

Supporting Information

Regioselective Access to CF₃S-substituted Dihydrofurans from Homopropargylic Alcohols with Trifluoromethanesulfenamide

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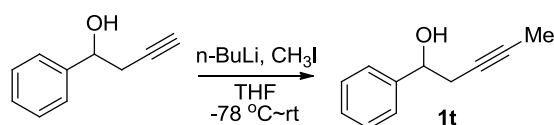
1. General remarks

Column chromatography was carried out on silica gel and analytical TLC was performed with silica gel GF254 plates. NMR spectra were recorded on a Bruker advance III 400 spectrometer in CDCl_3 at 400 MHz (^1H NMR), 100 MHz (^{13}C NMR), 376 MHz (^{19}F NMR). IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1} . Data collections for crystal structure were performed at room temperature (295 K). Melting points were determined on a microscopic apparatus and were uncorrected. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. All products were further characterized by high resolution mass spectra (HRMS). Copies of their ^1H NMR, ^{13}C NMR are provided.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Homopropargylic alcohols were prepared according to literature procedures.¹ CH_2Cl_2 was dried and distilled from CaH_2 . Room temperature is 27 °C.

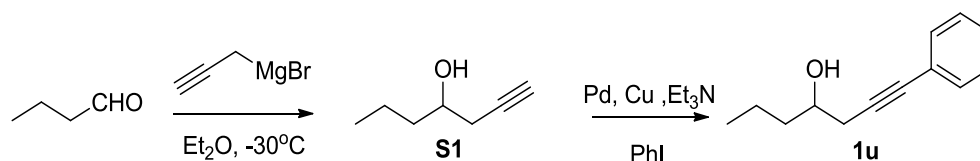
2. General procedure for the synthesis of 1t-1w:

1 1t were prepared in the method²:



$n\text{-BuLi}$ (2.5 M in hexanes, 6 mL, 15 mmol) was slowly added to a stirred solution of the propargyl alcohol (876 mg, 6 mmol) prepared in dry THF (20 mL) at $-78\text{ }^\circ\text{C}$ under Ar. After being stirred at $-78\text{ }^\circ\text{C}$ for 1 h, the reaction mixture was treated with CH_3I (1.12 mL, 18 mmol) and then allowed to warm to rt over night. The reaction mixture was then cooled to $-78\text{ }^\circ\text{C}$ again, quenched with sat. NH_4Cl (aq) (10 mL), and extracted with Et_2O (3 * 20 mL). The combined organic phases were dried over Na_2SO_4 , filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give **1t** as a yellow oil.

2 1u-1y were prepared in the same method³:



Under a argon atmosphere, magnesium turnings (0.67 g, 27.5 mmol) and mercury chloride (0.34 g,

1.3 mmol) were mixed in dry diethyl ether (40 mL) in a 250 mL round-bottom flask. To the solution, propargyl bromide (2.0 mL, 25 mmol) was then added dropwise at 60 °C over about 1 h. The reaction was kept at the same temperature until the yellow solution turned cloudy. This solution was cooled to -30 °C and a solution of butyraldehyde (6 mmol) in Et₂O (12 mL) was added dropwise. After addition the reaction was moved to room temperature for further 30 min then quenched with sat. NH₄Cl (aq). The aqueous layer was extracted with ether and the extracts were combined with the above organic layer. The combined solution was dried over Na₂SO₄. After evaporation of the solvent the residue was purified by column chromatography (silica gel, appropriate mixture of *n*-hexane/ethyl acetate) to afford **S1**.

To a dried schlenk flask was added **S1** (10.0 mmol), Pd(PPh₃)₂Cl₂ (0.2 mmol), CuI (0.4 mmol), iodoarene (11.0 mmol) and freshly distilled Et₃N (50 mL) under argon. The resulting mixture was stirred for 16 h at rt. The reaction mixture was quenched with sat. NH₄Cl (aq) and 50 mL of ethyl acetate were added and the mixture filtered. After removal of solvent using rotary evaporator, the crude compound was purified by column chromatography on silica gel to give **1u**.

3. General experimental procedure

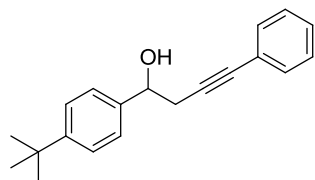
General procedure for synthesis of 4-((trifluoromethyl)thio)-2,3-dihydrofuran from homopropargylic alcohol: homopropargylic alcohol **1a** (44.4 mg, 0.2 mmol), *p*-toluenesulfonic acid (0.6 mmol), BiCl₃ (0.2 mmol) were successively added to a solution of trifluoromethanesulfenamide **2** (0.4 mmol) in CH₂Cl₂ (2.0 mL). The reactor was flushed with argon and sealed. The reaction mixture was stirring at 50 °C for 5 hour. The reaction mixture was quenched with 2 mL sat. NaHCO₃ (aq) and extracted with ethyl acetate (3 * 20 mL). The organic phases were combined and dried over sodium sulfate. The mixture was concentrated in vacuo and then purified by column chromatography on silica gel to afford **3a**.

Dehydrogenation of 2,5-diphenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (**3a**)⁴:

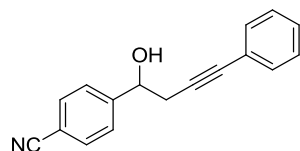
2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (59 mg, 0.26 mmol) was added to a solution of **3a** (64.4 mg, 0.2 mmol) in toluene (3 mL). The mixture was refluxed for 5 h and then cooled to r.t. The solution was hydrolyzed and neutralized with aq 5% NaOH solution. The organic phases

were extracted with ethyl acetate (3 * 15 mL) and the combined extracts were dried (Na₂SO₄). After evaporation of the solvent, the residue was purified by column chromatography on silica gel to give **4** (57.4 mg, 90 %) as a white solid.

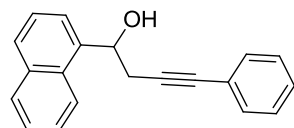
4. Characterization data of **1c**, **1f**, **1h-1k**, **1n**, **1s-1y**



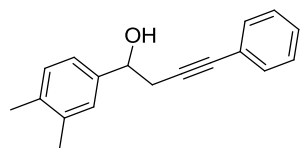
1-(4-(tert-butyl)phenyl)-4-phenylbut-3-yn-1-ol (1c): ¹H NMR (400 MHz, CDCl₃) δ 1.32 (s, 9H), 2.52 (d, *J* = 2.0 Hz, 1H), 2.84 (d, *J* = 6.4 Hz, 2H), 4.89-4.93 (m, 1H), 7.27 (t, *J* = 3.2 Hz, 3H), 7.34-7.40 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 139.7, 131.6, 128.2, 127.9, 125.5, 125.3, 123.3, 86.3, 83.0, 72.4, 34.5, 31.3, 30.4.



1-(4-cyanophenyl)-4-phenylbut-3-yn-1-ol (1f): ¹H NMR (400 MHz, CDCl₃) δ 2.64 (d, *J* = 4.0 Hz, 1H), 2.80-2.92 (m, 2H), 4.99-5.03 (m, 1H), 7.28-7.32 (m, 3H), 7.35-7.38 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 147.8, 132.2, 131.6, 128.3, 128.3, 126.6, 122.8, 118.7, 111.6, 84.6, 83.9, 71.8, 30.5.

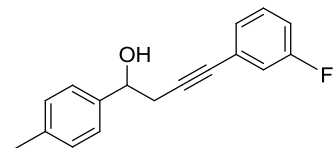


1-(naphthalen-1-yl)-4-phenylbut-3-yn-1-ol (1h): ¹H NMR (400 MHz, CDCl₃) δ 2.65 (d, *J* = 3.6 Hz, 1H), 2.94-3.14 (m, 2H), 5.72-5.76 (m, 1H), 7.28-7.30 (m, 3H), 7.37-7.40 (m, 2H), 7.48-7.56 (m, 3H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.88-7.90 (m, 1H), 8.12 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.0, 133.7, 131.7, 130.2, 129.0, 128.4, 128.2, 128.0, 126.2, 125.6, 125.4, 123.2, 123.0, 122.9, 86.2, 83.5, 69.4, 29.8.

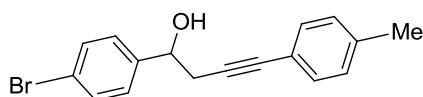


1-(3,4-dimethylphenyl)-4-phenylbut-3-yn-1-ol (1i): ¹H NMR (400 MHz, CDCl₃) δ 2.26 (d, *J* =

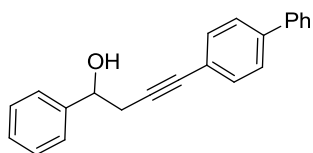
7.6 Hz, 6H), 2.42 (s, 1H), 2.83 (d, $J = 6.4$ Hz, 2H), 4.88 (t, $J = 6.4$ Hz, 1H), 7.11-7.16 (m, 2H), 7.20 (s, 1H), 7.27-7.29 (m, 3H), 7.37-7.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.2, 136.6, 136.2, 131.6, 129.6, 128.2, 127.9, 127.0, 123.3, 123.2, 86.3, 83.1, 72.5, 30.6, 19.8, 19.4.



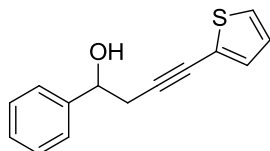
4-(3-fluorophenyl)-1-(p-tolyl)but-3-yn-1-ol (1j): ^1H NMR (400 MHz, CDCl_3) δ 2.34-2.37 (m, 4H), 2.84 (d, $J = 6.0$ Hz, 2H), 4.90-4.94 (m, 1H), 6.96-7.01 (m, 1H), 7.07 (d, $J = 9.6$ Hz, 1H), 7.15-7.23 (m, 4H), 7.32 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.3 (d, $J = 245$ Hz), 139.7, 137.7, 129.7 (d, $J = 8.0$ Hz), 129.1, 127.5 (d, $J = 2.0$ Hz), 125.7, 125.6 (d, $J = 92.0$ Hz), 118.4 (d, $J = 22.0$ Hz), 115.3 (d, $J = 21.0$ Hz), 87.3, 81.8 (d, $J = 2.0$ Hz), 72.4, 30.4, 21.1; ^{19}F NMR (376 MHz, CDCl_3) δ -113.1 (d, $J = 3.8$ Hz).



1-(4-bromophenyl)-4-(p-tolyl)but-3-yn-1-ol (1k): ^1H NMR (400 MHz, CDCl_3) δ 2.34 (s, 3H), 2.46 (d, $J = 3.6$ Hz, 1H), 2.76-2.87 (m, 2H), 4.88-4.92 (m, 1H), 7.10 (d, $J = 7.6$ Hz, 2H), 7.26-7.28 (m, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.7, 138.2, 131.5 (d, $J = 4.0$ Hz), 129.0, 127.5, 121.6, 119.9, 84.5, 83.6, 71.9, 30.6, 21.4.

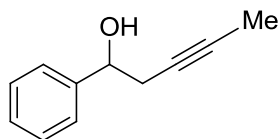


4-([1,1'-biphenyl]-4-yl)-1-phenylbut-3-yn-1-ol (1n): ^1H NMR (400 MHz, CDCl_3) δ 2.52 (s, 1H), 2.87 (d, $J = 6.4$ Hz, 2H), 4.95 (t, $J = 6.4$ Hz, 1H), 7.29-7.34 (m, 2H), 7.35-7.40 (m, 3H), 7.42-7.45 (m, 5H), 7.50-7.52 (m, 2H), 7.55-7.57 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.7, 140.7, 140.3, 132.0, 128.8, 128.4, 127.9, 127.5, 127.0, 126.9, 125.8, 122.1, 86.7, 83.0, 72.6, 30.6.

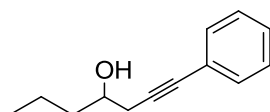


1-phenyl-4-(thiophen-2-yl)but-3-yn-1-ol (1s): ^1H NMR (400 MHz, CDCl_3) δ 2.63 (s, 1H), 2.83 (d, $J = 6.4$ Hz, 2H), 4.89 (t, $J = 6.4$ Hz, 1H), 6.89-6.92 (m, 1H), 7.11-7.21 (m, 1H), 7.15-7.16 (m,

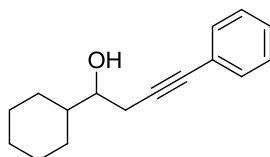
1H), 7.26-7.30 (m, 1H), 7.32-7.36 (m, 2H), 7.38-7.40 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 131.5, 128.4, 127.9, 126.7, 126.4, 125.7, 123.3, 90.2, 76.2, 72.4, 30.7.



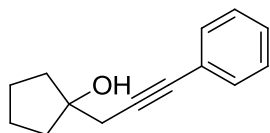
1-phenylpent-3-yn-1-ol (1t): ¹H NMR (400 MHz, CDCl₃) δ 1.77 (t, *J* = 2.4 Hz, 3H), 2.51-2.56 (m, 2H), 2.69 (s, 1H), 4.74-4.77 (m, 1H), 7.23-7.28 (m, 1H), 7.30-7.36 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 142.8, 128.2, 127.6, 125.6, 78.5, 75.2, 72.5, 29.8, 3.4.



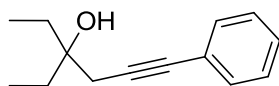
phenylhept-1-yn-4-ol (1u): ¹H NMR (400 MHz, CDCl₃) δ 0.95 (t, *J* = 7.2 Hz, 3H), 1.35-1.60 (m, 4H), 2.14 (s, 1H), 2.51-2.67 (m, 2H), 3.84 (t, *J* = 5.6 Hz, 1H), 7.27-7.29 (m, 3H), 7.40-7.42 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 131.6, 128.2, 127.8, 123.4, 86.2, 82.9, 69.9, 38.5, 28.3, 18.8, 14.0.



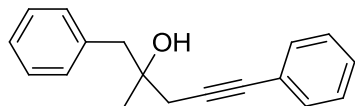
1-cyclohexyl-4-phenylbut-3-yn-1-ol (1v): ¹H NMR (400 MHz, CDCl₃) δ 0.98-1.11 (m, 2H), 1.12-1.32 (m, 3H), 1.46-1.55 (m, 1H), 1.65-1.78 (m, 4H), 1.91-1.94 (m, 1H), 2.21 (m, 1H), 2.56 (dd, *J*₁ = 16.8 Hz, *J*₂ = 7.4 Hz, 1H), 2.66 (dd, *J*₁ = 16.8 Hz, *J*₂ = 4.4 Hz, 1H), 3.54-3.58 (m, 1H), 7.25-7.28 (m, 3H), 7.38-7.43 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 131.5, 128.1, 127.7, 123.4, 86.6, 82.7, 74.1, 42.5, 29.0, 28.0, 26.3, 26.1, 25.9, 25.5.



1-(3-phenylprop-2-yn-1-yl)cyclopentanol (1w): ¹H NMR (400 MHz, CDCl₃) δ 1.67-1.87 (m, 8H), 2.00 (s, 1H), 2.71 (s, 2H), 7.29 (t, *J* = 3.2 Hz, 3H), 7.40-7.43 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 131.6, 128.2, 127.8, 123.4, 86.8, 82.5, 81.2, 39.2, 32.4, 24.1.

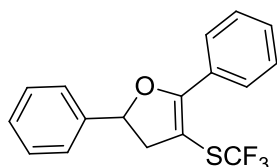


3-ethyl-6-phenylhex-5-yn-3-ol (1x): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 0.93 (t, J = 7.6 Hz, 6H), 1.57-1.72 (m, 4H), 1.80 (s, 1H), 2.57 (s, 2H), 7.27-7.28 (m, 3H), 7.40-7.42 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 131.6, 128.2, 127.8, 123.5, 86.2, 83.2, 74.1, 30.8, 30.2, 7.9.

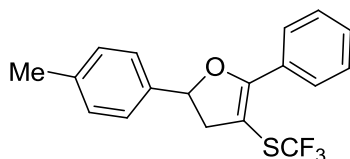


2-methyl-1,5-diphenylpent-4-yn-2-ol (1y): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.33 (s, 3H), δ 1.94 (s, 1H), 2.53 (dd, J_1 = 24.0 Hz, J_2 = 16.8 Hz, 2H), 2.94 (q, J_1 = 13.6 Hz, 2H), 7.23-7.34 (m, 8H), 7.43-7.46 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 137.1, 131.6, 130.4, 128.3, 128.2, 127.9, 126.6, 123.4, 86.4, 83.8, 72.4, 46.9, 32.7, 26.7.

5. Characterization data of 3a-3y, 3aa, 4

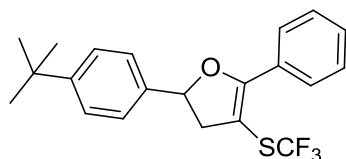


2,5-diphenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3a): Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.09 (dd, J_1 = 15.2 Hz, J_2 = 8.8 Hz, 1H), 3.54 (dd, J_1 = 15.2 Hz, J_2 = 10.8 Hz, 1H), 5.72 (dd, J_1 = 10.8 Hz, J_2 = 8.8 Hz, 1H), 7.31-7.35 (m, 1H), 7.37-7.43 (m, 7H), 7.91-7.93 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 162.3 (d, J = 1.0 Hz), 141.5, 130.2, 129.7 (q, J = 310.0 Hz), 129.1, 128.8, 128.3, 128.2, 125.7, 90.0 (d, J = 2.0 Hz), 81.9, 45.0; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -42.4; IR (thin film, cm^{-1}) 3361, 3064, 2925, 2371, 1599, 1493, 1448, 1330, 1236, 1124, 919, 770, 694; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{13}\text{F}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 323.0639, found: 323.0712.

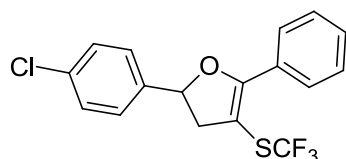


5-phenyl-2-(p-tolyl)-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3b): Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.36 (s, 3H), 3.08 (dd, J_1 = 15.2 Hz, J_2 = 8.8 Hz, 1H), 3.51 (dd, J_1 = 14.8 Hz, J_2 = 10.8 Hz, 1H), 5.70 (dd, J_1 = 10.4 Hz, J_2 = 8.8 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.39-7.41 (m, 3H), 7.90-7.92 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 162.3, 138.5, 138.1, 130.1, 129.7 (q, J = 310.0 Hz), 129.4, 129.2, 128.3, 128.1, 125.7, 89.8, 81.9, 44.9, 21.2; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -42.5; IR (thin film, cm^{-1}) 3373, 2925, 2372, 1901, 1768,

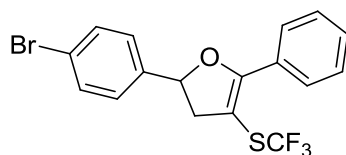
1598, 1492, 1331, 1236, 1123, 917, 816, 770, 692; HRMS (ESI) m/z calcd for $C_{18}H_{15}F_3OS$ $[M+H]^+$: 337.0796, found: 337.0868.



2-(4-(tert-butyl)phenyl)-5-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3c): Pale yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 3.12 (dd, $J_1 = 15.2$ Hz, $J_2 = 8.8$ Hz, 1H), 3.51 (dd, $J_1 = 15.2$ Hz, $J_2 = 10.8$ Hz, 1H), 5.70 (t, $J = 9.6$ Hz, 1H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.39-7.43 (m, 5H), 7.90-7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 151.4, 138.4, 130.1, 129.7 (q, $J = 310.0$ Hz), 129.2, 128.3, 128.2, 125.7, 125.6, 89.9 (d, $J = 2.0$ Hz), 81.9, 44.8, 34.6, 31.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.4; IR (thin film, cm^{-1}) 3363, 2962, 2373, 1598, 1493, 1331, 1237, 1123, 913, 833, 770, 692; HRMS (ESI) m/z calcd for $C_{21}H_{21}F_3OS$ $[M+H]^+$: 379.1265, found: 379.1338.

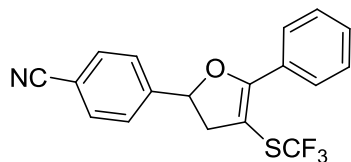


2-(4-chlorophenyl)-5-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3d): Pale yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.03 (dd, $J_1 = 15.2$ Hz, $J_2 = 8.8$ Hz, 1H), 3.53 (dd, $J_1 = 15.2$ Hz, $J_2 = 10.8$ Hz, 1H), 5.69 (dd, $J_1 = 10.8$ Hz, $J_2 = 8.8$ Hz, 1H), 7.31-7.37 (m, 4H), 7.40-7.42 (m, 3H), 7.90-7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 140.0, 134.1, 131.9, 130.3, 129.6 (q, $J = 310.0$ Hz), 129.0, 128.9, 128.2, 127.0, 90.0 (d, $J = 2.0$ Hz), 81.1, 44.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.4; IR (thin film, cm^{-1}) 3374, 3061, 2926, 2369, 1899, 1599, 1492, 1446, 1329, 1236, 1124, 1015, 917, 827, 770, 692; HRMS (ESI) m/z calcd for $C_{17}H_{12}ClF_3OS$ $[M+H]^+$: 357.0249, found: 357.0322.

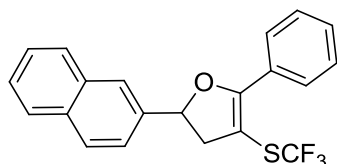


2-(4-bromophenyl)-5-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3e): Pale yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.03 (dd, $J_1 = 15.2$ Hz, $J_2 = 8.4$ Hz, 1H), 3.54 (dd, $J_1 = 15.2$ Hz, $J_2 = 10.8$ Hz, 1H), 5.68 (dd, $J_1 = 10.8$ Hz, $J_2 = 8.4$ Hz, 1H), 7.26 (d, $J = 8.4$ Hz, 2H), 7.40-7.43 (m,

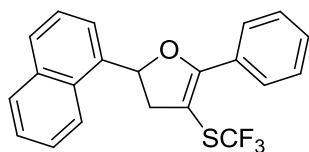
3H), 7.50-7.52 (m, 2H), 7.89-7.92 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.1, 140.5, 131.9, 130.3, 129.6 (q, $J = 310.0$ Hz), 128.9, 128.2, 128.1, 127.4, 122.2, 90.0, 81.2, 44.9; ^{19}F NMR (376 MHz, CDCl_3) δ -42.4; IR (thin film, cm^{-1}) 3371, 2925, 2374, 1893, 1597, 1491, 1328, 1237, 1122, 824, 770, 692; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{BrF}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 400.9744, found: 400.9817.



4-(5-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran-2-yl)benzonitrile (3f): Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.02 (dd, $J_1 = 15.2$ Hz, $J_2 = 8.4$ Hz, 1H), 3.60 (dd, $J_1 = 15.2$ Hz, $J_2 = 10.8$ Hz, 1H), 5.78 (dd, $J_1 = 10.8$ Hz, $J_2 = 8.4$ Hz, 1H), 7.42-7.45 (m, 3H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.91-7.94 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.0 (d, $J = 2.0$ Hz), 146.7, 132.6, 130.4, 129.5 (q, $J = 310.0$ Hz), 128.5, 128.3, 128.1, 126.1, 118.5, 112.0, 90.1 (d, $J = 2.0$ Hz), 80.6, 44.8; ^{19}F NMR (376 MHz, CDCl_3) δ -42.3; IR (thin film, cm^{-1}) 3405, 3062, 2924, 2230, 1920, 1611, 1493, 1327, 1238, 1124, 919, 838, 770, 693; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{12}\text{F}_3\text{NOS}$ $[\text{M}+\text{H}]^+$: 348.0592, found: 348.0664.

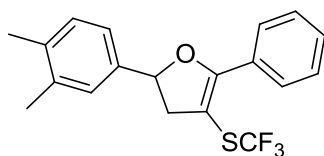


2-(naphthalen-2-yl)-5-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3g): White solid. $\text{Mp} = 86\text{-}88^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 3.17 (dd, $J_1 = 15.2$ Hz, $J_2 = 8.8$ Hz, 1H), 3.60 (dd, $J_1 = 14.8$ Hz, $J_2 = 10.8$ Hz, 1H), 5.76 (t, $J = 9.6$ Hz, 1H), 7.41-7.51 (m, 6H), 7.83-7.89 (m, 4H), 7.95-7.97 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.3, 138.6, 133.2, 133.2, 130.2, 129.7 (q, $J = 310.0$ Hz), 129.1, 128.9, 128.3, 128.2, 128.1, 127.7, 126.4, 126.3, 124.7, 123.4, 90.1 (d, $J = 2.0$ Hz), 82.1, 44.9; ^{19}F NMR (376 MHz, CDCl_3) δ -42.4; IR (thin film, cm^{-1}) 3376, 2924, 2371, 1796, 1597, 1384, 1262, 1121, 856, 770, 748, 690; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{15}\text{F}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 373.0796, found: 373.0868.

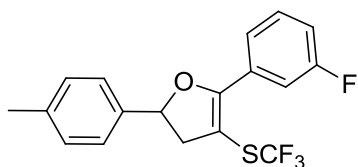


2-(naphthalen-1-yl)-5-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3h): Pale yellow oil;

¹H NMR (400 MHz, CDCl₃) δ 3.14 (dd, $J_1 = 15.2$ Hz, $J_2 = 8.8$ Hz, 1H), 3.76 (dd, $J_1 = 15.2$ Hz, $J_2 = 11.2$ Hz, 1H), 6.40 (dd, $J_1 = 10.8$ Hz, $J_2 = 9.2$ Hz, 1H), 7.44-7.49 (m, 4H), 7.52-7.55 (m, 2H), 7.63 (d, $J = 7.2$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.88-7.92 (m, 2H), 8.00-8.03 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 159.7, 148.3, 140.7, 135.0, 129.3 (q, $J = 310.0$ Hz), 129.1, 128.9, 128.6, 125.7, 123.4, 94.2 (d, $J = 2.0$ Hz), 82.4, 45.0; **¹⁹F NMR** (376 MHz, CDCl₃) δ -42.3; IR (thin film, cm⁻¹) 3370, 3059, 2926, 2370, 1808, 1598, 1493, 1321, 1236, 1124, 920, 775, 692; HRMS (ESI) m/z calcd for C₂₁H₁₅F₃OS [M+H]⁺: 373.0796, found: 373.0868.

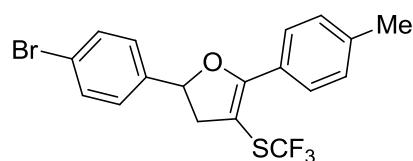


2-(3,4-dimethylphenyl)-5-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3i): Pale yellow oil; **¹H NMR** (400 MHz, CDCl₃) δ 2.27 (d, $J = 8.0$ Hz, 6H), 3.10 (dd, $J_1 = 15.2$ Hz, $J_2 = 8.8$ Hz, 1H), 3.50 (dd, $J_1 = 15.2$ Hz, $J_2 = 10.8$ Hz, 1H), 5.67 (dd, $J_1 = 9.6$ Hz, $J_2 = 8.8$ Hz, 1H), 7.14-7.17 (m, 3H), 7.39-7.41 (m, 3H), 7.90-7.92 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 162.3, 138.9, 137.1, 136.8, 130.1, 130.0, 129.7 (q, $J = 310.0$ Hz), 129.2, 128.3, 128.1, 127.1, 123.3, 89.9, 82.1, 44.9, 19.8, 19.5; **¹⁹F NMR** (376 MHz, CDCl₃) δ -42.5; IR (thin film, cm⁻¹) 3340, 2924, 2369, 1720, 1598, 1447, 1265, 1125, 910, 801, 741, 656; HRMS (ESI) m/z calcd for C₁₉H₁₇F₃OS [M+H]⁺: 351.0952, found: 351.1025.

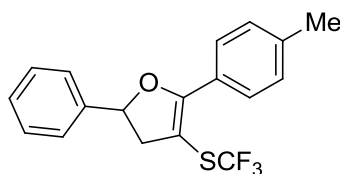


5-(3-fluorophenyl)-2-(p-tolyl)-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3j): Colorless oil; **¹H NMR** (400 MHz, CDCl₃) δ 2.36 (s, 3H), 3.10 (dd, $J_1 = 15.2$ Hz, $J_2 = 8.8$ Hz, 1H), 3.52 (dd, $J_1 = 15.2$ Hz, $J_2 = 10.8$ Hz, 1H), 5.70 (dd, $J_1 = 10.8$ Hz, $J_2 = 8.8$ Hz, 1H), 7.08-7.13 (m, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.34-7.39 (m, 1H), 7.62-7.65 (m, 1H), 7.73-7.75 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 162.3 (d, $J = 244.0$ Hz), 160.7, 138.2 (d, $J = 12.0$ Hz), 131.1 (d, $J = 8.0$ Hz), 129.8, 129.7, 129.6 (q, $J = 310.0$ Hz), 129.5, 125.7, 124.0 (d, $J = 2.0$ Hz), 117.1 (d, $J = 21.0$ Hz), 115.2 (d, $J = 23.0$ Hz), 91.2 (d, $J = 2.0$ Hz), 82.1, 44.9, 21.2; **¹⁹F NMR** (376 MHz, CDCl₃) δ -42.3, -112.4; IR (thin film, cm⁻¹) 3341, 2926, 2373, 1900, 1583, 1447, 1327, 1252, 1126,

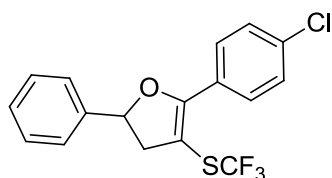
957, 841, 789, 697; HRMS (ESI) m/z calcd for $C_{18}H_{14}F_4OS$ $[M+H]^+$: 355.0701, found: 355.0774.



2-(4-bromophenyl)-5-(p-tolyl)-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3k): Pale yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.01 (dd, $J_1 = 14.8$ Hz, $J_2 = 8.4$ Hz, 1H), 3.52 (dd, $J_1 = 14.8$ Hz, $J_2 = 10.8$ Hz, 1H), 5.66 (dd, $J_1 = 10.8$ Hz, $J_2 = 8.4$ Hz, 1H), 7.20-7.26 (m, 4H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.81 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 140.6, 140.6, 131.9, 129.7 (q, $J = 310.0$ Hz), 128.9, 128.1, 127.3, 126.0, 122.1, 89.0 (d, $J = 2.0$ Hz), 81.0, 44.9, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.5; IR (thin film, cm^{-1}) 3365, 2924, 2370, 1895, 1607, 1490, 1327, 1237, 1123, 915, 822, 661; HRMS (ESI) m/z calcd for $C_{18}H_{14}BrF_3OS$ $[M+H]^+$: 414.9901, found: 414.9974.

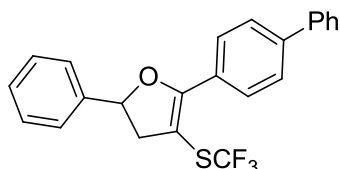


2-phenyl-5-(p-tolyl)-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3l): Pale yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.07 (dd, $J_1 = 14.8$ Hz, $J_2 = 8.4$ Hz, 1H), 3.52 (dd, $J_1 = 15.2$ Hz, $J_2 = 10.8$ Hz, 1H), 5.71 (dd, $J_1 = 10.8$ Hz, $J_2 = 8.4$ Hz, 1H), 7.20-7.22 (m, 2H), 7.30-7.36 (m, 1H), 7.38-7.39 (m, 4H), 7.83 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 141.6, 140.4, 129.7 (q, $J = 310.0$ Hz), 128.9, 128.8, 128.2, 126.3, 125.7, 89.0 (d, $J = 1.0$ Hz), 81.8, 45.0, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.5; IR (thin film, cm^{-1}) 3358, 2925, 2372, 1801, 1606, 1509, 1329, 1237, 1123, 919, 822, 756, 698; HRMS (ESI) m/z calcd for $C_{18}H_{15}F_3OS$ $[M+H]^+$: 337.0796, found: 337.0868.

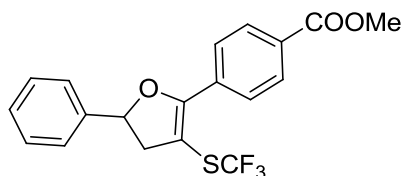


5-(4-chlorophenyl)-2-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3m): Pale yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.09 (dd, $J_1 = 15.2$ Hz, $J_2 = 8.8$ Hz, 1H), 3.53 (dd, $J_1 = 15.2$ Hz, $J_2 = 10.8$ Hz, 1H), 5.72 (dd, $J_1 = 9.6$ Hz, $J_2 = 9.2$ Hz, 1H), 7.33-7.38 (m, 7H), 7.88 (d, $J = 8.8$ Hz, 2H);

¹³C NMR (100 MHz, CDCl₃) δ 161.1, 141.2, 136.2, 129.6 (q, *J* = 310.0 Hz), 129.5, 128.8, 128.5, 128.4, 127.5, 125.7, 90.6, 82.0, 45.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -42.4; IR (thin film, cm⁻¹) 3368, 2926, 2371, 1907, 1614, 1489, 1328, 1239, 1125, 1014, 919, 834, 755, 698; HRMS (ESI) *m/z* calcd for C₁₇H₁₂ClF₃OS [M+H]⁺: 357.0249, found: 357.0322.



