Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Regio- and Chemoselective Rearrangement of Terminal Epoxides into Methyl Alkyl and Aryl Ketones

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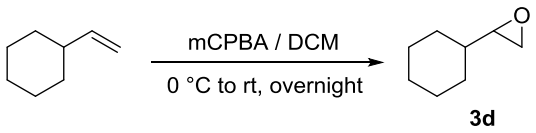
1. General information

Unless otherwise noted, all reactions were carried out under an argon atmosphere in dried and degassed solvents using Schlenk technique. Toluene, Pentane, dichloromethane and tetrahydrofuran were purchased from Sigma Aldrich and dried using an MBraun SPS-800 solvent purification system. All lithium salts used were obtained from commercial suppliers, dried in vacuum and used without further purification. Epoxides obtained from commercial suppliers and synthesised epoxides were degassed through freeze-pump-thaw cycles prior to use. **Hbimca^{Homo}·2HBr** [1,2] and rhodium complex **1**[3] were synthesised according to the literature procedures. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker ARX 250 and AVANCE II+ 400 spectrometer. Chemical shifts δ (ppm) are given relative to the solvent's residual proton and carbon signal respectively: THF-d_8: 3.58 ppm (^{1}H NMR) and 67.57 ppm (^{13}C NMR); C_6D_6: 7.16 ppm (^{1}H NMR) and 128.39 ppm (^{13}C NMR); $CDCl_3$: 7.27 ppm (^{1}H NMR) and 77.00 ppm (^{13}C NMR); DMSO-d_6: 2.50 ppm (^{1}H NMR) and 39.51 ppm (^{13}C NMR). Coupling constants (*J*) are expressed in Hz. Multiplets were assigned as br s (broad singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplets), m (multiplet), q (quartet), qd (quartet of doublets) s (singlet), t (triplet) and tt (triplet of triplets). Assignment of peaks was made using 2D NMR correlation and NOE spectra.

2. Synthesis of terminal epoxides

2-Cyclohexyloxirane (3d)[4]

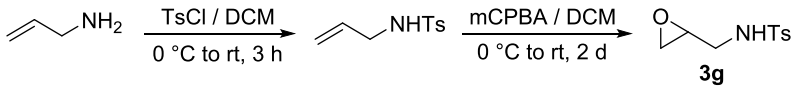


3d

To a solution of vinylcyclohexane (1.10 g, 10.0 mmol) in DCM (30 mL), *meta*-chloroperoxybenzoic acid (2.72 g, <77 % purity, 11.0 mmol) was added at 0 °C and the resulting mixture was stirred overnight at room temperature. The reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (50 mL) and washed with 10% Na_2SO_3 (3 × 25 mL), 10% $NaHCO_3$ (4 × 25 mL), water (25 mL) and brine (25 mL). The organic phase was dried over Na_2SO_4, filtered and evaporated *in vacuo* to obtain **3d** (59%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.72–2.70 (m, 2H), 2.53–2.51 (m, 1H), 1.89-1.86 (m, 1H), 1.76-1.63 (m, 4H), 1.30–1.05 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 56.6, 46.0, 40.4, 29.7, 28.8, 26.3, 25.7, 25.5.

4-Methyl-*N*-(oxiran-2-ylmethyl)benzenesulfonamide (3g)[5]

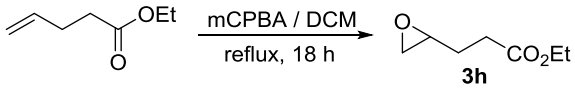


3g

To a solution of 4-toluenesulfonyl chloride (1.90 g, 10.0 mmol) in anhydrous dichloromethane (50 mL), allylamine (1.20 g, 21.0 mmol) was added dropwise at 0 °C and the resulting mixture was stirred for 3 h at room temperature. The reaction mixture was washed with 10% citric acid (2 × 25 mL), water (25 mL) and brine (25 mL). The organic phase was dried over Na_2SO_4, filtered and evaporated *in vacuo* to obtain *N*-allyl-4-methylbenzenesulfonamide. The compound obtained was used directly without purification. To a solution of *N*-allyl-4-methylbenzenesulfonamide in DCM (30 mL), *meta*-chloroperoxybenzoic acid (2.72 g, <77% purity, 11.0 mmol) was added at 0 °C and the resulting mixture was stirred for 48 h at room temperature. The reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (50 mL) and washed with 10% Na_2SO_3 (3 × 25 mL), 10% $NaHCO_3$ (4 × 25 mL), water (25 mL) and brine (25 mL). The organic phase was dried over Na_2SO_4, filtered and evaporated *in vacuo* to obtain **3g** (87%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77–7.74 (m, 2H), 7.33–7.31 (m, 2H), 4.76–4.74 (m, 1H), 3.38–3.32 (m, 1H), 3.09–3.01 (m, 2H), 2.77–2.75 (m, 1H), 2.64 (dd, *J* = 4.7, 2.3 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.7, 136.8, 129.8, 127.0, 50.2, 45.1, 44.3, 21.5.

Ethyl 3-(oxiran-2-yl)propanoate (3h)[4]

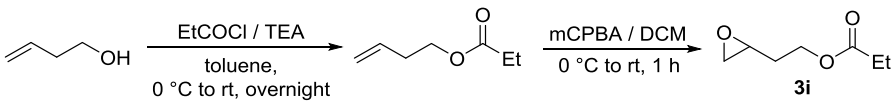


3h

Ethyl pent-4-enoate (3.00 g, 23.4 mmol) and *meta*-chloroperoxybenzoic acid (5.77 g, <77% purity, 23.4 mmol) were dissolved in CH_2Cl_2 (90 mL) and stirred for 18 h in an oil bath at 50 °C. The white solid was filtered off and the filtrate was washed with 10% $NaHSO_3$ (100 mL), 10% $NaHCO_3$ (3 × 50 mL) and H_2O (2 × 50 mL). The crude product was dried over Na_2SO_4 then carefully concentrated without external heating. The desired product **3h** (59%) was obtained as a colorless liquid by distillation, b.p. 30-33 °C (9.0×10^{-2} mbar).

^{1}H NMR (400 MHz, DMSO-d_6) δ = 4.06 (q, *J* = 7.1 Hz, 2H), 2.93–2.90 (m, 1H), 2.68–2.66 (m, 1H), 2.46 (dd, *J* = 5.1, 2.7 Hz, 1H), 2.39 (t, *J* = 7.4 Hz, 2H), 1.82–1.64 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.8, 60.5, 51.2, 47.1, 30.4, 27.6, 14.2.

2-(Oxiran-2-yl)ethyl propionate (3i)[6]



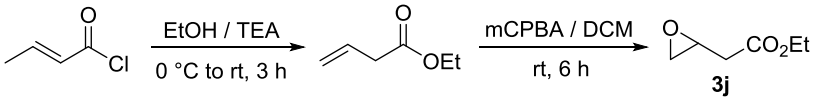
3i

To a mixture of 3-buten-1-ol (3.00 g, 41.6 mmol) and triethylamine (5.06 g, 50.0 mmol) in toluene (30 mL), propionyl chloride (4.04 g, 43.7 mmol) was added dropwise with vigorous stirring at 0 °C. The reaction was allowed to warm to room temperature and stirred overnight. The solution was washed with cold water (3 × 20 mL) and brine (100 mL). After drying over Na_2SO_4, the solvent was removed under reduced pressure to yield but-3-en-1-yl propionate as a crude oil. To a stirred solution of crude but-3-en-1-yl propionate (2.75 g, 21.5 mmol) in CH_2Cl_2 (20 mL) at 0 °C, *meta*-chloroperoxybenzoic acid (5.55 g, <77% purity, 23.2 mmol) was added and the reaction was allowed to warm to room temperature. After stirred for 1 h, excess peroxide was quenched by the slow addition of 10% $NaHSO_3$

(50 mL) at 0 °C, followed by slow addition of $NaHCO_3$ until bubbling ceased. The product was extracted with CH_2Cl_2 (3 × 30 mL) and washed with brine (50 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by distillation and the desired product **3i** (26%) was obtained as a colorless liquid, b.p. 27-33 °C (9.0×10^{-2} mbar).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.24 (t, *J* = 6.2, 2H), 3.04–2.99 (m, 1H), 2.80–2.78 (m, 1H), 2.51 (dd, *J* = 5.0, 2.7 Hz, 1H), 2.35 (q, *J* = 7.6 Hz, 2H), 1.97–1.78 (m, 2H), 1.15 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.3, 61.2, 49.5, 46.8, 31.9, 27.5, 9.1.

Ethyl 2-(oxiran-2-yl)acetate (3j)[7]

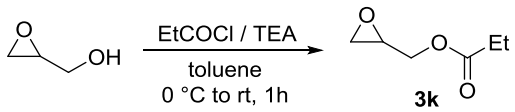


3j

To the cooled mixture of triethylamine (4.84 g, 47.8 mmol) and ethanol (3.31 g, 71.7 mmol), crotonoyl chloride (4.50 g, 47.8 mmol) was added dropwise at 0 °C and the reaction was allowed to warm to room temperature. After stirring for 3 h, 10% $NaHCO_3$ (10 mL) was added to the reaction mixture, followed by water (20 mL). The reaction mixture was extracted with diethyl ether and pentane (70 mL). The organic layers were combined and washed with brine. The crude product was dried over Na_2SO_4 then carefully concentrated without external heating. The compound obtained was used directly without further purification. To a stirred solution of crude ethyl but-3-enoate (3.54 g, 31.0 mmol) in CH_2Cl_2 (20 mL), *meta*-chloroperoxybenzoic acid (7.64 g, <77% purity, 31.0 mmol) was added and the solution was stirred for 6 h. The reaction mixture was washed with 10% $NaHSO_3$ (30 mL), $NaHCO_3$ (sat., 30 mL) and brine (3 × 30 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by distillation and the desired product **3j** (32%) was obtained as a colorless liquid, b.p. 25-27 °C (3.1×10^{-2} mbar).

^{1}H NMR (400 MHz, C_6D_6) δ = 3.89 (q, *J* = 7.1 Hz, 2H), 3.03–2.99 (m, 1H), 2.30–2.26 (m, 1H), 2.09-2.21 (m, 2H), 2.00 (dd, *J* = 5.1, 2.5 Hz, 1H), 0.90 (t, *J* =7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.4, 60.9, 48.0, 46.7, 38.1, 14.2.

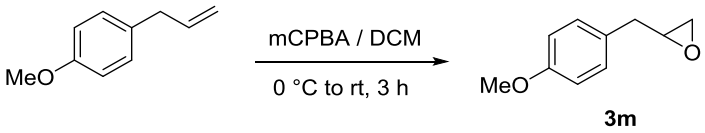
Oxiran-2-ylmethyl propionate (3k)[6]



Propionyl chloride (6.24 g, 67.5 mmol) was added dropwise with vigorous stirring to a mixture of glycidol (5.00 g, 67.5 mmol) and triethylamine (8.26 g, 81.0 mmol) in toluene (30 mL) at 0 °C. After 1 h, the mixture was allowed to warm to room temperature. The solution was rapidly washed with cold water (3 × 20 mL) and brine (20 mL). The organic phase was collected, dried over Na_2SO_4 and distilled twice to obtain the desired product **3k** (53%) as a colorless liquid, b.p. 82-85 °C (12.0 mbar).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.42 (dd, *J* = 12.3, 3.1 Hz, 1H), 3.93 (dd, *J* = 12.3, 6.3 Hz, 1H), 3.23–3.19 (m, 1H), 2.85 (t, *J* = 4.5 Hz, 1H), 2.65 (dd, *J* = 4.9, 2.6 Hz, 1H), 2.39 (q, *J* = 7.6 Hz, 2H), 1.18–1.14 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.2, 64.8, 49.4, 44.6, 27.3, 9.0.

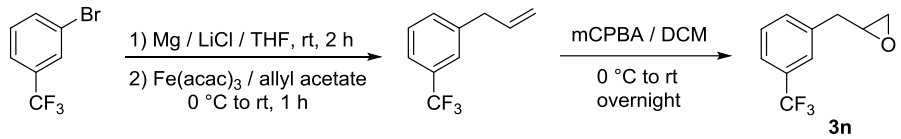
2-(4-Methoxybenzyl)oxirane (3m)[8]



A solution of 1-allyl-4-methoxybenzene (3.00 g, 20.3 mmol) in CH_2Cl_2 (75 mL) was cooled to 0 °C with an ice bath and *meta*-chloroperoxybenzoic acid (3.50 g, <77% purity; 20.3 mmol) was added portion wise. The mixture was allowed to warm to room temperature and then stirred until TLC indicated complete consumption of the starting material. After completion, $NaHCO_3$ (sat., 75 mL) was slowly added and the mixture was stirred vigorously until bubbling ceased. The organic layer was separated and washed with 10% $NaHSO_3$ (100 mL) and brine (70 mL), and then dried over Na_2SO_4. After removal of the solvent by rotary evaporation, the crude product was purified by chromatography on silica gel (EtOAc/hexane, gradient 5:95 to 20:80) to afford the desired product **3m** (87%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20–7.16 (m, 2H), 6.89–6.85 (m, 2H), 3.81 (s, 3H), 3.16–3.13 (m, 1H), 2.91–2.75 (m, 3H), 2.55–2.53 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.4, 130.0, 129.1, 113.9, 55.2, 52.6, 46.8, 37.8.

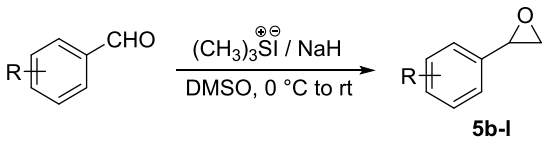
2-(3-(Trifluoromethyl)benzyl)oxirane (3n)[8,9]



Freshly distilled THF (40 mL) and 1-bromo-3-(trifluoromethyl)benzene (6.14 g, 27.3 mmol) were added dropwise to a mixture of magnesium ribbons (822 mg, 33.8 mmol), dry LiCl (1.45 g, 33.8 mmol) and THF under argon protection. The mixture was stirred at room temperature for 2 h and then cooled to 0 °C in an ice bath. A solution of $Fe(acac)_3$ (473 mg, 1.30 mmol, 5 mol %) in dry THF (20 mL) was added, the solution stirred for 5 min, and allyl acetate (2.63 g, 26.0 mmol) was added. After stirring for 45 min at 0 °C, the reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over Na_2SO_4, concentrated in vacuo and the crude product was purified by vacuum distillation. A solution of 1-allyl-3-(trifluoromethyl)benzene (7.41 g, 50.0 mmol) in CH_2Cl_2 (75 mL) was cooled to 0 °C with an ice bath. *Meta*-chloroperoxybenzoic acid (12.1 g, <77% purity, 50.0 mmol) was added portion wise. The mixture was allowed to warm to room temperature and then stirred until TLC indicated complete consumption of the starting material. After completion, $NaHCO_3$ (sat., 75 mL) was slowly added and the mixture was stirred vigorously until bubbling ceased. The organic layer was separated and washed with 10% $NaHSO_3$ (100 mL), brine (70 mL), and then dried over Na_2SO_4. After removal of the solvent by rotary evaporation, the crude product was purified by chromatography on silica gel (EtOAc/hexane, gradient 5:95 to 20:80) to afford the desired product **3n** (36%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53–7.51 (m, 2H), 7.48–7.44 (m, 2H), 3.21–3.16 (m, 1H), 3.00–2.89 (m, 2H), 2.85–2.82 (m, 1H), 2.56 (dd, *J* = 4.9, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.1, 132.4, 130.9 (q, $^2J_{CF}$ = 32.0 Hz), 128.9, 125.7 (q, $^3J_{CF}$ = 3.8 Hz), 124.1 (q, $^1J_{CF}$ = 272.3 Hz), 123.6 (q, $^3J_{CF}$ = 3.8 Hz), 51.9, 46.7, 38.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.62.

***α*-Aryl oxiranes (5b-l)**[10]



Trimethylsulfonium iodide (20.0 mmol) and sodium hydride (60% in oil, 20.0 mmol) were dissolved in DMSO (15 mL) at 0 °C under an argon atmosphere. After stirring for 20 minutes, the corresponding aldehyde (12.0 mmol) dissolved in DMSO (20 mL) was added dropwise. The reaction was then stirred at room temperature overnight. The mixture was poured into cold water (60 mL), and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water (30 mL) and brine (30 mL × 2), and dried over Na_2SO_4. The crude epoxide was purified using flash chromatography.

The desired product 2-(3-(trifluoromethyl)phenyl)oxirane (**5b**) was obtained as a colorless liquid (73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59–7.55 (m, 2H), 7.49–7.48 (m, 2H), 3.94–3.93 (m, 1H), 3.21–3.18 (m, 1H), 2.81–2.79 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.8, 131.1 (q, $^2J_{CF}$ = 32.5 Hz), 129.0, 128.8, 125.0 (q, $^3J_{CF}$ = 3.8 Hz), 124.0 (q, $^1J_{CF}$ = 270.0 Hz), 122.3 (q, $^2J_{CF}$ = 3.8 Hz), 51.8, 51.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.79.

The desired product 2-(2-(trifluoromethyl)phenyl)oxirane (**5c**) was obtained as a colorless liquid (58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.57–7.53 (m, 1H), 7.49–7.46 (m, 1H), 7.43–7.39 (m, 1H), 4.24–4.22 (m, 1H), 3.21–3.18 (m, 1H), 2.67–2.65 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.6, 132.3, 128.3 (q, $^2J_{CF}$ = 31.1 Hz), 127.7, 125.5 (q, $^3J_{CF}$ = 5.7 Hz), 125.3, 124.3 (q, $^1J_{CF}$ = 273.6 Hz), 51.1, 49.2 (q, $^4J_{CF}$ = 3.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -59.92.

The desired product 2-(4-(trifluoromethyl)phenyl)oxirane (**5d**) was obtained as a colorless liquid (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 3.93 (dd, *J* = 4.1, 2.5 Hz, 1H), 3.20 (dd, *J* = 5.5, 4.1 Hz, 1H), 2.78 (dd, *J* = 5.5, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.8, 130.4 (q, $^2J_{CF}$ = 32.5 Hz), 125.7, 125.4 (q, $^3J_{CF}$ = 3.8 Hz), 124.0 (q, $^1J_{CF}$ = 272.2 Hz), 51.7, 51.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.62.

The desired product 2-(3-fluorophenyl)oxirane (**5e**) was obtained as a colorless liquid (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.29 (m, 1H), 7.10 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.03-6.96 (m, 2H), 3.87 (dd, *J* = 4.0, 2.8 1H), 3.16 (dd, *J* = 5.6, 4.0 Hz, 1H), 2.77 (dd, *J* = 5.6, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.1 (d, $^1J_{CF}$ = 246.3 Hz), 140.4 (d, $^3J_{CF}$ = 7.5 Hz), 130.1 (d, $^3J_{CF}$ = 8.0 Hz), 121.3 (d,

$^{4}J_{CF}$ = 2.8 Hz), 115.2 (d, $^{2}J_{CF}$ = 21.2 Hz), 112.2 (d, $^{2}J_{CF}$ = 22.6 Hz), 51.8 (d, $^{4}J_{CF}$ = 2.4 Hz), 51.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -112.93.

The desired product 2-(3-chlorophenyl)oxirane (**5f**) was obtained as a colorless liquid (76%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-7.27 (m, 3H), 7.21-7.16 (m, 1H), 3.85 (dd, *J* = 4.0, 2.5 Hz, 1H), 3.16 (dd, *J* = 5.5, 4.0 Hz, 1H), 2.77 (dd, *J* = 5.5, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.8, 134.6, 129.8, 128.3, 125.5, 123.7, 51.7, 51.2.

The desired product 2-(3-bromophenyl)oxirane (**5g**) was obtained as a colorless liquid (82%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.42 (m, 2H), 7.24-7.21 (m, 2H), 3.83 (dd, *J* = 4.0, 2.5 Hz, 1H), 3.15 (dd, *J* = 5.5, 4.0 Hz, 1H), 2.76 (dd, *J* = 5.5, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 140.1, 131.2, 130.0, 128.4, 124.2, 122.7, 51.6, 51.2.

The desired product 2-(4-fluorophenyl)oxirane (**5h**) was obtained as a colorless liquid (71%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28-7.23 (m, 2H), 7.07-7.02 (m, 2H), 3.86 (dd, *J* = 4.0, 2.6 Hz, 1H), 3.15 (dd, *J* = 5.4, 4.0, 1H), 2.78 (dd, *J* = 5.4, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.7 (d, $^{1}J_{CF}$ = 246.3 Hz), 133.3 (d, $^{4}J_{CF}$ = 2.8 Hz), 127.2 (d, $^{3}J_{CF}$ = 8.5 Hz), 115.5 (d, $^{2}J_{CF}$ = 21.7 Hz), 51.8, 51.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -113.94.

The desired product 2-(4-chlorophenyl)oxirane (**5i**) was obtained as a colorless liquid (48%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36–7.30 (m, 2H), 7.26–7.20 (m, 2H), 3.90–3.82 (m, 1H), 3.19–3.13 (m, 1H), 2.76 (dd, *J* = 5.5, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.2, 133.9, 128.7, 126.8, 51.8, 51.2.

The desired product 2-(4-bromophenyl)oxirane (**5j**) was obtained as a colorless liquid (71%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51-7.46 (m, 2H), 7.18-7.15 (m, 2H), 3.84 (dd, *J* = 4.0, 2.5 Hz, 1H), 3.16 (dd, *J* = 5.5, 4.0 Hz, 1H), 2.76 (dd, *J* = 5.5, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.7, 131.6, 127.1, 122.0, 51.8, 51.2.

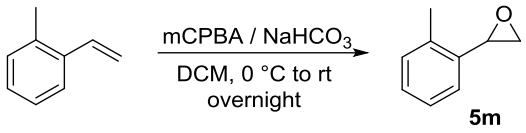
The desired product 2-(p-tolyl)oxirane (**5k**) was obtained as a colorless liquid (39%) and stored in fridge.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21–7.15 (m, 4H), 3.84 (dd, *J* = 4.1, 2.6 Hz, 1H), 3.14 (dd, *J* = 5.4, 4.1, 1H), 2.81 (dd, *J* = 5.4, 2.6 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.0, 134.5, 129.2, 125.5, 52.3, 51.1, 21.2.

The desired product 2-(4-methoxyphenyl)oxirane (**5l**) was obtained as a colorless liquid (78%) and stored in fridge.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.23–7.20 (m, 2H), 6.93–6.90 (m, 2H), 3.86 (dd, *J* = 4.1, 2.6 Hz, 1H), 3.74 (s, 3H), 3.07 (dd, *J* = 5.3, 4.1 Hz, 1H), 2.84 (dd, *J* = 5.3, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.7, 129.4, 126.8, 114.0, 55.3, 52.2, 51.0.

2-(*o*-Tolyl)oxirane (5m)[11]

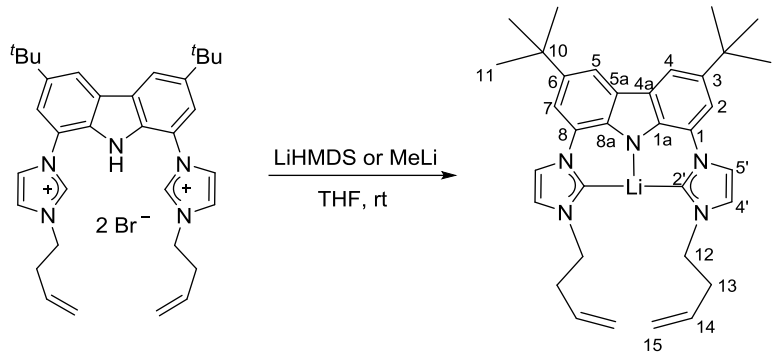


To a solution of 1-methyl-2-vinylbenzene (2.00 g, 16.9 mmol) in CH_2Cl_2 (75 mL) was added solid $NaHCO_3$ (2.80 g, 33.8 mmol). The reaction was cooled to 0 °C with an ice bath and *meta*-chloroperoxybenzoic acid (4.60 g, <77% purity; 18.6 mmol) dissolved in CH_2Cl_2 (70 mL) was added dropwise. The mixture was allowed to warm to room temperature and then stirred until TLC indicated complete consumption of the starting material. After completion, the mixture was washed with aqueous $NaHCO_3$ solution (sat., 75 mL), aqueous $Na_2S_2O_3$ solution (sat., 100 mL) and then dried over Na_2SO_4. After removal of the solvent by rotary evaporation, the crude product was purified by distillation to afford the desired product **5m** (82%) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25–7.16 (m, 4H), 4.02 (dd, *J* = 4.1, 2.7 Hz, 1H), 3.18 (dd, *J* = 5.7, 4.1, 1H), 2.71 (dd, *J* = 5.7, 2.7 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.1, 135.8, 129.8, 127.6, 126.1, 124.1, 50.4, 50.1, 18.7.

3. Preparation of the rhodium complexes 2 and 2^{LiX}

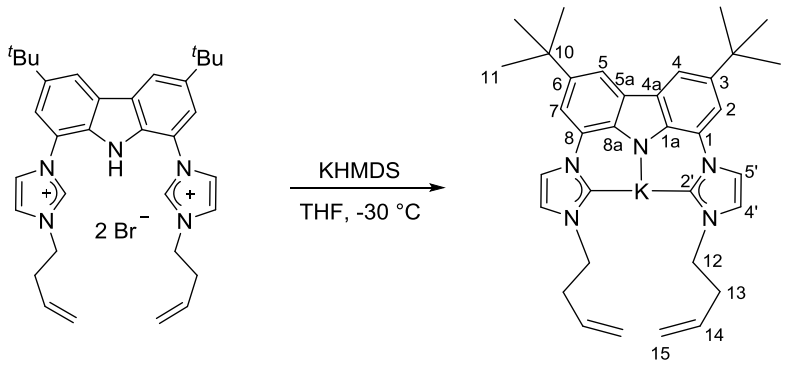
3.1. Deprotonation of $Hbimca^{Homo}$·2HBr with different bases



$Hbimca^{Homo}$·2HBr **[Li($bimca^{Homo}$)]**

Lithium bis(trimethylsilyl)amide (7.4 mg, 44 µmol) or methyl lithium (1.0 mg, 44 µmol) was added to the suspension of **$Hbimca^{Homo}$·2HBr** (10.0 mg, 14.7 µmol) in 0.5 mL of THF-d_8 at room temperature and a light yellow solution with blue fluorescence was formed. After 30 min, the quantitative formation of **[Li($bimca^{Homo}$)]** was confirmed by ^{1}H NMR spectroscopy.[1]

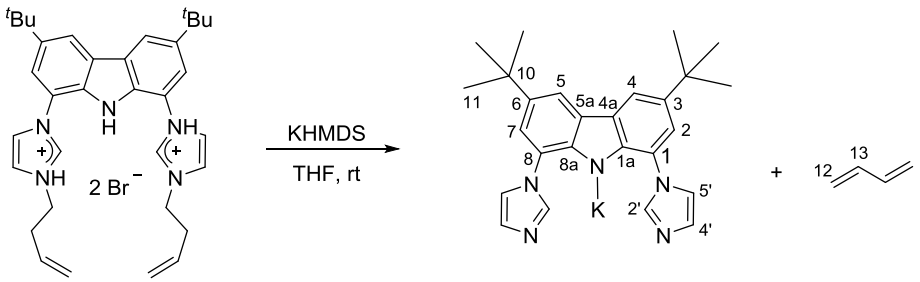
^{1}H NMR (400 MHz, THF-d_8) δ = 8.00 (s, 2H, H-4/5), 7.73 (s, 2H, H-5'), 7.40 (s, 2H, H-2/7), 7.21 (s, 2H, H-4'), 5.98-5.88 (m, 2H, H-14), 5.15 (d, $^3J_{HH}$ = 17.1 Hz, 2H, H-15$_{trans}$), 5.04 (d, $^3J_{HH}$ = 10.1 Hz, 2H, H-15$_{cis}$), 4.29 (t, $^3J_{HH}$ = 7.2 Hz, 4H, H-12), 2.72 (q, $^3J_{HH}$ = 6.3 Hz, 4H, H-13), 1.50 (s, 18H, H-11). ^{13}C NMR (101 MHz, THF-d_8) δ = 205.3 (C2'), 143.8 (C1a/8a), 136.4 (C14), 135.8 (C3/6), 128.6 (C4a/5a), 128.4 (C1/8), 119.6 (C5'), 119.4 (C15), 117.3 (C4'), 114.3 (C4/5), 111.8 (C2/7), 51.9 (C12), 37.0 (C13), 35.4 (C10), 33.1 (C11).



$Hbimca^{Homo}$·2HBr **[K($bimca^{Homo}$)]**

Potassium bis(trimethylsilyl)amide (10.4 mg, 52.0 µmol) was added to the suspension of **$Hbimca^{Homo}$·2HBr** (10.0 mg, 14.7 µmol) in 0.5 mL of THF-d_8 at –30 °C and a yellow solution formed. After 10 min, the formation of **[K($bimca^{Homo}$)]** was checked by low temperature ^{1}H NMR spectroscopy at –30 °C.

^{1}H NMR (400 MHz, THF-d_8) δ = 8.02 (s, 2H, H-4/5), 7.50 (br s, 2H, H-5'), 7.24 (s, 2H, H-2/7), 7.12 (s, 2H, H-4'), 5.91-5.83 (m, 2H, H-14), 5.12 (d, $^{3}J_{HH}$ = 17.2 Hz, 2H, H-15$_{trans}$), 5.03 (d, $^{3}J_{HH}$ = 10.3 Hz, 2H, H-15$_{cis}$), 4.13 (t, $^{3}J_{HH}$ = 7.6 Hz, 4H, H-12), 2.57 (ps q, $^{3}J_{HH}$ = 7.0 Hz, 4H, H-13), 1.46 (s, 18H, H-11). ^{13}C NMR (101 MHz, THF-d_8) δ = 146.5 (C1a/8a), 136.7 (C14), 134.3 (C3/6), 130.0 (C4a/5a), 128.5 (C1/8), 122.6 (C5'), 118.5 (C15), 117.0 (C4'), 116.3 (C4/5), 114.6 (C2/7), 51.2 (C12), 37.6 (C13), 35.3 (C10), 33.1 (C11). The signal of C2' is not observed.

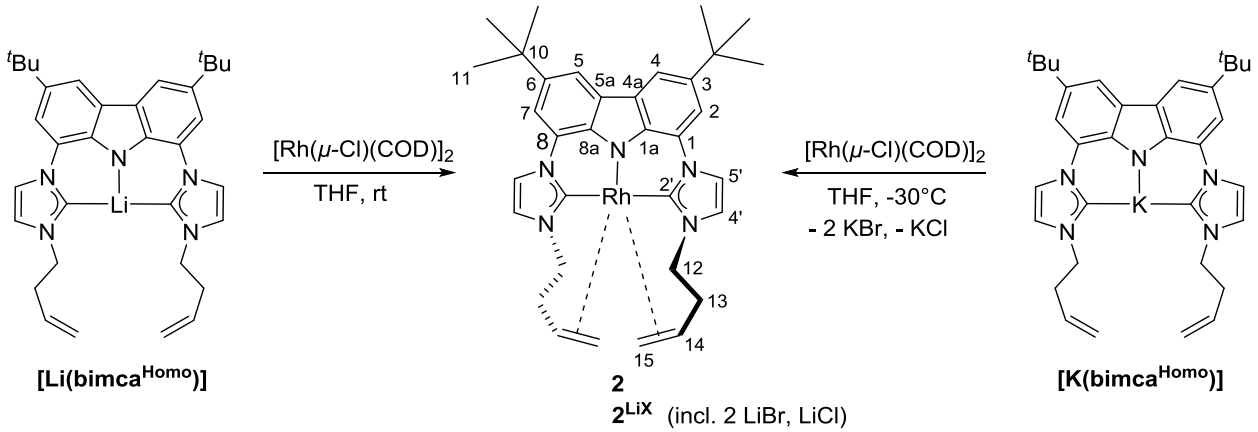


Hbimca^{Homo}·2HBr **[K(imi)$_2$carb]**

Potassium bis(trimethylsilyl)amide (8.8 mg, 44 µmol) was added to the suspension of **Hbimca^{Homo}·2HBr** (10.0 mg, 14.7 µmol) in 0.5 mL of THF-d_8 at room temperature and a yellow solution was formed. After 10 min, the formation of **[K(imi)$_2$carb)]** and 1,3-butadiene was confirmed by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, THF-d_8) δ = 8.93 (s, 2H, H-2'), 8.03 (d, $^{3}J_{HH}$ = 1.9 Hz, 2H, H-4/5), 7.72 (t, $^{3}J_{HH}$ = 1.2 Hz, 2H, H-5'), 7.28 (d, $^{3}J_{HH}$ = 1.9 Hz, 2H, H-2/7), 7.04 (d, $^{3}J_{HH}$ = 1.2 Hz, 2H, H-4'), 6.42-6.25 (m, 2H, H-13), 5.21-5.14 (m, 2H, H-12$_{trans}$), 5.10-5.02 (m, 2H, H-12$_{cis}$), 1.47 (s, 18H, H-11). ^{13}C NMR (101 MHz, THF-d_8) δ = 145.9 (C1a/8a), 139.9 (C2'), 138.9 (C13), 135.4 (C3/6), 128.7 (C4'), 128.6 and 124.9, (C1/8 and C4a/5a), 119.9 (C5'), 117.9 (C12), 115.2 (C4/5), 113.5 (2/7), 35.3 (C10), 33.1 (C11).

3.2. Preparation of catalysts 2 and 2^{LiX}



[Li(bimca^{Homo})] **2** **[K(bimca^{Homo})]**

2^{LiX} (incl. 2 LiBr, LiCl)

From **[Li(bimca^{Homo})]**:

[Rh(μ-Cl)(COD)]$_2$ (0.5 eq) was added to the previous prepared solution of **[Li(bimca^{Homo})]** (1.0 eq) at the given temperature. The solution was stirred for 1 h. Catalyst **2** was obtained as an orange solution in quantitative yield as determined by NMR spectroscopy.

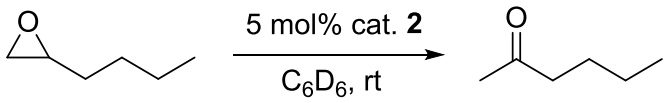
^{1}H NMR (400 MHz, THF-d_8) δ = 8.02 (d, $^4J_{HH}$ = 1.5 Hz, 2H, H-4/5), 7.92 (d, $^3J_{HH}$ = 2.2 Hz, 2H, H-5'), 7.52 (d, $^4J_{HH}$ = 1.5 Hz, 2H, H-2/7), 7.11 (d, $^3J_{HH}$ = 2.2 Hz, 2H, H-4'), 4.21 (br ps t,$^{2/3}J$ = 12.0 Hz, 2H, H-12$_{ax}$), 4.14–4.06 (m, 2H, H-14), 3.77 (br d, ^2J = 12.7 Hz, 2H, H-12$_{eq}$), 2.74–2.65 (m, 2H, H-13$_{eq}$), 2.38 (dd, $^3J_{HH}$ = 8.0, $^2J_{HH}$ = 1.3 Hz, 2H, H-15$_{cis}$), 1.64 (br d, $^3J_{HH}$ = 9.9 Hz, 2H, H-15$_{trans}$), 1.48 (s, 18H, H-11), 1.41–1.32 (m, 2H, H-13$_{ax}$). ^{13}C NMR (101 MHz, THF-d_8) δ = 185.5 (d, $^1J_{RhC}$ = 33.9 Hz, C2'), 137.8 (C3/6), 136.6 (C1a/8a), 128.4 (C4a/5a), 126.2 (C1/8), 121.7 (C4'), 116.3 (C5'), 115.0 (C4/5), 109.1 (C2/7), 55.9 (d, $^1J_{RhC}$ = 6.7 Hz, C15), 52.6 (C12), 51.1 (d, $^1J_{RhC}$ = 11.3 Hz, C14), 36.0 (C13), 35.5 (C10), 33.0 (C11).

From **[K(bimca^{Homo})]**:

[Rh(μ-Cl)(COD)]$_2$ (0.5 eq) was added to the previous prepared solution of **[K(bimca^{Homo})]** (1.0 eq) at –30 °C. The solution was stirred for 1 h. After completion, the solvent was removed in vacuo. The residue was washed with pentane (3 × 1 mL) and redissolved in THF (1 mL). The solution was dried in vacuo to obtain catalyst **2** as a yellow solid. The NMR data correspond to the results obtained from using **[Li(bimca^{Homo})]**.

$C_{34}H_{40}N_5Rh$ (621.62): calcd C 65.69, H 6.49, N 11.27; found C 65.19, H 6.36, N 11.03. m.p.: 183-187 °C (dec). (From **[K(bimca^{Homo})]**)

4. Reactivity comparison between catalyst 1 and catalyst 2



To a solution of catalyst **2** (2.0 µmol) and 1,3,5-trimethoxybenzene (certain amount) as the internal standard in C_6D_6 (0.4 mL), 1,2-epoxyhexane (4.1 mg, 40 µmol) was added. The reaction at room temperature was followed by ^{1}H NMR spectroscopy every 30 min.

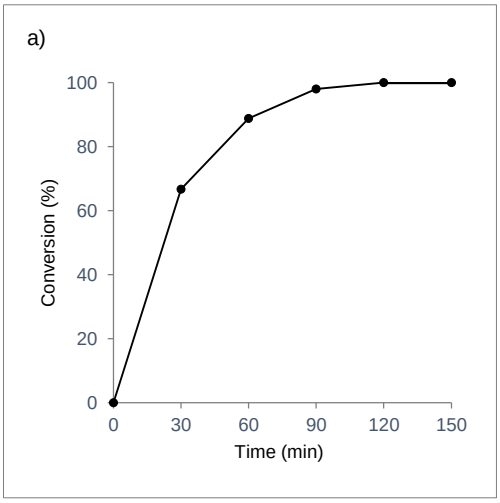


Figure S1. Monitoring the conversion of 1,2-epoxyhexane with catalyst **2.**

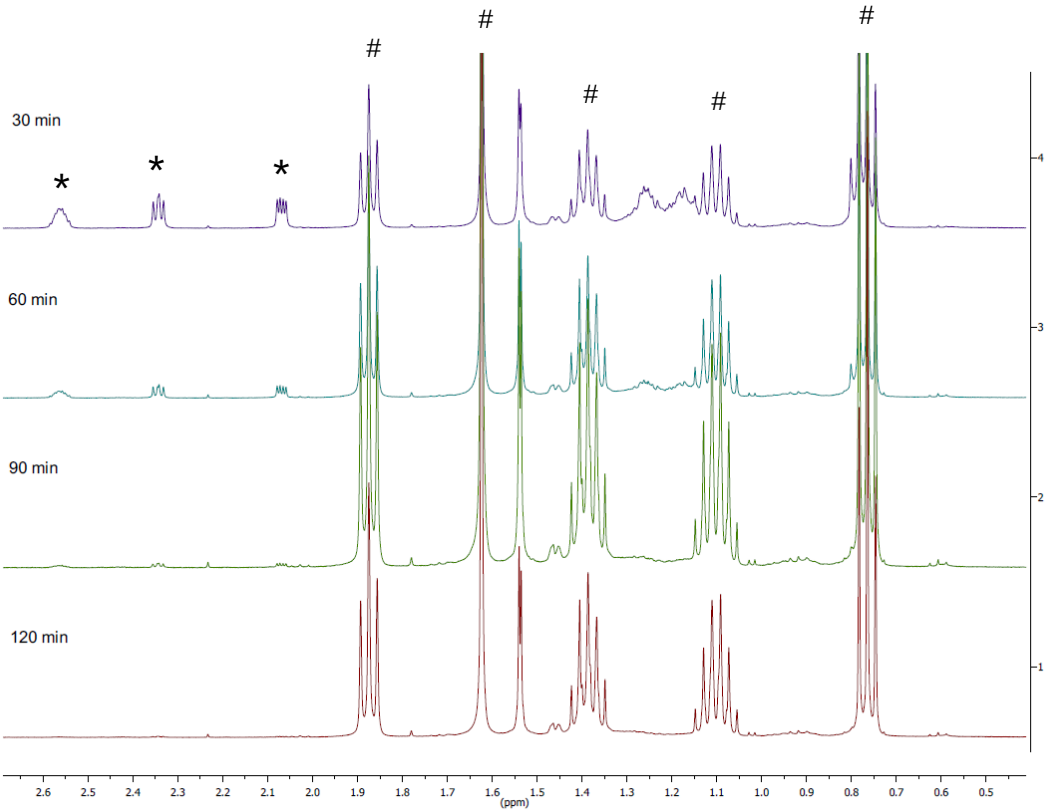
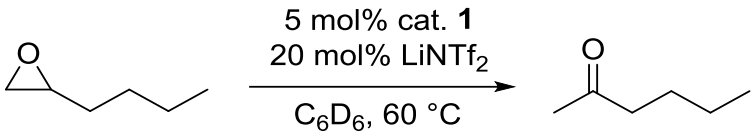


Figure S2. Monitoring the rearrangement of 1,2-epoxyhexane (*) into hexan-2-one (#) with catalyst **2** by ^{1}H NMR spectroscopy.



1,2-Epoxyhexane (4.1 mg, 40 μmol), catalyst **1** (1.1 mg, 2.0 μmol) and $LiNTf_2$ (2.3 mg, 8.0 μmol) were added into a *J. Young* NMR tube. 1,3,5-trimethoxybenzene (certain amount) was added as the internal standard and C_6D_6 was used as the solvent. The reaction was carried out at 60 °C and monitored by ^1H NMR spectroscopy every 30 min.

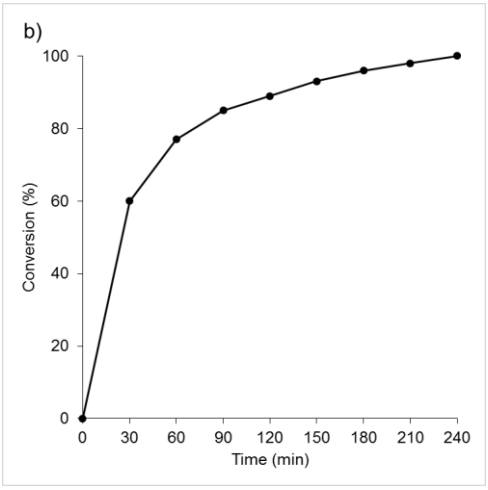


Figure S3. Monitoring the conversion of 1,2-epoxyhexane with catalyst **1**.

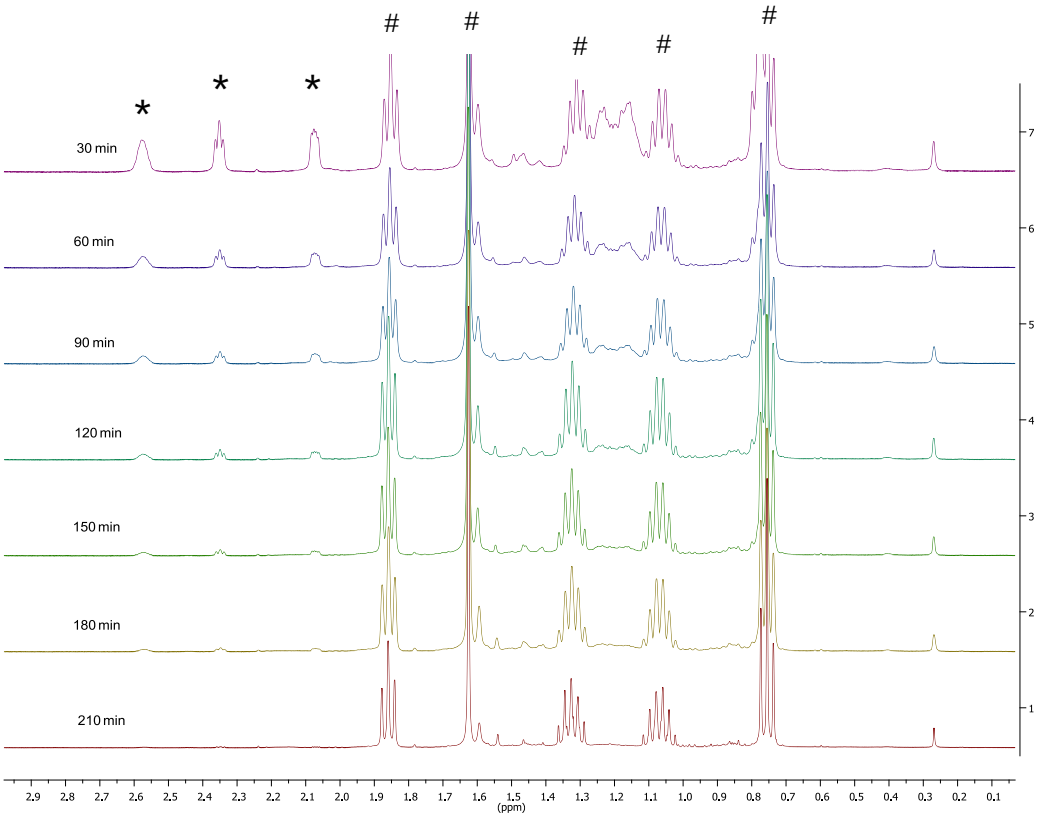
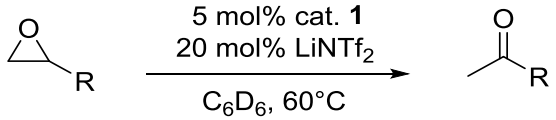
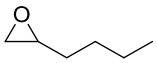
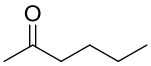
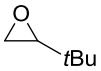
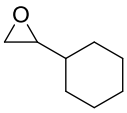
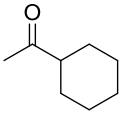
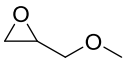
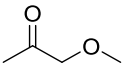
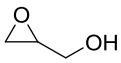
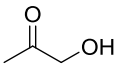
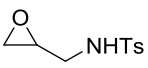
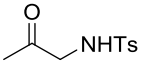
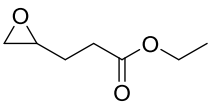
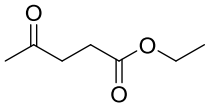
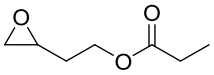
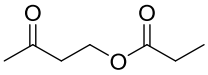
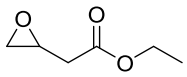
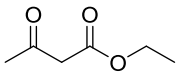
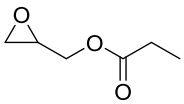
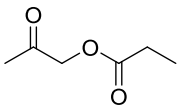
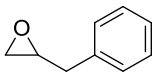
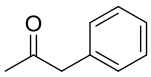
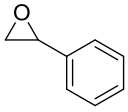
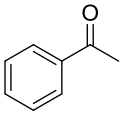


Figure S4. Monitoring the rearrangement of 1,2-epoxyhexane (*) into hexan-2-one (#) with catalyst **1** by ^1H NMR spectroscopy.

