

Supporting Information

Table of Contents

1. General information	2
2. Optimization of the bases for the nucleophilic addition of TMSCF ₃ with conjugated enyne aldehyde 1c	3
3. Typical procedure for the one pot trifluoromethylation and cyclization of conjugated enyne aldehydes	4
4. Typical procedure for the one pot trifluoromethylation and cyclization of conjugated enyne ketones	4
5. General datas for 2 and 4	5
6. References.....	17
7. ¹ H, ¹³ C, ¹⁹ F spectra for 2 and 4	18

1. General information

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere; materials obtained from commercial suppliers were used directly without further purification. ^1H NMR spectra, ^{13}C NMR spectra, and ^{19}F NMR spectra were recorded on a Bruker 400 (or 300) MHz spectrometer in chloroform- d_3 . Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl_3 as an internal standard. ^{13}C -NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl_3 ($\delta = 77.00$ ppm). The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration).

Trichloromethane (CHCl_3), dichloromethane, dichloroethane and acetonitrile were freshly distilled from CaH_2 ; tetrahydrofuran (THF), toluene and ether were dried with sodium benzophenone and distilled before use.

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate.

2. Optimization of the bases for the nucleophilic addition of TMSCF_3

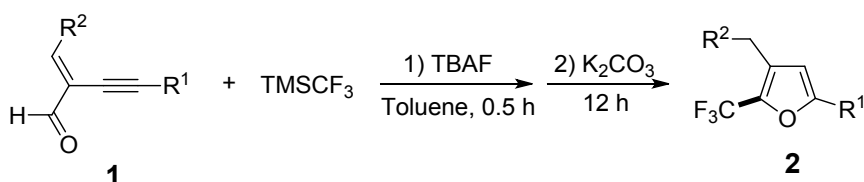
with conjugated enyne aldehyde **1c**.^a

Reaction scheme: **1c** + TMSCF_3 (1.5 equiv) $\xrightarrow[\text{Toluene, 25 } ^\circ\text{C, 8 h}]{\text{base 1.5 equiv}}$ **2-OTMS** + **2-OH** + **2c**

Entry	Base	Yield (%) ^b (2-OTMS)	Yield (%) ^b (2-OH)	Yield (%) ^b (2c)
1	LiOAc	0	0	0
2	NaOAc	0	0	0
3	KOAc	0	0	0
4	Li_2CO_3	0	0	0
5	Na_2CO_3	0	0	0
6	K_2CO_3	0	0	0
7	K_3PO_4	0	0	0
8	KF	0	0	0
9	CsF	96	0	0

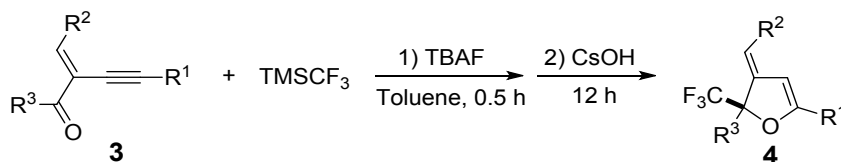
Unless otherwise specified, all reactions were carried out with **1c** (0.1 mmol), TMSCF_3 (0.15 mmol), base (0.15 mmol), in solvent (2 mL) at 25 °C. [b] Yield of isolated products.

3. Typical procedure for the one pot trifluoromethylation and cyclization of conjugated enyne aldehydes



A stirred solution of **1**^[1] (0.2 mmol) and TMSCF₃ (0.3 mmol) in toluene (2 mL) was cooled to 0 °C. Subsequently, TBAF (0.3 mmol) was added slowly through a syringe. The mixture was stirred at this temperature until completion of conjugated enyne aldehyde **1** as indicated by TLC. Then the reaction mixture was warmed to room temperature and K₂CO₃ (0.4 mmol) was added in one portion. The mixture was stirred at this temperature for 12 h and directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the desired product **2**.

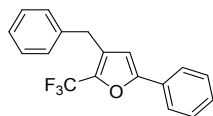
4. Typical procedure for the one pot trifluoromethylation and cyclization of conjugated enyne ketones



A stirred solution of **3**^[2] (0.2 mmol) and TMSCF₃ (0.3 mmol) in toluene (2 mL) was cooled to 0 °C. Subsequently, TBAF (0.3 mmol) was added slowly through a syringe. The mixture was stirred at this temperature until completion of conjugated enyne ketone **3** as indicated by TLC. Then the reaction mixture was warmed to room temperature and CsOH (0.4 mmol) was added in one portion. The mixture was stirred at this temperature for 12 h and directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the desired product **4**.

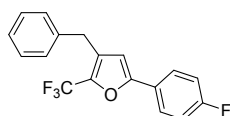
5. General datas for 2 and 4

2a 3-benzyl-5-phenyl-2-(trifluoromethyl)furan



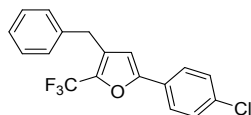
2a; colourless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, $J = 7.6$ Hz, 2H), 7.36–7.27 (m, 5H), 7.22–7.21 (m, 3H), 6.40 (s, 1H), 3.92 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.11, 138.75, 136.15 (q, $J_{\text{CF}} = 40.1$ Hz), 129.23, 128.72, 128.69, 128.67, 128.57, 128.34, 126.62, 124.39, 120.31 (q, $J_{\text{CF}} = 266.2$ Hz), 107.86, 30.53; ^{19}F NMR (376 MHz, CDCl_3), δ -60.84; HRMS (EI) m/z calcd. for $\text{C}_{18}\text{H}_{13}\text{OF}_3$ $[\text{M}]^+ = 302.0918$, found = 302.0915.

2b 3-benzyl-5-(4-fluorophenyl)-2-(trifluoromethyl)furan



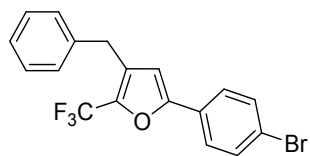
2b; colourless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.49–7.44 (m, 2H), 7.23–7.19 (m, 2H), 7.15–7.10 (m, 3H), 6.96–6.90 (m, 2H), 6.24 (s, 1H), 3.82 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.84 (d, $J_{\text{CF}} = 247.4$ Hz), 154.23, 138.68, 136.16 (q, $J_{\text{CF}} = 40.3$ Hz), 128.72, 128.57, 128.47, 126.67, 126.31 (d, $J_{\text{CF}} = 8.2$ Hz), 125.61 (d, $J_{\text{CF}} = 3.3$ Hz), 120.26 (q, $J_{\text{CF}} = 266.1$ Hz), 115.84 (d, $J_{\text{CF}} = 22$ Hz), 107.57, 30.51; ^{19}F NMR (376 MHz, CDCl_3), δ -60.90, -111.91; HRMS (EI) m/z calcd. for $\text{C}_{18}\text{H}_{12}\text{OF}_4$ $[\text{M}]^+ = 320.0824$, found = 320.0822.

2c 3-benzyl-5-(4-chlorophenyl)-2-(trifluoromethyl)furan



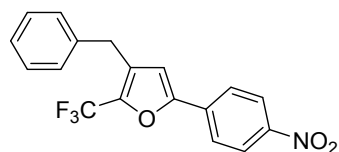
2c; white solid, m.p. = 39–41 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, $J = 8.4$ Hz, 2H), 7.34–7.30 (m, 4H), 7.26–7.21 (m, 3H), 6.41 (s, 1H), 3.93 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 153.98, 138.58, 136.38 (q, $J_{\text{CF}} = 40.2$ Hz), 134.53, 129.00, 128.74, 128.57, 128.48, 127.71, 126.70, 125.64, 120.16 (q, $J_{\text{CF}} = 266.2$ Hz), 108.25, 30.50; ^{19}F NMR (376 MHz, CDCl_3), δ -60.96; HRMS (EI) m/z calcd. for $\text{C}_{18}\text{H}_{12}\text{OF}_3\text{Cl}$ $[\text{M}]^+ = 336.0529$, found = 336.0526.

2d 3-benzyl-5-(4-bromophenyl)-2-(trifluoromethyl)furan



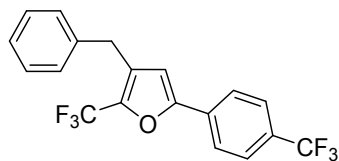
2d; white solid, m.p. = 44-46 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.47–7.42 (m, 4H), 7.33–7.29 (m, 2H), 7.25–7.20 (m, 3H), 6.40 (s, 1H), 3.91 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 153.98, 137.00, 136.40 (q, $J_{\text{CF}} = 40.2$ Hz), 131.90, 128.73, 128.56, 128.51, 128.10, 126.70, 125.82, 122.70, 120.16 (q, $J_{\text{CF}} = 266.2$ Hz), 108.33, 30.48; ^{19}F NMR (376 MHz, CDCl_3), δ -60.89; HRMS (EI) m/z calcd. for $\text{C}_{18}\text{H}_{12}\text{OF}_3\text{Br}[\text{M}]^+ = 380.0024$, found = 380.0027.

2e 3-benzyl-5-(4-nitrophenyl)-2-(trifluoromethyl)furan



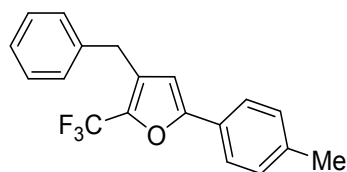
2e; white solid, m.p. = 107-109 °C; ^1H NMR (300 MHz, CDCl_3): δ 8.26 (d, $J = 8.7$ Hz, 2H), 7.79 (d, $J = 8.7$ Hz, 2H), 7.42–7.37 (m, 2H), 7.33–7.28 (m, 3H), 6.70 (s, 1H), 4.01 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 152.48, 147.27, 138.16, 137.82 (q, $J_{\text{CF}} = 40.43$ Hz), 134.64, 128.91, 128.79, 128.52, 126.82, 124.75, 124.17, 119.84 (q, $J_{\text{CF}} = 266.7$ Hz), 111.25, 30.36; ^{19}F NMR (282 MHz, CDCl_3), δ -61.13; HRMS (EI) m/z calcd. for $\text{C}_{18}\text{H}_{12}\text{O}_3\text{NF}_3[\text{M}]^+ = 347.0769$, found = 347.0764.

2f 3-benzyl-2-(trifluoromethyl)-5-(4-(trifluoromethyl)phenyl)furan



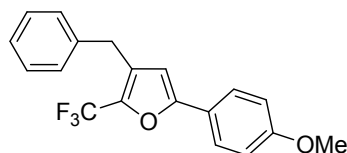
2f; white solid, m.p. = 78-80 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.78–7.68 (m, 4H), 7.49–7.44 (m, 2H), 7.40–7.35 (m, 3H), 6.63 (s, 1H), 4.06 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 153.46, 138.51, 137.11 (q, $J_{\text{CF}} = 40.28$ Hz), 132.30, 130.33 (q, $J_{\text{CF}} = 32.25$ Hz), 129.38, 128.81, 128.69, 128.66, 128.60, 126.81, 125.78, 125.74, 125.69, 125.64, 124.44, 122.17, 121.92, 118.57, 118.37, 114.82, 109.63, 30.45; ^{19}F NMR (282 MHz, CDCl_3), δ -61.05, -62.74; HRMS (EI) m/z calcd. for $\text{C}_{19}\text{H}_{12}\text{OF}_6[\text{M}]^+ = 370.0792$, found = 370.0789.

2g 3-benzyl-5-(p-tolyl)-2-(trifluoromethyl)furan



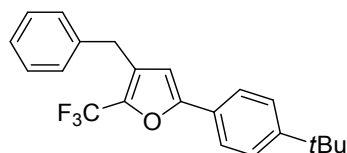
2g; colourless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.49 (d, J = 8.0 Hz, 2H), 7.31–7.28 (m, 2H), 7.23–7.20 (m, 3H), 7.14 (d, J = 7.6 Hz, 2H), 6.34 (s, 1H), 3.90 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.38, 138.83, 138.73, 135.76 (q, J_{CF} = 40.1 Hz), 129.41, 128.67, 128.58, 128.32, 126.59, 124.35, 120.38 (q, J_{CF} = 266.0 Hz), 107.17, 30.54, 21.25; ^{19}F NMR (376 MHz, CDCl_3), δ -60.75; HRMS (EI) m/z calcd. for $\text{C}_{19}\text{H}_{15}\text{OF}_3$ $[\text{M}]^+ = 316.1075$, found = 316.1074.

2h 3-benzyl-5-(4-methoxyphenyl)-2-(trifluoromethyl)furan

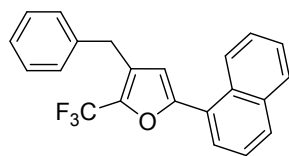


2h; colourless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.46–7.43 (m, 2H), 7.22–7.18 (m, 2H), 7.13–7.11 (m, 3H), 6.79–6.76 (m, 2H), 6.18 (s, 1H), 3.81 (s, 2H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.02, 155.24, 138.86, 135.45 (q, J_{CF} = 40.0 Hz), 128.65, 128.56, 128.37, 126.56, 125.92, 122.21, 120.42 (q, J_{CF} = 265.9 Hz), 114.17, 106.34, 55.23, 30.54; ^{19}F NMR (376 MHz, CDCl_3), δ -60.72; HRMS (EI) m/z calcd. for $\text{C}_{19}\text{H}_{15}\text{O}_2\text{F}_3$ $[\text{M}]^+ = 332.1024$, found = 332.1020.

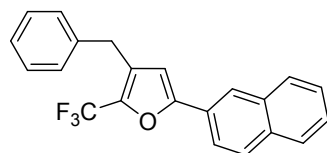
2i 3-benzyl-5-(4-(tert-butyl)phenyl)-2-(trifluoromethyl)furan



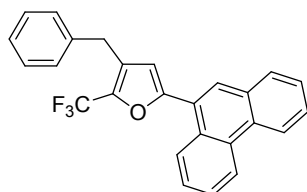
2i; white solid, m.p. = 112–114 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.67 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.45–7.41 (m, 2H), 7.37–7.33 (m, 3H), 6.50 (s, 1H), 4.05 (s, 2H), 1.43 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 155.36, 151.95, 138.83, 135.85 (q, J_{CF} = 40.05 Hz), 128.66, 128.56, 128.25, 126.58, 126.53, 125.65, 124.22, 120.39 (q, J_{CF} = 265.88 Hz), 107.30, 34.67, 31.12, 30.52; ^{19}F NMR (282 MHz, CDCl_3), δ -60.71; HRMS (EI) m/z calcd. for $\text{C}_{22}\text{H}_{21}\text{OF}_3$ $[\text{M}]^+ = 358.1545$, found = 358.1542.

2j 3-benzyl-5-(naphthalen-1-yl)-2-(trifluoromethyl)furan

2j; white solid, m.p. = 49-51 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.24 (d, J = 8.0 Hz, 1H), 7.81–7.77 (m, 2H), 7.64 (d, J = 6.8 Hz, 1H), 7.50–7.38 (m, 3H), 7.32–7.21 (m, 5H), 6.48 (s, 1H), 3.98 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 154.85, 138.77, 136.60 (q, J_{CF} = 40.0 Hz), 133.83, 130.15, 129.72, 128.71, 128.61, 128.57, 127.99, 127.03, 126.89, 126.80, 126.62, 126.11, 125.08, 124.94, 117.74 (q, J_{CF} = 266.2 Hz), 112.14, 30.57; ^{19}F NMR (376 MHz, CDCl_3), δ -60.65; HRMS (EI) m/z calcd. for $\text{C}_{22}\text{H}_{15}\text{OF}_3$ $[\text{M}]^+ = 352.1075$, found = 352.1078.

2k 3-benzyl-5-(naphthalen-2-yl)-2-(trifluoromethyl)furan

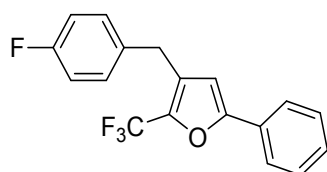
2k; colourless oil; ^1H NMR (300 MHz, CDCl_3): δ 8.20 (s, 1H), 7.93–7.86 (m, 3H), 7.76–7.72 (m, 1H), 7.59–7.52 (m, 2H), 7.47–7.43 (m, 2H), 7.38–7.35 (m, 3H), 6.60 (s, 1H), 4.06 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 155.12, 138.72, 136.24 (q, J_{CF} = 39.98 Hz), 133.18, 133.17, 128.71, 128.59, 128.47, 128.29, 127.72, 126.64, 126.54, 126.44, 123.36, 122.08, 120.32 (q, J_{CF} = 263.63 Hz), 108.32, 30.52; ^{19}F NMR (282 MHz, CDCl_3), δ -60.66; HRMS (EI) m/z calcd. for $\text{C}_{22}\text{H}_{15}\text{OF}_3$ $[\text{M}]^+ = 352.1075$, found = 352.1072.

2l 3-benzyl-5-(phenanthren-9-yl)-2-(trifluoromethyl)furan

2l; colourless oil; ^1H NMR (300 MHz, CDCl_3): δ 8.76 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 8.34 (d, J = 8.7 Hz, 1H), 8.01 (s, 1H), 7.93–7.91 (m, 1H), 7.76–7.62 (m, 4H), 7.46–7.34 (m, 5H), 6.64 (s, 1H), 4.12 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 154.75, 138.77, 136.60 (q, J_{CF} = 40.20 Hz), 130.81, 130.64, 130.50, 129.06, 128.96,

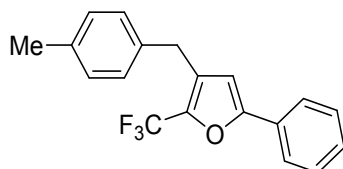
128.73, 128.59, 128.43, 127.95, 127.92, 127.58, 127.09, 126.99, 126.82, 126.64, 125.71, 125.59, 123.04, 122.50, 120.37 (q, J_{CF} = 266.24 Hz), 112.47, 30.59; ^{19}F NMR (282 MHz, CDCl_3), δ -60.65; HRMS (EI) m/z calcd. for $\text{C}_{26}\text{H}_{17}\text{OF}_3$ $[\text{M}]^+ = 402.1232$, found = 402.1229.

2m, 3-(4-fluorobenzyl)-5-phenyl-2-(trifluoromethyl)furan



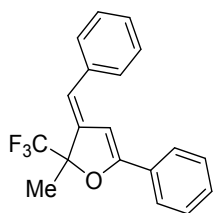
2m; white solid, m.p. = 33–35 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.72–7.69 (m, 2H), 7.46–7.34 (m, 3H), 7.27–7.22 (m, 2H), 7.09–7.04 (m, 2H), 6.47 (s, 1H), 3.97 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 161.68 (d, J_{CF} = 243.23 Hz), 155.23, 136.11 (q, J_{CF} = 40.2 Hz), 134.43 (d, J_{CF} = 3.08 Hz), 134.49 (d, J_{CF} = 7.8 Hz), 129.12, 128.75, 128.19, 124.38, 120.24 (q, J_{CF} = 266.1 Hz), 115.49 (d, J_{CF} = 21.15 Hz), 107.65, 29.72; ^{19}F NMR (282 MHz, CDCl_3), δ -60.90, -116.32; HRMS (EI) m/z calcd. for $\text{C}_{18}\text{H}_{12}\text{OF}_4$ $[\text{M}]^+ = 320.0824$, found = 320.0823.

2n 3-(4-methylbenzyl)-5-phenyl-2-(trifluoromethyl)furan



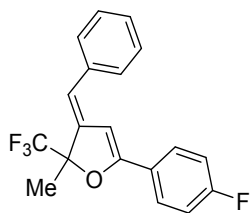
2n; colourless oil; ^1H NMR (300 MHz, CDCl_3): δ 7.73–7.70 (m, 2H), 7.47–7.35 (m, 3H), 7.22 (s, 4H), 6.51 (s, 1H), 3.99 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 155.04, 136.18, 135.94 (q, J_{CF} = 36.38 Hz), 135.70, 129.37, 129.25, 128.70, 128.62, 128.45, 124.36, 120.32 (q, J_{CF} = 266.1 Hz), 107.86, 30.08, 20.97; ^{19}F NMR (282 MHz, CDCl_3), δ -60.80; HRMS (EI) m/z calcd. for $\text{C}_{19}\text{H}_{15}\text{OF}_3$ $[\text{M}]^+ = 316.1075$, found = 316.1074.

4a (E)-3-benzylidene-2-methyl-5-phenyl-2-(trifluoromethyl)-2,3-dihydrofuran



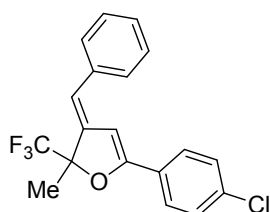
4a; yellow solid, m.p. = 50-52 °C; ^1H NMR (300 MHz, CD_3COCD_3): δ 7.84–7.81 (m, 2H), 8.76 (d, $J = 7.5$ Hz, 2H), 7.49–7.38 (m, 5H), 7.28–7.23 (m, 1H), 7.01 (s, 1H), 6.32 (s, 1H), 1.82 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3): δ 163.76, 141.85, 138.33, 130.97, 130.18, 129.57, 129.52, 129.01, 127.71, 126.60, 125.44 (q, $J_{\text{CF}} = 281.4$ Hz), 118.13, 100.64, 88.23 (q, $J_{\text{CF}} = 29.7$ Hz), 21.31; ^{19}F NMR (282 MHz, CD_3COCD_3), δ -82.74; HRMS (EI) m/z calcd. for $\text{C}_{19}\text{H}_{15}\text{OF}_3$ $[\text{M}]^+ = 316.1075$, found = 316.1075.

4b (E)-3-benzylidene-5-(4-fluorophenyl)-2-methyl-2-(trifluoromethyl)-2,3-dihydrofuran



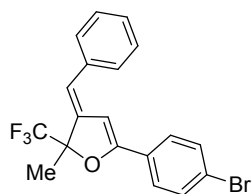
4b; yellow solid, m.p. = 86-88 °C; ^1H NMR (400 MHz, CD_3COCD_3): δ 7.88–7.85 (m, 2H), 7.53 (d, $J = 7.2$ Hz, 2H), 7.40–7.36 (m, 2H), 7.26–7.21 (m, 3H), 7.00 (s, 1H), 6.30 (s, 1H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 164.56 (d, $J_{\text{CF}} = 247.4$ Hz), 162.70, 141.70, 138.25, 129.53, 128.99, 128.90, 127.75, 126.72 (d, $J_{\text{CF}} = 3.3$ Hz), 125.39 (q, $J_{\text{CF}} = 281.4$ Hz), 118.22, 116.56 (d, $J_{\text{CF}} = 22.1$ Hz), 100.52, 88.36 (q, $J_{\text{CF}} = 30.0$ Hz), 21.24; ^{19}F NMR (376 MHz, CD_3COCD_3), δ -94.61, -123.02; HRMS (EI) m/z calcd. for $\text{C}_{19}\text{H}_{14}\text{OF}_4$ $[\text{M}]^+ = 334.0981$, found = 334.0986.

4c (E)-3-benzylidene-5-(4-chlorophenyl)-2-methyl-2-(trifluoromethyl)-2,3-dihydrofuran



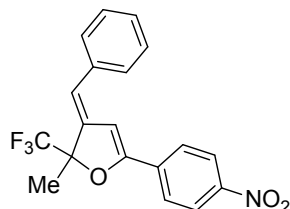
4c; yellow solid, m.p. = 83-85 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.41–7.37 (m, 2H), 7.28–7.24 (m, 1H), 7.11 (s, 1H), 6.35 (s, 1H), 1.81 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 162.51, 141.48, 138.15, 132.73, 129.54, 129.32, 129.04, 128.37, 127.85, 125.35 (q, *J*_{CF} = 281.4 Hz), 124.57, 118.86, 101.52, 88.36 (q, *J*_{CF} = 29.8 Hz), 21.24; ¹⁹F NMR (376 MHz, CD₃COCD₃), δ -94.58; HRMS (EI) *m/z* calcd. for C₁₉H₁₄OF₃Cl [M]⁺ = 350.0685, found = 350.0684.

4d (*E*)-3-benzylidene-5-(4-bromophenyl)-2-methyl-2-(trifluoromethyl)-2,3-dihydrofuran



4d; yellow solid, m.p. = 132-134 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.41–7.37 (m, 2H), 7.28–7.24 (m, 1H), 7.10 (s, 1H), 6.34 (s, 1H), 1.81 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 162.46, 141.51, 138.16, 136.21, 129.75, 129.54, 129.05, 128.95, 128.19, 127.84, 125.36 (q, *J*_{CF} = 281.4 Hz), 118.78, 101.43, 88.37 (q, *J*_{CF} = 29.9 Hz), 21.23; ¹⁹F NMR (376 MHz, CD₃COCD₃), δ -94.58; HRMS (EI) *m/z* calcd. for C₁₉H₁₄OF₃Br [M]⁺ = 394.0180, found = 394.0179.

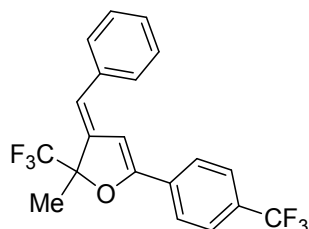
4e (*E*)-3-benzylidene-2-methyl-5-(4-nitrophenyl)-2-(trifluoromethyl)-2,3-dihydrofuran



4e; red solid, m.p. = 144-146 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.42–7.38 (m, 2H), 7.34 (s, 1H), 7.31–7.27 (m, 1H), 6.47 (s, 1H), 1.85 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 161.17, 149.03, 141.00, 137.80, 135.89, 129.57, 129.18, 128.24, 127.43, 125.24 (q,

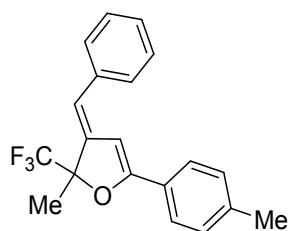
$J_{CF} = 281.4$ Hz), 124.74, 120.99, 104.76, 88.59 (q, $J_{CF} = 30.0$ Hz), 21.15; ^{19}F NMR (376 MHz, CD_3COCD_3), δ -94.49; HRMS (EI) m/z calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_3\text{NF}_3$ $[\text{M}]^+ = 361.0926$, found = 361.0925.

4f (E)-3-benzylidene-2-methyl-2-(trifluoromethyl)-5-(4-(trifluoromethyl)phenyl)-2,3-dihydrofuran



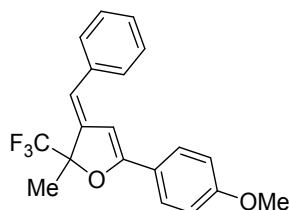
4f, yellow solid, m.p. = 103-105 °C; ^1H NMR (400 MHz, CD_3COCD_3): δ 8.04 (d, $J = 8.8$ Hz, 2H), 7.80 (d, $J = 7.6$ Hz, 2H), 7.57 (d, $J = 7.6$ Hz, 2H), 7.42–7.38 (m, 2H), 7.30–7.25 (m, 2H), 6.42 (s, 1H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 161.91, 141.28, 138.02, 133.87, 131.61 (q, $J_{CF} = 32.1$ Hz), 129.60, 129.17, 128.09, 127.16, 126.53 (q, $J_{CF} = 3.8$ Hz), 125.36 (q, $J_{CF} = 281.3$ Hz), 125.16 (q, $J_{CF} = 281.0$ Hz), 120.00, 103.15, 88.50 (q, $J_{CF} = 29.8$ Hz), 21.23; ^{19}F NMR (376 MHz, CD_3COCD_3), δ -74.70, -94.49; HRMS (EI) m/z calcd. for $\text{C}_{20}\text{H}_{14}\text{OF}_6$ $[\text{M}]^+ = 384.0949$, found = 384.0952.

4g (E)-3-benzylidene-2-methyl-5-(p-tolyl)-2-(trifluoromethyl)-2,3-dihydrofuran



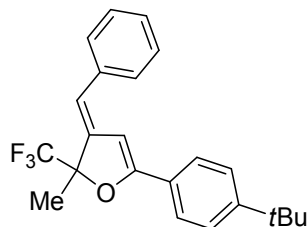
4g, yellow oil; ^1H NMR (400 MHz, CD_3COCD_3): δ 7.70 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 7.6$ Hz, 2H), 7.41–7.37 (m, 2H), 7.27–7.23 (m, 3H), 6.95 (s, 1H), 6.28 (s, 1H), 2.36 (s, 2H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 164.05, 141.99, 141.30, 138.45, 130.23, 129.52, 128.98, 127.60, 127.48, 126.63, 125.48 (q, $J_{CF} = 281.4$ Hz), 117.53, 99.85, 88.19 (q, $J_{CF} = 29.9$ Hz), 21.52, 21.32; ^{19}F NMR (376 MHz, CD_3COCD_3), δ -94.72; HRMS (EI) m/z calcd. for $\text{C}_{20}\text{H}_{17}\text{OF}_3$ $[\text{M}]^+ = 330.1232$, found = 330.1230.

4h (E)-3-benzylidene-5-(4-methoxyphenyl)-2-methyl-2-(trifluoromethyl)-2,3-dihydrofuran



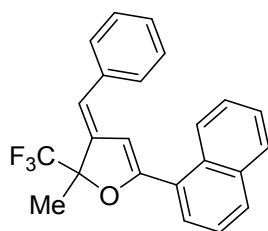
4h; yellow solid, m.p. = 74-76 °C; ^1H NMR (400 MHz, CD_3COCD_3): δ 7.79–7.75 (m, 2H), 7.53 (d, $J = 7.2$ Hz, 2H), 7.40–7.36 (m, 2H), 7.25–7.22 (m, 1H), 7.03–6.99 (m, 2H), 6.88 (s, 1H), 6.23 (s, 1H), 3.83 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 163.97, 162.31, 142.16, 138.57, 129.49, 128.91, 128.36, 127.46, 125.50 (q, $J_{\text{CF}} = 281.5$ Hz), 122.70, 116.77, 115.03, 98.76, 88.20 (q, $J_{\text{CF}} = 29.5$ Hz), 55.81, 21.31; ^{19}F NMR (376 MHz, CD_3COCD_3), δ -94.76; HRMS (EI) m/z calcd. for $\text{C}_{20}\text{H}_{17}\text{O}_2\text{F}_3$ $[\text{M}]^+ = 346.1181$, found = 346.1175.

4i (E)-3-benzylidene-5-(4-(tert-butyl)phenyl)-2-methyl-2-(trifluoromethyl)-2,3-dihydrofuran



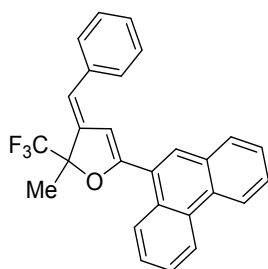
4i; yellow solid, m.p. = 81-83 °C; ^1H NMR (400 MHz, CD_3COCD_3): δ 7.77 (d, $J = 8.8$ Hz, 2H), 7.55–7.50 (m, 4H), 7.41–7.37 (m, 2H), 7.26–7.23 (m, 1H), 6.99 (s, 1H), 6.29 (s, 1H), 1.81 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 163.98, 154.32, 141.97, 138.43, 129.51, 128.96, 127.60, 127.45, 126.52, 126.49, 125.45 (q, $J_{\text{CF}} = 281.4$ Hz), 117.56, 117.55, 99.98, 88.17 (q, $J_{\text{CF}} = 29.7$ Hz), 35.46, 31.45, 21.31; ^{19}F NMR (376 MHz, CD_3COCD_3), δ -94.68; HRMS (EI) m/z calcd. for $\text{C}_{23}\text{H}_{23}\text{OF}_3$ $[\text{M}]^+ = 372.1701$, found = 372.1703.

4j (E)-3-benzylidene-2-methyl-5-(naphthalen-1-yl)-2-(trifluoromethyl)-2,3-dihydrofuran



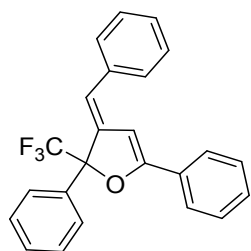
4j; yellow solid, m.p. = 74-76 °C; ^1H NMR (400 MHz, CD_3COCD_3): δ 8.45 (d, J = 8.4 Hz, 1H), 8.04–7.98 (m, 2H), 7.90–7.88 (m, 1H), 7.64–7.55 (m, 5H), 7.41–7.37 (m, 2H), 7.28–7.23 (m, 1H), 6.84 (s, 1H), 6.39 (s, 1H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 164.62, 141.82, 138.30, 134.88, 131.64, 131.40, 129.60, 129.55, 128.99, 128.17, 128.13, 127.97, 127.78, 127.21, 126.09, 125.51 (q, J_{CF} = 281.5 Hz), 118.42, 104.97, 88.23 (q, J_{CF} = 29.8 Hz), 21.32; ^{19}F NMR (376 MHz, CD_3COCD_3), δ -94.79; HRMS (EI) m/z calcd. for $\text{C}_{23}\text{H}_{17}\text{OF}_3$ $[\text{M}]^+ = 366.1232$, found = 366.1236.