5-([1,1'-biphenyl]-4-yl)-2-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3n): White solid. *Mp* = 80-82 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.10 (dd, *J*₁ = 15.2 Hz, *J*₂ = 8.8 Hz, 1H), 3.54 (dd, *J*₁ = 15.2 Hz, *J*₂ = 10.8 Hz, 1H), 5.73 (dd, *J*₁ = 9.6 Hz, *J*₂ = 8.8 Hz, 1H), 7.33-7.45 (m, 8H), 7.59-7.64 (m, 4H), 8.02 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 161.9, 142.8, 141.5, 140.2, 129.7 (q, *J* = 310.0 Hz), 128.9, 128.8, 128.7, 128.3, 127.9, 127.8, 127.1, 126.8, 125.7, 89.9, 81.9, 45.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -42.3; IR (thin film, cm⁻¹) 3366, 2925, 2374, 1878, 1604, 1487, 1326, 1241, 1123, 846, 766, 697; HRMS (ESI) *m/z* calcd for C₂₃H₁₇F₃OS [M+H]⁺: 399.0952, found: 399.1025.

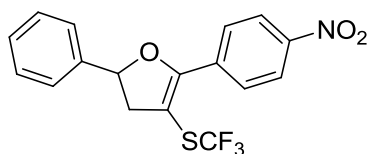


Methyl 4-(5-phenyl-3-((trifluoromethyl)thio)-4,5-dihydrofuran-2-yl)benzoate (3o): Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 3.12 (dd, *J*₁ = 15.2 Hz, *J*₂ = 8.8 Hz, 1H), 3.56 (dd, *J*₁ = 15.6 Hz, *J*₂ = 10.8 Hz, 1H), 3.92 (s, 3H), 5.75 (dd, *J*₁ = 10.8 Hz, *J*₂ = 8.8 Hz, 1H), 7.32-7.37 (m, 1H), 7.39-7.41 (m, 4H), 8.00 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 161.0, 141.1, 133.2, 131.3, 129.5 (q, *J* = 310.0 Hz), 129.3, 128.8, 128.4, 128.2, 125.7, 92.3 (q, *J* = 2.0 Hz), 82.2, 52.2, 45.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -42.2; IR (thin film, cm⁻¹) 3428, 2953, 2377, 1940, 1724, 1605, 1437, 1279, 1124, 1018, 862, 776, 700; HRMS (ESI) *m/z* calcd for C₁₉H₁₅F₃O₃S [M+H]⁺: 381.0694, found: 381.0767.

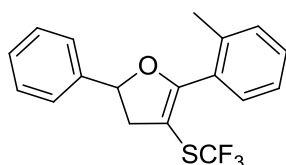


2-phenyl-5-(4-(trifluoromethyl)phenyl)-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3p):

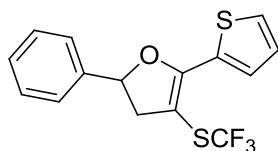
Yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.13 (dd, $J_1 = 15.2$ Hz, $J_2 = 8.8$ Hz, 1H), 3.56 (dd, $J_1 = 15.2$ Hz, $J_2 = 10.8$ Hz, 1H), 5.76 (dd, $J_1 = 10.8$ Hz, $J_2 = 8.8$ Hz, 1H), 7.33-7.43 (m, 5H), 7.66 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.0$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.7, 141.1, 132.5, 131.8 (q, $J = 32.0$ Hz), 129.5 (q, $J = 310.0$ Hz), 128.9, 128.6, 128.5, 125.7, 125.2 (q, $J = 4.0$ Hz), 123.8 (q, $J = 270.0$ Hz), 92.4, 82.3, 45.0; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -42.3, -62.9; IR (thin film, cm^{-1}) 3364, 2926, 2374, 1928, 1611, 1410, 1326, 1169, 1126, 920, 848, 756, 698; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{12}\text{F}_6\text{OS}$ $[\text{M}+\text{H}]^+$: 391.0513, found: 391.0586.



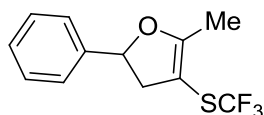
5-(4-nitrophenyl)-2-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3q): Yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.16 (dd, $J_1 = 15.6$ Hz, $J_2 = 8.8$ Hz, 1H), 3.59 (dd, $J_1 = 15.6$ Hz, $J_2 = 10.8$ Hz, 1H), 5.77 (t, $J = 10.0$ Hz, 1H), 7.36-7.44 (m, 5H), 8.12 (d, $J = 8.8$ Hz, 2H), 8.26 (d, $J = 8.8$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.6, 148.3, 140.7, 135.0, 129.3 (q, $J = 309.0$ Hz), 129.1, 128.9, 128.6, 125.7, 123.4, 94.2 (d, $J = 2.0$ Hz), 82.4, 45.0; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -42.0; IR (thin film, cm^{-1}) 3363, 2926, 2372, 1802, 1590, 1523, 1457, 1328, 1124, 919, 853, 755, 697; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{F}_3\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 368.0490, found: 368.0563.



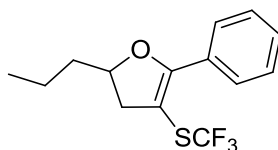
2-phenyl-5-(o-tolyl)-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3r): Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.34 (s, 3H), 3.15 (dd, $J_1 = 14.8$ Hz, $J_2 = 9.2$ Hz, 1H), 3.49 (dd, $J_1 = 14.8$ Hz, $J_2 = 10.8$ Hz, 1H), 5.76-5.81 (m, 1H), 7.21-7.24 (m, 2H), 7.30-7.35 (m, 3H), 7.37-7.44 (m, 4H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.5, 141.1, 137.5, 130.3, 130.2, 129.9, 129.6 (q, $J = 309.0$ Hz), 128.9, 128.8, 128.4, 126.0, 125.4, 92.8 (d, $J = 2.0$ Hz), 83.3, 43.3, 19.7; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -42.7; IR (thin film, cm^{-1}) 3344, 2925, 2372, 1806, 1637, 1458, 1327, 1241, 1125, 919, 755, 698; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 337.0796, found: 337.0868.



2-phenyl-5-(thiophen-2-yl)-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3s): Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.05 (dd, $J_1 = 15.2$ Hz, $J_2 = 8.4$ Hz, 1H), 3.51 (dd, $J_1 = 15.2$ Hz, $J_2 = 9.6$ Hz, 1H), 5.75 (dd, $J_1 = 9.6$ Hz, $J_2 = 8.4$ Hz, 1H), 7.07-7.09 (m, 1H), 7.31-7.35 (m, 1H), 7.38-7.39 (m, 4H), 7.44 (d, $J = 4.8$ Hz, 1H), 7.76 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.8, 141.3, 130.6, 129.7, 129.5 (q, $J = 311.0$ Hz), 128.9, 128.8, 128.3, 127.0, 125.6, 88.2, 82.7, 44.7; ^{19}F NMR (376 MHz, CDCl_3) δ -42.4; IR (thin film, cm^{-1}) 3341, 2925, 2373, 1806, 1612, 1425, 1245, 1125, 934, 849, 699; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{11}\text{F}_3\text{OS}_2$ $[\text{M}+\text{H}]^+$: 329.0203, found: 329.0276.

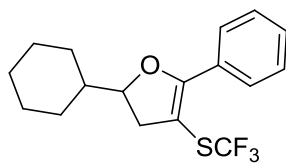


5-methyl-2-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3t): Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 2.06 (s, 3H), 2.84-2.90 (m, 1H), 3.26-3.33 (m, 1H), 5.60 (dd, $J_1 = 10.4$ Hz, $J_2 = 8.4$ Hz, 1H), 7.30-7.33 (m, 3H), 7.36-7.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 141.4, 129.8 (q, $J = 309.0$ Hz), 128.8, 128.3, 125.7, 89.3 (d, $J = 2.0$ Hz), 82.7, 42.8, 12.4; ^{19}F NMR (376 MHz, CDCl_3) δ -43.9; IR (thin film, cm^{-1}) 3343, 3034, 2926, 2371, 1872, 1646, 1495, 1384, 1227, 1113, 966, 757, 698, 607; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 261.0483, found: 261.0555.



5-phenyl-2-propyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3u): Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 0.99 (t, $J = 7.6$ Hz, 3H), 1.44-1.56 (m, 2H), 1.60-1.67 (m, 1H), 1.78-1.85 (m, 1H), 2.71 (dd, $J_1 = 14.8$ Hz, $J_2 = 8.0$ Hz, 1H), 3.17 (dd, $J_1 = 14.8$ Hz, $J_2 = 10.0$ Hz, 1H), 4.74-4.78 (m, 1H), 7.39 (t, $J = 3.6$ Hz, 3H), 7.82-7.84 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.3, 129.9, 129.8 (q, $J = 309.0$ Hz), 129.5, 128.2, 128.1, 89.8 (d, $J = 3.0$ Hz), 81.0, 42.3, 38.1, 18.3, 13.9; ^{19}F NMR (376 MHz, CDCl_3) δ -42.7; IR (thin film, cm^{-1}) 3339, 2961, 2372, 1889, 1598, 1493, 1341, 1236, 1127, 918, 770, 692; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 289.0796, found:

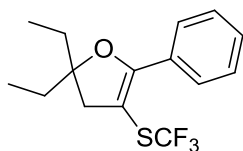
289.0868.



2-cyclohexyl-5-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3v): Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.04-1.14 (m, 2H), 1.17-1.30 (m, 3H), 1.61-1.65 (m, 1H), 1.67-1.71 (m, 2H), 1.77-1.80 (m, 2H), 1.93-1.96 (m, 1H), 2.82 (dd, $J_1 = 14.8$ Hz, $J_2 = 8.8$ Hz, 1H), 3.06 (dd, $J_1 = 14.8$ Hz, $J_2 = 10.4$ Hz, 1H), 4.46-4.52 (m, 1H), 7.38-7.40 (m, 3H), 7.83-7.85 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.5, 129.9, 129.8 (q, $J = 310.0$ Hz), 129.5, 128.1, 128.1, 89.8 (d, $J = 2.0$ Hz), 85.2, 43.1, 39.9, 28.1, 27.9, 26.4, 25.9, 25.7; ^{19}F NMR (376 MHz, CDCl_3) δ -42.6; IR (thin film, cm^{-1}) 3343, 2927, 2855, 2364, 1598, 1493, 1448, 1238, 1126, 770, 692; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{19}\text{F}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 329.1109, found: 329.1181.

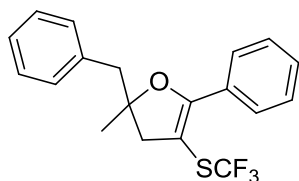


2-phenyl-3-((trifluoromethyl)thio)-1-oxaspiro[4.4]non-2-ene compound with 5-phenyl-2-propyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (1:1) (3w): Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 1.67-1.79 (m, 4H), 1.83-1.92 (m, 2H), 2.11-2.16 (m, 2H), 3.03 (s, 2H), 7.38 (t, $J = 3.2$ Hz, 3H), 7.80-7.82 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.8, 129.8, 129.8 (q, $J = 310.0$ Hz), 128.2, 128.1, 128.0, 94.9, 89.3 (d, $J = 2.0$ Hz), 46.9, 39.5, 23.7; ^{19}F NMR (376 MHz, CDCl_3) δ -42.9; IR (thin film, cm^{-1}) 3357, 2960, 2373, 1597, 1492, 1447, 1257, 1125, 767, 692; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 301.0796, found: 301.0868.

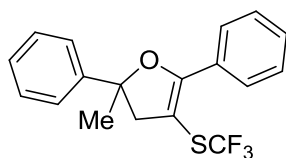


2,2-diethyl-5-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3x): Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.96 (t, $J = 7.6$ Hz, 6H), 1.66-1.81 (m, 4H), 2.85 (s, 2H), 7.38-7.39 (m, 3H), 7.81-7.83 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.3, 129.8 (q, $J = 310.0$ Hz), 129.8, 128.2, 128.0, 89.6, 89.1 (d, $J = 1.0$ Hz), 44.7, 31.8, 7.5; ^{19}F NMR (376 MHz, CDCl_3) δ -42.7; IR (thin film, cm^{-1}) 3309, 2972, 2371, 1598, 1493, 1338, 1254, 1125, 953, 895, 692; HRMS (ESI) m/z

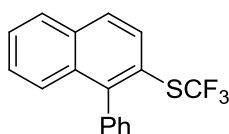
calcd for C₁₅H₁₇F₃OS [M+H]⁺: 303.0952, found: 303.1015.



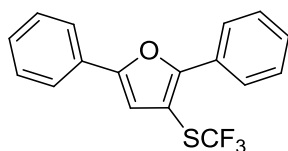
2-benzyl-2-methyl-5-phenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3y): Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.46 (s, 3H), 2.77 (m, 1H), 3.01 (s, 2H), 3.05 (m, 1H), 7.23-7.30 (m, *J*, 5H), 7.38-7.39 (m, 3H), 7.79-7.83 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 136.4, 130.4, 129.9, 129.7 (q, *J* = 310.0 Hz), 129.6, 128.3, 128.2, 128.1, 126.7, 89.5 (d, *J* = 2.0 Hz), 86.6, 47.4, 46.6, 26.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -42.7; IR (thin film, cm⁻¹) 3400, 2927, 2251, 1952, 1887, 1810, 1598, 1493, 1267, 1128, 909, 735, 651; HRMS (ESI) *m/z* calcd for C₁₉H₁₇F₃OS [M+H]⁺: 351.0952, found: 351.1022.



2-methyl-2,5-diphenyl-4-((trifluoromethyl)thio)-2,3-dihydrofuran (3z): Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 1.79 (s, 3H), 3.20-3.34 (m, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.36-7.39 (m, 2H), 7.42-7.46 (m, 5H), 7.93-7.96 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 161.4, 146.1, 130.1, 129.7 (q, *J* = 310.0 Hz), 129.5, 128.5, 128.4, 128.3, 127.4, 124.3, 89.4, 87.2, 51.1, 29.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -42.6; IR (thin film, cm⁻¹) 3340, 2926, 2374, 1953, 1599, 1493, 1327, 1247, 1125, 918, 852, 762, 696; HRMS (ESI) *m/z* calcd for C₁₈H₁₅F₃OS [M+H]⁺: 337.0796, found: 337.0868.



(1-phenylnaphthalen-2-yl)(trifluoromethyl)sulfane (3aa): Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.27 (m, 2H), 7.39-7.43 (m, 1H), 7.45-7.51 (m, 4H), 7.53-7.57 (m, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 146.7, 138.2, 133.9, 133.3, 131.6, 130.3, 129.5 (q, *J* = 307.0 Hz), 128.6, 128.1, 127.9, 127.6, 127.5, 126.8, 121.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -41.4; IR (thin film, cm⁻¹) 3370, 3058, 2924, 2367, 1585, 1492, 1443, 1115, 1096, 965, 908, 815, 747, 700; HRMS (ESI) *m/z* calcd for C₁₇H₁₁F₃S [M+H]⁺: 305.0534, found: 305.0606.

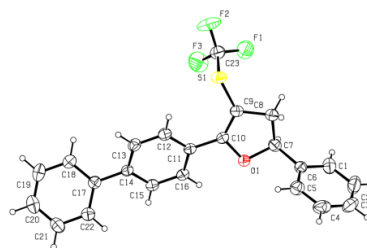
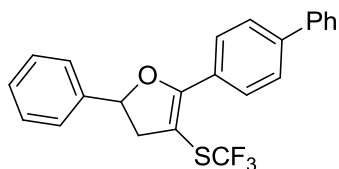


2,5-diphenyl-3-((trifluoromethyl)thio)furan (4): White solid. Mp = 71-72 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.84 (s, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.36-7.47 (m, 5H), 7.10 (t, J = 7.6 Hz, 2H), 8.05 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 153.1, 129.5, 129.2 (q, J = 309.0 Hz), 129.1, 129.0, 128.8, 128.6, 128.3, 126.6, 124.0, 113.0, 103.1 (d, J = 3.0 Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -43.0; IR (thin film, cm^{-1}) 3337, 3113, 2925, 2373, 1951, 1739, 1587, 1480, 1136, 1103, 818, 767, 690; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{11}\text{F}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 321.0483, found: 321.0555.

6. References

1. (a) P. Gao, Y.-W. Shen, R. Fang, X.-H. Hao, Z.-H. Qiu, F. Yang, X.-B. Yan, Q. Wang, X.-J. Gong, X.-Y. Liu and Y.-M. Liang, *Angew. Chem., Int. Ed.*, 2014, **53**, 7629. (b) P. Gao, H.-X. Li, X.-H. Hao, D.-P. Jin, D.-Q. Chen, X.-B. Yan, X.-X. Wu, X.-R. Song, X.-Y. Liu and Y.-M. Liang, *Org. Lett.*, 2014, **16**, 6214.
2. S.-S. Liu, J.-B. Zhao, L. Kaminsky, R. J. Wilson, N. Marino and D. A. Clark, *Org. Lett.*, 2014, **16**, 4456.
3. Y.-Z. Chen, L.-Z. Wu, M.-L. Peng, D. Zhang, L.-P. Zhang and C.-H. Tung, *Tetrahedron*, 2006, **62**, 10688.
4. A. Arrault, F. Touzeau, G. Guillaumet, J.-Y. M  our, *Synthesis*, 1999, **7**, 1241.

7. Crystallographic data of 3n



Bond precision:

C-C = 0.0043 Å

Wavelength=0.71073

Cell:

a=9.4049(15)

b=10.3048(12)

c=10.563(2)

alpha=79.807(13)

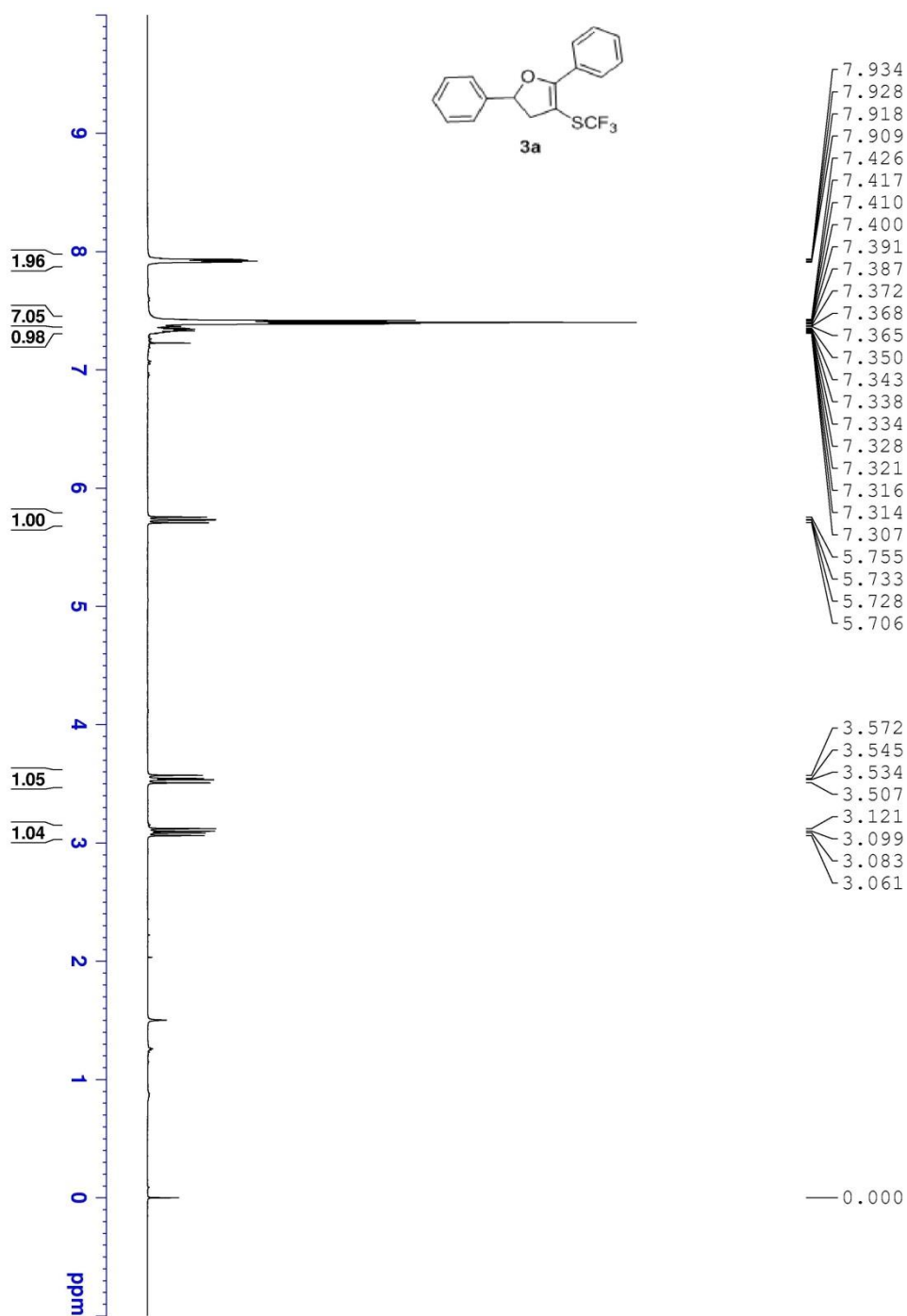
beta=74.337(16)

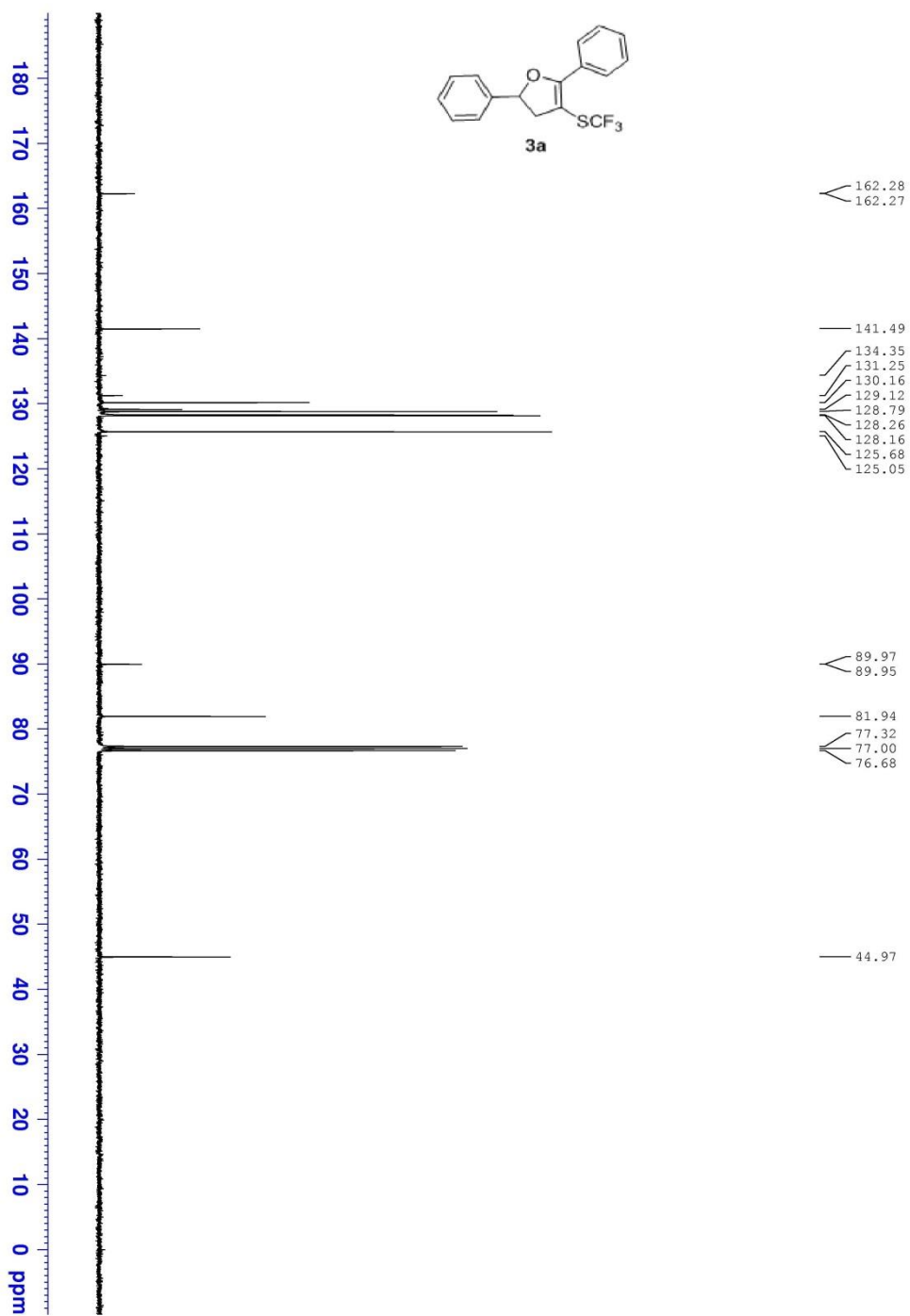
gamma=82.314(11)

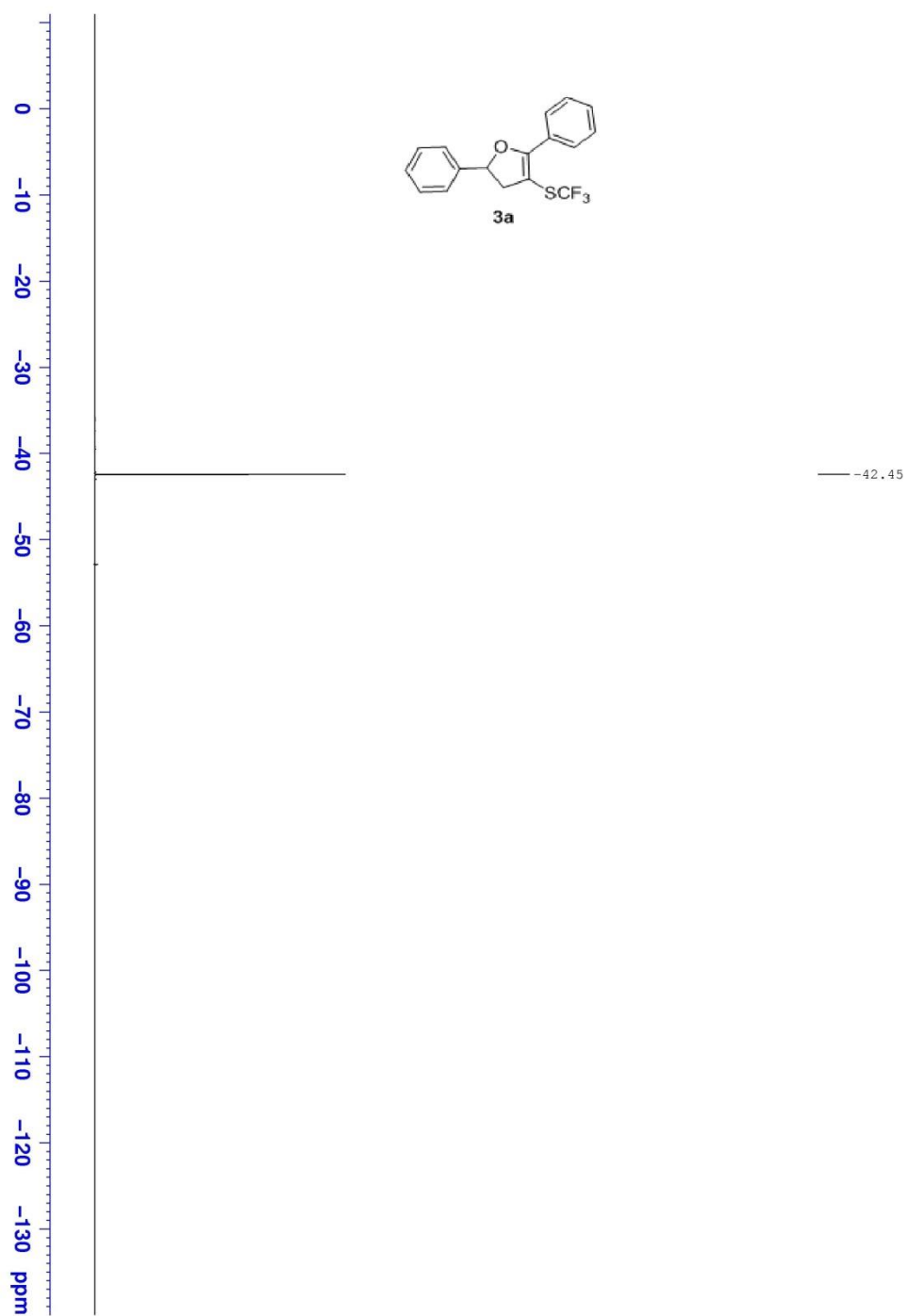
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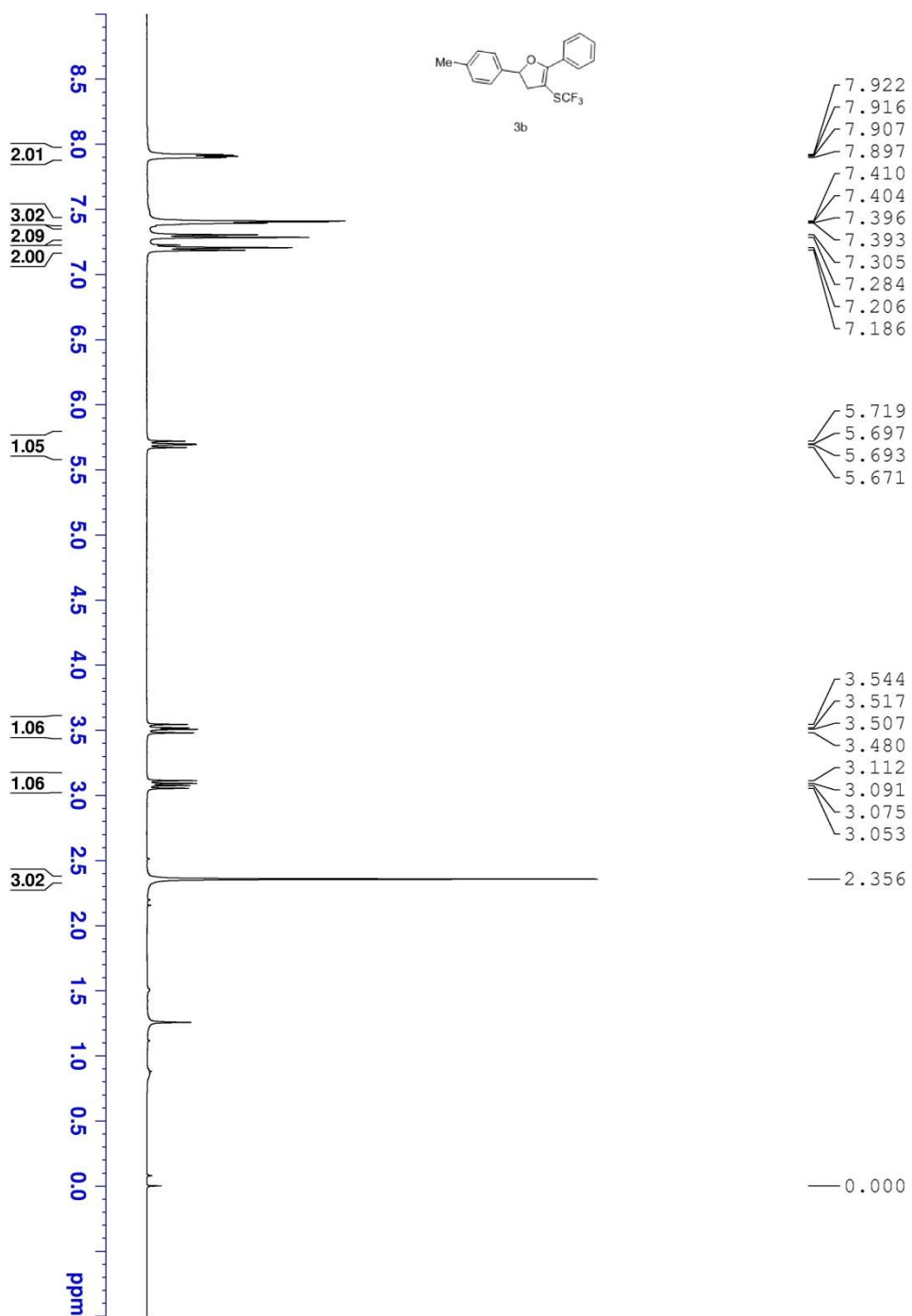
	Calculated	Reported
Volume	966.2(3)	966.2(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C ₂₃ H ₁₇ F ₃ O S	C ₂₃ H ₁₇ F ₃ O S
Sum formula	C ₂₃ H ₁₇ F ₃ O S	C ₂₃ H ₁₇ F ₃ O S
Mr	398.43	398.43
D _x , g cm ⁻³	1.370	1.370
Z	2	2
Mu (mm ⁻¹)	0.206	0.206
F ₀₀₀	412.0	412.0
F ₀₀₀ '	412.48	
h,k,l _{max}	11,12,13	11,12,13
N _{ref}	3794	3781
T _{min} , T _{max}	0.930, 0.944	0.858, 1.000
T _{min} '	0.930	
Correction method= MULTI-SCAN		
Data completeness= 0.977	Theta(max)= 26.020	
R(reflections)= 0.0522 (2393)	wR2(reflections)= 0.1488 (3781)	
S = 1.034	N _{par} = 253	

