Supporting Information

Regioselective ring-opening of epoxides towards Markovnikov alcohols: A metal-free catalytic approach using abnormal N-heterocyclic carbene

Sreejyothi P[a], Pallavi Sarkar[b], Supriti Dutta[b], Arpan Das[a], Swapan K Pati[b]* and Swadhin K Mandal[a]*

[a] Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur Campus, Nadia, 741246, West Bengal, India.

[b] Theoretical Sciences Unit, School of Advanced Materials (SAMat), Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India

*Correspondence to: swadhin.mandal@iiserkol.ac.in, pati@jncasr.ac.in

Contents: **Page**

1. General considerations and instrumentations ……S2
2. Experimental Details…….....S3
3. Characterization of products……..……S9
4. X-ray crystallographic details……...S16
5. ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra of products…… ……S18
6. Computational study...……...S45
7. References……..S75

1. General considerations and instrumentations

1.1 Materials and Methods

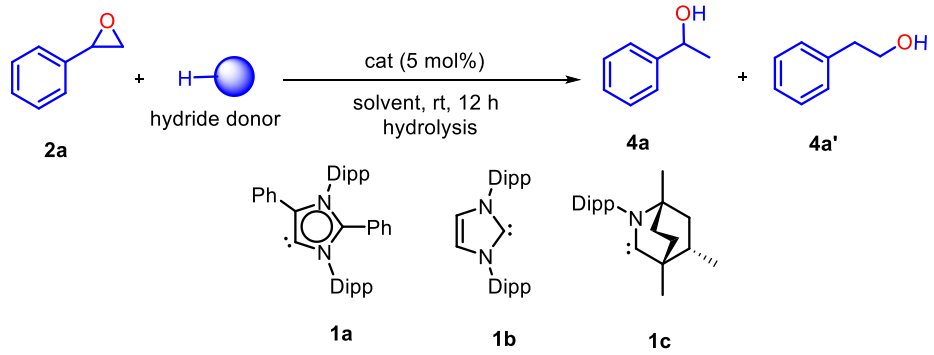
All reactions were carried out in oven-dried glassware (130 °C) under a dry and oxygen-free atmosphere (Argon) using the standard Schlenk line technique or inside an Ar-filled MBraun glovebox with a level of O_2 and H_2O maintained at 0.1 ppm. Before use, the reaction solvents were dried with a Na/benzophenone mixture or CaH_2. aNHC (**1a)**[1], iPr (**1b**)[2] BICAAC (**1c**)[3], was synthesized according to the literature procedure. All chemicals were either purchased from Sigma-Aldrich, Alfa Aesar, Merck or Spectrochem or used as received or synthesized following the reported procedure. The substrates (**2c-2f**,[4] **2i**,[5] **2y**,[6] **2z,**[7] **2aa**[8] were synthesised according to the literature procedure. Thin-layer chromatography (TLC) was performed on a Merck 60 F254 silica gel plate (0.25 mm thickness). Column chromatography was performed on a Merck 60 silica gel (100−200 mesh). The ^{1}H,$^{13}C\{^{1}H\}$,$^{19}F\{^{1}H\}$, $^{11}B\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectra were recorded on Bruker Avance III 500 MHz spectrometer with residual undeuterated solvent as internal standard. Chemical shifts (δ) are given in ppm, and J values are given in Hz. X-ray crystallographic measurements were performed using XtaLAB Synergy, Dualflex, HyPix3000 diffractometer at 100K. High-resolution mass spectrometry (HRMS) was obtained on a Bruker maXis impact spectrometer.

2. Experimental Details

2.1 Optimization study for Markovnikov ring-opening of epoxides.

A 25 mL Schlenk tube equipped with a stir bar was charged with styrene oxide (**2a**, 0.3 mmol) and catalyst (5 mol%) in the solvent under an argon atmosphere. In order to achieve optimized reaction conditions, various catalysts, hydride donors, and solvents were screened at room temperature for 12 h. Conversion to the product was analyzed using ^{1}H NMR spectroscopy. Detailed optimization is given in table S1.

Table S1: Optimization of reaction conditions for ring-opening of epoxide

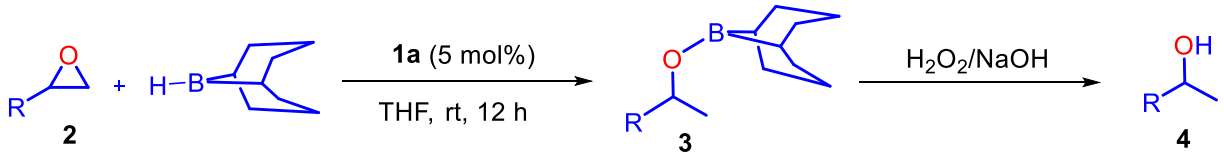


Entry	Catalyst	Hydride source	Solvent	Ratio (b:l)	Conversion (%)
1.	aNHC	HBPin	THF	n.d	NR
2.	aNHC	BH_3.THF	THF	n.d	NR
3.	aNHC	$PhSiH_3$	THF	n.d	NR
4.	aNHC	Ph_2SiH_2	THF	n.d	NR
5.	aNHC	$NH_3.BH_3$	THF	n.d	NR
6.	**aNHC**	**9-BBN**	**THF**	**94:6**	**99**
7.	aNHC	9-BBN	Toluene	n.d	NR
8.	aNHC	9-BBN	Acetonitrile	n.d	NR
9.	aNHC	9-BBN	Dioxane	85:15	99
10.	iPr	9-BBN	THF	87:13	99
11.	BICAAC	9-BBN	THF	85:15	99
12.	--	9-BBN	THF		24%

Reaction conditions: Epoxide (0.3 mmol), Hydride donor (0.33 mmol), Cat (0.015 mmol, 5 mol%), and solvent (1 mL), n.d stands for “not detected”, NR stands for “No Reaction”

2.2. General Procedure for the aNHC (1a) catalysed Markovnikov ring-opening of epoxides.

A 25 mL Schlenk tube equipped with a stir bar was charged with corresponding epoxide (0.3 mmol) and catalyst **1a** (5 mol%) in tetrahydrofuran under an argon atmosphere. After 2 minutes of stirring, the 9-BBN was added to the reaction mixture. The reaction tube was sealed, and the reaction mixture was stirred at room temperature for 12 hours. Upon completion of the reaction, the solvent was evaporated under reduced pressure. The reaction mixture was hydrolyzed with either H_2O_2 or NaOH. The final product was purified using silica gel column chromatography (Merck, 100-200 mesh). Using a hexane-ethyl acetate mixture as the eluent, analytically pure secondary alcohols were collected and identified using ^{1}H and ^{13}C NMR spectroscopy in $CDCl_3$ solvent.



R = aromatic, alkyl

2.3. Interaction between aNHC and epoxide

A screw cap NMR tube is charged with aNHC (**1a**, 15mg, 0.05 mmol) in C_6D_6(500 µL) and an equimolar amount of 4-Chlorophenyl glycidyl ether (**2g,** 0.05 mmol) is added to it. The reaction was monitored using ^{1}H NMR spectroscopy which shows that, a new set of peaks appeared, which were assigned to ring-opened epoxide-hydrogens with a downfield shift along with unreacted epoxide hydrogens. A stacked plot for ^{1}H NMR spectra for **1a**, **2g** and reaction mixture is given below (Figure S1.)

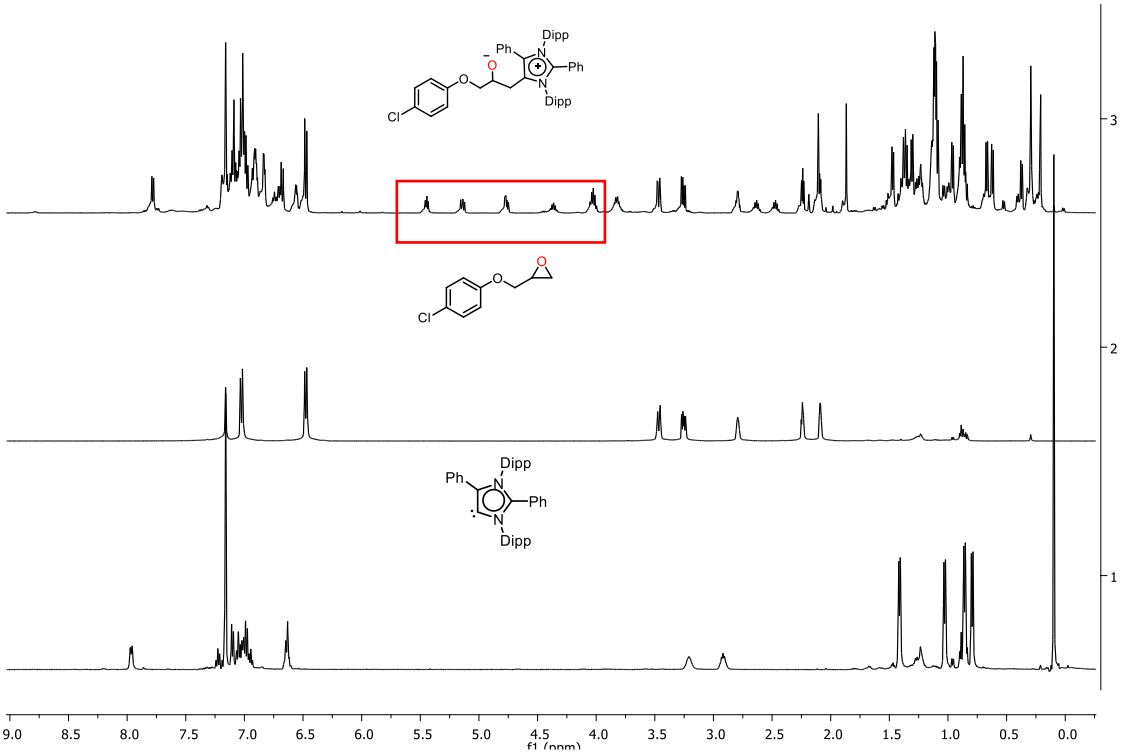
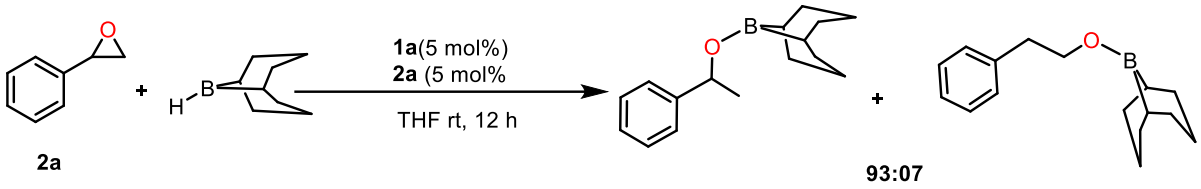


Figure S1. Stack plot indicating the interaction between **1a** and **2g.** ^{1}H NMR spectrum of **1a** is given at the bottom, **2g** in the middle, and a reaction mixture of **1a** and **2g** on top. All NMR spectra are recorded in C_6D_6. The peaks marked in the red box represent the new peaks that appeared as a result of the interaction between aNHC and epoxide.

2.4. Control reaction using aNHC-epoxide as catalyst.

A 25 mL Schlenk tube is equipped with **1a** (10 mg, 0.018 mmol) and **2a** (2.1µL, 0.018 mmol) in THF and stirred at rt for 10 min. In to the green solution added **2a** (43 µL, 0.37 mmol) and 9-BBN (50 mg, 0.40 mmol) sequentially and kept for stirring at room temperature for 12 h. After completion of the reaction, reaction mixture ^{1}H NMR analysis shows that **2a** was successfully converted to corresponding hydroborated compounds with Markovnikov product as major product (93:07).



2.5. General procedure for the synthesis of ring-opened epoxide trapped with BCF (5)

A 25 mL Schlenk flask equipped with a stir bar is charged with aNHC (**1a**, 30mg, 0.05 mmol) in toluene (5 mL) and an equimolar amount of 4-chlorophenyl glycidyl ether (**2g,** 0.05 mmol) was added under argon atmosphere. The reaction colour changed from brown to deep green. After 10 minutes of stirring, an equimolar amount of tris(pentafluorophenyl)borane (0.05 mmol) was added to the reaction mixture resulting in precipitation of the white colour compound. The solvent was evaporated under reduced pressure and the white precipitate was washed with hexane thrice to obtain the Markovnikov aNHC-ring-opened adduct trapped with tris(pentafluorophenyl)borane (**5**). The colourless crystals of **5** were successfully grown from THF/Hexane mixture under an argon atmosphere at -25 ^{o}C. The compound **5** was characterized through SCXRD, as well as 1H, ^{13}C{1H}, ^{11}B{1H} and ^{19}F{^{1}H} NMR and HRMS spectroscopies.

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.57-7.54 (t, 1H), 7.48-7.45 (t, 1H), 7.35-7.29 (m, 3H), 7.23-7.22 (m, 1H), 7.19-7.13 (m, 8H), 7.08-7.06 (m, 2H), 7.00-6.98 (m, 2H), 6.53-6.51 (d, 2H), 3.96-3.94 (m, 1H), 3.89-3.87(m, 1H), 3.69-3.66 (m, 1H), 3.21-3.17 (m, 1H), 3.00-2.95 (m, 1H), 2.87-2.84 (sep, 1H), 2.70-2.64 (s, 1H), 2.45-2.40 (sep, 1H), 2.16-2.14 (sep, 1H), 1.16-1.12 (m, 6H), 0.97-0.93 (m, 6H), 0.89-0.81 (m, 6H), 0.65-0.55 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 157.1, 149.0, 147.2, 146.2, 145.2, 145.1, 144.8, 144.7, 139.4, 137.5, 135.4. 134.8, 132.3, 132.1, 130.2, 130.1, 129.4, 129.0, 128.7, 128.4, 128.2, 126.2, 126.0, 125.7, 125.6, 125.5, 125.3, 124.1, 121.6. 115.3, 71.9, 68.5, 32.9, 29.1, 28.9, 28.8, 28.5, 25.0, 24.3, 24.1, 24.0, 23.7, 23.7, 23.6, 23.5. ^{19}F NMR (470 MHz, $CDCl_3$, 25 ^{o}C): δ = -132.1 (d), -161.7 (t), -166.1 (t). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ = -3.49 ppm.

HRMS: m/z calc. for $C_{66}H_{53}BClF_{15}N_2O_2$ $[M+Na]^+$ 1259.3541, found 1259.3554.

Figure S2. ^1H NMR (in $CDCl_3$) spectrum of **5**

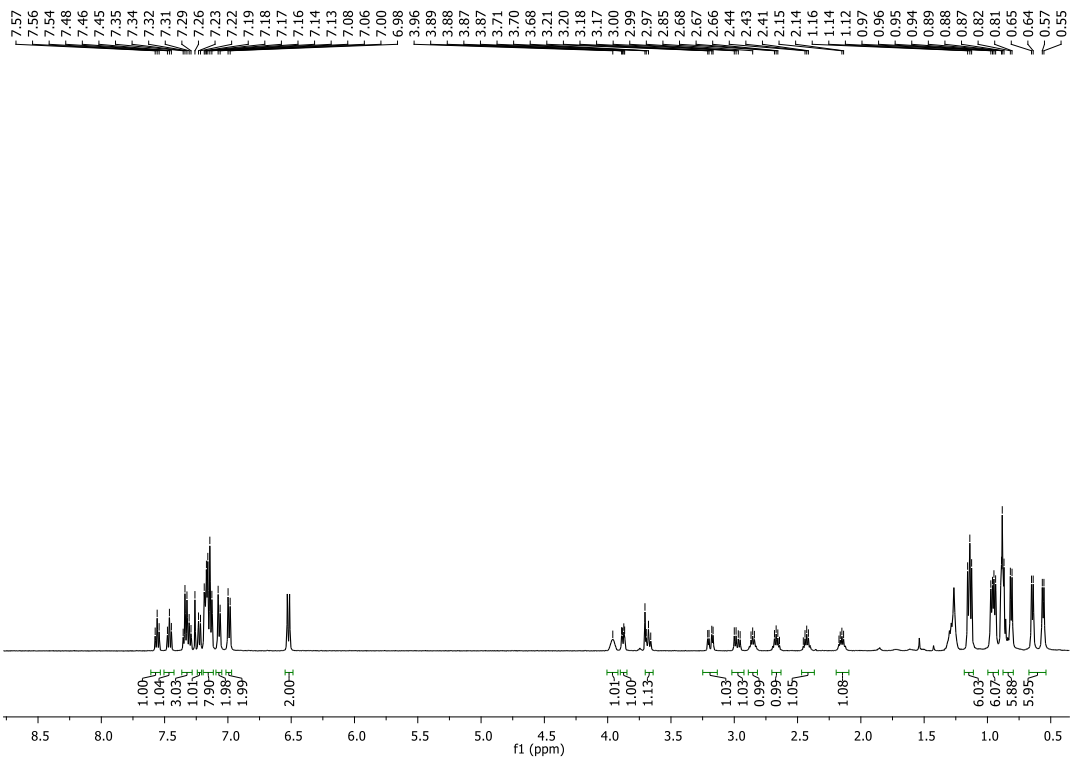


Figure S3. $^{13}C\{^1H\}$ NMR (in $CDCl_3$) spectrum of **5**

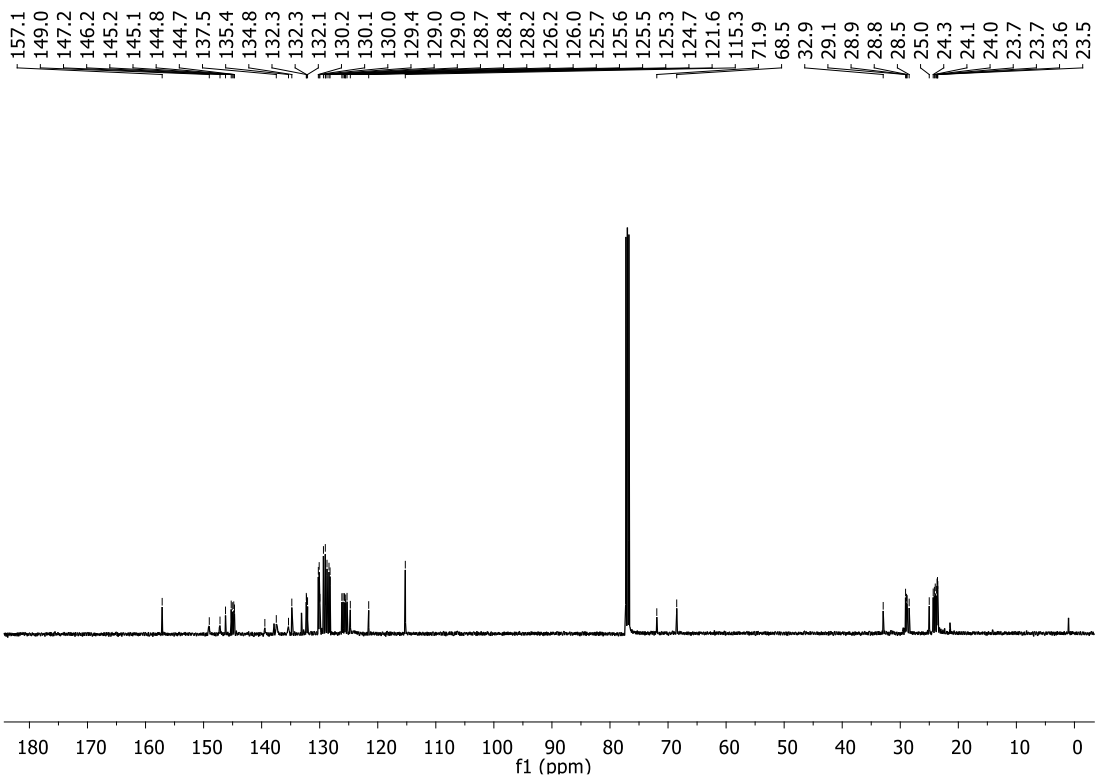


Figure S4. $^{11}B\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of **5**

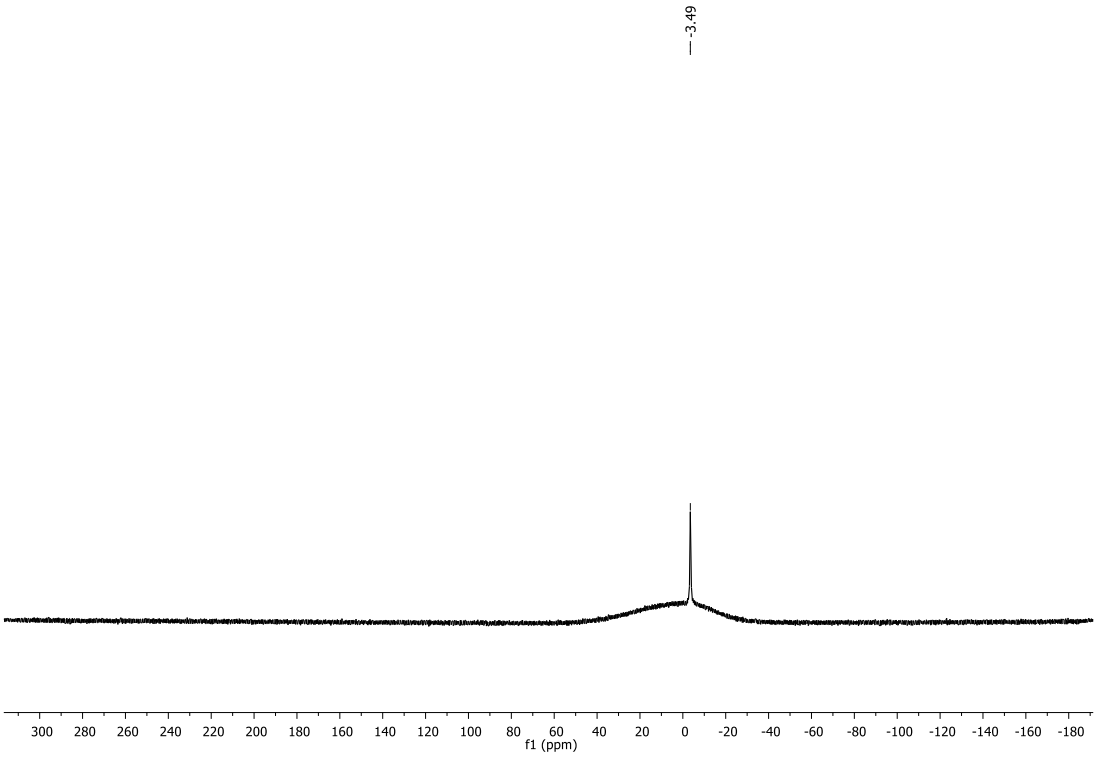
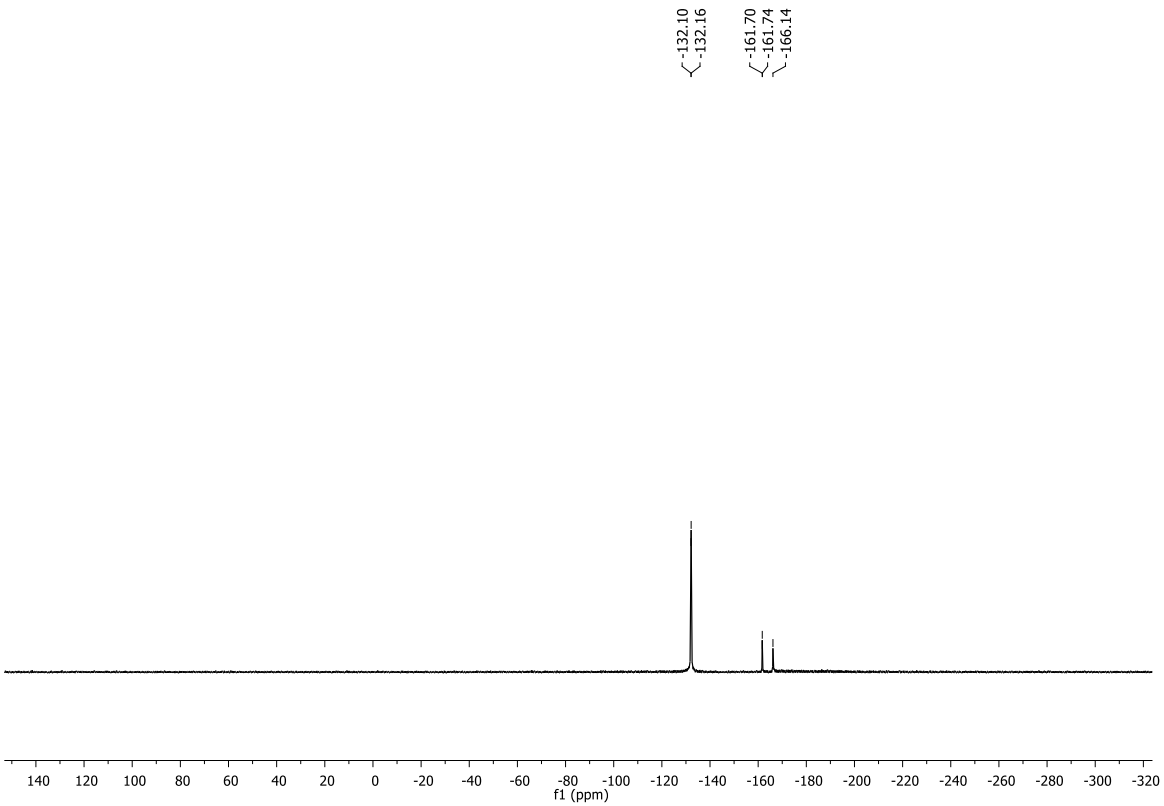


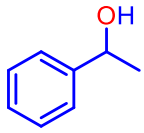
Figure S5. $^{19}F\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of **5**



3. Characterization of Products.

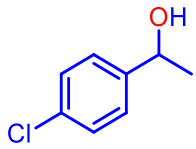
3.1 Characterization of secondary alcohols

1-phenylethan-1-ol (4a)[9]



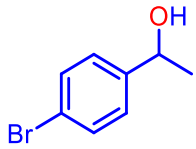
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.39-734 (m, 4H), 7.29-7.28 (m, 1H), 4.92 (q, 1H), 1.80 (bs, 1H), 1.51-1.50 (d, J = 5.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 145.8, 128.5, 127.5, 125.4, 70.7, 25.1 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (95:5 v/v) as an eluent.

1-(4-chlorophenyl)ethan-1-ol (4b)[9]



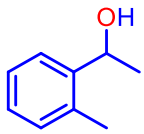
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.32-7.28 (m, 4H), 4.86 (q, 1H), 2.09 (bs, 1H), 1.46 (d, J = 10.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 144.2, 133.1, 128.6, 126.8, 69.7, 25.3 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (95:5 v/v) as an eluent.

1-(4-bromophenyl)ethan-1-ol (4c)[9]



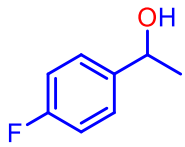
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.40 (d, J = 10.0 Hz, 2H), 7.18 (d, J = 10.0 Hz, 2H), 4.80 (q, 1H), 1.78 (bs, 1H), 1.40 (d, J = 10.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 144.8, 131.6, 127.1, 121.2, 69.8, 25.2 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (95:5 v/v) as an eluent.

1-(o-tolyl)ethan-1-ol (4d)[10]



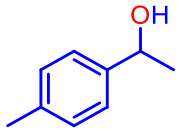
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.52 (d, J = 10.0 Hz, 1H), 7.24 (t, J = 5.0 Hz, 1H), 7.19-7.13 (m, 2H), 5.14 (q, 1H), 2.35 (s, 3H), 1.72 (bs, 1H), 1.48 (d, J = 10.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 143.8, 134.2, 130.4, 127.2, 126.4, 124.4, 66.8, 23.9, 18.9 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (95:5 v/v) as an eluent.

1-(4-fluorophenyl)ethan-1-ol (4e)[11]



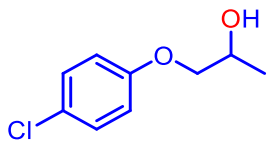
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.35-7.27 (m, 2H), 7.04-7.01 (m, 2H), 4.89 (q, 1H), 1.81 (bs, 1H), 1.48 (d, J = 5.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 163.1, 161.1, 145.1 (d), 127.1 (d), 115.3 (d), 69.8, 25.3. ^{19}F NMR (470 MHz, $CDCl_3$, 25 ^{o}C): δ = -115.4 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (95:5 v/v) as an eluent.

1-(p-tolyl)ethan-1-ol (4f)[9]



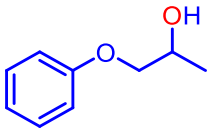
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ =7.19 (d, J = 10.0 Hz, 2H), 7.09 (d, J = 10.0 Hz, 2H), 4.79 (q, 1H), 2.27 (s, 3H), 1.72 (bs, 1H), 1.41 (d, J = 10.0 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ =142.9, 137.2, 129.2, 125.3, 70.3, 25.1, 21.1 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (95:5 v/v) as an eluent.

1-(4-chlorophenoxy)propan-2-ol (4g)[12]



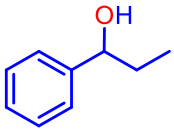
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.23 (d, J = 10.0 Hz, 2H), 6.83 (d, J = 10.0 Hz, 2H), 4.20-4.17 (m, 1H), 3.91-3.89 (m, 1H), 3.78-3.75 (m, 1H), 2.40 (bs, 1H), 1.28 (d, J = 5.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 157.2, 129.4, 126.0, 115.8, 73.6, 66.2, 18.8 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (95:5 v/v) as an eluent.

1-phenoxypropan-2-ol (4h)[9]



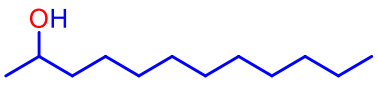
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.30 (t, J = 10.0 Hz, 2H), 6.98 (t, J = 10.0 Hz, 2H), 6.92 (d, J = 10.0 Hz, 2H), 4.21-4.18 (m, 1H), 3.95-3.93 (m, 1H), 3.80-3.78 (m, 1H), 2.51 (bs, 1H), 1.29 (d, J = 10.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 158.5, 129.5, 121.1, 114.5, 73.2, 66.2, 18.7 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (92:8 v/v) as an eluent.