4k (E)-3-benzylidene-2-methyl-5-(phenanthren-9-yl)-2-(trifluoromethyl)-2,3-dihydrofuran



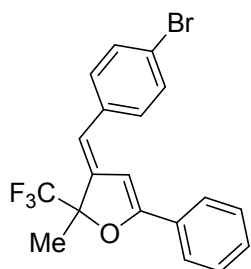
4k; yellow solid, m.p. = 145-147 °C; ^1H NMR (400 MHz, CD_2Cl_2): δ 8.77–8.68 (m, 2H), 8.47–8.44 (m, 1H), 8.13 (s, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.76–7.64 (m, 4H), 7.51 (d, J = 7.6 Hz, 2H), 7.44–7.40 (m, 2H), 7.30–7.27 (m, 1H), 6.77 (s, 1H), 6.34 (s, 1H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 164.07, 141.74, 137.98, 131.43, 131.26, 131.10, 129.78, 129.52, 129.18, 129.03, 128.54, 127.68, 127.53, 127.43, 126.74, 126.53, 125.03 (q, J_{CF} = 281.4 Hz), 123.63, 123.13, 117.88, 105.05, 87.83 (q, J_{CF} = 29.9 Hz), 21.55; ^{19}F NMR (376 MHz, CD_2Cl_2), δ -91.93; HRMS (EI) m/z calcd. for $\text{C}_{27}\text{H}_{19}\text{OF}_3$ $[\text{M}]^+ = 416.1388$, found = 416.1385.

4l (E)-3-benzylidene-2,5-diphenyl-2-(trifluoromethyl)-2,3-dihydrofuran



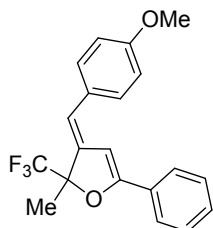
4l; yellow solid, m.p. = 146-148 °C; ^1H NMR (400 MHz, CD_3COCD_3): δ 7.94–7.92 (m, 2H), 7.86 (d, J = 7.6 Hz, 2H), 7.57–7.45 (m, 8H), 7.41–7.37 (m, 2H), 7.28–7.25 (m, 1H), 7.13 (s, 1H), 6.56 (s, 1H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 163.66, 141.50, 138.05, 136.72, 131.18, 130.33, 129.96, 129.72, 129.71, 129.57, 129.21, 127.98, 126.99, 126.98, 126.69, 125.04 (q, J_{CF} = 281.6 Hz), 120.65, 100.98, 90.53 (q, J_{CF} = 32.2 Hz); ^{19}F NMR (376 MHz, CD_3COCD_3), δ -100.03; HRMS (EI) m/z calcd. for $\text{C}_{24}\text{H}_{17}\text{OF}_3$ $[\text{M}]^+ = 378.1232$, found = 378.1228.

4m (E)-3-(4-bromobenzylidene)-2-methyl-5-phenyl-2-(trifluoromethyl)-2,3-dihydrofuran



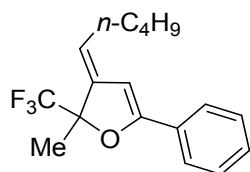
4m; yellow solid, m.p. = 55-57 °C; ^1H NMR (400 MHz, CD_3COCD_3): δ 7.84–7.82 (m, 2H), 7.55–7.45 (m, 7H), 7.03 (s, 1H), 6.27 (s, 1H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 164.33, 142.76, 137.50, 132.52, 131.16, 130.83, 130.03, 129.60, 128.09 (q, J_{CF} = 282.2 Hz), 123.87, 120.81, 116.65, 100.46, 88.36 (q, J_{CF} = 29.7 Hz), 55.60, 21.17; ^{19}F NMR (376 MHz, CD_3COCD_3), δ -94.73; HRMS (EI) m/z calcd. for $\text{C}_{19}\text{H}_{14}\text{OF}_3\text{Br}$ $[\text{M}]^+ = 394.0180$, found = 394.0182.

4n (E)-3-(4-methoxybenzylidene)-2-methyl-5-phenyl-2-(trifluoromethyl)-2,3-dihydrofuran



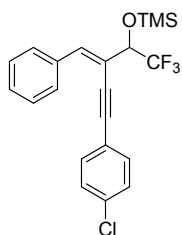
4n; yellow solid, m.p. = 79-81 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.83–7.80 (m, 2H), 7.51–7.42 (m, 5H), 7.01 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.26 (s, 1H), 3.81 (s, 3H), 1.79 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 162.93, 159.69, 139.56, 130.94, 130.77, 130.33, 129.57, 126.46, 125.51 (q, *J*_{CF} = 281.5 Hz), 117.94, 117.93, 114.92, 100.74, 88.12 (q, *J*_{CF} = 29.6 Hz), 21.31; ¹⁹F NMR (376 MHz, CD₃COCD₃), δ -94.54; HRMS (EI) *m/z* calcd. for C₂₀H₁₇O₂F₃ [M]⁺ = 346.1181, found = 346.1179.

4o (*E*)-2-methyl-3-pentylidene-5-phenyl-2-(trifluoromethyl)-2,3-dihydrofuran



4o; colorless oil; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.73–7.70 (m, 2H), 7.45–7.37 (m, 3H), 6.54 (s, 1H), 5.30 (t, *J* = 7.6 Hz, 1H), 2.29–2.23 (m, 2H), 1.65 (s, 3H), 1.48–1.34 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 160.39, 141.65, 130.72, 130.41, 129.53, 126.24, 125.56 (q, *J*_{CF} = 281.1 Hz), 119.88, 100.20, 88.63 (q, *J*_{CF} = 29.8 Hz), 32.67, 30.02, 22.89, 21.58, 14.29; ¹⁹F NMR (376 MHz, CD₃COCD₃), δ -94.06; HRMS (EI) *m/z* calcd. for C₁₇H₁₉OF₃ [M]⁺ = 296.1388, found = 296.1392.

(*E*)-((3-benzylidene-5-(4-chlorophenyl)-1,1,1-trifluoropent-4-yn-2-yl)oxy)-trimethylsilane



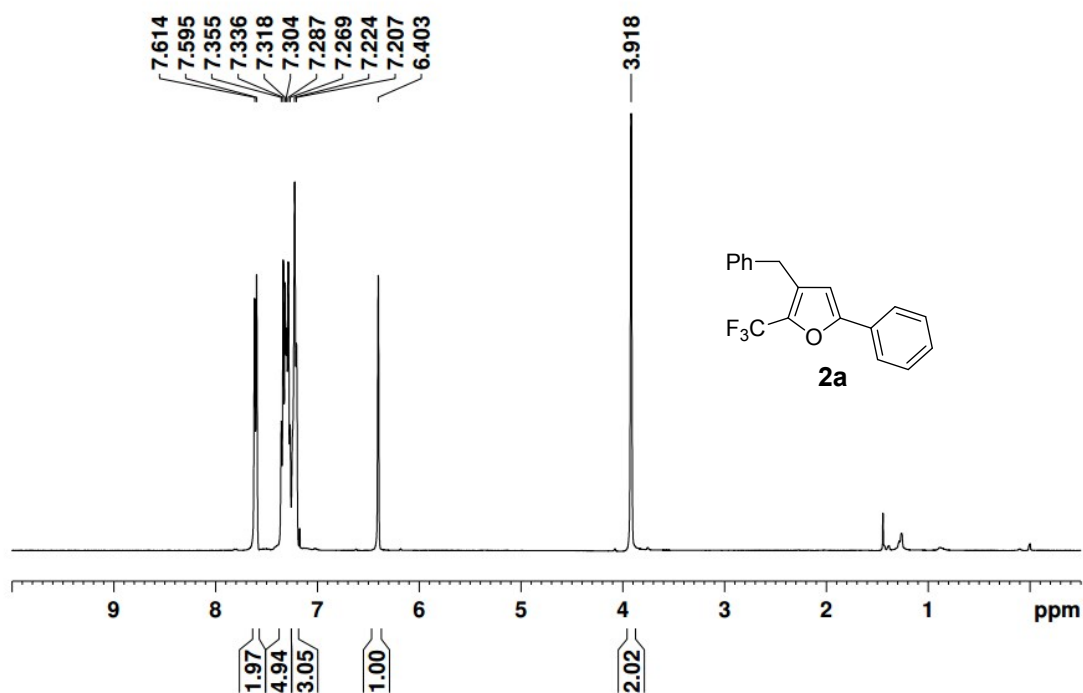
colorless oil; ¹H NMR (400 MHz, CD₃COCD₃): δ 8.04–8.01 (m, 2H), 7.59–7.56 (m, 2H), 7.51–7.47 (m, 4H), 7.44–7.39 (m, 1H), 7.28 (s, 1H), 5.04–4.99 (m, 1H), 0.27 (s, 9H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 140.08, 136.29, 135.45, 133.85, 130.33, 130.13, 129.96, 125.38 (q, *J*_{CF} = 281.0 Hz), 122.66, 117.22, 97.33, 88.27, 75.26 (q, *J*_{CF} = 31.4 Hz), -0.09; ¹⁹F NMR (376 MHz, CD₃COCD₃), δ -99.76; HRMS (EI) *m/z* calcd. for C₂₁H₂₀OF₃ClSi [M]⁺ = 408.0924, found = 408.0922.

6. References

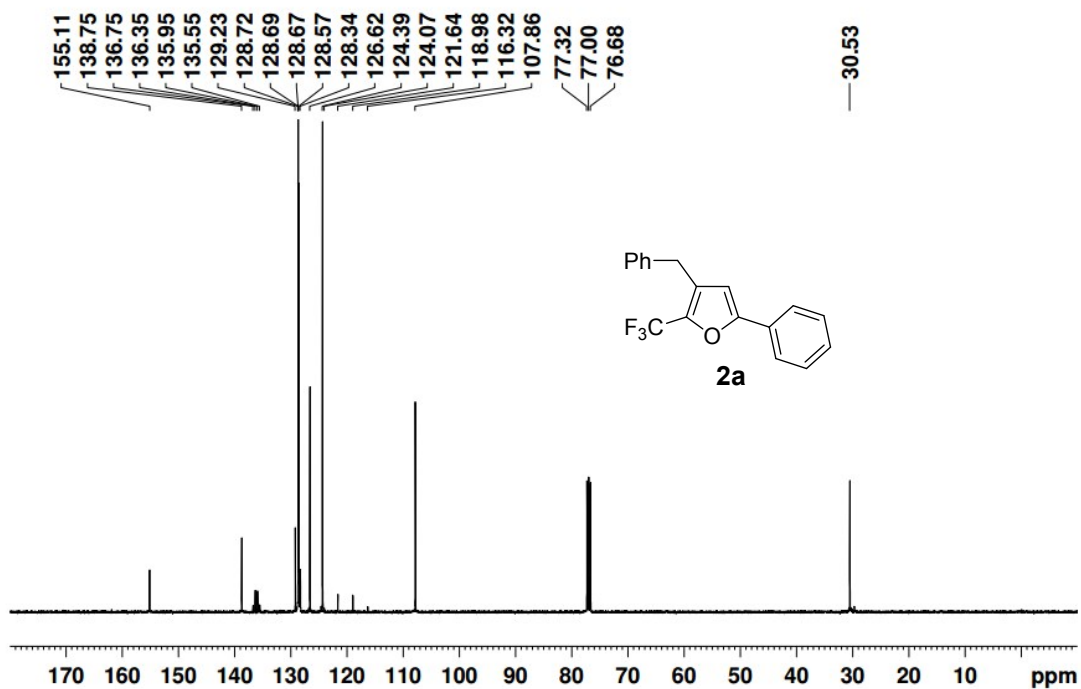
- [1] a) T. Yao, X. Zhang, R. C. Larock, *J. Am. Chem. Soc.* **2004**, *126*, 11164; b) N. T. Patil, H. Wu, Y. Yamamoto, *J. Org. Chem.* **2005**, *70*, 4531; c) Y. Liu, S. Zhou, *Org. Lett.* **2005**, *7*, 4609.
- [2] a) Y. Chen, Y. Liu, *J. Org. Chem.* **2011**, *76*, 5274; b) M. Lautens, M. L. Maddess, E. L. O. Sauer, S. G. Ouellet, *Org. Lett.* **2002**, *4*, 83.

7. ^1H , ^{13}C , ^{19}F spectra for 2 and 4

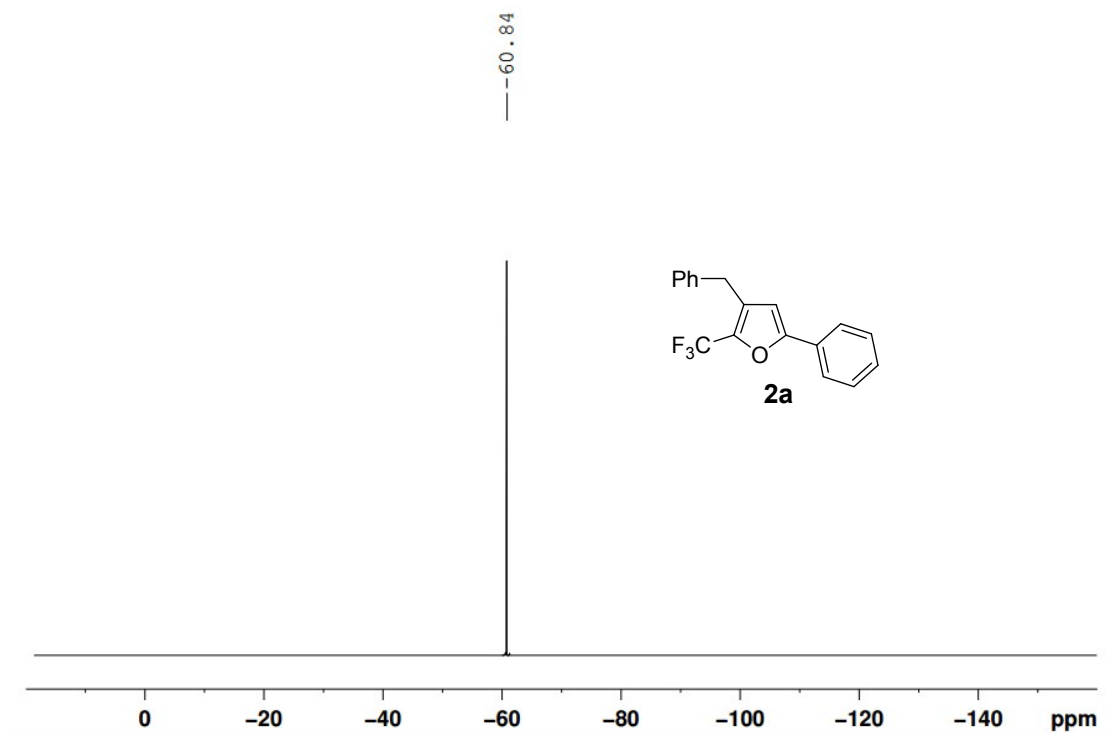
zw-3-51



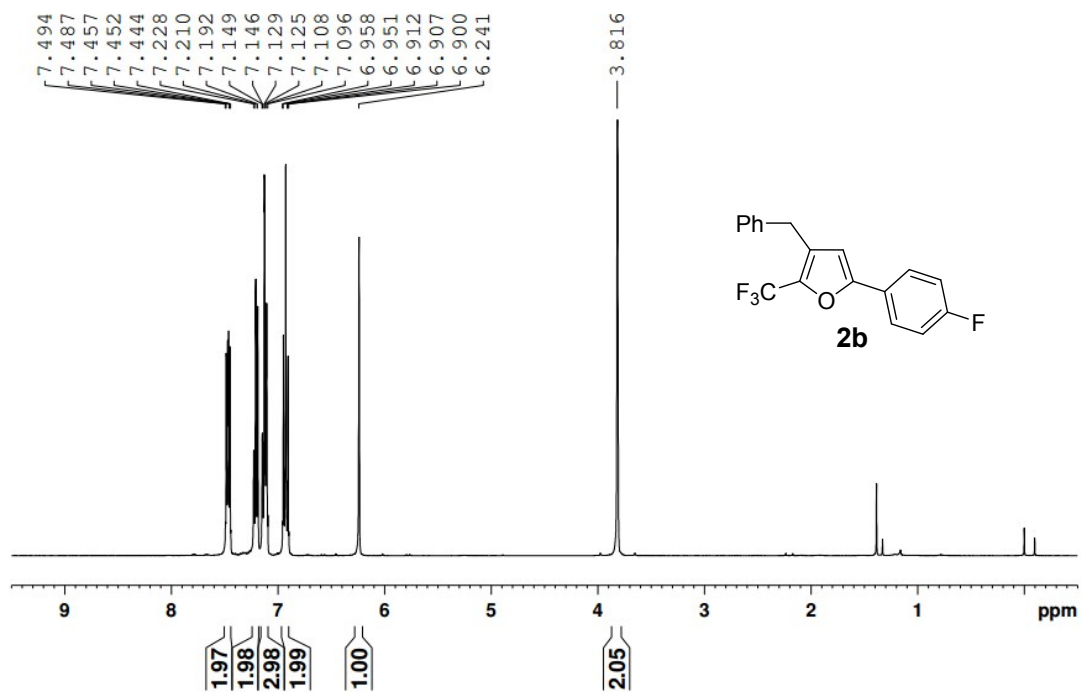
zw-3-51c



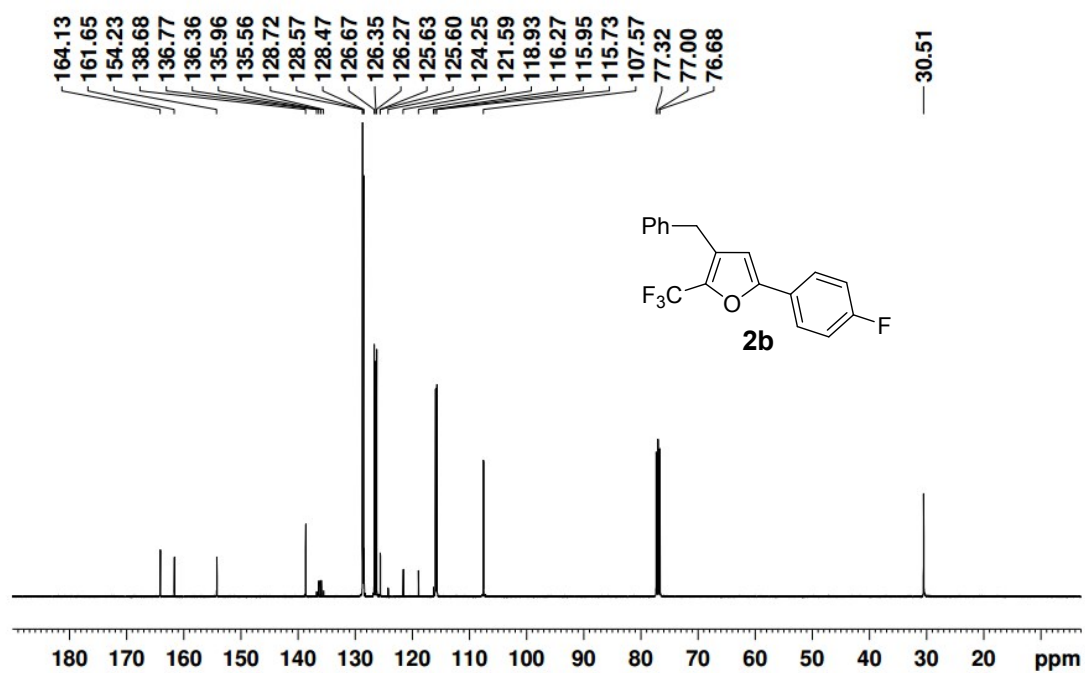
zw-3-51f



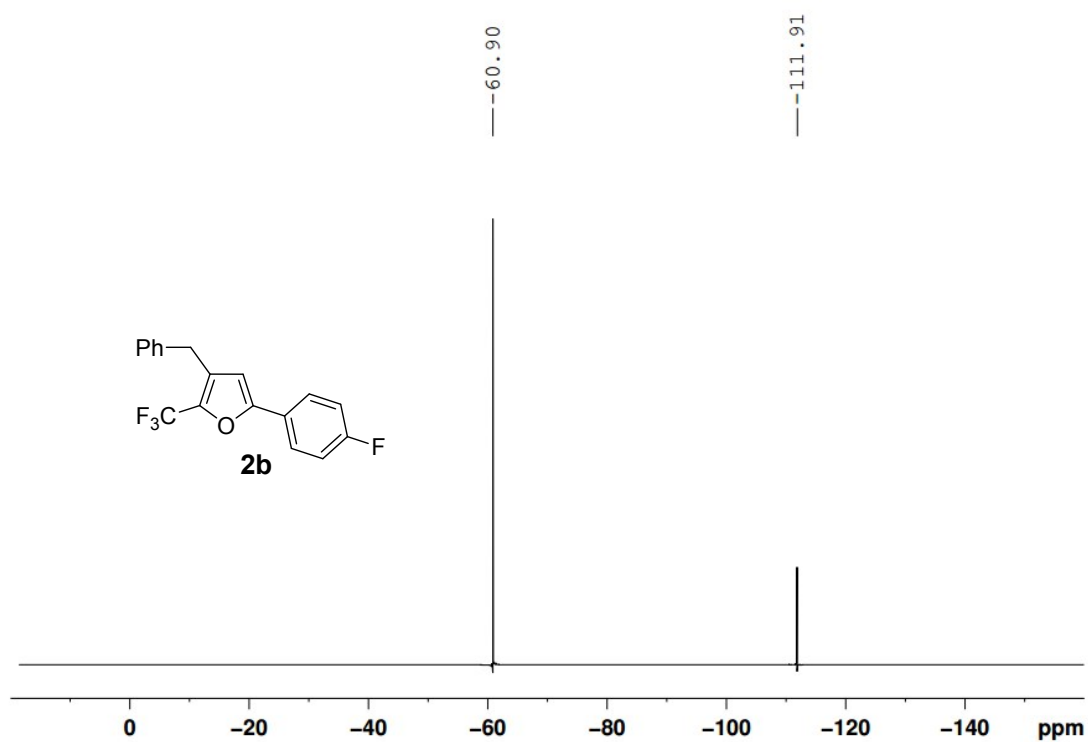
zw-3-55



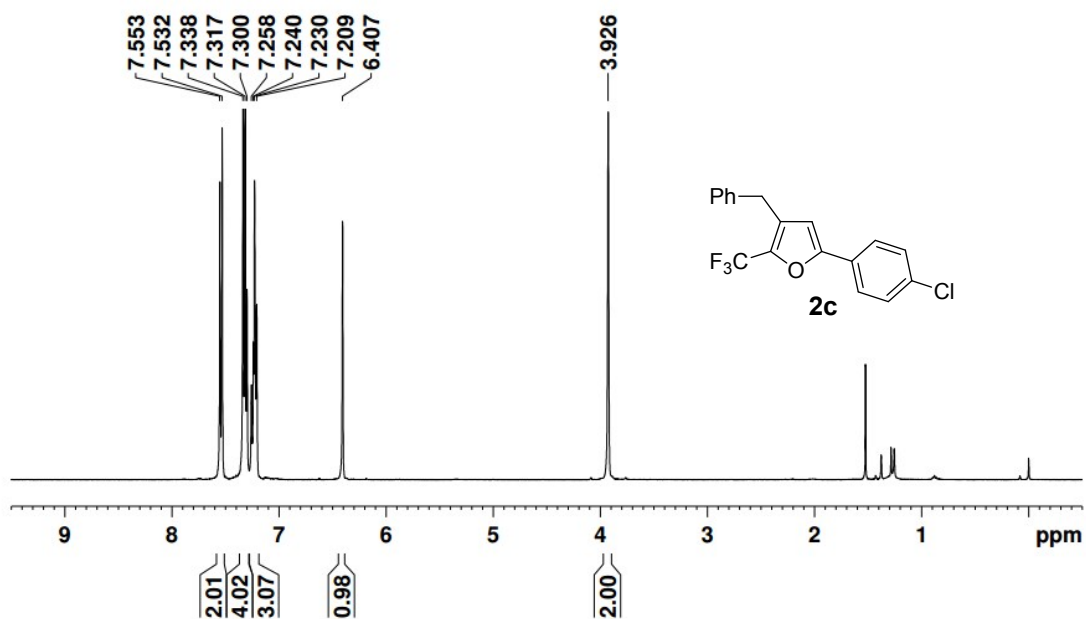
zw-3-55c



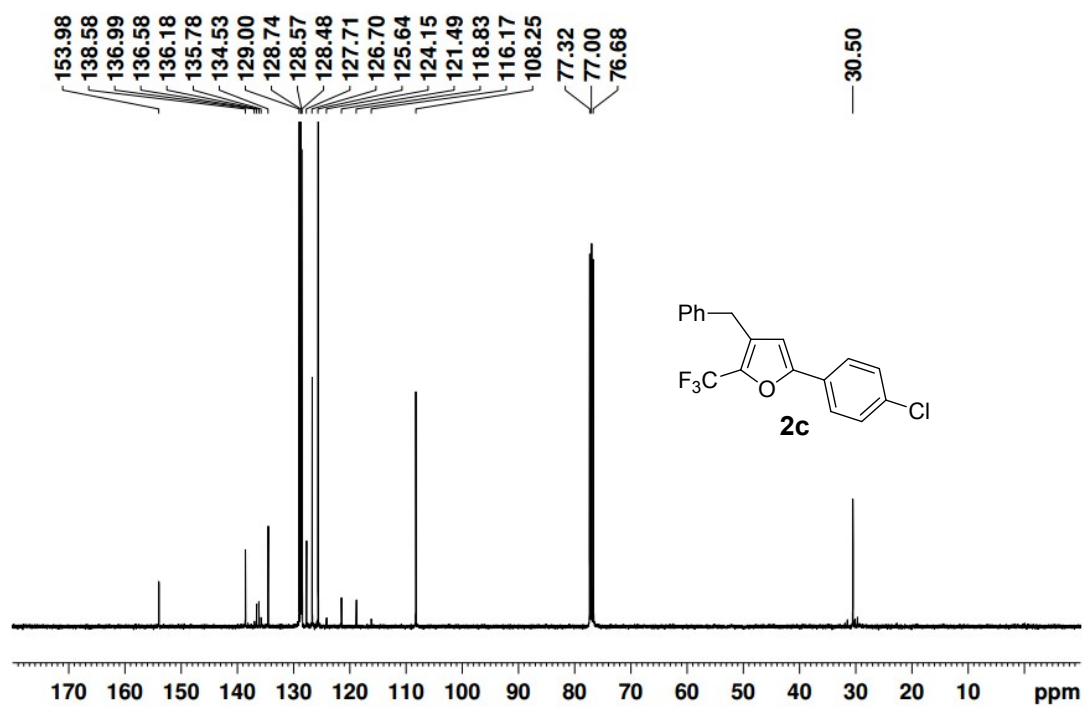
zw-3-55f



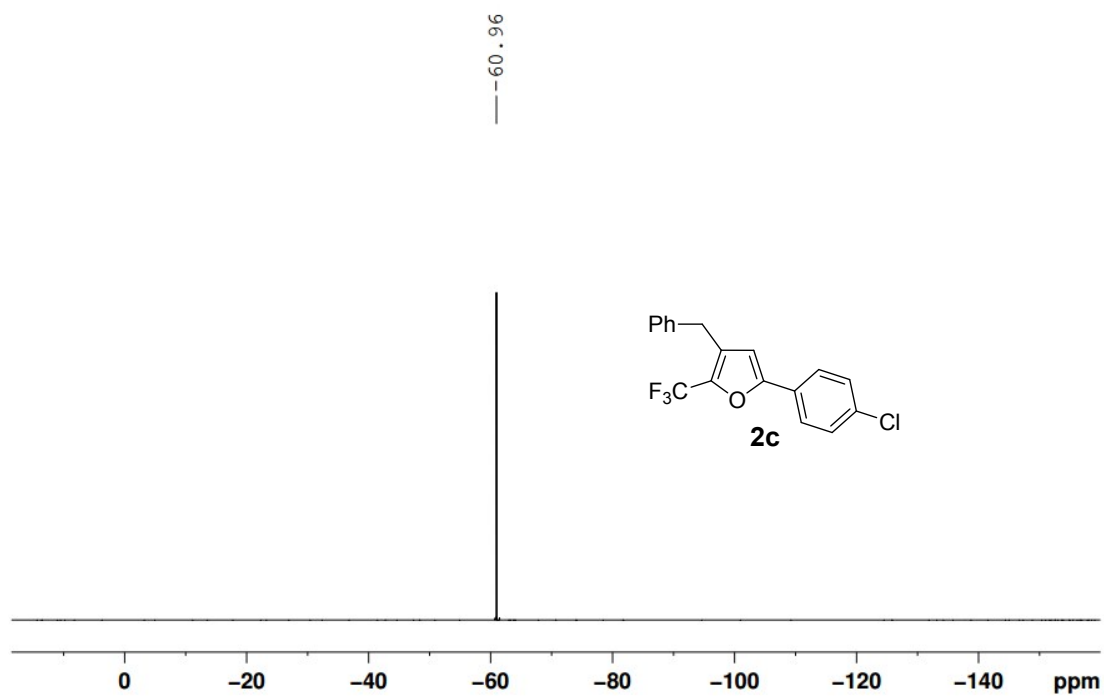
zw-3-50



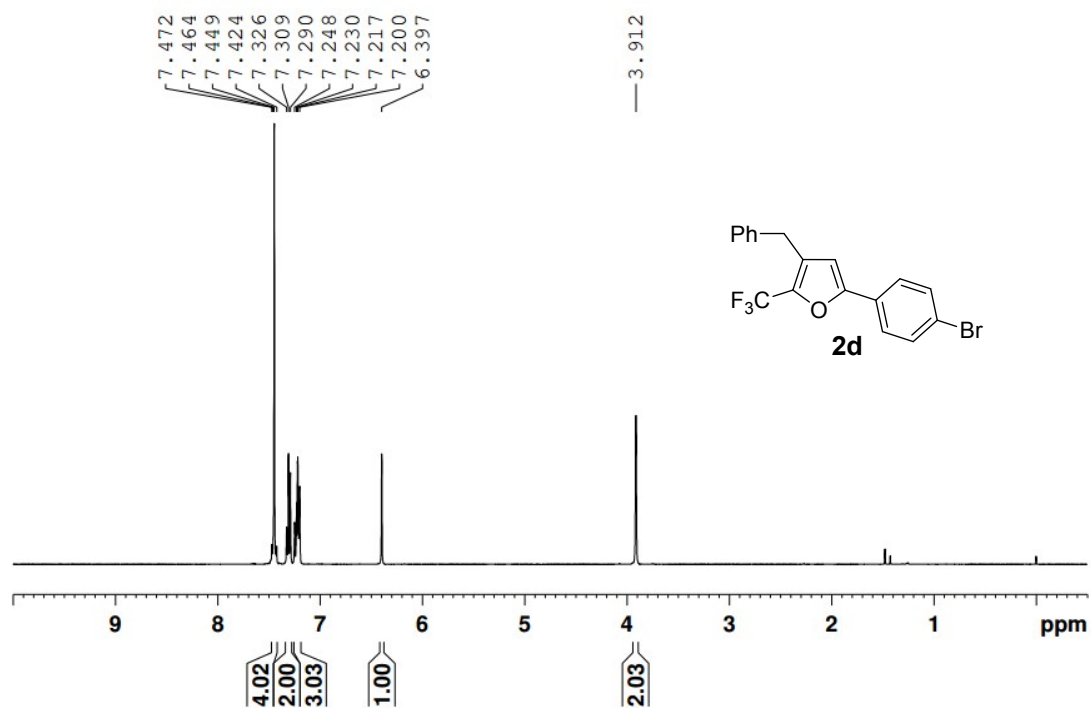
zw-3-50c



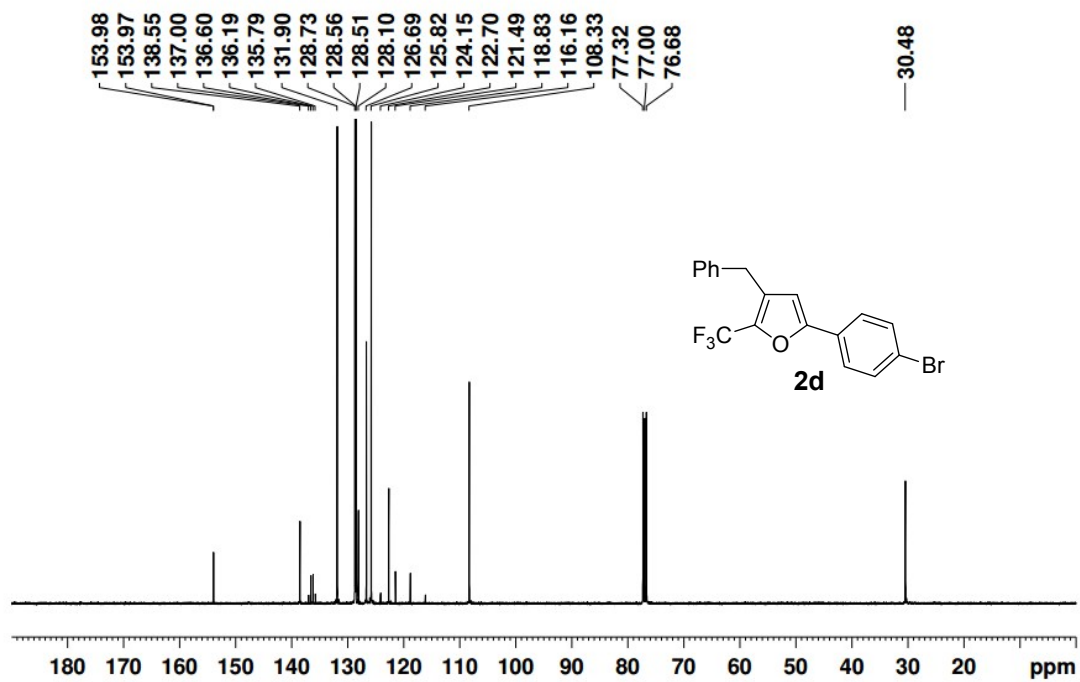
zw-3-50f



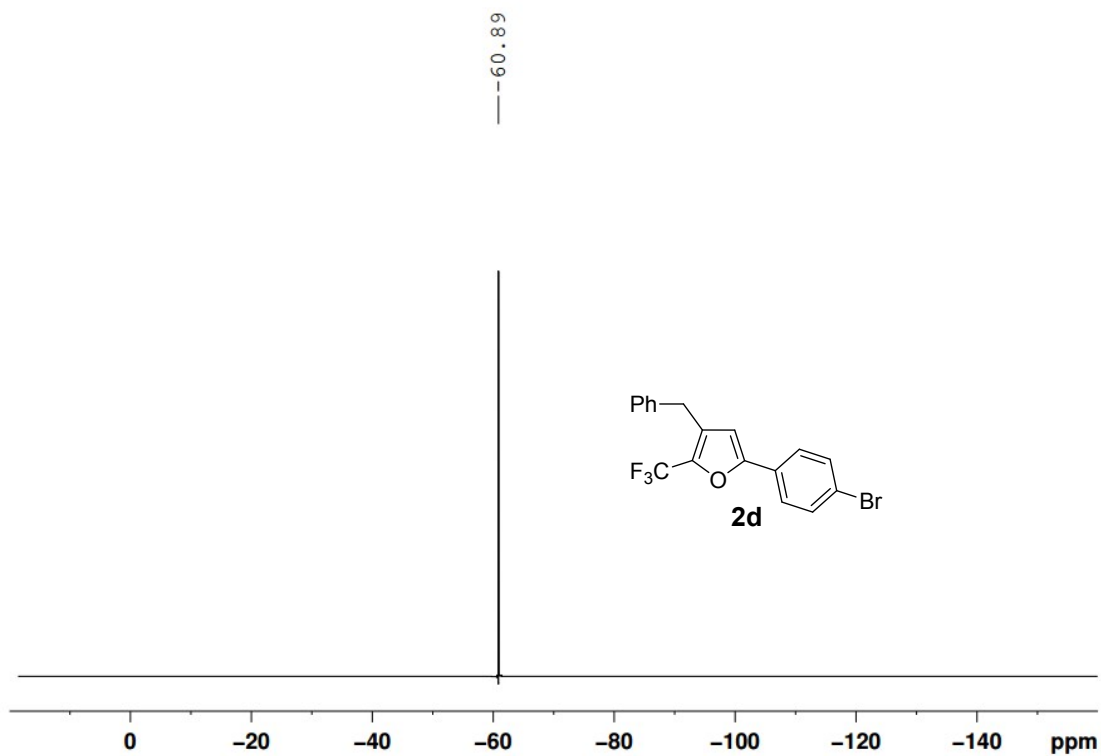
zw-3-57



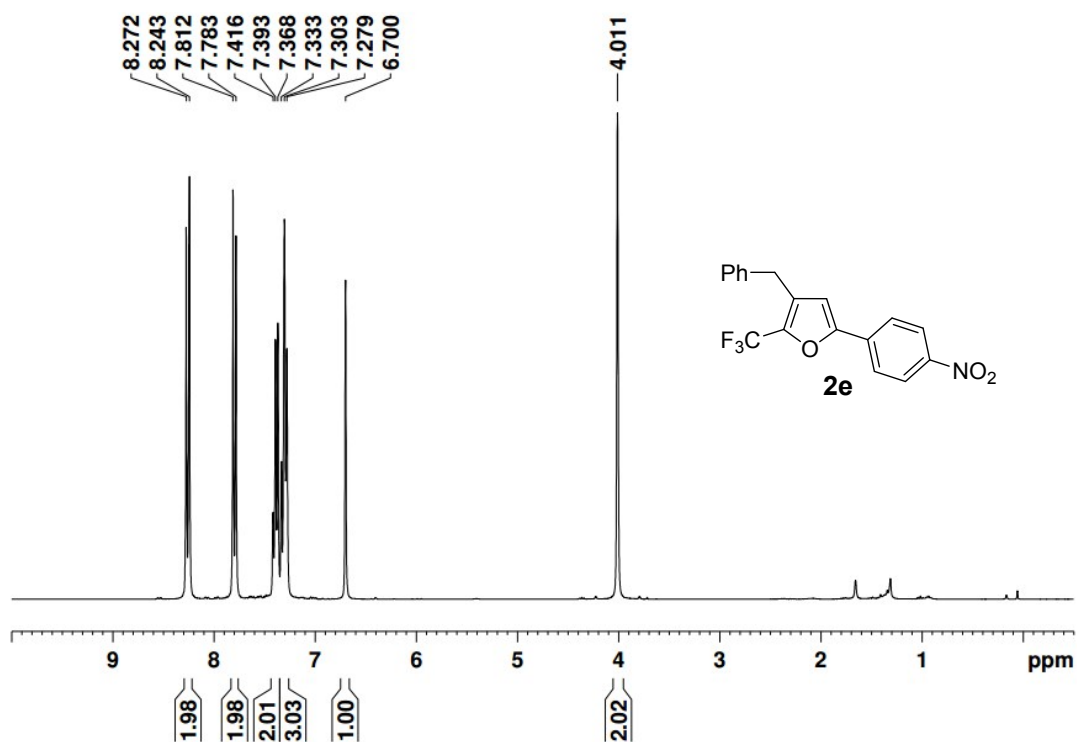
zw-3-57c



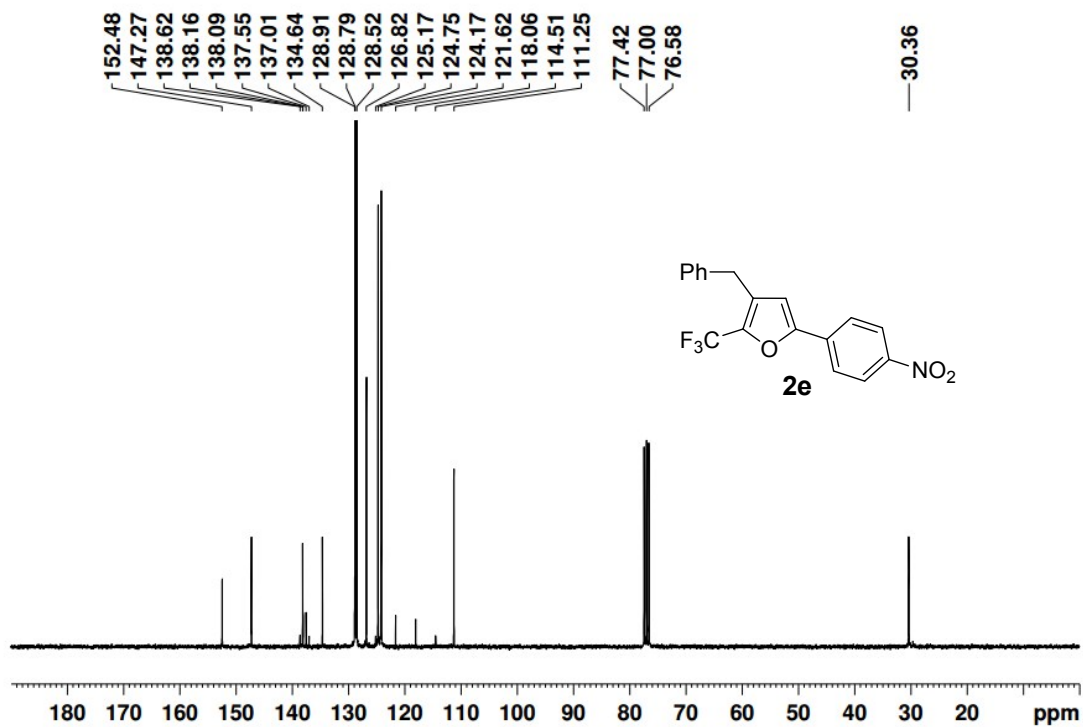
zw-3-57f



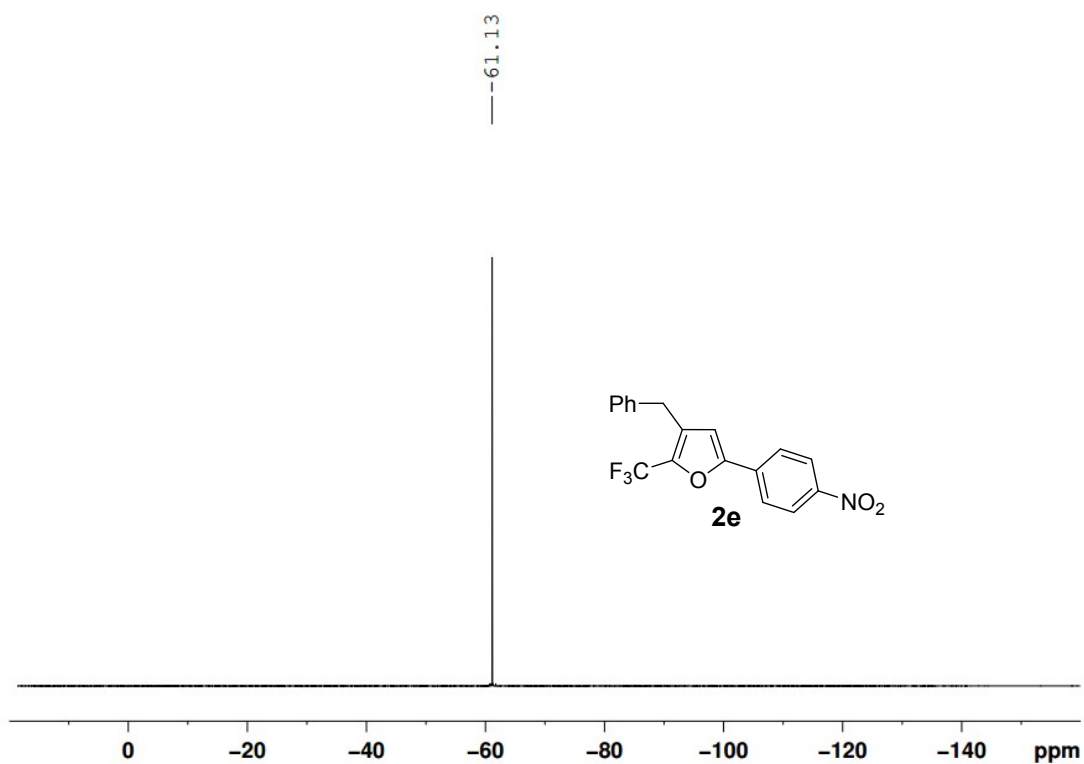
zw-3-62



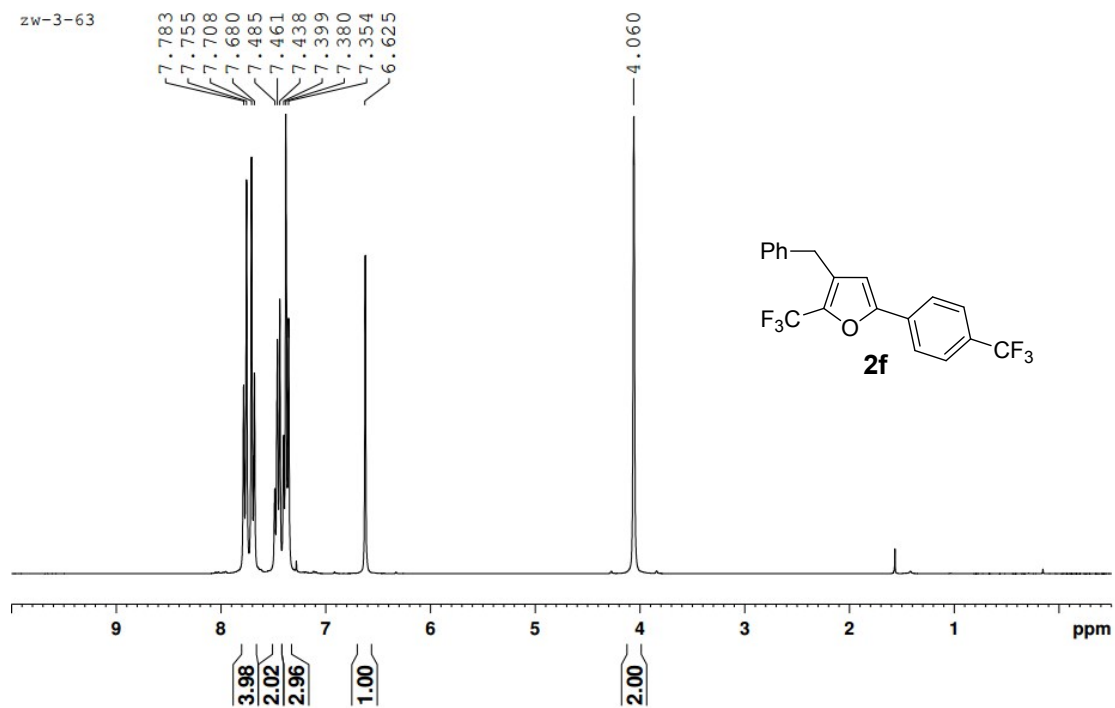
zw-3-62c