5. Additional substrate scope for catalyst 1 in the Meinwald reaction



	Epoxide		Methyl ketone	Time	Yield [%][a,b]
3a		**4a**		3 h	95
3b		**4b**		3 h	95
3c		**4c**		9.7 d	50
3d		**4d**		24 h	92
3e		**4e**		3 h	98
3f		**4f**		2 h	50
3g		**4g**		24 h	20
3h		**4h**		24 h	67
3i		**4i**		24 h	37
3j		**4j**		24 h	33[c]
3k		**4k**		24 h	17[c]
3l		**4l**		24 h	99
5a		**6a**		24 h	26 (Ketone) 44 (Aldehyde)

[a] Standard reaction conditions: Substrates (40 µmol), Cat. **1** (2.0 µmol), C_6D_6 (0.4 mL), 60 °C. All reactions were carried out using a *J. Young* NMR tube. [b] Yield of methyl ketones was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard. [c] at 80 °C.

6. Stability of 2-(4-methoxyphenyl)oxirane (5l) against lithium halides and catalyst 2

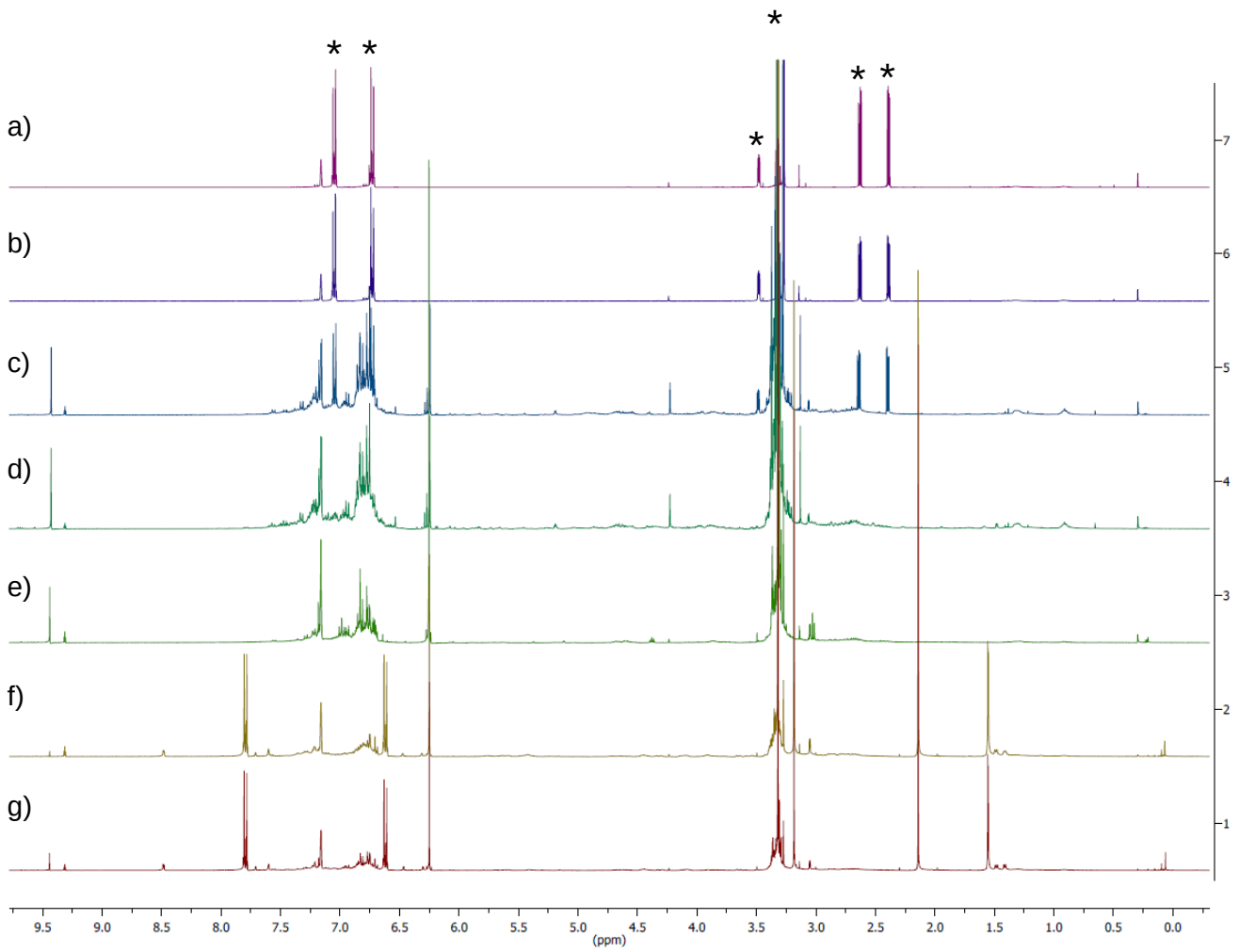
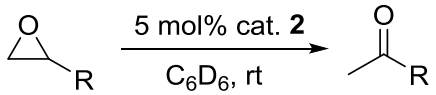


Figure S5. a) **5l** (*) in C_6D_6; b) **5l** in C_6D_6 after 8 days; c) **5l** in C_6D_6 with 10 mol% LiBr and 5 mol% LiCl after 4 days; d) **5l** in C_6D_6 with 10 mol% LiBr and 5 mol% LiCl after 18 days; e) **5l** in C_6D_6 with 10 mol% LiI after 23 h; f) **5l** in C_6D_6 with 5 mol% catalyst **2** after 2 h; g) **5l** in C_6D_6 with 5 mol% catalyst **2** after 48 h.

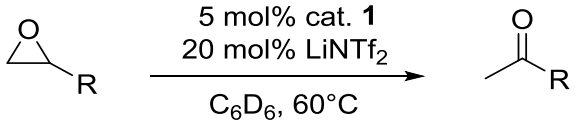
7. Experimental procedures for the Meinwald reaction of terminal epoxides with catalyst 2^{LiX}



Method 1

A defined amount of an in situ prepared solution containing catalyst $\mathbf{2^{LiX}}$ (2.5 µmol) was injected into a *J. Young* NMR tube containing a defined amount of the internal standard 1,3,5-trimethoxybenzene and THF was removed under vacuum. C_6D_6 (0.5 mL) and the respective epoxide (50 µmol) were added successively. The reaction at room temperature was monitored by ^{1}H NMR spectroscopy. All yields were determined by 1,3,5-trimethoxybenzene (certain amount) as the internal standard. The NMR signals of the obtained ketones were confirmed with literature data.

The up-scaling of this method was tested with **3l** (1.0 mmol). Lithium bis(trimethylsilyl)amide (25.1 mg, 150.0 µmol) was added to a suspension of $\mathbf{Hbimca^{Homo}\cdot 2HBr}$ (34.1 mg, 50.0 µmol) in 0.7 mL of THF-*d8* at room temperature. After 10 min, [Rh(*µ*-Cl)(COD)]$_2$ (12.3 mg, 25.0 µmol) was added and the solution was stirred for another 10 min. The successful formation of the catalyst was checked by ^{1}H NMR. After the THF-*d8* was removed in the oil-pump vacuum, the catalyst was transferred to a dry round flask with toluene (10 mL) and the epoxide **3l** (134.2 mg, 1.0 mmol) was added. The reaction was stirred for 2 h. After removal of the solvent by rotary evaporation, the crude product was purified by column chromatography on silica gel (EtOAc/hexane, 1:8) to afford the desired product **4l** (82%) as a colourless liquid.

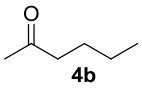


Method 2

Catalyst **1** (1.1 mg, 2.0 µmol), lithium bis(trifluoromethanesulfonimide) (2.3 mg, 8.0 µmol) and 1,3,5-trimethoxybenzene (certain amount) were added into a *J. Young* NMR tube. C_6D_6 (0.4 mL) was added as the solvent. The solution was then mixed with the respective epoxide (40 µmol) and heated at 60 °C for a defined period of time. The reaction was monitored by ^{1}H NMR spectroscopy and the yields were determined by 1,3,5-trimethoxybenzene as the internal standard. The NMR signals of the obtained ketones were compared with literature values.

4a

Propan-2-one (**4a**). ^{1}H NMR (400 MHz, C_6D_6) δ = 1.57 (s, 3H).



4b

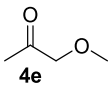
Hexan-2-one (**4b**). ^{1}H NMR (400 MHz, C_6D_6) δ = 1.89 (t, *J* = 7.4 Hz, 2H), 1.64 (s, 3H), 1.44–1.37 (m, 2H), 1.17–1.07 (m, 2H), 0.78 (t, *J* = 7.4 Hz, 3H).

4c

3,3-Dimethylbutan-2-one (**4c**). ^{1}H NMR (400 MHz, C_6D_6) δ = 1.73 (s, 3H), 0.89 (s, 9H).

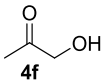
4d

1-Cyclohexylethan-1-one (**4d**). ^{1}H NMR (400 MHz, C_6D_6) δ = 1.88 (tt, *J* = 11.4, 3.5 Hz, 1H), 1.71 (s, 3H), 1.64–1.42 (m, 5H), 1.26–1.16 (m, 2H), 1.07-0.96 (m, 3H).



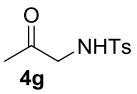
4e

1-Methoxypropan-2-one (**4e**). ^{1}H NMR (400 MHz, C_6D_6) δ = 3.43 (s, 2H), 2.96 (s, 3H), 1.71 (s, 3H).



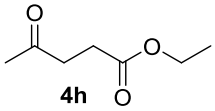
4f

1-Hydroxypropan-2-one (**4f**). ^{1}H NMR (400 MHz, C_6D_6) δ = 3.57 (s, 2H), 2.97 (br s, 1H), 1.27 (s, 3H).



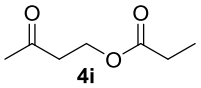
4g

4-Methyl-*N*-(2-oxopropyl)benzenesulfonamide (**4g**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.79 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 5.71 (s, 1H), 3.38 (s, 2H), 1.87 (s, 3H), 1.32 (s, 3H).



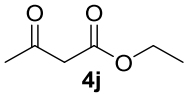
4h

Ethyl-4-oxopentanoate (**4h**). ^{1}H NMR (400 MHz, C_6D_6) δ = 3.93 (q, *J* = 7.1 Hz, 2H), 2.34 (t, *J* = 6.4 Hz, 2H), 2.16 (t, *J* = 6.4 Hz, 2H), 1.62 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H).



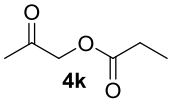
4i

3-Oxobutyl-propionate (**4i**). ^{1}H NMR (400 MHz, C_6D_6) δ = 4.18 (t, *J* = 6.3 Hz, 2H), 2.07 (t, *J* = 6.3 Hz, 2H), 1.98 (q, *J* = 7.6 Hz, 2H), 1.55 (s, 3H), 0.93 (t, *J* = 7.6 Hz, 3H).



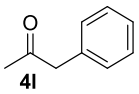
4j

Ethyl-3-oxobutanoate (**4j**). ^{1}H NMR (400 MHz, C_6D_6) δ = 3.88 (q, *J* = 7.1 Hz, 2H), 2.90 (s, 2H), 1.66 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H).



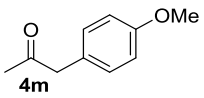
4k

2-Oxopropylpropionate (**4k**). ^{1}H NMR (400 MHz, C_6D_6) δ = 4.11 (s, 2H), 2.12 (q, *J* = 7.6 Hz, 2H), 1.42 (s, 3H), 0.96 (t, *J* = 7.6 Hz, 3H).



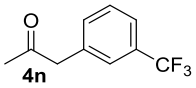
4l

1-Phenylpropan-2-one (**4l**). ^{1}H NMR (400 MHz, **C_6D_6**) δ = 7.11–7.01 (m, 3H), 6.98–6.96 (m, 2H), 3.20 (s, 2H), 1.63 (s, 3H). Up-scaling result: 82% isolated yield. ^{1}H NMR (400 MHz, **$CDCl_3$**) δ = 7.37-7.33 (m, 2H), 7.30-7.26 (m, 1H), 7.23-7.21 (m, 2H), 3.71 (s, *2*H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 206.4, 134.2, 129.4, 128.7, 127.0, 51.0, 29.2.

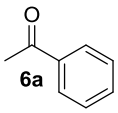


4m

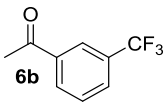
1-(4-Methoxyphenyl)propan-2-one (**4m**). ^{1}H NMR (400 MHz, C_6D_6) δ = 6.91 (dt, *J* = 8.0, 4.0 Hz, 2H), 6.73 (dt, *J* = 8.0, 4.0 Hz, 2H), 3.29 (s, 3H), 3.21 (s, 2H), 1.68 (s, 3H).



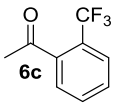
1-(3-(Trifluoromethyl)phenyl)propan-2-one (**4n**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.23–7.23 (m, 2H), 6.92–6.85 (m, 2H), 2.97 (s, 2H), 1.54 (s, 3H).



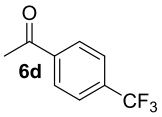
Acetophenone (**6a**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.77–7.74 (m, 2H), 7.13–7.09 (m, 1H), 7.06–7.00 (m, 2H), 2.09 (s, 3H).



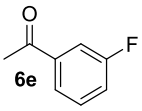
1-(3-(Trifluoromethyl)phenyl)ethan-1-one (**6b**). ^{1}H NMR (400 MHz, C_6D_6) δ = 8.00 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.80 (t, *J* = 7.8 Hz, 1H), 1.90 (s, 3H).



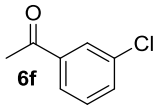
1-(2-(Trifluoromethyl)phenyl)ethan-1-one (**6c**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.26 (d, *J* = 7.7 Hz, 1H), 6.85–6.76 (m, 3H), 2.06 (s, 3H).



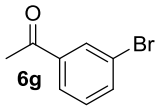
1-(4-(Trifluoromethyl)phenyl)ethan-1-one (**6d**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.48 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 1.95 (s, 3H).



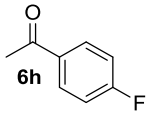
1-(3-Fluorophenyl)ethan-1-one (**6e**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.47-7.44 (m, 1H), 7.38-7.34 (m, 1H), 6.79-6.76 (m, 2H), 1.94 (s, 3H).



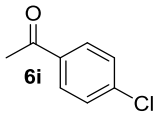
1-(3-Chlorophenyl)ethan-1-one (**6f**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.75 (t, *J* = 1.7 Hz, 1H), 7.45-7.43 (m, 1H), 7.08-7.06 (m, 1H), 6.71 (t, *J* = 7.9, 1H), 1.91 (s, 3H).



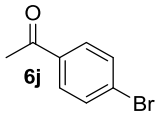
1-(3-Bromophenyl)ethan-1-one (**6g**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.92-7.91 (m, 1H), 7.49-7.46 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.24-7.21 (m, 1H), 6.64 (t, *J* = 7.9, 1H), 1.89 (s, 3H).



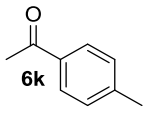
1-(4-Fluorophenyl)ethan-1-one (**6h**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.56-7.51 (m, 2H), 6.66-6.60 (m, 2H), 1.99 (s, 3H).



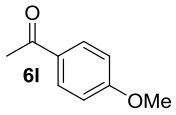
1-(4-Chlorophenyl)ethan-1-one (**6i**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.43 (dt, *J* = 8.7, 2.3 Hz, 2H), 6.98 (dt, *J* = 8.7, 2.3 Hz, 2H), 1.95 (s, 3H).



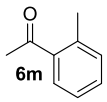
1-(4-Bromophenyl)ethan-1-one (**6j**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.34 (dt, *J* = 8.8, 2.3 Hz, 2H), 7.15 (dt, *J* = 8.8, 2.3 Hz, 2H), 1.94 (s, 3H).



1-(p-Tolyl)ethan-1-one (**6k**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.76-7.73 (m, 2H), 6.89-6.86 (m, 2H), 2.13 (s, 3H), 1.99 (s, 3H).



1-(4-Methoxyphenyl)ethan-1-one (**6l**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.80 (dt, *J* = 8.9, 2.9 Hz, 2H), 6.62 (dt, *J* = 8.9, 2.9 Hz, 2H), 3.18 (s, 3H), 2.14 (s, 3H).



1-(*o*-Tolyl)ethan-1-one (**6m**). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.26 (d, *J* = 7.5 Hz, 1H), 7.05-7.01 (m, 1H), 6.93-6.91 (m, 2H), 2.53 (s, 3H), 2.11 (s, 3H).

8. NMR spectra

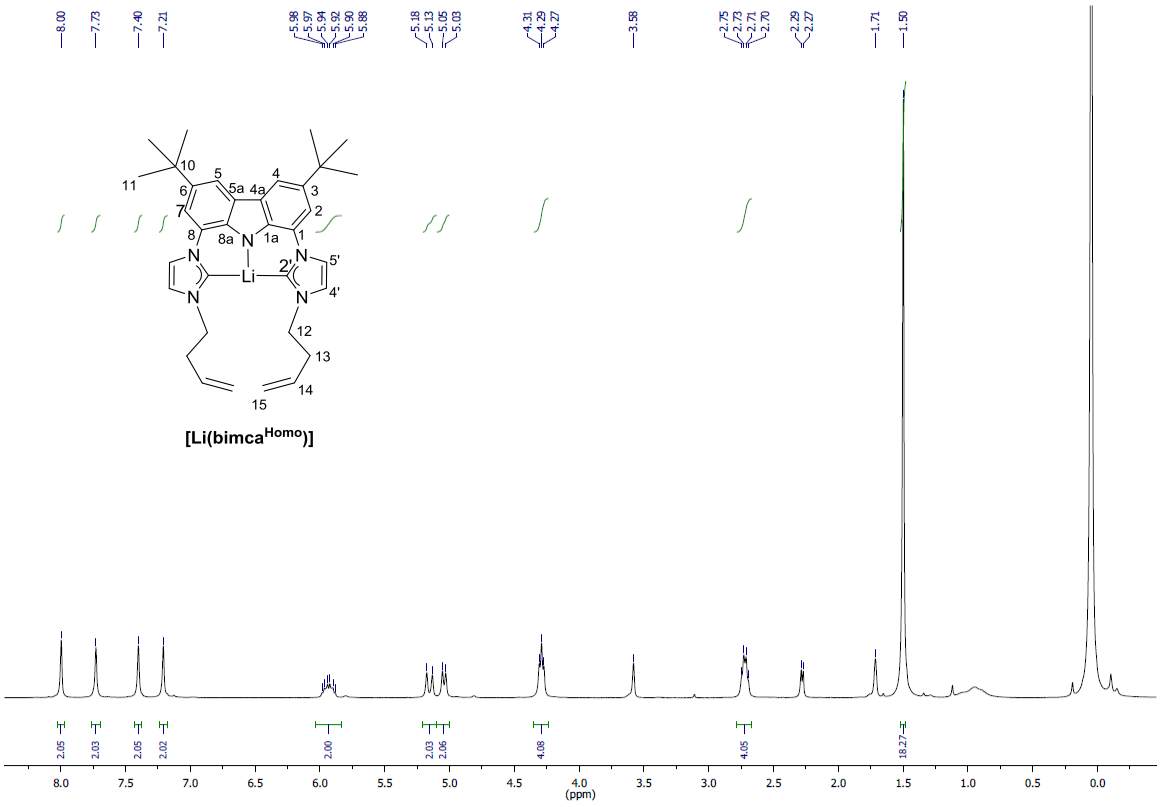


Figure S6. ^{1}H NMR (THF-d_8, 400 MHz) spectrum: deprotonation of **Hbimca^{Homo}·2HBr** with LiHMDS.

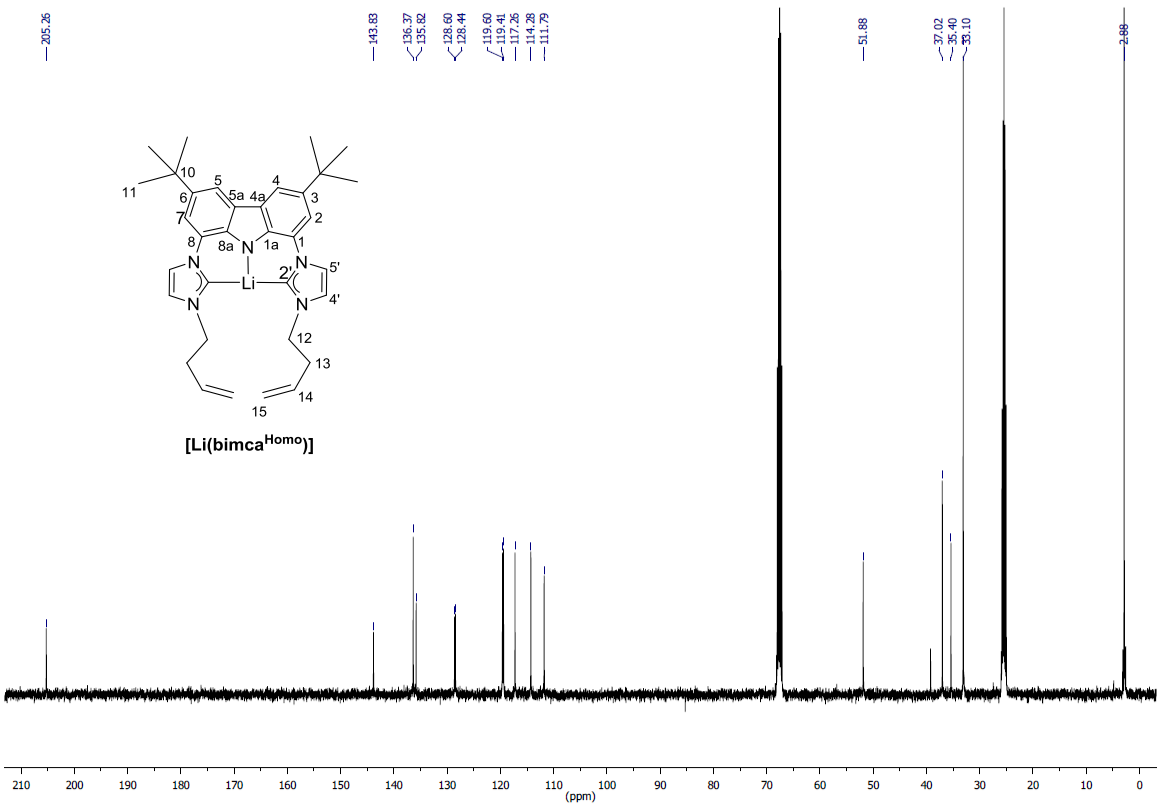


Figure S7. ^{13}C NMR (THF-d_8, 101 MHz) spectrum: deprotonation of **Hbimca^{Homo}·2HBr** with LiHMDS.

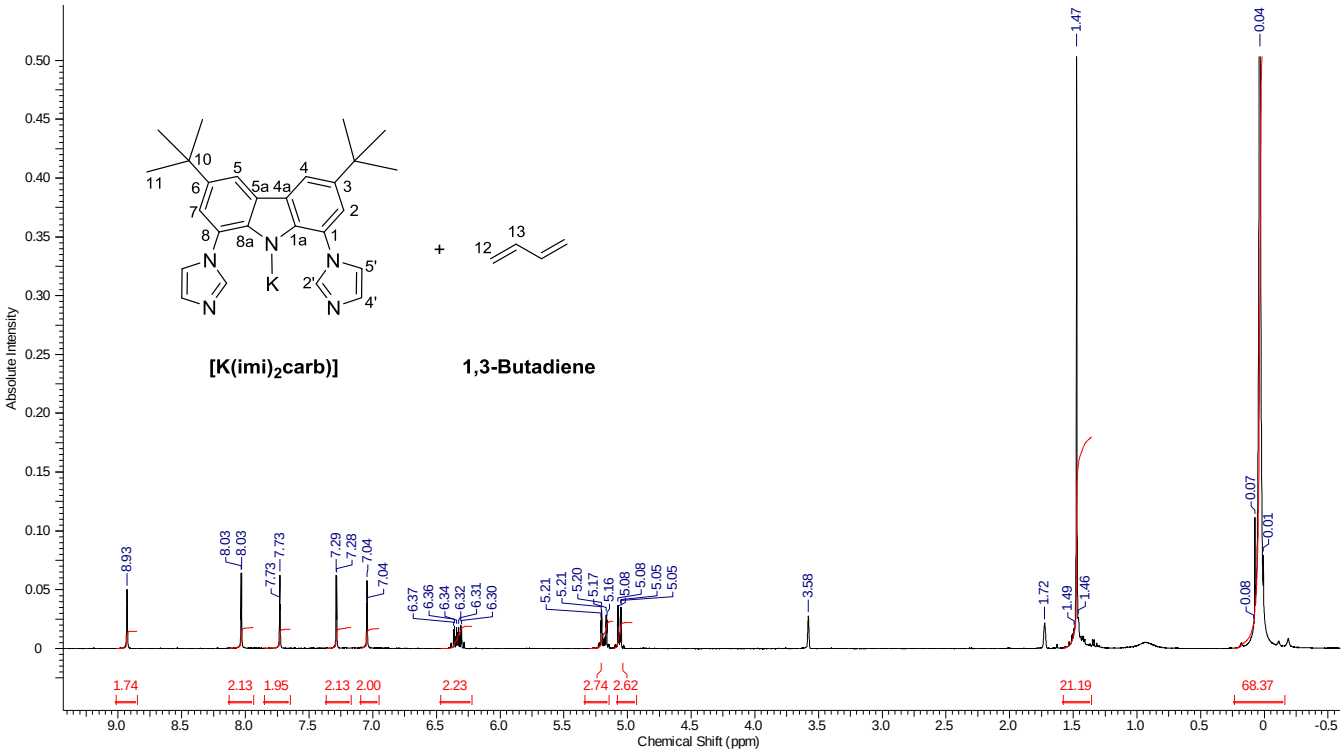


Figure S8. ^{1}H NMR (THF-d_8, 400 MHz) spectrum: deprotonation of **Hbimca^{Homo}·2HBr** with KHMDS at room temperature.

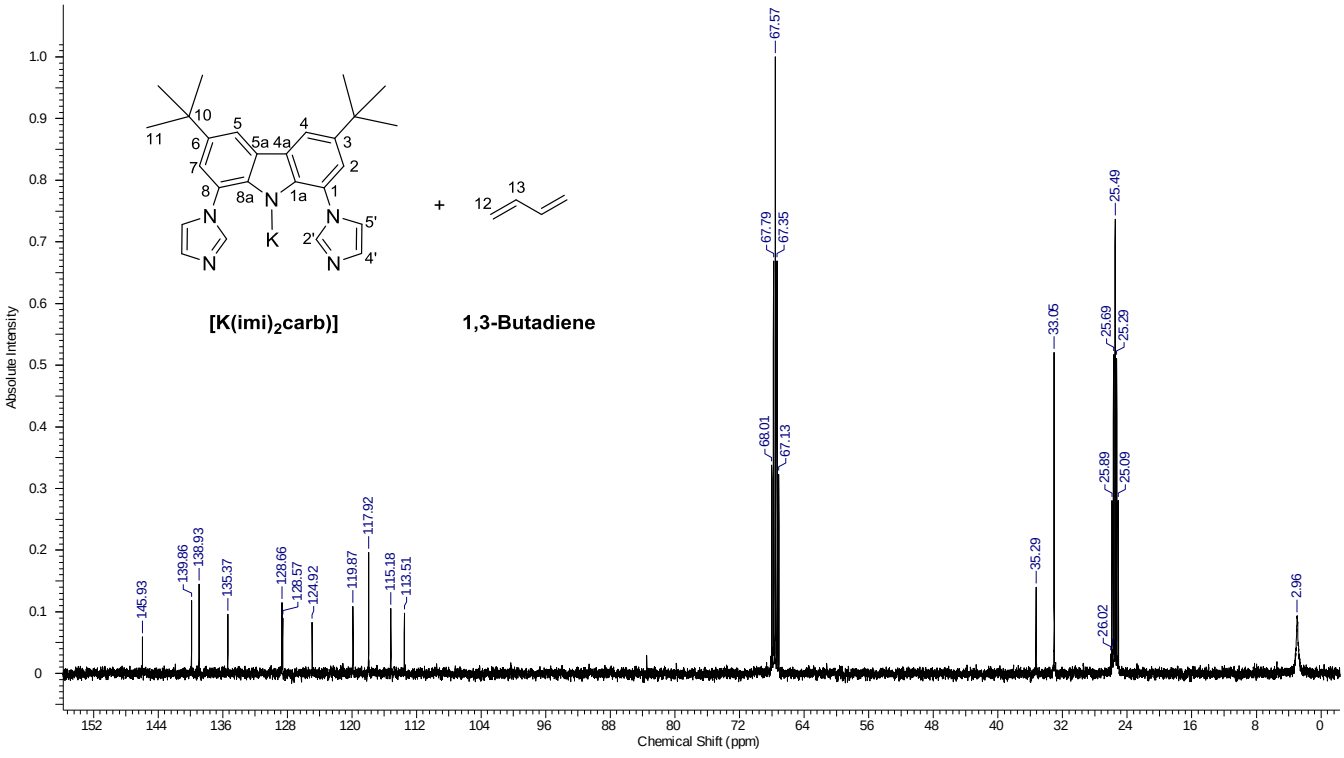


Figure S9. ^{13}C NMR (THF-d_8, 101 MHz) spectrum: deprotonation of **Hbimca^{Homo}·2HBr** with KHMDS at room temperature.

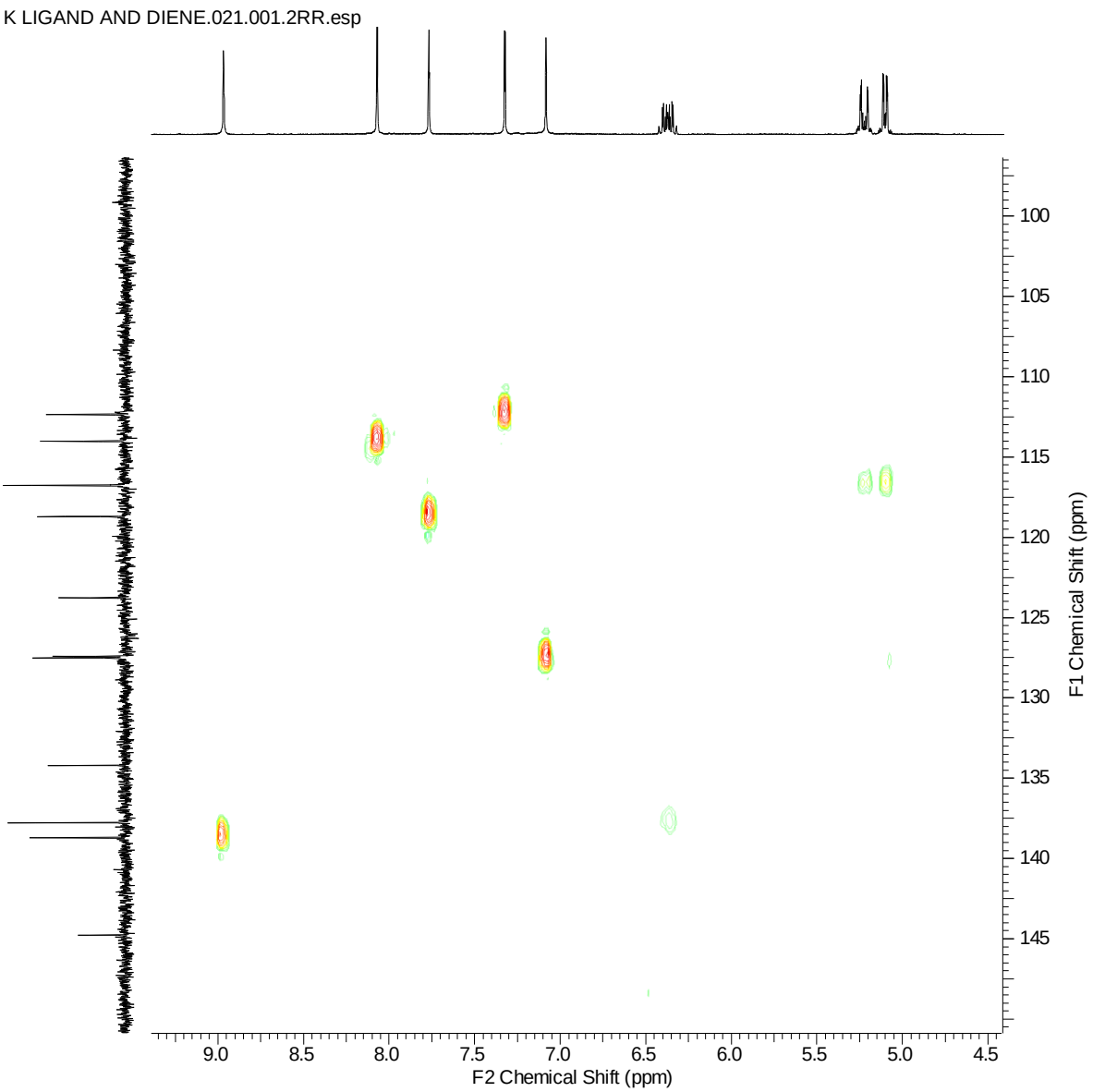


Figure S10. ^{1}H,^{1}H -HSQC (THF-d_8, 400 MHz) spectrum: deprotonation of **Hbimca^{Homo}·2HBr** with KHMDS at room temperature.

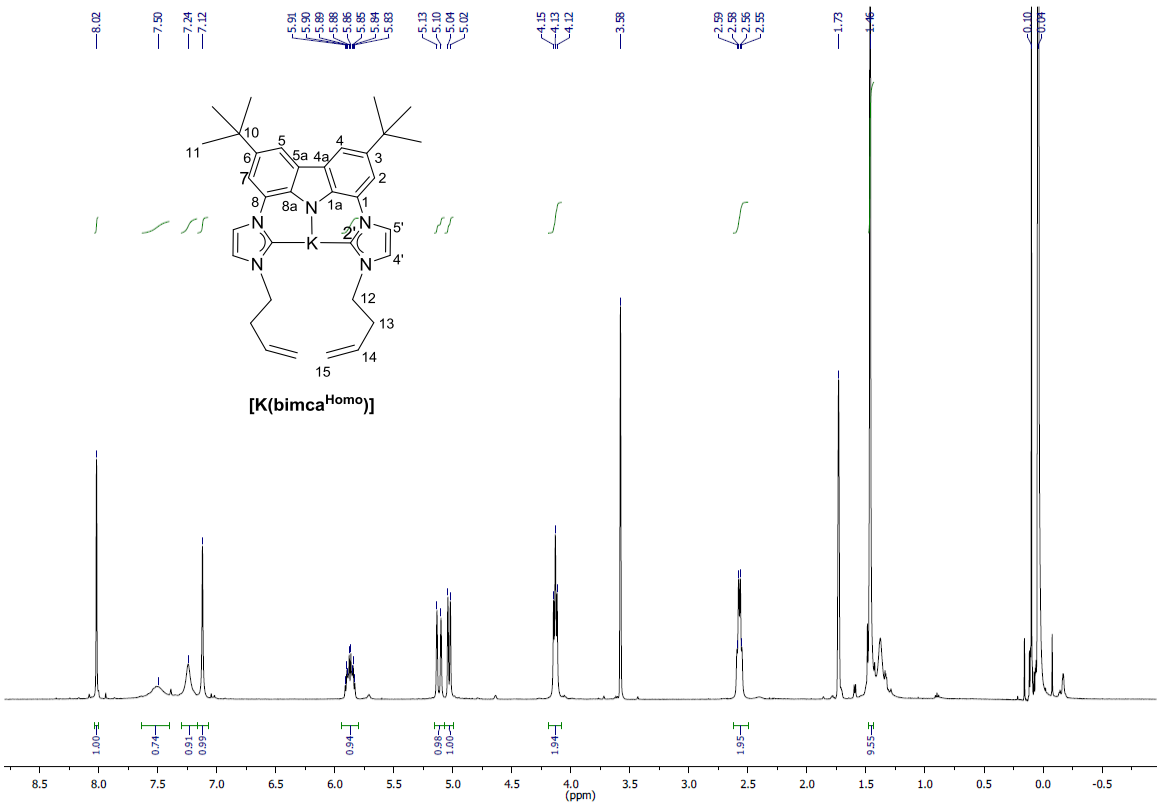


Figure S11. ^{1}H NMR (THF-d_8, 400 MHz) spectrum: deprotonation of **Hbimca^{Homo}·2HBr** with KHMDS at –30 °C.

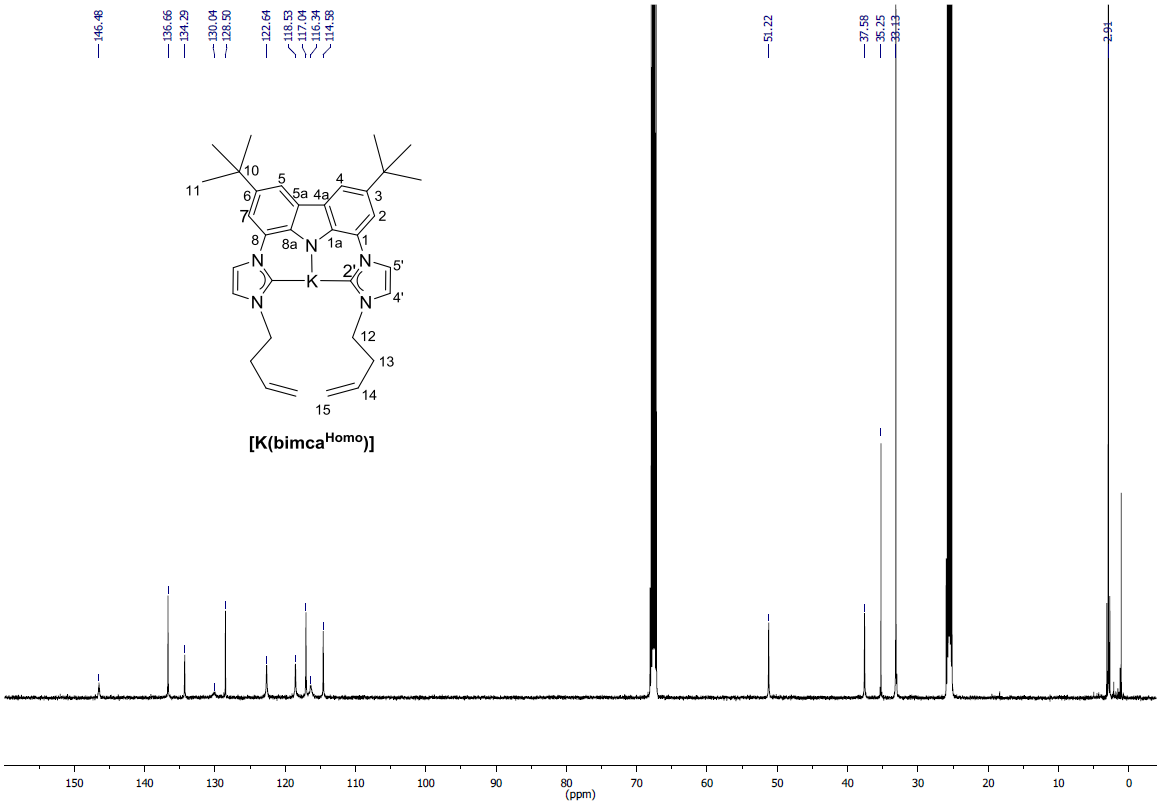


Figure S12. ^{13}C NMR (THF-d_8, 101 MHz) spectrum: deprotonation of **Hbimca^{Homo}·2HBr** with KHMDS at –30 °C.

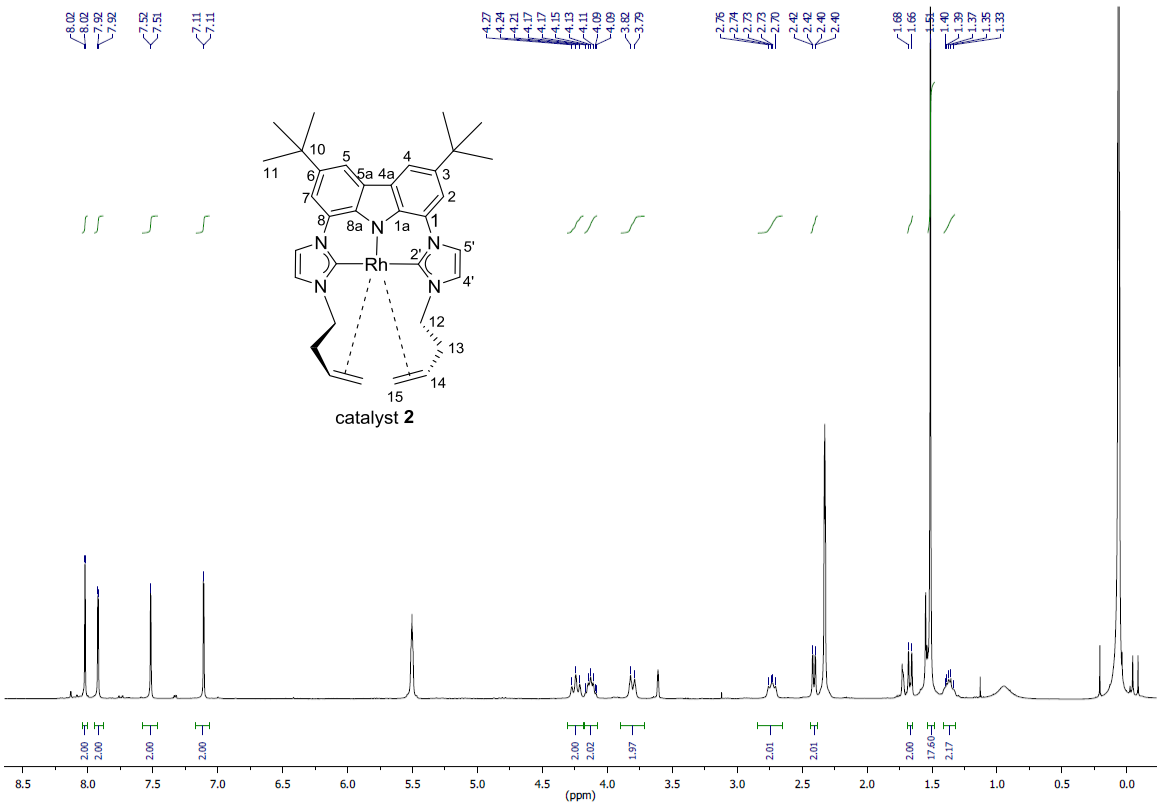


Figure S13. ^{1}H NMR (THF-d_8, 400 MHz) spectrum: transmetalation of **[Li(bimca^{Homo})]** with [Rh(μ-Cl)(COD)]$_2$.

