

Electronic Supplementary Information

Merging Visible-light Photoredox and Micellar catalysis: Arylation Reactions with Anilines Nitrosated in Situ

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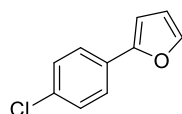
1. General Information

Unless otherwise noted, all commercially available reagents were used without further purification. Deionized water was degassed by sparging with argon prior to use. Solutions of 2 wt% surfactant in degassed water was prepared by dissolving 2 g surfactant in 98 g degassed water and stored in a glass container with a septum on the bench-top. Starting materials were prepared applying reference procedures. Photoredox-catalyzed were conducted in a sealed 10 mL tube irradiated with a 20 W household white CFL. The CFL was purchased directly from supermarket shelves. Analytical thin-layer chromatography was performed on glass plates precoated with silica gel, and compounds were detected by visualization under an ultraviolet lamp (254 nm). Starting materials were prepared applying reference procedures. Column chromatography was carried out using Silica gel. NMR solvents were purchased from Cambridge Isotopes Laboratories. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on an AVANCE III 500 Bruker spectrometer operating at 500 MHz, 125 MHz and 470 MHz, respectively. Chemical shifts were reported in ppm. Coupling constants (J values) are reported in Hz. UV-vis absorption measurements were performed using a Perkin Elmer Lambda 750 spectrophotometer at room temperature.

2. General Methods and Product Characterization

Typical procedure for photocatalytic arylation of heteroarenes in water. Aniline (0.5 mmol) and Eosin B (1 mol%, 3 mg) were added to an oven dried 10 mL tube containing a PTFE-coated magnetic stir bar. 2 mL aqueous solution of 2 wt% Triton X-100 was added *via* syringe, and heteroarene (2.5 mmol or 1.5 mmol) was then added. The reaction tube was closed with a rubber septum. The mixture was stirred for 1 min before *tert*-Butyl nitrite (1 mmol, 120 μL) was added slowly *via* syringe while stirring. The resulting mixture was stirred and irradiated under a 20 W household white CFL at room temperature for 2 h. After completion, the mixture was extracted in flask with ethyl acetate (5 mL x 3). The organic phase was collected and the volatiles was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the title compounds.

2-(4-Chlorophenyl)furan (3a).



Chemical Formula: $\text{C}_{10}\text{H}_7\text{ClO}$
Exact Mass: 178.0185
Elemental Analysis: C, 67.25; H, 3.95; Cl, 19.85; O, 8.96

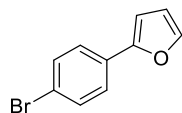
White solid, yield 83%.

^1H NMR (500 MHz, CDCl_3) δ 7.60 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 1.7$ Hz, 1H), 7.35 (d, $J = 8.5$ Hz, 2H), 6.64 (d, $J = 3.3$ Hz, 1H), 6.48 (dd, $J = 3.4, 1.8$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 153.1, 142.5, 133.1, 129.5, 129.0, 125.1, 111.9, 105.6.

Analytical data are in accordance with literature values.¹

2-(4-Bromophenyl)furan (3b).



Chemical Formula: $\text{C}_{10}\text{H}_7\text{BrO}$
Exact Mass: 221.9680
Elemental Analysis: C, 53.84; H, 3.16; Br, 35.82; O, 7.17

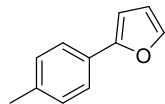
White solid, yield 79%.

^1H NMR (500 MHz, CDCl_3) δ 7.52 (qd, $J = 8.6, 1.6$ Hz, 4H), 7.48 (s, 1H), 6.65 (d, $J = 3.4$ Hz, 1H), 6.51 – 6.44 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 153.1, 142.5, 131.9, 129.9, 125.4, 121.2, 111.9, 105.7.

Analytical data are in accordance with literature values.¹

2-(*p*-Tolyl)furan (3c).



Chemical Formula: $\text{C}_{11}\text{H}_{10}\text{O}$
Exact Mass: 158.0732
Elemental Analysis: C, 83.52; H, 6.37; O, 10.11

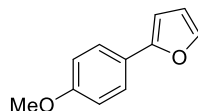
Colorless oil, yield 67%.

^1H NMR (500 MHz, CDCl_3) δ 7.58 (d, $J = 8.1$ Hz, 2H), 7.45 (d, $J = 1.8$ Hz, 1H), 7.20 (d, $J = 7.9$ Hz, 2H), 6.60 (d, $J = 3.4$ Hz, 1H), 6.46 (dd, $J = 3.4, 1.8$ Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 154.4, 141.8, 137.3, 129.5, 128.4, 123.9, 111.7, 104.3, 21.4.

Analytical data are in accordance with literature values.¹

2-(4-Methoxyphenyl)furan (3d).



Chemical Formula: $\text{C}_{11}\text{H}_{10}\text{O}_2$
Exact Mass: 174.0681
Elemental Analysis: C, 75.84; H, 5.79; O, 18.37

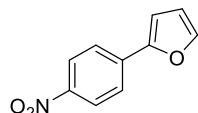
Yellowish oil, yield 32%.

^1H NMR (500 MHz, CDCl_3) δ 7.62 (dt, $J = 8.8, 2.1$ Hz, 2H), 7.44 (d, $J = 1.8$ Hz, 1H), 6.94 (d, $J = 8.5$ Hz, 2H), 6.62 – 6.36 (m, 2H), 3.84 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 159.2, 154.2, 141.5, 125.4, 124.2, 114.3, 111.7, 103.5, 55.4.

Analytical data are in accordance with literature values.¹

2-(4-Nitrophenyl)furan (3e).



Chemical Formula: $\text{C}_{10}\text{H}_7\text{NO}_3$
Exact Mass: 189.0426
Elemental Analysis: C, 63.49; H, 3.73; N, 7.40; O, 25.37

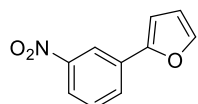
Yellow solid, yield 86%.

^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.21 (d, $J = 9.0$ Hz, 2H), 7.88 (d, $J = 8.7$ Hz, 3H), 7.25 (d, $J = 3.5$ Hz, 1H), 6.67 (dd, $J = 3.5, 1.8$ Hz, 1H).

^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 151.0, 145.8, 145.1, 136.0, 124.3, 123.9, 112.8, 110.2.

Analytical data are in accordance with literature values.¹

2-(3-Nitrophenyl)furan (3f).



Chemical Formula: $\text{C}_{10}\text{H}_7\text{NO}_3$
Exact Mass: 189.0426
Elemental Analysis: C, 63.49; H, 3.73; N, 7.40; O, 25.37

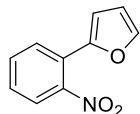
Yellow solid, yield 81%.

^1H NMR (500 MHz, CDCl_3) δ 8.46 (t, $J = 2.0$ Hz, 1H), 8.07 (dd, $J = 8.3, 2.2$ Hz, 1H), 7.93 (dt, $J = 7.9, 1.2$ Hz, 1H), 7.56 – 7.49 (m, 2H), 6.79 (d, $J = 3.4$ Hz, 1H), 6.52 (dd, $J = 3.5, 1.8$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 151.6, 148.8, 143.4, 132.4, 129.8, 129.3, 121.7, 118.6, 112.2, 107.4.

Analytical data are in accordance with literature values.¹

2-(2-Nitrophenyl)furan (3g).



Chemical Formula: C₁₀H₇NO₃
Exact Mass: 189.0426
Elemental Analysis: C, 63.49; H, 3.73; N, 7.40; O, 25.37

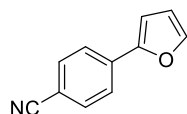
Yellow solid, yield 84%.

¹H NMR (500 MHz, CDCl₃) δ 7.73 – 7.62 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 6.67 (d, *J* = 3.5 Hz, 1H), 6.49 (dd, *J* = 3.5, 1.8 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 148.4, 147.5, 143.8, 131.9, 128.9, 128.3, 124.1, 123.8, 111.9, 109.7.

Analytical data are in accordance with literature values.¹

4-(Furan-2-yl)benzonitrile (3h).



Chemical Formula: C₁₁H₇NO
Exact Mass: 169.0528
Elemental Analysis: C, 78.09; H, 4.17; N, 8.28; O, 9.46

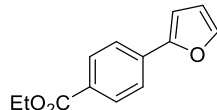
White solid, yield 90%.

¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.53 (s, 1H), 6.80 (d, *J* = 3.3 Hz, 1H), 6.52 (s, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 152.0, 143.8, 134.7, 132.6, 124.0, 119.0, 112.3, 110.3, 108.3.

Analytical data are in accordance with literature values.¹

Ethyl 4-(furan-2-yl)benzoate (3i).



Chemical Formula: C₁₃H₁₂O₃
Exact Mass: 216.0786
Elemental Analysis: C, 72.21; H, 5.59; O, 22.20

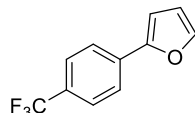
Yellowish oil, yield 87%.

¹H NMR (500 MHz, CDCl₃) δ 8.09 – 8.01 (m, 2H), 7.76 – 7.65 (m, 2H), 7.54 – 7.46 (m, 1H), 6.80 – 6.72 (m, 1H), 6.49 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 166.4, 153.0, 143.1, 134.7, 130.1, 129.0, 123.4, 112.1, 107.2, 61.0, 14.4.

Analytical data are in accordance with literature values.¹

2-(4-(Trifluoromethyl)phenyl)furan (3j).



Chemical Formula: C₁₁H₇F₃O
Exact Mass: 212.0449
Elemental Analysis: C, 62.27; H, 3.33; F, 26.86; O, 7.54

White solid, yield 91%.

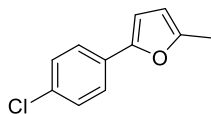
¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 1.6 Hz, 1H), 6.77 (d, *J* = 3.3 Hz, 1H), 6.51 (dd, *J* = 3.4, 1.8 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 152.7, 143.2, 134.1, 129.1 (q, *J* = 32.7 Hz), 125.9 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.9 Hz), 123.9, 112.1, 107.1.

¹⁹F NMR (470 MHz, CDCl₃) δ -61.7.

Analytical data are in accordance with literature values.²

2-(4-Chlorophenyl)-5-methylfuran (3k).



Chemical Formula: C₁₁H₉ClO

Exact Mass: 192.0342

Elemental Analysis: C, 68.58; H, 4.71; Cl, 18.40; O, 8.31

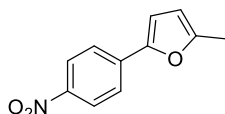
White solid, yield 75%.

¹H NMR (500 MHz, CDCl₃) δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 3.3 Hz, 1H), 6.06 (dd, *J* = 3.1, 1.2 Hz, 1H), 2.36 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 152.4, 151.4, 132.4, 129.8, 128.9, 124.6, 108.0, 106.5, 13.8.

Analytical data are in accordance with literature values.³

2-Methyl-5-(4-nitrophenyl)furan (3l).



Chemical Formula: C₁₁H₉NO₃

Exact Mass: 203.0582

Elemental Analysis: C, 65.02; H, 4.46; N, 6.89; O, 23.62

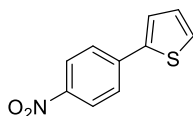
Yellow solid, yield 78%.

¹H NMR (500 MHz, CDCl₃) δ 8.24 – 8.14 (m, 2H), 7.74 – 7.67 (m, 2H), 6.76 (d, *J* = 3.3 Hz, 1H), 6.14 (dd, *J* = 3.4, 1.1 Hz, 1H), 2.40 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 154.8, 150.2, 146.0, 136.8, 124.4, 123.3, 110.4, 108.9, 13.9.

Analytical data are in accordance with literature values.⁴

2-(4-Nitrophenyl)thiophene (3m).



Chemical Formula: C₁₀H₇NO₂S

Exact Mass: 205.0197

Elemental Analysis: C, 58.52; H, 3.44; N, 6.82; O, 15.59; S, 15.62

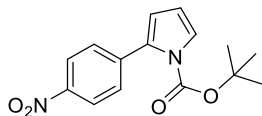
Yellow solid, yield 75%.

¹H NMR (500 MHz, DMSO-*d*₆) δ 8.21 – 8.18 (m, 2H), 7.89 – 7.84 (m, 2H), 7.76 – 7.70 (m, 2H), 7.20 (dd, *J* = 5.1, 3.7 Hz, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 146.0, 140.7, 140.0, 129.1, 128.8, 126.8, 125.9, 124.4.

Analytical data are in accordance with literature values.¹

tert-Butyl 2-(4-nitrophenyl)-1*H*-pyrrole-1-carboxylate (3n).



Chemical Formula: C₁₅H₁₆N₂O₄

Exact Mass: 288.1110

Elemental Analysis: C, 62.49; H, 5.59; N, 9.72; O, 22.20

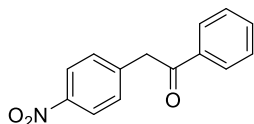
Yellowish solid, yield 80%.

¹H NMR (500 MHz, CDCl₃) δ 8.27 – 8.12 (m, 2H), 7.56 – 7.46 (m, 2H), 7.41 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.32 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.27 (t, *J* = 3.3 Hz, 1H), 1.44 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 148.9, 146.6, 140.7, 132.8, 129.6, 124.4, 123.0, 116.6, 111.2, 84.6, 27.8.

Analytical data are in accordance with literature values.¹

2-(4-Nitrophenyl)-1-phenylethan-1-one (5a).



Chemical Formula: C₁₄H₁₁NO₃
Exact Mass: 241.0739
Elemental Analysis: C, 69.70; H, 4.60; N, 5.81; O, 19.90

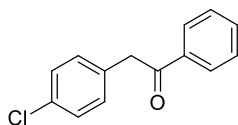
Pale white solid, yield 91%.

¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 6.9 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 4.42 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 196.1, 147.1, 142.2, 136.2, 133.8, 130.7, 128.9, 128.5, 123.8, 45.0.

Analytical data are in accordance with literature values.⁵

2-(4-Chlorophenyl)-1-phenylethan-1-one (5b).



Chemical Formula: C₁₄H₁₁ClO
Exact Mass: 230.0498
Elemental Analysis: C, 72.89; H, 4.81; Cl, 15.37; O, 6.94

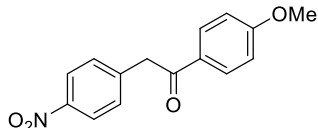
Yellowish oil, yield 43%.

¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.26 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 197.2, 136.6, 133.5, 133.1, 131.0, 128.9, 128.9, 128.7, 44.8.

Analytical data are in accordance with literature values.⁵

1-(4-Methoxyphenyl)-2-(4-nitrophenyl)ethan-1-one (5c).



Chemical Formula: C₁₅H₁₃NO₄
Exact Mass: 271.0845
Elemental Analysis: C, 66.41; H, 4.83; N, 5.16; O, 23.59

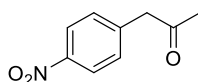
White solid, yield 88%.

¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 8.7 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.34 (s, 2H), 3.86 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 194.6, 164.0, 147.0, 142.6, 130.8, 130.6, 129.2, 123.7, 114.1, 55.6, 44.7.

Analytical data are in accordance with literature values.⁵

1-(4-Nitrophenyl)propan-2-one (5d).



Chemical Formula: C₉H₉NO₃
Exact Mass: 179.0582
Elemental Analysis: C, 60.33; H, 5.06; N, 7.82; O, 26.79

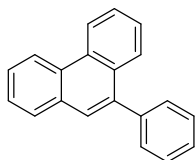
Yellow oil, yield 89%.

¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 2H), 2.24 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 204.5, 147.1, 141.6, 130.5, 123.7, 50.0, 29.9.

Analytical data are in accordance with literature values.⁵

9-Phenylphenanthrene (7a).



Chemical Formula: C₂₀H₁₄
Exact Mass: 254.1096
Elemental Analysis: C, 94.45; H, 5.55

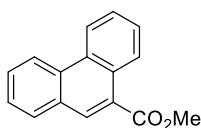
White solid, yield 76%.

¹H NMR (500 MHz, CDCl₃) δ 8.82 (d, *J* = 8.3 Hz, 1H), 8.77 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.81 – 7.69 (m, 3H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.64 – 7.54 (m, 5H), 7.52 (dd, *J* = 7.8, 2.2 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 140.9, 138.9, 131.7, 131.3, 130.8, 130.2, 130.1, 128.8, 128.4, 127.6, 127.5, 127.1, 127.0, 126.7, 126.6, 126.6, 123.0, 122.7.

Analytical data are in accordance with literature values.⁶

Methyl phenanthrene-9-carboxylate (7b).



Chemical Formula: C₁₆H₁₂O₂
Exact Mass: 236.0837
Elemental Analysis: C, 81.34; H, 5.12; O, 13.54

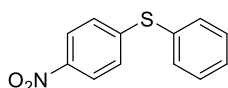
Yellowish solid, yield 67%.

¹H NMR (500 MHz, CDCl₃) δ 9.04 – 8.89 (m, 1H), 8.74 – 8.68 (m, 1H), 8.65 (d, *J* = 8.3 Hz, 1H), 8.47 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.79 – 7.66 (m, 3H), 7.62 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 4.05 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 168.1, 132.5, 132.2, 130.7, 130.1, 130.0, 129.1, 129.0, 127.5, 127.1, 127.0, 126.7, 126.2, 122.9, 122.7, 52.3.

Analytical data are in accordance with literature values.⁶

(4-Nitrophenyl)(phenyl)sulfane (9a).



Chemical Formula: C₁₂H₉NO₂S
Exact Mass: 231.0354
Elemental Analysis: C, 62.32; H, 3.92; N, 6.06; O, 13.84; S, 13.86

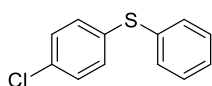
Yellowish solid, yield 81%.

¹H NMR (500 MHz, CDCl₃) δ 8.12 – 8.03 (m, 2H), 7.59 – 7.51 (m, 2H), 7.50 – 7.42 (m, 3H), 7.23 – 7.13 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 148.6, 145.5, 134.9, 130.5, 130.2, 129.8, 126.8, 124.2.

Analytical data are in accordance with literature values.⁷

(4-Chlorophenyl)(phenyl)sulfane (9b).



Chemical Formula: C₁₂H₉ClS
Exact Mass: 220.0113
Elemental Analysis: C, 65.30; H, 4.11; Cl, 16.06; S, 14.53

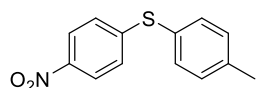
White solid, yield 74%.

¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.32 (m, 4H), 7.31 – 7.23 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 135.3, 134.8, 133.1, 132.2, 131.5, 129.5, 127.6.

Analytical data are in accordance with literature values.⁷

(4-Nitrophenyl)(*p*-tolyl)sulfane (9c).



Chemical Formula: C₁₃H₁₁NO₂S
Exact Mass: 245.0510
Elemental Analysis: C, 63.65; H, 4.52; N, 5.71; O, 13.04; S, 13.07

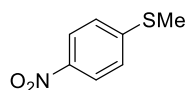
White solid, yield 79%.

¹H NMR (500 MHz, CDCl₃) δ 8.11 – 7.96 (m, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.20 – 7.09 (m, 2H), 2.45 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 149.4, 145.2, 140.3, 135.1, 130.9, 126.5, 126.2, 124.0, 21.4.

Analytical data are in accordance with literature values.⁷

Methyl(4-nitrophenyl)sulfane (9d).



Chemical Formula: C₇H₇NO₂S
Exact Mass: 169.0197
Elemental Analysis: C, 49.69; H, 4.17; N, 8.28; O, 18.91; S, 18.95

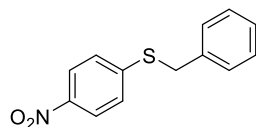
Yellowish oil, yield 85%.

¹H NMR (500 MHz, CDCl₃) δ 8.17 – 8.08 (m, 2H), 7.32 – 7.26 (m, 2H), 2.55 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 149.0, 144.9, 125.1, 124.0, 14.9.

Analytical data are in accordance with literature values.⁷

Benzyl(4-nitrophenyl)sulfane (9e).



Chemical Formula: C₁₃H₁₁NO₂S
Exact Mass: 245.0510
Elemental Analysis: C, 63.65; H, 4.52; N, 5.71; O, 13.04; S, 13.07

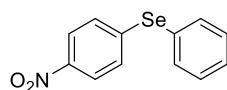
Pale white solid, yield 72%.

¹H NMR (500 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.27 (m, 5H), 4.25 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 147.3, 145.2, 135.5, 128.8, 128.7, 127.8, 126.6, 126.6, 123.9, 37.0.

Analytical data are in accordance with literature values.⁷

(4-Nitrophenyl)(phenyl)selane (9f).



Chemical Formula: C₁₂H₉NO₂Se
Exact Mass: 278.9799
Elemental Analysis: C, 51.81; H, 3.26; N, 5.04; O, 11.50; Se, 28.39

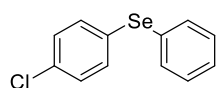
Yellow oil, yield 87%.

¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 6.5 Hz, 2H), 7.40 (dt, *J* = 14.1, 6.7 Hz, 3H), 7.32 (d, *J* = 8.6 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 146.0, 143.9, 135.8, 130.0, 129.5, 129.3, 127.1, 123.8.

Analytical data are in accordance with literature values.⁷

(4-Chlorophenyl)(phenyl)selane (9g).



