Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Atom-Economical Cobalt-Catalysed Regioselective Coupling of Epoxides and Aziridines with Alkenes

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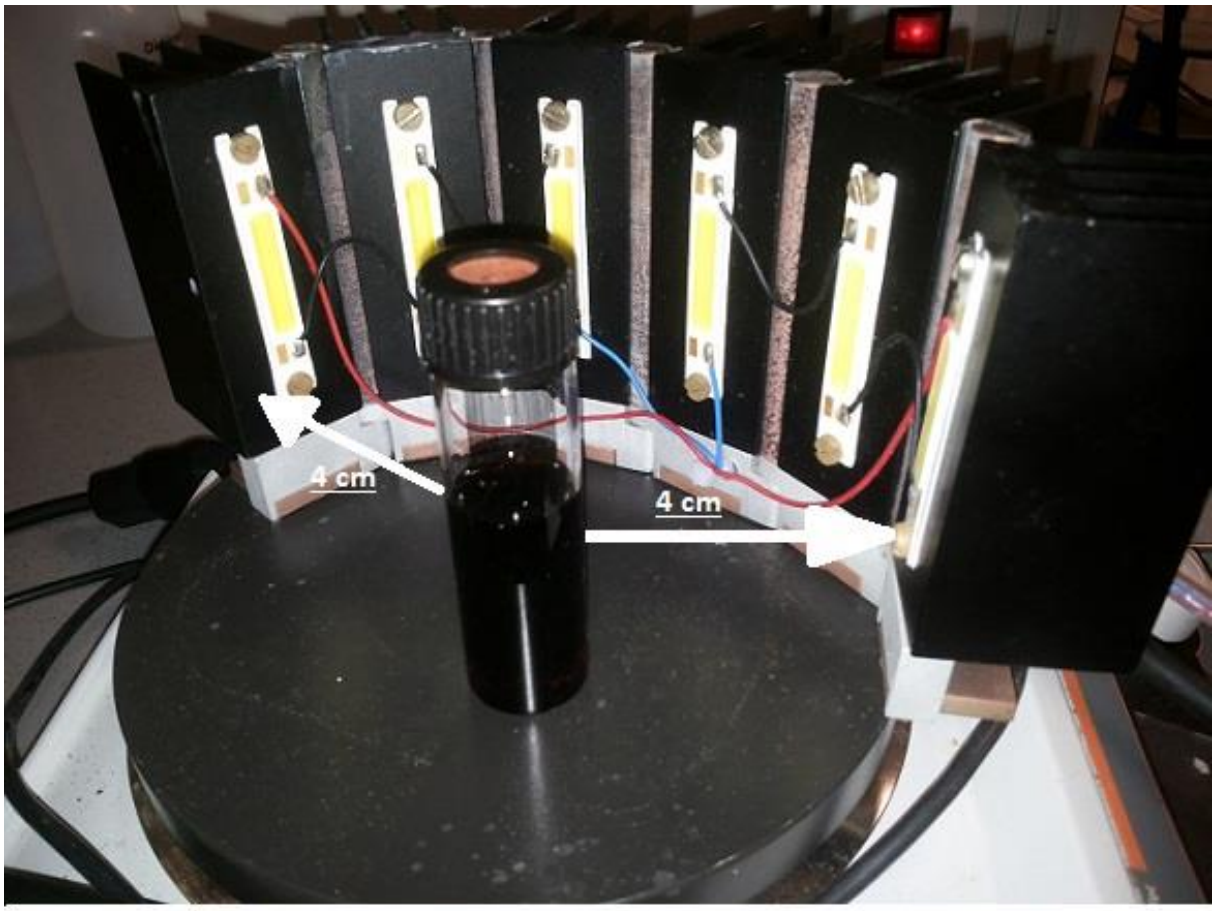
Materials and methods

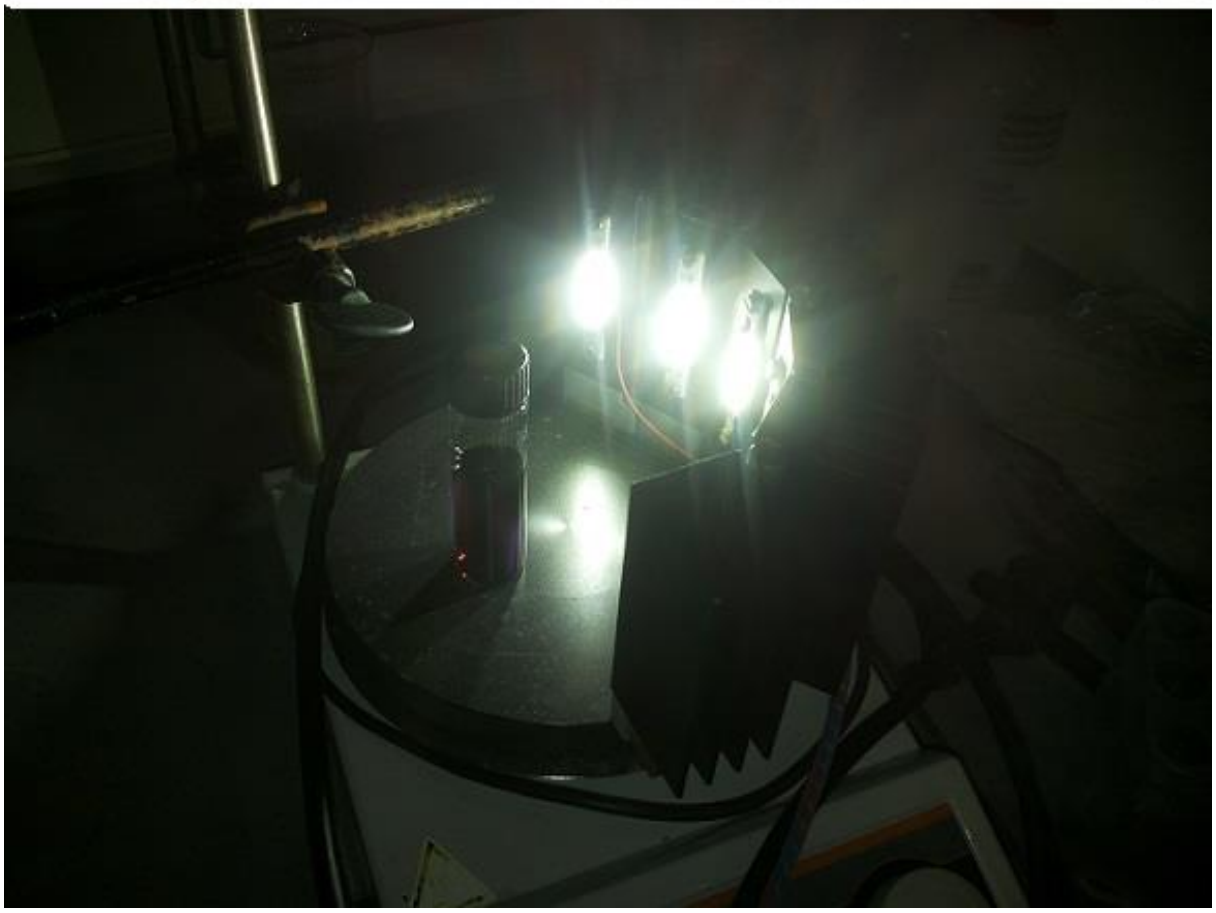
Commercially available materials were used as received without any further purification. Starting materials were synthesized as reported. Catalyst, $Co(dmg)_2(py)iPr$, was synthesized following reported literature procedure[1].

Nuclear Magnetic Resonance spectra were measured using a 500 MHz or 300 MHz spectrometer. ^{1}H-NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, p = pentuplet, h= sextuplet, m =multiplet and br = broad), coupling constant (J values) in Hz and integration. Chemical shifts (δ) were reported with respect to the corresponding solvent residual peak at 7.26 ppm for $CDCl_3$ for ^{1}H-NMR. ^{13}C-NMR spectra (^{1}H-broadband decoupled) were reported in ppm using the central peak of $CDCl_3$ (77.16 ppm). High-resolution mass spectrometric measurements were provided by the Mass Spectrometry Department of the Max-Planck-Institut für Kohlenforschung. The molecular ion $[M+H]^+$, $[M+Na]^+$ respectively or the anion $[M–H]^-$ are given in m/z units. Enantiomeric excess measurements were provided by the GC Department of the Max-Planck-Institut für Kohlenforschung.

Thin Layer Chromatography analyses were performed on silica gel coated glass plates (0.25 mm) with fluorescence-indicator UV254 (Macherey-Nagel, TLC plates SIL G-25 UV_{254}). For detection of spots, irradiation of UV light at 254 nm, oxidative staining using potassium permanganate solution ($KMnO_4$) or a solution of vanillin in ethanol and sulfuric acid were used. Flash column chromatography was conducted with Silicagel 60 (particle size 40–63 µM, Merck) at room temperature and under elevated pressure (compressed air). Organic solutions were concentrated under reduced pressure on a rotary evaporator.

Catalytic reactions were performed using a white LED-lamp apparatus (6 x 6W LED lamp in a row: CCT 5000K, forward current 700 mA, Voltage 9.3 V, Viewing angle 120°) built by the Mechanical Department of the Max-Planck-Institut für Kohlenforschung and shown in the following picture.


4 cm
4 cm



Experimental Procedures

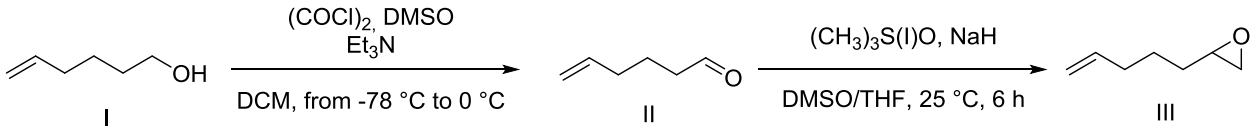
General procedure (A): Optimization table (Table 1)

A screw-cap vial charged with $Co(dmg)_2(py)$*i*Pr (21 mg, 0.05 mmol), KO*t*Bu (11 mg, 0.10 mmol) and a stirring bar, was purged with Ar for 10 mins. Degassed MeOH was then added to afford a final 0.1 M solution (based on the amount of epoxide). After purging the solution with Ar for additional 5 mins, commercially available 1,2-Epoxy-5-hexene (97 % purity, 0.50 mmol) was added and the reaction mixture was stirred in front of the LED reactor (approx. 4 cm, internal reached temperature 34 °C). After 24 h the LED reactor was switched off, nitrobenzene as internal standard was added and 0.20 mL of solution were collected and diluted with additional 0.20 mL of distilled water and 0.20 mL of $CDCl_3$. The aqueous phase was then extracted with $CDCl_3$ (3 x 0.20 mL) and the resulting organic phase filtered over Celite and directly used for the ^{1}H-NMR analysis. The yields of the corresponding products were determined by ^{1}H-NMR analysis of the crude reaction mixture comparing with the internal standard.

General procedure (B): Substrate scope (Table 2)

A screw-cap vial charged with $Co(dmg)_2(py)$*i*Pr (21 mg, 0.05 mmol, 0.10 eq.), KO*t*Bu (11 mg, 0.10 mmol, 0.20 eq.) and a stirring bar, was purged with Ar for 10 mins. Degassed MeOH (10 mL, 0.05 M solution) was then added. After purging the solution with Ar for additional 5 mins, commercially available 1,2-Epoxy-5-hexene (97 % purity, 58 µL, 0.50 mmol, 1.0 eq.) was added and the reaction mixture was stirred in front of the LED reactor (approx. 4 cm, internal reached temperature 34 °C). After 24 h the LED reactor was switched off and the solution was diluted with additional 8.0 mL of distilled water and 10 mL of $CHCl_3$. The aqueous phase was then extracted with $CHCl_3$ (3 x 10 mL) and the combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified via flash column chromatography (DCM as eluent) to afford the desired product.

General procedure (C): Synthesis of 2-(pent-4-en-1-yl)oxirane (compound III)

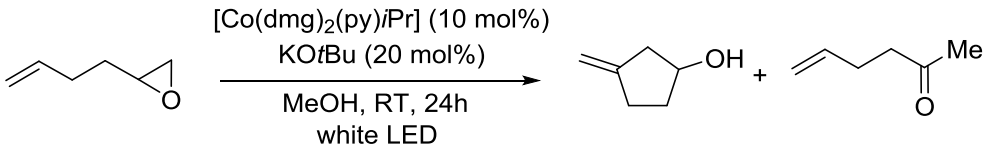


I II III

Compound **II** was synthesized from commercially available compound **I** according to reported procedure[2]. NaH (60 % in oil, 1.2 g, 30 mmol) was added to a solution of trimethylsulfoxonium iodide (6.6 g, 30 mmol) in dried DMSO (24 mL). After 1 h, a solution of aldehyde **II** (2.0 g, 20 mmol) in 24 mL THF was added at 25 °C. After stirring for 5 h, ice was added to the reaction mixture, and the reaction mixture was extracted with ethyl acetate (2 x 100 mL). The organic layer was washed with water (2 x 50 mL) and then with brine. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo.* The crude

product was purified by column chromatography (hexanes/MTBE 95:5) to get 2-(pent-4-en-1-yl)oxirane (compound **III**, 1.25 g, 56 % yield).

Optimization Table



All the reactions were performed following general procedure A, with all the relative deviations.

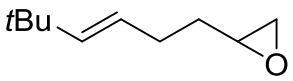
Entry	Deviation from Standard Conditions	Yield
1	-	73/8
2	No Base	0/0
3	10 mol% KO*t*Bu, 15 mol% [Co(dmg)$_2$(py)*i*Pr]	72/8
4	NEt_3 instead of KO*t*Bu	8/0
5	No LED	0/0
6	No LED, 80 °C	0/70
7	LED for 1 h, then no LED	traces/0
8	MeCN instead of MeOH	0/19
9	EtOH instead of MeOH	33/17
10	No Base, 1. Equiv Zn(0), Co-salen (5 mol%) instead of [Co(dmg)$_2$(py)*i*Pr]	0/0
11	No Base, 1. Equiv Zn(0), $B12_a$ (5 mol%) instead of [Co(dmg)$_2$(py)*i*Pr]	73/8

Initial rate study

A screw-cap was charged with Co(dmg)$_2$(py)*i*Pr (21 mg, 0.05 mmol, 0.10 eq.), KO*t*Bu (11 mg, 0.10 mmol, 0.20 eq.) and a stirring bar, then purged with Ar for 10 mins. A second screw-cap vial was charged with Co(dmg)$_2$(py)*i*Pr (31 mg, 0.075 mmol, 0.15 eq.) and KO*t*Bu (11 mg, 0.05 mmol, 0.10 eq.). Degassed MeOH (5 mL, 0.1 M solutions) was then added. After purging the solutions with Ar for additional 5 mins, commercially available 1,2-Epoxy-5-hexene (97 % purity, 58 µL, 0.50 mmol, 1.0 eq.) and trifluoromethyl-benzene (0.2 mmol) were added in both the vials and the reaction mixtures were stirred in front of the LED reactor (approx. 4 cm, internal reached temperature 34 °C). Different aliquots (0.2 mL) from the two solutions were collected after: 1h, 3h, 5h, 7h and 24h. To the 0.20 mL of solution was added 0.20 mL of distilled water and 0.20 mL of $CDCl_3$. The aqueous phase were then extracted with $CDCl_3$ (3 x 0.20 mL) and the resulting organic phases filtered over Celite and directly used for the ^{1}H-NMR analysis. The yields of the corresponding products were determined by ^{1}H-NMR analysis of the crude reaction mixture comparing with the internal standard.

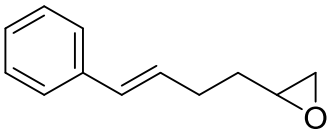
Time	**Vial A** (yield) $Co(dmg)_2(py)$*i*Pr(10mol%) KOtBu (20 mol %)	**Vial B** (yield) $Co(dmg)_2(py)$*i*Pr(15mol%) KOtBu (10 mol %)
1h	2%	1%
3h	12%	12%
5h	22%	22%
7h	30%	29%
24h	71%	72%

2-(5,5-dimethylhex-3-en-1-yl)oxirane, Table **2**, Entry **4**, Substrate



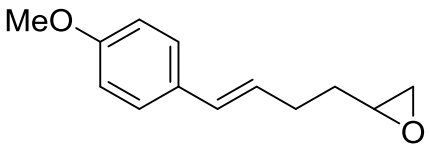
A solution of 1,2-Epoxy-5-hexene (0.15 g, 1.5 mmol) and Hoveyda-Grubbs 2nd generation catalyst (38 mg, 0.06 mmol, 4.0 mol%) in 3,3-Dimethyl-1-butene (7.8 mL) was stirred at 25 ºC for 16 h. The volatile 3,3-Dimethyl-1-butene was removed in vacuo to give the crude product as a black oil. Purification of the crude product by column chromatography (hexanes/MTBE 96:4) gave 2-(5,5-dimethylhex-3-en-1-yl)oxirane as a colorless oil (0.20 g; 86 % yield; *E*-alkene, 82:18 mixture of isomers). **^{1}H NMR** (500 MHz, $CDCl_3$); **[**minor isomer**]** δ = 5.49 [5.58] (dt, *J* = 15.6, 1.4 Hz, 1H), 5.37 – 5.28 (m, 1H), 2.97 – 2.90 (m, 1H), 2.76 – 2.74 (m, 1H), 2.47 [2.50] (dd, *J* = 5.0, 2.8 Hz, 1H), 2.31 – 2.09 (m, 2H), 1.65 – 1.52 (m, 2H), 0.98 [1.00] (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) **[**minor isomer**]** δ = [144.94] , 142.59 , 123.46 , [118.86] , 52.11 , [52.07] , 47.42 , [46.79] , 35.66 , [32.93] , 32.79 , 29.85 , [29.77] , 29.20. **HR-MS (ESI+)** calc. for $C_{10}H_{18}O_1Na_1$ $[M+Na]^+$ 177.124984, found 177.125100.

2-(4-phenylbut-3-en-1-yl)oxirane, Table **2**, Entry **5**, Substrate



A 25 mL flask was charged with a stirring bar, Hoveyda-Grubbs catalyst 2nd generation (16 mg, 0.03 mmol, 0.50 mol%) and 10 mL of anhydrous toluene. Commercially available 1,2-Epoxy-5-hexene (1.0 eq, 5.0 mmol, 0.60 mL) and styrene (5.0 eq, 25 mmol, 2.9 mL) were simultaneously added and the resulting solution was stirred at 95 °C for 5 h. The mixture was cooled down to room temperature and dichloromethane (10 mL) was added. The solvent was removed under vacuum and the crude purified on silica (hexanes → hexanes/MTBE 95:5) to afford the clean product as a colorless oil (0.35 g ; 40 % yield; 20:1 mixture of *E:Z* diastereoisomers). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.38 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.22 – 7.19 (m, 1H), 6.45 (dt, *J* = 15.8, 1.6 Hz, 1H), 6.24 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.01 – 2.97 (m, 1H), 2.78 (dd, *J* = 5.0, 3.9 Hz, 1H), 2.52 (dd, *J* = 5.0, 2.7 Hz, 1H), 2.46 – 2.34 (m, 2H), 1.79 – 1.67 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 137.63 , 130.73 , 129.52 , 128.64 , 127.17 , 126.11 , 52.00 , 47.36 , 32.44 , 29.63. **HR-MS (ESI+)** calc. for $C_{12}H_{14}O_1Na_1$ $[M+Na]^+$ 197.093684, found 197.093670.

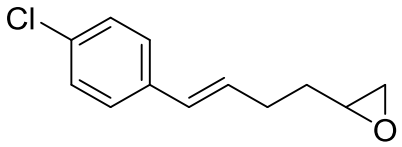
2-(4-(4-methoxyphenyl)but-3-en-1-yl)oxirane, Table **2**, Entry **6**, Substrate



A screw-cap vial was charged with a stirring bar, Hoveyda-Grubbs catalyst 2nd generation (9.4 mg, 0.50 mol%) and 6.0 mL of anhydrous toluene. Commercially available 1,2-Epoxy-5-hexene (0.34 mL, 3.0 mmol, 1.0 eq.) and 4-Vinylanisole (1.6 mL, 12 mmol, 4.0 eq.) were simultaneously added and the resulting solution was stirred at 95 °C for 5 h. The mixture was cooled down to room temperature and

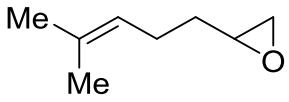
dichloromethane (6.0 mL) was added. The solvent was removed under vacuum and the crude purified on silica (hexanes → hexanes/MTBE, 95:5) to afford the clean product (0.23 g; 38 % yield; 20:1 mixture of *E:Z* diastereoisomers). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.29 – 7.26 (m, 2H), 6.85 – 6.82 (m, 2H), 6.38 (dt, *J* = 15.8, 1.6 Hz, 1H), 6.09 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.80 (s, 3H), 3.00 – 2.97 (m, 1H), 2.78 (dd, *J* = 5.0, 4.0 Hz, 1H), 2.52 (dd, *J* = 5.0, 2.8 Hz, 1H), 2.43 – 2.30 (m, 2H), 1.76 – 1.65 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.91 , 130.47 , 130.08 , 127.34 , 127.20 , 114.06 , 55.43 , 52.05 , 47.38 , 32.59 , 29.61. **HR-MS (ESI+)** calc. for $C_{13}H_{16}O_2Na_1$ $[M+Na]^+$ 227.104249, found 227.104130.

2-(4-(4-chlorophenyl)but-3-en-1-yl)oxirane, Table **2**, Entry **7**, Substrate



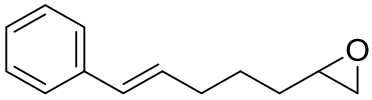
A screw-cap vial was charged with a stirring bar, Hoveyda-Grubbs catalyst 2nd generation (6.3 mg, 0.50 mol%) and 4.0 mL of anhydrous toluene. Commercially available 1,2-Epoxy-5-hexene (0.23 mL, 2.0 mmol, 1.0 eq.) and 4-Chlorostyrene (1.3 mL, 10 mmol, 5.0 eq,) were simultaneously added and the resulting solution was stirred at 95 °C for 5 h. The mixture was cooled down at room temperature and dichloromethane (4.0 mL) was added. The solvent was removed under vacuum and the crude purified on silica (hexanes → hexanes/MTBE 95:5) to afford the clean product (0.27 g; 64 % yield; 20:1 mixture of *E:Z* diastereoisomers).**^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.26 (s, 4H), 6.39 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.21 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.00 – 2.96 (m, 1H), 2.78 (dd, *J* = 5.0, 4.0 Hz, 1H), 2.52 (dd, *J* = 5.0, 2.7 Hz, 1H), 2.45 – 2.32 (m, 2H), 1.80 – 1.73 (m, 1H), 1.71 – 1.64 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 136.12 , 132.71 , 130.27 , 129.57 , 128.76 , 127.32 , 51.96 , 47.32 , 32.33 , 29.63. **HR-MS (ESI+)** calc. for $C_{12}H_{13}O_1Cl_1Na_1$ $[M+Na]^+$ 231.054712, found 231.054520.

2-(4-methylpent-3-en-1-yl)oxirane, Table **2**, Entry **8**, Substrate



2-(4-methylpent-3-en-1-yl)oxirane was synthesized according to literature[3].

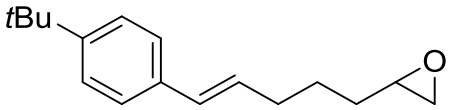
2-(5-phenylpent-4-en-1-yl)oxirane, Table **2**, Entry **9**, Substrate



A screw-cap vial was charged with a stirring bar, Hoveyda-Grubbs catalyst 2nd generation (8.8 mg, 1.0 mol%) and 2.8 mL of toluene. 2-(pent-4-en-1-yl)oxirane (compound **III**, 0.16 g, 1.4 mmol, 1.0 eq.) and styrene (0.64 mL, 5.6 mmol, 4.0 eq.) were simultaneously added and the resulting solution was stirred at 95 °C for 5 h. The mixture was cooled down at room temperature and dichloromethane (2.8 mL) was added. The solvent was removed under vacuum and the crude purified on silica (hexanes →

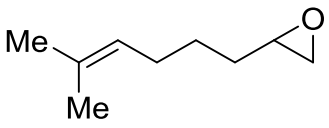
hexanes/MTBE 90:10) to afford the clean product (99 mg; 38 % yield; E-alkene).**^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.35 – 7.28 (m, 4H), 7.22 – 7.18 (m, 1H), 6.40 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.21 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.96 – 2.93 (m, 1H), 2.77 (dd, *J* = 5.0, 3.9 Hz, 1H), 2.49 (dd, *J* = 5.0, 2.7 Hz, 1H), 2.31 – 2.26 (m, 2H), 1.73 – 1.54 (m, 4H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ = 137.79 , 130.49 , 130.33 , 128.63 , 127.06 , 126.07, 52.36 , 47.26 , 32.84 , 32.10 , 25.84 .**HR-MS (ESI+)** calc. for $C_{13}H_{16}O_1Na_1$ $[M+Na]^+$ 211.109334, found 211.109250.

2-(5-(4-(*tert*-butyl)phenyl)pent-4-en-1-yl)oxirane, Table **2**, Entry **10**, Substrate



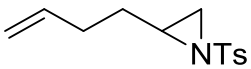
A screw-cap vial was charged with a stirring bar, Hoveyda-Grubbs catalyst 2nd generation (9.4 mg, 0.50 mol%) and 6.0 mL of anhydrous toluene. 2-(pent-4-en-1-yl)oxirane (compound **III**, 0.34 g, 3.0 mmol,1.0 eq.) and 4-*tert*-Butylstyrene (2.7 mL, 15 mmol, 5.0 eq.) were simultaneously added and the resulting solution was stirred at 95 °C for 5 h. The mixture was cooled down at room temperature and dichloromethane (6.0 mL) was added. The solvent was removed under vacuum and the crude purified on silica (hexanes → hexanes/MTBE 96:4) to afford the clean product (0.26 g; 36 % yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.33 – 7.27 (m, 4H), 6.38 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.17 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.96 – 2.92 (m, 1H), 2.76 (dd, *J* = 5.0, 3.9 Hz, 1H), 2.48 (dd, *J* = 5.0, 2.7 Hz, 1H), 2.29 – 2.25 (m, 2H), 1.72 – 1.53 (m, 4H), 1.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 150.08 , 135.03 , 130.20 , 129.55 , 125.76, 125.54, 52.37 , 47.27 , 34.64 , 32.85 , 32.07 , 31.45, 25.90 . **HR-MS (ESI+)** calc. for $C_{17}H_{24}O_1Na_1$ $[M+Na]^+$ 267.171934, found 267. 172150.

2-(5-methylhex-4-en-1-yl)oxirane, Table **2**, Entry **11**, Substrate



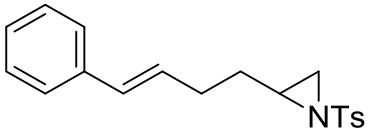
A solution of 2-(pent-4-en-1-yl)oxirane (compound **III**, 0.20 g, 1.8 mmol, 1.0 eq.) and Hoveyda-Grubbs 2nd generation catalyst (47 mg, 0.08 mmol, 4.2 mol%) in isoamylene (3.0 mL) was stirred at 25 ºC for 16 h. The volatile isoamylene was removed in vacuum to give the crude product as a black oil. Purification of the crude product by column chromatography (hexanes/MTBE 96:4) gave 2-(5-methylhex-4-en-1-yl)oxirane as a colorless oil (0.17 g, 67% yield). The spectra match with literature data [4,5].

2-(but-3-en-1-yl)-1-tosylaziridine, Table **2**, Entry **12**, Substrate



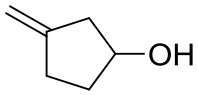
2-(but-3-en-1-yl)-1-tosylaziridine was synthesized according to literature[6].

2-(4-phenylbut-3-en-1-yl)-1-tosylaziridine, Table **2**, Entry **13**, Substrate



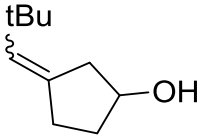
A screw-cap vial was charged with a stirring bar, Hoveyda-Grubbs catalyst 2nd generation (9.4 mg, 1.0 mol%) and 3.0 mL of anhydrous toluene. 2-(but-3-en-1-yl)-1-tosylaziridine (0.38 g, 1.5 mmol, 1.0 eq.) and styrene (0.69 mL, 6.0 mmol, 4.0 eq.) were simultaneusly added and the resulting solution was stirred at 95 °C for 5 h. The mixture was cooled down at room temperature and dichloromethane (3.0 mL) was added. The solvent was removed under vacuum and the crude purified on silica (pentane → pentane/MTBE 6:1) to afford the clean product (0.31 g ; 62 % yield; E-alkene). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.80 – 7.76 (m, 2H), 7.32 – 7.11 (m, 7H), 6.31 – 6.27 (m, 1H), 6.08 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.78 – 2.74 (m, 1H), 2.61 (d, *J* = 7.0 Hz, 1H), 2.40 (s, 3H), 2.20 – 2.10 (m, 2H), 2.06 (d, *J* = 4.6 Hz, 1H), 1.75 – 1.68 (m, 1H), 1.51 – 1.44 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 144.66 , 137.50 , 135.14 , 131.05 , 129.81 , 128.81 , 128.65 , 128.16 , 127.25 , 126.11 , 39.90 , 34.03 , 31.32 , 30.34 , 21.81 . **HR-MS (ESI+)** calc. for $C_{19}H_{21}N_1O_2S_1Na_1$ $[M+Na]^+$ 350.118520, found 350.118820.

3-methylenecyclopentan-1-ol, Table **2**, Entry **2**, Product



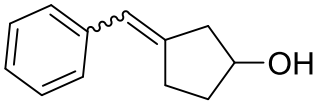
Was prepared from commercially available 1,2-Epoxy-5-hexene according to general procedure (B) in a 2.0 mmol scale. The clean product was obtained as colorless oil with 53 % isolated yield due to its high volatility (73 % ^{1}H-NMR yield). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 4.92 (p, *J* = 2.3 Hz, 2H), 4.36 (p, *J* = 4.4 Hz , 1H), 2.57 – 2.46 (m, 2H), 2.35 – 2.26 (m, 2H), 1.93 – 1.86 (m, 1H), 1.77 – 1.70 (m, 1H), 1.58 – 1.47 (br, 1H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 149.85 , 107.17 , 73.36 , 42.77 , 35.36 , 29.81. **HR-MS (ESI+)** calc. for $C_6H_{10}O_1Na_1$ $[M+Na]^+$ 121.062384, found 121.062440.

3-(2,2-dimethylpropylidene)cyclopentan-1-ol, Table **2**, Entry **4**, Product



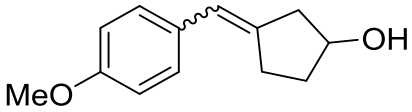
Was prepared from 2-(5,5-dimethylhex-3-en-1-yl)oxirane according to general procedure (B). The crude product was purified via flash column chromatography (DCM/MTBE; 97:3) and obtained as a 1:1 mixture of *E*:*Z* isomers (colorless oil, 69 % isolated yield). **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* = 5.33 - 5.30 (m, 2H), 4.40 – 4.35 (m, 1H), 4.27 – 4.23 (m, 1H), 2.67 – 2.61 (m, 1H), 2.58 – 2.45 (m, 3H), 2.44 – 2.32 (m, 2H), 2.30 – 2.23 (m, 2H), 1.90 – 1.83 (m, 1H), 1.80 – 1.72 (m, 2H), 1.63 – 1.56 (m, 1H), 1.43 (d, *J* = 4.3 Hz, 1H), 1.36 (d, *J* = 4.2 Hz, 1H), 1.07 (s, 9H), 1.06 (s, 9H). **^{13}C-NMR** (125 MHz, $CDCl_3$): *δ* = 136.51 , 136.26 , 133.29 , 133.08 , 74.35 , 72.07 , 45.29 , 38.93 , 35.93 , 34.30 , 33.30 , 33.09 , 32.57 , 30.75 , 30.70 , 26.10 . **HR-MS (ESI+)** calc. for $C_{10}H_{18}O_1Na_1$ $[M+Na]^+$ 177.124984, found 177.125020.

3-benzylidenecyclopentan-1-ol, Table **2**, Entry **5**, Product



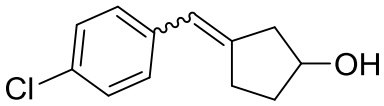
Was prepared from 2-(4-phenylbut-3-en-1-yl)oxirane according to general procedure (B). The product was obtained as a 1:1 mixture of *E:Z* isomers (colorless oil, 83 % isolated yield). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.34 – 7.30 (m, 6H), 7.29 – 7.27 (m, 2H), 7.20 – 7.16 (m, 2H), 6.42 – 6.39 (m, 2H), 4.47 (p, *J* = 4.2 Hz, 1H), 4.41 – 4.38 (m, 1H), 2.88 – 2.71 (m, 4H), 2.66 – 2.50 (m, 4H), 2.02 – 1.86(m, 3H), 1.79 – 1.73 (m, 1H), 1.53 (br, 2H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 143.44 , 143.25 , 138.50 , 138.45 , 128.35, 128.16 , 128.07 , 126.06 , 123.00 , 122.92 , 73.93 , 72.14 , 45.15 , 41.00 , 35.80 , 34.32 , 32.40 , 28.43 . **HR-MS (ESI+)** calc. for $C_{12}H_{14}O_1Na_1$ $[M+Na]^+$ 197.093684, found 197.093690.