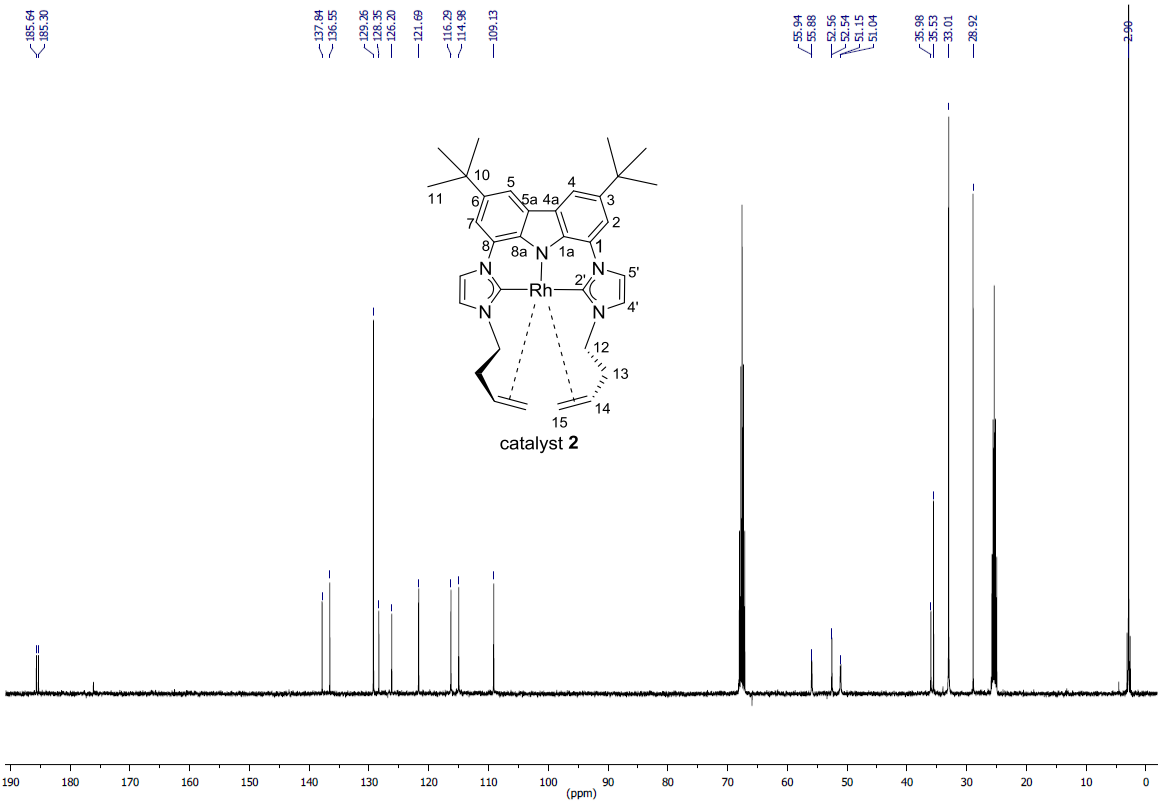


Figure S14. ^{13}C NMR (THF-d_8, 101 MHz) spectrum: transmetalation of **[Li(bimca^{Homo})]** with [Rh(μ-Cl)(COD)]$_2$.

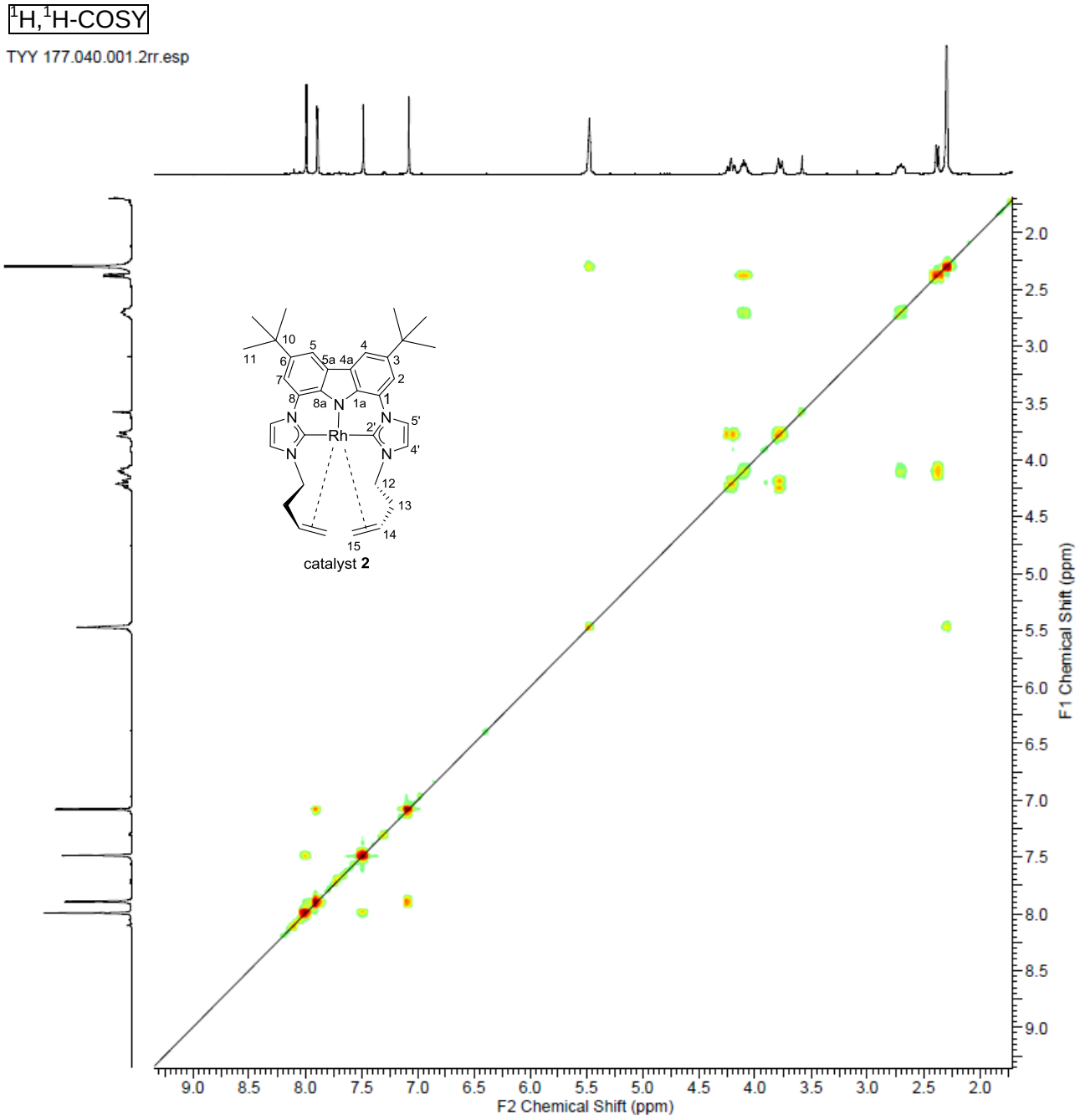


Figure S15. ^{1}H,^{13}C-COSY NMR (THF-d_8, 400 MHz) spectrum: transmetalation of **[Li(bimca^{Homo})]** with [Rh(μ-Cl)(COD)]$_2$.

^{1}H,^{13}C-HSQC

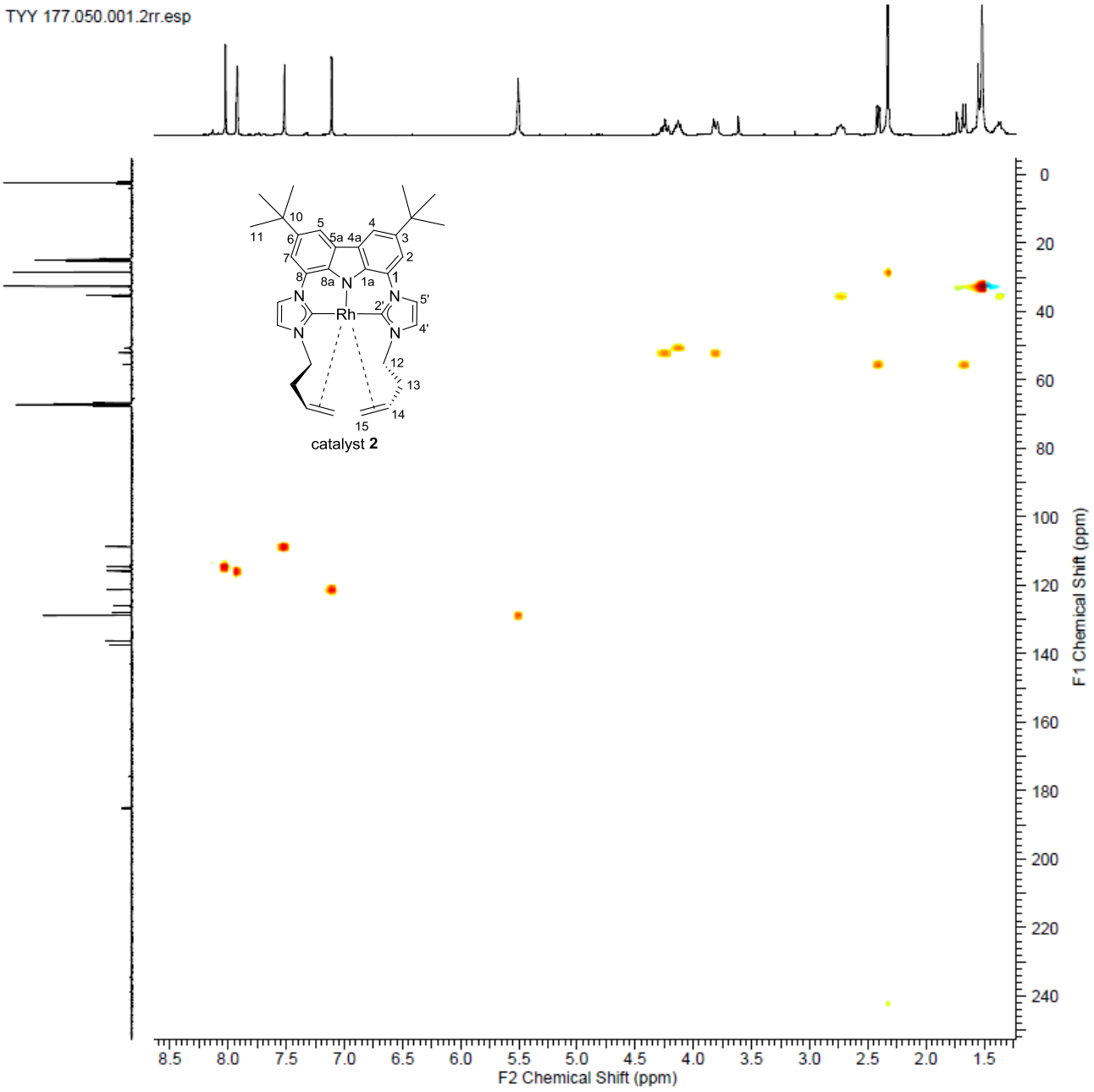


Figure S16. ^{1}H,^{13}C-HSQC NMR (THF-d_8, 400 MHz) spectrum: transmetalation of **[Li(bimca^{Homo})]** with [Rh(μ-Cl)(COD)]$_2$.

^{1}H, ^{13}C-HMBC

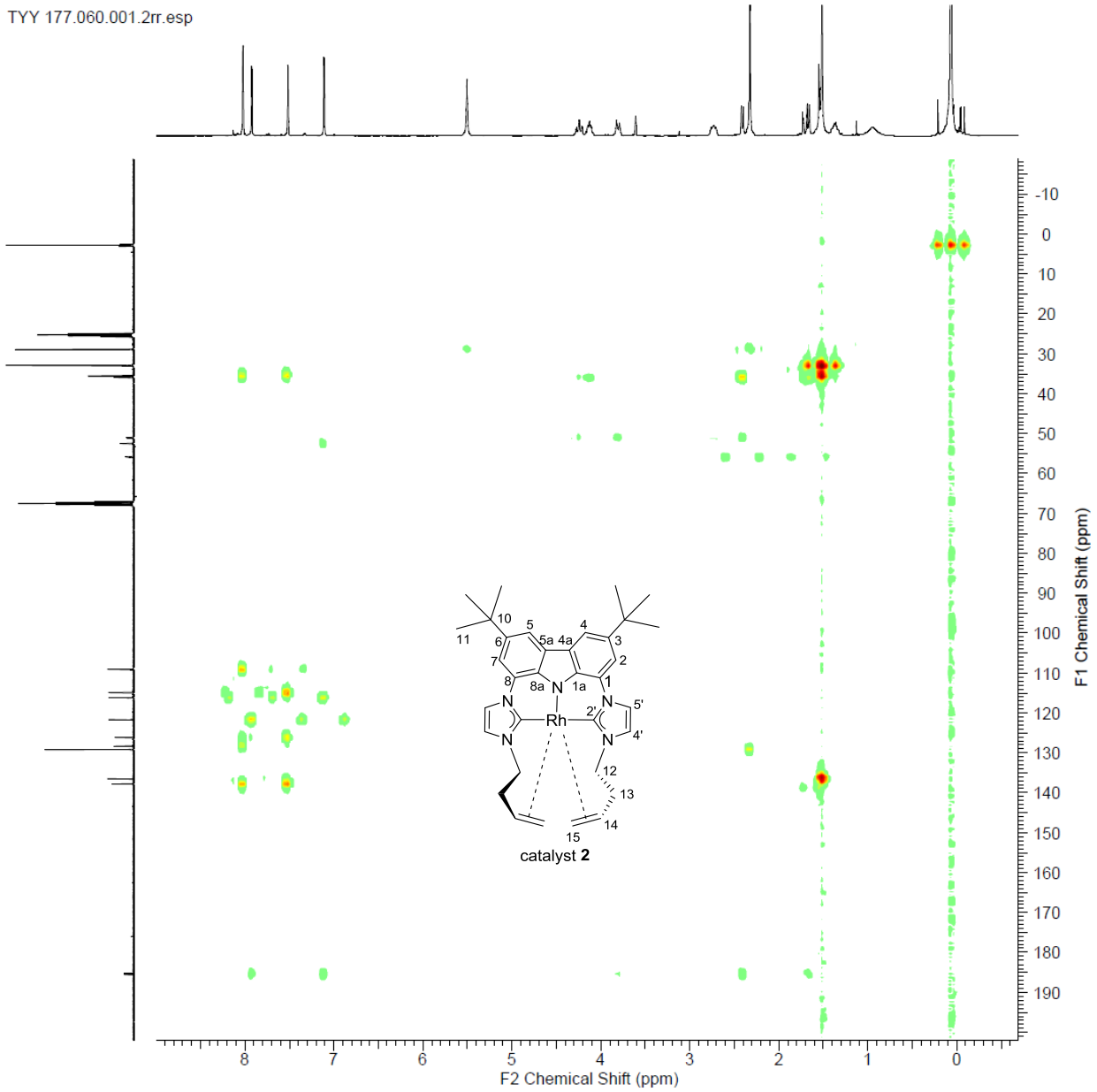


Figure S17. ^{1}H,^{13}C-HMBC NMR (THF-d_8, 400 MHz) spectrum: transmetalation of **[Li(bimca^{Homo})]** with [Rh(μ-Cl)(COD)]$_2$.

^{1}H,^{1}H-NOE

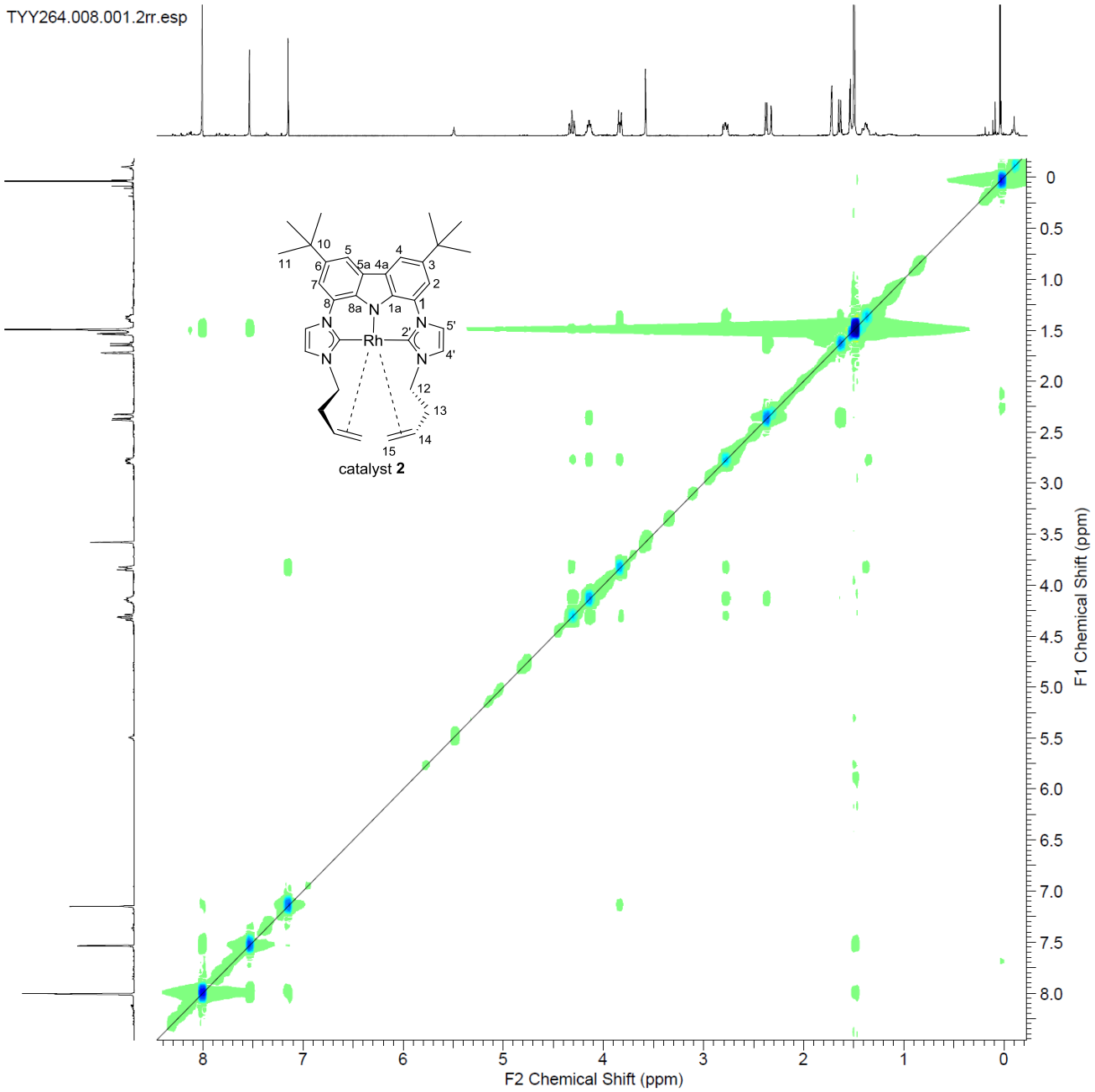


Figure S18. ^{1}H,^{1}H-NOE NMR (THF-d_8, 400 MHz) spectrum at 0 °C: transmetalation of **[Li(bimca^{Homo})]** with [Rh(μ-Cl)(COD)]$_2$.

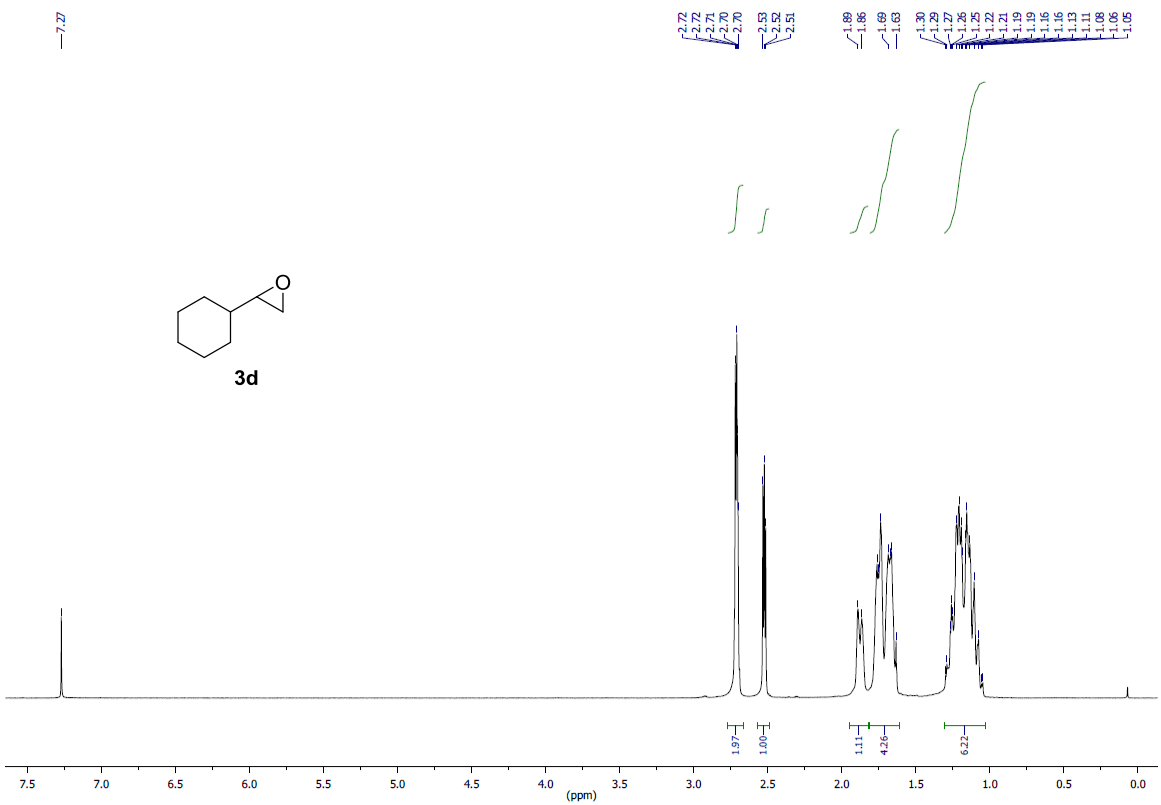


Figure S19. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **3d**.

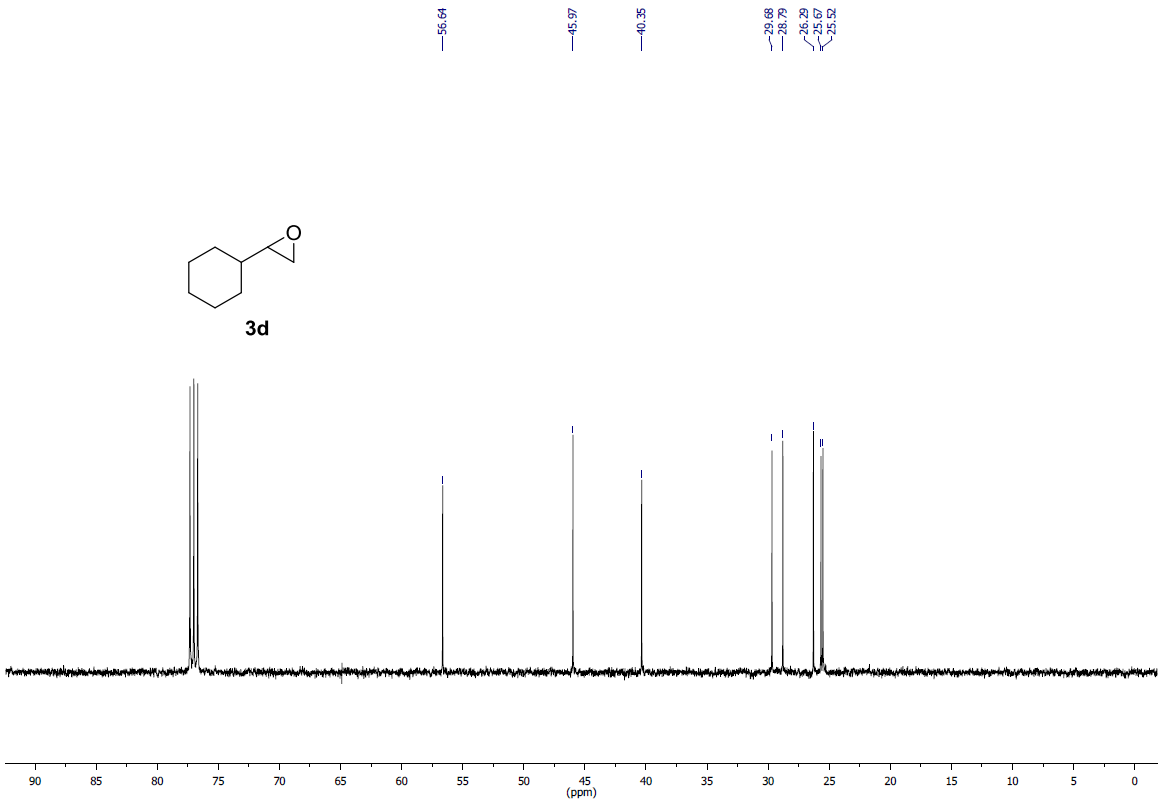


Figure S20. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **3d**.

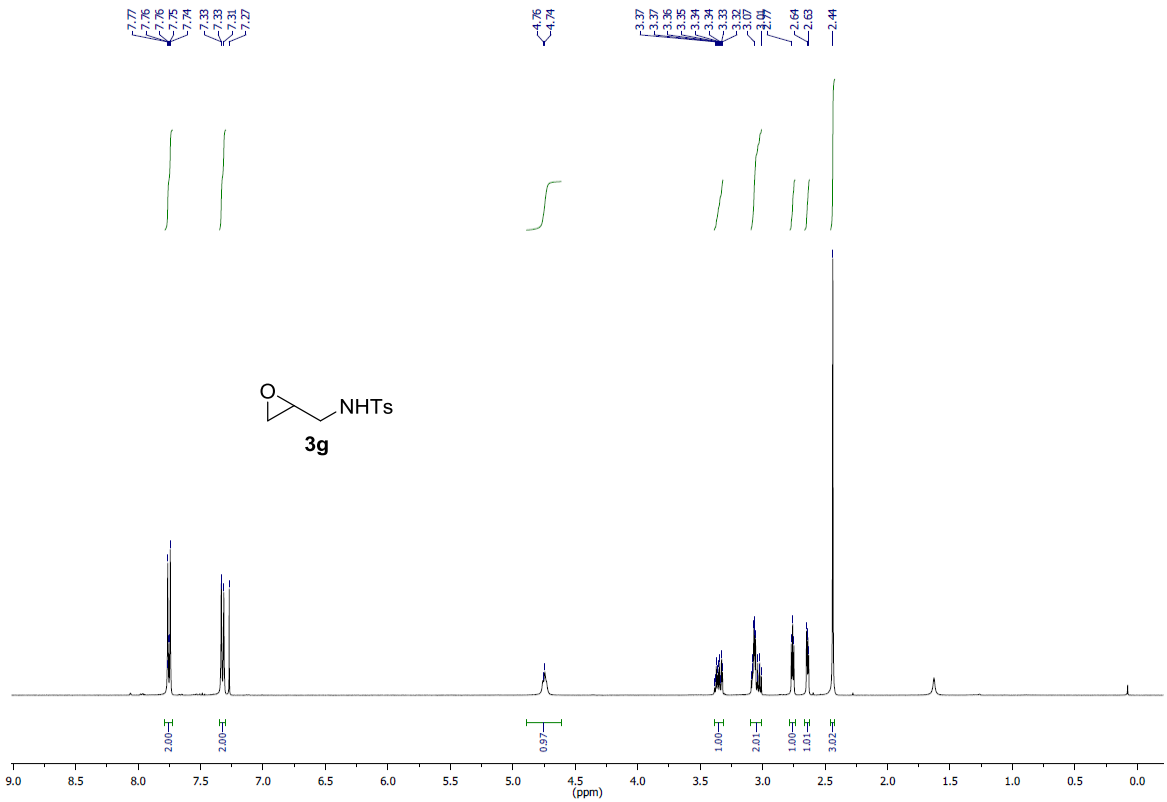


Figure S21. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **3g**.

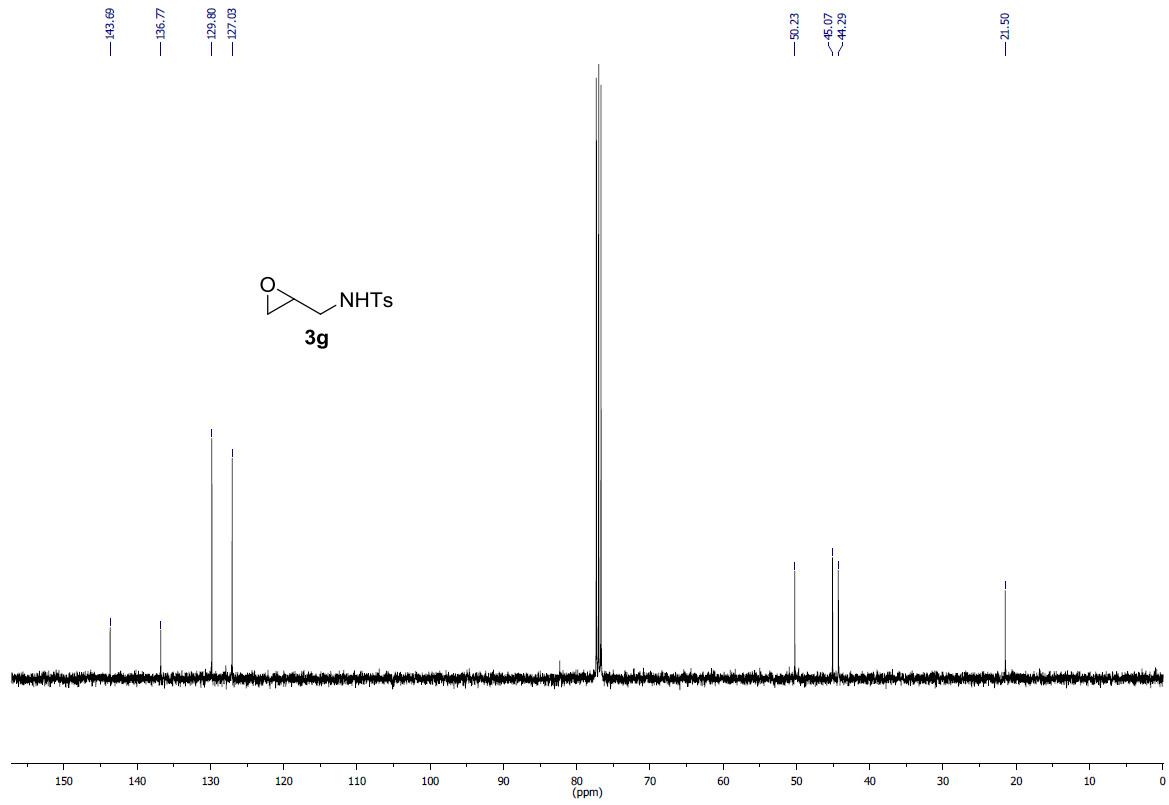


Figure S22. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **3g**.

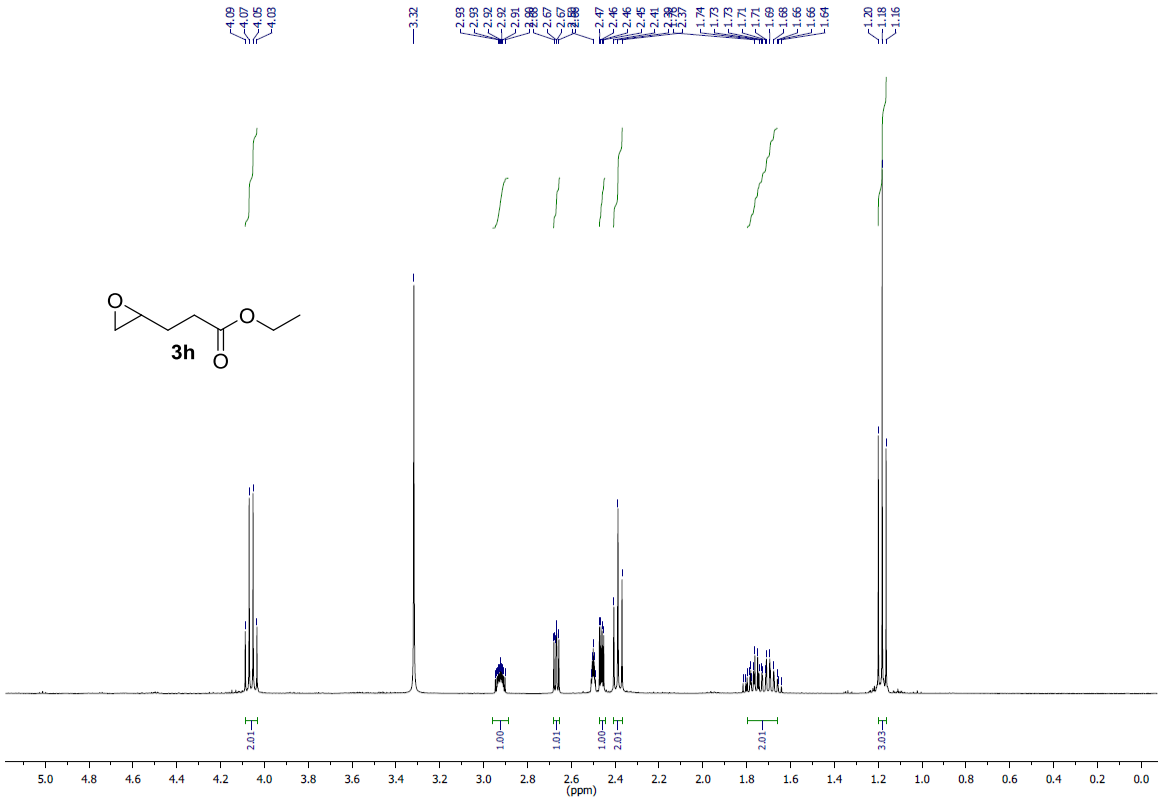


Figure S23. ^{1}H NMR (d_6-DMSO, 400 MHz) spectrum: compound **3h**.

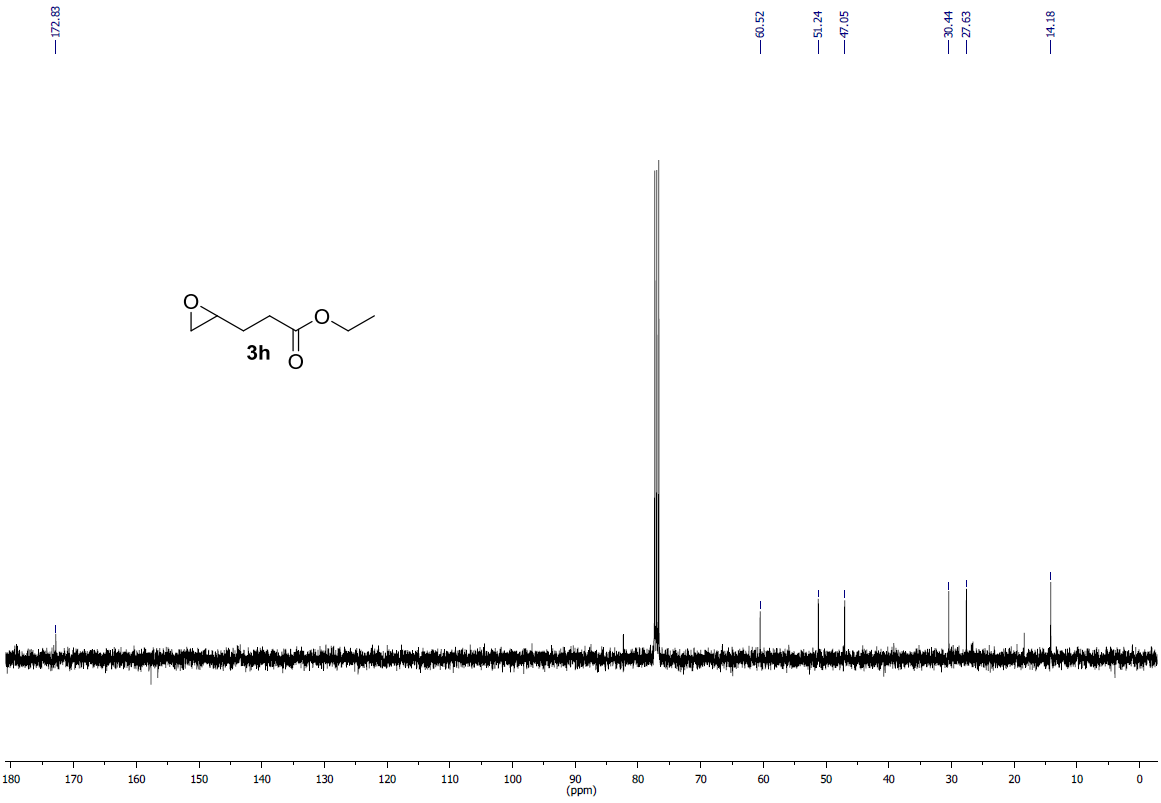


Figure S24. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **3h**.

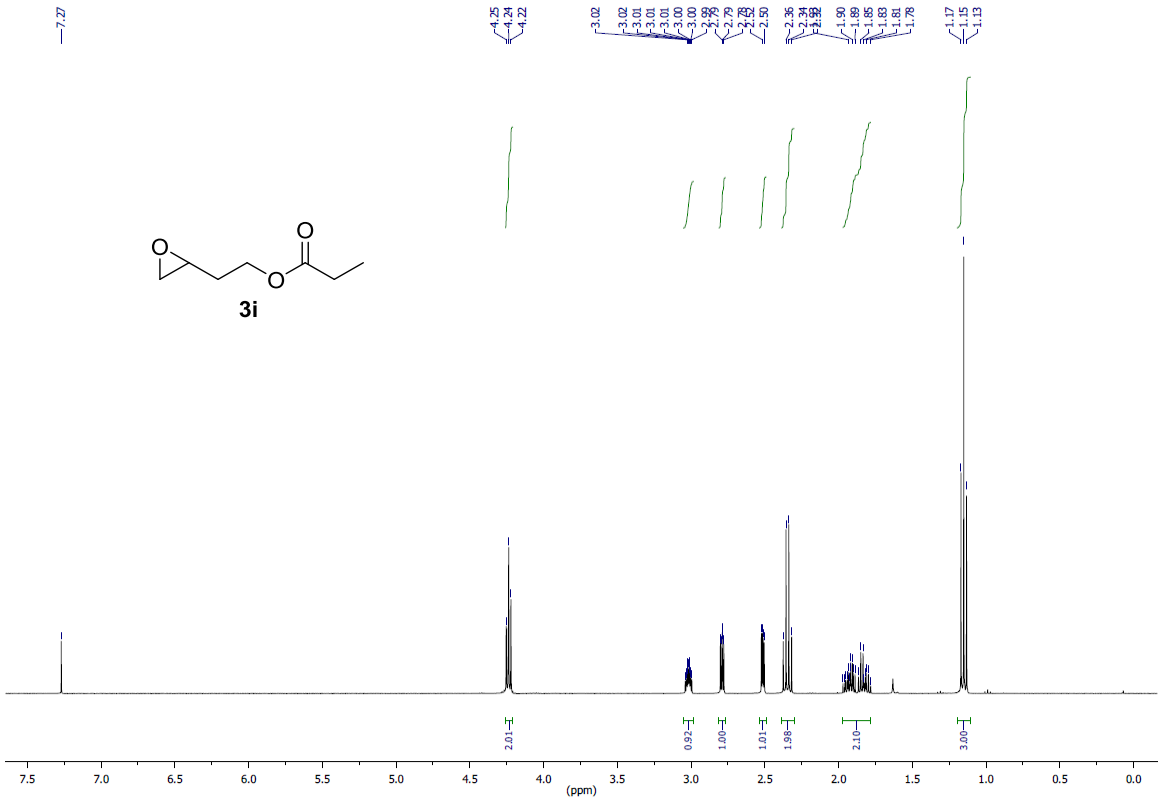


Figure S25. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **3i**.

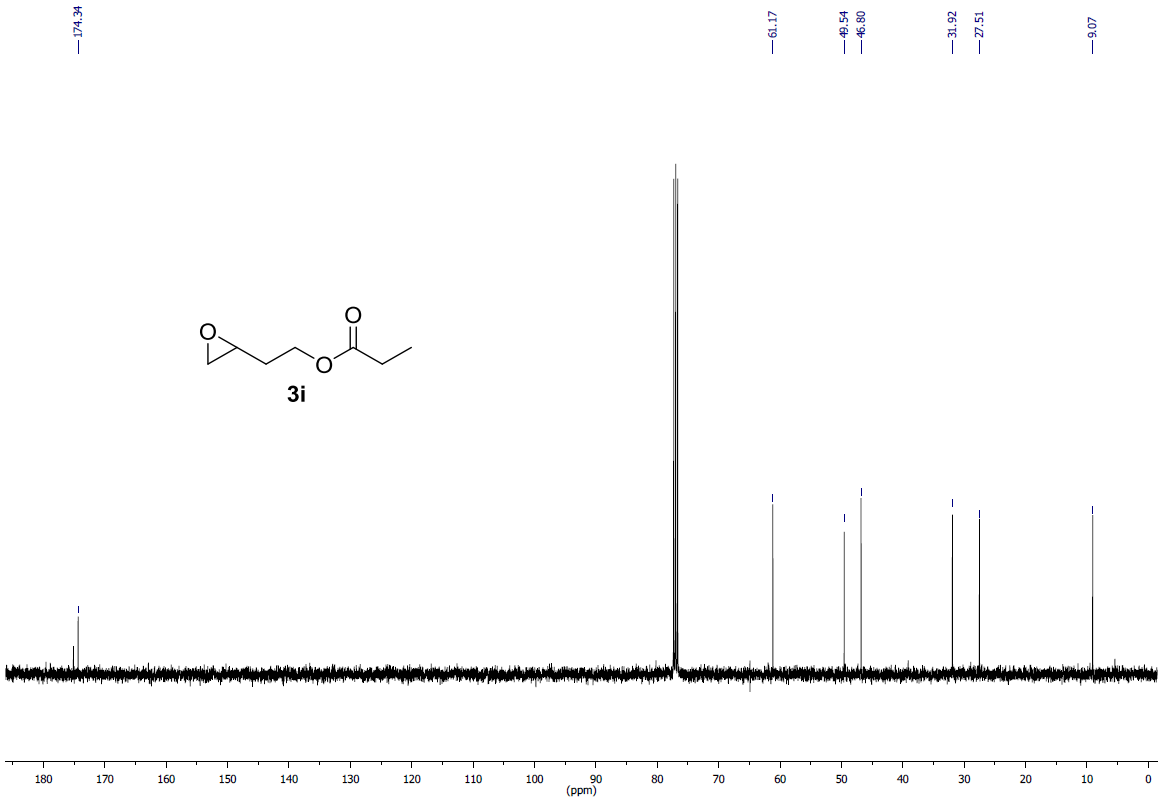


Figure S26. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **3i**.

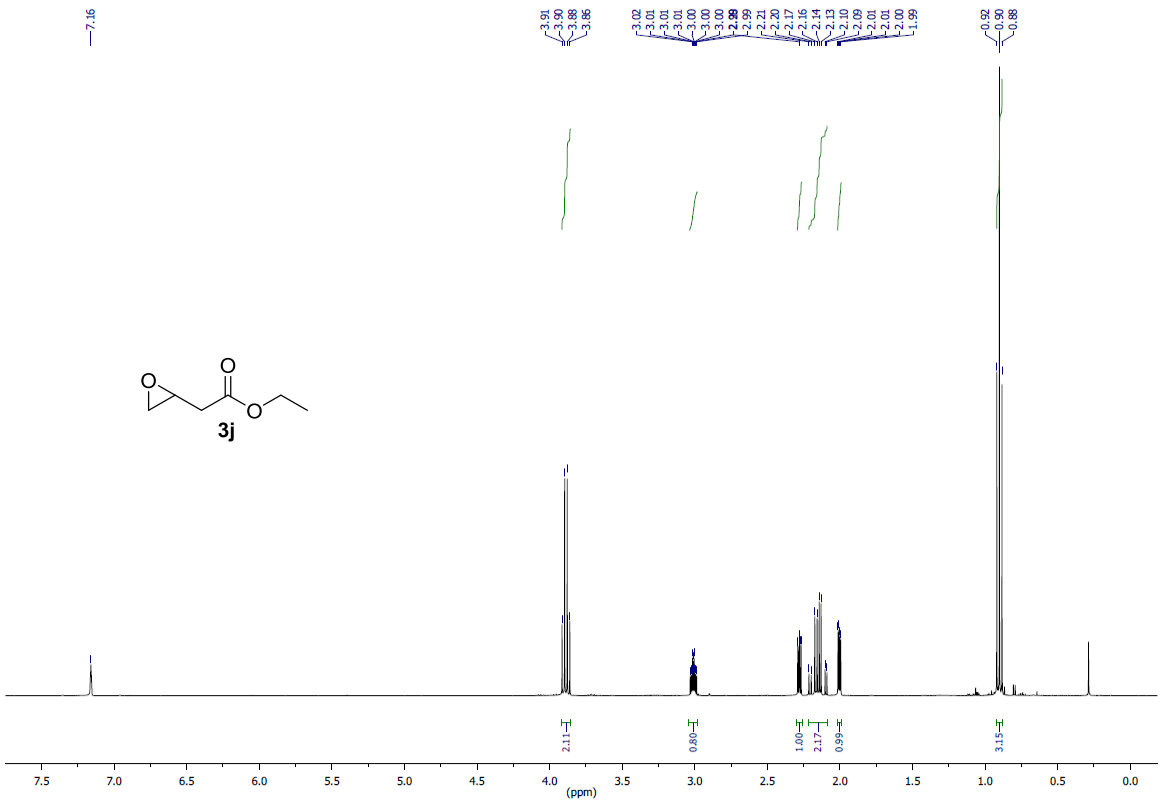


Figure S27. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **3j**.