Chemical Formula: C₁₂H₉ClSe
Exact Mass: 267.9558
Elemental Analysis: C, 53.86; H, 3.39; Cl, 13.25; Se, 29.51

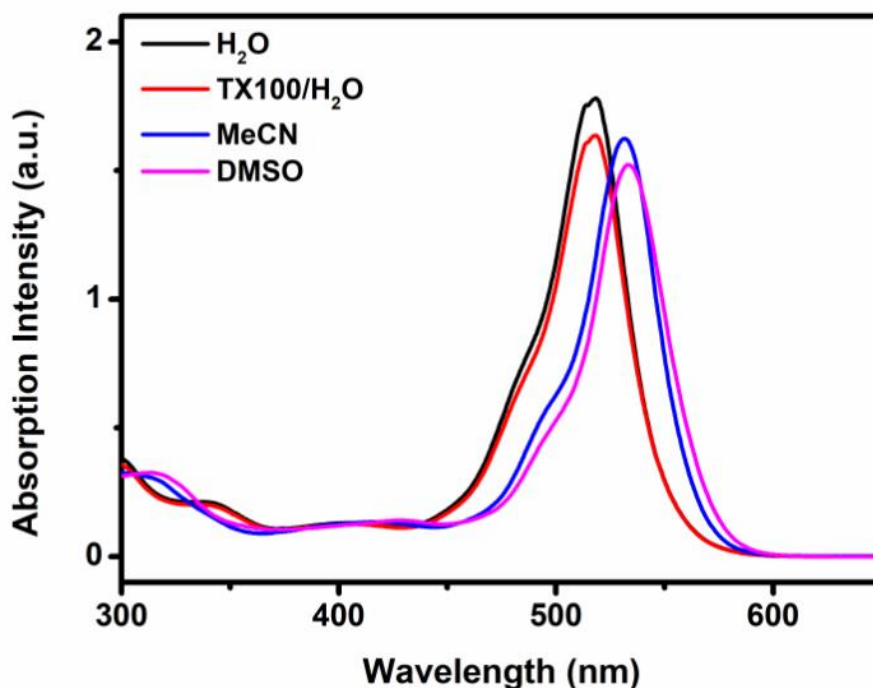
Colorless oil, yield 72%.

^1H NMR (500 MHz, CDCl_3) δ 7.49 (ddd, $J = 6.6, 3.2, 1.5$ Hz, 2H), 7.42 – 7.37 (m, 2H), 7.31 (tt, $J = 3.9, 2.6$ Hz, 3H), 7.27 – 7.23 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 134.2, 133.6, 133.3, 130.8, 129.6, 127.8.

Analytical data are in accordance with literature values.⁷

3. UV-Vis Absorptions of Eosin B in Different Solvents



Note: For UV-vis measurements, solutions were processed with the concentration of 20 μM . The molar ratio of Eosin B to Triton X-100 was kept at 3:40, in accordance of the ratio as applied in the photoredox catalysis setting. TX100 is short for Triton X-100.

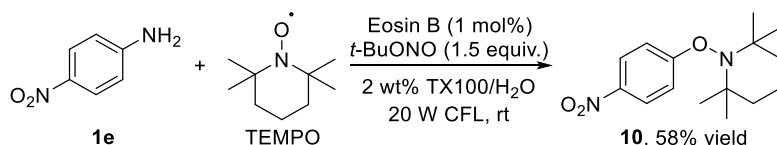
4. Recycling of the Aqueous Reaction Medium

4-Chloroaniline (0.5 mmol, 64 mg) and Eosin B (1 mol%, 3 mg) were added to an oven dried 10 mL tube containing a PTFE-coated magnetic stir bar. 2 mL aqueous solution of 2 wt% Triton X-100 was added *via* syringe, and furan (2.5 mmol, 181 μL) was then added. The reaction tube was closed with a rubber septum. The mixture was stirred for 1 min before *tert*-Butyl nitrite (1 mmol, 120 μL) was added slowly *via* syringe while stirring. The resulting mixture was stirred and irradiated under a 20 W household white CFL at room temperature for 2 h. After completion, the mixture was extracted in flask with ethyl acetate (3 mL x 3). The organic phase was collected and the volatiles was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the title compounds. To the aqueous phase containing the surfactant was added 4-Chloroaniline (0.5 mmol) and Eosin B (1 mol%, 3 mg). The mixture was then deoxygenated by three freeze-pump-thaw cycles before the addition of furan (2.5 mmol, 181

μL). *tert*-Butyl nitrite (1 mmol, 120 μL) was added slowly *via* syringe while stirring. The resulting mixture was stirred under a 20 W household white CFL at room temperature for 2 h. The work up was conducted in exactly the same way as described for the first run, and the aqueous phase containing the surfactant was reused to start the next cycle. The next two cycles were conducted according to the second run.

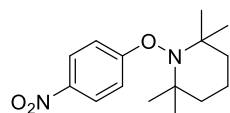
5. Experiments for the Mechanistic Study

Radical capturing experiment with TEMPO.



4-Nitroaniline (0.5 mmol, 69 mg), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (0.75 mmol, 118 mg) and Eosin B (1 mol%, 3mg) were added to an oven dried 10 mL tube containing a PTFE-coated magnetic stir bar. 2 mL aqueous solution of 2 wt% Triton X-100 was added *via* syringe. The reaction tube was closed with a rubber septum. The mixture was stirred for 1 min before *tert*-Butyl nitrite (1 mmol, 120 μL) was added slowly *via* syringe while stirring. The resulting mixture was stirred and irradiated under a 20 W household white CFL at room temperature for 2 h. After completion, the mixture was extracted in flask with ethyl acetate (5 mL x 3). The organic phase was collected and the volatiles was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the adduct **10**.

2,2,6,6-Tetramethyl-1-(4-nitrophenoxy)piperidine (**10**).



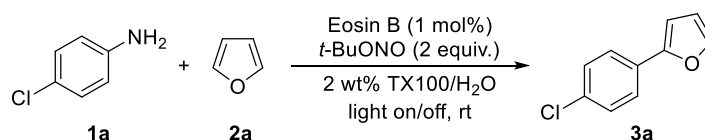
Chemical Formula: $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_3$
 Exact Mass: 278.1630
 Elemental Analysis: C, 64.73; H, 7.97; N, 10.06; O, 17.24

^1H NMR (500 MHz, CDCl_3) δ 8.12 (dt, $J = 9.4, 1.4$ Hz, 2H), 7.73 – 6.75 (m, 2H), 1.69 – 1.55 (m, 5H), 1.42 (dq, $J = 9.7, 3.3$ Hz, 1H), 1.22 (s, 6H), 0.96 (s, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 168.7, 141.2, 125.6, 114.2, 60.9, 39.7, 32.3, 20.5, 16.9.

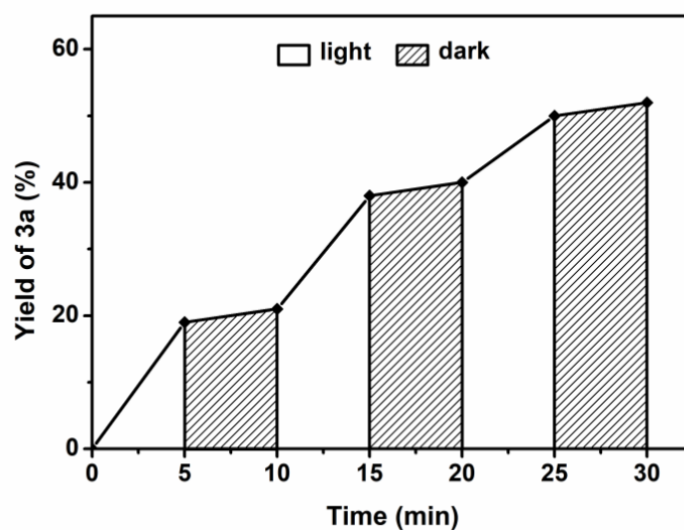
Analytical data are in accordance with literature values.⁵

Light on/off experiment.



4-Chloroaniline (0.5 mmol, 64 mg) and Eosin B (1 mol%, 3 mg) were added to an oven dried 10 mL tube containing a PTFE-coated magnetic stir bar. 2 mL aqueous solution of 2 wt% Triton X-100 was added *via* syringe, and furan (2.5 mmol, 181 μL) was then added. The reaction tube was closed with a rubber septum. The mixture was stirred for 1 min before *tert*-Butyl nitrite (1 mmol, 120 μL) was added slowly *via* syringe while stirring. The resulting mixture was stirred under a 20 W household white CFL at room temperature for 5 min. 50 μL of the reaction mixture was taken from the reaction tube and was analyzed by GC with *n*-dodecane as internal standard. The tube was then

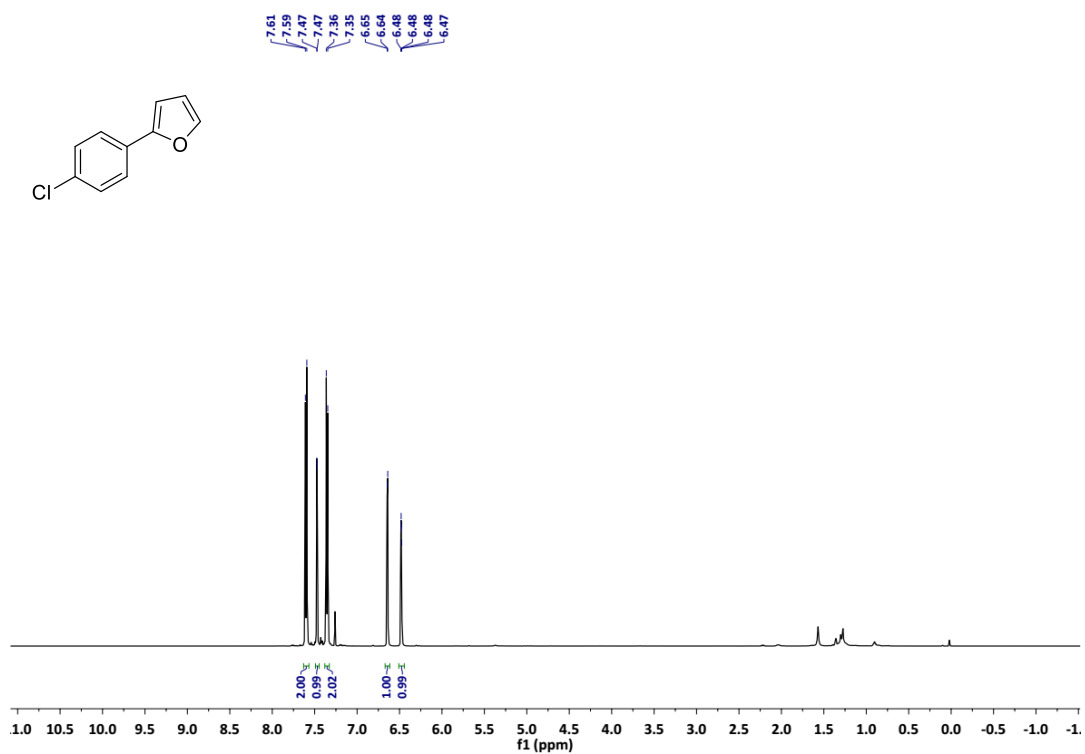
covered with aluminum foil and the reaction mixture was stirred in the dark for 5 min. Another 50 μL of the reaction mixture was taken and analyzed by GC. This procedure was repeated for two runs. The time profile is shown in the following figure.



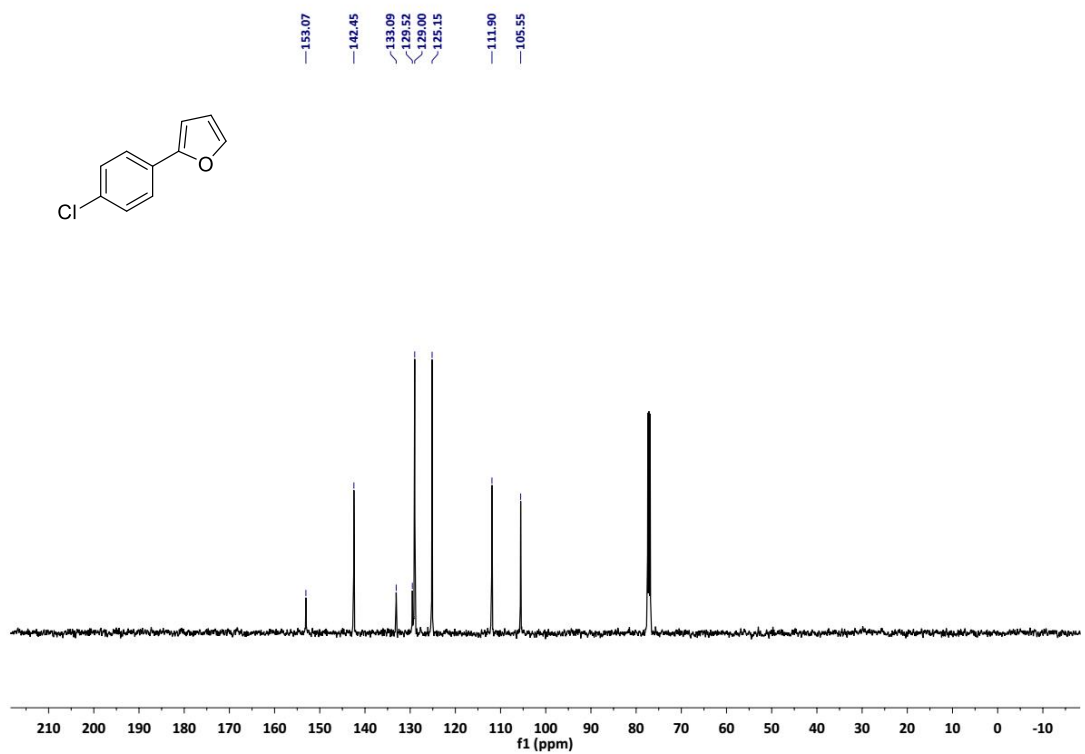
6. References

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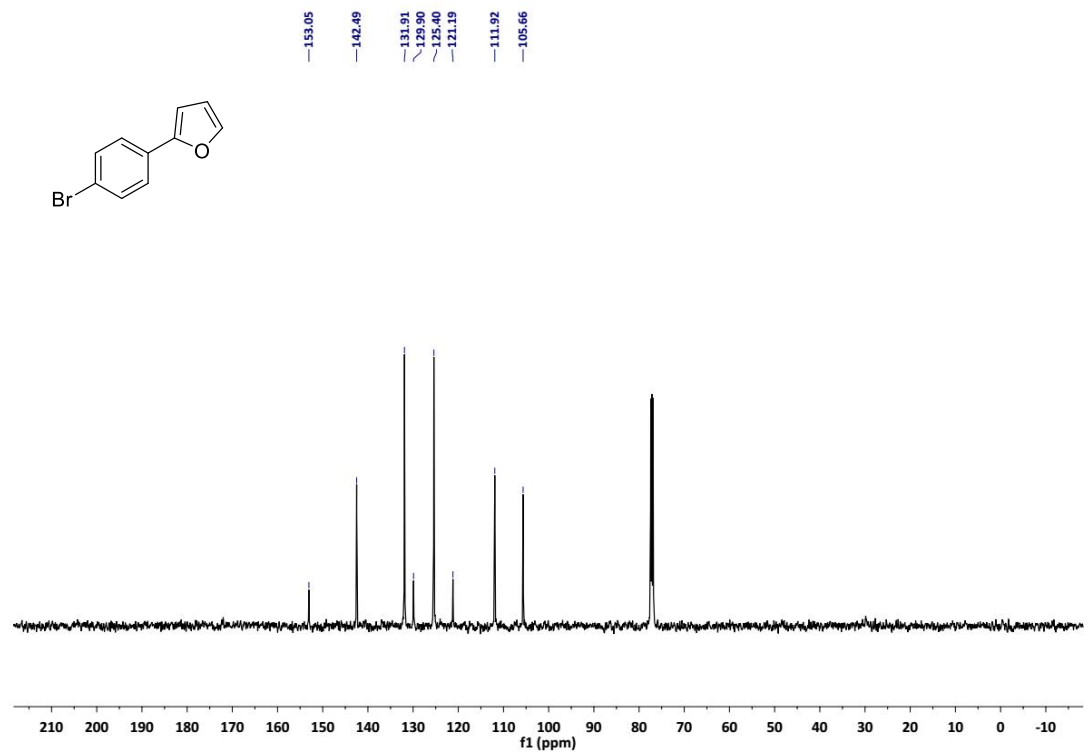
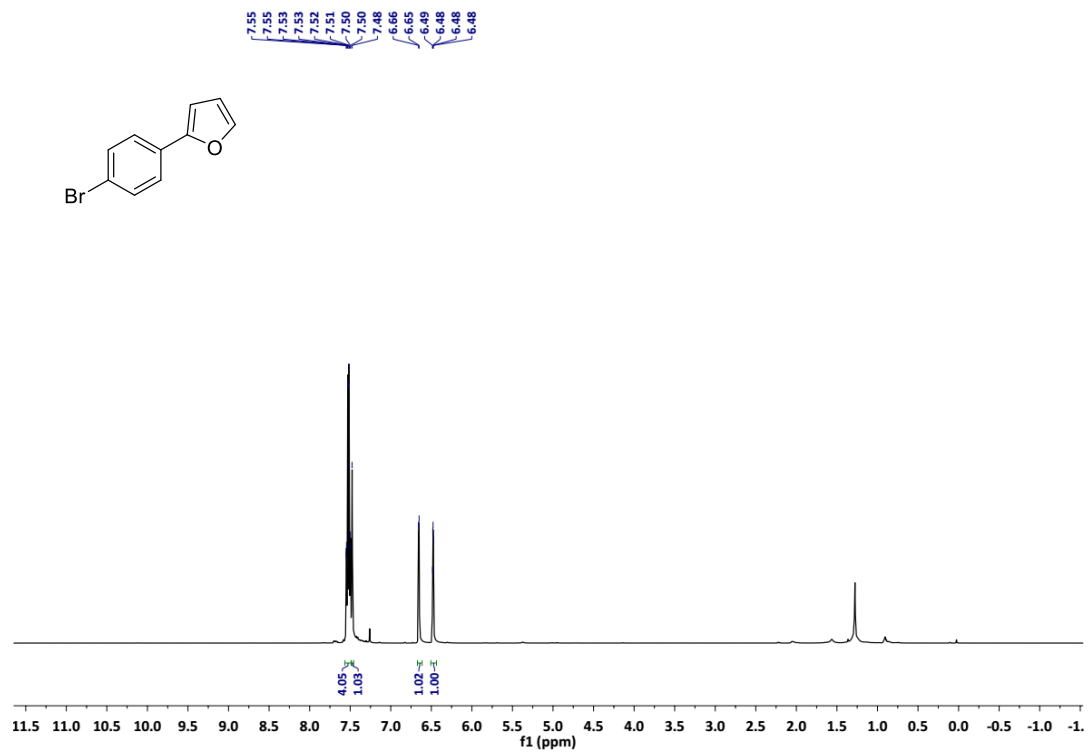
7. NMR Spectra