3-(4-methoxybenzylidene)cyclopentan-1-ol, Table **2**, Entry **6**, Product



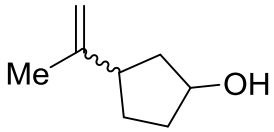
Was prepared from 2-(4-(4-methoxyphenyl)but-3-en-1-yl)oxirane according to general procedure (B) in a 0.25 mmol scale. The product was obtained as a 1:1 mixture of *E:Z* isomers (clear oil, 82 % isolated yield). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.26 – 7.20 (m, 4H), 6.88 – 6.84 (m, 4H), 6.35 – 6.32 (m, 2H), 4.46 (p, *J*=4.4 Hz, 1H), 4.39 – 4.36 (m, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.85 – 2.66 (m, 4H), 2.62 – 2.43 (m, 4H), 2.00 – 1.93 (m, 1H), 1.92 – 1.84 (m, 2H), 1.77 – 1.71 (m, 1H), 1.68 – 1.58 (br, 2H) **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 157.84 , 157.82 , 141.02 , 140.90 , 131.35 , 129.28 , 129.18 , 122.34 , 122.22 , 113.78 , 113.77 , 73.96 , 72.16 , 55.37 , 45.06 , 40.85 , 35.79 , 34.36 , 32.29 , 28.27. **HR-MS (ESI+)** calc. for $C_{13}H_{16}O_2Na_1$ $[M+Na]^+$ 227.104249, found 227.104360.

3-(4-chlorobenzylidene)cyclopentan-1-ol, Table **2**, Entry **7**, Product



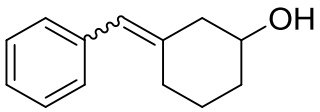
Was prepared from 2-(4-(4-chlorophenyl)but-3-en-1-yl)oxirane according to general procedure (B). The product was obtained as a 1:1 mixture of *E:Z* isomers (white solid, 83 % isolated yield). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.29-7.26 (m, 4H), 7.23 – 7.17 (m, 4H), 6.36 – 6.33 (m, 2H), 4.50 – 4.46 (m, 1H), 4.42 – 4.38 (m, 1H), 2.82-2.70 (m, 4H), 2.61 – 2.48 (m, 4H), 2.01 – 1.86 (m, 3H), 1.79 – 1.73 (m, 1H), 1.51 (br, 2H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 144.33 , 144.13 , 136.95 , 136.91 , 131.61 , 131.59 , 129.36 , 129.27 , 128.47 , 121.89 , 121.82 , 73.85 , 72.07 , 45.17 , 40.96 , 35.78 , 34.32 , 32.44 , 28.44 . **HR-MS (ESI+)** calc. for $C_{12}H_{13}O_1Cl_1Na_1$ $[M+Na]^+$ 231.054712, found 231.054900.

3-(prop-1-en-2-yl)cyclopentan-1-ol, Table **2**, Entry **8**, Product



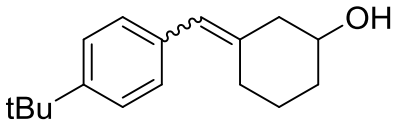
Was prepared from 2-(4-methylpent-3-en-1-yl)oxirane according to general procedure (B). The crude product was purified via flash column chromatography (DCM/MTBE; 97:3) and obtained as a 1:1 mixture of diastereoisomers (clear oil, 55 % isolated yield). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 4.75 – 4.68 (m, 4H), 4.42 – 4.39 (m, 1H), 4.36 – 4.32 (m, 1H), 2.82 – 2.75 (m, 1H), 2.50 – 2.43 (m, 1H), 2.22 – 2.15 (m, 1H), 2.08 – 1.93 (m, 2H), 1.90 – 1.77 (m, 2H), 1.74 (s, 3H), 1.73 (s, 3H), 1.69 – 1.56 (m, 5H), 1.48 – 1.38 (m, 4H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 148.41 , 108.77 , 108.48 , 73.72 , 73.67 , 45.63 , 44.37 , 41.12 , 40.85 , 35.64 , 35.47 , 29.31 , 28.96 , 21.33 , 21.02 . **HR-MS (ESI+)** calc. for $C_8H_{14}O_1Na_1$ $[M+Na]^+$ 149.093684, found 149.093800.

3-benzylidenecyclohexan-1-ol, Table **2**, Entry **9**, Product



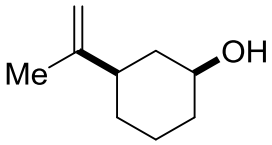
Was prepared from 2-(5-phenylpent-4-en-1-yl)oxirane according to general procedure (B) in a 0.21 mmol scale. The product was obtained as a 1:1 mixture of *E:Z* isomers (clear oil, 78 % isolated yield). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.33 – 7.30 (m, 4H), 7.22 – 7.19 (m, 6H), 6.39 (s, 1H), 6.32 (s, 1H), 3.87 – 3.82 (m, 1H), 3.76 – 3.71 (m, 1H), 2.90 (dd, *J* = 13.0, 4.0, 1H), 2.62 (dd, *J* = 12.8, 4.0 Hz, 1H), 2.55 – 2.51 (m, 1H), 2.29 – 2.11 (m, 5H), 1.99 – 1.92 (m, 2H), 1.90 – 1.84 (m, 1H), 1.81 – 1.74 (m, 1H), 1.67 (br, 2H), 1.59 – 1.36 (m, 4H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 139.36 , 139.18 , 137.97 , 137.79 , 129.00 , 128.98 , 128.26 , 128.21 , 126.32 , 126.30 , 125.15 , 125.10 , 70.54 , 70.35 , 46.18 , 38.33 , 36.41 , 35.01 , 34.85 , 28.50 , 24.18 , 23.65 . **HR-MS (ESI+)** calc. for $C_{13}H_{16}O_1Na_1$ $[M+Na]^+$ 211.109334, found 211. 109420.

3-(4-(*tert*-butyl)benzylidene)cyclohexan-1-ol, Table **2**, Entry **10**, Product



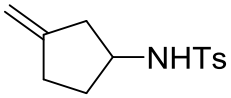
Was prepared from 2-(5-(4-(*tert*-butyl)phenyl)pent-4-en-1-yl)oxirane according to general procedure (B). The product was obtained as a 1:1 mixture of *E:Z* isomers (clear oil, 66 % isolated yield). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.35 – 7.32 (m, 4H), 7.17 – 7.13 (m, 4H), 6.35 (s, 1H), 6.28 (s, 1H), 3.86 – 3.81 (m, 1H), 3.76 – 3.71 (m, 1H), 2.93 (dd, *J* = 13.0, 4.3 Hz, 1H), 2.61 (dd, *J* = 12.8, 4.5 Hz, 1H), 2.57 – 2.53 (m, 1H), 2.28 – 2.13 (m, 5H), 1.99 – 1.91 (m, 2H), 1.88 – 1.82 (m, 1H), 1.80 - 1.73 (m, 1H), 1.58 – 1.37 (m, 6H), 1.32 (s, 18H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 149.19 , 138.78 , 138.63 , 135.06 , 134.89 , 128.70 , 128.68 , 125.18 , 125.14 , 124.99 , 124.95 , 70.55 , 70.41 , 46.25 , 38.42 , 36.42 , 35.05 , 34.86 , 34.62 , 31.49 , 28.56 , 24.22 , 23.67. **HR-MS (ESI+)** calc. for $C_{17}H_{24}O_1Na_1$ $[M+Na]^+$ 267.171934, found 267. 172040.

***cis*-3-(prop-1-en-2-yl)cyclohexan-1-ol,** Table **2**, Entry **11**, Product



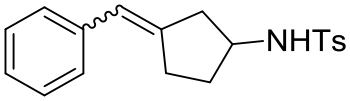
Was prepared from 2-(5-methylhex-4-en-1-yl)oxirane according to general procedure (B). The product was obtained as a clear oil (55 % isolated yield).**^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 4.69 (p, *J* = 1.1 Hz, 2H), 3.65 – 3.59 (m, 1H), 2.05 – 1.92 (m, 3H), 1.85 – 1.79 (m, 1H), 1.72 (t, *J* = 1.2 Hz, 3H), 1.70 – 1.67 (m, 1H), 1.48 (br, 1H), 1.36 – 1.27 (m, 1H), 1.19 – 1.12 (m, 2H), 1.11 – 1.02 (m, 1H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 149.62 , 108.78 , 71.14 , 43.92 , 41.10 , 35.69 , 30.84 , 24.34 , 20.99. **HR-MS (ESI+)** calc. for $C_9H_{16}O_1Na_1$ $[M+Na]^+$ 163.109334, found 163.109360.

4-methyl-*N*-(3-methylenecyclopentyl)benzenesulfonamide, Table **2**, Entry **12**, Product



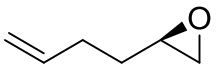
Was prepared from 2-(but-3-en-1-yl)-1-tosylaziridine according to general procedure (B) (83 % isolated yield). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.77 – 7.75 (m, 2H), 7.32 – 7.30 (m, 2H), 4.85 – 4.83 (m, 2H), 4.54 (d, *J* = 7.3 Hz, 1H), 3.66 (h, *J* = 6.8 Hz, 1H), 2.51 – 2.46 (m, 1H), 2.43 (s, 3H), 2.37 – 2.30 (m, 1H), 2.25 – 2.17 (m, 1H), 2.10 – 2.04 (m, 1H), 1.92 – 1.85 (m, 1H), 1.57 – 1.51 (m, 1H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 147.98 , 143.53 , 137.86 , 129.85 , 127.22 , 107.73 , 54.61 , 40.63 , 33.45 , 29.94 , 21.69. **HR-MS (ESI+)** calc. for $C_{13}H_{18}N_1O_2S_1$ $[M+H]^+$ 252.105276, found 252.105320.

***N*-(3-benzylidenecyclopentyl)-4-methylbenzenesulfonamide,** Table **2**, Entry **13**, Product



Was prepared from 2-(4-phenylbut-3-en-1-yl)-1-tosylaziridine according to general procedure (B) in a 0.28 mmol scale. The product was obtained as a 1:1 mixture of *E:Z* isomers (viscous oil, 74 % isolated yield). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 15.7, 8.4 Hz, 4H), 7.32 – 7.12 (m, 14H), 6.31 (p, *J* = 2.4 Hz, 1H), 6.28 (p, *J* = 2.5 Hz, 1H), 4.61 (t, *J* = 7.0 Hz, 2H) 3.79 – 3.67 (m, 2H), 2.78 (dd, *J* = 17.2, 7.1 Hz, 1H), 2.71 – 2.49 (m, 4H), 2.44 (s, 3H), 2.42 (s, 3H), 2.40 – 2.26 (m, 3H), 2.03 – 1.89 (m, 2H), 1.73 – 1.66 (m, 1H), 1.60 – 1.53 (m, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 143.54 , 141.40 , 141.21 , 138.00 , 137.97 , 137.92 , 129.87 , 129.83 , 128.41 , 128.36 , 128.17 , 128.06 , 127.26 , 126.35 , 126.31 , 123.47 , 123.44 , 55.30 , 53.68 , 43.06 , 38.81 , 33.81 , 32.52 , 32.44 , 28.50 , 21.66. **HR-MS (ESI-)** calc. for $C_{19}H_{20}N_1O_2S_1$ $[M-H]^-$ 326.122026, found 326. 122360.

(*R*)-1,2-Epoxy-5-hexene, Table **2**, Entry **16**, Substrate



(*R*)-1,2-Epoxy-5-hexene was prepared by the Jacobsen hydrolytic kinetic resolution of the commercially available (±)-1,2-Epoxy-5-hexene, according to literature[7].

enantiomeric excess**:** 96.40 % *ee*

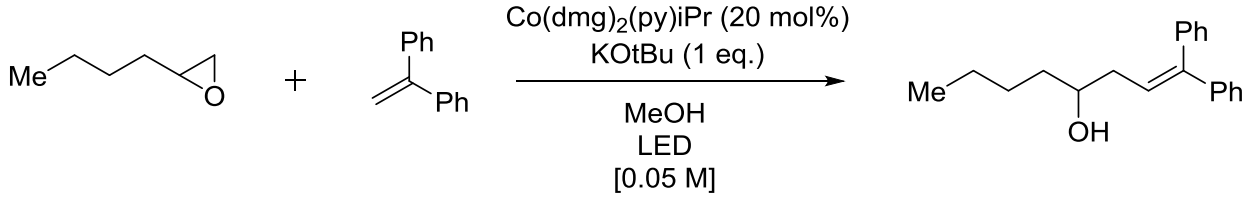
Retention of *ee*: Synthesis of (*R*)-3-methylenecyclopentan-1-ol, Table **2,** Entry **16,** Product

The reaction to test the retention of *ee* was performed following general procedure **B** using (*R*)-1,2-Epoxy-5-hexene as starting material. The isolated product was submitted to chiral GC analysis.

Enantiomeric excess: 97.36 % *ee*

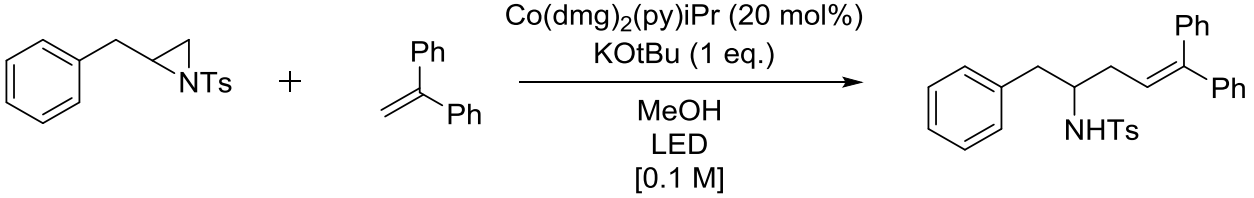
Specific rotation: $[\alpha]_D^{25}$ = -42.667

Intermolecular reactivity: Synthesis of 1,1-diphenyloct-1-en-4-ol, Table **2,** Entry **14,** Product



A screw-cap vial charged with Co(dmg)$_2$(py)*i*Pr (33 mg, 0.08 mmol, 0.20 eq.), KO*t*Bu (45 mg, 0.40 mmol, 1.0 eq.) and a stirring bar, was purged with Ar for 10 mins. Degassed MeOH (8.0 mL, 0.05 M solution) was then added and commercially available 1,2-Epoxyhexane (48 µL, 0.40 mmol, 1.0 eq.) and 1,1-Diphenylethylene (0.35 mL, 2.0 mmol, 5.0 eq.) were added. The reaction mixture was stirred in front of the LED reactor (approx. 4 cm, internal reached temperature 34 °C). After 24 h the LED reactor was switched off and the solution was diluted with additional 6.4 mL of distilled water and 8.0 mL of $CHCl_3$. The aqueous phase was then extracted with $CHCl_3$ (3 x 8.0 mL) and the combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified via flash column chromatography (DCM as eluent) to afford the desired product in 40 % isolated yield. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.34 – 7.31 (m, 2H), 7.28 – 7.13 (m, 8H), 6.13 (t, *J* = 7.5 Hz, 1H), 3.70 – 3.66 (m, 1H), 2.31 – 2.20 (m, 2H), 1.45 – 1.19 (m, 7H), 0.83 (t, *J* = 6.9 Hz, 3H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 144.16 , 142.63 , 140.03 , 130.04 , 128.37 , 128.24 , 127.35 , 127.20 , 127.16 , 125.60 , 72.12 , 37.84 , 36.87 , 27.93 , 22.83 , 14.20. **HR-MS (ESI+)** calc. for $C_{20}H_{24}O_1Na_1$ $[M+Na]^+$ 303.171934, found 303.172010.

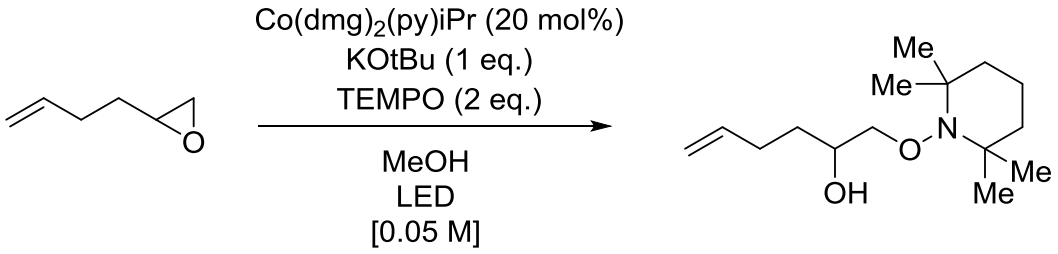
Intermolecular reactivity: Synthesis of 4-methyl-*N*-(1,5,5-triphenylpent-4-en-2-yl) benzenesulfonamide, Table **2,** Entry **15,** Product



A screw-cap vial charged with Co(dmg)$_2$(py)*i*Pr (25 mg, 0.06 mmol, 0.20 eq.), KO*t*Bu (34 mg, 0.30 mmol, 1.0 eq.) and a stirring bar, was degassed with Ar for 10 mins. Degassed MeOH (3.0 mL, 0.1 M solution) was then added and the solution was kept under argon flow for additional 5 mins. Commercially available (*S*)-(+)-2-Benzyl-1-(*p*-tolylsulfonyl)aziridine (86 mg, 0.30 mmol, 1.0 eq.) and 1,1-diphenylethylene (0.27 mL, 1.5 mmol, 5.0 eq.) were injected and the reaction mixture was stirred in front of the LED reactor

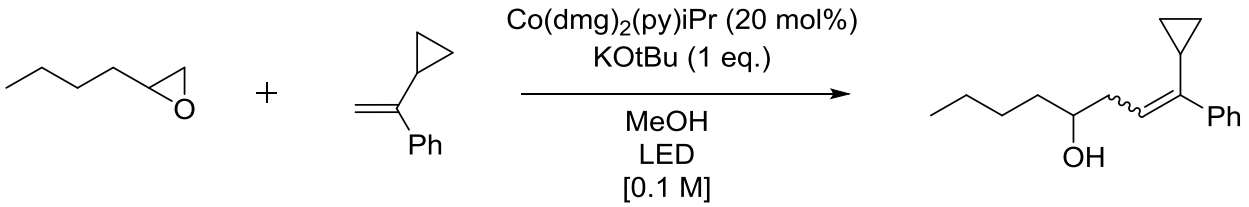
(approx. 4 cm, internal reached temperature 34 °C). After 24 h the LED reactor was switched off and the solution was diluted with additional 2.4 mL of distilled water and 3.0 mL of $CHCl_3$. The aqueous phase was then extracted with $CHCl_3$ (3 x 3.0 mL) and the combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified via flash column chromatography (DCM as eluent) to afford the desired product in 48 % isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.59 – 7.57 (m, 2H), 7.36 – 7.29 (m, 3H), 7.26 – 7.22 (m, 3H), 7.19 – 7.16 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.05 (m, 4H), 6.98 – 6.95 (m, 2H), 5.88 (t, *J* = 7.4 Hz, 1H), 4.43 (d, *J* = 7.4 Hz, 1H), 3.53 – 3.46 (m, 1H), 2.77 (dd, *J* = 13.7, 5.8 Hz, 1H), 2.70 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.36 (s, 3H), 2.34 – 2.28 (m, 1H), 2.24 – 2.16 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 144.67 , 143.21 , 142.12 , 139.58 , 137.48 , 137.09 , 129.81 , 129.70 , 129.50 , 128.63 , 128.49 , 128.19 , 127.34 , 127.32 , 127.07 , 126.70 , 124.33 , 55.50 , 41.56 , 34.31 , 21.66 . **HR-MS (ESI-)** calc. for $C_{30}H_{28}N_1O_2S_1$ $[M-H]^-$ 466.184626, found 466.184800.

Mechanistic experiment: TEMPO as radical trap, compound **19**, Scheme **4**



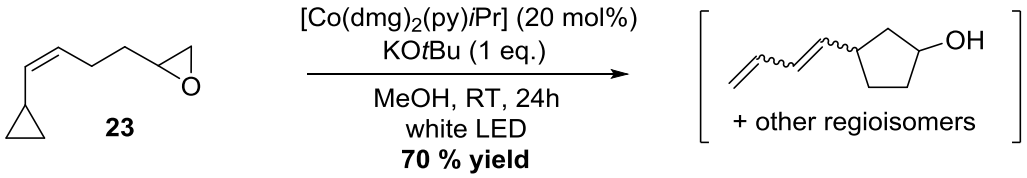
A screw-cap vial charged with $Co(dmg)_2(py)$*i*Pr (0.17 g, 0.40 mmol, 1.0 eq.), KO*t*Bu (45 mg, 0.4 mmol, 1.0 eq.) and a stir bar, was degassed with Ar for 10 mins. Degassed MeOH (8 mL, 0.05 M solution) was then added. After degassing the solution with Ar for additional 5 mins, commercially available 1,2-Epoxy-5-hexene (47 µL, 0.40 mmol, 1.0 eq.) was injected and the reaction mixture was stirred in front of the LED reactor (approx. 4 cm, internal reached temperature 34 °C). A solution of TEMPO in degassed MeOH (0.13 g, 0.80 mmol, 2.0 eq.; 0.30 mL MeOH) was prepared and added after 3 h to the reaction mixture. After additional 20 h the LED reactor was switched off and the solution was filtered in a plug of silica, eluted with additional MTBE and concentrated *in vacuo*. The crude product was purified via flash column chromatography (DCM as eluent) to afford the desired product in 34 % isolated yield. The moderate yield is due to competing formation of ketone as a sideproduct as well as some amount of cyclized product (Table 2, entry 2, product) . **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* = 5.87 – 5.79 (m, 1H), 5.06 – 4.96 (m, 2H), 3.86 – 3.81 (m, 1H), 3.77 (dd, *J* = 9.1, 3.1 Hz, 1H), 3.71 (dd, *J* = 9.1, 7.9 Hz, 1H), 2.27 (d, *J* = 3.1 Hz, 1H), 2.25 – 2.10 (m, 2H), 1.61 – 1.48 (m, 3H), 1.47 – 1.42 (m, 4H), 1.36 – 1.29 (m, 1H)1.19 (s, 3H), 1.16 (s, 3H), 1.10 (s, 6H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 138.48 , 114.94 , 80.69 , 69.98 , 60.10 , 39.86 , 39.79 , 33.25 , 33.20 , 32.61 , 29.93 , 20.33 , 20.22 , 17.17. **HR-MS (ESI+)** calc. for $C_{15}H_{30}N_1O_2$ $[M+H]^+$ 256.227104, found 256.227010.

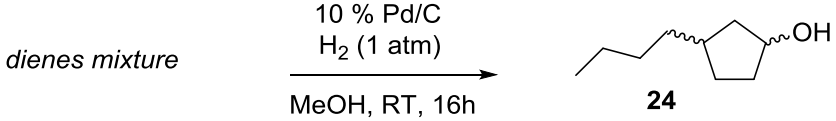
Mechanistic experiment: (1-cyclopropylvinyl)benzene as radical clock, compound **22**, Scheme **4**



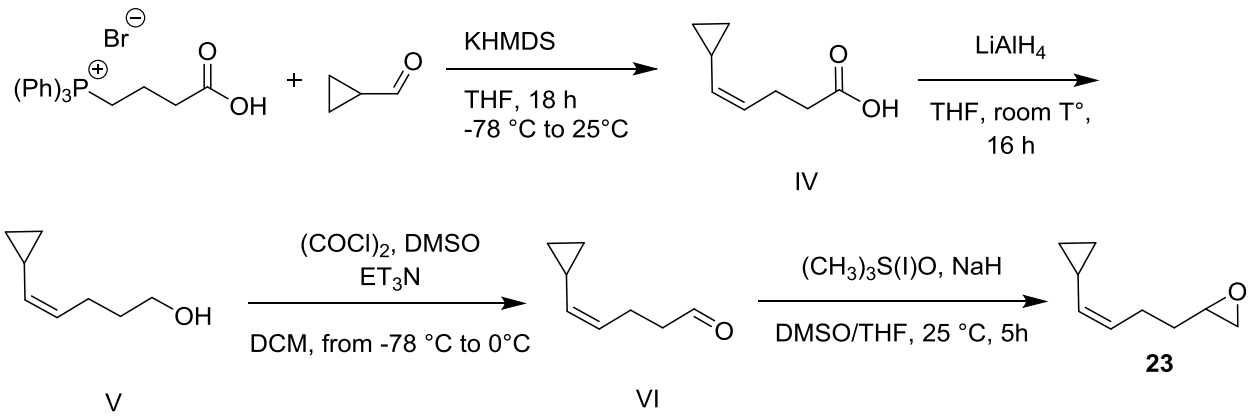
A screw-cap vial charged with $Co(dmg)_2(py)$*i*Pr (21 mg, 0.05 mmol, 0.20 eq.), KO*t*Bu (28 mg, 0.25 mmol, 1.0 eq.) and a stirring bar, was degassed with Ar for 10 mins. Degassed MeOH (5.0 mL, 0.05 M solution) was then added. After purging the solution with Ar for additional 5 mins, commercially available 1,2-Epoxyhexane (30 µL, 0.25 mmol, 1.0 eq.) and (1-cyclopropylvinyl)benzene (0.14 g, 1.0 mmol, 4.0 eq.) were injected and the reaction mixture was stirred in front of the LED reactor (approx. 4 cm, internal reached temperature 34 °C). After 24 h the LED reactor was switched off and the solution was diluted with additional 4.0 mL of distilled water and 5.0 mL of $CHCl_3$. The aqueous phase was then extracted with $CHCl_3$ (3 x 5.0 mL) and the combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified via flash column chromatography (DCM as eluent) to afford the desired product as a 1:1 mixture of *E:Z* isomers (38 % isolated yield). The moderate yield is due to the competing intramolecular formation of ketone as a sideproduct. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.34 – 7.19 (m, 8H), 7.13 – 7.11 (m, 2H), 5.73 (td, *J* = 7.4, 1.7 Hz, 1H), 5.51 (t, *J* = 7.9 Hz, 1H), 3.78 – 3.73 (m, 1H), 3.59 – 3.54 (m, 1H), 2.57 – 2.54 (m, 2H), 2.11 – 2.06 (m, 1H), 2.04 – 1.98 (m, 1H), 1.81 – 1.73 (m, 1H), 1.64 – 1.17 (m, 15H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.83 – 0.79 (m, 2H), 0.65 – 0.62 (m, 2H), 0.43 – 0.40 (m, 2H), 0.33 – 0.30 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 145.15 , 143.75 , 142.29 , 139.90 , 128.99 , 128.09 , 127.86 , 127.56 , 127.08 , 126.80 , 126.60 , 121.18 , 72.05 , 71.99 , 36.98 , 36.94 , 36.71 , 36.67 , 28.12 , 27.93 , 22.91 , 22.82 , 18.80 , 14.26 , 14.19 , 11.82 , 6.83 , 6.74 , 5.36 , 5.34 . **HR-MS (ESI+)** calc. for $C_{17}H_{24}O_1Na_1$ $[M+Na]^+$ 267.171934, found 267.172070.

Mechanistic experiment: 2-(4-cyclopropylbut-3-en-1-yl)oxirane as radical clock, compound **24,** Scheme **4**





Synthesis of 2-(4-cyclopropylbut-3-en-1-yl)oxirane, compound **23**, Scheme **4:**



Compound IV:

(3-carboxypropyl)triphenylphosphonium bromide (11 mmol, 1.1 eq.) was suspended in THF (60 mL) at -20 °C. KHMDS (22 mmol, 2.2 eq) was added dropwise into the suspension and further stirred for 20 min. The reaction mixture was then cooled to -78 °C and the corresponding aldehyde (10 mmol, 1.0 eq.) was added. After 18 h, the solvent was removed in vacuo. H_2O (300 mL) was added to the residue and extracted with diethyl ether (3 x 100 mL). The diethyl ether layers were discarded while the H_2O layer was acidified to pH 2 using HCl (1 M). The acidified aqueous layer was further extracted with ethyl acetate (3 x 100 mL). The organic layers were combined, dried over sodium sulfate, filtered and concentrated to dryness. Compound IV was obtained (78:22 *cis/trans* mixture) and used in the next step without further purification.

Compound V:

To a stirred suspension of $LiAlH_4$ (13 mmol, 1.0 eq.) in anhydrous THF (22 mL) was added dropwise a solution of enoic acid (13 mmol, 1.0 eq.) in THF (2.2 mL). After 16 h at room temperature, the reaction mixture was cooled to 0 °C and slowly treated with water (0.4 mL), then with a 15% aqueous solution of NaOH (0.4 mL), and with water (1.2 mL). The reaction mixture was additionally stirred for 1 h. The resulting suspension was filtered through Celite, then the insoluble salts were washed with diethyl ether (2 x 4.0 mL) and the filtrate was dried over $MgSO_4$. Filtration and concentration gave the compound V (80 % yield, 78:22 *cis/trans* mixture), which was directly used in the next step without further purification.

Compound VI:

To a solution of oxalylchloride (1.3 ml, 15 mmol, 1.5 eq.) in DCM (25 mL) was added DMSO (2.1 mL, 30 mmol, 3.0 eq.) dropwise within 5 minutes at -78°C. The mixture was stirred at -78°C for 10 min and a solution of compound V (1.3 g, 10 mmol, 1.0 eq.) in DCM (3.7 mL) was added dropwise within 10 min. After stirring for 1 h at -78°C TEA (4.2 mL, 30 mmol, 3.0 eq.) was added within 10 minutes and the reaction mixture was allowed to reach 0°C. Water (30 mL) and DCM (30 mL) were then added and the phases were separated. The aqueous solution was extracted with DCM (2 x 30 mL) and the combined

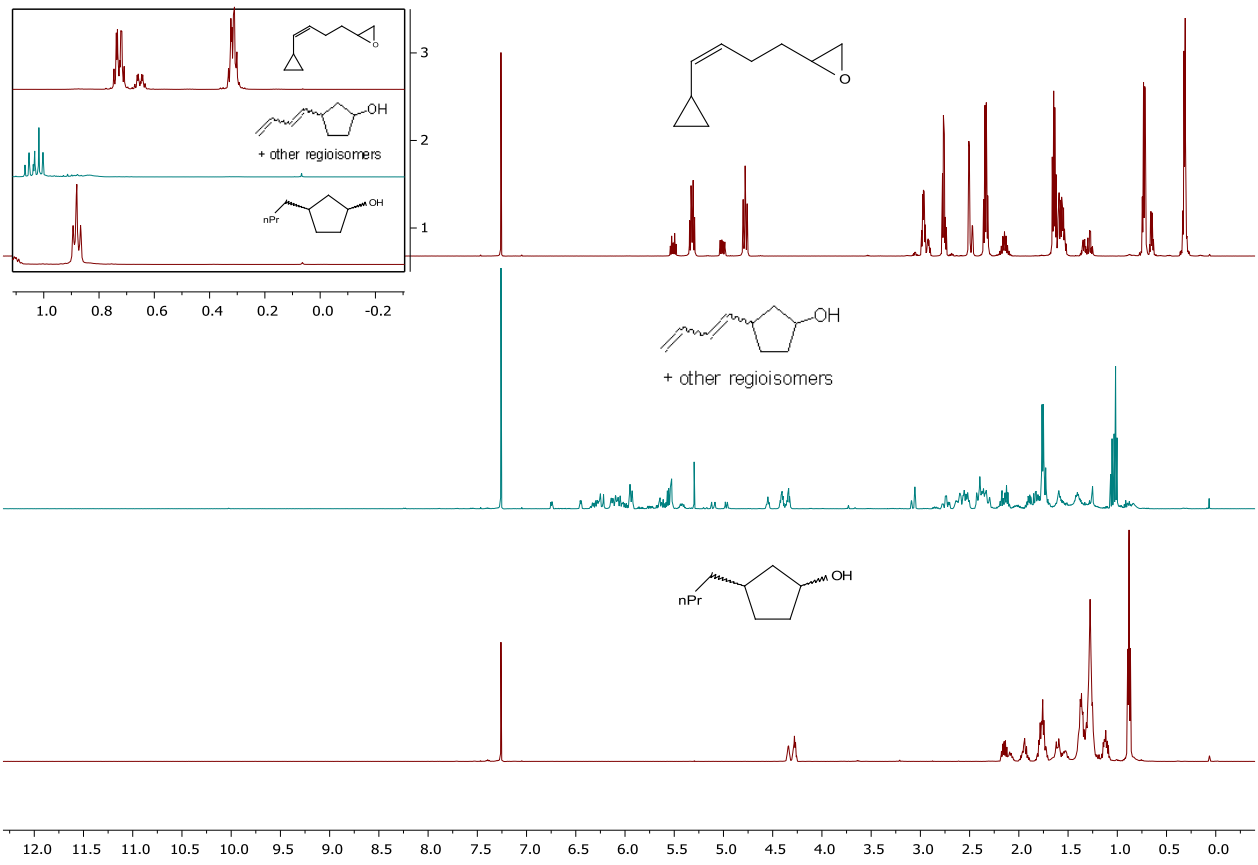
organic extracts were dried over $MgSO_4$, filtered and the solvent was evaporated in vacuo. The crude product was purified by FC (pentane/MTBE 9:1) to give compound VI (85 % yield, 78:22 *cis/trans* mixture) as a clear oil.