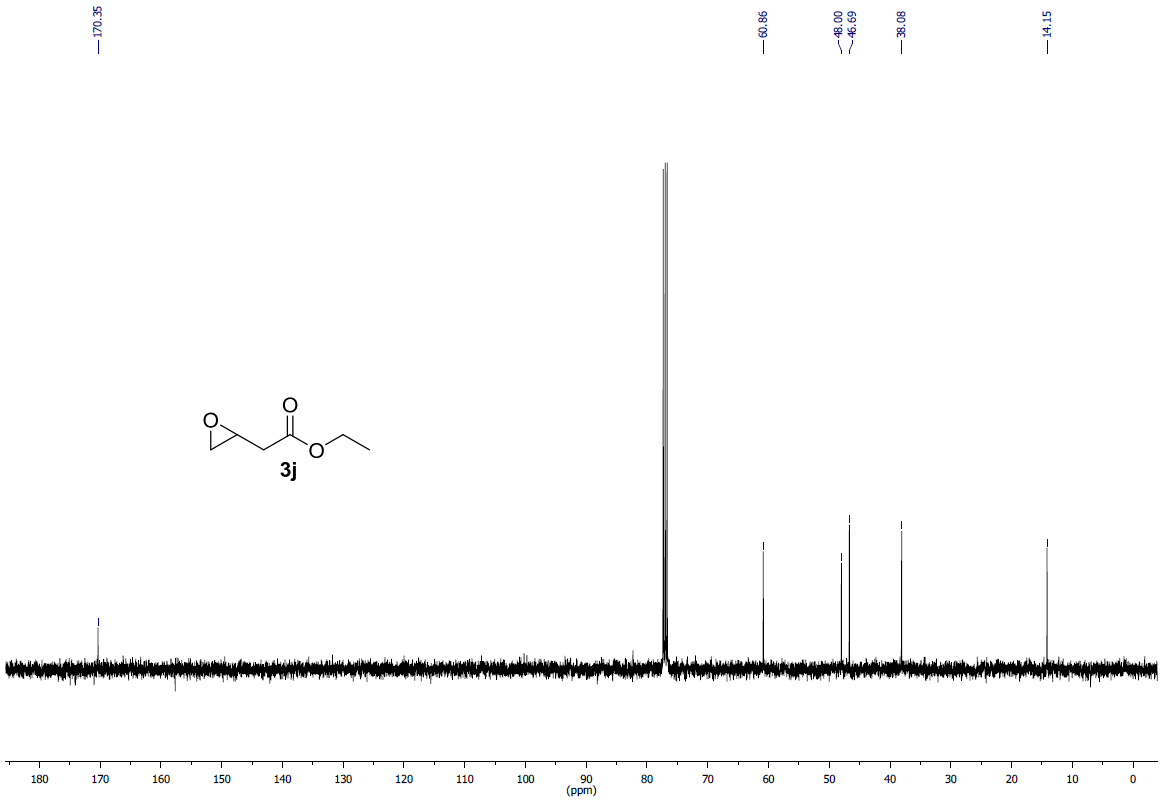


Figure S28. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **3j**.

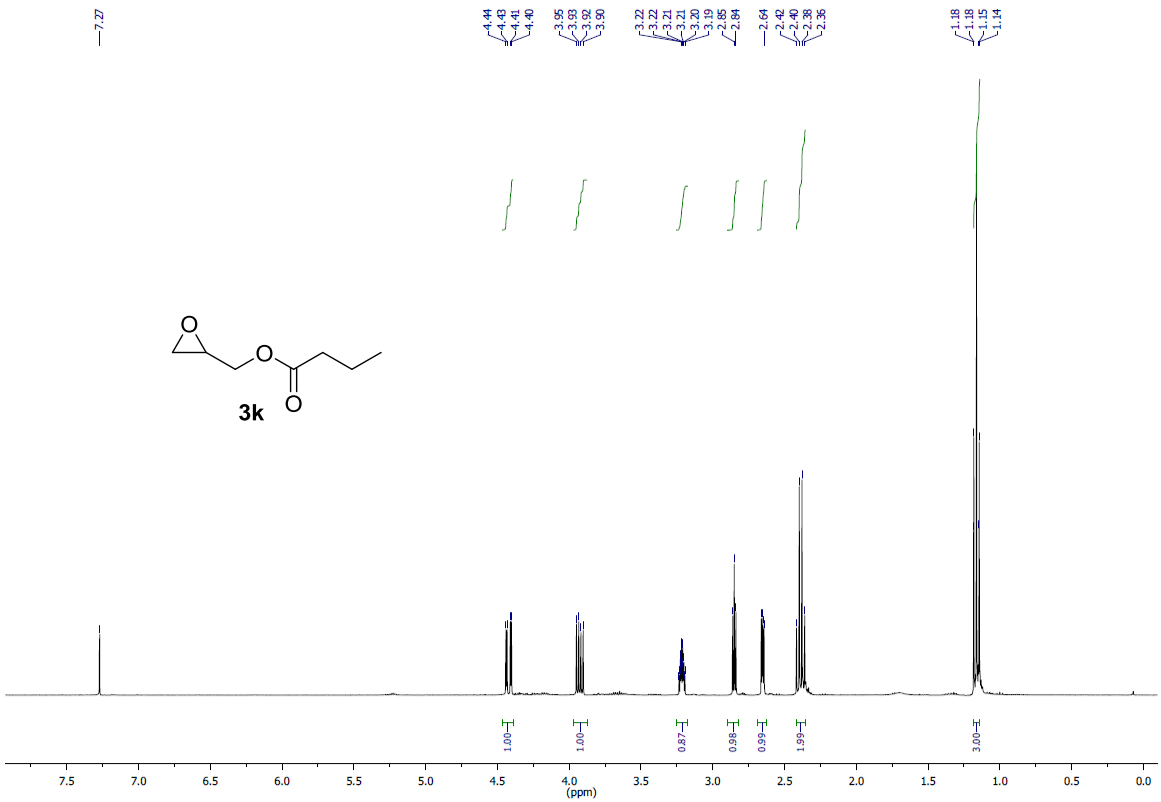


Figure S29. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **3k**.

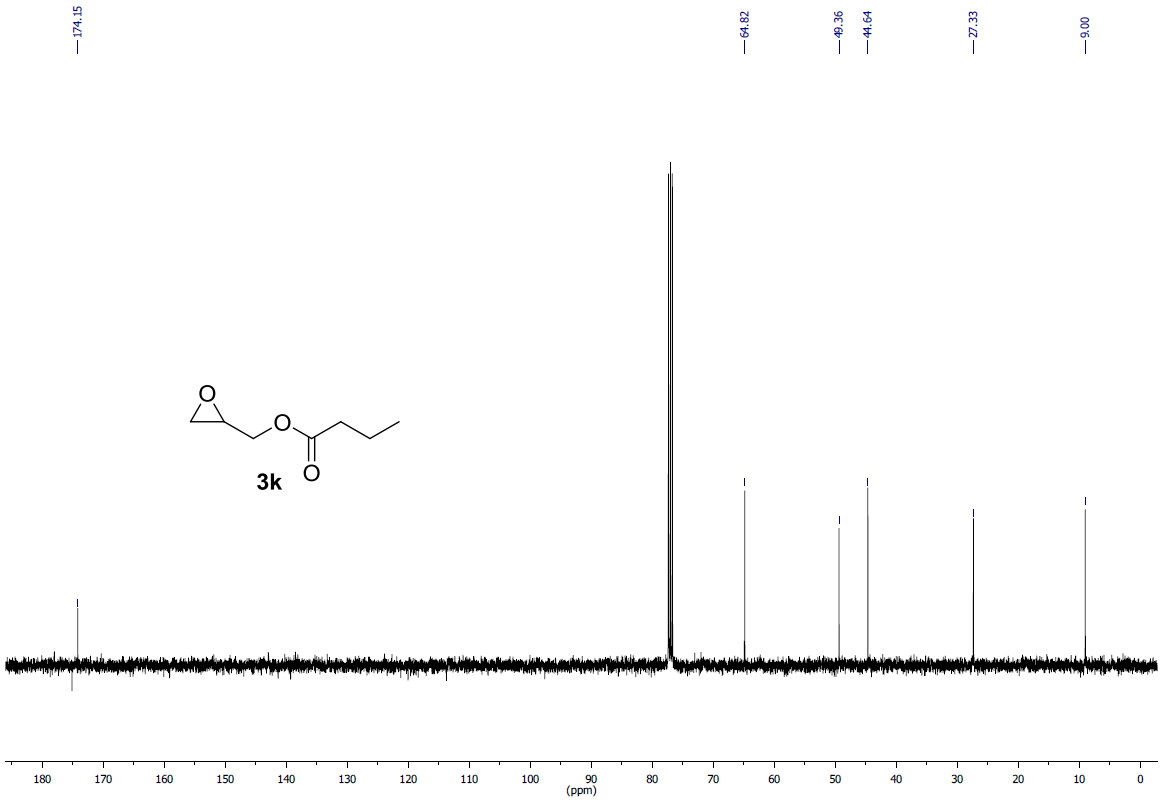


Figure S30. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **3k**.

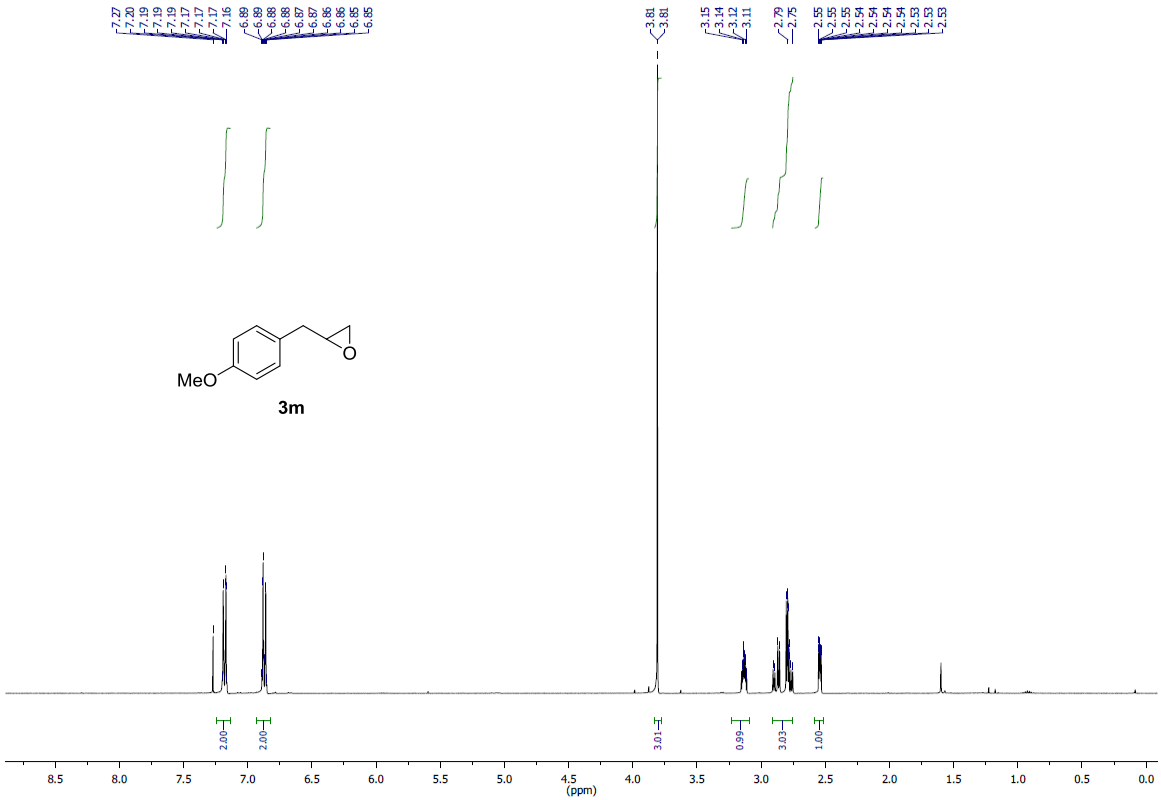


Figure S31. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **3m**.

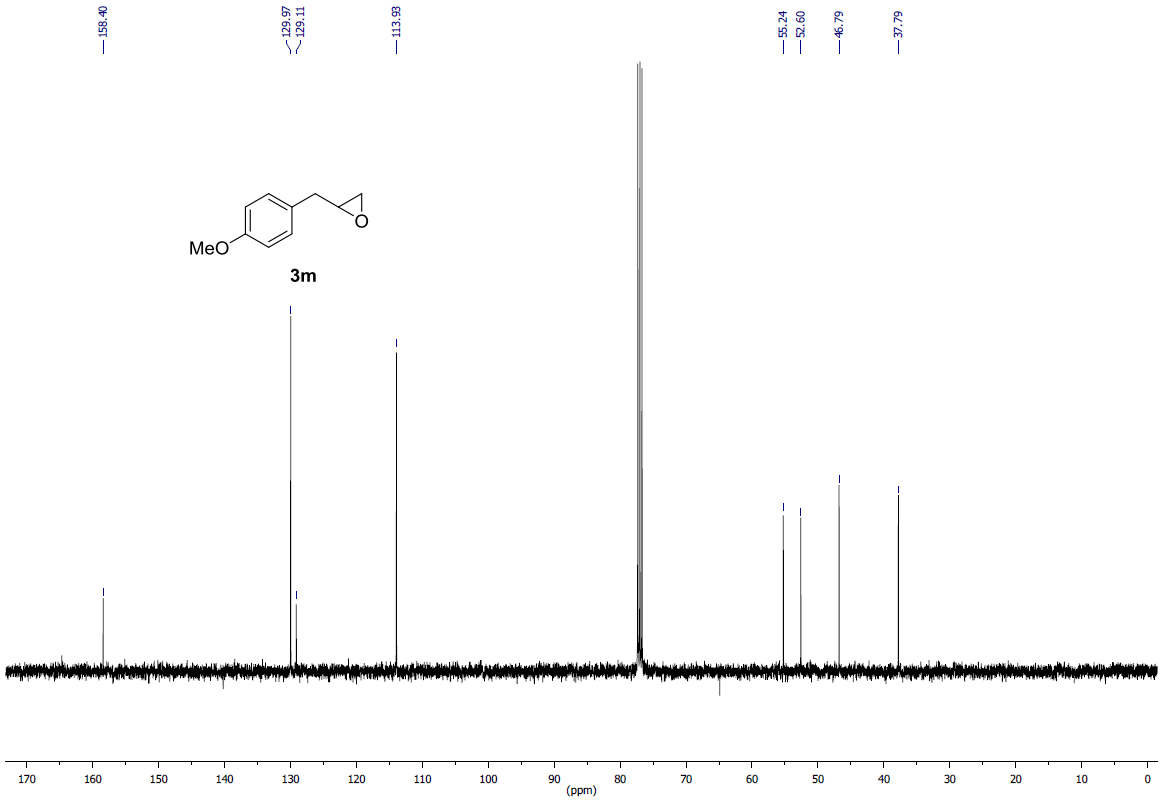


Figure S32. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **3m**.

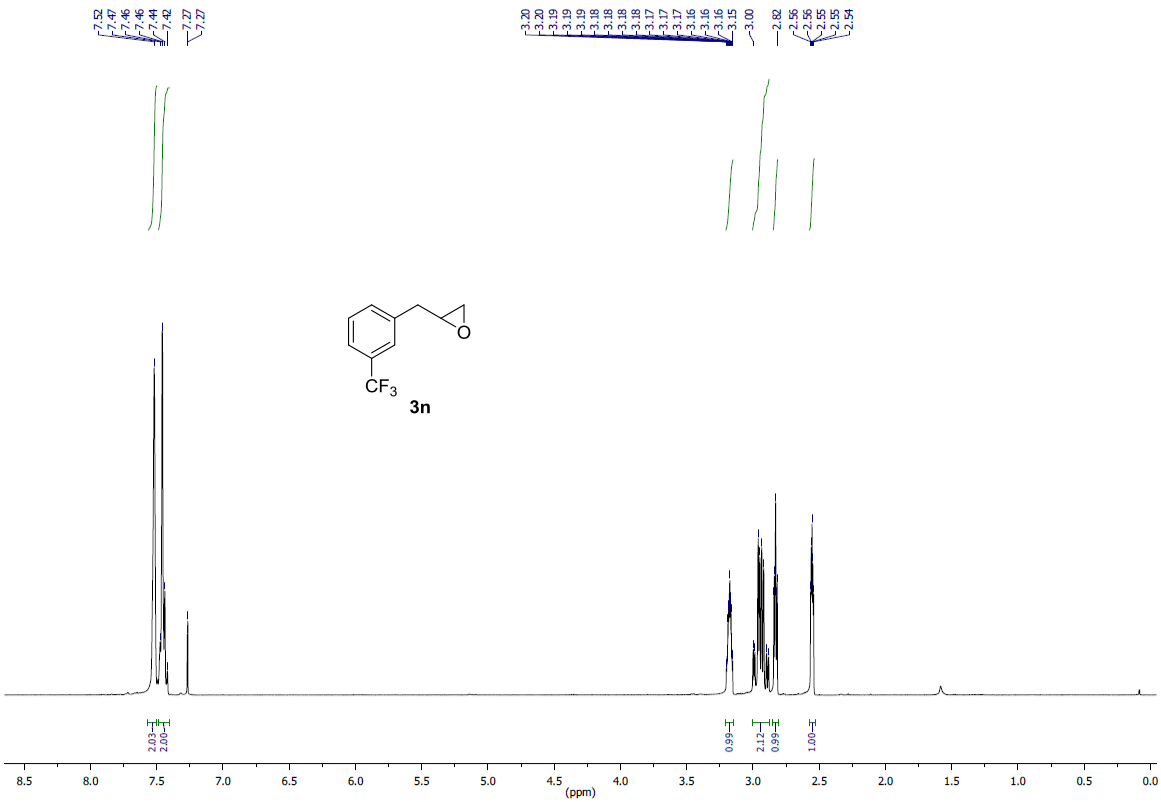


Figure S33. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **3n**.

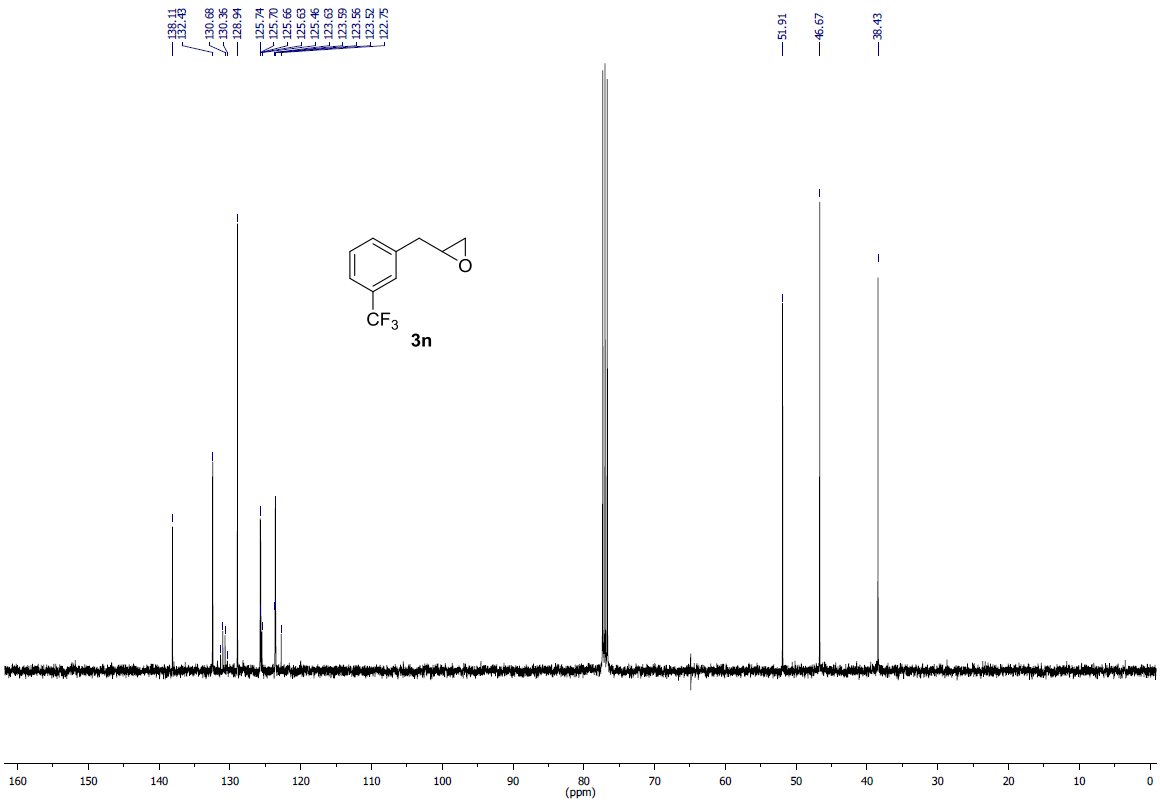


Figure S34. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **3n**.

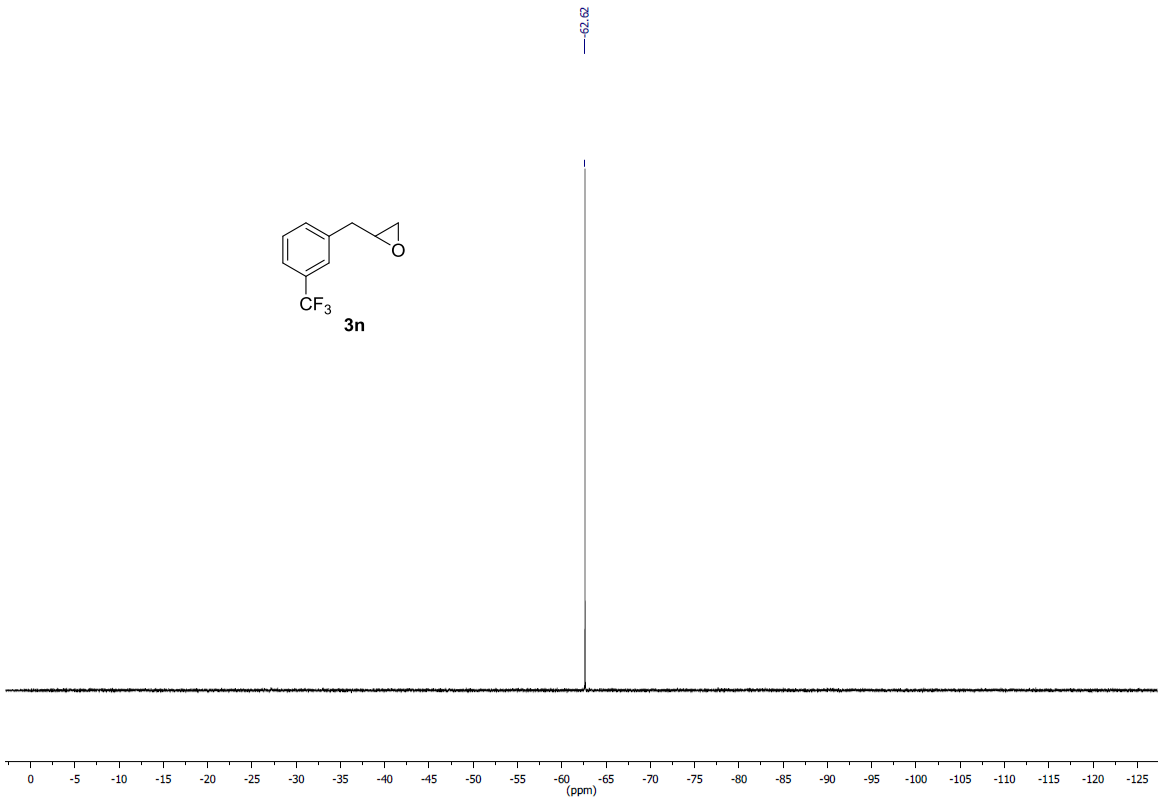


Figure S35. ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum: compound **3n**.

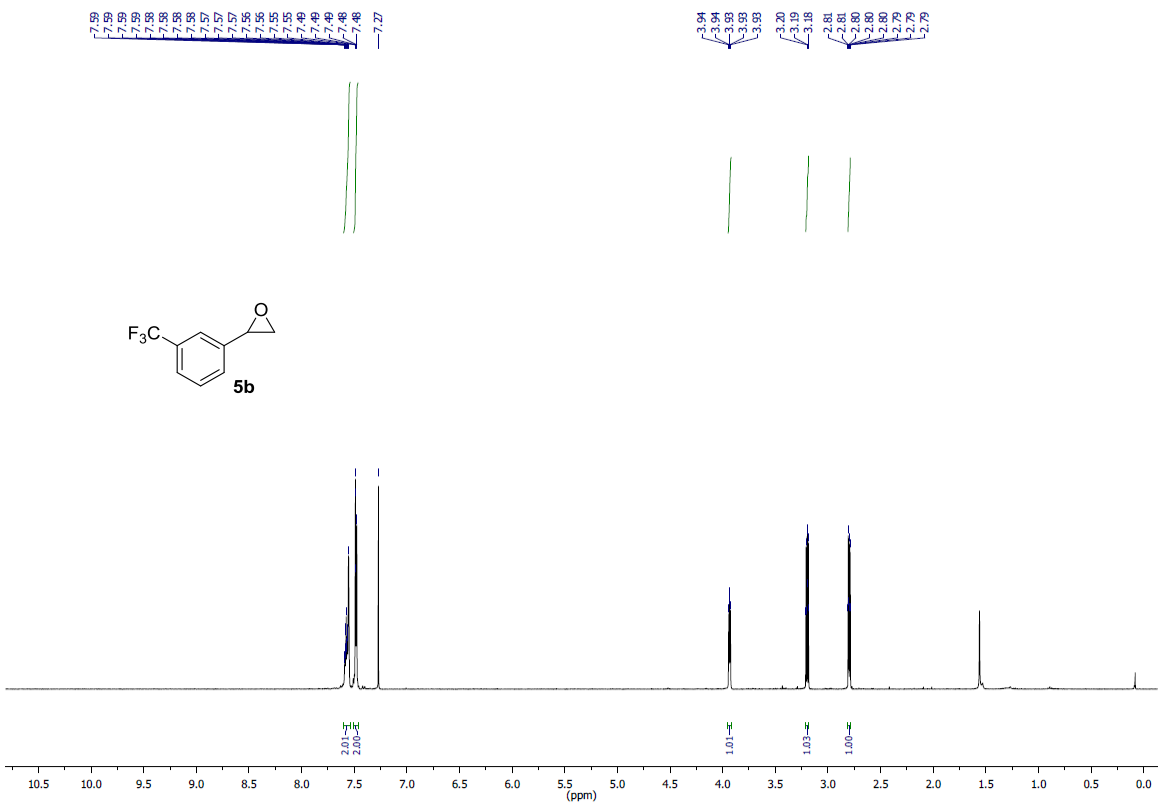


Figure S36. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5b**.

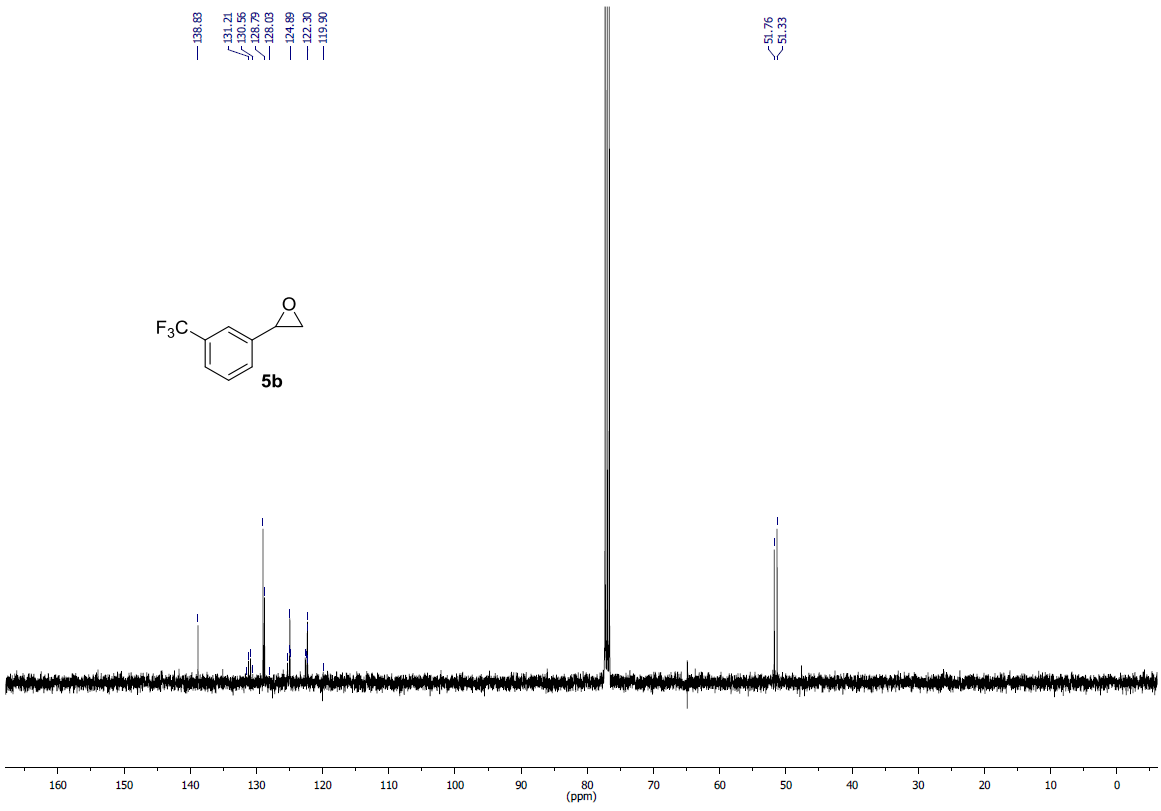


Figure S37. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5b**.

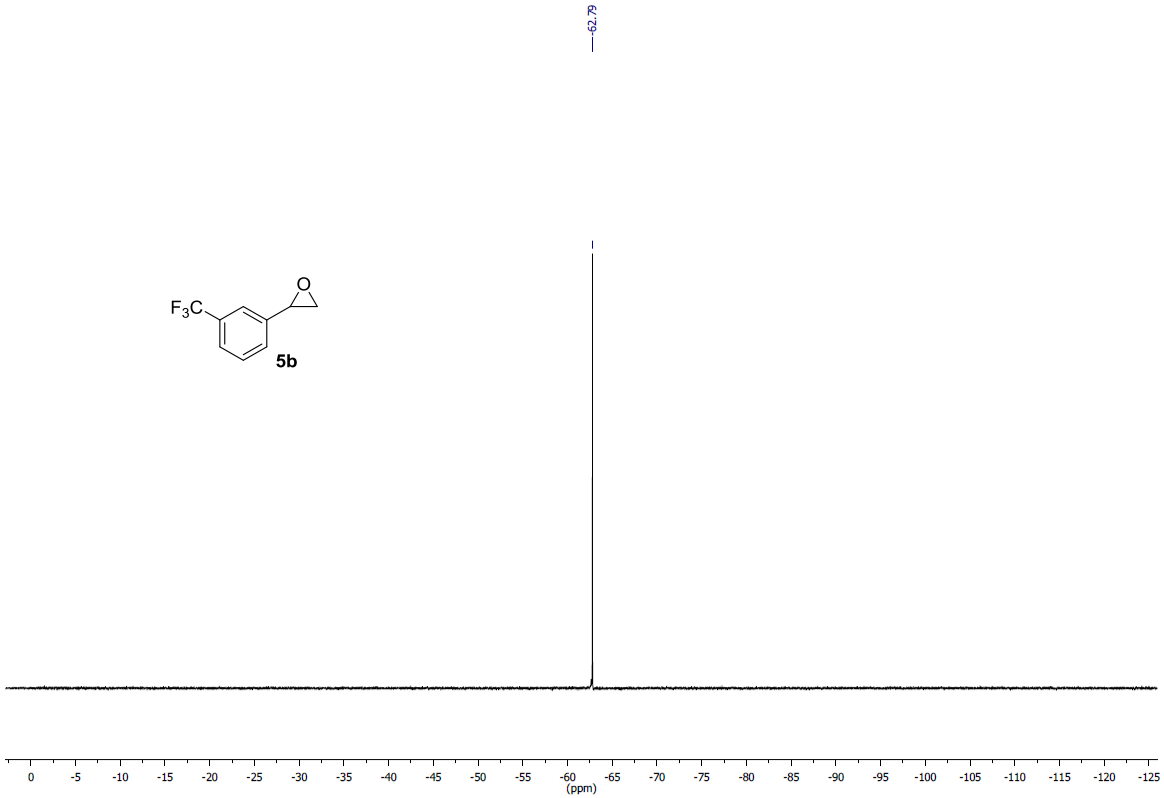


Figure S38. ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum: compound **5b**.

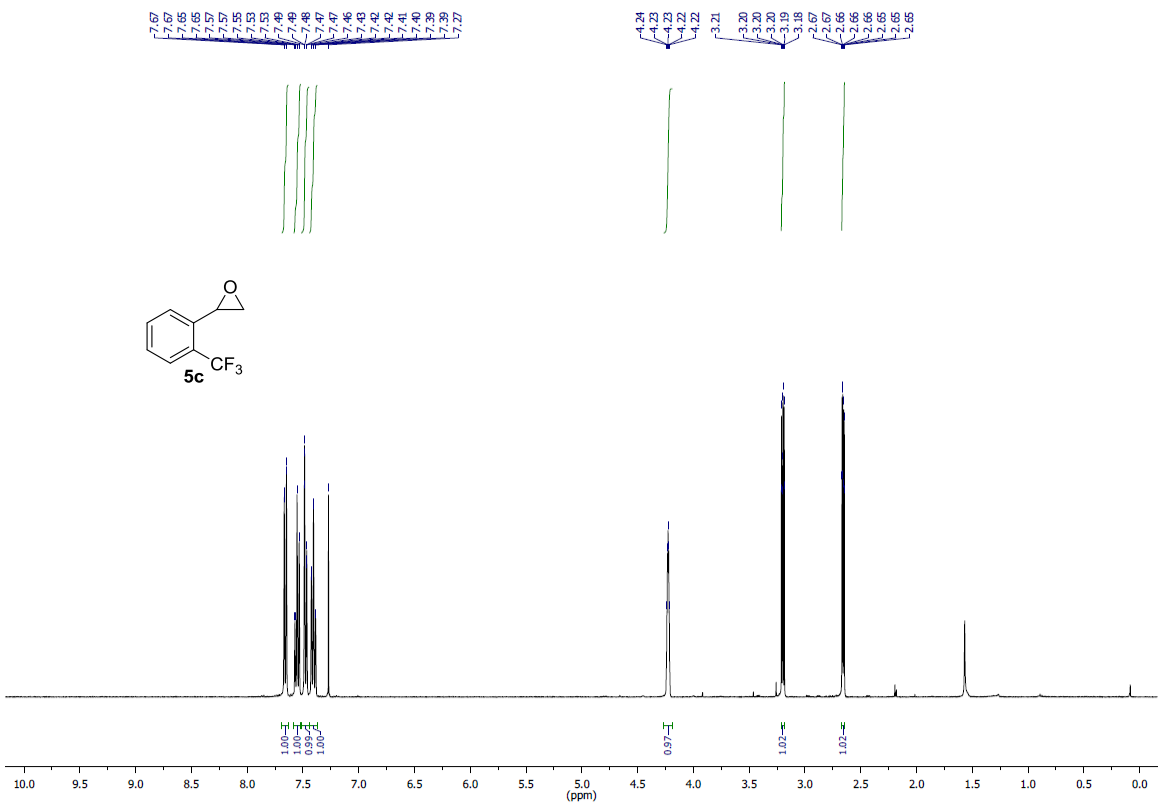


Figure S39. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5c**.

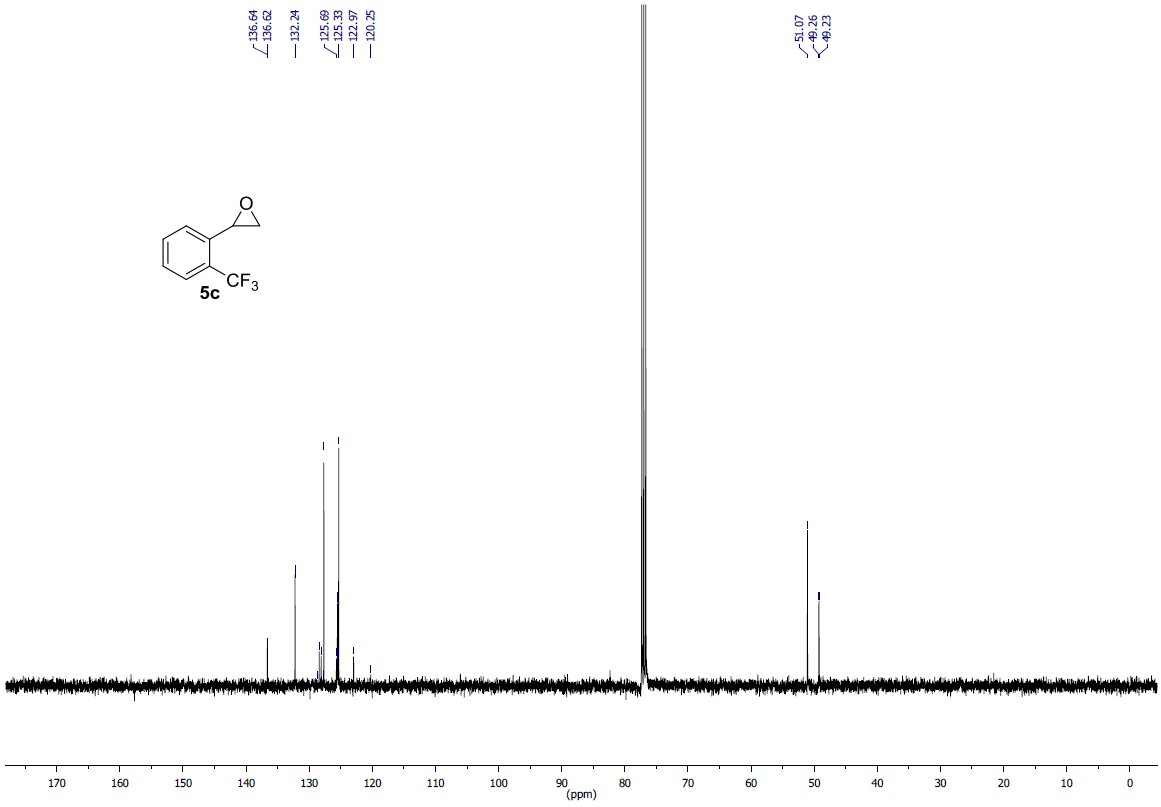


Figure S40. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5c**.

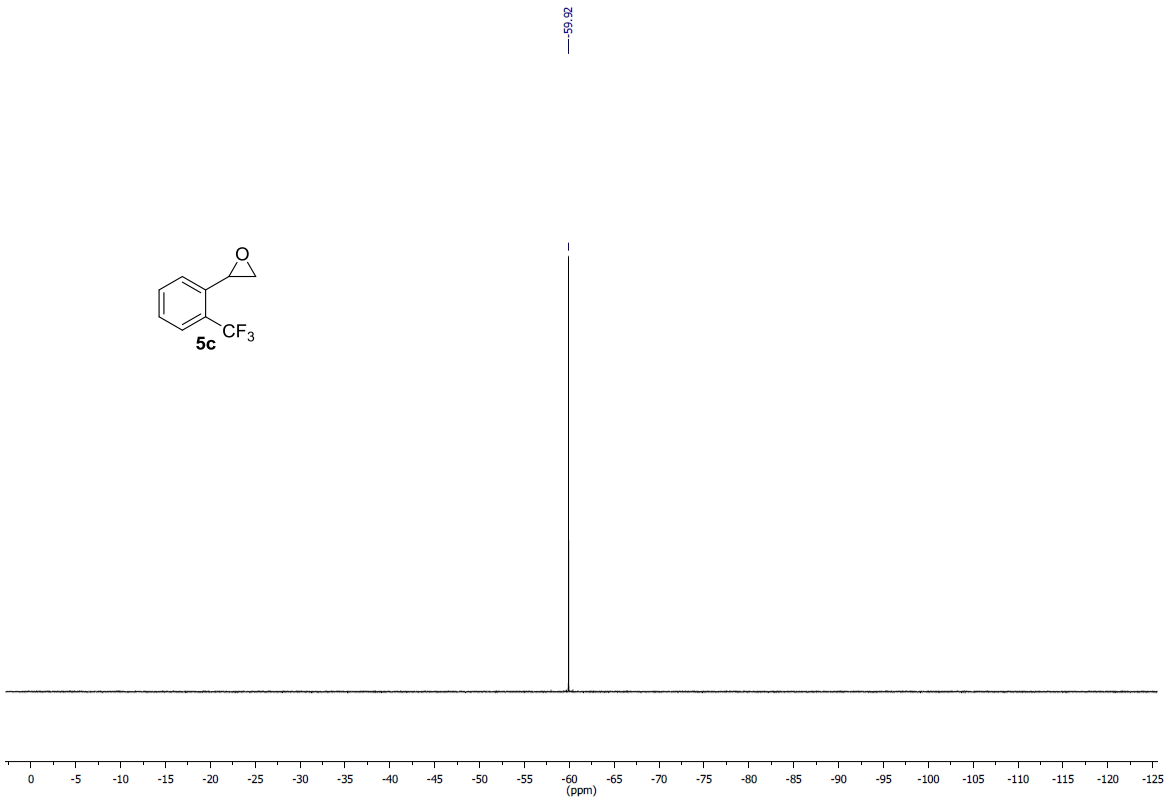


Figure S41. ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum: compound **5c**.

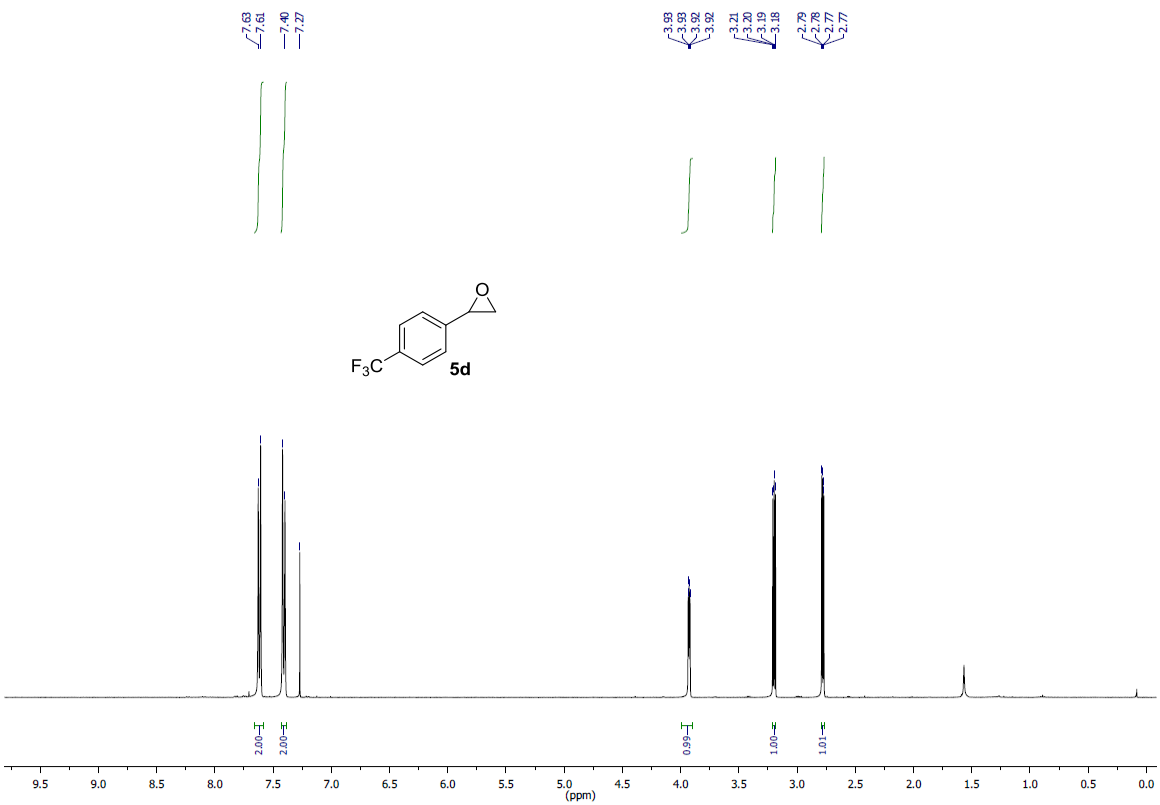


Figure S42. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5d**.