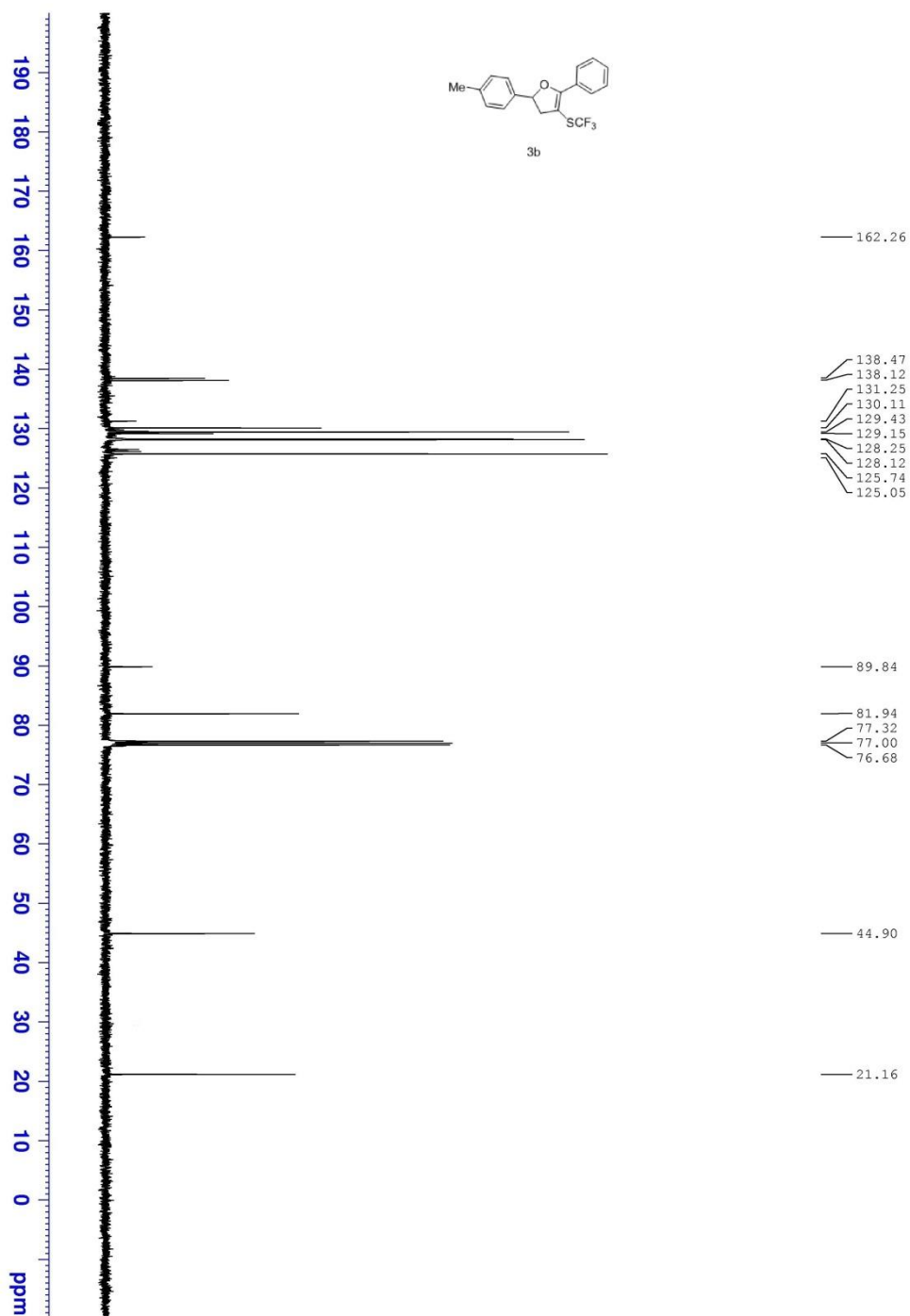
8. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of 3a-3z, 3aa, 4

