Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Organocatalytic epoxidation and allylic oxidation of alkenes by molecular oxygen

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Abbreviations

Ac	Acetyl
CSA	10-Camphorsulfonic acid
DCM	Dichloromethane
DIBAL-H	Diisobutylaluminium hydride
DKP	2,5-diketopiperazine
DMAP	4-Dimethylaminopyridine
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
EDC	N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride
EtOAc	Ethyl acetate
Et_2O	Diethylether
GC	Gas Chromatography
HFIP	1,1,1,3,3,3-Hexafluoro-2-propanol
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometry
NMR	Nuclear Magnetic Resonance
n-BuLi	n-Butyllithium
o/n	Overnight
RT	Room Temperature
TBS	tert-Butyldimethyl sillyl
THF	Tetrahydrofuran
THP	Tetrahydropyran
TLC	Thin Layer Chromatography
t-BuOOH	tert-Butyl hydroperoxide
UV	Ultraviolet-Visible

1. Materials and Methods

Reactions for preparation of prolinamides (section 2) were conducted under a positive pressure of dry argon round bottomed flasks or oven-dried/flame-dried glassware, unless specified otherwise. All reactions for preparation of 2,5-diketopiperazine (DKP) unless specified otherwise were conducted in Schlenk tubes under positive argon pressure. The solvents and materials in these cases were carefully degassed with the use of liquid nitrogen under freeze-pump-thaw technique. DKP was kept in sealed tubes under positive pressure of dry argon upon preparation and was used in caution of atmospheric air when tubes are opened. DKP can be weighted without the use of a glovebox but they need to be protected from air as soon as they are in contact with polar solvents or base. Oxidation reactions were performed in 4mL screw cap vials equipped with rubber septum in the absence of a stirring bar unless otherwise noted. Bubbling of dioxygen was achieved by balloon inserted through a pipette in the rubber septum. All materials weighted for oxidation reaction are taking care to avoid contact with metals (spatula, needles etc). Also, no magnetic stirrer was used for oxidation reactions.

Anhydrous solvents were either obtained from commercial sources (dry DMF, dioxane, DMSO and MeOH) or dried accordingly. Dry THF was readily distilled before its use from sodium (Na) and benzophenone, dry acetonitrile from P_2O_5, whereas dry DCM was distilled from CaH_2 prior its use. Commercially obtained solvents were kept under argon using molecular sieves 4Å upon their opening. Petroleum ether refers to the 40-60 °C boiling fraction. Commercially available reagents were purchased at the highest commercial quality and used without further purification or where specified, purified by standard techniques. All reactions were monitored by thin-layer chromatography (TLC) carried out on S-2 0.25 mm E. Merck silica gel plates, pre-coated with silica gel (60-F254). Preparative TLC plates (S-2 0.5mm E. Merck silica gel plates precoated with silica gel 60-F254) were used in cases where the separation with usual flash column chromatography were inadequate.

Visualization was affected by UV fluorescence (λ_{max}= 254 nm or 360 nm) and by staining with *Seebach* or anisaldehyde TLC stain solutions, followed by heating. Flash chromatography employed Merck 60, (particle size 0.040-0.063 mm) silica gel.

NMR spectra were recorded at 298 K using an Agilent 500 spectrometer. ^{1}H NMR spectra were recorded at 500 MHz and residual solvent peaks were used as an internal reference ($CDCl_3$ δ 7.26). Data are reported as follows: chemical shift in ppm, multiplicity (s = singlet, brs = broad singlet, d = doublet, brd = broad doublet, t = triplet, brt = broad triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances, coupling constants are reported in Hz, integration is included. ^{13}C NMR spectra were recorded at 125 MHz and residual solvent peaks were used as an internal reference ($CDCl_3$ δ 77.00). Data are reported as follows: chemical

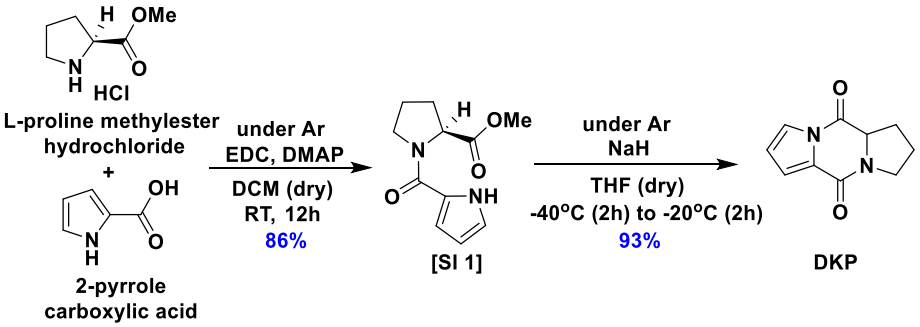
shift in ppm, multiplicity deduced. The assignment of ^{1}H and ^{13}C signals was assisted by COSY, HSQC and HMBC experiments where necessary.

GC chromatograms were recorded using Shimadzu Nexis GC-2030 Gas Chromatograph (Shimadju Corporation) to monitor reaction kinetics. For alkene to epoxide transformation, the column temperature was set at 60 °C (equilibration time: 1 min), held isothermally for 4 min, raised to 280 °C with a rate of 6 °C/min, and finally held at 280 °C for 20 min. The detector temperature was 290 °C and the temperature at the injector was 250 °C.

Column details: Column max temp.: 320.0 °C; Length: 30.0 m; Inner Diameter: 0.25 mm ID; Film Thickness: 0.25 µm; Column flow: 1.00 mL/min; FID Makeup Gas: He, FID Makeup flow: 20.0 mL/min; FID H_2 flow: 40.0 mL/min, FID Air flow: 400.0 mL/min.

Infusion experiments were carried out on an Agilent Q-TOF Mass Spectrometer, G6540B model with Dual AJS ESI-MS. All the compounds (dissolved in LC-MS grade, methanol) were introduced into the ESI source of the MS with a single injection of 15 µL of the sample and with a flow rate of 300 µL/min of 100% methanol as a solvent in the binary pump. The experiments were run using a Dual AJS ESI source, operating in a positive ionization mode. Source operating conditions were 330 ^{o}C Gas Temp, 8 l/min Gas Flow, Sheath Gas Temp 250 ^{o}C, Sheath Gas Flow 10 l/min and 150 V Fragmentor. Data-dependent MS/MS analysis was performed in parallel with the MS analysis, in a centroid mode, using different collision energies (10, 20, 30, 40 V). All accurate mass measurement of the $[M+H]^{+}$ ions, were carried out by scanning from 100 to 500 m/z. The Q-TOF was calibrated 1 h prior to the infusion experiments by using a calibration mixture. Data were acquired in an external calibration mode.

2. Preparation of Catalyst[2]



1st step:

To a mixture of 2-pyrrolecarboxylic acid (2.80 mmol, 1.0 equiv.) and L-proline methyl ester (3.64 mmol, 1.3 equiv.) in anhydrous DCM (12 mL), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (3.64 mmol, 1.3 equiv.) and DMAP (2.5 mmol%) were added under argon at 0°C. After 30 min stirring at 0°C and 12hr at room temperature, the reaction mixture was quenched with water, extracted with DCM (2 x 10 mL), the combined organic layers washed with $NaHCO_3$ (2 x 10 mL) and then dried with $MgSO_4$. After removal of the solvent under reduced pressure and subsequent flash column chromatography of the obtained residue on silica-gel with Hexane:EtOAc (1:1) [Rf: 0.3] as eluent gave **SI 1** in 86% yield as a white foam.

Recorded NMR was found identical to the reported values.[1]

MW (g/mol): 222.24

Molecular formula: $C_{11}H_{14}N_2O_3$

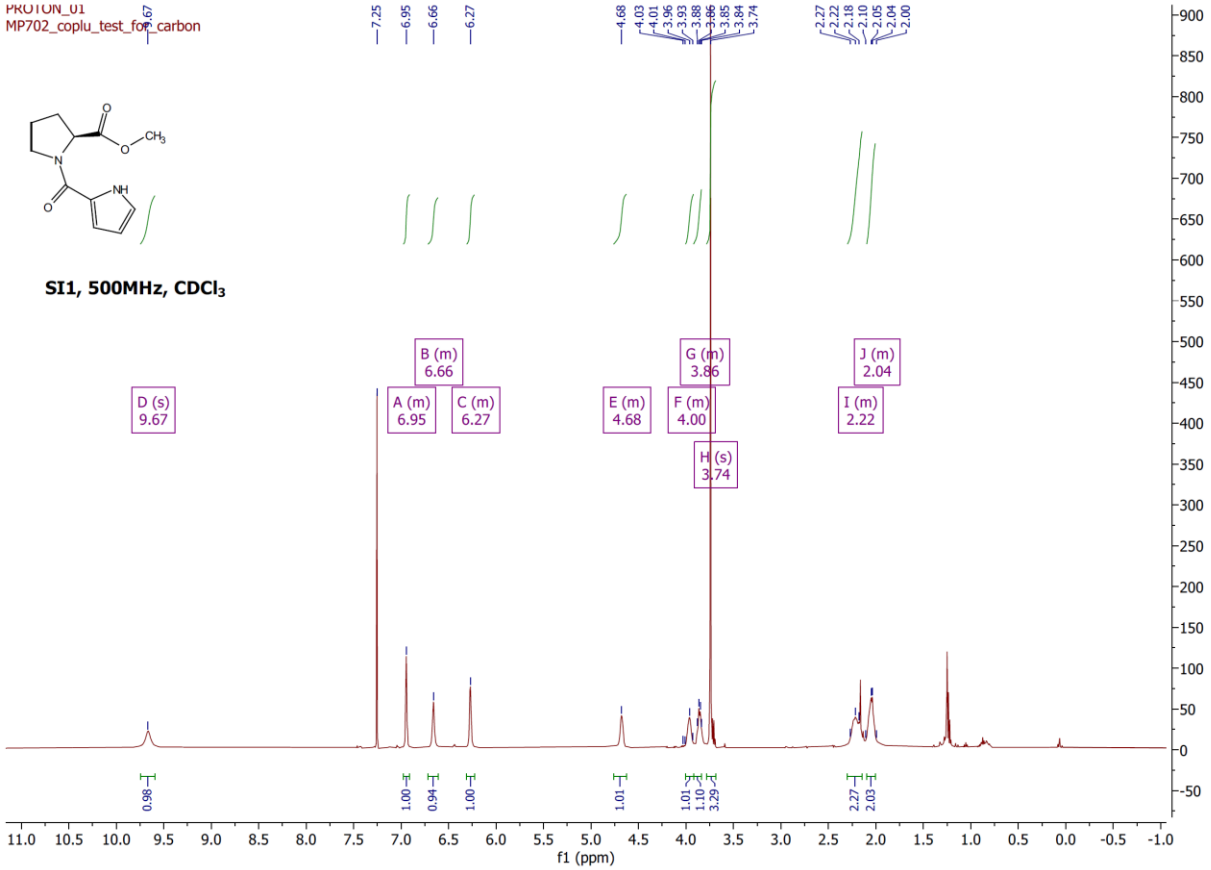
^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ_H 2.00-2.10 (m, 2H), 2.18-2.27 (m, 2H), 3.74 (s, 3H), 3.84-3.88 (m, 1H), 3.93-4.01 (m, 1H), 4.68 (s, 1H), 6.27 (m, 1H), 6.66 (m, 1H), 6.95 (m, 1H), 9.67 (bs, 1H)

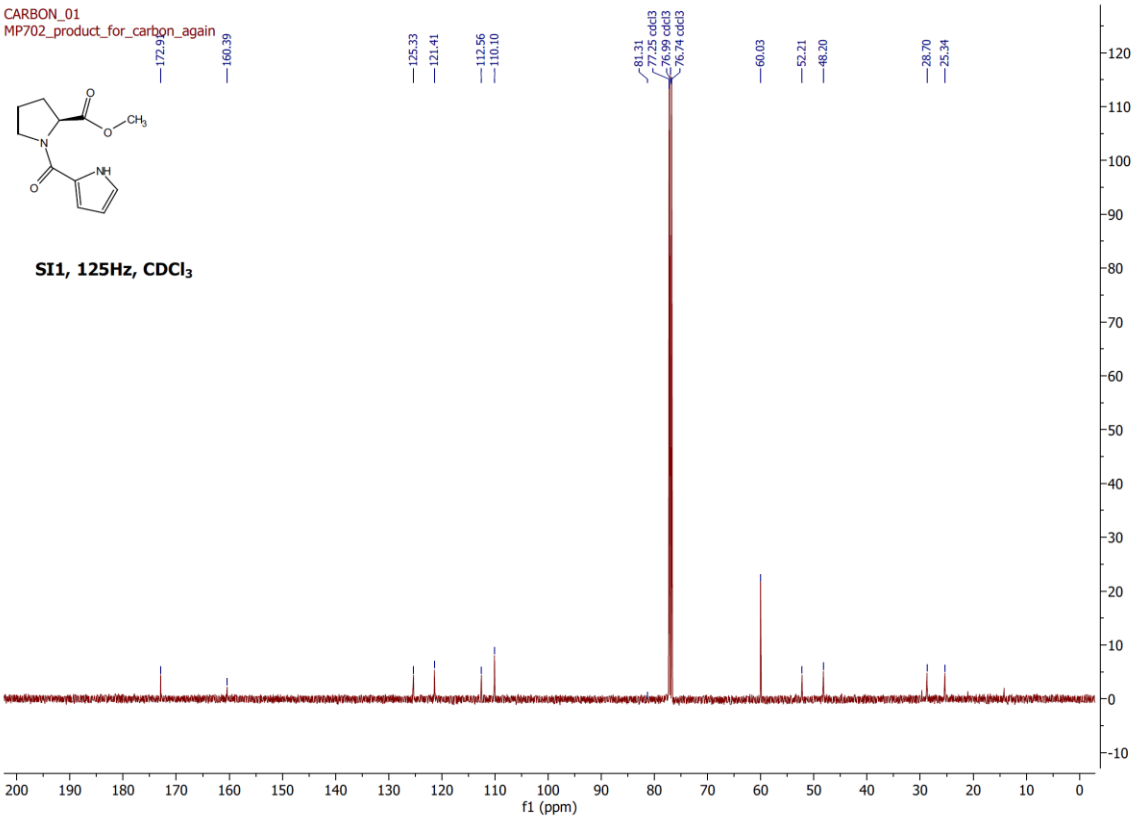
^{13}C NMR (125 MHz, $CDCl_3$, 25°C): δ_C 25.34, 28.70, 48.20, 52.21, 60.03, 110.10, 112.56, 121.41, 125.33, 160.39, 172.91

2nd step:

Methyl ester **SI 1** (1.63 mmol, 1.0 equiv.) was dissolved in THF (8 mL) in a Schlenk tube under argon, which was connected to a vacuum pump and immersed in a liquid nitrogen bath at -100°C. There, the substrate was deoxygenated 4 times and then sodium hydride (2.28 mmol, 1.4 equiv., 57% dispersion in paraffin liquid) was added as a dispersion in THF (1 mL) and the mixture was stirred for 2 hr at -40°C and 2 more hours at -20°C. The mixture was quenched with CH_3COOH/CH_3COONa buffer pH 3.7 (12 mL) and the products were extracted with EtOAc (5 x 10). After removal of the solvents under reduced pressure, the desirable DKP product was received as a white solid in 93% yield [DCM:EtOAc (1:2), Rf: 0.35]. Recorded NMR was found identical to the reported values.[2]

MW (g/mol): 190.20 Molecular formula: $C_{10}H_{10}N_2O_2$ ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ_H 1.96-2.10 (m, 2H), 2.13-2.19 (m, 1H), 2.54-2.60 (m, 1H), 3.61-3.70 (m, 1H), 3.80-3.88 (m, 1H), 4.49 (dd, *J* 9.5, 6.2 Hz, 1H), 6.48 (dd, *J* 3.3, 3.3 Hz, 1H), 7.07 (dd, *J* 3.3, 1.8 Hz,1H), 7.46 (dd, *J* 3.3, 1.8 Hz, 1H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$, 25°C):** δ_C 22.29, 29.05, 44.77, 61.51, 115.57, 117.91, 118.85, 127.40, 155.24, 164.50 ppm.





PROTON_01
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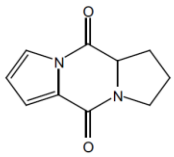
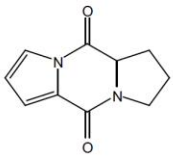
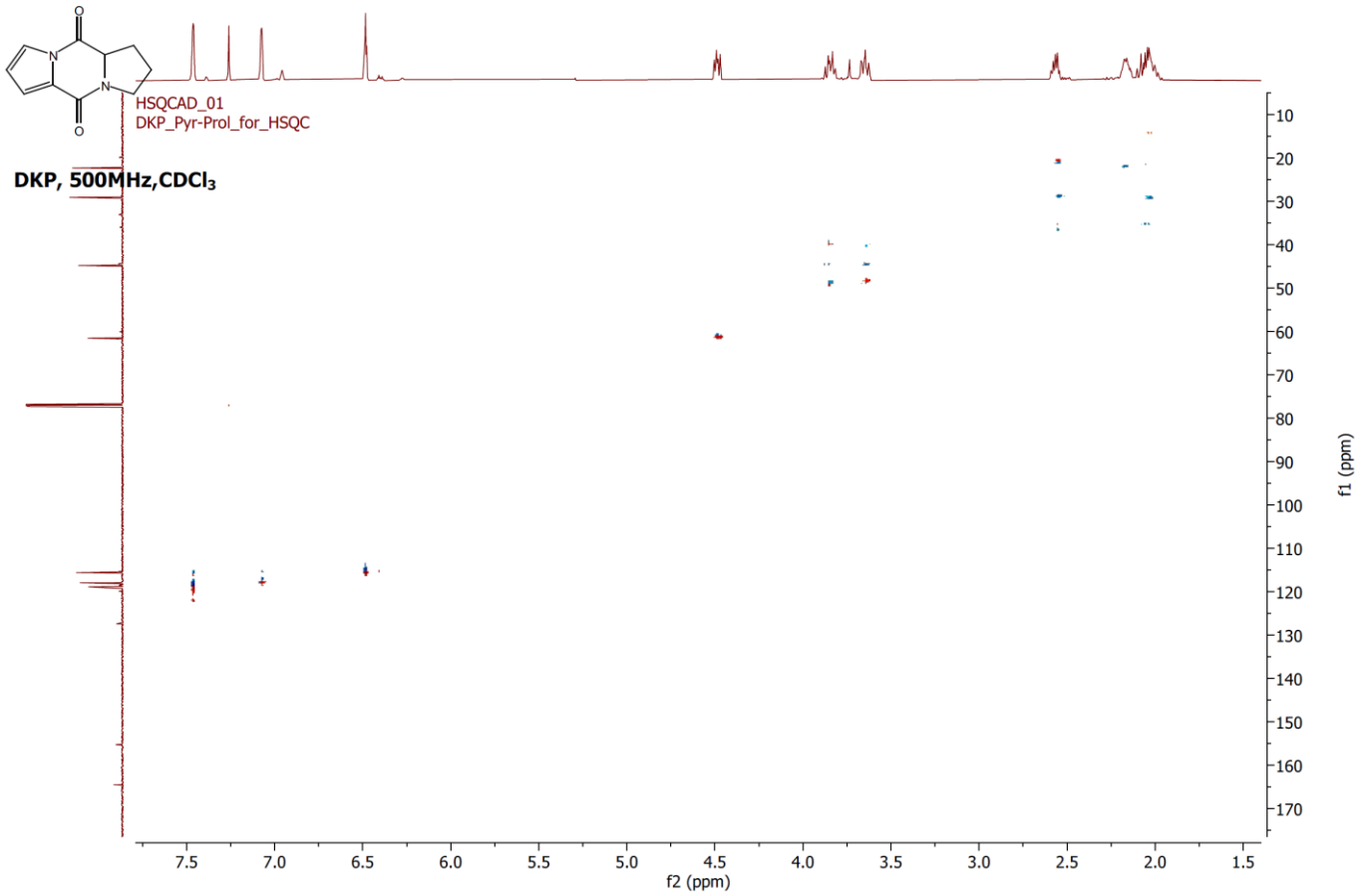


DKP, 500MHz, $CDCl_3$

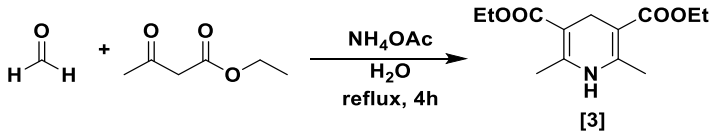
CARBON_01
DKP_Pyr-Prol_for_carbon



DKP, 125Hz, $CDCl_3$



3. Preparation of the Reductant[3]



According to literature,[3] formaldehyde (0.05 mmol, 1.0 equiv.), ethylacetoacetate (0.08 mmol, 1.5 equiv.) and ammonium acetate (0.04 mmol, 0.8 equiv.) were dissolved in H_2O (40 ml) in a round bottom flask and stirred at 80°C for 4 hours. After the completion of time yellow balls were formed and the reaction mixture cooled to room temperature. The resulting solid was filtered, washed with cold water (30 ml) and cold acetone (30 ml) to afford diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate or Hantzsch ester (**3**) as a yellow fine solid. In Section 7, **3** was used in its recrystallized form from hot EtOH.

MW (g/mol): 253.30

Molecular formula: $C_{13}H_{19}NO_4$

NMR spectra were fully consistent with reported literature values.[3]

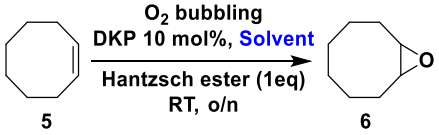
^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ_H 1.28 (t, *J* 7.1 Hz, 6H), 2.19 (s, 6H), 3.26 (s, 2H), 4.16 (q, *J* 7.1 Hz, 4H), 5.17 (brs, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25°C): δ_C 14.5, 19.2, 24.8, 59.6, 99.5, 144.7, 168.0 ppm

It is worth noting that in case of blank reactions, Hantzsch ester (**3**) was used as crude material, unless otherwise noted. The synthesis of different Hantzsch ester batches led to different results in blank reactions. When a blank reaction ran in the presence of recrystallized Hantzsch ester, higher yield of the epoxide was evidenced. That is the reason why it was crucial to search for the proper conditions where the oxidation of Hantzsch would be prohibited (Section 7).

4. Solvent Screening

Conditions: (*Z*)-cyclooctene (**5**, 0.23 mmol, 1.0 equiv.), Hantzsch ester (**3**, 0.23 mmol, 1.0 equiv.) and DKP (0.023 mmol, 0.1 equiv.) were dissolved in different solvents or mixture of solvents (1.2 ml) in the presence of dioxygen (bubbling) and stirred overnight at room temperature. The crude product was obtained by quenching the reaction with water (1.5 ml) and extracting it with pentane (3 x 2 ml). Then, the organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure in an ice bath, until a pale-yellow solid residue was left in the flask. All reactions were performed in 4mL screw capped vials equipped with rubber septum, pipette, and dioxygen balloon and the reactions monitored via GC with 1,3,5-trimethoxybenzene as internal standard.

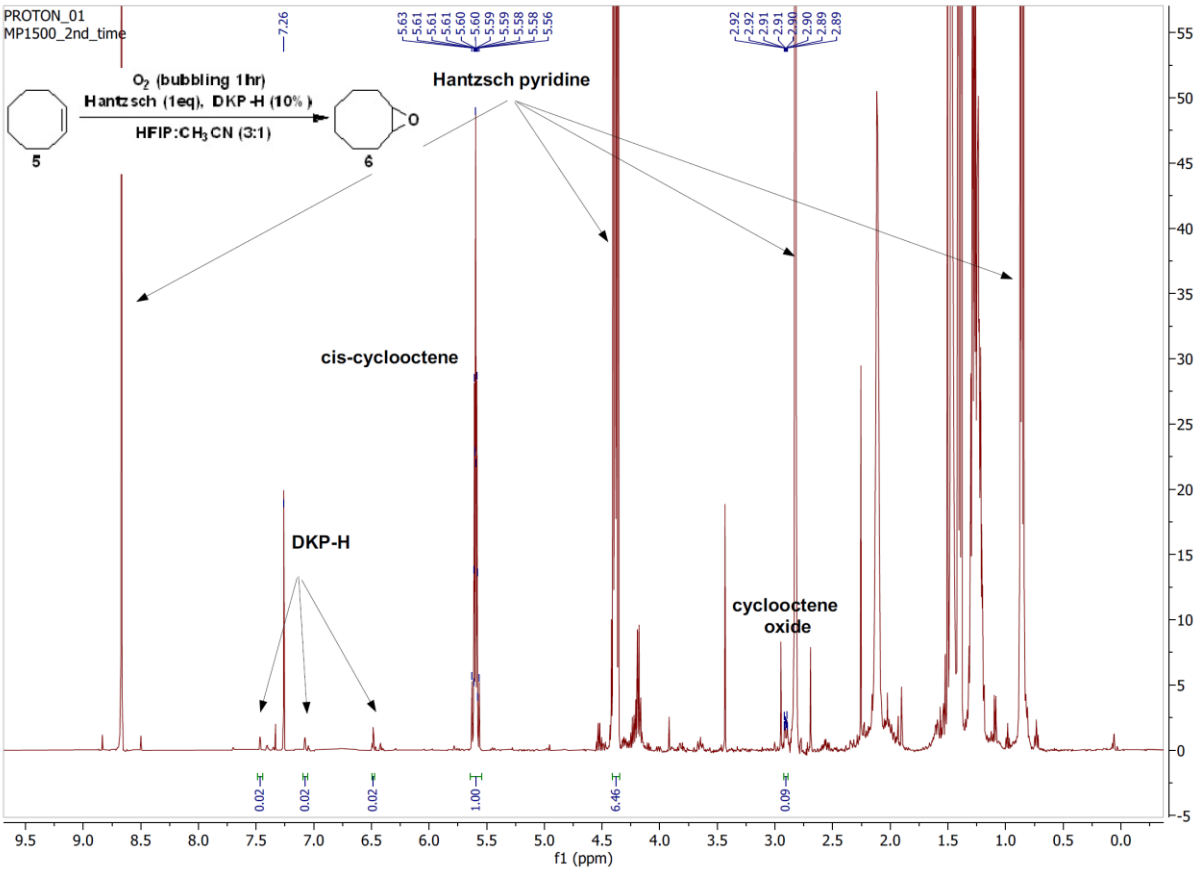


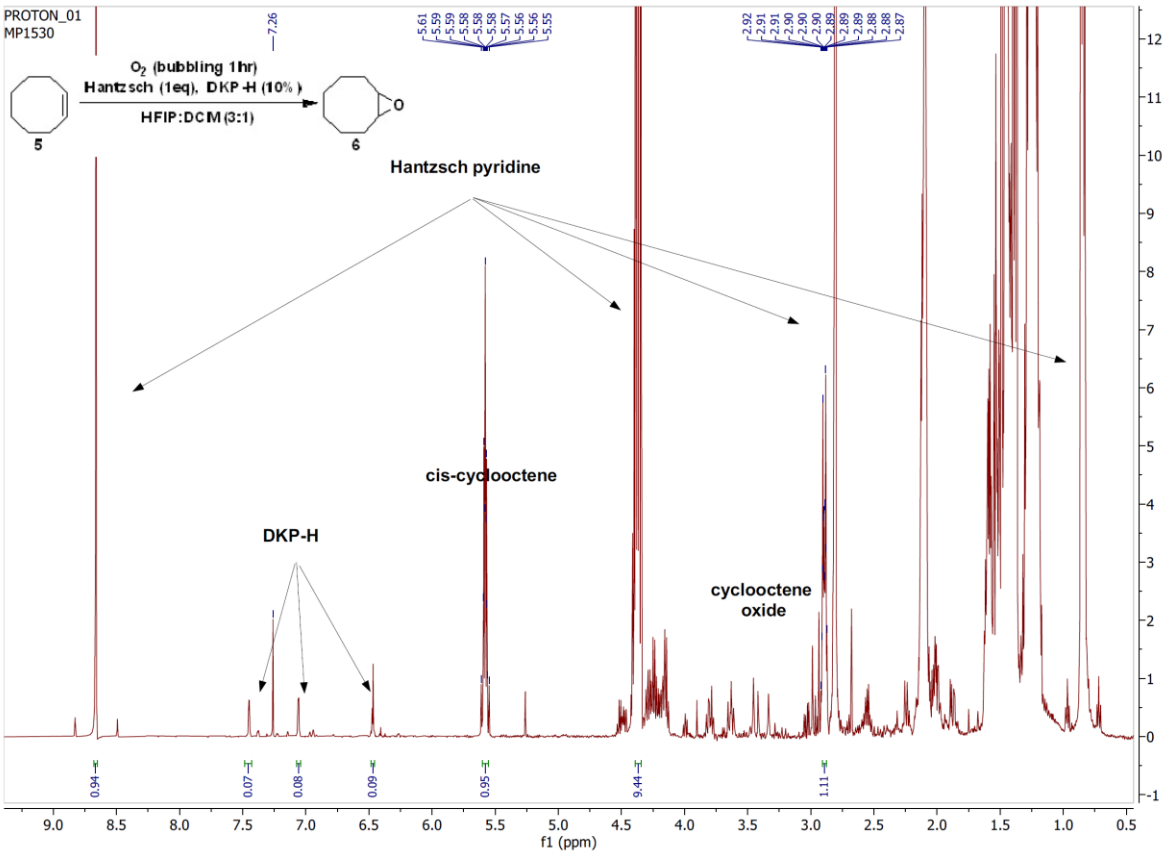
A/A	Solvent	Conversion (%)	Yield (%)
1	DCM	**20**	**12**
2	DMSO	**10**	**6**
3	DMF	**35**	**10**
4	HFIP	**100**	**93**
5	HFIP:H_2O (3:1)	**16**	**8**
6	HFIP:DMF (3:1)	**42**	**15**
7	HFIP:DCM (3:1)	**93**	**56**
8	HFIP:CH_3CN (3:1)	**32**	**8**

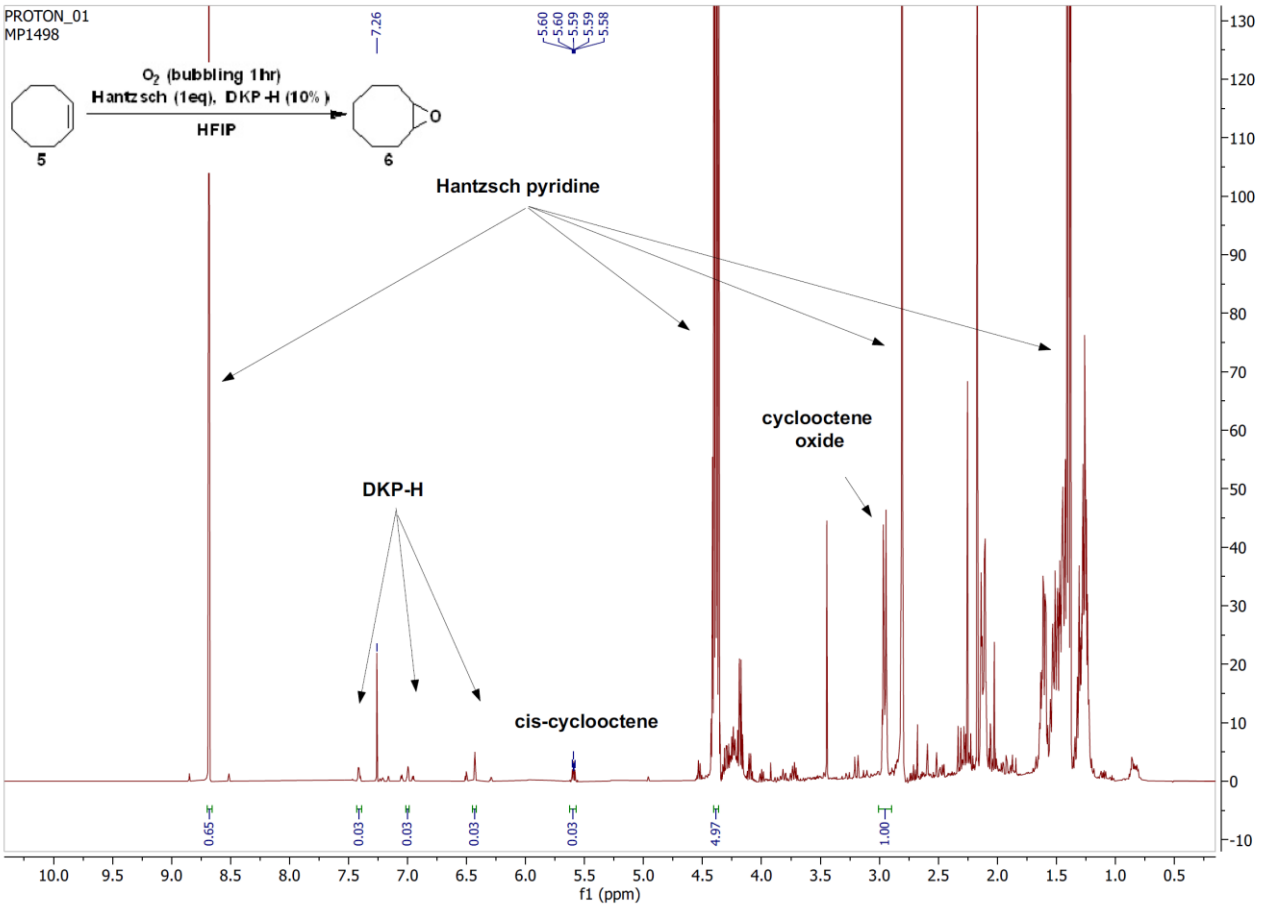
Table S1. Solvent Screening

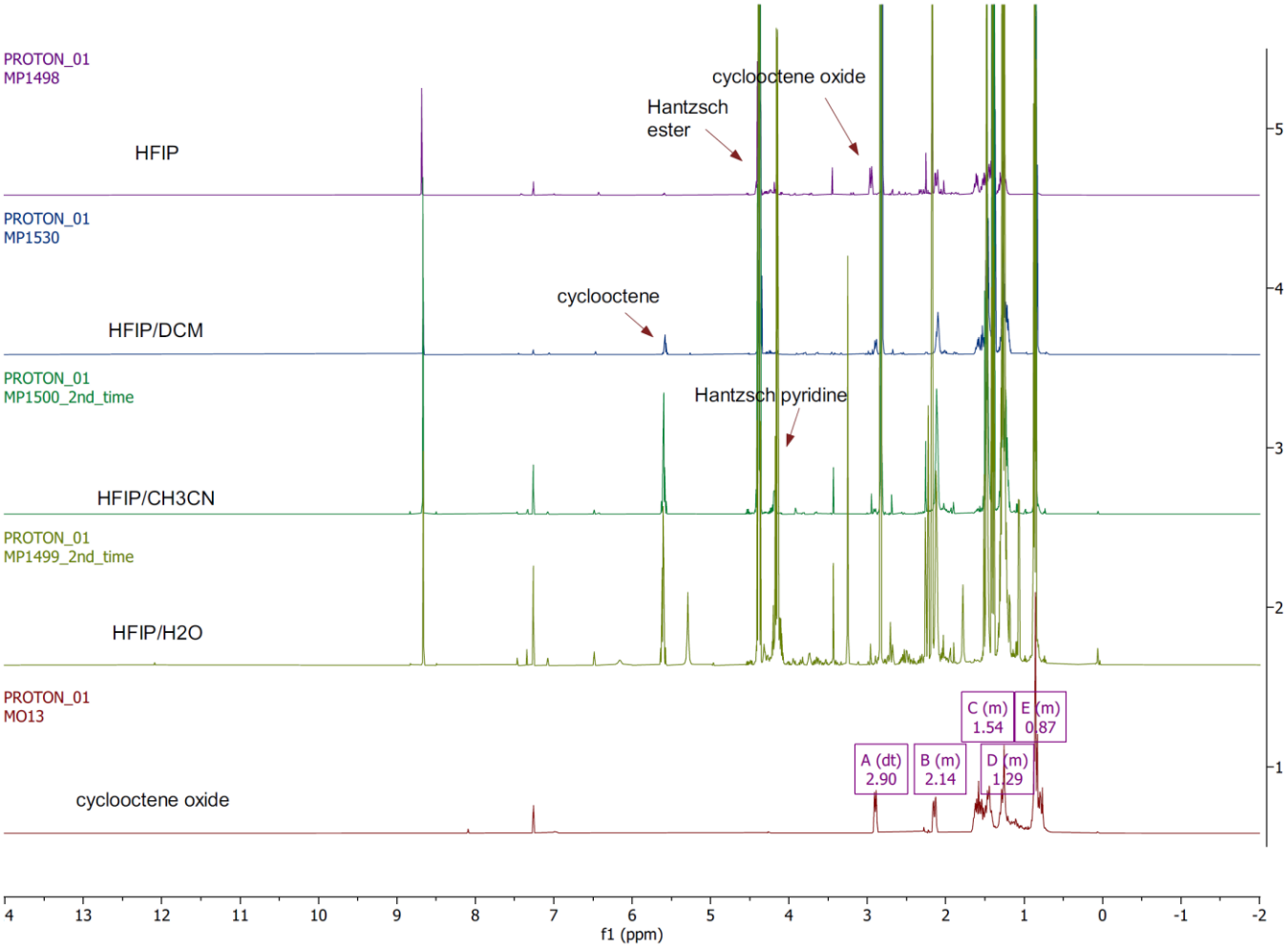
Results: Highly polar aprotic solvents (DMSO, DMF; entries: 2, 3) are able to initiate the epoxidation reaction but fail to retain the integration of the catalytic cycle. The enhanced basic profile of these solvents shutters the hemiaminal (**2**) reduction and the same is performed when mixtures of solvents with HFIP are used (entry 6). Acidity provided with HFIP can retain reduction of hemiaminal without diminishing the oxidation

potential of the starting catalyst (entry 4). Mixture of HFIP and DCM (entry 7) was found effective to retain DKP catalytic activity, a result that is highly beneficial in cases of insoluble alkenes in HFIP. Water mixtures were also tested in the presence of HFIP (entry 5) but failed to produce useful yields of **6**.






PROTON_01
MP1498
O2 (bubbling 1hr)
Hantzsch (1eq), DKP-H (10%)
HFIP
5
6
Hantzsch pyridine
cyclooctene oxide
DKP-H
cis-cyclooctene
f1 (ppm)


PROTON_01
MP1498
HFIP
cyclooctene oxide
Hantzsch ester
PROTON_01
MP1530
HFIP/DCM
cyclooctene
PROTON_01
MP1500_2nd_time
HFIP/CH3CN
Hantzsch pyridine
PROTON_01
MP1499_2nd_time
HFIP/H2O
PROTON_01
MO13
cyclooctene oxide
C (m) 1.54
E (m) 0.87
A (dt) 2.90
B (m) 2.14
D (m) 1.29
f1 (ppm)

5. Conditions Screening

Conditions:

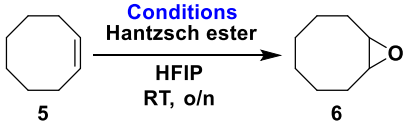
Entry 1. (*Z*)-cyclooctene (**5**, 0.23 mmol, 1.0 equiv.), Hantzsch ester (**3**, 0.46 mmol, 2.0 equiv.) and DKP (0.023 mmol, 0.1 equiv.) were dissolved in HFIP (1.2 ml) in the presence of dioxygen (bubbling) and stirred overnight at room temperature.

Entry 2. (*Z*)-cyclooctene (**5**, 0.23 mmol, 1.0 equiv.), Hantzsch ester (**3**, 0.23 mmol, 1.0 equiv.) and DKP (0.023 mmol, 0.1 equiv.) were dissolved in HFIP (1.2 ml) without bubbling with dioxygen, the vial was capped and stirred overnight at room temperature.

Entry 3. (*Z*)-cyclooctene (**5**, 0.23 mmol, 1.0 equiv.), Hantzsch ester (**3**, 0.23 mmol, 1.0 equiv.) and DKP (0.023 mmol, 0.1 equiv.) were dissolved in HFIP (1.2 ml). After 1 hour in the presence of dioxygen (bubbling), the vial was capped, and the reaction mixture stirred overnight at 45 ^{o}C.

Entry 4. (*Z*)-cyclooctene (**5**, 0.23 mmol, 1.0 equiv.), Hantzsch ester (**3**, 0.23 mmol, 1.0 equiv.) and H_2O_2 (0.23 mmol, 1.0 equiv.) were dissolved in HFIP (1.2 ml) without bubbling with dioxygen and stirred overnight at room temperature.

The crude product from every trial was obtained by quenching the reaction with water (1.5 ml) and extracting it with pentane (3 x 2 ml). Then, the organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure in an ice bath, until a pale-yellow solid residue was left in the flask. All reactions were performed in 4mL screw capped vials equipped with rubber septum, pipette, and dioxygen balloon and the reactions monitored via GC.

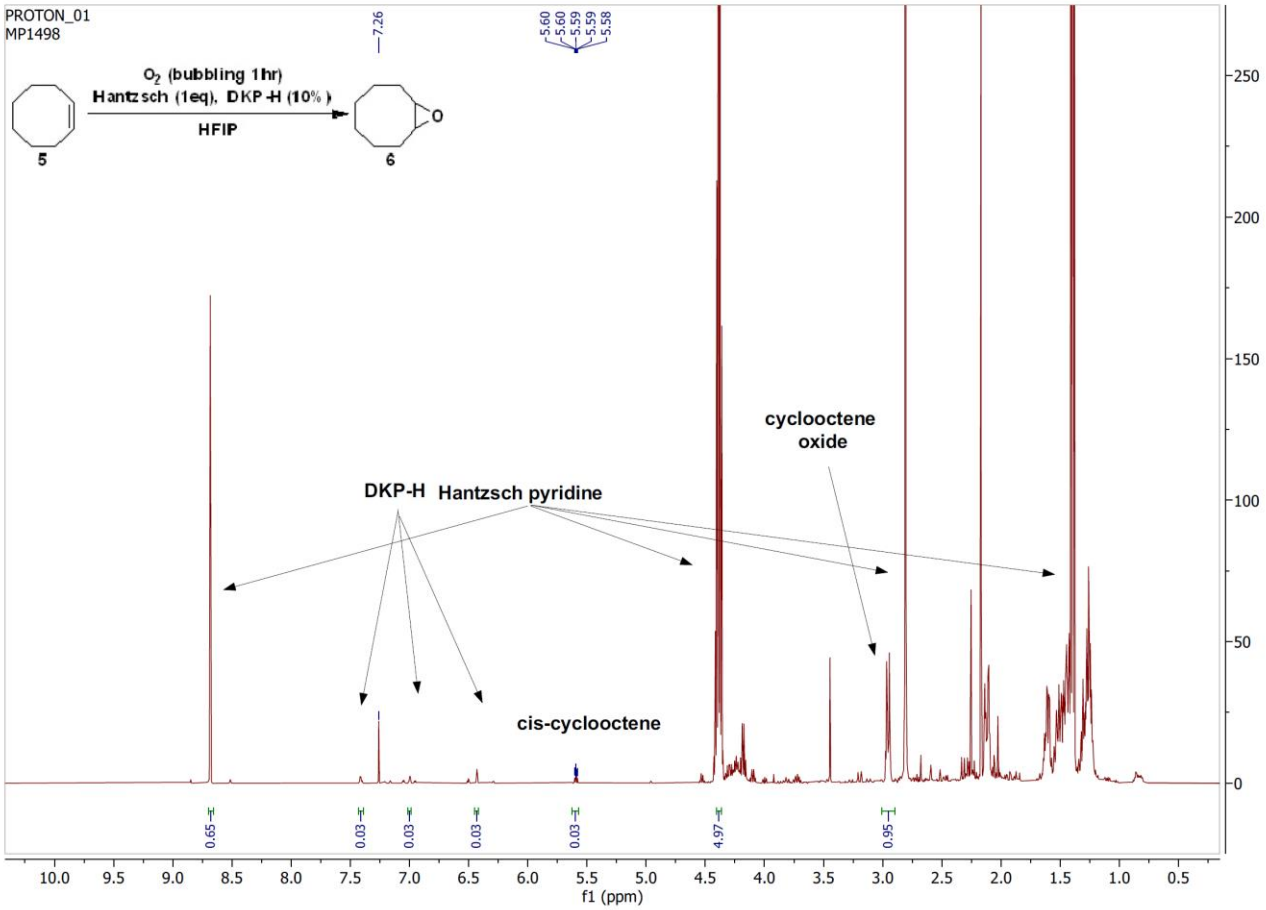


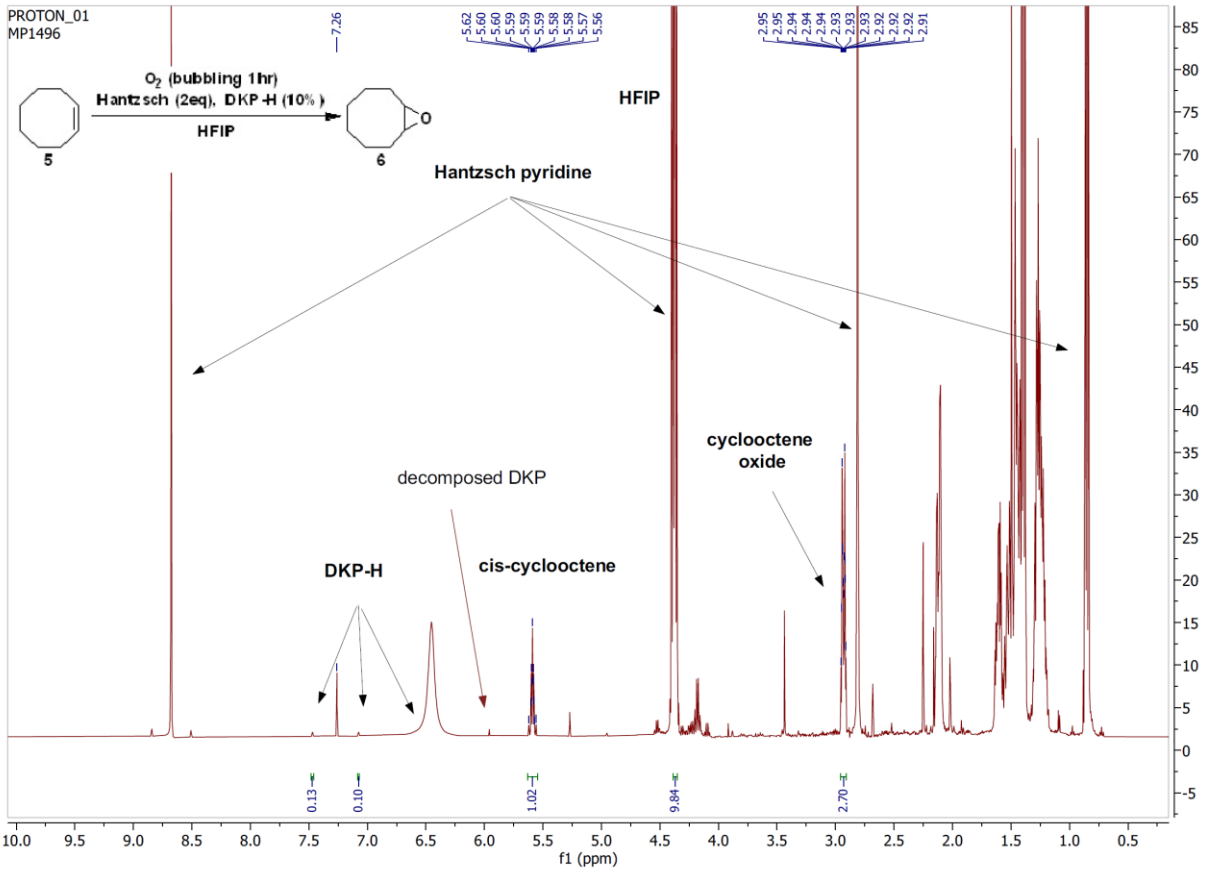
A/A	Conditions	Conversion (%)	Yield (%)
1	Hantzsch (2eq), DKP (10% mol) O_2 (bubbling)	75	**73**
2	Hantzsch (1eq), DKP (10% mol) no bubbling/capped vial	55	**50**
3	Hantzsch (1eq), DKP (10% mol) O_2 (1h bubbling) Heat 45 ^{o}C	55	**54**
4	Hantzsch (1eq), H_2O_2 (1eq)	30	**28**

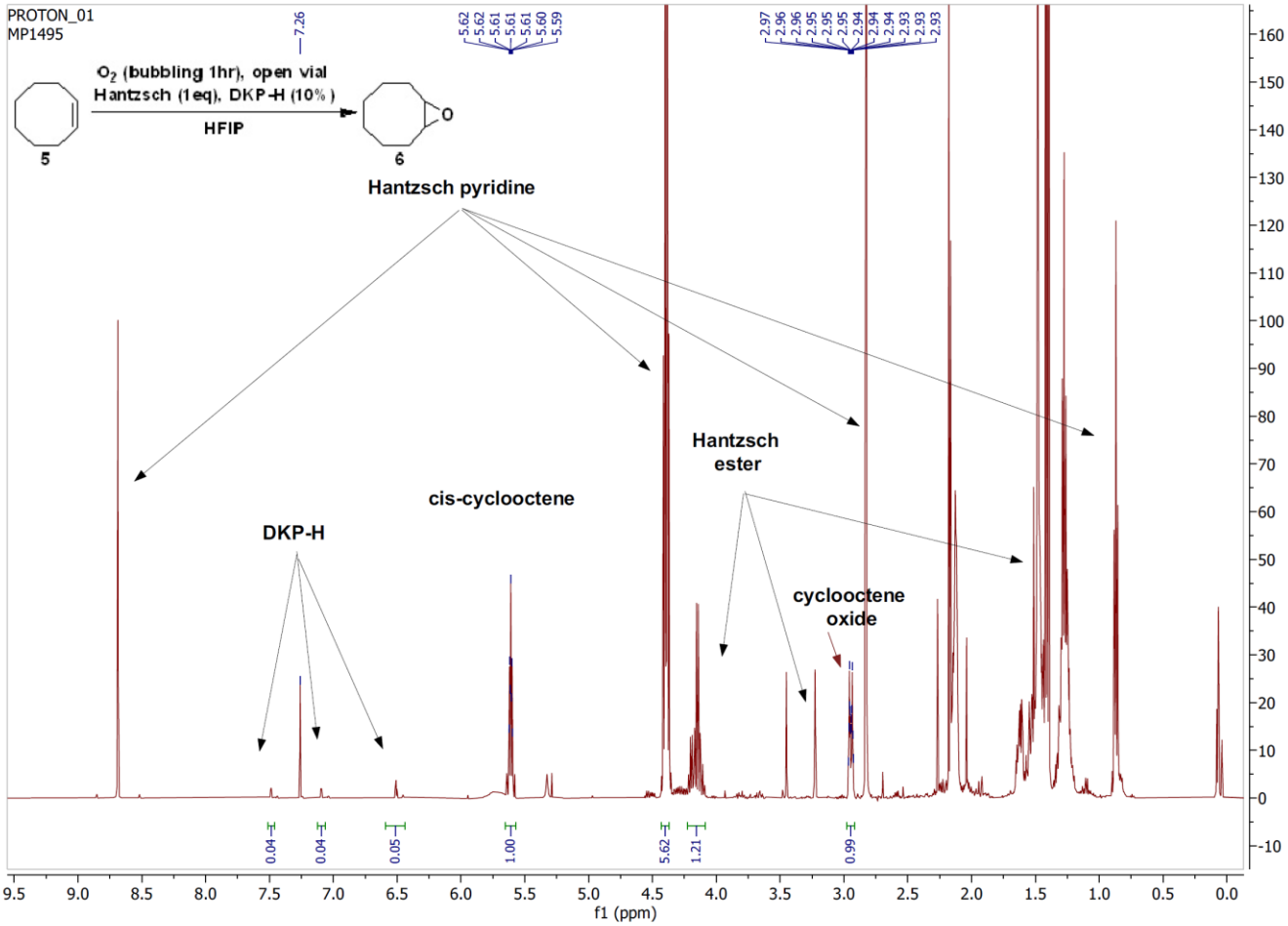
Table S2. Conditions screening

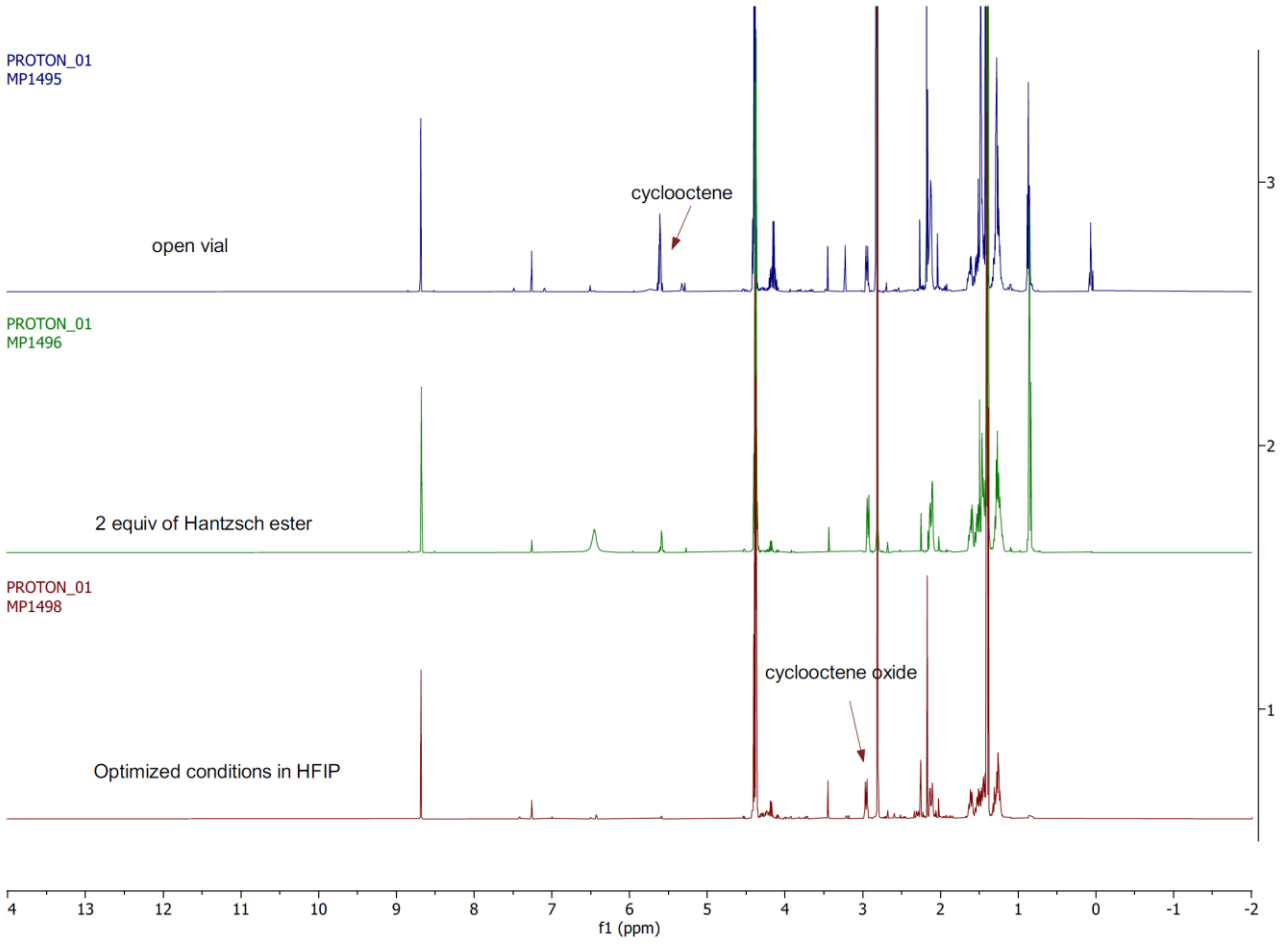
Results: Additional equivalents of Hantzsch ester (entry 1) or conducting the reaction in an capped vial without dioxygen bubbling (entry 2) resulted in diminished yields of **6**. Heating the reaction mixture led to complete oxidation of Hantzsch ester affording **4**, which caused the decomposition of DKP catalyst (entry 3),

whereas addition of hydrogen peroxide as the terminal oxidant led only to low yields of the desired cyclooctene oxide (**6**, entry 4).



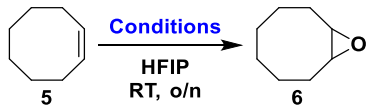



PROTON_01
MP1495
O_2 (bubbling 1hr), open vial
Hantzsch (1eq), DKP-H (10%)
HFIP
5
6
Hantzsch pyridine
Hantzsch ester
cis-cyclooctene
DKP-H
cyclooctene oxide
f1 (ppm)


PROTON_01
MP1495
open vial
cyclooctene
PROTON_01
MP1496
2 equiv of Hantzsch ester
PROTON_01
MP1498
cyclooctene oxide
Optimized conditions in HFIP
f1 (ppm)

6. Blank Reactions

Conditions: (*Z*)-cyclooctene (**5**, 0.23 mmol, 1.0 equiv.) and the additive that each trial included, were dissolved in HFIP (1.2 ml) in the presence of dioxygen (bubbling) and stirred overnight at room temperature. The crude product from every trial was obtained by quenching the reaction with water (1.5 ml) and extracting it with pentane (3 x 2 ml). Then, the organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure in an ice bath, until a pale-yellow solid residue was left in the flask. All reactions were performed in 4mL screw capped vials equipped with rubber septum, pipette, and dioxygen balloon and the reactions monitored via GC.



A/A	Conditions	Conversion (%)	Yield (*%*)
1	O_2 (bubbling)	0	**0**
2	O_2 (bubbling), DKP-H (10%)	12	**8**
3	O_2 (bubbling), Hantzsch (1eq)	10-44	**5-35**
4*	Hantzsch (1eq) Hantzsch pyridine (**4**, 0.25eq), H_2O (25eq) O_2 (bubbling)	10	**5**

*Note: recrystallized Hantzsch ester is used.

Table S3. Evaluating blank reactions

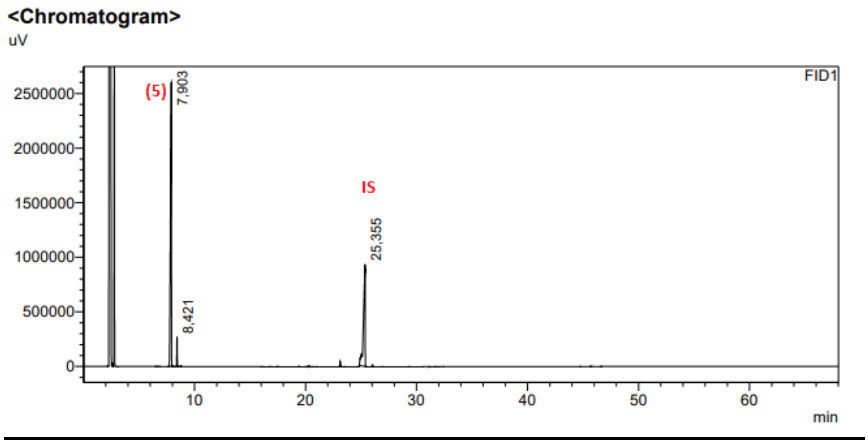
Results: In the presence only of dioxygen (bubbling) no evidence of epoxidation was observed (entry 1). Without Hantzsch ester (**3**) the epoxide was obtained at about 8% yield (entry 2), because no catalytic activity could proceed without the reduction of hemiaminal **2** and the recycle of the catalyst. On the other hand, the range of epoxide yields witnessed when Hantzsch ester was used in HFIP in the presence of dioxygen was highly depended on its purity and the existence of metal-traces and light (entry 3). When recrystallized Hantzsch ester was used, higher yield of the epoxide was evidenced (35% yield of entry 4).

The blank reactions as well as the reactions for monitoring the progress of the epoxidation of cyclooctene (**5**) were monitored with the use of GC. As internal standard (**IS**) was used 1,3,5-trimethoxybenzene (t_{IS}= 25.355 min) and the information about the analytical column or the method information are shown in Section 1.

For the analysis of the above experiments via GC, 0.01 mmol scale reaction was ran overnight at room temperature. The crude product from every trial was obtained by extracting each reaction mixture with pentane (3 x 2 ml), evaporation under reduced pressure in an ice bath and dissolving it in 1 ml CH_3CN.

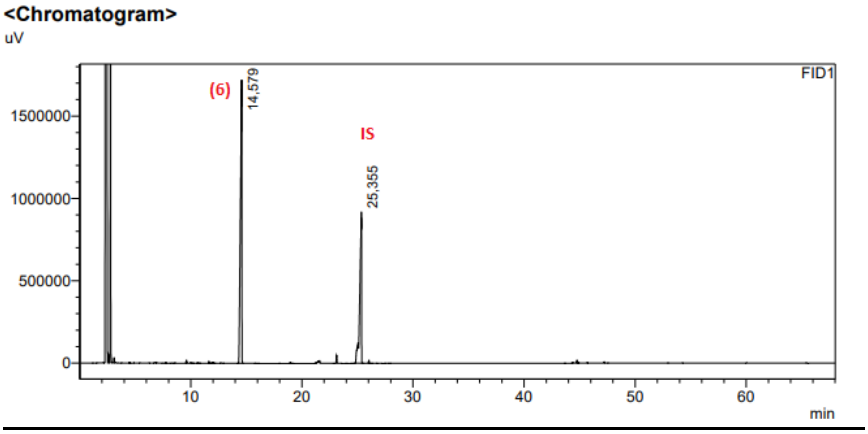
Chromatogram 1: Cyclooctene (**5**) with Internal standard (IS) trimethoxybenzene

t_1= 7.903 min



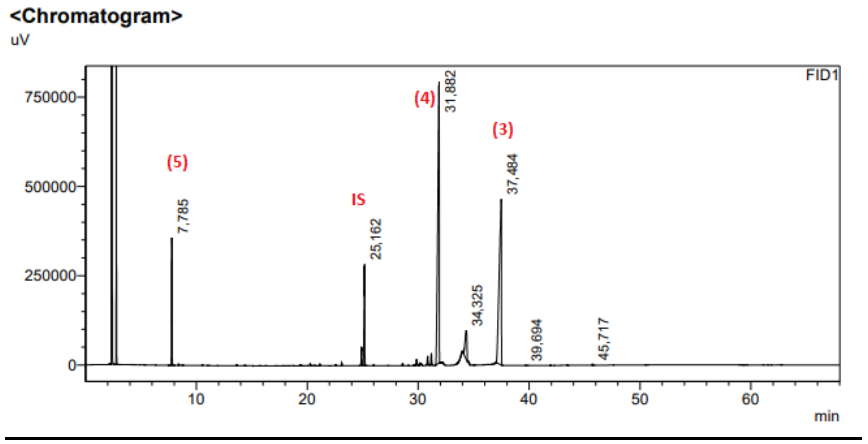
Chromatogram 2: Cyclooctene oxide (**6**)

t_2= 14.579 min



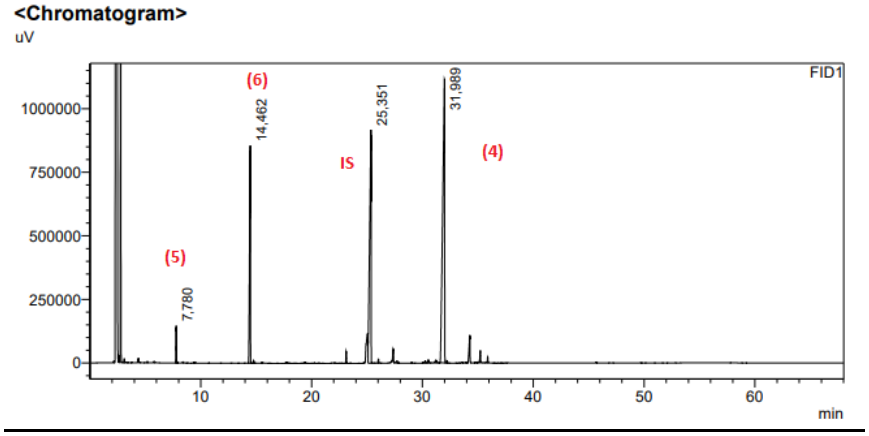
Chromatogram 3: Blank reaction (Section 6, entry 3)

t_1= 7.785 min (**5**); t_3= 31.882 min (Hantzsch pyridine, **4**); t_4= 37484 min (Hantzsch ester, **3**)

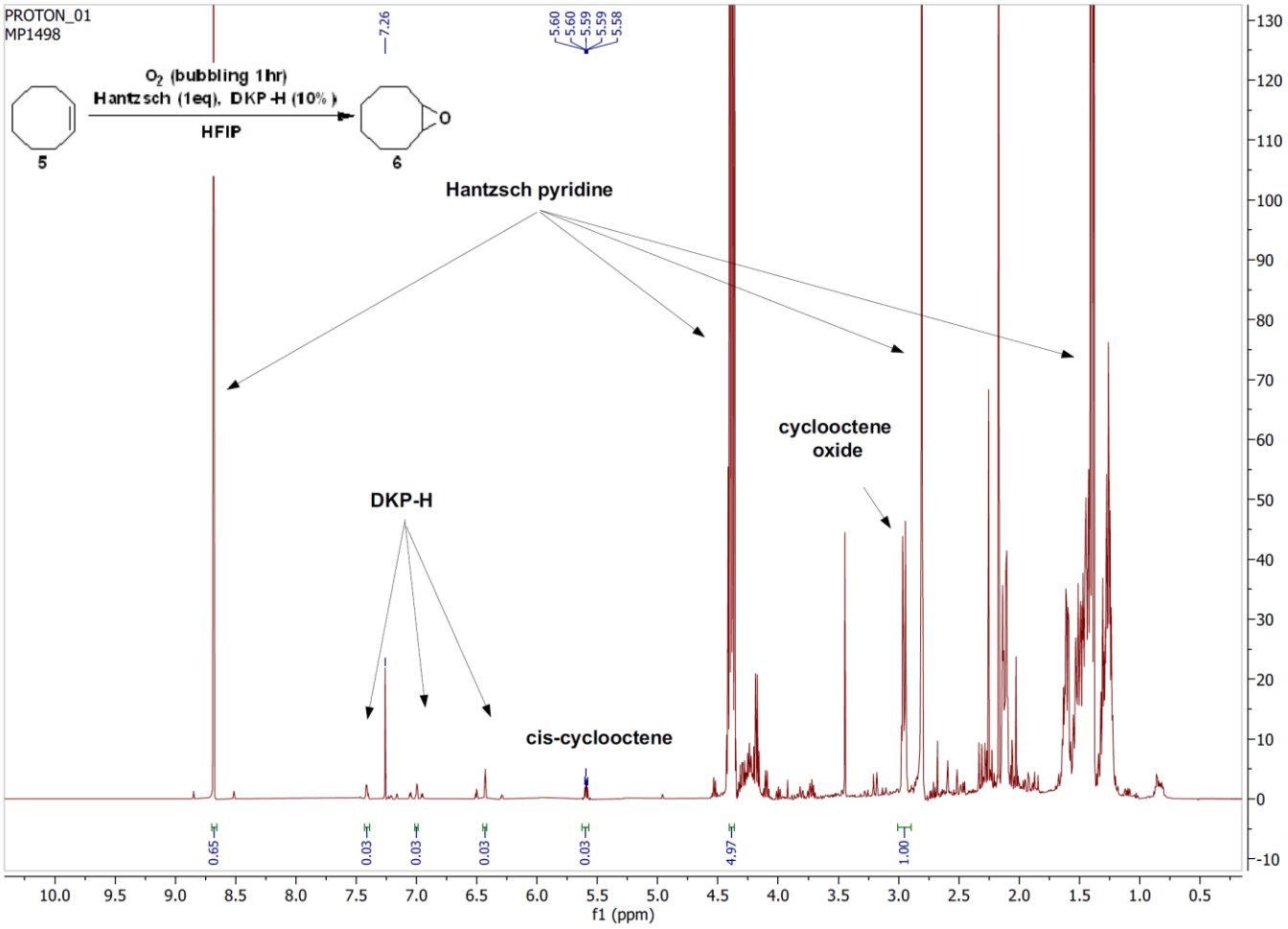


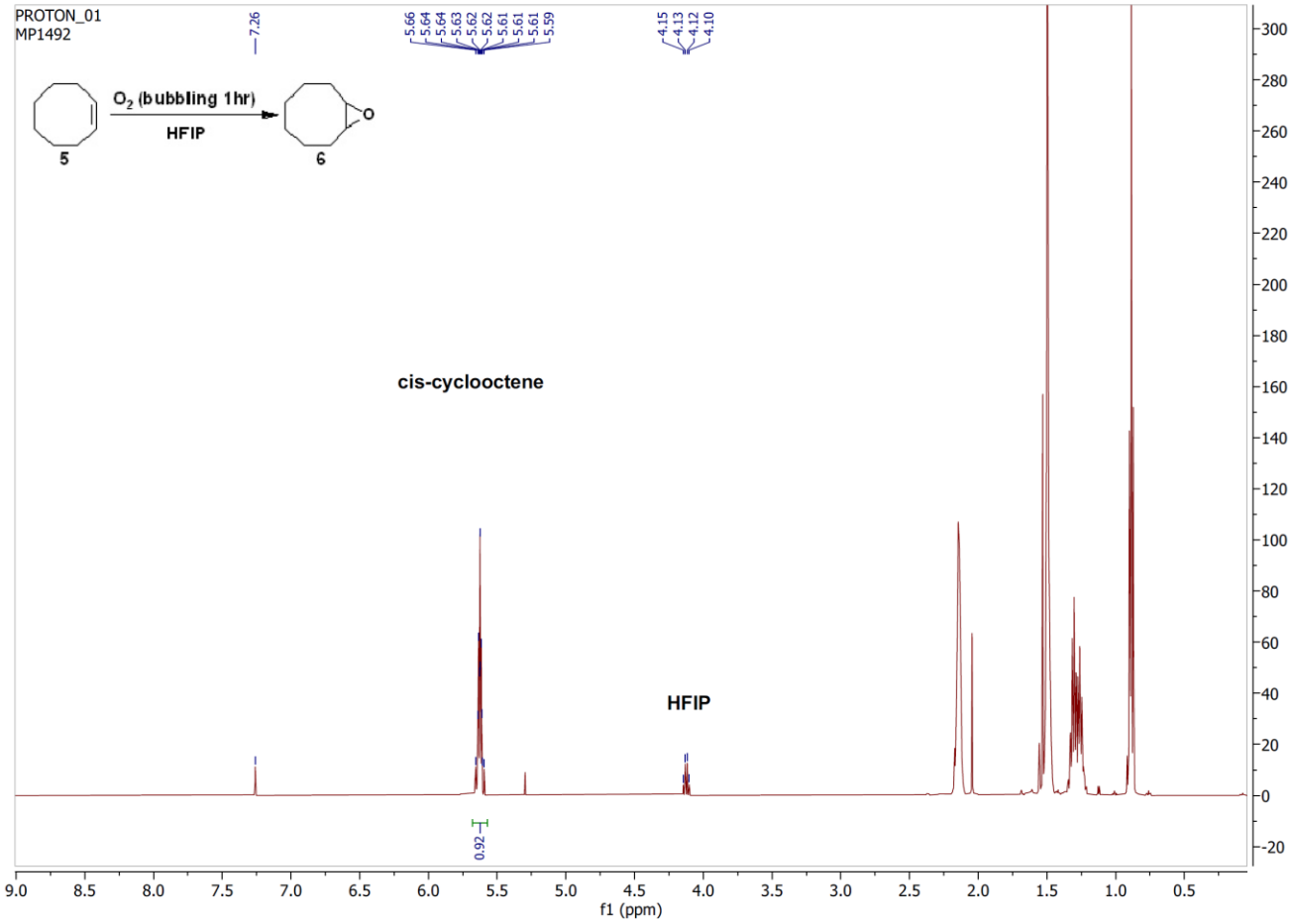
Chromatogram 4: Catalytic reaction

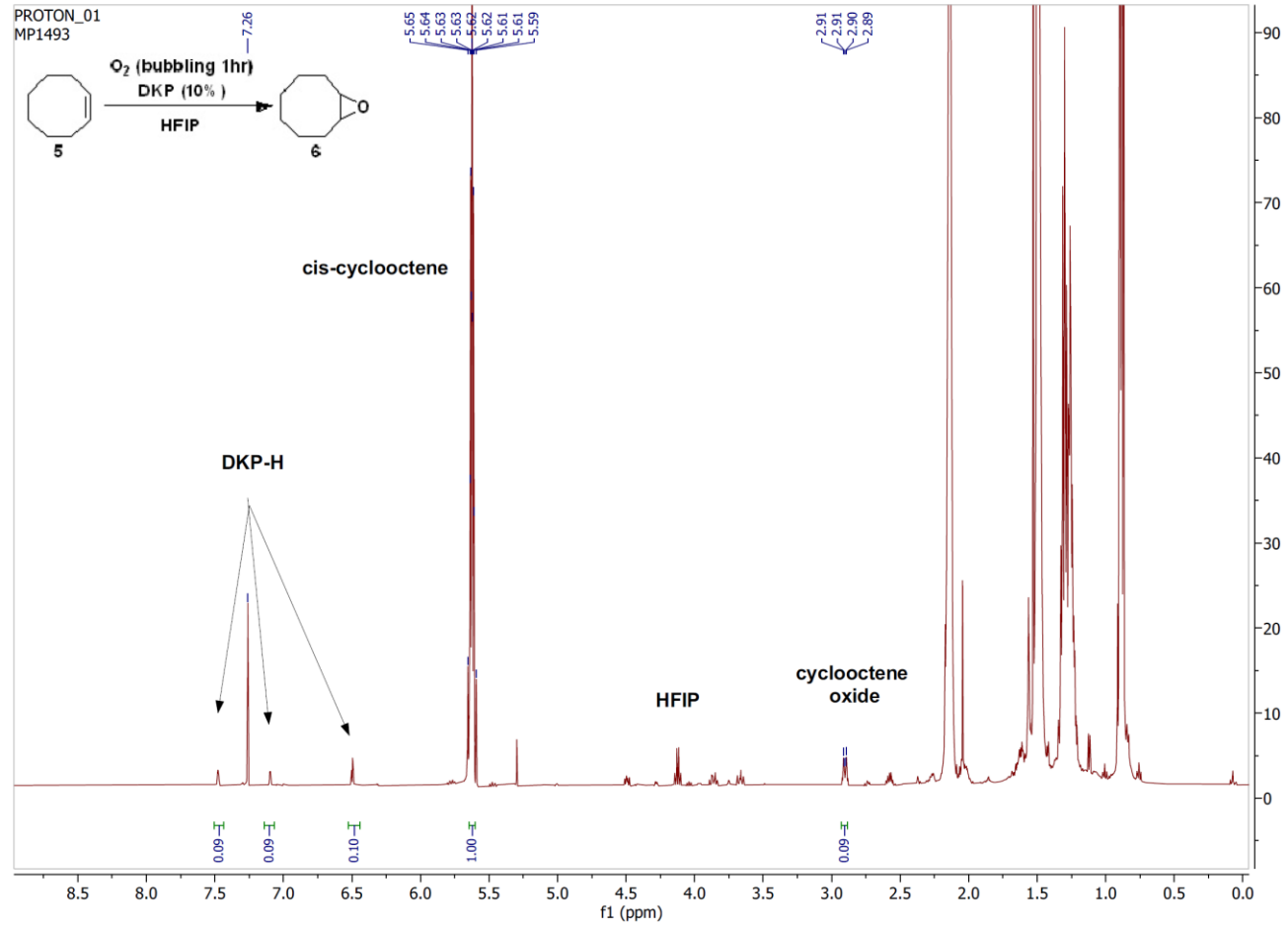
t_1= 7.780 min (**5**); t_2= 14.462 min (**6**); t_3= 31.989 min (Hantzsch pyridine, **4**)

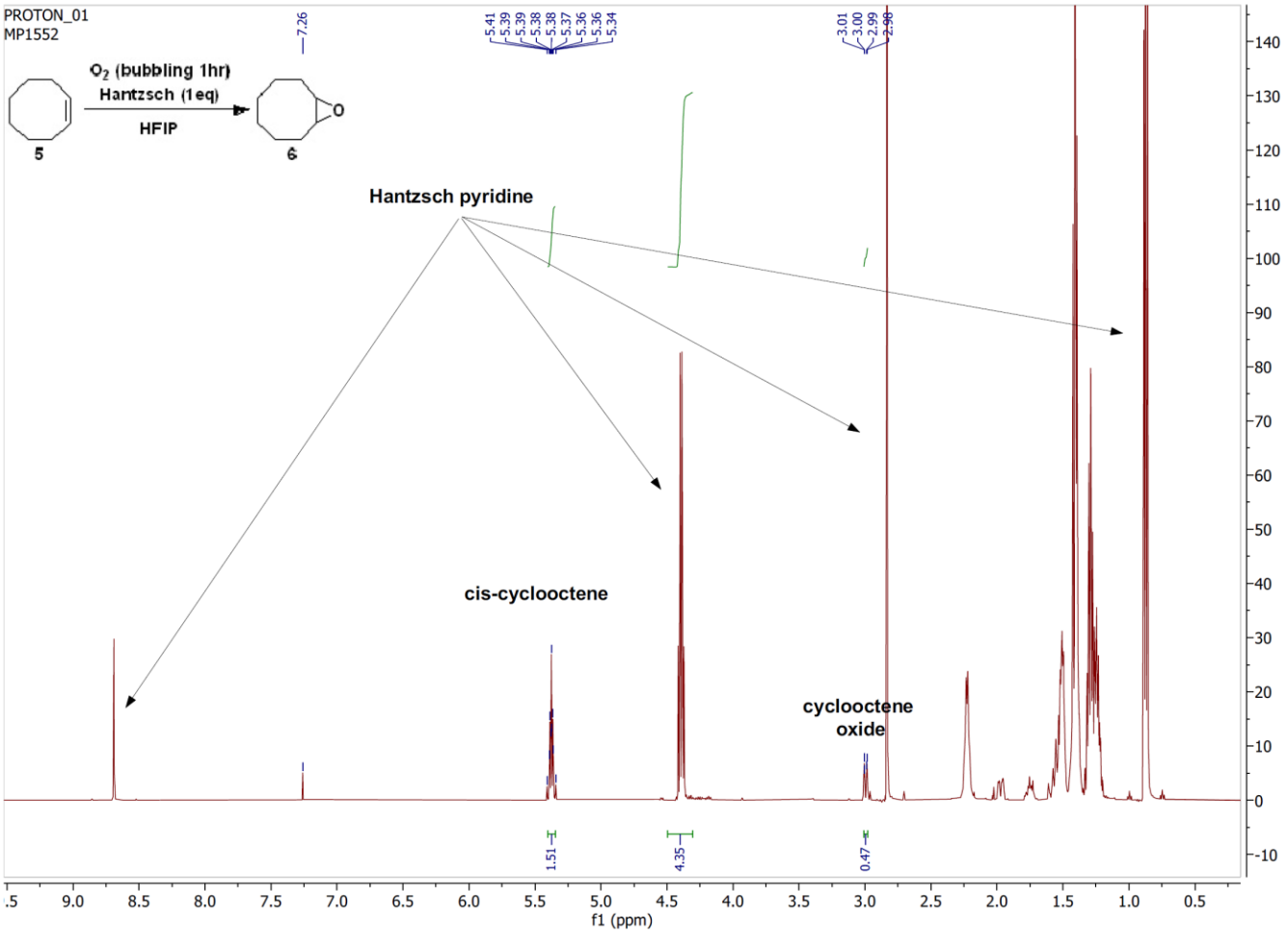


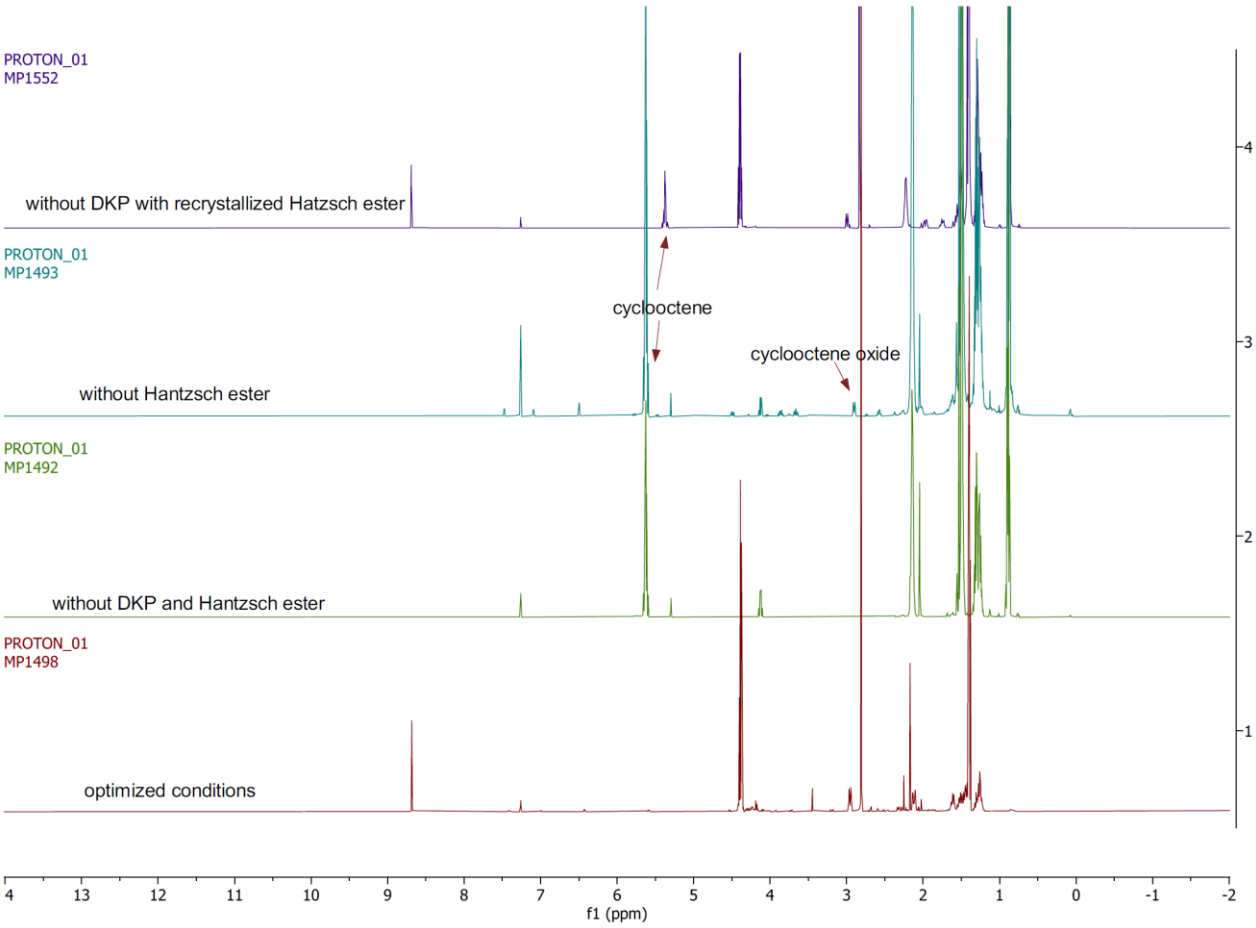
Several batches of Hantzsch ester were tried in the absence of DKP catalyst. In most cases the product varies from 5-35%. Indicative is the fact that batches bearing water stop the epoxidation reaction (chromatogram 3). In all cases Hantzsch ester oxidizes slowly to pyridine **4** in the presence of dioxygen in HFIP. The existence of pyridine **4** shows to accelerate production of epoxide **6** in the presence of catalytic amount of DKP (chromatogram 4).