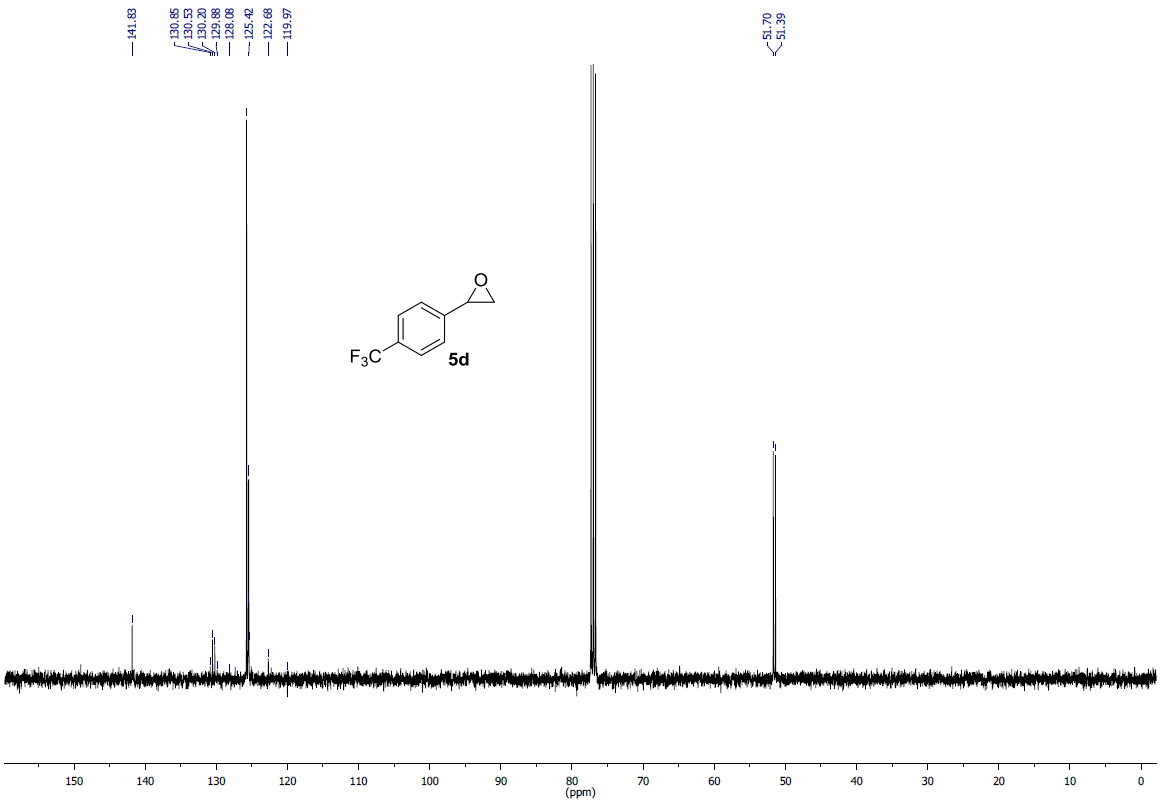


Figure S43. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5d**.

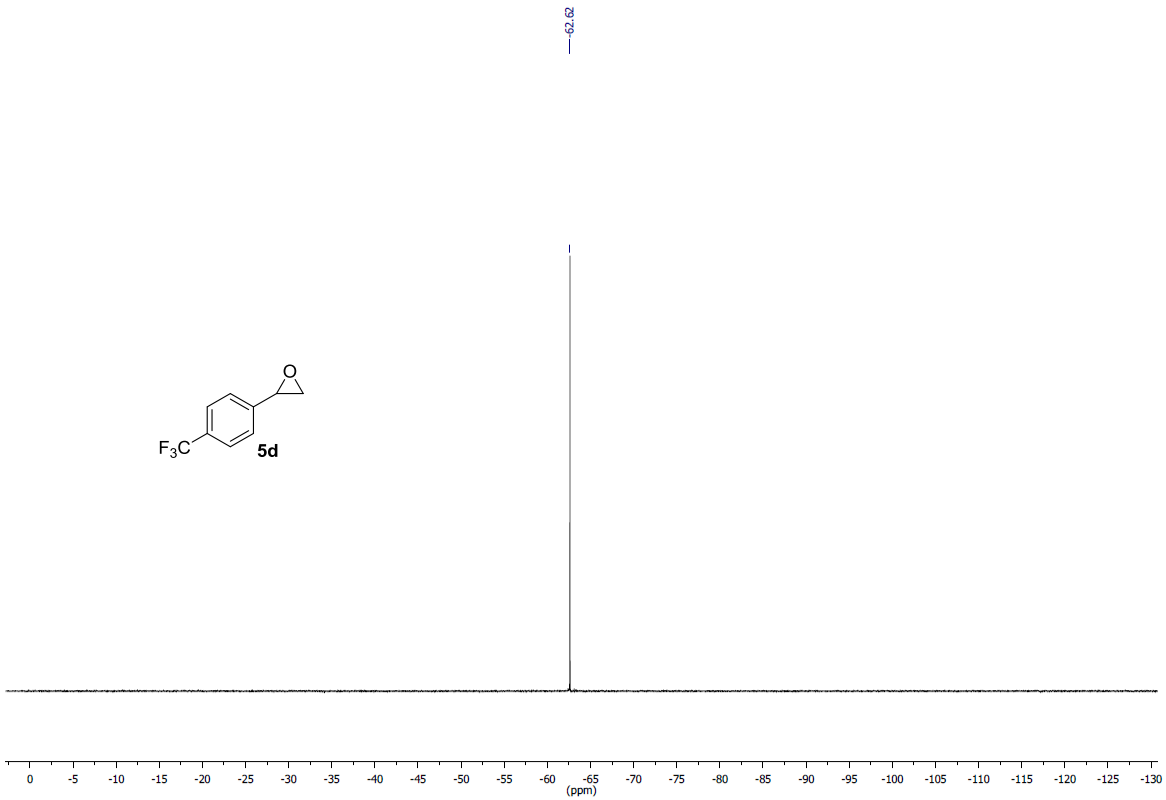


Figure S44. ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum: compound **5d**.

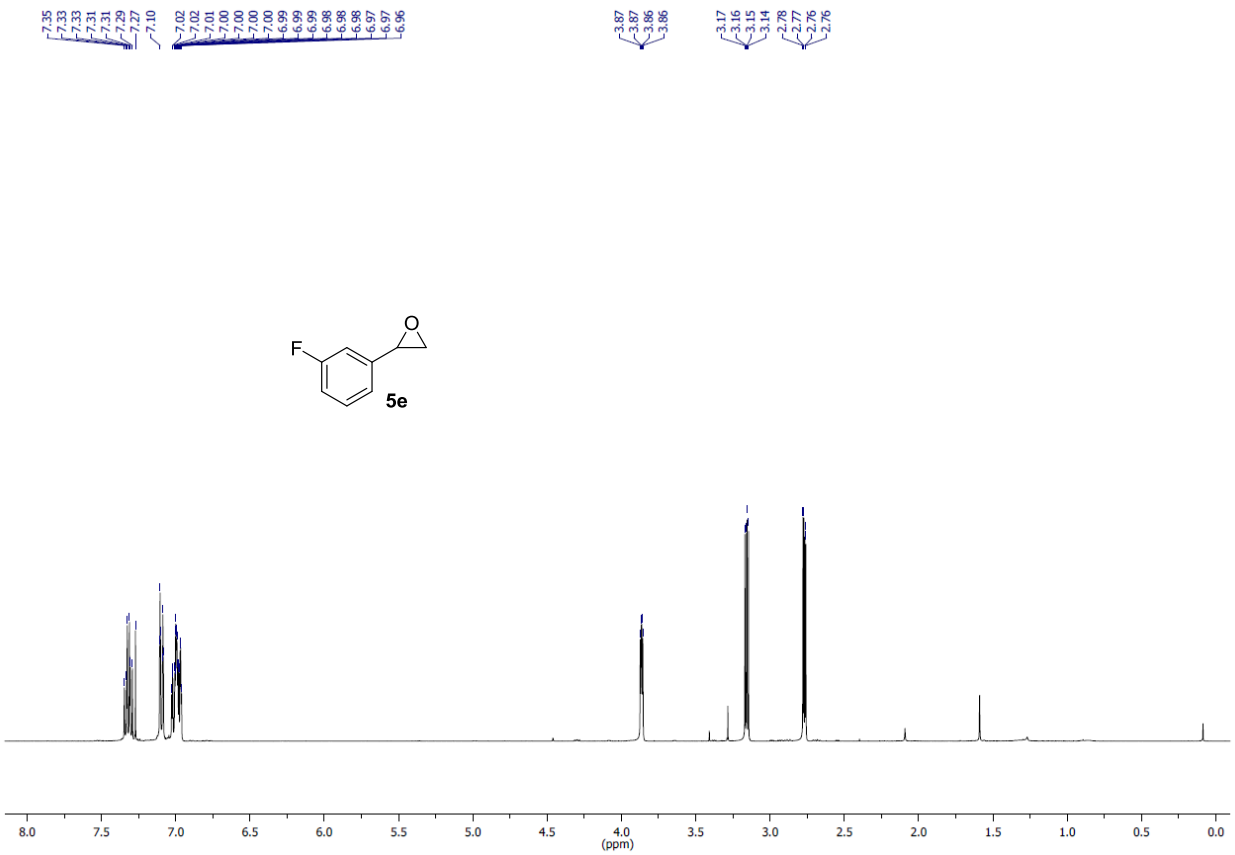


Figure S45. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5e**.

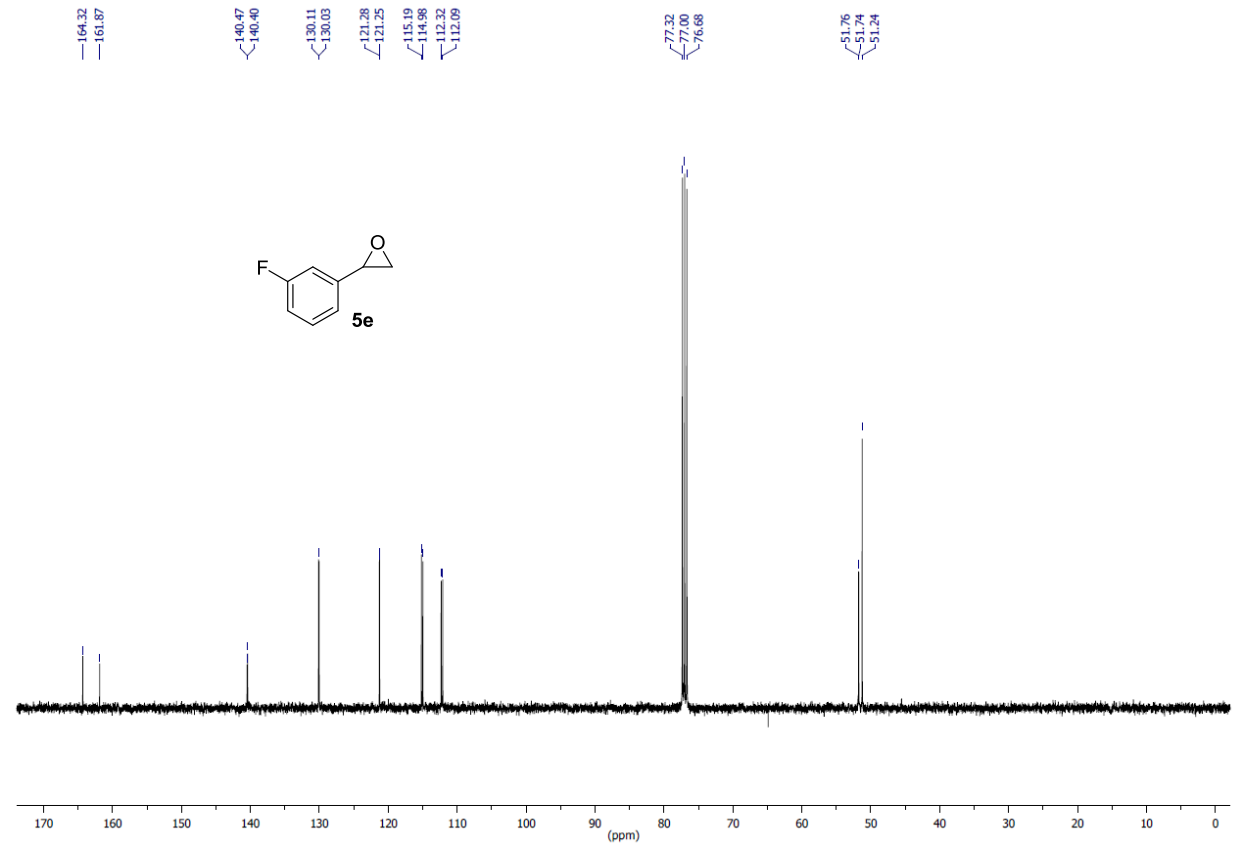


Figure S46. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5e**.

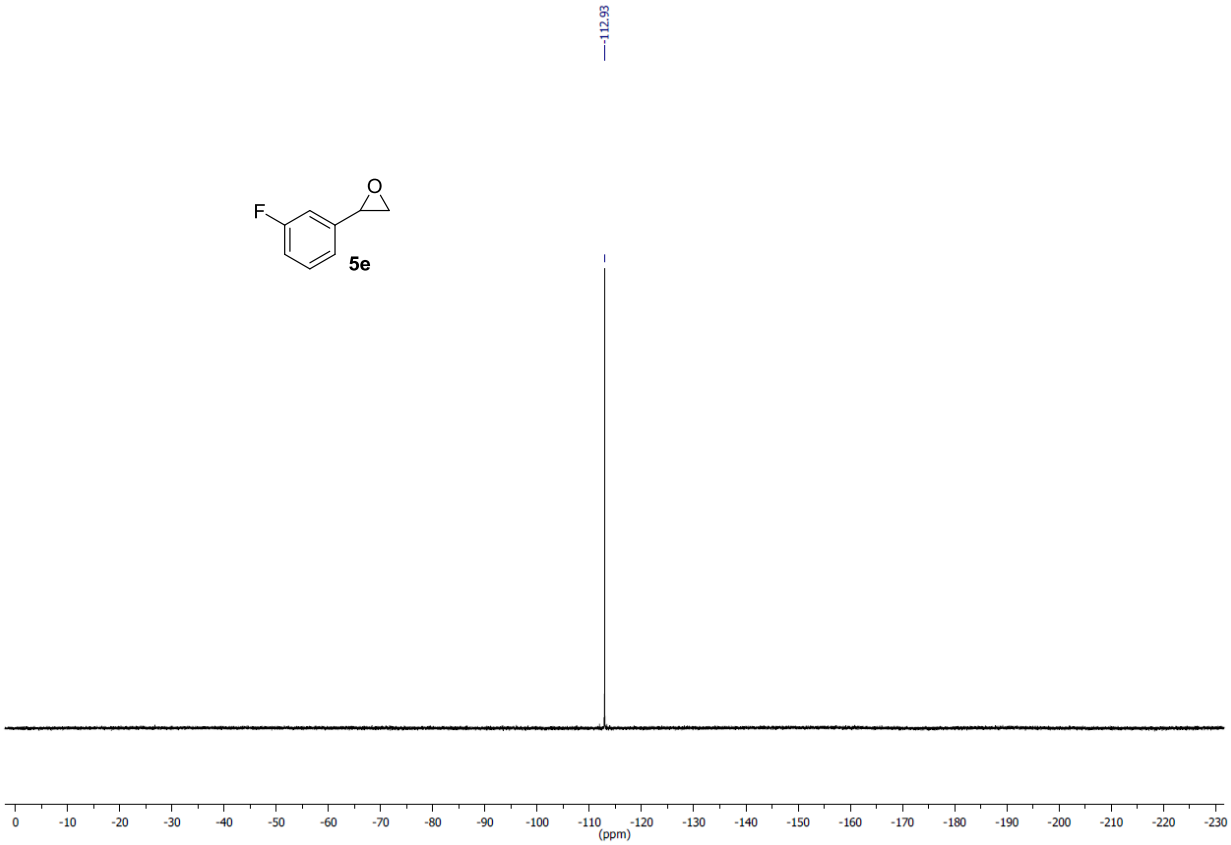


Figure S47. ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum: compound **5e**.

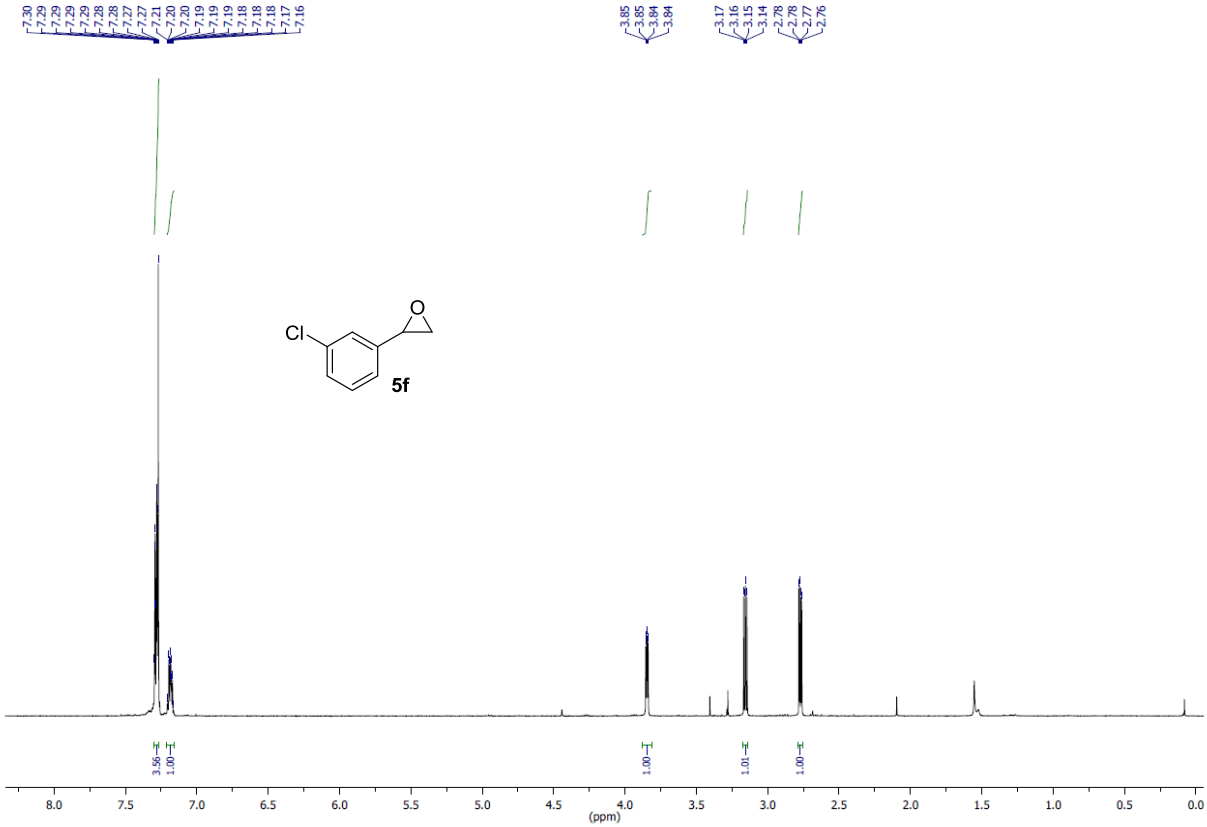


Figure S48. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5f**.

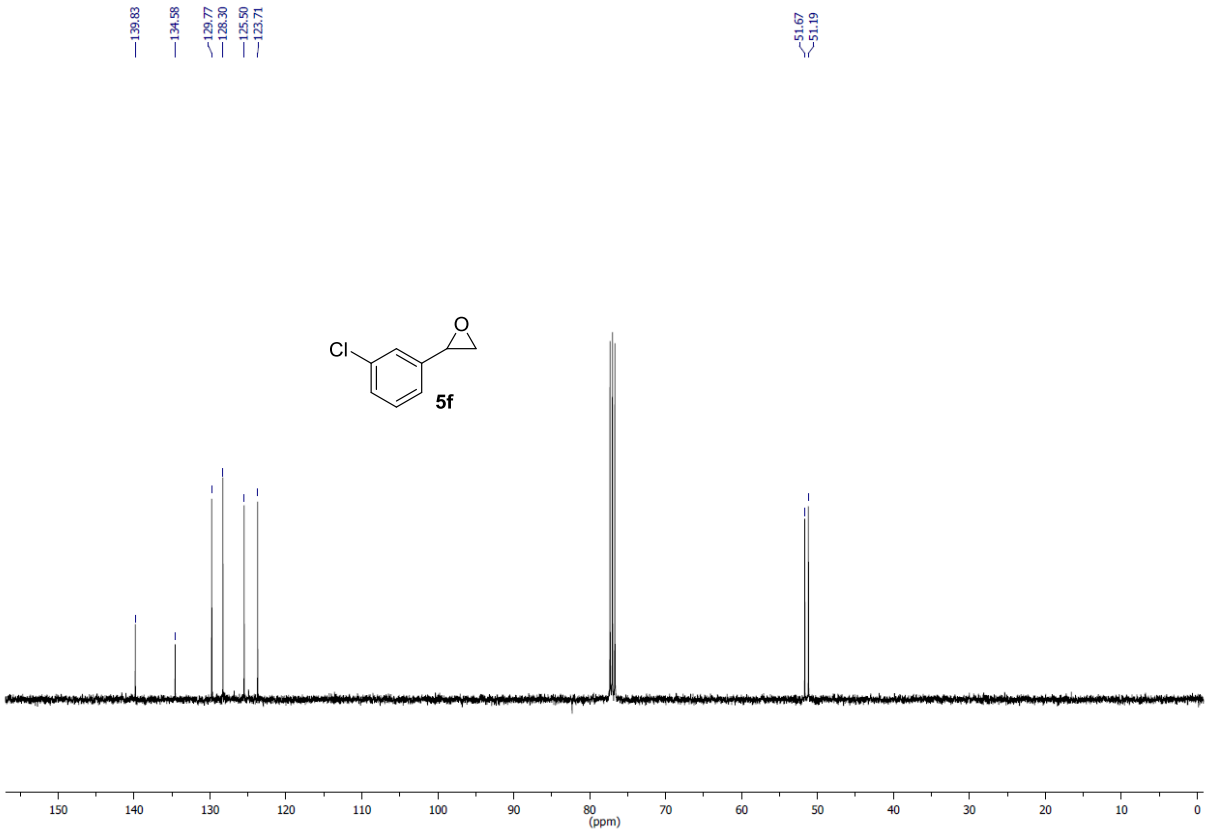


Figure S49. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5f**.

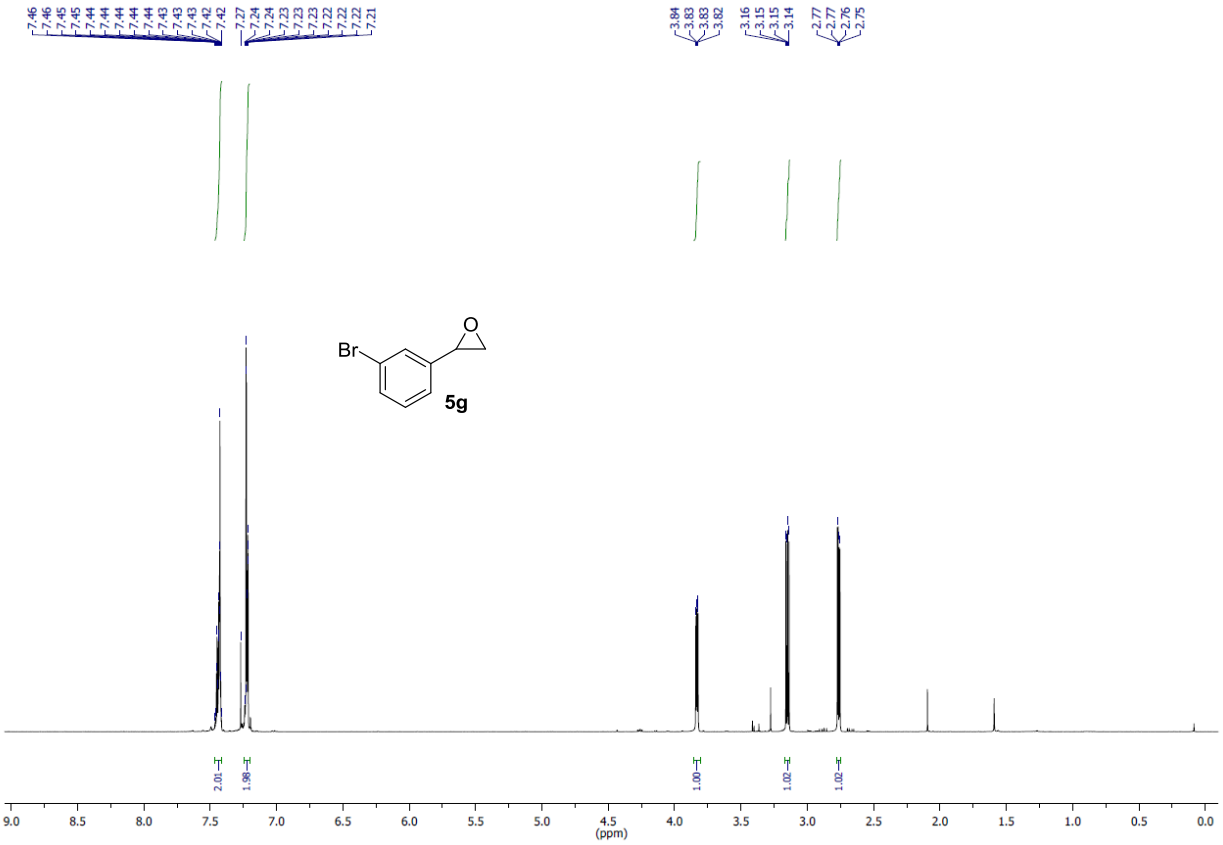


Figure S50. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5g**.

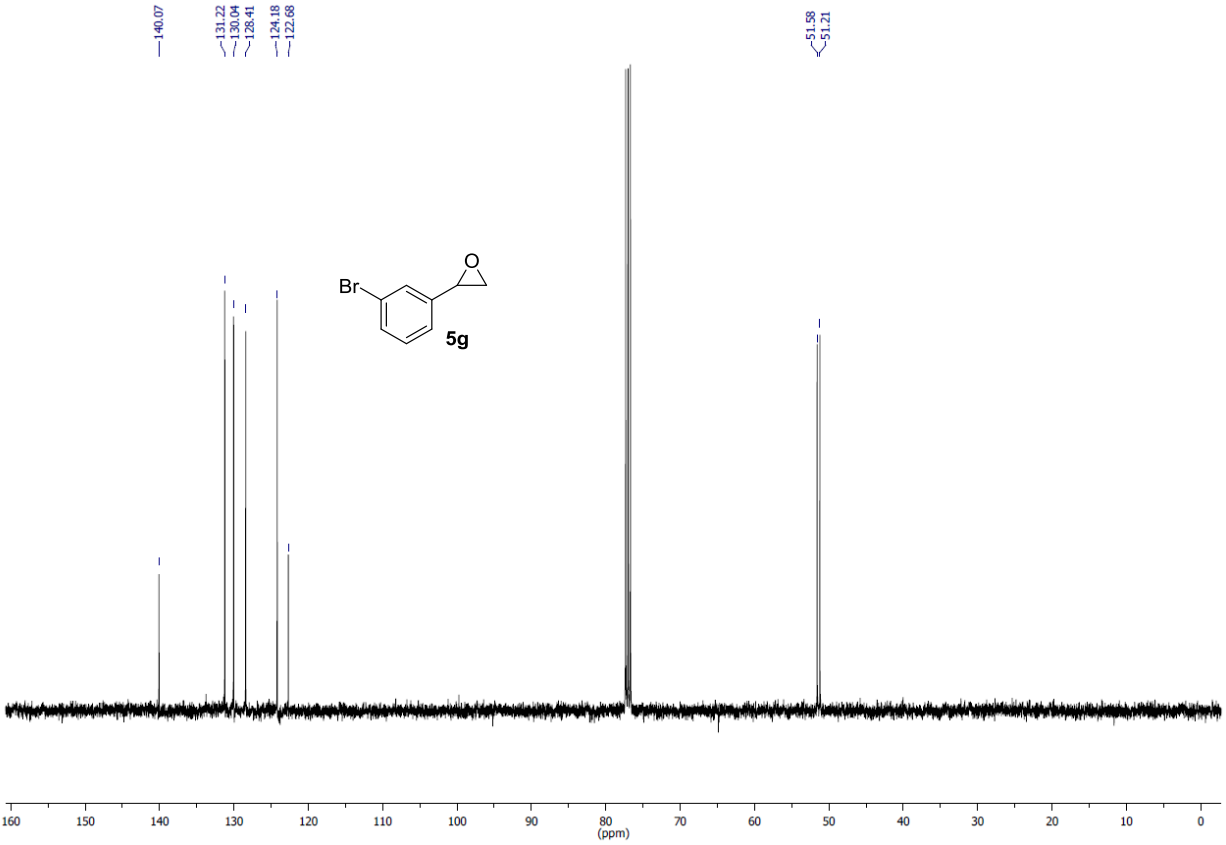


Figure S51. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5g**.

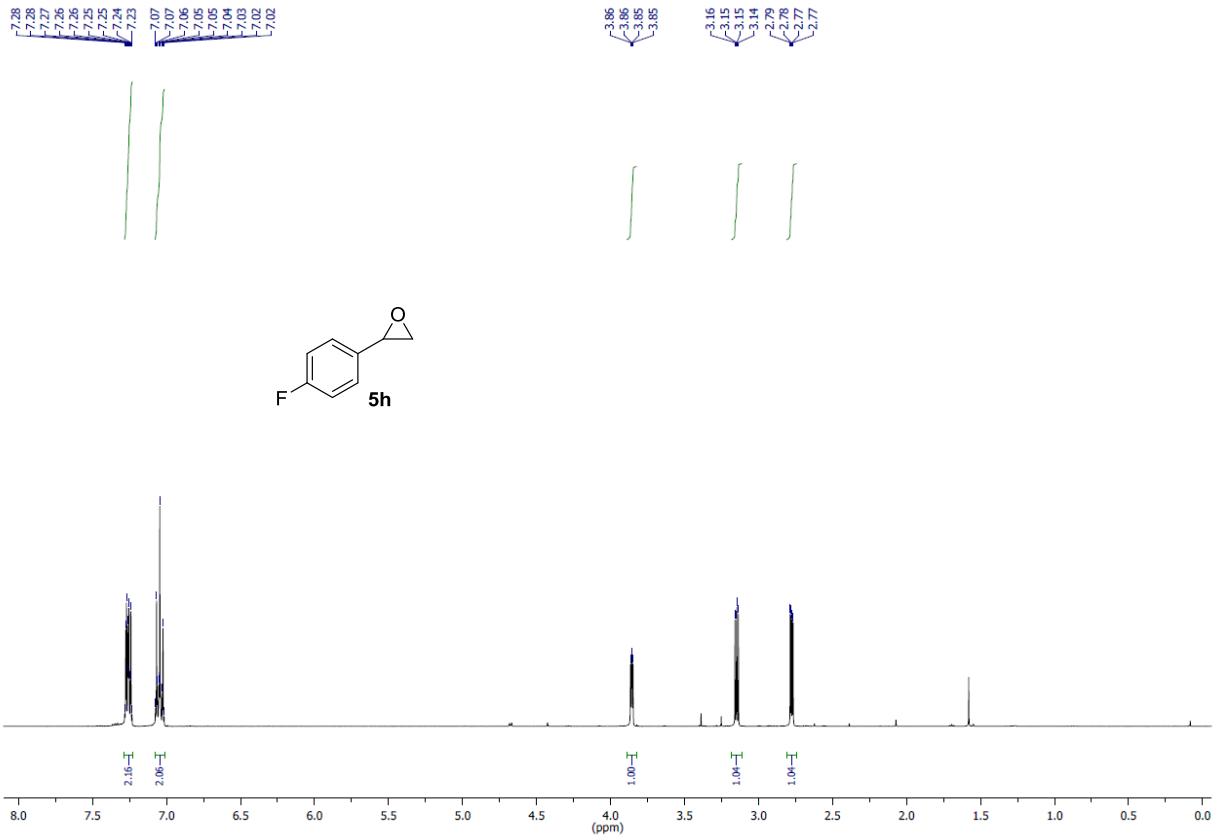


Figure S52. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5h**.

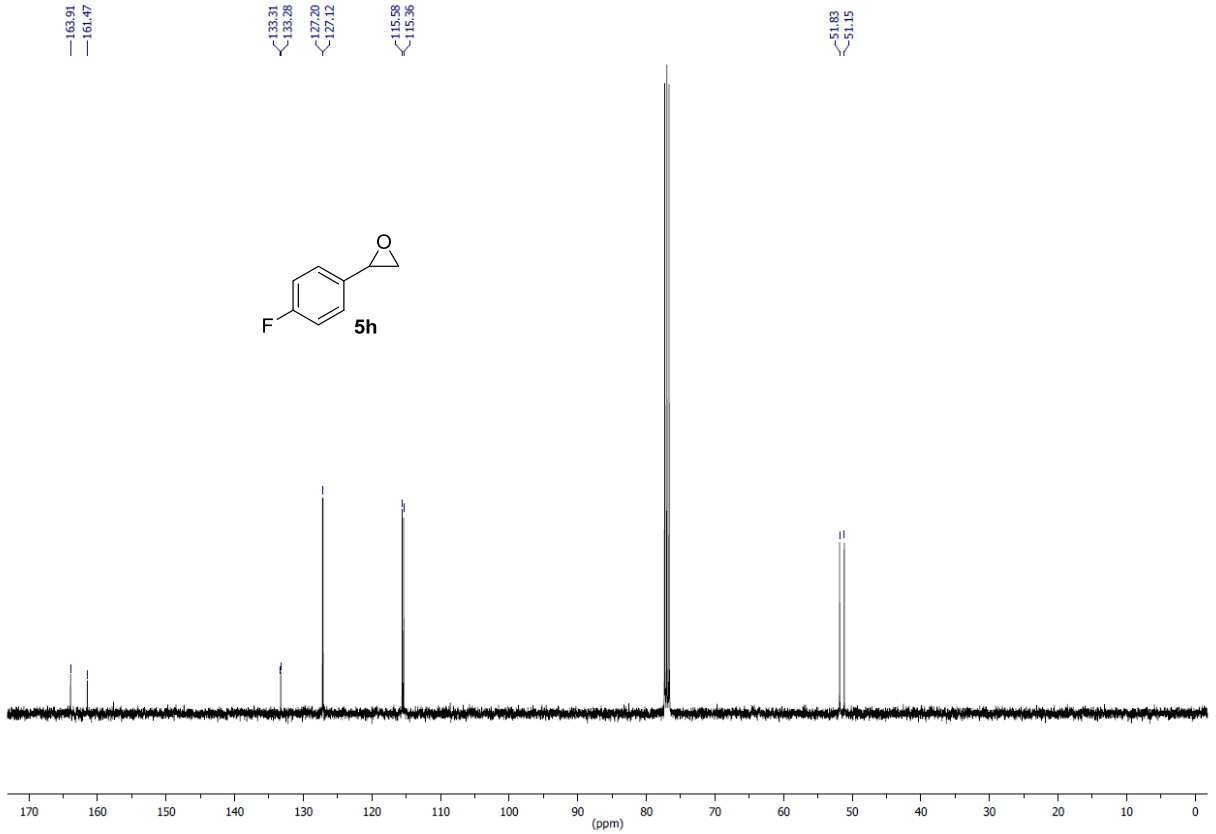


Figure S53. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5h**.

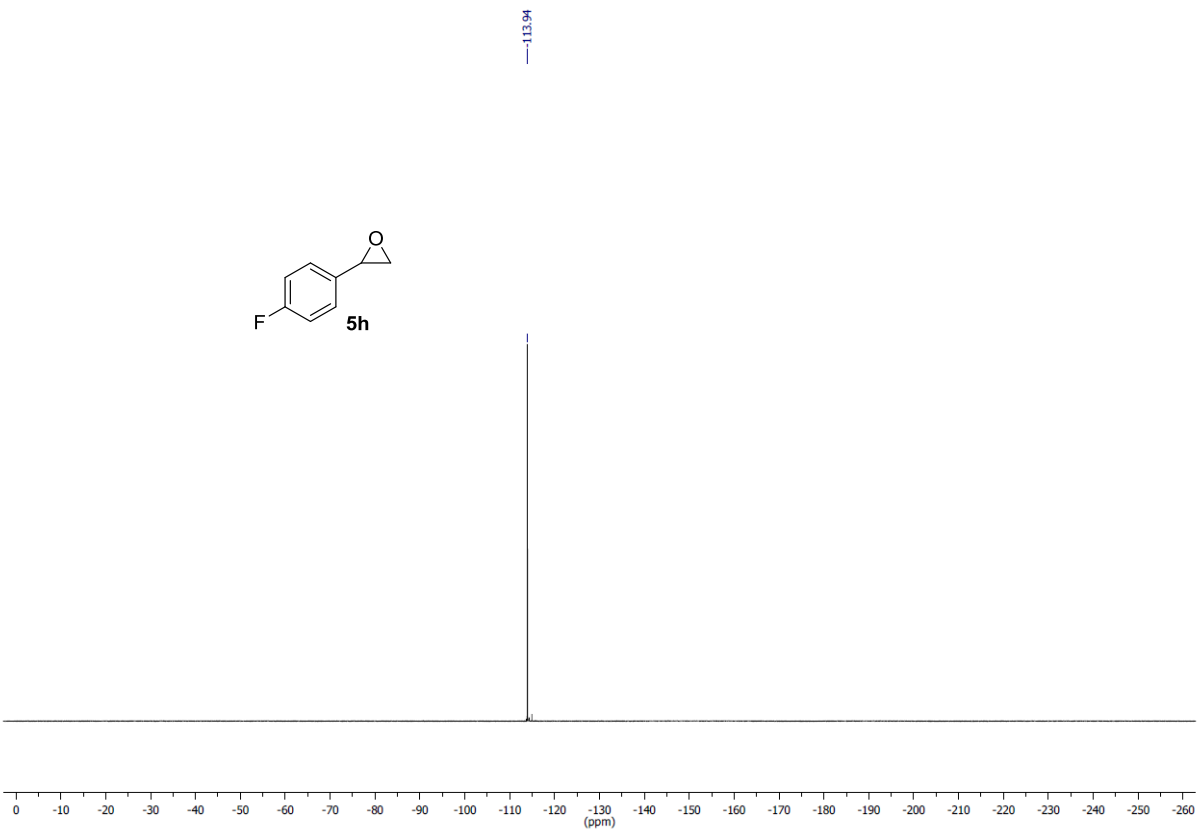


Figure S54. ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum: compound **5h**.

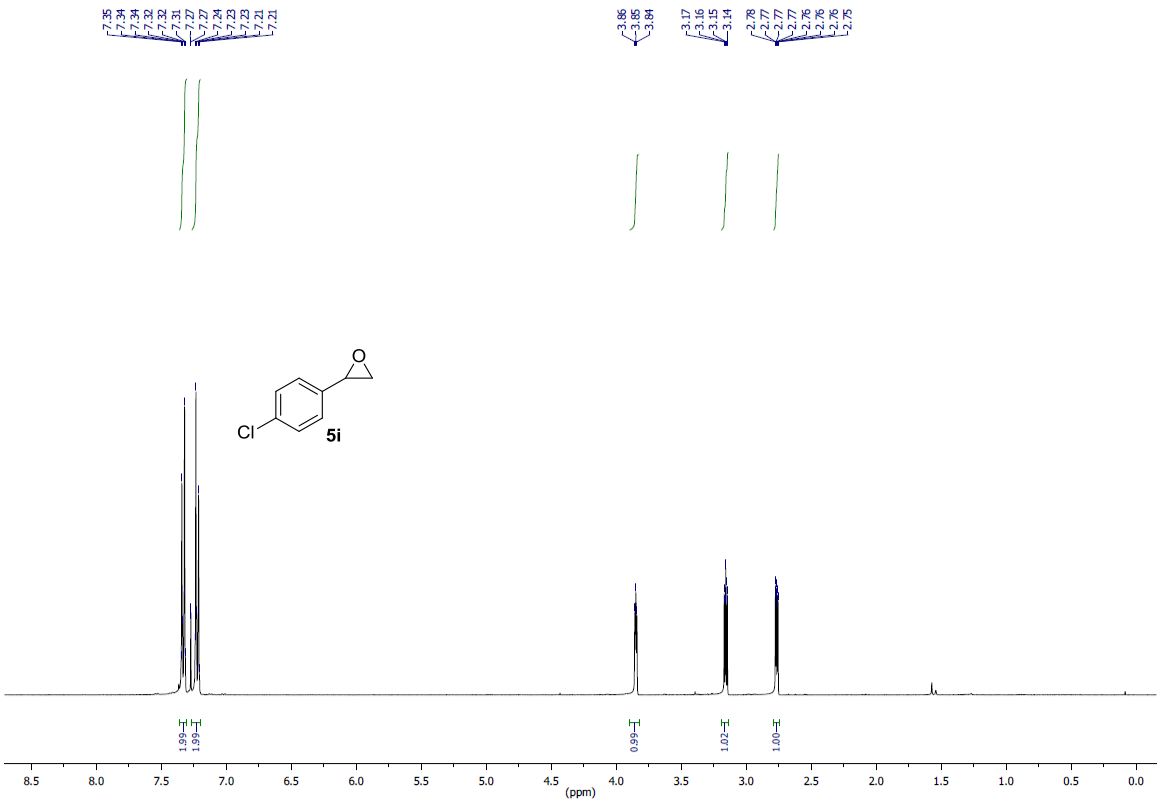


Figure S55. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5i**.

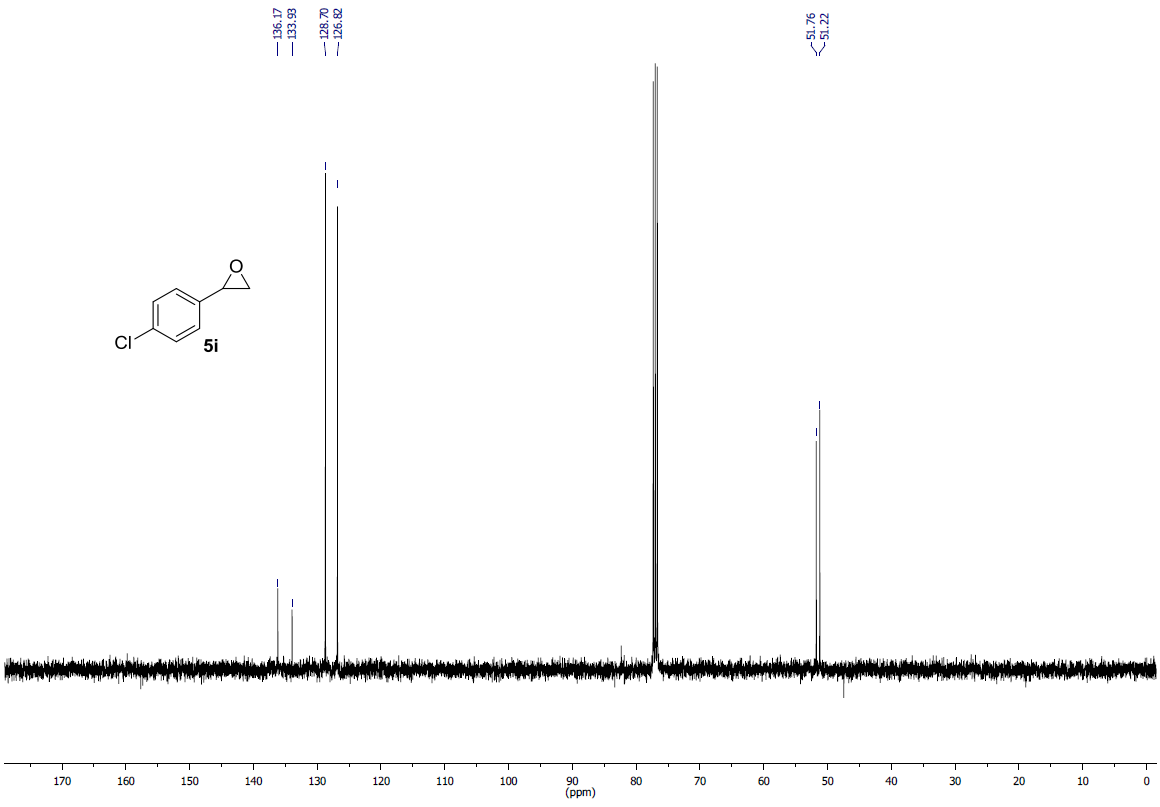


Figure S56. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5i**.

