Electronic Supplementary Material

Unusual Regiodivergence in Metal-Catalysed Intramolecular Cyclisation of γ-Allenols

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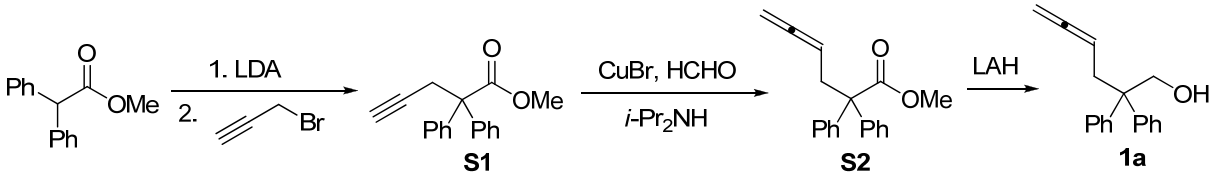
Contents

General Experimental. Preparative chemistry was performed under a dry nitrogen atmosphere, unless noted otherwise. Catalytic reactions were generally performed in air, using a Radley's 12-place reaction carousel. NMR spectra were recorded on a Bruker AVANCE 400 MHz machine operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR in $CDCl_3$ at room temperature, unless otherwise stated. Melting points were recorded using an Electrothermal Gallenhamp apparatus, and were uncorrected. Infrared spectra were recorded using a Perkin Elmer 100 series FT-IR spectrometer, equipped with a beam-condensing accessory (samples were sandwiched between diamond compressor cells). MS were recorded on a Micromass Autospec Premier Spectrometer or a VG Platform II spectrometer using EI, CI or ESI techniques. Chiral HPLC were performed on a Gilson HPLC chromatograph equipped with a Daicel Chiralcel OJ-H column, where UV detection was attained at 254 nm.

Materials. Solvents were dried by passing through columns of molecular sieves in a solvent purification system. All precursors and reagents were used as received from commercial suppliers, unless otherwise stated. Lithium diisopropyl amide (LDA) was generated *in situ* from reaction of *n*-BuLi and diisopropylamine in THF at -78 °C.

Synthesis of terminal allenic alcohols:



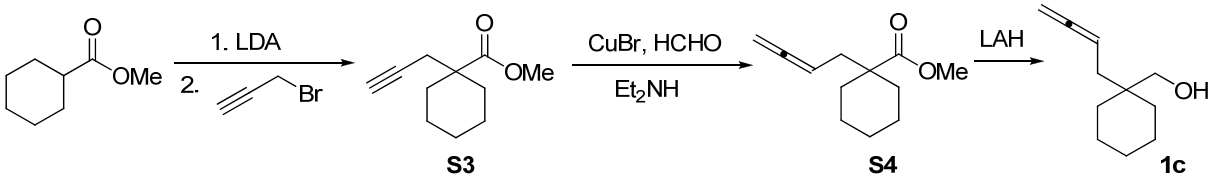
2,2-Diphenylhexa-4,5-dien-1-ol, 1a. Synthesised in three steps using a modified procedure:[1]

(i) Propargylation: A solution of methyl 2,2-diphenylacetate[2] (5.0 g, 22.1 mmol) in dry THF (20 mL) was added dropwise (90 min) to a solution of LDA (2M in THF, 16.6 mL, 33.2 mmol), keeping the temperature below -65 °C. Stirring was continued for 5 hours, before the addition of propargyl bromide (80% in toluene, 2.9 mL, 26.5 mmol). The reaction mixture was left to warm slowly to room temperature and stirred overnight. The resulting mixture was treated with sat. NH_4Cl and extracted with Et_2O (2 x 50 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated under vacuum. The residue was subjected to column chromatography to afford methyl 2,2-diphenylpent-4-ynoate, **S1** as a pale yellow oil (3.0 g, 85%). R_f = 0.38 (hexanes: acetone, 30:1); ν_{max} (thin film)/cm^{-1}: 3317, 3028, 2992, 1736, 1466, 1379, 1229, 1056, 698; δ_H (400 MHz, $CDCl_3$): 7.42-7.25 (10 H, m), 3.77 (3 H, s), 3.32 (2 H, d, J = 2.6), 1.95 (1 H, t, J = 2.6); δ_C (100 MHz, $CDCl_3$): 173.8, 141.3, 128.8, 127.9, 127.3, 80.9, 71.8, 52.7, 29.3; *m/z* (EI): 264 (M^+, 5 %), 225 (83 %), 205 (100 %).

(ii) Crabbé reaction: **S1** (5.3 g, 20.0 mmol) was added to a suspension of paraformaldehyde (1.2 g, 40.0 mmol), copper bromide (1.4 g, 10.0 mmol) and diisopropylamine (2.8 mL, 40.0 mmol) in dioxane (120 mL). The reaction mixture was refluxed for 24 hours, before cooling to room temperature and concentrated under vacuum. The residue was purified by column chromatography to furnish methyl 2,2-diphenylhexa-4,5-dienoate, **S2** as a yellow oil (2.4 g, 43%). R_f = 0.40 (hexanes/ acetone, 40:1); ν_{max} (thin film)/cm^{-1}: 3089, 3058, 2950, 1956, 1731, 1494, 1445, 1223, 1202, 1057, 845, 699; δ_H (400 MHz, $CDCl_3$): δ 7.37-7.22 (10H, m), 4.95-4.83 (1 H, m) 4.48 (1 H, t, *J* = 2.5), 4.46 (1 H, t, *J* = 2.5), 3.73 (3 H, s), 3.14 (2 H, dt, *J* = 2.5, 7.7); δ_C (100 MHz, $CDCl_3$): 210.1, 174.4, 142.2, 129.0, 127.9, 126.9, 85.8, 73.8, 60.6, 52.4, 38.1; *m/z* (CI): 296 ($[MNH_4]^+$, 100%), 279 ($[MH]^+$, 26%), 219 (22%).

(iii) Reduction: A solution of **S2** (5.4 g, 19.4 mmol) in dry Et_2O (70 mL) was added dropwise to a cooled (0 °C) suspension of $LiAlH_4$ (1.2 g, 38.8 mmol) in dry Et_2O (140 mL). The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The mixture was treated with water (1.2 mL), 1M NaOH (1.2 mL) then water (3.6 mL) at 0 °C. The resulting residue was filtered, treated with sat. NH_4Cl and extracted with Et_2O (2 x 25 mL). The combined organic extracts were dried over $MgSO_4$, concentrated under vacuum, and purified by column chromatography to afford pure **1a** (4.1 g, 75%) as a colourless oil. R_f = 0.55 (hexanes/EtOAc, 3:1); ν_{max} (thin film)/cm^{-1}: 3424, 3057, 2932, 2882, 1954, 1495, 1438, 1021, 844, 699; δ_H (400 MHz, $CDCl_3$): 7.41-7.17 (10H, m), 4.79-4.68 (1H, m), 4.55 (1H, t, *J* = 2.4), 4.53 (1H, t, *J* = 2.4), 4.23 (2H d, *J* 5.0), 2.96 (2H, dt, *J* = 2.5, 7.7), 1.47 (1H, br s); δ_C (100 MHz, $CDCl_3$); 209.6, 144.9, 128.3, 126.5, 85.6, 73.9, 68.1, 51.9, 36.3; *m/z* (CI): 268 ($[MNH_4]^+$, 100%), 251 ($[MH]^+$, 3%).

Allenic alcohol **1c** was similarly prepared from methyl cyclohexanecarboxylate:



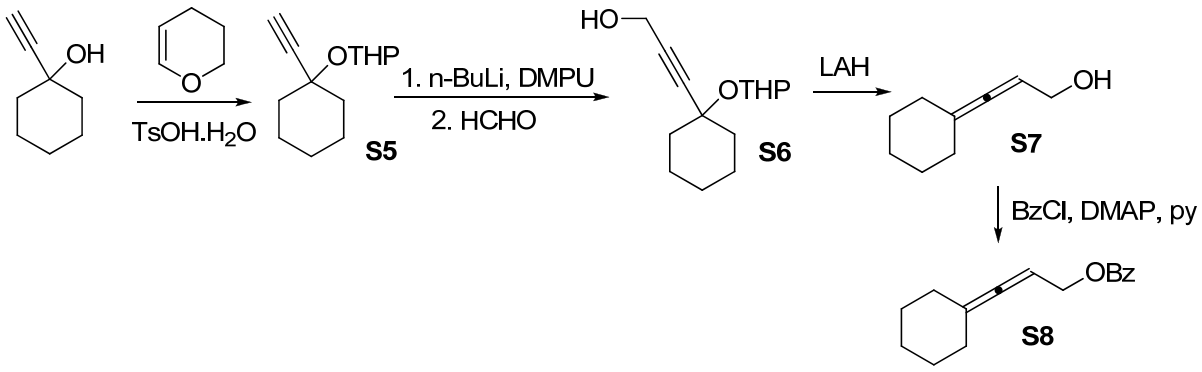
Methyl 1-(prop-2-ynyl)cyclohexanecarboxylate, S3: Yellow oil (5.19 g, 73%). R_f = 0.07 (hexanes: acetone, 20:1); ν_{max} (thin film)/cm^{-1}: 3419, 2923, 2851, 1718, 1599, 1495, 1444, 1026, 979, 754, 696. δ_H (400 MHz, $CDCl_3$): 3.73 (3 H, s), 2.43 (2 H, d, *J* 2.6), 2.09 (2 H, m), 2.03 (1 H, t, *J* 2.7), 1.64-1.51 (3 H, m), 1.50-1.36 (4 H, m), 1.28-1.25 (1 H, m); δ_C (100 MHz, $CDCl_3$): 176.0, 80.3, 70.8, 51.8, 46.7, 33.1, 29.0, 25.5, 22.9; *m/z* (CI): 198 ($[MNH_4]^+$, 100%), 181 ($[MH]^+$, 18%), 52% (11%); HRMS (ESI) 181.1228 (MH^+, $C_{11}H_{17}O_2$ requires 181.1229).

Methyl 1-(buta-2,3-dienyl)cyclohexanecarboxylate, S4: Yellow oil (2.3 g, 40%). R_f = 0.33 (hexanes/ethyl acetate, 20:1); ν_{max} (thin film)/cm^{-1}: 2932, 22854, 1956, 1727, 1453, 1194, 1131, 1079, 841; δ_H (400 MHz,

$CDCl_3$): δ_H (400 MHz, $CDCl_3$) 4.98 (1 H, tt, *J* 6.7, 8.1), 4.65 (1 H, t, *J* 2.5), 4.63 (1 H, t, *J* 2.5) 3.70 (3 H, s), 2.23 (2 H, dt, *J* 2.4, 8.0), 2.14 - 2.01 (2 H, m), 1.65 - 1.50 (3 H, m), 1.43- 1.23 (5 H, m); δ_C (100 MHz, $CDCl_3$): 209.6, 176.7, 85.1, 73.9, 51.5, 47.5, 39.2, 33.6, 25.8, 23.1; *m/z* (CI): 212 ($[MNH_4]^+$, 100%), 195 ($[MH]^+$, 49%), 135 (8%), 52 (11%); HRMS (CI) 195.1388 (MH^+, $C_{12}H_{19}O_2$ requires 195.1385).

(1-(Buta-2,3-dienyl)cyclohexyl)methanol, 1c. The product was obtained as a colourless oil (3.5 g, 76%). R_f = 0.54 (hexanes/ EtOAc, 7.5:2.5); ν_{max} (thin film)/cm^{-1}: 3339, 2922, 2851, 1953, 1452, 1042, 1028, 836; δ_H (400 MHz, $CDCl_3$): 5.11 (1H, tt, *J* = 6.7, 8.3), 4.69 (1H, t, *J* = 2.4), 4.67 (1H, t, *J* = 2.4), 3.48 (2H, close AB), 2.11 (2H, dt, *J* = 2.4, 8.3) 1.47 (6H, m), 1.36 (4H, m); δ_C (100 MHz, $CDCl_3$): 209.4, 85.72, 73.7, 68.6, 38.0, 34.5, 32.2, 26.3, 21.5; *m/z* (CI): 184 ($[MNH_4]^+$, 100%), 167 ($[MH]^+$, 9%), 95 (19%), 52 (20%); HRMS (CI) 184.1704 ($[MH]^+$ requires 184.1701).

Synthesis of internal allenic alcohols:



Preparation of benzoic acid 3-cyclohexylidene-allyl ester, S8. Compounds **S5-S7** were synthesised in 4 steps by modified procedures:[3, 4]

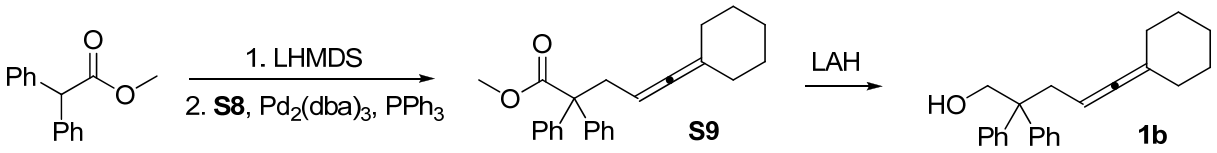
(i) THP protection: p-TsOH.H_2O (30 mg, 0.02 mmol) was added to a cooled (0 °C) solution of 1-ethylnyl-1-cyclohexanol (8.85 g, 71.3 mmol) and 3,4-dihydro-2H-pyran (9.0 g, 107 mmol) in $CHCl_3$ (60 mL), and the mixture was stirred for 2 hours. The resulting solution was washed with sat. $NaHCO_3$ (2 x 50 mL), dried over $MgSO_4$ and concentrated. The residue was purified by distillation to afford compound **S5** as a colourless oil (9.52g, 64%). bp: (120-121 °C, 8 torr) (lit.[5] 101-103, 3.6 torr); ν_{max} (thin film)/cm^{-1}: 3307, 2937, 2860, 1450, 1124, 1070, 909, 869, 850, 625; δ_H (400 MHz, $CDCl_3$): 5.15 (1H, dd, *J* 3.5, 5.0), 4.01-3.94 (1H, m), 3.56-3.49 (1H, m), 2.50 (1H, s), 2.13-2.00 (1H, m), 1.97-1.81 (2H, m), 1.78-1.62 (6H, m) 1.61-1.45 (6H m), 1.33-1.18 (1H, m); δ_C (100 MHz, $CDCl_3$): 95.7, 85.4, 73.9, 72.0, 63.5, 38.6, 38.4, 32.1, 25.4, 25.3, 23.1, 22.9, 20.4; MS (CI): 226 ($[MNH_4]^+$, 15%), 209 ($[MH]^+$, 5%), 102 (100%), 85 (36%).

(ii) Formylation: To a stirring solution of **S5** (9.5 g, 43.2 mmol) in dry THF (65 mL) at -78 °C, *n*-BuLi (1.6M in hexanes, 35.1 mL, 56.2 mmol) was added slowly, keeping the internal temperature below -65°C. After stirring

for 2 hours at -78°C, the solution was warmed to 0 °C and DMPU (10 mL) was added. This was stirred for a further 30 minutes before paraformaldehyde (2.6 g, 86.4 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature and stirred overnight, before quenching with sat. NH_4Cl (15 mL). The solution was extracted with Et_2O and the combined organic extracts washed with brine, dried over $MgSO_4$ and the solvent evaporated. The crude material was purified by column chromatography to afford compound **S6** as a colourless oil (6.4 g, 63%). R_f = 0.37 (hexanes/EtOAc 7.5:2.5); ν_{max} (thin film)/cm^{-1}: 3350, 3310, 2974, 2928, 2890, 1455, 1381, 1330, 1090, 1050, 881; δ_H (400 MHz, $CDCl_3$): 5.14 (1H, t, *J* = 4.2), 4.34 (2H, d, *J* = 5.6), 4.02-3.93 (1H, m), 3.56-3.49 (1H, m), 2.0-1.97 (2H, m), 1.87-1.85 (2H, m), 1.75-1.65 (5H, m), 1.60-1.47 (7H, m), 1.32-1.21 (1H, m); δ_C (100 MHz, $CDCl_3$): 95.4, 87.2, 84.3, 74.7, 63.3, 51.2, 38.8, 32.1, 25.4, 23.3, 20.2; *m/z* (CI): 256 ($[MNH_4]^+$, 100%), 239 ($[MH]^+$, 5%), 221 (78%), 203 (60%), 102 (93%).

(iii) Reduction: A solution of **S6** (6.0 g, 25.2 mmol) in THF (30 mL) was added slowly to a stirred suspension of $LiAlH_4$ (3.8 g, 100.7 mmol, 4 equiv) in THF (65 mL) at 0 °C. The reaction was stirred overnight, quench with water (3.5 mL), 2N NaOH (3.5 mL) and water (10.5 mL). The crude product was purified by column chromatography to afford **S7** as a colourless oil (2.55 g, 73%). R_f = 0.4 (hexanes/EtOAc, 7.5:2.5); ν_{max} (thin film)/cm^{-1}: 3400, 2924, 2854, 1959, 1719, 1458, 1377, 1047, 721; δ_H (400 MHz, $CDCl_3$): 5.23 (1H, m), 4.09 (2H, d, *J* = 5.6), 2.22-2.09 (4H, m), 1.65-1.52 (6H, m), 1.48 (1H, s); δ_C (100 MHz, $CDCl_3$): 197.2, 105.9, 89.7, 61.1, 32.8, 27.4, 26.0; *m/z* (EI): 138 (M^+, 8%), 84 (72%), 55 (78%), 49 (100%).

(iv) Benzoylation: To a stirred solution of **S7** (2.5 g, 18.5 mmol), DMAP (226 mg, 1.85 mmol) and pyridine (1.79 mL, 22.2 mmol) in CH_2Cl_2 (20 mL) at 0 °C, benzoyl chloride (3.2 mL, 27.8 mmol) was added dropwise. After stirring overnight at room temperature, the resulting suspension was diluted with CH_2Cl_2 (100 mL), washed with 1N HCl (2 x 50 mL), water (50 mL) and aq. $NaHCO_3$ (50 mL). The organic extracts were combined, dried over $MgSO_4$ and concentrated under vacuum. The crude material proved to be unstable on silica gel, so was purified to a moderate standard, and used immediately in the next step. Compound **S10** was obtained as a pale yellow oil (4.40 g, 98%). R_f = 0.38 (hexanes/EtOAc, 20:1); δ_H (400 MHz, $CDCl_3$): 8.23-7.99 (2 H, m), 7.62-7.55 (1H, m), 7.50-7.43 (2 H, m), 5.26 (1H, m), 4.80 (2H, d, *J* = 6.4), 2.25-2.10 (4H, m), 1.71-1.44 (6H, m).



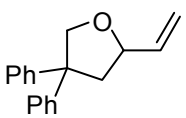
S9 was synthesised by a modified procedure:[4] At -78 °C, LHMDS (1 M in THF, 50.7 mL, 50.7 mmol) was added dropwise, over 1 h, to a solution of methyl 2,2-diphenylacetate (11.5 g, 50.7 mmol) in dry THF (100

mL). Stirring was continued for 2 hours at -78 °C. Meanwhile, a mixture of $Pd_2(dba)_3$[6] (0.583 g, 10 mol%) and PPh_3 (0.798 g, 30 mol%) was stirred in dry THF (30 mL) for 1 h at room temperature. **S8** (2.5 g, 10.1 mmol) was added to this catalytic mixture and stirred for a further 2 h, before the mixture was transferred by syringe into the first solution at -78 °C. The combined mixture was warmed to room temperature stirred overnight. The reaction was quenched with sat. NH_4Cl and extracted with Et_2O. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography to afford **S9** as a colourless oil (2 g, 58%). R_f = 0.38 (hexanes: EtOAc, 20:1); ν_{max} (thin film)/cm^{-1}: 2926, 2852, 1965, 1728, 1599, 1495, 1445, 1219, 1058, 1025, 728, 696; δ_H (400 MHz, $CDCl_3$) 7.37-7.18 (10H, m), 4.73 (1H, s), 3.72 (3H, s), 3.12 (2H, d, *J* 7.4), 1.96-1.84 (4H, m), 1.56-1.41 (6 H, m); δ_C (100 MHz, $CDCl_3$): 200.5, 174.6, 142.5, 129.1, 127.8, 126.7, 101.8, 84.4, 60.5, 52.4, 39.5, 31.1, 27.3, 26.1; *m/z* (CI): 364 ($[MNH_4]^+$, 100%), 347 ($[MH]^+$, 17%), 287 (21%), 268 (34%); HRMS (EI) 347.2015 (MH^+ $C_{24}H_{27}O_2$ requires 347.2011).

Reduction: A solution of **S9** (1.6 g, 7.2 mmol) in Et_2O (100 mL) was added slowly to a stirring suspension of $LiAlH_4$ (1.09 g, 28.8 mmol) in Et_2O (15 mL) at 0 °C and left overnight. The reaction was quenched by successive addition of H_2O (3.5 mL), 1N NaOH (3.5 mL), and H_2O (10.5 mL). The resulting suspension was filtered and the filtrate was extracted with Et_2O (2 x 15 mL). The combined organic extracts were dried over $MgSO_4$, concentrated under vacuum and purified by column chromatography, to afford **1b** as a white solid (0.80 g, 47%). R_f = 0.13 (hexanes/EtOAc, 20:1); mp 49-55 °C. ν_{max} (thin film)/cm^{-1}: 3558, 3058, 2921, 2851, 1964, 1494, 1444, 1234, 1069, 1044, 1044, 754, 695; δ_H (400 MHz, $CDCl_3$): 7.36-7.16 (10 H, m), 4.70-4.60 (1H, m), 4.21 (2H, s), 2.90 (2H, d, *J* 7.6), 1.98 (4H, d, *J* 4.9), 1.54-1.46 (6H, m); δ_C (100 MHz, $CDCl_3$): 200.2, 145.2, 128.4, 128.2, 122.9, 101.7, 84.2, 68.4, 52.2, 37.8, 31.3, 27.4, 26.1; *m/z* (EI): 318 (M^+,5%), 287 (64%), 227 (40%), 197 (100%), 105 (91%), 91 (82%); HRMS (EI) 318.1983 (M^+, $C_{23}H_{26}O$ requires 318.1984).

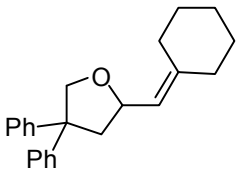
Typical procedure for catalytic reactions:

A Radley's reaction tube was charged with a magnetic stir bar, the catalyst AgOTf, $Sn(OTf)_2$ or $Zn(OTf)_2$ (0.06 mmol) and the corresponding γ-allenic alcohol (**1a**, **1b** or **1c**) (0.4 mmol). A PTFE screwcap was fitted, and DCE (0.3 mL) was added to the contents of the tube *via* syringe through the rubber septum. The tube was then positioned in a reaction carousel, and left to stir at room temperature. Conversions were monitored by TLC and/or NMR integration. Upon completion, the solvent was evaporated and the residue purified by column chromatography (hexanes/EtOAc, 20:1).

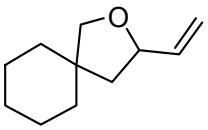


4,4-Diphenyl-2-vinyltetrahydrofuran, 2a.[1] Colourless oil. R_f = 0.26; 5% IPA in *n*-hexane, 1.0 mL/min, t_R(major) = 13.5, t_R(minor) = 17.9; ν_{max} (thin film)/cm^{-1}: 2866, 1493, 1445,

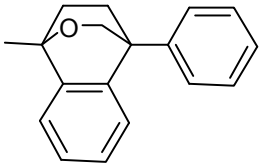
1054, 987, 925, 874, 842, 755, 696; δ_H (400 MHz, $CDCl_3$): 7.40-7.17 (10 H, m), 5.93 (1H, ddd, *J* 6.9, 10.2, 17.1), 5.28 (1H, d, *J* 17.1), 5.14 (1H, d, *J* 10.2), 4.71 (1H, d, *J* 8.7), 4.52-4.42 (1H, m), 4.19 (1H, d, *J* 8.7), 2.69 (1H, dd, *J* 5.9, 12.1), 2.48 (1H, dd, *J* 9.7, 12.1); δ_C (100 MHz, $CDCl_3$): 146.0, 145.6, 138.8, 128.5, 128.4, 127.3, 127.2, 126.5, 126.3, 115.9, 79.72, 76.7, 56.2, 45.2; (CI): 268 ($[MNH_4]^+$, 100%), 251 ($[MH]^+$, 4%), 269 (33%).



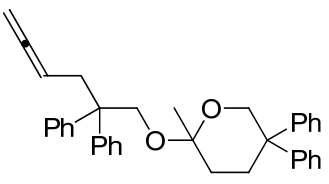
2-(Cyclohexylidenemethyl)-4,4-diphenyltetrahydrofuran, 2b. Colourless oil. R_f = 0.31; ν_{max} (thin film)/cm^{-1}: 2924, 2863, 1668, 1486, 1446, 1143, 1045, 1003, 754, 702, 696; δ_H (400 MHz, $CDCl_3$): 7.40-7.18 (10 H, m), 5.26 (1H, d, *J* 8.7), 4.80 (1H, td, *J* 5.9, 9.3), 4.66 (1H, d, *J* 8.7), 4.18 (1H, d, *J* 8.7), 2.64 (1H, dd, *J* 5.9, 12.2), 2.42 (1H, dd, *J* 9.7, 12.2), 2.26-2.03 (4 H, m), 1.53 (7H, dd, *J* 11.5, 40.4); δ_C (100 MHz, $CDCl_3$): 146.3, 146.1, 144.1, 128.4, 128.3, 127.2, 126.4, 126.2, 122.5, 76.9, 74.3, 56.4, 45.8, 37.1, 29.2, 28.31, 27.8, 26.7; *m/z* (EI): 318 (M^+, 100%), 288 (54%), 241 (48%), 205 (60%), 81 (68%); HRMS (EI) 318.1985 (M^+, $C_{23}H_{26}O$ requires 318.1984).



3-Vinyl-2-oxaspiro[4.5]decane, 2c. Colourless oil. R_f = 0.28; ν_{max} (thin film)/cm^{-1}: 2922, 2880, 1605, 1449, 1051, 987, 917, 848; δ_H (400 MHz, $CDCl_3$): 5.88 (1H, ddd, *J* 6.7, 10.3, 17.0), 5.27-5.20 (1H, m), 5.11-5.08 (1H, m), 4.37 (1H, dd, *J* 6.7, 15.5), 3.62 (2H, dd, *J* 8.4, 27.9), 1.95 (1H, dd, *J* 6.8, 12.5), 1.58-1.35 (11H, m); δ_C (100 MHz, $CDCl_3$): 139.5, 115.1, 79.7, 78.6, 44.8, 44.1, 36.8, 35.5, 26.0, 24.1, 23.6; *m/z* (CI): 350 ($[MNH_4]^+$, 4%), 333 ($[MH]^+$, 2%), 184 (23%), 167 (100%), 153 (18%); HRMS (CI) 167.1430 (MH^+, $C_{11}H_{19}O$ requires 167.1436).

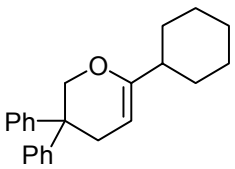


4: Isolated as a crystalline solid (recrystallised from hexane). mp: 83-86°C; R_f = 0.23; ν_{max} (thin film)/cm^{-1}: 2950, 2932, 2858, 1459, 1377, 1072, 1045, 767, 756, 708; δ_H (400 MHz, $CDCl_3$) 7.49-7.15 (8H, m), 6.76 (1H, d, *J* 7.4), 4.07 (1H, d, *J* 7.7), 3.88 (1H, dd, *J* 3.5, 7.7), 2.34-2.18 (2H, m), 2.09-1.94 (1H, m), 1.75 (3H, s), 1.69-1.59 (1H, m); δ_C (100 MHz, $CDCl_3$): 143.24, 142.57, 140.25, 128.54, 127.44, 127.18, 127.14, 126.24, 123.32, 120.30, 72.23, 71.35, 42.83, 33.69, 29.27, 21.87. *m/z* (CI): 268 ($[MNH_4]^+$, 100%), 251 ($[MH]^+$, 33%), 220 (11%), 52 (57%); HRMS (ESI) 251.1431 (MH^+, $C_{18}H_{19}O$ requires 251.1436).

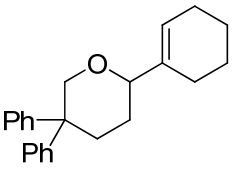


5: Isolated as a crystalline solid (recrystallised from hexane). R_f = 0.27; mp: 102-108°C. ν_{max} (thin film)/cm^{-1}: 2924, 2853, 1954, 1493, 1445, 1204, 1055, 1039, 1021, 879, 750, 696; δ_H (400 MHz, $CDCl_3$): 7.37 - 7.09 (17 H, m), 7.00-6.95 (1H, m), 6.89 - 6.82 (2H, m), 4.70 - 4.56 (1H, m), 4.54 - 4.36 (2H, m), 4.15 (1H, d, *J* = 8.4), 3.94 (1H, dd, *J* = 2.8, 11.9), 3.89 (1H, d, *J* = 8.4), 3.20 - 3.08 (1H, m), 2.95 - 2.87 (1H, m), 2.85 (1H, d, *J* =

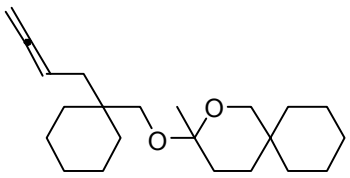
11.9), 2.42 - 2.32 (1H, m), 1.97 (1H, dd, *J* = 3.2, 12.6), 1.62 (1H, dt, *J* = 3.3, 13.3), 1.29 (1H, dd, *J* = 3.8, 13.3), 1.22 (3H, s); δ_C (100 MHz, $CDCl_3$): 209.7, 146.5, 146.2, 146.1, 145.6, 128.5, 128.2 , 128.0, 127.9, 127.8, 127.7, 127.2, 126.0, 125.9, 125.6, 97.0, 85.9, 73.6, 67.5, 64.9, 50.3, 45.0, 36.3, 32.3, 29.3, 23.9; Product fragmentised using MS. *m/z* (CI): 268 ([MNH_4^+], 20%), 251 ([MH^+], 100%).



6-cyclohexyl-3,3-diphenyl-3,4-dihydro-2H-pyran, 6a: Isolated as a white solid. R_f = 0.28; mp: 82-84°C. ν_{max} (thin film)/cm^{-1}: 2922, 2856, 1598, 1493, 1445, 1131, 1074, 1056, 1005, 772, 755, 697; δ_H (400 MHz, CDCl3) 7.52 - 7.11 (10 H, m), 5.75-5.71 (1 H, m), 4.69 (1 H, d, *J* 12.0), 3.80 (1 H, d, *J* 10.9), 3.59 (1 H, d, *J* 12.0), 2.49 (2 H, dd, *J* 3.6, 9.0), 2.03 (3 H, s), 1.90 (1 H, s), 1.68 - 1.40 (11 H, m); δ_C (100 MHz, $CDCl_3$): 146.73, 145.98, 138.53, 129.07, 128.24, 127.89, 127.04, 126.26, 125.59, 123.36, 82.38, 75.10, 45.88, 34.92, 29.69, 26.54, 24.97, 24.29, 22.63, 22.52; *m/z* (CI): 336 ([MNH_4]$^+$, 100%), 319 ([MH]$^+$, 51%), 301 (49%); HRMS (ESI) 319.2054 (MH^+, $C_{23}H_{27}O$ requires 319.2062).



2-cyclohexenyl-5,5-diphenyltetrahydro-2H-pyran, 6b: Isolated as a colourless oil. R_f = 0.26; ν_{max} (thin film)/cm^{-1}: 3023, 2924, 2862, 1668, 1597, 1492, 1446, 1144, 1044, 1003, 939, 857, 780, 753, 696, 680; δ_H (400 MHz, $CDCl_3$): 7.53 - 6.99 (10 H, m), 5.50 (1 H, m), 4.61 (1 H, d, *J* 8.7), 4.26 - 4.19 (1 H, m), 4.19-4.16 (1 H, m), 2.62 (1 H, dd, *J* 5.8, 12.2), 2.40 - 2.28 (2 H, m), 2.14 (1 H, dd, *J* 5.9, 14.0), 2.03 - 1.93 (4 H, m), 1.67 - 1.52 (4 H, m); δ_C (100 MHz, $CDCl_3$): 146.44, 146.18, 134.78, 128.35, 128.28, 127.18, 127.14, 126.34, 126.14, 123.22, 55.87, 44.87, 44.68, 28.83, 25.25, 22.89, 22.33. *m/z* (CI): 336 ([MNH_4]$^+$, 100%), 319 ([MH]$^+$, 38%), 240 (78%), 223 (33%); HRMS (ESI) 319.2053 (MH^+, $C_{23}H_{27}O$ requires 319.2062).



7: Isolated as a colourless oil. R_f = 0.56; ν_{max} (thin film)/cm^{-1}: 2921, 2850, 1954, 1451, 1371, 1245, 1201, 1104, 1044, 883, 836, 765; Two conformational isomers can be identified in solution (ratio = 1 : 1.26); δ_H (400 MHz, C_7D_8, 373K), 5.05 (minor, 1 H, tt, *J* 6.7, 8.0), 4.92 (major, 1 H, tt, *J* 6.7, 8.1), 4.47 (minor, 2 H, dt, *J* 2.6, 6.7), 4.43 (major, 2 H, dt, *J* 2.5, 6.7), 3.46 - 3.44 (minor, 2 H, m), 3.38-3.26 (major, 2 H, m), 3.22-3.14 (major, 2 H, m), 3.16-3.15 (minor, 2 H, m), 2.14-2.07 (minor, 2 H, m), 1.93 (major, 2 H, dt, *J* 2.5, 8.1), 1.63 - 1.59 (3 H, m), 1.52-1.49 (2 H, m), 1.40- 1.10 (48 H, m), 1.04-0.97 (1 H, m); Due to the existence of two conformational isomers the carbon spectra was too complicated to be assigned. *m/z* (CI): 350 ([MNH_4]$^+$, 2%), 333 ([MH]$^+$, 4%), 184 (24%), 167 (100%), 153 (17%); HRMS (CI) 333.2798 (MH^+, $C_{22}H_{37}O_2$ requires 333.2794).

X-Ray Crystallography

Crystal data for **4**: $C_{18}H_{18}O$, $M = 250.32$, orthorhombic, $Pna2_1$ (no. 33), $a = 14.1920(13)$, $b = 12.8979(13)$, $c = 7.4178(6)$ Å, $V = 1357.8(2)$ Å^3, $Z = 4$, $D_c = 1.225$ g cm^{-3}, μ(Mo-Kα) = 0.074 mm^{-1}, $T = 173$ K, colourless platy needles, Oxford Diffraction Xcalibur 3 diffractometer; 2203 independent measured reflections ($R_{int} = 0.0798$), F^2 refinement, R_1(obs) = 0.050, wR_2(all) = 0.098, 1140 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 55°$], 172 parameters. The absolute structure of **3** could not be determined by either *R*-factor tests [$R_1^+ = 0.0497$, $R_1^- = 0.0497$] or by use of the Flack parameter [$x^+ = +0(3)$, $x^- = +1(3)$]. CCDC726110.

Crystal data for **5**: $C_{36}H_{36}O_2$, $M = 500.65$, monoclinic, $P2_1/c$ (no. 14), $a = 6.3771(3)$, $b = 19.8345(8)$, $c = 23.2868(12)$ Å, $\beta = 97.321(4)°$, $V = 2921.5(2)$ Å^3, $Z = 4$, $D_c = 1.138$ g cm^{-3}, μ(Cu-Kα) = 0.530 mm^{-1}, $T = 293$ K, colourless needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 4532 independent measured reflections ($R_{int} = 0.0278$), F^2 refinement, R_1(obs) = 0.048, wR_2(all) = 0.128, 2460 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 126°$], 357 parameters. CCDC726111.

The crystals of **4** and **5**, neither of which contains any atoms heavier than oxygen, both grew as thin needles. It was not surprising, therefore, that they were both weak scatterers of X-rays, and this led to the data collections being trimmed to 45° and 120° in 2θ for **4** and **5** respectively. Compound **4** crystallised in a polar space group, $Pna2_1$ (no. 33), but it proved impossible to determine the correct absolute structure, which was not surprising given the lack of any atoms heavier than oxygen and the use of Mo-Kα radiation. The terminal C(11)=C(12)=C(13) unit in the structure of **5** was found to be disordered. Two orientations were identified of *ca.* 80 and 20% occupancy, and the equivalent bond lengths and angles of the two orientations were lightly restrained to be equal. Only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically. The positions of the C(13) and C(13') protons in the structure of **5** were calculated on the basis of trigonal planar geometries at C(13) and C(13'), and the assumption that these planes would be coplanar with the C(10)–C(11) bond. Once placed, these protons were allowed to ride on their parent atoms.

Fig. S1 The molecular structure of **4** (50% probability ellipsoids).

Fig. S2 The molecular structure of **5** (30% probability ellipsoids).

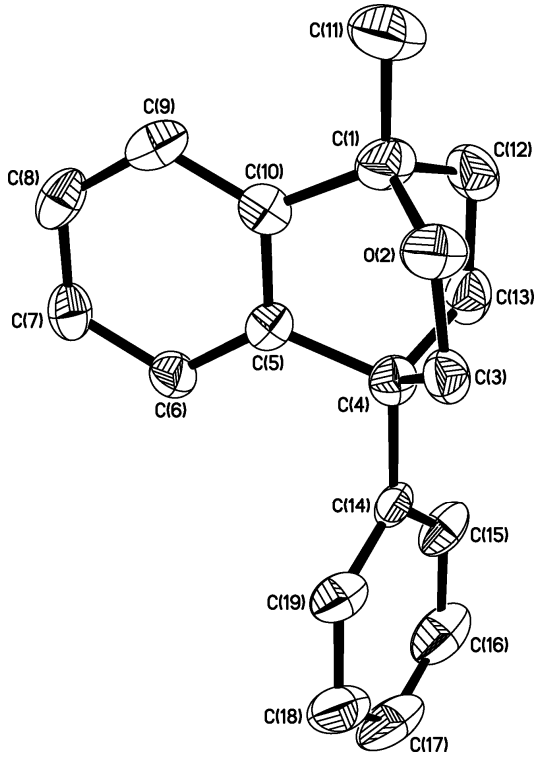

C(11)
C(9)
C(1)
C(12)
C(8)
C(10)
O(2)
C(13)
C(7)
C(5)
C(3)
C(6)
C(4)
C(14)
C(15)
C(19)
C(16)
C(18)
C(17)

Fig. S1

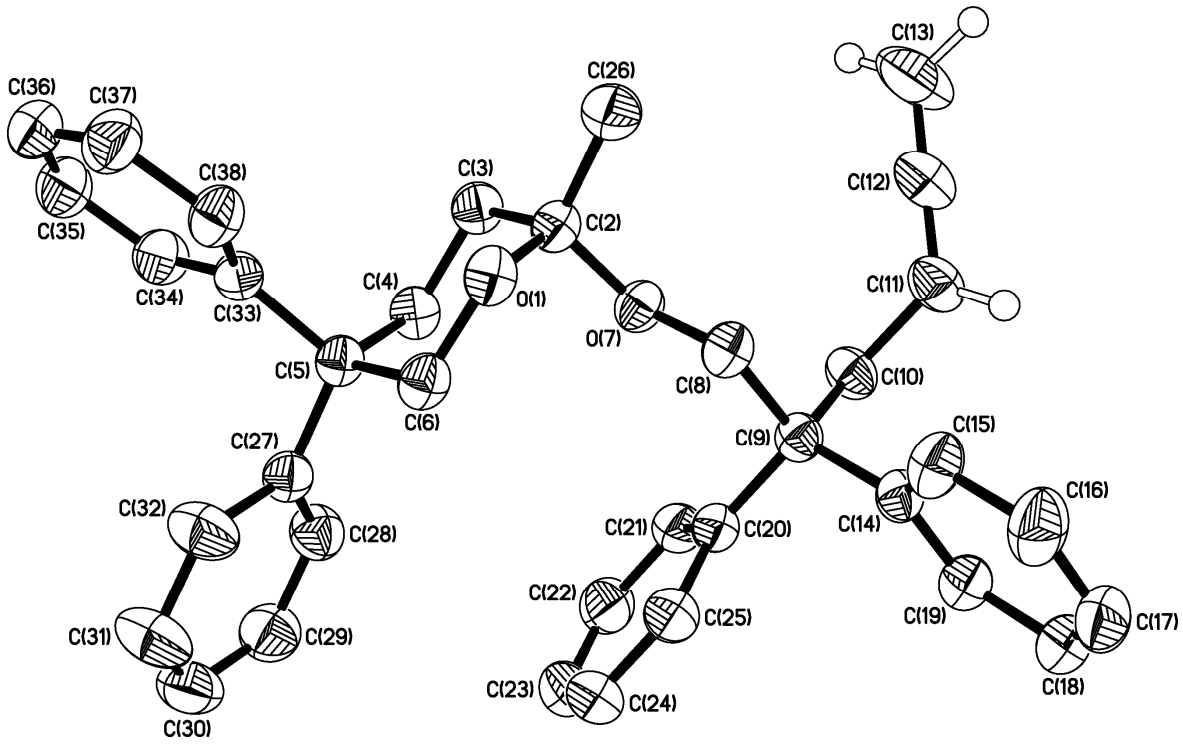

C(13)
C(26)
C(36)
C(37)
C(3)
C(12)
C(38)
C(2)
C(35)
C(4)
O(1)
C(11)
C(34)
C(33)
O(7)
C(5)
C(8)
C(10)
C(6)
C(27)
C(9)
C(15)
C(32)
C(28)
C(21)
C(20)
C(14)
C(16)
C(22)
C(25)
C(19)
C(17)
C(31)
C(29)
C(23)
C(24)
C(18)
C(30)

Fig. S2

References

1. Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc*. **2006**, *128*, 9066.

2. Klamo, S. B.; Wendt, O. F.; Henling, L. M.; Day, M. W.; Bercaw, J. E. *Organometallics* **2007**, *26,* 3018.

3. Zhang, Z.; Bender, C. F.; Widenhoefer, R. A. *Org. Lett*., **2007**, *9*, 2887.

4. Löfstedt, J.; Franzén, J.; Bäckvall, J-E. *J. Org. Chem*. **2001**, *66*, 8015.

Figure S3a. ^{1}H NMR spectra of **1a**.

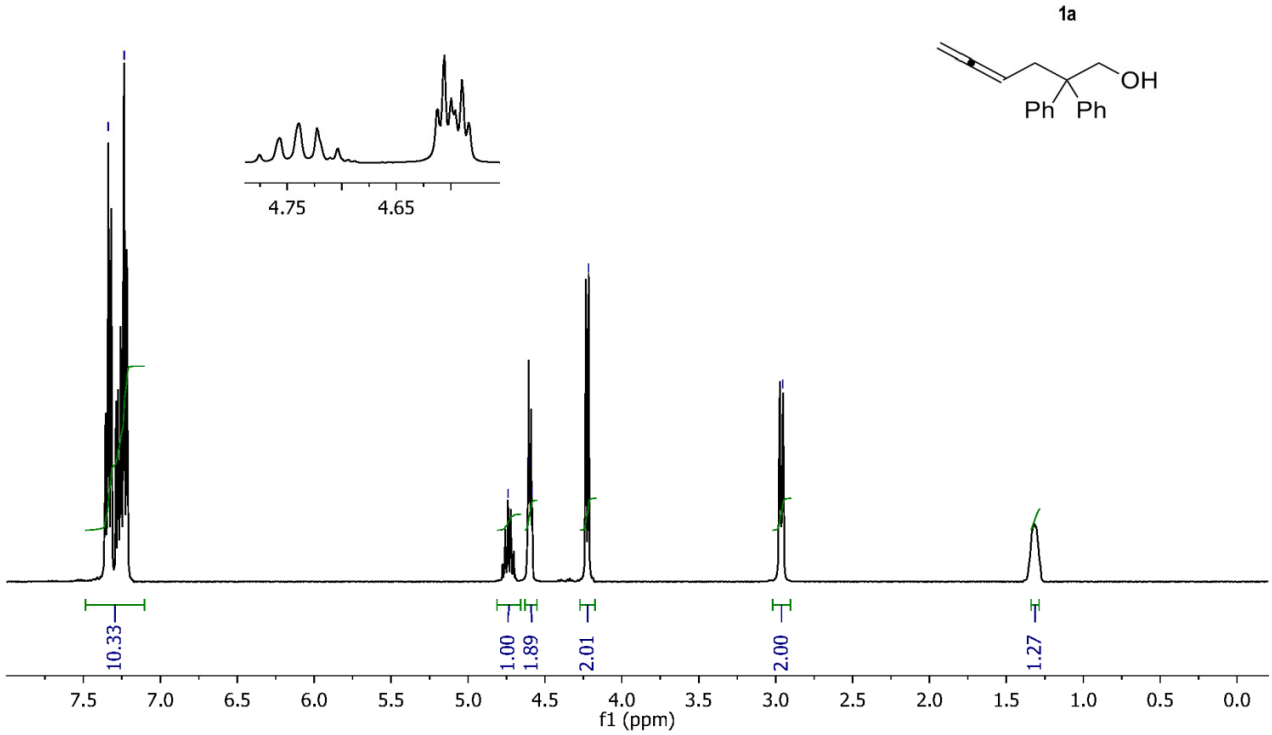


Figure S3a. ^{13}C NMR spectra of **1a**.

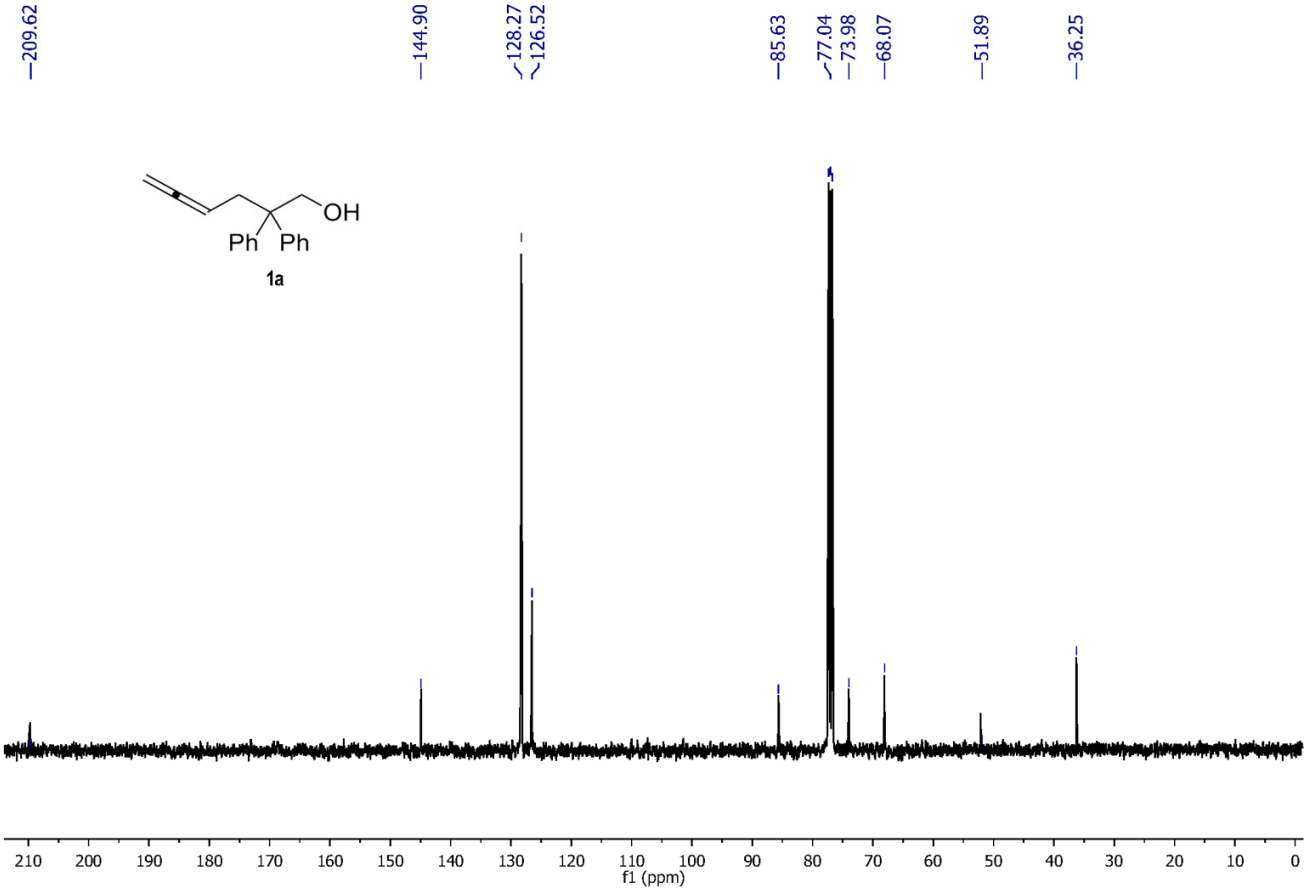


Figure S4a. ^{1}H NMR spectra of **1b**.

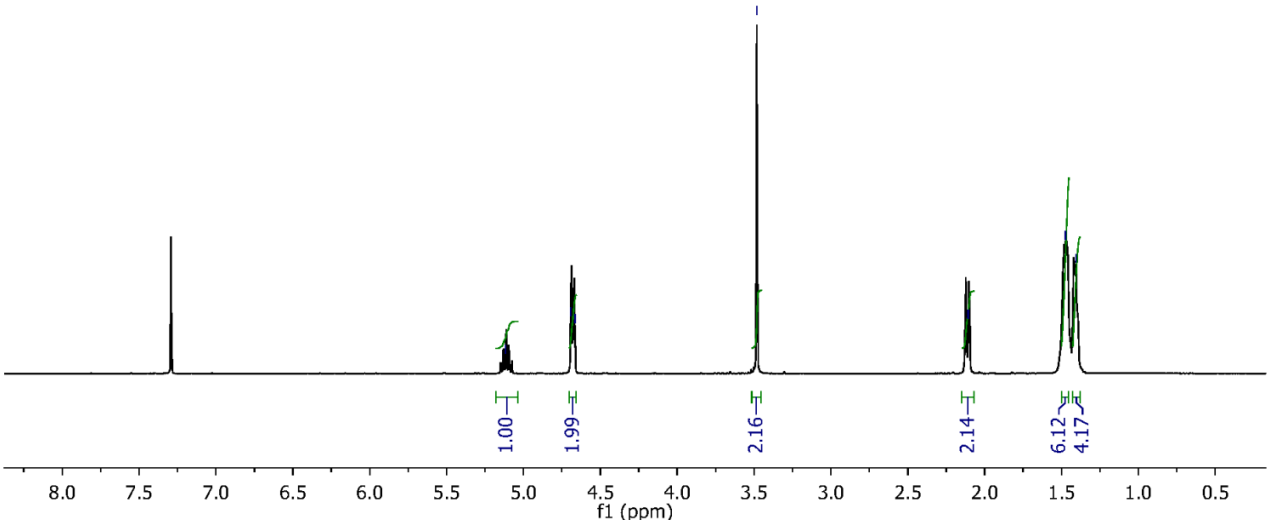


Figure S4b. ^{13}C NMR spectra of **1b**.

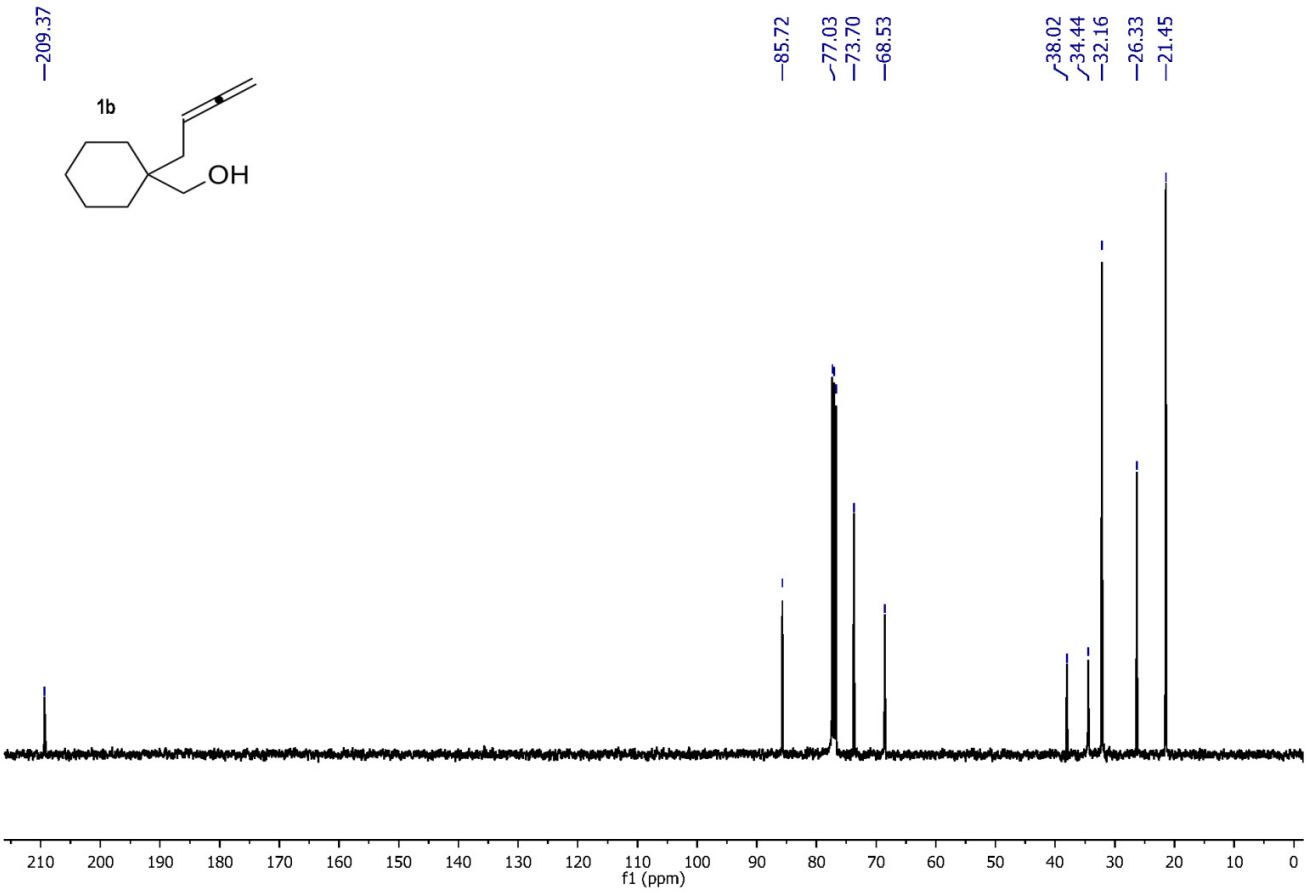


Figure S5a. ^{1}H NMR spectra of **1c**.

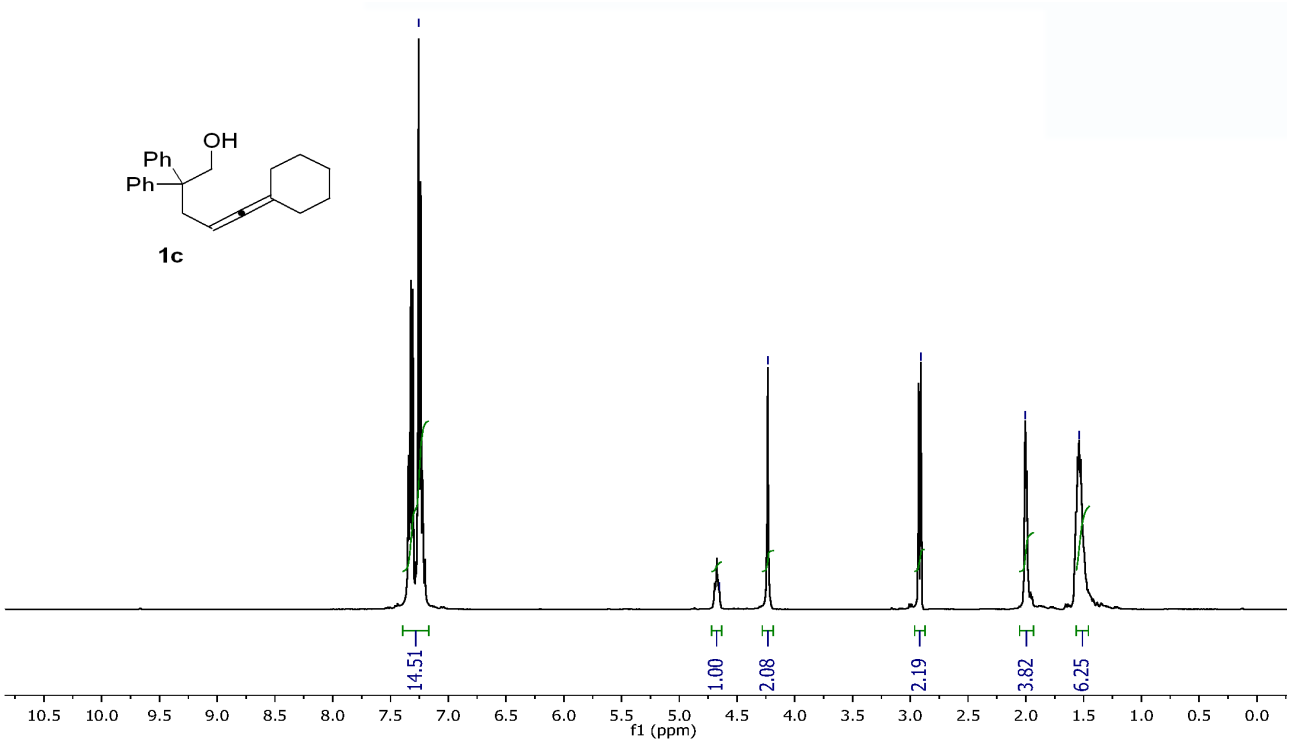


Figure S5b. ^{13}C NMR spectra of **1c**.

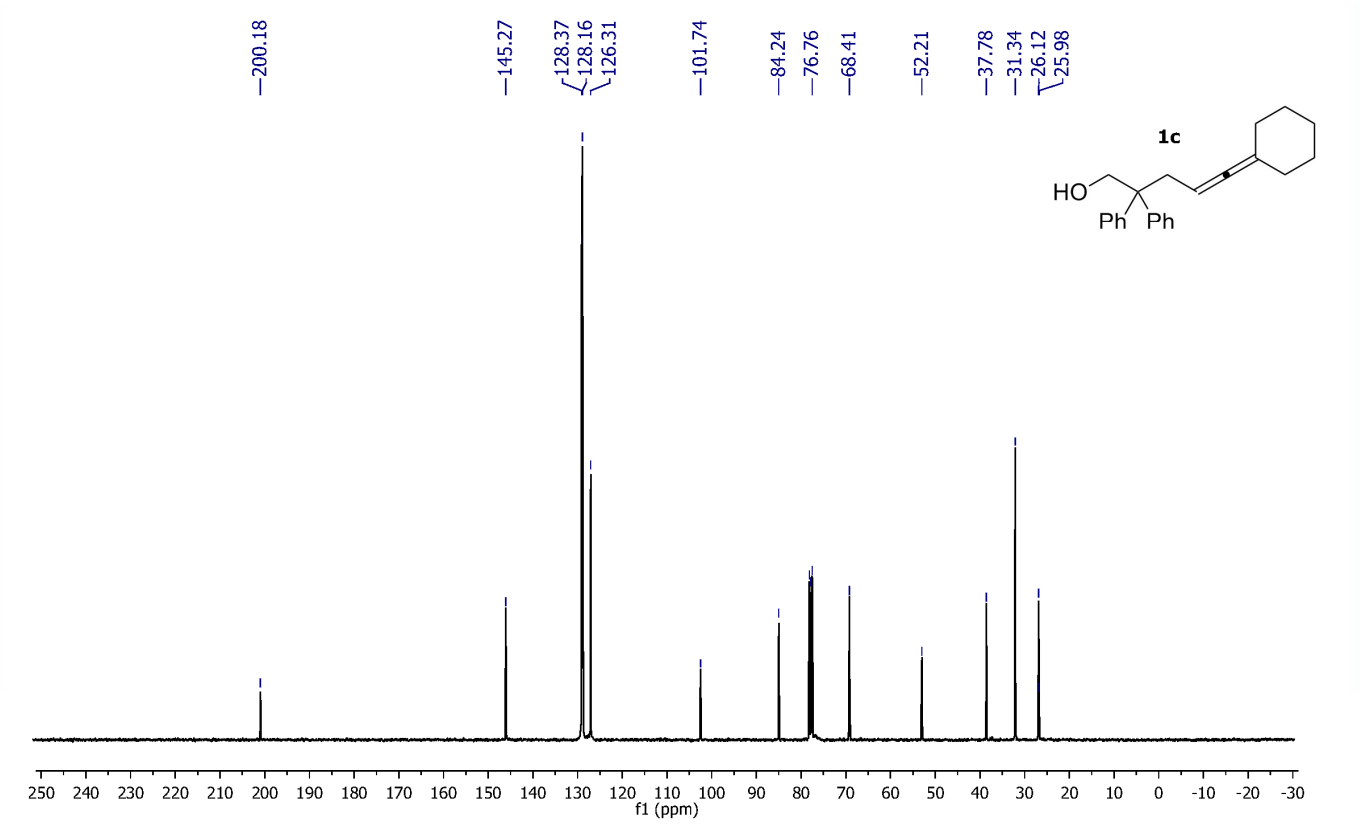


Figure S6a. ^{1}H NMR spectra of **2a**.

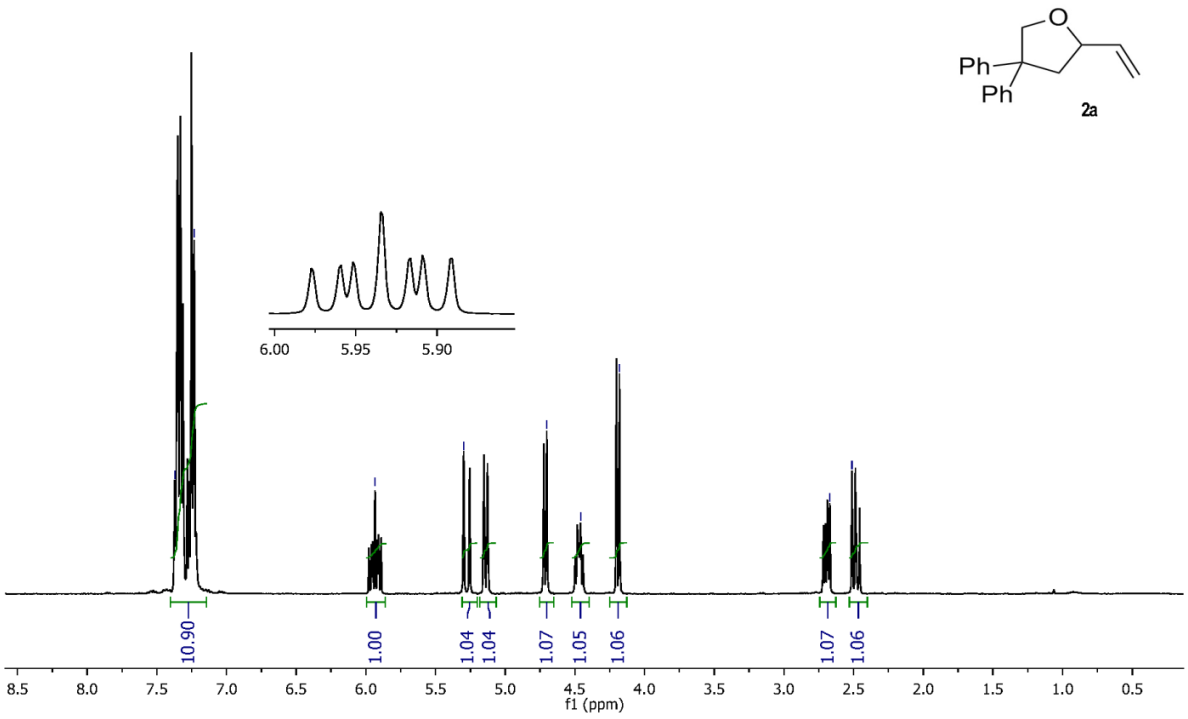


Figure S6b. ^{13}C NMR spectra of **2a**.

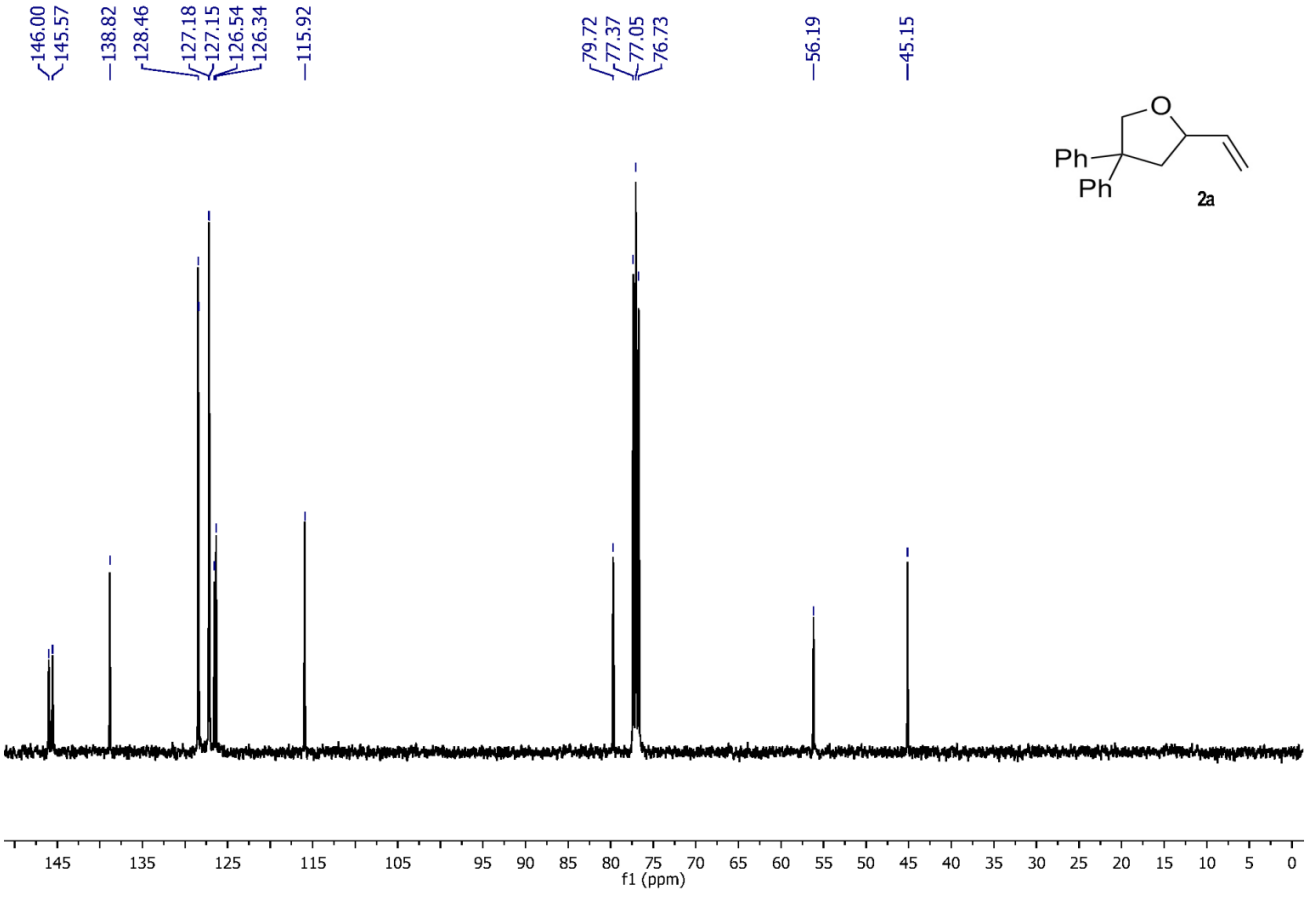


Figure S7a. ^{1}H NMR spectra of **2b**.

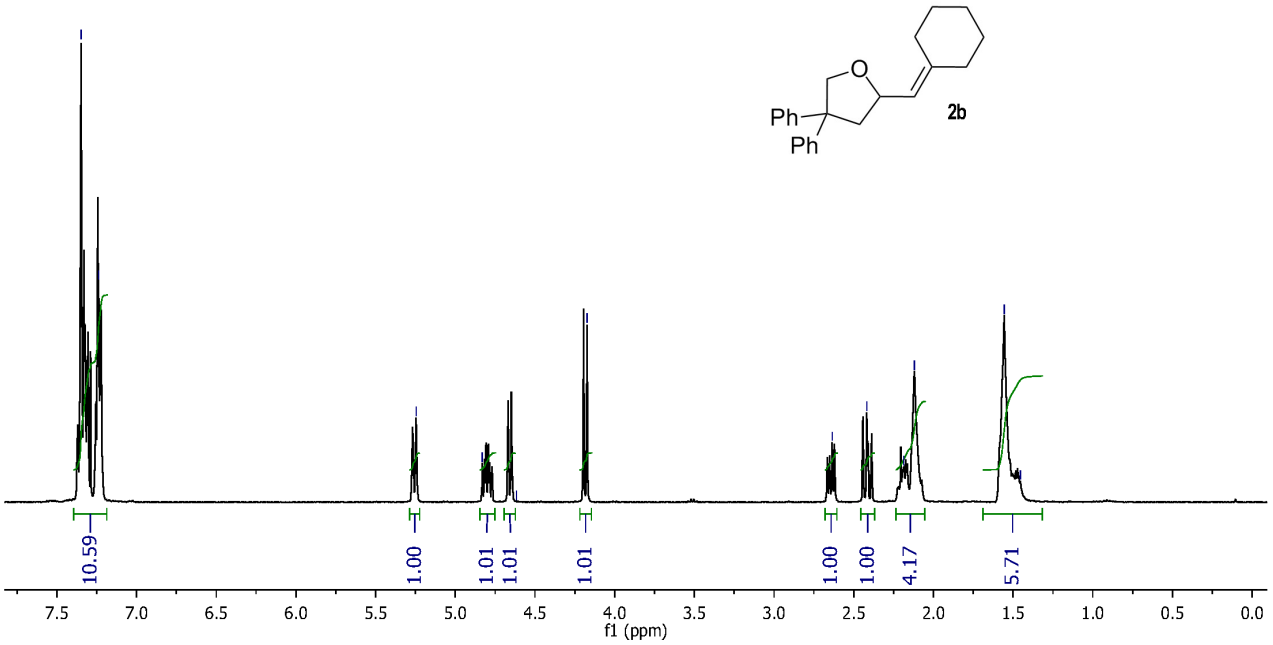


Figure S7b. ^{13}C NMR spectra of **2b**.

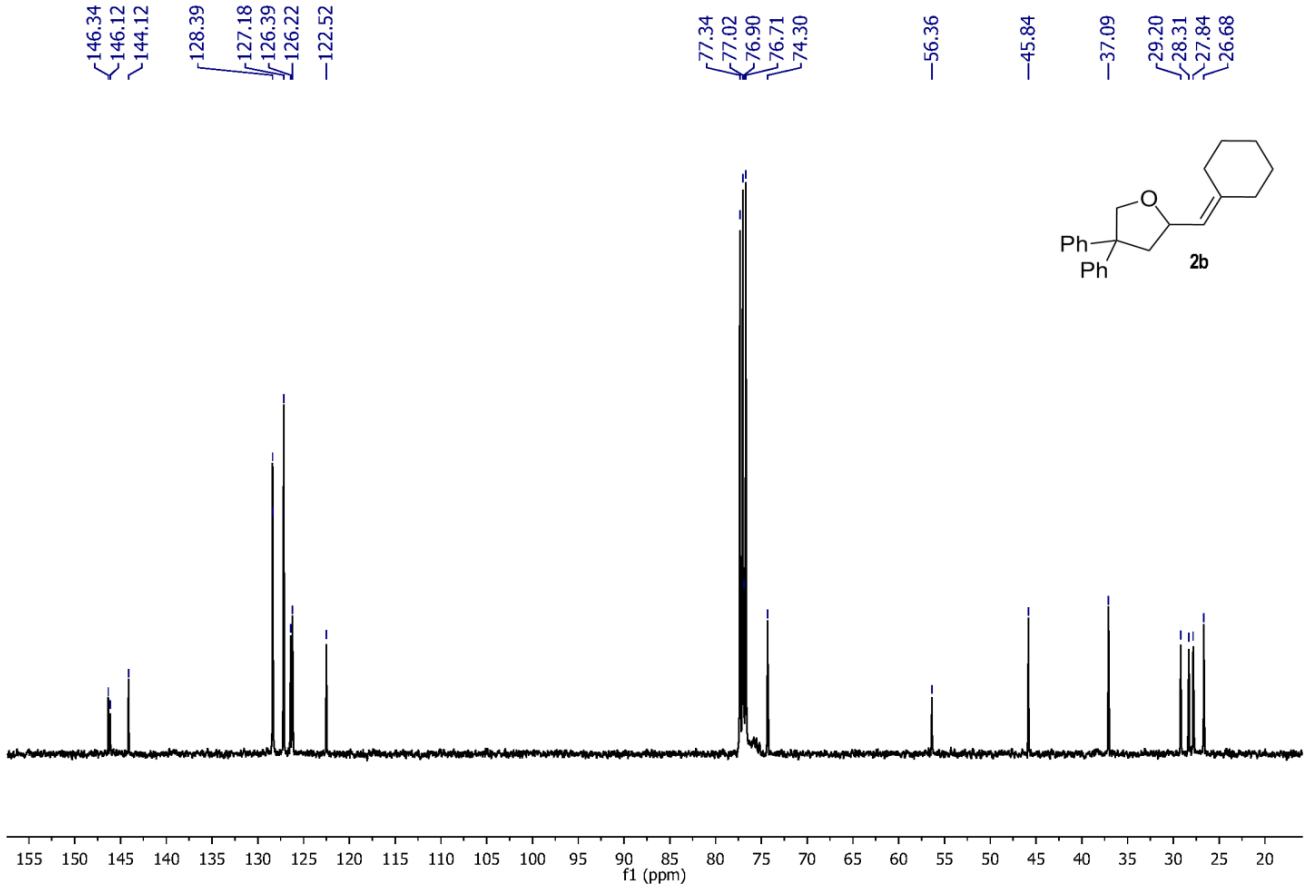


Figure S8a. ^{1}H NMR spectra of **2c**.

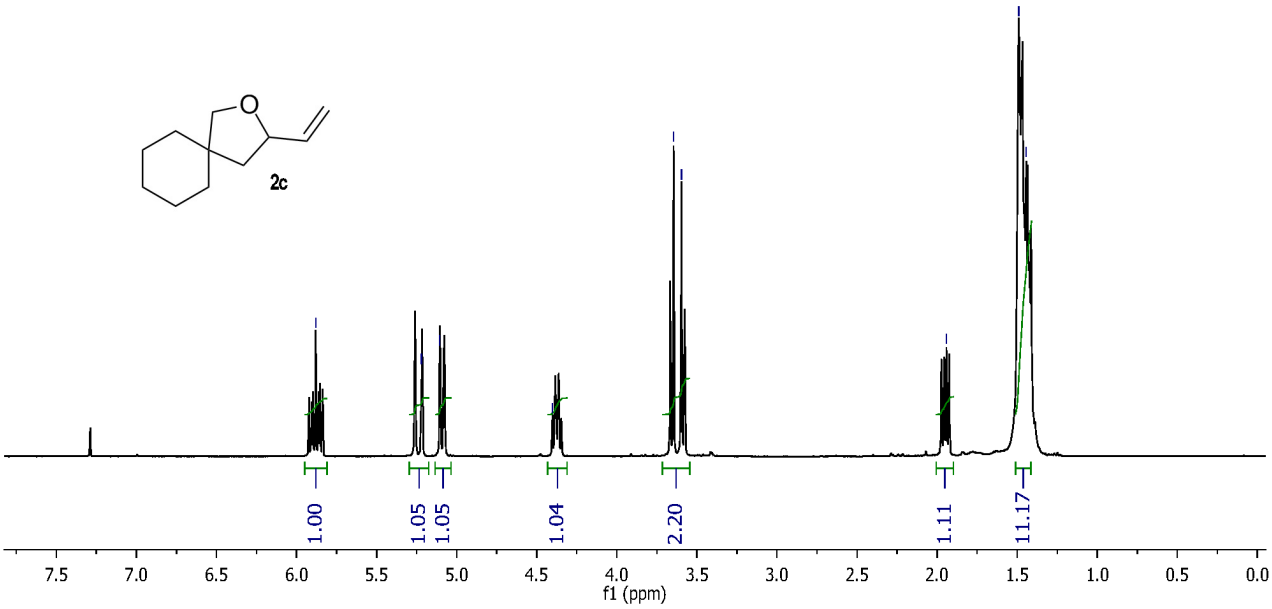


Figure S8b. ^{13}C NMR spectra of **2c**.

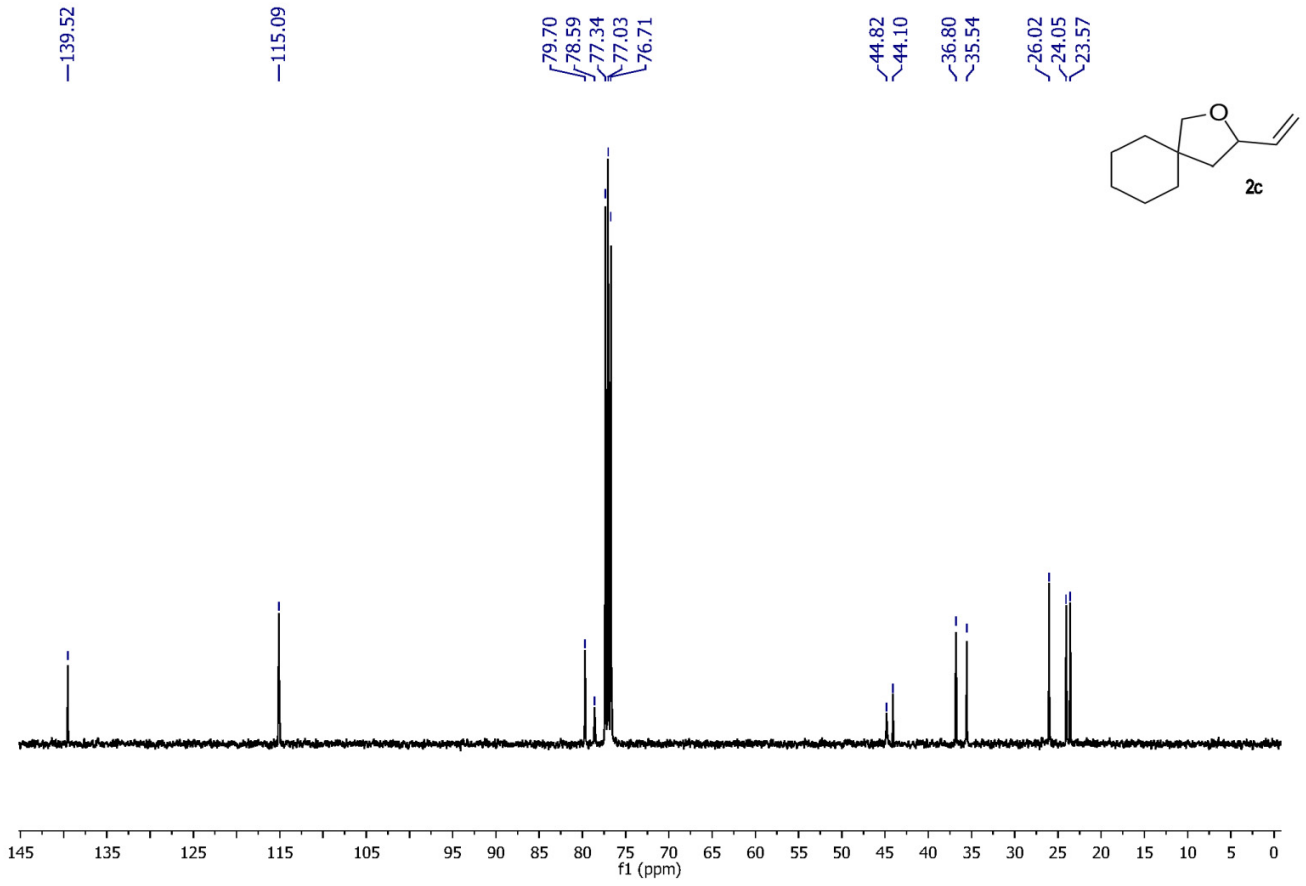


Figure S9a. ^{1}H NMR spectra of **4**.

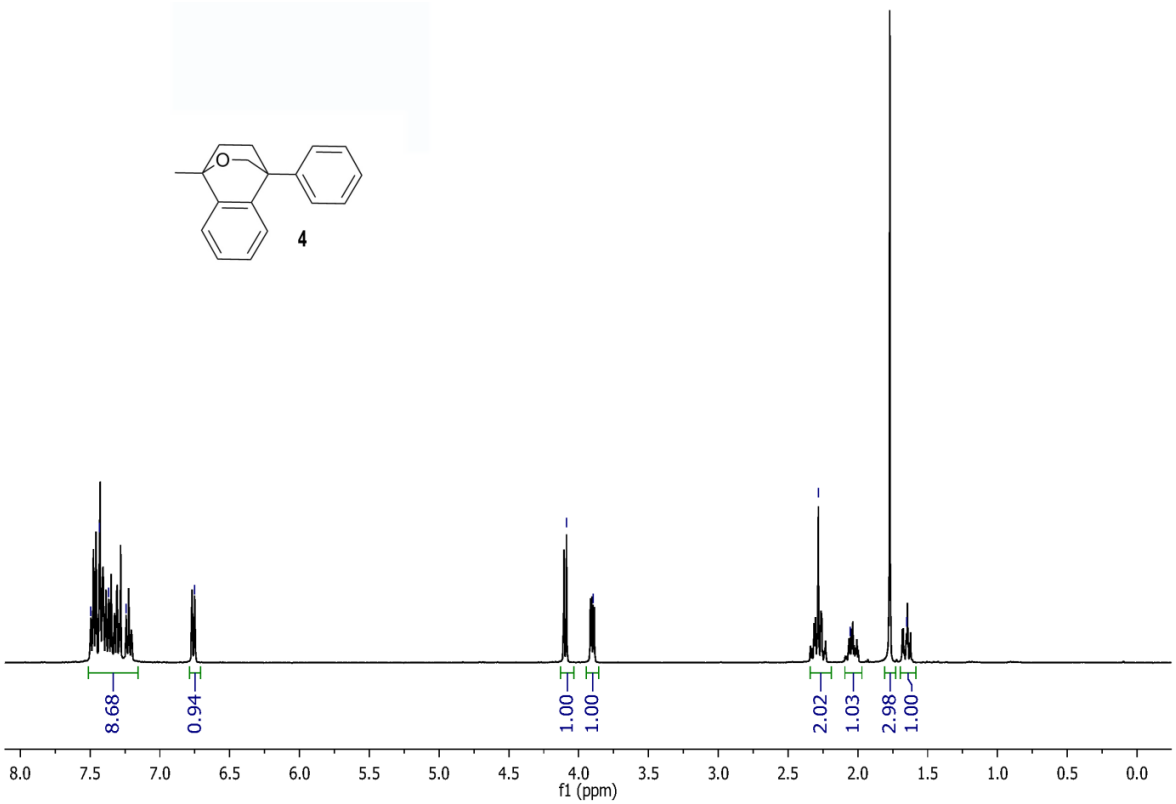


Figure S9b. ^{13}C NMR spectra of **4**.

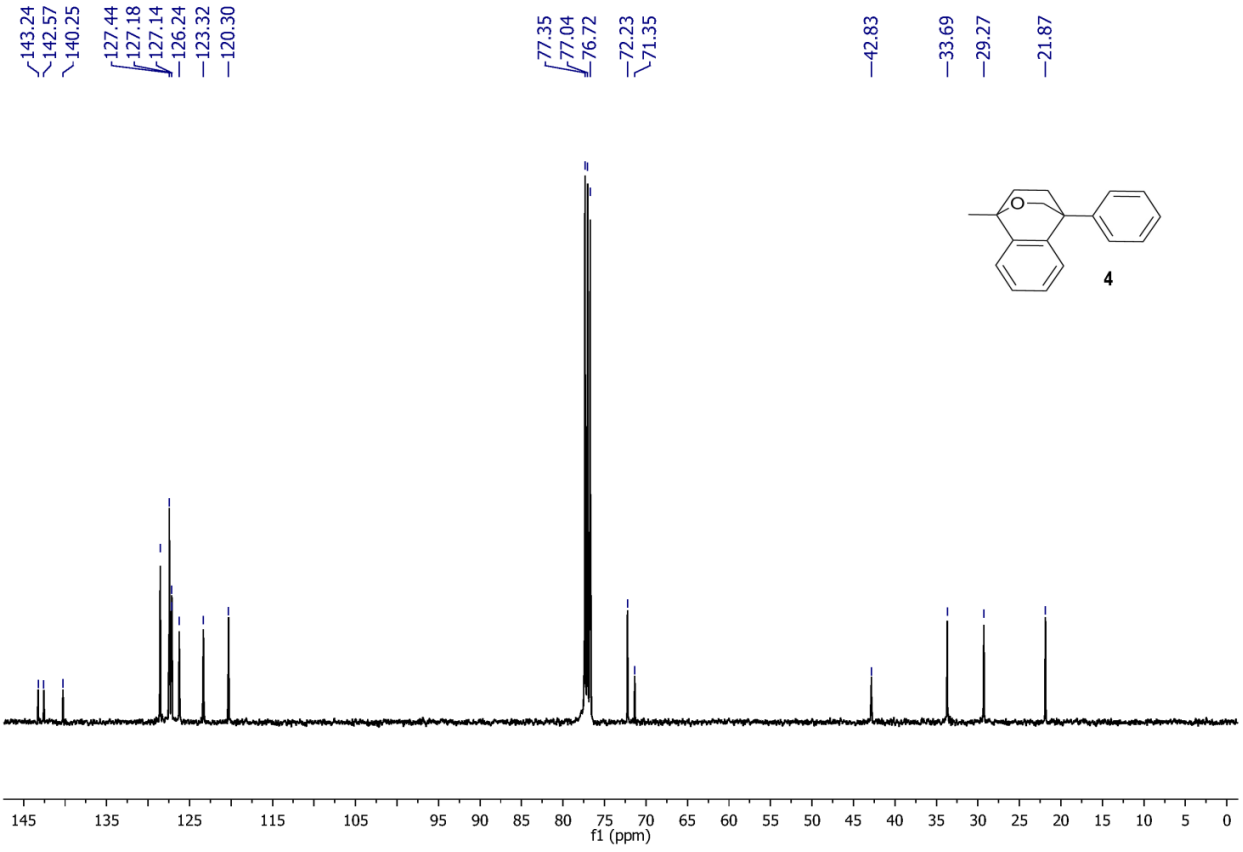


Figure S10a. ^{1}H NMR spectra of **5.**

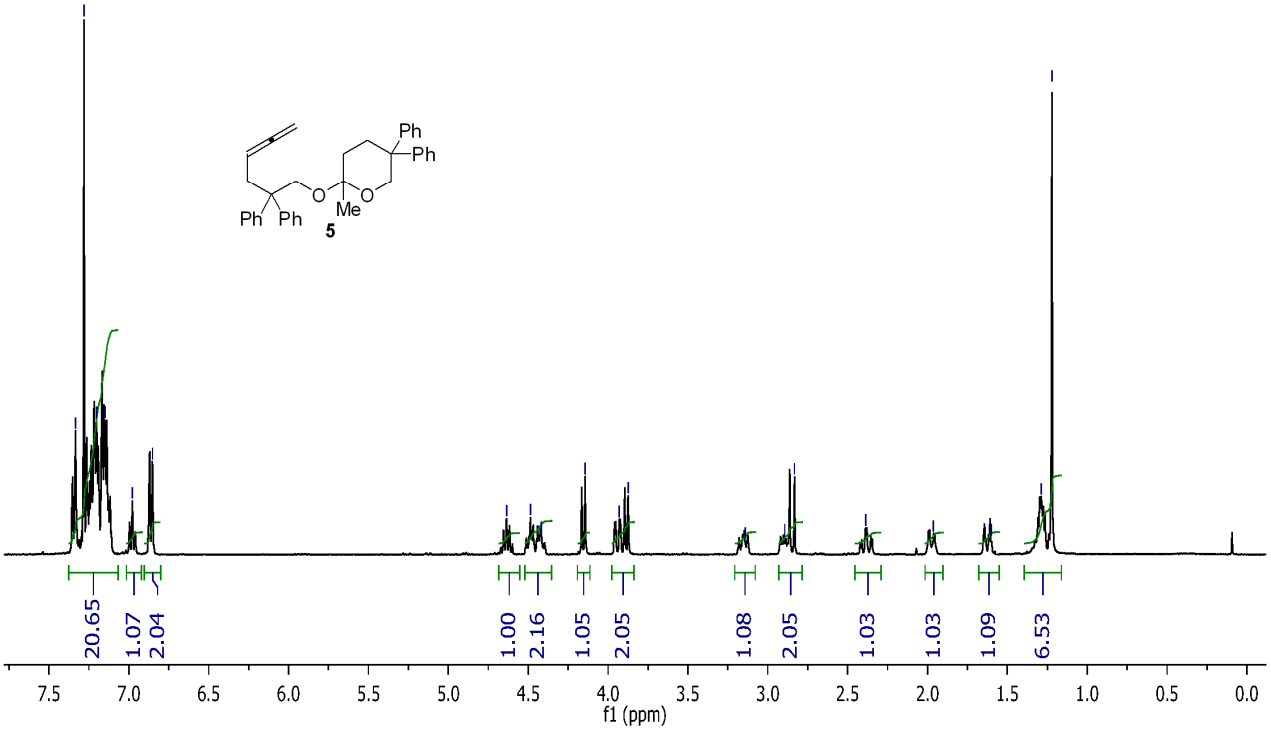


Figure S10b. ^{13}C NMR spectra of **5.**

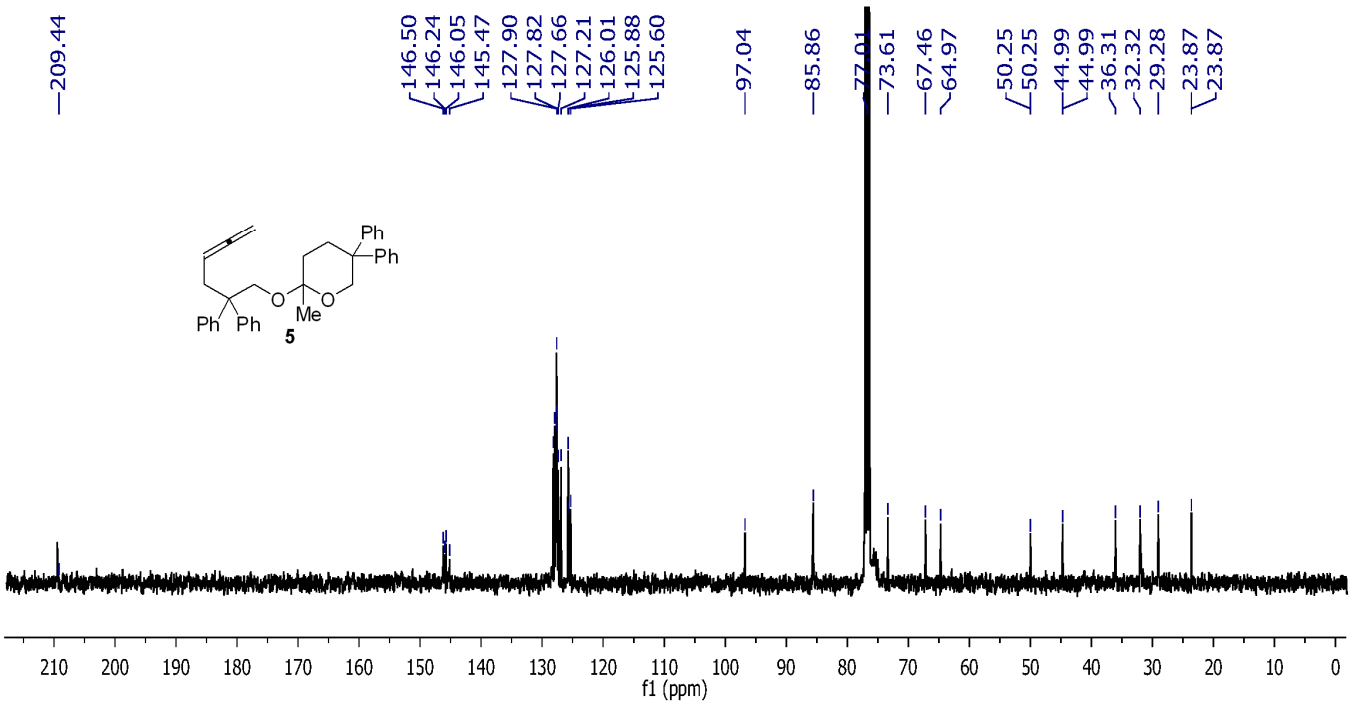


Figure S11a. ^{1}H NMR spectra of **6a**.

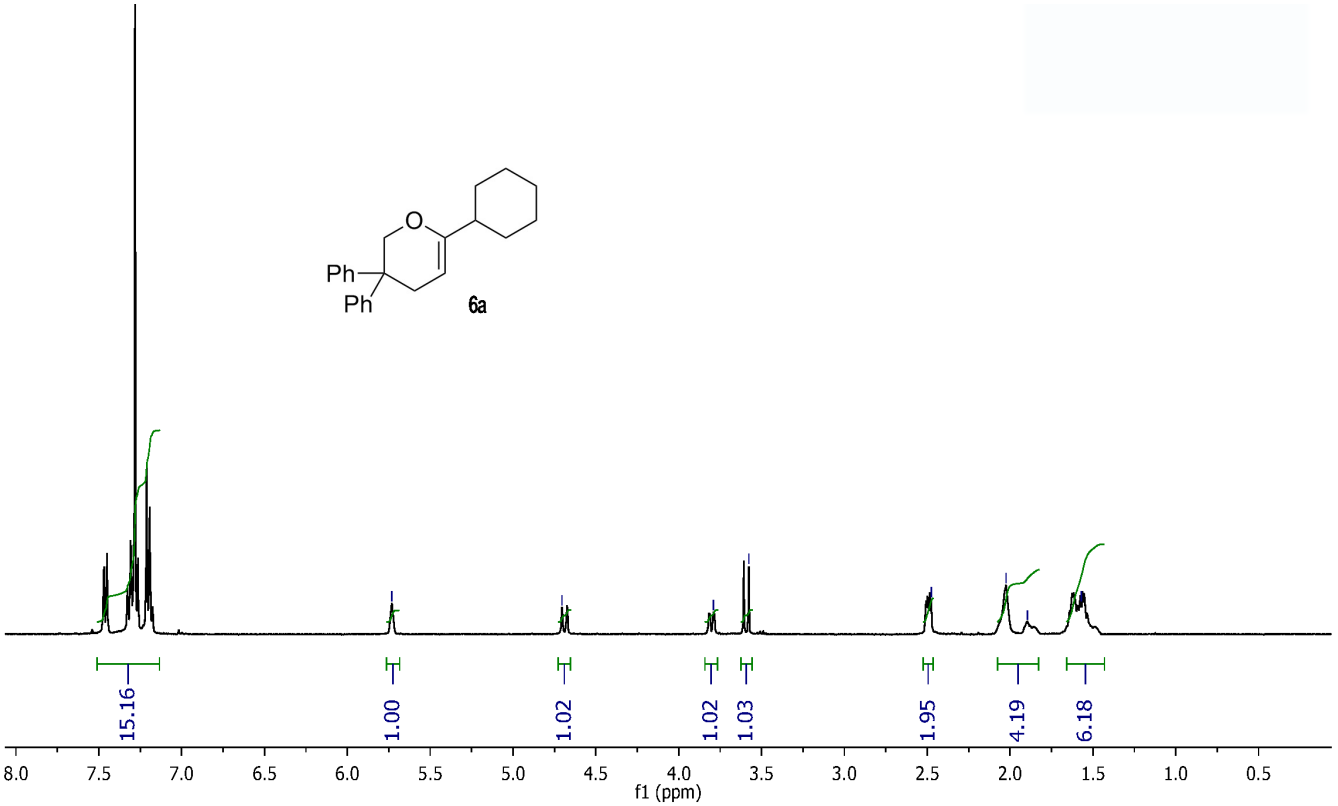


Figure S11b. ^{13}C NMR spectra of **6a**.

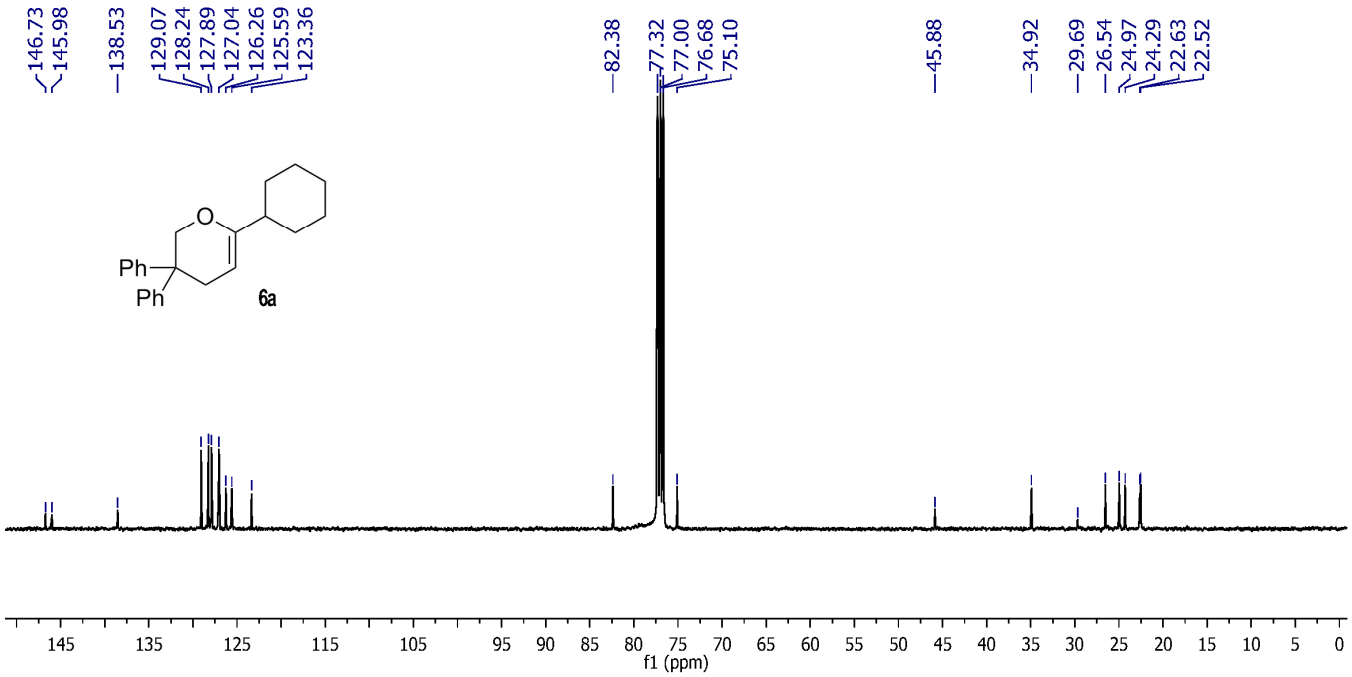


Figure S12a. ^{1}H NMR spectra of **6b**.

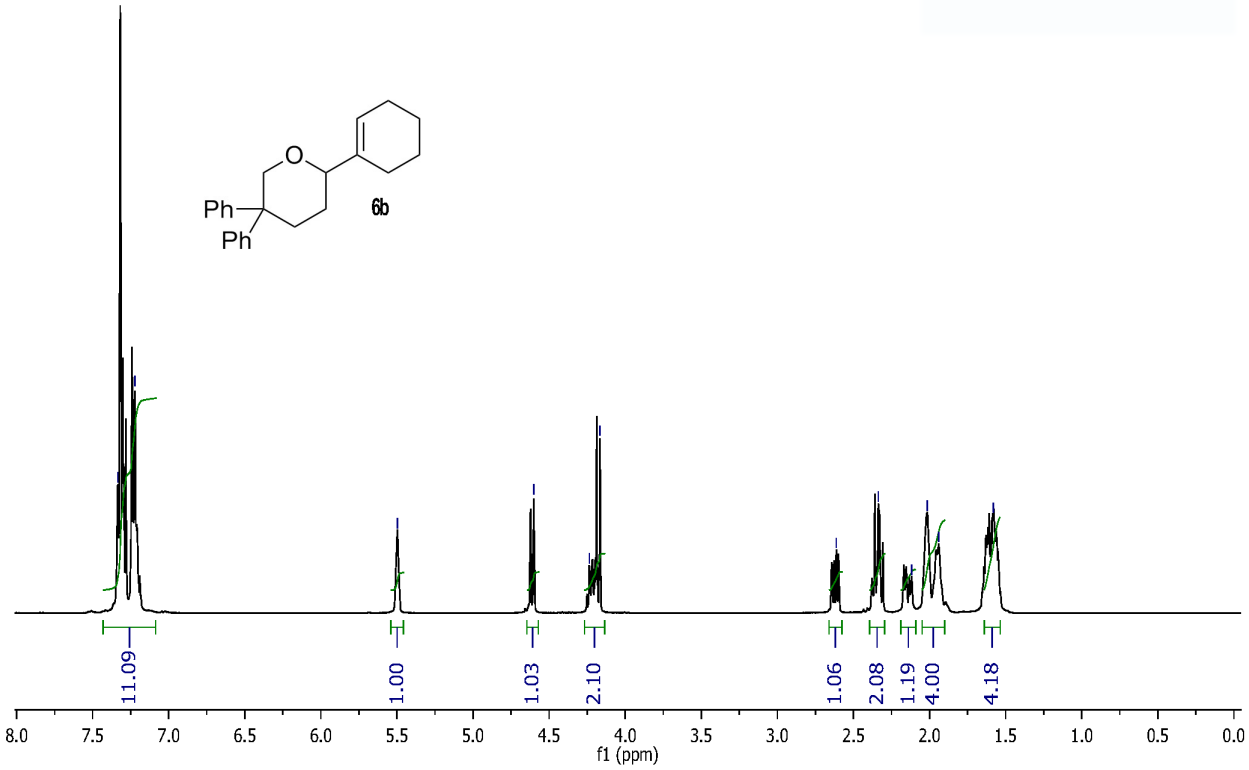


Figure S12b. ^{13}C NMR spectra of **6b**.

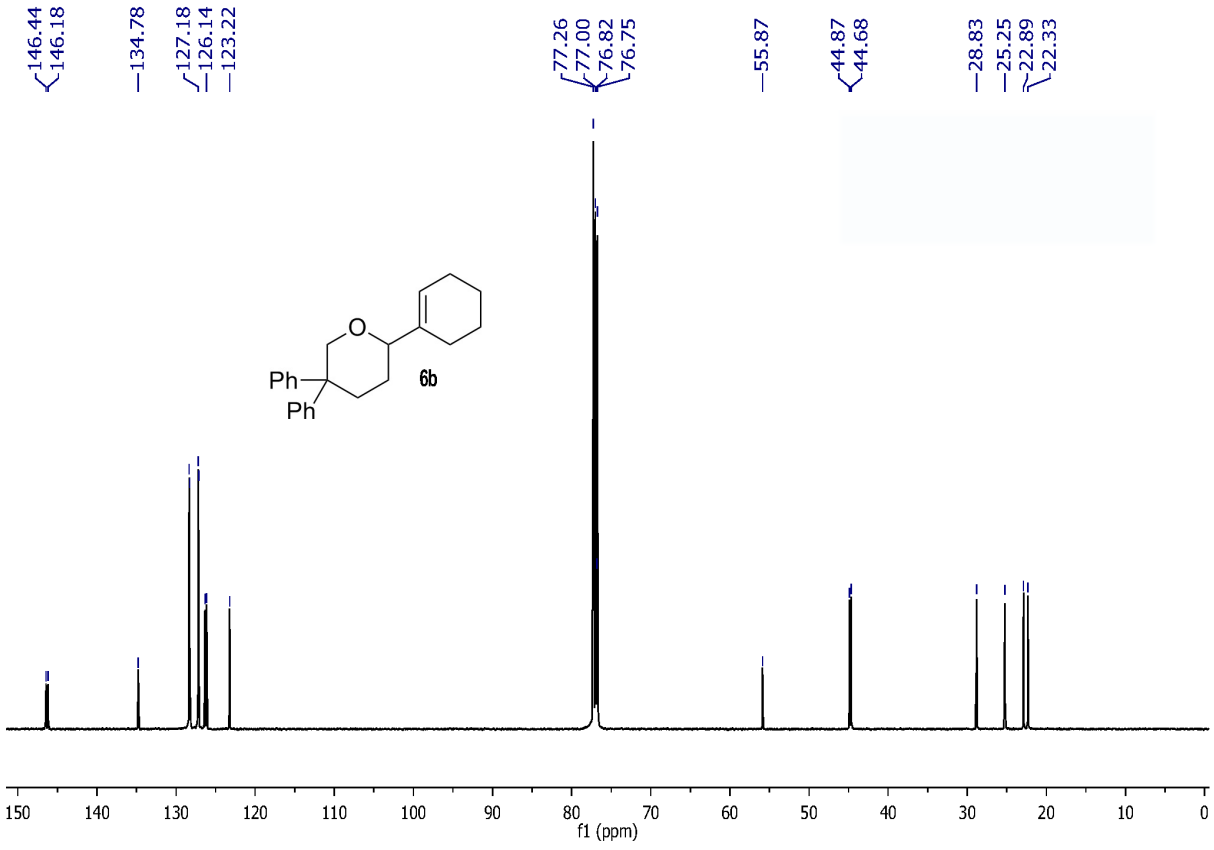


Figure S13a. ^{1}H NMR spectra of **7**.

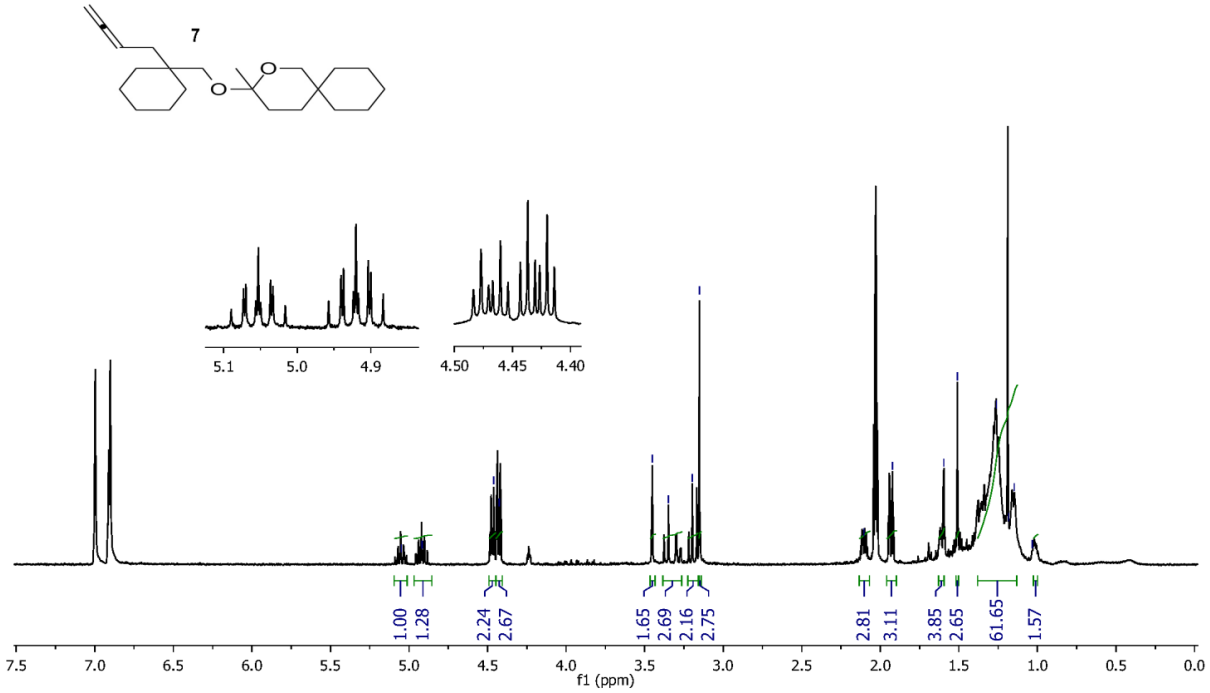


Figure S13b. ^{13}C NMR spectra of **7**.