1-phenylpropan-1-ol (4i)[13]



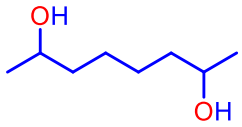
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.36 (m, 4H), 7.28-7.25 (m, 1H), 4.58 (t, J = 6.6 Hz, 1H), 1.92 (bs, 1H), 1.83-1.73 (m, 2H), 0.91 (t, J = 5.0 Hz, 3H).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 144.6, 128.4, 127.5, 126.0, 76.0, 31.9, 10.1 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (92:8 v/v) as an eluent.

dodecan-2-ol (4j)[9]



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 3.80-3.77 (m, 1H), 1.42 (bs, 1H), 1.26-1.21 (m, 17H), 1.18 (d, J = 5.0 Hz, 1H), 0.87 (t, J = 5.0 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 68.2, 39.4, 29.7, 29.6, 29.3, 25.8, 23.5, 22.7, 14.1 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (90:10 v/v) as an eluent.

octane-2,7-diol (4k)[9]



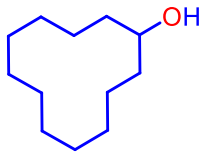
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 3.81-3.78 (m, 2H), 1.61-1.57 (bs, 2H), 1.44-1.33 (m, 8H), 1.19-1.18 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 68.1, 68.0, 39.2, 25.7, 25.7, 23.5 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (90:10 v/v) as an eluent.

1,1'-((2,2-dimethylpropane-1,3-diyl)bi9s(oxy))bis(propan-2-ol) (4l)

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 3.96-3.93 (m, 2H), 3.58-3.54 (m, 2H), 3.40-3.38 (m, 2H), 3.30-3.27 (m, 2H), 3.23-3.19 (m, 2H) 1.11-1.10 (m, 6H), 0.89-0.87 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 77.2 (d), 76.9 (d), 68.1, 66.2, 36.2, 22.2, 18.5 (d) ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (90:10 v/v) as an eluent.

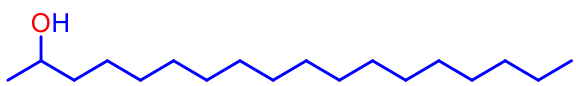
HRMS: m/z calc. for $C_{11}H_{24}O_4$ $[M+Na]^+$ 243.1567, found 243.1595.

Cyclododecanol (4m)[14]



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 3.83 (m, 1H), 1.66-1.64 (m, 2H), 1.44-1.36 (m, 21H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 69.1, 32.4, 24.2, 23.8, 23.3, 23.3, 20.9 ppm. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (90:10 v/v) as an eluent.

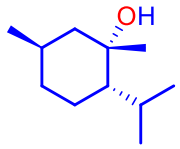
octadecan-2-ol (4n)[15]



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 3.80-3.76 (m, 1H), 1.46 (m, 4H), 1.28-1.25 (m, 26H), 1.18 (d, J = 5.0 Hz, 1H), 0.87 (t, J = 5.0 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 68.2, 39.4, 31.9, 29.7-29.4 (5C), 25.8, 23.5, 22.7, 14.1 ppm. The compound was

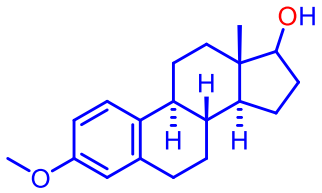
purified by column chromatography on silica gel with hexane and ethyl acetate mixture (90:10 v/v) as an eluent.

(1S,2S,5R)-2-isopropyl-1,5-dimethylcyclohexan-1-ol (4y)[13]



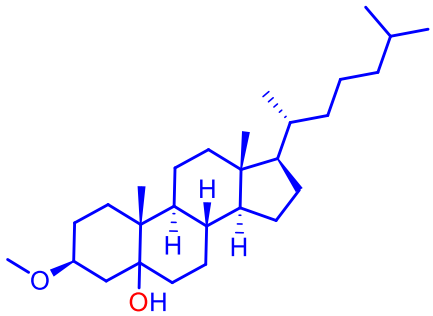
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 2.17-2.12 (m, 1H), 1.78-1.75 (m, 1H), 1.69-1.65 (m, 1H), 1.59-1.56 (m, 2H), 1.50-1.49 (m, 1H), 1.37-1.34 (m, 1H), 1.23 (s, 3H), 1.17 (s, 1H), 1.07-1.01 (m, 2H), 0.91 (d, *J* = 5.0 Hz, 3H), 0.89 (d, *J* = 5.0 Hz, 3H), 0.86 (d, *J* = 5.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 73.1, 50.7, 50.5, 35.2, 28.9, 28.2, 26.1, 23.8, 22.3, 20.9, 18.2. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (98:2 v/v) as an eluent.

17ß-Estradiol-3-methylether (4aa)[16]



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.22 (d, *J* = 10.0 Hz, 1H), 6.73 (d, *J* = 5.0 Hz, 1H), 6.64 (s, 1H), 3.79 (s, 3H), 3.74 (t, *J* = 10.0 Hz, 1H), 2.89-2.85 (m, 2H), 2.34-2.31 (m, 2H), 2.22-2.18 (m, 1H), 2.13-2.11(m, 1H), 1.97-1.95 (m, 1H), 1.91-1.87 (m, 1H), 1.72-1.70 (m, 1H), 1.51-1.33 (m, 6H), 1.30-1.27 (m, 1H), 1.19-1.17 (m, 1H), 0.79 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 157.3, 137.9, 132.6, 126.2, 113.7, 111.4, 81.7, 55.1, 49.9, 43.8, 43.1, 38.7, 36.6, 30.4, 29.7, 27.2, 26.2, 23.0, 11.0. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (85:15 v/v) as an eluent.

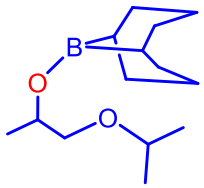
(3S,8S,9S,10R,13R,14S,17R)-3-methoxy-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-5H-cyclopenta[a]phenanthren-5-ol (4ab)[17]



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 3.62 (m. 1H), 3.33 (s, 3H), 1.99-1.96 (m, 2H), 1.85-1.79 (m, 1H), 1.72-1.68 (m, 2H), 1.56-1.32 (m, 19H), 1.28-1.03 (m, 7H), 0.97 (s, 3H), 0.89 (d, J = 10.0 Hz, 3H), 0.85 (dd, 6H), 0.64 (s, 3H).). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 76.0, 75.1, 56.2, 56.2, 55.7, 46.0, 42.7, 40.4, 40.0, 39.5, 39.0, 36.1, 35.8, 34.7, 34.5, 30.6, 28.2, 28.0, 27.1, 26.0, 24.1, 23.8, 22.8, 22.5, 21.3, 18.6, 16.2, 12.1. The compound was purified by column chromatography on silica gel with hexane and ethyl acetate mixture (85:15 v/v) as an eluent.

3.2. Characterization of hydroborated epoxides

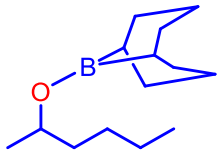
9-((1-isopropoxypropan-2-yl)oxy)-9-borabicyclo[3.3.1]nonane (3o)



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 4.41 (q, 1H), 3.59-3.54 (m, 1H), 3.40-3.34 (m, 2H), 1.89-1.69 (m, 12H), 1.34-1.30 (m, 2H), 1.21 (d, J = 10.0 Hz, 3H), 1.12 (d, J = 10.0 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 73.0, 71.9, 70.6, 33.2, 33.1, 23.1, 22.1, 21.9, 19.9. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ = -57.11 ppm. HRMS was recorded in MeOH as solvent so corresponding alcohol product was detected.

HRMS: m/z calc. for $C_6H_{14}O_2$ $[M+Na]^+$ 141.0886, found 141.0881.

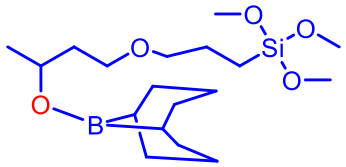
9-(hexan-2-yloxy)-9-borabicyclo[3.3.1]nonane (3p)



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 4.29-4.26 (m, 1H), 1.89-1.71 (m, 12H), 1.58-1.54 (m, 1H), 1.50-1.45 (m, 1H), 1.37-1.26 (m, 6H), 1.22 (d, J = 10.0 Hz, 3H), 0.90 (t, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 71.5, 38.1, 33.3, 33.2, 28.1, 23.3, 23.2, 22.6, 14.0. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ = -55.96 ppm. HRMS was recorded in MeOH as solvent so corresponding alcohol product was detected.

HRMS: m/z calc. for $C_6H_{14}O$ $[M+Na]^+$ 125.0937, found 125.0943.

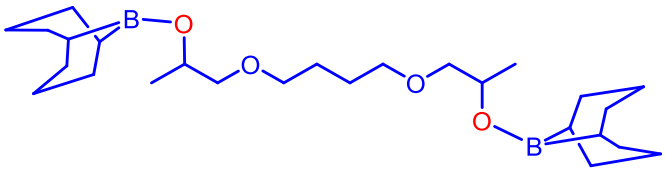
3-(3-(((1s,5s)-9-borabicyclo[3.3.1]nonan-9-yl)oxy)butoxy)propyl)trimethoxysilane (3q)



^{1}H NMR (500 MHz, C_6D_6, 25 ^{o}C, TMS): δ = 4.41 (q, 1H), 3.43 (s, 9H), 3.35-3.27 (m, 3H), 3.20-3.17 (m, 1H), 1.93-1.83 (m, 11H), 1.79-1.73 (m, 3H), 1.42-1.37 (m, 4H) 1.12 (d, *J* = 10.0 Hz, 3H), 0.70 (dd, 2H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 ^{o}C, TMS): δ = 76.0, 73.6, 70.7, 50.3, 33.7, 33.6, 23.7, 23.5, 20.1, 6.0. ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 25 ^{o}C): δ = -56.26. ^{29}Si NMR (79.3 MHz, C_6D_6, 25 °C): δ -42.35 ppm. HRMS was recorded in MeOH as solvent so corresponding alcohol product was detected.

HRMS: m/z calc. for $C_{10}H_{24}O_5Si$ $[M+Na]^+$ 275.1285, found 275.1233.

1,4-bis(2-(((1s,5s)-9-borabicyclo[3.3.1]nonan-9-yl)oxy)propoxy)butane (3r)



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 4.45 (q, 2H), 3.45-3.43 (m, 4H), 3.41-3.39 (m, 2H), 3.37-3.35 (m, 2H), 1.85-1.73 (m, 24H), 1.60-1.59 (m, 4H), 1.34-1.30 (m, 4H), 1.21 (d, *J* = 5.0 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 75.6, 71.1, 70.3, 33.2, 33.1, 26.3, 23.1, 19.8. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ = -56.54 ppm. HRMS was recorded in MeOH as solvent so corresponding alcohol product was detected.

HRMS: m/z calc. for $C_{10}H_{22}O_4$ $[M+Na]^+$ 229.1410, found 229.1402.

4. X-ray crystallographic details

A suitable crystal of **5** was mounted on an XtaLAB Synergy, Dualflex, HyPix 3000 diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2[18], the structure was solved with the SHELXT[19] structure solution program using Intrinsic Phasing and refined with the SHELXL[20] refinement package using Least Squares minimisation.

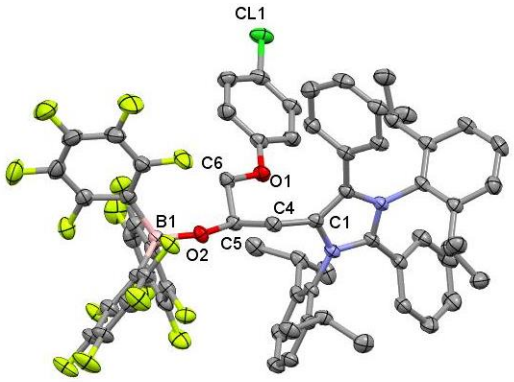


Figure S6. View of the molecular structure of **5**. Ellipsoids are set at the 50% probability level; hydrogen atoms have been omitted for the sake of clarity.

Table S2: Crystal data and structure refinement for 5

CCDC	2180180
Empirical formula	$C_{66}H_{53}BClF_{15}N_2O_2$
Formula weight	1237.36
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.88130(10)
b/Å	15.85180(10)
c/Å	26.0785(2)
α/°	90
β/°	98.1380(10)
γ/°	90
Volume/Å3	7317.53(9)
Z	4
ρ_{calc}g/cm3	1.123
μ/mm-1	1.130
F(000)	2544.0
Crystal size/mm3	0.15 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)

2Θ range for data collection/°	6.442 to 136.472
Index ranges	$-21 \leq h \leq 21$, $-19 \leq k \leq 17$, $-31 \leq l \leq 31$
Reflections collected	79533
Independent reflections	13311 [R_{int} = 0.0408, R_{sigma} = 0.0234]
Data/restraints/parameters	13311/0/793
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0494, wR_2 = 0.1314
Final R indexes [all data]	R_1 = 0.0542, wR_2 = 0.1346
Largest diff. peak/hole / e Å^{-3}	0.43/-0.41

5. ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra of compounds

Figure S7. ^{1}H NMR (in $CDCl_3$) spectrum of 1-phenylethan-1-ol (**4a**)

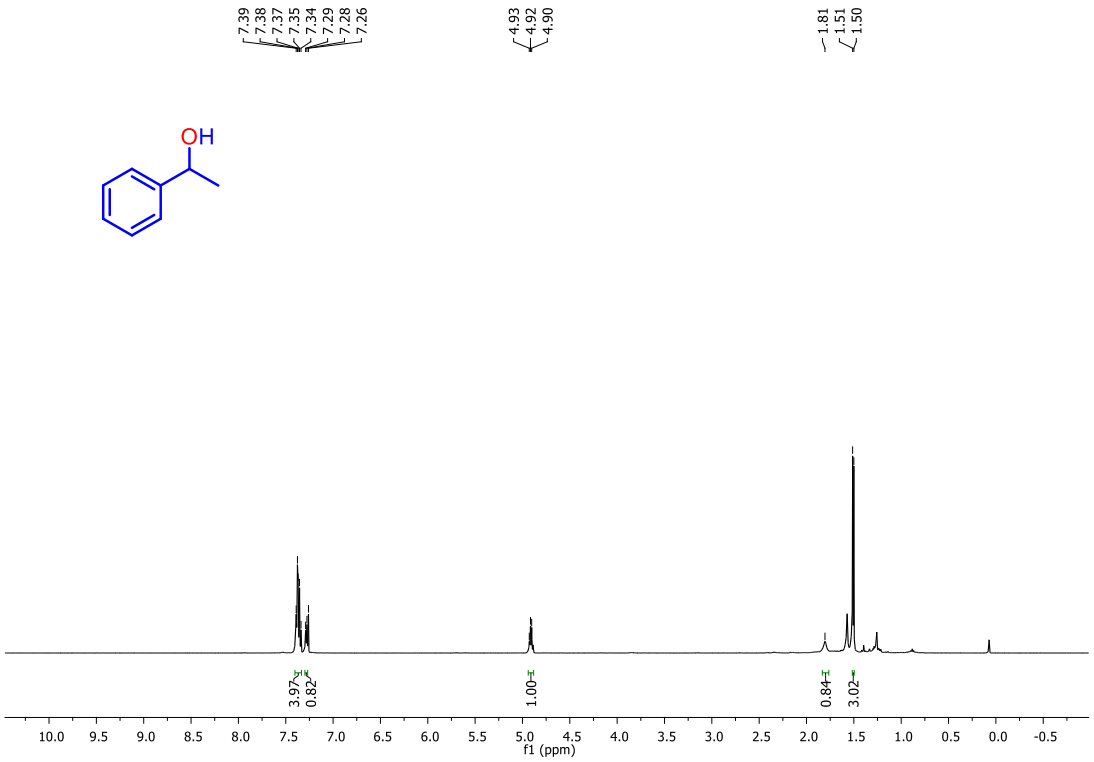


Figure S8. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1-phenylethan-1-ol (**4a)**

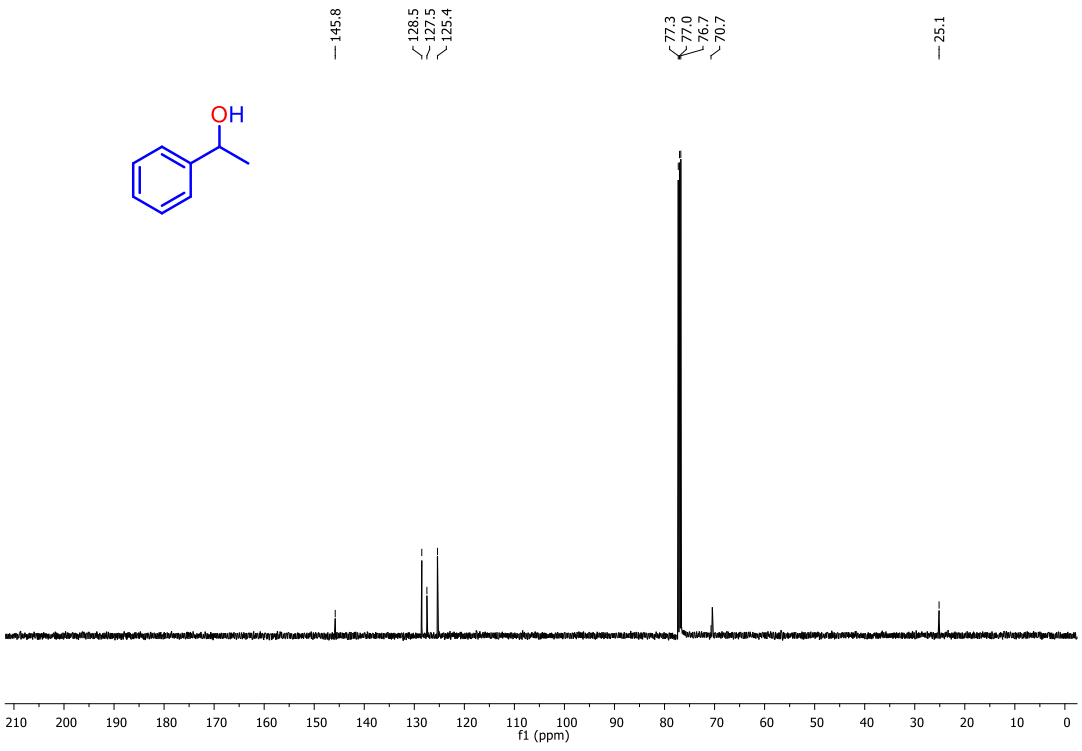


Figure S9. ^{1}H NMR (in $CDCl_3$) spectrum of 1-(4-chlorophenyl)ethan-1-ol (**4b**)

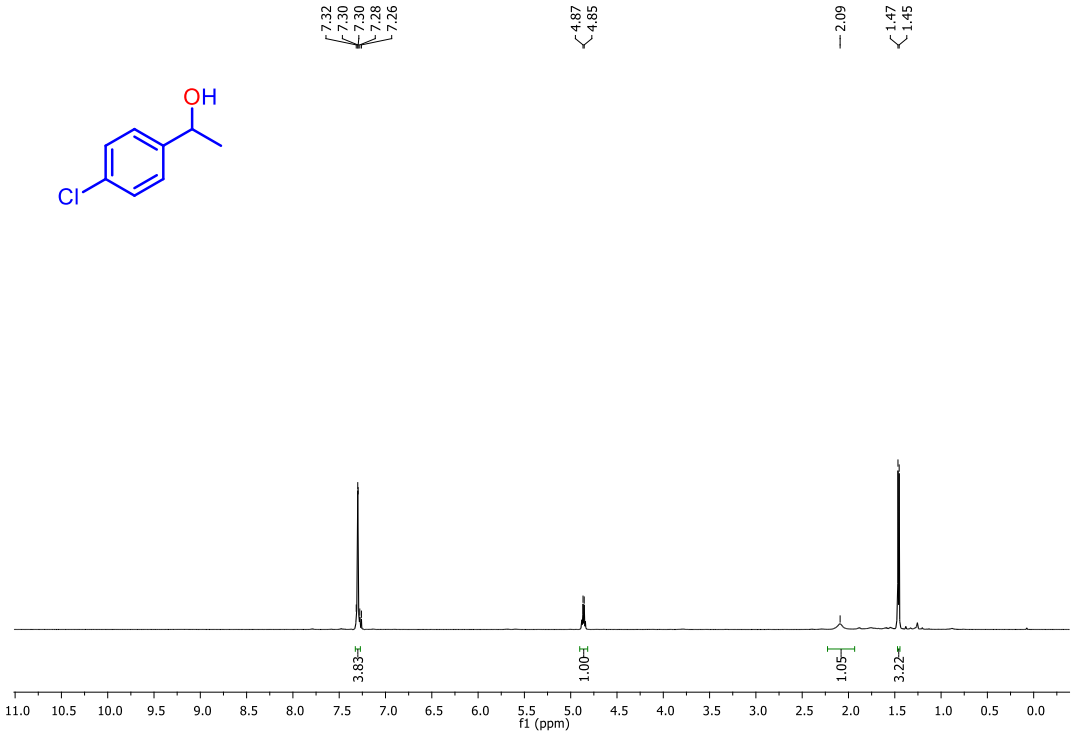


Figure S10. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1-(4-chlorophenyl)ethan-1-ol (**4b**)

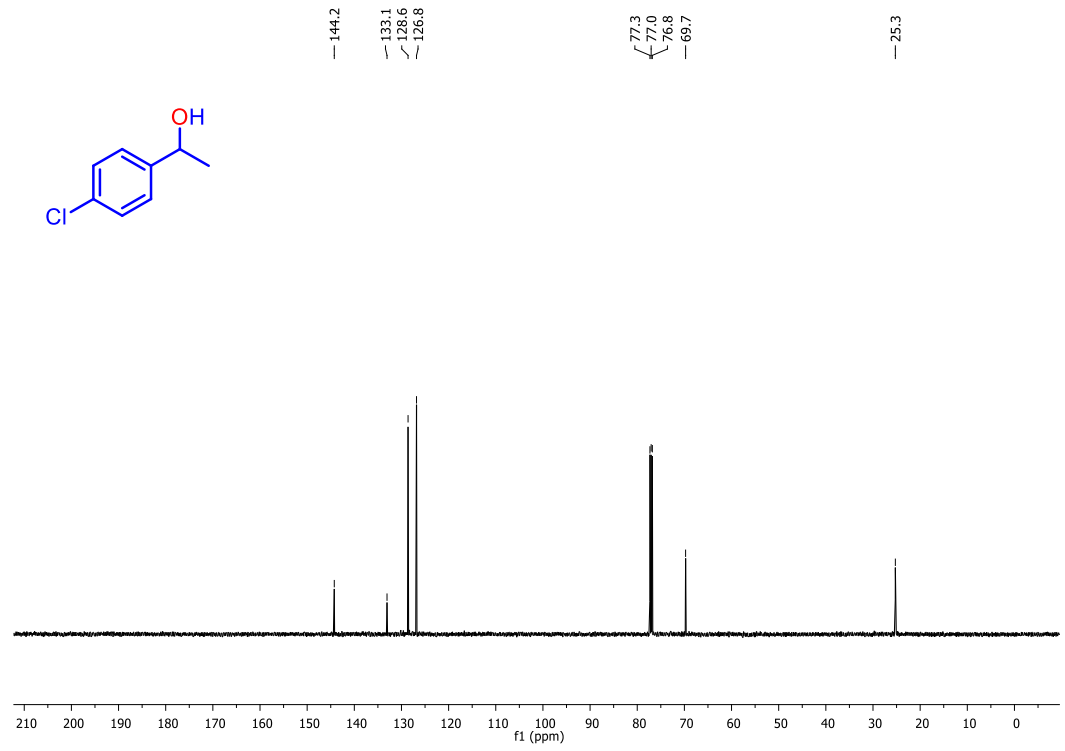


Figure S11. ^{1}H NMR (in $CDCl_3$) spectrum of 1-(4-bromophenyl)ethan-1-ol (**4c**)

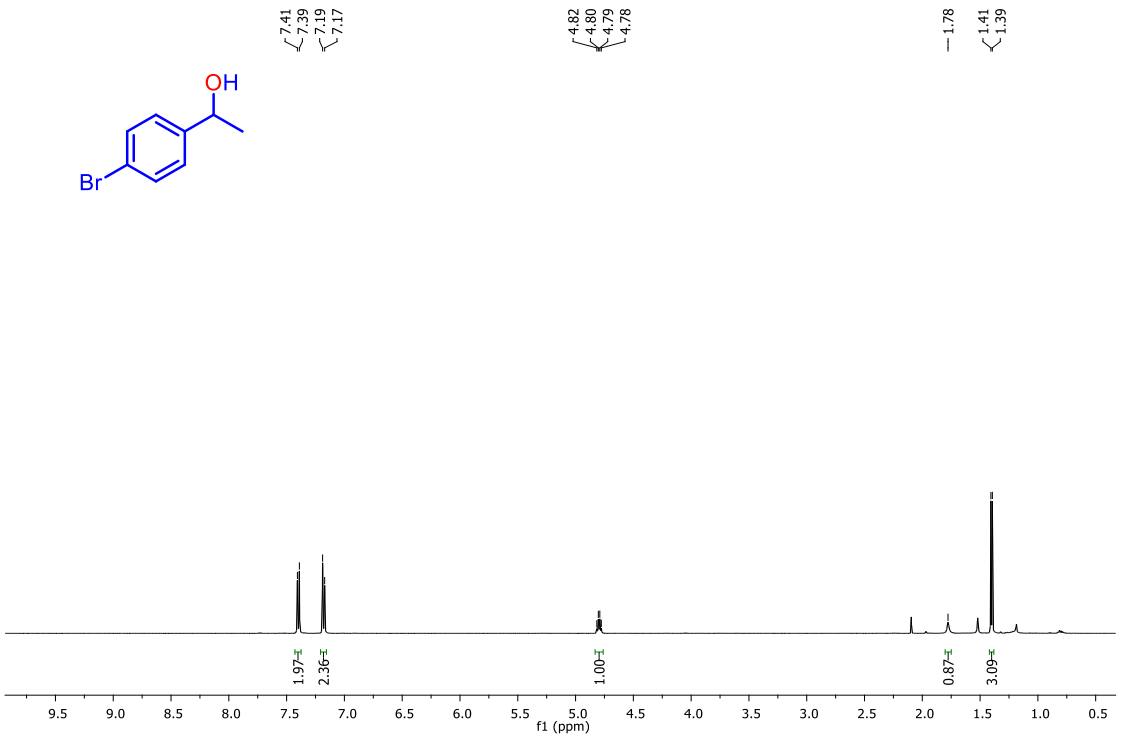


Figure S12. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1-(4-bromophenyl)ethan-1-ol (**4c**)

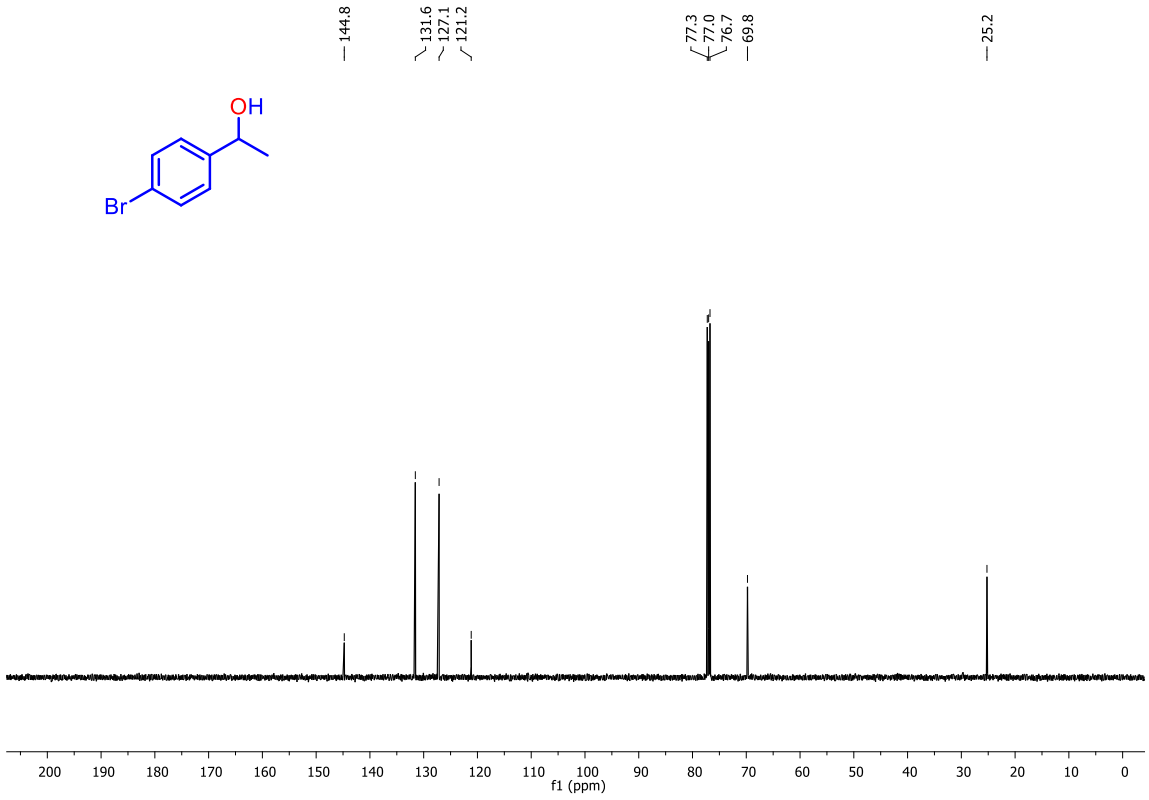


Figure S13. ^{1}H NMR (in $CDCl_3$) spectrum of 1-(o-tolyl)ethan-1-ol (**4d**)