2-(4-cyclopropylbut-3-en-1-yl)oxirane, compound **23**:

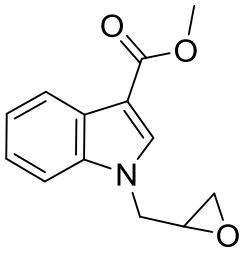
60 % NaH in oil (0.51 g, 13 mmol) was added to a solution of trimethylsulfoxonium iodide (2.8 g, 13 mmol) in dry DMSO (10 mL). After 1 h, aldehyde, compound VI (1.1 g, 8.5 mmol), dissolved in anhydrous THF (10 mL) was added at 25°C. The reaction was stirred overnight, then ice was added, and the reaction mixture was extracted with ethyl acetate (2x40 mL). The organic layer was washed with water (2x20 mL) and then with brine solution (20 mL). Extract was dried over sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (pentane/MTBE 97:3) to get 2-(4-cyclopropylbut-3-en-1-yl)oxirane, compound **23** (34 % yield, 78:22 *cis/trans* mixture), as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$); **[**minor *trans* isomer**]** δ [5.51; dt, *J* = 15.2, 6.9 Hz, 0.22H] 5.32 (dt, *J* = 10.7, 7.3 Hz, 0.78H), [5.01; ddt, *J* = 15.2, 8.5, 1.5 Hz, 0.22H] 4.78 (ddt, *J* = 11.2, 9.8, 1.5 Hz, 0.78H), 2.99 – 2.95 (m, 0.78H) [2.94 – 2.90; m, 0.22H], 2.77 – 2.74 (m, 1H), 2.51 (dd, *J* = 5.0, 2.7 Hz, 0.78H) [2.47; dd, *J* = 5.0, 2.7 Hz, 0.22H], 2.36 – 2.31 (m, 1.56H) [2.20 – 2.08; m, 0.44H], 1.66 – 1.52 (m, 3H), 0.75 – 0.71 (m, 1.56H) [0.67 – 0.64; m, 0.44H], 0.33 – 0.29 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) **[**minor *trans* isomer**]** δ 135.03 [134.87], [126.77] 126.69, 52.16 [52.08], 47.35 [47.34], 32.82 [32.73], 29.07, 24.25, 13.62, 9.72, 7.00, 6.52. **HR-MS (ESI+)** calc. for $C_9H_{14}O_1$ $[M]^+$ 138.104429, found 138.104465.

Mechanistic experiment: compound **24**, Scheme **4**

The mechanistic experiment was performed following general procedure **B** using 2-(4-cyclopropylbut-3-en-1-yl)oxirane, compound **23** (prepared following the procedure previously described), as starting material in a 0.5 mmol scale. The product showed complete cyclopropyl opening and was obtained as a complex mixture of different dienes isomers (oil, 70 % isolated yield). The NMR spectrum of this mixture is reported, showing complete opening of cyclopropyl (in the zoomed area is pointed up the loss of the cyclopropyl signals in ^{1}H-NMR between 0.2 -0.8 ppm). To facilitate understanding, the dienes mixture was treated with 20 mg of Pd/C in presence of H_2 (1 atm) for 16 h at 20 °C. Complete hydrogenation of the mixture occurred after this time, giving 3-butylcyclopentan-1-ol (compound **24**) as an inseparable 62:38 mixture of two diastereoisomers. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.36 – 4.32 (m, 1H; minor isomer), 4.30 – 4.26 (m, 1H; major isomer), 2.18 – 2.06 (m, 2H), 2.00 – 1.71 (m, 6H), 1.63 – 1.49 (m, 2H), 1.39 – 1.24 (m, 16H), 1.16 – 1.08 (m, 2H), 0.88 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 74.02 (minor isomer), 73.99, 42.86, 42.68, 38.63, 37.53, 36.66, 36.05, 35.63, 35.39, 30.97, 30.67, 30.43, 23.04 (minor isomer), 23.01, 14.28. **HR-MS (ESI+)** calc. for $C_9H_{18}O_1$ $[M]^+$ 142.135618, found 142.135765.

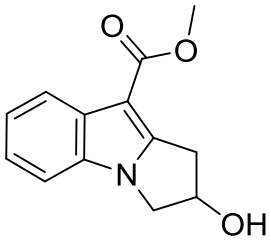


methyl 1-(oxiran-2-ylmethyl)-1H-indole-3-carboxylate, compound **17**, Scheme **3**



Powdered KOH (0.623 g, 11.1 mmol) was added to a solution of Methyl indole-3-carboxylate (1.62 g, 9.24 mmol) in DMF (9.0 mL) at ambient temperature and stirred for 30 min until dissolved. Epichlorohydrin (1.79 mL, 22.8 mmol) was added via syringe and the reaction was stirred at room temperature overnight. Upon completion, the solution was partitioned between EtOAc and H_2O. The aqueous layer was washed 3xEtOAc, and the combined organics were washed with saturated aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude was purified on silica (DCM/MTBE, 97:3) to give the pure compound (1.07 g ; 50 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22 – 8.17 (m, 1H), 7.86 (s, 1H), 7.45 – 7.38 (m, 1H), 7.34 – 7.28 (m, 2H), 4.48 (dd, *J* = 15.2, 3.0 Hz, 1H), 4.19 (dd, *J* = 15.2, 5.5 Hz, 1H), 3.91 (s, 3H), 3.34 – 3.29 (m, 1H), 2.84 (dd, *J* = 4.7, 3.9 Hz, 1H), 2.49 (dd, *J* = 4.7, 2.5 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.42, 137.01, 134.69, 126.78, 123.24, 122.27, 122.00, 109.99, 108.08, 51.15, 50.50, 48.53, 45.33. **HR-MS (ESI+)** calc. for $C_{13}H_{13}N_1O_3Na_1$ $[M+Na]^+$ 254.078763, found 254.078920. The spectra match with literature data[8].

methyl 2-hydroxy-2,3-dihydro-1H-pyrrolo[1,2-a]indole-9-carboxylate, compound **18**, Scheme **3**



A screw-cap vial charged with $Co(dmg)_2(py)$*i*Pr (16.5 mg, 0.04 mmol), KO*t*Bu (5.61 mg, 0.05 mmol) and a stirring bar, was purged with Ar for 10 mins. Degassed MeOH (10.0 mL) was then added to afford a final 0.02 M solution (based on the amount of epoxide). After purging the solution with Ar for additional 5 mins, methyl 1-(oxiran-2-ylmethyl)-1H-indole-3-carboxylate (46.2 mg, 0.20 mmol) was added and the reaction mixture was stirred in front of the LED reactor (approx. 4 cm, internal reached temperature 34 °C). After 36 h the LED reactor was switched off and the solution was diluted with additional 10.0 mL of distilled water and 10.0 mL of EtOAc. The aqueous phase was then extracted with EtOAc (4 x 10.0 mL) and the combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude was purified via flash column chromatography (EtOAc/hexane, 1:1) to afford the desired product (26.0 mg, 56 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 1H), 7.25 – 7.21 (m, 3H), 5.14 (tt, *J* = 5.5, 2.5 Hz, 1H), 4.29 (dd, *J* = 11.4, 5.6 Hz, 1H), 4.08 (dd, *J* = 11.4, 2.5 Hz, 1H), 3.86 (s, 3H), 3.55 (dd, *J* = 18.2, 6.3 Hz, 1H), 3.30 (dd, *J* = 18.2, 2.6 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.95, 149.96, 133.03, 130.64, 122.21, 121.93, 121.66, 109.97, 100.35, 74.10, 53.64, 50.93, 37.19. **HR-MS (ESI+)** calc. for $C_{13}H_{13}N_1O_3Na_1$ $[M+Na]^+$ 254.078763, found 254.078860.

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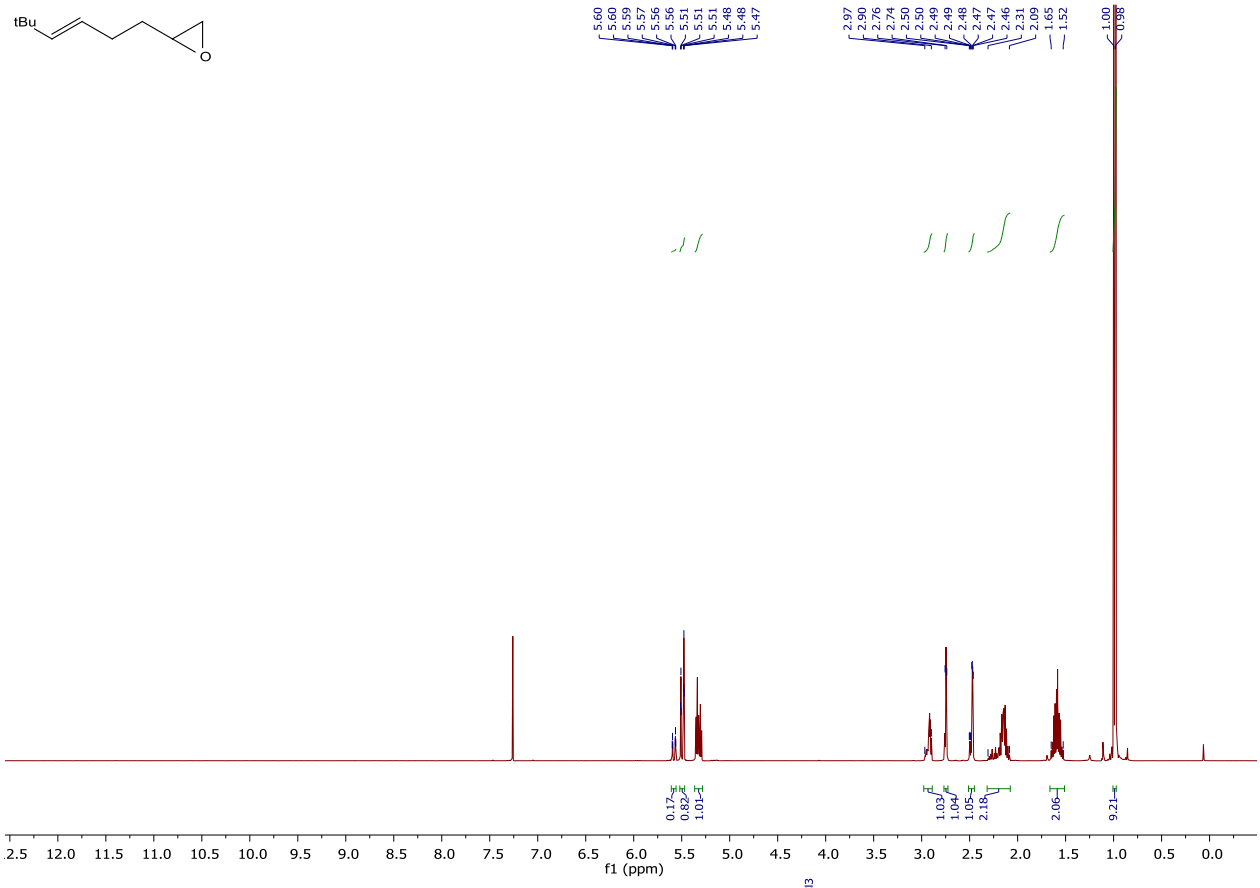
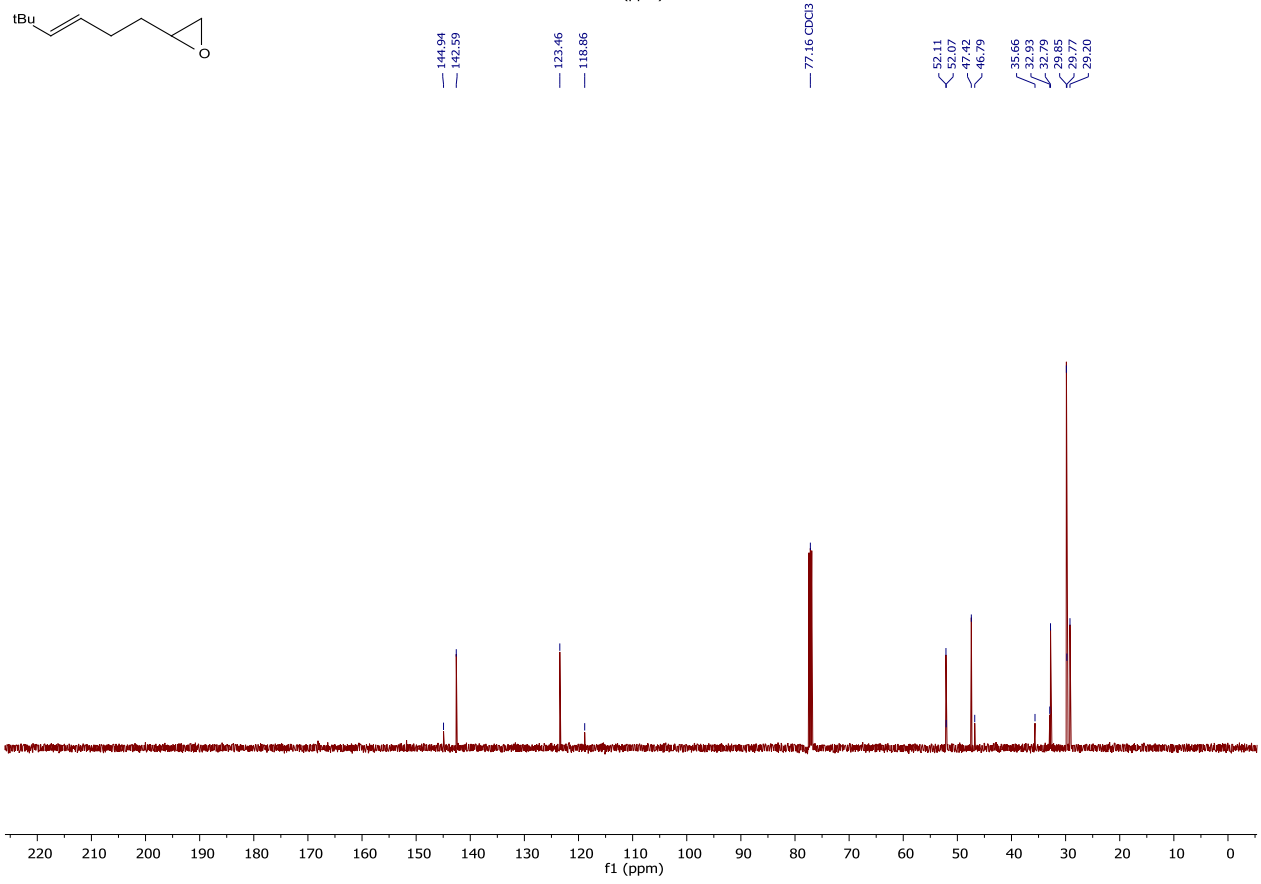
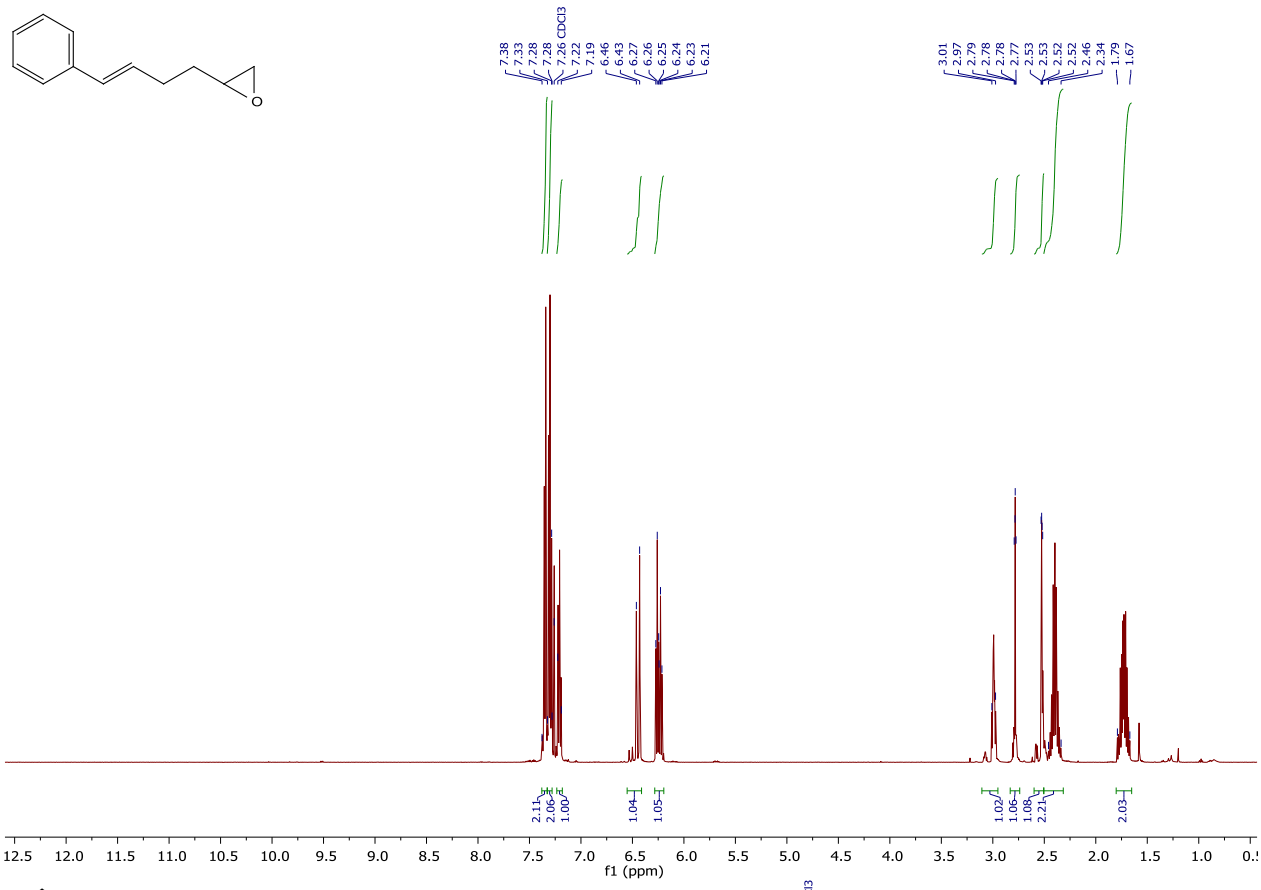
Characterization



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7.33
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7.28
7.26 CDCl3
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7.19
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6.26
6.25
6.24
6.23
6.21
3.01
2.97
2.79
2.78
2.78
2.77
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2.53
2.52
2.52
2.46
2.34
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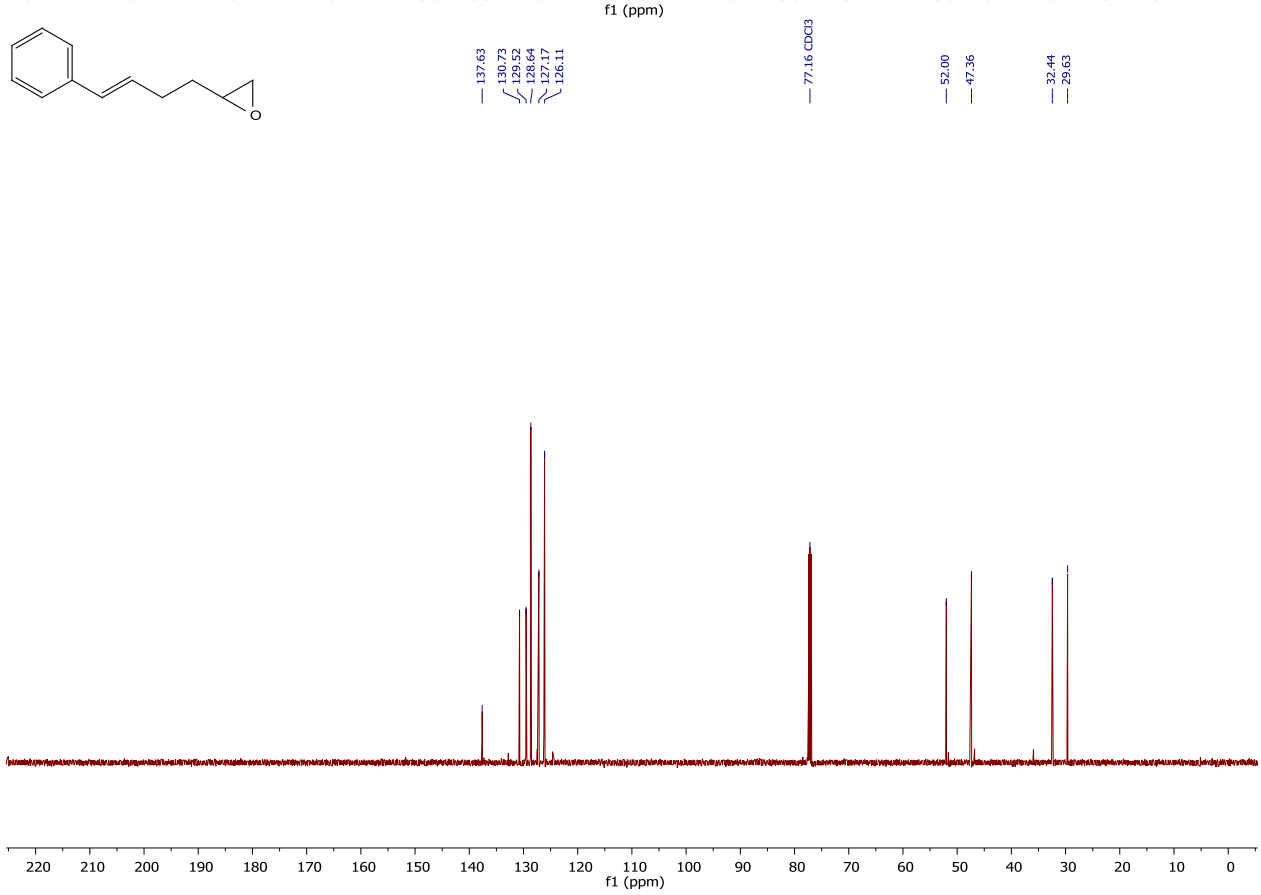
f1 (ppm)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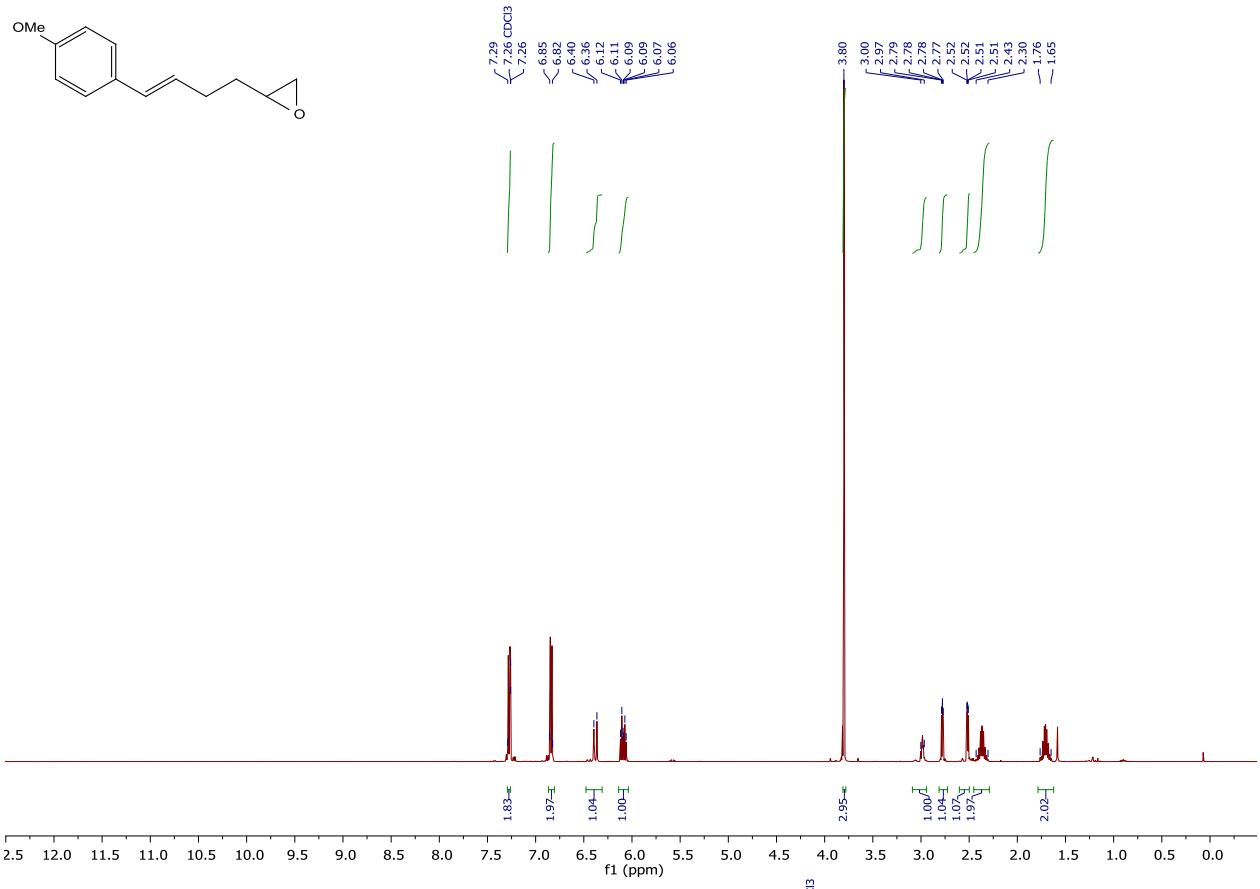
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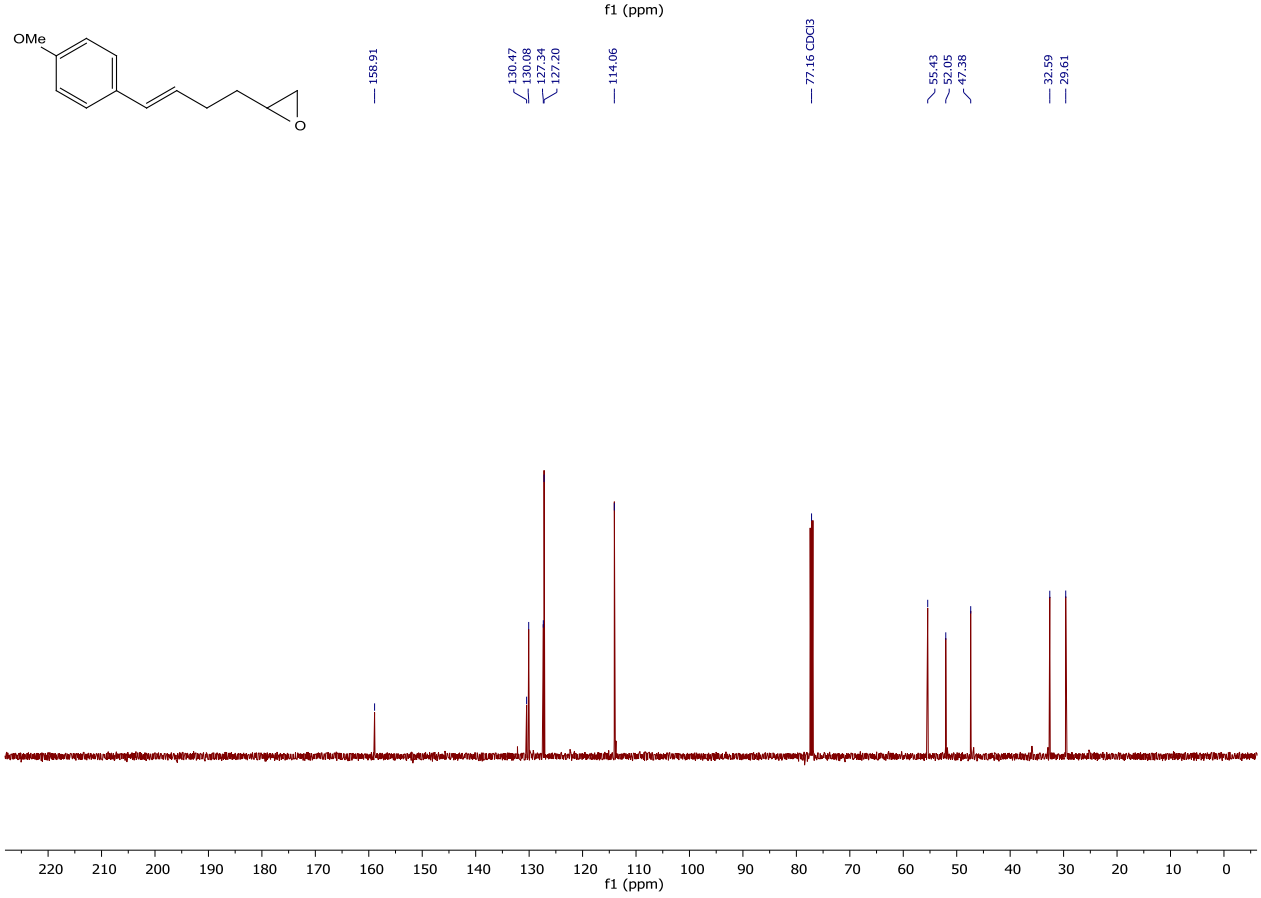
f1 (ppm)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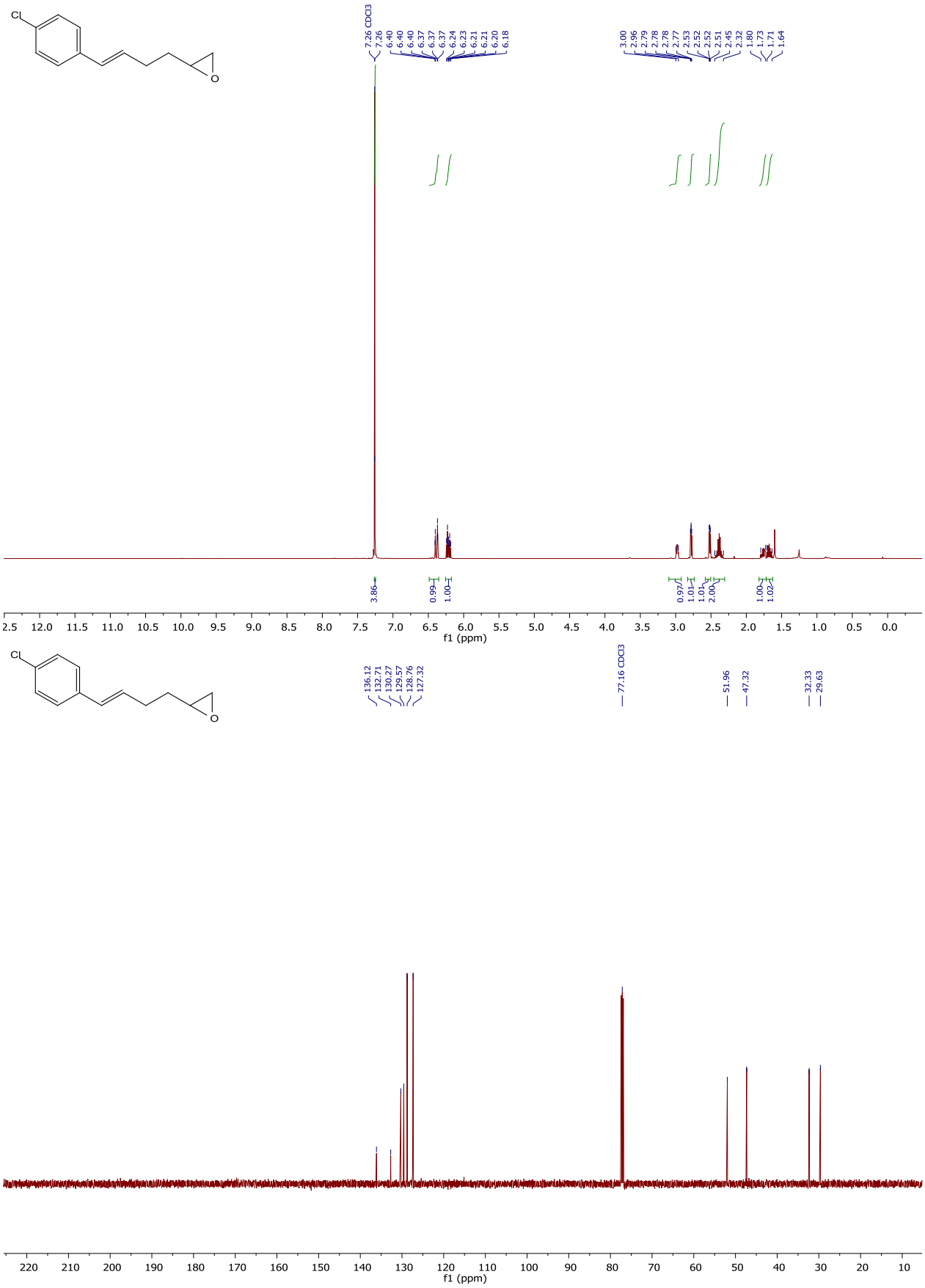
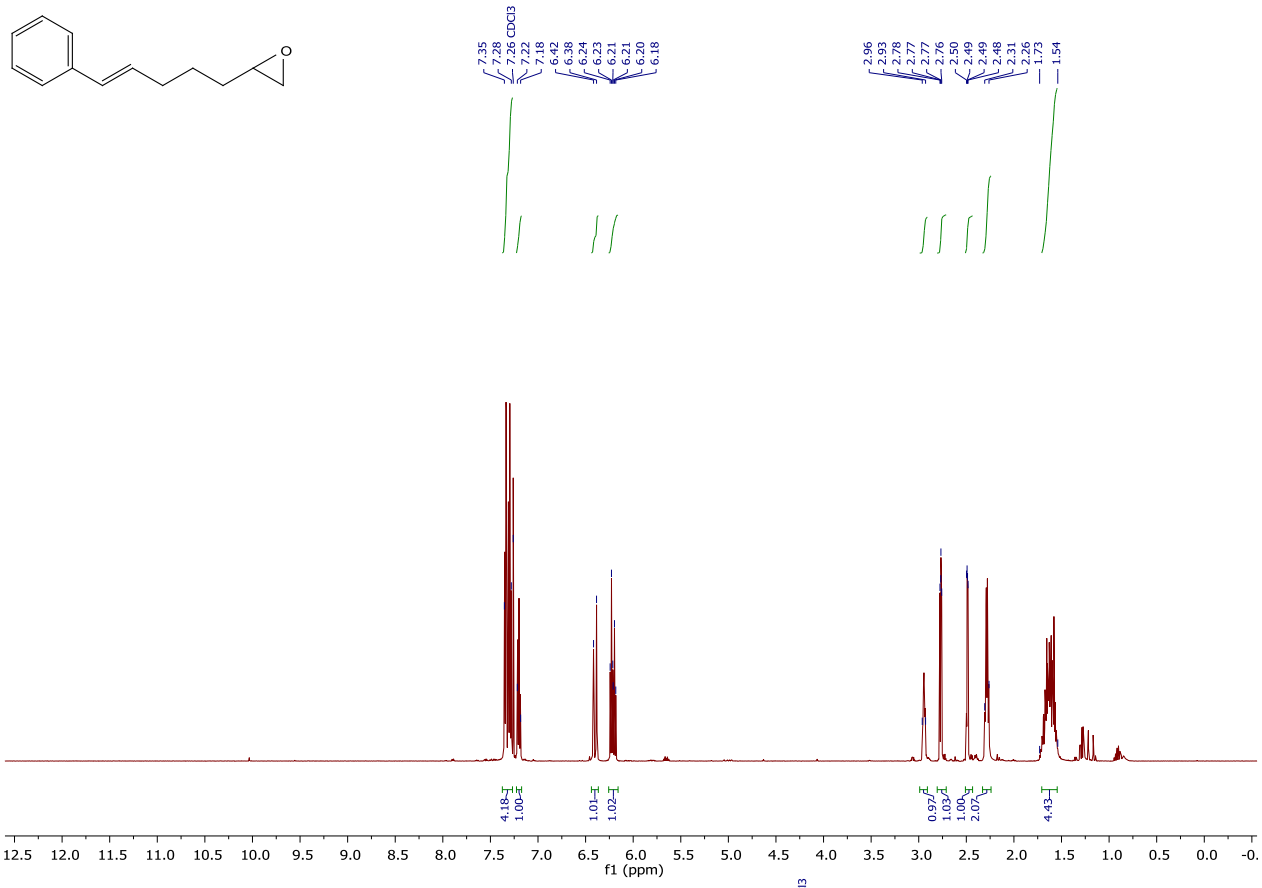
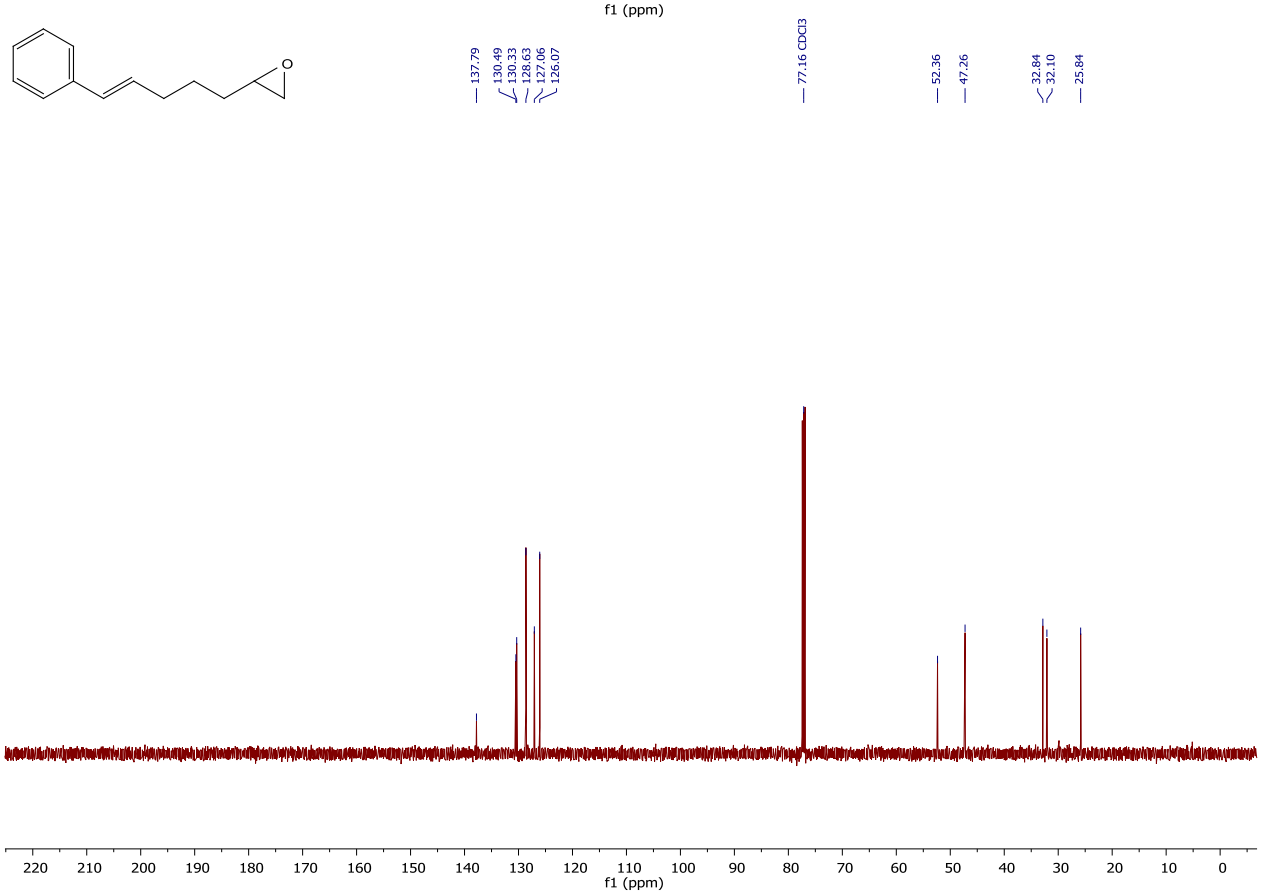
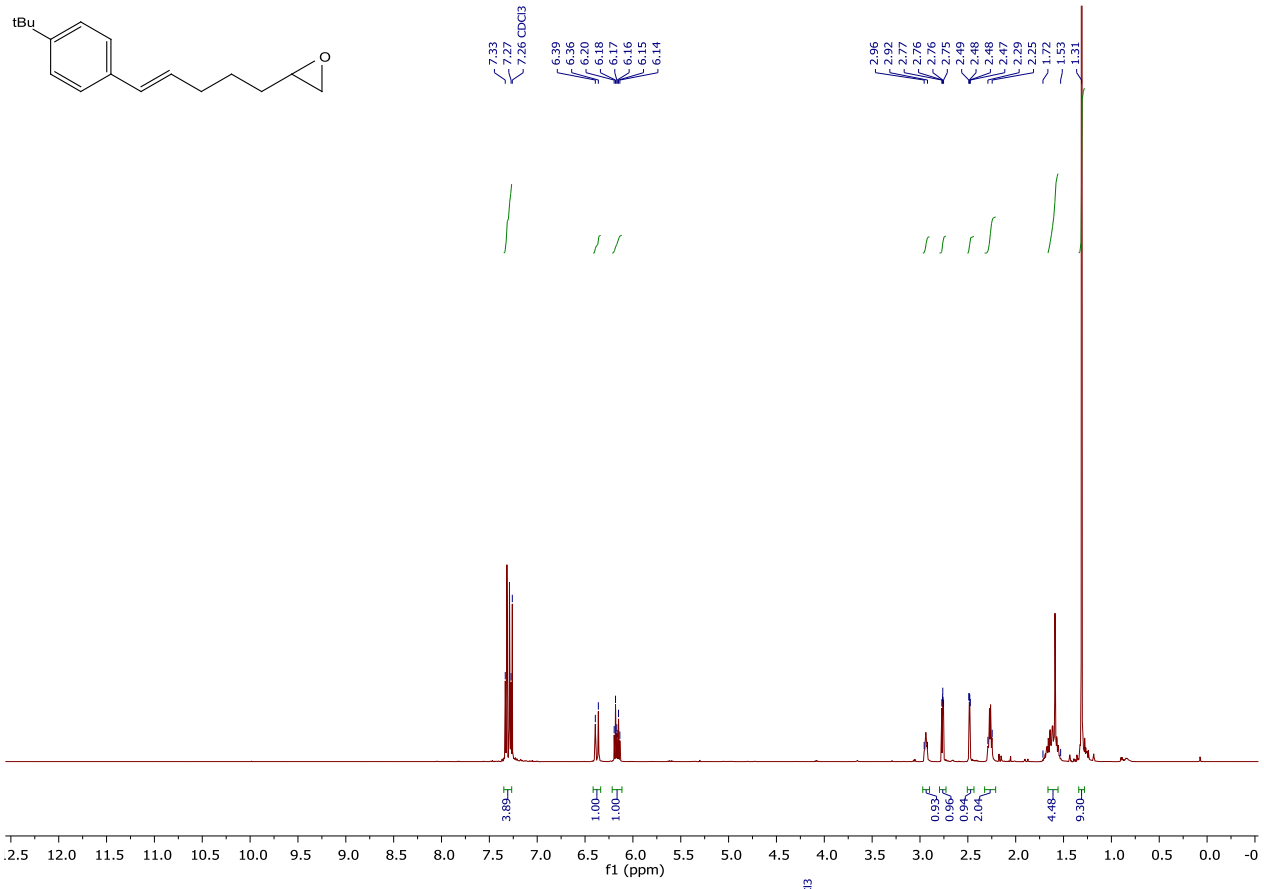
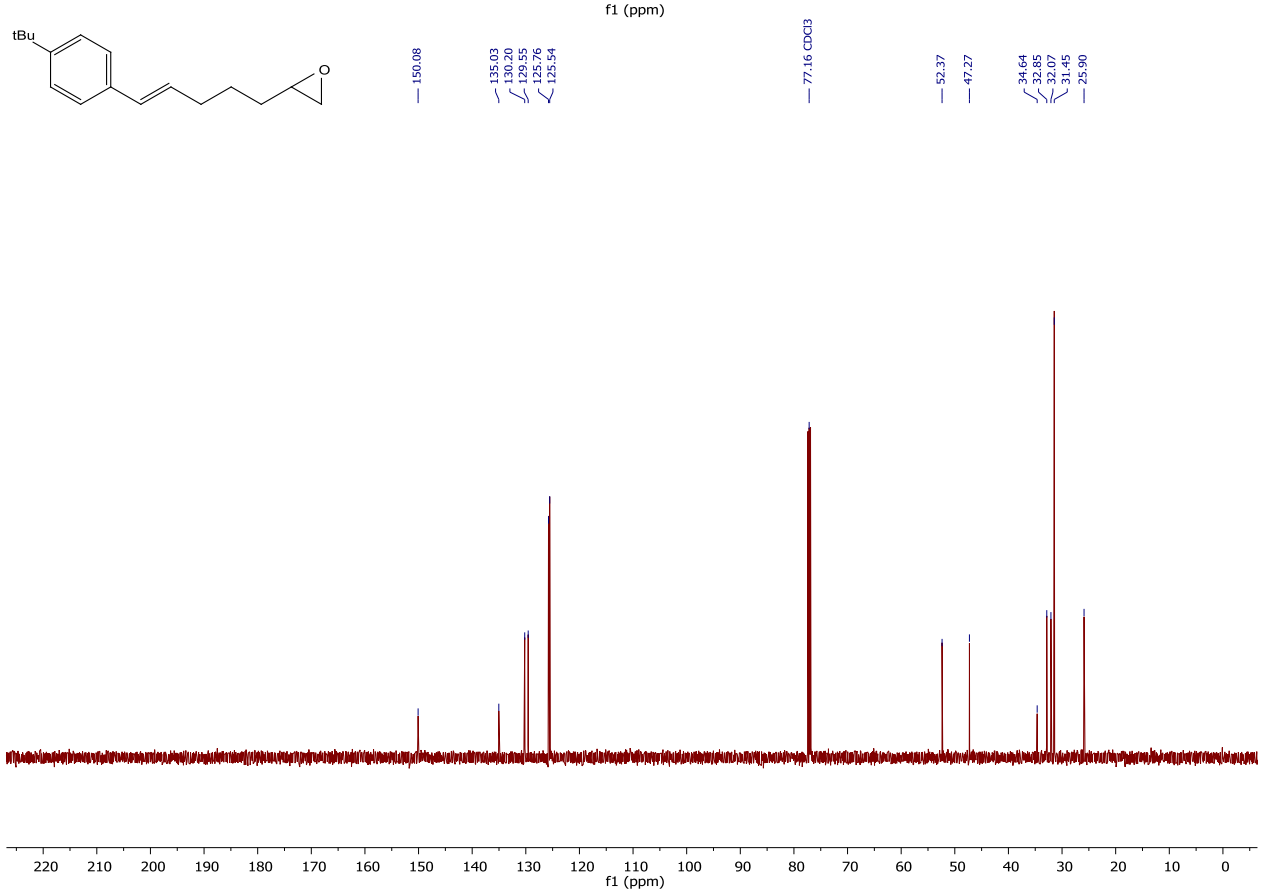
32.59
29.61
f1 (ppm)

