Supporting Information

Catalyst Controlled Site-Selective Asymmetric Epoxidation of Nerylamine and Geranylamine Derivatives

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Content

1. General Information

All dry solvents were obtained from Kanto Kagaku Co., Ltd. Other chemicals were obtained from Tokyo Kasei Kogyo Co., Ltd., Wako Pure Chemical Industries, Ltd., and Nacalai Tesque. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL ECZ 400S (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal Me_4Si. Mass spectra were obtained on Thermo Scientific Exactive Plus. Optical rotations were determined on JASCO P-2200. Flash column chromatography was performed on Silica Gel 60N (spherical, neutral, Kanto Kagaku Co., Ltd.) or CHROMATOREX Q-PACK (Fuji Silysia).

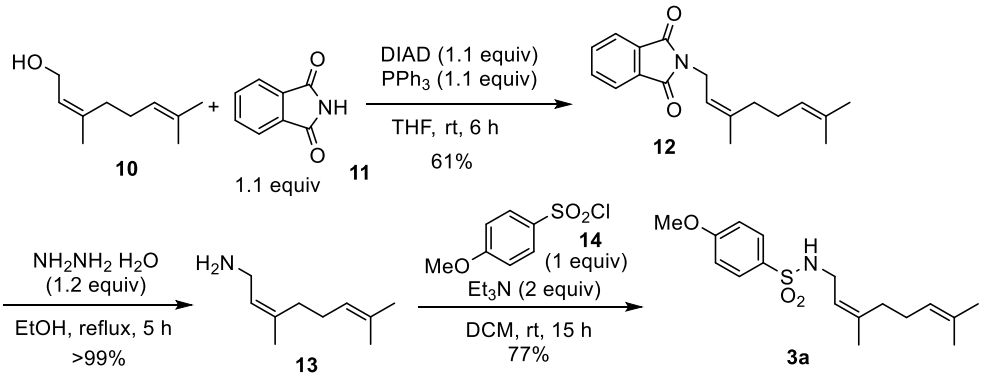
List of abbreviation

DIAD	diisopropyl azodicarboxylate
DCM	dichloromethane
THF	tetrahydrofuran
DMEAD	di-2-methoxyethyl azodicarboxylate
DMF	*N*,*N*-dimethylformamide
DIBAH	diisobutylaluminum hydride
HOBt	1-hydroxybenzotriazole
NMM	*N*-methylmorpholine
WSCI·HCl	1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride
DMAP	4-dimethylaminopyridine
HBTU	2-(1H-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate
DIC	*N*,*N*-Dissopropylcarbodiimide

2. General Procedure

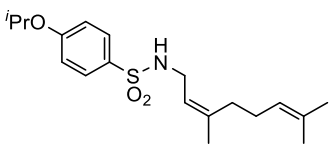
2. 1. Preparation of starting materials

Preparation of 3a, 3d, 3g, 3h and 3i

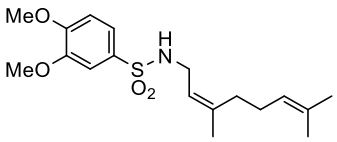


To a solution of nerol (**10**) (2.6 mL, 15 mmol), phthalimide (**11**) (2.4 g, 16.5 mmol, 1.1 equiv) and PPh_3 (4.3 g, 16.5 mmol, 1.1 equiv) in THF (30 mL) was added DIAD (3.3 mL, 16.5 mmol, 1.1 equiv) at 0 °C. After being stirred for 5 h at rt, the reaction mixture was concentrated in *vacuo*. Purification of the crude product by flash

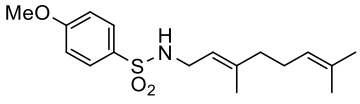
chromatography on silica gel provided *N*-nerylphthalimide (**12**) (3.1 g, 74%). A solution of **12** (3.1 g, 11.1 mmol) and hydrazine monohydrate (0.65 mL, 13.3 mmol, 1.2 equiv) in EtOH (60 mL) was refluxed for 6 h. After cooling, 10% aq. NaOH was added and extracted with $CHCl_3$. The organic later was washed with H_2O, dried over Na_2SO_4, and concentrated *in vacuo*. To a solution of nerylamine (**13**) (613.0 mg, 4 mmol) and Et_3N (1.12 mL, 8 mmol, 2 equiv) in DCM (6 mL) was added *p*-methoxybenzenesulfonyl chloride (**14**) (826.4 mg, 4 mmol, 1 equiv) at 0 °C. After being stirred for 0.5 h at rt, sat. $NaHCO_3$ was added and extracted with DCM. The organic later was washed with 2NHCl, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **3a** (1.13 g, 87%) as a colorless oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.78-7.81 (m, 2H), 6.96-7.00 (m, 2H), 5.10 (t, J = 7.2 Hz, 1H), 4.96-5.00 (m, 1H), 4.11-4.14 (m, 1H), 3.88 (s, 3H), 3.48-3.51 (m, 2H), 1.91-2.04 (m, 4H), 1.69 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.84, 141.20, 132.61, 131.60, 129.29, 123.50, 119.59, 114.16, 55.59, 40.66, 31.77, 26.17, 25.69, 23.22, 17.63; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{25}NO_3SNa$ (M+Na)$^+$ 346.1447, found 346.1446.