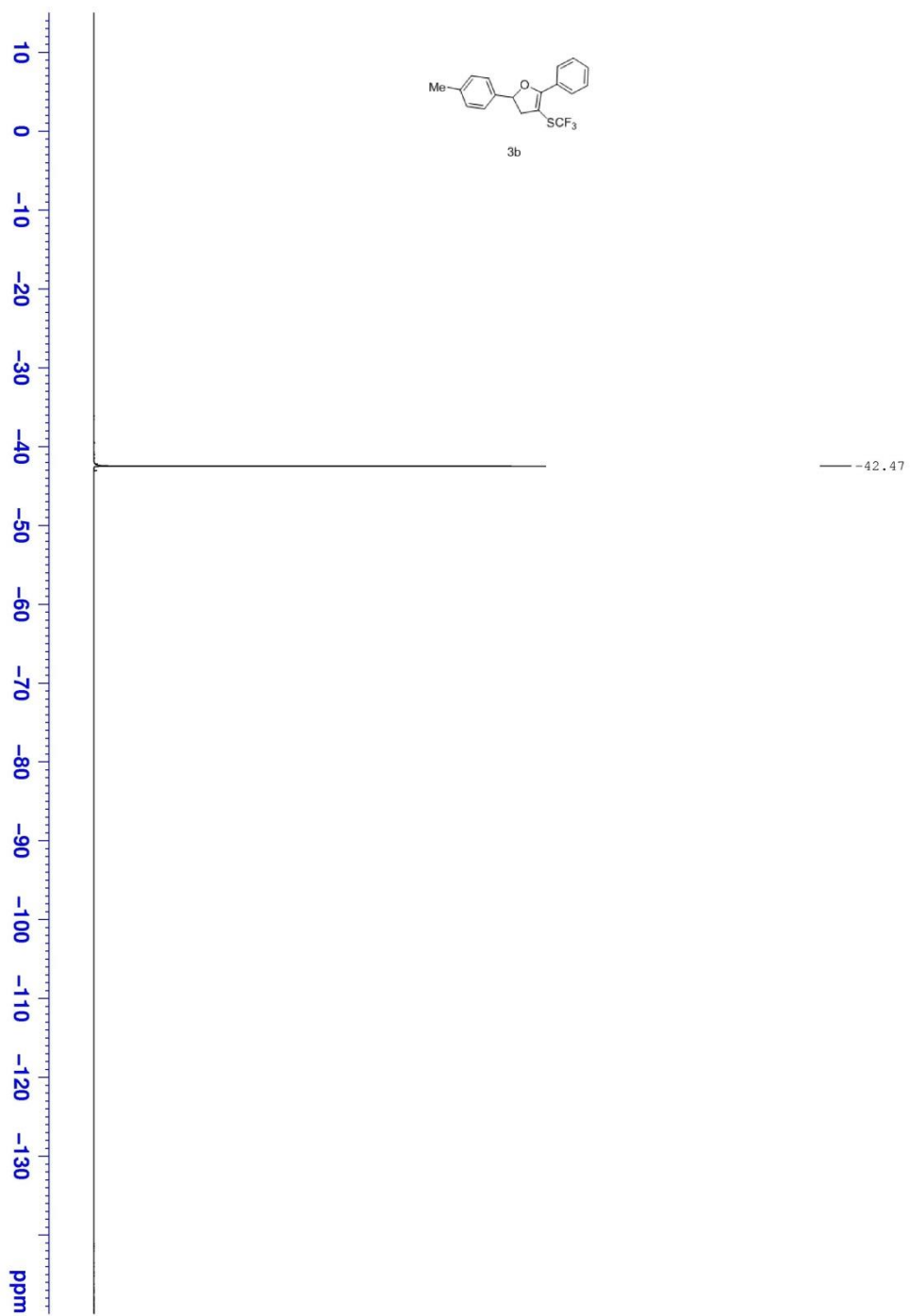


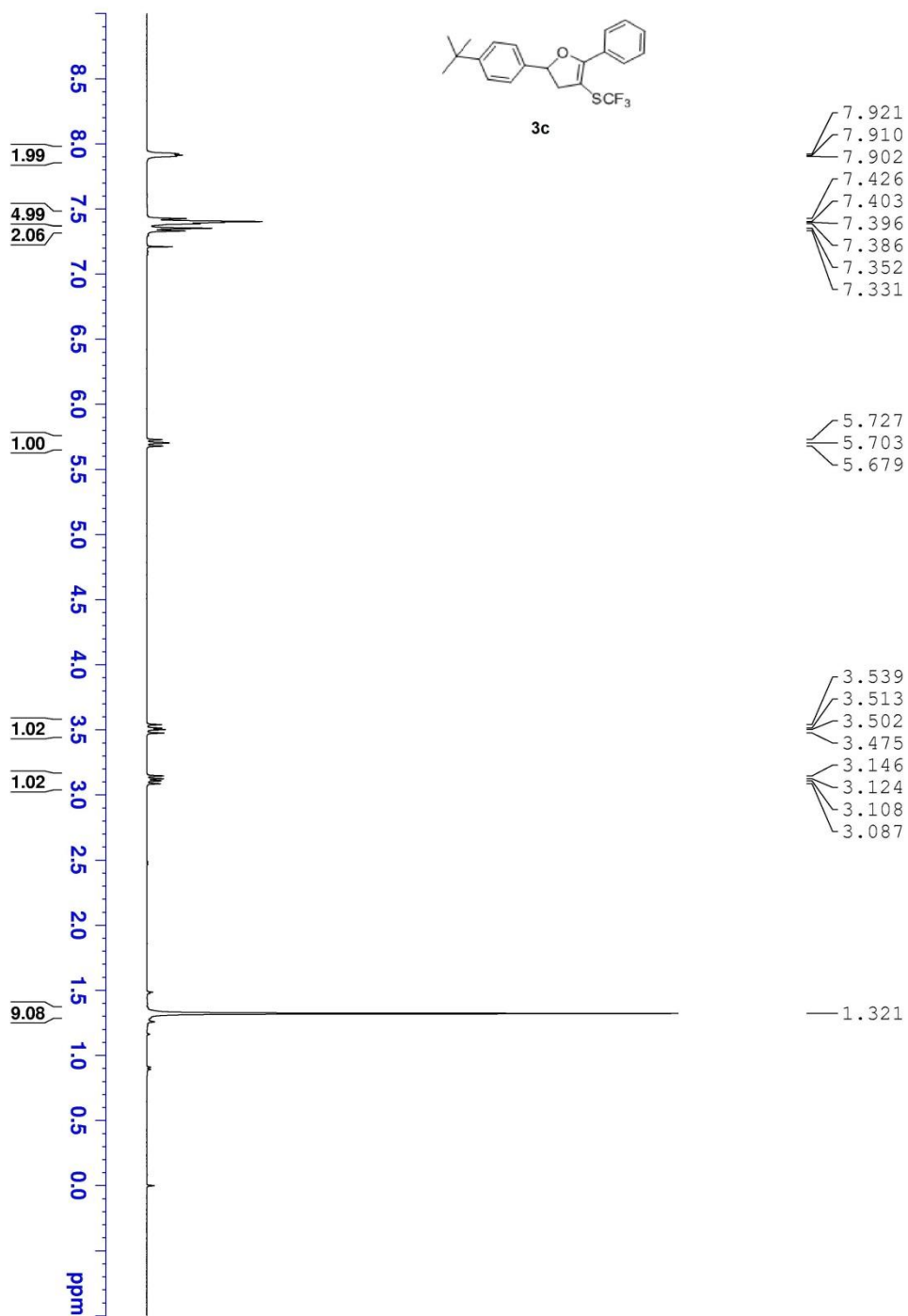


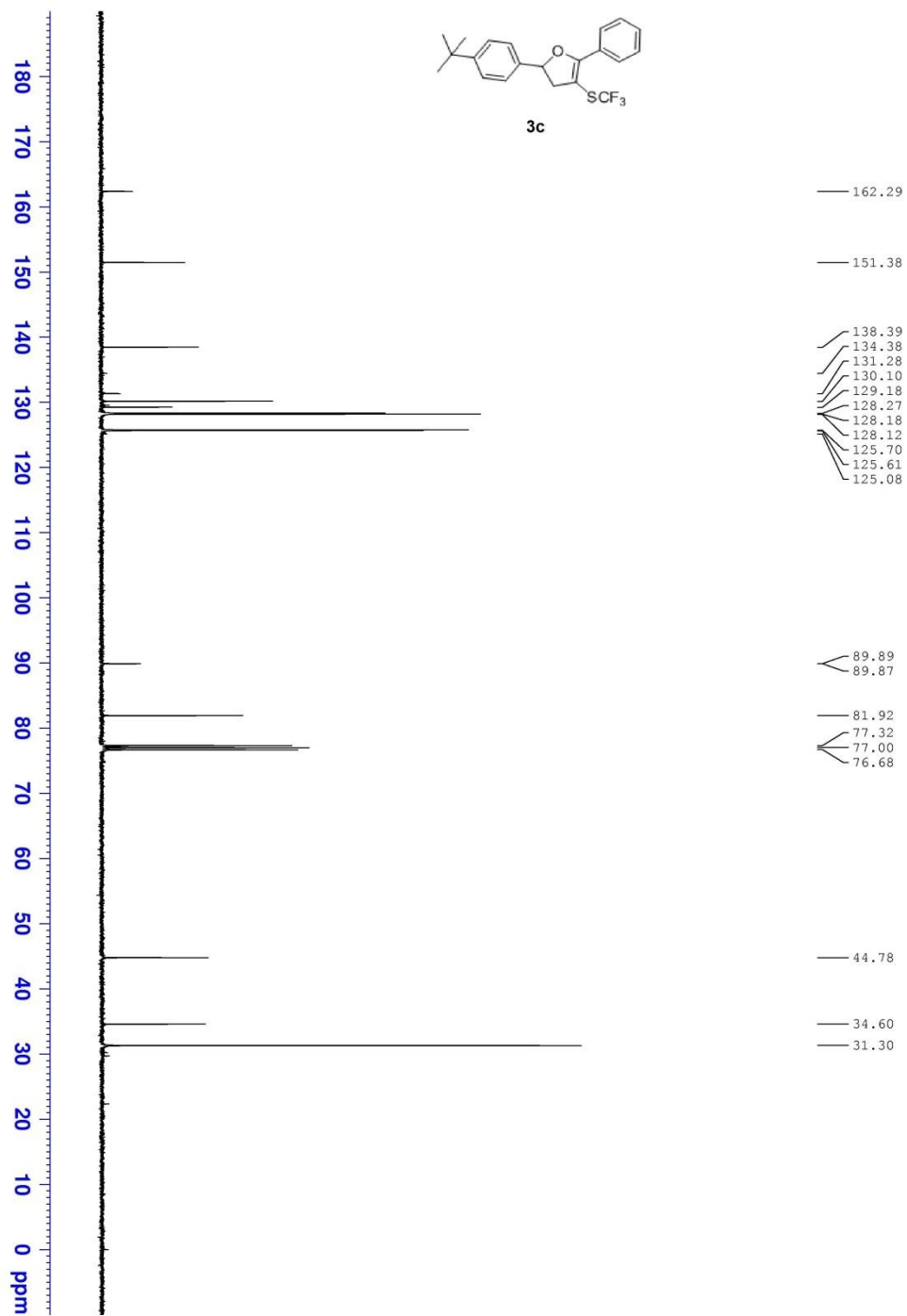


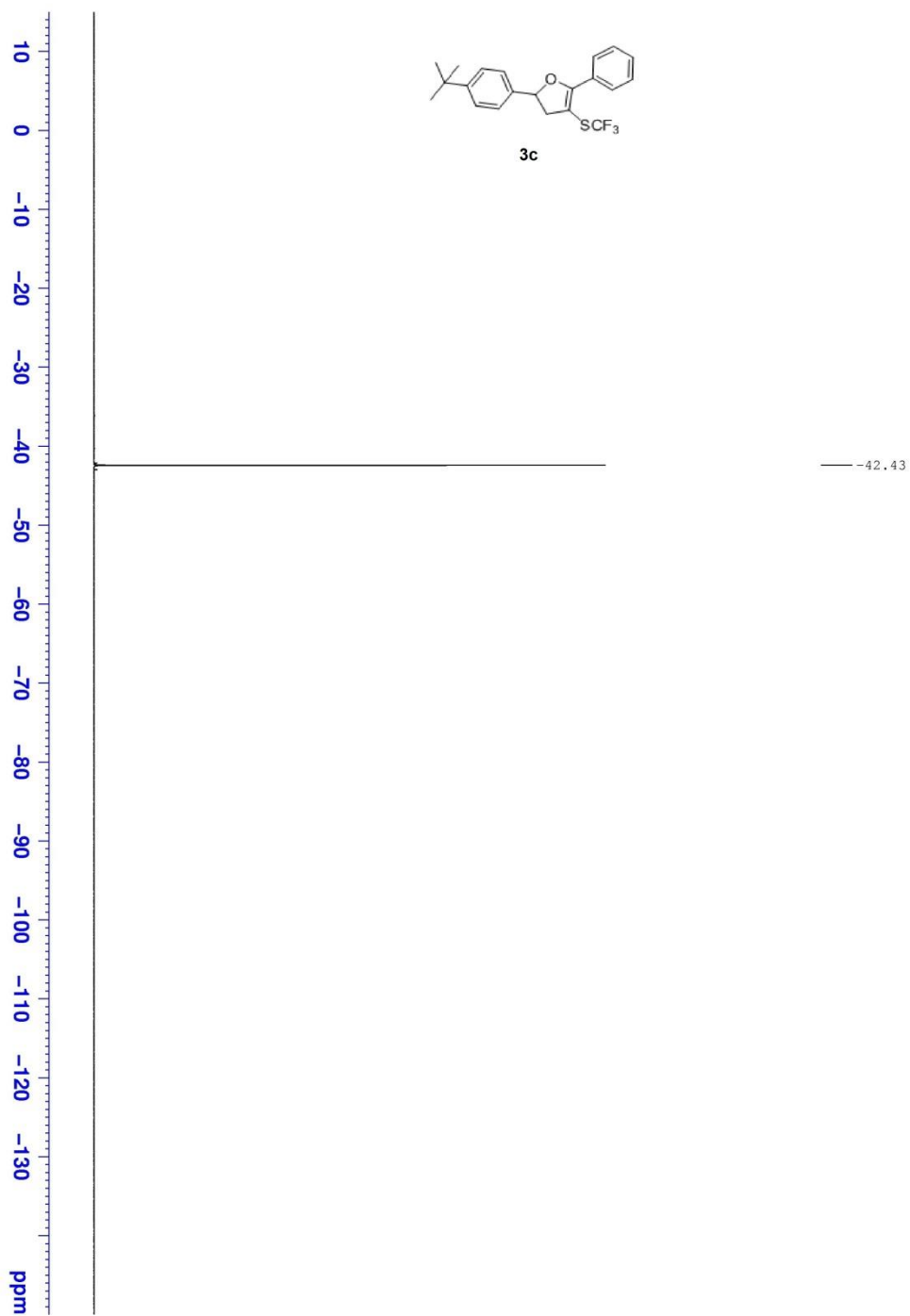


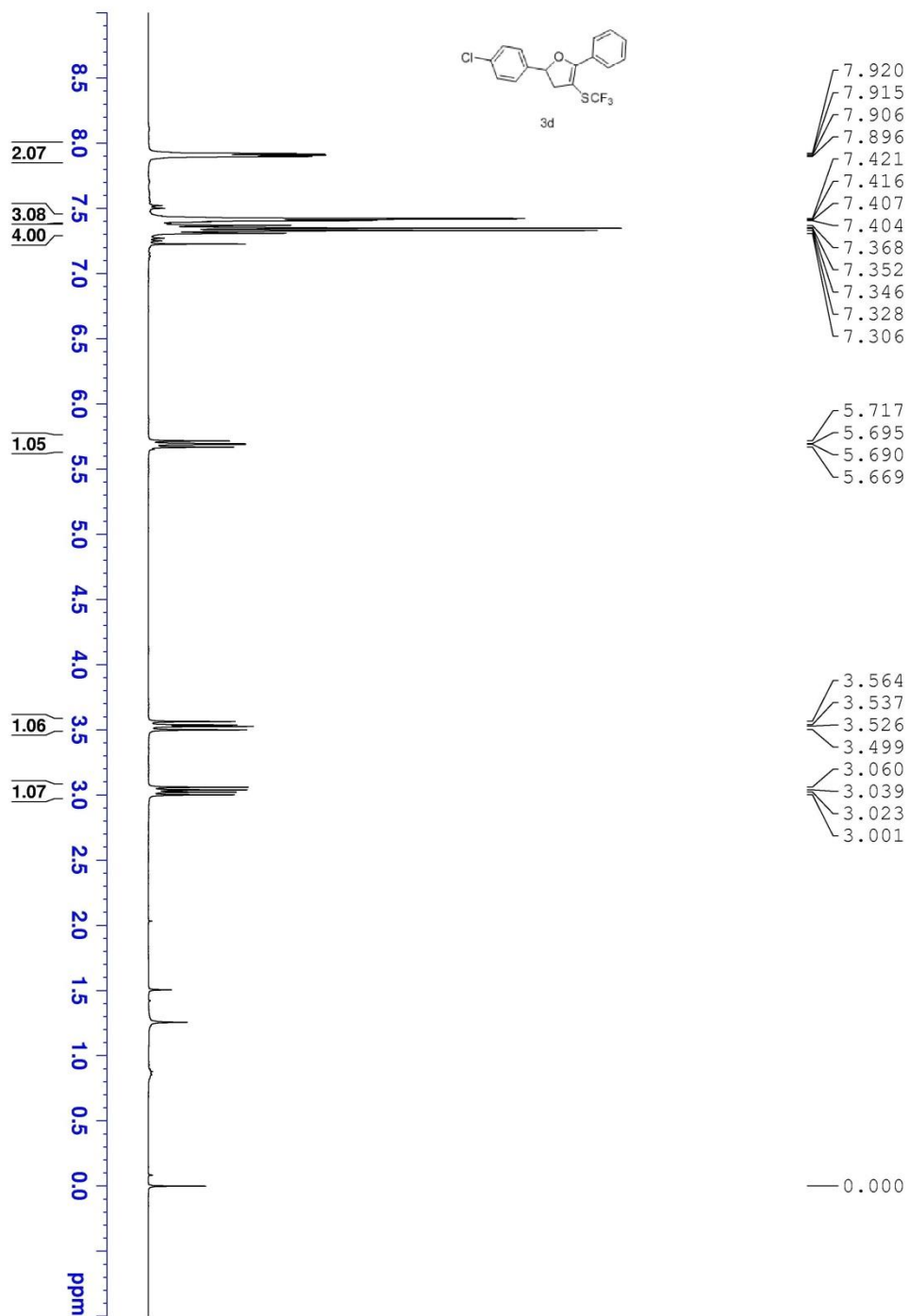


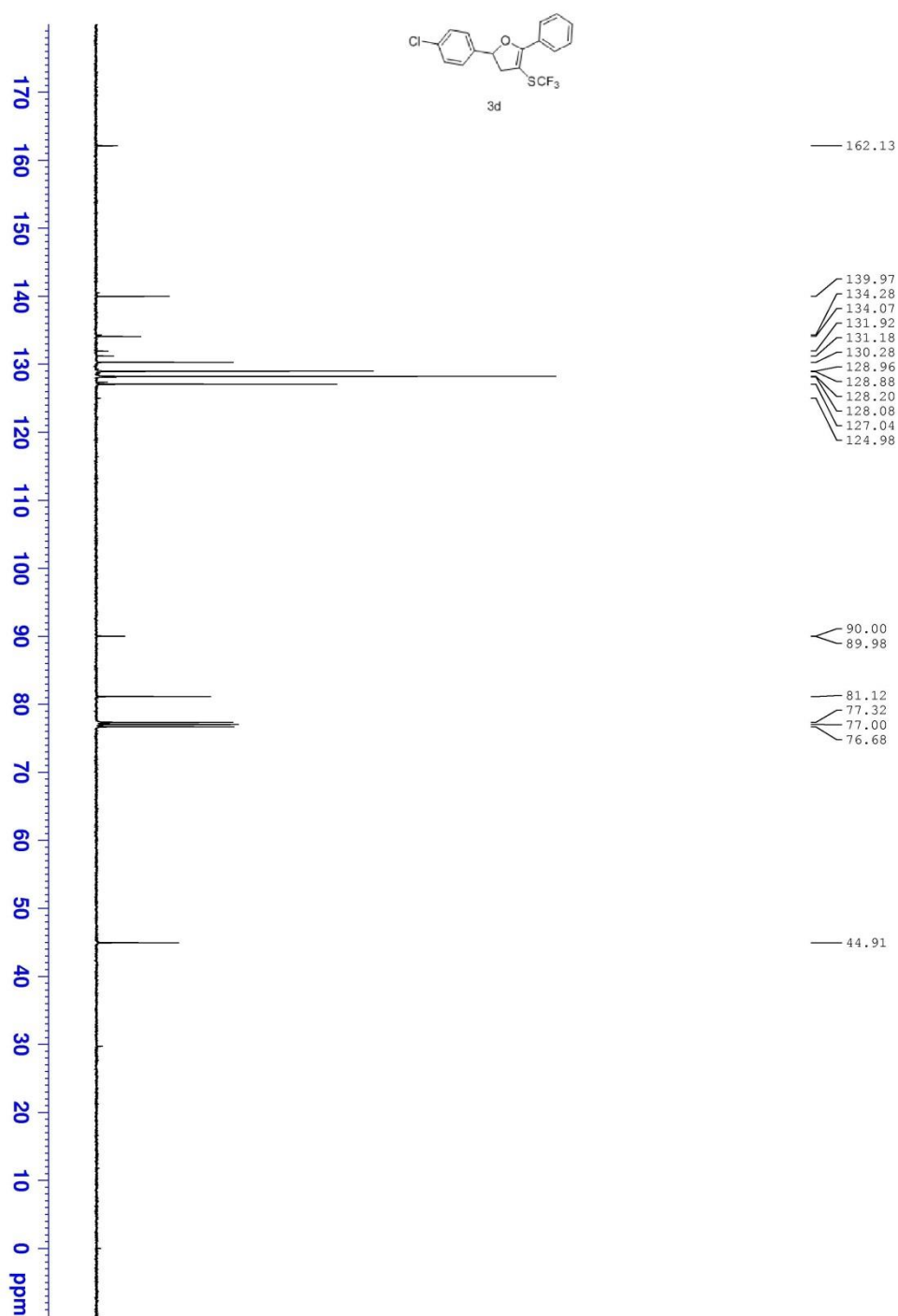


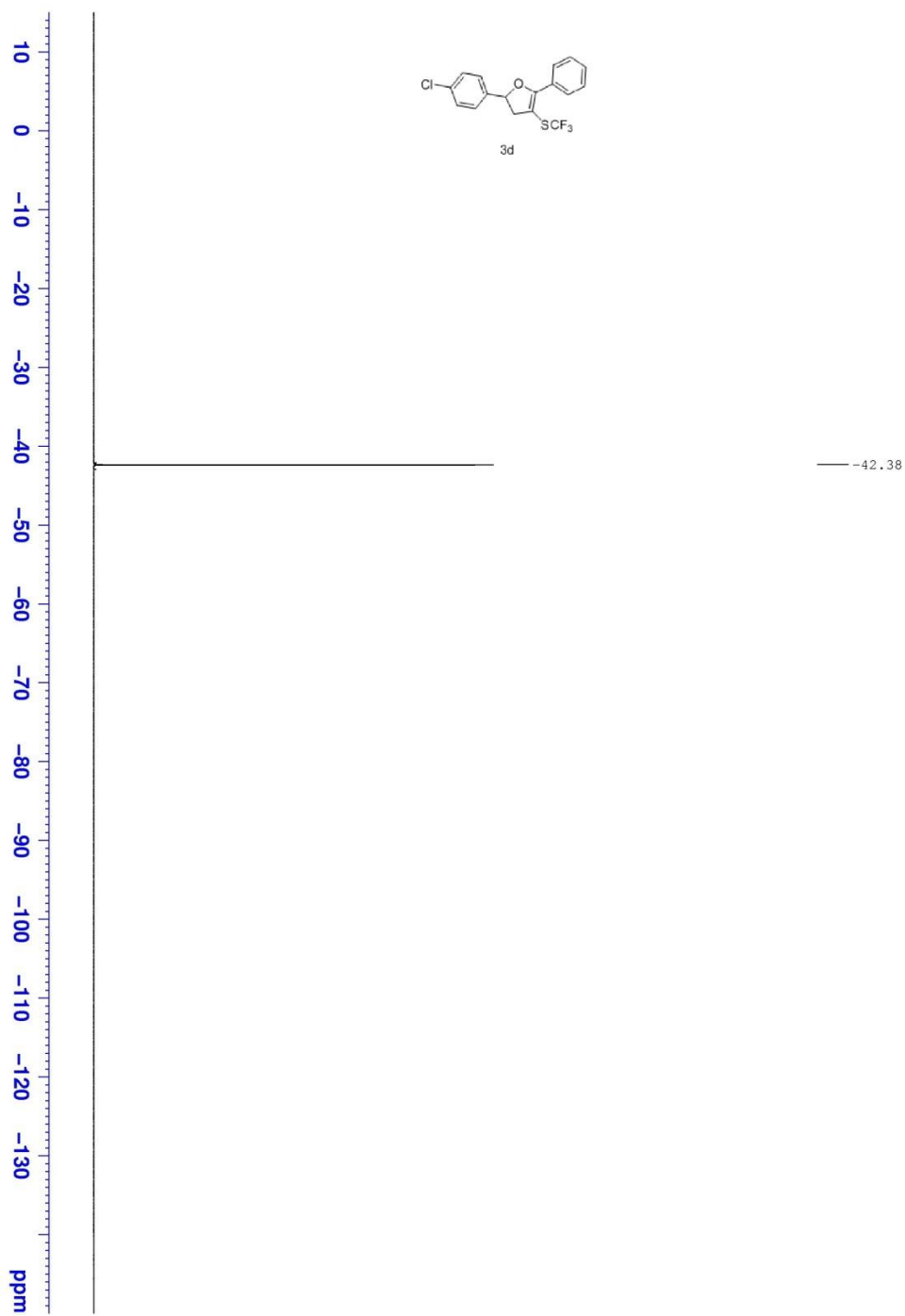


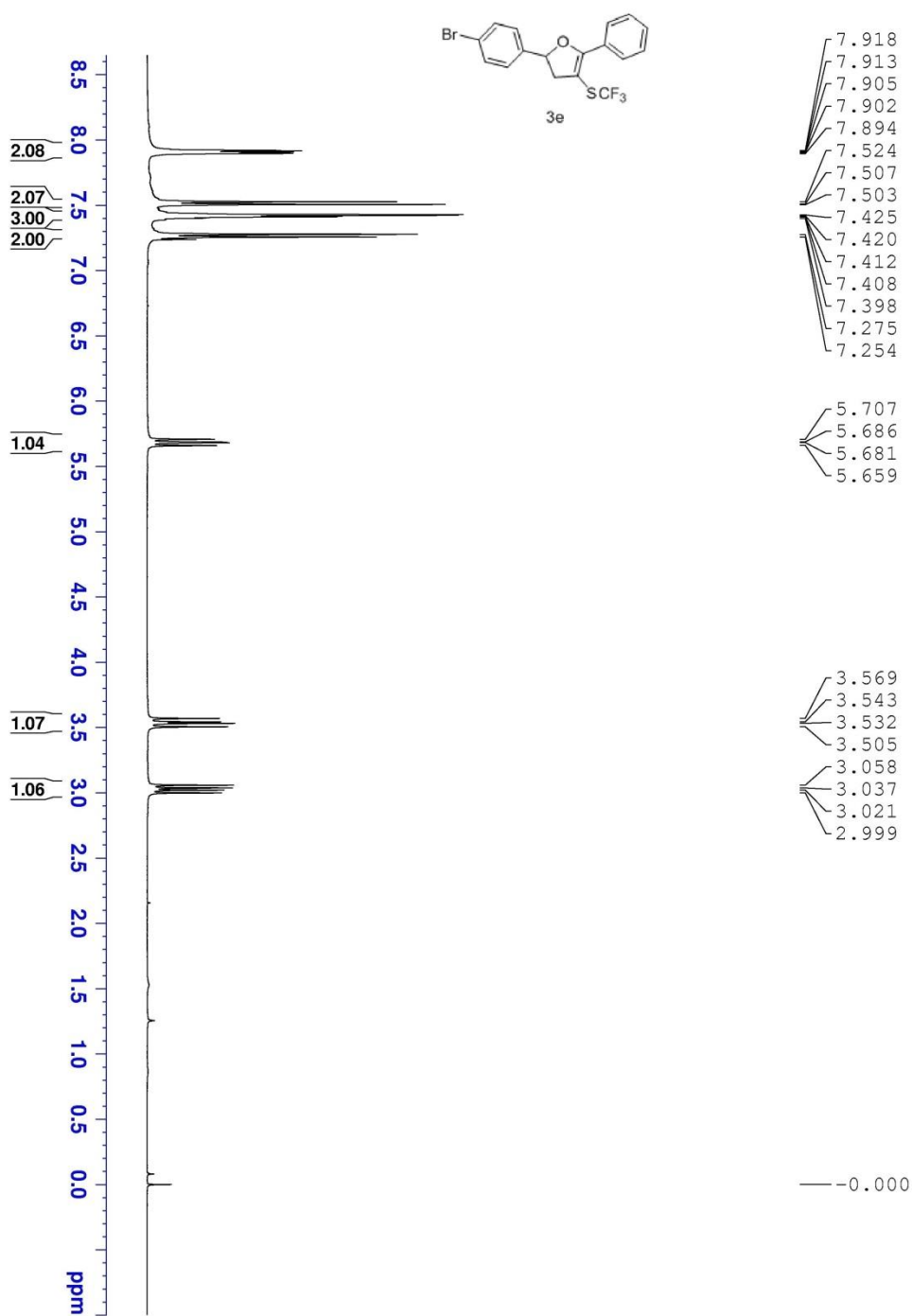


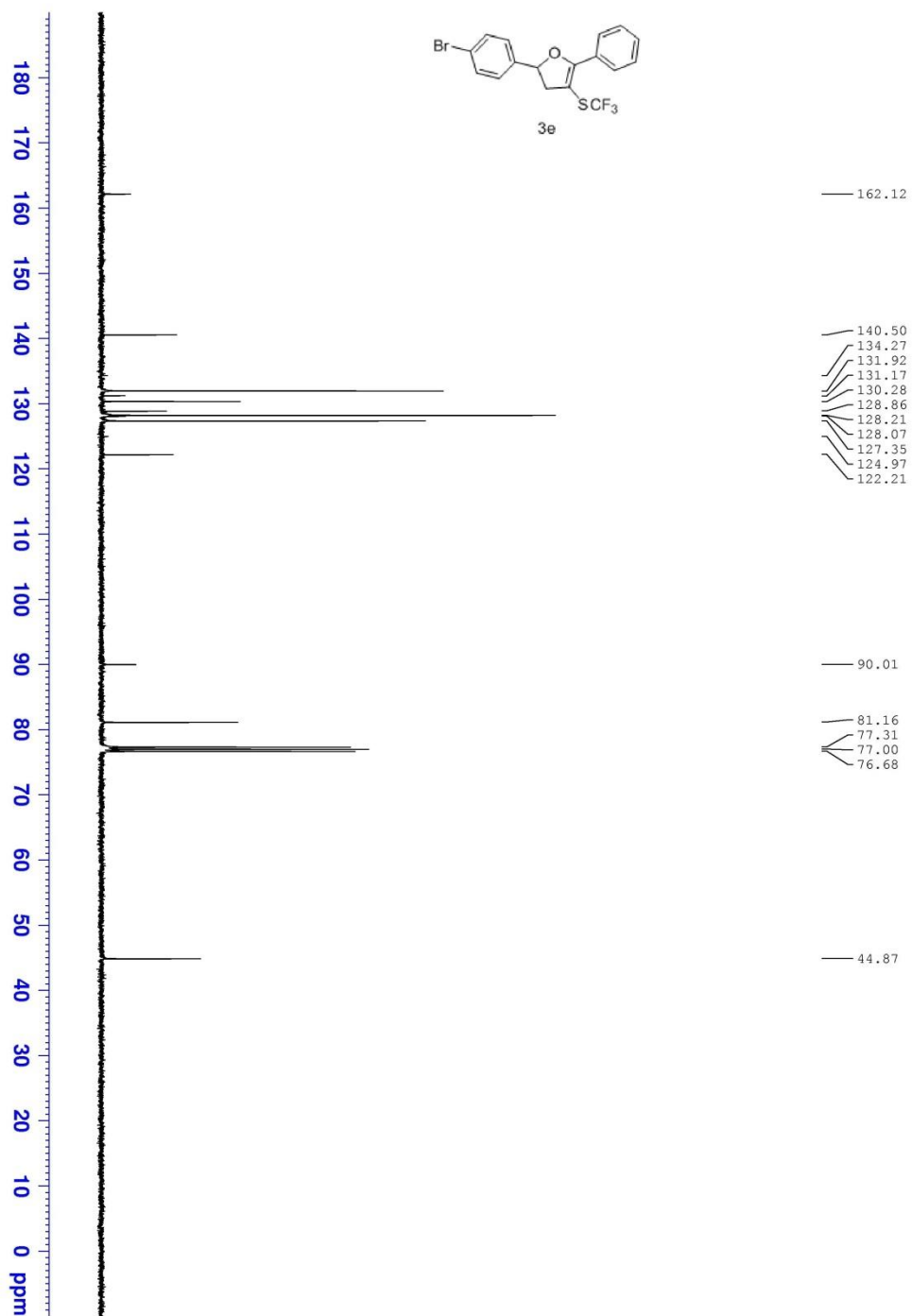


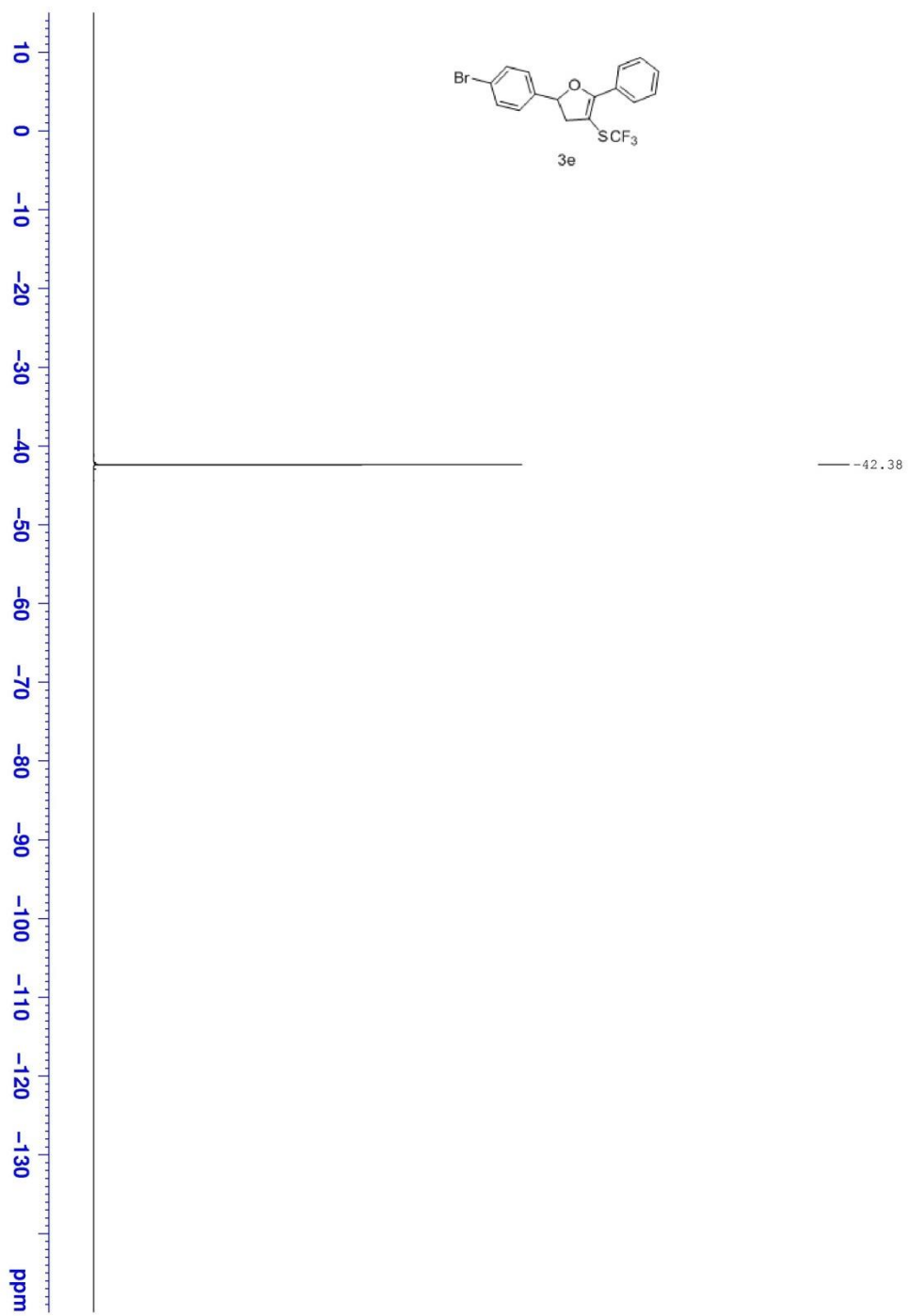


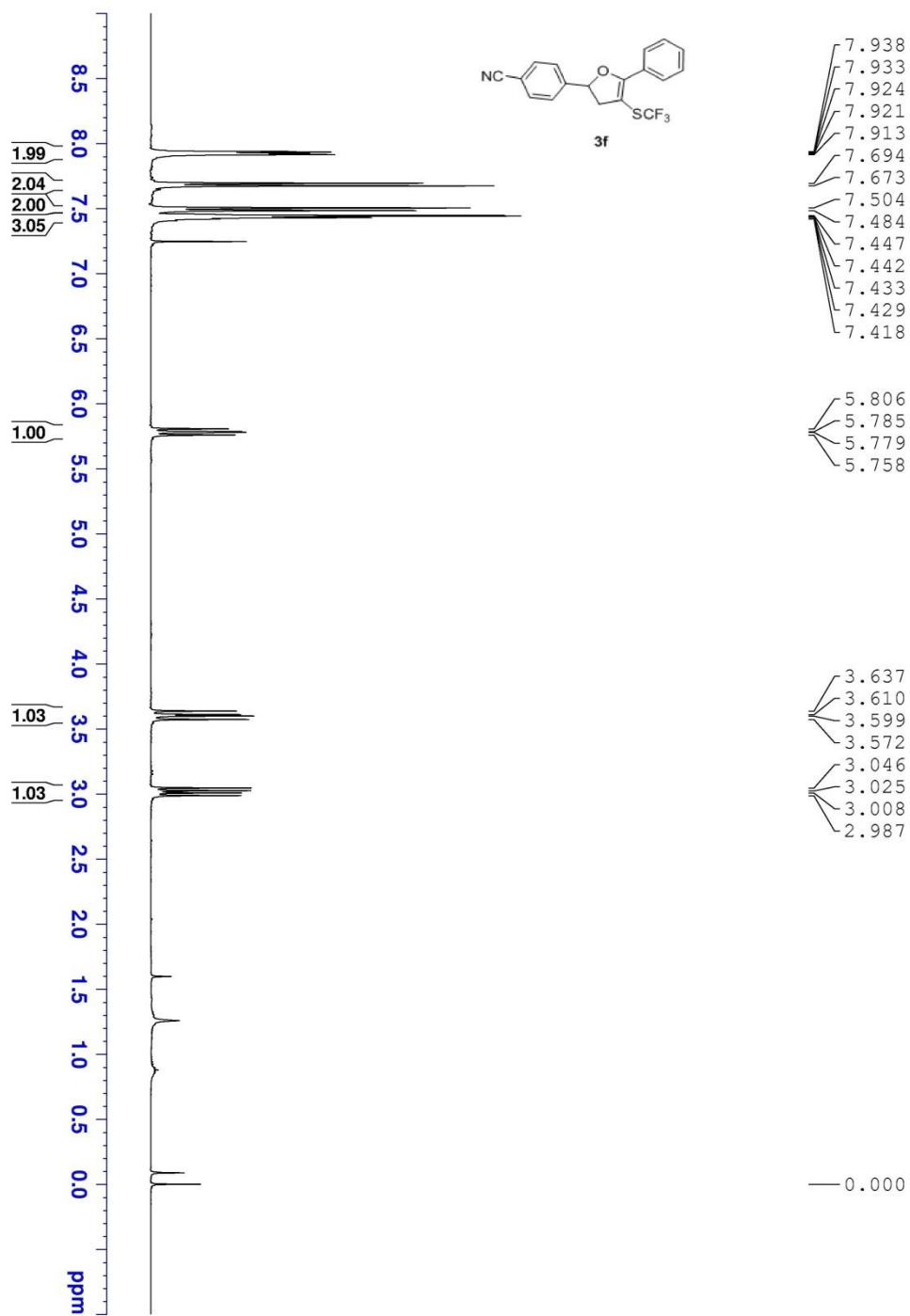