PROTON_01
MP1492
7.26
5.66
5.64
5.64
5.63
5.62
5.62
5.61
5.61
5.59
4.15
4.13
4.12
4.10
O2 (bubbling 1hr)
HFIP
5
6
cis-cyclooctene
HFIP
0.92
f1 (ppm)


PROTON_01
MP1493
7.26
5.65
5.64
5.63
5.63
5.62
5.62
5.61
5.61
5.59
2.91
2.91
2.90
2.89
O2 (bubbling 1hr)
DKP (10%)
HFIP
5
6
cis-cyclooctene
DKP-H
HFIP
cyclooctene
oxide
0.09
0.09
0.10
1.00
0.09
f1 (ppm)


PROTON_01
MP1552
O_2 (bubbling 1hr)
Hantzsch (1eq)
HFIP
5
6
Hantzsch pyridine
cis-cyclooctene
cyclooctene oxide
f1 (ppm)


PROTON_01
MP1552
without DKP with recrystallized Hatzsch ester
PROTON_01
MP1493
cyclooctene
cyclooctene oxide
without Hantzsch ester
PROTON_01
MP1492
without DKP and Hantzsch ester
PROTON_01
MP1498
optimized conditions
f1 (ppm)

7. Hantzsch ester Screening Activity

Willing to confirm the above observations, a different substrate was selected to avoid problems of volatility. A wide selection of conditions employed to reveal the appropriate equivalents of Hantzsch pyridine **4** and water to shut down the competitive epoxidation by Hantzsch ester and allow the DKP-promoted epoxidation. The current study might find application in a future development of an asymmetric epoxidation variant.

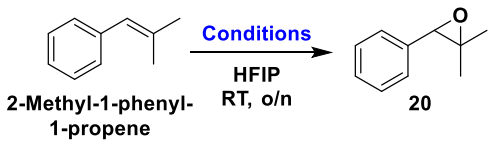
Observation: the synthesis of different Hantzsch ester batches led to different results in blank reactions (Section 6, entry 3). When a blank reaction ran in the presence of recrystallized Hantzsch ester, higher yield of the epoxide was evidenced.

Conditions:

Blank reaction: 2-Methyl-1-phenyl-1-propene (0.38 mmol, 1.0 equiv.), Hantzsch ester (**3**, 0.38 mmol, 1.0 equiv.), Hantzsch pyridine (**4**) (depending on the Table below.) and H_2O (depending on the Table below.) were dissolved in HFIP (1.2 ml) in the presence of dioxygen (bubbling) and stirred overnight at room temperature.

Catalytic reactions: 2-Methyl-1-phenyl-1-propene (0.38 mmol, 1.0 equiv.) and Hantzsch ester (**3**, 0.38 mmol, 1.0 equiv.) followed by the addition of Hantzsch pyridine (**4**) (depending on the Table below.), H_2O (depending on the Table below.) and DKP (0.038 mmol, 0.1 equiv.) were dissolved in HFIP (1.2 ml) in the presence of dioxygen (bubbling) and stirred overnight at room.

The crude product from every trial was obtained by quenching the reaction with water (1.5 ml) and extracting it with pentane (3 x 2 ml). Then, the organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure in an ice bath, until a pale-yellow solid residue was left in the flask. All reactions were performed in 4mL screw capped vials equipped with rubber septum, pipette, and dioxygen balloon and the reactions monitored via GC.



A/A*	Hantzsch ester (3)	Hantzsch pyridine (4)	H_2O	Catalyst	Yield %
1	1eq	-	50eq	-	**0**
2	1eq	-	50eq	10%	**6.5**
3	1eq	1eq	-	-	**0**
4	1eq	1eq	-	10%	**20**
5	1eq	0.5eq	10eq	-	**12**
6	1eq	0.5eq	10eq	10%	**22**
7	1eq	0.5eq	50eq	-	**0**
8	1eq	0.5eq	50eq	10%	**14**
9	1eq	0.25eq	50eq	-	**0**
10	1eq	0.25eq	50eq	10%	**traces**

11	1eq	-	25eq	-	**6%**
12	1eq	0.25eq	25eq	-	**9%**
13	1eq	0.25eq	25eq	10%	**56%**

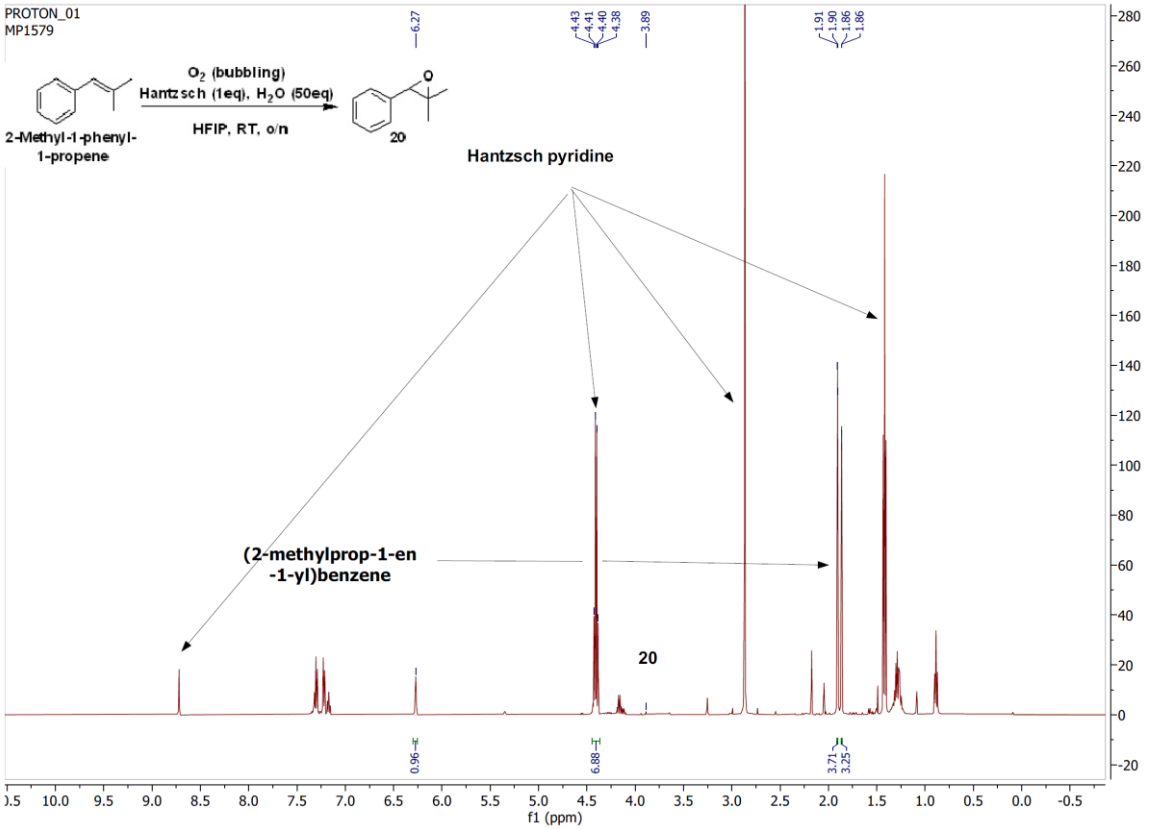
Note: Trials indicated by circle correspond to blank reactions (no use of DKP).
*All reactions ran in the presence of recrystallized Hantzsch ester (**3**).

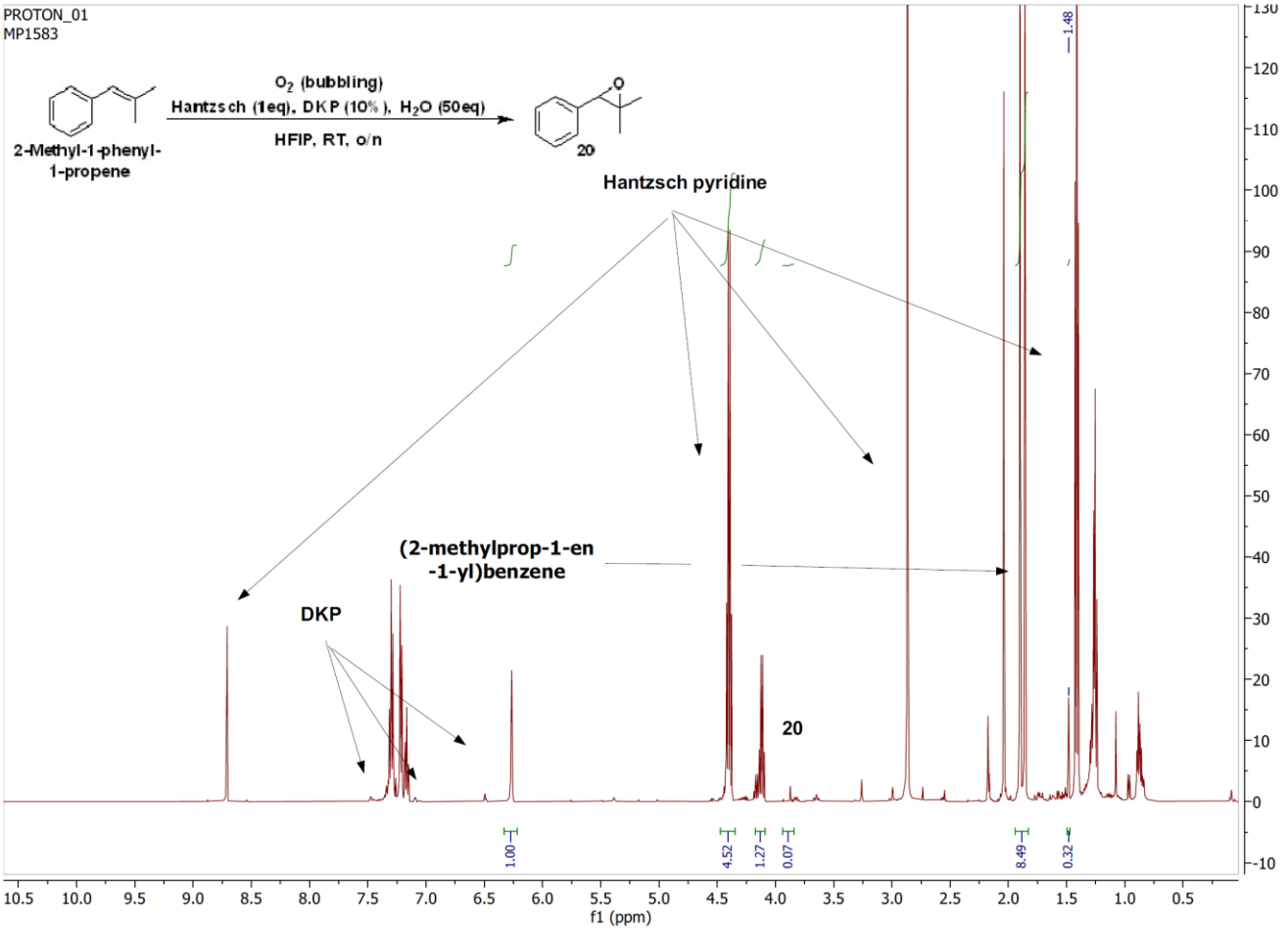
Table S4. Evaluating Hantzsch ester promoted epoxidation and conditions to shutter it

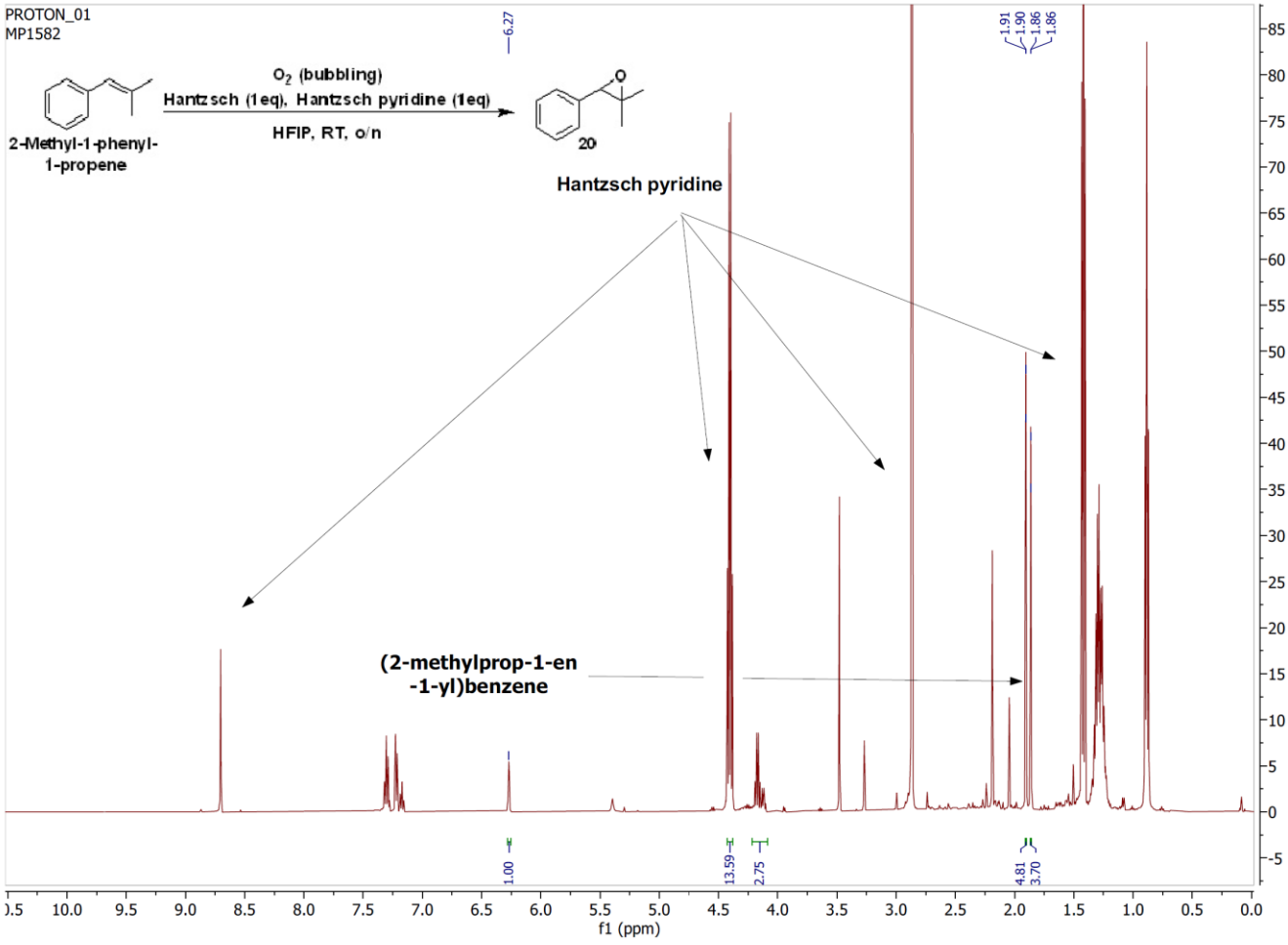
Results: From comparison of blank and catalytic reactions is evidenced that in the presence of large volume of H_2O, catalytic reaction stopped immediately (entry 2, 8, 10). When large amount of **4** was used (entry 4, 6) enhanced the decomposition of the catalyst and led to lower yields of epoxidation reaction. More equivalents of H_2O interrupt the oxidation process of Hantzsch ester (entry 1, 7, 9) but at the same time water reduces the capacity of DKP for epoxidation. As it is already mentioned before[2] Hantzsch pyridine (**4**), produced from Hantzsch ester (**3**) in the catalytic cycle promotes the ability of DKP to activate dioxygen, so when the smallest quantity of **4** and H_2O were used, the proper operation of the catalytic system was achieved (entry 13).

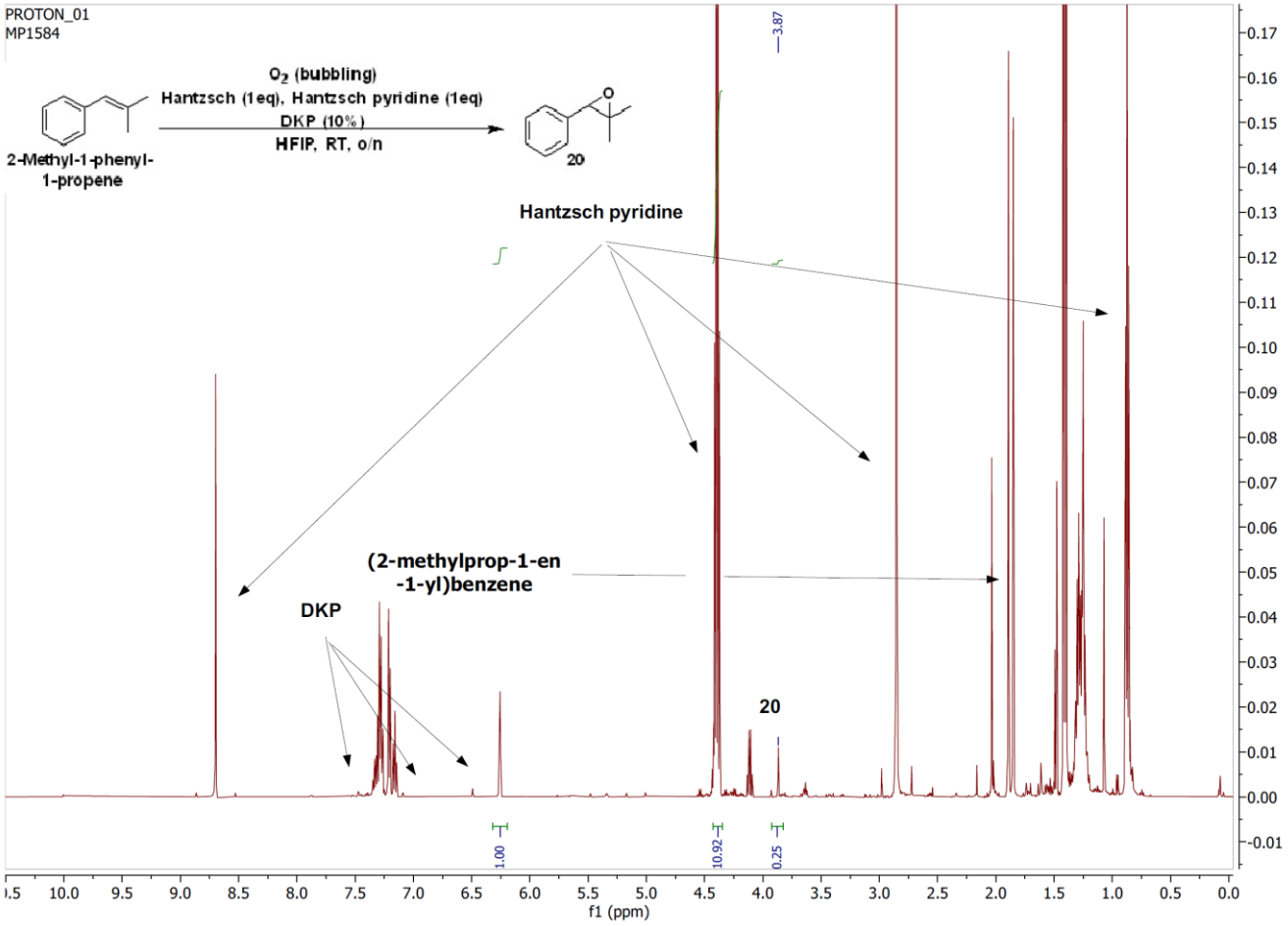
To conclude, this survey aims to reveal the participation of Hantzsch ester in oxidation process. This might be particularly helpful for the development of enantioselective reactions and does not affect current non-asymmetric catalytic epoxidation reactions which advised to be proceeded without the addition of Hantzsch pyridine (**4**) and water.

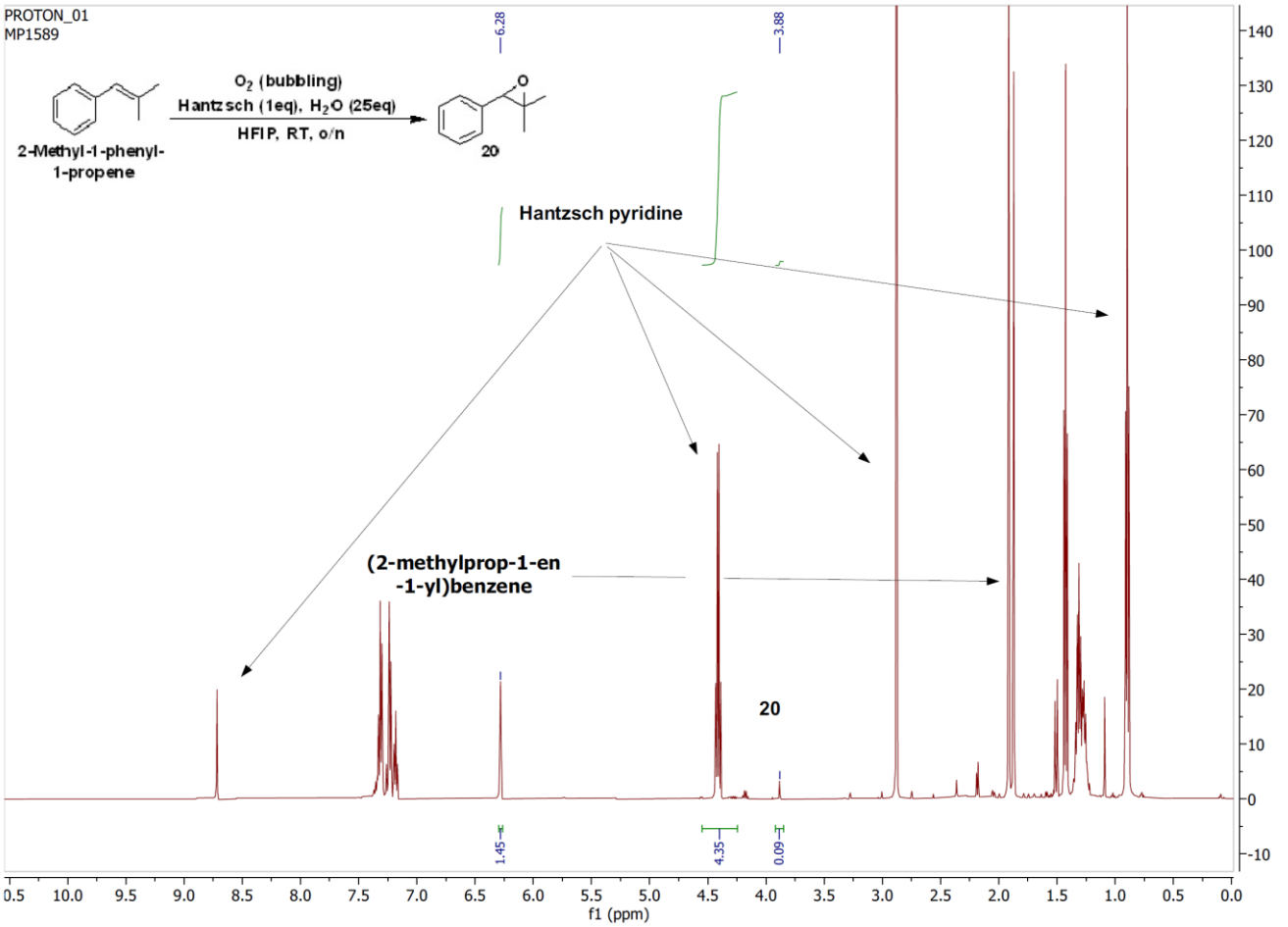
Please find below indicative spectra of crude reaction mixtures corresponding to entries of Table S4.

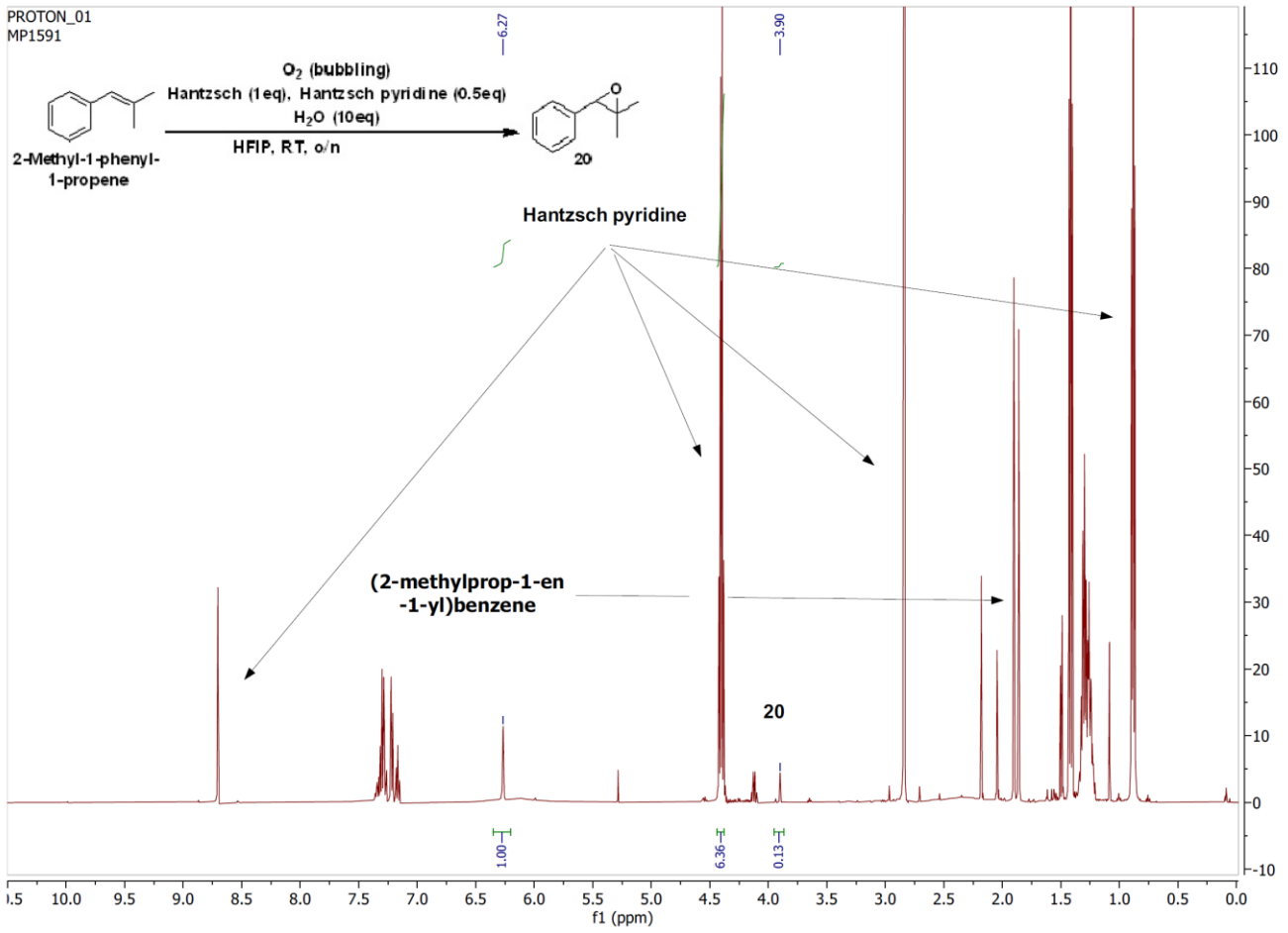


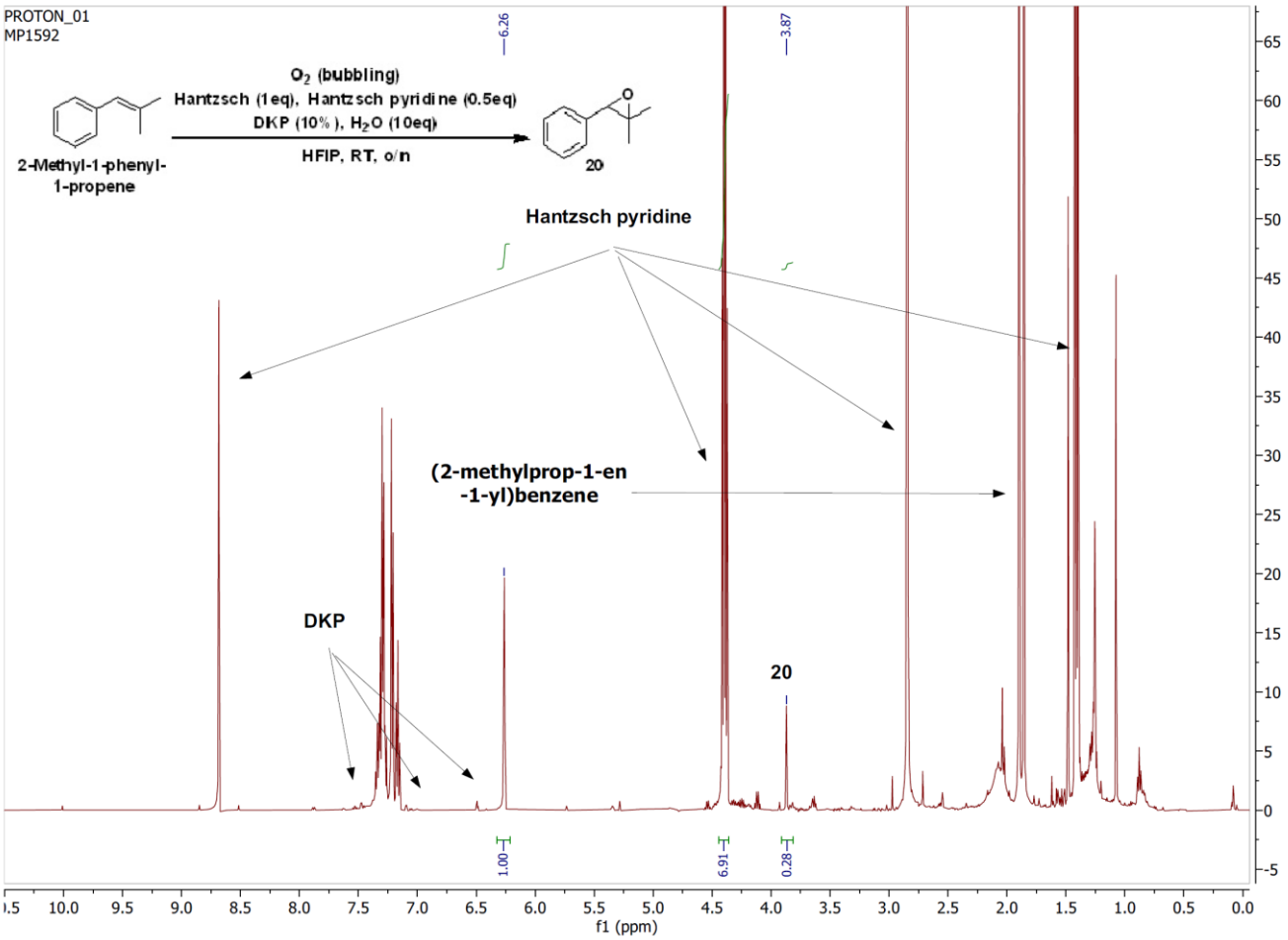

PROTON_01
MP1583
2-Methyl-1-phenyl-1-propene
O2 (bubbling)
Hantzsch (1eq), DKP (10%), H2O (50eq)
HFIP, RT, o/n
20
Hantzsch pyridine
(2-methylprop-1-en-1-yl)benzene
DKP
20
1.48
1.00
4.52
1.27
0.07
8.49
0.32
f1 (ppm)

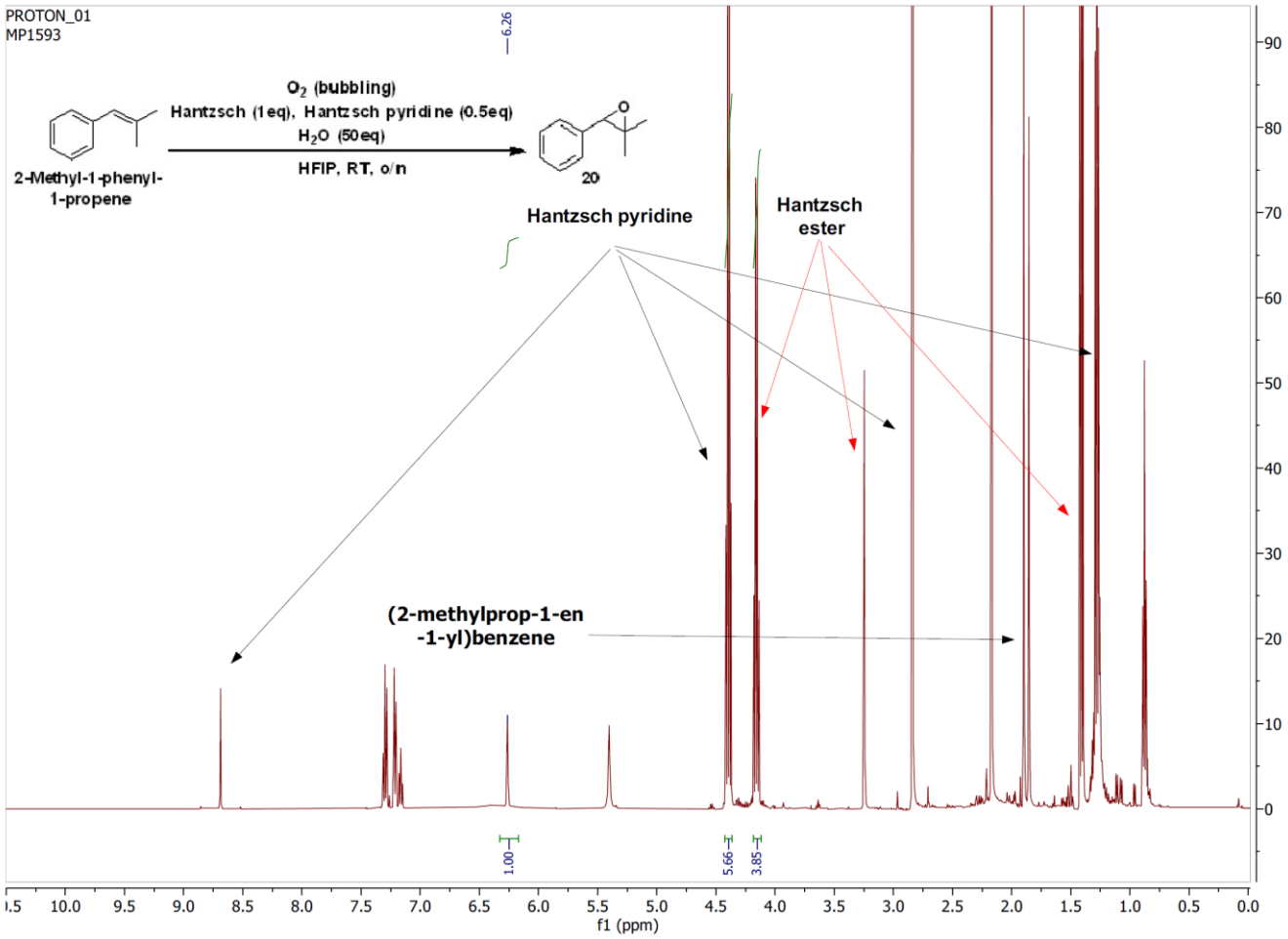

PROTON_01
MP1582
2-Methyl-1-phenyl-1-propene
O2 (bubbling)
Hantzsch (1eq), Hantzsch pyridine (1eq)
HFIP, RT, o/n
20
Hantzsch pyridine
(2-methylprop-1-en-1-yl)benzene
6.27
1.91
1.90
1.86
1.86
1.00
13.59
2.75
4.81
3.70
f1 (ppm)

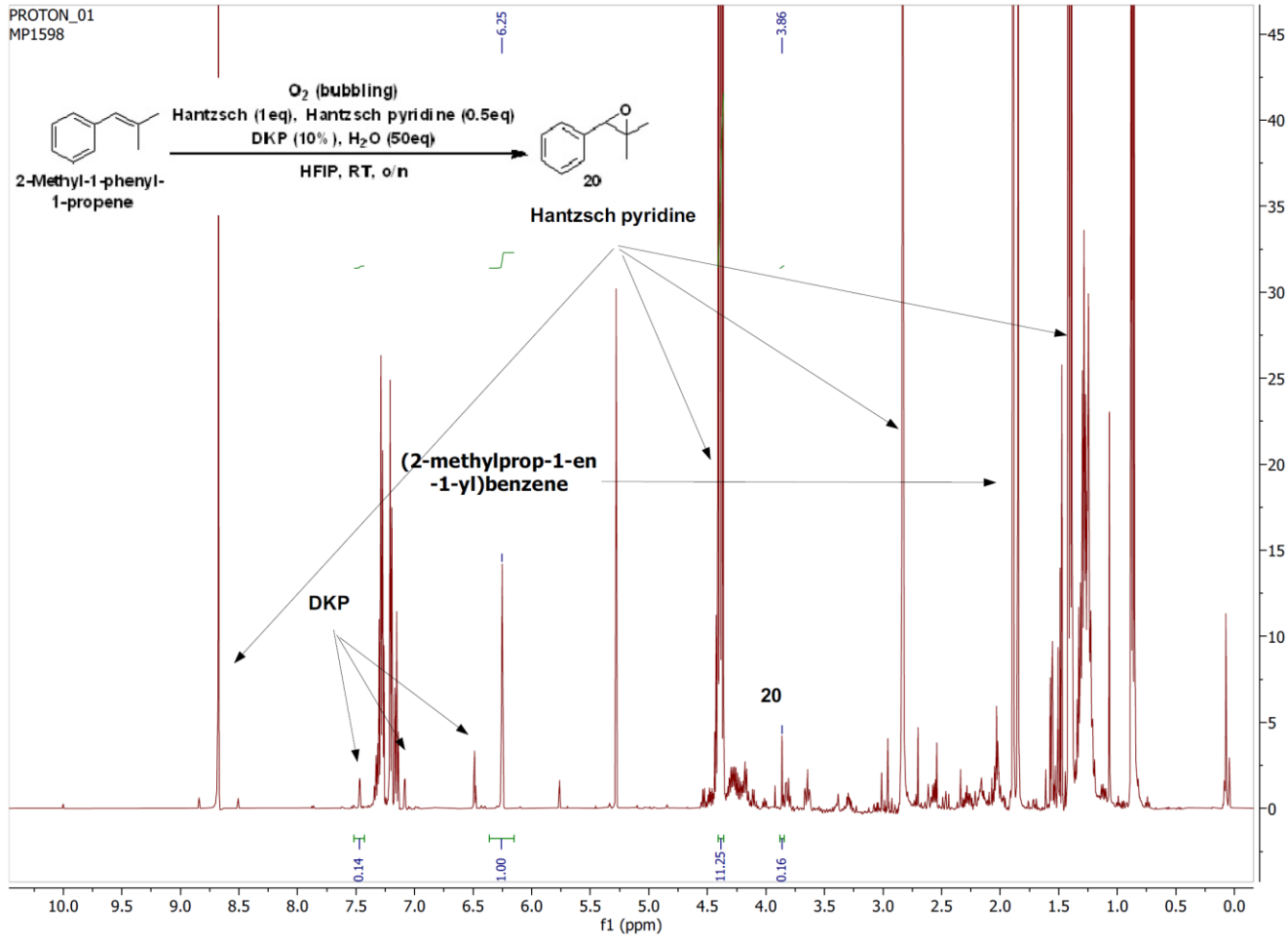

PROTON_01
MP1584
O2 (bubbling)
Hantzsch (1eq), Hantzsch pyridine (1eq)
DKP (10%)
HFIP, RT, o/n
2-Methyl-1-phenyl-1-propene
20
Hantzsch pyridine
(2-methylprop-1-en-1-yl)benzene
DKP
20
f1 (ppm)

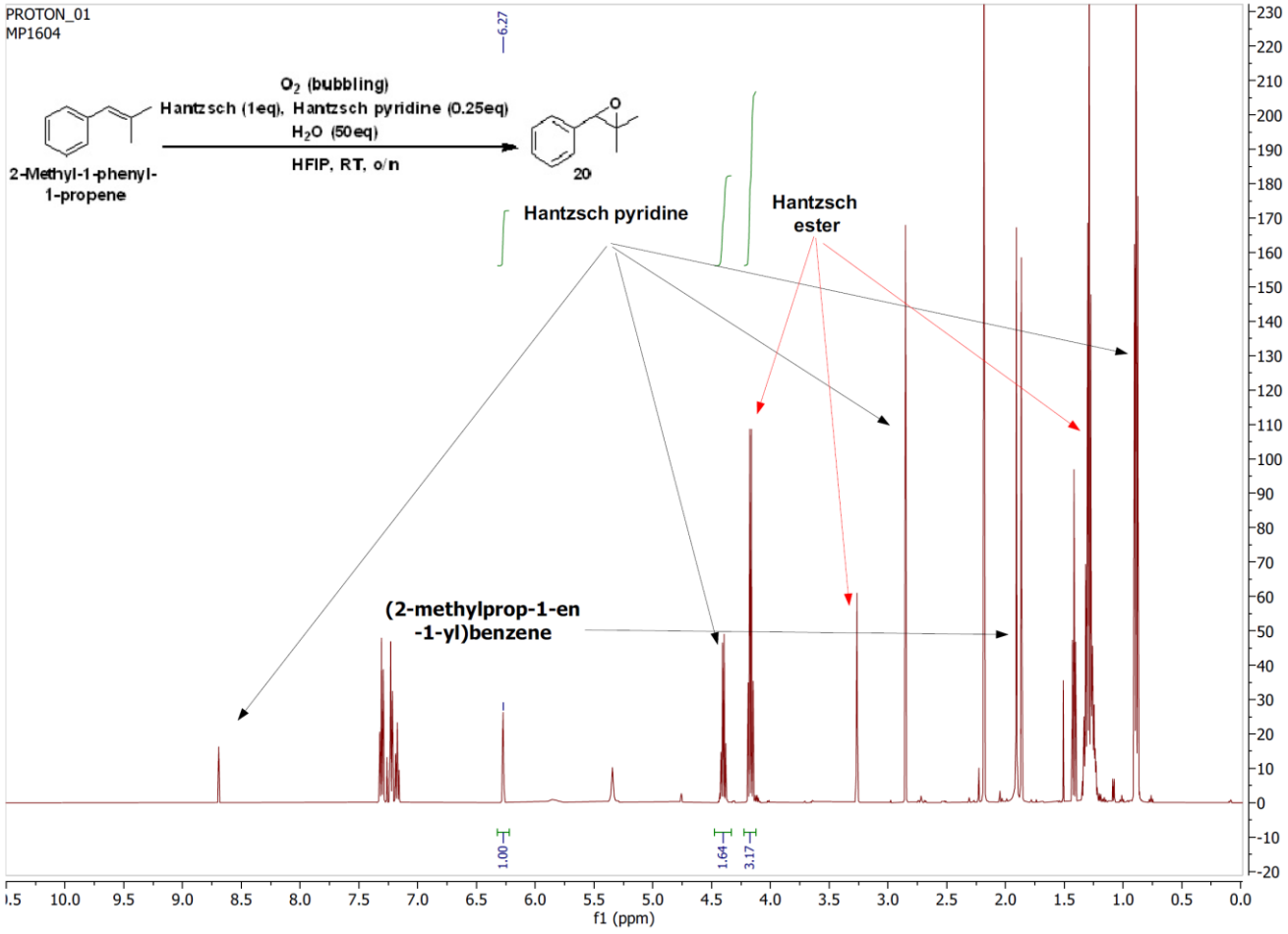

PROTON_01
MP1589
O2 (bubbling)
Hantzsch (1eq), H2O (25eq)
HFIP, RT, o/n
2-Methyl-1-phenyl-1-propene
20
Hantzsch pyridine
(2-methylprop-1-en-1-yl)benzene
20
f1 (ppm)

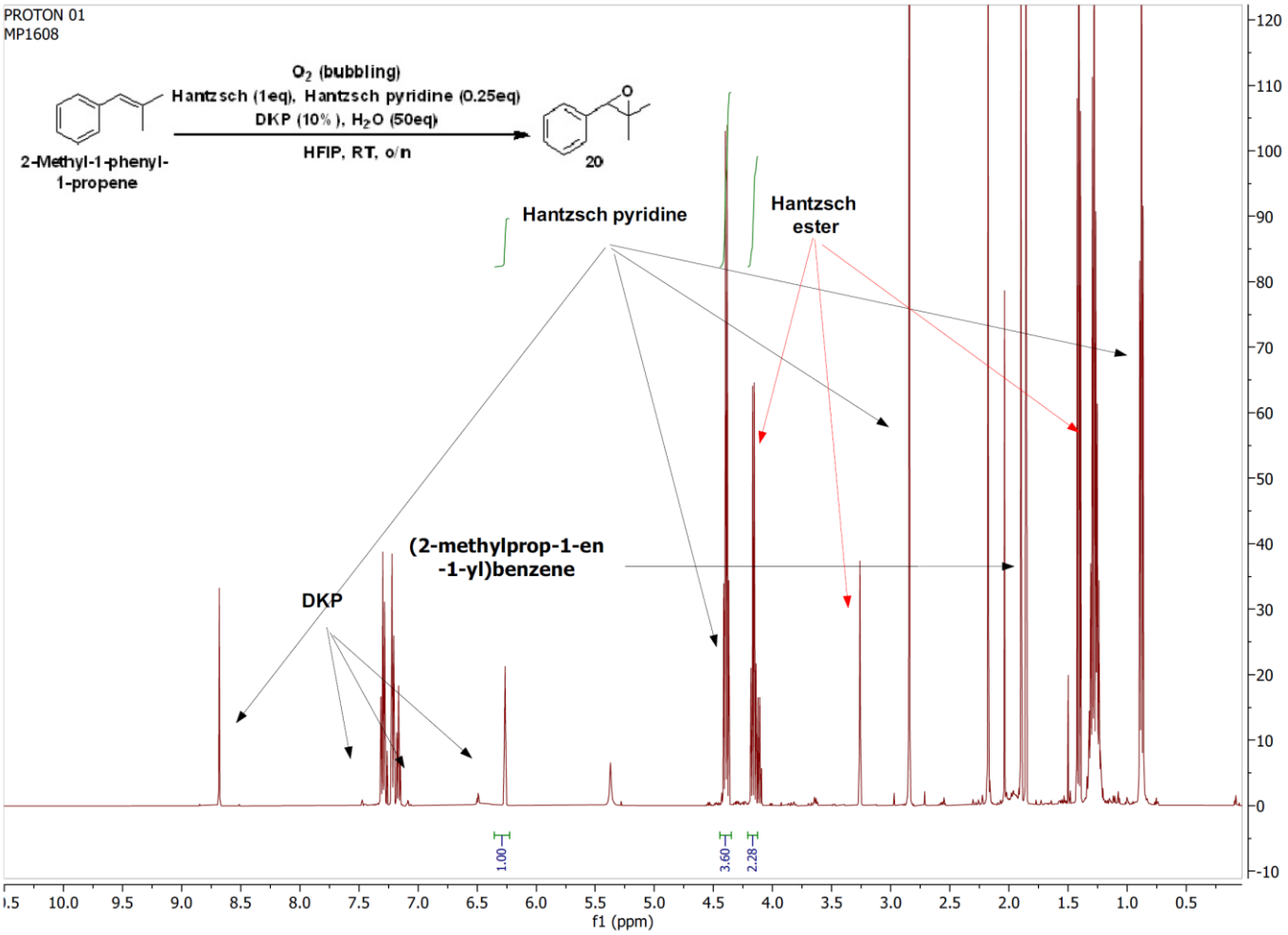

PROTON_01
MP1591
6.27
3.90
O_2 (bubbling)
Hantzsch (1eq), Hantzsch pyridine (0.5eq)
H_2O (10eq)
HFIP, RT, o/n
2-Methyl-1-phenyl-1-propene
20
Hantzsch pyridine
(2-methylprop-1-en-1-yl)benzene
20
1.00
6.36
0.13
f1 (ppm)

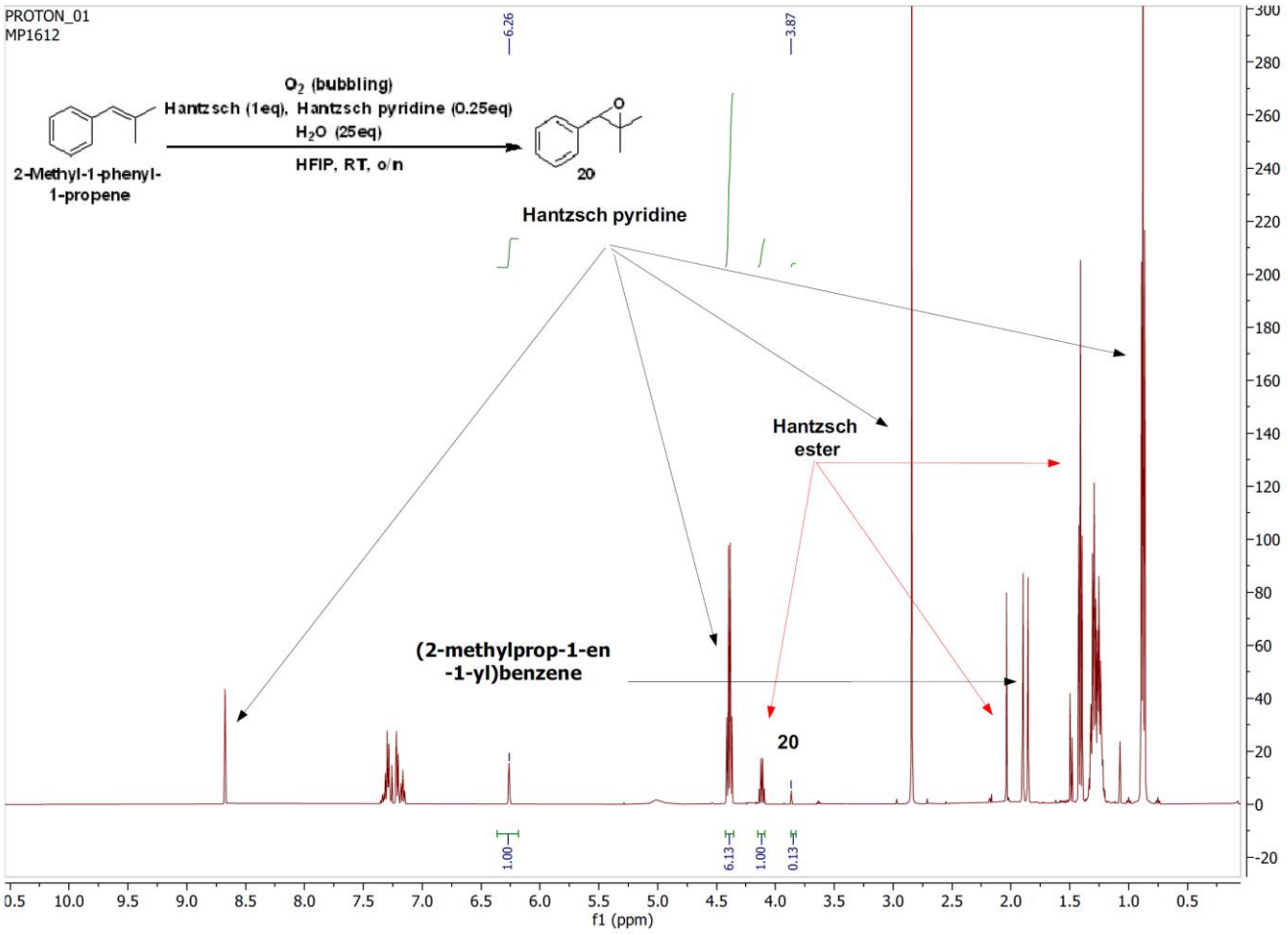

PROTON_01
MP1592
6.26
3.87
O_2 (bubbling)
Hantzsch (1eq), Hantzsch pyridine (0.5eq)
DKP (10%), H_2O (10eq)
HFIP, RT, o/n
2-Methyl-1-phenyl-1-propene
20
Hantzsch pyridine
(2-methylprop-1-en-1-yl)benzene
DKP
20
1.00
6.91
0.28
f1 (ppm)

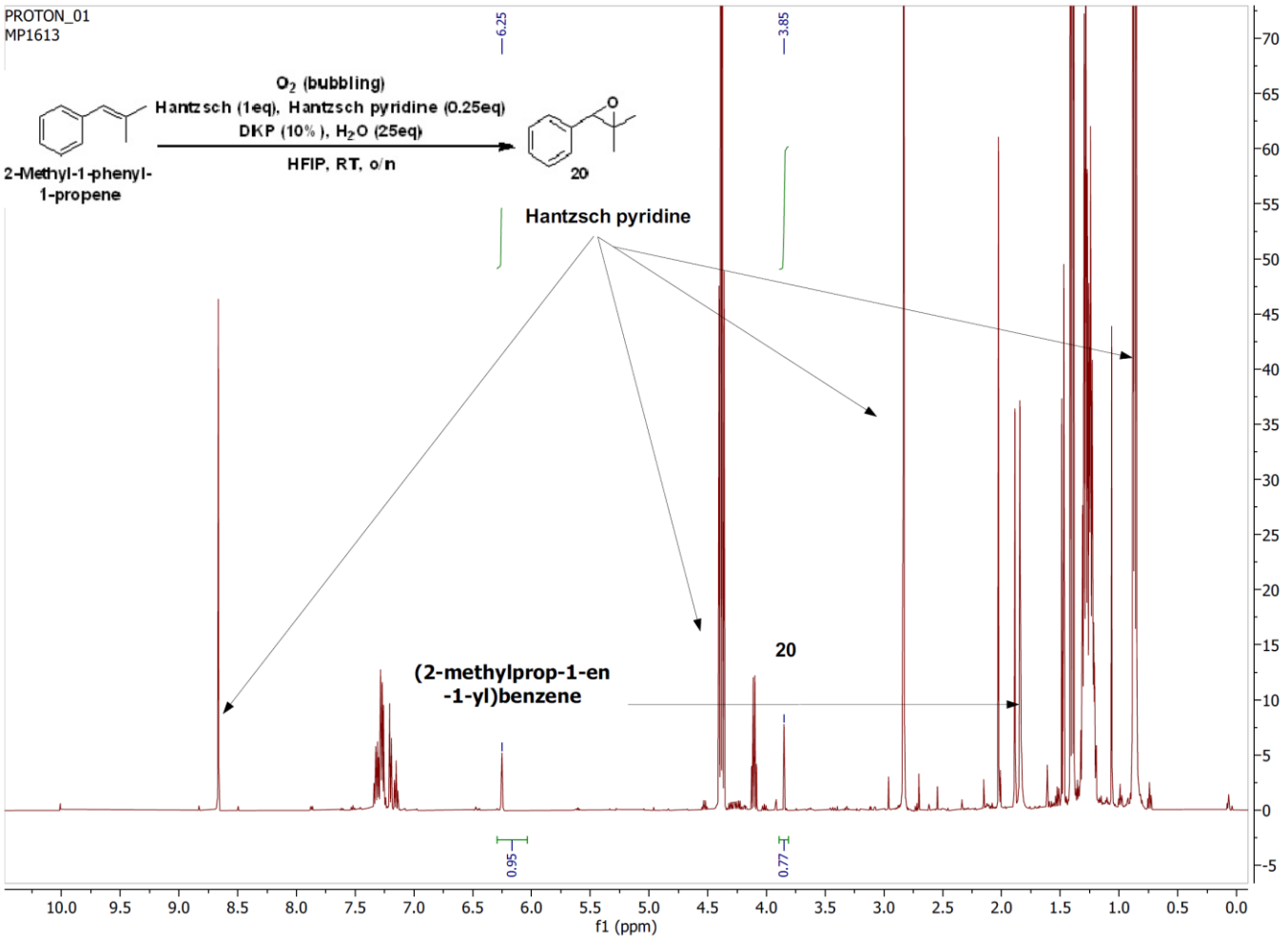

PROTON_01
MP1593
6.26
O2 (bubbling)
Hantzsch (1eq), Hantzsch pyridine (0.5eq)
H2O (50eq)
HFIP, RT, o/n
2-Methyl-1-phenyl-1-propene
20
Hantzsch pyridine
Hantzsch ester
(2-methylprop-1-en-1-yl)benzene
1.00
5.66
3.85
f1 (ppm)

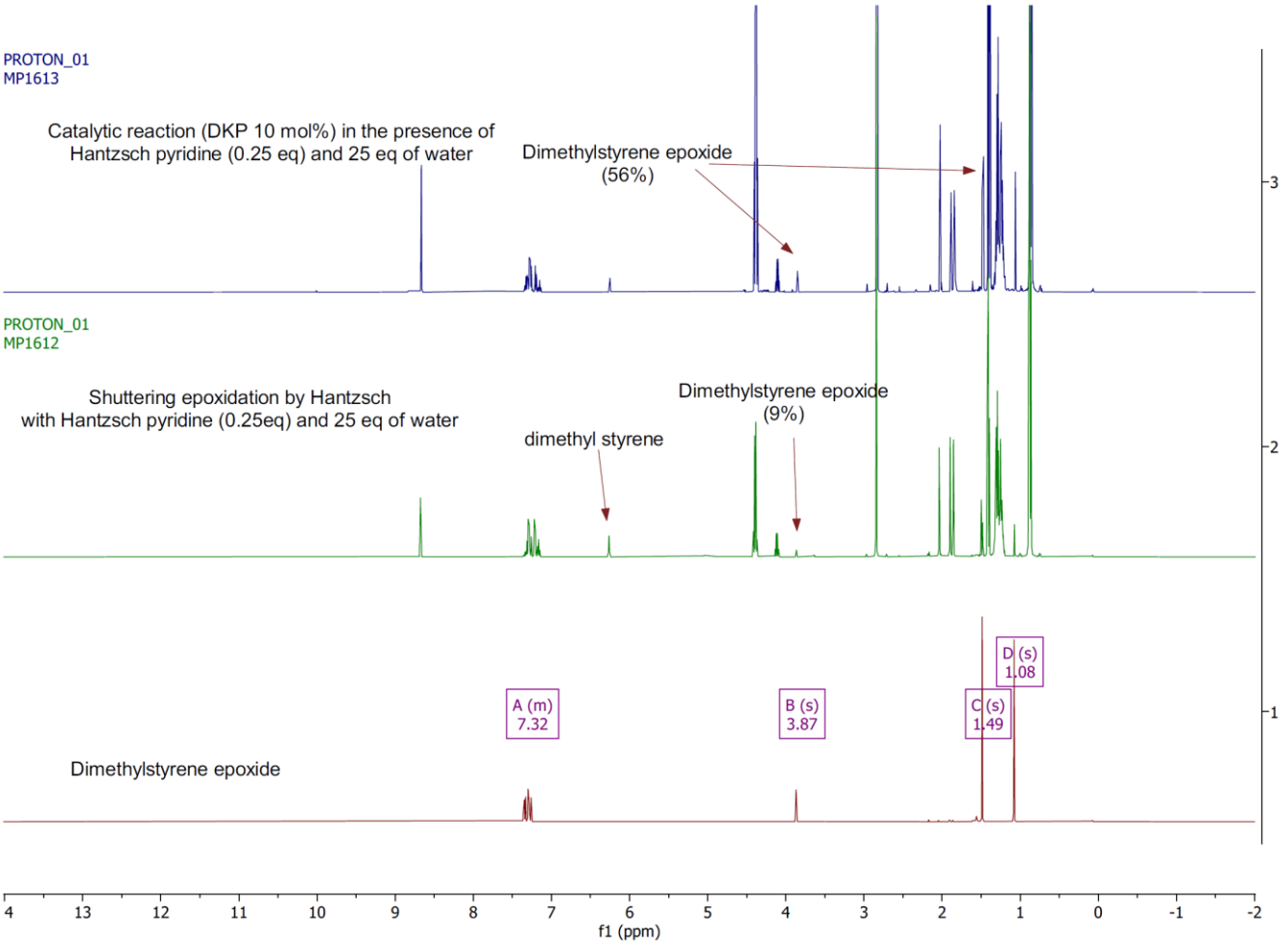

PROTON_01
MP1598
6.25
3.86
O2 (bubbling)
Hantzsch (1eq), Hantzsch pyridine (0.5eq)
DKP (10%), H2O (50eq)
HFIP, RT, o/n
2-Methyl-1-phenyl-1-propene
20
Hantzsch pyridine
(2-methylprop-1-en-1-yl)benzene
DKP
20
0.14
1.00
11.25
0.16
f1 (ppm)


PROTON_01
MP1604
6.27
O2 (bubbling)
Hantzsch (1eq), Hantzsch pyridine (0.25eq)
H2O (50eq)
HFIP, RT, o/n
2-Methyl-1-phenyl-1-propene
20
Hantzsch pyridine
Hantzsch ester
(2-methylprop-1-en-1-yl)benzene
1.00
1.64
3.17
f1 (ppm)


PROTON 01
MP1608
O2 (bubbling)
Hantzsch (1eq), Hantzsch pyridine (0.25eq)
DKP (10%), H2O (50eq)
HFIP, RT, o/n
2-Methyl-1-phenyl-1-propene
20
Hantzsch pyridine
Hantzsch ester
(2-methylprop-1-en-1-yl)benzene
DKP
1.00
3.60
2.28
f1 (ppm)


PROTON_01
MP1612
6.26
3.87
O2 (bubbling)
Hantzsch (1eq), Hantzsch pyridine (0.25eq)
H2O (25eq)
HFIP, RT, o/n
2-Methyl-1-phenyl-1-propene
20
Hantzsch pyridine
Hantzsch ester
(2-methylprop-1-en-1-yl)benzene
20
1.00
6.13
1.00
0.13
f1 (ppm)


PROTON_01
MP1613
6.25
3.85
O2 (bubbling)
Hantzsch (1eq), Hantzsch pyridine (0.25eq)
DKP (10%), H2O (25eq)
HFIP, RT, o/n
2-Methyl-1-phenyl-1-propene
20
Hantzsch pyridine
20
(2-methylprop-1-en-1-yl)benzene
0.95
0.77
f1 (ppm)

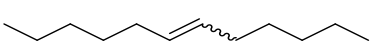


It is worth noting that in case of blank reactions and reaction conditions monitoring in Sections 4, 5, 6, Hantzsch ester (**3**) was used without further purification, unless otherwise noted.

8. Preparation of Alkene Substrates

Isolated epoxides

(*E*)-Dodec-6-ene[4] (as a mixture of *E,Z*-isomers→ 85%:15%) (SI 2)



MW (g/mol): 168.32 **Molecular formula: $C_{12}H_{24}$**

In a typical cross metathesis reaction, to a solution of 1-heptene (0.30 mL, 2.04 mmol, 1.0 equiv.) in dry CH_2Cl_2 (2 mL) placed in a sealed tube, Grubb's catalyst 2nd generation (17 mg, 0.02 mmol, 0.015 equiv.) was added in one portion. The mixture was stirred at 50 °C for 12 hours and after the completion of time, the solvent was removed by evaporation under vacuo and the residue was purified by flash column chromatography on silica gel [Hexane:EtOAc (30:1)] to give the desired alkene **SI 2** as a mixture of *E,Z* isomers

(85%:15%) in 68% yield (231 mg), as a colorless oil. Compound was used as isomeric mixture in epoxidation reaction.

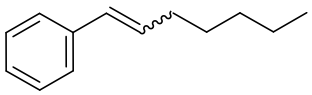
Rf: 0.65 Hexane:EtOAc (20:1), **Yield: 68%**, Colorless liquid

NMR identical to previous reported spectra.[4]

^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ_H 0.88 (t, *J* 7.0 Hz, 6H), 1.26-1.36 (m, 12H), 1.95-1.99 (m, 4H), 1.99-2.04 (m, 0.8H of *Z*), 5.33-5.36 (m, 0.4H of *Z*), 5.37-5.40 (m, 2H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25°C): δ_C 13.95 (*Z*), 14.1, 22.2 (*Z*), 22.6, 29.3, 29.5 (*Z*), 31.4, 31.8 (*Z*), 32.3 (*Z*), 32.6, 129.9 (*Z*), 130.4 ppm

(*E*)-Hept-1-en-1-ylbenzene[5] **(as a mixture of *E,Z*-isomers→ 72%:18%) (SI 3)**



MW (g/mol): 174.29 **Molecular formula: $C_{13}H_{18}$**

In a typical cross metathesis reaction, to a solution of styrene (0.1 mL, 0.87 mmol, 1.0 equiv.) and 1-heptene (0.25 mL, 1.74 mmol, 2.0 equiv.) in dry CH_2Cl_2 (2 mL) placed in a sealed tube, Grubb's catalyst 2nd generation (15 mg, 0.017 mmol, 0.02 equiv.) was added in one portion. The mixture was stirred at 50 °C for 12 hours and after the completion of time, the solvent was removed by evaporation under vacuo and the residue was purified by flash column chromatography on silica gel [Hexane:Et_2O (50:1)] to give the desired alkene **SI 3** as a mixture of *E*,*Z*-isomers (72%:18%) in 68% yield (102 mg), as a colorless oil. Compound was used as isomeric mixture in epoxidation reaction.

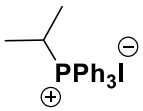
Rf: 0.85, Hexane (100%), **Yield: 68%**, Colorless liquid

NMR identical to previous reported spectra.[5]

^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ_H 0.93-1.02 (m, 3H), 1.38-1.44 (m, 3H), 1.47-1.55 (m, 2H), 1.92 (dd, *J* 6.6, 1.7 Hz, 1H), 2.22-2.28 (m, 2H), 6.24-6.30 (m, 1H), 6.42 (d, *J* 15.7 Hz, 1H), 7.20-7.24 (m, 1H), 7.31-7.39 (m, 4H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25°C): δ_C 13.9 (*Z*), 14.1, 18.5 (*Z*), 22.3 (*Z*), 22.6, 29.1, 31.4, 31.5 (*Z*), 32.7 (*Z*), 33.0, 125.8 (*Z*), 125.9, 126.7, 128.4, 129.67, 129.68 (*Z*), 131.21 (*Z*), 131.23, 137.91 (*Z*), 137.94 ppm

Isopropyltriphenylphosphonium iodide[6] **(SI 4)**



MW (g/mol): 432.29 **Molecular formula: $C_{21}H_{22}IP$**

A solution of 2-iodopropane (3.5 g, 20.4 mmol, 1.0 equiv.) and triphenylphosphine (5.3 g, 20.3 mmol, 0.9 equiv.) in acetonitrile (32 mL) was refluxed for 5 days. The solution was allowed to cool to room temperature. After evaporation of the solvent under vacuo, the residue was filtrated and washed with Et_2O (3 x 20 ml) to afford 7.5 g (yield: **85%**) of **SI 4** as pale yellow powder.

Rf: 0.05, Hexane:AcOEt (4:1)

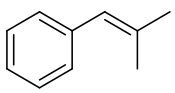
NMR identical to previous reported spectra.[6]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.32 (d, *J* 6.9 Hz, 3H), 1.36 (d, *J* 6.9 Hz, 3H), 4.94-5.02 (m, 1H), 7.69 (td, *J* 7.7, 3.2 Hz, 6H), 7.77 (td, *J* 7.4, 1.7 Hz, 3H), 7.90 (ddd, *J* 11.9, 7.2, 1.7 Hz, 5H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 16.3, 16.4, 21.7, 22.1, 117.0, 117.7, 130.5, 130.6, 133.7, 133.8, 134.8, 134.9

^{15}P (500 MHz, $CDCl_3$, 25°C): δ_P 31.9

(2-Methylprop-1-en-1-yl)benzene[7] **(SI 5)**



MW (g/mol): 132.21 **Molecular formula: $C_{10}H_{12}$**

To a solution of $(CH_3)_2CHP(Ph)_3I$ (6.1 g, 14.1 mmol, 1.5 equiv.) in THF (50 mL), n-BuLi (9.4 mL, 1.5 M in hexanes, 14.1 mmol, 1.5 equiv.) was added dropwise at -78 °C under N_2 atmosphere, until a dark red solution was formed. After stirring for 30 min at -78 °C, the reaction mixture was placed in an ice bath (0 °C) where benzaldehyde (1.0 ml, 9.4 mmol, 1.0 equiv.) was added. The mixture was stirred at room temperature for more 12 h and then quenched with aqueous saturated NH_4Cl (30 mL). The reaction mixture was transferred to a separation funnel, diluted with EtOAc (20 ml) and extracted (3 x 30 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the desired alkene **SI 5** in 92% yield (1.1 g), as a colorless oil.

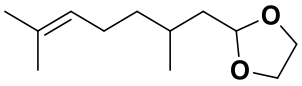
Rf: 0.74, 100% Hexanes

NMR identical to previous reported spectra.[7]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.87 (d, *J* 1.4 Hz, 3H), 1.91 (d, *J* 1.4 Hz, 3H), 6.28 (s, 1H), 7.18 (t, *J* 7.2 Hz, 1H), 7.23 (d, *J* 7.1 Hz, 2H), 7.31 (t, *J* 7.4 Hz, 2H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 19.4, 26.8, 125.1, 125.7, 128.0, 128.7, 135.4, 138.7 ppm

2-(2,6-Dimethylhept-5-en-1-yl)-1,3-dioxolane[8] (SI 6)



MW (g/mol): 198.31 **Molecular formula: $C_{12}H_{22}O_2$**

Triethylorthoformate (2.7 mL, 16.5 mol, 3.0 equiv.) and ethylene glycol (4.6 mL, 82.5 mmol, 15.0 equiv.) were added to a solution of CSA (64 mg, 0.3 mmol, 5 mol%) in dry CH_2Cl_2 (35 ml), under argon atmosphere. Neat (*R*, *S*)-citronellal (1.0 mL, 5.5 mmol, 1.0 equiv.) was added dropwise via syringe over 10 min. The colorless solution was stirred at ambient temperature for 12 hours before the reaction was quenched with aqueous saturated $NaHCO_3$ (2 x 30 mL). The aqueous phase was separated and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine (2 × 80 mL), dried over $MgSO_4$ and concentrated to a colorless liquid in vacuo. This crude reaction mixture was purified by flash chromatography on silica gel to give the desired alkene **SI 6** in 91% yield (1.0 g), as a colorless oil as a racemic mixture.

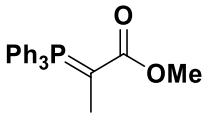
Rf: 0.30, Hexanes:CH_2Cl_2 (2:1)

NMR identical to previous reported spectra.[8]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.95 (d, *J* 6.5 Hz, 3H), 1.18-1.25 (m, 2H), 1.34-1.38 (m, 2H), 1.49 (td, *J* 10.1, 4.9 Hz, 1H), 1.59 (s, 3H), 1.68 (s, 3H), 1.98 (dq, *J* 15.4, 7.4 Hz, 2H), 3.84 (m, 2H), 3.96 (m, 2H), 4.89 (t, *J* 5.0 Hz, 1H), 5.09 (dt, *J* 8.5, 7.0, 1.4 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 17.6, 19.7, 25.3, 25.7, 29.1, 37.4, 40.9, 64.6, 64.7, 103.8, 124.6, 131.2 ppm

Methyl 2-(triphenyl-λ^5-phosphanylidene)propanoate[9] (SI 7)

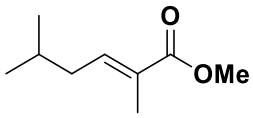


MW (g/mol): 348.38 **Molecular formula: $C_{22}H_{21}O_2P$**

To a solution of triphenylphosphine (2.0 g, 7.6 mmol, 1.0 equiv.) in 15 mL EtOAc, was added methyl-2-bromopropionate (1.4 g, 8.3 mmol, 1.1 equiv.), and the mixture was refluxed for 72 hours. The resulting precipitate was collected by filtration and redissolved in a minimal amount of CH_2Cl_2. With stirring, fresh

EtOAc (5 mL) was added dropwise using a funnel to reprecipitate the product. The precipitate was collected by filtration and washed with 10 mL fresh EtOAc. The precipitate was then dissolved in 15 mL CH_2Cl_2 and transferred to a separatory funnel. Aqueous KOH (850 mg in 30 mL water) was added, and the separatory funnel was shaken vigorously to ensure complete mixing. During this step, the organic layer developed a bright yellow color, while the aqueous layer became cloudy white. The organic layer was collected, dried with $MgSO_4$, filtered, and evaporated to give the desired Wittig reagent (**SI 7**) as a yellow solid (2.1 g, 81%), which could be stored in the dark at room temperature in a closed container.

Methyl (*E*)-2,5-dimethylhex-2-enoate[10] (SI 8)



MW (g/mol): 156.22 **Molecular formula: $C_9H_{16}O_2$**

To a refluxing solution of the Wittig reagent **SI 7** (526 mg, 1.5 mmol, 1.3 equiv.) in 5 mL CH_2Cl_2, isovarealdehyde (100 mg, 1.2 mmol, 1.0 equiv.) was added dropwise. The reaction was allowed to reflux for 24 hours, and when TLC indicated that aldehyde was fully consumed, the solvent was evaporated and the reaction mixture was loaded onto a silica gel column. Elution with Hexane:EtOAc (20:1) gave the desired product **SI 8** (160 mg, 1.0 mmol, 86%).

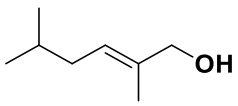
Rf: 0.68, Hexane: EtOAc (5:1)

NMR identical to previous reported spectra.[10]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.01 (d, *J* 6.7 Hz, 6H), 1.83 (d, *J* 1.5 Hz, 3H), 2.63 (dp, *J* 9.7, 6.7 Hz, 1H), 3.72 (s, 3H), 6.57 (dd, *J* 9.8, 1.5 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 12.3, 21.9, 27.9, 51.7, 125.3, 149.1, 169.0 ppm

(*E*)-2,5-Dimethylhex-2-en-1-ol[11] (SI 9)



MW (g/mol): 128.22 **Molecular formula: $C_8H_{16}O$**

In a flame-dried flask, ester **SI 8** (100 mg, 0.64 mmol, 1.0 equiv.) was dissolved in 6 mL anhydrous CH_2Cl_2. Commercially available DIBAL-H solution (1.6 mmol, 1.0 M in hexane, 2.5 equiv.) was added dropwise using a syringe at -78 °C via a period of 45 min, and the reaction was allowed to stir for 30 min at 0 °C and more 30 min at room temperature. When all the starting material had reacted, the reaction mixture was cooled

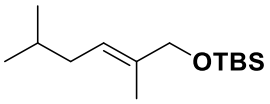
to 0 °C, and saturated aqueous tartaric acid K^+, Na^+ (10 ml) was added dropwise using a funnel. Then, the reaction mixture was diluted with CH_2Cl_2 (3 x 12 ml) and the organic layer was collected, dried over $MgSO_4$, filtered, and concentrated in vacuo to give the desired product (**SI 9**, 76 mg, 0.59 mmol, **92%**). The crude product was used in the next step without further purification.

Rf: 0.36, Hexane:EtOAc (5:1)

NMR identical to previous reported spectra.[11]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.88 (d, *J* 6.8 Hz, 6H), 1.59-1.64 (ddd, *J* 13.4, 7.4, 2.9 Hz, 1H), 1.65 (s, 3H), 1.91 (t, *J* 7.1 Hz, 2H), 4.00 (s, 2H), 5.42 (t, *J* 7.0 Hz, 1H) ppm

(*E*)-*tert*-Butyl((2,5-dimethylhex-2-en-1-yl)oxy)dimethylsilane (SI 10)



MW (g/mol): 242.28 **Molecular formula: $C_{14}H_{30}OSi$**

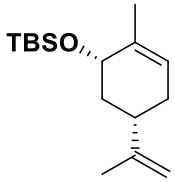
In a flame-dried flask was added **SI 9** (50 mg, 0.39 mmol, 1.0 equiv.) in dry CH_2Cl_2 (3 ml). Then imidazole (50 mg, 0.74 mmol, 1.9 equiv.) and *tert*-butyldimethylsillyl chloride (65 mg, 0.43 mmol, 1.1 equiv.) were added. The reaction was stirred at room temperature for 18 h under argon atmosphere. The reaction was quenched with water (2 ml), extracted with CH_2Cl_2 (2 x 5 mL) and the organic layers were combined, washed with brine (5 mL) and dried over $MgSO_4$. After filtration, the crude reaction mixture was concentrated in vacuum under reduced pressure to provide an oily mixture which was purified by flash chromatography on silica gel to afford 0.36 mmol of **SI 10**, in **93%** yield, as a colorless oil.

Rf: 0.85, Hexane:EtOAc (4:1)

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.02 (s, 6H), 0.87 (s, 9H), 0.89 (d, *J* 6.7 Hz, 3H), 1.59 (s, 3H), 1.60-1.64 (m, 1H), 1.89-1.93 (m, 2H), 4.03 (s, 2H), 5.41 (tq, *J* 7.3, 1.4 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C -5.3, -2.9, 13.5, 18.1, 22.4, 25.7, 26.0, 28.8, 36.7, 68.8, 123.6, 134.8 ppm

tert-**Butyldimethyl(((1*S*,5*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)oxy)silane**[12] **(SI 11)**



MW (g/mol): 266.50 **Molecular formula: $C_{16}H_{30}OSi$**

A solution of (*S,S*)-carveol (120 mg, 0.79 mmol, 1.0 equiv.) and imidazole (107 mg, 1.58 mmol, 2.0 equiv.) in anhydrous CH_2Cl_2 (4 mL) was stirred for 10 min. Then, *tert*-butyldimethylsilyl chloride (179 mg, 1.19 mmol, 1.5 equiv.) was added and the mixture was stirred overnight at room temperature. After the completion of time, the reaction mixture quenched with H_2O (5 mL), and then extracted with CH_2Cl_2 (3 × 5 mL). The organic phases were combined, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give silyl ether **SI 11** (206 mg, 98%) as a colorless oil.

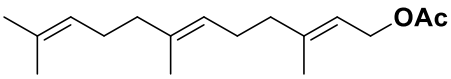
Rf: 0.79, Hexane:EtOAc (4:1)

NMR identical to previous reported spectra.[12]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.09 (d, *J* 3.8 Hz,6H), 0.91 (s, 9H), 1.52 (td, *J* 12.6, 9.9 Hz, 1H), 1.69 (s, 3H), 1.72 (s, 3H), 1.94 (dddd, *J* 16.9, 11.1, 2.9 Hz, 1H), 1.99-2.05 (m, 2H), 2.22-2.28 (m, 1H), 4.25 (d, *J* 8.1 Hz, 1H), 4.72 (s, 2H), 5.46 (s, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C -4.9, -4.1, 18.2, 19.7, 20.3, 25.9, 31.1, 38.5, 40.9, 71.6, 108.9, 123.3, 137.1, 149.2 ppm

(2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl acetate[13] (SI 12)



MW (g/mol): 264.41 **Molecular formula: $C_{17}H_{28}O_2$**

To a solution of (*trans*,*trans*)-farnesol (100 mg, 0.45 mmol, 1.0 equiv.), Et_3N (94 µL, 0.67 mmol, 1.5 equiv.) and a catalytic amount of DMAP in CH_2Cl_2 (3 mL), freshly distilled Ac_2O (68 µL, 0.72 mmol, 1.6 equiv.) was added dropwise at 0 °C with vigorous stirring. Stirring was continued at room temperature for 30 min until the reaction was complete. The resulting mixture was diluted with H_2O (3 mL) and extracted with Et_2O (5 mL × 3). The combined organic layer was washed with 10% HCl aqueous solution, H_2O, and brine and then dried over $MgSO_4$. Evaporation of the solvent followed by purification on silica gel and elution with CH_2Cl_2 (100%) afforded farnesol acetyl acetate **SI 12** (116 mg, 98%) as a colorless oil.

Rf: 0.87, Hexane:EtOAc (3:1)

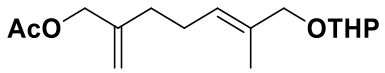
NMR identical to previous reported spectra.[13]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.60 (s, 6H), 1.68 (s, 3H), 1.70 (s, 3H), 1.97 (dd, *J* 9.0, 6.0 Hz, 2H), 2.04-2.14 (m, 5H), 2.05 (s, 3H), 4.59 (d, *J* 7.1 Hz, 2H), 5.09 (dtq, *J* 5.8, 4.6, 1.4 Hz, 2H), 5.34 (ddq, *J* 7.1, 5.7, 1.3 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 16.0, 16.4, 17.6, 21.0, 25.6, 26.1, 26.7, 39.5, 39.6, 61.3, 118.2, 123.6, 124.3, 131.2, 135.4, 142.2, 171.1 ppm

Additional alkenes were provided from collaborators of Laboratory of Organic Chemistry at Aristotle University of Thessaloniki. Spectra were provided by them.

(*E*)-6-Methyl-2-methylene-7-((tetrahydro-2*H*-pyran-2-yl)oxy)hept-5-en-1-yl acetate (SI 13)

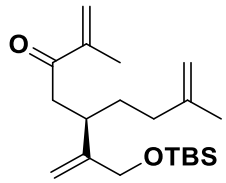


MW (g/mol): 282.38 **Molecular formula: $C_{16}H_{26}O_4$**

Rf: 0.39, Hexane:EtOAc (4:1), Colorless liquid

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.52-1.62 (m, 5H), 1.67 (s, 3H), 1.68-1.72 (m, 1H), 1.81-1.87 (m, 1H), 2.09 (s, 3H), 2.12-2.14 (m, 2H), 2.22 (q, *J* 7.2 Hz, 2H), 3.48-3.52 (m, 1H), 3.85 (d, *J* 11.7 Hz, 1H), 4.10 (d, *J* 11.8 Hz, 1H), 4.52 (s, 2H), 4.60 (t *J* 3.7 Hz, 1H), 4.95 (t, *J* 1.2 Hz, 1H), 5.04 (m, 1H), 5.42-5.44 (m, 1H) ppm

(*R*)-5-(3-((*tert*-Butyldimethylsilyl)oxy)prop-1-en-2-yl)-2,8-dimethylnona-1,8-dien-3-one (SI 14)



MW (g/mol): 336.59 **Molecular formula: $C_{20}H_{36}O_2Si$**

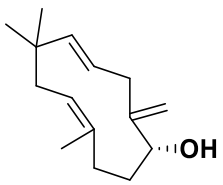
Rf: 0.64, Hexane:EtOAc (50:1), Colorless liquid

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.07 (s, 9H), 0.91 (s, 6H), 1.47-1.53 (m, 4H), 1.86 (s, 3H), 1.96 (q, J 8.0 Hz, 2H), 2.56 (p, J 8.0, 7.4 Hz, 1H), 2.75 (m, 1H), 2.90 (dd, J 16.3, 6.9 Hz, 1H), 4.12 (s, 2H), 4.88 (s, 1H), 5.14 (s, 1H), 5.74 (s, 1H), 5.93 (s, H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C -5.43, -5.41, 17.7, 18.4, 23.3, 25.9, 29.2, 32.3, 38.2, 43.0, 65.4, 108.6, 119.0, 124.4, 135.8, 144.9, 151.1, 201.1 ppm

HRMS (ESI, m/z): calcd. for $C_{20}H_{36}O_2SiK^+$ ($[M+K]^+$): 375.6797, found: 375.6755.

(*R*,4*E*,8*E*)-6,6,9-Trimethyl-2-methylenecycloundeca-4,8-dien-1-ol (SI 15)

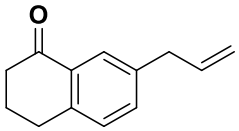


MW (g/mol): 220.36 **Molecular formula: $C_{15}H_{24}O$**

Rf: 0.46, Hexane:EtOAc (4:1), Colorless liquid

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ_H 1.07 (d, *J* 8.4 Hz, 6H), 1.61 (s, 3H), 1.69-1.76 (m, 3H), 1.88-1.98 (m, 2H), 2.06-2.09 (td, *J* 5.4, 4.7, 2.2 Hz, 2H), 2.82 (tt, *J* 21.2, 9.4 Hz, 2H), 3.92 (brs, 1H), 4.92 (d, *J* 2.5 Hz, 1H), 4.98-5.06 (m, 2H), 5.04 (s, 1H), 5.13 (d, *J* 15.3 Hz, 1H) ppm

tert-**Butyldimethyl(((2*R*,4*S*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptan-2-yl)oxy)silane (SI 16)**



MW (g/mol): 186.25 **Molecular formula: $C_{13}H_{14}O$**

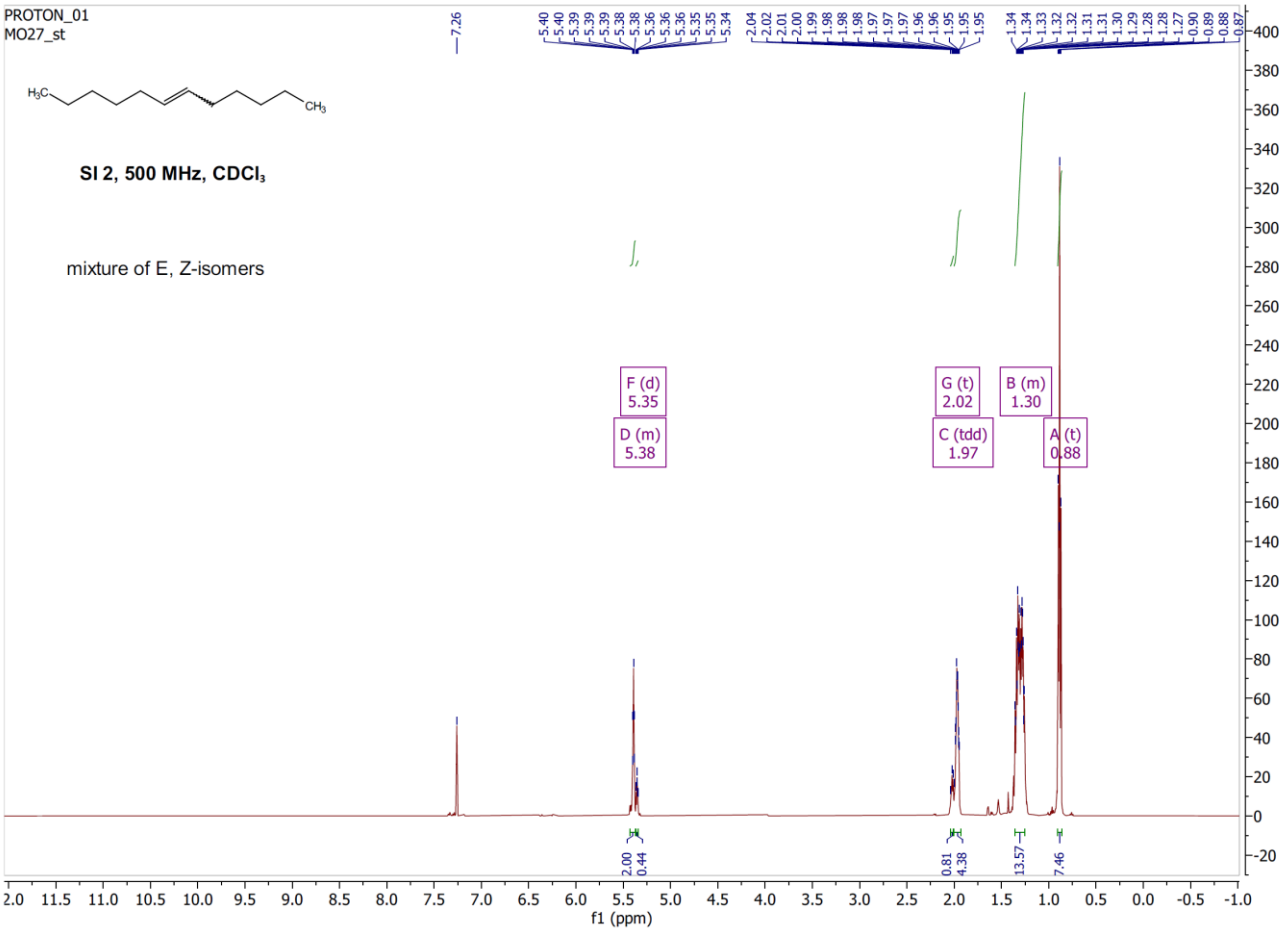
Rf: 0.46, Hexane:EtOAc (4:1), Yellow oil

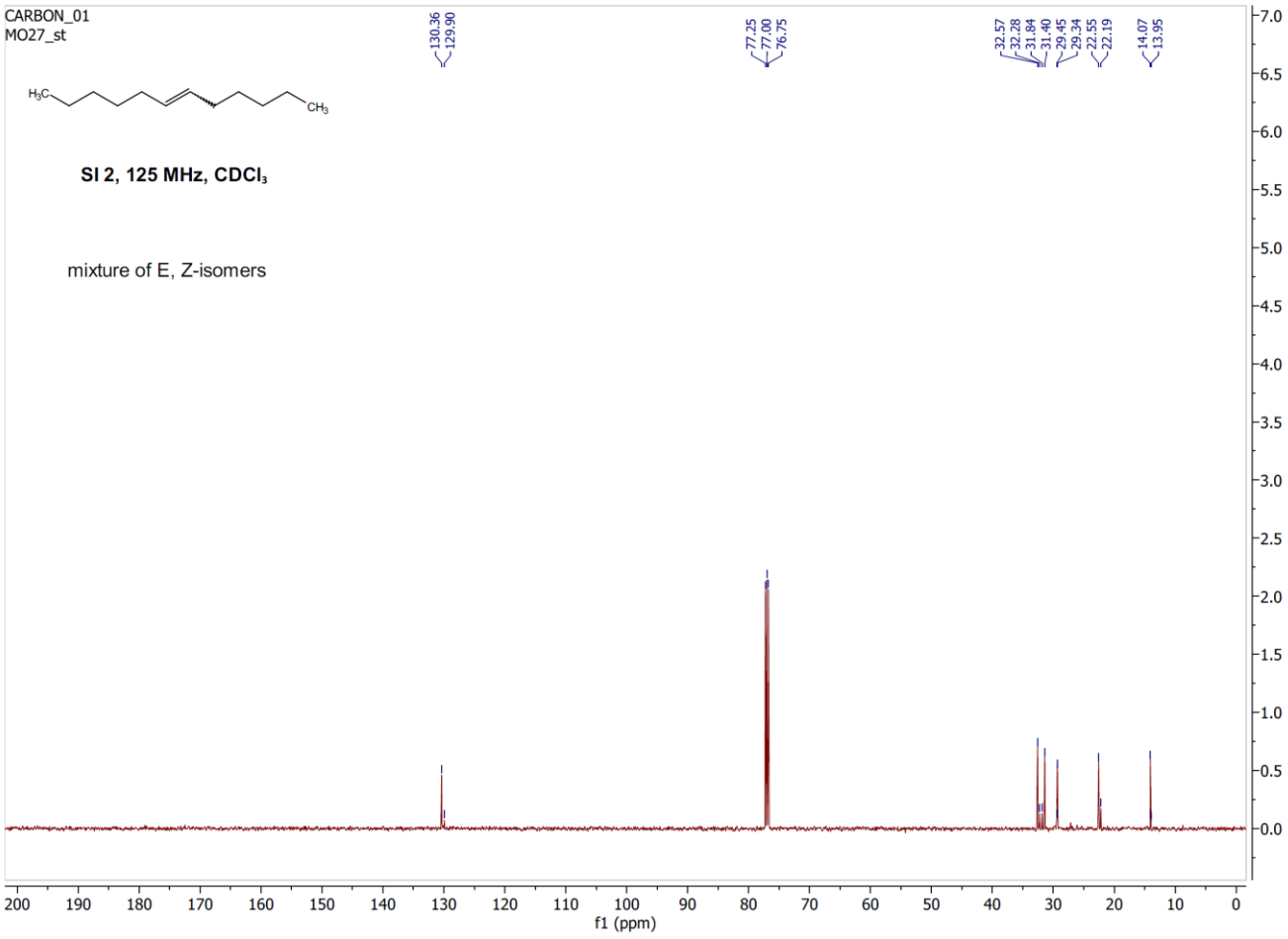
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ_H 2.03 (p, *J* 6.4 Hz, 2H), 2.55 (t, *J* 6.6 Hz, 2H), 2.84 (t, *J* 6.1 Hz, 2H), 3.30 (d, *J* 6.7 Hz, 2H), 4.95-5.01 (m, 2H), 5.85 (ddt, *J* 16.8, 10.2, 6.8 Hz, 1H), 7.10 (d, *J* 7.8 Hz, 1H), 7.22 (d, *J* 7.8 Hz, 1H), 7.77 (s, 1H) ppm

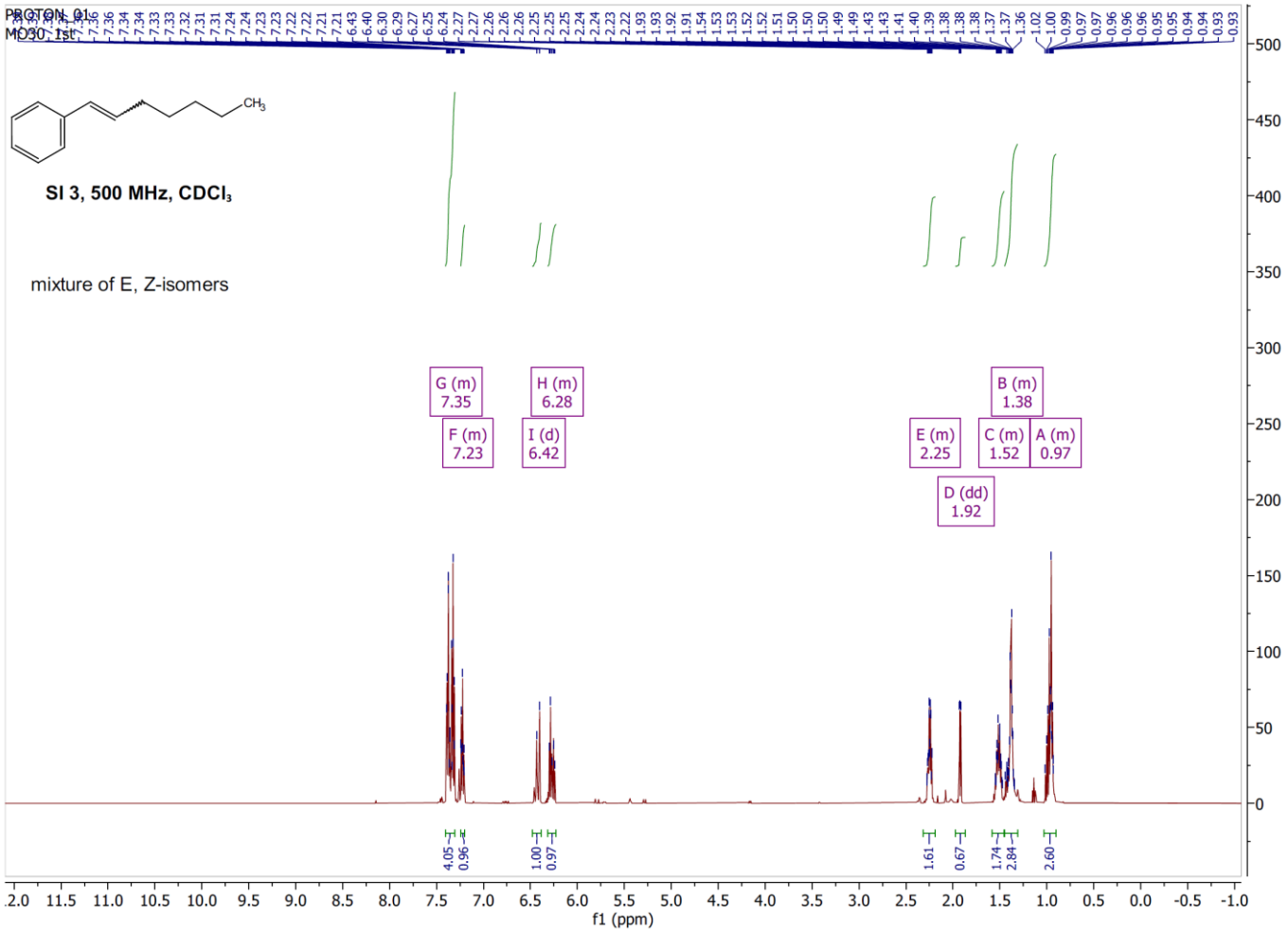
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ_C 23.3, 29.3, 39.1, 39.6, 116.2, 126.8, 128.9, 132.4, 133.8, 136.8, 138.5, 142.3, 198.6 ppm

HRMS (ESI, m/z): calcd. for $C_{13}H_{15}O^+$ $[M]^+$: 187.1117, found: 187.1127.

Spectra of prepared or provided alkenes






PROTON_01
MO30_1st
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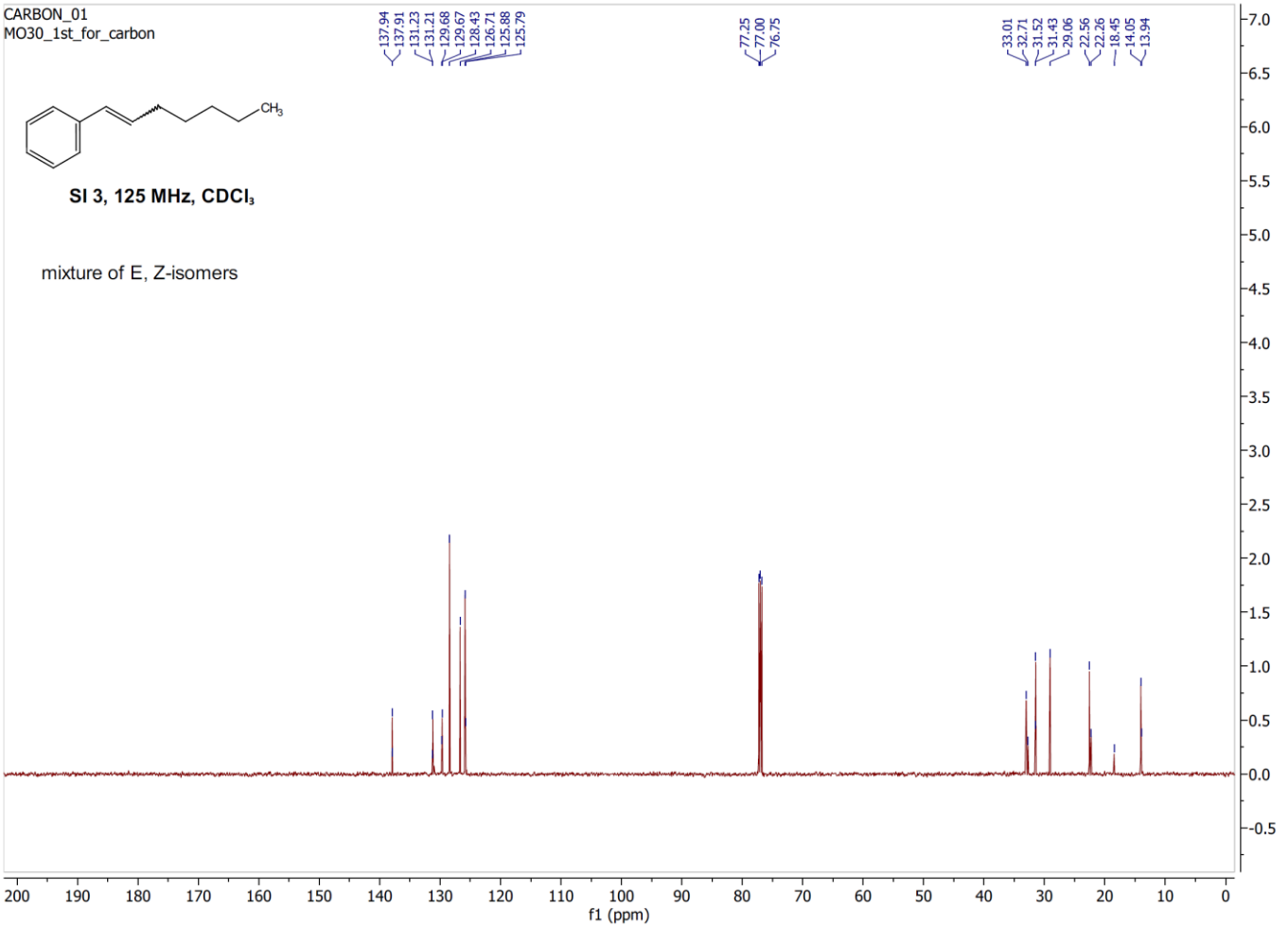
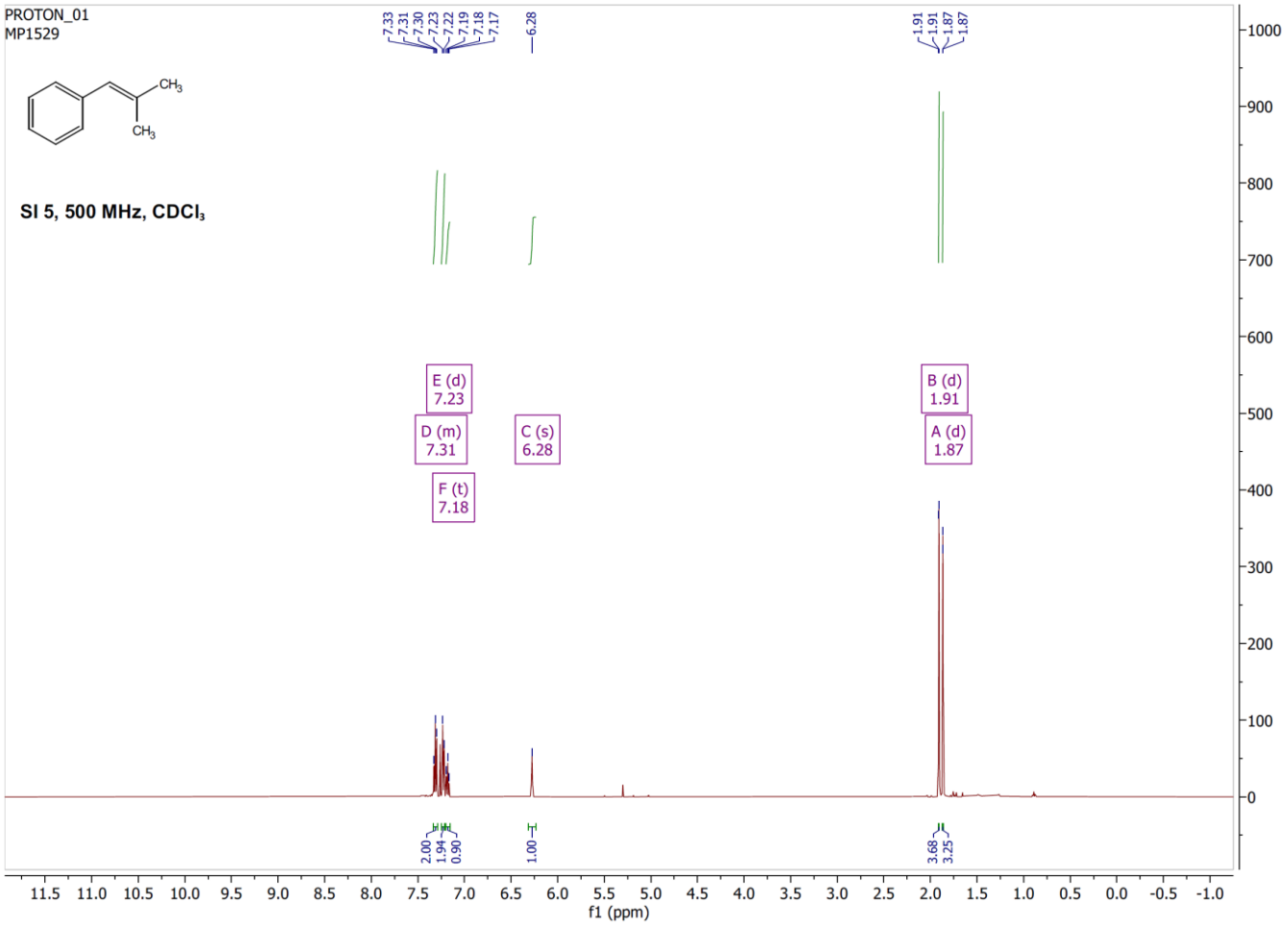
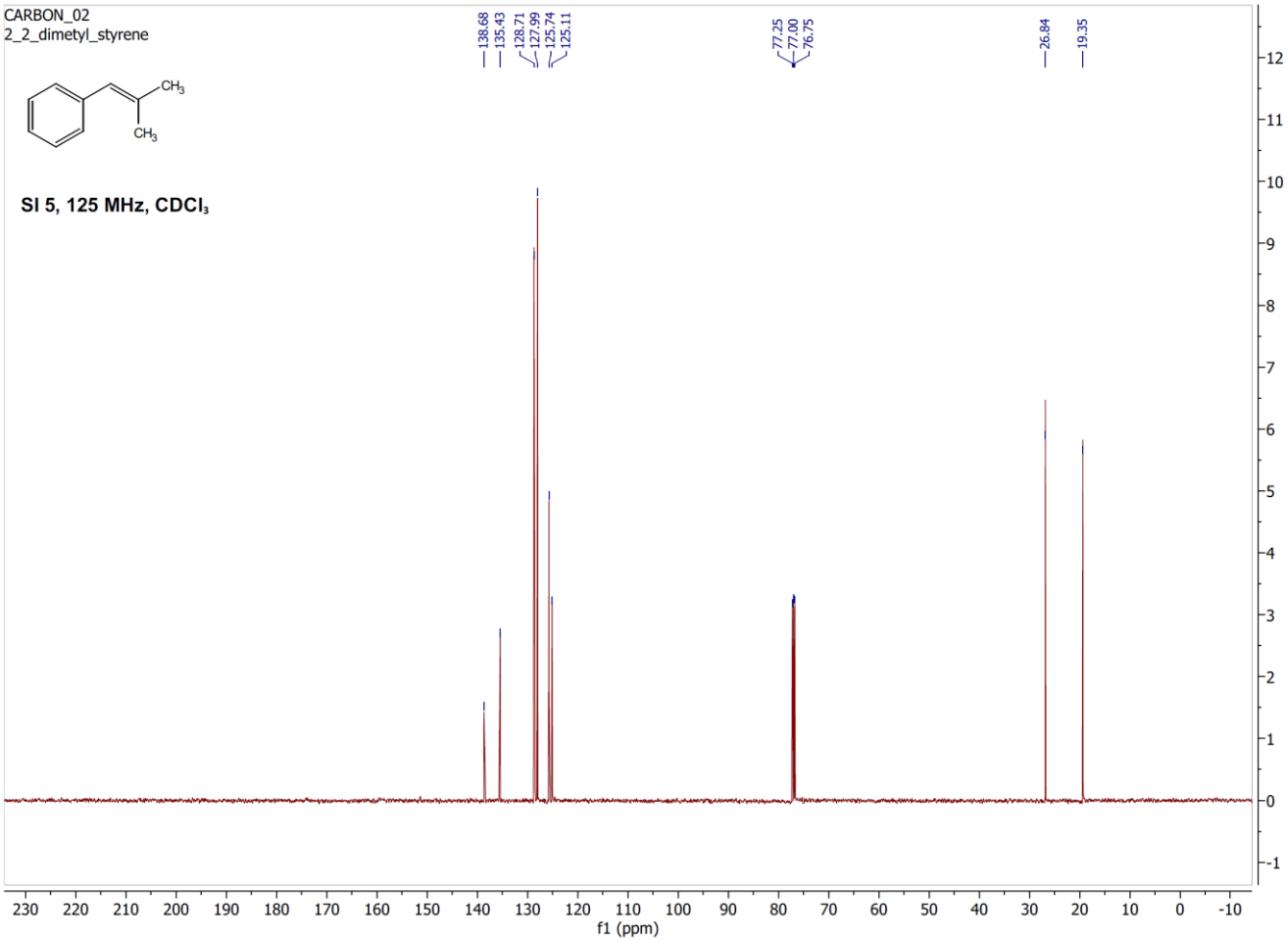
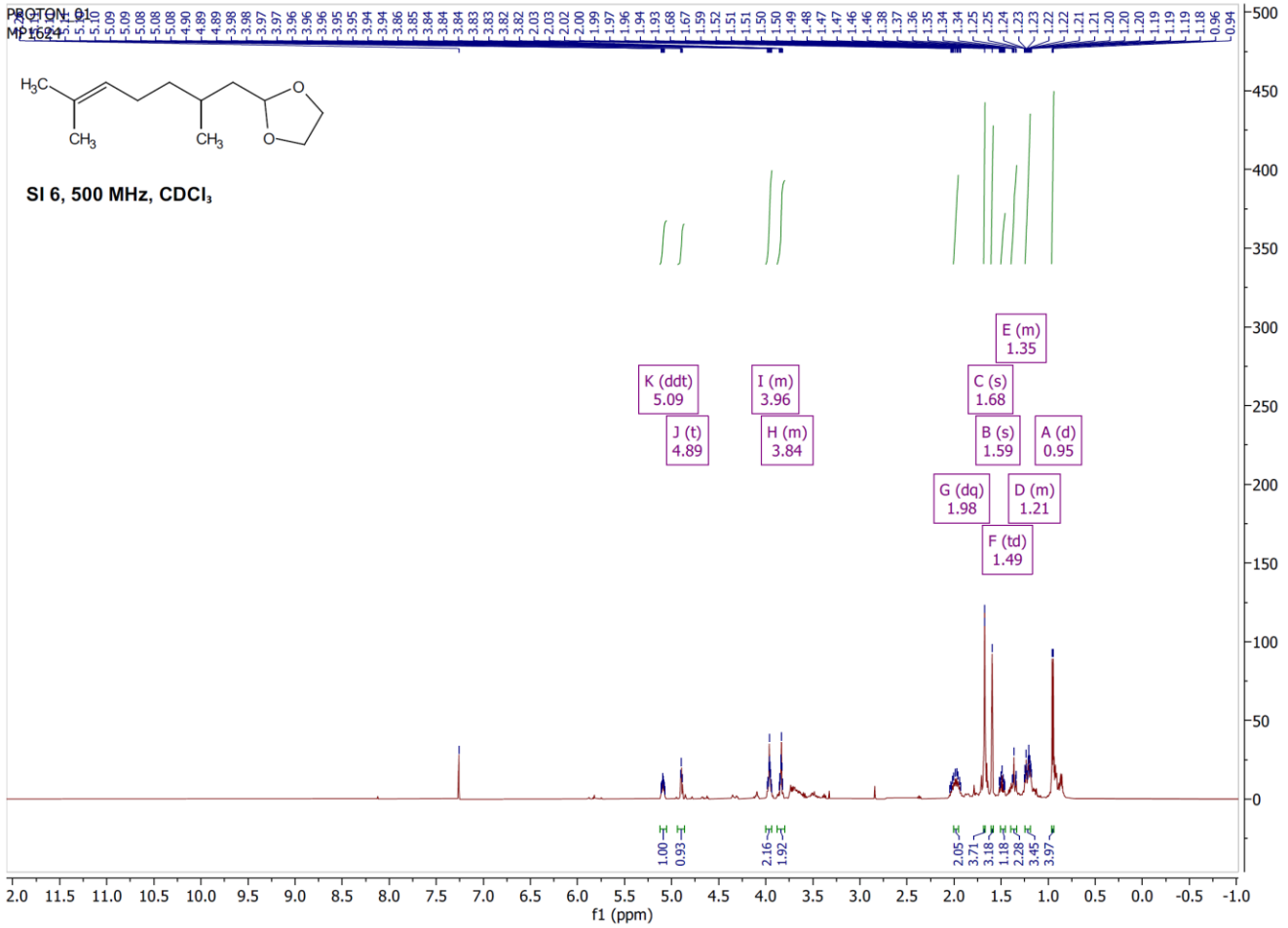
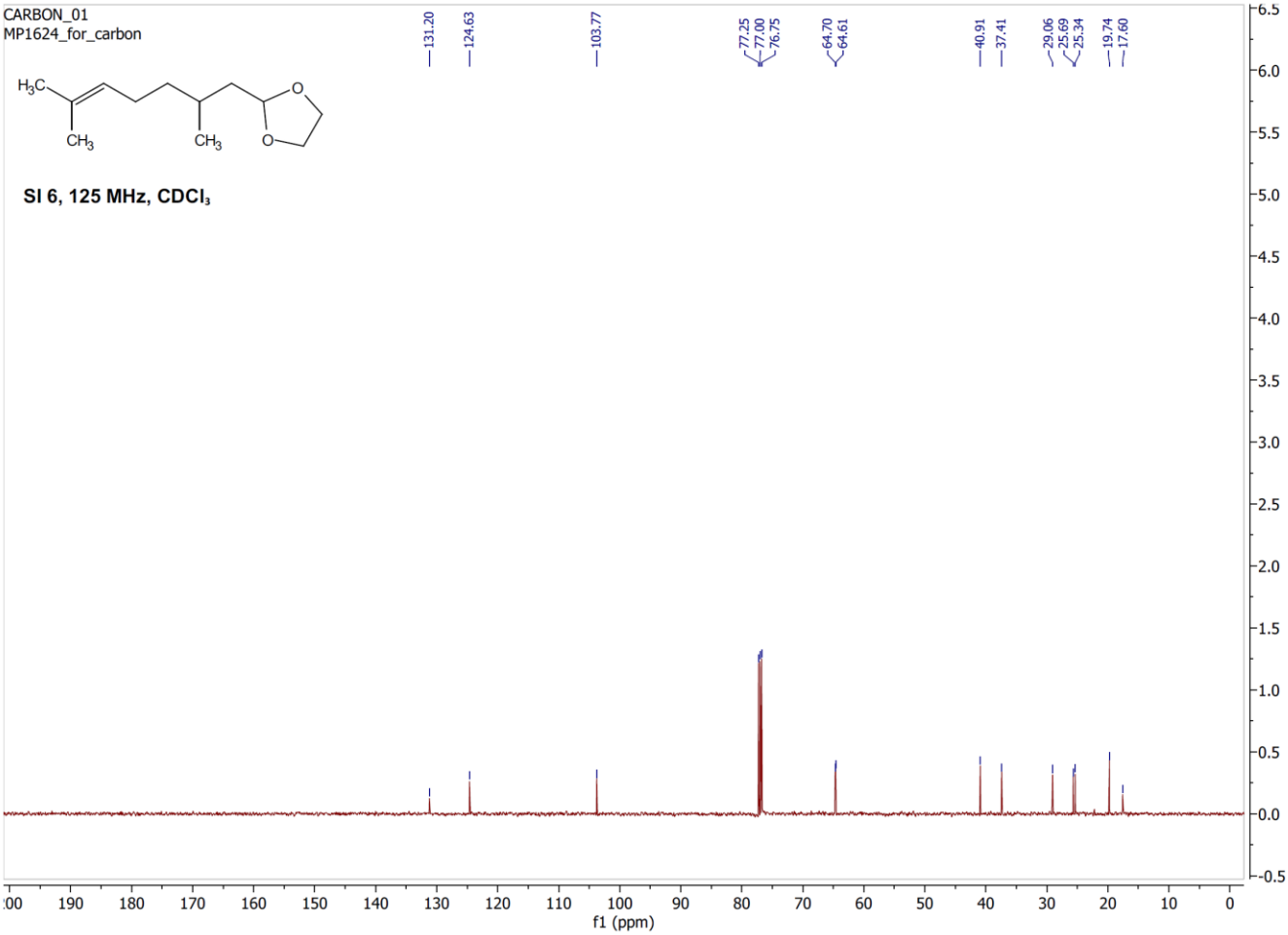
SI 3, 500 MHz, CDCl3
mixture of E, Z-isomers
G (m) 7.35
F (m) 7.23
H (m) 6.28
I (d) 6.42
B (m) 1.38
E (m) 2.25
C (m) 1.52
A (m) 0.97
D (dd) 1.92
4.05
0.96
1.00
0.97
1.61
0.67
1.74
2.84
2.60
f1 (ppm)

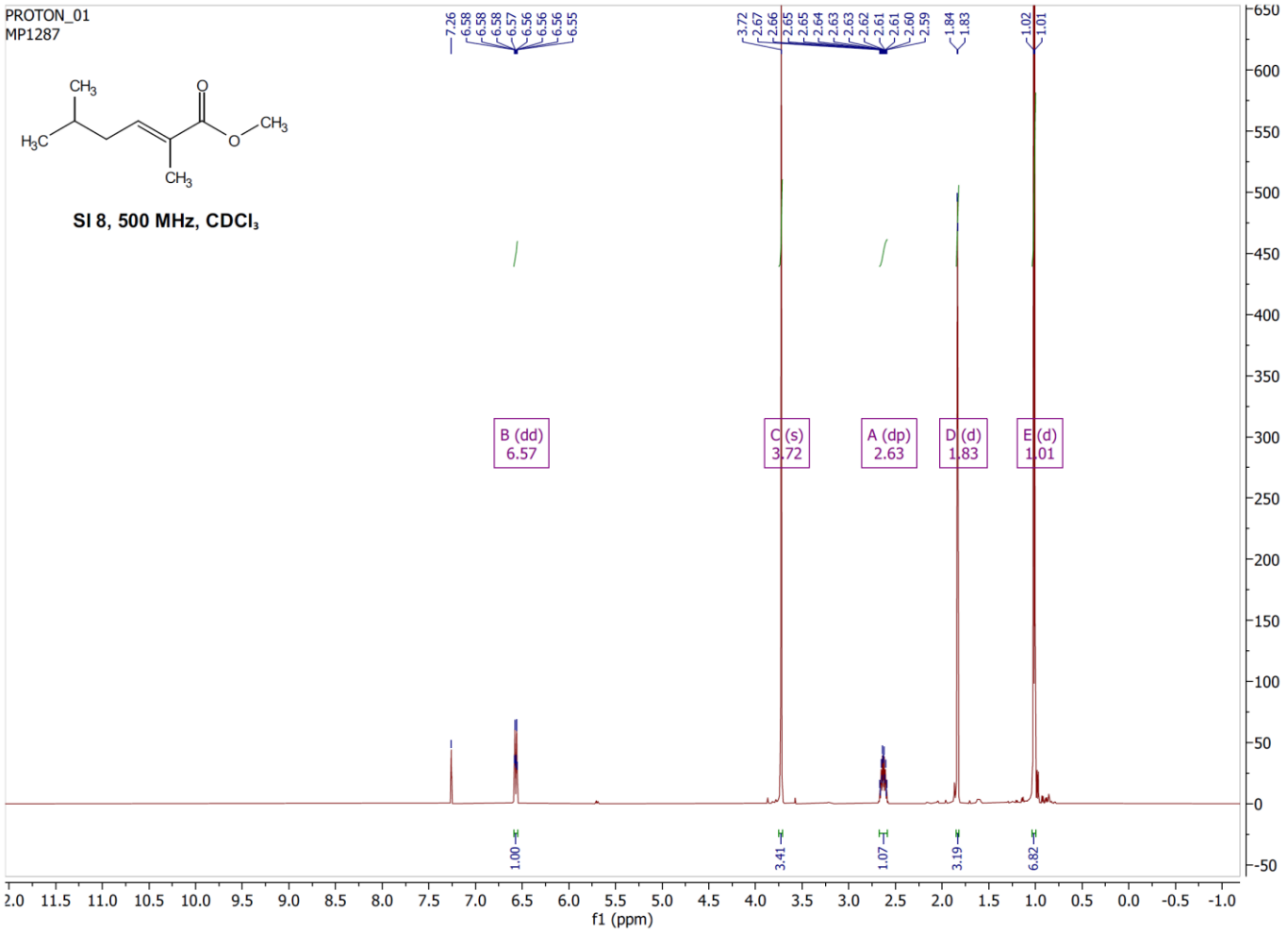

CARBON_01
MO30_1st_for_carbon
137.94
137.91
131.23
131.21
129.68
129.67
128.43
126.71
125.88
125.79
77.25
77.00
76.75
33.01
32.71
31.52
31.43
29.06
22.56
22.26
18.45
14.05
13.94
CH3
SI 3, 125 MHz, CDCl3
mixture of E, Z-isomers
f1 (ppm)

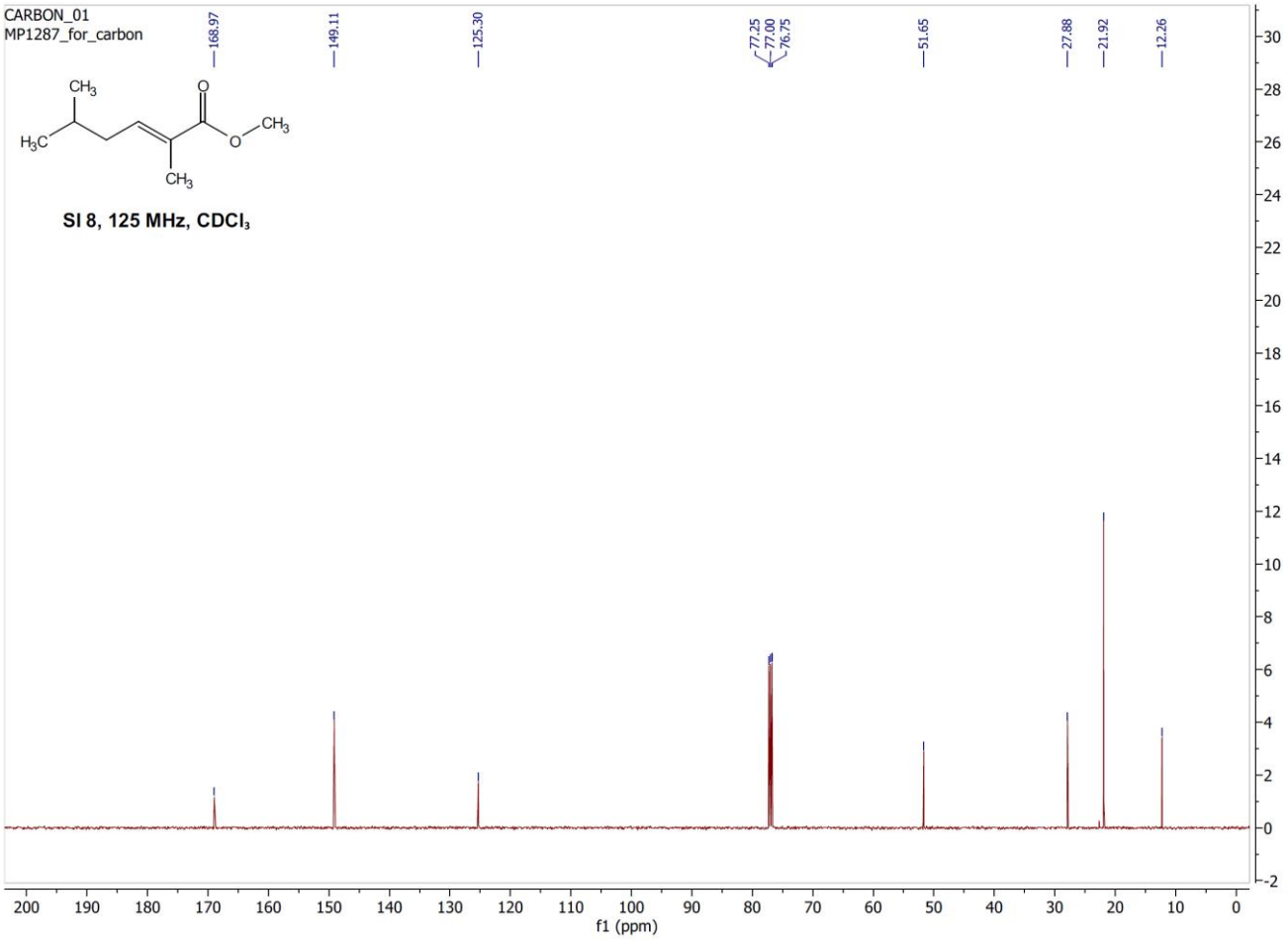

PROTON_01
MP1529
SI 5, 500 MHz, CDCl3
7.33
7.31
7.30
7.23
7.22
7.19
7.18
7.17
6.28
1.91
1.91
1.87
1.87
E (d)
7.23
D (m)
7.31
F (t)
7.18
C (s)
6.28
B (d)
1.91
A (d)
1.87
2.00
1.94
0.90
1.00
3.68
3.25
f1 (ppm)

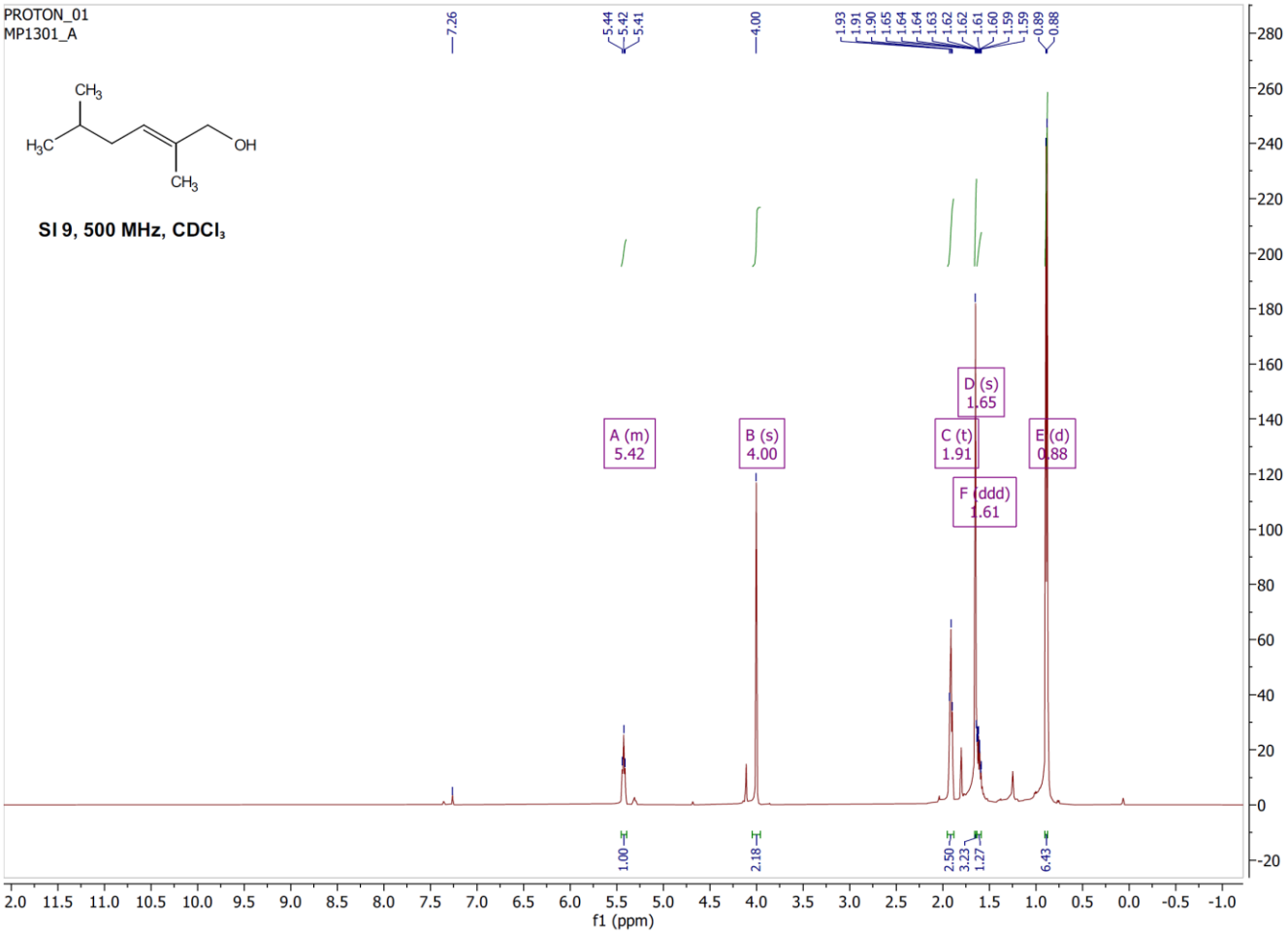

CARBON_02
2_2_dimetyl_styrene
SI 5, 125 MHz, CDCl3
138.68
135.43
128.71
127.99
125.74
125.11
77.25
77.00
76.75
26.84
19.35
f1 (ppm)


PROTON_01
MP1624_1
SI 6, 500 MHz, CDCl3
K (ddt) 5.09
J (t) 4.89
I (m) 3.96
H (m) 3.84
E (m) 1.35
C (s) 1.68
B (s) 1.59
A (d) 0.95
G (dq) 1.98
D (m) 1.21
F (td) 1.49
1.00
0.93
2.16
1.92
2.05
3.71
3.18
1.18
2.28
3.45
3.97
f1 (ppm)

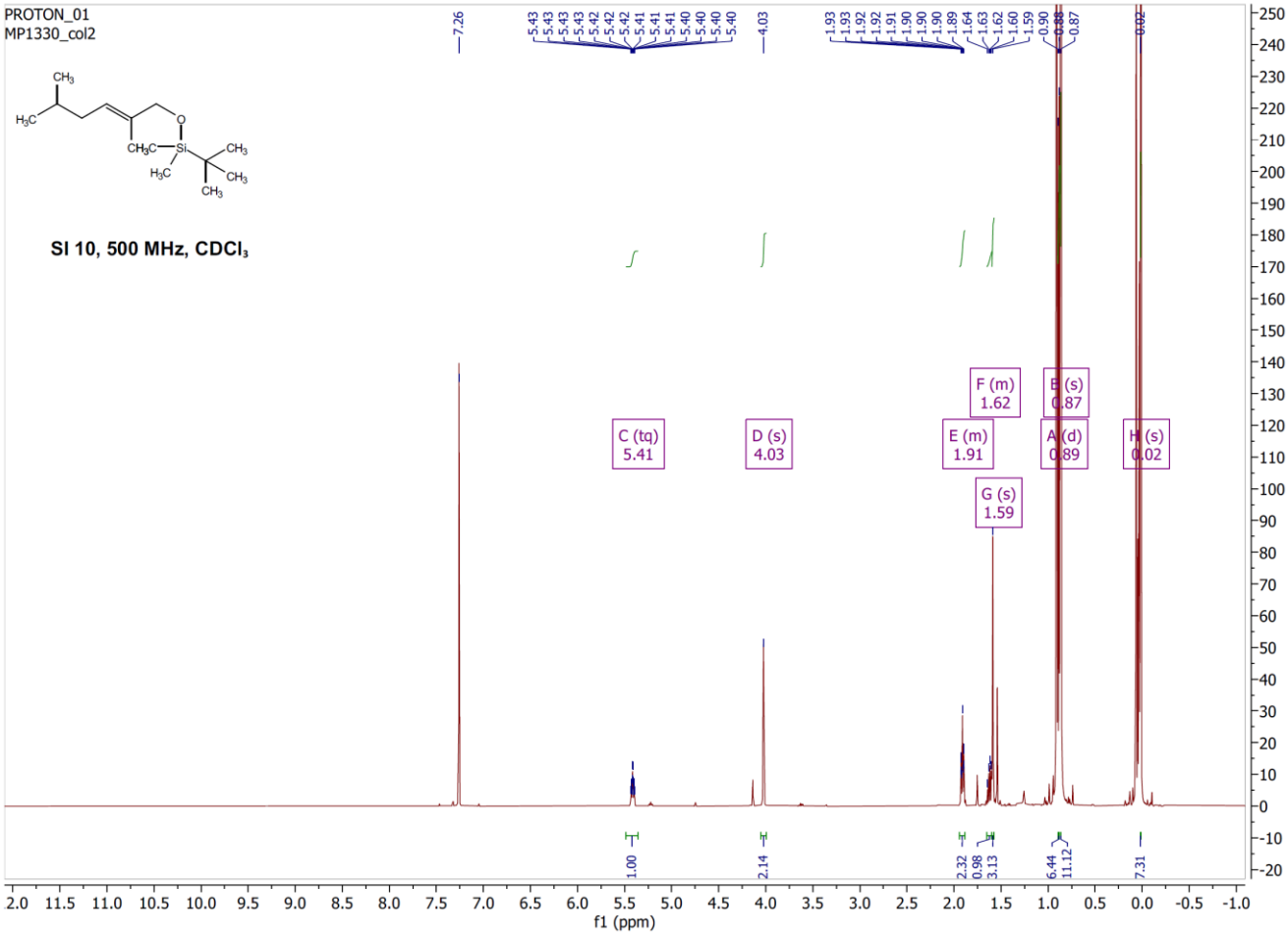

CARBON_01
MP1624_for_carbon
SI 6, 125 MHz, CDCl3
131.20
124.63
103.77
77.25
77.00
76.75
64.70
64.61
40.91
37.41
29.06
25.69
25.34
19.74
17.60
f1 (ppm)


PROTON_01
MP1287
SI 8, 500 MHz, CDCl3
B (dd) 6.57
C (s) 3.72
A (dp) 2.63
D (d) 1.83
E (d) 1.01
f1 (ppm)

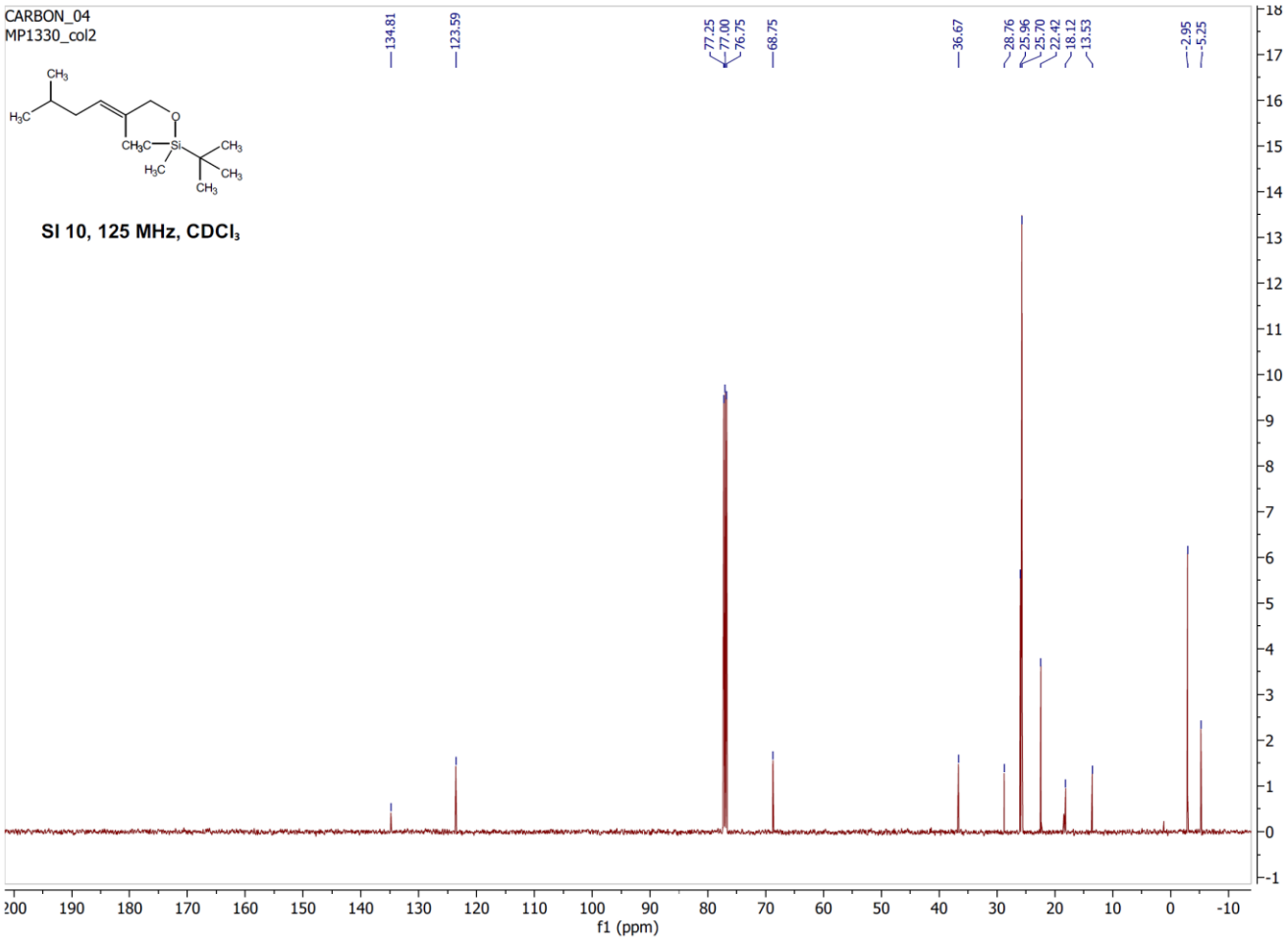

CARBON_01
MP1287_for_carbon
SI 8, 125 MHz, CDCl3
f1 (ppm)



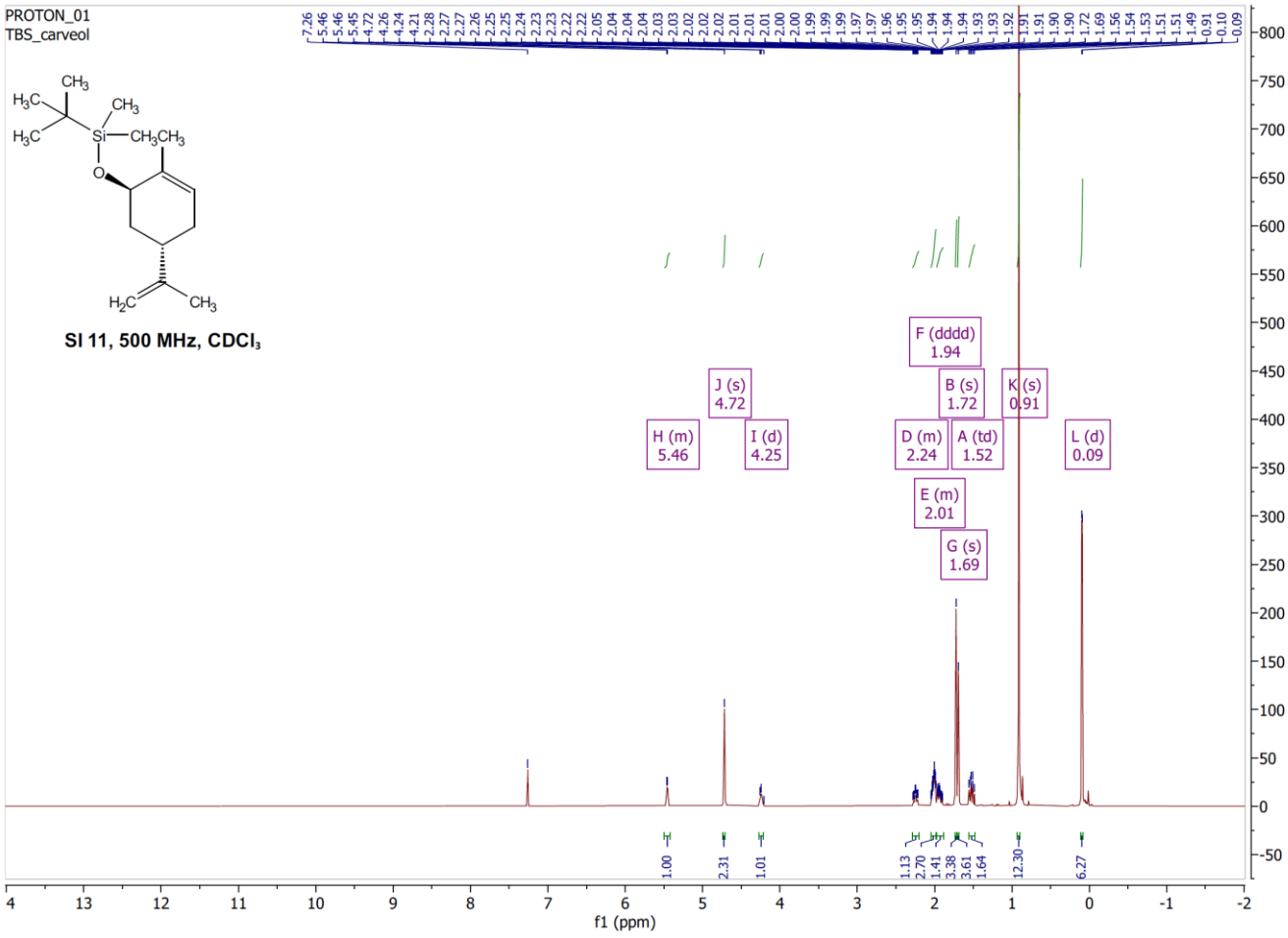
SI 9, 500 MHz, $CDCl_3$



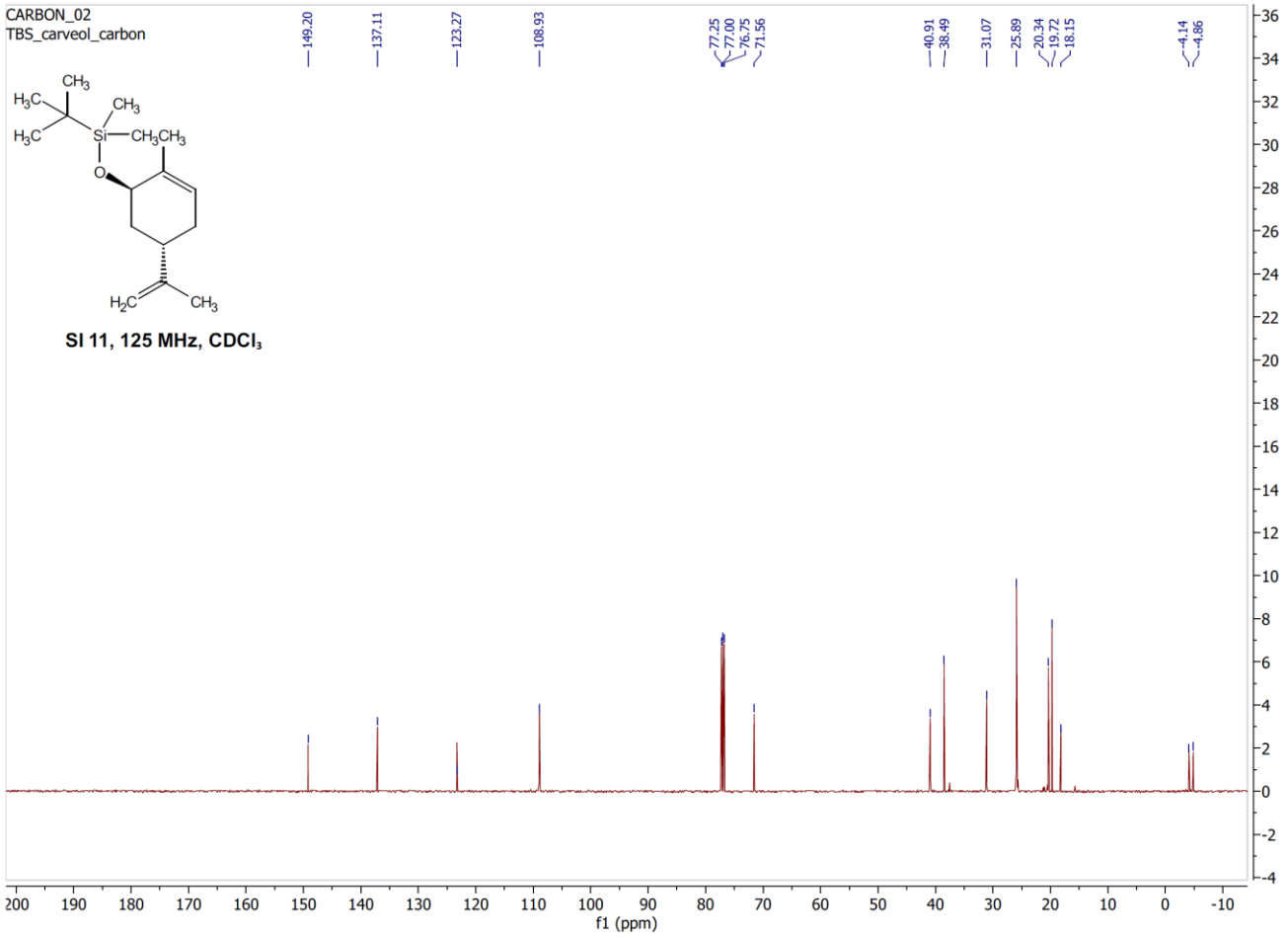
SI 10, 500 MHz, $CDCl_3$



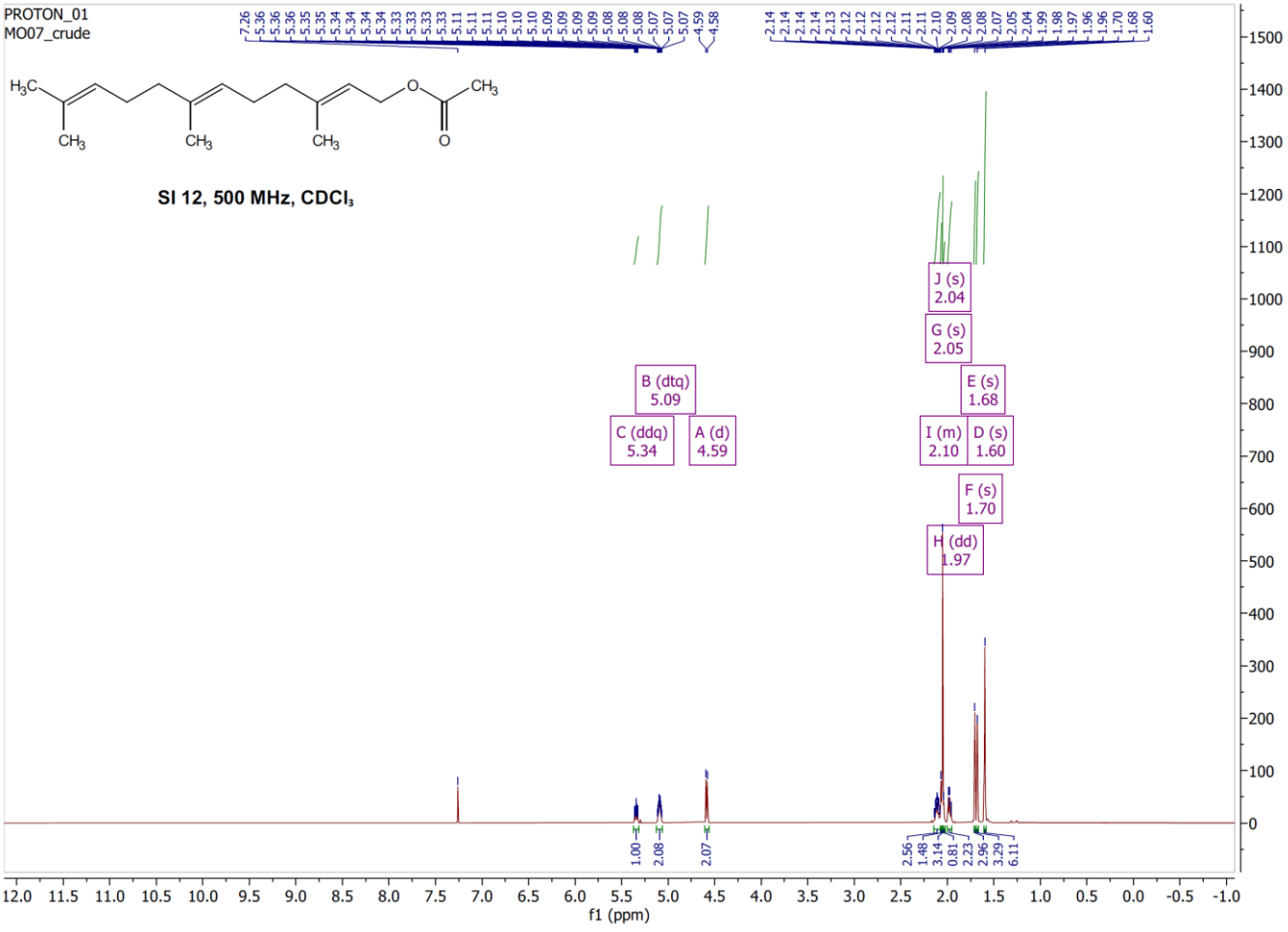
SI 10, 125 MHz, $CDCl_3$



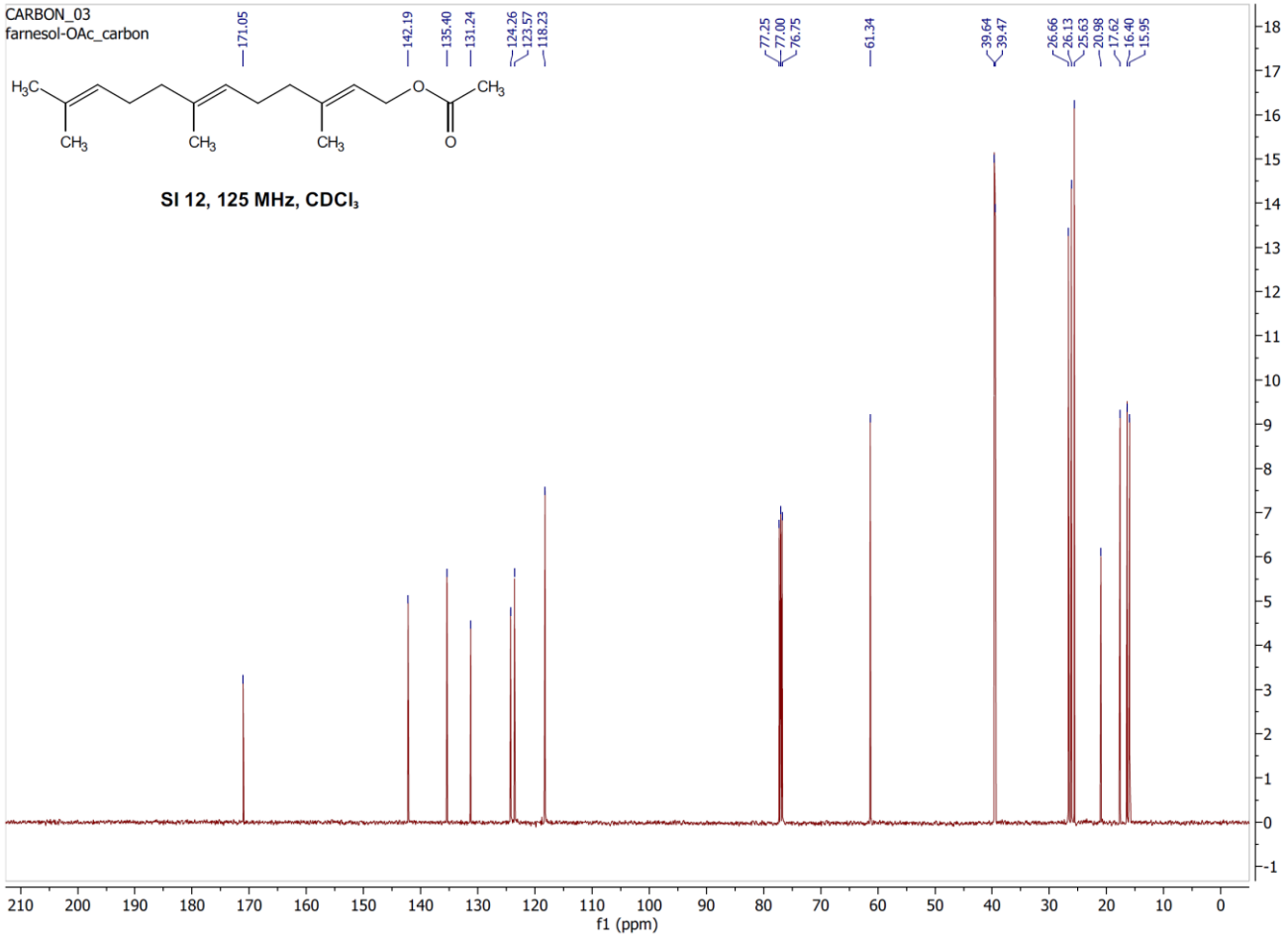
SI 11, 500 MHz, $CDCl_3$



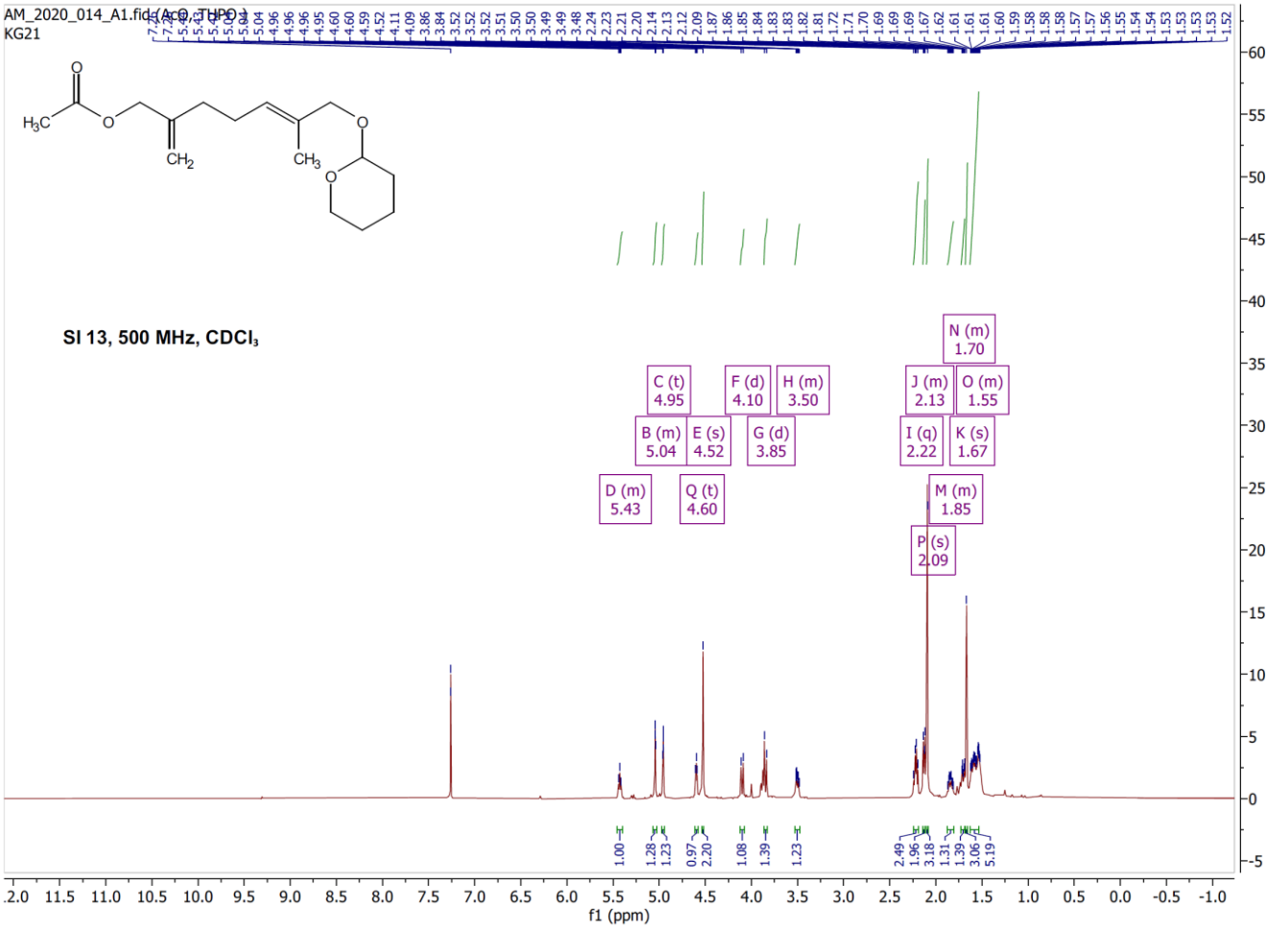
SI 11, 125 MHz, $CDCl_3$



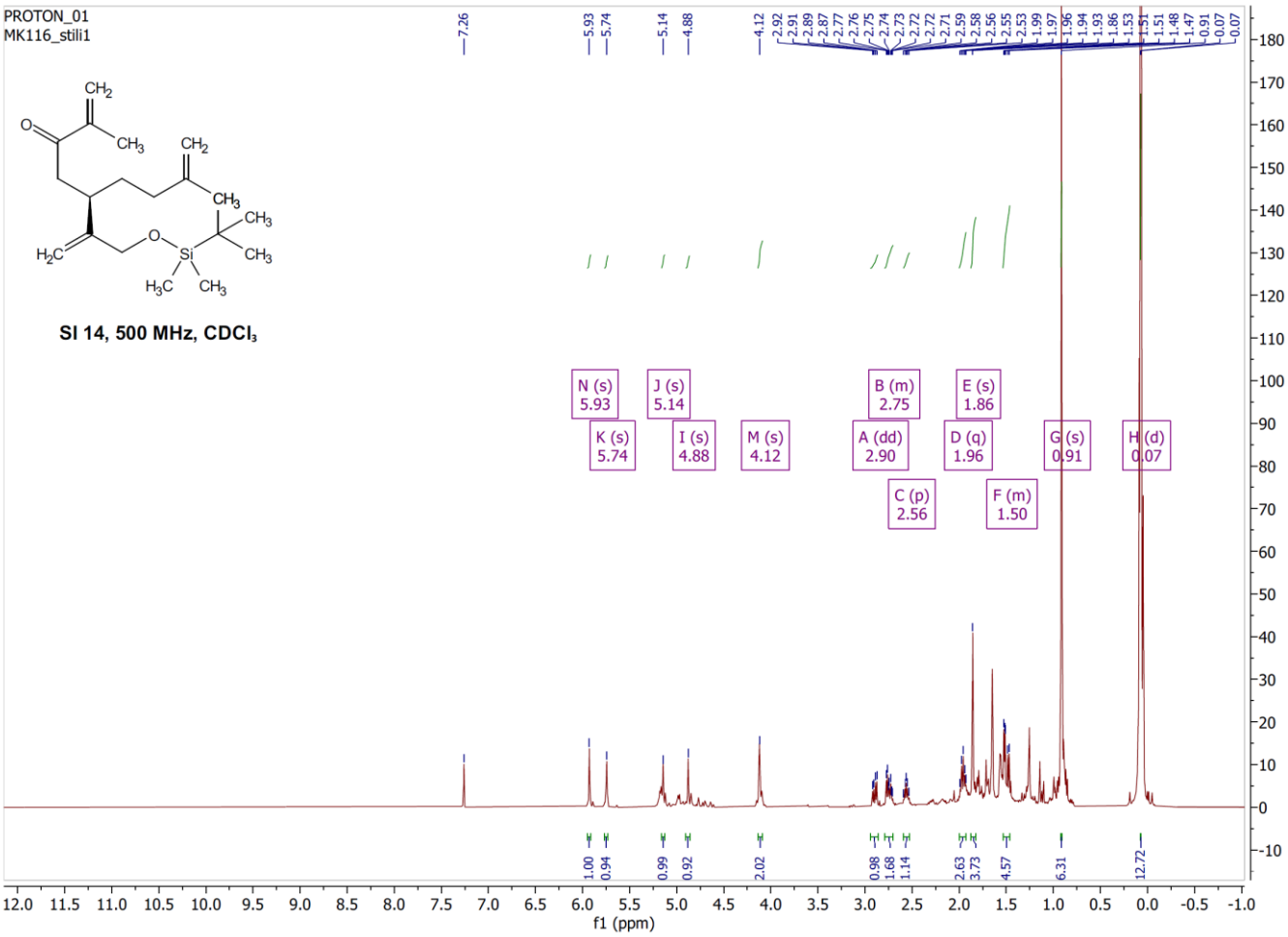
SI 12, 500 MHz, $CDCl_3$

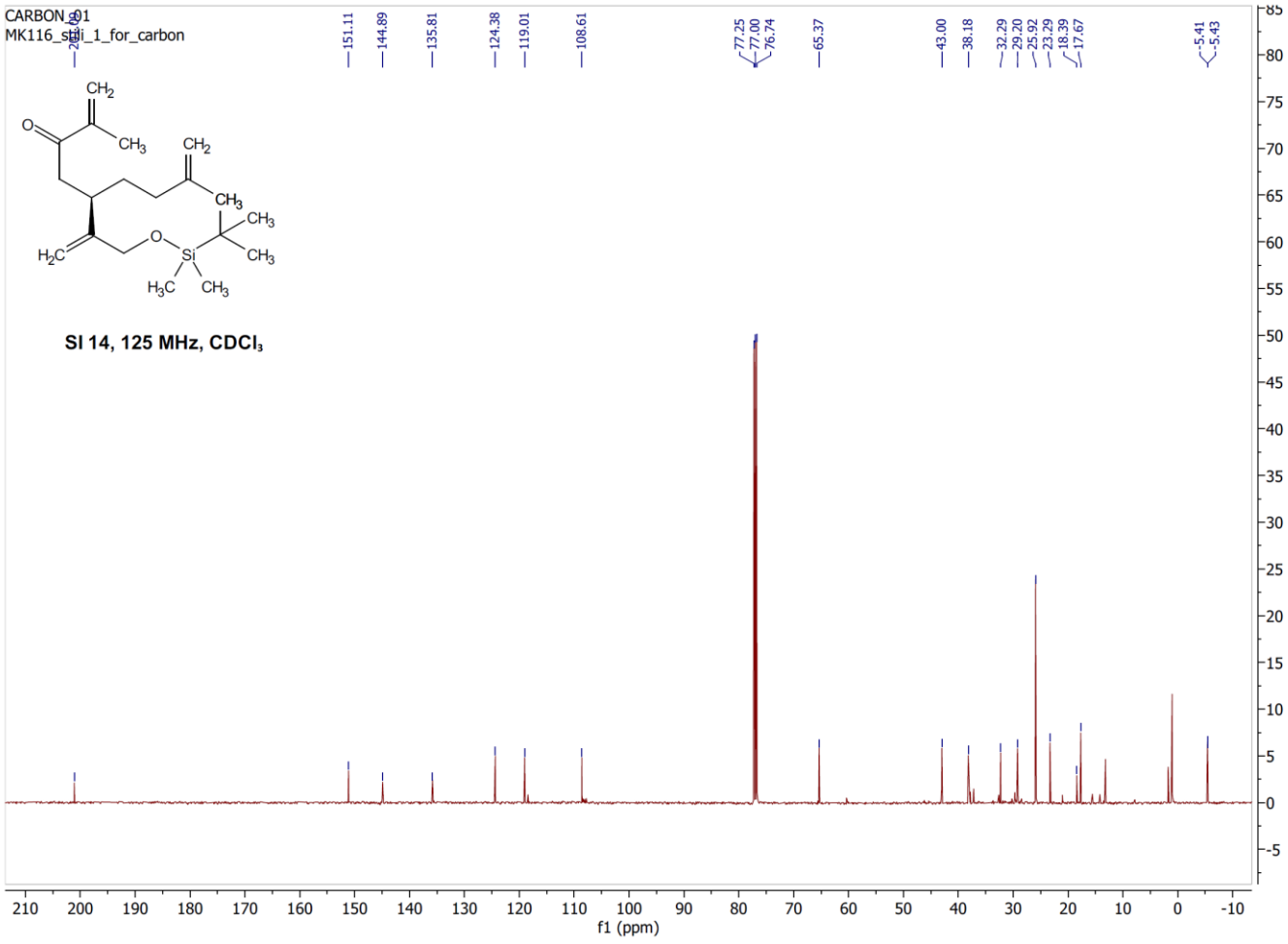


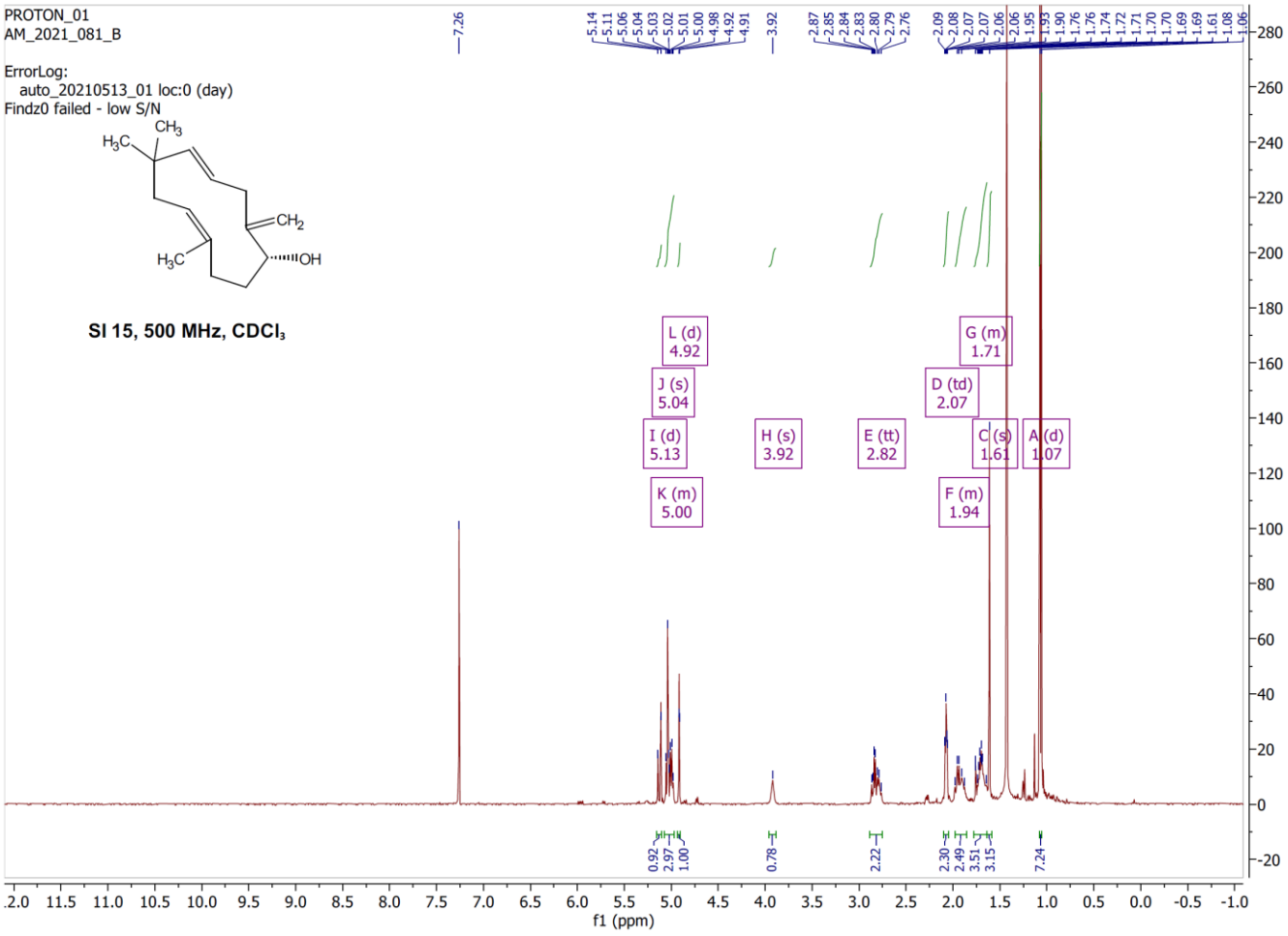
SI 12, 125 MHz, $CDCl_3$

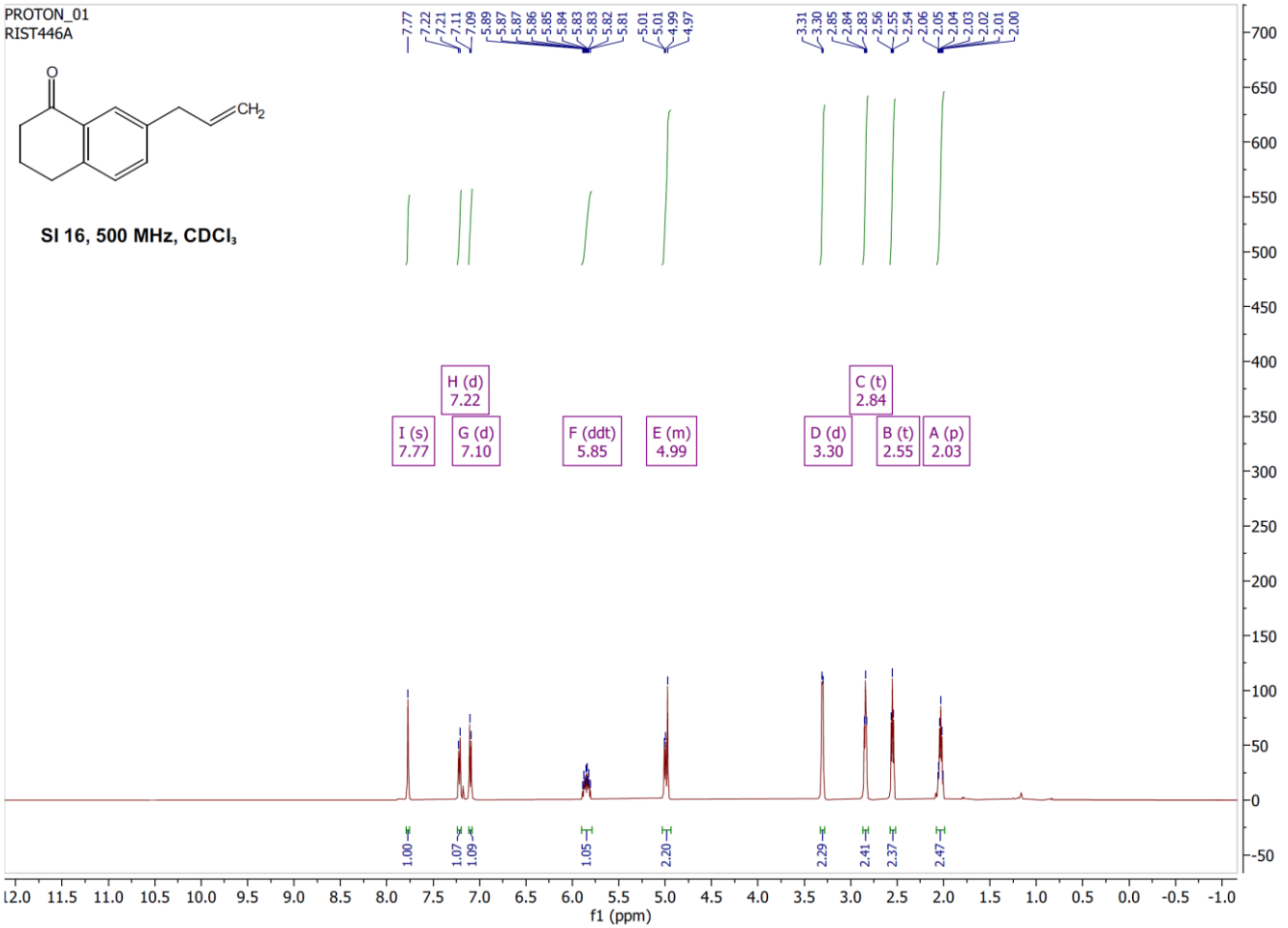


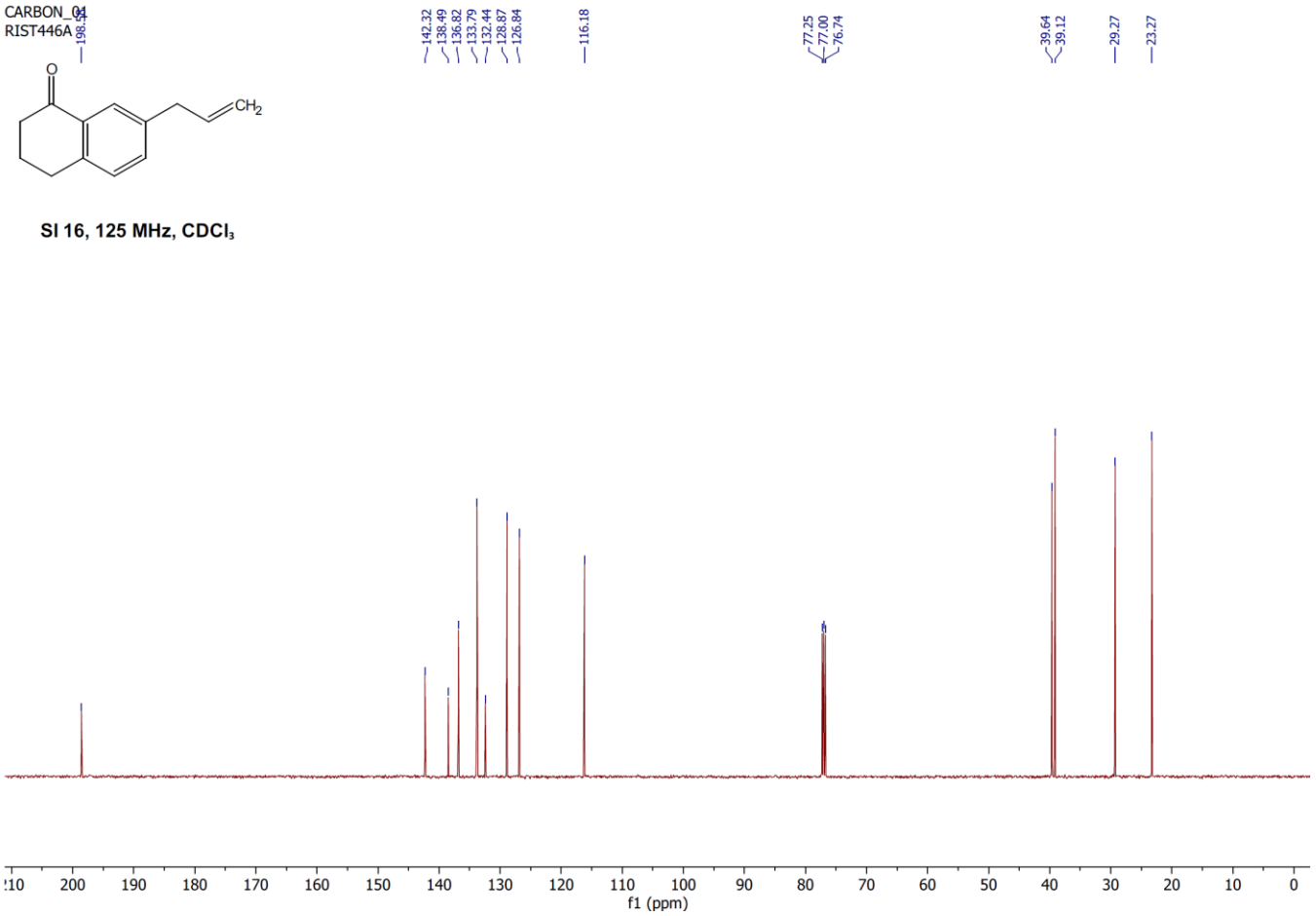
SI 13, 500 MHz, $CDCl_3$


PROTON_01
MK116_stili1
SI 14, 500 MHz, CDCl3
N (s) 5.93
K (s) 5.74
J (s) 5.14
I (s) 4.88
M (s) 4.12
B (m) 2.75
A (dd) 2.90
C (p) 2.56
E (s) 1.86
D (q) 1.96
F (m) 1.50
G (s) 0.91
H (d) 0.07
f1 (ppm)


CARBON_01
MK116_stili_1_for_carbon
SI 14, 125 MHz, CDCl3
f1 (ppm)


PROTON_01
AM_2021_081_B
ErrorLog:
auto_20210513_01 loc:0 (day)
Findz0 failed - low S/N
CH3
H3C
CH2
H3C
OH
SI 15, 500 MHz, CDCl3
L (d) 4.92
J (s) 5.04
I (d) 5.13
K (m) 5.00
H (s) 3.92
E (tt) 2.82
G (m) 1.71
D (td) 2.07
C (s) 1.61
A (d) 1.07
F (m) 1.94
f1 (ppm)


PROTON_01
RIST446A
O
CH2
SI 16, 500 MHz, CDCl3
H (d) 7.22
I (s) 7.77
G (d) 7.10
F (ddt) 5.85
E (m) 4.99
C (t) 2.84
D (d) 3.30
B (t) 2.55
A (p) 2.03
f1 (ppm)



SI 16, 125 MHz, $CDCl_3$

9. Epoxidation of Alkenes

Method A.

The corresponding commercially, provided or synthesized alkene (0.36 mmol, 1.0 equiv.) was dissolved in HFIP (1.5 mL) in a 4 mL screw capped vial without a stirring bar. Then, Hantzsch ester (0.36 mmol, 1.0 equiv.), followed by the addition of DKP (0.04 mmol, 0.1 equiv.) were added in one portion and the vial was tightly capped by a rubber septum. In the septum was introduced a thin exit needle and a pipette through which dioxygen was bubbled continuously either by a balloon or by gas cyclinder and a finely tuned gas controller. Care was taken to adjust slow bubbling in the reaction vial in order to avoid evaporation of HFIP. The reaction was stirred for 12 hours at room temperature and after the completion of time, the reaction was quenched with water and extracted with pentane (3 x 2 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure in an ice bath, until a pale-yellow solid residue was left in the flask. Flash chromatography on deactivated silica gel gave epoxides in moderate to good yields.

Method B.

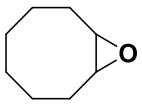
(used for alkenes insoluble in HFIP)

The corresponding commercially, provided or synthesized alkene (0.36 mmol, 1.0 equiv.) was dissolved in a mixture of HFIP:CH_2Cl_2 (4:1) of overall volume 2 mL, in a 4 mL screw capped vial without a stirring bar. Then, Hantzsch ester (0.36 mmol, 1.0 equiv.), followed by the addition of DKP (0.04 mmol, 0.1 equiv.) were added in one portion and the vial was tightly capped by a rubber septum. In the septum was introduced a thin exit needle and a pipette through which dioxygen was bubbled continuously either by a balloon or by gas cyclinder and a finely tuned gas controller. Care was taken to adjust slow bubbling in the reaction vial in order to avoid evaporation of HFIP. The reaction was stirred for 12 hours at room temperature and after the completion of time, the reaction was quenched with water and extracted with Et_2O (3 x 2 ml). The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure, until a pale-yellow solid residue was left in the flask. Flash chromatography on deactivated silica gel gave epoxides in moderate to good yields.

The optimal method applying the appropriate conditions mentioned above, was tested on a 2 mmol alkene scale with DKP 2% mmol and proved to be functional. The solvent and the catalyst can be effectively recovered. Practically, the reaction was quenched with pentane (3 x 15 ml) where the HFIP-pentane phases are not mixed and separated from its other. The pentane phase was treated and extracted with H_2O (2 x 10 ml), whereas the HFIP phase was collected and recycled through distillation to be reused (80% recovery). The catalyst, on the other hand, recovered through column chromatography of the crude reaction mixture (65% recovery). Catalyst was tested in a new epoxidation reaction and was found active to induce epoxidation.

Isolated epoxides

9-Oxabicyclo[6.1.0]nonane[14] **(6)**



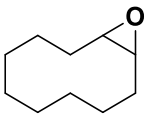
MW (g/mol): 126.20 **Molecular formula: $C_8H_{14}O$**

From cyclooctene. **Rf:** 0.75 [CH_2Cl_2:EtOAc (1:2)], CH_2Cl_2:Et_2O (50:1), Yield: **93%,** Colorless liquid (Method A) NMR identical to previous reported spectra.[14]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.82-0.89 (m, 4H), 1.24-1.31 (m, 2H), 1.42-1.65 (m, 6H), 2.12-2.18 (m, 1H), 2.90 (dt, *J* 7.4, 4.2 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 25.6, 26.3, 26.5, 55.6 ppm

11-Oxabicyclo[8.1.0]undecane[15] **(7)**



MW (g/mol): 152.24 **Molecular formula: $C_{10}H_{16}O$**

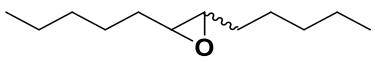
From cyclodecene. **Rf:** 0.60 [Hexane:CH_2Cl_2 (1:1)], Hexane:CH_2Cl_2 (50:1), Yield: **82%,** Colorless liquid (Method A)

NMR identical to previous reported spectra.[15]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.35-1.43 (m, 6H), 1.46-1.56 (m, 6H), 1.74 (dt, *J* 10.2, 6.2 Hz, 2H), 1.97 (d, *J* 9.6 Hz, 2H), 2.96 (d, *J* 10.4 Hz, 2H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 21.9, 24.7, 25.1, 26.0, 58.5 ppm

2,3-Dipentyloxirane[16] **(8)**



MW (g/mol): 184.32 **Molecular formula: $C_{12}H_{24}O$**

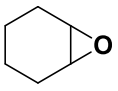
From (*E*,*Z*)-6-dodecene. **Rf:** 0.75 [Hexane:Et_2O (5:1)], isolated in Hexane:Et_2O (30:1) by maintaining stereochemistry from starting material as *E*,*Z*- mix of isomers, Yield: **88%,** Colorless liquid (Method A). Ratio of *E*,*Z*-starting alkene was retained in the epoxidation reaction providing the same ratio of diastereomeric epoxides.

NMR identical to previous reported spectra.[16]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.89 (dd, *J* 8.9, 5.3 Hz, 6H), 1.28-1.55 (m, 16H), 2.65 (t, *J* 4.8 Hz, 2H), 2.90 (t, *J* 4.5 Hz, 0.5H$_Z$) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 14.0, 22.6, 25.7, 26.3 (*Z*), 27.8 (*Z*), 31.6, 31.7 (*Z*), 31.8 (*Z*), 32.1, 57.3 (*Z*), 58.9 ppm

7-Oxabicyclo[4.1.0]heptane[17] **(9)**



MW (g/mol): 98.14 **Molecular formula: C_6H_8O**

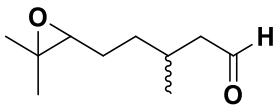
From cyclohexene. **Rf:** 0.56 [Hexane:EtOAc (20:1)], Hexane:EtOAc (10:1) Yield: **89%,** Colorless oil (Method A)

NMR identical to previous reported spectra.[17]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.15-1.25 (m, 2H), 1.33-1.45 (m, 2H), 1.72-1.83 (m, 2H), 1.87-1.99 (m, 2H), 3.09 (s, 2H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 19.4, 24.4, 52.1 ppm

5-(3,3-Dimethyloxiran-2-yl)-3-methylpentanal (as a mixture of diastereoisomers)[18] (10)



MW (g/mol): 170.25 **Molecular formula: $C_{10}H_{18}O_2$**

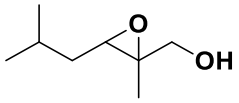
From (*R*,*S*)-citronellal. **Rf:** 0.3 [Hexane:EtOAc (4:1)], Hexane:EtOAc (7:1), Yield: **65%**, as a mixture of diastereoisomers dr=1.1:1. Colorless liquid (Method B)

NMR identical to previous reported spectra.[18]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.25 (s, 3H), 1.28 (s, 3H), 1.66-1.60 (m, 2H), 1.67 (s, 3H), 2.08-2.21 (m, 2H), 2.74-2.62 (m, 1H), 4.20-4.07 (m, 2H), 5.45-5.41 (m, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 18.6, 18.7, 19.8, 19.9, 24.7, 24.9, 26.3, 26.4, 27.9, 33.5, 50.8, 51.0, 64.2, 64.2, 202.5, 202.6 ppm

(3-Isobutyl-2-methyloxiran-2-yl)methanol[19] (11)



MW (g/mol): 144.21 **Molecular formula: $C_8H_{16}O_2$**

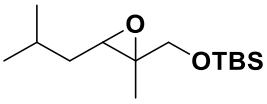
From (*E*)-2,5-dimethyl hex-2-en-1-ol. **Rf:** 0.54 [CH_2Cl_2:EtOAc (1:2)], CH_2Cl_2:EtOAc (15:1), Yield: **68%**, Colorless liquid (Method B)

NMR identical to previous reported spectra.[19]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.98 (dd, *J* 15.9, 6.6 Hz, 6H), 1.28 (s, 3H), 1.44-1.52 (m, 2H), 1.67 (brs, 1H), 1.73-1.88 (m, 1H), 3.08 (t, *J* 6.1 Hz, 1H), 3.59 (dd, *J* 12.3, 7.0 Hz, 1H), 3.69 (d, *J* 13.1Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 14.4, 22.4, 22.8, 26.6, 36.9, 59.1, 60.5, 65.3 ppm

tert-**Butyl((3-isobutyl-2-methyloxiran-2-yl)methoxy)dimethylsilane (12)**



MW (g/mol): 258.48 **Molecular formula: $C_{14}H_{30}O_2Si$**

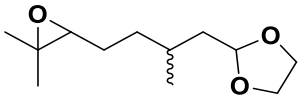
From (*E*)-tert-butyl((2,5-dimethylhex-2-en-1-yl)oxy)dimethylsilane. **Rf:** 0.26 [Hexane:CH_2Cl_2 (5:1)], CH_2Cl_2:EtOAc (20:1), Yield: **48%**, Colorless liquid (Method B)

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.06 (d, *J* 5.0 Hz, 6H), 0.89 (s, 9H), 0.97 (dd, *J* 13.2, 6.7 Hz, 6H), 1.26 (s, 3H), 1.36-1.45 (m, 1H), 1.48-1.53 (m, 1H), 1.80 (dq, *J* 7.6, 6.5 Hz, 1H), 2.88 (t, *J* 6.2 Hz, 1H), 3.57 (q, *J* 11.0, 2H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C -5.4, 14.4, 18.3, 22.4, 22.9, 25.8, 26.6, 37.0, 60.2, 60.7, 68.1 ppm

HRMS (ESI, m/z): calcd. for $C_{20}H_{31}O_2Si^+$ ($[M]^+$): 259.2088, found: 259.2080.

2-(4-(3,3-Dimethyloxiran-2-yl)-2-methylbutyl)-1,3-dioxolane (13)



MW (g/mol): 214.31 **Molecular formula: $C_{12}H_{22}O_3$**

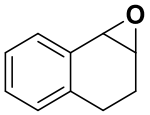
From (*R*,*S*)-2-(2,6-dimethylhept-5-en-1-yl)-1,3-dioxolane. **Rf:** 0.48 [Hexane:EtOAc (4:1)], Hexane:EtOAc (10:1), Yield: **64%**, as a mixture of diastereoisomers dr=1.1:1. Colorless liquid (Method B)

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.97 (d, *J* 6.5 Hz, 3H), 1.26 (s, 6H), 1.47-1.60 (m, 4H), 1.63-1.76 (m, 3H), 2.70 (t, *J* 6.2 Hz, 1H), 3.82-3.85 (m, 2H), 3.95-3.98 (m, 2H), 4.88-4.93 (m, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 18.6, 18.7, 19.7, 19.8, 24.9, 26.2, 26.3, 29.3, 29.7, 33.8, 33.8, 40.7, 40.8, 58.2, 64.5, 64.6, 64.7, 64.8, 103.6, 103.6 ppm

HRMS (ESI, m/z): calcd. for $C_{12}H_{22}O_3Na^+$ ($[M+Na]^+$): 237.1461, found: 237.1455.

1a,2,3,7b-Tetrahydronaphtho[1,2-*b*]oxirene[20] (15)



MW (g/mol): 146.19 **Molecular formula: $C_{10}H_{10}O$**

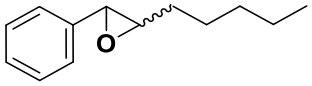
From 1,2-dihydronaphthalene. **Rf:** 0.34 [Hexane:EtOAc (30:1)], Hexane:EtOAc (50:1), Yield: **54%**, Yellowish oil (Method B)

NMR identical to previous reported spectra.[20]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.73-1.81 (m, 1H), 2.42 (dddd, *J* 14.5, 6.6, 2.9, 1.7 Hz, 1H), 2.56 (dd, *J* 15.6, 5.5 Hz, 1H), 2.80 (dd, *J* 28.8, 6.5 Hz, 1H), 3.74 (t, *J* 3.5 Hz, 1H), 3.86 (d, *J* 4.2 Hz, 1H), 7.10 (d, *J* 7.3 Hz, 1H), 7.21 (t, *J* 7.2 Hz, 1H), 7.27 (td, *J* 7.2, 1.5 Hz, 1H), 7.40 (dd, *J* 7.3, 1.5 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 21.8, 24.4, 52.7, 55.1, 126.1, 128.3, 128.4, 129.5, 132.5, 136.7 ppm

2-Pentyl-3-phenyloxirane[21] **(16)**



MW (g/mol): 190.29 **Molecular formula: $C_{13}H_{18}O$**

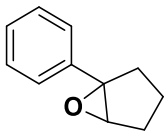
From (*E*,*Z*)-hept-1-en-1-ylbenzene. **Rf:** 0.7 [Hexane:CH_2Cl_2 (1:1)], isolated in Hexane:CH_2Cl_2 (30:1) by maintaining stereochemistry from starting material as *E*,*Z*- mix of isomers. Ratio of *E*,*Z*-starting alkene was retained in the epoxidation reaction providing the same ratio of diastereomeric epoxides. Yield: **66%**, Colorless liquid (Method B)

NMR identical to previous reported spectra.[21]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.91 (t, *J* 2.5 Hz, 3H), 1.51-1.26 (m, 4H), 1.77-1.64 (m, 4H), 2.43 (t, J 7.4 Hz, 0.4H_{minor}), 2.94 (td, *J* 5.6, 2.3 Hz, 1H), 3.60 (d, *J* 2.4 Hz, 1H), 3.67 (s, 0.3H_{minor}), 7.46-7.19 (m, 5H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 14.0, 22.6, 25.6, 31.6, 32.3, 58.6, 63.2, 125.5, 127.9, 128.4, 137.9 ppm

1-Phenyl-6-oxabicyclo[3.1.0]hexane[22] **(17)**



MW (g/mol): 160.22 **Molecular formula: $C_{11}H_{12}O$**

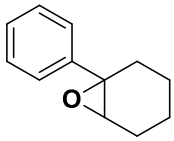
From 1-phenyl-cyclopentene. **Rf:** 0.85 [Hexane:EtOAc (4:1)], Pentane:Et_2O (85:1), Yield: **51%**, Colorless liquid (Method A)

NMR identical to previous reported spectra.[22]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.75-1.80 (m, 2H), 1.94 (ddt, *J* 6.5, 5.3, 2.5 Hz, 2H), 2.15 (ddd, *J* 4.5, 3.7, 1.6 Hz, 2H), 3.98 (t, *J* 2.5 Hz, 1H), 7.01-7.06 (m, 1H), 7.20-7.24 (m, 2H), 7.34-7.38 (m, 2H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 19.9, 27.1, 30.2, 58.5, 62.3, 125.7, 128.1, 128.6, 141.2 ppm

1-Phenyl-7-oxabicyclo[4.1.0]heptane[23] **(18)**



MW (g/mol): 174.24 **Molecular formula: $C_{12}H_{14}O$**

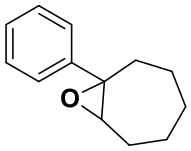
From 1-phenyl-cyclohexene. **Rf:** 0.78 [Hexane:EtOAc (4:1)], Pentane:Et_2O (80:1), Yield: **58%**, Colorless liquid (Method A)

NMR identical to previous reported spectra.[23]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.28-1.37 (m, 1H), 1.44-1.53 (m, 1H), 1.55-1.67 (m, 2H), 1.97-2.03 (m, 2H), 2.09-2.15 (m, 1H), 2.29 (ddd, *J* 14.5, 8.6, 5.4 Hz, 1H), 3.08 (d, *J* 2.6 Hz, 1H), 7.27-7.39 (m, 5H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 19.8, 20.1, 24.7, 28.9, 60.2, 61.9, 125.3, 127.1, 128.2, 142.5 ppm

1-Phenyl-8-oxabicyclo[5.1.0]octane[24] (19)



MW (g/mol): 188.27 **Molecular formula: $C_{13}H_{16}O$**

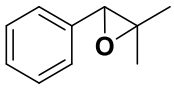
From 1-phenyl-cycloheptene. **Rf:** 0.85 [Hexane:EtOAc (4:1)], Pentane:Et_2O (90:1), Yield: **55%**, Colorless liquid (Method A)

NMR identical to previous reported spectra.[24]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.35 (td, J Hz, 1H), 1.50-1.85 (m, 5H), 1.90-2.20 (m, 3H), 2.38-2.50 (m, 1H), 3.04 (q, J 3.8 Hz, 1H), 7.25-7.40 (m, 5H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 24.5, 25.1, 29.5, 31.4, 33.6, 63.2, 65.5, 125.1, 127.0, 128.2, 143.7 ppm

2,2-Dimethyl-3-phenyloxirane[25] (20)



MW (g/mol): 148.20 **Molecular formula: $C_{10}H_{12}O$**

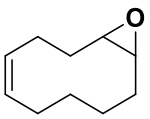
From 2-Methyl-1-phenylpropene. **Rf:** 0.88 [Hexane:EtOAc (4:1)], Pentane: Et_2O (100:1), Yield: **56%**, Colorless liquid (Method A)

NMR identical to previous reported spectra.[25]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.08 (s, 3H), 1.49 (s, 3H), 3.87 (s, 1H), 7.27-7.38 (m, 5H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 17.9, 24.7, 61.1, 64.6, 126.4, 127.3, 128.0, 136.6 ppm

(*Z*)-11-Oxabicyclo[8.1.0]undec-4-ene[26] (21)



MW (g/mol): 154.25 **Molecular formula: $C_{10}H_{18}O$**

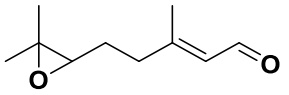
From 1,5-cyclodecadiene. **Rf:** 0.75 [Hexane:Et_2O (5:1)], Hexane:Et_2O (30:1), Yield: **59%,** Colorless liquid (Method A)

NMR identical to previous reported spectra.[26]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.84-0.95 (m, 2H), 1.41-1.55 (m, 4H), 1.70-1.78 (m, 3H), 2.07-2.10 (m, 2H), 2.20-2.30 (m, 2H), 2.33-2.38 (m, 2H), 2.53 (d, *J* 10.2 Hz, 1H), 2.76 (d, *J* 9.9 Hz, 1H), 5.36-5.50 (m, 2H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 21.89, 23.12, 25.33, 28.45, 31.08, 31.20, 60.90, 60.95, 127.48, 132.10 ppm

(*E,Z*)-5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-2-enal[27] (22)



MW (g/mol): 168.24 **Molecular formula: $C_{10}H_{16}O_2$**

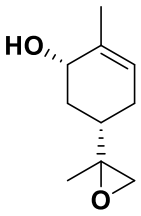
From (*E*,*Z*)-geranial. **Rf:** 0.26 [CH_2Cl_2:Et_2O (10:1)], CH_2Cl_2:Et_2O (8:1), Ratio of *E*,*Z*-starting alkene was retained in the epoxidation reaction providing the same ratio of diastereomeric epoxides. Yield: **53%**, Colorless liquid (Method B)

NMR identical to previous reported spectra.[27]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.28 (s, 3H), 1.31 (s, 3H), 1.43 (s, 3H), 1.74-1.82 (m, 2H), 2.30-2.45 (m, 1H), 2.70-2.77 (m, 1H), 5.91 (d, *J* 7.9 Hz, 1H), 10.00 (dd, *J* 11.4, 8.0 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 17.6, 18.7, 24.7, 24.8, 25.0, 26.7, 28.1, 29.5, 30.3, 37.3, 58.5, 63.25, 63.34, 127.5, 128.7, 162.5, 190.4, 191.1 ppm

(1*S*,5*S*)-2-Methyl-5-((*S*)-2-methyloxiran-2-yl)cyclohex-2-en-1-ol[28] (23)



MW (g/mol): 168.24 **Molecular formula: $C_{10}H_{16}O_2$**

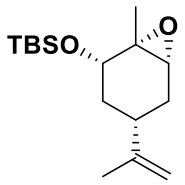
From (1*S*,5*S*)-carveol. **Rf:** 0.15 [Hexane:EtOAc (4:1)], Hexane:EtOAc (5:1), Yield: **72%**, as a mixture of diastereoisomers dr=1:1 Colorless liquid (Method B)

NMR identical to previous reported spectra.[28]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.29 (s, 3H), 1.79 (brs, 3H), 1.93 (ddt, *J* 11.5, 9.3, 2.0 Hz, 1H), 2.04-2.17 (m, 2H), 2.56 (dd, *J* 6.3, 4.7 Hz, 1H), 2.68 (dd, *J* 9.8, 4.8, 1H), 3.75 (q, *J* 7.2 Hz, 1H), 3.99-4.05 (m, 1H), 5.56 (ddt, *J* 7.3, 5.8, 1.8 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 8.0, 18.6, 18.7, 20.9, 27.4, 27.8, 33.7, 34.1, 52.8, 53.0, 57.8, 58.8, 59.0, 67.9, 68.0, 124.5, 124.8, 134.4, 134.6 ppm

***tert*-Butyldimethyl(((2*S*,4*S*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptan-2-yl)oxy)silane[29] (24)**



MW (g/mol): 282.50 **Molecular formula: $C_{16}H_{30}O_2Si$**

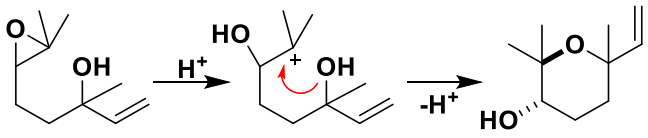
From *tert*-butyldimethyl(((2*S*,4*S*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptan-2-yl)oxy)silane. **Rf:** 0.75 [Hexane:EtOAc (4:1)], Hexane:EtOAc (50:1), Yield: **58%**, as a single diastereoisomer. Colorless liquid (Method B)

NMR identical to previous reported spectra.[29]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.10 (d, J 9.4 Hz, 6H), 0.92 (s, 9H), 1.14 (d, J 7.2 Hz, 1H), 1.36 (s, 3H), 1.48-1.55 (m, 2H), 1.67 (s, 3H), 1.89-1.96 (m, 1H), 1.98-2.04 (m, 1H), 3.04 (d, J 5.1 Hz, 1H), 3.89-3.94 (m, 1H), 4.68 (s, 2H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C -4.7, -4.1, 18.1, 19.7, 20.0, 25.9, 29.1, 33.8, 40.6, 60.2, 60.9, 109.6, 148.1 ppm

2,2,6-Trimethyl-6-vinyltetrahydro-2H-pyran-3-ol[30] (25)



MW (g/mol): 170.25 **Molecular formula: $C_{10}H_{18}O_2$**

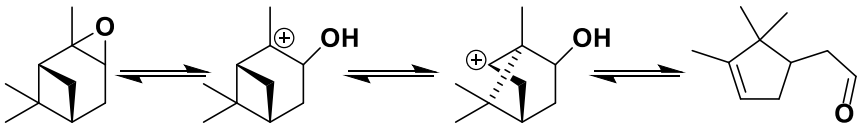
From (*R*,*S*)-linalool. **Rf:** 0.56 [Hexane:EtOAc (4:1)], Hexane:EtOAc (2:1), Yield: **62%**, as a mixture of diastereoisomers dr=1.5:1. Colorless liquid (Method B)

NMR identical to previous reported spectra.[30]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.17 (d, *J* 4.0 Hz, 6H), 1.22 (s, 3H), 1.25 (s, 3H), 1.58 (m, 1H), 1.72 (m, 2H), 2.12 (dt, *J* 13.8, 3.8 Hz, 1H), 3.44 (m, 1H), 5.00 (m, 2H), 5.96 (m, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 20.7, 24.2, 25.7, 26.4, 27.1, 27.5, 29.5, 30.9, 31.6, 32.5, 71.2, 73.5, 73.6, 74.9, 75.2, 75.9, 110.5, 110.7, 146.3, 146.8 ppm

2-(2,2,3-Trimethylcyclopent-3-en-1-yl)acetaldehyde[31] (26)



MW (g/mol): 152.24 **Molecular formula: $C_{10}H_{16}O$**

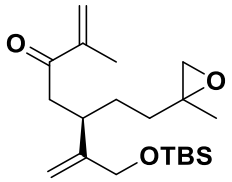
From (+)-a-pinene. **Rf:** 0.52 [Cyclohexane:EtOAc (10:1)], Cyclohexane:EtOAc (50:1), Yield: **68%**, Colorless liquid (Method B)

NMR identical to previous reported spectra.[31]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.79 (s, 3H), 1.00 (s, 3H), 1.62-1.63 (m, 3H), 1.89 (dt, *J* 11.2, 4.7, 2.3 Hz, 1H), 2.8-2.60 (m, 1H), 2.53 (ddd, *J* 15.7, 4.3, 2.1 Hz, 1H), 5.24 (s, 1H), 9.80 (t, *J* 2.3 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 12.6, 19.5 (C_{minor}), 20.0, 21.1 (C_{minor}), 25.6, 29.7 (C_{minor}), 35.5, 42.1 (C_{minor}), 44.2, 45.1, 46.9, 111.7 (C_{minor}), 121.6, 145.4 (C_{minor}), 148.0, 203.0 ppm

(5*R*)-6-(((*tert*-Butyldimethylsilyl)oxy)methyl)-2-methyl-5-(2-(2-methyloxiran-2-yl)ethyl)hepta-1,6-dien-3-one (27)



MW (g/mol): 352.59 **Molecular formula: $C_{20}H_{36}O_3Si$**

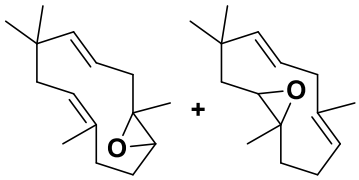
From (*R*)-5-(3-((*tert*-butyldimethylsilyl)oxy)prop-1-en-2-yl)-2,8-dimethylnona-1,8-dien-3-one. **Rf:** 0.40 [Cyclohexane:EtOAc (50:1)], Cyclohexane:EtOAc (50:1), Yield: **84%**, as a mixture of diastereoisomers dr=1:1 Colorless liquid (Method B)

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.06 (dd, *J* 2.8, 1.6 Hz, 6H), 0.91 (s, 9H), 1.25 (d, *J* 3.5 Hz, 3H), 1.51-1.58 (m, 3H), 1.86 (d, *J* 1.2 Hz, 3H), 2.58 (dt, *J* 13.1, 6.3 Hz, 1H), 2.74 (td, *J* 16.4, 7.2 Hz, 1H), 2.81 (qd, *J* 5.5, 2.5 Hz, 1H), 4.86 (dd, *J* 3.7, 1.7 Hz, 2H), 5.13 (t, *J* 1.7 Hz, 1H), 5.75 (dt, *J* 1.6, 1.0 Hz, 1H), 5.93 (dt, *J* 1.8, 1.0 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C -5.4, 13.95, 14.0, 17.7, 18.4, 22.1, 22.2, 25.9, 29.69, 29.73, 30.0, 30.32, 30.34, 37.9, 38.2, 42.9, 43.0, 60.1, 60.2, 60.6, 65.4, 65.5, 108.8, 109.2, 124.5, 124.52, 144.8, 150.6, 151.0, 200.8, 200.9 ppm

HRMS (ESI, m/z): calcd. for $C_{20}H_{36}O_3SiK^+$ ($[M+K]^+$): 391.6789, found: 391.6781.

(3*E*,7*E*)-1,5,5,8-Tetramethyl-12-oxabicyclo[9.1.0]dodeca-3,7-diene (major isomer) : (4*Z*,7*E*)-1,5,9,9-tetramethyl-12-oxabicyclo[9.1.0]dodeca-4,7-diene (minor isomer)[32] (28)



major **minor**

(9:1)

MW (g/mol): 220.36 **Molecular formula: $C_{15}H_{24}O$**

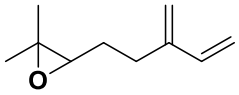
From humulene. **Rf:** 0.9 [Hexane:EtOAc (10:1)], Hexane:EtOAc (30:1), Yield: **98%**, as a mixture of 1,2- and 8,9-monoepoxides in a ratio of 9:1. Colorless liquid (Method B)

NMR identical to previous reported spectra.[32]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.03 (s, $3H_{minor}$), 1.07 (s, 3H), 1.10 (s, 3H), 1.18 (d, *J* 2.6 Hz, $6H_{minor}$), 1.30 (s, 3H), 1.30-1.38 (m, 1H), 1.39-1.42 (m, $1H_{minor}$), 1.56 (s, 3H), 1.60 (d, *J* 5.9 Hz, $1H_{minor}$), 1.64 (dd, *J* 12.3, 10.2 Hz, 1H), 1.69 (s, $3H_{minor}$), 1.86 (dd, *J* 13.8, 5.7, 1H), 1.99 (dd, *J* 13.7, 9.1 Hz, 1H), 2.06-2.27 (m, $3H_{major}$ + $1H_{minor}$), 2.48-2.60 (m, 2H), 4.96-5.01 (m, 1H), 5.15 (d, *J* 15.8 Hz, 1H), 5.19 (d, *J* 7.2 Hz, $1H_{minor}$), 5.23-5.31 (m, 1H), 5.37 (d, *J* 16.0 Hz, $1H_{minor}$), 5.77 (dt, *J* 16.1, 7.2 Hz, $1H_{minor}$)

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 15.1, 16.1 (C_{minor}), 17.2, 18.1 (C_{minor}), 23.4 (C_{minor}), 23.8 (C_{minor}), 24.7, 25.5, 29.0, 30.7 (C_{minor}), 35.1 (C_{minor}), 36.5, 36.6, 38.6 (C_{minor}), 39.7 (C_{minor}), 40.2, 41.1 (C_{minor}), 42.6, 61.5 (C_{minor}), 61.9, 63.2, 63.5 (C_{minor}), 122.1, 125.7, 125.9 (C_{minor}), 128.1 (C_{minor}), 131.9, 139.6 (C_{minor}), 141.4 (C_{minor}), 143.1 ppm

2,2-Dimethyl-3-(3-methylenepent-4-en-1-yl)oxirane[33] (29)



MW (g/mol): 152.24 **Molecular formula: $C_{10}H_{16}O$**

From β-myrcene. **Rf:** 0.8 [Hexane:EtOAc (4:1)], Hexane:EtOAc (10:1), Yield: **72%**, White liquid (Method B)

NMR identical to previous reported spectra.[33]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.26 (s, 3H), 1.31 (s, 3H), 1.71-1.76 (m, 2H), 2.29-2.35 (td, *J* 14.9, 7.9 Hz, 1H), 2.41-2.47 (m, 1H), 2.76 (t, *J* 6.2 Hz, 1H), 5.03 (s, 1H), 5.05 (s, 1H), 5.09 (d, *J* 10.9 Hz, 1H), 5.25 (d, *J* 17.6 Hz, 1H), 6.39 (dd, *J* 17.7, 10.8 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 18.8, 24.9, 27.6, 28.1, 58.5, 64.1, 113.4, 116.1, 138.6, 145.4 ppm

(2*E*,6*E*)-9-(3,3-Dimethyloxiran-2-yl)-3,7-dimethylnona-2,6-dien-1-ol[34] (30)

MW (g/mol): 238.37 **Molecular formula: $C_{15}H_{26}O_2$**

From (*E*,*E*,*E*)-farnesol. **Rf**: 0.41 [CH_2Cl_2:Et_2O (20:1)], CH_2Cl_2:Et_2O (10:1) Yield: **56%**, as a mixture of two monoepoxides. 10,11-epoxide: 6,7-epoxide= 1.2:1. Colorless liquid (Method B)

NMR identical to previous reported spectra.[34]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.24 (d, *J* 2.2 Hz, 3H), 1.29 (s, 3H), 1.60 (d, *J* 6.1 Hz, 3H), 1.64-1.69 (m, 5H), 2.09 (ddt, *J* 38.4, 15.1, 7.5 Hz, 6H), 2.69 (td, *J* 6.1, 3.8 Hz, 1H), 4.14 (t, *J* 7.3 Hz, 2H), 5.11 (dt, *J* 42.2, 7.0 Hz, 1H), 5.42 (dt, *J* 25.1, 7.0 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 15.9, 16.17, 16.2, 16.5, 17.6, 18.7, 23.8, 24.8, 25.6, 26.1, 27.0, 27.2, 36.2, 36.3, 38.7, 39.3, 58.4, 59.2, 59.3, 60.8, 63.2, 64.2, 123.6, 123.9, 124.5, 134.3, 138.6, 139.2 ppm

(2*E*,6*E*)-9-(3,3-Dimethyloxiran-2-yl)-3,7-dimethylnona-2,6-dien-1-yl acetate[35] (31)

(1:0.75)

MW (g/mol): 238.37 **Molecular formula: $C_{15}H_{26}O_2$**

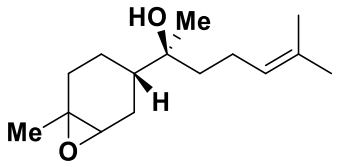
From (*E*,*E*,*E*)-farnesol acetate. **Rf:** 0.65 [CH_2Cl_2:Et_2O (50:1)], CH_2Cl_2:Et_2O (20:1) Yield: **52%**, as a mixture of two monoepoxides. 10,11-epoxide: 6,7-epoxide= 2:1. Colorless liquid (Method B)

NMR identical to previous reported spectra.[35]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.25 (s, 3H), 1.30 (s, 3H), 1.57-1.64 (m, 5H), 1.59-1.65 (m, 5H), 1.69 (d, *J* 0.6 Hz, 3H), 2.05 (s, 3H), 2.07-2.22 (m, 6H), 2.69 (t, *J* 6.2 Hz, 1H), 4.58 (dd, *J* 7.2, 4.0 Hz, 2H), 5.10 (m, 1H), 5.36 (dddd, *J* 22.3, 8.4, 5.7, 1.4 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 16.0, 16.4, 16.5, 17.6, 18.7, 20.9, 21.0, 23.8, 24.9, 25.7, 26.1, 26.9,27.4, 36.1, 36.3, 38.7, 39.4, 58.3, 60.8, 61.2, 61.4, 63.1, 64.1, 118.3, 118.8, 123.6, 124.2, 131.9, 134.6, 141.2, 142.1, 171.0, 171.1 ppm

(2*S*)-6-Methyl-2-((3*S*)-6-methyl-7-oxabicyclo[4.1.0]heptan-3-yl)hept-5-en-2-ol[36] (32).



MW (g/mol): 238.37 **Molecular formula: $C_{15}H_{26}O_2$**

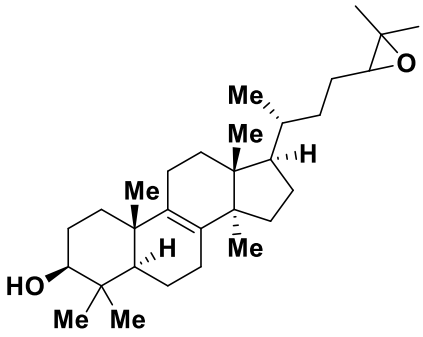
From a-(-)-bisabolole. **Rf:** 0.52 [Hexane:EtOAc (2:1)], Hexane:EtOAc (8:1), Yield: **67%**, as a mixture of diastereoisomers dr=1.2:1. Colorless liquid (Method B)

NMR identical to previous reported spectra.[36]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.18 (s, 3H), 1.31 (d, *J* 3.9 Hz, 3H), 1.46-1.54 (m, 2H), 1.55-1.58 (m, 1H), 1.61 (d, *J* 4.1 Hz, 2H), 1.62-1.66 (m, 2H), 1.68 (s, 3H), 1.79-1.90 (m, 2H), 1.98-2.06 (m, 2H), 2.10-2.18 (m, 1H), 2.98 (d, *J* 5.2 Hz, 1xOH), 3.04 (d, *J* 5.3 Hz, 1xOH), 5.11 (dtq, *J* 7.1, 4.2, 1.4 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 17.7, 19.4, 21.8, 21.9, 22.1, 22.2, 22.9, 23.1, 23.4, 25.7, 25.8, 27.2, 29.5, 30.9, 31.8, 38.3, 39.8, 40.1, 41.7, 42.3, 57.6, 57.7, 59.2, 61.2, 73.97, 74.04, 124.32, 124.35, 131.9 ppm

(3*S*,5*R*,10*S*,13*R*,14*R*,17*R*)-17-((2*R*)-4-(3,3-Dimethyloxiran-2-yl)butan-2-yl)-4,4,10,13,14-pentamethyl-2,3,4,5,6,7,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol[37] (33)



MW (g/mol): 442.73 **Molecular formula: $C_{30}H_{50}O_2$**

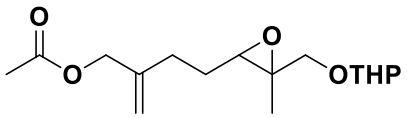
From lanosterol. **Rf:** 0.5 [Hexane:EtOAc (4:1)], Hexane:EtOAc (12:1), Yield: **67%**, White liquid (Method B)

NMR identical to previous reported spectra.[37]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.70 (s, 3H), 0.81 (s, 3H), 0.88 (s, 3H), 0.91 (d, *J* 6.2 Hz, 3H), 0.98 (s, 3H), 1.00 (s, 3H), 1.26 (s, 3H), 1.31 (s, 3H), 1.32-1.74 (m, 18H), 1.90-2.06 (m, 5H), 2.69 (t, *J* 6.4 Hz, 1H), 3.23 (dd, *J* 11.7, 4.6 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 15.4, 15.8, 18.2, 18.5, 18.6, 18.7, 18.7, 19.1, 21.0, 24.2, 24.9, 24.9, 25.6, 25.9, 26.5, 27.8, 27.9, 28.1, 28.2, 30.8, 30.9, 31.0, 32.6, 32.8, 35.6, 36.2, 36.3, 37.0, 38.9, 44.5, 49.8, 50.2, 50.3, 50.4, 58.1, 58.4, 64.8, 64.9, 78.9, 134.3, 134.4 ppm

4-(3-Methyl-3-(((tetrahydro-2*H*-pyran-2-yl)oxy)methyl)oxiran-2-yl)-2-methylenebutyl acetate (34)



MW (g/mol): 298.38 **Molecular formula: $C_{16}H_{26}O_5$**

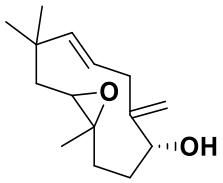
From (*E*)-6-methyl-2-methylene-7-((tetrahydro-2*H*-pyran-2-yl)oxy)hept-5-en-1-yl acetate. **Rf:** 0.45 [Hexane:EtOAc (4:1)], Hexane:EtOAc (12:1), Yield: **56%** , as a mixture of diastereoisomers dr=xx:xx. Colorless liquid (Method B)

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.33 (d, *J* 18.5 Hz, 3H), 1.49-1.63 (m, 5H), 1.64-1.89 (m, 3H), 2.09 (s, 3H), 2.18-2.31 (m, 2H), 2.86 (dd, *J* 7.0, 5.4 Hz, 0.5H), 2.99 (dd, *J* 7.1, 5.4 Hz, 0.5H), 3.40 (dd, *J* 15.1, 11.2, 1H), 3.47-3.55 (m, 1H), 3.72 (dd, *J* 11.1, 8.3 Hz, 1H), 3.84 (ddt, *J* 11.2, 8.6, 2.9 Hz, 1H), 4.55 (s, 2H), 4.61 (dt, *J* 12.6, 3.5 Hz, 1H), 5.04 (d, *J* 41.6 Hz, 2H)

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 14.6, 14.7, 19.2, 19.4, 20.9, 25.4, 26.4, 26.5, 29.9, 30.0, 30.4, 30.5, 59.7, 59.9, 60.3, 60.6, 62.1, 62.2, 66.7, 66.8, 70.6, 72.3, 98.6, 98.9, 113.0, 113.1, 142.9, 143.0, 170.7

HRMS (ESI, m/z): calcd. for $C_{16}H_{27}O_5^+$ ($[M]^+$): 299.1853, found: 299.1874.

(4*R*,*E*)-1,9,9-Trimethyl-5-methylene-12-oxabicyclo[9.1.0]dodec-7-en-4-ol (35)



MW (g/mol): 236.35 **Molecular formula: $C_{15}H_{24}O_2$**

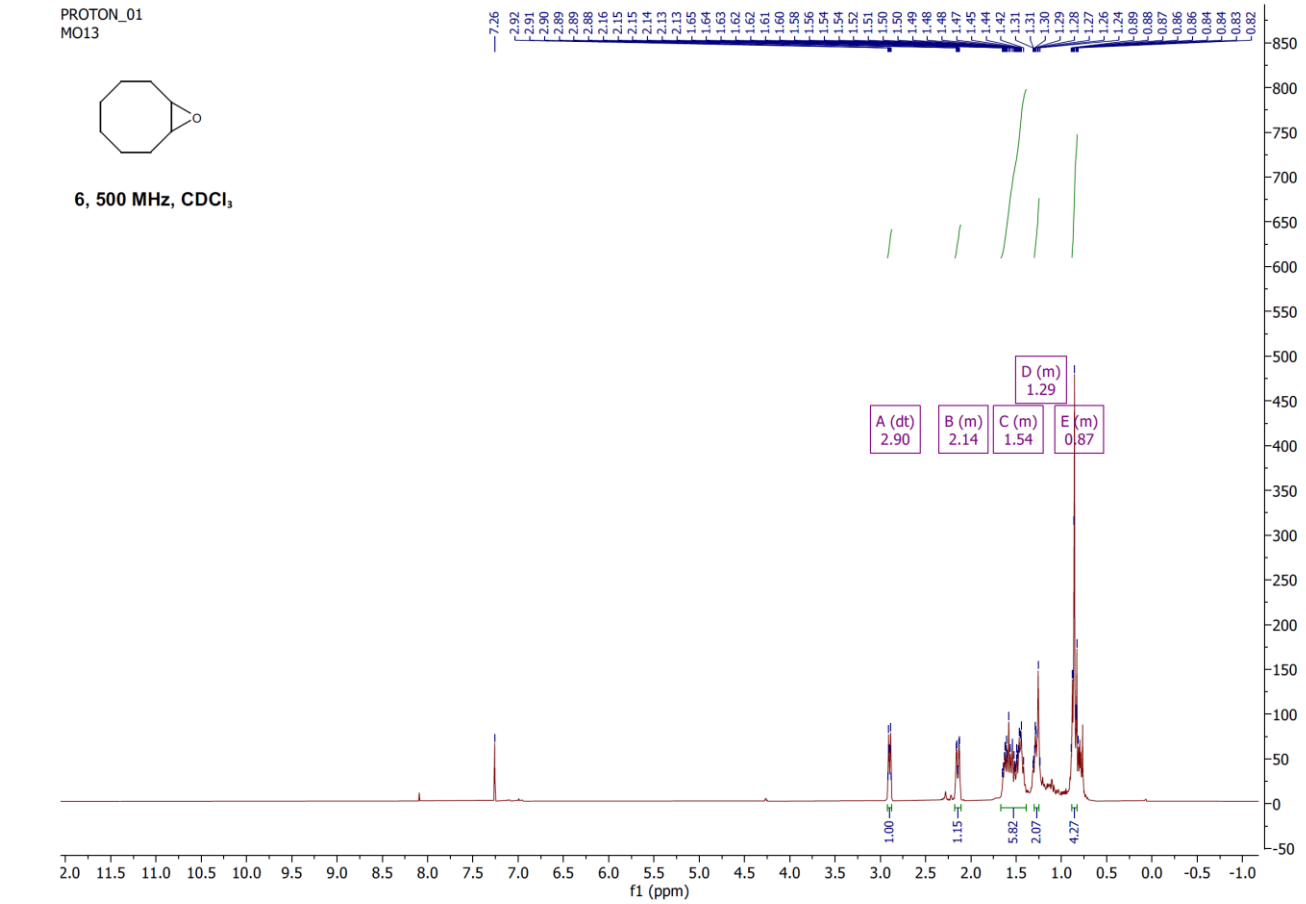
From (*R*,4*E*,8*E*)-6,6,9-trimethyl-2-methylenecycloundeca-4,8-dien-1-ol. **Rf:** 0.38 [CH_2Cl_2:EtOAc (5:1)], CH_2Cl_2:EtOAc (5:1), Yield: **71%**, White oil (Method B)

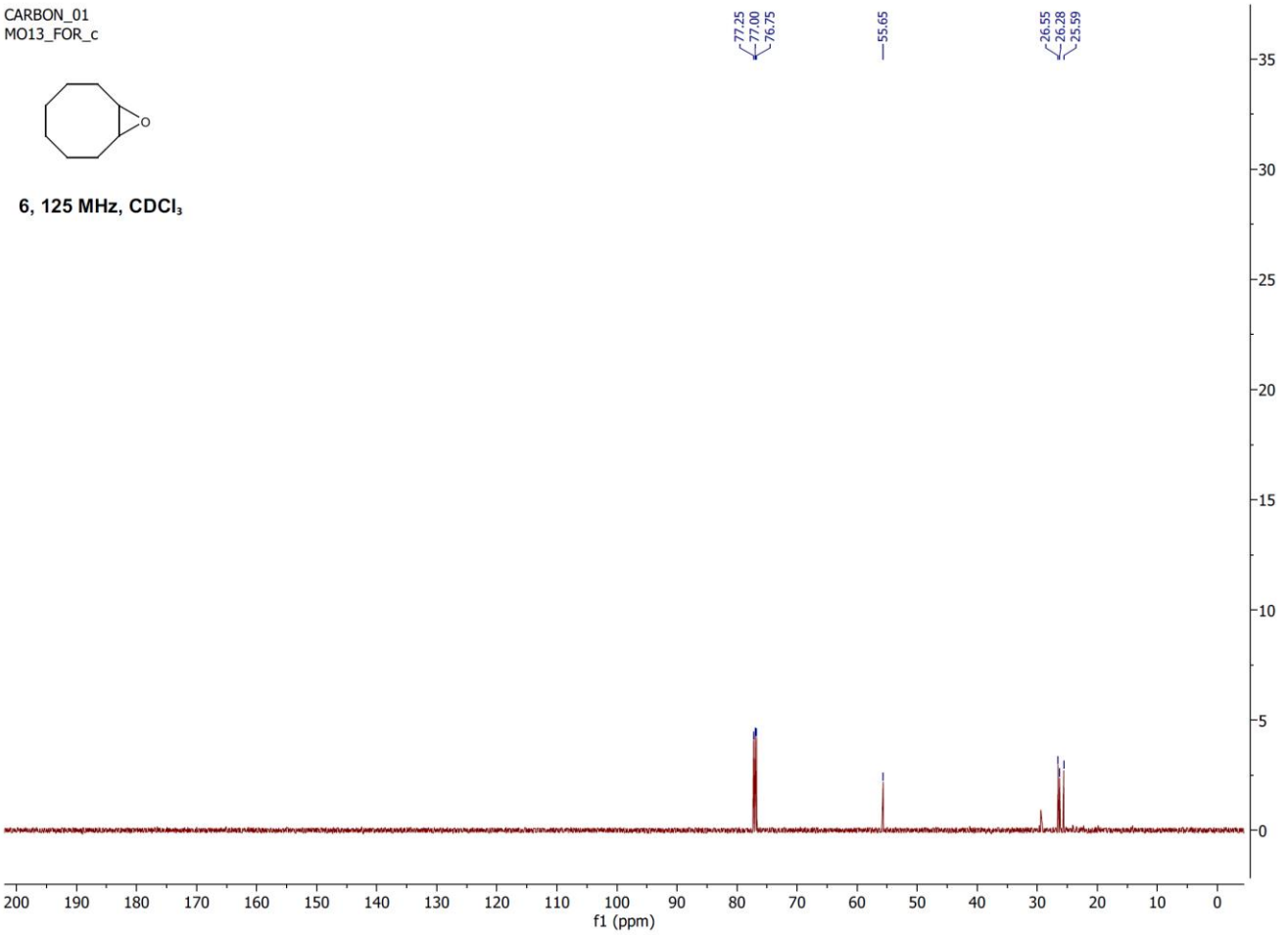
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.07 (s, 3H), 1.19 (s, 3H), 1.37 (s, 3H), 1.55-1.61 (m, 2H), 1.68 (d, *J* 12.5 Hz, 1H), 1.82 (dddd, *J* 14.6, 10.1, 4.6, 3.5 Hz, 1H), 2.12 (ddd, *J* 13.7, 10.0, 3.3 Hz, 1H), 3.35 (qd, *J* 7.1, 4.7 Hz, 1H), 4.07 (dd, *J* 7.3, 4.6 Hz, 1H), 4.95 (s, 1H), 5.06 (s, 1H), 5.25 (ddd, *J* 20.4, 10.0, 4.8 Hz, 1H), 5.36 (dd, *J* 15.6, 1.3 Hz, 1H) ppm

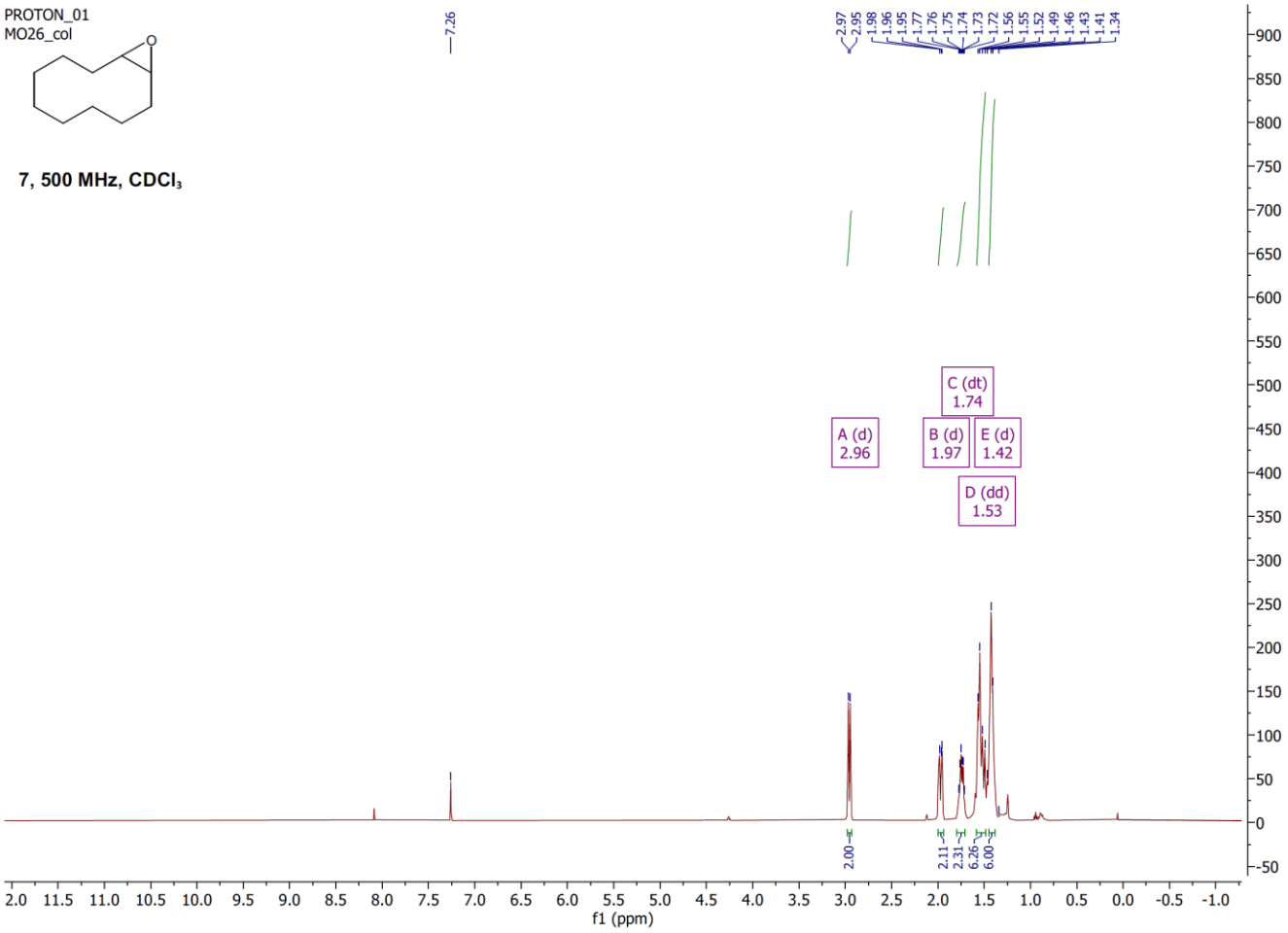
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 19.8, 23.7, 31.3, 34.6, 34.8, 35.7, 38.7, 41.0, 61.3, 61.5, 70.2, 109.7, 125.0, 140.4, 150.5 ppm

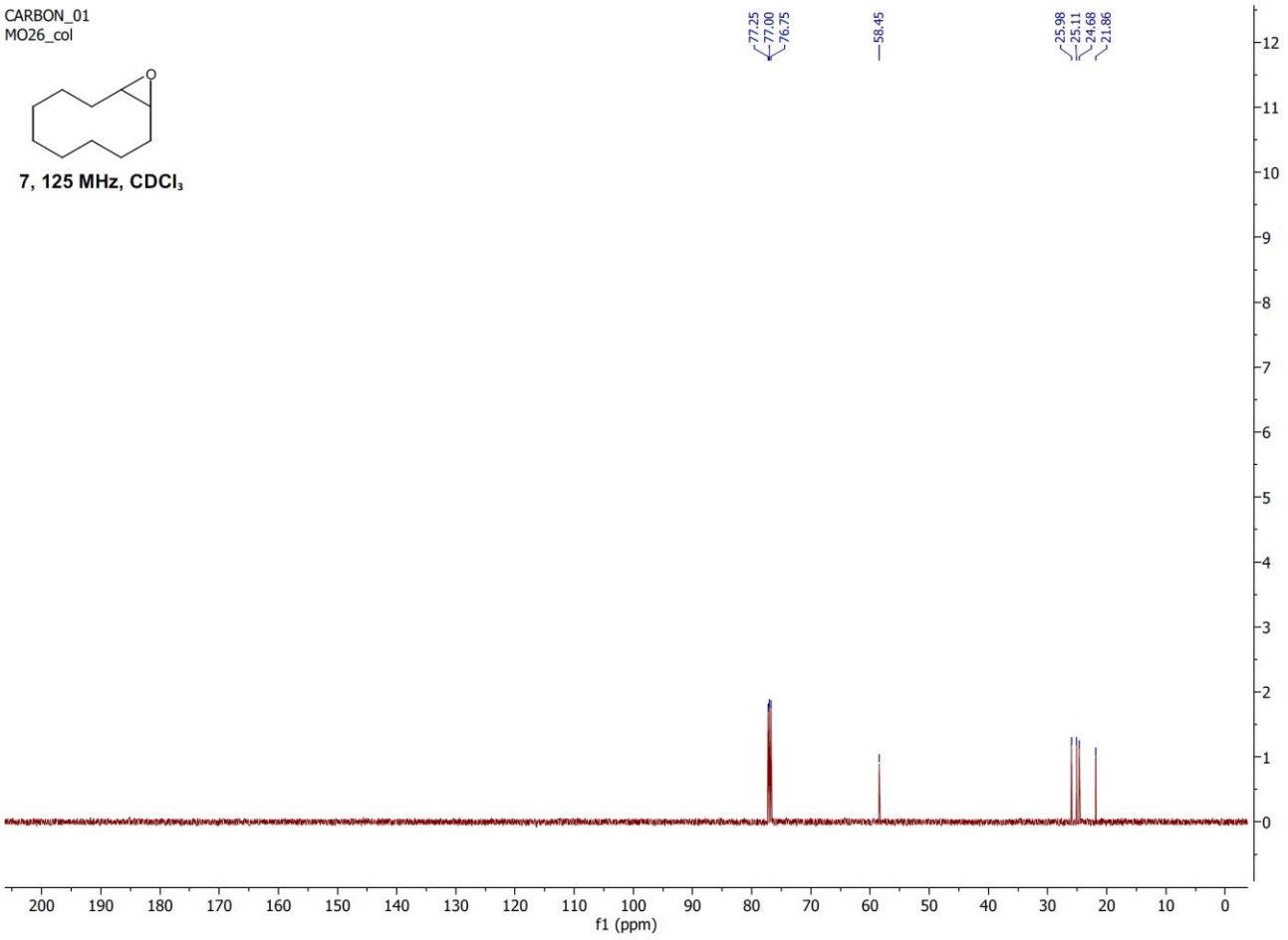
HRMS (ESI, m/z): calcd. for $C_{15}H_{24}O_2Na^+$ ($[M+Na]^+$): 259.3392, found: 258.1479.

Spectra for catalytic epoxidation reaction

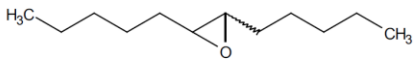





PROTON_01
MO26_col
7, 500 MHz, CDCl3
7.26
2.97
2.95
1.98
1.96
1.95
1.77
1.76
1.75
1.74
1.73
1.72
1.56
1.55
1.52
1.49
1.46
1.43
1.41
1.34
C (dt)
1.74
A (d)
2.96
B (d)
1.97
E (d)
1.42
D (dd)
1.53
2.00
2.11
2.31
6.26
6.00
f1 (ppm)


CARBON_01
MO26_col
7, 125 MHz, CDCl3
77.25
77.00
76.75
58.45
25.98
25.11
24.68
21.86
f1 (ppm)

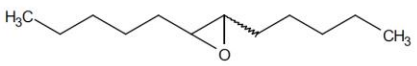
PROTON_01
MO28_st



8, 500 MHz, $CDCl_3$

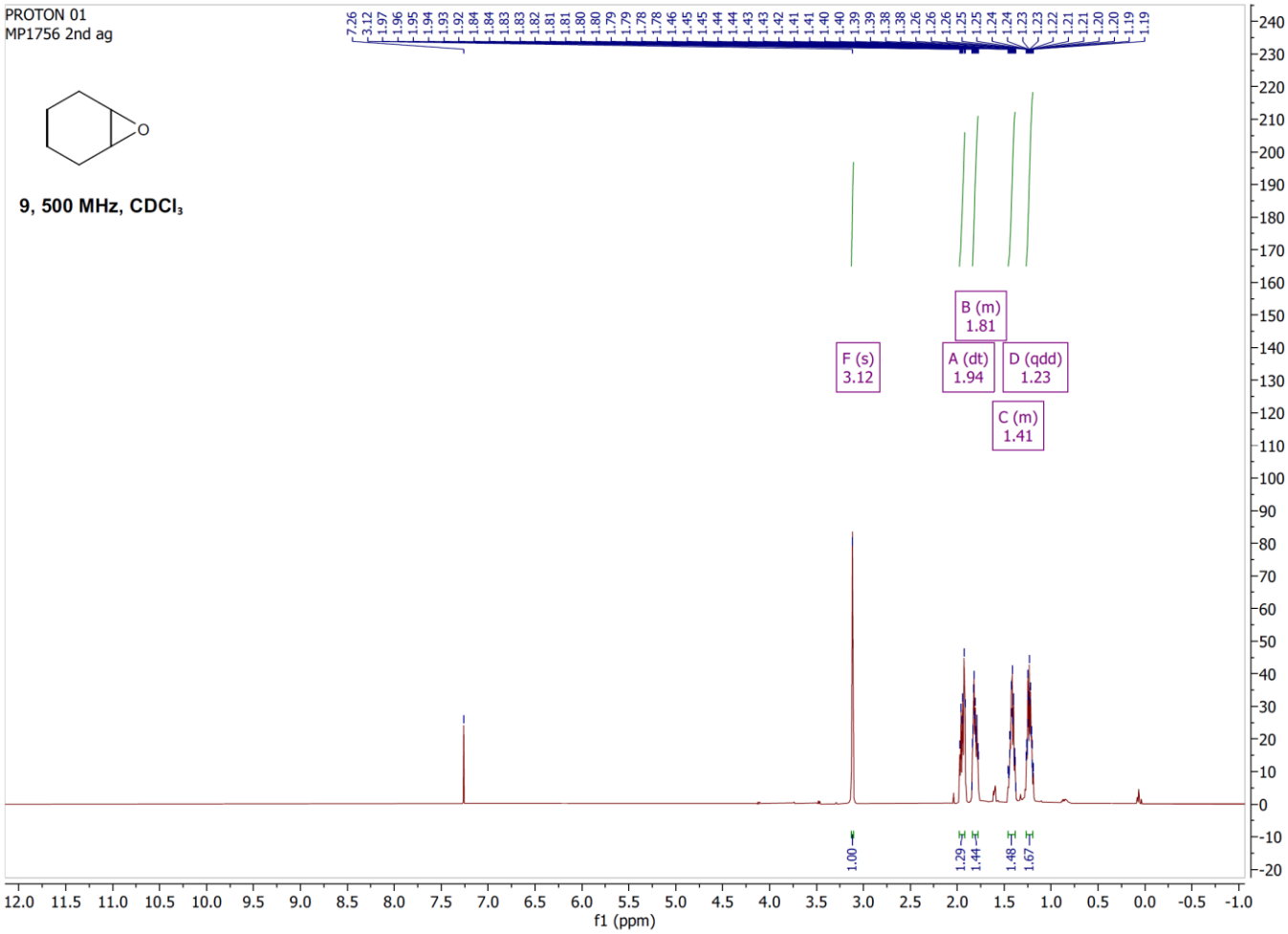
mixture of diastereoisomers

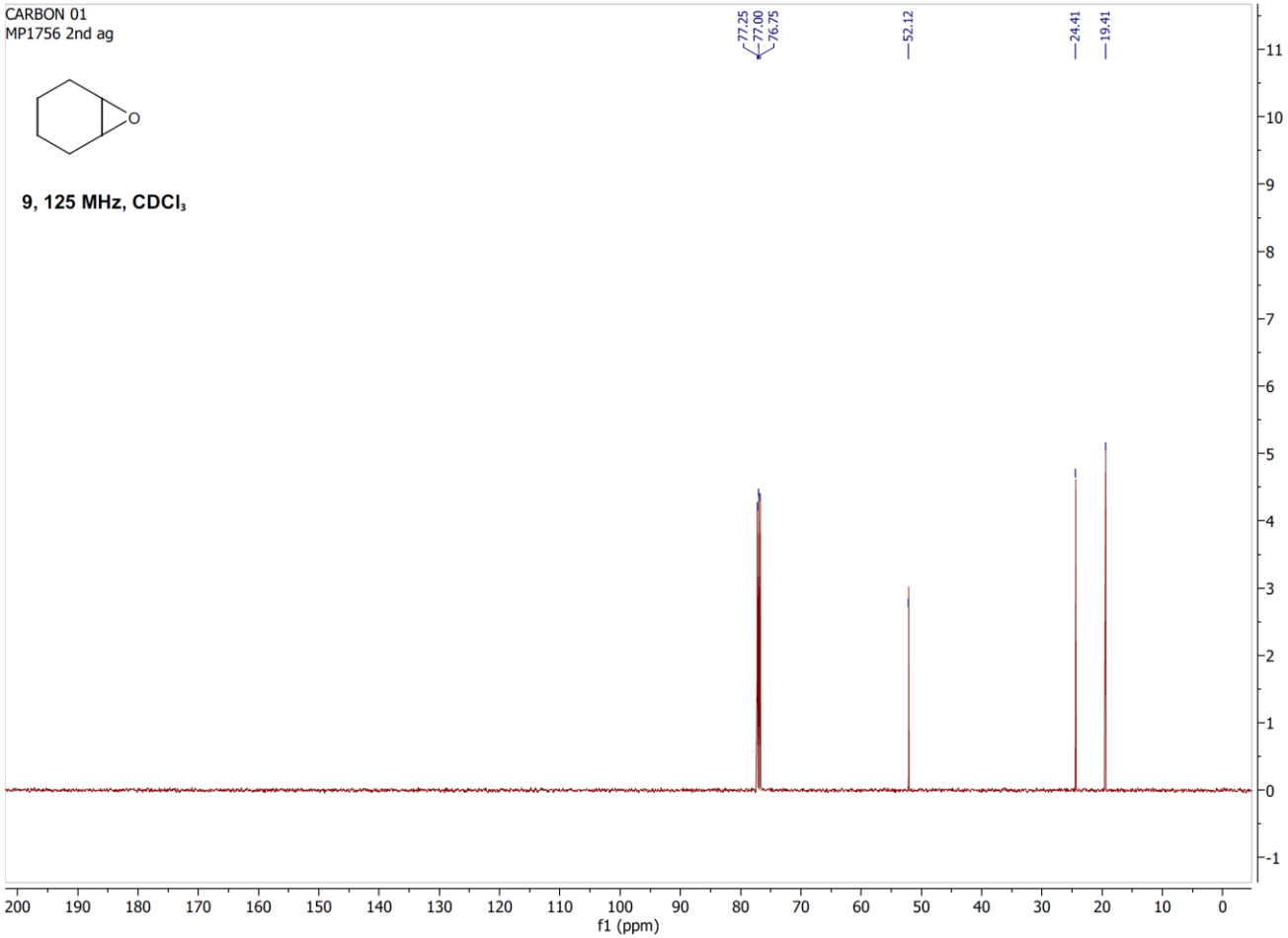
CARBON_01
MP28_st_for_carbon

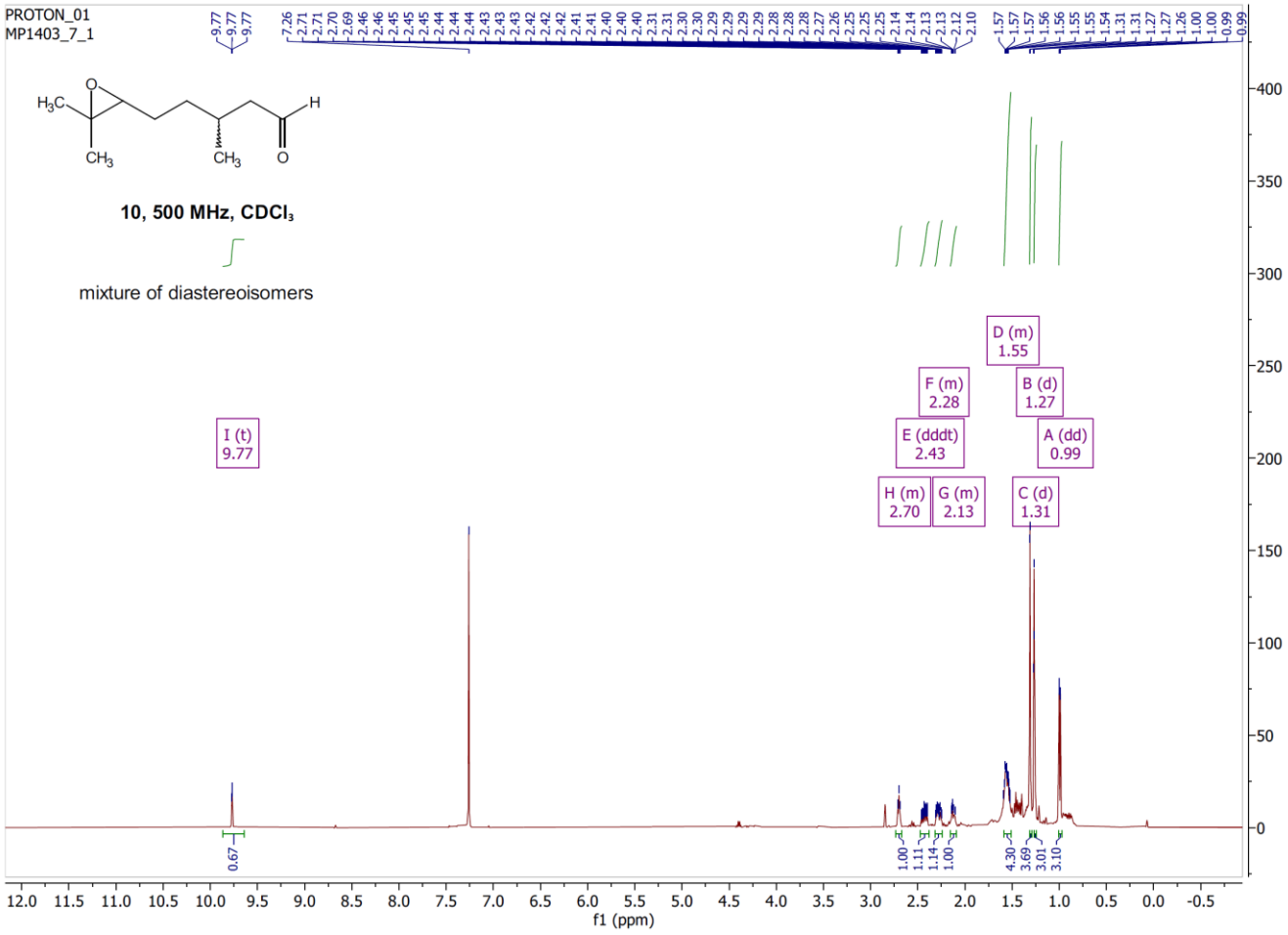


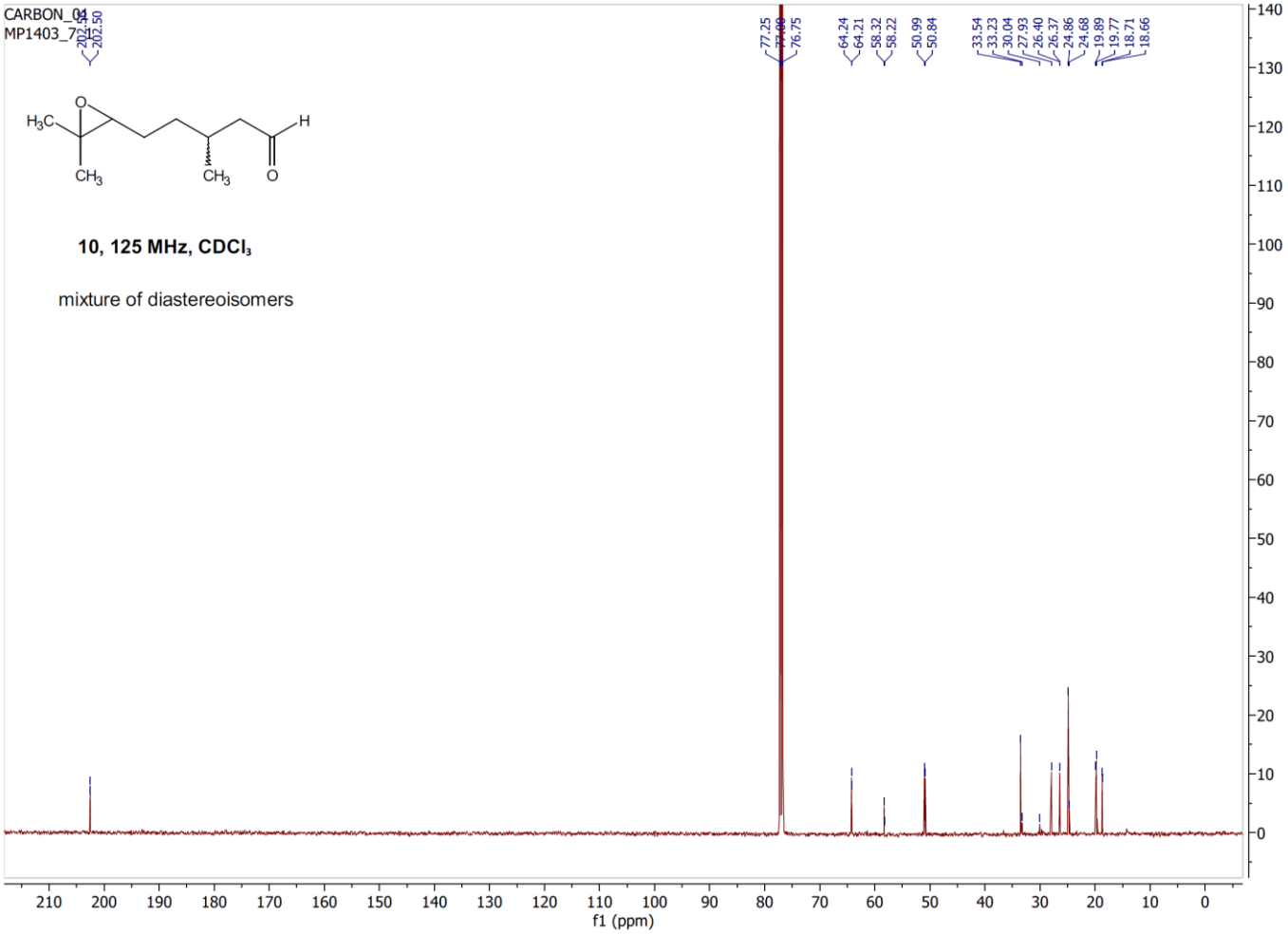
8, 125 MHz, $CDCl_3$

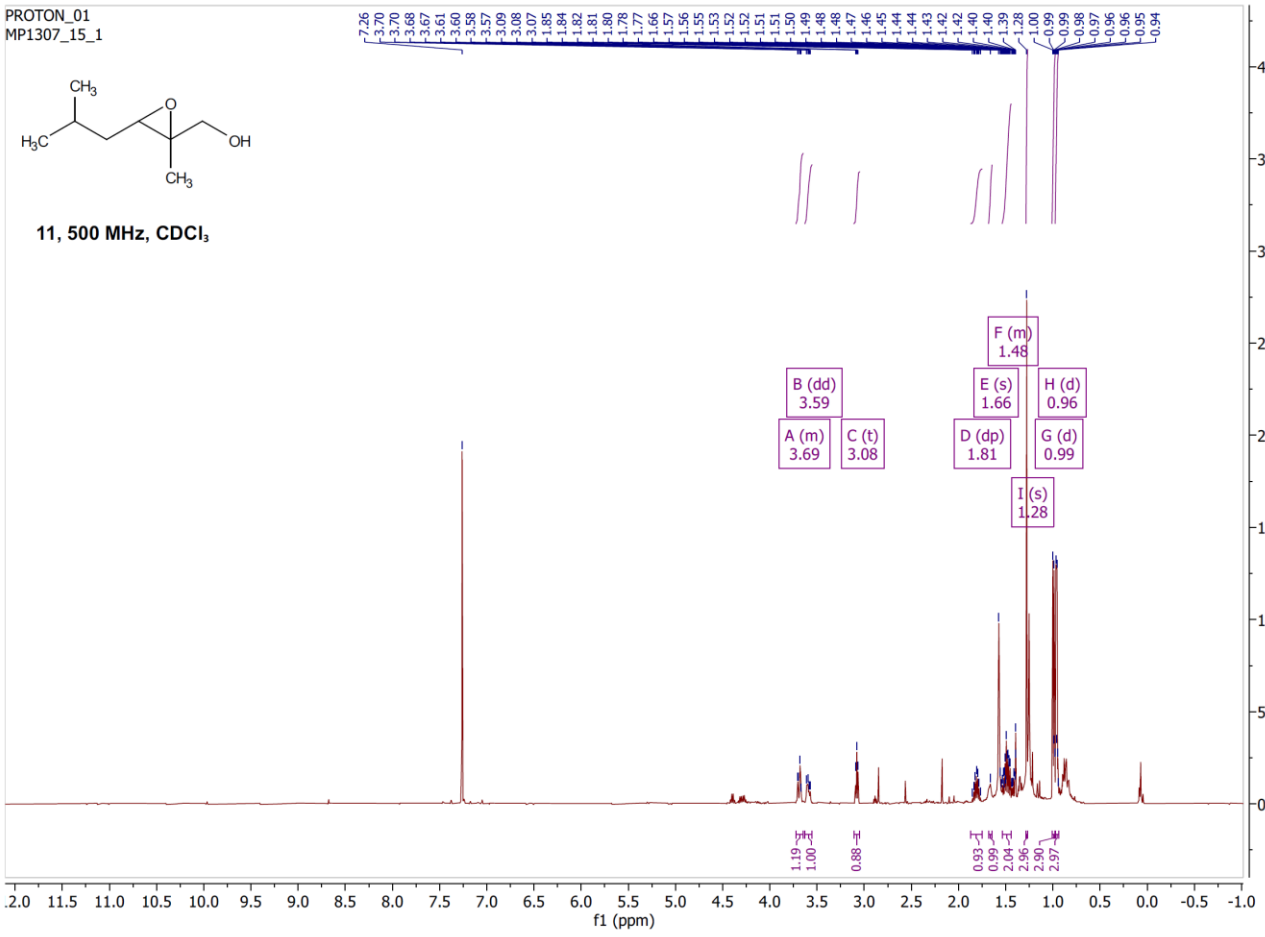
mixture of diastereoisomers

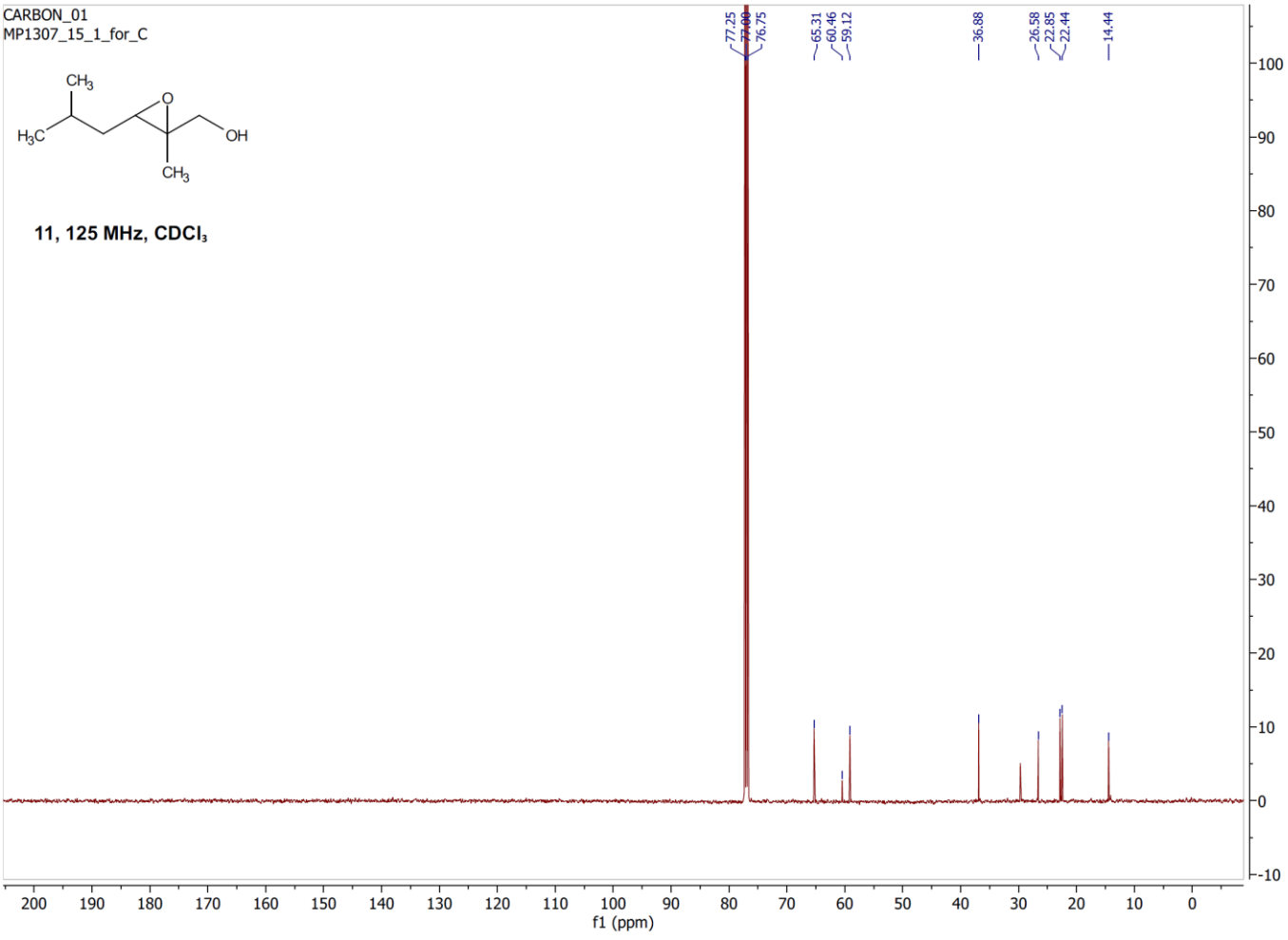

PROTON 01
MP1756 2nd ag
9, 500 MHz, CDCl3
B (m)
1.81
F (s)
3.12
A (dt)
1.94
D (qdd)
1.23
C (m)
1.41
1.00
1.29
1.44
1.48
1.67
f1 (ppm)

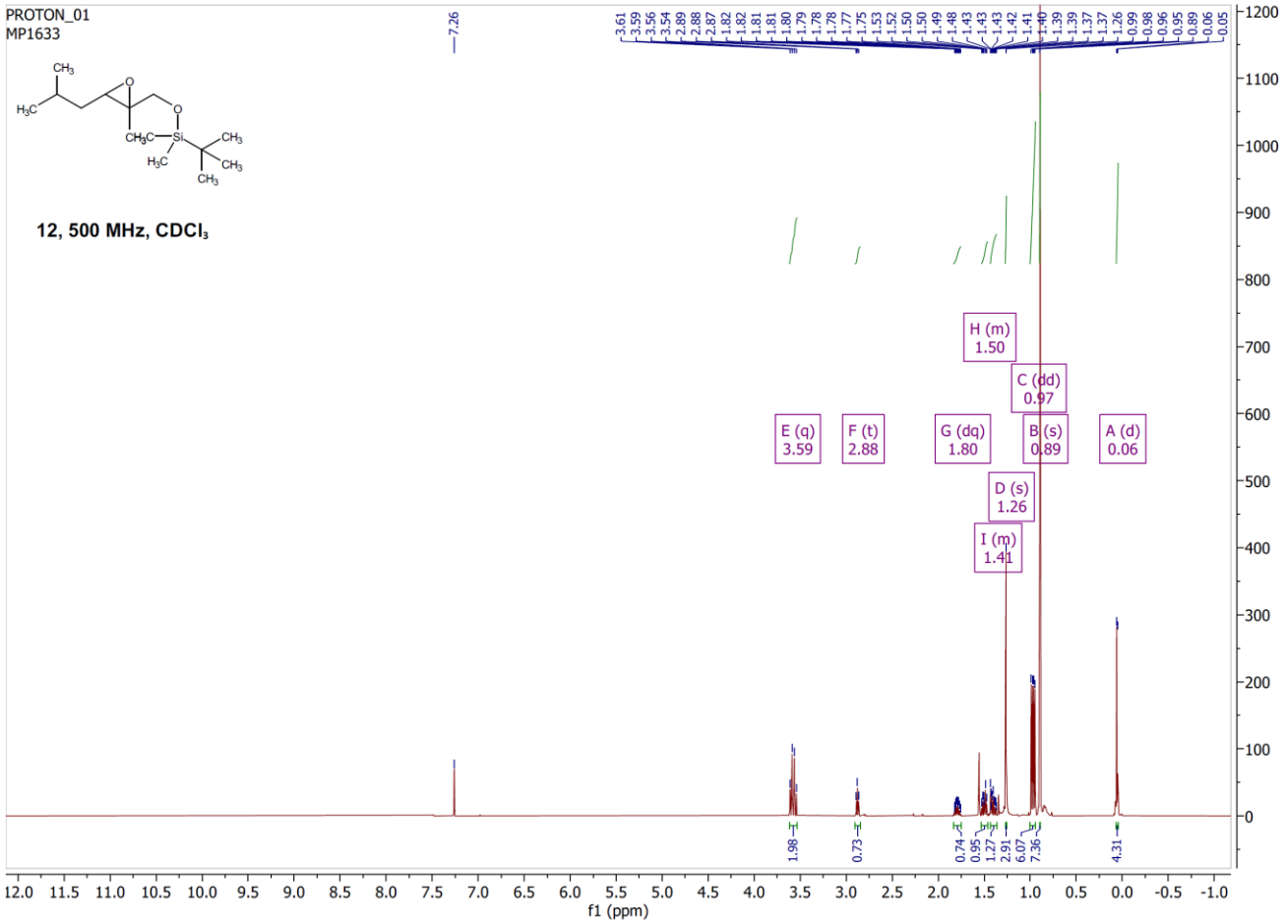

CARBON 01
MP1756 2nd ag
9, 125 MHz, CDCl3
77.25
77.00
76.75
52.12
24.41
19.41
f1 (ppm)

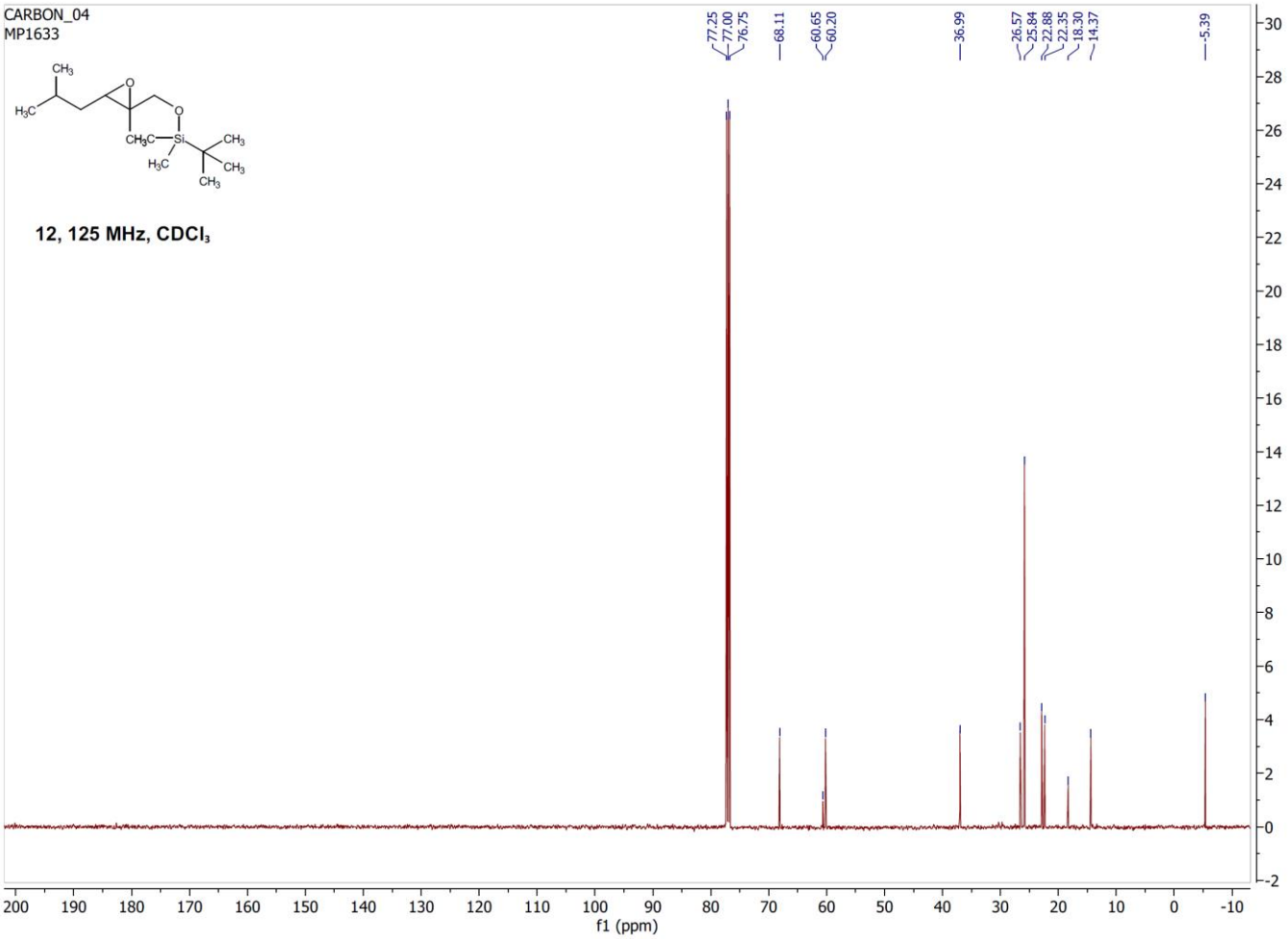

PROTON_01
MP1403_7_1
10, 500 MHz, CDCl3
mixture of diastereoisomers
I (t) 9.77
F (m) 2.28
E (dddt) 2.43
H (m) 2.70
G (m) 2.13
D (m) 1.55
B (d) 1.27
A (dd) 0.99
C (d) 1.31
f1 (ppm)

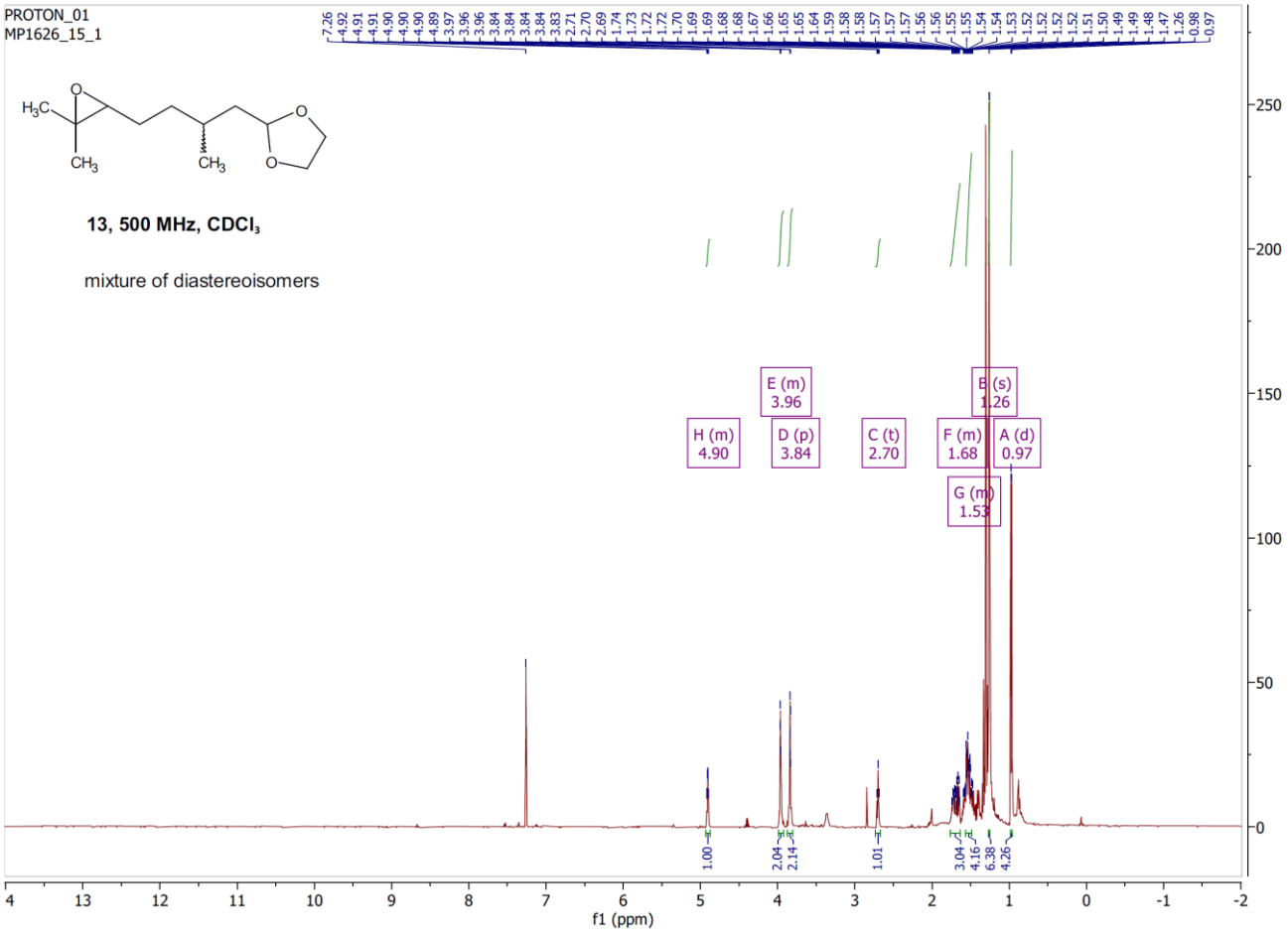

CARBON_01
MP1403_7_1
10, 125 MHz, CDCl3
mixture of diastereoisomers
f1 (ppm)

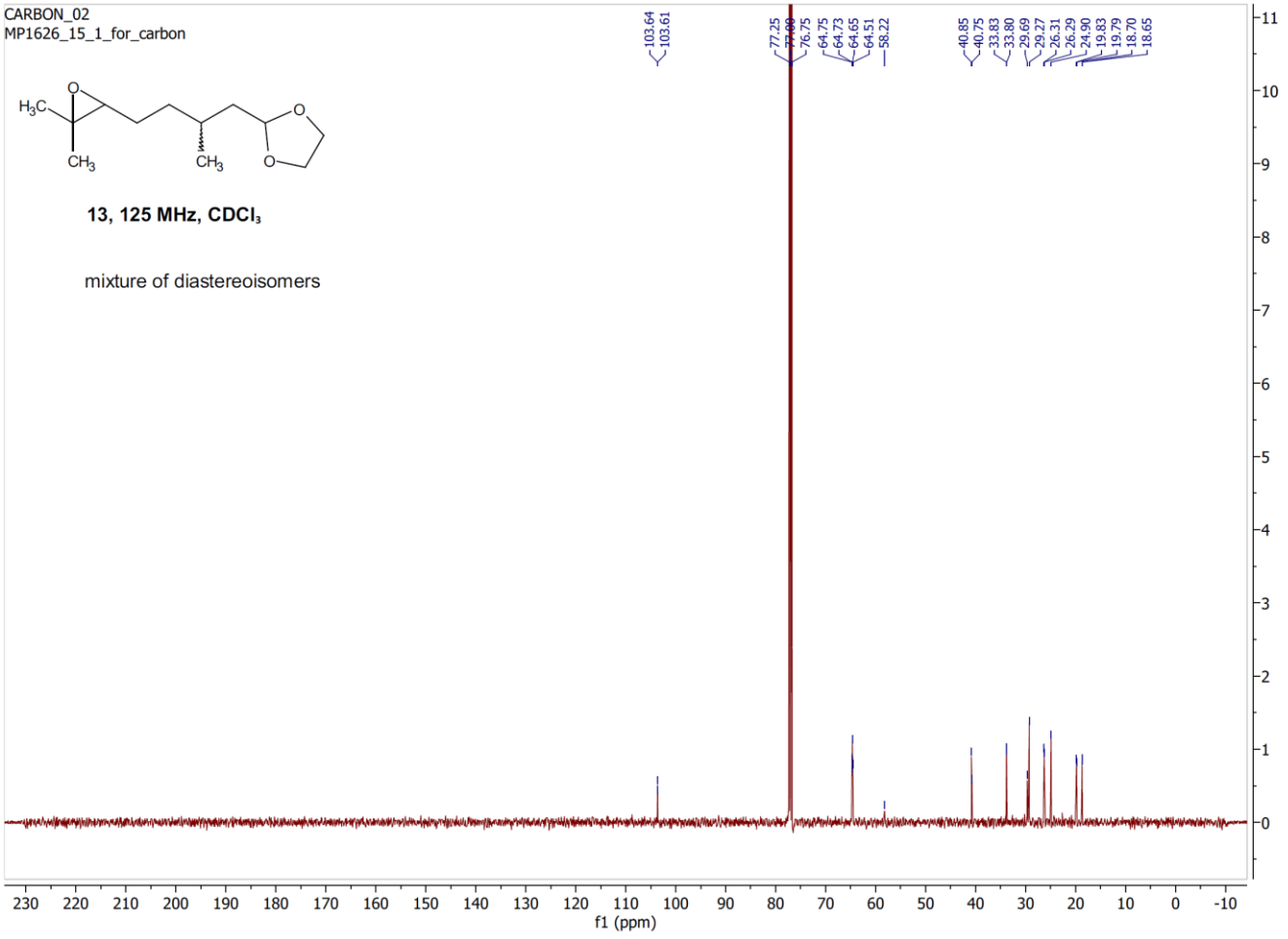

PROTON_01
MP1307_15_1
11, 500 MHz, CDCl₃
F (m) 1.48
B (dd) 3.59
E (s) 1.66
H (d) 0.96
A (m) 3.69
C (t) 3.08
D (dp) 1.81
G (d) 0.99
I (s) 1.28
f1 (ppm)

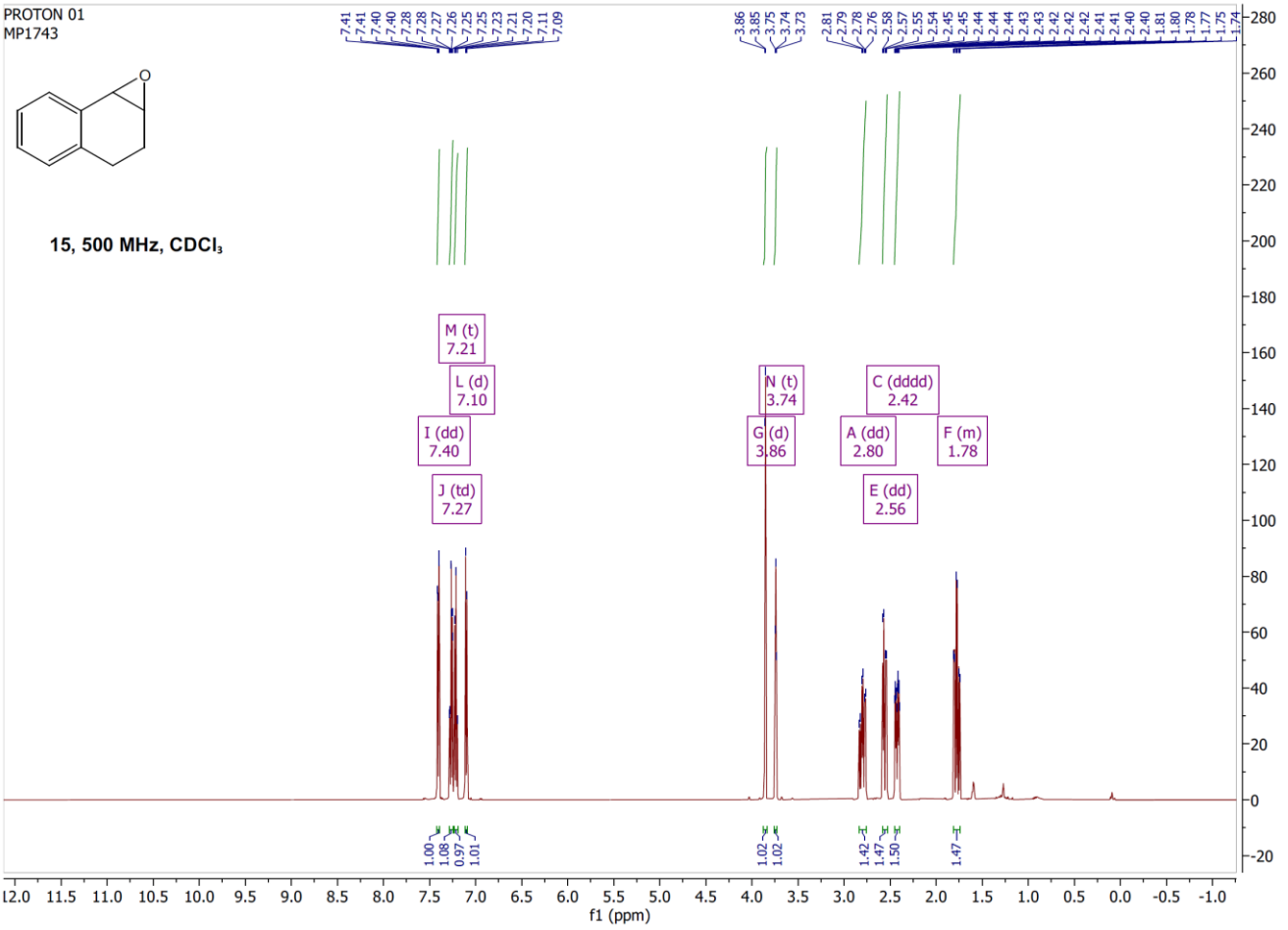

CARBON_01
MP1307_15_1_for_C
11, 125 MHz, CDCl₃
f1 (ppm)

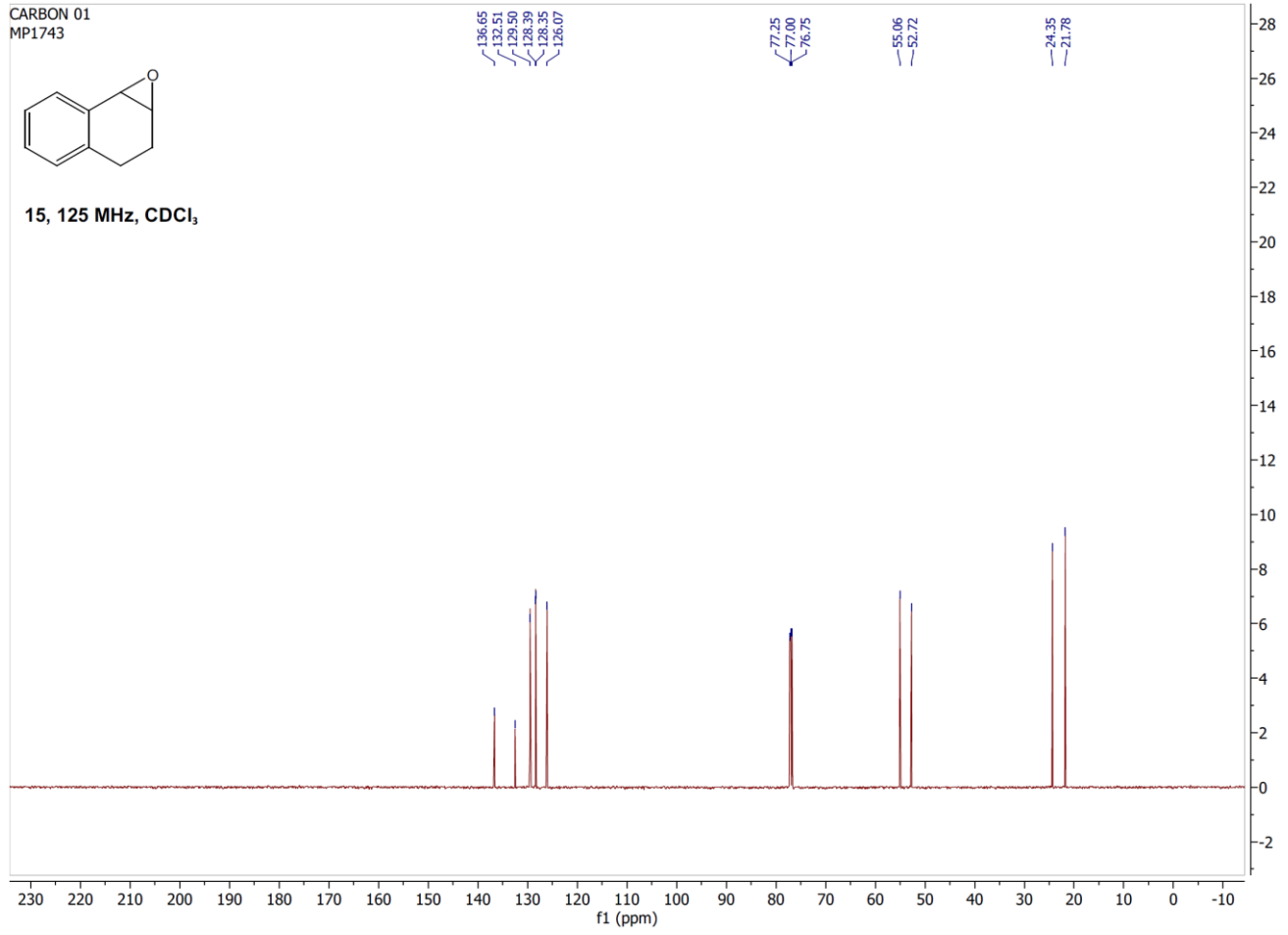

PROTON_01
MP1633
12, 500 MHz, CDCl3
H (m) 1.50
C (dd) 0.97
E (q) 3.59
F (t) 2.88
G (dq) 1.80
B (s) 0.89
A (d) 0.06
D (s) 1.26
I (m) 1.41
f1 (ppm)

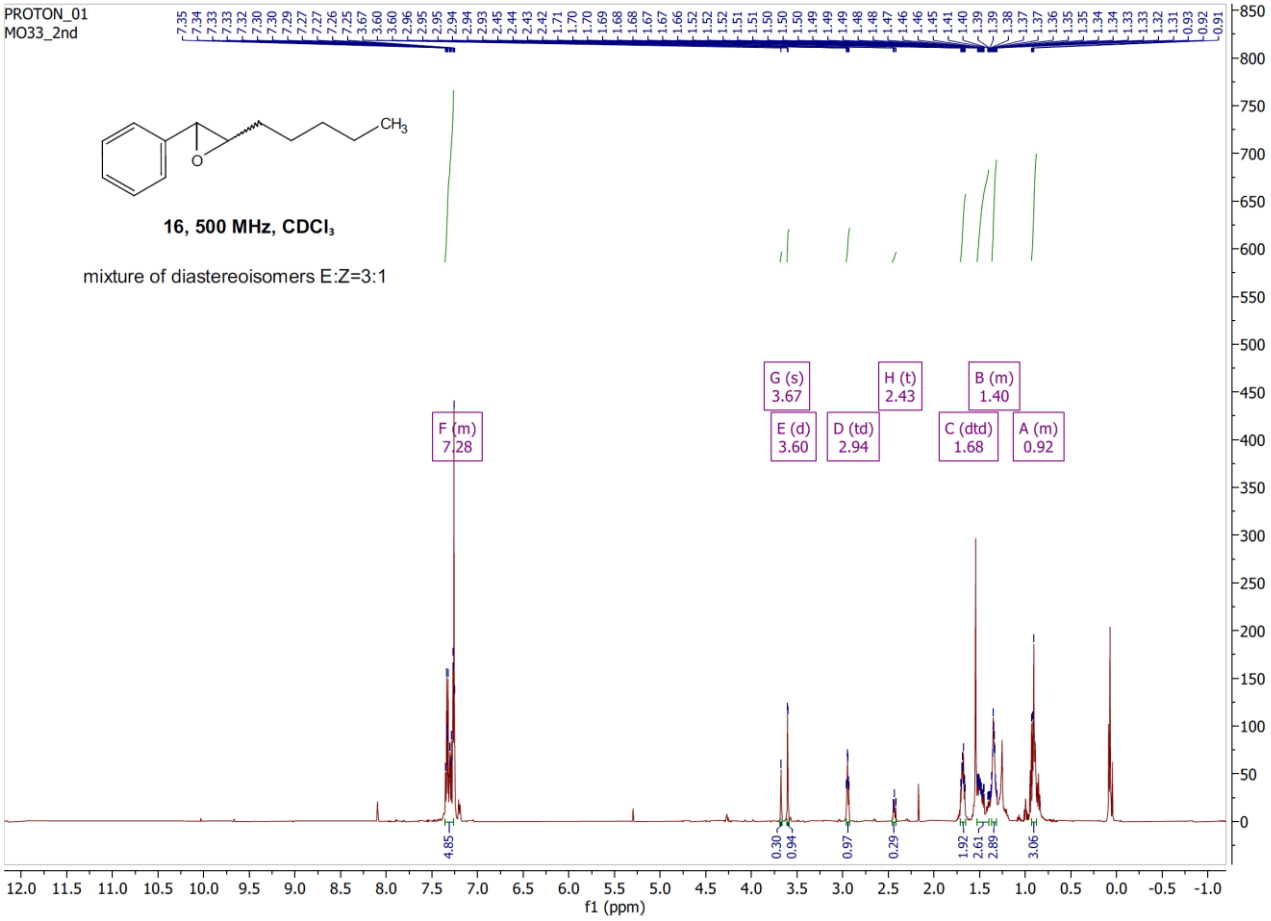

CARBON_04
MP1633
12, 125 MHz, CDCl3
f1 (ppm)

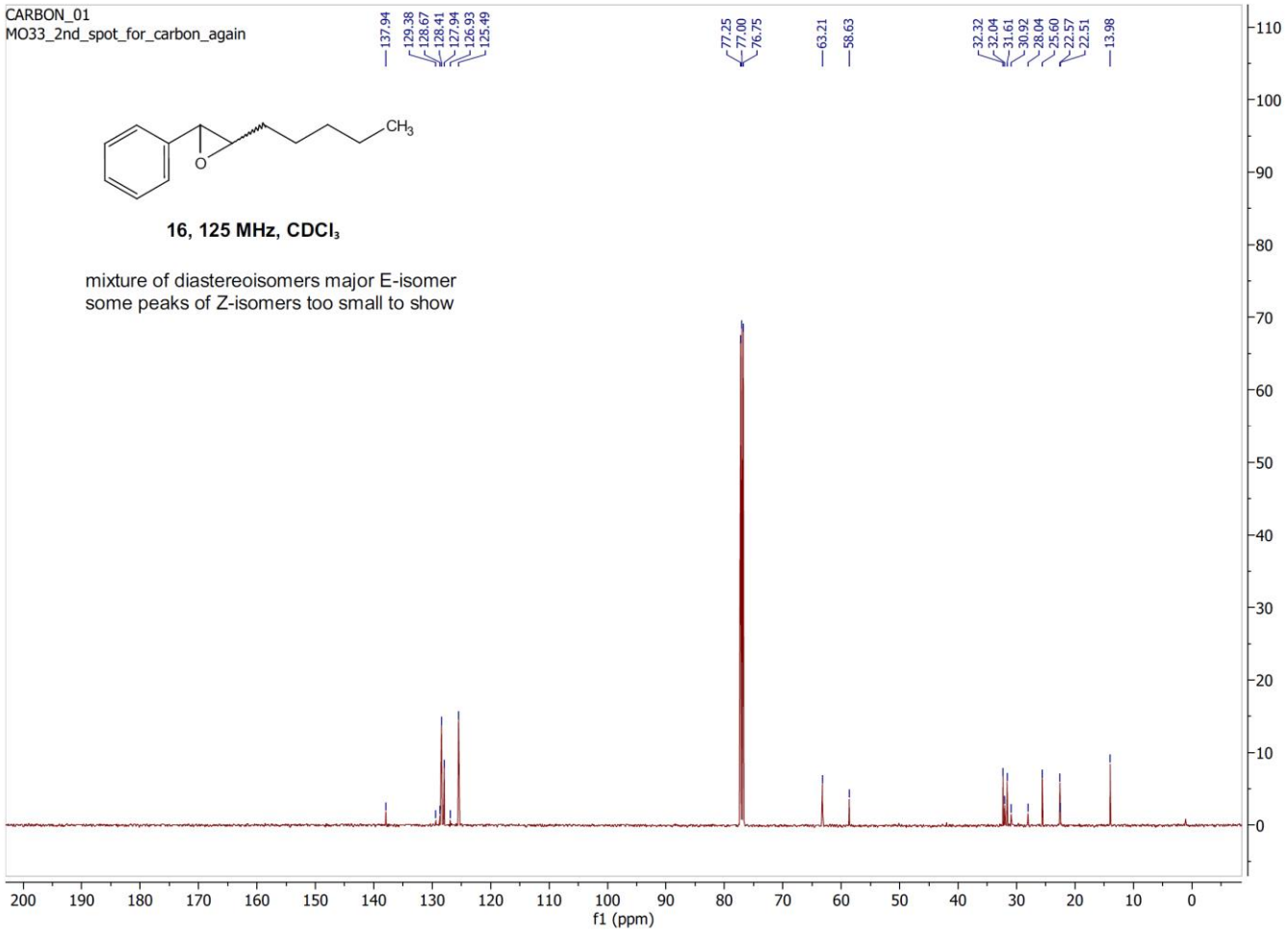

PROTON_01
MP1626_15_1
13, 500 MHz, CDCl3
mixture of diastereoisomers
E (m) 3.96
B (s) 1.26
H (m) 4.90
D (p) 3.84
C (t) 2.70
F (m) 1.68
A (d) 0.97
G (m) 1.53
1.00
2.04
2.14
1.01
3.04
4.16
6.38
4.26
f1 (ppm)

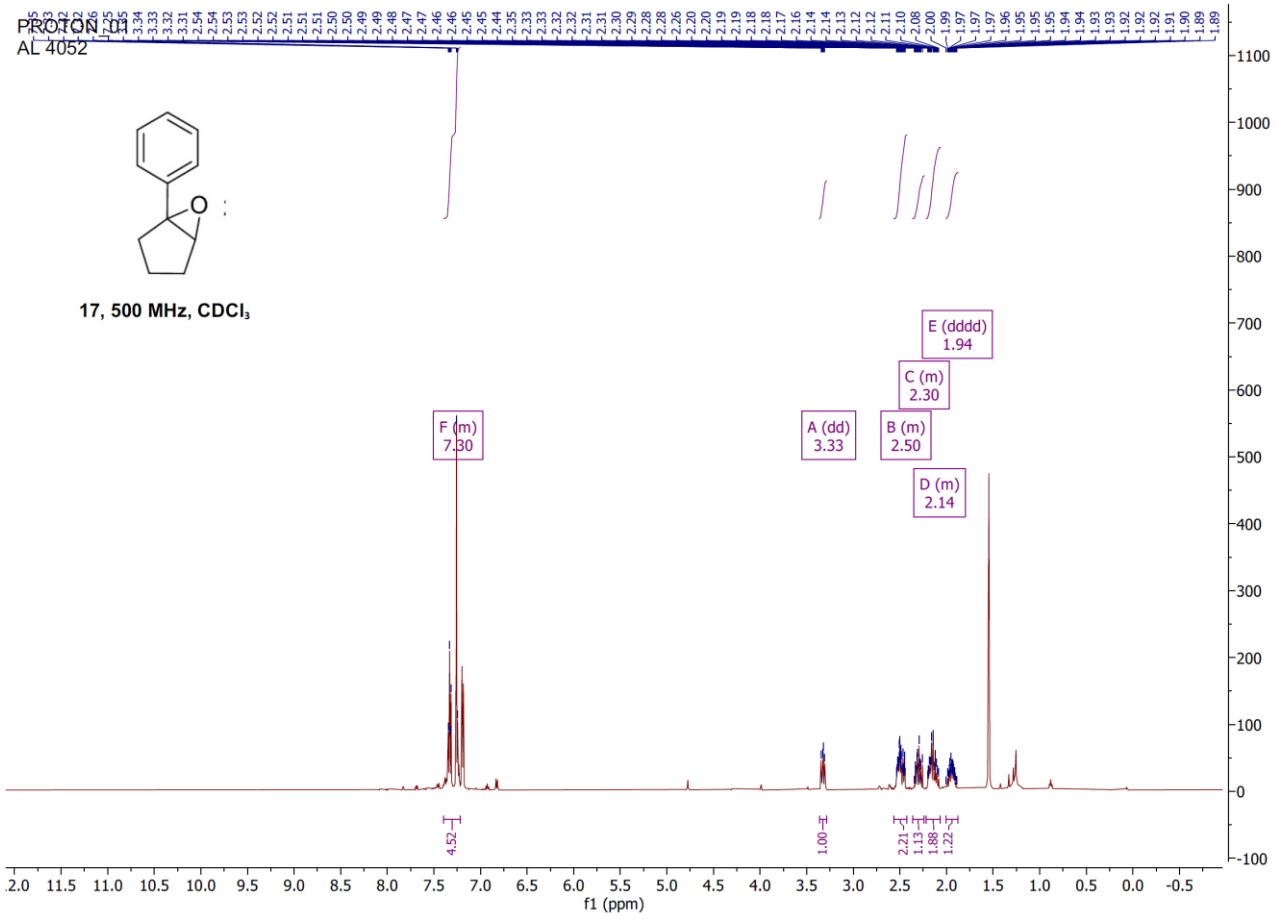

CARBON_02
MP1626_15_1_for_carbon
13, 125 MHz, CDCl3
mixture of diastereoisomers
103.64
103.61
77.25
77.00
76.75
64.75
64.73
64.65
64.51
58.22
40.85
40.75
33.83
33.80
29.69
29.27
26.31
26.29
24.90
19.83
19.79
18.70
18.65
f1 (ppm)

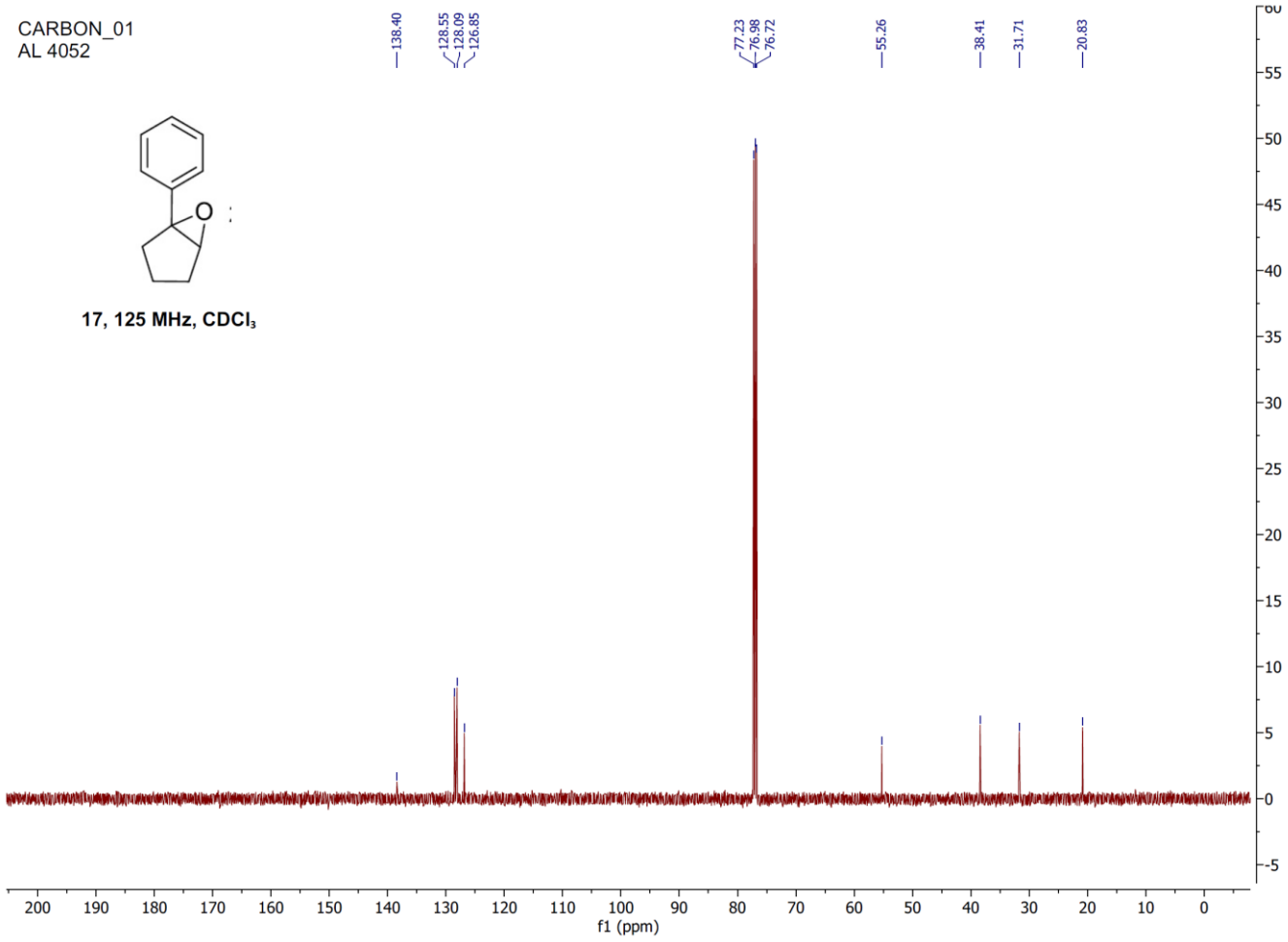

PROTON 01
MP1743
15, 500 MHz, CDCl3
M (t) 7.21
L (d) 7.10
I (dd) 7.40
J (td) 7.27
N (t) 3.74
G (d) 3.86
C (dddd) 2.42
A (dd) 2.80
F (m) 1.78
E (dd) 2.56
f1 (ppm)

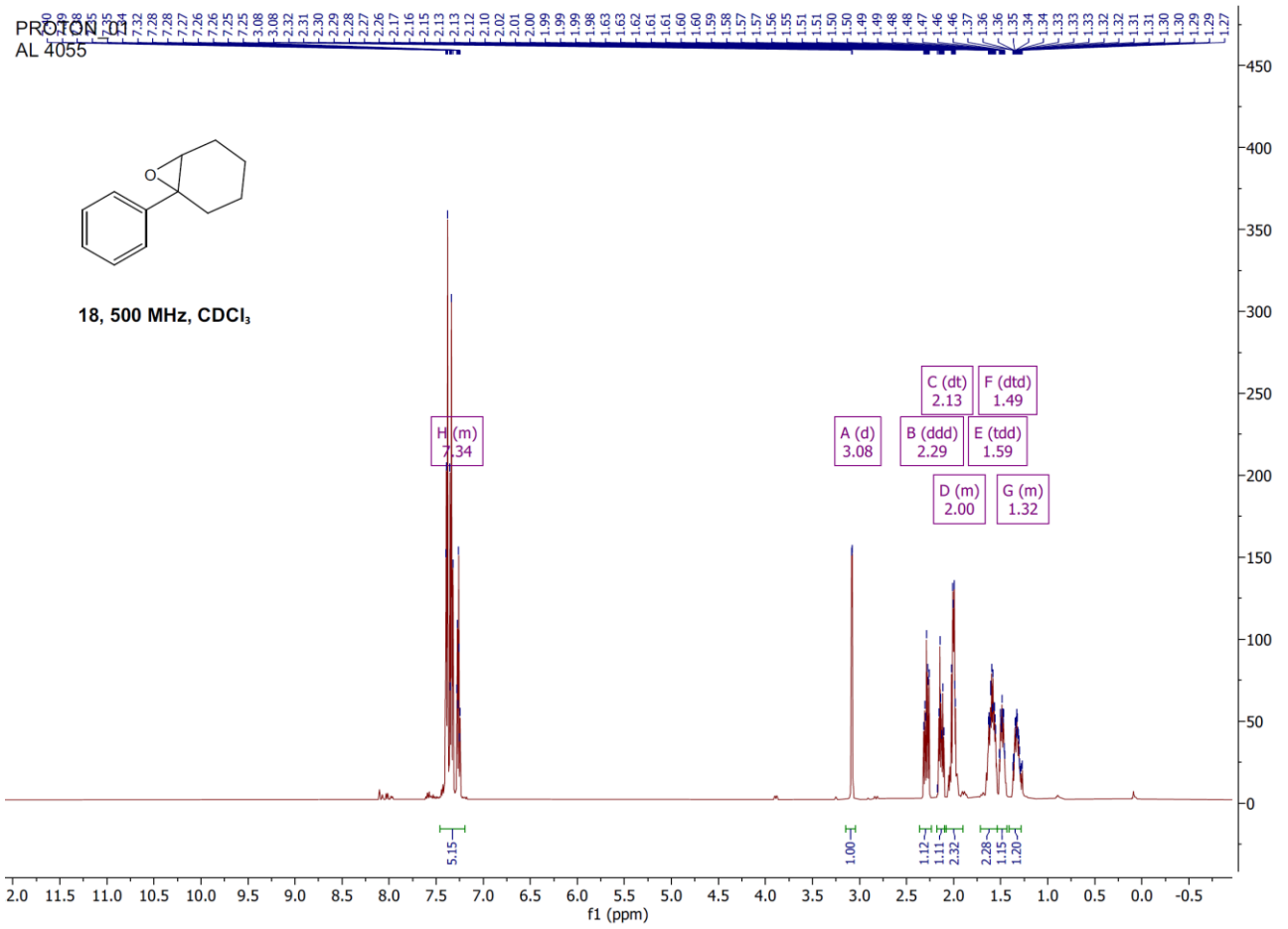

CARBON 01
MP1743
15, 125 MHz, CDCl3
f1 (ppm)

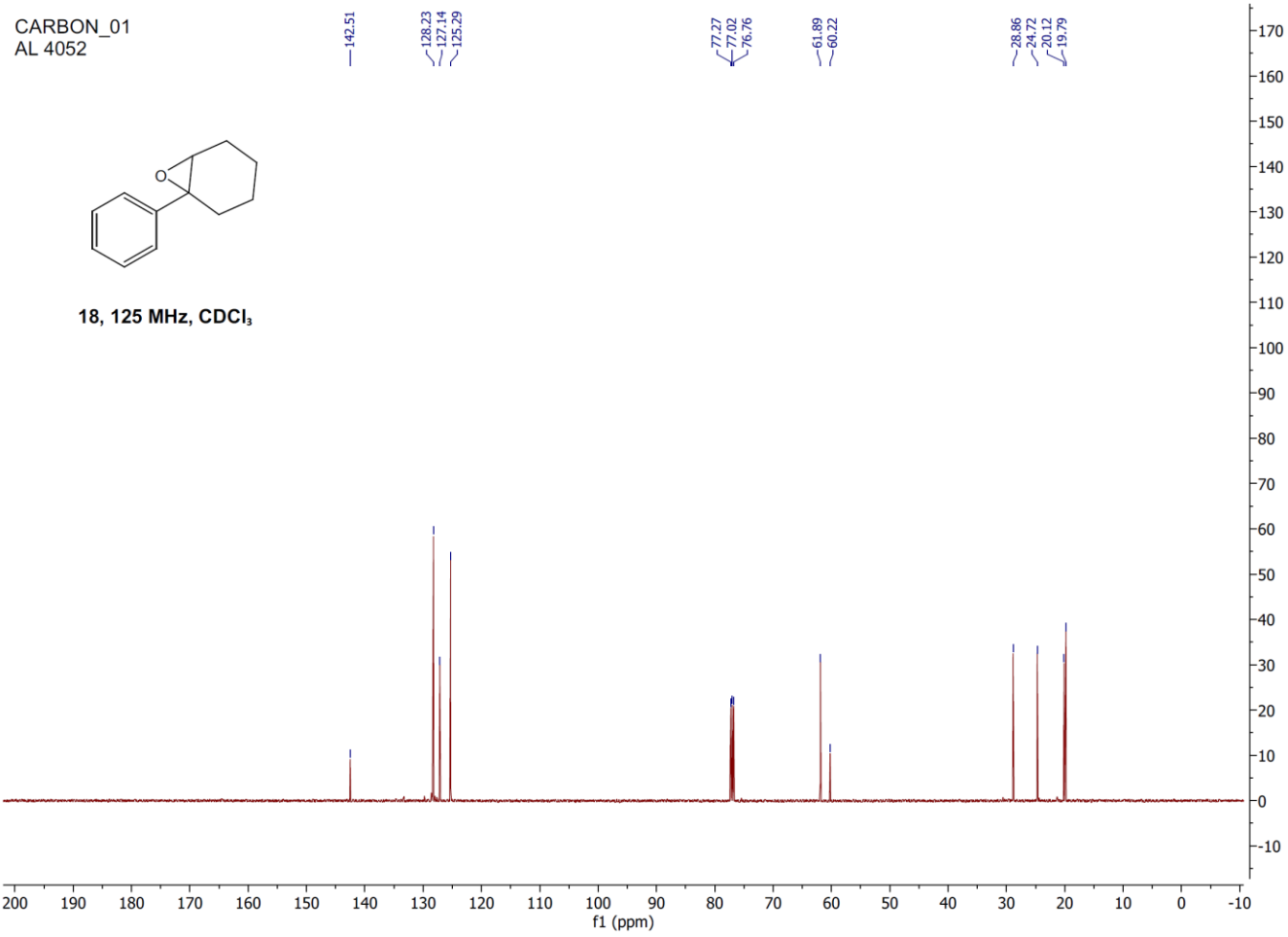

PROTON_01
MO33_2nd
16, 500 MHz, CDCl3
mixture of diastereoisomers E:Z=3:1
F (m) 7.28
G (s) 3.67
E (d) 3.60
D (td) 2.94
H (t) 2.43
C (dtd) 1.68
B (m) 1.40
A (m) 0.92
f1 (ppm)

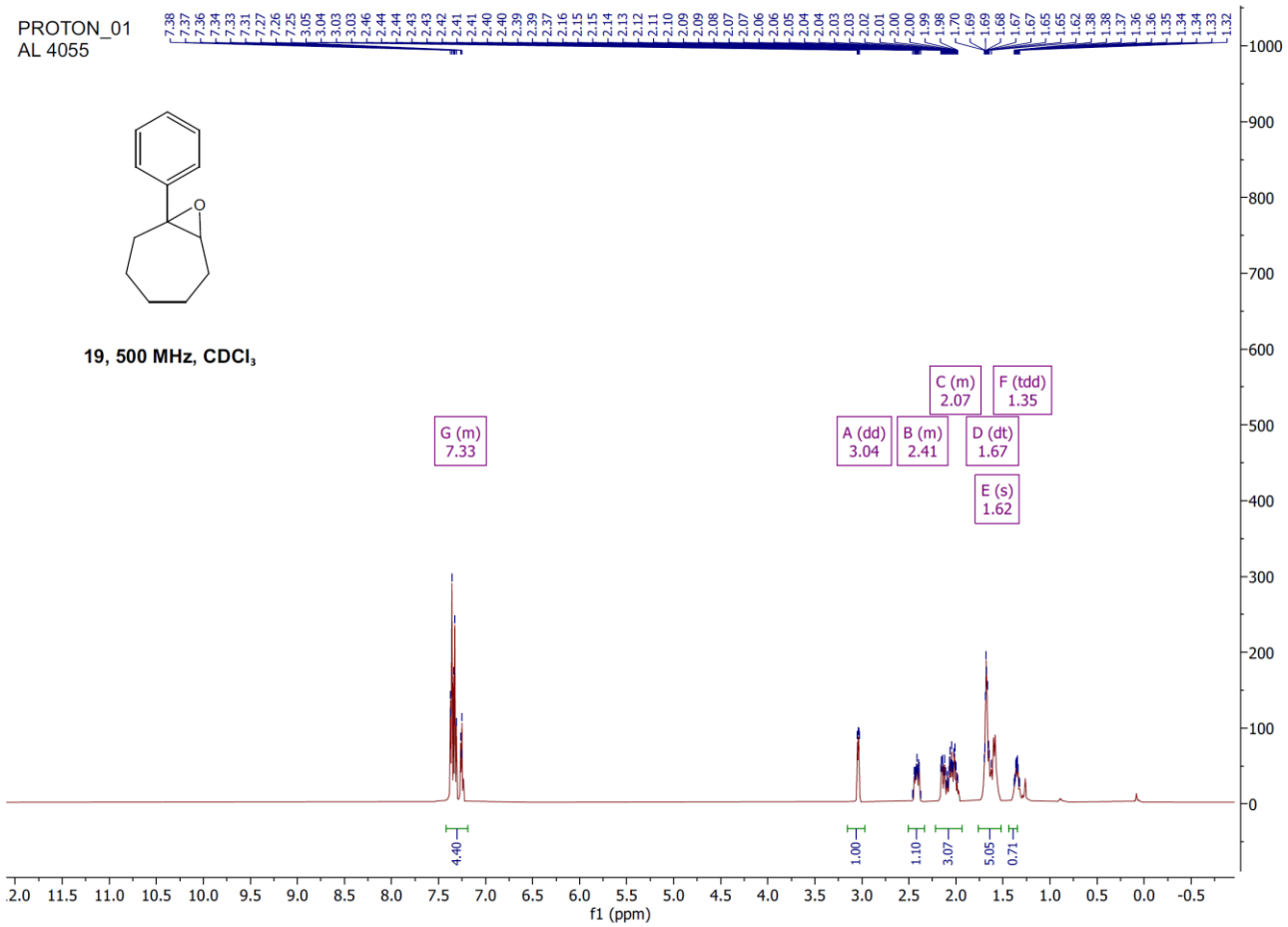

CARBON_01
MO33_2nd_spot_for_carbon_again
16, 125 MHz, CDCl3
mixture of diastereoisomers major E-isomer
some peaks of Z-isomers too small to show
f1 (ppm)


PROTON_01
AL 4052
17, 500 MHz, CDCl3
F (m)
7.30
A (dd)
3.33
B (m)
2.50
C (m)
2.30
D (m)
2.14
E (dddd)
1.94
4.52
1.00
2.21
1.13
1.88
1.22
f1 (ppm)

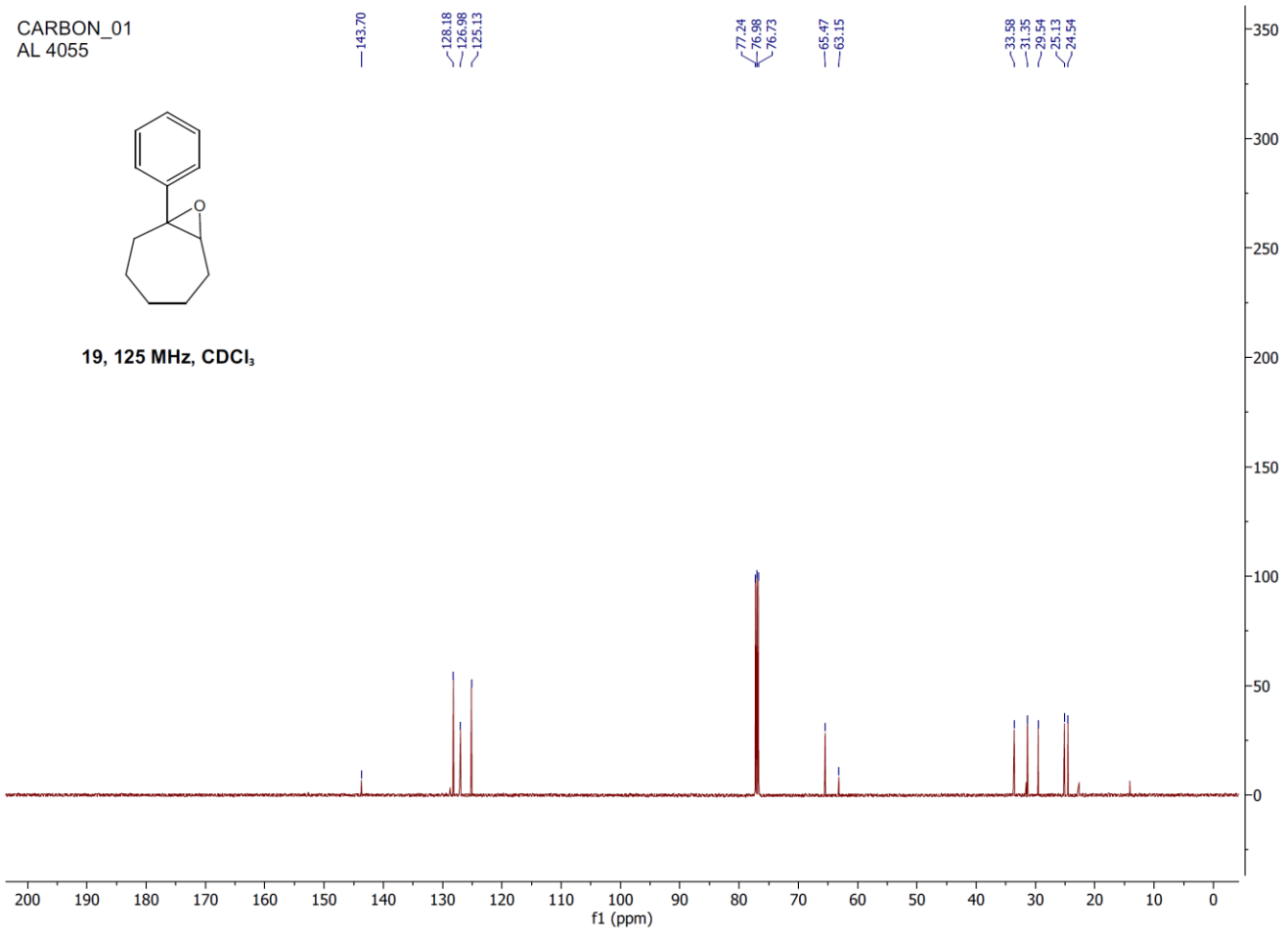

CARBON_01
AL 4052
17, 125 MHz, CDCl3
138.40
128.55
128.09
126.85
77.23
76.98
76.72
55.26
38.41
31.71
20.83
f1 (ppm)


PROTON_02
AL 4055
18, 500 MHz, CDCl3
H (m)
7.34
A (d)
3.08
C (dt)
2.13
F (dtd)
1.49
B (ddd)
2.29
E (tdd)
1.59
D (m)
2.00
G (m)
1.32
5.15
1.00
1.12
1.11
2.32
2.28
1.15
1.20
f1 (ppm)

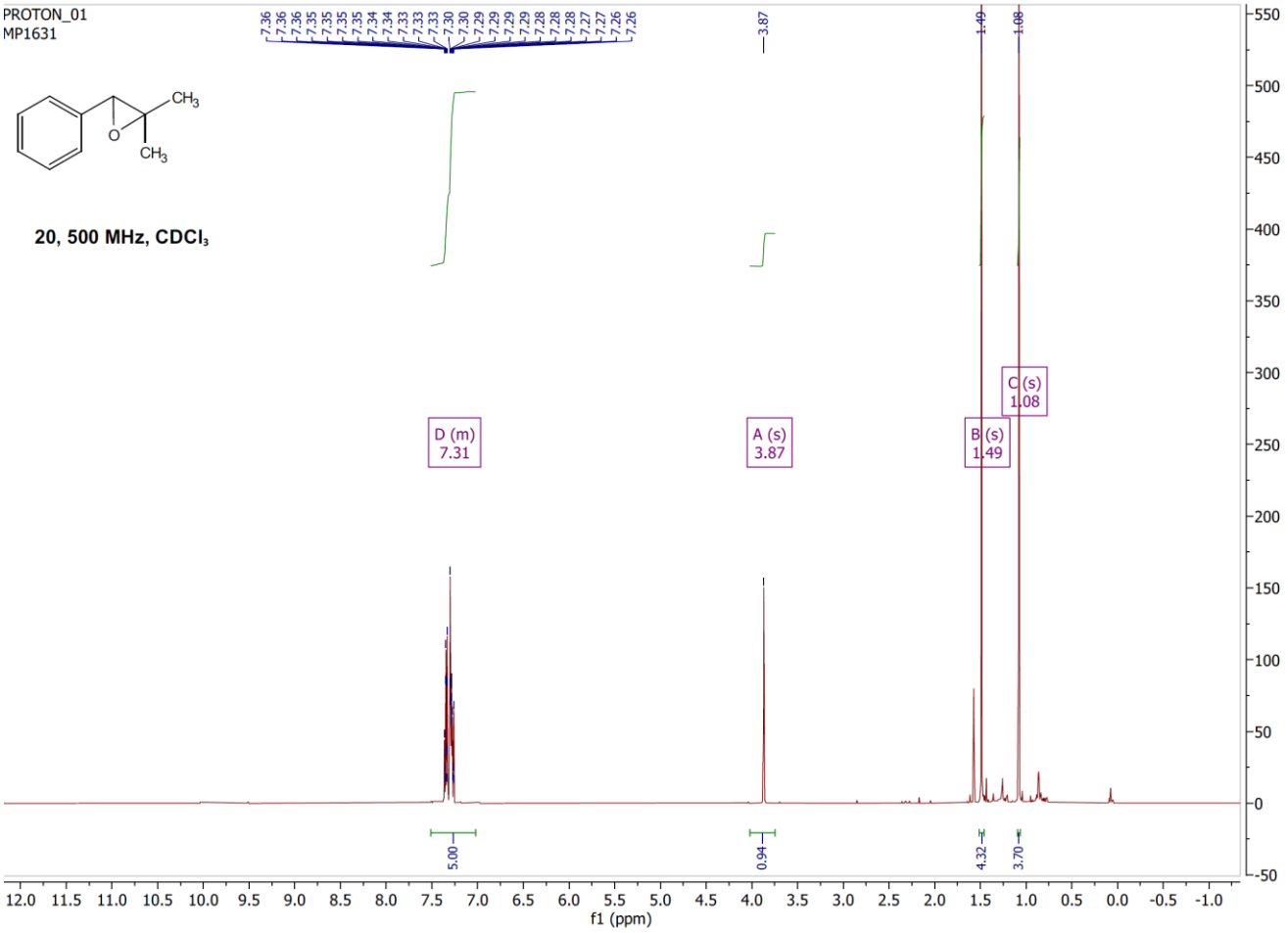

CARBON_01
AL 4052
142.51
128.23
127.14
125.29
77.27
77.02
76.76
61.89
60.22
28.86
24.72
20.12
19.79
18, 125 MHz, CDCl3
f1 (ppm)

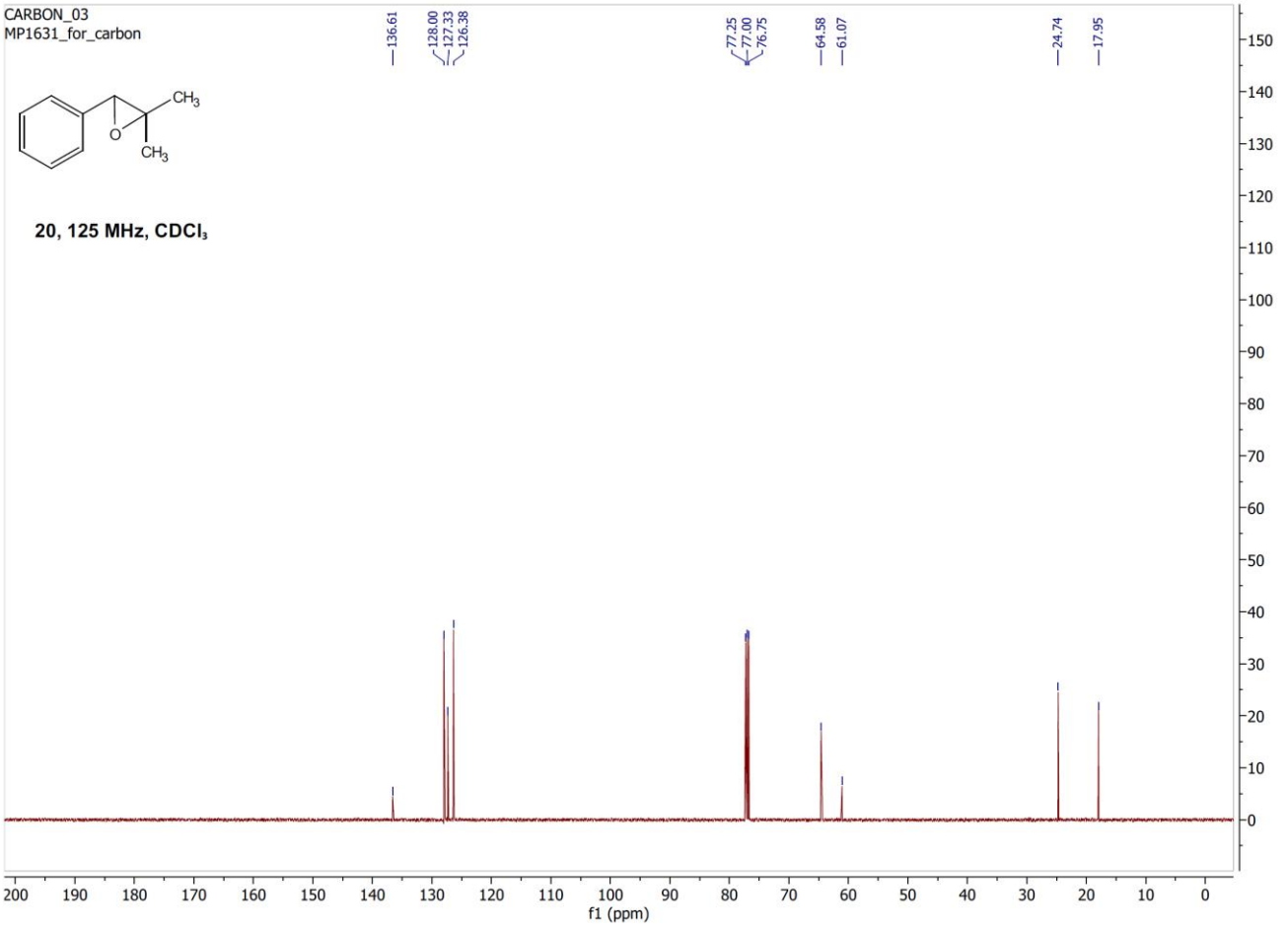


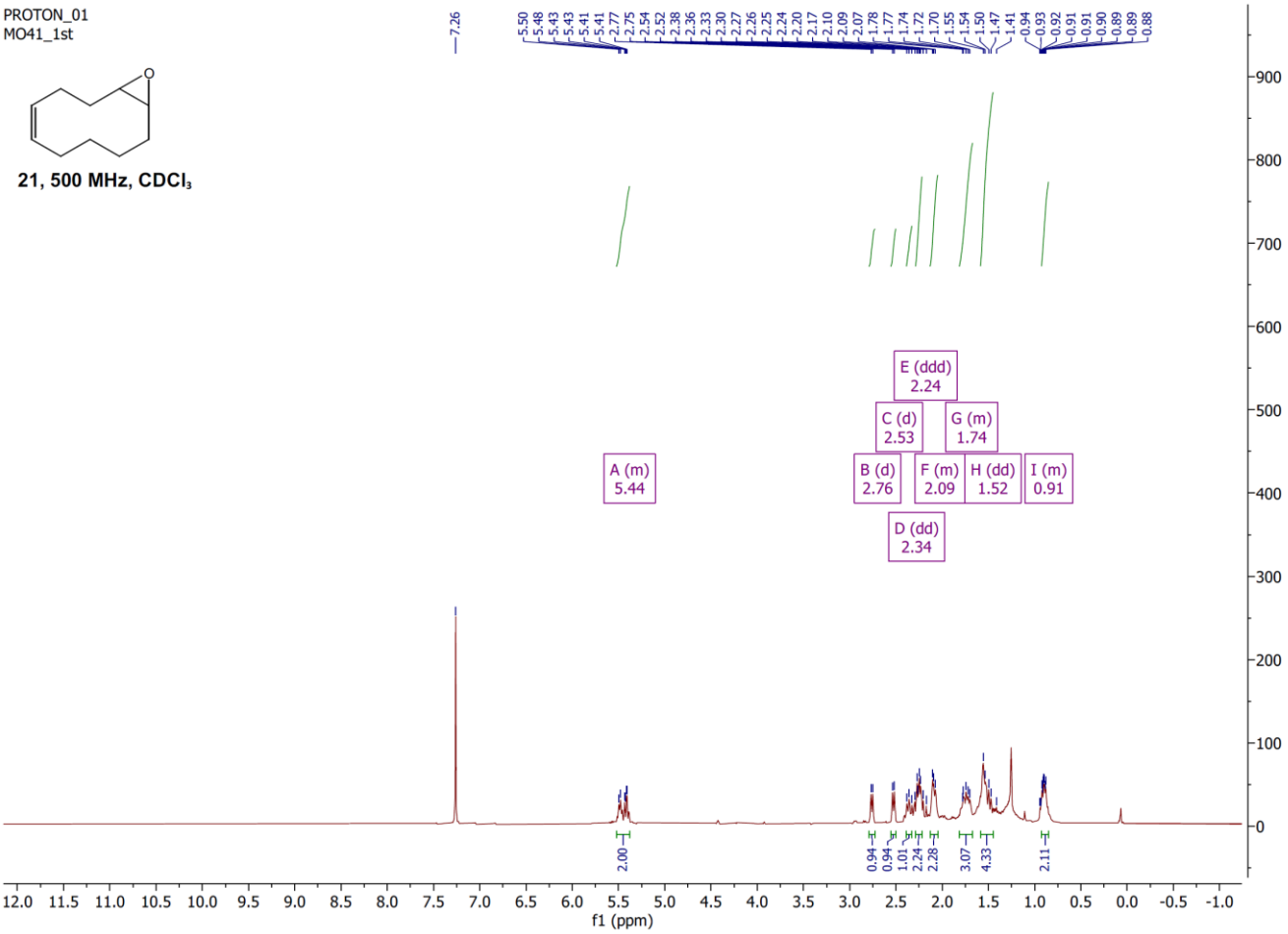
19, 500 MHz, $CDCl_3$

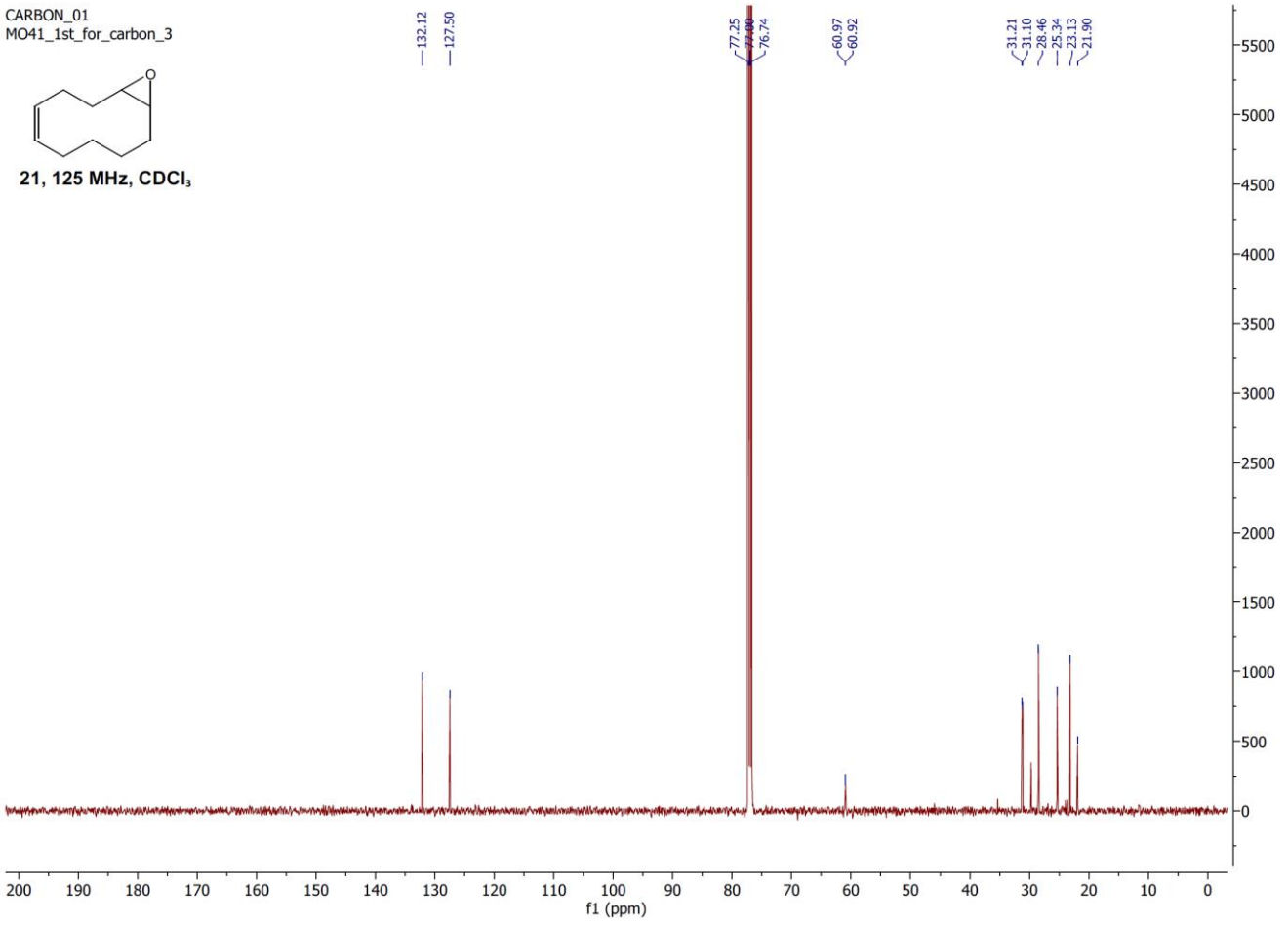


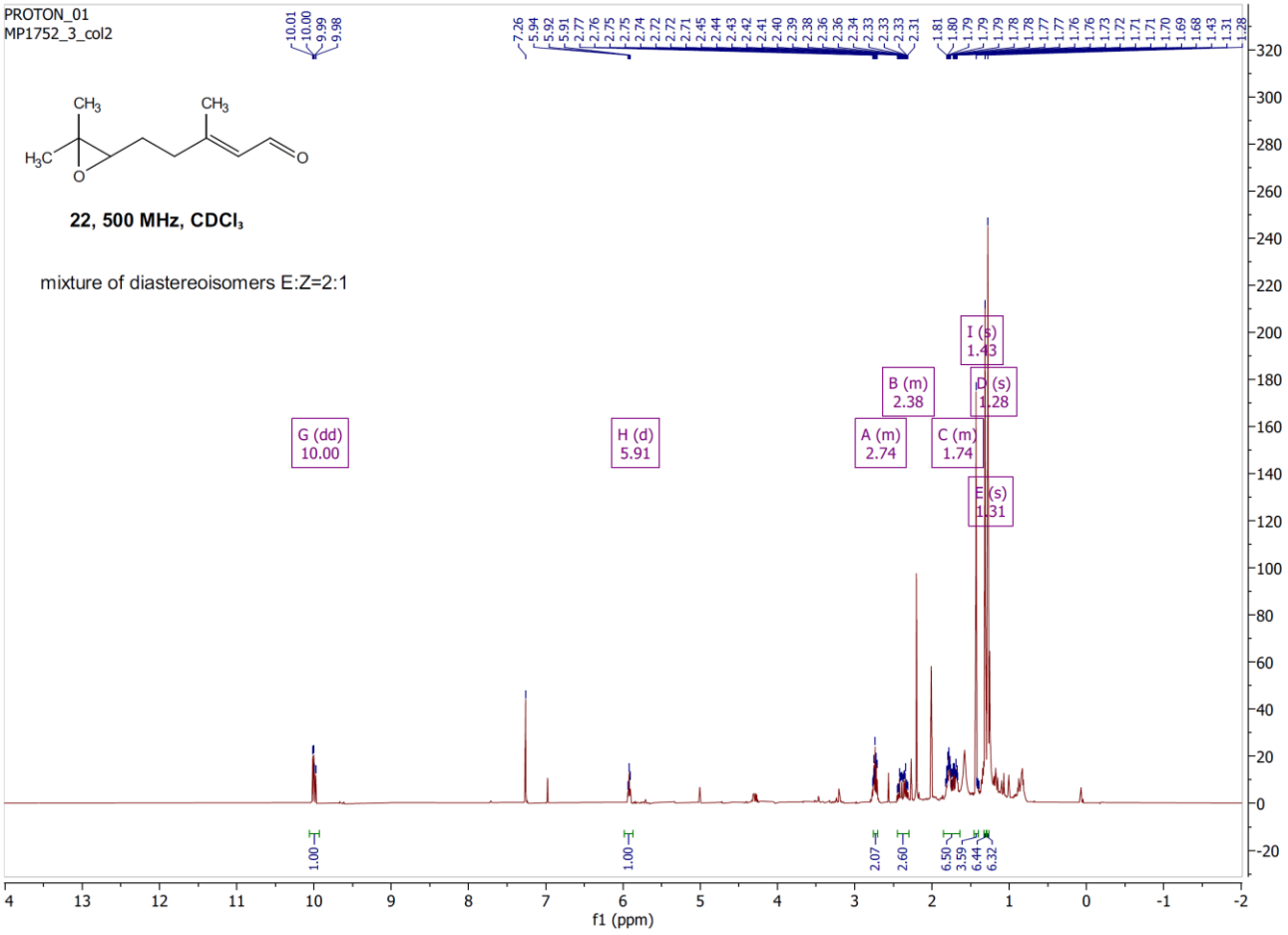
19, 125 MHz, $CDCl_3$

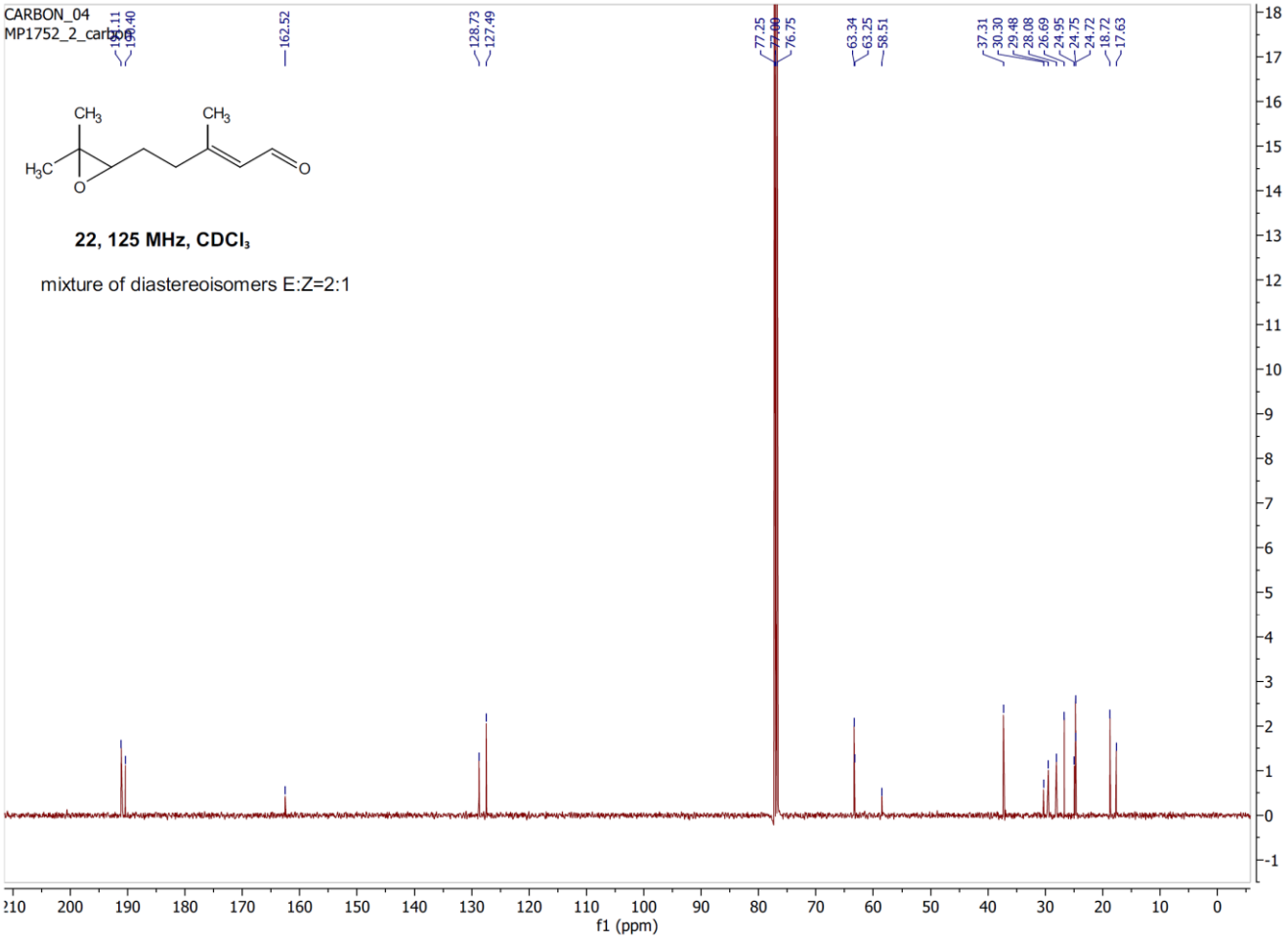

PROTON_01
MP1631
20, 500 MHz, CDCl3
D (m)
7.31
A (s)
3.87
B (s)
1.49
C (s)
1.08
5.00
0.94
4.32
3.70
f1 (ppm)

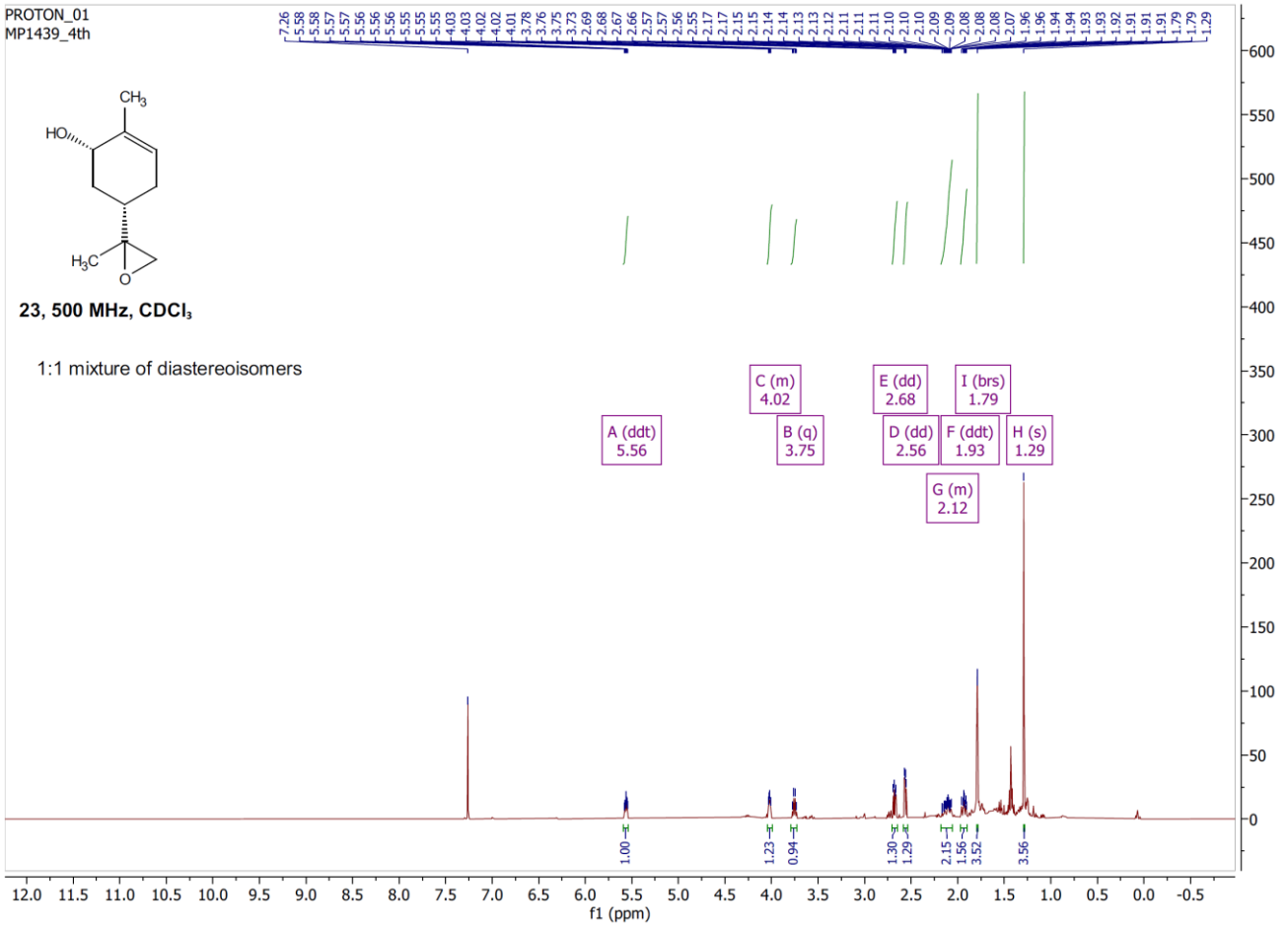

CARBON_03
MP1631_for_carbon
20, 125 MHz, CDCl3
f1 (ppm)

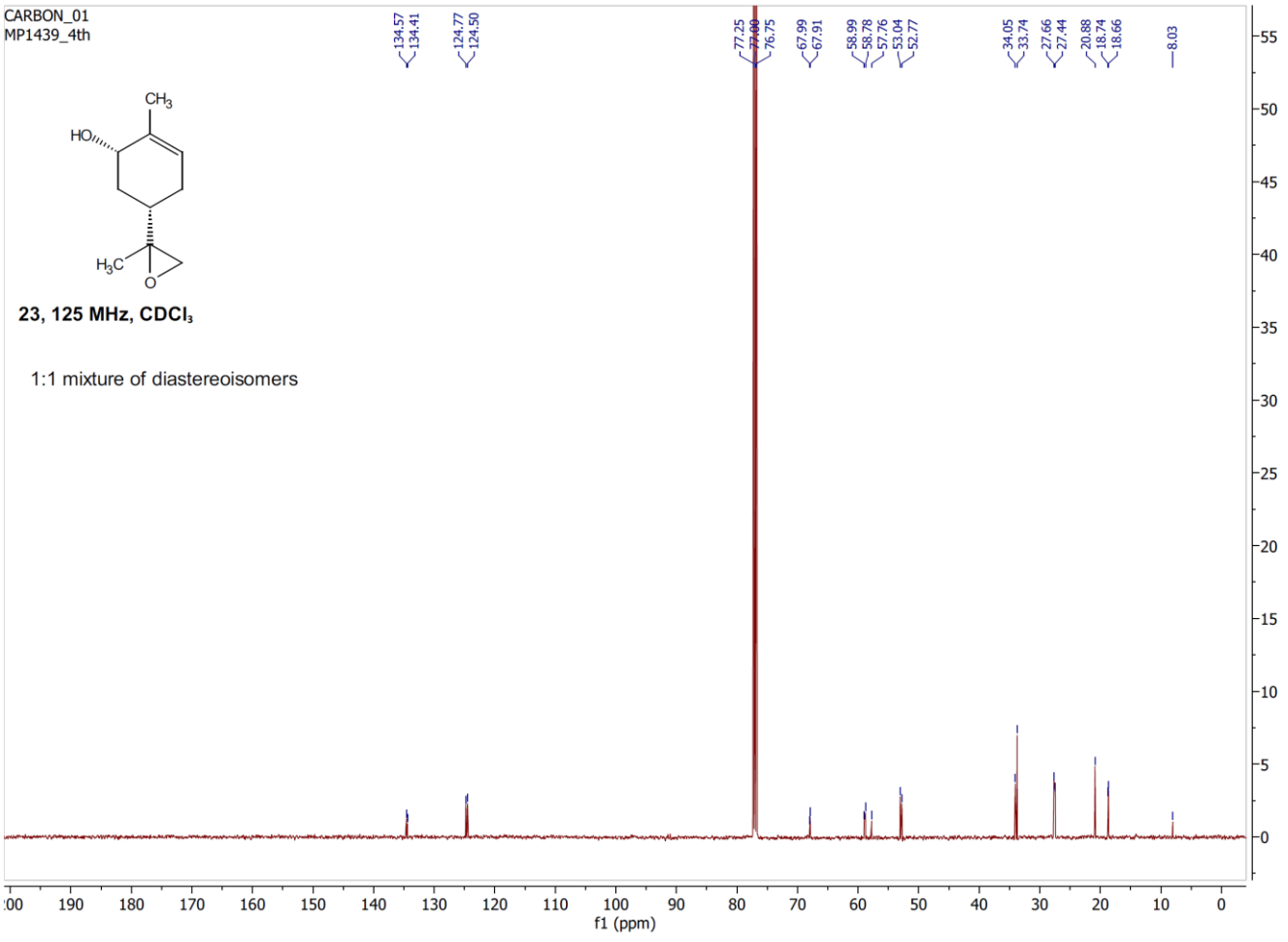

PROTON_01
MO41_1st
21, 500 MHz, CDCl3
7.26
5.50 5.48 5.43 5.43 5.41 5.41 2.77 2.75 2.54 2.52 2.38 2.36 2.33 2.30 2.27 2.26 2.25 2.24 2.20 2.17 2.10 2.09 2.07 1.78 1.77 1.74 1.72 1.70 1.55 1.54 1.50 1.47 1.41 0.94 0.93 0.92 0.91 0.90 0.89 0.88
E (ddd) 2.24
C (d) 2.53
G (m) 1.74
A (m) 5.44
B (d) 2.76
F (m) 2.09
H (dd) 1.52
I (m) 0.91
D (dd) 2.34
2.00 0.94 0.94 1.01 2.24 2.28 3.07 4.33 2.11
f1 (ppm)

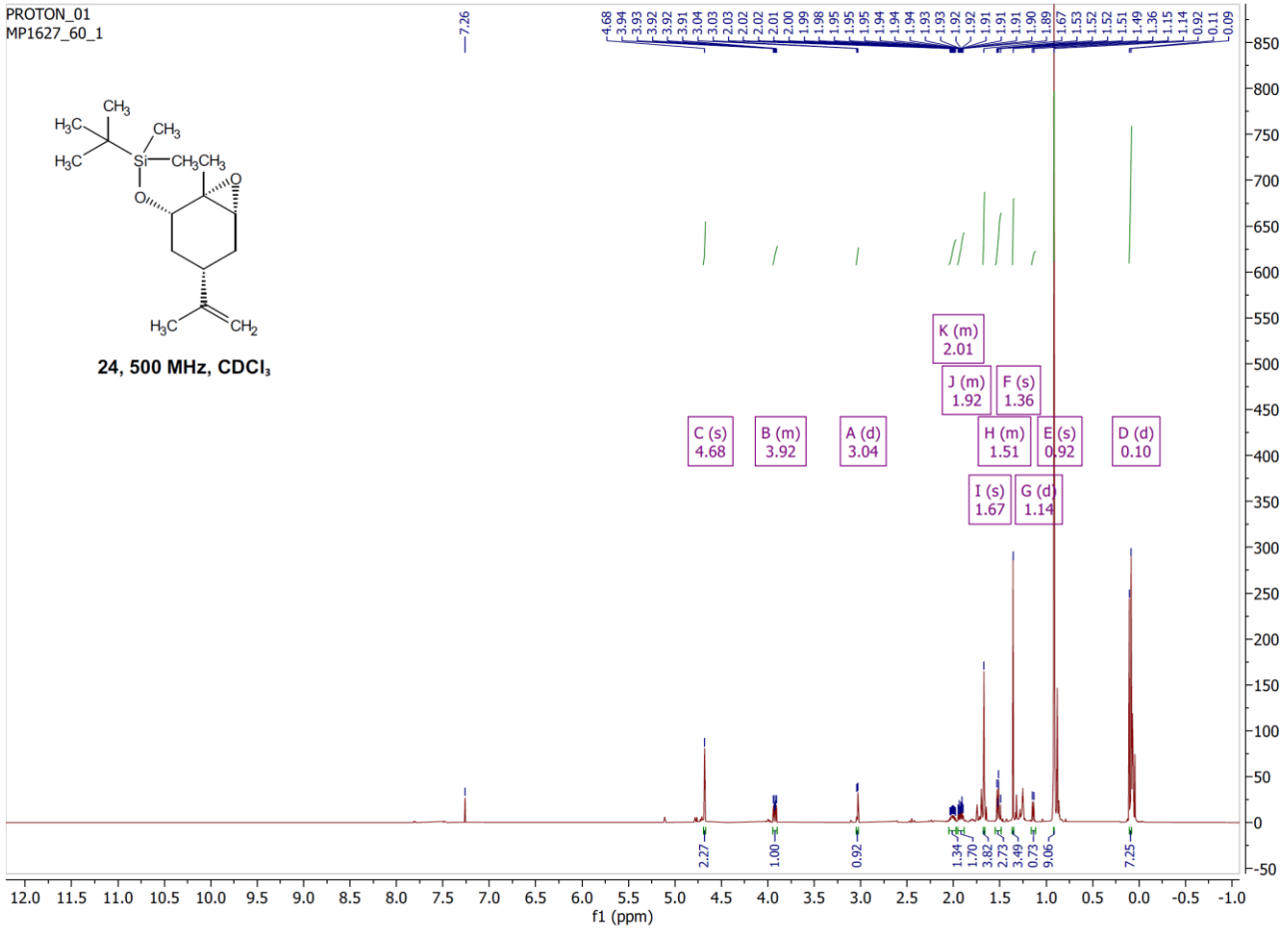

CARBON_01
MO41_1st_for_carbon_3
21, 125 MHz, CDCl3
132.12 127.50 77.25 77.00 76.74 60.97 60.92 31.21 31.10 28.46 25.34 23.13 21.90
f1 (ppm)

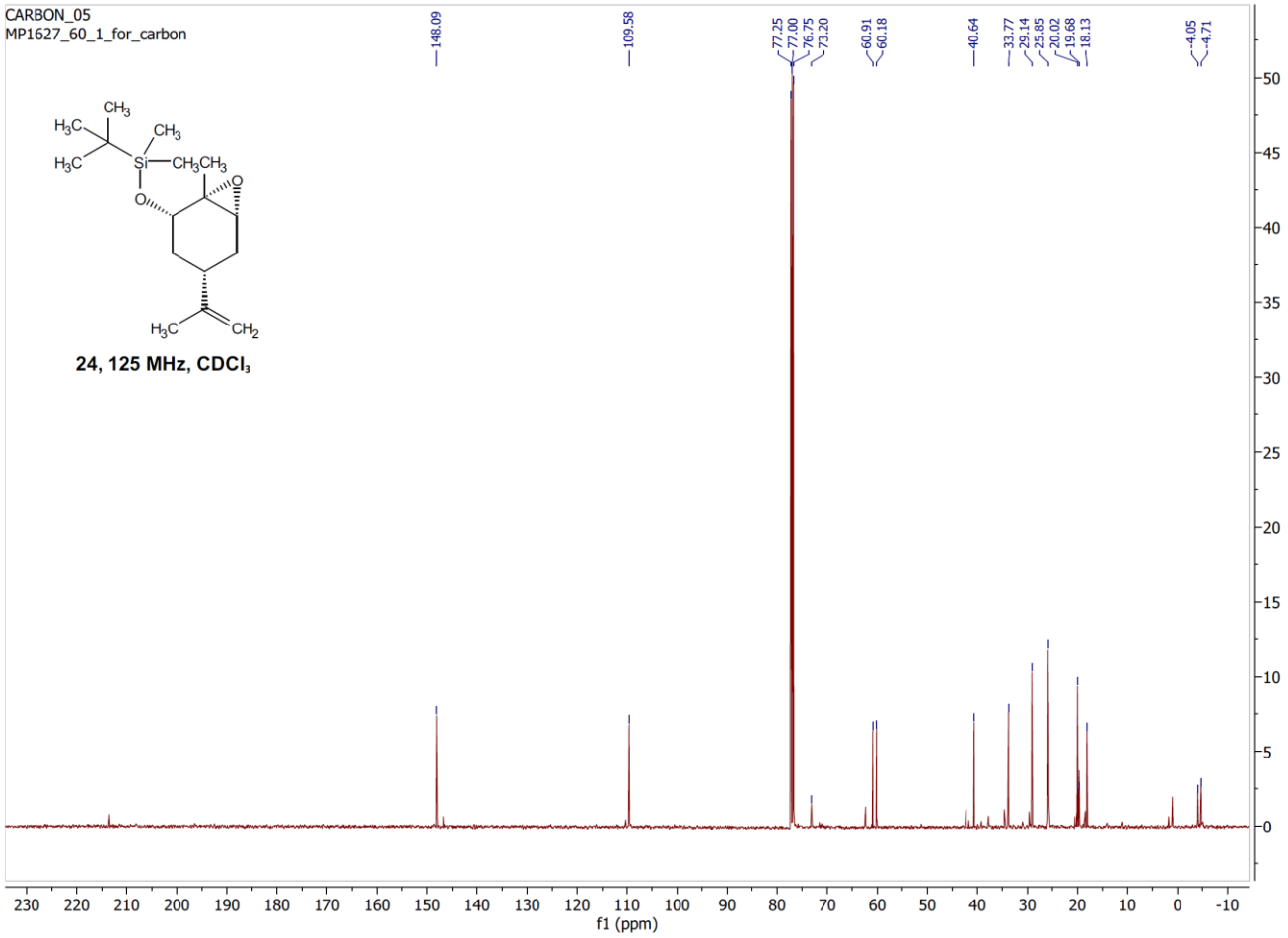

PROTON_01
MP1752_3_col2
22, 500 MHz, CDCl3
mixture of diastereoisomers E:Z=2:1
G (dd) 10.00
H (d) 5.91
A (m) 2.74
B (m) 2.38
C (m) 1.74
D (s) 1.28
I (s) 1.43
f1 (ppm)

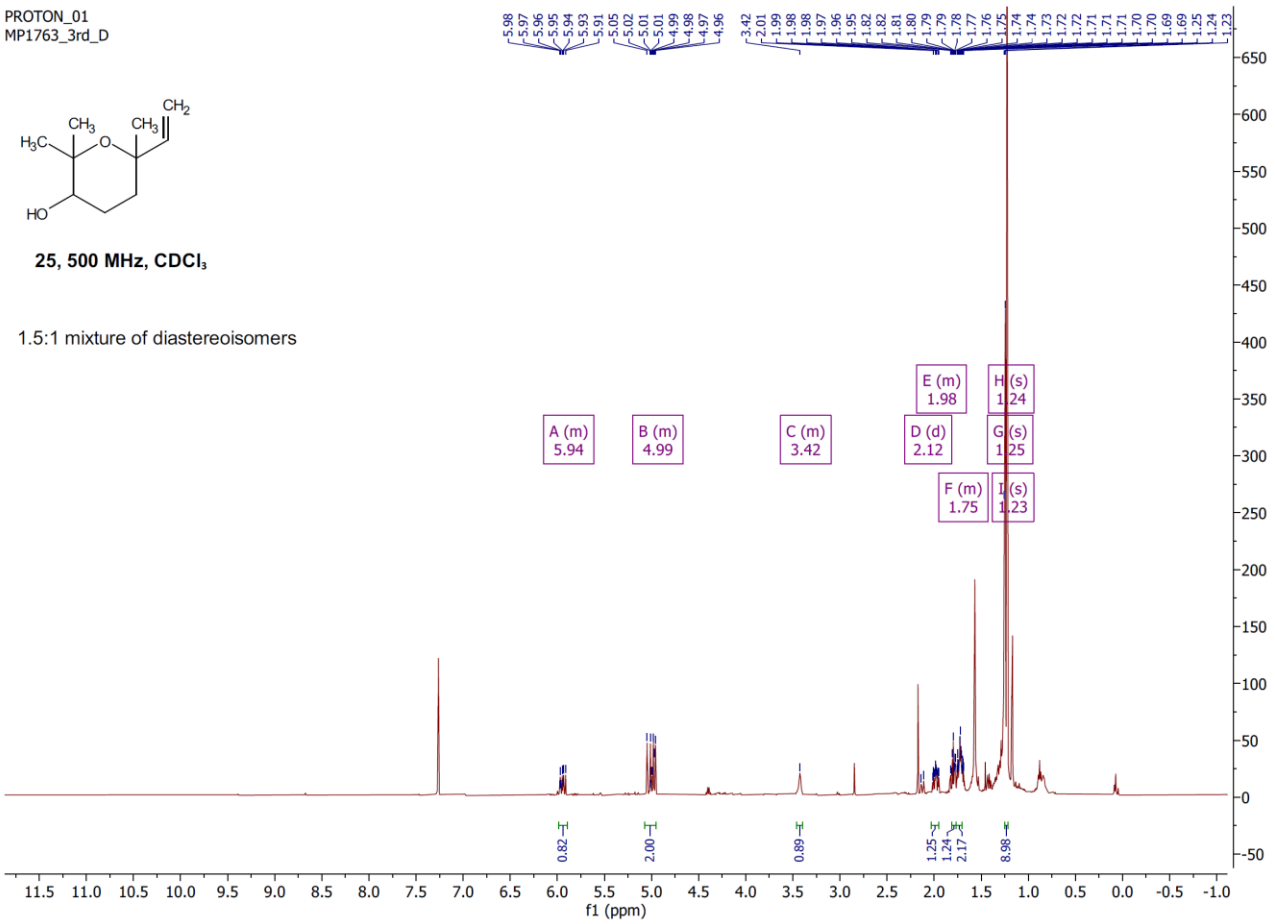

CARBON_04
MP1752_2_carbon
22, 125 MHz, CDCl3
mixture of diastereoisomers E:Z=2:1
f1 (ppm)

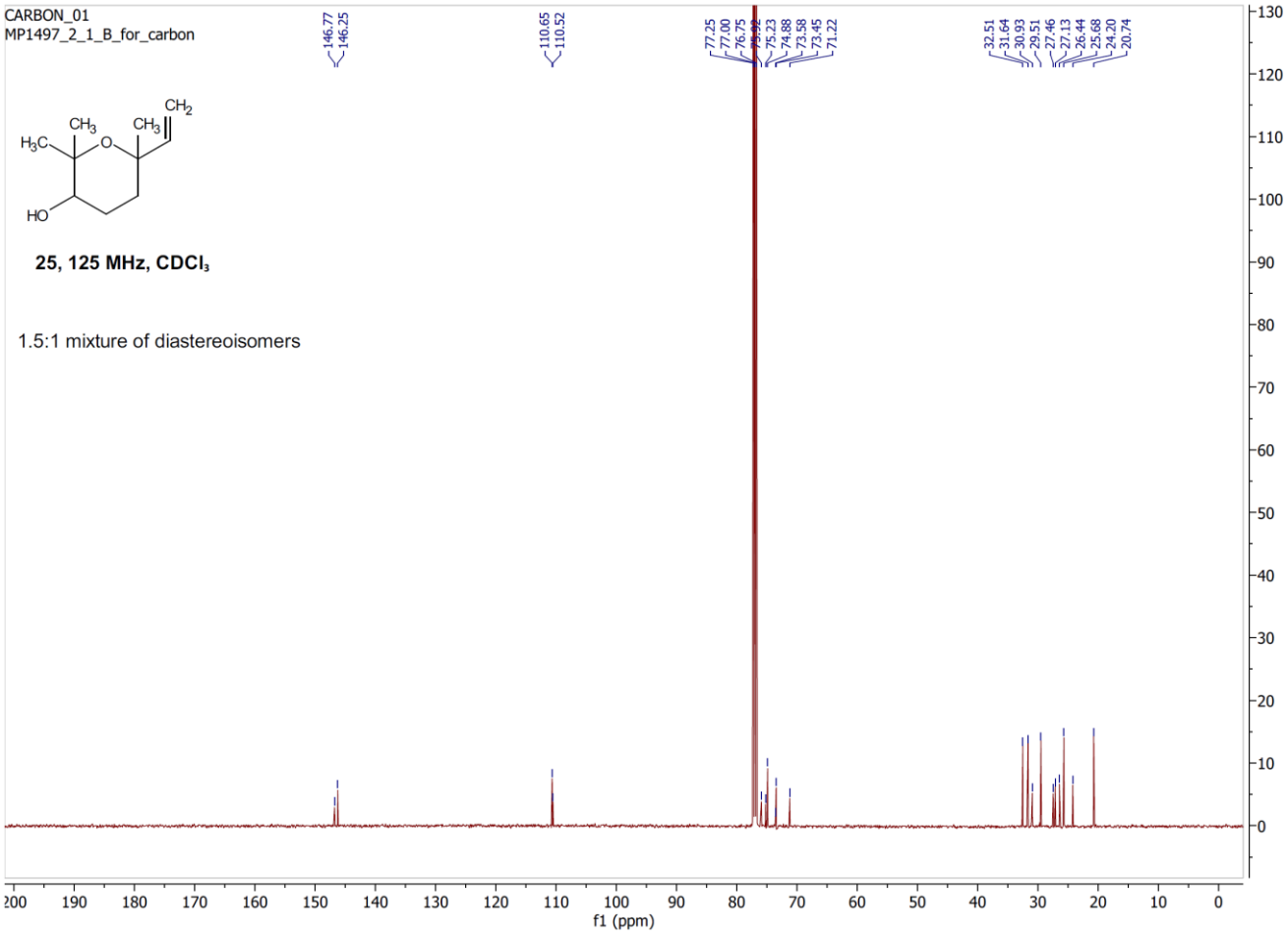

PROTON_01
MP1439_4th
23, 500 MHz, CDCl3
1:1 mixture of diastereoisomers
A (ddt) 5.56
B (q) 3.75
C (m) 4.02
D (dd) 2.56
E (dd) 2.68
F (ddt) 1.93
G (m) 2.12
H (s) 1.29
I (brs) 1.79
f1 (ppm)

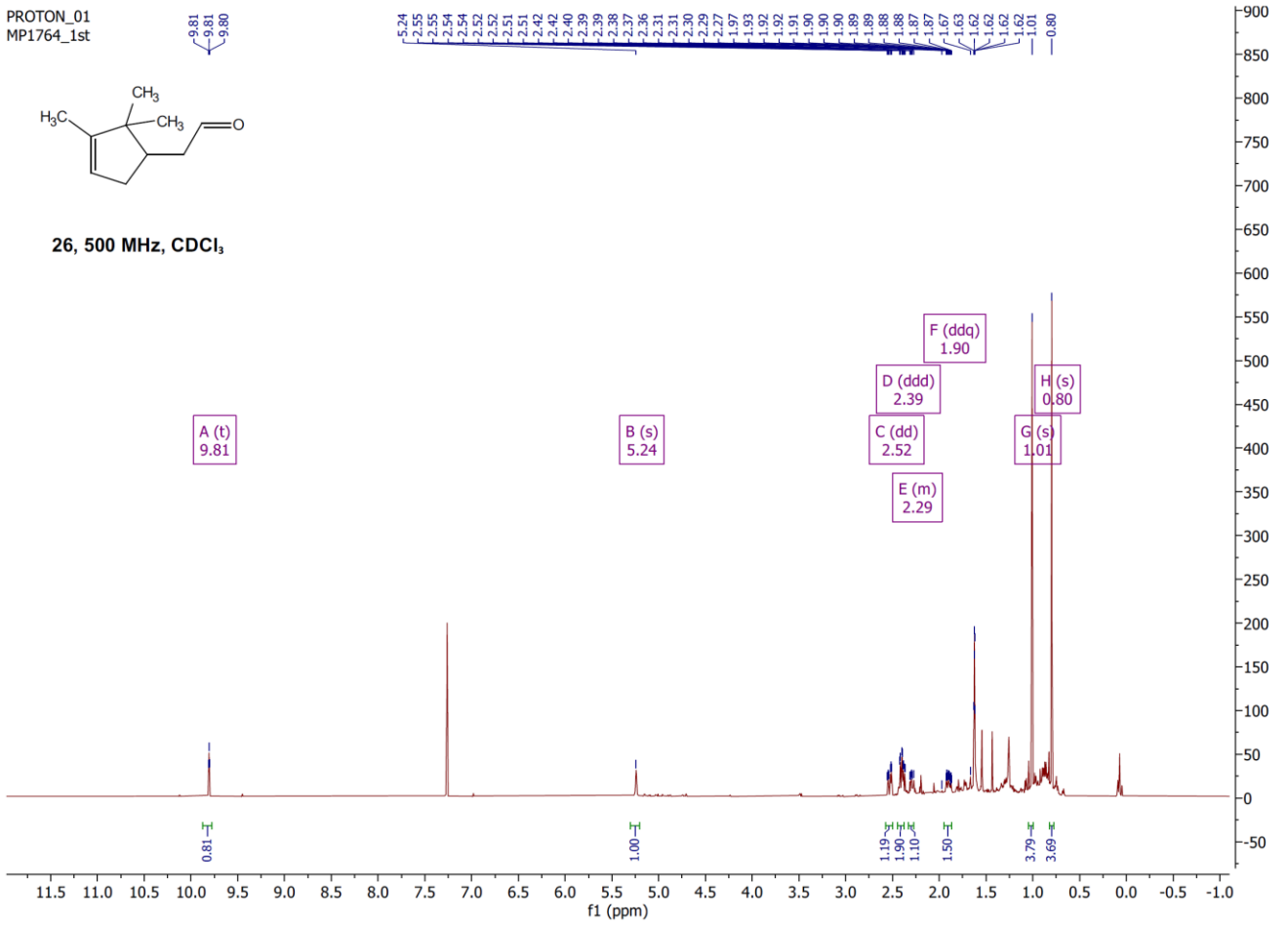

CARBON_01
MP1439_4th
23, 125 MHz, CDCl3
1:1 mixture of diastereoisomers
f1 (ppm)

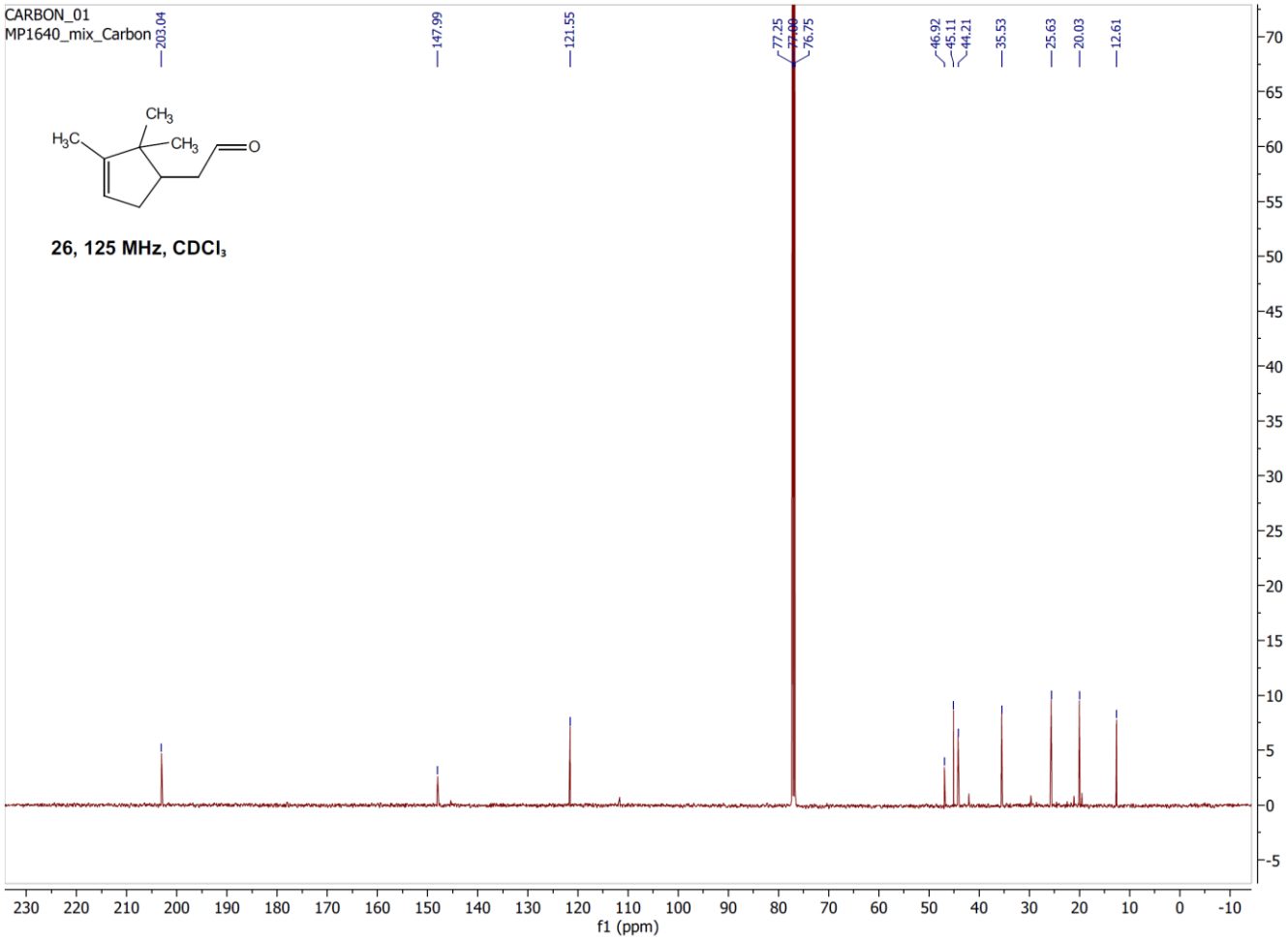

PROTON_01
MP1627_60_1
24, 500 MHz, CDCl3
K (m) 2.01
J (m) 1.92
F (s) 1.36
C (s) 4.68
B (m) 3.92
A (d) 3.04
H (m) 1.51
E (s) 0.92
D (d) 0.10
I (s) 1.67
G (d) 1.14
f1 (ppm)

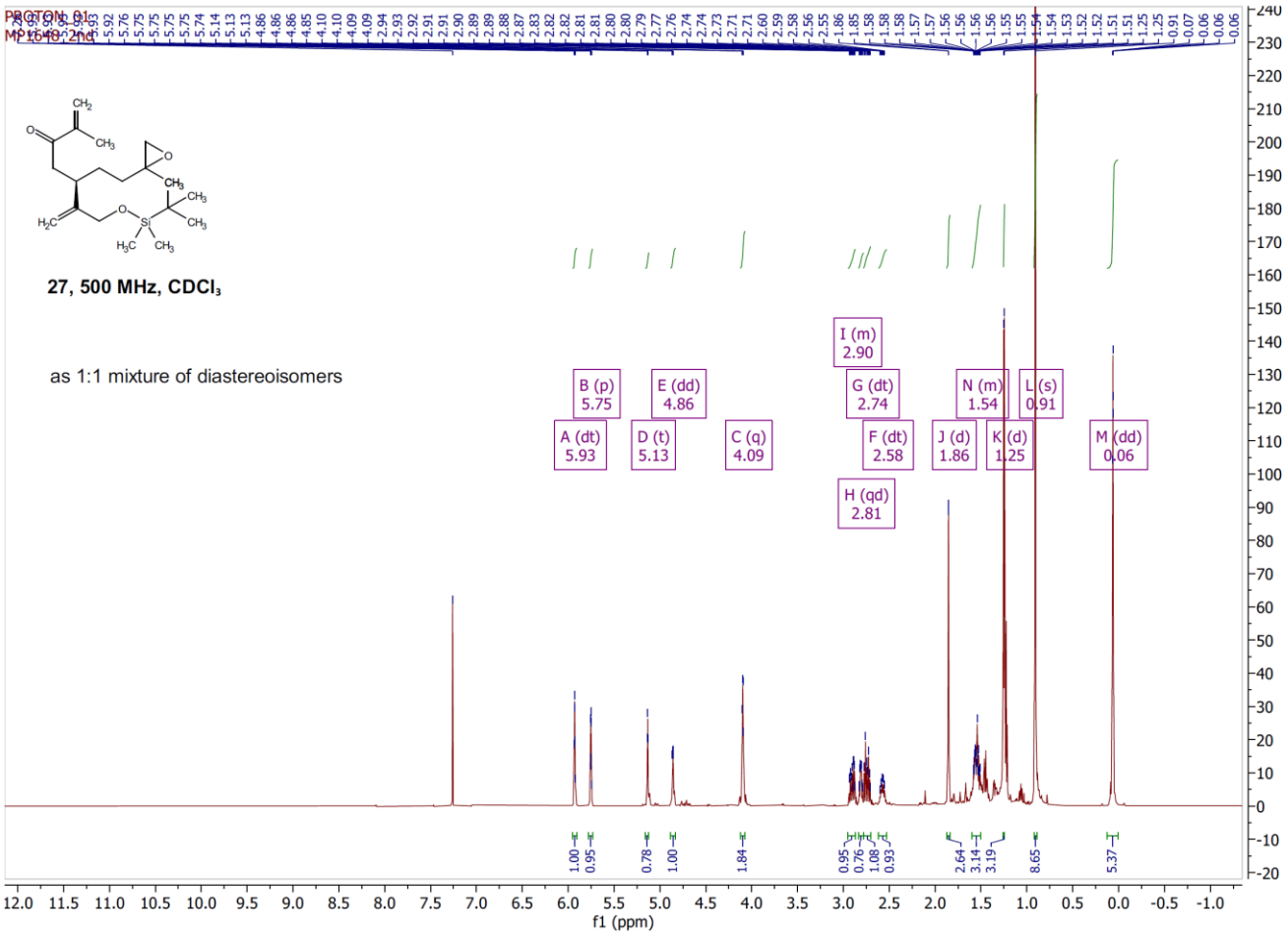

CARBON_05
MP1627_60_1_for_carbon
24, 125 MHz, CDCl3
f1 (ppm)

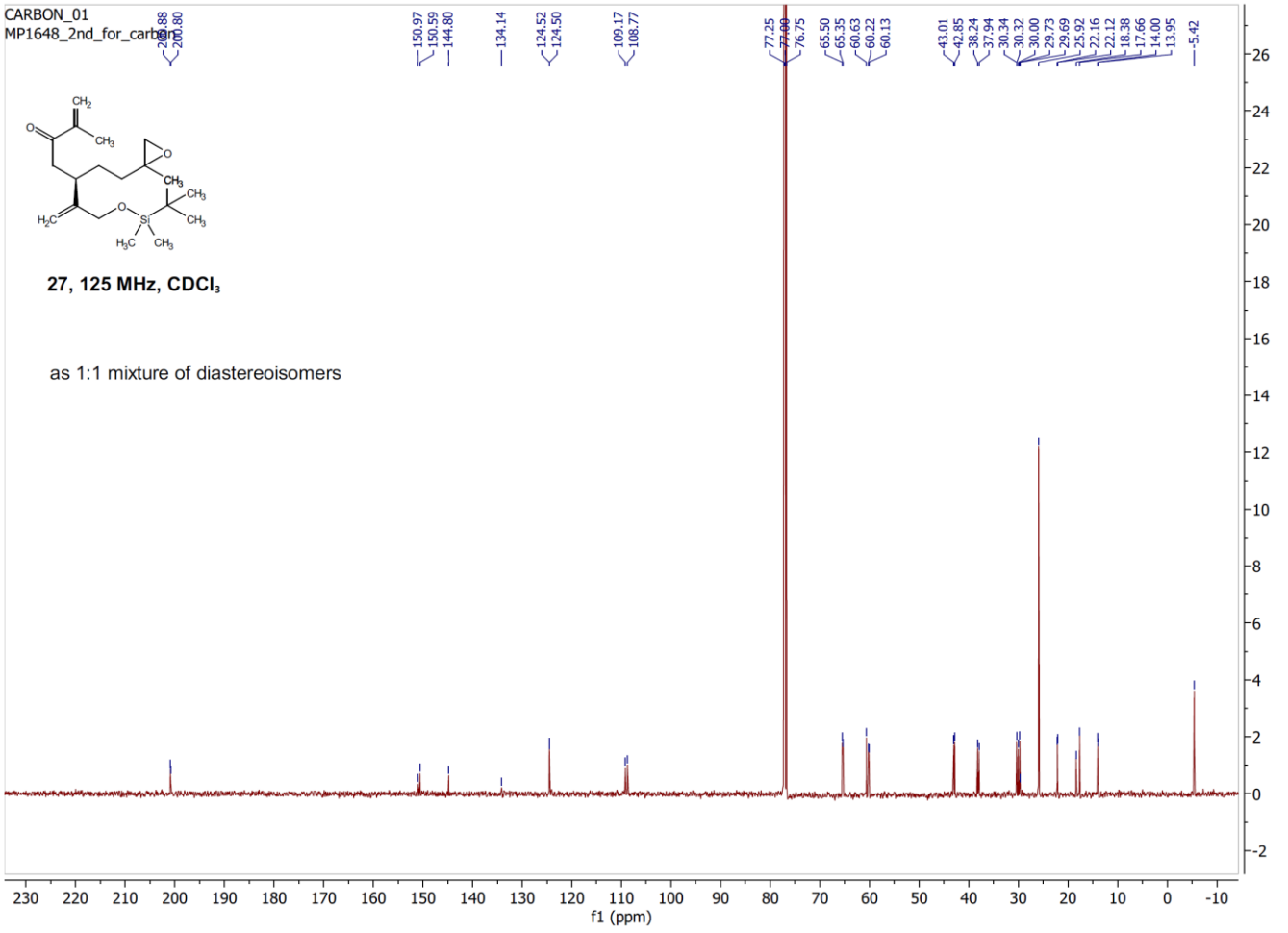

PROTON_01
MP1763_3rd_D
25, 500 MHz, CDCl3
1.5:1 mixture of diastereoisomers
A (m) 5.94
B (m) 4.99
C (m) 3.42
D (d) 2.12
E (m) 1.98
F (m) 1.75
G (s) 1.25
H (s) 1.24
I (s) 1.23
f1 (ppm)

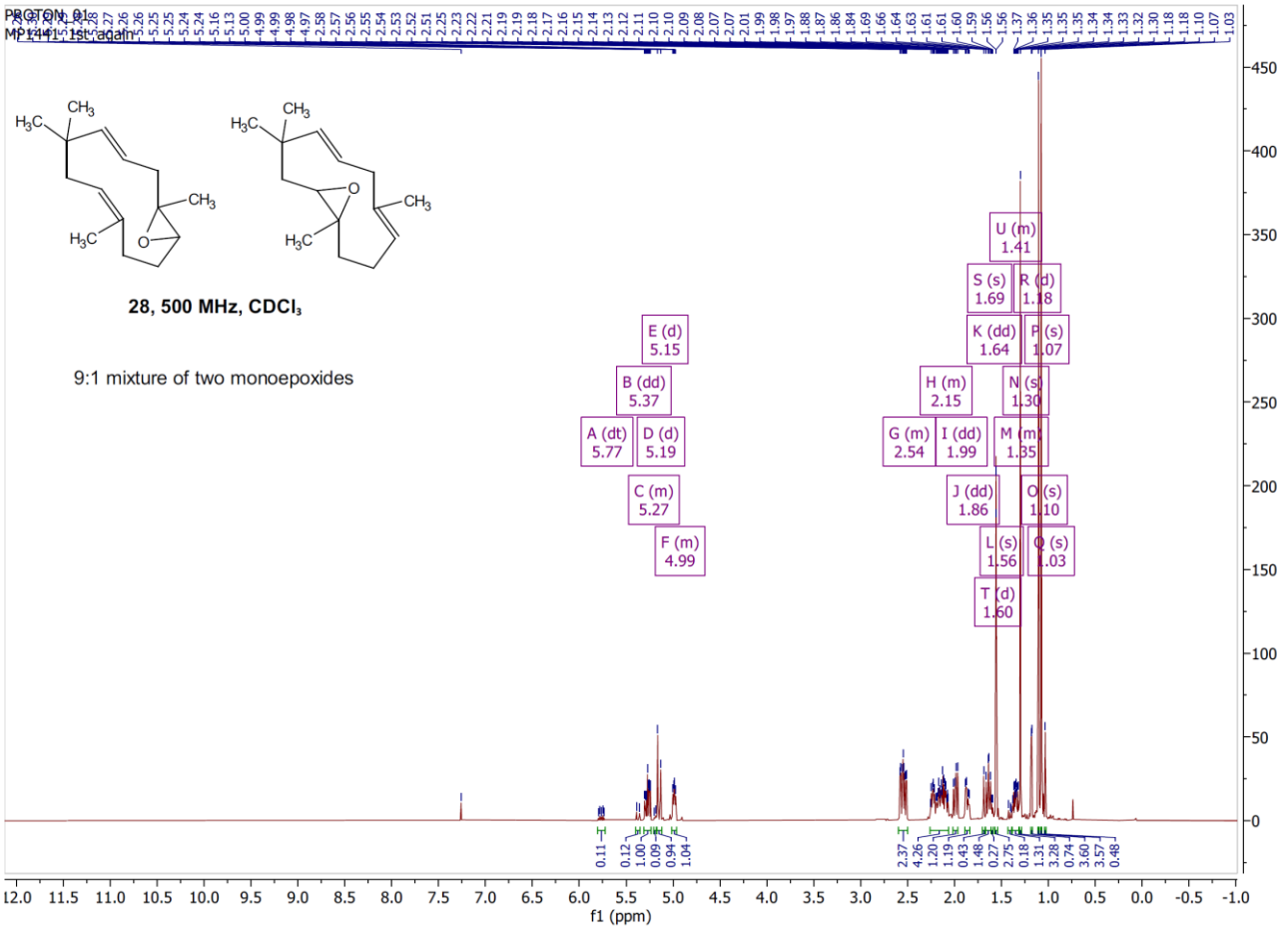

CARBON_01
MP1497_2_1_B_for_carbon
25, 125 MHz, CDCl3
1.5:1 mixture of diastereoisomers
f1 (ppm)


PROTON_01
MP1764_1st
26, 500 MHz, CDCl₃
A (t) 9.81
B (s) 5.24
C (dd) 2.52
D (ddd) 2.39
E (m) 2.29
F (ddq) 1.90
G (s) 1.01
H (s) 0.80
f1 (ppm)


CARBON_01
MP1640_mix_Carbon
26, 125 MHz, CDCl₃
f1 (ppm)

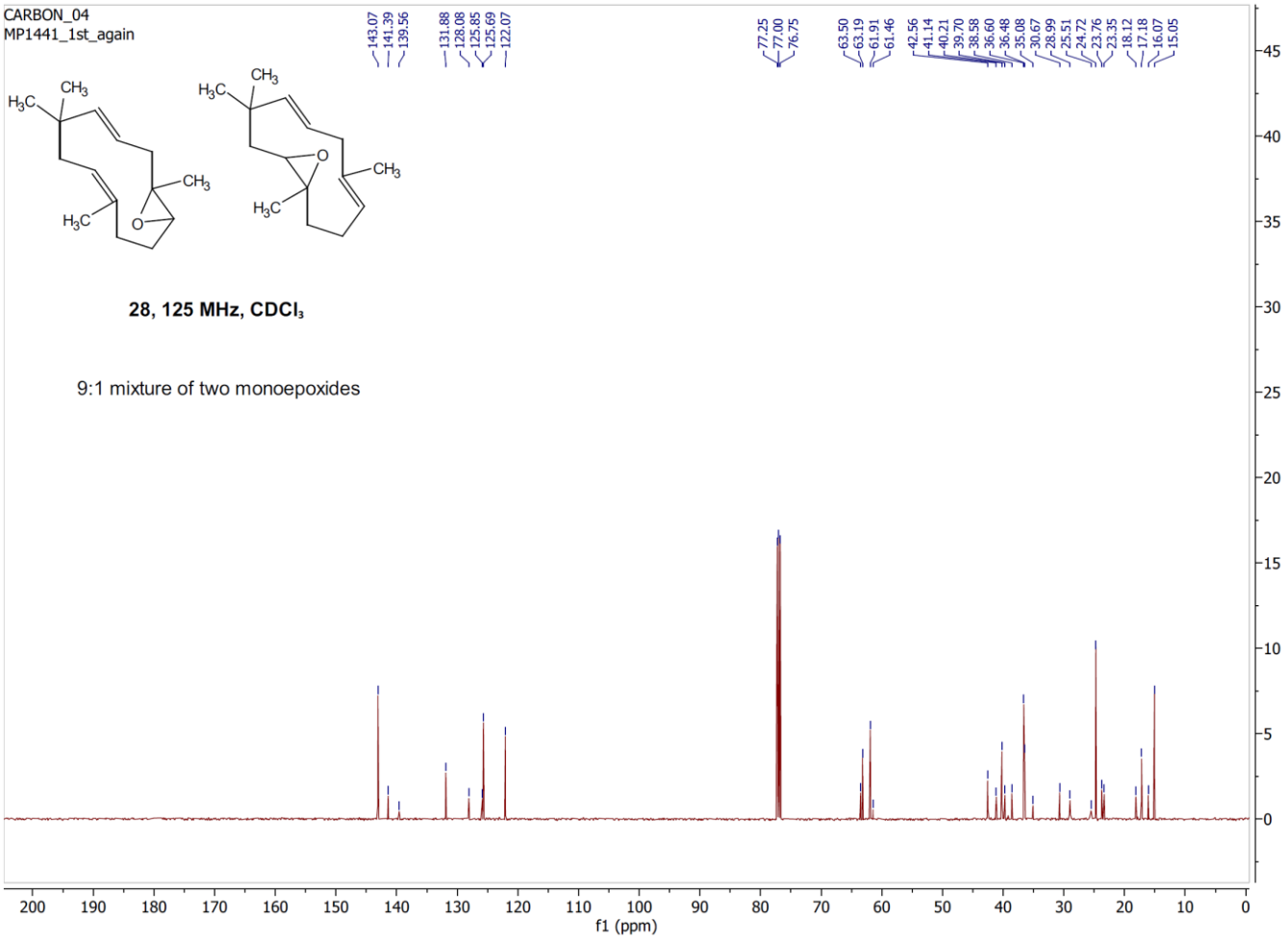

PROTON_01
MP1648_2nd
27, 500 MHz, CDCl3
as 1:1 mixture of diastereoisomers
A (dt) 5.93
B (p) 5.75
C (q) 4.09
D (t) 5.13
E (dd) 4.86
F (dt) 2.58
G (dt) 2.74
H (qd) 2.81
I (m) 2.90
J (d) 1.86
K (d) 1.25
L (s) 0.91
M (dd) 0.06
N (m) 1.54
f1 (ppm)


CARBON_01
MP1648_2nd_for_carbon
27, 125 MHz, CDCl3
as 1:1 mixture of diastereoisomers
f1 (ppm)



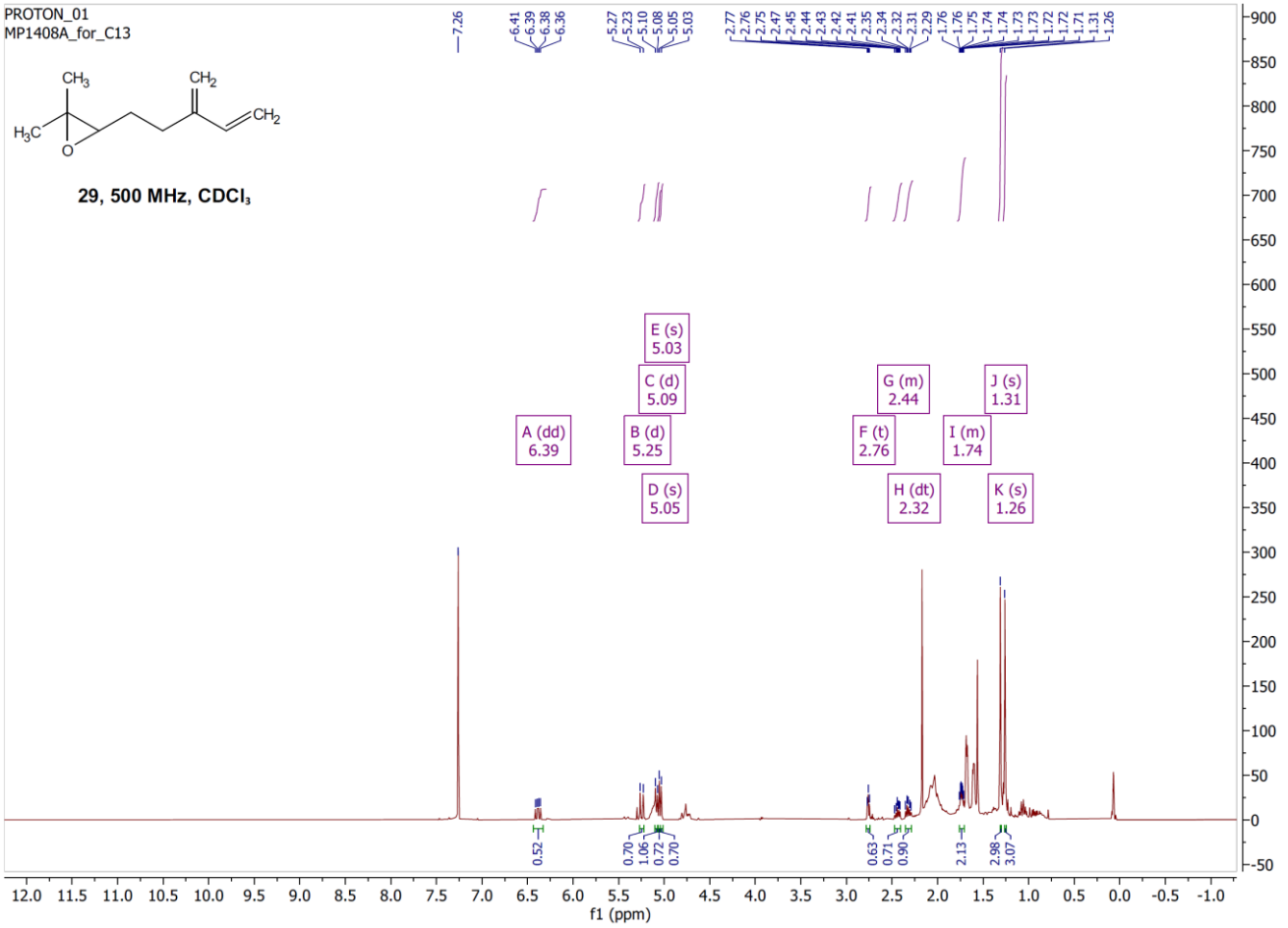
28, 500 MHz, $CDCl_3$

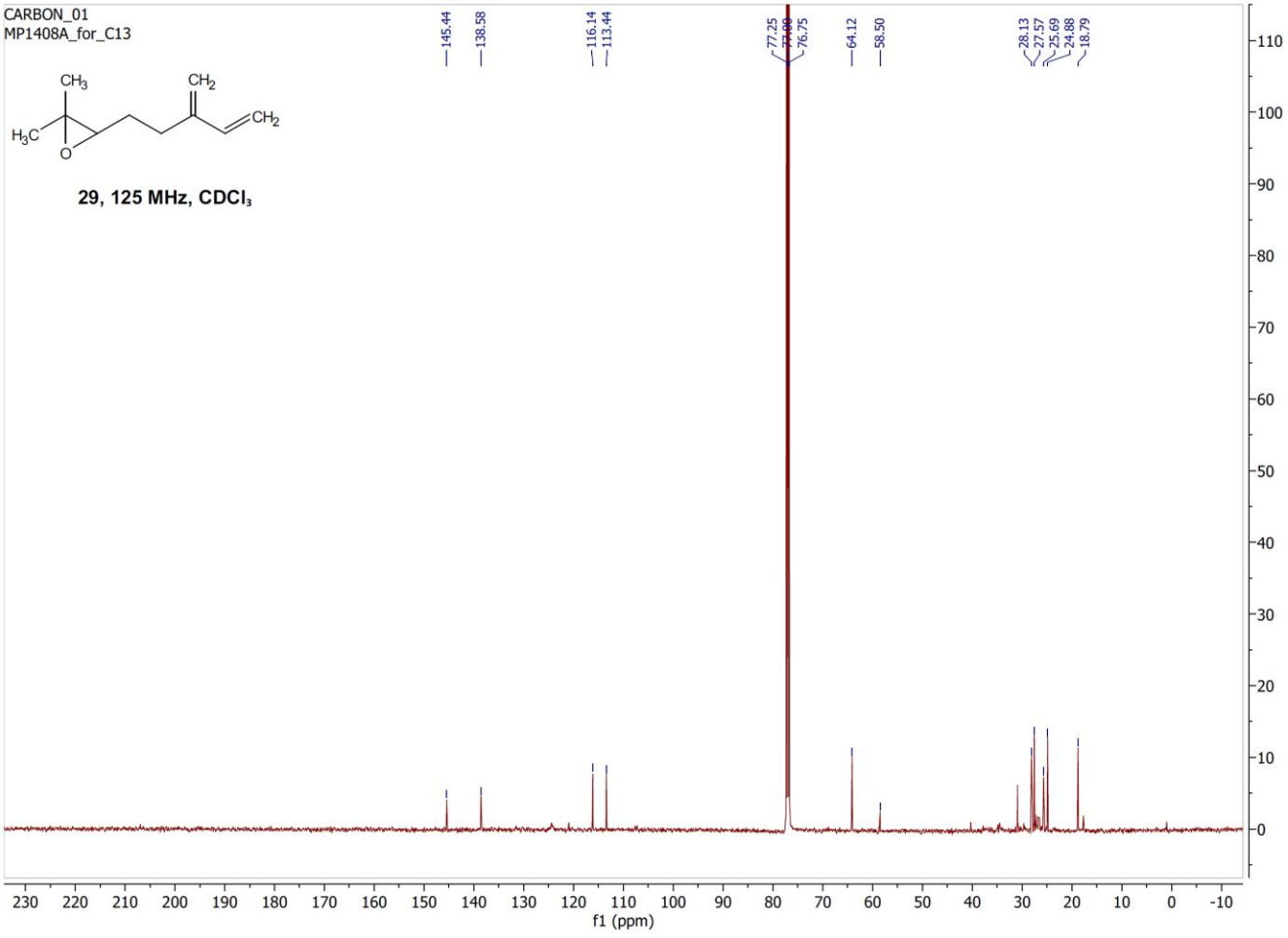
9:1 mixture of two monoepoxides

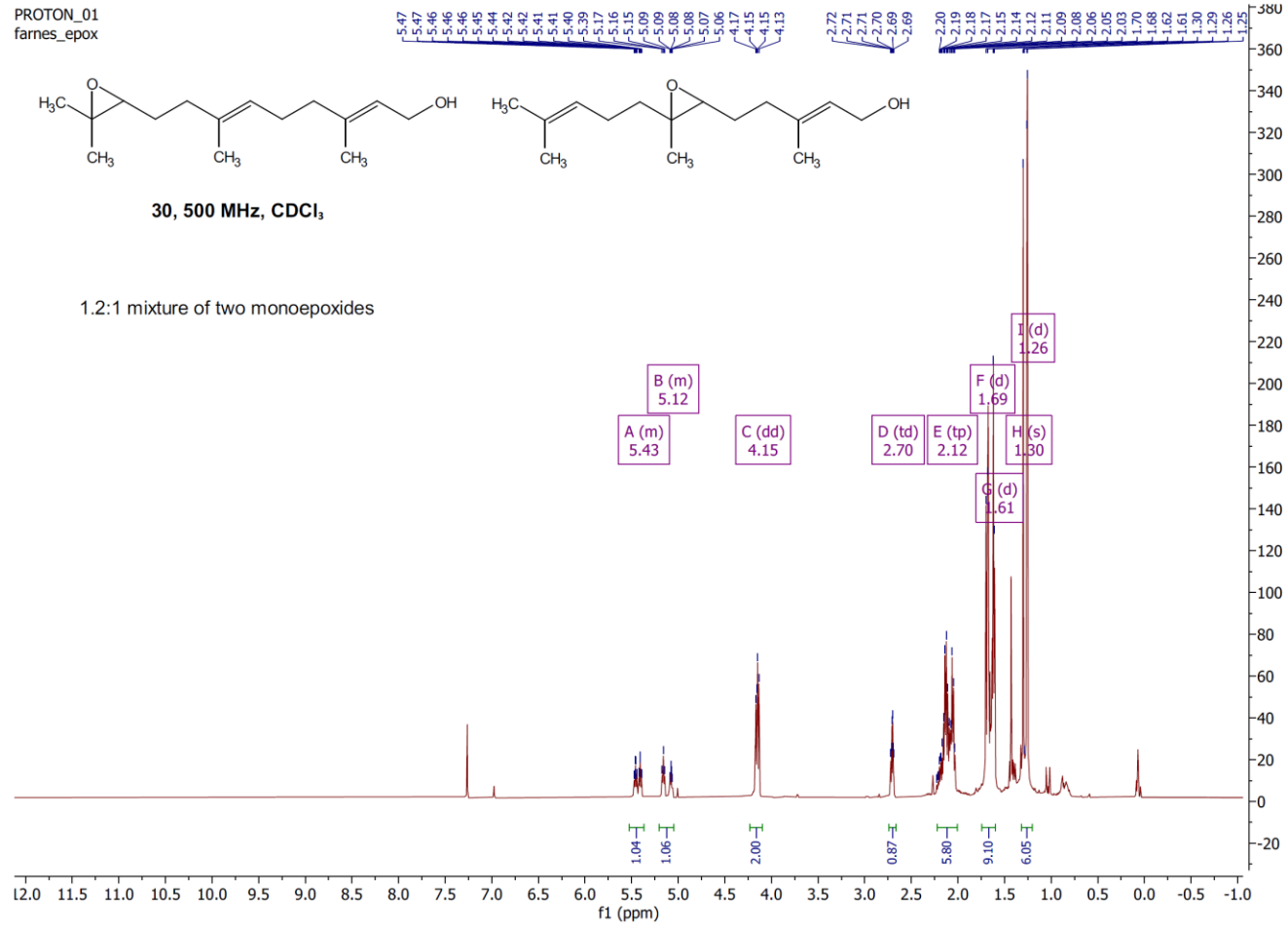


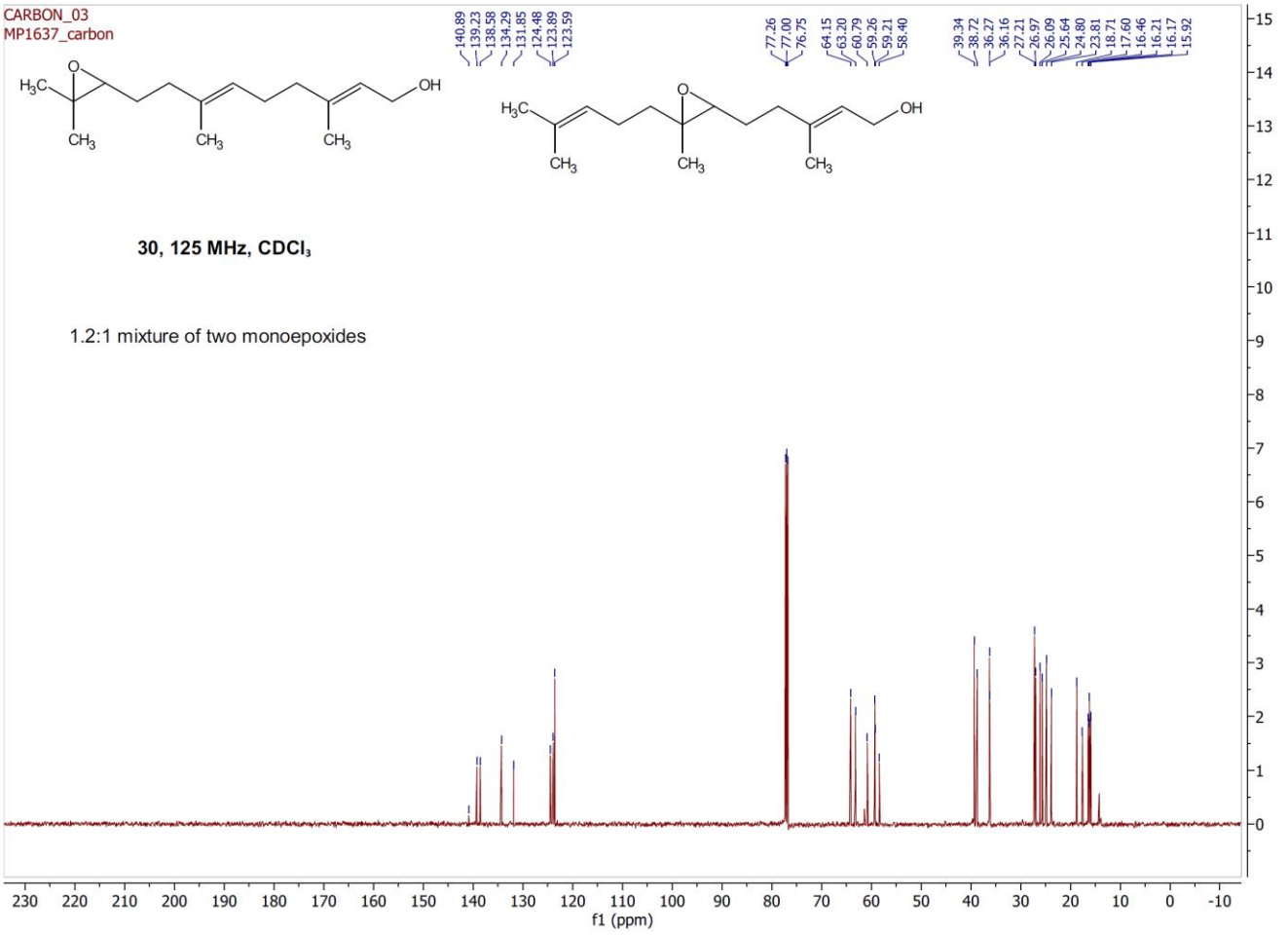
28, 125 MHz, $CDCl_3$

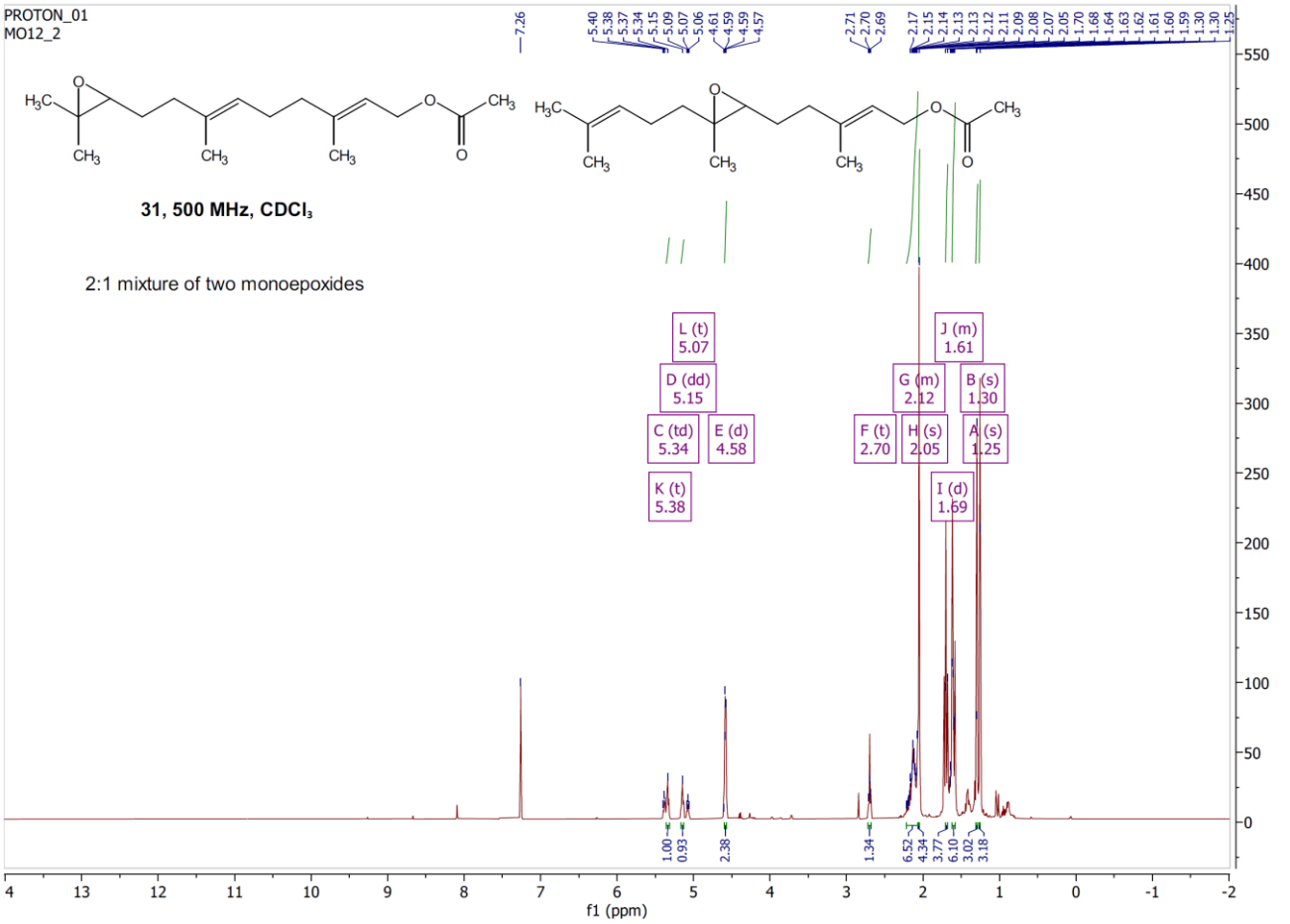
9:1 mixture of two monoepoxides

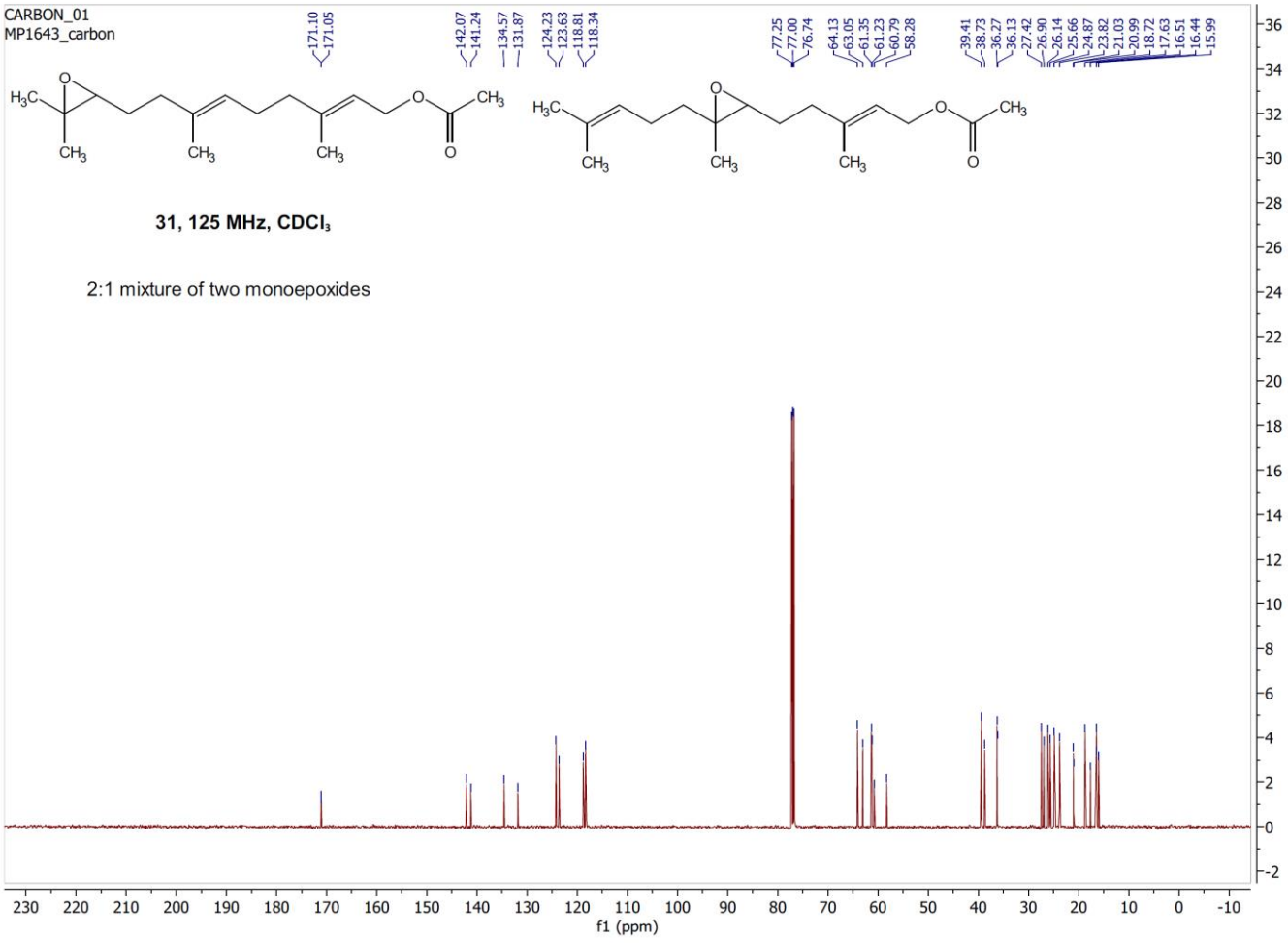

PROTON_01
MP1408A_for_C13
29, 500 MHz, CDCl3
E (s) 5.03
C (d) 5.09
G (m) 2.44
J (s) 1.31
A (dd) 6.39
B (d) 5.25
F (t) 2.76
I (m) 1.74
D (s) 5.05
H (dt) 2.32
K (s) 1.26
f1 (ppm)

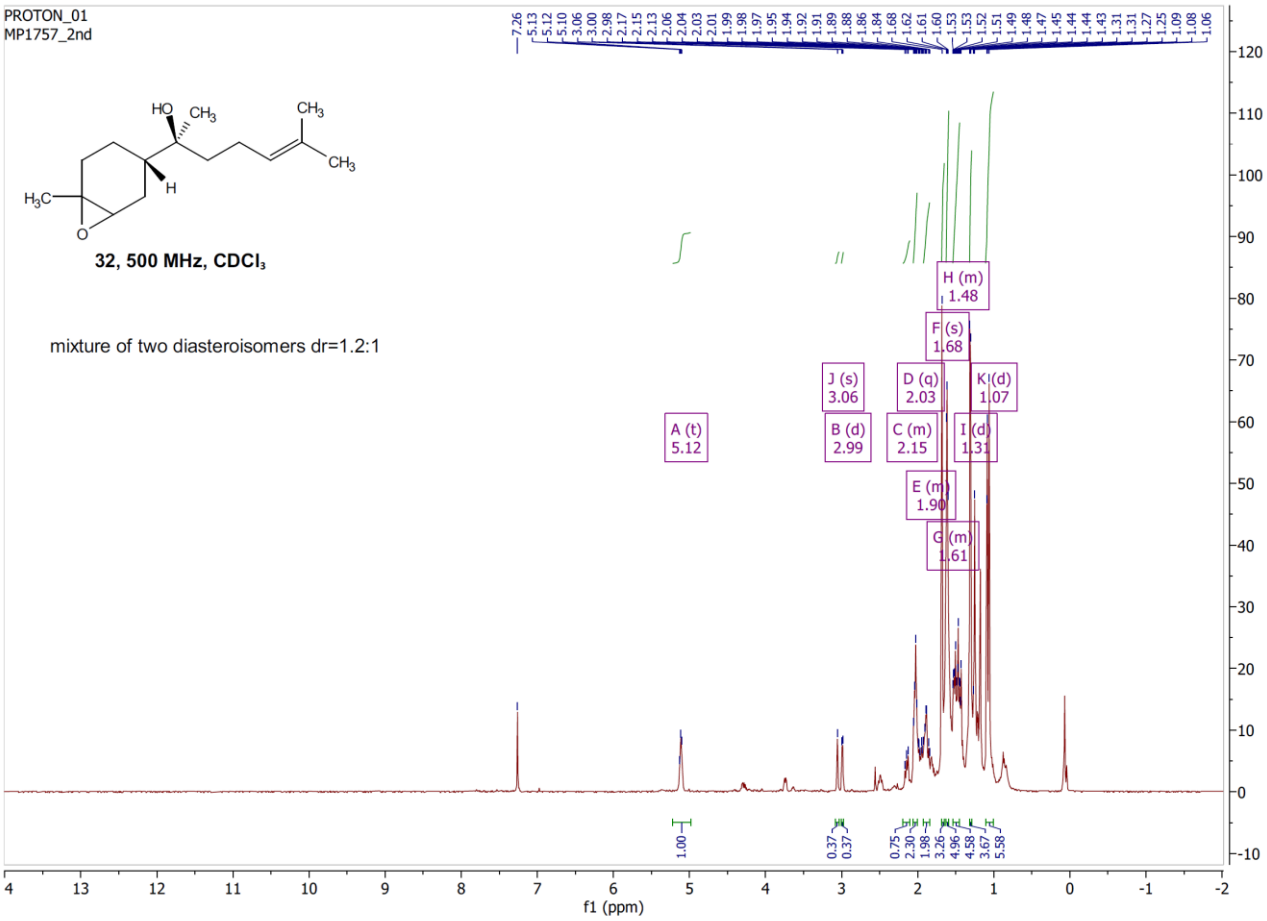

CARBON_01
MP1408A_for_C13
29, 125 MHz, CDCl3
f1 (ppm)

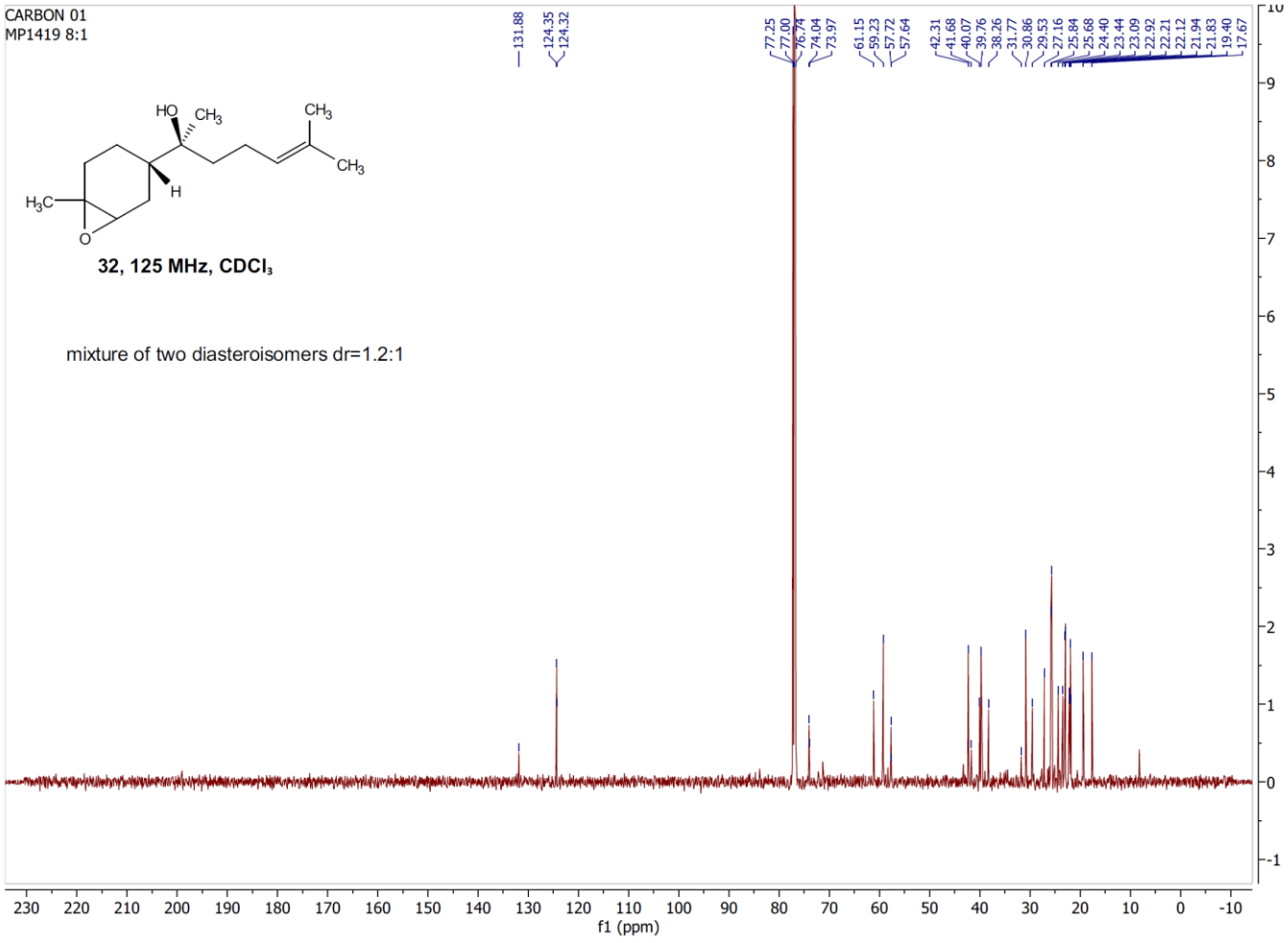

PROTON_01
farnes_epox
30, 500 MHz, CDCl3
1.2:1 mixture of two monoepoxides
A (m) 5.43
B (m) 5.12
C (dd) 4.15
D (td) 2.70
E (tp) 2.12
F (d) 1.69
G (d) 1.61
H (s) 1.30
I (d) 1.26
f1 (ppm)

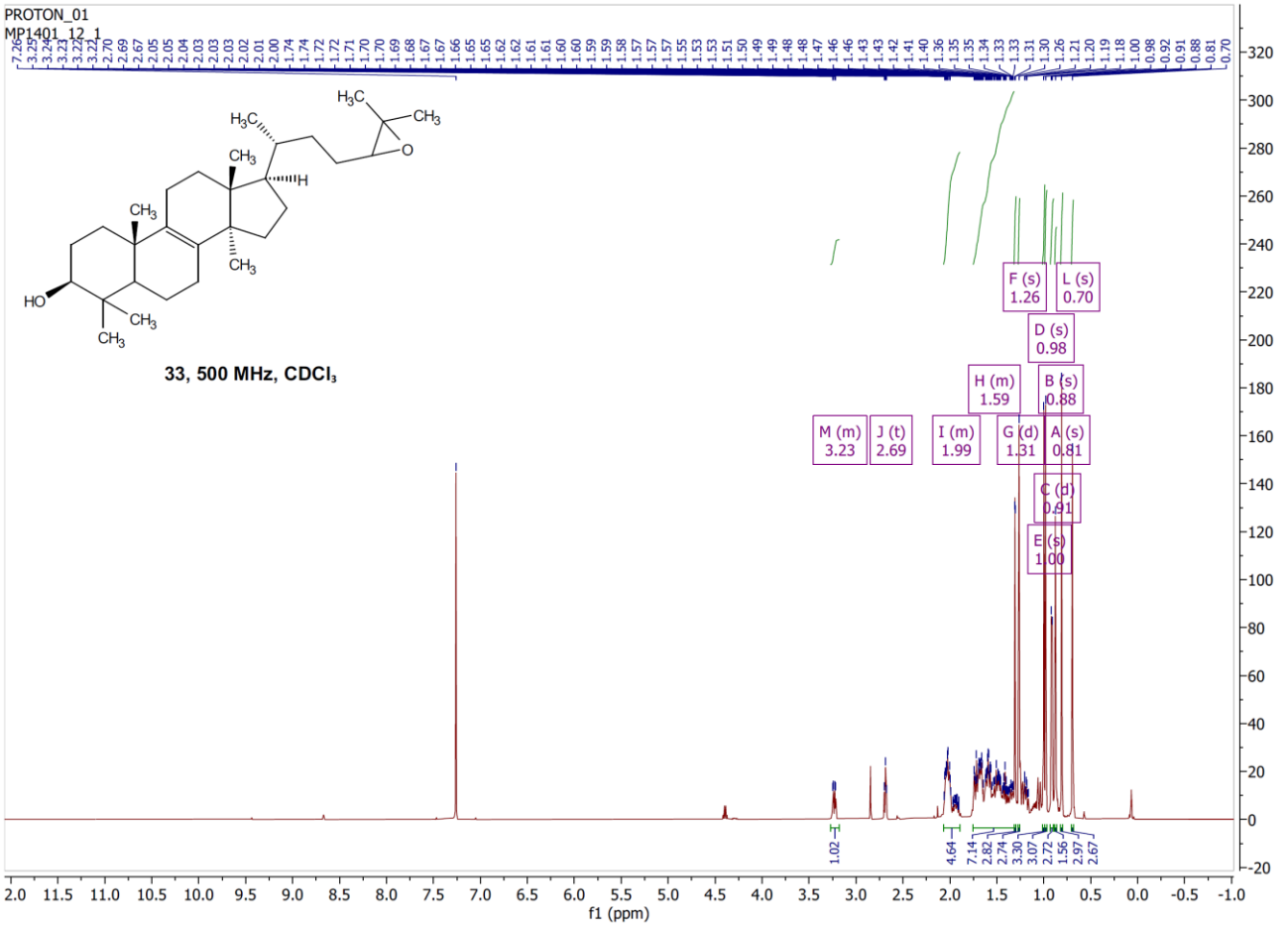

CARBON_03
MP1637_carbon
30, 125 MHz, CDCl3
1.2:1 mixture of two monoepoxides
f1 (ppm)


PROTON_01
MO12_2
31, 500 MHz, CDCl3
2:1 mixture of two monoepoxides
L (t) 5.07
D (dd) 5.15
C (td) 5.34
E (d) 4.58
K (t) 5.38
J (m) 1.61
G (m) 2.12
B (s) 1.30
F (t) 2.70
H (s) 2.05
A (s) 1.25
I (d) 1.69
f1 (ppm)

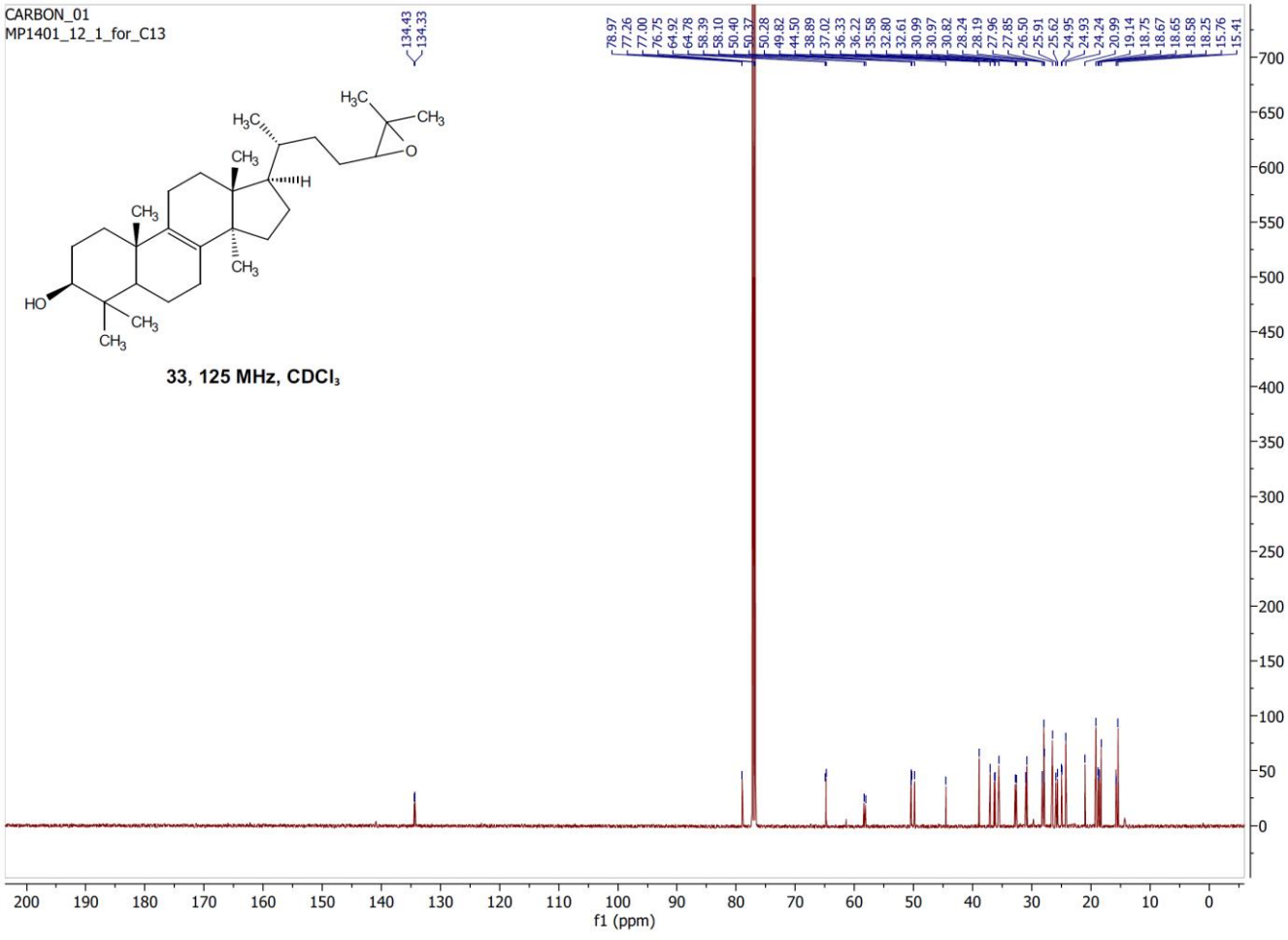

CARBON_01
MP1643_carbon
31, 125 MHz, CDCl3
2:1 mixture of two monoepoxides
f1 (ppm)


PROTON_01
MP1757_2nd
HO
CH3
CH3
CH3
H3C
H
O
32, 500 MHz, CDCl3
mixture of two diasteroisomers dr=1.2:1
H (m) 1.48
F (s) 1.68
J (s) 3.06
D (q) 2.03
K (d) 1.07
A (t) 5.12
B (d) 2.99
C (m) 2.15
I (d) 1.31
E (m) 1.90
G (m) 1.61
f1 (ppm)

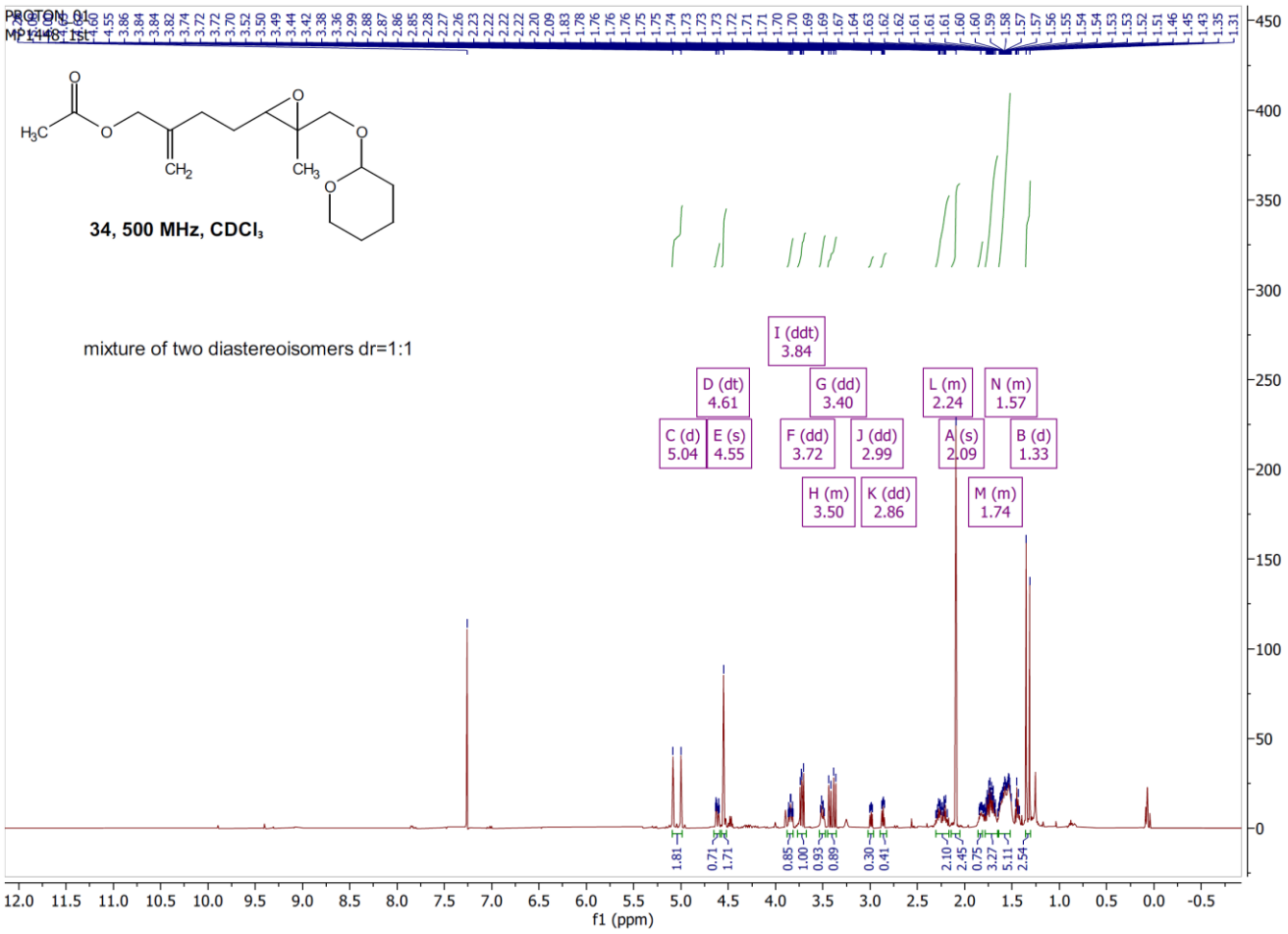

CARBON 01
MP1419 8:1
HO
CH3
CH3
CH3
H3C
H
O
32, 125 MHz, CDCl3
mixture of two diasteroisomers dr=1.2:1
f1 (ppm)

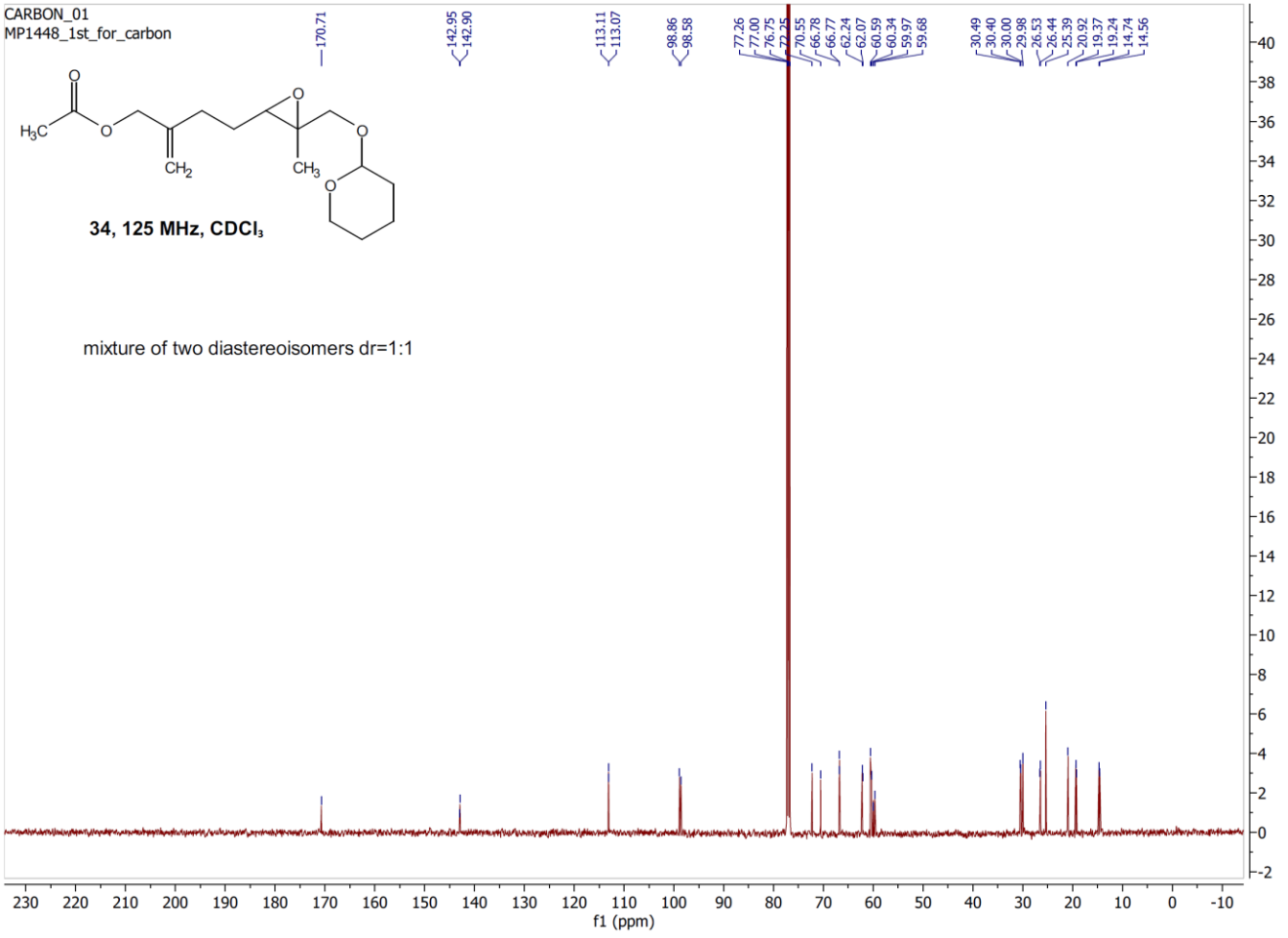


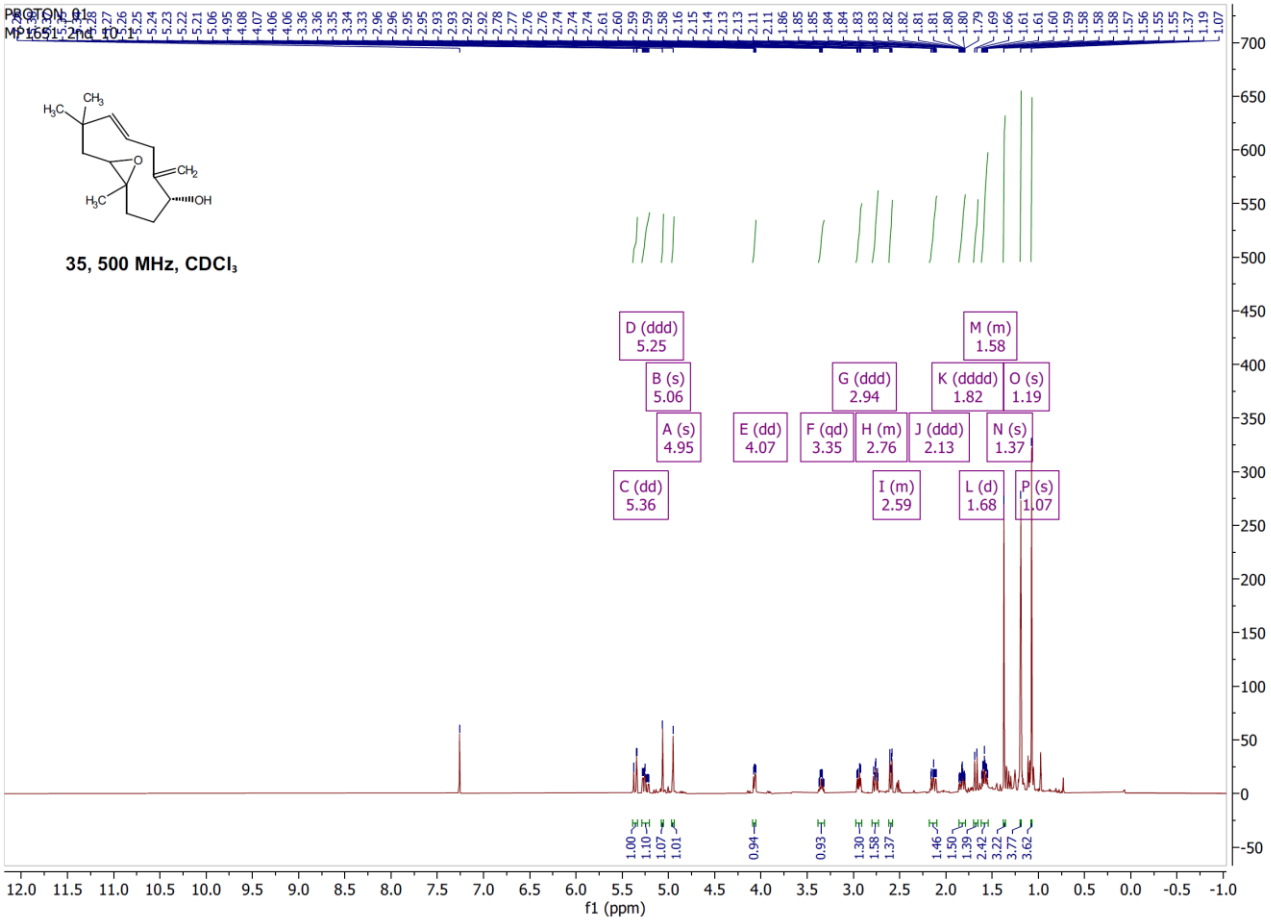
33, 500 MHz, $CDCl_3$

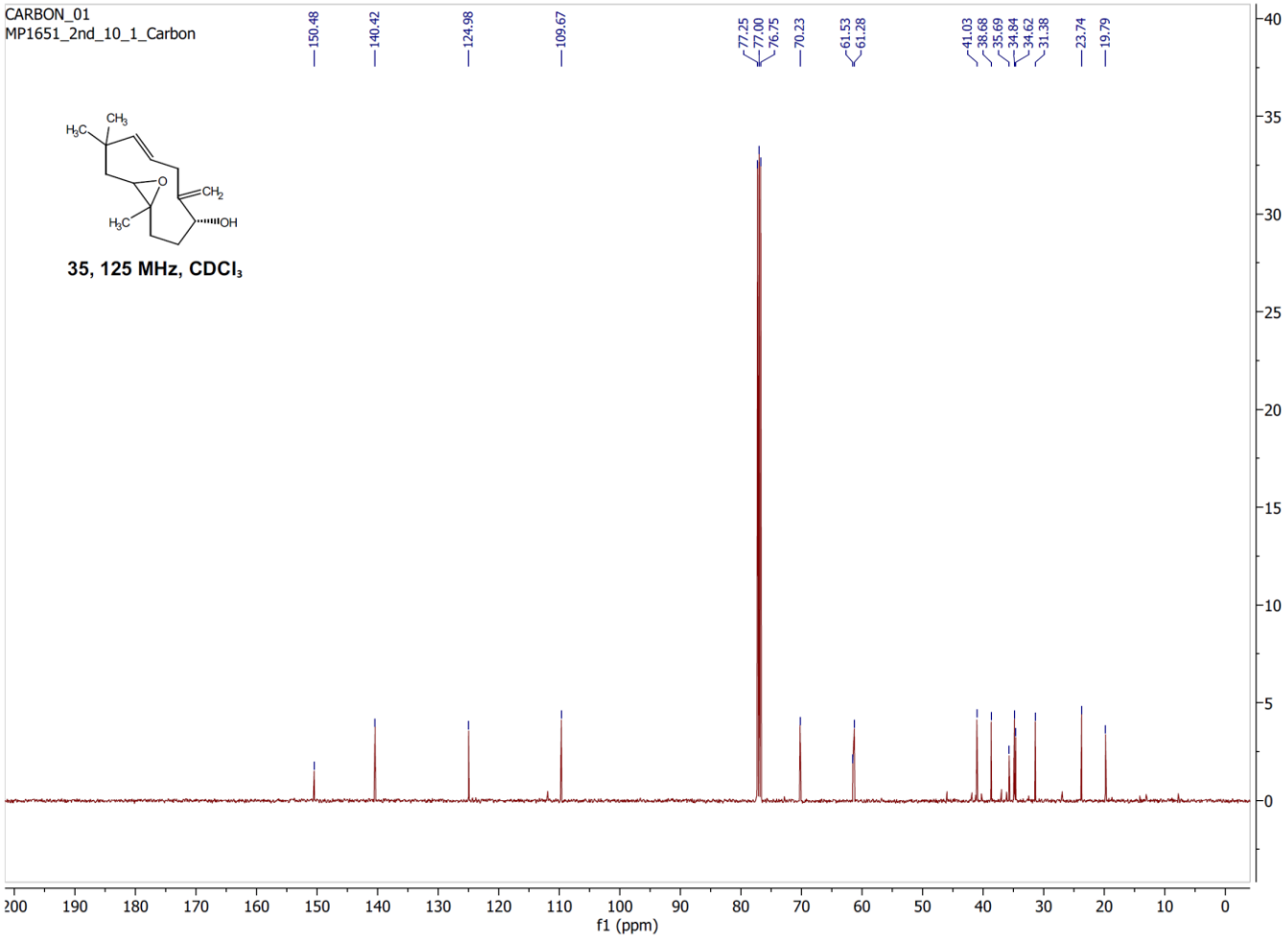


33, 125 MHz, $CDCl_3$


PROTON_01
MP1448_1st
34, 500 MHz, CDCl3
mixture of two diastereoisomers dr=1:1
I (ddt) 3.84
D (dt) 4.61
G (dd) 3.40
L (m) 2.24
N (m) 1.57
C (d) 5.04
E (s) 4.55
F (dd) 3.72
J (dd) 2.99
A (s) 2.09
B (d) 1.33
H (m) 3.50
K (dd) 2.86
M (m) 1.74
f1 (ppm)


CARBON_01
MP1448_1st_for_carbon
34, 125 MHz, CDCl3
mixture of two diastereoisomers dr=1:1
f1 (ppm)


PROTON_01
MP1651_2nd_10_1_Proton
35, 500 MHz, CDCl3
D (ddd) 5.25
B (s) 5.06
A (s) 4.95
C (dd) 5.36
E (dd) 4.07
F (qd) 3.35
G (ddd) 2.94
H (m) 2.76
I (m) 2.59
J (ddd) 2.13
K (dddd) 1.82
L (d) 1.68
M (m) 1.58
N (s) 1.37
O (s) 1.19
P (s) 1.07
f1 (ppm)


CARBON_01
MP1651_2nd_10_1_Carbon
150.48
140.42
124.98
109.67
77.25
77.00
76.75
70.23
61.53
61.28
41.03
38.68
35.69
34.84
34.62
31.38
23.74
19.79
35, 125 MHz, CDCl3
f1 (ppm)

10. Allylic Oxidation of Alkenes

Conditions were surveyed for achieving aerobic allylic oxidation of alkenes with the aid of DKP. For analysis purposes, the known reaction of cyclohexene with selenium dioxide and t-butylhydroperoxide was set up to identify potential products. The reaction products were identified from ^{1}H-NMR signal position by comparison with commercial references materials and a previous report.[38] The ^{1}H-NMR spectra of the reaction mixtures contained some signals assigned as cyclohexene (δ 5.64, m, 2H), 2-cyclohexen-1-peroxide (**SI 17**, δ 5.96, m, 1H; 5.75 m, 1H), 2-cyclohexen-1-ol (**39**, δ 4.19, q, 1H), and 1,2-epoxycyclohexane (**9**, δ 3.17, m, 1H) in $CDCl_3$.

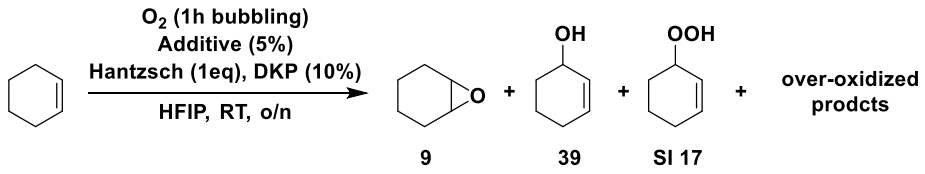
Known Experimental Procedure that was used:[38] Cyclohexene (2.0 mmol, 1.0 equiv.) reacted with SeO_2 (1.00 mmol, 0.5 equiv.) and tert-butyl hydroperoxide (5.0-6.0 M soln in decane, 4.0 mmol, 2.0 equiv.) in dry CH_2Cl_2 (2 ml) at room temperature for 1 hour. After the completion of time, the reaction was quenched with H_2O (2 ml) and extracted with pentane (3 x 3 mL). The organic layers were collected, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure in an ice bath, until a yellowish residue was left in the flask.

- In first spectra the major products were the allylic tert-butyl ether (**SI 18**) and the tert-butyl peroxide (**SI 19**) along with the expected allylic alcohol **39**. The peroxide products appear to arise from a radical-chain mechanism. This is not surprising, since selenenic acids are known to induce the radical-chain decomposition of tert-butyl hydroperoxide.[39]

NMR showing the products

Screening additives to achieve aerobic allylic oxidation based on DKP catalysis

Having a reliable trace of potential oxidations for cyclohexene we next moved on screening additives in our DKP-catalytic protocol, wishing to shutter the competent epoxidation over the production of allylic alcohols. Selected examples of additives tested are shown in Table S5. In most cases of screened metal salts or complexes (entries 2-5) reaction profile was bad, producing many overoxidized products or decomposition. On the other hand, selenium dioxide was found appropriate for producing allylic alcohol and allylic hydroperoxide, minimizing the formation of competent epoxide.

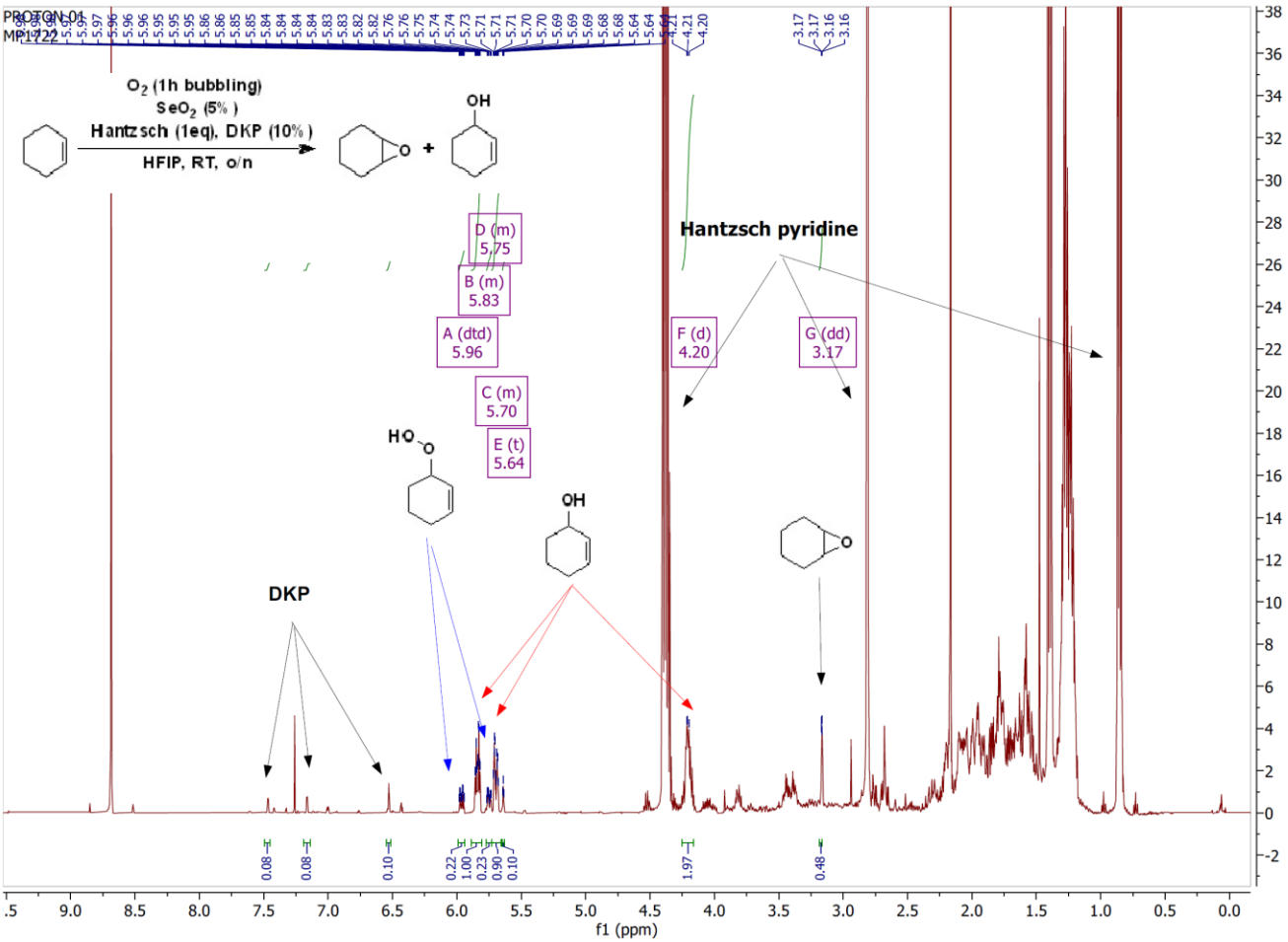


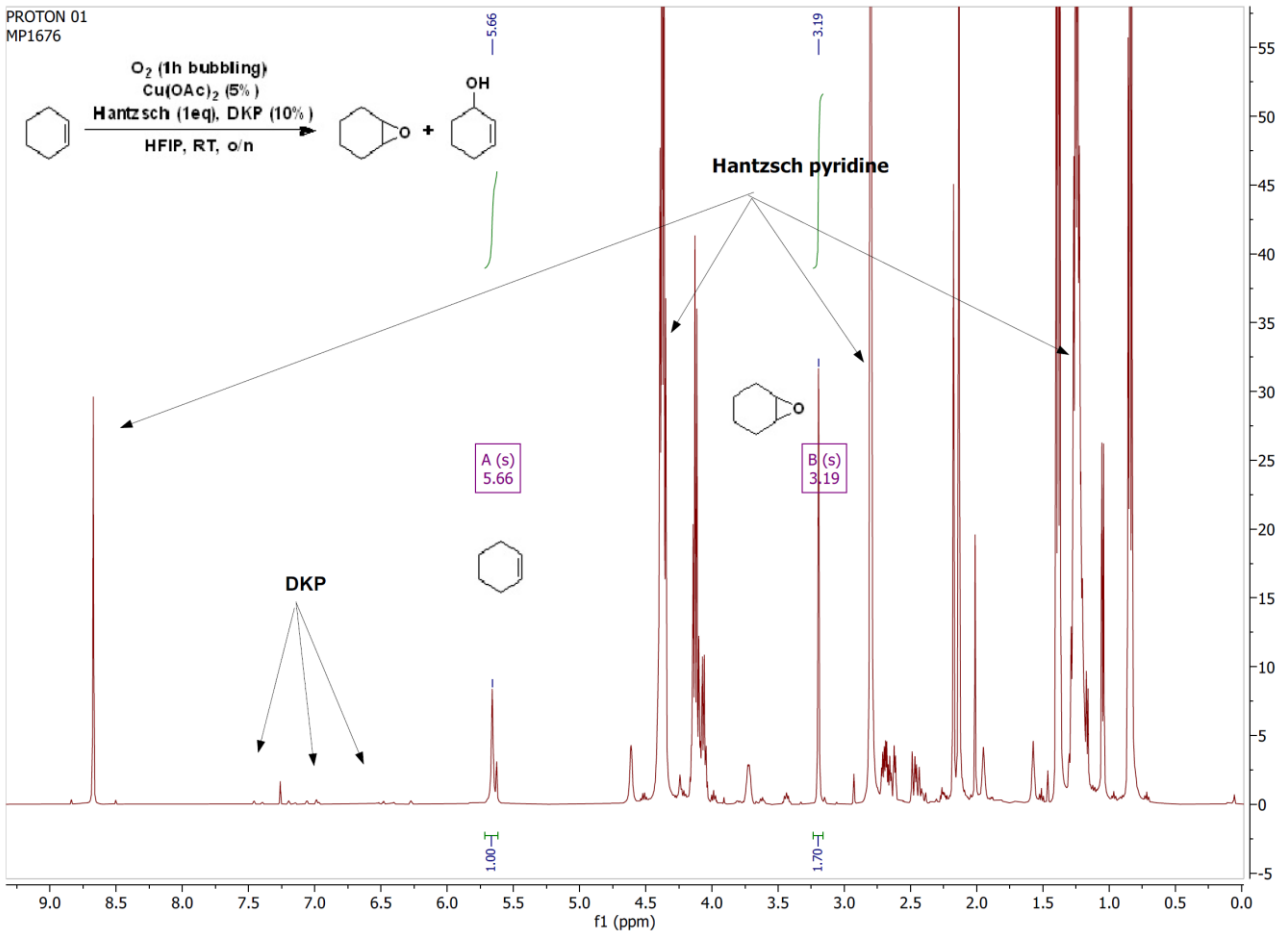
A/A	Additive (5% mol)	Conversion (%)	9	39	SI 17	DEC
1	SeO_2	97	15%	72%	10%	-
2	$Cu(OTf)_2$	65	50%	10%	5%	-
3	$Cu(OAc)_2$	70	63%	-	-	-
4	$FeCl_3$	75	12%	-	-	62%
5	Fe(TPP)Cl	90	-	-	-	90%

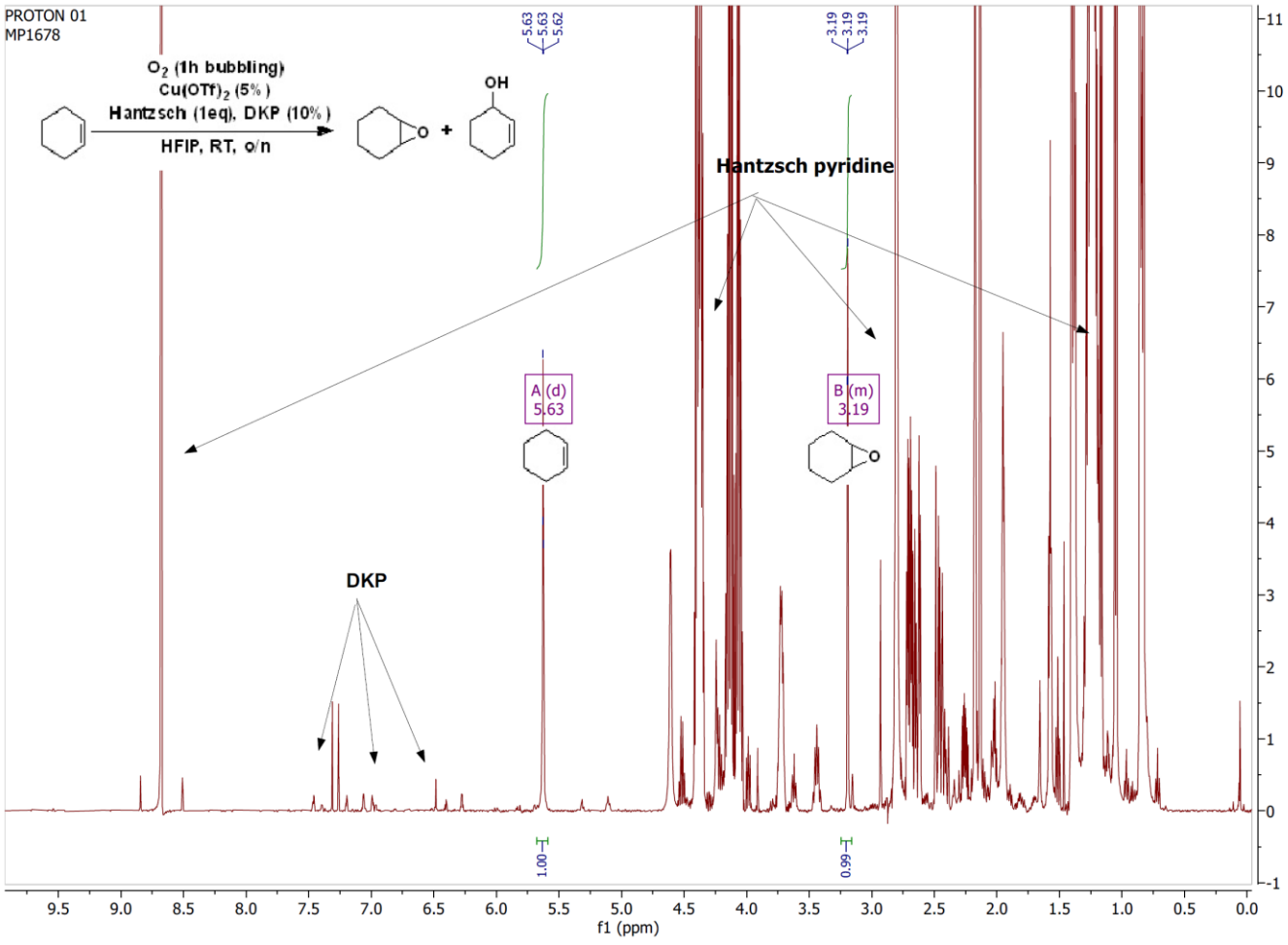
Conditions: Cyclohexene (1.0 equiv.), **3** (1.0 equiv.) and DKP (0.1 equiv.) were dissolved in 1.2 ml HFIP and then lewis acid (0.05 equiv.) was added. The reaction was bubbled with O_2 for 1 h and then the vial was capped at 25°C for o/n.

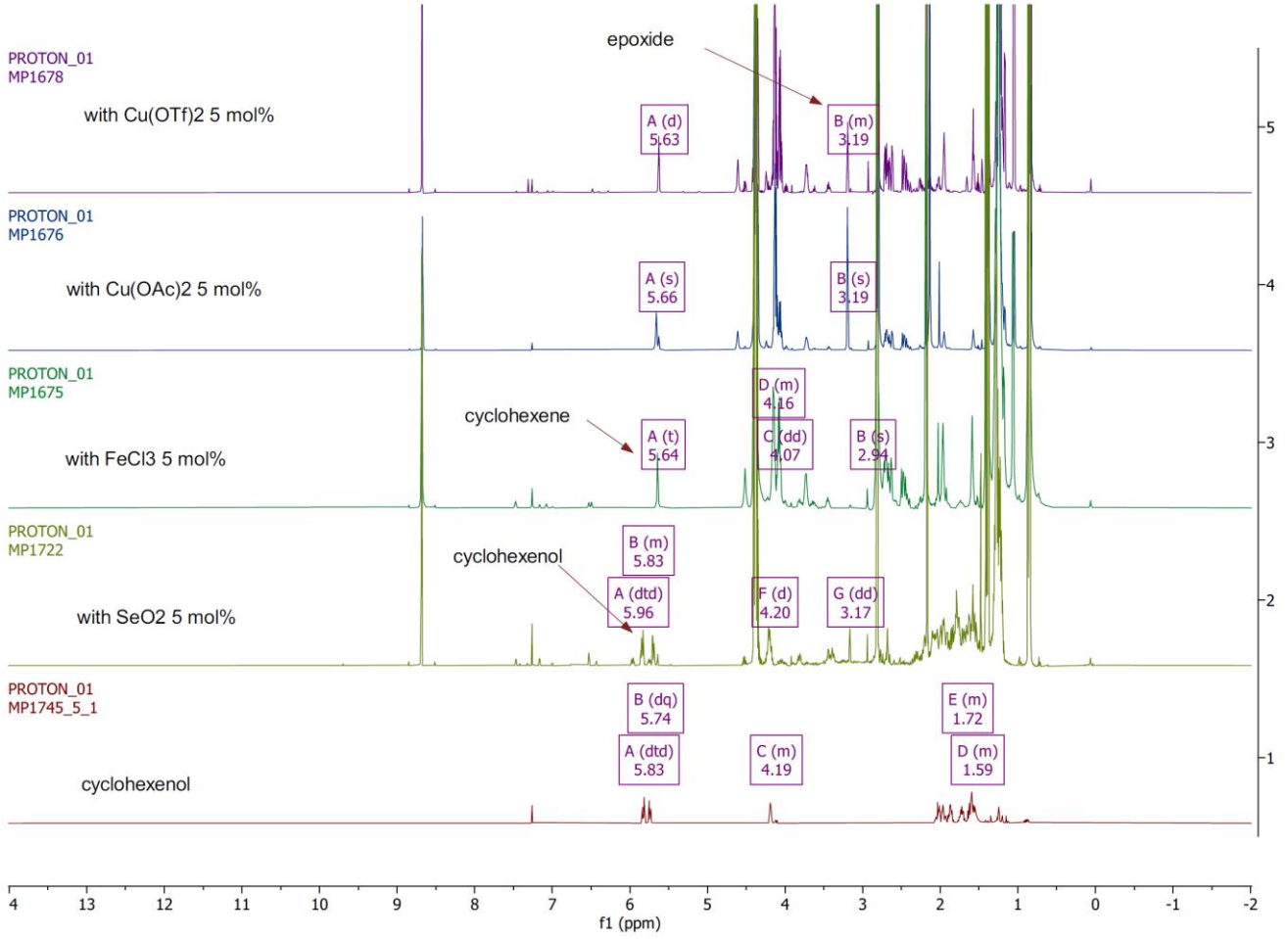
Table S5. Screening additives for allylic oxidation

The dominance of SeO_2 is obvious if someone compares the spectra from different additives as the spectra that are provided below.

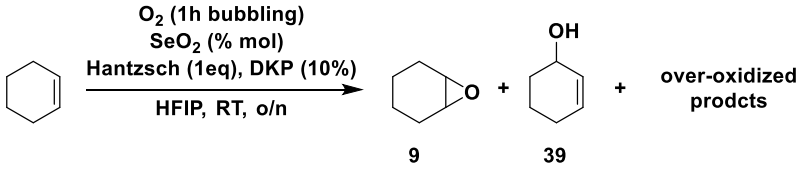



PROTON 01
MP1676
O_2 (1h bubbling)
$Cu(OAc)_2$ (5%)
Hantzsch (1eq), DKP (10%)
HFIP, RT, o/n
OH
Hantzsch pyridine
DKP
A (s)
5.66
B (s)
3.19
1.00
1.70
f1 (ppm)


PROTON 01
MP1678
O_2 (1h bubbling)
$Cu(OTf)_2$ (5%)
Hantzsch (1eq), DKP (10%)
HFIP, RT, o/n
OH
Hantzsch pyridine
DKP
A (d)
5.63
B (m)
3.19
1.00
0.99
f1 (ppm)



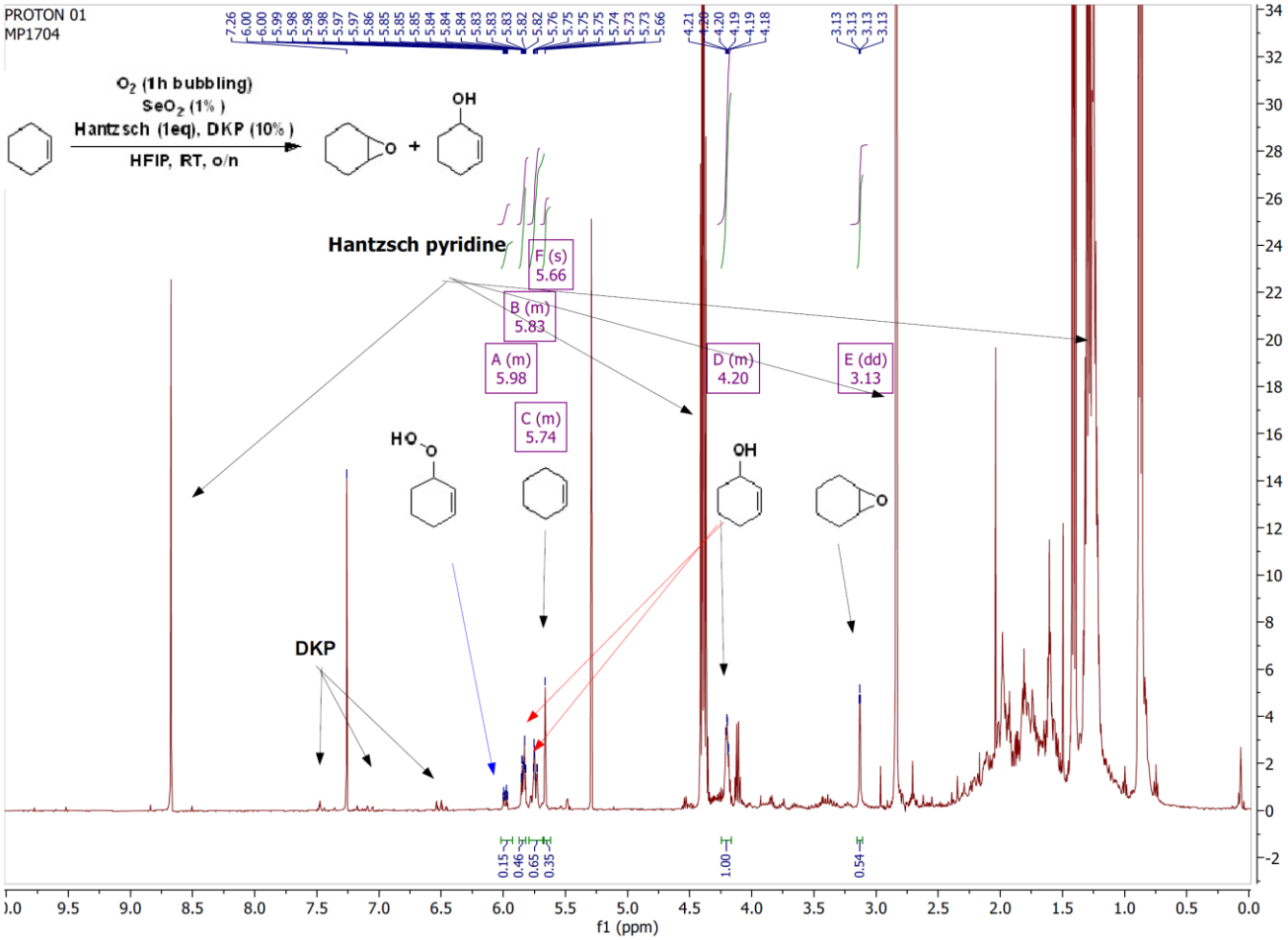
Attempts to optimize the yields by altering the equivalents of selenium dioxide resulted worse reaction profiles when higher amounts of SeO_2 were tried, attributed to the production of several overoxidized products as shown in Table S6 and the spectra provided below. Optimal amount of selenium dioxide was found to be 5 mol% while the amount of DKP remained to 10 mol%. Allylic oxidation can efficiently work even if SeO_2 lowered to 1 mol%. The formed hydroperoxide **SI17** produced by selenium dioxide reaction was able to be transformed to the desired **39** by allowing reaction mixture to stir with NH_4Cl or HCl 3N.

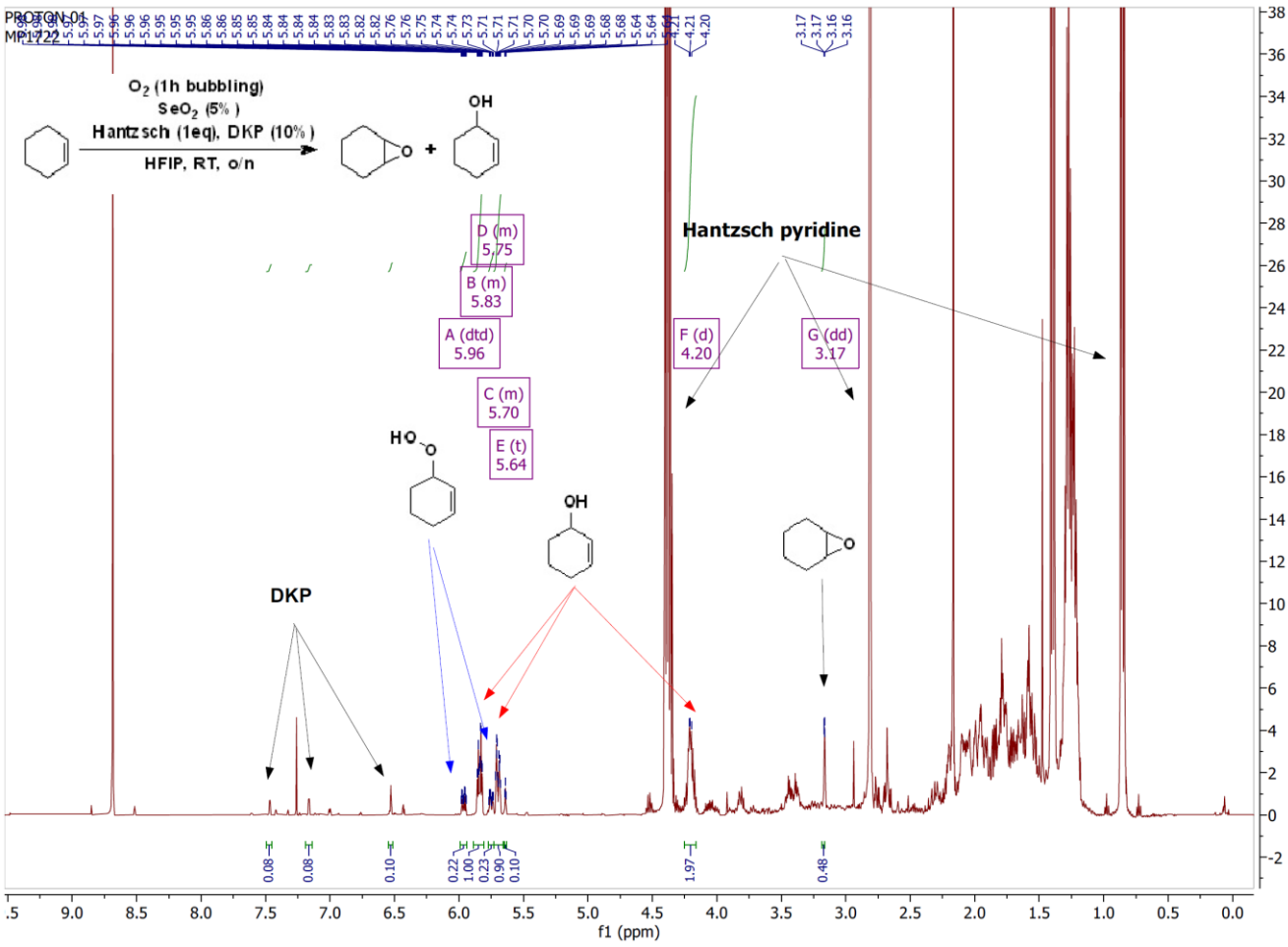


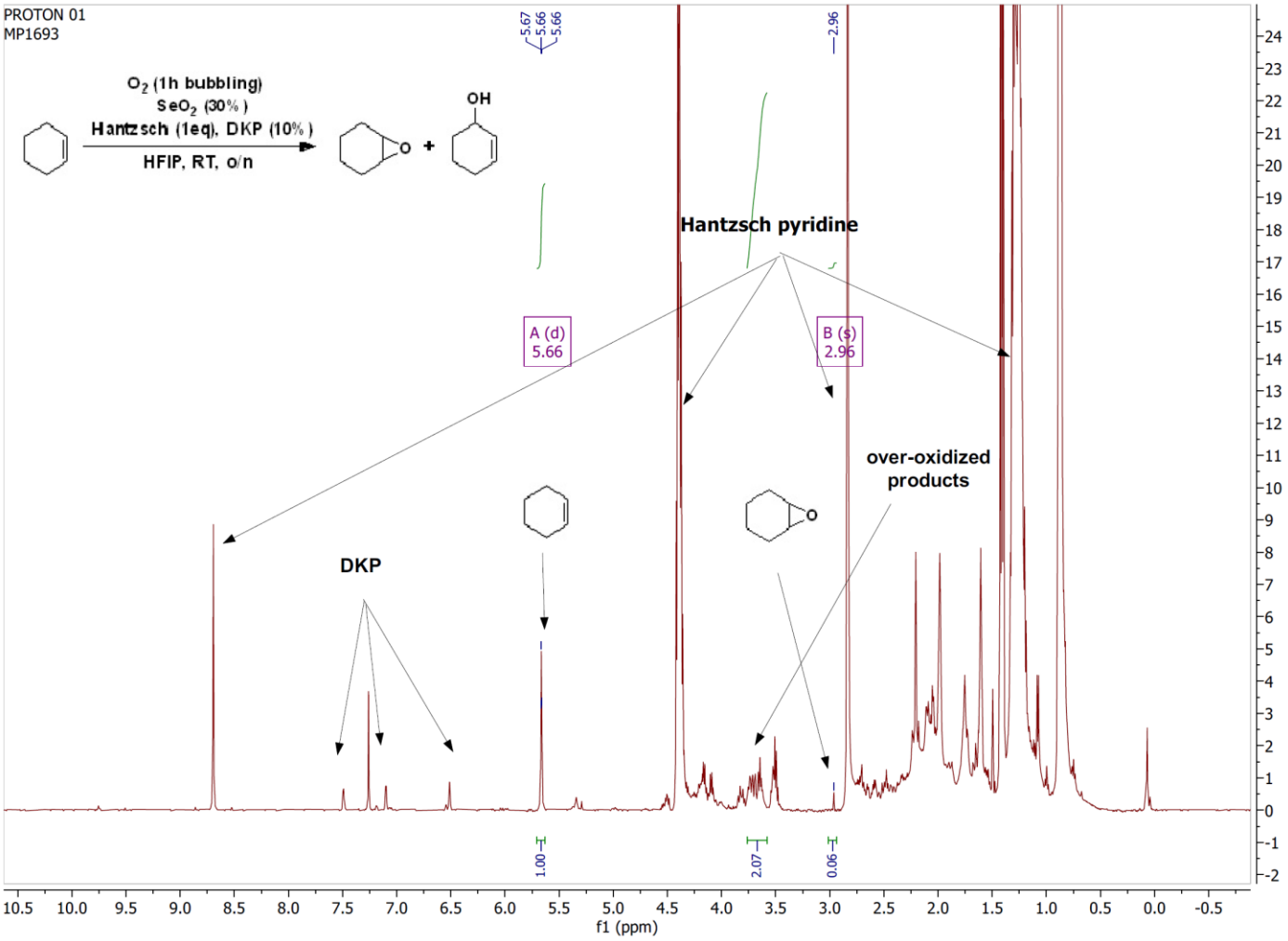
A/A	SeO_2 (% mol)	Conversion (%)	9	39	OVEROX
1	-	92	89%	-	-
2	1	72	22%	44%	-
3	5	97	15%	82%	-
4	30	80	5%	-	60%

Conditions: Cyclohexene (1.0 equiv.), **3** (1.0 equiv.) and DKP (0.1 equiv.) were dissolved in 1.2 ml HFIP and then SeO_2 (as mentioned in the table) was added. The reaction was bubbled with O_2 for 1 h and then the vial was capped at 25°C for o/n.

Table S6. Evaluating quantity of selenium dioxide

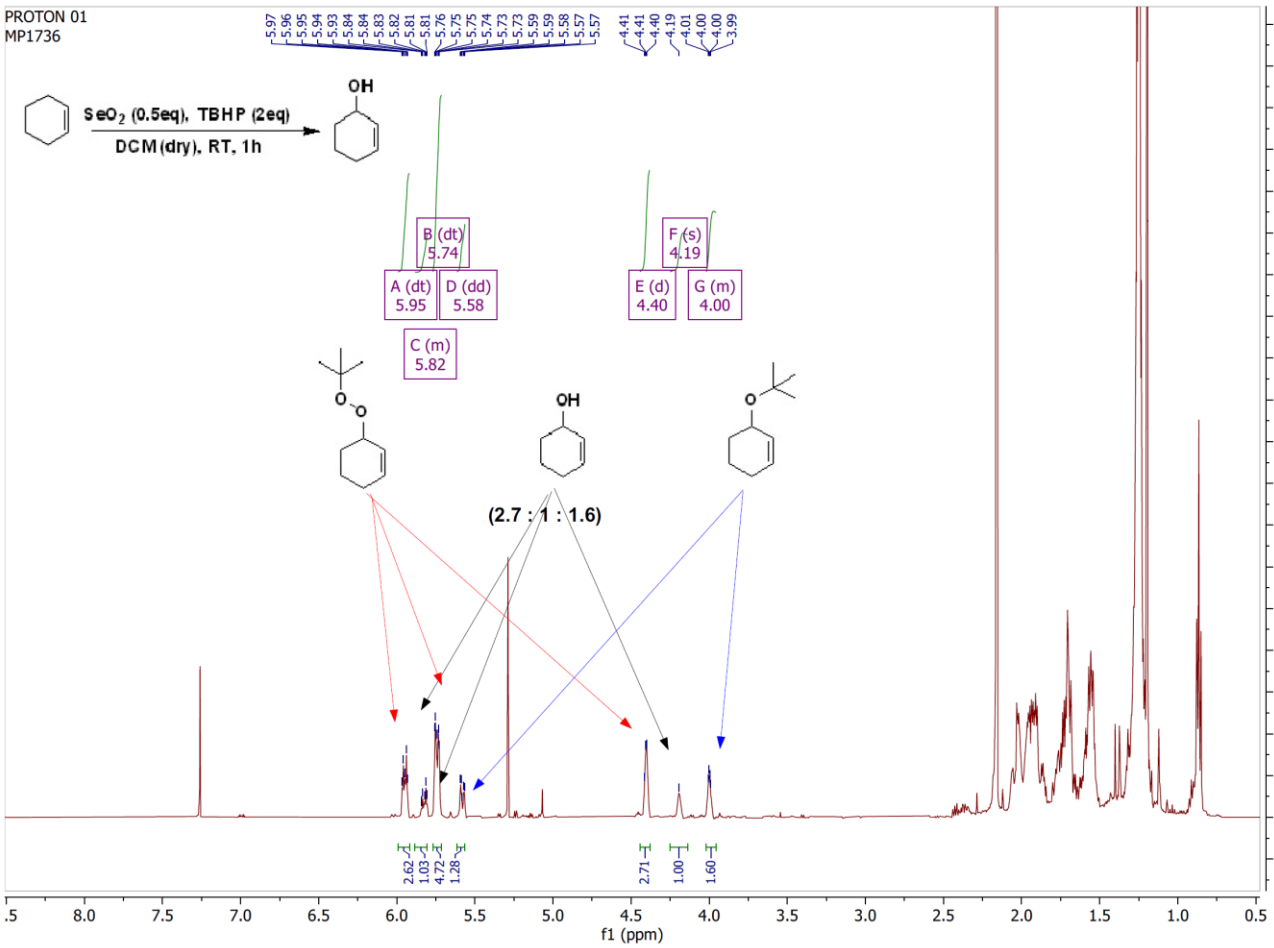

PROTON 01
MP1704
O2 (1h bubbling)
SeO2 (1%)
Hantzsch (1eq), DKP (10%)
HFIP, RT, o/n
OH
Hantzsch pyridine
F (s)
5.66
B (m)
5.83
A (m)
5.98
D (m)
4.20
E (dd)
3.13
C (m)
5.74
HO
OH
DKP
0.15
0.46
0.65
0.35
1.00
0.54
f1 (ppm)

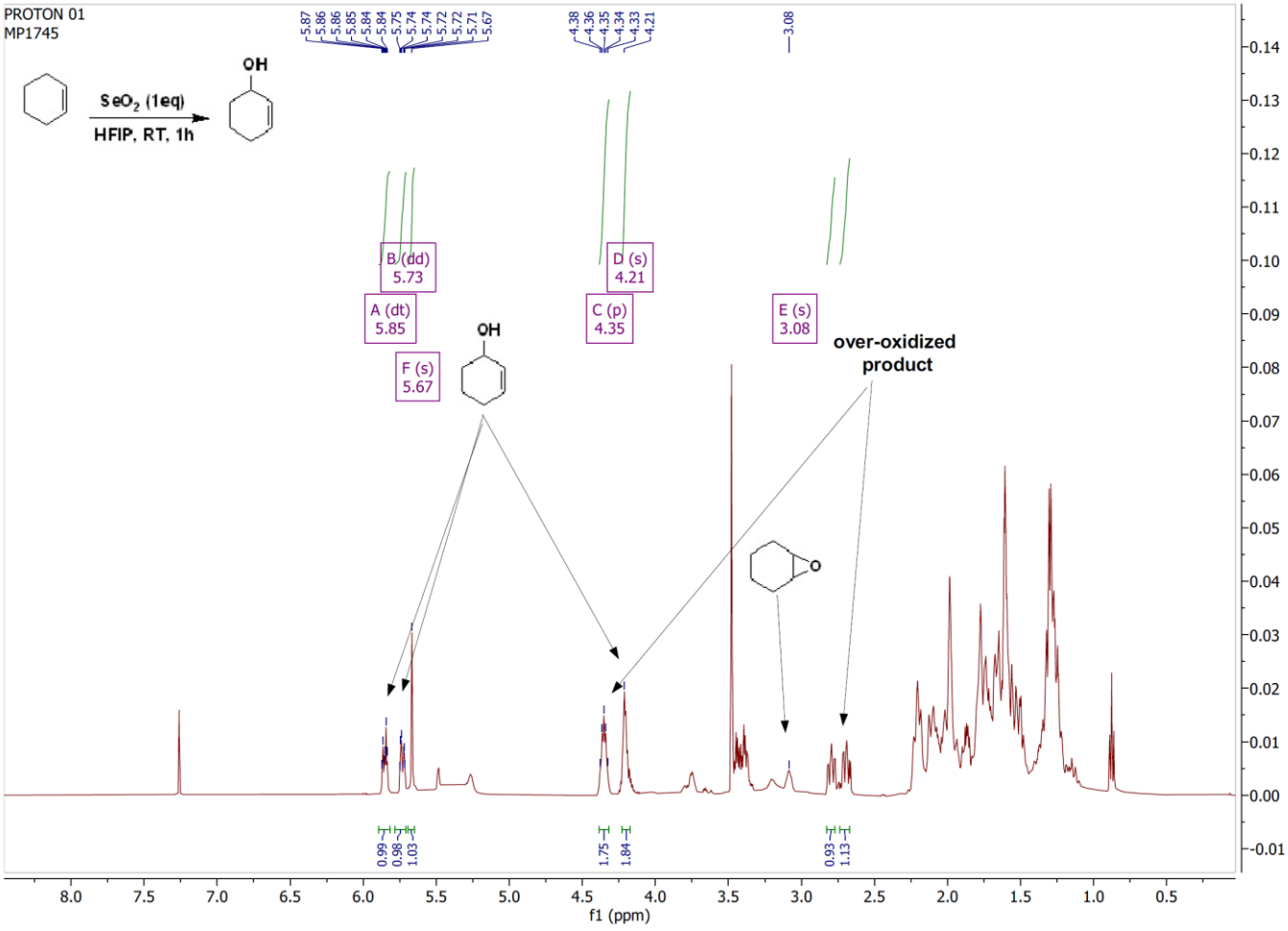

PROTON 01
MP1722
O2 (1h bubbling)
SeO2 (5%)
Hantzsch (1eq), DKP (10%)
HFIP, RT, o/n
OH
D (m)
5.75
B (m)
5.83
A (dtd)
5.96
C (m)
5.70
E (t)
5.64
Hantzsch pyridine
F (d)
4.20
G (dd)
3.17
HO
OH
DKP
0.08
0.08
0.10
0.22
1.00
0.23
0.90
0.10
1.97
0.48
f1 (ppm)

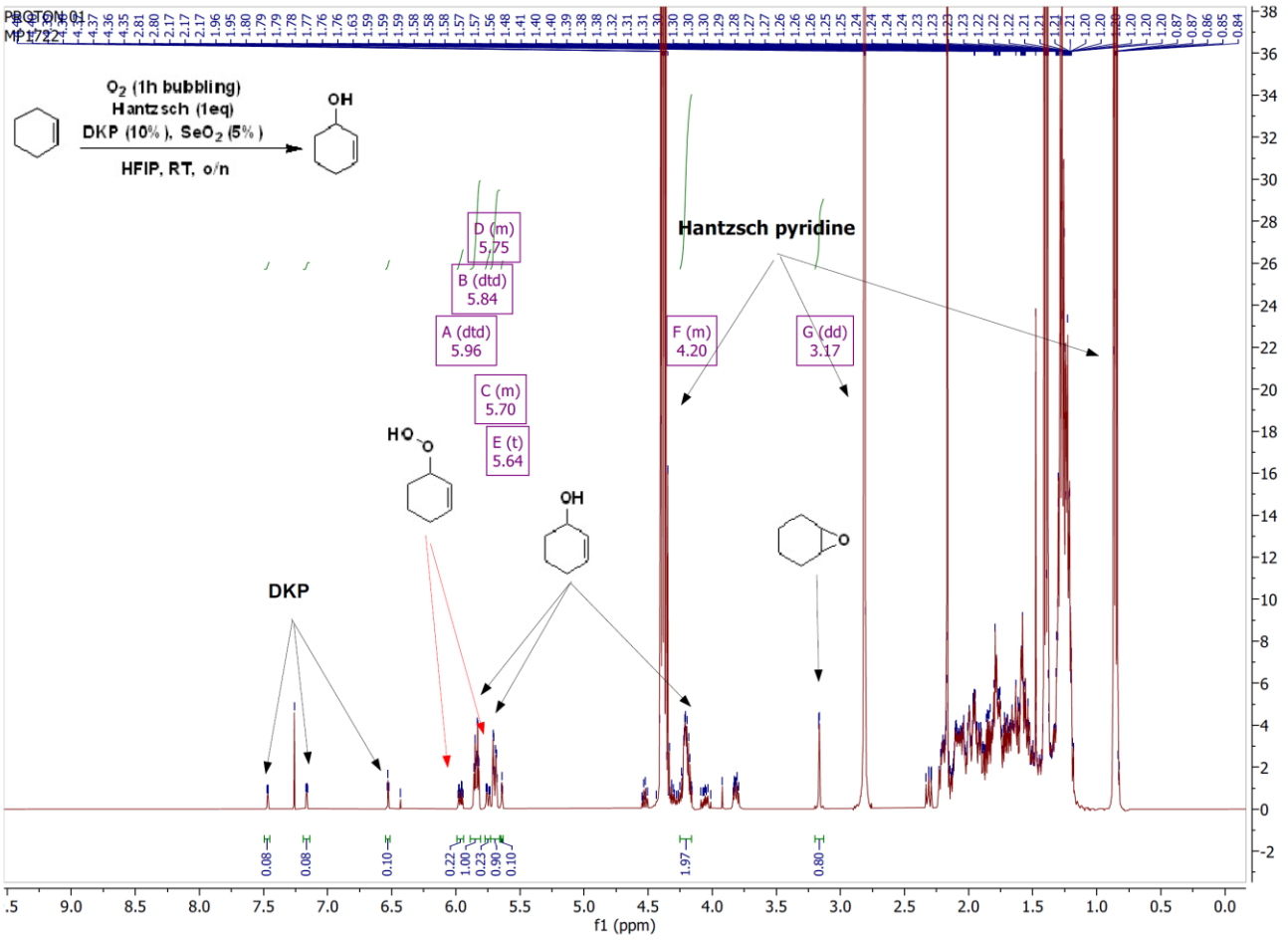


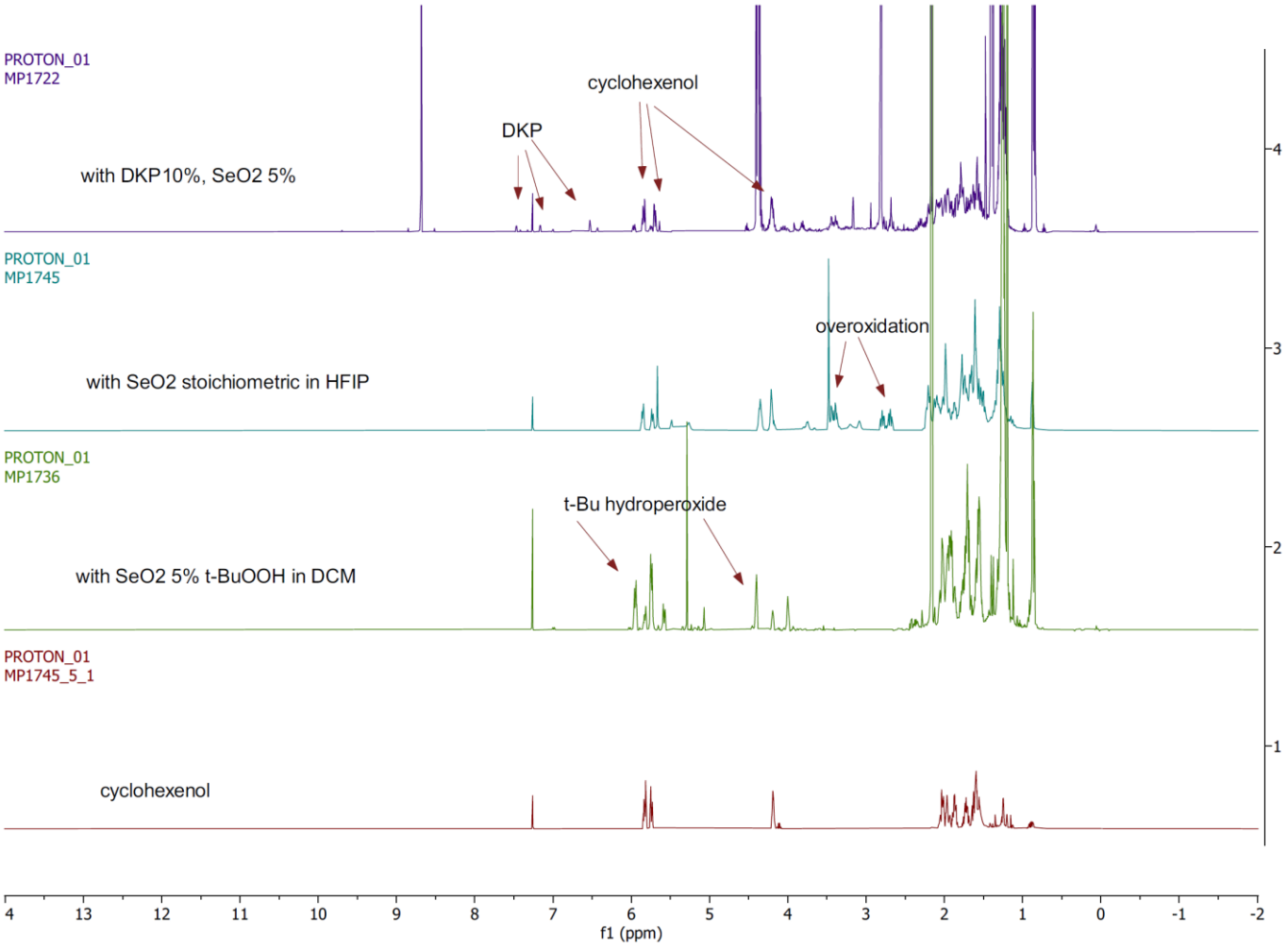
Willing to understand the observed reaction profile, a stoichiometric on selenium oxide reaction was attempted in HFIP (**MP1745)**. The reaction proceeded smoothly resulting cyclohexen-1-ol (**39**) and an over oxidizing product, in 1:1 yield. The overall conversion of the starting material to its oxidized products was at about 61%, where allylic alcohol (**39**) and cyclohexene-oxide (**9**) were formed in 1.1:1 yield.

