Electronic Supporting Information

Deprotonative C-H Silylation of Functionalized Arenes and Heteroarenes Using Trifluoromethyltrialkylsilane with Fluoride

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General Comments

Reactions were carried out under an Ar atmosphere using dry solvents. Melting points (mp) were determined with a Yazawa micro melting point apparatus and uncorrected. Infrared (IR) data were recorded on SensIR ATR (Attenuated Total Reflectance) FT-IR. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). NMR data were recorded on a JEOL AL400 spectrometer or a JEOL ECA600 spectrometer. Chemical shifts are expressed in δ (parts per million, ppm) values and coupling constants are expressed in herts (Hz). ^{1}H NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal ($CDCl_3$: 7.26 ppm). ^{13}C NMR spectra were referenced to a solvent signal ($CDCl_3$: 77.0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet. Low and high resolution mass spectra (LRMS and HRMS) were obtained from Mass Spectrometry Resource, Graduate School of Pharmaceutical Sciences, Tohoku University, on a JEOL JMS-DX 303 and JMS-700/JMS-T 100 GC spectrometer.

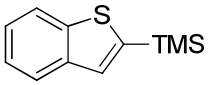
Materials

Materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used as received. Flash column chromatography was performed with Kanto silica gel 60 N (spherical, neutral, 70–230 mesh).

Representative Procedure for Trimethylsilylation of Aromatic Compounds using CF_3TMS (Table 1, Entry 10)

Under an Ar atmosphere, a mixture of benzo[b]thiophene (**1a**) (40.3 mg, 0.30 mmol), CsF (22.8 mg, 0.15 mmol) and CF_3TMS (133 µl, 0.90 mmol) in DMI (0.3 mL) was stirred at 0 °C for 2 h. The reaction mixture was quenched with saturated NH_4Cl aq. and extracted with diethylether (10 ml x 3). The combined organic phase was washed with brine and dried over $MgSO_4$. The organic phase was concentrated under a reduced pressure and the crude material was purified by silica gel column chromatography (1% AcOEt in hexane) to 2-trimethylsilylbenzo[b]thiophene (**2a**) (58.2 mg, 94%).

2-Trimethylsilylbenzo[*b*]thiophene (2a)[i]



Yellow oil. (58.2 mg, 94%)

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.38 (s, 9H), 7.28–7.36 (m, 2H), 7.46 (s, 1H), 7.80 (d, J = 7.8 Hz, 2H), 7.88 (d, J = 7.8 Hz, 2H).

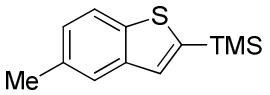
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): –0.3, 122.2, 123.4, 124.0, 124.1, 130.8, 141.1, 142.1, 143.5.

LRMS (EI) *m/z*: 206 (M^+).

HRMS: Calcd. for $C_{11}H_{14}SSi$: 206.0585. Found: 206.0573.

IR (neat): 3075, 2956, 2900, 1493, 1453, 1249, 1017, 869, 826, 755, 742, 726 cm^{-1}.

5-Methyl-2-trimethylsilylbenzo[*b*]thiophene (2b)



Colorless oil. (53.6 mg, 81%)

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.36 (s, 9H), 2.45 (s, 3H), 7.13 (d, J = 8.3 Hz, 1H), 7.37 (s, 1H), 7.58 (s, 1H), 7.74 (d, J = 8.3 Hz, 1H).

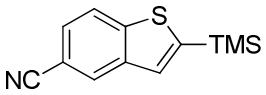
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): –0.3, 21.3, 121.8, 123.3, 126.0, 130.4, 133.6, 140.8, 141.8, 142.3.

LRMS (EI) *m/z*: 220 (M^+).

HRMS: Calcd. for $C_{11}H_{14}SSi$: 220.0742. Found: 220.0739.

IR (neat): 3075, 3050, 2956, 2910, 1502, 1449, 1070, 973, 834, 828, 794, 754 cm^{-1}.

5-Carbonitrile-2-trimethylsilylbenzo[*b*]thiophene (2c)



Recrystallized from hexane/acetone, white solid, mp 88–90 °C. (54.8 mg, 79%)

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.40 (s, 9H), 7.49–7.52 (m, 2H), 7.95 (d, J = 9.3 Hz, 1H), 8.11 (s, 1H).

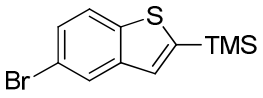
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): –0.5, 107.6, 119.5, 123.1, 125.9, 127.9, 130.3, 140.8, 146.0, 147.5.

LRMS (EI) *m/z*: 231 (M^+).

HRMS: Calcd. for $C_{12}H_{13}NSSi$: 231.0538. Found: 231.0512.

IR (neat): 2955, 2897, 2218, 1408, 1285, 1250, 1243, 1069, 973, 835, 805, 756 cm^{-1}.

5-Bromo-2-trimethylsilylbenzo[*b*]thiophene (2d)[ii]



Yellow oil. (79.6 mg, 93%)

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.37 (s, 9H), 7.36–7.41 (m, 2H), 7.72 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 1.5 Hz, 1H).

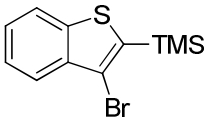
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): –0.4, 118.0, 123.4, 125.9, 127.1, 129.8, 142.1, 142.7, 144.7.

LRMS (EI) *m/z*: 284 (M^+).

HRMS: Calcd. for $C_{11}H_{13}BrSSi$: 283.9691. Found: 283.9672.

IR (neat): 3075, 2955, 2900, 1578, 1491, 1249, 1068, 969, 881, 836, 795, 755 cm^{-1}.

3-Bromo-2-trimethylsilylbenzo[*b*]thiophene (2e)[iii]



Yellow oil. (55.6 mg, 65%)

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.47 (s, 9H), 7.39 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 7.43 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 7.81–7.85 (m, 2H).

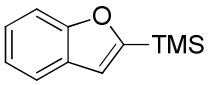
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): –0.8, 114.7, 122.1, 122.9, 124.8, 125.1, 136.1, 139.8, 141.4.

LRMS (EI) *m/z*: 284 (M^+).

HRMS: Calcd. for $C_{11}H_{13}BrSSi$: 283.9691. Found: 283.9669.

IR (neat): 3057, 2956, 2897, 1482, 1290, 1248, 1242, 1020, 991, 881, 835, 749, 726 cm^{-1}.

2-Trimethylsilylbenzo[*b*]furan (2f)[iv]



Colourless oil. (29.1mg, 51%)

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.35 (s, 9H), 6.96 (s, 1H), 7.19 (dd, *J* = 7.3 Hz, 7.3 Hz, 1H), 7.27 (dd, *J* = 7.3 Hz, 8.5 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 7.3 Hz,

1H).

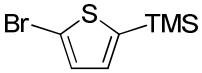
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): –1.8, 111.3, 116.0, 120.9, 122.3, 124.3, 128.0, 158.1, 163.5.

LRMS (EI) *m/z*: 190 (M^+).

HRMS: Calcd. for $C_{11}H_{14}OSi$: 190.0814. Found: 190.0789.

IR (neat): 3065, 2960, 2926, 1529, 1471, 1443, 1250, 1111, 1066, 920, 837, 750, 740 cm^{-1}.

2-Bromo-5-trimethylsilylthiophene (4a)[v]



Yellow oil. (50.1 mg, 71%)

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.29 (s, 9H), 6.98 (d, J = 3.4 Hz, 1H), 7.08 (d, J = 3.4 Hz, 1H).

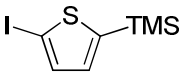
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): –0.3, 116.7, 131.1, 134.3, 143.3.

LRMS (EI) *m/z*: 234 (M^+).

HRMS: Calcd. for $C_7H_{11}BrSSi$: 233.9534. Found: 233.9533.

IR (neat): 2956, 2900, 1406, 1250, 1203, 1067, 954, 834, 794, 754 cm^{-1}.

2-Iodo-5-trimethylsilylthiophene (4b)[vi]



Red oil. (60.7 mg, 72%)

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.29 (s, 9H), 6.91 (d, J = 3.4 Hz, 1H), 7.25 (d, J = 3.4 Hz, 1H).

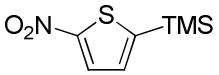
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): –0.2, 78.0, 135.5, 138.1, 148.1.

LRMS (EI) *m/z*: 282 (M^+).

HRMS: Calcd. for $C_7H_{11}SSiI$: 281.9395. Found: 281.9397.

IR (neat): 2955, 2900, 2875, 1396, 1248, 1202, 1067, 990, 936, 834, 795, 754 cm^{-1}.

2-Nitro-5-trimethylsilylthiophene (4c)[vii]



Red oil. (41.1 mg, 68%)

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.37 (s, 9H), 7.14 (d, *J* = 3.9 Hz, 1H), 7.92 (d, *J* = 3.9 Hz, 1H).

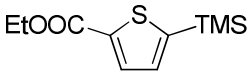
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm): –0.6, 129.2, 132.8, 151.1, 156.3.

LRMS (EI) *m/z*: 201 (M^+).

HRMS: Calcd. for $C_7H_{11}O_2NSSi$: 201.0280. Found: 201.0293.

IR (neat): 2958, 2875, 1525, 1494, 1340, 1253, 1046, 1041, 983, 837, 814, 754, 733 cm^{-1}.

Ethyl 5-trimethylsilylthiophene-2-carboxylate (4d)



Yellow oil. (25.3 mg, 37%)

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.34 (s, 9H), 1.37 (t, *J* = 7.2 Hz, 3H), 4.34 (q, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 3.7 Hz, 1H), 7.92 (d, *J* = 3.7 Hz, 1H).