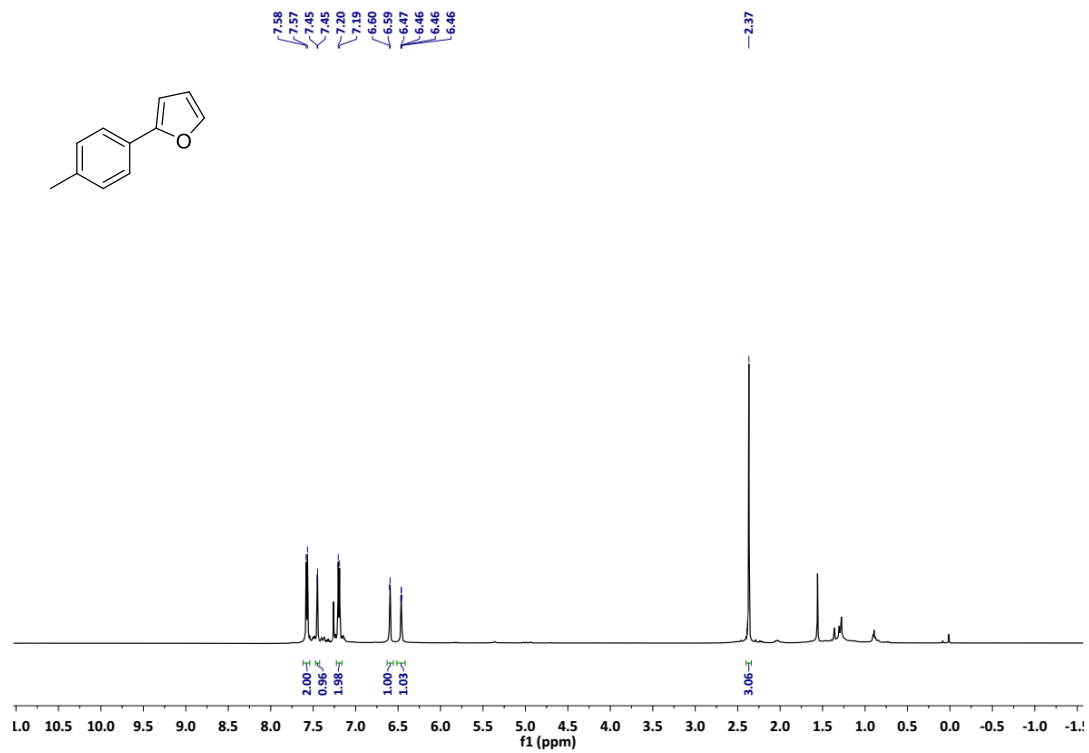


¹H NMR spectrum (500 MHz, CDCl₃) of **3a**

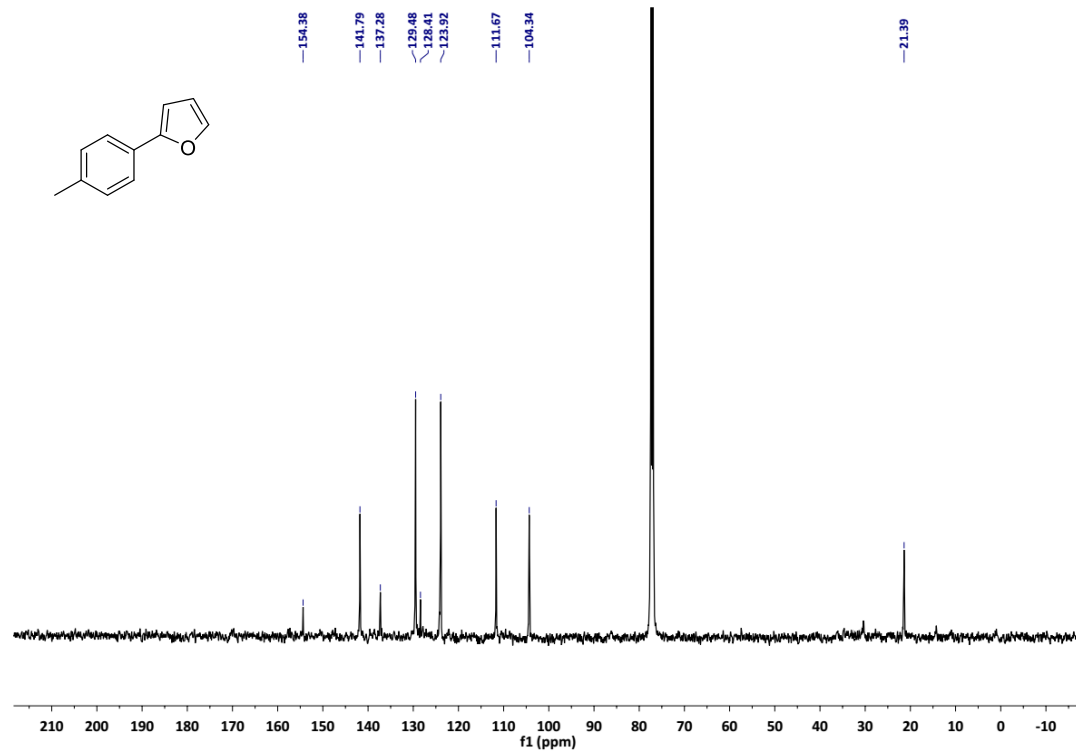


¹³C NMR spectrum (126 MHz, CDCl₃) of **3a**

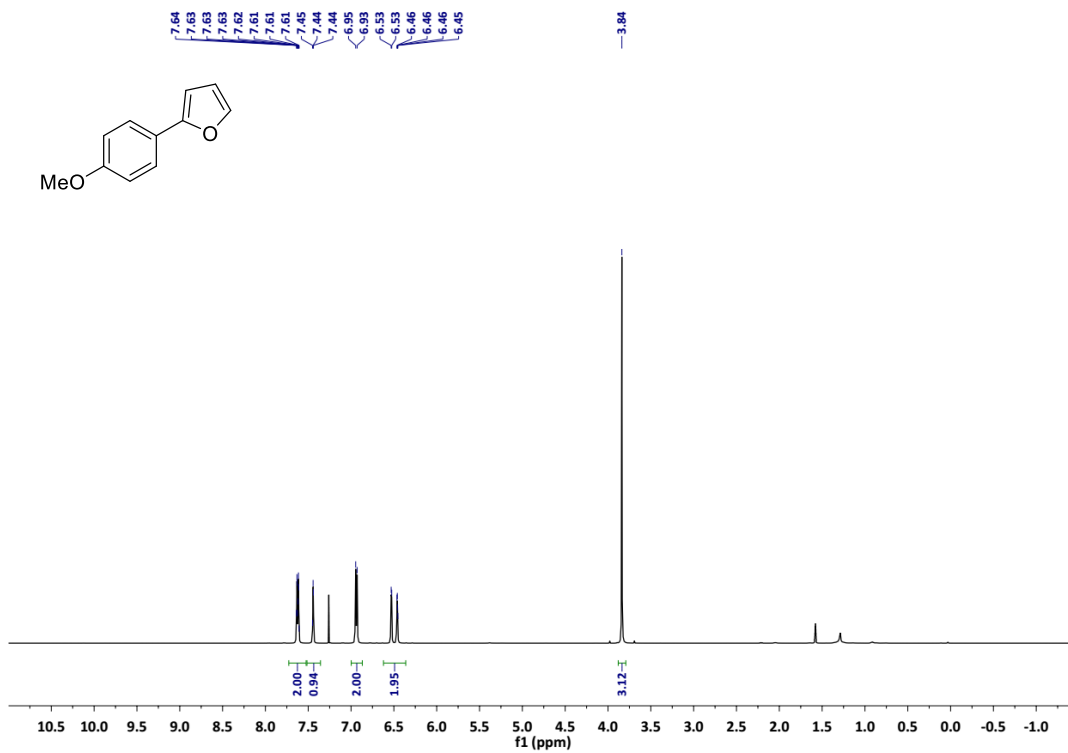




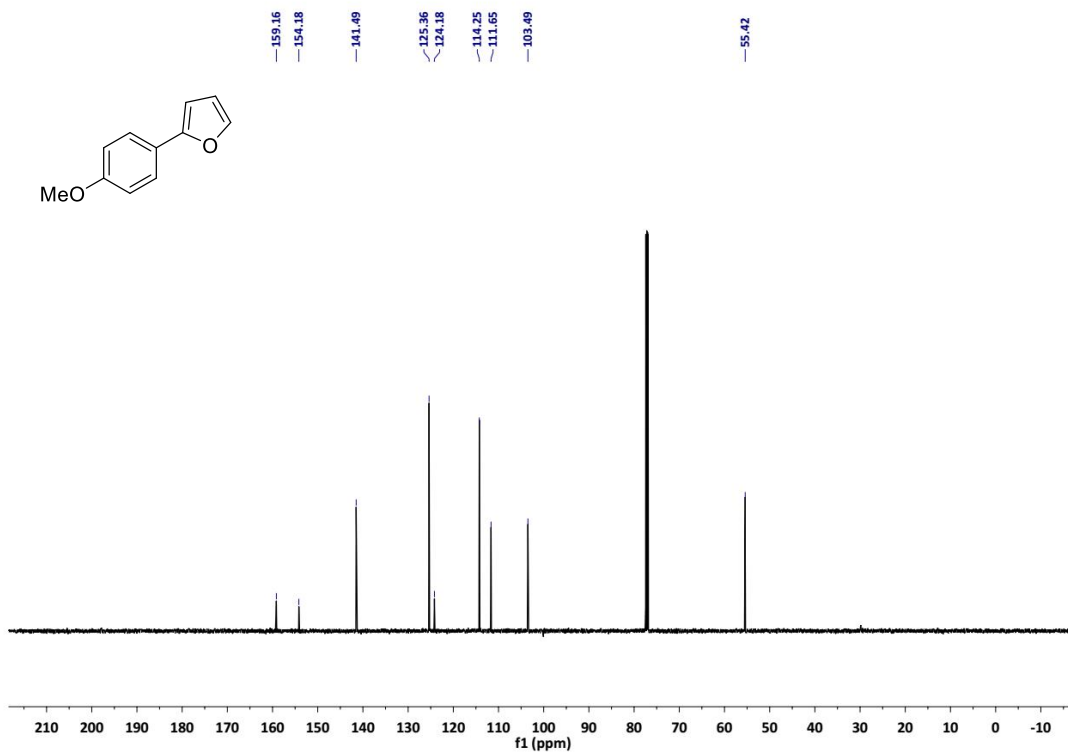
¹H NMR spectrum (500 MHz, CDCl₃) of **3c**



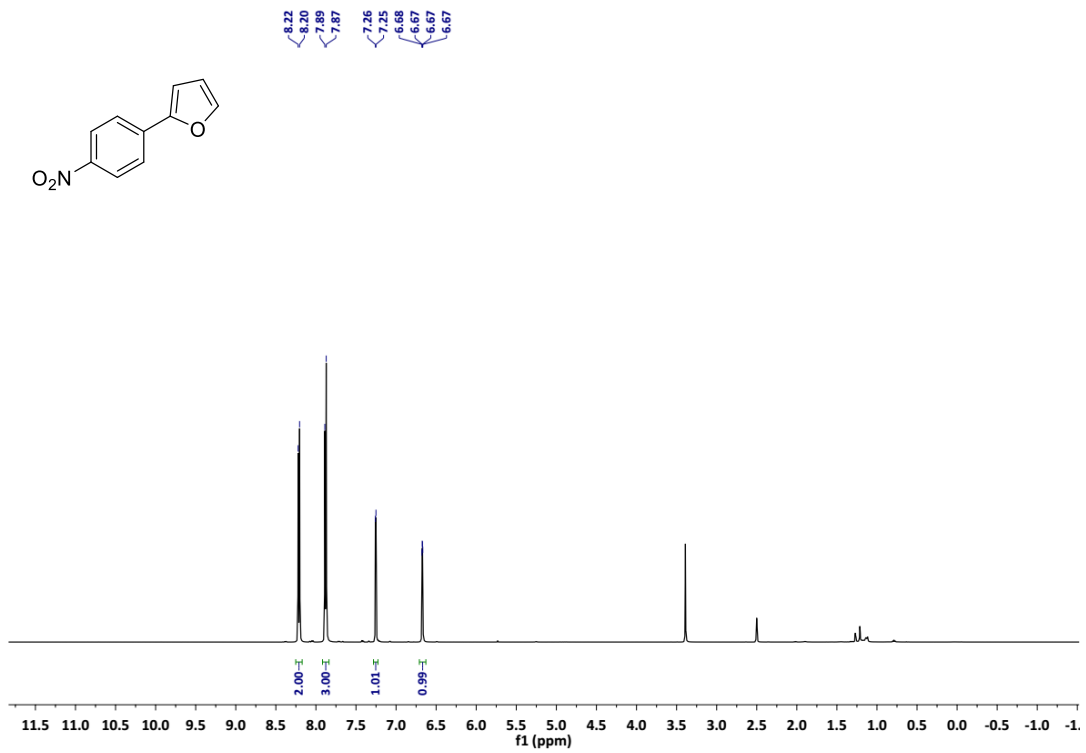
¹³C NMR spectrum (126 MHz, CDCl₃) of **3c**



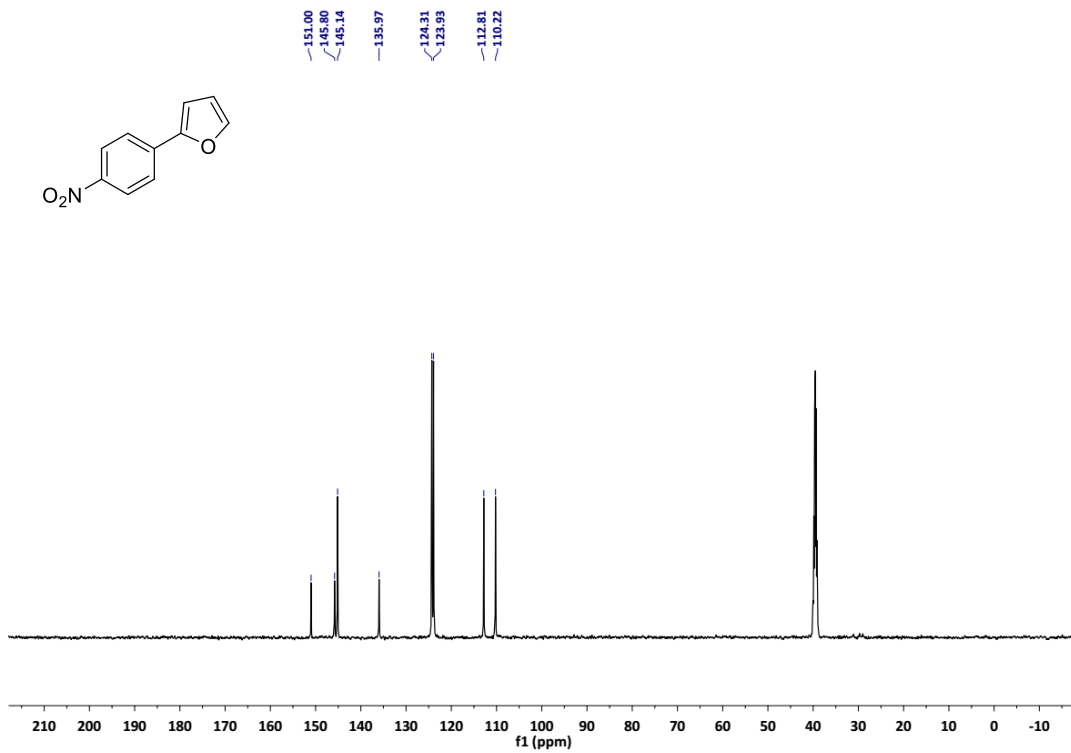
¹H NMR spectrum (500 MHz, CDCl₃) of **3d**



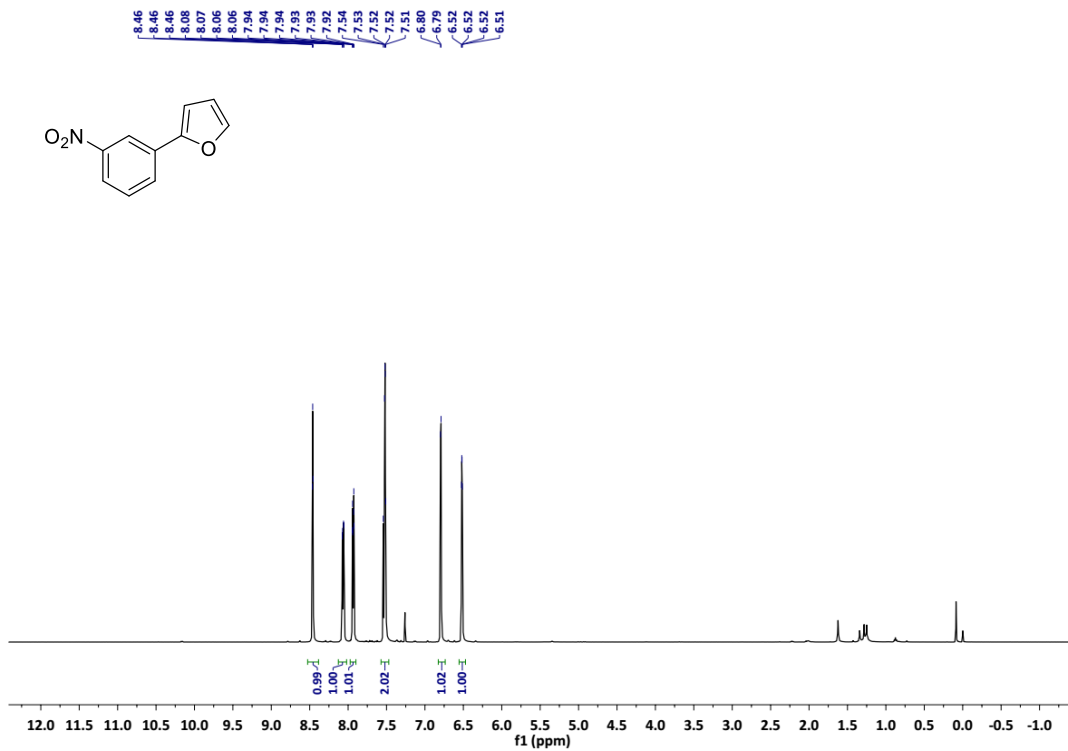
¹³C NMR spectrum (126 MHz, CDCl₃) of **3d**



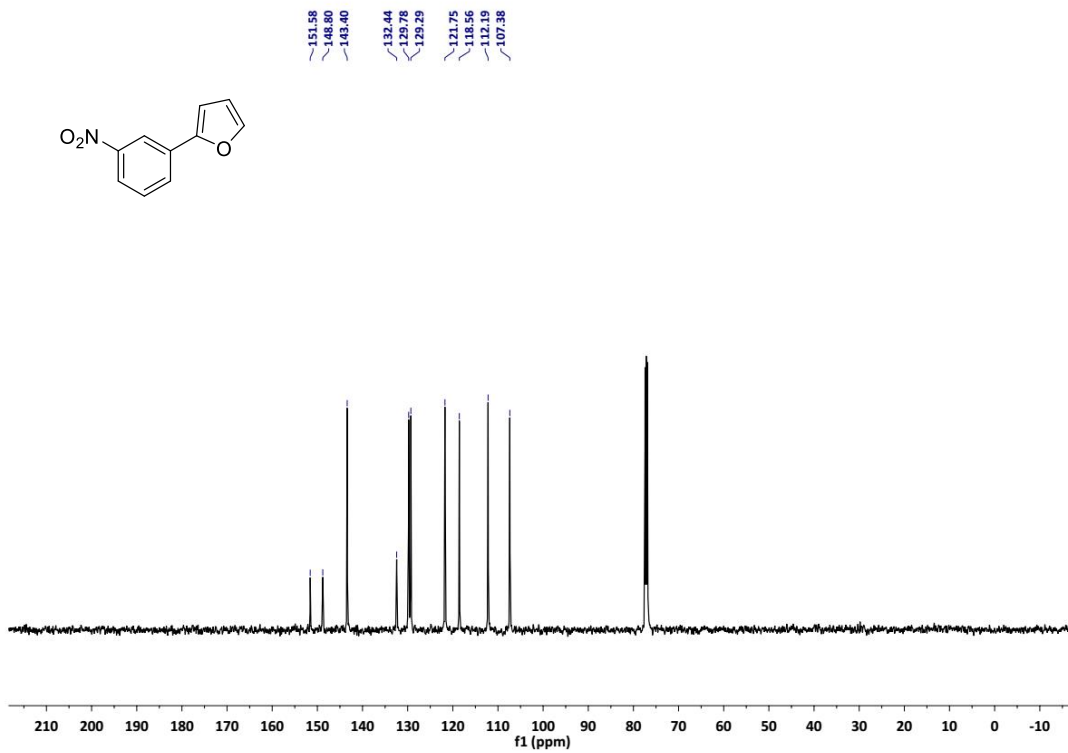
¹H NMR spectrum (500 MHz, DMSO-*d*₆) of **3e**



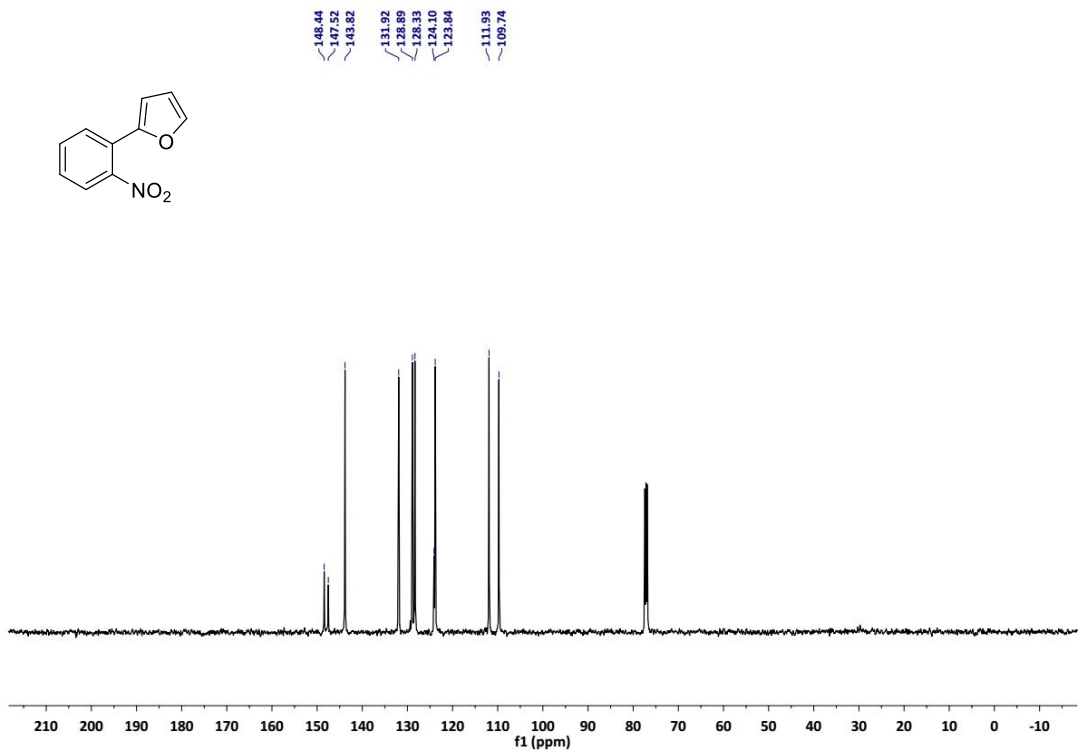
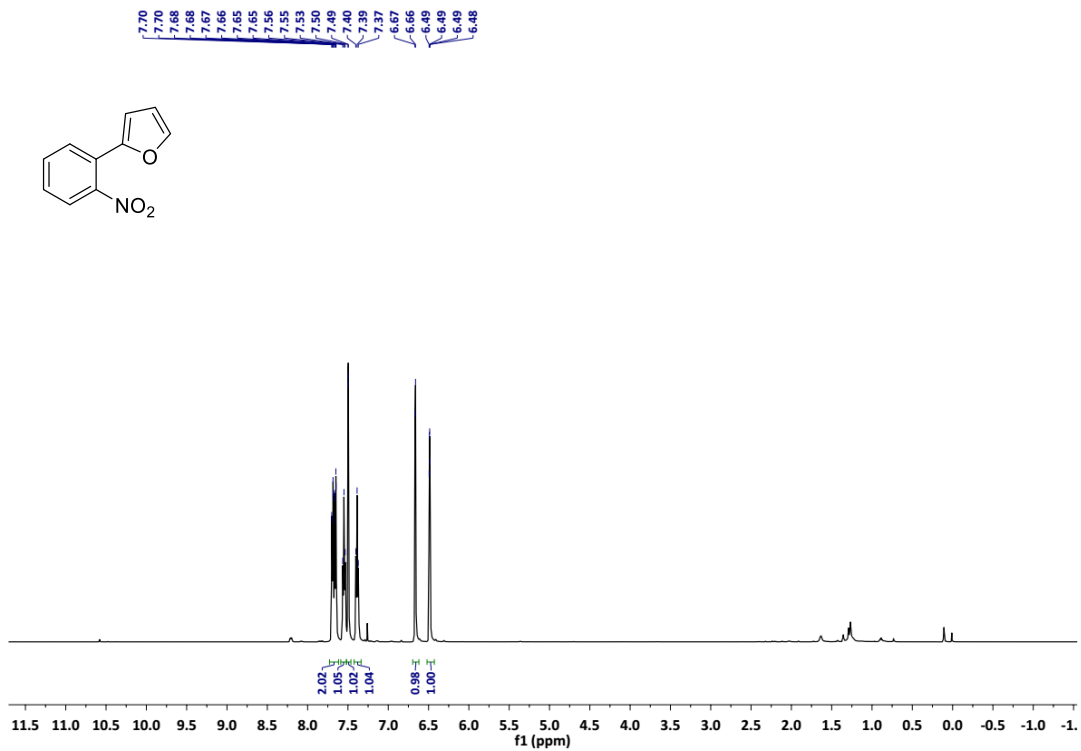
¹³C NMR spectrum (126 MHz, DMSO-*d*₆) of **3e**

