

Supporting Information

Asymmetric Hydrogenation of Thiophenes and Benzothiophenes

Slawomir Urban,[‡] Bernhard Beiring,[‡] Nuria Ortega, Daniel Paul, Frank Glorius*

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1 General information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flame-dried glassware. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon: *n*-hexane (CaH₂), THF (Na-benzophenone), toluene (CaH₂). DME and DMA were purchased as dry compounds, transferred under argon and stored over 4 Å molecular sieve.

All hydrogenation reactions were carried out in Berghof High Pressure Reactors using hydrogen gas. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV₂₅₄ plates. Flash chromatography was either performed on Merck silica gel (40-63 mesh) by standard technique eluting with solvents as indicated.

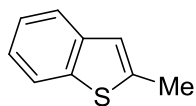
GC-MS Spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm × 30 m, Film: 0.25 µm). The major signals are quoted in *m/z* with the relative intensity in parentheses. The methods used start with the injection temperature *T*₀; after holding this temperature for 3 min, the column is heated to temperature *T*₁ (ramp) and this temperature is held for an additional time *t*:

Method **50_40**: *T*₀ = 50 °C, *T*₁ = 290 °C, ramp = 40 °C/min, *t* = 4 min.

¹H and ¹³C-NMR spectra were recorded on a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicate. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD₂Cl₂: δ_H = 5.33 ppm, δ_C = 54.24 ppm). ESI mass spectra were recorded on a Bruker Daltonics MicroTof. Infrared spectra were recorded on a Varian Associates FT-IR 3100 Excalibur and Shimadzu FTIR 8400S. The wave numbers (ν) of recorded IR-signals are quoted in cm⁻¹. Specific rotation was measured on a Perkin Elmer 341 polarimeter at 24 °C using a quartz glass cell (100 mm path length). The enantiomeric ratio (e.r.) was determined by HPLC analysis using chiral column OD-H and OJ-H. No attempts were made to optimize yields for substrate synthesis.

2 Synthesis and characterization of benzothiophenes

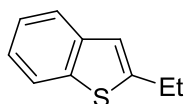
2-Methylbenzo[*b*]thiophene (1b)



In a dry Schlenk *t*-BuLi (1.7 M in pentane, 5.9 mL, 16 mmol, 1.6 equiv) was added to a solution of benzo[*b*]thiophene (1.34 g, 10.0 mmol, 1.00 equiv) in THF (10 mL) at -78°C . The resulting suspension was stirred for 30 min at -78°C . Then iodomethane (1.2 mL, 20 mmol, 2.0 equiv) was added dropwise and the reaction mixture was allowed to warm up to rt and stirred over night. The reaction mixture was carefully quenched with water and extracted several times with Et₂O. The combined organic layers were dried over anhydrous MgSO₄, concentrated under reduced pressure and purified by flash column chromatography (silica, pentane). 2-Methylbenzo[*b*]thiophene (**1b**) was obtained as a white solid in 96% yield (1.43 g, 9.63 mmol).

R_F (pentane): 0.49; **¹H NMR (300 MHz, CDCl₃)**: 7.75 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.35 – 7.18 (m, 3H), 6.98 (s, 1H), 2.59 (d, *J* = 1.2 Hz, 4H); **¹³C NMR (75 MHz, CDCl₃)**: 141.19, 140.77, 140.00, 124.38, 123.67, 122.85, 122.32, 121.91, 16.50; **GC-MS: R_t (50_40)**: 7.2 min; **EI**: 149 (10), 148 (67), 147 (100); **ATR-FTIR (cm⁻¹)**: 2944, 1457, 1432, 1300, 1254, 1198, 1158, 1120, 1065, 1031, 1016, 934, 866, 829, 742, 724, 707, 669.

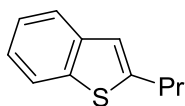
2-Ethylbenzo[*b*]thiophene (1c)



Compound **1c** was synthesized following the procedure described for the preparation of 2-Methylbenzo[*b*]thiophene (**1b**) using *t*-BuLi (1.7 M in pentane, 9.4 mL, 16 mmol, 2.0 equiv), benzo[*b*]thiophene (1.07 g, 8.00 mmol, 1.00 equiv) and bromoethane (2.4 mL, 32 mmol, 4.0 equiv). 2-Ethylbenzo[*b*]thiophene (**1c**) was obtained as a colorless liquid in 82% yield (1.06 g, 6.53 mmol).

R_F (pentane): 0.37; **¹H NMR (300 MHz, CDCl₃)**: 7.78 (d, *J* = 8.0, 1H), 7.68 (d, *J* = 7.5, 1H), 7.35 – 7.22 (m, 1H), 7.02 (s, 1H), 2.95 (qd, *J* = 7.5, 1.1, 1H), 1.40 (t, *J* = 7.5, 1H); **¹³C NMR (75 MHz, CDCl₃)**: 148.6, 140.6, 139.5, 124.4, 123.7, 123.0, 122.5, 120.0, 24.5, 15.8; **GC-MS: R_t (50_40)**: 7.5 min; **EI**: 162 (40), 148 (11), 147 (100); **ATR-FTIR (cm⁻¹)**: 3058, 2968, 2932, 1457, 1436, 1310, 1248, 1192, 1126, 1065, 855, 825, 744, 726, 361, 542, 535.

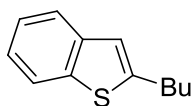
2-Propylbenzo[*b*]thiophene (**1d**)



Compound **1d** was synthesized following the procedure described for the preparation of 2-Methylbenzo[*b*]thiophene (**1b**) using propyl bromide (3.6 mL, 40 mmol, 4.0 equiv). 2-Propylbenzo[*b*]thiophene (**1d**) was obtained as a colorless liquid in 62% yield (1.10 g, 6.20 mmol).

R_F (pentane): 0.42; **¹H NMR (300 MHz, CDCl₃)**: 7.78 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.38 – 7.20 (m, 2H), 7.02 (s, 1H), 2.89 (t, *J* = 7.5 Hz, 2H), 1.80 (h, *J* = 7.4 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)**: 146.7, 140.3, 139.4, 124.1, 123.4, 122.8, 122.2, 120.6, 33.0, 24.5, 13.8; **GC-MS: R_t (50_40)**: 7.9 min; **EI**: 176 (31), 148 (15), 147 (100); **ATR-FTIR (cm⁻¹)**: 3059, 2959, 2930, 2872, 1458, 1436, 1189, 1067, 855, 820, 744, 726, 631, 531, 505.

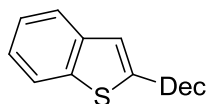
2-Butylbenzo[*b*]thiophene (**1e**)



Compound **1e** was synthesized following the procedure described for the preparation of 2-Methylbenzo[*b*]thiophene (**1b**) using *n*-BuLi (1.6 M in pentane, 15.1 mL, 24.1 mmol, 1.30 equiv), benzo[*b*]thiophene (2.48 g, 18.5 mmol, 1.00 equiv) in THF (25 mL) and butyl bromide (5.9 mL, 56 mmol, 3.0 equiv). 2-Butylbenzo[*b*]thiophene (**1e**) was obtained as a colorless liquid in 98% yield (3.46 g, 18.2 mmol).

R_F (pentane): 0.42; **¹H NMR (300 MHz, CDCl₃)**: 7.76 (d, *J* = 7.7, 1H), 7.66 (d, *J* = 7.3, 1H), 7.34 – 7.20 (m, 2H), 7.00 (s, 1H), 2.91 (t, *J* = 7.6, 2H), 1.74 (p, *J* = 7.6, 2H), 1.43 (h, *J* = 7.4, 2H), 0.96 (t, *J* = 7.3, 3H); **¹³C NMR (75 MHz, CDCl₃)**: 147.0, 140.3, 139.4, 124.1, 123.4, 122.8, 122.2, 120.5, 33.4, 30.6, 22.3, 14.0; **GC-MS: R_t (50_40)**: 8.2 min; **EI**: 190 (26), 148 (49), 147 (100); **ATR-FTIR (cm⁻¹)**: 3059, 2957, 2930, 1458, 1436, 823, 744, 726, 634, 548, 540, 533, 508, 498.

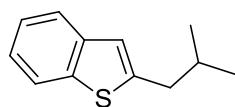
2-Decylbenzo[*b*]thiophene (**1f**)



Compound **1f** was synthesized following the procedure described for the preparation of 2-Methylbenzo[*b*]thiophene (**1b**) using *n*-BuLi (1.6 M in pentane, 3.3 mL, 5.2 mmol, 1.3 equiv), benzo[*b*]thiophene (577 mg, 4.00 mmol, 1.00 equiv) in THF (20 mL) and decyl bromide (4.1 mL, 20 mmol, 5.0 equiv). 2-decylbenzo[*b*]thiophene (**1f**) was obtained as a colorless solid in 83% yield (912 mg, 3.32 mmol).

R_F (pentane): 0.43; **¹H NMR (300 MHz, CDCl₃)**: 7.88 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.39 (dtd, *J* = 19.6, 7.2, 1.2 Hz, 3H), 7.10 (s, 1H), 3.01 (t, *J* = 7.5 Hz, 2H), 1.87 (p, *J* = 7.5 Hz, 2H), 1.43 (s, 14H), 1.05 (t, *J* = 6.7 Hz, 3H). **¹³C NMR (75 MHz, CDCl₃)**: 146.9, 140.3, 139.4, 124.1, 123.4, 122.7, 122.2, 120.5, 32.1, 31.3, 30.9, 29.8, 29.7, 29.6, 29.5, 29.30, 22.9, 14.3; **GC-MS: R_t (50_40)**: 9.9 min; **EI**: 274 (30), 161 (11), 149 (12), 148 (73), 147 (100); **ATR-FTIR (cm⁻¹)**: 3054, 2953, 2918, 2850, 1564, 1537, 1456, 1434, 1378, 1311, 1255, 1191, 1157, 1135, 1064, 1015, 936, 836, 749, 726, 681, 653, 583.

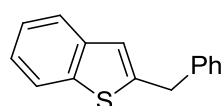
2-Isobutylbenzo[*b*]thiophene (1g)



Compound **1g** was synthesized following the procedure described for the preparation of 2-Methylbenzo[*b*]thiophene (**1b**) using 1-Bromo-2-Methylpropane (4.3 mL, 40 mmol, 4.0 equiv). 2-Isobutylbenzo[*b*]thiophene (**1g**) was obtained as a colorless liquid in 47% yield (0.89 g, 4.69 mmol).

R_F (pentane): 0.42; **¹H NMR (300 MHz, CDCl₃)**: 7.78 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.38 – 7.20 (m, 3H), 7.00 (s, 1H), 2.78 (dd, *J* = 7.1, 0.8 Hz, 3H), 2.01 (n, *J* = 6.7 Hz, 1H), 1.01 (d, *J* = 6.6 Hz, 6H); **¹³C NMR (75 MHz, CDCl₃)**: 145.7, 140.3, 139.6, 124.1, 123.4, 122.8, 122.2, 121.5, 40.2, 30.5, 22.5; **GC-MS: R_t (50_40)**: 8.0 min; **EI**: 190 (26), 148 (17), 147 (100); **ATR-FTIR (cm⁻¹)**: 3059, 2955, 2925, 2868, 1458, 1436, 1385, 1367, 1306, 1189, 1126, 1067, 1015, 966, 855, 831, 806, 743, 726, 664, 631, 538.

2-Benzylbenzo[*b*]thiophene (1h)



Compound **1h** was synthesized following the procedure described for the preparation of 2-Methylbenzo[*b*]thiophene (**1b**) using benzyl bromide (4.8 mL, 40 mmol, 4.0 equiv). 2-Benzylbenzo[*b*]thiophene (**1h**) was obtained as a white solid in 77% yield (1.72 g, 7.67 mmol).

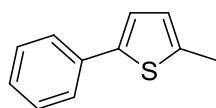
R_F (pentane): 0.17; **¹H NMR (300 MHz, CDCl₃)**: 7.71 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.39 – 7.17 (m, 7H), 6.98 (s, 1H), 4.20 (s, 2H); **¹³C NMR (75 MHz, CDCl₃)**: 145.3, 140.16, 139.9, 139.6, 128.9, 128.7, 126.8, 124.3, 123.8, 123.1, 122.3, 121.8, 37.1; **GC-MS: R_t (50_40)**: 9.4 min; **EI**: 225 (19), 224 (100), 223 (80), 222 (10), 221 (24), 147 (53); **ATR-FTIR (cm⁻¹)**: 3059, 1491, 1454, 1437, 1421, 1310, 1283, 1254, 1204, 1112, 1064, 1025, 1012, 939, 917, 837, 756, 744, 726, 701, 671, 640, 602.

3 Synthesis and characterization of thiophenes

3.1 General procedure I for the synthesis of 2,5-disubstituted thiophenes from 2-alkylthiophenes and aryl bromides

Following a modified procedure of Fagnou *et al.*¹ a flame dried Schlenk tube was charged with Pd(OAc)₂ (2 mol %), PCy₃ (4 mol %) and K₂CO₃ (1.50 equiv) in a glovebox. Outside the glovebox PivOH (30 mol %), DMA (0.42 M), thiophene (1.00 equiv) and the aromatic bromide (1.0 equiv) were added successively under argon. The reaction mixture was then vigorously stirred at 100 °C over 16 h. The solution was then cooled to rt, diluted with EtOAc, extracted with H₂O (3 times), dried over anhydrous MgSO₄, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (pentane) to afford the corresponding product.

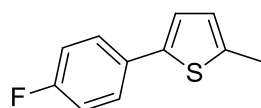
2-Methyl-5-phenylthiophene (3e)



2-Methyl-5-phenylthiophene (**3e**) was synthesized following the general procedure **I** using 2-methylthiophene (431 μ L, 5.00 mmol) and bromobenzene (527 μ L, 5.00 mmol). 2-Methyl-5-phenylthiophene (**3e**) was obtained as a white solid in 77% yield (670 mg, 3.84 mmol).

R_F (pentane): 0.27; **¹H NMR (300 MHz, CDCl₃)**: 7.60 – 7.54 (m, 2H), 7.40 – 7.32 (m, 2H), 7.28 – 7.21 (m, 1H), 7.12 (d, *J* = 3.5 Hz, 1H), 6.74 (dq, *J* = 3.5, 1.1 Hz, 1H), 2.52 (d, *J* = 0.9 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)**: 142.1, 139.6, 134.8, 128.9, 127.1, 126.3, 125.6, 123.0, 15.6; **GC-MS: R_t (50_20)**: 10.7 min; **EI**: 175 (17), 174 (99), 173 (100), 171 (6), 141 (13), 128 (8), 121 (7), 115 (11), 97 (7), 87 (6), 77 (7), 51 (6); **ATR-FTIR (cm⁻¹)**: 3058, 3025, 2913, 2854, 1743, 1598, 1497, 1469, 1443, 1261, 1212, 1186, 1098, 1073, 1027, 946, 902, 872, 799, 749, 734, 684.

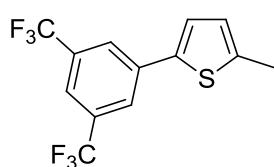
2-(4-Fluorophenyl)-5-methylthiophene (3f)



2-(4-Fluorophenyl)-5-methylthiophene (**3f**) was synthesized following the general procedure **I** using 2-methylthiophene (431 μ L, 5.00 mmol) and 1-bromo-4-fluorobenzene (550 μ L, 5.00 mmol). 2-(4-Fluorophenyl)-5-methylthiophene (**3f**) was obtained as a white solid in 70% yield (674 mg, 3.51 mmol).

R_F (pentane): 0.29; **¹H NMR (500 MHz, CDCl₃)**: 7.53 – 7.47 (m, 2H), 7.08 – 7.02 (m, 3H), 6.72 (dq, *J* = 3.4, 1.1 Hz, 1H), 2.51 (d, *J* = 1.1 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)**: 162.33 (d, *J_F* = 246.4 Hz), 141.0, 139.6, 131.3 127.41 (d, *J_F* = 8.0 Hz), 126.3, 123.0, 116.04 (d, *J_F* = 21.8 Hz), 15.6; **¹⁹F NMR (282 MHz, CDCl₃)**: -115.4; **GC-MS: R_t (50_40)**: 7.8 min; **EI**: 193(16), 192 (99), 191 (100), 159 (14), 133 (10); **ATR-FTIR (cm⁻¹)**: 3078, 3034, 2918, 2860, 2738, 2036, 1886, 1750, 1601, 1551, 1506, 1468, 1411, 1261, 1219, 1159, 1098, 1011, 948, 830, 799, 636, 627, 534.

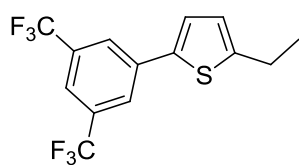
2-(3,5-Bis(trifluoromethyl)phenyl)-5-methylthiophene (3g)



2-(3,5-Bis(trifluoromethyl)phenyl)-5-methylthiophene (**3g**) was synthesized following the general procedure **I** using 2-methylthiophene (431 μL, 5.00 mmol) and 1-bromo-3,5-bis(trifluoromethyl)benzene (857 μL, 5.00 mmol). 2-(3,5-Bis(trifluoromethyl)phenyl)-5-methyl-thiophene (**3g**) was obtained as a white solid in 37% yield (571 mg, 1.84 mmol).

R_F (pentane): 0.43; **¹H NMR (300 MHz, CDCl₃)**: 7.92 (s, 2H), 7.72 (s, 1H), 7.24 (d, *J* = 3.6 Hz, 1H), 6.79 (dq, *J* = 3.5, 1.1 Hz, 1H), 2.54 (d, *J* = 1.1 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)**: 142.3, 138.5, 136.9, 132.51 (q, *J_F* = 33.3 Hz), 126.9, 125.3, 125.48 – 125.29 (m), 123.5 (q, *J_F* = 273 Hz), 120.46 (p, *J_F* = 3.9 Hz), 15.6; **¹⁹F NMR (282 MHz, CDCl₃)**: -63.1; **GC-MS: R_t (50_40)**: 7.4 min; **EI**: 312 (9), 311 (29), 310 (100), 309 (100), 291 (25), 277 (8), 257 (10), 241 (11), 239 (6), 171 (9), 155 (6), 145 (11), 97 (22), 71 (6), 69 (10), 59 (9), 45 (9); **ATR-FTIR (cm⁻¹)**: 3103, 2932, 2868, 1617, 1484, 1375, 1333, 1275, 1217, 1160, 1108, 1015, 886, 843, 799, 705, 695, 680.

2-(3,5-Bis(trifluoromethyl)phenyl)-5-ethylthiophene (3h)

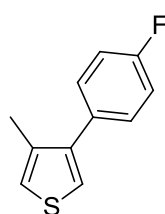


2-(3,5-Bis(trifluoromethyl)phenyl)-5-ethylthiophene (**3h**) was synthesized following the general procedure **I** using 2-ethylthiophene (678 μL, 6.00 mmol) and 1-bromo-3,5-bis(trifluoromethyl)benzene (1,03 mL, 6.00 mmol). 2-(3,5-Bis(trifluoromethyl)phenyl)-5-methyl-thiophene (**3h**) was obtained as a colorless liquid in 53% yield (1.023 g, 3.15 mmol).

R_F (pentane): 0.45; **¹H NMR (300 MHz, CD₂Cl₂)**: 7.99 (s, 2H), 7.75 (s, 1H), 7.32 (d, *J* = 3.7 Hz, 1H), 6.89 – 6.82 (m, 1H), 2.91 (q, *J* = 7.5 Hz, 2H), 1.35 (t, *J* = 7.5 Hz, 3H);

^{13}C NMR (75 MHz, CD_2Cl_2): 150.9, 138.7, 137.7, 132.8 (q, $J_{\text{F}} = 33$ Hz), 126.0, 125.9, 125.8, 124.0 (q, $J_{\text{F}} = 273$ Hz), 121.5 – 120.7 (m), 24.4, 16.4.; **^{19}F NMR (282 MHz, CD_2Cl_2):** -63.4; **GC-MS: R_{t} (50_40):** 7.7 min; **EI:** 324 (31), 310 (15), 309 (100); **ATR-FTIR (cm^{-1}):** 1617, 1488, 1377, 1276, 1172, 1129, 1005, 890, 846, 805, 683, 631, 540.

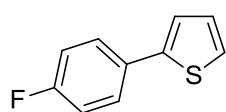
3-(4-Fluorophenyl)-4-methylthiophene (3i)



Following a modified procedure of Cashman *et al.*² a flame dried Schlenk tube was charged with $\text{Pd}(\text{PPh}_3)_4$ (2.5 mol%) in a glovebox. Outside the glovebox DME (6.15 mL) and 3-bromo-4-methylthiophene (447 μL , 4.00 mmol, 1.00 equiv) were added successively under argon. To this reaction mixture an aqueous solution of Na_2CO_3 (2 M, 4.00 mL, 8.00 mmol, 2.0 equiv) was added under argon. The resultant mixture was stirred at room temperature for 5 min. To this, a solution of (4-fluorophenyl)boronic acid (700 mg, 5.00 mmol, 1.25 equiv) in ethanol (6.15 mL) was added and the mixture was heated to 90 $^\circ\text{C}$ and stirred for 5 h. The solution was cooled to room temperature and filtered through a pad of Celite (washing with dichloromethane). The filtrate was dried over anhydrous MgSO_4 (~5 g), filtered and the solvent was removed in vacuo to afford the crude product, which was chromatographed on silica gel (pentane). 3-(4-Fluorophenyl)-4-methylthiophene (**3i**) was obtained as a colorless liquid in 94% yield (726 mg, 3.78 mmol).

R_{F} (pentane): 0.33; **^1H NMR (300 MHz, CDCl_3):** 7.44 – 7.40 (m, 2H), 7.20 (d, $J = 5.1$ Hz, 1H), 7.10 (t, $J = 8.7$ Hz, 1H), 6.92 (d, $J = 5.2$ Hz, 1H), 2.30 (s, 3H); **^{13}C NMR (75 MHz, CDCl_3):** 163.41, 161.45, 137.07, 133.57, 131.33, 131.03 (d, $J_{\text{F}} = 8.0$ Hz), 123.69, 115.78 (d, $J_{\text{F}} = 21.6$ Hz), 14.90; **^{19}F NMR (282 MHz, CDCl_3):** -114.6; **GC-MS: R_{t} (50_20):** 10.2 min; **EI:** 193 (16), 192 (100), 191 (82), 189 (9), 171 (6), 159 (14), 147 (8), 146 (11), 139 (7), 133 (13), 97 (14), 96 (5), 95 (5); **ATR-FTIR (cm^{-1}):** 3066, 2924, 2867, 2360, 1894, 1601, 1550, 1504, 1455, 1430, 1232, 1159, 1099, 1013, 926, 832, 813, 722, 708, 631, 615, 605, 539, 527.

2-(4-Fluorophenyl)thiophene (3d)



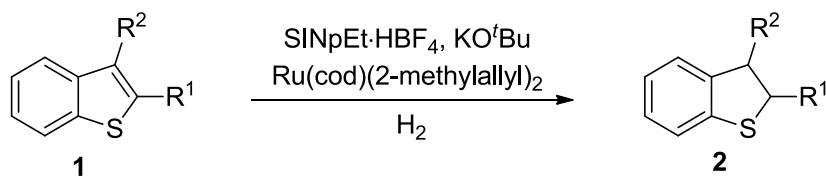
Following a procedure from Vachal *et al.*³ a 1 M aqueous solution of Na_2CO_3 (5.0 equiv) was added to a solution of thiophenes-2-boronic acid (4.01 mmol, 1.10 equiv) and 1-fluoro-4-iodobenzene (3.65 mmol, 1.00 equiv) in DMF p.a. (0.05 M). The resulting suspension was degassed for 10 min. and $\text{Pd}(\text{PPh}_3)_4$ (10 mol%) was added. The reaction mixture was degassed again for 5 min and then

heated to 85 °C. The course of the reaction was monitored by GC-MS and, upon complete consumption of the aryl halide (usually after 2-4 h) the reaction was diluted with EtOAc (110 mL/mmol) and 1 N HCl (aq) (55 mL/mmol). The organic phase was washed with 1 N HCl (aq) (3 x 55 mL/mmol) and brine, dried over MgSO₄ and concentrated *in vacuo*. The obtained crude product was purified by flash column chromatography (silica, pentane) yielding pure product as a white solid (559 mg, 3.14 mmol, 86%).

R_f (pentane): 0.34; **¹H NMR (300 MHz, CDCl₃):** 7.62 – 7.53 (m, 2H), 7.28 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.25 (dd, *J* = 4.0, 1.0 Hz, 1H), 7.04 – 7.12 (m, 3H); **¹³C NMR (75 MHz, CDCl₃):** 162.4 (d, *J_F* = 247 Hz), 143.4, 130.8 (d, *J_F* = 3 Hz), 128.2, 127.7 (d, *J_F* = 8 Hz), 124.9, 123.2 (d, *J_F* = 1 Hz), 116.0 (d, *J_F* = 22 Hz); **¹⁹F{¹H} (282 MHz, CDCl₃):** –114.7; **GC-MS: t_R (50_40):** 7.6 min; **EI-MS:** 178 (100), 147 (45), 146 (11), 133 (36), 74 (10), 73 (82); **ATR-FTIR (cm⁻¹):** 1599, 1528, 1491, 1431, 1216, 1160, 1100, 1010, 850, 838, 819, 809, 691, 659.

4 Hydrogenation of benzothiophenes 1a-1i to the corresponding dihydrobenzothiophenes 2a-2i

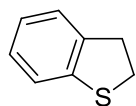
4.1 General procedure II for the hydrogenation of benzothiophenes



To a flame-dried screw-capped tube equipped with a magnetic stir bar was added [Ru(cod)(2-methylallyl)₂] (4.8 mg, 0.015 mmol), imidazolinium salt **5a** (14.9 mg, 0.032 mmol) and dry KO^{*t*}-Bu (5.0 mg, 0.045 mmol) in a glove box. The mixture was suspended in hexane (1 mL) and stirred at 70 °C for 16 h under argon. Then the mixture was transferred under argon to a glass vial containing benzothiophene **1** (0.3 mmol) and a magnetic stirring bar. The glass vial was placed in a 150 mL stainless-steel reactor. The autoclave was carefully pressurized/depressurized with hydrogen gas three times before the reaction pressure of 90 bar was adjusted. The hydrogenation was performed at rt for 24 h. The autoclave was depressurized carefully and the crude mixture was filtered through a plug of silica using a mixture of pentane/ethyl acetate (19:1). The yield of compound **2** was determined by ¹H NMR after addition of dibromomethane (21 μL, 0.3 mmol) as internal standard. The analytically

pure dihydrobenzothiophene **2** was obtained by flash column chromatography (silica, pentane). The enantiomeric ratio of all compounds was determined by HPLC on a chiral stationary phase.

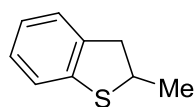
2,3-Dihydrobenzo[*b*]thiophene (**2a**)



Following the general procedure **II**, the hydrogenation reaction was carried out and full conversion to 2,3-Dihydrobenzo[*b*]thiophene (**2a**) was observed in GC-MS.

R_F (pentane): 0.19; **¹H NMR (300 MHz, CDCl₃)**: 7.25 – 7.17 (m, 2H), 7.16 – 7.09 (m, 1H), 7.02 (td, *J* = 7.4, 1.2 Hz, 1H), 3.41 – 3.33 (m, 2H), 3.32 – 3.25 (m, 2H); **¹³C NMR (75 MHz, CDCl₃)**: 141.6, 140.1, 127.4, 124.5, 124.2, 122.2, 36.3, 33.4; **GC-MS: R_t (50_20)**: 9.1 min; **EI**: 137 (12), 136 (80), 135 (100), 134 (19), 91 (27); **ATR-FTIR (cm⁻¹)**: 3060, 3006, 2977, 2940, 2893, 2833, 1722, 1586, 1461, 1445, 1427, 1256, 1121, 1059, 1028, 930, 862, 742, 697, 630, 531, 486.