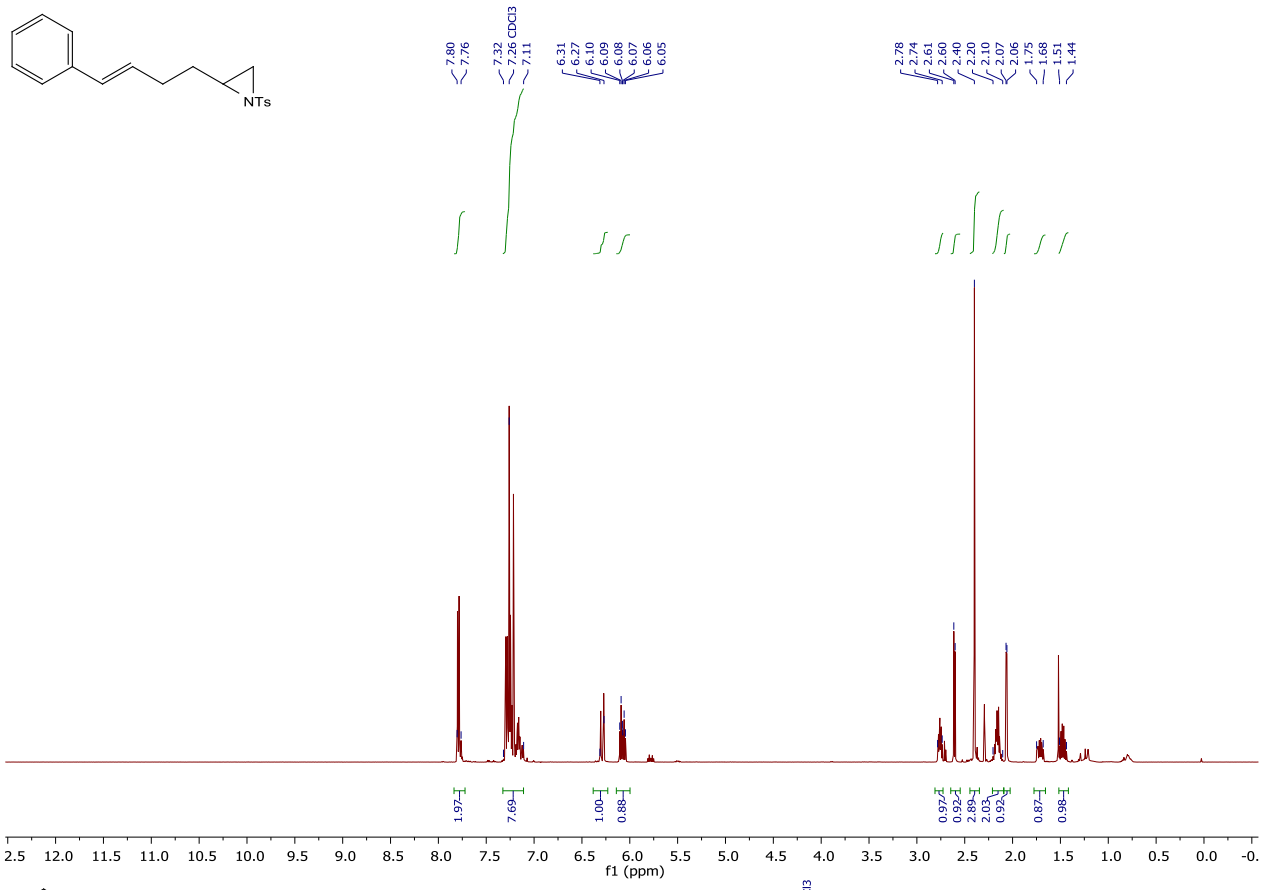

Cl
O
7.26 CDCl3
7.26
6.40
6.40
6.40
6.37
6.37
6.37
6.24
6.23
6.21
6.21
6.20
6.18
3.00
2.96
2.79
2.78
2.78
2.77
2.53
2.52
2.52
2.51
2.45
2.32
1.80
1.73
1.71
1.64
3.86
0.99
1.00
0.97
1.01
1.01
2.00
1.00
1.02
f1 (ppm)
136.12
132.71
130.27
129.57
128.76
127.32
77.16 CDCl3
51.96
47.32
32.33
29.63
f1 (ppm)

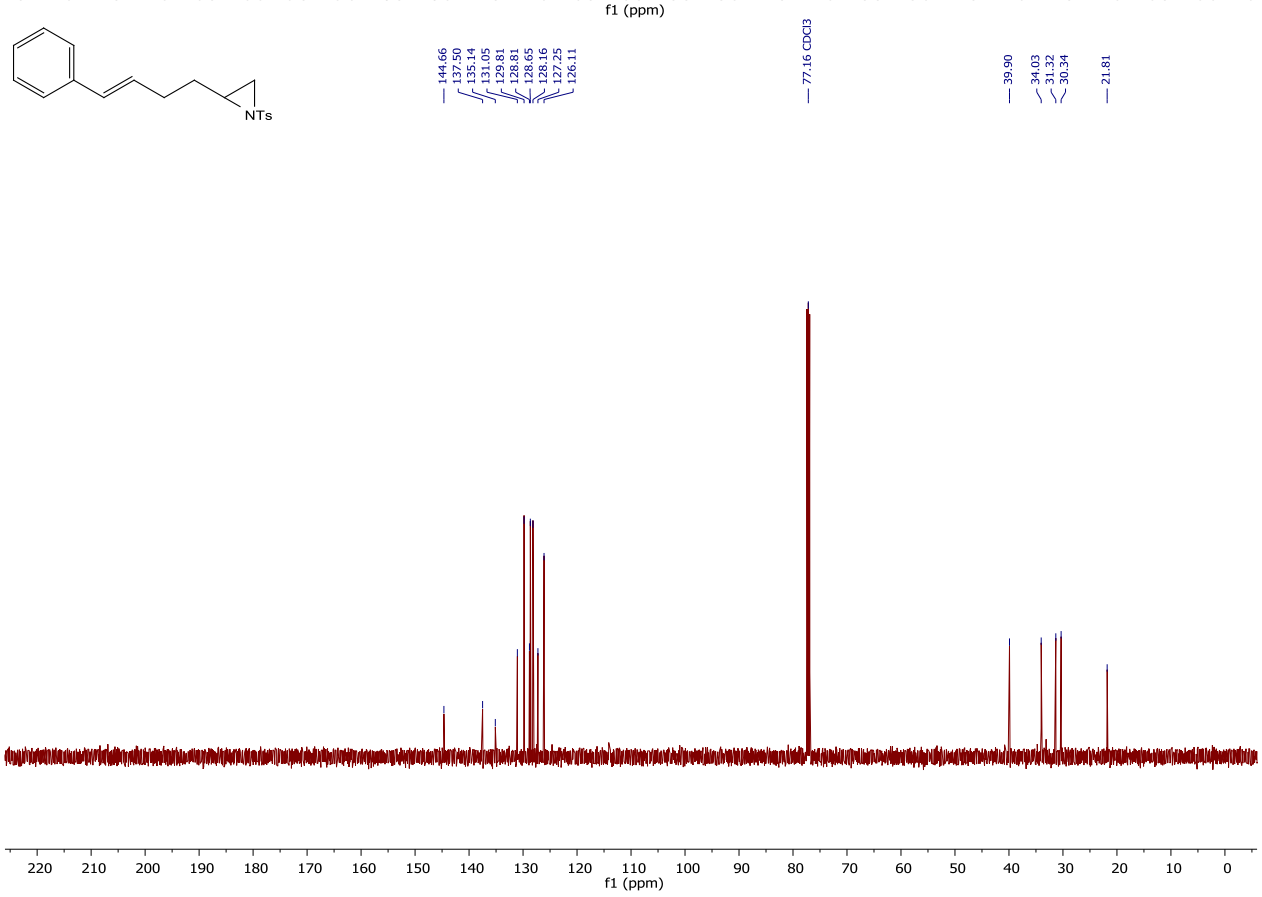

7.35
7.28
7.26 CDCl3
7.22
7.18
6.42
6.38
6.24
6.23
6.21
6.21
6.20
6.18
2.96
2.93
2.78
2.77
2.77
2.76
2.50
2.49
2.49
2.48
2.31
2.26
1.73
1.54
4.18
1.00
1.01
1.02
0.97
1.03
1.00
2.07
4.43
f1 (ppm)

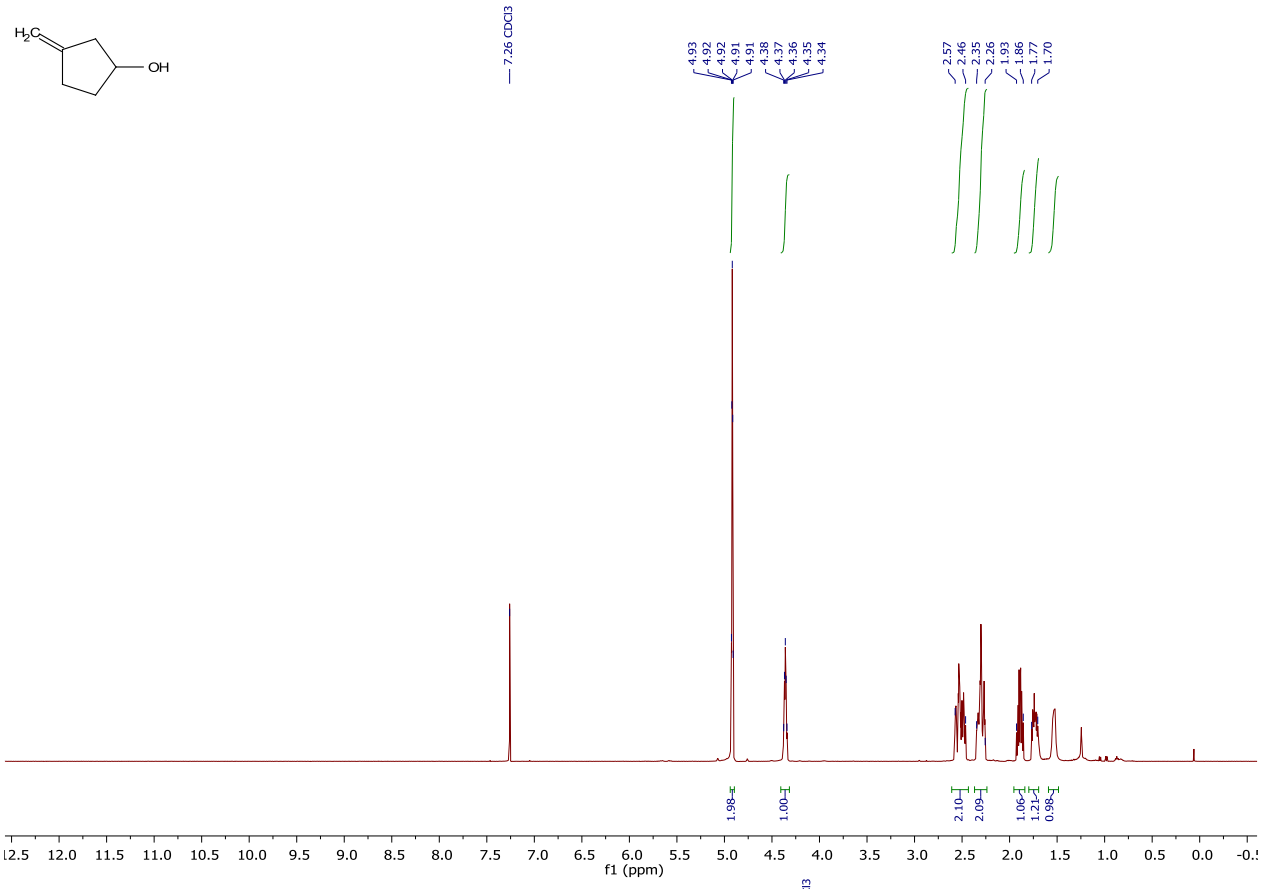

137.79
130.49
130.33
128.63
127.06
126.07
77.16 CDCl3
52.36
47.26
32.84
32.10
25.84
f1 (ppm)

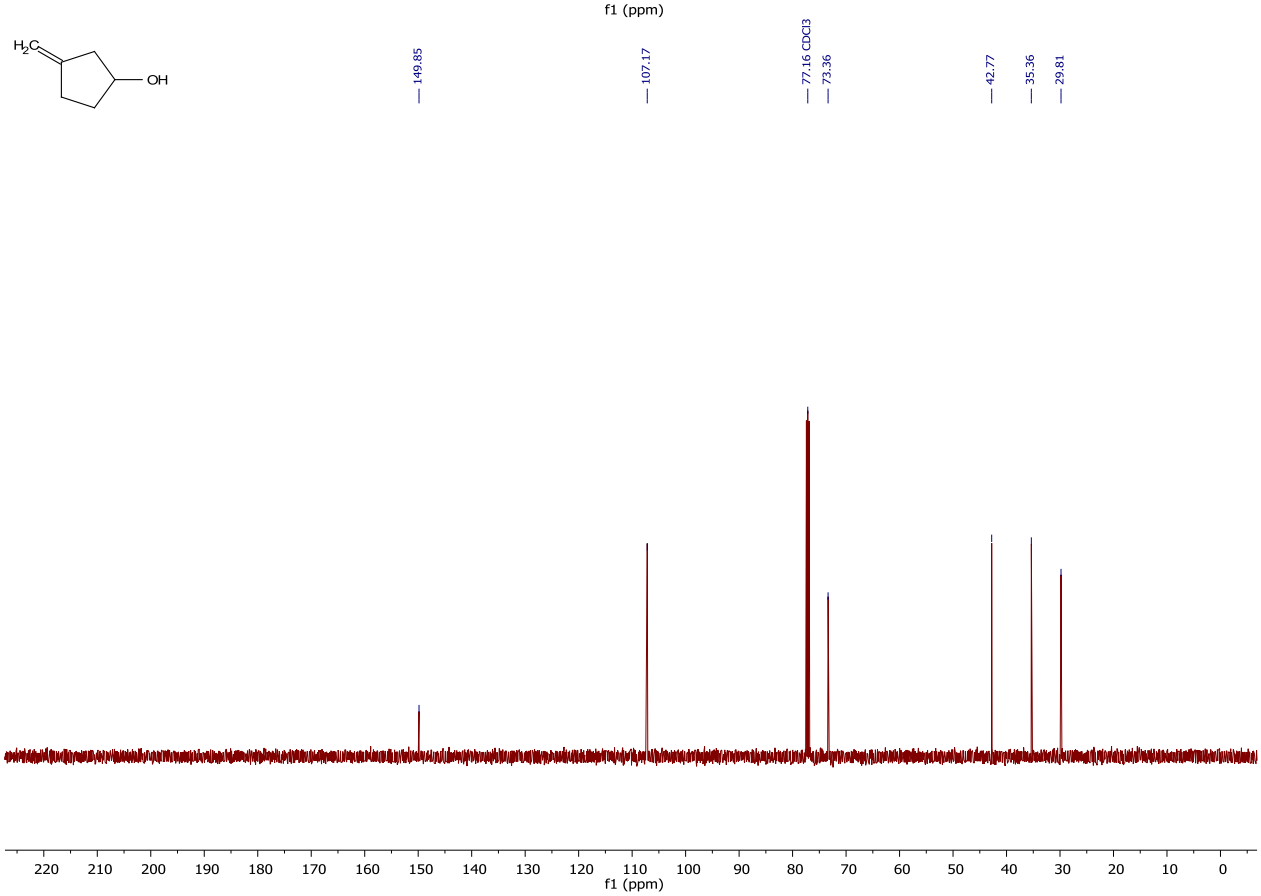

tBu
O
7.33
7.27
7.26 CDCl3
6.39
6.36
6.20
6.18
6.17
6.16
6.15
6.14
2.96
2.92
2.77
2.76
2.76
2.75
2.49
2.48
2.48
2.47
2.29
2.25
1.72
1.53
1.31
3.89
1.00
1.00
0.93
0.96
0.94
2.04
4.48
9.30
f1 (ppm)

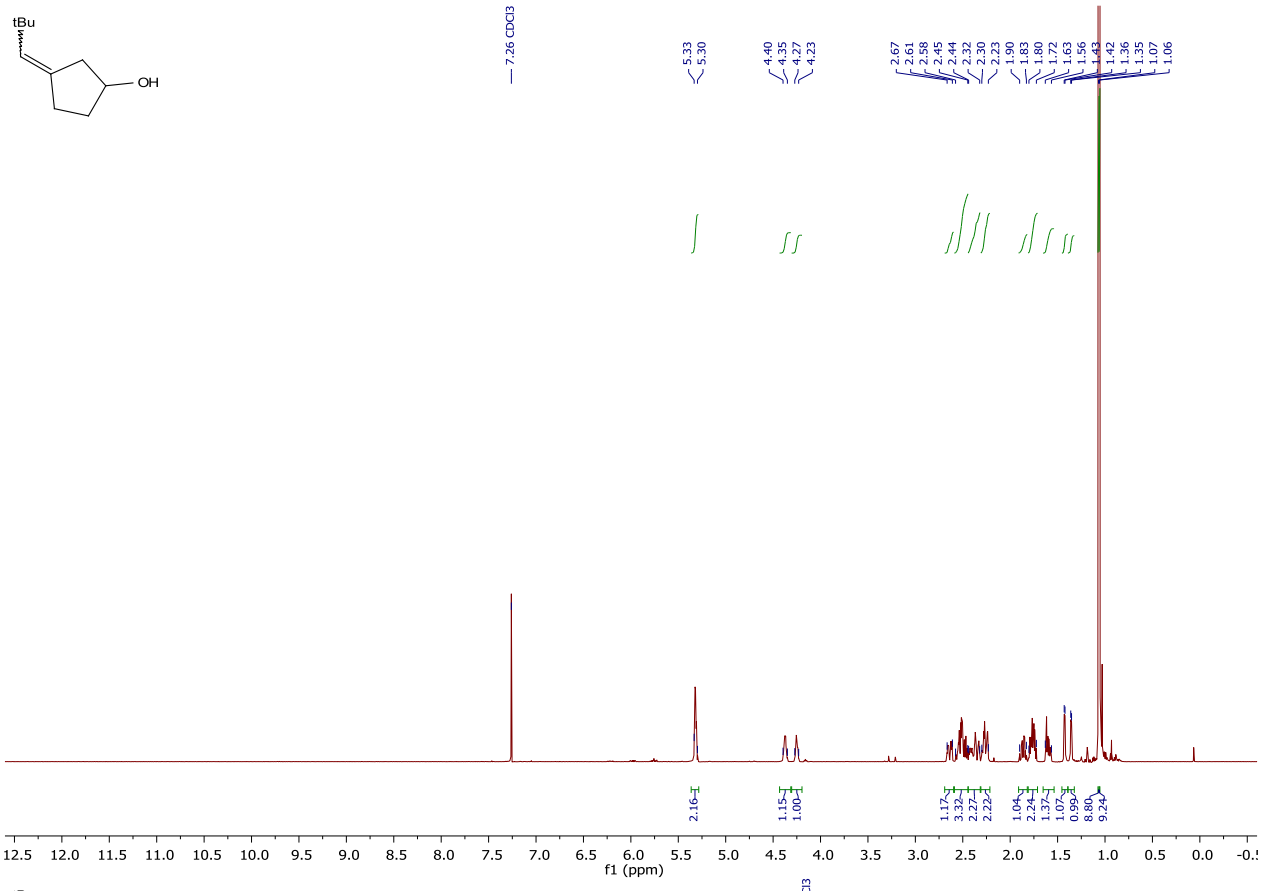

tBu
O
150.08
135.03
130.20
129.55
125.76
125.54
77.16 CDCl3
52.37
47.27
34.64
32.85
32.07
31.45
25.90
f1 (ppm)