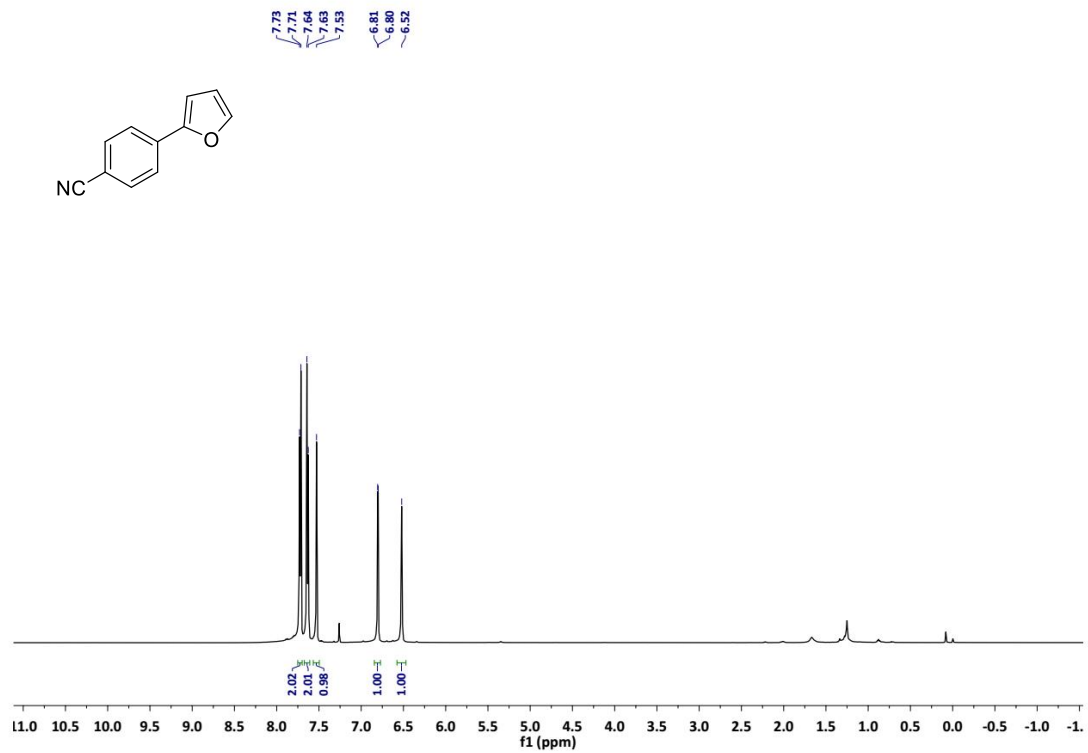


¹H NMR spectrum (500 MHz, CDCl₃) of 3f

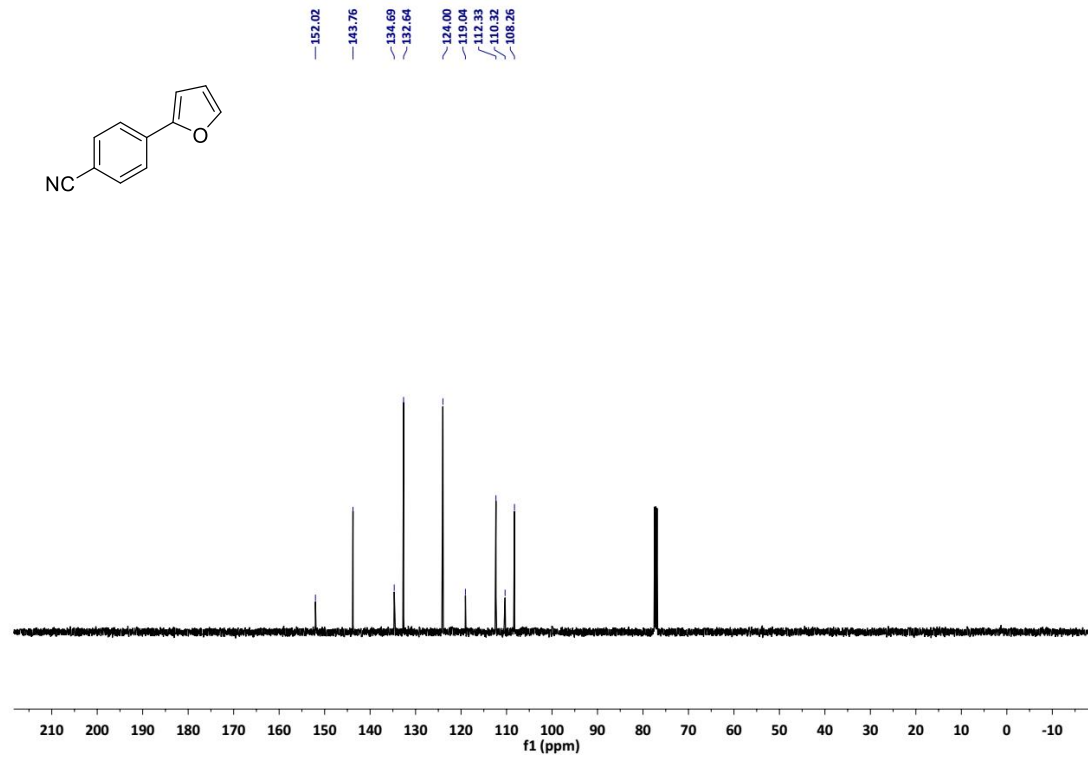


¹³C NMR spectrum (126 MHz, CDCl₃) of 3f

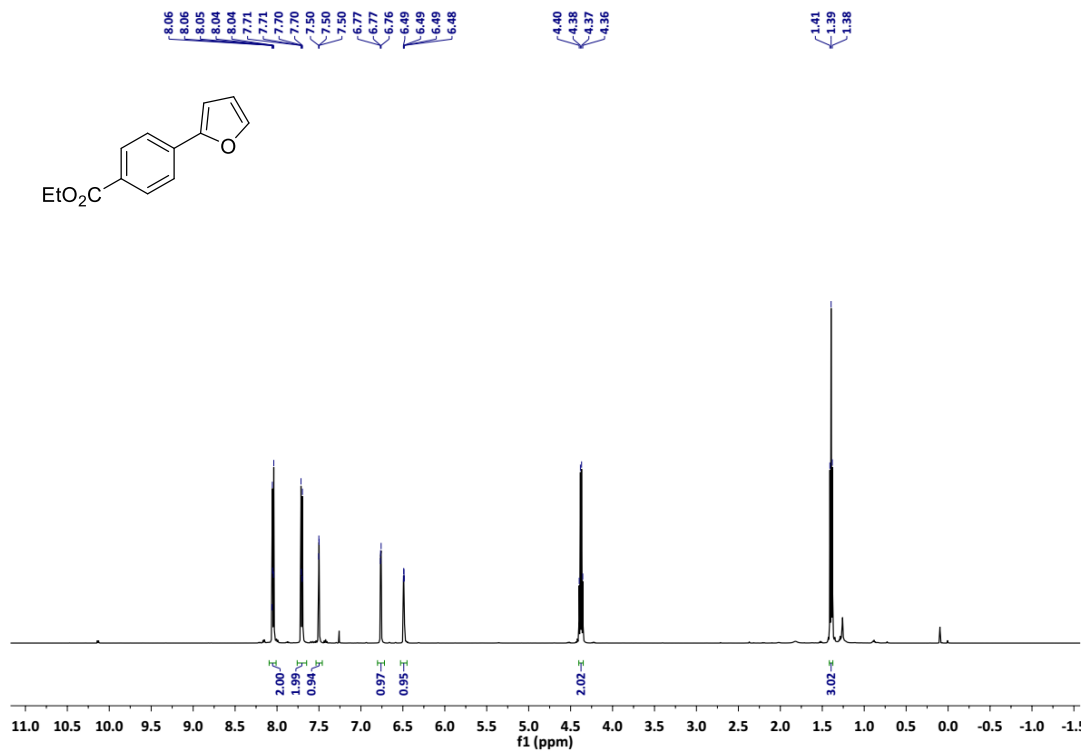




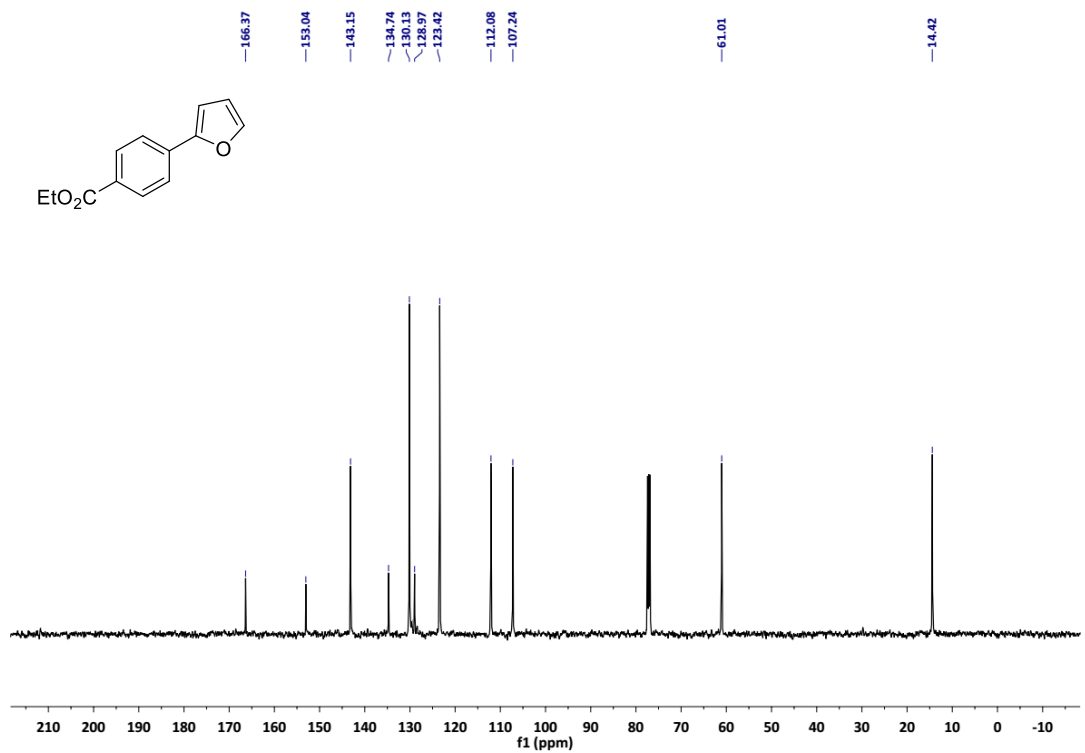
^1H NMR spectrum (500 MHz, CDCl_3) of **3h**



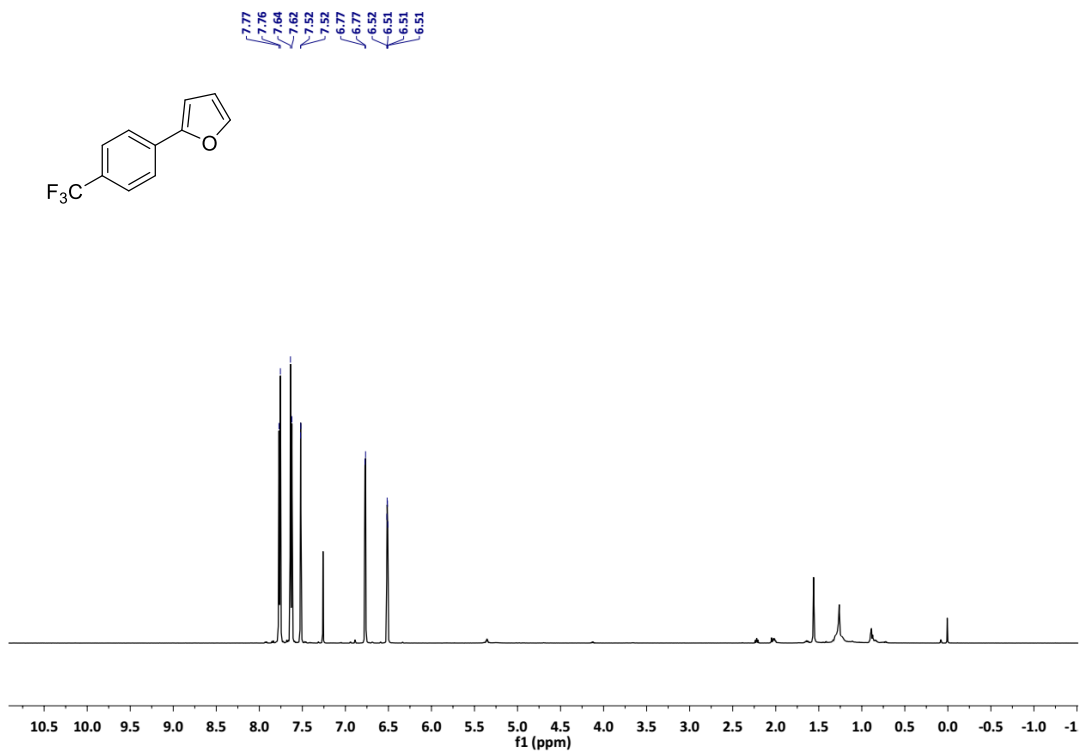
^{13}C NMR spectrum (126 MHz, CDCl_3) of **3h**



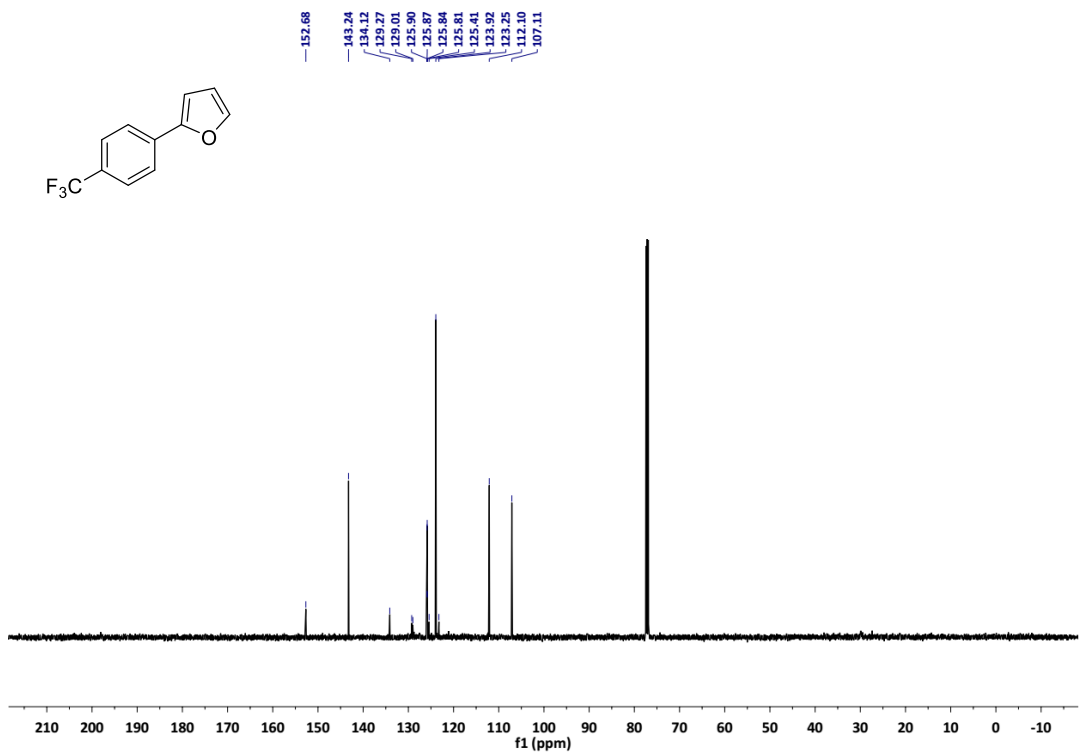
^1H NMR spectrum (500 MHz, CDCl_3) of **3i**



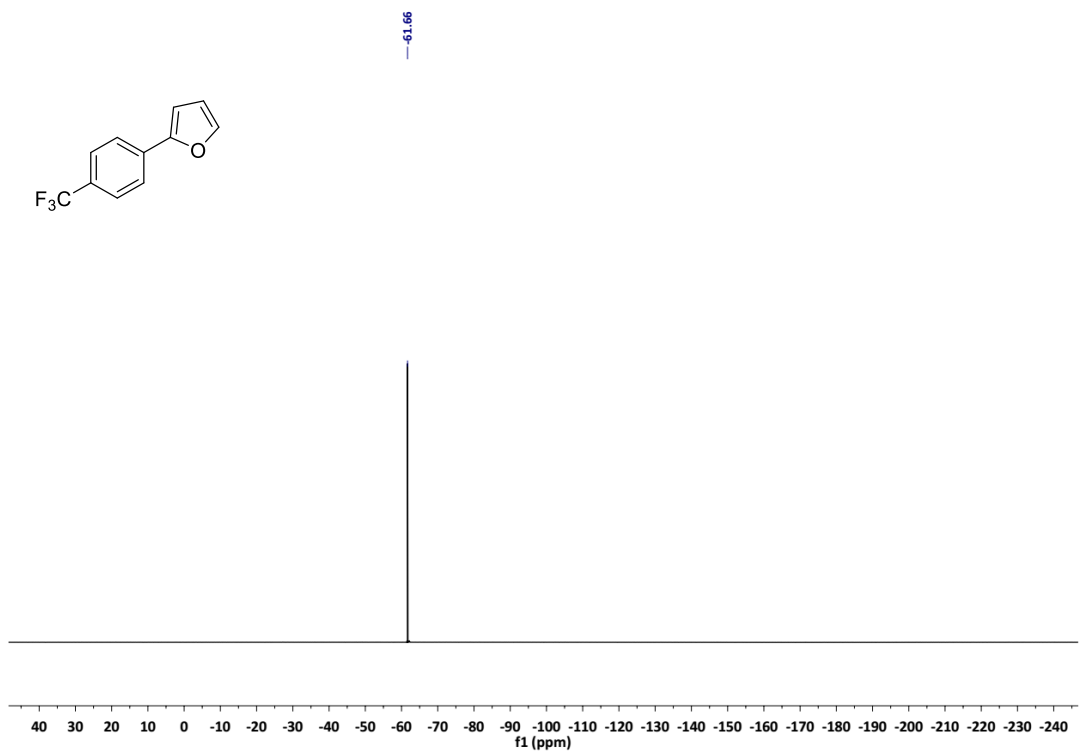
^{13}C NMR spectrum (126 MHz, CDCl_3) of **3i**



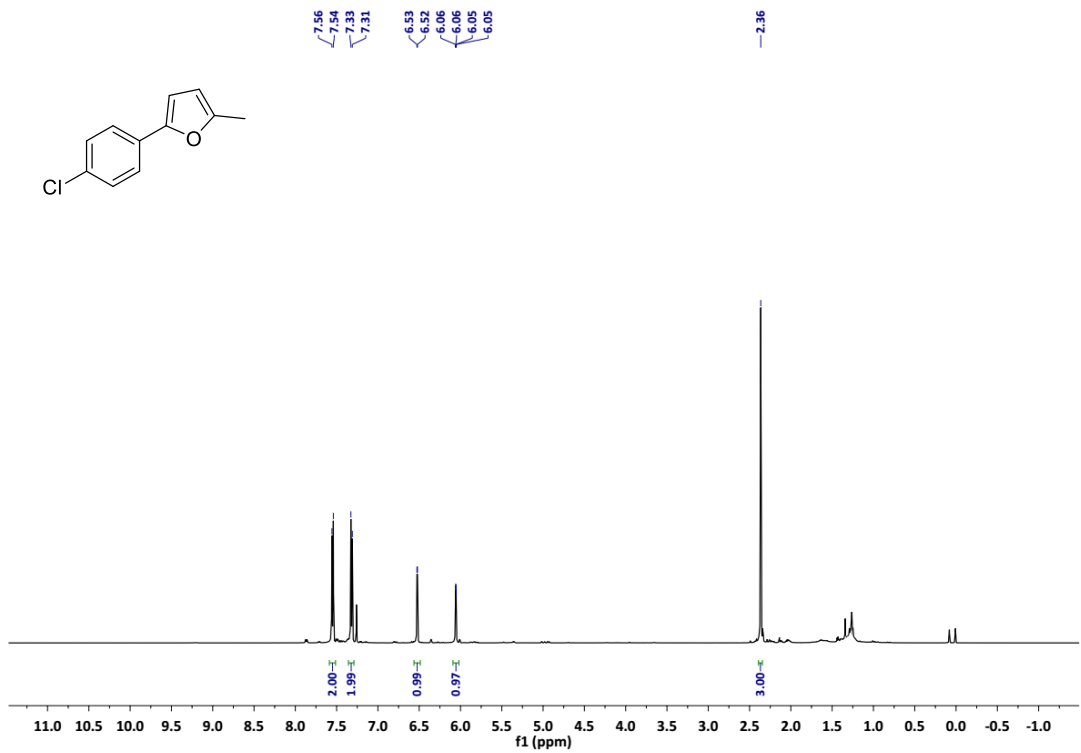
^1H NMR spectrum (500 MHz, CDCl_3) of **3j**



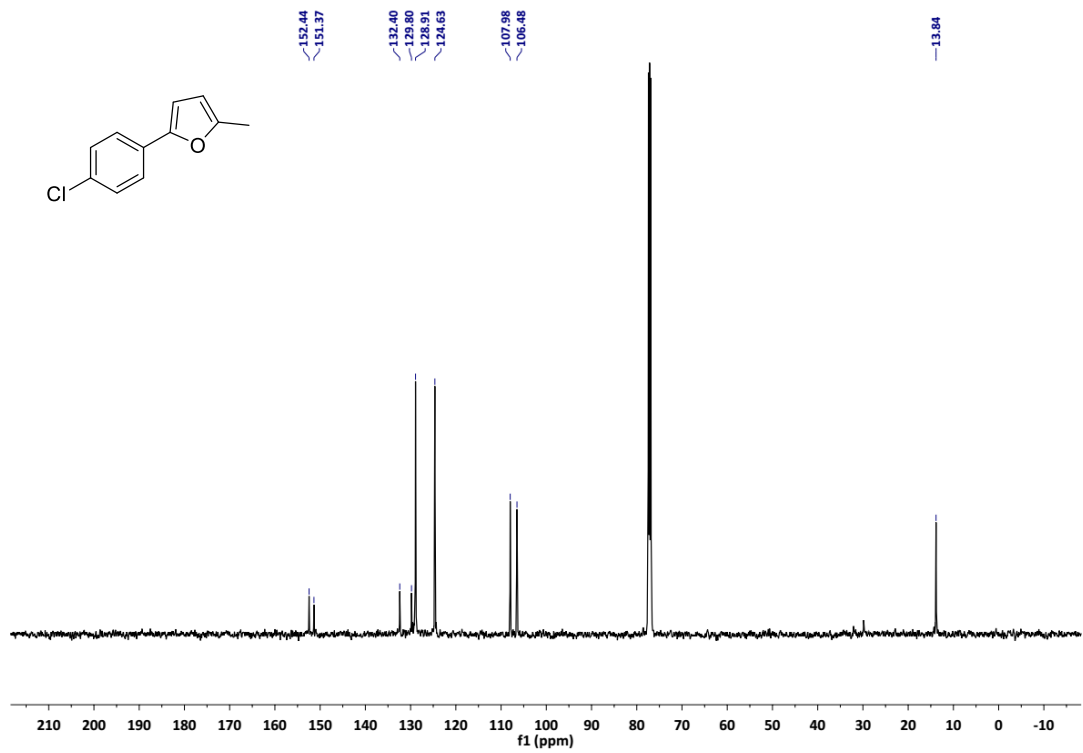
^{13}C NMR spectrum (126 MHz, CDCl_3) of **3j**