(R)-(+)-2-Methyl-2,3-dihydrobenzo[*b*]thiophene (**2b**)

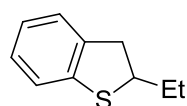


Following the general procedure **II**, the hydrogenation reaction was carried out and 2-Methyl-2,3-dihydrobenzo[*b*]thiophene (**2b**) was formed in 98% yield. In a second experiment the compound **2b** was isolated with 90% yield.

The absolute configuration of **2b** was obtained by comparison of optical rotation data with the literature,⁴ showing that we obtained (R)-(+)-2-Methyl-2,3-dihydrobenzo[*b*]thiophene (**2b**).

99:1 e.r. [α]_D²⁴ = +129.1 (c 1.00, CH₂Cl₂), **R_F** (pentane): 0.25; **¹H NMR (300 MHz, CDCl₃)**: 7.14 – 6.97 (m, 3H), 6.92 (td, *J* = 7.4, 1.1 Hz, 1H), 3.97 – 3.84 (m, 1H), 3.30 (dd, *J* = 15.3, 7.4 Hz, 1H), 2.87 (dd, *J* = 15.3, 6.7 Hz, 1H), 1.37 (d, *J* = 6.7 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)**: 141.4, 139.6, 127.4, 124.8, 124.2, 122.4, 45.6, 44.5, 21.9; **GC-MS: R_t (50_40)**: 7.1 min; **EI**: 150 (501), 147 (20), 135 (100), 91 (22); **ATR-FTIR (cm⁻¹)**: 3061, 2960, 2922, 1724, 1588, 1461, 1447, 1374, 1279, 1256, 1120, 1063, 740, 697, 639, 620, 596; **HPLC** (OJ-H, eluents: hexane/*i*-PrOH = 99:1, detector: 254 nm, flowrate: 0.4 mL/min), *t*_{1(minor)} = 14.8 min, *t*_{2(major)} = 15.3 min.

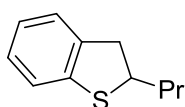
2-Ethyl-2,3-dihydrobenzo[*b*]thiophene (**2c**)



Following the general procedure **II**, the hydrogenation reaction was carried out and 2-Ethyl-2,3-dihydrobenzo[*b*]thiophene (**2c**) was formed in 95% yield.

98:2 e.r. $[\alpha]_D^{24} = +150.6$ (c 0.50, CH_2Cl_2), \mathbf{R}_F (pentane): 0.25; $^1\text{H NMR}$ (300 MHz, CD_2Cl_2): 7.21 – 7.11 (m, 2H), 7.15 – 7.03 (m, 1H), 6.99 (td, $J = 7.3, 1.4$, 1H), 3.89 – 3.75 (m, 1H), 3.38 (dd, $J = 15.5, 7.6$, 1H), 3.01 (dd, $J = 15.5, 6.9$, 1H), 1.87 – 1.63 (m, 2H), 1.01 (t, $J = 7.3$, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 141.1, 139.8, 127.4, 124.6, 124.1, 122.2, 53.1, 42.3, 29.4, 12.8; **GC-MS**: \mathbf{R}_t (50_40): 7.3 min; **EI**: 164 (35), 136 (10), 135 (100), 134 (13), 91 (16); **ATR-FTIR** (cm^{-1}): 3062, 2961, 2929, 1586, 1461, 1446, 1378, 1278, 1238, 1121, 1060, 741, 698, 635, 624; **HPLC** (OD-H, eluents: hexane/*i*-PrOH = 100:0, detector: 254 nm, flowrate: 0.4 mL/min), $t_{1(\text{minor})} = 25.8$ min, $t_{2(\text{major})} = 27.7$ min.

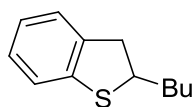
2-Propyl-2,3-dihydrobenzo[*b*]thiophene (2d)



Following the general procedure **II**, the hydrogenation reaction was carried out and 2-Propyl-2,3-dihydrobenzo[*b*]thiophene (**2d**) was formed in 87% yield.

98.5:1.5 e.r. $[\alpha]_D^{24} = +172.5$ (c 1.00, CH_2Cl_2), \mathbf{R}_F (pentane): 0.28; $^1\text{H NMR}$ (300 MHz, CDCl_3): 7.22 – 7.07 (m, 3H), 7.00 (td, $J = 7.4, 1.2$, 1H), 3.91 (p, $J = 7.3$, 1H), 3.38 (dd, $J = 15.4, 7.5$, 1H), 3.01 (dd, $J = 15.4, 7.3$, 1H), 1.75 (q, $J = 7.6$, 2H), 1.58 – 1.35 (m, 2H), 0.96 (t, $J = 7.3$, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 141.2, 139.8, 127.4, 124.6, 124.1, 122.2, 51.2, 42.7, 38.4, 21.6, 14.0; **GC-MS**: \mathbf{R}_t (50_40): 7.8 min; **EI**: 178 (33), 136 (11), 135 (100), 134 (16), 91 (16); **ATR-FTIR** (cm^{-1}): 3062, 2957, 2929, 2872, 1587, 1462, 1447, 1379, 1121, 1062, 909, 739, 698, 630, 562; **HPLC** (OD-H, eluents: hexane/*i*-PrOH = 99:1, detector: 254 nm, flowrate: 0.5 mL/min), $t_{1(\text{minor})} = 9.0$ min, $t_{2(\text{major})} = 9.4$ min.

2-Butyl-2,3-dihydrobenzo[*b*]thiophene (2e)

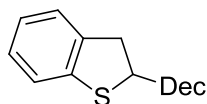


Following the general procedure **II**, the hydrogenation reaction was carried out and 2-Butyl-2,3-dihydrobenzo[*b*]thiophene (**2e**) was formed in 89% yield.

99:1 e.r. $[\alpha]_D^{24} = +162.6$ (c 1.00, CH_2Cl_2), \mathbf{R}_F (pentane): 0.19; $^1\text{H NMR}$ (300 MHz, CDCl_3): 7.23 – 7.07 (m, 3H), 7.00 (td, $J = 7.3, 1.3$ Hz, 1H), 3.89 (p, $J = 7.4$ Hz, 1H), 3.38 (dd, $J = 15.4, 7.5$ Hz, 1H), 3.01 (dd, $J = 15.4, 7.3$ Hz, 1H), 1.83 – 1.71 (m, 2H), 1.48 – 1.30 (m, 4H), 0.93 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 141.2, 139.8, 127.4, 124.6, 124.1, 122.3, 51.5, 42.7, 36.0, 30.7, 22.6, 14.1; **GC-MS**: \mathbf{R}_t (50_40): 8.1 min; **EI**: 192 (25), 147 (11), 136 (10), 135 (100), 134 (14), 91 (17); **ATR-FTIR** (cm^{-1}): 3061, 2956, 2927, 2857, 1587,

1461, 1447, 1121, 1063, 739, 698, 629; **HPLC** (OD-H, eluents: hexane/*i*-PrOH = 99:1, detector: 254 nm, flowrate: 0.4 mL/min), $t_{1(\text{minor})}$ = 10.5 min, $t_{2(\text{major})}$ = 10.9 min.

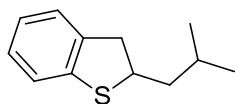
2-Decyl-2,3-dihydrobenzo[*b*]thiophene (2f)



Following the general procedure **II**, the hydrogenation reaction was carried out and 2-Decyl-2,3-dihydrobenzo[*b*]thiophene (**2f**) was formed in 92% yield.

98:2 e.r. $[\alpha]_D^{24}$ = +112.4 (c 1.00, CH₂Cl₂), **R_F** (pentane): 0.23; **¹H NMR (300 MHz, CDCl₃)**: 7.19 – 7.06 (m, 3H), 6.99 (td, *J* = 7.3, 1.2 Hz, 1H), 3.89 (p, *J* = 7.6 Hz, 1H), 3.36 (dd, *J* = 15.4, 7.6 Hz, 1H), 3.00 (dd, *J* = 15.4, 7.4 Hz, 1H), 1.83 – 1.65 (m, 2H), 1.50 – 1.37 (m, 2H), 1.29 (s, 14H), 0.90 (t, *J* = 6.9 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)**: 141.7, 140.4, 127.7, 125.1, 124.5, 122.5, 54.0, 52.0, 43.1, 36.8, 32.5, 30.2, 30.2, 30.1, 30.0, 29.9, 29.0, 23.3, 14.5; **GC-MS: R_t (50_40)**: 8.4 min; **EI**: 277 (12), 276 (58), 136 (11), 135 (100), 134 (10); **ATR-FTIR (cm⁻¹)**: 3062, 2922, 2852, 1734, 1717, 1700, 1684, 1653, 1636, 1587, 1559, 1541, 1541, 1507, 1461, 1447, 1121, 1062, 740, 698; **HPLC** (OD-H, eluents: hexane/*i*-PrOH = 99:1, detector: 210 nm, flowrate: 0.4 mL/min), $t_{1(\text{minor})}$ = 9.6 min, $t_{2(\text{major})}$ = 9.9 min.

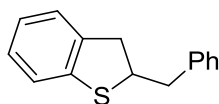
2-Isobutyl-2,3-dihydrobenzo[*b*]thiophene (2g)



Following the general procedure **II**, the hydrogenation reaction was carried out and 2-Isobutyl-2,3-dihydrobenzo[*b*]thiophene (**2g**) was formed in 38% yield.

98:2 e.r. $[\alpha]_D^{24}$ = +149 (c 0.75, CH₂Cl₂), **R_F** (pentane): 0.31; **¹H NMR (300 MHz, CD₂Cl₂)**: 7.15 (d, *J* = 8.3, 2H), 7.11 – 7.05 (m, 1H), 6.98 (td, *J* = 7.3, 1.2, 1H), 4.04 – 3.94 (m, 1H), 3.35 (dd, *J* = 15.4, 7.4, 1H), 2.97 (dd, *J* = 15.4, 7.8, 1H), 1.80 – 1.55 (m, 3H), 0.94 (dd, *J* = 6.4, 1.0, 6H); **¹³C NMR (75 MHz, CD₂Cl₂)**: 141.7, 140.5, 127.7, 125.1, 124.5, 122.5, 50.1, 45.6, 43.3, 27.7, 23.2, 22.2; **GC-MS: R_t (50_40)**: 7.9 min; **EI**: 192 (33), 135 (100), 134 (16), 91 (14); **ATR-FTIR (cm⁻¹)**: 3061, 2955, 2870, 1588, 1462, 1447, 1385, 1367, 1122, 1064, 741, 698, 631, 538; **HPLC** (OD-H, eluents: hexane/*i*-PrOH = 99:1, detector: 254 nm, flowrate: 0.4 mL/min), $t_{1(\text{minor})}$ = 11.4 min, $t_{2(\text{major})}$ = 11.9 min.

2-Benzyl-2,3-dihydrobenzo[*b*]thiophene (2h)

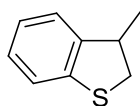


Following the general procedure **II**, the hydrogenation reaction was carried out and 2-Benzyl-2,3-dihydrobenzo[*b*]thiophene (**2h**) was formed

in 63% yield.

98.5:1.5 e.r. $[\alpha]_D^{24} = +105.3$ (c 0.7, CH_2Cl_2), R_F (pentane): 0.13; $^1\text{H NMR}$ (300 MHz, CDCl_3): 7.31 – 7.19 (m, 2H), 7.23 – 6.98 (m, 6H), 6.93 (td, $J = 7.3, 1.3$ Hz, 1H), 4.08 – 3.97 (m, 1H), 3.21 (dd, $J = 15.5, 7.4$ Hz, 1H), 3.06 – 2.88 (m, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 140.9, 139.5, 139.2, 129.1, 128.6, 127.5, 126.7, 124.8, 124.3, 122.4, 52.1, 42.2, 41.8; **GC-MS: R_t (50_40):** 9.3 min; **EI:** 226 (20), 136 (11), 135 (100), 134 (28), 91 (29); **ATR-FTIR (cm^{-1}):** 3057, 3028, 2959, 2931, 2902, 2876, 2844, 2822, 1950, 1878, 1807, 1789, 1755, 1723, 1601, 1587, 1573, 1494, 1448, 1271, 1229, 1198, 1160, 1120, 1068, 1026, 1016, 864, 748, 696, 623, 594; **HPLC** (OJ-H, eluents: hexane/*i*-PrOH = 99:1, detector: 254 nm, flowrate: 1 mL/min), $t_{1(\text{minor})} = 24.1$ min, $t_{2(\text{major})} = 26.2$ min.

3-Methyl-2,3-dihydrobenzo[*b*]thiophene (2i)

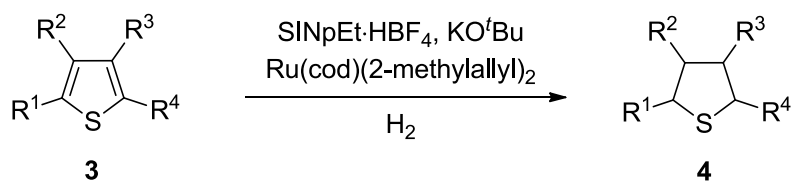


Following the general procedure **II**, the hydrogenation reaction was carried out and 3-Methyl-2,3-dihydrobenzo[*b*]thiophene (**2i**) was formed in 79% yield.

99:1 e.r. $[\alpha]_D^{24} = +23.3$ (c 0.72, CH_2Cl_2), R_F (pentane): 0.42; $^1\text{H NMR}$ (300 MHz, CD_2Cl_2): 7.21 – 7.00 (m, 4H), 3.60 – 3.43 (m, 2H), 3.04 – 2.93 (m, 1H), 1.36 (d, $J = 6.6$, 3H); $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2): 145.1, 141.8, 127.8, 124.7, 124.2, 122.6, 43.3, 41.3, 19.1; **GC-MS: R_t (50_40):** 7.1 min; **EI:** 150 (41), 135 (100), 134 (19), 91 (23); **ATR-FTIR (cm^{-1}):** 3061, 2962, 2925, 1587, 1462, 1442, 1375, 1313, 1237, 1126, 1073, 1024, 931, 743, 693; **HPLC** (OJ-H, eluents: hexane/*i*-PrOH = 99:1, detector: 254 nm, flowrate: 0.4 mL/min), $t_{1(\text{major})} = 13.6$ min, $t_{1(\text{minor})} = 14.2$ min.

5 Hydrogenation of thiophenes 3a-3i to the corresponding tetrahydrothiophenes 4a-4i

5.1 General procedure III for the hydrogenation of thiophenes



To a flame-dried screw-capped tube equipped with a magnetic stir bar was added $[\text{Ru}(\text{cod})(2\text{-methylallyl})_2]$ (4.8 mg, 0.015 mmol), $\text{SINpEt}\cdot\text{HBF}_4$ (14.9 mg, 0.032 mmol) and dry $\text{KO}^t\text{-Bu}$

(5.0 mg, 0.045 mmol) in a glove box. The mixture was suspended in hexane (1 mL) and stirred at 70 °C for 16 h under argon. Then the mixture was transferred under argon to a glass vial containing thiophene **3** (0.15 mmol) and a magnetic stirring bar. The glass vial was placed in a 150 mL stainless-steel reactor. The autoclave was carefully pressurized/depressurized with hydrogen gas three times before the reaction pressure of 90 bar was adjusted. The hydrogenation was performed at rt for 24 h. The autoclave was depressurized carefully and the crude mixture was filtered through a plug of silica using a mixture of pentane/ethyl acetate (18:2). The yield of compound **4** was determined by ¹H NMR after addition of dibromomethane (21 µL, 0.3 mmol) as internal standard. The analytically pure tetrahydrothiophene **4** was obtained by flash column chromatography (silica, pentane). The enantiomeric ratio of all compounds was determined by HPLC on a chiral stationary phase.

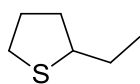
Tetrahydrothiophene (4a)



Following the general procedure **III**, the hydrogenation reaction was carried out and after filtration of the crude reaction mixture full conversion was observed by GC and GC-MS.

GC: R_t (50_20): 4.3 min; **GC-MS: R_t (50_20):** 4.3 min; **EI:** 88 (85), 87 (24), 60 (100), 59 (31), 58 (14), 55 (13), 54 (12), 47 (19), 46 (25), 45 (34), 41 (17), 40 (36).

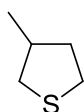
2-Ethyl-tetrahydrothiophene (4b)



Following the general procedure **III**, the hydrogenation reaction was carried out and after filtration of the crude reaction mixture full conversion was observed by GC-MS.

GC-MS: R_t (50_40): 5.3 min; **EI:** 116 (32), 87 (100), 45 (12).

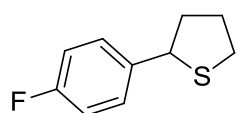
3-Methyl-tetrahydrothiophene (4c)



Following the general procedure **III**, the hydrogenation reaction was carried out and after filtration of the crude reaction mixture full conversion was observed by GC.

GC: R_t (50_20): 5.1 min.

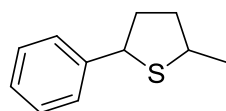
2-(4-Fluorophenyl)-tetrahydrothiophene (4d)



Following the general procedure **III**, the hydrogenation reaction was carried out and tetrahydrothiophene **4d** was formed in 99% yield.

R_F (pentane): 0.11; **¹H NMR (300 MHz, CD₂Cl₂)**: 7.46 – 7.34 (m, 2H), 7.07 – 6.94 (m, 2H), 4.49 (dd, *J* = 8.6, 6.0, 1H), 3.21 – 3.09 (m, 1H), 3.04 – 2.94 (m, 1H), 2.44 – 2.32 (m, 1H), 2.32 – 2.20 (m, 1H), 2.07 – 1.79 (m, 2H); **¹³C NMR (75 MHz, CD₂Cl₂)**: 162.4 (d, *J_F* = 242 Hz), 139.8, 130.0 (d, *J_F* = 8 Hz), 115.7 (d, *J_F* = 21 Hz), 52.7, 41.5, 34.2, 31.8; **¹⁹F NMR (564 MHz, CD₂Cl₂)** -117.0; **GC-MS: R_t (50_40)**: 9.7 min; **EI**: 276 (39), 136 (11), 135 (100), 134 (10); **ATR-FTIR (cm⁻¹)**: 2951, 2862, 1604, 1508, 1442, 1261, 1224, 1156, 1095, 1015, 832, 798.

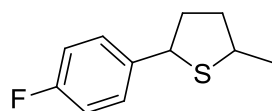
2-Methyl-5-phenyl tetrahydrothiophene (4e)



Following the general procedure **III**, the hydrogenation reaction was carried out for 40 h and tetrahydrothiophene **4e** was formed in 37% yield.

95:5 e.r. [α]_D²⁴ = +12.9 (c 4.1, CH₂Cl₂), **R_F** (pentane): 0.09; **¹H NMR (300 MHz, CD₂Cl₂)**: 7.48 – 7.40 (m, 2H), 7.36 – 7.27 (m, 2H), 7.25 – 7.17 (m, 1H), 4.63 – 4.48 (m, 1H), 3.71 – 3.55 (m, 1H), 2.39 – 2.26 (m, 1H), 2.22 – 2.00 (m, 2H), 1.94 – 1.81 (m, 1H), 1.45 (d, *J* = 6.7, 3H); **¹³C NMR (75 MHz, CD₂Cl₂)**: 143.3, 128.5, 127.8, 127.0, 54.2, 44.6, 38.8, 38.5, 24.0; **GC-MS: R_t (50_40)**: 7.7 min; **EI**: 178 (100), 177 (23), 136 (68), 135 (32), 129 (37), 121 (47), 117 (40), 115 (24), 104 (29), 91 (28); **ATR-FTIR (cm⁻¹)**: 2954, 2923, 2857, 1600, 1492, 1453, 1028, 759, 699; **HPLC** (OJ-H, eluents: hexane/*i*-PrOH = 90:10, detector: 210 nm, flowrate: 1 mL/min), *t*_{1(major)} = 7.2 min, *t*_{2(minor)} = 9.1 min.

2-(4-Fluorophenyl)-5-methyl tetrahydrothiophene (4f)

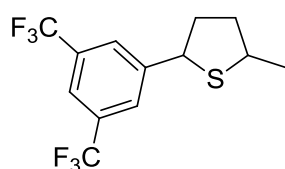


Following the general procedure **III**, the hydrogenation reaction was carried out for 40 h at 75 bar and tetrahydrothiophene **4f** was formed in 55% yield.

96:4 e.r. [α]_D²⁴ = +28.6 (c 4.7, CH₂Cl₂), **R_F** (pentane): 0.11; **¹H NMR (300 MHz, CD₂Cl₂)**: 7.44 – 7.35 (m, 2H), 6.98 (t, *J*=8.7, 2H), 4.55 (br, 1H), 3.64 (br, 1H), 2.38 – 2.24 (m, 1H), 2.20 – 1.97 (m, 1H), 1.91 – 1.78 (m, 2H), 1.45 (d, *J* = 6.7, 3H); **¹³C NMR (75 MHz, CD₂Cl₂)**: 161.75 (d, *J_F* = 245.3 Hz), 138.84, 129.13 (d, *J_F* = 7.9 Hz), 115.07 (d, *J_F* = 21.4 Hz), 53.3, 44.5, 38.8, 38.3, 23.8; **¹⁹F NMR (282 MHz, CDCl₃)** -116.2; **GC-MS: R_t (50_40)**: 7.6 min; **EI**: 196 (100), 154 (78), 153 (35), 147 (34), 139 (58), 136 (20), 135 (53), 122 (30), 121 (21),

109 (39); **ATR-FTIR** (cm^{-1}): 2924, 2858, 1604, 1508, 1375, 1223, 1157, 831; **HPLC** (OJ-H, eluents: hexane/*i*-PrOH = 90:10, detector: 210 nm, flowrate: 1.0 mL/min), $t_{1(\text{major})} = 5.2$ min, $t_{1(\text{minor})} = 7.0$ min.

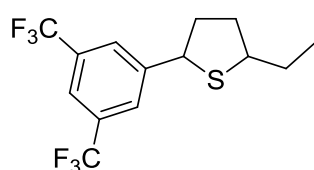
2-(3,5-Bis(trifluoromethyl)phenyl)-5-methyl tetrahydrothiophene (4g)



Following the general procedure **III**, the hydrogenation reaction was carried out and tetrahydrothiophene **4g** was formed in 98% yield.

~97:3 e.r. (The separation of the enantiomers was not perfect, see hplc-traces, but indicated the shown e.r. value) $[\alpha]_D^{24} = +23.8$ (c 1.0, CH_2Cl_2), R_F (pentane): 0.22; **^1H NMR (300 MHz, CD_2Cl_2)**: 7.93 (s, 2H), 7.77 (s, 1H), 4.64 (t, $J = 6.9$, 1H), 3.74 – 3.61 (m, 1H), 2.47 – 2.34 (m, 1H), 2.25 – 1.99 (m, 2H), 1.90 – 1.77 (m, 1H), 1.46 (d, $J = 6.7$, 3H); **^{13}C NMR (75 MHz, CD_2Cl_2)**: 147.3, 131.90 (q, $J_F = 33.1$), 128.87 – 128.53 (m), 124.0 (q, $J_F = 273$ Hz), 121.58 – 121.28 (m), 53.5, 45.7, 39.5, 38.8, 23.9; **^{19}F NMR (564 MHz, CD_2Cl_2)** -63.2; **GC-MS: R_t (50_40)**: 7.3 min; **EI**: 314 (100), 299 (49), 295 (26), 272 (99), 258 (21), 257 (76), 245 (51), 203 (22); **ATR-FTIR** (cm^{-1}): 2961, 2865, 1622, 1376, 1277, 1167, 1129, 1024, 944, 898, 846, 707, 682, 547; **HPLC** (OJ-H, eluents: hexane/*i*-PrOH = 99:1, detector: 254 nm, flowrate: 0.4 mL/min), $t_{1(\text{major})} = 9.2$ min, $t_{1(\text{minor})} = 9.4$ min.

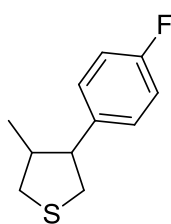
2-(3,5-Bis(trifluoromethyl)phenyl)-5-ethyl tetrahydrothiophene (4h)



Following the general procedure **III**, the hydrogenation reaction was carried out and tetrahydrothiophene **4h** was formed in 98% yield.

97:3 e.r. $[\alpha]_D^{24} = +29$ (c 0.97, CH_2Cl_2), R_F (pentane): 0.24; **^1H NMR (300 MHz, CD_2Cl_2)**: 7.92 (s, 2H), 7.76 (s, 1H), 4.62 (t, $J = 6.9$, 1H), 3.52 – 3.39 (m, 1H), 2.46 – 2.33 (m, 1H), 2.22 – 1.96 (m, 2H), 1.95 – 1.62 (m, 3H), 1.02 (t, $J = 7.3$, 3H); **^{13}C NMR (75 MHz, CD_2Cl_2)**: 147.2, 131.81 (q, $J_F = 33.0$), 128.99 – 128.39 (m), 124.0 (q, $J_F = 273$ Hz), 121.55 – 121.17 (m), 53.4, 52.6, 39.5, 36.3, 31.6, 13.5; **^{19}F NMR (282 MHz, CD_2Cl_2)** -63.17. **GC-MS: R_t (50_40)**: 7.5 min; **EI**: 328 (36), 299 (100), 257 (20), 245 (57); **ATR-FTIR** (cm^{-1}): 2963, 2935, 2874, 1622, 1464, 1376, 1335, 1276, 1171, 1129, 899, 846, 707, 682, 632; **HPLC** (OJ-H, eluents: hexane/*i*-PrOH = 100/0, detector: 254 nm, flowrate: 0.5 mL/min), $t_{1(\text{major})} = 7.9$ min, $t_{1(\text{minor})} = 8.3$ min.

3-(4-Fluorophenyl)-4-methyl tetrahydrothiophene (**4i**)



Following the general procedure **III**, the hydrogenation reaction was carried out and tetrahydrothiophene **4i** was formed in 81% yield. A second signal set in the ^1H NMR indicates 6% of the trans diastereoisomer.

63.5:35.5 e.r., R_F (pentane): 0.11; ^1H NMR (300 MHz, CDCl_3): 7.37 – 7.28 (m, 2H), 7.05 – 6.91 (m, 2H), 4.52 (d, $J = 6.4$ Hz, 2H), 3.20 – 2.87 (m, 2H), 2.59 – 2.39 (m, 1H), 2.18 – 2.01 (m, 1H), 1.96 – 1.82 (m, 1H), 0.68 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): 161.9 (d, $J_F = 245.1$), 136.7, 130.5 (d, $J_F = 7.9$ Hz), 114.76 (d, $J_F = 21.2$ Hz), 55.32, 43.40, 36.69, 30.84, 14.98; ^{19}F NMR (282 MHz, CDCl_3) -116.3; GC-MS: R_t (50_40): 7.9 min; EI: 196 (100), 154 (68), 153 (84), 140 (32), 139 (75), 135 (35), 133 (23), 109 (58); HPLC (OJ-H, eluents: hexane/*i*-PrOH = 99.5:0.5, detector: 210 nm, flowrate: 0.4 mL/min), $t_{1(\text{major})} = 13.9$ min, $t_{1(\text{minor})} = 17.5$ min.