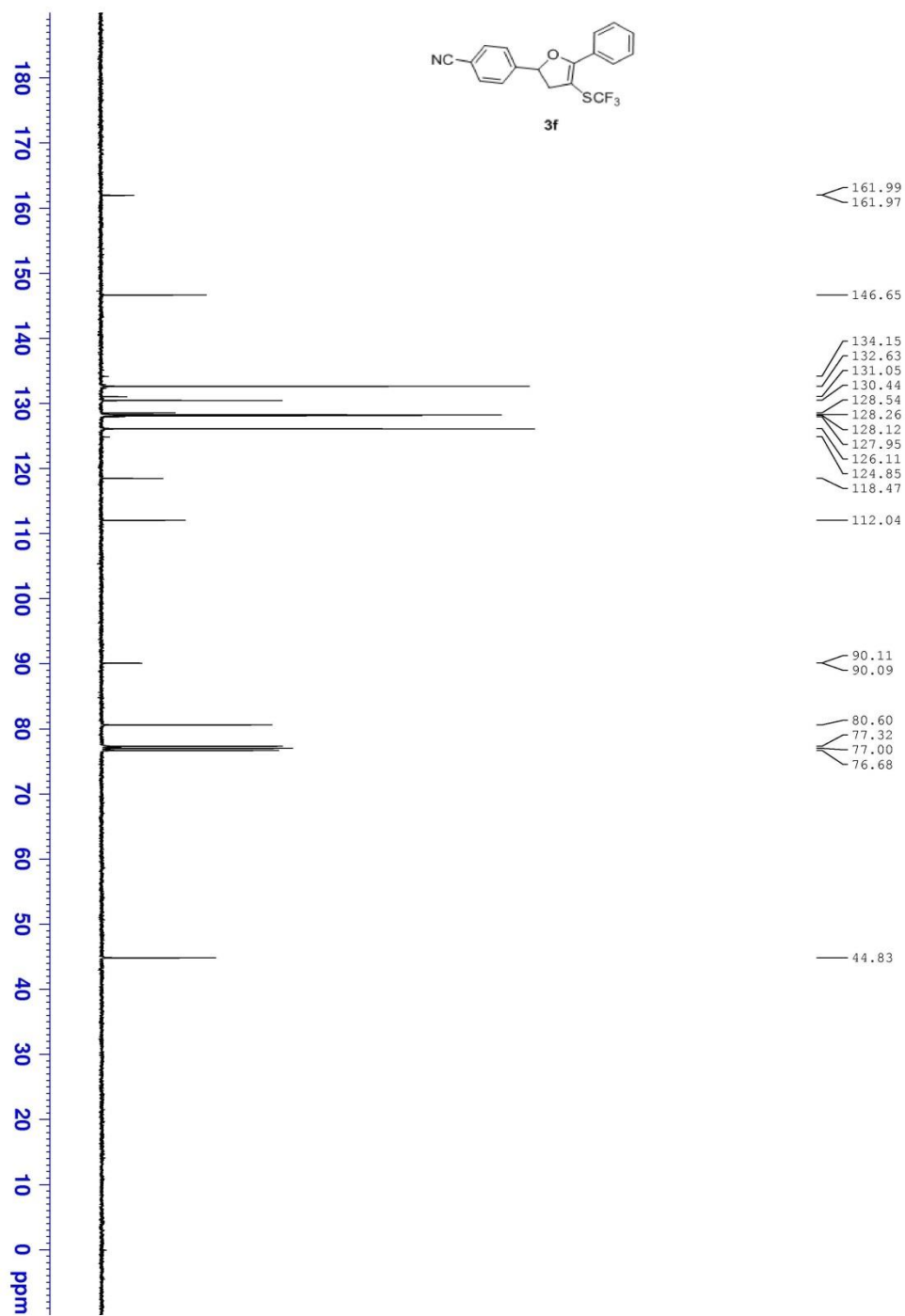


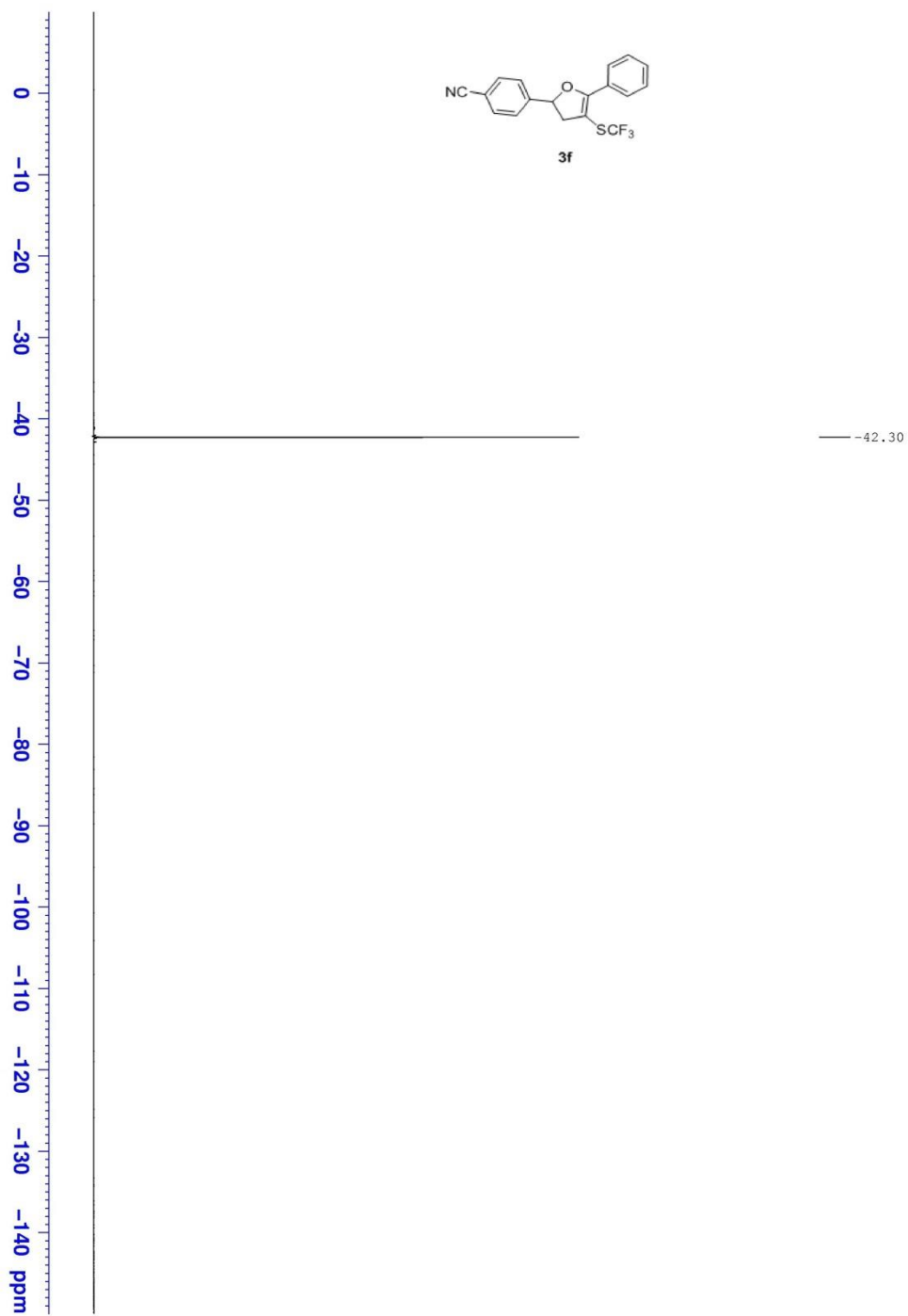


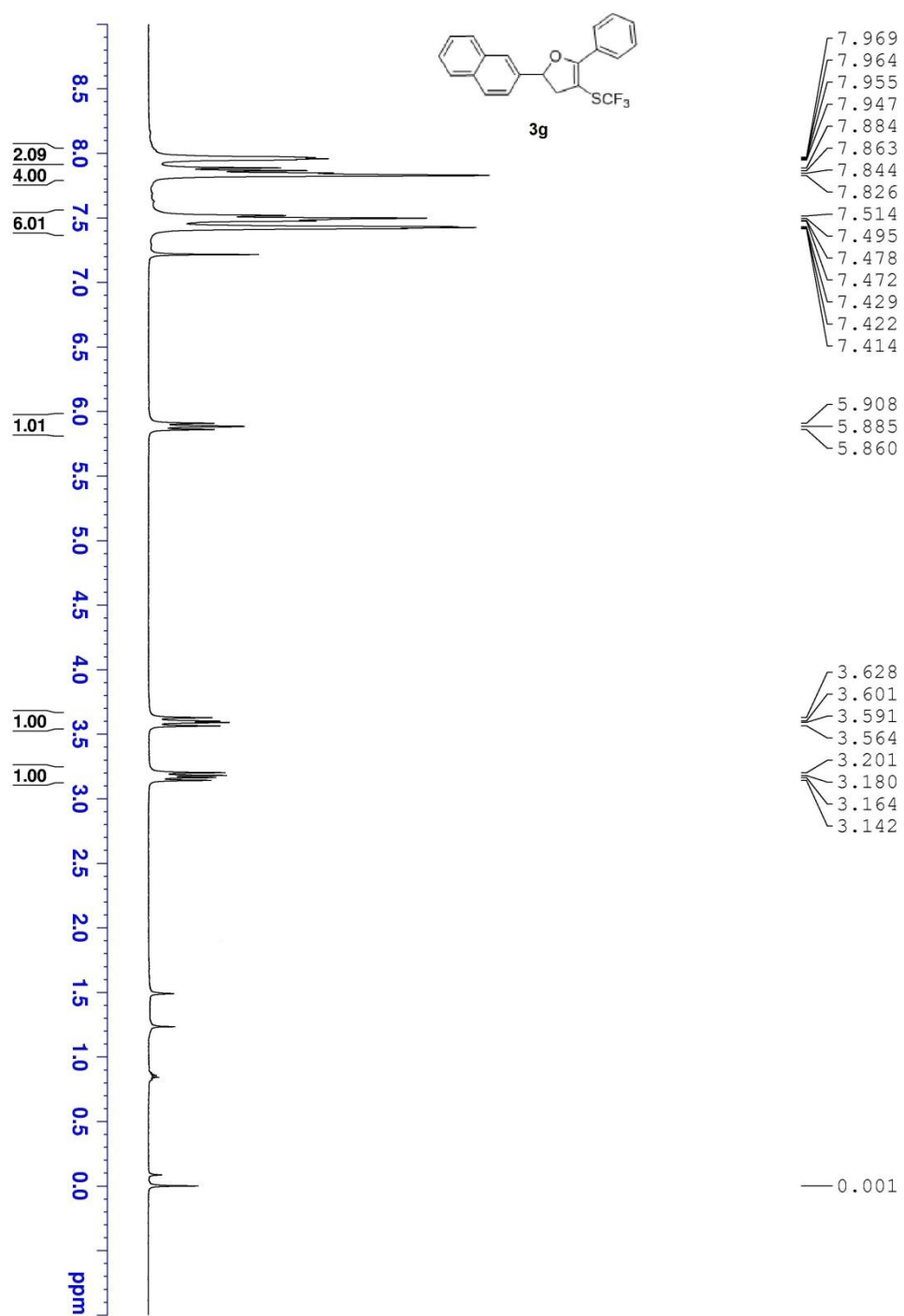


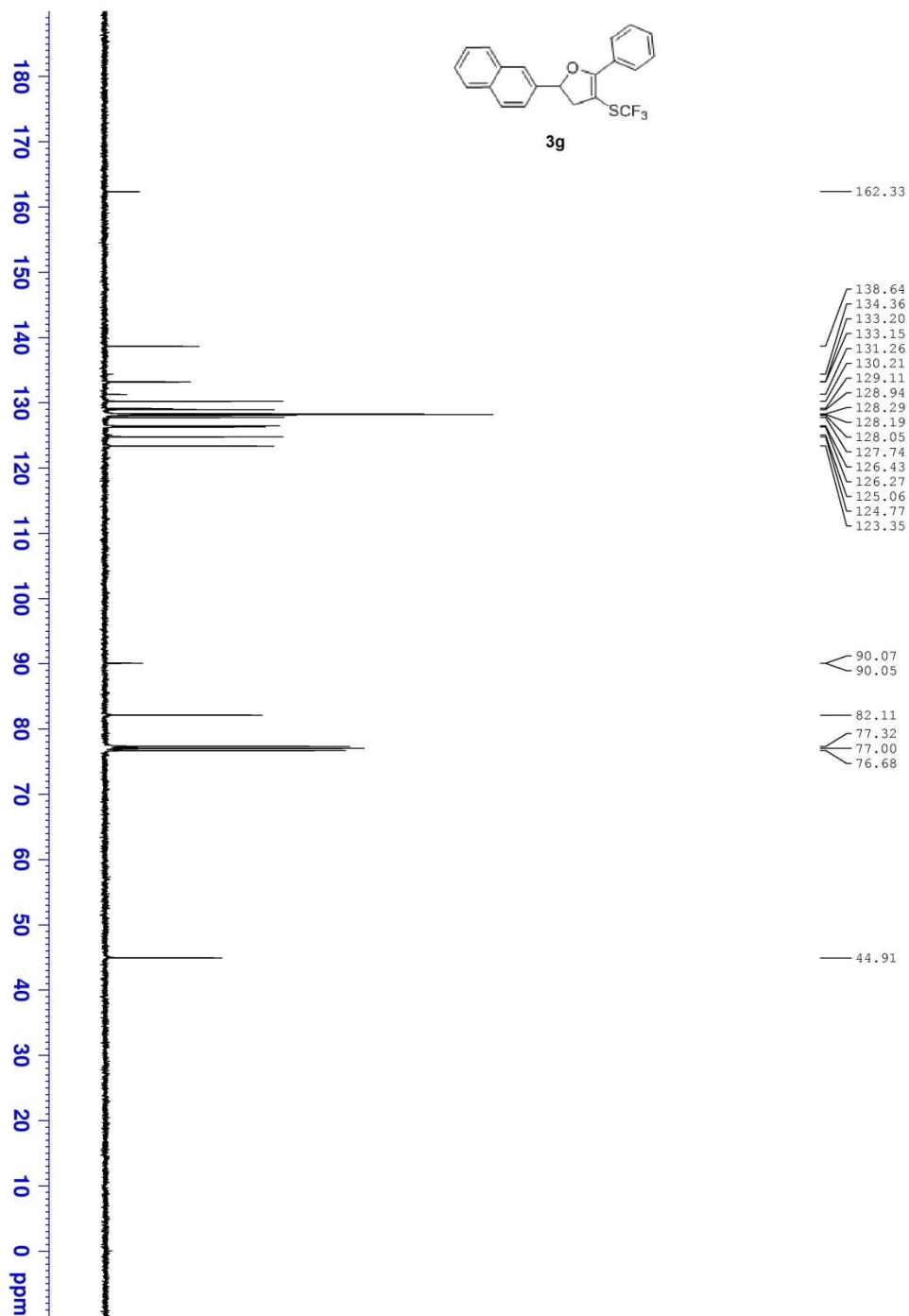


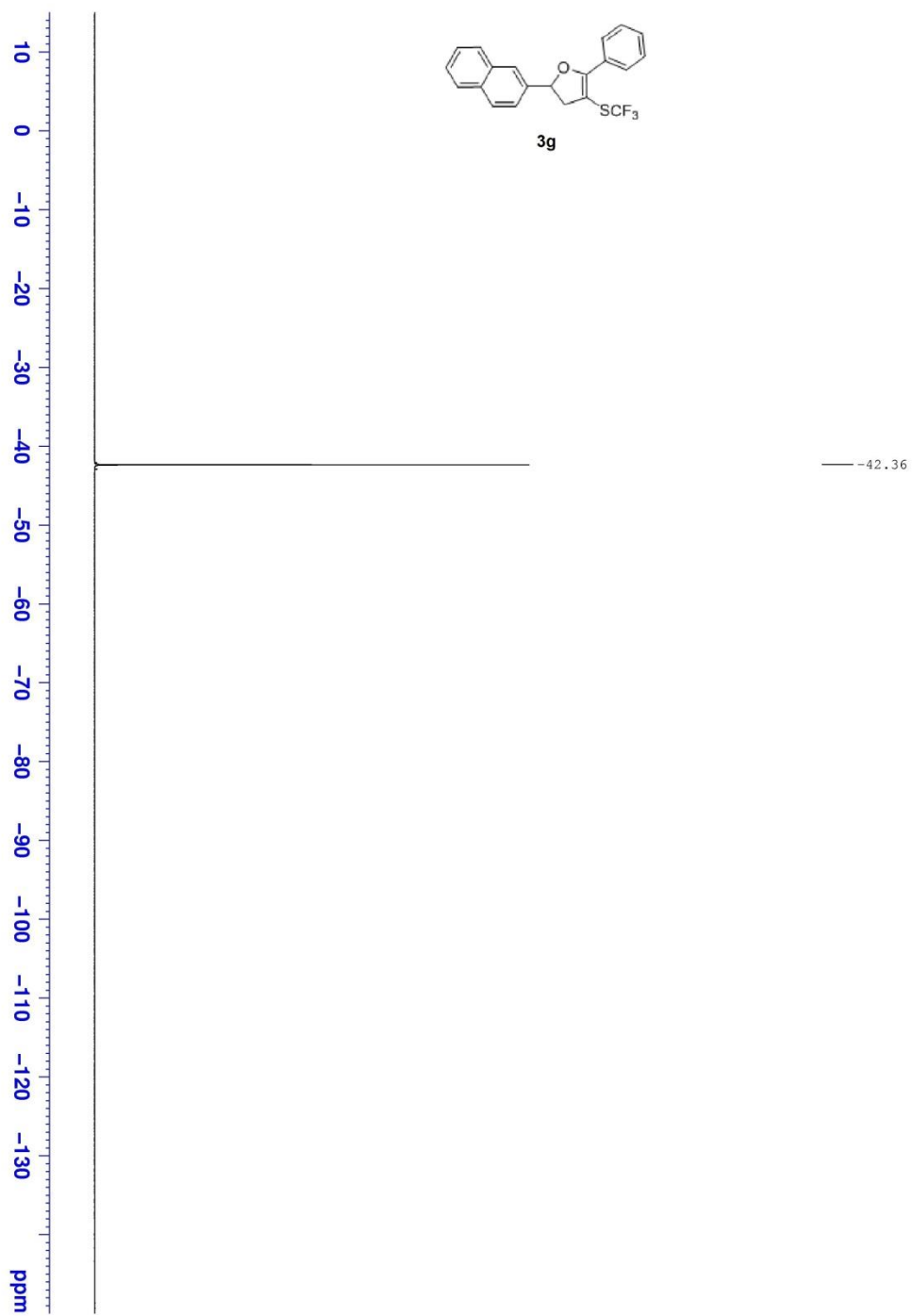


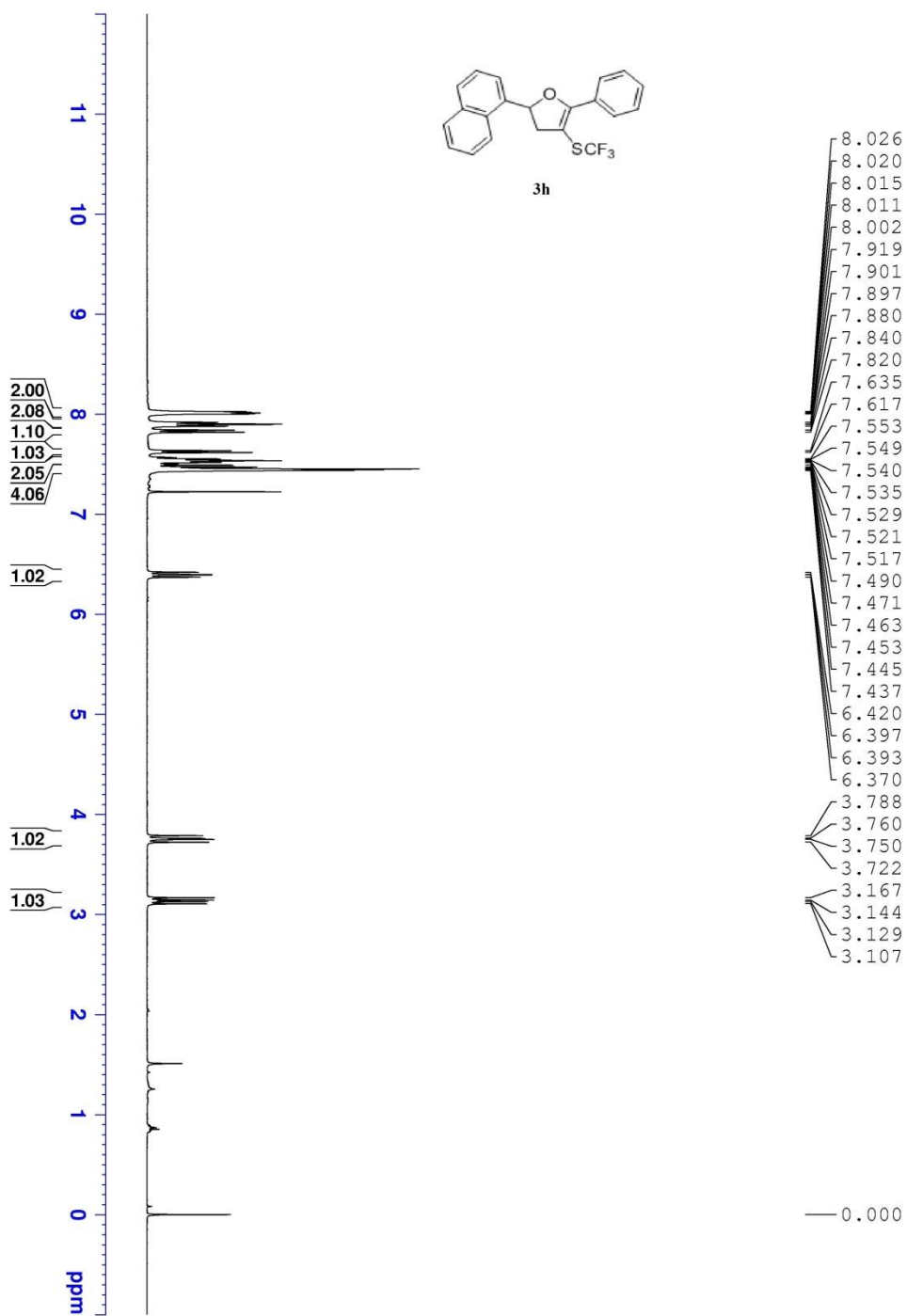


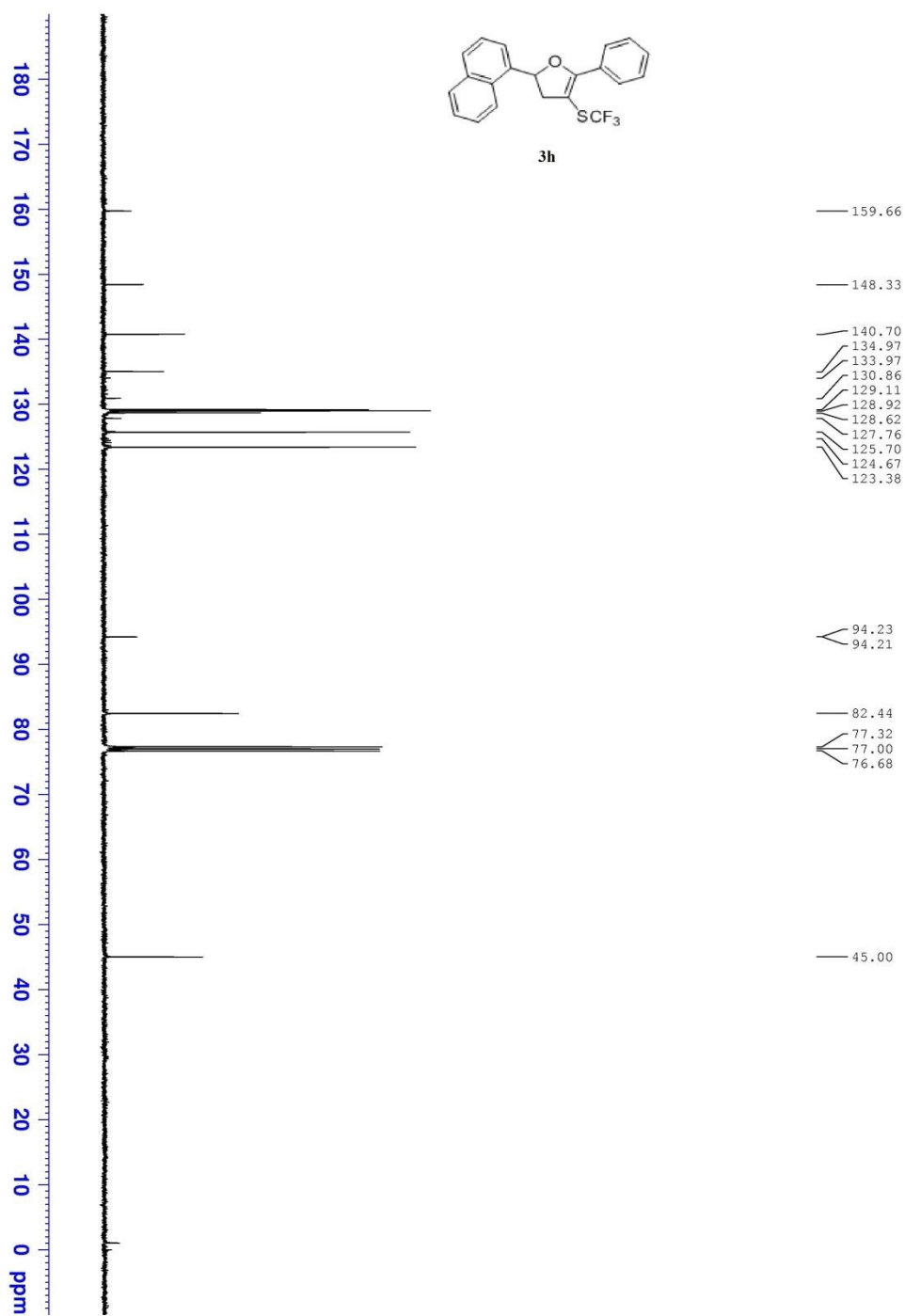


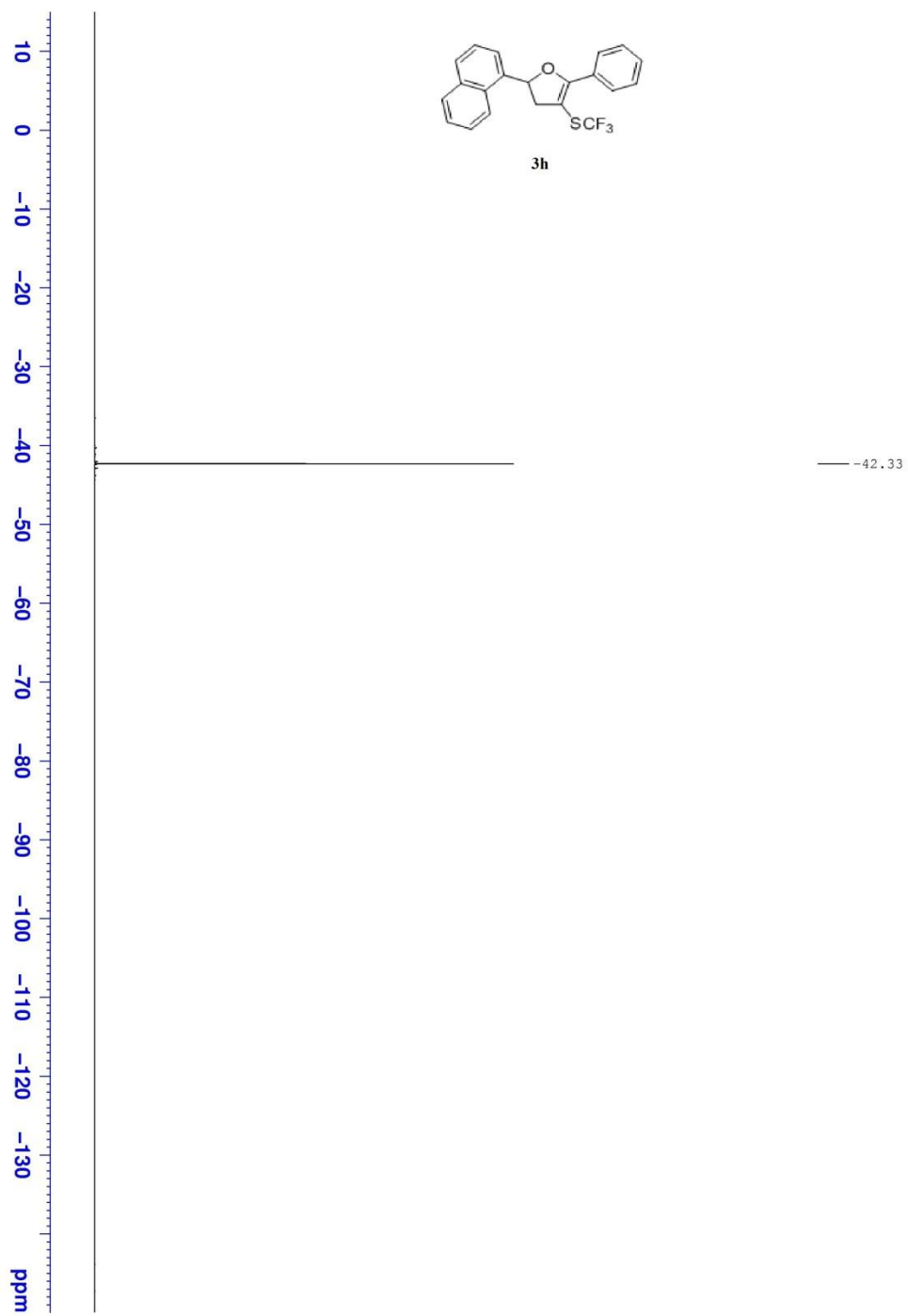


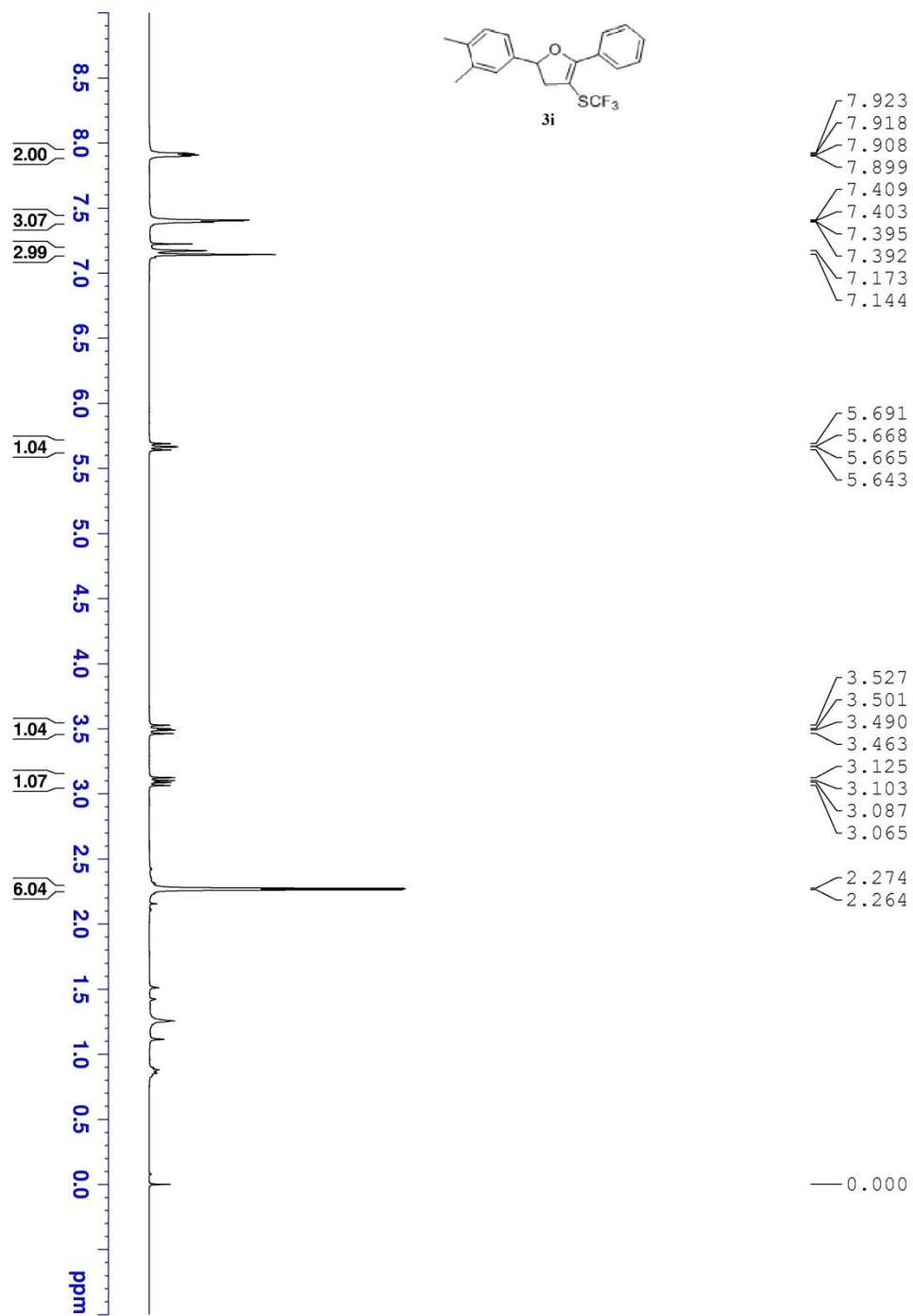


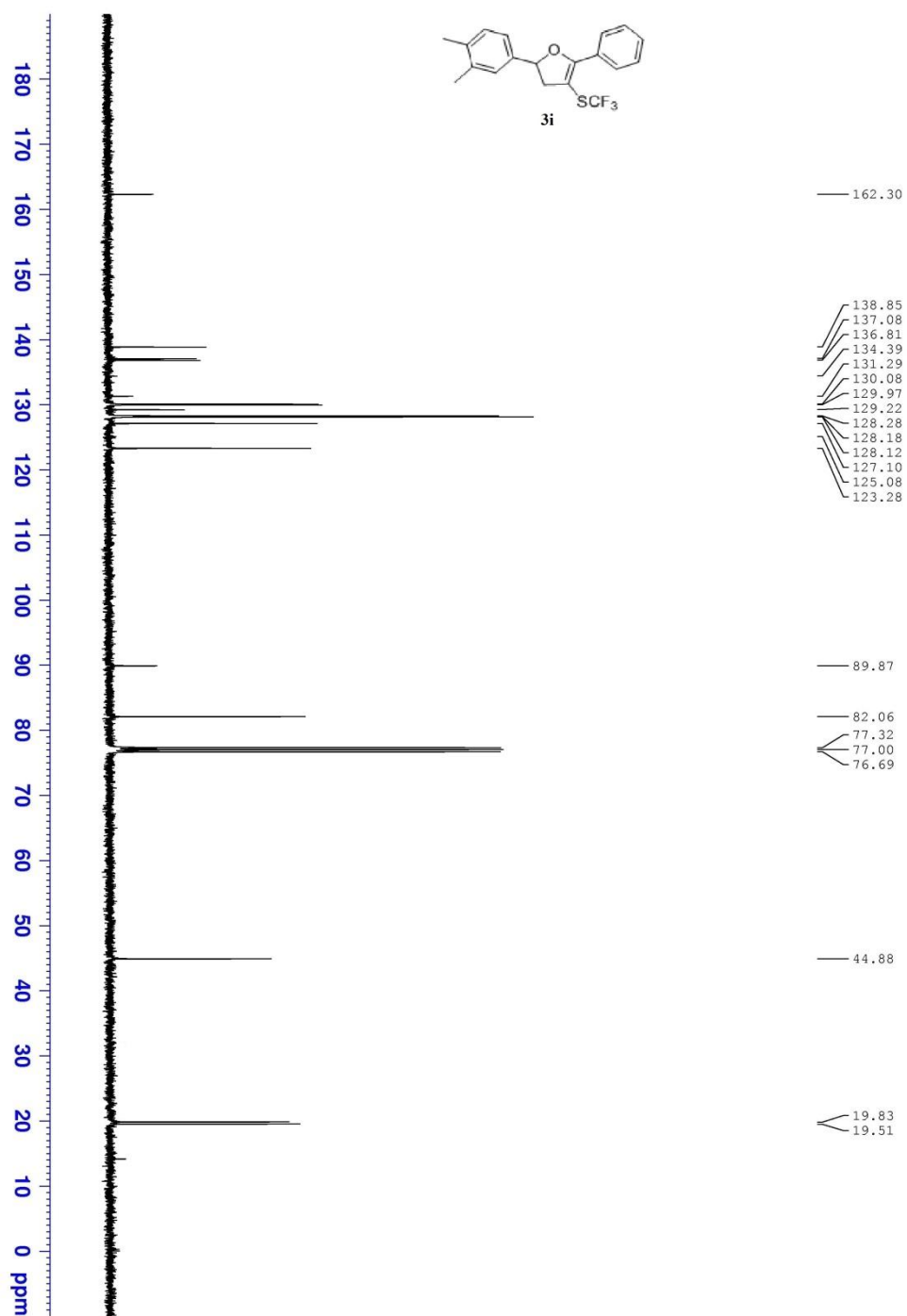