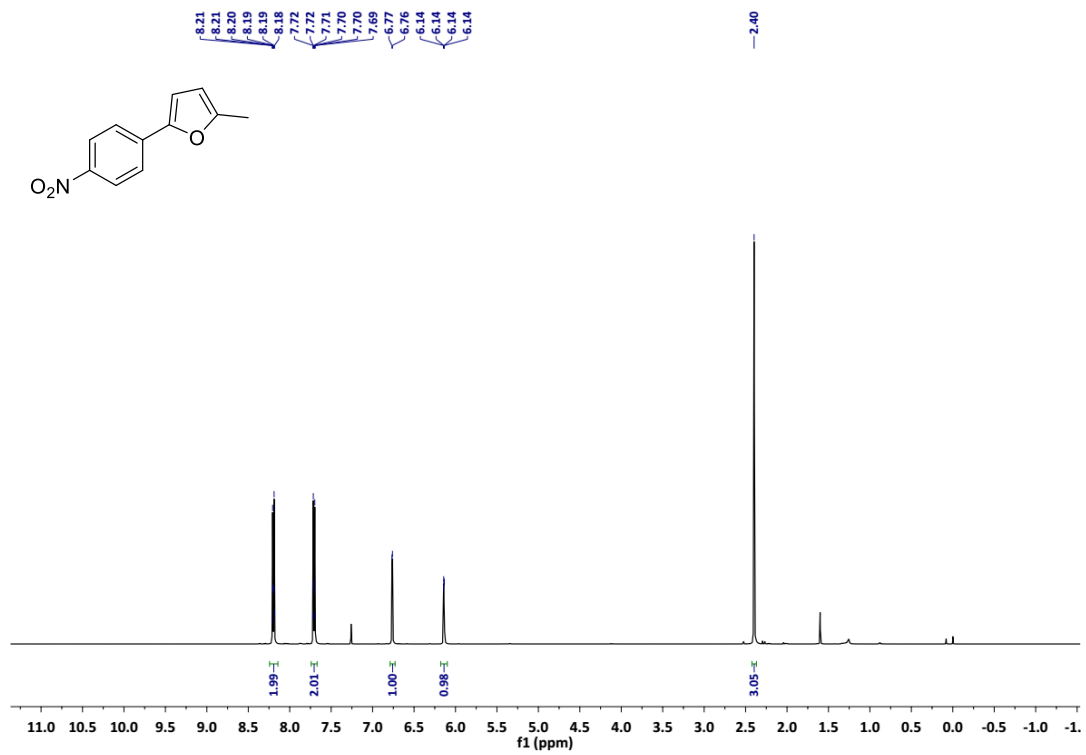
^{19}F NMR spectrum (470 MHz, CDCl_3) of **3j**



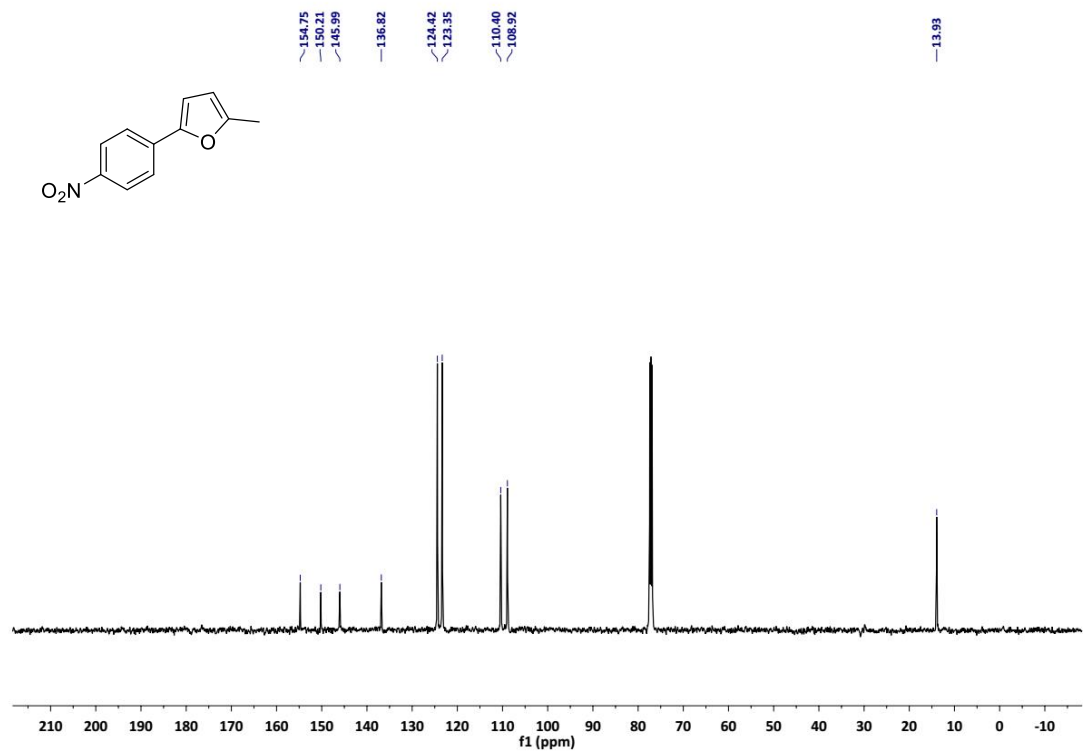
^1H NMR spectrum (500 MHz, CDCl_3) of **3k**



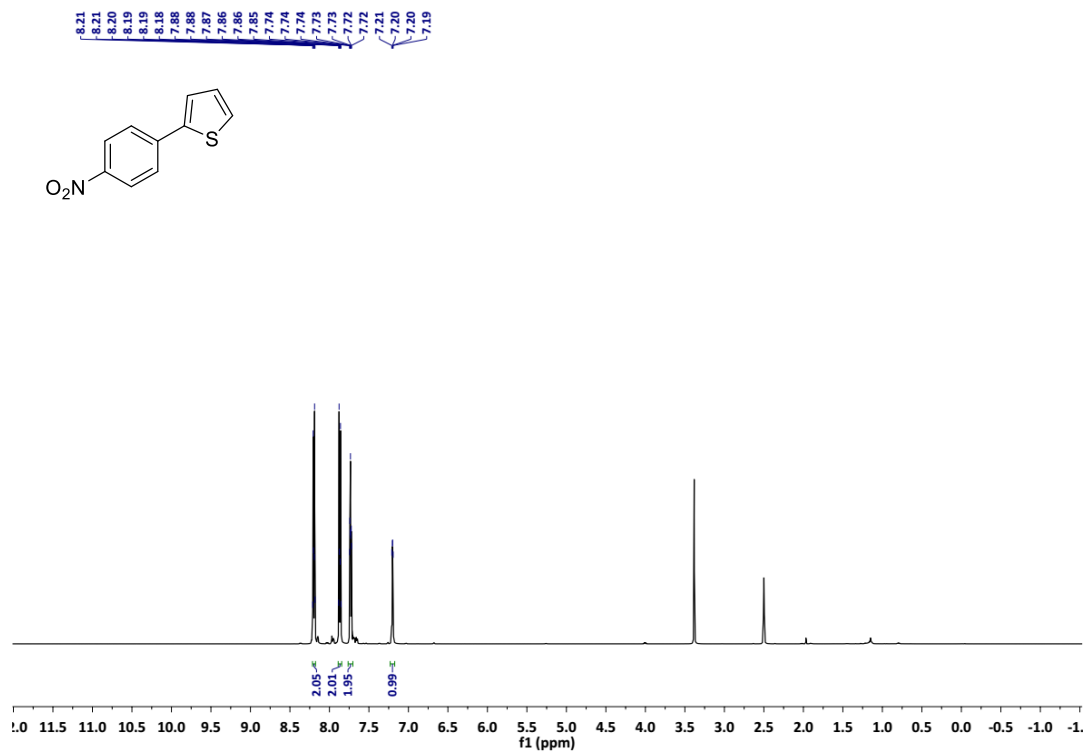
^{13}C NMR spectrum (126 MHz, CDCl_3) of **3k**



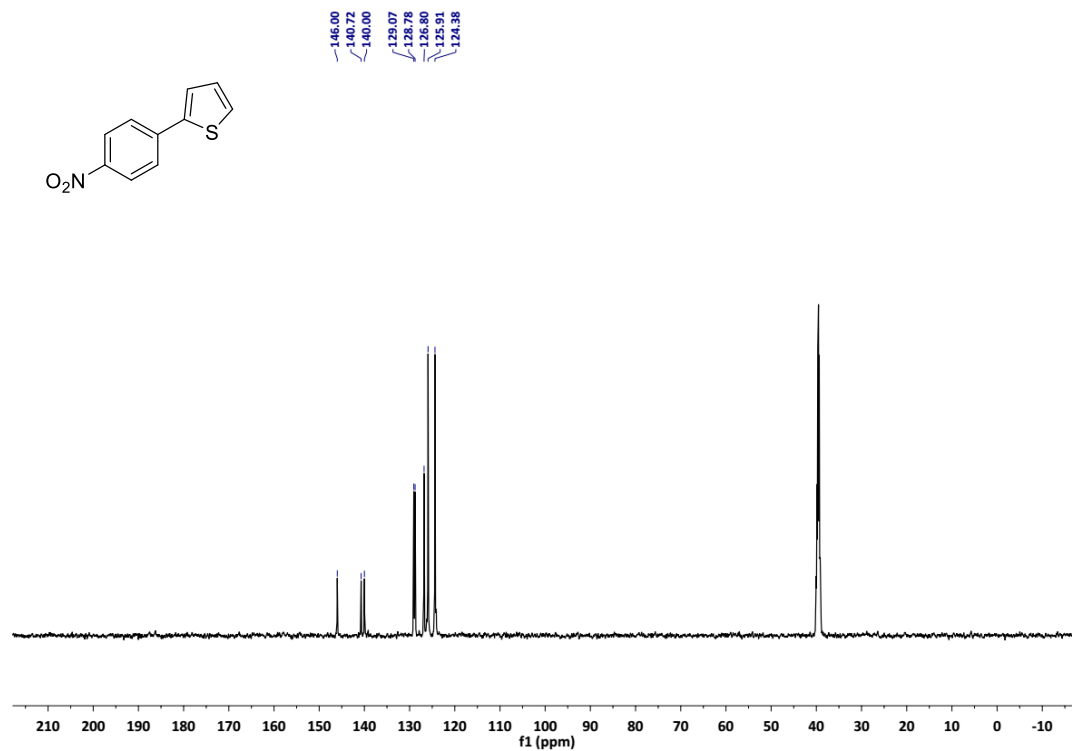
^1H NMR spectrum (500 MHz, CDCl_3) of **3l**



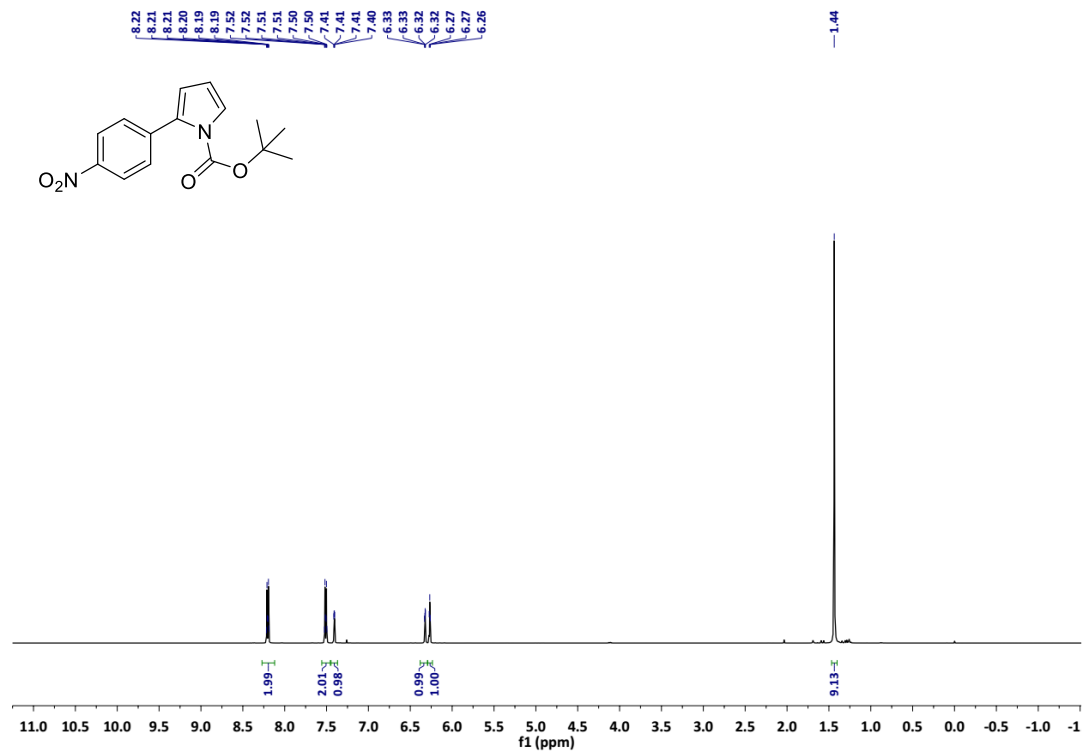
^{13}C NMR spectrum (126 MHz, CDCl_3) of **3l**



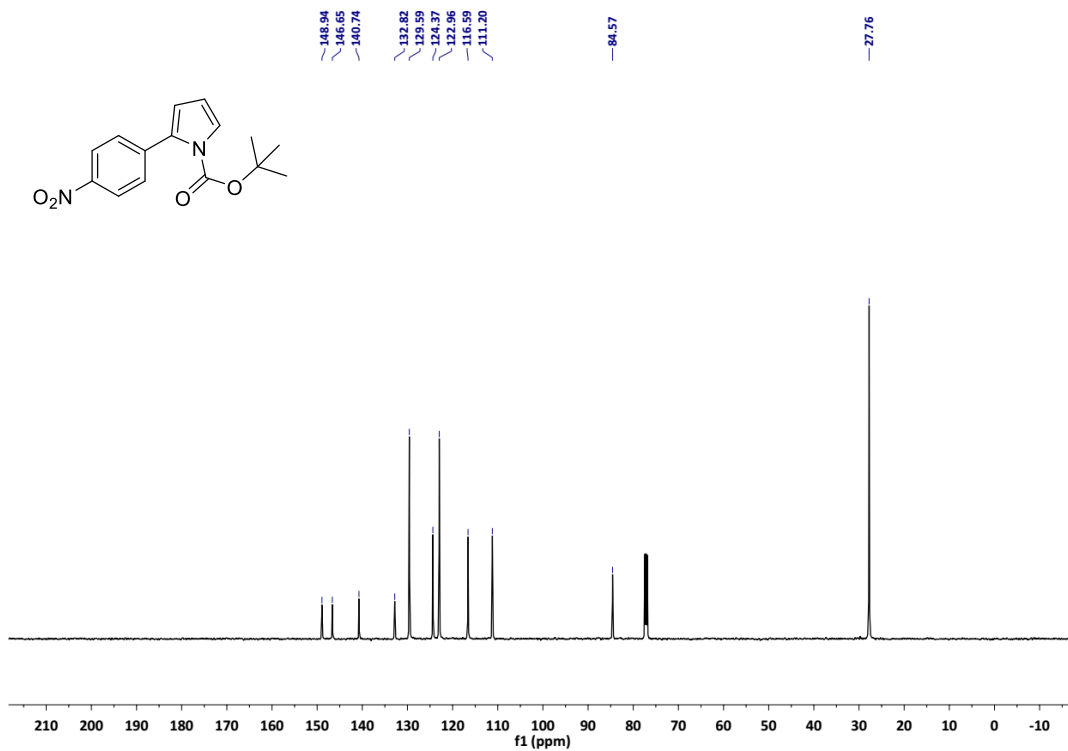
^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of **3m**



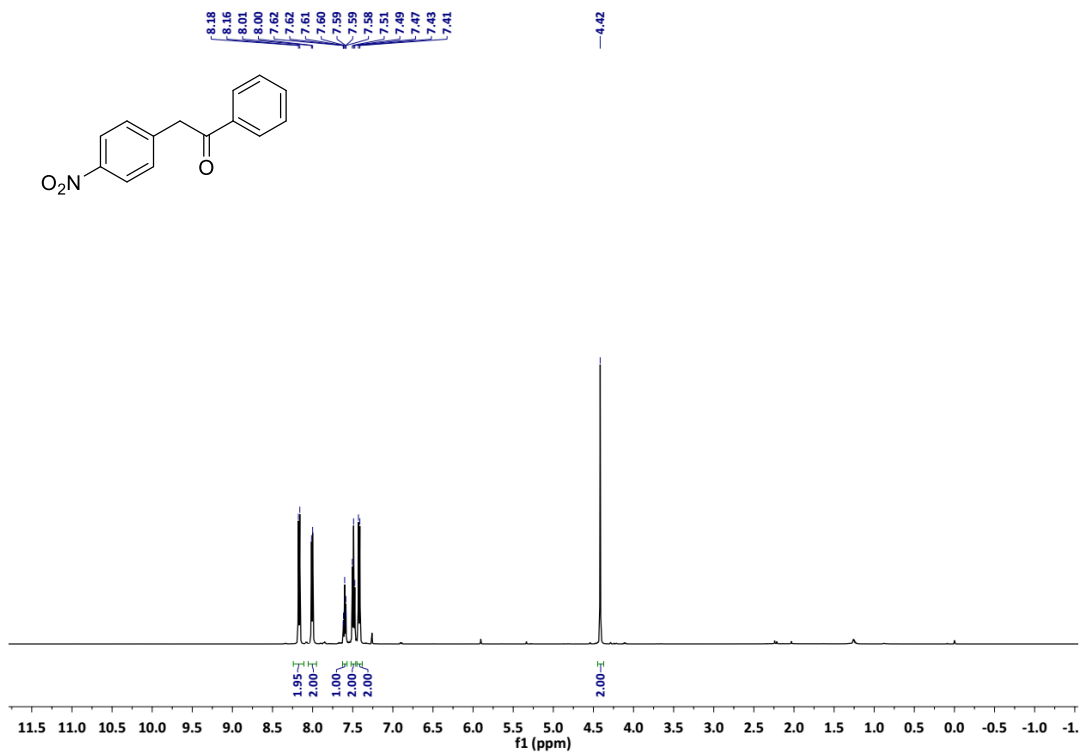
^{13}C NMR spectrum (126 MHz, $\text{DMSO-}d_6$) of **3m**



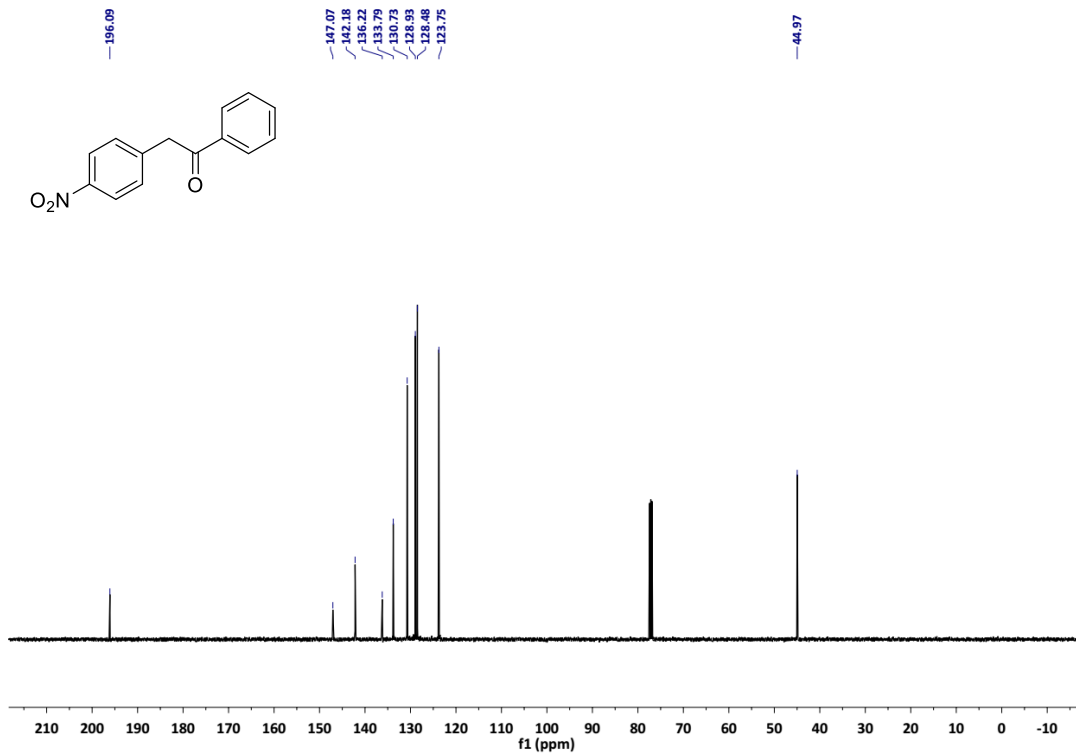
^1H NMR spectrum (500 MHz, CDCl_3) of **3n**