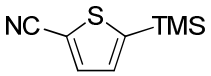
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): –0.3, 14.3, 61.0, 134,0, 134.1, 138.6, 149.2, 162.2.

LRMS (EI) *m/z*: 228 (M^+).

HRMS: Calcd. for $C_{10}H_{16}O_2SSi$: 228.0640. Found: 228.0649.

IR (neat): 2958, 2900, 1710, 1519, 1426, 1312, 1274, 1239, 1089, 988, 838, 750 cm^{-1}.

2-Cyano-5-trimethylsilylthiophene (4e)[7]



Yellow oil. (45.7 mg, 84%)

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.35 (s, 9H), 7.20 (d, J = 3.9 Hz, 1H), 7.65 (d, J = 3.9 Hz, 1H).

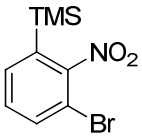
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): –0.4, 114.1, 114.4, 133.7, 137.9, 150.5.

LRMS (EI) *m/z*: 181 (M^+).

HRMS: Calcd. for $C_8H_{11}NSSi$: 181.0381. Found: 181.0379.

IR (neat): 2958, 2900, 2211, 1252, 1003, 873, 840, 821, 757 cm^{-1}.

1-Bromo-2-nitro-3-trimethylbenzene (6a)



Yellow oil. (28.8 mg, 35%)

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.31 (s, 9H), 7.32 (dd, J = 7.8 Hz, 7.3 Hz, 1H), 7.52 (d, J = 7.3 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H).

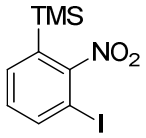
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): –1.3, 113.3, 130.9, 134.2, 134.5, 135.1, 155.8.

LRMS (EI) *m/z*: 258 (M^+–15).

HRMS: Calcd. for $C_8H_9O_2NBrSi$: 257.9586. Found: 257.9584.

IR (neat): 2957, 2902, 1532, 1366, 1253, 1075, 840, 762 cm^{-1}.

1-Iodo-2-nitro-3-trimethylbenzene (6b)



Yellow oil. (16.3 mg, 17%)

^{1}H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 0.29 (s, 9H), 7.16 (dd, J = 6.4 Hz, 6.4 Hz, 1H), 7.55 (d, J = 6.4 Hz, 1H), 7.90 (d, J = 6.4 Hz, 1H).

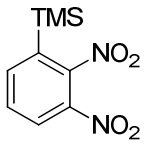
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ (ppm): –1.3, 86.1, 130.9, 134.9, 135.0, 141.2, 159.6.

LRMS (EI) *m/z*: 306 (M^+–15).

HRMS: Calcd. for $C_8H_9O_2NISi$: 305.9447. Found: 305.9447.

IR (neat): 2957, 2901, 1529, 1364, 1252, 1067, 1054, 840, 768, 758 cm^{-1}.

1,2-Dinitro-3-trimethylsilylbenzene (6c)



Recrystallized from hexane, yellow prisms, mp 57–59 °C. (23.1 mg, 32%)

Anal. Calcd. for: C, 44.99; H, 5.03; N, 11.66. Found: C, 44.82; H, 5.03; N, 11.66.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.36 (s, 9H), 7.66 (dd, J = 7.8 Hz, 7.8 Hz, 1H), 7.88 (dd, J = 1.4 Hz, 7.8 Hz, 1H), 8.04 (dd, J = 1.4 Hz, 7.8 Hz, 1H).

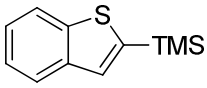
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ (ppm): –1.3, 125.9, 130.9, 136.6, 140.5, 141.4, 148.5.

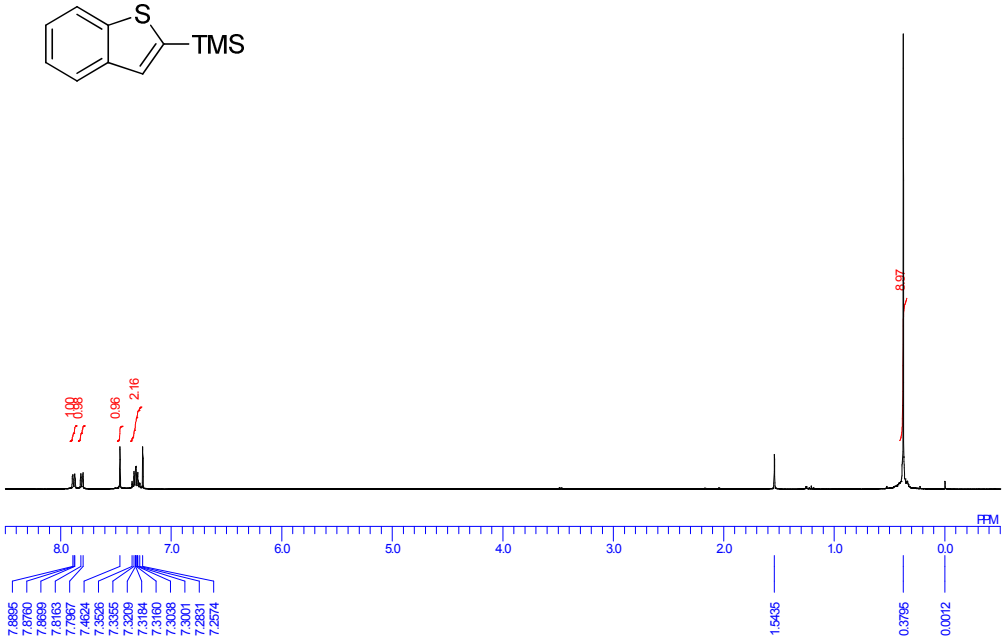
LRMS (EI) *m/z*: 225 (M^+–15).

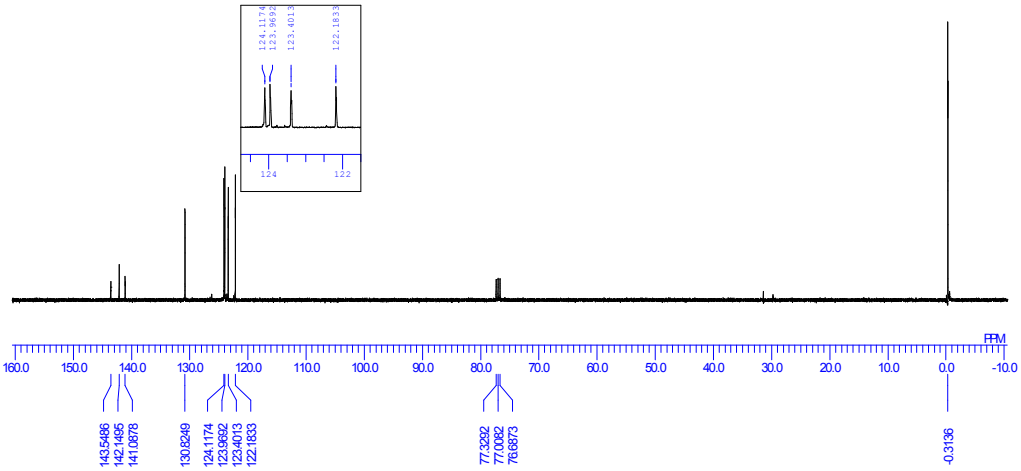
HRMS: Calcd. for $C_8H_9O_4N_2Si$: 225.0332. Found: 225.0317.

IR (neat): 3078, 2957, 1565, 1526, 1353, 1256, 1222, 1149, 885, 841, 813, 751 cm^{-1}.

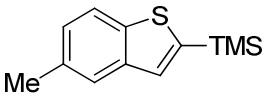
2-Trimethylsilylbenzo[*b*]thiophene(2a)