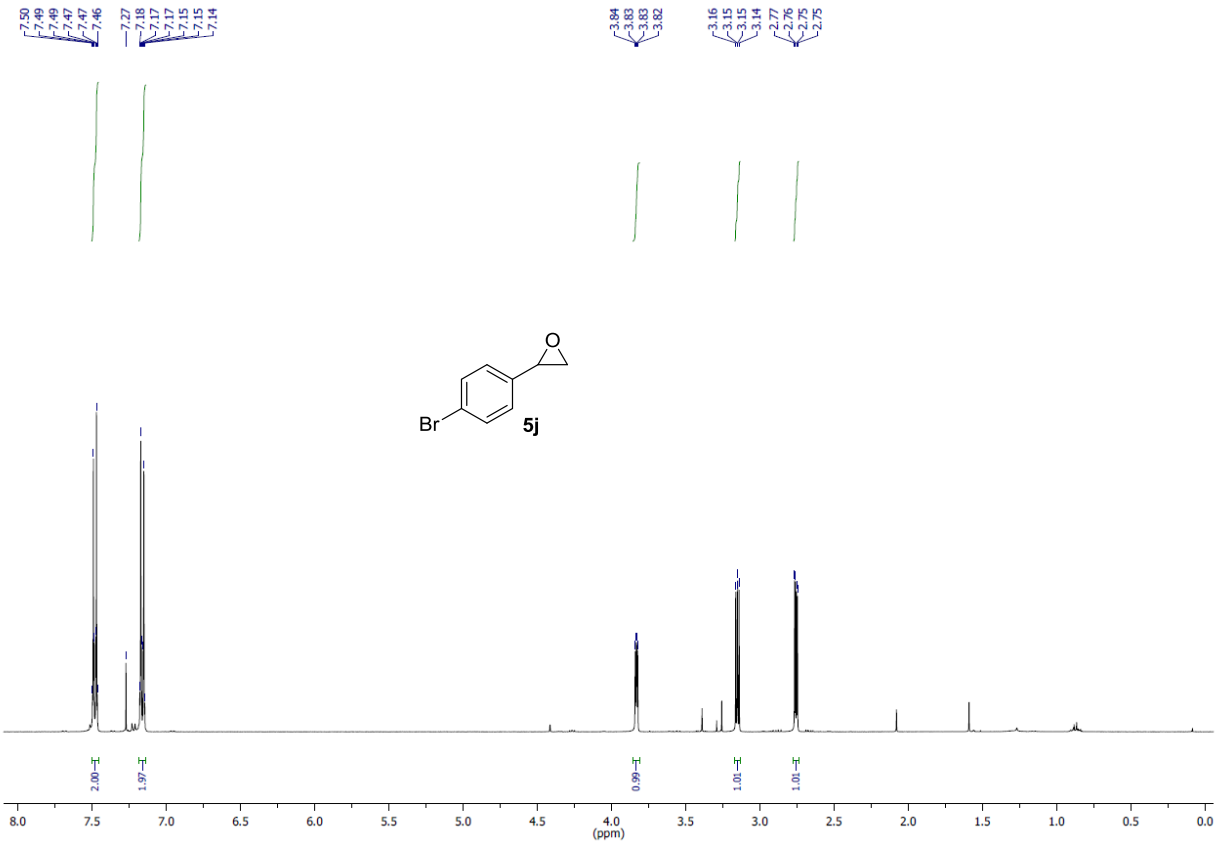


Figure S57. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5j**.

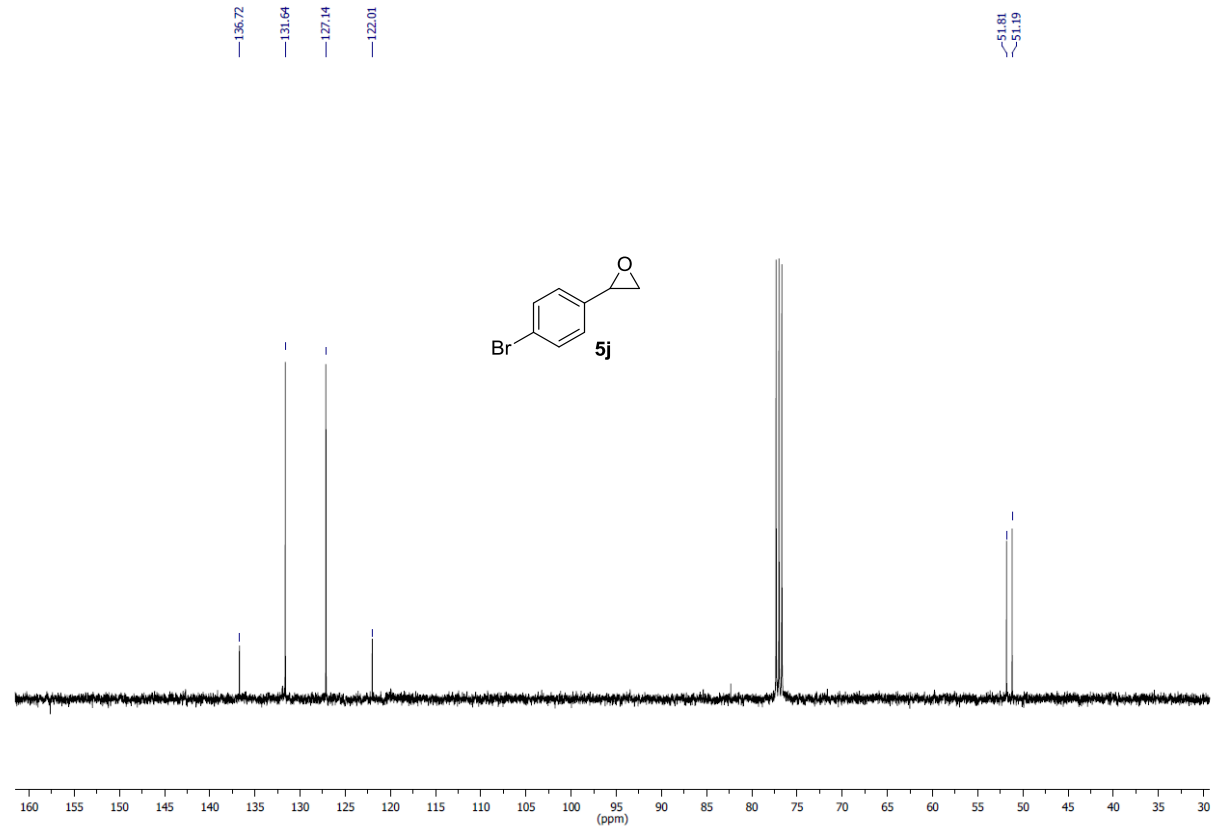


Figure S58. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5j**.

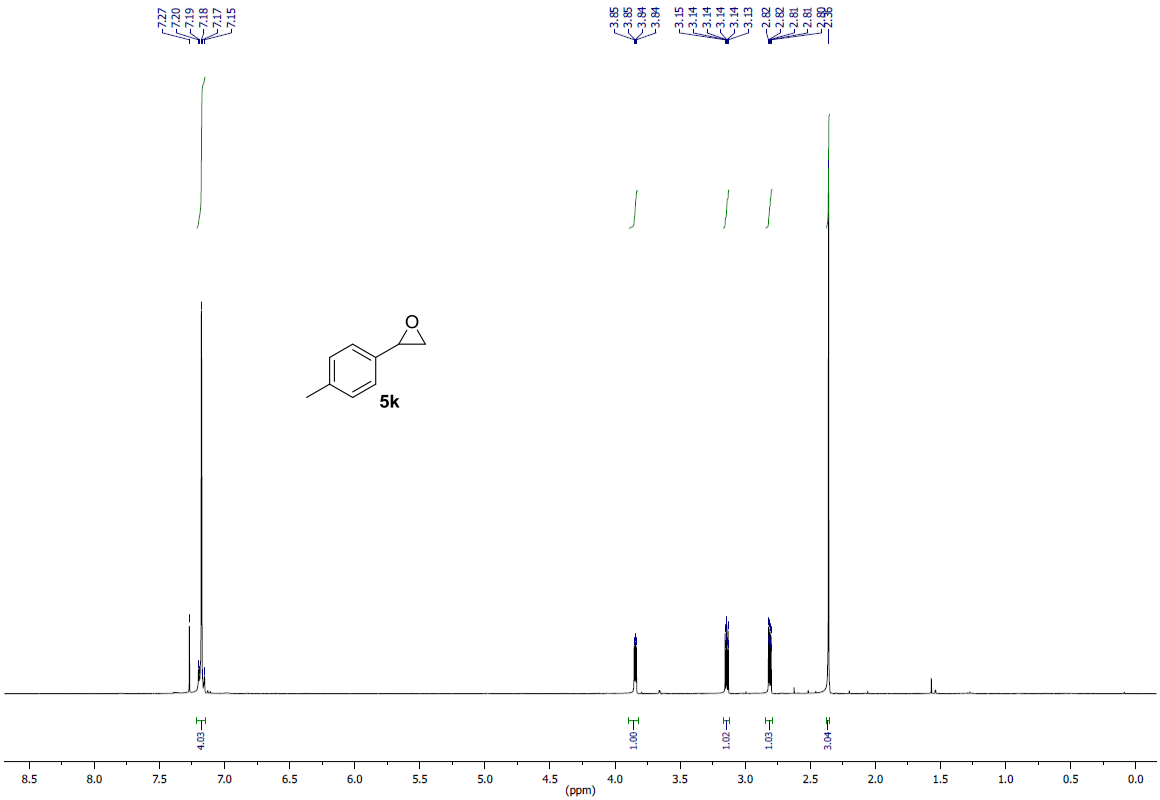


Figure S59. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5k**.

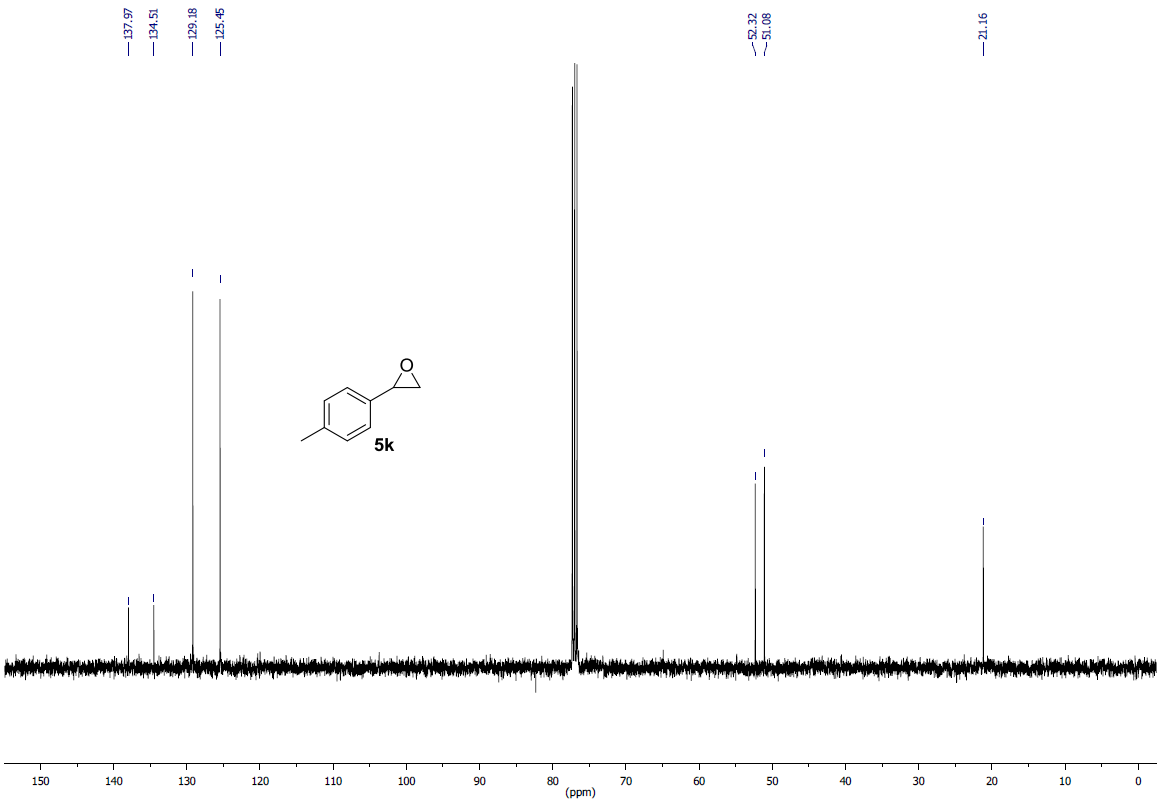


Figure S60. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5k**.

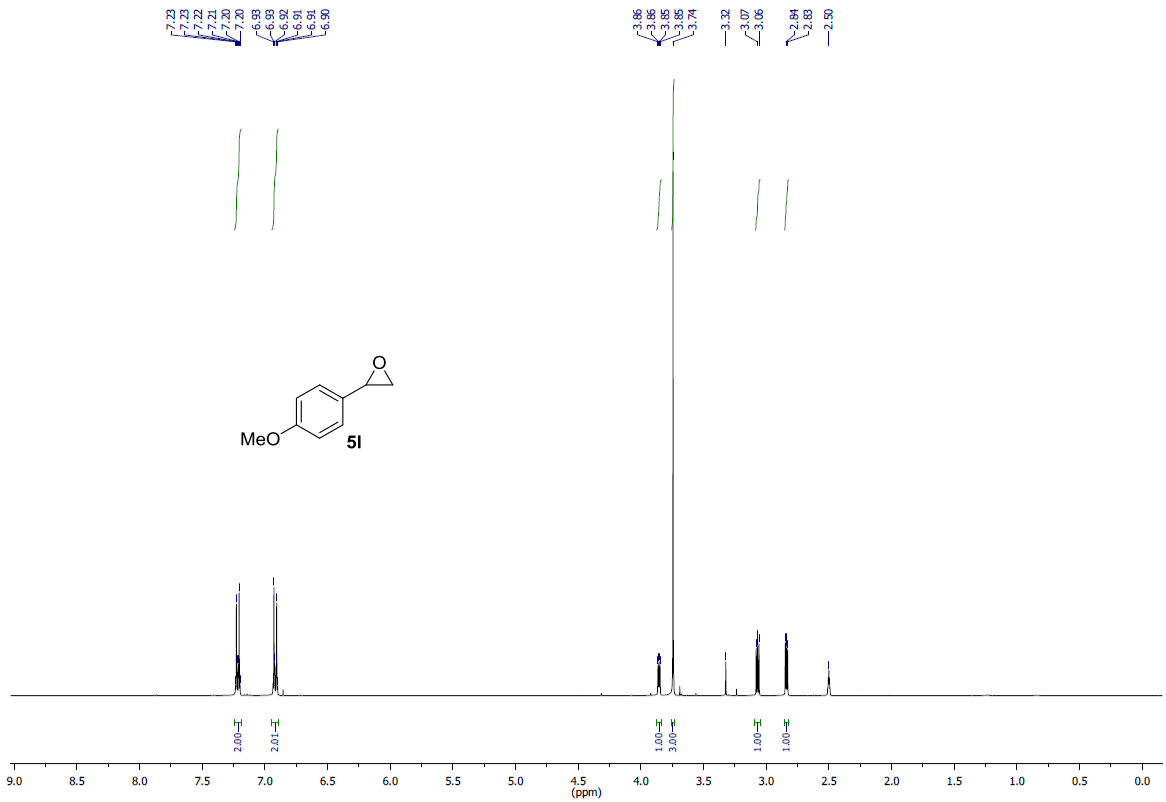


Figure S61. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5l**.

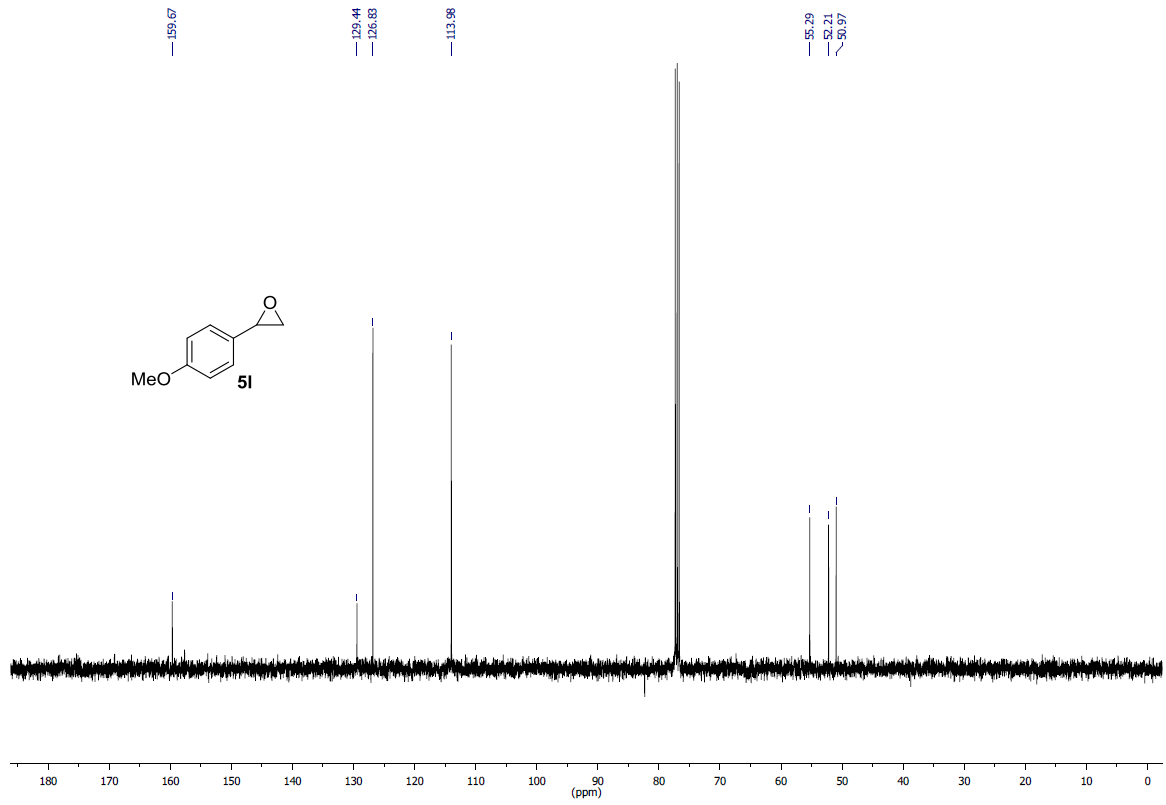


Figure S62. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5l**.

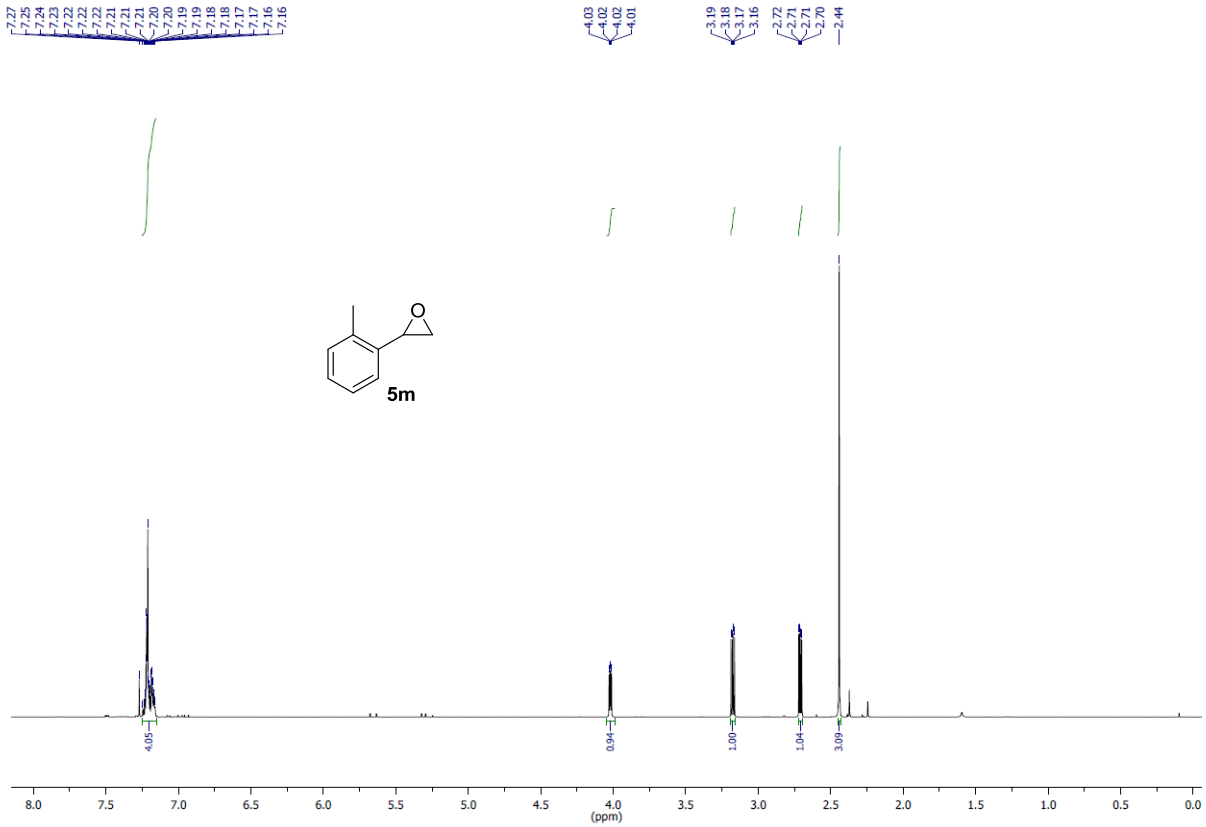


Figure S63. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: compound **5m**.

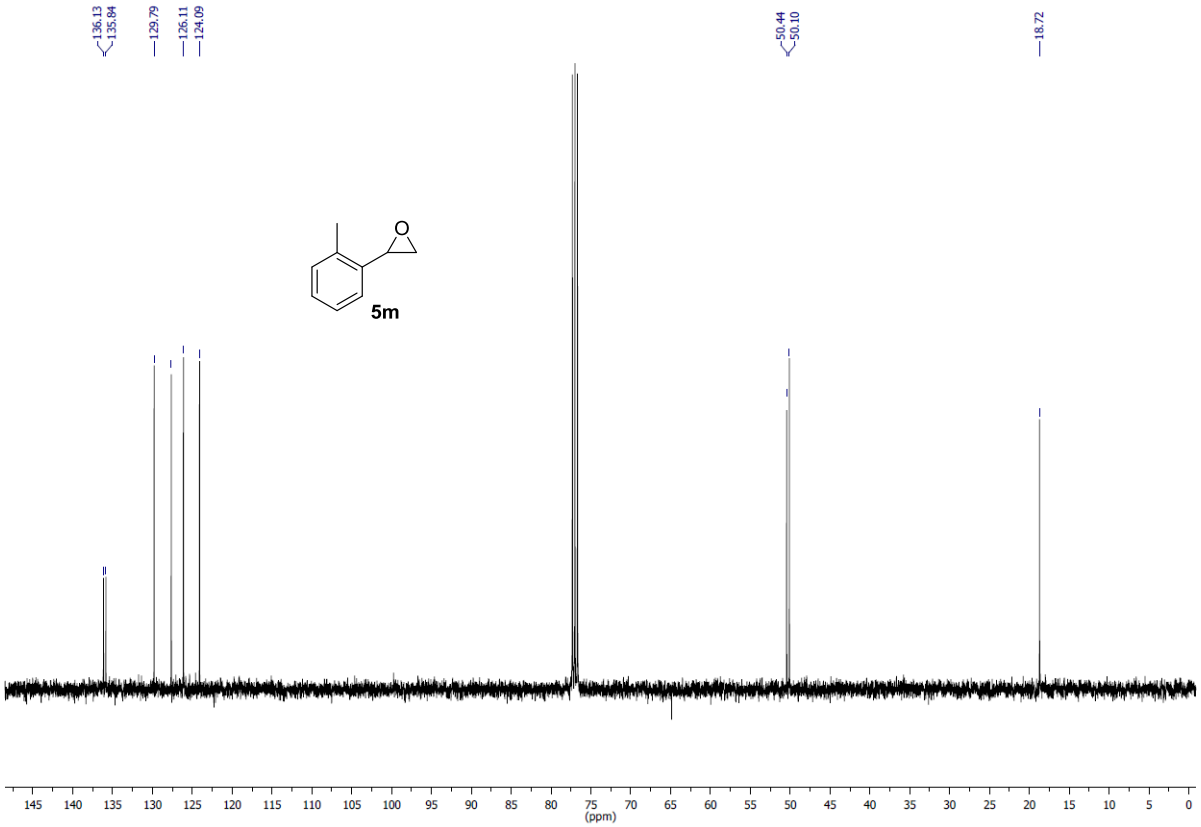


Figure S64. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: compound **5m**.

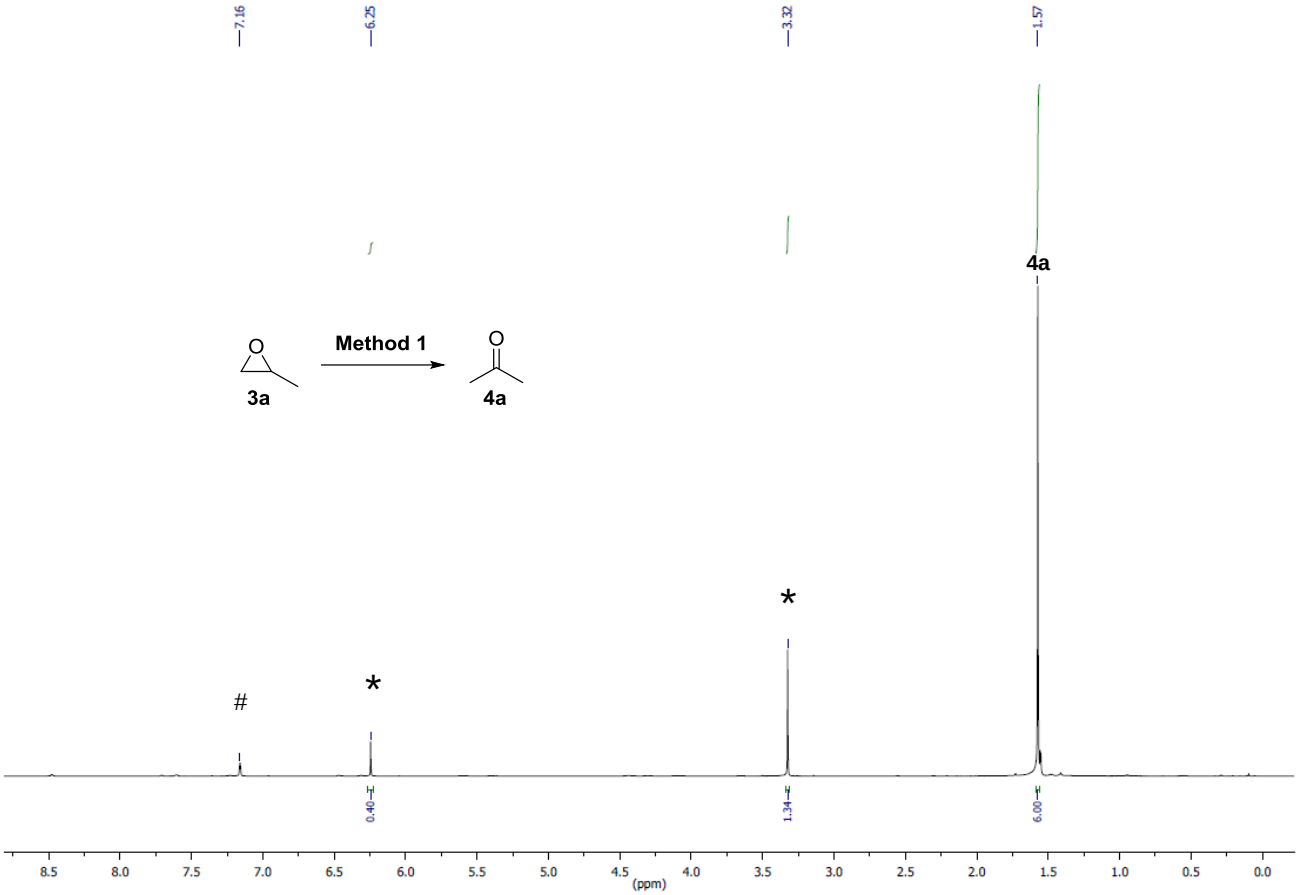


Figure S65. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3a** into **4a** with **Method 1** including the internal standard (*).

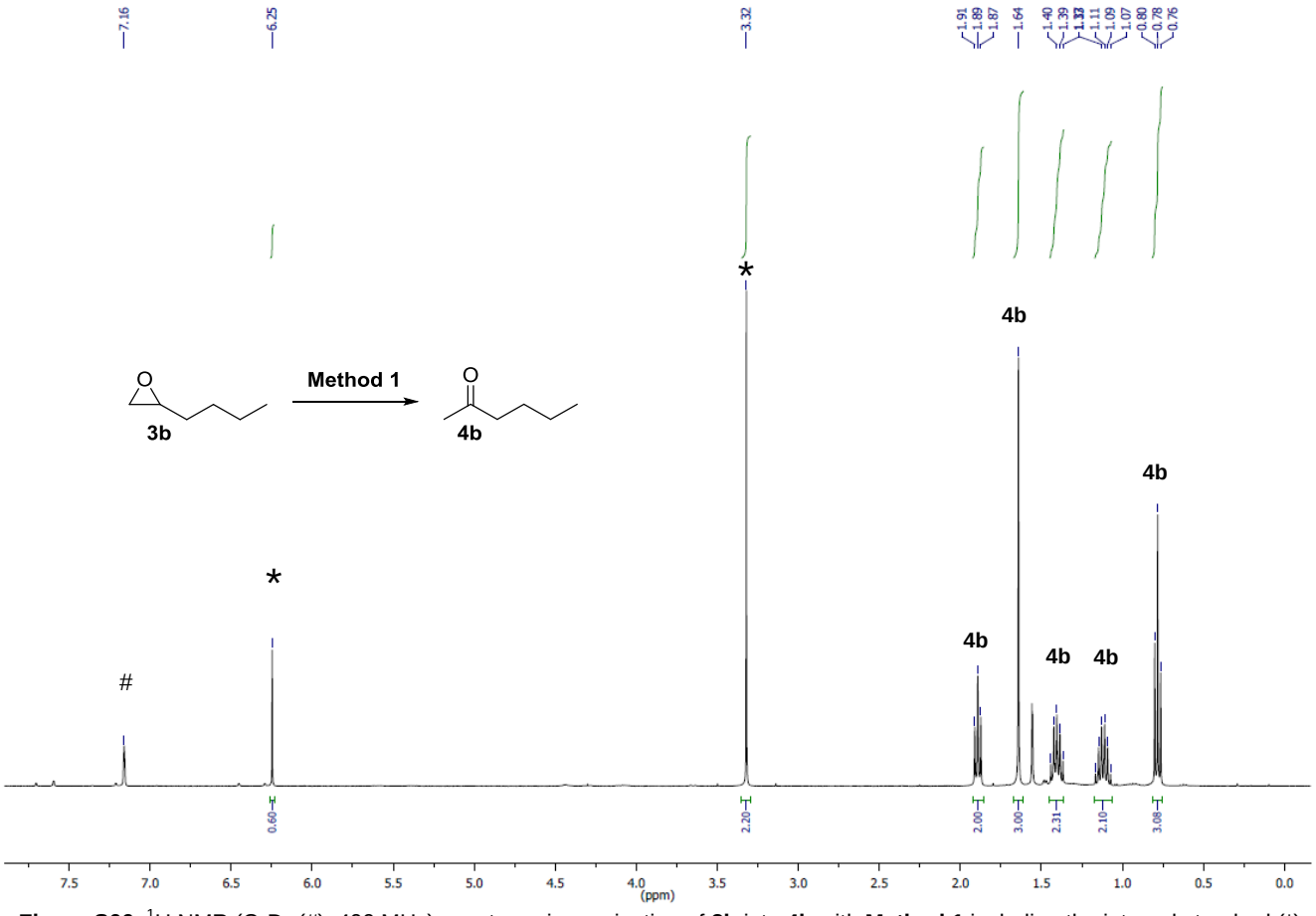


Figure S66. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3b** into **4b** with **Method 1** including the internal standard (*).

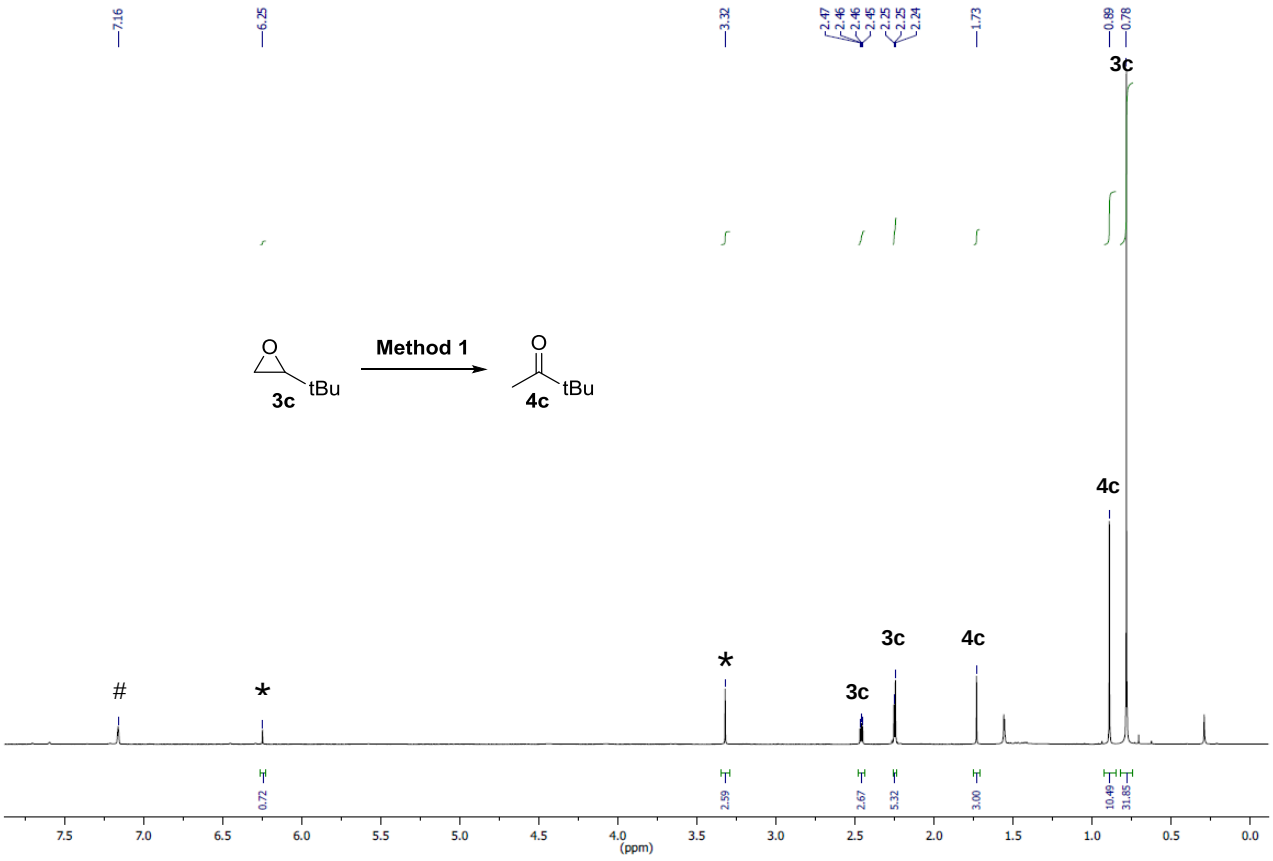


Figure S67. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3c** into **4c** with **Method 1** including the internal standard (*).

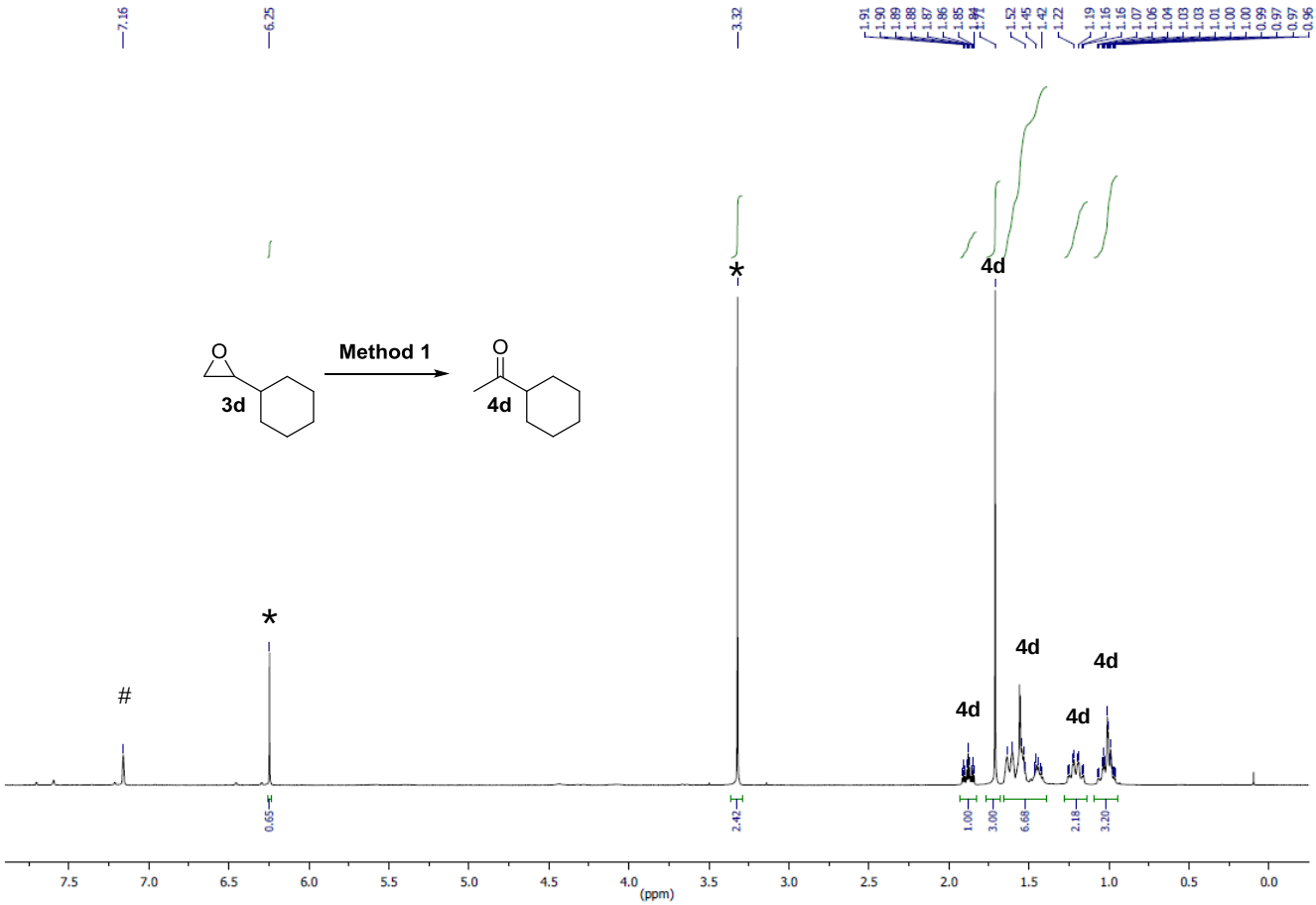


Figure S68. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3d** into **4d** with **Method 1** including the internal standard (*).

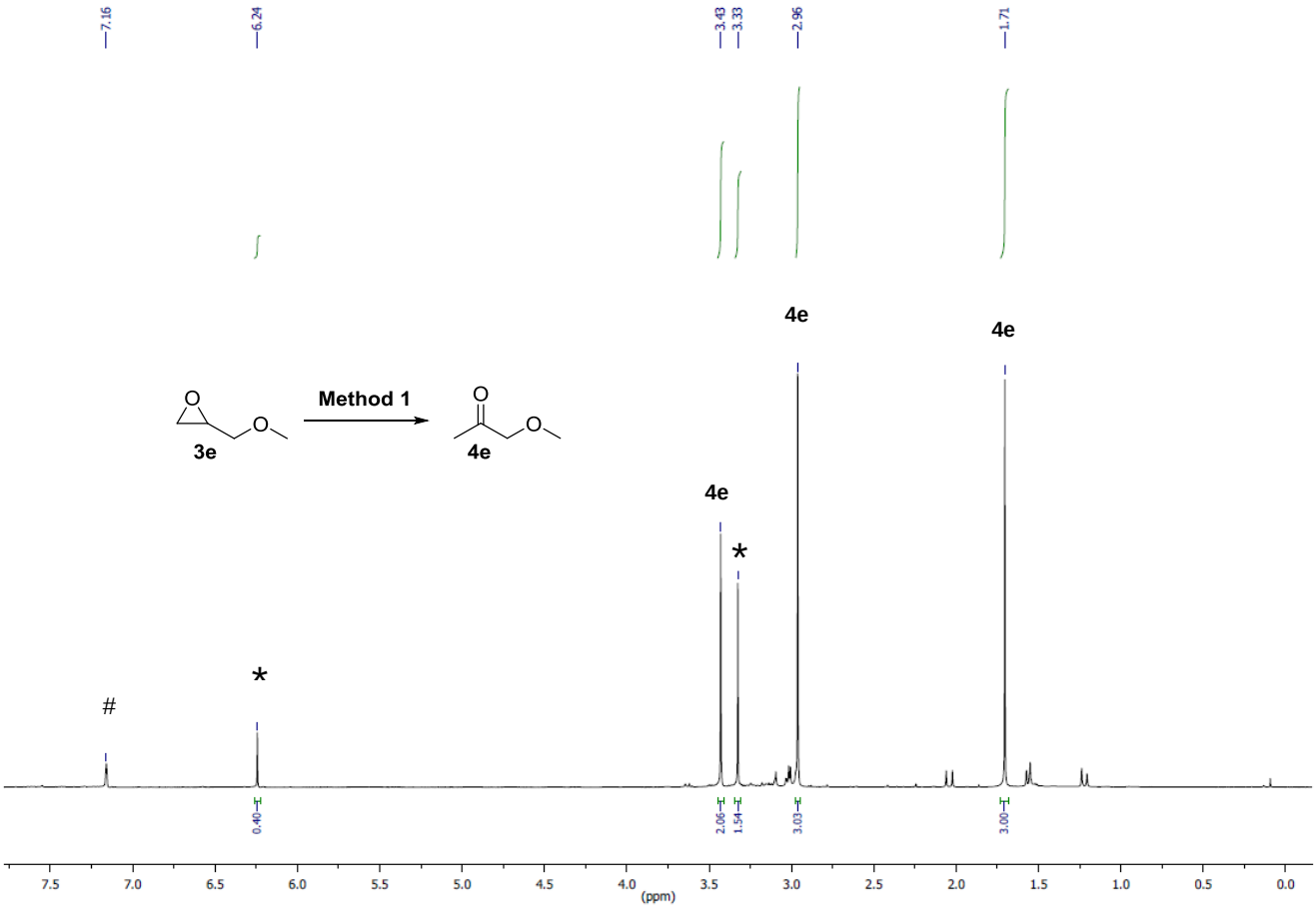


Figure S69. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3e** into **4e** with **Method 1** including the internal standard (*).

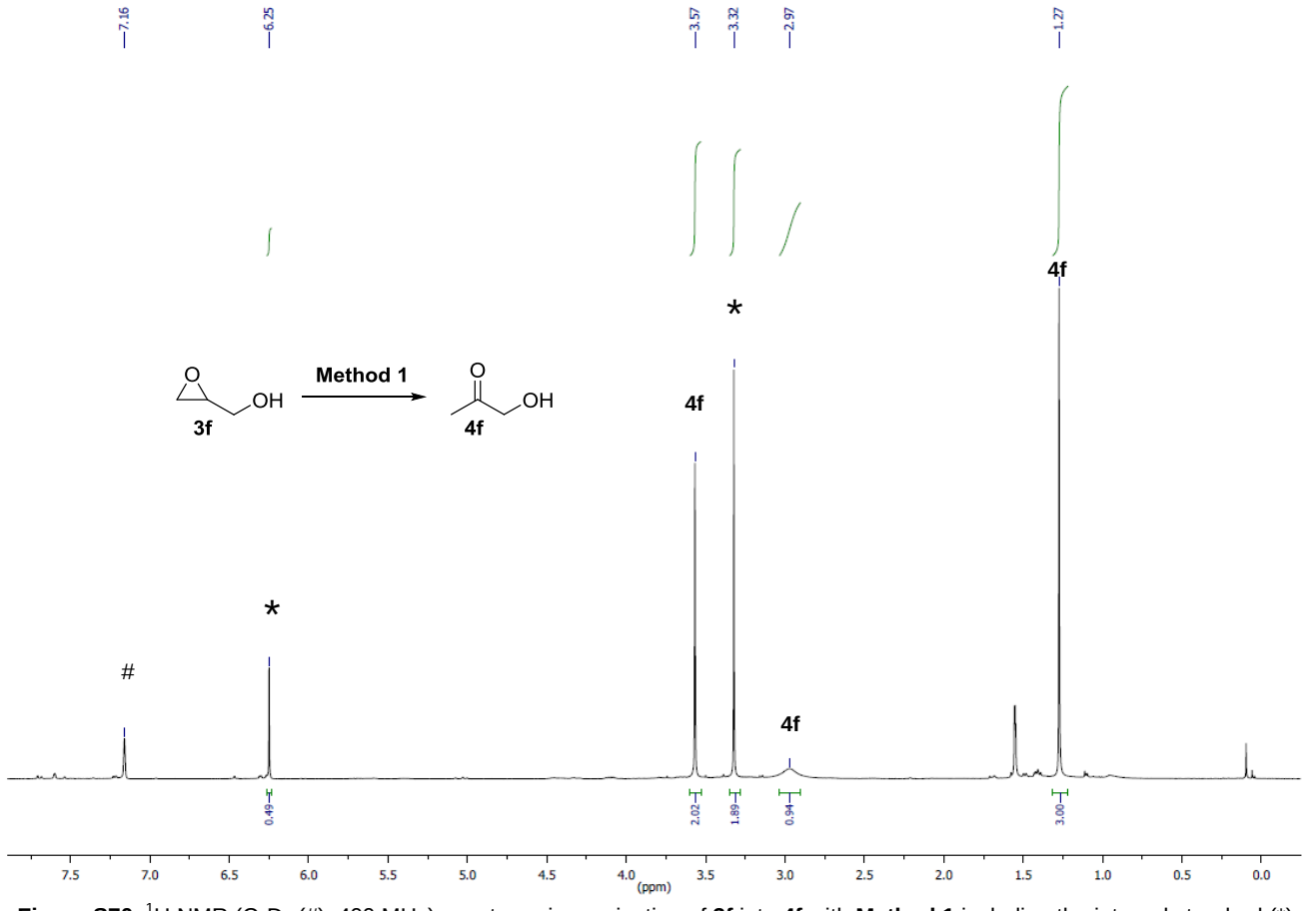


Figure S70. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3f** into **4f** with **Method 1** including the internal standard (*).