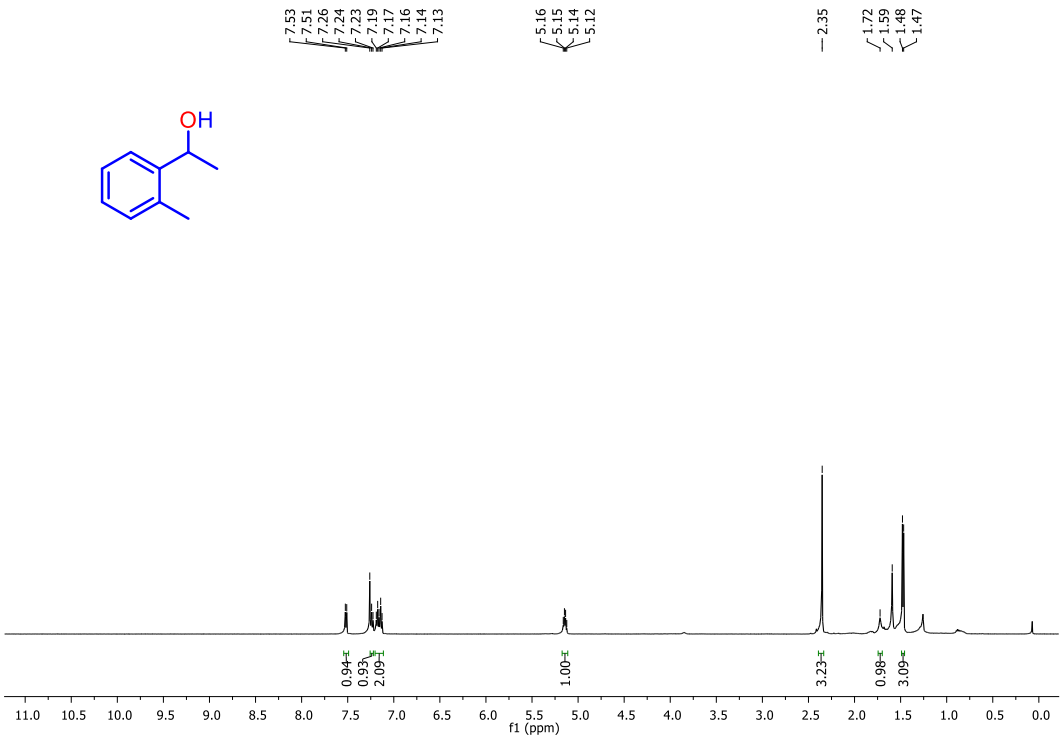


Figure S14. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1-(o-tolyl)ethan-1-ol (**4d)**

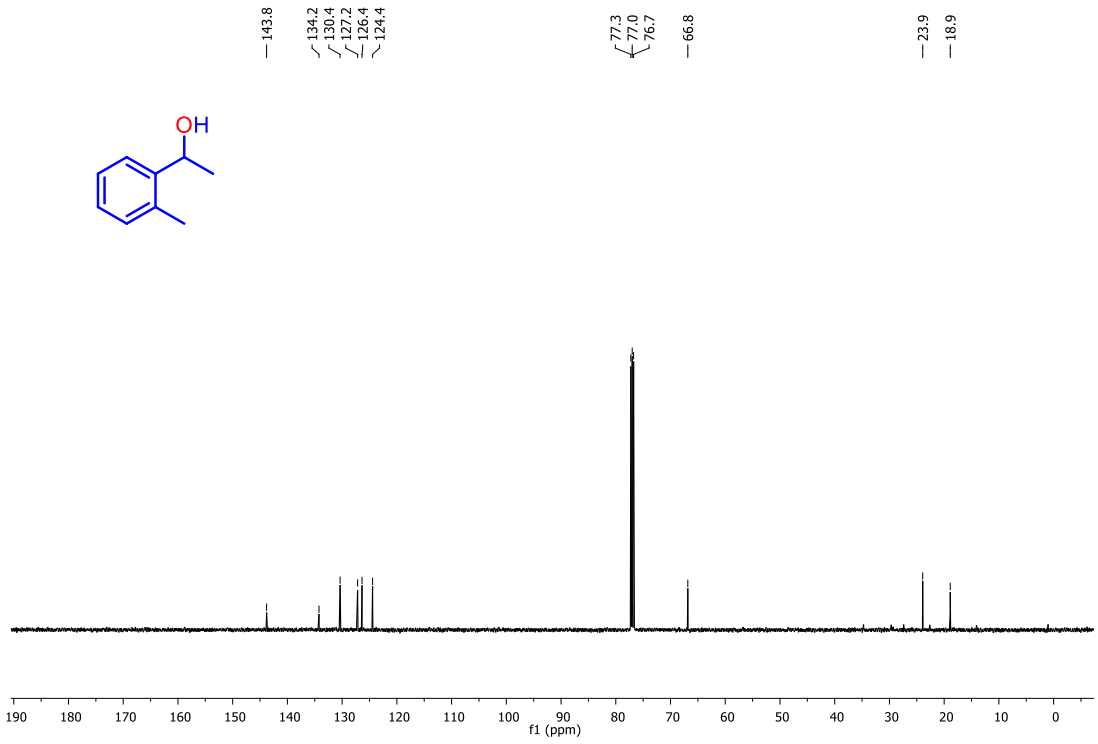


Figure S15. ^{1}H NMR (in $CDCl_3$) spectrum of 1-(4-fluorophenyl)ethan-1-ol (**4e**)

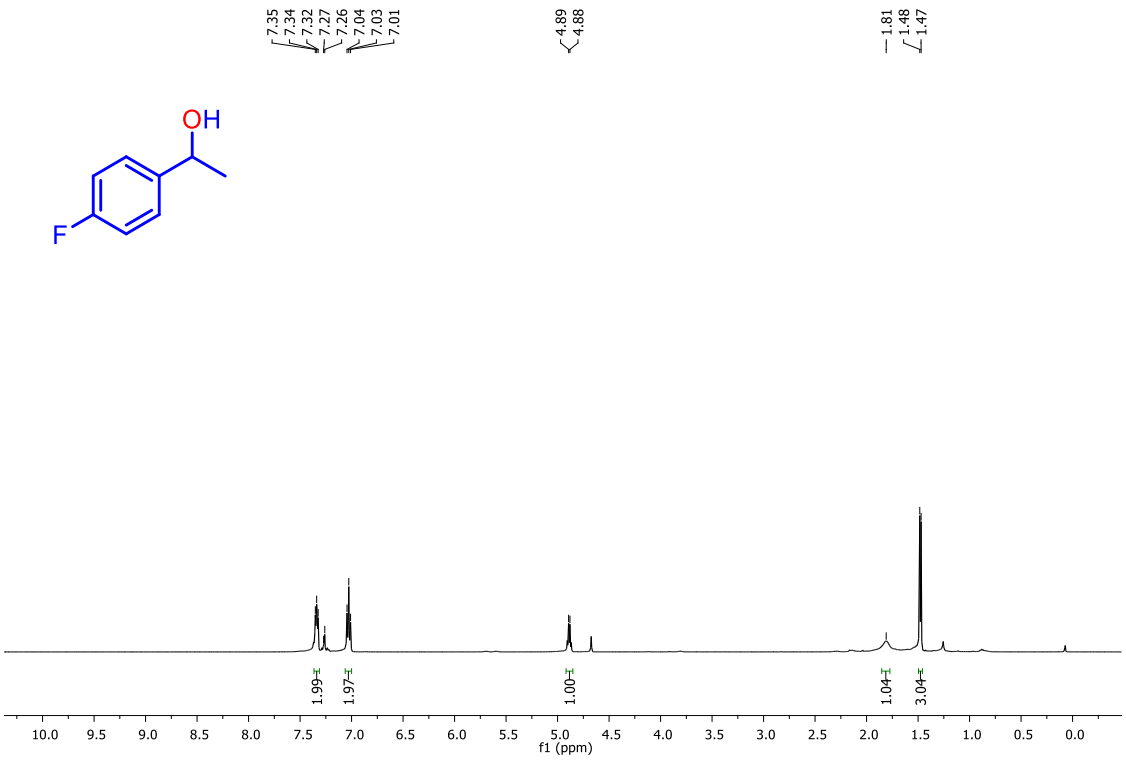


Figure S16. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1-(4-fluorophenyl)ethan-1-ol (**4e**)

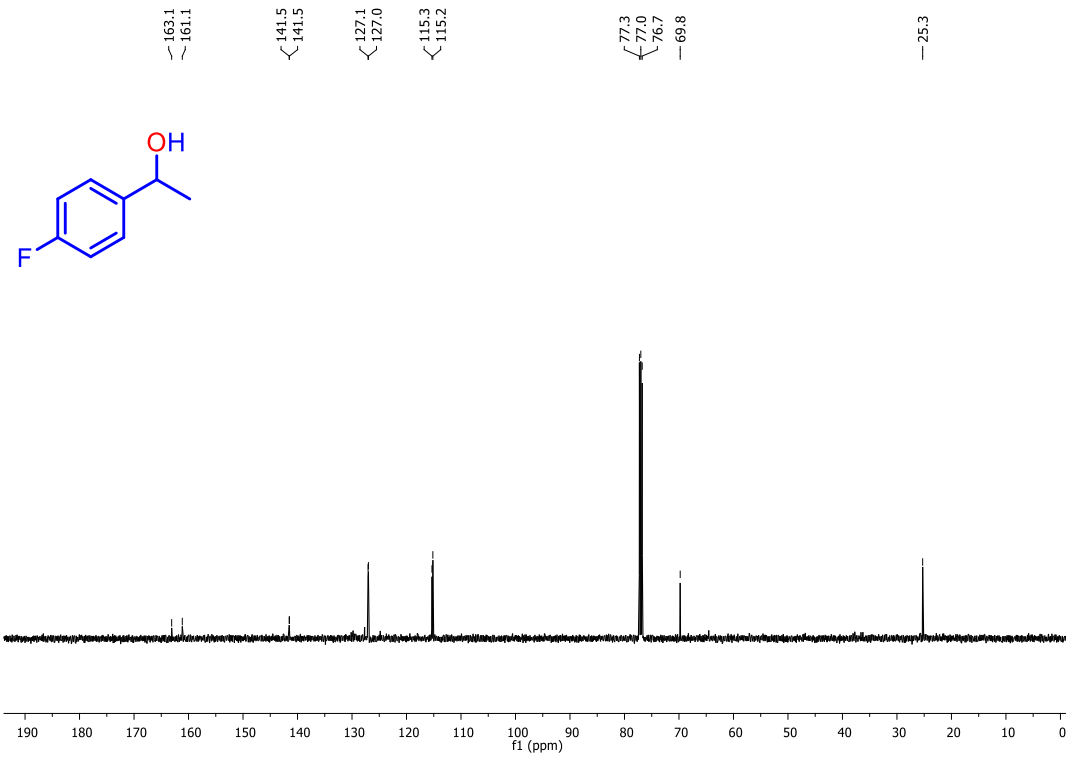


Figure S17. $^{19}F\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1-(4-fluorophenyl)ethan-1-ol (**4e**)

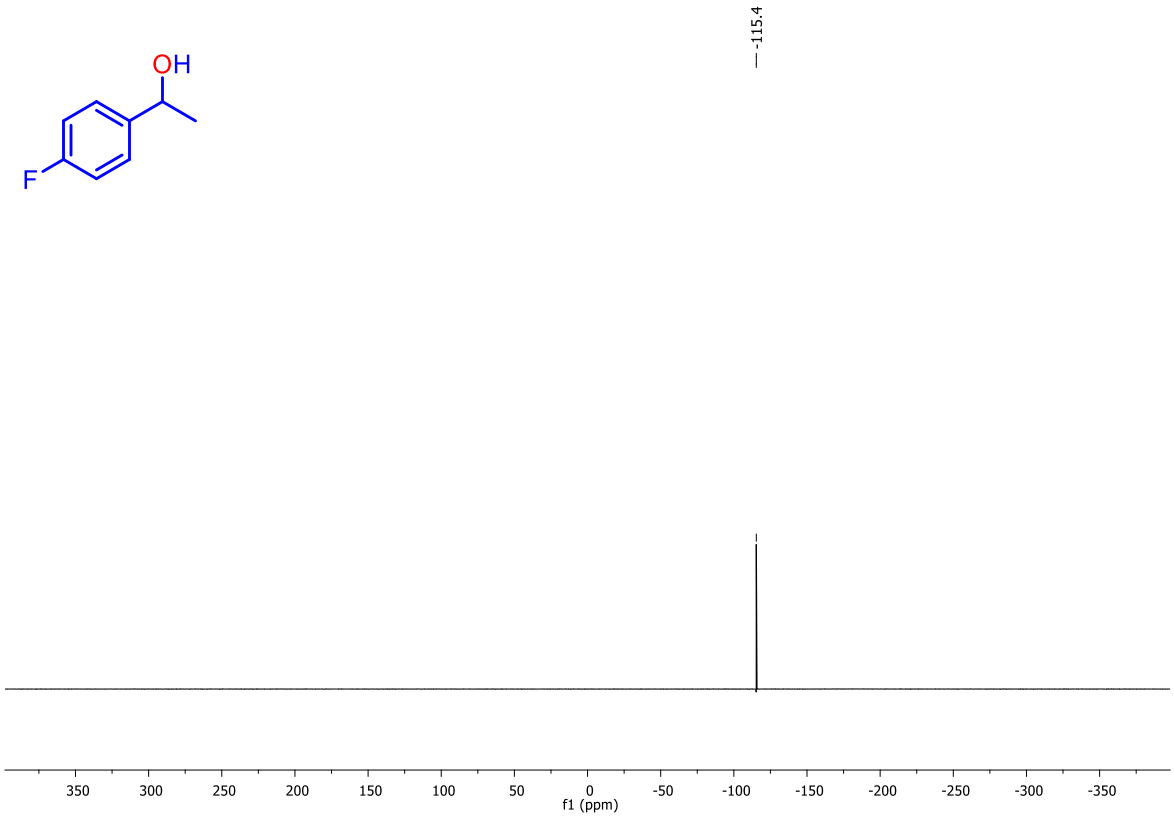


Figure S18. ^{1}H NMR (in $CDCl_3$) spectrum of 1-(p-tolyl)ethan-1-ol (**4f**)

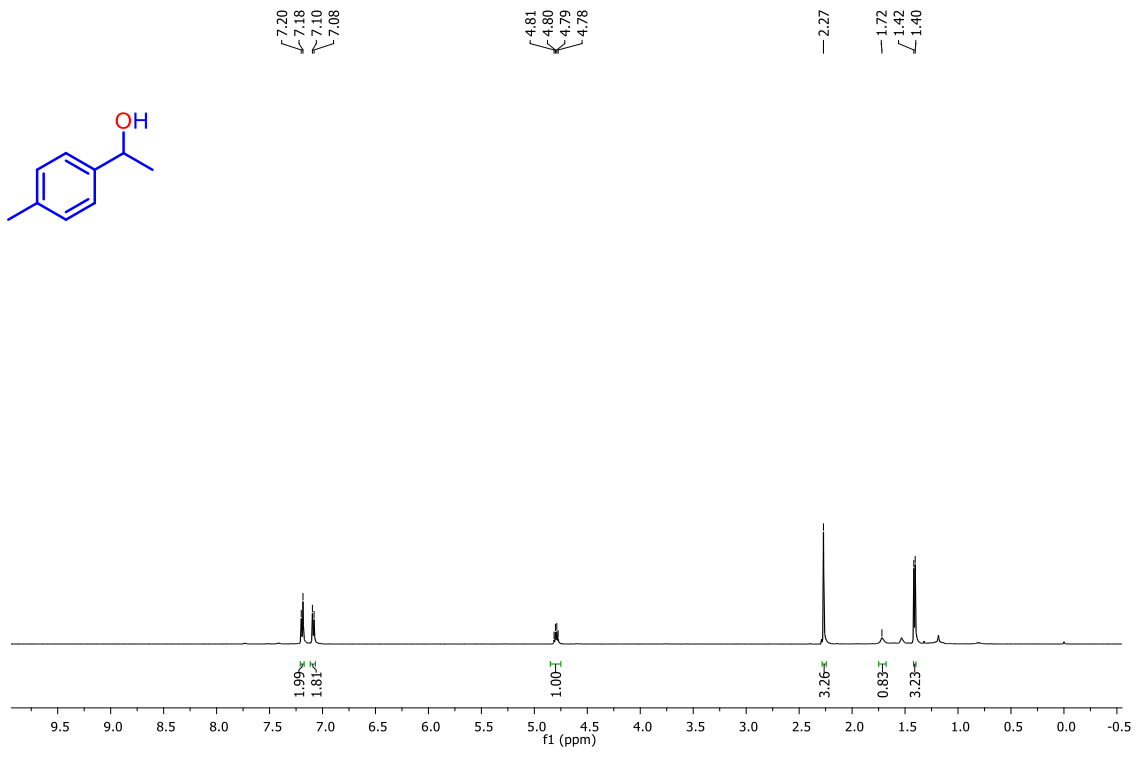


Figure S19. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1-(p-tolyl)ethan-1-ol (**4f**)

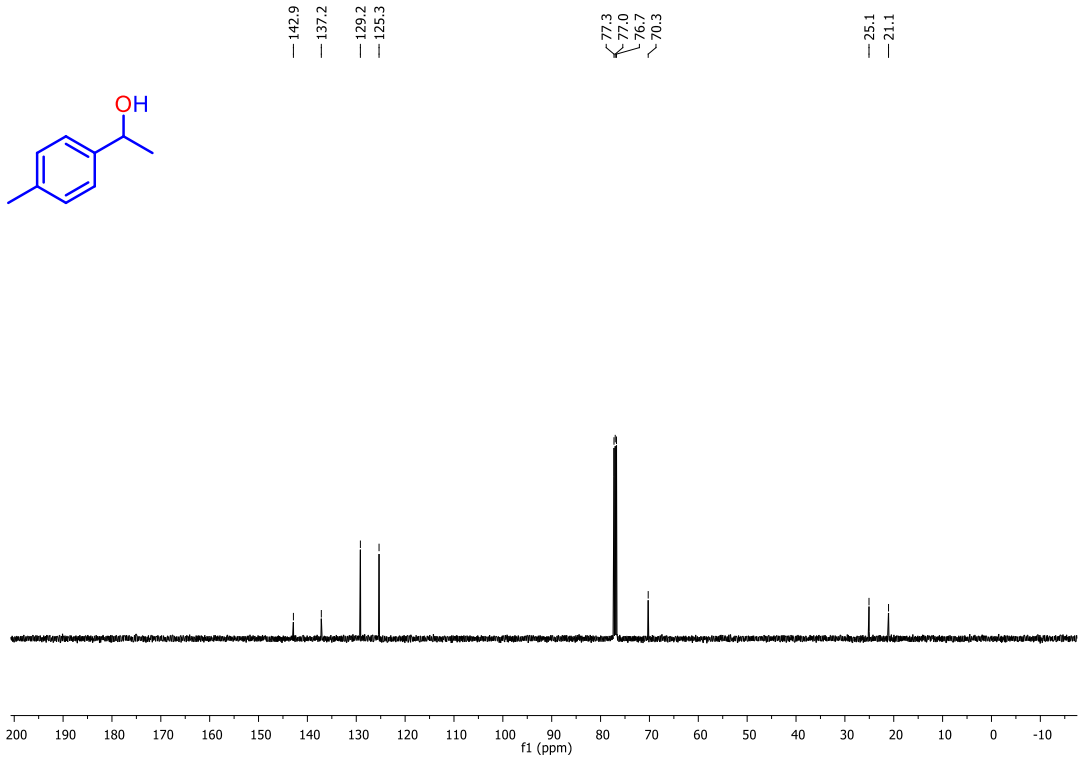


Figure S20. ^{1}H NMR (in $CDCl_3$) spectrum of 1-(4-chlorophenoxy)propan-2-ol (**4g**)

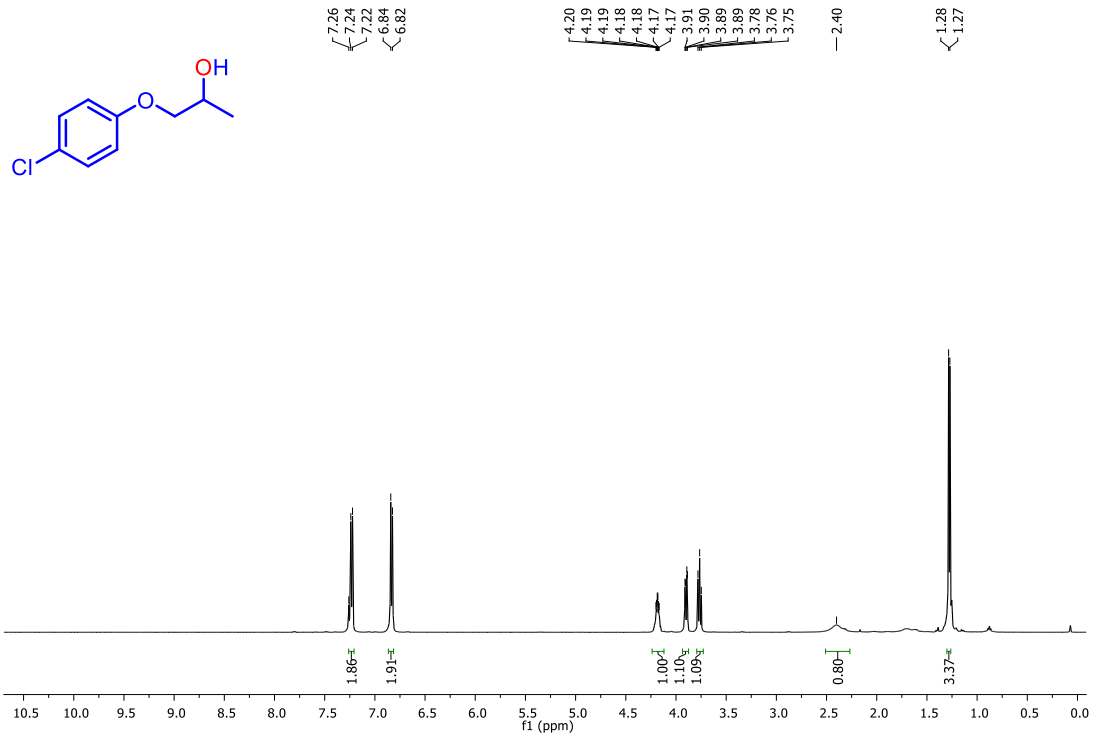


Figure S21. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1-(4-chlorophenoxy)propan-2-ol (**4g**)

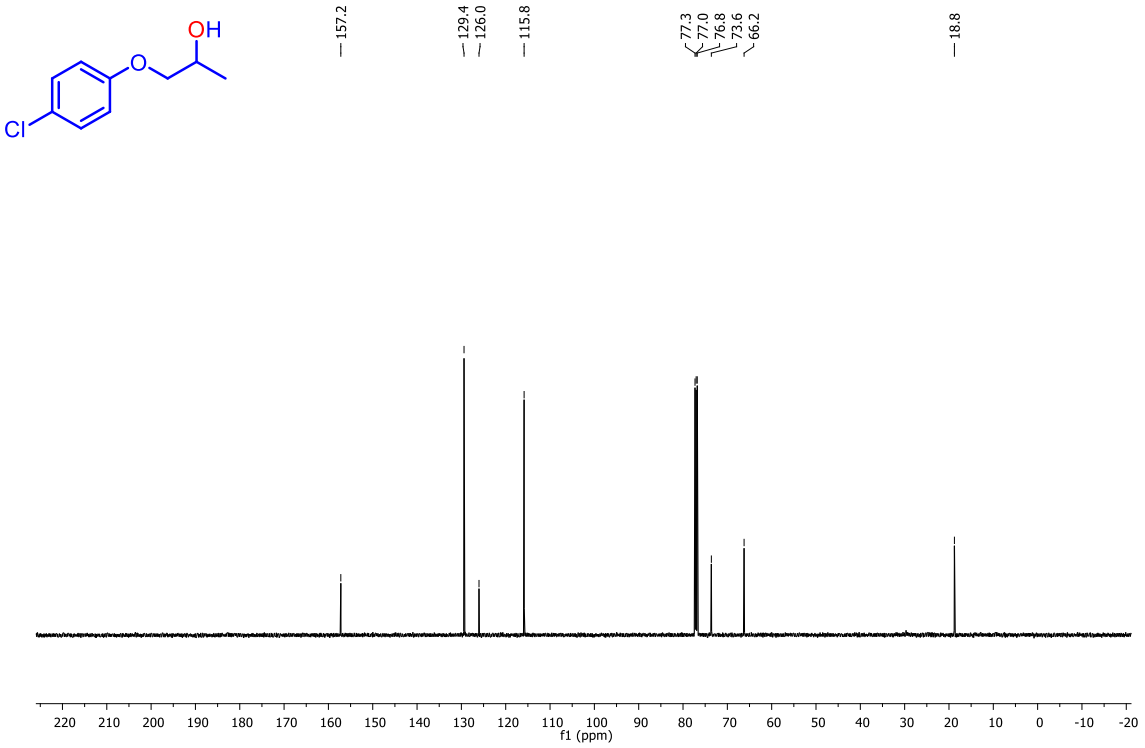


Figure S22. ^{1}H NMR (in $CDCl_3$) spectrum of 1-phenoxypropan-2-ol (**4h**)

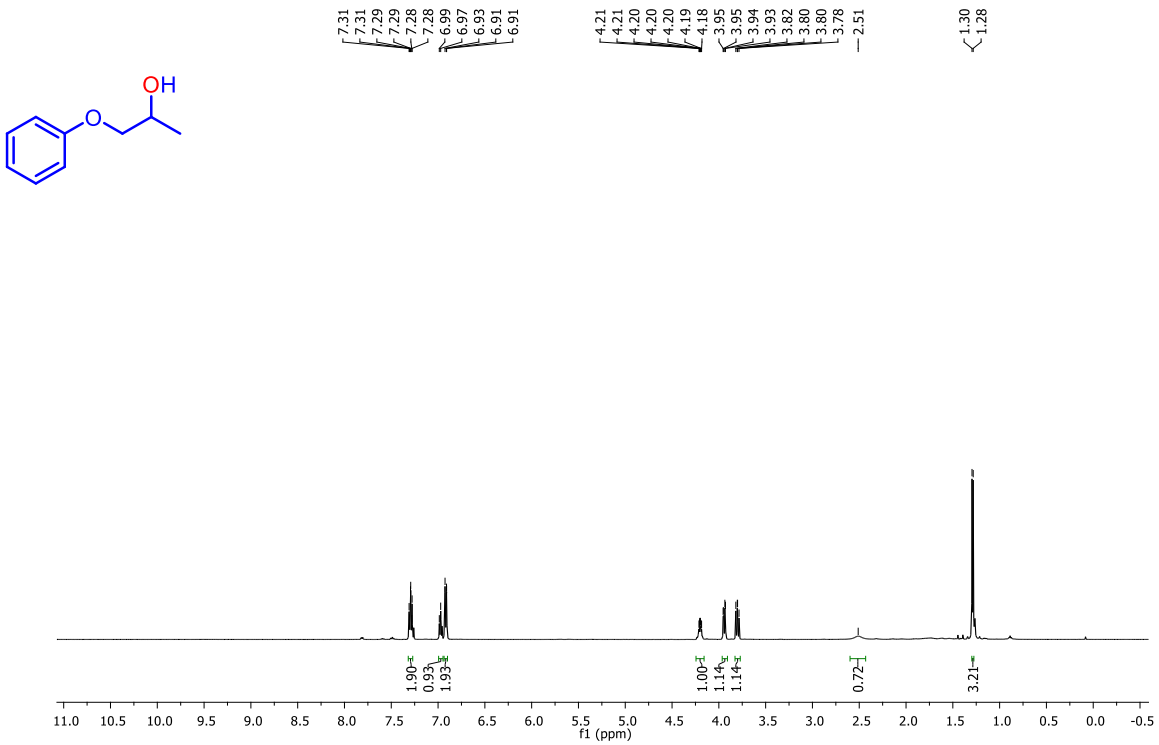


Figure S23. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1-phenoxypropan-2-ol (**4h**)

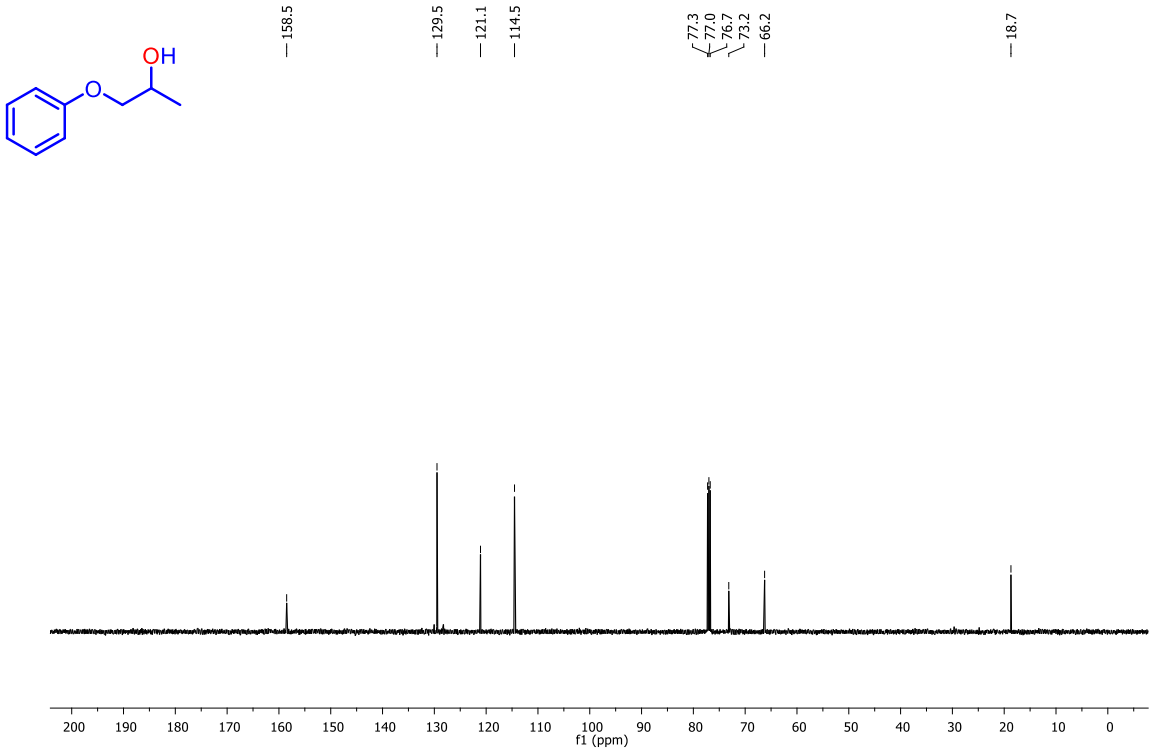


Figure S24. ^{1}H NMR (in $CDCl_3$) spectrum of 1-phenoxypropan-2-ol (**4i**)