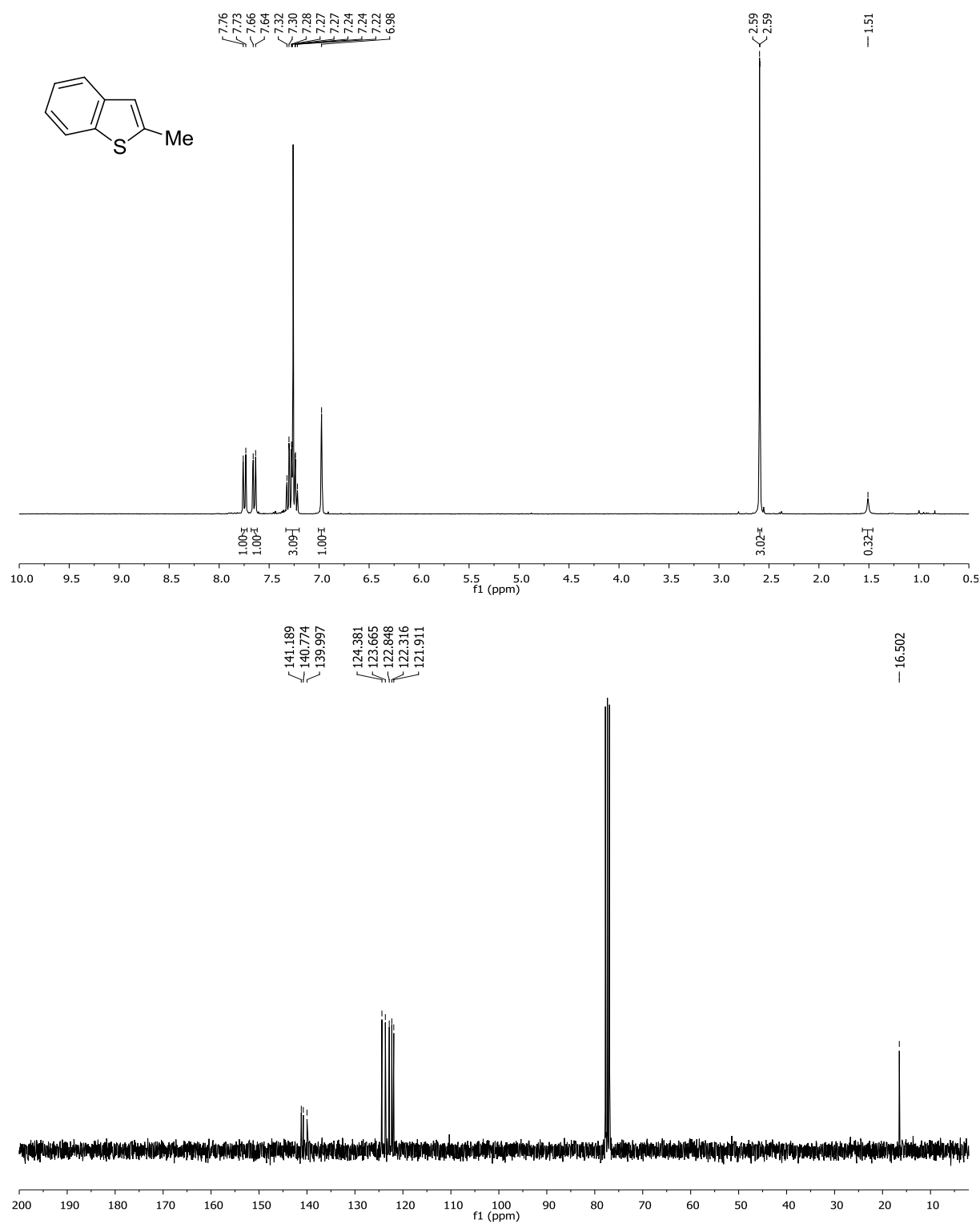
6 References

- [1] , B. t.; Lapointe, D.; Caron, L.; Vlassova, A.; Fagnou, K. *J. Org. Chem.* **2009**, *74*, 1826-1834.
- [2] Denton, T. T.; Zhang, X.; Cashman, J. R. *J. Med. Chem.* **2005**, *48*, 224-239.
- [3] Vachal, P.; Toth, L. M. *Tetrahedron Lett.* **2004**, *45*, 7157-7161.
- [4] Fujimori, K.; Matsuura, T.; Mikami, A.; Watanabe, Y.; Oae, S.; Iyanagi, T. *J. Chem. Soc. Perkin Trans. 1*, **1990**, 1435-1440.
- [5] Jurcik, V.; Gilani, M.; Wilhelm, R. *Eur. J. Org. Chem.*, **2006**, 5103-5109.

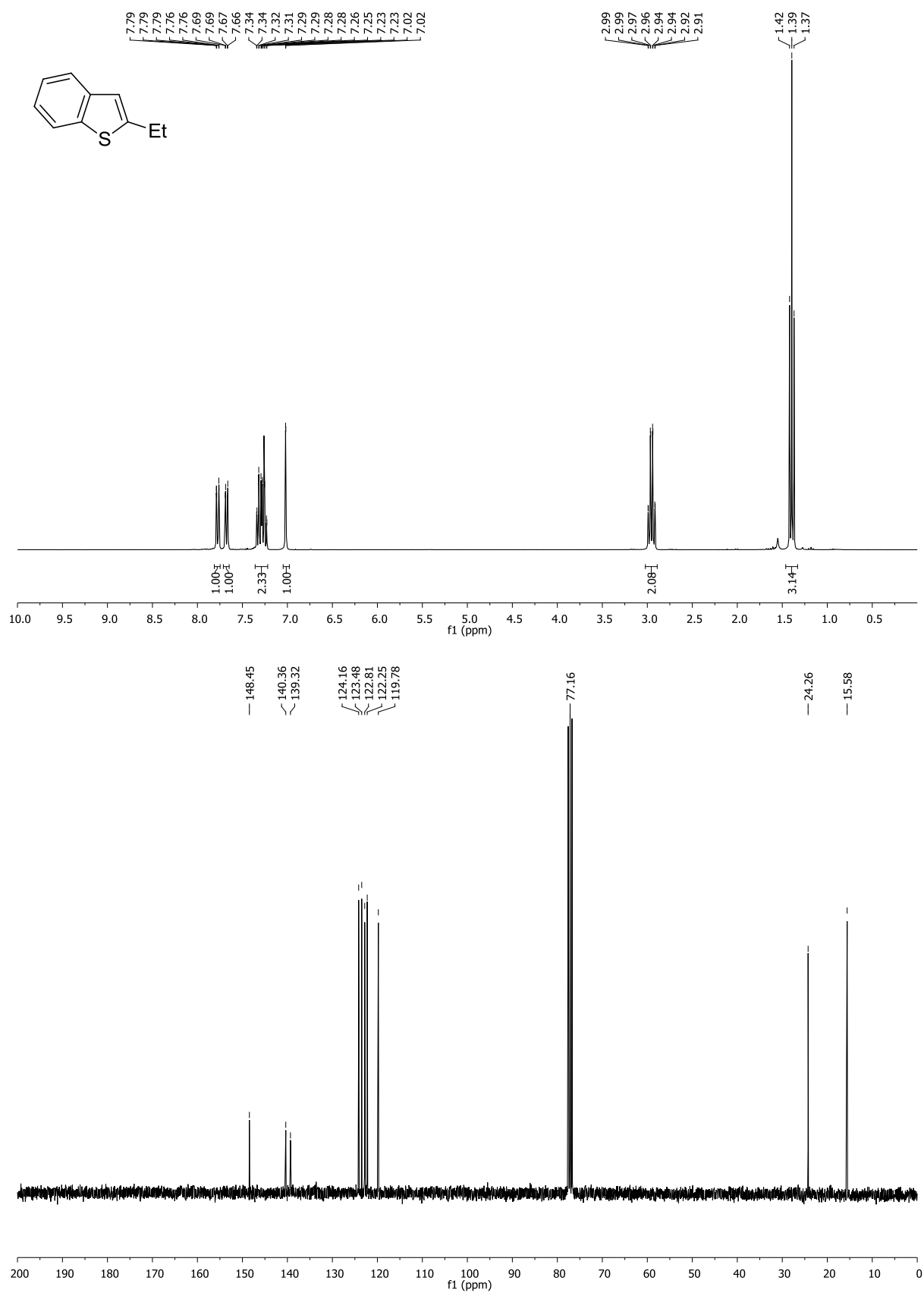
7 NMR spectra

7.1 Substrates

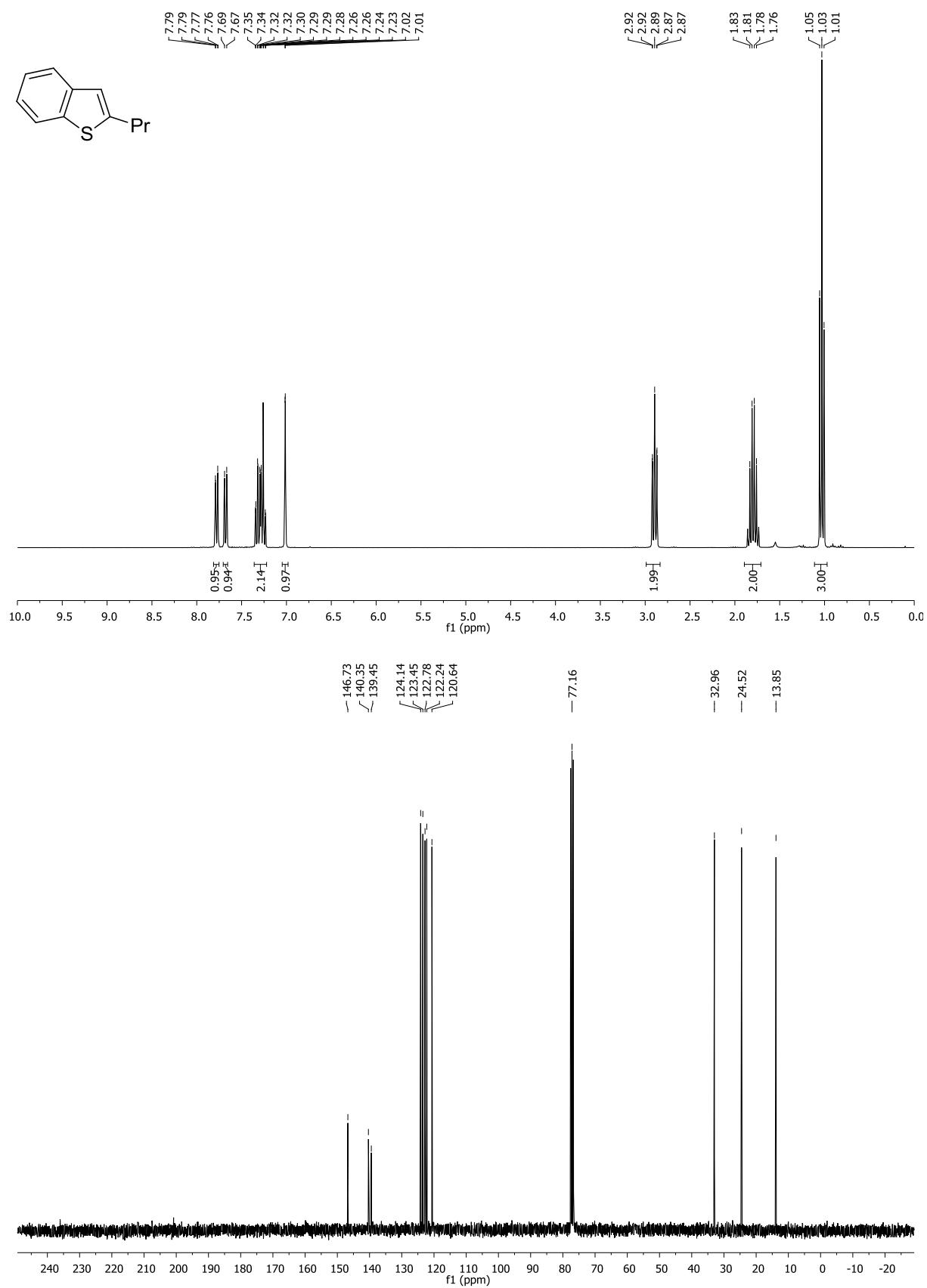
2-Methylbenzo[*b*]thiophene (1b)



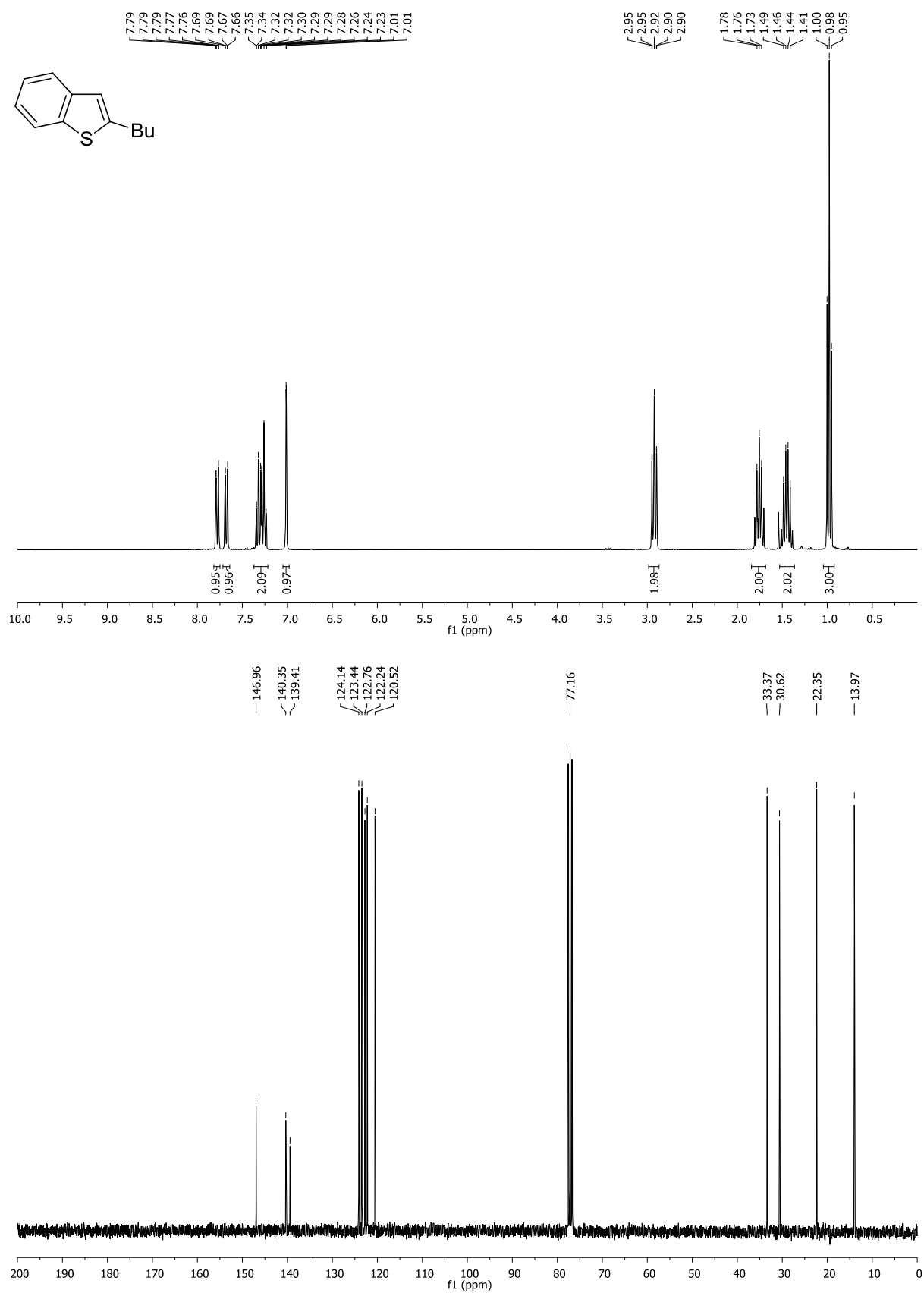
2-Ethylbenzo[*b*]thiophene (1c)



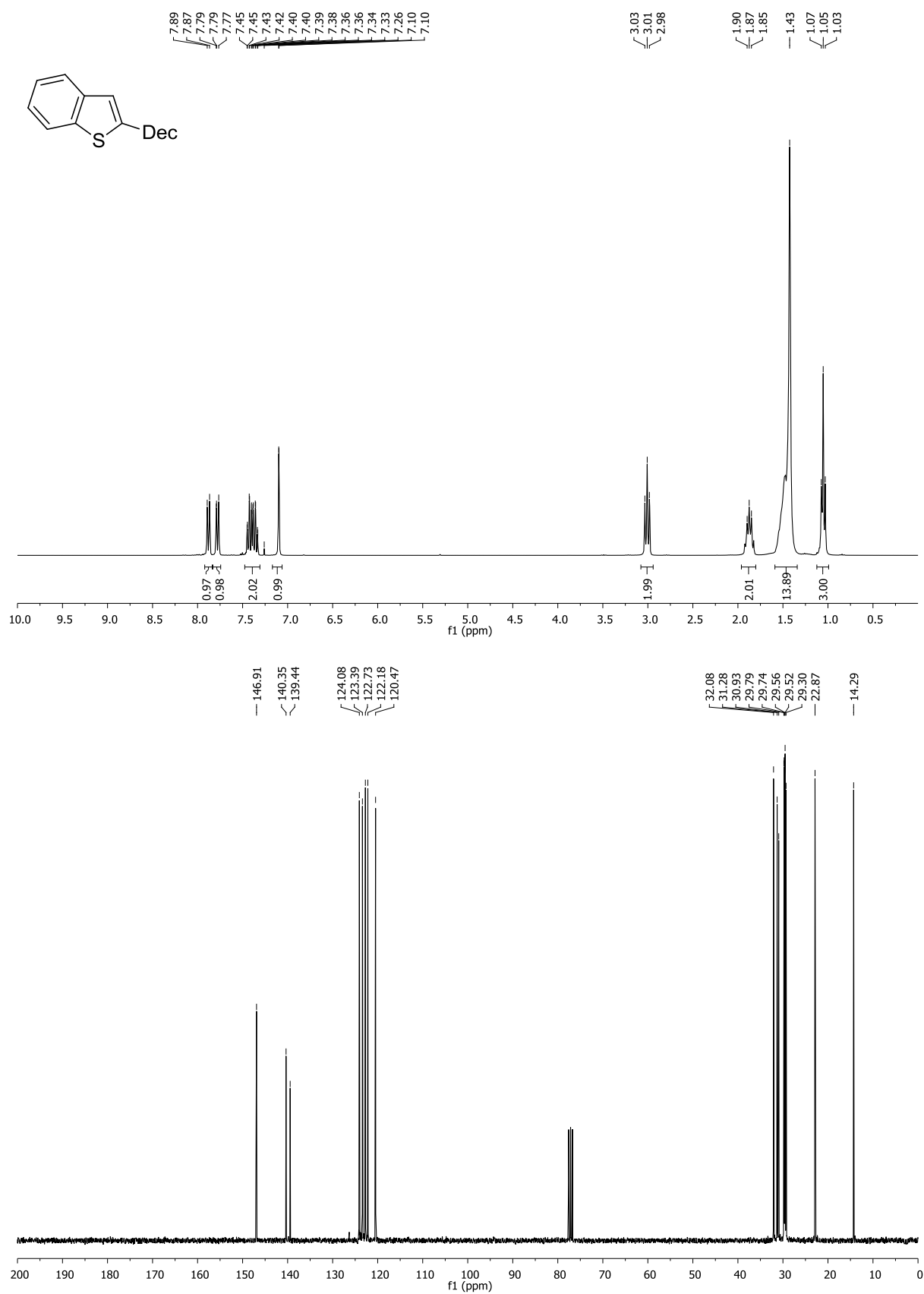
2-Propylbenzo[b]thiophene (1d)



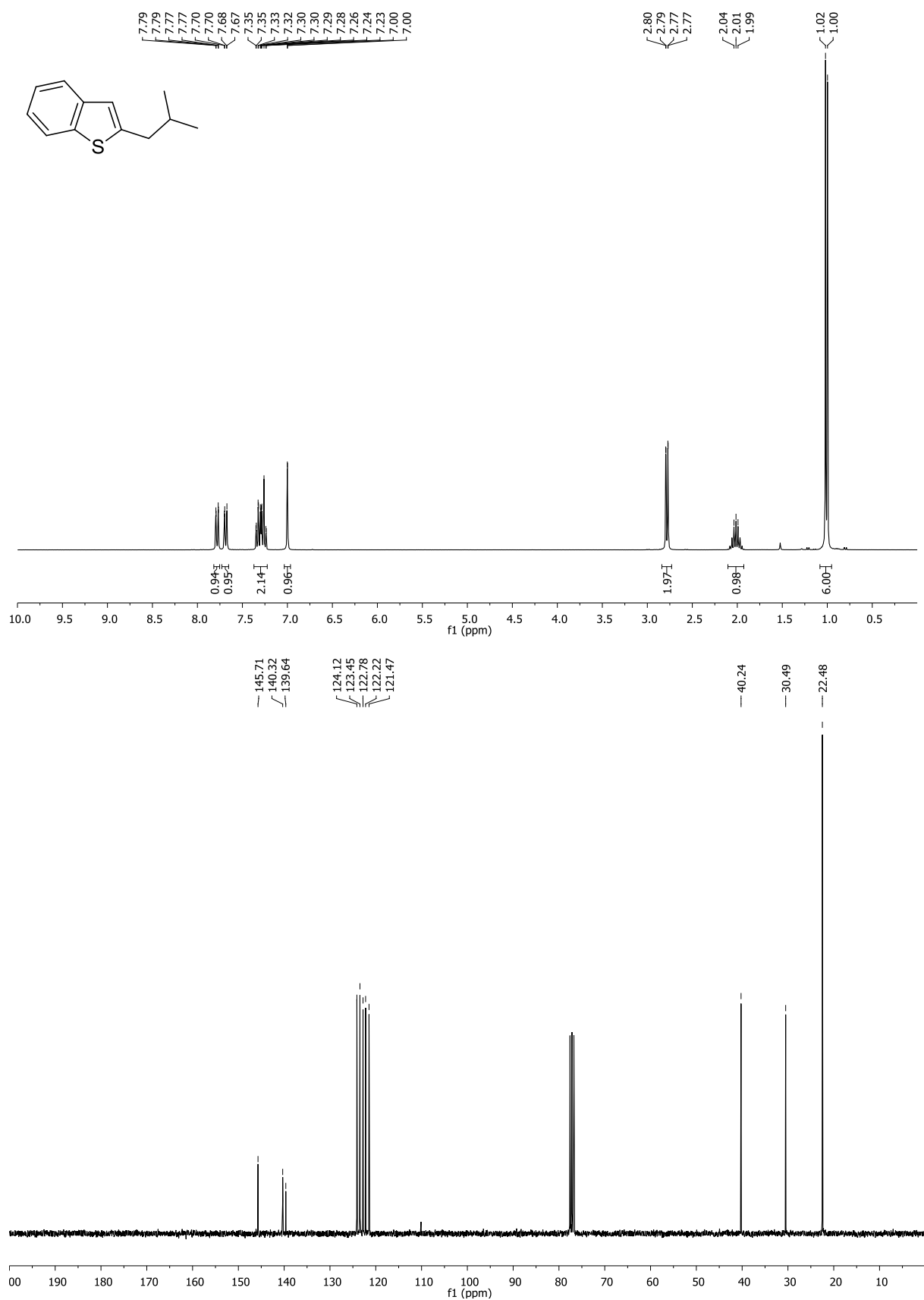
2-Butylbenzo[*b*]thiophene (1e)



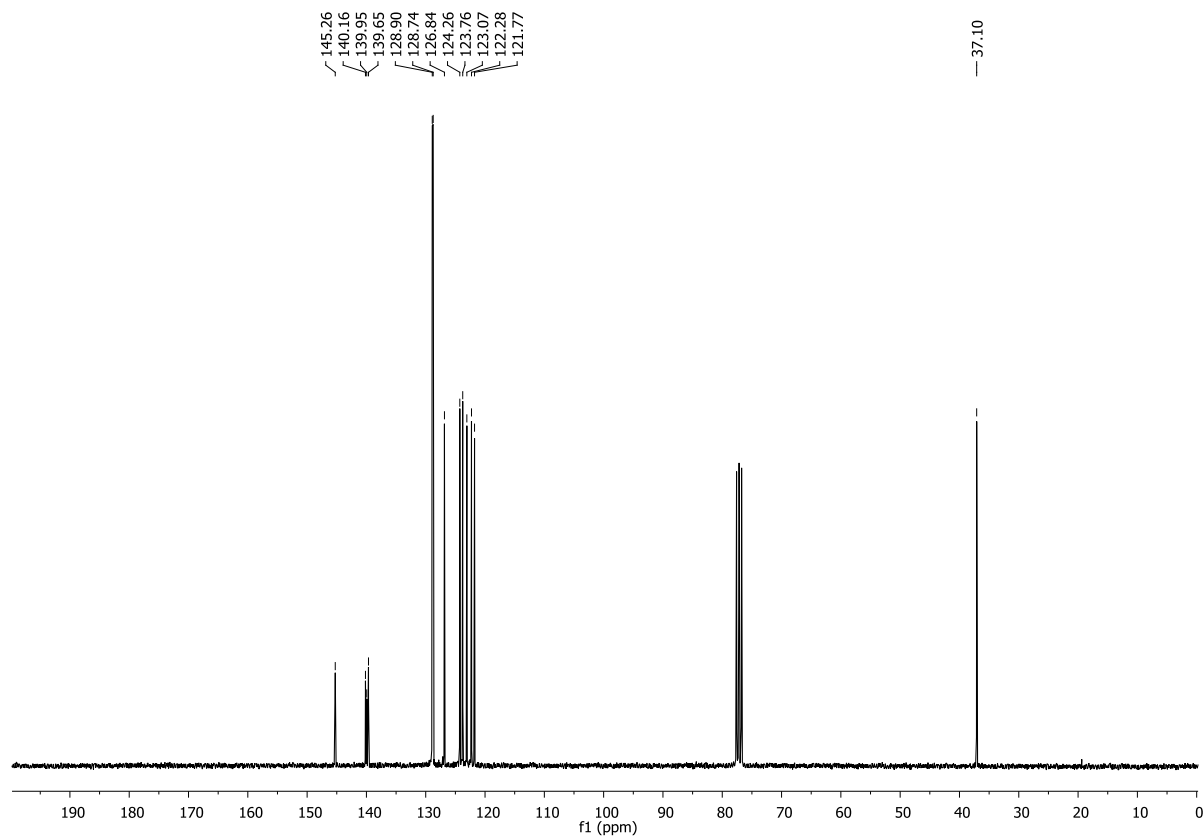
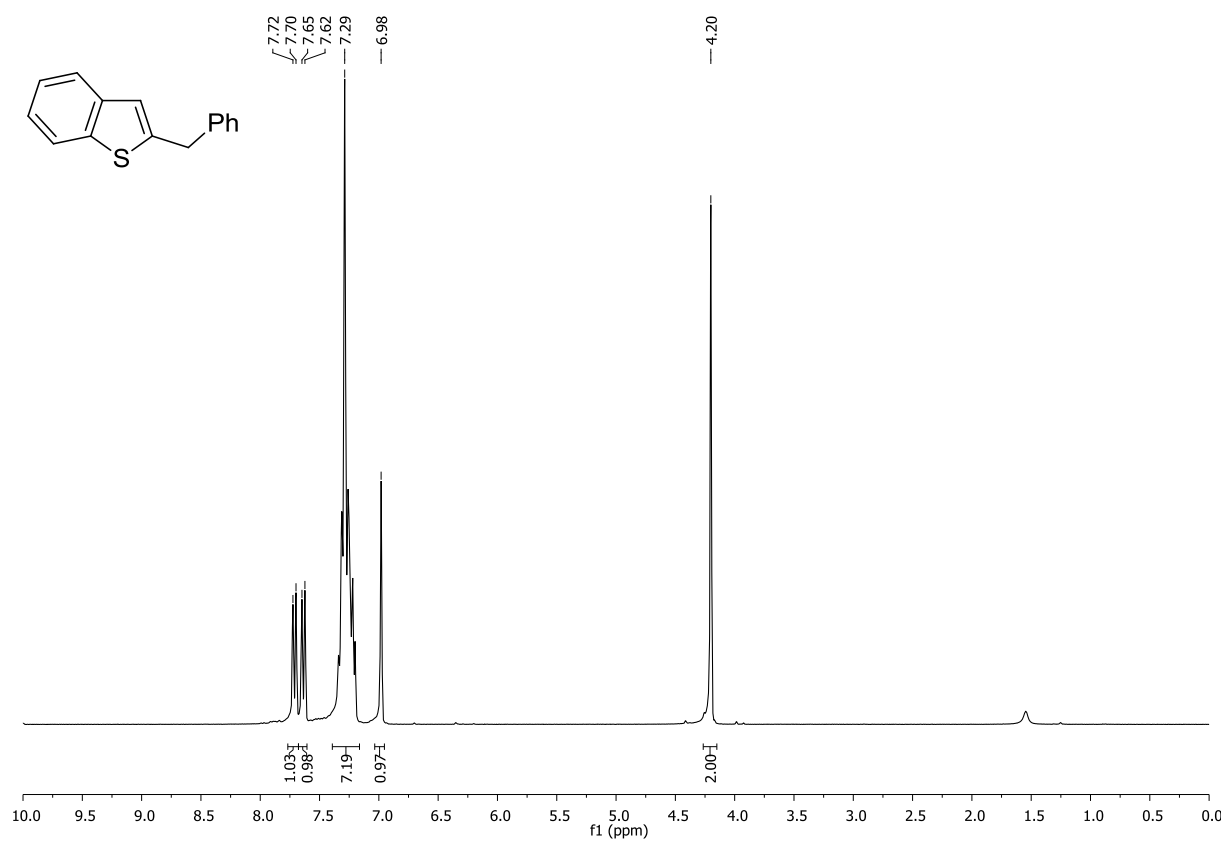
2-Decylbenzo[*b*]thiophene (1f)



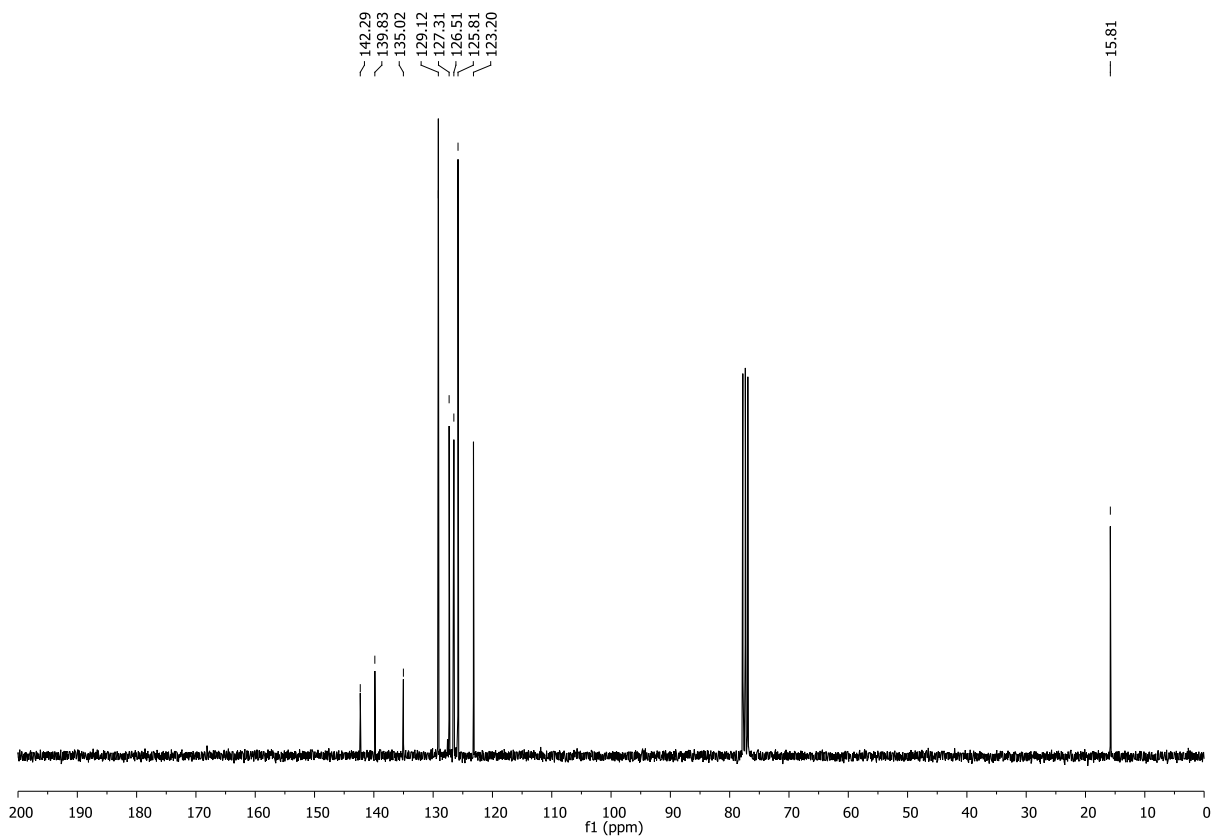
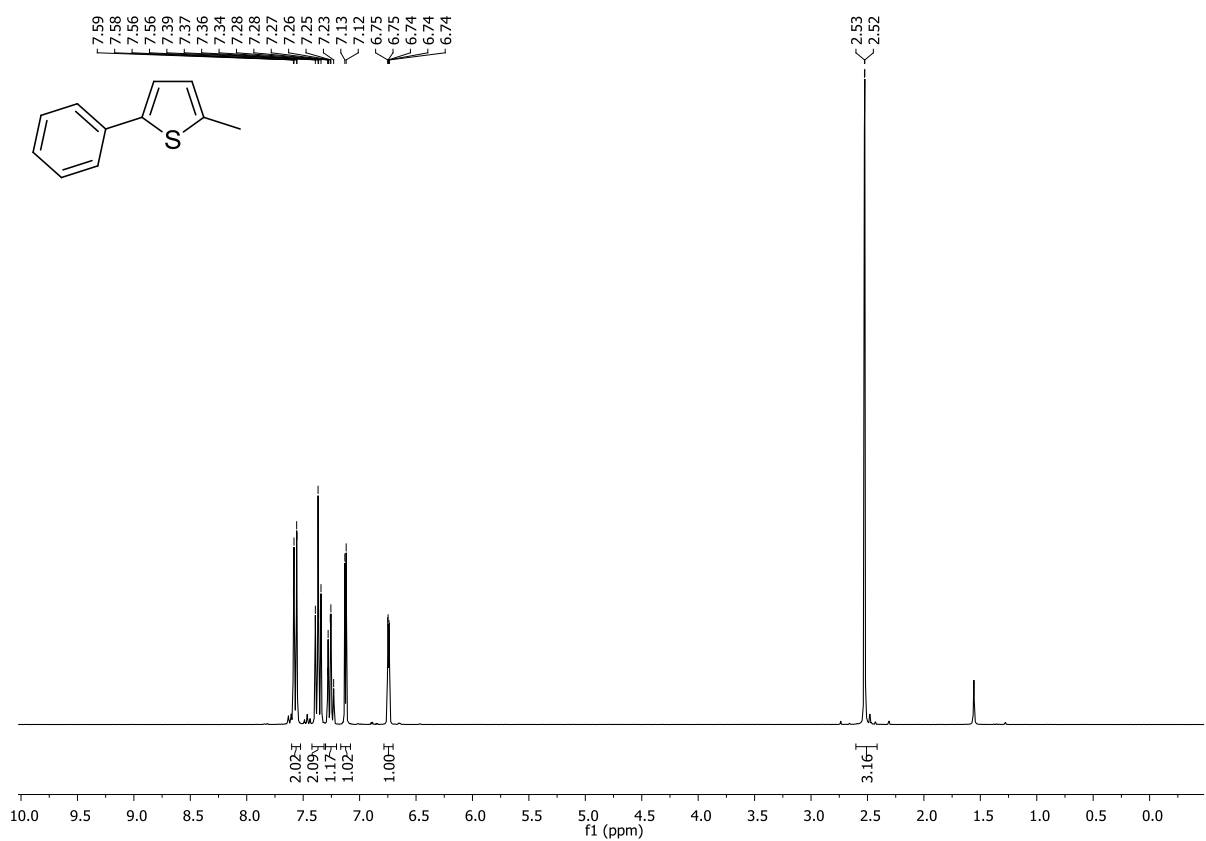
2-Isobutylbenzo[*b*]thiophene (1g)



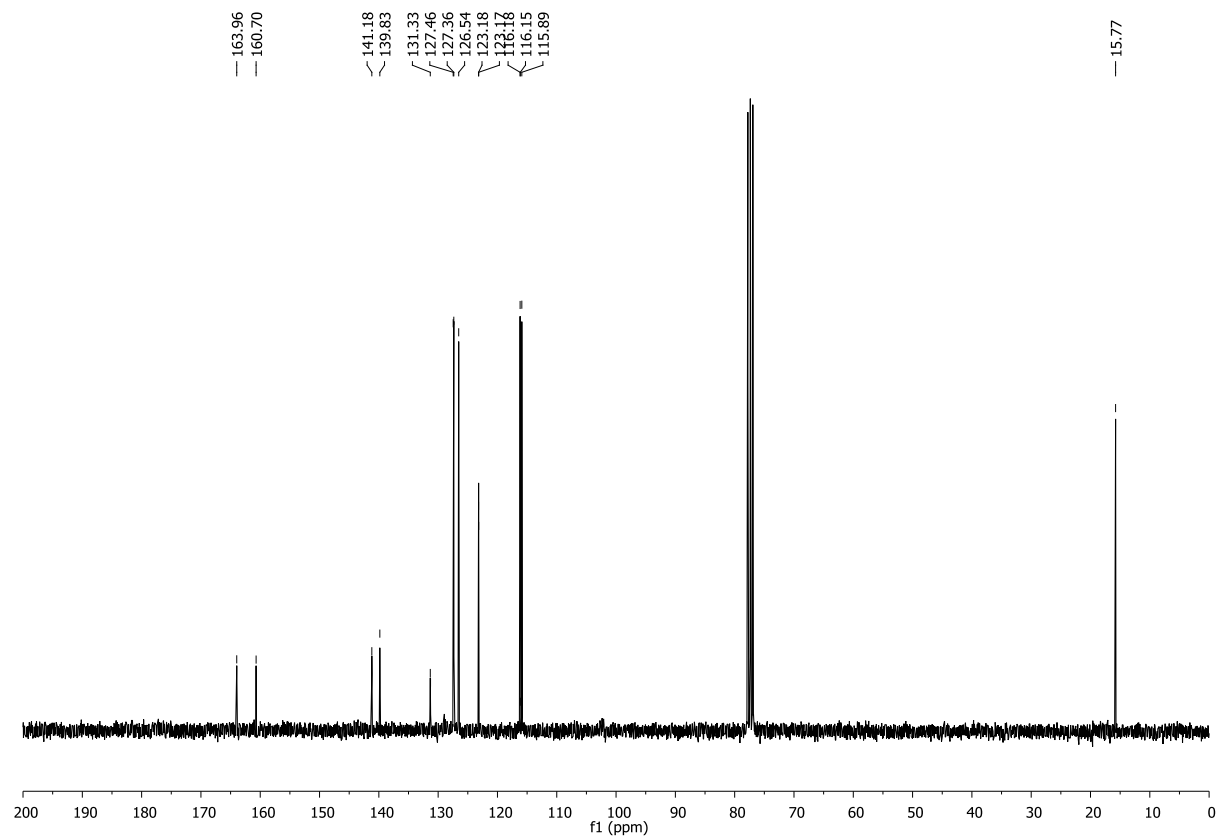
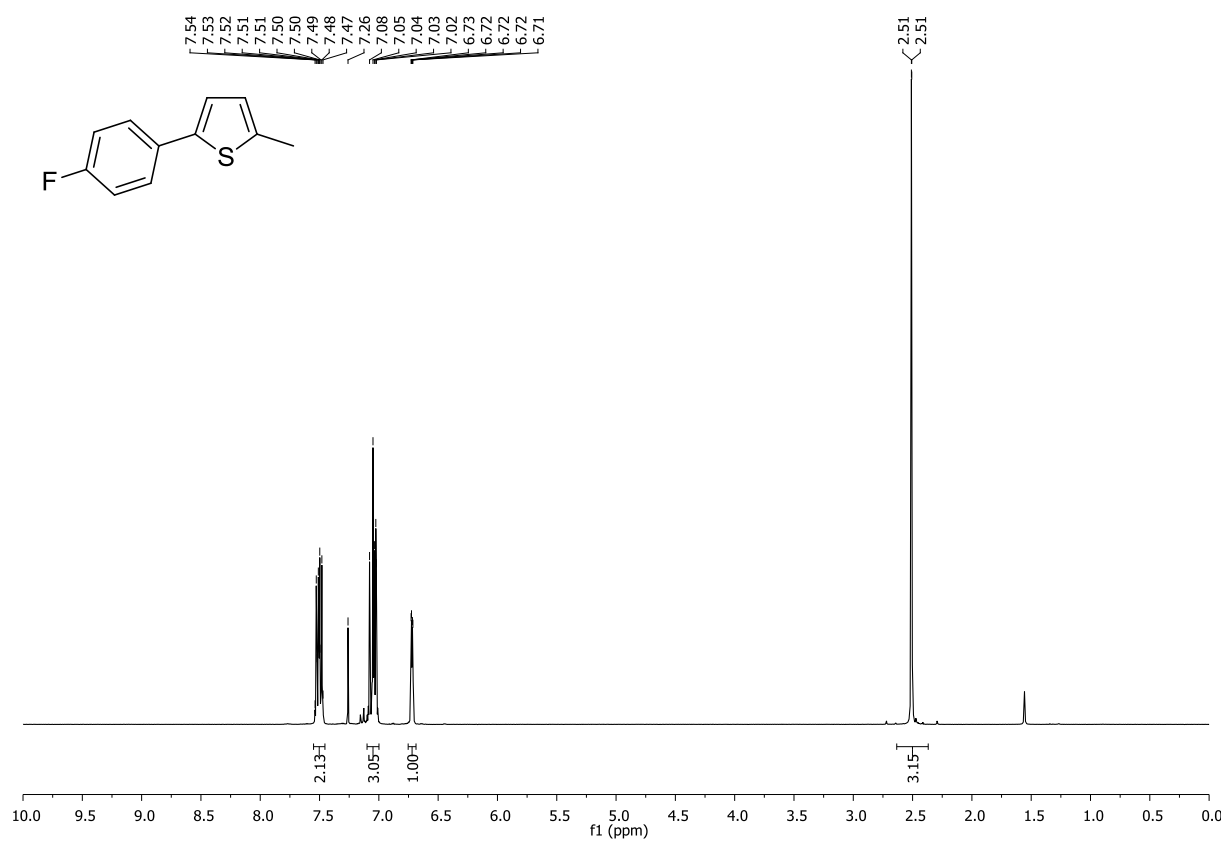
2-Benzylbenzo[*b*]thiophene (1h)



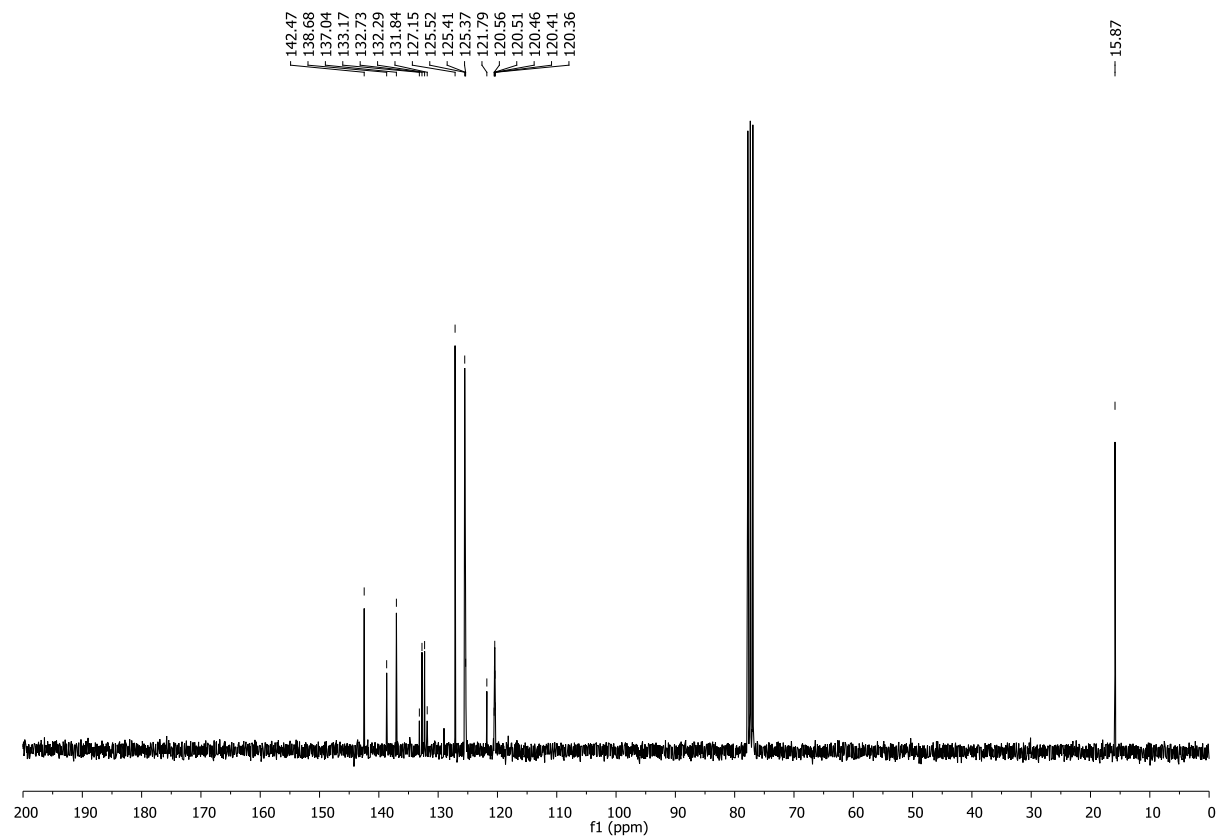
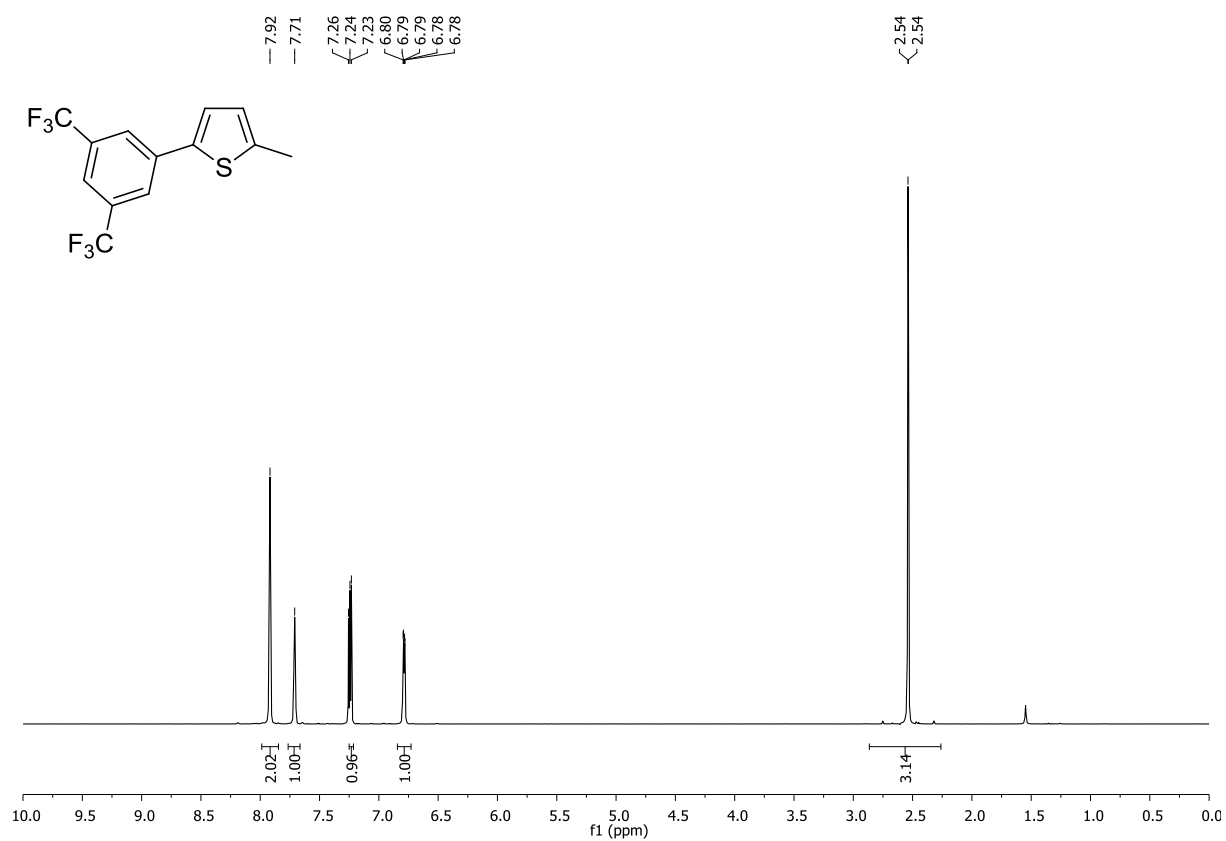
2-Methyl-5-phenylthiophene (3e)



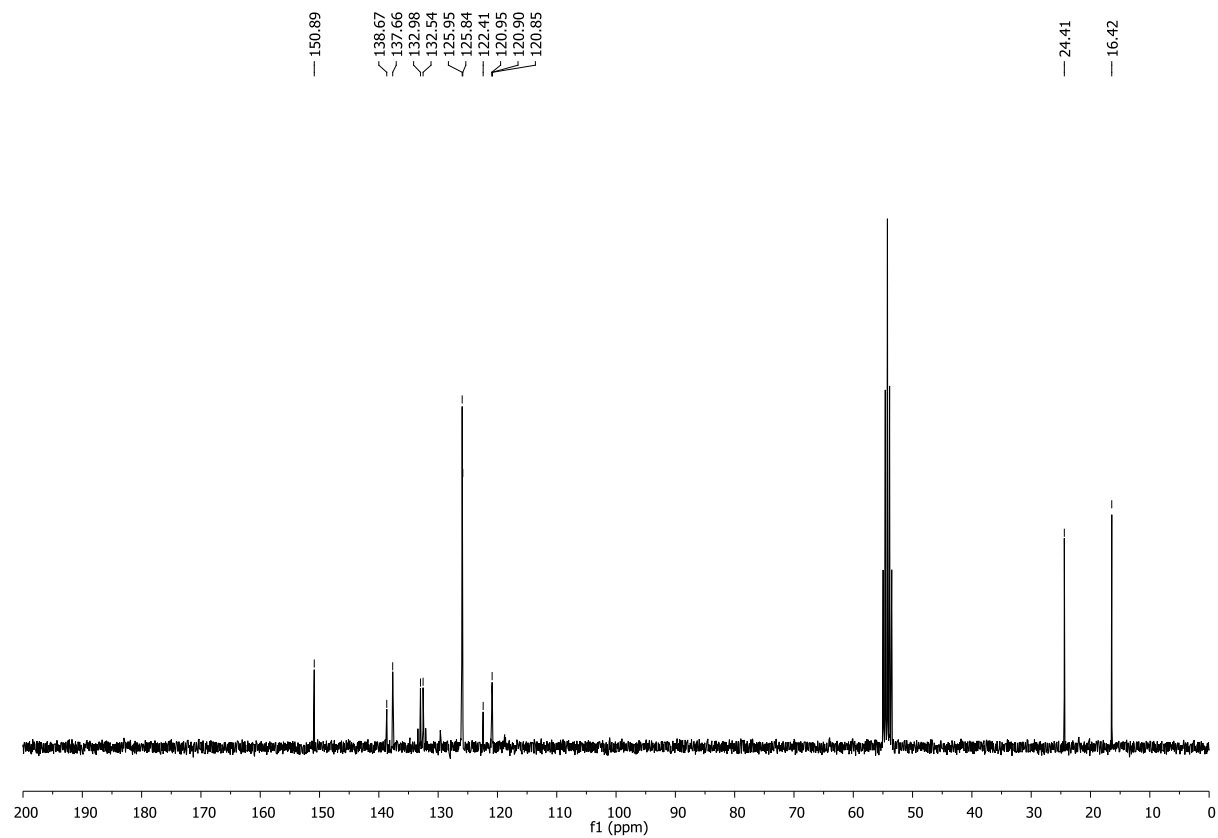
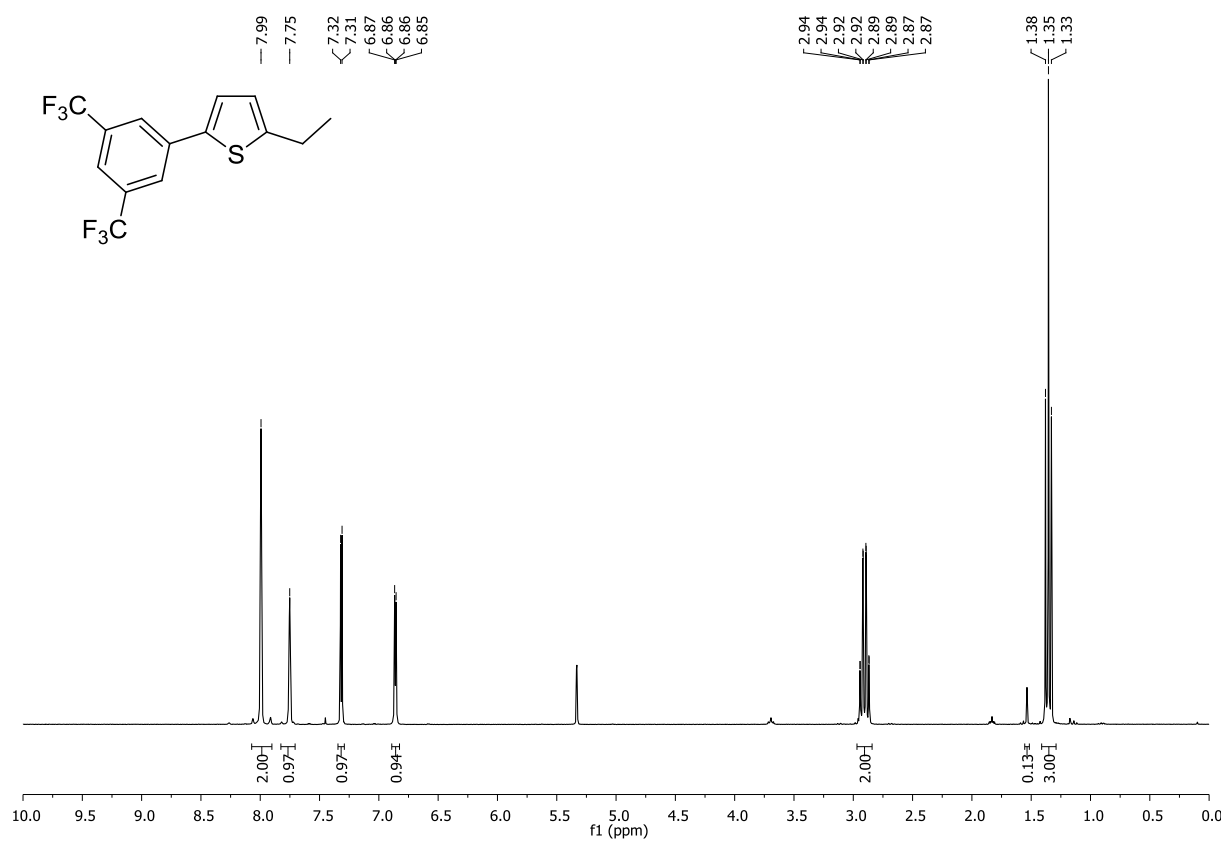
2-(4-Fluorophenyl)-5-methylthiophene (3f)



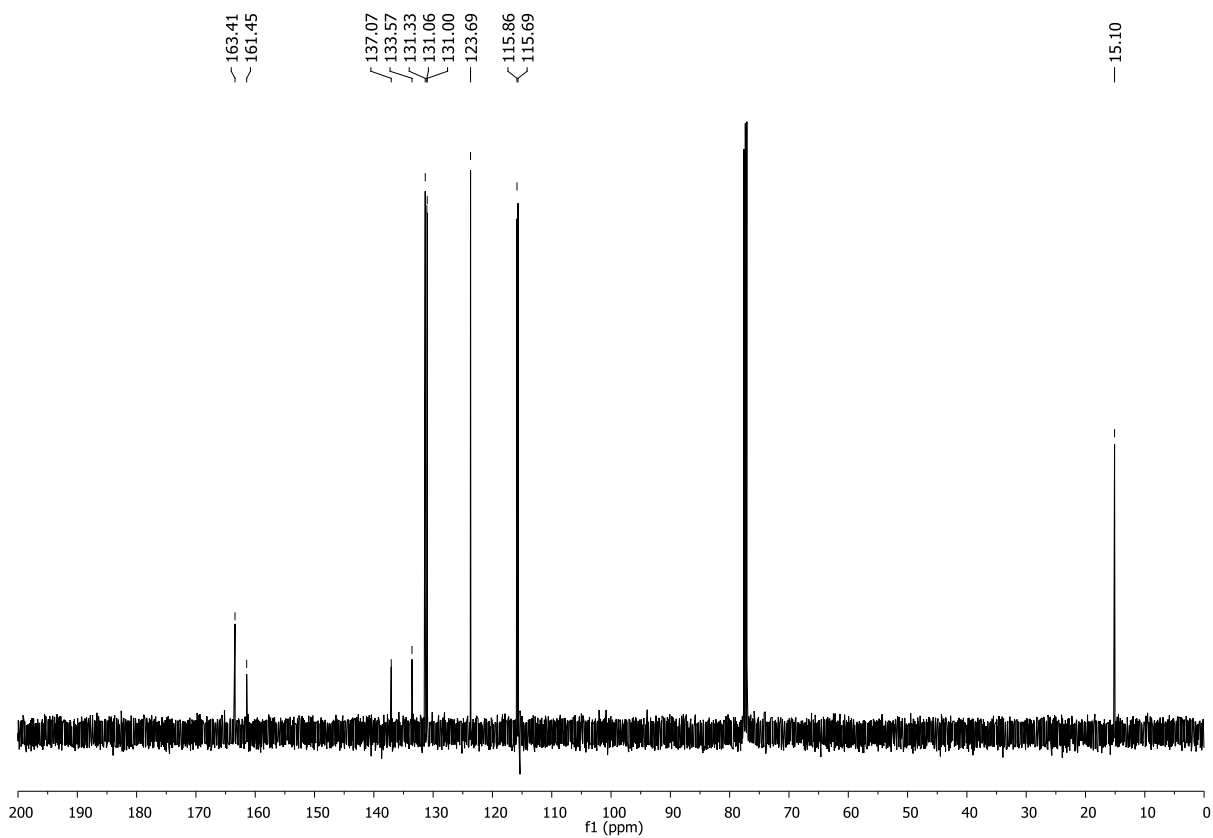
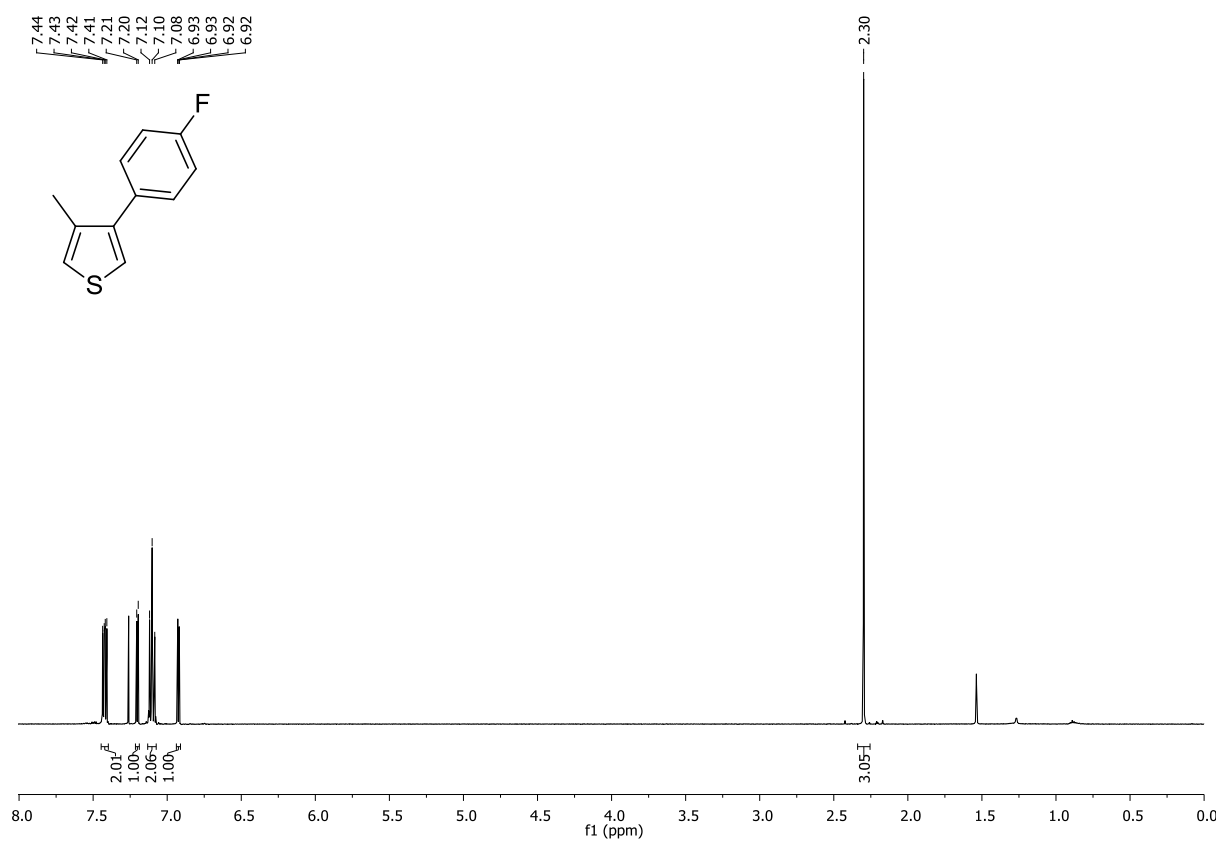
2-(3,5-Bis(trifluoromethyl)phenyl)-5-methylthiophene (3g)



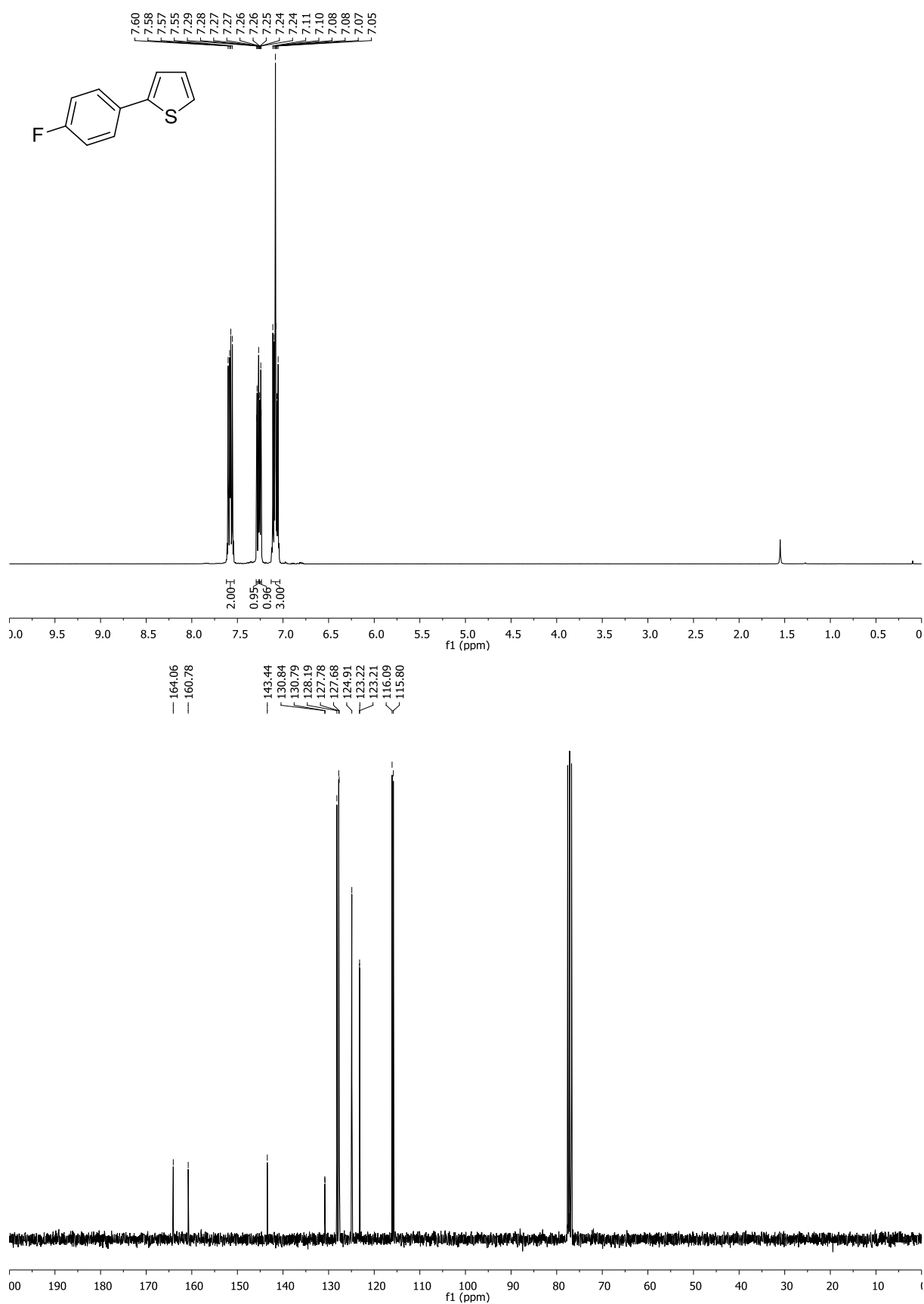
2-(3,5-Bis(trifluoromethyl)phenyl)-5-ethylthiophene (3h)



3-(4-Fluorophenyl)-4-methylthiophene (3i)

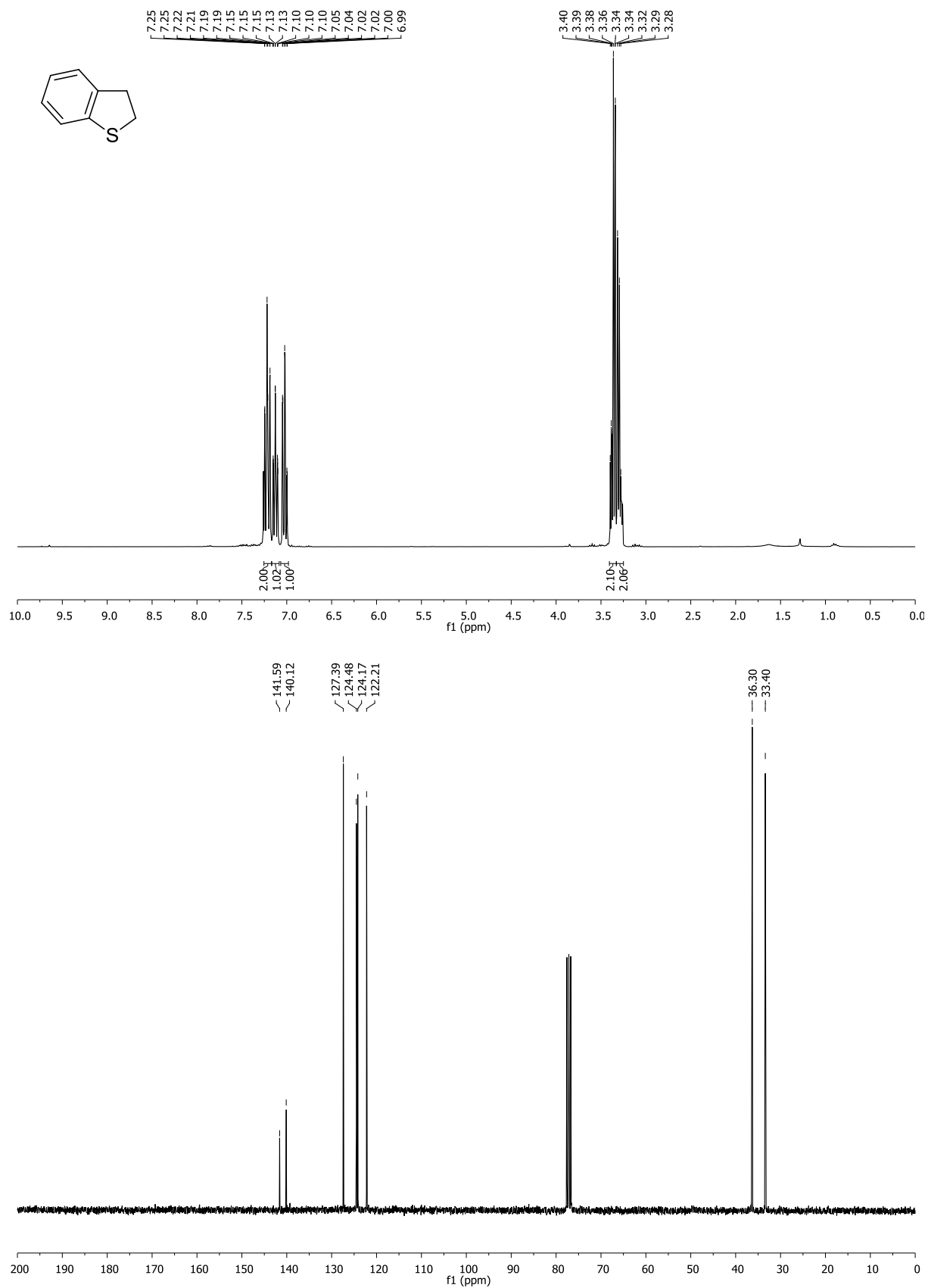


2-(4-Fluorophenyl)thiophene (3d)

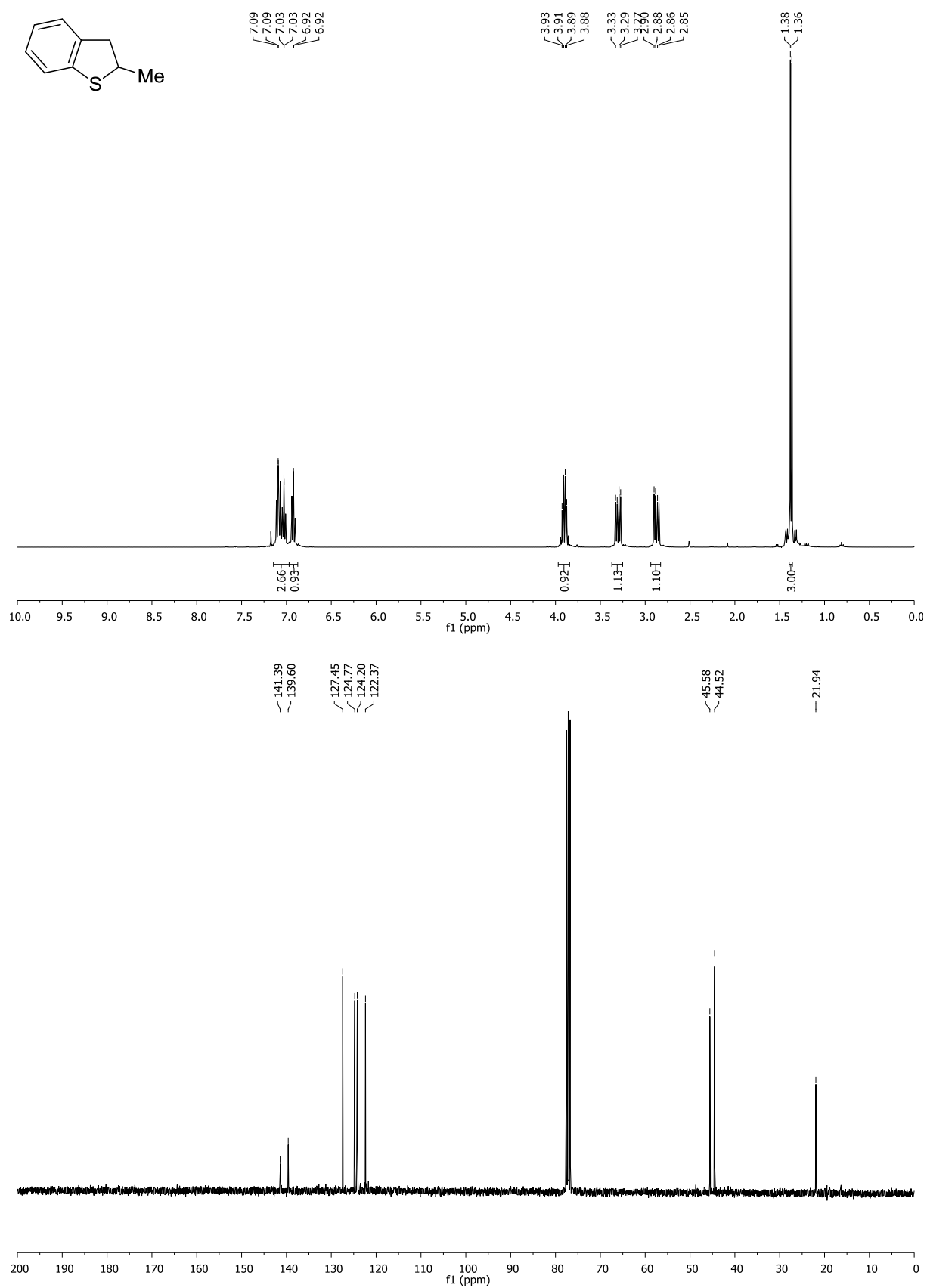


7.2 Products

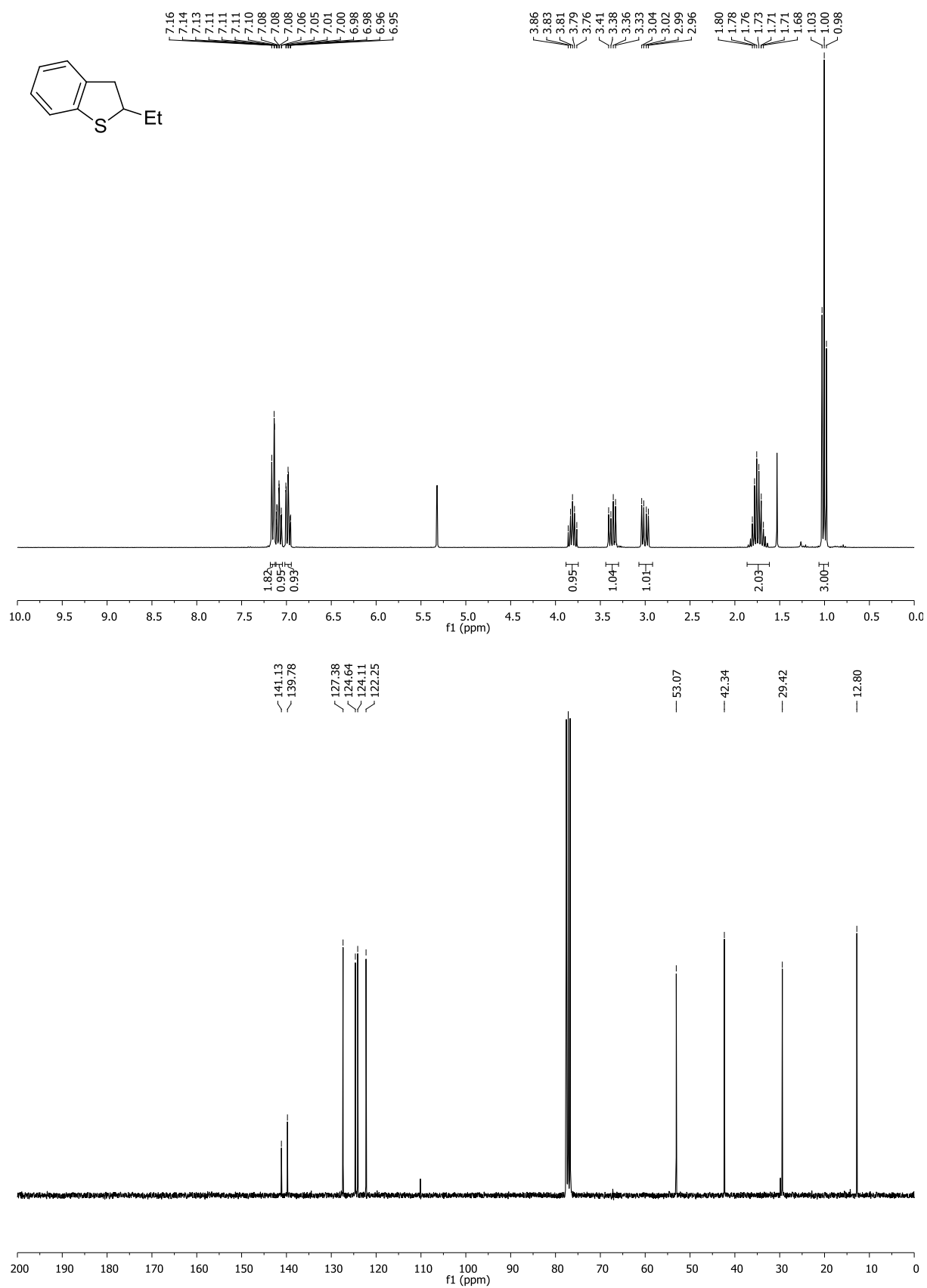
2,3-Dihydrobenzo[*b*]thiophene (2a)



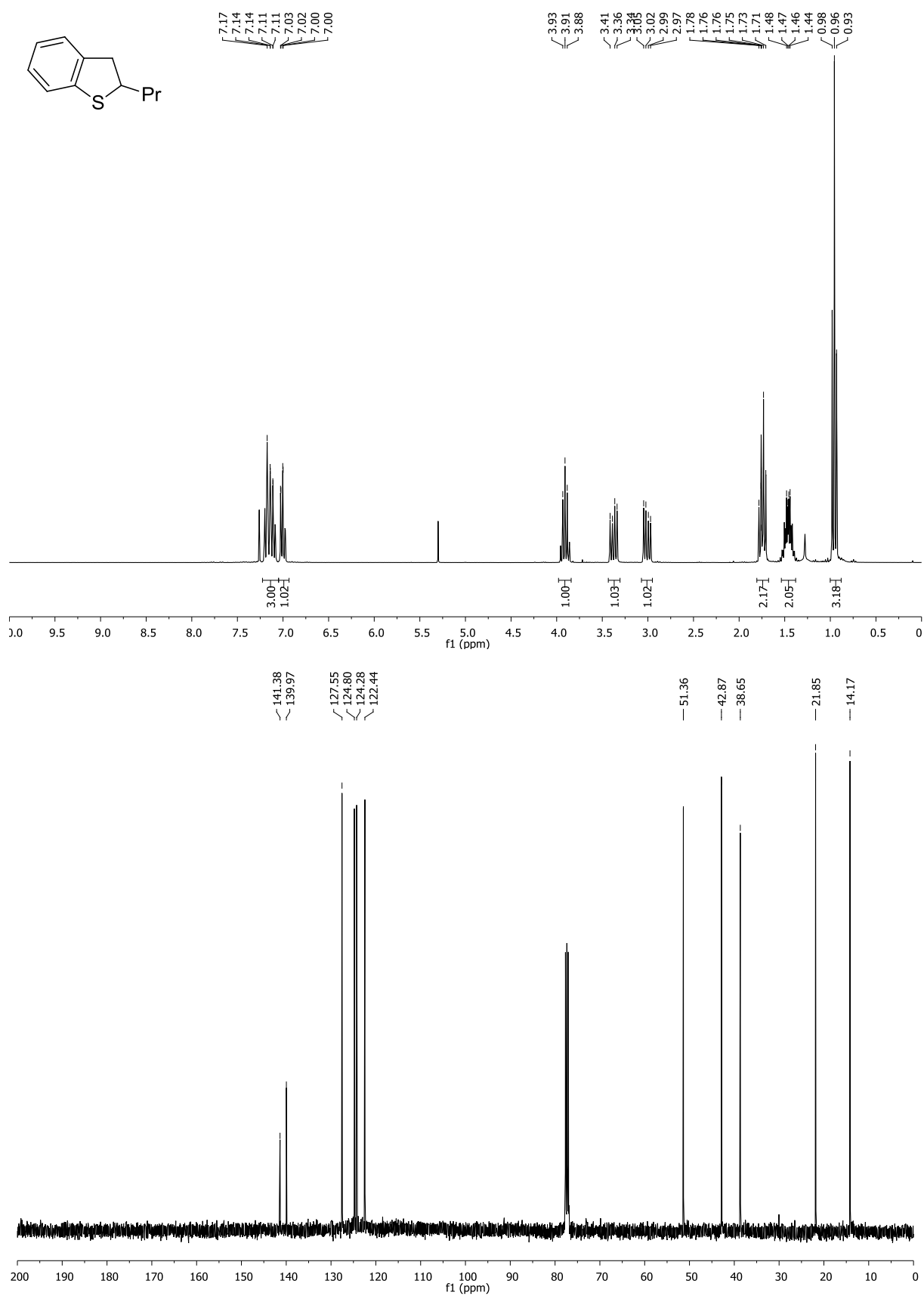
2-Methyl-2,3-dihydrobenzo[*b*]thiophene (2b)



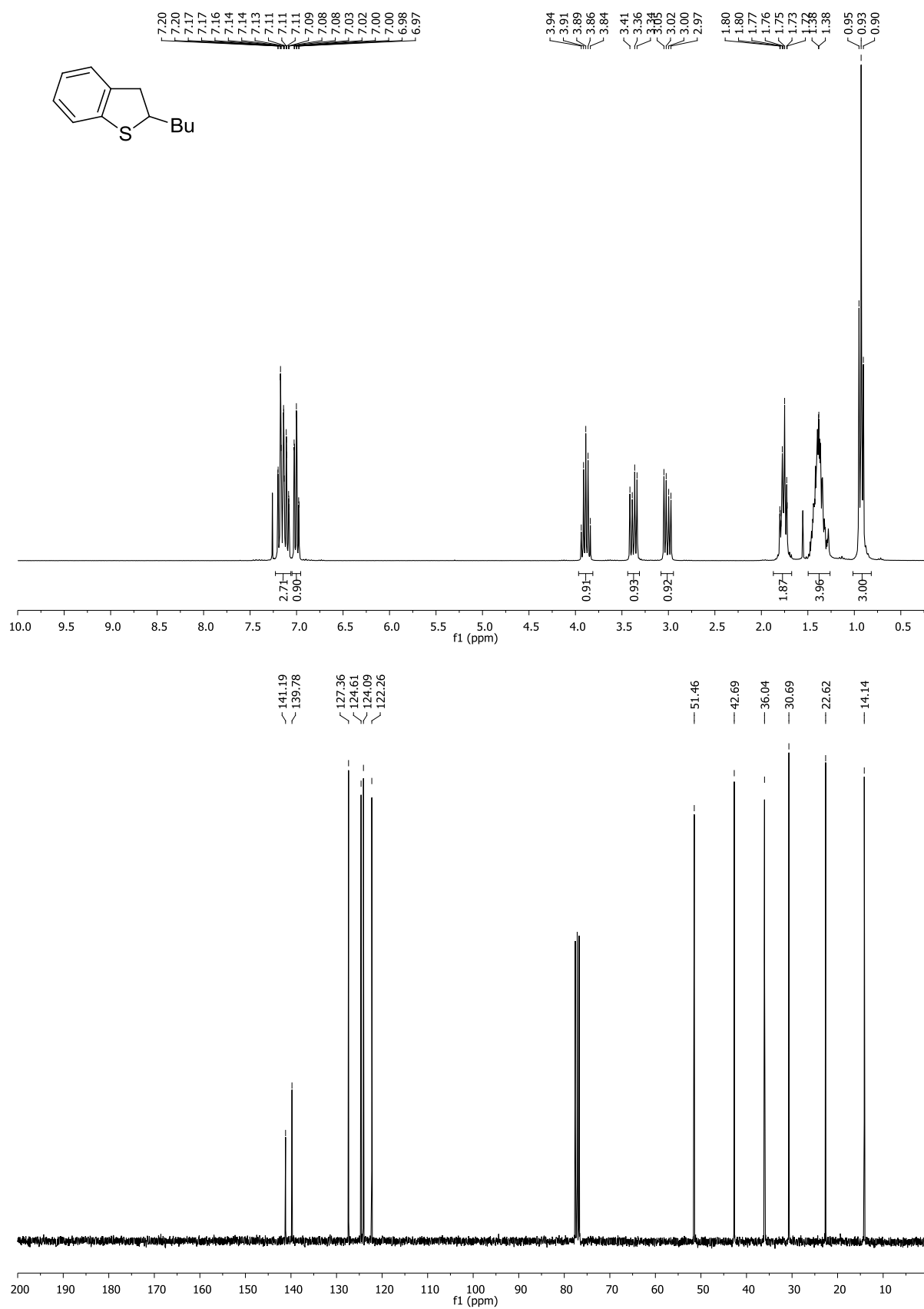
2-Ethyl-2,3-dihydrobenzo[*b*]thiophene (2c)



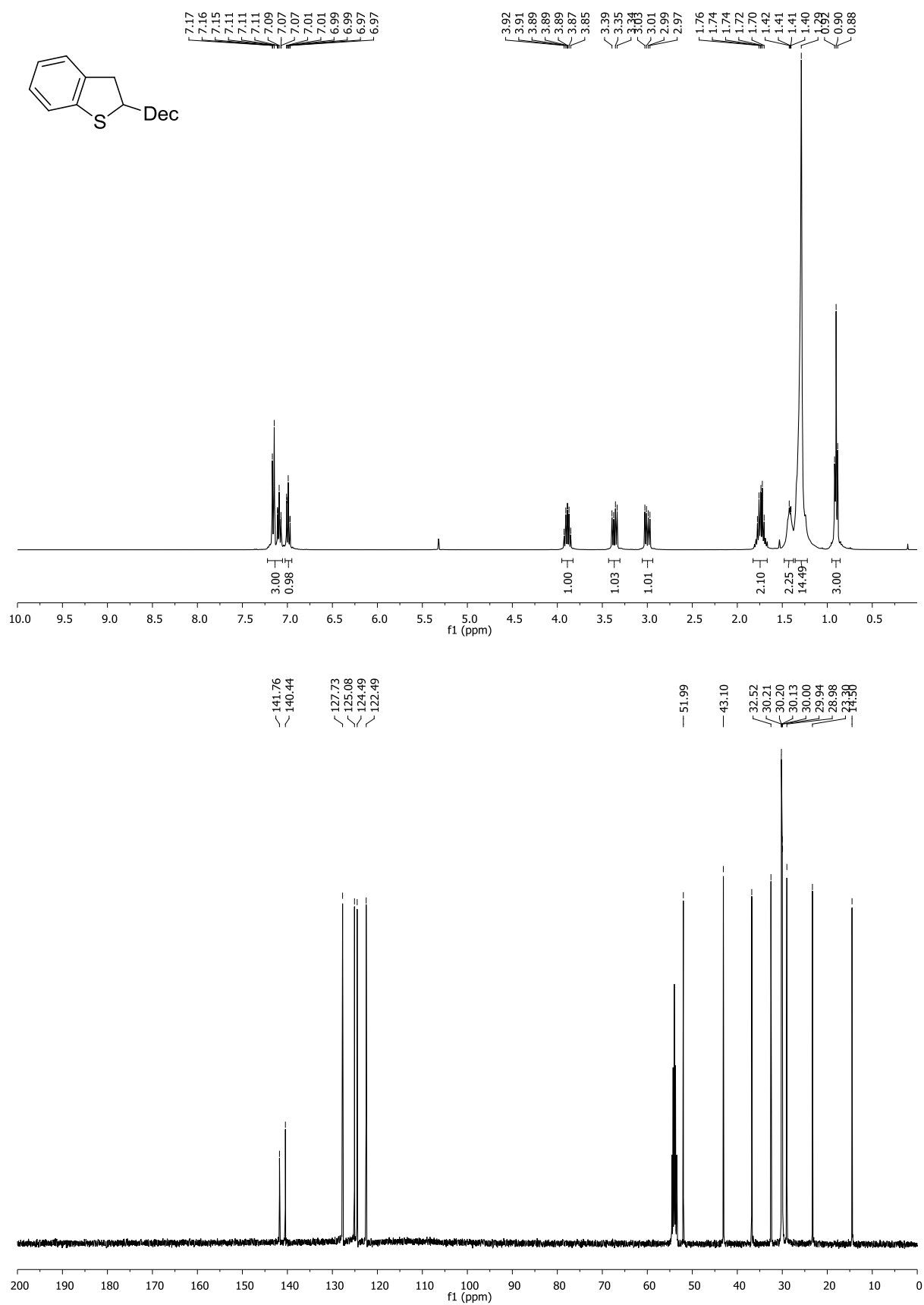
2-Propyl-2,3-dihydrobenzo[*b*]thiophene (2d)



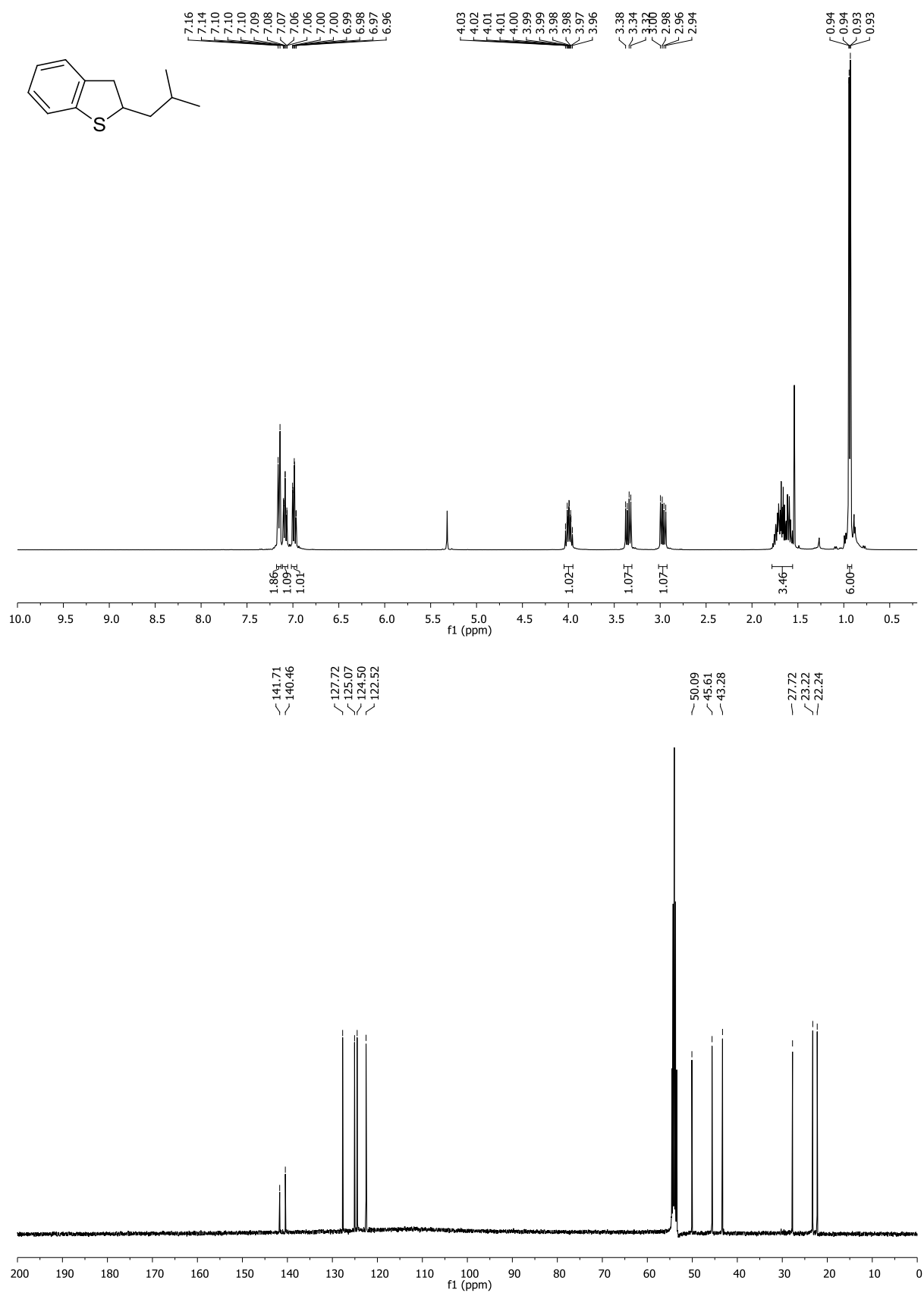
2-Butyl-2,3-dihydrobenzo[b]thiophene (2e)



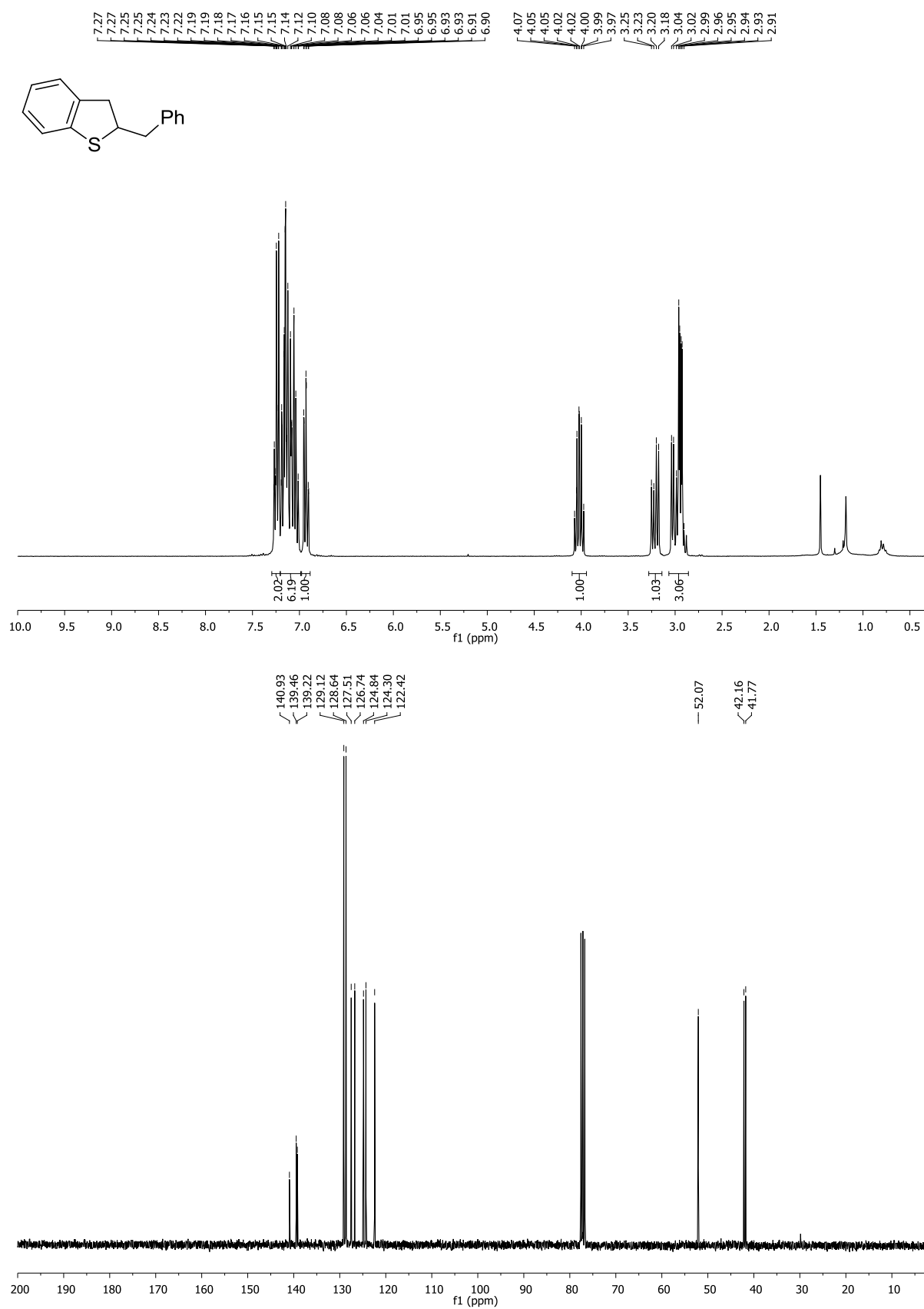
2-Decyl-2,3-dihydrobenzo[*b*]thiophene (2f)



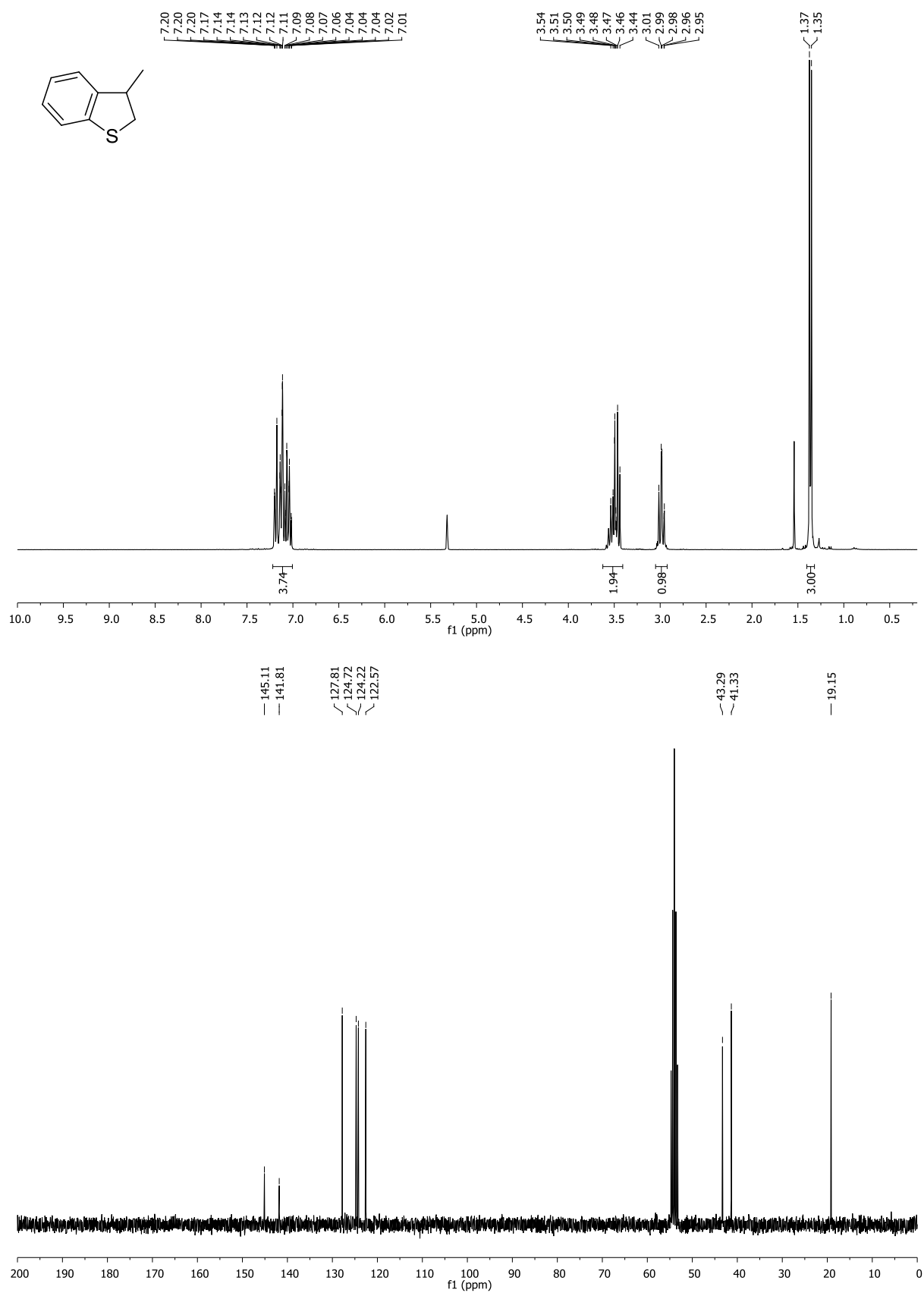
2-Isobutyl-2,3-dihydrobenzo[b]thiophene (2g)



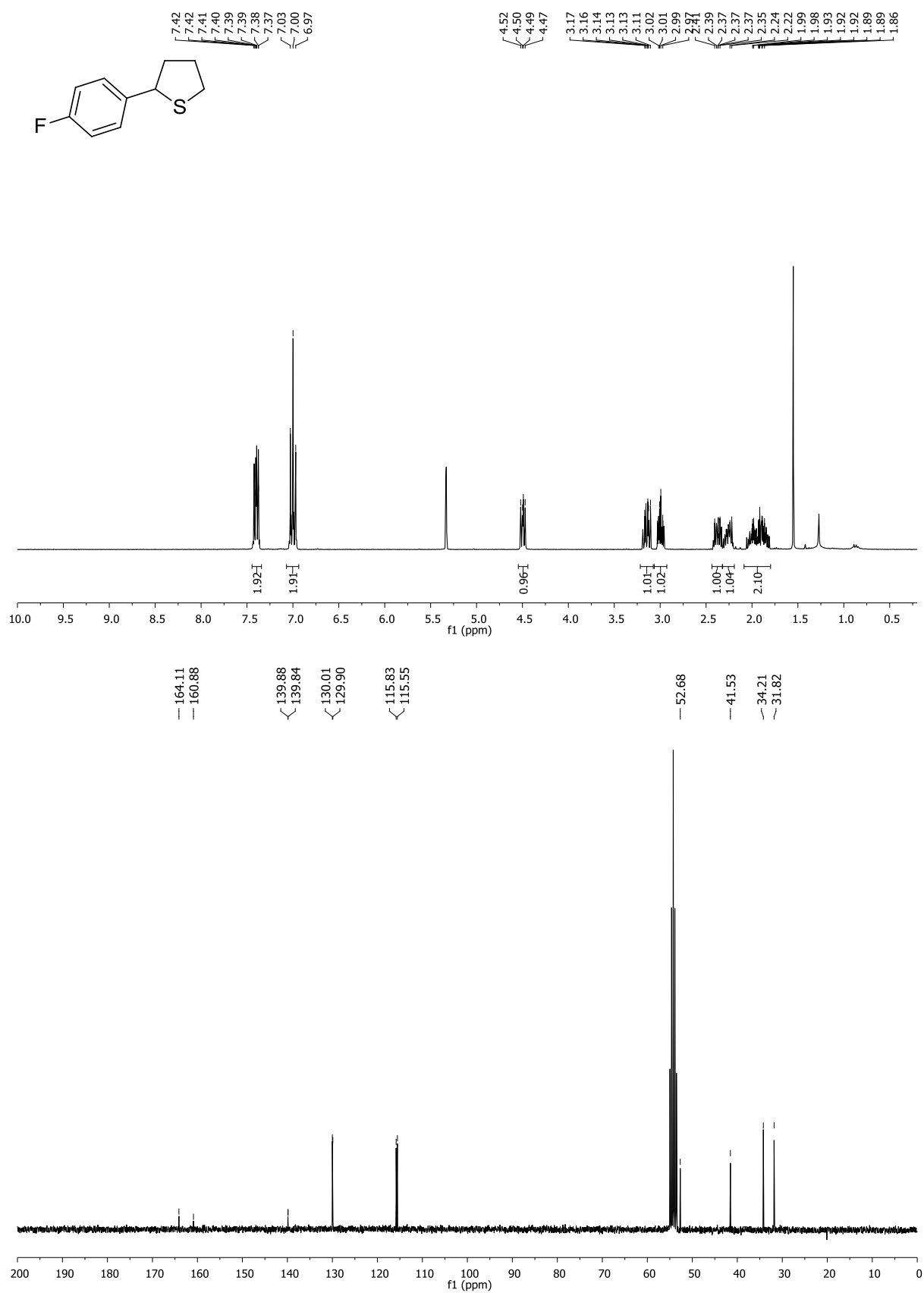
2-Benzyl-2,3-dihydrobenzo[*b*]thiophene (2h)



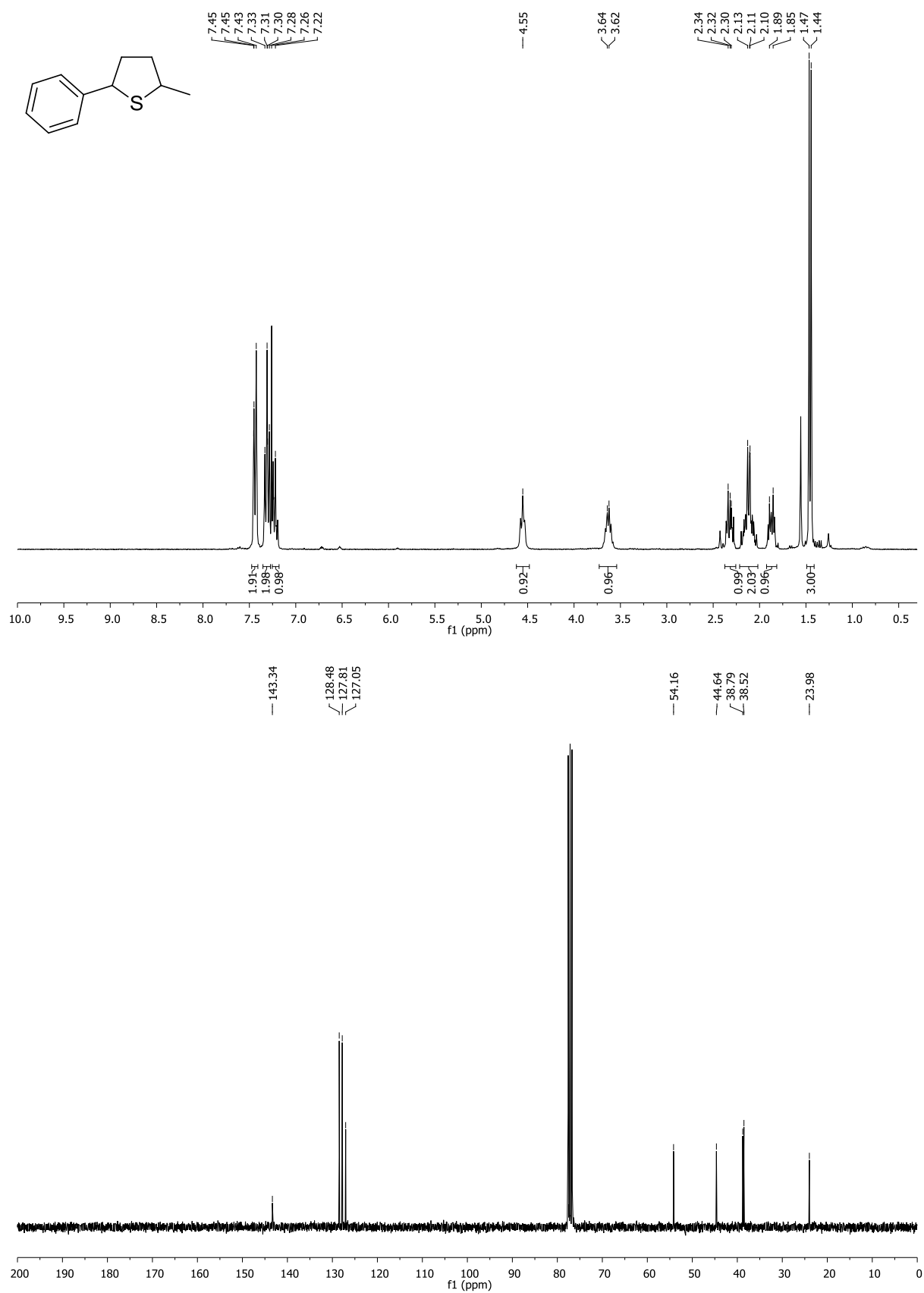
3-Methyl-2,3-dihydrobenzo[*b*]thiophene (2i)



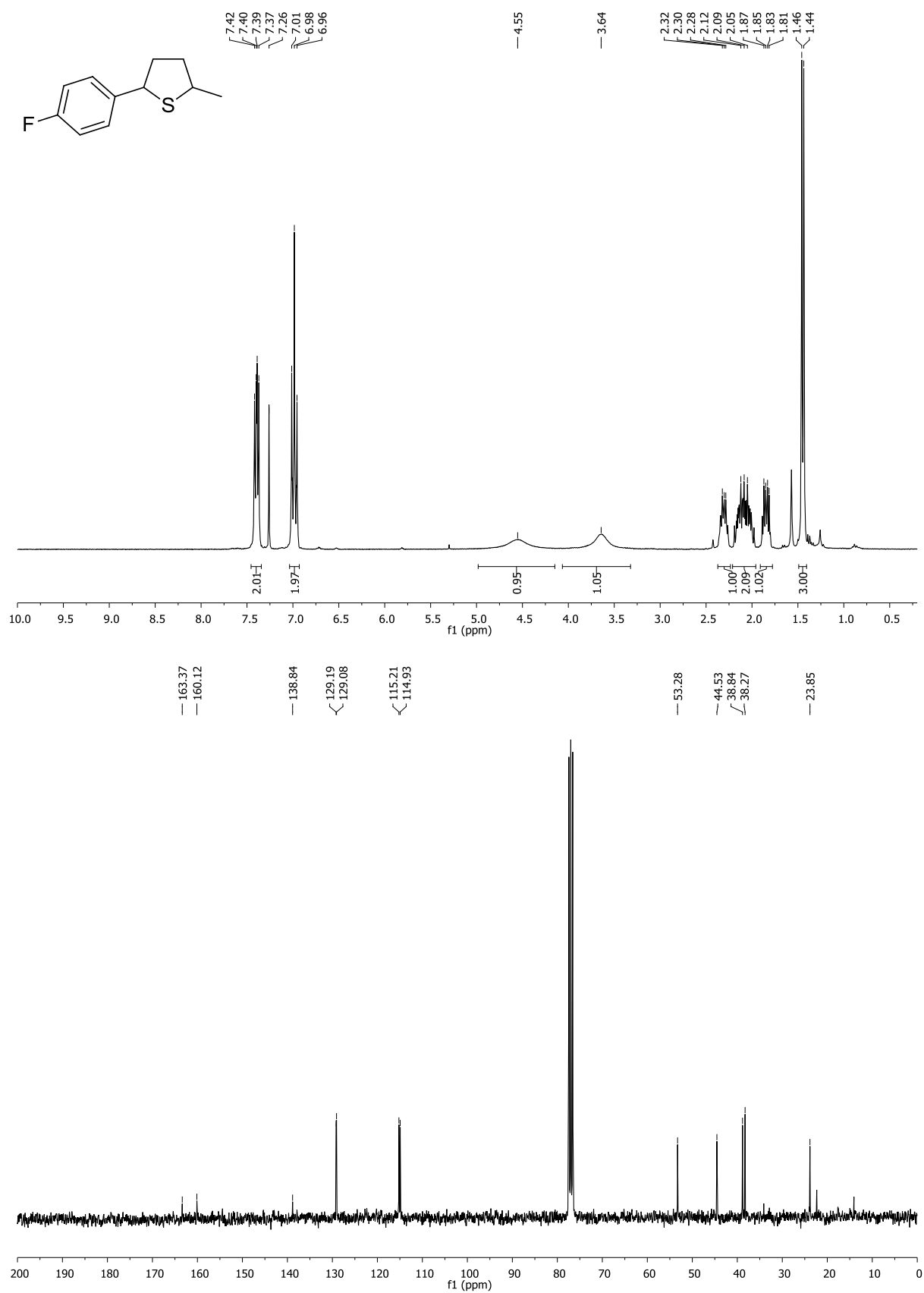
2-(4-Fluorophenyl)-tetrahydrothiophene (4d)



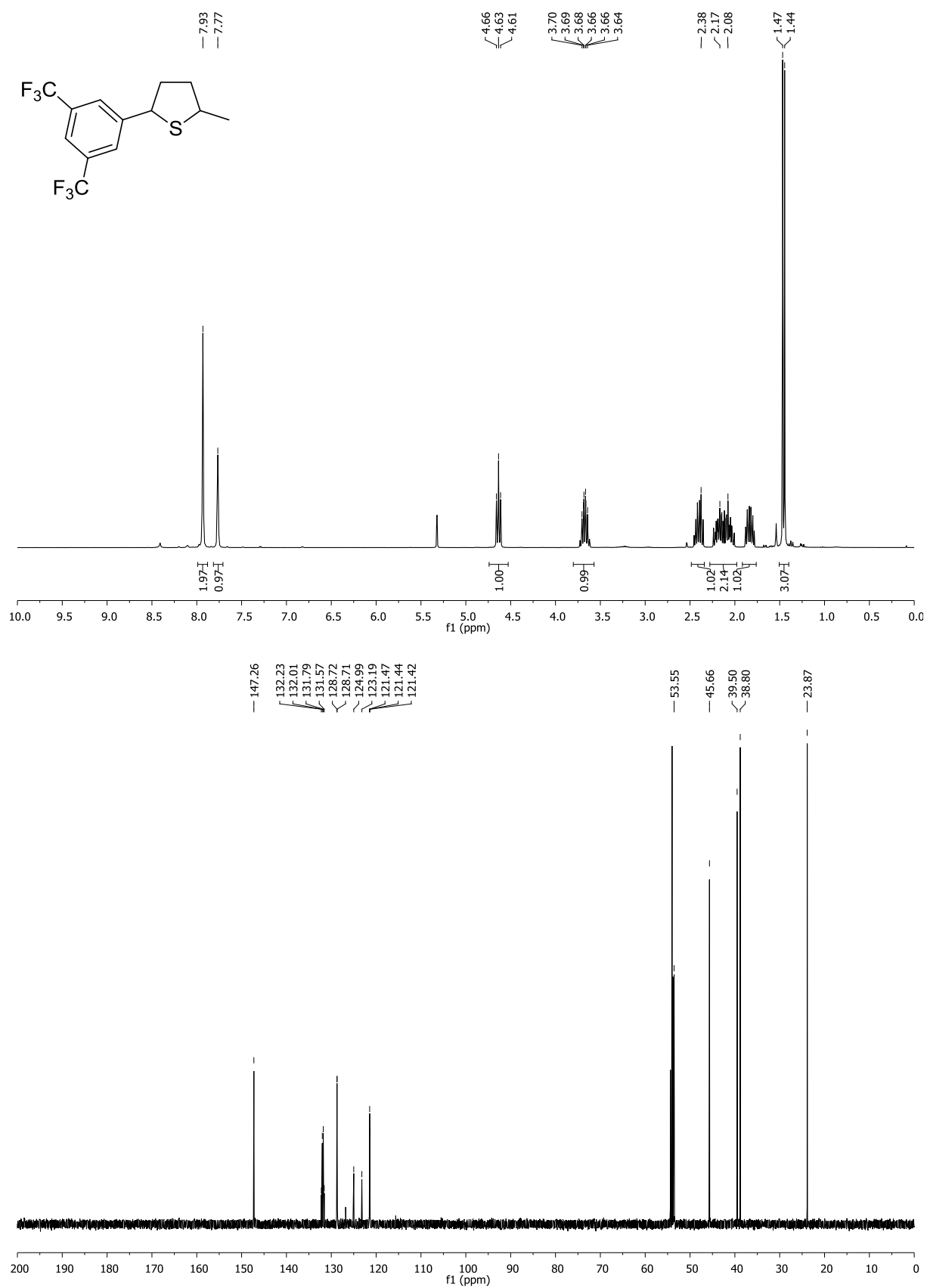
2-Methyl-5-phenyl-tetrahydrothiophene (4e)



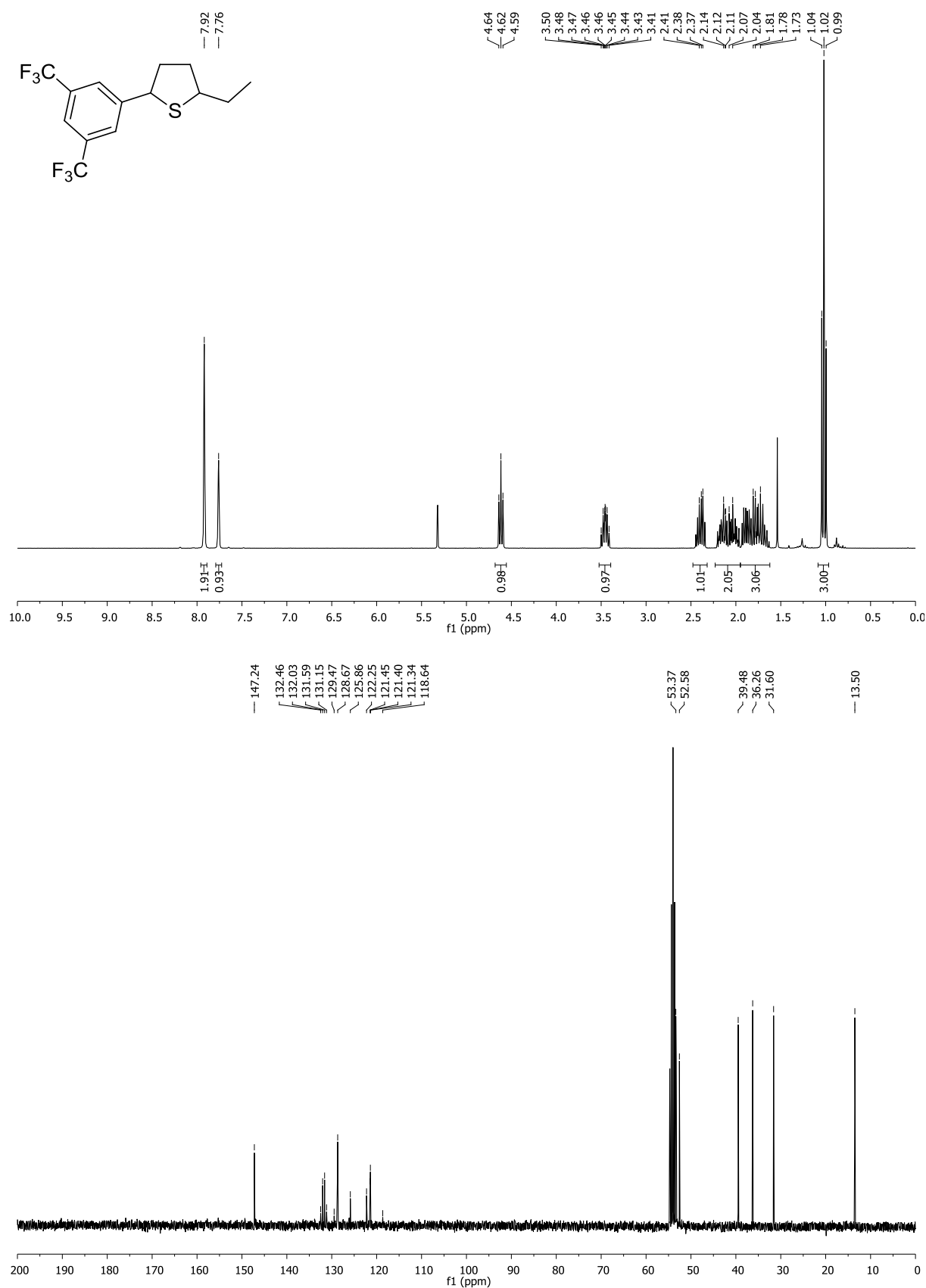
2-(4-Fluorophenyl)-5-methyl-tetrahydrothiophene (4f)



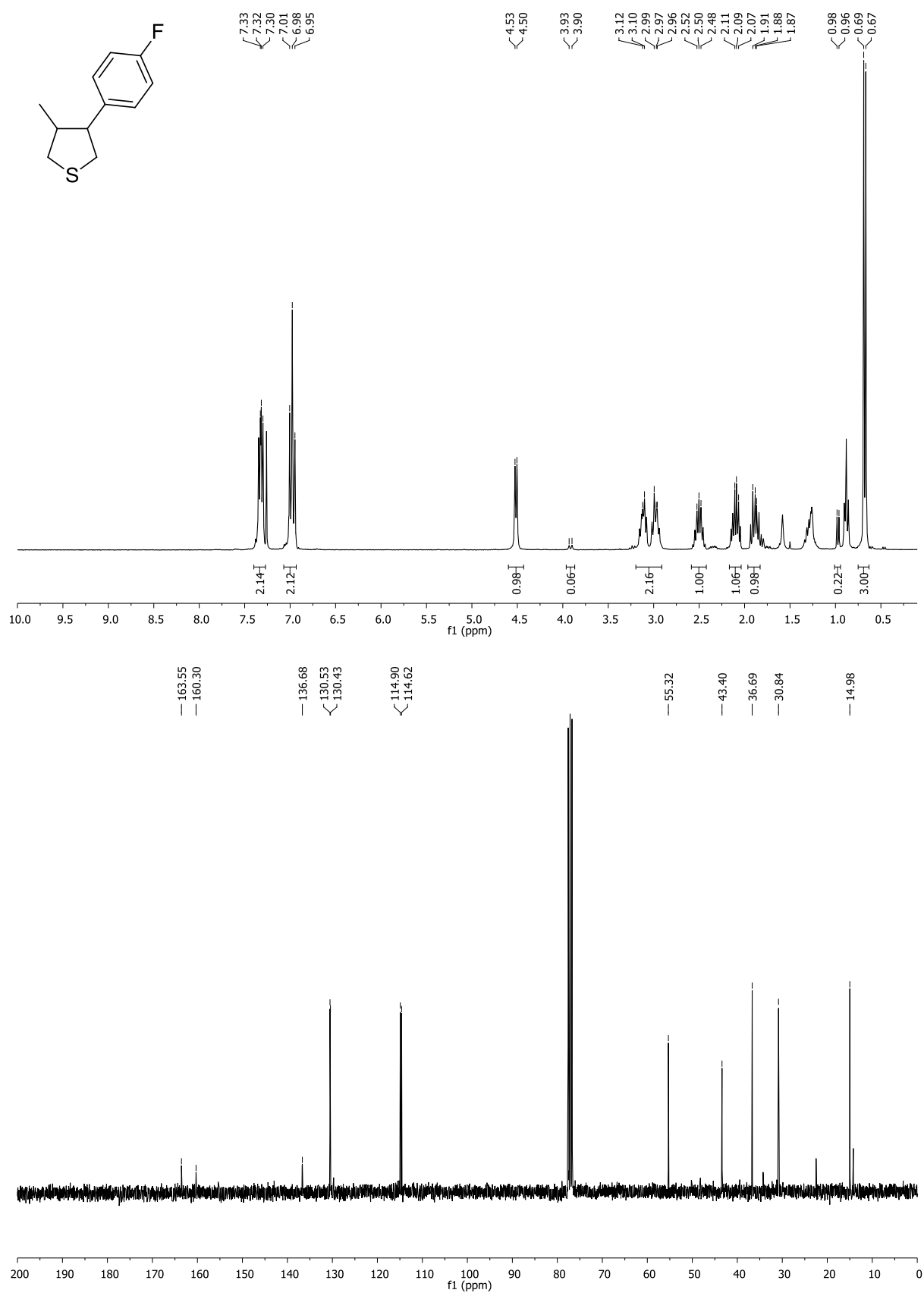
2-(3,5-Bis(trifluoromethyl)phenyl)-5-methyl-tetrahydrothiophene (4g)



2-(3,5-Bis(trifluoromethyl)phenyl)-5-ethyl-tetrahydrothiophene (4h)



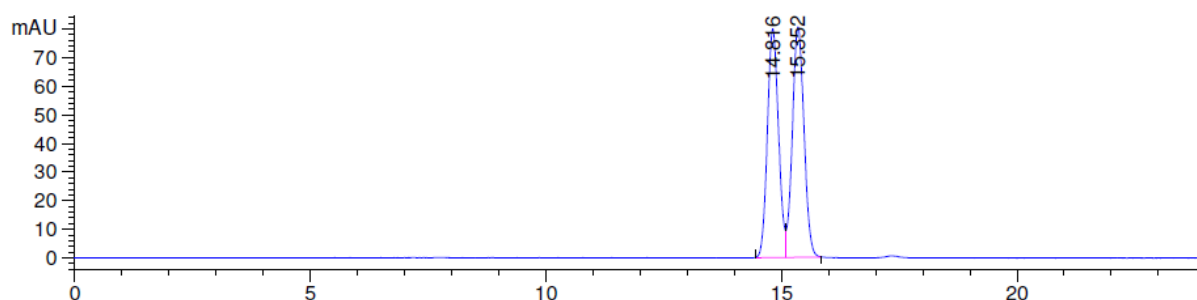
3-(4-Fluorophenyl)-4-methyl-tetrahydrothiophene (4i)



8 HPLC traces

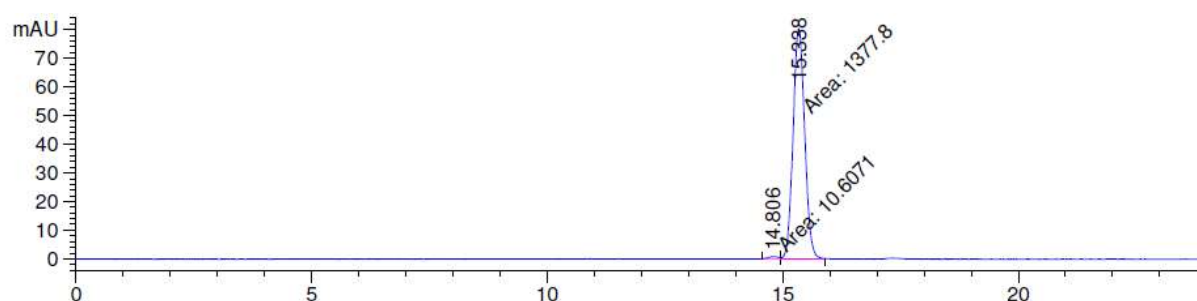
The racemic products were obtained, running the hydrogenation reactions with the achiral imidazolium salt ICy·HCl.

2-Methyl-2,3-dihydrobenzo[*b*]thiophene (2b)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.816	BV	0.2551	1308.81201	79.91222	48.6149
2	15.352	VB	0.2684	1383.38928	80.53651	51.3851

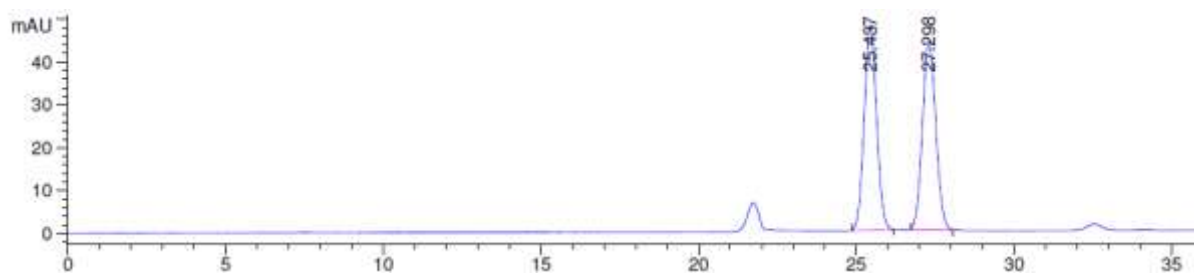
Totals : 2692.20129 160.44873



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.806	MM	0.2340	10.60707	7.55475e-1	0.7640
2	15.338	MM	0.2861	1377.80249	80.26729	99.2360

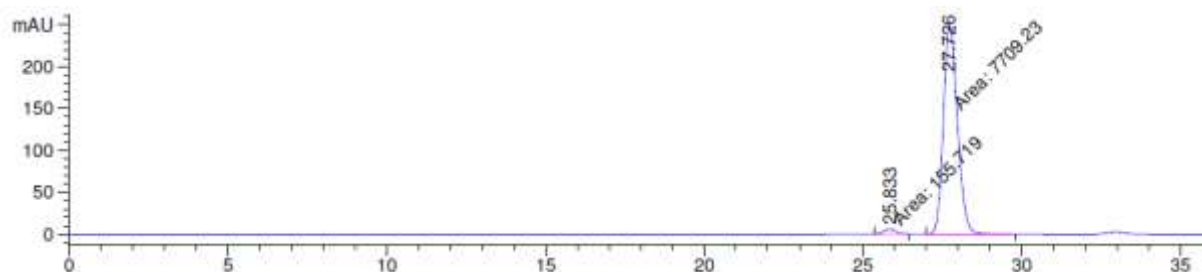
Totals : 1388.40956 81.02276

2-Ethyl-2,3-dihydrobenzo[b]thiophene (2c)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.437	BB	0.4209	1307.22205	47.67954	49.9742
2	27.298	BB	0.4338	1308.57068	44.14630	50.0258

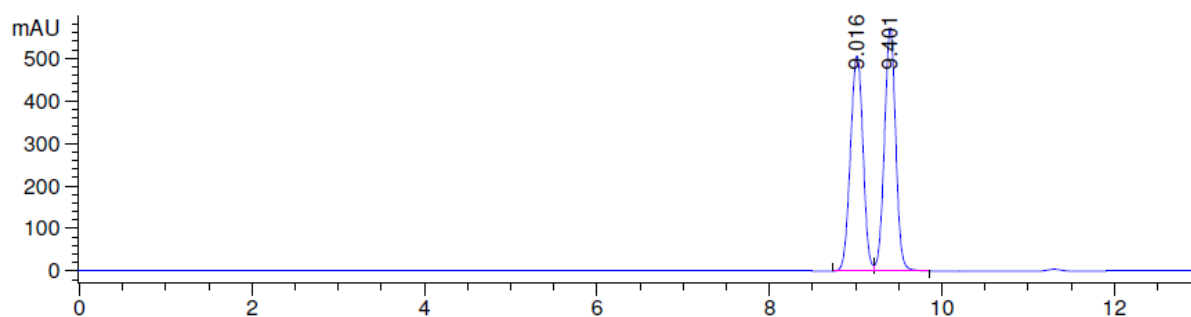
Totals : 2615.79272 91.82584



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.833	MM	0.4433	155.71877	5.85401	1.9799
2	27.726	MM	0.5153	7709.23193	249.32269	98.0201

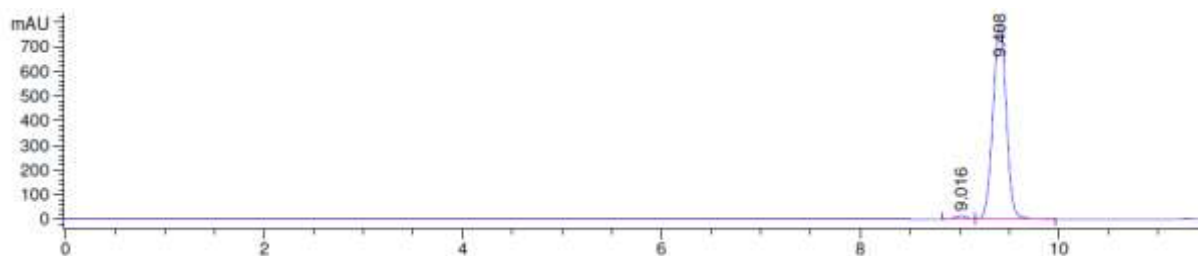
Totals : 7864.95070 255.17670

2-Propyl-2,3-dihydrobenzo[*b*]thiophene (2d)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.016	BV	0.1610	5110.24561	505.21826	49.6747
2	9.401	VB	0.1409	5177.16553	570.44165	50.3253

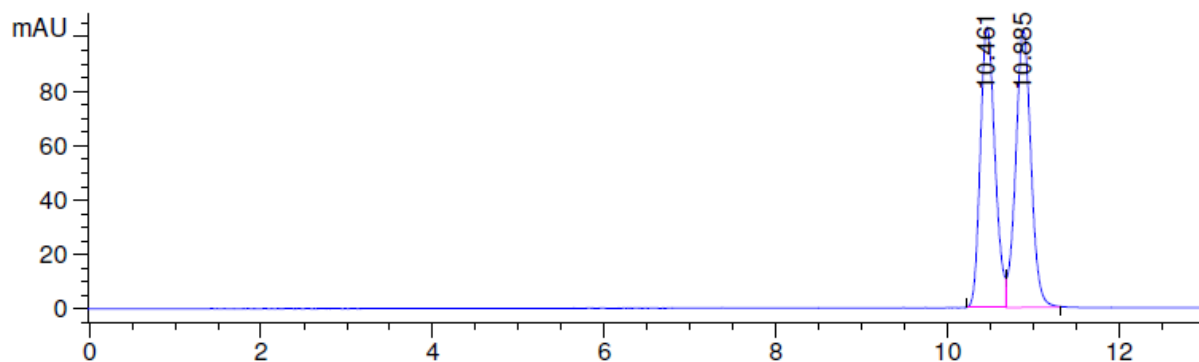
Totals : 1.02874e4 1075.65991



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.016	BV	0.1353	117.18853	13.23565	1.5635
2	9.408	VB	0.1455	7377.84814	792.98419	98.4365

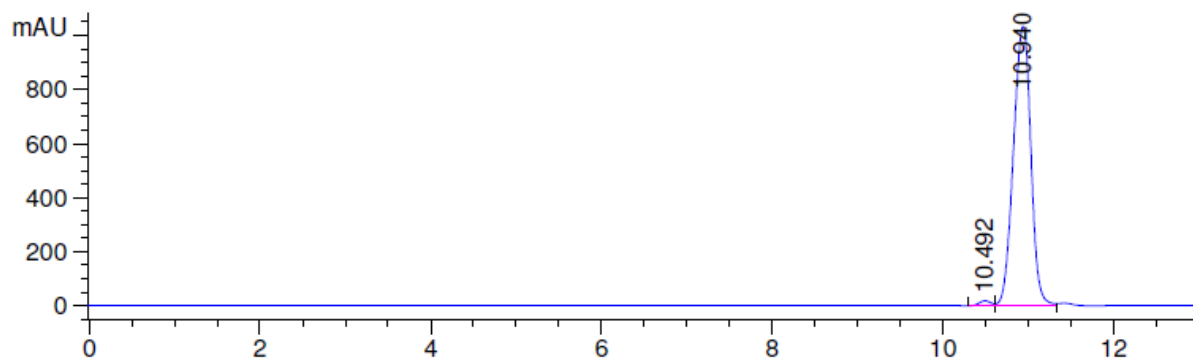
Totals : 7495.03667 806.21984

2-Butyl-2,3-dihydrobenzo[*b*]thiophene (2e)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.461	BV	0.1850	1219.65125	103.09299	49.1645
2	10.885	VB	0.1904	1261.10645	101.86798	50.8355

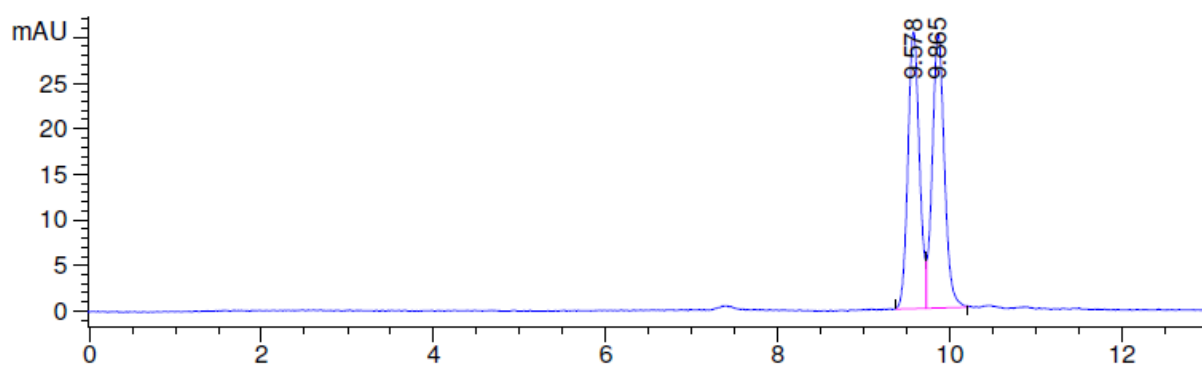
Totals : 2480.75769 204.96097



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.492	BV	0.1485	174.47749	18.09382	1.1780
2	10.940	VV	0.2255	1.46369e4	1031.68530	98.8220

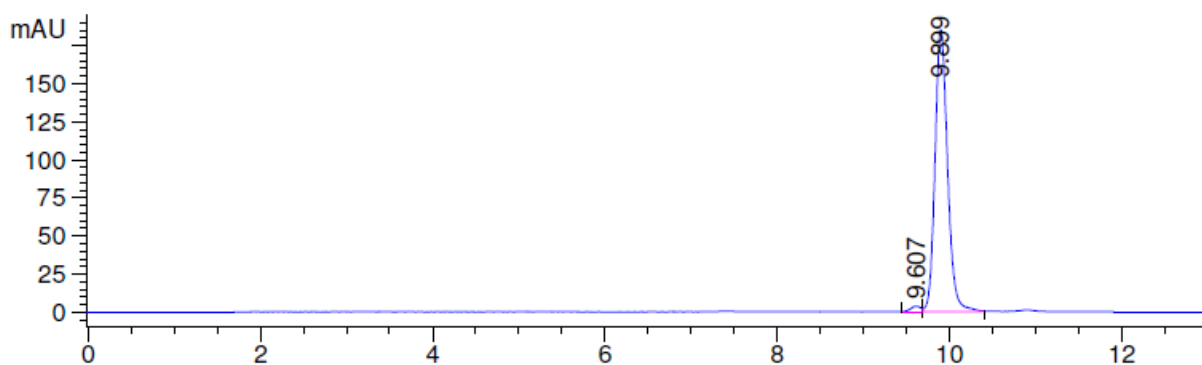
Totals : 1.48114e4 1049.77912

2-Decyl-2,3-dihydrobenzo[*b*]thiophene (2f)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.578	BV	0.1448	280.49881	30.36077	48.7192
2	9.865	VB	0.1496	295.24707	30.06149	51.2808

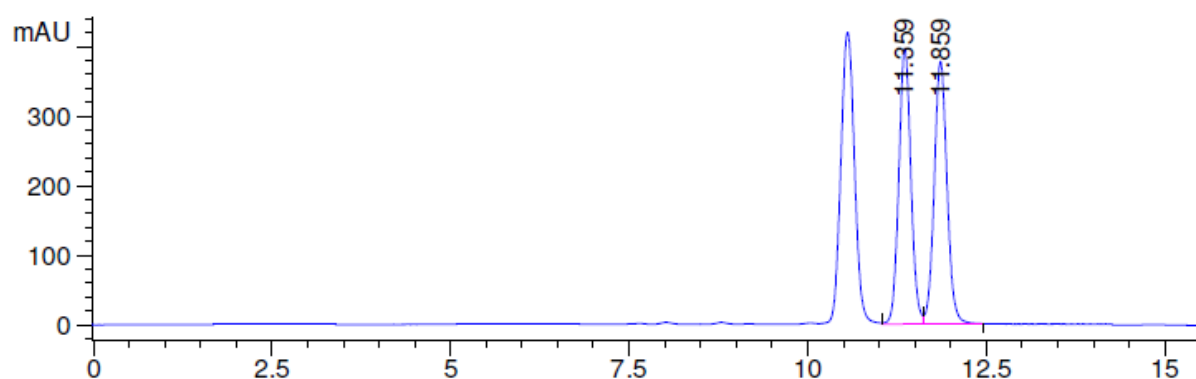
Totals : 575.74588 60.42226



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.607	BV	0.1219	29.68814	3.57280	1.5575
2	9.899	VB	0.1551	1876.47986	185.32983	98.4425

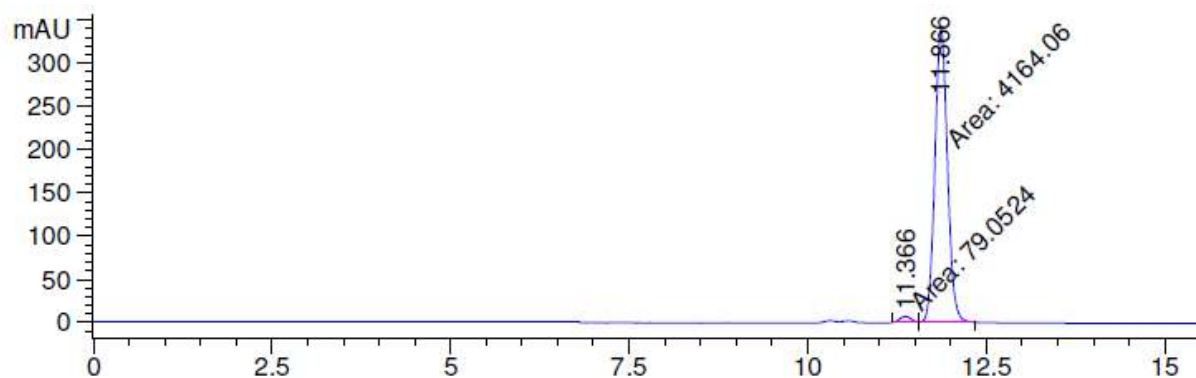
Totals : 1906.16800 188.90264

2-Isobutyl-2,3-dihydrobenzo[b]thiophene (2g)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.359	VV	0.1812	4658.54980	396.23260	49.6707
2	11.859	VB	0.1939	4720.31152	377.34698	50.3293

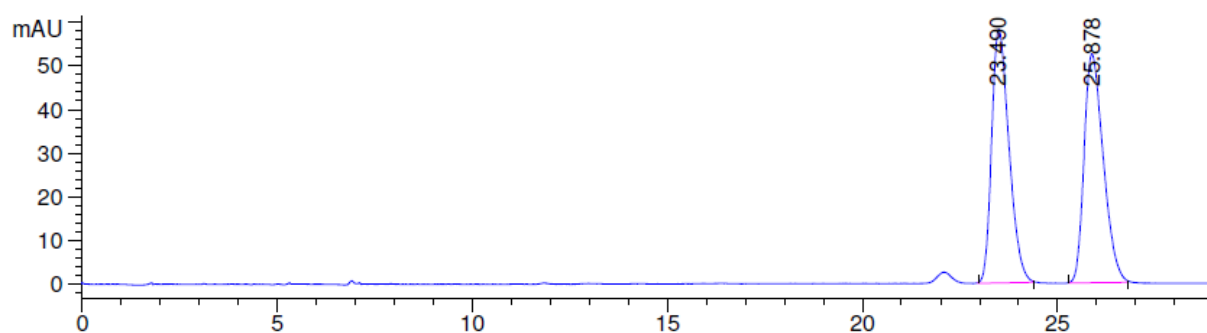
Totals : 9378.86133 773.57959



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.366	MM	0.1877	79.05241	7.02086	1.8631
2	11.866	MM	0.2049	4164.06250	338.70572	98.1369

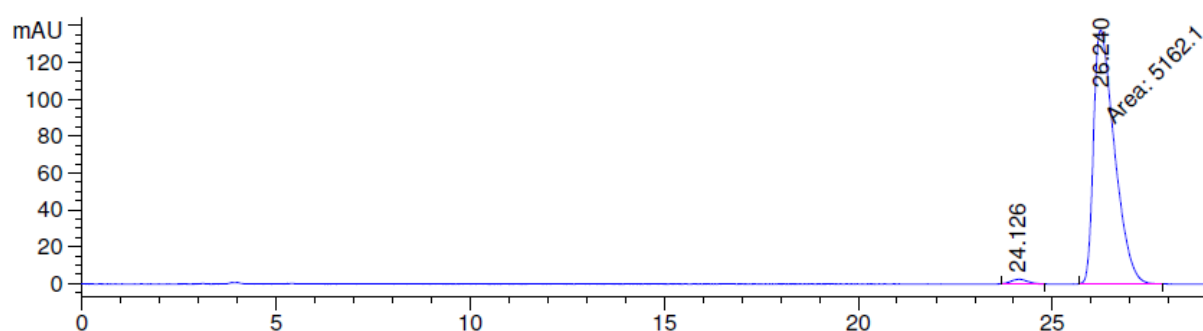
Totals : 4243.11491 345.72658

2-Benzyl-2,3-dihydrobenzo[*b*]thiophene (2h)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.490	BB	0.4610	1794.04651	57.98209	50.0494
2	25.878	BB	0.4984	1790.50623	52.30663	49.9506

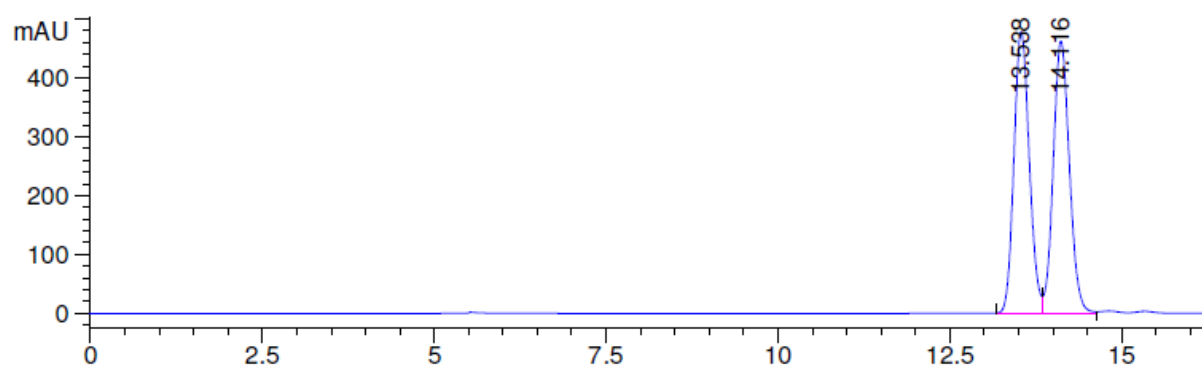
Totals : 3584.55273 110.28872



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.126	BB	0.3536	72.79885	2.44322	1.3906
2	26.240	MM	0.6247	5162.10352	137.71411	98.6094

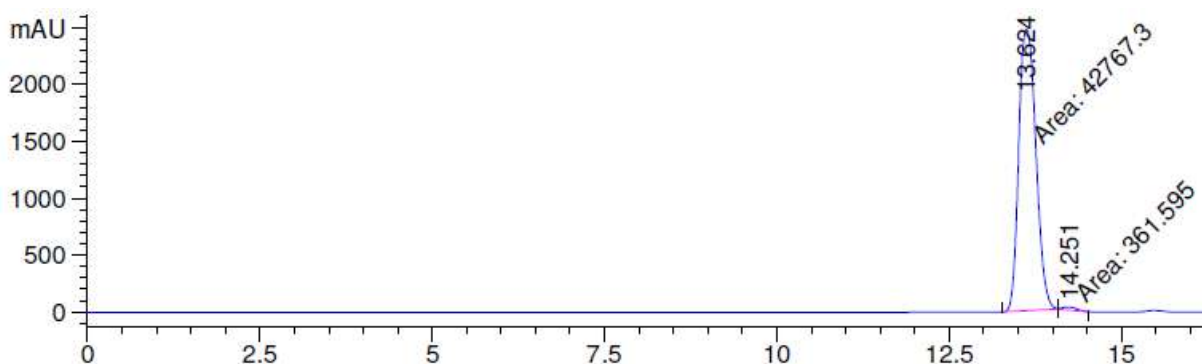
Totals : 5234.90237 140.15733

3-Methyl-2,3-dihydrobenzo[*b*]thiophene (2i)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.538	BV	0.2422	7433.65723	478.66443	49.5489
2	14.116	VB	0.2538	7569.00879	462.73083	50.4511

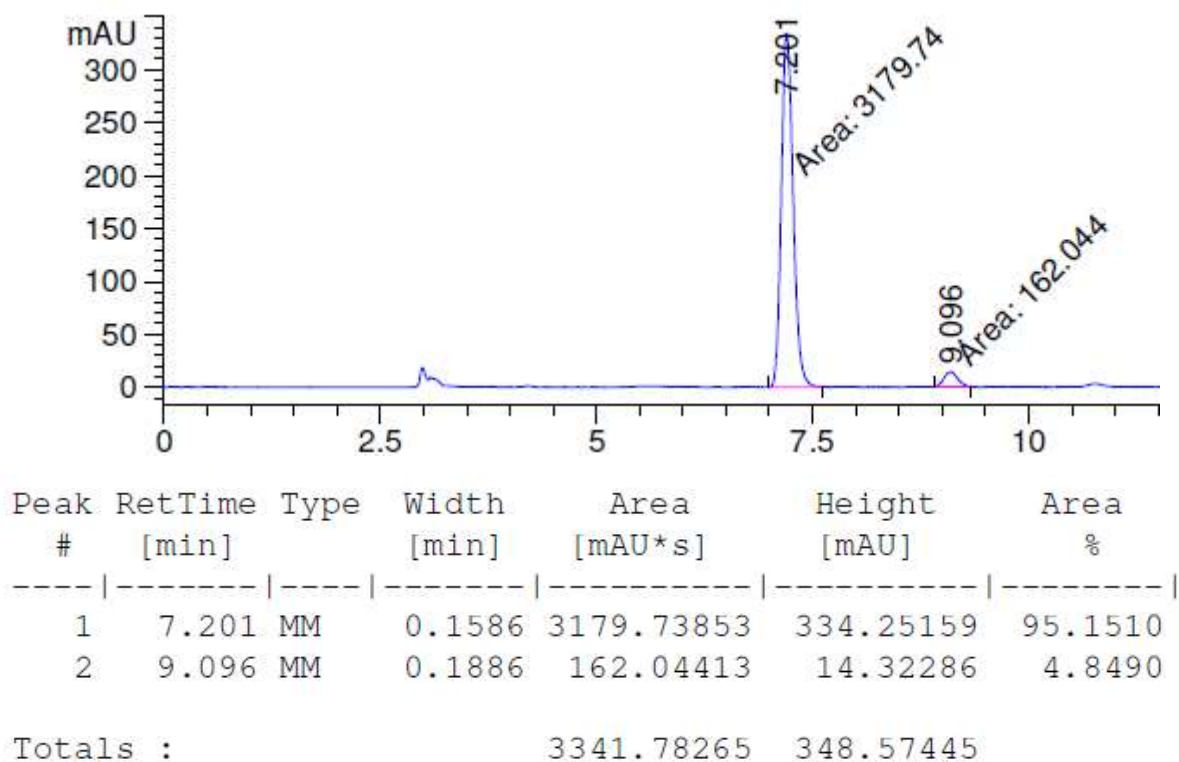
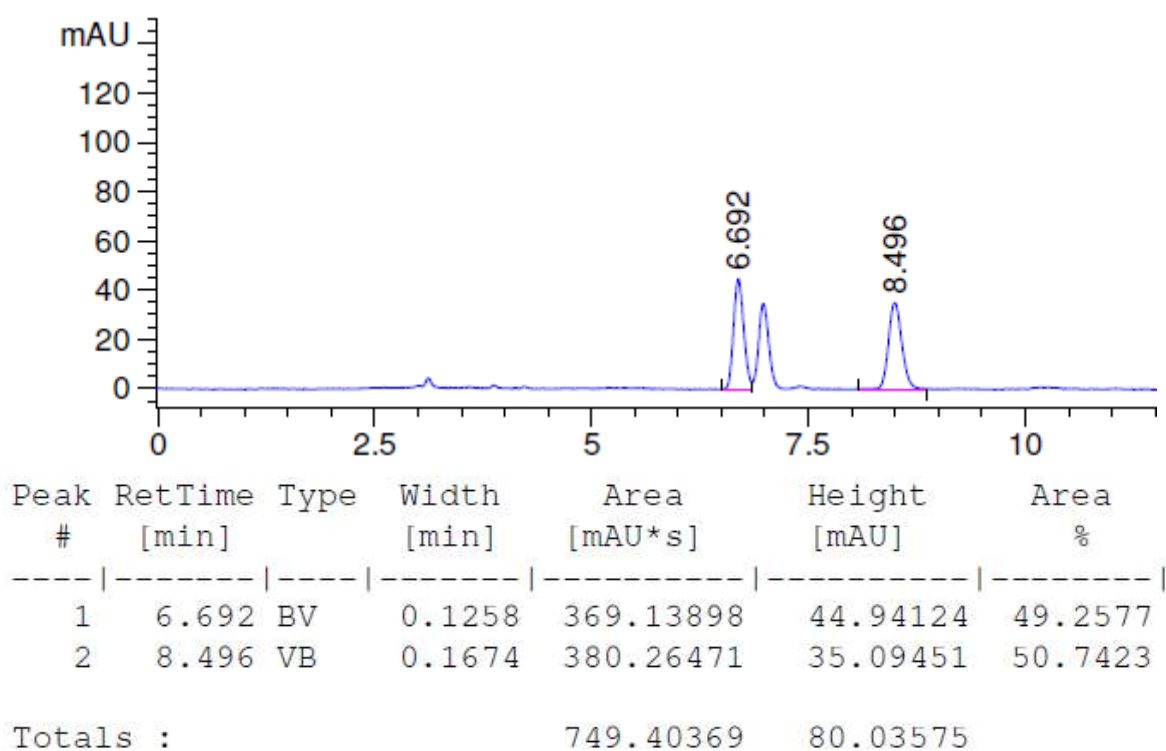
Totals : 1.50027e4 941.39526



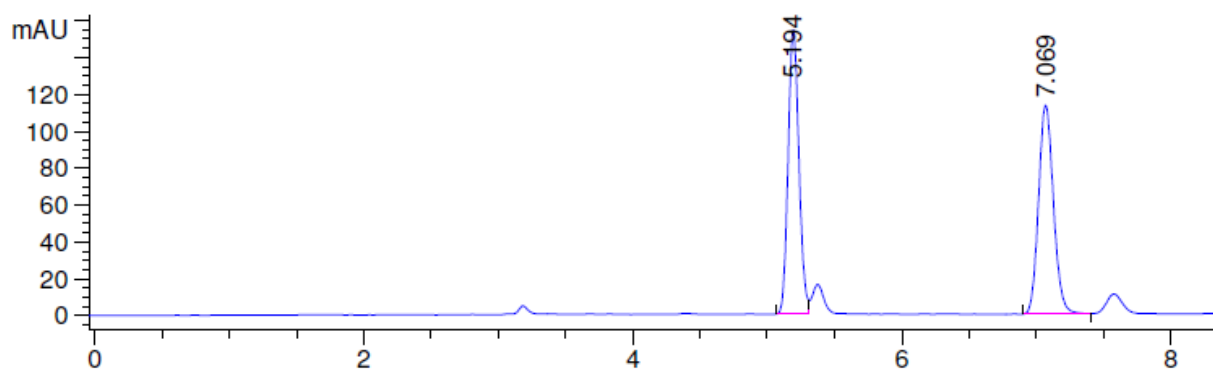
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.624	MM	0.2887	4.27673e4	2469.34814	99.1616
2	14.251	MM	0.2265	361.59454	26.60483	0.8384

Totals : 4.31289e4 2495.95297

2-Methyl-5-phenyl-tetrahydrothiophene (4e)

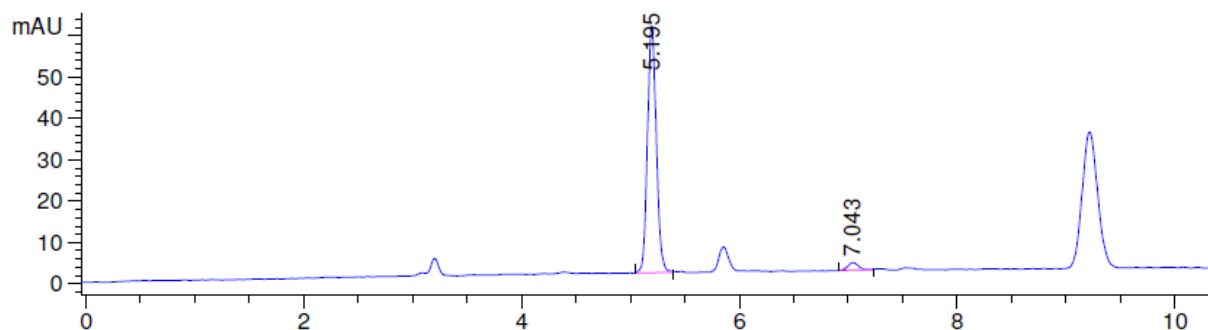


2-(4-Fluorophenyl)-5-methyl-tetrahydrothiophene (4f)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.194	BV	0.0871	861.05109	154.29105	49.6224
2	7.069	BB	0.1179	874.15576	113.40108	50.3776

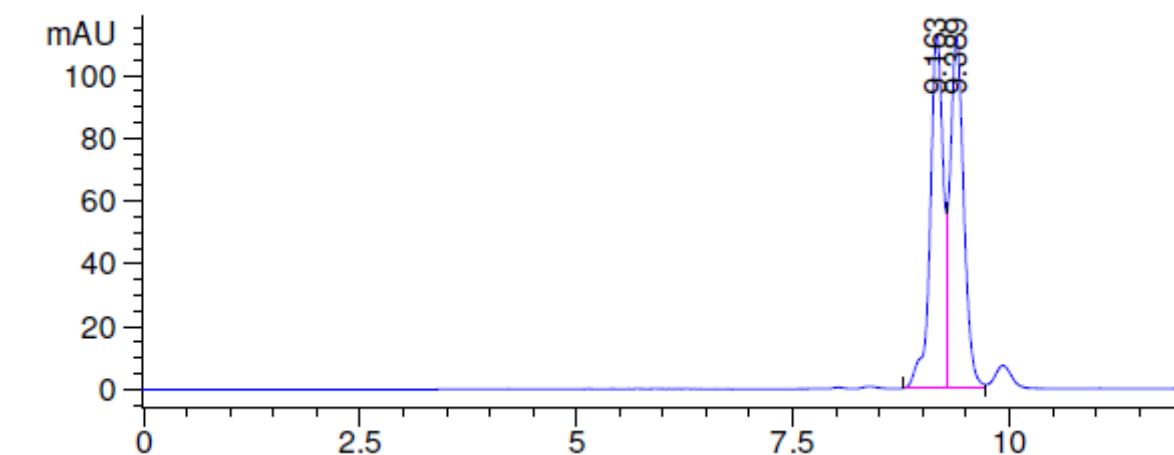
Totals : 1735.20685 267.69213



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.195	BB	0.0859	337.68454	59.81295	96.4536
2	7.043	BB	0.1071	12.41590	1.83162	3.5464

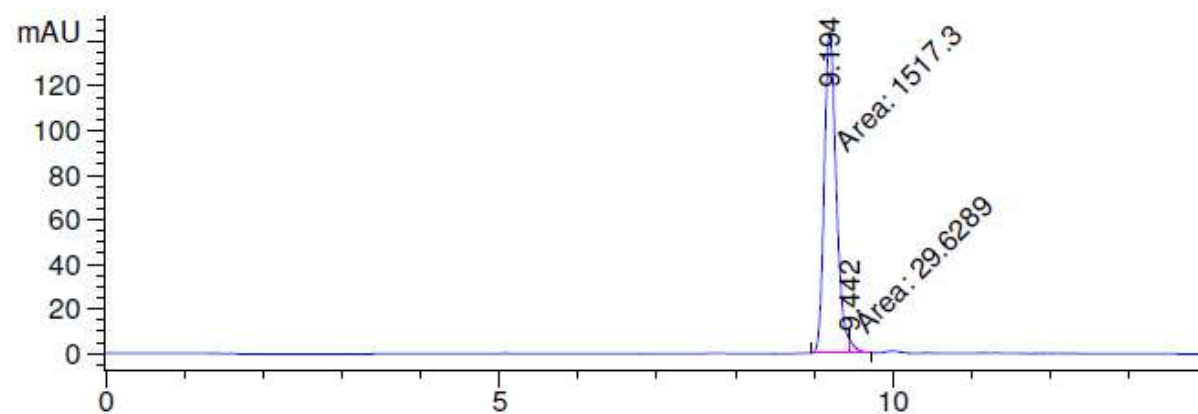
Totals : 350.10044 61.64457

2-(3,5-Bis(trifluoromethyl)phenyl)-5-methyl-tetrahydrothiophene (4g)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.163	BV	0.1581	1181.98877	112.89834	48.7280
2	9.389	VV	0.1678	1243.69592	111.76457	51.2720

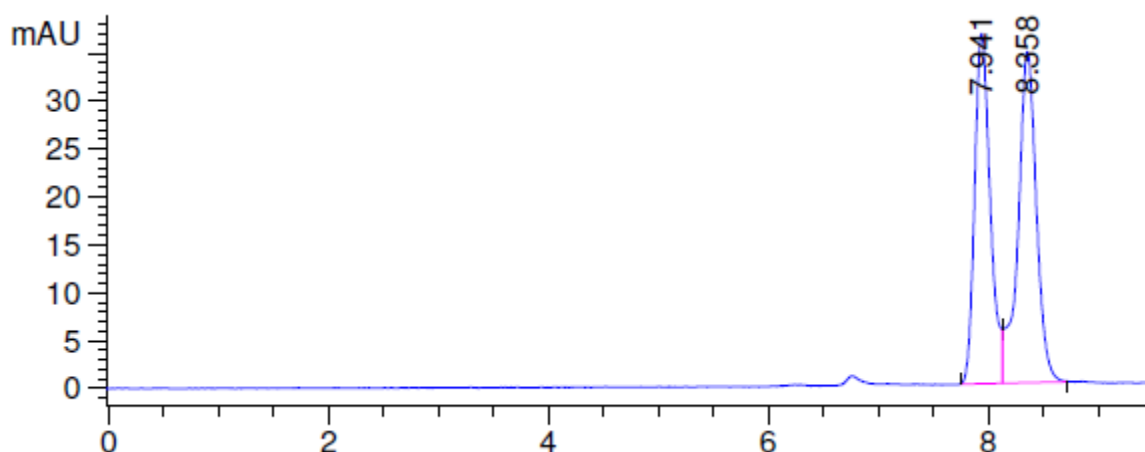
Totals : 2425.68469 224.66291



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.194	MF	0.1758	1517.29919	143.86662	98.0847
2	9.442	FM	0.0770	29.62889	6.41299	1.9153

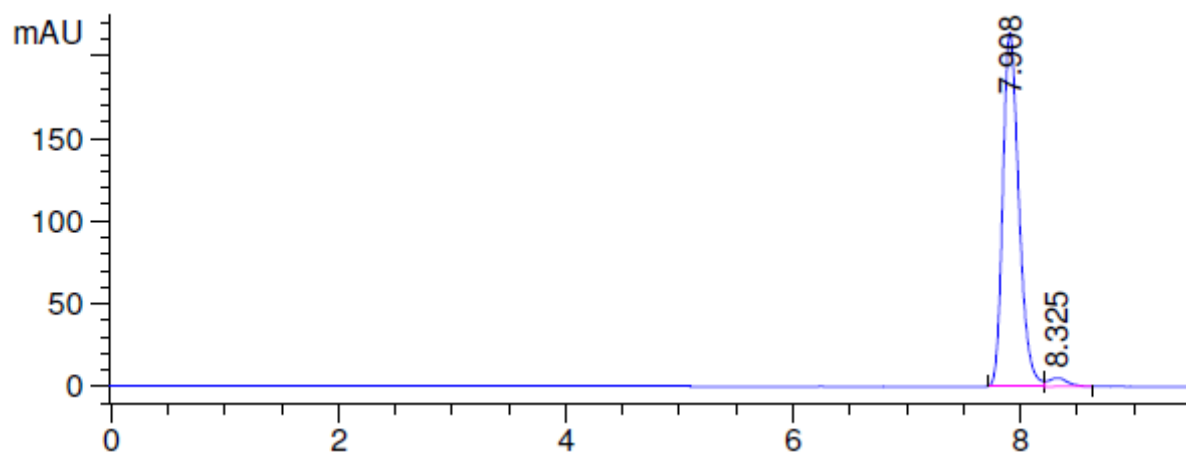
Totals : 1546.92808 150.27962

2-(3,5-Bis(trifluoromethyl)phenyl)-5-ethyl-tetrahydrothiophene (4h)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.941	BV	0.1519	359.89914	36.55708	47.1306
2	8.358	VB	0.1754	403.72223	34.53363	52.8694

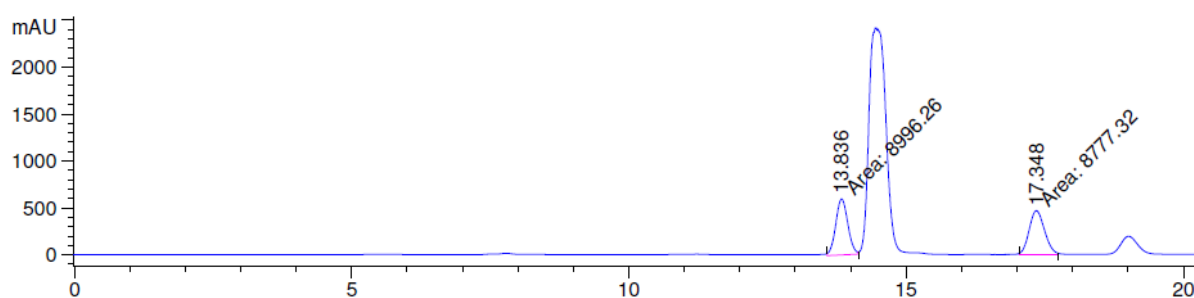
Totals : 763.62137 71.09071



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.908	BV	0.1514	2096.44873	213.75233	97.2152
2	8.325	VB	0.1732	60.05521	5.18200	2.7848

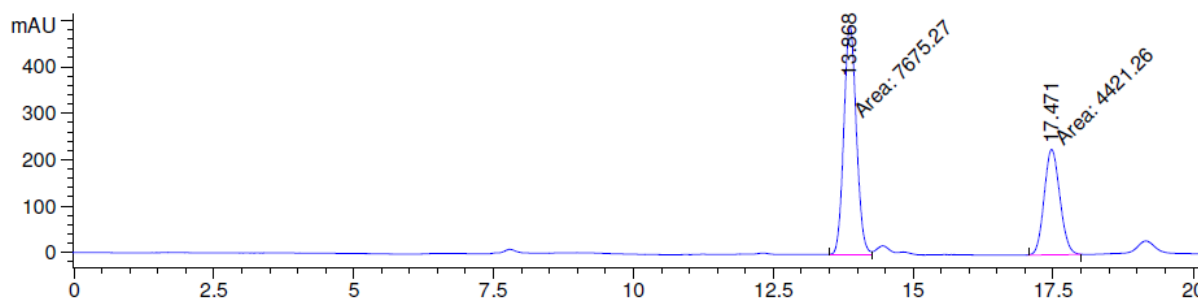
Totals : 2156.50394 218.93434

3-(4-Fluorophenyl)-4-methyl-tetrahydrothiophene (4i)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.836	MM	0.2516	8996.25781	595.84125	50.6159
2	17.348	MM	0.3164	8777.31543	462.41913	49.3841

Totals : 1.77736e4 1058.26038



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.868	MM	0.2592	7675.26807	493.45752	63.4502
2	17.471	MM	0.3248	4421.26221	226.85692	36.5498

Totals : 1.20965e4 720.31444