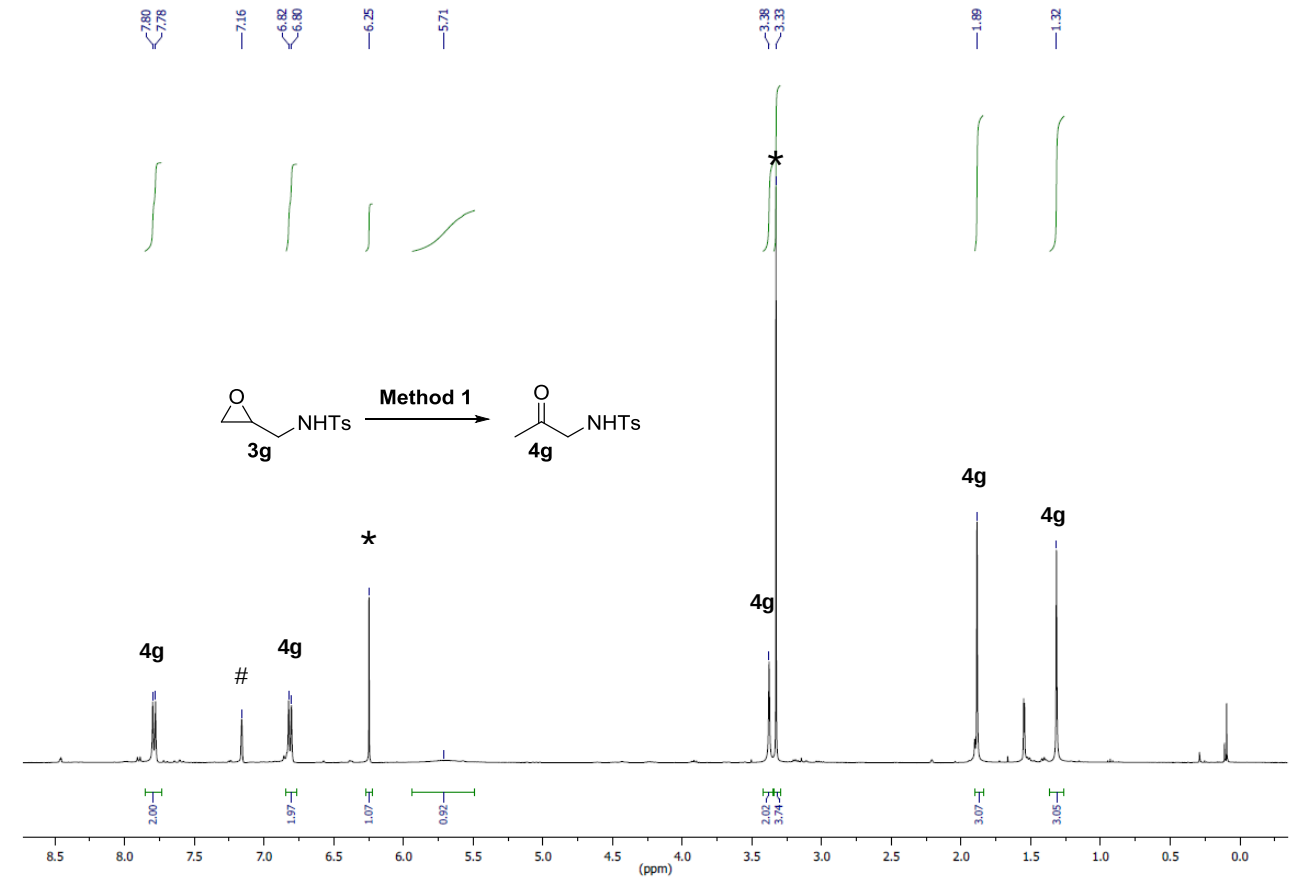


Figure S71. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3g** into **4g** with **Method 1** including the internal standard (*).

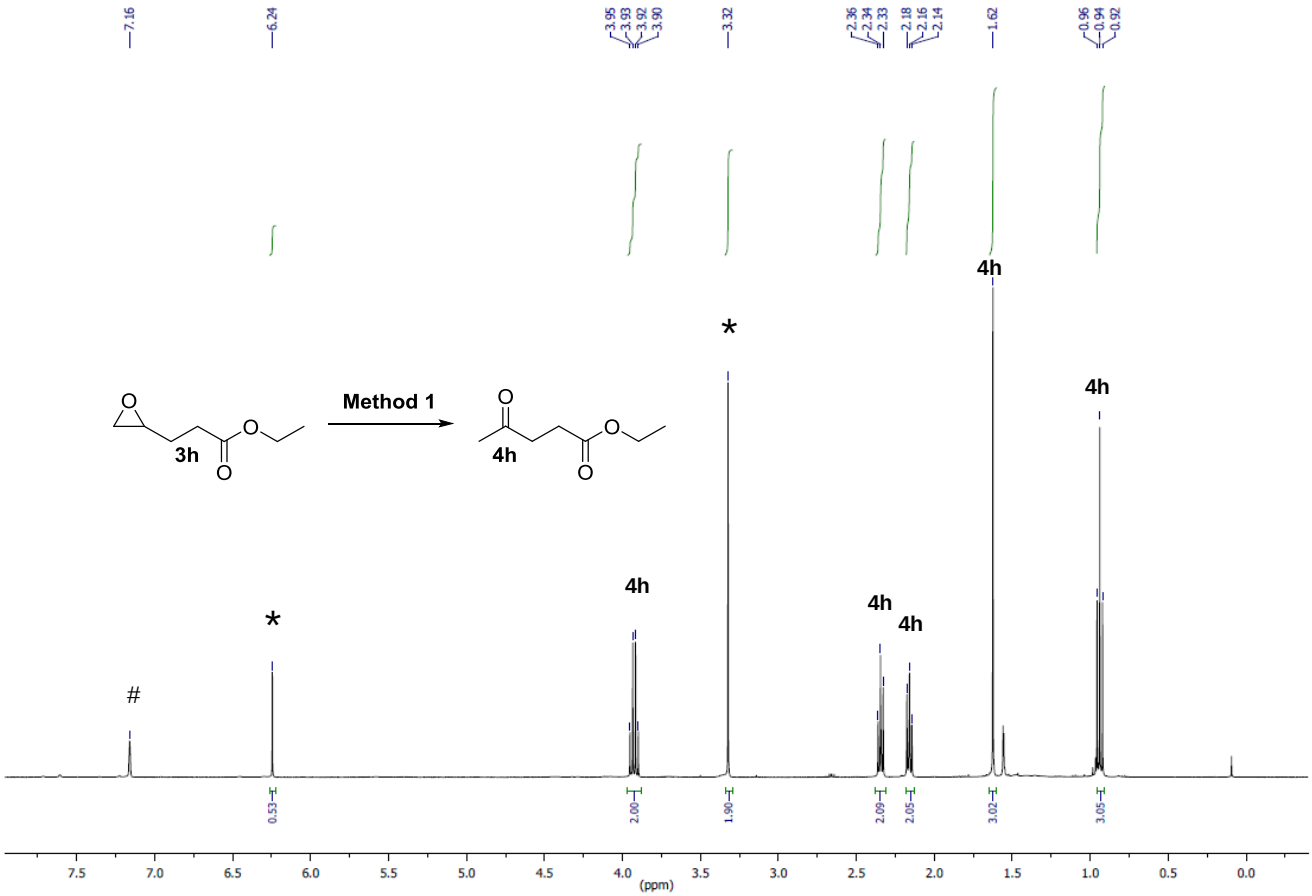


Figure S72. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3h** into **4h** with **Method 1** including the internal standard (*).

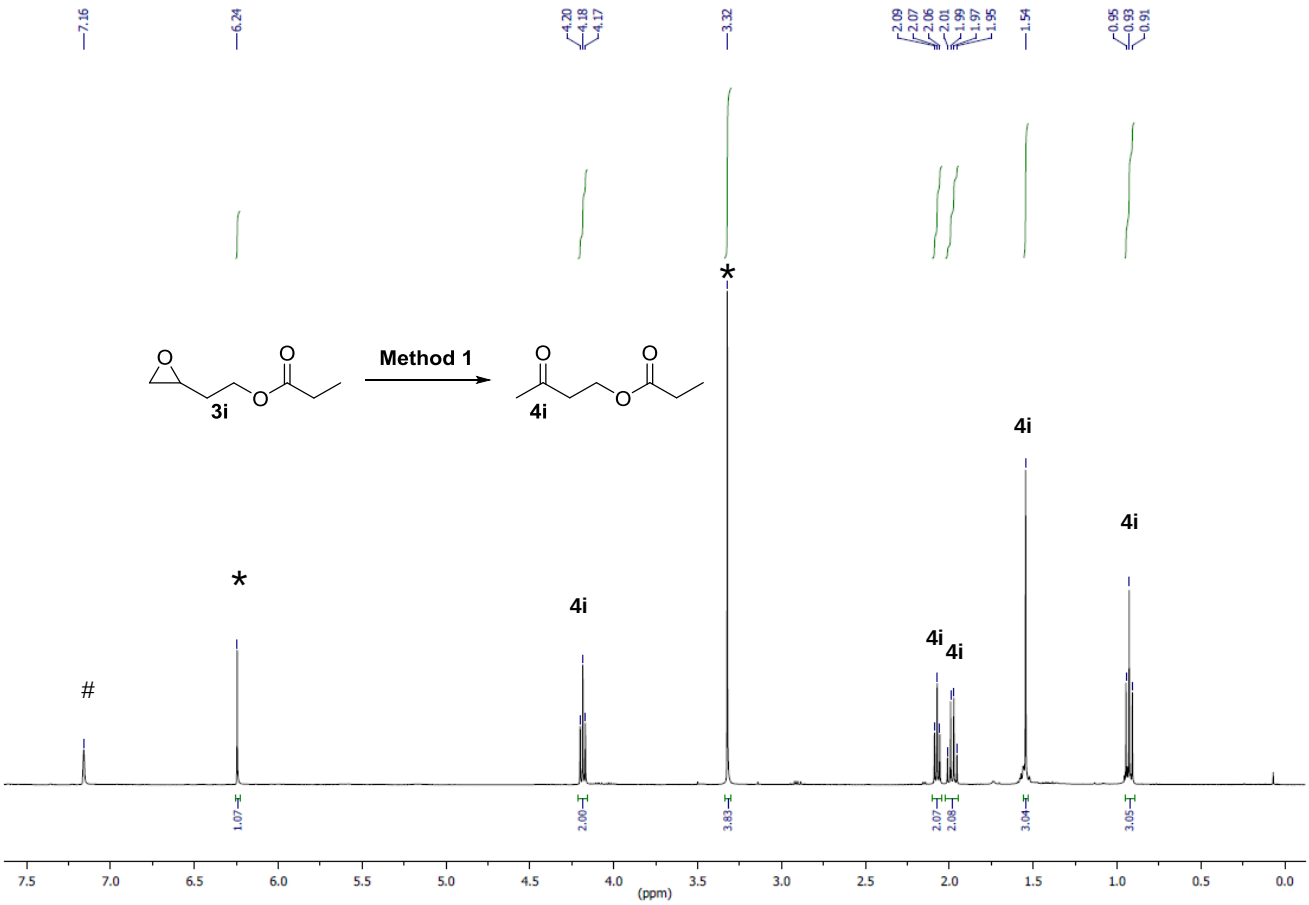


Figure S73. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3i** into **4i** with **Method 1** including the internal standard (*).

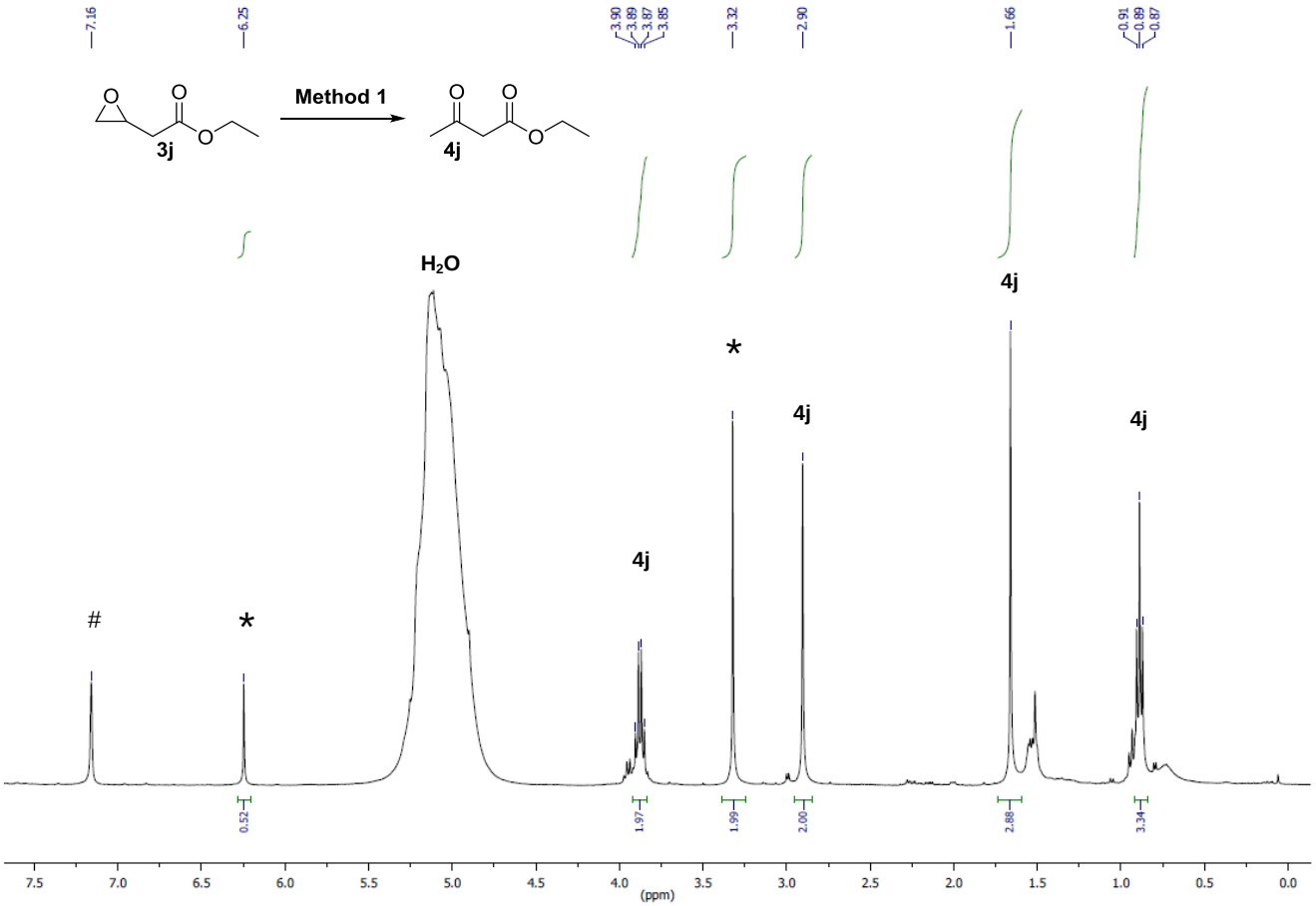


Figure S74. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3j** into **4j** with **Method 1** including the internal standard (*). Notably, this reaction should be quenched with a drop of water otherwise there were all broad peaks in the spectrum.

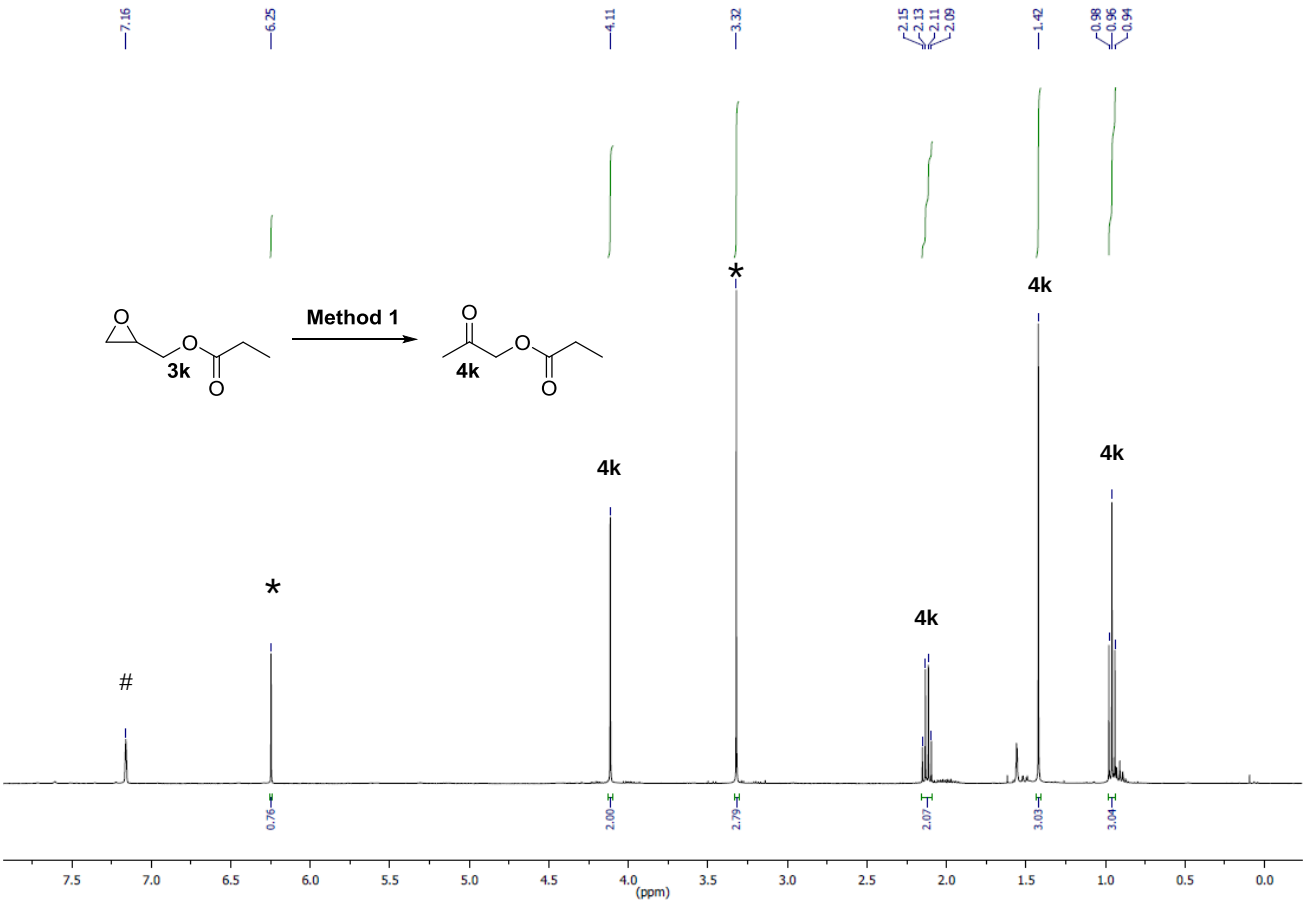


Figure S75. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3k** into **4k** with **Method 1** including the internal standard (*).

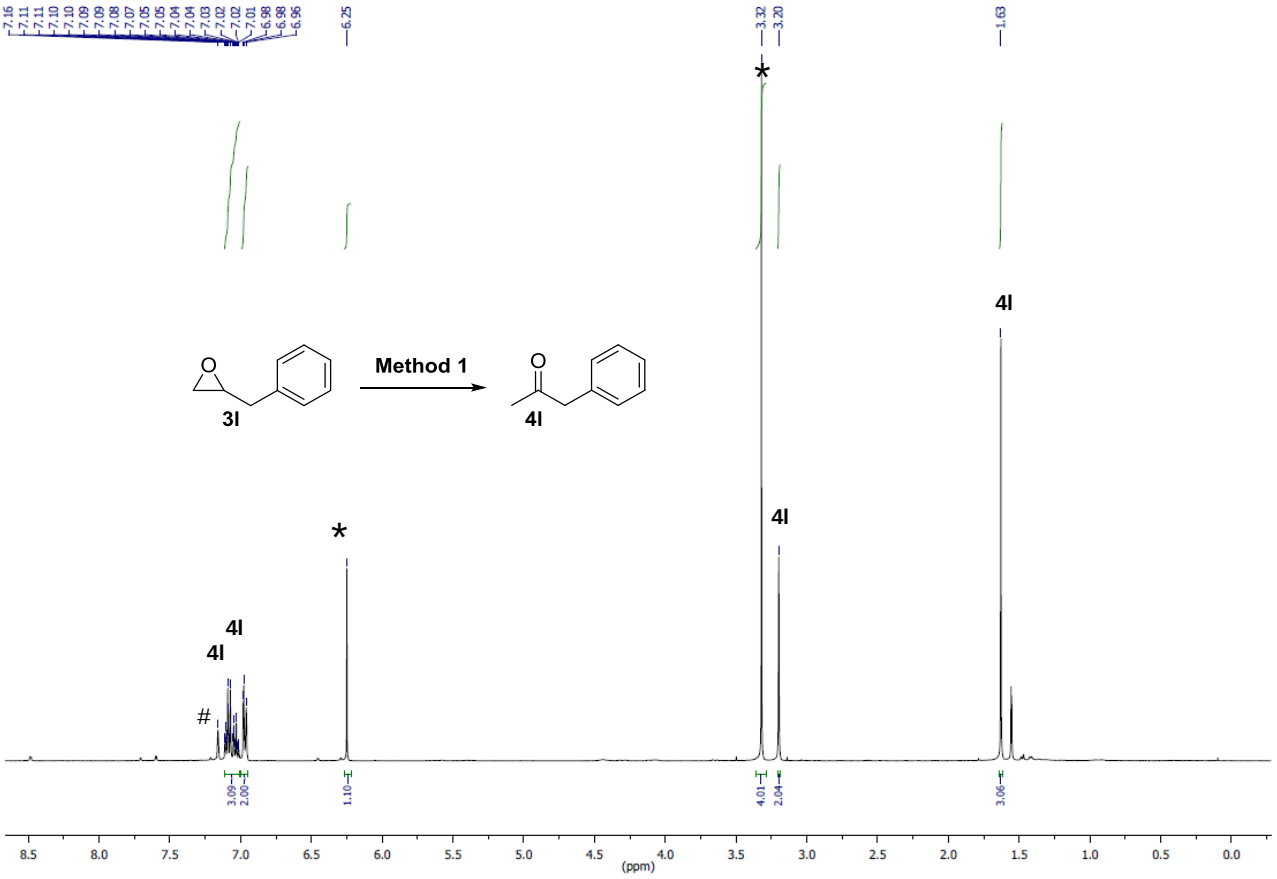


Figure S76. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3l** into **4l** with **Method 1** including the internal standard (*).

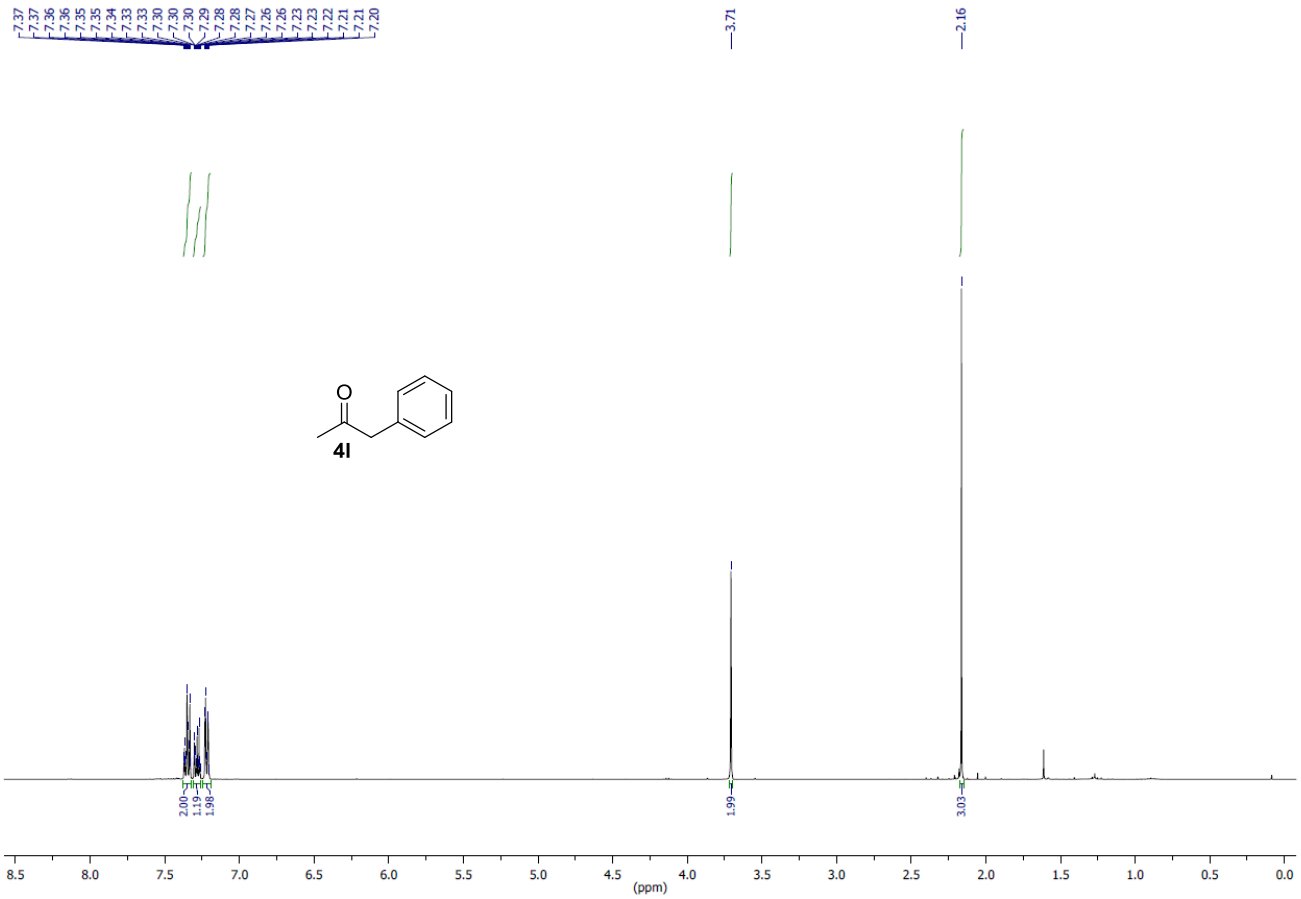


Figure S77. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum: isolated **4l** from the up-scaling experiment.

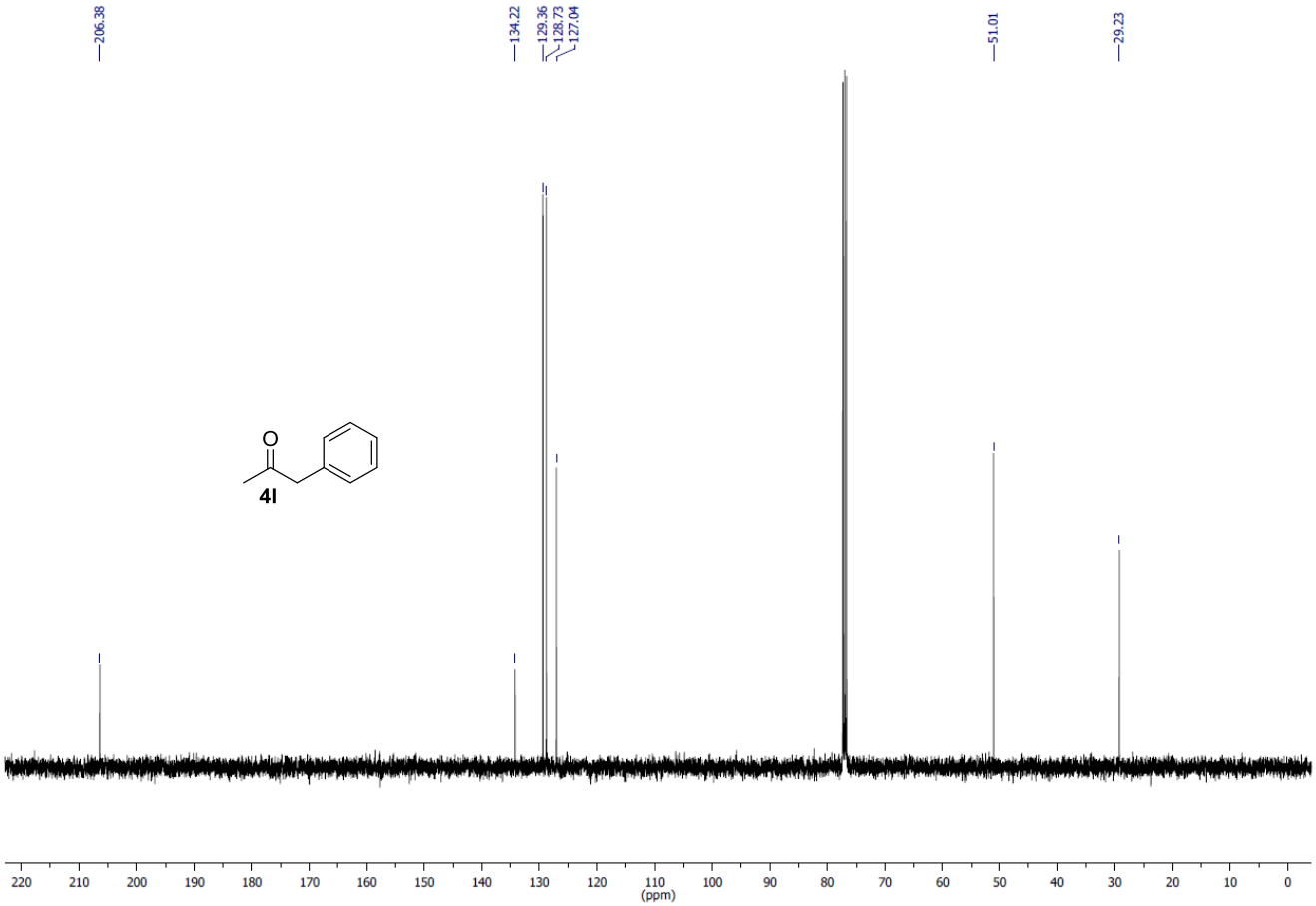


Figure S78. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum: isolated **4l** from the up-scaling experiment.

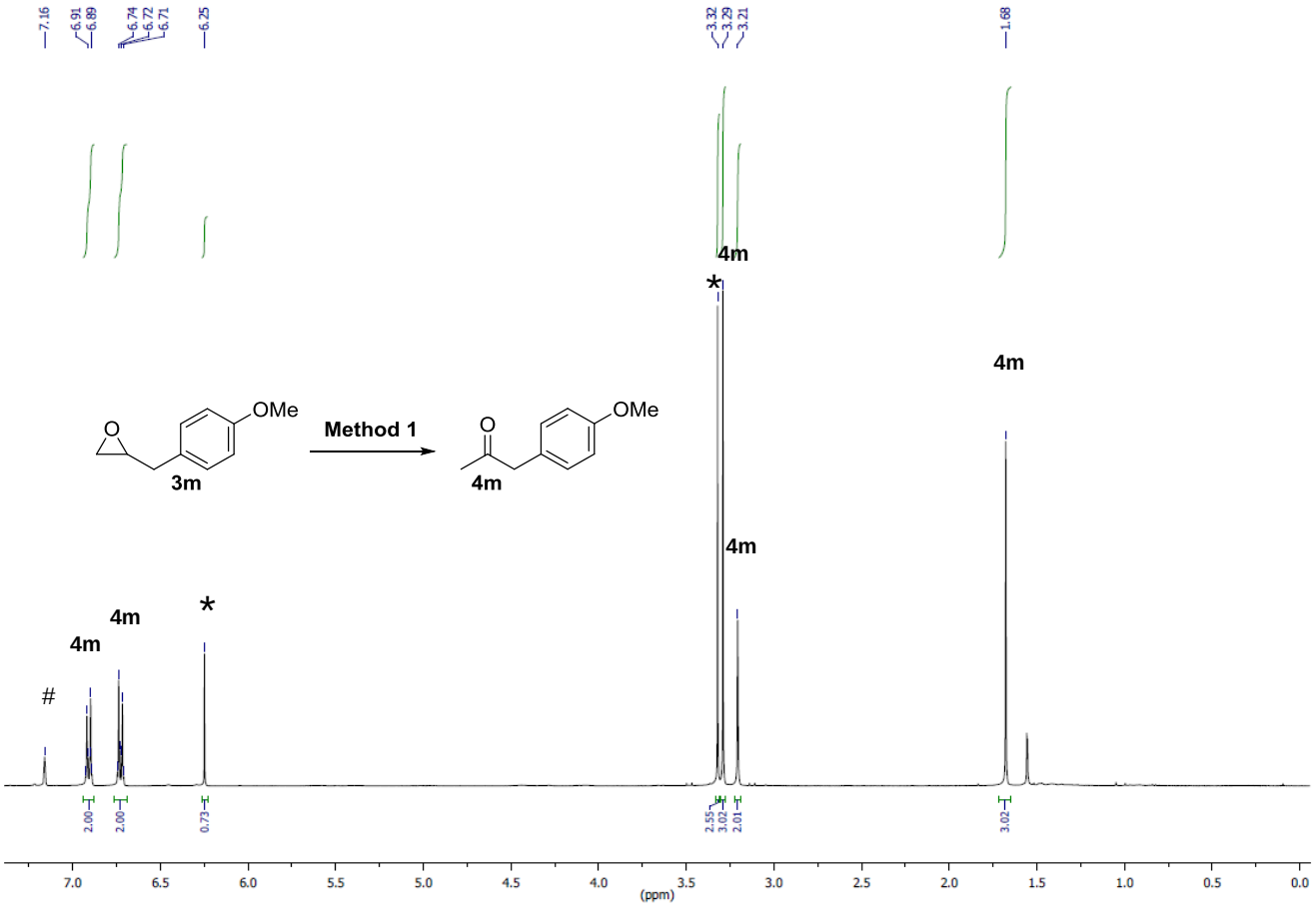


Figure S79. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3m** into **4m** with **Method 1** including the internal standard (*).

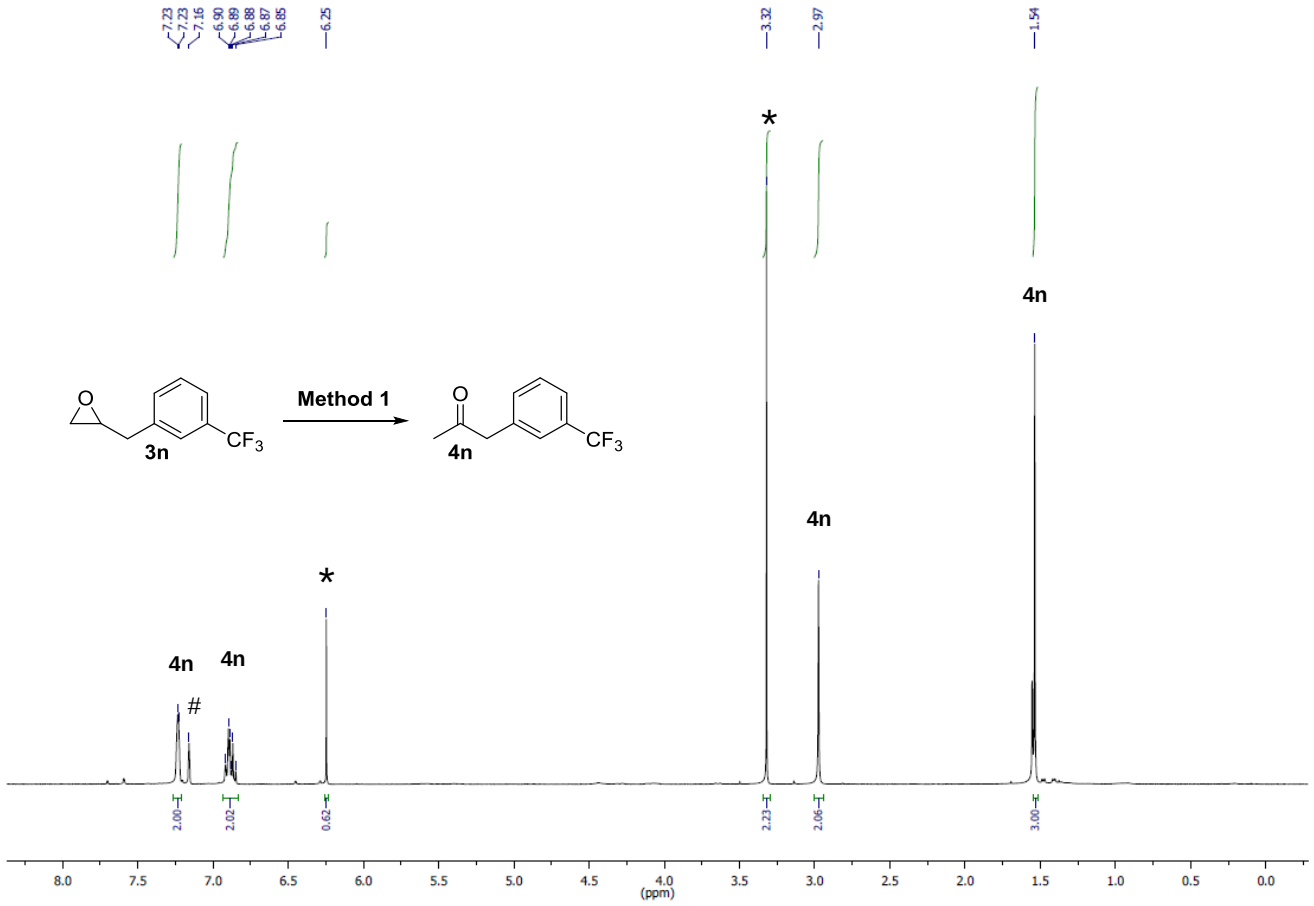


Figure S80. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **3n** into **4n** with **Method 1** including the internal standard (*).

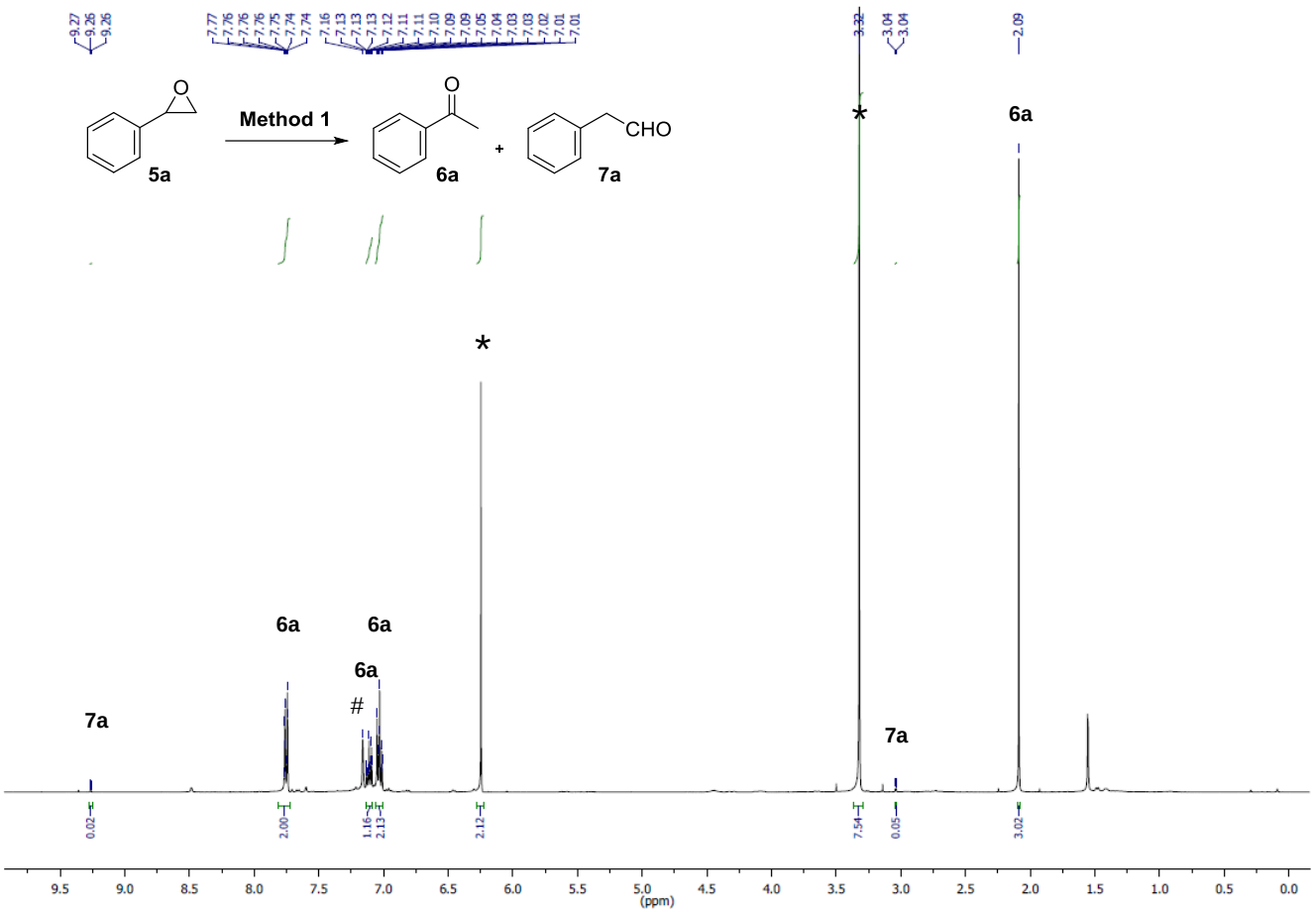


Figure S81. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5a** into **6a** with **Method 1** including the internal standard (*).

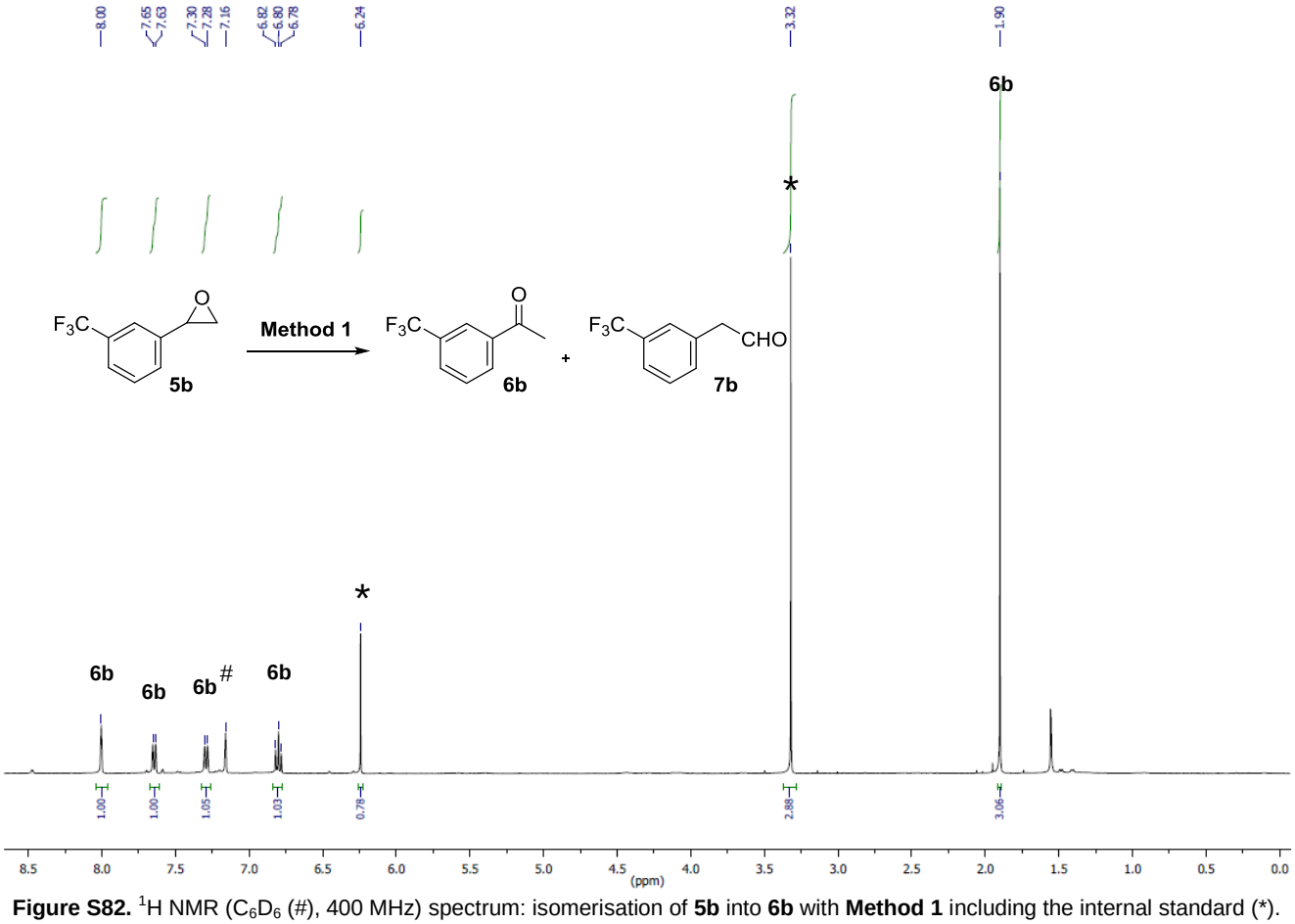


Figure S82. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5b** into **6b** with **Method 1** including the internal standard (*).