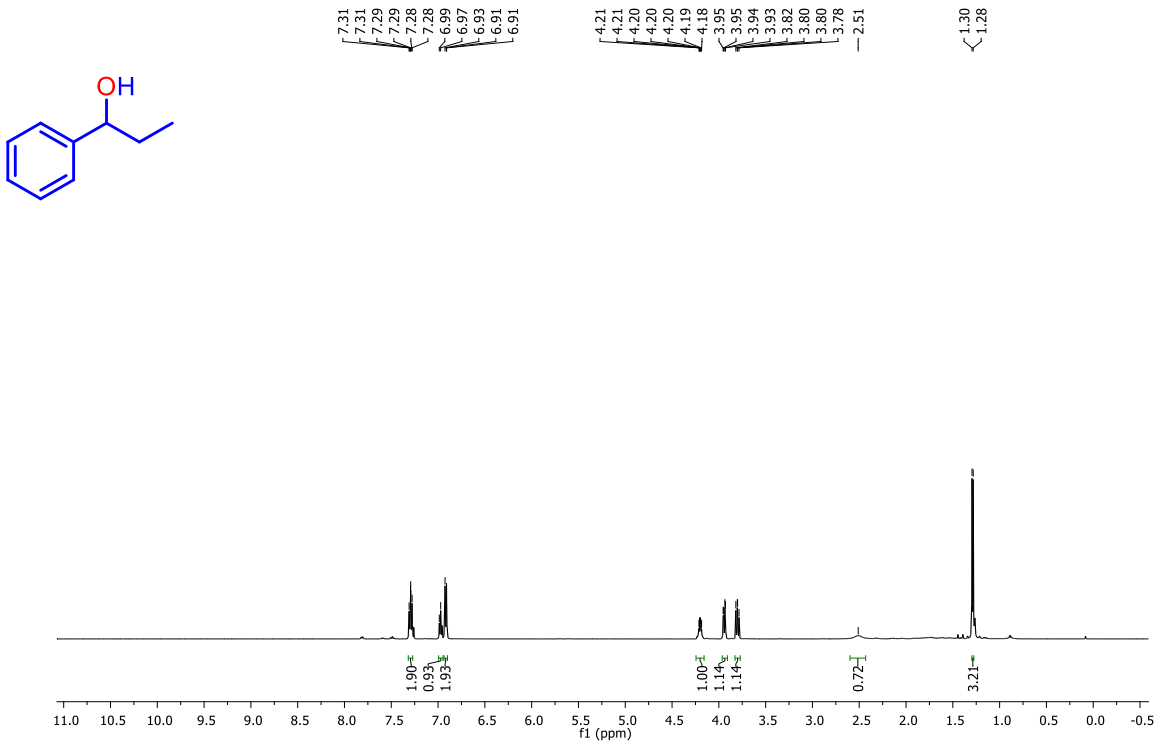


Figure S25. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1-phenoxypropan-2-ol (**4i**)

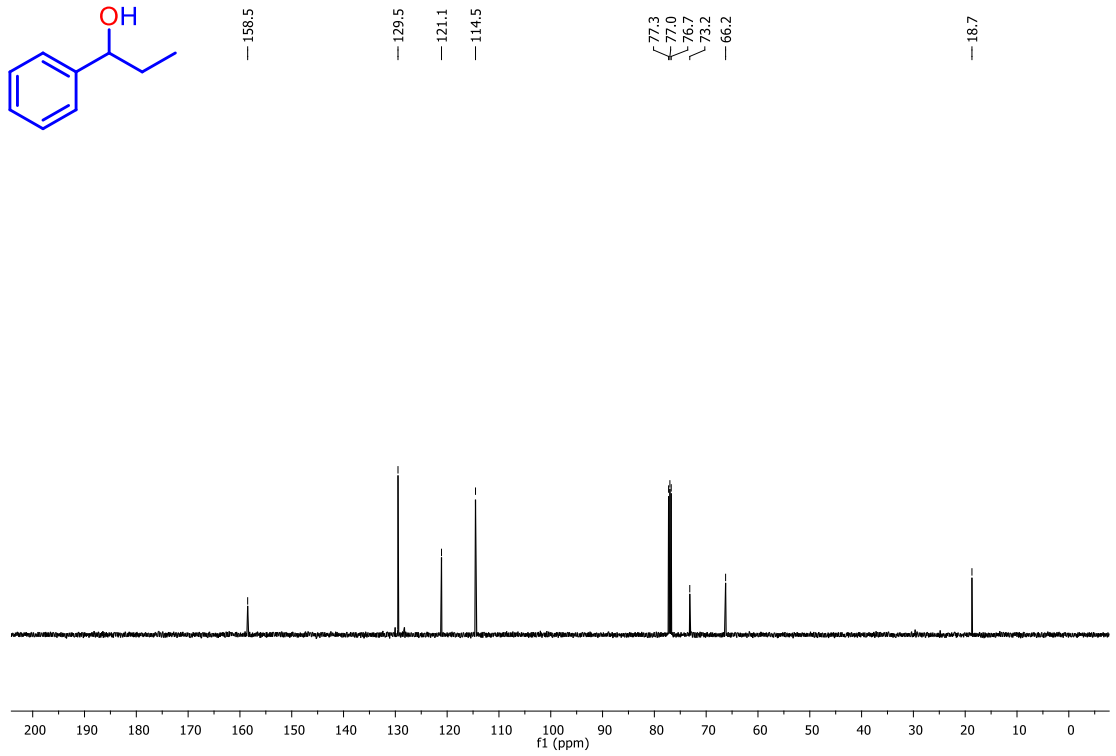


Figure S26. ^{1}H NMR (in $CDCl_3$) spectrum of dodecan-2-ol (**4j**)

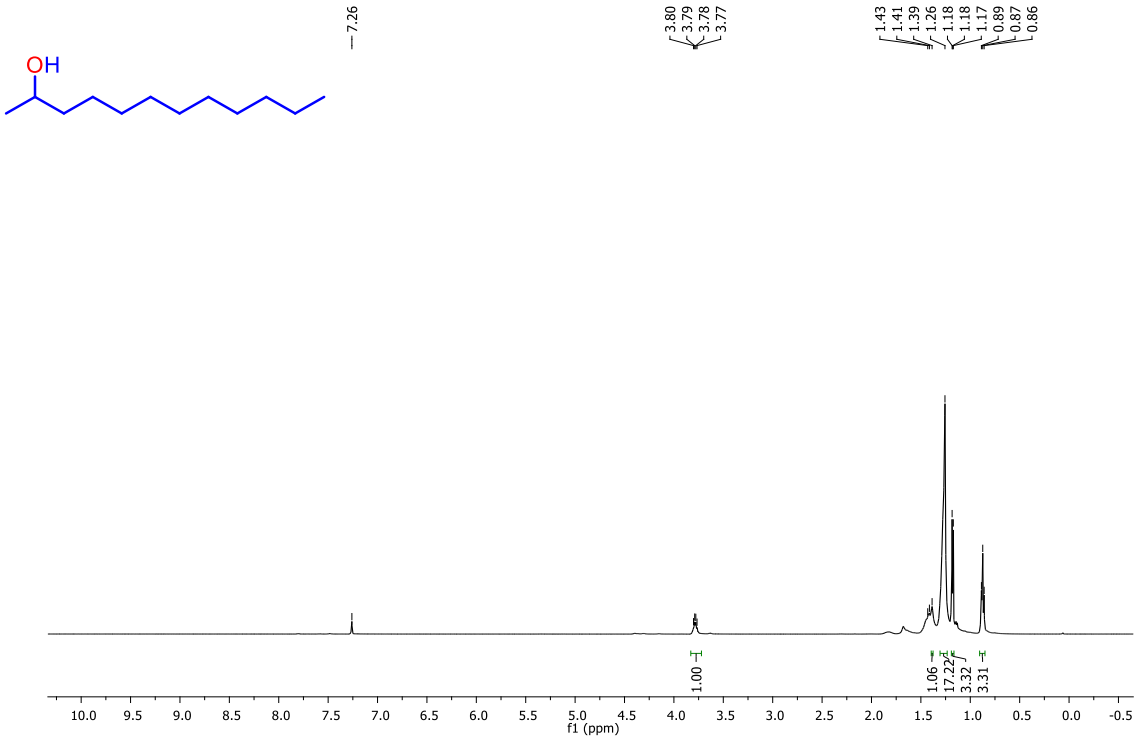


Figure S27. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of dodecan-2-ol (**4j**)

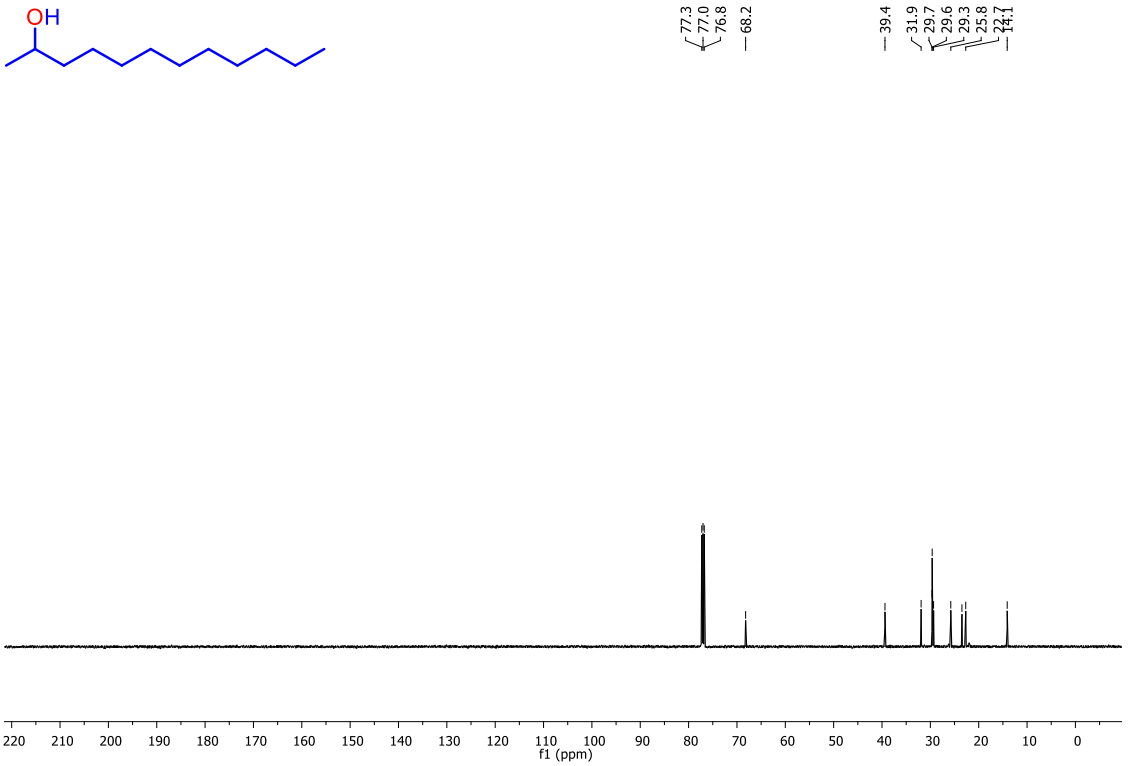


Figure S28. ^{1}H NMR (in $CDCl_3$) spectrum of octane-2,7-diol (**4k**)

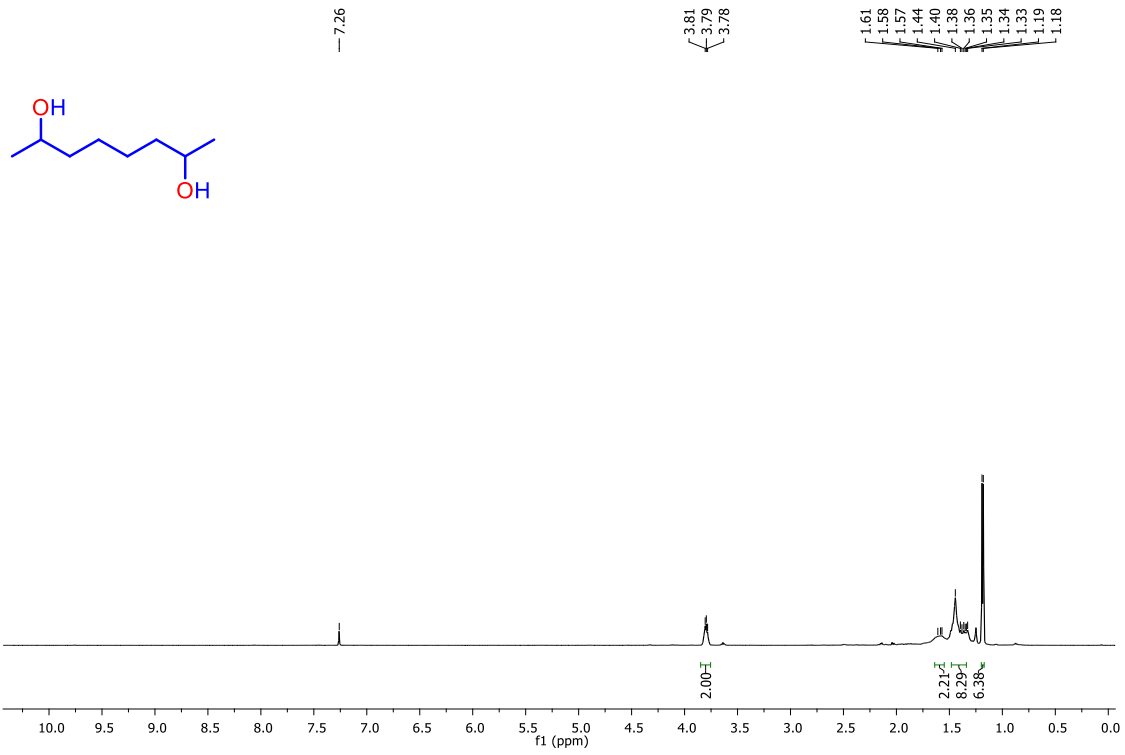


Figure S29. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of octane-2,7-diol (**4k**)

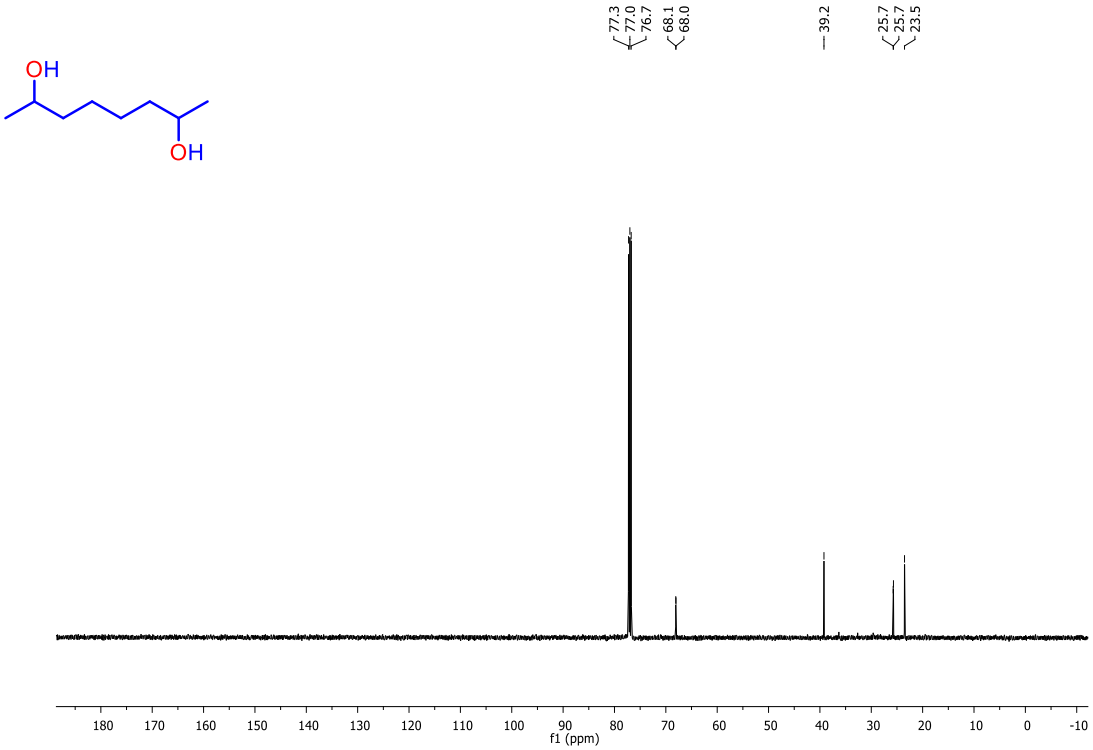


Figure S30. ^{1}H NMR (in $CDCl_3$) spectrum of 1,1'-((2,2-dimethylpropane-1,3-diyl)bis(oxy))bis(propan-2-ol) (**4l**)

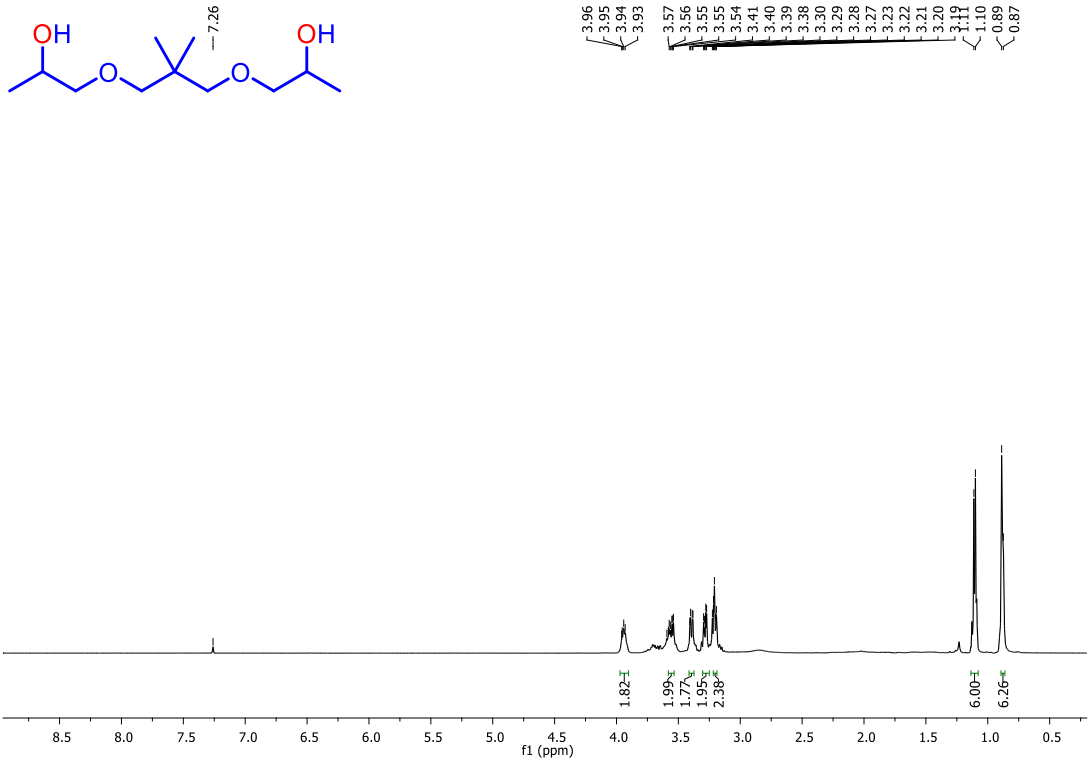


Figure S31. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1,1'-((2,2-dimethylpropane-1,3-diyl)bis(oxy))bis(propan-2-ol) (**4l**)

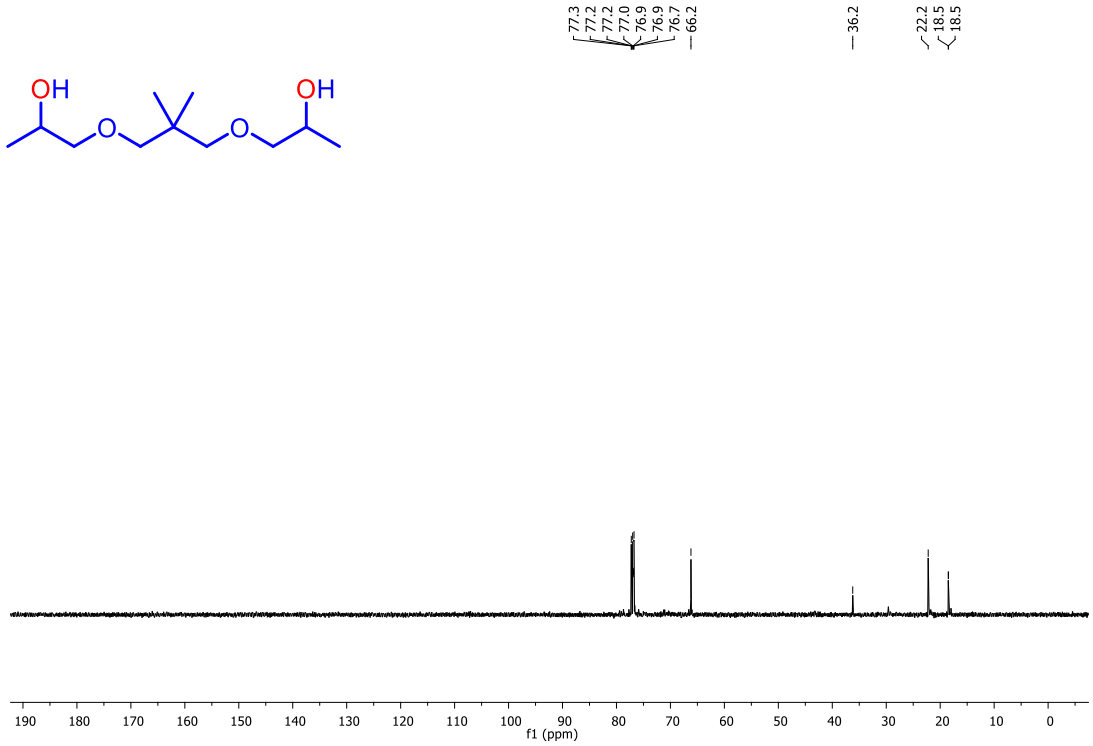


Figure S32. ^{1}H NMR (in $CDCl_3$) spectrum of cyclododecanol (**4m**)

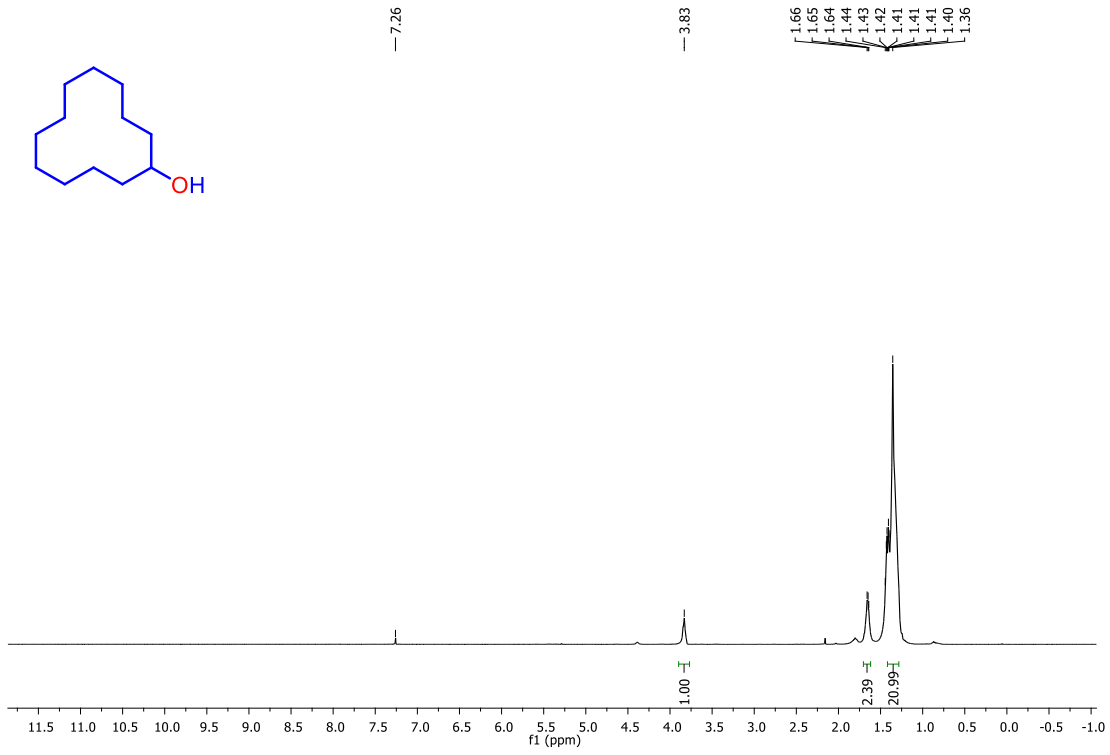


Figure S33. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of cyclododecanol (**4m**)

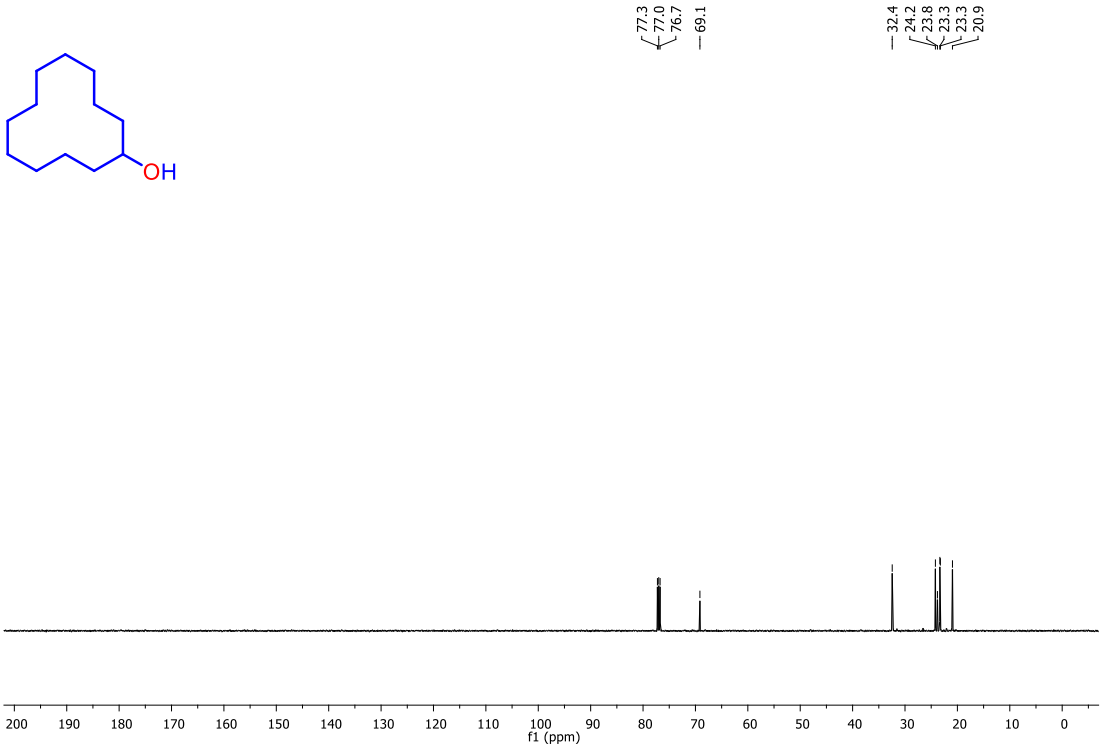


Figure S34. ^{1}H NMR (in $CDCl_3$) spectrum of octadecan-2-ol (**4n**)

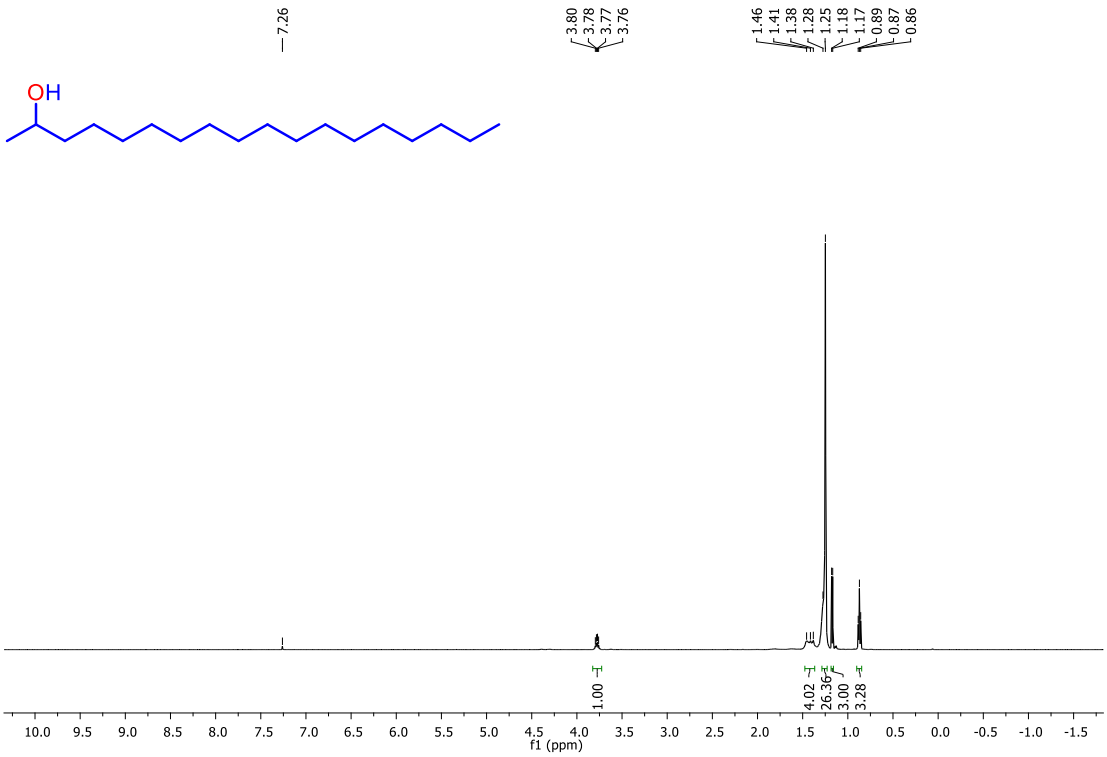


Figure S35. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of octadecan-2-ol(**4n**)

