Supporting Information

Ligand-Enabled Gold-Catalyzed 1,2-Heteroarylation of Alkenes

Akash G. Tathe, Chetan C. Chintawar, Vivek W. Bhoyare and Nitin T. Patil*

Contents

1. General Information:

1.1 Practical considerations:

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under nitrogen atmosphere. Gold-catalyzed heteroarylation reactions were performed in 2.5 mL glass vials with a PTFE-lined cap, whereas all other reactions were performed in round-bottom flasks with rubber septa. All experiments were monitored by analytical thin layer chromatography (TLC). The TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining iodine, potassium permanganate solution and charring on a hot plate. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in petroleum ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

1.2 Materials:

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. DCM, DCE, and petroleum ether were dried by using standard protocol under nitrogen atmosphere. Gold and silver salts were purchased from Sigma-Aldrich and stored under nitrogen atmosphere.

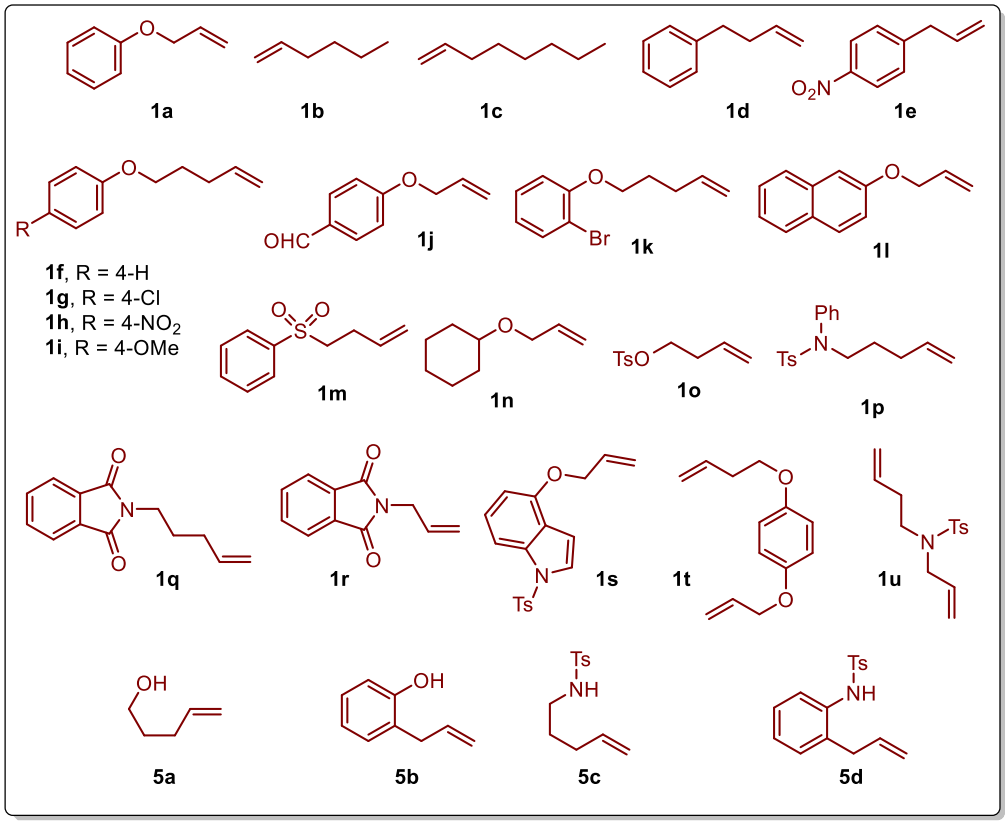
1.3 Instrumentation:

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on Bruker Avance III, 400, 500 and 700 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^{1}H NMR signals are designated as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), dq (doublet of quartet), ddd (doublet of doublet of doublet), dtd (doublet of triplet of doublet), dddd (doublet of doublet of doublet of doublet), tdd (triplet of

doublet of doublet), q (quartet), qd (quartet of doublet), quin (quintet), br.s. (broad singlet), m (multiplet), etc. HRMS data were recorded on a Bruker Daltonics MicroTOF-Q-II with Electron Spray Ionization (ESI). Single crystal X-ray diffraction measurements were carried out on Bruker D8 Venture Dual source X-ray diffractometer and Bruker APEX-II CCD systems.

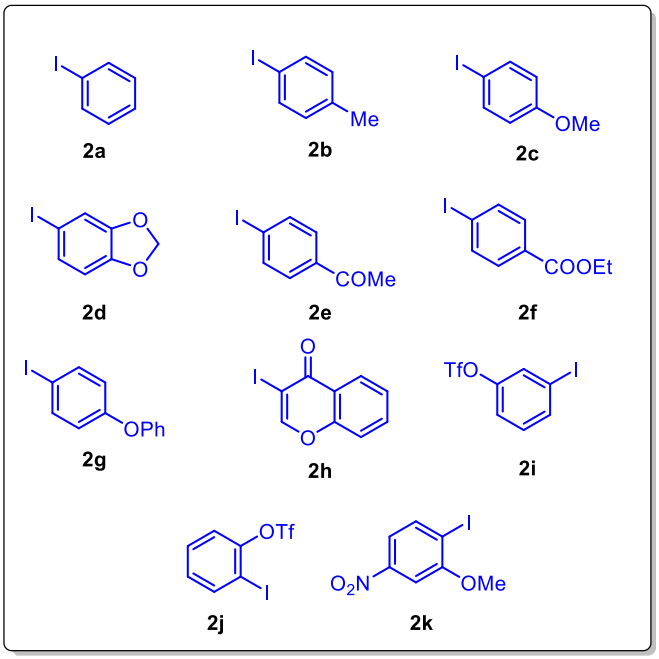
2. Synthesis of starting materials:

2.1 Synthesis of alkenes:



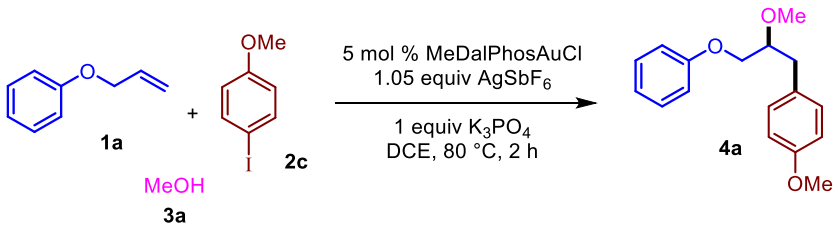
Alkenes	Sources
1b, 1c and 5a	Commercially available
1a, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1l, 1m, 1n, 1o,1p 1q, 1r, 1s, 1t, 1u, 5b, 5c and 5d	Reported in the literature. Prepared by the literature known procedures

2.2 Synthesis of aryl iodide:



Aryl iodide	Sources
2a, 2b, 2c and 2e	Commercially available
2d, 2f, 2g, 2h, 2i, 2j and 2k	Reported in the literature. Prepared by the literature known procedures

3. Gold-catalyzed three-component 1,2-oxyarylation of alkenes:

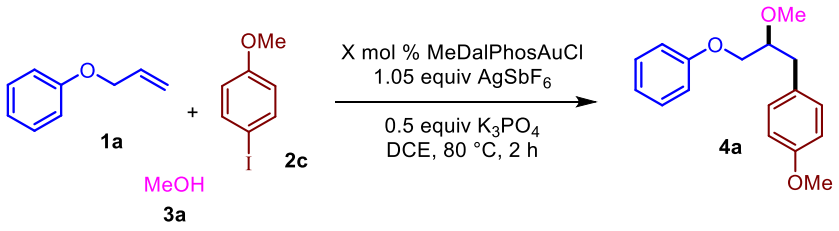


An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the (allyloxy)benzene (**1a**, 1 equiv, 0.2 mmol), 4-iodoanisole (**2a**, 1 equiv, 0.2 mmol), (Me-DalPhos)AuCl (0.05 equiv, 0.01 mmol), K_3PO_4 (1 equiv, 0.2 mmol), methanol (**3a**, 10 equiv, 2

mmol) and 1,2-dichloroethane (DCE) (0.1 M). The resulting reaction mixture was stirred at room temperature for 5 min then $AgSbF_6$ (1.05 equiv, 0.21 mmol) was added and allowed to stir at 80 °C for 2 h. After completion of the reaction, it was diluted with DCM (5 mL), filtered through a short pad of celite, concentrated and subsequently purified by silica gel column chromatography to afford the desired 1,2- oxyrylation product **4a** in 75% yield. The optimization studies are given below.

3.1 Optimization studies:

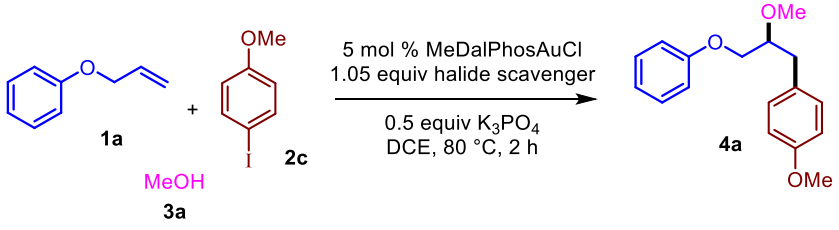
a) Effect of catalyst loading:[a]



Sr.no	X	Yield %[b]
1	2.5	48
2	1	20

[a]Reaction conditions: 0.2 mmol **1a**, 0.2 mmol **2a**, 2 mmol **3a**, x mol % (Me-DalPhos)AuCl, 0.21 mmol $AgSbF_6$, 0.1 mmol K_3PO_4, DCE (0.1 M), 80 ºC, 2 h. [b]Isolated yields.

b) Effect of halide scavengers:[a]

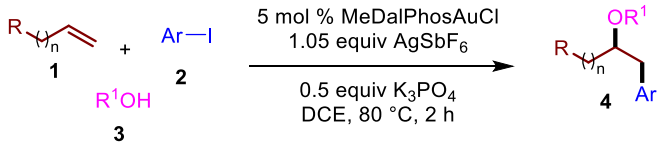


Sr.no	Halide scavenger	Yield %[b]

1	AgOTf	--[c]
2	$AgNTf_2$	--[c]
3	$AgBF_4$	52
4	$AgPF_6$	--[c]
5	AgOTs	--[c]
6	AgOAc	--[c]
7	NaBArF	--[c]

[a]Reaction conditions: 0.2 mmol **1a**, 0.2 mmol **2a**, 2 mmol **3a**, 5 mol % (Me-DalPhos)AuCl, 0.21 mmol halide scavenger, 0.1 mmol K_3PO_4, DCE (0.1 M), 80 ºC, 2 h. [b]Isolated yields. [C] no reaction

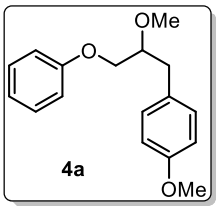
4. General procedure for the gold-catalyzed three-component 1,2-oxyarylation of alkenes:



An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the aryl iodide (**2**, 1 equiv, 0.2 mmol), alkene (**1**, 1 equiv, 0.2 mmol), (MeDalPhos)AuCl (0.05 equiv, 0.01 mmol), K_3PO_4 (0.5 equiv, 0.1 mmol), alcohol (**3**, 10 equiv, 2 mmol) and 1,2-dichloroethane (DCE) (0.1 M). The resulting reaction mixture was stirred at room temperature for 5 min then $AgSbF_6$ (1.05 equiv, 0.21 mmol) was added and allowed to stir at 80 °C for 2 h. After completion of the reaction, it was diluted with DCM (5 mL), filtered through a short pad of celite, concentrated and subsequently purified by silica gel column chromatography to afford the desired 1,2-oxyarylation product **4**.

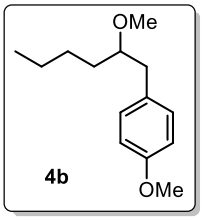
- **Characterization data:**

1-Methoxy-4-(2-methoxy-3-phenoxypropyl)benzene (4a):



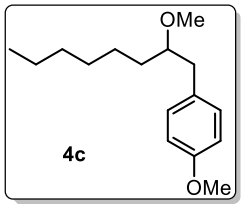
Colourless liquid, 40 mg, 75% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (500MHz, CHLOROFORM-d)** δ = 7.31 - 7.26 (m, 2 H), 7.19 - 7.15 (m, *J* = 8.4 Hz, 2 H), 6.96 (t, *J* = 7.4 Hz, 1 H), 6.93 - 6.88 (m, *J* = 8.2 Hz, 2 H), 6.84 (d, *J* = 8.4 Hz, 2 H), 4.00 - 3.90 (m, 2 H), 3.80 (s, 3 H), 3.76 - 3.70 (m, 1 H), 3.47 (s, 3 H), 2.93 (d, *J* = 6.4 Hz, 2 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.7, 158.1, 130.4, 130.0, 129.4, 120.8, 114.6, 113.8, 80.7, 68.3, 57.9, 55.2, 36.5; **HRMS (ESI)** calcd for $C_{17}H_{20}O_3$ $(M + Na)^+$ 295.1305, found 295.1313;

1-Methoxy-4-(2-methoxyhexyl)benzene (4b):



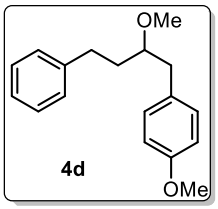
Colourless liquid, 24 mg, 54% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 98/02); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.15 - 7.10 (m, 2 H), 6.86 - 6.81 (m, 2 H), 3.80 (s, 3 H), 3.37 - 3.28 (m, 4 H), 2.78 (dd, *J* = 6.2, 13.8 Hz, 1 H), 2.66 (dd, *J* = 6.1, 13.9 Hz, 1 H), 1.54 - 1.39 (m, 3 H), 1.35 - 1.25 (m, 3 H), 0.92 - 0.86 (m, 3 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 157.9, 131.2, 130.3, 113.6, 82.5, 56.9, 55.2, 39.1, 33.1, 27.5, 22.8, 14.1; **HRMS (ESI)** calcd for $C_{14}H_{22}O_2$ $(M + Na)^+$ 245.1512, found 245.1483.

1-Methoxy-4-(2-methoxyoctyl)benzene (4c):



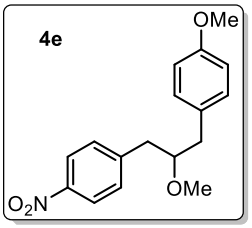
Colourless liquid, 29 mg, 58% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 98/02); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.15 - 7.10 (m, 2 H), 6.87 - 6.81 (m, 2 H), 3.80 (s, 3 H), 3.34 - 3.29 (m, 4 H), 2.78 (dd, *J* = 6.1, 13.9 Hz, 1 H), 2.66 (dd, *J* = 6.1, 13.9 Hz, 1 H), 1.44 (d, *J* = 5.3 Hz, 3 H), 1.35 - 1.24 (m, 7 H), 0.88 (t, *J* = 6.9 Hz, 3 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 157.9, 131.2, 130.3, 113.6, 82.5, 56.9, 55.2, 39.1, 33.4, 31.8, 29.4, 25.3, 22.6, 14.1; **HRMS (ESI)** calcd for $C_{16}H_{26}O_2$ $(M + Na)^+$ 273.1825, found 273.1847.

1-Methoxy-4-(2-methoxy-4-phenylbutyl)benzene (4d):



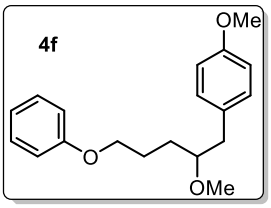
Colourless liquid, 35 mg, 66% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (400 MHz, CHLOROFORM-d)** δ = 7.33 - 7.26 (m, 2 H), 7.23 - 7.16 (m, 3 H), 7.15 - 7.10 (m, *J* = 8.7 Hz, 2 H), 6.88 - 6.83 (m, 2 H), 3.82 (s, 3 H), 3.46 - 3.31 (m, 4 H), 2.90 - 2.61 (m, 4 H), 1.82 - 1.73 (m, 2 H); **^{13}C NMR (100 MHz, CHLOROFORM-d)** δ = 158.0, 142.3, 130.8, 130.3, 128.4, 128.3, 125.7, 113.7, 81.6, 57.0, 55.2, 39.0, 35.3, 31.6; **HRMS (ESI)** calcd for $C_{18}H_{22}O_2$ $(M + Na)^+$ 293.1512, found 293.1505.

1-Methoxy-4-(2-methoxy-3-(4-nitrophenyl)propyl)benzene (4e):



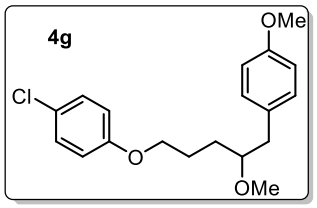
Colourless liquid, 45 mg, 75% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 8.17 - 8.11 (m, 2 H), 7.37 - 7.33 (m, *J* = 8.7 Hz, 2 H), 7.15 - 7.09 (m, 2 H), 6.88 - 6.83 (m, 2 H), 3.81 (s, 3 H), 3.62 - 3.56 (m, 1 H), 3.26 (s, 3 H), 2.90 - 2.82 (m, 2 H), 2.81 - 2.76 (m, 1 H), 2.68 (dd, *J* = 6.3, 14.0 Hz, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.2, 147.2, 146.5, 130.3, 130.2, 130.1, 123.3, 113.8, 83.0, 57.5, 55.2, 39.9, 39.1; **HRMS (ESI)** calcd for $C_{17}H_{19}NO_4$ $(M + H)^+$ 302.1419, found 302.1423.

1-Methoxy-4-(2-methoxy-5-phenoxypentyl)benzene (4f):



Colourless liquid, 32 mg, 56% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 98/02); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.31 - 7.26 (m, 2 H), 7.17 - 7.12 (m, *J* = 8.4 Hz, 2 H), 6.97 - 6.92 (m, 1 H), 6.91 - 6.87 (m, 2 H), 6.87 - 6.83 (m, *J* = 8.4 Hz, 2 H), 3.96 (dt, *J* = 3.1, 6.4 Hz, 2 H), 3.81 (s, 3 H), 3.41 (dd, *J* = 4.7, 6.3 Hz, 1 H), 3.36 (s, 3 H), 2.85 (dd, *J* = 6.0, 13.9 Hz, 1 H), 2.70 (dd, *J* = 6.3, 13.8 Hz, 1 H), 2.00 - 1.91 (m, 1 H), 1.87 - 1.78 (m, 1 H), 1.73 - 1.65 (m, 1 H), 1.62 - 1.50 (m, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 159.0, 158.0, 130.8, 130.3, 129.4, 120.5, 114.5, 113.7, 82.1, 67.8, 57.0, 55.2, 39.0, 29.9, 25.2; **HRMS (ESI)** calcd for $C_{19}H_{24}O_3$ $(M + Na)^+$ 323.1618, found 323.1636.

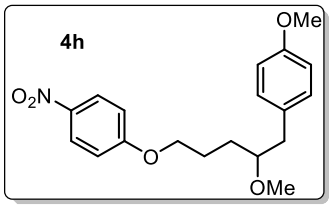
1-Chloro-4-((4-methoxy-5-(4-methoxyphenyl)pentyl)oxy)benzene (4g):



Colourless liquid, 47 mg, 71% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 98/02); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.24 - 7.20 (m, 2 H), 7.15 - 7.11 (m, 2 H), 6.87 - 6.83 (m, 2 H), 6.82 - 6.78 (m, 2 H), 3.91 (dt, *J* = 1.8, 6.5 Hz, 2 H), 3.81 (s, 3 H), 3.43 - 3.38 (m, 1 H), 3.36 (s, 3 H), 2.85 (dd, *J* = 5.8, 13.9 Hz, 1 H), 2.68 (dd, *J* = 6.5, 13.8 Hz, 1 H), 1.98 - 1.89 (m, 1 H),

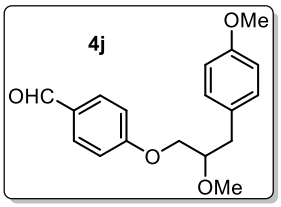
1.85 - 1.75 (m, 1 H), 1.68 - 1.61 (m, 1 H), 1.59 - 1.50 (m, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.0, 157.6, 130.7, 130.3, 129.2, 125.3, 115.7, 113.7, 82.0, 68.2, 57.0, 55.2, 39.0, 29.8, 25.1; **HRMS (ESI)** calcd for $C_{19}H_{23}ClO_3$ $(M + Na)^+$ 357.1228, found 357.1241.

1-Methoxy-4-(2-methoxy-5-(4-nitrophenoxy)pentyl)benzene (4h):



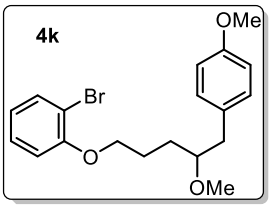
Colourless liquid, 40 mg, 61% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 8.21 - 8.16 (m, 2 H), 7.14 - 7.09 (m, 2 H), 6.94 - 6.89 (m, 2 H), 6.86 - 6.81 (m, 2 H), 4.07 - 4.00 (m, 2 H), 3.80 (s, 3 H), 3.44 - 3.38 (m, 1 H), 3.37 (s, 3 H), 2.87 (dd, *J* = 5.6, 13.9 Hz, 1 H), 2.67 (dd, *J* = 6.7, 13.7 Hz, 1 H), 2.03 - 1.93 (m, 1 H), 1.90 - 1.79 (m, 1 H), 1.71 - 1.62 (m, 1 H), 1.54 (dddd, *J* = 5.3, 7.7, 10.2, 14.0 Hz, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 164.1, 158.0, 141.3, 130.5, 130.3, 125.8, 114.4, 113.7, 81.9, 68.8, 57.0, 55.2, 38.9, 29.7, 24.9; **HRMS (ESI)** calcd for $C_{19}H_{23}NO_5$ $(M + Na)^+$ 368.1468, found 368.1476.

4-((4-methoxy-5-(4-methoxyphenyl)pentyl)oxy)benzaldehyde (4j):



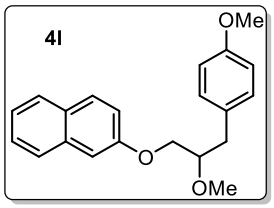
Colourless liquid, 32 mg, 56% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 98/02); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 9.89 (s, 1 H), 7.83 (d, *J* = 8.9 Hz, 2 H), 7.20 - 7.08 (m, *J* = 8.7 Hz, 2 H), 7.01 - 6.96 (m, *J* = 8.7 Hz, 2 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 4.10 - 3.91 (m, 2 H), 3.79 (s, 3 H), 3.76 - 3.72 (m, 1 H), 3.47 (s, 3 H), 2.99 - 2.86 (m, 2 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 190.8, 163.8, 158.3, 131.9, 130.3, 130.1, 129.6, 114.8, 113.9, 80.5, 68.8, 58.0, 55.2, 36.3; **HRMS (ESI)** calcd for $C_{18}H_{20}O_4$ $(M + Na)^+$ 323.1254, found 323.1269.

1-Bromo-2-((4-methoxy-5-(4-methoxyphenyl)pentyl)oxy)benzene (4k)



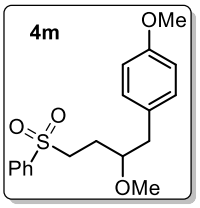
Colourless liquid, 48 mg, 65% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.15 - 7.11 (m, 3 H), 7.08 - 7.05 (m, 1 H), 7.03 (t, *J* = 2.1 Hz, 1 H), 6.87 - 6.84 (m, 2 H), 6.80 (ddd, *J* = 1.1, 2.4, 8.2 Hz, 1 H), 3.95 - 3.91 (m, 2 H), 3.81 (s, 3 H), 3.43 - 3.38 (m, 1 H), 3.36 (s, 3 H), 2.85 (dd, *J* = 5.8, 13.9 Hz, 1 H), 2.68 (dd, *J* = 6.5, 13.8 Hz, 1 H), 1.97 - 1.88 (m, 1 H), 1.85 - 1.77 (m, 1 H), 1.70 - 1.64 (m, 1 H), 1.58 - 1.49 (m, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 159.8, 158.0, 130.7, 130.4, 130.3, 123.6, 122.7, 117.7, 113.7, 113.5, 82.0, 68.2, 57.0, 55.2, 39.0, 29.8, 25.0; **HRMS (ESI)** calcd for $C_{19}H_{23}BrO_3$ $(M + Na)^+$ 401.0723, found 401.0736.

2-(2-Methoxy-3-(4-methoxyphenyl)propoxy)naphthalene (4l):



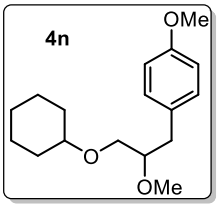
Colourless liquid, 42 mg, 66% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.79 (d, *J* = 8.2 Hz, 2 H), 7.70 (d, *J* = 8.1 Hz, 1 H), 7.45 (ddd, *J* = 1.2, 6.9, 8.2 Hz, 1 H), 7.36 (ddd, *J* = 1.1, 6.9, 8.1 Hz, 1 H), 7.25 - 7.18 (m, 3 H), 7.06 (d, *J* = 2.4 Hz, 1 H), 6.91 - 6.83 (m, 2 H), 4.12 (dd, *J* = 4.0, 10.0 Hz, 1 H), 4.05 (dd, *J* = 5.1, 10.0 Hz, 1 H), 3.83 - 3.79 (m, 4 H), 3.52 (s, 3 H), 2.99 (d, *J* = 6.6 Hz, 2 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.1, 156.7, 134.4, 130.4, 129.9, 129.3, 129.0, 127.6, 126.7, 126.3, 123.6, 119.0, 113.8, 106.6, 80.7, 68.3, 57.9, 55.2, 36.5; **HRMS (ESI)** calcd for $C_{21}H_{22}O_3$ $(M + Na)^+$ 345.1461, found 345.1474.

1-Methoxy-4-(2-methoxy-4-(phenylsulfonyl)butyl)benzene (4m):



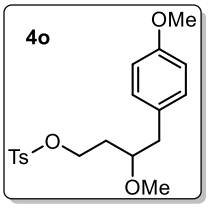
Colourless liquid, 35 mg, 53% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.86 - 7.83 (m, 2 H), 7.67 - 7.62 (m, 1 H), 7.56 - 7.52 (m, 2 H), 7.05 - 7.01 (m, 2 H), 6.83 - 6.79 (m, 2 H), 3.80 (s, 3 H), 3.46 - 3.41 (m, 1 H), 3.28 (s, 3 H), 3.11 (s, 2 H), 2.82 (dd, *J* = 5.5, 13.9 Hz, 1 H), 2.54 (dd, *J* = 7.1, 13.8 Hz, 1 H), 1.99 - 1.90 (m, 1 H), 1.71 (dddd, *J* = 5.3, 8.0, 10.2, 14.1 Hz, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.2, 139.0, 133.6, 130.2, 129.5, 129.2, 128.0, 113.9, 80.0, 57.0, 55.2, 52.4, 38.7, 26.3; **HRMS (ESI)** calcd for $C_{18}H_{22}O_4S$ $(M + Na)^+$ 357.1131, found 357.1144.

1-(3-(Cyclohexyloxy)-2-methoxypropyl)-4-methoxybenzene (4n):



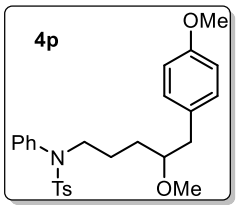
Colourless liquid, 30 mg, 55% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.17 - 7.12 (m, *J* = 8.7 Hz, 2 H), 6.86 - 6.81 (m, *J* = 8.7 Hz, 2 H), 3.80 (s, 3 H), 3.51 - 3.43 (m, 2 H), 3.39 (s, 3 H), 3.23 - 3.16 (m, 1 H), 2.85 - 2.73 (m, 2 H), 1.94 - 1.85 (m, 2 H), 1.74 (dd, *J* = 3.3, 8.0 Hz, 2 H), 1.65 - 1.60 (m, 1 H), 1.54 (br. s., 1 H), 1.33 - 1.19 (m, 5 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 157.9, 130.8, 130.4, 113.6, 81.7, 78.1, 68.7, 57.7, 55.2, 36.6, 32.2, 25.8, 24.1; **HRMS (ESI)** calcd for $C_{17}H_{26}O_3$ $(M + Na)^+$ 301.1774, found 301.1788.

3-Methoxy-4-(4-methoxyphenyl)butyl 4-methylbenzenesulfonate (4o):



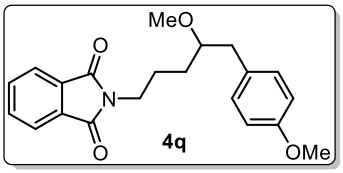
Colourless liquid, 38 mg, 56% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.79 - 7.75 (m, 2 H), 7.36 - 7.31 (m, *J* = 7.9 Hz, 2 H), 7.07 - 7.03 (m, 2 H), 6.84 - 6.80 (m, 2 H), 4.14 (dt, *J* = 5.3, 9.2 Hz, 1 H), 4.07 (ddd, *J* = 4.7, 6.1, 9.7 Hz, 1 H), 3.79 (s, 3 H), 3.46 - 3.40 (m, 1 H), 3.23 (s, 3 H), 2.76 (dd, *J* = 5.6, 13.9 Hz, 1 H), 2.62 (dd, *J* = 6.6, 13.9 Hz, 1 H), 2.44 (s, 3 H), 1.80 (dddd, *J* = 3.4, 6.2, 8.6, 14.7 Hz, 1 H), 1.67 - 1.57 (m, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.1, 144.6, 133.0, 130.3, 129.7, 127.8, 113.7, 77.9, 67.5, 57.2, 55.1, 38.7, 33.2, 21.5; **HRMS (ESI)** calcd for $C_{19}H_{24}O_5S$ $(M + Na)^+$ 387.1237, found 387.1245.

N-(4-methoxy-5-(4-methoxyphenyl)pentyl)-4-methyl-N-phenylbenzenesulfonamide (4p):



Colourless liquid, 62 mg, 69% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.47 - 7.43 (m, *J* = 8.2 Hz, 2 H), 7.31 - 7.27 (m, 3 H), 7.25 - 7.22 (m, *J* = 8.1 Hz, 2 H), 7.07 - 7.03 (m, 2 H), 7.01 - 6.96 (m, 2 H), 6.84 - 6.80 (m, 2 H), 3.80 (s, 3 H), 3.56 - 3.46 (m, 2 H), 3.31 - 3.27 (m, 1 H), 3.27 - 3.24 (m, 3 H), 2.75 (dd, *J* = 6.0, 13.9 Hz, 1 H), 2.55 (dd, *J* = 6.6, 13.9 Hz, 1 H), 2.42 (s, 3 H), 1.57 - 1.35 (m, 4 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 157.9, 143.2, 139.0, 135.2, 130.7, 130.2, 129.3, 128.9, 128.7, 127.7, 113.7, 81.7, 56.8, 55.2, 55.2, 50.4, 38.9, 29.9, 24.0, 21.5; **HRMS (ESI)** calcd for $C_{26}H_{31}NO_4S$ $(M + Na)^+$ 476.1866, found 476.1867.

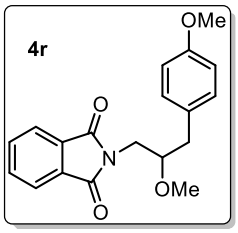
2-(4-Methoxy-5-(4-methoxyphenyl)pentyl)isoindoline-1,3-dione (4q):



White solid, 42 mg, 60% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.85 - 7.80 (m, 2 H), 7.74 - 7.68 (m, 2 H), 7.11 - 7.05 (m, 2 H),

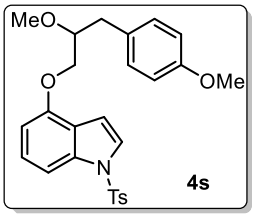
6.81 - 6.76 (m, 2 H), 3.76 (s, 3 H), 3.71 - 3.63 (m, 2 H), 3.39 - 3.33 (m, 1 H), 3.31 (s, 3 H), 2.78 (dd, *J* = 6.0, 13.9 Hz, 1 H), 2.62 (dd, *J* = 6.4, 13.7 Hz, 1 H), 1.91 - 1.79 (m, 1 H), 1.73 - 1.64 (m, 1 H), 1.56 - 1.41 (m, 2 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 168.3, 157.9, 133.8, 132.1, 130.6, 130.2, 123.1, 113.6, 81.8, 57.1, 55.1, 39.0, 37.9, 30.5, 24.4; **HRMS (ESI)** calcd for $C_{21}H_{23}NO_4$ $(M + Na)^+$ 376.1519, found 376.1533.

2-(2-Methoxy-3-(4-methoxyphenyl)propyl)isoindoline-1,3-dione (4r):



White solid, 36 mg, 55% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.86 - 7.82 (m, 2 H), 7.73 - 7.69 (m, 2 H), 7.18 - 7.15 (m, *J* = 8.5 Hz, 2 H), 6.82 - 6.78 (m, *J* = 8.7 Hz, 2 H), 3.85 - 3.78 (m, 2 H), 3.76 (s, 3 H), 3.74 - 3.67 (m, 1 H), 3.30 (s, 3 H), 2.88 - 2.82 (m, 1 H), 2.78 - 2.73 (m, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 168.3, 157.9, 133.8, 132.1, 130.6, 130.2, 123.1, 113.6, 81.8, 57.1, 55.1, 37.9, 24.4; **HRMS (ESI)** calcd for $C_{19}H_{19}NO_4$ $(M + Na)^+$ 348.1206, found 348.1221.

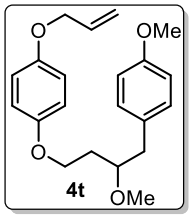
4-(2-Methoxy-3-(4-methoxyphenyl)propoxy)-1-tosyl-1H-indole (4s):



Colourless liquid, 51 mg, 55% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.78 - 7.74 (m, 2 H), 7.59 (d, *J* = 8.4 Hz, 1 H), 7.48 (d, *J* = 3.7 Hz, 1 H), 7.24 - 7.17 (m, 3 H), 7.14 (d, *J* = 8.5 Hz, 2 H), 6.84 - 6.78 (m, 3 H), 6.56 (d, *J* = 8.1 Hz, 1 H), 4.02 (dq, *J* = 4.8, 9.9 Hz, 2 H), 3.79 - 3.75 (m, 4 H), 3.45 (s, 3 H), 2.92 (d, *J* = 6.4 Hz, 2 H), 2.35 (s, 3 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.2, 152.2, 144.9, 136.2, 135.3, 130.4, 129.9, 129.8, 126.8, 125.5, 124.8, 121.3, 113.8, 106.7, 106.2, 104.4, 80.7, 69.0,

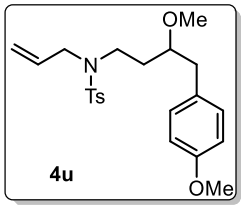
58.1, 55.2, 36.7, 21.5; **HRMS (ESI)** calcd for $C_{26}H_{27}NO_5S$ $(M + Na)^+$ 488.1502, found 488.1529.

1-(Allyloxy)-4-(3-methoxy-4-(4-methoxyphenyl)butoxy)benzene (4t):



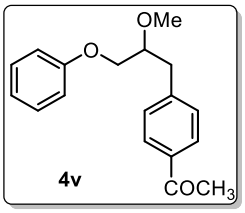
Colourless liquid, 18 mg, 48% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.16 (d, *J* = 8.5 Hz, 2 H), 6.85 - 6.81 (m, 6 H), 5.91 (tdd, *J* = 6.7, 10.3, 17.1 Hz, 1 H), 5.20 - 5.09 (m, 2 H), 3.99 - 3.95 (m, 2 H), 3.94 - 3.83 (m, 2 H), 3.80 (s, 3 H), 3.73 - 3.63 (m, 1 H), 3.45 (s, 3 H), 2.91 (d, *J* = 6.4 Hz, 2 H), 2.56 - 2.50 (m, 2 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.1, 153.2, 153.0, 134.6, 130.4, 130.1, 116.9, 115.5, 113.8, 80.8, 69.1, 67.9, 57.8, 55.2, 36.5, 33.7; **HRMS (ESI)** calcd for $C_{21}H_{26}O_4$ $(M + Na)^+$ 365.1723, found 365.1733.

N-allyl-N-(3-methoxy-4-(4-methoxyphenyl)butyl)-4-methylbenzenesulfonamide (4u):



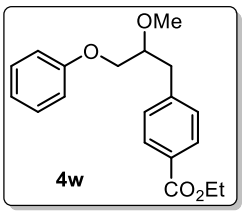
Colourless liquid, 35 mg, 43% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.67 (d, *J* = 8.2 Hz, 2 H), 7.29 (s, 2 H), 7.11 - 7.07 (m, *J* = 8.5 Hz, 2 H), 6.85 - 6.82 (m, *J* = 8.5 Hz, 2 H), 5.54 (tdd, *J* = 6.4, 10.3, 16.9 Hz, 1 H), 5.11 - 5.04 (m, 2 H), 3.80 (s, 3 H), 3.71 (dd, *J* = 1.3, 6.5 Hz, 2 H), 3.44 - 3.38 (m, 1 H), 3.35 - 3.32 (m, 3 H), 3.32 - 3.26 (m, 1 H), 3.11 (ddd, *J* = 5.0, 8.9, 13.9 Hz, 1 H), 2.81 (dd, *J* = 5.6, 13.8 Hz, 1 H), 2.61 (dd, *J* = 6.8, 13.8 Hz, 1 H), 2.42 (s, 3 H), 1.75 - 1.68 (m, 2 H), 1.55 (dtd, *J* = 4.9, 8.5, 13.6 Hz, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.0, 143.1, 136.9, 133.2, 130.3, 129.6, 127.1, 118.6, 113.7, 79.5, 56.8, 55.2, 50.7, 44.0, 38.6, 31.9, 21.4; **HRMS (ESI)** calcd for $C_{22}H_{29}NO_4S$ $(M + Na)^+$ 426.1710, found 426.1730.

1-(4-(2-Methoxy-3-phenoxypropyl)phenyl)ethan-1-one (4v):



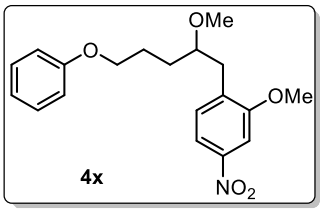
Colourless liquid, 34 mg, 60% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.92 - 7.88 (m, 2 H), 7.37 - 7.34 (m, *J* = 8.2 Hz, 2 H), 7.32 - 7.26 (m, 2 H), 6.97 (t, *J* = 7.4 Hz, 1 H), 6.91 (dd, *J* = 0.8, 8.6 Hz, 2 H), 3.95 (d, *J* = 4.9 Hz, 2 H), 3.82 - 3.76 (m, 1 H), 3.44 (s, 3 H), 3.11 - 2.99 (m, 2 H), 2.59 (s, 3 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 197.8, 158.6, 144.0, 135.5, 129.7, 129.5, 128.4, 121.0, 114.5, 80.2, 68.2, 58.0, 37.7, 26.5; **HRMS (ESI)** calcd for $C_{18}H_{20}O_3$ $(M + Na)^+$ 307.1305, found 307.1316.

Ethyl 4-(2-methoxy-3-phenoxypropyl)benzoate (4w):



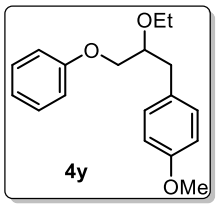
Colourless liquid, 34 mg, 54% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 8.00 - 7.96 (m, 2 H), 7.34 - 7.32 (m, 2 H), 7.31 - 7.27 (m, 2 H), 6.99 - 6.95 (m, 1 H), 6.90 (dd, *J* = 0.8, 8.6 Hz, 2 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 3.95 (d, *J* = 4.7 Hz, 2 H), 3.80 - 3.76 (m, 1 H), 3.44 (s, 3 H), 3.09 - 2.99 (m, 2 H), 1.40 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 166.6, 158.6, 143.5, 129.7, 129.6, 129.4, 128.7, 121.0, 114.5, 80.3, 68.2, 60.8, 58.0, 37.7, 14.3; **HRMS (ESI)** calcd for $C_{19}H_{22}O_4$ $(M + Na)^+$ 337.1410, found 337.1391.

2-Methoxy-1-(2-methoxy-5-phenoxypentyl)-4-nitrobenzene (4x):



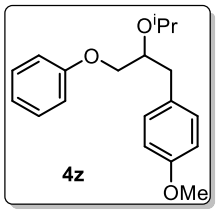
Colourless liquid, 38 mg, 56% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.81 (dd, *J* = 2.3, 8.2 Hz, 1 H), 7.70 (d, *J* = 2.1 Hz, 1 H), 7.33 (d, *J* = 8.2 Hz, 1 H), 7.31 - 7.27 (m, 2 H), 6.95 (t, *J* = 7.3 Hz, 1 H), 6.90 - 6.85 (m, 2 H), 3.99 - 3.95 (m, 2 H), 3.93 (s, 3 H), 3.57 - 3.48 (m, 1 H), 3.33 (s, 3 H), 2.98 (dd, *J* = 6.4, 13.4 Hz, 1 H), 2.85 (dd, *J* = 6.0, 13.4 Hz, 1 H), 2.00 - 1.92 (m, 1 H), 1.88 - 1.81 (m, 1 H), 1.72 - 1.62 (m, 2 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.9, 157.7, 147.6, 135.5, 131.4, 129.4, 120.6, 115.7, 114.4, 105.1, 79.9, 67.6, 57.1, 55.8, 34.8, 30.4, 25.1; **HRMS (ESI)** calcd for $C_{19}H_{23}NO_5$ $(M + Na)^+$ 368.1468, found 368.1473.

1-(2-Ethoxy-3-phenoxypropyl)-4-methoxybenzene (4y):



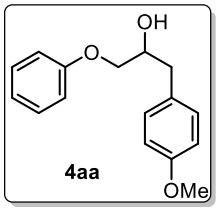
Colourless liquid, 38 mg, 66% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.31 - 7.27 (m, 2 H), 7.20 - 7.16 (m, 2 H), 6.99 - 6.93 (m, 1 H), 6.93 - 6.89 (m, 2 H), 6.86 - 6.82 (m, 2 H), 3.94 (d, *J* = 5.0 Hz, 2 H), 3.80 (s, 4 H), 3.69 - 3.63 (m, 1 H), 3.55 (qd, *J* = 7.0, 9.3 Hz, 1 H), 2.97 - 2.86 (m, 2 H), 1.18 (t, *J* = 7.0 Hz, 3 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.8, 158.1, 130.5, 130.3, 129.4, 120.7, 114.6, 113.7, 79.1, 68.9, 65.7, 55.2, 37.2, 15.5; **HRMS (ESI)** calcd for $C_{18}H_{22}O_3$ $(M + Na)^+$ 309.1461, found 309.1481.

1-(2-Isopropoxy-3-phenoxypropyl)-4-methoxybenzene (4z):



Pale yellow liquid, 35 mg, 58% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.31 - 7.26 (m, 2 H), 7.20 - 7.16 (m, 2 H), 6.95 (t, *J* = 7.3 Hz, 1 H), 6.92 - 6.88 (m, 2 H), 6.86 - 6.82 (m, 2 H), 3.95 - 3.88 (m, 2 H), 3.87 - 3.83 (m, 1 H), 3.80 (s, 3 H), 3.64 (td, *J* = 6.1, 12.2 Hz, 1 H), 2.94 (dd, *J* = 5.5, 13.7 Hz, 1 H), 1.16 (d, *J* = 6.1 Hz, 3 H), 1.02 (d, *J* = 6.1 Hz, 3 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.8, 158.1, 130.6, 130.5, 129.4, 120.7, 114.5, 113.6, 71.4, 69.7, 55.2, 38.1, 22.7, 22.5; **HRMS (ESI)** calcd for $C_{19}H_{24}O_3$ $(M + Na)^+$ 323.1618, found 323.1622.

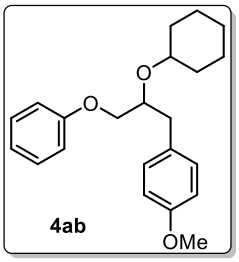
1-(4-Methoxyphenyl)-3-phenoxypropan-2-ol (4aa):[1]



White solid, 27 mg, 53% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.33 - 7.28 (m, 2 H), 7.20 - 7.17 (m, 2 H), 6.98 (t, *J* = 7.3 Hz, 1 H), 6.92 (dd, *J* = 0.9, 8.7 Hz, 2 H), 6.89 - 6.85 (m, 2 H), 4.25 - 4.17 (m, 1 H), 3.98 (dd, *J* = 3.6, 9.4 Hz, 1 H), 3.89 (dd, *J* = 6.7, 9.3 Hz, 1 H), 3.81 (s, 3 H), 2.90 (dd, *J* = 2.2, 6.8 Hz, 2 H), 2.31 (d, *J* = 4.3 Hz, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.5, 158.4, 130.3, 129.5, 129.4, 121.1, 114.6, 114.0, 71.2, 70.9, 55.2, 38.9; **HRMS (ESI)** calcd for $C_{16}H_{18}O_3$ $(M + Na)^+$ 281.1148, found 281.1161.

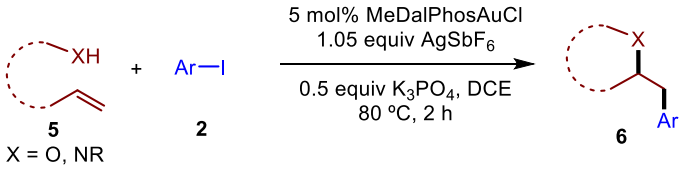
1-(2-(Cyclohexyloxy)-3-phenoxypropyl)-4-methoxybenzene (4ab):

[1] A. Ebrahim-Alkhalil, Z.-Q. Zhang, T.-J. Gong, W. Su, X.-Y. Lu, B. Xiao, Y. Fu, *Chem. Commun.*, 2016, **52**, 4891.



Colourless liquid, 35 mg, 51% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.31 - 7.26 (m, 2 H), 7.20 - 7.17 (m, 2 H), 6.98 - 6.93 (m, 1 H), 6.92 - 6.89 (m, 2 H), 6.86 - 6.82 (m, 2 H), 3.92 - 3.90 (m, 2 H), 3.81 (s, 3 H), 3.34 - 3.27 (m, 1 H), 2.98 - 2.91 (m, 1 H), 2.84 - 2.78 (m, 1 H), 1.93 - 1.85 (m, 1 H), 1.76 - 1.69 (m, 2 H), 1.66 (br. s., 1 H), 1.53 - 1.47 (m, 1 H), 1.35 - 1.11 (m, 6 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.8, 158.0, 130.6, 130.5, 129.4, 120.7, 114.5, 113.6, 69.6, 55.2, 38.2, 33.0, 32.6, 25.7, 24.2, 24.2; **HRMS (ESI)** calcd for $C_{22}H_{28}O_3$ $(M + Na)^+$ 363.1931, found 363.1940.

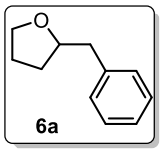
5. General procedure for the gold-catalyzed two-component 1,2-oxy- and 1,2-aminoarylation of alkenes:



An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the alkene (**5**, 1 equiv, 0.2 mmol), aryl iodide (**2**, 1 equiv, 0.2 mmol), (MeDalPhos)AuCl (0.05 equiv, 0.01 mmol), K_3PO_4 (0.5 equiv, 0.1 mmol) and 1,2-dichloroethane (DCE) (0.1 M). The resulting reaction mixture was stirred at room temperature for 5 min then $AgSbF_6$ (1.05 equiv, 0.21 mmol) was added and allowed to stir at 80 °C for 2 h. After completion of the reaction, it was diluted with DCM (5 mL), filtered through a short pad of celite, concentrated and subsequently purified by silica gel column chromatography to afford the desired 1,2-oxy- or 1,2-aminoarylation product **6**.

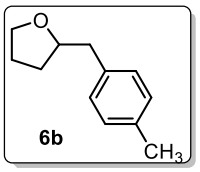
- **Characterization data:**

2-Benzyltetrahydrofuran (6a):[2]



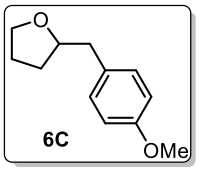
Colourless liquid, 28 mg, 86% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 98/02); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.32 - 7.20 (m, 5 H), 4.08 (quin, *J* = 6.7 Hz, 1 H), 3.94 - 3.88 (m, 1 H), 3.75 (dt, *J* = 6.4, 7.9 Hz, 1 H), 2.94 (dd, *J* = 6.4, 13.6 Hz, 1 H), 2.76 (dd, *J* = 6.6, 13.6 Hz, 1 H), 1.97 - 1.83 (m, 3 H), 11.58 (s, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 139.0, 129.2, 128.3, 126.1, 80.0, 67.9, 41.9, 31.0, 25.6.

2-(4-Methylbenzyl)tetrahydrofuran (6b):[2]



Colourless liquid, 34 mg, 96% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 98/02); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.14 - 7.09 (m, 4 H), 4.05 (quin, *J* = 6.7 Hz, 1 H), 3.94 - 3.87 (m, 1 H), 3.74 (dt, *J* = 6.2, 7.9 Hz, 1 H), 2.90 (dd, *J* = 6.4, 13.6 Hz, 1 H), 2.72 (dd, *J* = 6.6, 13.6 Hz, 1 H), 2.33 (s, 3 H), 1.96 - 1.82 (m, 3 H), 1.61 - 1.52 (m, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 135.9, 135.6, 129.0, 129.0, 80.2, 67.9, 41.5, 30.9, 25.6, 21.0; **HRMS (ESI)** calcd for $C_{12}H_{16}O$ $(M + Na)^+$ 199.1093, found 199.1123.

2-(4-Methoxybenzyl)tetrahydrofuran (6c):[3]

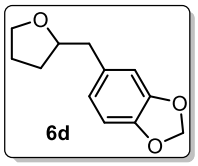


[2] B. Sahoo, M. N. Hopkinson, F. Glorius, *J. Am. Chem. Soc.,* 2013, **135**, 5505.

[3] D. S. Hamilton, D. A. Nicewicz, *J. Am. Chem. Soc*. 2012, **134**, 45, 18577.

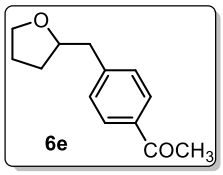
Pale yellow liquid, 37 mg, 96% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.17 - 7.14 (m, *J* = 8.5 Hz, 2 H), 6.86 - 6.83 (m, 2 H), 4.07 - 4.00 (m, 1 H), 3.93 - 3.87 (m, 1 H), 3.79 (s, 3 H), 3.77 - 3.71 (m, 1 H), 2.87 (dd, *J* = 6.4, 13.7 Hz, 1 H), 2.70 (dd, *J* = 6.4, 13.7 Hz, 1 H), 1.95 - 1.82 (m, 3 H), 1.59 - 1.51 (m, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 158.0, 131.0, 130.1, 113.7, 80.2, 67.9, 55.2, 40.9, 30.9, 25.6; **HRMS (ESI)** calcd for $C_{12}H_{16}O_2$ $(M + Na)^+$ 215.1043, found 215.1051.

5-((Tetrahydrofuran-2-yl)methyl)benzo[d][1,3]dioxole (6d):[4]



Colourless liquid, 30 mg, 73% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 6.74 (d, *J* = 7.5 Hz, 2 H), 6.70 - 6.65 (m, 1 H), 5.92 (s, 2 H), 4.02 (quin, *J* = 6.6 Hz, 1 H), 3.89 (q, *J* = 7.1 Hz, 1 H), 3.74 (q, *J* = 7.6 Hz, 1 H), 2.82 (dd, *J* = 6.6, 13.7 Hz, 1 H), 2.68 (dd, *J* = 6.2, 13.7 Hz, 1 H), 1.97 - 1.81 (m, 3 H), 1.59 - 1.49 (m, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 147.4, 145.8, 132.8, 122.0, 109.6, 108.1, 100.7, 80.1, 67.9, 41.5, 30.9, 25.6.

1-(4-((Tetrahydrofuran-2-yl)methyl)phenyl)ethan-1-one (6e):

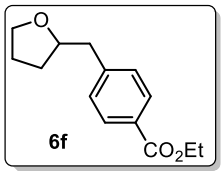


Pale yellow liquid, 19 mg, 57% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.91 - 7.88 (m, 2 H), 7.36 - 7.31 (m, *J* = 8.2 Hz, 2 H), 4.09 (td, *J* = 6.5, 13.6 Hz, 1 H), 3.89 (td, *J* = 6.8, 8.2 Hz, 1 H), 3.77 - 3.71 (m, 1 H), 2.93 (dd, *J* = 6.9, 13.7 Hz, 1 H), 2.84 (dd, *J* = 5.8, 13.6 Hz, 1 H), 2.58 (s, 3 H), 2.00 - 1.92 (m, 1 H), 1.91 - 1.82 (m, 2 H), 1.62 - 1.50 (m, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 197.9,

[4] N. Hoffmann, J.-P. Pete, *J. Org. Chem*. 1997, **62**, 20, 6952.

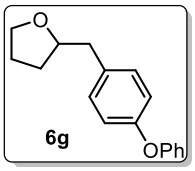
144.8, 135.3, 129.4, 128.4, 79.4, 68.0, 41.8, 31.0, 26.5, 25.6; **HRMS (ESI)** calcd for $C_{13}H_{16}O_2$ $(M + Na)^+$ 227.1043, found 227.1043.

Ethyl 4-((tetrahydrofuran-2-yl)methyl)benzoate (6f):[2]



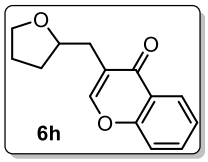
Pale yellow liquid, 22 mg, 56% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500MHz, CHLOROFORM-d)** δ = 7.99 - 7.95 (m, 2 H), 7.32 - 7.28 (m, *J* = 8.2 Hz, 2 H), 4.37 (q, *J* = 7.1 Hz, 2 H), 4.13 - 4.05 (m, 1 H), 3.89 (td, *J* = 6.8, 8.2 Hz, 1 H), 3.77 - 3.70 (m, 1 H), 2.94 (dd, *J* = 6.7, 13.6 Hz, 1 H), 2.83 (dd, *J* = 6.0, 13.6 Hz, 1 H), 1.98 - 1.82 (m, 3 H), 1.60 - 1.51 (m, 1 H), 1.40 - 1.36 (m, 3 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 166.6, 144.3, 129.6, 129.2, 128.5, 79.5, 68.0, 60.8, 41.8, 31.0, 25.6, 14.3; **HRMS (ESI)** calcd for $C_{14}H_{18}O_3$ $(M + Na)^+$ 257.1148, found 257.1175.

2-(4-Phenoxybenzyl)tetrahydrofuran (6g):



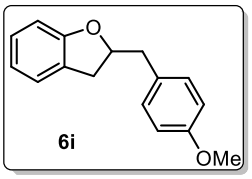
Colourless liquid, 31 mg, 62% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.33 (t, *J* = 7.9 Hz, 2 H), 7.24 - 7.18 (m, *J* = 8.4 Hz, 2 H), 7.12 - 7.06 (m, 1 H), 7.05 - 6.99 (m, 2 H), 6.98 - 6.93 (m, *J* = 8.4 Hz, 2 H), 4.08 (quin, *J* = 6.6 Hz, 1 H), 3.92 (q, *J* = 7.1 Hz, 1 H), 3.81 - 3.73 (m, 1 H), 2.90 (dd, *J* = 6.7, 13.7 Hz, 1 H), 2.76 (dd, *J* = 6.1, 13.7 Hz, 1 H), 2.00 - 1.86 (m, 3 H), 1.62 - 1.53 (m, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 157.5, 155.4, 134.0, 130.4, 129.6, 122.9, 118.9, 118.6, 80.0, 67.9, 41.1, 31.0, 25.6; **HRMS (ESI)** calcd for $C_{17}H_{18}O_2$ $(M + Na)^+$ 277.1199, found 277.1226.

3-((Tetrahydrofuran-2-yl)methyl)-4H-chromen-4-one (6h):



Colourless liquid, 38 mg, 80% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 8.21 (dd, *J* = 1.7, 7.9 Hz, 1 H), 7.93 (s, 1 H), 7.62 (ddd, *J* = 1.7, 7.1, 8.5 Hz, 1 H), 7.41 (d, *J* = 8.4 Hz, 1 H), 7.39 - 7.34 (m, 1 H), 4.16 - 4.08 (m, 1 H), 3.91 - 3.84 (m, 1 H), 3.72 (dt, *J* = 6.3, 8.0 Hz, 1 H), 2.83 (dd, *J* = 4.0, 14.4 Hz, 1 H), 2.51 (dd, *J* = 8.1, 14.5 Hz, 1 H), 2.08 - 2.00 (m, 1 H), 1.92 - 1.80 (m, 2 H), 1.61 - 1.51 (m, 1 H); **^{13}C NMR (125 MHz, CHLOROFORM-d)** δ = 177.7, 156.4, 153.5, 133.2, 125.8, 124.8, 123.8, 121.6, 118.0, 77.2, 67.8, 31.2, 31.1, 25.7; **HRMS (ESI)** calcd for $C_{14}H_{14}O_3$ $(M + H)^+$ 231.1032, found 231.1043.

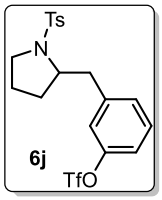
2-(4-Methoxybenzyl)-2,3-dihydrobenzofuran (6i):[5]



Colourless liquid, 28 mg, 58% yield, ***Rf*** = 0.20 (petroleum ether/ethyl acetate = 95/05); **^{1}H NMR (700 MHz, CHLOROFORM-d)** δ = 7.22 - 7.18 (m, 2 H), 7.15 (dd, *J* = 0.9, 7.3 Hz, 1 H), 7.13 - 7.10 (m, 1 H), 6.89 - 6.87 (m, 2 H), 6.83 (dt, *J* = 1.0, 7.4 Hz, 1 H), 6.79 (d, *J* = 8.0 Hz, 1 H), 4.98 (qd, *J* = 7.0, 8.8 Hz, 1 H), 3.81 (s, 3 H), 3.21 (dd, *J* = 8.8, 15.5 Hz, 1 H), 3.13 (dd, *J* = 6.8, 13.9 Hz, 1 H), 2.96 (dd, *J* = 7.5, 15.5 Hz, 1 H), 2.89 (dd, *J* = 6.8, 13.9 Hz, 1 H); **^{13}C NMR (175 MHz, CHLOROFORM-d)** δ = 159.4, 158.3, 130.3, 129.5, 127.9, 126.7, 125.0, 120.2, 113.9, 109.4, 83.7, 55.2, 41.1, 34.8; **HRMS (ESI)** calcd for $C_{16}H_{16}O_2$ $(M + Na)^+$ 263.1043, found 263.1056.

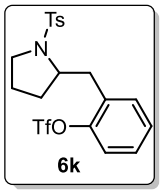
3-((1-Tosylpyrrolidin-2-yl)methyl)phenyl trifluoromethanesulfonate (6j):

[5] J. T. Hutta, J. P. Wolfe, *Org. Chem. Front*., 2016,**3**, 1314.



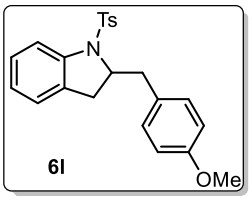
Colourless thick liquid, 78 mg, 84% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, CHLOROFORM-d)** δ = 7.75 (d, *J* = 8.2 Hz, 2 H), 7.43 - 7.37 (m, 1 H), 7.36 - 7.30 (m, 3 H), 7.16 (br. s., 2 H), 3.85 - 3.76 (m, 1 H), 3.42 - 3.29 (m, 1 H), 3.23 (dd, *J* = 3.4, 13.5 Hz, 1 H), 3.14 (td, *J* = 6.8, 9.9 Hz, 1 H), 2.91 (dd, *J* = 8.8, 13.4 Hz, 1 H), 2.44 (s, 3 H), 1.60 - 1.36 (m, 4 H); **^{13}C NMR (175 MHz, CHLOROFORM-d)** δ = 149.5, 143.6, 141.3, 134.3, 130.1, 129.8, 129.7, 127.5, 122.5, 119.3, 60.9, 49.3, 42.2, 30.0, 23.8, 21.5; **HRMS (ESI)** calcd for $C_{19}H_{20}F_3NO_5S_2$ $(M + Na)^+$ 486.0627, found 486.0629.

2-((1-Tosylpyrrolidin-2-yl)methyl)phenyl trifluoromethanesulfonate (6k):



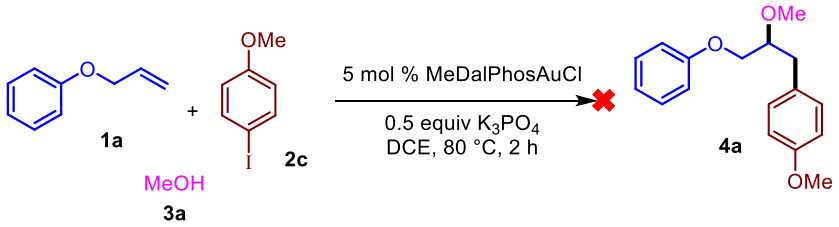
Colourless liquid, 60 mg, 65% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (700 MHz, CHLOROFORM-d)** δ = 7.75 (d, *J* = 8.2 Hz, 2 H), 7.51 (d, *J* = 7.3 Hz, 1 H), 7.38 - 7.35 (m, 1 H), 7.34 - 7.31 (m, 3 H), 7.31 - 7.28 (m, 1 H), 3.91 (tt, *J* = 4.1, 8.0 Hz, 1 H), 3.41 (ddd, *J* = 4.4, 6.6, 10.5 Hz, 1 H), 3.27 (dd, *J* = 4.7, 14.0 Hz, 1 H), 3.20 - 3.14 (m, 1 H), 2.99 (dd, *J* = 8.6, 14.0 Hz, 1 H), 2.43 (s, 3) 1.76 - 1.67 (m, 1 H), 1.56 - 1.43 (m, 3 H); **^{13}C NMR (175 MHz, CHLOROFORM-d)** δ = 148.4, 143.5, 134.4, 132.8, 131.1, 129.7, 128.5, 128.4, 127.5, 121.1, 60.5, 49.1, 36.1, 30.1, 23.8, 21.5; **HRMS (ESI)** calcd for $C_{19}H_{20}F_3NO_5S_2$ $(M + H)^+$ 464.0824, found 464.0833.

2-(4-Methoxybenzyl)-1-tosylindoline (6l):

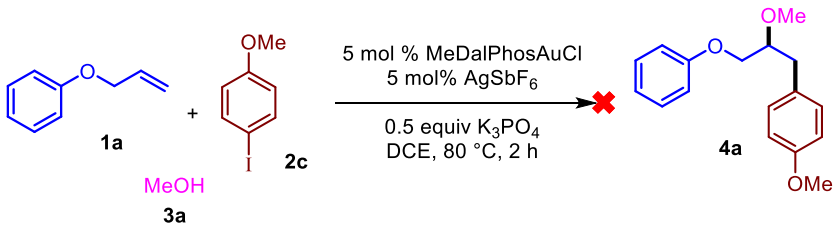


Colourless thick liquid, 45 mg, 58% yield, ***Rf*** = 0.30 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, CHLOROFORM-d)** δ = 7.68 (d, *J* = 8.1 Hz, 1 H), 7.60 - 7.55 (m, *J* = 8.2 Hz, 2 H), 7.23 - 7.14 (m, 5 H), 7.02 (d, *J* = 4.3 Hz, 2 H), 6.88 - 6.83 (m, *J* = 8.4 Hz, 2 H), 4.47 - 4.38 (m, 1 H), 3.80 (s, 3 H), 3.29 (dd, *J* = 4.2, 13.4 Hz, 1 H), 2.75 (dd, *J* = 10.1, 13.4 Hz, 1 H), 2.60 (d, *J* = 5.0 Hz, 2 H), 2.34 (s, 3 H); **^{13}C NMR (100 MHz, CHLOROFORM-d)** δ = 158.4, 143.7, 141.3, 135.3, 131.7, 130.6, 129.5, 129.3, 127.7, 126.9, 125.2, 124.6, 117.3, 113.9, 63.7, 55.2, 41.6, 32.7, 21.5; **HRMS (ESI)** calcd for $C_{23}H_{23}NO_3S$ $(M + Na)^+$ 416.1291, found 416.1281.

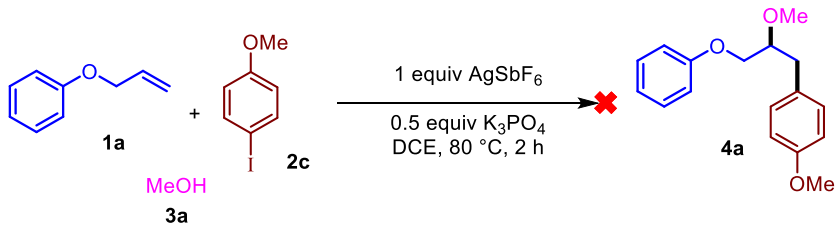
6. Control experiments:



An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the (allyloxy)benzene (**1a**, 1 equiv, 0.2 mmol), 4-iodoanisole (**2a**, 1 equiv, 0.2 mmol), methanol (**3a**, 10 equiv, 2 mmol), (Me-DalPhos)AuCl (0.05 equiv, 0.01 mmol), K_3PO_4 (0.5 equiv, 0.1 mmol) and 1,2-dichloroethane (0.1 M). The resulting reaction mixture was stirred at room temperature for 5 min then stir at 80 °C for 2 h. However, formation of desired product **4a** was not observed and starting material was isolated in quantitative yield.

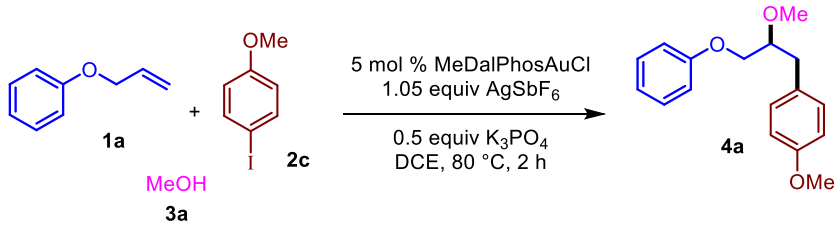


An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the (allyloxy)benzene (**1a**, 1 equiv, 0.2 mmol), 4-iodoanisole (**2a**, 1 equiv, 0.2 mmol), methanol (**3a**, 10 equiv, 2 mmol), (Me-DalPhos)AuCl (0.05 equiv, 0.01 mmol), K_3PO_4 (0.5 equiv, 0.1 mmol) and 1,2-dichloroethane (0.1 M). The resulting reaction mixture was stirred at room temperature for 5 min then $AgSbF_6$ (0.05 equiv, 0.01 mmol) was added and allowed to stir at 80 °C for 2 h. However, the formation of desired product **4a** was not observed and starting material was isolated in quantitative yield.



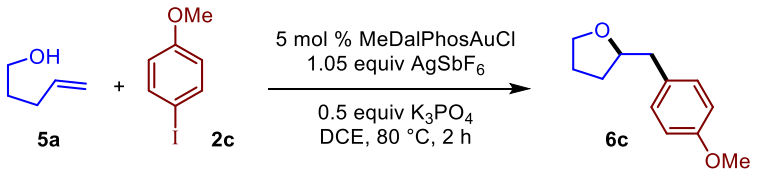
An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the (allyloxy)benzene (**1a**, 1 equiv, 0.2 mmol), 4-iodoanisole (**2a**, 1 equiv, 0.2 mmol), methanol (**3a**, 10 equiv, 2 mmol), K_3PO_4 (0.5 equiv, 0.1 mmol) and 1,2-dichloroethane (0.1 M). The resulting reaction mixture was stirred at room temperature for 5 min then $AgSbF_6$ (1 equiv, 0.2 mmol) was added and allowed to stir at 80 °C for 2 h. However, the formation of desired product **4a** was not observed and starting material was isolated in quantitative yield.

7. Large scale synthesis:



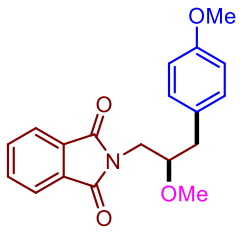
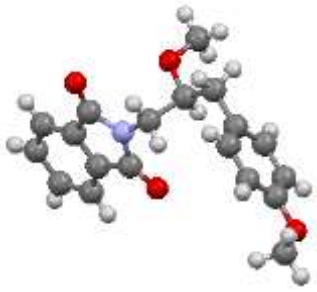
An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the 4-iodoanisole (**2a**, 1 equiv, 1 mmol), (allyloxy)benzene (**1a**, 1 equiv, 1 mmol), (MeDalPhos)AuCl (0.05 equiv, 0.0.5 mmol), K_3PO_4 (0.5 equiv, 0.5 mmol), methanol (**3a**, 10 equiv, 10 mmol) and 1,2-dichloroethane (DCE) (0.1 M). The resulting reaction mixture was stirred at room temperature for 5 min then $AgSbF_6$ (1.05 equiv, 1.05 mmol) was added and allowed to stir at 80

°C for 2 h. After completion of the reaction, it was diluted with DCM (15 mL), filtered through a short pad of celite, concentrated and subsequently purified by silica gel column chromatography to afford the desired 1,2-oxyarylation product **4a** in 68% yield.

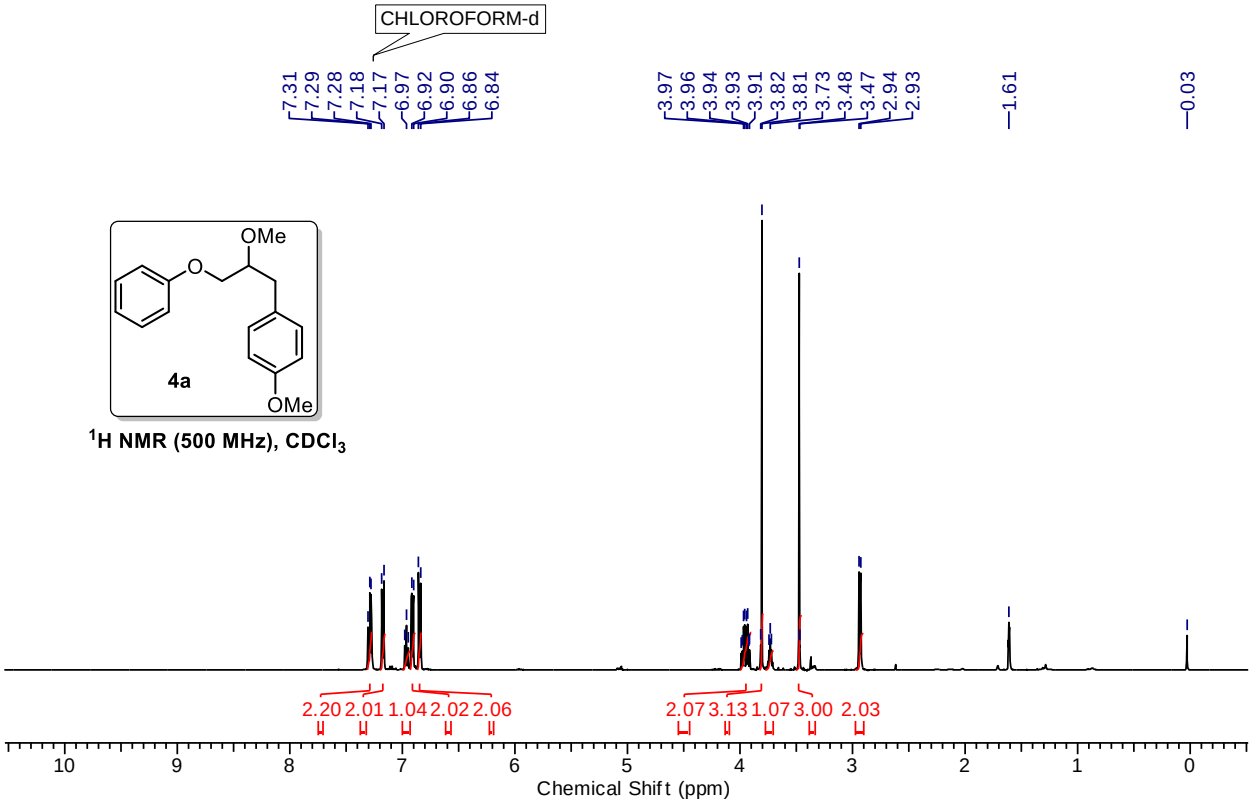


An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the pent-4-en-1-ol (**5a**, 1 equiv, 1 mmol), 4-iodoanisole (**2c**, 1 equiv, 1 mmol), (Me-DalPhos)AuCl (0.05 equiv, 0.05 mmol), K_3PO_4 (0.5 equiv, 0.5 mmol) and 1,2-dichloroethane (DCE) (0.1 M). The resulting reaction mixture was stirred at room temperature for 5 min then $AgSbF_6$ (1.05 equiv, 1.05 mmol) was added and allowed to stir at 80 °C for 2 h. After completion of the reaction, it was diluted with DCM (15 mL), filtered through a short pad of celite, concentrated and subsequently purified by silica gel column chromatography to afford the desired 2-(4-methoxybenzyl)tetrahydrofuran **6c** in 89% yield.

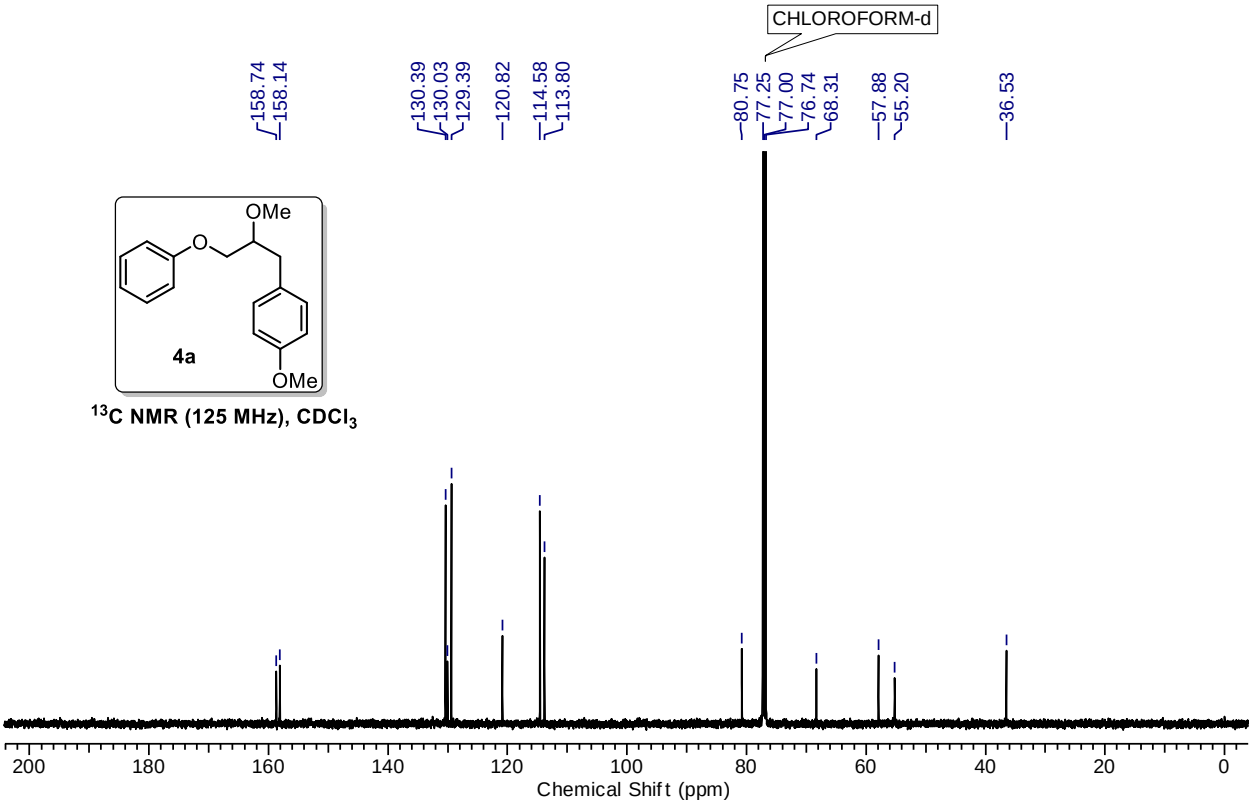
8. X-ray crystallography data:

Compound Structure	ORTEP Diagram
 **4r**	 CCDC = 1973104

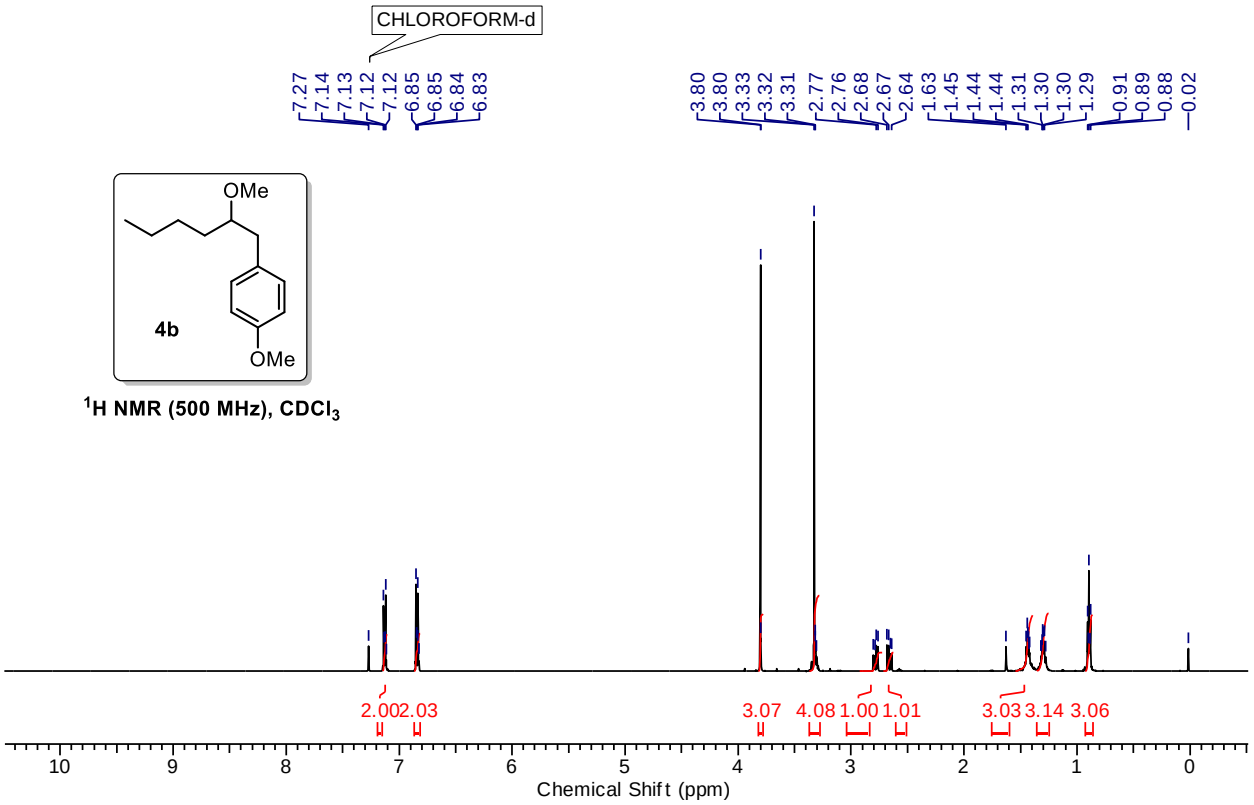
9. NMR spectra:



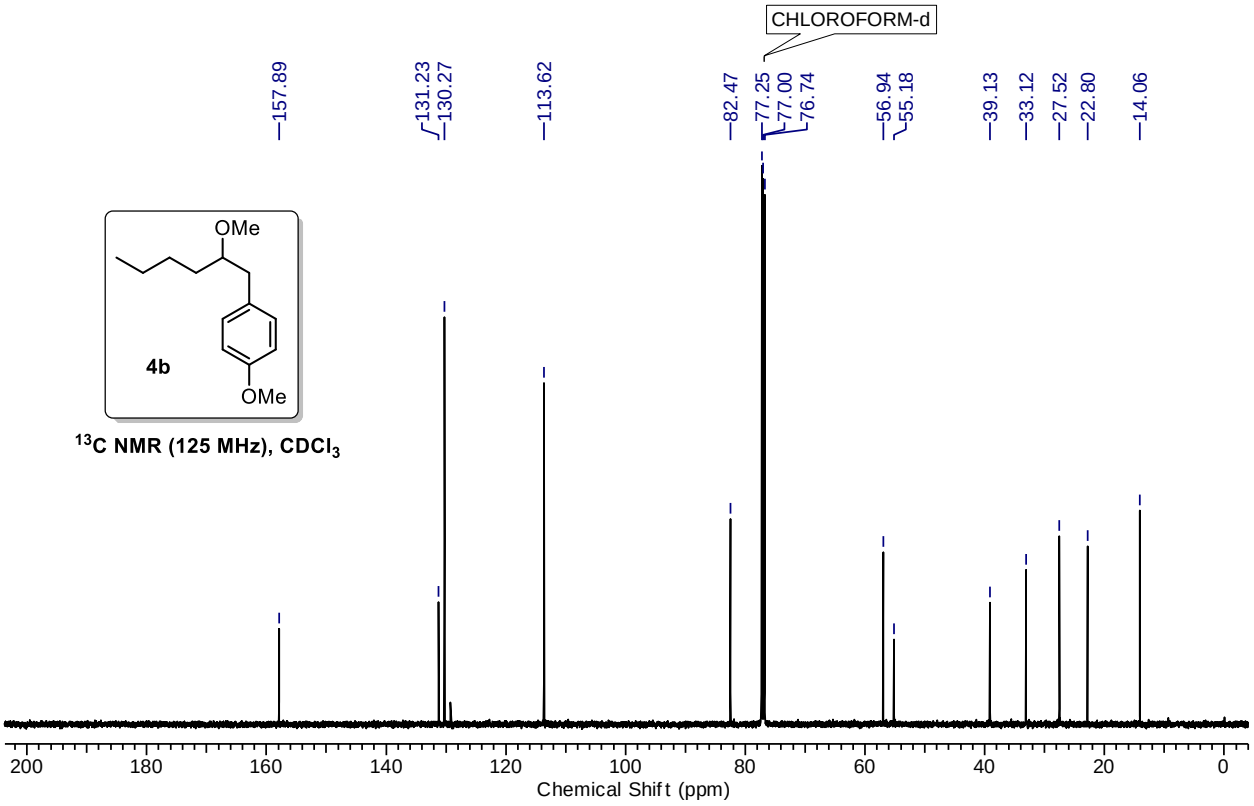
^{1}H NMR (500 MHz), $CDCl_3$



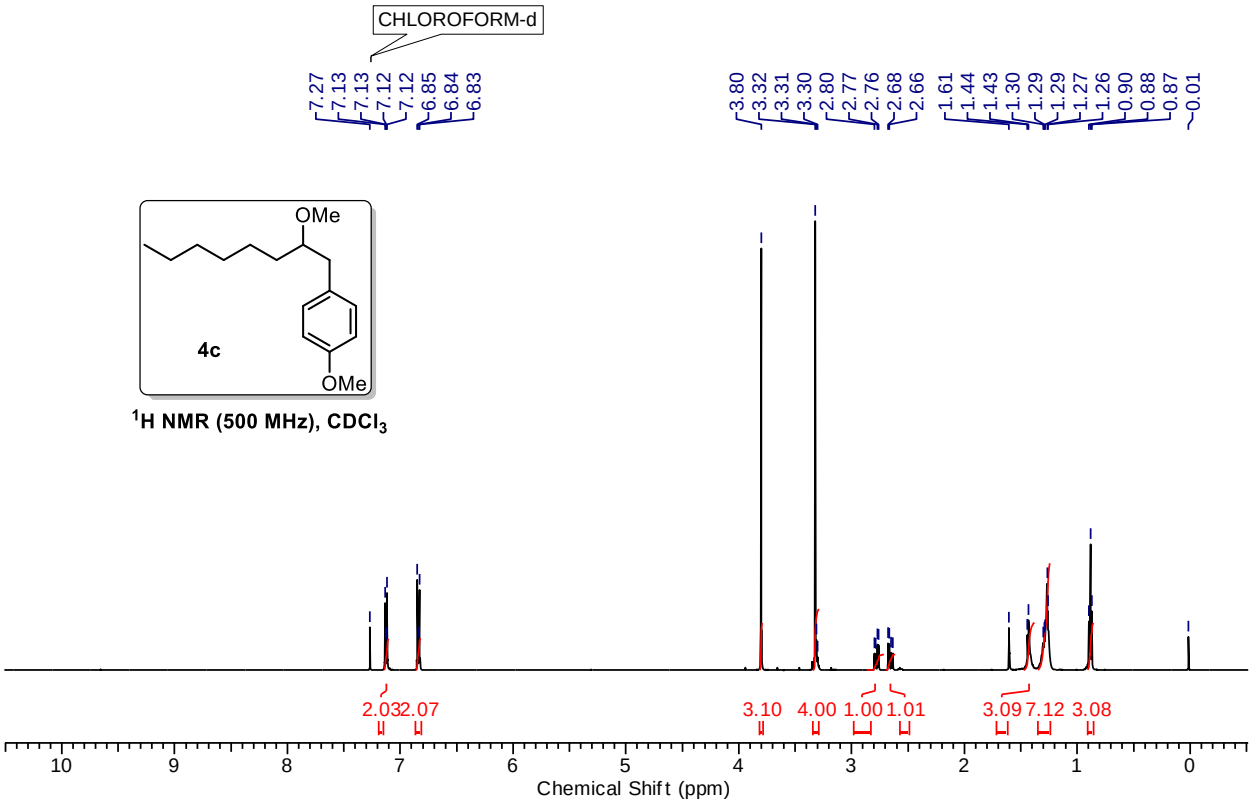
^{13}C NMR (125 MHz), $CDCl_3$



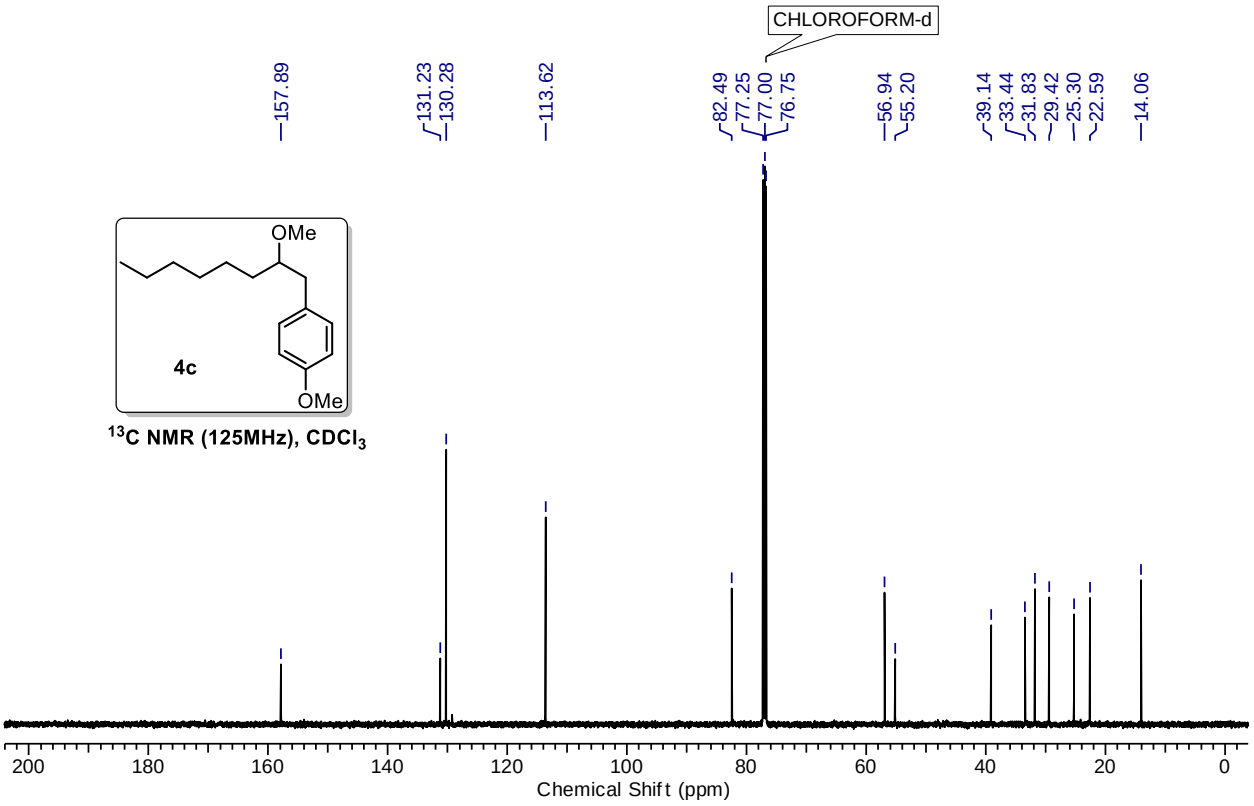
^{1}H NMR (500 MHz), $CDCl_3$



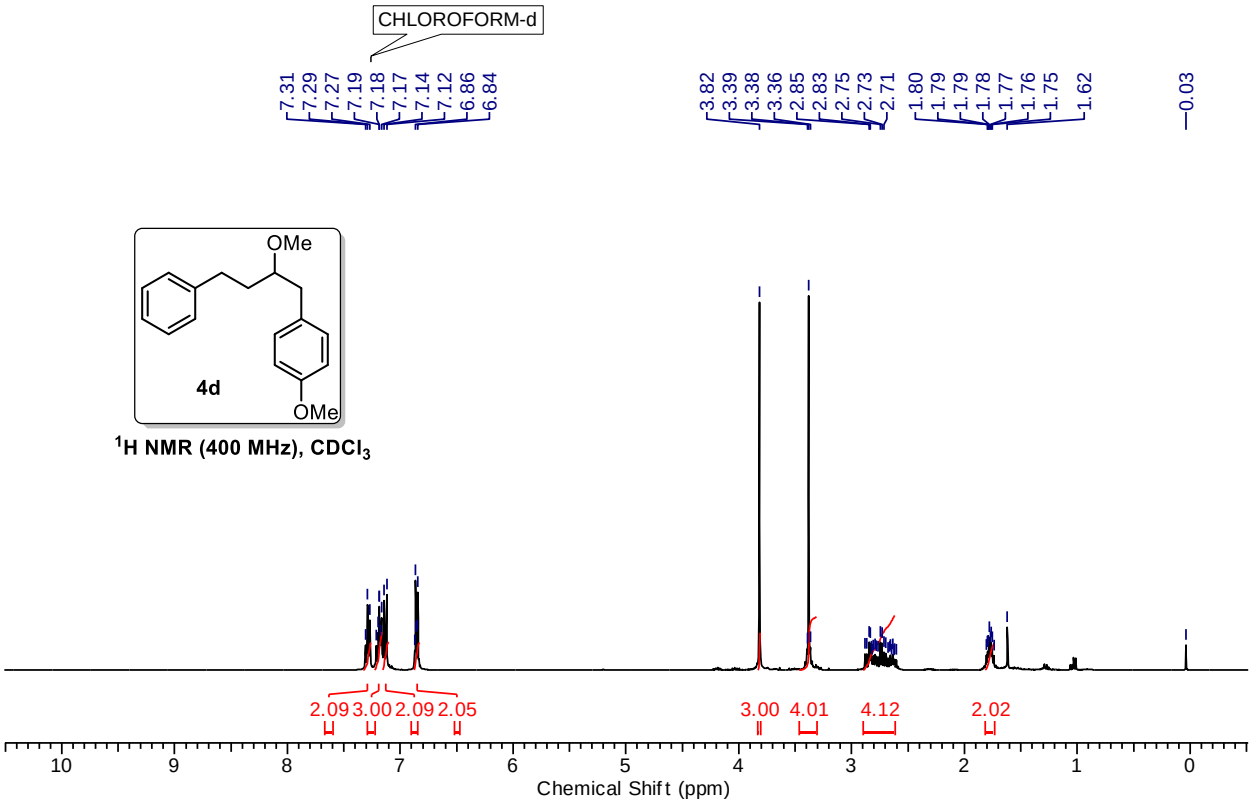
^{13}C NMR (125 MHz), $CDCl_3$



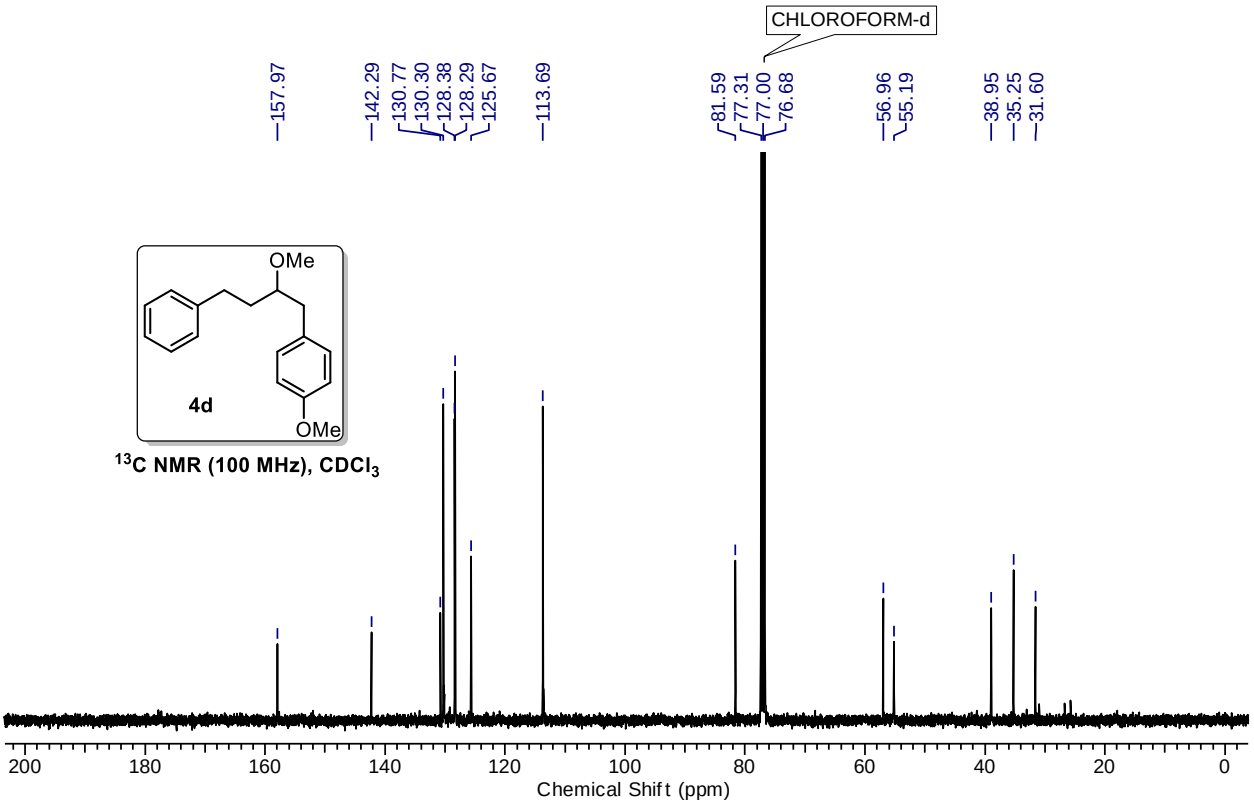
^{1}H NMR (500 MHz), $CDCl_3$



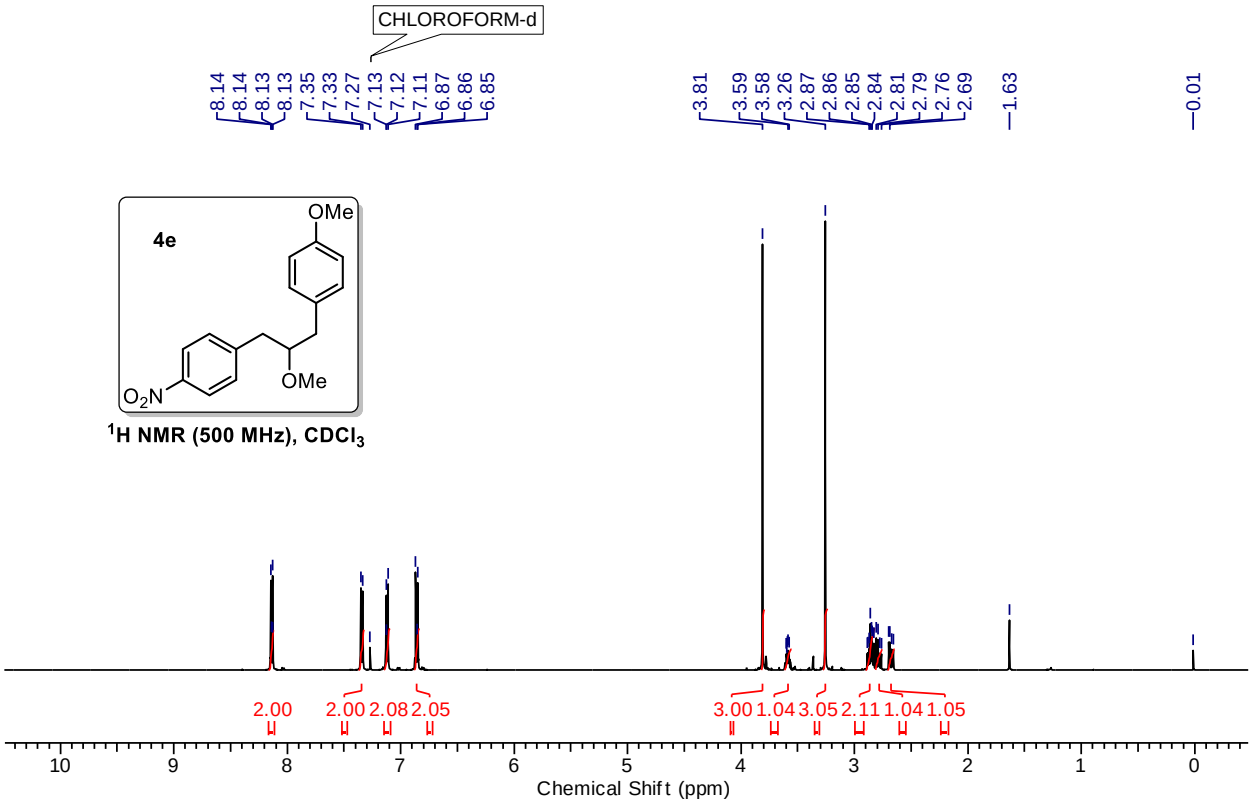
^{13}C NMR (125MHz), $CDCl_3$

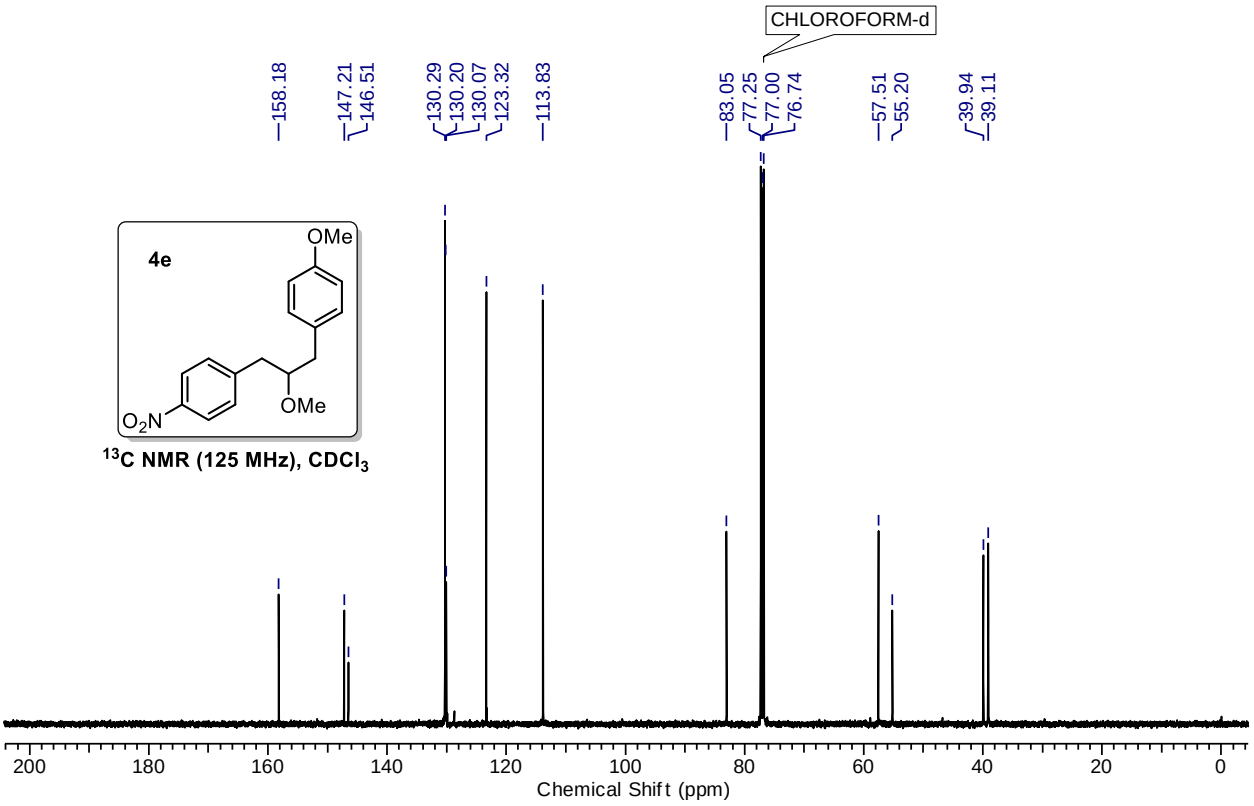


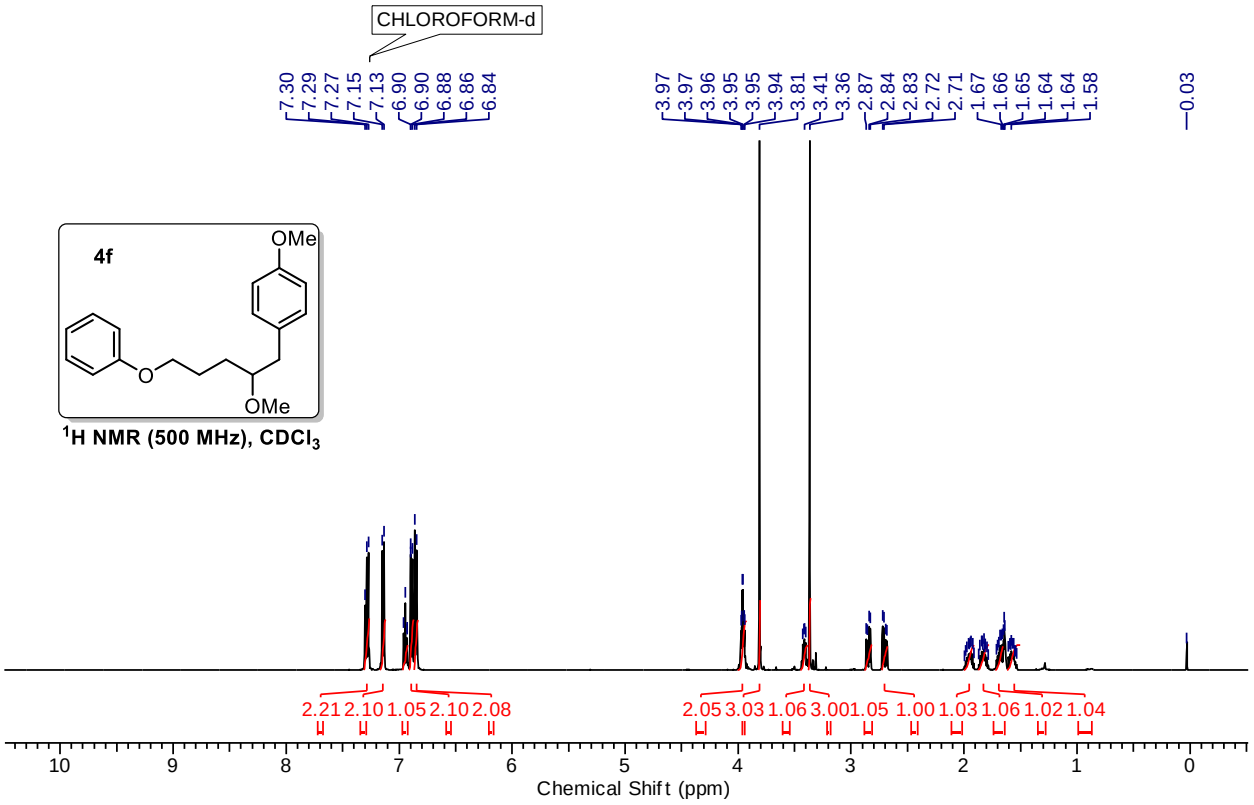
^{1}H NMR (400 MHz), $CDCl_3$

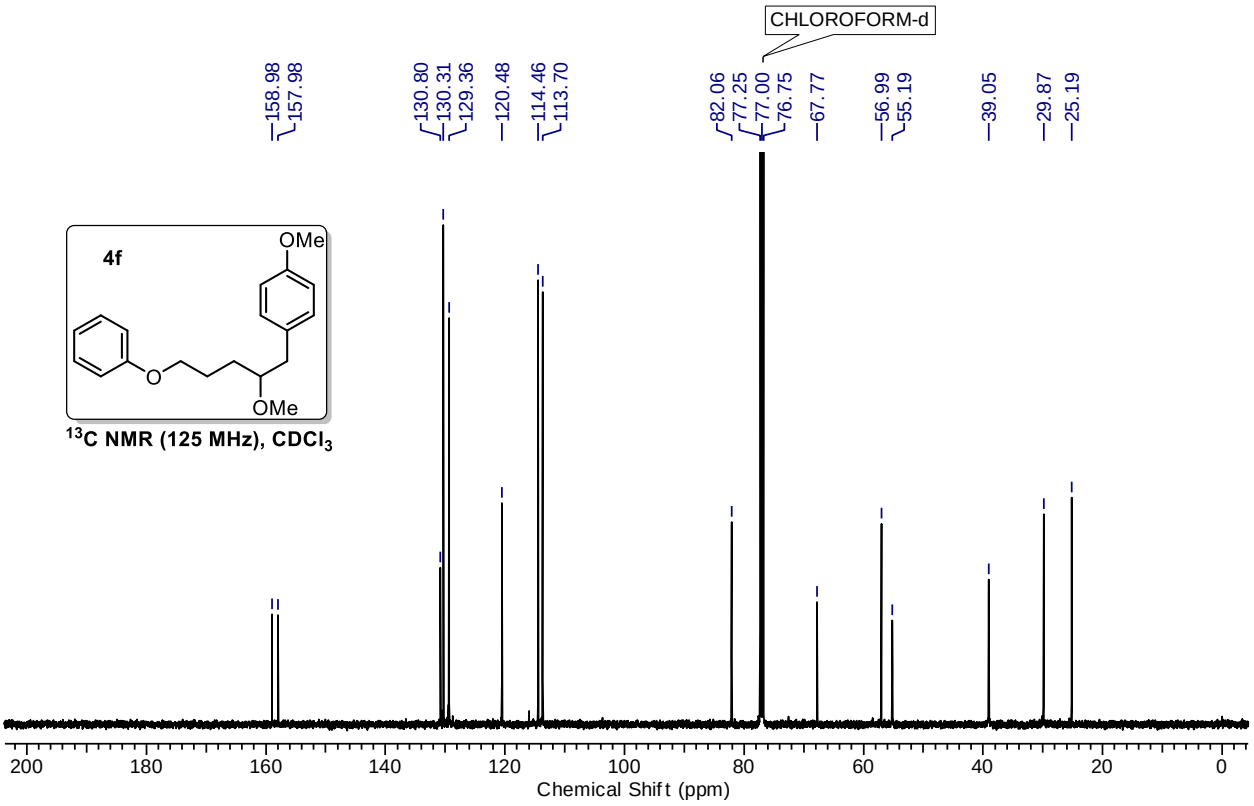


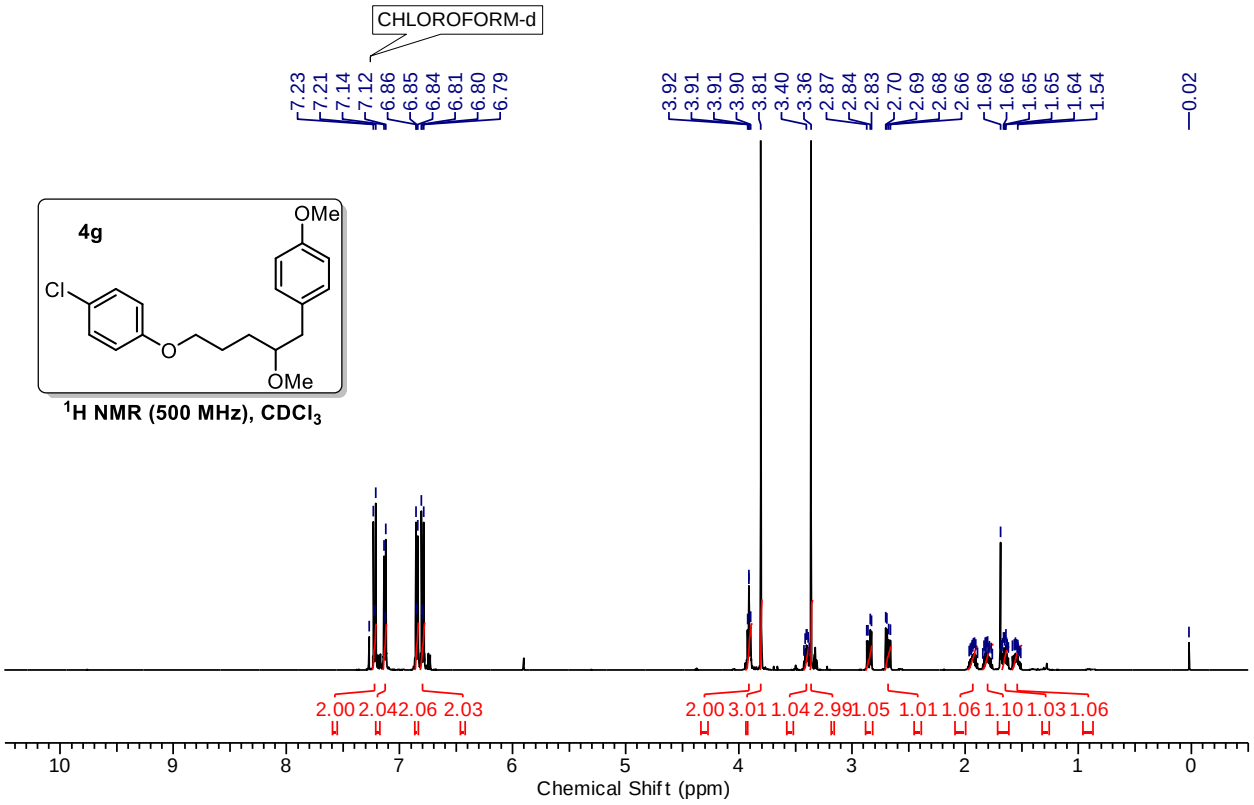
^{13}C NMR (100 MHz), $CDCl_3$


CHLOROFORM-d
8.14
8.14
8.13
8.13
7.35
7.33
7.27
7.13
7.12
7.11
6.87
6.86
6.85
3.81
3.59
3.58
3.26
2.87
2.86
2.85
2.84
2.81
2.79
2.76
2.69
1.63
0.01
OMe
4e
OMe
O2N
1H NMR (500 MHz), CDCl3
2.00
2.00
2.08
2.05
3.00
1.04
3.05
2.11
1.04
1.05
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

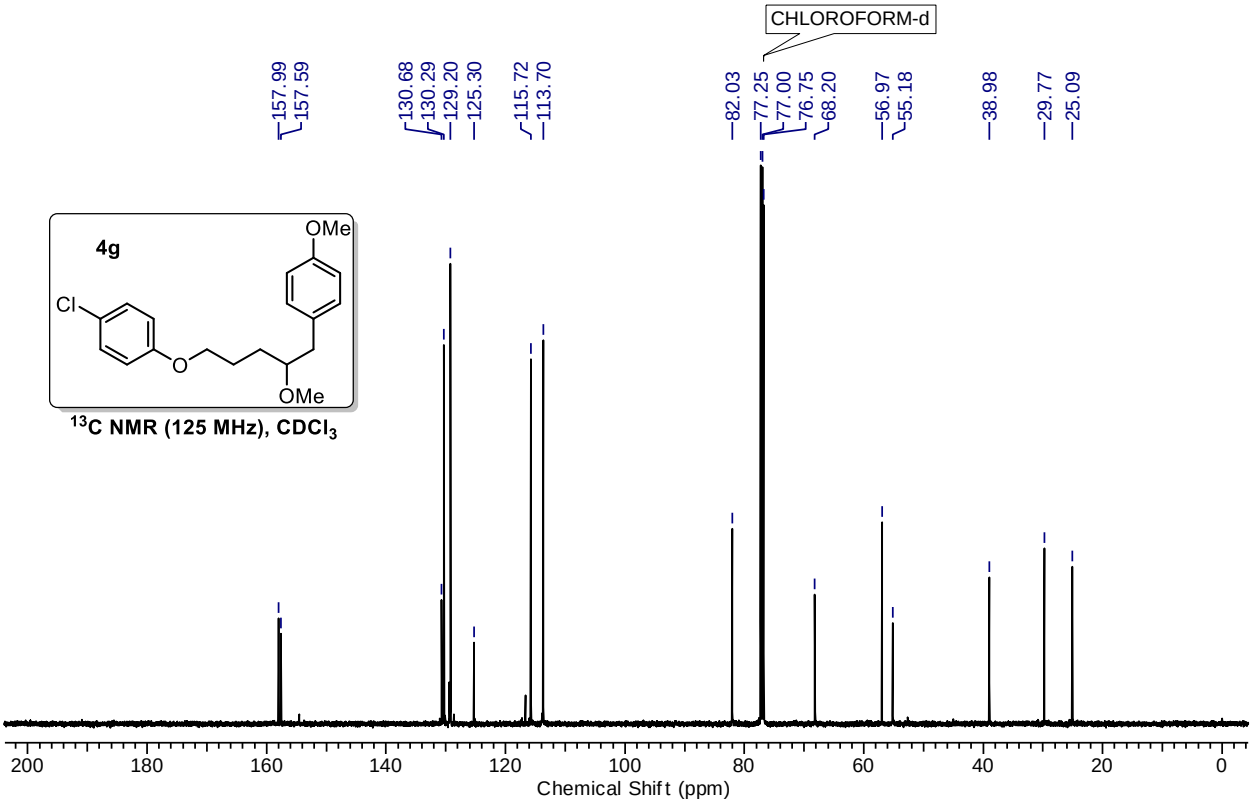

CHLOROFORM-d
158.18
147.21
146.51
130.29
130.20
130.07
123.32
113.83
83.05
77.25
77.00
76.74
57.51
55.20
39.94
39.11
OMe
4e
OMe
O2N
13C NMR (125 MHz), CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


CHLOROFORM-d
7.30
7.29
7.27
7.15
7.13
6.90
6.90
6.88
6.86
6.84
3.97
3.97
3.96
3.95
3.95
3.94
3.81
3.41
3.36
2.87
2.84
2.83
2.72
2.71
1.67
1.66
1.65
1.64
1.64
1.58
0.03
4f
OMe
OMe
O
1H NMR (500 MHz), CDCl3
2.21 2.10 1.05 2.10 2.08
2.05 3.03 1.06 3.00 1.05 1.00 1.03 1.06 1.02 1.04
Chemical Shift (ppm)

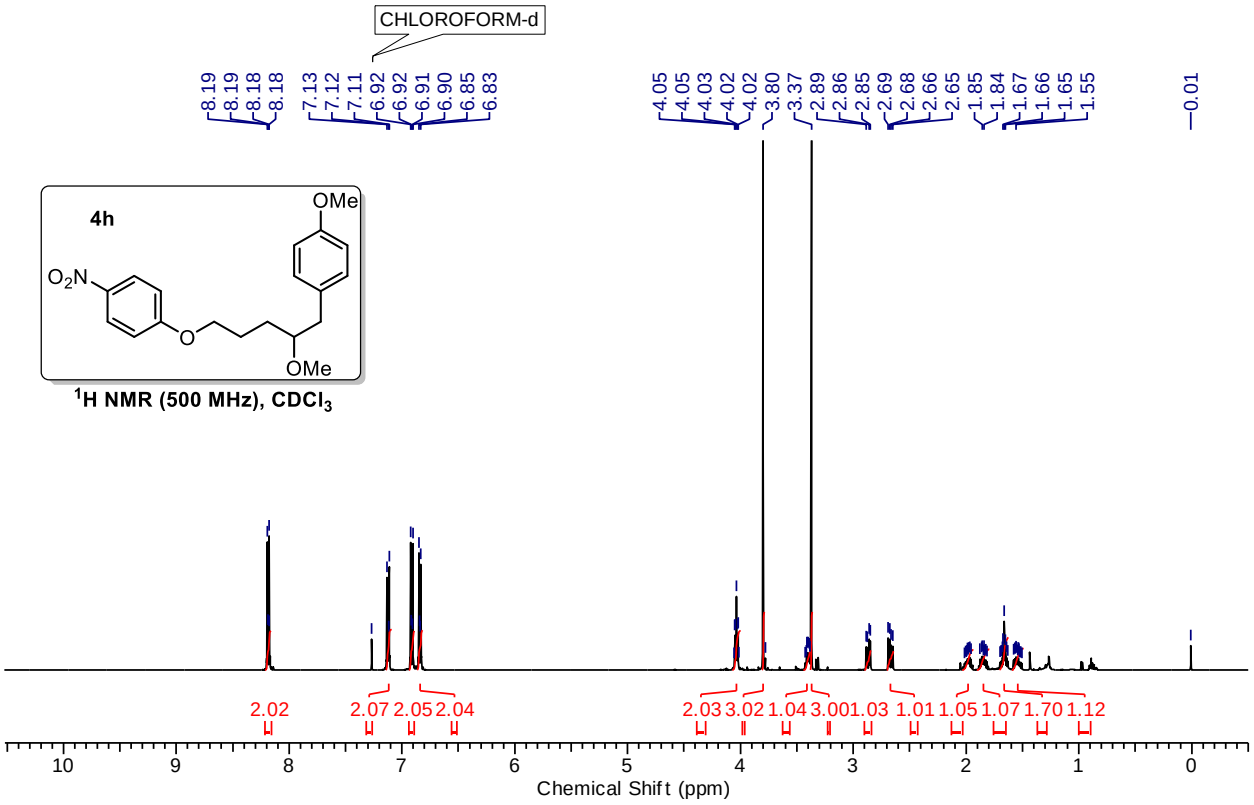

CHLOROFORM-d
158.98
157.98
130.80
130.31
129.36
120.48
114.46
113.70
82.06
77.25
77.00
76.75
67.77
56.99
55.19
39.05
29.87
25.19
4f
OMe
OMe
O
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)

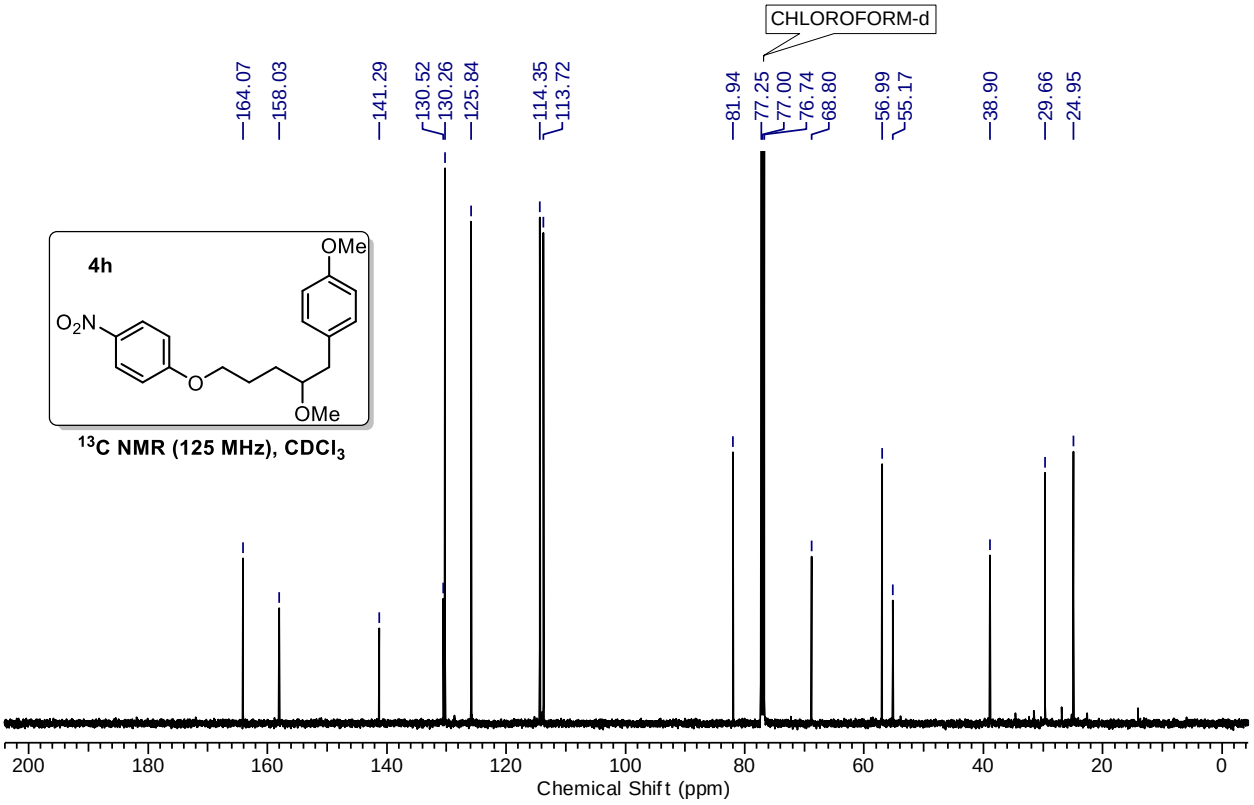


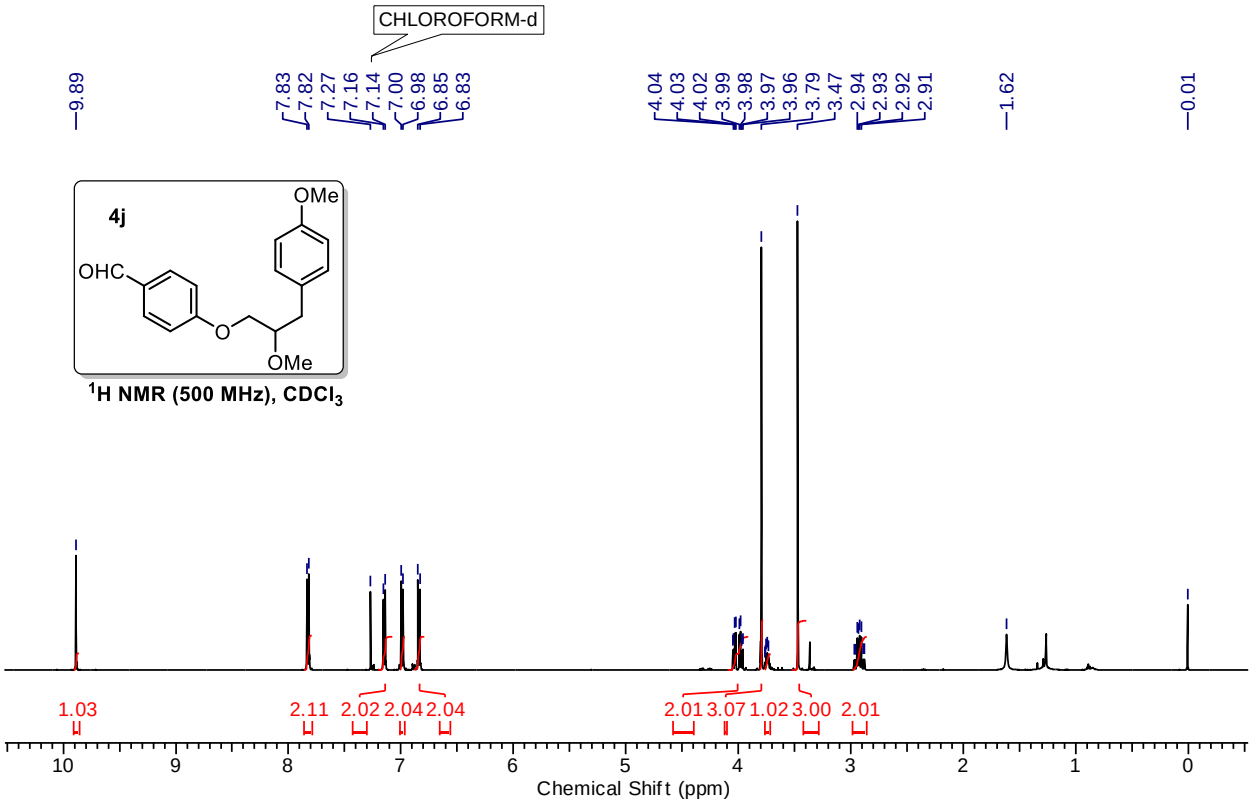
^{1}H NMR (500 MHz), $CDCl_3$

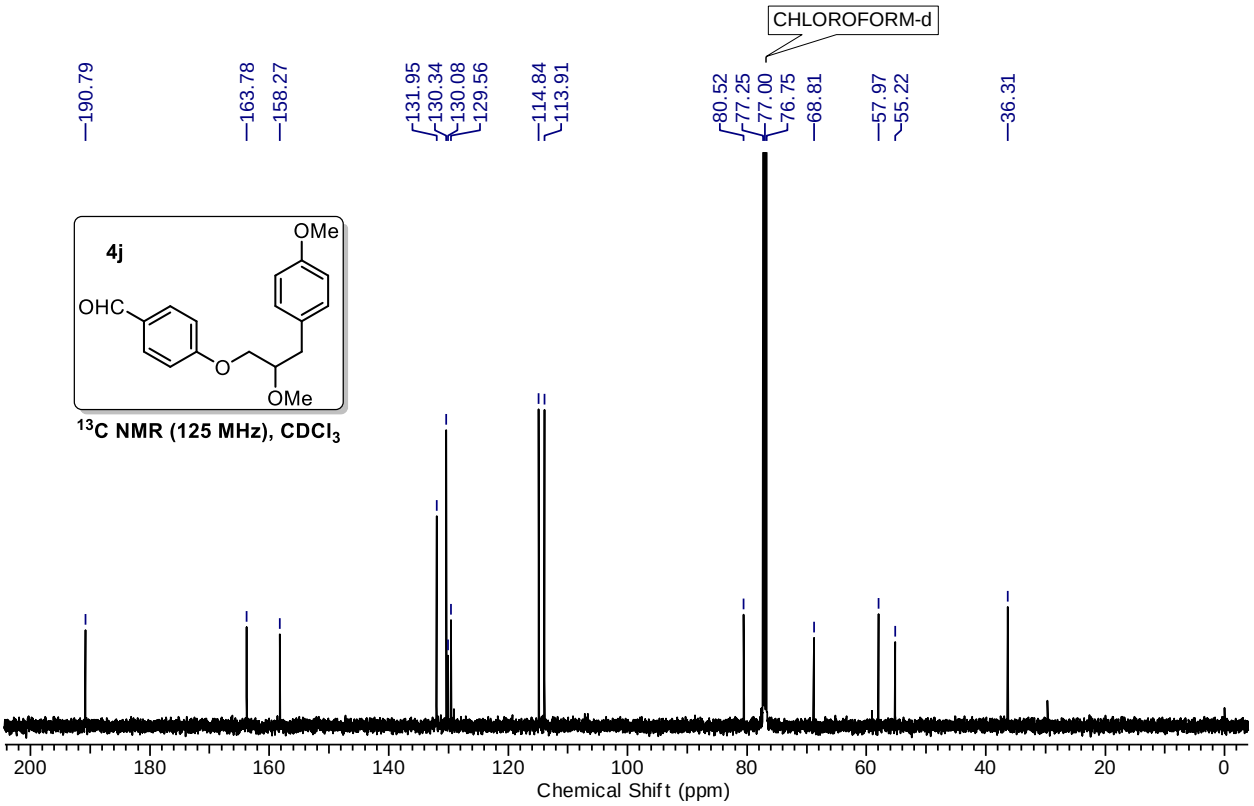


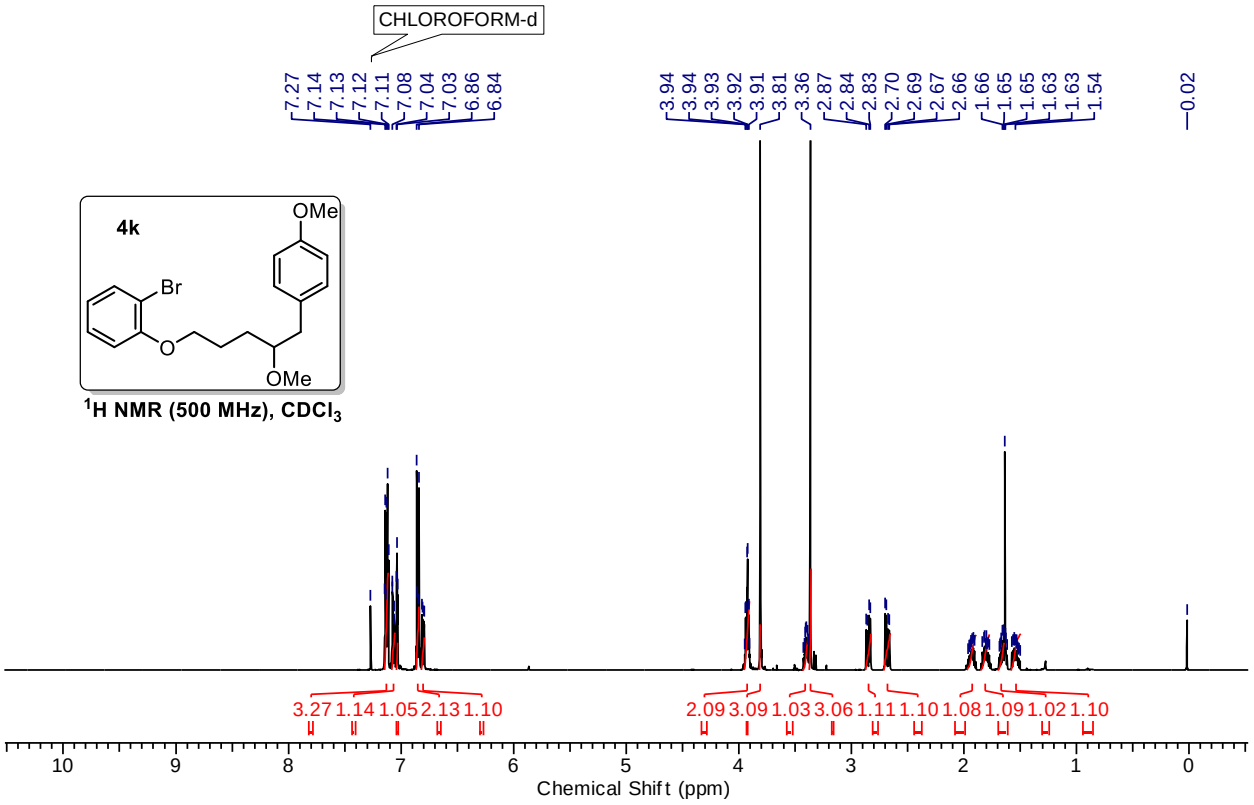
^{13}C NMR (125 MHz), $CDCl_3$

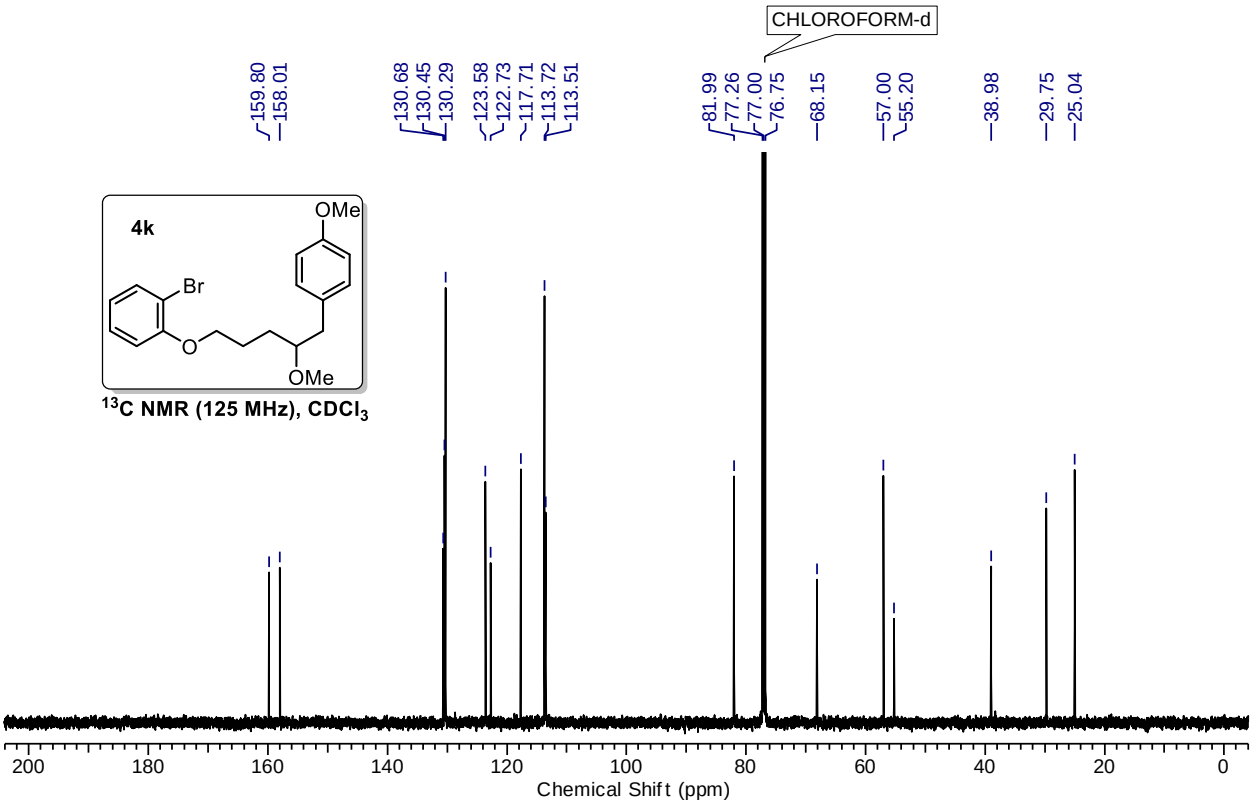

CHLOROFORM-d
8.19
8.19
8.18
8.18
7.13
7.12
7.11
6.92
6.92
6.91
6.90
6.85
6.83
4.05
4.05
4.03
4.02
4.02
3.80
3.37
2.89
2.86
2.85
2.69
2.68
2.66
2.65
1.85
1.84
1.67
1.66
1.65
1.55
0.01
4h
OMe
O2N
O
OMe
1H NMR (500 MHz), CDCl3
2.02
2.07
2.05
2.04
2.03
3.02
1.04
3.00
1.03
1.01
1.05
1.07
1.70
1.12
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

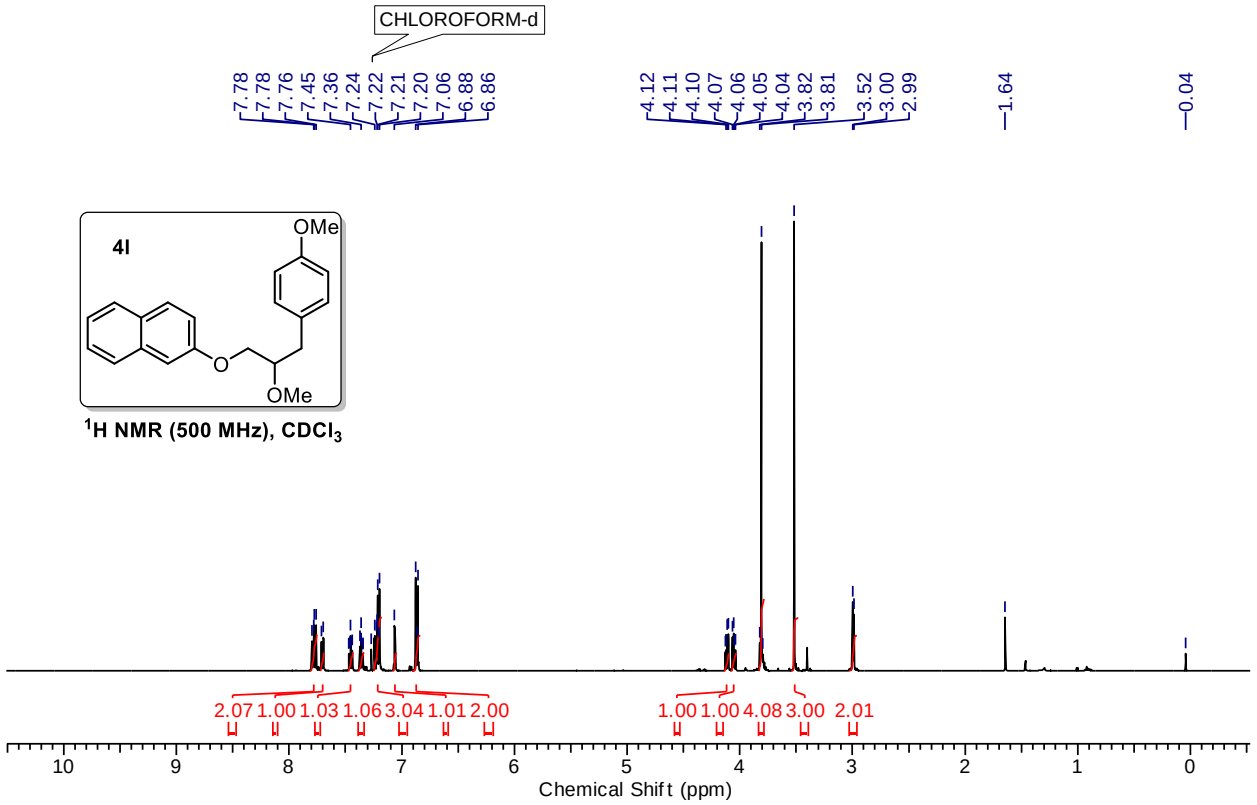

CHLOROFORM-d
164.07
158.03
141.29
130.52
130.26
125.84
114.35
113.72
81.94
77.25
77.00
76.74
68.80
56.99
55.17
38.90
29.66
24.95
4h
OMe
O2N
O
OMe
13C NMR (125 MHz), CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

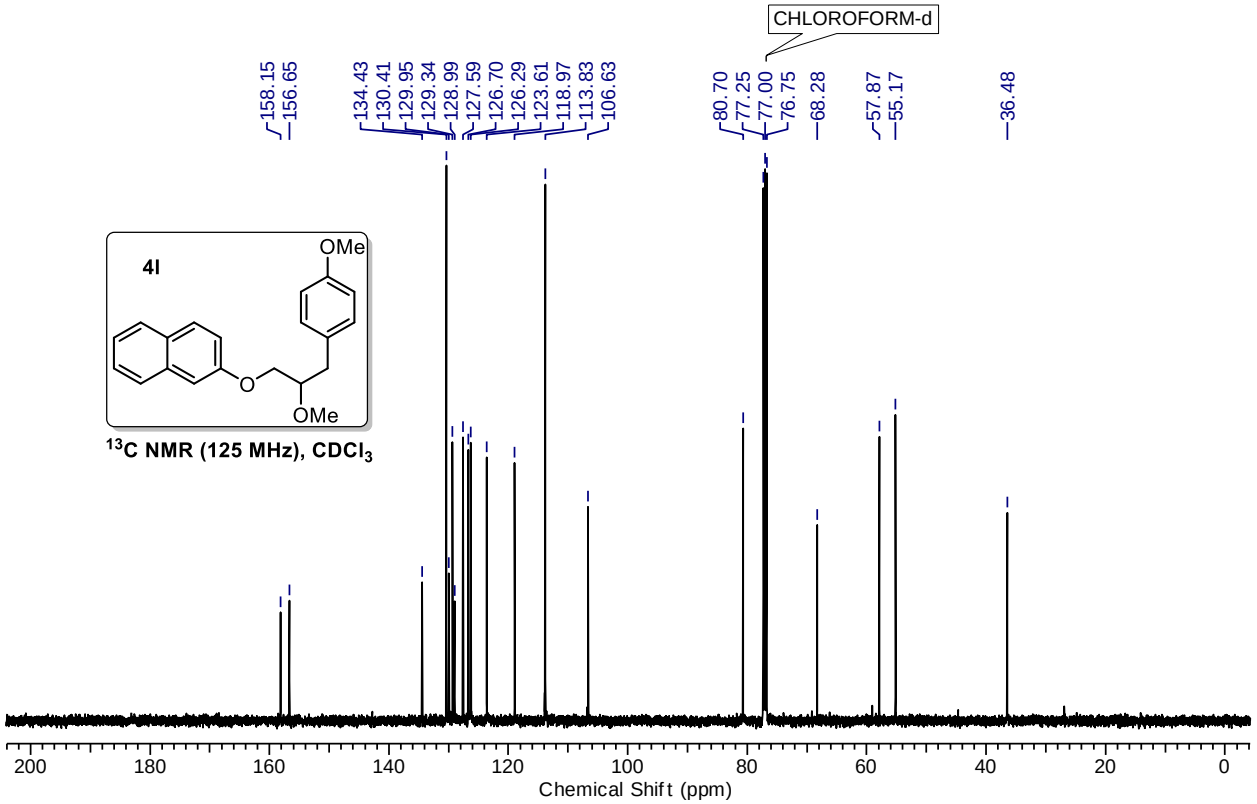

CHLOROFORM-d
9.89
7.83
7.82
7.27
7.16
7.14
7.00
6.98
6.85
6.83
4.04
4.03
4.02
3.99
3.98
3.97
3.96
3.79
3.47
2.94
2.93
2.92
2.91
1.62
0.01
4j
OMe
OHC
O
OMe
1H NMR (500 MHz), CDCl3
1.03
2.11
2.02
2.04
2.04
2.01
3.07
1.02
3.00
2.01
Chemical Shift (ppm)

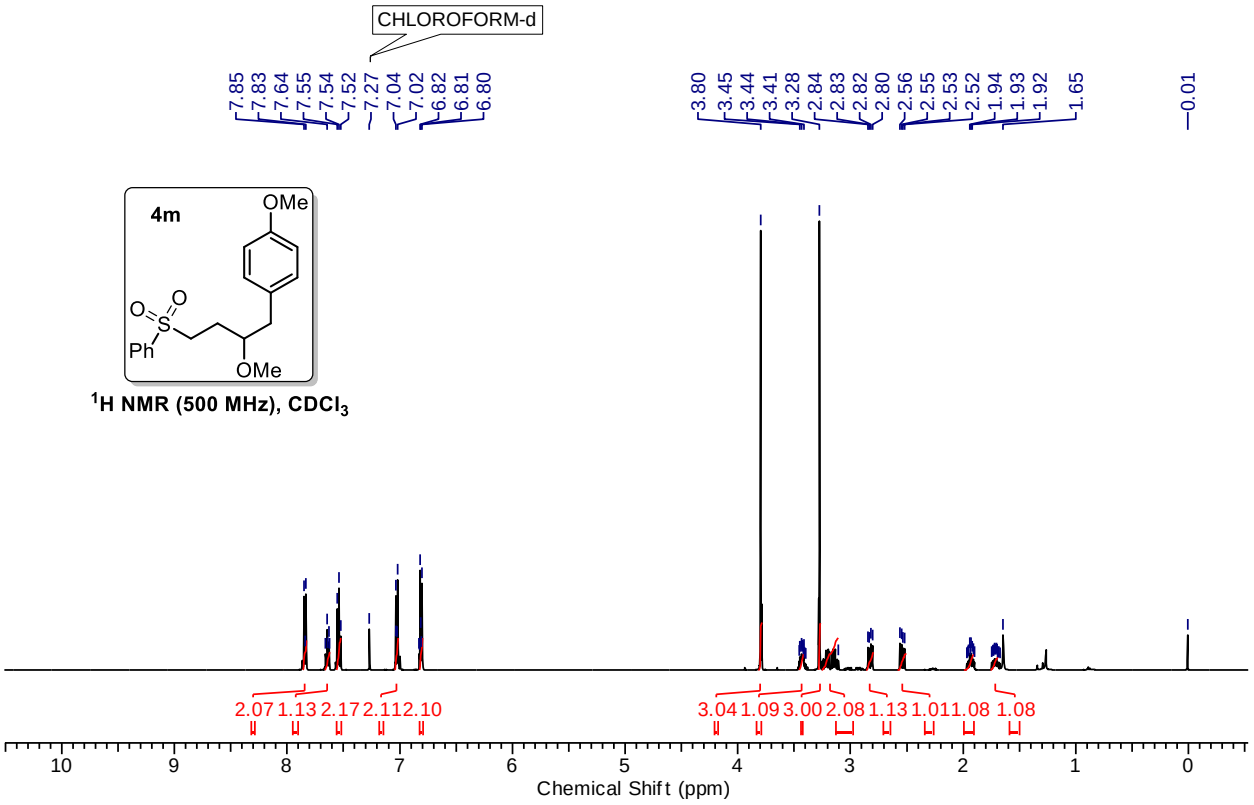

CHLOROFORM-d
190.79
163.78
158.27
131.95
130.34
130.08
129.56
114.84
113.91
80.52
77.25
77.00
76.75
68.81
57.97
55.22
36.31
4j
OMe
OHC
O
OMe
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)


CHLOROFORM-d
7.27
7.14
7.13
7.12
7.11
7.08
7.04
7.03
6.86
6.84
3.94
3.94
3.93
3.92
3.91
3.81
3.36
2.87
2.84
2.83
2.70
2.69
2.67
2.66
1.66
1.65
1.65
1.63
1.54
0.02
4k
OMe
Br
O
OMe
1H NMR (500 MHz), CDCl3
3.27 1.14 1.05 2.13 1.10
2.09 3.09 1.03 3.06 1.11 1.10 1.08 1.09 1.02 1.10
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

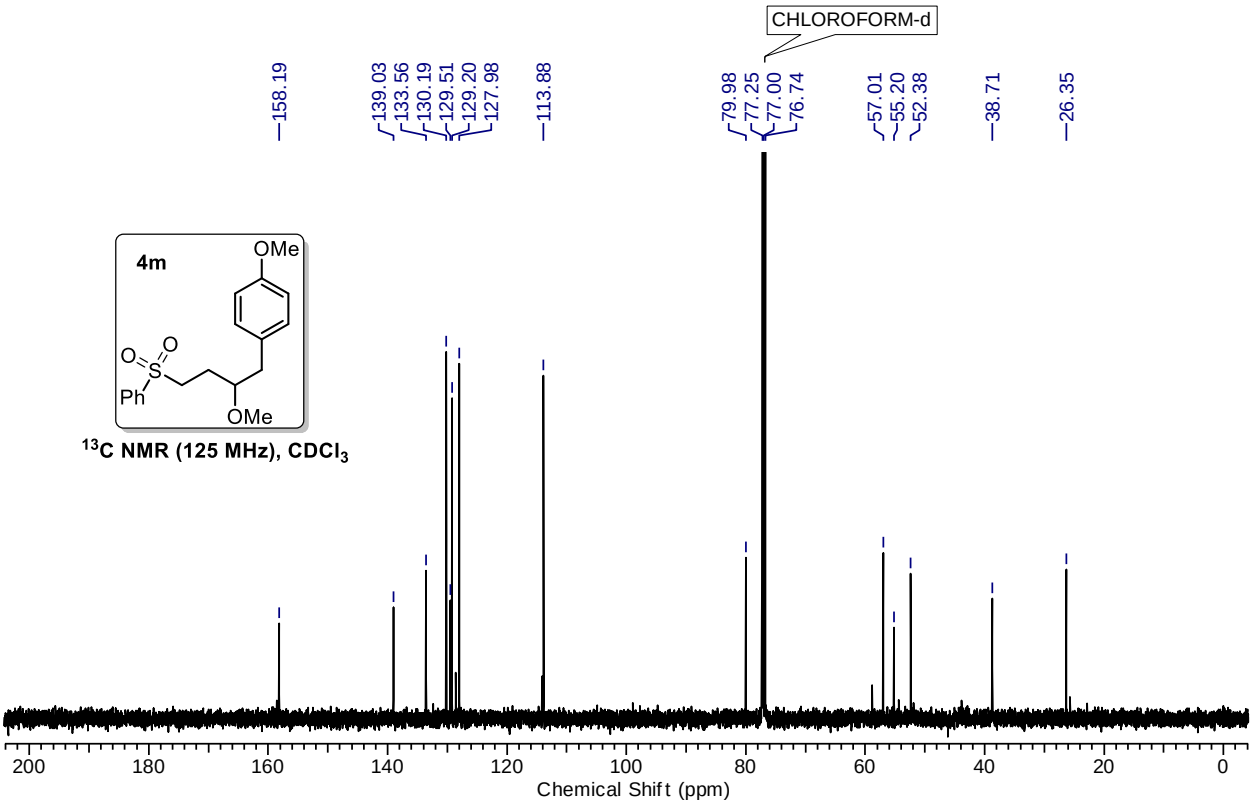

CHLOROFORM-d
159.80
158.01
130.68
130.45
130.29
123.58
122.73
117.71
113.72
113.51
81.99
77.26
77.00
76.75
68.15
57.00
55.20
38.98
29.75
25.04
4k
OMe
Br
O
OMe
13C NMR (125 MHz), CDCl3
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)


CHLOROFORM-d
7.78
7.78
7.76
7.45
7.36
7.24
7.22
7.21
7.20
7.06
6.88
6.86
4.12
4.11
4.10
4.07
4.06
4.05
4.04
3.82
3.81
3.52
3.00
2.99
1.64
0.04
4l
OMe
OMe
O
1H NMR (500 MHz), CDCl3
2.07 1.00 1.03 1.06 3.04 1.01 2.00
1.00 1.00 4.08 3.00 2.01
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

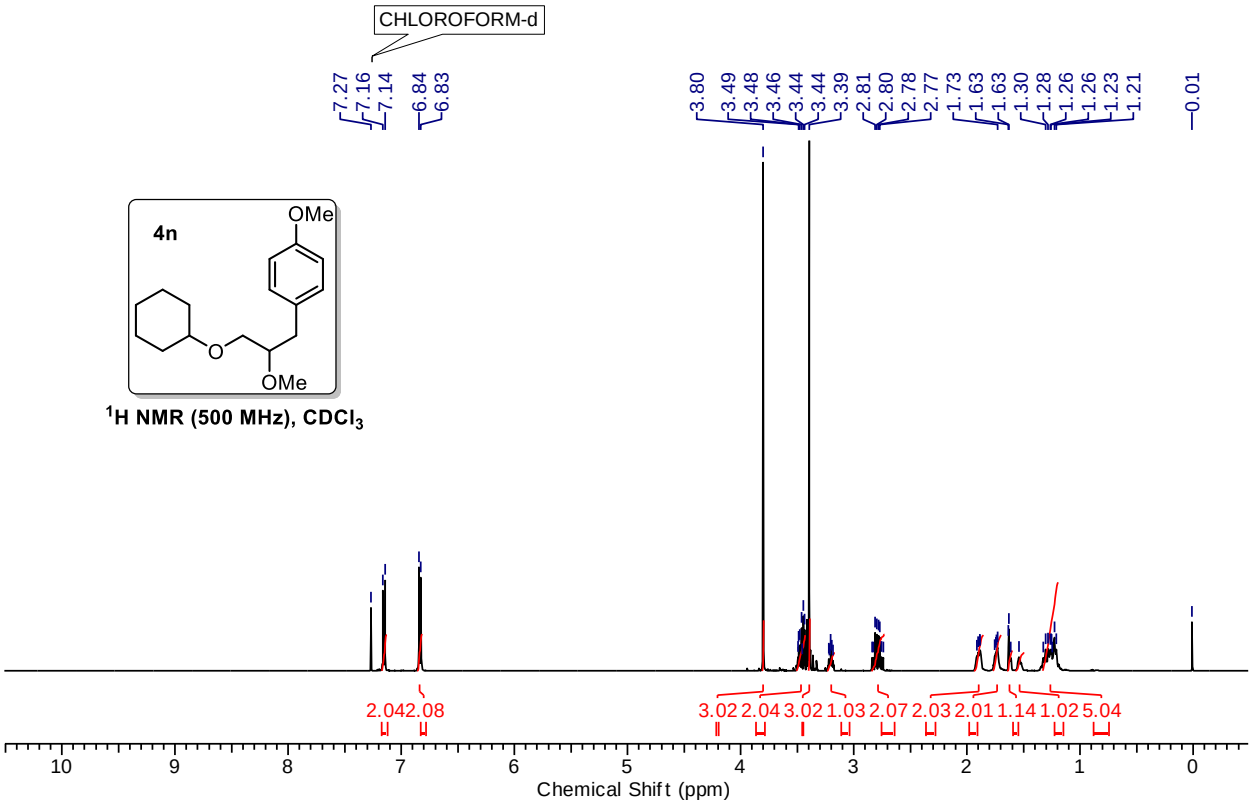

CHLOROFORM-d
158.15
156.65
134.43
130.41
129.95
129.34
128.99
127.59
126.70
126.29
123.61
118.97
113.83
106.63
80.70
77.25
77.00
76.75
68.28
57.87
55.17
36.48
4l
OMe
OMe
O
13C NMR (125 MHz), CDCl3
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)



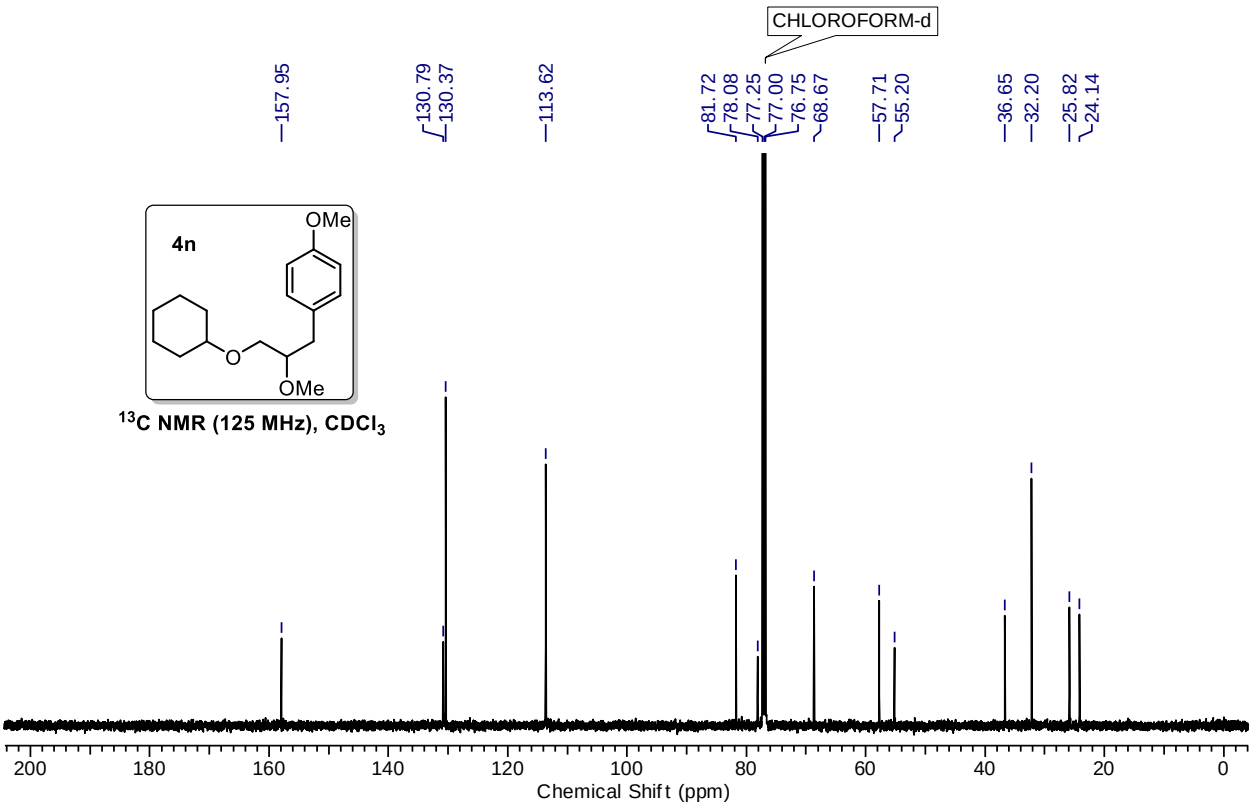
^{1}H NMR (500 MHz), $CDCl_3$



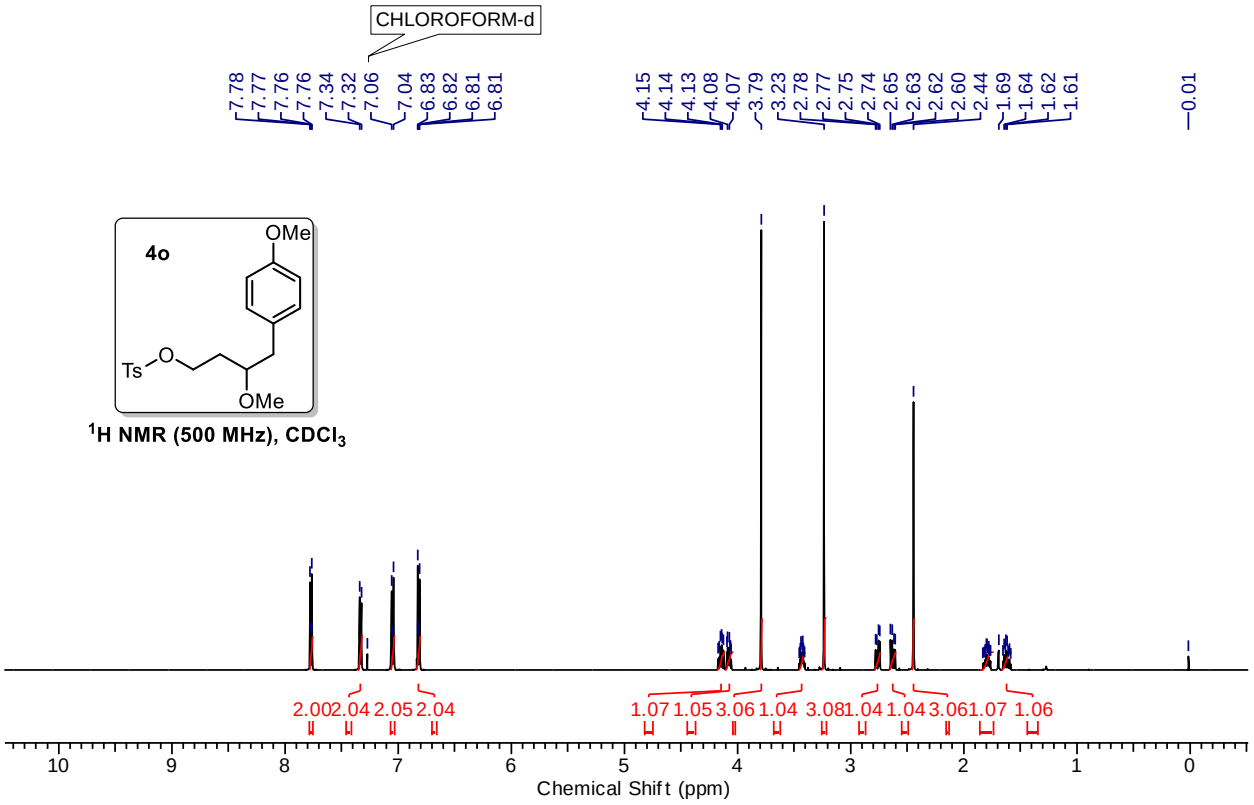
^{13}C NMR (125 MHz), $CDCl_3$



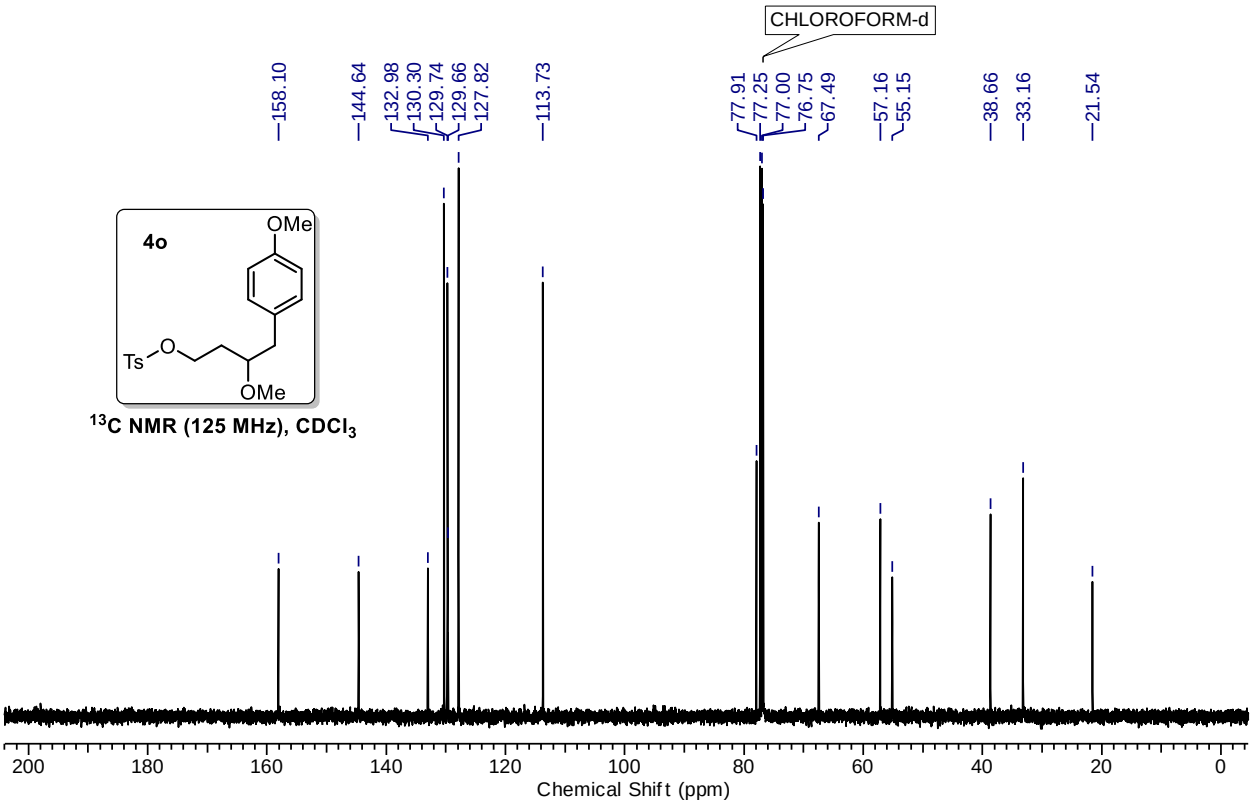
^{1}H NMR (500 MHz), $CDCl_3$



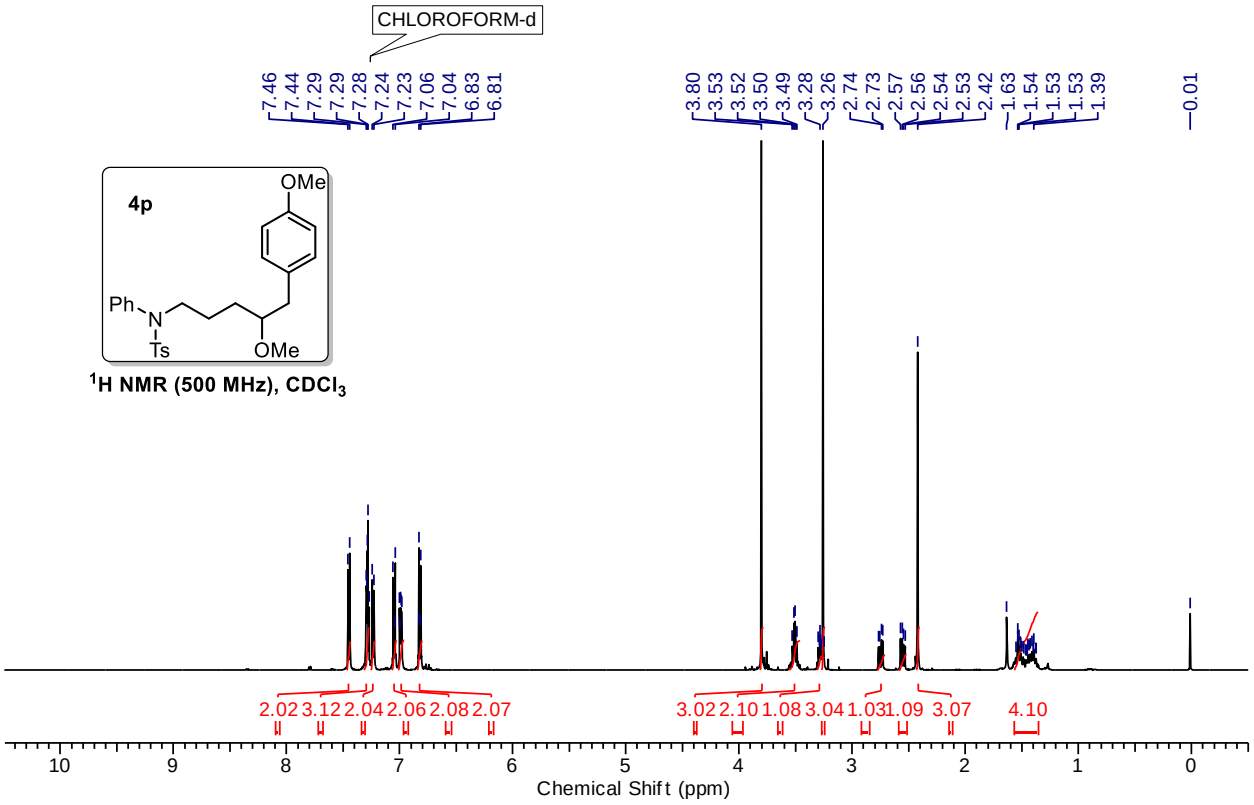
^{13}C NMR (125 MHz), $CDCl_3$



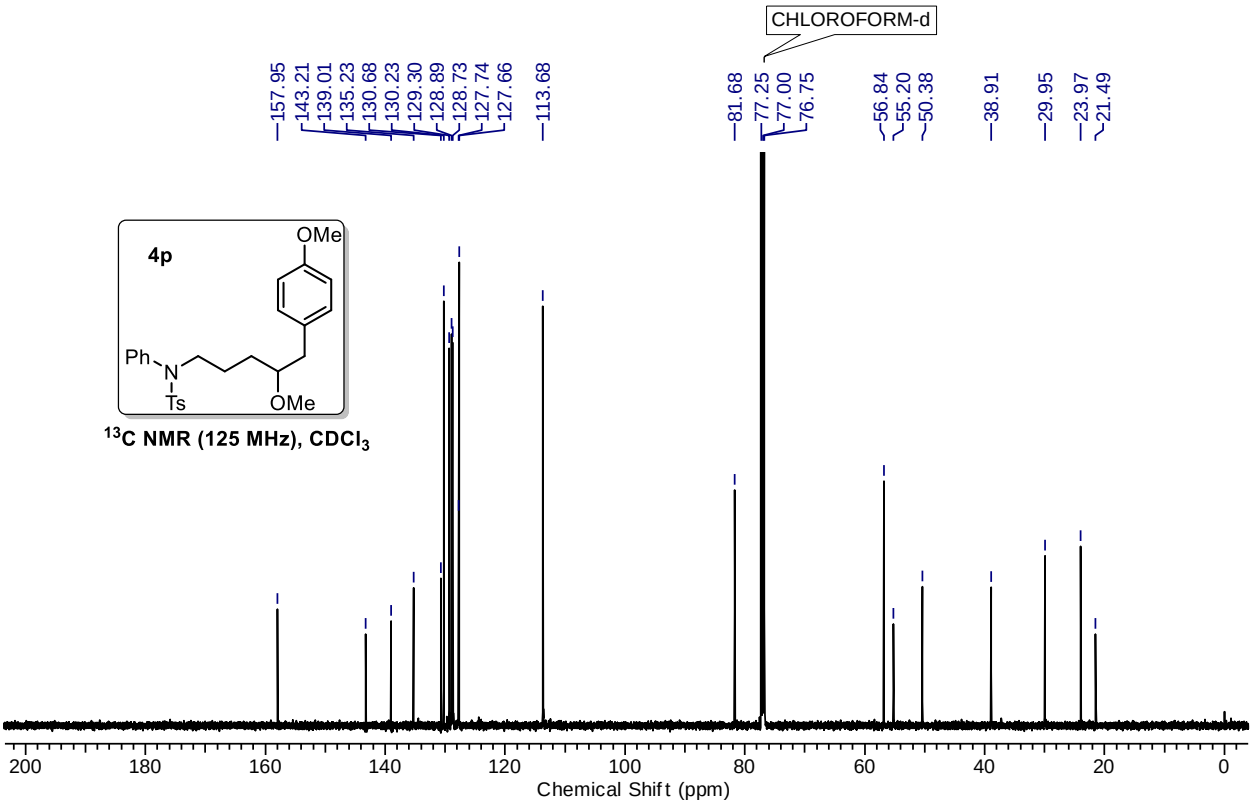
^{1}H NMR (500 MHz), $CDCl_3$



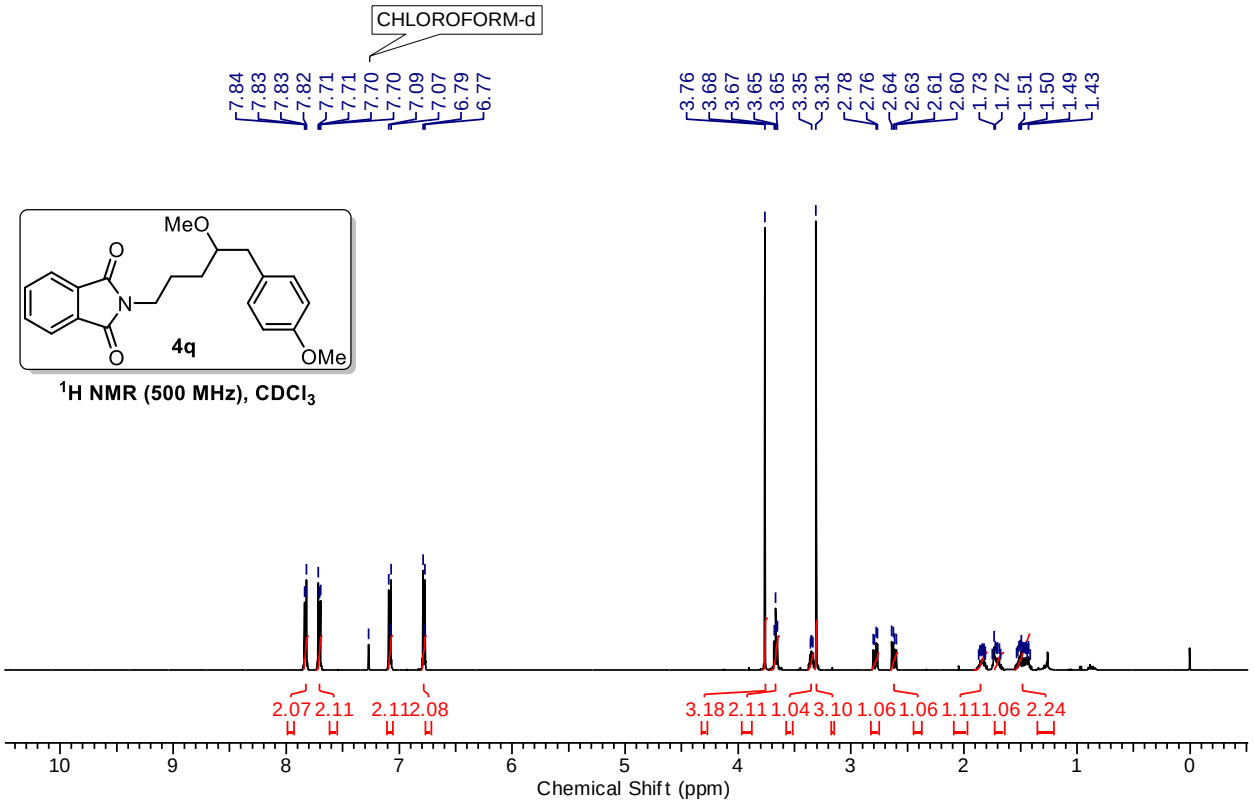
^{13}C NMR (125 MHz), $CDCl_3$



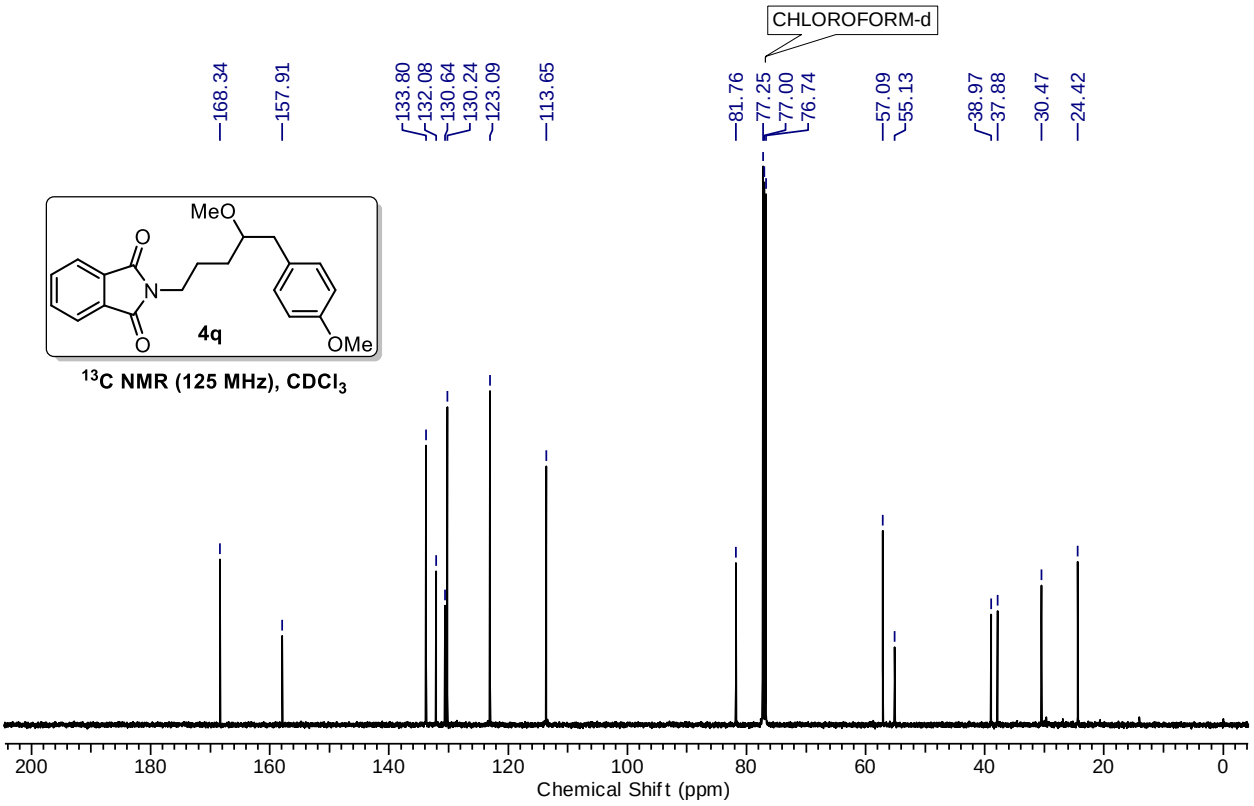
^{1}H NMR (500 MHz), $CDCl_3$



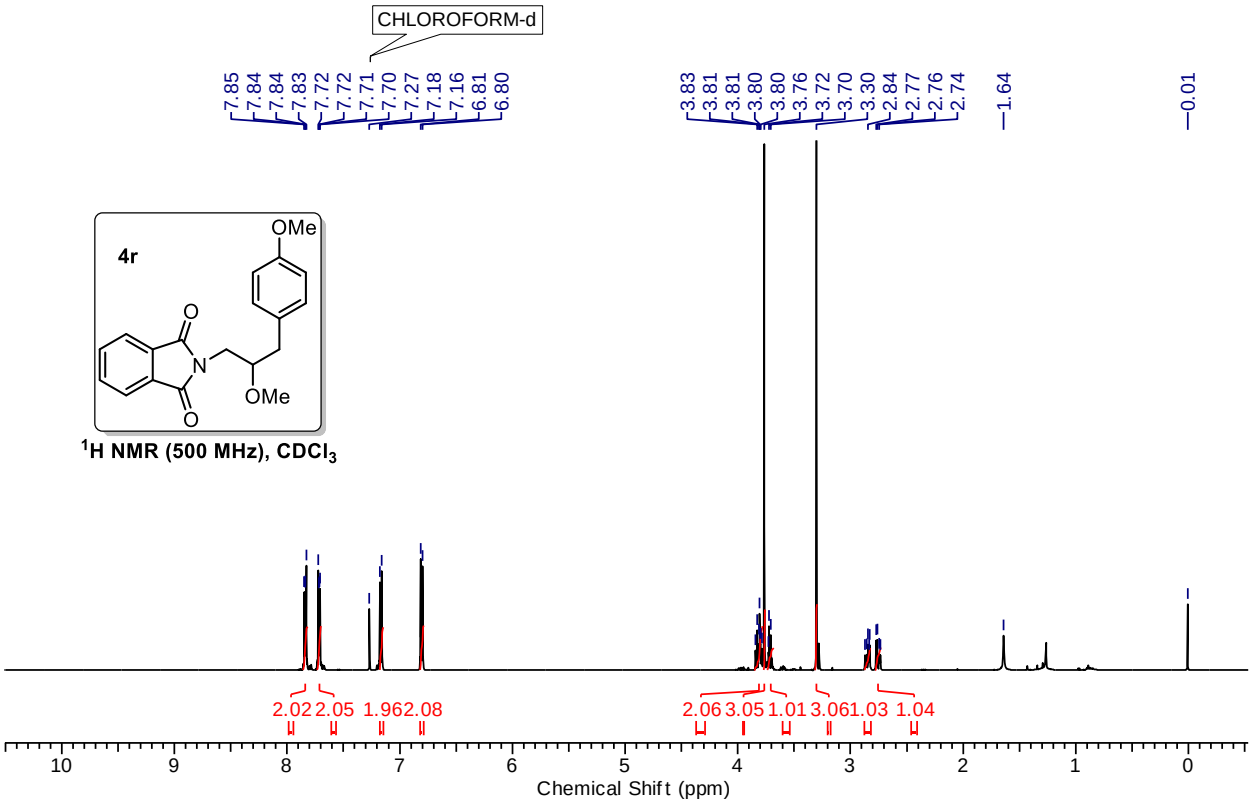
^{13}C NMR (125 MHz), $CDCl_3$



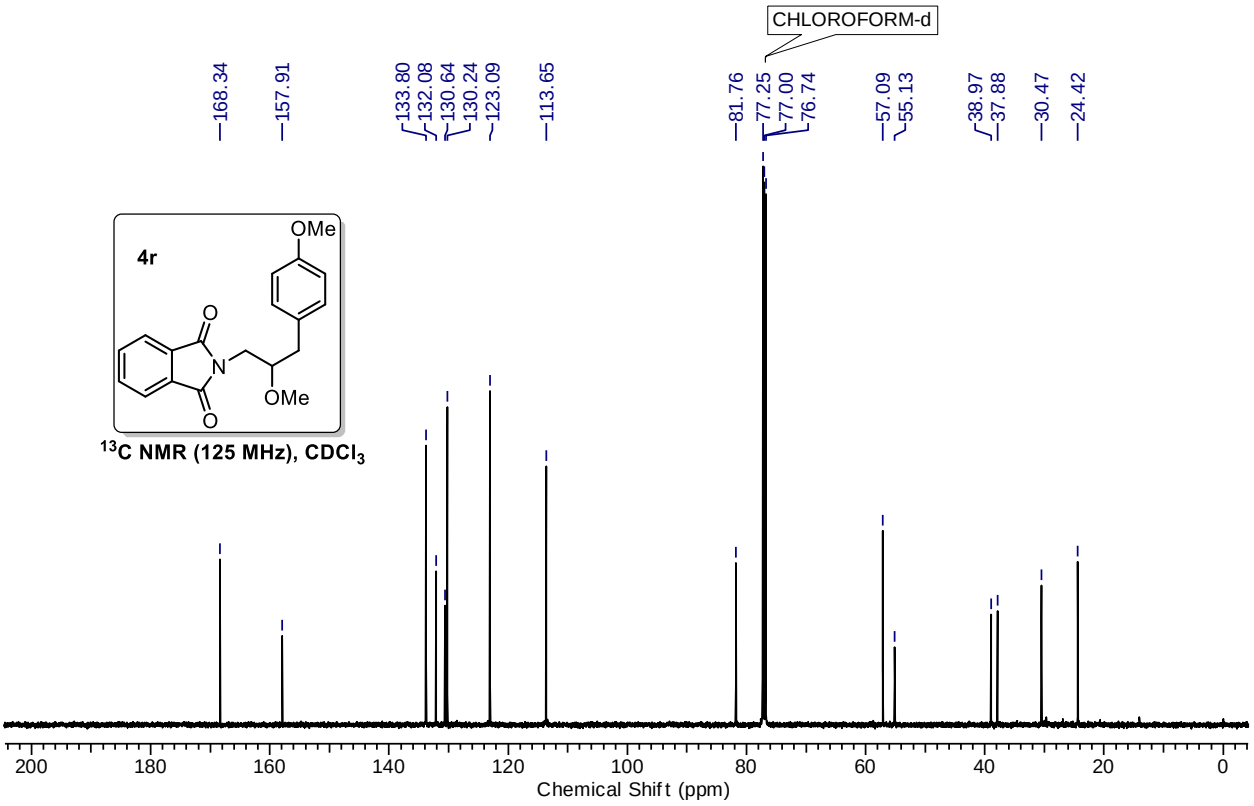
^{1}H NMR (500 MHz), $CDCl_3$



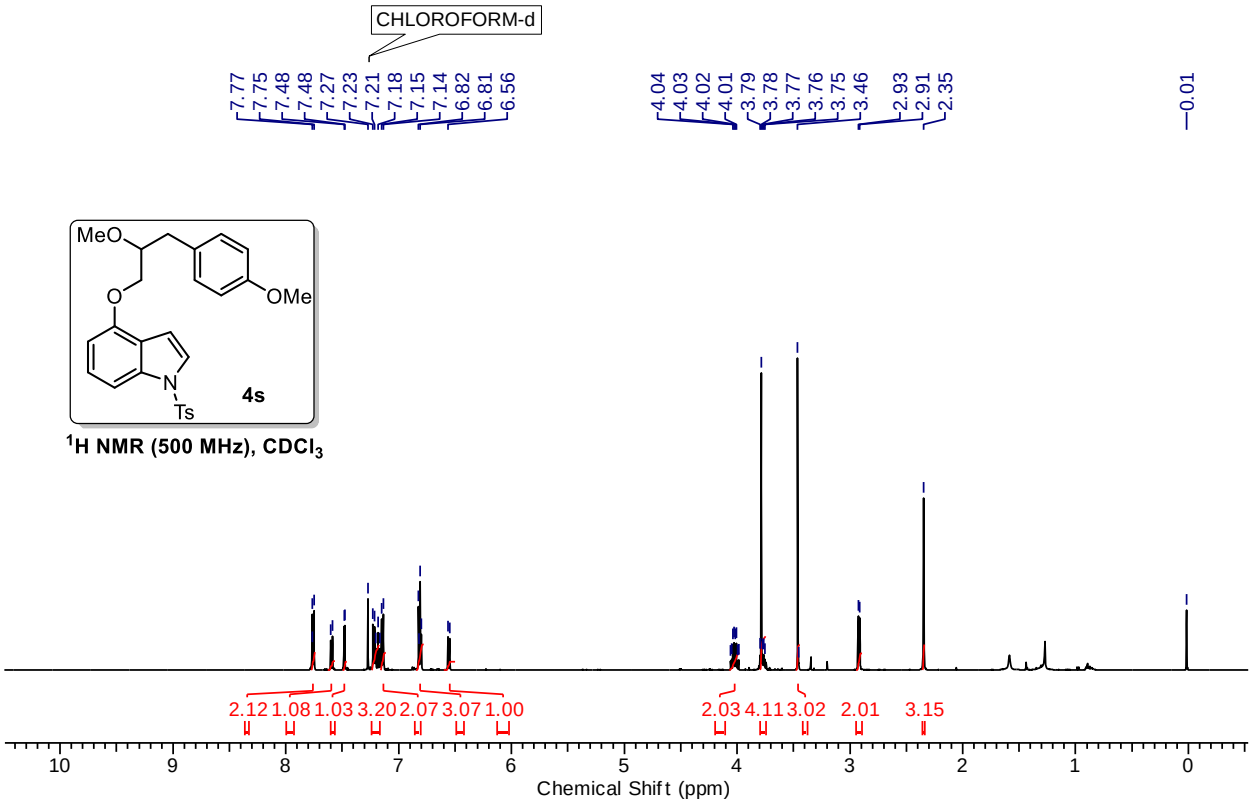
^{13}C NMR (125 MHz), $CDCl_3$



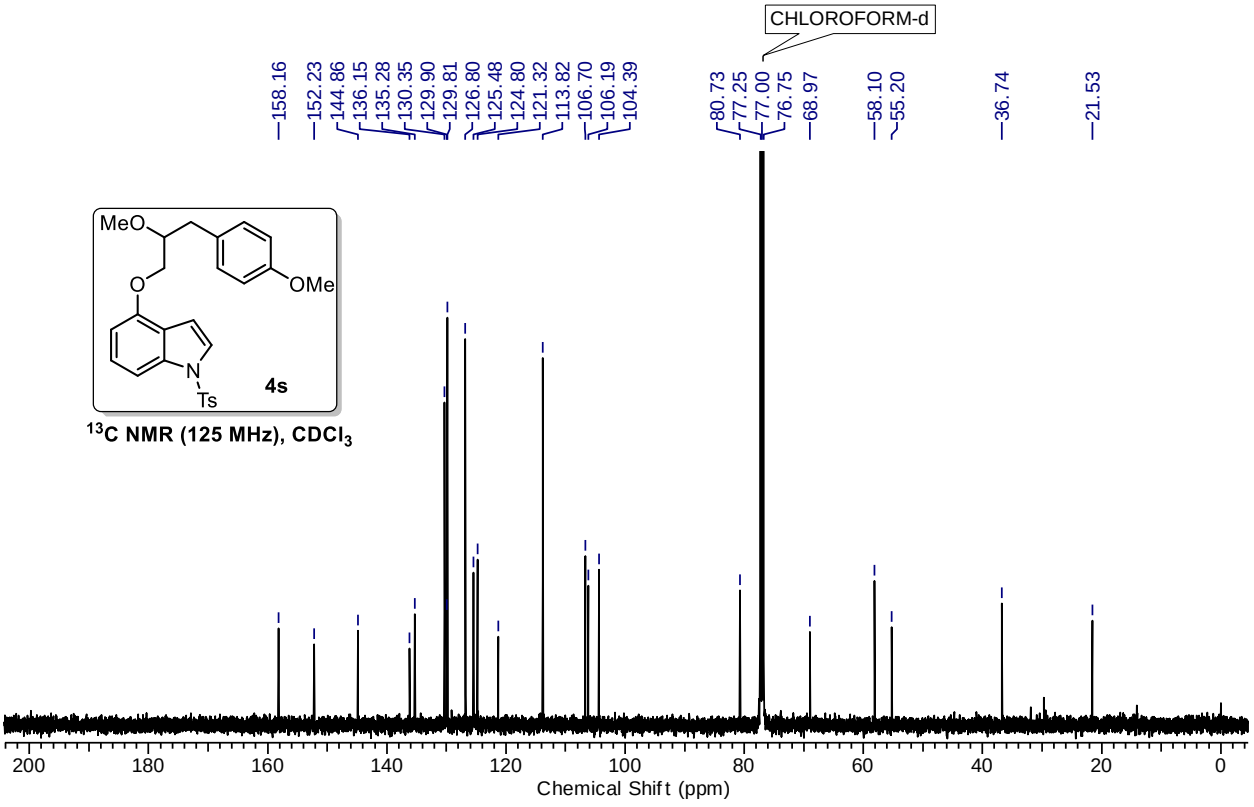
^{1}H NMR (500 MHz), $CDCl_3$



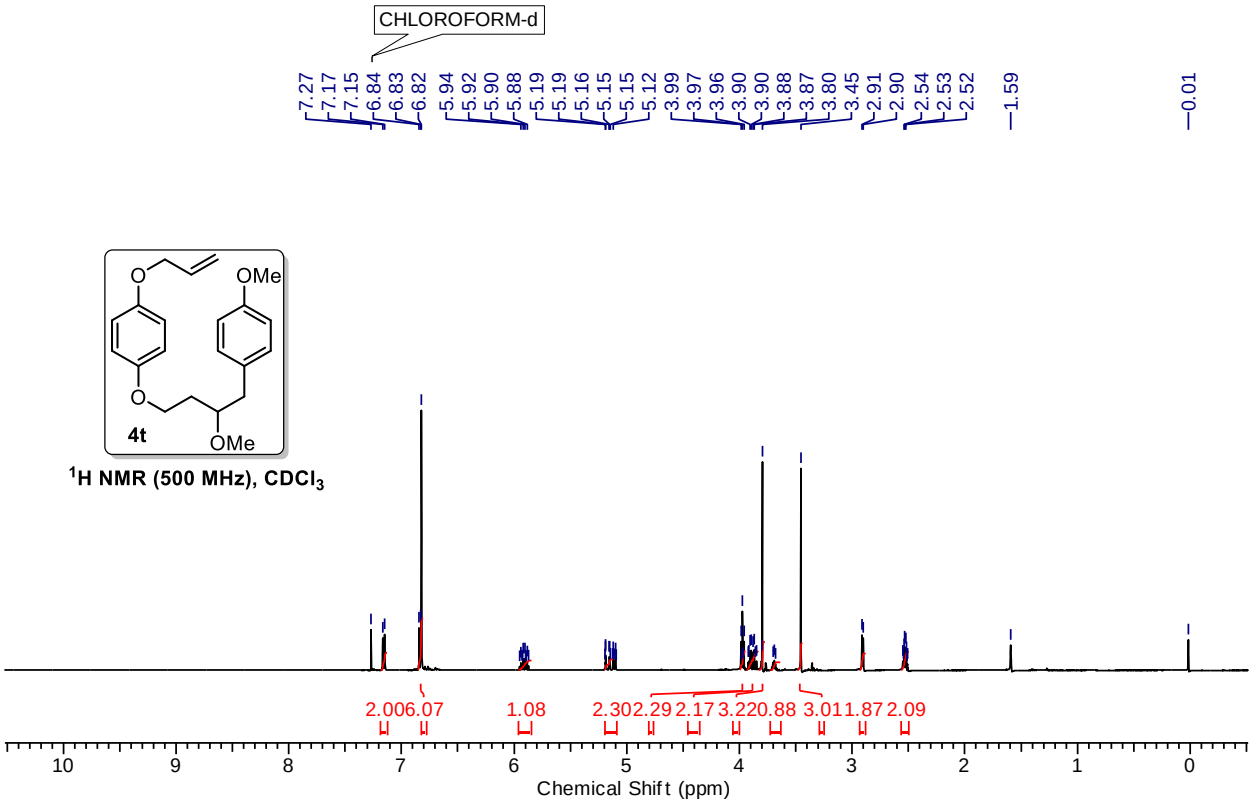
^{13}C NMR (125 MHz), $CDCl_3$



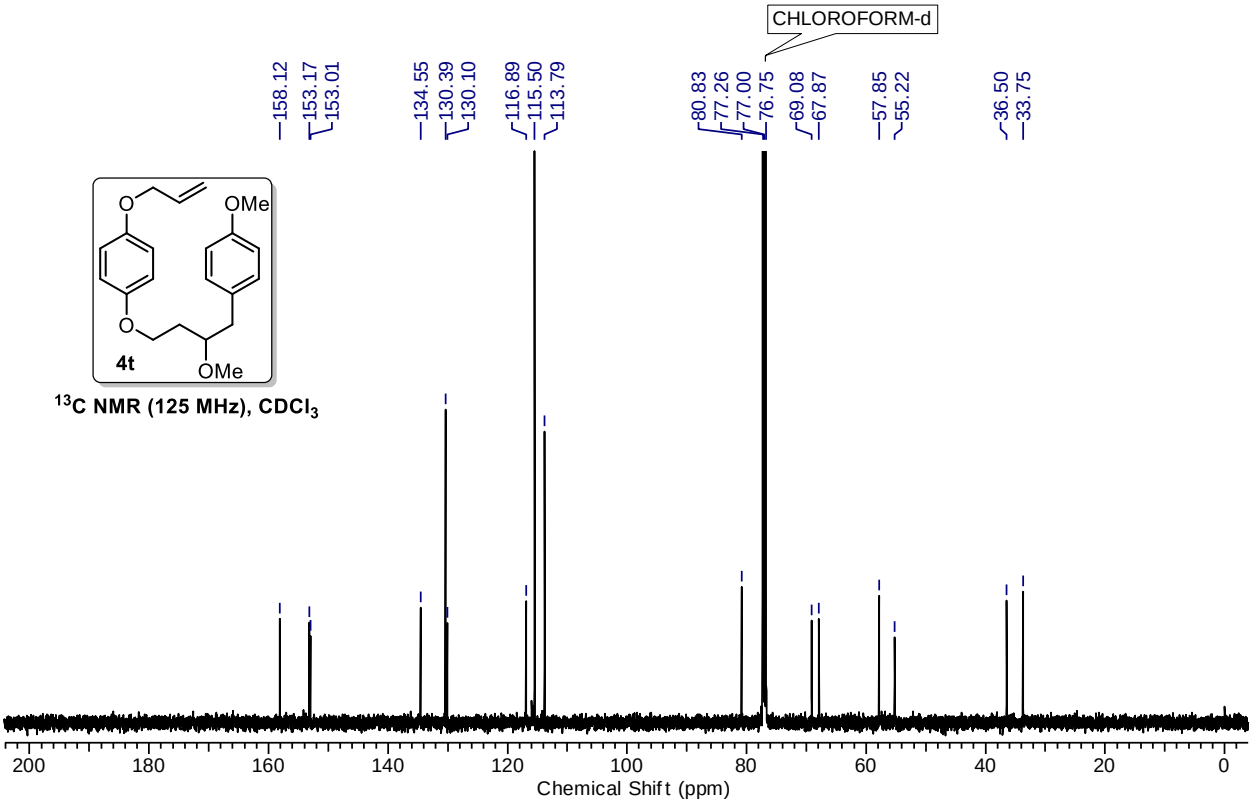
^{1}H NMR (500 MHz), $CDCl_3$



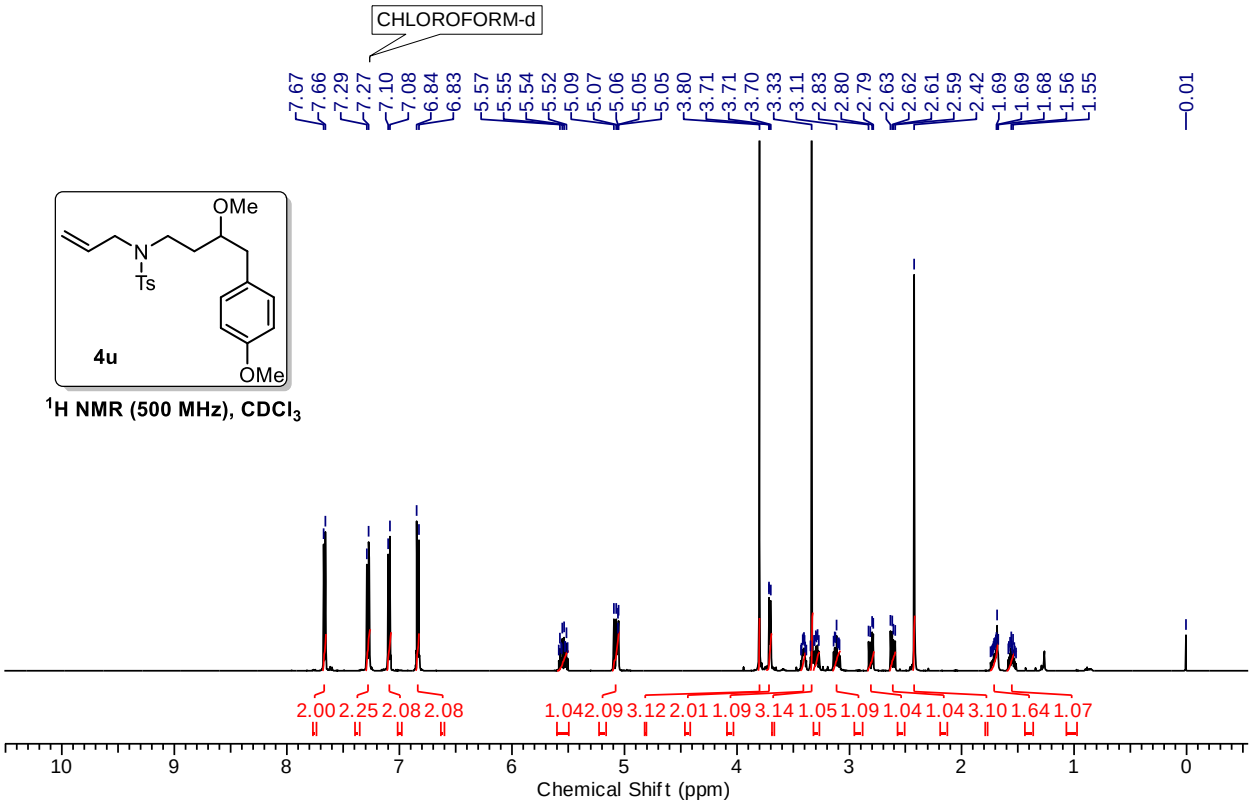
^{13}C NMR (125 MHz), $CDCl_3$



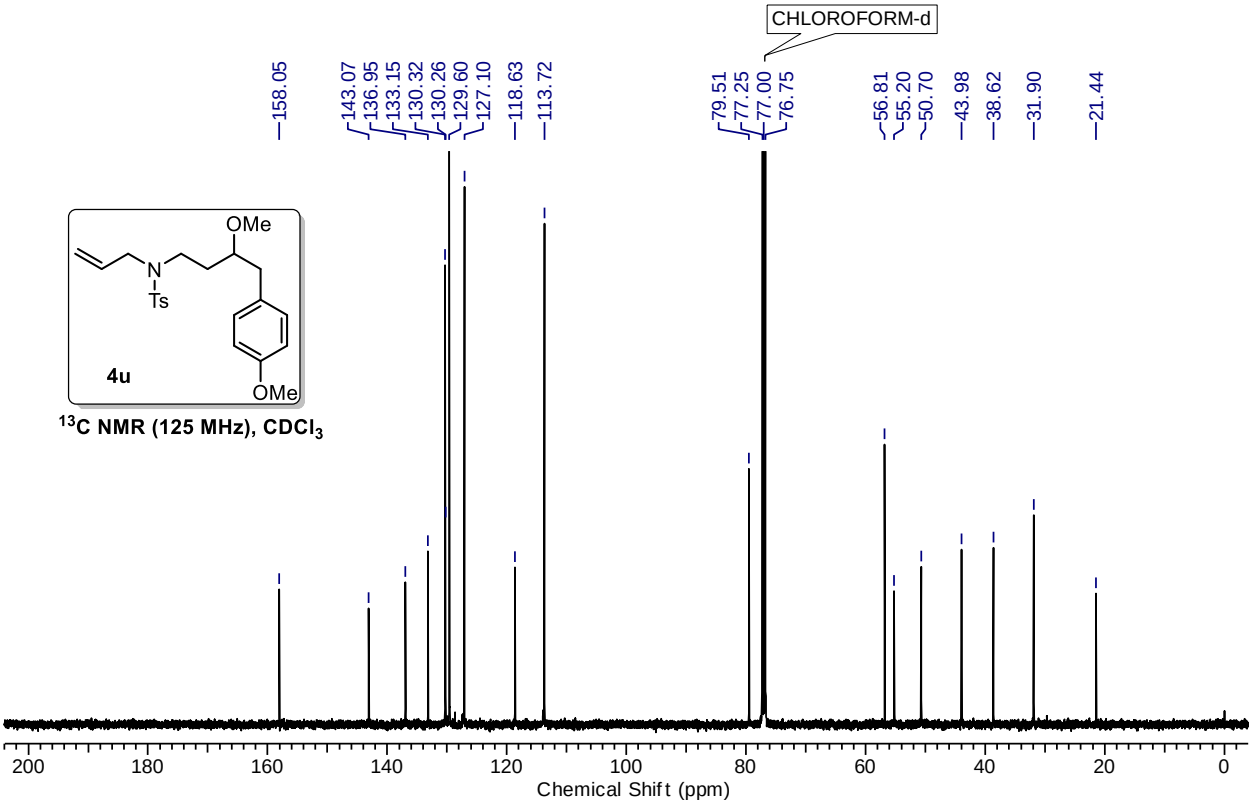
^{1}H NMR (500 MHz), $CDCl_3$



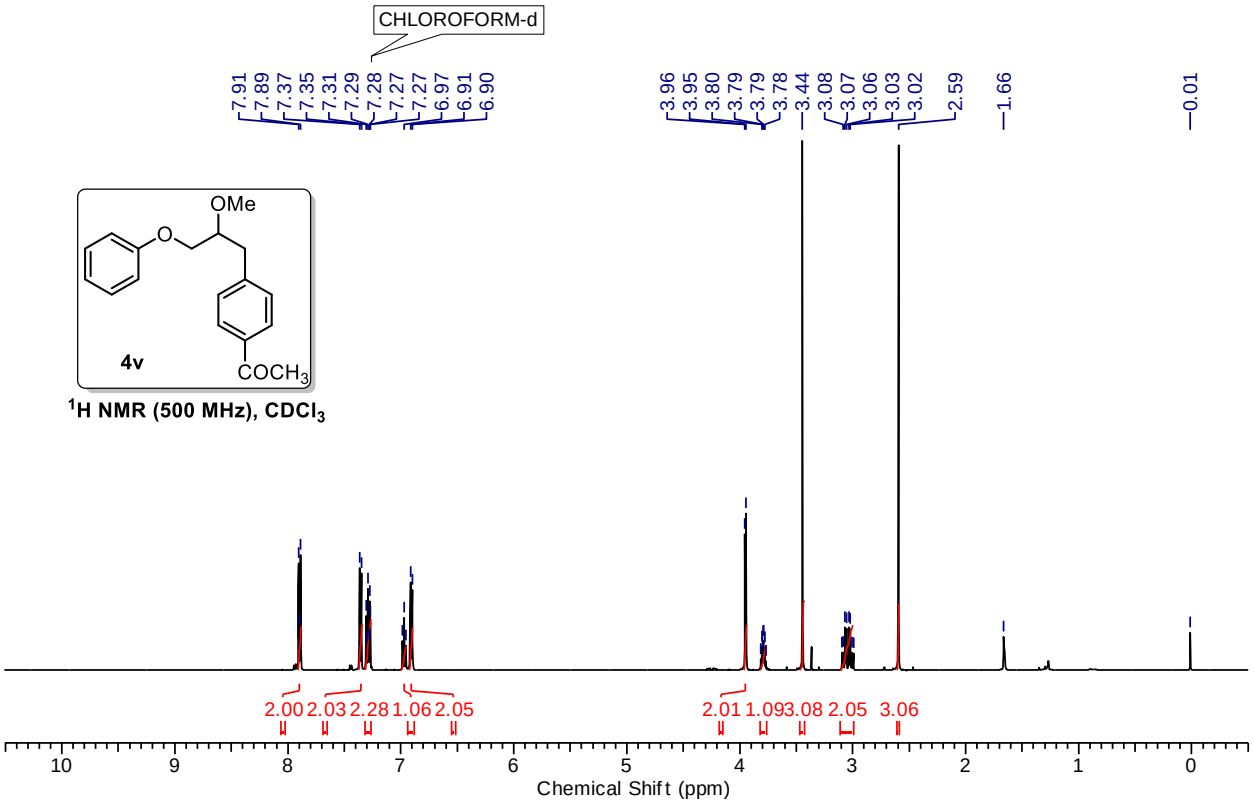
^{13}C NMR (125 MHz), $CDCl_3$

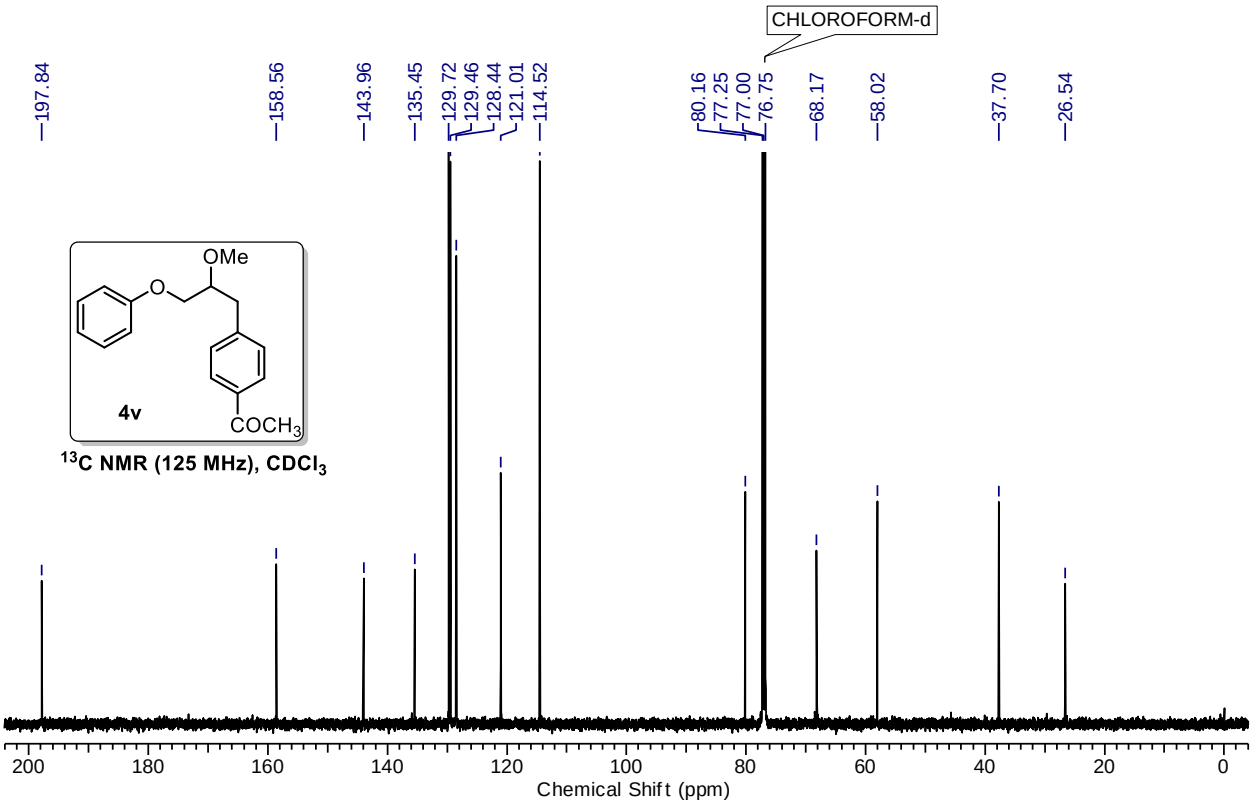


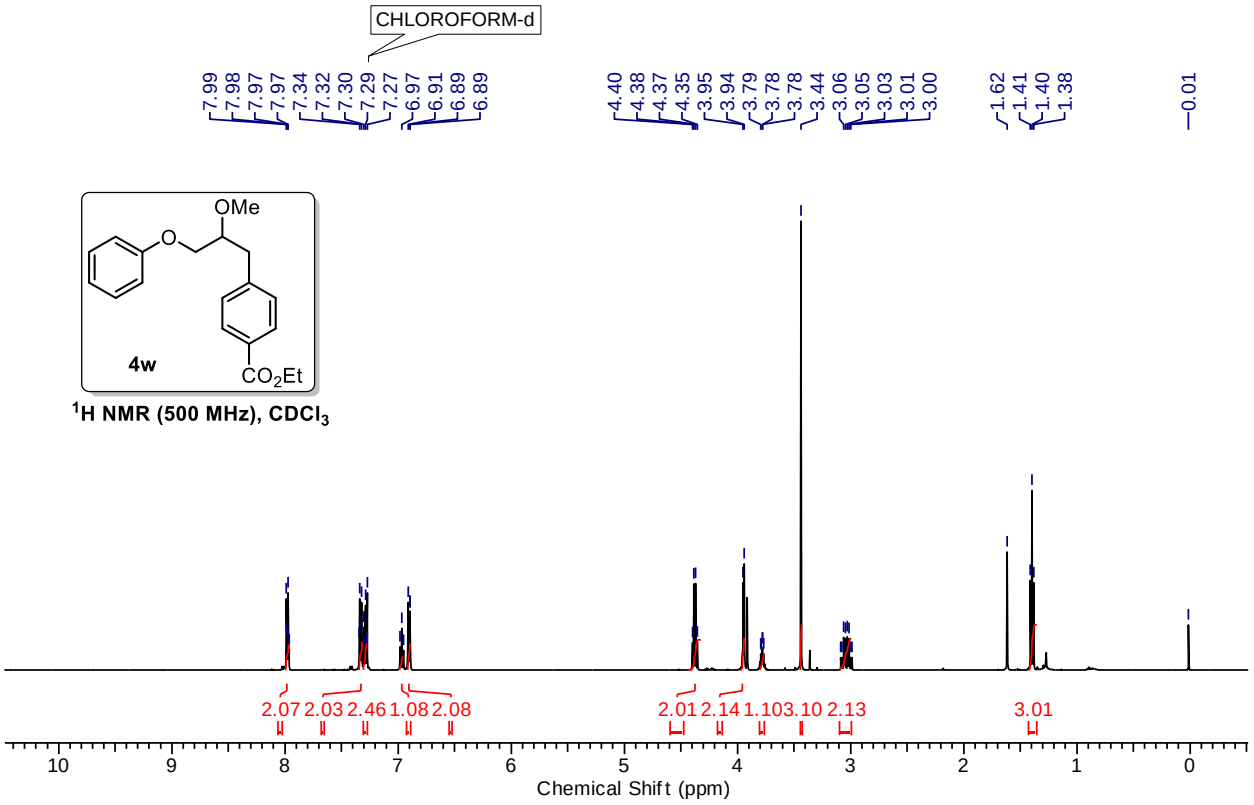
^{1}H NMR (500 MHz), $CDCl_3$

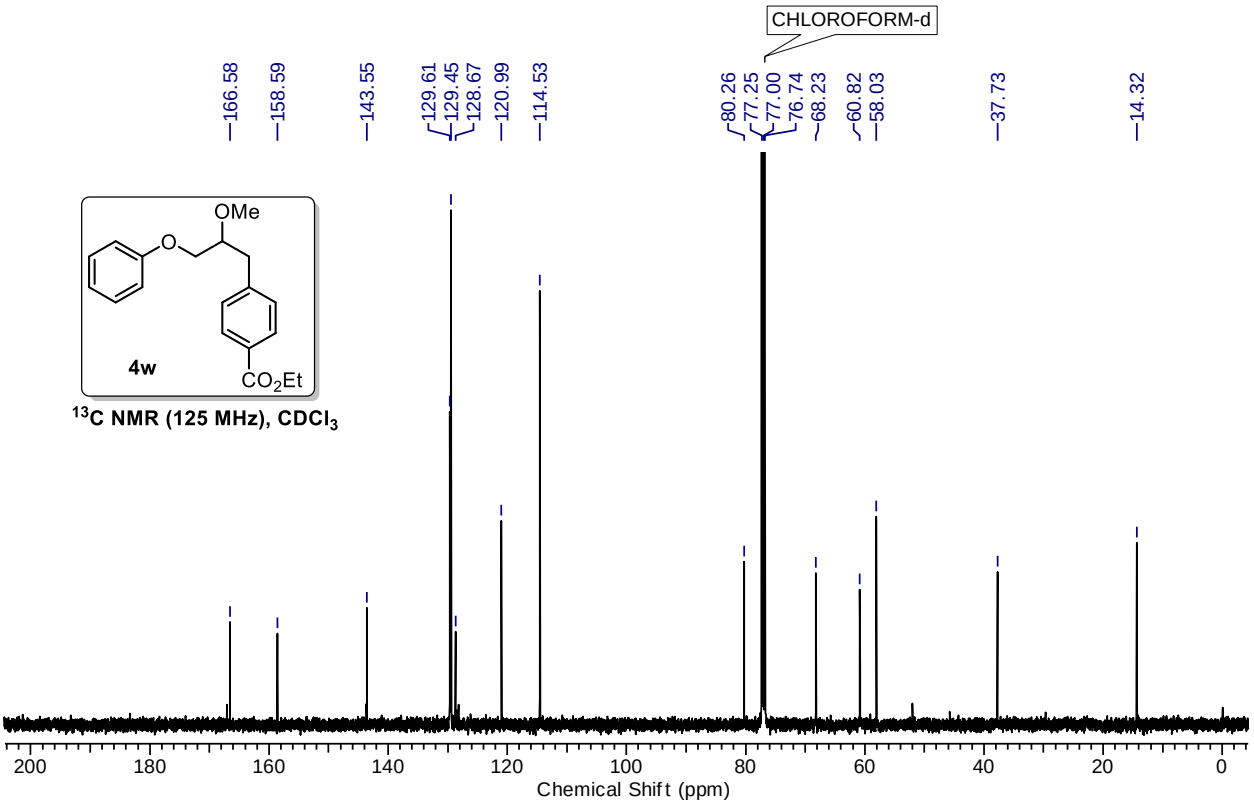


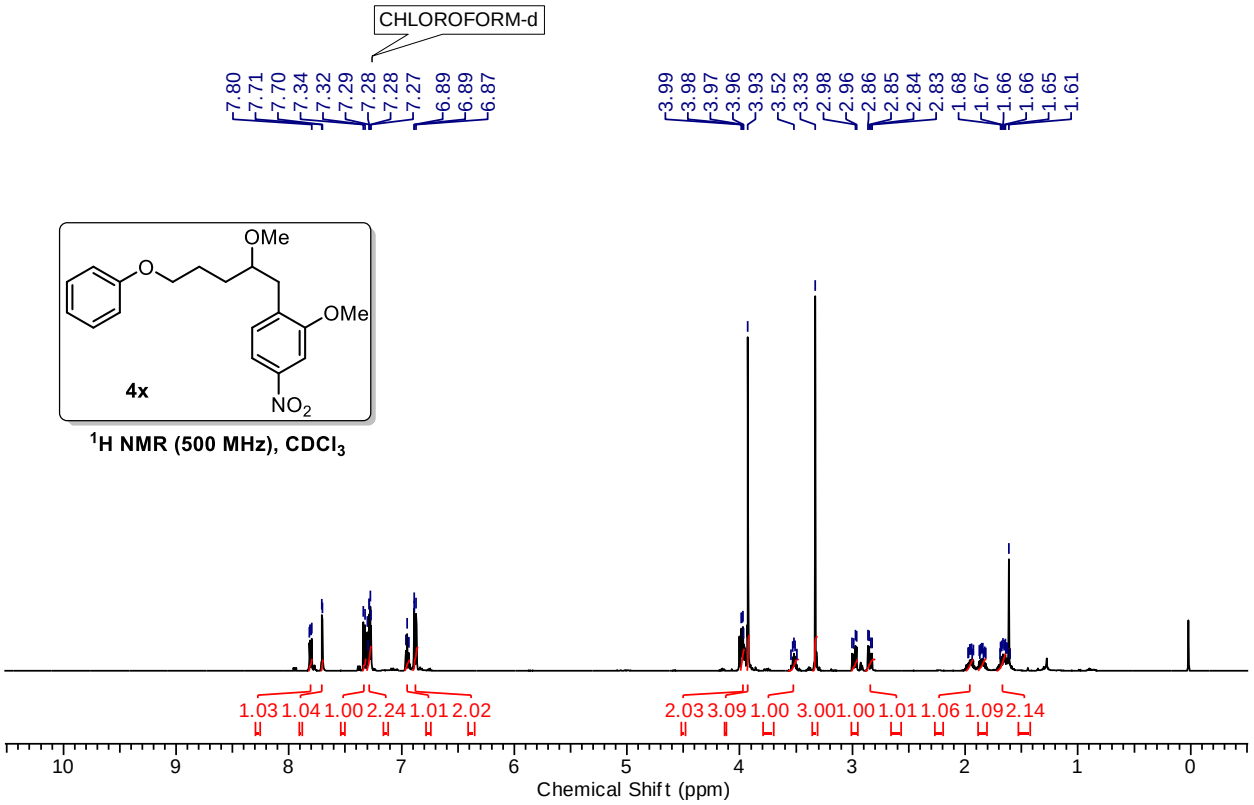
^{13}C NMR (125 MHz), $CDCl_3$

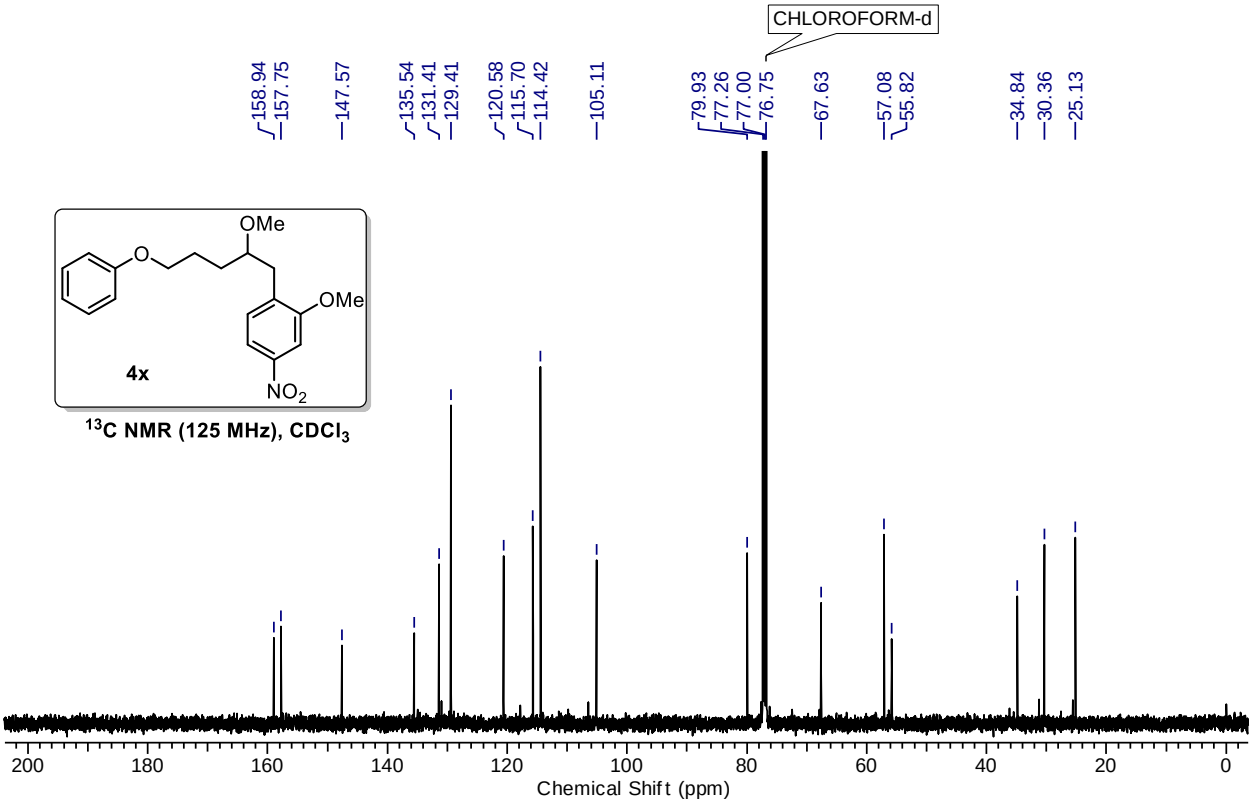

CHLOROFORM-d
7.91
7.89
7.37
7.35
7.31
7.29
7.28
7.27
7.27
6.97
6.91
6.90
3.96
3.95
3.80
3.79
3.79
3.78
3.44
3.08
3.07
3.06
3.03
3.02
2.59
1.66
0.01
OMe
O
4v
COCH3
1H NMR (500 MHz), CDCl3
2.00 2.03 2.28 1.06 2.05
2.01 1.09 3.08 2.05 3.06
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

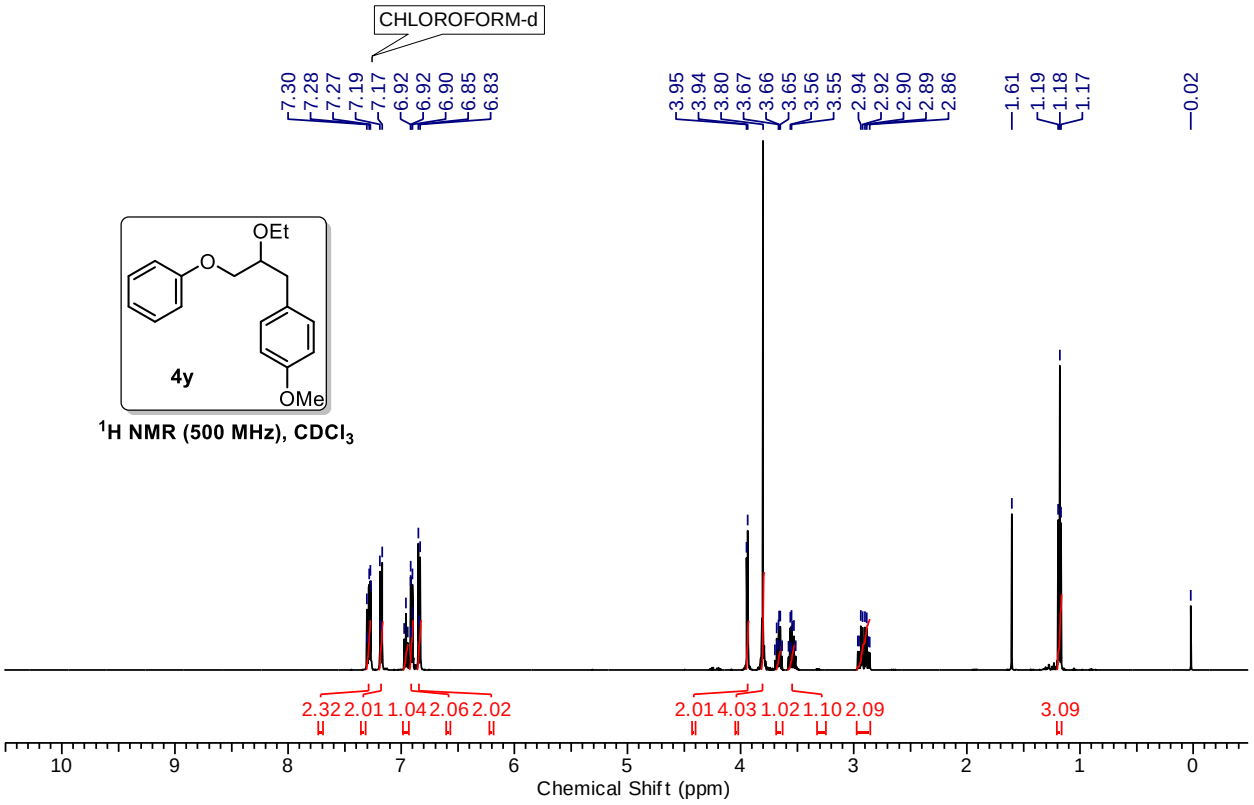

CHLOROFORM-d
197.84
158.56
143.96
135.45
129.72
129.46
128.44
121.01
114.52
80.16
77.25
77.00
76.75
68.17
58.02
37.70
26.54
OMe
O
4v
COCH3
13C NMR (125 MHz), CDCl3
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)


CHLOROFORM-d
7.99
7.98
7.97
7.97
7.34
7.32
7.30
7.29
7.27
6.97
6.91
6.89
6.89
4.40
4.38
4.37
4.35
3.95
3.94
3.79
3.78
3.78
3.44
3.06
3.05
3.03
3.01
3.00
1.62
1.41
1.40
1.38
0.01
OMe
O
4w
CO2Et
1H NMR (500 MHz), CDCl3
2.07 2.03 2.46 1.08 2.08
2.01 2.14 1.10 3.10 2.13
3.01
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

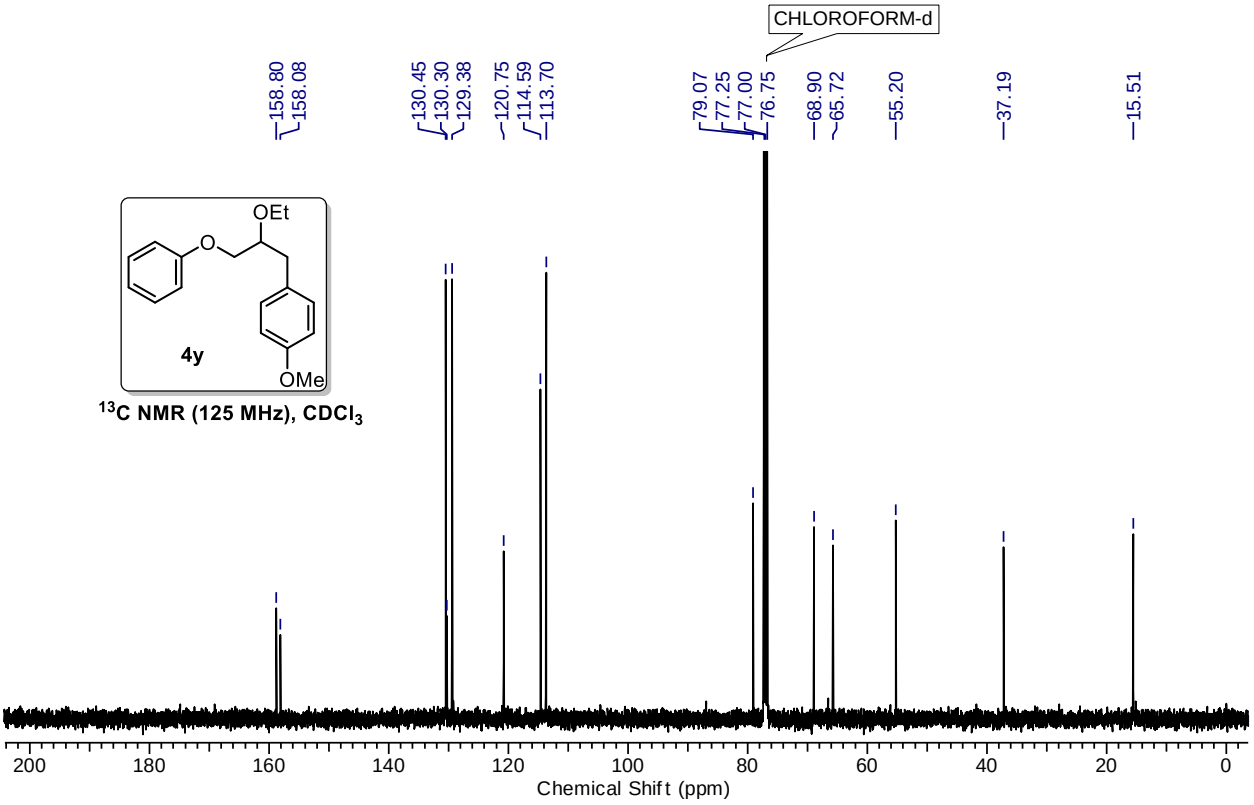

CHLOROFORM-d
166.58
158.59
143.55
129.61
129.45
128.67
120.99
114.53
80.26
77.25
77.00
76.74
68.23
60.82
58.03
37.73
14.32
OMe
O
4w
CO2Et
13C NMR (125 MHz), CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


CHLOROFORM-d
7.80
7.71
7.70
7.34
7.32
7.29
7.28
7.28
7.27
6.89
6.89
6.87
3.99
3.98
3.97
3.96
3.93
3.52
3.33
2.98
2.96
2.86
2.85
2.84
2.83
1.68
1.67
1.66
1.66
1.65
1.61
OMe
O
OMe
4x
NO2
1H NMR (500 MHz), CDCl3
1.03 1.04 1.00 2.24 1.01 2.02
2.03 3.09 1.00 3.00 1.00 1.01 1.06 1.09 2.14
Chemical Shift (ppm)

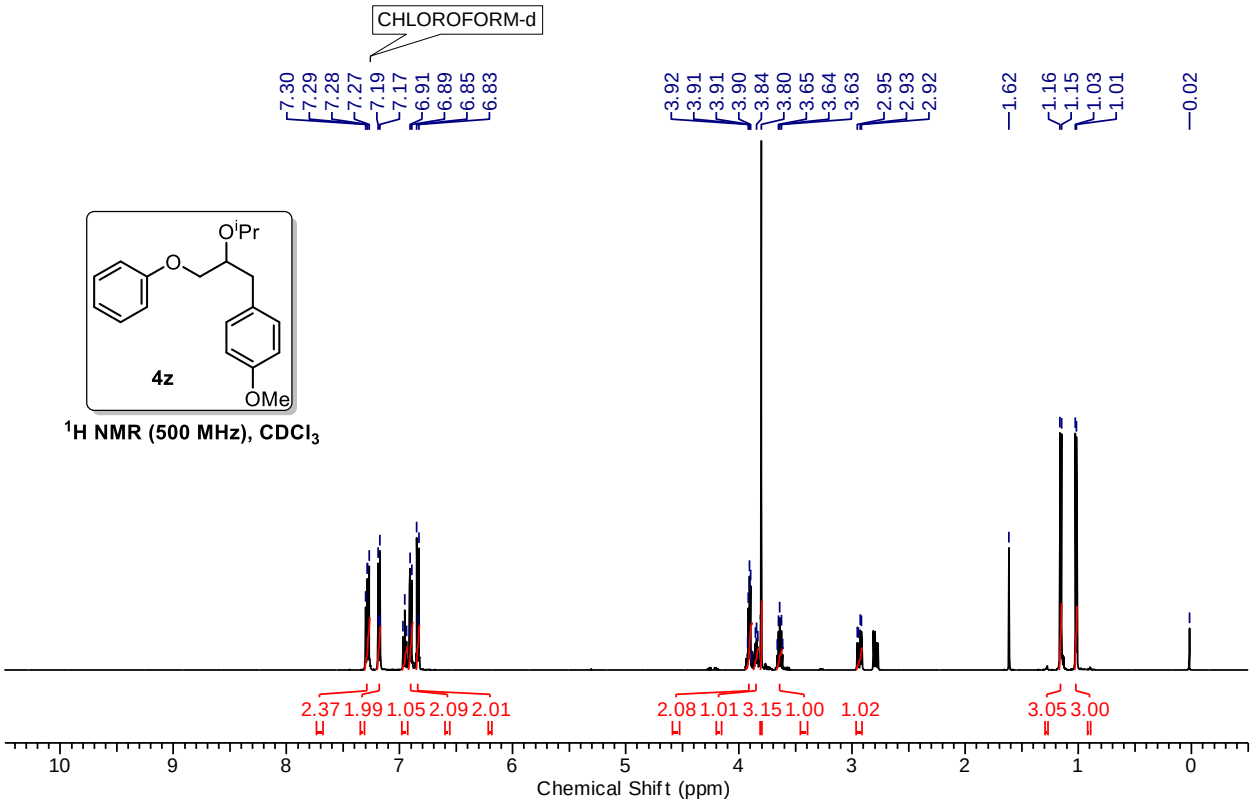

CHLOROFORM-d
158.94
157.75
147.57
135.54
131.41
129.41
120.58
115.70
114.42
105.11
79.93
77.26
77.00
76.75
67.63
57.08
55.82
34.84
30.36
25.13
OMe
O
OMe
4x
NO2
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)



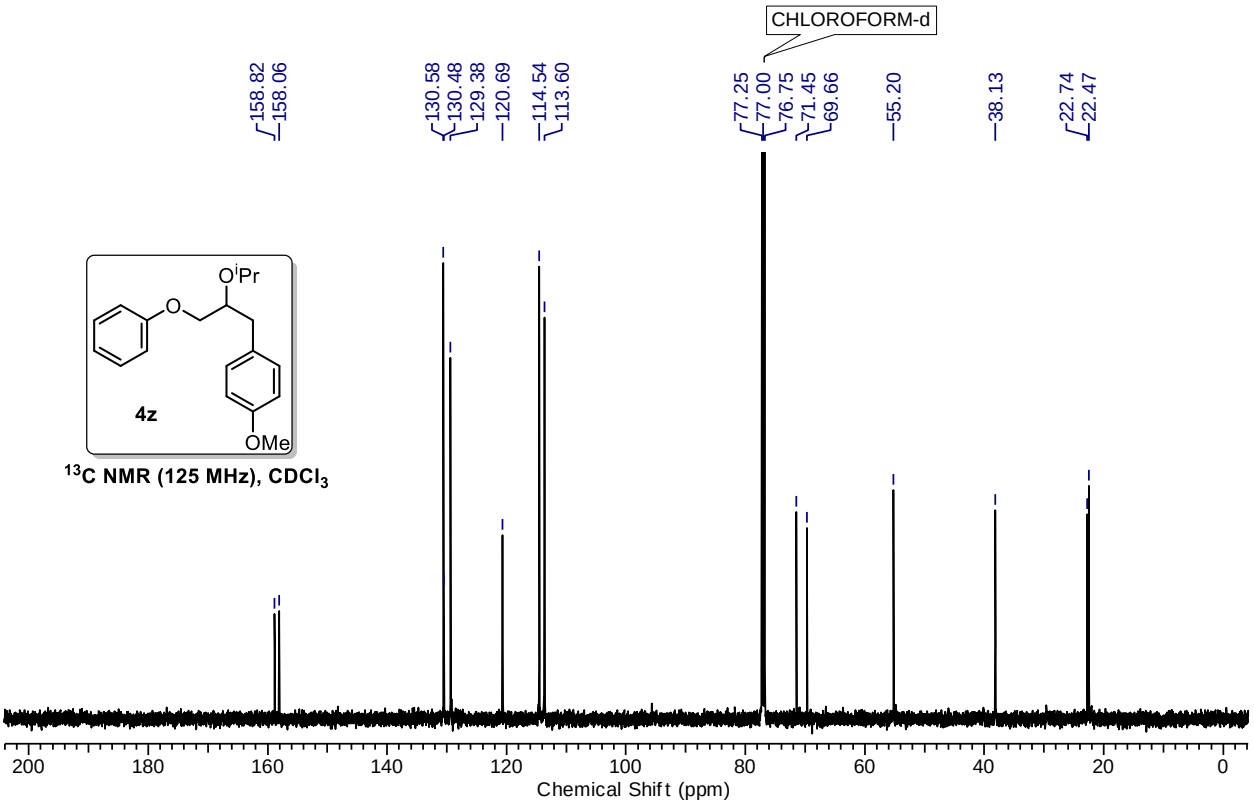
^{1}H NMR (500 MHz), $CDCl_3$



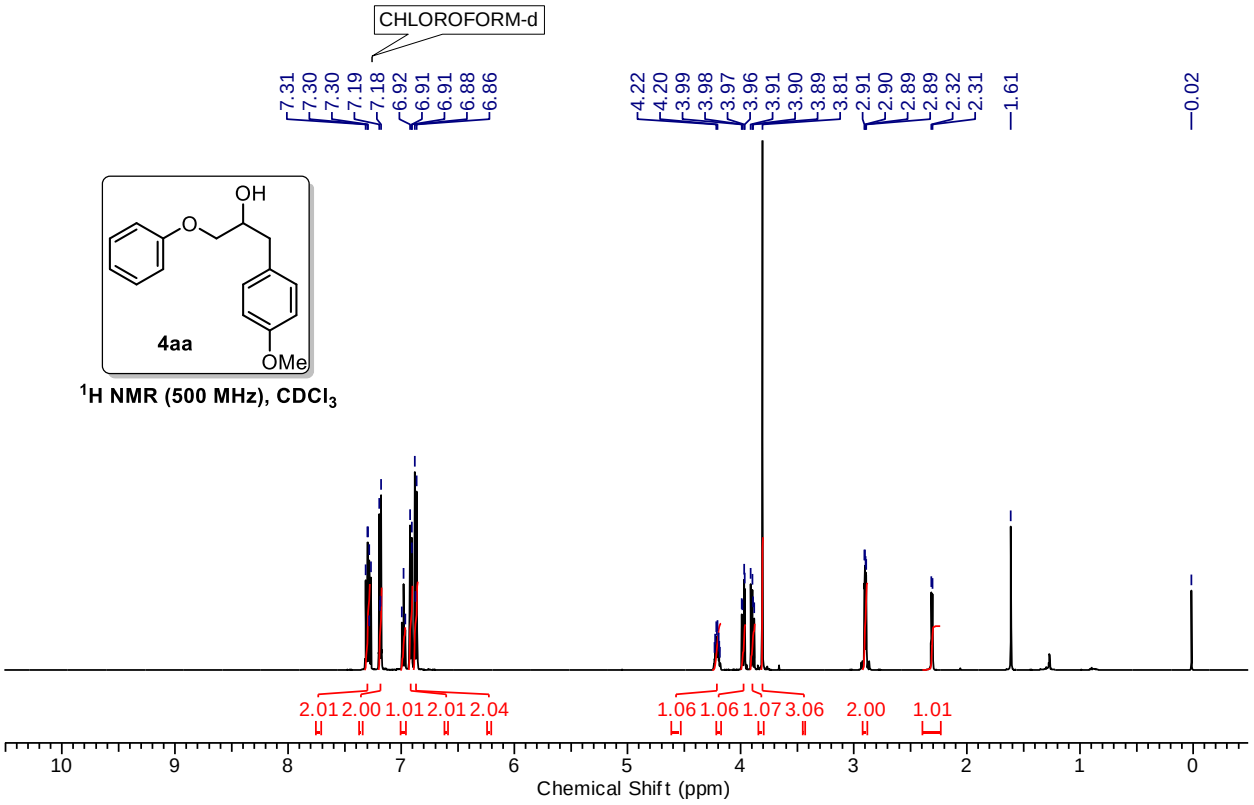
^{13}C NMR (125 MHz), $CDCl_3$



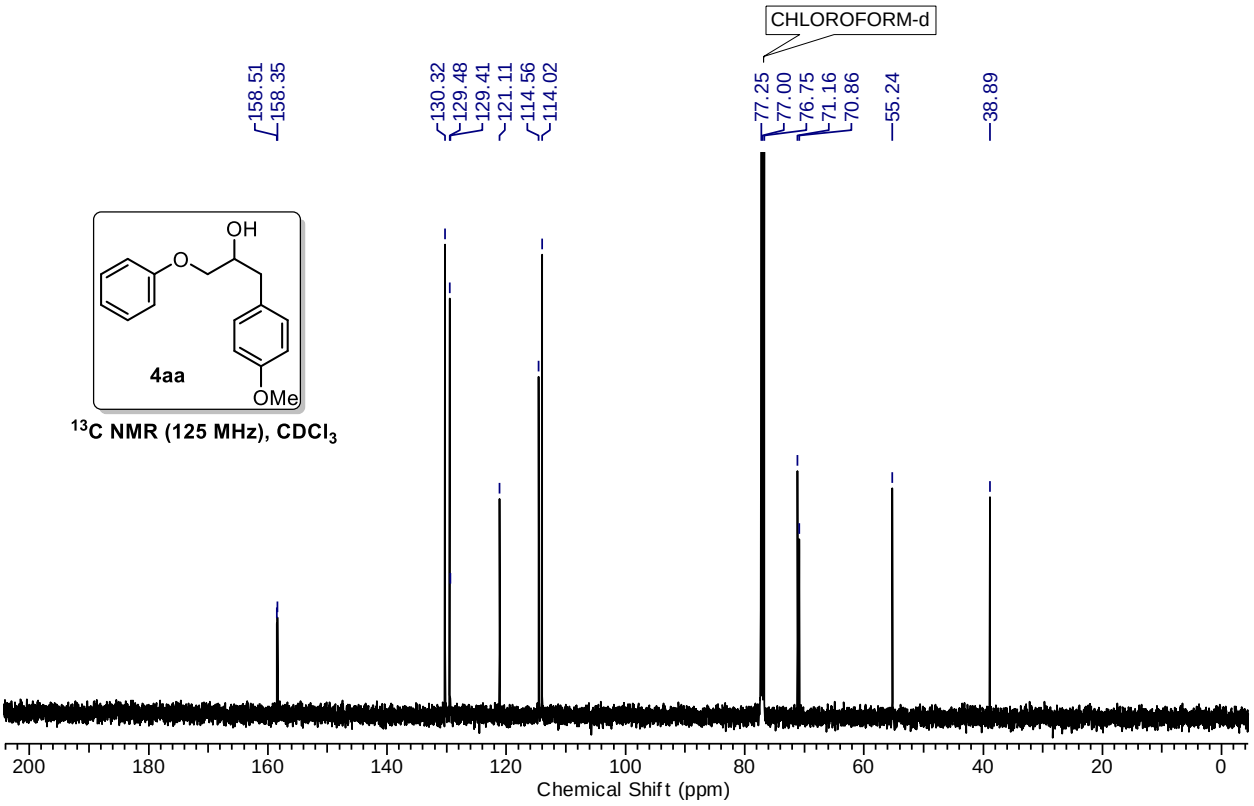
^{1}H NMR (500 MHz), $CDCl_3$



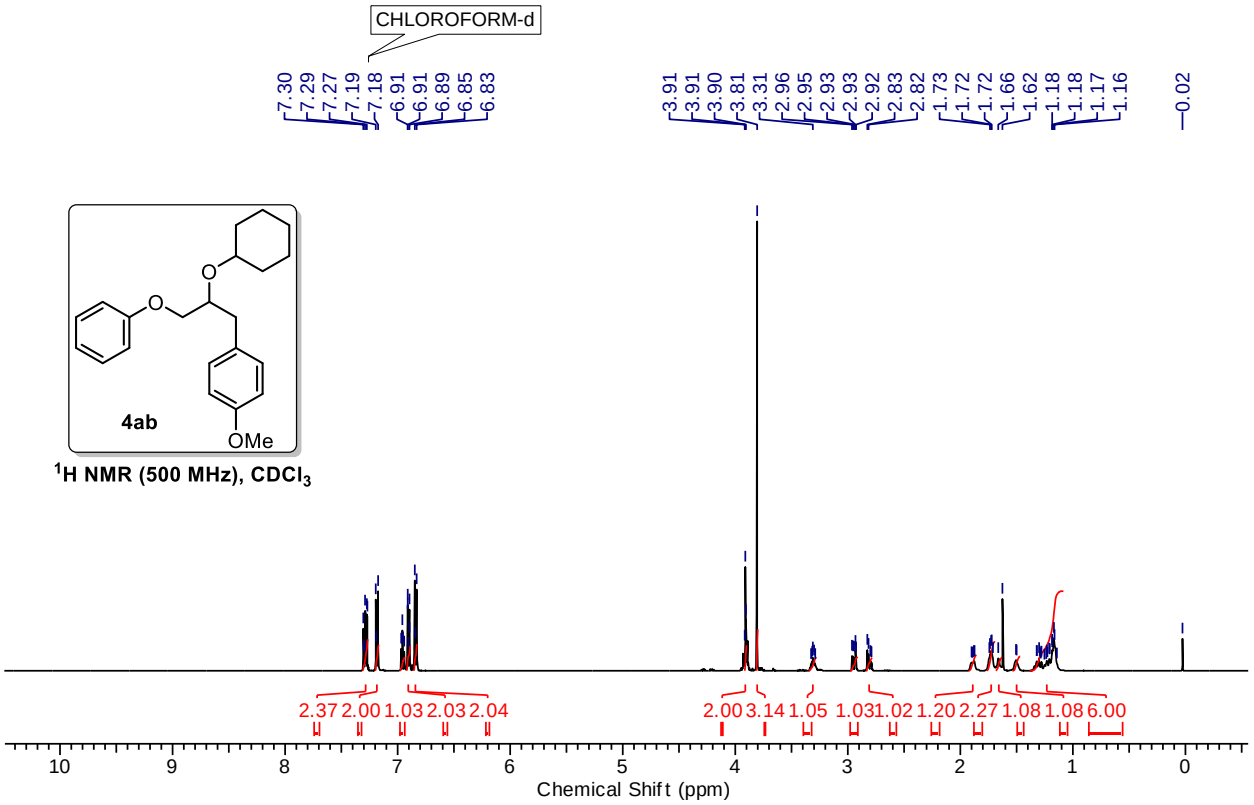
^{13}C NMR (125 MHz), $CDCl_3$

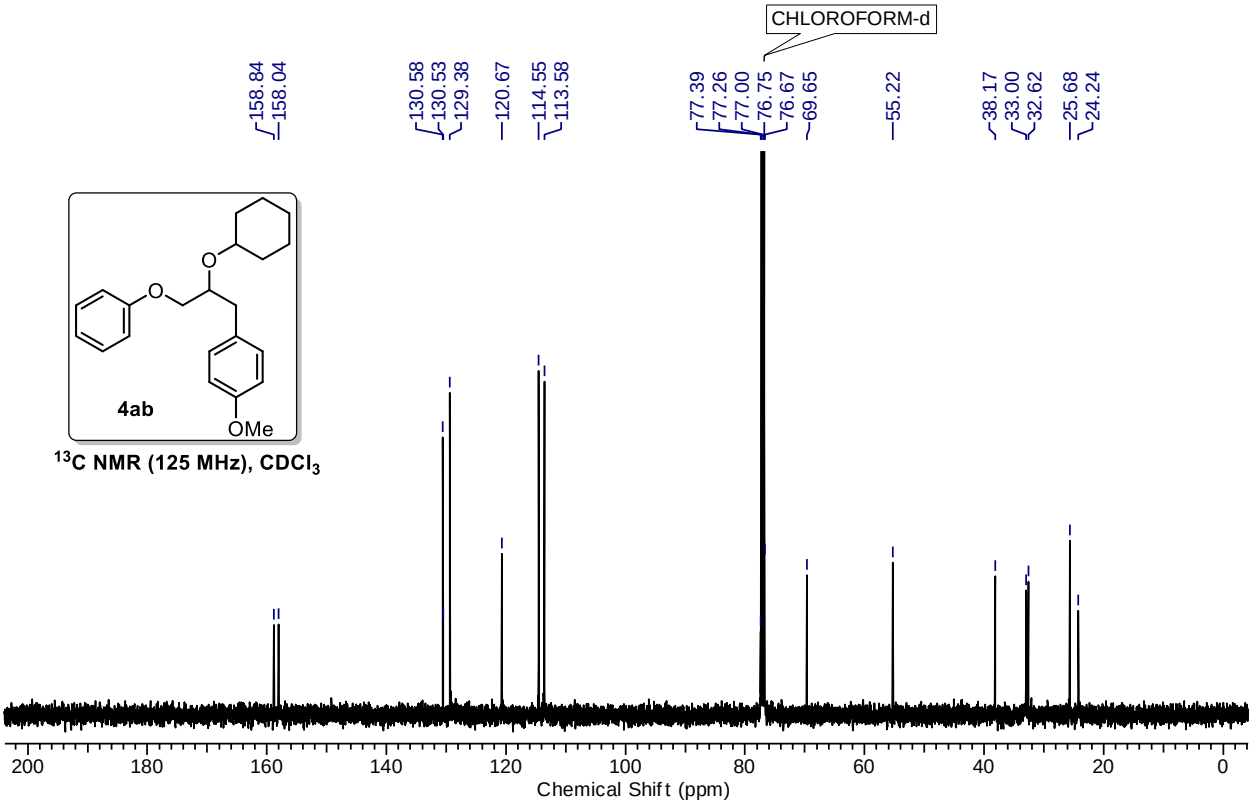


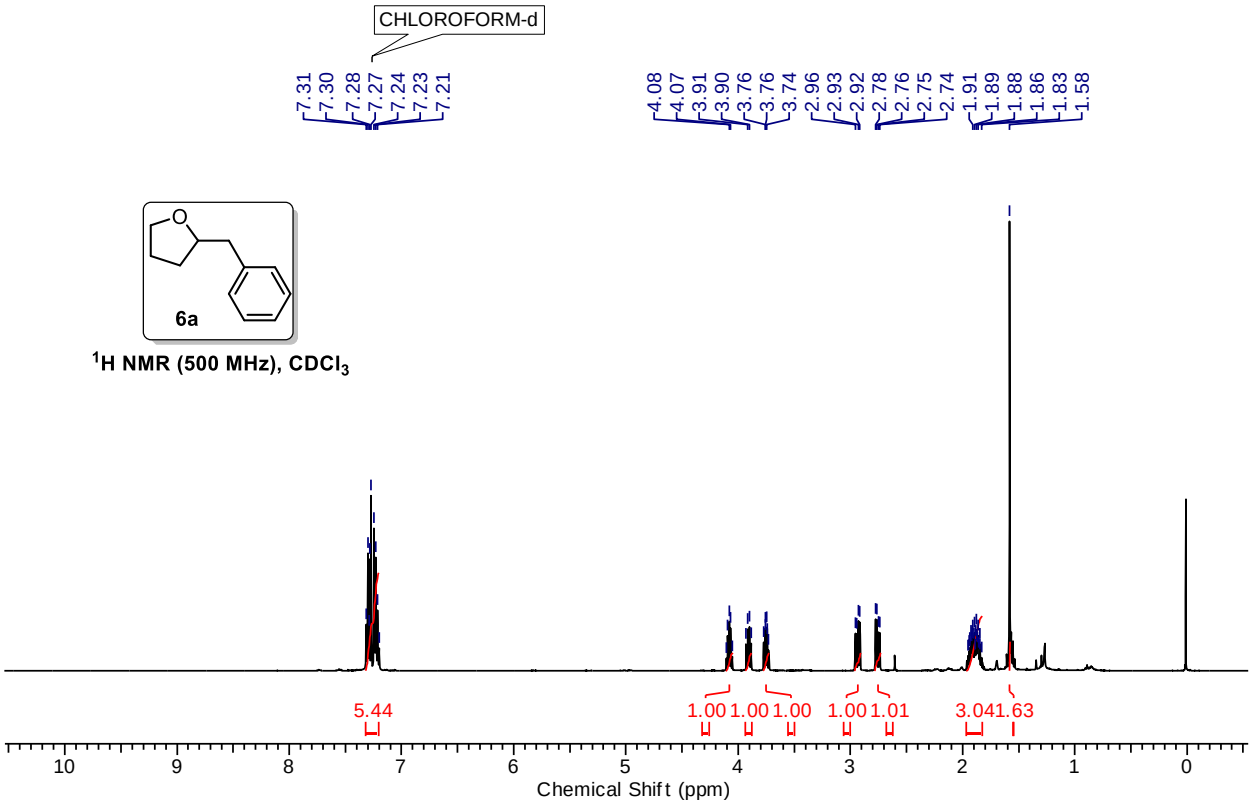
^{1}H NMR (500 MHz), $CDCl_3$

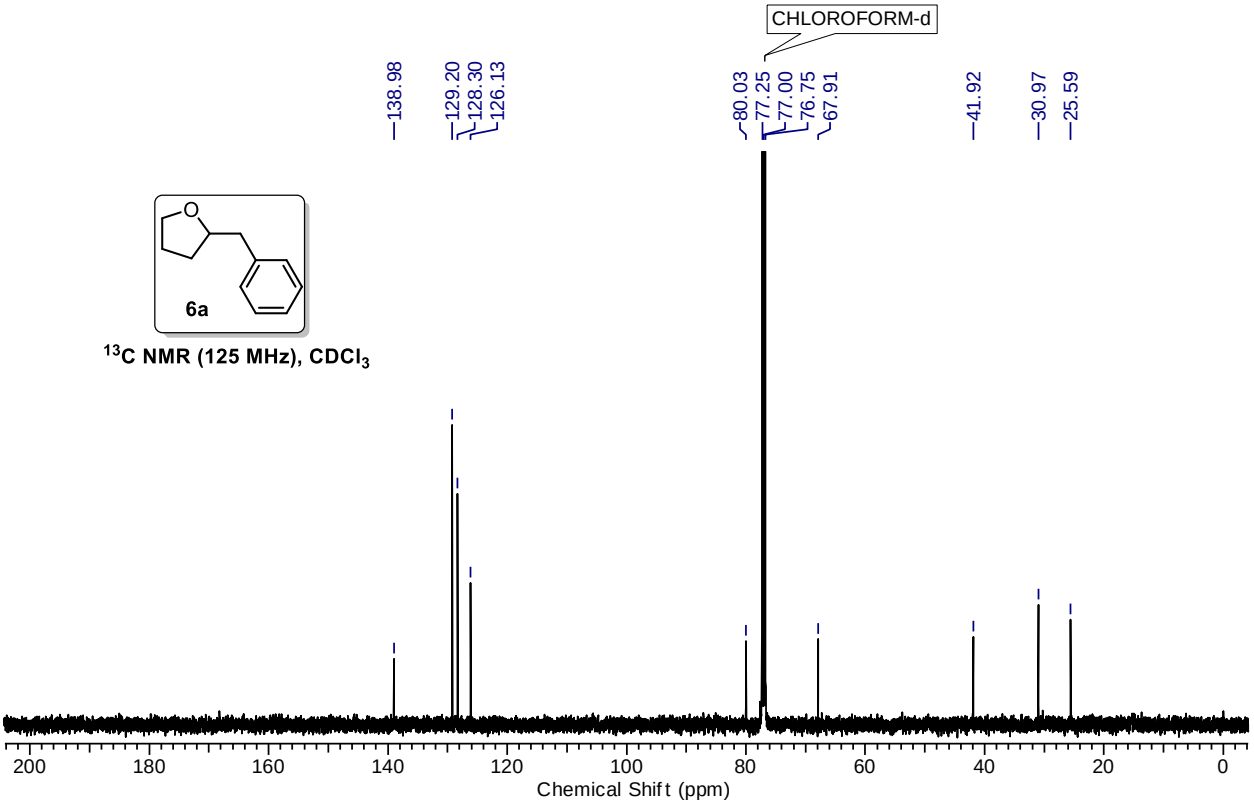


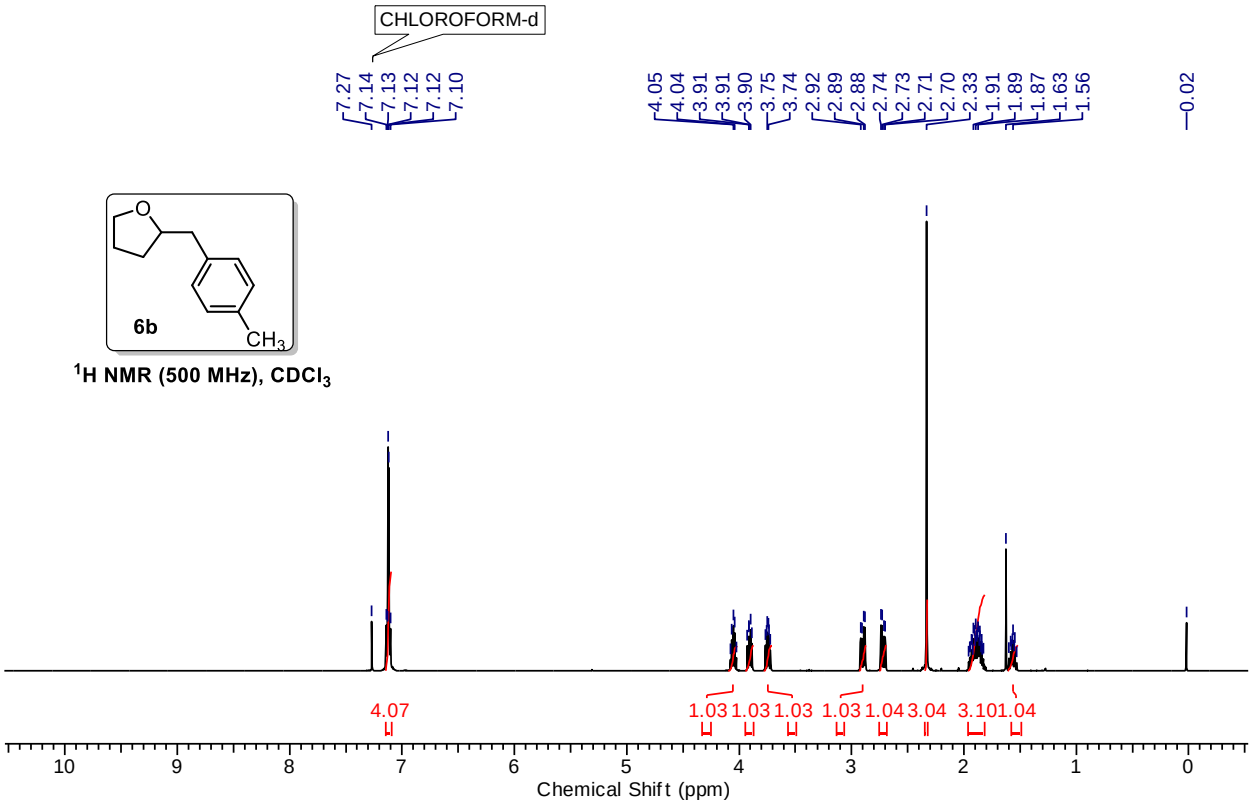
^{13}C NMR (125 MHz), $CDCl_3$


CHLOROFORM-d
7.30
7.29
7.27
7.19
7.18
6.91
6.91
6.89
6.85
6.83
3.91
3.91
3.90
3.81
3.31
2.96
2.95
2.93
2.92
2.83
2.82
1.73
1.72
1.72
1.66
1.62
1.18
1.18
1.17
1.16
0.02
4ab
OMe
^{1}H NMR (500 MHz), CDCl$_3$
2.37 2.00 1.03 2.03 2.04
2.00 3.14 1.05 1.03 1.02 1.20 2.27 1.08 1.08 6.00
Chemical Shift (ppm)

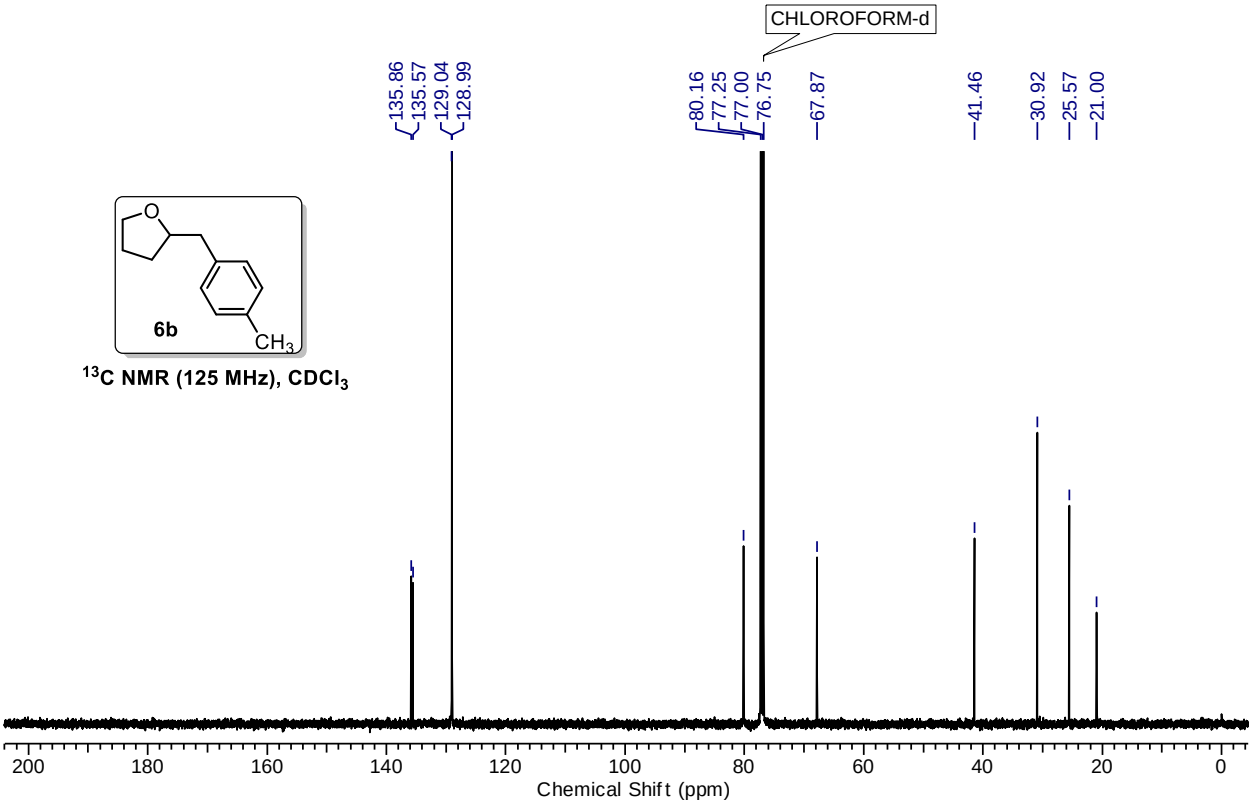

CHLOROFORM-d
158.84
158.04
130.58
130.53
129.38
120.67
114.55
113.58
77.39
77.26
77.00
76.75
76.67
69.65
55.22
38.17
33.00
32.62
25.68
24.24
4ab
OMe
^{13}C NMR (125 MHz), CDCl$_3$
Chemical Shift (ppm)


CHLOROFORM-d
7.31
7.30
7.28
7.27
7.24
7.23
7.21
4.08
4.07
3.91
3.90
3.76
3.76
3.74
2.96
2.93
2.92
2.78
2.76
2.75
2.74
1.91
1.89
1.88
1.86
1.83
1.58
6a
1H NMR (500 MHz), CDCl3
5.44
1.00
1.00
1.00
1.00
1.01
3.04
1.63
Chemical Shift (ppm)

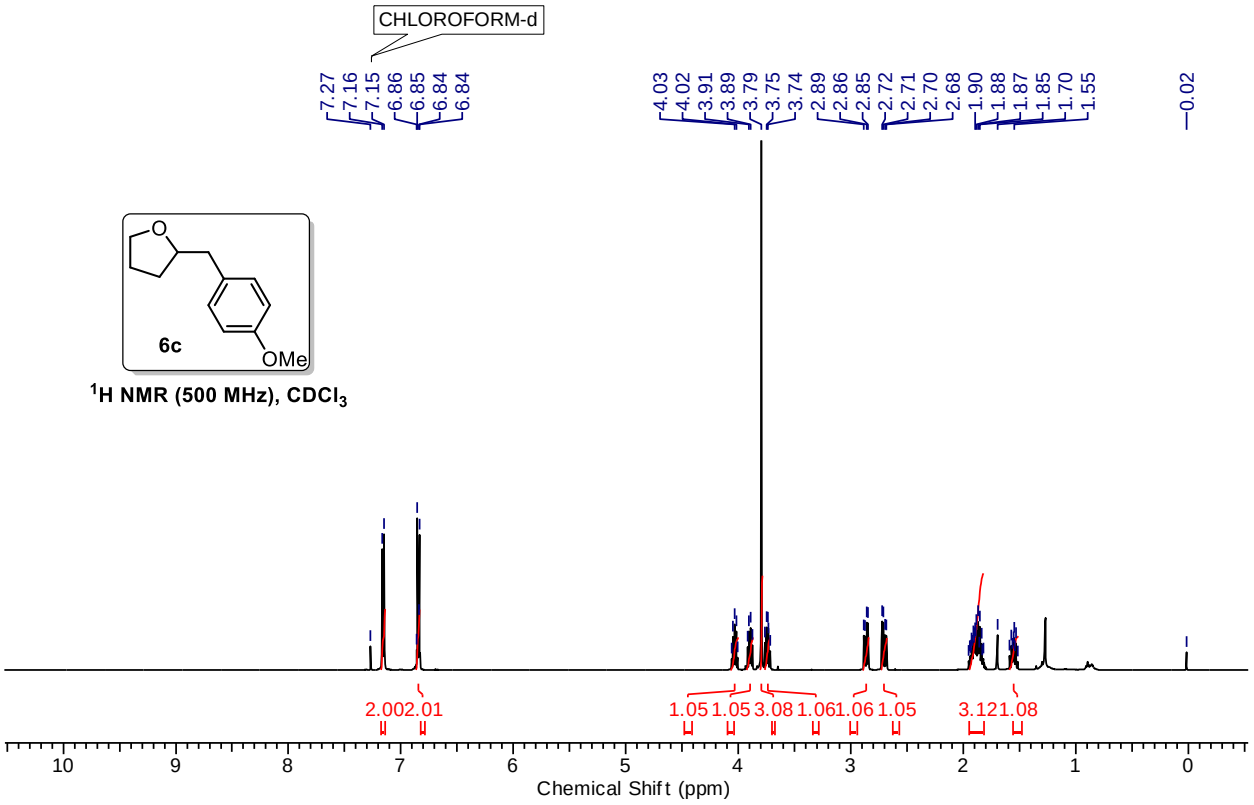

CHLOROFORM-d
138.98
129.20
128.30
126.13
80.03
77.25
77.00
76.75
67.91
41.92
30.97
25.59
6a
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)



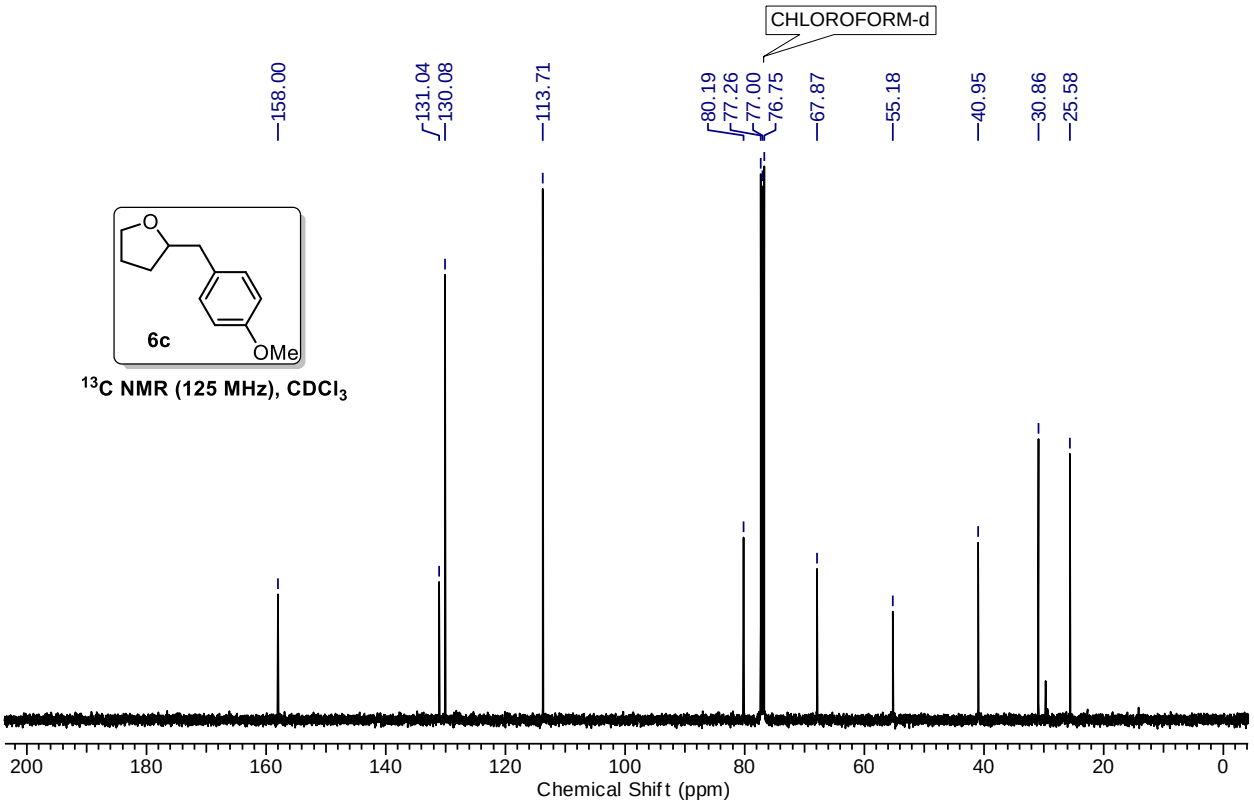
^{1}H NMR (500 MHz), $CDCl_3$



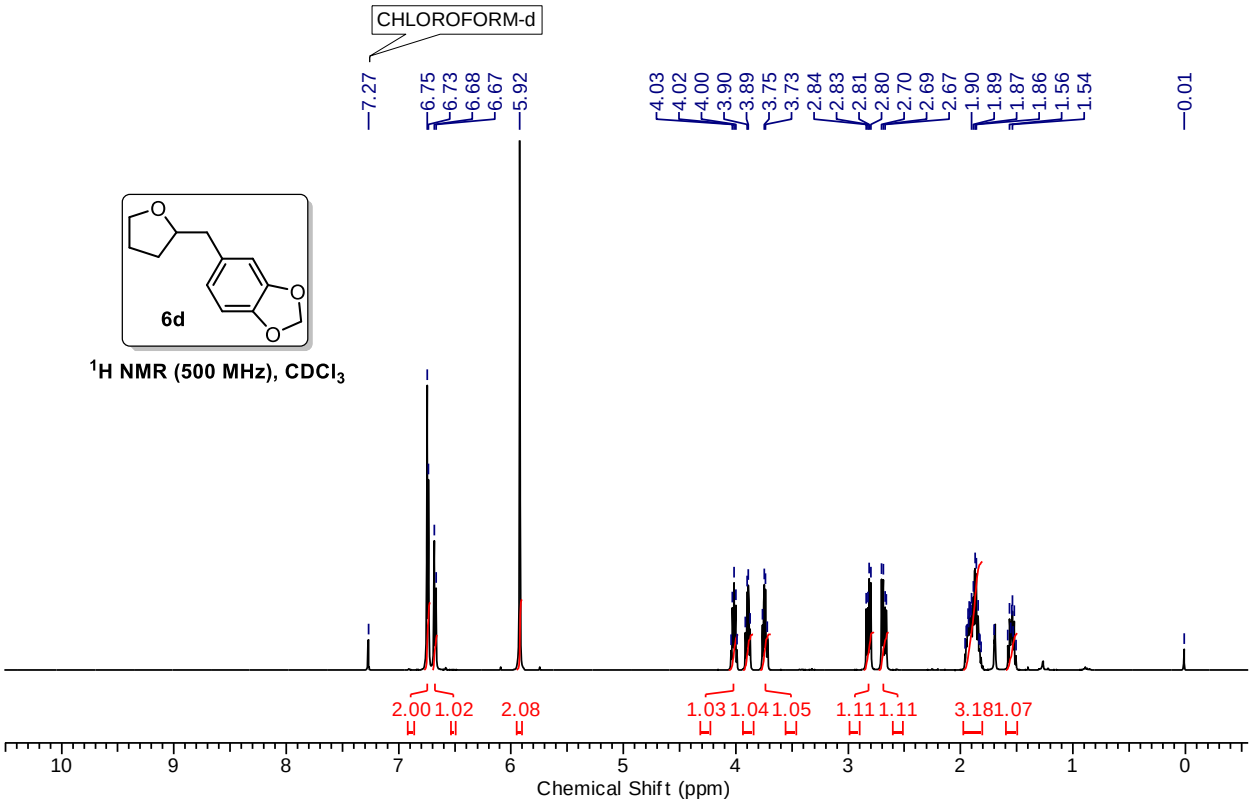
^{13}C NMR (125 MHz), $CDCl_3$

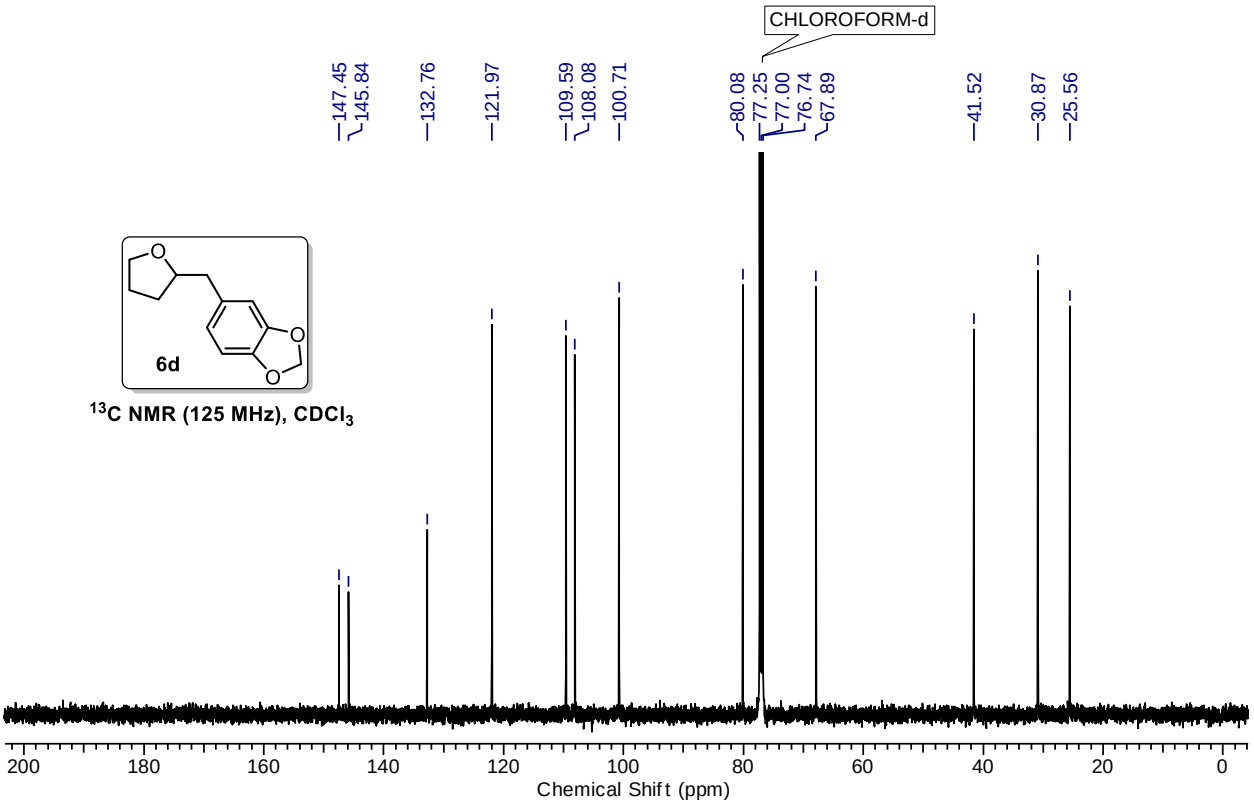


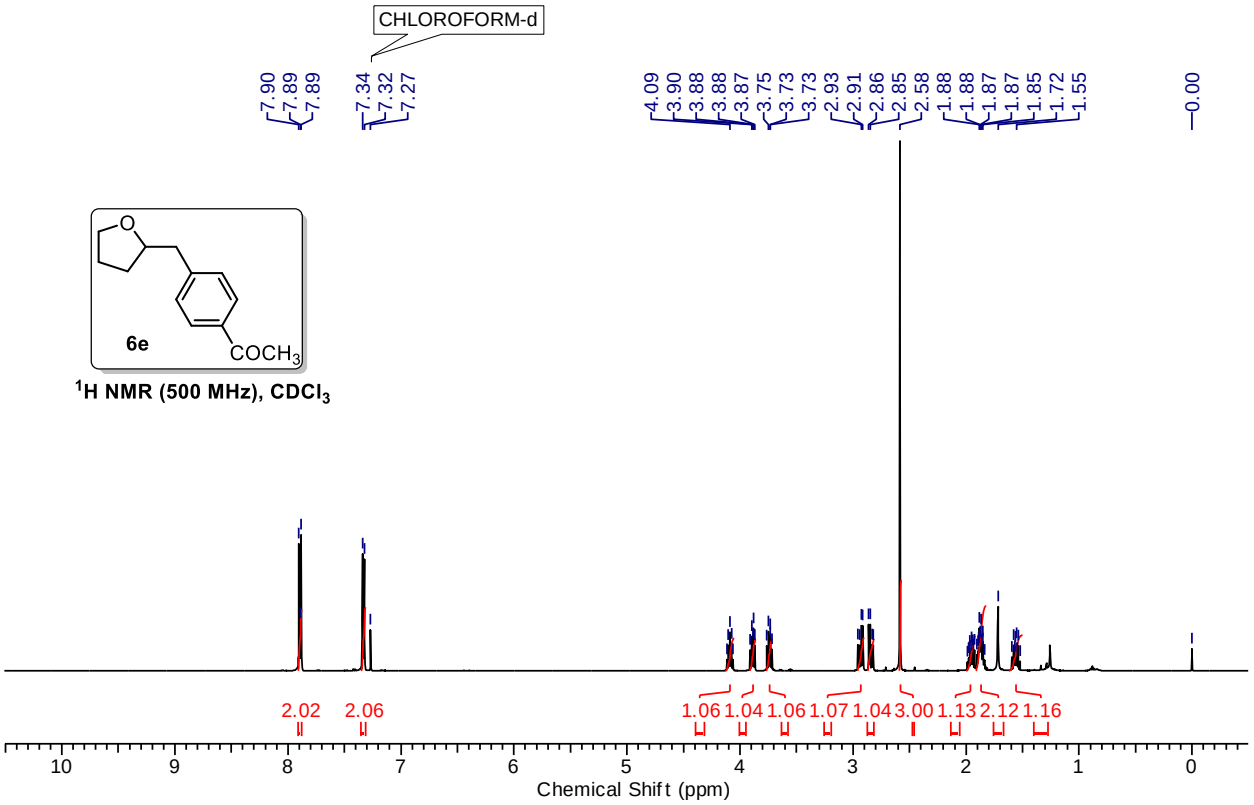
^{1}H NMR (500 MHz), $CDCl_3$

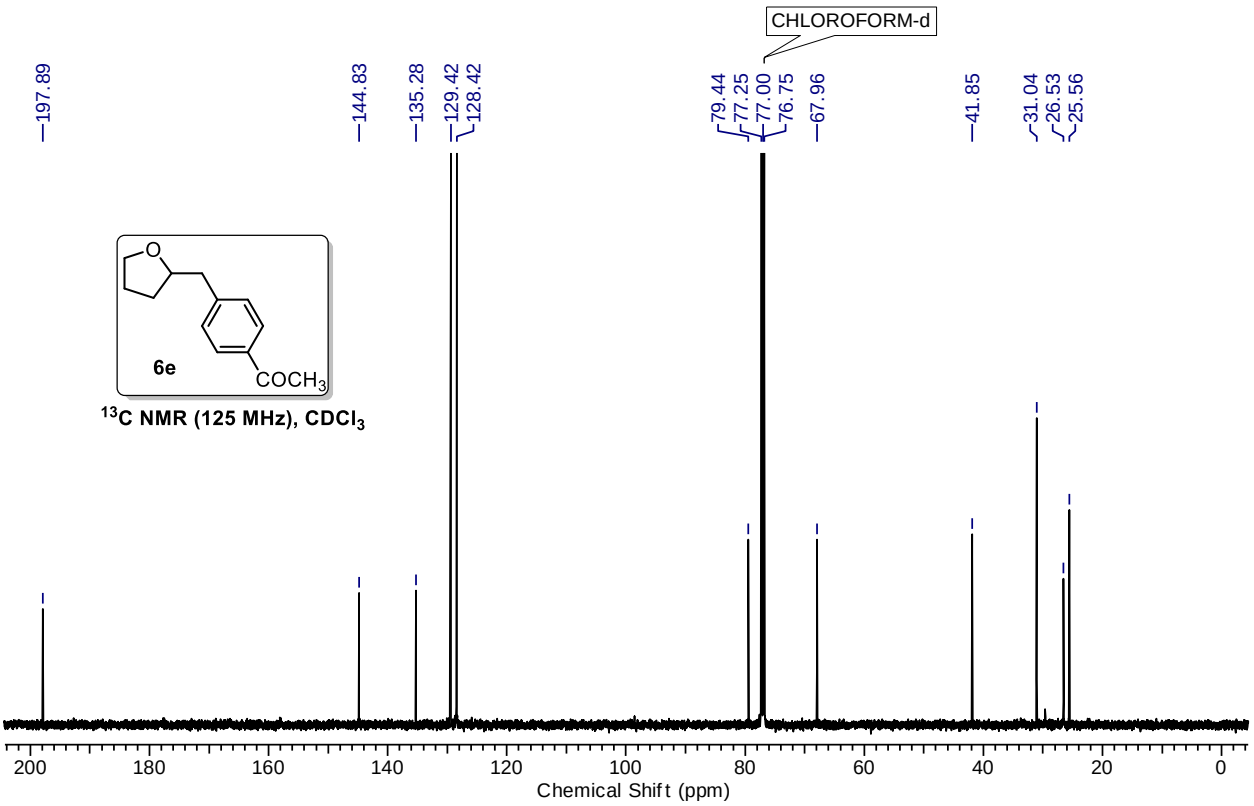


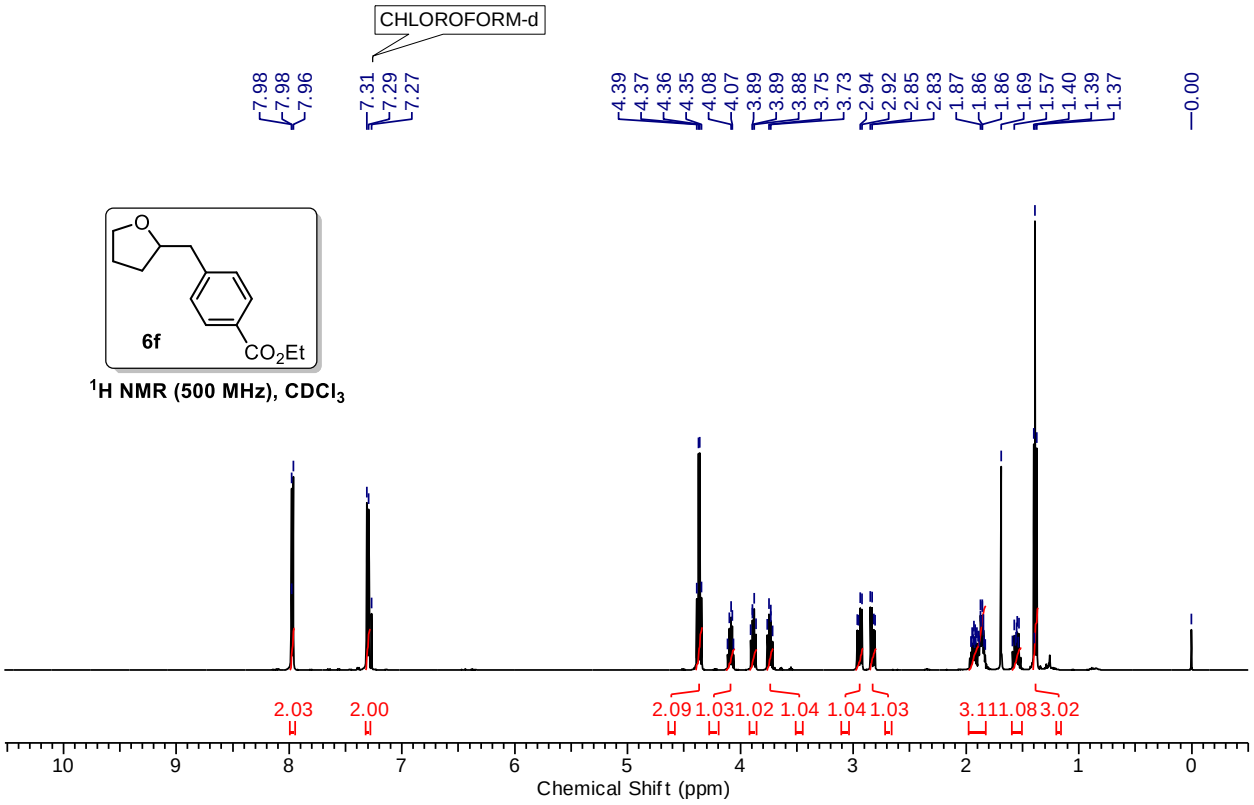
^{13}C NMR (125 MHz), $CDCl_3$

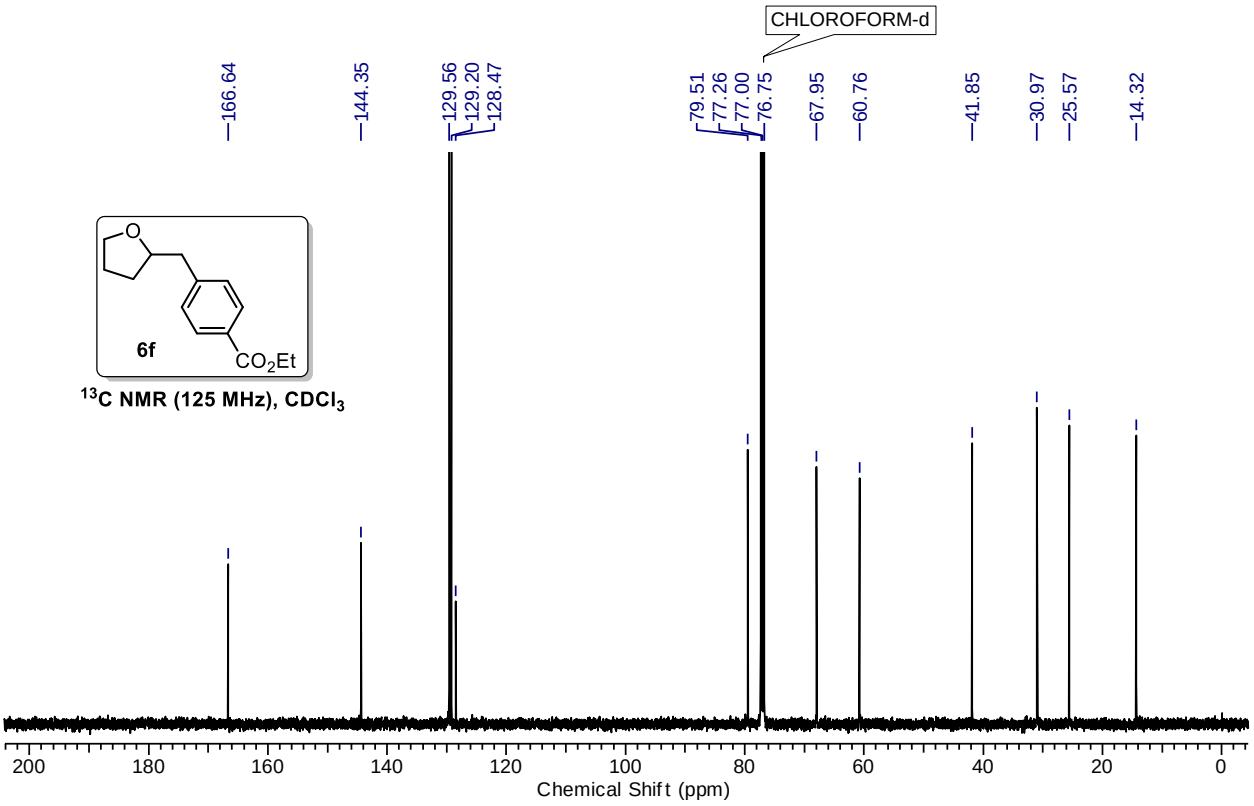

CHLOROFORM-d
7.27
6.75
6.73
6.68
6.67
5.92
4.03
4.02
4.00
3.90
3.89
3.75
3.73
2.84
2.83
2.81
2.80
2.70
2.69
2.67
1.90
1.89
1.87
1.86
1.56
1.54
0.01
6d
1H NMR (500 MHz), CDCl3
2.00
1.02
2.08
1.03
1.04
1.05
1.11
1.11
3.18
1.07
Chemical Shift (ppm)

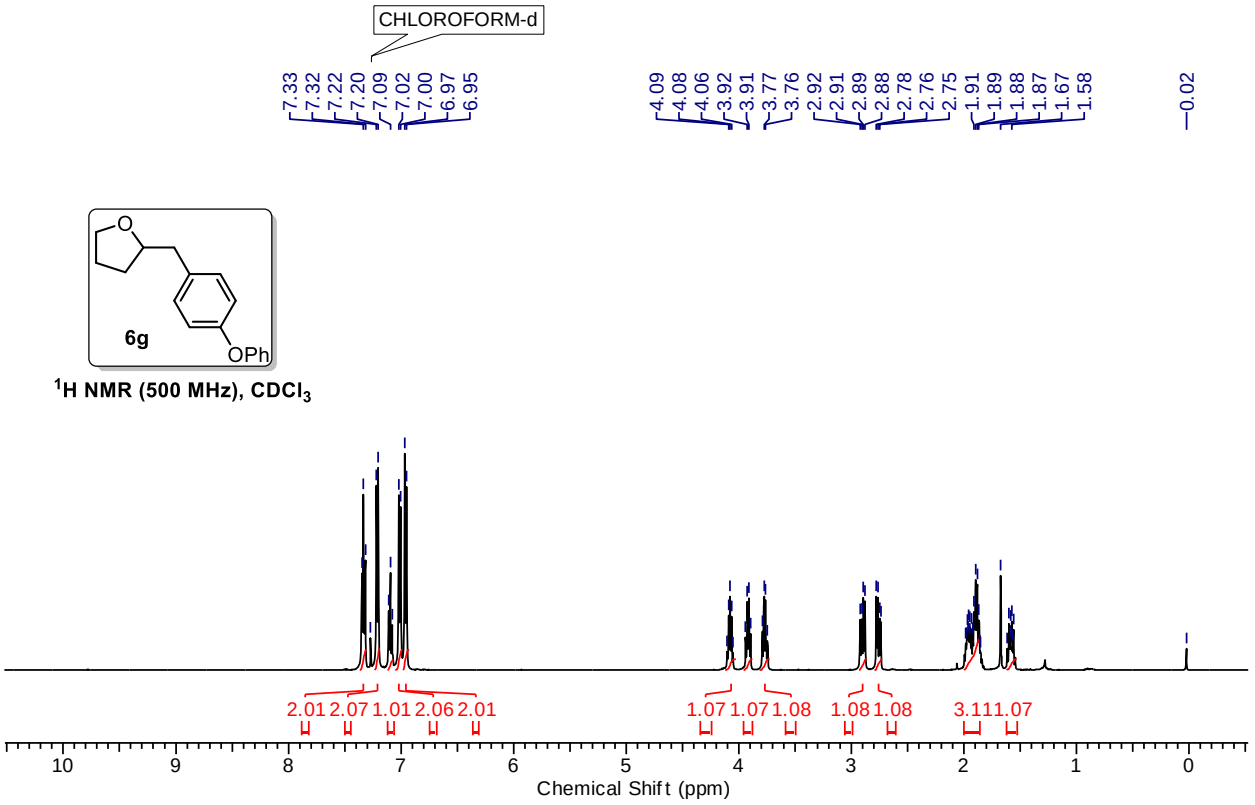

CHLOROFORM-d
147.45
145.84
132.76
121.97
109.59
108.08
100.71
80.08
77.25
77.00
76.74
67.89
41.52
30.87
25.56
6d
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)


CHLOROFORM-d
7.90
7.89
7.89
7.34
7.32
7.27
4.09
3.90
3.88
3.88
3.87
3.75
3.73
3.73
2.93
2.91
2.86
2.85
2.58
1.88
1.88
1.87
1.87
1.85
1.72
1.55
0.00
6e
COCH3
1H NMR (500 MHz), CDCl3
2.02
2.06
1.06
1.04
1.06
1.07
1.04
3.00
1.13
2.12
1.16
Chemical Shift (ppm)

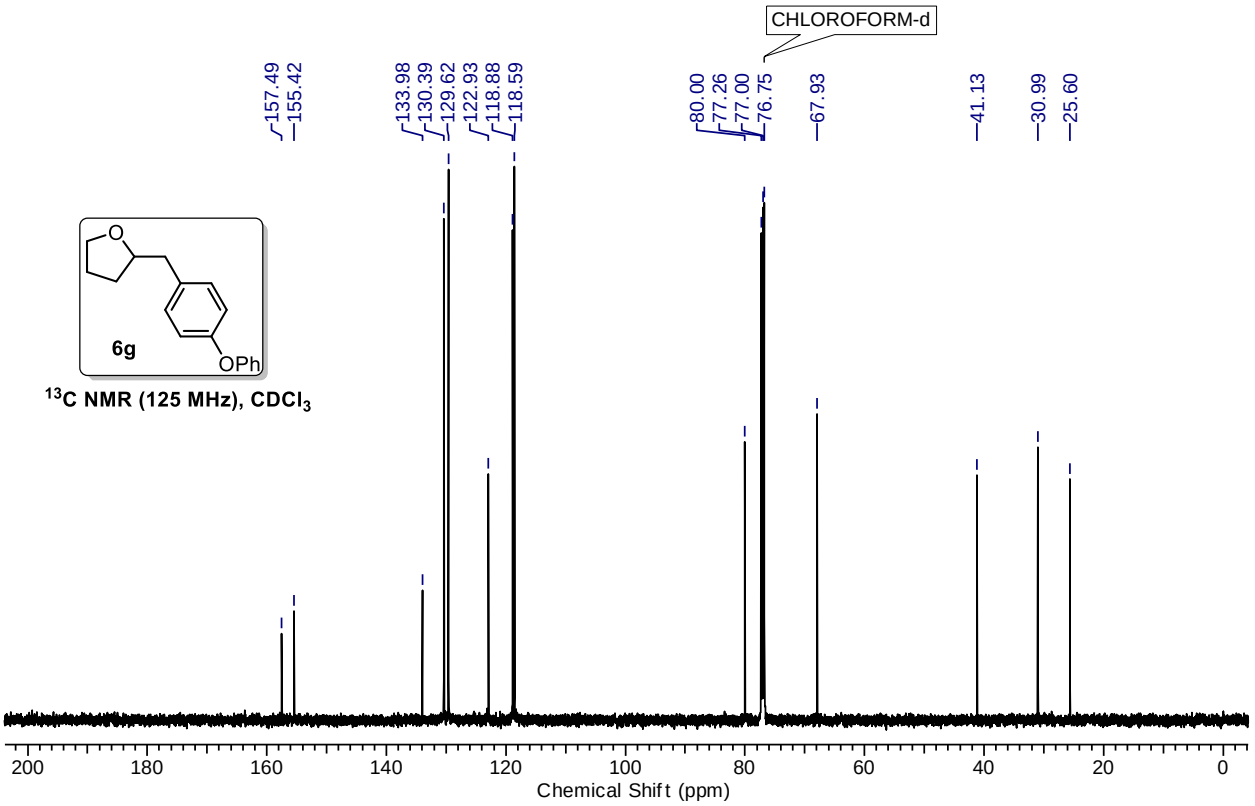

CHLOROFORM-d
197.89
144.83
135.28
129.42
128.42
79.44
77.25
77.00
76.75
67.96
41.85
31.04
26.53
25.56
6e
COCH3
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)


CHLOROFORM-d
7.98
7.98
7.96
7.31
7.29
7.27
4.39
4.37
4.36
4.35
4.08
4.07
3.89
3.89
3.88
3.75
3.73
2.94
2.92
2.85
2.83
1.87
1.86
1.86
1.69
1.57
1.40
1.39
1.37
0.00
6f
CO2Et
1H NMR (500 MHz), CDCl3
2.03
2.00
2.09
1.03
1.02
1.04
1.04
1.03
3.11
1.08
3.02
Chemical Shift (ppm)

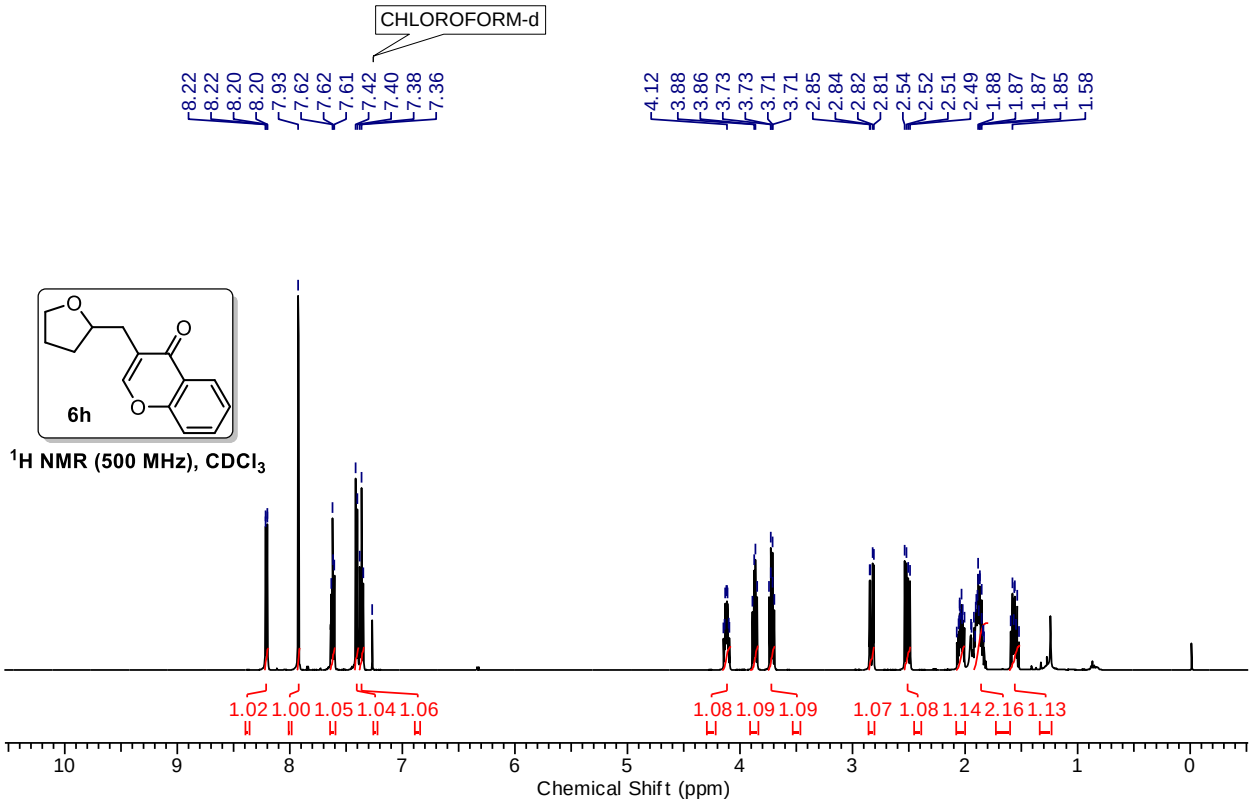

CHLOROFORM-d
166.64
144.35
129.56
129.20
128.47
79.51
77.26
77.00
76.75
67.95
60.76
41.85
30.97
25.57
14.32
6f
CO2Et
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)

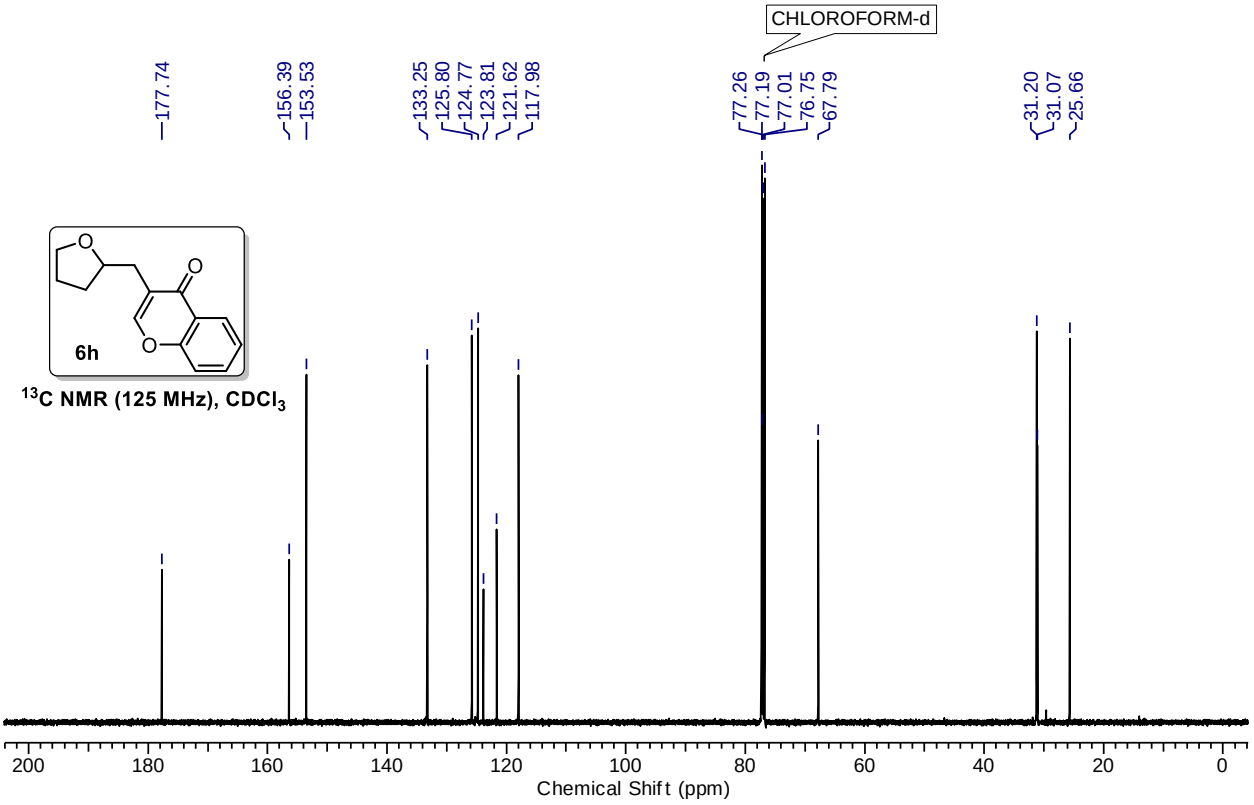


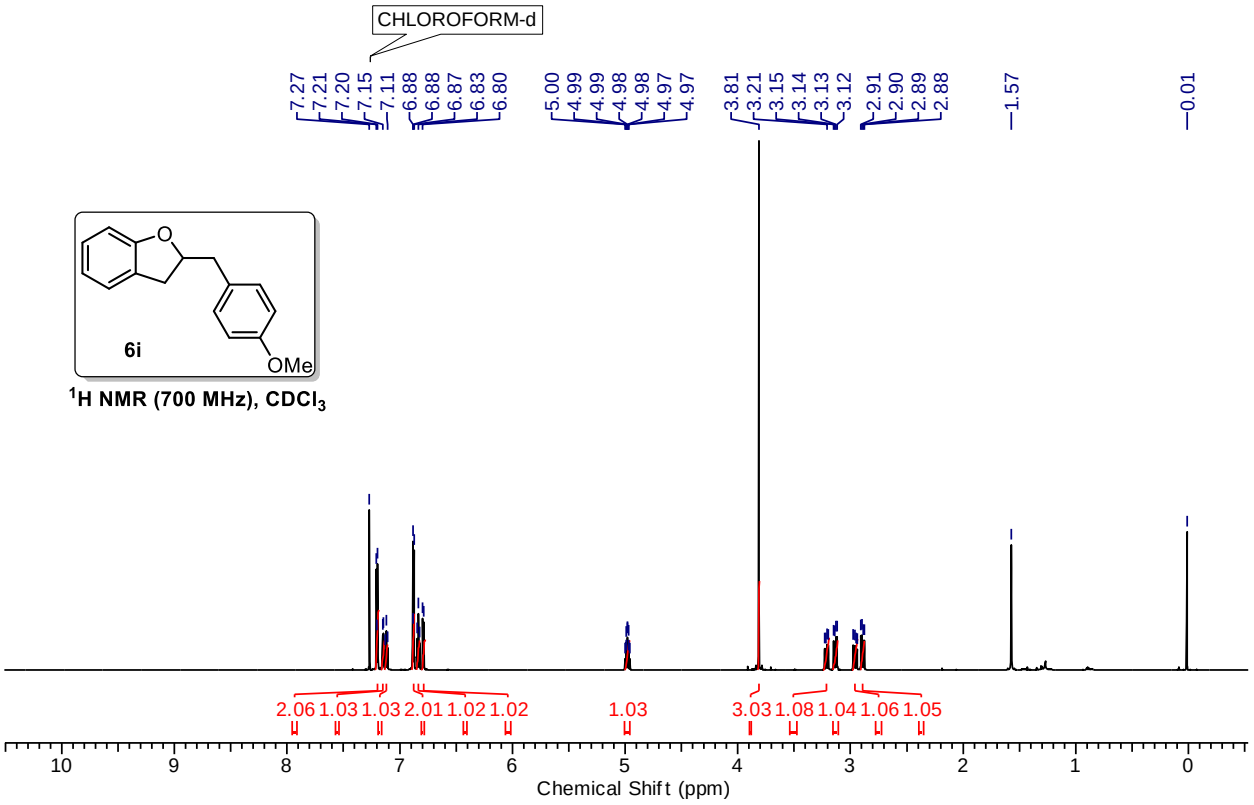
^{1}H NMR (500 MHz), $CDCl_3$



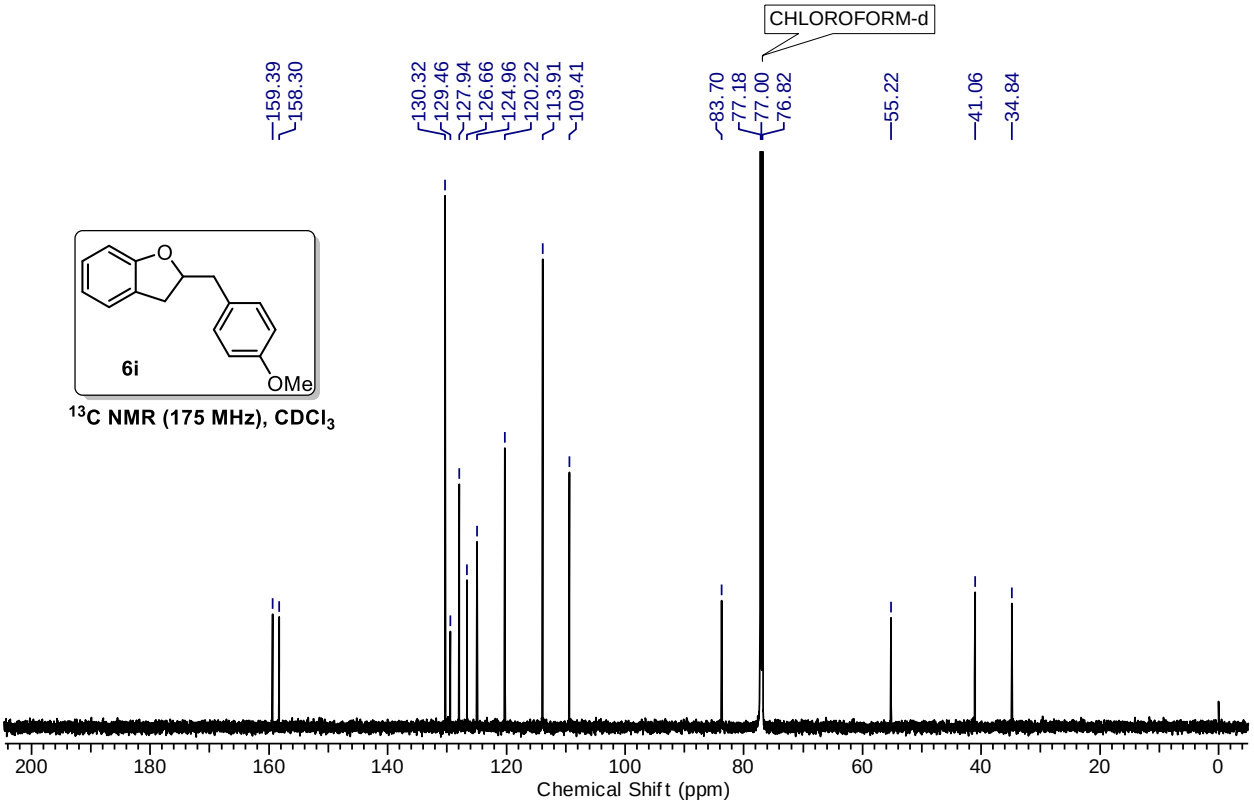
^{13}C NMR (125 MHz), $CDCl_3$


CHLOROFORM-d
8.22
8.22
8.20
8.20
7.93
7.62
7.62
7.61
7.42
7.40
7.38
7.36
4.12
3.88
3.86
3.73
3.73
3.71
3.71
2.85
2.84
2.82
2.81
2.54
2.52
2.51
2.49
1.88
1.87
1.87
1.85
1.58
6h
1H NMR (500 MHz), CDCl3
1.02 1.00 1.05 1.04 1.06
1.08 1.09 1.09
1.07 1.08 1.14 2.16 1.13
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

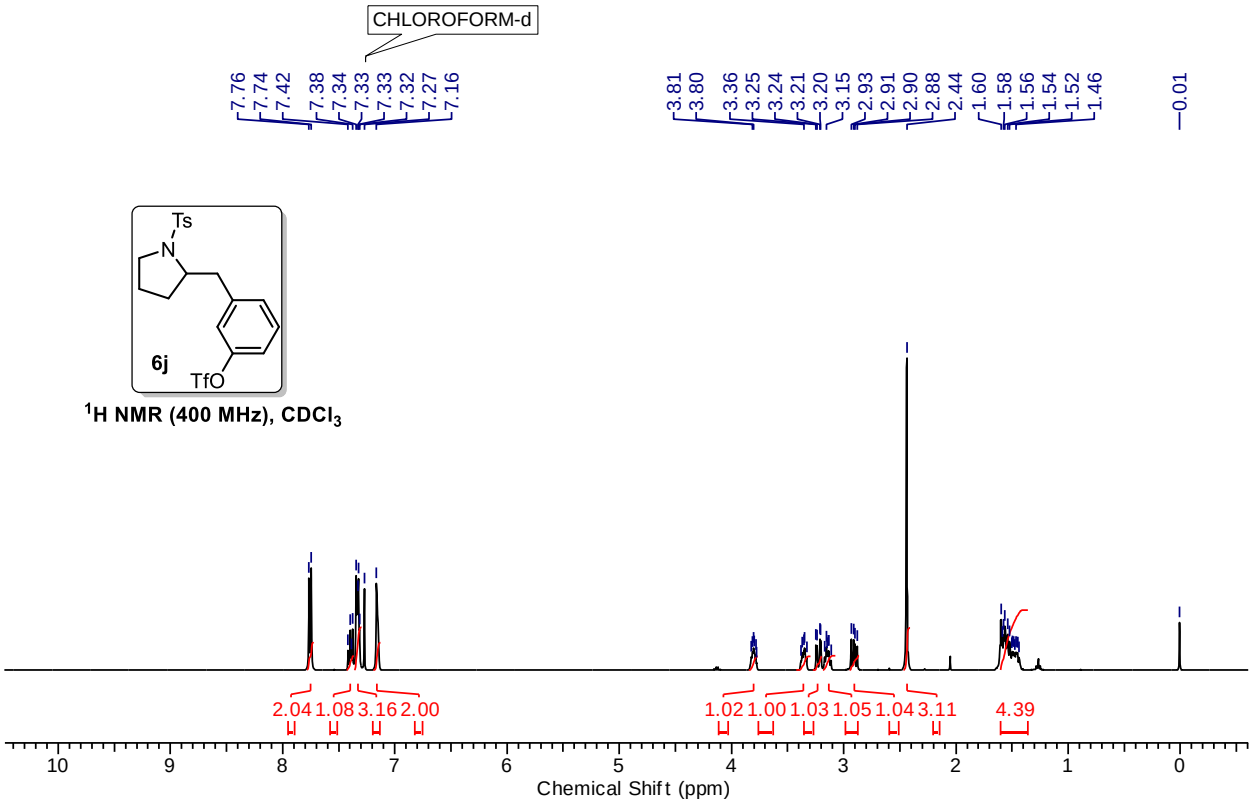

CHLOROFORM-d
177.74
156.39
153.53
133.25
125.80
124.77
123.81
121.62
117.98
77.26
77.19
77.01
76.75
67.79
31.20
31.07
25.66
6h
13C NMR (125 MHz), CDCl3
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)



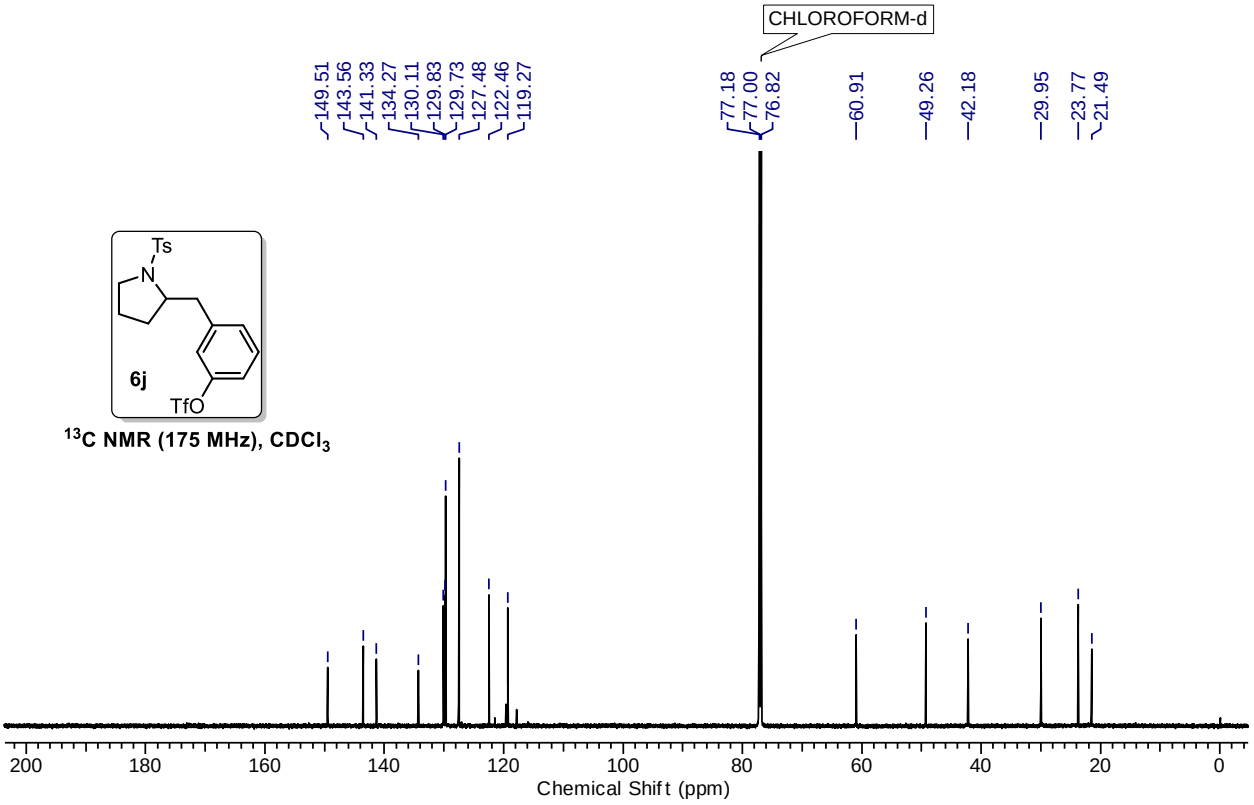
^{1}H NMR (700 MHz), $CDCl_3$



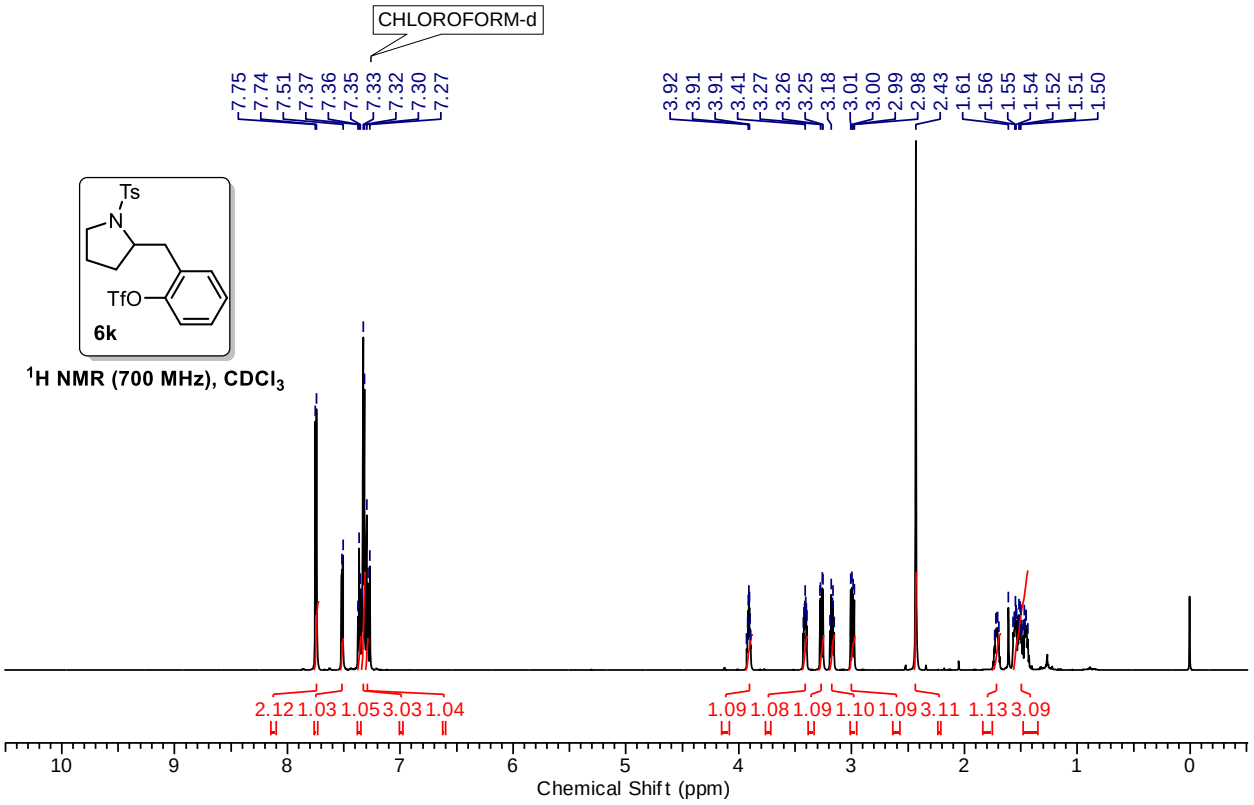
^{13}C NMR (175 MHz), $CDCl_3$



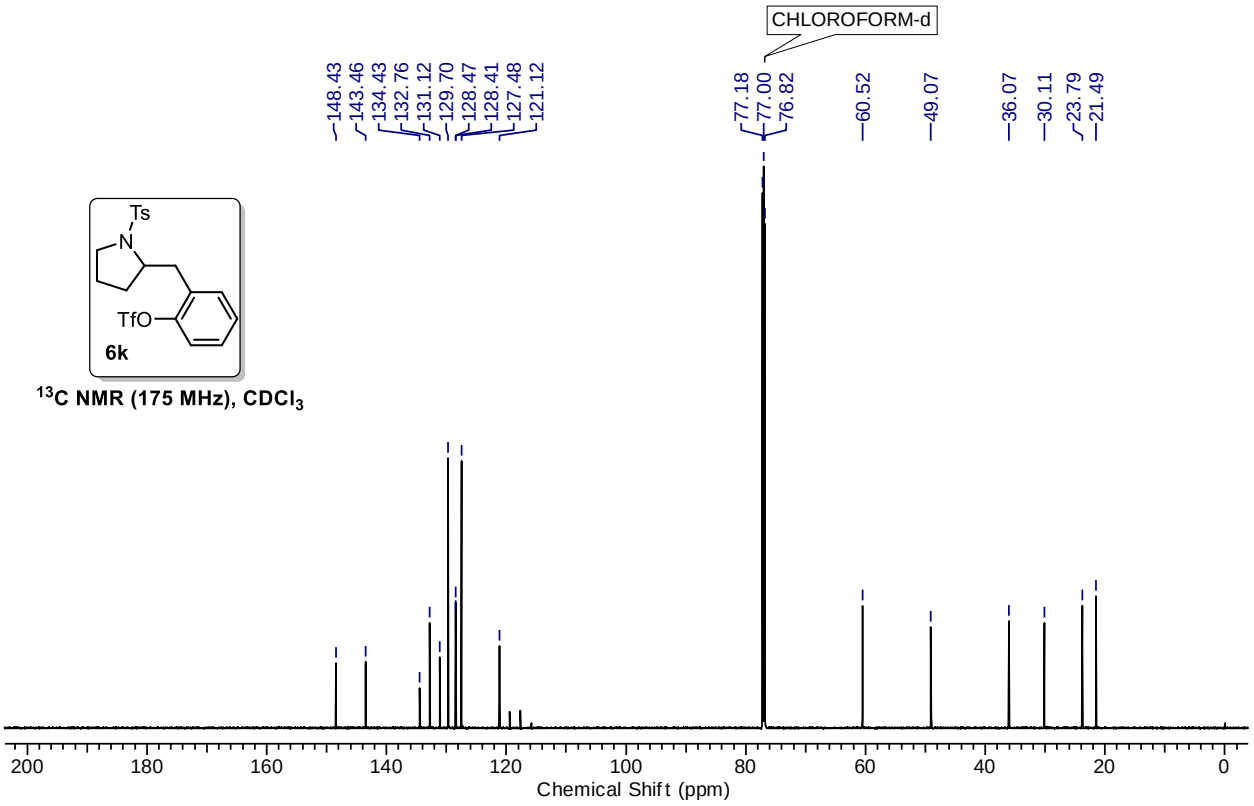
^{1}H NMR (400 MHz), $CDCl_3$



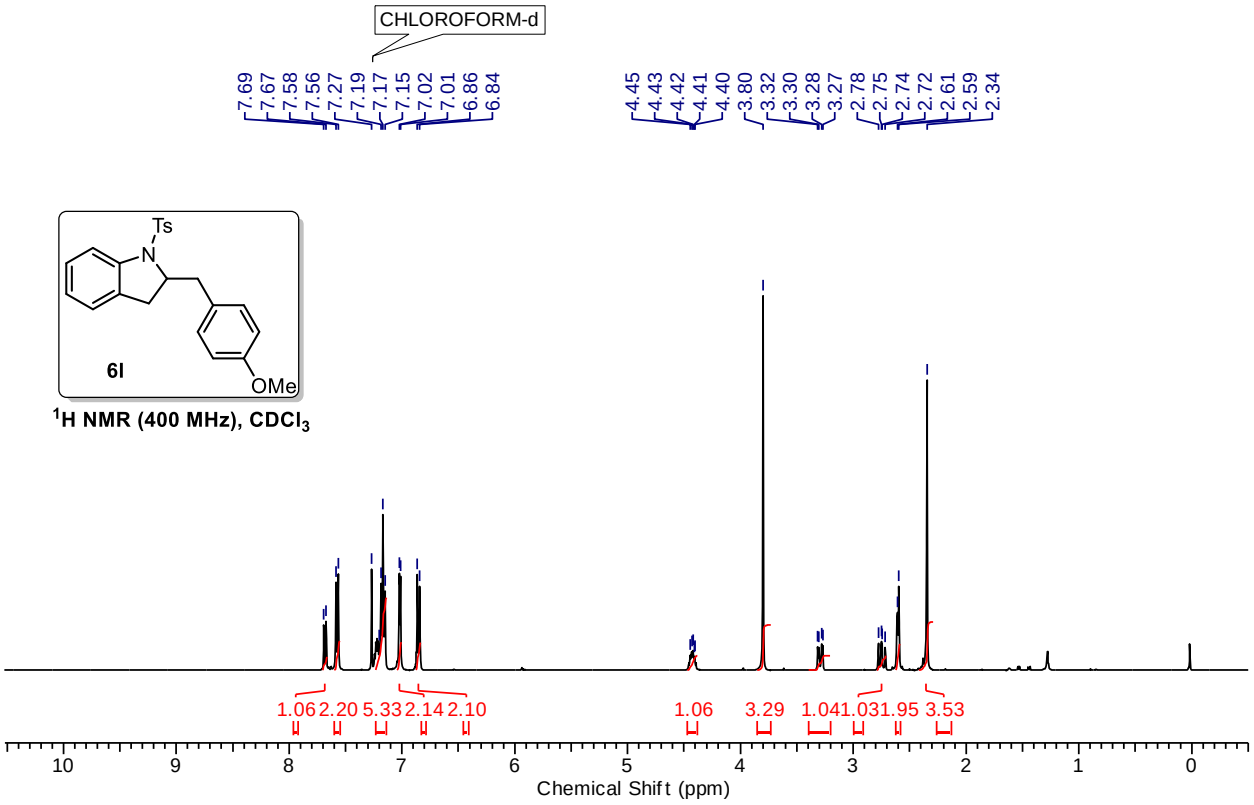
^{13}C NMR (175 MHz), $CDCl_3$

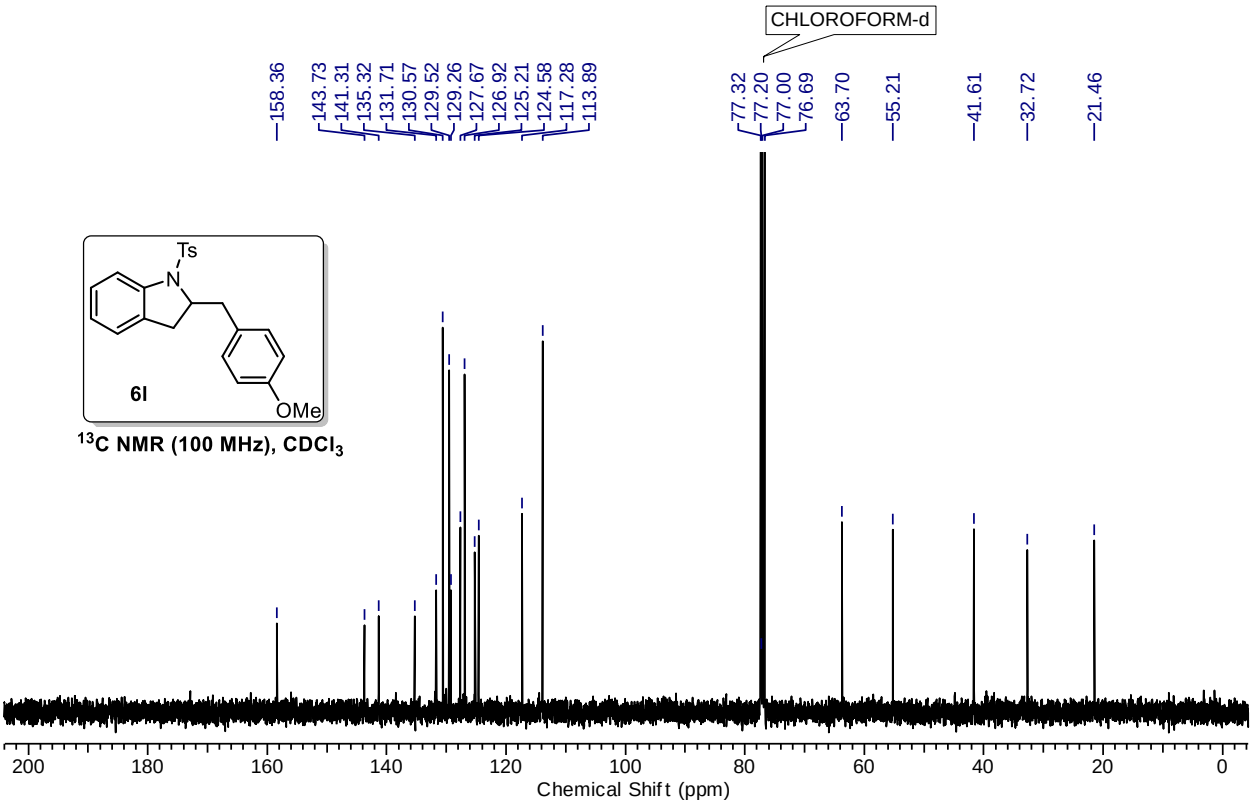


^{1}H NMR (700 MHz), $CDCl_3$



^{13}C NMR (175 MHz), $CDCl_3$


CHLOROFORM-d
7.69
7.67
7.58
7.56
7.27
7.19
7.17
7.15
7.02
7.01
6.86
6.84
4.45
4.43
4.42
4.41
4.40
3.80
3.32
3.30
3.28
3.27
2.78
2.75
2.74
2.72
2.61
2.59
2.34
Ts
N
6l
OMe
1H NMR (400 MHz), CDCl3
1.06
2.20
5.33
2.14
2.10
1.06
3.29
1.04
1.03
1.95
3.53
Chemical Shift (ppm)


CHLOROFORM-d
158.36
143.73
141.31
135.32
131.71
130.57
129.52
129.26
127.67
126.92
125.21
124.58
117.28
113.89
77.32
77.20
77.00
76.69
63.70
55.21
41.61
32.72
21.46
Ts
N
6l
OMe
13C NMR (100 MHz), CDCl3
Chemical Shift (ppm)