Comparison of SeO_2 methods including the classic approach of SeO_2 with t-BuOOH with SeO_2 in HFIP and with the aid of DKP is provided below.


PROTON 01
MP1736
SeO2 (0.5eq), TBHP (2eq)
DCM (dry), RT, 1h
OH
B (dt) 5.74
A (dt) 5.95
D (dd) 5.58
C (m) 5.82
F (s) 4.19
E (d) 4.40
G (m) 4.00
(2.7 : 1 : 1.6)
f1 (ppm)


PROTON 01
MP1745
SeO2 (1eq)
HFIP, RT, 1h
OH
B (dd) 5.73
A (dt) 5.85
F (s) 5.67
D (s) 4.21
C (p) 4.35
E (s) 3.08
over-oxidized product
f1 (ppm)


PROTON_01
MP1722
O2 (1h bubbling)
Hantzsch (1eq)
DKP (10%), SeO2 (5%)
HFIP, RT, o/n
OH
D (m)
5.75
B (dtd)
5.84
A (dtd)
5.96
C (m)
5.70
E (t)
5.64
Hantzsch pyridine
F (m)
4.20
G (dd)
3.17
HO
O
OH
O
DKP
0.08
0.08
0.10
0.22
1.00
0.23
0.90
0.10
1.97
0.80
f1 (ppm)


PROTON_01
MP1722
with DKP10%, SeO2 5%
cyclohexenol
DKP
PROTON_01
MP1745
with SeO2 stoichiometric in HFIP
overoxidation
PROTON_01
MP1736
with SeO2 5% t-BuOOH in DCM
t-Bu hydroperoxide
PROTON_01
MP1745_5_1
cyclohexenol
f1 (ppm)

Experimental Procedure: Cyclohexene (2.0 mmol, 1.0 equiv.) reacted with SeO_2 (2.00 mmol, 1.0 equiv.) in HFIP (2ml) at room temperature for 1 hour. After the completion of time, the reaction was quenched with H_2O (2 ml) and extracted with pentane (3 x 3 mL). The organic layers were collected, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure in an ice bath, until a yellowish residue was left in the flask. The crude reaction mixture was analyzed by NMR and GC.

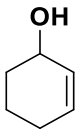
Results: As it is mentioned before (Section 9) cyclohexene can easily be epoxidized with the aim of DKP in the presence of dioxygen in HFIP almost quantitively without the formation of more oxidized products (entry 1). With the use of 1 mol% of SeO_2, a reduction in the reaction rate was observed while the reaction retains the preference for allylic alcohol formation over epoxide **9** (entry 2). Increasing the amount of SeO_2 to 30 mol% diminishing the formation of allylic alcohol **39** by the production of over oxidized products (entry 4). It was thus considered that the ideal amount of selenium dioxide is 5 mol%, the one that leads to a satisfactory preference of allylic **39** to epoxy product **9** without the formation of over-oxidizing products (entry 3).

General procedure for the aerobic allylic oxidation of alkenes with the aid of DKP and selenium dioxide

The corresponding commercially or synthesized alkene (0.36 mmol, 1.0 equiv.) was dissolved in HFIP (1.5 mL) in a 4 mL screw capped vial without a stirring bar. Then, Hantzsch ester (**3**, 0.36 mmol, 1.0 equiv.), followed by the addition of DKP (0.04 mmol, 0.1 equiv.) were added in one portion. When the reaction mixture became homogeneous SeO_2 (0.018 mmol, 0.05 equiv.) was added, and the vial was tightly capped by a rubber septum. In the septum was introduced an exit needle and a pipette through which dioxygen was bubbled continuously either by a balloon or by gas cyclinder and a gas controller. Care was taken to adjust slow bubbling in the reaction vial in order to avoid evaporation of HFIP. The reaction was stirred for 12 hours at room temperature and after the completion of time, the reaction was quenched with HCl 3N and extracted with pentane (3 x 2 mL). The organic layers were collected and re-extracted with HCl 3N (2 x 5 ml), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure in an ice bath, until a pale-yellow solid residue was left in the flask. Flash chromatography on silica gel gave alcohols (**39**-**42**) in good yields. For non-volatile alkenes, after the completion of time, the reaction was quenched with water and extracted with Et_2O (3 x 2 ml). The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure, until a pale-yellow solid residue was left in the flask. Flash chromatography on silica gel gave alcohols (**43**-**45**) in good yields.

Isolated allylic alcohols

Cyclohex-2-en-1-ol[38] **(39)**



MW (g/mol): 98.14 **Molecular formula: $C_6H_{10}O$**

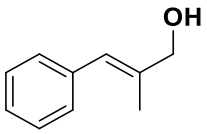
From cyclohexene. **Rf:** 0.18 [Hexane:EtOAc (10:1)], Hexane:EtOAc (5:1), **Yield: 82%**, Yellowish oil

NMR identical to previous reported spectra.[40]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.54-1.64 (m, 2H), 1.69-1.74 (m, 1H), 1.84-1.89 (m, 1H), 1.93-1.95 (m, 1H), 1.99-2.04 (m, 1H), 4.16-4.21 (m, 1H), 5.74 (dq, *J* 10.0, 2.4 Hz, 1H), 5.83 (dtd, *J* 10.2, 3.7, 1.3 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 18.9, 25.0, 32.0, 65.5, 129.8, 130.6 ppm

(*E*)-2-Methyl-3-phenylprop-2-en-1-ol[39] **(40)**



MW (g/mol): 148.20 **Molecular formula: $C_{10}H_{12}O$**

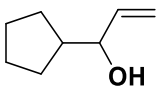
From 2-Methyl-1-phenylpropene. **Rf:** 0.52 [Cyclohexane:EtOAc (20:1)], Cyclohexane:EtOAc (10:1), **Yield: 58%**, Colorless oil

NMR identical to previous reported spectra.[41]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.91 (s, 3H), 4.20 (s, 2H), 6.53 (s, 1H), 7.22 (t, *J* 7.3 Hz, 1H), 7.29 (d, *J* 7.8 Hz, 2H), 7.34 (t, *J* 7.5 Hz, 2H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 15.3, 69.0, 125.0, 126.4, 128.1, 128.9, 137.5, 137.6 ppm

1-Cyclopentylprop-2-en-1-ol[40] **(41)**



MW (g/mol): 126.20 **Molecular formula: $C_8H_{14}O$**

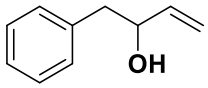
From allylcyclopentane. **Rf:** 0.43 [CH_2Cl_2 (100%)], Pentane:Et_2O (40:1), **Yield: 91%**, Colorless oil

NMR identical to previous reported spectra.[42]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.20-1.29 (m, 1H), 1.34-1.42 (m, 1H), 1.52-1.68 (m, 5H), 1.79 (tdd, *J* 11.9, 5.3, 2.4 Hz, 2H), 1.95 (p, *J* 8.0 Hz, 1H), 3.90 (ddt, *J* 7.7, 6.4, 1.3 Hz, 1H), 5.11 (dt, *J* 10.5, 1.4 Hz, 1H), 5.22 (dt, *J* 17.1, 1.5 Hz, 1H), 5.88 (ddd, *J* 17.1, 10.4, 6.5 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 25.61, 25.66, 28.69, 28.71, 30.9, 45.7, 114.9, 140.4 ppm

1-Phenylbut-3-en-2-ol[41] (42)



MW (g/mol): 148.20 **Molecular formula: $C_{10}H_{12}O$**

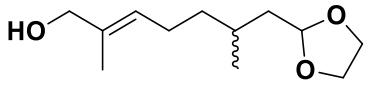
From but-3-en-1-ylbenzene. **Rf:** 0.41 [CH_2Cl_2 (100%)], Pentane:Et_2O (40:1), **Yield: 85%**, Colorless oil

NMR identical to previous reported spectra.[43]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 2.80 (dd, *J* 13.6, 8.0 Hz, 1H), 2.89 (dd, *J* 13.6, 5.1 Hz, 1H), 4.33-4.39 (m, 1H), 5.14 (dt, *J* 10.6, 1.4 Hz, 1H), 5.26 (dt, *J* 17.1, 1.5 Hz, 1H), 5.94 (ddd, *J* 17.3, 10.4, 5.8 Hz, 1H), 7.21-7.28 (m, 3H), 7.32 (dd, *J* 8.6, 6.6 Hz, 2H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 43.8, 73.6, 115.0, 126.6, 128.5, 129.5, 137.7, 140.1 ppm

(*E*)-7-(1,3-Dioxolan-2-yl)-2,6-dimethylhept-2-en-1-ol[42] (43)



MW (g/mol): 214.31 **Molecular formula: $C_{12}H_{22}O_3$**

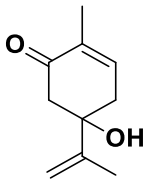
From 2-(2,6-dimethylhept-5-en-1-yl)-1,3-dioxolane. **Rf:** 0.19 [Hexane:EtOAc (4:1)], Hexane:EtOAc (4:1), **Yield: 68%**, Colorless oil

NMR identical to previous reported spectra.[44]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 0.96 (d, *J* 6.5 Hz, 3H), 1.48-1.54 (m, 2H), 1.64-1.69 (m, 3H), 1.67 (s, 3H), 1.97-2.12 (m, 2H), 3.81-3.86 (m, 2H), 3.94-3.97 (m, 2H), 3.99 (d, *J* 5.4 Hz, 2H), 4.90 (t, *J* 5.0 Hz, 1H), 5.40 (t, *J* 7.2 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 13.7, 19.8, 29.0, 29.7, 30.9, 36.9, 40.8, 64.7, 69.1, 103.7, 126.5, 134.7 ppm

5-Hydroxy-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one[43] (44)



MW (g/mol): 166.22 **Molecular formula: $C_{10}H_{14}O_2$**

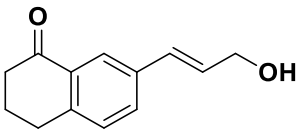
From *R*-carvone. **Rf:** 0.31 [Hexane:EtOAc (2:1)], Hexane:EtOAc (4:1) **Yield: 73%**, Colorless oil

NMR identical to previous reported spectra.[45]

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 1.81 (q, *J* 1.8 Hz, 3H), 1.83 (d, *J* 1.3 Hz, 3H), 2.49 (dt, *J* 5.1, 1.7 Hz, 0.6H), 2.52 (dt, *J* 5.1, 1.7 Hz, 0.8H), 2.62 (d, *J* 1.8 Hz, 0.6H), 2.65 (d, *J* 1.7 Hz, 0.8H), 2.69 (dt, *J* 4.5, 2.3 Hz, 0.8H), 2.73 (dd, *J* 3.3, 2.3 Hz, 0.6H), 2.80 (s, 0.8H), 2.83 (s, 0.6H), 4.90-4.92 (m, 1H), 5.02-5.03 (t, *J* 0.9 Hz, 1H), 6.62 (ddq, *J* 4.8, 3.0, 1.5 Hz, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 15.5, 18.6, 37.3, 49.2, 76.1, 111.6, 135.3, 140.9, 148.1, 198.1 ppm

(*E*)-7-(3-Hydroxyprop-1-en-1-yl)-3,4-dihydronaphthalen-1(2*H*)-one (45)



MW (g/mol): 202.25 **Molecular formula: $C_{13}H_{14}O_2$**

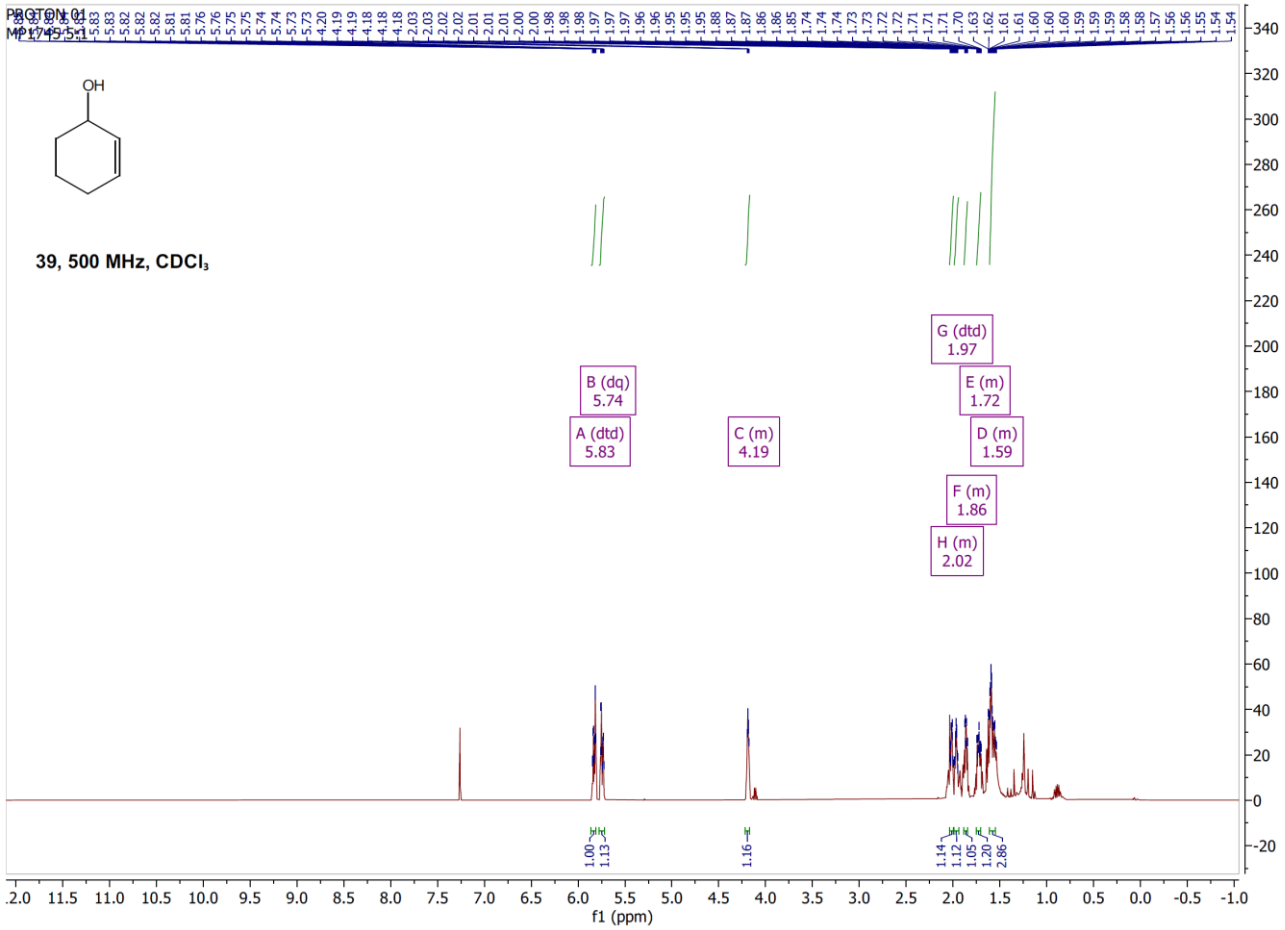
From 7-allyl-3,4-dihydronaphthalen-1(2H)-one. **Rf:** 0.44 [Hexane:EtOAc (2:1)], Hexane:EtOAc (3:1), **Yield: 87%**, Colorless oil

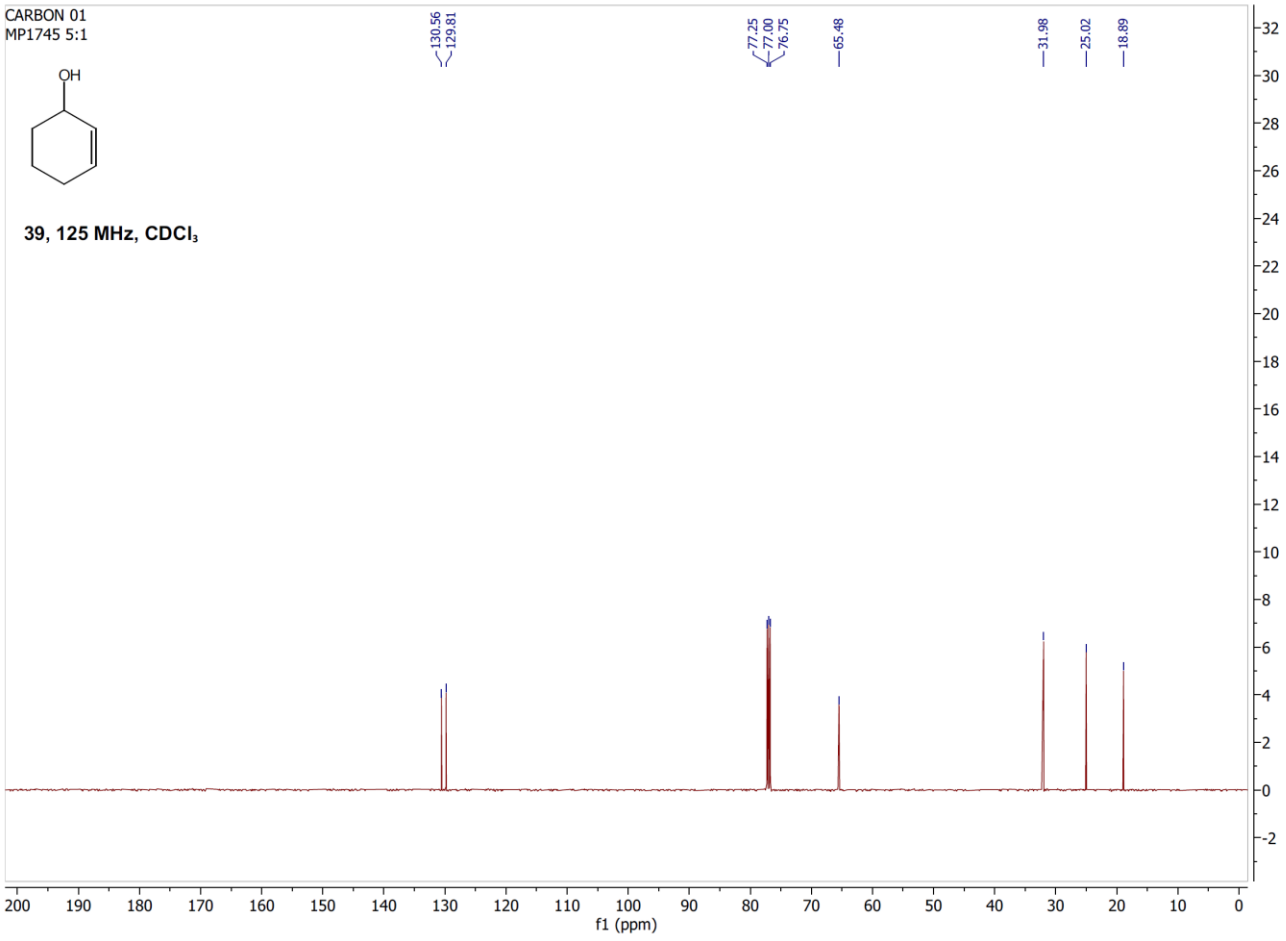
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ_H 2.13 (p, *J* 6.5 Hz, 3H), 2.65 (dd, *J* 7.3, 5.8 Hz, 2H), 2.94 (t, *J* 6.1 Hz, 2H), 4.33 (dd, *J* 5.6, 1.6 Hz, 2H), 6.41 (dt, *J* 15.9, 5.6 Hz, 1H), 6.62 (dt, *J* 16.0, 1.6 Hz, 1H), 7.21 (d, *J* 7.9 Hz, 1H), 7.49 (dd, *J* 7.9, 2.0 Hz, 1H), 8.03 (d, *J* 2.0 Hz, 1H) ppm

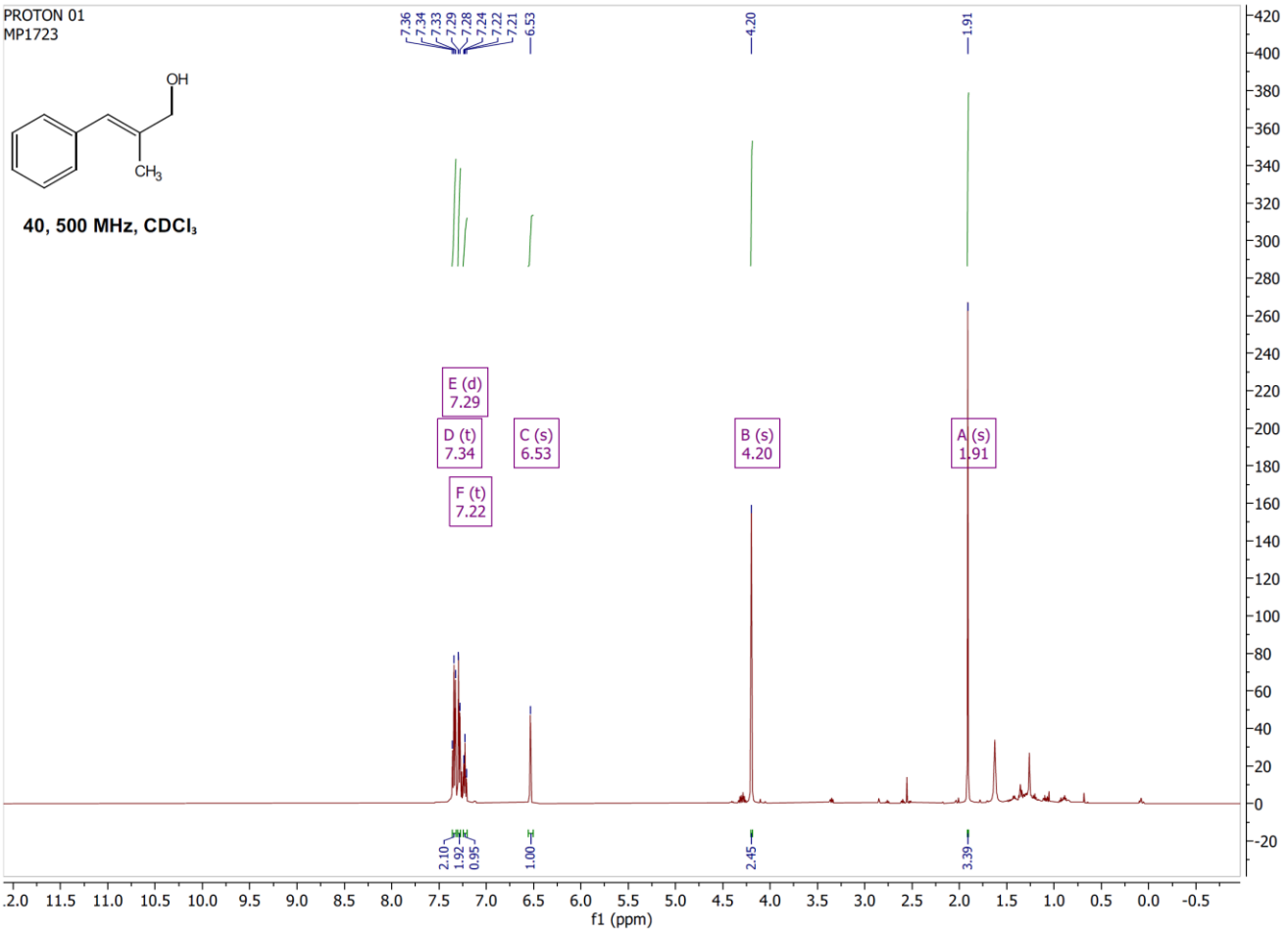
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 23.2, 29.5, 39.1, 63.5, 125.0, 129.1, 129.3, 129.9, 131.1, 132.7, 135.3, 143.8, 198.4 ppm

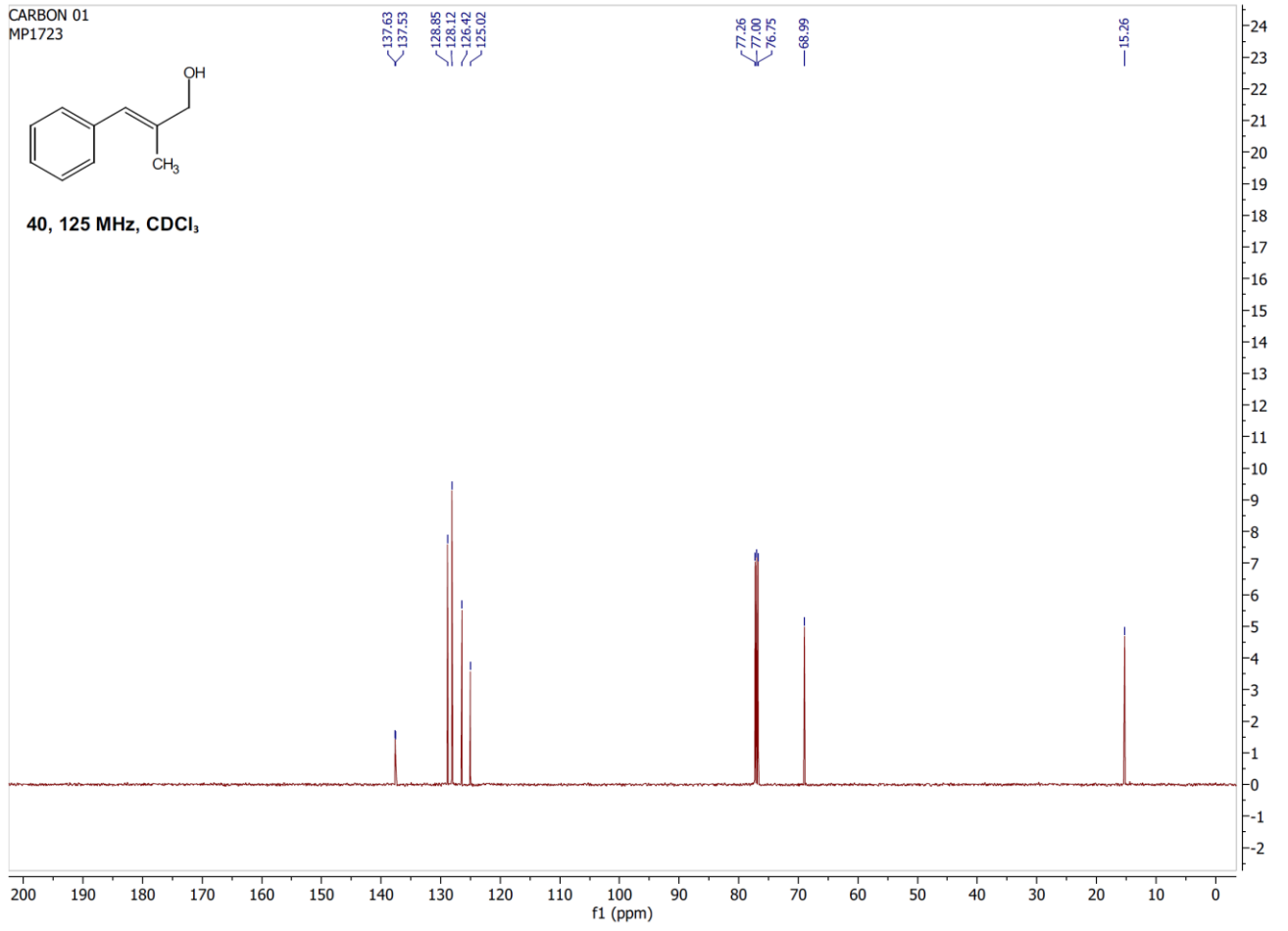
HRMS (ESI, m/z): calcd. for $C_{13}H_{15}O_2^+$ ($[M]^+$): 203.1067, found: 203.1080.

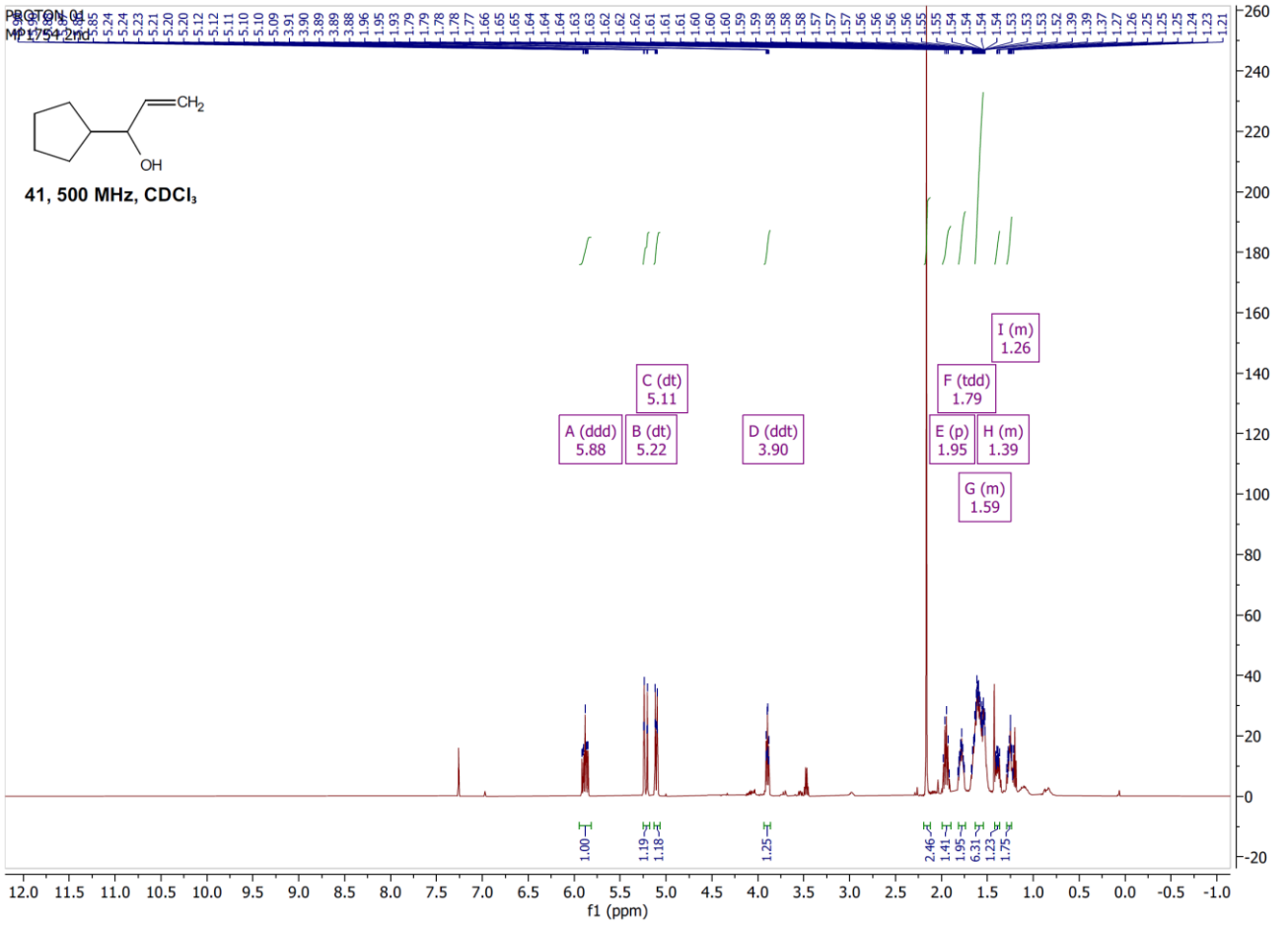
Spectra for allylic hydroxylation

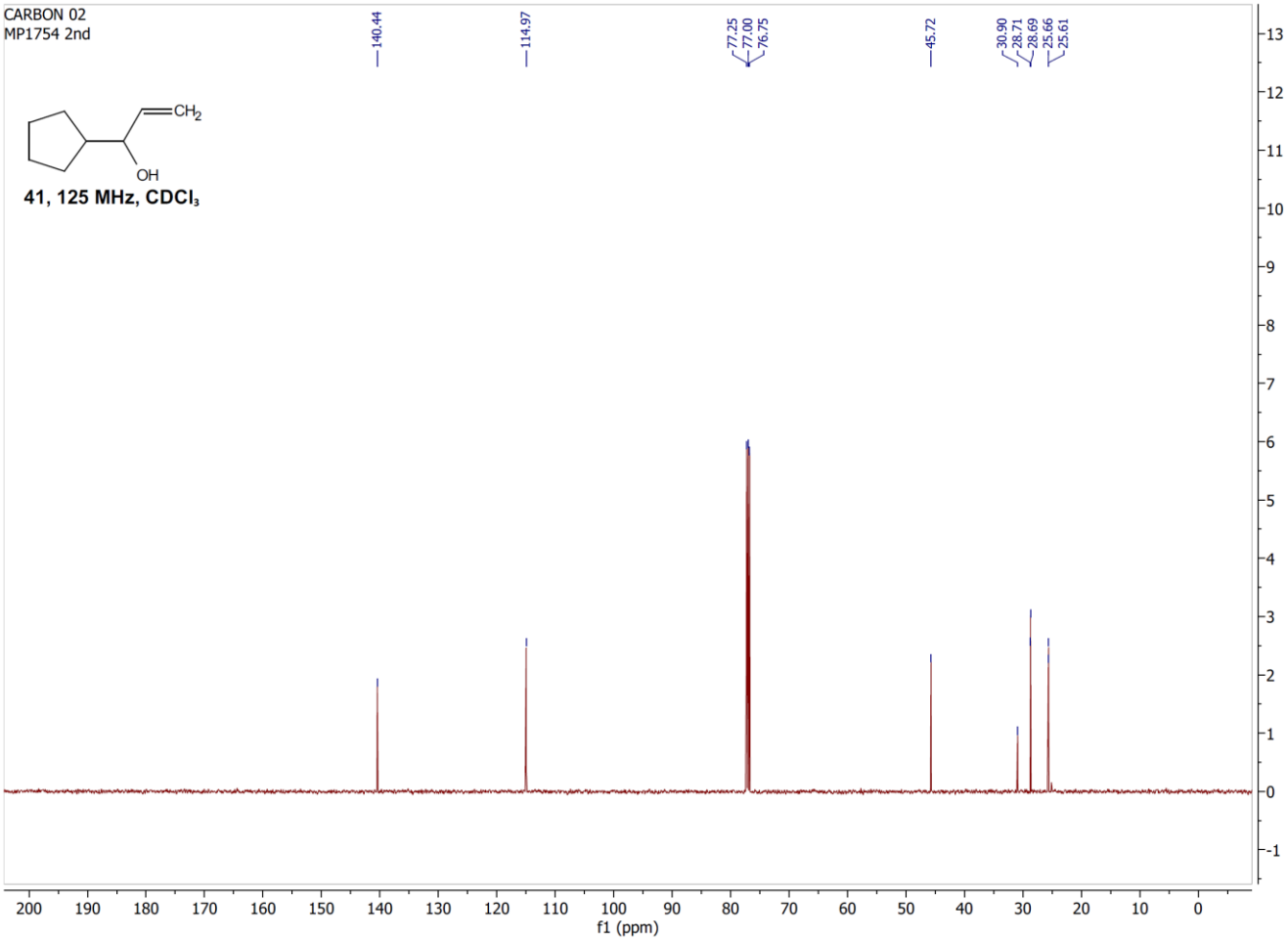


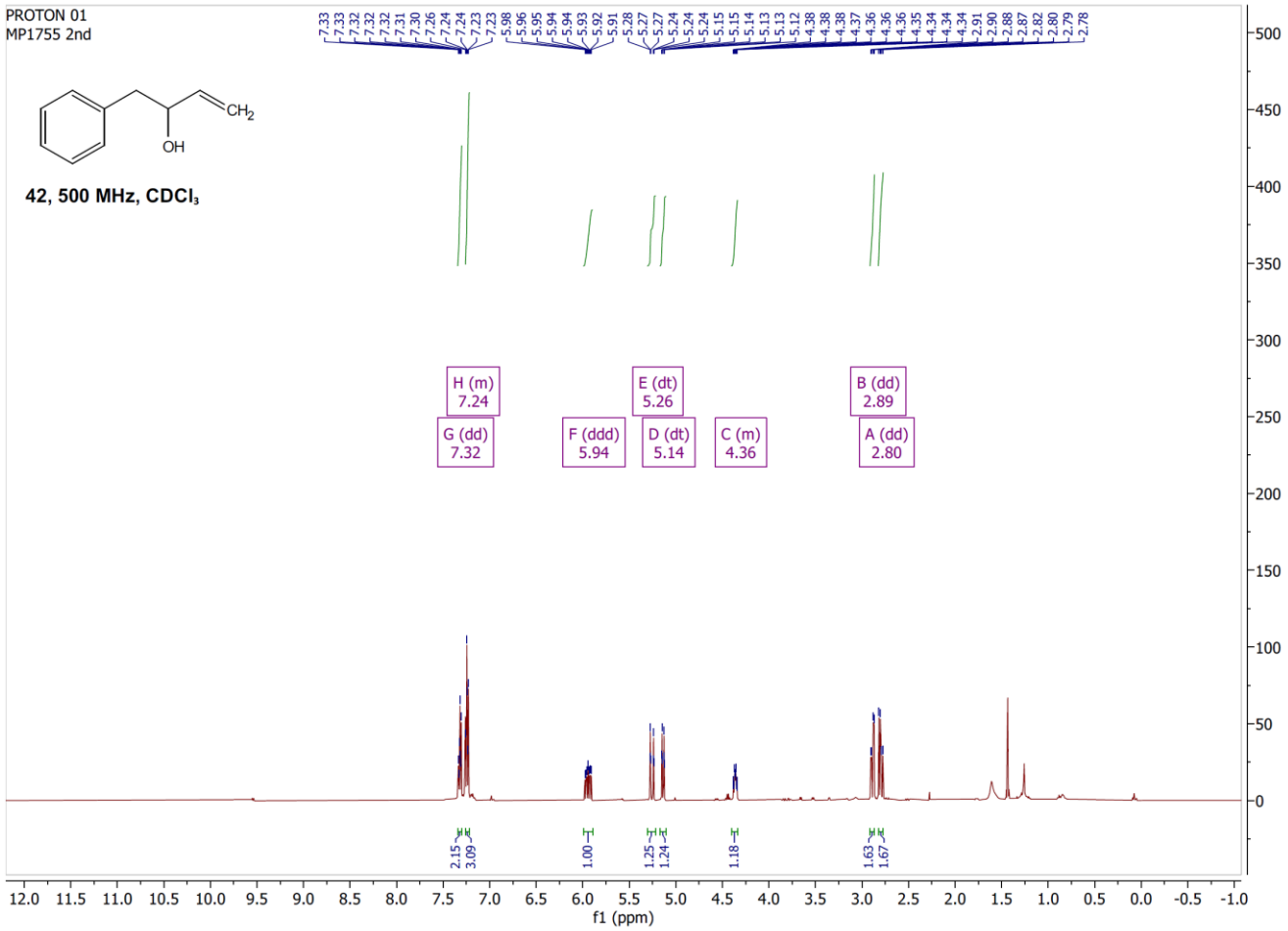


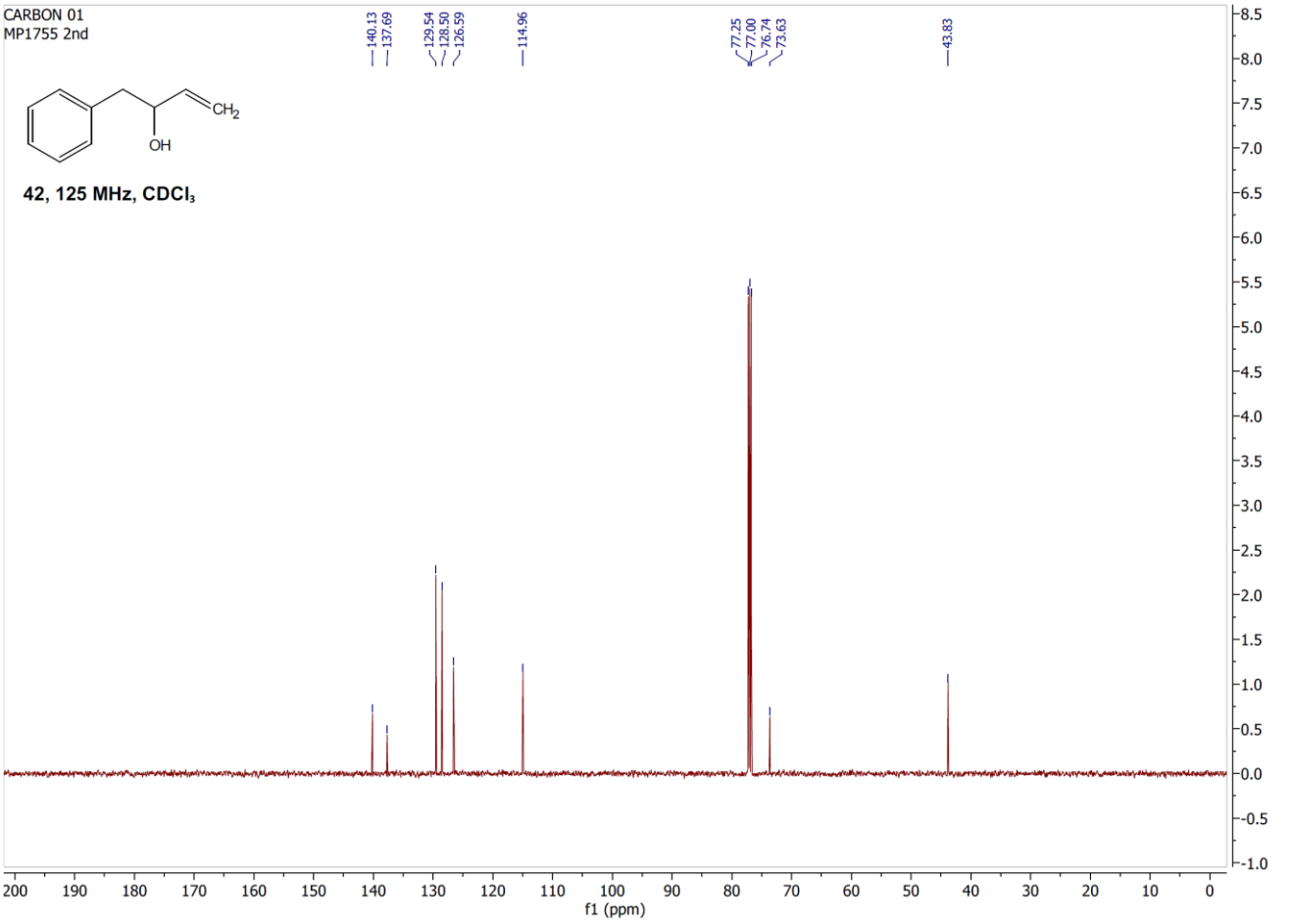

PROTON 01
MP1723
OH
CH3
40, 500 MHz, CDCl3
7.36
7.34
7.33
7.29
7.28
7.24
7.22
7.21
6.53
4.20
1.91
E (d)
7.29
D (t)
7.34
C (s)
6.53
B (s)
4.20
A (s)
1.91
F (t)
7.22
2.10
1.92
0.95
1.00
2.45
3.39
f1 (ppm)

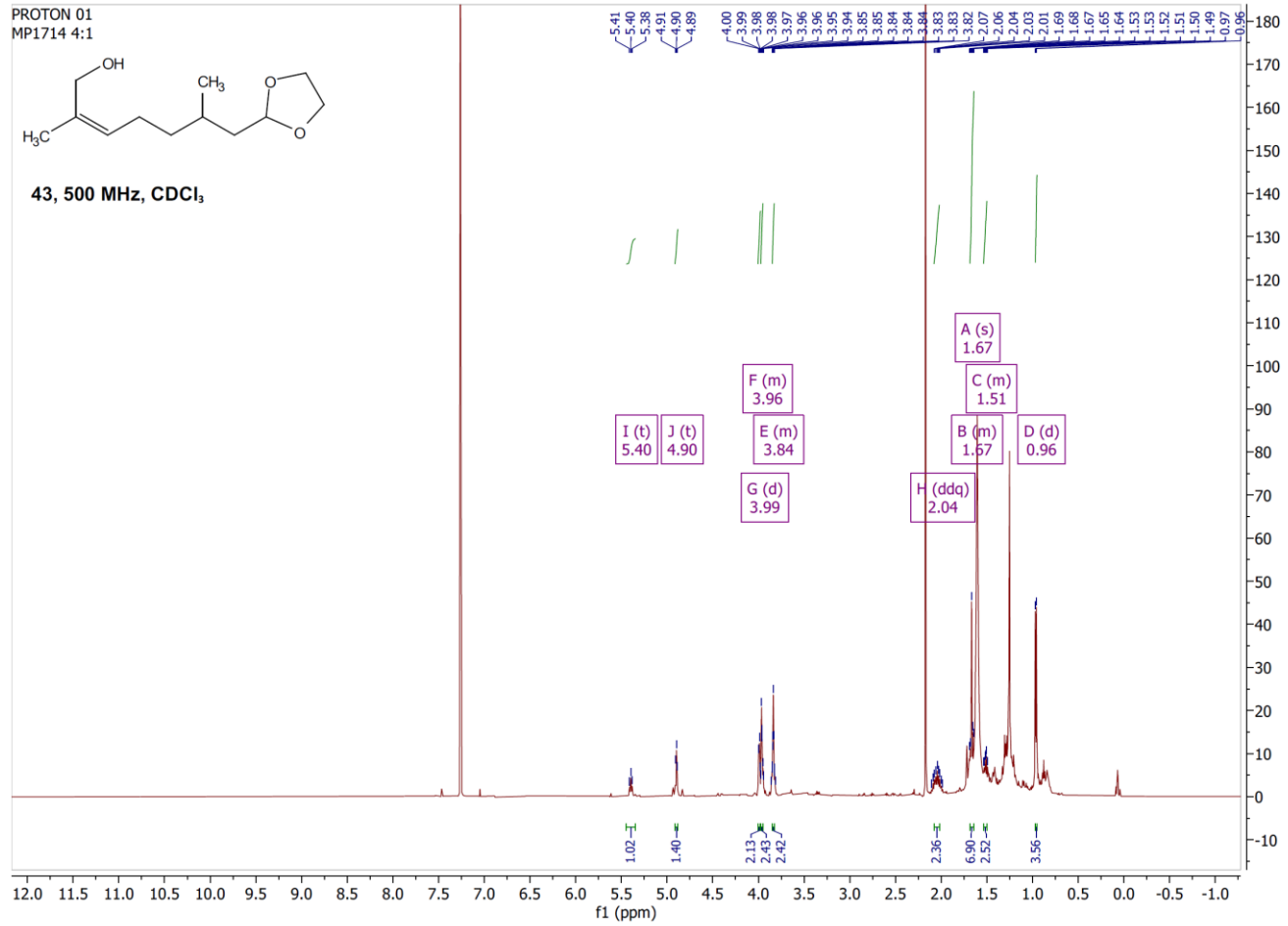

CARBON 01
MP1723
OH
CH3
40, 125 MHz, CDCl3
137.63
137.53
128.85
128.12
126.42
125.02
77.26
77.00
76.75
68.99
15.26
f1 (ppm)

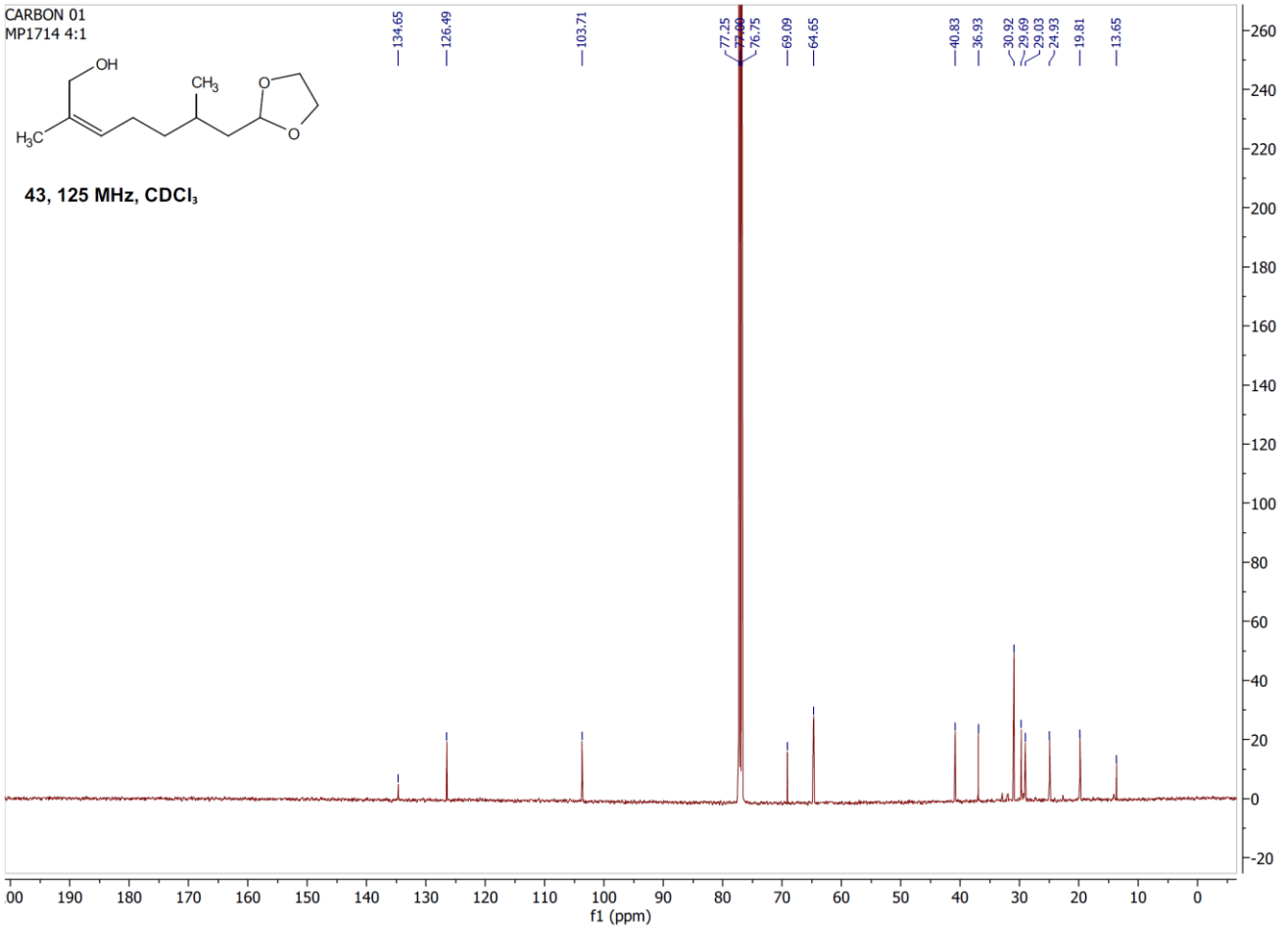

PROTON 01
MP1754 2nd
41, 500 MHz, CDCl3
A (ddd) 5.88
B (dt) 5.22
C (dt) 5.11
D (ddt) 3.90
E (p) 1.95
F (tdd) 1.79
G (m) 1.59
H (m) 1.39
I (m) 1.26
f1 (ppm)

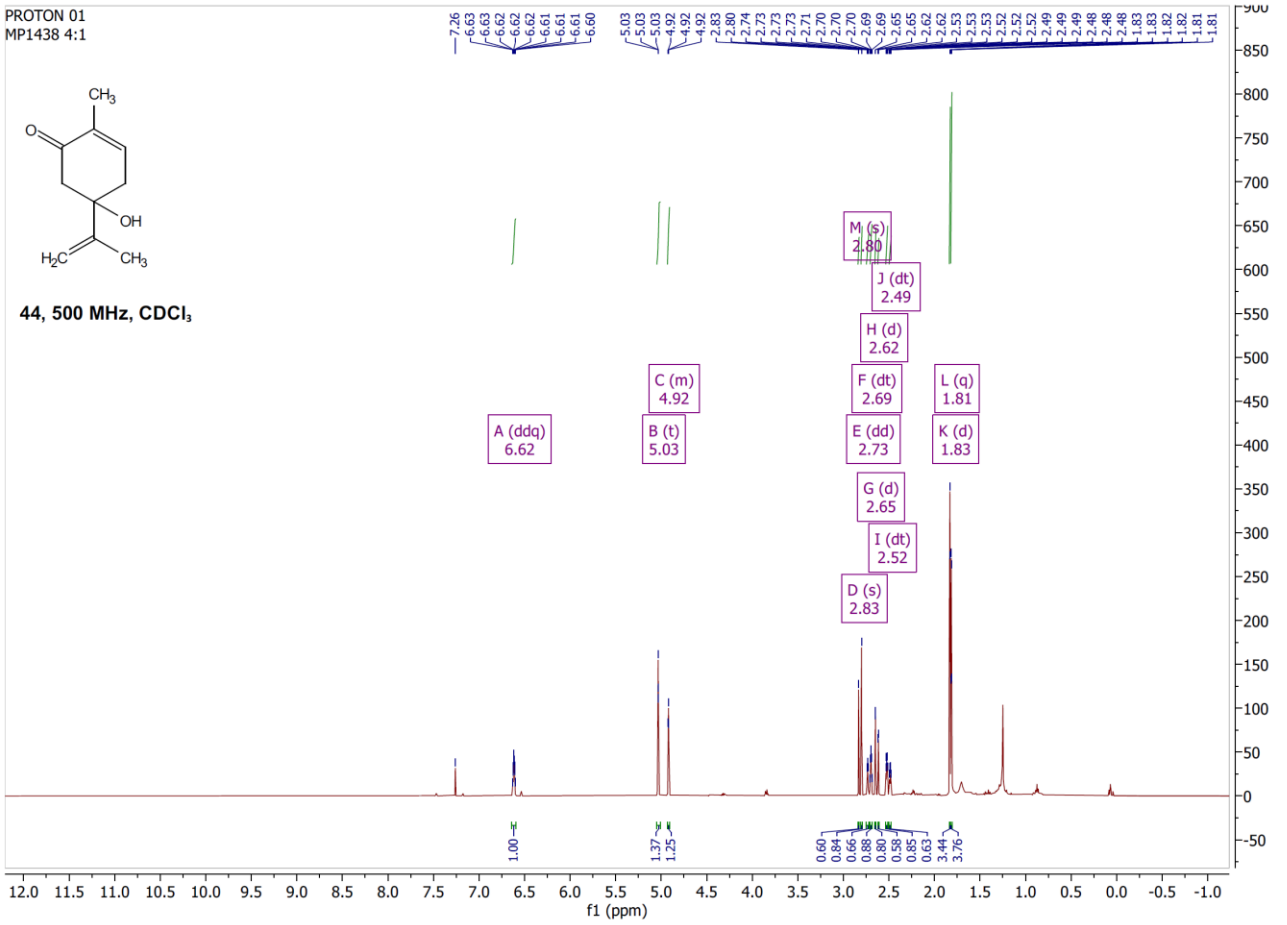

CARBON 02
MP1754 2nd
41, 125 MHz, CDCl3
140.44
114.97
77.25
77.00
76.75
45.72
30.90
28.71
28.69
25.66
25.61
f1 (ppm)

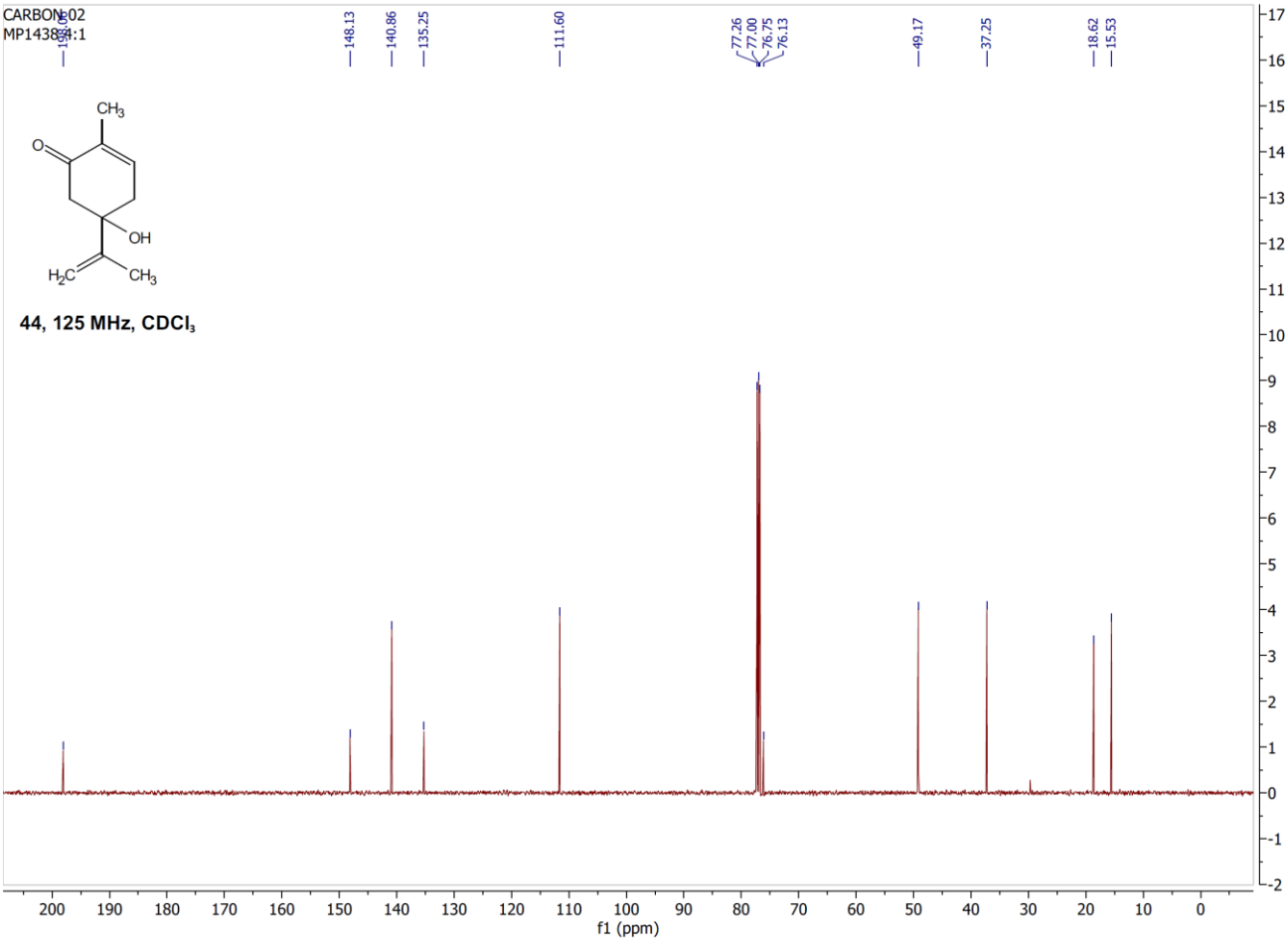

PROTON 01
MP1755 2nd
42, 500 MHz, CDCl3
H (m) 7.24
G (dd) 7.32
F (ddd) 5.94
E (dt) 5.26
D (dt) 5.14
C (m) 4.36
B (dd) 2.89
A (dd) 2.80
f1 (ppm)

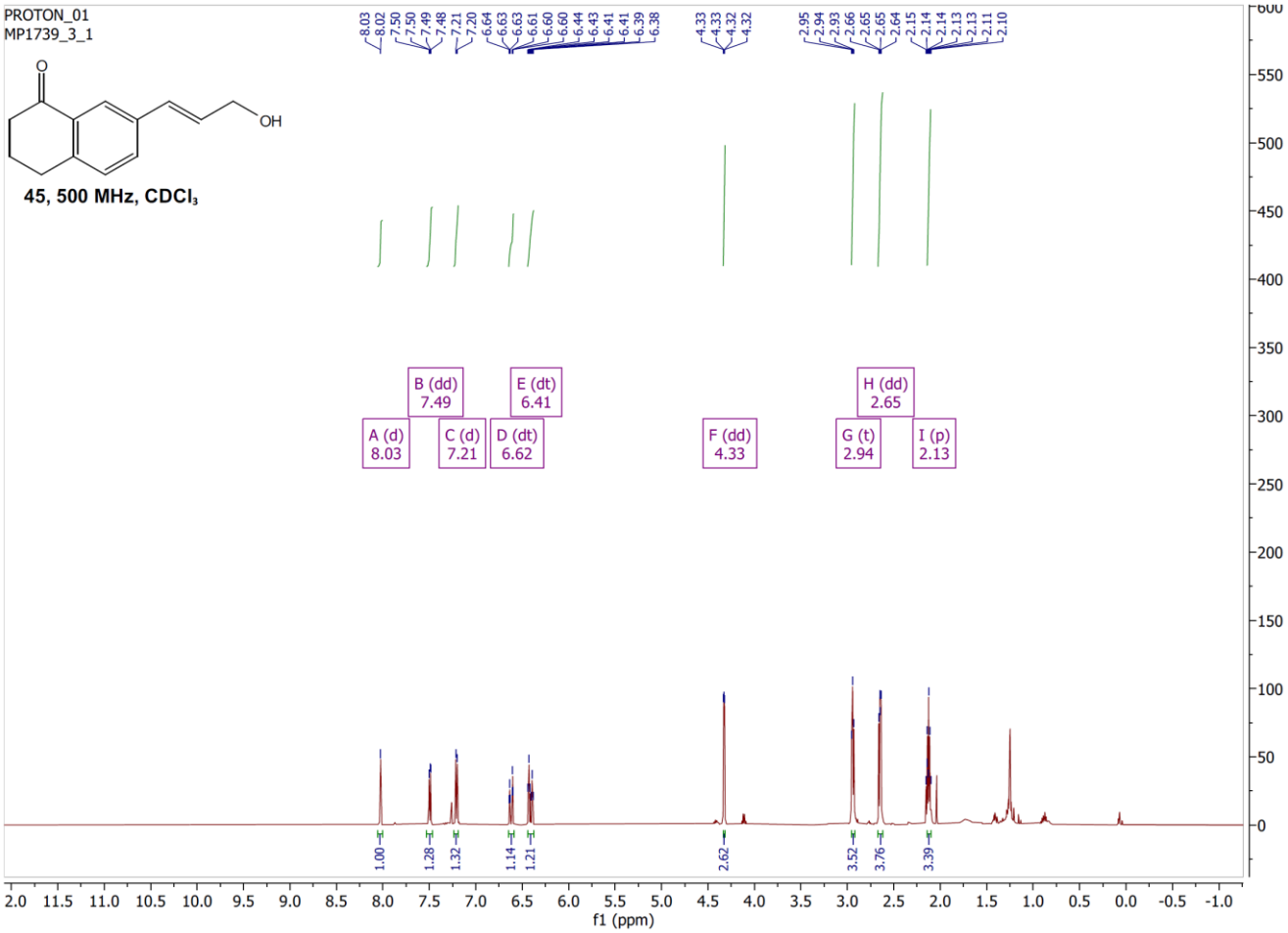

CARBON 01
MP1755 2nd
42, 125 MHz, CDCl3
140.13
137.69
129.54
128.50
126.59
114.96
77.25
77.00
76.74
73.63
43.83
f1 (ppm)

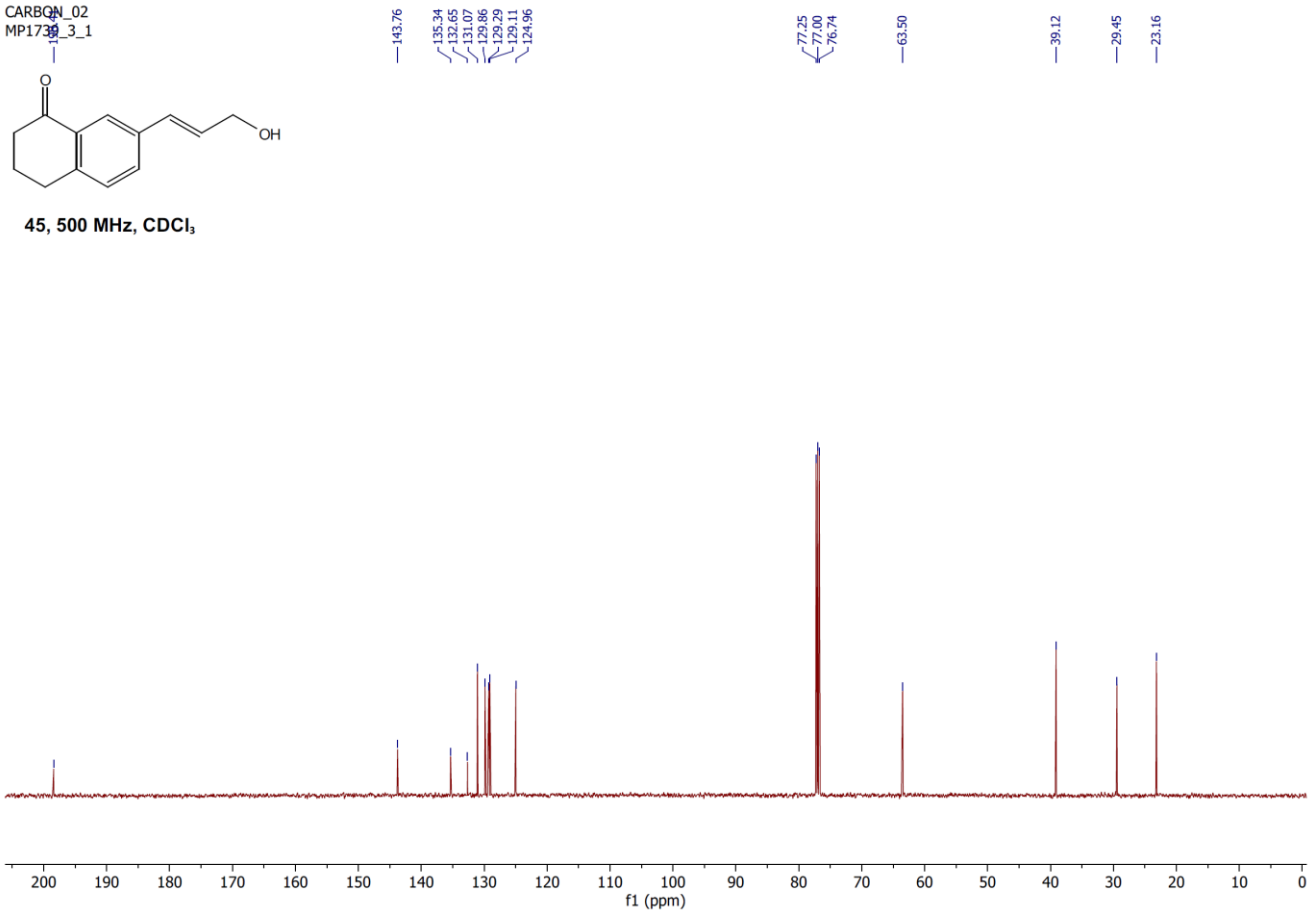

PROTON 01
MP1714 4:1
OH
CH3
H3C
O
O
43, 500 MHz, CDCl3
A (s)
1.67
C (m)
1.51
F (m)
3.96
I (t)
5.40
J (t)
4.90
E (m)
3.84
B (m)
1.67
D (d)
0.96
G (d)
3.99
H (ddq)
2.04
f1 (ppm)


CARBON 01
MP1714 4:1
OH
CH3
H3C
O
O
43, 125 MHz, CDCl3
134.65
126.49
103.71
77.25
76.75
69.09
64.65
40.83
36.93
30.92
29.69
29.03
24.93
19.81
13.65
f1 (ppm)


PROTON 01
MP1438 4:1
44, 500 MHz, CDCl3
M (s) 2.80
J (dt) 2.49
H (d) 2.62
C (m) 4.92
F (dt) 2.69
L (q) 1.81
A (ddq) 6.62
B (t) 5.03
E (dd) 2.73
K (d) 1.83
G (d) 2.65
I (dt) 2.52
D (s) 2.83
f1 (ppm)


CARBON 02
MP1438 4:1
44, 125 MHz, CDCl3
f1 (ppm)


PROTON_01
MP1739_3_1
O
OH
45, 500 MHz, CDCl3
8.03
8.02
7.50
7.50
7.49
7.48
7.21
7.20
6.64
6.63
6.63
6.61
6.60
6.60
6.44
6.43
6.41
6.41
6.39
6.38
4.33
4.33
4.32
4.32
2.95
2.94
2.93
2.66
2.65
2.65
2.64
2.15
2.14
2.14
2.13
2.13
2.11
2.10
A (d) 8.03
B (dd) 7.49
C (d) 7.21
D (dt) 6.62
E (dt) 6.41
F (dd) 4.33
G (t) 2.94
H (dd) 2.65
I (p) 2.13
1.00
1.28
1.32
1.14
1.21
2.62
3.52
3.76
3.39
f1 (ppm)


CARBON_02
MP1739_3_1
O
OH
45, 500 MHz, CDCl3
143.76
135.34
132.65
131.07
129.86
129.29
129.11
124.96
77.25
77.00
76.74
63.50
39.12
29.45
23.16
f1 (ppm)

12. References

[1] C. Vergne; J. Appenzeller; C. Ratinaud; M-T. Martin; C. Debitus, A. Zaparucha; A. Al-Mourabit, *Org. Letters* **2008**, 10, 493-496
[2] M. Petsi; A. L. Zografos, *ACS Catalysis* **2020**, 10, 7093-7099
[3] S. Chen; M. S. Hossain; F. Jr W. Foss, *ACS Sustainable Chem. Eng*. **2013**, 1, 1048-1051
[4] K. Semba; R. Kameyama; Y. Nakao, *Synlett* **2015**, 26, 318-322
[5] C. M. Latham; Blake, A. J. Blake; W. Lewis; M. Lawrence; S. Woodward, *Eur. J. Org. Chem*. **2012**, 4, 699-707
[6] *Eur. J. Inorg. Chem*. **2018**, 4234-4244
[7] *J. Org. Chem*. **2020**, 85, 4906; *J. Am. Chem. Soc*. **2011**, 133, 4710-4713
[8] *J. Am. Chem. Soc*. **2020**, 142, 6409-6422; *Angew. Chem. Int. Ed*. **2018**, 57, 13575-13581
[9] K-H. Altmann; M. Liniger; C. M. Neuhaus, *Molecules* **2020**, 25, 4527; T. Boisse; B. Rigo; R. Millet; J-P. Hénichart, *Tetrahedron* **2007**, 63, 10511-10520
[10] B. Das; J. Banerjee; A. Majhi; G. Mahender, *Tetrah.Lett*. **2004**, 45, 9225-9227
[11] A. S. Kumar; P. Srihari; J. S. Yadav; A. A Alghamdi, *Synthesis* **2017,** 49, 1702-1706
[12] S. Jin; V. T. Nguyen; H. T. Dang; D. P. Nguyen; H. D. Arman; O. V. Larionov, *J. Am. Chem. Soc.* **2017**, 139, 11365-11368
[13] S. A. Snyder; D. S. Treitler; A. P. Brucks, *J. Am. Chem. Soc.* **2010**, 132, 14303-14314
[14] M. Kazemnejadi; Boshra Mahmoudi; Zeinab Sharafi; Mohammad Ali Nasseri; Ali Allahresani; M. Esmaeilpour, *J. Organomet. Chem*. **2019**, 896, 59-69; M. Nayak; P. Nayak; K. Sahu; S. Kar, *J. Org. Chem*. **2020**, 85, 11654–11662
[15] H-J. Schneider; P. K. Agrawal, *Magn. Res. Chem.* **1986**, 24,718-722; D. M. Pawar, E. A. Noe, *J. Am. Chem. Soc.* **1998**, 120, 5312-5314
[16] T. Hamatani; S. Matsubara; H. Matsuda; M. Schlosser, *Tetrahedron* **1988**, 44, 2875-2882
[17] M. Kazemnejadi; Boshra Mahmoudi; Zeinab Sharafi; Mohammad Ali Nasseri; Ali Allahresani; M. Esmaeilpour, *J. Organomet. Chem*. **2019**, 896, 59-69
[18] C. Ai; F. Zhu; Y. Wang; Z. Yan; S. Lin, *J. Org. Chem.* **2019**, 84, 11928-11934; Chudasama, Vijay; A. R. Akhbar; A. K. Bahou; R. J. Fitzmaurice; S. Caddick, *Org. Biomol. Chem*. **2013**, 11, 7301-7317
[19] A. S. Kumara; P. Srihari; J. S. Yadav; A. A Alghamdi, *Synthesis* **2017**, 49, 1702-1706
[20] W. Dai; J. Li; G. Li; H. Yang; L. Wang; S. Gao, *Org. Lett*. **2013**, 15, 4138-4141
[21] L. Oudeyer; N. Paugam, *Synthesis* **2004**, 3, 389-400
[22] R. Novikov; G. Bernardinelli; J. Lacour, *Adv. Synth. Catal.* **2009**, 351, 596-606
[23] J. C. Ianni; V. Annamalai; P.-W. Phuan; M. Panda; M. C. Kozlowski, *Angew. Chem. Int. Ed*. **2006**, 45, 5502-5505
[24] P. C. B. Page; B. R. Buckley; A. J. Blacker, *Org. Lett*. **2004**, 6, 1543-1546
[25] C. Ebner; C. A. Muller; C. Markert; A. Pfaltz, *J. Am. Chem. Soc*. **2011**, 133, 4710-4713
[26] E. Alvarez; M. T. Diaz; R. Perez; J. L. Ravelo; A. Regueiro; J. A. Vera; D. Zurita; J. D. Martin, *J. Org. Chem*. **1994**, 59, 2848–2876
[27] J. Holz; S. Doerfelt; A. Boerner, *Adv. Syn. Catal*. **2017**, 359, 4379-4387
[28] O. Smitt; H-E. Högberg, *Tetrahedron* **2002**, 58, 7691-7700
[29] S. Kirsch; T. Bach, *Synthesis* **2003**, 12, 1827-1836
[30] T. M. Khomenko; L. E. Tatarova; D. V. Korchagina; V. A. Barkhash, *Rus. J. Org. Chem*. **2002**, 38, 498-506
[31] C. J. A. Ribeiroa; M. M. Pereira; E. F. Kozhevnikova; I. V. Kozhevnikov; E. V. Gusevskaya; K. A. da Silva Rocha, *Catal. Today* **2020**, 344, 166-170; M. Stekrova; N. Kumar; S.F. Díaz; P. Mäki-Arvelaa; D. Y. Murzin, *Catal. Today* **2015**, 241, 237-245
[32] N. Zigon; M. Hoshino; S. Yoshioka; Y. Inokuma; M. Fujita, *Angew. Chem. Int. Ed*. **2015**, 54, 9033-9037
[33] W. B. Cunningham; J. D. Tibbetts; M. Hutchby; K. A. Maltby; M. G. Davidson; U. Hintermair; P. Plucinski; S. D. Bull, *Green Chem*. **2020**, 22, 513-524
[34] K. Surendra; Corey, *J. Am. Chem. Soc*. **2008**, 130, 8865-8869
[35] J. A. Marshall; R. K. Hann, *J. Org. Chem*. **2008**, 73, 6753-6757; C. Tsangarakis; E. Arkoudis; C. Raptis; M. Stratakis *Org. Lett*. **2007**, 9, 583-586
[36] K. Mori; M. Kato, *Tetrahedron* **1986**, 42, 5895-5900
[37] C. E. Davis; J. L. Bailey; J. W. Lockner; R. M. Coates, *J. Org. Chem*. **2003**, 68, 1, 75-82
[38] U. Atmaca; H. K. Usanmaz; M. Celik, *Tetrah. Lett*. **2014**, 55, 2230-2232
[39] M. A. Warpehoski; B. Chabaud; K. B. Sharpless, J. Org. Chem. 1982, 47, 2897-2900
[40] T. Kambe; T. Moriai; M. Tanabe; T. Tsukamoto; K. Yamamoto, *Angew. Chem. Int. Ed*. **2020**, 59, 23051-23055; Angew. Chem., **2020**, 132, 23251-23255; A. J. Ruddy; C. M. Kelly; S. M. Crawford; G. A. Wheaton; O. L. Sydora; B. L. Small; M. L. Stradiotto; L. Turculet, *Organometallics* **2013**, 32, 5581-5588
[41] Q. Wang; X. Li; X. Liu; B. Li; H. Nie; S. Zhang; W. Chen, *Chem. Commun.***, 2014**, 50, 978-980; M. Cavallo; D. Arnodo; A. Mannua; M. Blangettia; C. Prandia; W. Barattab; S. Baldino, *Tetrahedron* **2021**, 83, 131997
[42] M. Lafrance; M. Roggen, E. M. Carreira, *Angew. Chem. Int. Ed*. **2012**, 51, 3470-3473; M. S. Kirillova.; M. E. Muratore; R. E. Dorel; A. M. Echavarren, *J. Am. Chem. Soc.* **2016**, 138, 3671-3674
[43] D. K. Ahn; Y. W. Kang; S. K. Woo, *J. Org. Chem.* **2019**, 84, 3612-3623; A. Gontala, S. K. Woo, *Adv. Syn. Catal*. **2020**, 362, 3223-3228
[44] W. G. Taylor; *Can. J. Chem*. **1982**, 60, 1847–1852

[45] H. Hamada; H. Yasumune; Y. Fuchikami; T. Hirata; I. Sattler; H. J. Williams; A. I. Scott, *Phytochemistry* **1997**, 44, 615-621