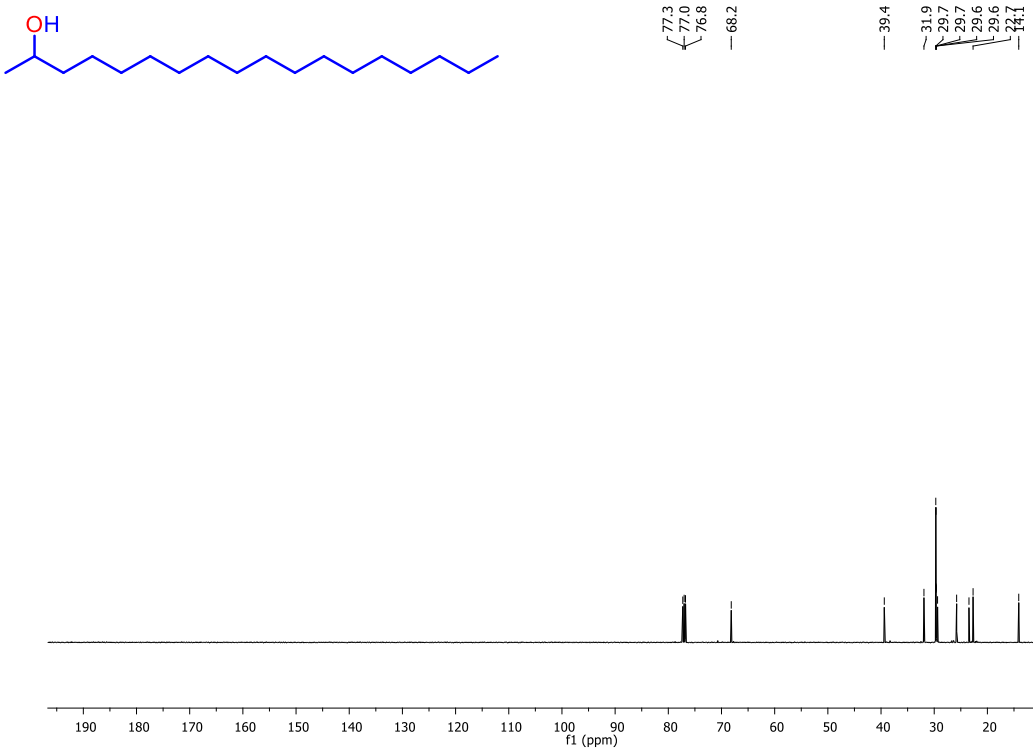


Figure S36. ^{1}H NMR (in $CDCl_3$) spectrum of (1S,2S,5R)-2-isopropyl-1,5-dimethylcyclohexan-1-ol (**4y**)

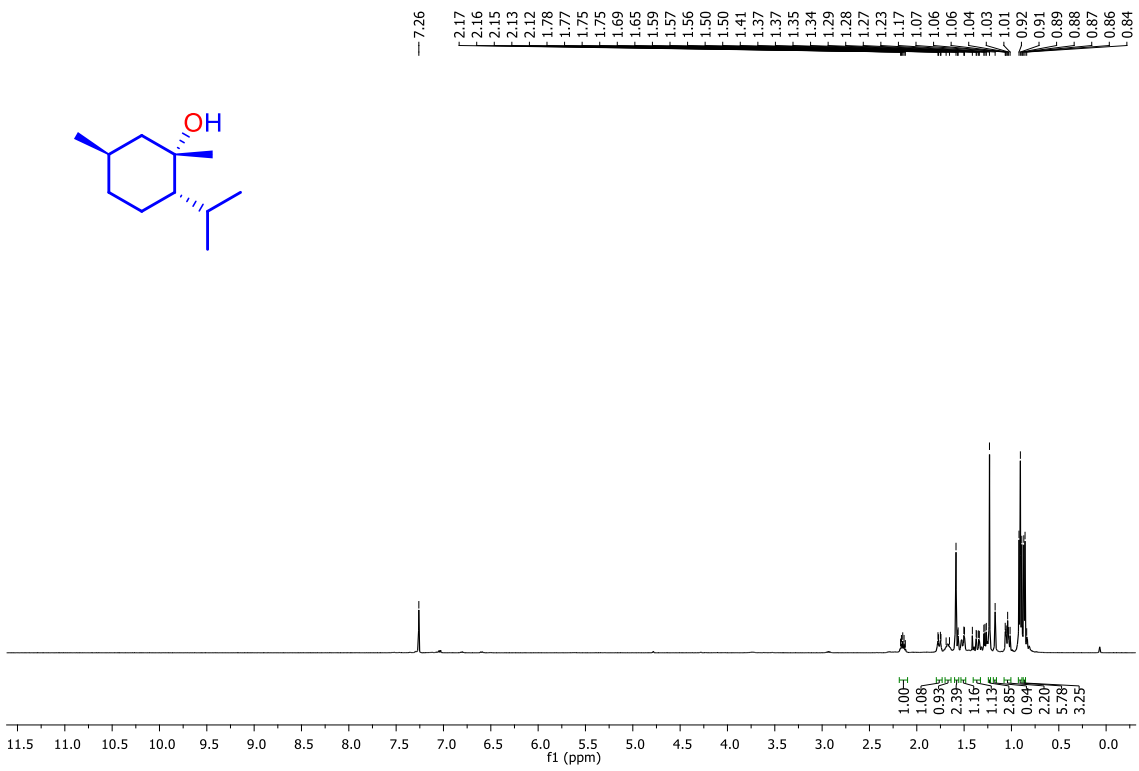


Figure S37. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of (1S,2S,5R)-2-isopropyl-1,5-dimethylcyclohexan-1-ol (**4y**)

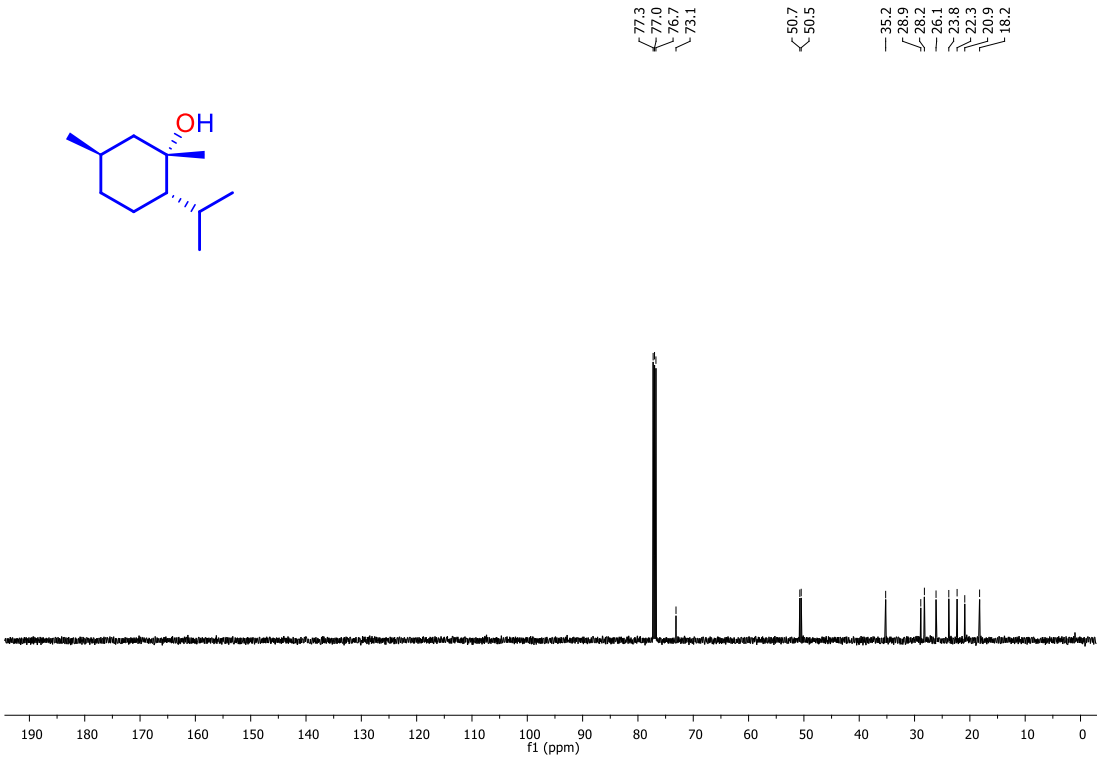


Figure S38 ^{1}H NMR (in $CDCl_3$) spectrum of (8R,9S,13S,14S,17S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-ol (**4z**)

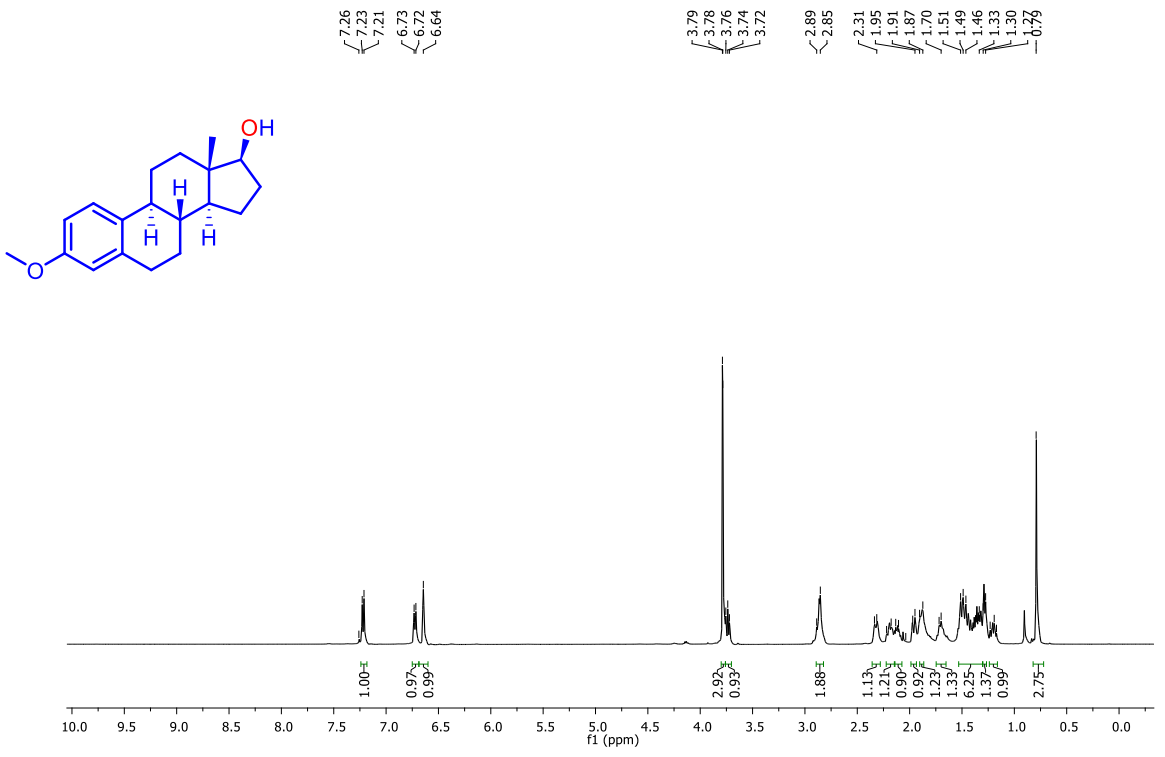


Figure S39. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of (8R,9S,13S,14S,17S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-ol (**4z**)

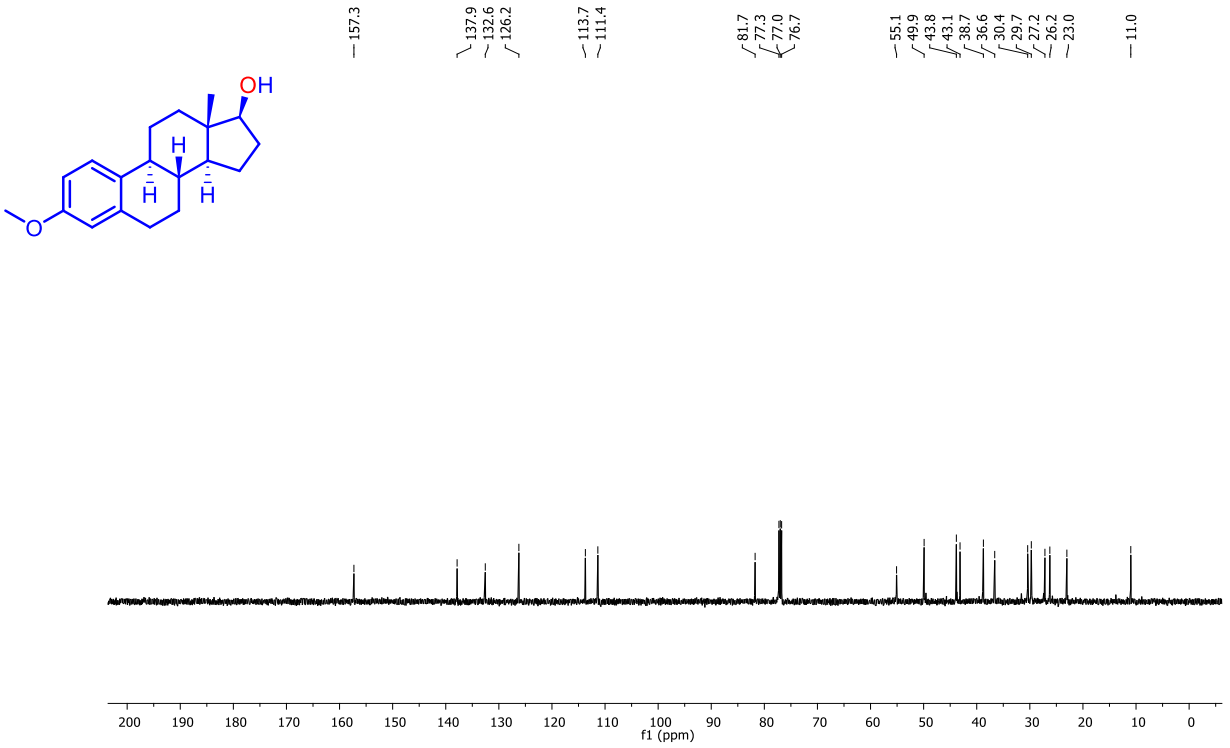


Figure S40. ^{1}H NMR (in $CDCl_3$) spectrum of (3S,8S,9S,10R,13R,14S,17R)-3-methoxy-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-5H-cyclopenta[a]phenanthren-5-ol (**4aa**)

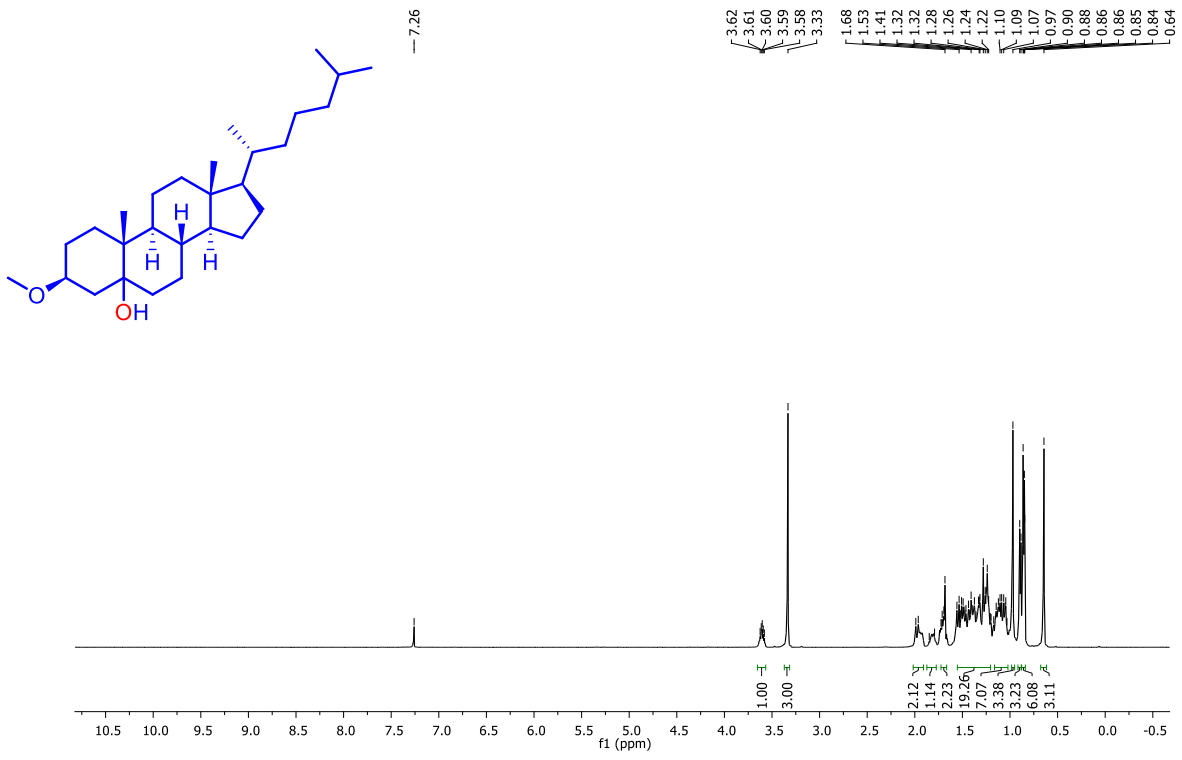
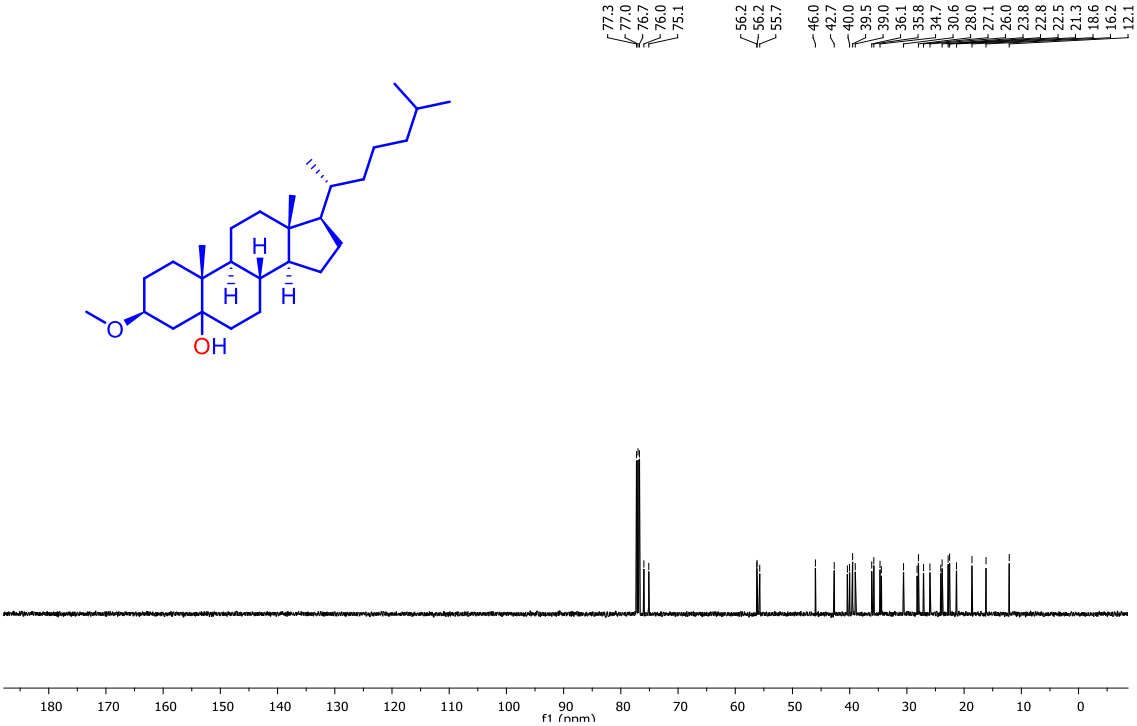


Figure S41. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of (3S,8S,9S,10R,13R,14S,17R)-3-methoxy-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-5H-cyclopenta[a]phenanthren-5-ol (**4aa**)



6. ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$ NMR spectra of hydroborated epoxides

Figure S42. ^{1}H NMR (in $CDCl_3$) spectrum of 9-((1-isopropoxypropan-2-yl)oxy)-9-borabicyclo[3.3.1]nonane (**3o**)

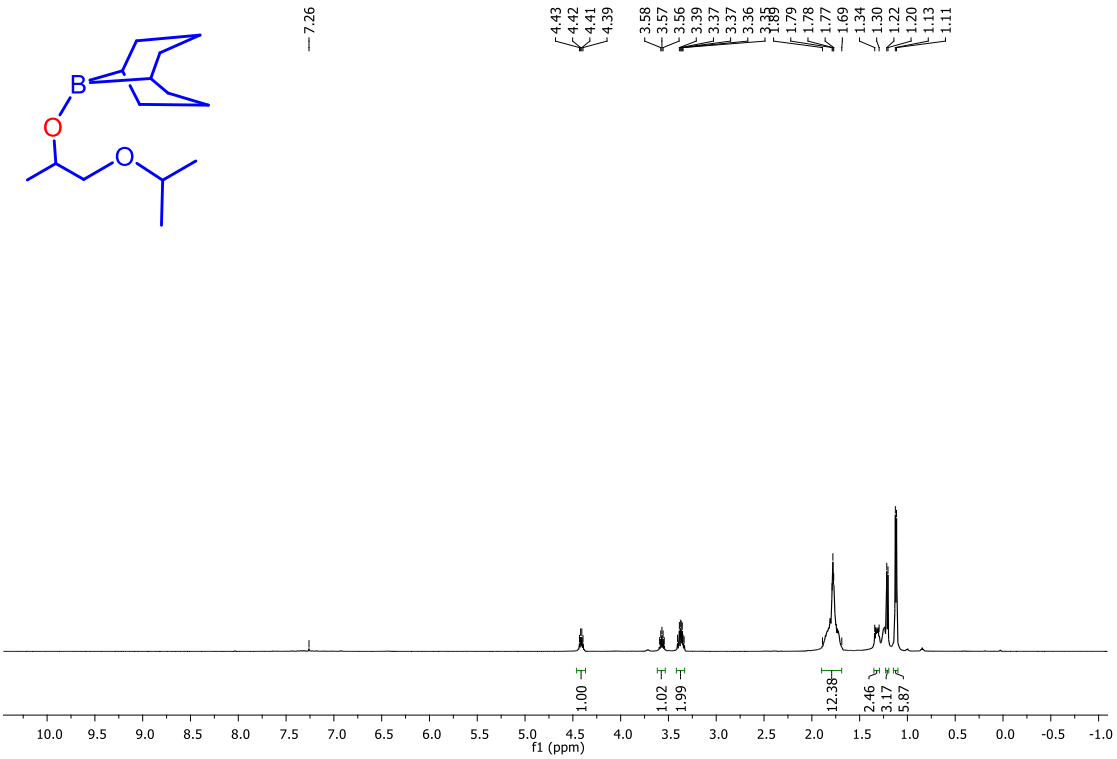


Figure S43. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 9-((1-isopropoxypropan-2-yl)oxy)-9-borabicyclo[3.3.1]nonane (**3o**)

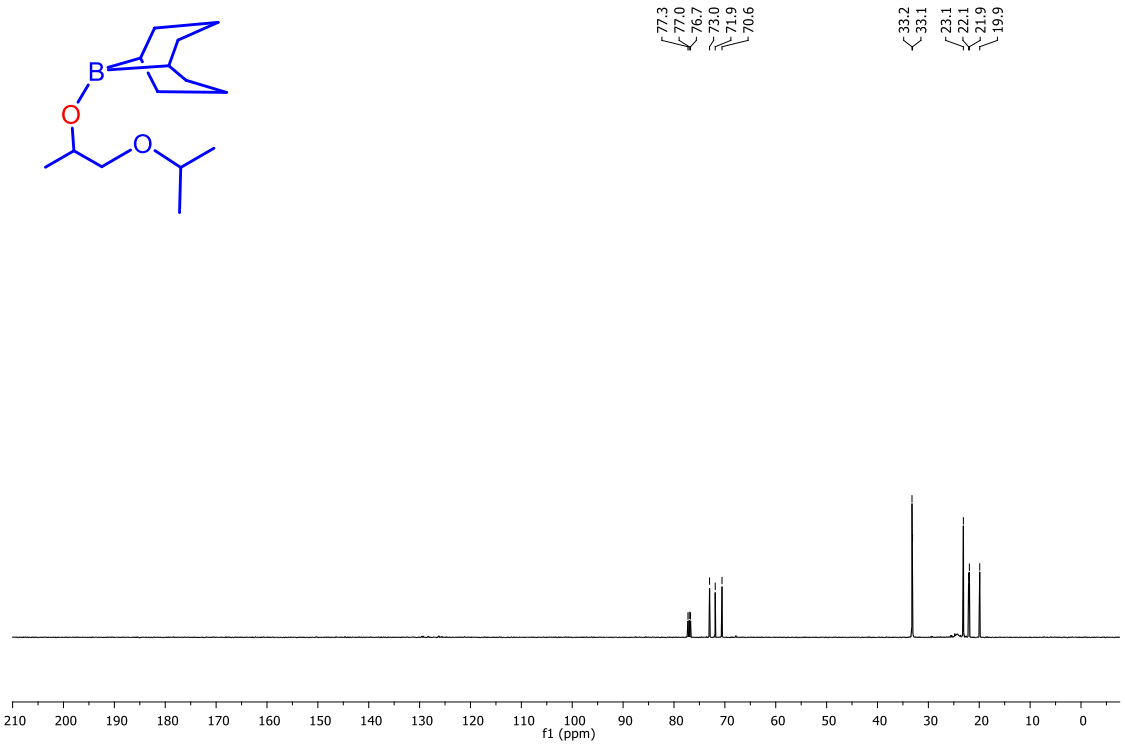


Figure S44. $^{11}B\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 9-((1-isopropoxypropan-2-yl)oxy)-9-borabicyclo[3.3.1]nonane (**3o**)

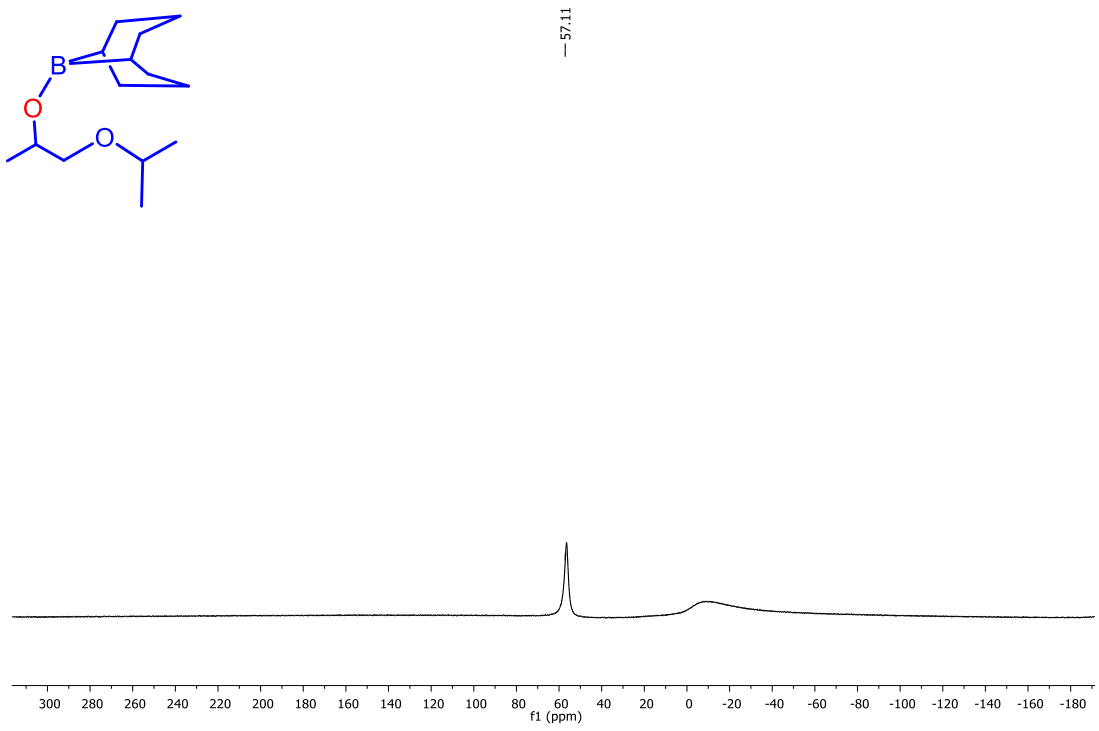


Figure S45. ^{1}H NMR (in $CDCl_3$) spectrum of 9-(hexan-2-yloxy)-9-borabicyclo[3.3.1]nonane (**3p**)

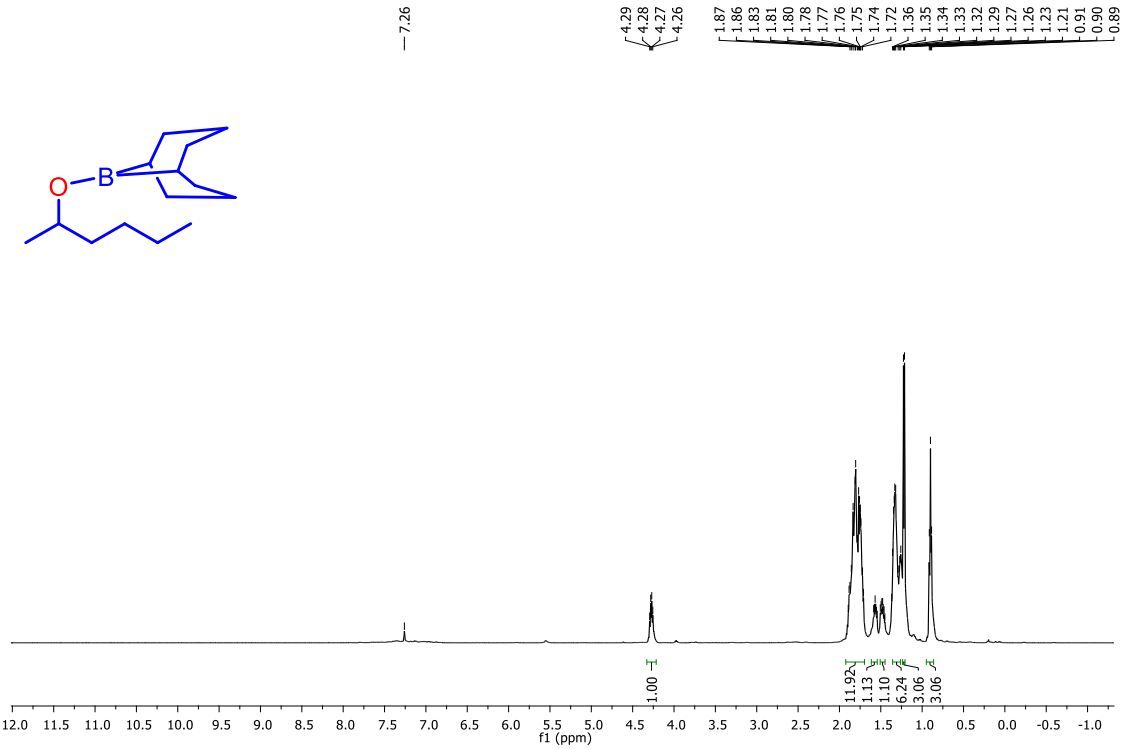


Figure S46. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum 9-(hexan-2-yloxy)-9-borabicyclo[3.3.1]nonane (**3p**)

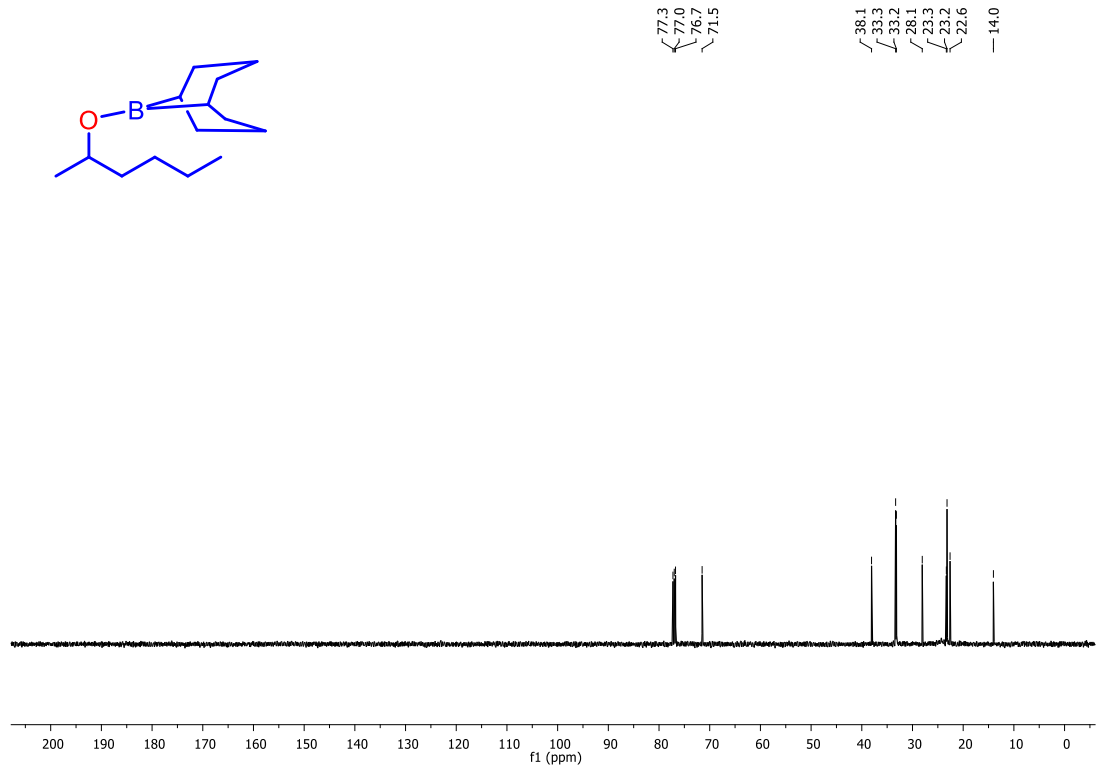


Figure S47. $^{11}B\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 9-(hexan-2-yloxy)-9-borabicyclo[3.3.1]nonane (**3p**)

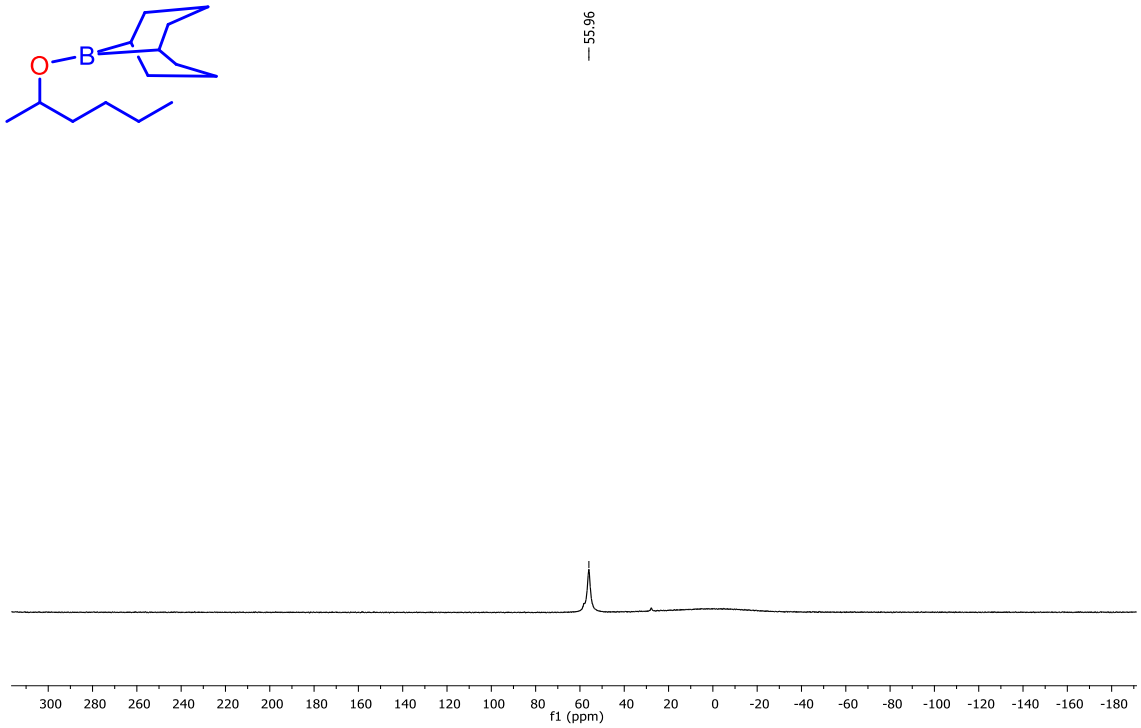


Figure S48. ^{1}H NMR (in C_6D_6) spectrum of 3-(3-(((1s,5s)-9-borabicyclo[3.3.1]nonan-9-yl)oxy)butoxy)propyl)trimethoxysilane (**3q**)

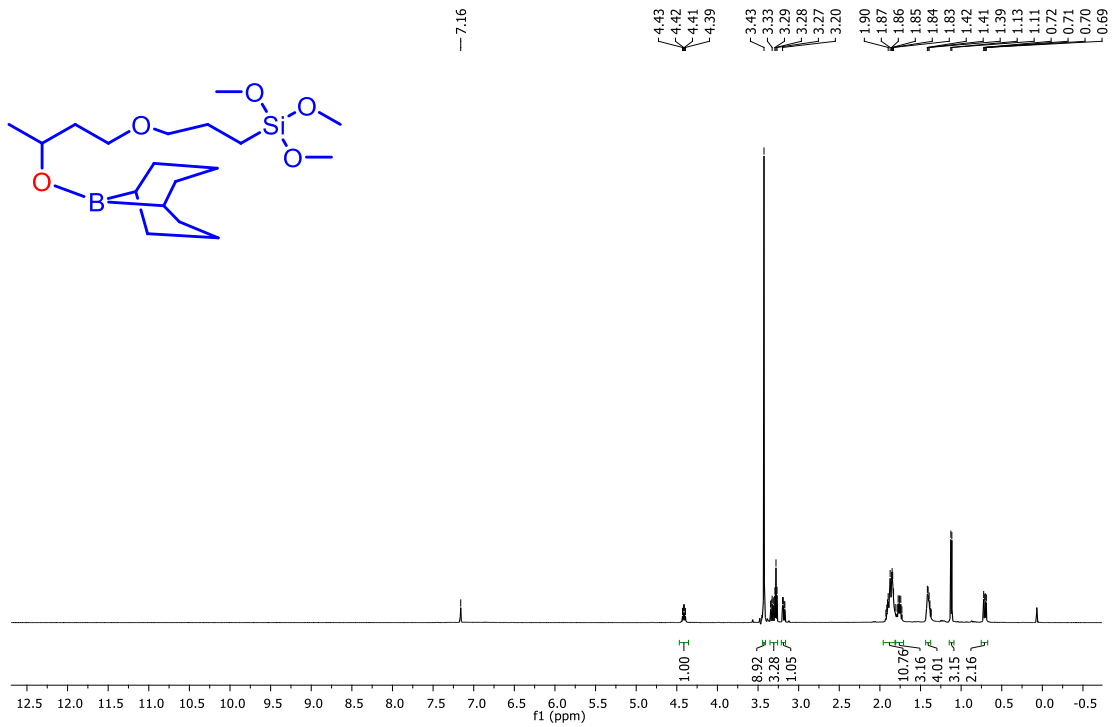


Figure S49. $^{13}C\{^{1}H\}$ NMR (in C_6D_6) spectrum of 3-(3-(((1s,5s)-9-borabicyclo[3.3.1]nonan-9-yl)oxy)butoxy)propyl)trimethoxysilane (**3q**)

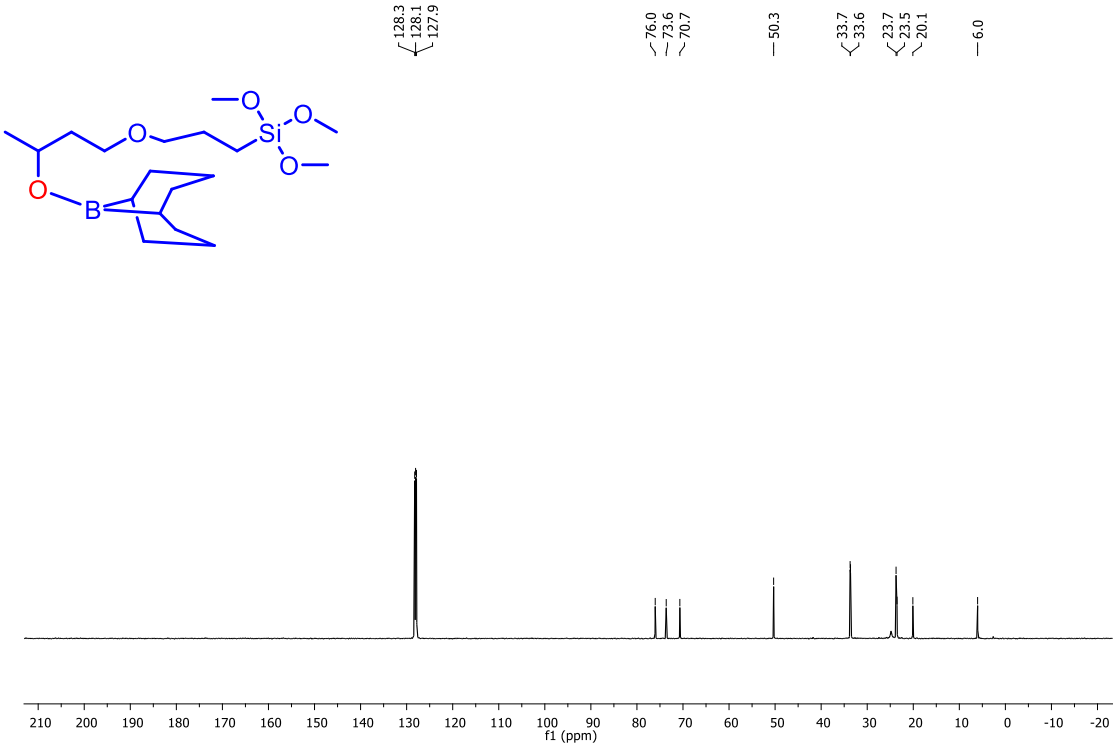


Figure S50. $^{11}B\{^{1}H\}$ NMR (in C_6D_6) spectrum of 3-(3-(((1s,5s)-9-borabicyclo[3.3.1]nonan-9-yl)oxy)butoxy)propyl)trimethoxysilane (**3q**)

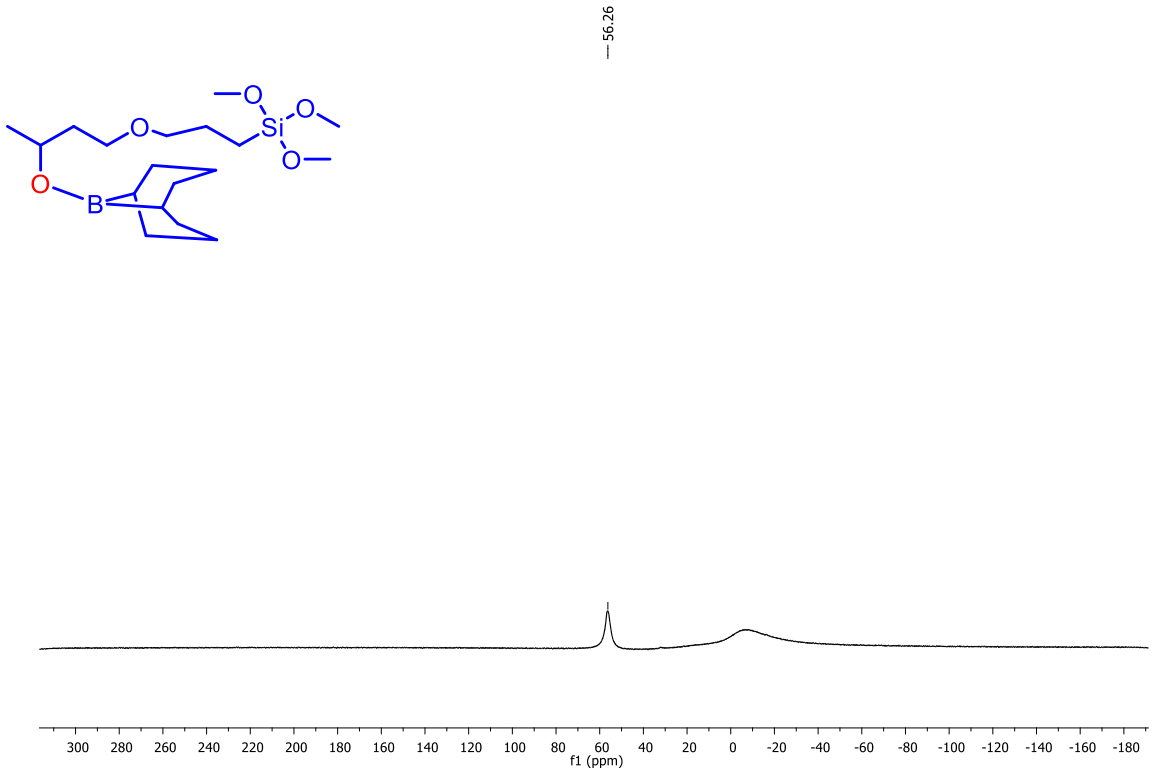


Figure S51. $^{29}Si\{^{1}H\}$ NMR (in C_6D_6) spectrum of 3-(3-(((1s,5s)-9-borabicyclo[3.3.1]nonan-9-yl)oxy)butoxy)propyl)trimethoxysilane (**3q**)

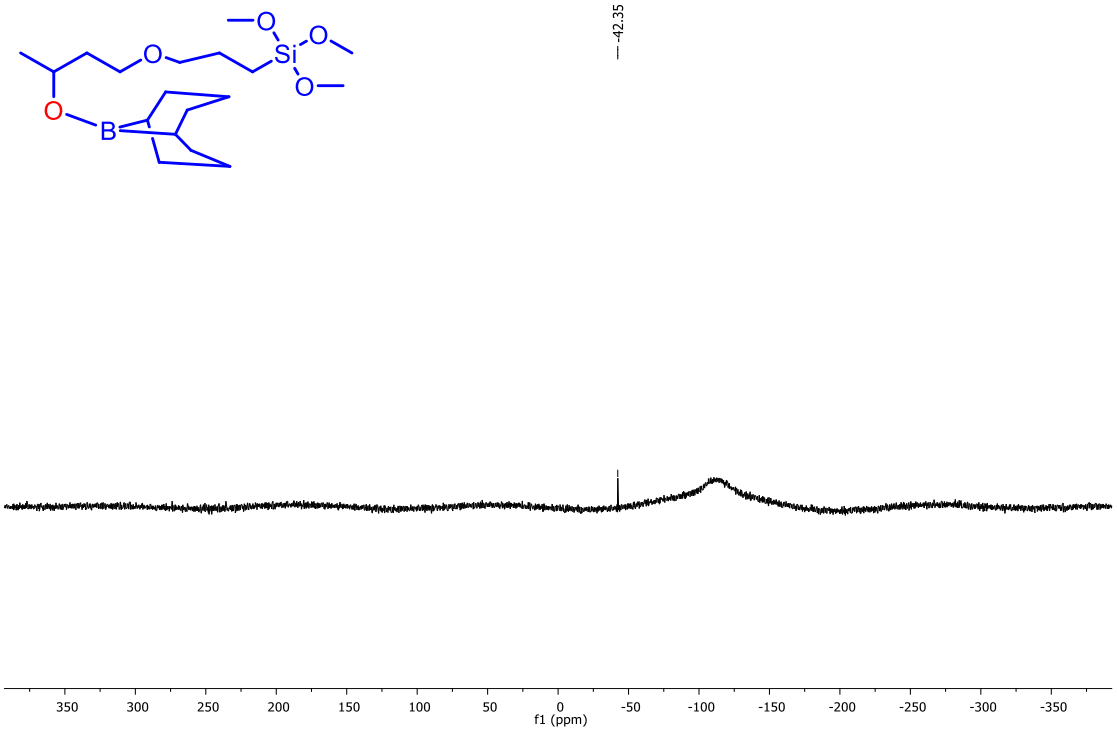


Figure S52. ^{1}H NMR (in $CDCl_3$) spectrum of 1,4-bis(2-(((1s,5s)-9-borabicyclo[3.3.1]nonan-9-yl)oxy)propoxy)butane (**3q**)

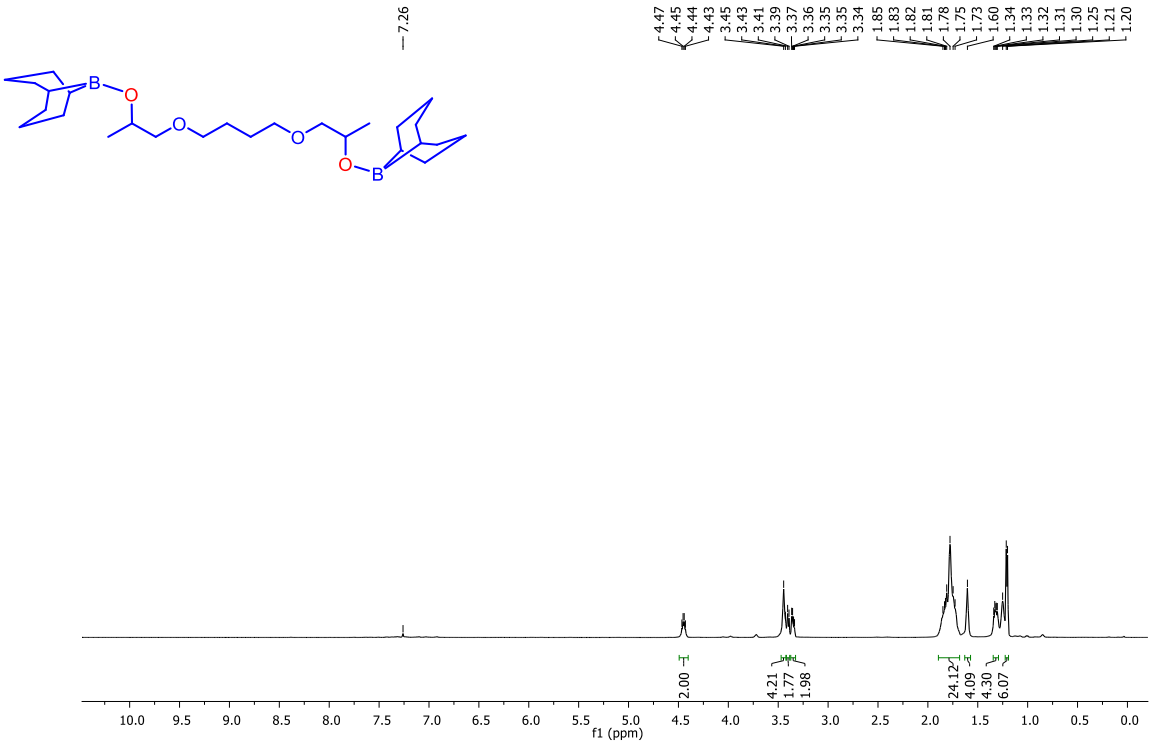


Figure S53. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1,4-bis(2-(((1s,5s)-9-borabicyclo[3.3.1]nonan-9-yl)oxy)propoxy)butane (**3r**)

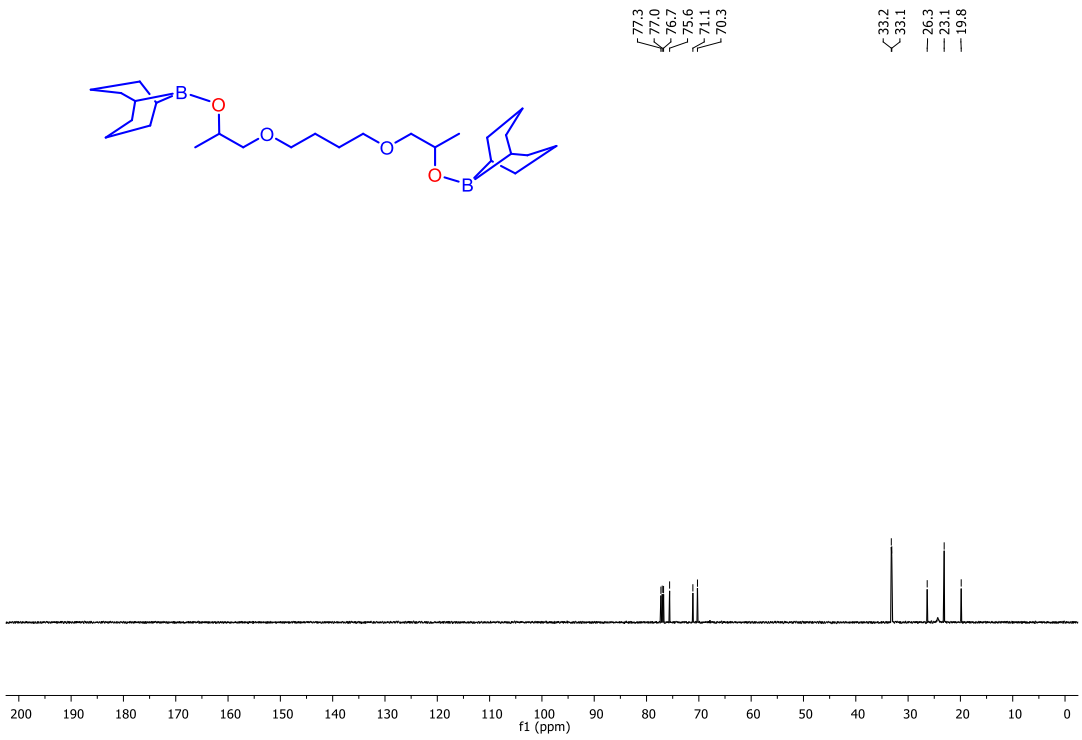


Figure S54. $^{11}B\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of 1,4-bis(2-(((1s,5s)-9-borabicyclo[3.3.1]nonan-9-yl)oxy)propoxy)butane (**3t**)

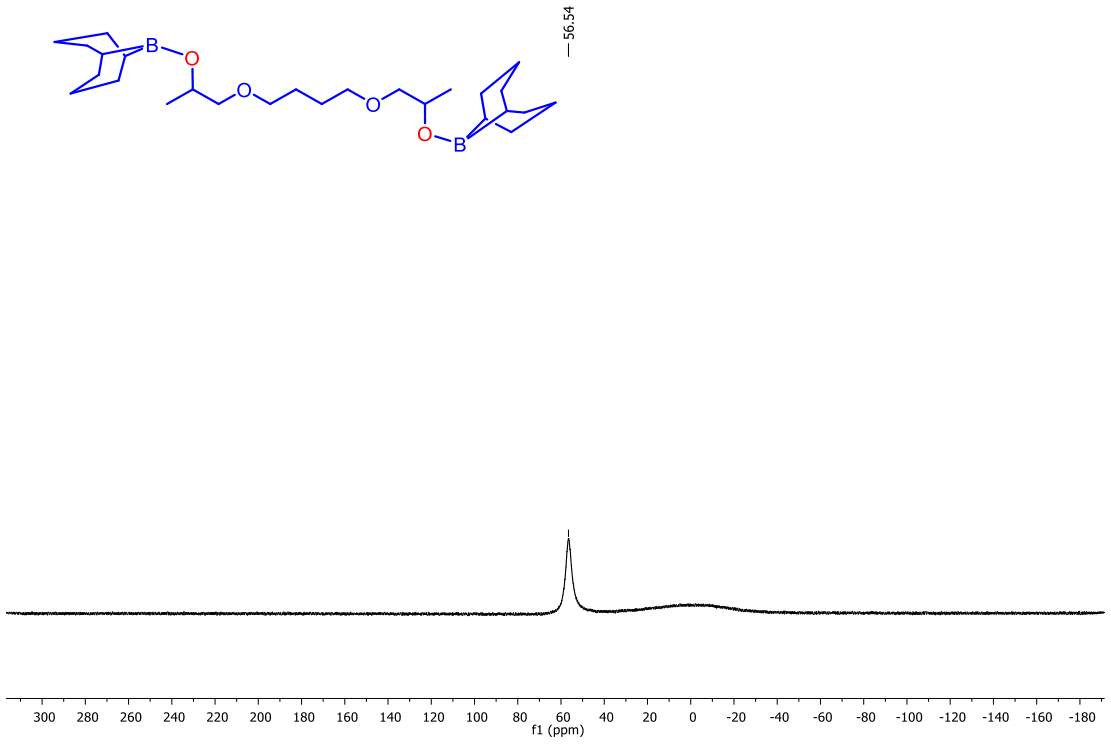


Figure S55. ^{1}H NMR (in $CDCl_3$) spectrum of reaction mixture of hydroborated product of butylene-oxide with internal standard. (**3s**)

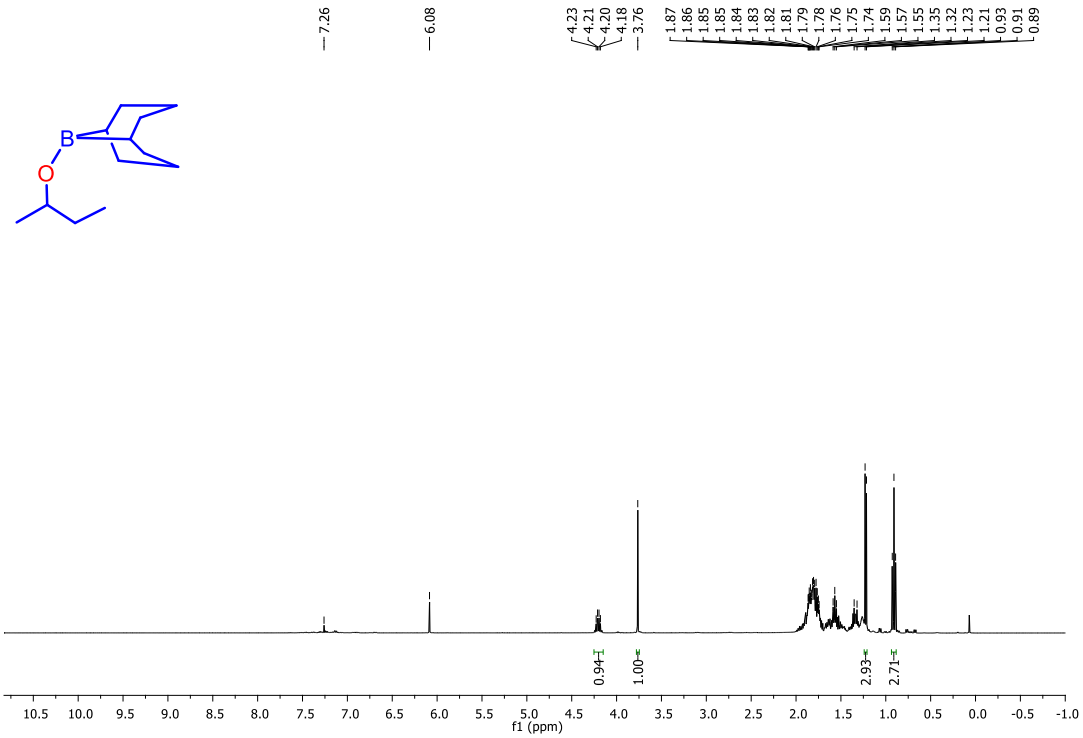


Figure S56. ^{1}H NMR (in $CDCl_3$) spectrum of the reaction mixture of the hydroborated product of epichlorohydrin (**3t**) with internal standard.

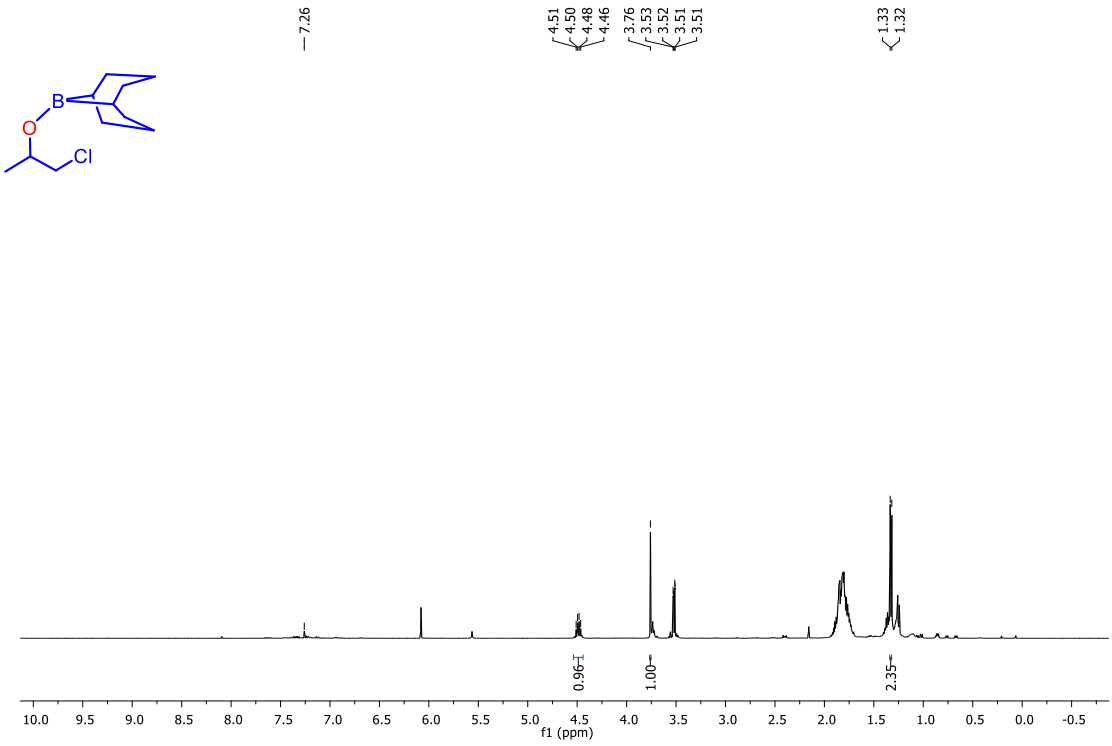


Figure S57. ^{1}H NMR (in $CDCl_3$) spectrum of reaction mixture of hydroborated product of cyclohexene oxide (**3u**) with internal standard

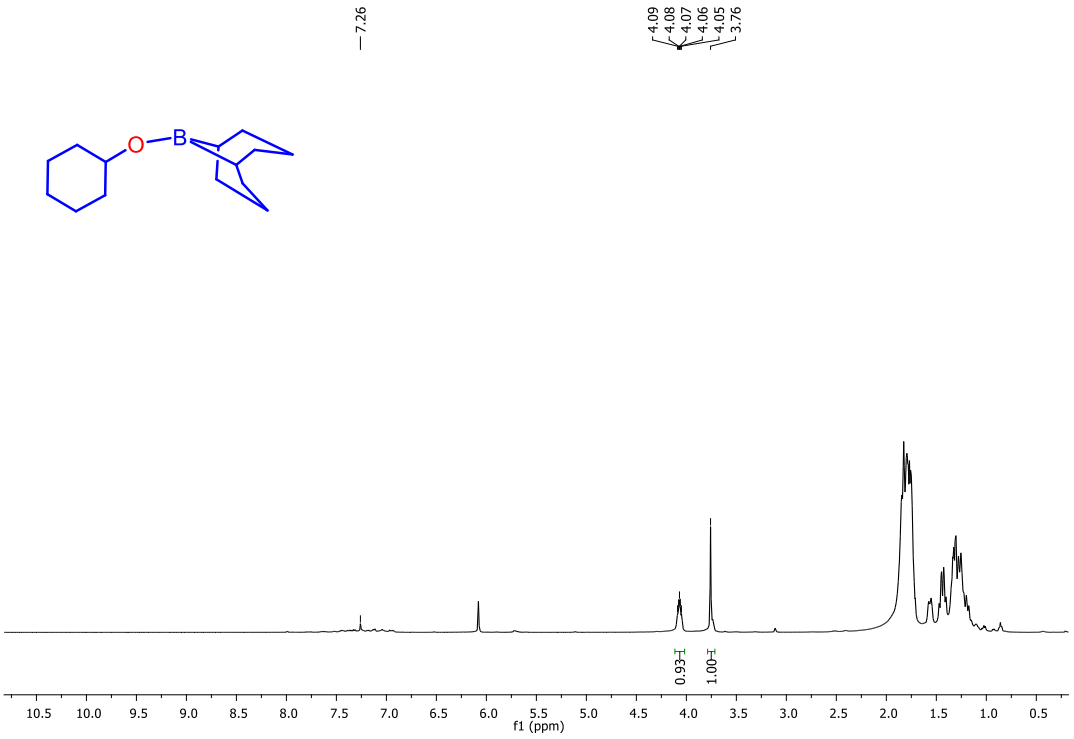


Figure S58. ^{1}H NMR (in $CDCl_3$) spectrum of the reaction mixture of the hydroborated product of cyclopentene oxide (**3v**) with internal standard

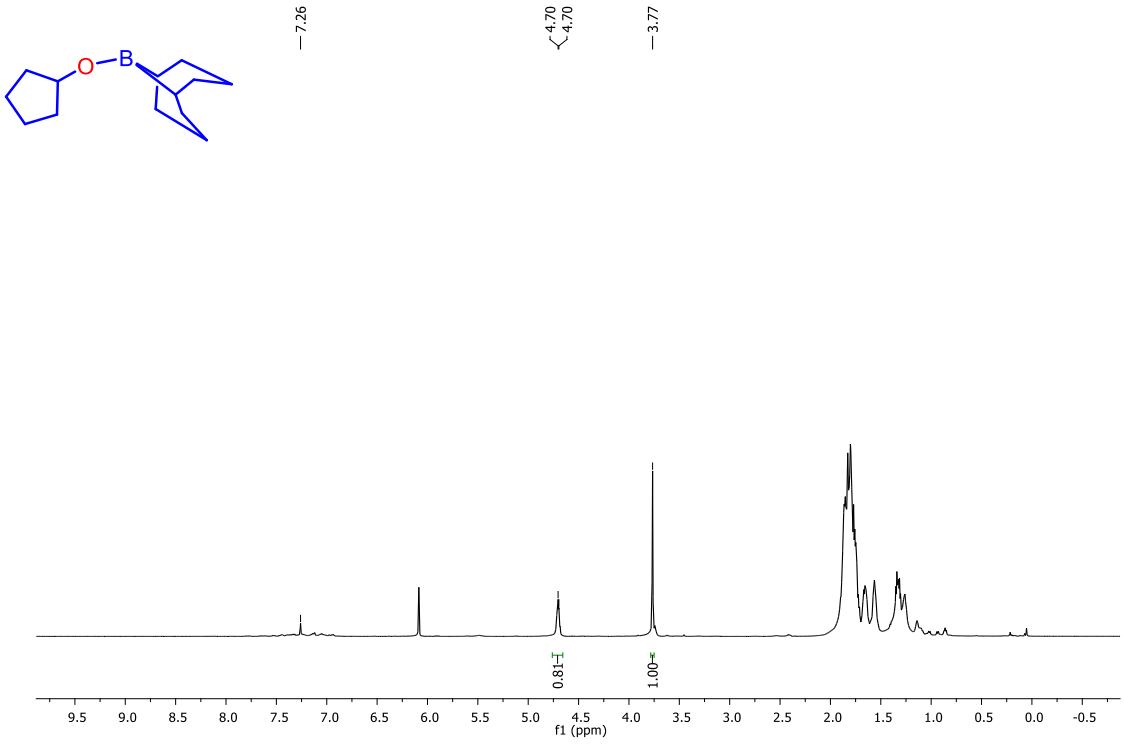


Figure S59. ^{1}H NMR (in $CDCl_3$) spectrum of the reaction mixture of the hydroborated product of t-butyl glycidal ether (**3w**) with internal standard

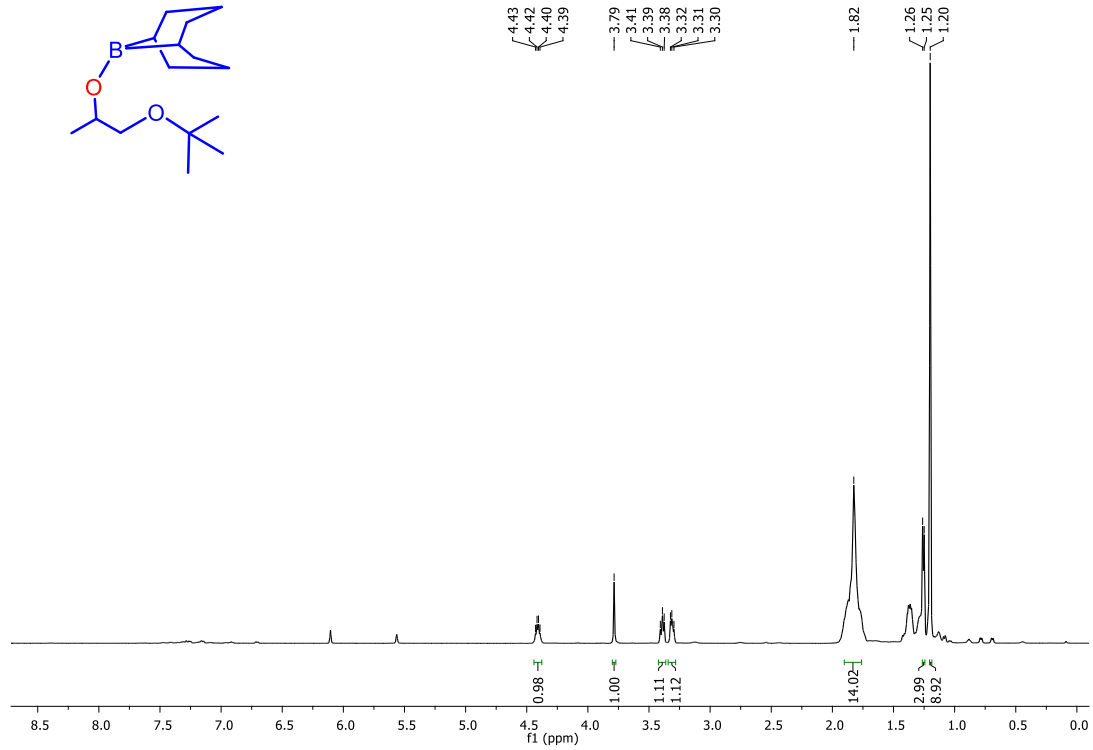
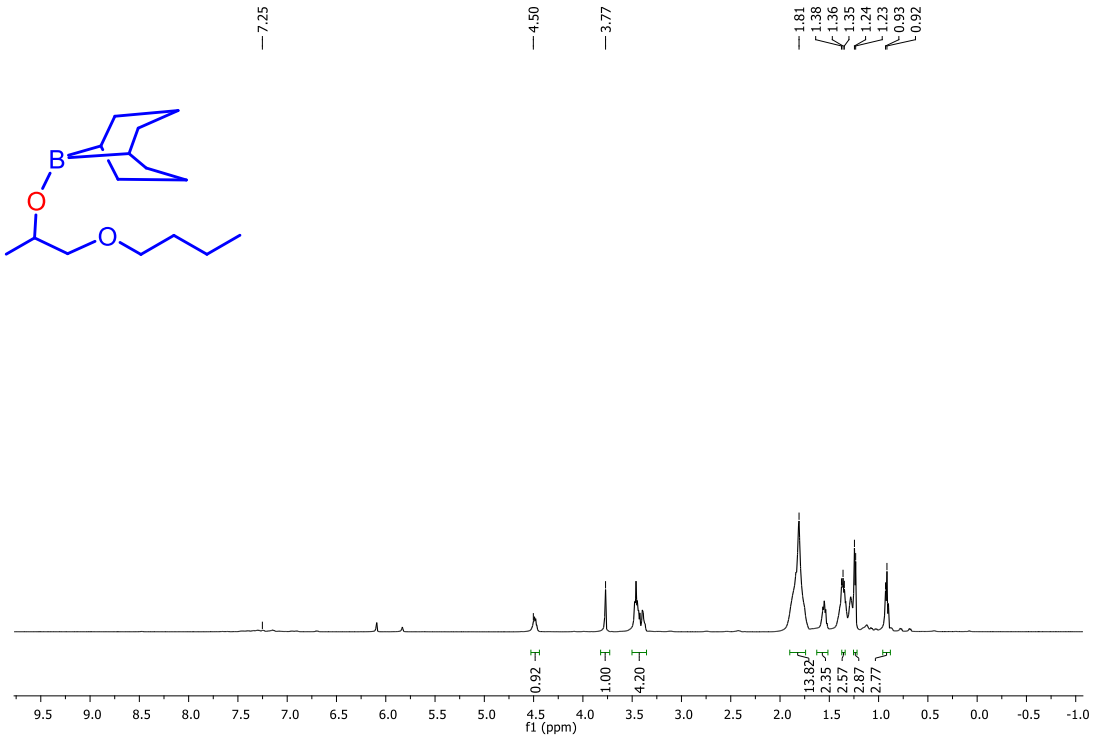


Figure S60. ^{1}H NMR (in $CDCl_3$) spectrum of the reaction mixture of the hydroborated product of n-butyl glycidal ether(**3x**) with internal standard



6. Computational Study

Computational Details

All the calculations are performed with the Gaussian 16 suite of programs under the framework of Density functional theory.[21] The geometry optimizations of all the compounds are carried out with M06-2X functional with 6-311G(d,p) basis set.[22,23] Harmonic vibrational frequency analysis is performed to characterize the optimized structures to be minima (zero imaginary frequency) or transition states (one imaginary frequency). Transition states (TSs) are further verified by intrinsic reaction coordinate (IRC) calculations to confirm their connection to two respective minimum structures. The optimized geometries are further refined with single-point energy calculations at the M062X/6-311++g(d,p) level of theory. The SMD[24] solvation model is used to account for the solvent effects. All thermochemical data are obtained with the ideal gas-rigid rotor-simple harmonic oscillator approximations at 298.15 K and 1 atm. Zero point-energy corrections are included in the Gibbs free energy values along with a concentration correction for c = 1 mol/ dm^3 condition in the solvent.

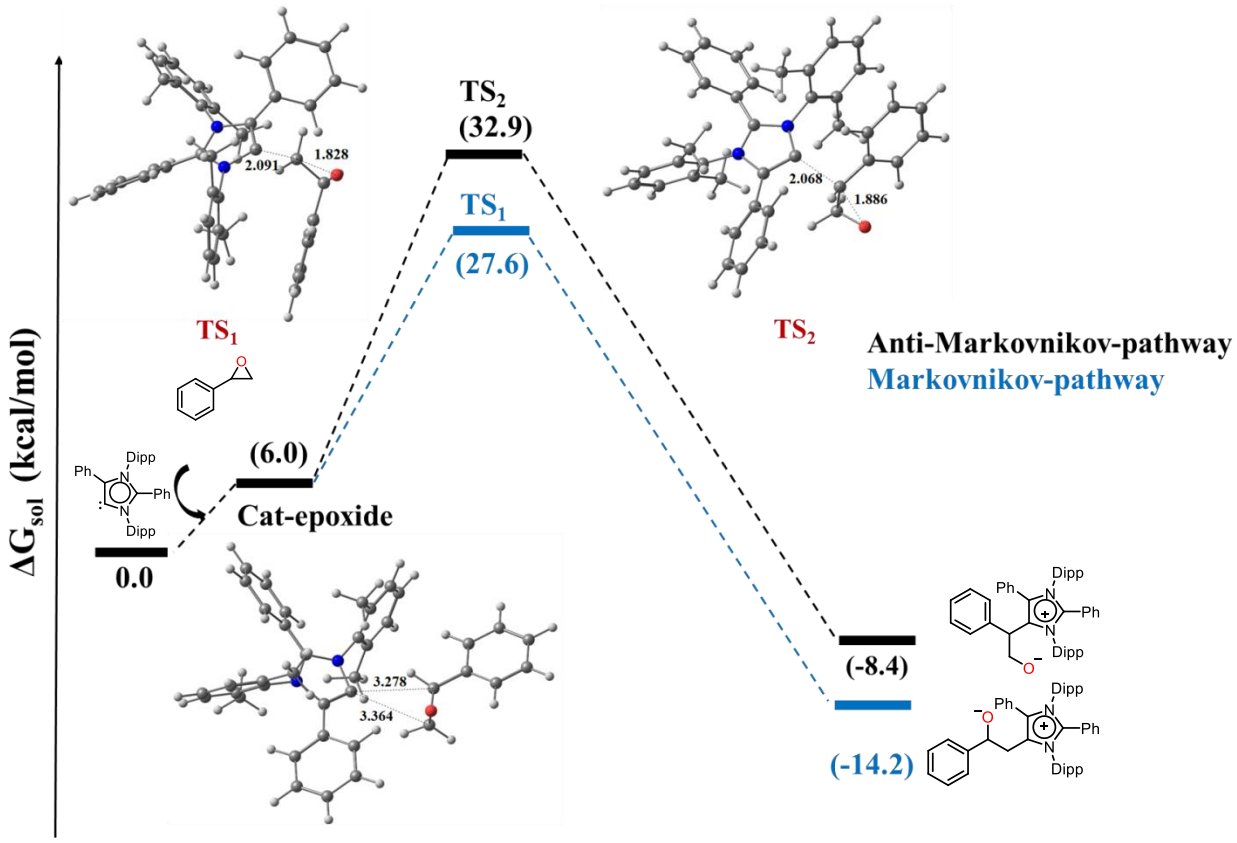
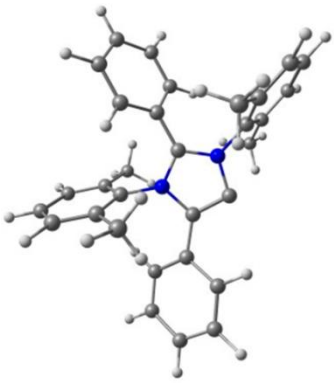


Figure S61: Figure: Gibbs free energy profile for the ring-opening of epoxide by Markovnikov and anti-Markovnikov pathway using aNHC computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d,p) level of theory. All energies are reported in kcal/mol.

Cartesian Coordinates of the optimized geometries in standard XYZ format

Catalyst **1a**

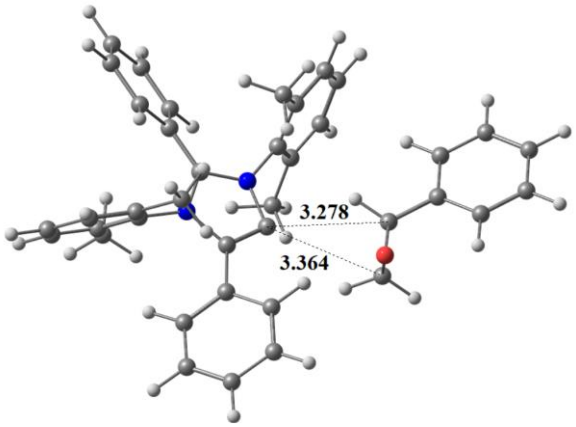


N	0.00000000	0.00000000	0.00000000
N	0.00000000	0.00000000	2.15115200
C	0.81295976	0.00000000	1.07079749
C	2.28214817	-0.00348653	1.05735903
C	2.99866153	0.82089565	0.17842165
H	2.46588871	1.47706713	-0.50179248
C	-1.33067572	-0.00442399	0.45814812
C	2.98624588	-0.83217420	1.94238455
H	2.44078123	-1.47330376	2.62716479
C	4.38875678	0.80665814	0.18123180
H	4.93121613	1.45010111	-0.50341094
C	0.47102131	0.07632892	3.50433403
C	-2.49985488	0.00574117	-0.43519626
C	0.45348241	0.01183801	-1.36026786
C	-1.36893382	0.00669408	1.84720188
C	5.08107363	-0.02013333	1.06206590

H	6.16607162	-0.02647516	1.06385588
C	4.37606535	-0.83638799	1.94299919
H	4.90836089	-1.48313943	2.63238747
C	0.34184468	-1.05707555	4.31417275
C	1.00190285	-1.15742089	-1.89754891
C	-2.53808831	-0.57352780	-1.71145062
H	-1.66937783	-1.08535934	-2.11040402
C	0.29733482	1.18990062	-2.09925255
C	-0.30875020	2.41825570	-1.47519096
H	0.11485562	2.61048048	-0.48358456
C	-3.66706862	0.61243340	0.05674399
H	-3.63380622	1.03464818	1.05550387
C	1.00597322	1.28047527	3.96834973
C	0.72081166	1.17827297	-3.42812590
H	0.61191672	2.07972852	-4.02369532
C	1.11992901	-2.40866540	-1.06872740
H	0.21035820	-2.57774687	-0.48357293
C	1.41325155	-1.12405662	-3.23047077
H	1.83867355	-2.01967606	-3.67335142
C	1.27418633	0.03240546	-3.99018372
H	1.59589502	0.04008743	-5.02655244
C	-3.69956794	-0.51909031	-2.47811099
H	-3.70737215	-0.97334001	-3.46409853
C	0.80535514	-0.97275218	5.62612849
H	0.71878408	-1.84089877	6.27303494

C	-0.28292848	-2.31190216	3.76754713
H	0.27942168	-2.69204248	2.90583849
C	-4.82478467	0.65423622	-0.70772286
H	-5.71496877	1.12933738	-0.30715513
C	-4.84521633	0.09633121	-1.98527514
H	-5.74778995	0.13481364	-2.58670426
C	1.45966434	1.32315472	5.28798741
H	1.87861378	2.24885667	5.67174852
C	1.36742168	0.20558461	6.10881522
H	1.72258575	0.25570794	7.13315296
C	1.06572668	2.49184065	3.07601834
H	1.88383604	2.41429806	2.35092529
H	1.95604506	-2.33688172	-0.36445938
H	1.28959887	-3.27638485	-1.70877631
H	-0.31587582	-3.09325305	4.52900846
H	-1.29395179	-2.09594013	3.41113032
H	-0.13572085	3.29290786	-2.10484193
H	-1.38879862	2.29318028	-1.34376426
H	1.22535193	3.39528095	3.66777747
H	0.13106341	2.59947294	2.51676398

Cat-epoxide



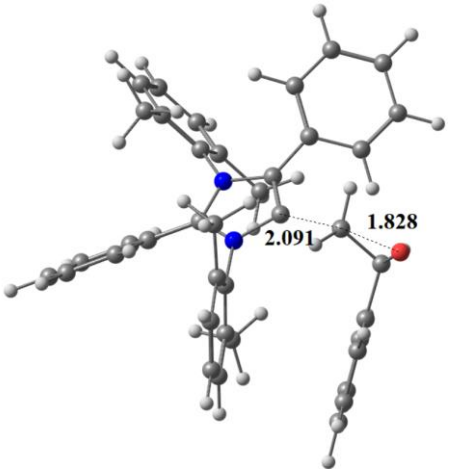
N	-1.89971390	-0.24423225	-0.10091568
N	0.00894391	0.68369515	-0.45265961
C	-1.27556638	0.94656034	-0.12486912
C	-1.87515403	2.26048207	0.14135404
C	-2.76918002	2.44571543	1.20496570
H	-3.02298578	1.61025839	1.84901019
C	-0.96220976	-1.24159754	-0.42241744
C	-1.54373878	3.35325254	-0.67184900
H	-0.85314643	3.21791406	-1.49804795
C	-3.32466996	3.69806037	1.44111041
H	-4.01476604	3.82948428	2.26777897
C	1.05612711	1.66506314	-0.46886489
C	-1.27893411	-2.67828460	-0.45685463
C	-3.28904947	-0.43065619	0.20406152
C	0.28235918	-0.67680738	-0.65163137
C	-2.99196211	4.77881045	0.62855465
H	-3.42548144	5.75531742	0.81754031

C	-2.09901591	4.60328672	-0.42566942
H	-1.83587049	5.44071578	-1.06307379
C	1.62013297	2.01693244	-1.70034817
C	-4.24283142	-0.05611663	-0.74815952
C	-2.50004734	-3.20428871	-0.89907856
H	-3.28749937	-2.54400668	-1.24741917
C	-3.62407702	-1.00709670	1.43431268
C	-2.55789981	-1.39737083	2.42251704
H	-1.80821053	-0.60635354	2.53213408
C	-0.26760530	-3.56392762	-0.05022722
H	0.68081336	-3.15390908	0.28900171
C	1.51112191	2.18384639	0.74748880
C	-4.97832133	-1.20207370	1.70594433
H	-5.26645840	-1.64642589	2.65389399
C	-3.82795450	0.53587951	-2.06899582
H	-2.97485008	-0.00515633	-2.49087209
C	-5.58550746	-0.26843723	-0.43402682
H	-6.34641026	0.00967414	-1.15715616
C	-5.95125265	-0.83659992	0.78145742
H	-7.00002290	-0.99814282	1.00847068
C	-2.70969201	-4.58051075	-0.91568874
H	-3.66163773	-4.97120118	-1.26161262
C	2.64352425	2.96437600	-1.69789834
H	3.09375753	3.25681584	-2.64192406
C	1.13100595	1.37587256	-2.97048714

H	1.26748012	0.29217133	-2.91385613
C	-0.48146813	-4.93657753	-0.08058523
H	0.31104594	-5.60629126	0.23842106
C	-1.70473354	-5.45157365	-0.50646225
H	-1.87190348	-6.52389377	-0.52276808
C	2.53587453	3.13176540	0.70598018
H	2.90695566	3.54755923	1.63801519
C	3.09077267	3.52794589	-0.50571235
H	3.88878853	4.26348897	-0.52081938
C	0.93134674	1.70942932	2.05369584
H	0.81121914	0.62103066	2.04553991
C	4.81942769	-0.96367916	0.30893324
C	5.76324852	-1.90691471	0.71761911
C	7.06955425	-1.51392276	0.99050188
C	7.44249769	-0.17746743	0.85914889
C	6.49984679	0.76660730	0.45859973
C	5.19174703	0.37597055	0.18904011
H	5.45070273	-2.94057759	0.83272142
H	7.79920983	-2.25100097	1.31168162
H	8.46193199	0.12717616	1.07389755
H	6.78210708	1.81066928	0.36119663
H	4.44906075	1.10906269	-0.11863232
C	3.42468457	-1.36058273	-0.01881994
C	3.13411267	-2.42879437	-0.98963894
O	2.99941299	-2.64888274	0.40831090

H	2.65791575	-0.59243179	0.06687179
H	3.96859298	-2.95019647	-1.45612385
H	2.19220226	-2.36609002	-1.53106023
H	1.58700877	1.98063610	2.88302324
H	-0.05254079	2.15502524	2.23930917
H	1.66551558	1.77097256	-3.83606883
H	0.05795905	1.54881463	-3.11550113
H	-2.02874722	-2.29618975	2.08878532
H	-2.99801259	-1.59851465	3.40083334
H	-3.52930731	1.58383851	-1.95472017
H	-4.65341109	0.49512053	-2.78193425

Markovnikov-TS



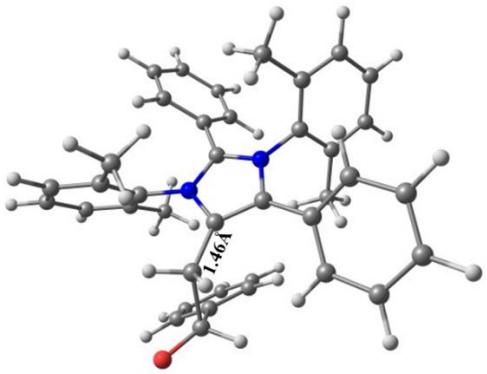
N	1.62832300	-0.03290200	-0.09595100
N	-0.44963600	-0.42345400	-0.51441500
C	0.71680600	-1.01705800	-0.19107400
C	0.95173800	-2.45144600	0.03056100
C	1.72762400	-2.88806900	1.11269600
H	2.15805800	-2.16456200	1.79695900

C	0.99552100	1.19063600	-0.36979200
C	0.38450300	-3.39647500	-0.83441700
H	-0.22162700	-3.06746300	-1.67173300
C	1.93656100	-4.24673000	1.31790300
H	2.53623000	-4.57450000	2.16025200
C	-1.70403200	-1.11035100	-0.67157400
C	1.69615200	2.48495300	-0.36369500
C	3.01419200	-0.22779500	0.22749200
C	-0.33887700	0.96151600	-0.63041400
C	1.37240700	-5.18161600	0.45357100
H	1.53518600	-6.24157800	0.61815200
C	0.59568900	-4.75355300	-0.61990800
H	0.15243700	-5.47679200	-1.29587800
C	-2.21064300	-1.25529000	-1.96808900
C	3.85180400	-0.80521400	-0.73264600
C	2.99637000	2.65996300	-0.85531700
H	3.54460500	1.81778000	-1.26424100
C	3.46573600	0.19523800	1.48237000
C	2.52434400	0.81789000	2.47860700
H	1.58309200	0.26146000	2.54183700
C	1.00292100	3.60063100	0.12544700
H	-0.00523200	3.46189700	0.50296100
C	-2.36258700	-1.58012400	0.46686200
C	4.81821600	0.01474700	1.77229000
H	5.19587100	0.33136700	2.73976500

C	3.32302100	-1.21837500	-2.08076900
H	2.64086000	-0.46409700	-2.48641500
C	5.19673300	-0.96676700	-0.39886900
H	5.87074600	-1.40898400	-1.12628200
C	5.67660400	-0.56117500	0.84175900
H	6.72626400	-0.69172400	1.08367900
C	3.58898700	3.91857300	-0.84127300
H	4.59652600	4.03865000	-1.22631000
C	-3.45146300	-1.87537700	-2.10637600
H	-3.87362200	-1.99570500	-3.09954300
C	-1.41748900	-0.80053200	-3.16674700
H	-1.24595900	0.27913500	-3.15543900
C	1.59421600	4.85833400	0.12430700
H	1.03899100	5.71115800	0.50074600
C	2.89275100	5.02057100	-0.35253100
H	3.35747100	6.00111100	-0.34877600
C	-3.59843700	-2.20088500	0.27951400
H	-4.14309200	-2.55611600	1.14881900
C	-4.14274100	-2.33864600	-0.99108300
H	-5.11230900	-2.81013000	-1.11485800
C	-1.74718600	-1.45928000	1.83504300
H	-1.28646400	-0.47681700	1.97189700
C	-3.53765100	1.91453100	0.62855400
C	-3.21394600	1.60693700	1.94903400
C	-4.03353500	0.76814300	2.70295700

C	-5.18245600	0.22316400	2.13491300
C	-5.50912300	0.52710500	0.81264300
C	-4.69424400	1.37092400	0.06643400
H	-2.32415100	2.04817200	2.39572400
H	-3.78112800	0.54863300	3.73711300
H	-5.82834600	-0.42198100	2.72376700
H	-6.40958100	0.11079400	0.36935600
H	-4.93704200	1.66444900	-0.95057400
C	-2.69302300	2.84939300	-0.20891100
C	-1.87474900	2.23180900	-1.26333800
O	-3.28876600	3.38895000	-1.31268400
H	-2.15188400	3.55018100	0.45856200
H	-2.36433000	1.43441700	-1.80416400
H	-1.16383700	2.86539500	-1.77545800
H	-2.51265100	-1.57942800	2.60295000
H	-0.97979700	-2.22774900	1.98525400
H	-1.93867100	-1.05938900	-4.08983900
H	-0.42833400	-1.27453000	-3.18817300
H	2.27311800	1.84346200	2.18777900
H	2.97978400	0.84387700	3.47001000
H	2.76974100	-2.16158900	-2.01461100
H	4.14411800	-1.35769700	-2.78603600

Markovnikov-product



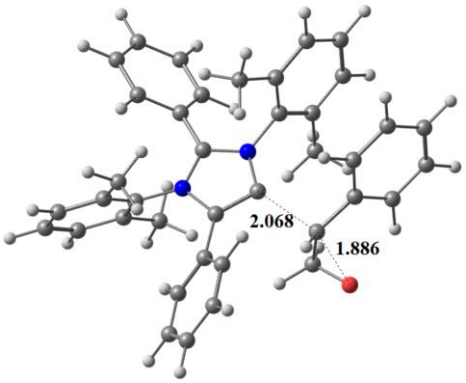
N	1.23498500	-0.37931300	-0.22510800
N	-0.86512900	-0.20836500	-0.71816300
C	0.07439300	-1.05158800	-0.24921600
C	-0.13119500	-2.44718000	0.16583500
C	0.37857800	-2.89776800	1.38952700
H	0.92068600	-2.21390300	2.03410800
C	1.03761400	0.92359600	-0.69140000
C	-0.85131600	-3.32717700	-0.65222100
H	-1.25051100	-2.98246000	-1.60066400
C	0.17069800	-4.21339100	1.78643400
H	0.56271900	-4.55362500	2.73872200
C	-2.21845300	-0.59255500	-1.03460500
C	2.12897300	1.88806700	-0.87963900
C	2.47455000	-0.92775300	0.26095300
C	-0.31020100	1.04835100	-0.99023400
C	-0.54752200	-5.08535200	0.97200900
H	-0.71240400	-6.11036400	1.28702700
C	-1.05710500	-4.64029400	-0.24543400

H	-1.61678500	-5.31610100	-0.88286700
C	-2.54664100	-0.71275000	-2.39390600
C	3.13024700	-1.89091400	-0.51319500
C	3.38414600	1.49353100	-1.36896600
H	3.56874100	0.45601100	-1.62443100
C	2.96386700	-0.46366100	1.48636700
C	2.22490100	0.57939600	2.27981800
H	1.14363000	0.40374900	2.27872000
C	1.91127100	3.24513100	-0.60538500
H	0.94306400	3.56882100	-0.23847400
C	-3.11801600	-0.87303900	-0.00399000
C	4.16311600	-1.01045800	1.94417100
H	4.56535200	-0.67241900	2.89421800
C	2.58135900	-2.33879500	-1.84227900
H	2.18528500	-1.49365900	-2.41502700
C	4.32555100	-2.40886000	-0.01455900
H	4.85887700	-3.15499500	-0.59562500
C	4.83750600	-1.97438100	1.20314900
H	5.76954800	-2.38713000	1.57494100
C	4.39559000	2.42793800	-1.55225600
H	5.35921700	2.10357300	-1.93143800
C	-3.85182600	-1.07978900	-2.71147700
H	-4.13398500	-1.17184800	-3.75575600
C	-1.52023800	-0.48832200	-3.47376400
H	-1.28299700	0.57411600	-3.58375400

C	2.92436900	4.17760500	-0.80392600
H	2.73230300	5.22329400	-0.58794400
C	4.17178100	3.77335200	-1.26853300
H	4.96295800	4.50097200	-1.41643700
C	-4.41622500	-1.23548900	-0.37418600
H	-5.13983800	-1.44485800	0.40757400
C	-4.78469000	-1.32761500	-1.70861100
H	-5.80071800	-1.60255700	-1.97217100
C	-2.71357500	-0.85986900	1.44246900
H	-1.95169000	-0.10432900	1.64819500
C	-1.97776000	2.66940100	1.06068000
C	-0.92425600	2.35519700	1.92471800
C	-1.17081400	1.89162100	3.21729200
C	-2.48383900	1.73991600	3.66281800
C	-3.53927900	2.05103200	2.80573500
C	-3.28619900	2.50955700	1.51489200
H	0.10213300	2.52113900	1.59792700
H	-0.34120700	1.67655100	3.88711600
H	-2.68054700	1.39756700	4.67449700
H	-4.56360800	1.94999500	3.15582500
H	-4.07067400	2.81422700	0.82763200
C	-1.77413700	3.34335000	-0.31036300
C	-1.12388300	2.18134400	-1.41985200
O	-2.81326100	3.85240800	-0.85458800
H	-0.88001100	4.01732200	-0.17173900

H	-2.06419500	1.84607600	-1.85479700
H	-0.58120600	2.79964000	-2.13780000
H	-3.57440500	-0.64040500	2.07443000
H	-2.31969200	-1.84208400	1.73005000
H	-1.89165800	-0.85838600	-4.43081100
H	-0.58181000	-1.00768500	-3.24593700
H	2.38656600	1.57578300	1.85227200
H	2.57525800	0.59207000	3.31356300
H	1.76736700	-3.05980500	-1.71093800
H	3.36329100	-2.81812200	-2.43381600

Anti-Markovnikov-TS



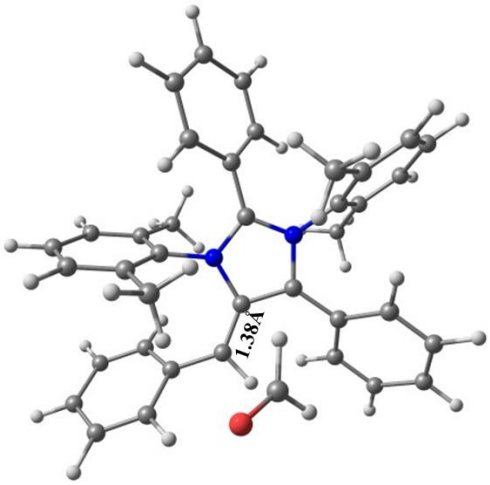
N	1.51939200	0.09440700	-0.04165500
N	-0.60541400	0.46989200	-0.08892800
C	0.59863700	1.06938000	0.01758800
C	0.86614800	2.50951800	0.13184900
C	1.84923100	3.11165600	-0.66347700
H	2.41616100	2.51091500	-1.36757600
C	0.86061100	-1.13238500	-0.19872700
C	0.13255200	3.29227700	1.03200700

H	-0.62157000	2.82667300	1.65731600
C	2.09412200	4.47562600	-0.55557200
H	2.85600000	4.93424400	-1.17668700
C	-1.83192800	1.20046100	-0.29194700
C	1.57468400	-2.41267100	-0.33090800
C	2.93415700	0.28966700	0.10983600
C	-0.50298500	-0.91821400	-0.24174600
C	1.36113400	5.24963600	0.34034700
H	1.55297700	6.31442800	0.42119000
C	0.38128300	4.65589000	1.13227500
H	-0.19007200	5.25447900	1.83352500
C	-2.71782300	1.39349300	0.76756500
C	3.42850800	0.58571700	1.38474600
C	2.64315300	-2.77831300	0.49730400
H	2.97566300	-2.10665200	1.28233700
C	3.75248200	0.13938600	-1.01381100
C	3.17268300	-0.20689900	-2.35934000
H	2.25327800	0.35399100	-2.55846100
C	1.14386900	-3.31153400	-1.31579600
H	0.32058000	-3.01960200	-1.96149500
C	-2.08974600	1.65123600	-1.59268700
C	5.12506700	0.31424400	-0.83551600
H	5.78508200	0.20731100	-1.69102900
C	2.50420200	0.69615500	2.56883100
H	1.75758600	-0.10587900	2.56539100

C	4.80718000	0.75122300	1.51632500
H	5.22003300	0.97781400	2.49464800
C	5.64825600	0.61854700	0.41650500
H	6.71878700	0.74829800	0.53707500
C	3.26867300	-4.00953000	0.33407300
H	4.09218100	-4.28196900	0.98601000
C	-3.91575100	2.05721400	0.48983400
H	-4.63091600	2.20253100	1.29450000
C	-2.41774700	0.93501600	2.17001200
H	-2.49395900	1.77387200	2.87018100
C	1.76288600	-4.54705000	-1.46713700
H	1.41217000	-5.23485100	-2.22944200
C	2.83140200	-4.89691600	-0.64580600
H	3.31733300	-5.85977900	-0.76417000
C	-3.28924200	2.31870200	-1.82250000
H	-3.51390900	2.67426200	-2.82382900
C	-4.20016100	2.51590100	-0.78844200
H	-5.13930900	3.02326100	-0.98441900
C	-1.09974400	1.40373800	-2.70031100
H	-0.77888300	0.35644900	-2.70849000
C	-3.09285300	-1.92245900	0.17647900
C	-3.41518000	-1.44573000	-1.09673800
C	-4.67496800	-0.92296300	-1.37025500
C	-5.63717500	-0.86133500	-0.36594200
C	-5.33285800	-1.35221400	0.90194200

C	-4.07831600	-1.89312500	1.16878100
H	-2.65113800	-1.46484200	-1.87016100
H	-4.89903500	-0.54997500	-2.36529900
H	-6.61852700	-0.44491600	-0.57259100
H	-6.08561100	-1.33629400	1.68489300
H	-3.85151700	-2.35512200	2.12369300
C	-1.71657000	-2.43766500	0.46134500
C	-1.27893000	-2.66544200	1.84989900
O	-2.09530100	-3.74817200	1.76362000
H	-1.29451300	-3.14167100	-0.24321200
H	-1.57968000	-1.85989100	2.55231000
H	-0.19148600	-2.84473000	1.96275200
H	-1.53957500	1.64204400	-3.67028100
H	-0.20420600	2.02478900	-2.57499100
H	-1.42181300	0.49553800	2.25685000
H	-3.14051100	0.17505900	2.47764100
H	2.91546500	-1.27057400	-2.40585400
H	3.89076200	0.00757800	-3.15284600
H	1.96397600	1.64916700	2.55963600
H	3.06911600	0.63791100	3.50069200

Anti-Markovnikov-product



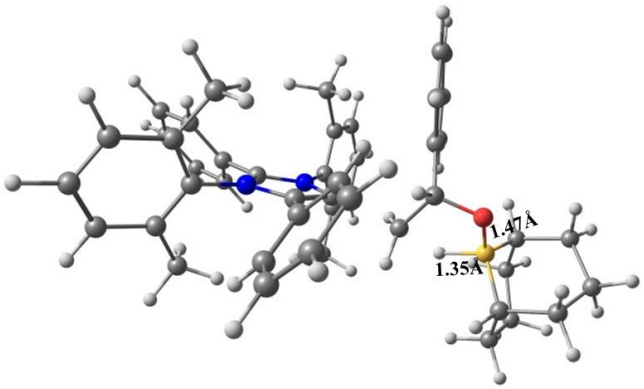
N	1.46341600	0.08580900	-0.12452200
N	-0.67728500	0.46596200	-0.16662900
C	0.55177200	1.05989900	-0.08004500
C	0.82073400	2.49135300	0.08263200
C	1.83664200	3.11783300	-0.65571000
H	2.40767200	2.54562900	-1.37910900
C	0.85842200	-1.15909000	-0.25407900
C	0.07398700	3.25445200	0.99472600
H	-0.71161600	2.78393300	1.57590400
C	2.10583900	4.46905100	-0.47419200
H	2.89421000	4.93868000	-1.05293500
C	-1.91052900	1.18822700	-0.08415700
C	1.58187800	-2.42239000	-0.32690100
C	2.88243100	0.30416000	-0.05976900
C	-0.55405900	-0.94304700	-0.30765500
C	1.36039800	5.21890400	0.43207400
H	1.56866900	6.27505100	0.56706500

C	0.34373700	4.60720700	1.16180500
H	-0.24056900	5.18316000	1.87157800
C	-2.68877900	1.04761300	1.07171000
C	3.44594300	0.66980100	1.16645900
C	2.70713200	-2.70551900	0.46996000
H	3.05714200	-1.97169300	1.18839700
C	3.63397500	0.11793000	-1.22438800
C	2.98119100	-0.28537100	-2.51926200
H	2.04046900	0.25277600	-2.67571400
C	1.13927800	-3.42069900	-1.21683500
H	0.27815400	-3.21611700	-1.84488900
C	-2.29383600	1.99455600	-1.16166200
C	5.01067700	0.32527100	-1.13837200
H	5.61918600	0.19267300	-2.02781400
C	2.59764800	0.83048100	2.39996500
H	1.81712500	0.06344800	2.44546800
C	4.82672300	0.86676800	1.20517900
H	5.29235400	1.14854200	2.14476700
C	5.60264000	0.69702800	0.06403000
H	6.67555100	0.85202100	0.11249500
C	3.36463600	-3.92562700	0.36745700
H	4.22810200	-4.11839000	0.99653100
C	-3.90958000	1.72104300	1.11233400
H	-4.53922600	1.61273600	1.99027600
C	-2.22936500	0.20561800	2.22961300

H	-2.74887900	0.49725500	3.14444100
C	1.79249500	-4.64372100	-1.30226200
H	1.42897900	-5.39480700	-1.99662400
C	2.91115600	-4.90460000	-0.51336100
H	3.41931000	-5.86077300	-0.57968400
C	-3.51364800	2.66334900	-1.07111000
H	-3.83699000	3.28639100	-1.89995300
C	-4.32148100	2.51895700	0.05130900
H	-5.27685500	3.03151100	0.09961000
C	-1.43655500	2.10467600	-2.39476000
H	-1.03604900	1.12722900	-2.68326800
C	-3.01184400	-1.70042300	-0.49240400
C	-3.59401600	-0.89294500	-1.48471500
C	-4.97079600	-0.72545900	-1.56777000
C	-5.81666200	-1.39805300	-0.68785200
C	-5.26312400	-2.24545200	0.26941900
C	-3.88378200	-2.39239600	0.36782700
H	-2.94616300	-0.40056100	-2.20406400
H	-5.38534900	-0.07688900	-2.33449800
H	-6.89264700	-1.27359700	-0.75627400
H	-5.90897000	-2.78615100	0.95515000
H	-3.45902900	-3.02960700	1.14019200
C	-1.56375900	-1.88263500	-0.35927900
C	-0.61294700	-2.90701900	2.31311600
O	-1.54836100	-3.03714400	3.06273600

H	-1.22483100	-2.90968100	-0.28091400
H	-0.09058600	-1.94004800	2.17635200
H	-0.19672000	-3.75104200	1.72872900
H	-2.01863300	2.49988300	-3.22962500
H	-0.58466700	2.77381700	-2.22987100
H	-1.15063900	0.31206700	2.39461400
H	-2.42768400	-0.85553000	2.04959100
H	2.74571100	-1.35490500	-2.51743400
H	3.64529300	-0.07956000	-3.36078600
H	2.10184100	1.80722300	2.41181500
H	3.21287900	0.75170500	3.29819500

Hydride transfer-TS



N	2.48950256	0.62135982	-0.20257124
N	0.97365814	-0.90821284	-0.27308996
C	2.30370756	-0.69952856	-0.33953372
C	3.35908672	-1.71383282	-0.48509424
C	4.47431813	-1.69043262	0.36139358
H	4.55522428	-0.92392394	1.12558369

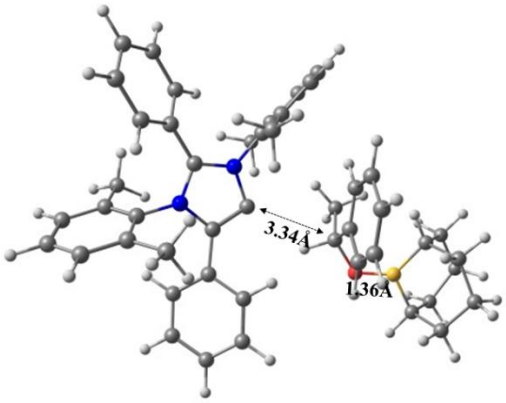
C	1.23836874	1.23740379	-0.03714543
C	3.25490295	-2.71130063	-1.46227046
H	2.39568609	-2.73168790	-2.12408799
C	5.47046374	-2.65068624	0.22829089
H	6.32951755	-2.62735624	0.89002799
C	0.38102240	-2.22201448	-0.28388965
C	1.12849801	2.69823641	0.14233425
C	3.75987727	1.28928757	-0.28189248
C	0.25369824	0.27394332	-0.06637194
C	5.36233452	-3.64055187	-0.74514235
H	6.14035594	-4.38996921	-0.84582865
C	4.25435967	-3.66901644	-1.58837227
H	4.16690128	-4.43750370	-2.34874657
C	-0.18043909	-2.70944616	-1.46902498
C	4.36880980	1.40829650	-1.53612417
C	1.65335564	3.59305254	-0.79615310
H	2.14838471	3.21186187	-1.68473628
C	4.31767320	1.80732267	0.89124610
C	3.62365507	1.66925266	2.22030334
H	3.10841642	0.70783415	2.31350098
C	0.48831676	3.20435043	1.27887611
H	0.10731899	2.50437756	2.01612551
C	0.38015750	-2.94115990	0.91488179
C	5.54507329	2.46212701	0.78315679
H	6.00397993	2.87016260	1.67864745

C	3.72356276	0.84220749	-2.77380269
H	2.64597111	1.03745219	-2.78791763
C	5.59339347	2.07257107	-1.59677018
H	6.08687925	2.18228936	-2.55764822
C	6.17739787	2.59487303	-0.44772747
H	7.13032290	3.10968520	-0.51260614
C	1.53357943	4.96509192	-0.60302654
H	1.94046261	5.64952298	-1.34006607
C	-0.75705674	-3.98011742	-1.43189885
H	-1.20482670	-4.38190468	-2.33592640
C	-0.19552685	-1.89505314	-2.73802461
H	-0.15907167	-2.54926535	-3.61202910
C	0.35889015	4.57669988	1.46561507
H	-0.14844479	4.95506731	2.34676222
C	0.88275853	5.45928212	0.52479675
H	0.78309966	6.53005143	0.66903395
C	-0.19973638	-4.20934759	0.90426929
H	-0.21998996	-4.78536463	1.82450527
C	-0.76493324	-4.72430184	-0.25719254
H	-1.21945562	-5.70958534	-0.24669583
C	0.95564689	-2.34120980	2.16804679
H	0.50216662	-1.36217903	2.36139323
C	-2.11299961	-0.17296398	1.95993098
C	-1.67289735	0.27270525	3.20771631
C	-1.58008523	-0.59709528	4.29226536

C	-1.93635532	-1.93453457	4.14090860
C	-2.38574877	-2.38973038	2.90261795
C	-2.47288091	-1.51631332	1.82212203
H	-1.42282671	1.32368352	3.33401986
H	-1.23807298	-0.22978515	5.25515475
H	-1.87184764	-2.61622081	4.98351499
H	-2.67173900	-3.42984156	2.77546085
H	-2.83487523	-1.88244930	0.86381927
C	-2.27910854	0.82003232	0.81438043
C	-1.78485453	0.22147590	-0.52002915
O	-3.59919367	1.23535128	0.69225959
H	-1.64991085	1.69024879	1.03493801
H	-1.64286403	-0.83890322	-0.66460704
H	-1.58858775	0.88125803	-1.35776498
H	0.75384630	-2.98221569	3.02726637
H	2.04099097	-2.20996917	2.08097846
H	0.64516971	-1.19717924	-2.78884445
H	-1.11363643	-1.30098737	-2.80750785
H	2.86706930	2.45140903	2.34063904
H	4.34167011	1.76104371	3.03747742
H	3.86155484	-0.24349232	-2.82679839
H	4.16536567	1.28142311	-3.66986076
C	-4.76339977	1.68315754	-1.59235855
H	-3.99363312	2.43229334	-1.83554527
C	-5.73822960	-1.17500678	-1.53935695

H	-4.86691393	-1.78619590	-1.82214152
H	-6.56995092	-1.88060080	-1.39336055
C	-5.38417165	-0.45149032	-0.22876704
H	-5.07394340	-1.21397165	0.50086660
C	-5.11948799	0.94057737	-2.89223938
H	-5.54009786	1.62731518	-3.64217137
H	-4.17880350	0.56187744	-3.32169279
C	-6.54931248	0.32752388	0.42312103
H	-6.18365137	0.68311275	1.39547209
H	-7.39991173	-0.33849602	0.63255017
C	-6.07648298	-0.25352439	-2.72473798
H	-7.10226773	0.10958956	-2.62528918
H	-6.06984434	-0.84602900	-3.64909080
C	-5.93429067	2.44153202	-0.93148556
H	-5.50829378	3.01476222	-0.09732775
H	-6.37543828	3.17502714	-1.62323682
C	-7.05516989	1.54588321	-0.37162941
H	-7.70854631	1.21586742	-1.18365515
H	-7.69463578	2.15112023	0.28374438
B	-4.22783057	0.63836000	-0.49315917
H	-3.17613996	0.00073774	-1.04622192

Product



N	2.85577676	0.73377022	-0.21463601
N	1.56371762	-0.96531716	-0.47211472
C	2.84416144	-0.61040353	-0.22957841
C	3.99120599	-1.50201328	-0.01440104
C	4.93350369	-1.23279244	0.98804267
H	4.81729097	-0.35706337	1.61769976
C	1.54585062	1.18790735	-0.45101731
C	4.14444266	-2.64870943	-0.80584221
H	3.41918518	-2.86625446	-1.58301421
C	6.01069566	-2.08913762	1.18395820
H	6.73256767	-1.87033962	1.96364507
C	1.06882581	-2.31049322	-0.44476980
C	1.17816439	2.61229911	-0.45677439
C	4.02157188	1.54280228	-0.00613614
C	0.68197174	0.11578581	-0.61716088
C	6.15799887	-3.22510544	0.39226833

H	6.99835986	-3.89308809	0.54973150
C	5.22119554	-3.50318574	-0.59986140
H	5.32915315	-4.38666752	-1.22004216
C	0.66344264	-2.89347625	-1.65002590
C	4.96946123	1.63246279	-1.03127683
C	1.96693734	3.62506688	-1.01730346
H	2.91567412	3.38177893	-1.48485900
C	4.14235608	2.23058621	1.20663820
C	3.09272278	2.10404840	2.27818092
H	2.77700728	1.06326274	2.40637699
C	-0.05712631	2.95828906	0.11191500
H	-0.65631335	2.16858424	0.55655955
C	0.94003953	-2.95058394	0.79084416
C	5.27074592	3.03150462	1.38279701
H	5.39045129	3.57435161	2.31561146
C	4.78159875	0.88930882	-2.32735170
H	3.74605624	0.96045458	-2.67536982
C	6.08242924	2.44461384	-0.81173064
H	6.83153377	2.53473764	-1.59273128
C	6.23266181	3.13890325	0.38388128
H	7.10298698	3.76864132	0.53727246
C	1.53365815	4.94781101	-0.99747507
H	2.15653383	5.72046300	-1.43719153
C	0.11166138	-4.17371978	-1.59634537
H	-0.21862482	-4.64555325	-2.51711251

C	0.82476570	-2.14803308	-2.94851541
H	0.38353663	-2.70836078	-3.77484048
C	-0.49170220	4.27771002	0.11656475
H	-1.45264946	4.52459064	0.55708854
C	0.30527731	5.27991318	-0.43357515
H	-0.03016419	6.31195923	-0.42527712
C	0.39912786	-4.23779802	0.79855747
H	0.28842286	-4.75746263	1.74630801
C	-0.01566559	-4.84377403	-0.38245131
H	-0.44648940	-5.83952889	-0.35752192
C	1.32388839	-2.24408356	2.06321318
H	0.88891001	-1.23849805	2.07720060
C	-2.50622313	-0.29491697	0.66444670
C	-2.75394917	0.60432990	1.70773102
C	-2.62063394	0.21401846	3.03695358
C	-2.24768771	-1.09242328	3.34562920
C	-1.99677156	-1.99264822	2.31426135
C	-2.11274474	-1.59532431	0.98353712
H	-3.06472748	1.61787070	1.46539367
H	-2.81672620	0.92729959	3.83169663
H	-2.15500322	-1.40527967	4.38091805
H	-1.70363657	-3.01457573	2.53938479
H	-1.89958459	-2.31267577	0.19563206
C	-2.65153243	0.18920139	-0.76789300
C	-2.64232990	-0.90418950	-1.82245366

O	-3.80446382	1.03255849	-0.90389604
H	-1.78906914	0.83187794	-0.97105408
H	-1.66913118	-1.40114688	-1.81163860
H	-2.79088486	-0.45032791	-2.80525875
H	0.95111106	-2.78996988	2.93224664
H	2.41170365	-2.15225461	2.15852435
H	1.88421284	-1.97771539	-3.17670979
H	0.35503357	-1.16255393	-2.88144920
H	2.19865800	2.67955796	2.01580713
H	3.47360533	2.47378533	3.23196182
H	5.01595478	-0.17429265	-2.20814918
H	5.43755669	1.29567140	-3.09931621
C	-6.24377025	1.69099767	-0.70044759
H	-5.88359977	2.66116750	-1.06300074
C	-6.58046118	-1.26394041	-1.18122150
H	-6.01254471	-1.44185360	-2.10645737
H	-6.99604450	-2.23738743	-0.88813723
C	-5.58879867	-0.76787742	-0.09979685
H	-4.80393891	-1.52327055	0.00838085
C	-7.29631872	1.16272164	-1.70218162
H	-8.18441927	1.80970126	-1.69947600
H	-6.86252260	1.24818614	-2.70759423
C	-6.22084486	-0.57790815	1.30203033
H	-5.39464301	-0.41929432	2.00793144
H	-6.71452193	-1.50835492	1.61438078

C	-7.73538438	-0.29889967	-1.49451567
H	-8.48316121	-0.35882557	-0.70104428
H	-8.24660834	-0.64362609	-2.40116055
C	-6.77088291	1.88511808	0.74166036
H	-5.96576999	2.34362113	1.33402032
H	-7.60151238	2.60393737	0.75008645
C	-7.21472758	0.59122744	1.44353528
H	-8.19938398	0.29681655	1.07405698
H	-7.35709213	0.79982200	2.51049636
B	-5.06760517	0.64328000	-0.59489636
H	-3.42630642	-1.64909635	-1.65636339

7. References

[1] E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking and G. Bertrand, *Science*, 2009, **326,** 18124-18137.

[2] A. J. Arduengo III, R. Krafczyk and R. Schmultzer, *Tetrahedron*, 1999, **55**, 14523-14534.

[3] E. Tomás-Mendivil , M. M. Hansmann , C. M. Weinstein , R. Jazzar , M. Melaimi and G. Bertrand , *J. Am. Chem. Soc*., **2017**, 139 , 7753-7756.

[4] Y. Hao, D. Yuan and Y. Yao, *ChemCatChem*, 2020, **12**, 4346-4351.

[5] K. Okuma, Y. Tanaka, S. Kaji and H. Ohta, *J. Org. Chem.*, 1983, **48**, 5133-5134.

[6]J. Duran, N. Brugat, A. Polo, J. Real, X. Fontrodona and J. Benet-Buchholz, *Organometallics*, 2003, **22**, 3432-3438.

[7] W. P. Liu, W. Li, A. Spannenberg, K. Junge and M. Beller, *Nat. Catal.*, 2019, **2**, 523–528.

[8] B. Wang, H. Du and J. Zhang, *Steroids,* 2011, **76**, 204-209.

[9] S. Thiyagarajan and C. Gunanathan, *Org. Lett.*, 2019, **21**, 9774-9778.

[10] M. Trose, F. Lazreg, T. Chang, F. Nahra, D. B. Cordes, A. M. Z. Slawin and C. S. J. Cazin, *ACS Catal*., 2017, **7**, 238-242.

[11] Z.-W. Xi, L. Yang, D.-Y. Wang, C.-W. Feng, Y. Qin, Y.-M. Shen, C. Pu and X. Peng, *J. Org. Chem.*, 2021, **86**, 2474-2488.

[12] H.-F. Lu, J.-T. Zhou, H.-L. Cheng, L.-L. Sun, F.-F. Yang, R.-Z. Wu, Y.-h. Gao and Z.-b. Luo, *Tetrahedron*, 2013, **69**, 11174-11184.

[13] M. Magre, E. Paffenholz, B. Maity, L. Cavallo and M. Rueping, *J. Am. Chem. Soc*., 2020, **142**, 14286-14294.

[14] C. Huang, W. Ma, X. Zheng, M. Xu, X. Qi and Q. Lu, *J. Am. Chem. Soc*., 2022, **144**, 1389-1395.

[15] F. Puls, P. Linke, O. Kataeva and H. Knölker, *Angew. Chem., Int. Ed.*, 2021, **60** , 14083-14090.

[16] P. Rühl, A. S. Rosato, N. Urban, S. Gerndt, R. Tang, C. Abrahamian, C. Leser, J. Sheng, A. Jha, G. Vollmer, M. Schaefer, F. Bracher, C. Grimm, *Sci. Rep*. 2021, **11**, 8313.

[17] A. Bhunia, K. Bergander, C. G. Daniliuc and A. Studer, *Angew. Chem., Int. Ed.*, 2021, **60**, 8313-8320.

[18] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–342

[19] G. M .Sheldrick, *Acta Cryst.* 2015, **A71**, 3-8.

[20] G. M .Sheldrick, *Acta Cryst.* 2015, **C71**, 3-8.

[21] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell,

J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[22] Y. Zhao and D. G. Truhlar, *Theor. Chim. Acta*, 2008, **120**, 215–241.

[23] Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41**, 157–167.

[24] A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.