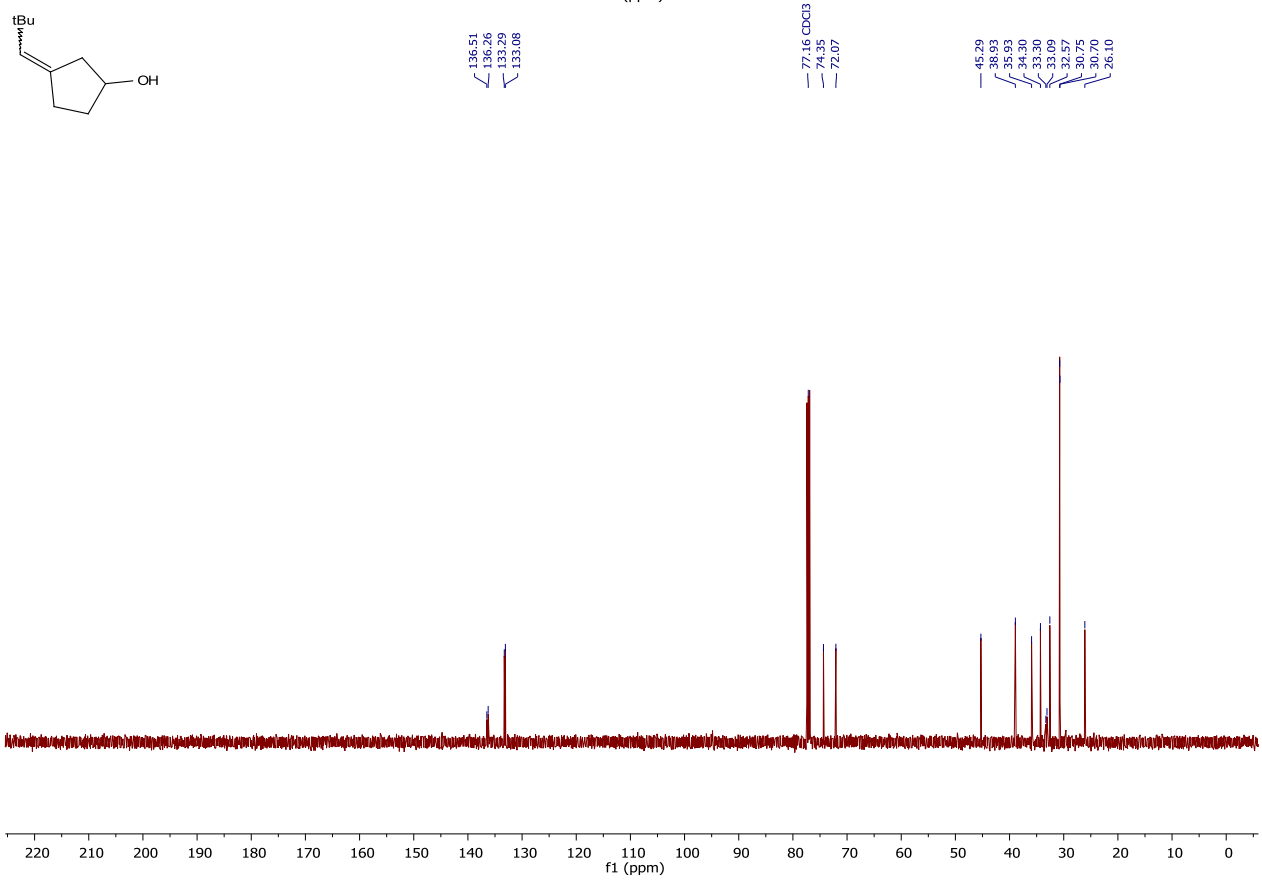

NTs
7.80
7.76
7.32
7.26 CDCl3
7.11
6.31
6.27
6.10
6.09
6.08
6.07
6.06
6.05
2.78
2.74
2.61
2.60
2.40
2.20
2.10
2.07
2.06
1.75
1.68
1.51
1.44
1.97
7.69
1.00
0.88
0.97
0.92
2.89
2.03
0.92
0.87
0.98
f1 (ppm)

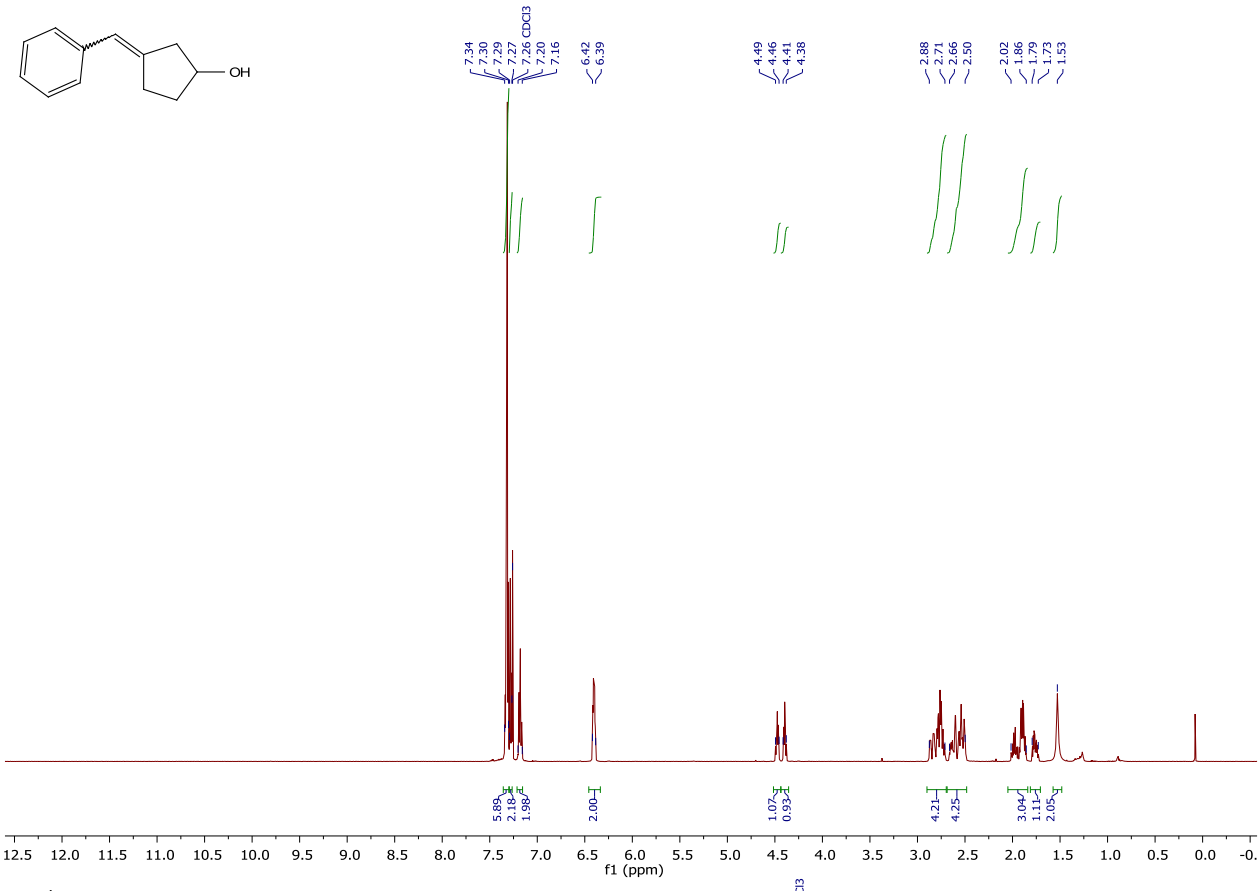

NTs
144.66
137.50
135.14
131.05
129.81
128.81
128.65
128.16
127.25
126.11
77.16 CDCl3
39.90
34.03
31.32
30.34
21.81
f1 (ppm)

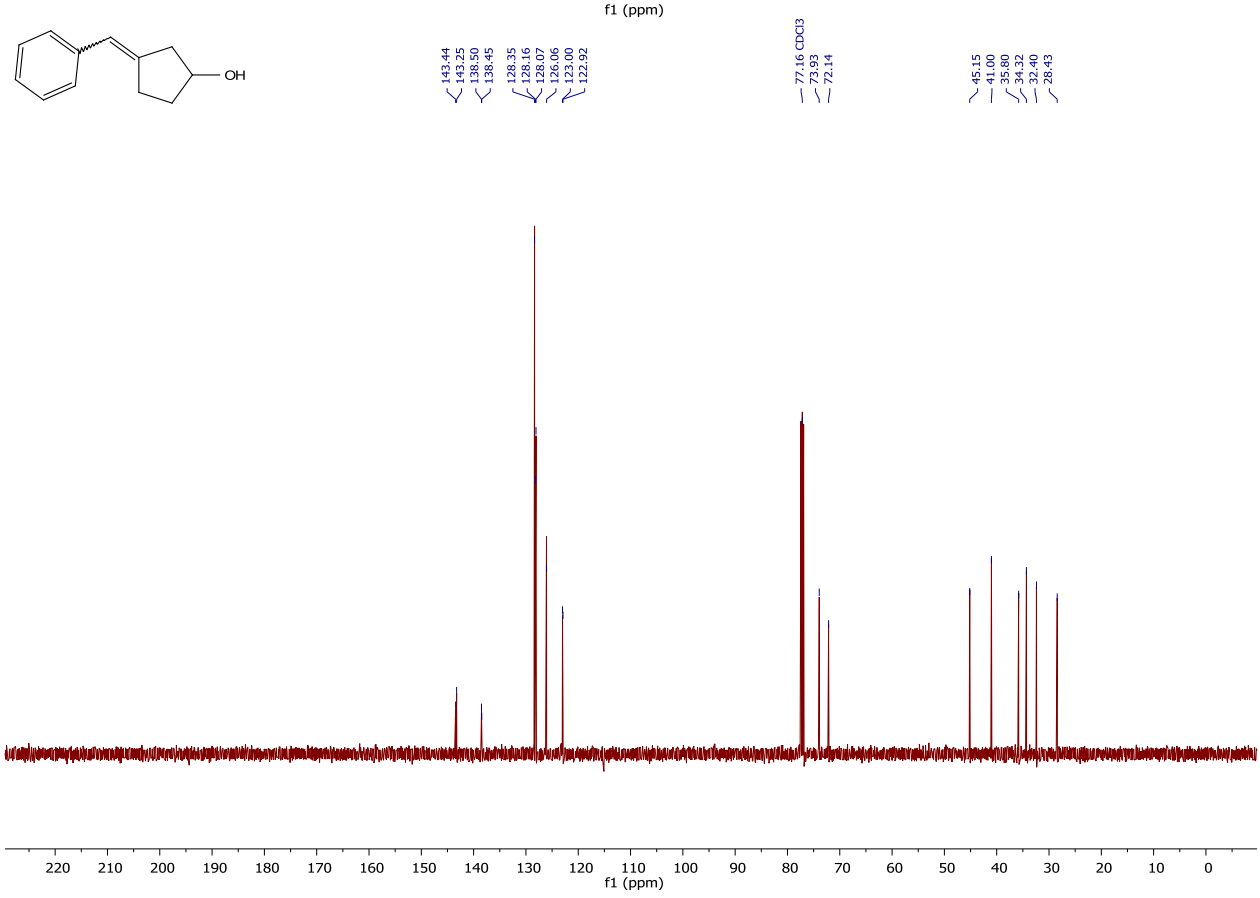

H2C
OH
7.26 CDCl3
4.93
4.92
4.92
4.91
4.91
4.38
4.37
4.36
4.35
4.34
2.57
2.46
2.35
2.26
1.93
1.86
1.77
1.70
1.98
1.00
2.10
2.09
1.06
1.21
0.98
f1 (ppm)

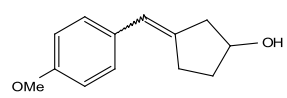

H2C
OH
149.85
107.17
77.16 CDCl3
73.36
42.77
35.36
29.81
f1 (ppm)


tBu
OH
7.26 CDCl3
5.33
5.30
4.40
4.35
4.27
4.23
2.67
2.61
2.58
2.45
2.44
2.32
2.30
2.23
1.90
1.83
1.80
1.72
1.63
1.56
1.43
1.42
1.36
1.35
1.07
1.06
2.16
1.15
1.00
1.17
3.32
2.27
2.22
1.04
2.24
1.32
1.07
0.99
8.80
9.24
f1 (ppm)

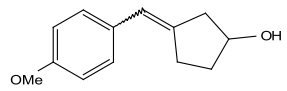

tBu
OH
136.51
136.26
133.29
133.08
77.16 CDCl3
74.35
72.07
45.29
38.93
35.93
34.30
33.30
33.09
32.57
30.75
30.70
26.10
f1 (ppm)


OH
7.34
7.30
7.29
7.27
7.26 CDCl3
7.20
7.16
6.42
6.39
4.49
4.46
4.41
4.38
2.88
2.71
2.66
2.50
2.02
1.86
1.79
1.73
1.53
5.89
2.18
1.98
2.00
1.07
0.93
4.21
4.25
3.04
1.11
2.05
f1 (ppm)

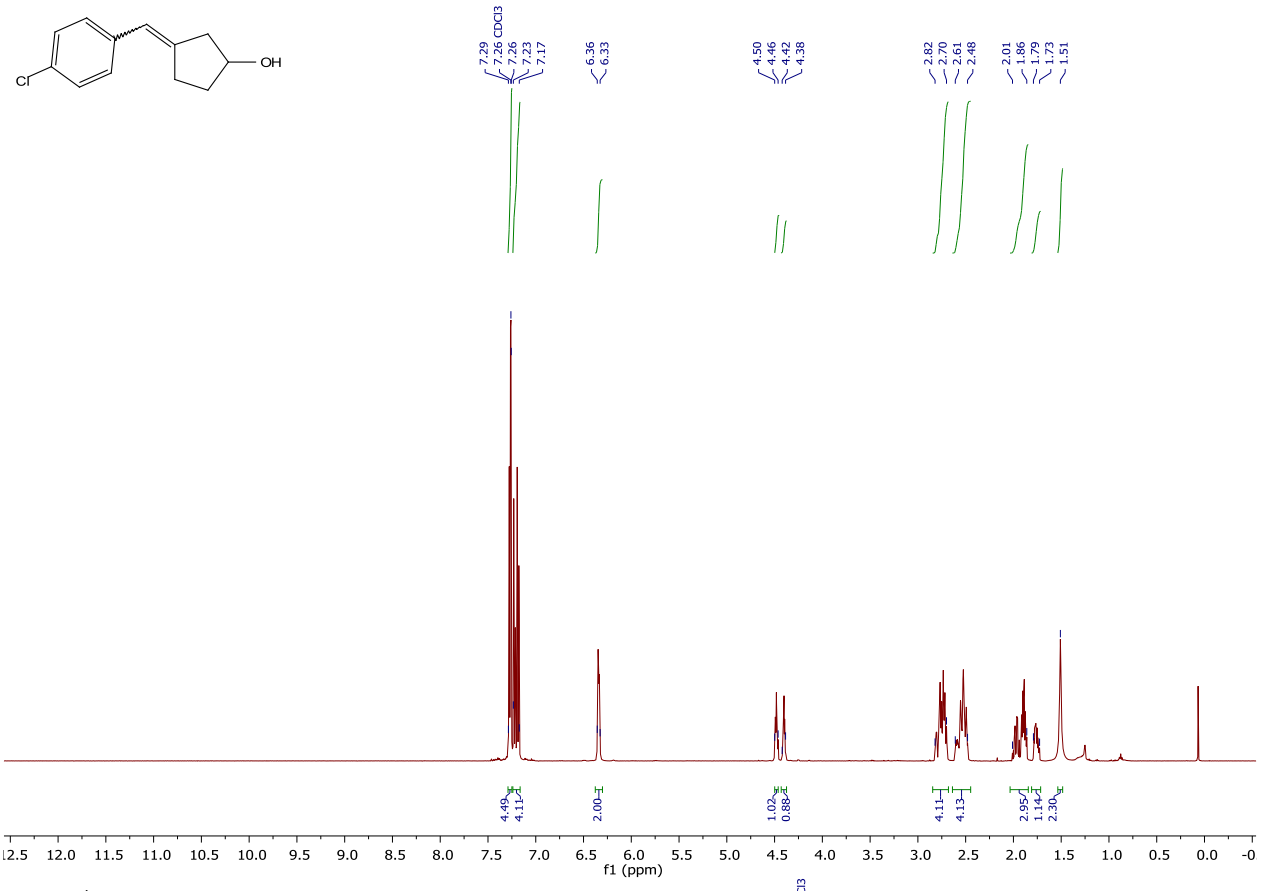

OH
143.44
143.25
138.50
138.45
128.35
128.16
128.07
126.06
123.00
122.92
77.16 CDCl3
73.93
72.14
45.15
41.00
35.80
34.32
32.40
28.43
f1 (ppm)

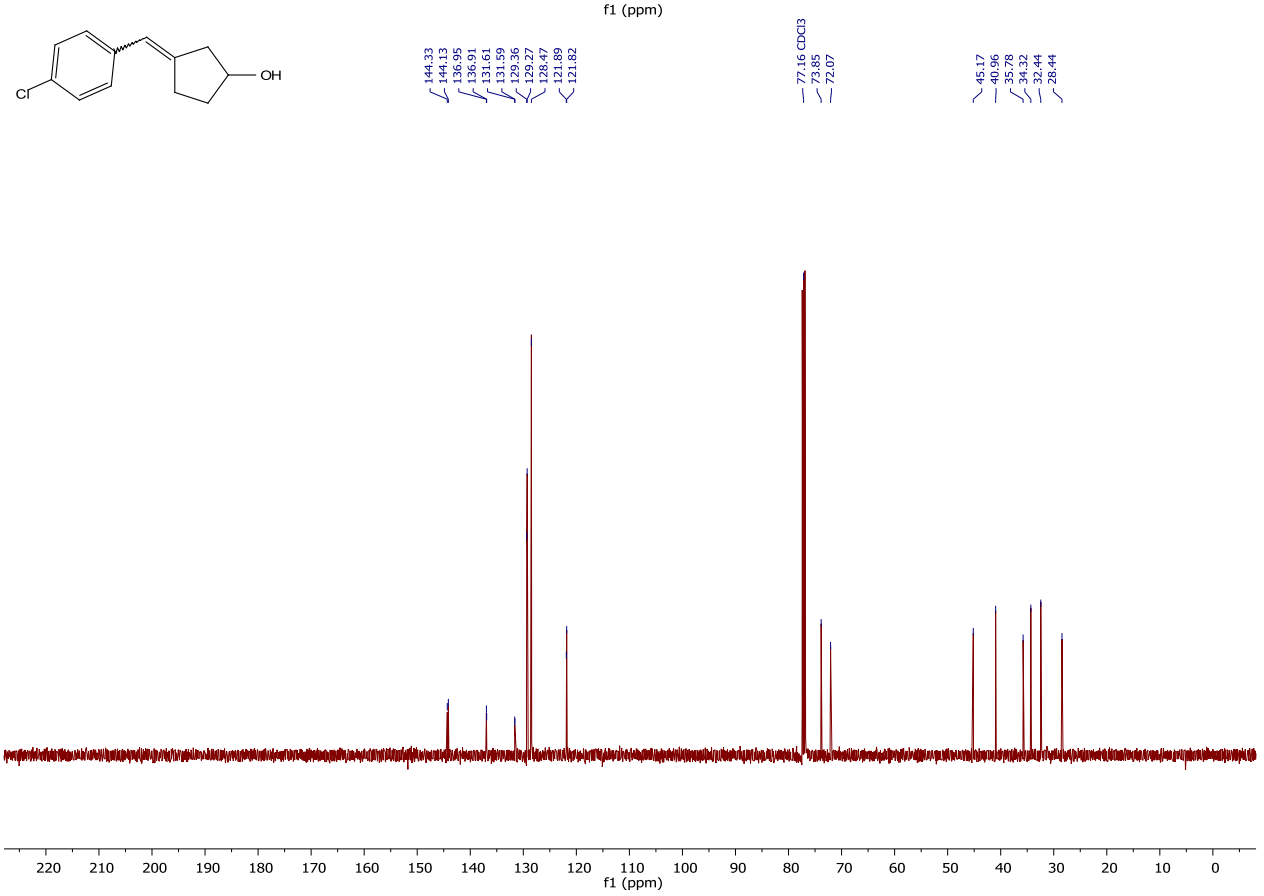

OH
OMe

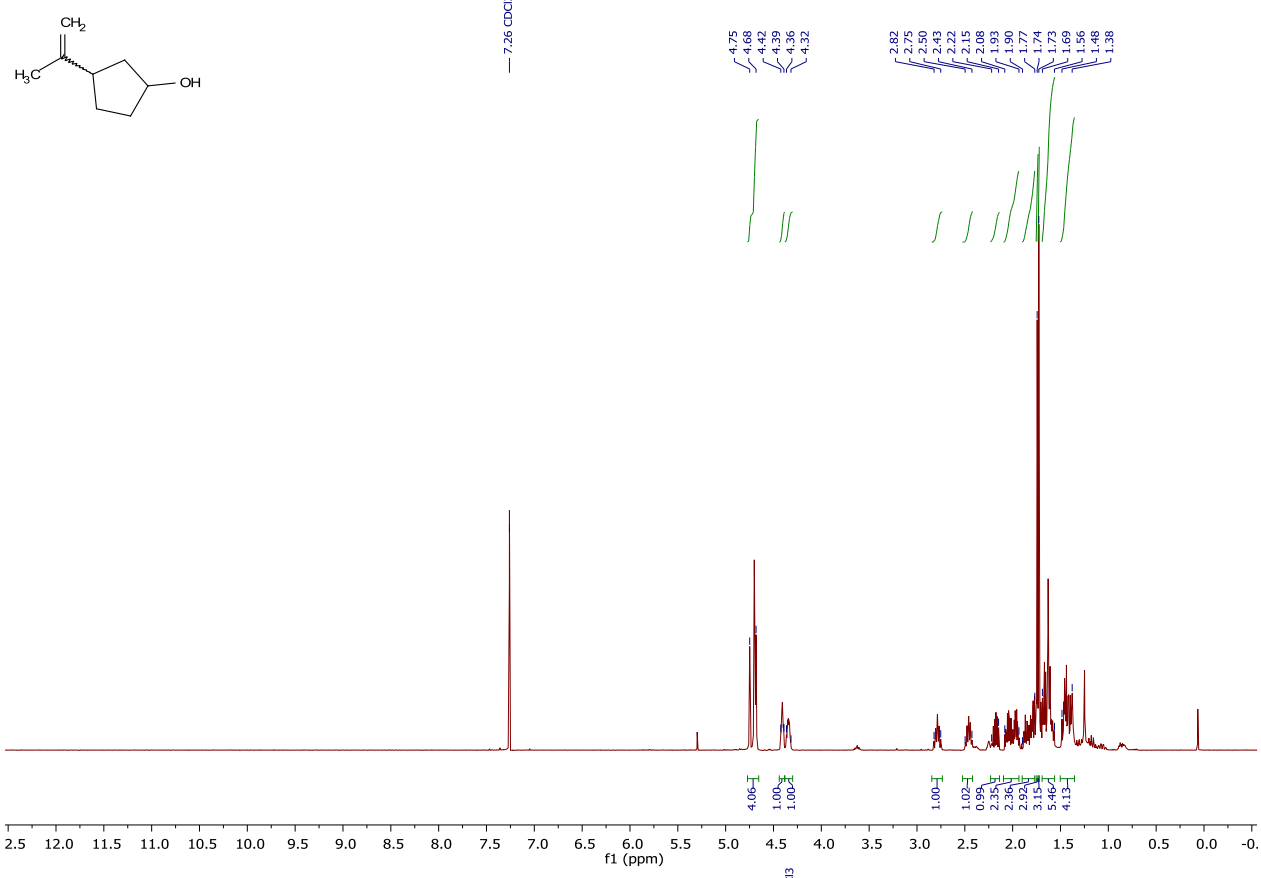
7.26 CDCl3
7.26
7.20
6.88
6.84
6.35
6.32
4.48
4.44
4.39
4.36
3.81
3.80
2.85
2.66
2.62
2.43
2.00
1.93
1.92
1.84
1.77
1.71
1.68
1.58
3.94
3.99
2.00
1.04
0.90
2.87
3.10
4.21
4.22
0.96
2.02
1.20
2.28
f1 (ppm)

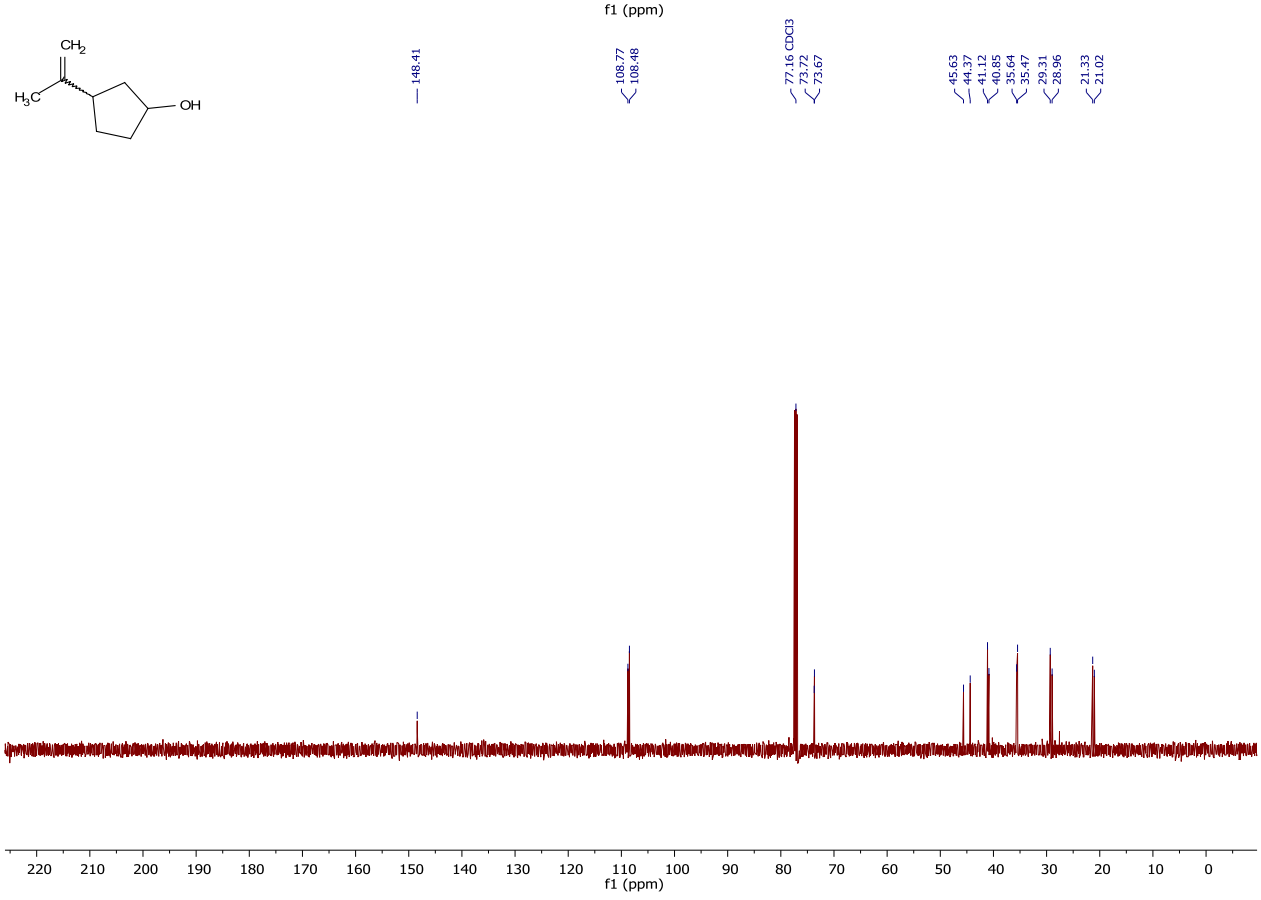

OH
OMe

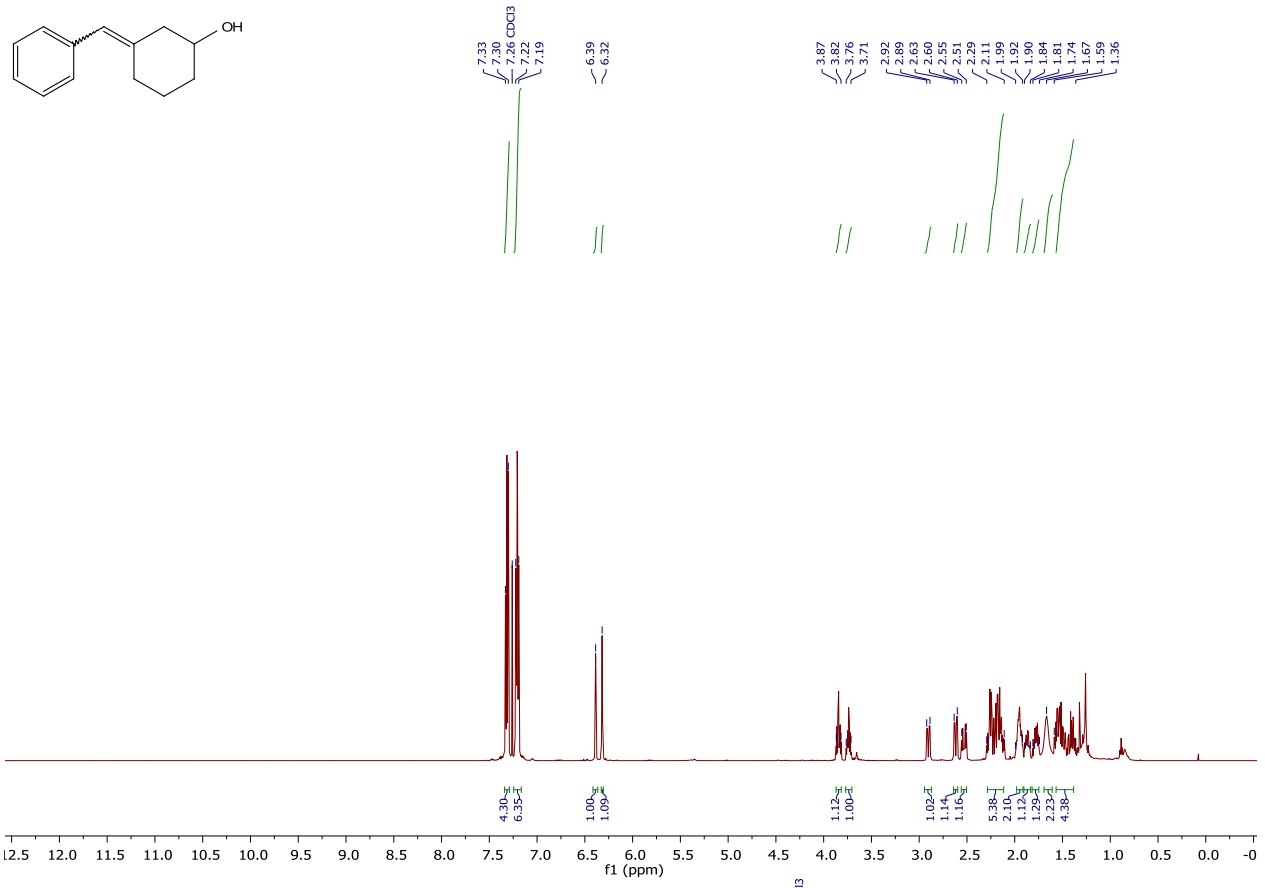
157.84
157.82
141.02
140.90
131.35
129.28
129.18
122.34
122.22
113.78
113.77
77.16 CDCl3
73.96
72.16
55.37
45.06
40.85
35.79
34.36
32.29
28.27
f1 (ppm)

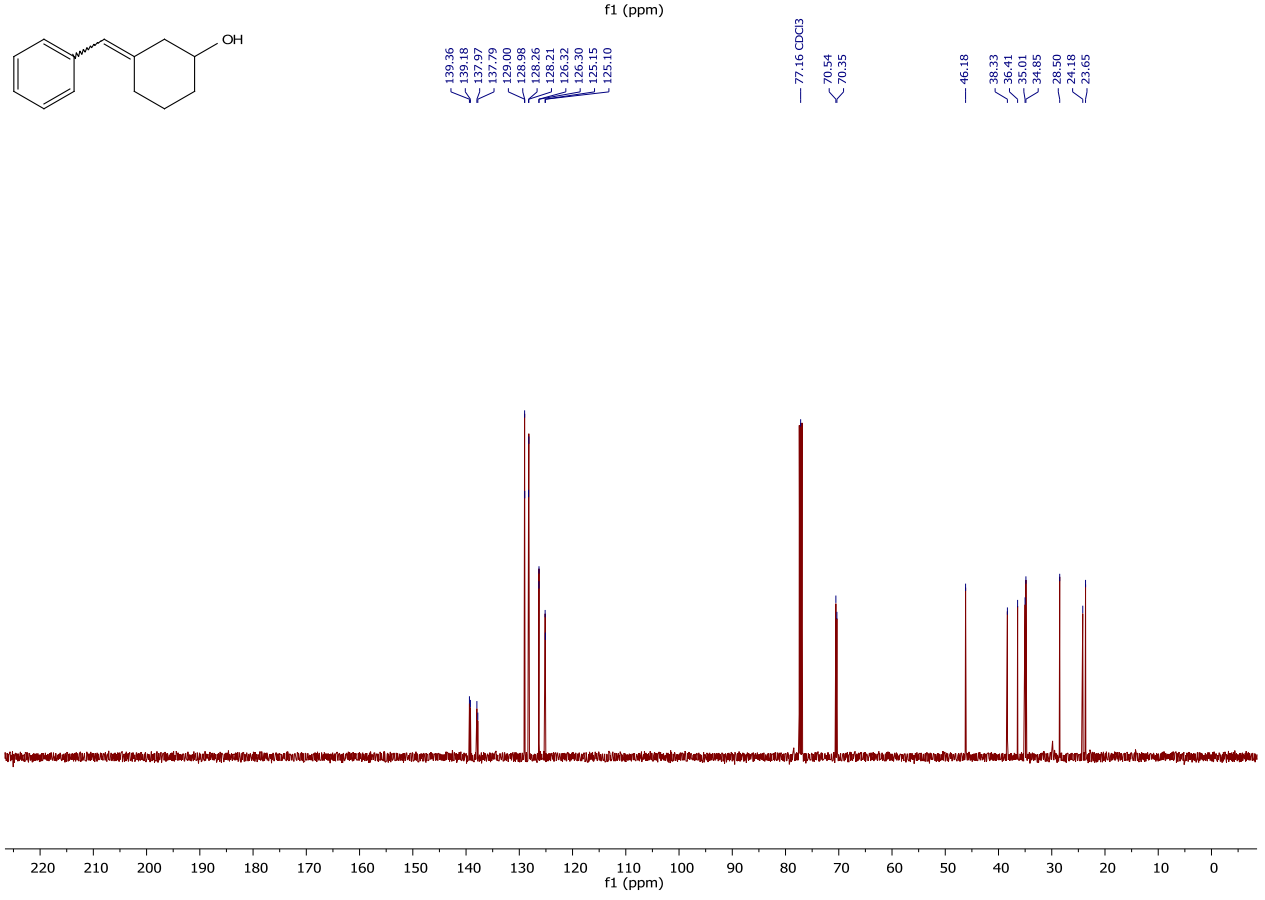

Cl
OH
7.29
7.26 CDCl3
7.26
7.23
7.17
6.36
6.33
4.50
4.46
4.42
4.38
2.82
2.70
2.61
2.48
2.01
1.86
1.79
1.73
1.51
4.49
4.11
2.00
1.02
0.88
4.11
4.13
2.95
1.14
2.30
f1 (ppm)

