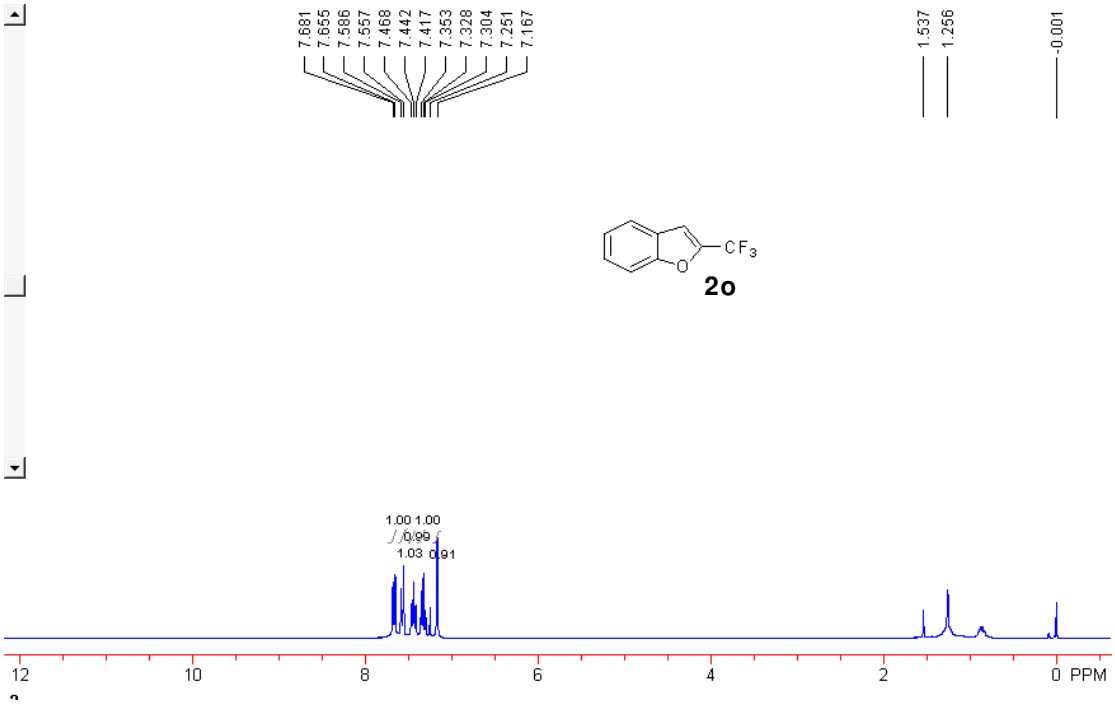


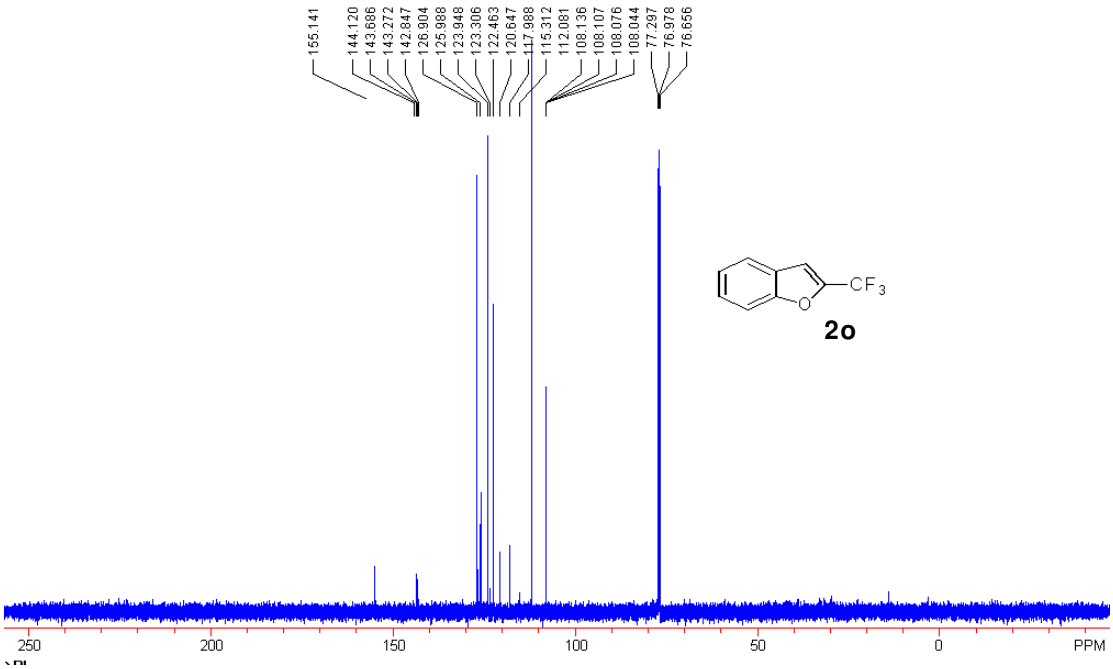
2-(trifluoromethyl)benzo[b]thiophene 2n:



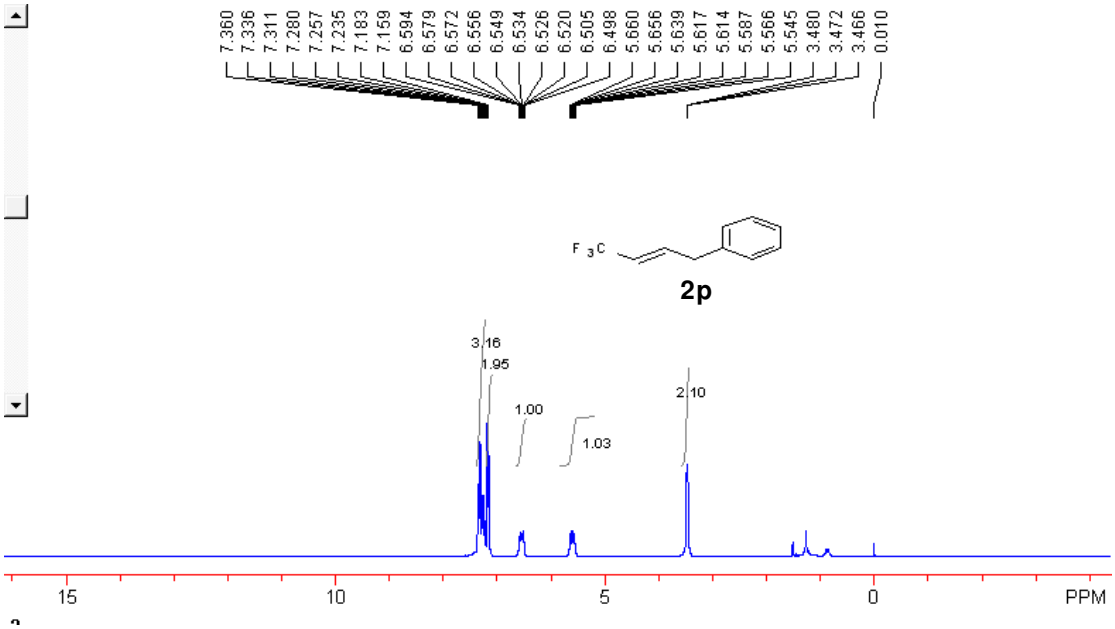


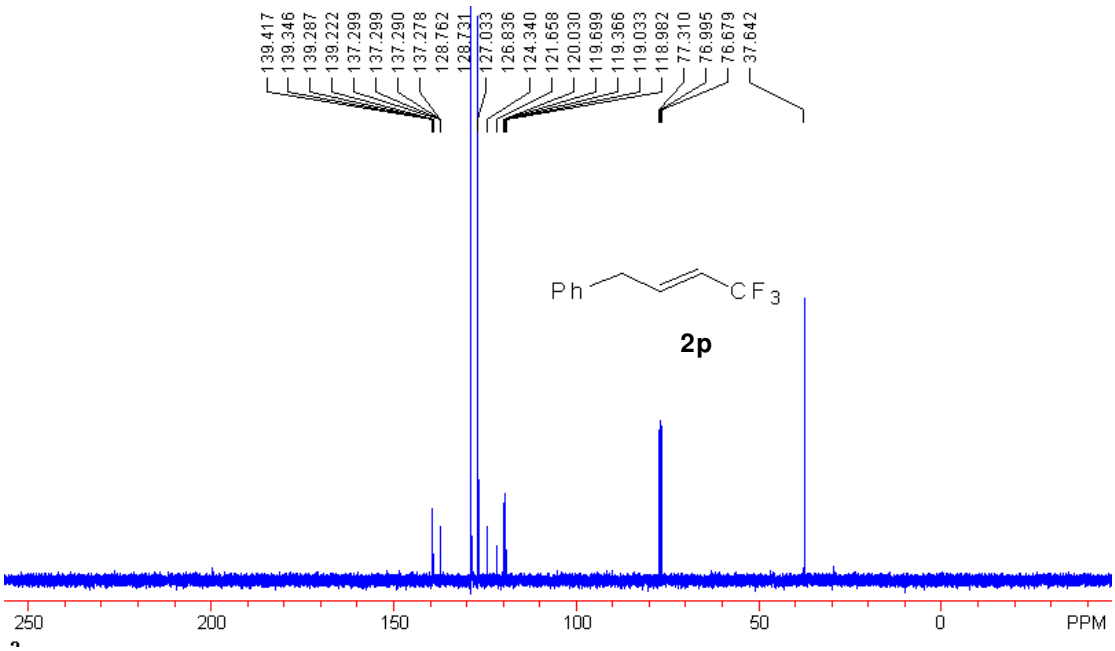
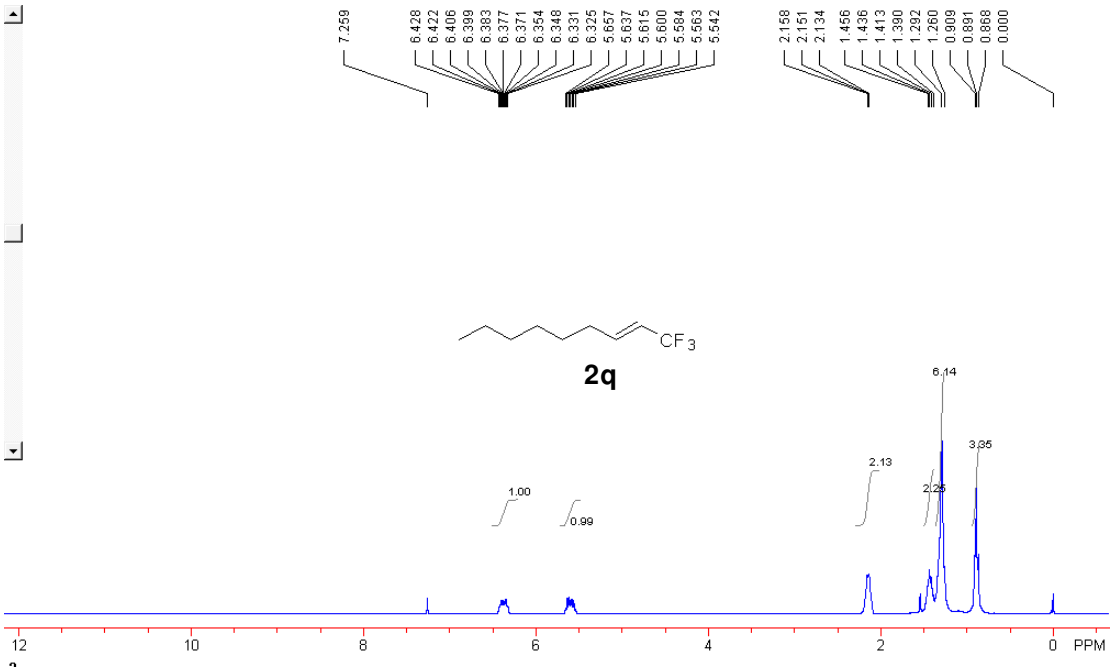