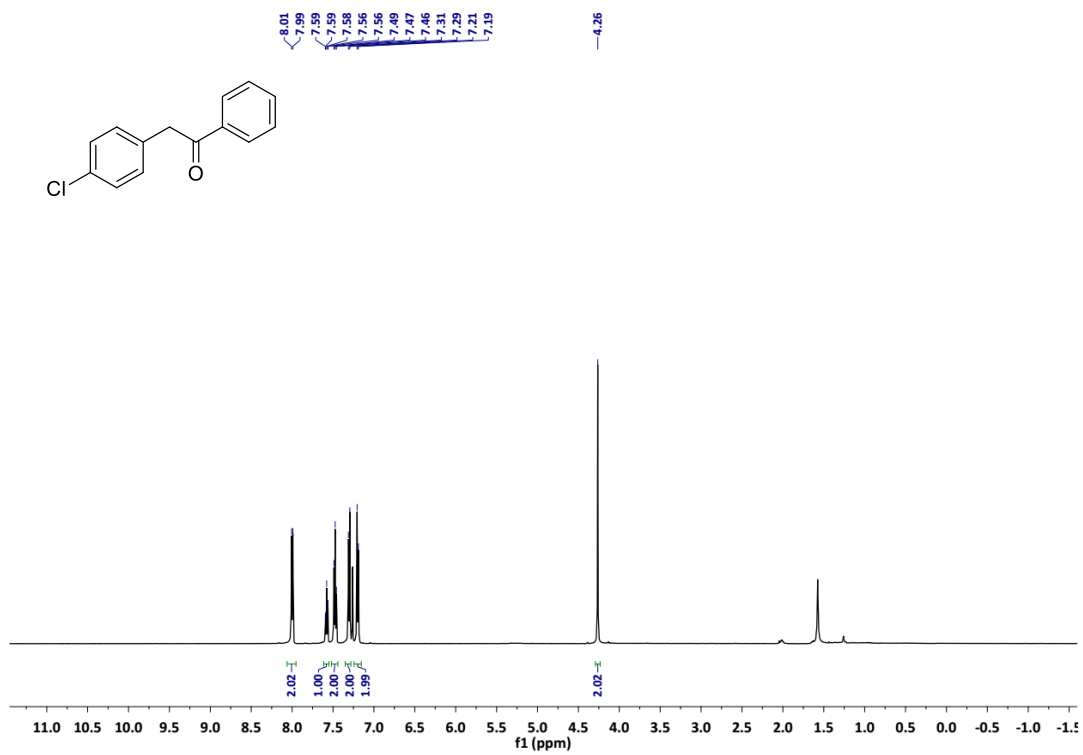
¹³C NMR spectrum (126 MHz, CDCl₃) of **3n**



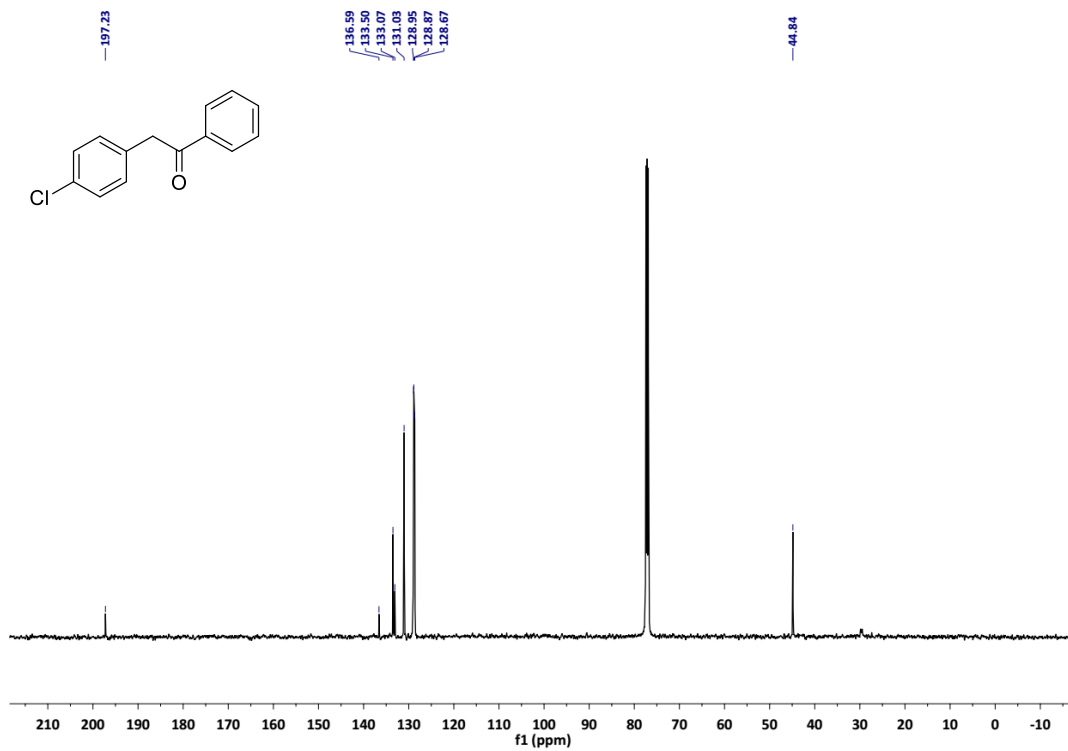
¹H NMR spectrum (500 MHz, CDCl₃) of **5a**



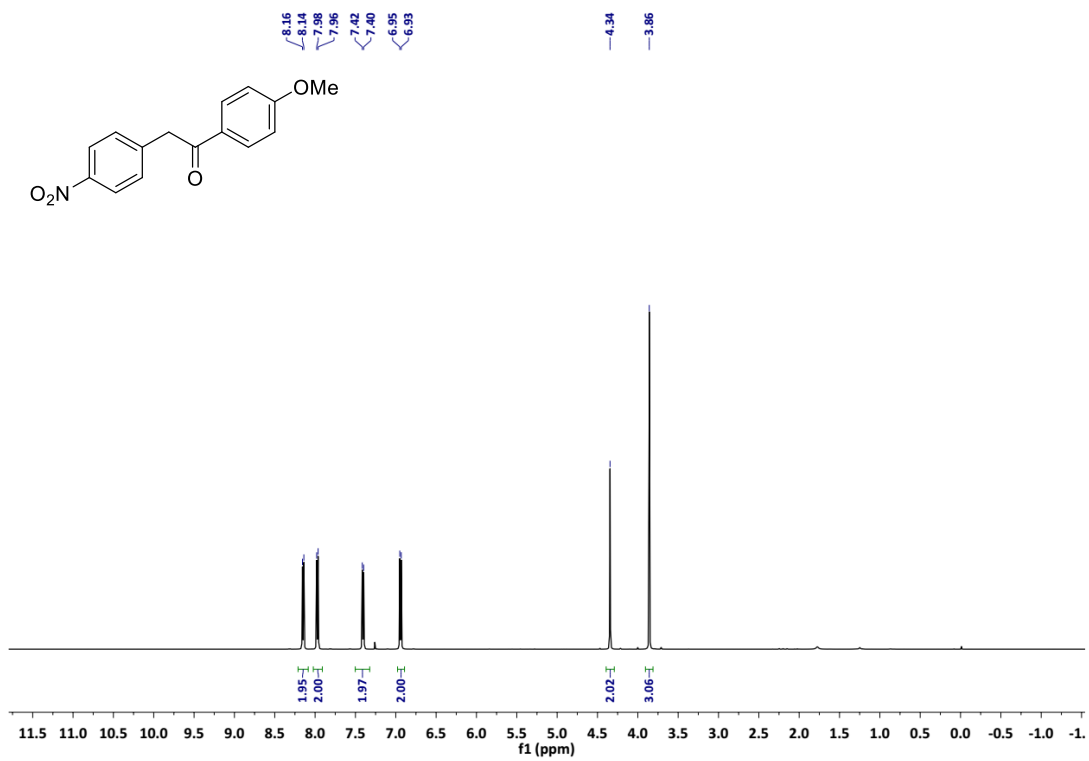
^{13}C NMR spectrum (126 MHz, CDCl_3) of **5a**



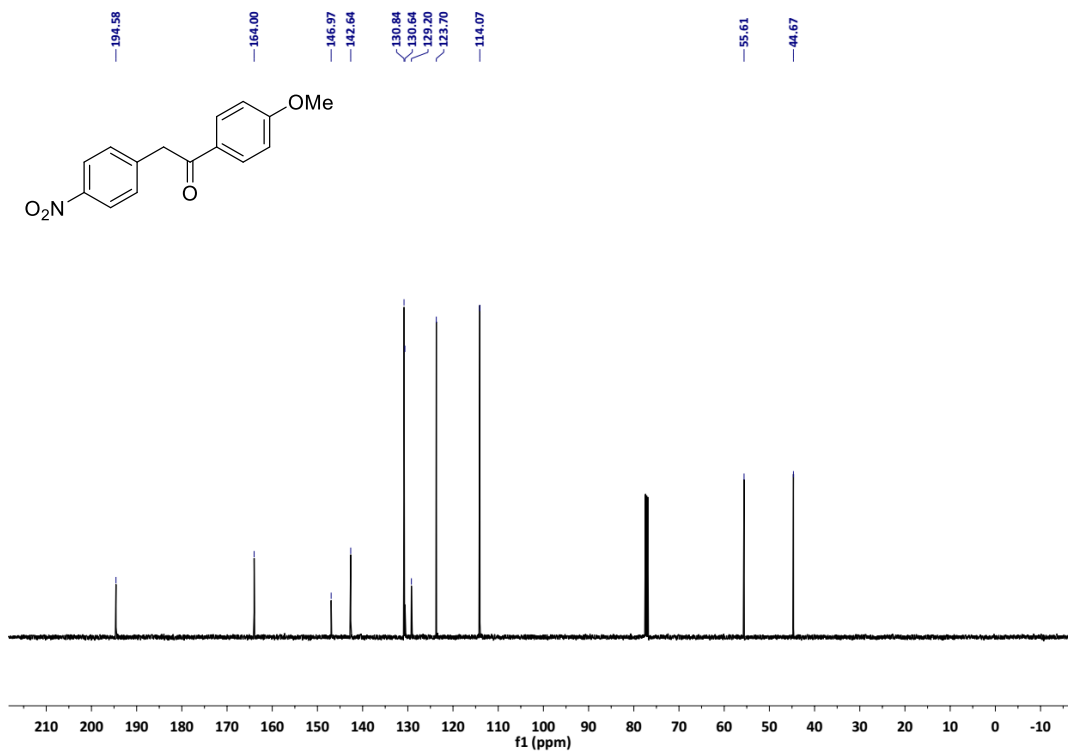
^1H NMR spectrum (500 MHz, CDCl_3) of **5b**



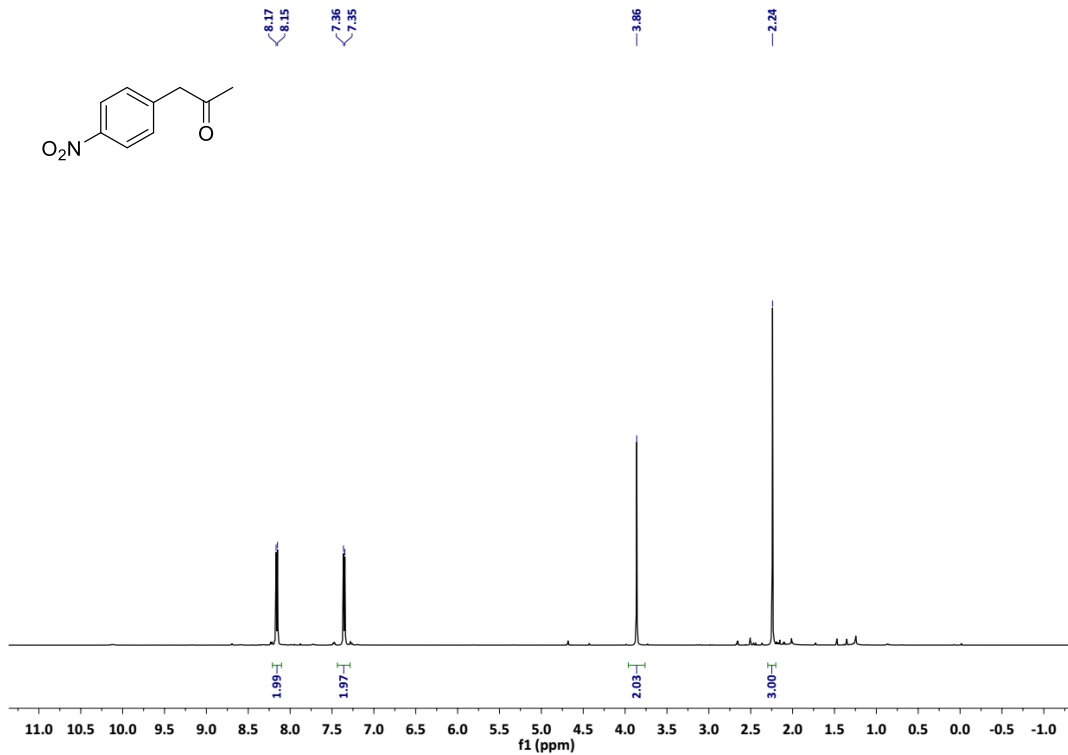
^{13}C NMR spectrum (126 MHz, CDCl_3) of **5b**



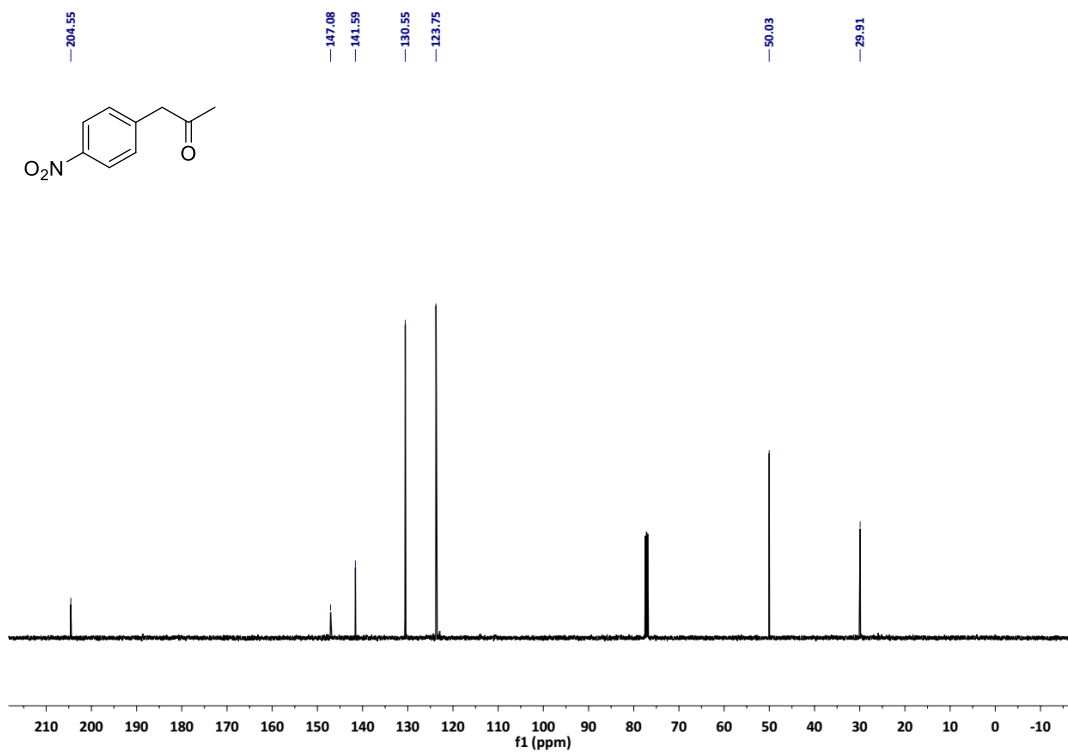
^1H NMR spectrum (500 MHz, CDCl_3) of **5c**



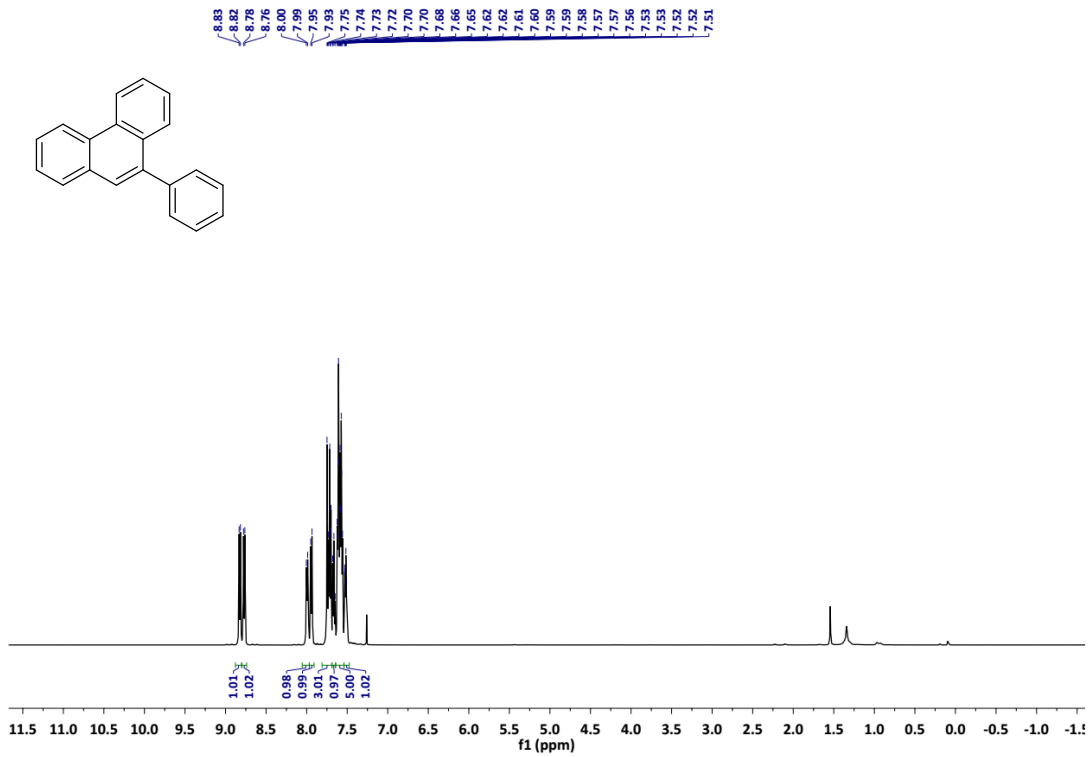
^{13}C NMR spectrum (126 MHz, CDCl_3) of **5c**



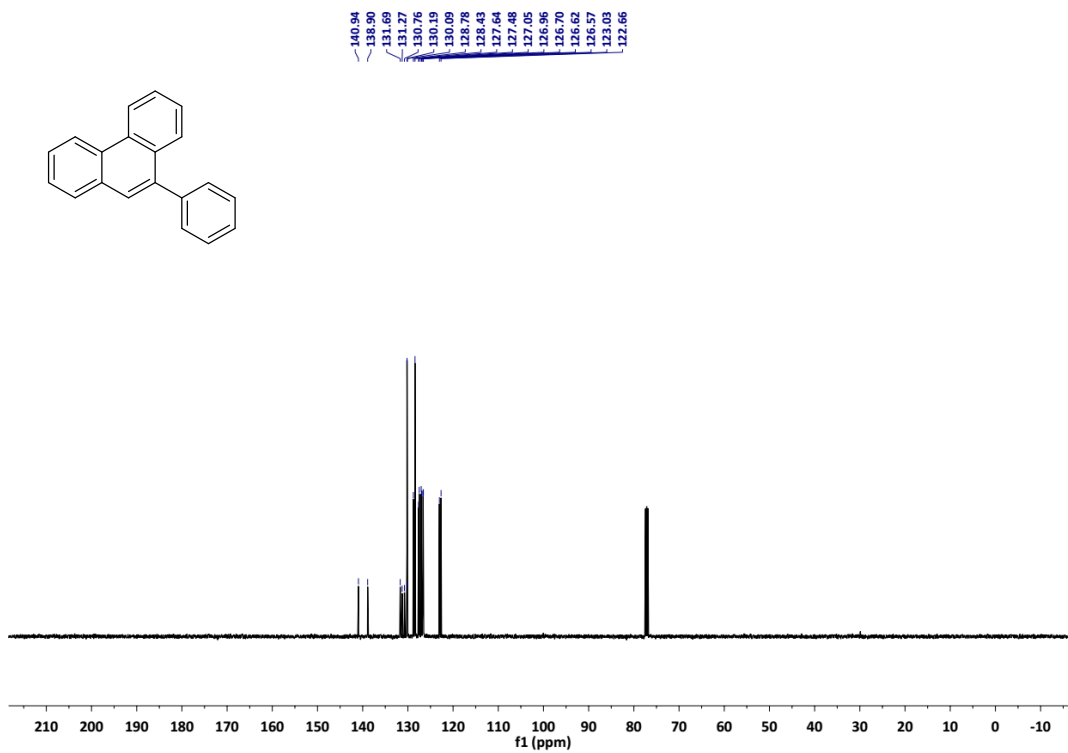
^1H NMR spectrum (500 MHz, CDCl_3) of **5d**



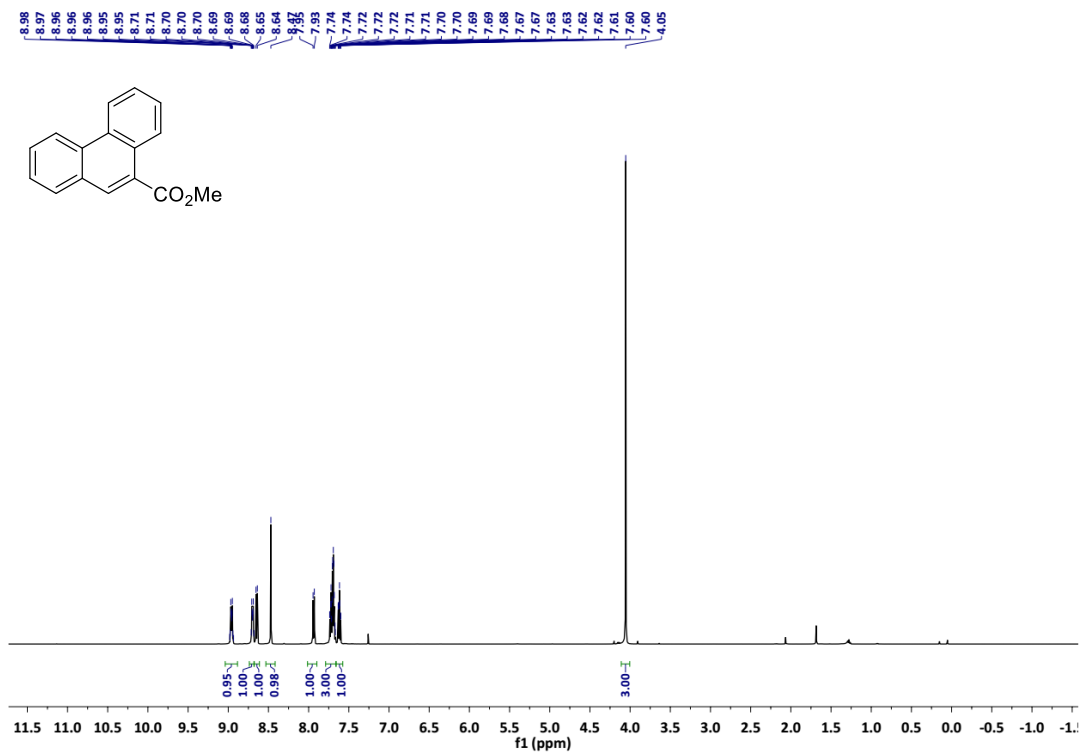
¹³C NMR spectrum (126 MHz, CDCl₃) of **5d**



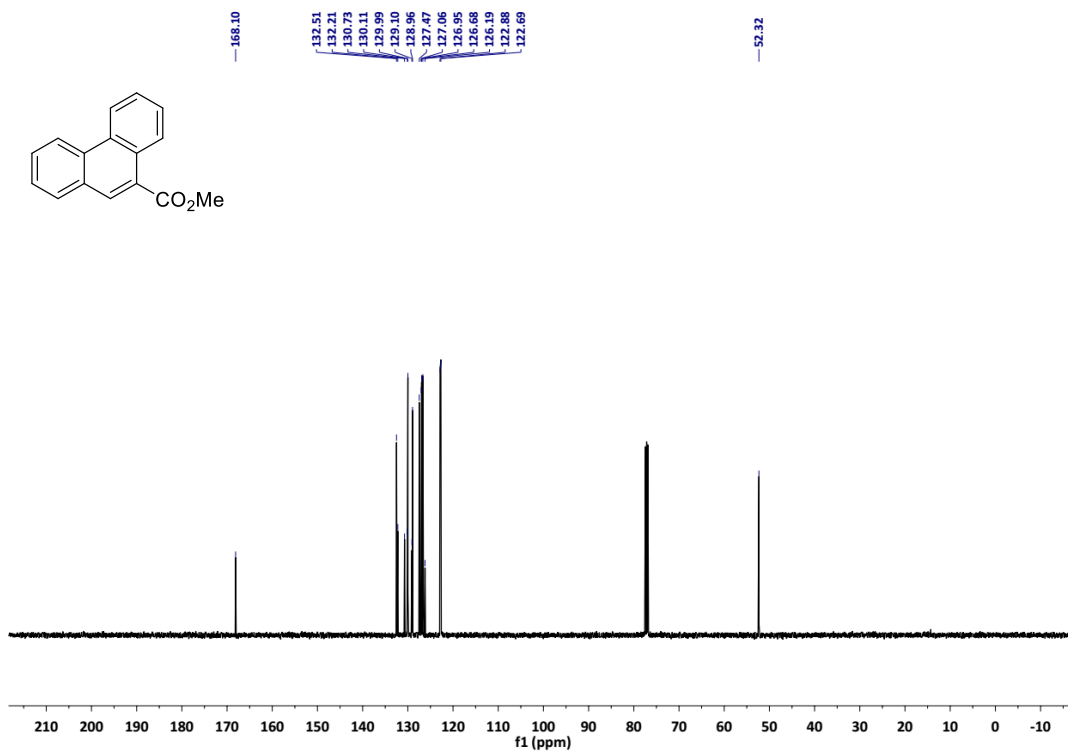
¹H NMR spectrum (500 MHz, CDCl₃) of **7a**



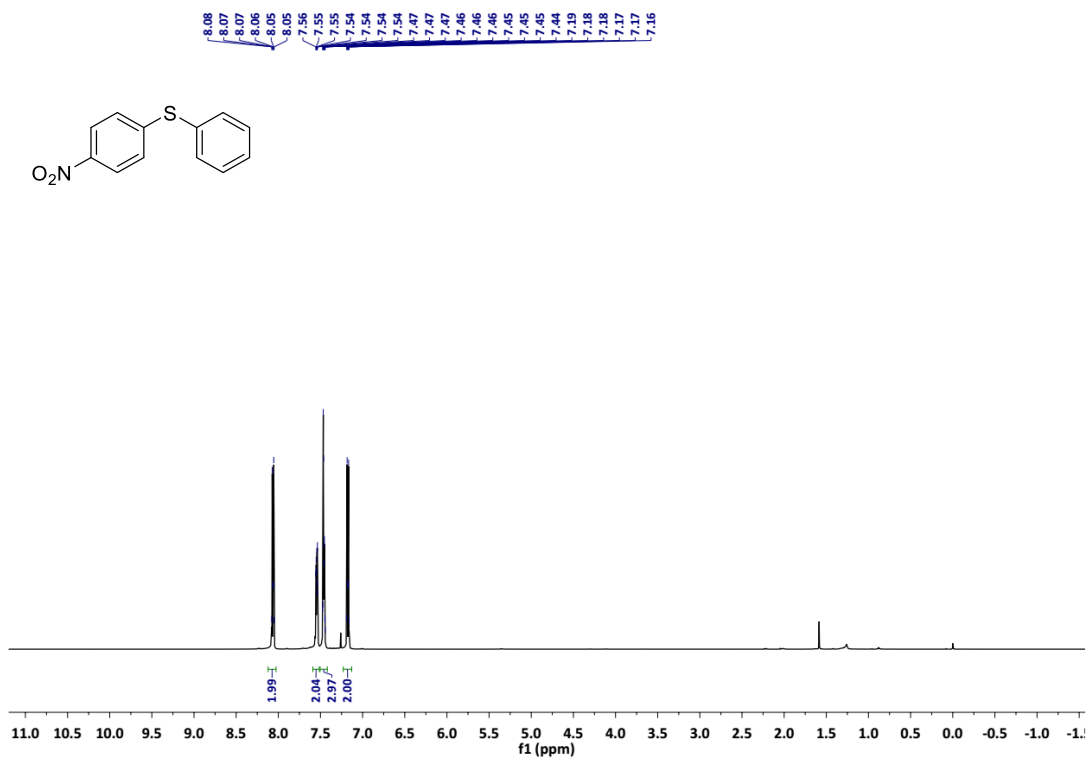
^{13}C NMR spectrum (126 MHz, CDCl_3) of **7a**



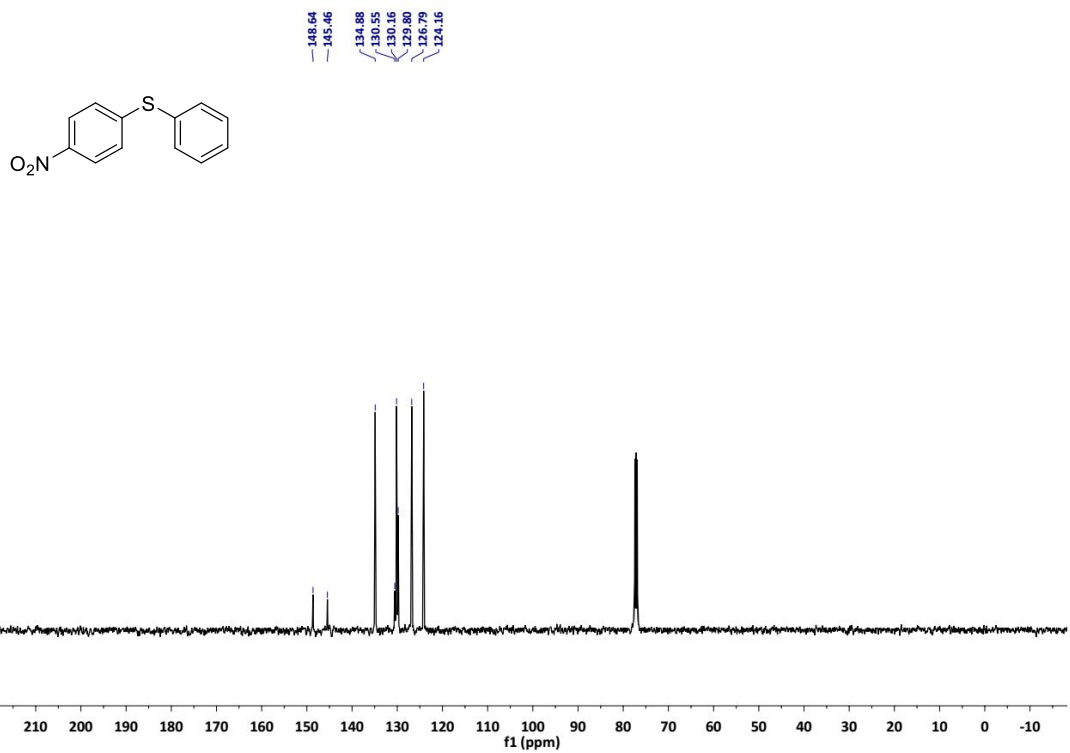
^1H NMR spectrum (500 MHz, CDCl_3) of **7b**



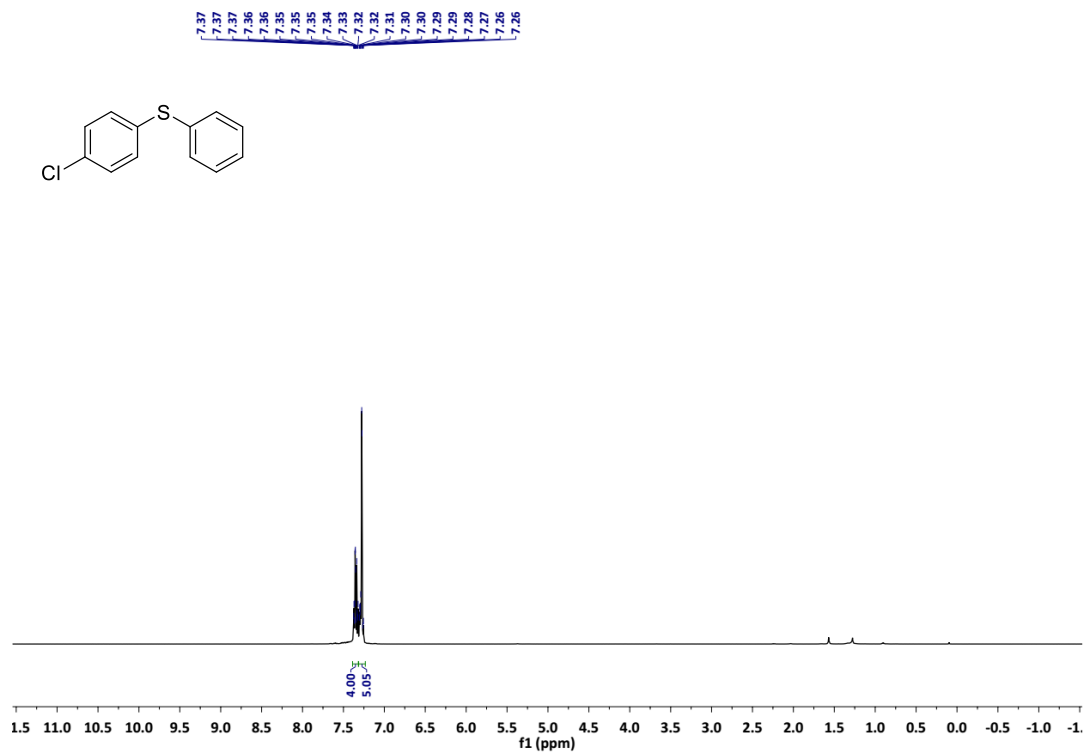
¹³C NMR spectrum (126 MHz, CDCl₃) of **7b**



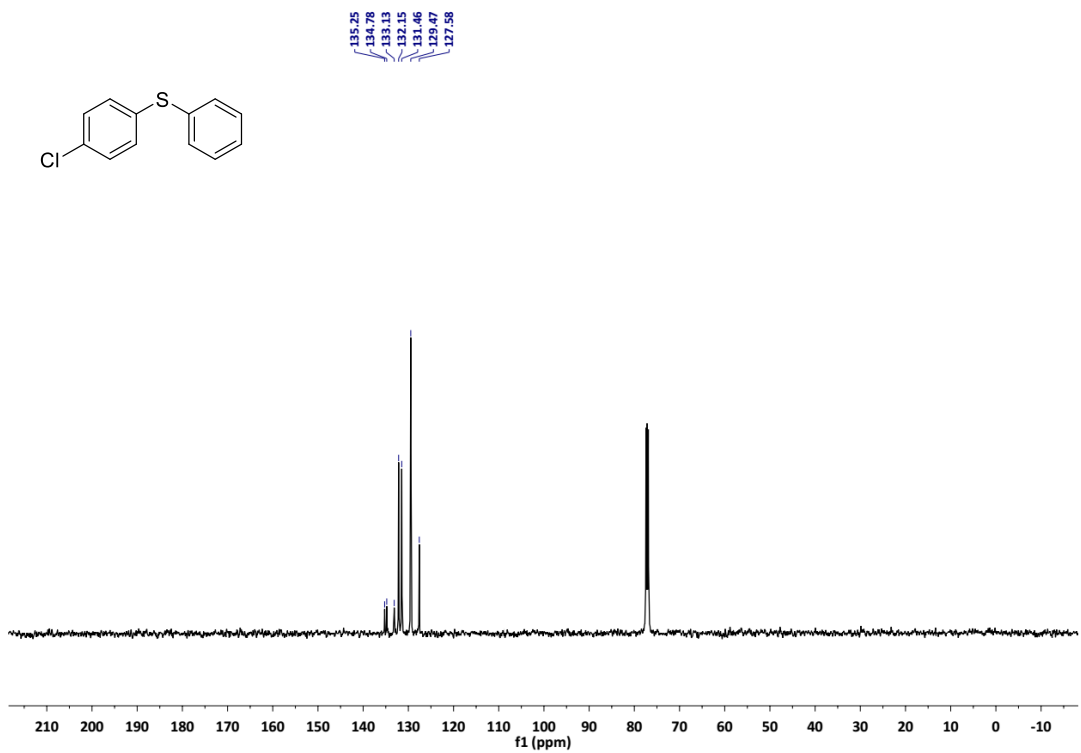
¹H NMR spectrum (500 MHz, CDCl₃) of **9a**



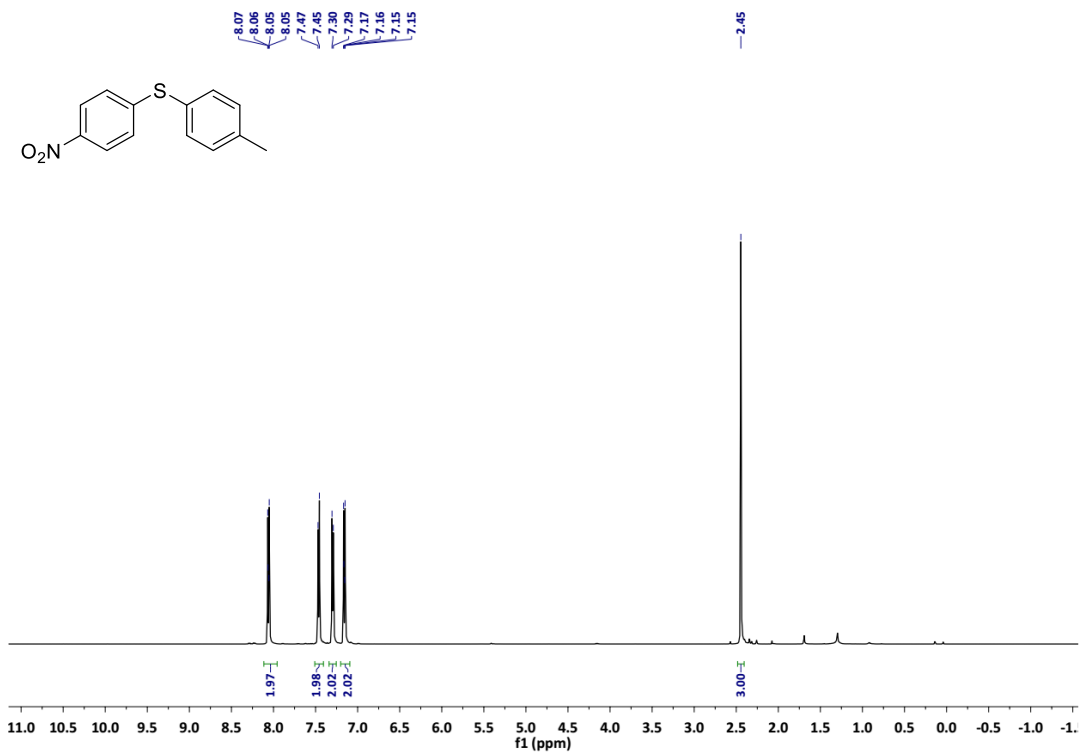
^{13}C NMR spectrum (126 MHz, CDCl_3) of **9a**



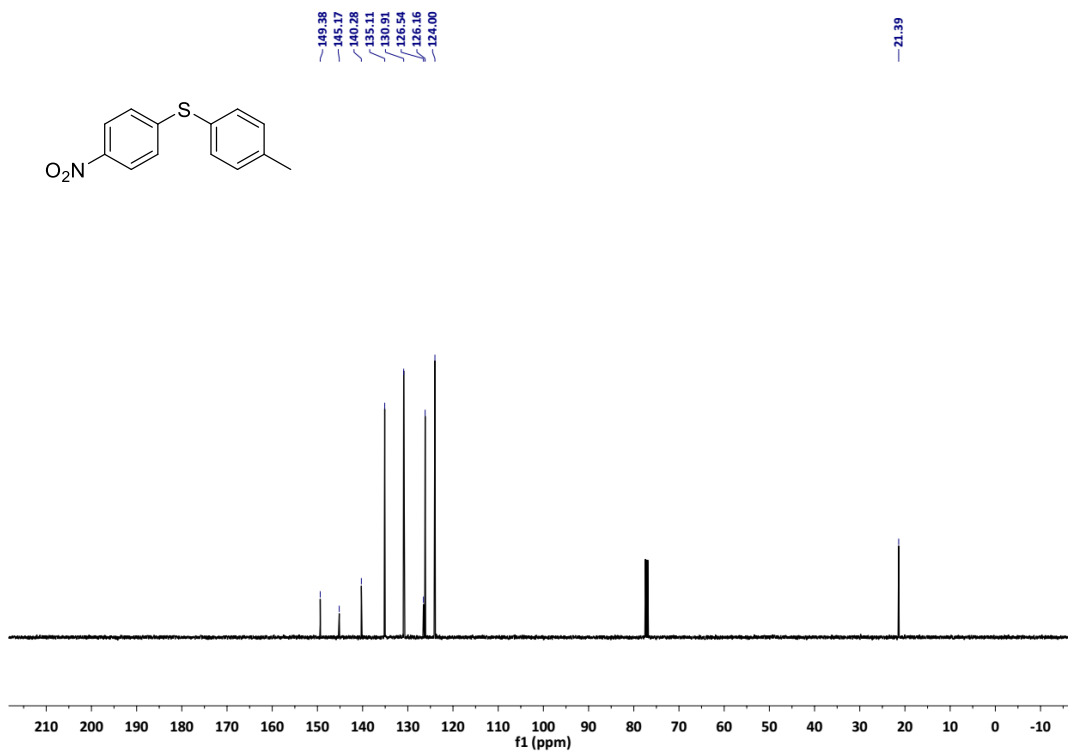
^1H NMR spectrum (500 MHz, CDCl_3) of **9b**



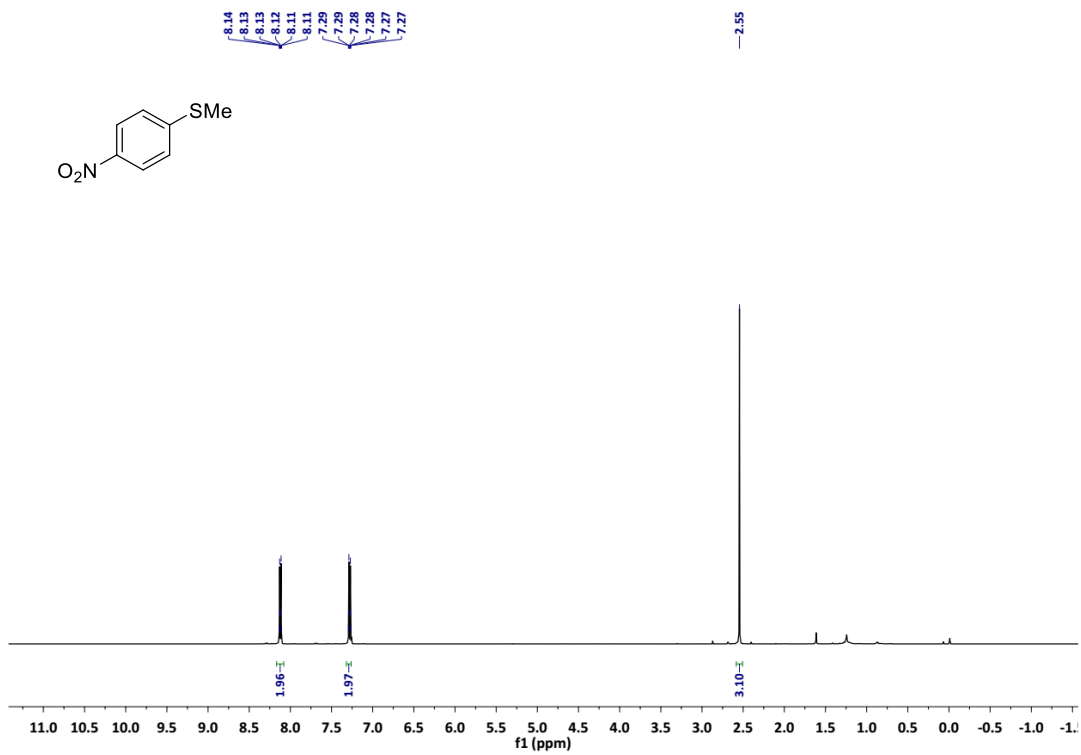
^{13}C NMR spectrum (126 MHz, CDCl_3) of **9b**



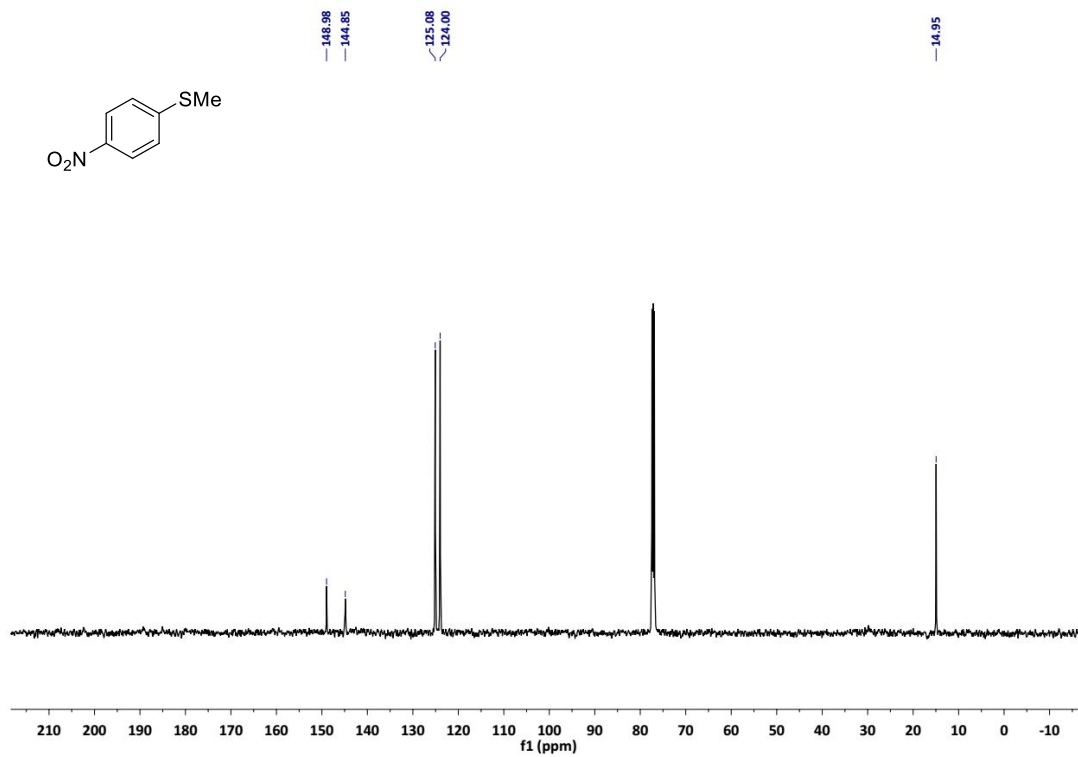
^1H NMR spectrum (500 MHz, CDCl_3) of **9c**



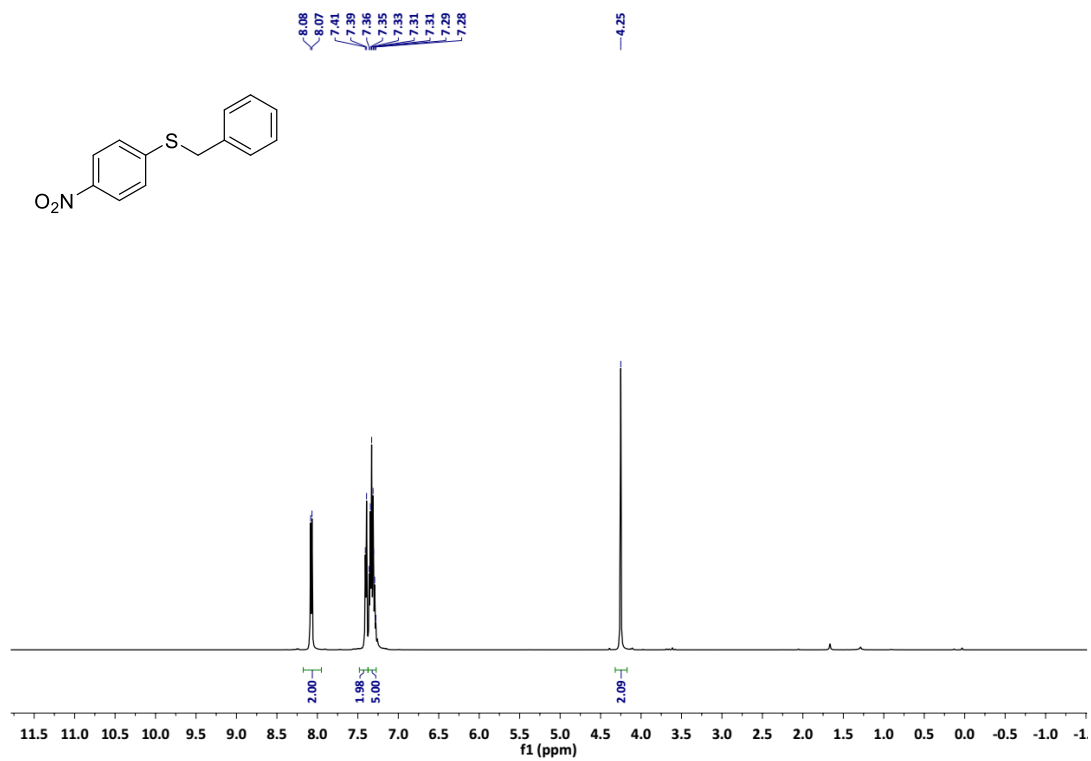
^{13}C NMR spectrum (126 MHz, CDCl_3) of **9c**



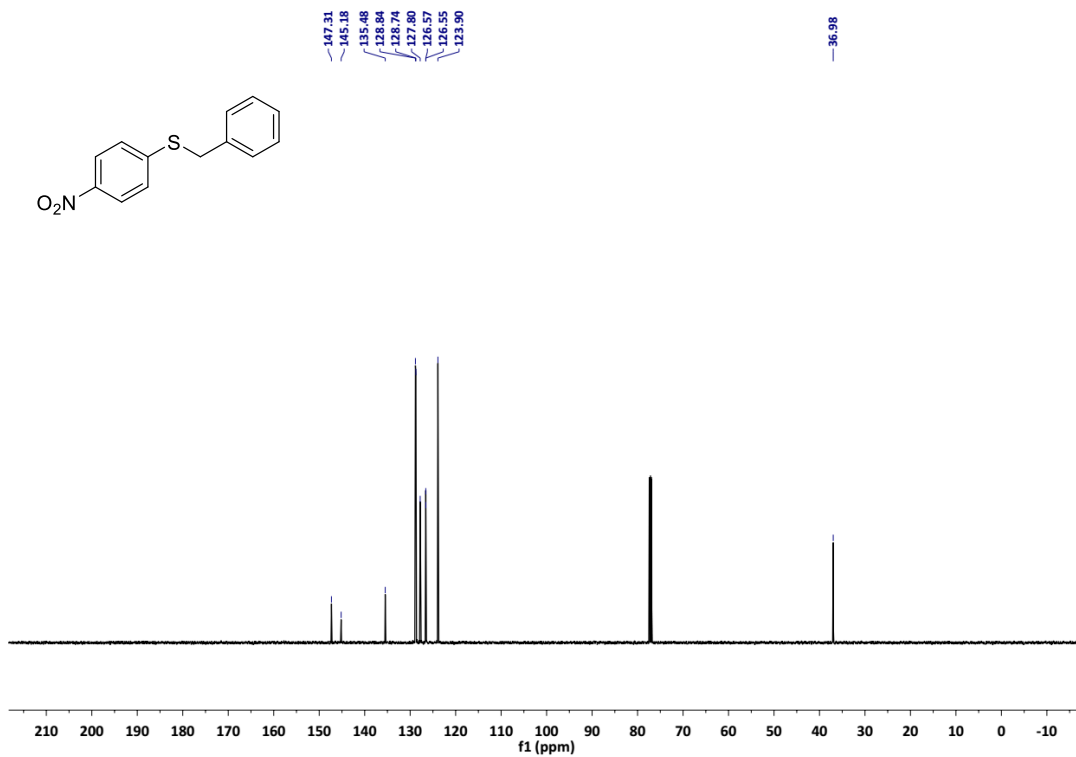
^1H NMR spectrum (500 MHz, CDCl_3) of **9d**



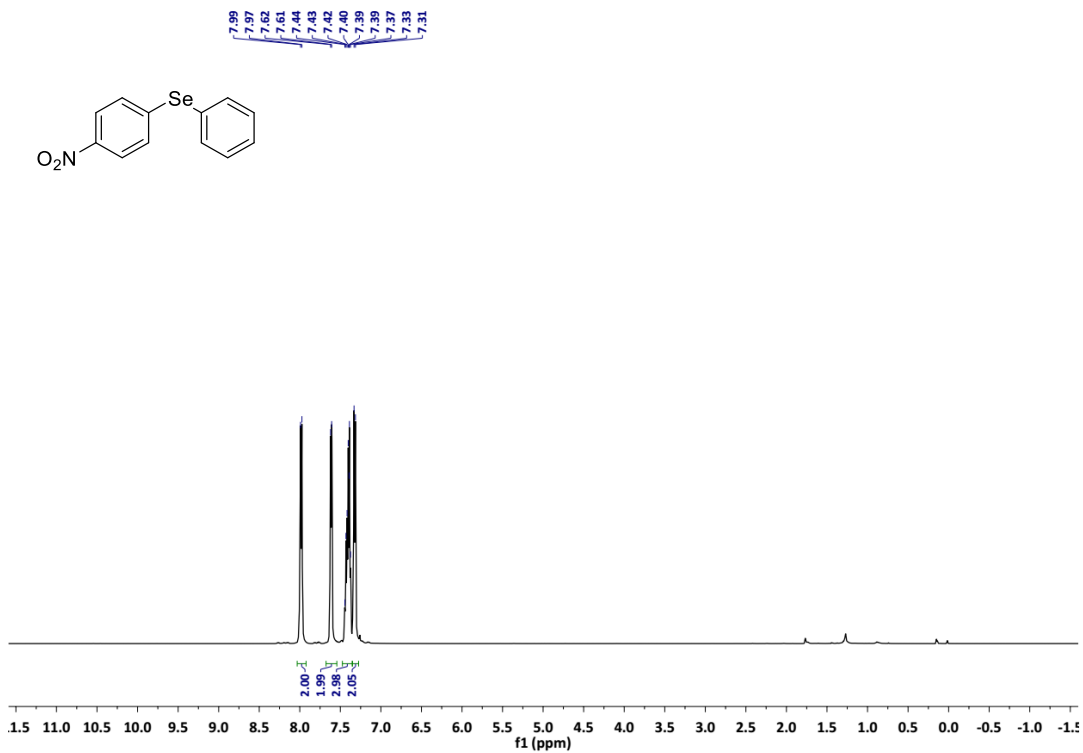
^{13}C NMR spectrum (126 MHz, CDCl_3) of **9d**



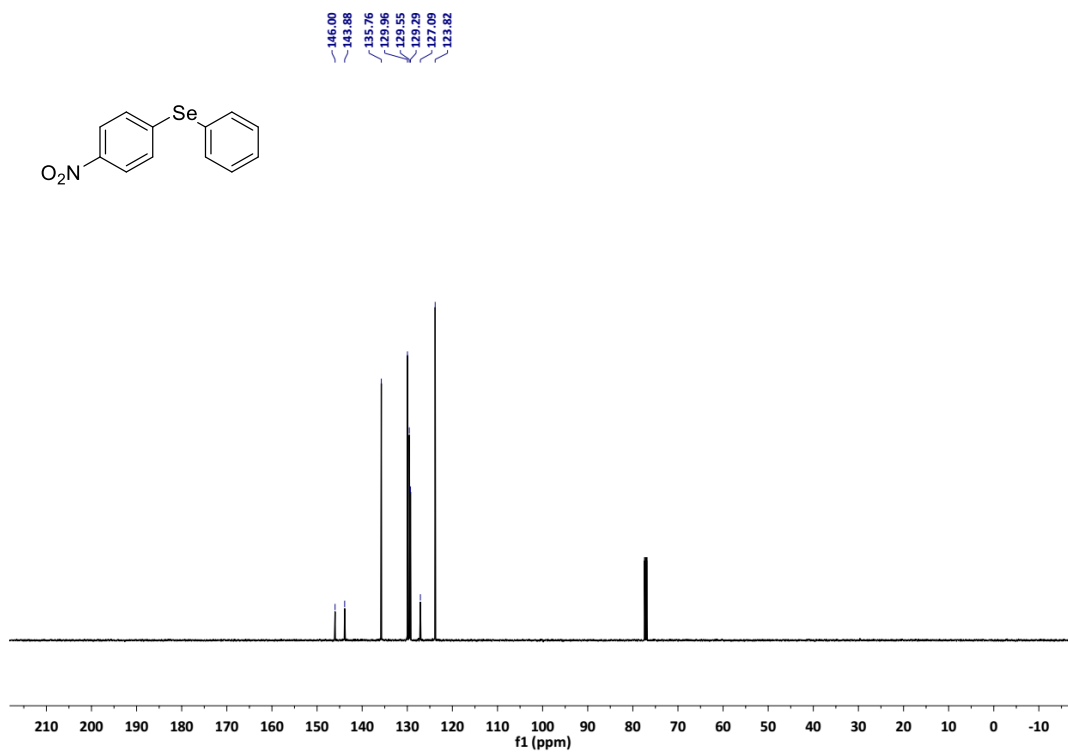
^1H NMR spectrum (500 MHz, CDCl_3) of **9e**



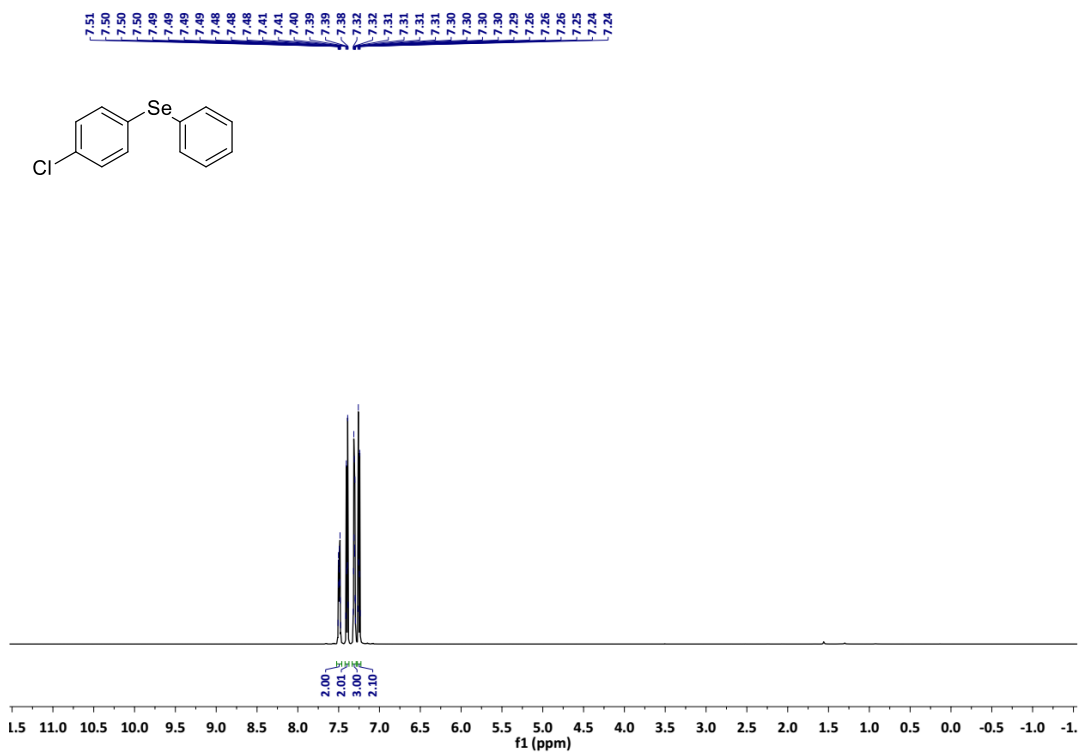
^{13}C NMR spectrum (126 MHz, CDCl_3) of **9e**



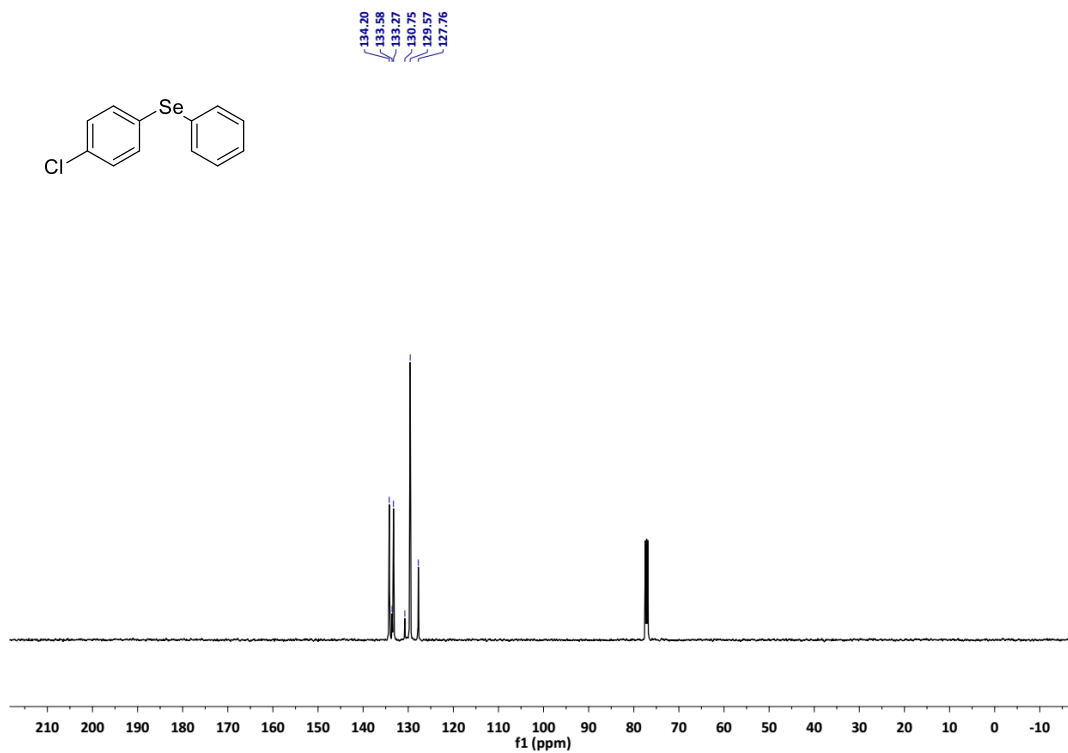
^1H NMR spectrum (500 MHz, CDCl_3) of **9f**



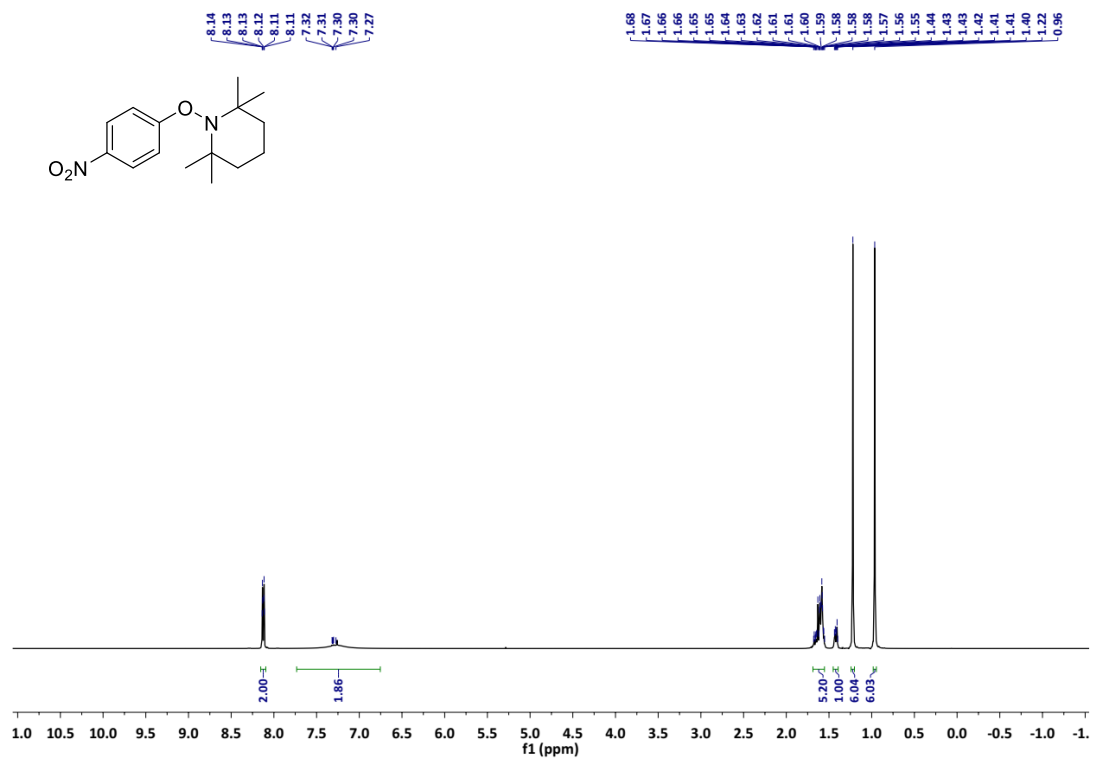
^{13}C NMR spectrum (126 MHz, CDCl_3) of **9f**



^1H NMR spectrum (500 MHz, CDCl_3) of **9g**



¹³C NMR spectrum (126 MHz, CDCl₃) of **9g**



¹H NMR spectrum (500 MHz, CDCl₃) of **10**