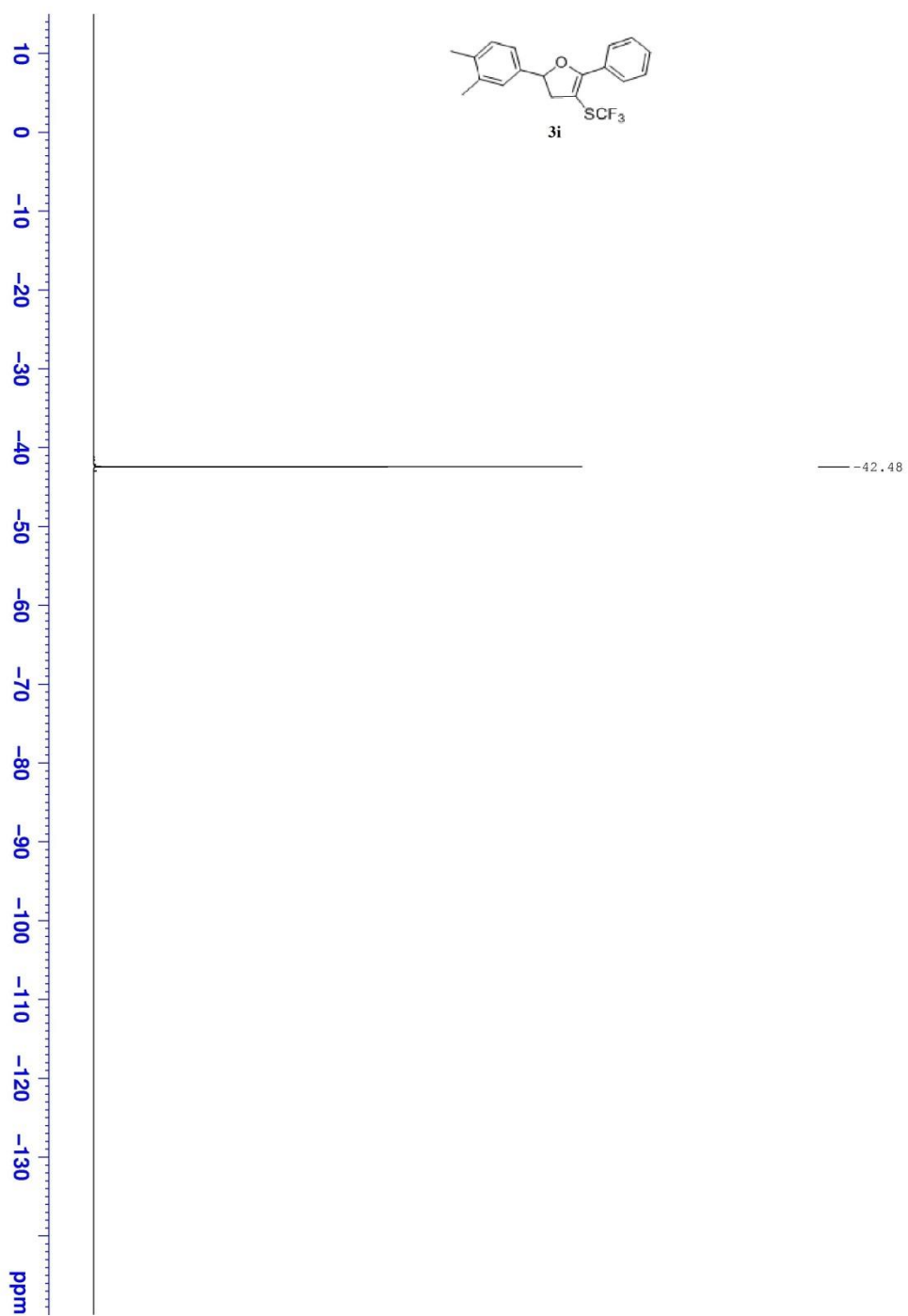


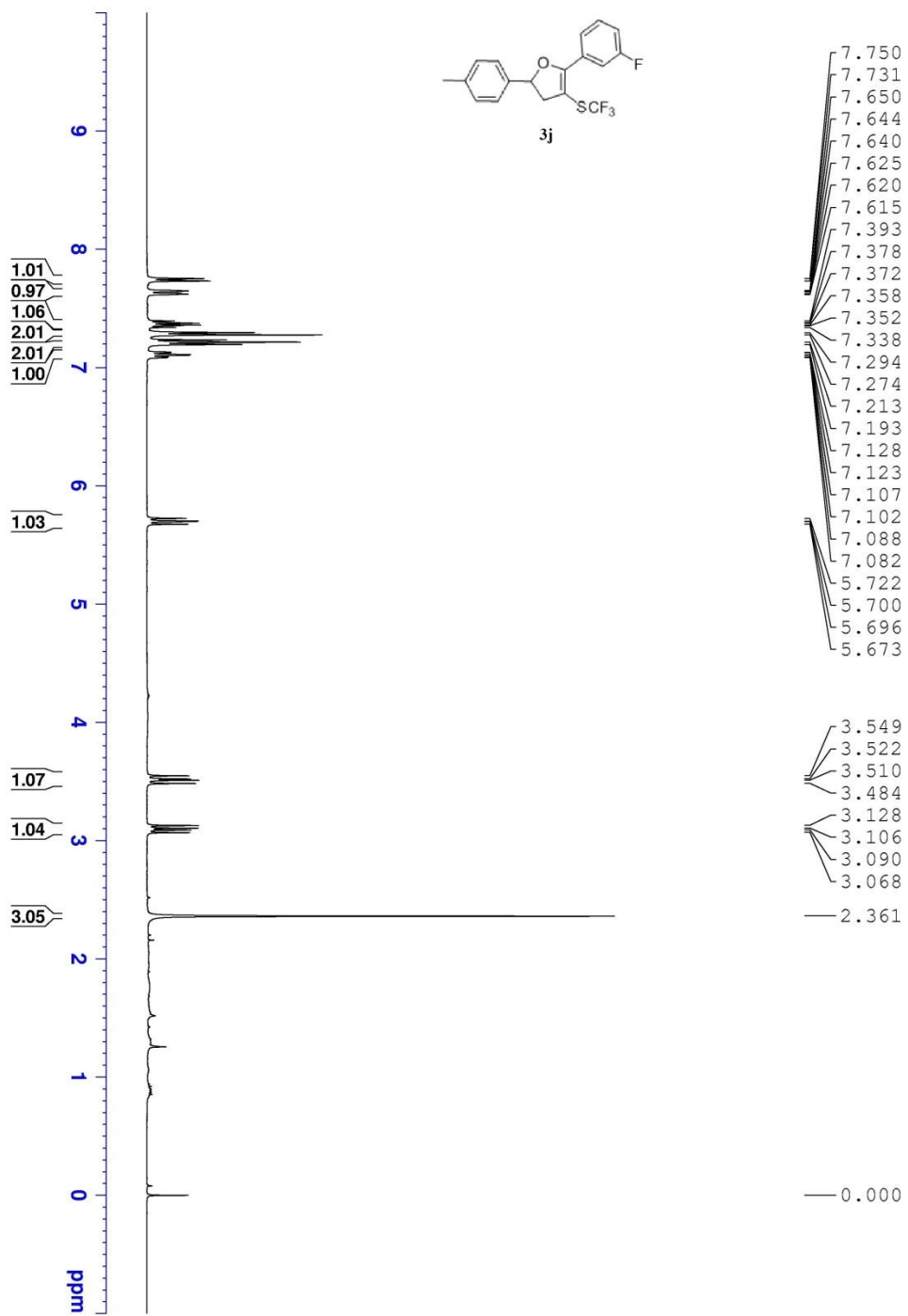


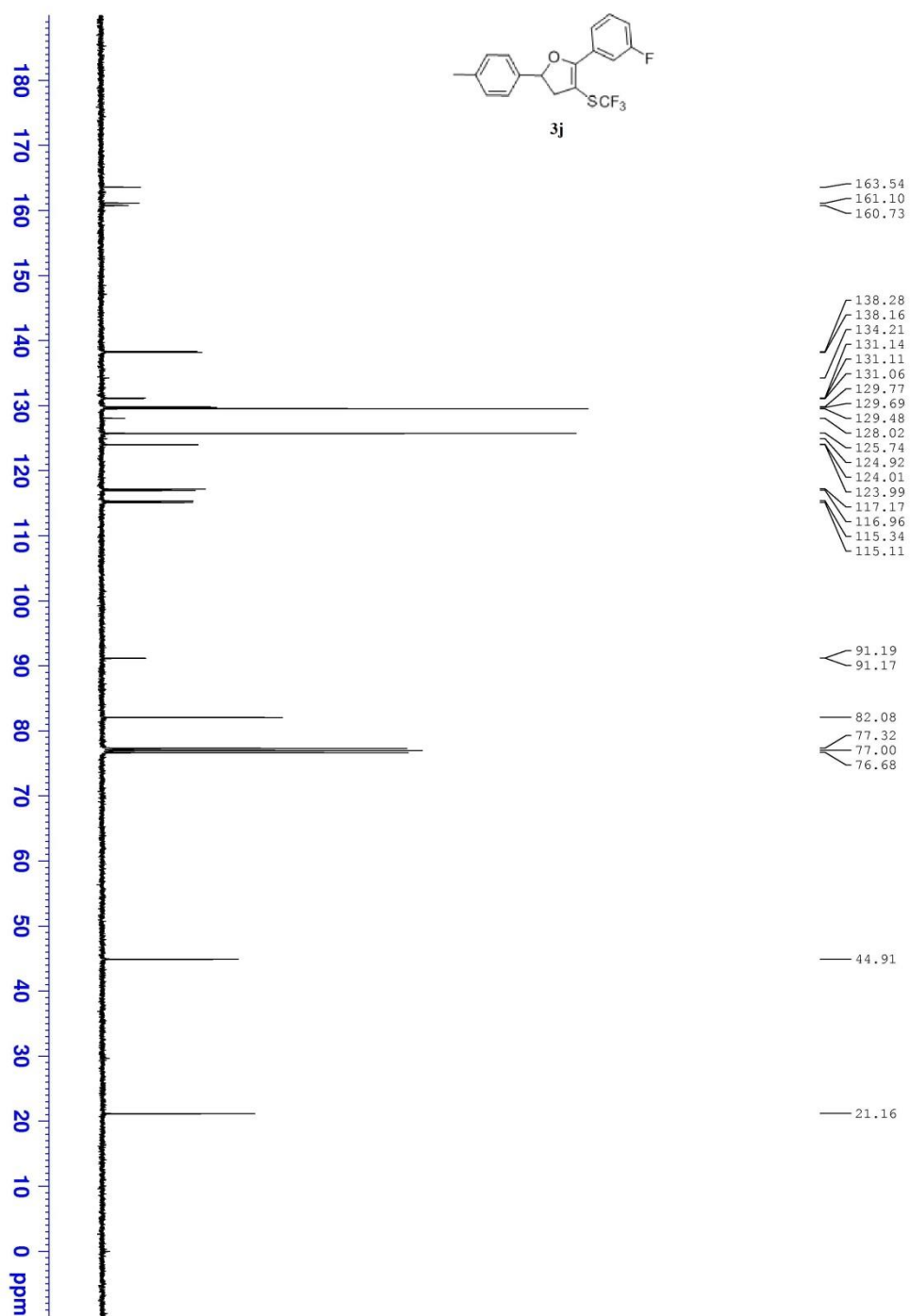


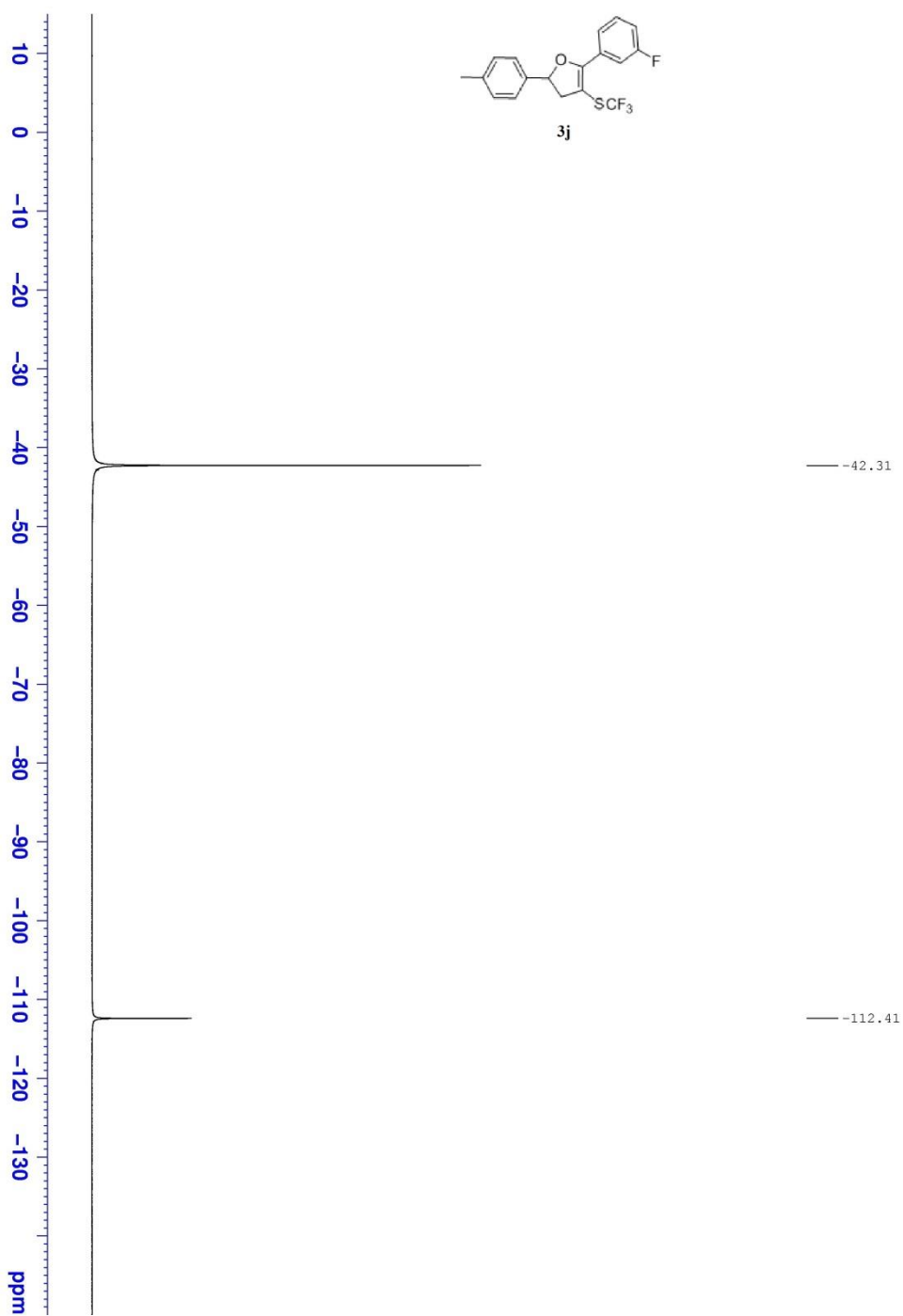


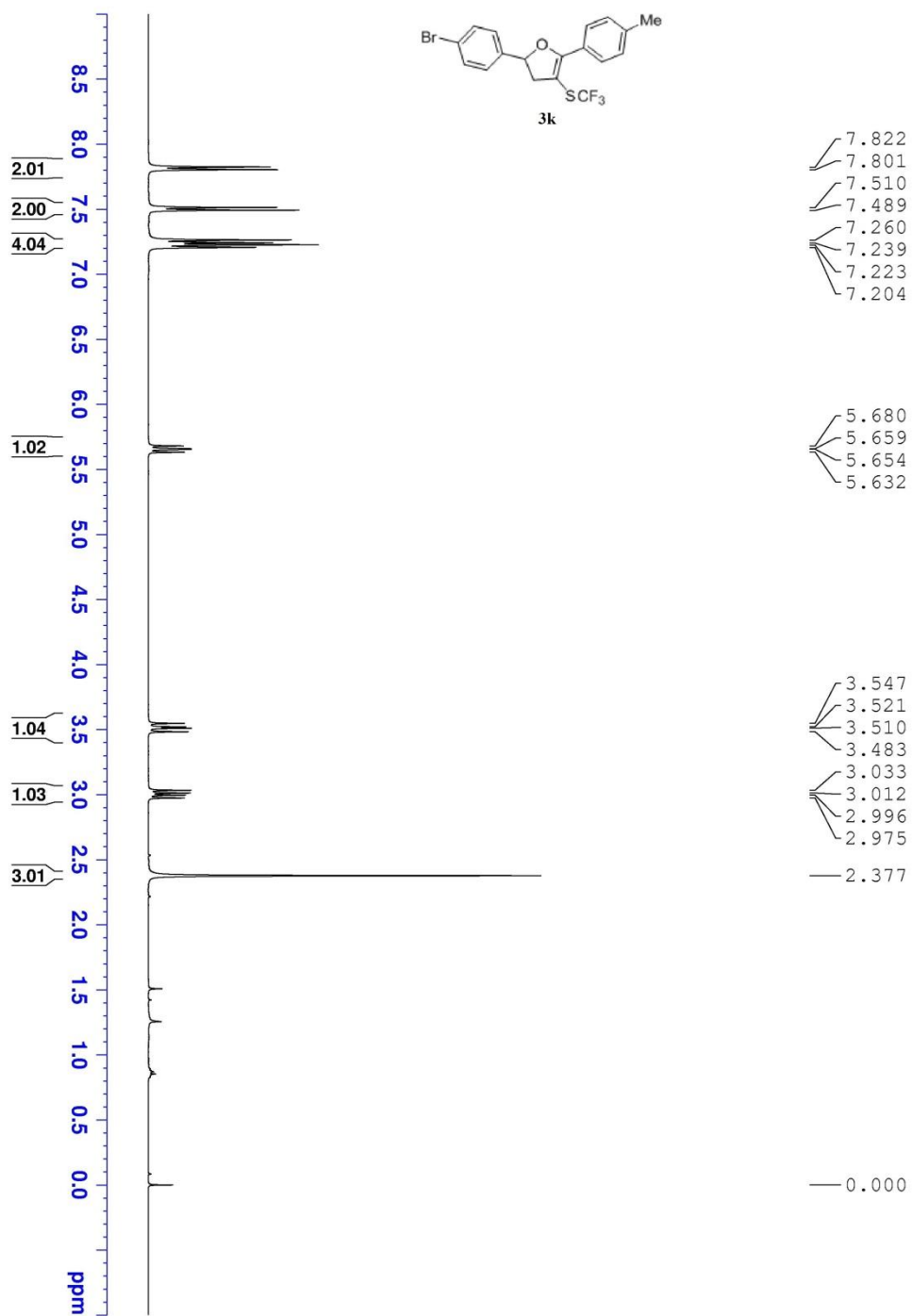


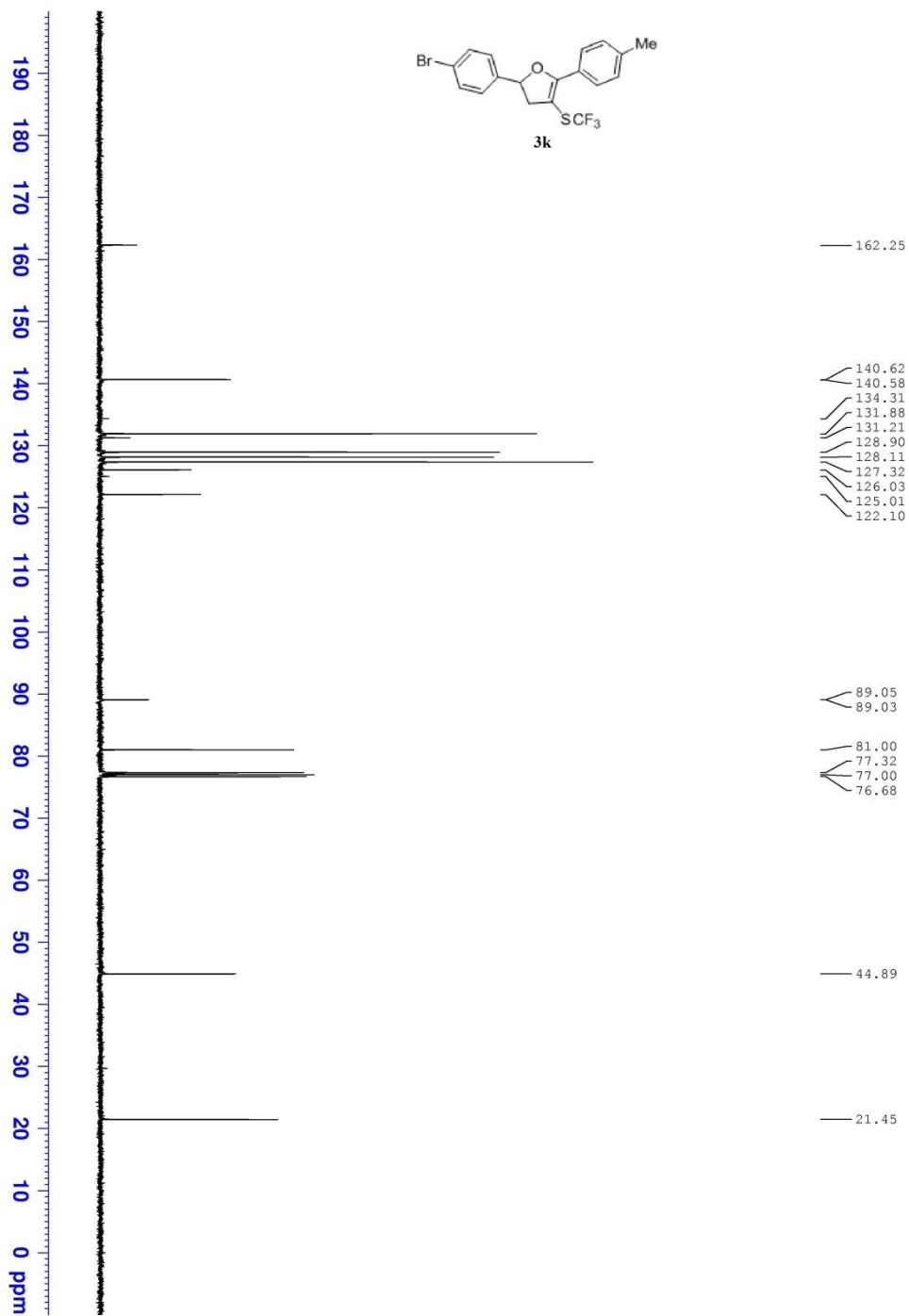


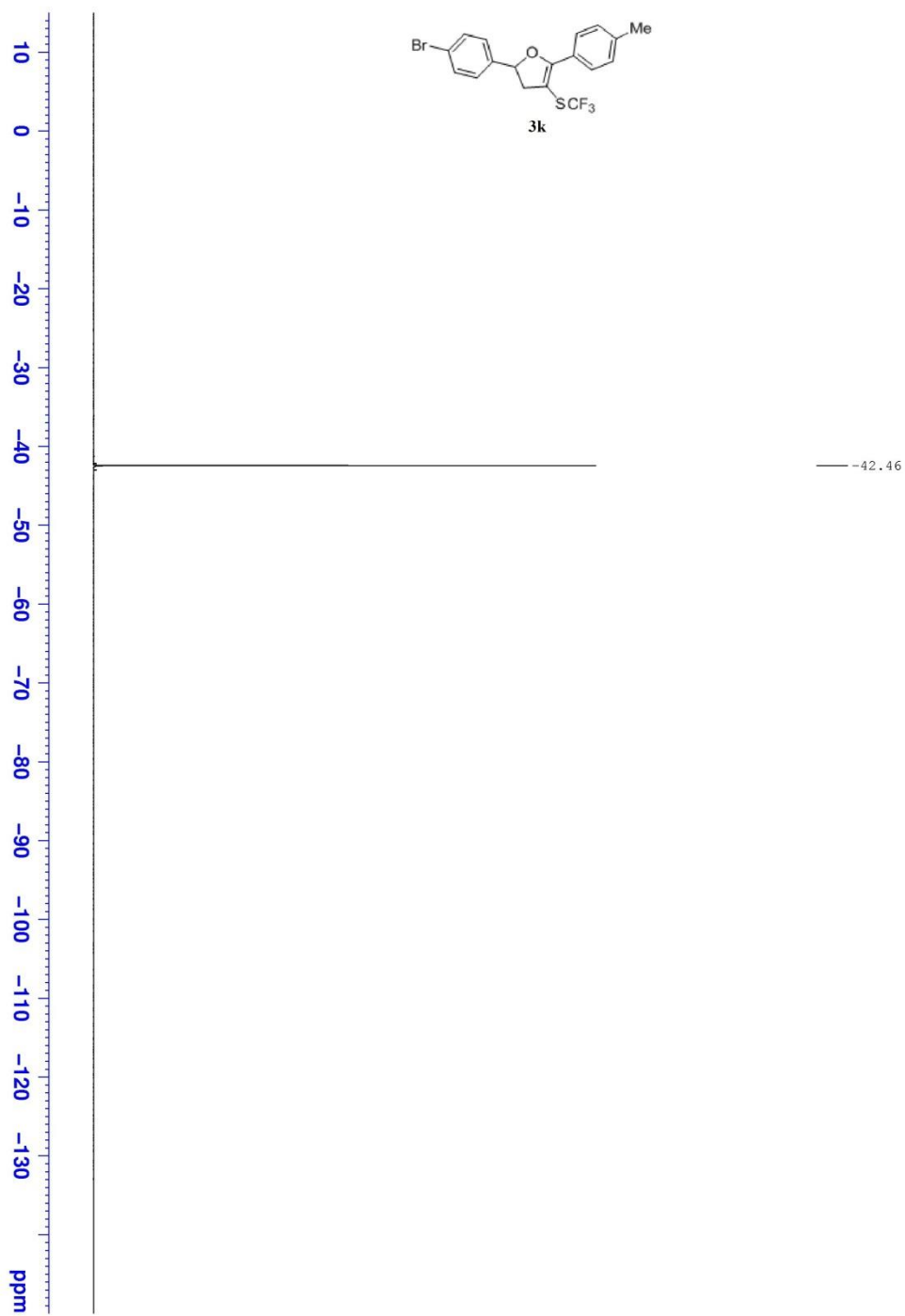


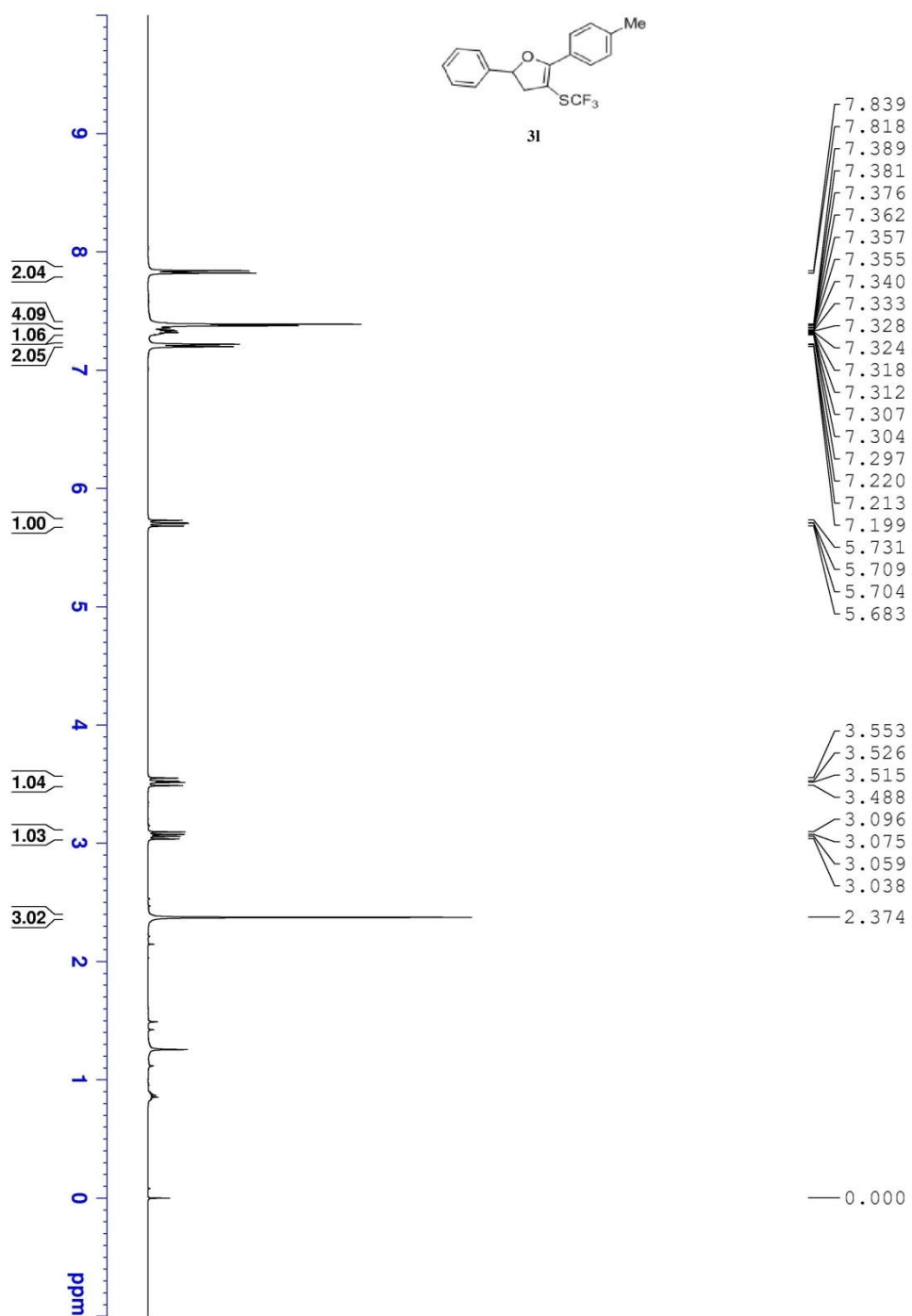


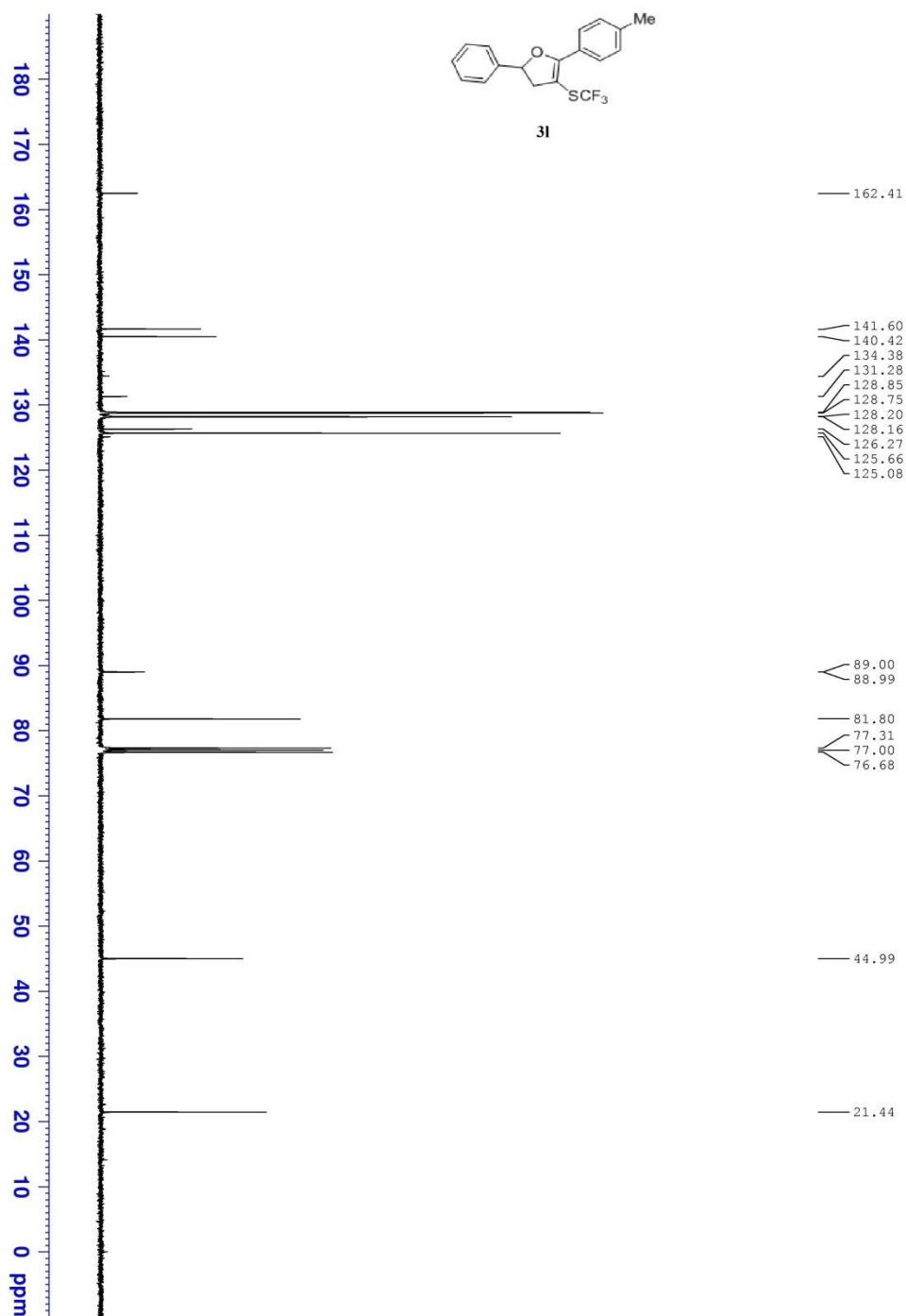


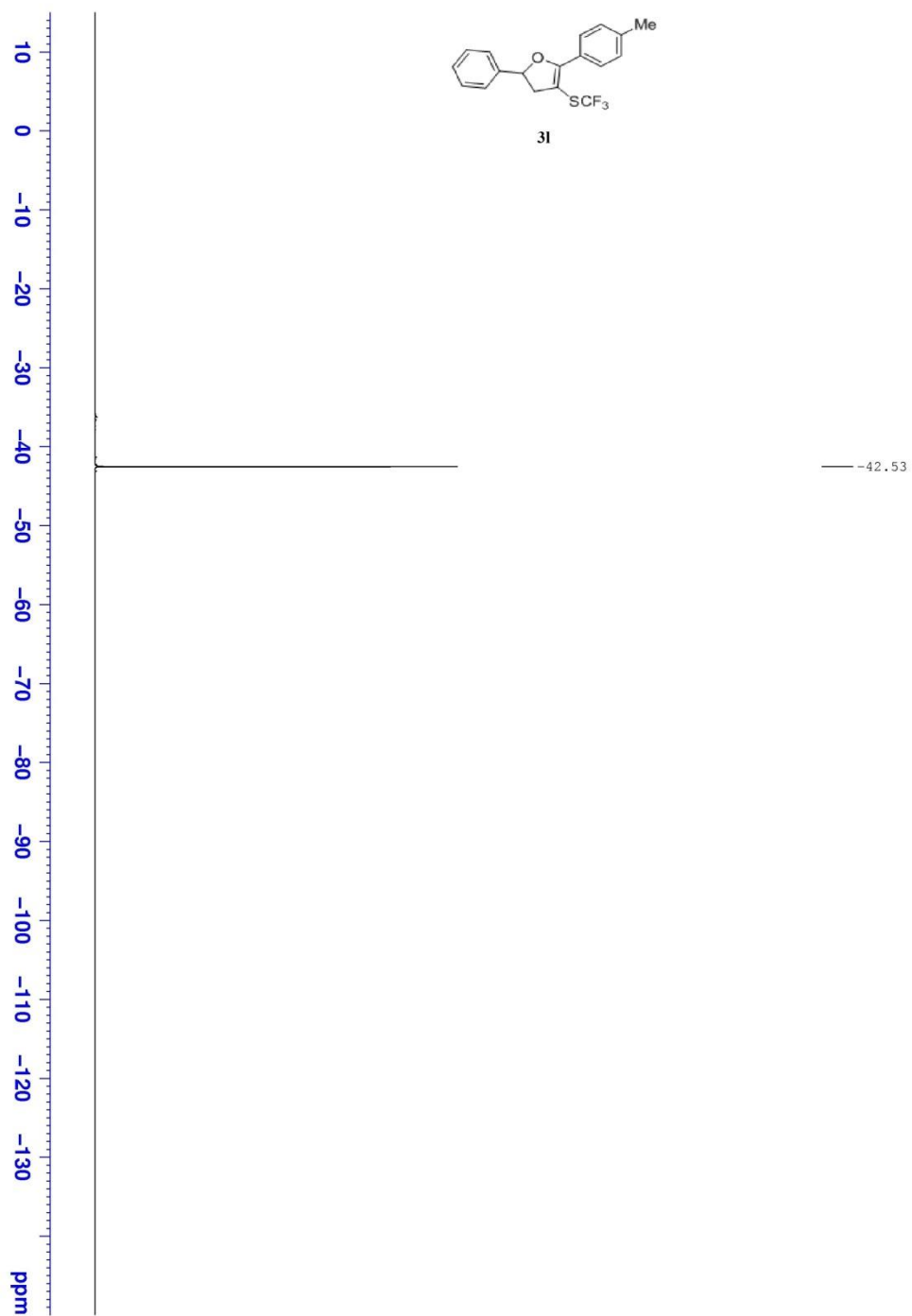


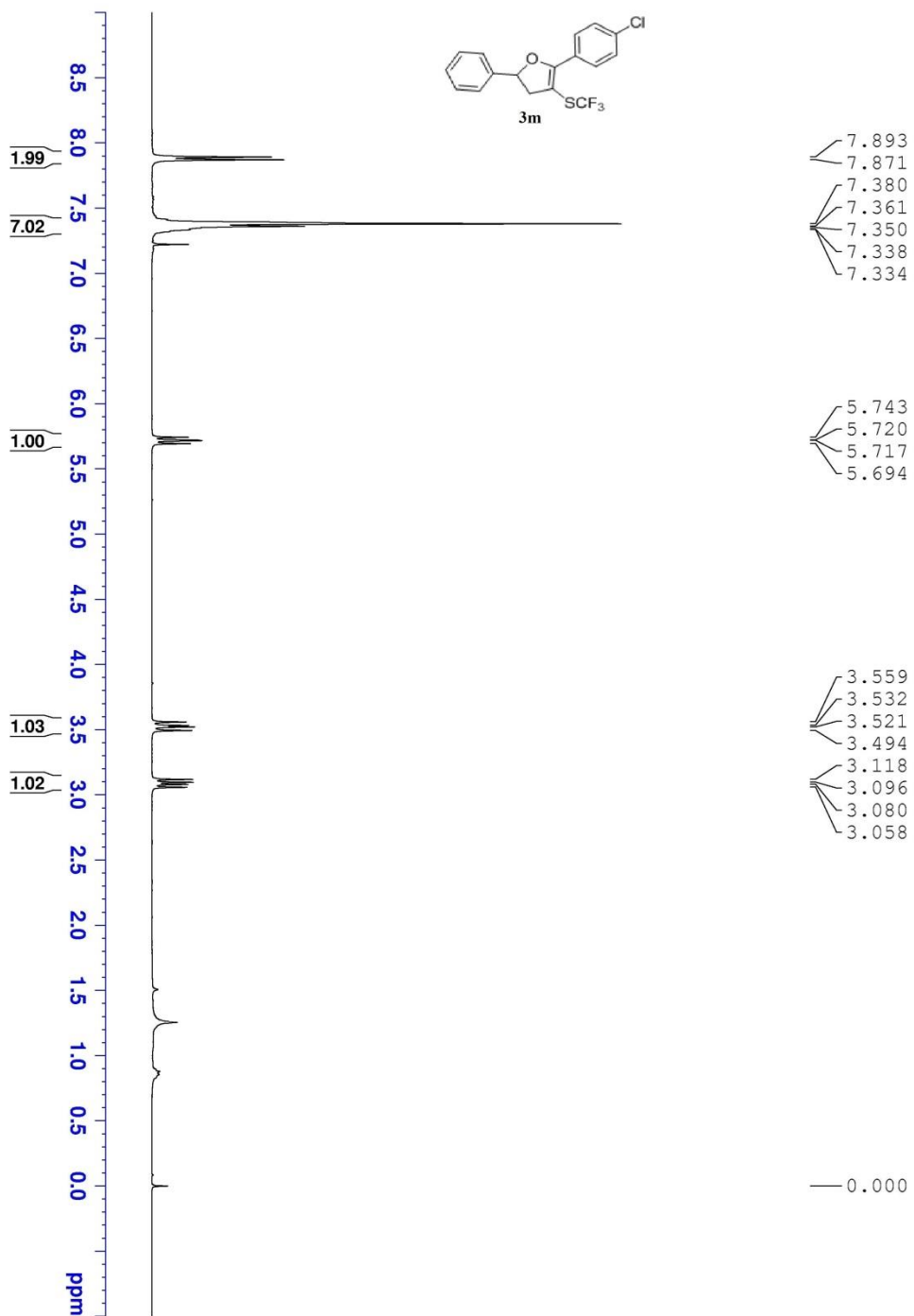