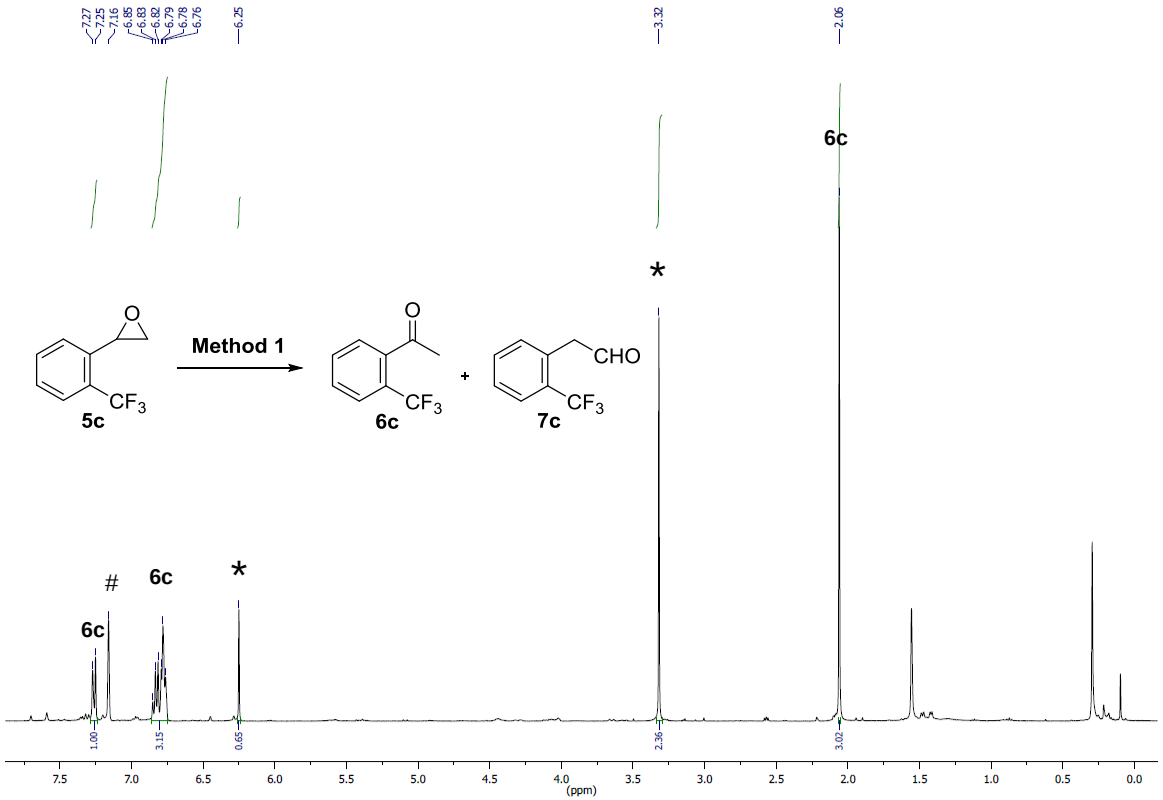


Figure S83. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5c** into **6c** with **Method 1** including the internal standard (*).

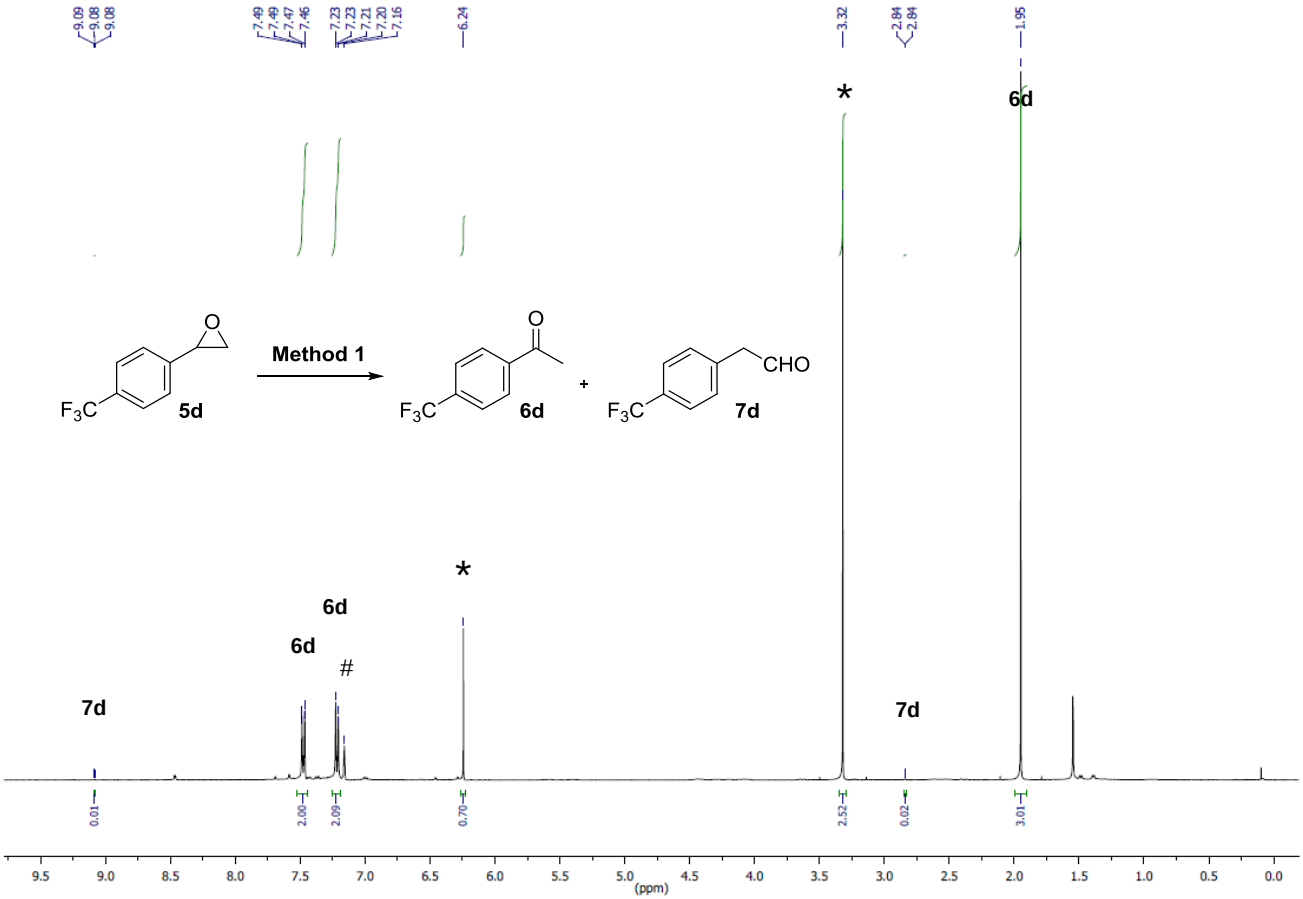


Figure S84. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5d** into **6d** with **Method 1** including the internal standard (*).

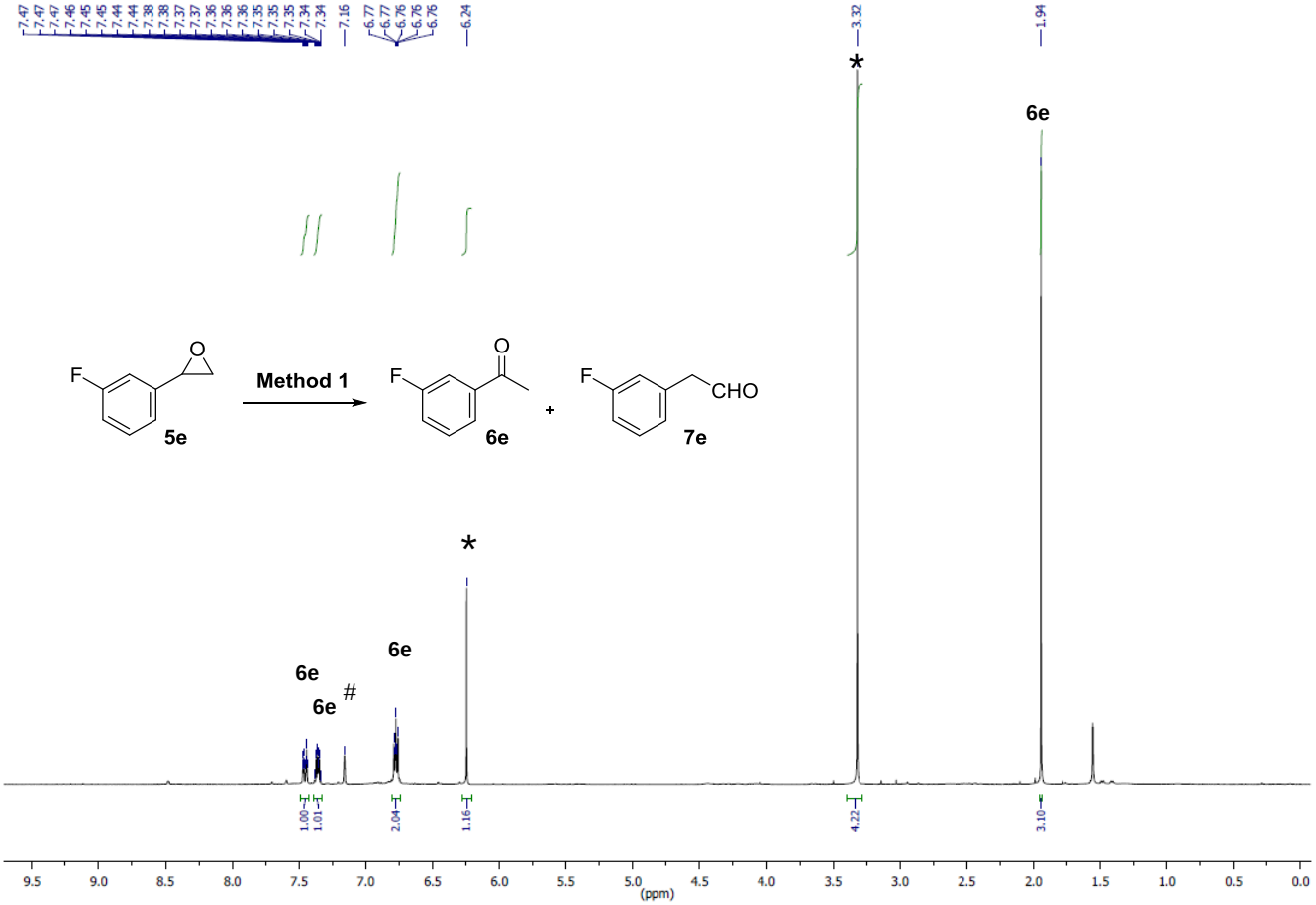


Figure S85. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5e** into **6e** with **Method 1** including the internal standard (*).

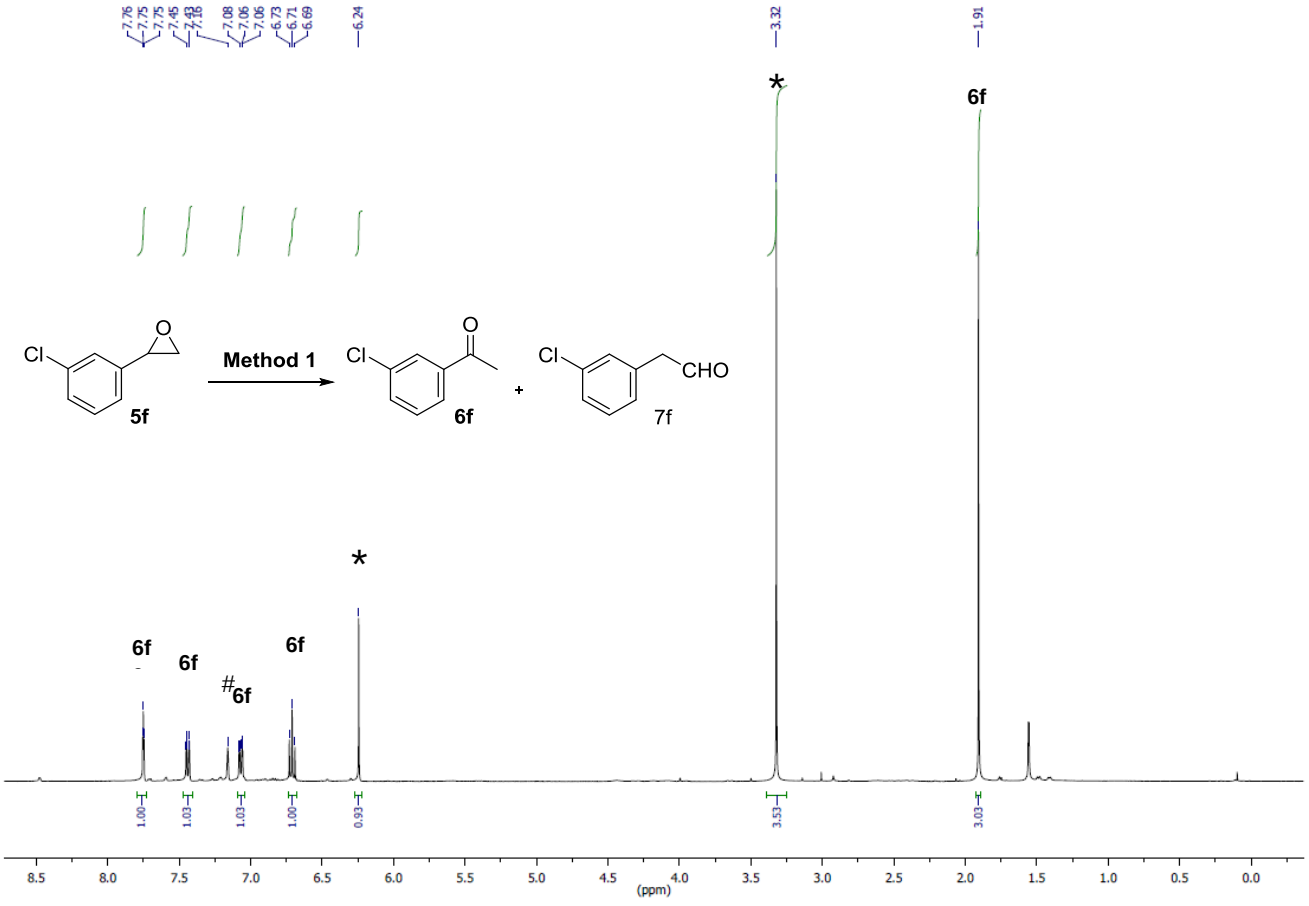


Figure S86. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5f** into **6f** with **Method 1** including the internal standard (*).

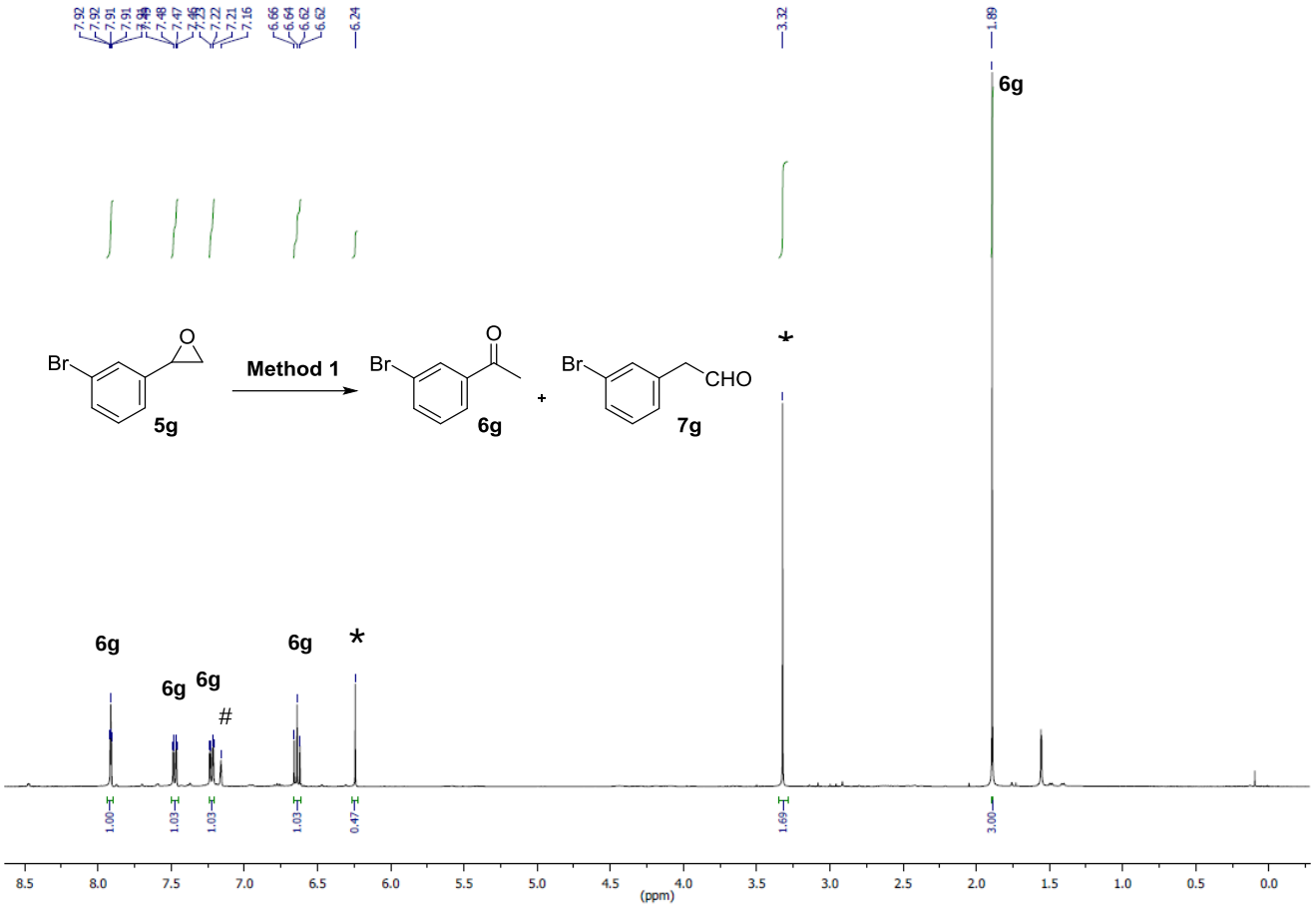


Figure S87. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5g** into **6g** with **Method 1** including the internal standard (*).

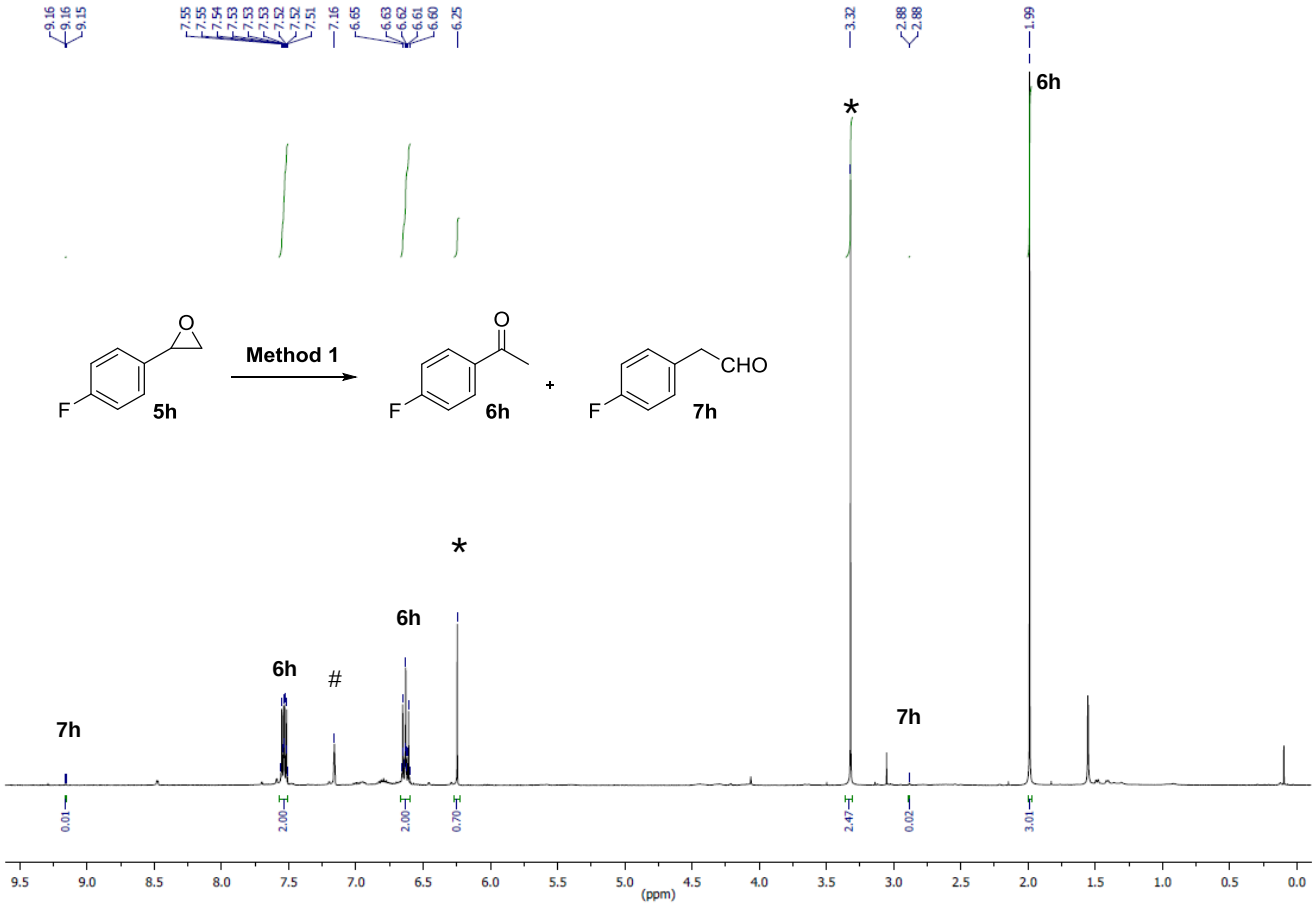


Figure S88. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5h** into **6h** with **Method 1** including the internal standard (*).

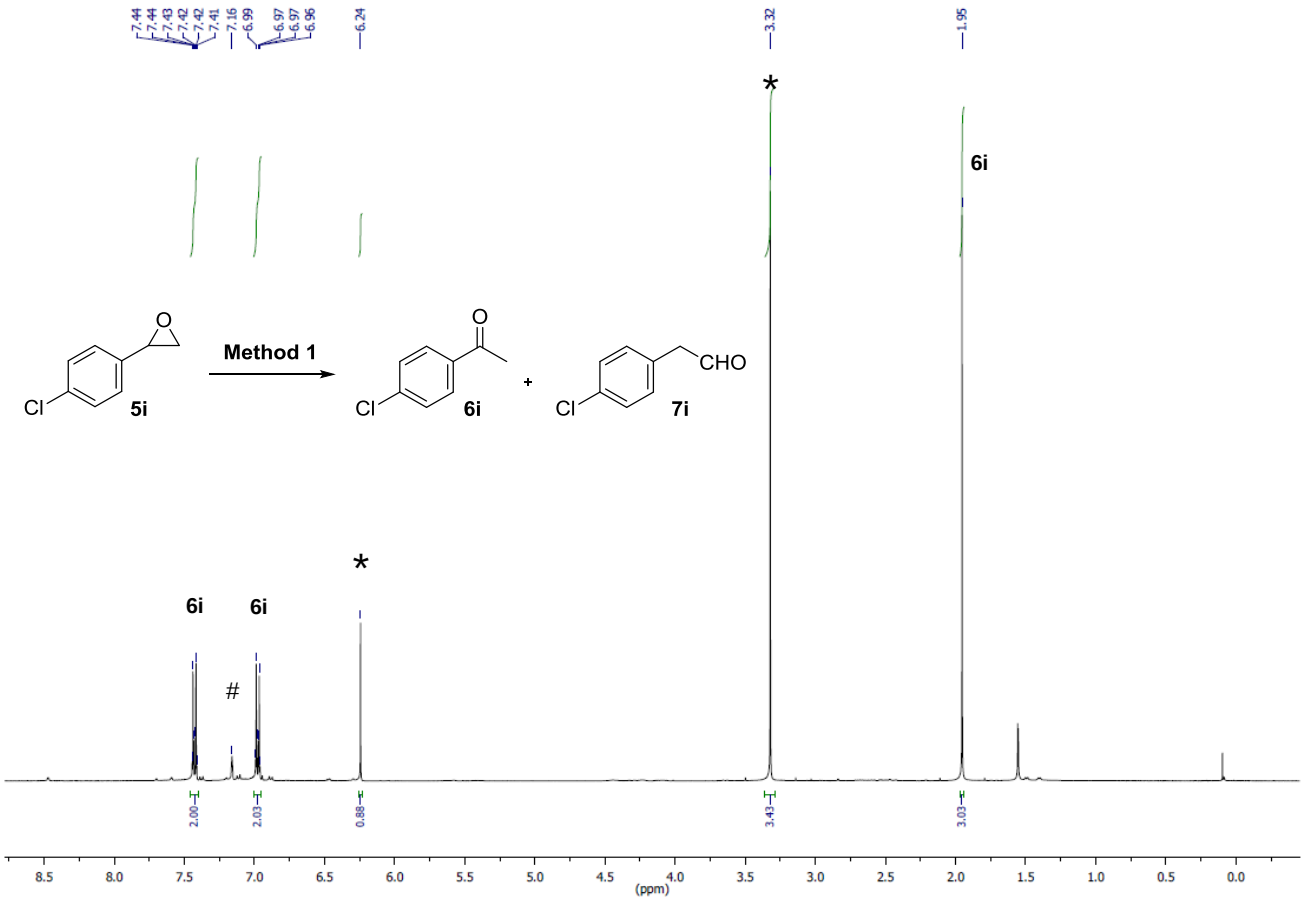


Figure S89. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5i** into **6i** with **Method 1** including the internal standard (*).

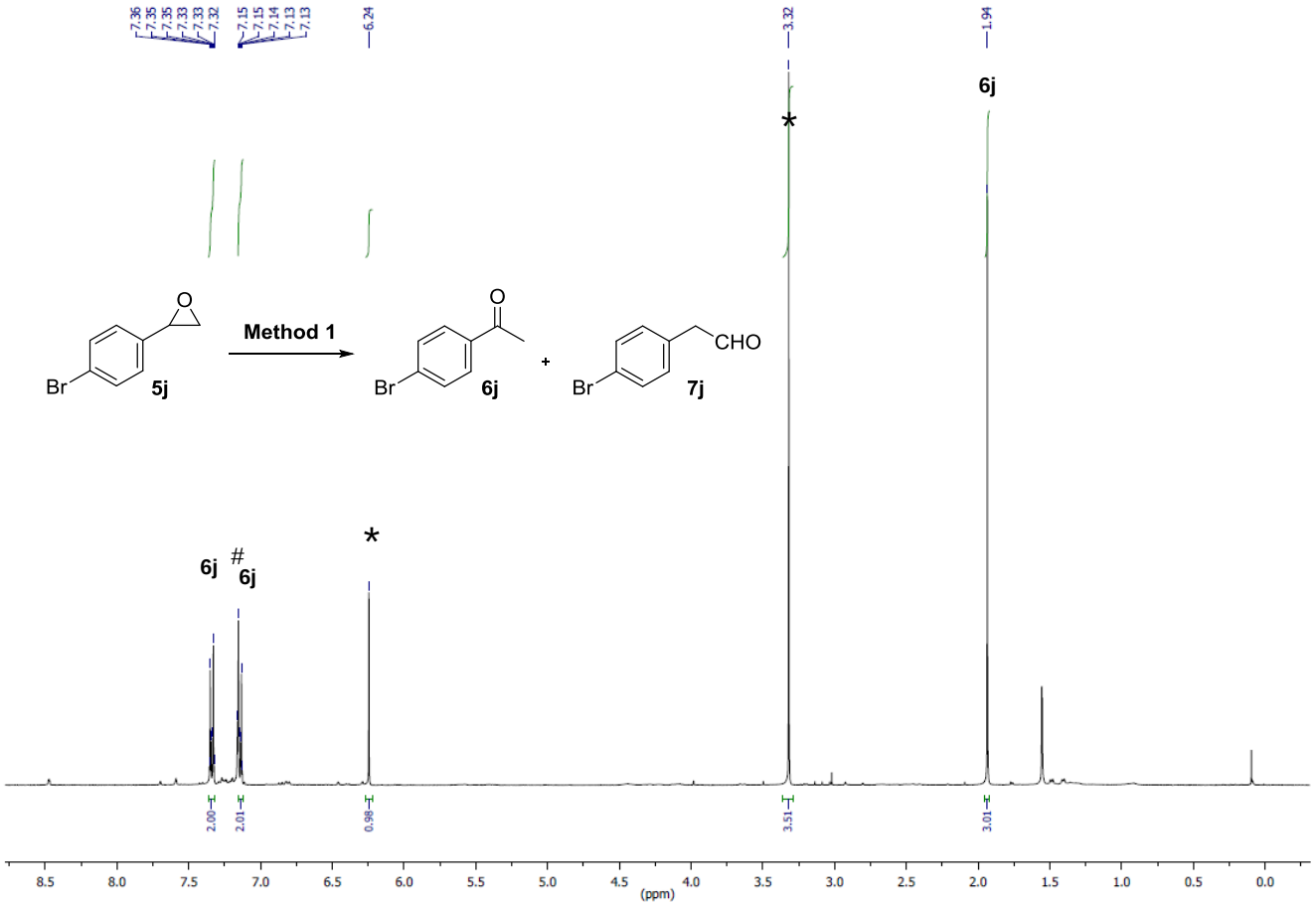


Figure S90. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5j** into **6j** with **Method 1** including the internal standard (*).

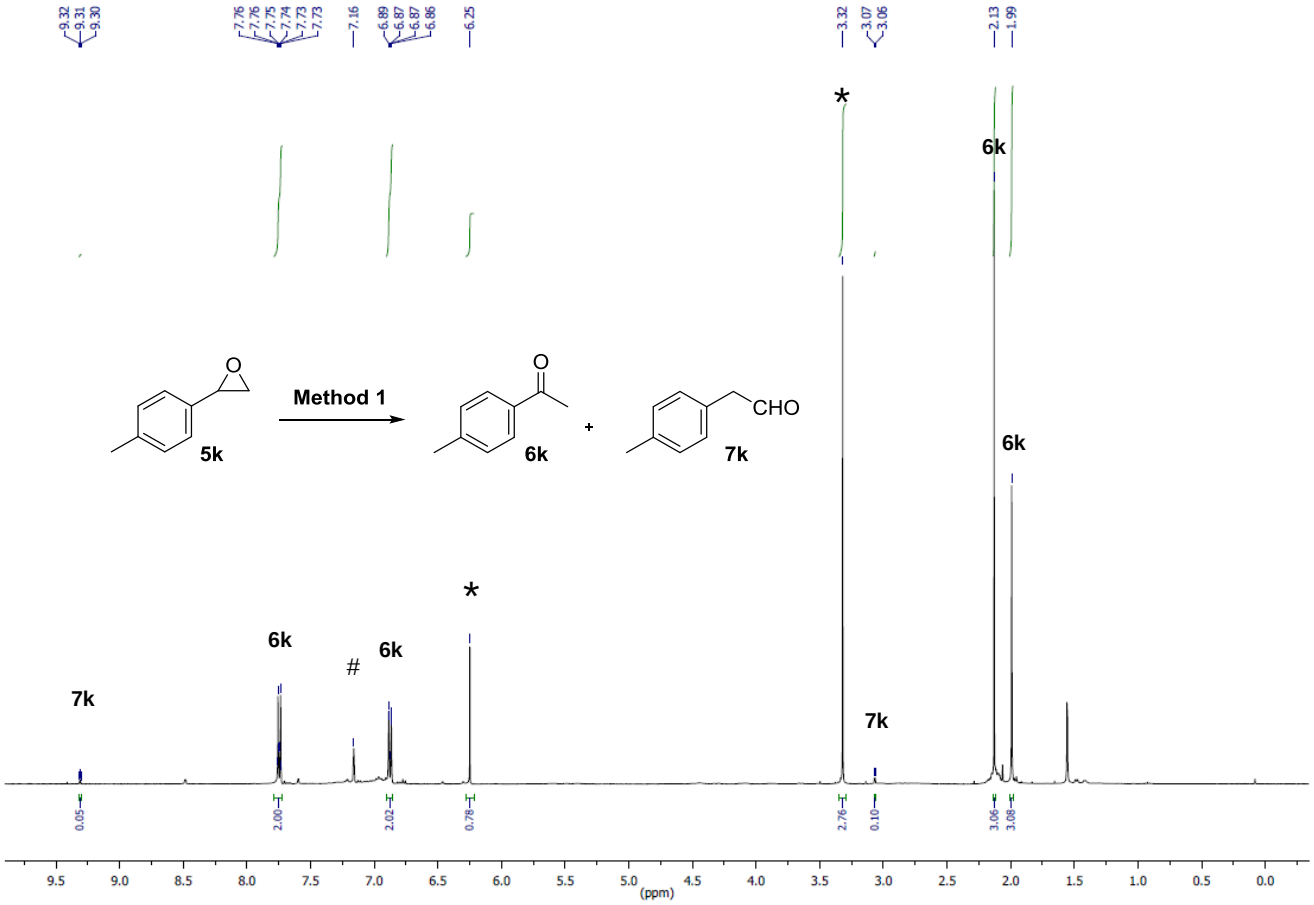


Figure S91. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5k** into **6k** with **Method 1** including the internal standard (*).

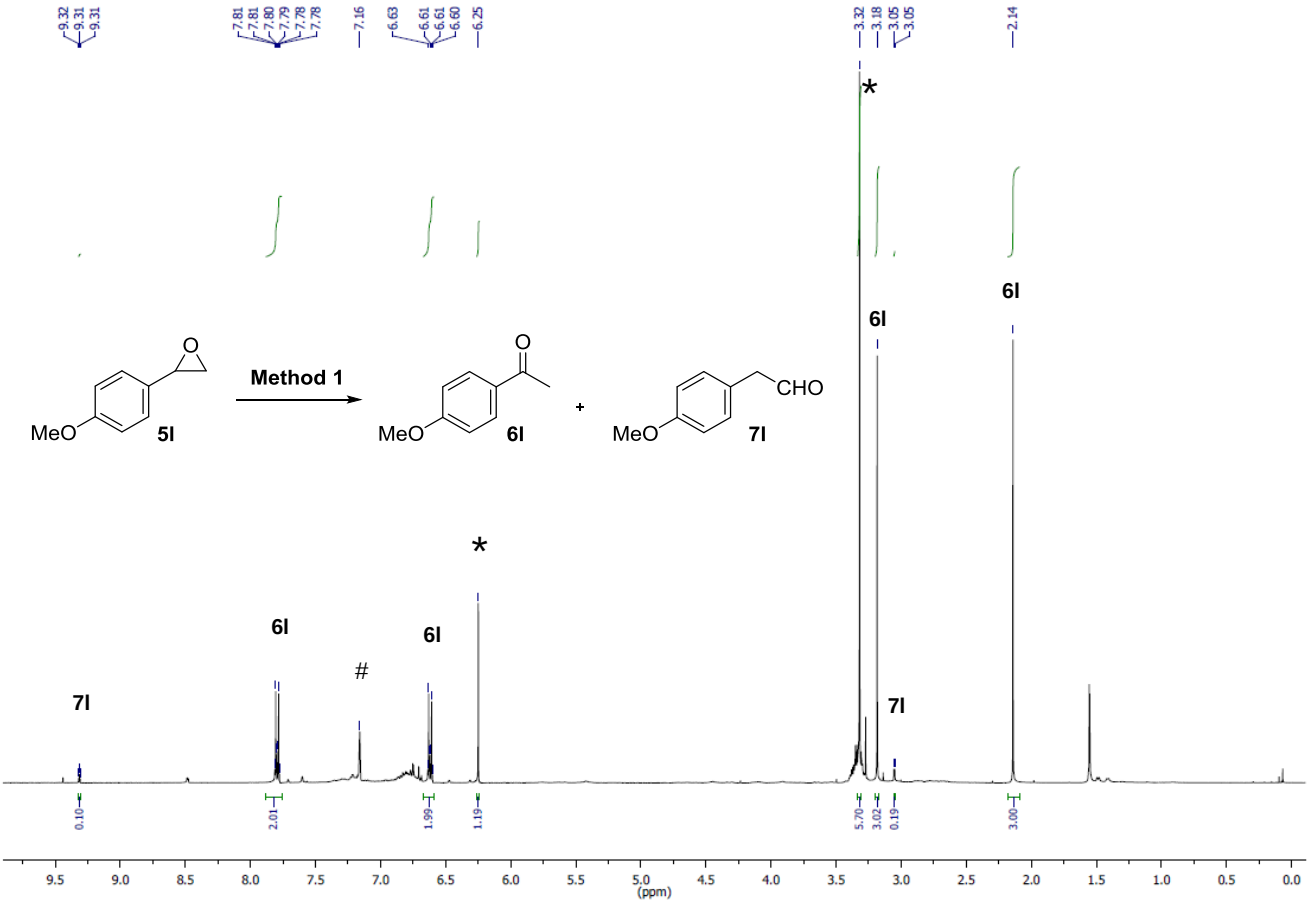


Figure S92. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5l** into **6l** with **Method 1** including the internal standard (*).

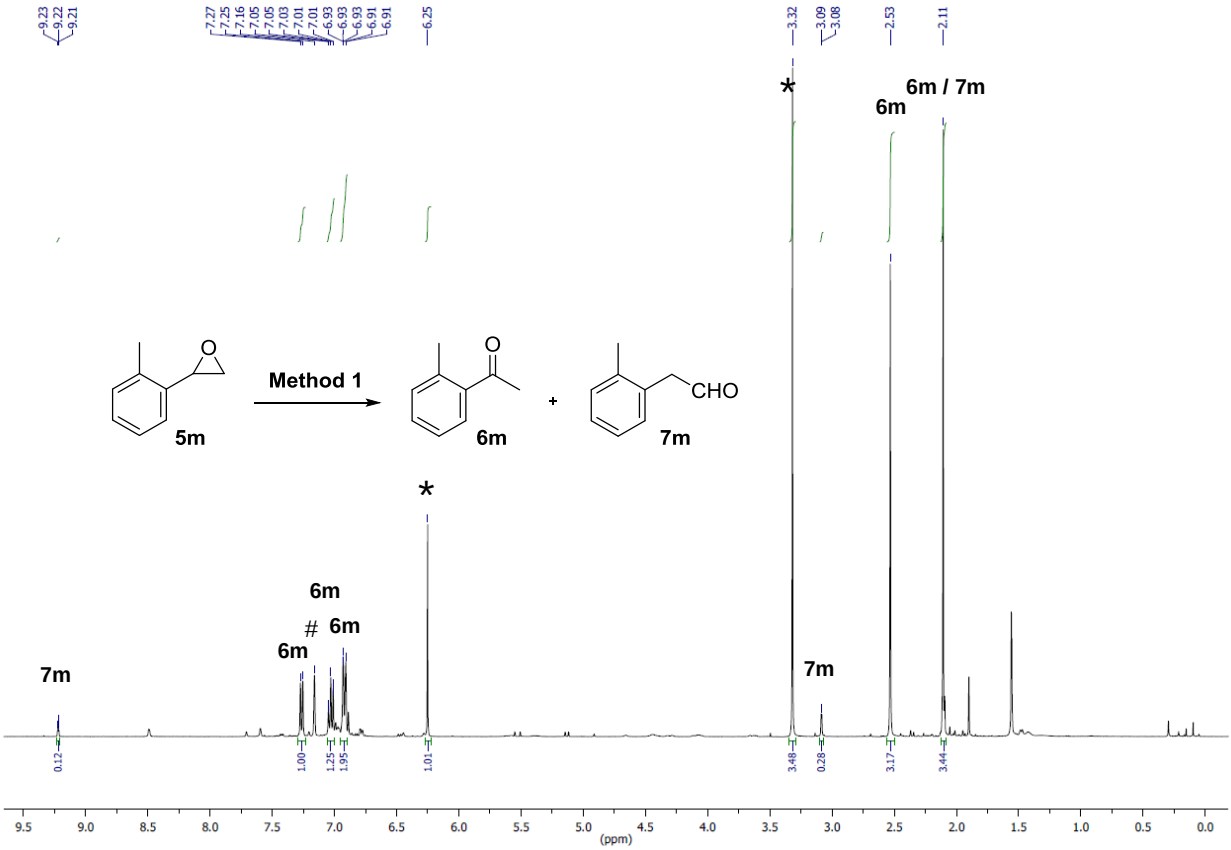
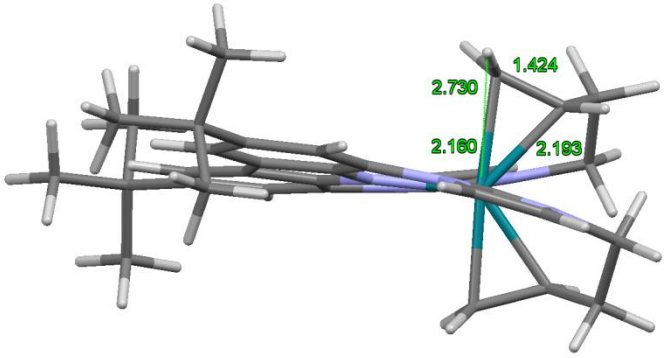


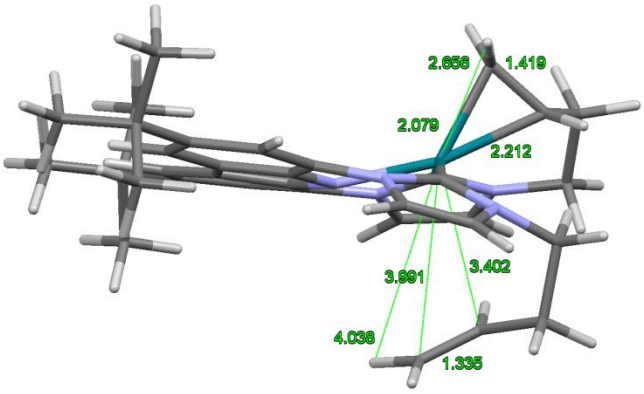
Figure S93. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum: isomerisation of **5m** into **6m** with **Method 1** including the internal standard (*).

9. DFT calculations

General information. Calculations were performed based on density functional theory at the BP86/def2-SVP and/or BP86/def2-TZVP[12-17] level implemented in Turbomole[18-26]. The RI-approximation[27-32] was used all over and the Grimme dispersion correction D3-BJ[33-34]. Several structures were optimised differing in the conformation of the rings formed by the coordination of the double bonds. The two conformers **2** and **2-mono** were verified to be minimum structures at the BP86/def2-SVP level by calculating the Hessian matrix and ensuring that it has no imaginary frequency. The Cartesian coordinates are provided as a separate xyz-file.



2



2-mono

Thermodynamics of the two conformers of 2

No. in Manuscript	**2**		**2-mono**
SCF	-1705,0810914		-1705,0601104
SCF+E_{vib}0	-1704,4236066		-1704,4052447
H (298K, 1 bar)	0,6950860		0,6941540
SCF+H (298K, 1 bar)	-1704,3860054		-1704,3659564
G (298K, 1 bar)	0,5922243		0,5838385
SCF+G (298K, 1 bar)	-1704,4888671		-1704,4762719
Δ (SCF) a.u.	0,0209810	55,09 kJ/mol	
Δ (SCF+E_{vib}0) a.u.	0,0183619	48,21 kJ/mol	
$\Delta H_{(298\ K,\ 1\ bar)\ a.u.}$	0,0200490	52,64 kJ/mol	
$\Delta G_{(298\ K,\ 1\ bar)\ a.u.}$	0,0125952	33,07 kJ/mol	

The unsymmetric complex **2-mono** is about 53 kJ/mol higher in energy ($\Delta H^{\ominus}$) ($\Delta G^{\ominus}$ = 33 kJ/mol) than complex **2** and is also not supported by the experimental NMR data for symmetry reasons.

10. References

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