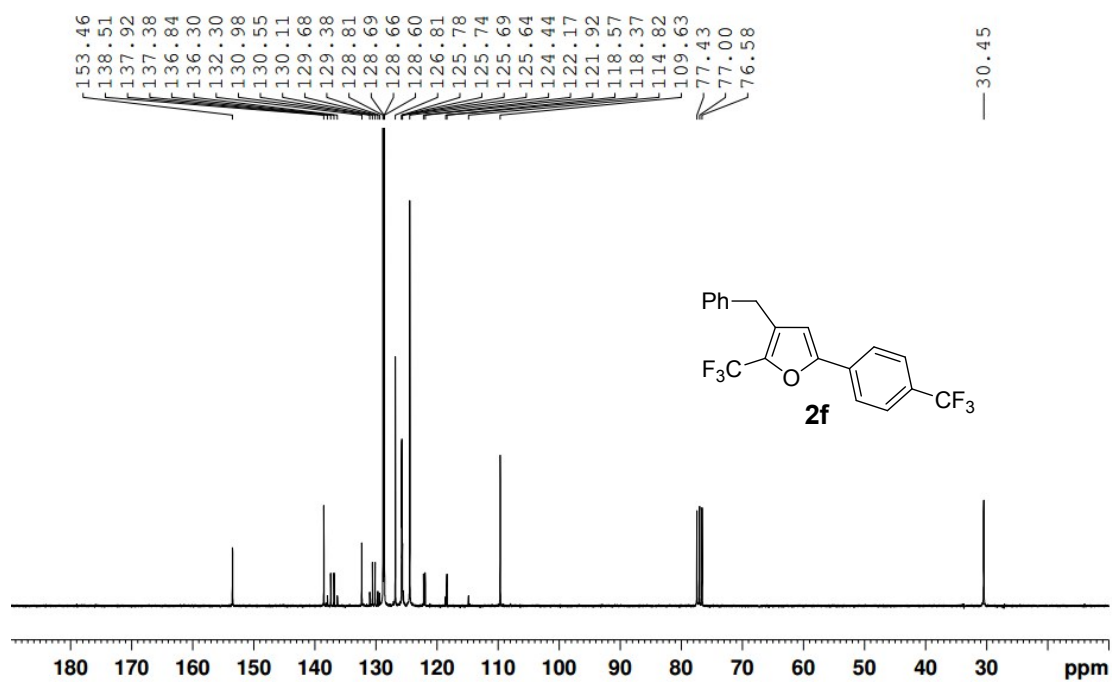
zw-3-62f



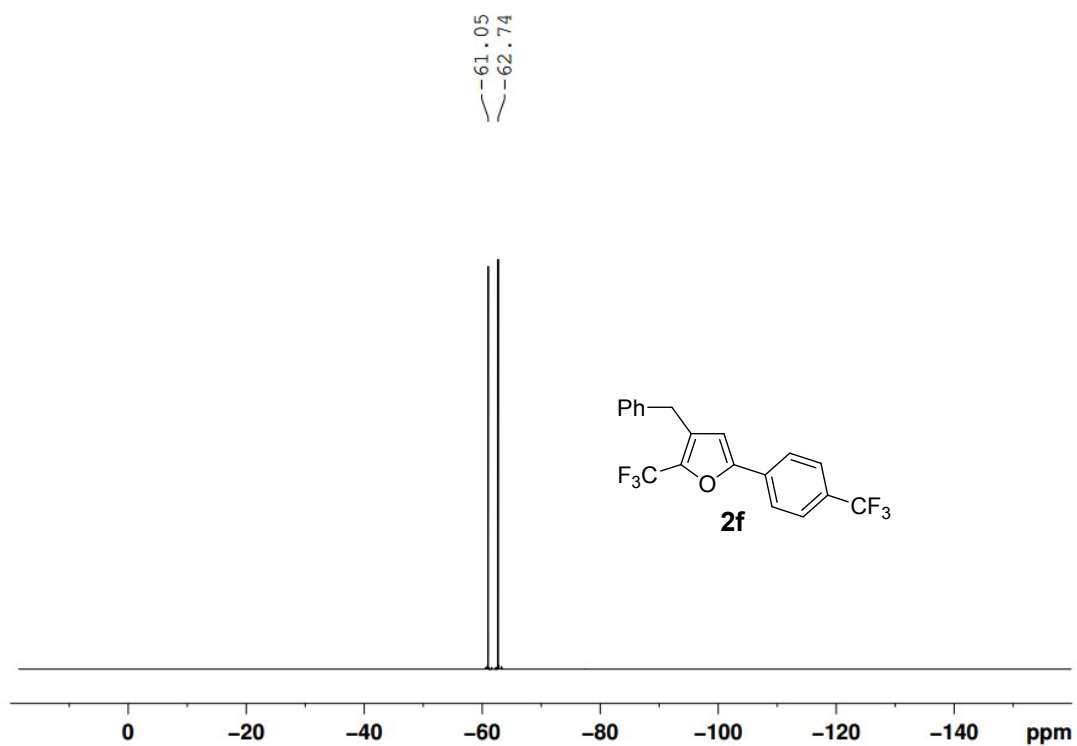
zw-3-63



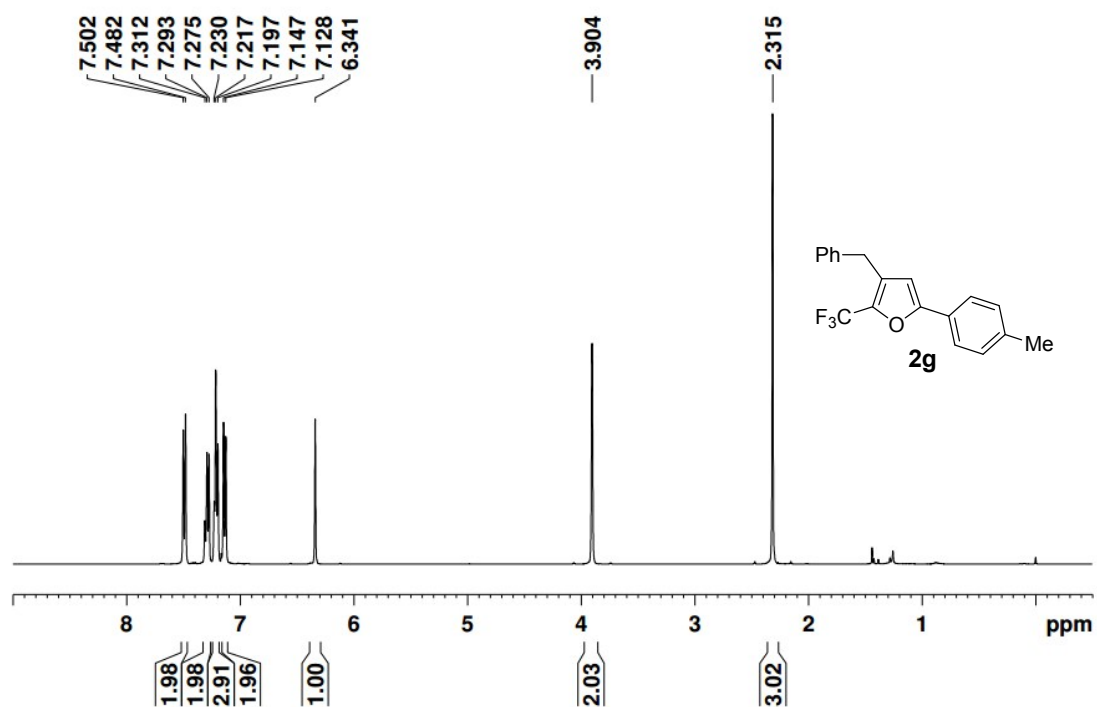
zw-3-63c



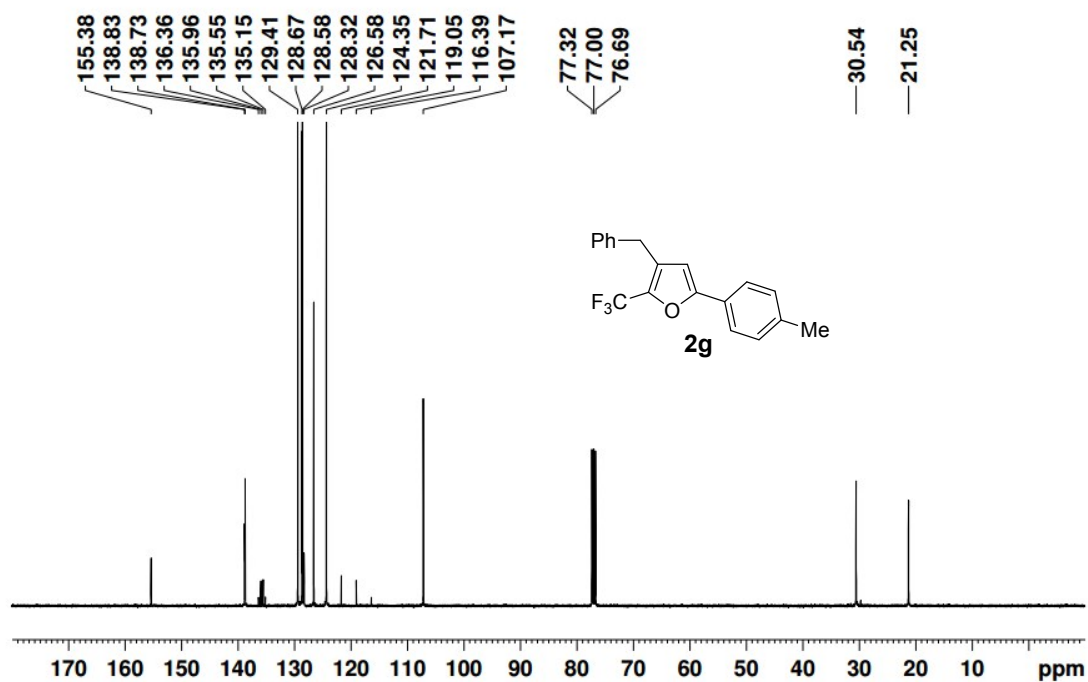
zw-3-63f



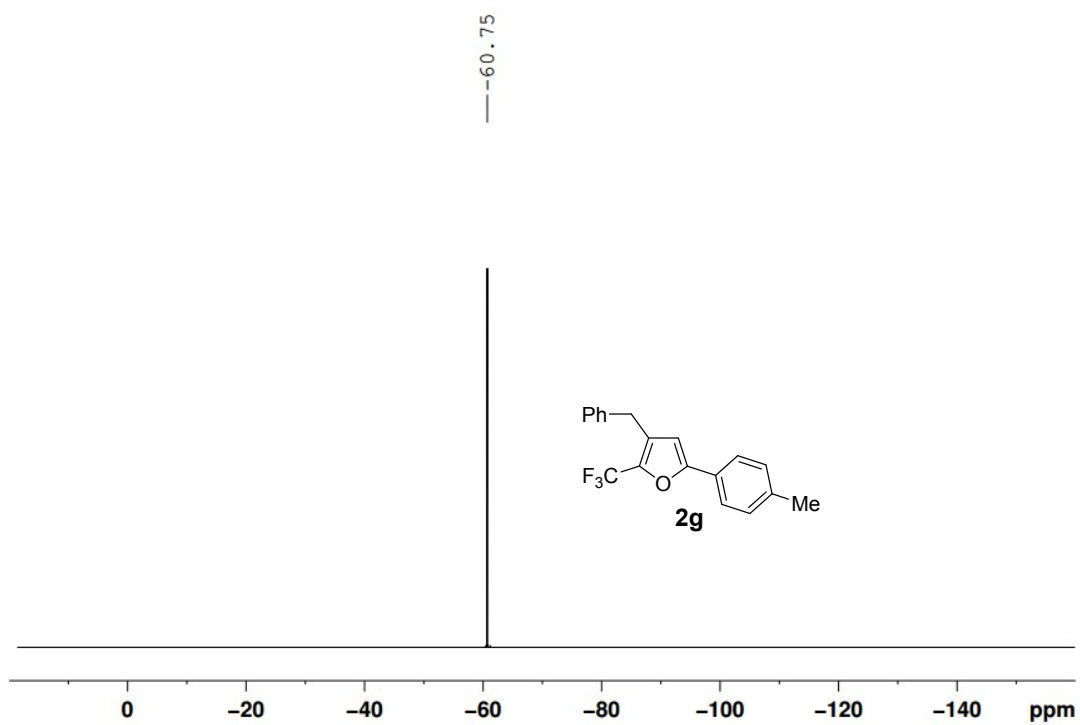
zw-3-52



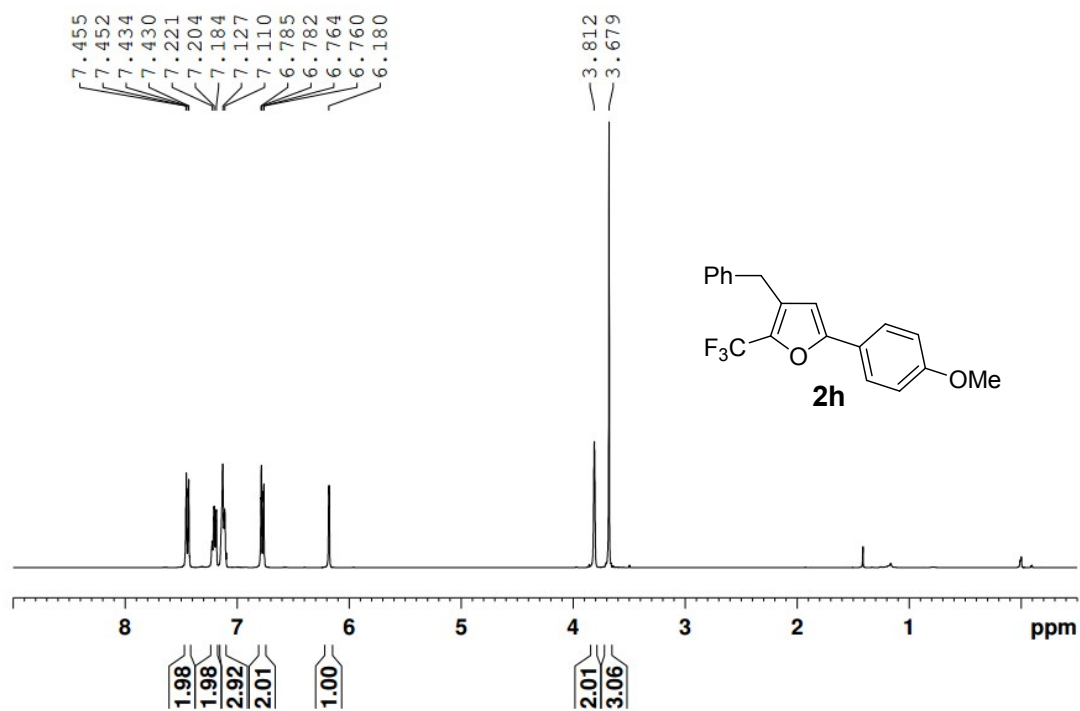
zw-3-52c



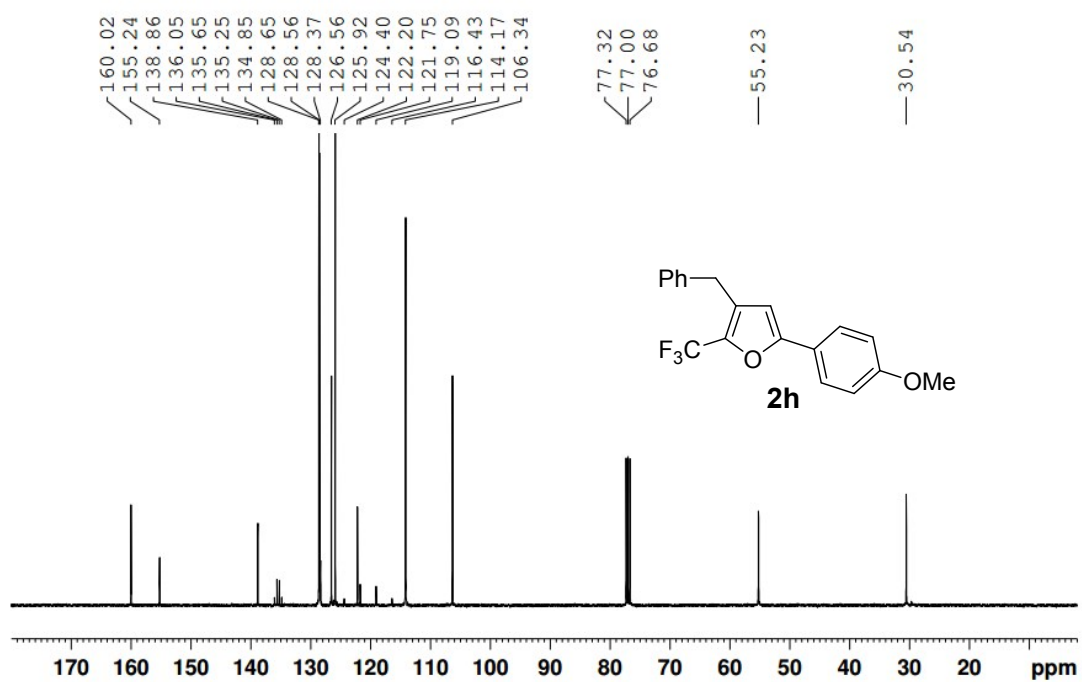
zw-3-52f



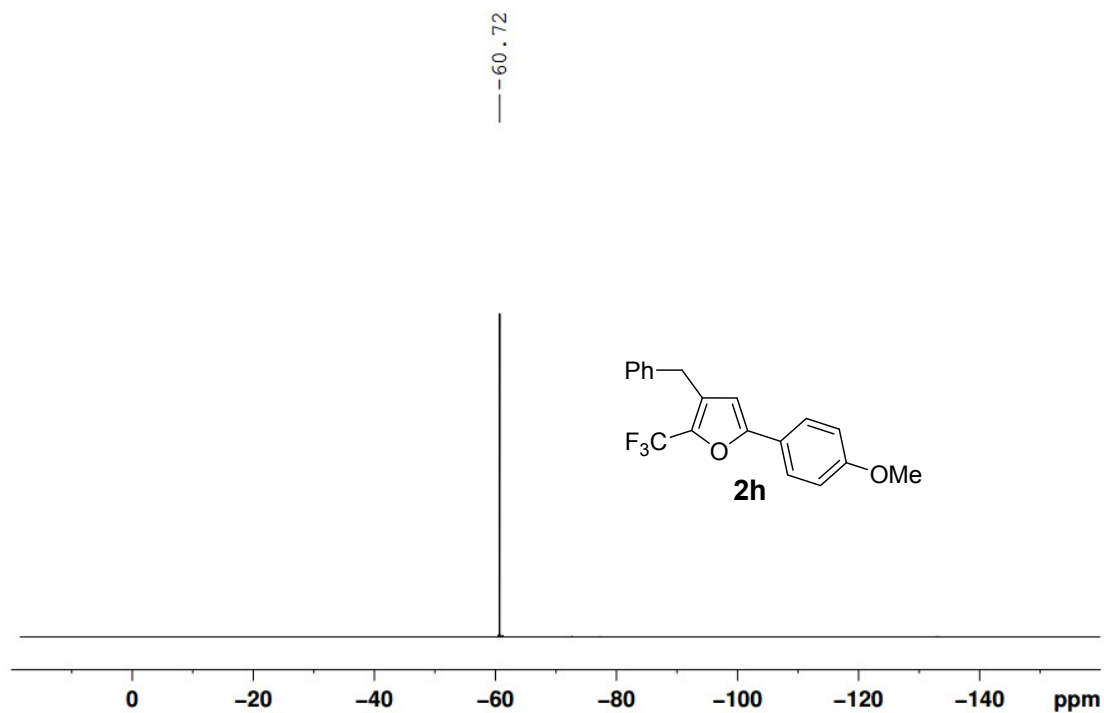
zw-3-54



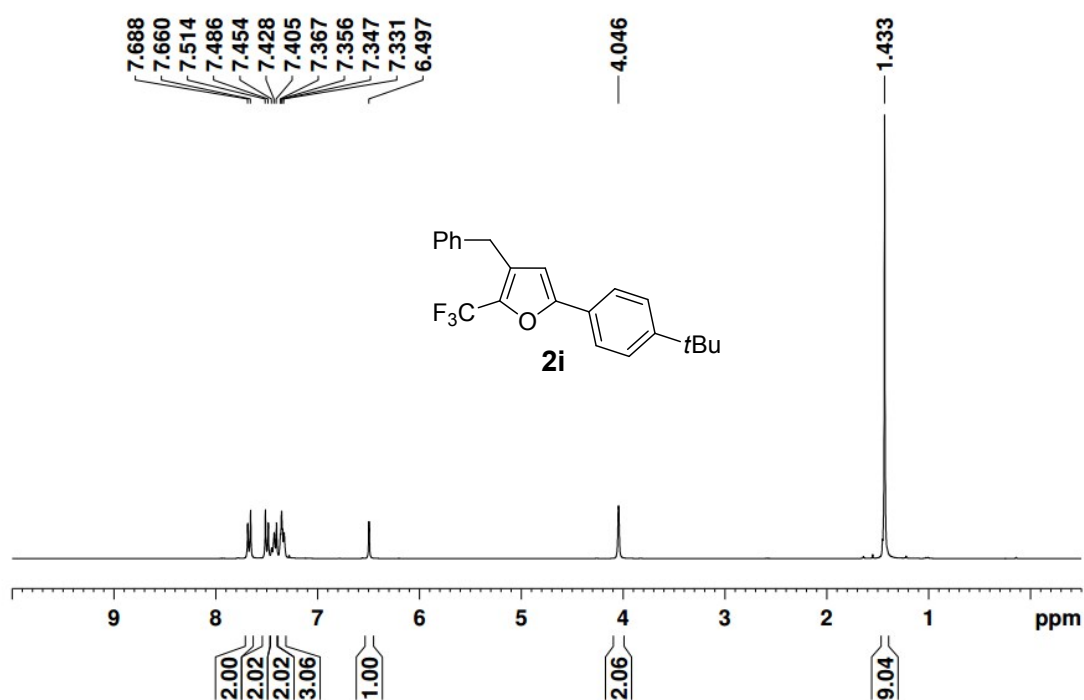
zw-3-54c



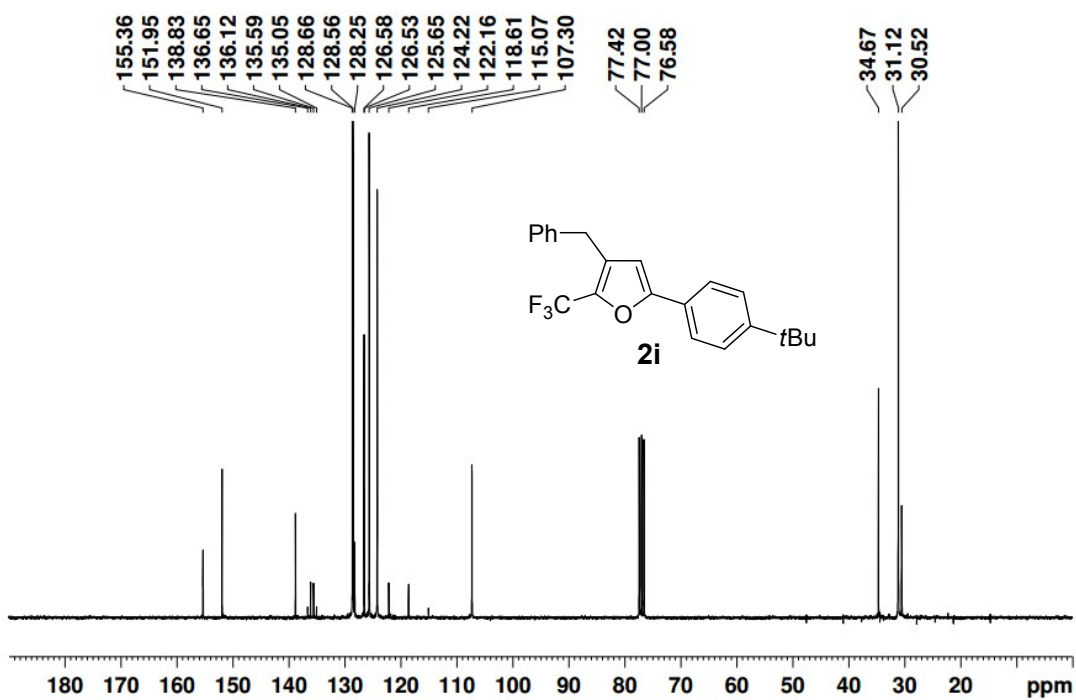
zw-3-54f



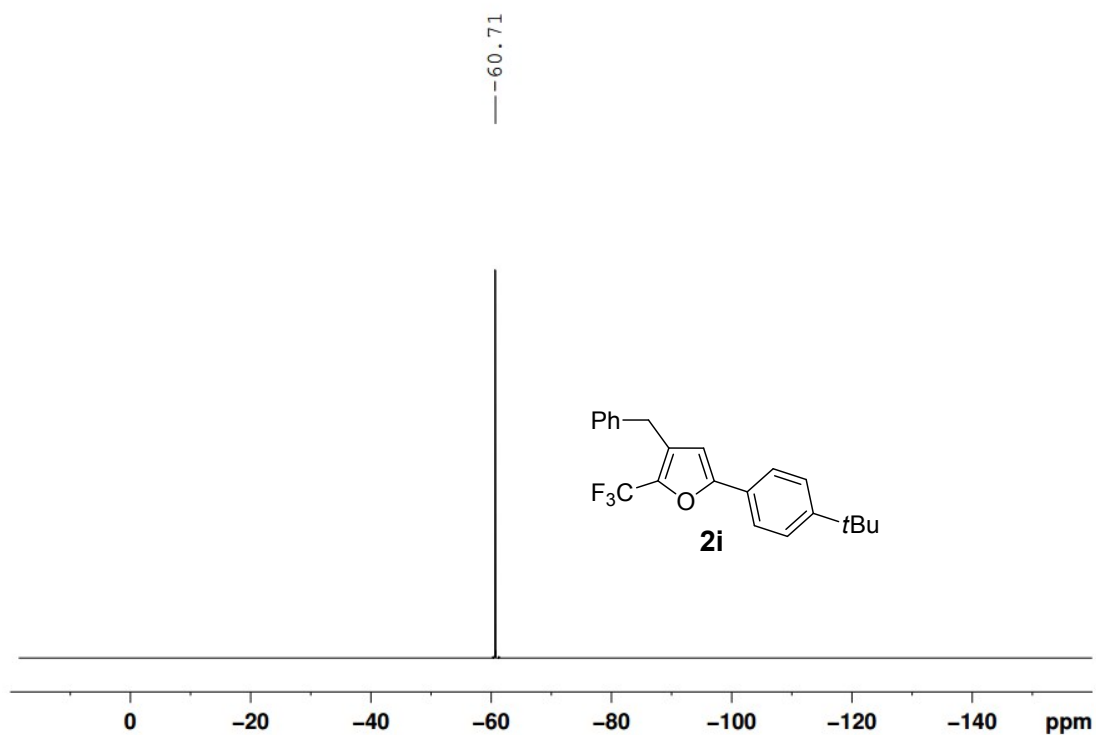
zw-3-61



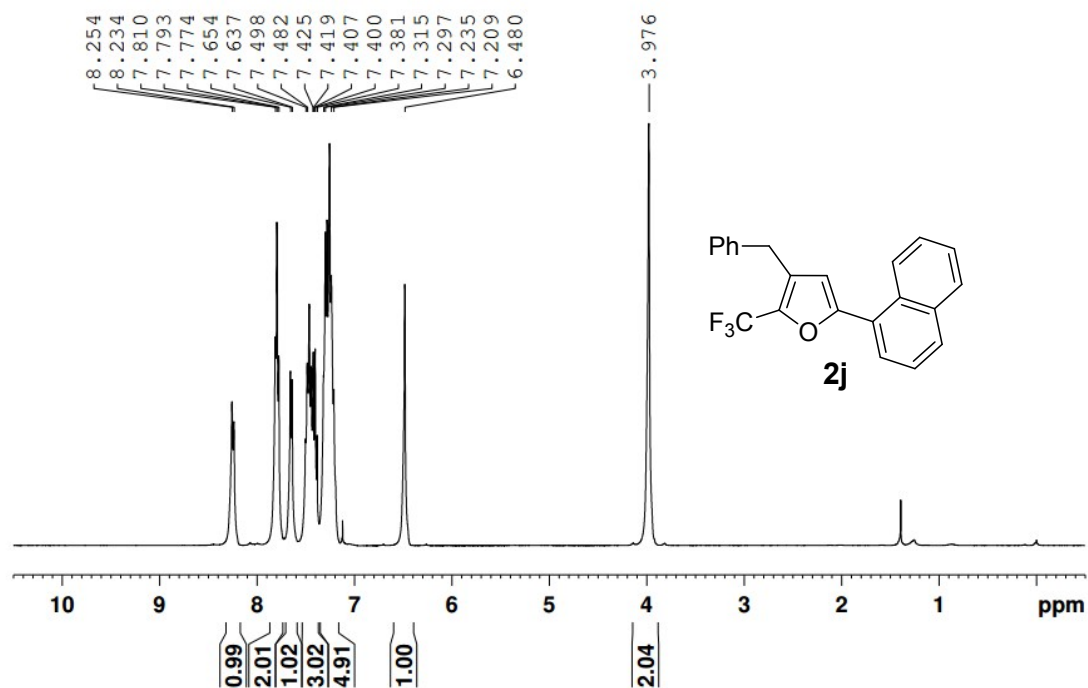
zw-3-61c



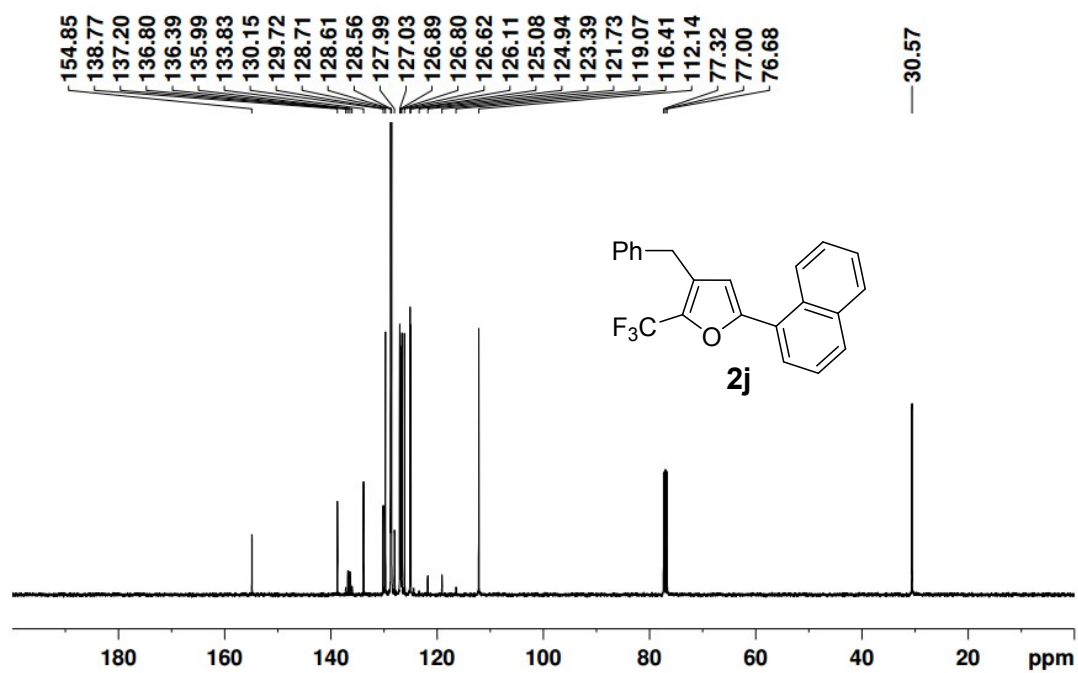
zw-3-61f



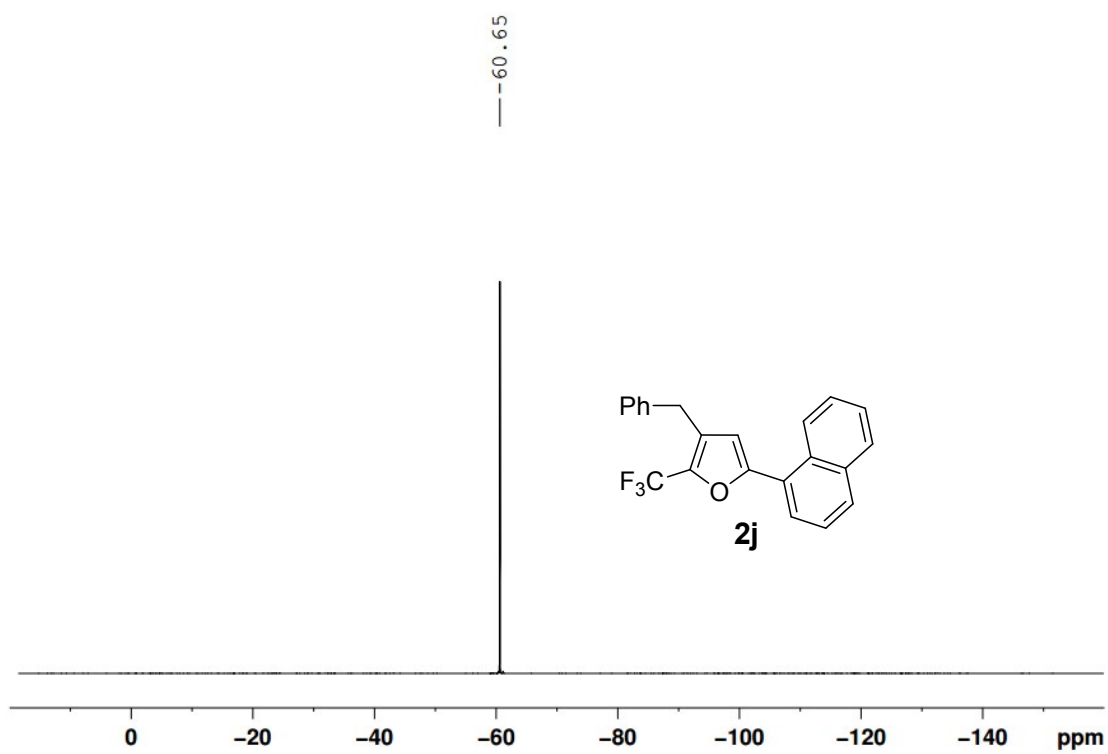
zw-3-56



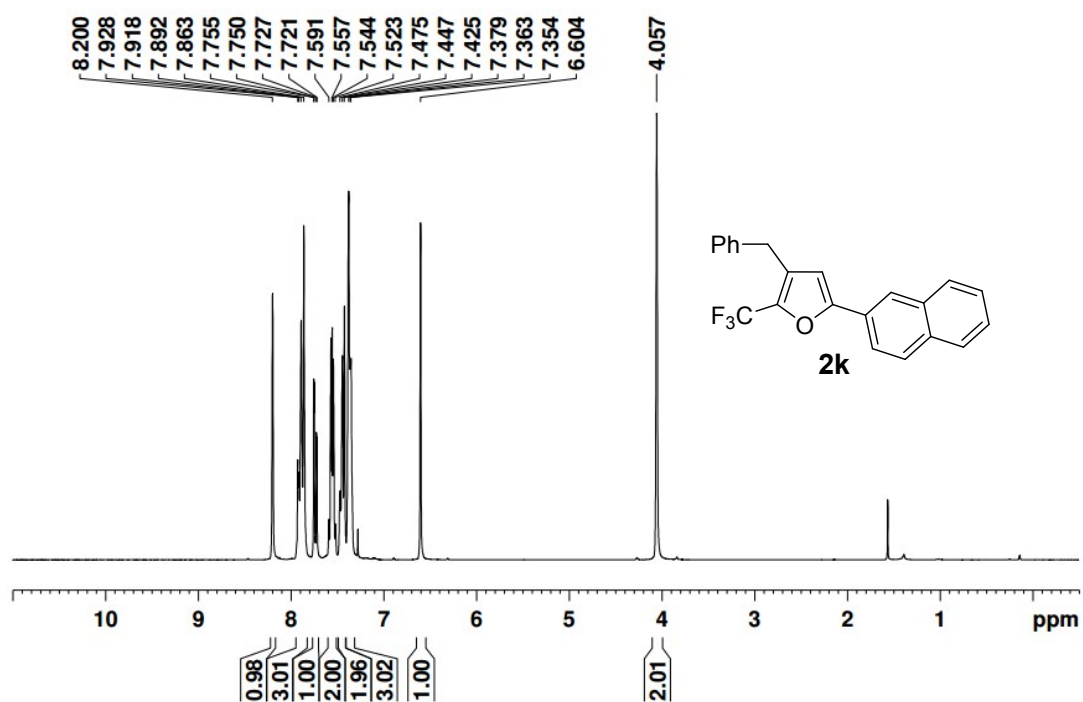
zw-3-56c



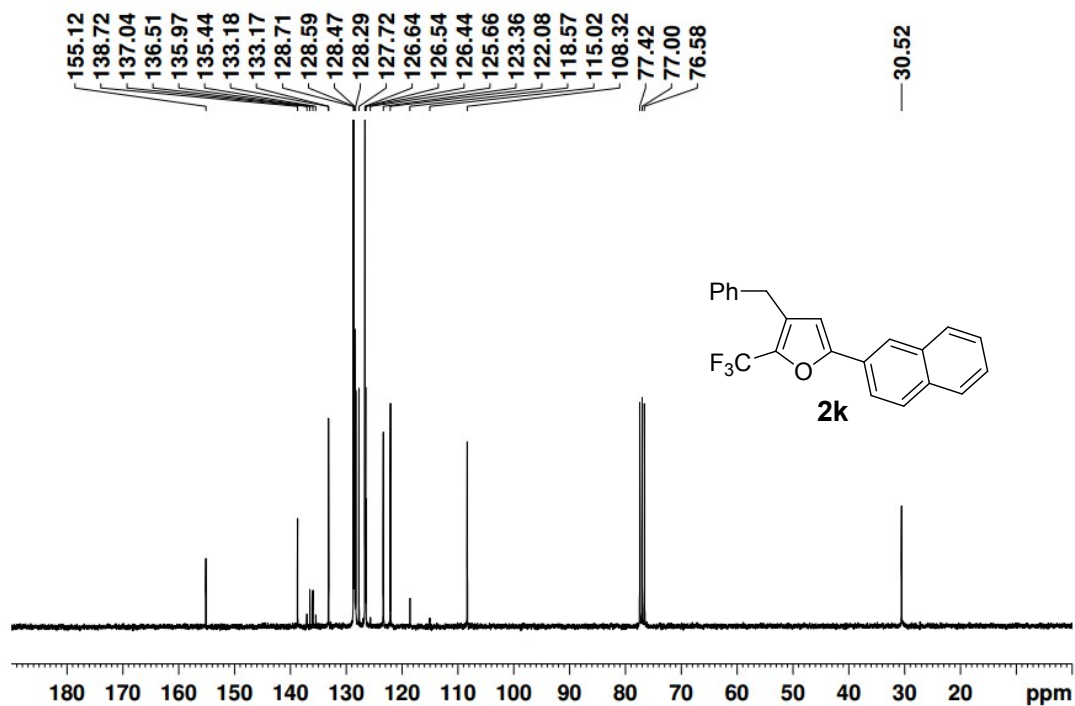
zw-3-56f



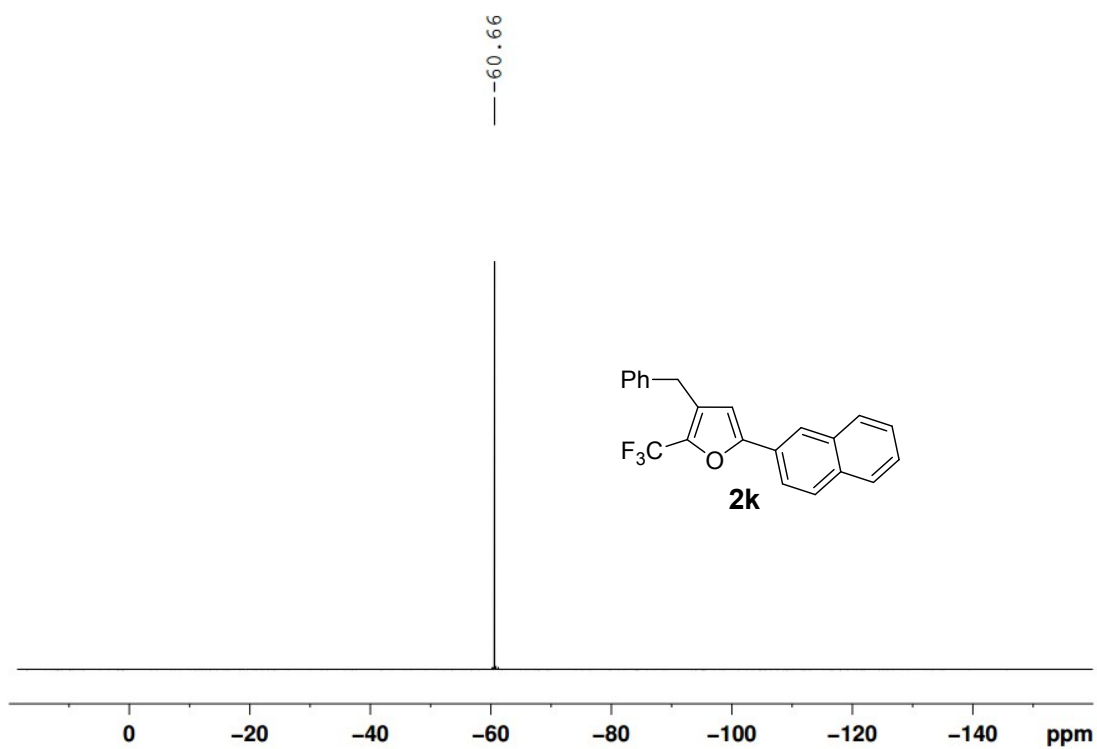
zw-3-58



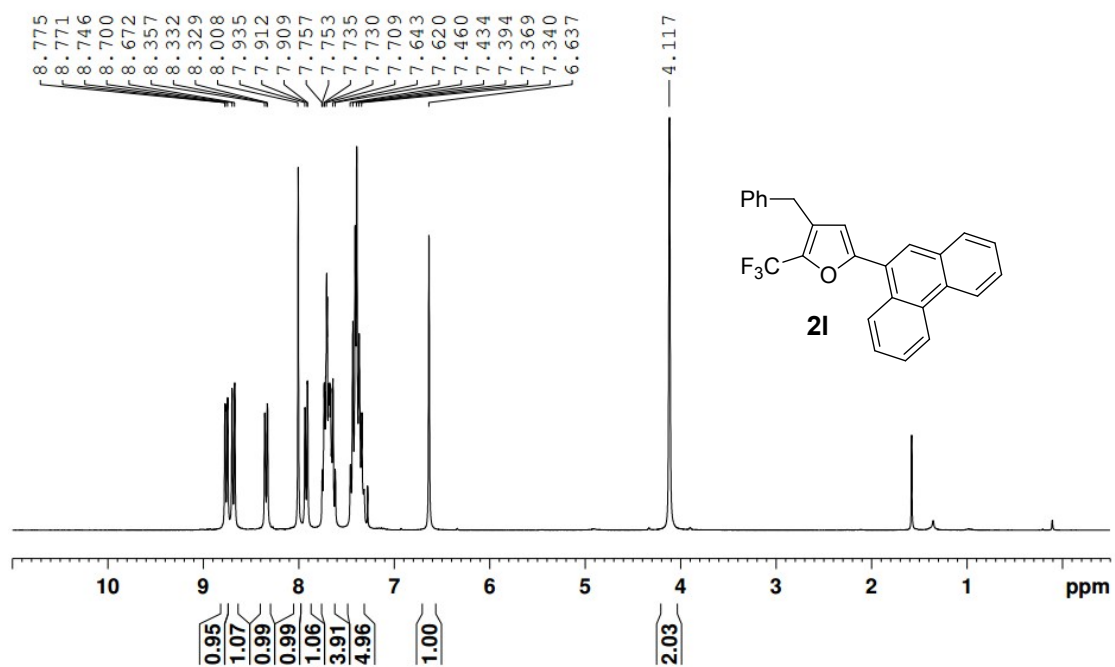
zw-3-58c



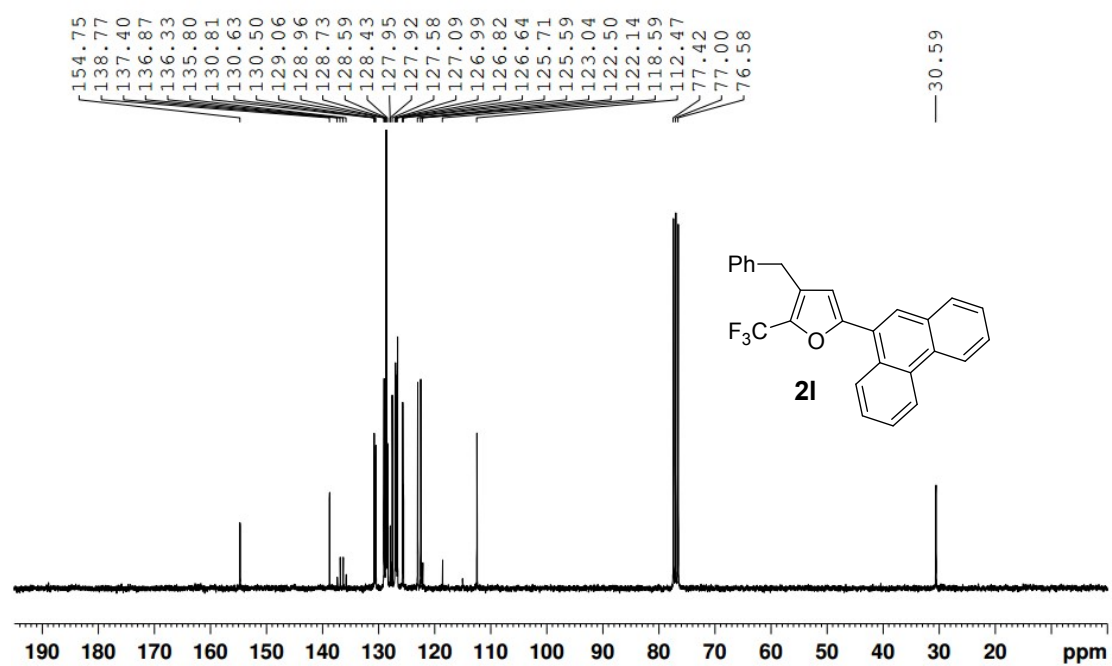
zw-3-58f



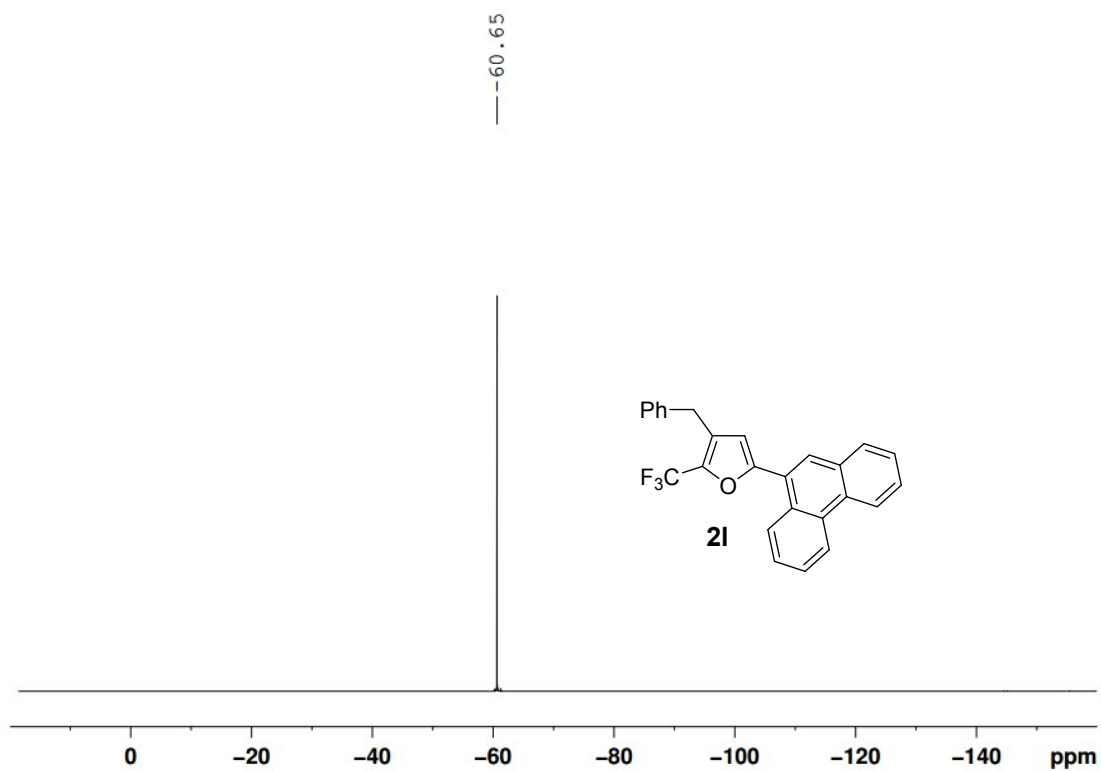
zw-3-64



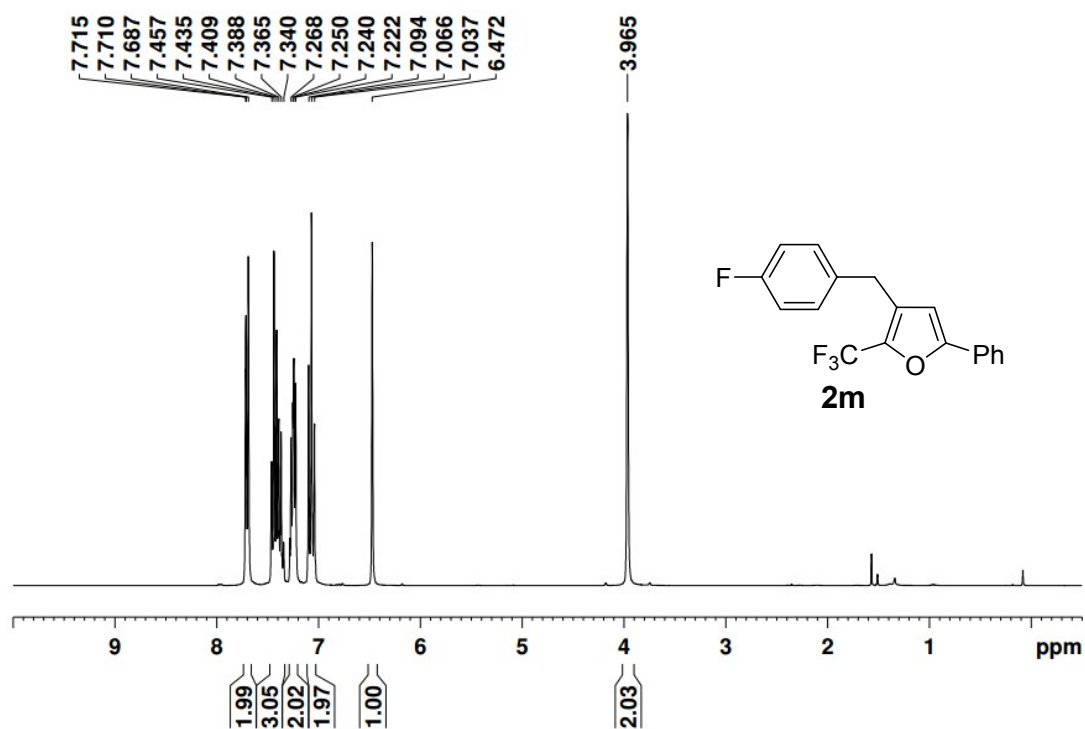
zw-3-64c



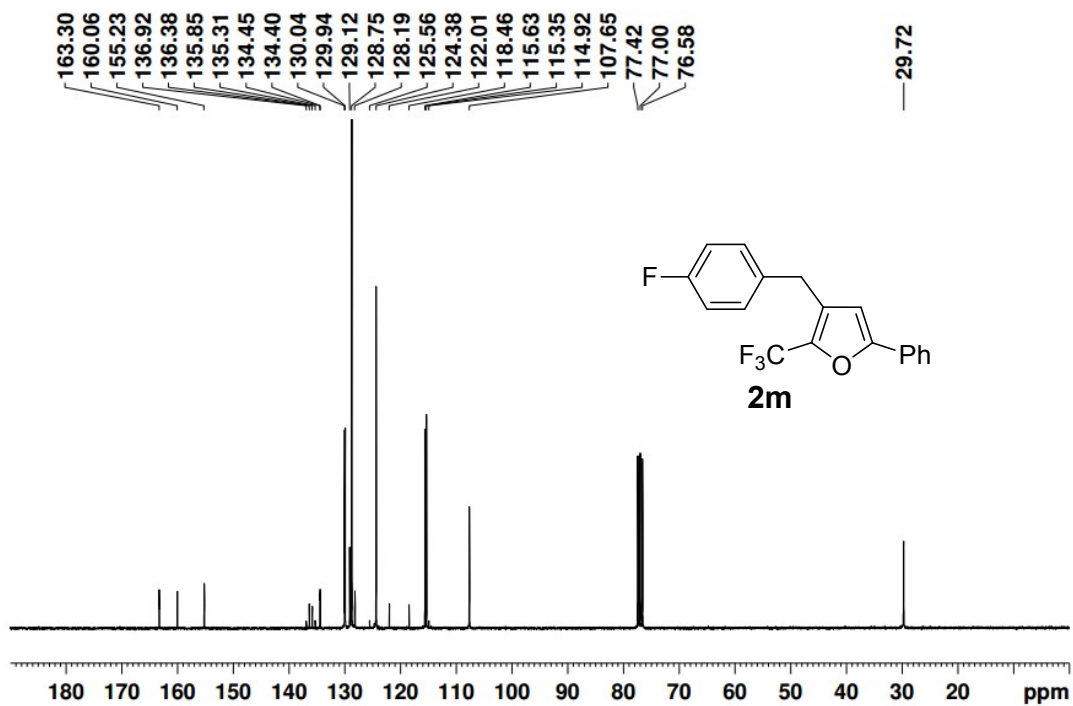
zw-3-64f



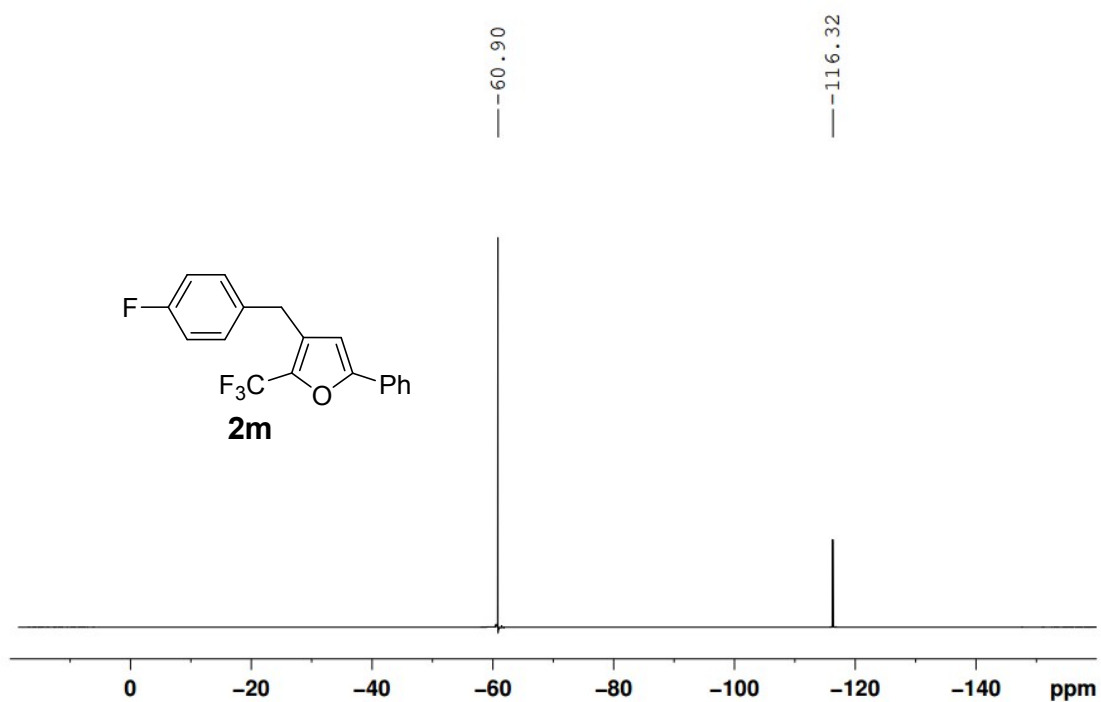
zw-3-60



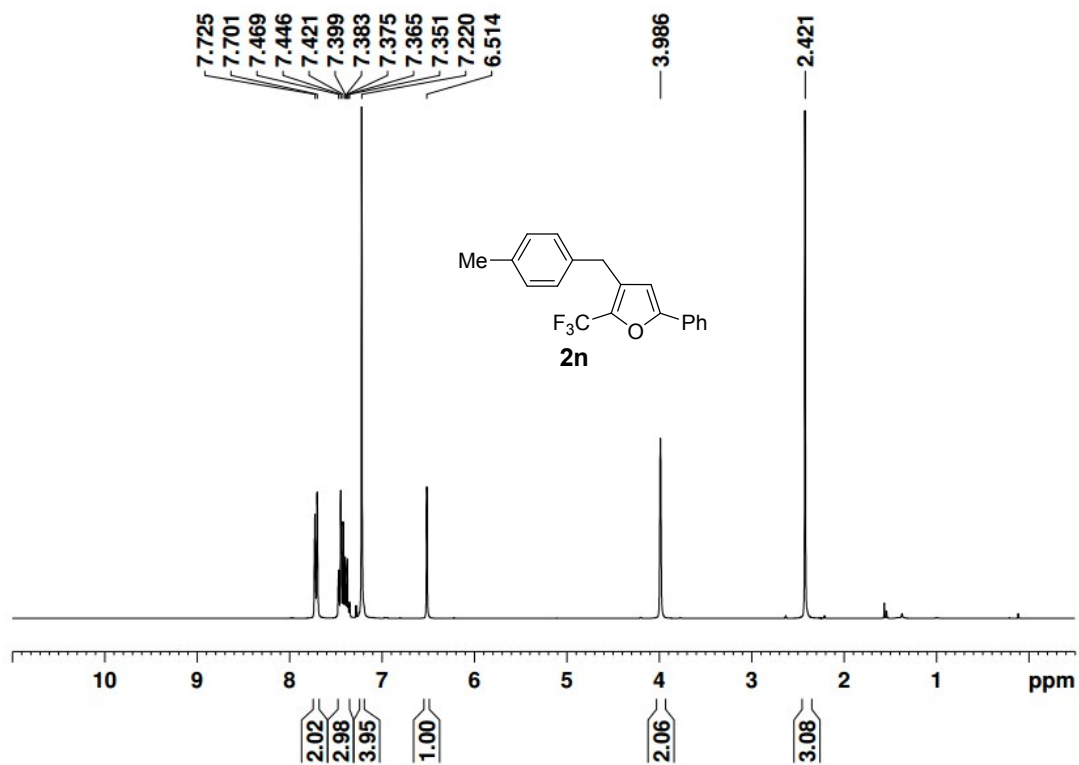
zw-3-60c



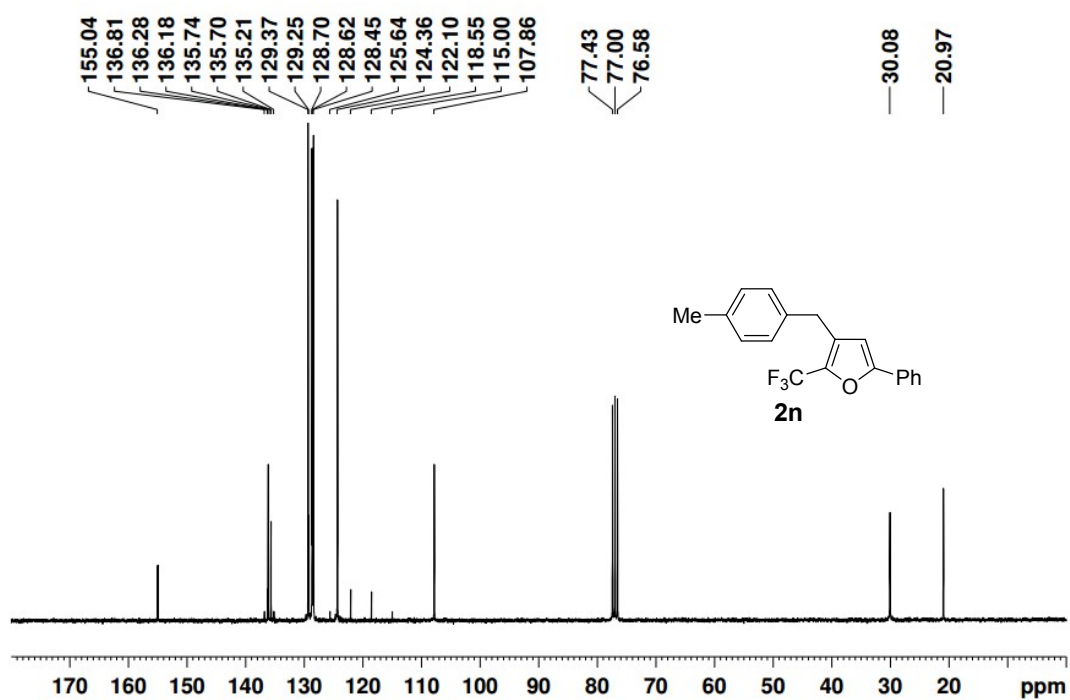
zw-3-60f



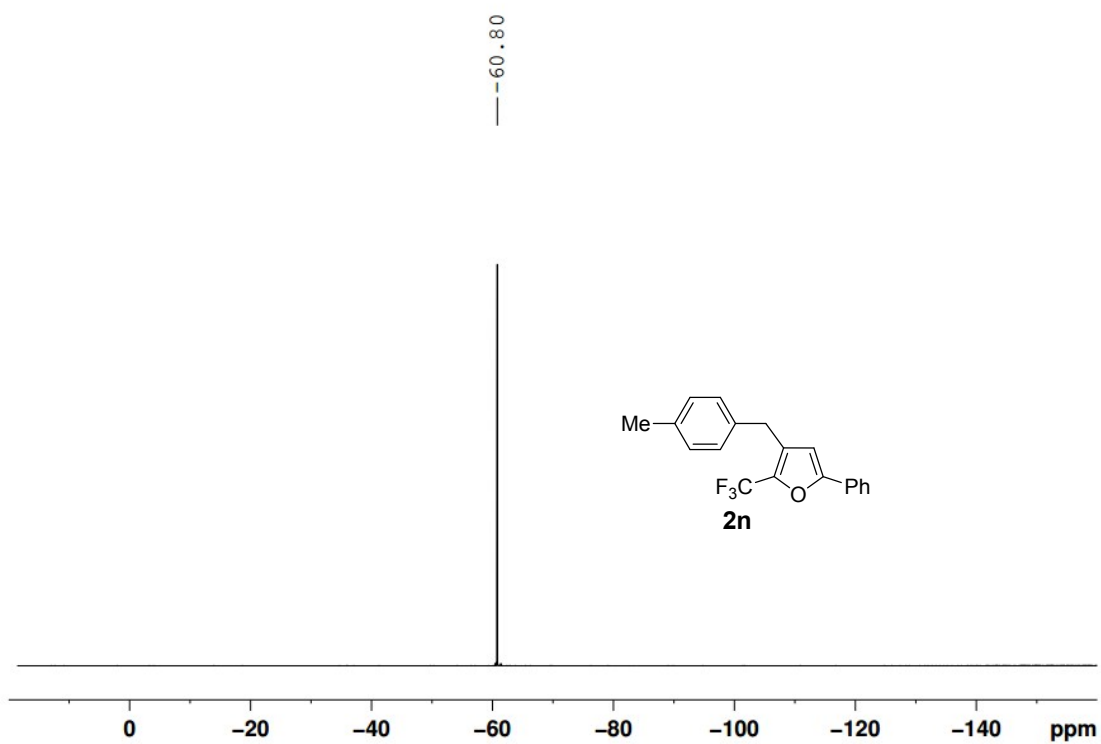
zw-3-59



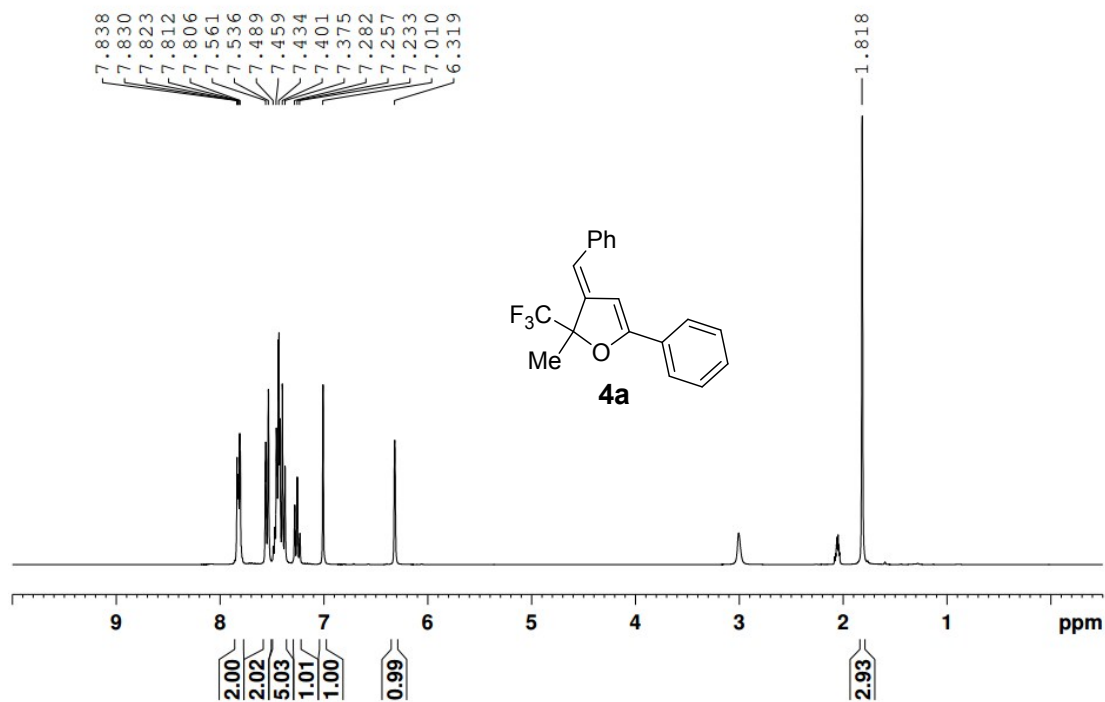
zw-3-59c



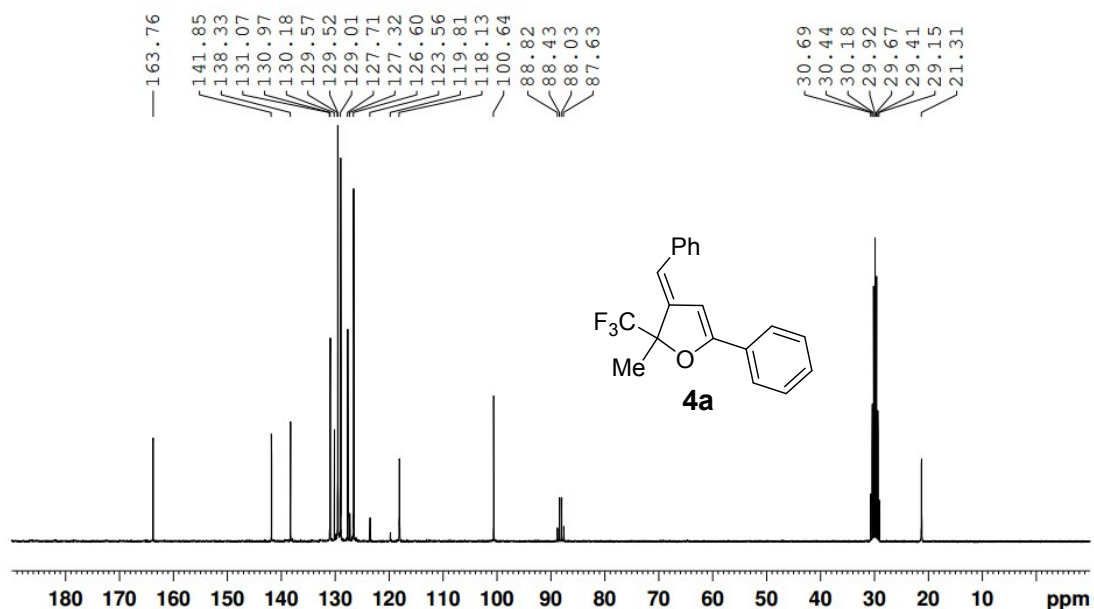
zw-3-59f



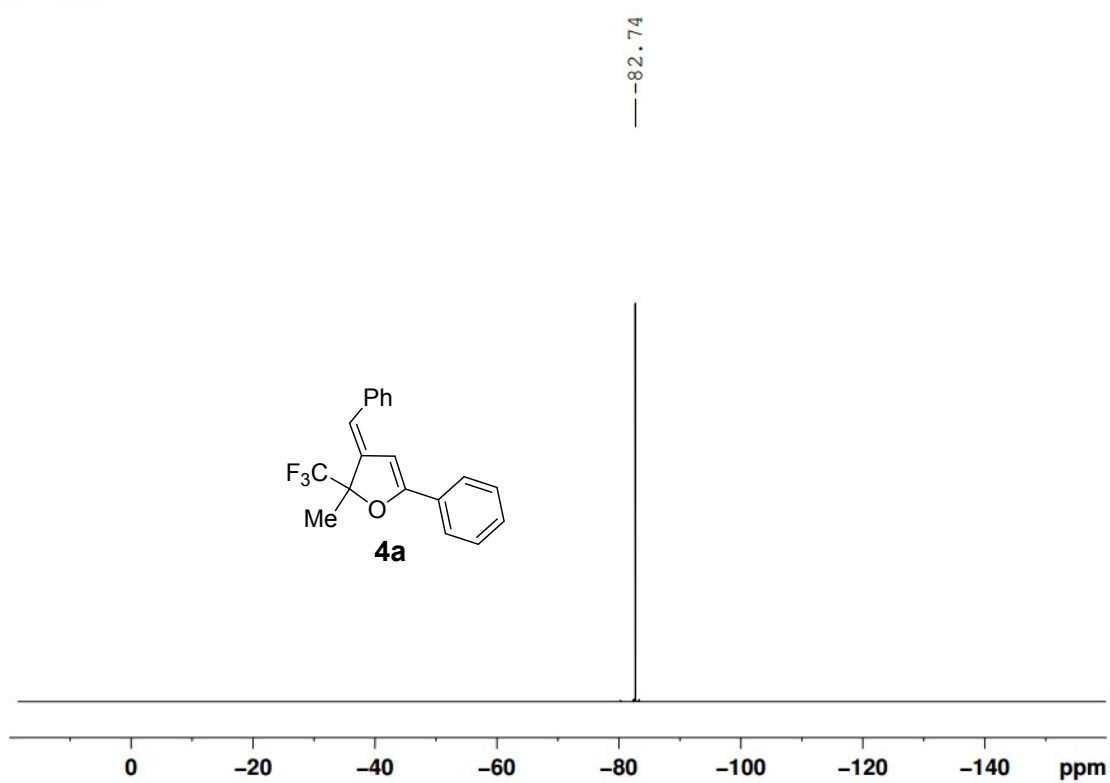
zw-3-65



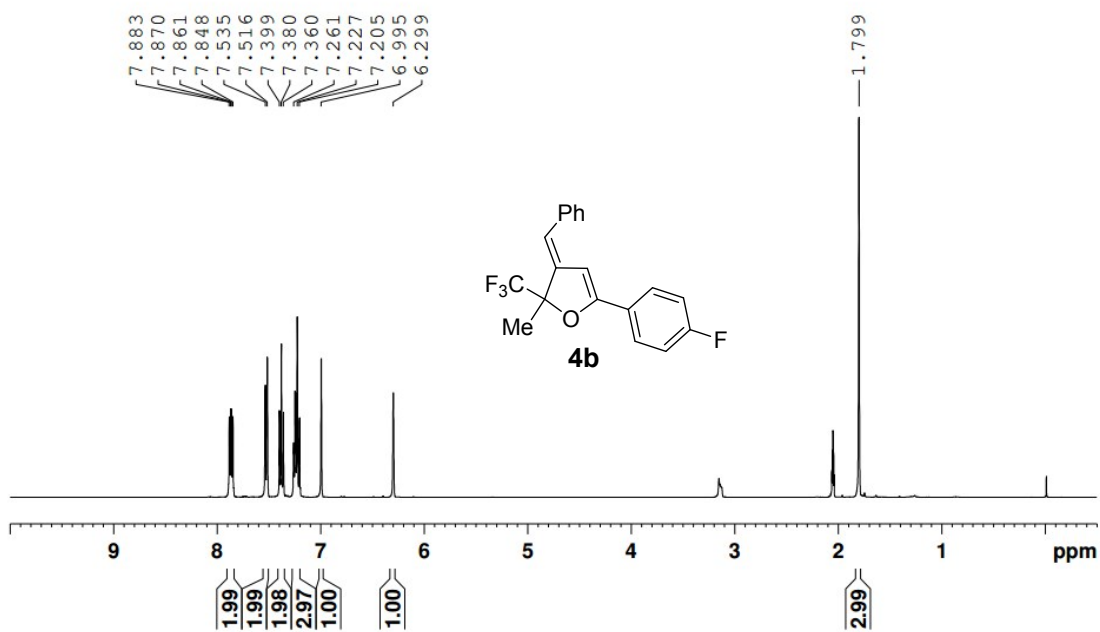
zw-3-65c



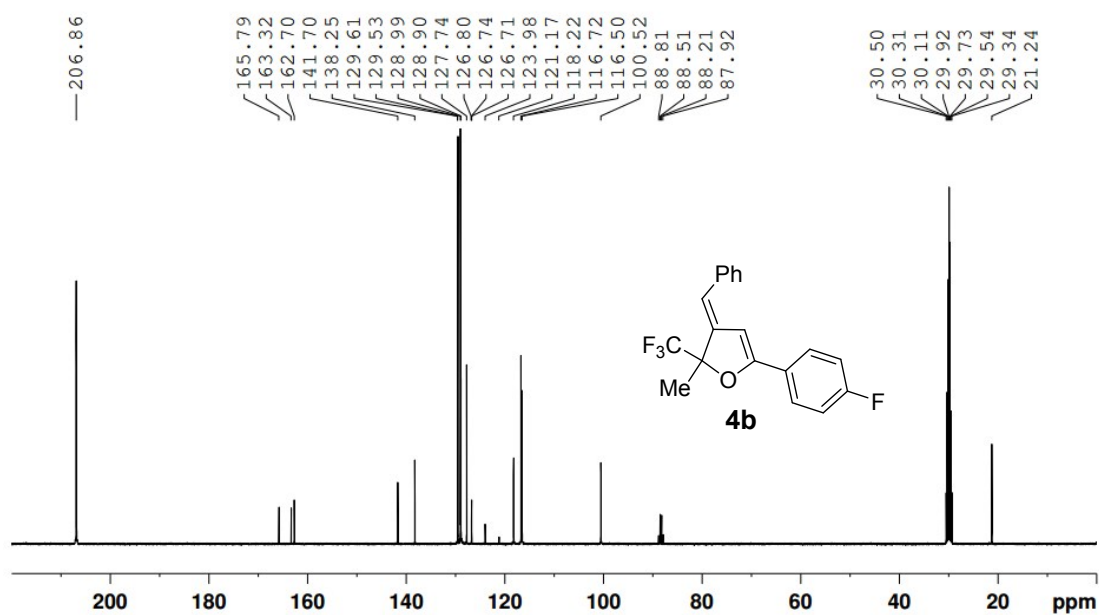
zw-3-65f



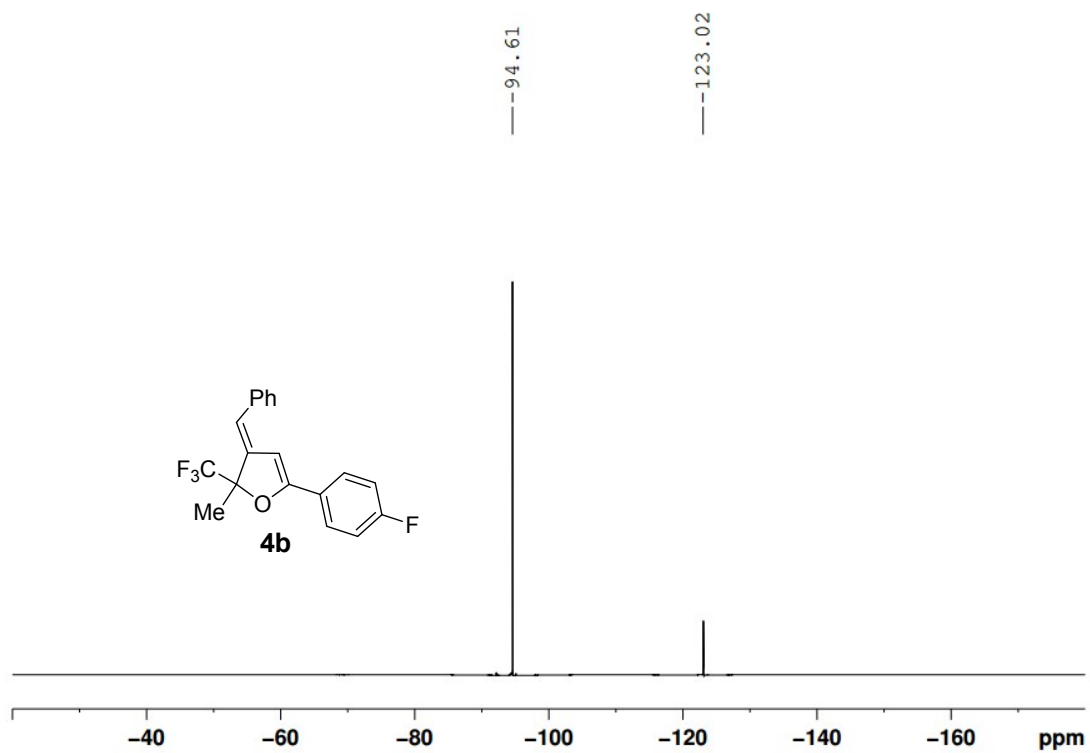
zw-3-68



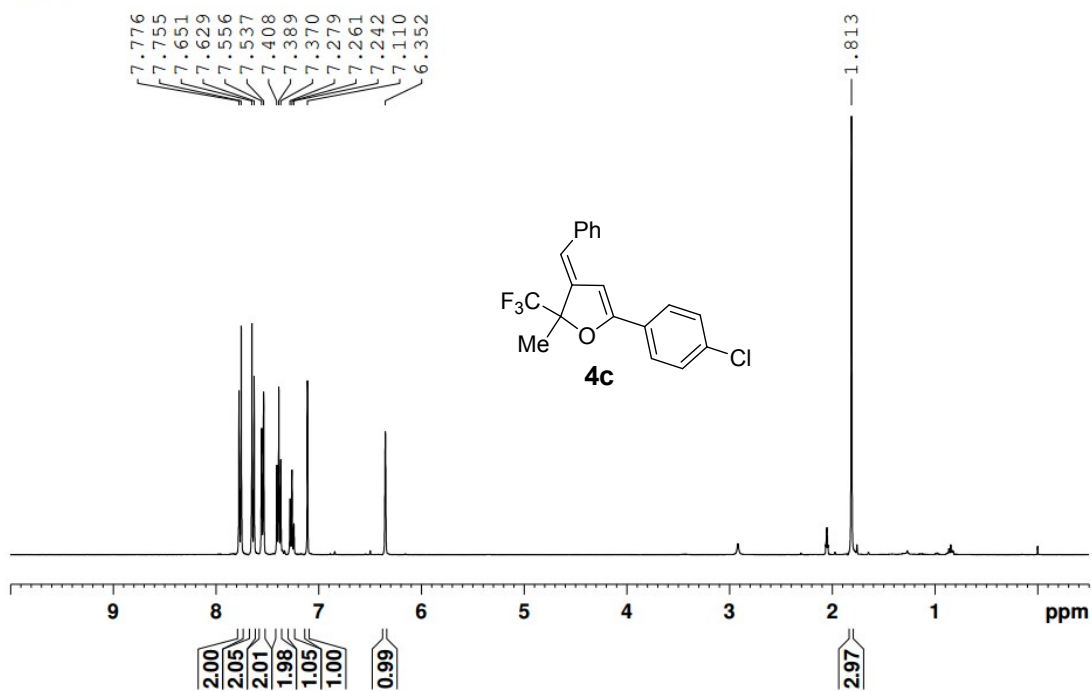
zw-3-68c



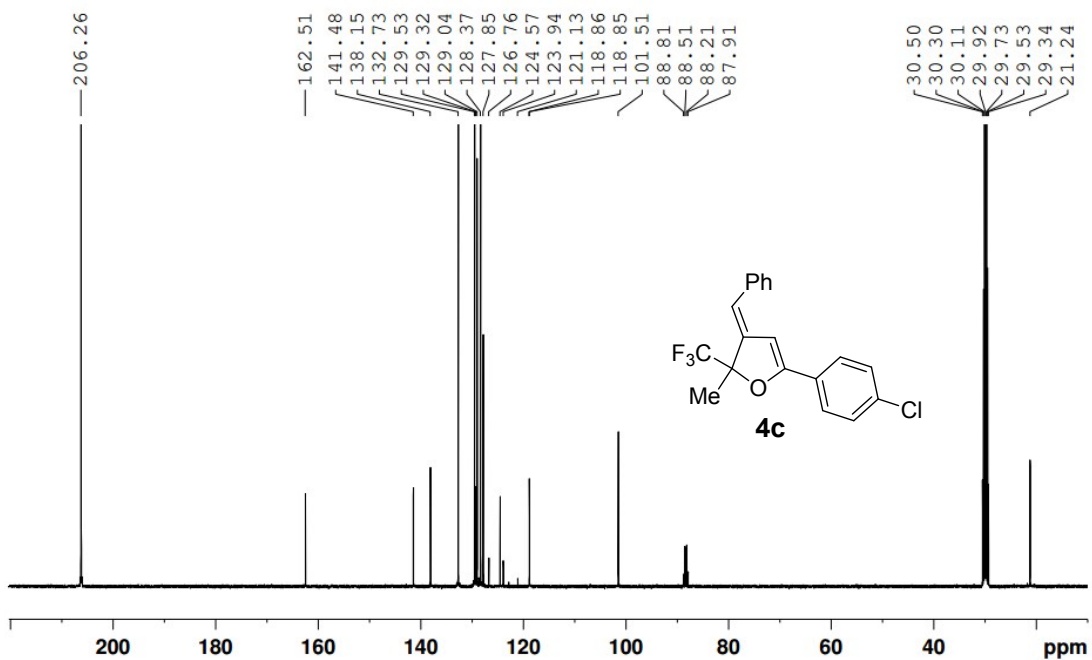
zw-3-68f



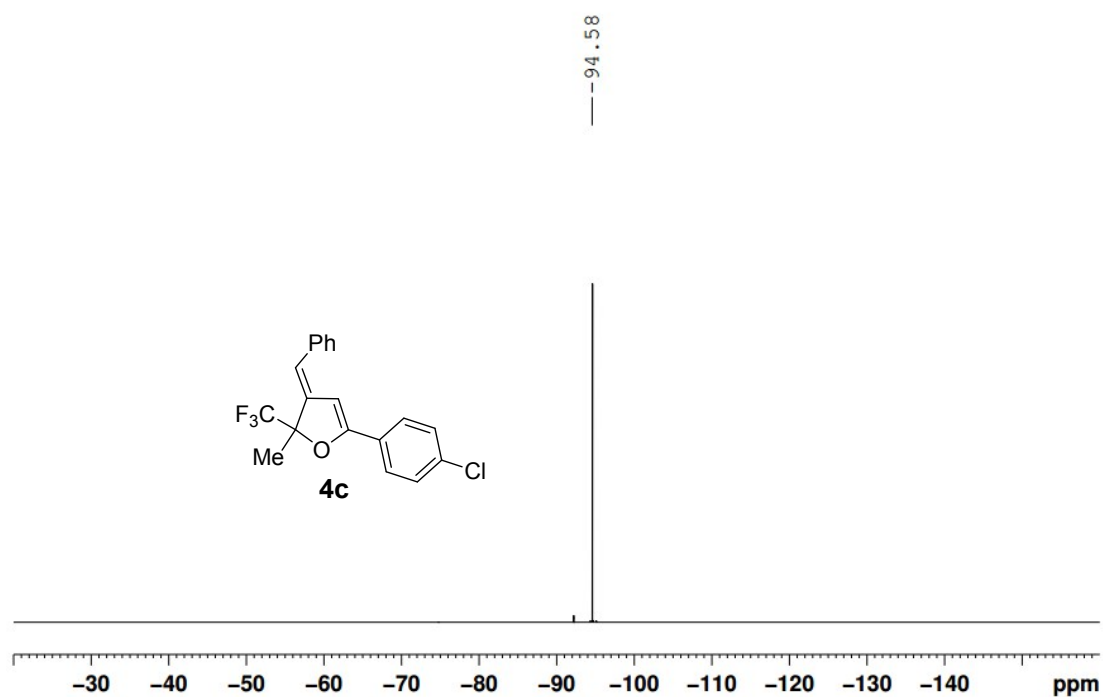
zw-4-3



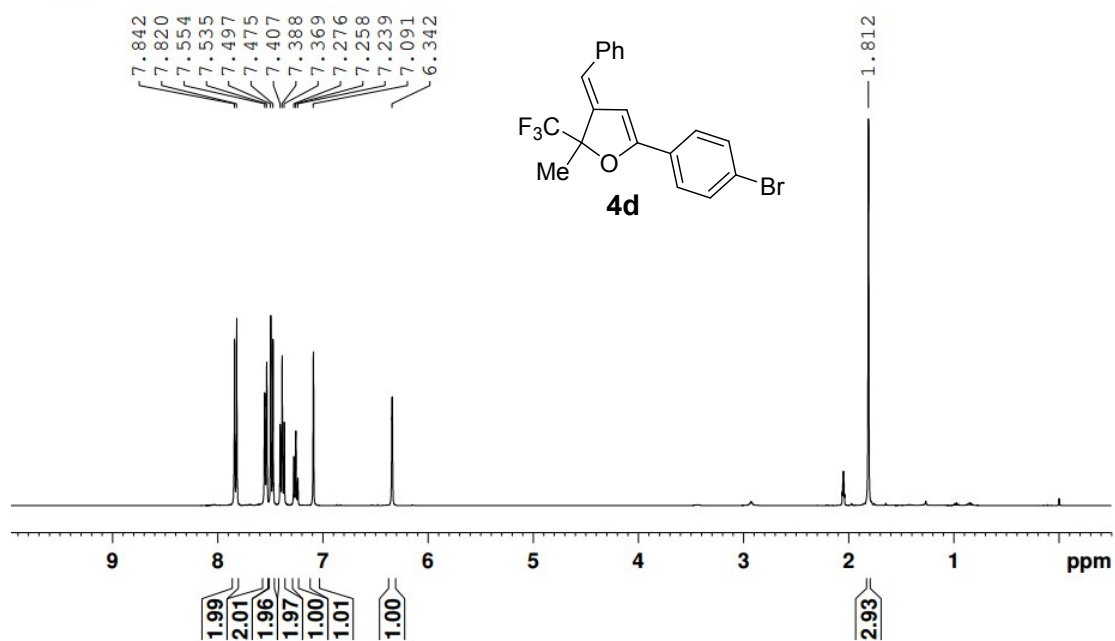
zw-4-3c



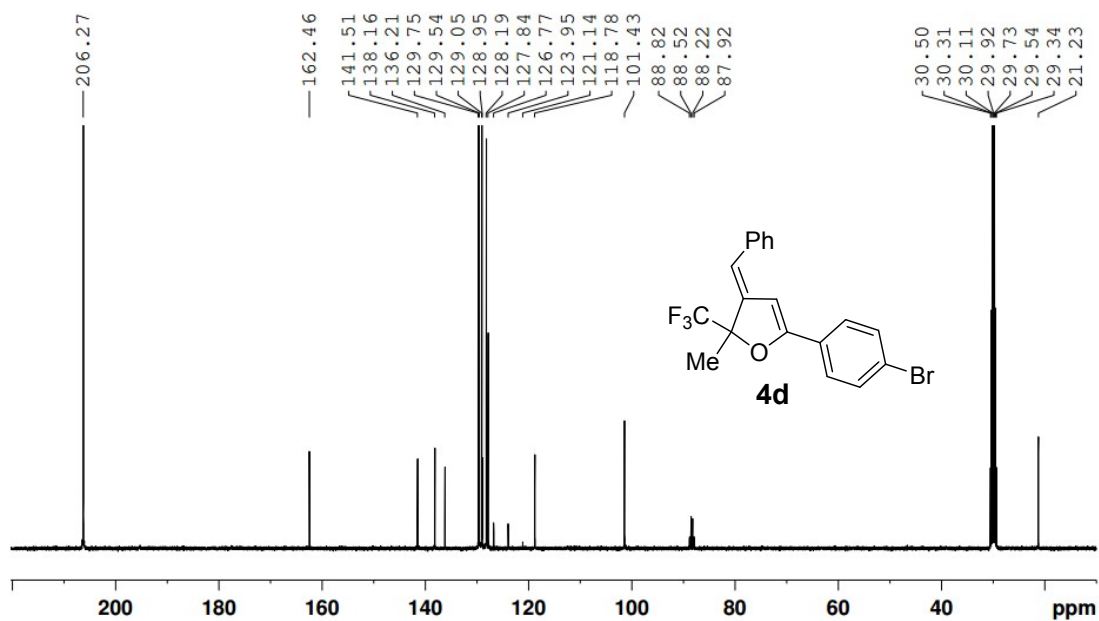
zw-4-3f



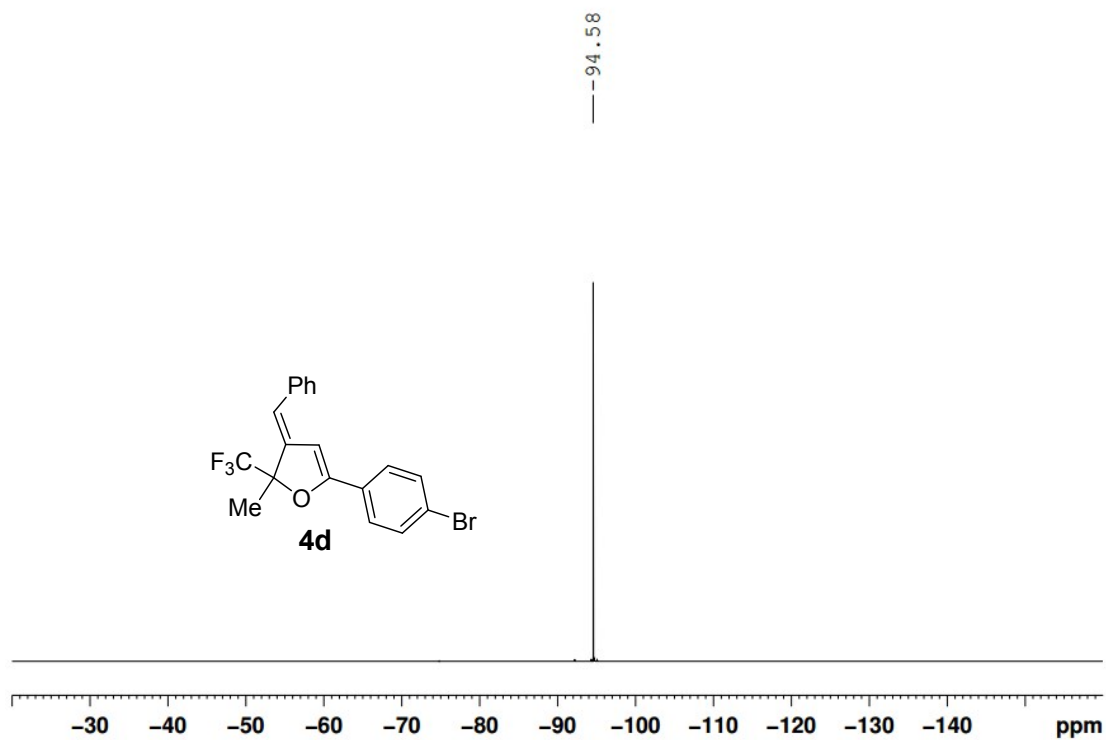
zw-4-4



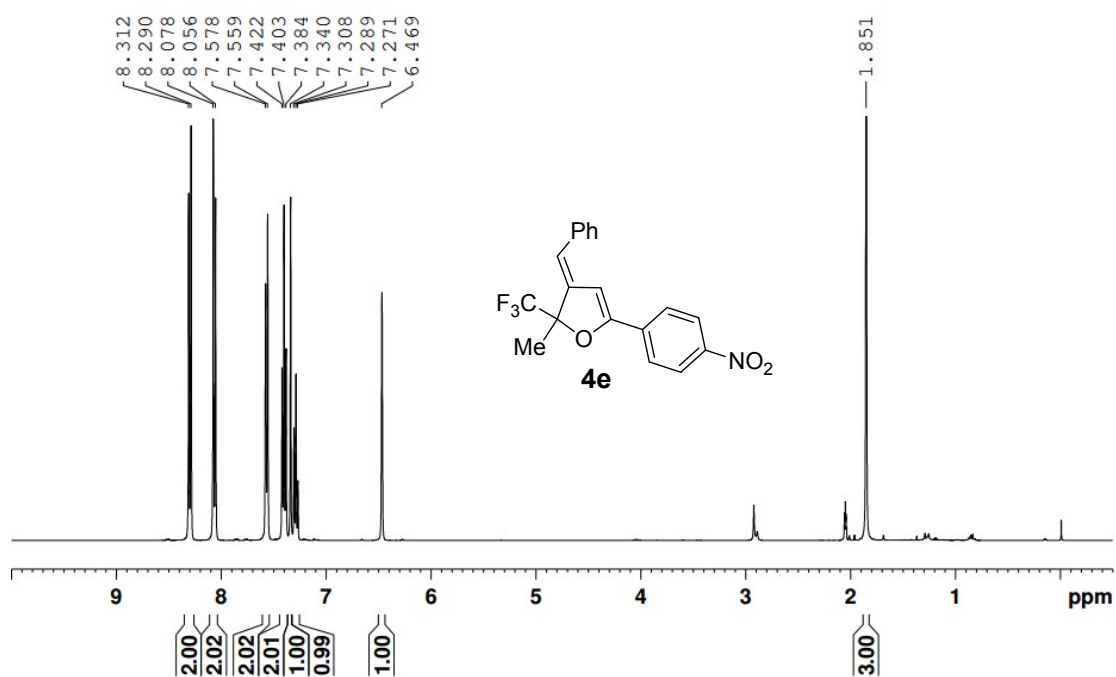
zw-4-4c



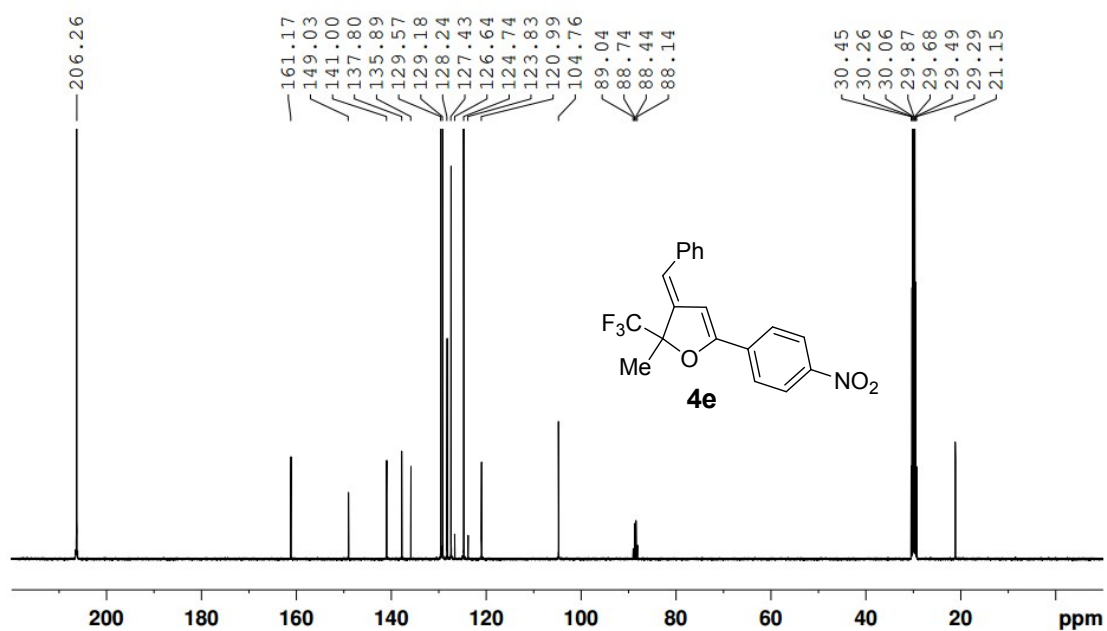
zw-4-4f



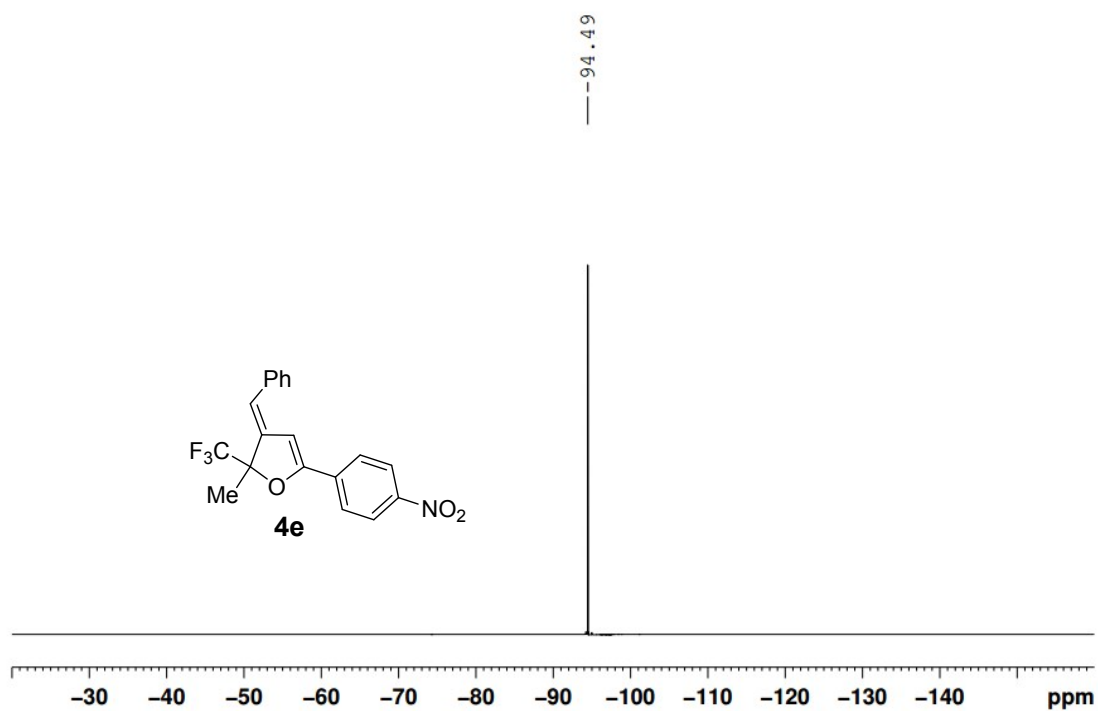
zw-4-7



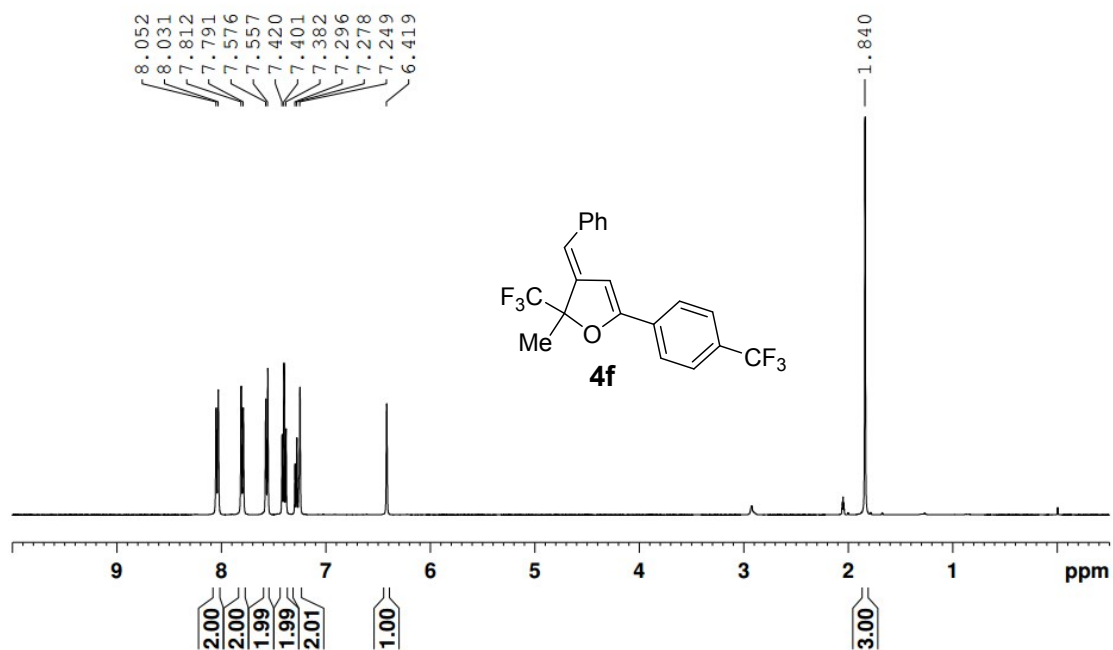
zw-4-7c



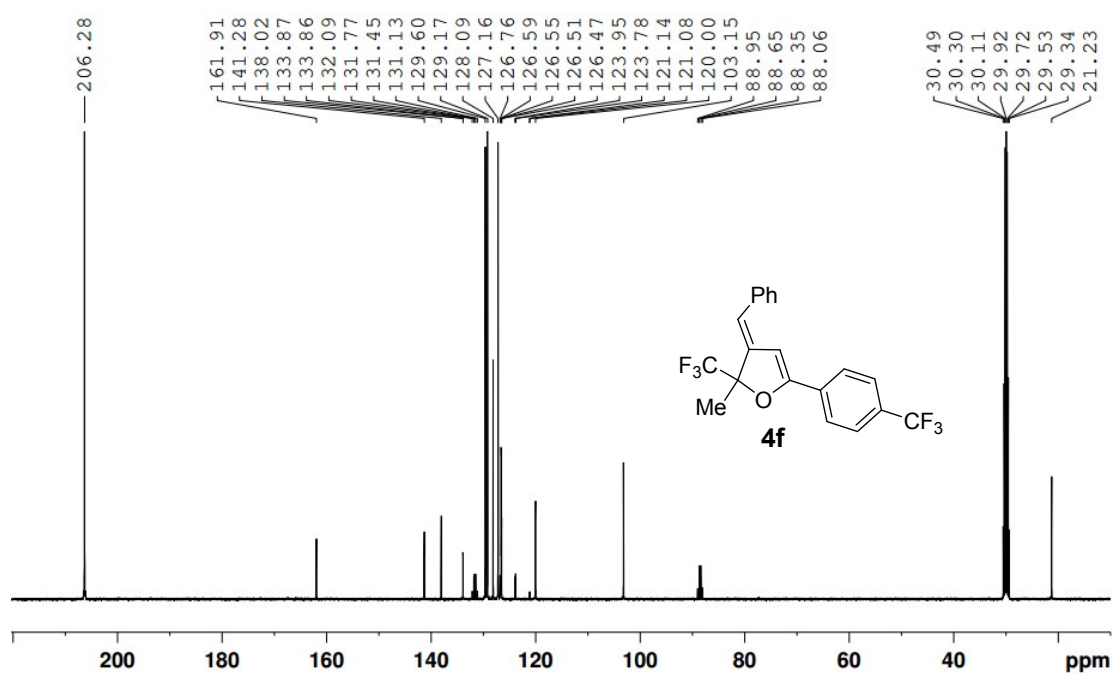
zw-4-7f



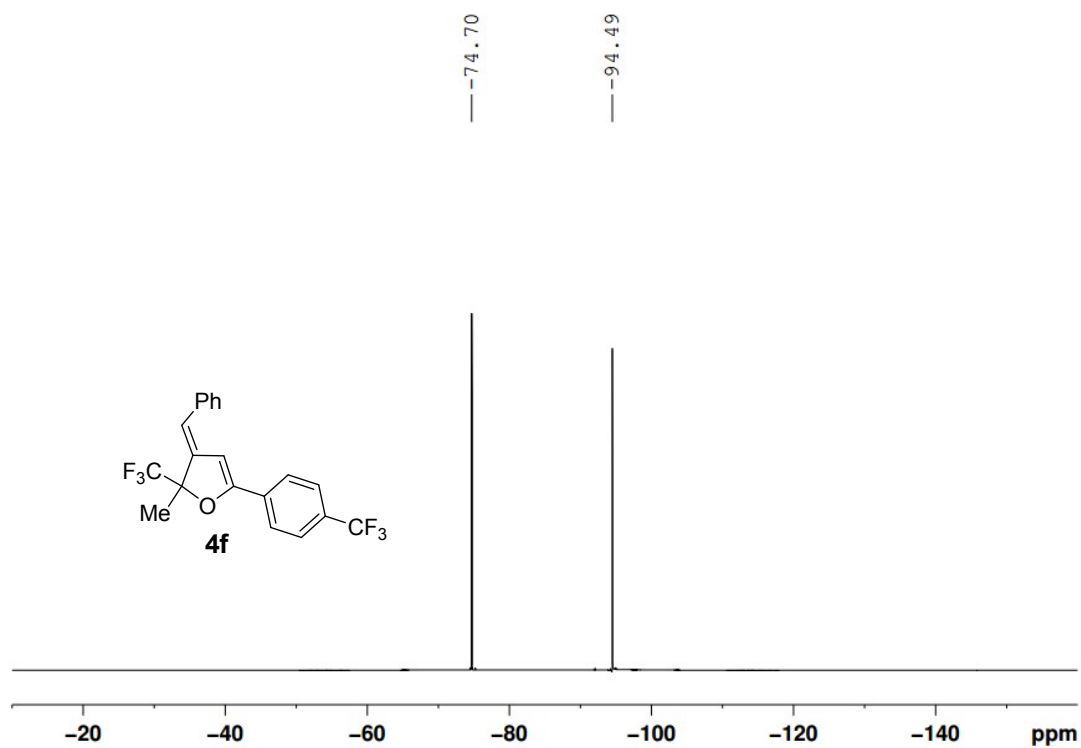
zw-4-6



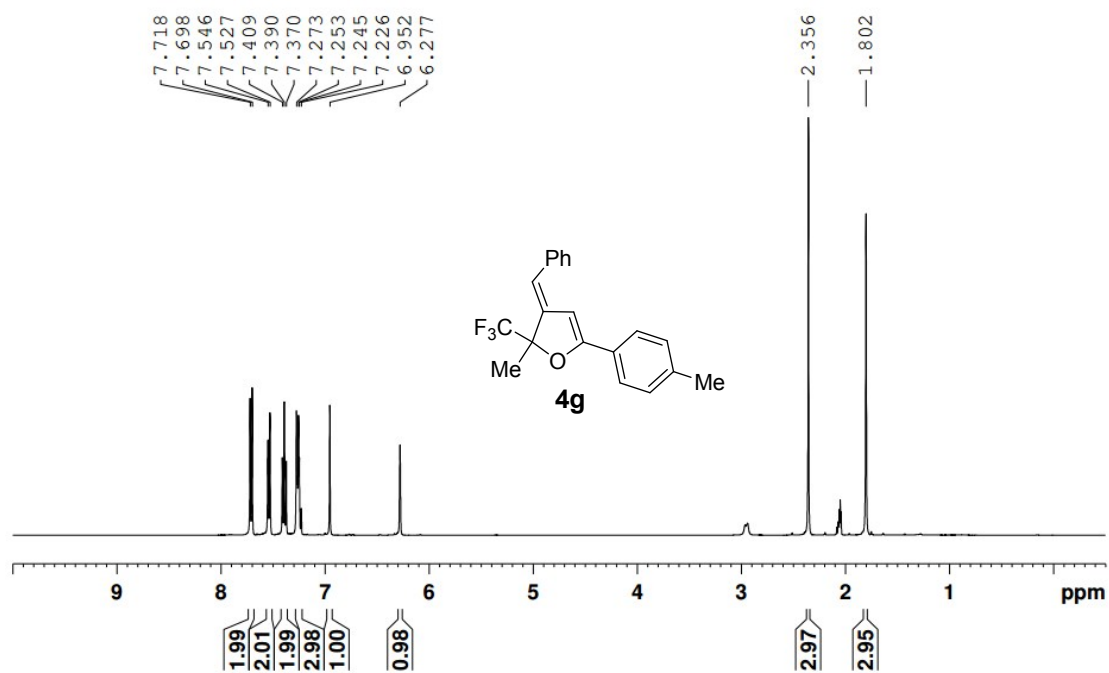
zw-4-6c



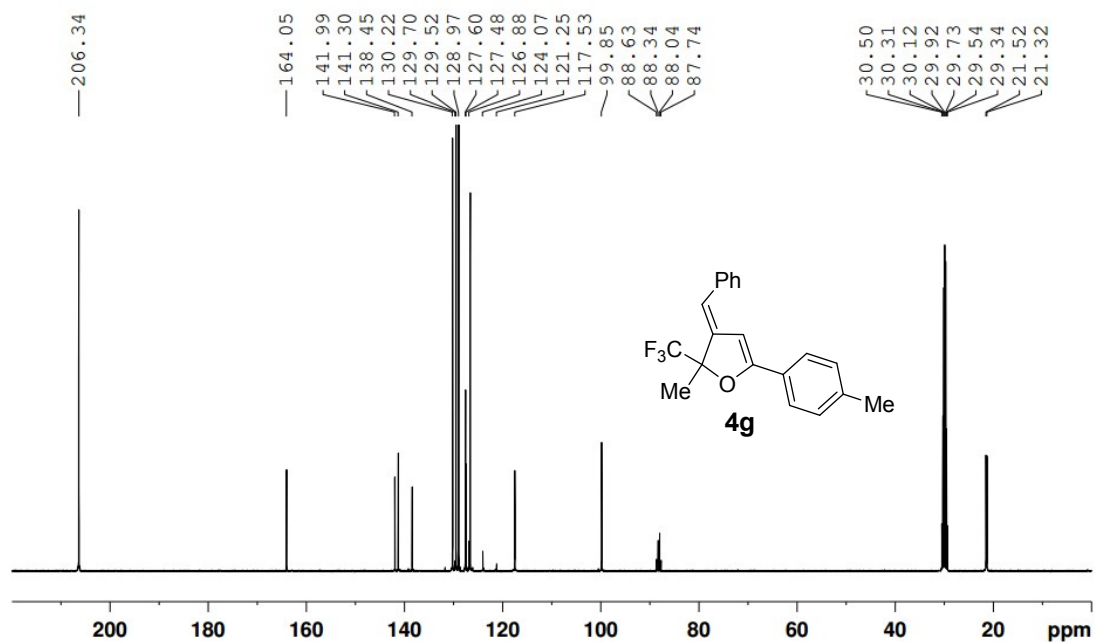
zw-4-6f



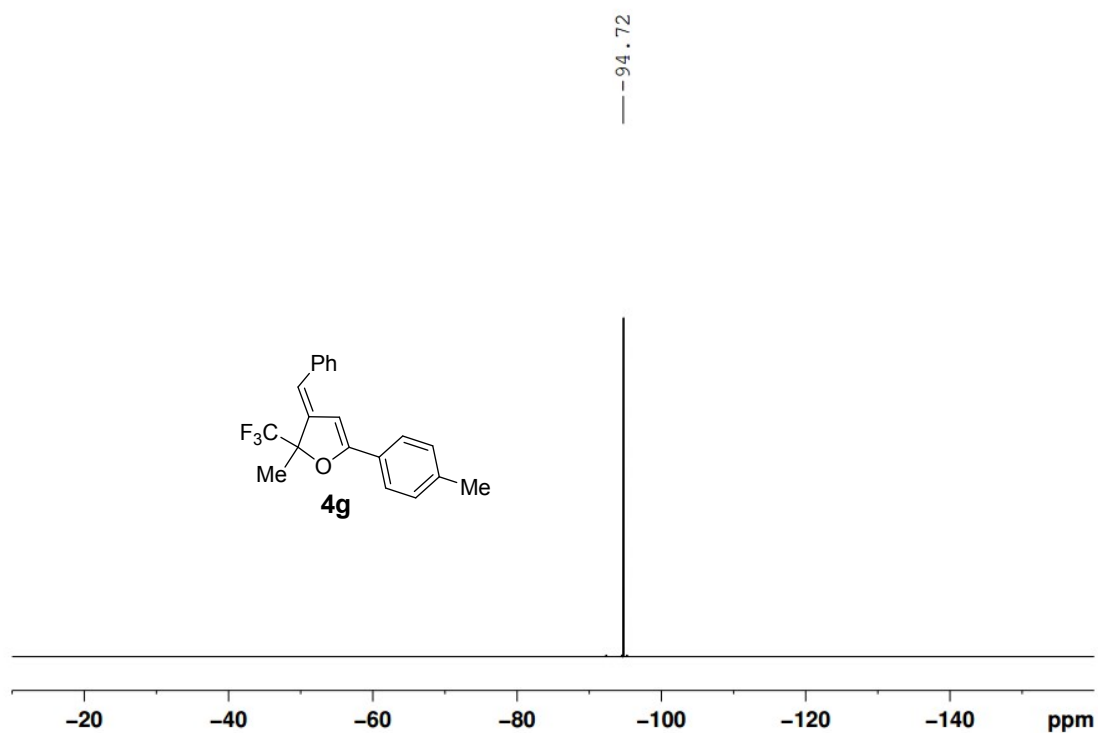
zw-3-67



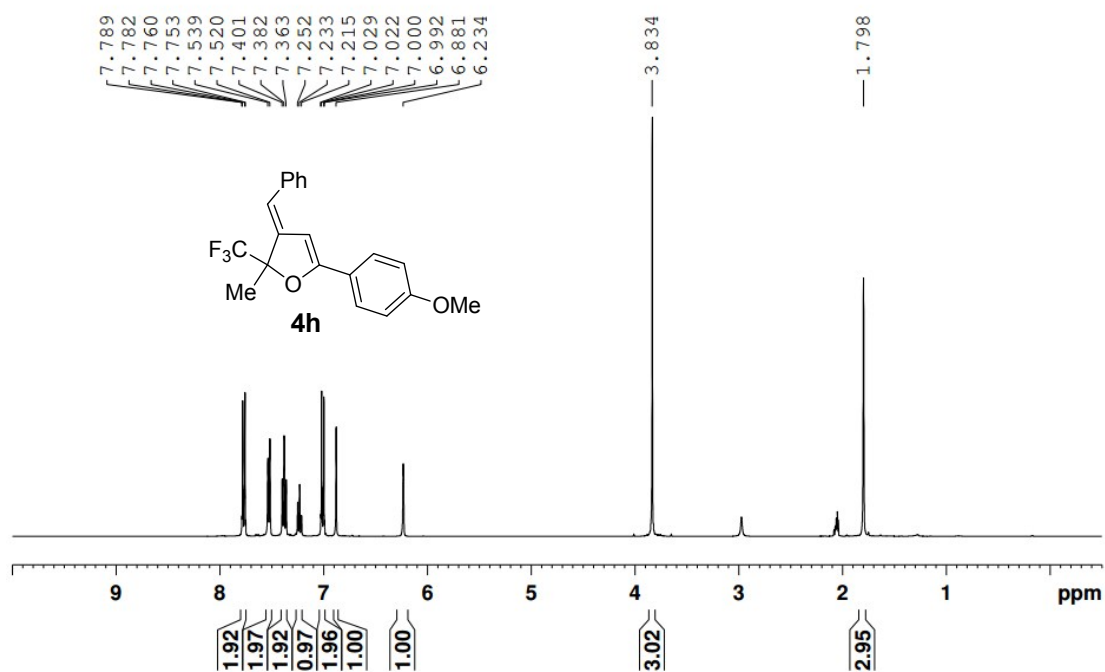
zw-3-67c



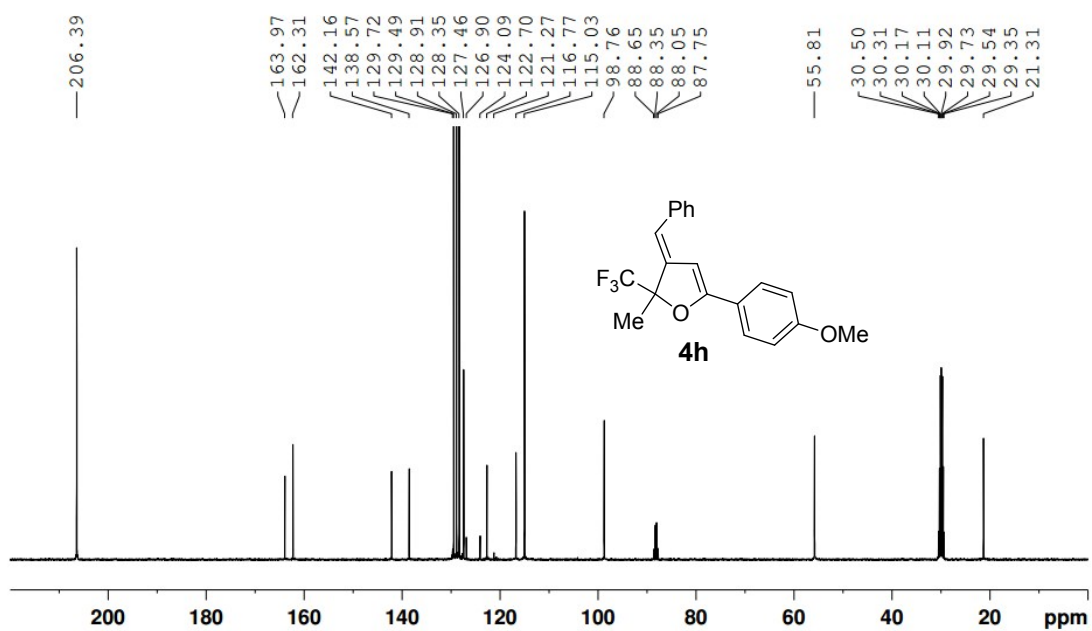
zw-3-67f



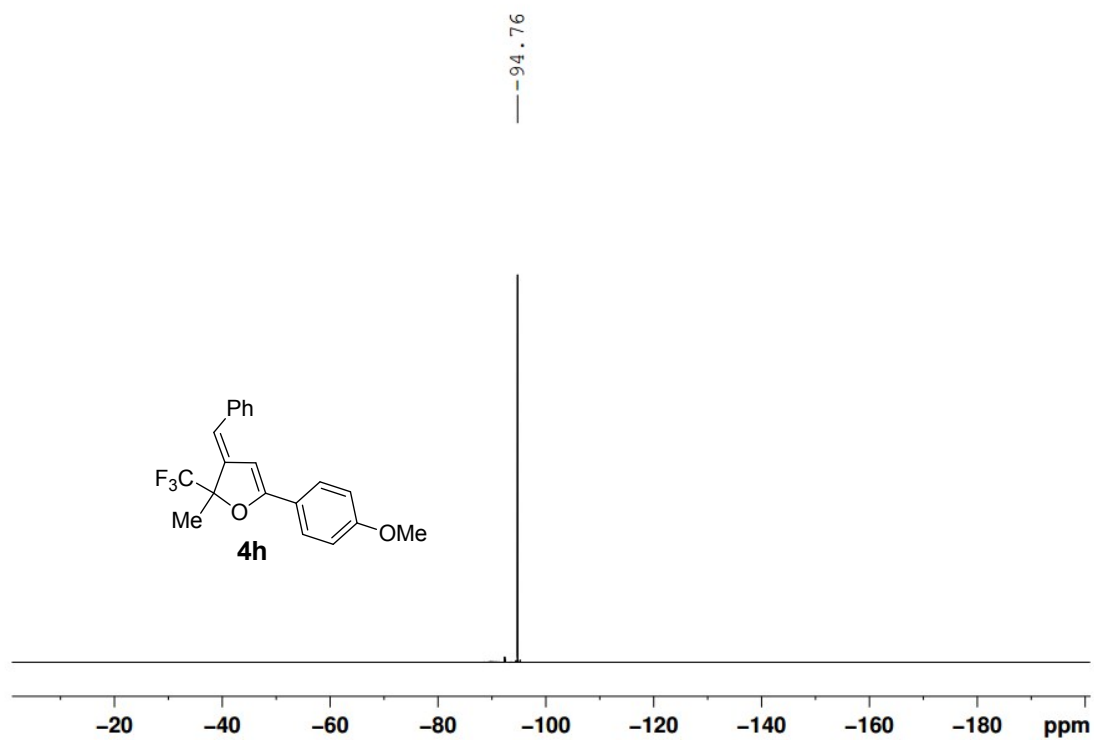
zw-3-66



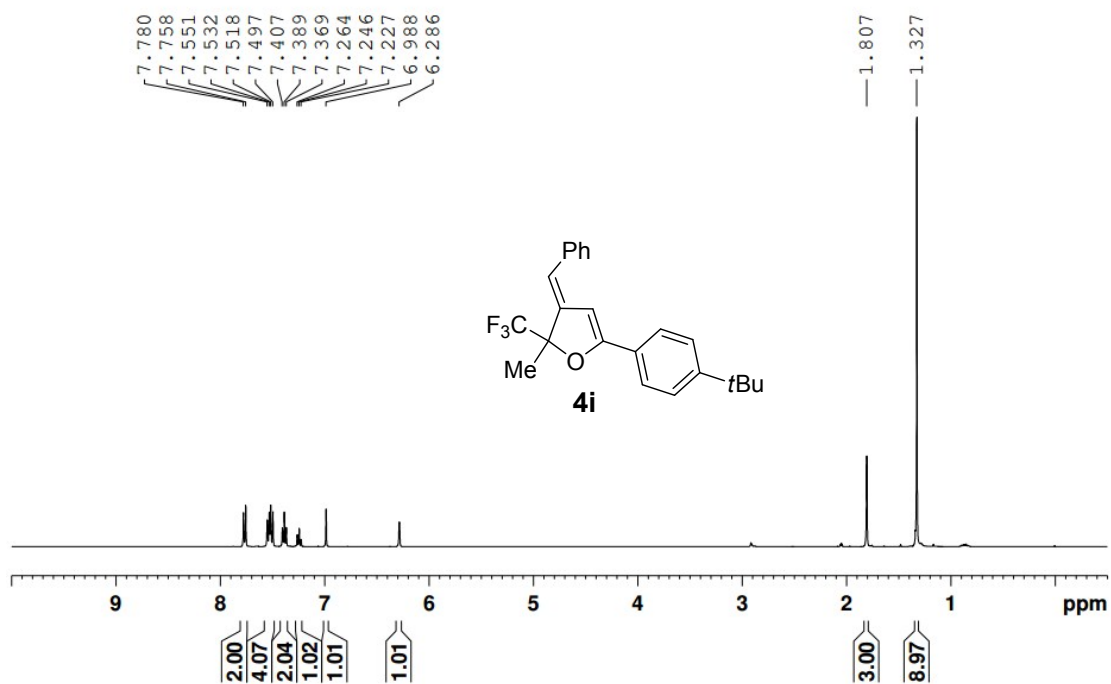
zw-3-66c



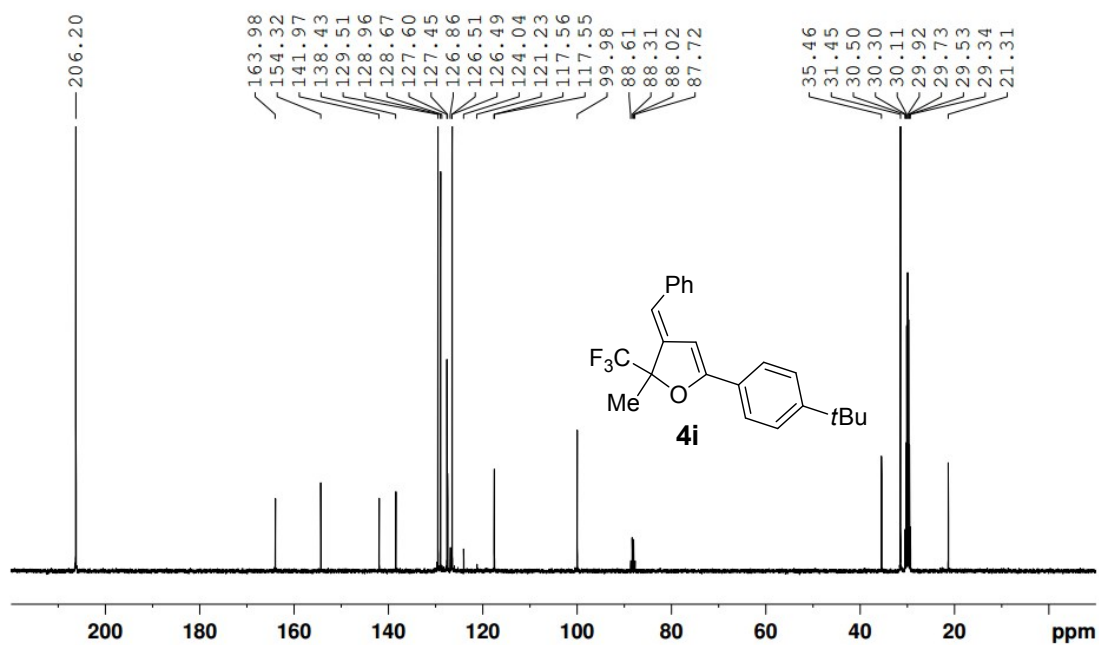
zw-3-66f



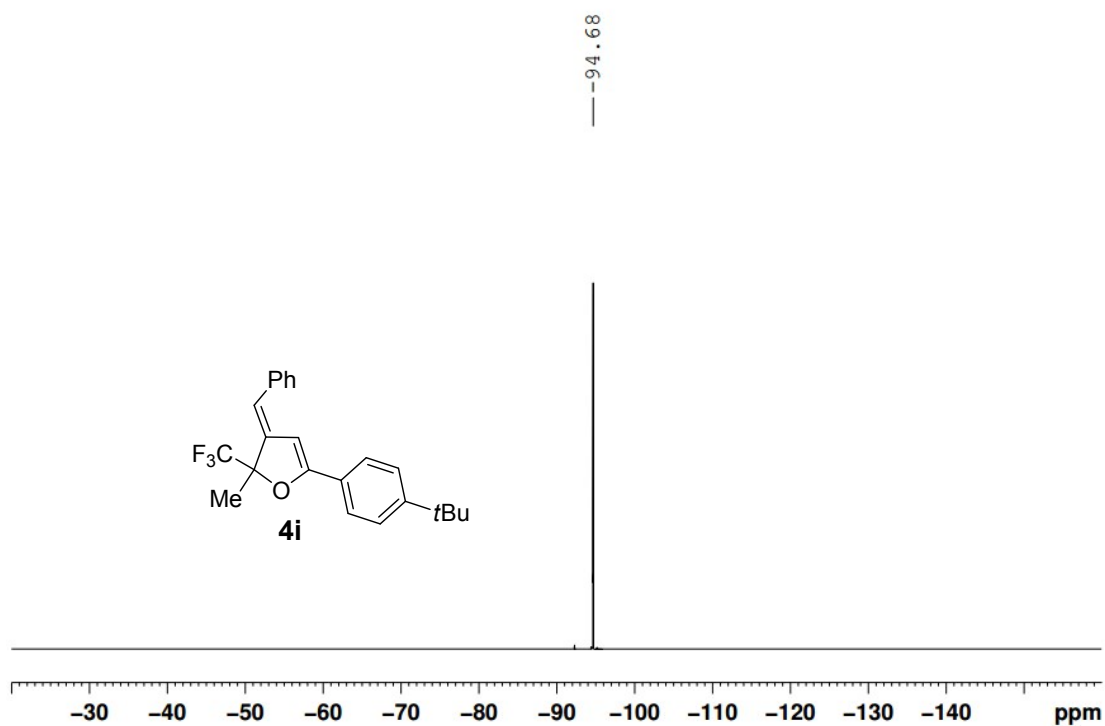
zw-4-11



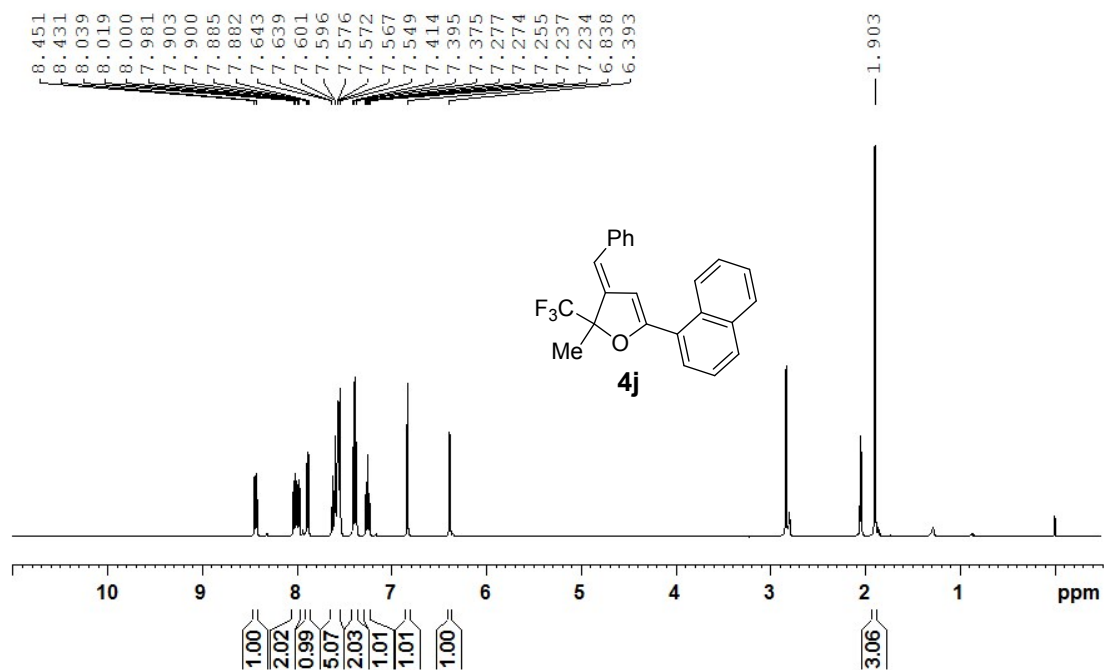
zw-4-11c



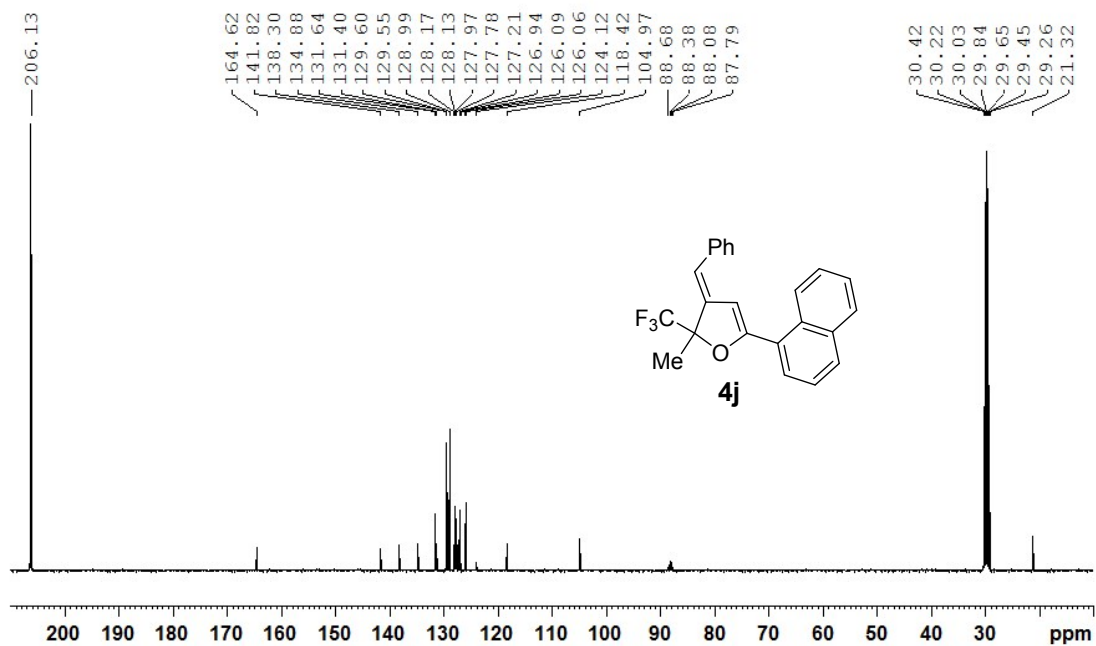
zw-4-11f



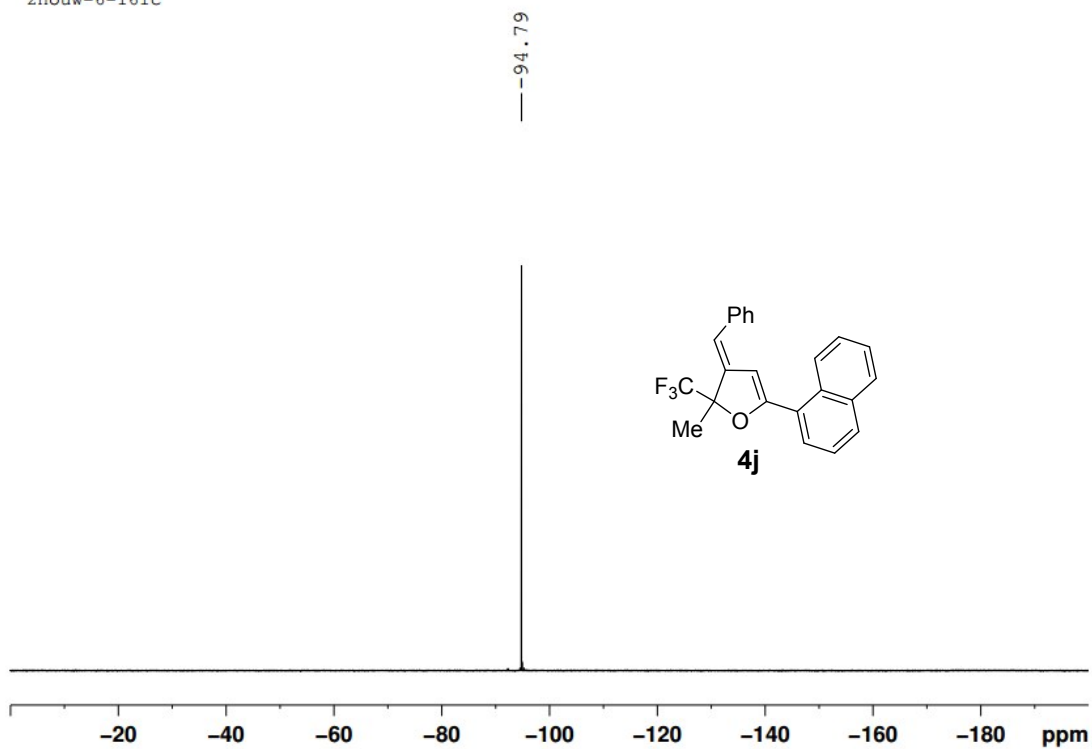
zhouw-6-161



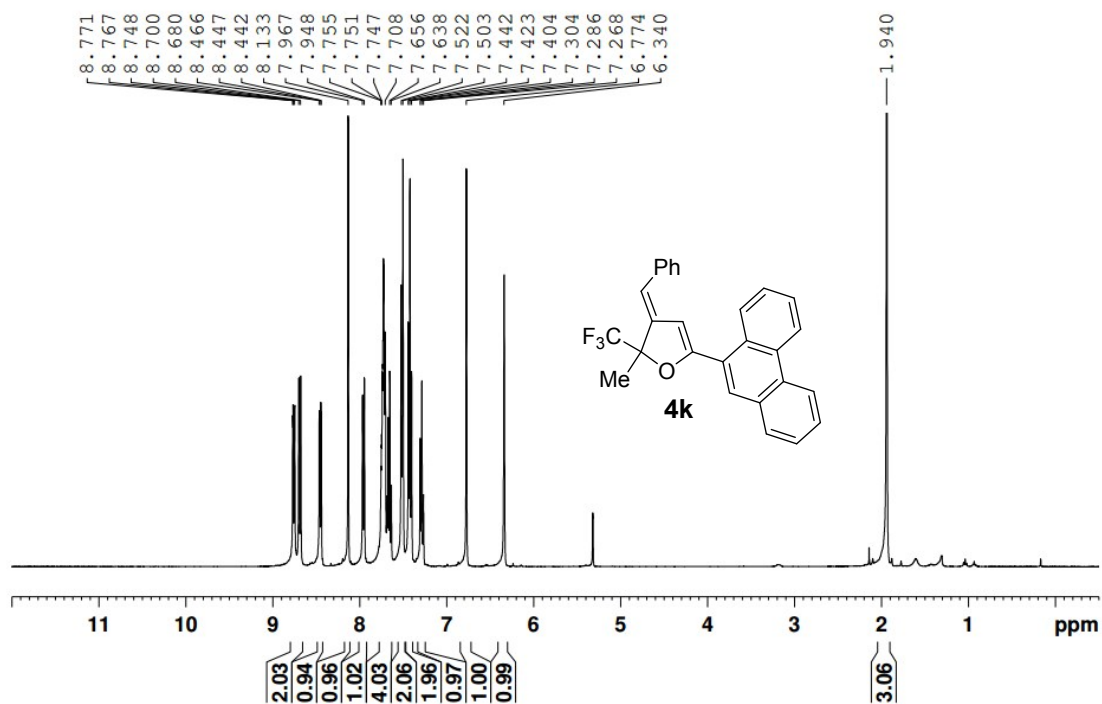
zhouw-6-161



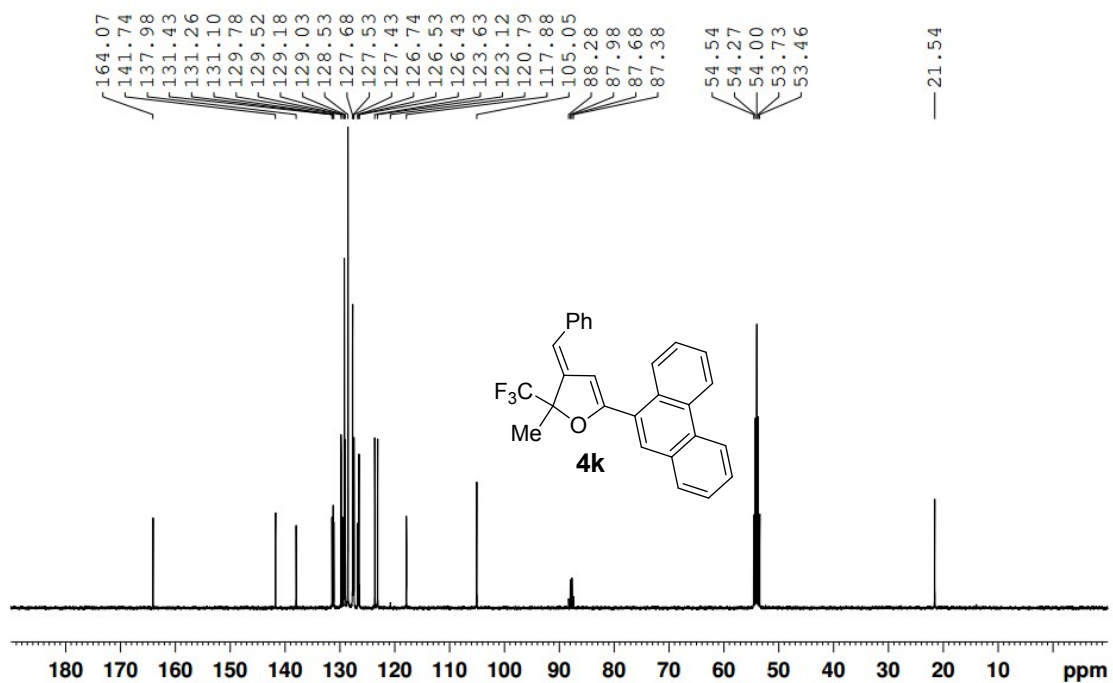
zhouw-6-161c



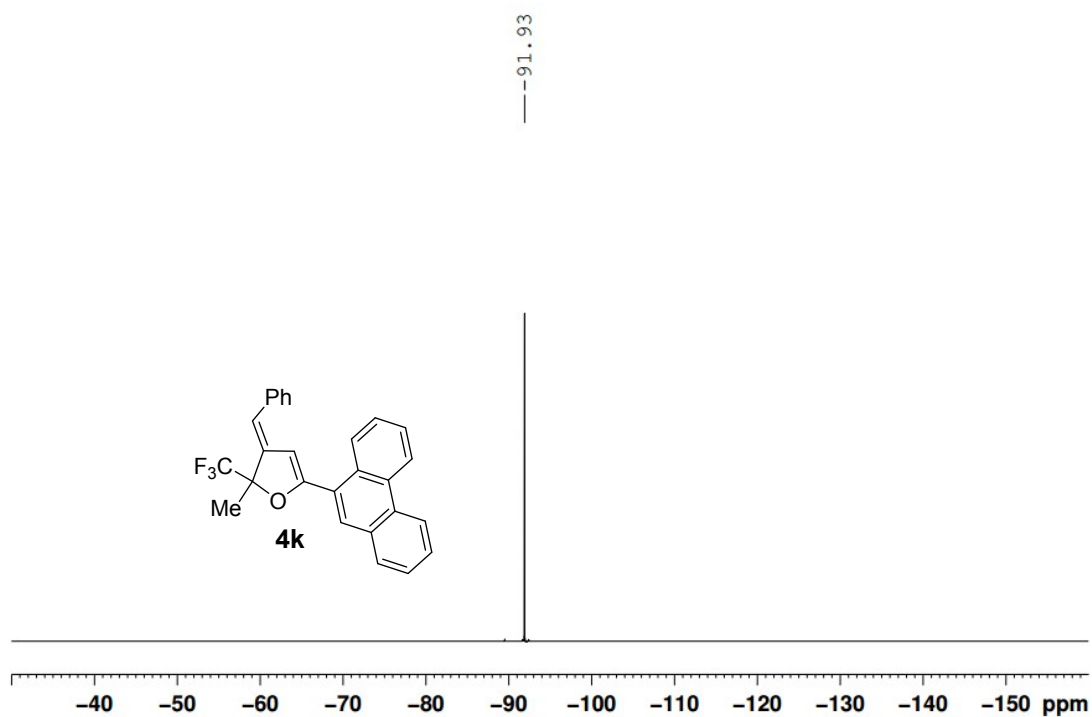
zw-4-16



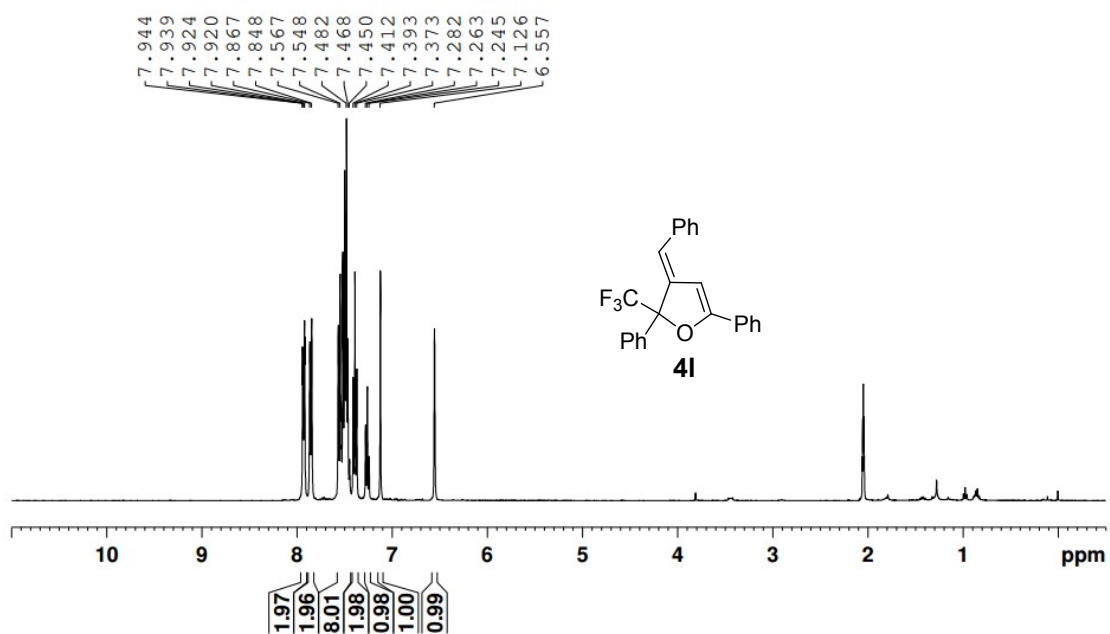
zw-4-16c



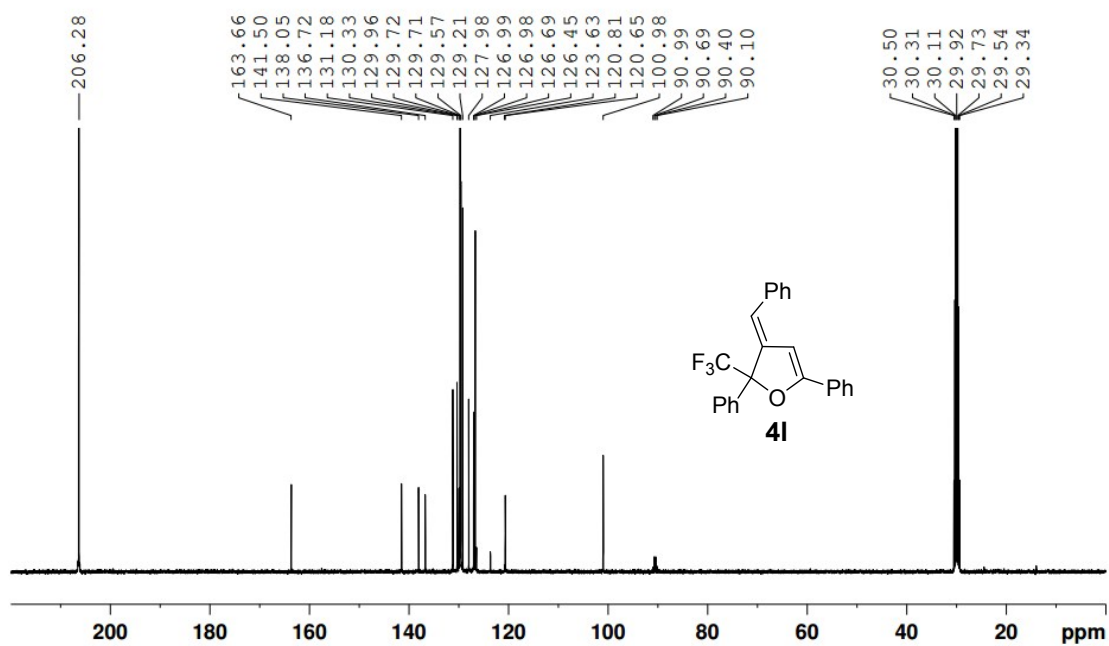
zw-4-16f



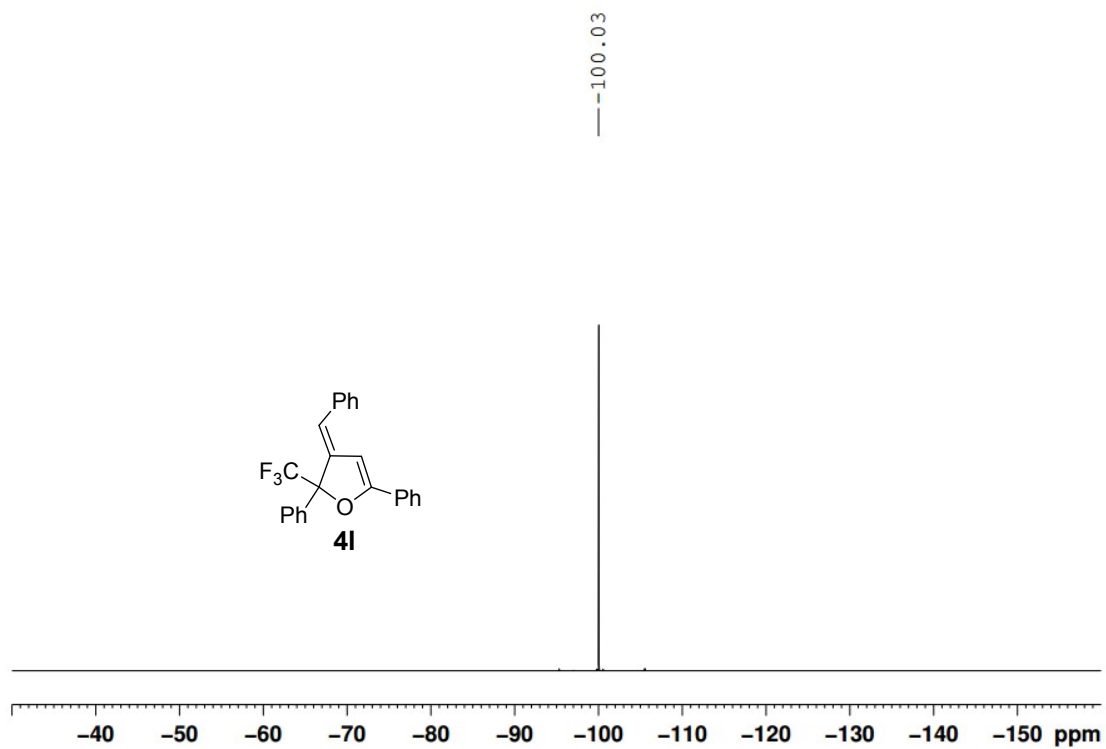
zw-4-10



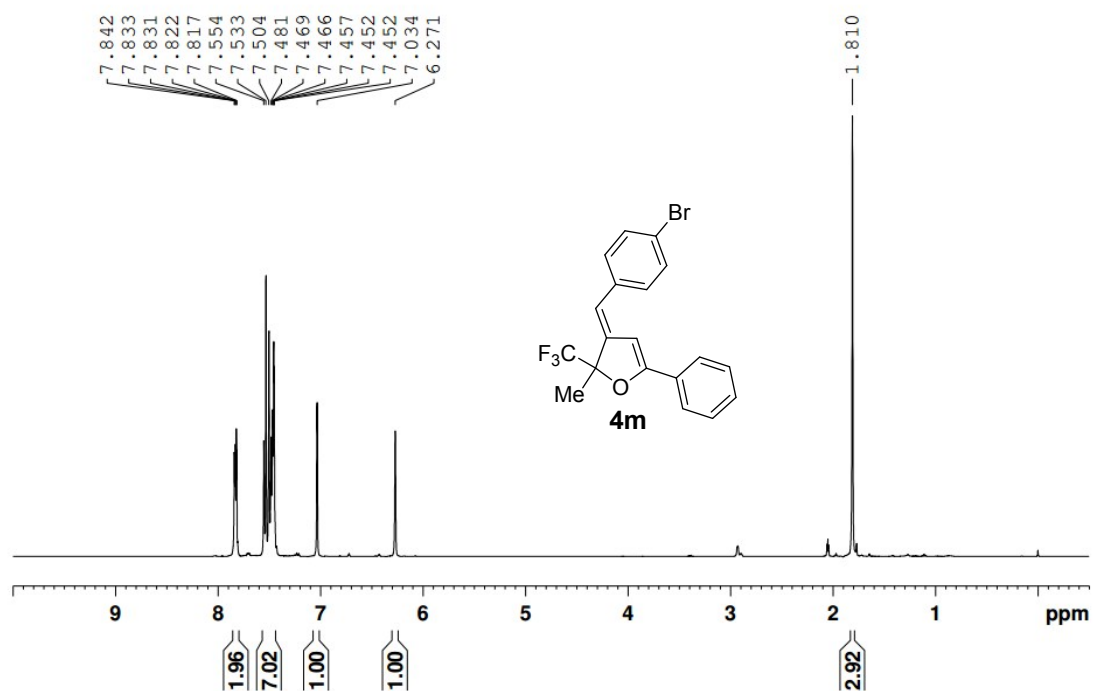
zw-4-10c



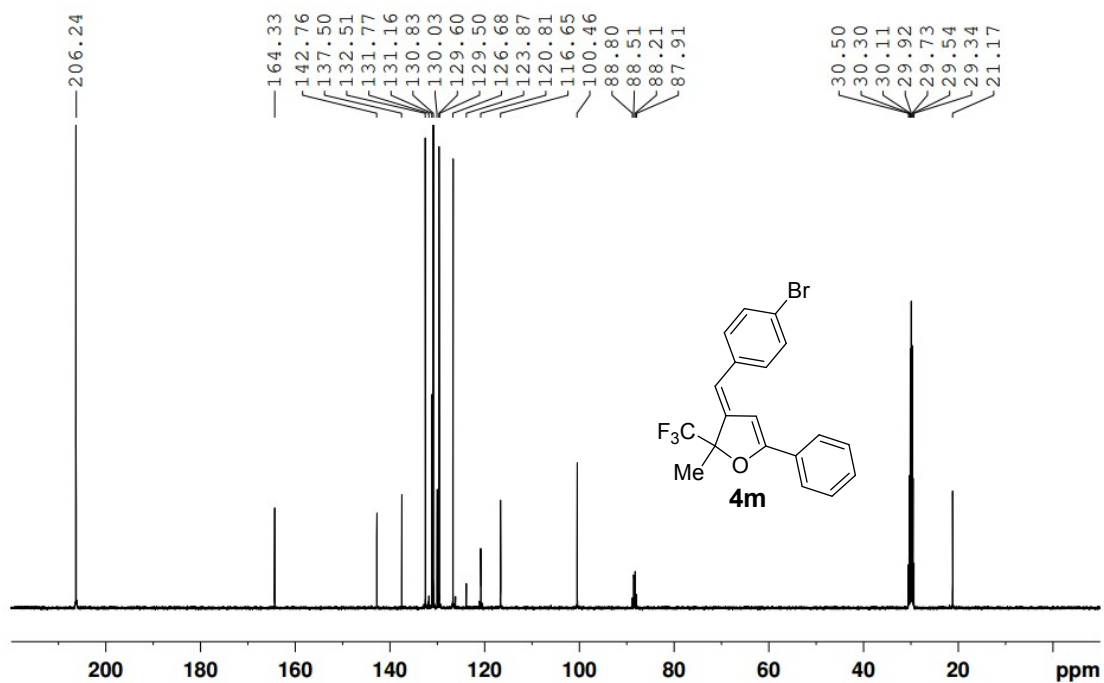
zw-4-10f



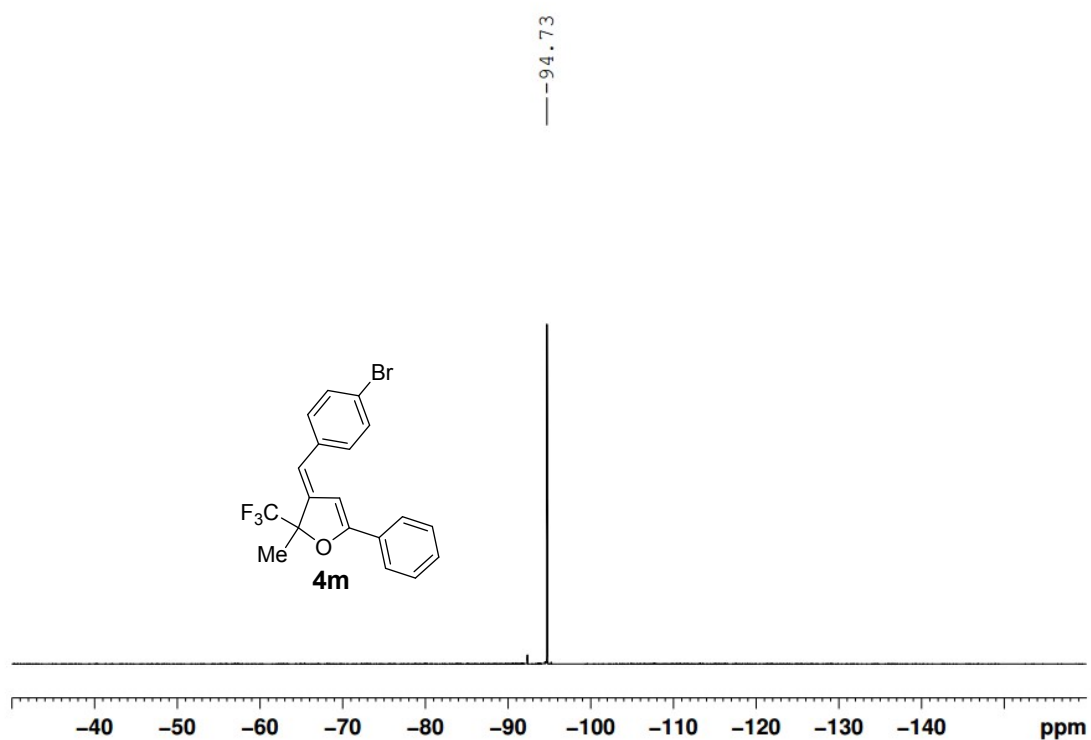
zw-4-14



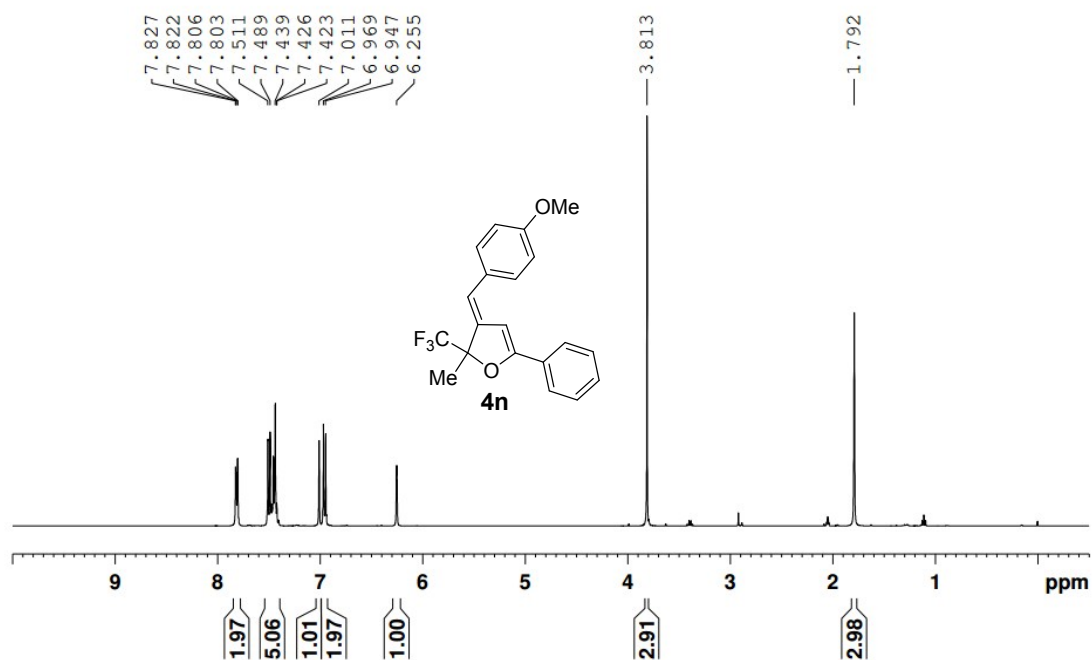
zw-4-14c



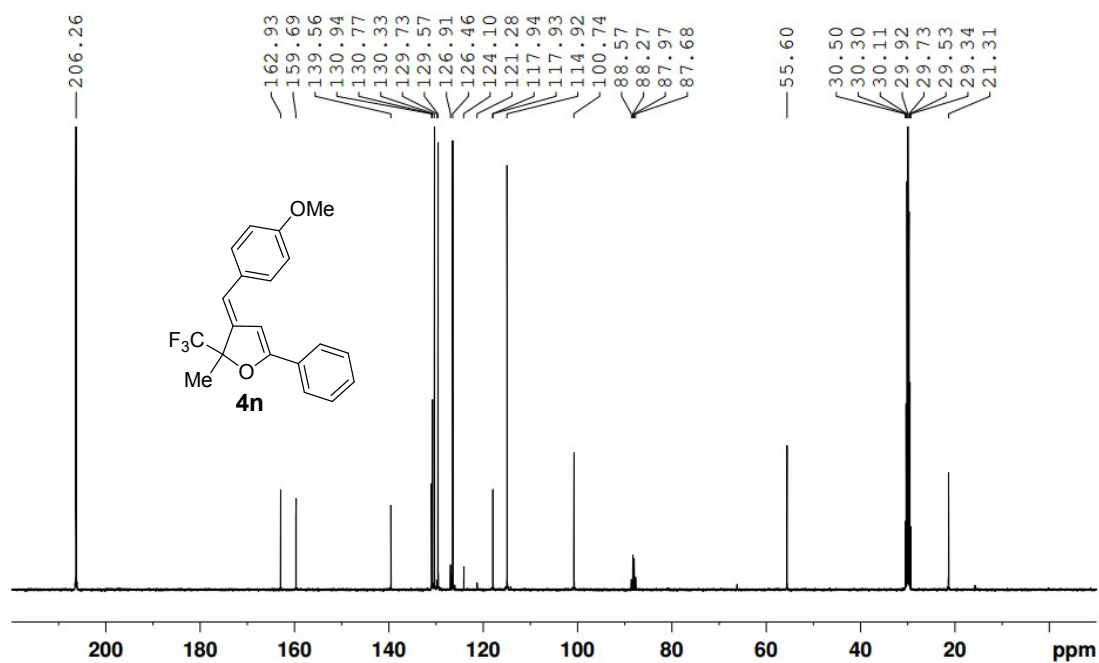
zw-4-14f



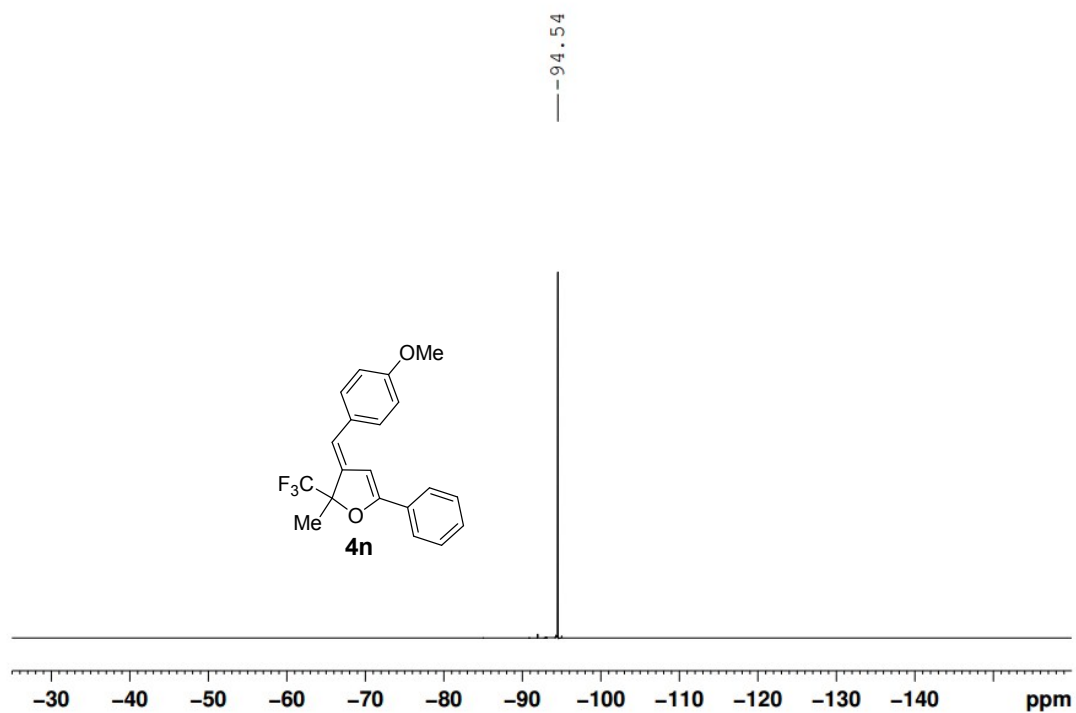
zw-4-12



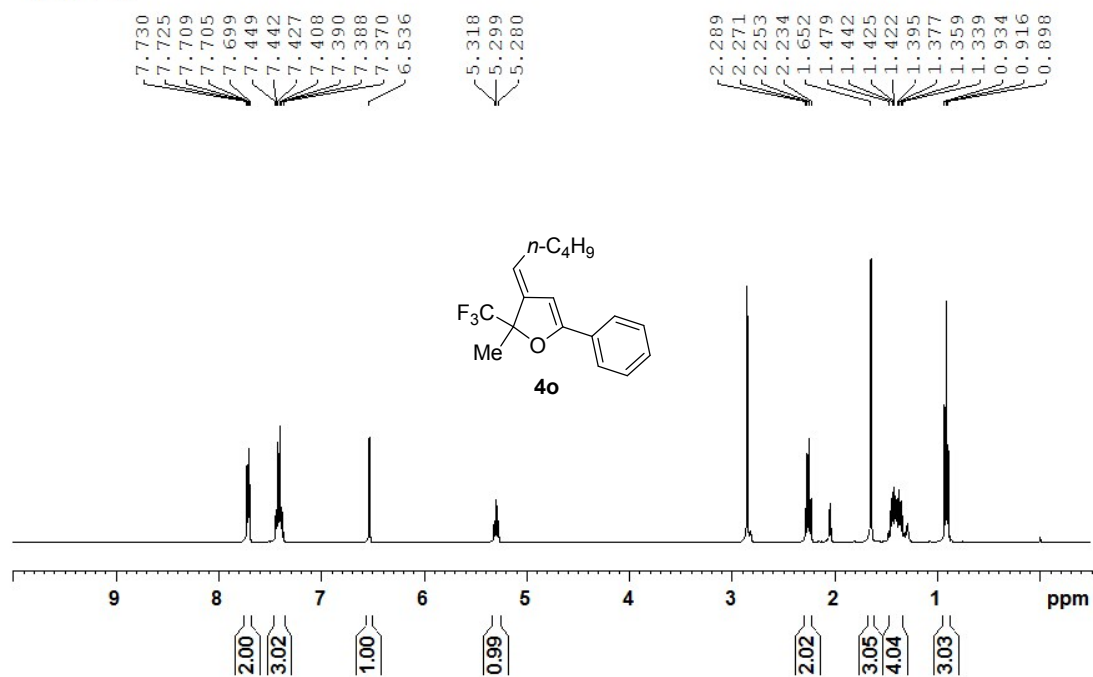
zw-4-12c



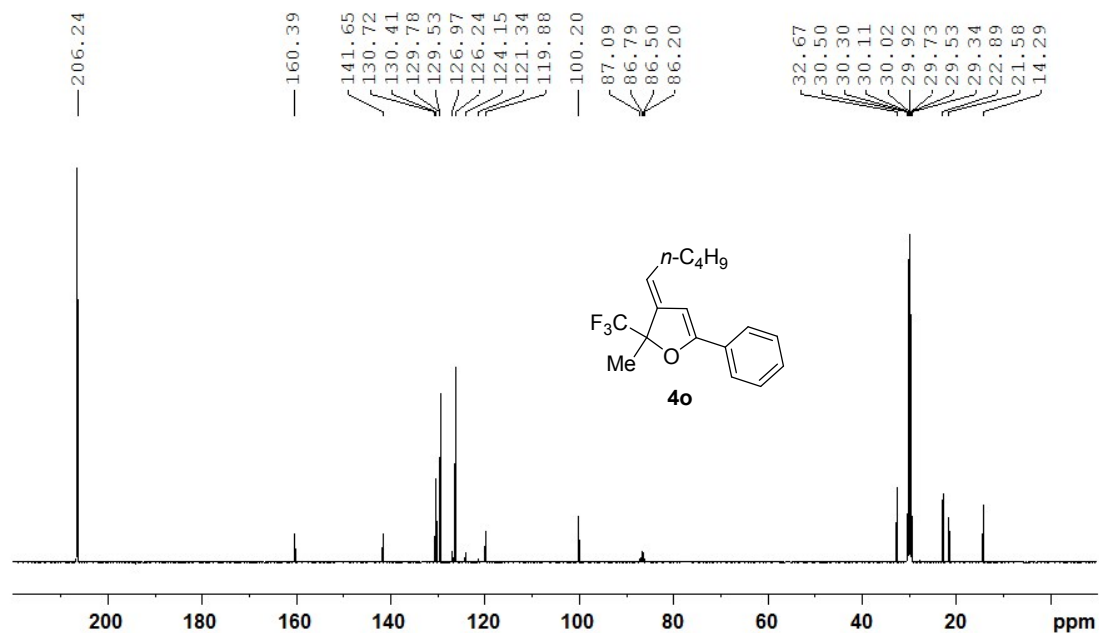
zw-4-12f



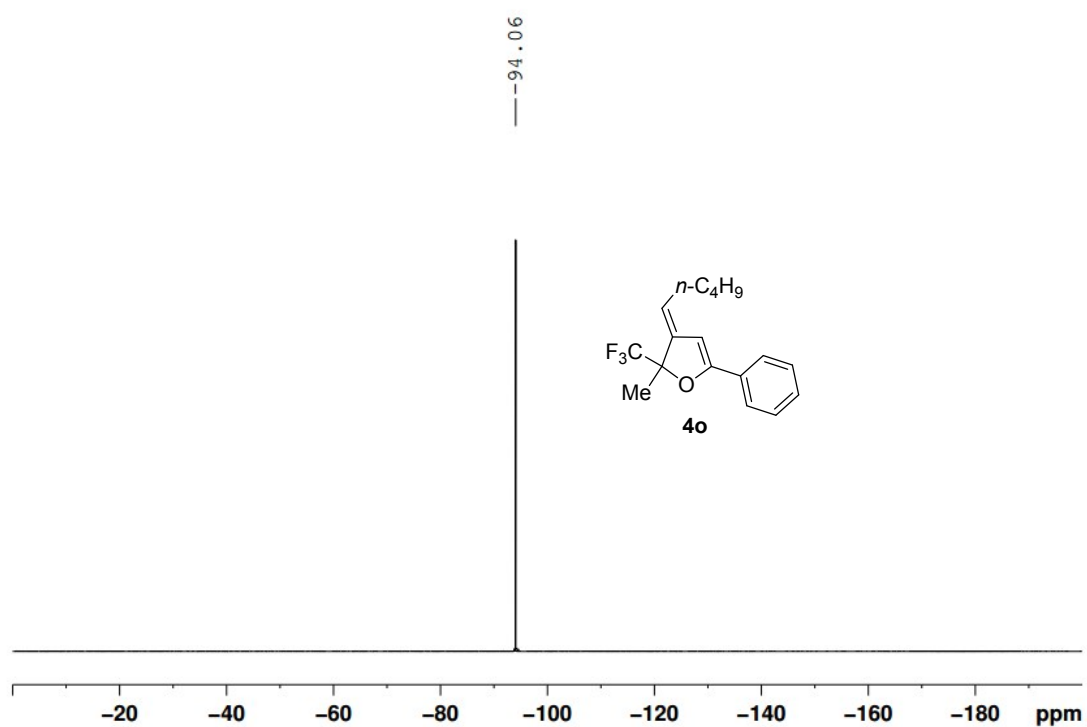
zhouw-6-158



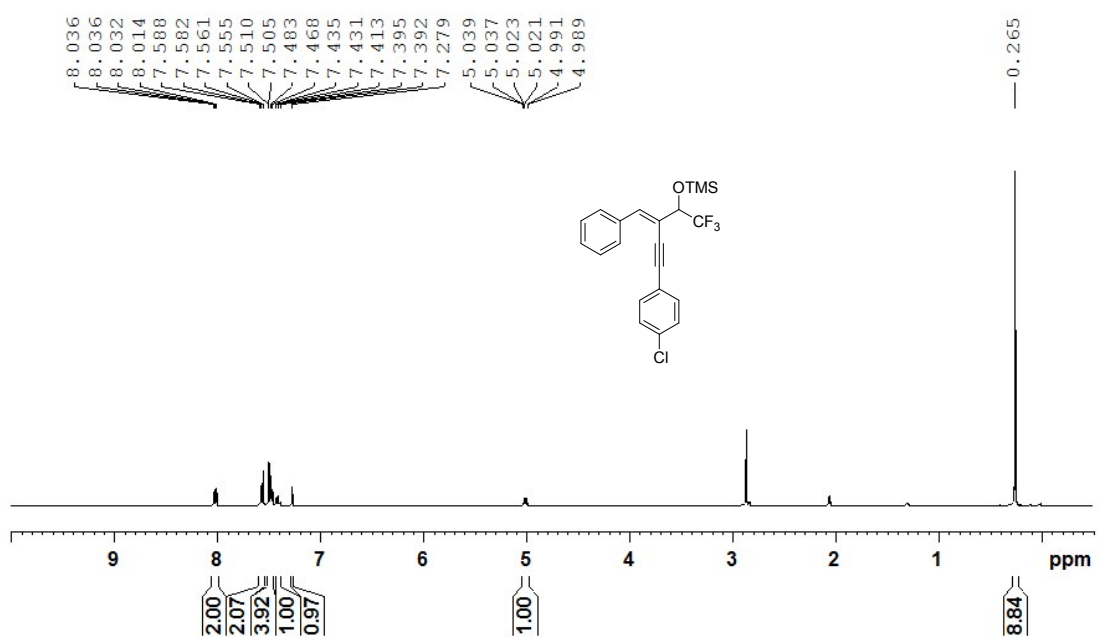
zhouw-6-158c



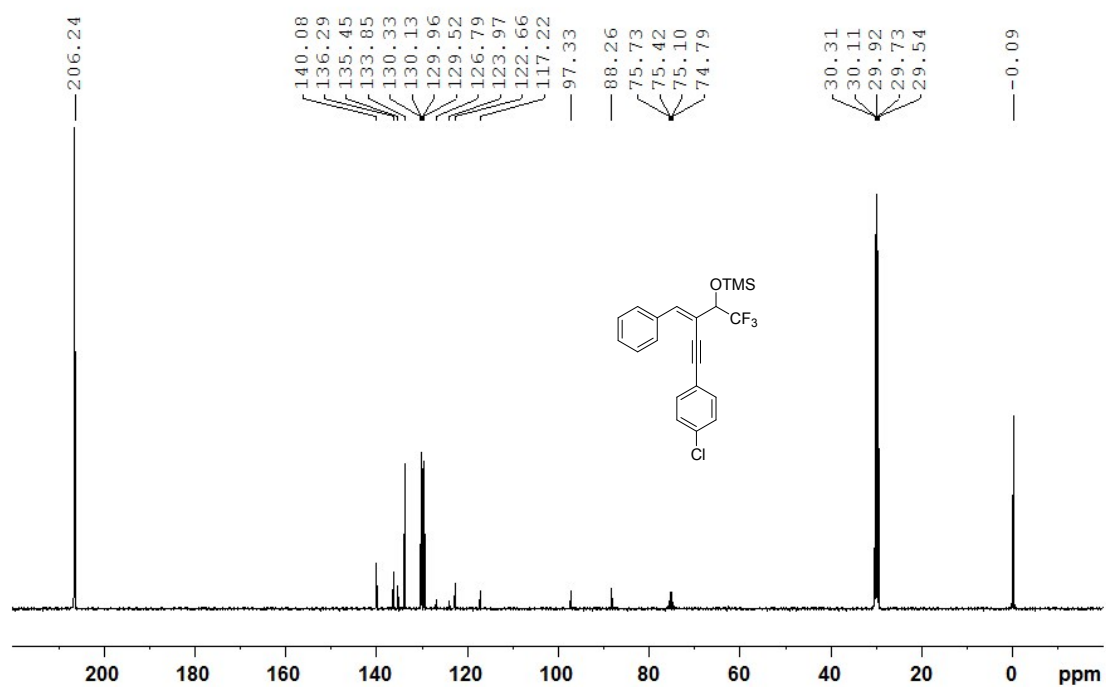
zhouw-6-158f



zhouw-6-159



zhouw-6-158c



zhouw-6-159f