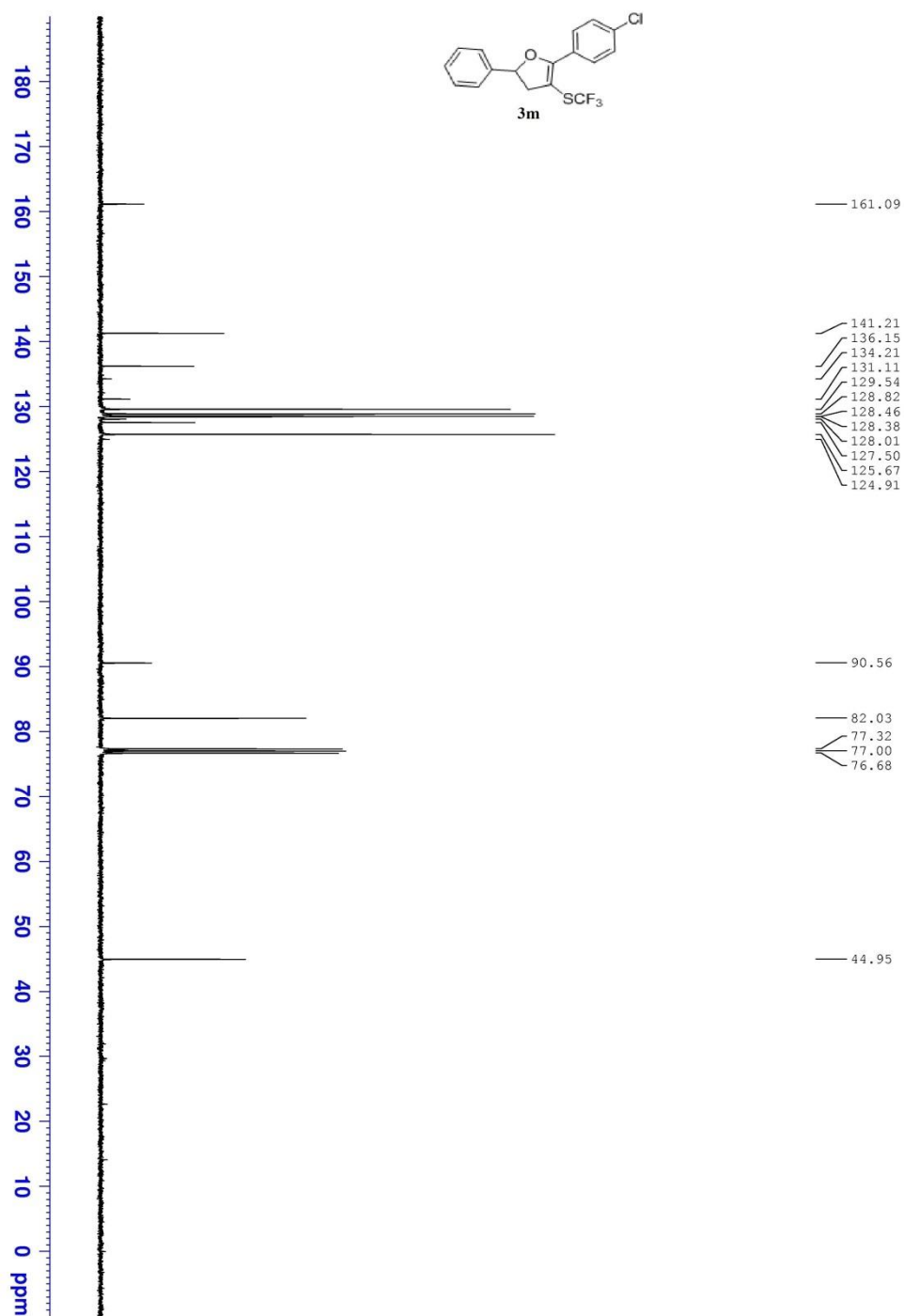


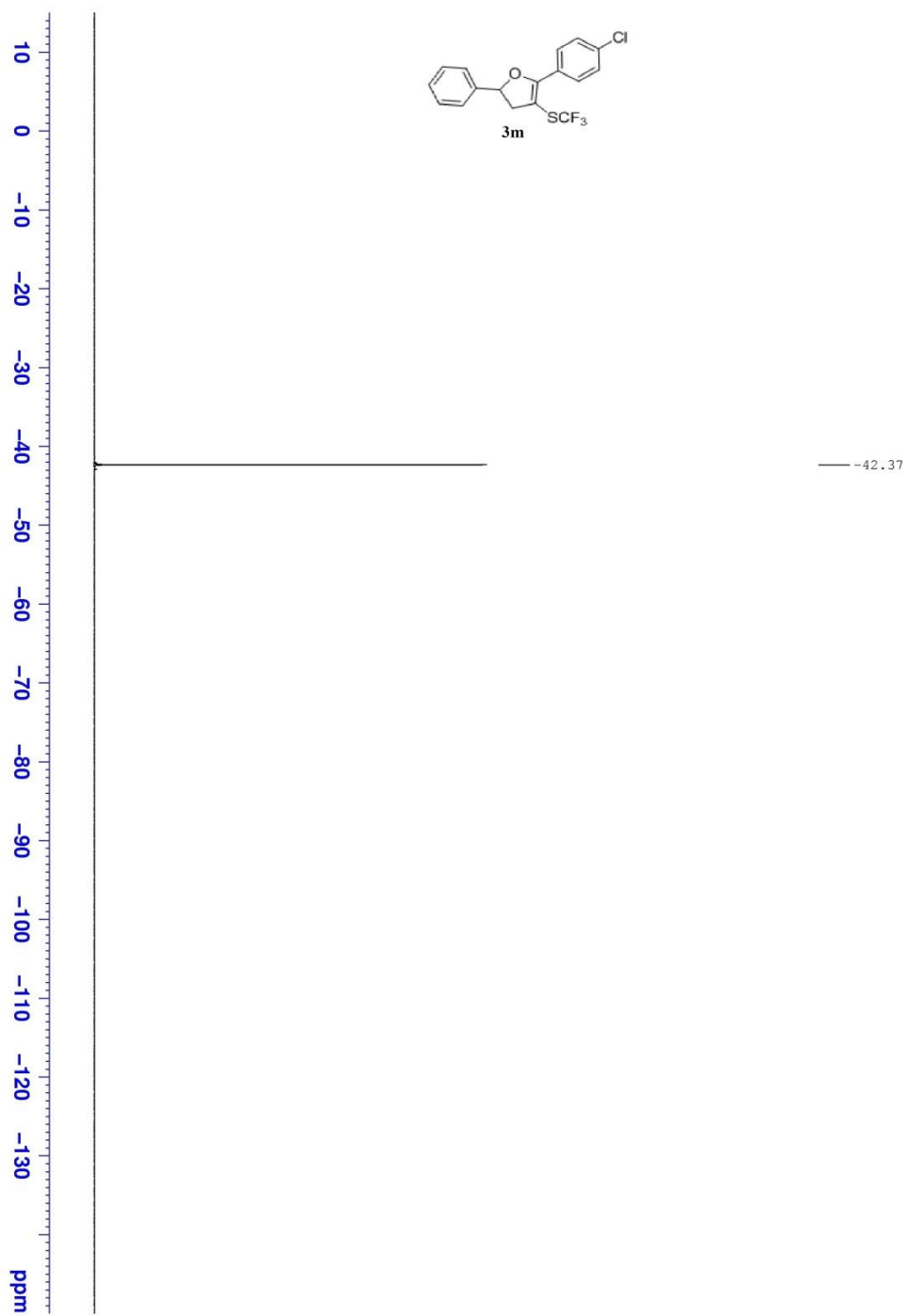


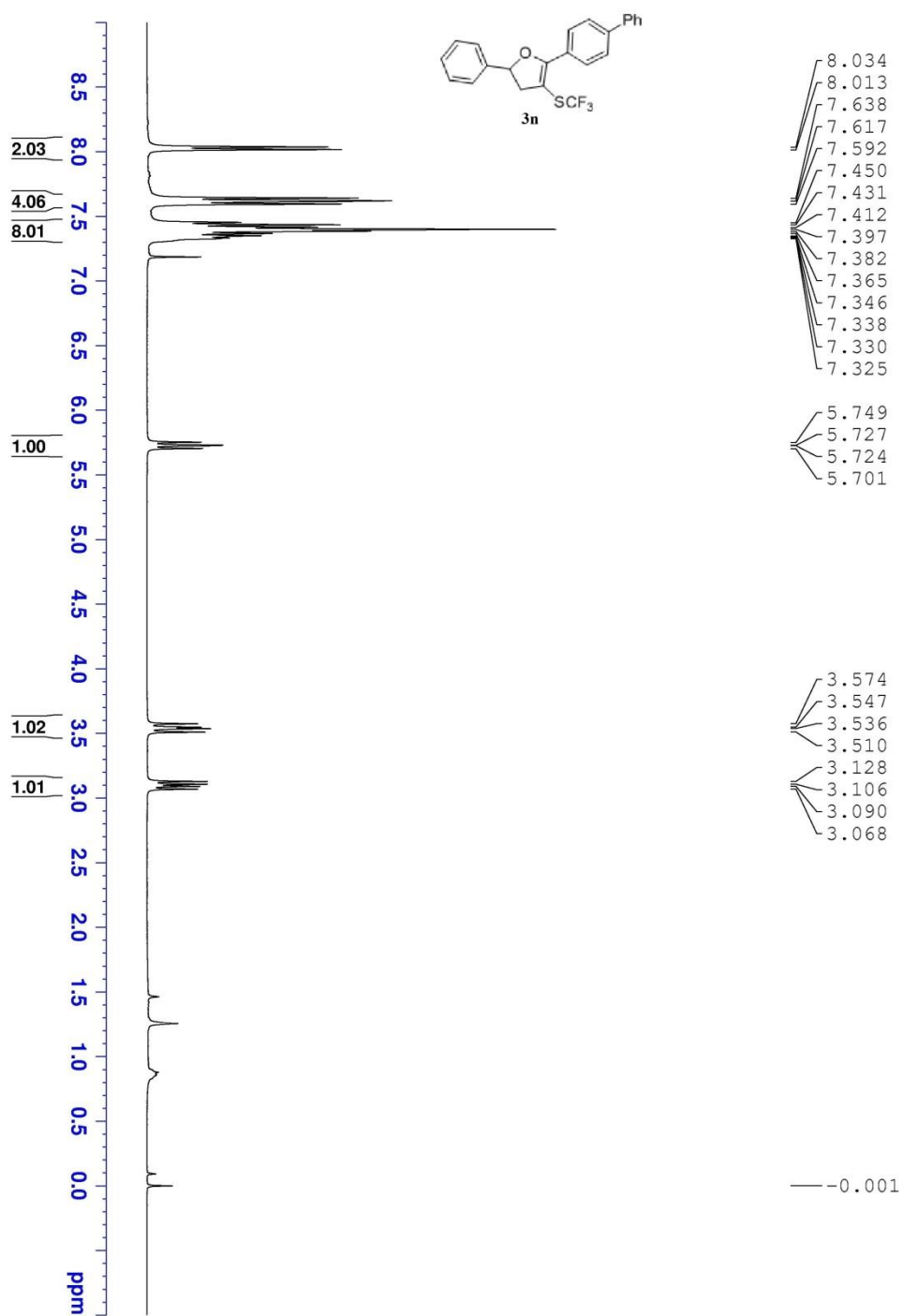


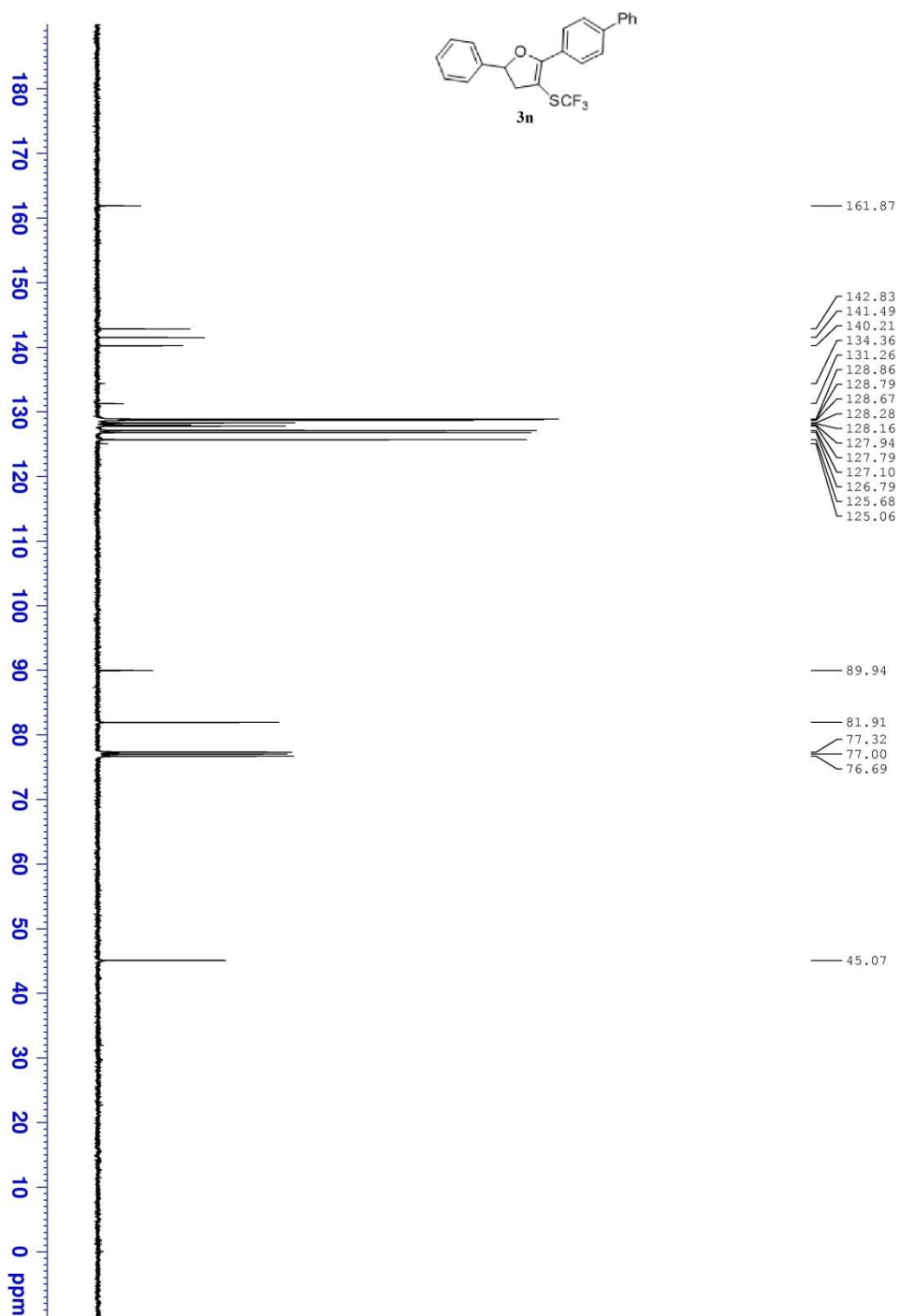


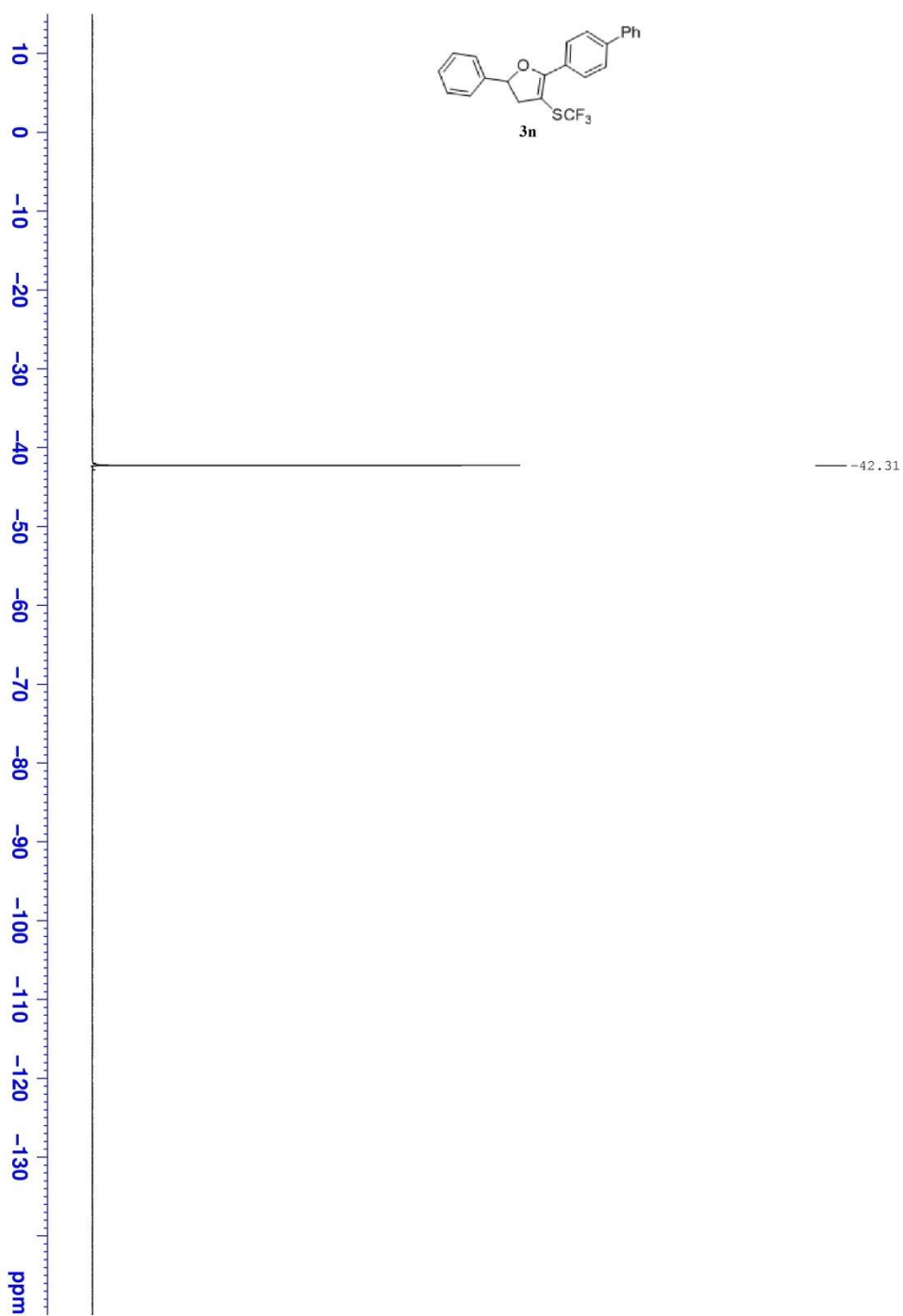


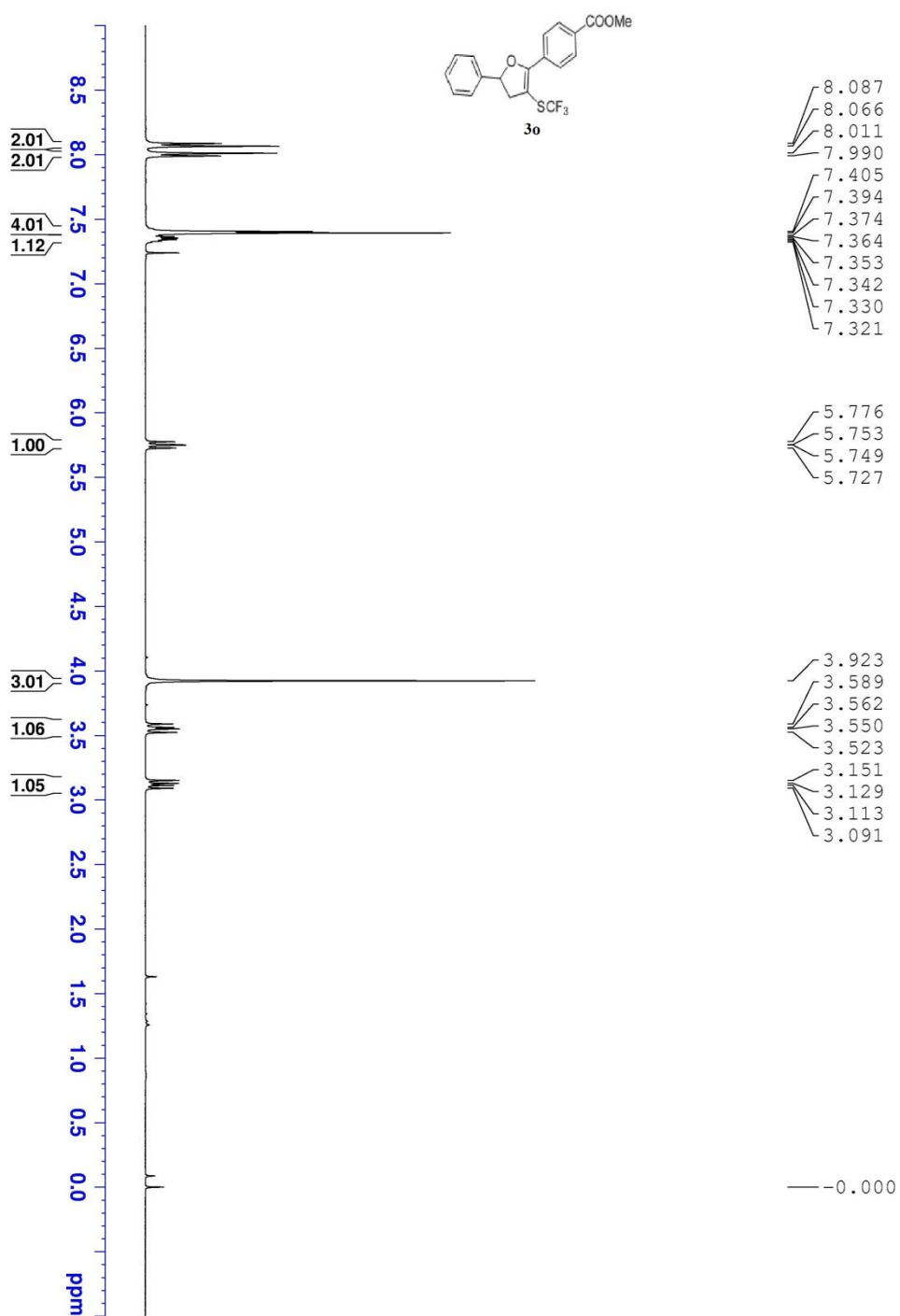


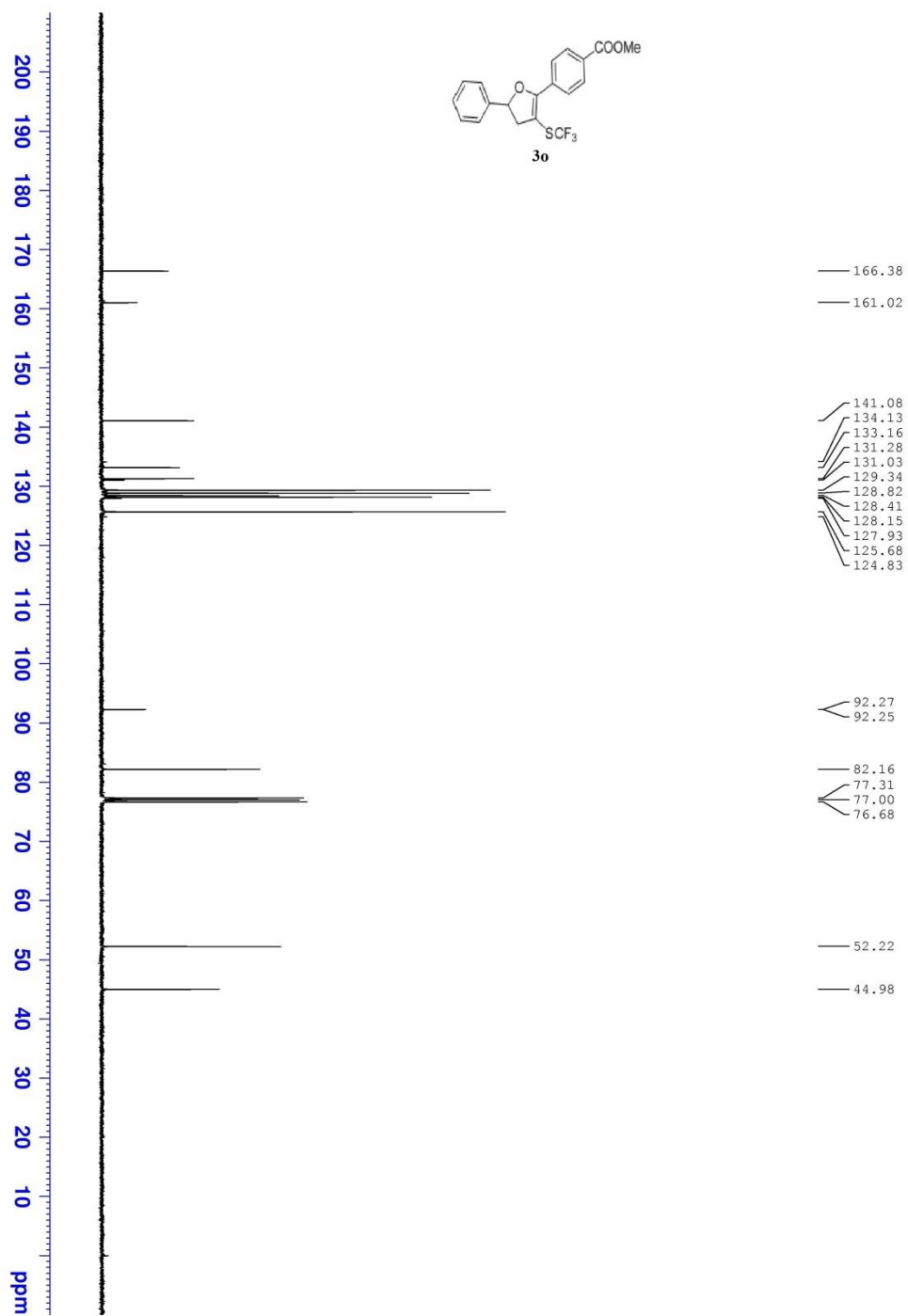




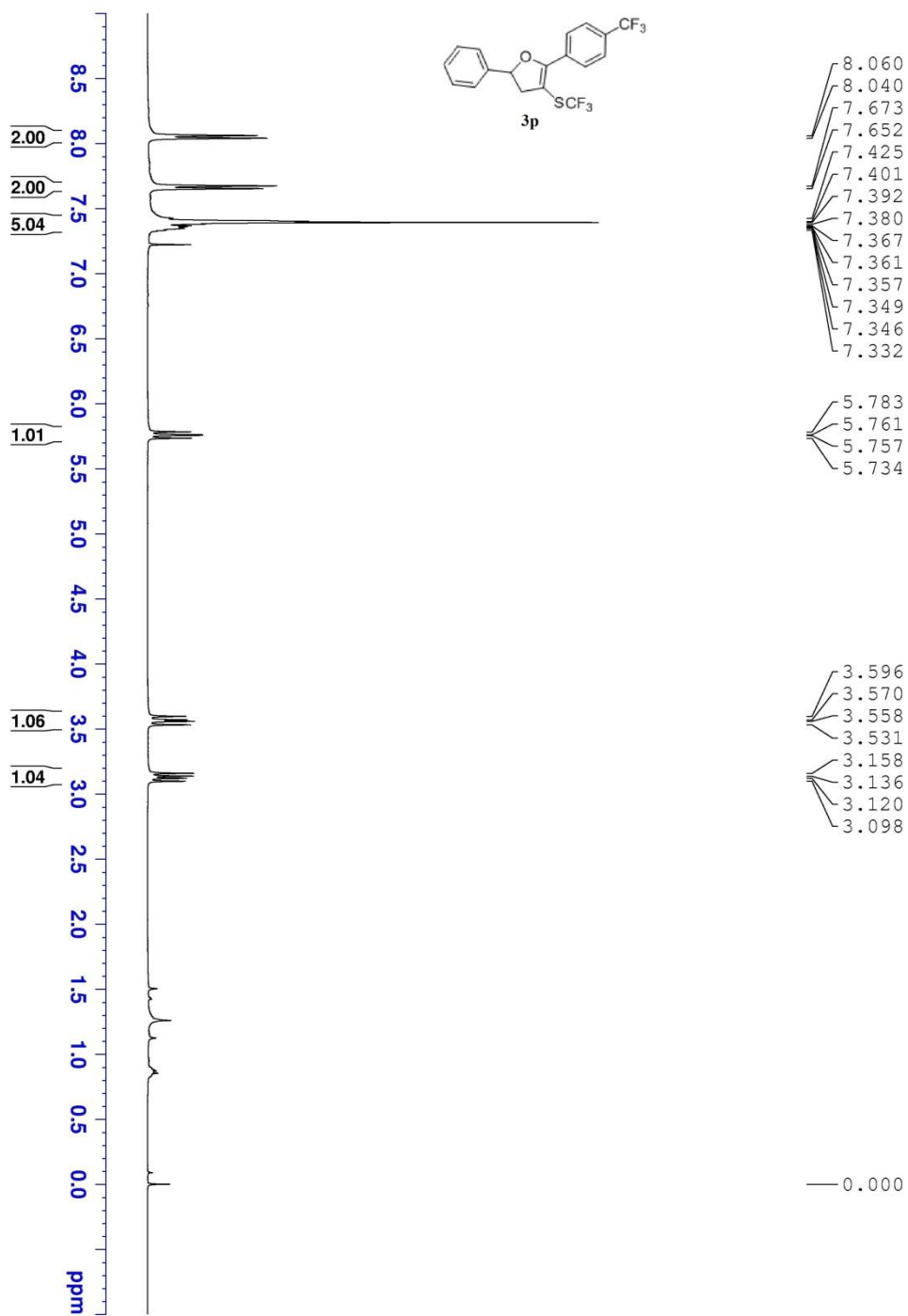


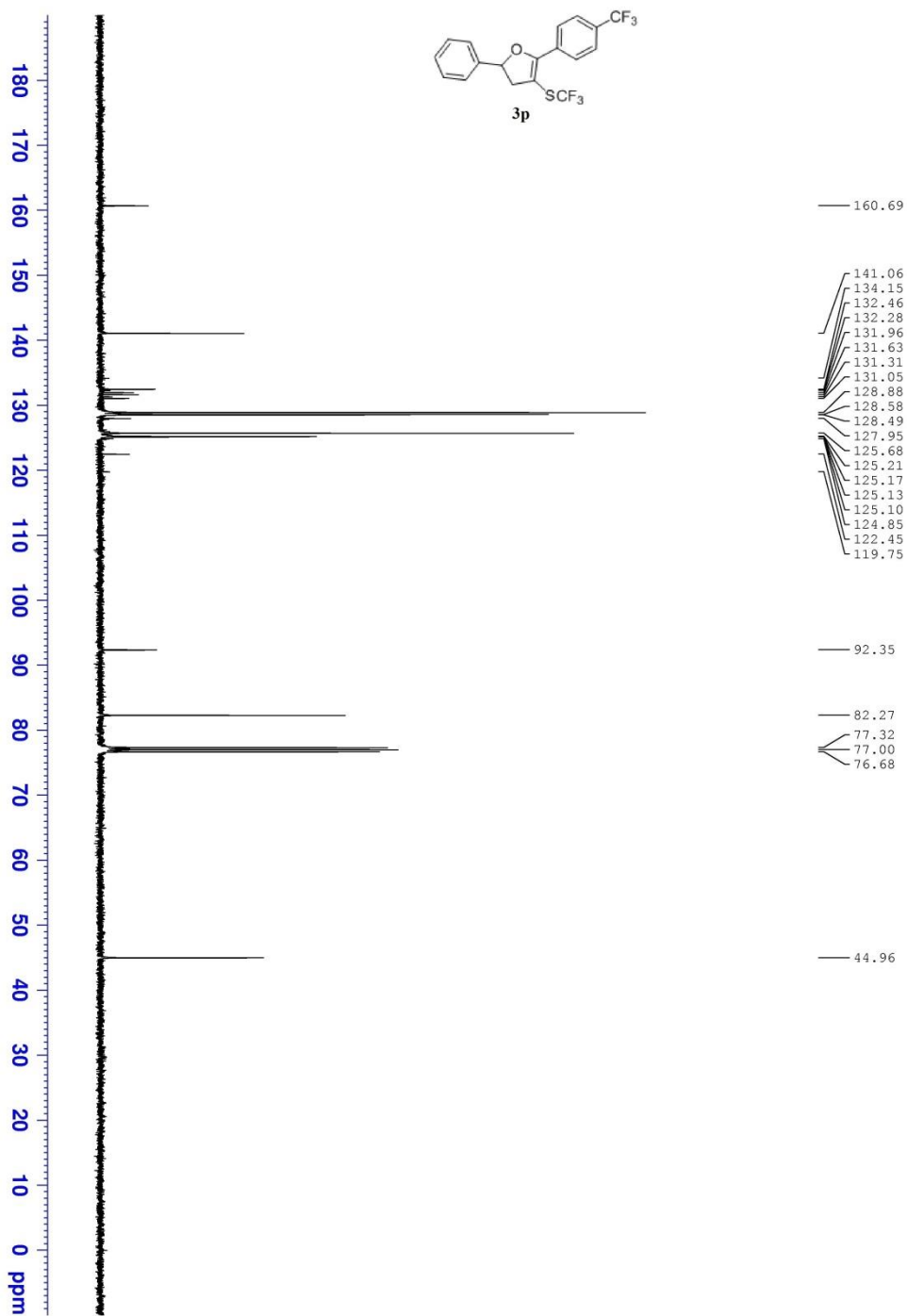


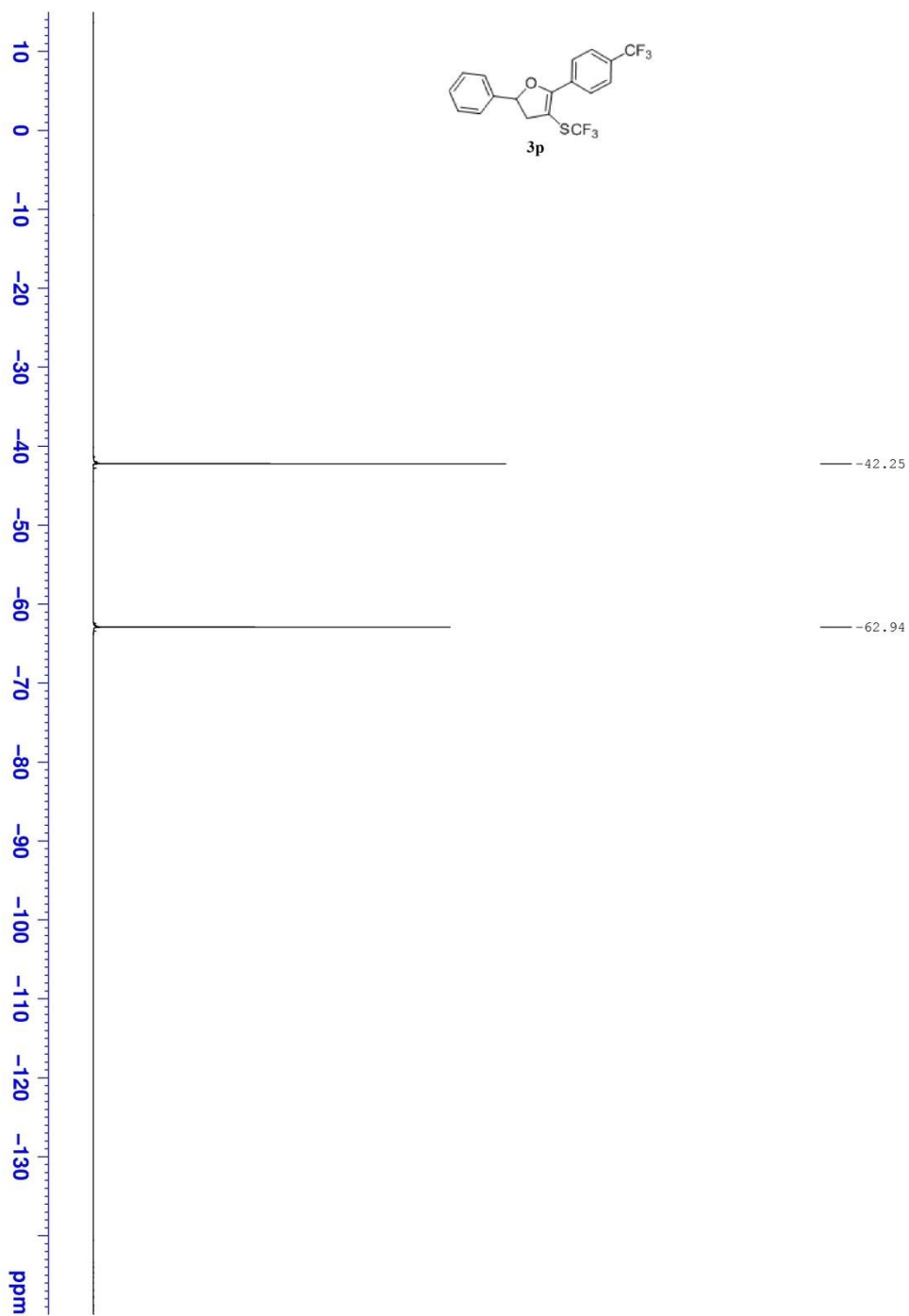


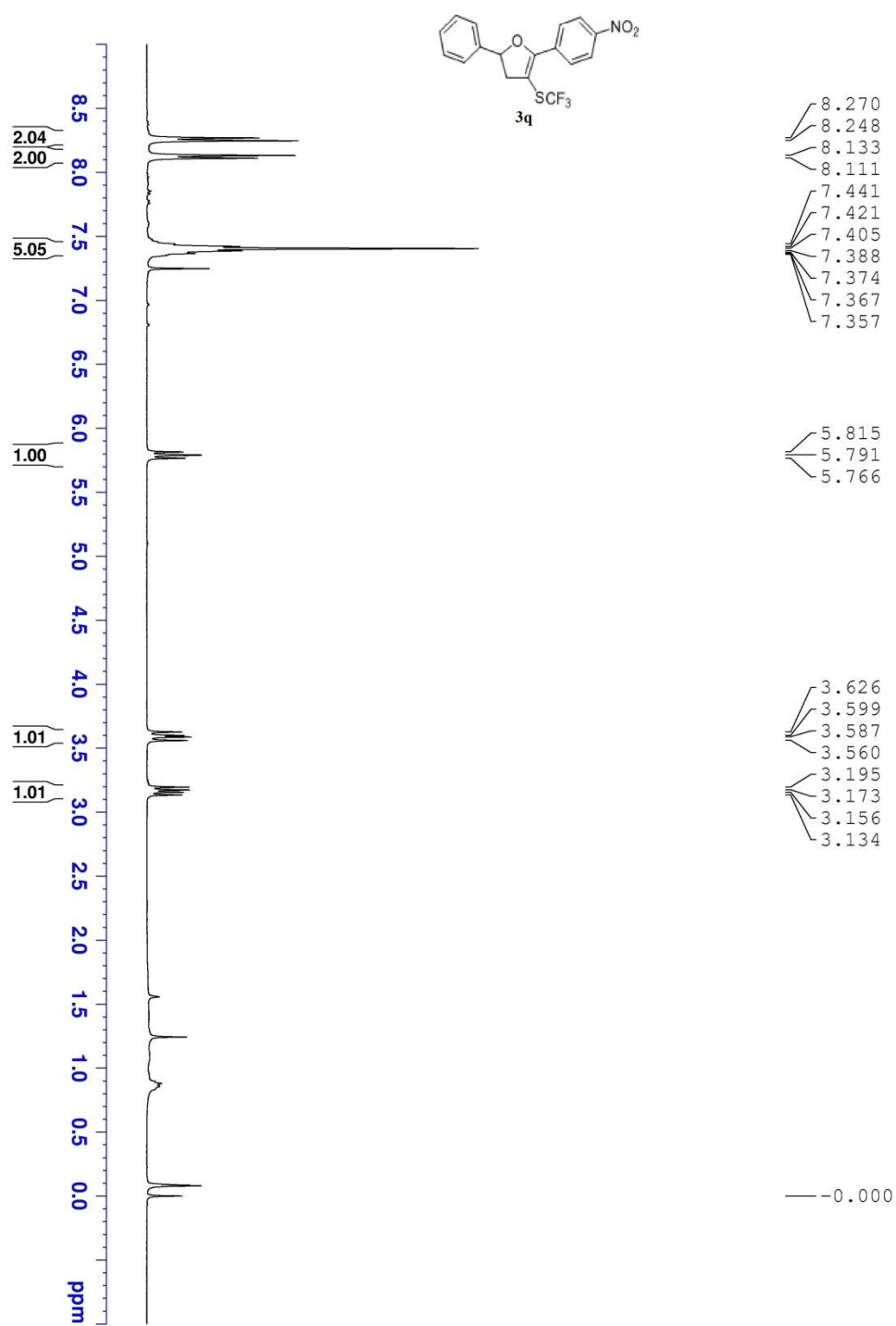


