Electronic Supporting Information for

Diastereoselective Synthesis of Tetrahydropyranes via Ag(I)-Catalyzed Dimerization of Cinnamyl Ethers

Davide Ruggeri, Elena Motti, Nicola Della Ca' and Giovanni Maestri

Table of contents

General remarks

All chemicals were purchased from commercial sources and used as received. Solvents were dried passing through alumina columns using an Inert® system and were stored under nitrogen. Chromatographic purifications were performed under gradient or isocratic regimes using a Combiflash system and prepacked disposable silica cartridges. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 K on Bruker 400 MHz spectrometer using the solvent as internal standard (7.26 ppm for ^{1}H NMR and 77.00 ppm for ^{13}CNMR for $CDCl_3$). Reported assignments are based on decoupling, COSY, NOESY, HSQC, and HMBC correlation experiments. The terms m, s, d, t, q, and quint represent multiplet, singlet, doublet, triplet, quadruplet, and quintuplet, respectively, and the term br means a broad signal. Exact masses were recorded on an LTQ ORBITRAP XL Thermo Mass Spectrometer (electrospray source). Cinnamyl ethers **3a**-**m** were synthesized according to literature procedures.[1–4] Spectroscopic data of **3a**-**c**,**e**,**g**,**i**-**l** correspond to those described in the literature.

Calculations were performed at the DFT level using Gaussian16.[5] Optimization were performed without any constraint using the hybrid M06 functional described by Zhao and Truhlar[6] in combination with the the Def2-SVP basis set described by Weigend and Ahlrichs.[7] Solvated structures were modeled using DCM as implicit solvent through the use of the CPCM method introduced by Barone and Cossi.[8] All values and geometries reported hereafter are those of freely optimized solvated structures, calculated at the M06/Def2-SVP level. All intermediates were characterized by the absence of any imaginary frequency in their Hessian matrix. All transition states were characterized by the presence of a single imaginary frequency in their Hessian matrix, which corresponds to the molecular vibration connecting the reactant with the product.

Synthesis and characterization of substrates

Synthesis of Diendiyne 1

To a stirred solution of 4-methylbenzenesulfonamide (260 mg, 1.52 mmol, 1 eq.) in acetone (16 mL) was added (E)-(3-((4-bromobut-2-yn-1-yl)oxy)prop-1-en-1-yl)benzene (807 mg, 3.04 mmol, 2.0 eq.) and K_2CO_3 (630 mg, 4.56 mmol, 3.0 eq.). The reaction mixture was stirred overnight under reflux. The mixture was quenched by addition of water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (*n*-hexane/ EtOAc, gradient).

General Procedure I for the Synthesis of Cynnamyl Ethers 3a-b, j

A solution of cinnamyl alcohol (387 µL, 3 mmol, 1 equiv) in THF (5 mL) was added to a suspension of NaH (60% in mineral oil, 160 mg, 4 mmol, 1.3 equiv) in THF (10 mL). The resulting mixture was stirred for 30 min prior to the addition of the corresponding halide (4 mmol, 1.3 equiv). The mixture was then stirred at r.T. overnight. After completion, the reaction was quenched with NH_4Cl acqueous solution. The mixture was extracted with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude was purified by chromatography on silica gel (*n*-hexane/ EtOAc, gradient).

General Procedure II for the Synthesis of Cynnamyl Ethers 3c-d, l

A solution of the desired alcohol (2.6 mmol, 1 equiv) in THF (4 mL) was added to a suspension of NaH (60% in mineral oil, 136 mg, 3.4 mmol, 1.3 equiv) in THF (8 mL). The resulting mixture was stirred for 30 min prior to the addition of cinnamyl bromide (3.4 mmol, 1.3 equiv). The mixture was then stirred at r.T. overnight. After completion, the reaction was quenched with NH_4Cl acqueous solution. The mixture was extracted with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude was purified by chromatography on silica gel (*n*-hexane/ EtOAc, gradient).

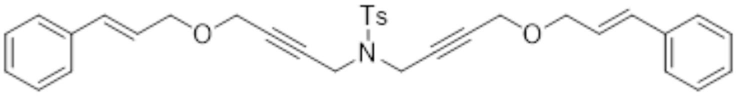
General Procedure III for the Synthesis of Cynnamyl Ethers 3e, g, i, k, m

A solution of the desired alcohol (0.82 mmol, 1 equiv) in THF (4 mL) was added to a suspension of NaH (60% in mineral oil, 43 mg, 1.1 mmol, 1.3 equiv) in DMF (1 mL). The resulting mixture was stirred for 30 min prior to the addition of benzyl bromide (0.96 mmol, 1.1 equiv). The mixture was then stirred at r.T. overnight. After completion, the reaction was quenched with NH_4Cl acqueous solution. The mixture was extracted with diethyl ether. The combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude was purified by chromatography on silica gel (*n*-hexane/ EtOAc, gradient).

General Procedure IV for the Synthesis of Cynnamyl Ethers 3h, f

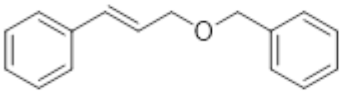
A solution of the desired alcohol (1.32 mmol, 1 equiv) in THF (4 mL) was added to a suspension of NaH (60% in mineral oil, 79 mg, 1.97 mmol, 1.5 equiv) in DMF (4 mL). The resulting mixture was stirred for 30 min prior to the addition of 1-iodo propane (335 mg, 1.97 mmol, 1.5 equiv). The mixture was then stirred at r.T. overnight. After completion, the reaction was quenched with NH_4Cl acqueous solution. The mixture was extracted with diethyl ether. The combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude was purified by chromatography on silica gel (*n*-hexane/ EtOAc, gradient).

N,N-bis(4-(cinnamyloxy)but-2-yn-1-yl)-4-methylbenzenesulfonamide (1)



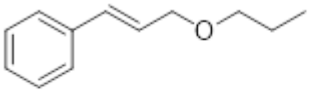
Diendiyne **1** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (552 mg, 1.02 mmol, 67%). The NMR data was consistent with previously reported spectra.[9] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.23 (m, 12H), 6.59 (d, *J* = 16.0 Hz, 2H), 6.22 (dt, *J* = 15.9, 6.2 Hz, 2H), 4.24 – 4.21 (m, 4H), 4.10 (dd, *J* = 6.2, 1.4 Hz, 4H), 4.06 – 4.03 (m, 4H), 2.37 (s, 3H).

(E)-(3-(benzyloxy)prop-1-en-1-yl)benzene (3a)



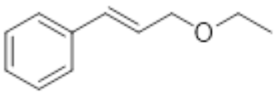
Following general procedure **I**, **3a** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (656 mg, 2.92 mmol, 78%). The NMR data was consistent with previously reported spectra.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 6H), 7.36 – 7.30 (m, 3H), 7.27 – 7.22 (m, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.34 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.59 (s, 2H), 4.21 (dd, *J* = 6.0, 1.5 Hz, 2H).

(E)-(3-propoxyprop-1-en-1-yl)benzene (3b)



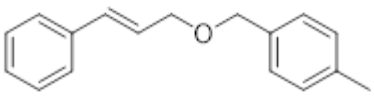
Following general procedure **I**, **3b** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (129 mg, 0.73 mmol, 33%). The NMR data was consistent with previously reported spectra.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.21 (m, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.14 (dd, *J* = 6.0, 1.5 Hz, 2H), 3.45 (t, *J* = 6.7 Hz, 2H), 1.71 – 1.58 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

(E)-(3-ethoxyprop-1-en-1-yl)benzene (3c)



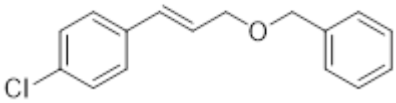
Following general procedure **II**, **3c** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (377 mg, 2.32 mmol, 70%). The NMR data was consistent with previously reported spectra.[2] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.26 – 7.21 (m, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.15 (dd, *J* = 6.0, 1.5 Hz, 2H), 3.56 (q, *J* = 7.0 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 3H).

1-((cinnamyloxy)methyl)-4-methylbenzene) (3d)



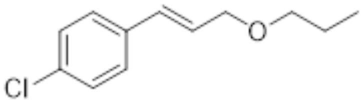
Following general procedure **II**, **3d** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (563 mg, 2.36 mmol, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.36 – 7.23 (m, 5H), 7.21 – 7.15 (m, 2H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.55 (s, 2H), 4.19 (dd, *J* = 6.0, 1.5 Hz, 2H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.5 (Cq), 136.9 (Cq), 135.4 (Cq), 132.6 (CH), 129.2 (2CH), 128.7 (2CH), 128.1 (2CH), 127.8 (CH), 126.6 (2CH), 126.3 (CH), 72.2 (CH_2), 70.7 (CH_2), 21.3 (CH_3). **(ESI)-HRMS** calcd for $C_{17}H_{18}O$ $[M + Na]^+$ 261.1256, found 261.1249.

(E)-1-(3-(benzyloxy)prop-1-en-1-yl)-4-chlorobenzene (3e)



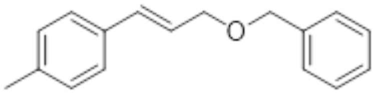
Following general procedure **III**, **3e** was isolated (silica gel, n-hexane/EtOAc, gradient) as a transparent oil (185 mg, 0.71 mmol, 87%). The NMR data was consistent with previously reported spectra.[1] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 4H), 7.33 – 7.26 (m, 5H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.58 (s, 2H), 4.19 (dd, *J* = 5.9, 1.5 Hz, 2H).

(E)-1-chloro-4-(3-propoxyprop-1-en-1-yl)benzene (3f)



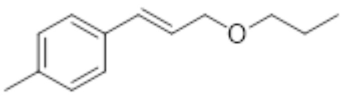
Following general procedure **IV**, **3f** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (105 mg, 0.50 mmol, 38%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 4H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.12 (dd, *J* = 5.9, 1.5 Hz, 2H), 3.44 (t, *J* = 6.7 Hz, 2H), 1.64 (h, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.5 (Cq), 133.3 (Cq), 130.8 (CH), 128.8 (2CH), 127.8 (2CH), 127.3 (CH), 72.5 (CH_2), 71.3 (CH_2), 23.1 (CH_2), 10.8 (CH_3). **(ESI)-HRMS** calcd for $C_{12}H_{15}ClO$ $[M + Na]^+$ 233.0709, found 233.0711.

(E)-1-(3-(benzyloxy)prop-1-en-1-yl)-4-methylbenzene (3g)



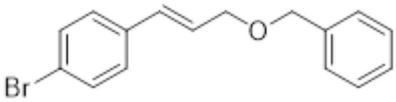
Following general procedure **III**, **3g** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (144 mg, 0.60 mmol, 90%). The NMR data was consistent with previously reported spectra.[1] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 7.33 – 7.28 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.29 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.58 (s, 2H), 4.20 (dd, *J* = 6.2, 1.4 Hz, 2H), 2.35 (s, 3H).

(E)-1-methyl-4-(3-propoxyprop-1-en-1-yl)benzene (3h)



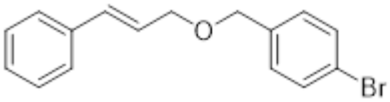
Following general procedure **IV**, **3h** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (53 mg, 0.28 mmol, 28%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.27 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.15 (dd, *J* = 6.0, 1.5 Hz, 2H), 3.47 (t, *J* = 6.7 Hz, 2H), 2.36 (s, 3H), 1.74 – 1.60 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.4 (Cq), 134.3 (Cq), 132.1 (CH), 129.3 (2CH), 126.5 (2CH), 125.7 (CH), 72.2 (CH_2), 71.6 (CH_2), 23.1 (CH_2), 21.2 (CH_3), 10.7 (CH_3). **(ESI)-HRMS** calcd for $C_{13}H_{18}O$ $[M + Na]^+$ 213.1256, found 213.1250.

(E)-1-(3-(benzyloxy)prop-1-en-1-yl)-4-bromobenzene (3i)



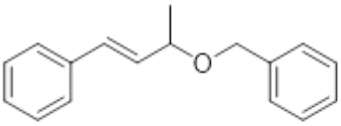
Following general procedure **III**, **3i** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (132 mg, 0.44 mmol, 87%). The NMR data was consistent with previously reported spectra.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.28 (m, 5H), 7.27 – 7.23 (m, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.32 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.58 (s, 2H), 4.19 (dd, *J* = 5.9, 1.5 Hz, 2H).

1-bromo-4-((cinnamyloxy)methyl)benzene (3j)



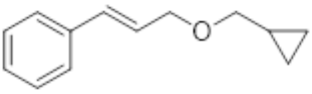
Following general procedure **I**, **3j** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (681 mg, 2.25 mmol, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.23 (m, 3H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.53 (s, 2H), 4.20 (dd, *J* = 6.1, 1.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.5 (Cq), 136.7 (Cq), 132.9 (CH), 131.6 (2CH), 129.5 (2CH), 128.7 (2CH), 127.9 (CH), 126.6 (2CH), 125.9 (CH), 121.6 (Cq), 71.5 (CH_2), 71.0 (CH_2). **(ESI)-HRMS** calcd for $C_{16}H_{15}BrO$ $[M + Na]^+$ 325.0204, found 325.0201.

(E)-(3-(benzyloxy)but-1-en-1-yl)benzene (3k)



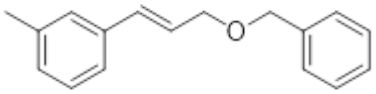
Following general procedure **III**, **3k** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (432 mg, 1.81 mmol, 60%). The NMR data was consistent with previously reported spectra.[1] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.39 – 7.32 (m, 6H), 7.31 – 7.24 (m, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.19 (dd, *J* = 15.9, 7.7 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 4.12 (p, *J* = 6.4 Hz, 1H), 1.40 (d, *J* = 6.4 Hz, 3H).

(E)-(3-(cyclopropylmethoxy)prop-1-en-1-yl)benzene (3l)



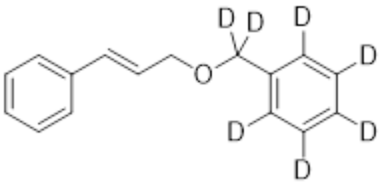
Following general procedure **II**, **3l** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (360 mg, 1.91 mmol, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.17 (dd, *J* = 6.1, 1.5 Hz, 2H), 3.33 (d, *J* = 6.9 Hz, 2H), 1.16 – 1.05 (m, 1H), 0.61 – 0.51 (m, 2H), 0.26 – 0.19 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9 (Cq), 132.4 (CH), 128.7 (2CH), 127.8 (CH), 126.6 (2CH), 126.5 (CH), 75.2 (CH_2), 71.3 (CH_2), 10.8 (CH), 3.2 ($2CH_2$). **(ESI)-HRMS** calcd for $C_{13}H_{16}O$ $[M + Na]^+$ 211.1100, found 211.1105.

(E)-1-(3-(benzyloxy)prop-1-en-1-yl)-3-methylbenzene (3m)



Following general procedure **III**, **3m** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (263 mg, 1.10 mmol, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 7.21 (dd, *J* = 4.7, 1.7 Hz, 3H), 7.11 – 7.04 (m, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.58 (s, 2H), 4.21 (dd, *J* = 6.1, 1.5 Hz, 2H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4 (Cq), 138.2 (Cq), 136.8 (Cq), 132.8 (CH), 128.62 (CH), 128.59 (CH), 128.56 (2CH), 127.9 (2CH), 127.8 (CH), 127.4 (CH), 126.0 (CH), 123.8 (CH), 72.2 (CH_2), 70.9 (CH_2), 21.5 (CH_3). **(ESI)-HRMS** calcd for $C_{17}H_{18}O$ [M + Na]$^+$ 261.1256, found 261.1258.

1-((cinnamyloxy)methyl-d2)benzene-2,3,4,5,6-d5 (*7d*-3a)



Following general procedure **I**, *7d*-**3a** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a transparent oil (522 mg, 2.26 mmol, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.35 – 7.29 (m, 2H), 7.27 – 7.22 (m, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.34 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.21 (dd, *J* = 6.0, 1.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1 (Cq), 136.9 (Cq), 132.7 (CH), 128.7 (2CH), 127.8 (CH), 126.6 (2CH), 126.2 (CH), 70.8 (CH_2). **(ESI)-HRMS** calcd for $C_{16}H_9D_7O$ [M + Na]+ 254.1538, found 254.1535.

Synthesis and characterization of products

Catalytic Synthesis of 2

A solution of **1** (81.0 mg, 0.15 mmol, 1 equiv) in DCM (45 mL) was stirred under nitrogen in a Schlenk-type flask equipped with a magnetic stirring bar and a septum. $AgSbF_6$ (5.2 mg, 0.015 mmol, 10 mol %) was added and the reaction's conversion was monitored by TLC. Upon complete conversion of the substrate, the mixture was directly purified by chromatography on silica gel (*n*-hexane/EtOAc, gradient).

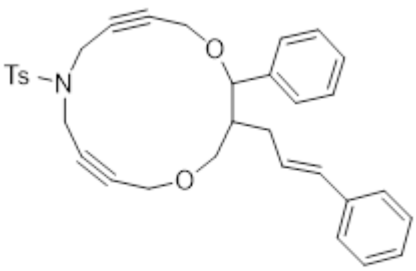
Catalytic Synthesis I (4a-d, f-h, j-m, *d14*-4a)

A solution of the desired substrate (0.4 mmol, 1 equiv) in DCM (4 mL) was stirred under nitrogen in a Schlenk-type flask equipped with a magnetic stirring bar and a septum. $AgSbF_6$ (6.9 mg, 0.02 mmol, 5 mol %) was added and the reaction's conversion was monitored by TLC. Upon complete conversion of the substrate, the mixture was directly purified by chromatography on silica gel (*n*-exane/EtOAc, gradient).

Catalytic Synthesis II (4e, i)

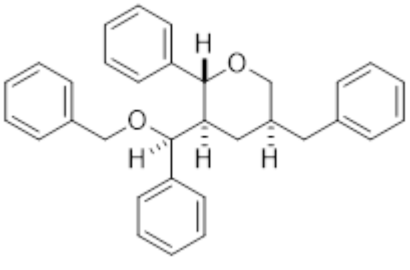
A solution of the desired substrate (0.4 mmol, 1 equiv) in DCM (4 mL) was stirred under nitrogen in a Schlenk-type flask equipped with a magnetic stirring bar and a septum. $AgSbF_6$ (20.6 mg, 0.06 mmol, 15 mol %) was added in three different batches (5 mol % each). The reaction's conversion was monitored by TLC. Upon complete conversion of the substrate, the mixture was directly purified by chromatography on silica gel (*n*-hexane/EtOAc, gradient).

3-cinnamyl-2-phenyl-10-tosyl-1,5-dioxa-10-azacyclotetradeca-7,12-diyne (2)



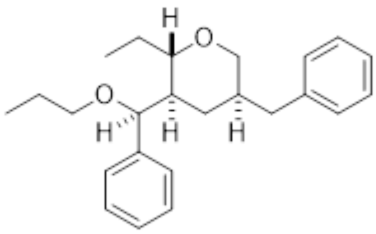
Macrocycle **2** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a white solid (26.8 mg, 0.050 mmol, 33% yield) from starting material **1** (81 mg, 0.15 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.39 – 7.14 (m, 12H), 6.18 (d, *J* = 15.8 Hz, 1H), 5.93 (ddd, *J* = 15.8, 7.8, 6.2 Hz, 1H), 4.48 (d, *J* = 8.9 Hz, 1H), 4.36 (dd, *J* = 17.6, 6.5 Hz, 2H), 4.30 – 4.23 (m, 1H), 4.19 – 4.10 (m, 2H), 4.04 (dd, *J* = 8.7, 1.7 Hz, 1H), 3.95 (dd, *J* = 16.5, 1.3 Hz, 1H), 3.78 (d, *J* = 16.4, 1H), 3.59 (d, *J* = 16.5, 1H), 3.31 (dd, *J* = 8.7, 3.4 Hz, 1H), 2.43 (s, 3H), 2.04 – 1.88 (m, 2H), 1.70 – 1.60 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0 (Cq), 139.7 (Cq), 137.8 (Cq), 134.9 (Cq), 131.5 (CH), 129.6 (2CH), 128.62 (2CH), 128.57 (2CH), 128.46 (CH), 128.29 (CH), 128.25 (2CH), 128.0 (2CH), 127.1 (CH), 126.0 (2CH), 83.9 (Cq), 83.6 (Cq), 80.1 (CH), 79.3 (Cq), 79.0 (Cq), 67.6 (CH_2), 58.3 (CH_2), 55.5 (CH_2), 45.4 (CH), 38.03 (CH_2), 37.99 (CH_2), 31.0 (CH_2), 21.7 (CH_3). **(ESI)-HRMS** calcd for $C_{33}H_{33}NO_4S$ $[M + Na]^+$ 562.2130, found 562.2137.

(±)(2R,3R,5R)-5-benzyl-3-((S)-(benzyloxy)(phenyl)methyl)-2-phenyltetrahydro-2H-pyran (4a)



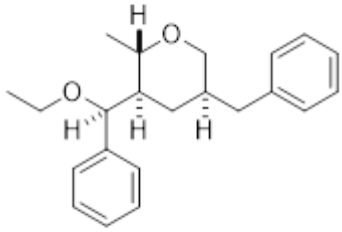
Following catalytic synthesis **I**, **4a** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a white solid (40.0 mg, 0.178 mmol, 60% yield, *dr* 73:27 based on ^{1}H NMR integration) from starting material **3a** (100 mg, 0.45 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 13H), 7.29 – 7.22 (m, 3H), 7.20 – 7.10 (m, 4H), 4.54 (d, *J* = 10.0 Hz, 1H), 4.40 (d, *J* = 11.5 Hz, 1H), 4.14 – 4.11 (m, 1H), 4.11 – 4.06 (m, 1H), 3.94 (ddd, *J* = 11.1, 4.3, 1.7 Hz, 1H), 3.28 (t, *J* = 11.1 Hz, 1H), 2.57 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.43 (dd, *J* = 13.7, 8.5 Hz, 1H), 1.99 – 1.81 (m, 2H), 1.73 – 1.63 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3 (Cq), 140.3 (Cq), 139.9 (Cq), 138.7 (Cq), 128.9 (2CH), 128.7 (2CH), 128.5 (2CH), 128.34 (2CH), 128.27 (2CH), 128.1 (CH), 127.71 (2CH), 127.69 (CH), 127.62 (2CH), 127.2 (CH), 126.7 (2CH), 126.1 (CH), 83.2 (CH), 80.2 (CH), 73.2 (CH_2), 71.0 (CH_2), 49.9 (CH), 39.6 (CH_2), 38.3 (CH), 29.1 (CH_2). **(ESI)-HRMS** calcd for $C_{32}H_{32}O_2$ [M + Na]$^+$ 471.2300, found 471.2309.

(±)(2S,3R,5R)-5-benzyl-2-ethyl-3-((S)-phenyl(propoxy)methyl)tetrahydro-2H-pyran (4b)



Following catalytic synthesis **I**, **4b** was isolated (silica gel, n-hexane/EtOAc, gradient) as a white solid (32.1 mg, 0.182 mmol, 73% yield, *dr* 90:10 based on ^{1}H NMR integration) from starting material **3b** (44 mg, 0.25 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.25 – 7.16 (m, 5H), 7.16 – 7.08 (m, 1H), 7.03 (d, *J* = 7.4 Hz, 2H), 4.48 (br s, 1H), 3.76 (dd, *J* = 11.2, 4.5 Hz, 1H), 3.45 – 3.34 (m, 2H), 3.15 – 3.07 (m, 1H), 3.02 (t, *J* = 11.1 Hz, 1H), 2.46 (dd, *J* = 13.6, 5.8 Hz, 1H), 2.30 (dd, *J* = 13.6, 8.6 Hz, 1H), 1.97 – 1.84 (m, 1H), 1.68 – 1.48 (m, 5H), 1.46 – 1.38 (m, 1H), 1.37 – 1.28 (m, 1H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1 (Cq), 140.1 (Cq), 128.9 (2CH), 128.3 (2CH), 128.2 (2CH), 127.0 (CH), 126.8 (2CH), 125.9 (CH), 80.9 (CH), 80.0 (CH), 72.7 (CH_2), 71.5 (CH_2), 46.8 (CH), 39.6 (CH_2), 38.4 (CH), 29.4 (CH_2), 25.8 (CH_2), 23.3 (CH_2), 11.0 (CH_3), 9.7 (CH_3). **(ESI)-HRMS** calcd for $C_{24}H_{32}O_2$ [M + Na]$^+$ 375.2300, found 375.2298.

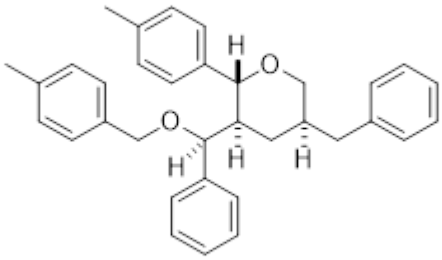
(±)(2S,3R,5R)-5-benzyl-3-((S)-ethoxy(phenyl)methyl)-2-methyltetrahydro-2H-pyran (4c)



Following catalytic synthesis **I**, **4c** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a white solid (42.2 mg, 0.260 mmol, 65% yield, *dr* 86:14 based on ^{1}H NMR integration) from starting material **3c**

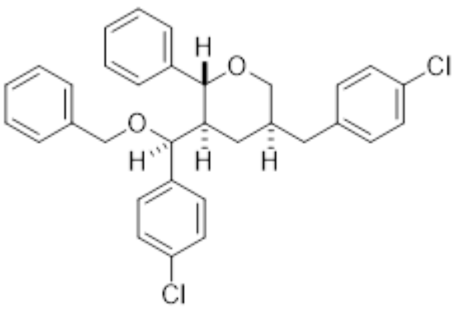
(65 mg, 0.40 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.25 – 7.17 (m, 5H), 7.15 – 7.07 (m, 1H), 7.06 – 7.01 (m, 2H), 4.49 (d, *J* = 2.3 Hz, 1H), 3.73 (ddd, *J* = 11.0, 4.3, 1.9 Hz, 1H), 3.62 – 3.53 (m, 1H), 3.51 – 3.43 (m, 1H), 3.31 – 3.20 (m, 1H), 3.06 (t, *J* = 11.1 Hz, 1H), 2.45 (dd, *J* = 13.6, 5.9 Hz, 1H), 2.31 (dd, *J* = 13.7, 8.6 Hz, 1H), 1.76 – 1.65 (m, 1H), 1.44 – 1.38 (m, 2H), 1.35 (d, *J* = 6.1 Hz, 3H), 1.32 – 1.25 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.0 (Cq), 140.0 (Cq), 128.9 (2CH), 128.3 (2CH), 128.2 (2CH), 127.1 (CH), 126.7 (2CH), 126.0 (CH), 81.0 (CH), 75.4 (CH), 72.6 (CH_2), 65.1 (CH_2), 49.5 (CH), 39.6 (CH_2), 38.3 (CH), 29.3 (CH_2), 19.8 (CH_3), 15.5 (CH_3). **(ESI)-HRMS** calcd for $C_{22}H_{28}O_2$ $[M + Na]^+$ 347.1987, found 347.1981.

(±)(2R,3R,5R)-5-benzyl-3-((S)-((4-methylbenzyl)oxy)(phenyl)methyl)-2-(p-tolyl)tetrahydro-2H-pyran (4d)



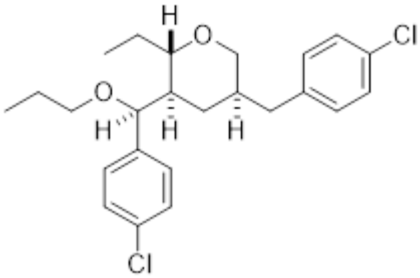
Following catalytic synthesis **I**, **4d** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a white solid (24.4 mg, 0.102 mmol, 26% yield, *dr* 86:14 based on ^{1}H NMR integration) from starting material **3d** (95 mg, 0.40 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.01 (m, 18H), 4.45 (d, *J* = 9.9 Hz, 1H), 4.30 (d, *J* = 11.2 Hz, 1H), 4.08 (d, *J* = 2.2 Hz, 1H), 3.99 (d, *J* = 11.3 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.21 (t, *J* = 11.1 Hz, 1H), 2.51 (dd, *J* = 13.7, 5.8 Hz, 1H), 2.41 (s, 3H), 2.40 – 2.36 (m, 1H), 2.36 (s, 3H), 1.91 – 1.76 (m, 2H), 1.66 – 1.58 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.5 (Cq), 140.0 (Cq), 138.3 (Cq), 137.7 (Cq), 137.4 (Cq), 135.7 (Cq), 129.3 (2CH), 129.2 (2CH), 128.9 (2CH), 128.3 (2CH), 128.2 (2CH), 127.9 (2CH), 127.5 (2CH), 127.1 (CH), 126.7 (2CH), 126.0 (CH), 83.0 (CH), 80.2 (CH), 73.2 (CH_2), 71.0 (CH_2), 49.8 (CH), 39.6 (CH_2), 38.3 (CH), 29.1 (CH_2), 21.4 ($2CH_3$). **(ESI)-HRMS** calcd for $C_{34}H_{36}O_2$ $[M + Na]^+$ 499.2613, found 499.2611.

(±)(2R,3R,5R)-3-((S)-(benzyloxy)(4-chlorophenyl)methyl)-5-(4-chlorobenzyl)-2-phenyltetrahydro-2H-pyran (4e)



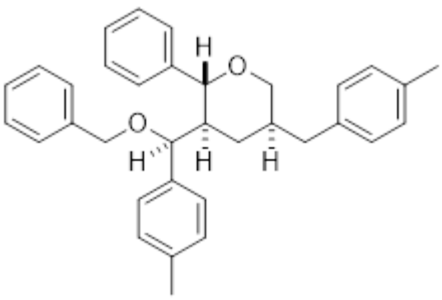
Following catalytic synthesis **II**, **4e** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a white solid (50.3 mg, 0.194 mmol, 50% yield, *dr* 90:10 based on ^{1}H NMR integration) from starting material **3e** (101 mg, 0.39 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.26 (m, 12H), 7.24 – 7.19 (m, 2H), 7.07 – 7.00 (m, 4H), 4.47 (d, *J* = 10.0 Hz, 1H), 4.33 (d, *J* = 11.3 Hz, 1H), 4.10 – 4.01 (m, 2H), 3.93 – 3.86 (m, 1H), 3.23 (t, *J* = 11.1 Hz, 1H), 2.50 (dd, *J* = 13.8, 5.9 Hz, 1H), 2.39 (dd, *J* = 13.8, 8.4 Hz, 1H), 1.92 – 1.73 (m, 2H), 1.64 – 1.55 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.0 (Cq), 138.8 (Cq), 138.3 (Cq), 138.2 (Cq), 133.0 (Cq), 131.9 (Cq), 130.2 (2CH), 128.8 (2CH), 128.6 (2CH), 128.53 (2CH), 128.51 (2CH), 128.3 (CH), 128.0 (2CH), 127.9 (CH), 127.7 (2CH), 127.6 (2CH), 83.1 (CH), 79.6 (CH), 73.0 (CH_2), 71.2 (CH_2), 49.8 (CH), 38.8 (CH_2), 38.1 (CH), 29.0 (CH_2). **(ESI)-HRMS** calcd for $C_{32}H_{30}Cl_2O_2$ $[M + Na]^+$ 539.1521, found 539.1515.

(±)(2S,3R,5R)-5-(4-chlorobenzyl)-3-((S)-(4-chlorophenyl)(propoxy)methyl)-2-ethyltetrahydro-2H-pyran (4f)



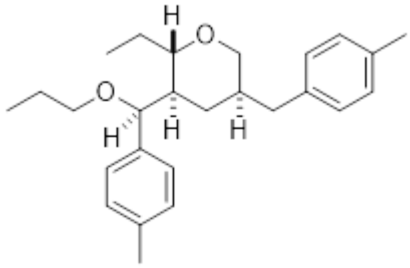
Following catalytic synthesis **I**, **4f** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a white solid (20.1 mg, 0.095 mmol, 38% yield, *dr* 93:7 based on ^{1}H NMR integration) from starting material **3f** (52 mg, 0.25 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.20 – 7.11 (m, 4H), 6.99 – 6.94 (m, 2H), 4.45 (d, *J* = 2.6 Hz, 1H), 3.74 (ddd, *J* = 11.1, 4.4, 2.0 Hz, 1H), 3.42 – 3.32 (m, 2H), 3.15 – 3.06 (m, 1H), 3.00 (t, *J* = 11.1 Hz, 1H), 2.41 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.28 (dd, *J* = 13.8, 8.6 Hz, 1H), 1.94 – 1.82 (m, 1H), 1.65 – 1.43 (m, 5H), 1.34 – 1.23 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.6 (Cq), 138.4 (Cq), 132.7 (Cq), 131.8 (Cq), 130.2 (2CH), 128.4 (4CH), 128.0 (2CH), 80.3 (CH), 79.9 (CH), 72.5 (CH_2), 71.6 (CH_2), 46.7 (CH), 38.9 (CH_2), 38.3 (CH), 29.2 (CH_2), 25.7 (CH_2), 23.3 (CH_2), 11.0 (CH_3), 9.7 (CH_3). **(ESI)-HRMS** calcd for $C_{24}H_{30}Cl_2O_2$ $[M + Na]^+$ 443.1521, found 443.1522.

(±)(2R,3R,5R)-3-((S)-(benzyloxy)(p-tolyl)methyl)-5-(4-methylbenzyl)-2-phenyltetrahydro-2H-pyran (4g)



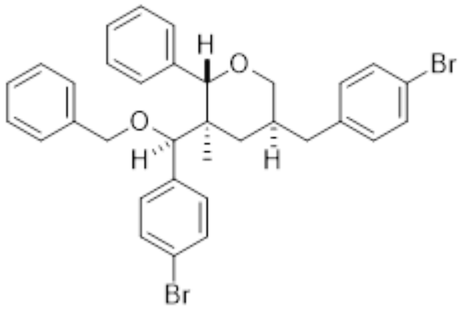
Following catalytic synthesis **I**, **4g** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a white solid (29.0 mg, 0.122 mmol, 22% yield, *dr* 87:13 based on ^{1}H NMR integration) from starting material **3g** (129 mg, 0.54 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 10H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.07 – 6.95 (m, 6H), 4.48 (d, *J* = 9.9 Hz, 1H), 4.35 (d, *J* = 11.6 Hz, 1H), 4.07 – 3.98 (m, 2H), 3.93 – 3.85 (m, 1H), 3.22 (t, *J* = 11.1 Hz, 1H), 2.51 (dd, *J* = 13.7, 5.5 Hz, 1H), 2.39 – 2.32 (m, 1H), 2.33 (s, 3H), 2.29 (s, 3H), 1.89 – 1.76 (m, 2H), 1.73 – 1.61 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4 (Cq), 138.9 (Cq), 137.3 (Cq), 136.88 (Cq), 136.84 (Cq), 135.5 (Cq), 129.04 (2CH), 128.99 (2CH), 128.8 (2CH), 128.7 (2CH), 128.5 (2CH), 128.1 (CH), 127.71 (2CH), 127.65 (3CH), 126.7 (2CH), 83.2 (CH), 80.1 (CH), 73.3 (CH_2), 70.9 (CH_2), 49.9 (CH), 39.2 (CH_2), 38.3 (CH), 29.2 (CH_2), 21.2 (CH_3), 21.1 (CH_3). **(ESI)-HRMS** calcd for $C_{34}H_{36}O_2$ $[M + Na]^+$ 499.2613, found 499.2618.

(±)(2S,3R,5R)-2-ethyl-5-(4-methylbenzyl)-3-((S)-propoxy(p-tolyl)methyl)tetrahydro-2H-pyran (4h)



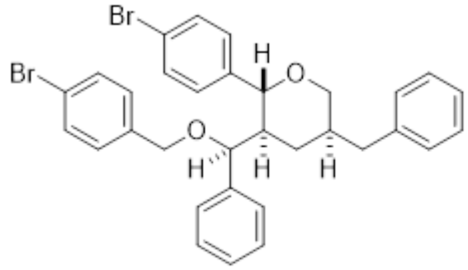
Following catalytic synthesis **I**, **4h** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a white solid (25.5 mg, 0.134 mmol, 52% yield, *dr* 88:12 based on ^{1}H NMR integration) from starting material **3h** (50 mg, 0.26 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 – 7.07 (m, 4H), 7.03 – 6.98 (m, 2H), 6.95 – 6.89 (m, 2H), 4.45 (d, *J* = 2.5 Hz, 1H), 3.76 (ddd, *J* = 11.0, 4.3, 2.0 Hz, 1H), 3.46 – 3.33 (m, 2H), 3.14 – 3.06 (m, 1H), 3.00 (t, *J* = 11.1 Hz, 1H), 2.43 (dd, *J* = 13.7, 5.5 Hz, 1H), 2.35 (s, 3H), 2.27 (s, 3H), 2.27 – 2.18 (m, 1H), 1.90 (ddd, *J* = 14.2, 7.4, 2.8 Hz, 1H), 1.65 – 1.49 (m, 4H), 1.49 – 1.41 (m, 2H), 1.36 – 1.27 (m, 1H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.0 (Cq), 137.0 (Cq), 136.6 (Cq), 135.3 (Cq), 128.94 (2CH), 128.87 (2CH), 128.78 (2CH), 126.8 (2CH), 80.9 (CH), 80.0 (CH), 72.8 (CH_2), 71.4 (CH_2), 46.8 (CH), 39.2 (CH_2), 38.5 (CH), 29.5 (CH_2), 25.8 (CH_2), 23.3 (CH_2), 21.3 (CH_3), 21.1 (CH_3), 11.0 (CH_3), 9.7 (CH_3). **(ESI)-HRMS** calcd for $C_{26}H_{36}O_2$ $[M + Na]^+$ 403.2613, found 403.2608.

(±)(2S,3R,5S)-3-((R)-(benzyloxy)(4-bromophenyl)methyl)-5-(4-bromobenzyl)-3-methyl-2-phenyltetrahydro-2H-pyran (4i)



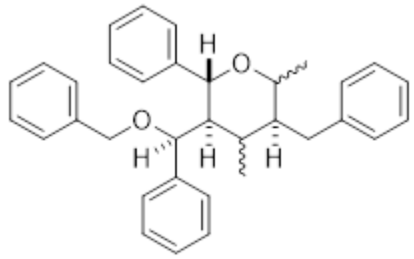
Following catalytic synthesis **II**, **4i** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a white solid (45.2 mg, 0.149 mmol, 38% yield, *dr* 92:8 based on ^{1}H NMR integration) from starting material **3i** (118 mg, 0.39 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.28 (m, 14H), 6.97 (dd, *J* = 8.4, 3.1 Hz, 4H), 4.46 (d, *J* = 9.9 Hz, 1H), 4.32 (d, *J* = 11.3 Hz, 1H), 4.07 – 4.02 (m, 2H), 3.92 – 3.85 (m, 1H), 3.22 (t, *J* = 11.1 Hz, 1H), 2.49 (dd, *J* = 13.8, 5.9 Hz, 1H), 2.37 (dd, *J* = 13.8, 8.4 Hz, 1H), 1.90 – 1.74 (m, 2H), 1.63 – 1.56 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9 (Cq), 139.3 (Cq), 138.7 (Cq), 138.3 (Cq), 131.5 (4CH), 130.6 (2CH), 128.8 (2CH), 128.6 (2CH), 128.35 (2CH), 128.27 (CH), 127.9 (CH), 127.7 (2CH), 127.6 (2CH), 83.1 (CH), 79.6 (CH), 73.0 (CH_2), 71.2 (CH_2), 49.7 (CH), 38.9 (CH_2), 38.1 (CH), 29.0 (CH_2). **(ESI)-HRMS** calcd for $C_{33}H_{32}Br_2O_2$ $[M + Na]^+$ 641.0667, found 641.0664.

(±)(2R,3R,5R)-5-benzyl-3-((S)-((4-bromobenzyl)oxy)(phenyl)methyl)-2-(4-bromophenyl)tetrahydro-2H-pyran (4j/4j')



Following catalytic synthesis **I**, **4j** (50.1 mg, 0.165 mmol, 41% yield) and **4j'** (14.8 mg, 0.049 mmol, 12% yield) were isolated (silica gel, *n*-hexane/EtOAc, gradient) as white solids from starting material **3j** (121 mg, 0.40 mmol). **4j**: ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.11 (m, 8H), 7.09 – 7.05 (m, 4H), 4.39 (d, *J* = 9.9 Hz, 1H), 4.33 (d, *J* = 11.8 Hz, 1H), 4.02 (d, *J* = 2.3 Hz, 1H), 3.96 (d, *J* = 11.9 Hz, 1H), 3.88 (ddd, *J* = 11.2, 4.3, 1.9 Hz, 1H), 3.21 (t, *J* = 11.2 Hz, 1H), 2.53 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.40 (dd, *J* = 13.6, 8.5 Hz, 1H), 1.90 – 1.82 (m, 1H), 1.80 – 1.72 (m, 1H), 1.70 – 1.63 (m, 1H), 1.63 – 1.54 (m, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 140.2 (Cq), 139.7 (Cq), 139.7 (Cq), 137.4 (Cq), 131.8 (2CH), 131.7 (2CH), 129.5 (2CH), 129.3 (2CH), 128.9 (2CH), 128.4 (4CH), 127.5 (CH), 126.7 (2CH), 126.1 (CH), 122.0 (Cq), 121.7 (Cq), 82.4 (CH), 80.1 (CH), 73.2 (CH_2), 70.2 (CH_2), 49.7 (CH), 39.5 (CH_2), 38.2 (CH), 29.1 (CH_2). **(ESI)-HRMS** calcd for $C_{32}H_{30}Br_2O_2$ $[M + Na]^+$ 627.0511, found 627.0514. **4j'**: ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.22 – 7.16 (m, 4H), 7.12 – 7.06 (m, 4H), 6.84 (d, *J* = 8.4 Hz, 2H), 4.13 (d, *J* = 11.8 Hz, 1H), 4.02 (d, *J* = 4.7 Hz, 1H), 3.90 – 3.80 (m, 3H), 3.03 (t, *J* = 11.1 Hz, 1H), 2.46 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.40 – 2.33 (m, 1H), 2.09 – 1.99 (m, 1H), 1.97 – 1.90 (m, 1H), 1.66 – 1.49 (m, 2H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 140.0 (Cq), 139.5 (Cq), 138.8 (Cq), 137.2 (Cq), 131.7 (2CH), 131.4 (2CH), 129.9 (2CH), 129.2 (2CH), 129.0 (2CH), 128.4 (2CH), 128.3 (2CH), 127.9 (CH), 127.8 (2CH), 126.2 (CH), 122.1 (Cq), 121.4 (Cq), 82.9 (CH), 81.5 (CH), 73.4 (CH_2), 69.6 (CH_2), 46.9 (CH), 39.3 (CH_2), 37.9 (CH), 32.7 (CH_2). **(ESI)-HRMS** calcd for $C_{32}H_{30}Br_2O_2$ $[M + Na]^+$ 627.0511, found 627.0515.

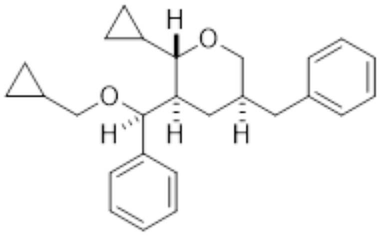
(±)(3S,5S,6R)-3-benzyl-5-((S)-(benzyloxy)(phenyl)methyl)-2,4-dimethyl-6-phenyltetrahydro-2H-pyran (4k/4k')



Following catalytic synthesis **I**, **4k** (26.1 mg, 0.110 mmol, 22% yield, *dr* 80:20 based on ^{1}H NMR integration) and **4k'** (21.8 mg, 0.091 mmol, 18% yield, *dr* 70:30 based on ^{1}H NMR integration) were isolated (silica gel, *n*-hexane/EtOAc, gradient) as white solids from starting material **3k** (119 mg, 0.50 mmol). **4k**: ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.42 – 7.28 (m, 10H), 7.25 – 7.18 (m, 4H), 7.15 – 7.09 (m, 2H), 7.06 – 6.98 (m, 4H), 6.81 – 6.75 (m, 2H), 5.00 (d, *J* = 10.4 Hz, 1H), 4.33 – 4.24 (m, 2H), 4.07 (d, *J* = 3.5 Hz, 1H), 3.84 (d, *J* = 11.7 Hz, 1H), 2.91 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.70 – 2.56 (m, 1H), 2.31 (dt, *J* = 10.4, 3.7 Hz, 1H), 1.32 (d, *J* = 7.1 Hz, 2H), 1.26 (d, *J* = 6.5 Hz, 2H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 141.8 (Cq), 141.2 (Cq), 140.0 (Cq), 139.2 (Cq), 129.1 (2CH), 128.7 (2CH), 128.4 (2CH), 128.3 (2CH), 128.2 (2CH), 128.1(CH), 127.6 (2CH), 127.2 (CH), 127.0 (CH), 126.6 (2CH), 126.1 (2CH), 125.5 (CH), 82.3 (CH), 78.4 (CH), 71.4 (CH_2), 70.3 (CH), 48.9 (CH), 47.6 (CH), 32.3 (CH_2), 28.0

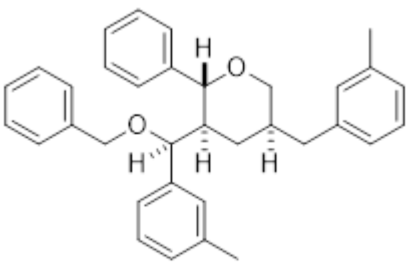
(CH), 19.5 (CH_3), 17.3 (CH_3). **(ESI)-HRMS** calcd for $C_{34}H_{36}O_2$ [M + Na]$^+$ 499.2613, found 499.2617. **4k'**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.22 – 7.14 (m, 9H), 7.09 – 7.06 (m, 2H), 6.89 – 6.85 (m, 2H), 6.80 – 6.75 (m, 2H), 4.76 (d, *J* = 10.3 Hz, 1H), 4.23 – 4.17 (m, 1H), 4.07 (d, *J* = 6.0 Hz, 1H), 3.94 (d, *J* = 11.1 Hz, 1H), 3.79 (d, *J* = 11.2 Hz, 1H), 3.02 (dd, *J* = 14.1, 4.7 Hz, 1H), 2.86 (dd, *J* = 14.1, 11.2 Hz, 1H), 2.71 – 2.63 (m, 1H), 1.70 – 1.63 (m, 1H), 1.61 – 1.55 (m, 1H), 1.23 (d, *J* = 6.5 Hz, 3H), 1.03 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.8 (Cq), 141.4 (Cq), 140.6 (Cq), 138.4 (Cq), 129.3 (2CH), 128.5 (2CH), 128.1 (2CH), 128.0 (2CH), 127.9 (2CH), 127.8 (2CH), 127.46 (2CH), 127.43 (CH), 127.37 (2CH), 127.1 (CH), 126.9 (CH), 125.9 (CH), 83.1 (CH), 79.4 (CH), 70.08 (CH), 70.05 (CH_2), 47.4 (CH), 45.1 (CH), 32.4 (CH), 32.2 (CH_2), 19.4 (CH_3), 14.8 (CH_3). **(ESI)-HRMS** calcd for $C_{34}H_{36}O_2$ [M + Na]$^+$ 499.2613, found 499.2619.

(±)(2S,3R,5R)-5-benzyl-2-cyclopropyl-3-((S)-(cyclopropylmethoxy)(phenyl)methyl)tetrahydro-2H-pyran (4l)



Following catalytic synthesis **I**, **4l** was isolated (silica gel, n-hexane/EtOAc, gradient) as a white solid (45.5 mg, 0.242 mmol, 40% yield, *dr* 87:13 based on ^{1}H NMR integration) from starting material **3l** (115 mg, 0.61 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.27 – 7.15 (m, 5H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.06 – 6.99 (m, 2H), 4.87 (d, *J* = 2.3 Hz, 1H), 3.77 (ddd, *J* = 11.1, 4.4, 2.1 Hz, 1H), 3.20 – 3.07 (m, 2H), 3.02 (t, *J* = 11.1 Hz, 1H), 2.78 (t, *J* = 9.1 Hz, 1H), 2.46 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.31 (dd, *J* = 13.7, 8.5 Hz, 1H), 1.72 – 1.61 (m, 1H), 1.62 – 1.58 (m, 1H), 1.50 – 1.45 (m, 1H), 1.38 (t, *J* = 12.3 Hz, 1H), 1.07 – 1.00 (m, 1H), 0.99 – 0.92 (m, 1H), 0.73 – 0.64 (m, 1H), 0.63 – 0.55 (m, 1H), 0.55 – 0.46 (m, 2H), 0.47 – 0.38 (m, 2H), 0.18 – 0.11 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1 (Cq), 140.0 (Cq), 128.9 (2CH), 128.3 (2CH), 128.2 (2CH), 127.0 (CH), 126.9 (2CH), 126.0 (CH), 83.8 (CH), 80.3 (CH), 73.6 (CH_2), 72.9 (CH_2), 49.5 (CH), 39.5 (CH_2), 38.2 (CH), 28.8 (CH_2), 14.9 (CH), 11.0 (CH), 4.5 (CH_2), 3.2 (CH_2), 3.1 (CH_2), 1.9 (CH_2). **(ESI)-HRMS** calcd for $C_{26}H_{32}O_2$ [M + Na]$^+$ 399.2300, found 399.2307.

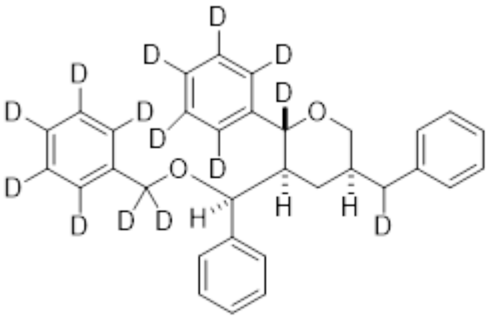
(±)(2R,3R,5R)-3-((S)-(benzyloxy)(m-tolyl)methyl)-5-(3-methylbenzyl)-2-phenyltetrahydro-2H-pyran (4m)



Following catalytic synthesis **I**, **4m** was isolated (silica gel, *n*-hexane/EtOAc, gradient) as a white solid (50.4 mg, 0.211 mmol, 53% yield, *dr* 87:13 based on ^{1}H NMR integration) from starting material **3m** (95 mg, 0.40 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.30 (m, 10H), 7.24 – 7.18 (m, 1H), 7.17 – 7.11 (m, 1H), 7.08 – 7.03 (m, 1H), 7.00 – 6.88 (m, 5H), 4.52 (d, *J* = 9.9 Hz, 1H), 4.39 (d, *J* = 11.4 Hz, 1H), 4.10 – 4.02 (m, 2H), 3.98 – 3.90 (m, 1H), 3.26 (t, *J* = 11.1 Hz, 1H), 2.51 (dd, *J* = 13.8, 5.8 Hz, 1H), 2.44 – 2.36 (m, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 1.94 – 1.79 (m, 2H), 1.76 – 1.54 (m, 2H). **^{13}C NMR** (101

MHz, $CDCl_3$) δ 141.3 (Cq), 140.3(Cq), 139.9 (Cq), 138.9 (Cq), 137.87 (Cq), 137.84 (Cq), 129.8 (CH), 128.7 (2CH), 128.5 (2CH), 128.2 (CH), 128.12 (CH), 128.06 (CH), 127.99 (CH), 127.70 (2CH), 127.66 (CH), 127.64 (2CH), 127.4 (CH), 126.7 (CH), 126.0 (CH), 123.8 (CH), 83.2 (CH), 80.3 (CH), 73.4 (CH_2), 71.0 (CH_2), 49.8 (CH), 39.5 (CH_2), 38.3 (CH), 29.2 (CH_2), 21.6 (CH_3), 21.5 (CH_3). **(ESI)-HRMS** calcd for $C_{34}H_{36}O_2$ [M + Na]$^+$ 499.2613, found 499.2609.

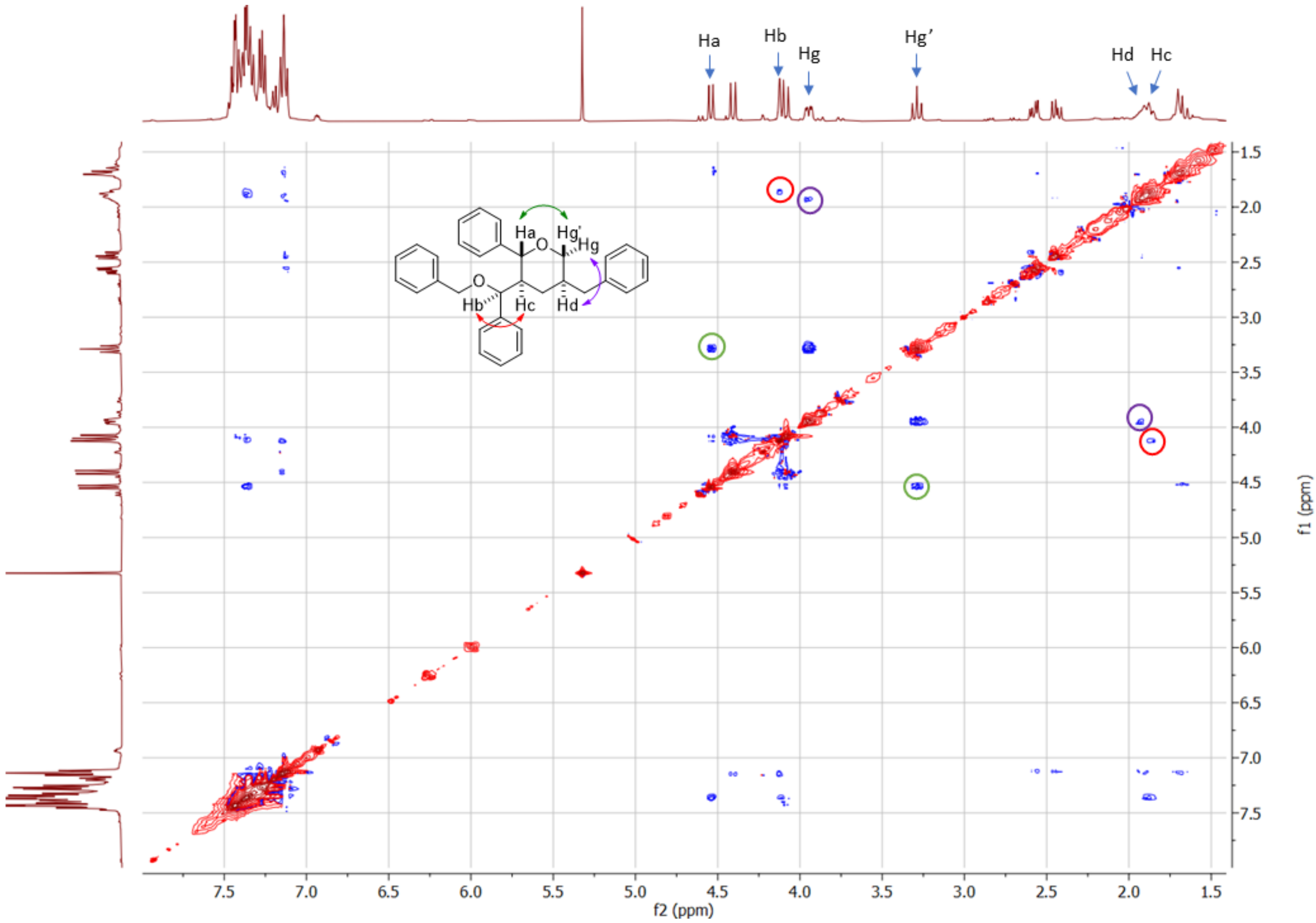
(±)(2R,3S,5R)-2-(phenyl-d5)-3-((S)-phenyl((phenyl-d5)methoxy-d2)methyl)-5-(phenylmethyl-d)tetrahydro-2H-pyran-2-d (*d14*-4a)



Following catalytic synthesis **I**, *d14*-**4a** was isolated (silica gel, ***n***-hexane/EtOAc, gradient) as a white solid (58.5 mg, 0.25 mmol, 58% yield, *dr* 83:17 based on ^{1}H NMR integration) from starting material *d7*-**3a** (100 mg, 0.43 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.11 (m, 10H), 4.11 (d, *J* = 2.2 Hz, 1H), 3.94 (ddd, *J* = 11.2, 4.3, 1.7 Hz, 1H), 3.28 (t, *J* = 11.1 Hz, 1H), 2.55 (d, *J* = 5.7 Hz, 1H), 1.95 – 1.84 (m, 1H), 1.74 – 1.60 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.0 (Cq), 140.3 (Cq), 139.9 (Cq), 138.4 (Cq), 128.9 (2CH), 128.3 (2CH), 128.3 (2CH), 127.2 (CH), 126.7 (2CH), 126.0 (CH), 80.1 (CH), 73.2 (CH2), 49.7 (CH), 39.2 (CHD, t, 19.8), 38.2 (CH), 29.1 (CH_2). **(ESI)-HRMS** calcd for $C_{32}H_{18}D_{14}O_2$ [M + Na]$^+$ 485.3179, found 485.3170.

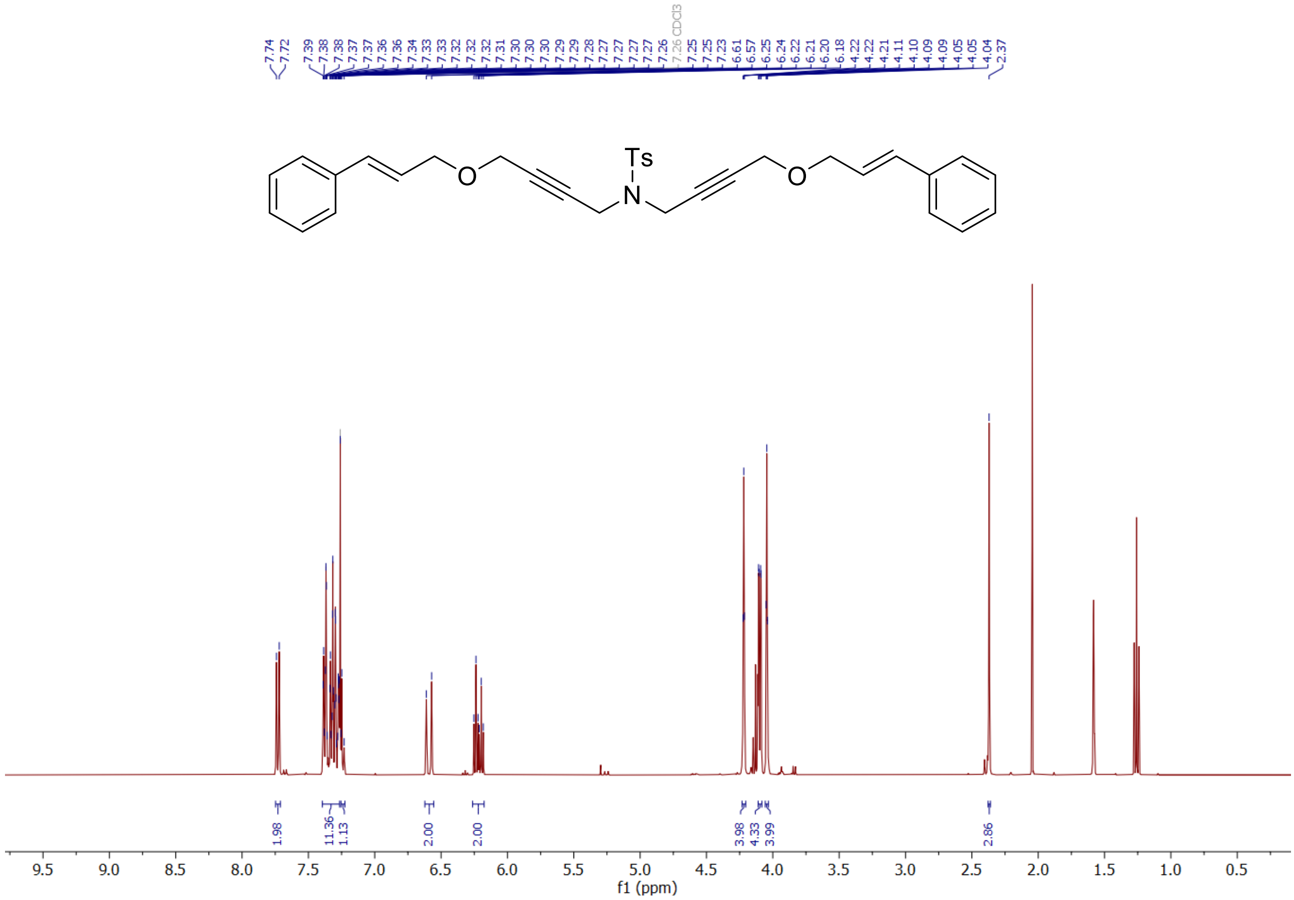
NOESY NMR experiment

4a, NOESY (400 MHz, $CDCl_3$)

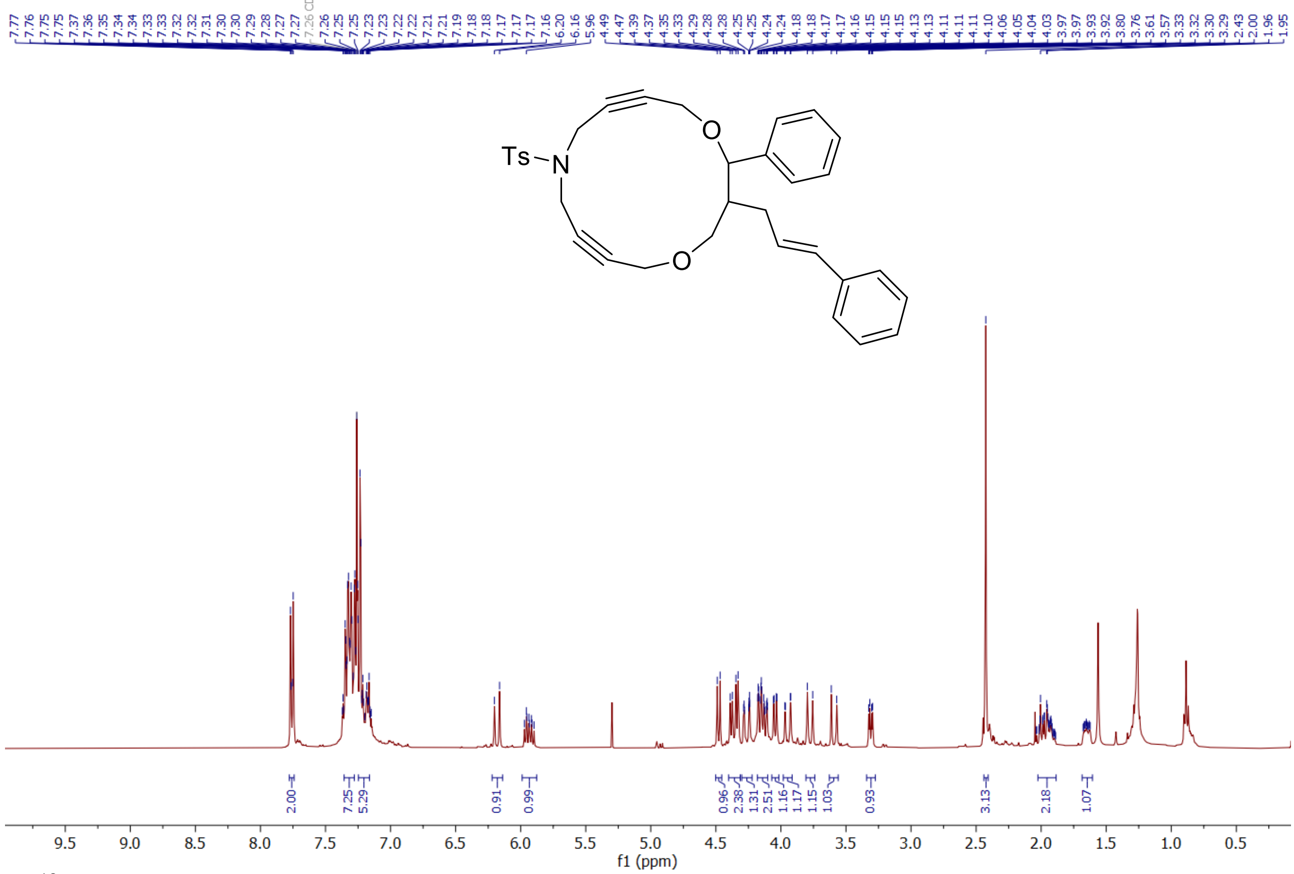


Copies of NMR spectra

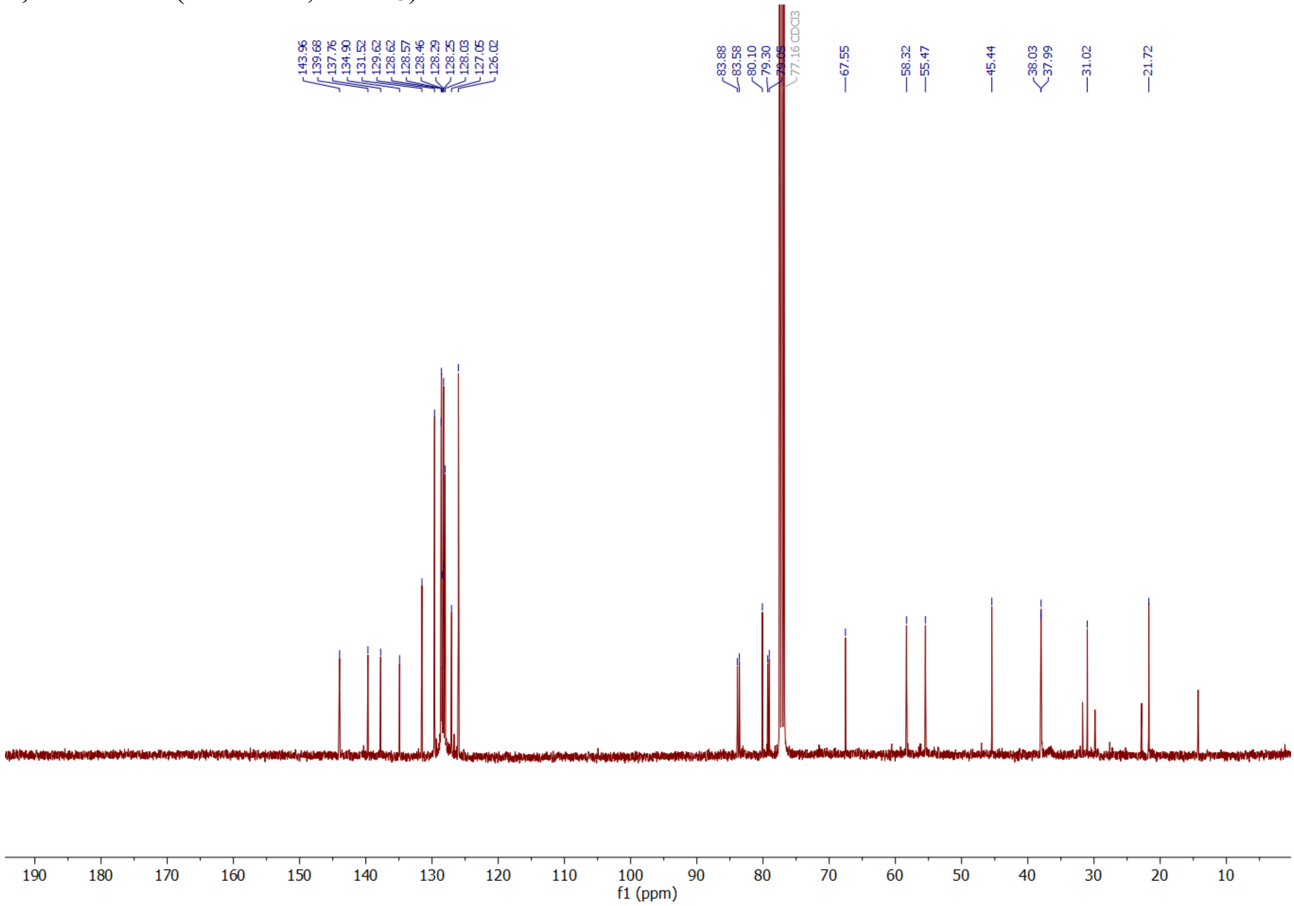
1, ^{1}H NMR (400 MHz, $CDCl_3$)



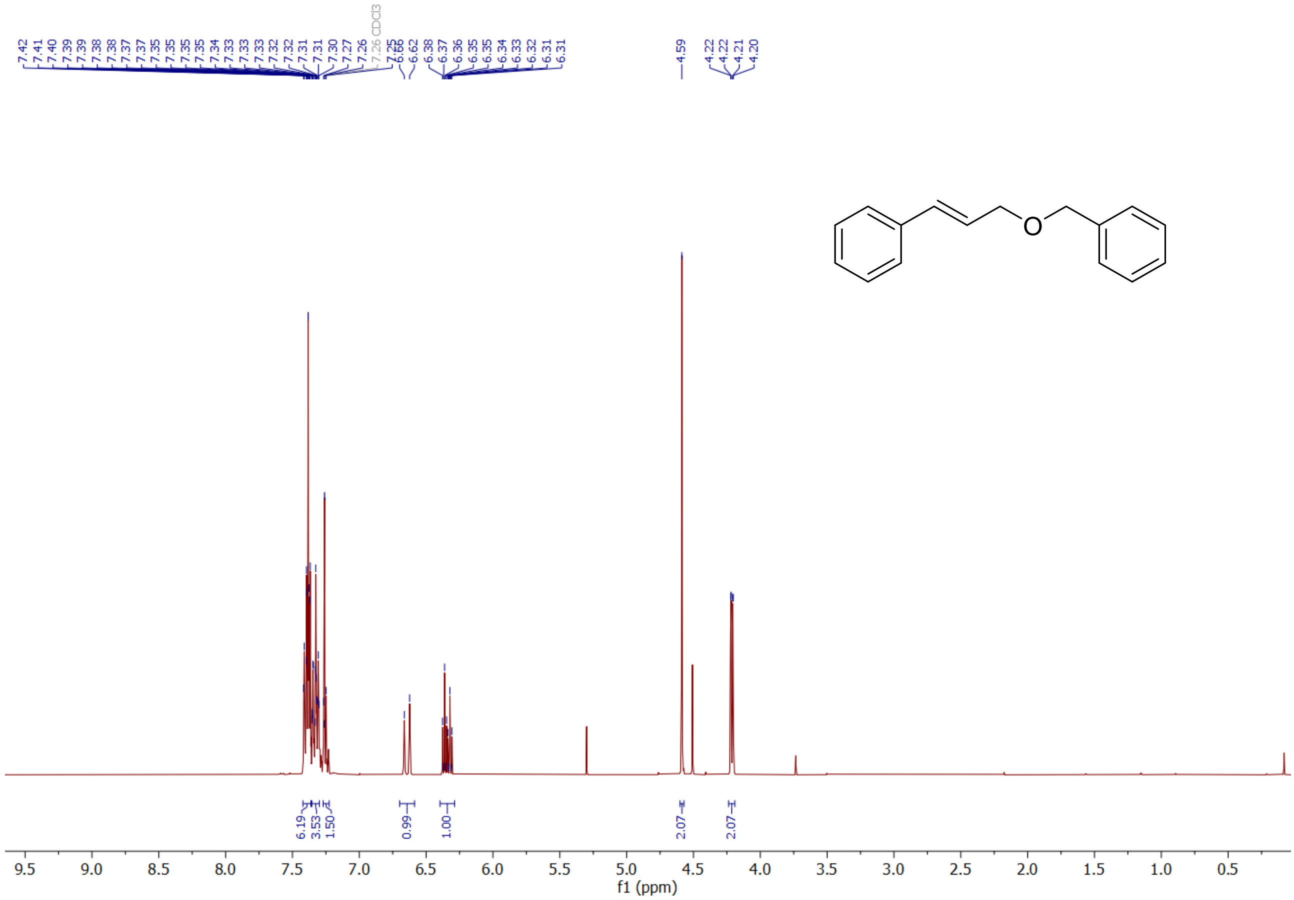
2, ^{1}H NMR (400 MHz, $CDCl_3$)



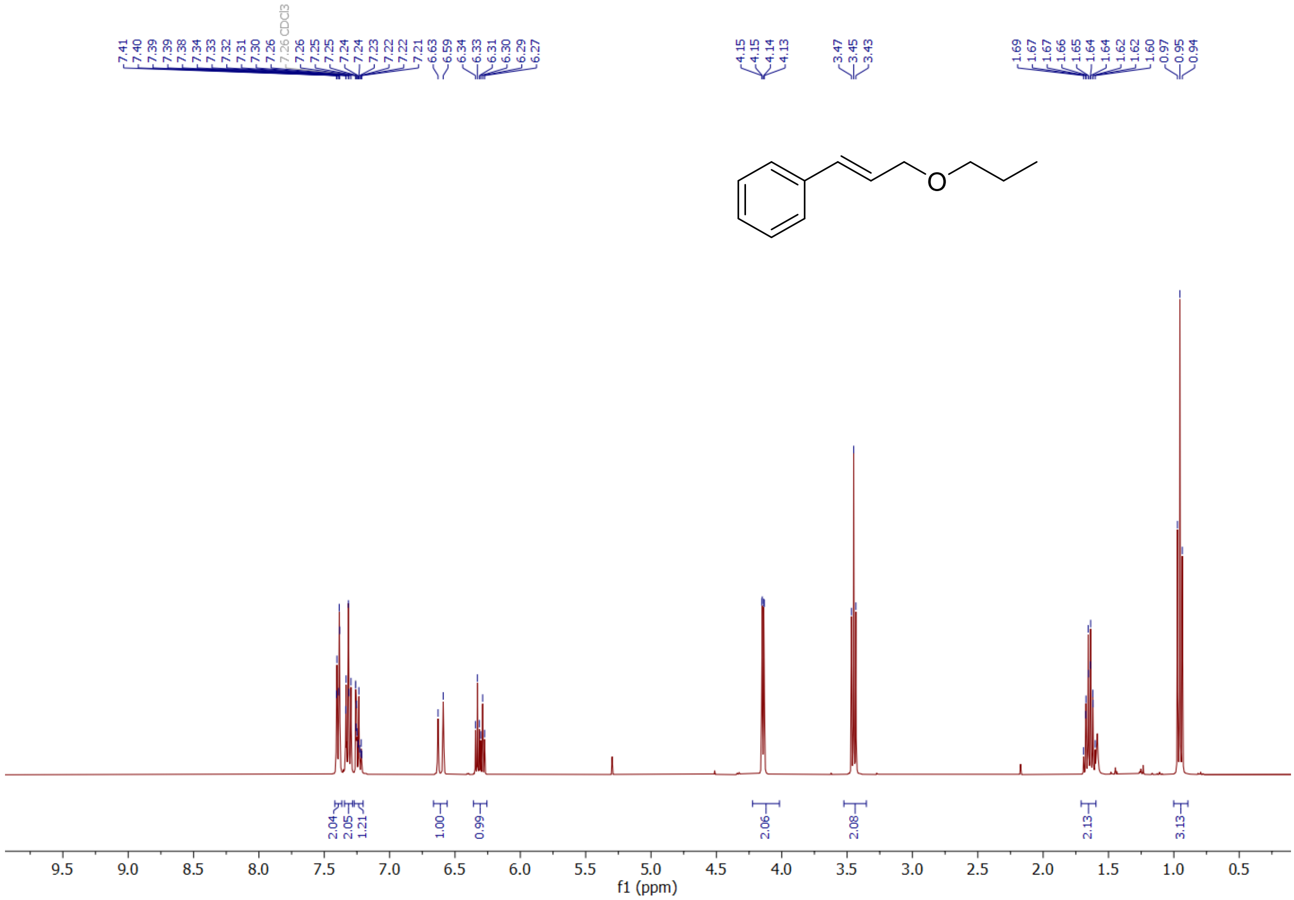
2, ^{13}C NMR (101 MHz, $CDCl_3$)



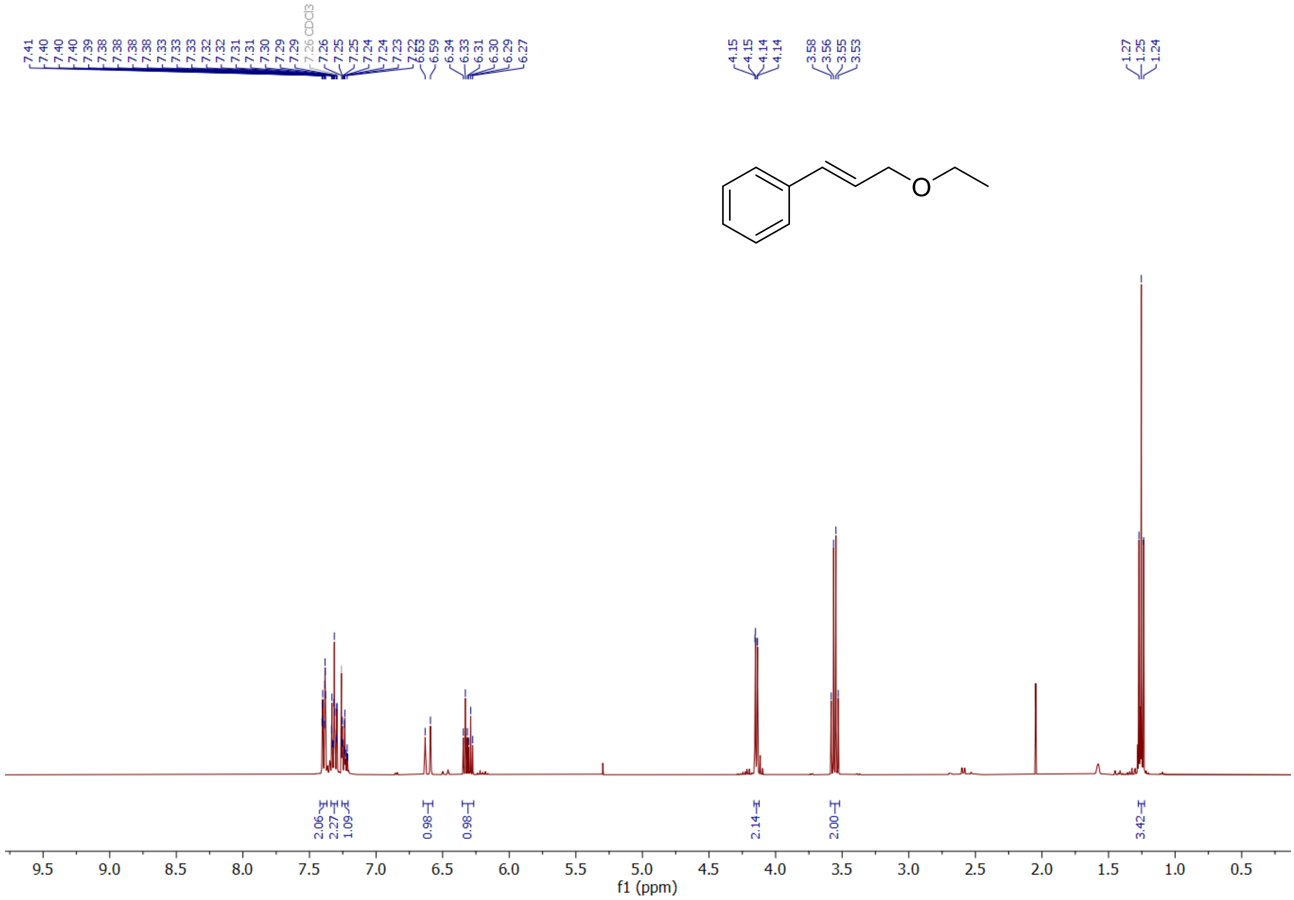
3a, ¹H NMR (400 MHz, $CDCl_3$)



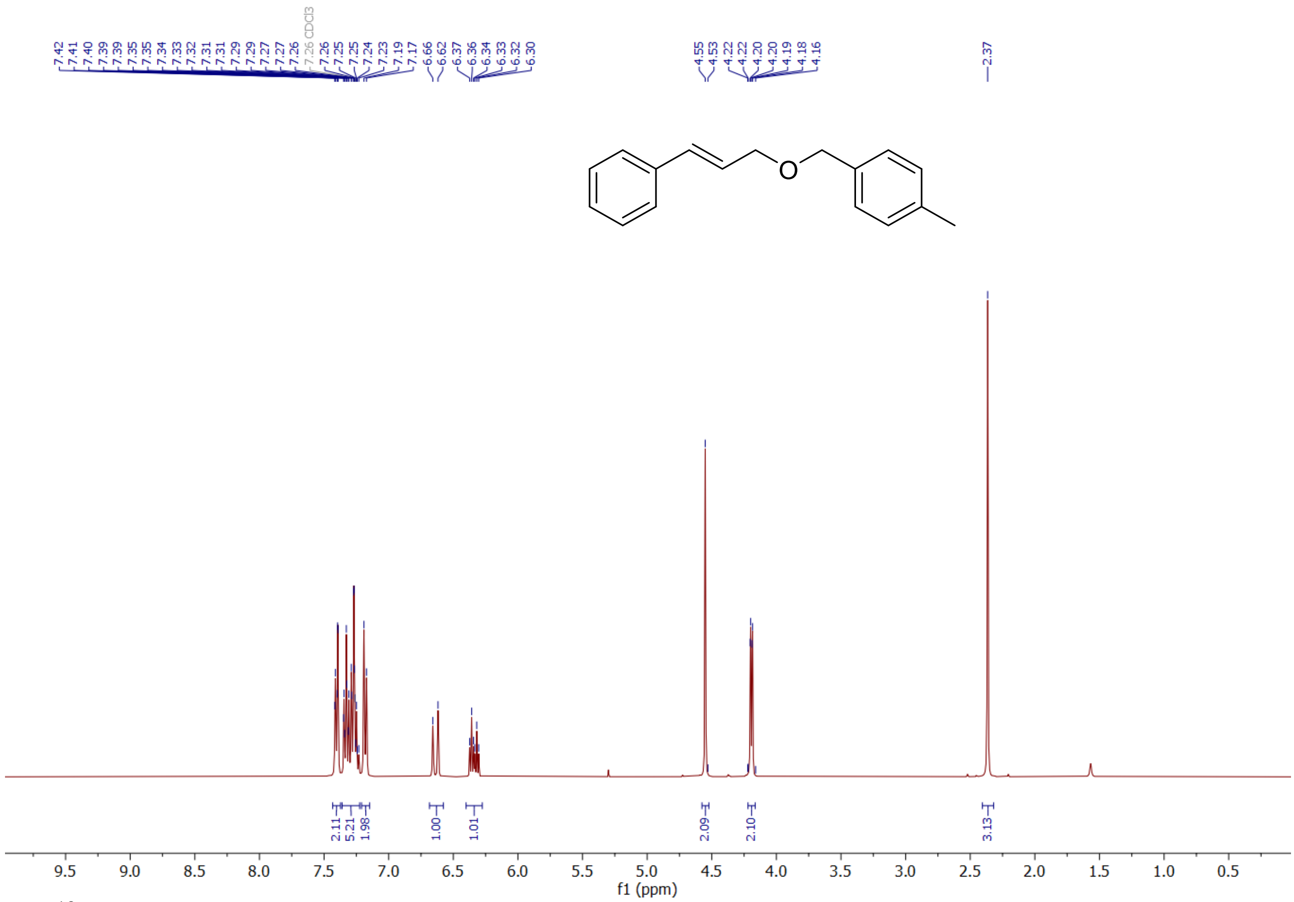
3b, ^{1}H NMR (400 MHz, $CDCl_3$)



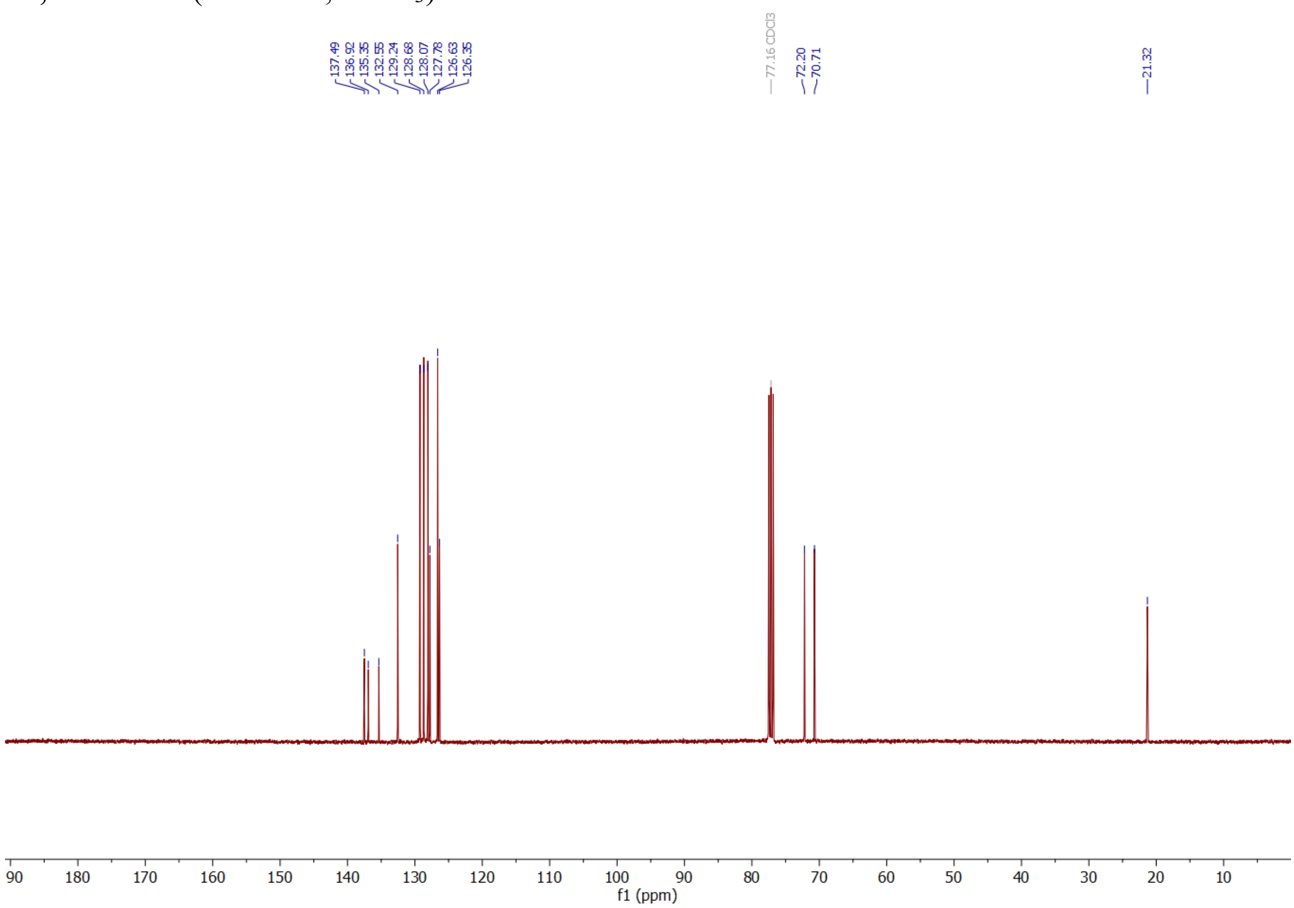
3c, ^{1}H NMR (400 MHz, $CDCl_3$)



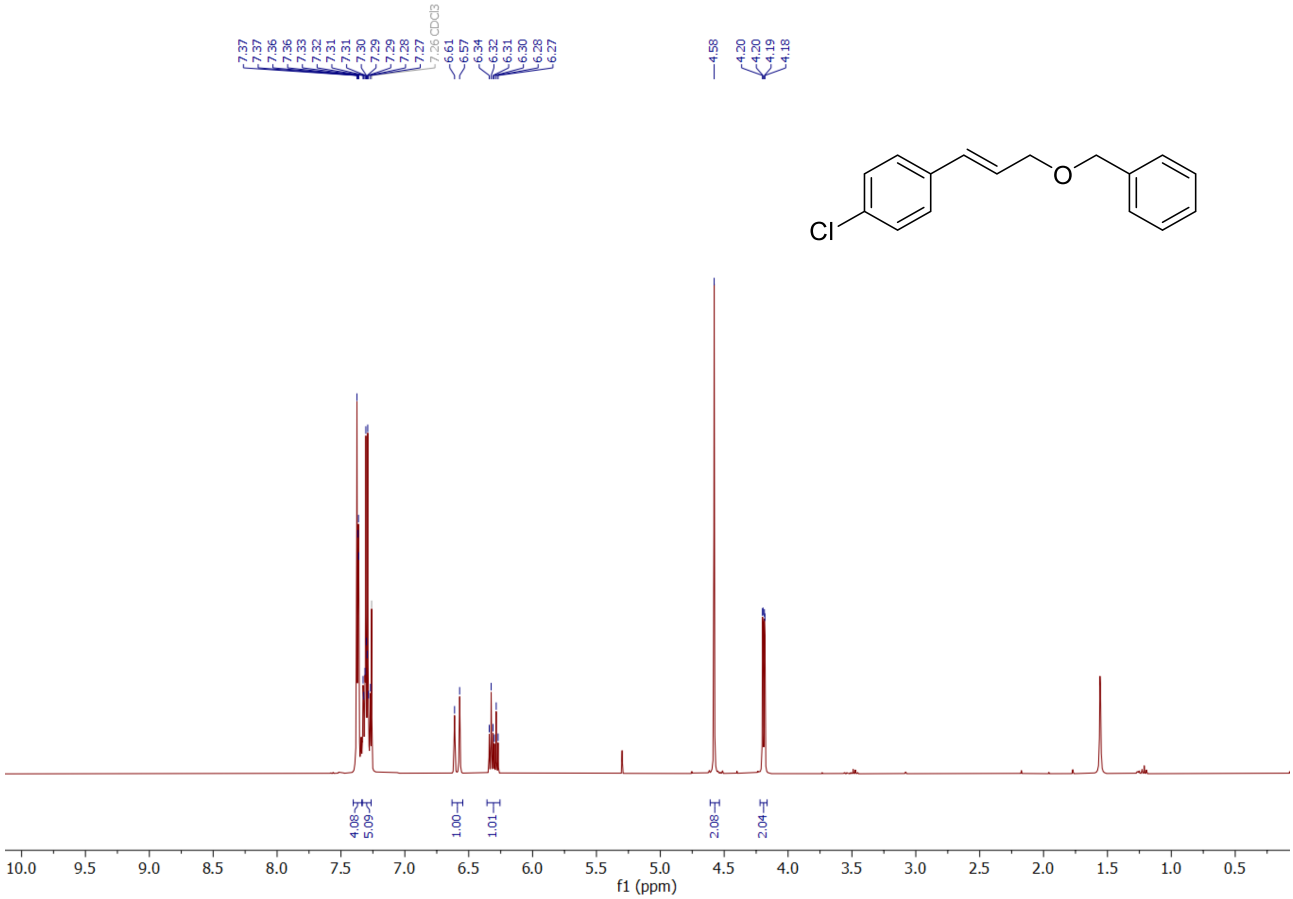
3d, ^{1}H NMR (400 MHz, $CDCl_3$)



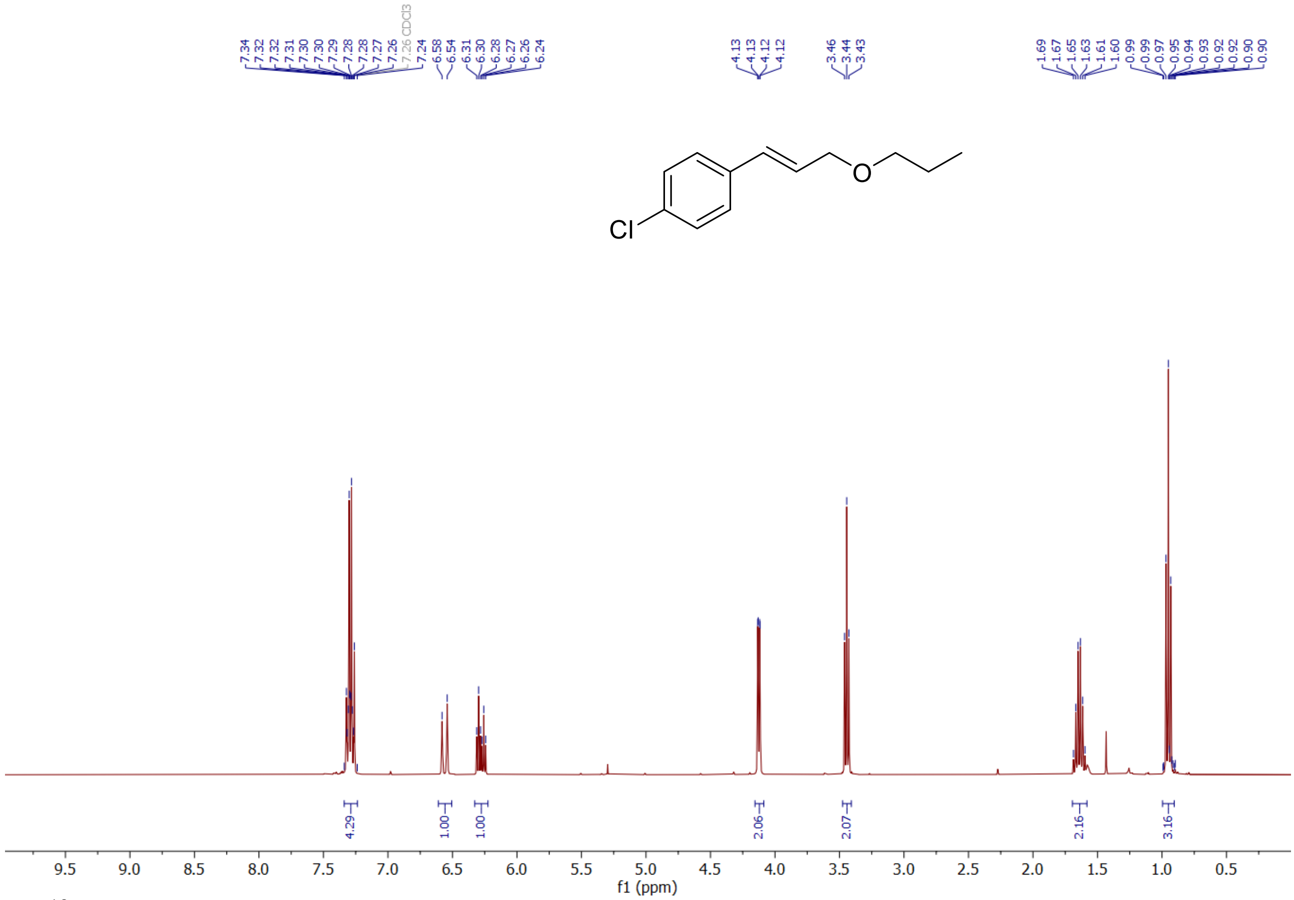
3d, ^{13}C NMR (101 MHz, $CDCl_3$)



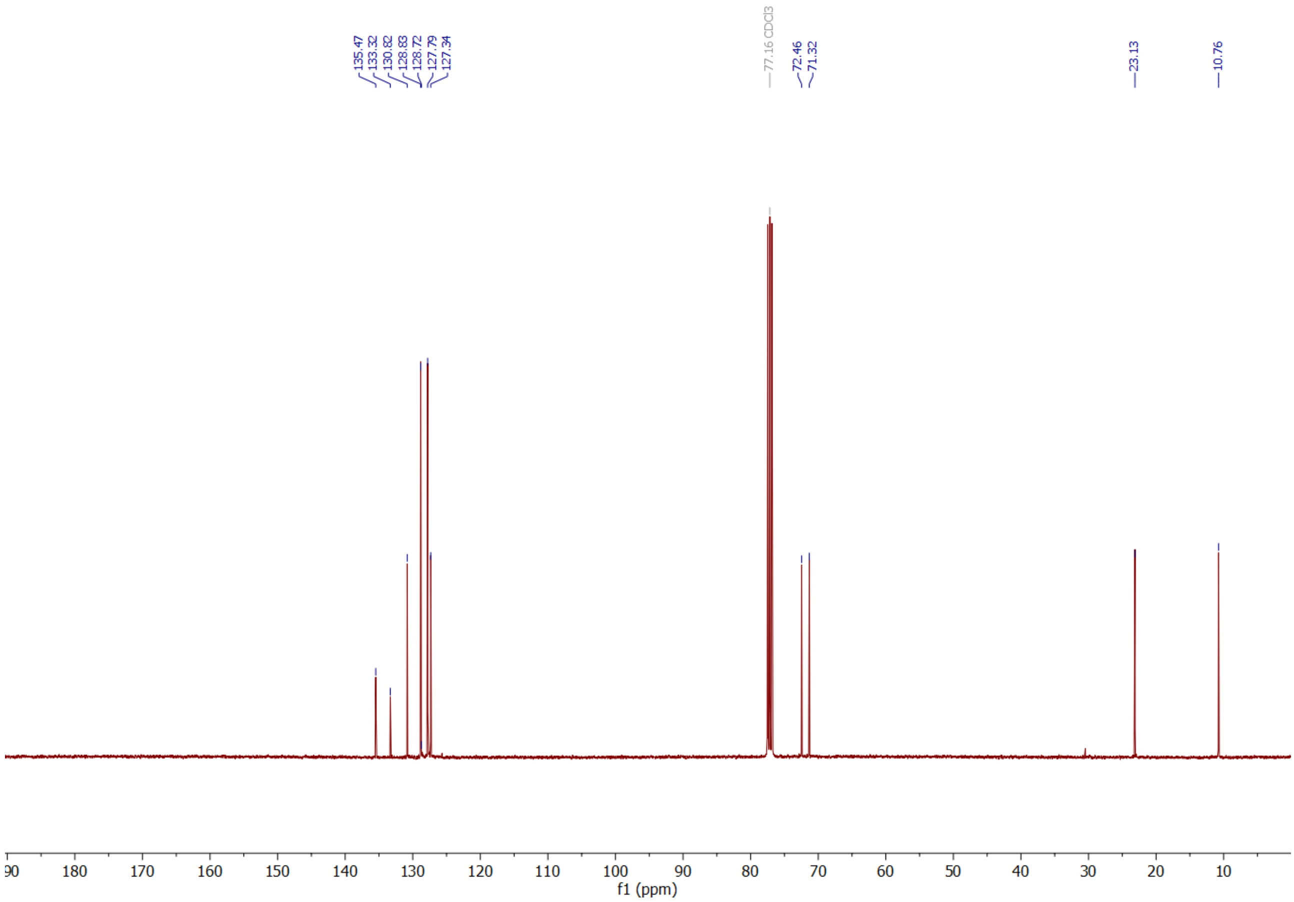
3e, ^{1}H NMR (400 MHz, $CDCl_3$)



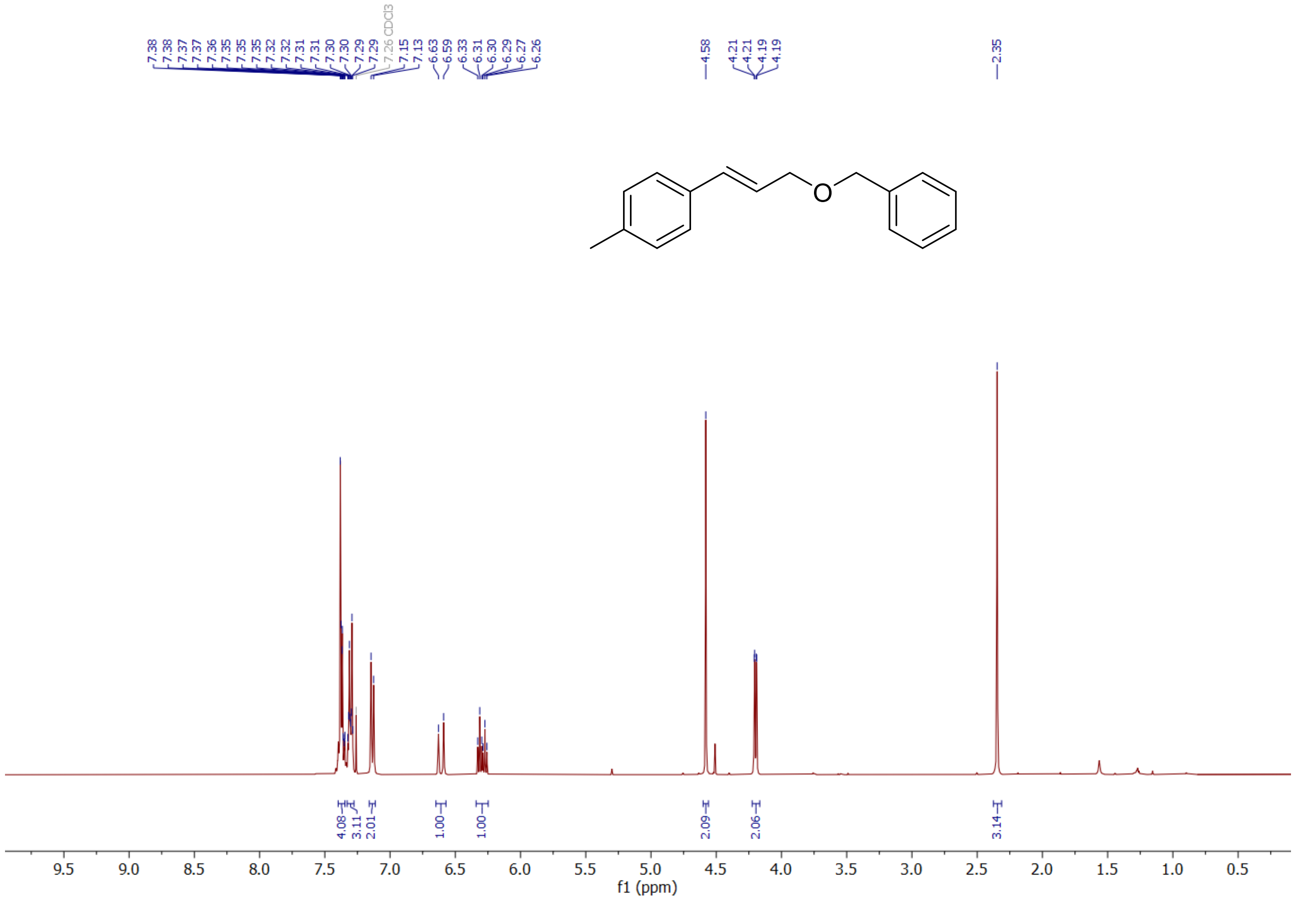
3f, ^{1}H NMR (400 MHz, $CDCl_3$)



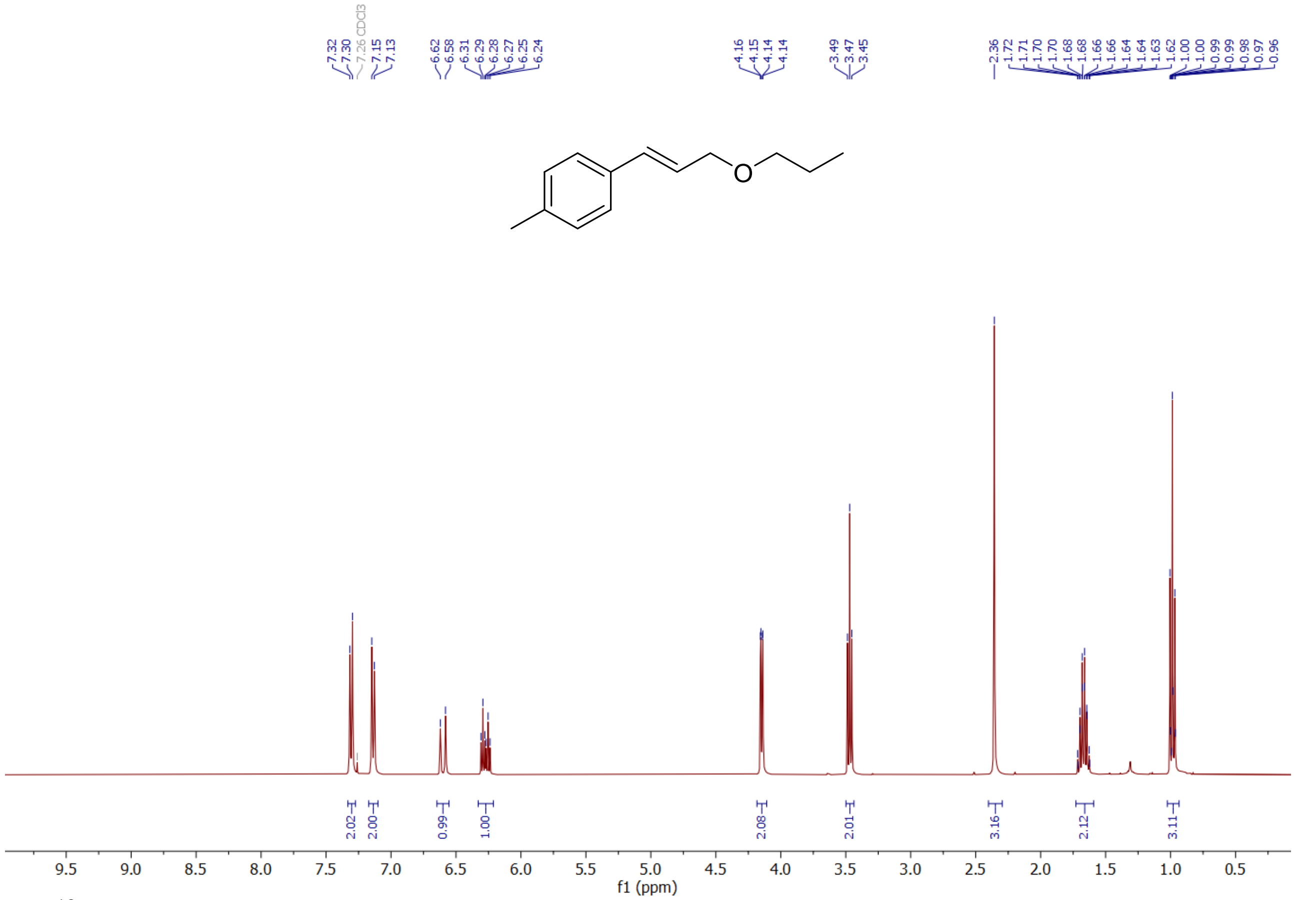
3f, ^{13}C NMR (101 MHz, $CDCl_3$)



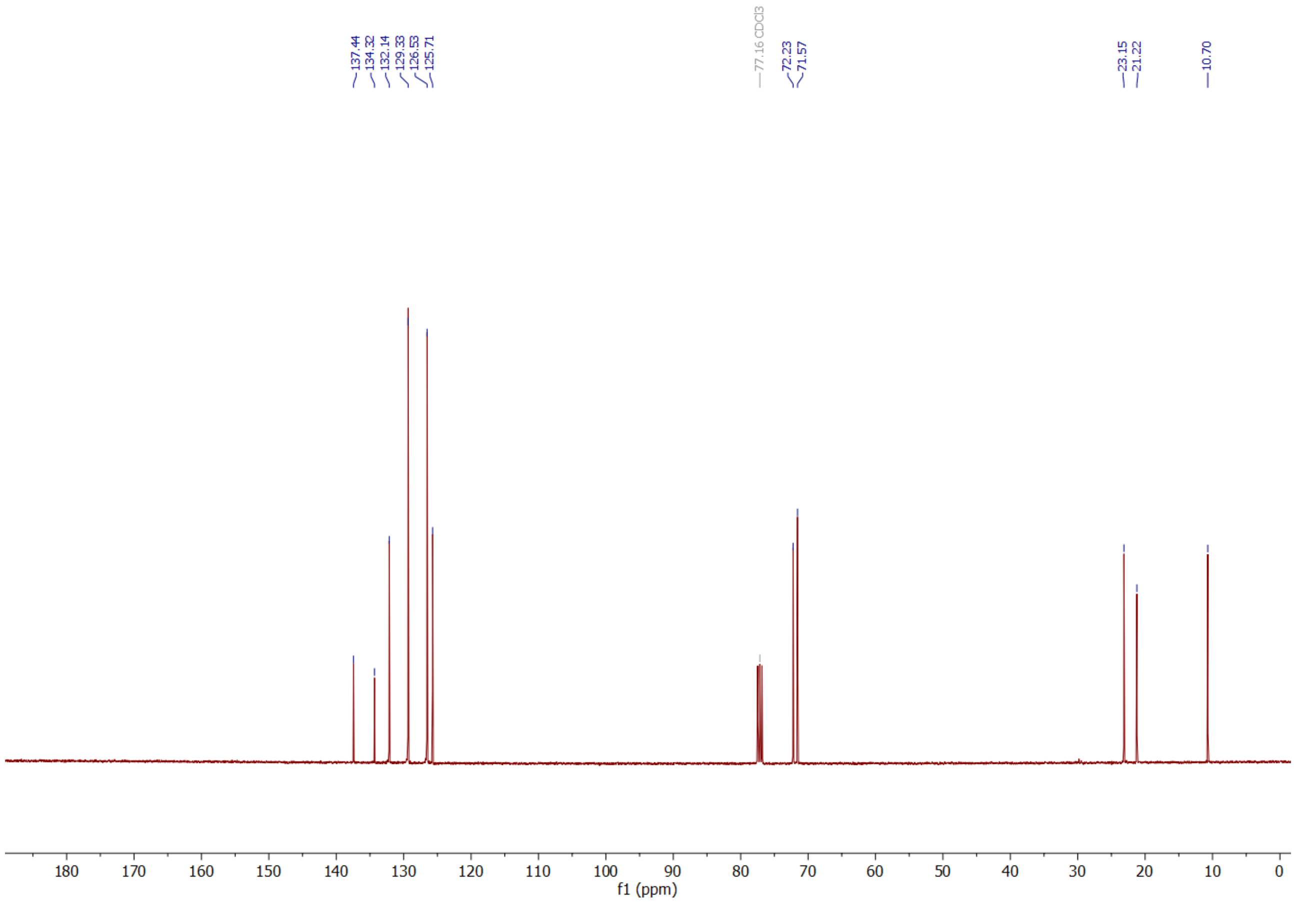
3g, ^{1}H NMR (400 MHz, $CDCl_3$)



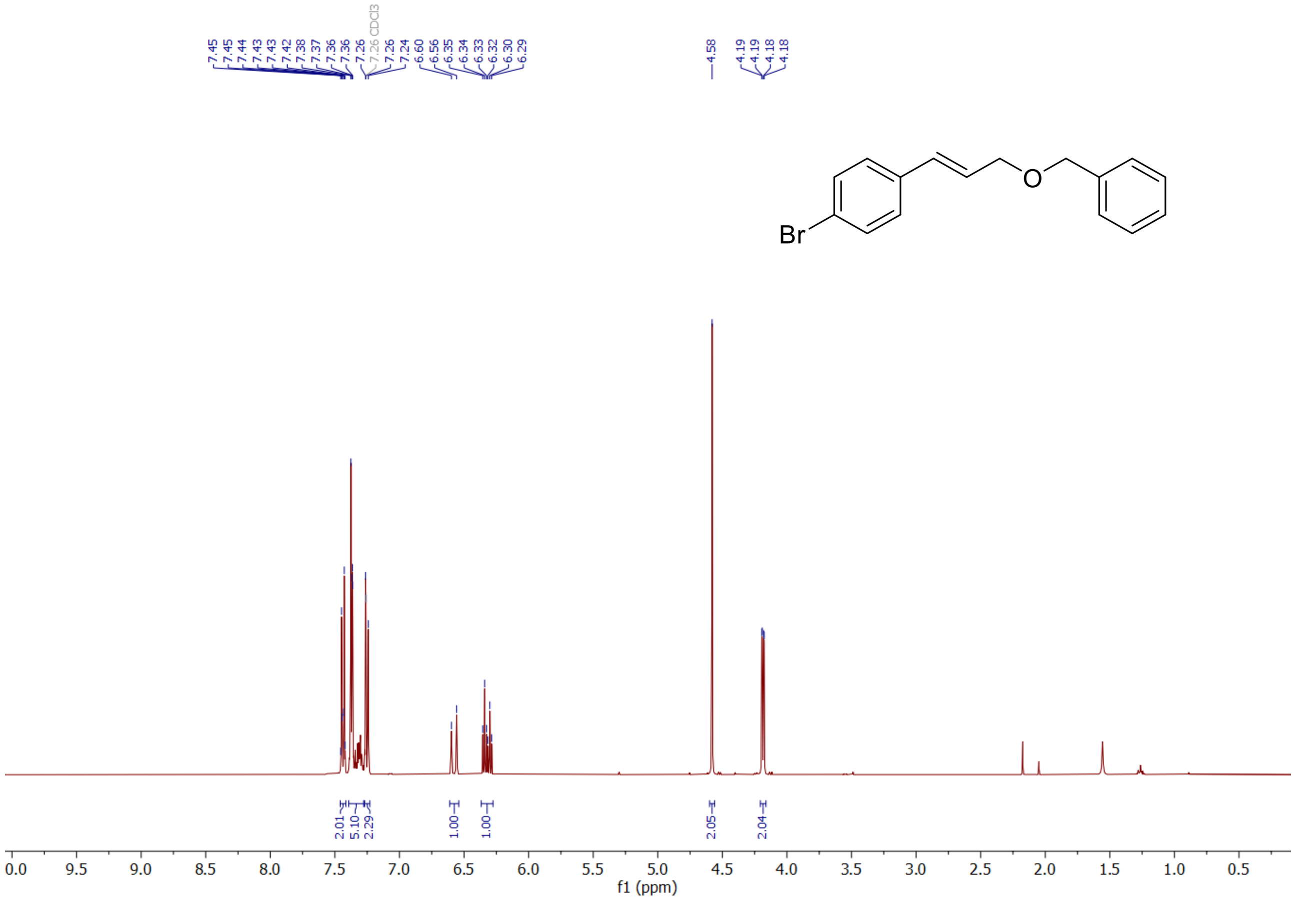
3h, ^{1}H NMR (400 MHz, $CDCl_3$)



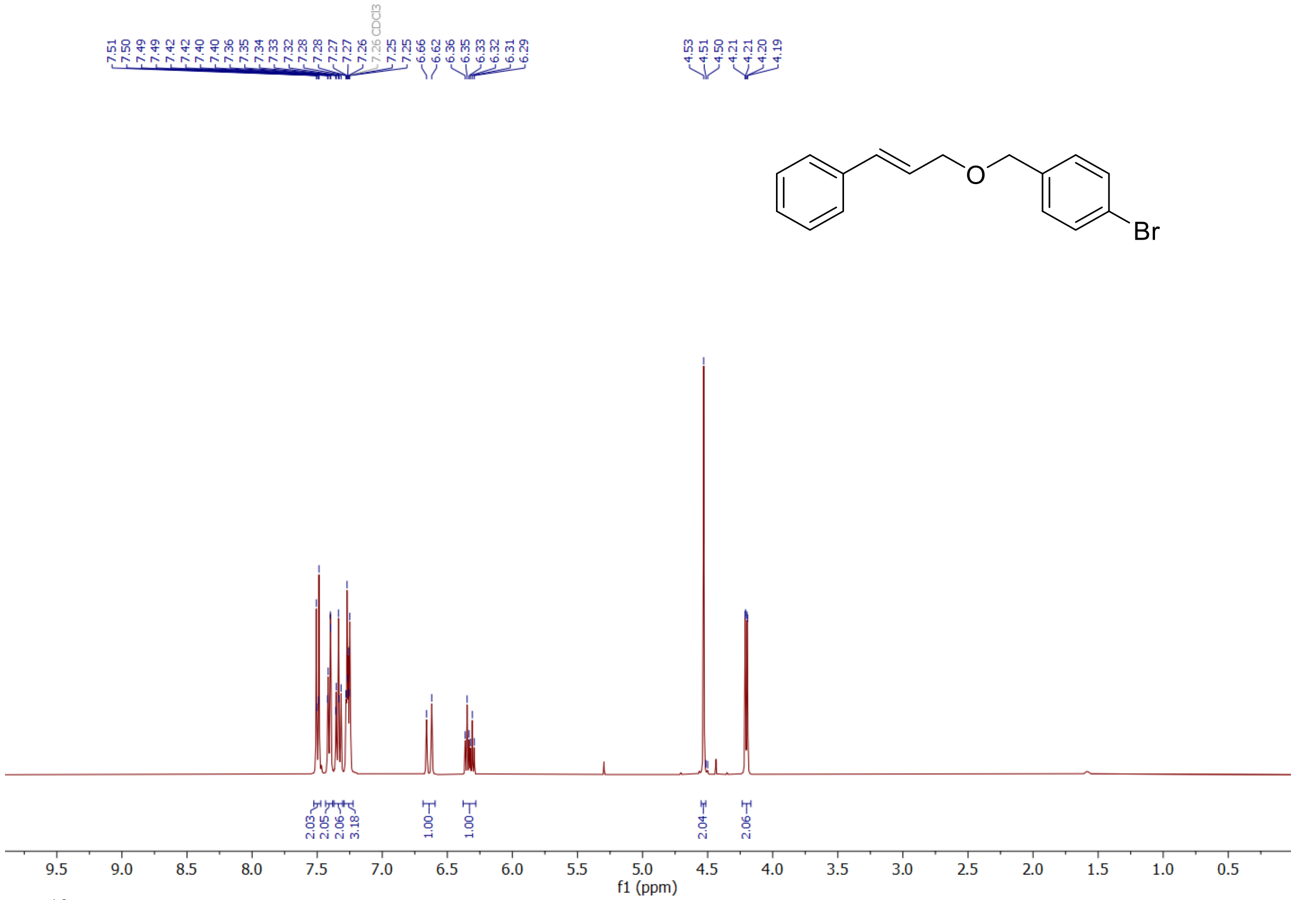
3h, ^{13}C NMR (101 MHz, $CDCl_3$)



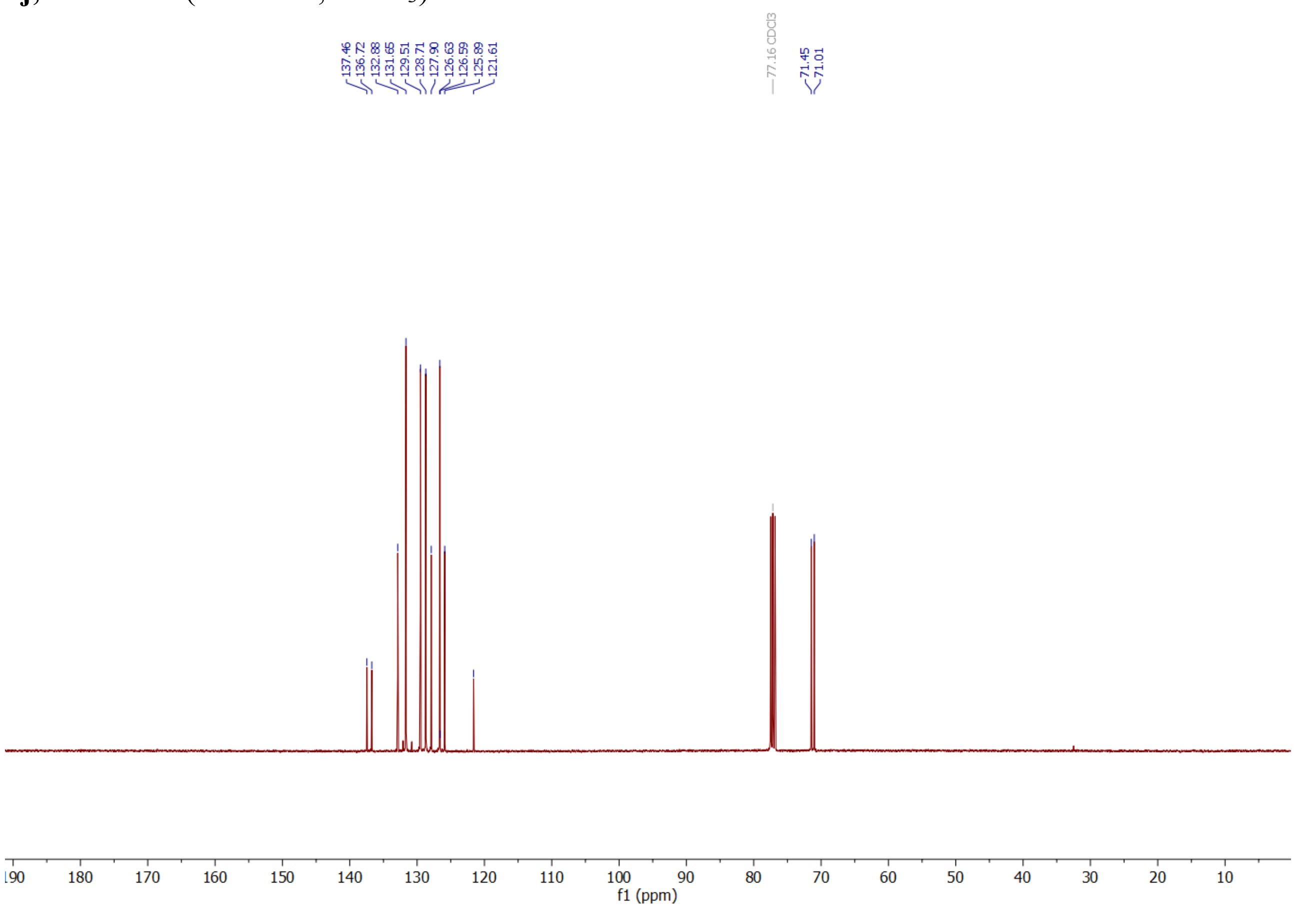
3i, ^{1}H NMR (400 MHz, $CDCl_3$)



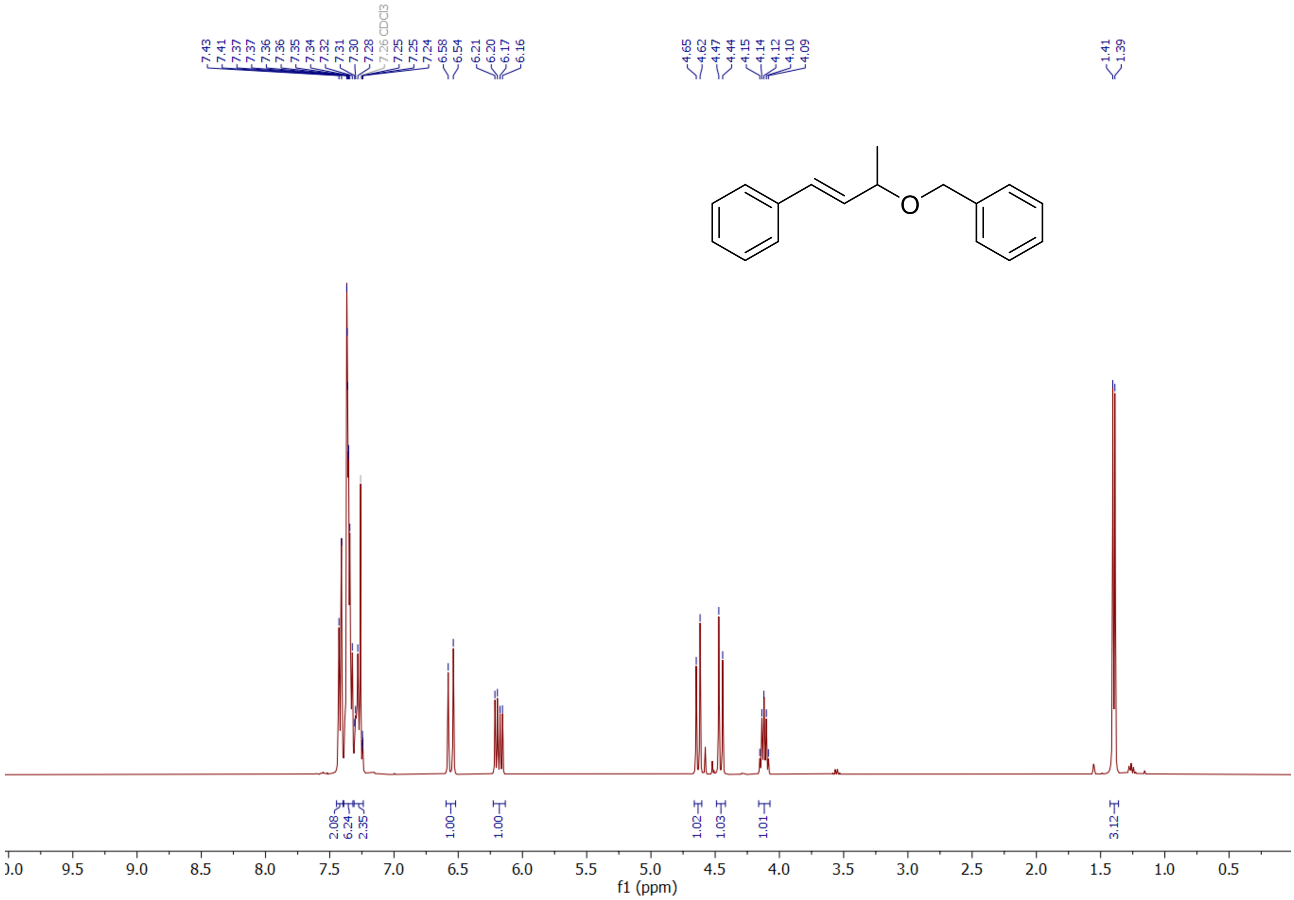
3j, ^{1}H NMR (400 MHz, $CDCl_3$)



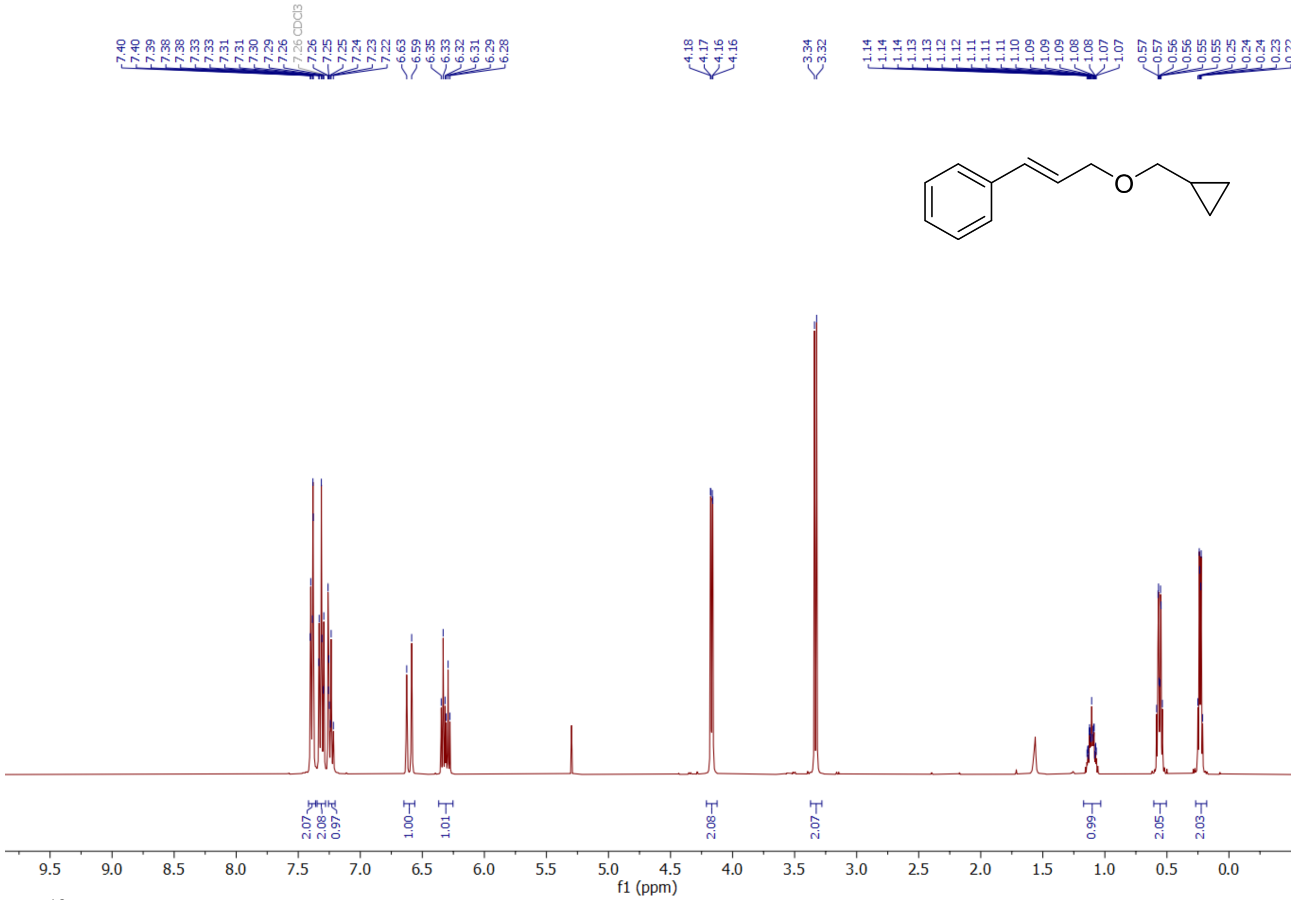
3j, ^{13}C NMR (101 MHz, $CDCl_3$)



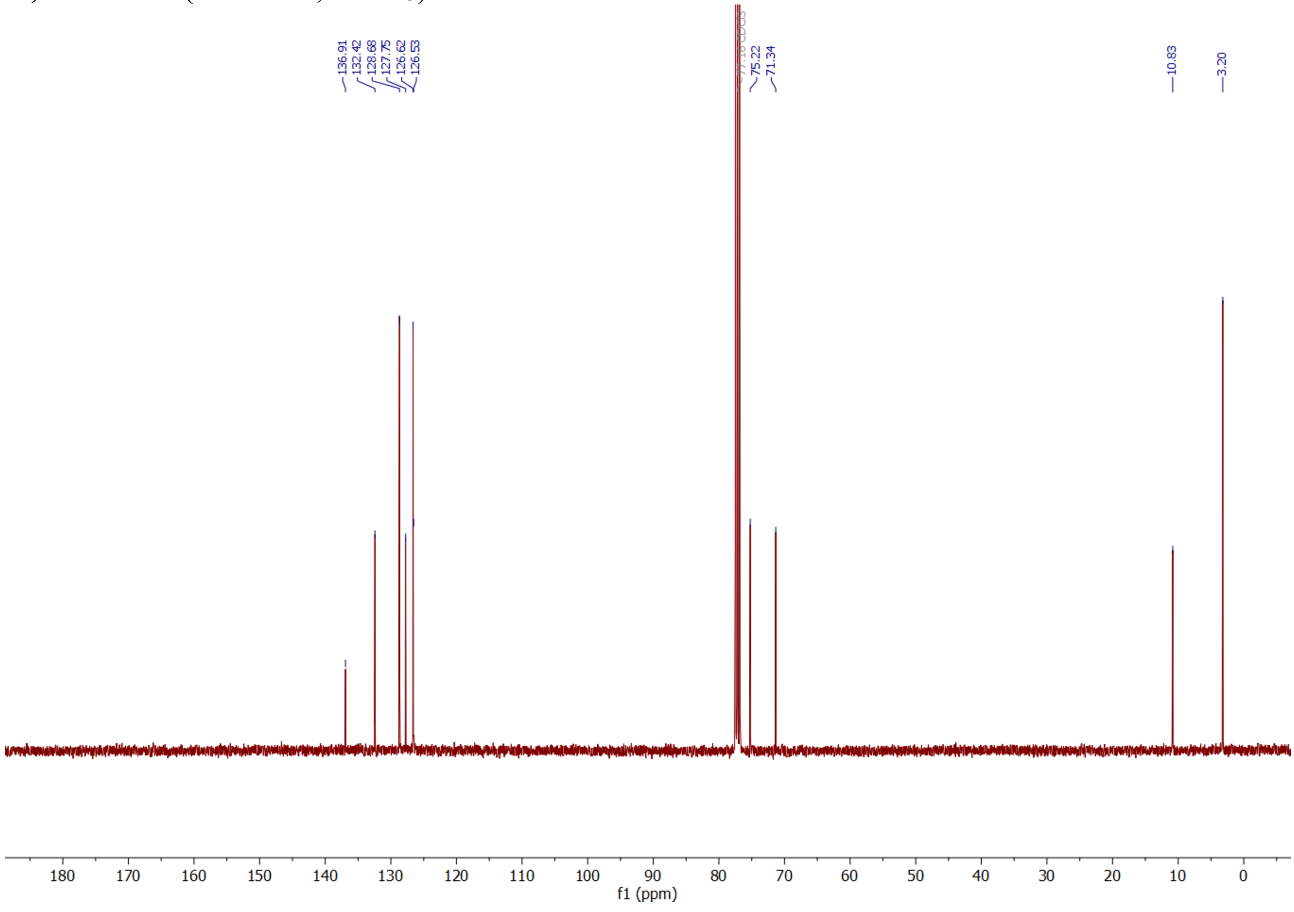
3k, ^{1}H NMR (400 MHz, $CDCl_3$)



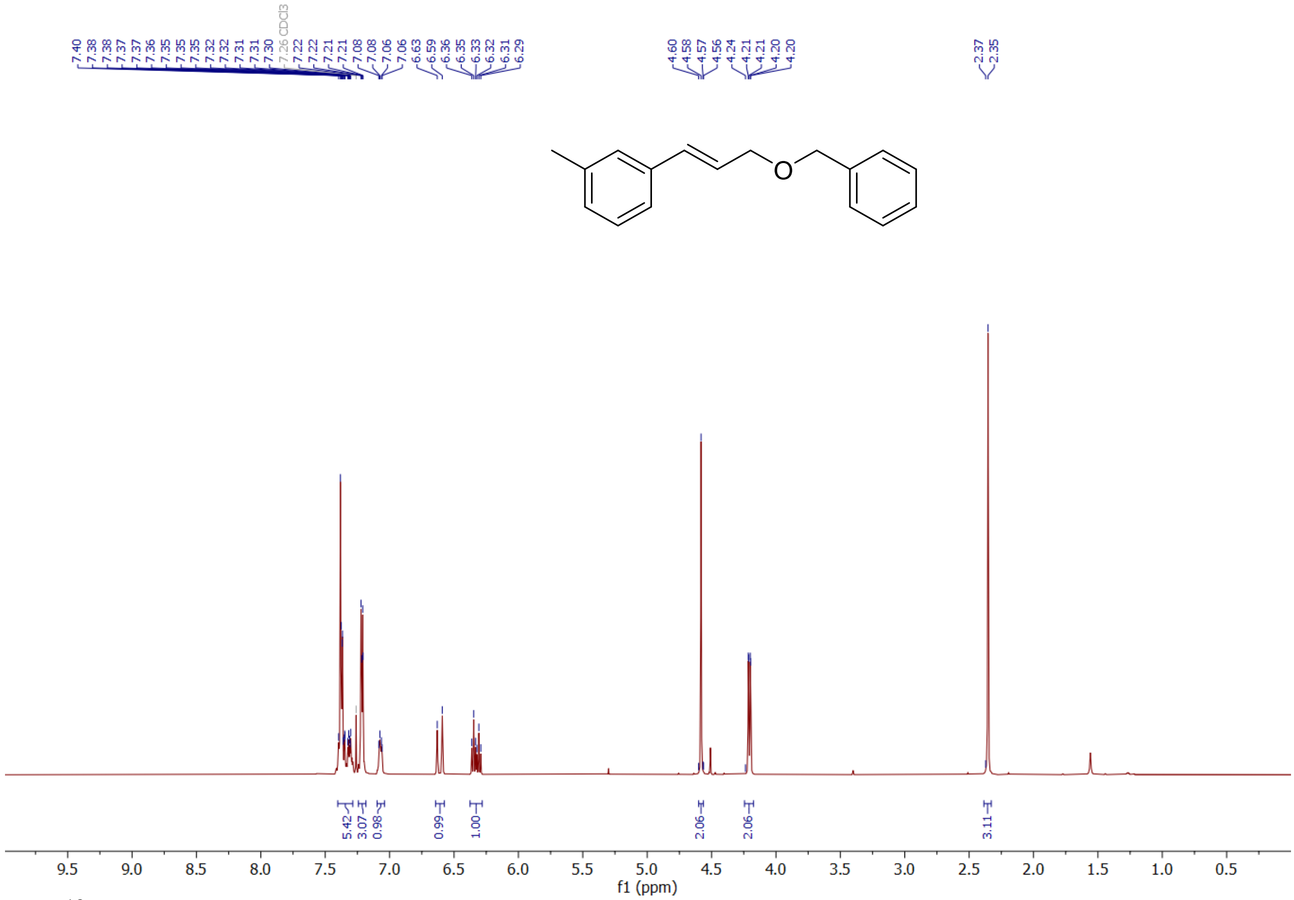
3l, ^{1}H NMR (400 MHz, $CDCl_3$)



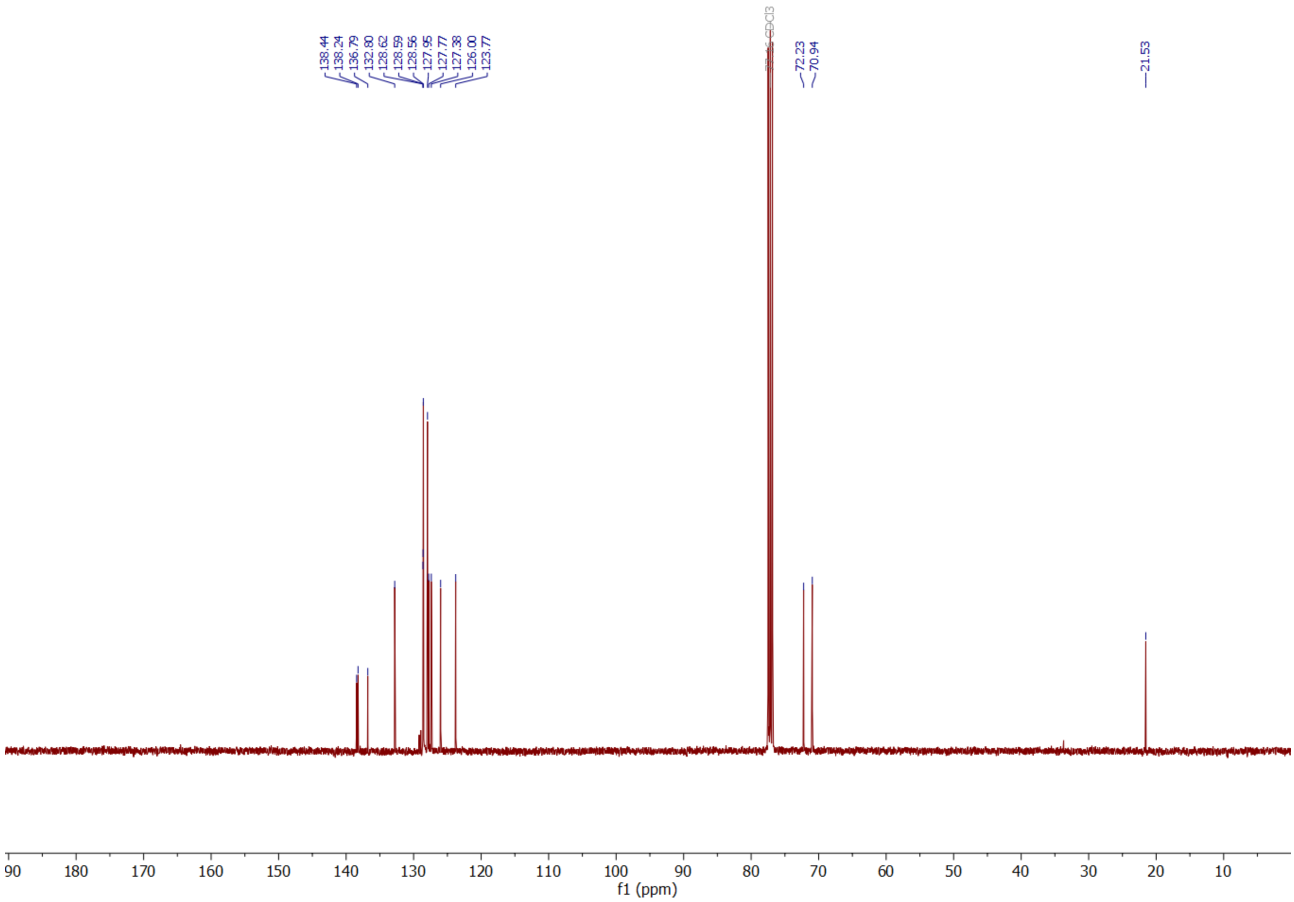
3l, ^{13}C NMR (101 MHz, $CDCl_3$)



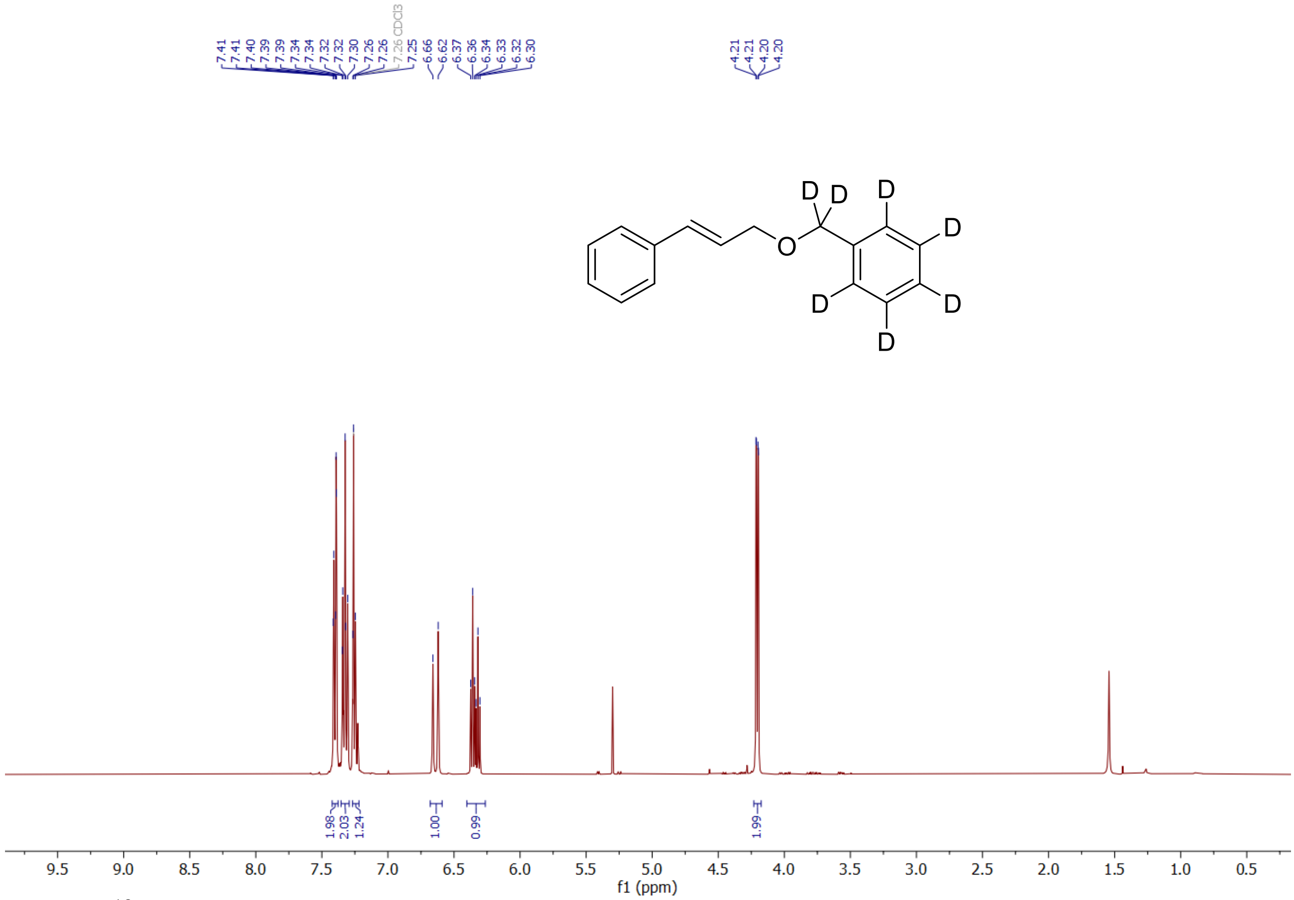
3m, ¹H NMR (400 MHz, $CDCl_3$)



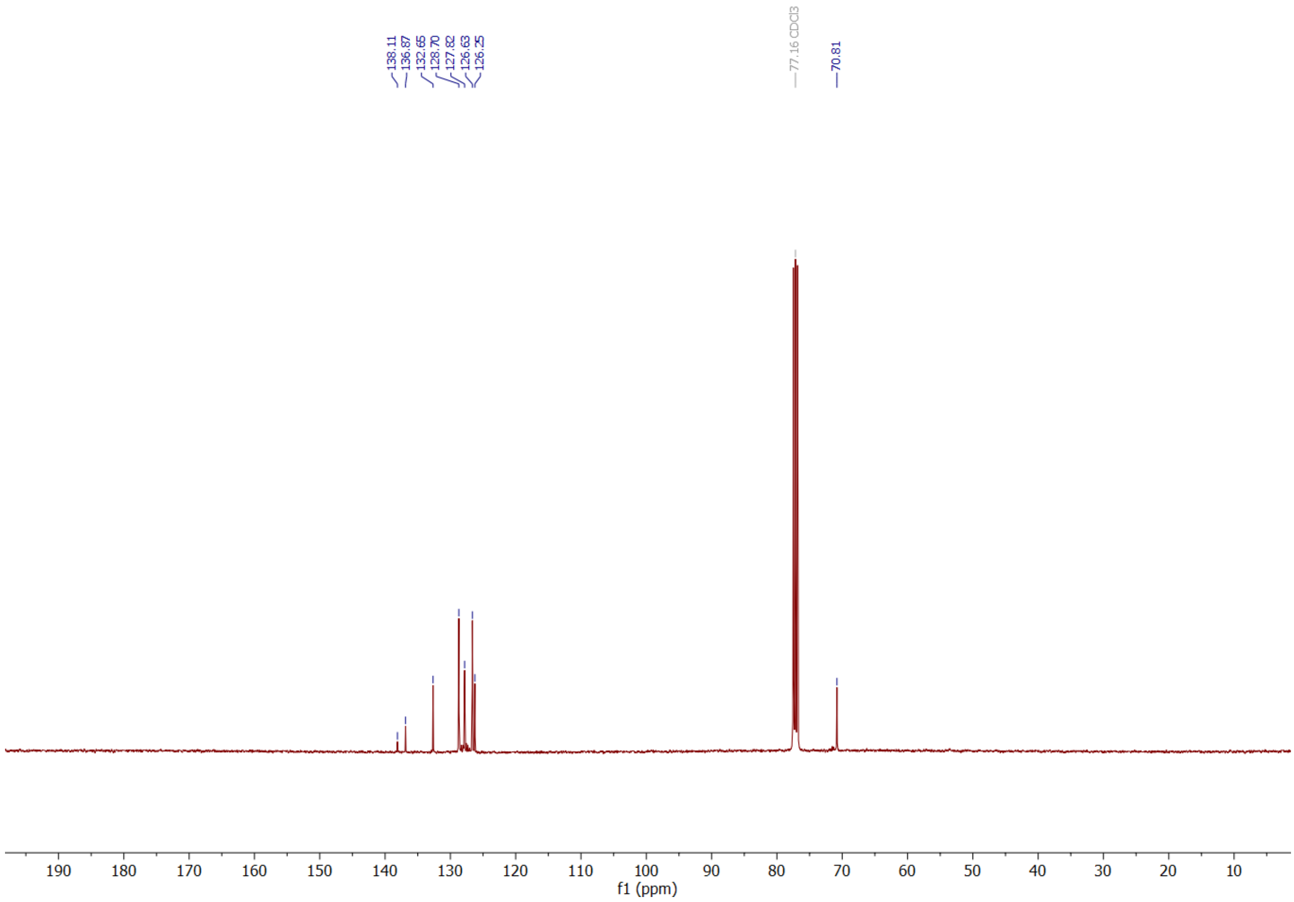
3m, ¹³C NMR (101 MHz, $CDCl_3$)



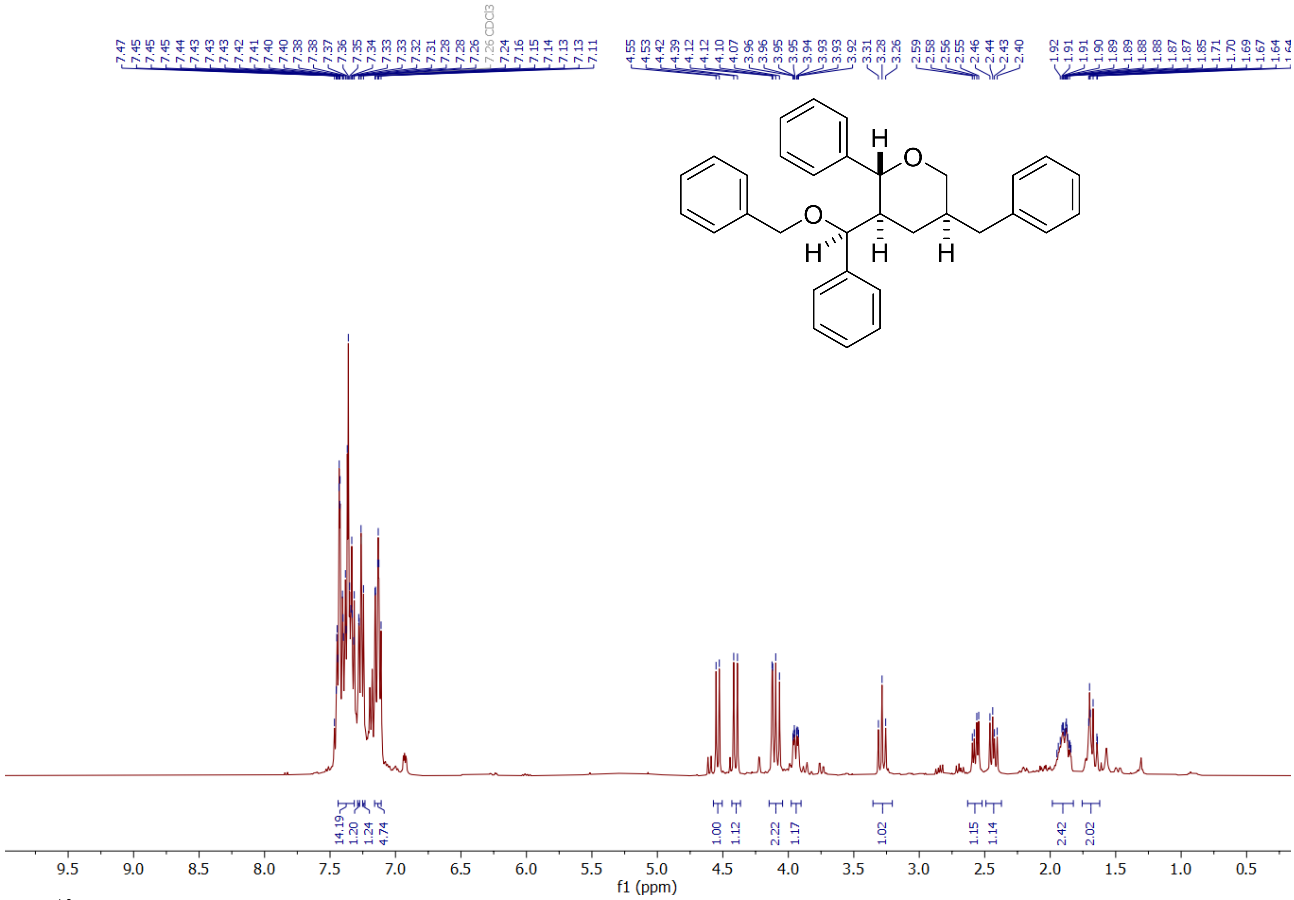
***7d*-3a, [1]H NMR** (400 MHz, CDCl$_3$)



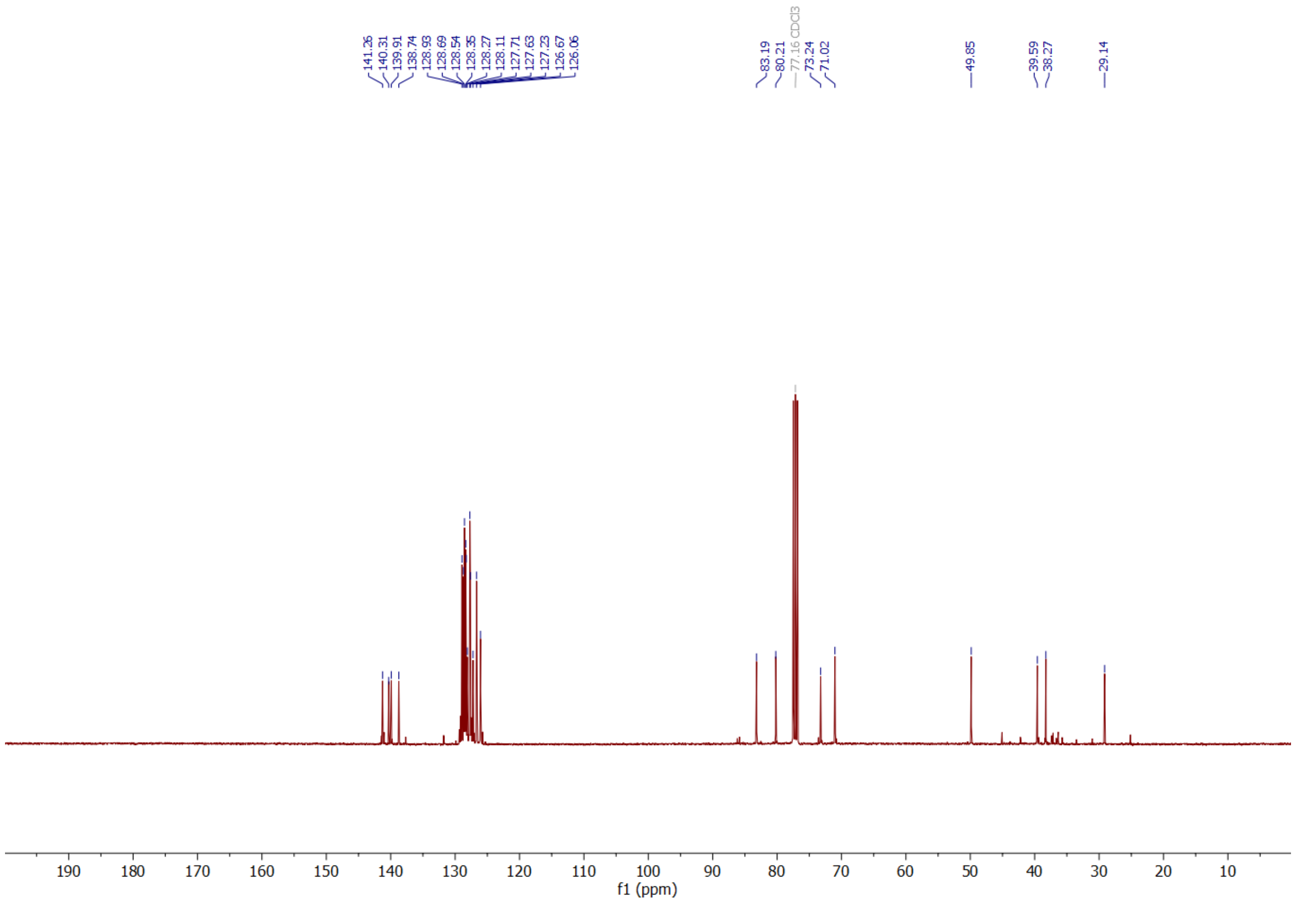
***7d*-3a , [13]C NMR** (101 MHz, CDCl$_3$)



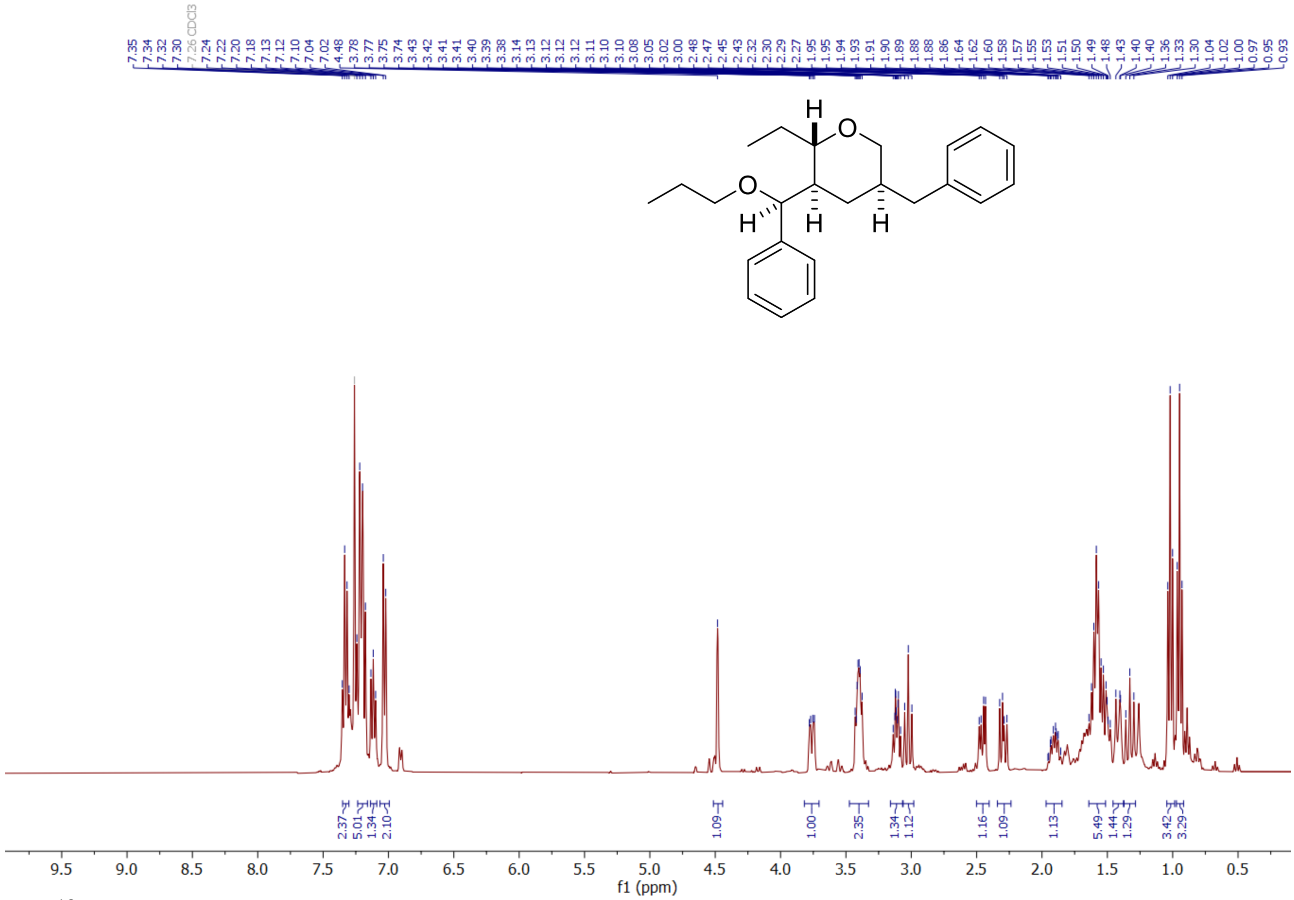
4a, ^{1}H NMR (400 MHz, $CDCl_3$)



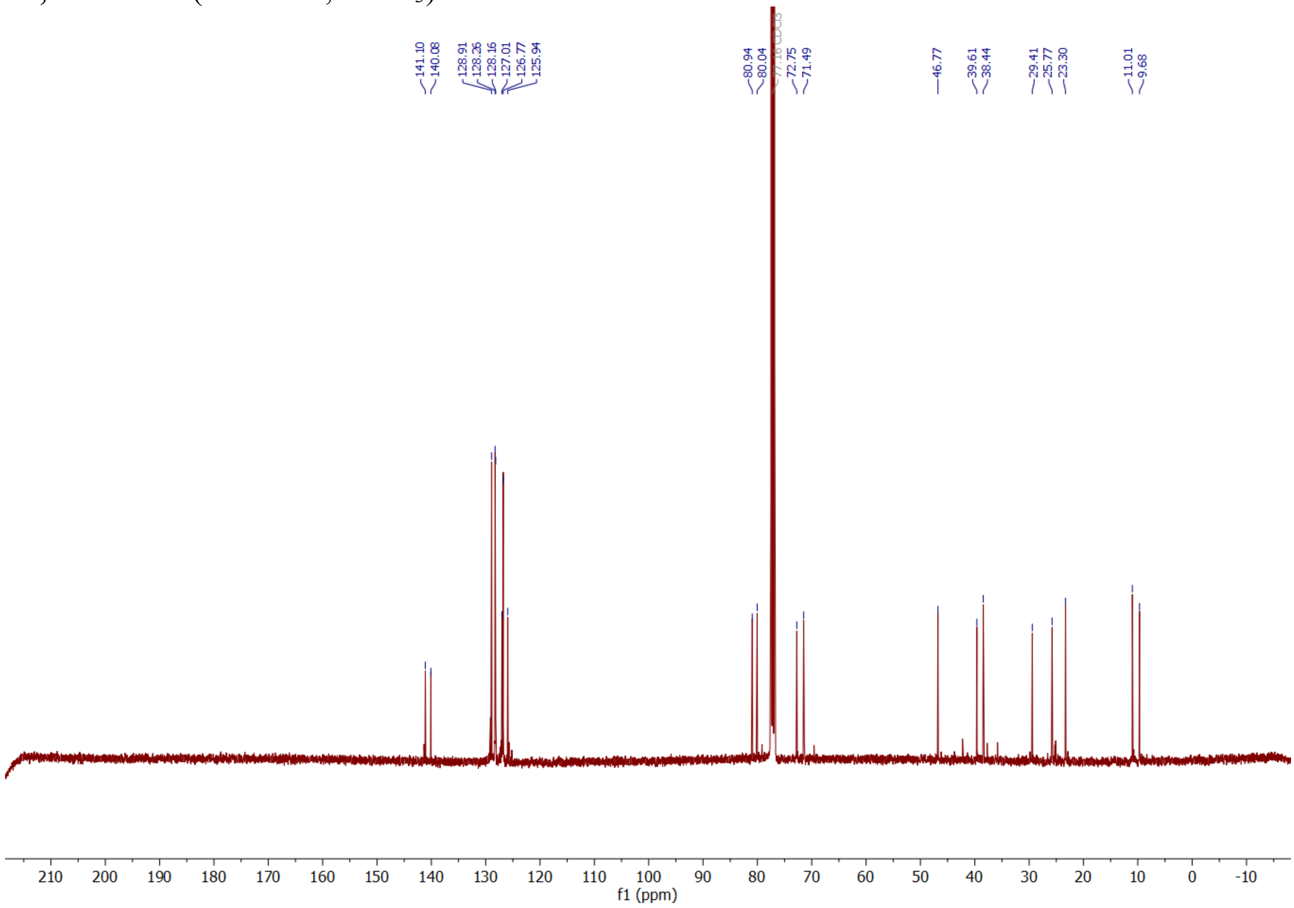
4a, ^{13}C NMR (101 MHz, $CDCl_3$)



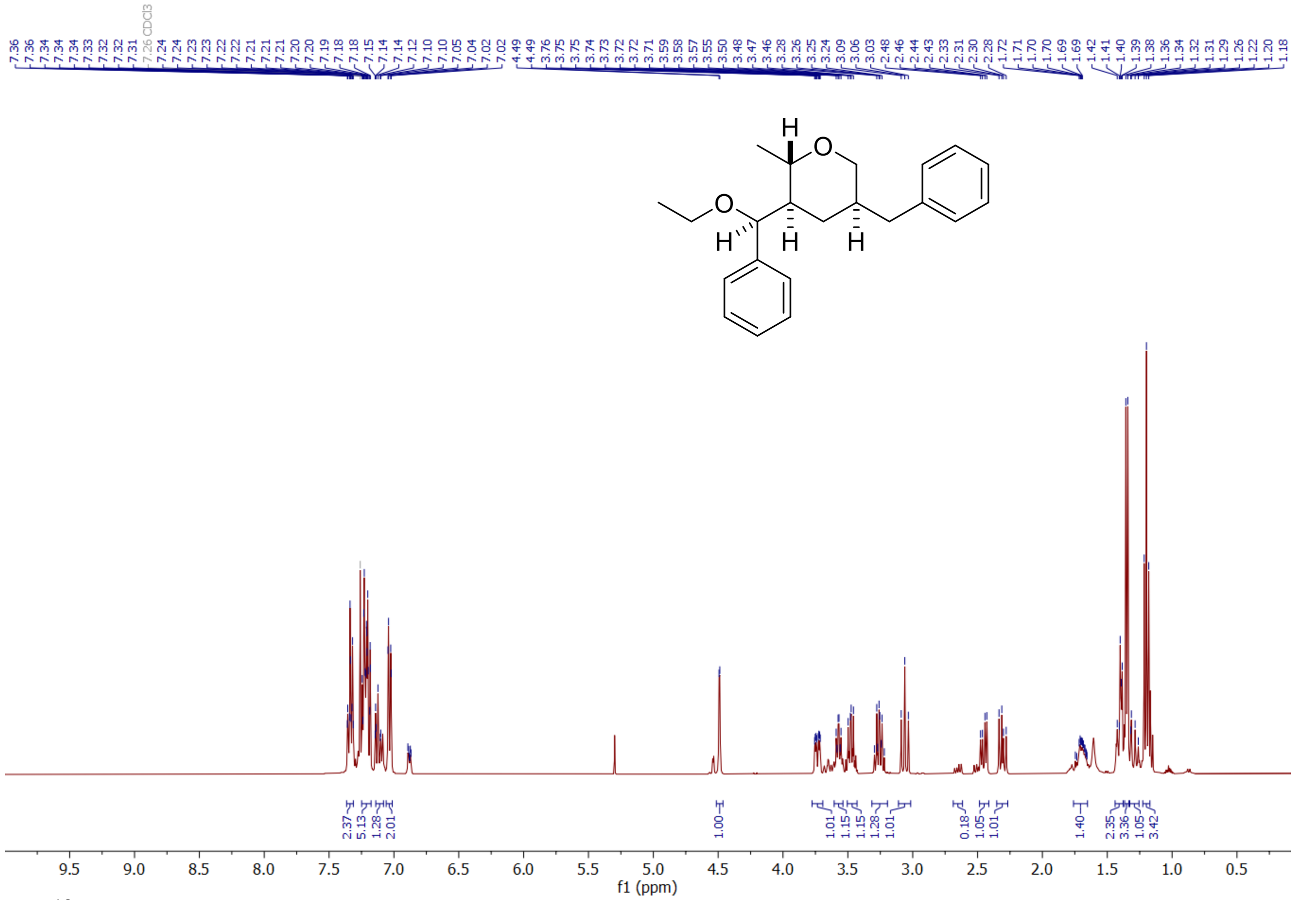
4b, ^{1}H NMR (400 MHz, $CDCl_3$)



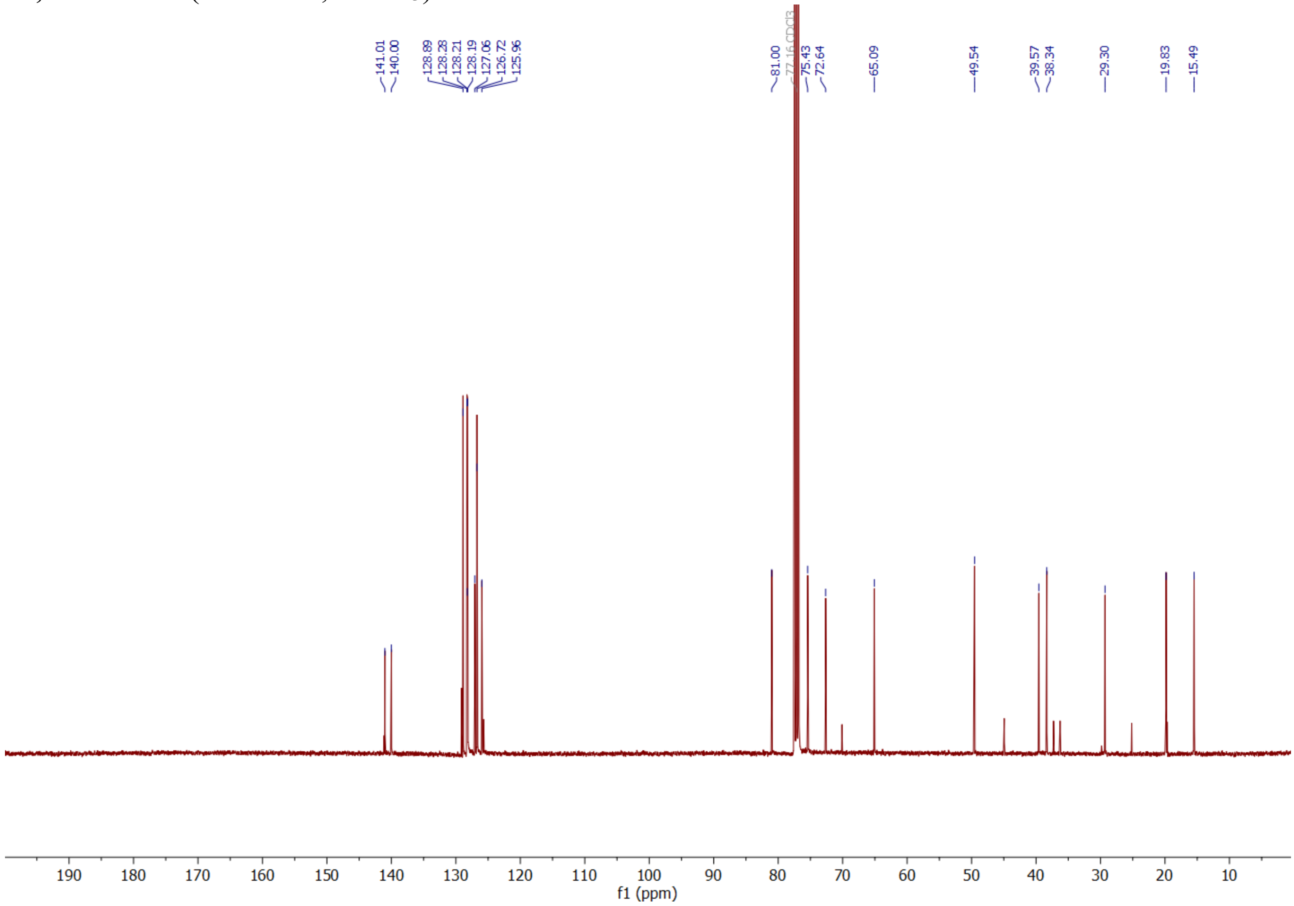
4b, ^{13}C NMR (101 MHz, $CDCl_3$)



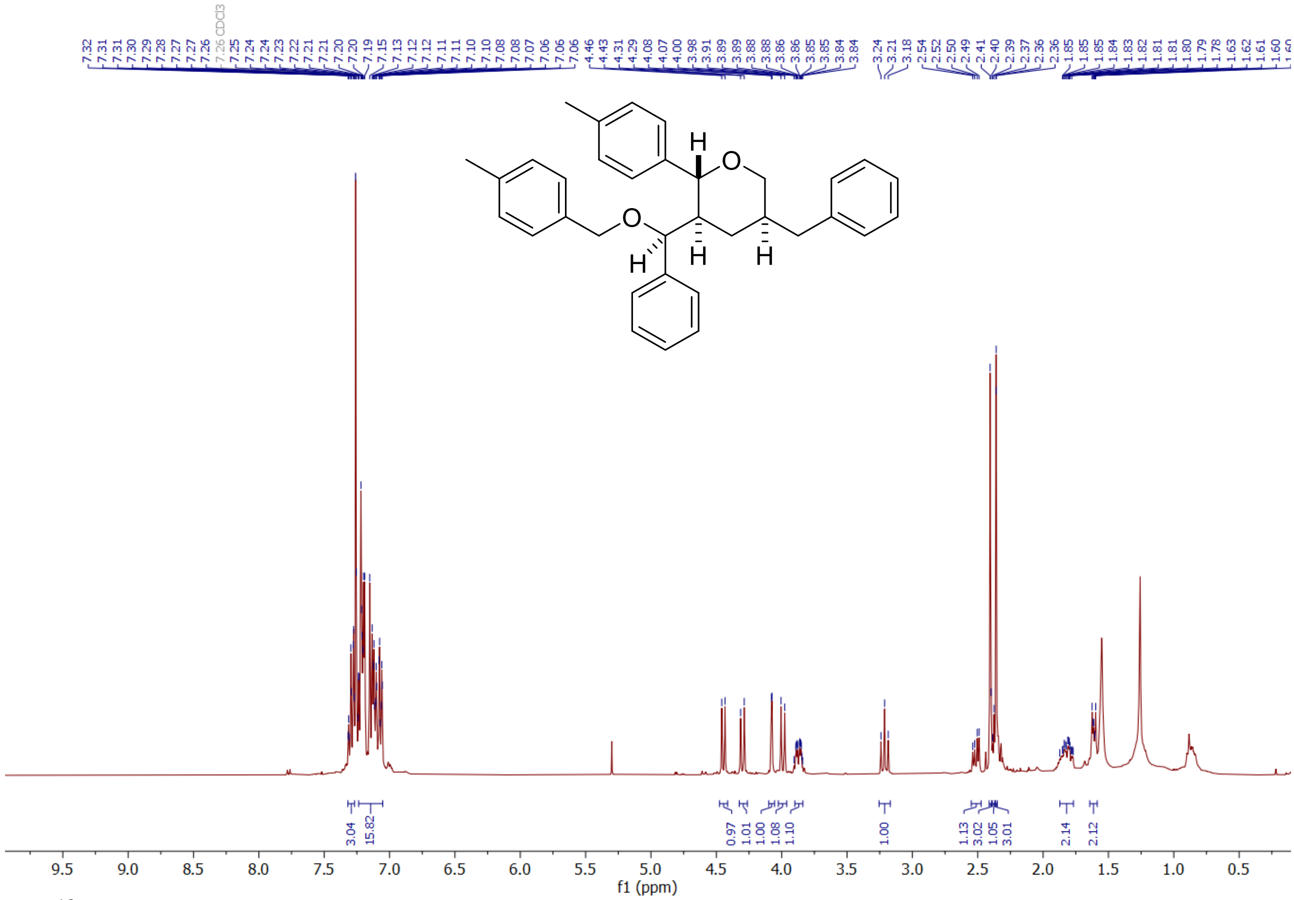
4c, ^{1}H NMR (400 MHz, $CDCl_3$)



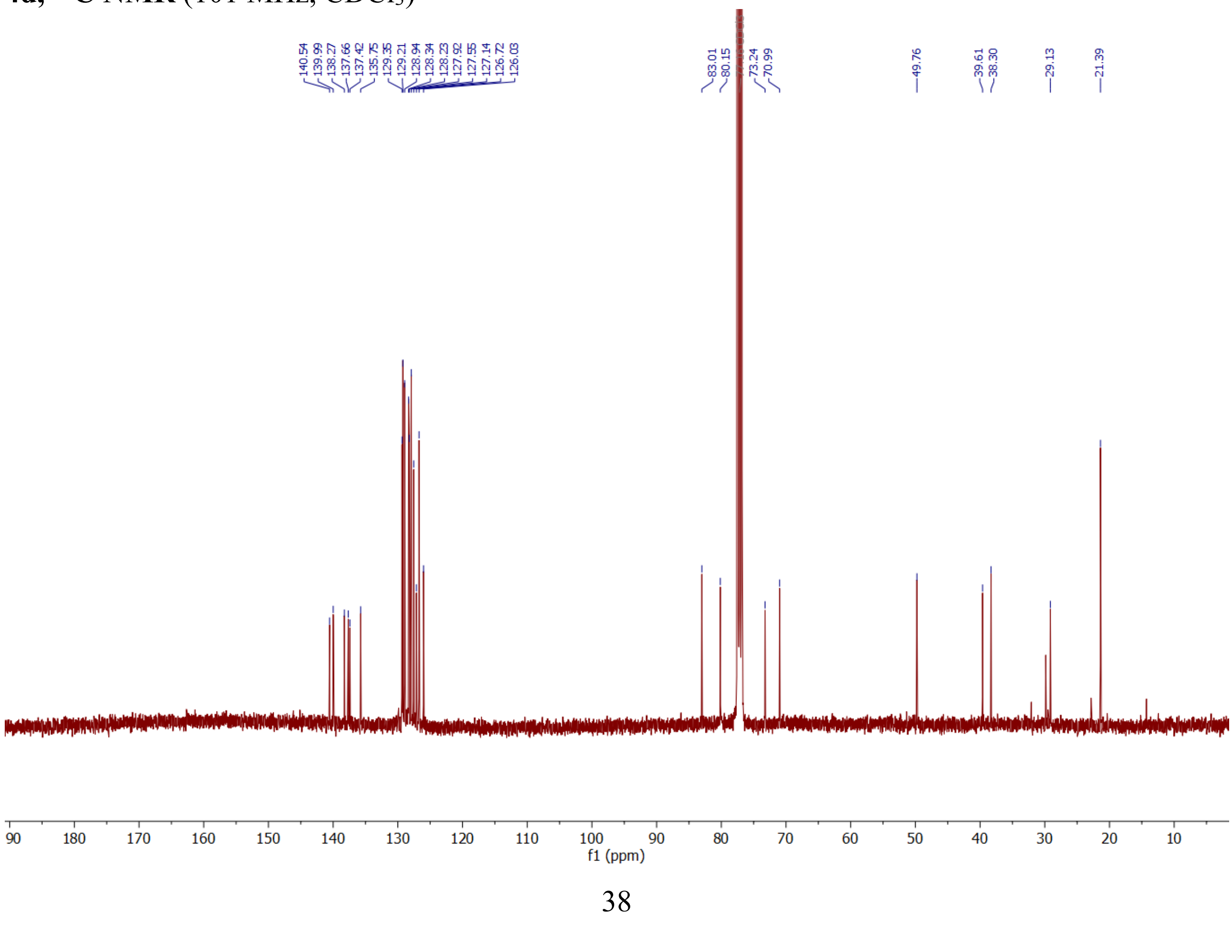
4c, ^{13}C NMR (101 MHz, $CDCl_3$)



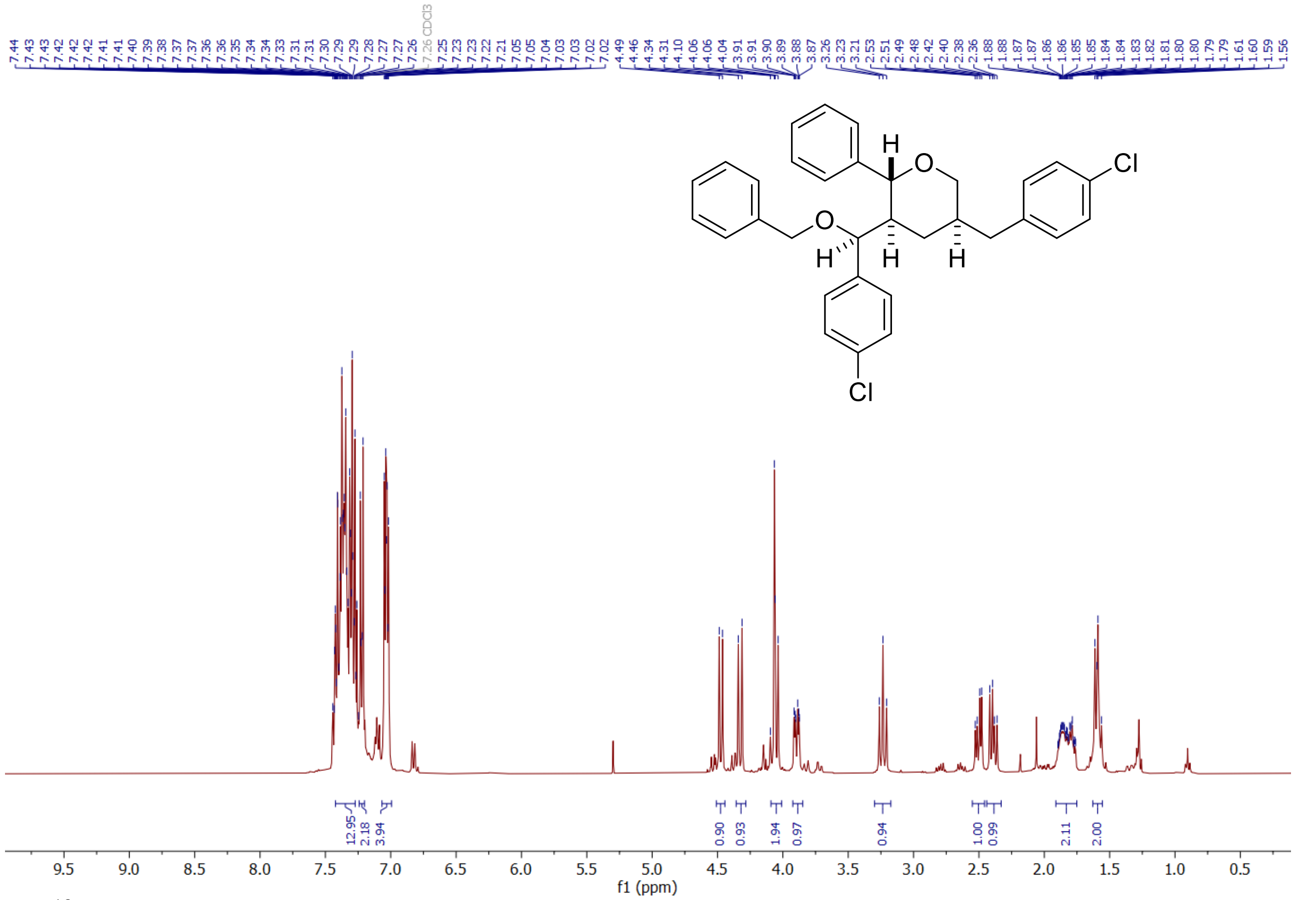
4d, ^{1}H NMR (400 MHz, $CDCl_3$)



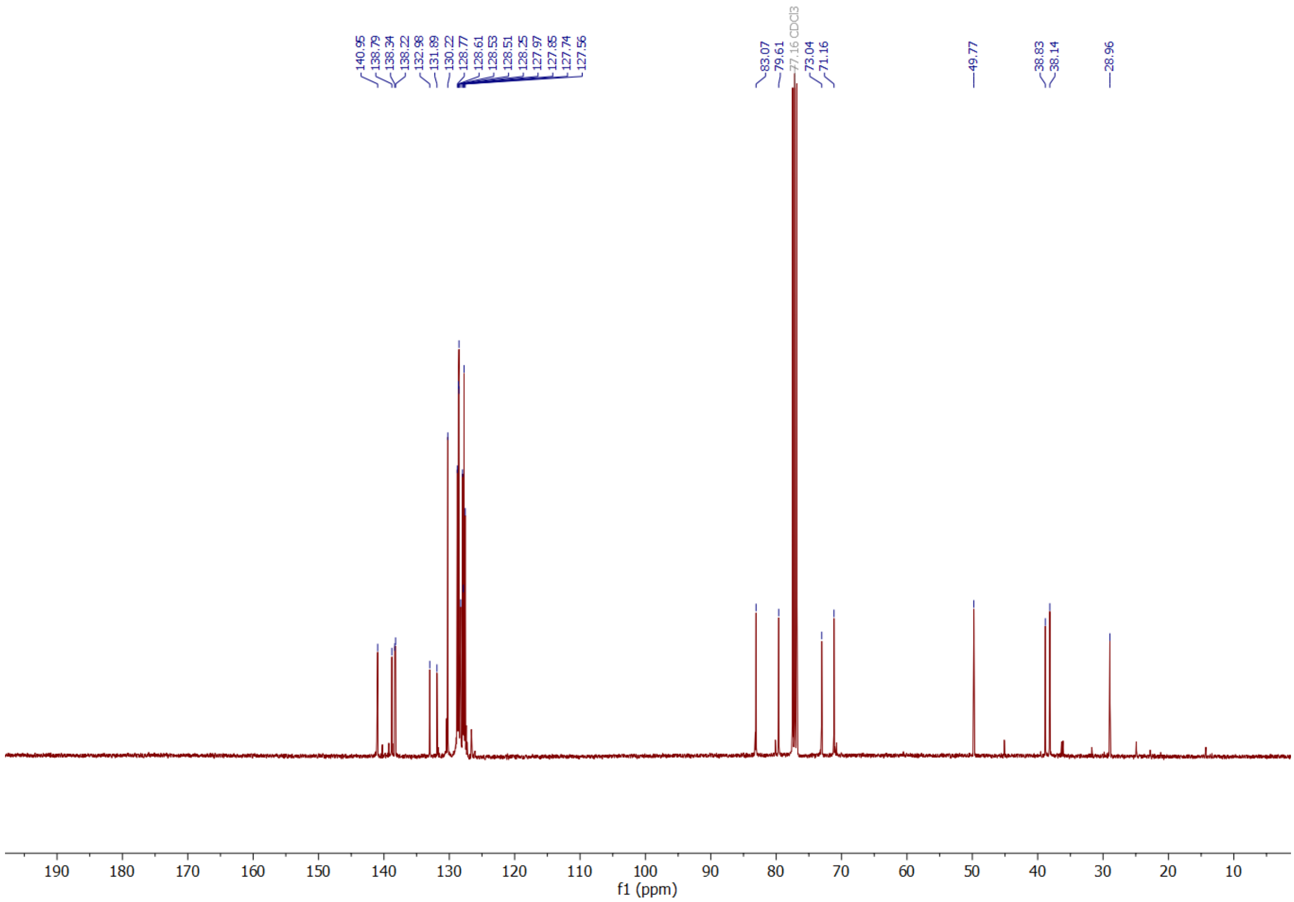
4d, ^{13}C NMR (101 MHz, $CDCl_3$)



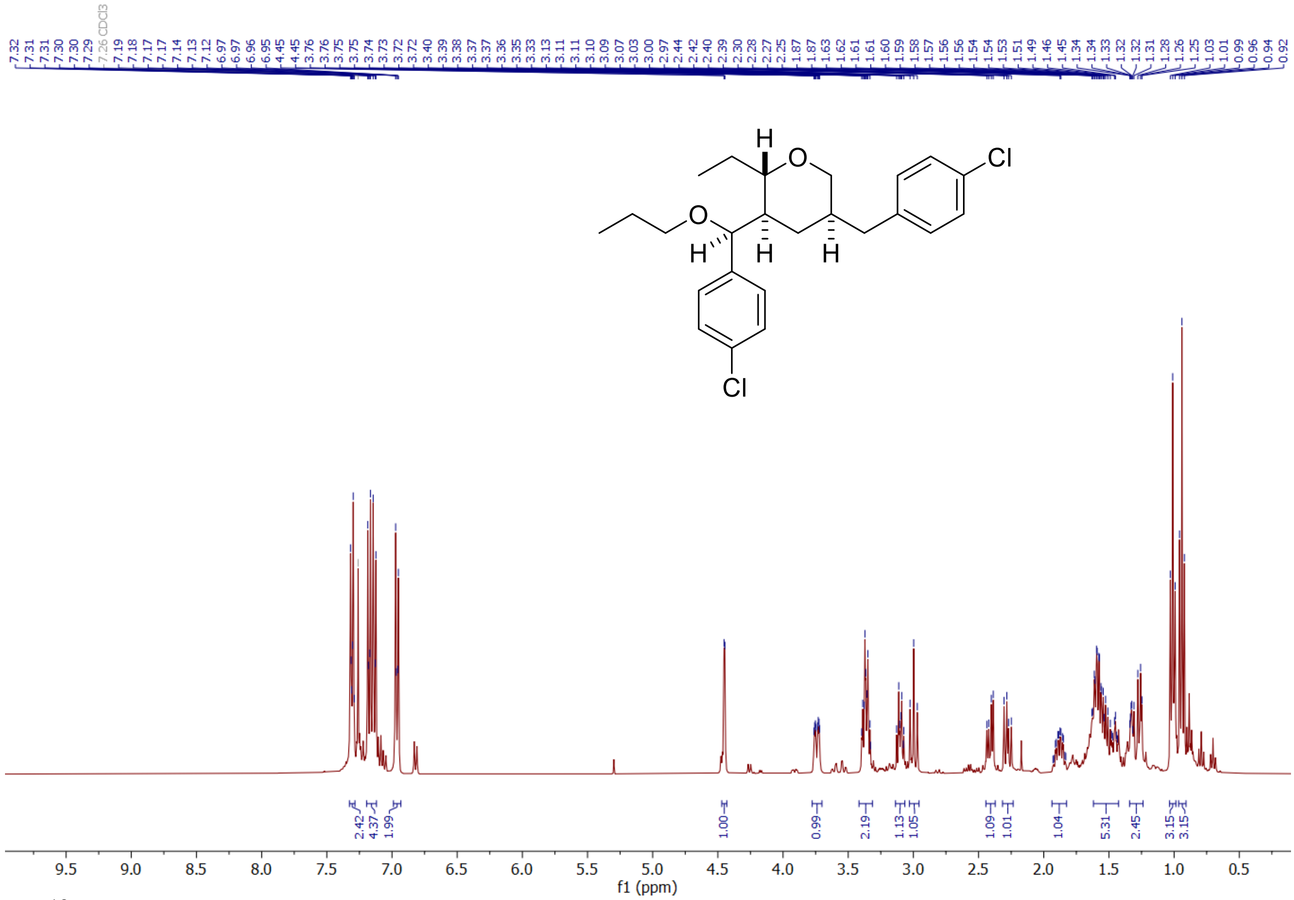
4e, ^{1}H NMR (400 MHz, $CDCl_3$)



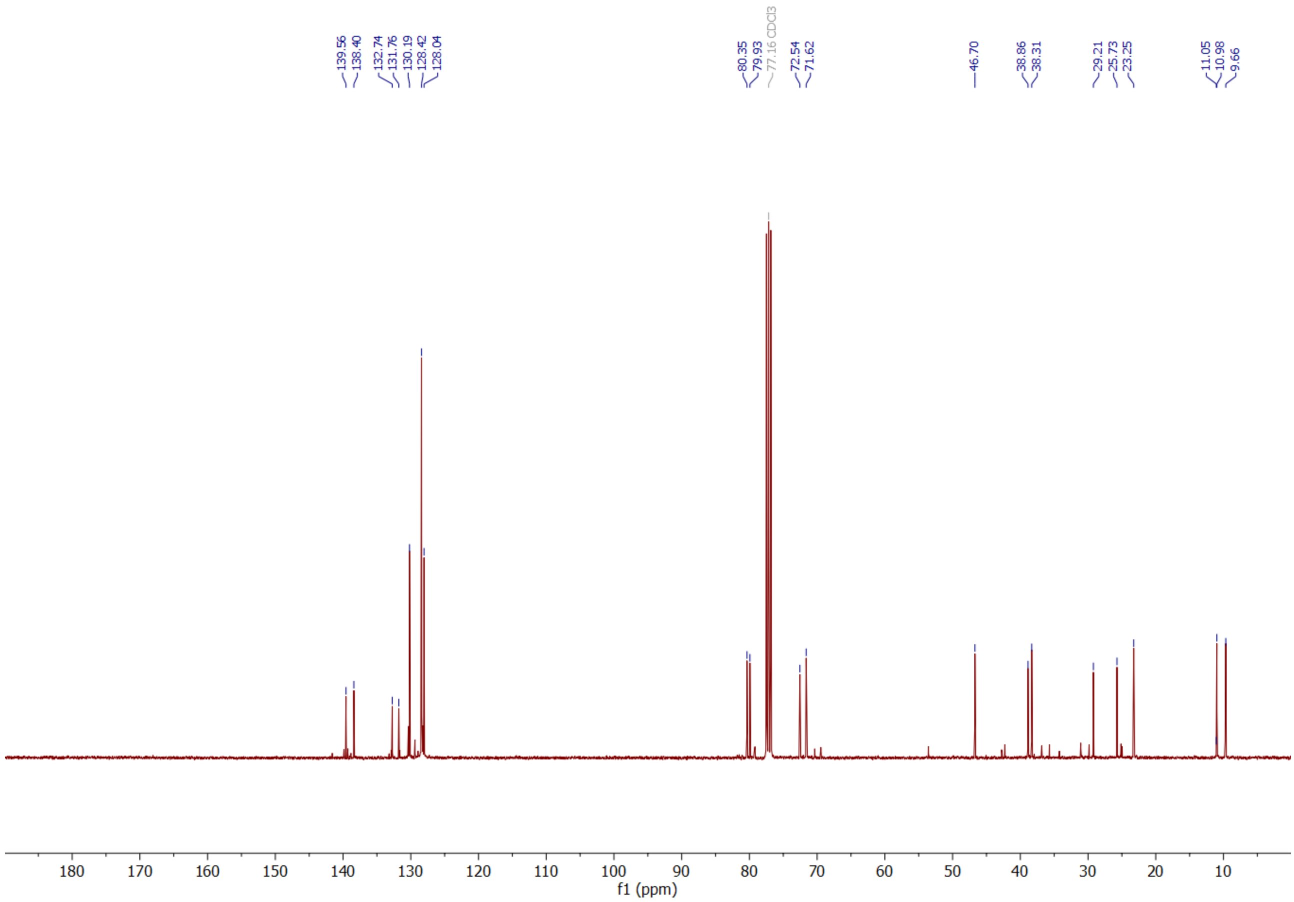
4e, ^{13}C NMR (101 MHz, $CDCl_3$)



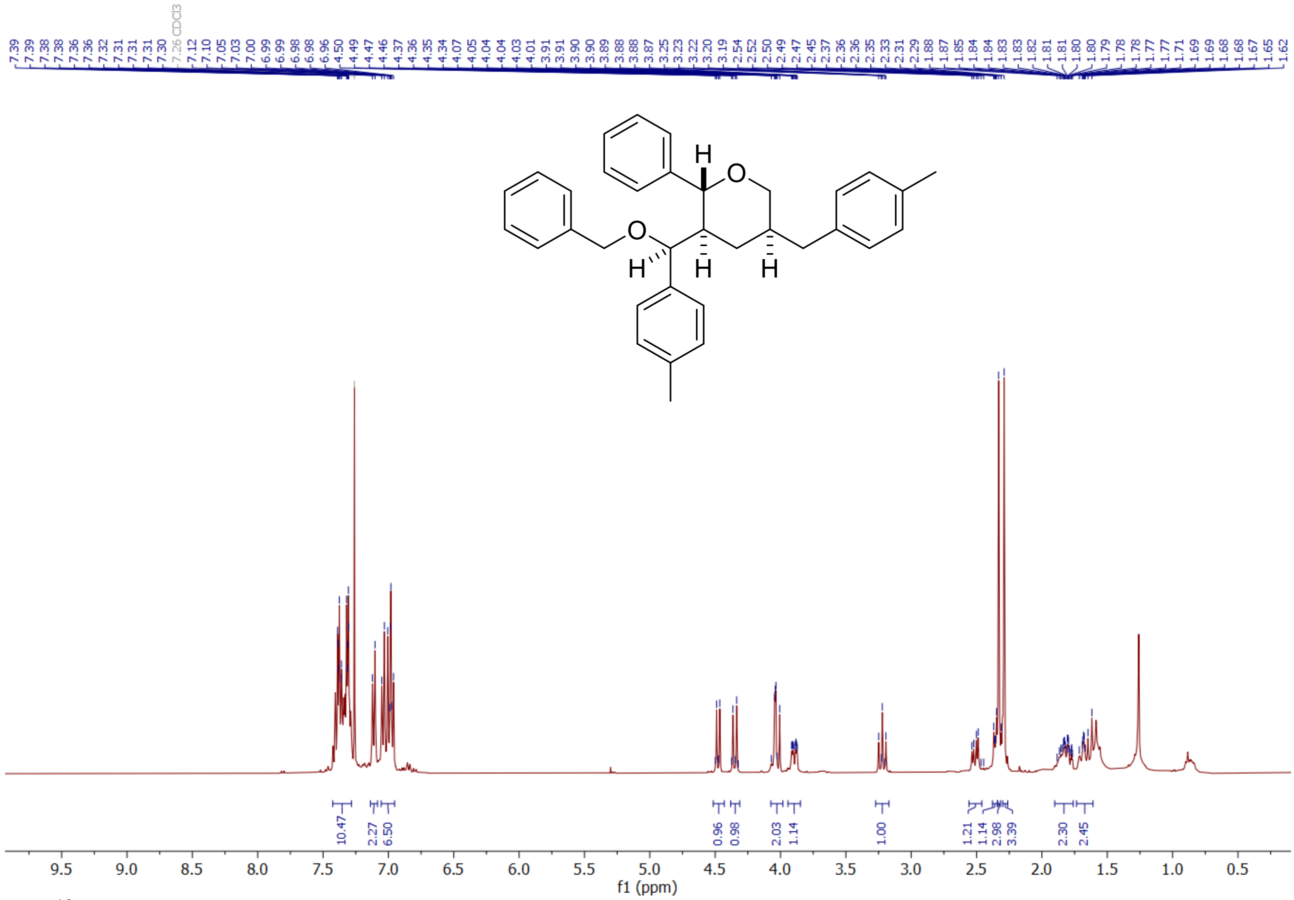
4f, ^{1}H NMR (400 MHz, $CDCl_3$)



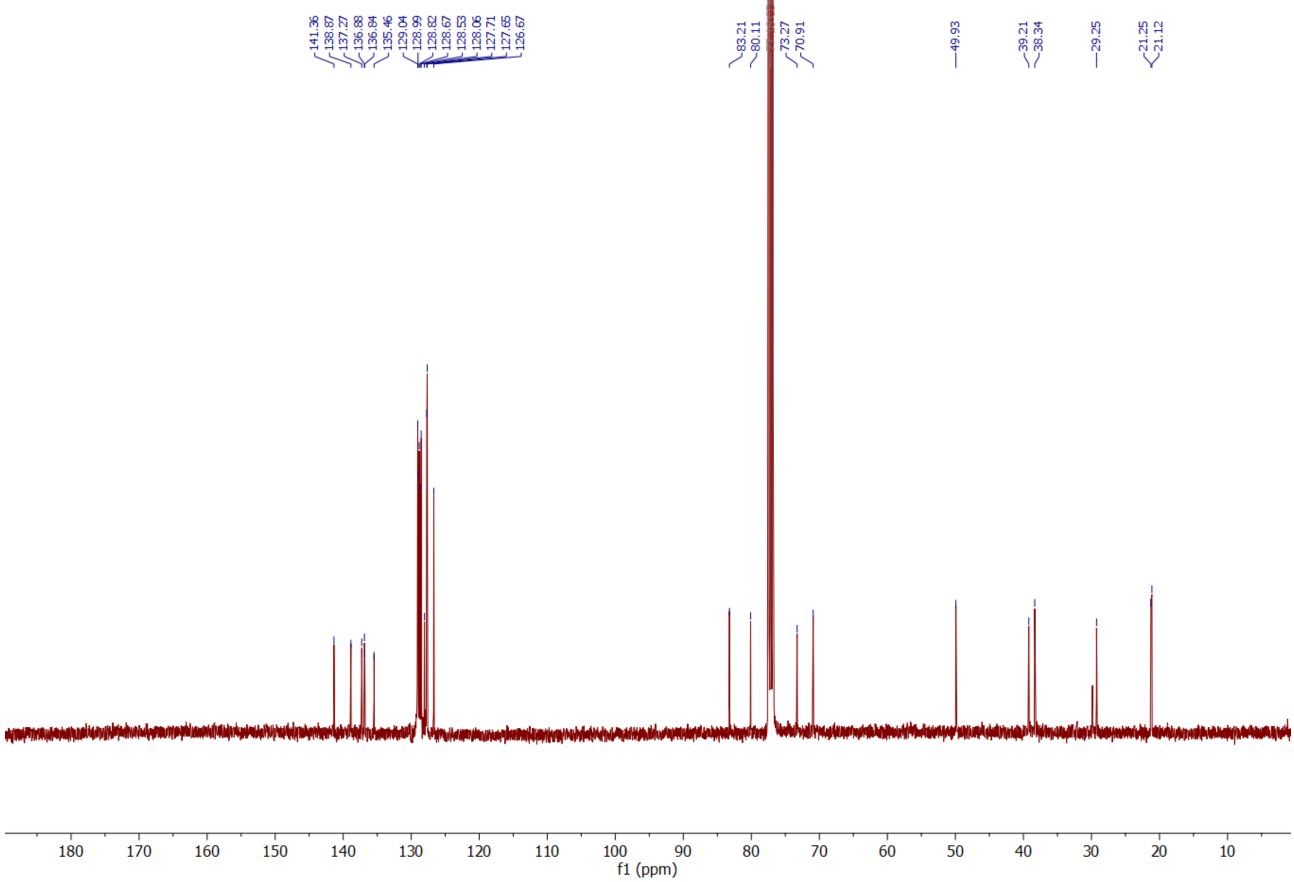
4f, ^{13}C NMR (101 MHz, $CDCl_3$)



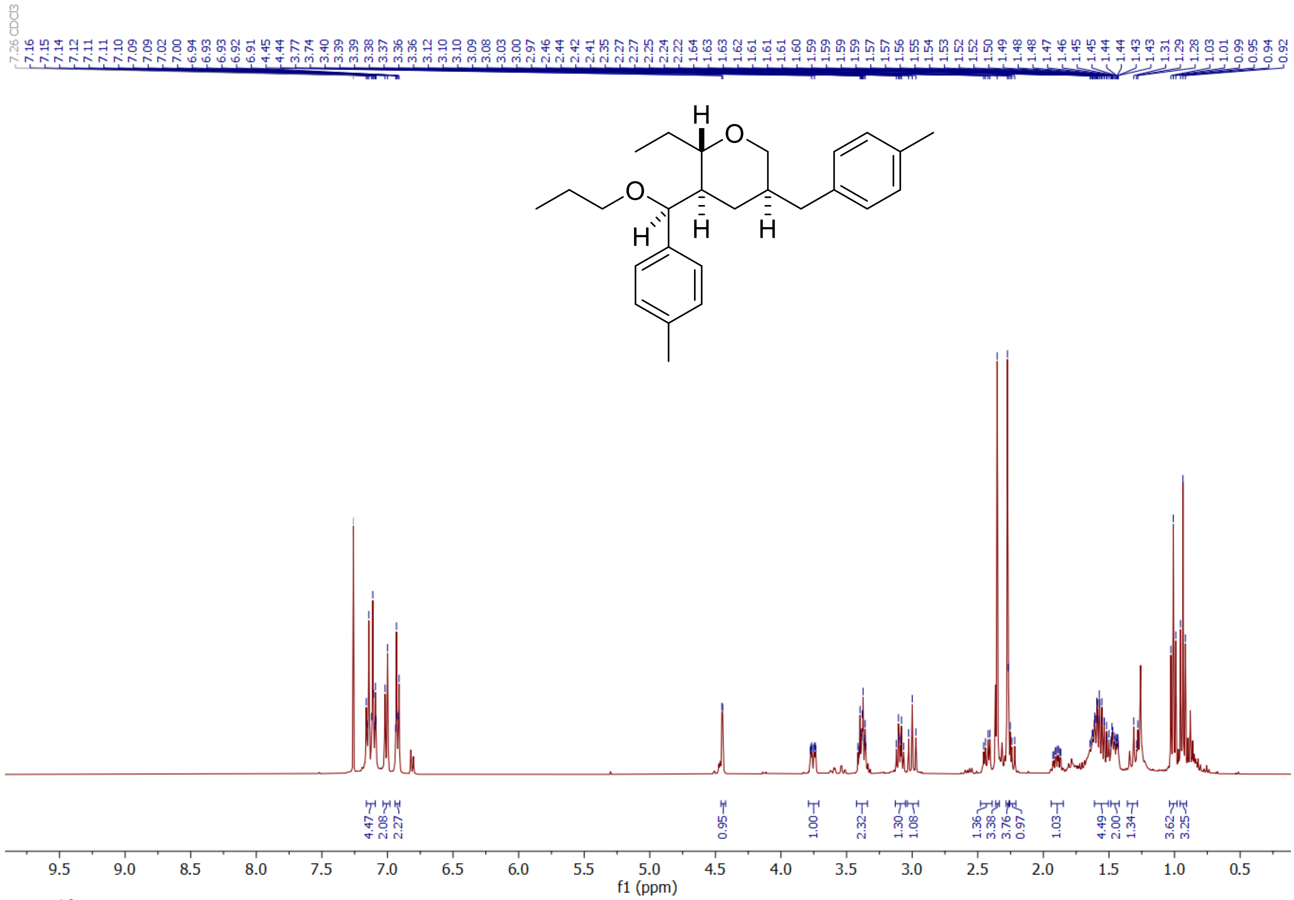
4g, ^{1}H NMR (400 MHz, $CDCl_3$)



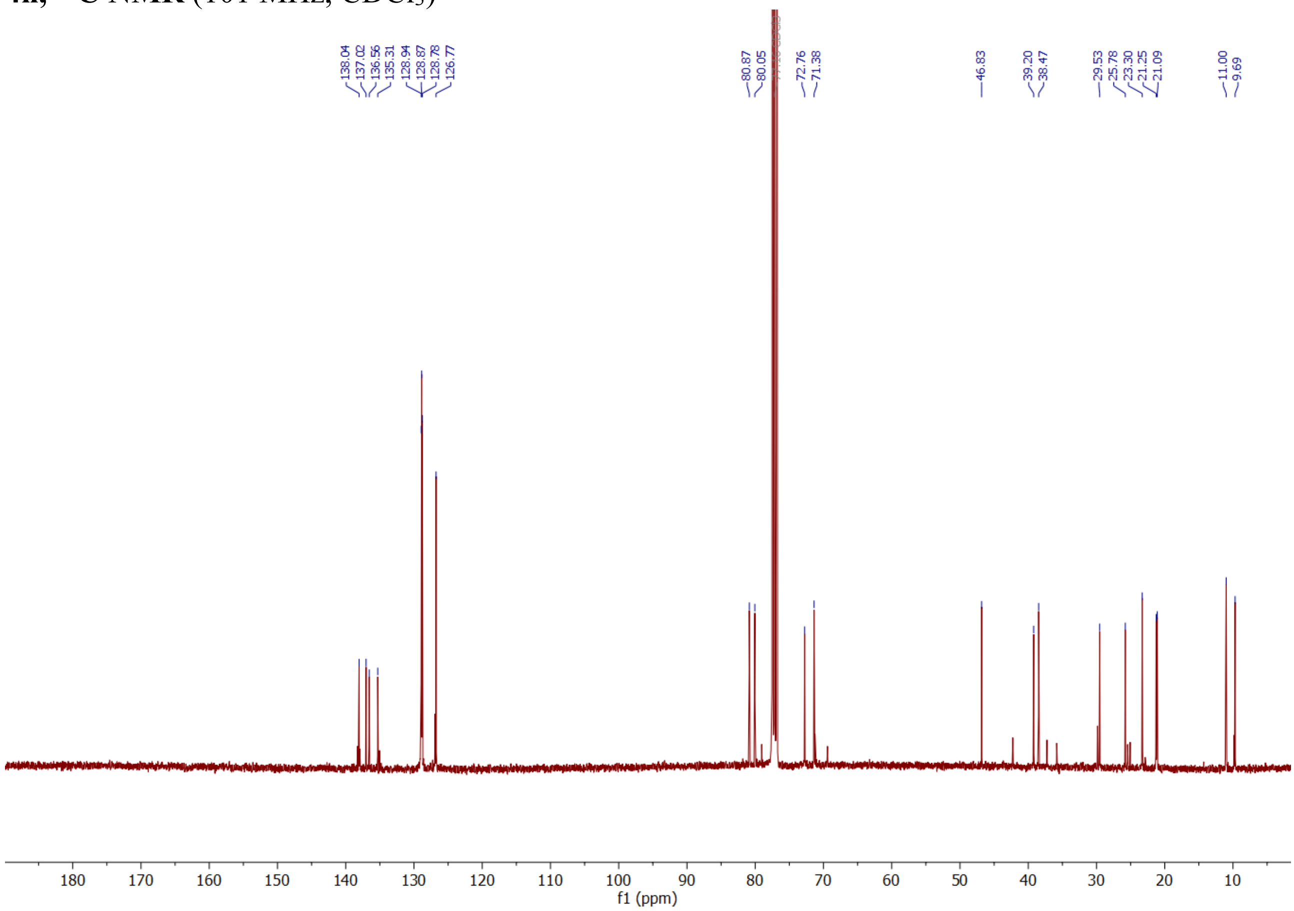
4g, ^{13}C NMR (101 MHz, $CDCl_3$)



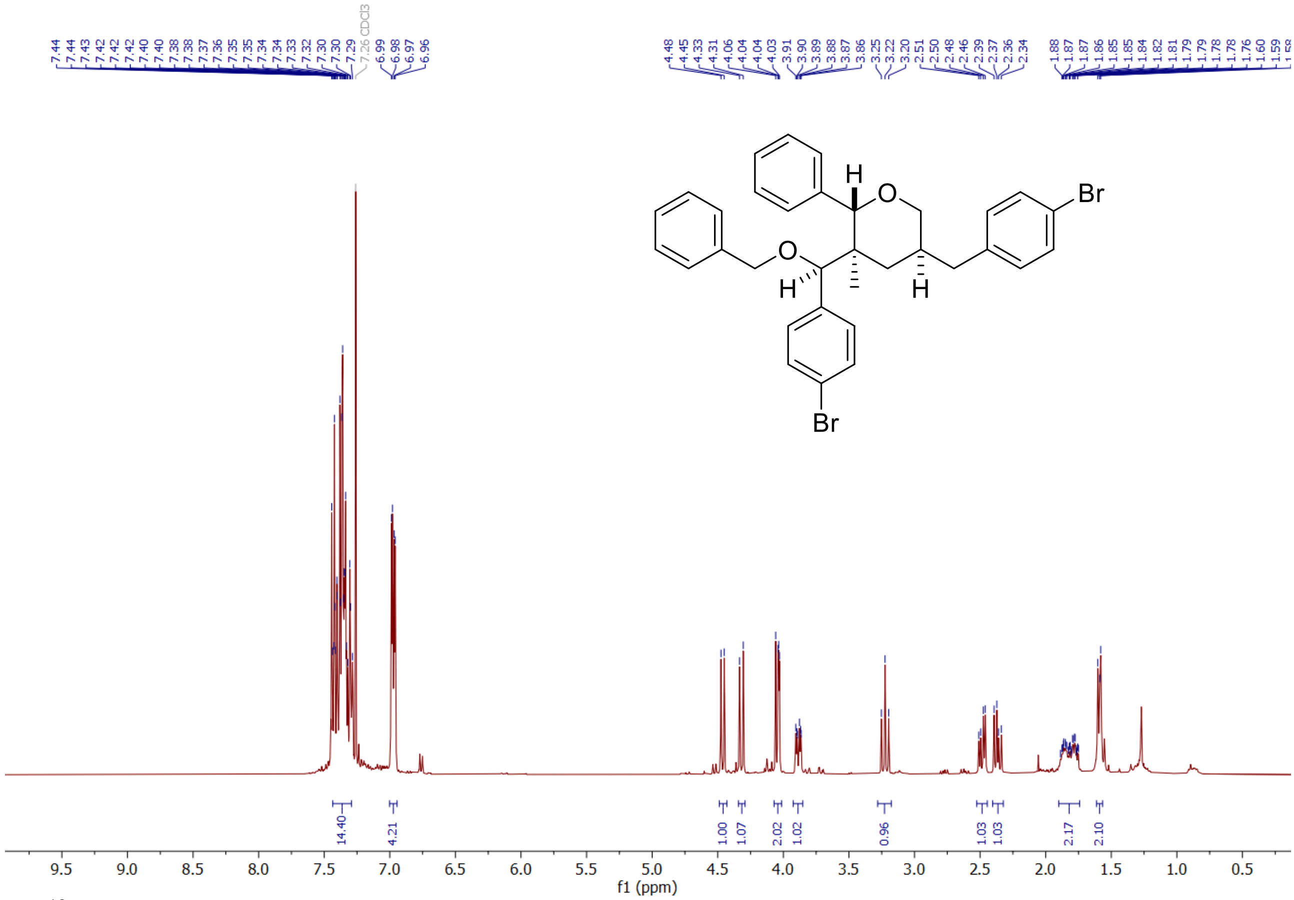
4h, ^{1}H NMR (400 MHz, $CDCl_3$)



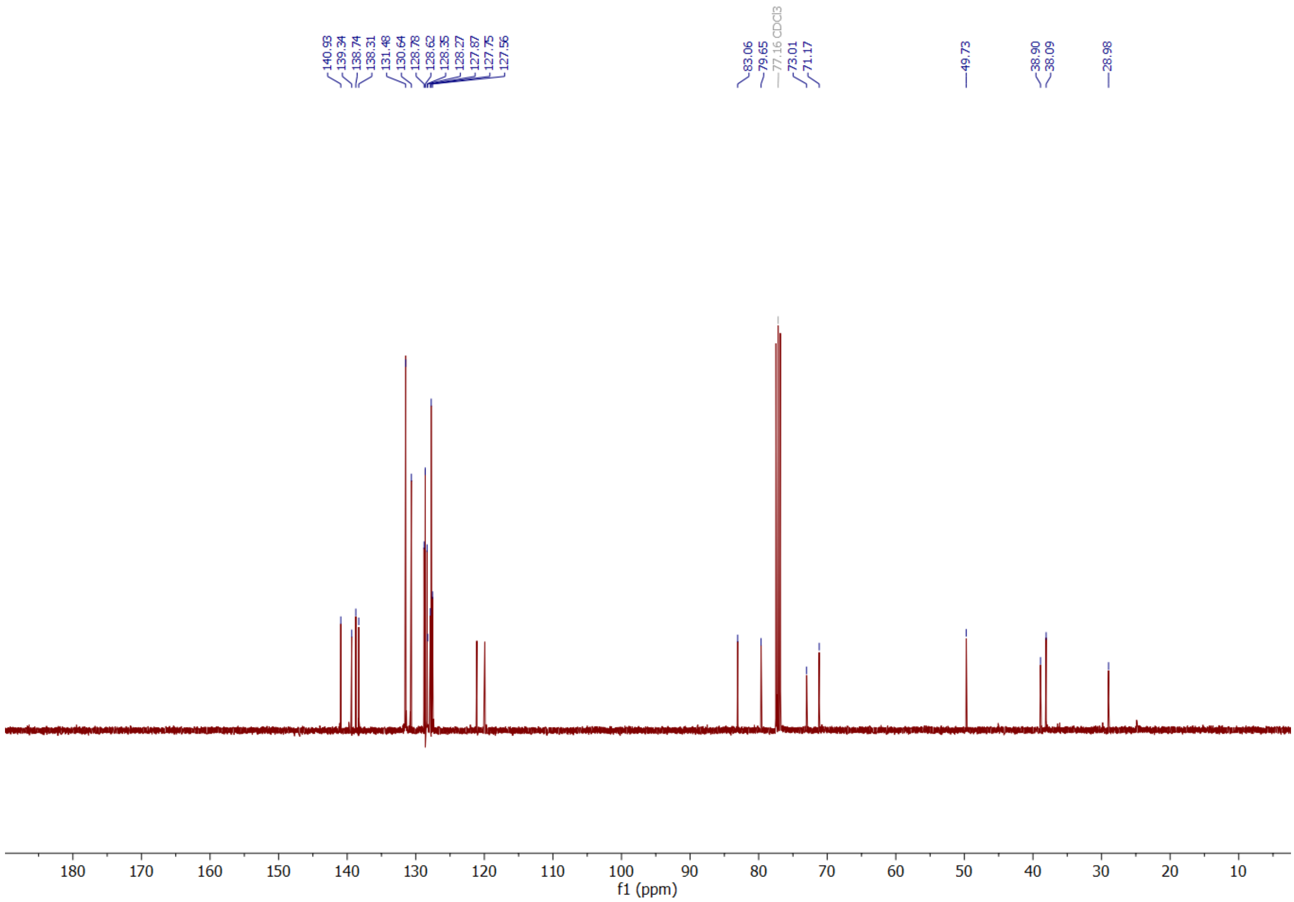
4h, ^{13}C NMR (101 MHz, $CDCl_3$)



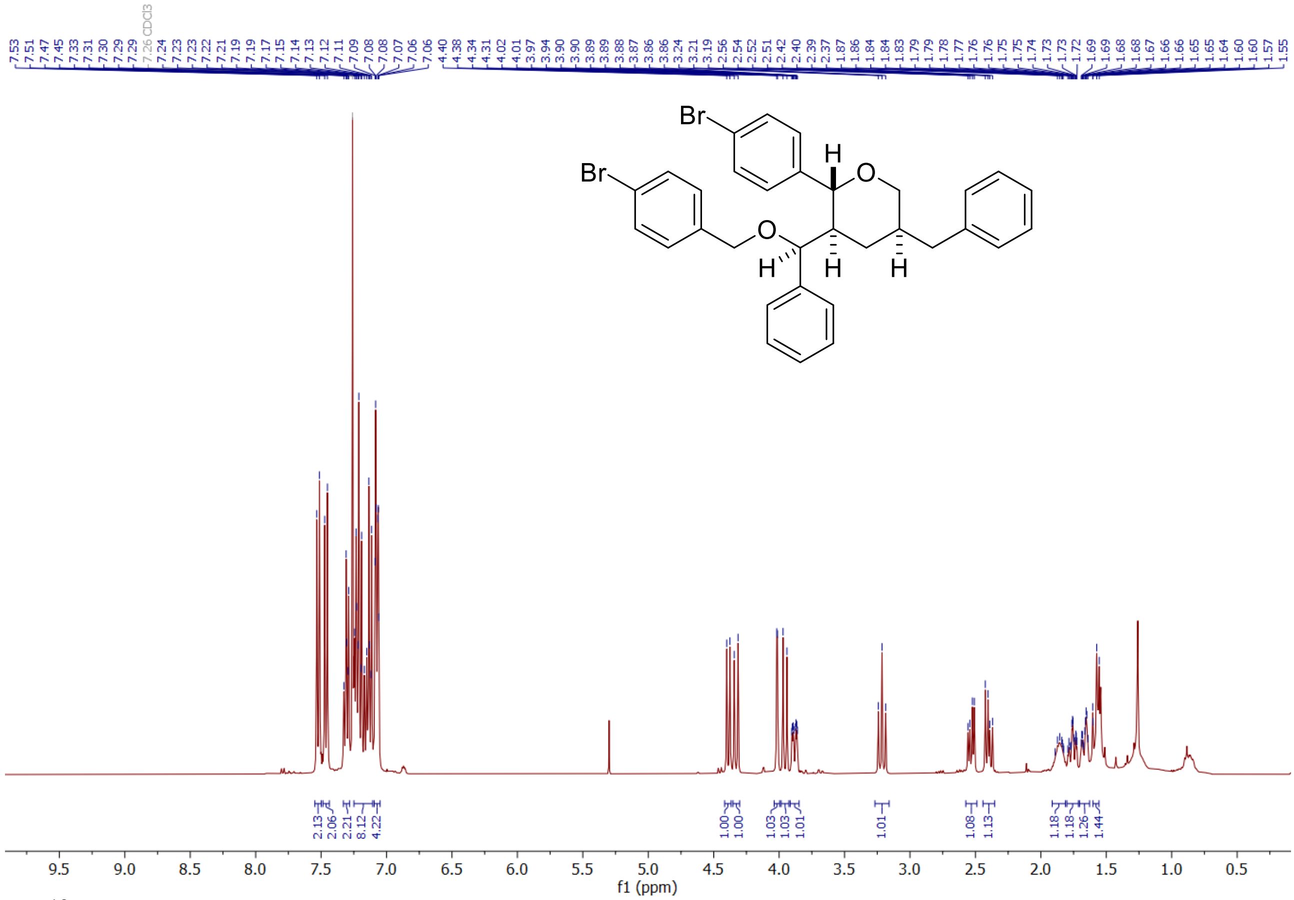
4i, ^{1}H NMR (400 MHz, $CDCl_3$)



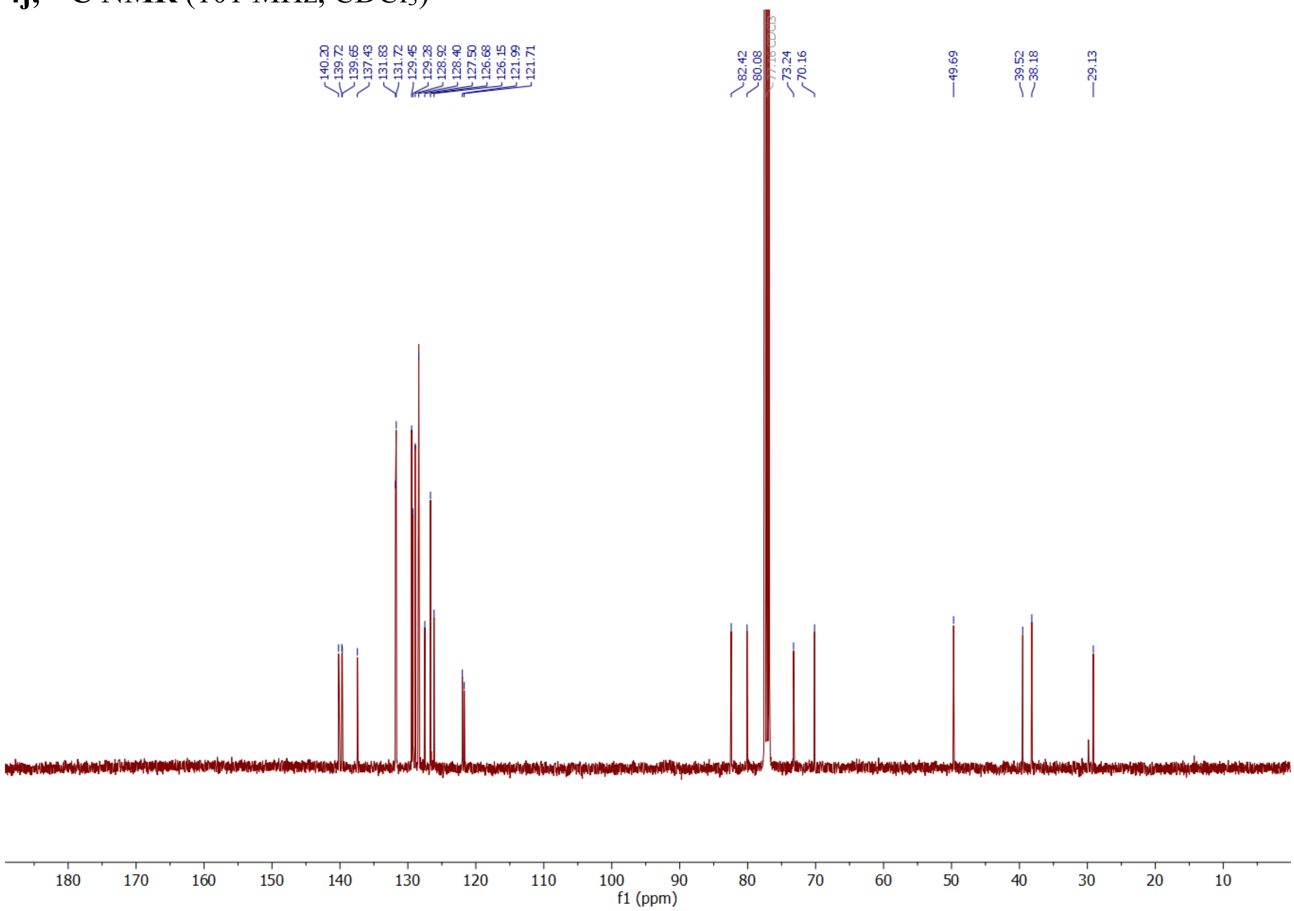
4i, ^{13}C NMR (101 MHz, $CDCl_3$)



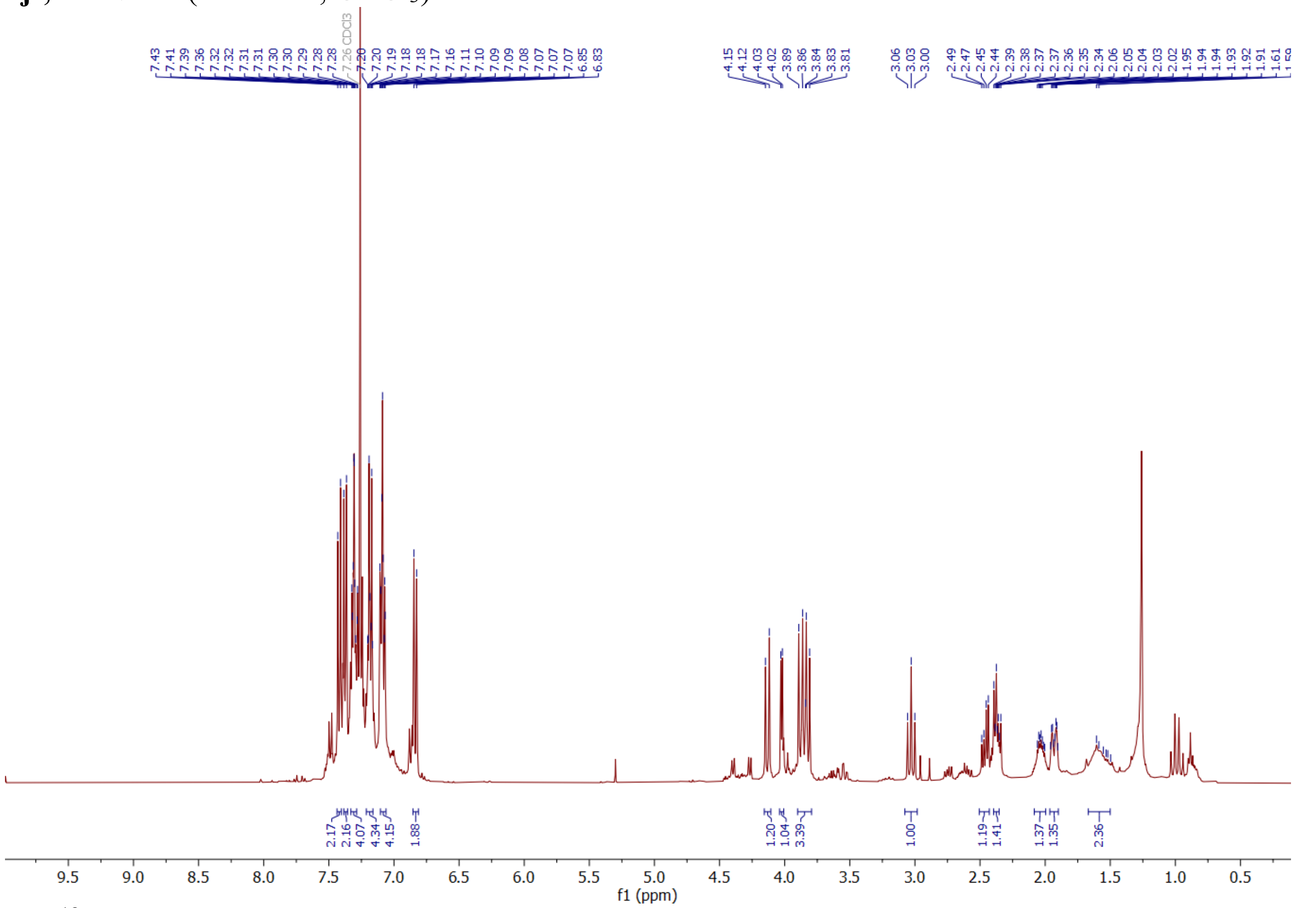
4j, ^{1}H NMR (400 MHz, $CDCl_3$)



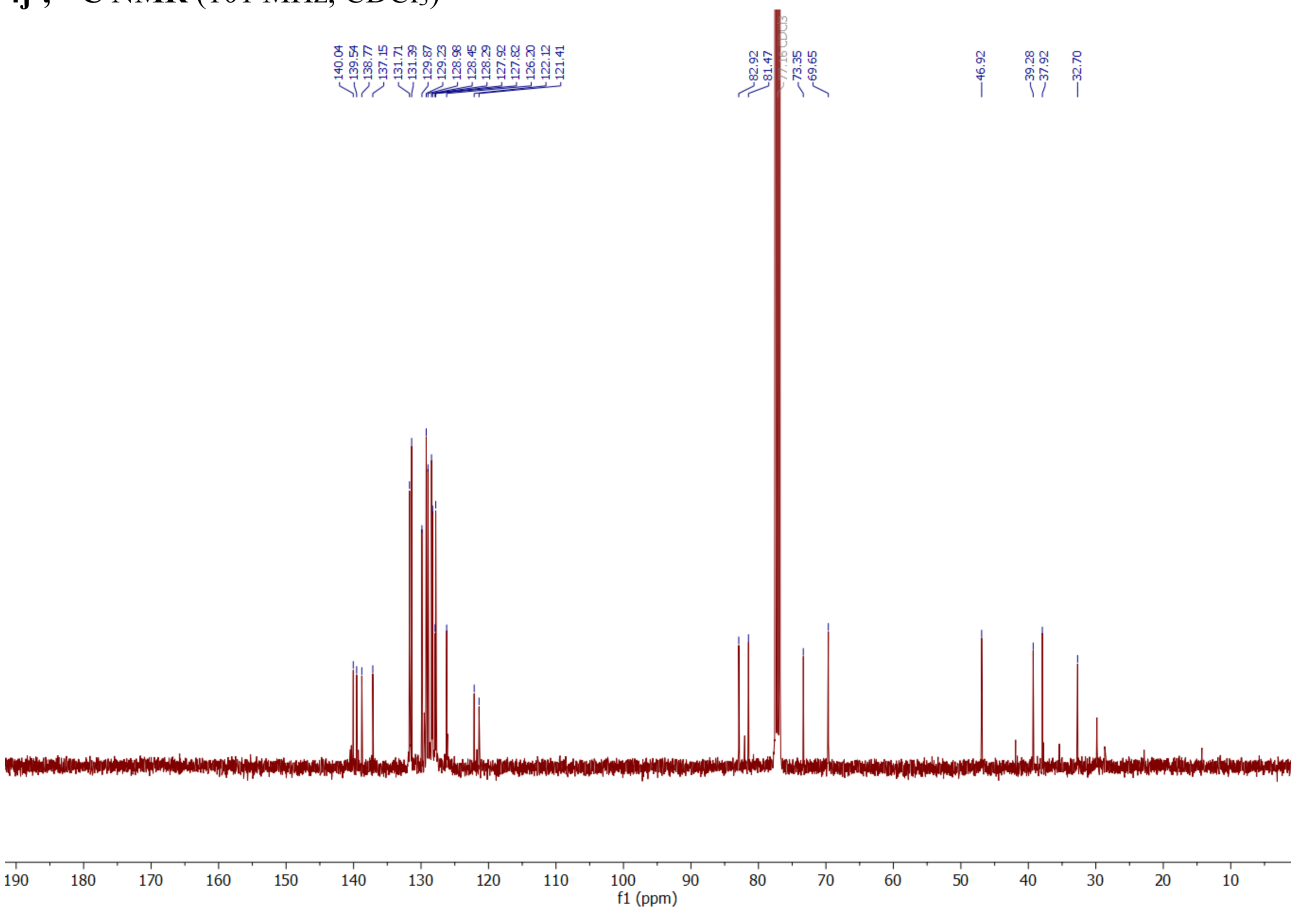
4j, ^{13}C NMR (101 MHz, $CDCl_3$)



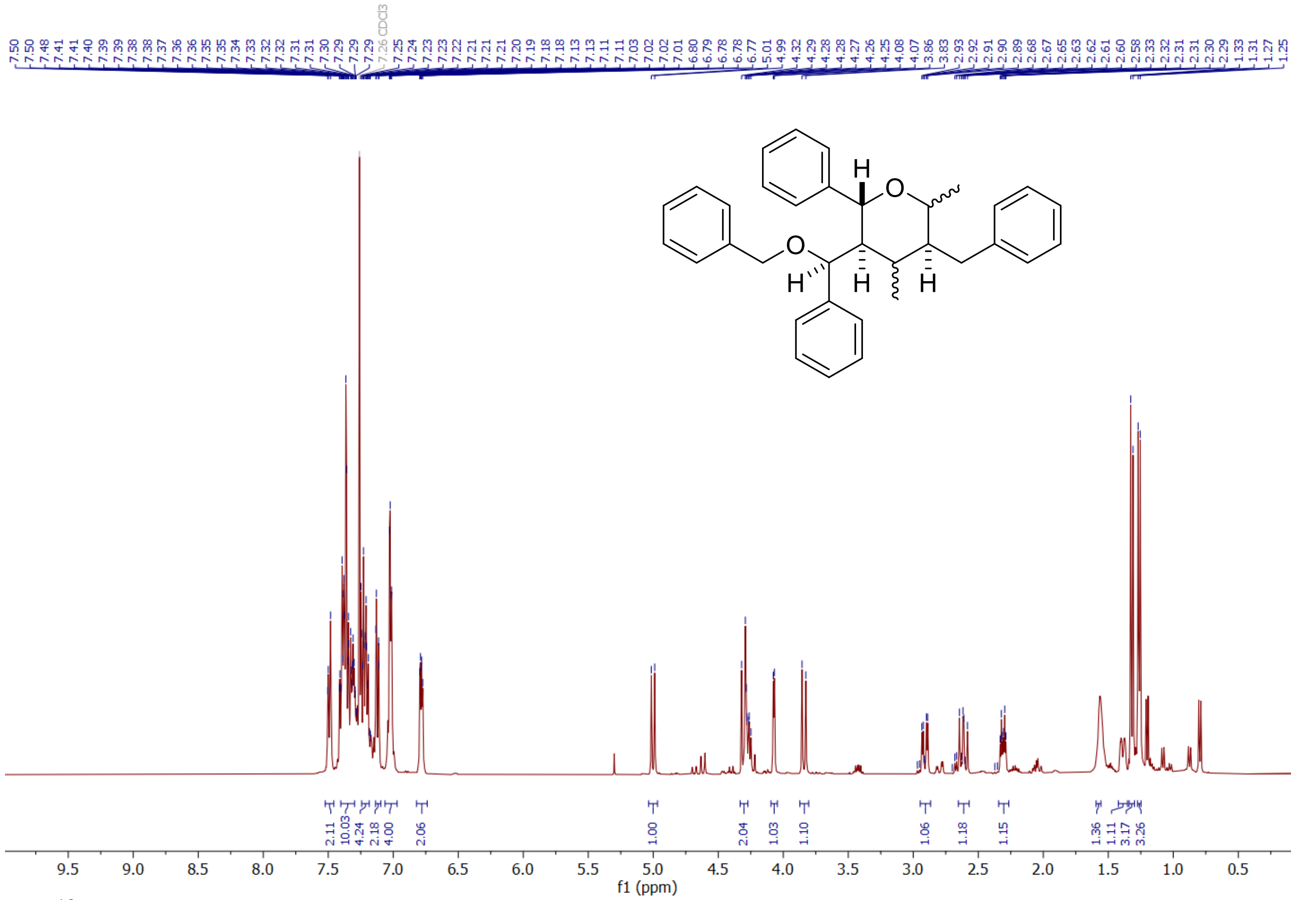
4j', ^{1}H NMR (400 MHz, $CDCl_3$)



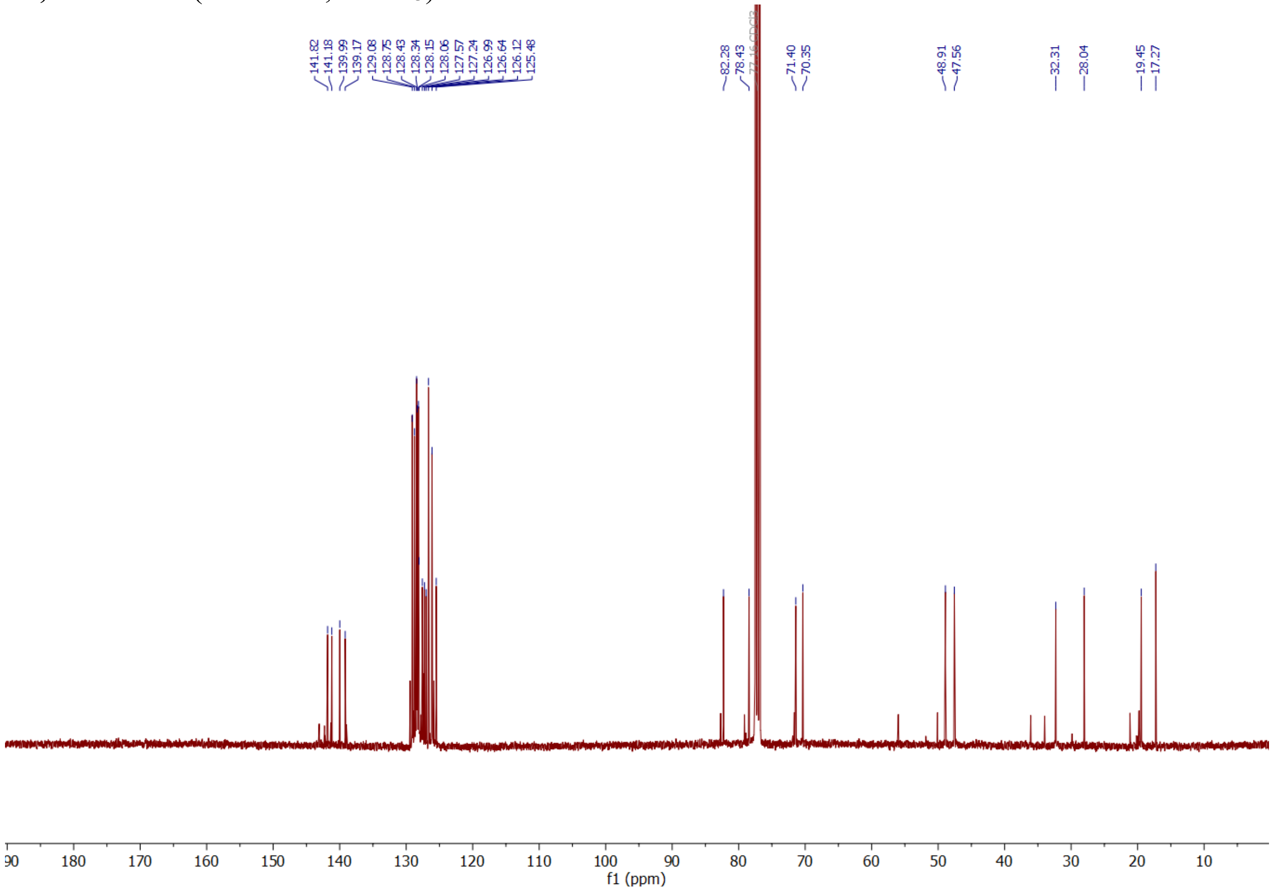
4j', ^{13}C NMR (101 MHz, $CDCl_3$)



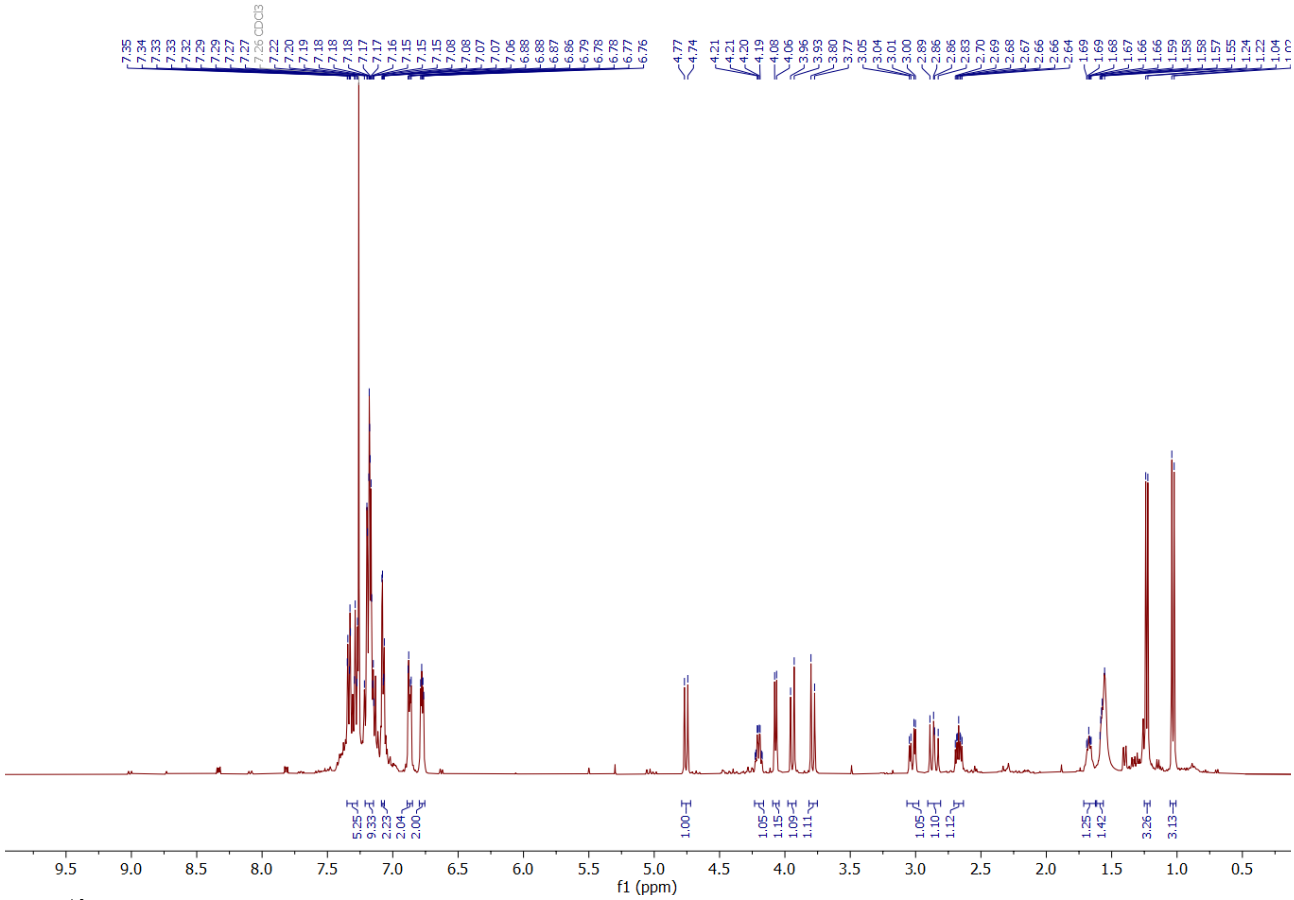
4k, ^{1}H NMR (400 MHz, $CDCl_3$)



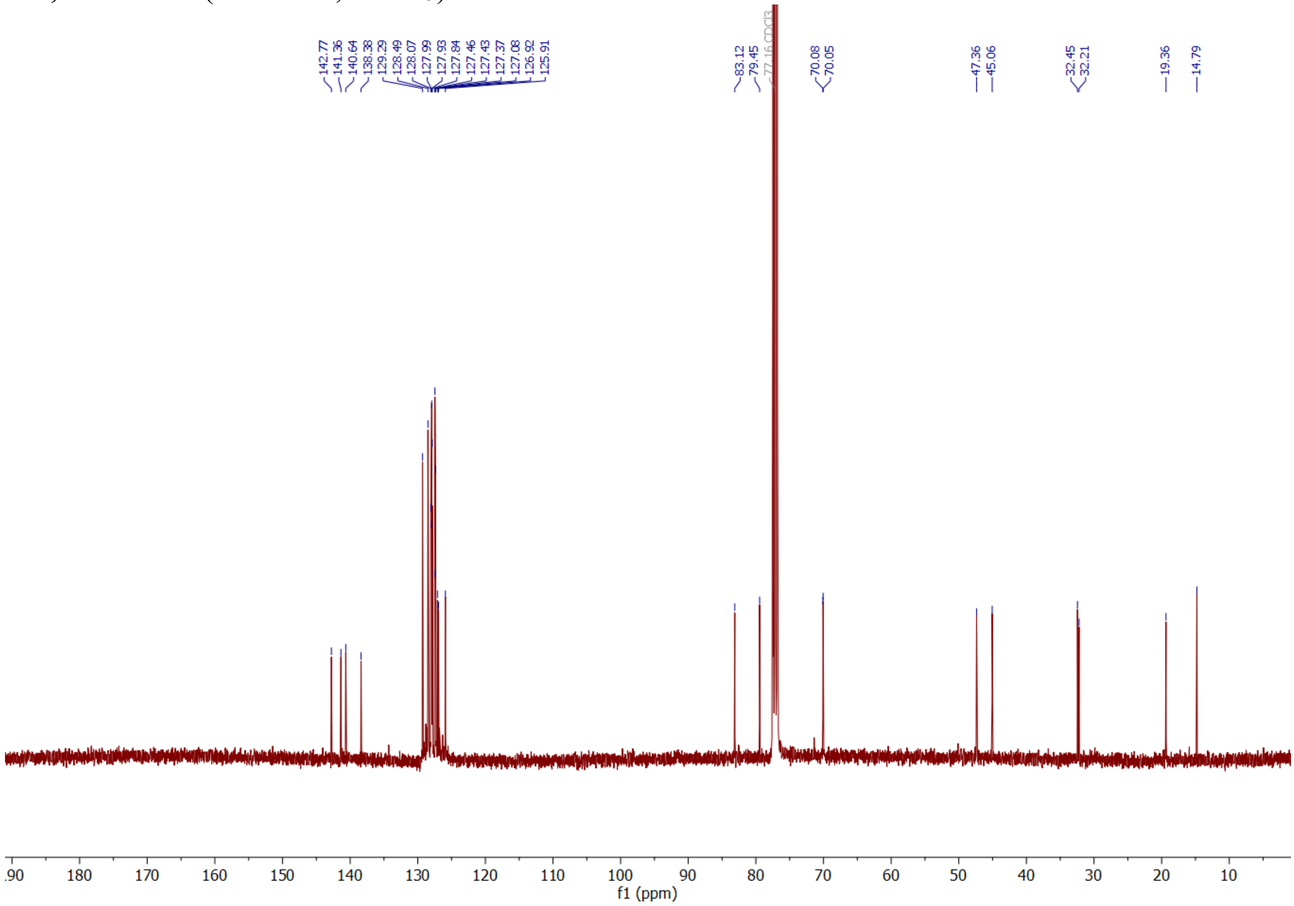
4k, ^{13}C NMR (101 MHz, $CDCl_3$)



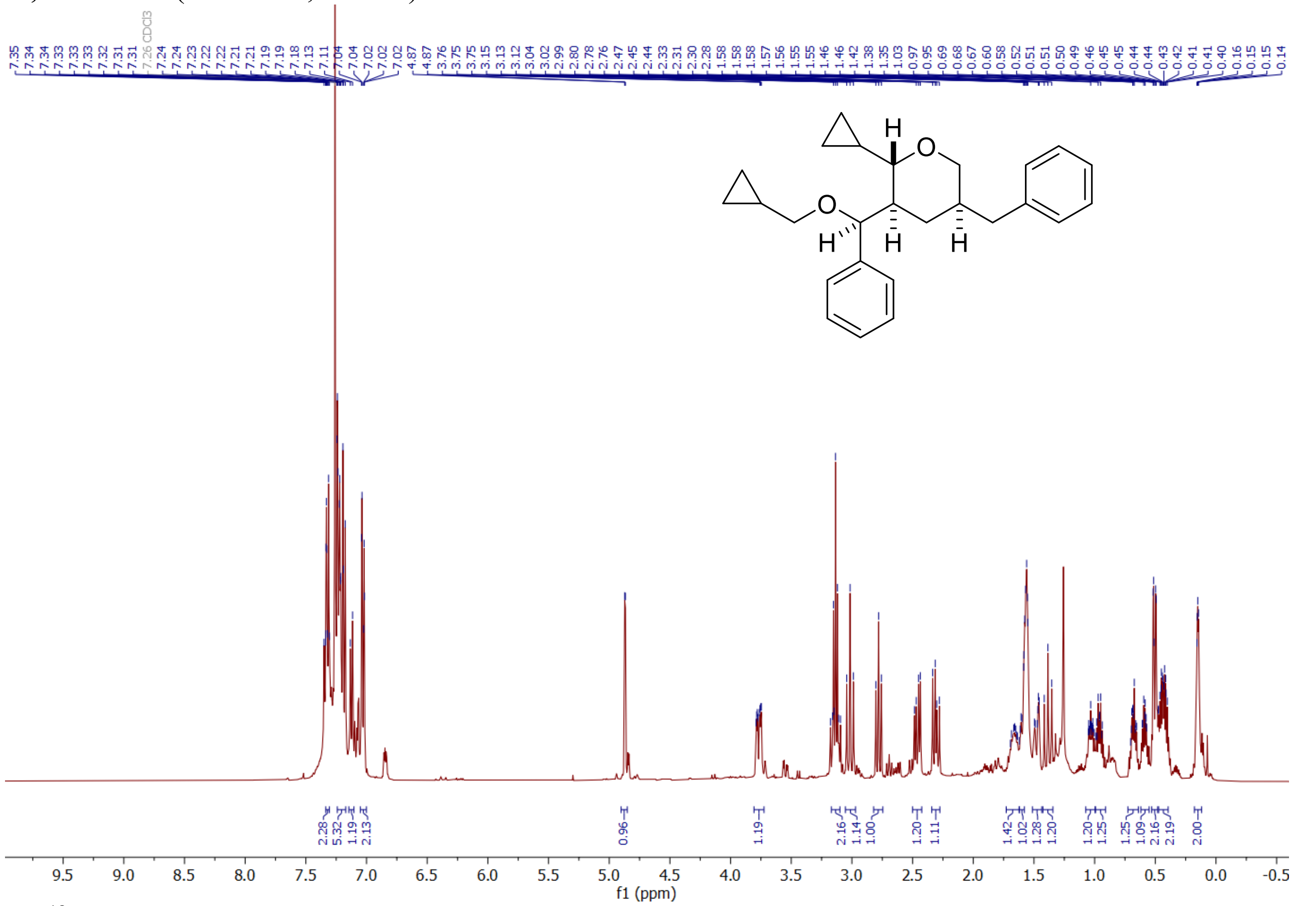
4k’, ^{1}H NMR (400 MHz, $CDCl_3$)



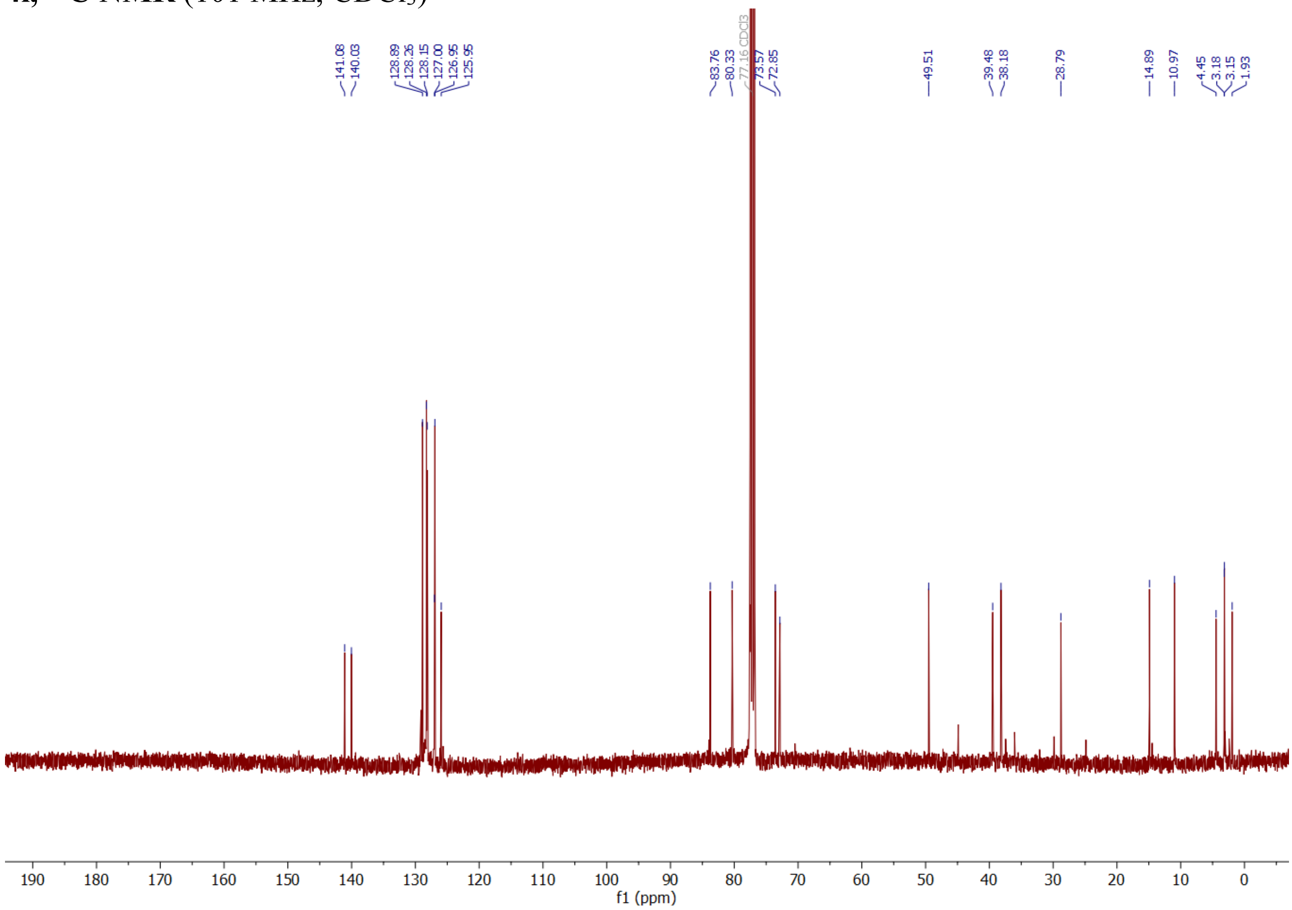
4k’, ^{13}C NMR (101 MHz, $CDCl_3$)



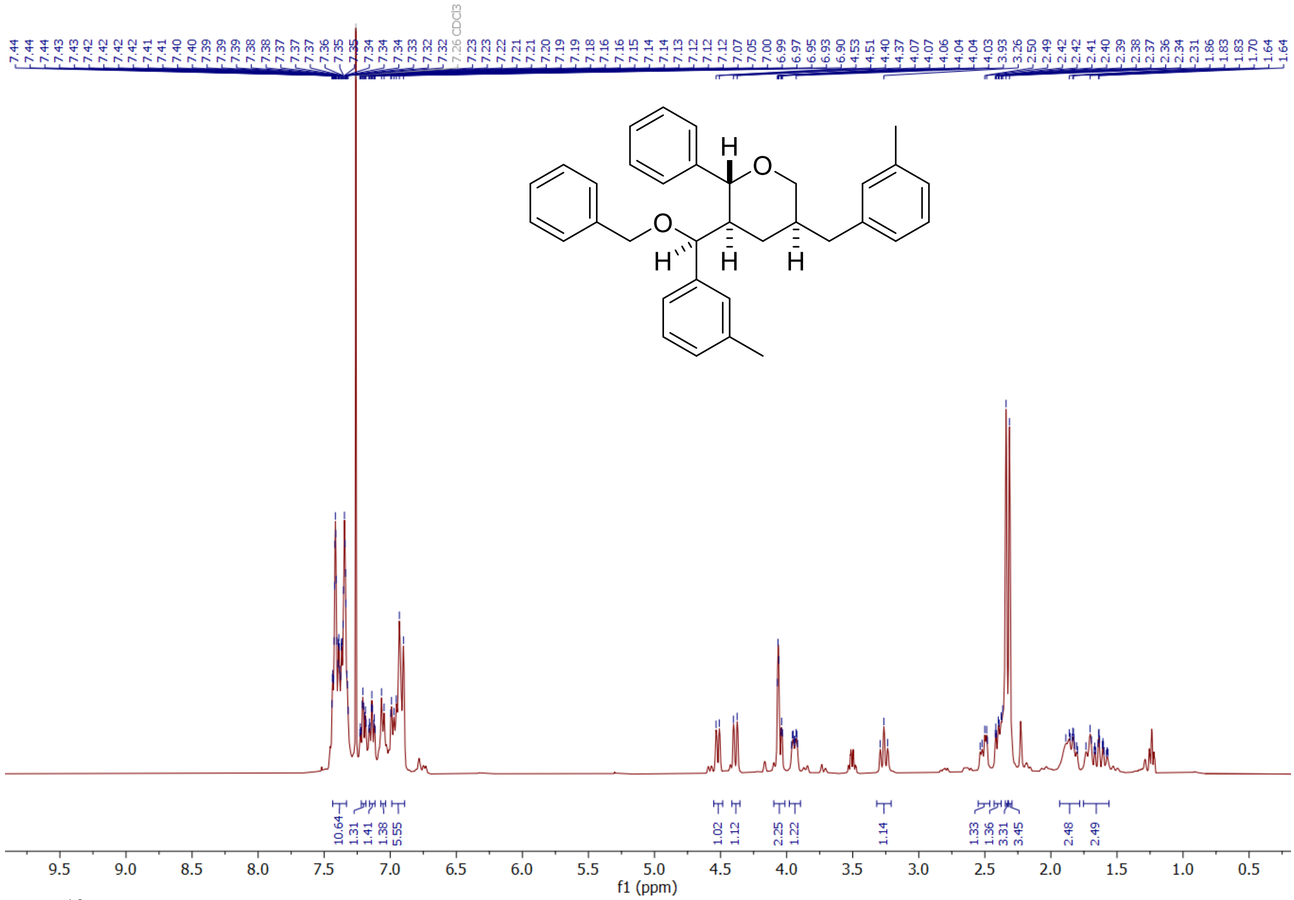
4l, ¹H NMR (400 MHz, $CDCl_3$)



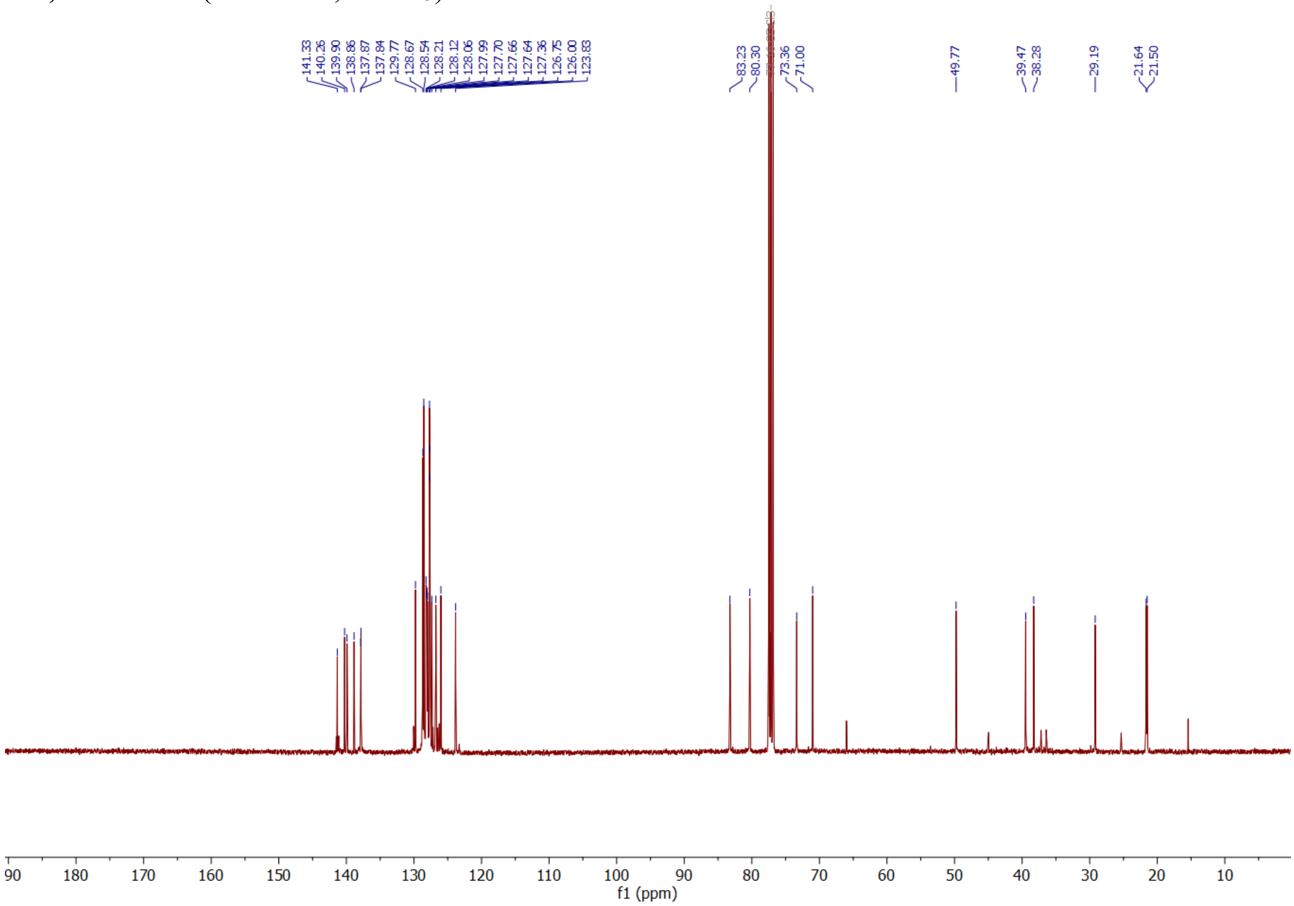
4l, ¹³C NMR (101 MHz, $CDCl_3$)



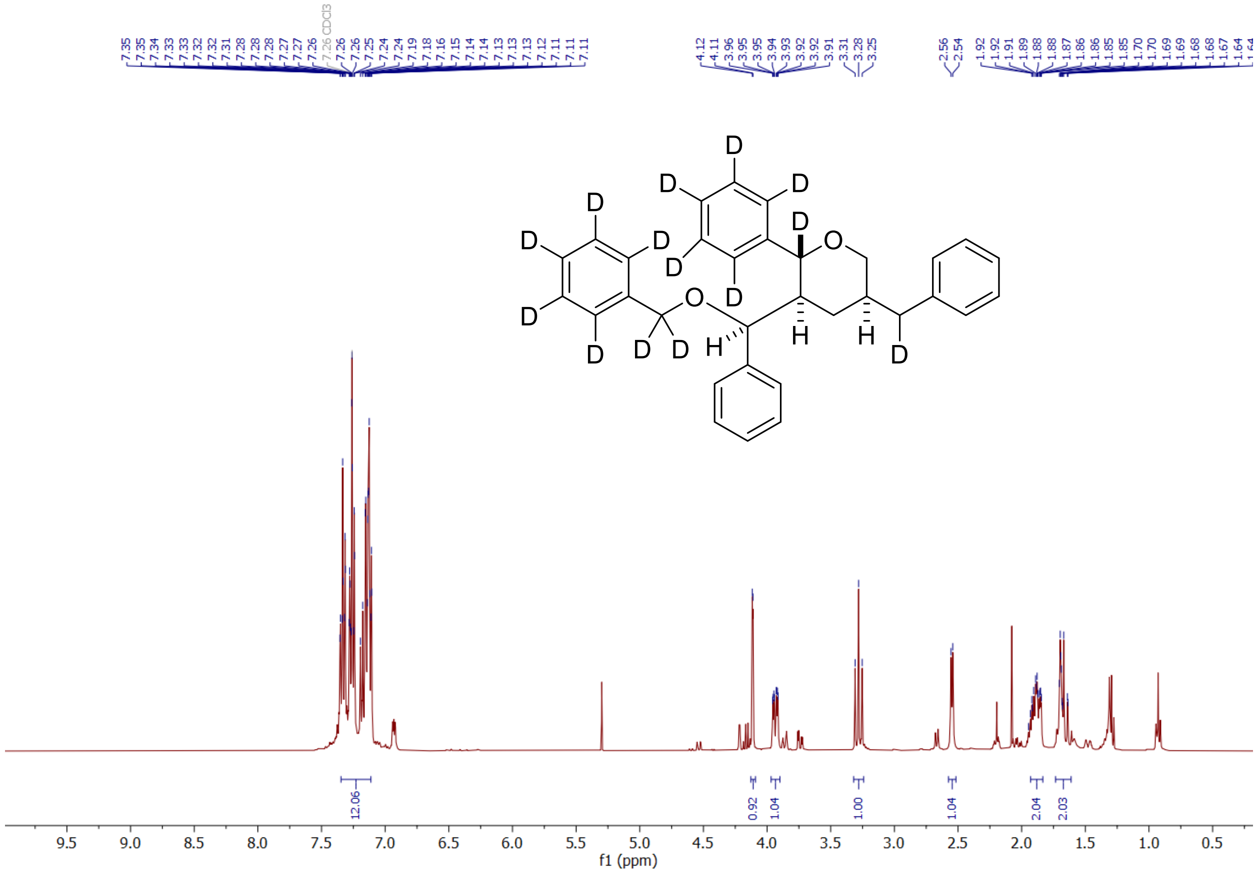
4m, ^{1}H NMR (400 MHz, $CDCl_3$)



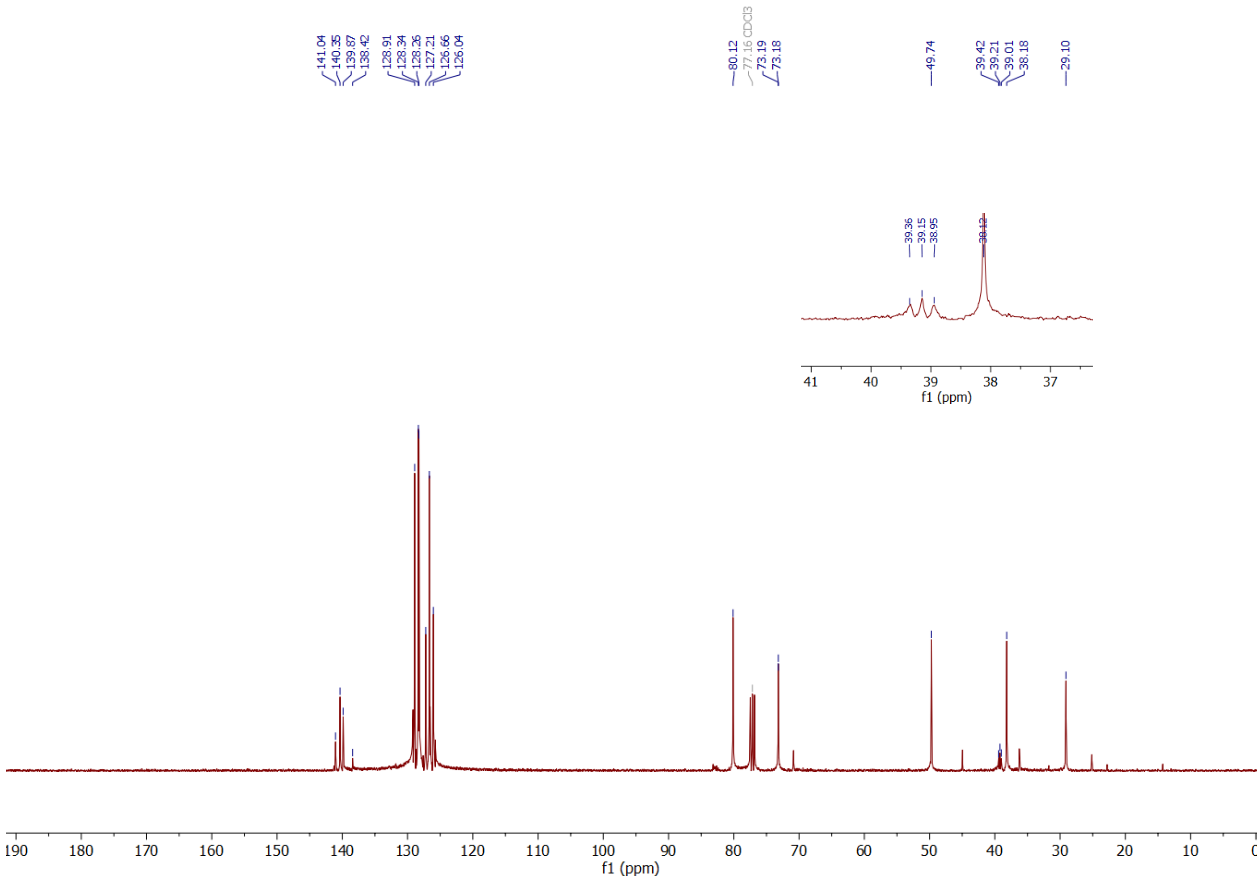
4m, ^{13}C NMR (101 MHz, $CDCl_3$)



***14d*-4a, ^{1}H NMR** (400 MHz, $CDCl_3$)



***14d*-4a, ^{13}C NMR** (101 MHz, $CDCl_3$)



XYZ coordinates

DCM

5
scf done: -2065.509311

C	-0.161483	3.629494	0.100909
Cl	-0.134190	2.117474	1.056507
Cl	-0.280737	3.298530	-1.650590
H	0.771669	4.178582	0.282206
H	-1.045809	4.202865	0.408222

$Ag(DCM)_2^+$

11
scf done: -2065.510770

C	-3.705513	0.981668	0.843739
Cl	-2.997056	-0.507244	0.142404
Ag	-1.463003	0.865179	-1.676896
Cl	-0.007759	3.162648	-1.601962
C	-0.336023	3.551607	0.120962
Cl	-0.358142	2.095839	1.126424
Cl	-3.702621	2.316877	-0.328030
H	-4.741062	0.759069	1.126082
H	-3.090810	1.278195	1.702697
H	0.465606	4.217056	0.462247
H	-1.321196	4.031186	0.170958

3c

26
scf done: -502.045902

C	1.191514	-0.102444	-0.695004
C	-0.015427	-0.056186	-0.002478
C	-0.005699	0.028062	1.390665
C	1.197071	0.065677	2.084151
C	2.423346	0.024332	1.401130
C	2.395666	-0.063491	0.001944
C	3.716918	0.070571	2.086541
C	3.932810	0.214191	3.399807
C	5.279376	0.199829	4.029053
O	5.399094	1.275940	4.912552
C	6.596525	1.268140	5.635584
H	5.425419	-0.758530	4.583155
H	6.074138	0.225854	3.249806
H	3.096458	0.339531	4.100339
H	4.593519	-0.023750	1.429032
H	3.344424	-0.099378	-0.544701
H	1.196334	-0.169846	-1.786749
H	-0.964480	-0.087568	-0.545339
H	-0.949668	0.061448	1.942779
H	1.187731	0.124736	3.176753
C	6.633511	2.474661	6.533780
H	6.679158	0.329203	6.228458
H	7.466093	1.267672	4.940740
H	7.559217	2.499351	7.128070
H	6.576874	3.399169	5.938675
H	5.776590	2.466211	7.224922

Ag(DCM)(**3c**)$^+$

32

scf done: -1608.257801

C	2.404786	-1.827953	-0.059005
C	2.446847	-0.871042	-1.066258
C	2.200947	-1.229539	-2.402026
C	1.919806	-2.572505	-2.695711
C	1.874933	-3.530933	-1.687219
C	2.115918	-3.160529	-0.365138
C	2.200677	-0.256174	-3.496336
Ag	-0.341570	1.203276	-3.243669
Cl	-0.686770	0.651053	-0.438181
C	-1.109733	-1.030519	-0.840284
Cl	-1.539690	-1.199123	-2.569017
C	2.376627	1.078818	-3.410302
C	2.283781	1.973902	-4.599007
O	1.002106	2.589921	-4.564514
H	3.066074	2.756322	-4.582099
H	-0.233558	-1.664067	-0.643157
H	-1.980627	-1.326163	-0.243920
H	2.398467	1.399006	-5.539629
H	2.037496	-0.681625	-4.498100
H	2.565897	1.560878	-2.441412
H	1.727866	-2.861772	-3.734322
H	1.652966	-4.572466	-1.934582
H	2.084251	-3.910587	0.429841
H	2.599232	-1.534476	0.976258
H	2.674170	0.167983	-0.809614
C	0.752330	3.519643	-5.609808
C	-0.652499	4.033871	-5.476894
H	1.492539	4.340262	-5.540090
H	0.910026	3.020174	-6.586099
H	-0.873599	4.766437	-6.266281
H	-1.380842	3.210336	-5.564879
H	-0.799190	4.526680	-4.502509

TS C-O cleavage

32

scf done: -1608.211128

C	0.046180	0.085974	-0.069818
C	-0.013847	0.036158	1.322890
C	1.163807	-0.039818	2.072607
C	2.397132	-0.059845	1.435482
C	2.473727	-0.009462	0.031657
C	1.280807	0.057901	-0.709272
C	3.735938	0.002143	-0.688459
C	4.985868	0.105739	-0.168041
C	6.127873	0.178764	-1.030177
O	6.329042	2.087821	-1.338417
Ag	4.391847	3.053233	-1.094274
Cl	3.118972	3.337177	1.712327
C	1.605400	3.474957	0.816645
Cl	1.893473	3.775913	-0.940828
C	7.178982	2.319363	-2.430558
C	7.234261	3.797497	-2.729674
H	7.125608	0.006274	-0.617869
H	1.047265	2.531467	0.896683

H	1.030884	4.328953	1.193993
H	5.998253	-0.113181	-2.078917
H	3.650743	-0.069290	-1.783176
H	5.144928	0.195129	0.912386
H	1.333721	0.095597	-1.802346
H	-0.873276	0.141528	-0.658114
H	-0.982547	0.050854	1.829759
H	1.115249	-0.084955	3.163691
H	3.310525	-0.120762	2.033976
H	8.196242	1.943398	-2.197187
H	6.837121	1.767583	-3.332797
H	7.919765	4.003948	-3.566101
H	6.237308	4.177957	-3.016401
H	7.582459	4.365001	-1.851824

Ag(DCM)(OEt)

14

scf done: -1260.549230

C	0.702614	1.305207	-4.721448
Cl	1.113699	0.748228	-3.050114
Ag	-1.184710	0.222300	-2.136751
Cl	-0.473191	0.258416	-5.503388
O	-3.021139	-0.148959	-1.287277
C	-3.920841	-0.916756	-1.984849
H	0.292121	2.317343	-4.626555
H	1.643827	1.297177	-5.283908
H	-4.720612	-1.284693	-1.294632
H	-4.478820	-0.339137	-2.767680
C	-3.319690	-2.134936	-2.666790
H	-4.080387	-2.755835	-3.171547
H	-2.579290	-1.823724	-3.430393
H	-2.791822	-2.767318	-1.931323

II

18

scf done: -347.603322

C	-5.553615	1.236707	-3.703538
C	-4.368575	0.532320	-3.443871
C	-3.206418	0.883268	-4.096915
C	-3.214000	1.957292	-5.030378
C	-4.428331	2.656081	-5.276567
C	-5.586175	2.296501	-4.616450
C	-2.064486	2.360772	-5.729472
C	-0.763198	1.817112	-5.632517
C	0.229986	2.333633	-6.397320
H	1.249612	1.942753	-6.353899
H	0.036690	3.161922	-7.087313
H	-0.556688	0.989276	-4.948198
H	-2.188356	3.194712	-6.433756
H	-4.428917	3.481765	-5.993713
H	-6.519296	2.831344	-4.803282
H	-6.470363	0.950563	-3.180797
H	-4.370168	-0.291054	-2.726924
H	-2.283503	0.333885	-3.897936

TS II-IIIc

44

scf done: -849.657720

C	-0.457393	0.558534	-0.267843
C	-0.065521	-0.022277	0.959596
C	1.289049	-0.373657	1.147612
C	2.220978	-0.154306	0.144954
C	1.815098	0.419331	-1.060937
C	0.476952	0.774495	-1.265486
C	-0.986386	-0.270541	2.026231
C	-2.335134	0.015591	2.057463
C	-3.086560	-0.244315	3.203591
C	-4.366640	-2.166821	2.916930
C	-4.628228	-2.088559	1.446074
O	-5.576439	-3.059933	1.124830
C	-5.969022	-3.024240	-0.228217
C	-6.976231	-4.113644	-0.471546
C	-3.337847	-2.899312	3.435154
C	-3.091091	-3.220534	4.823243
C	-1.908089	-3.907021	5.154162
C	-1.620021	-4.228023	6.475042
C	-2.509045	-3.864827	7.485719
C	-3.688098	-3.181619	7.173397
C	-3.980180	-2.862812	5.856088
H	-4.999848	-1.076421	1.169890
H	-3.680856	-2.246363	0.882394
H	-5.190699	-1.849332	3.568542
H	-2.576399	-3.256156	2.725069
H	-1.215481	-4.189892	4.354895
H	-0.699475	-4.764024	6.719455
H	-2.285496	-4.116535	8.525975
H	-4.384103	-2.901522	7.968192
H	-4.909577	-2.335283	5.622717
H	-6.393561	-2.026404	-0.470398
H	-5.079384	-3.151465	-0.881469
H	-7.306301	-4.113220	-1.520653
H	-6.543301	-5.100621	-0.246365
H	-7.861008	-3.974711	0.168847
H	-4.085939	0.182913	3.317787
H	-2.588576	-0.551665	4.128527
H	-2.832286	0.463372	1.190645
H	-0.558007	-0.737335	2.925198
H	1.594919	-0.821837	2.097813
H	3.267319	-0.428402	0.298163
H	2.548185	0.593817	-1.853048
H	0.169961	1.223520	-2.213003
H	-1.500065	0.840707	-0.434686

IIIc

44

scf done: -849.686114

C	3.043957	-0.015947	0.633198
C	2.001420	0.036752	-0.267191
C	0.686297	-0.060817	0.203873
C	0.399525	-0.210410	1.570760
C	1.430852	-0.261921	2.480544
C	2.781946	-0.171806	2.027647
C	3.864373	-0.259114	2.894707
C	3.833389	-0.537797	4.341784

C	5.024018	0.125410	5.003204
O	4.971340	1.476087	4.657883
C	6.053478	2.233927	5.154118
C	5.878482	3.667301	4.736543
H	4.983977	-0.024651	6.102184
H	5.971861	-0.337976	4.648450
H	2.911286	-0.124460	4.786852
H	4.861922	-0.171835	2.437934
H	4.081672	0.053960	0.295014
H	2.194086	0.153054	-1.335132
H	-0.140683	-0.016007	-0.510291
H	-0.637311	-0.278164	1.905160
H	1.217926	-0.365149	3.547519
H	6.092732	2.142059	6.259593
H	7.008167	1.817239	4.770029
H	6.708051	4.285167	5.109646
H	5.851936	3.753315	3.639113
H	4.937346	4.076340	5.135332
C	3.807142	-2.079492	4.536655
C	4.847789	-2.813429	3.750368
H	3.925884	-2.256474	5.620920
H	2.805157	-2.447356	4.259381
C	4.551996	-3.608012	2.710274
H	5.894938	-2.672673	4.050693
C	5.485908	-4.357234	1.865998
H	3.490809	-3.727265	2.443233
C	4.974477	-5.118219	0.804011
C	5.818303	-5.844439	-0.032189
C	7.194926	-5.824015	0.179660
C	7.719341	-5.073347	1.234088
C	6.876271	-4.348614	2.067667
H	3.891993	-5.136878	0.637539
H	5.397476	-6.431003	-0.853791
H	7.861619	-6.393356	-0.474059
H	8.799089	-5.055077	1.407891
H	7.306299	-3.769379	2.890571

TS IIIc-IVc

44

scf done: -849.679553

C	-0.550069	-0.026963	-0.622018
C	-0.111873	0.044495	0.711053
C	1.267287	-0.021656	0.960185
C	2.181168	-0.148820	-0.082550
C	1.730999	-0.214876	-1.399094
C	0.361058	-0.154101	-1.663453
C	-1.028150	0.180035	1.846724
C	-2.360782	0.338379	1.805668
C	-3.218932	0.445141	3.023069
C	-4.097691	-0.792858	3.285258
C	-5.206820	-0.925483	2.189333
O	-5.430059	-2.274484	1.872365
C	-4.339313	-2.873075	1.366374
C	-4.429789	-4.352654	1.296893
C	-3.282635	-2.036227	3.436519
C	-3.660090	-3.128448	4.309463
C	-2.698242	-4.118627	4.598885

C	-3.032861	-5.217286	5.374509
C	-4.333796	-5.345450	5.867504
C	-5.297042	-4.374005	5.589465
C	-4.967471	-3.269701	4.815744
H	-6.157198	-0.505264	2.540864
H	-4.894292	-0.374329	1.283764
H	-4.623328	-0.645535	4.243838
H	-2.197317	-1.919549	3.282962
H	-1.683948	-4.011240	4.200932
H	-2.282811	-5.979048	5.599206
H	-4.598958	-6.211275	6.480037
H	-6.310475	-4.479404	5.983496
H	-5.729344	-2.513914	4.607818
H	-3.885159	-2.349246	0.499890
H	-3.421555	-2.620328	2.174682
H	-3.499549	-4.788443	0.910063
H	-4.659331	-4.776878	2.288737
H	-5.252877	-4.629326	0.618311
H	-3.893725	1.316775	2.944646
H	-2.589165	0.620044	3.911460
H	-2.862093	0.396374	0.829318
H	-0.544575	0.159110	2.835137
H	1.623443	0.031511	1.994604
H	3.251937	-0.196085	0.135028
H	2.444991	-0.315149	-2.221357
H	0.000466	-0.207758	-2.694708
H	-1.619856	0.014269	-0.850076

IVc

44

scf done: -849.711434

C	-0.060882	0.193467	-0.678517
C	0.147155	0.487799	0.679473
C	1.458740	0.745946	1.106103
C	2.526603	0.712708	0.212951
C	2.303204	0.419398	-1.130313
C	1.003749	0.159911	-1.571053
C	-0.939346	0.538033	1.661915
C	-2.247241	0.334212	1.444992
C	-3.290766	0.413704	2.511915
C	-3.918578	-0.936130	2.901500
C	-4.581823	-1.555429	1.687855
O	-5.610559	-2.497079	2.134552
C	-5.479756	-3.737696	2.006367
C	-6.465487	-4.634867	2.568458
C	-2.884869	-1.852957	3.561002
C	-3.394607	-3.155471	4.120561
C	-2.931849	-4.381769	3.623734
C	-3.351834	-5.590074	4.183696
C	-4.255024	-5.589326	5.243512
C	-4.736316	-4.373646	5.739359
C	-4.308491	-3.171178	5.184563
H	-5.135215	-0.811437	1.097108
H	-3.882050	-2.101237	1.031129
H	-4.728359	-0.715254	3.622871
H	-2.414483	-1.278748	4.380644
H	-2.207406	-4.386511	2.800949

H	-2.964964	-6.534438	3.790949
H	-4.581529	-6.532332	5.690375
H	-5.441772	-4.365600	6.574941
H	-4.674553	-2.223345	5.594911
H	-4.609971	-4.122227	1.443904
H	-2.075367	-2.056323	2.836660
H	-5.954514	-5.202709	3.374433
H	-7.330405	-4.097337	2.974708
H	-6.752921	-5.390873	1.820969
H	-4.104716	1.088274	2.187907
H	-2.857677	0.858579	3.424161
H	-2.595897	0.103782	0.427226
H	-0.624230	0.779400	2.688158
H	1.637026	0.978112	2.161658
H	3.540042	0.918484	0.569319
H	3.138710	0.392969	-1.835510
H	0.819909	-0.070373	-2.624551
H	-1.071506	-0.011767	-1.044998

TS IVc-Vc

44

scf done: -849.707235

C	0.244506	-0.817158	0.361586
C	0.023283	0.090856	1.418608
C	1.073865	0.954539	1.793088
C	2.302832	0.884456	1.150378
C	2.512648	-0.045791	0.131406
C	1.479620	-0.895357	-0.265675
C	-1.285906	0.084767	2.034933
C	-1.688730	0.483349	3.283812
C	-0.924208	1.266293	4.310017
C	-1.435847	1.064335	5.733873
C	-1.221394	-0.365570	6.184325
O	-1.890561	-1.276949	5.287859
C	-1.360776	-1.523649	4.135616
C	-0.735969	2.023439	6.700425
C	-1.208315	1.910603	8.122873
C	-2.479519	2.373727	8.483722
C	-2.941179	2.242088	9.790844
C	-2.136124	1.643955	10.760467
C	-0.868124	1.182007	10.414349
C	-0.409613	1.315119	9.104317
C	-2.052902	-2.537156	3.320766
H	-2.065086	-0.395283	1.428178
H	-2.773139	0.429306	3.457770
H	0.154123	1.020075	4.282242
H	-0.988847	2.341634	4.055348
H	-2.525221	1.267271	5.757652
H	-0.145054	-0.621274	6.207772
H	-1.655992	-0.562403	7.173545
H	-0.270108	-1.381910	4.035702
H	-0.573926	-1.468928	0.038759
H	1.637278	-1.612471	-1.075038
H	3.484119	-0.097504	-0.367458
H	3.104431	1.568683	1.439623
H	0.917073	1.718548	2.556022
H	-1.585942	-2.666660	2.337545

H	-1.976138	-3.492206	3.869642
H	-3.122657	-2.303267	3.217652
H	0.354723	1.847228	6.650615
H	-0.900741	3.050238	6.328214
H	0.589379	0.952213	8.835789
H	-0.228872	0.715597	11.169576
H	-2.497224	1.541978	11.787796
H	-3.935121	2.613358	10.057019
H	-3.112070	2.852869	7.727149

Vc

44

scf done: -849.720358

C	-0.461135	-2.591555	1.021385
C	0.500932	-2.016978	0.181767
C	0.072638	-1.392408	-0.994071
C	-1.281119	-1.340626	-1.324003
C	-2.228613	-1.914667	-0.479054
C	-1.814168	-2.542070	0.695946
C	1.954098	-2.047632	0.563434
C	2.308779	-1.081395	1.694671
C	3.768748	-1.228407	2.093276
C	4.134138	-0.188191	3.170617
C	3.741105	1.251686	2.657980
O	2.389892	1.247382	2.342871
C	2.032535	0.360138	1.306375
C	5.514621	-0.222051	3.651803
C	6.715612	-0.094132	2.951070
C	6.809897	0.113690	1.540656
C	8.043502	0.257913	0.946179
C	9.208032	0.188219	1.726818
C	9.149282	-0.015702	3.110005
C	7.919519	-0.150310	3.718482
C	3.980495	2.319015	3.692610
H	5.639475	-0.327969	4.738169
H	3.471977	-0.359185	4.038047
H	4.400105	-1.106734	1.195116
H	3.963964	-2.242991	2.478346
H	1.678225	-1.316011	2.576027
H	2.596557	0.609944	0.379431
H	0.963240	0.523798	1.101889
H	4.345762	1.448902	1.742739
H	7.846610	-0.301544	4.799235
H	10.067519	-0.063154	3.698118
H	10.182157	0.296091	1.241999
H	8.118800	0.421024	-0.130482
H	5.908183	0.163146	0.928364
H	5.052012	2.422288	3.926643
H	3.614523	3.285847	3.318858
H	3.437302	2.080146	4.620965
H	2.579169	-1.811262	-0.318175
H	2.237335	-3.067541	0.880814
H	0.815217	-0.940723	-1.662098
H	-1.597022	-0.849236	-2.248952
H	-3.290889	-1.876533	-0.736841
H	-2.551551	-3.000251	1.361667
H	-0.138988	-3.092105	1.942191

TS Vc-VIc

70

scf done: -1351.788662

C	-0.051981	0.015891	-0.021134
C	-0.006036	0.034920	1.378188
C	1.244570	0.061955	2.003596
C	2.419314	0.071643	1.252100
C	2.359468	0.054612	-0.139914
C	1.118261	0.025851	-0.775721
C	-1.281783	0.060169	2.172413
C	-1.984145	1.416652	2.150170
C	-3.327578	1.342595	2.862183
C	-3.989191	2.740492	2.938201
C	-3.006887	3.723183	3.594835
O	-1.827469	3.733441	2.822875
C	-1.144824	2.505682	2.792283
C	-5.340594	2.461498	3.497886
C	-5.634856	2.109278	4.871617
C	-6.598067	1.104081	5.087149
C	-6.926009	0.703279	6.375539
C	-6.315496	1.321666	7.465577
C	-5.372478	2.333710	7.269116
C	-5.025107	2.722198	5.983907
C	-3.482245	5.152903	3.658489
O	-6.341083	4.083757	3.203026
C	-7.416055	4.408288	4.118381
C	-7.063643	5.594751	4.970754
C	-6.637848	4.333647	1.806214
C	-6.752590	5.788882	1.544293
C	-7.878066	6.359144	1.087616
C	-8.091819	7.773969	0.781937
C	-7.092696	8.747015	0.951257
C	-7.345411	10.080579	0.655592
C	-8.599890	10.471765	0.182576
C	-9.600301	9.518131	0.008207
C	-9.346767	8.181993	0.305722
H	-5.955314	1.897586	2.781908
H	-8.320582	4.587035	3.515144
H	-7.612287	3.512610	4.730385
H	-7.917389	5.849288	5.616465
H	-6.204205	5.380303	5.625408
H	-6.826185	6.475623	4.353748
H	-4.111060	3.084438	1.892954
H	-3.174125	0.962685	3.892236
H	-3.989378	0.619557	2.353719
H	-2.163663	1.710652	1.096153
H	-0.865917	2.191957	3.824703
H	-0.209180	2.670446	2.234037
H	-2.754128	3.350364	4.612619
H	-7.082966	0.632815	4.226394
H	-7.664781	-0.086058	6.531832
H	-6.579242	1.016808	8.481729
H	-4.905670	2.821003	8.128179
H	-4.298409	3.525796	5.847837
H	-4.372989	5.275000	4.288950
H	-2.676562	5.786257	4.057214

H	-3.724887	5.512632	2.644647
H	-1.079423	-0.221237	3.222984
H	-1.981430	-0.698631	1.776898
H	1.296520	0.074326	3.098555
H	3.388559	0.091033	1.759104
H	3.280143	0.060416	-0.730419
H	1.062462	0.006339	-1.868169
H	-1.025973	-0.014927	-0.523767
H	-5.796271	3.891682	1.249317
H	-7.558347	3.788808	1.528214
H	-5.852347	6.385431	1.742930
H	-8.748058	5.709202	0.912485
H	-10.133505	7.432492	0.168724
H	-10.585038	9.816100	-0.362438
H	-8.794869	11.522338	-0.050258
H	-6.556412	10.825228	0.793552
H	-6.103417	8.457721	1.318579

VIc

70

scf done: -1351.799045

C	-2.575602	6.948039	0.090149
C	-3.438815	5.873252	0.326800
C	-4.756646	6.149443	0.711453
C	-5.199119	7.461820	0.858006
C	-4.327207	8.524562	0.621387
C	-3.013778	8.263686	0.235868
C	-2.964767	4.451675	0.212602
C	-2.733478	3.773233	1.561556
C	-2.321912	2.319526	1.380833
C	-1.985369	1.660536	2.725539
C	-0.917311	2.506674	3.440392
O	-1.418067	3.817009	3.590327
C	-1.668841	4.482277	2.378823
C	-1.703023	0.185544	2.445323
C	-0.533881	-0.075975	1.542834
C	-0.786163	-0.577743	0.260830
C	0.256116	-0.774519	-0.641454
C	1.565380	-0.486786	-0.264371
C	1.828348	0.002679	1.014607
C	0.786036	0.215731	1.911521
C	-0.533313	2.050060	4.827730
O	-1.535708	-0.621803	3.731907
C	-1.016587	-2.019490	3.583064
C	0.266519	-2.189847	4.333476
C	-2.692029	-0.553599	4.692491
H	-2.612910	-0.248259	1.991424
H	-1.820054	-2.671689	3.952762
H	-0.910003	-2.187361	2.504223
H	0.587968	-3.237187	4.228798
H	1.065204	-1.552380	3.928076
H	0.147279	-1.981693	5.407564
H	-2.902218	1.744192	3.338392
H	-1.431966	2.284378	0.721011
H	-3.119269	1.756948	0.861086
H	-3.676793	3.804533	2.144535
H	-0.733952	4.554372	1.775759

H	-1.976176	5.509523	2.633460
H	-0.014251	2.545841	2.790416
H	-1.814434	-0.811333	-0.035837
H	0.042541	-1.160818	-1.641327
H	2.386434	-0.646775	-0.968183
H	2.854764	0.226105	1.316501
H	1.014335	0.599486	2.909969
H	-0.073441	1.050851	4.838318
H	0.183491	2.763894	5.258787
H	-1.419963	2.038637	5.483964
H	-2.024964	4.415543	-0.370107
H	-3.703297	3.854641	-0.353164
H	-1.541604	6.747484	-0.213752
H	-2.323570	9.090842	0.045065
H	-4.673267	9.556018	0.734527
H	-6.233612	7.657819	1.155441
H	-5.447134	5.317051	0.892361
H	-2.982778	0.502183	4.687974
H	-3.499188	-1.160606	4.249640
C	-2.273258	-1.006747	6.030003
C	-2.777746	-2.106451	6.614242
H	-1.541563	-0.375469	6.549172
C	-2.436195	-2.627839	7.935556
H	-3.527131	-2.689891	6.059524
C	-3.131759	-3.743007	8.426628
C	-2.831918	-4.277560	9.676263
C	-1.826723	-3.706578	10.453839
C	-1.122334	-2.599508	9.975570
C	-1.423050	-2.064550	8.729976
H	-3.919917	-4.192246	7.813424
H	-3.385236	-5.145675	10.044563
H	-1.587638	-4.125107	11.435384
H	-0.329975	-2.151596	10.581475
H	-0.857693	-1.200320	8.368399

TS VIc-II

70

scf done: -1351.788277

C	0.485455	-0.181527	0.251822
C	0.073582	-0.000258	1.588844
C	1.038993	-0.050093	2.614041
C	2.375962	-0.271347	2.315478
C	2.766560	-0.447895	0.988089
C	1.821047	-0.403780	-0.041458
C	-1.299726	0.221866	1.953811
C	-2.374332	0.352124	1.114282
C	-3.663145	0.573427	1.632029
O	-4.616094	-1.122922	1.692077
C	-3.710565	-2.165885	2.122157
C	-3.131153	-2.871152	0.929403
C	-5.881719	-1.061844	2.416165
C	-6.558915	-2.412476	2.398234
C	-7.028912	-2.953058	3.598914
C	-7.690072	-4.179548	3.617091
C	-7.874434	-4.888674	2.432786
C	-7.396048	-4.365282	1.232215
C	-6.745748	-3.134309	1.213100

C	-6.768026	0.081424	1.906489
C	-7.941343	0.247482	2.876789
C	-8.843956	1.407559	2.488079
C	-9.244935	1.237001	1.034761
O	-8.121157	1.110168	0.204025
C	-7.315419	-0.020185	0.471822
C	-10.056792	1.499826	3.411884
C	-10.946370	2.677062	3.127229
C	-12.169066	2.521459	2.465925
C	-12.972016	3.623926	2.175850
C	-12.562309	4.903700	2.544592
C	-11.345923	5.072865	3.206162
C	-10.547556	3.968549	3.493524
C	-6.287941	-0.046904	-0.636429
H	-5.631943	-0.822455	3.470918
H	-2.930664	-1.708753	2.757408
H	-4.269505	-2.860226	2.766867
H	-2.431104	-3.651587	1.263292
H	-3.923039	-3.353106	0.335519
H	-2.579710	-2.181737	0.271132
H	-6.189855	1.023581	1.955875
H	-8.549299	-0.679851	2.882011
H	-7.569509	0.381221	3.909519
H	-8.263618	2.350470	2.563058
H	-9.902013	0.340850	0.941515
H	-9.819061	2.104762	0.670250
H	-7.953875	-0.931657	0.417187
H	-6.875300	-2.403676	4.534263
H	-8.054906	-4.585687	4.564402
H	-8.387131	-5.854363	2.444616
H	-7.531578	-4.919591	0.299556
H	-6.371869	-2.740269	0.263420
H	-5.564351	-0.868728	-0.537507
H	-6.798575	-0.138456	-1.606465
H	-5.735982	0.908403	-0.653272
H	-10.638259	0.561919	3.330634
H	-9.694278	1.549104	4.455152
H	-12.495757	1.516325	2.174688
H	-13.925746	3.481034	1.659151
H	-13.191667	5.769658	2.319795
H	-11.019083	6.073616	3.504249
H	-9.595560	4.105571	4.020154
H	-4.416103	1.017426	0.981480
H	-3.777669	0.760612	2.706798
H	-2.252130	0.313167	0.026894
H	-1.491704	0.307243	3.033044
H	0.720968	0.088757	3.651944
H	3.118224	-0.307553	3.116386
H	3.819189	-0.622959	0.749897
H	2.135538	-0.544854	-1.078327
H	-0.246941	-0.150726	-0.559613

4c + II

70

scf done: -1351.793511

C	0.590516	-0.132386	0.556366
C	-0.080705	0.099025	1.786466

C	0.603048	-0.145142	3.006015
C	1.908322	-0.599094	2.996653
C	2.549872	-0.819862	1.773931
C	1.893067	-0.588243	0.557486
C	-1.415584	0.554414	1.848468
C	-2.260382	0.867384	0.769787
C	-3.563455	1.178811	1.010200
O	-4.774618	-1.201020	1.169854
C	-3.688511	-2.013269	1.560809
C	-2.958656	-2.486206	0.333774
C	-5.842655	-1.136857	2.100183
C	-6.493962	-2.490461	2.304320
C	-6.936538	-2.866480	3.575792
C	-7.570771	-4.091056	3.778554
C	-7.756341	-4.965277	2.709969
C	-7.300254	-4.608934	1.441329
C	-6.673824	-3.381415	1.240126
C	-6.820626	-0.036072	1.667572
C	-7.806717	0.258881	2.796669
C	-8.775550	1.375850	2.444734
C	-9.417295	1.045537	1.110042
O	-8.453144	0.824539	0.117059
C	-7.592469	-0.274715	0.360980
C	-9.812847	1.579975	3.547171
C	-10.742733	2.734578	3.302112
C	-12.052923	2.532169	2.855652
C	-12.897617	3.611712	2.600042
C	-12.443067	4.915435	2.788605
C	-11.139331	5.131642	3.234963
C	-10.299505	4.049906	3.488261
C	-6.748268	-0.400601	-0.884832
H	-5.434166	-0.817673	3.087043
H	-3.018446	-1.440325	2.242420
H	-4.048342	-2.874585	2.154180
H	-2.076924	-3.085104	0.607487
H	-3.621301	-3.108916	-0.288790
H	-2.622537	-1.638518	-0.285503
H	-6.217261	0.879216	1.501217
H	-8.398121	-0.653988	3.014191
H	-7.261068	0.501740	3.727799
H	-8.202755	2.317311	2.312096
H	-10.065997	0.146199	1.233188
H	-10.061845	1.868243	0.757650
H	-8.214960	-1.191225	0.492225
H	-6.778697	-2.188345	4.422081
H	-7.912729	-4.366770	4.780222
H	-8.248506	-5.929266	2.866677
H	-7.431531	-5.294589	0.599320
H	-6.306389	-3.115523	0.243766
H	-6.071202	-1.263704	-0.853623
H	-7.406585	-0.487119	-1.762443
H	-6.136396	0.508255	-1.014013
H	-10.396034	0.646639	3.662812
H	-9.277332	1.729872	4.502751
H	-12.415343	1.508144	2.707460
H	-13.919530	3.432132	2.252895
H	-13.105116	5.763528	2.591123
H	-10.775895	6.151830	3.391066

H	-9.277520	4.224099	3.845584
H	-4.256695	1.418886	0.200583
H	-3.942557	1.242631	2.036221
H	-1.889497	0.826704	-0.258659
H	-1.841889	0.673313	2.854730
H	0.082323	0.033305	3.951240
H	2.435626	-0.785306	3.934393
H	3.581874	-1.180700	1.765511
H	2.412435	-0.769256	-0.385771
H	0.078490	0.044883	-0.392571

4c

52

scf done: -1004.182576

C	7.220840	1.391271	2.579088
C	6.595765	0.215667	3.009887
C	7.075873	-1.008221	2.532855
C	8.130797	-1.059088	1.623152
C	8.733690	0.119114	1.187657
C	8.279314	1.344260	1.674632
C	5.425015	0.253922	3.974394
O	5.537053	1.300266	4.905059
C	6.537038	1.110826	5.877114
C	6.602650	2.336200	6.747502
C	4.045944	0.337676	3.303136
C	3.742309	-0.951776	2.544594
C	2.366032	-0.935290	1.900435
C	2.247486	0.328491	1.069133
O	2.500113	1.473515	1.834157
C	3.806449	1.543866	2.385378
C	2.120011	-2.194104	1.071505
C	3.882507	2.893979	3.056524
H	5.428703	-0.716268	4.523333
H	6.307105	0.204691	6.477991
H	7.518773	0.923727	5.394170
H	7.356923	2.215953	7.539156
H	6.869411	3.222470	6.149623
H	5.628553	2.528386	7.223975
H	3.318675	0.430318	4.135939
H	4.495592	-1.092197	1.741835
H	3.841400	-1.823920	3.217760
H	1.599511	-0.876422	2.700887
H	2.959455	0.263246	0.211697
H	1.234845	0.438967	0.645203
H	4.544360	1.491465	1.549072
H	6.620139	-1.939662	2.888042
H	8.490758	-2.026716	1.261230
H	9.565233	0.082773	0.477908
H	8.756783	2.273540	1.349893
H	6.880766	2.354660	2.972424
H	4.883479	3.108872	3.450530
H	3.598109	3.676260	2.336121
H	3.175232	2.930792	3.901645
C	0.733202	-2.283658	0.500338
H	2.866350	-2.234261	0.255312
H	2.315564	-3.073771	1.712264
C	0.482219	-2.028069	-0.851973

C	-0.814273	-2.080692	-1.362726
C	-1.883906	-2.391372	-0.525412
C	-1.647713	-2.649926	0.824975
C	-0.351115	-2.595951	1.329974
H	1.320698	-1.782927	-1.514456
H	-0.989201	-1.878382	-2.423710
H	-2.901462	-2.434882	-0.924587
H	-2.480895	-2.899508	1.488894
H	-0.169014	-2.805415	2.390821

Comprehensive table in AU

M06/Def2-svp CPCM = DCM	H (hartrees)	S (cal/K*mol)	imaginary freq. (cm-1)
DCM	-959.291172	65.937	
$Ag(DCM)_2^+$	-2065.451193	113.472	
3c	-501.829144	112.155	
Ag(DCM)(**3c**)$^+$	-1608.005336	150.085	
TS C-O cleavage	-1607.961310	148.238	-342.6528
Ag(DCM)(OEt)	-1260.451686	111.117	
Cinnamyl cation (**II**)	-347.453425	86.884	
TS II-IIIc	-849.285091	157.534	-204.6774
IIIc	-849.310607	155.746	
TS IIIc-IVc	-849.306473	145.416	-368.1151
IVc	-849.332457	146.745	
TS IVc-Vc	-849.329977	141.433	-271.8465
Vc	-849.341535	142.687	
TS Vc-VIc	-1351.185333	202.517	-168.5970
VIc	-1351.193065	200.259	
TS VIc-II	-1351.184646	200.335	-241.8321
4c + **II**	-1351.191185	207.894	
4c	-1003.732271	164.272	

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