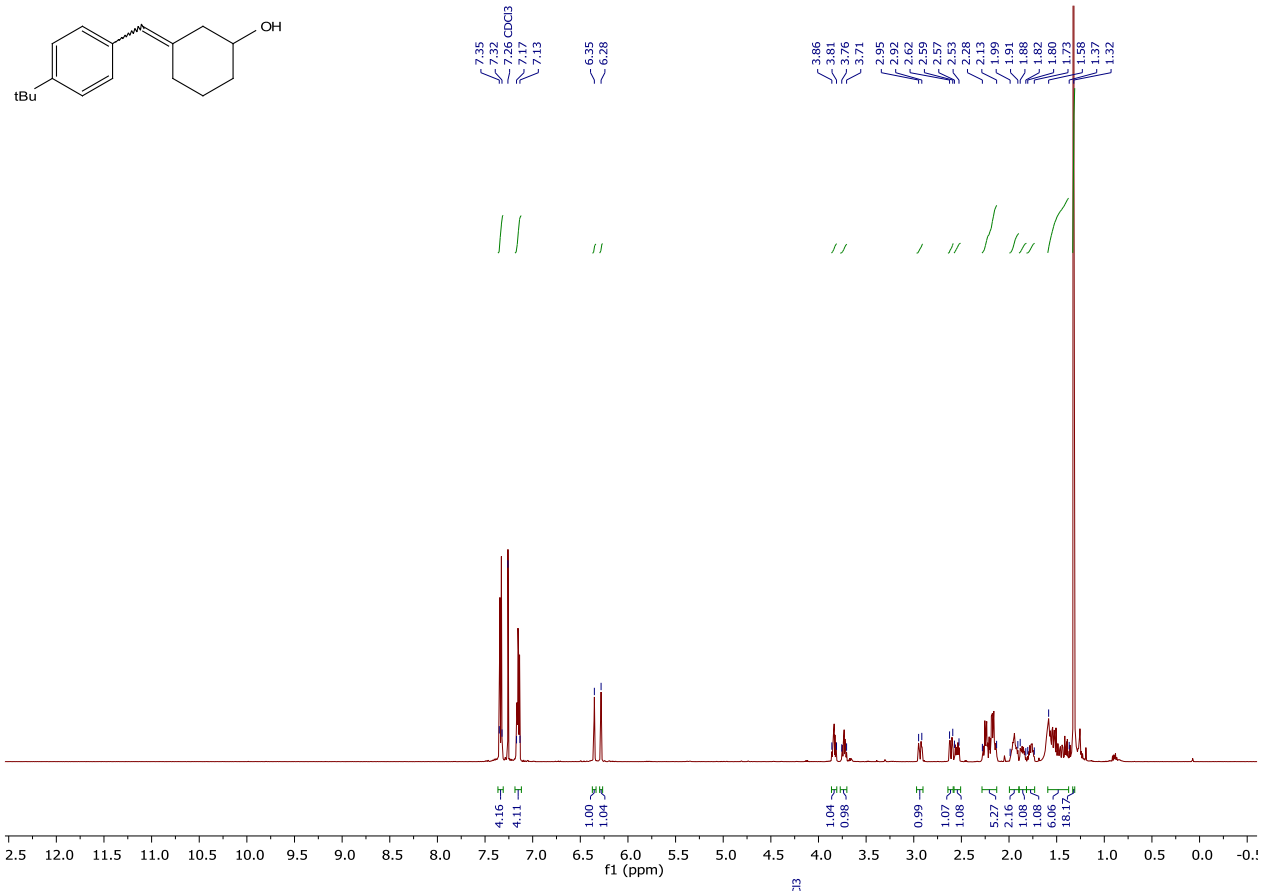

Cl
OH
144.33
144.13
136.95
136.91
131.61
131.59
129.36
129.27
128.47
121.89
121.82
77.16 CDCl3
73.85
72.07
45.17
40.96
35.78
34.32
32.44
28.44
f1 (ppm)

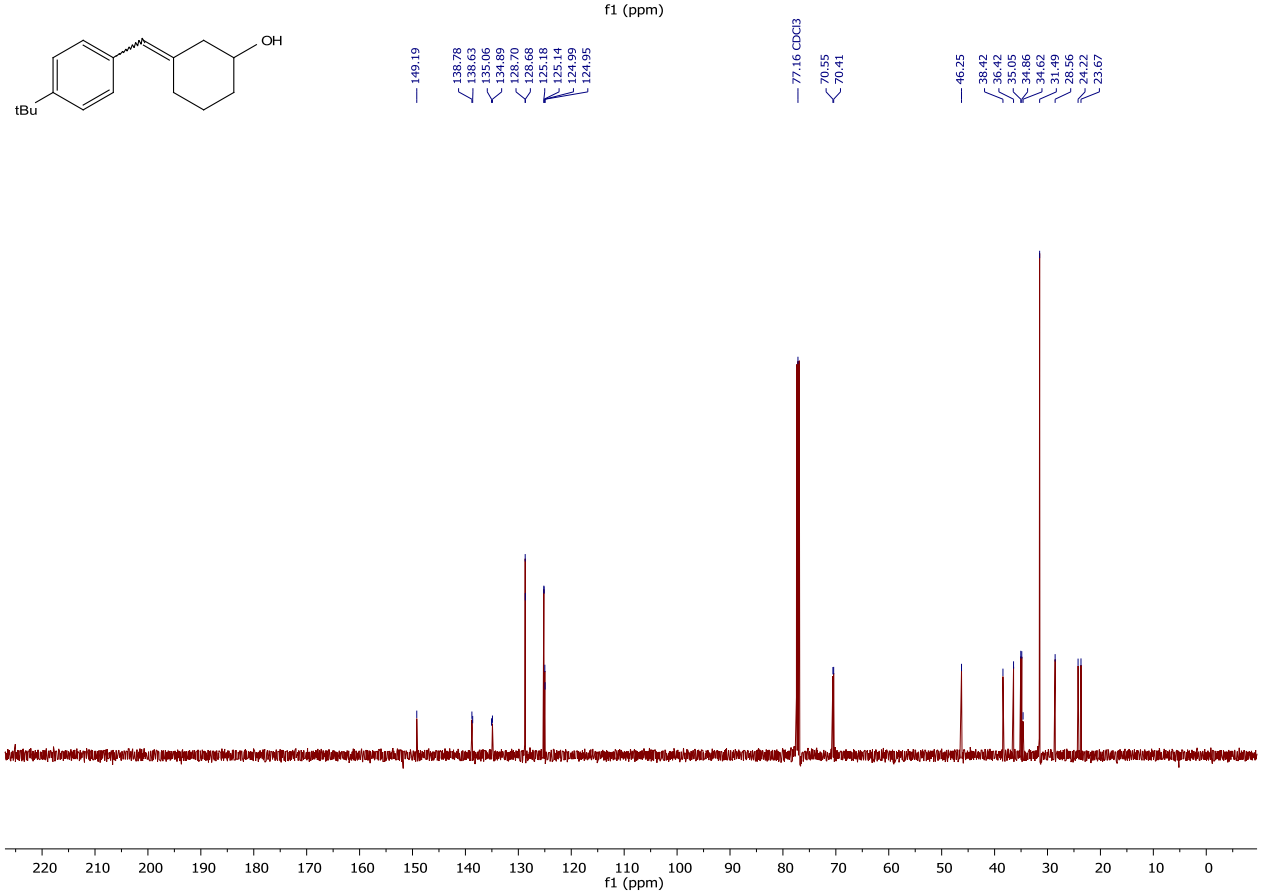

CH2
H3C
OH
7.26 CDCl3
4.75
4.68
4.42
4.39
4.36
4.32
2.82
2.75
2.50
2.43
2.22
2.15
2.08
1.93
1.90
1.77
1.74
1.73
1.69
1.56
1.48
1.38
4.06
1.00
1.00
1.00
1.02
0.99
2.35
2.36
2.92
3.15
5.46
4.13
f1 (ppm)

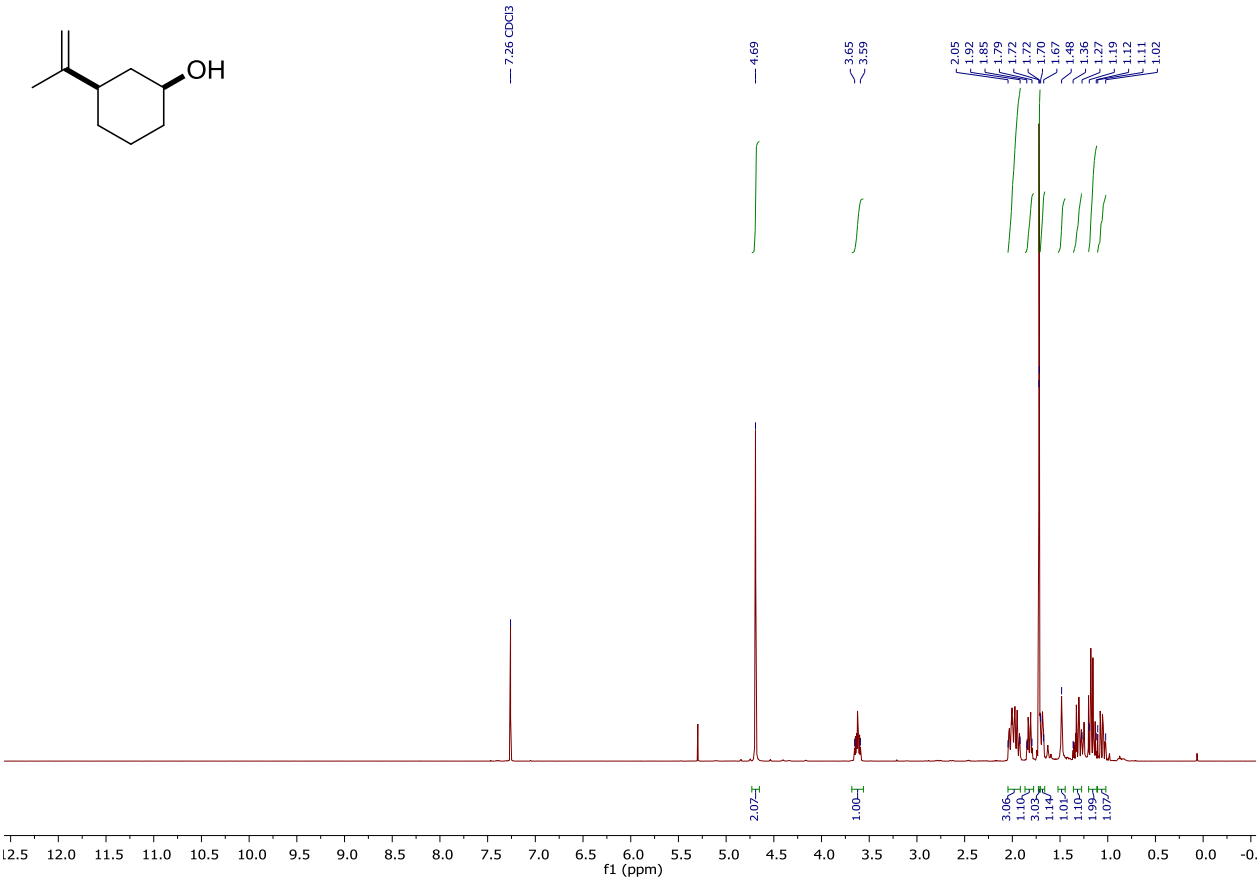

CH2
H3C
OH
148.41
108.77
108.48
77.16 CDCl3
73.72
73.67
45.63
44.37
41.12
40.85
35.64
35.47
29.31
28.96
21.33
21.02
f1 (ppm)

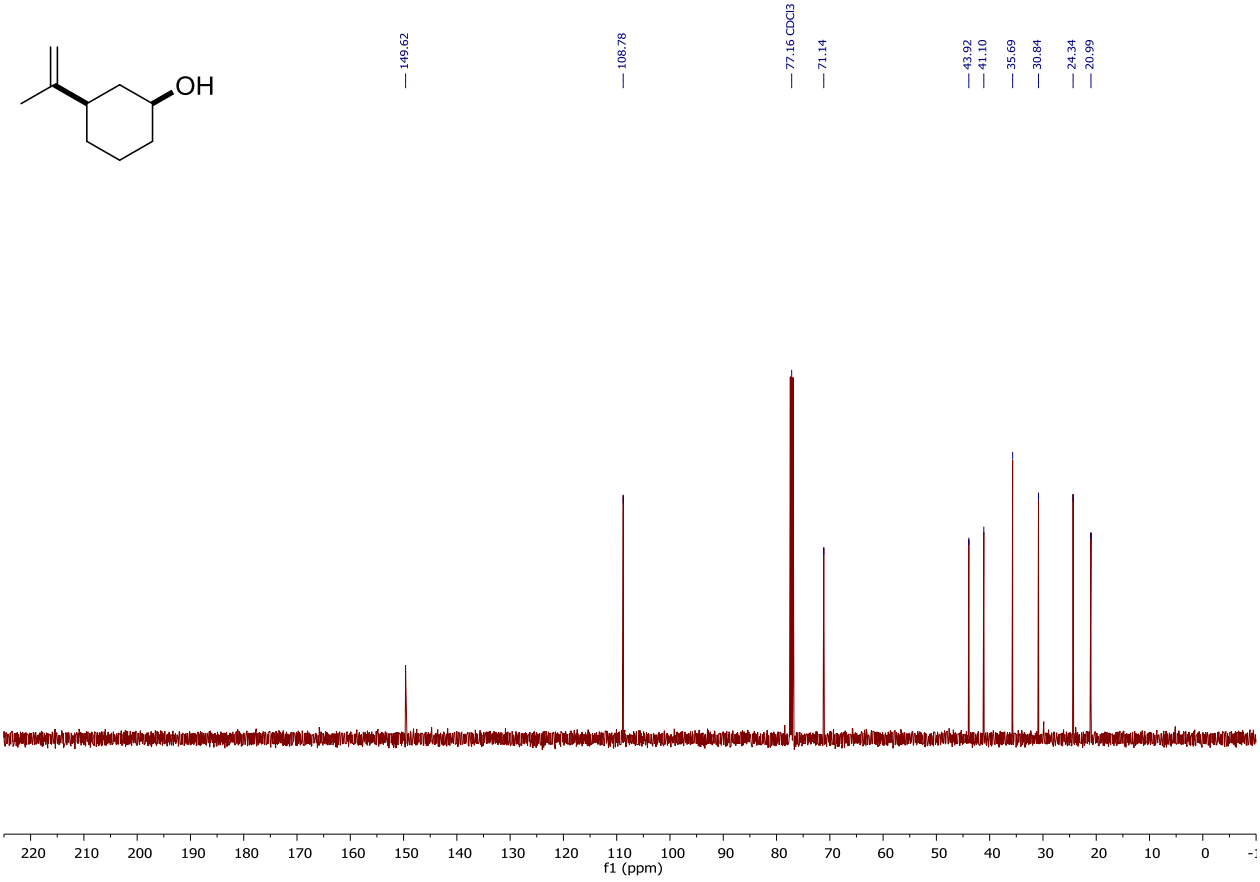

OH
7.33
7.30
7.26 CDCl3
7.22
7.19
6.39
6.32
3.87
3.82
3.76
3.71
2.92
2.89
2.63
2.60
2.55
2.51
2.29
2.11
1.99
1.92
1.90
1.84
1.81
1.74
1.67
1.59
1.36
4.30
6.35
1.00
1.09
1.12
1.00
1.02
1.14
1.16
5.38
2.10
1.12
1.29
2.23
4.38
f1 (ppm)

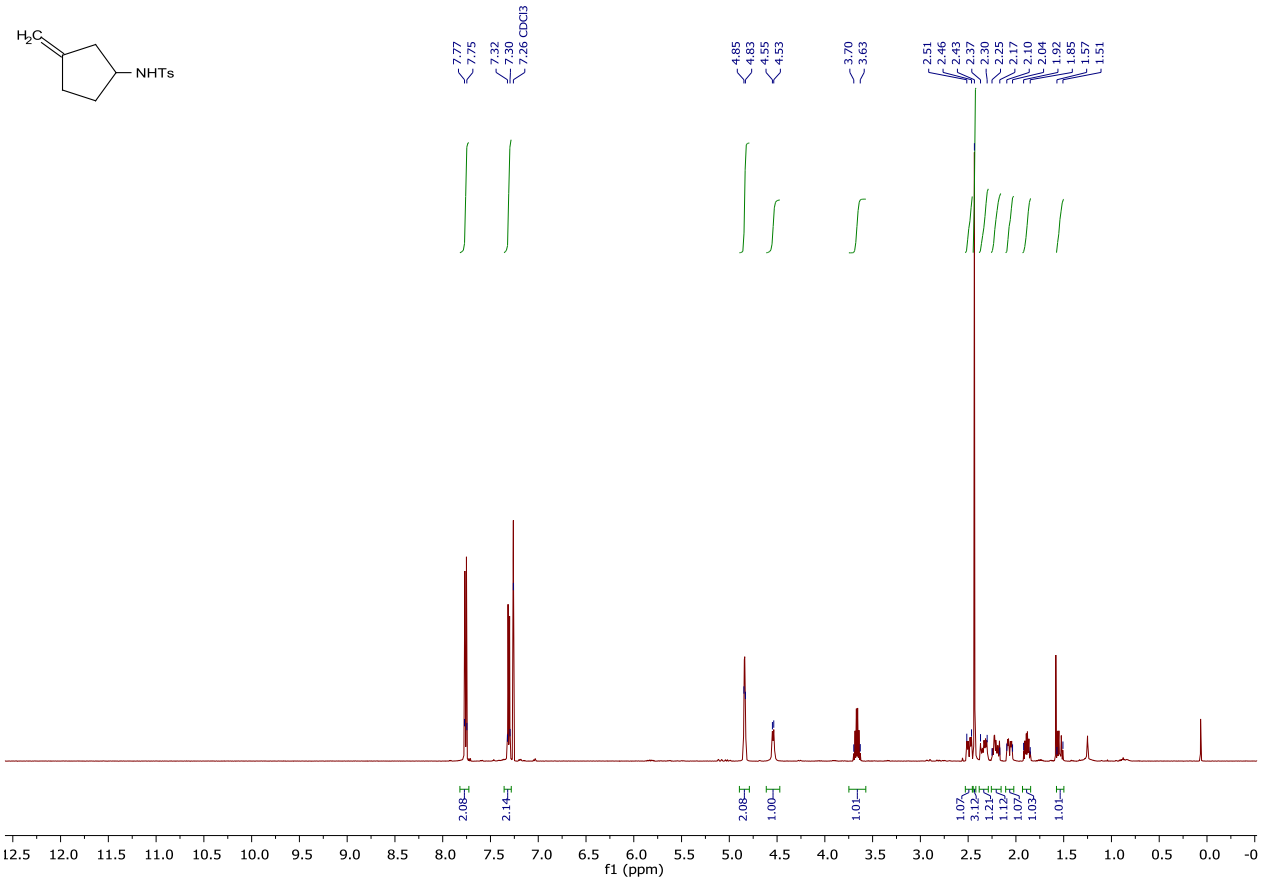

OH
139.36
139.18
137.97
137.79
129.00
128.98
128.26
128.21
126.32
126.30
125.15
125.10
77.16 CDCl3
70.54
70.35
46.18
38.33
36.41
35.01
34.85
28.50
24.18
23.65
f1 (ppm)

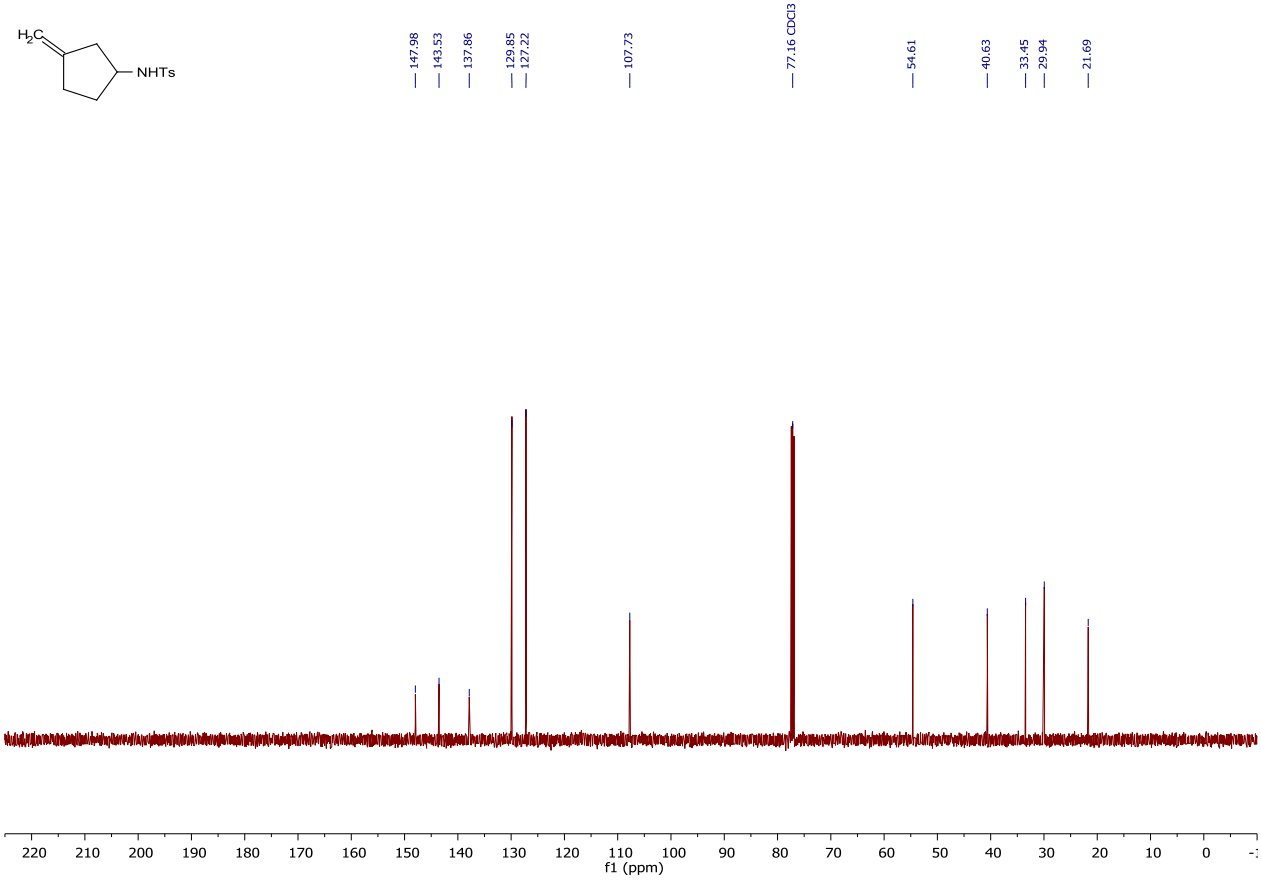

OH
tBu
7.35
7.32
7.26 CDCl3
7.17
7.13
6.35
6.28
3.86
3.81
3.76
3.71
2.95
2.92
2.62
2.59
2.57
2.53
2.28
2.13
1.99
1.91
1.88
1.82
1.80
1.73
1.58
1.37
1.32
4.16
4.11
1.00
1.04
1.04
0.98
0.99
1.07
1.08
5.27
2.16
1.08
1.08
6.06
18.17
f1 (ppm)

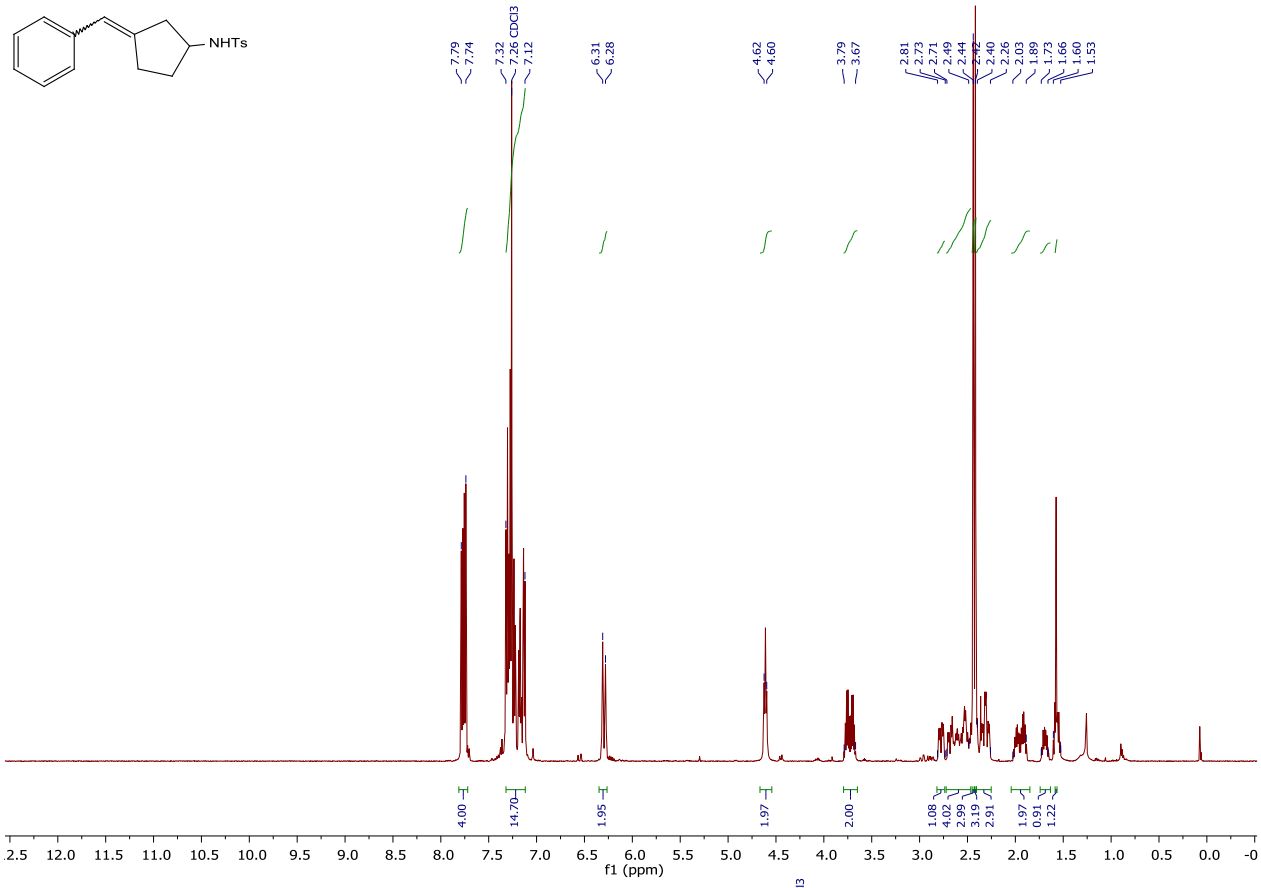

OH
tBu
149.19
138.78
138.63
135.06
134.89
128.70
128.68
125.18
125.14
124.99
124.95
77.16 CDCl3
70.55
70.41
46.25
38.42
36.42
35.05
34.86
34.62
31.49
28.56
24.22
23.67
f1 (ppm)

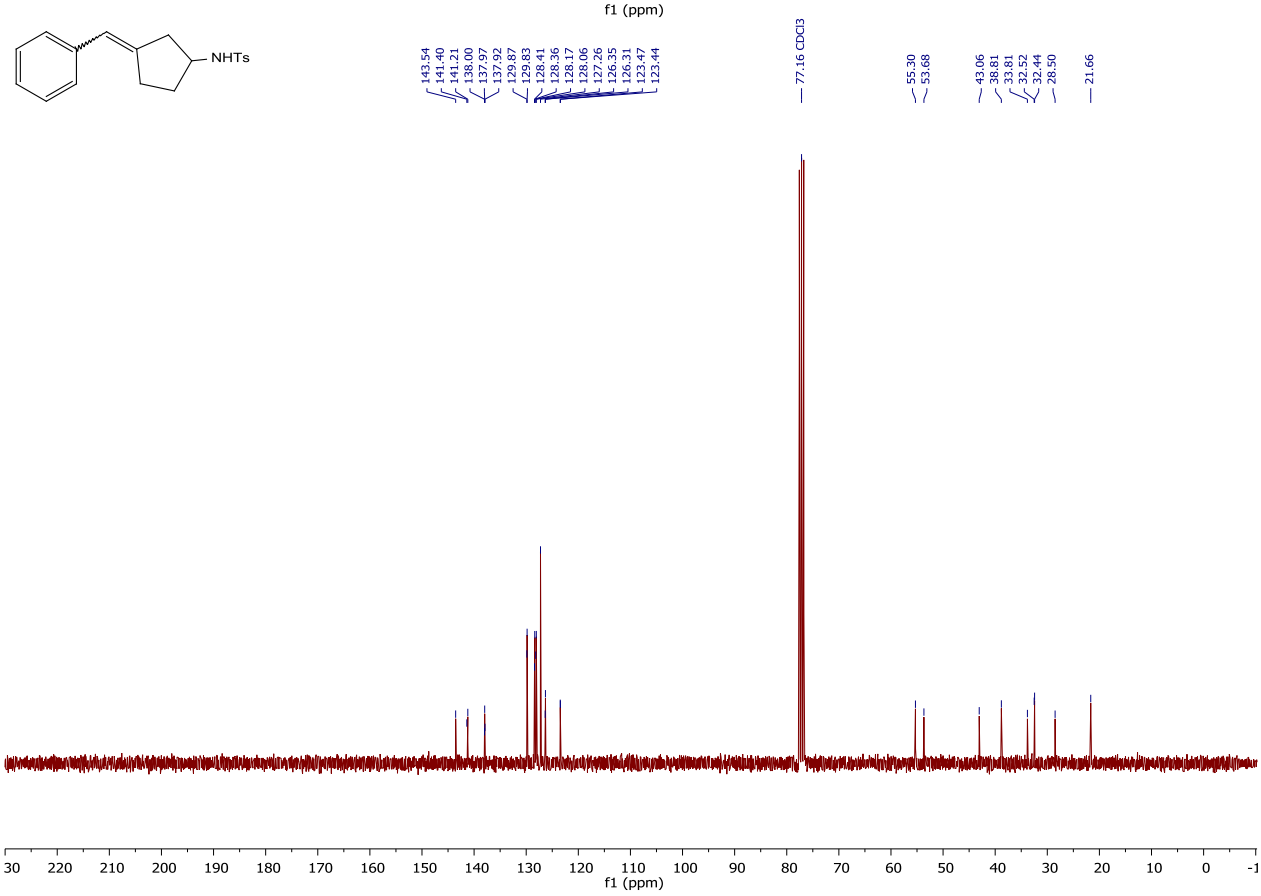

OH
7.26 CDCl3
4.69
3.65
3.59
2.05
1.92
1.85
1.79
1.72
1.72
1.72
1.70
1.67
1.48
1.36
1.27
1.19
1.12
1.11
1.02
2.07
1.00
3.06
1.10
1.10
3.03
1.14
1.01
1.10
1.99
1.07
f1 (ppm)

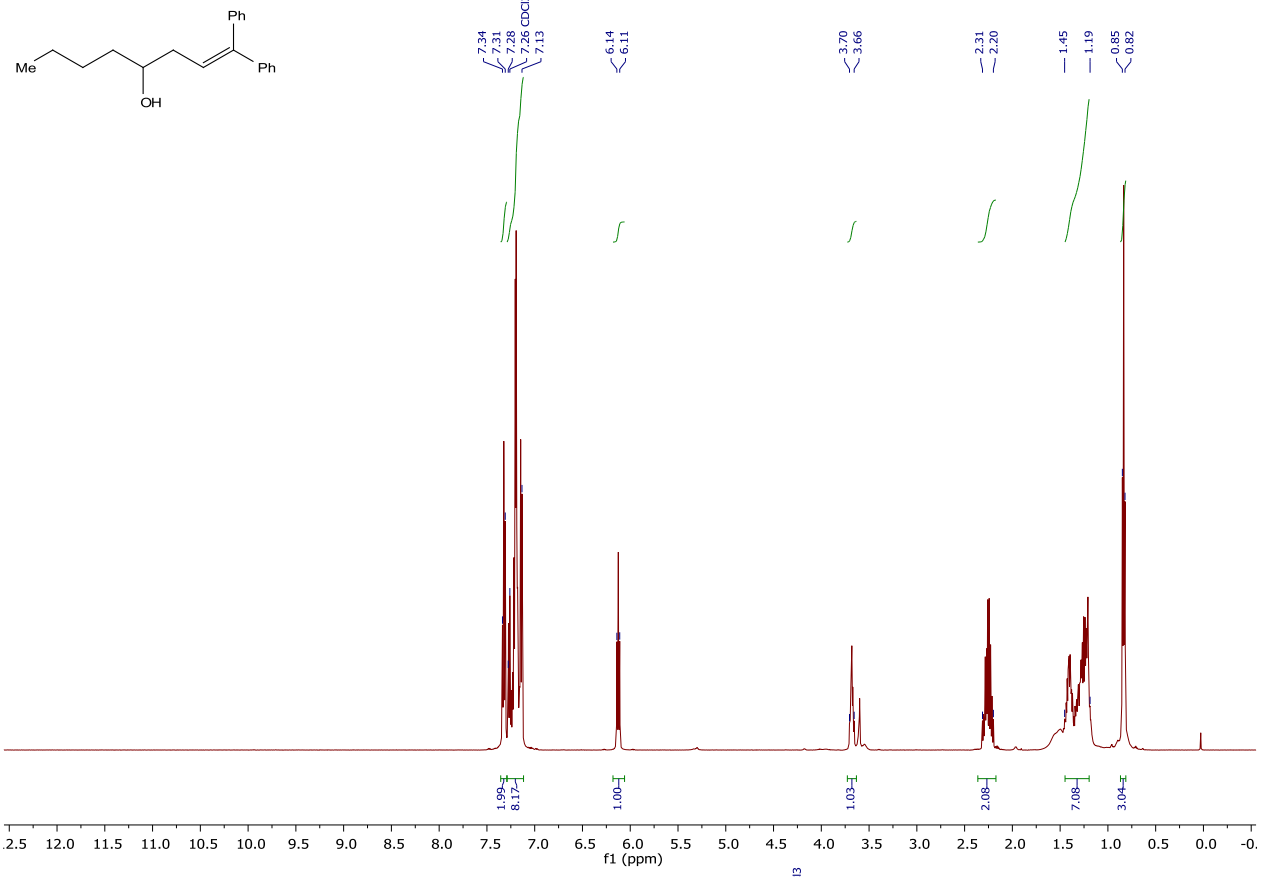

OH
149.62
108.78
77.16 CDCl3
71.14
43.92
41.10
35.69
30.84
24.34
20.99
f1 (ppm)