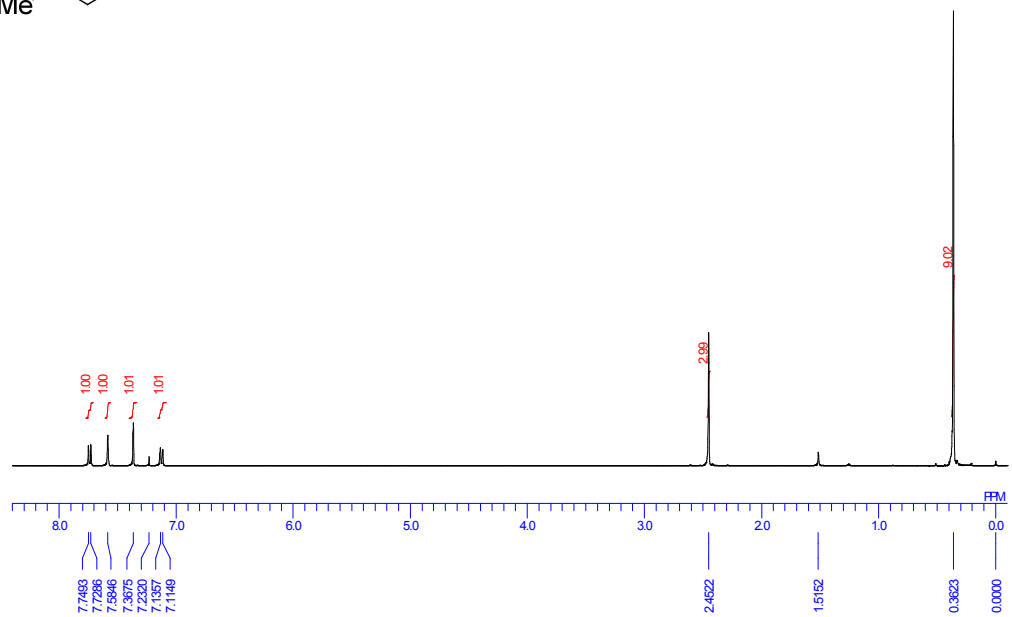


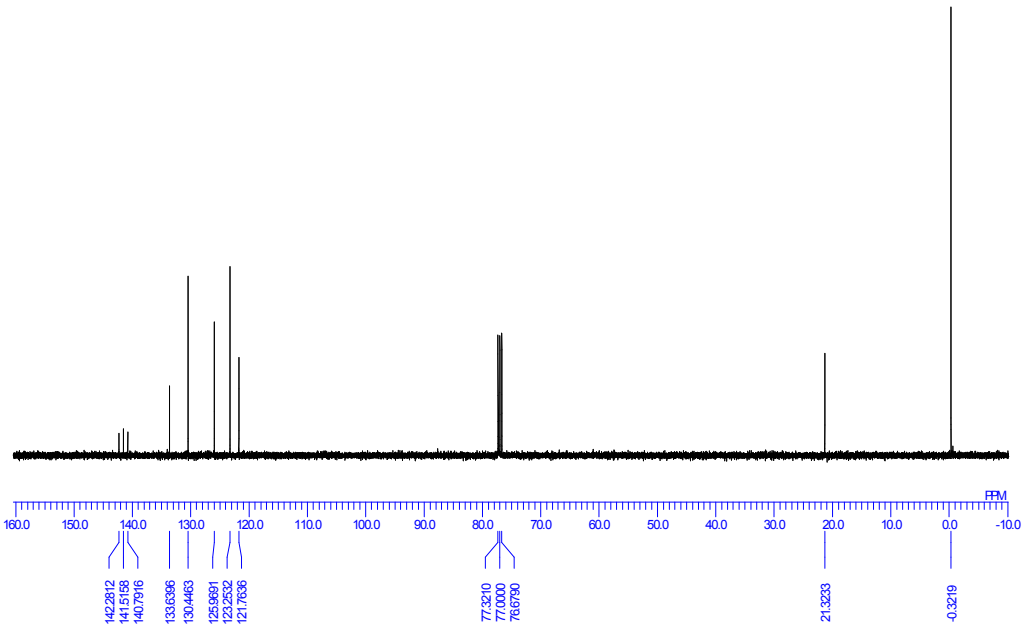




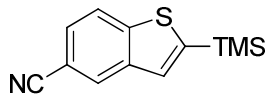
5-Methyl-2-trimethylsilylbenzo[*b*]thiophene(2b)

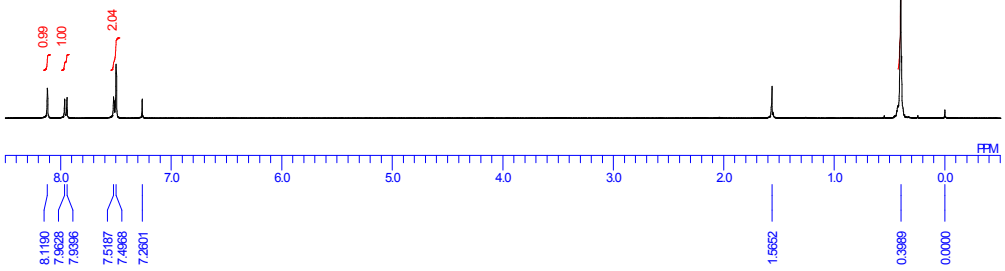


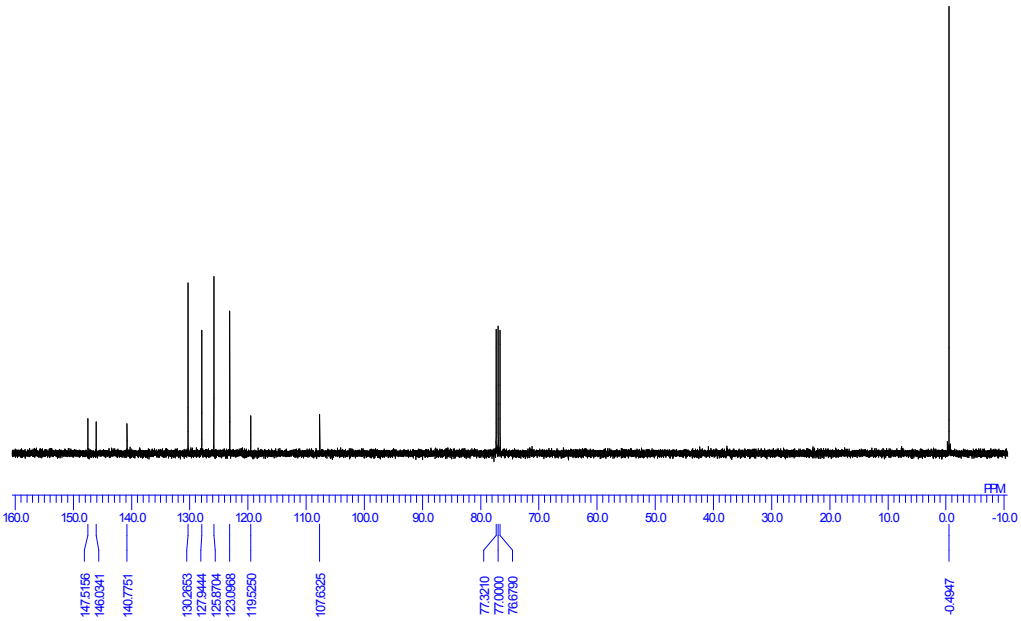




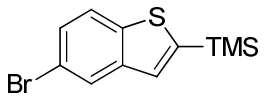
5-Carbonitrile-2-trimethylsilylbenzo[*b*]thiophene(2c)

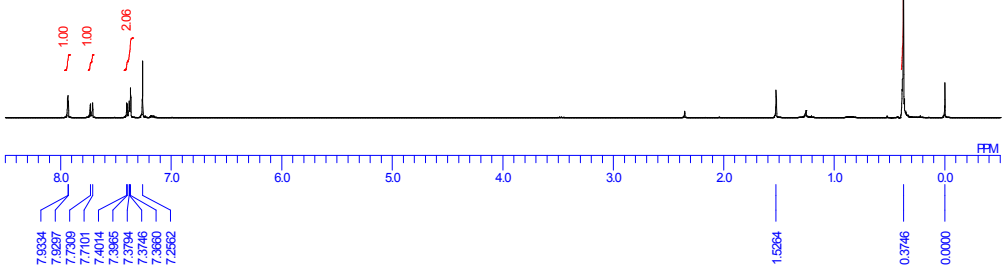


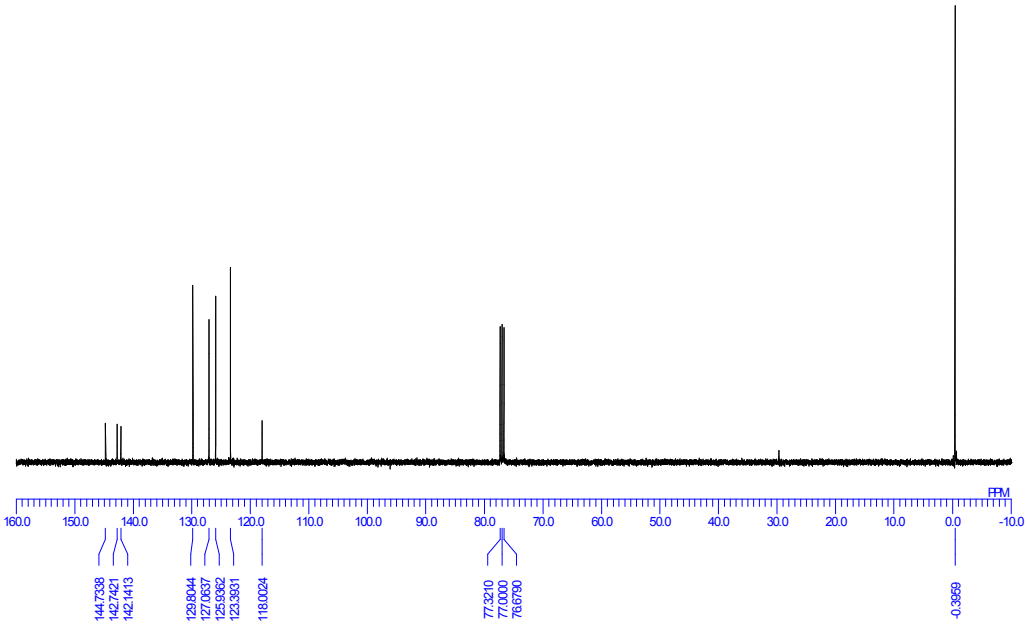




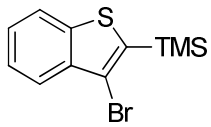
5-Bromo-2-trimethylsilylbenzo[*b*]thiophene(2d)