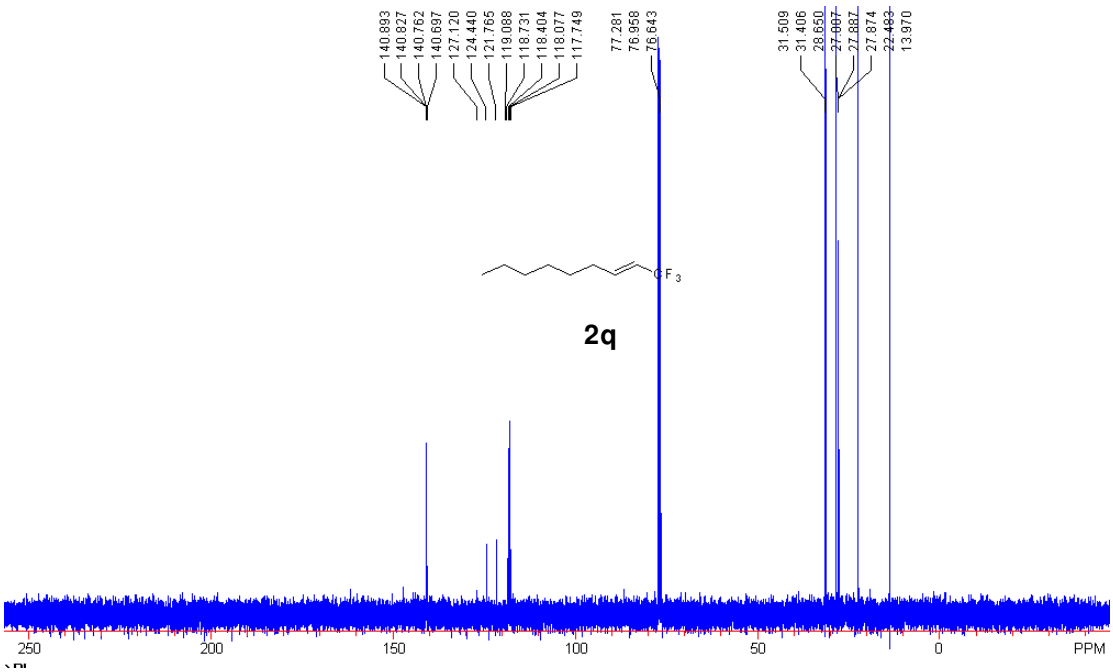
2-(trifluoromethyl)benzofuran 2o:





(E)-(4,4,4-trifluorobut-2-enyl)benzene 2p:





(E)-1,1,1-trifluoronon-2-ene 2q: