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Supporting information for Visible-light-mediated oxidative arylation of vinylarenes under aerobic conditions

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1 Experimental

1.1 General

All the reagents were commercially available and used without any further purification. The products were purified by column chromatography over silica gel. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. ^{1}H and ^{13}C NMR spectra were recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz, and chemical shifts were reported in ppm from internal TMS (δ).

1.2 Experimental Procedure

General procedure for the preparation of aryl diazonium tetrafluoroborates 1: Compounds were prepared according to literature.[1] The appropriate aniline (1 eq., 10 mmol) was dissolved in a mixture of absolute ethanol (3 mL) and an aqueous solution of HBF_4 (50%, 2.5 mL, 20 mmol). After cooling the reaction mixture to 0 °C *tert*-butyl nitrite (2.7 mL, 20 mmol) was added dropwise. The resulting mixture was stirred at room temperature for 1 hour and diethyl ether (20 mL) was added to precipitate the aryl diazonium tetrafluoroborate. It was then filtered off and washed with diethyl ether (3 × 10 mL). The aryl diazonium tetrafluoroborate was dried in vacuo and was directly used without further purification.

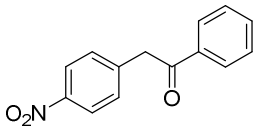
General procedure for the photocatalytic oxidative arylation reactions: A 10 mL reaction vessel with a magnetic stirring bar was equipped with $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2 mol %, 3 mg), aryl diazonium tetrafluoroborate 1 (0.2 mmol), vinylarene 2 (5 eq., 1.0 mmol) and methanol (1 mL). The mixture was irradiated with a blue LED (5 W) and stirred under at r.t. in an oxygen atmosphere for 10 h. After the reaction, the solvent was removed under reduced pressure. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate (5:1−10:1) as eluent.

General procedure for the reductive cyclization reactions: The reaction were conducted according to literature.[2] In a 50 mL reaction vessel were dissolved 0.5 mmol of the ketone, 1.7 mmol (3.5 equiv) iron powder, and 0.5 mmol (1 equiv) sodium acetate in 3.5 mmol (7 equiv) acetic acid and 10 mL of 80:20 (v/v) ethanol/water. The mixture was heated to reflux under argon. After a reaction time of 2 h, the reaction mixture was cooled to room temperature, ethanol was evaporated, and the residue was extracted three times with dichloromethane. The organic layer were combined, washed with brine, and dried over magnesium sulfate. Dichloromethane was evaporated, and the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate (10:1) as eluent.

1 G. Danoun, B. Bayarmagnai, M. F. Grünberg and L. J. Gooßen, *Angew. Chem. Int. Ed.*, 2013, **52**, 7972-7975.

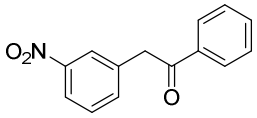
2 T. Hering, D. P. Hari and B. König, *J. Org. Chem.*, 2012, **77**, 10347-10352.

2 Characterization Data



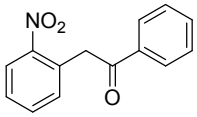
Chemical Formula: $C_{14}H_{11}NO_3$
Exact Mass: 241.07
Elemental Analysis: C, 69.70; H, 4.60; N, 5.81; O, 19.90

2-(4-Nitrophenyl)-1-phenylethan-1-one (**3a**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 4.42 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.1, 147.2, 142.1, 136.3, 133.8, 130.7, 129.0, 128.5, 123.9, 45.1.



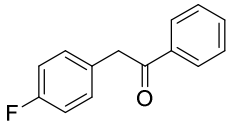
Chemical Formula: $C_{14}H_{11}NO_3$
Exact Mass: 241.07
Elemental Analysis: C, 69.70; H, 4.60; N, 5.81; O, 19.90

2-(3-Nitrophenyl)-1-phenylethan-1-one (**3b**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 6.5 Hz, 2H), 8.03 (d, *J* = 7.5 Hz, 2H), 7.64 – 7.58 (m, 2H), 7.55 – 7.48 (m, 3H), 4.42 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.0, 148.4, 136.4, 136.2, 136.0, 133.7, 129.4, 128.9, 128.4, 124.7, 122.1, 44.6.



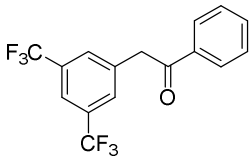
Chemical Formula: $C_{14}H_{11}NO_3$
Exact Mass: 241.07
Elemental Analysis: C, 69.70; H, 4.60; N, 5.81; O, 19.90

2-(2-Nitrophenyl)-1-phenylethan-1-one (**3c**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.50 (dd, *J* = 15.8, 8.0 Hz, 3H), 7.35 (d, *J* = 7.5 Hz, 1H), 4.74 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.4, 148.1, 135.5, 132.7, 132.5, 129.7, 127.8, 127.4, 127.3, 124.3, 43.1.



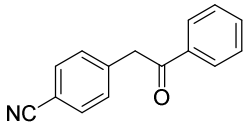
Chemical Formula: $C_{14}H_{11}FO$
Exact Mass: 214.08
Elemental Analysis: C, 78.49; H, 5.18; F, 8.87; O, 7.47

2-(4-Fluorophenyl)-1-phenylethan-1-one (**3d**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.17 (dd, *J* = 8.3, 5.5 Hz, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 4.21 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 161.9, 160.0, 135.6, 132.3, 130.1, 130.0, 129.2, 127.7, 127.5, 114.6, 114.4, 43.5.



Chemical Formula: $C_{16}H_{10}F_6O$
Exact Mass: 332.06
Elemental Analysis: C, 57.84; H, 3.03; F, 34.31; O, 4.82

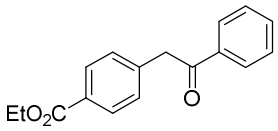
2-(3,5-Bis(trifluoromethyl)phenyl)-1-phenylethan-1-one (**3e**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.4 Hz, 2H), 7.83 (s, 1H), 7.74 (s, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 4.47 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.6, 135.7, 135.1, 132.9, 130.9, 130.6, 129.1, 128.0, 127.3, 123.4, 121.2, 120.1, 43.4.



Chemical Formula: $C_{15}H_{11}NO$
Exact Mass: 221.08
Elemental Analysis: C, 81.43; H, 5.01; N, 6.33; O, 7.23

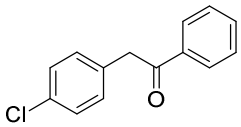
4-(2-Oxo-2-phenylethyl)benzonitrile (**3f**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.62 (dd, *J* = 17.8, 7.8 Hz, 3H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.36 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.1, 139.0, 135.3, 132.7, 131.4, 129.5, 127.9, 127.5, 117.8, 110.0,

44.2.



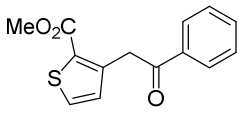
Chemical Formula: $C_{17}H_{16}O_3$
Exact Mass: 268.11
Elemental Analysis: C, 76.10; H, 6.01; O, 17.89

Ethyl 4-(2-oxo-2-phenylethyl)benzoate (**3g**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.7, 4.1 Hz, 4H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.36 (dd, *J* = 13.3, 6.2 Hz, 4H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.9, 165.4, 138.7, 135.4, 132.4, 128.9, 128.6, 128.3, 127.8, 127.6, 59.9, 44.4, 13.3.



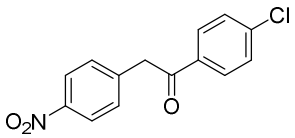
Chemical Formula: $C_{14}H_{11}ClO$
Exact Mass: 230.05
Elemental Analysis: C, 72.89; H, 4.81; Cl, 15.37; O, 6.94

2-(4-Chlorophenyl)-1-phenylethan-1-one (**3h**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.26 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.1, 135.5, 132.4, 131.9, 129.9, 127.8, 127.7, 127.5, 43.7.



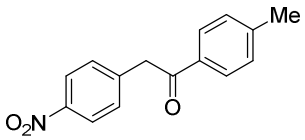
Chemical Formula: $C_{14}H_{12}O_3S$
Exact Mass: 260.05
Elemental Analysis: C, 64.60; H, 4.65; O, 18.44; S, 12.32

Methyl 3-(2-oxo-2-phenylethyl)thiophene-2-carboxylate (**3i**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.03 (d, *J* = 5.0 Hz, 1H), 4.77 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.6, 162.0, 141.4, 135.8, 132.3, 130.4, 129.5, 127.7, 127.4, 127.0, 50.9, 38.3.



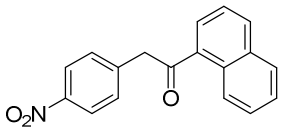
Chemical Formula: $C_{14}H_{10}ClNO_3$
Exact Mass: 275.03
Elemental Analysis: C, 60.99; H, 3.66; Cl, 12.86; N, 5.08; O, 17.41

1-(4-Chlorophenyl)-2-(4-nitrophenyl)ethan-1-one (**3l**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 4.38 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 146.2, 140.6, 139.3, 133.5, 129.6, 128.8, 128.3, 122.8, 43.9.



Chemical Formula: $C_{15}H_{13}NO_3$
Exact Mass: 255.09
Elemental Analysis: C, 70.58; H, 5.13; N, 5.49; O, 18.80

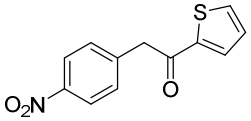
2-(4-Nitrophenyl)-1-(p-tolyl)ethan-1-one (**3m**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.38 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.6, 147.1, 144.7, 142.3, 133.7, 130.6, 129.5, 128.6, 123.7, 44.9, 21.7.



Chemical Formula: $C_{18}H_{13}NO_3$
Exact Mass: 291.09
Elemental Analysis: C, 74.22; H, 4.50; N, 4.81; O, 16.48

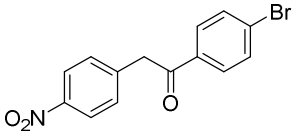
1-(Naphthalen-1-yl)-2-(4-nitrophenyl)ethan-1-one (**3n**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* =

8.4 Hz, 1H), 8.21 (d, *J* = 8.6 Hz, 2H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.48 (d, *J* = 8.5 Hz, 2H), 4.51 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 146.1, 141.1, 133.8, 133.1, 132.6, 129.6, 129.4, 127.6, 127.4, 127.2, 125.8, 124.6, 123.3, 122.8, 47.3.



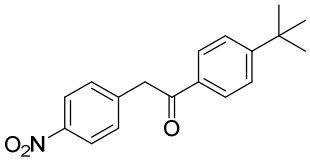
Chemical Formula: $C_{12}H_9NO_3S$
Exact Mass: 247.03
Elemental Analysis: C, 58.29; H, 3.67; N, 5.66; O, 19.41; S, 12.97

2-(4-Nitrophenyl)-1-(thiophen-2-yl)ethan-1-one (**3o**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 2.8 Hz, 1H), 7.72 (d, *J* = 4.7 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.16 (m, 1H), 4.34 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.7, 146.2, 142.3, 140.6, 133.8, 131.8, 129.5, 127.4, 122.8, 44.7.



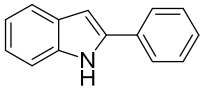
Chemical Formula: $C_{14}H_{10}BrNO_3$
Exact Mass: 318.98
Elemental Analysis: C, 52.52; H, 3.15; Br, 24.96; N, 4.38; O, 14.99

1-(4-Bromophenyl)-2-(4-nitrophenyl)ethan-1-one (**3p**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 4.39 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.0, 146.2, 140.5, 133.9, 131.3, 129.6, 128.9, 128.1, 122.8, 43.9.



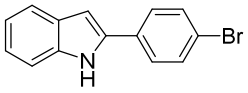
Chemical Formula: $C_{18}H_{19}NO_3$
Exact Mass: 297.14
Elemental Analysis: C, 72.71; H, 6.44; N, 4.71; O, 16.14

1-(4-(Tert-butyl)phenyl)-2-(4-nitrophenyl)ethan-1-one (**3q**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.3 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 4.40 (s, 2H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.6, 156.7, 146.1, 141.3, 132.6, 129.6, 127.5, 124.9, 122.8, 43.9, 34.2, 30.1.



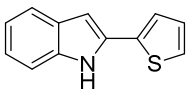
Chemical Formula: $C_{14}H_{11}N$
Exact Mass: 193.09
Elemental Analysis: C, 87.01; H, 5.74; N, 7.25

2-Phenyl-1H-indole (**6a**). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.36 (s, 1H), 7.67 (d, *J*=7.6, 2H), 7.63 (d, *J*=7.9, 1H), 7.44 (t, *J*=7.7, 2H), 7.40 (d, *J*=8.1, 1H), 7.32 (t, *J*=7.4, 1H), 7.19 (t, *J*=7.6, 1H), 7.12 (t, *J*=7.5, 1H), 6.83 (s, 1H).



Chemical Formula: $C_{14}H_{10}BrN$
Exact Mass: 271.00
Elemental Analysis: C, 61.79; H, 3.70; Br, 29.36; N, 5.15

2-(4-Bromophenyl)-1H-indole (**6b**). ^{1}H NMR (500 MHz, DMSO) δ = 11.57 (s, 1H), 7.80 (d, *J*=8.5, 2H), 7.63 (d, *J*=8.5, 2H), 7.52 (d, *J*=7.9, 1H), 7.39 (d, *J*=8.1, 1H), 7.10 (t, *J*=7.6, 1H), 6.99 (t, *J*=7.4, 1H), 6.92 (s, 1H).

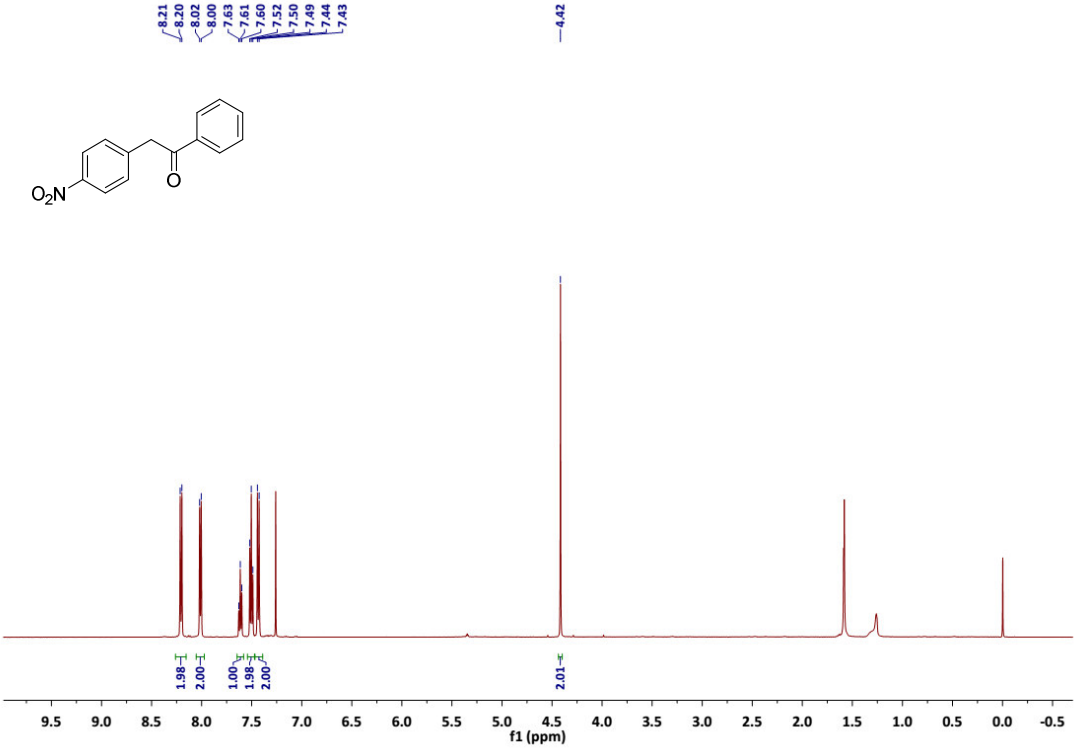


Chemical Formula: $C_{12}H_9NS$
Exact Mass: 199.05
Elemental Analysis: C, 72.33; H, 4.55; N, 7.03; S, 16.09

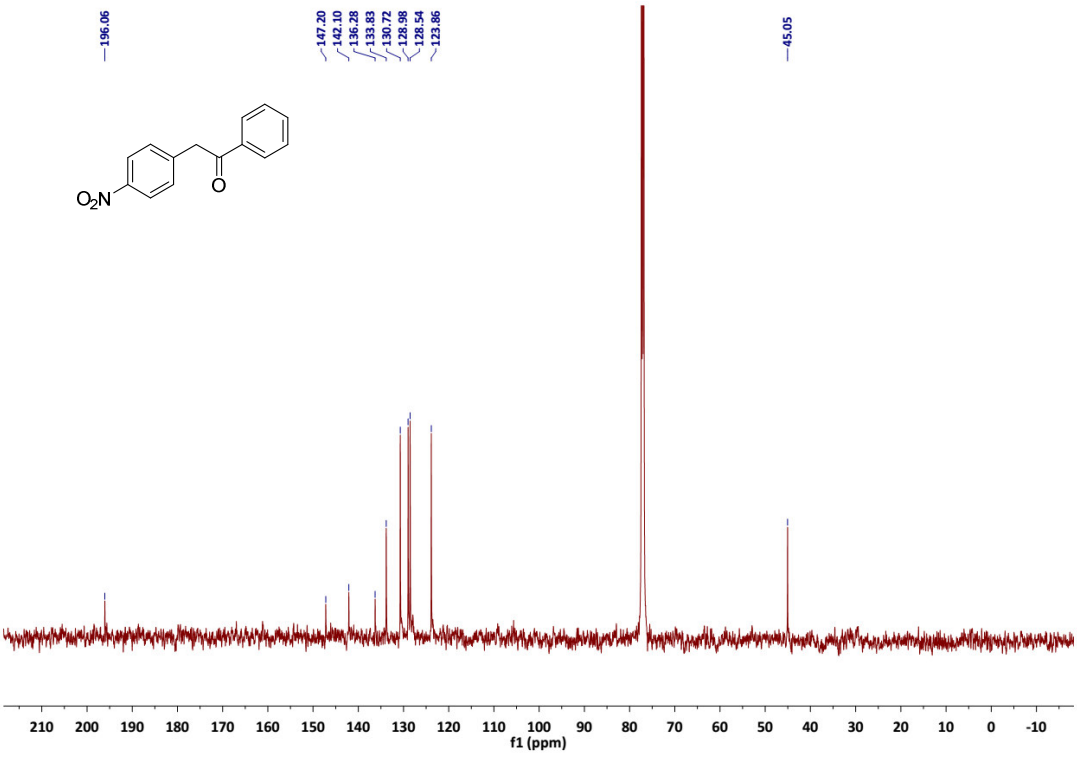
2-(Thiophen-2-yl)-1H-indole (**6c**). ^{1}H NMR (500 MHz, DMSO) δ = 11.55 (s, 1H), 7.56 – 7.46 (m, 3H), 7.37 (dd, *J*=8.1, 0.8, 1H), 7.14 (dd, *J*=5.0, 3.6, 1H), 7.10 (ddd, *J*=8.2, 7.1, 1.2, 1H), 7.00 (ddd,

J=8.0, 7.1, 1.0, 1H), 6.67 (s, 1H).

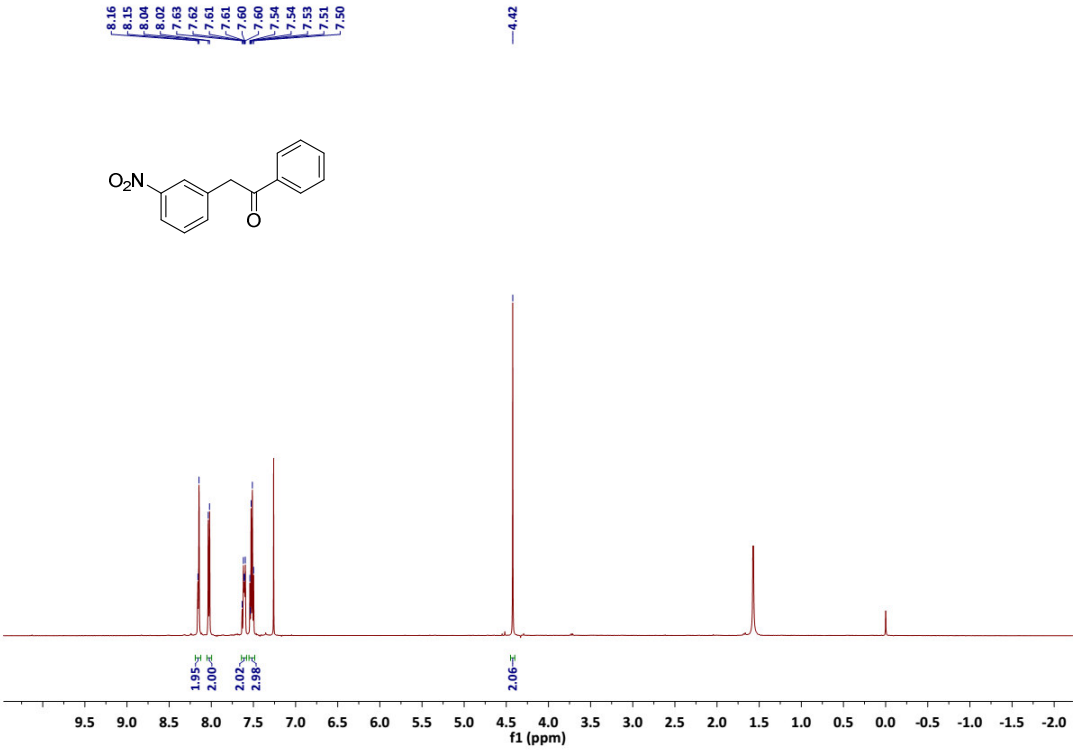
3 NMR Spectra of All Products



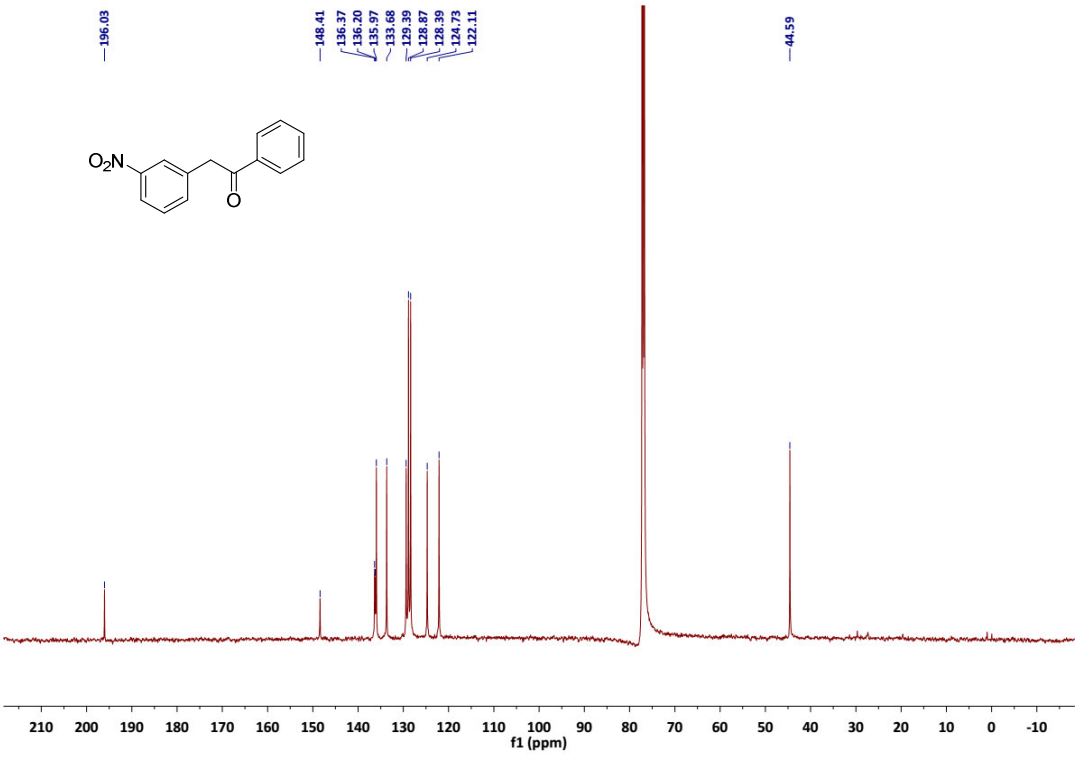
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3a**



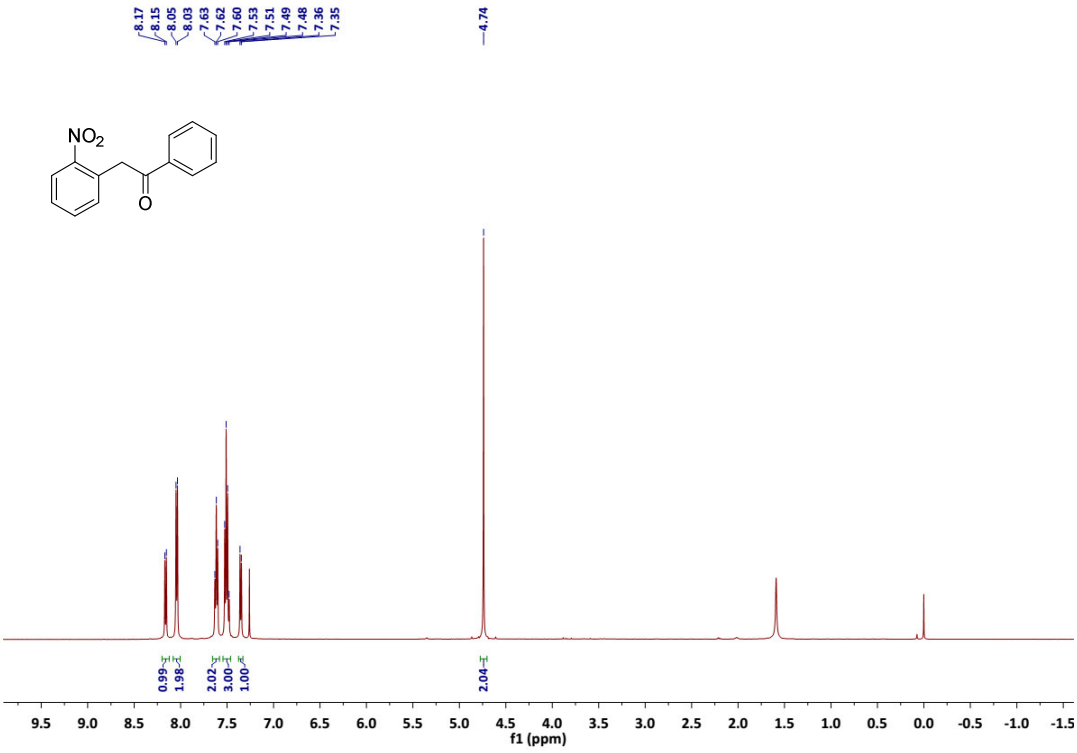
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3a**



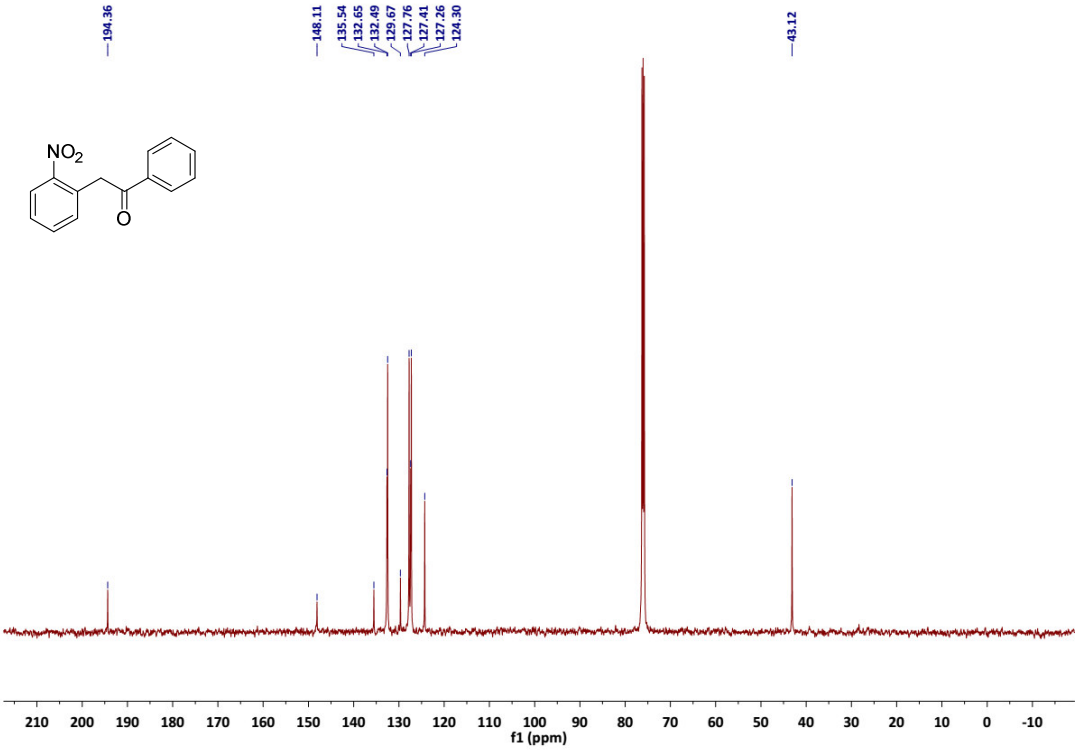
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3b**



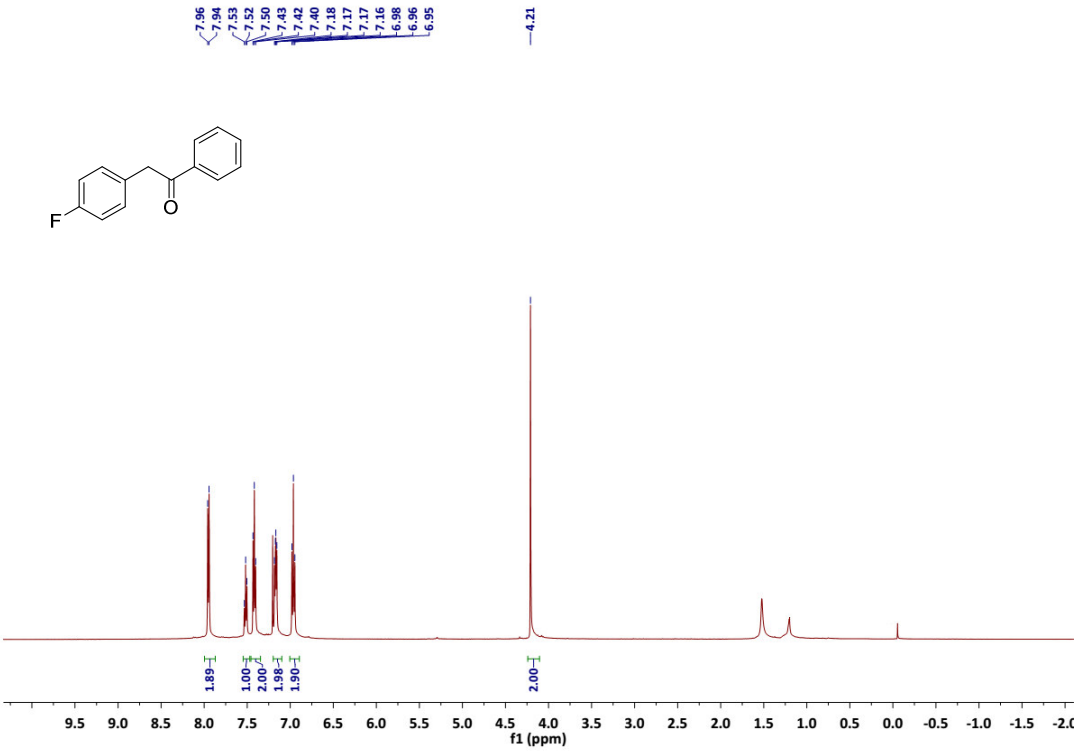
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3b**



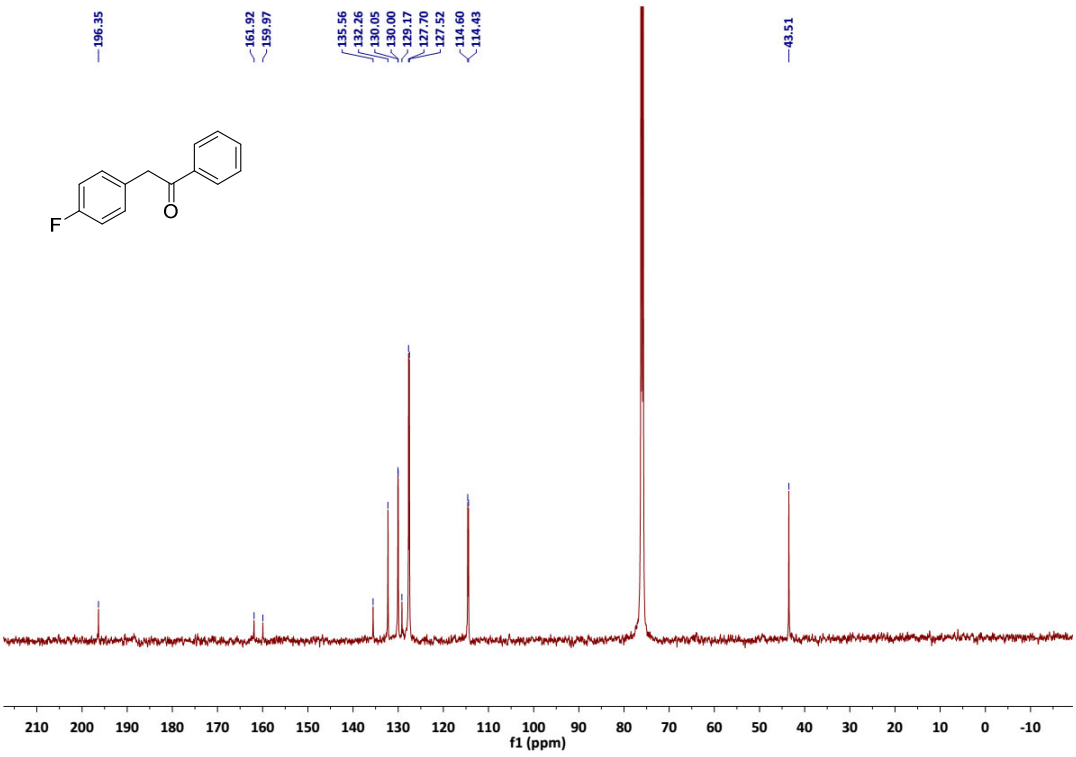
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3c**



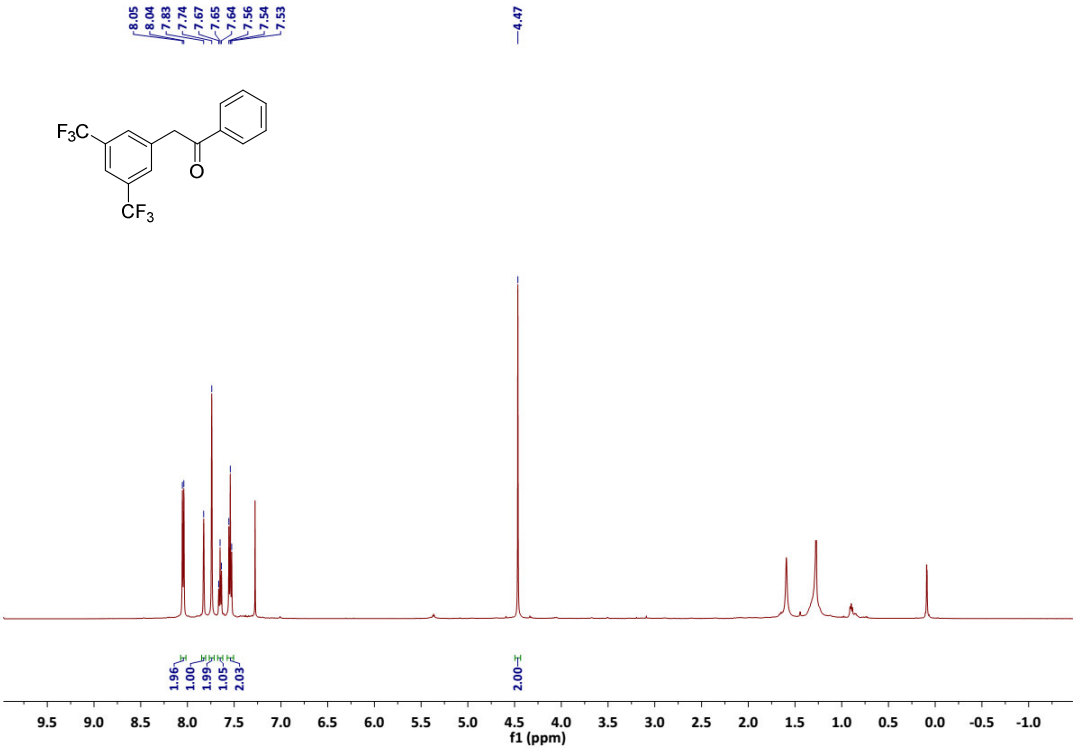
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3c**



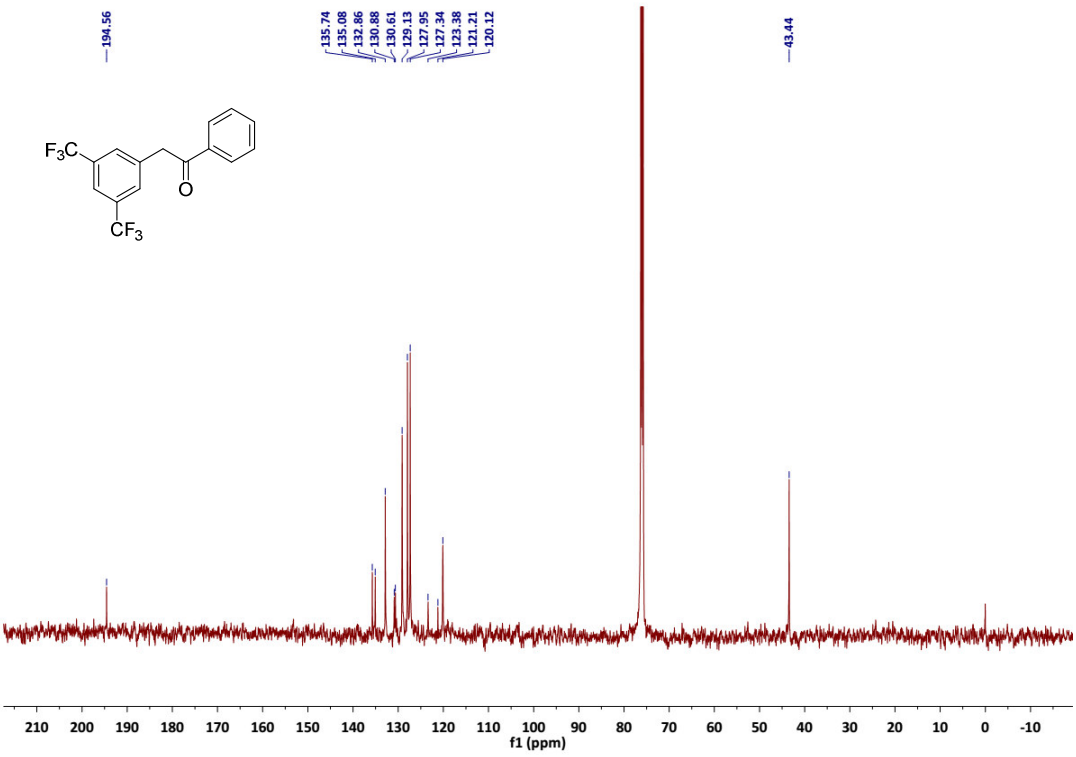
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3d**



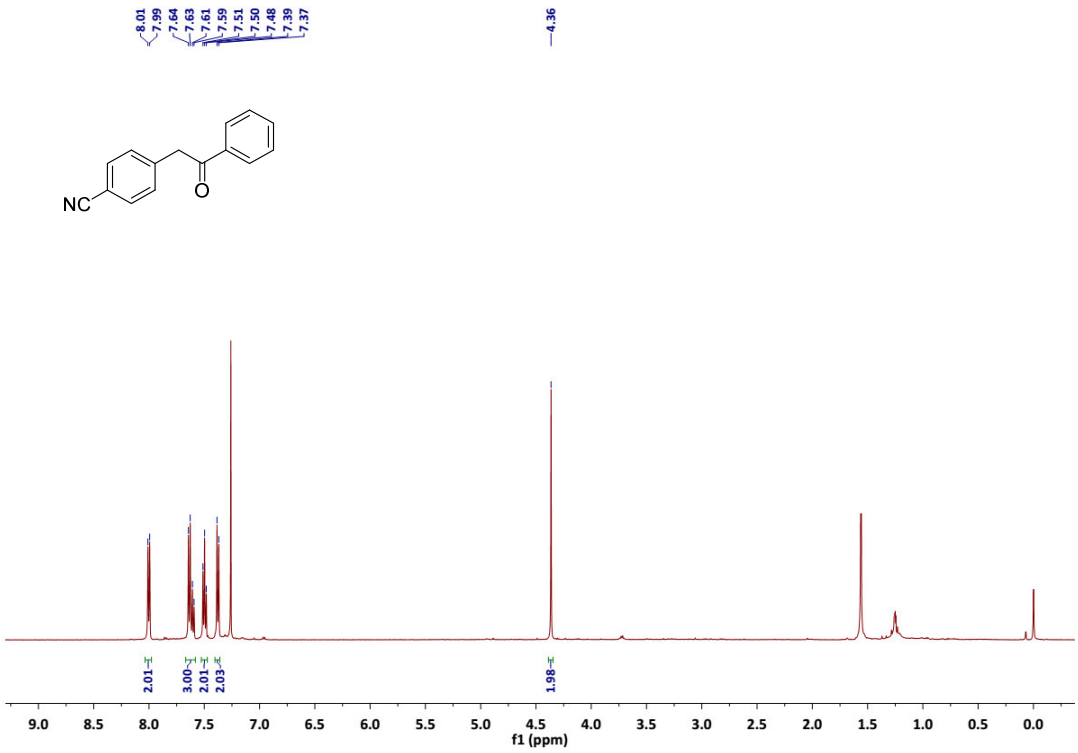
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3d**



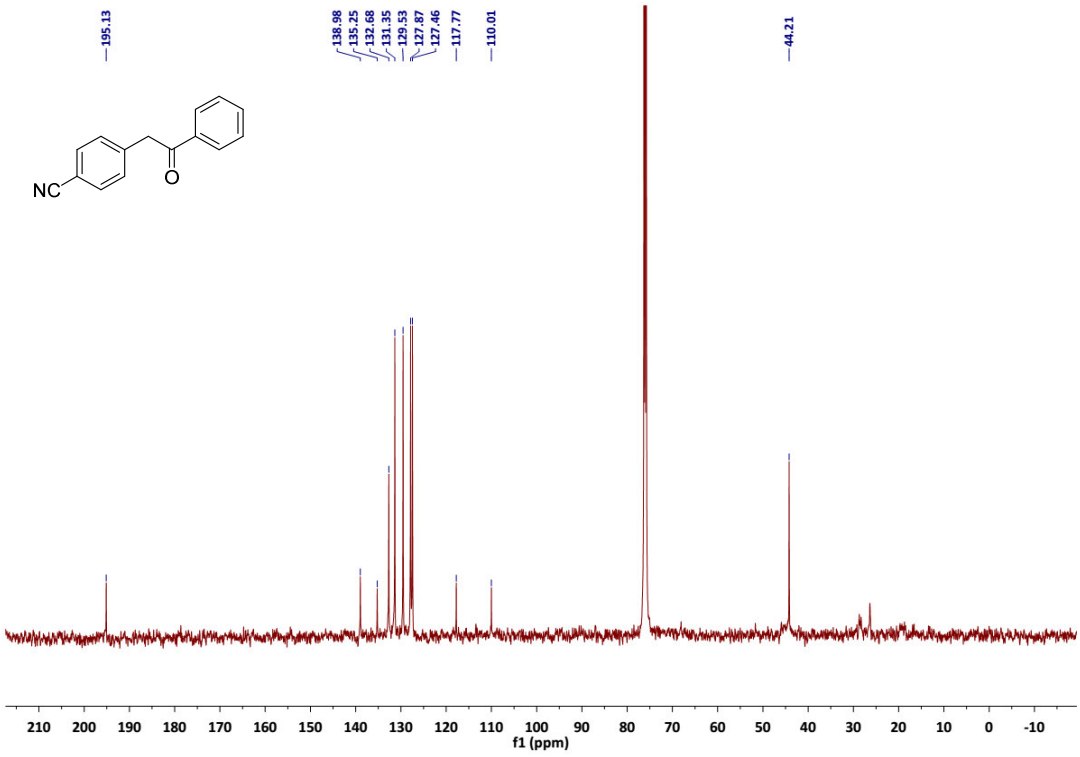
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3e**



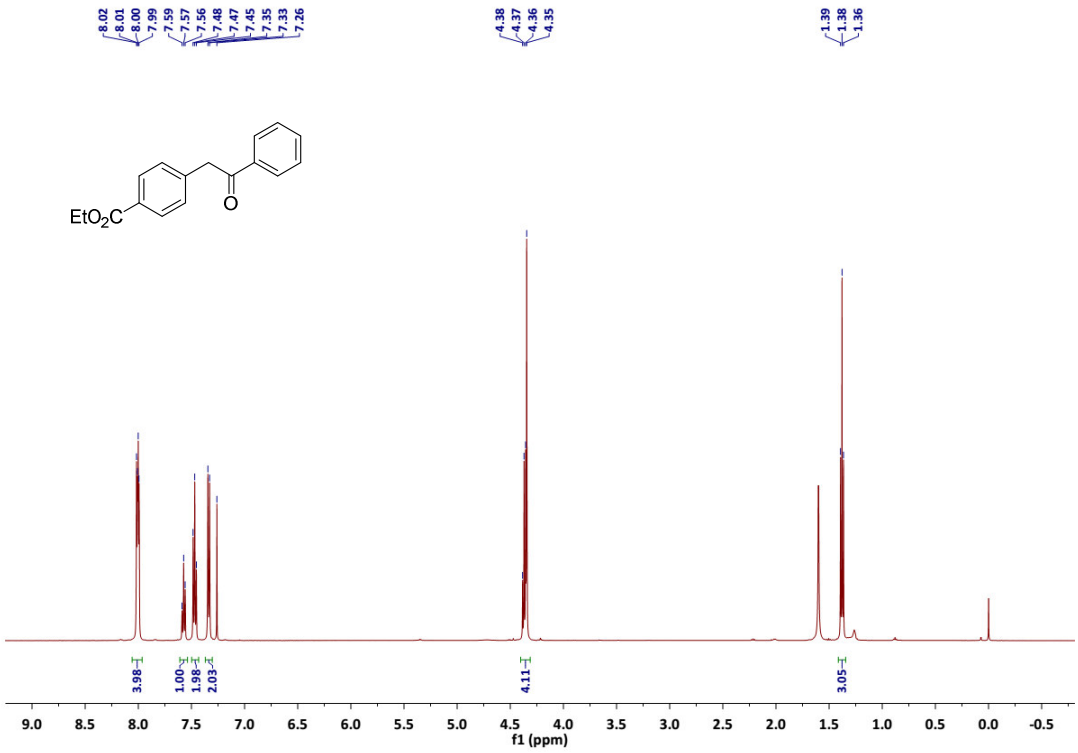
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3e**



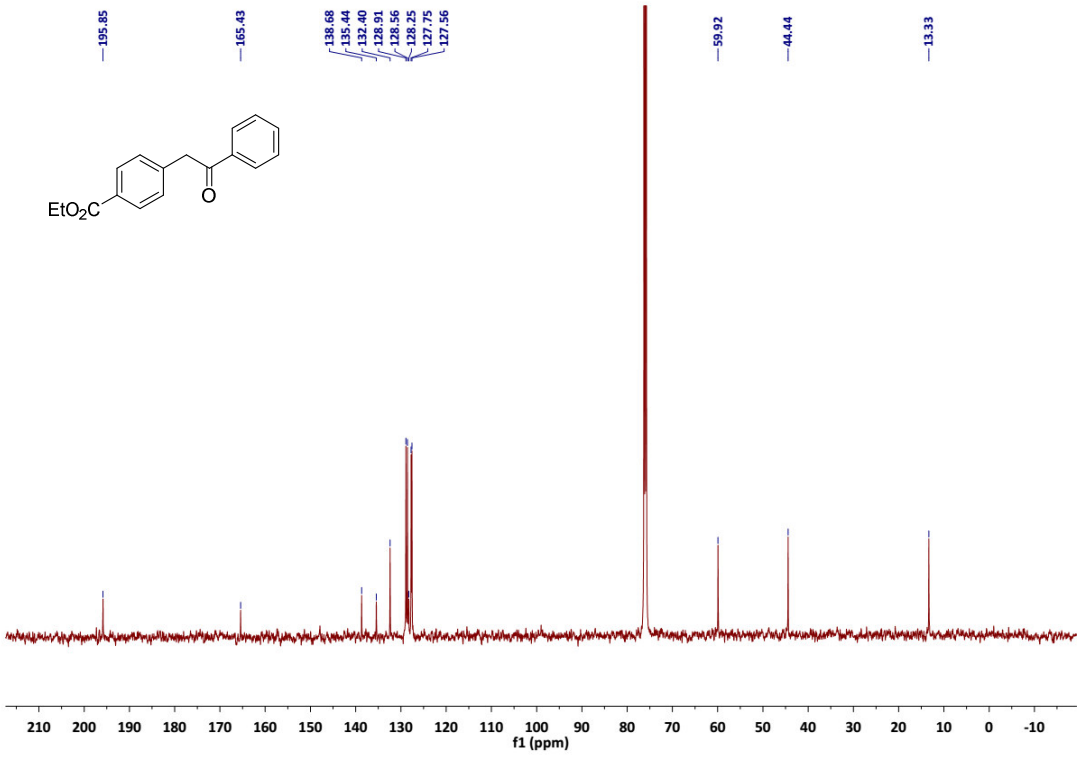
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3f**



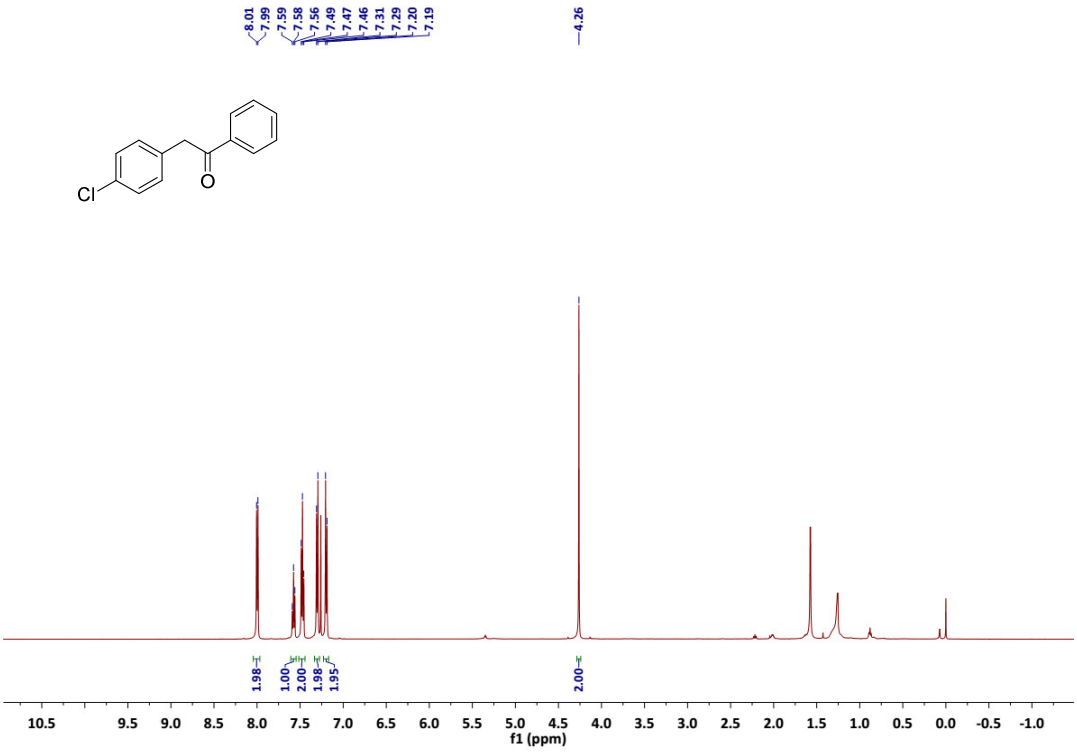
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3f**



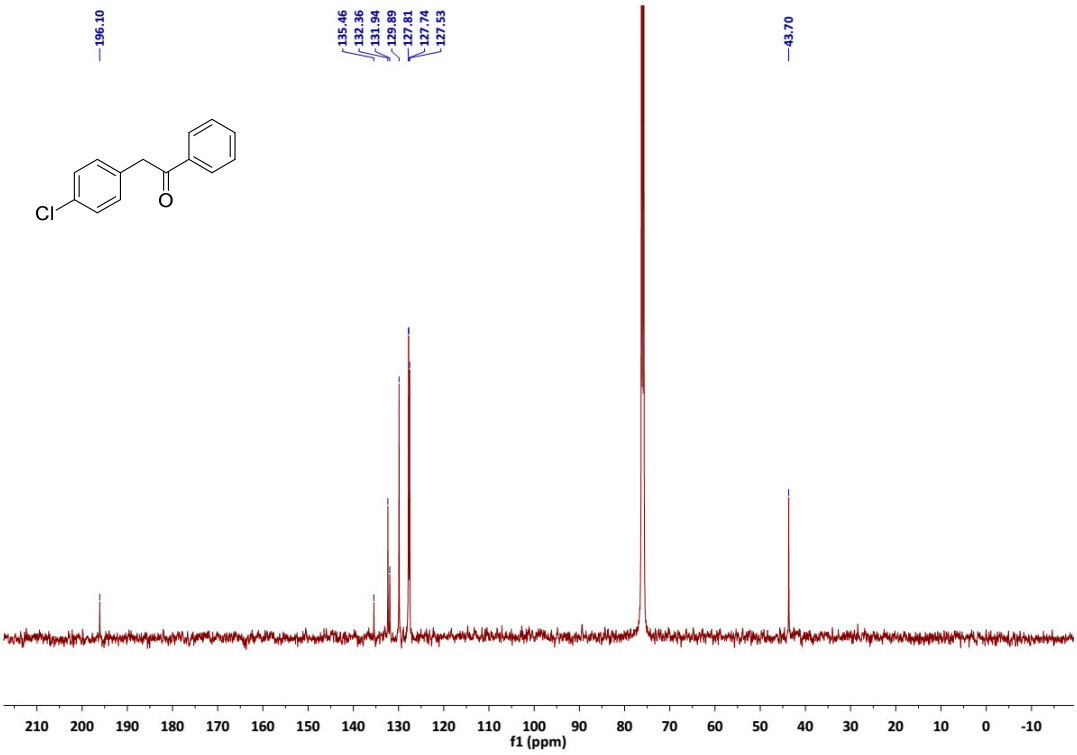
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3g**



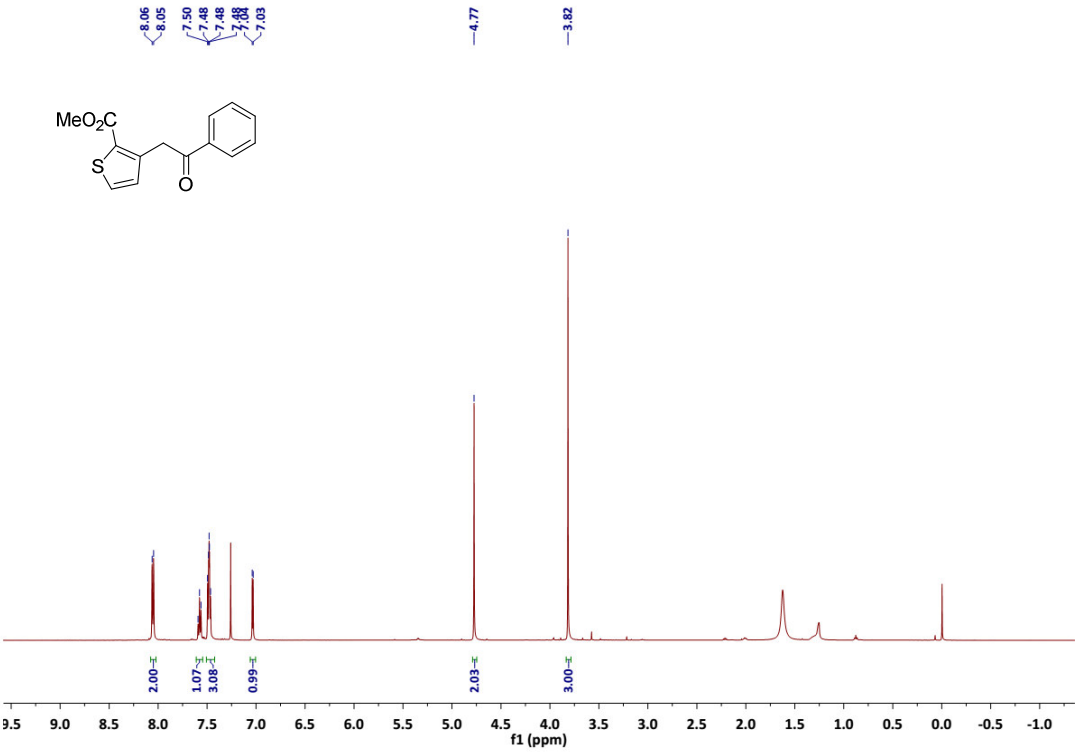
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3g**



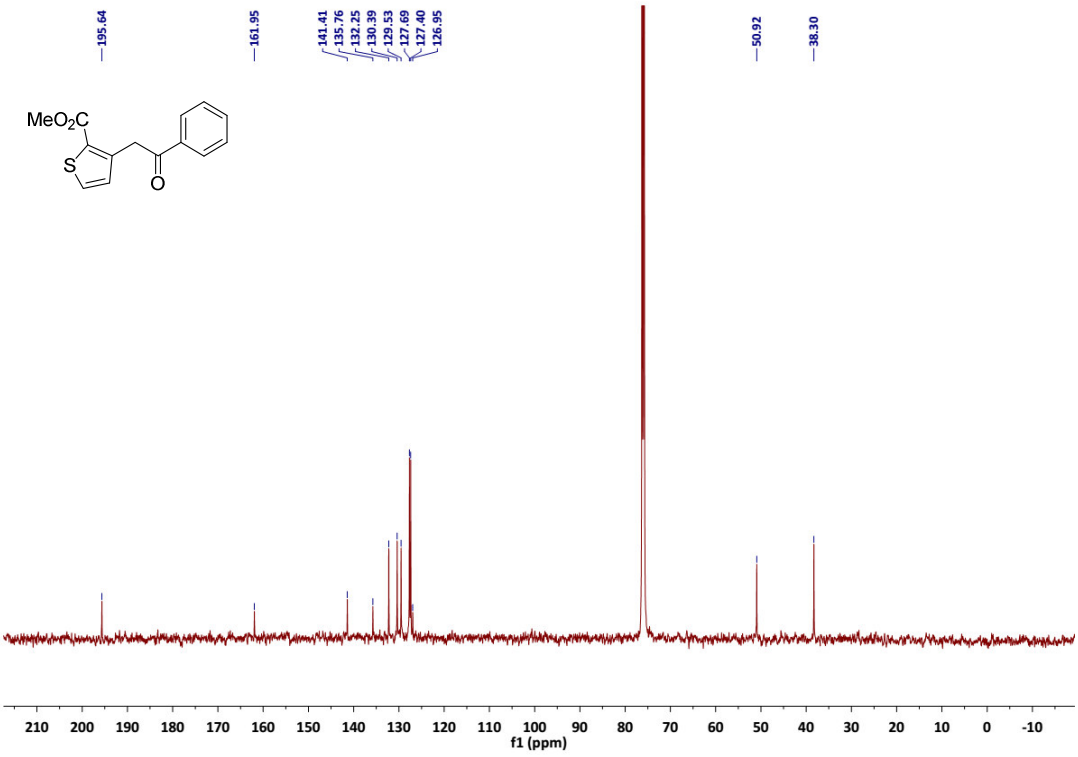
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3h**



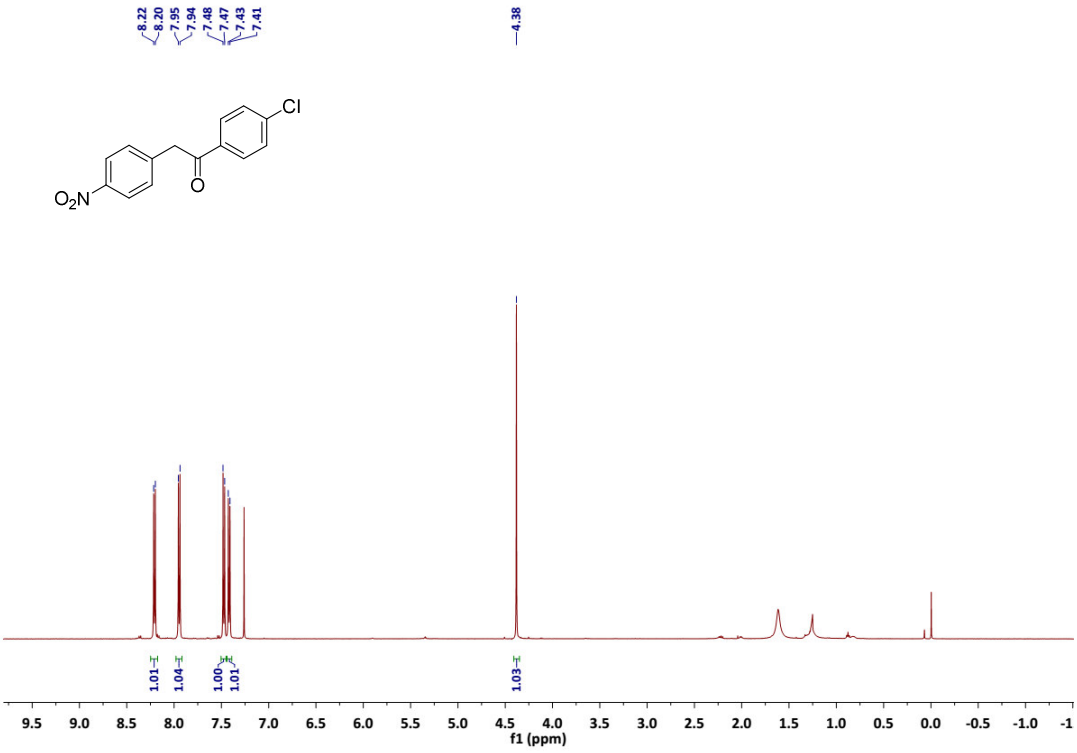
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3h**



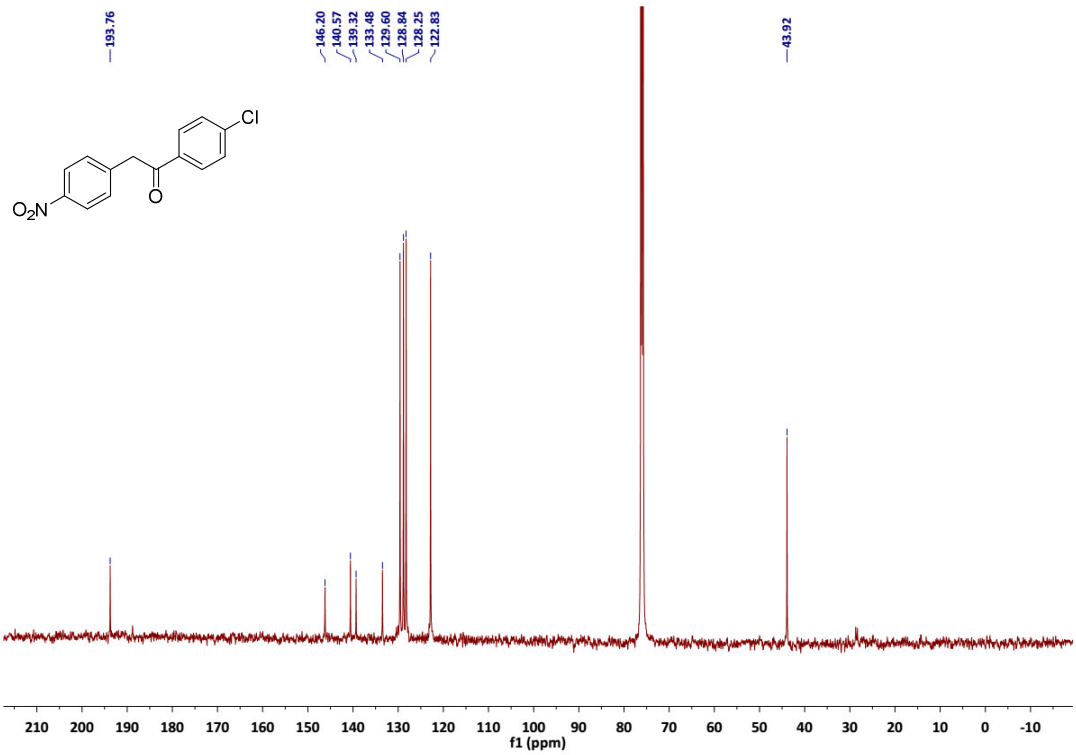
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3i**



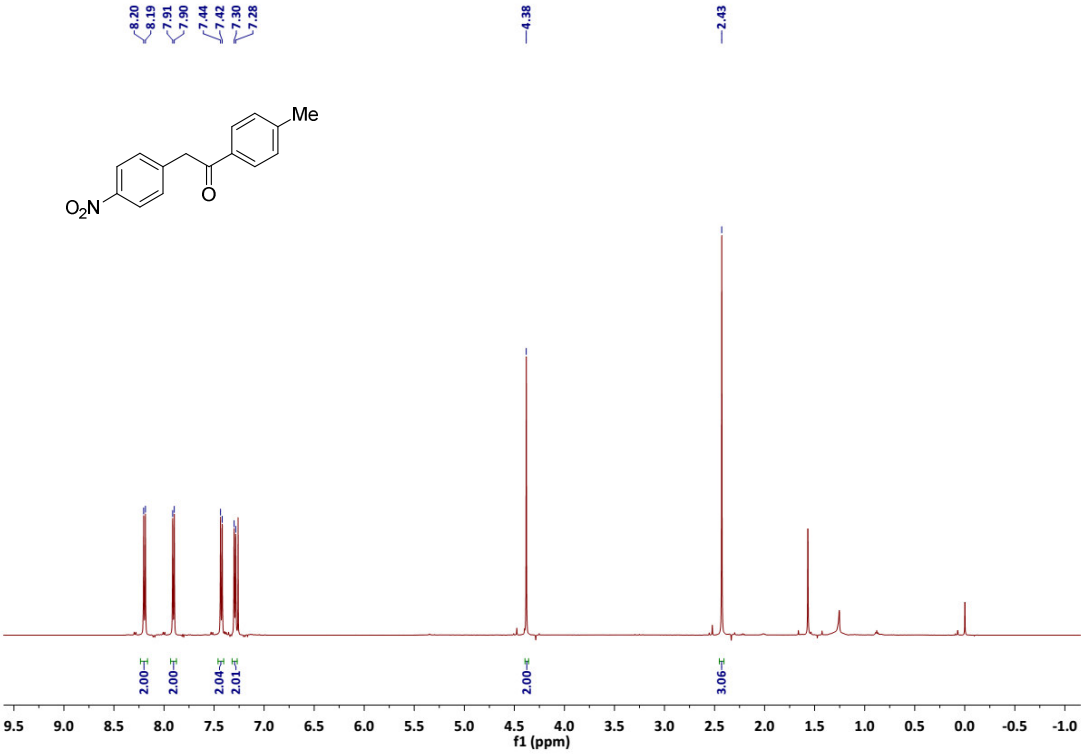
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3i**



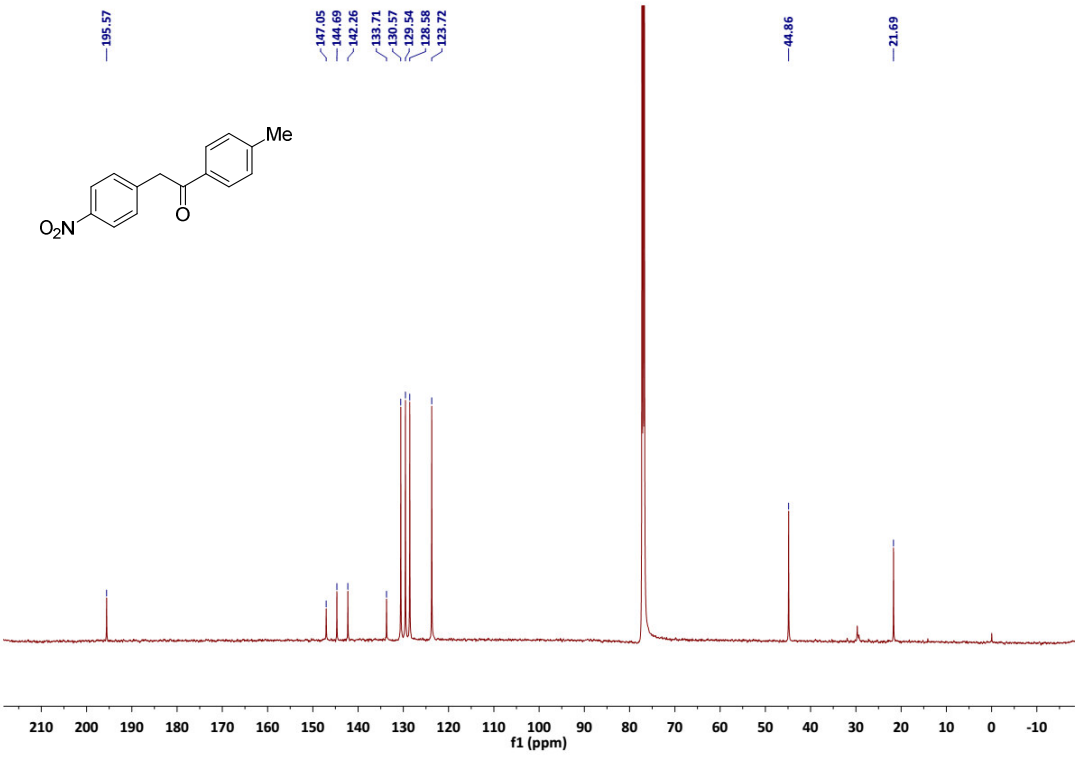
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3l**



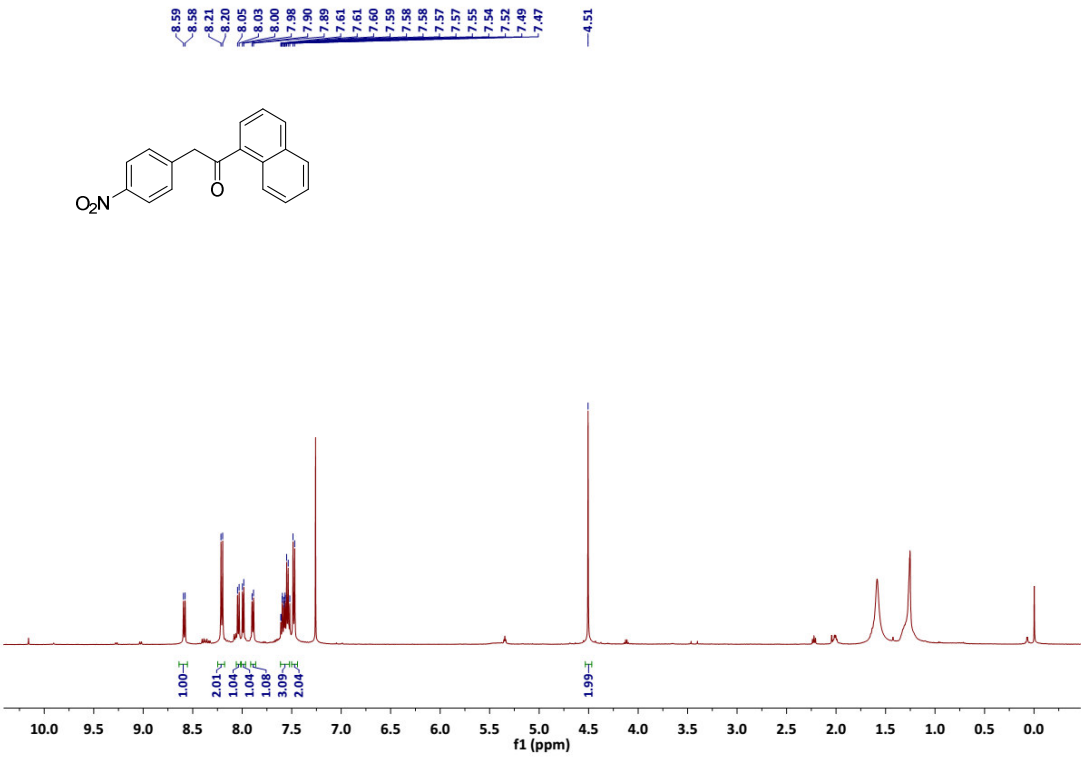
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3l**



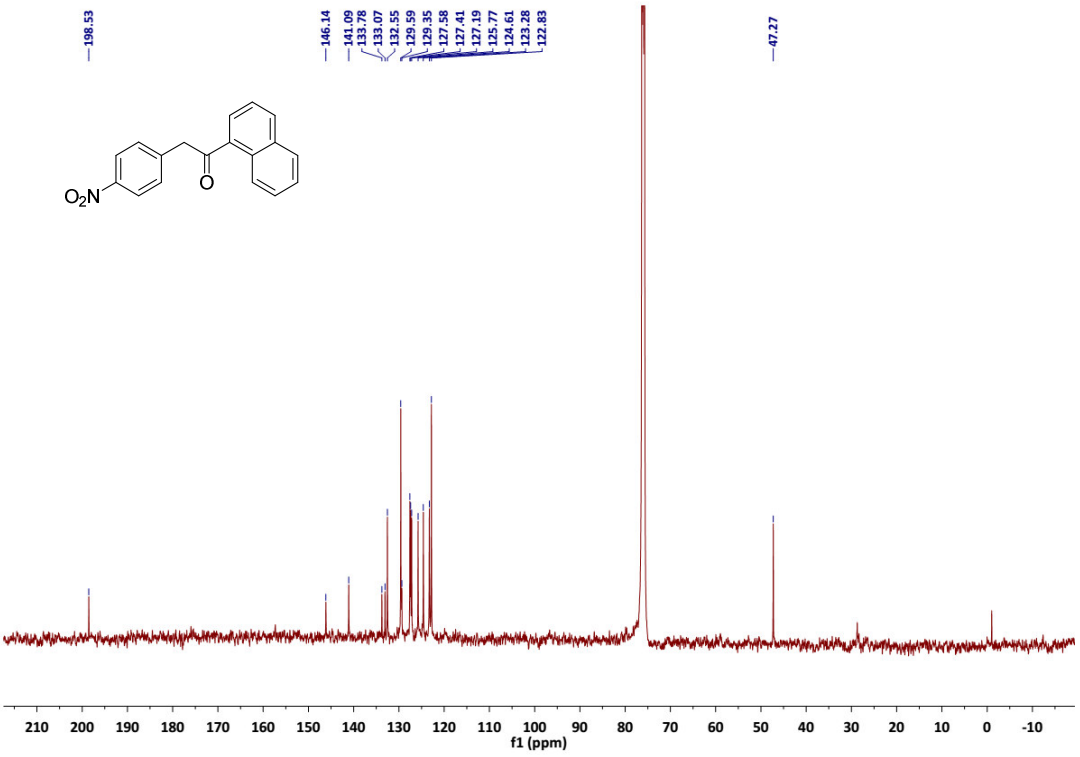
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3m**



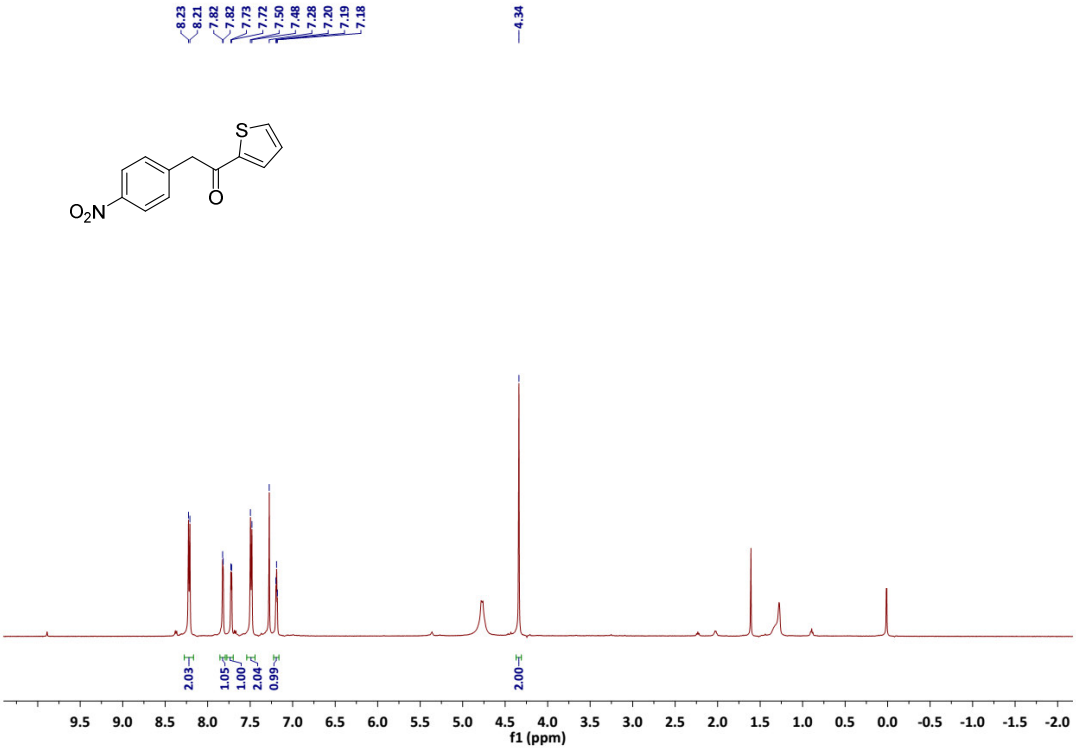
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3m**



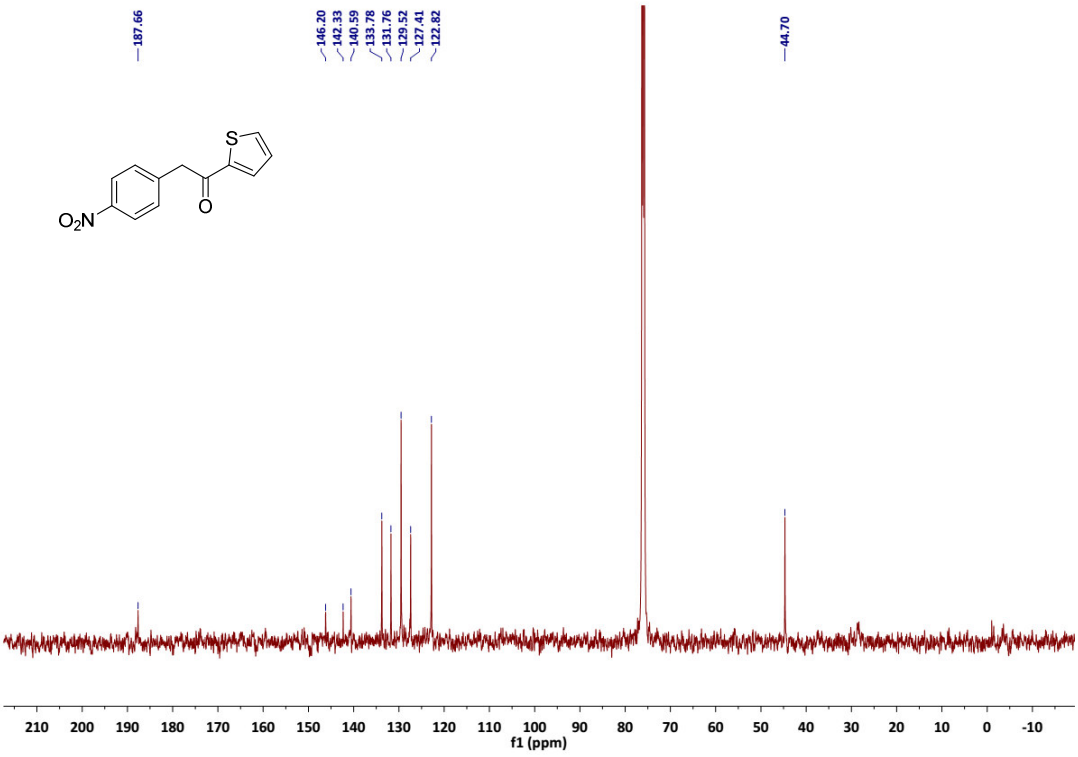
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3n**



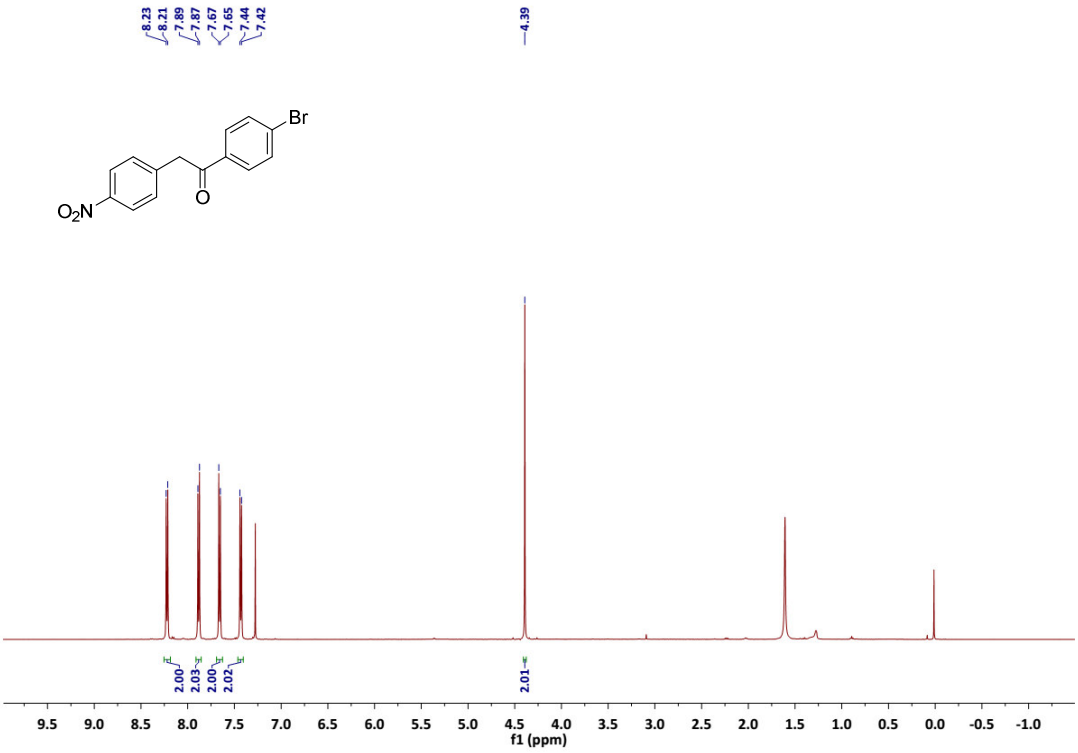
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3n**



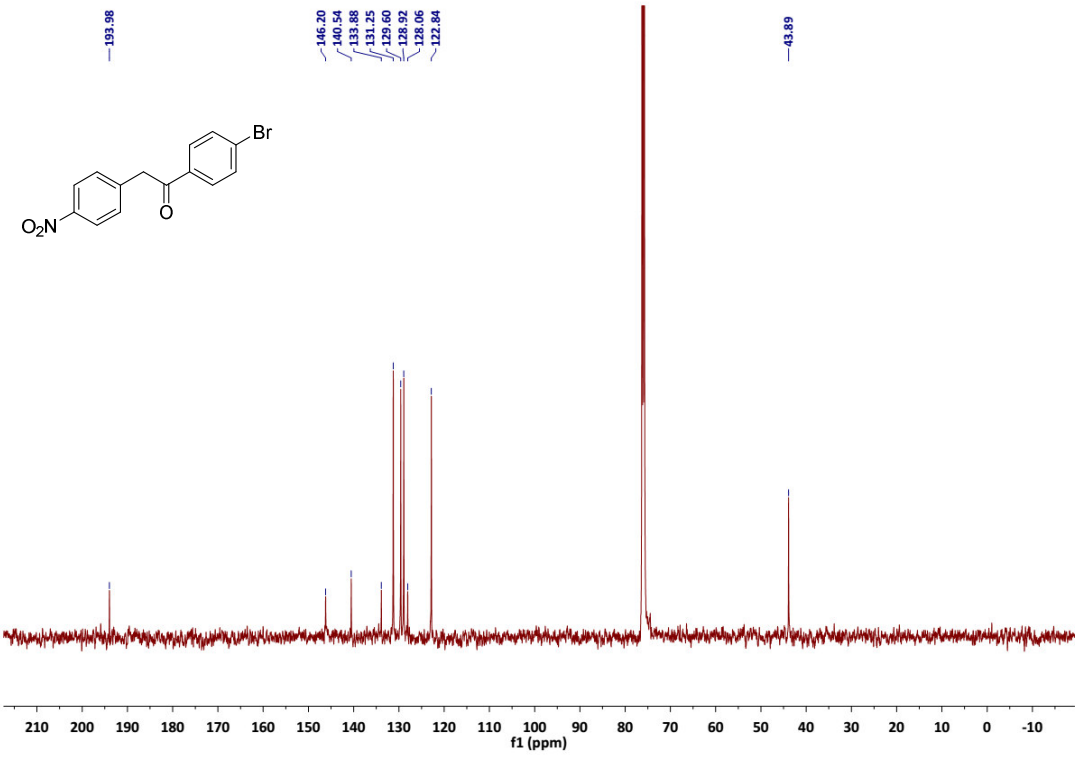
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3o**



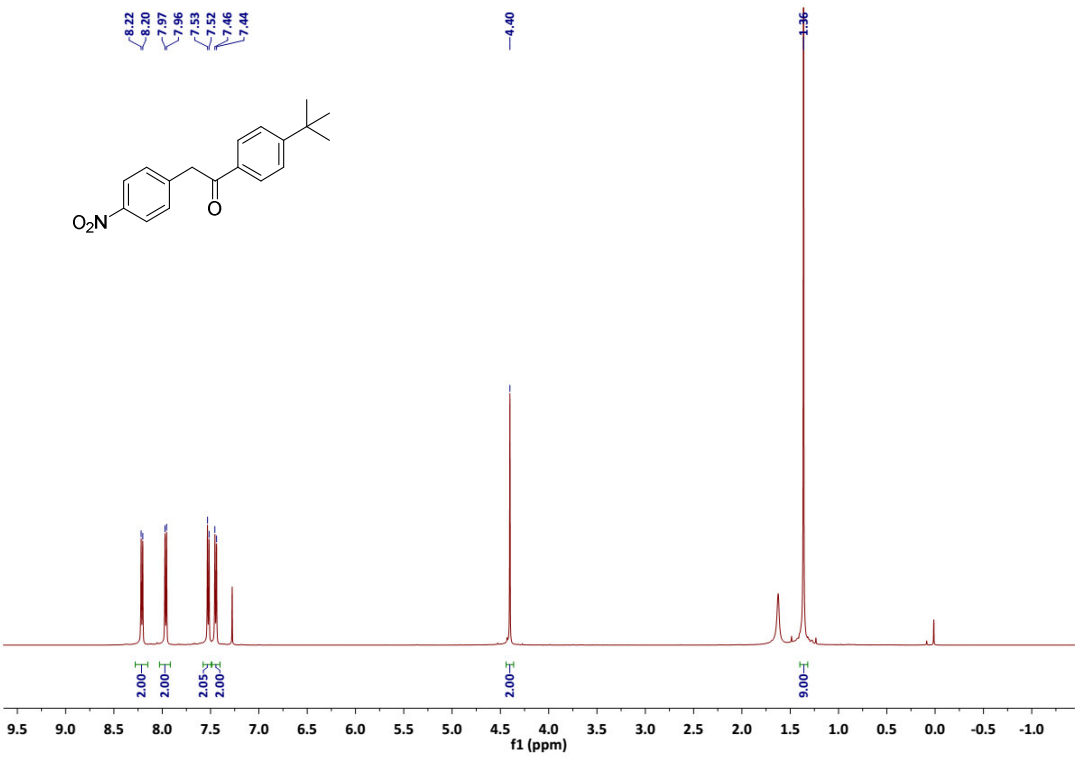
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3o**



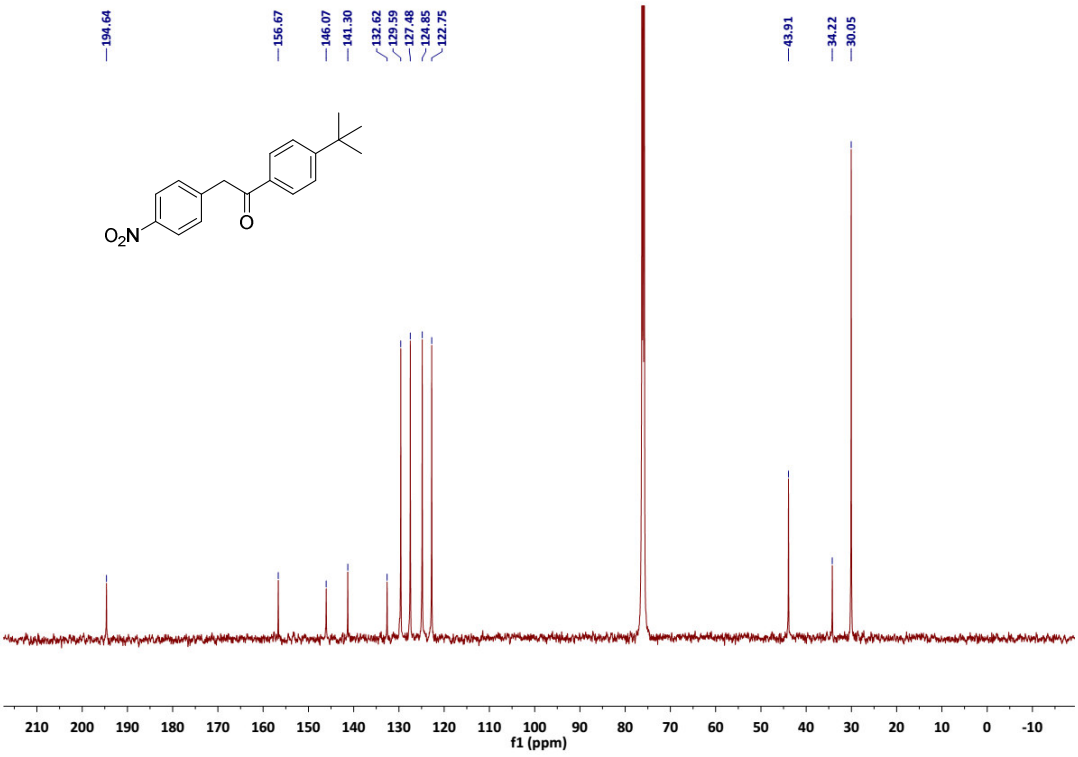
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3p**



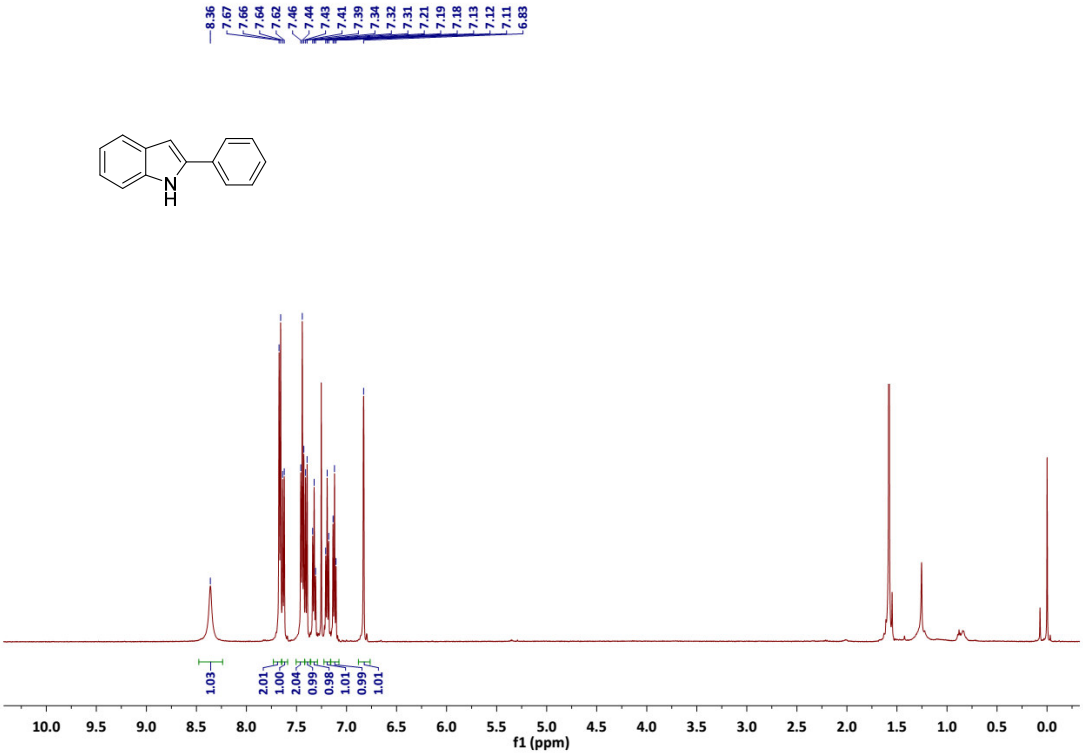
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3p**



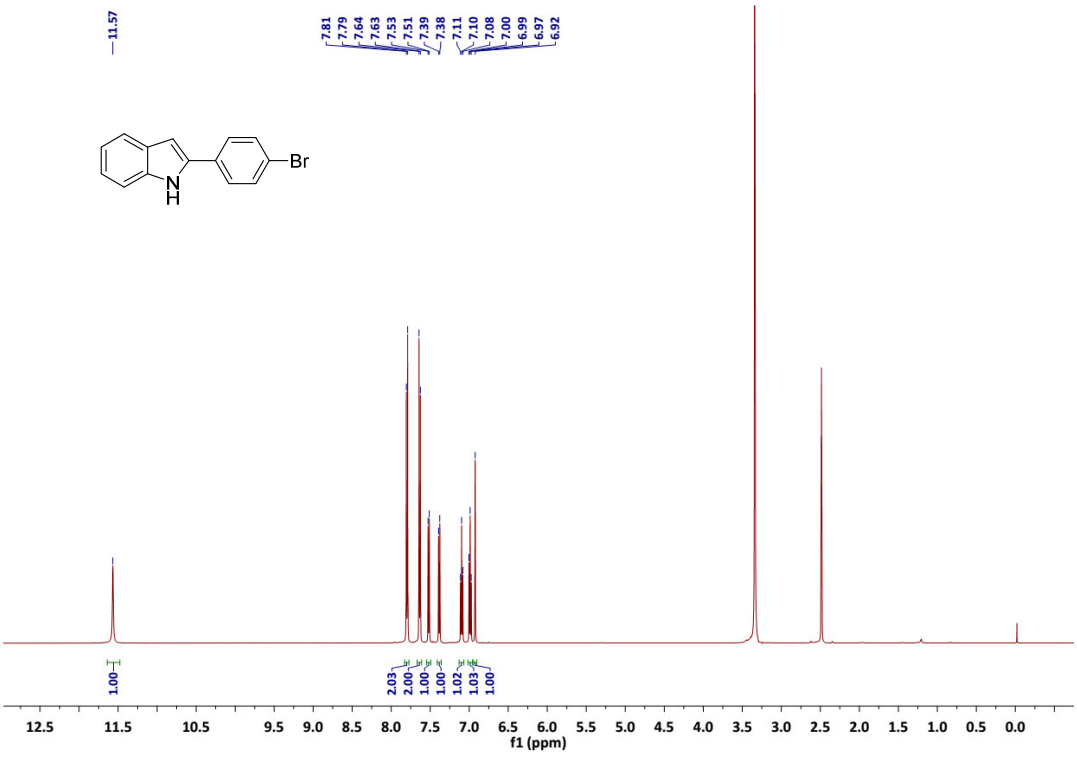
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3q**



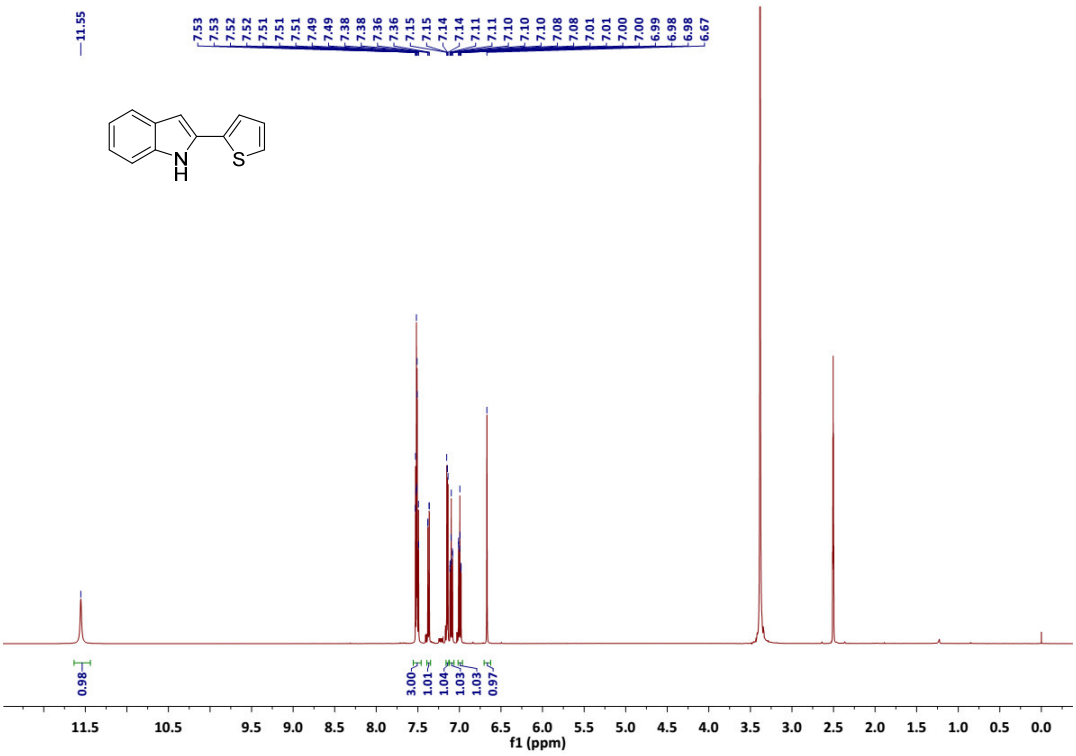
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3q**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **6a**



^{1}H NMR spectrum (500 MHz, DMSO) of **6b**



^{1}H NMR spectrum (500 MHz, DMSO) of **6c**