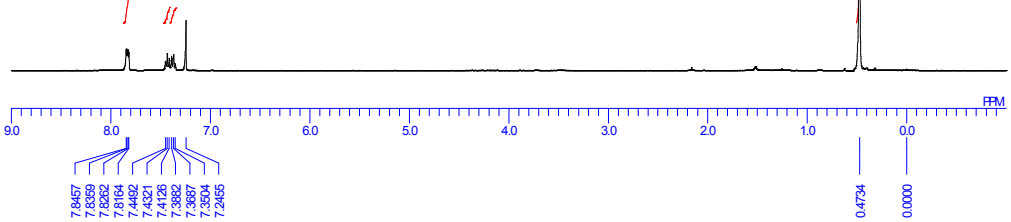


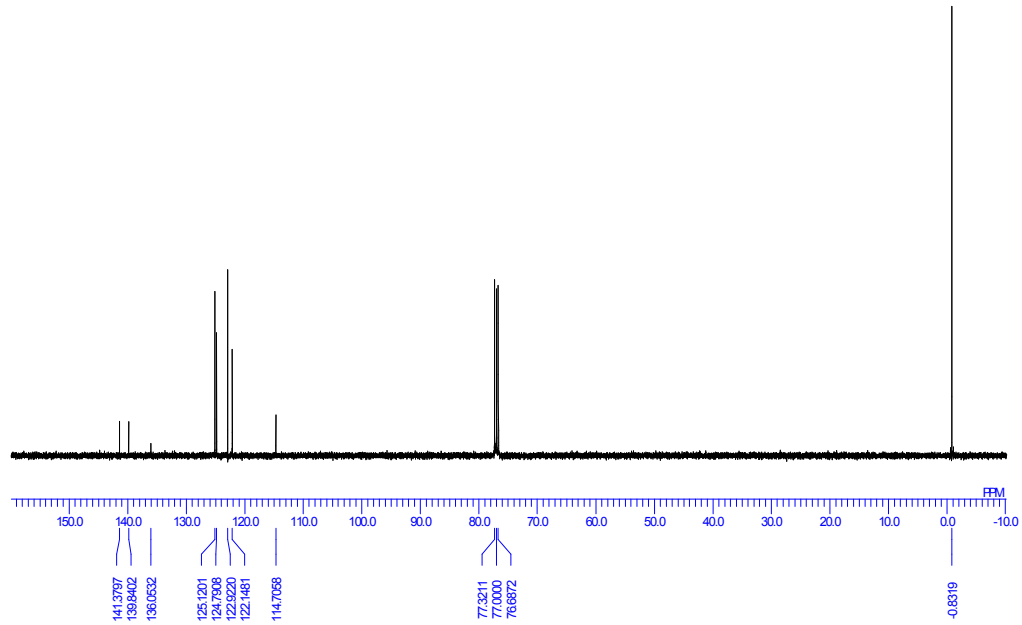




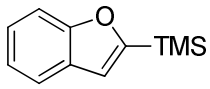
3-Bromo-2-trimethylsilylbenzo[*b*]thiophene(2e)

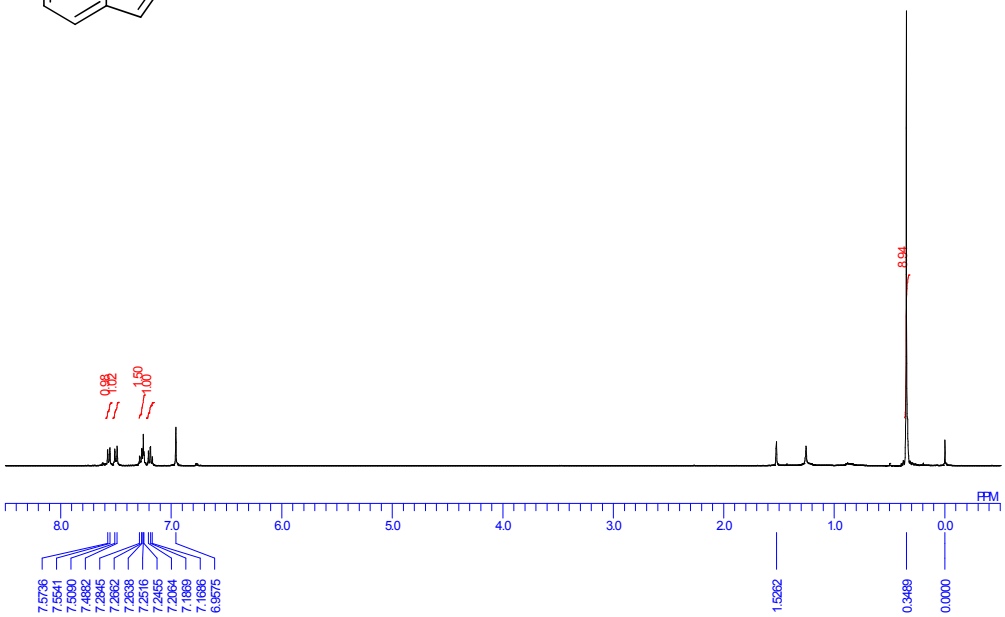


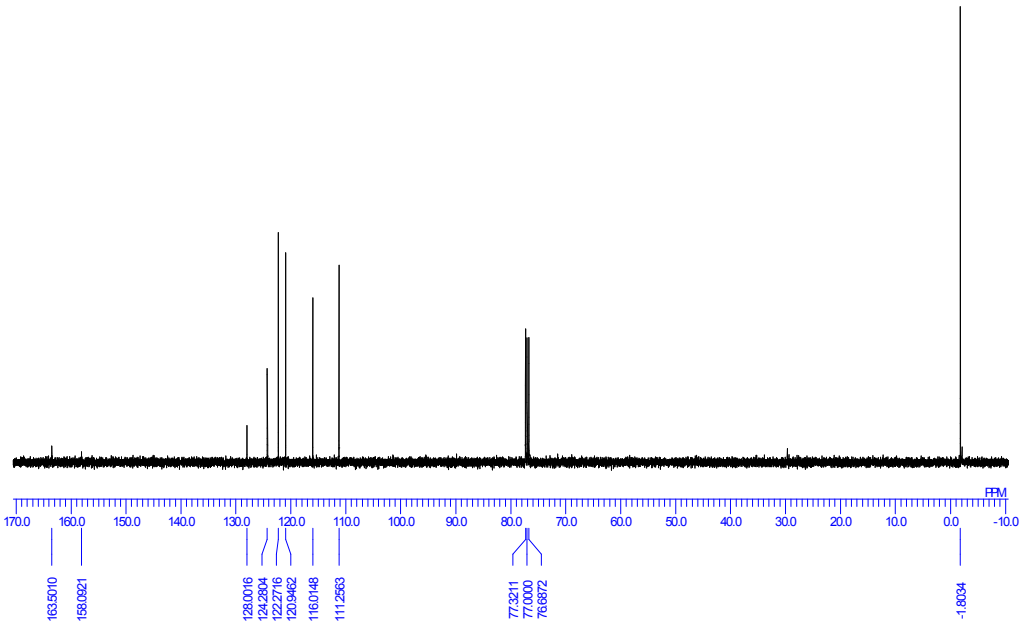




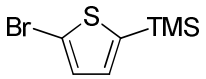
2-Trimethylsilylbenzo[*b*]furan(2f)

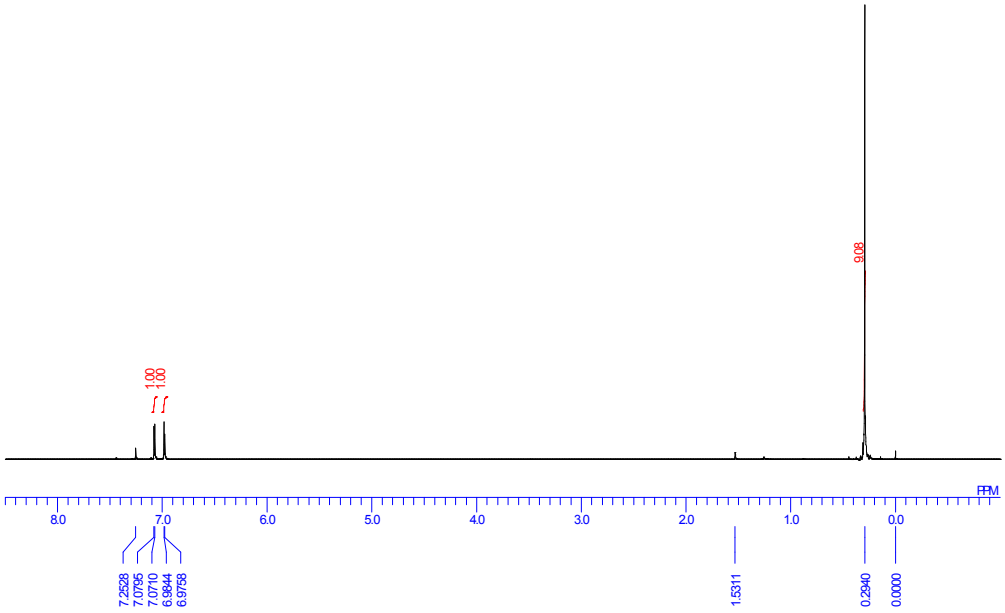


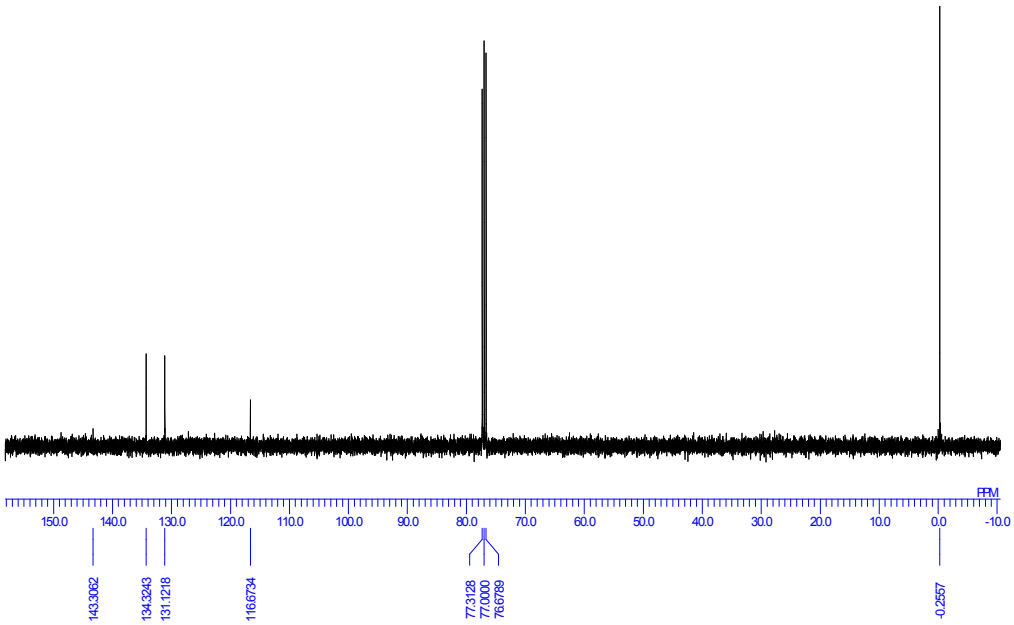




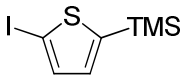
2-Bromo-5-trimethylsilylthiophene(4a)