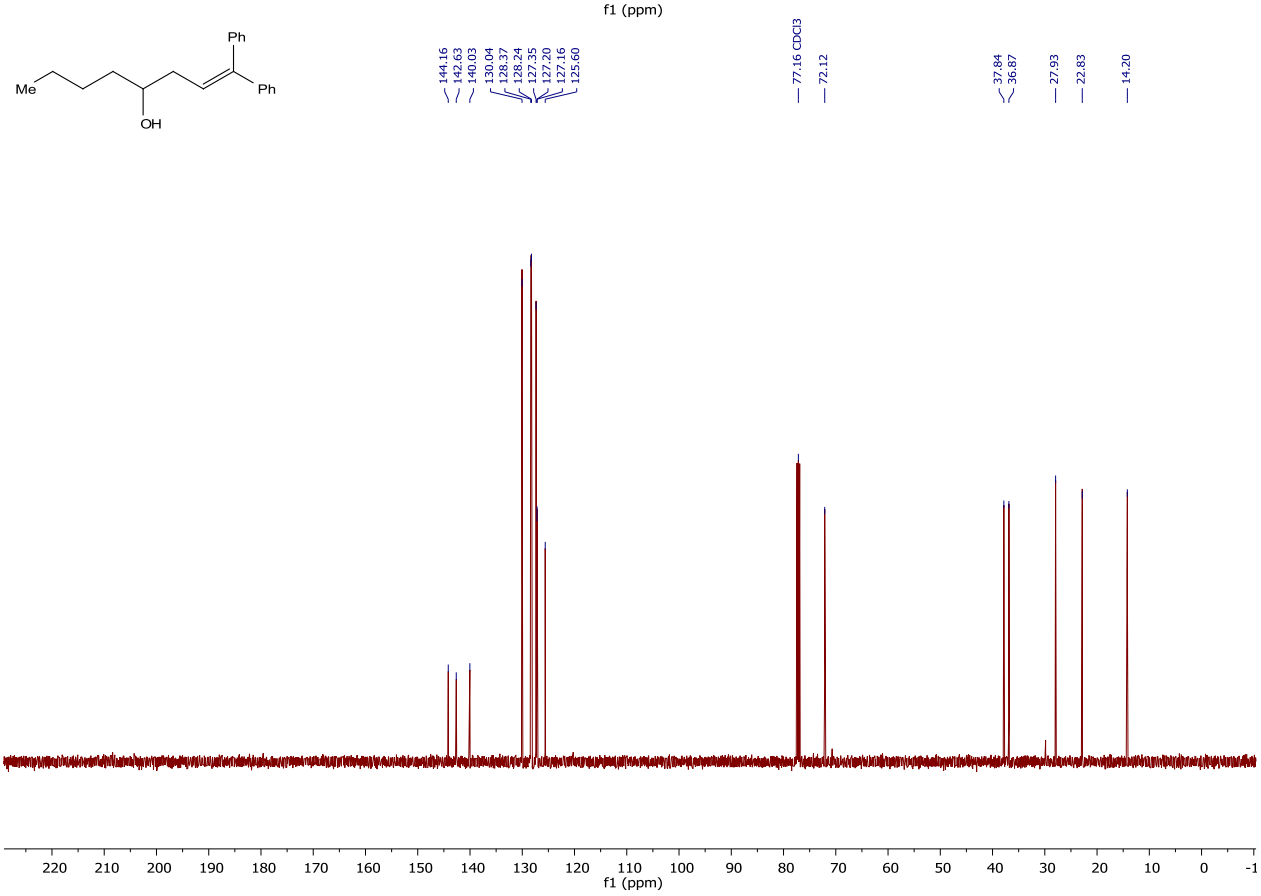

H2C
NHTs
7.77
7.75
7.32
7.30
7.26 CDCl3
4.85
4.83
4.55
4.53
3.70
3.63
2.51
2.46
2.43
2.37
2.30
2.25
2.17
2.10
2.04
1.92
1.85
1.57
1.51
2.08
2.14
2.08
1.00
1.01
1.07
3.12
1.21
1.12
1.07
1.03
1.01
f1 (ppm)

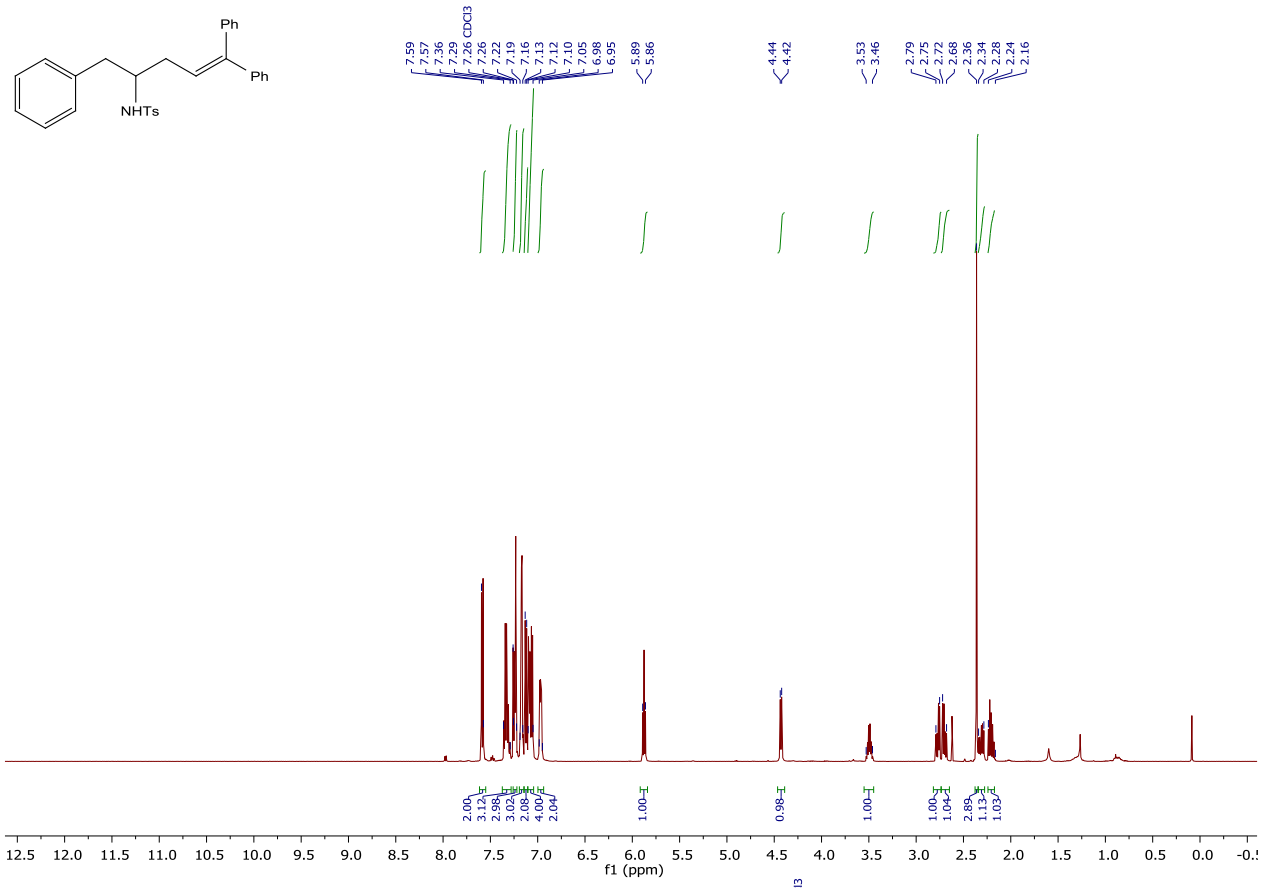

H2C
NHTs
147.98
143.53
137.86
129.85
127.22
107.73
77.16 CDCl3
54.61
40.63
33.45
29.94
21.69
f1 (ppm)

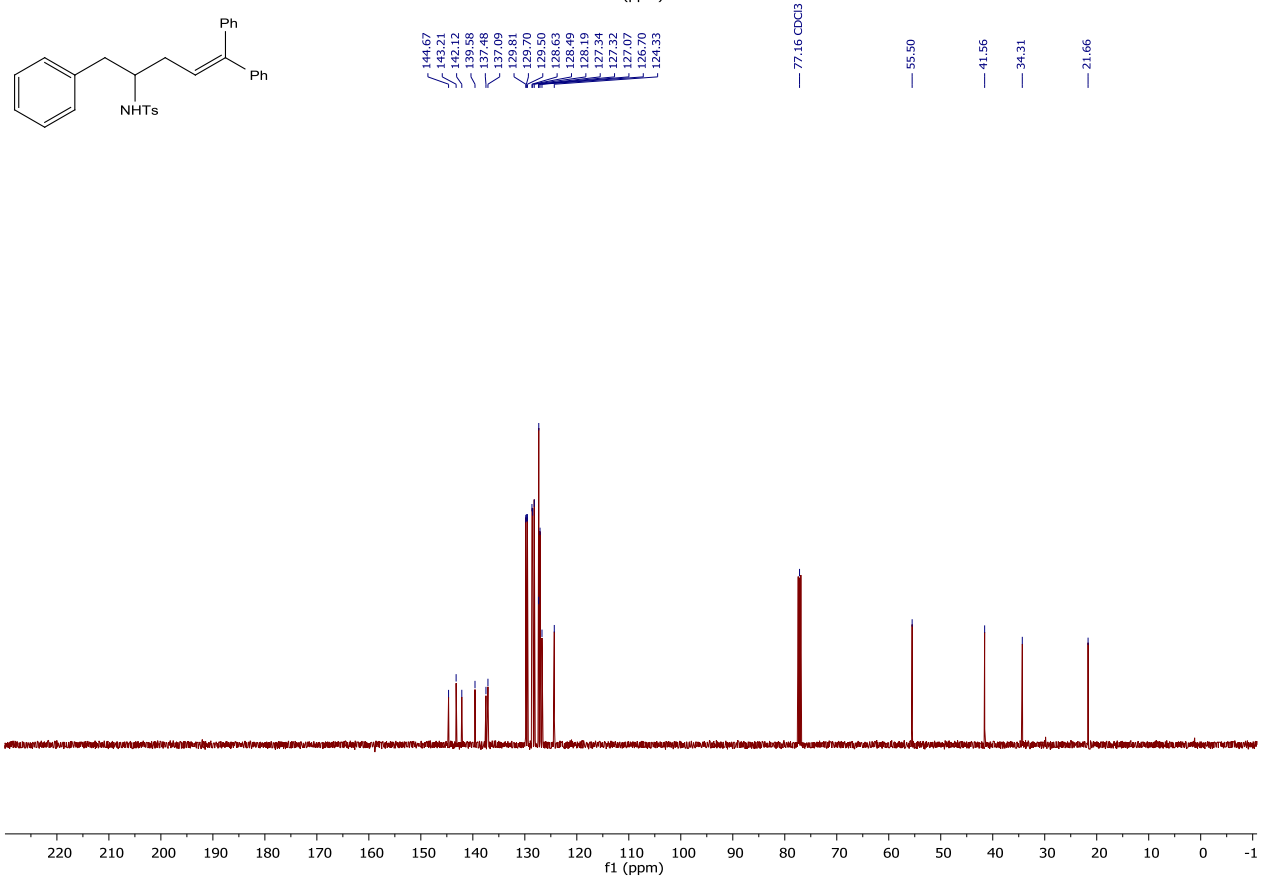

NHTs
7.79
7.74
7.32
7.26 CDCl3
7.12
6.31
6.28
4.62
4.60
3.79
3.67
2.81
2.73
2.71
2.49
2.44
2.42
2.40
2.26
2.03
1.99
1.73
1.66
1.60
1.53
4.00
14.70
1.95
1.97
2.00
1.08
4.02
2.99
3.19
2.91
1.97
0.91
1.22
f1 (ppm)

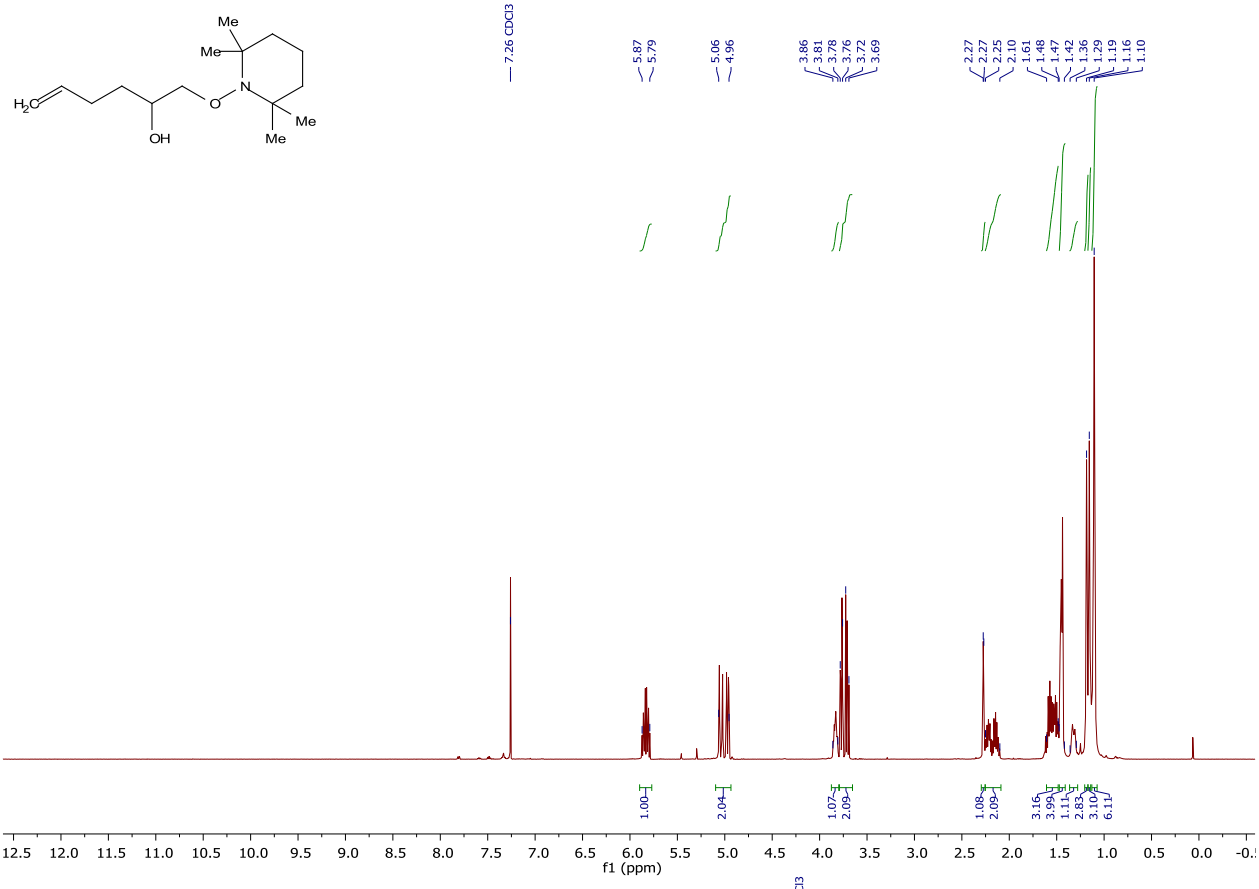

NHTs
143.54
141.40
141.21
138.00
137.97
137.92
129.87
129.83
128.41
128.36
128.17
128.06
127.26
126.35
126.31
123.47
123.44
77.16 CDCl3
55.30
53.68
43.06
38.81
33.81
32.52
32.44
28.50
21.66
f1 (ppm)

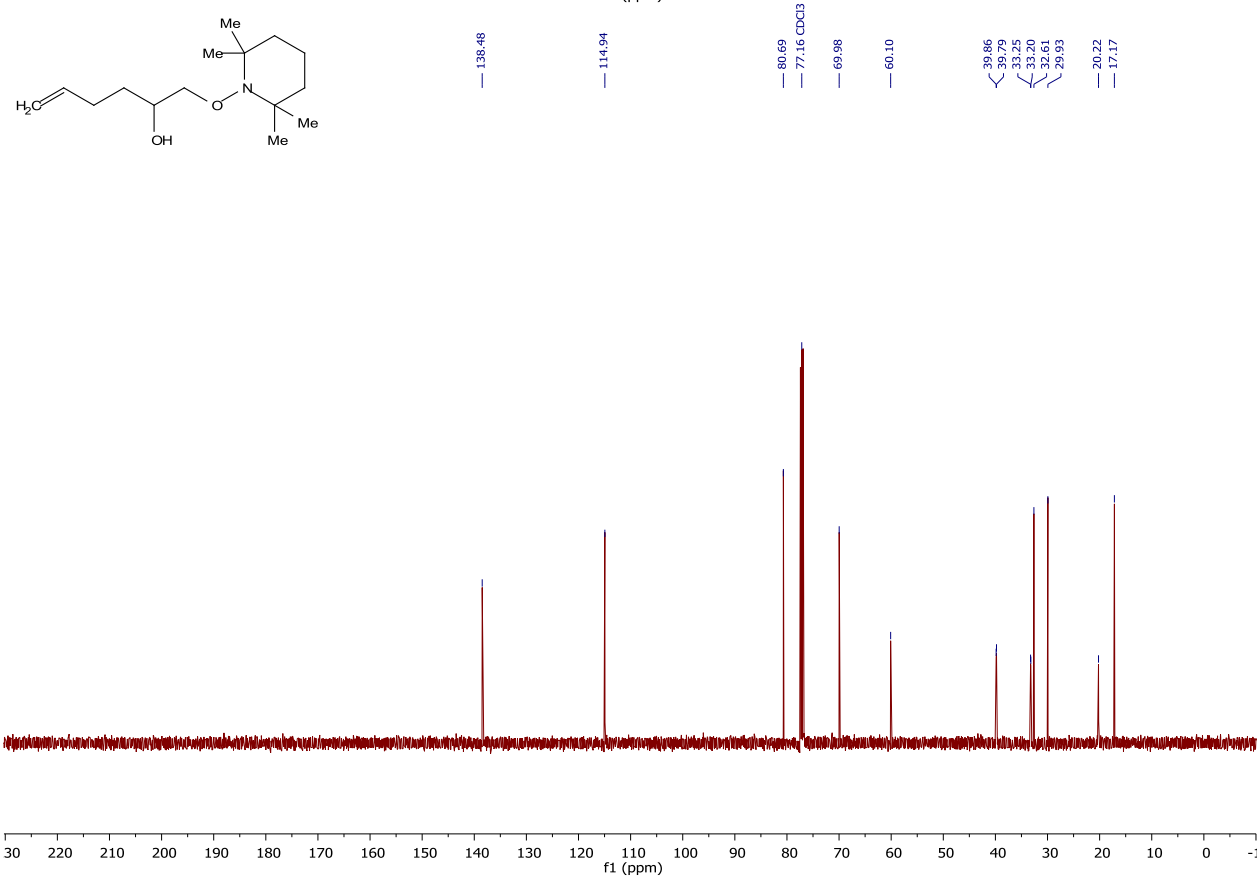

Ph
Me
Ph
OH
7.34
7.31
7.28
7.26 CDCl3
7.13
6.14
6.11
3.70
3.66
2.31
2.20
1.45
1.19
0.85
0.82
1.99
8.17
1.00
1.03
2.08
7.08
3.04
f1 (ppm)

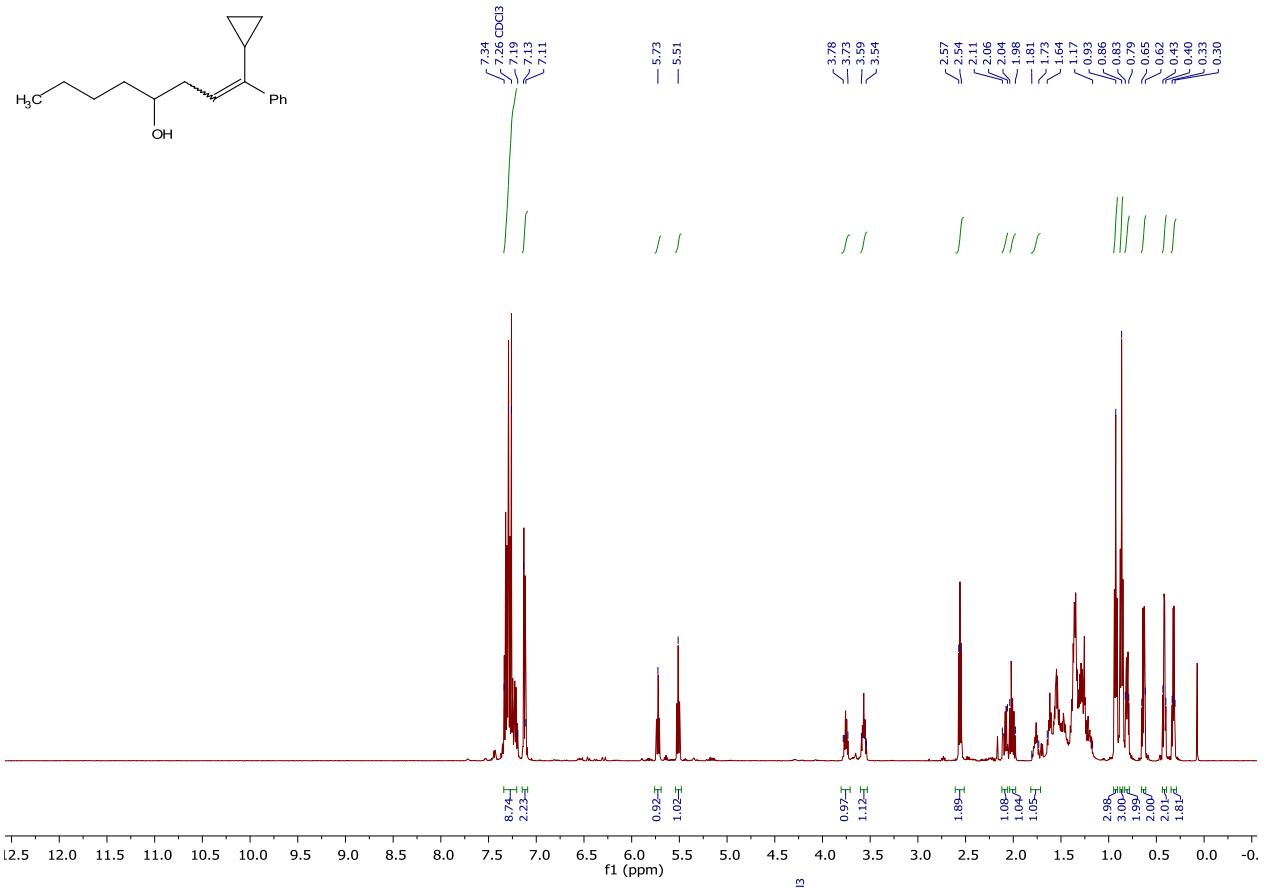

Ph
Me
Ph
OH
144.16
142.63
140.03
130.04
128.37
128.24
127.35
127.20
127.16
125.60
77.16 CDCl3
72.12
37.84
36.87
27.93
22.83
14.20
f1 (ppm)

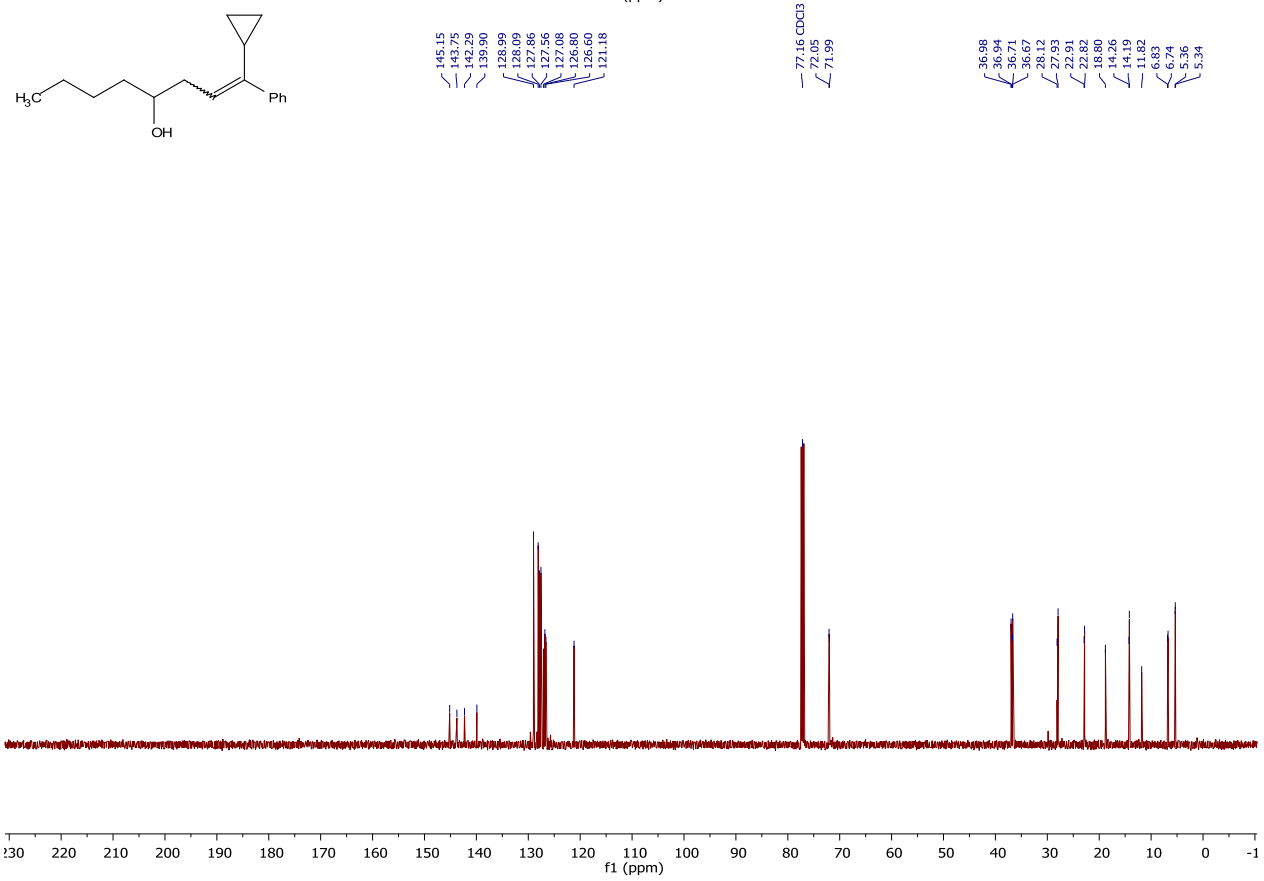

Ph
Ph
NHTs
7.59
7.57
7.36
7.29
7.26 CDCl3
7.26
7.22
7.19
7.16
7.13
7.12
7.10
7.05
6.98
6.95
5.89
5.86
4.44
4.42
3.53
3.46
2.79
2.75
2.72
2.68
2.36
2.34
2.28
2.24
2.16
2.00
3.12
2.98
3.02
2.08
4.00
2.04
1.00
0.98
1.00
1.00
1.04
2.89
1.13
1.03
f1 (ppm)

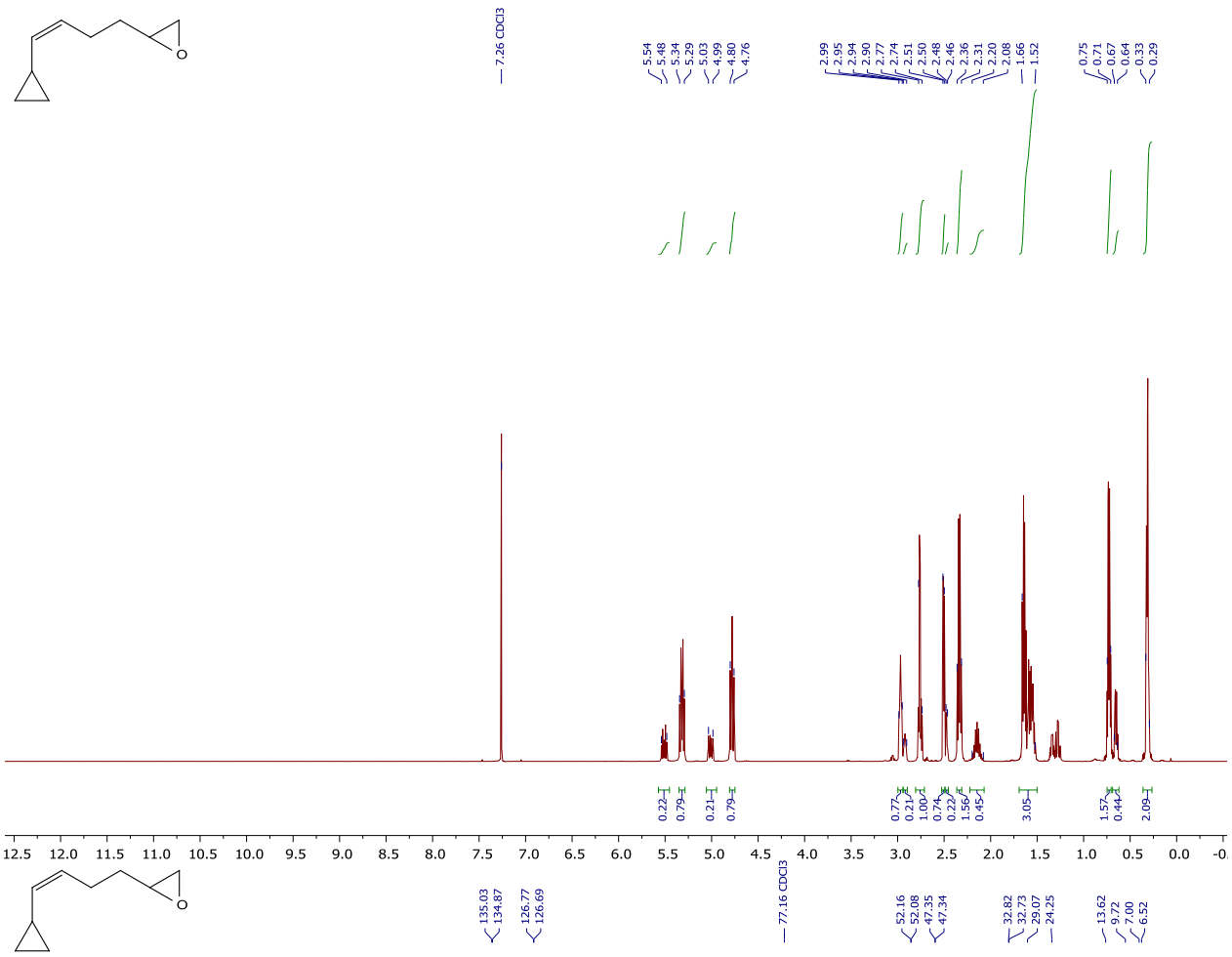

Ph
Ph
NHTs
144.67
143.21
142.12
139.58
137.48
137.09
129.81
129.70
129.50
128.63
128.49
128.19
127.34
127.32
127.07
126.70
124.33
77.16 CDCl3
55.50
41.56
34.31
21.66
f1 (ppm)

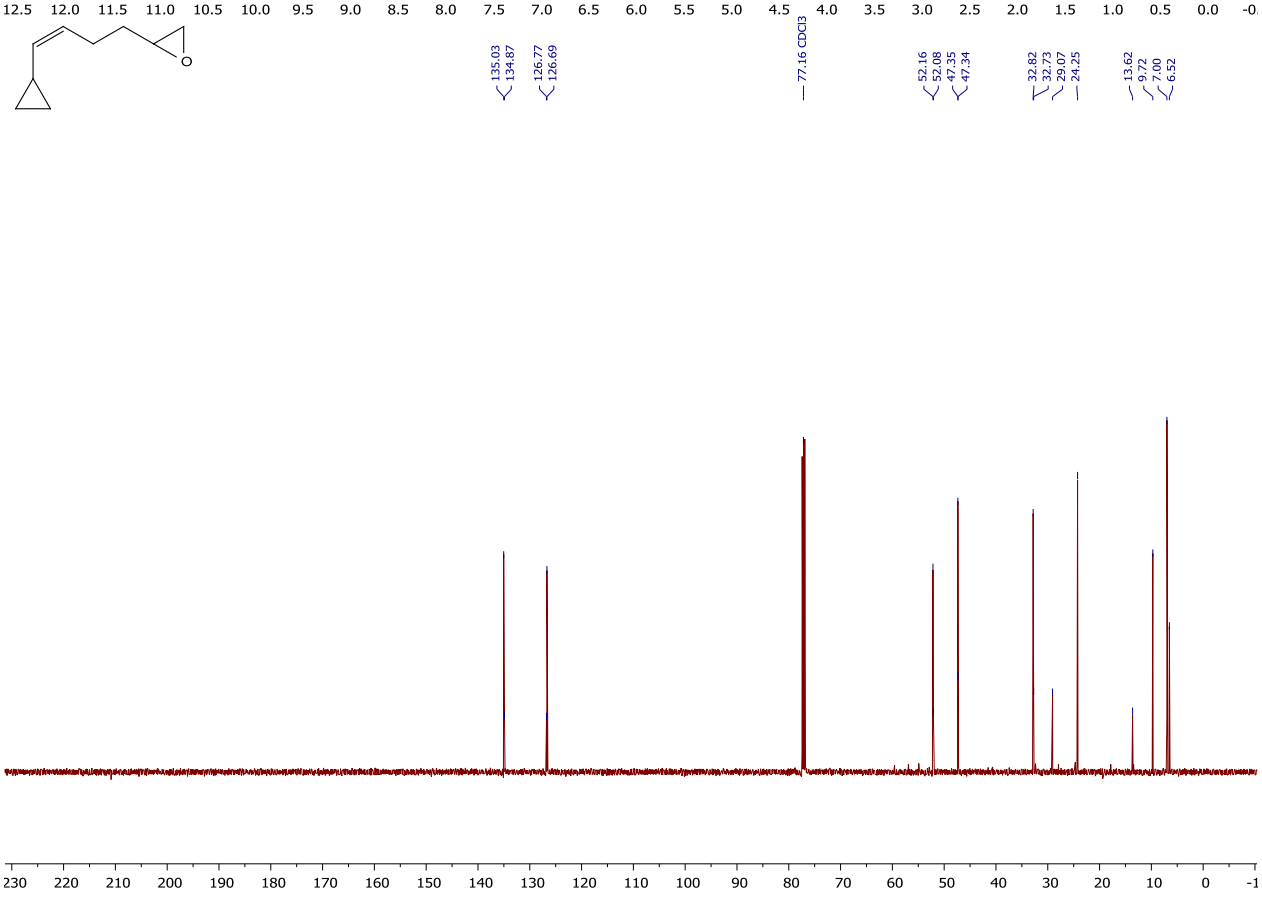

Me
Me
N
O
Me
Me
H2C
OH
7.26 CDCl3
5.87
5.79
5.06
4.96
3.86
3.81
3.78
3.76
3.72
3.69
2.27
2.27
2.25
2.10
1.61
1.48
1.47
1.42
1.36
1.29
1.19
1.16
1.10
1.00
2.04
1.07
2.09
1.08
2.09
3.16
3.99
1.11
2.83
3.10
6.11
f1 (ppm)

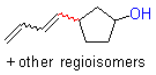

Me
Me
N
O
Me
Me
H2C
OH
138.48
114.94
80.69
77.16 CDCl3
69.98
60.10
39.86
39.79
33.25
33.20
32.61
29.93
20.22
17.17
f1 (ppm)


H3C
Ph
OH
7.34
7.26 CDCl3
7.19
7.13
7.11
5.73
5.51
3.78
3.73
3.59
3.54
2.57
2.54
2.11
2.06
2.04
1.98
1.81
1.73
1.64
1.17
0.93
0.86
0.83
0.79
0.65
0.62
0.43
0.40
0.33
0.30
8.74
2.23
0.92
1.02
0.97
1.12
1.89
1.08
1.04
1.05
2.98
3.00
1.99
2.00
2.01
1.81
f1 (ppm)


H3C
Ph
OH
145.15
143.75
142.29
139.90
128.99
128.09
127.86
127.56
127.08
126.80
126.60
121.18
77.16 CDCl3
72.05
71.99
36.98
36.94
36.71
36.67
28.12
27.93
22.91
22.82
18.80
14.26
14.19
11.82
6.83
6.74
5.36
5.34
f1 (ppm)

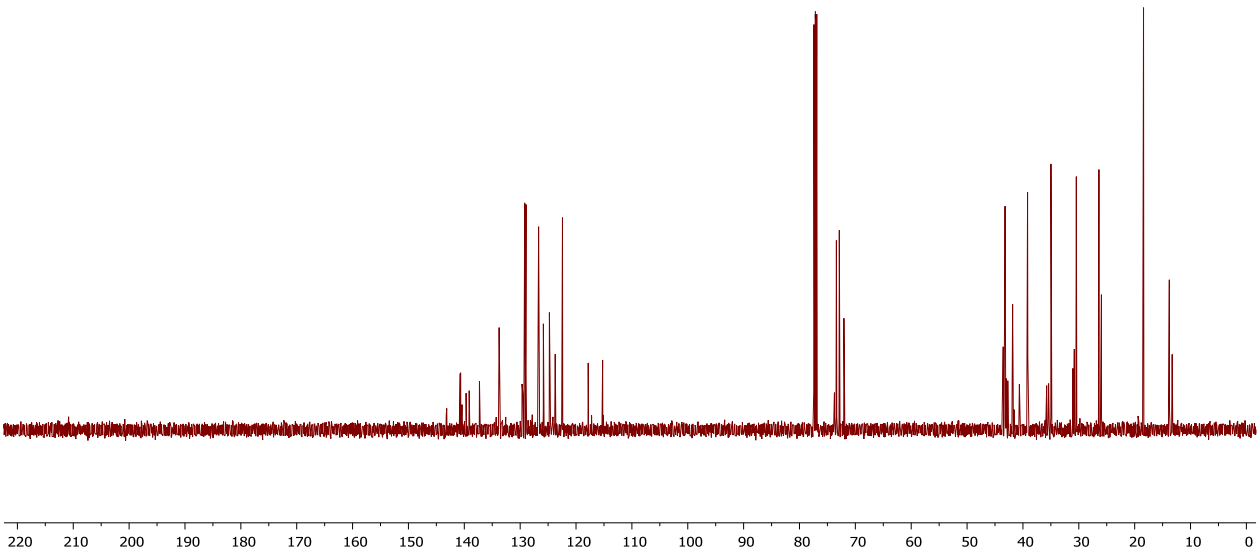

7.26 CDCl3
5.54
5.48
5.34
5.29
5.03
4.99
4.80
4.76
2.99
2.95
2.94
2.90
2.77
2.74
2.51
2.50
2.48
2.46
2.36
2.31
2.20
2.08
1.66
1.52
0.75
0.71
0.67
0.64
0.33
0.29
0.22
0.79
0.21
0.79
0.77
0.21
1.00
0.74
0.22
1.56
0.45
3.05
1.57
0.44
2.09
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

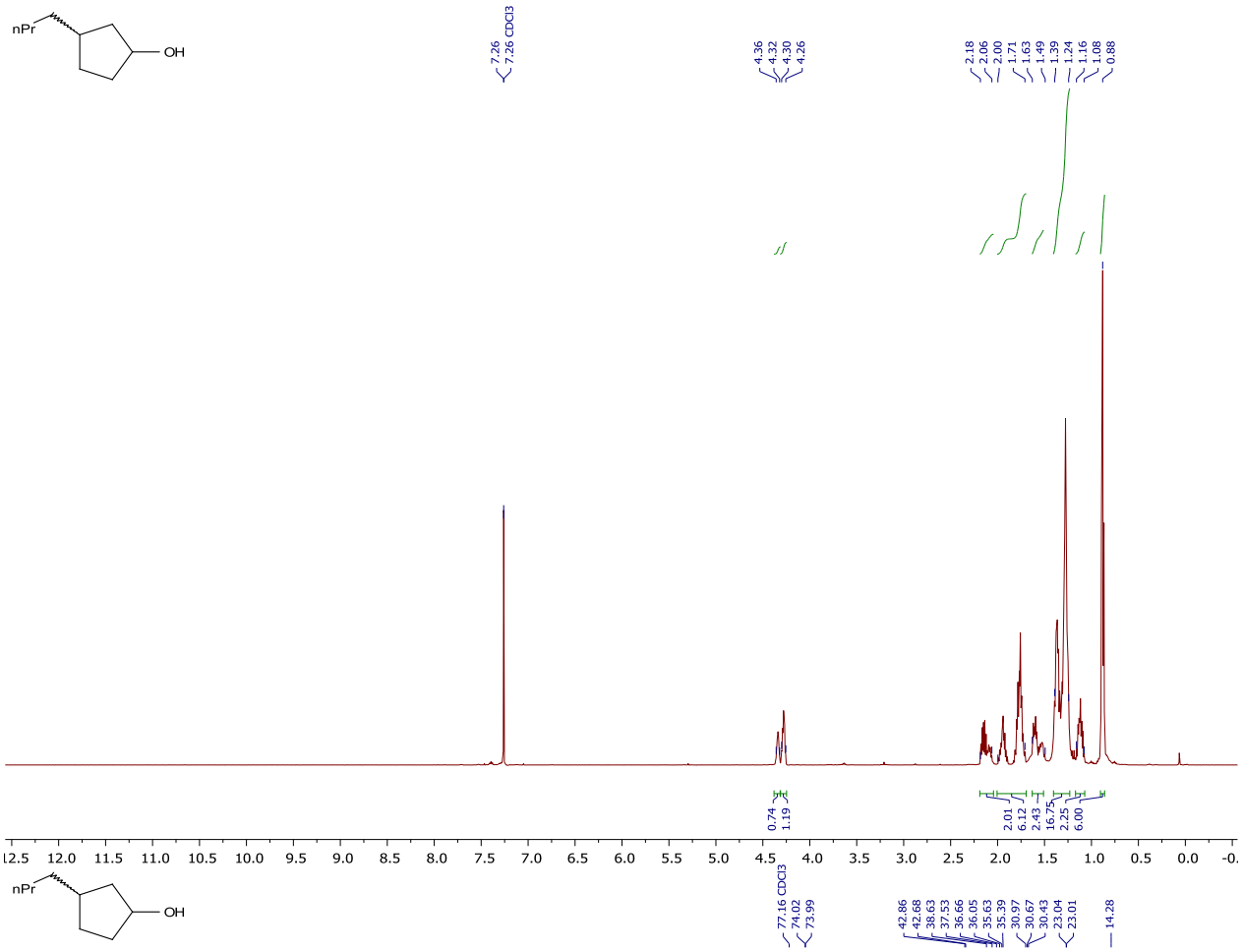

135.03
134.87
126.77
126.69
77.16 CDCl3
52.16
52.08
47.35
47.34
32.82
32.73
29.07
24.25
13.62
9.72
7.00
6.52
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1



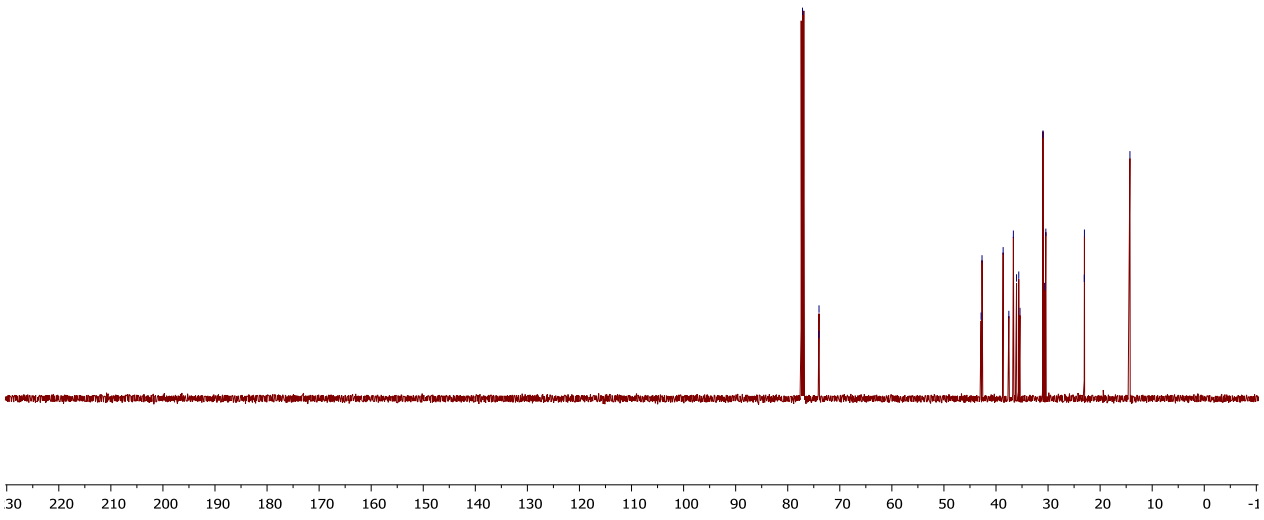
+other regioisomers

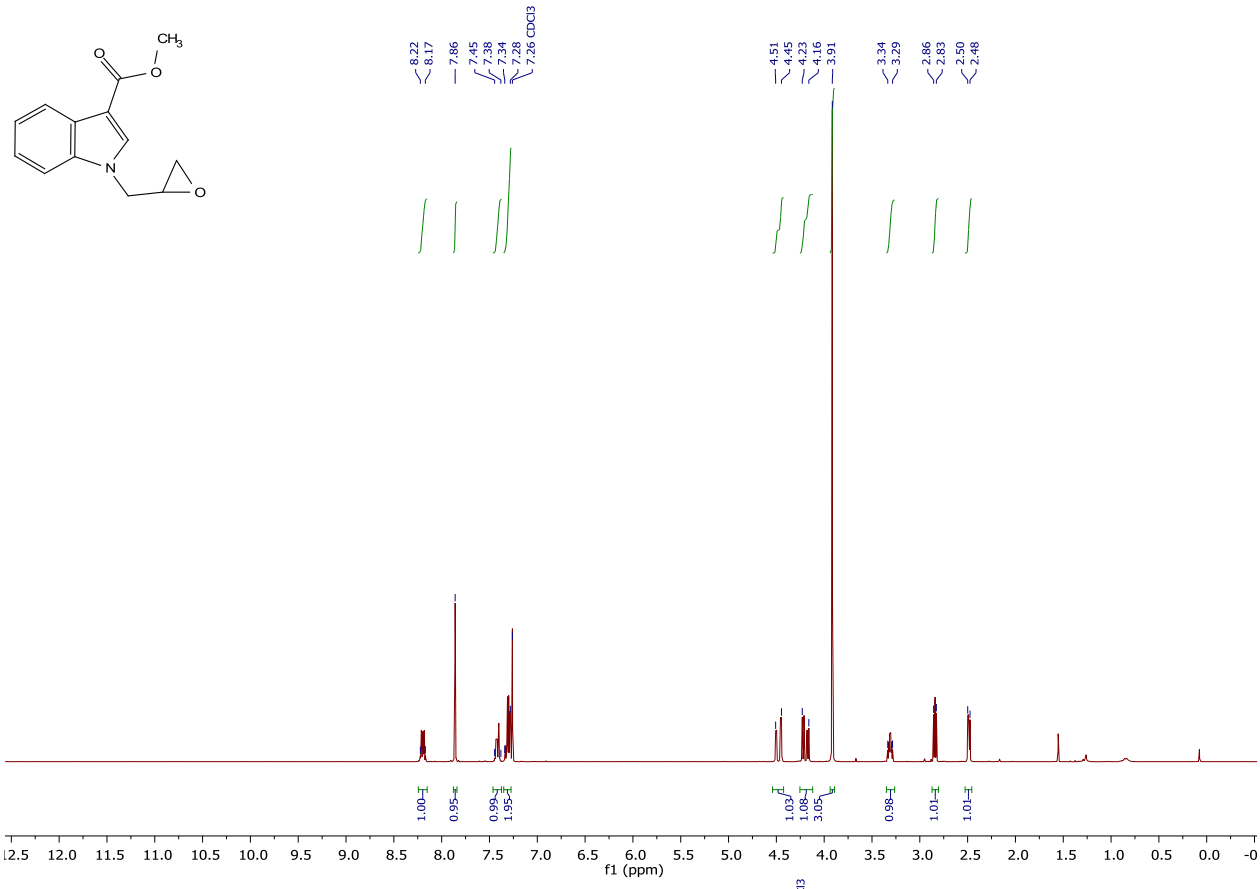
+other regioisomers

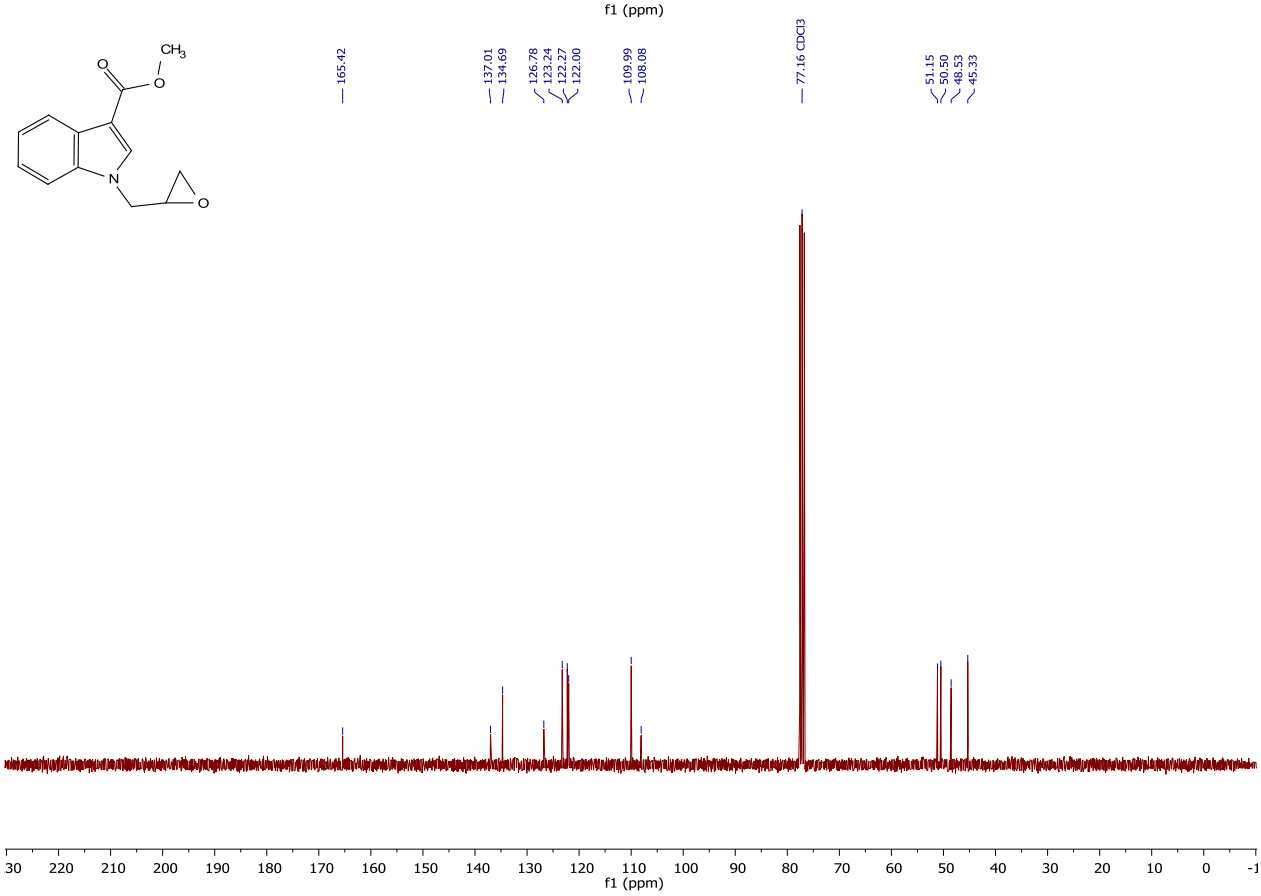


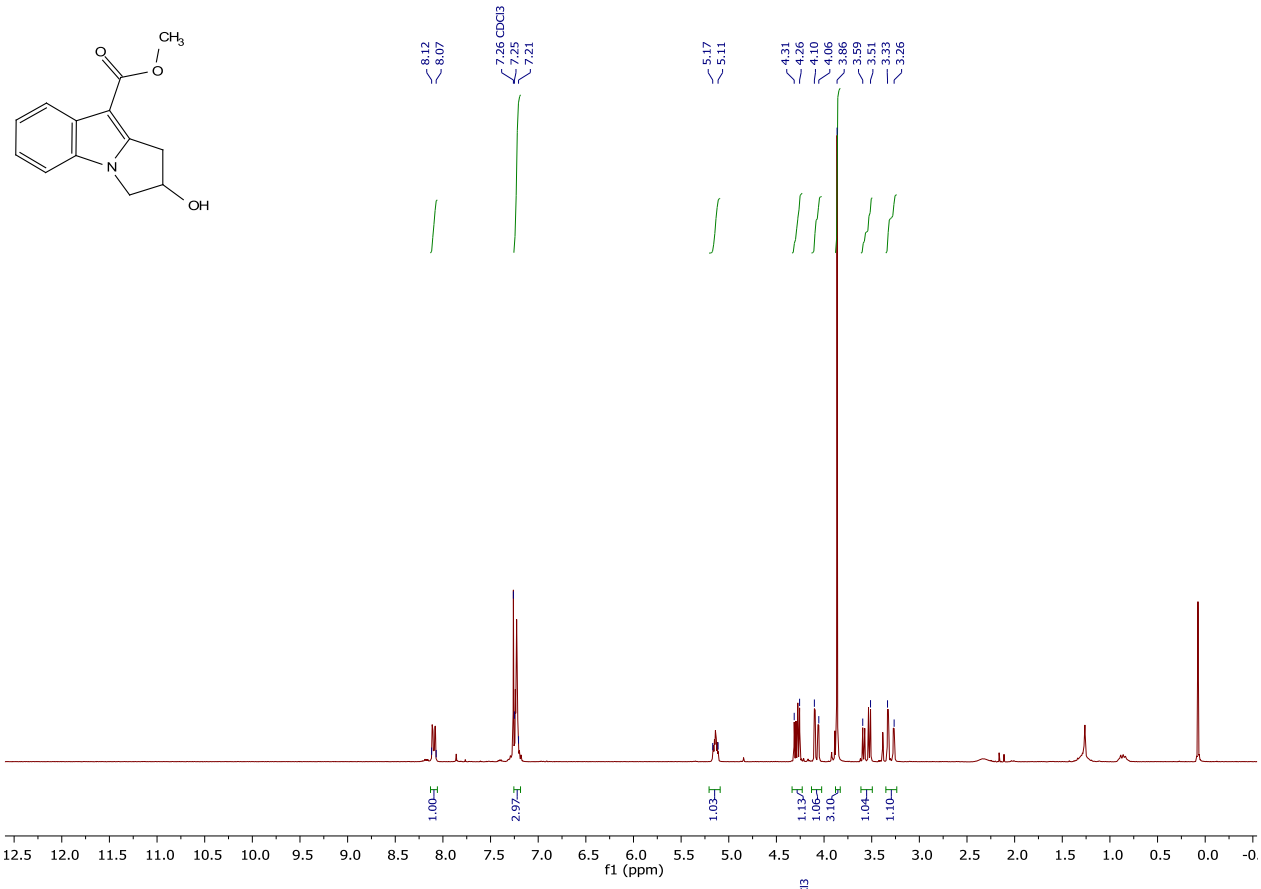

nPr
OH
7.26
7.26 CDCl3
4.36
4.32
4.30
4.26
2.18
2.06
2.00
1.71
1.63
1.49
1.39
1.24
1.16
1.08
0.88
0.74
1.19
2.01
6.12
2.43
16.75
2.25
6.00

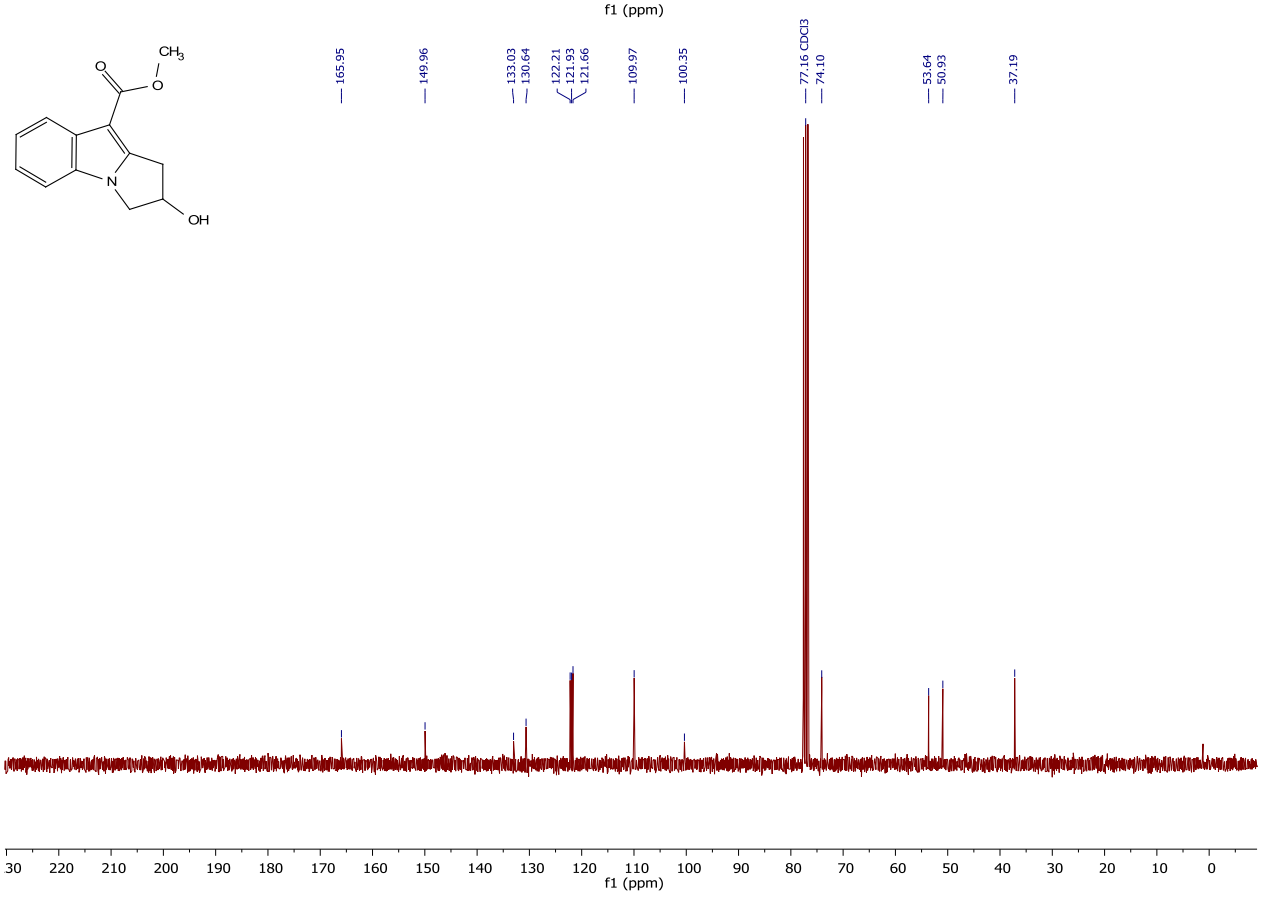
nPr
OH
77.16 CDCl3
74.02
73.99
42.86
42.68
38.63
37.53
36.66
36.05
35.63
35.39
30.97
30.67
30.43
23.04
23.01
14.28

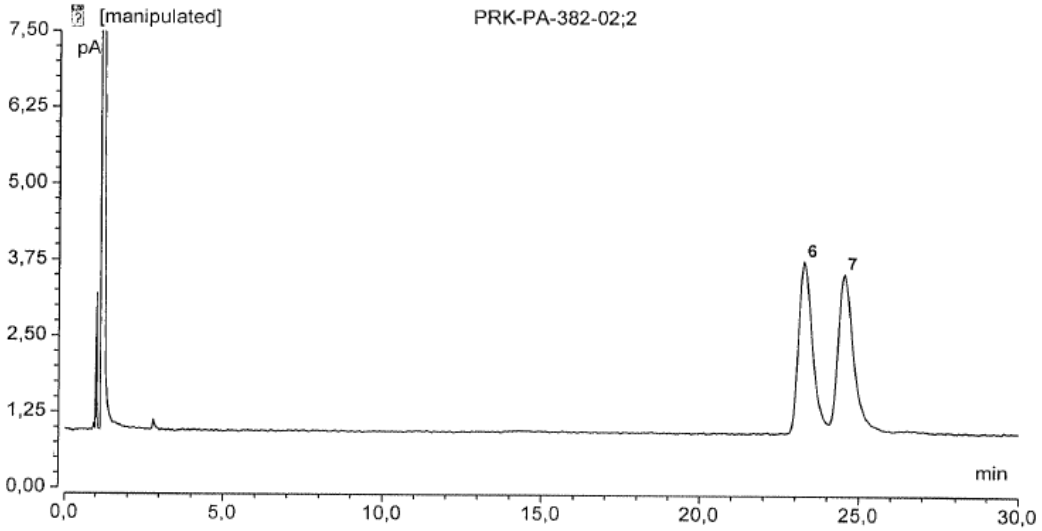



8.22
8.17
7.86
7.45
7.38
7.34
7.28
7.26 CDCl3
4.51
4.45
4.23
4.16
3.91
3.34
3.29
2.86
2.83
2.50
2.48
1.00
0.95
0.99
1.95
1.03
1.08
3.05
0.98
1.01
1.01
f1 (ppm)


165.42
137.01
134.69
126.78
123.24
122.27
122.00
109.99
108.08
77.16 CDCl3
51.15
50.50
48.53
45.33
f1 (ppm)


CH3
O
O
N
OH
8.12
8.07
7.26 CDCl3
7.25
7.21
5.17
5.11
4.31
4.26
4.10
4.06
3.86
3.59
3.51
3.33
3.26
1.00
2.97
1.03
1.13
1.06
3.10
1.04
1.10
f1 (ppm)


CH3
O
O
N
OH
165.95
149.96
133.03
130.64
122.21
121.93
121.66
109.97
100.35
77.16 CDCl3
74.10
53.64
50.93
37.19
f1 (ppm)



Sample:	**PRK-PA-382-02;2**	Instrument:	**GC_411**
Sequenz:	**95041 PRK-PA VD_634**	Measured:	**03.08.15 12:24**
Sequenz date:	**03.08.15**	Processing M.:	chiral 382-02
		Report-File:	ee-Verhältnis 382-01

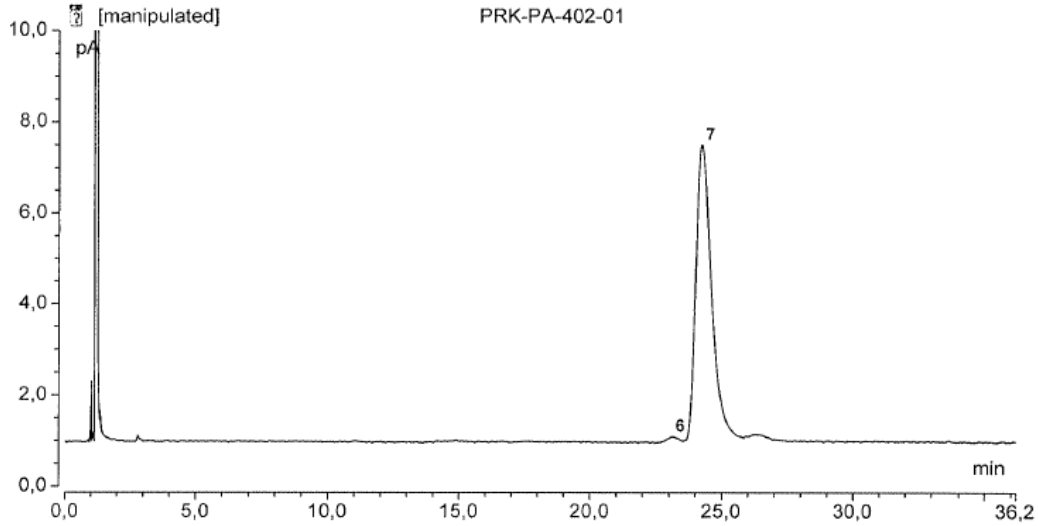
chirale Messung, Racematprobe
ee-Verhältnis, alpha-Wert: 1,057
gelöst in 200µL Dichlormethan
höher siedenden Komponenten im nachfolgenden Blindlauf ausgeheizt

No.	Ret.Time min	Rel.Area %	Peak Name
6	23,25	48,87	
7	24,52	51,13	

Instrument parameters:

Column:	25,0 m	Cyclodextrin-H/ in OV-1701 0,25 0,125df. G/632
Temperature:	220/ 45 iso/ 350	
Gas:	0,60 bar	Hydrogen
Sample size:	0,2 µL	

V. Diehl



Sample:	**PRK-PA-402-01**	Instrument:	**GC_411**
Sequenz:	**95218 PRK-PA VD_720**	Measured:	**04.09.15 08:59**
Sequenz date:	**04.09.15**	Processing M.:	chiral 382-02
		Report-File:	ee-Verhältnis 402-01

chirale Messung, gelöst in 200µL Dichlormethan
evtl. Verunreinigung unter Peak 7
höher siedenden Komponenten im nachfolgenden Blindlauf ausgeheizt
Zuordnung siehe Racematprobe PRK-PA-382-02;2 15/95041_634

No.	Ret.Time min	Rel.Area %	Peak Name
6	23,14	1,32	
7	24,27	98,68	

Instrument parameters:

Column:	25,0 m	Cyclodextrin-H/ in OV-1701 0,25 0,125df. G/632
Temperature:	220/ 45 iso/ 350	
Gas:	0,60 bar	Hydrogen
Sample size:	0,2 µL	

V. Diehl