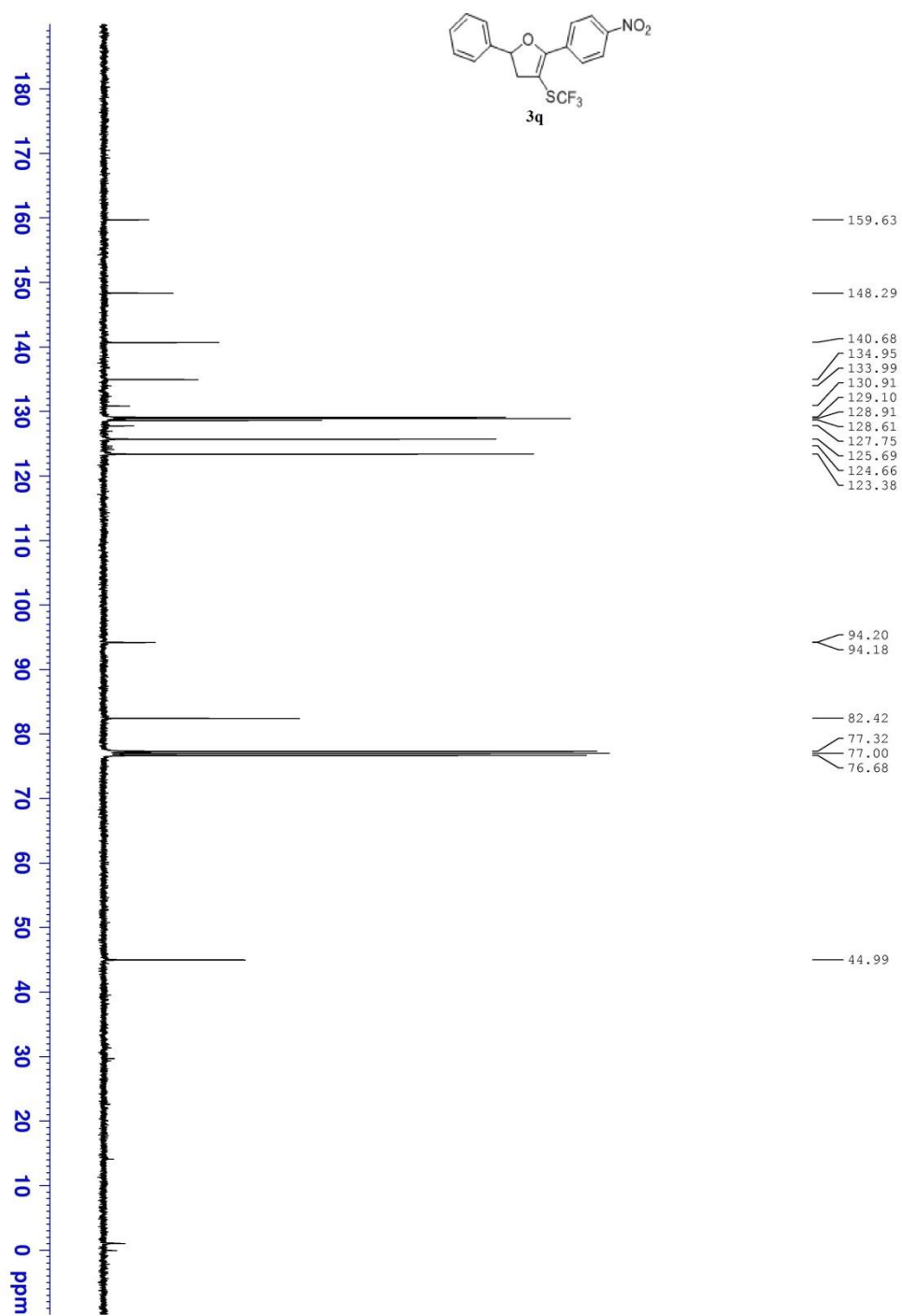


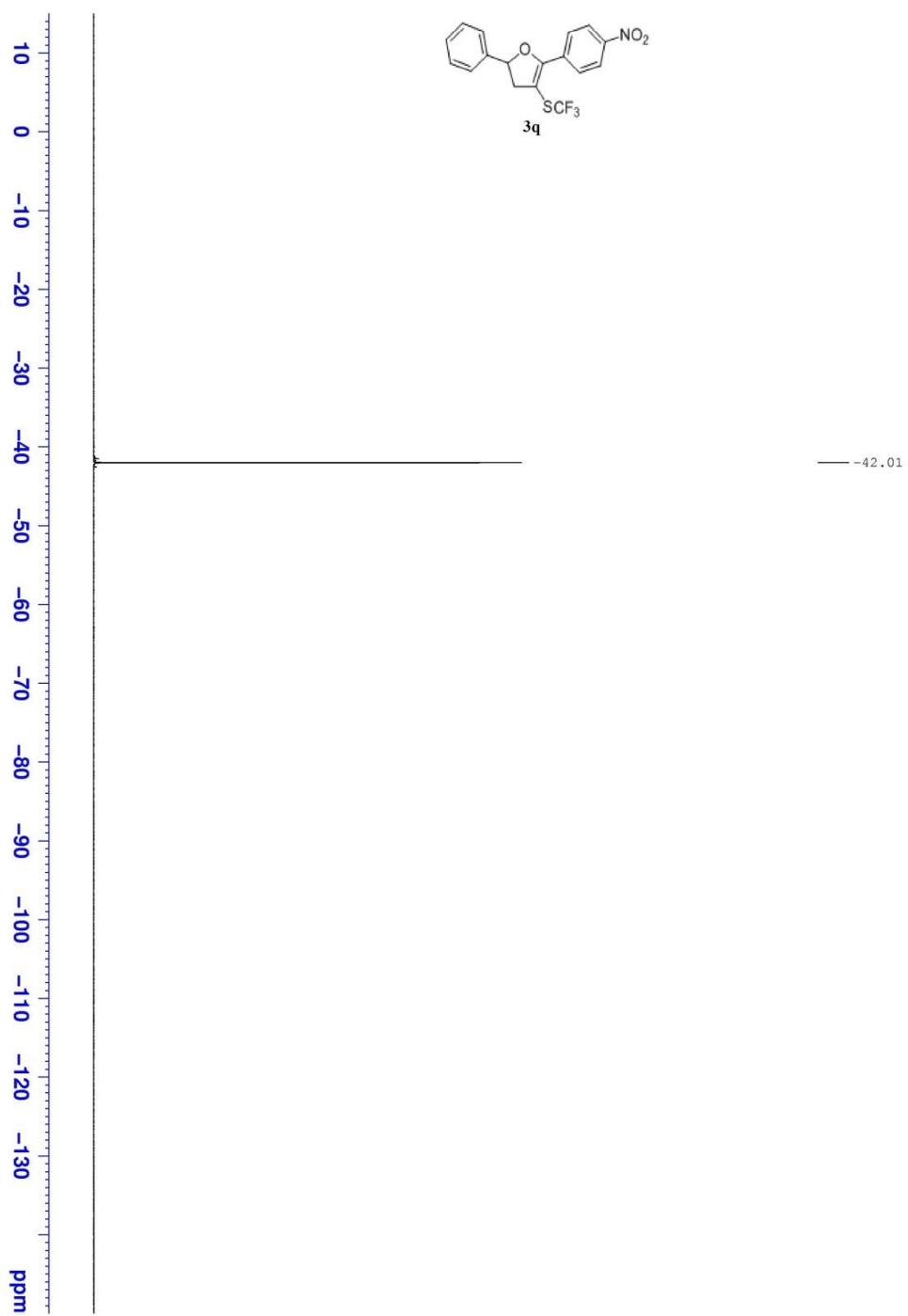


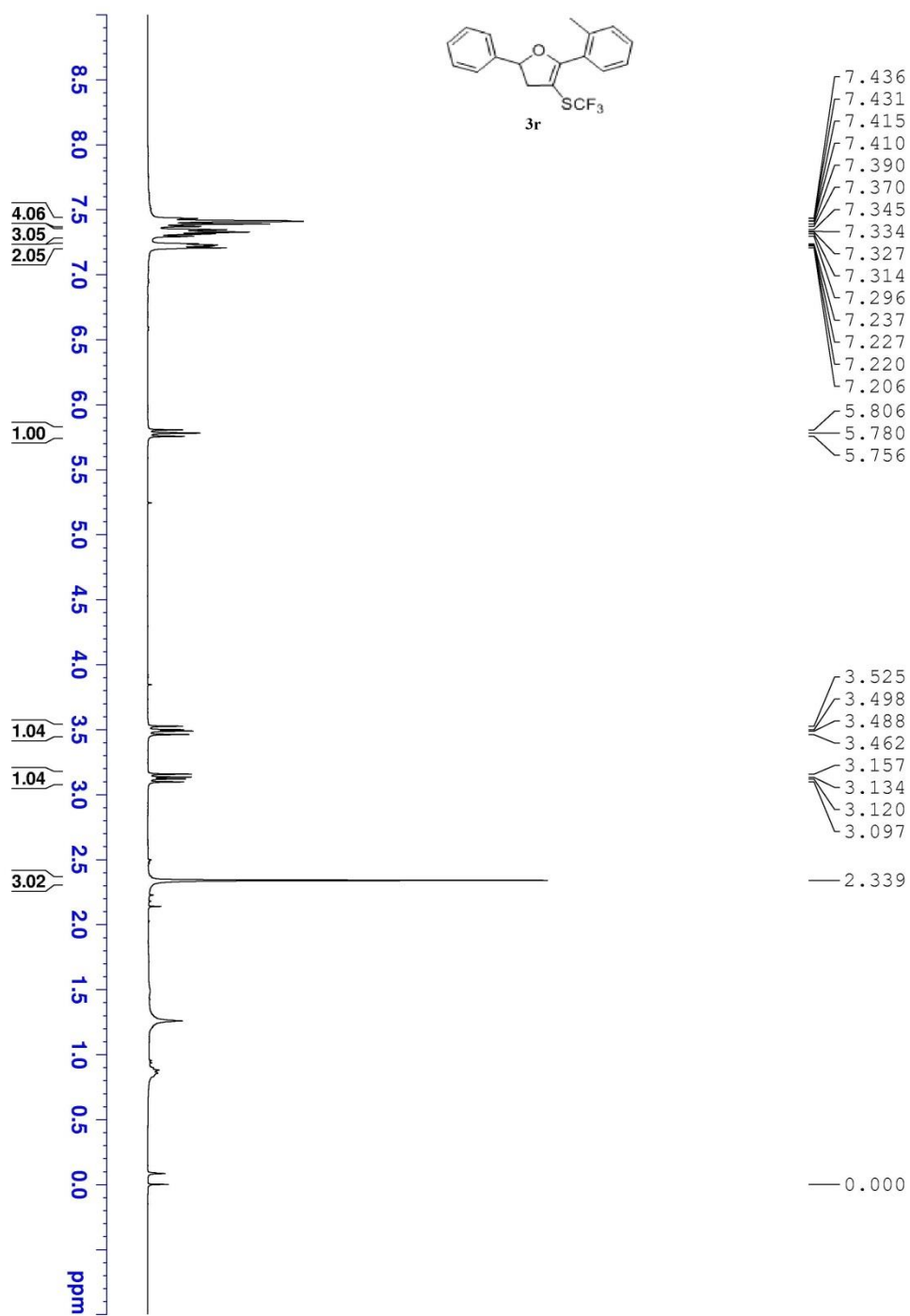


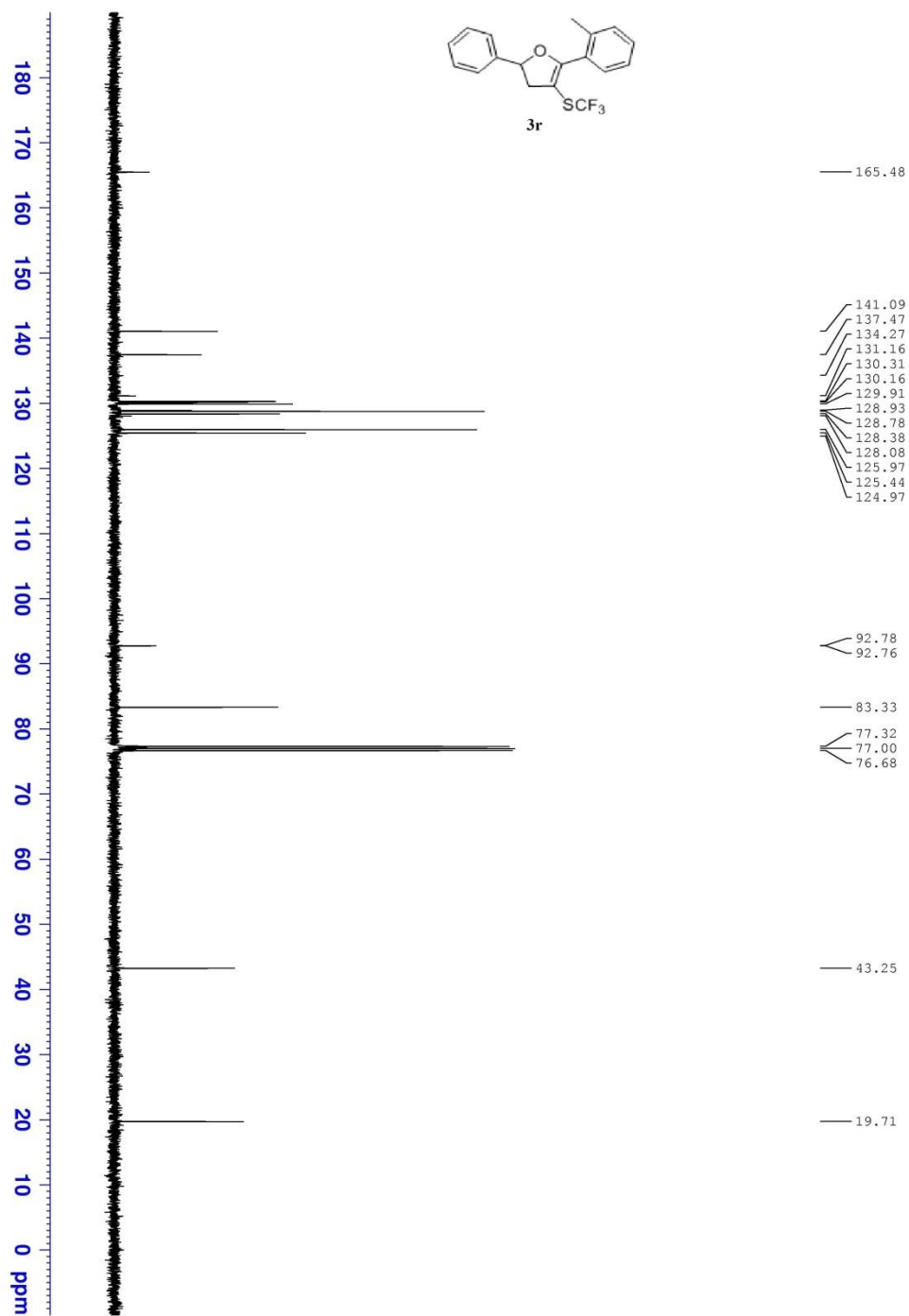


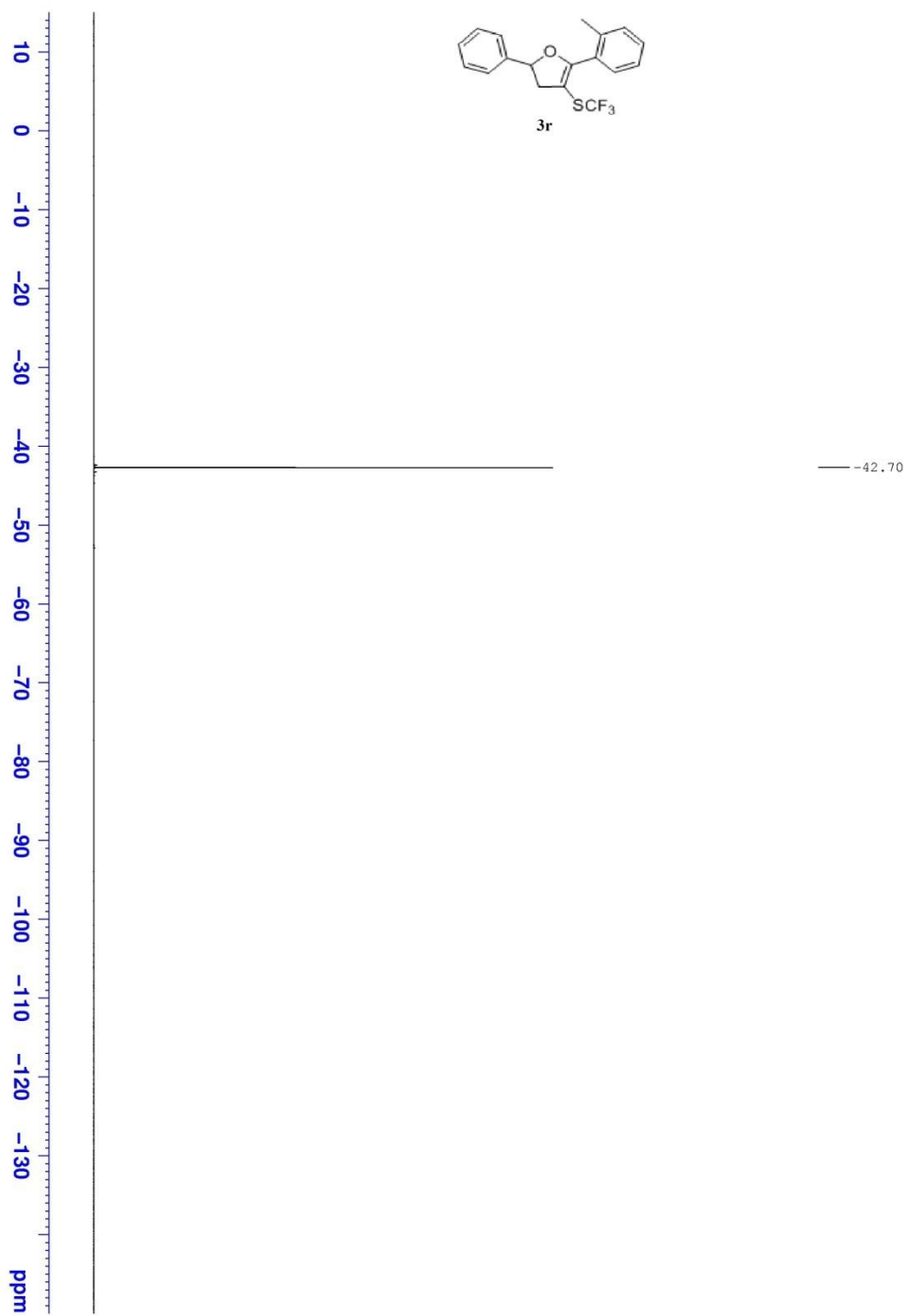


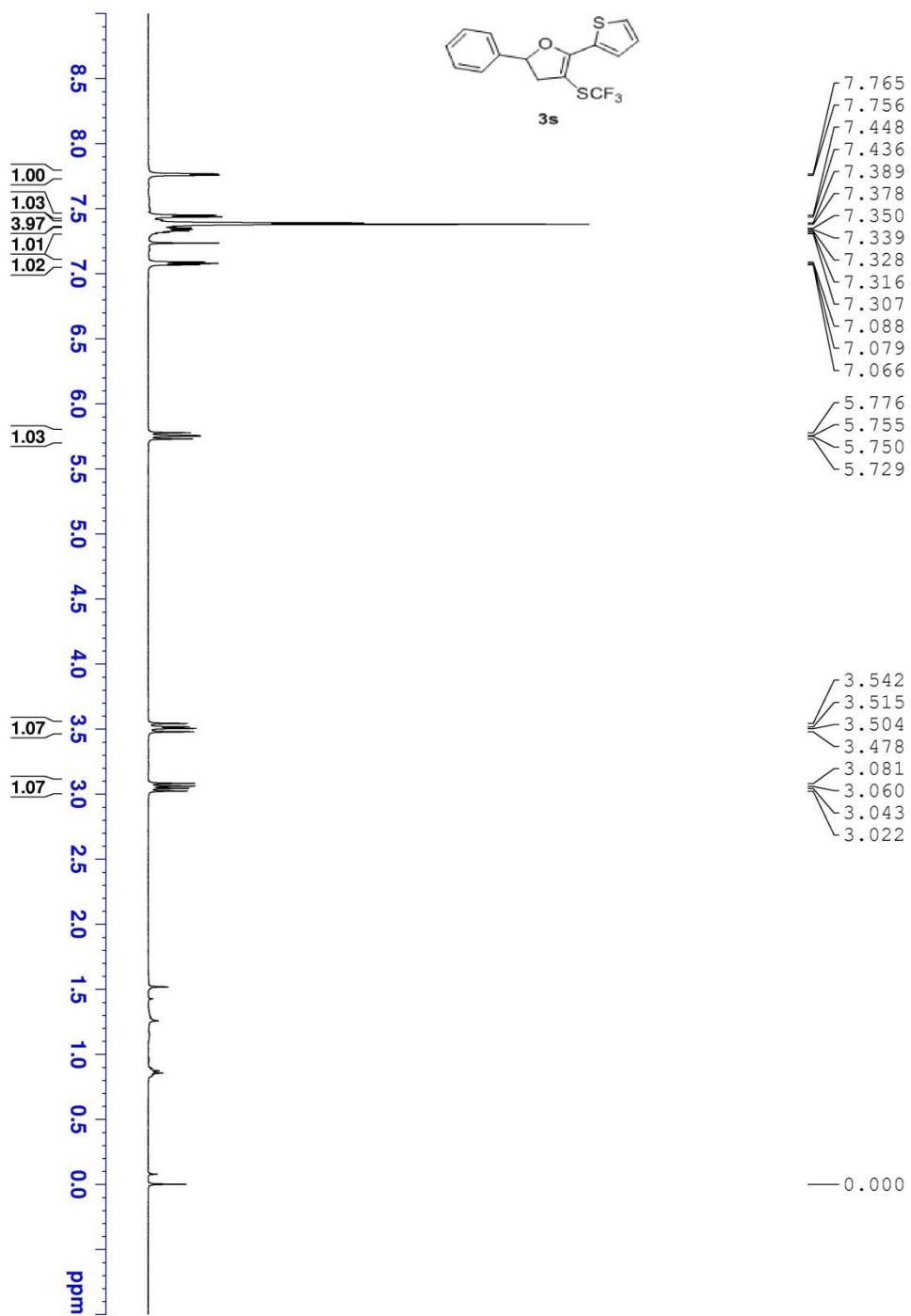


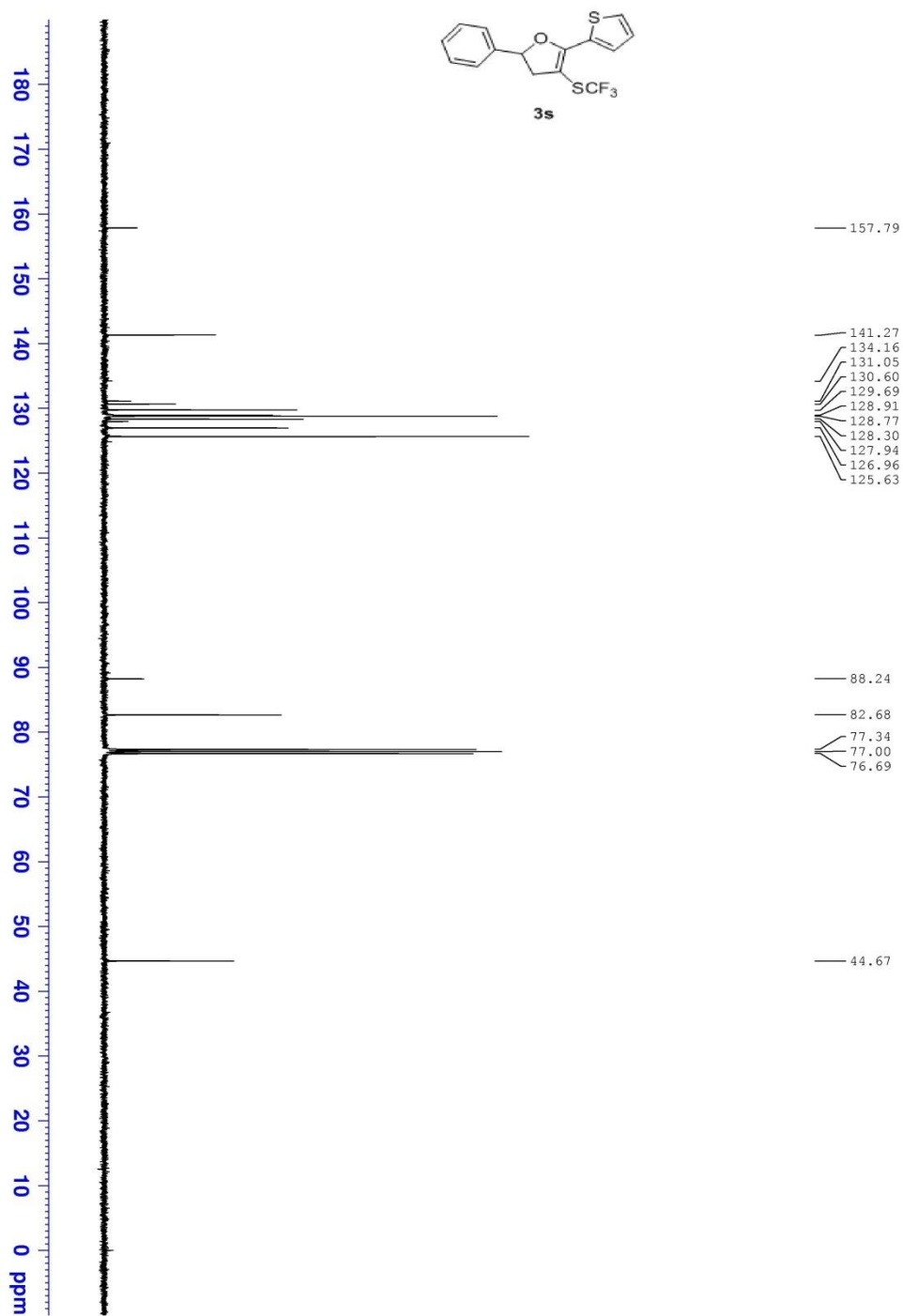


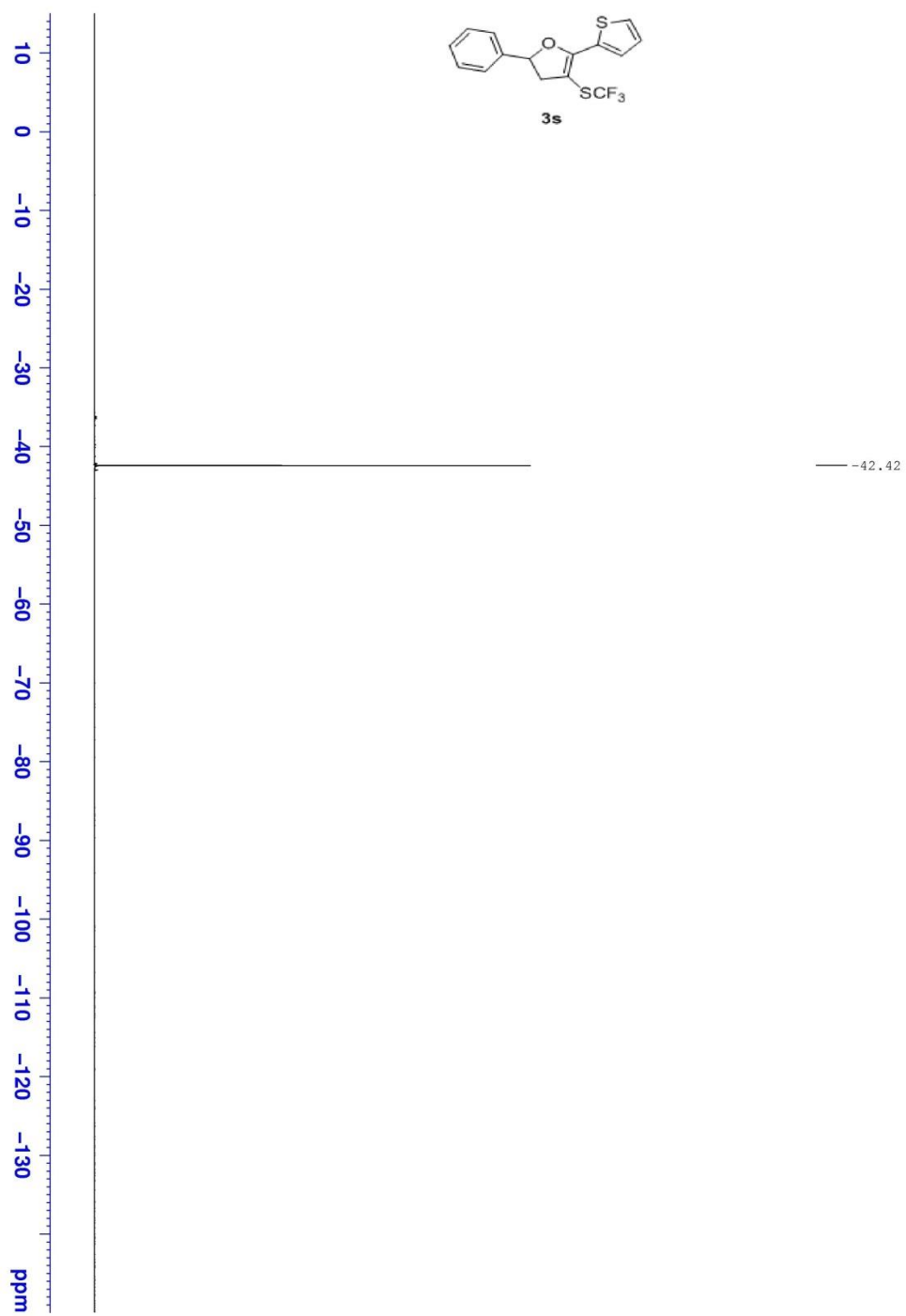


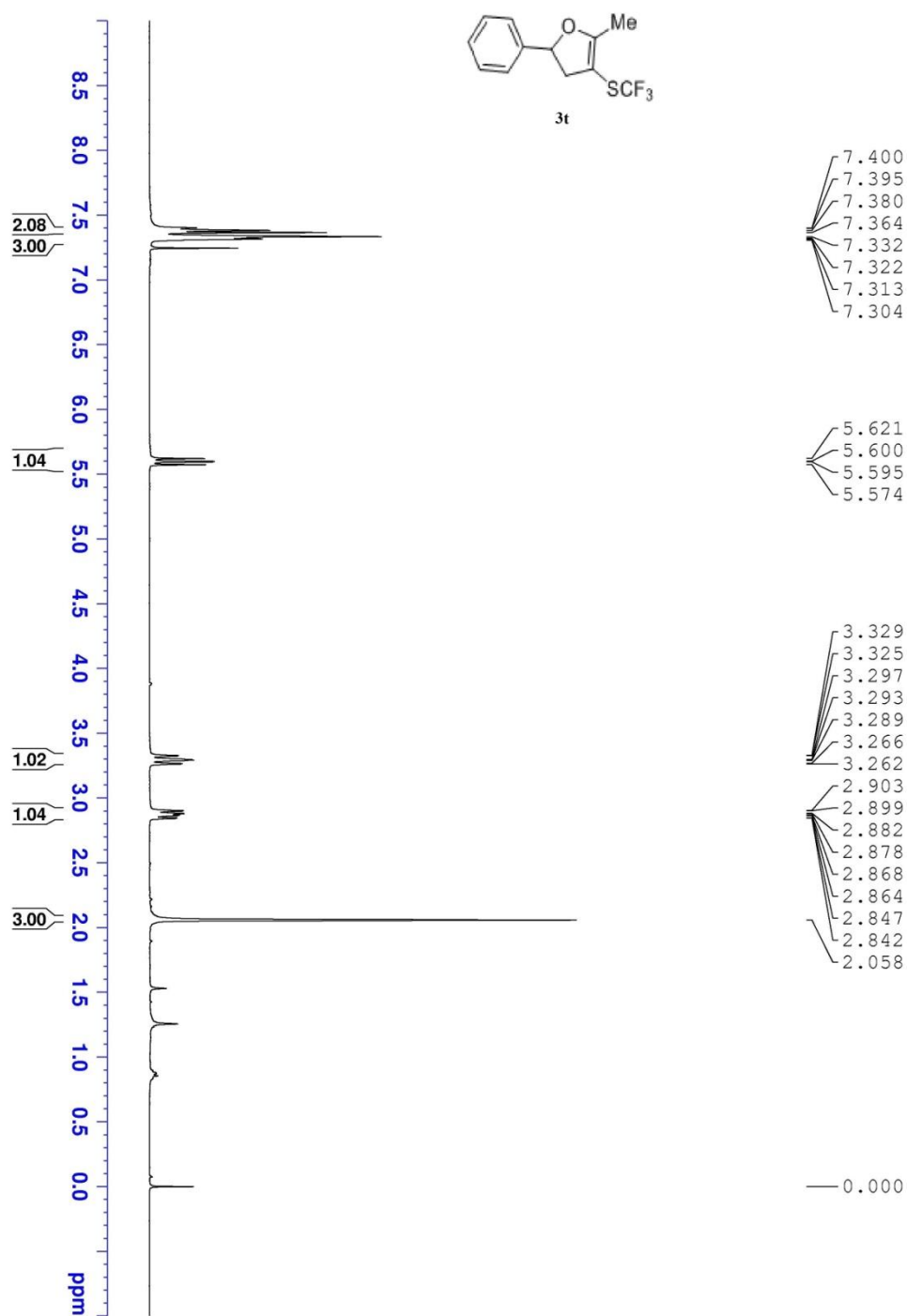












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