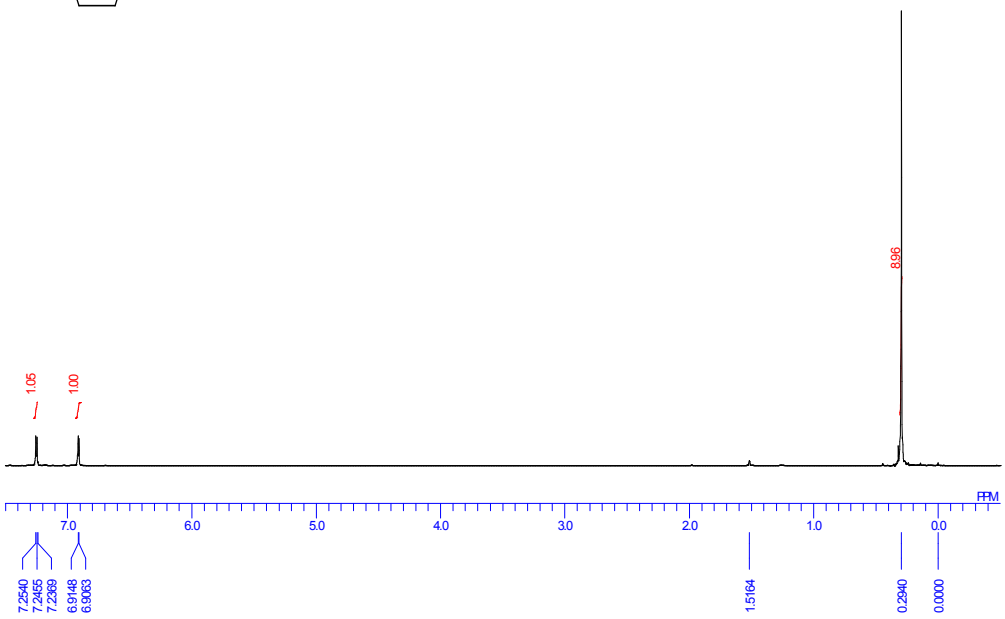


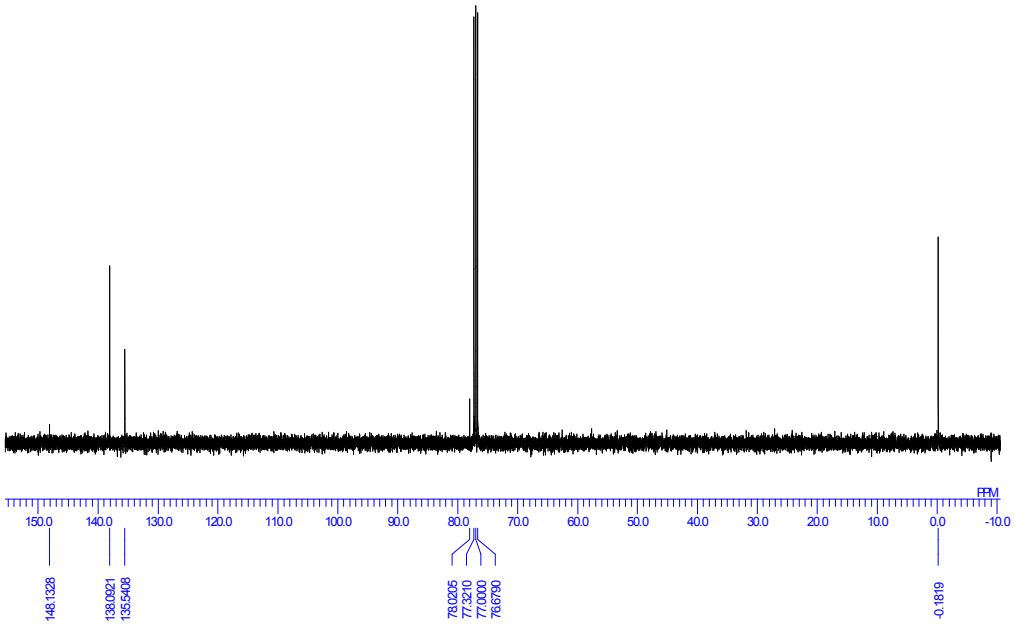




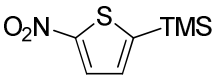
2-Iodo-5-trimethylsilylthiophene(4b)

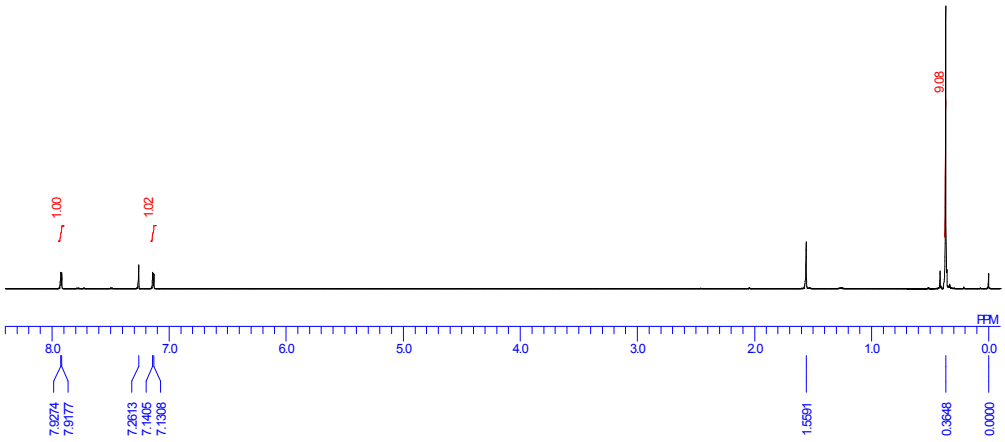


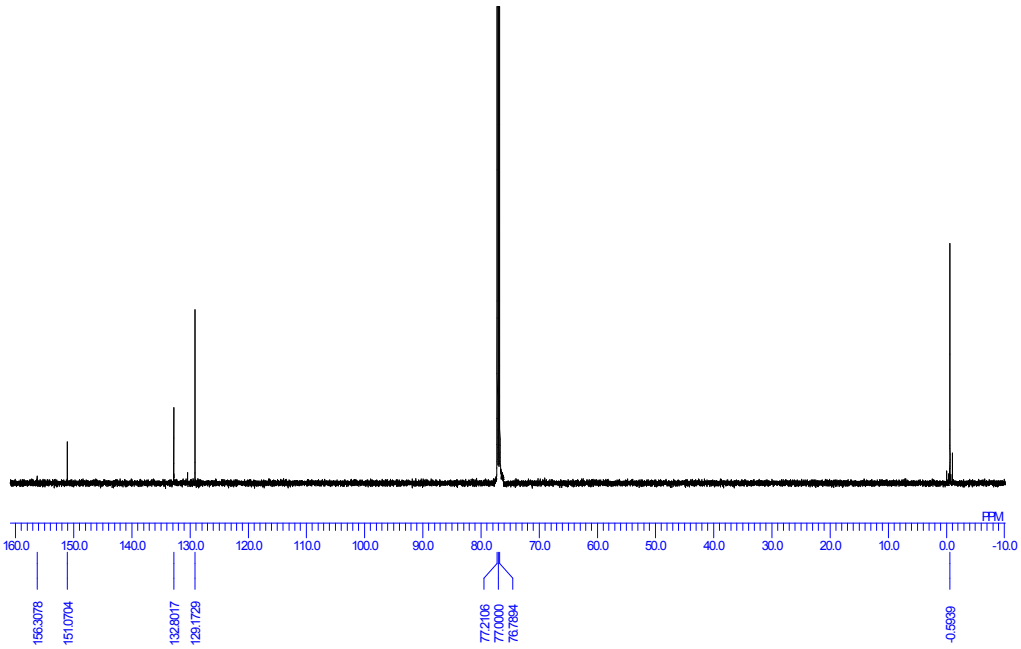




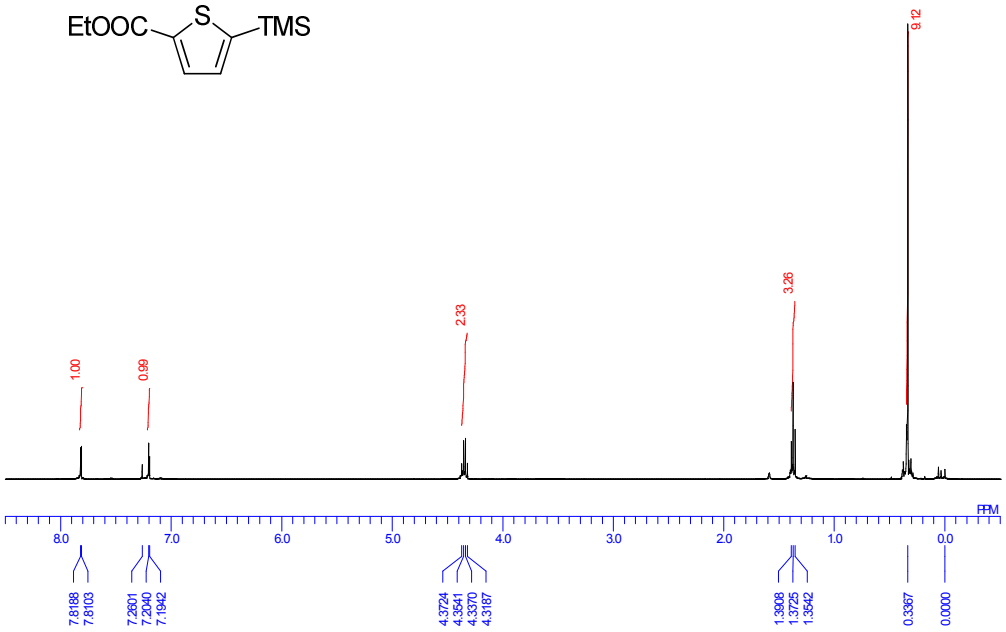
2-Nitro-5-trimethylsilylthiophene(4c)

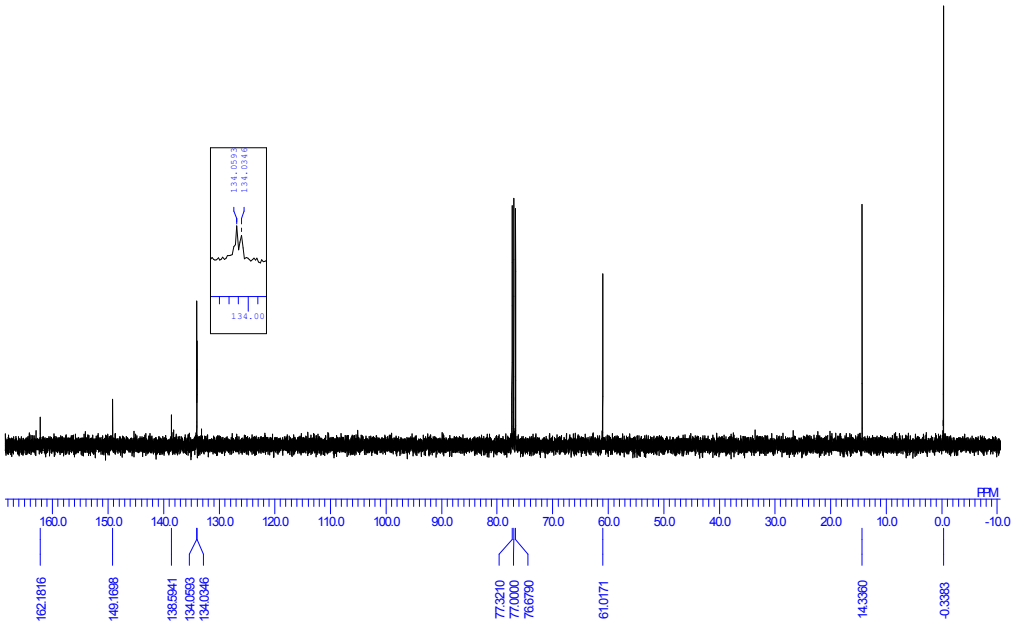




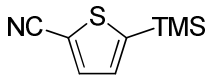


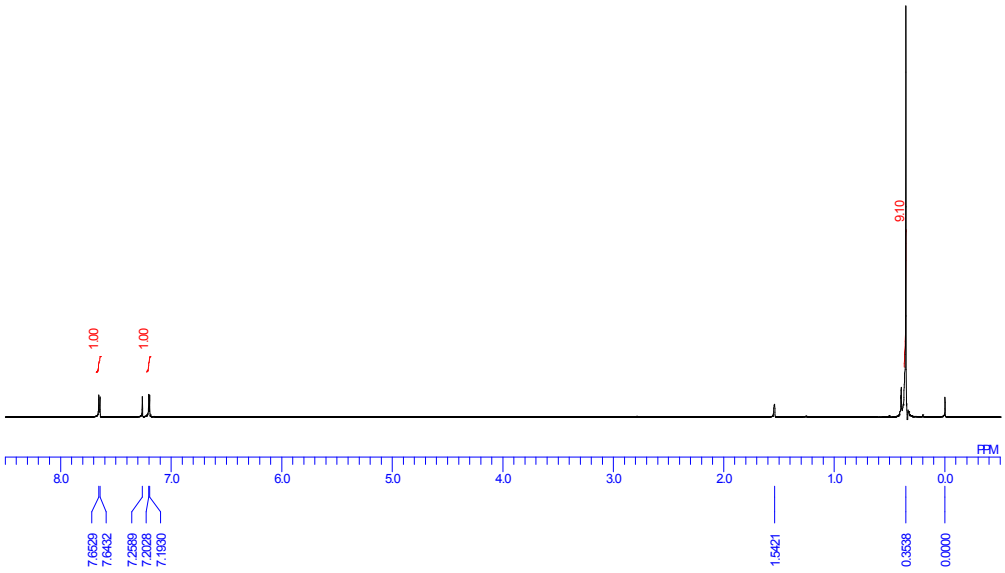
Ethyl 5-trimethylsilylthiophene-2-carboxylate(4d)

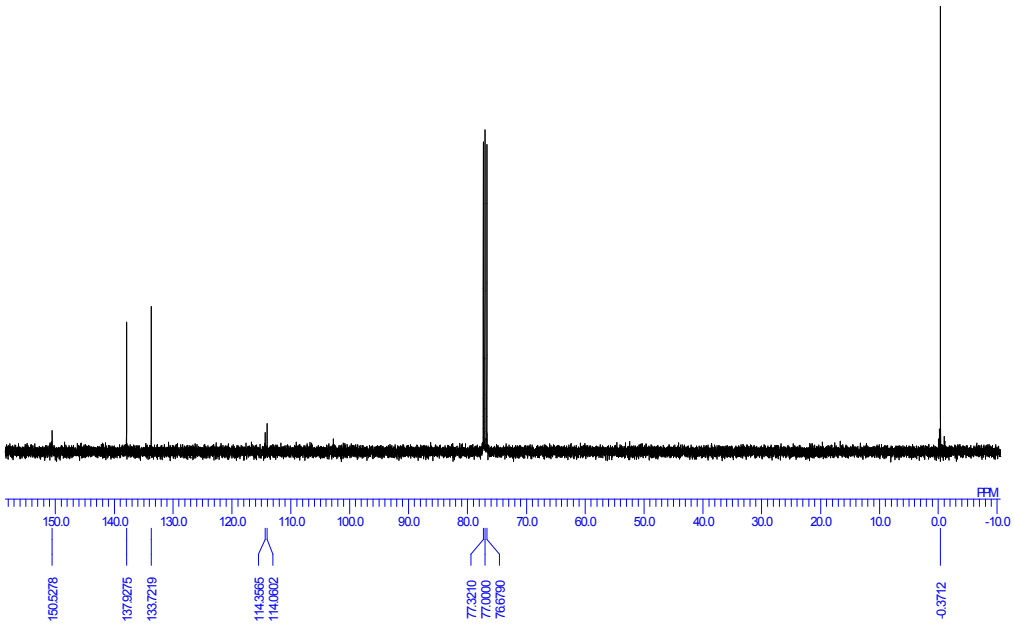




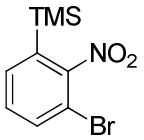
2-Cyano-5-trimethylsilylthiophene(4e)

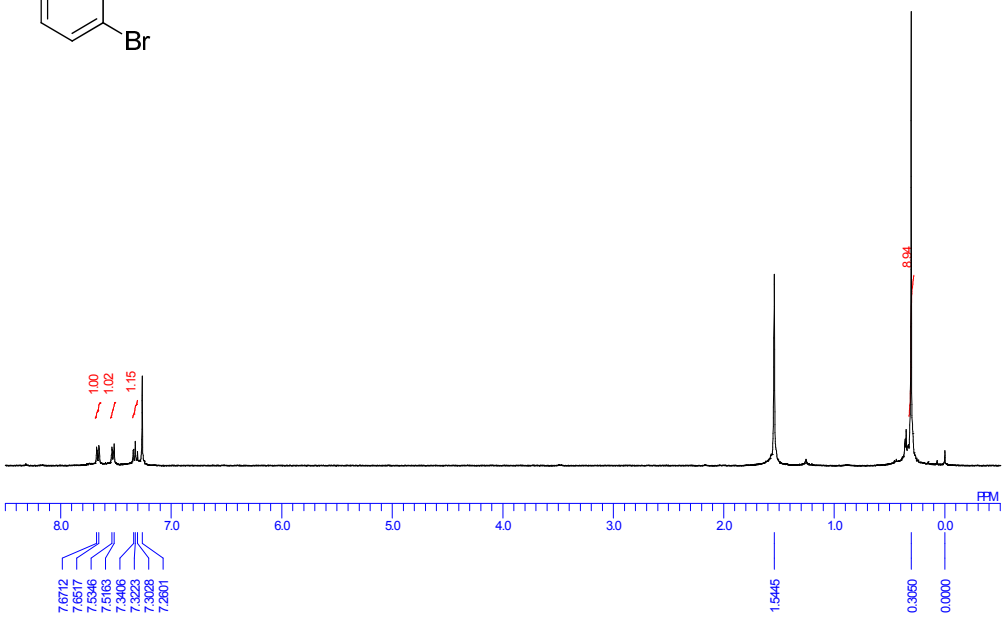


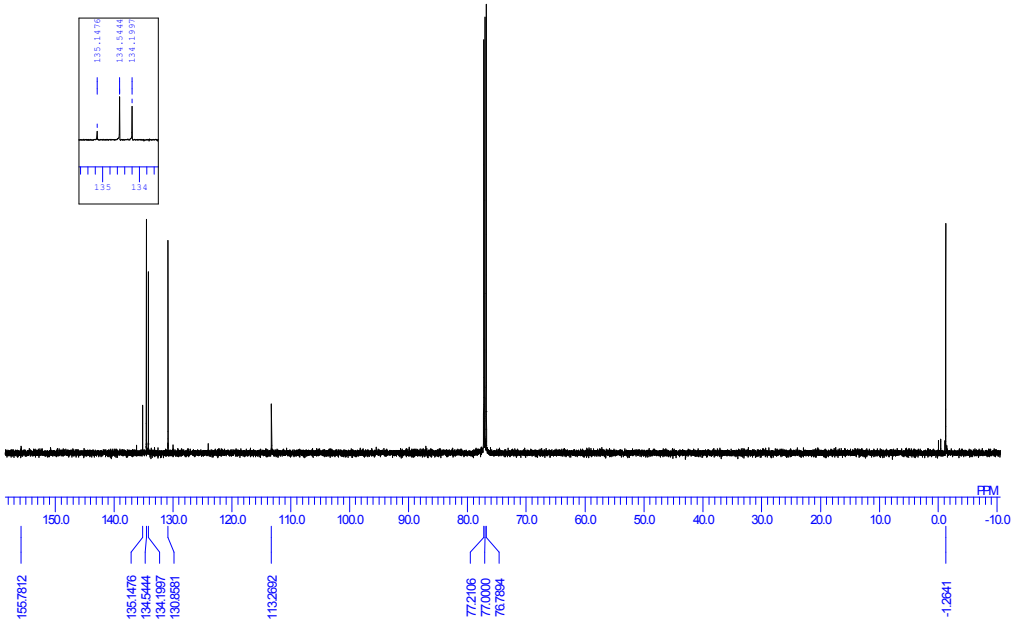




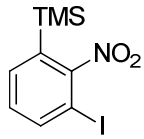
1-Bromo-2-nitro-3-trimethylbenzene(6a)

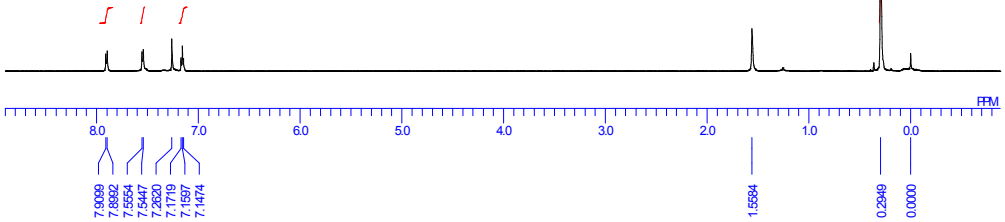


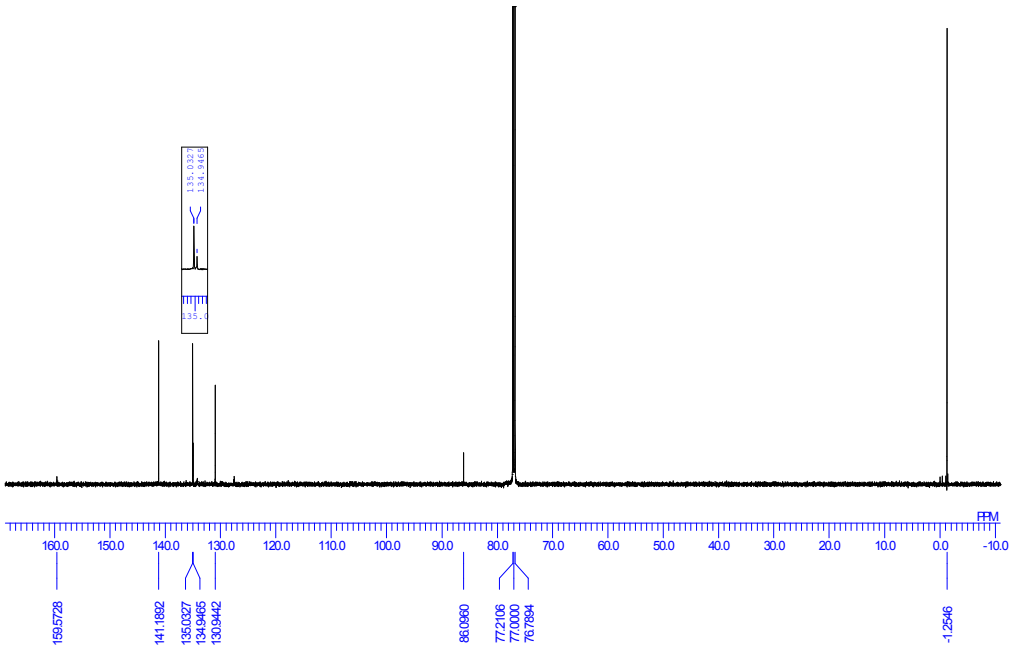




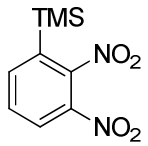
1-Iodo-2-nitro-3-trimethylbenzene(6b)

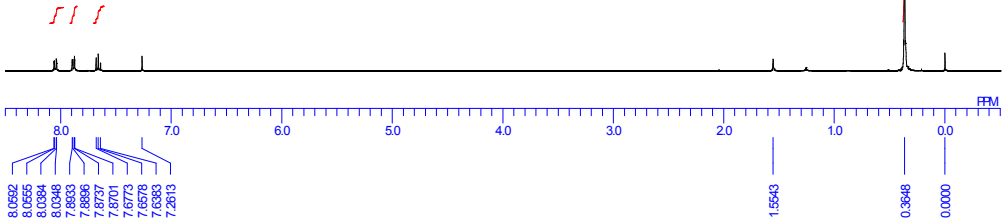


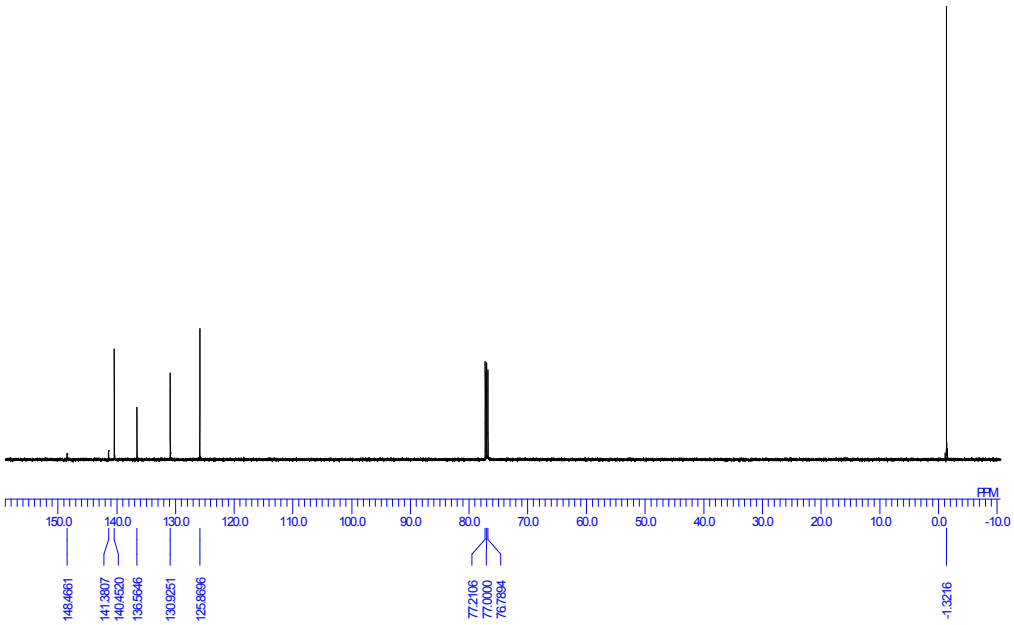




1,2-Dinitro-3-trimethylsilylbenzene(6c)



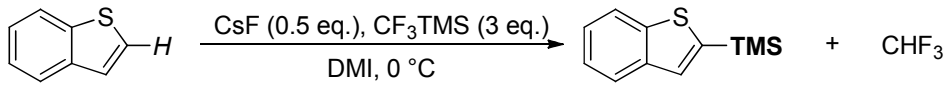




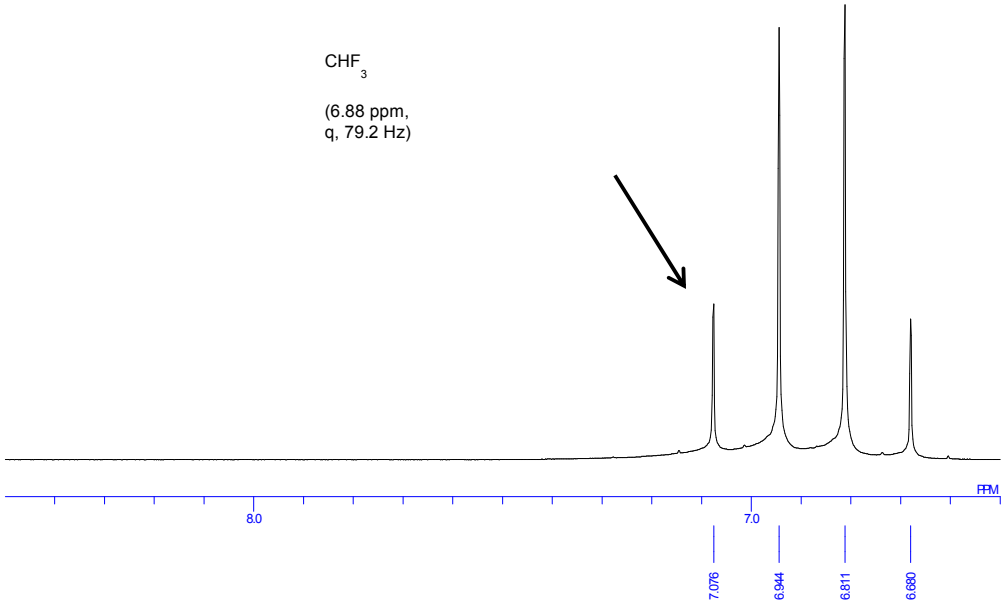
NMR Experiments for monitoring the formation of CHF_3

NMR data were recorded on a JEOL ECA600 spectrometer. Chemical shifts are expressed in δ (parts per million, ppm) values and coupling constants are expressed in herts (Hz). ^{1}H NMR spectra were referenced to a solvent signal (THF-d_8: 3.58 and 1.73 ppm respectively). ^{19}F NMR spectra were referenced to $PhCF_3$ as an internal standard (-63.0 ppm) in THF-d_8:

Reaction



CHF_3 bubbled into THF-d_8



Reaction mixture diluted with THF-d_8

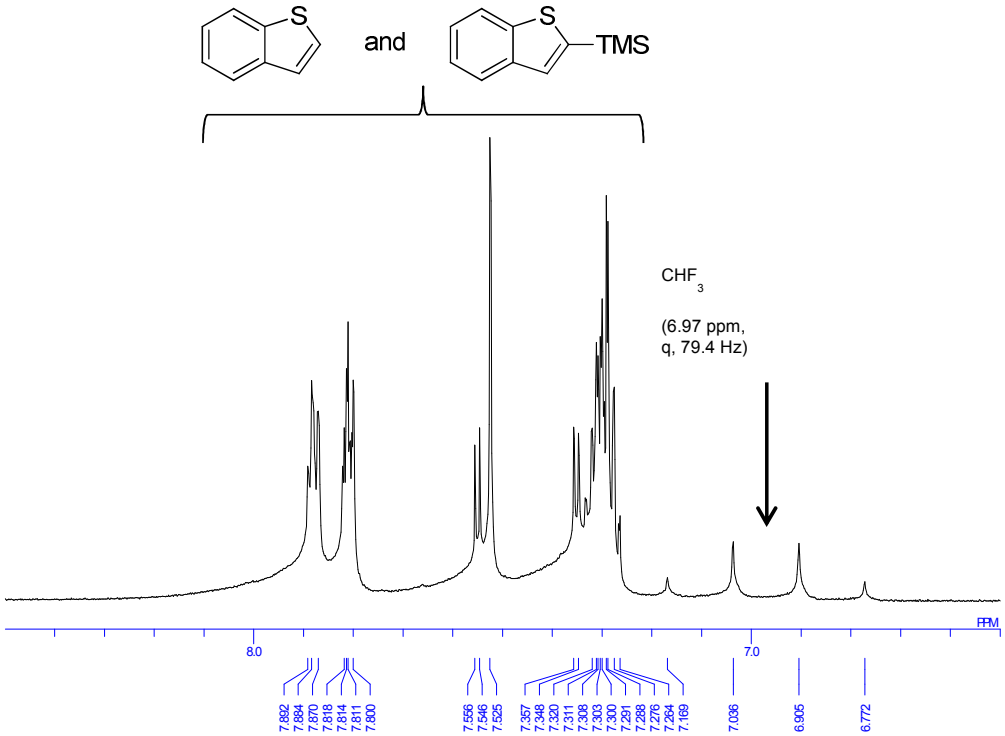
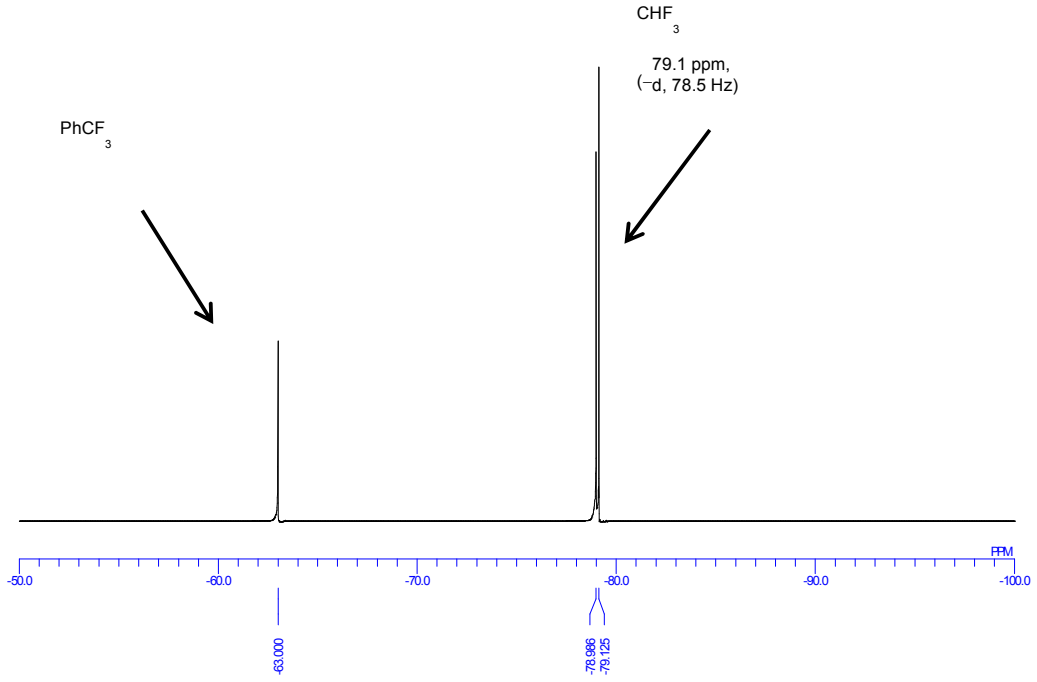


Figure 1. ^{1}H-NMR spectrums of CHF_3 and reaction mixture of benzo[*b*]thiophene and CF_3TMS in the presence of CsF in DMI at 0 °C from 1 h

CHF_3 bubbled into THF-d_8



Reaction mixture diluted with THF-d_8

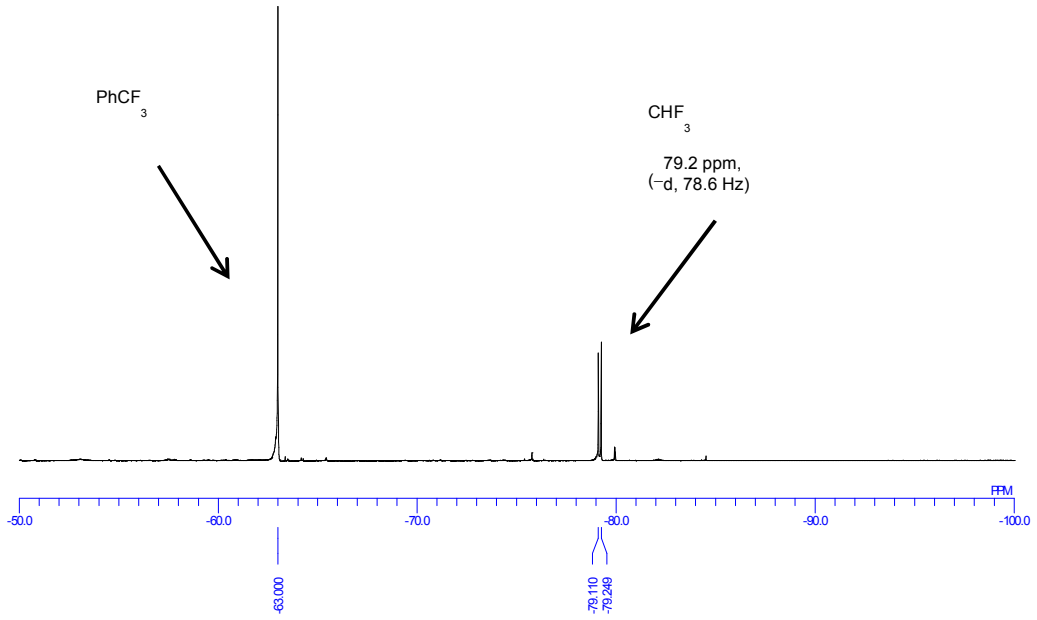


Figure 2. ^{19}F-NMR spectrums of CHF_3 and reaction mixture of benzo[*b*]thiophene and CF_3TMS in the presence of CsF in DMI at 0 °C from 1 h

[i] Hari, D. P.; Hering, T.; König, B. *Org. Lett.* **2012**, *14*, 5334.
[ii] AMR Technology, Inc. US2007/21408 A1, **2007**.
[iii] Liang, Y.; Geng, W.; Wei, J.; Xi, Z. *Angew. Chem, Int. Ed.* **2012**, *51*, 1934.
[iv] Crich, D.; Grant, D. *J. Org. Chem.* **2005**, *70*, 2384.
[v] Zhang, W.; Ng, G.; Tam, H.; Wong, M.; Zhu, F. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1865.
[vi] Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6906.
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