3d; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75-7.78 (m, 2H), 6.93-6.96 (m, 2H), 5.10 (t, J = 7.2 Hz, 1H), 4.99 (t, J = 7.0 Hz, 1H), 4.60-4.66 (m, 1H), 4.07 (d, J = 5.5 Hz, 1H), 3.50 (t, J = 6.4 Hz, 2H), 1.92-2.03 (m, 4H), 1.69 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H), 1.54 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.34, 141.14, 132.61, 131.01, 129.29, 123.50, 119.65, 115.53, 70.37, 40.66, 31.77, 26.17, 25.69, 23.22, 21.83, 17.62; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{29}NO_3SNa$ (M+Na)$^+$ 374.1760, found 374.1760.

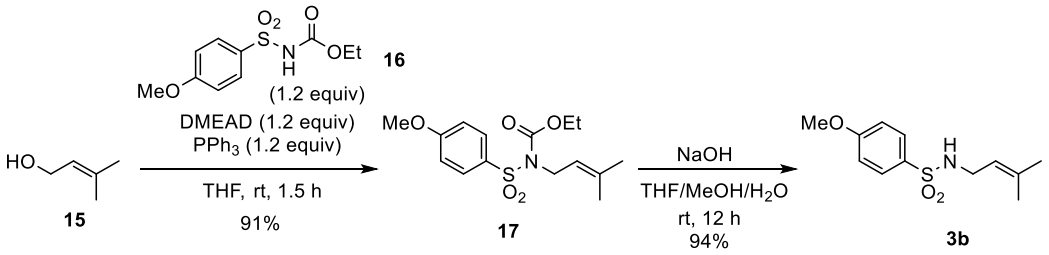


3g; Colorless oil ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.4 Hz, 1H), 7.33 (s, 1H), 6.94 (d, J = 8.4 Hz, 1H), 5.11 (t, J = 7.3 Hz, 1H), 4.97-5.00 (m, 1H), 4.14 (t, J = 5.6 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.51 (t, J = 6.5 Hz, 2H), 1.93-2.01 (m, 4H), 1.69 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.51, 149.12, 141.29, 132.65, 131.66, 123.47, 121.10, 119.55, 110.50, 109.70, 56.22, 56.18, 40.71, 31.79, 26.19, 25.69, 23.25, 17.62; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{27}NO_4SNa$ (M+Na)$^+$ 376.1553, found 376.1552.

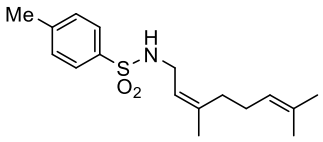


3h; Colorless oil ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79-7.82 (m, 2H), 6.96-6.99 (m, 2H), 5.00-5.08 (m, 2H), 4.20 (d, J = 4.3 Hz, 1H), 3.87 (s, 3H), 3.55 (t, J = 6.4 Hz, 2H), 1.91-2.02 (m, 4H), 1.67 (s, 3H), 1.57 (s, 3H), 1.54 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.85, 141.10, 131.87, 131.65, 129.30, 123.60, 118.61, 114.17, 55.59, 40.95, 39.32, 26.20, 25.65, 17.65, 16.22; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{25}NO_3SNa$ (M+Na)$^+$ 346.1447, found 346.1447.

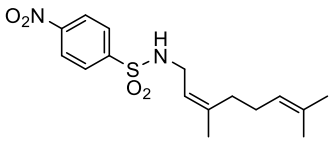
Preparation of 3b, 3e, 3f and 3j



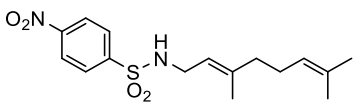
To a solution of 3-methyl-2-buten-1-ol (**15**) (125.2 μL, 1.25 mmol), **16** (388.9 mg, 1.5 mmol, 1.2 equiv) and PPh_3 (393.4 mg, 1.5 mmol, 1.2 equiv) in THF (10 mL) was added DMEAD (351.3 mg, 1.5 mmol, 1.2 equiv) at 0 °C. After being stirred for 1.5 h at rt, H_2O was added and extracted with toluene. The organic later was dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **17** (373.2 mg, 91%). To a solution of **17** (373.2 mg, 1.14 mmol) in THF (3 mL) and MeOH (6 mL) was added 50% aq. NaOH (4 mL) at 0 °C. After being stirred for 12 h at rt, aq. NH_4Cl was added and extracted with $CHCl_3$. The organic later was dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **3b** [1] (273.3 mg, 94%) as a colorless oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.78-7.82 (m, 2H), 6.96-7.00 (m, 2H), 5.04-5.08 (m, 1H), 4.11-4.17 (m, 1H), 3.88 (s, 3H), 3.53 (t, J = 6.4 Hz, 2H), 1.64 (s, 3H), 1.55 (s, 3H)



3d; Colorless oil ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.09 (t, J = 7.3 Hz, 1H), 4.98 (t, J = 7.0 Hz, 1H), 4.12 (br s, 1H), 3.51 (t, J = 6.4 Hz, 2H), 2.44 (s, 3H), 1.91-2.04 (m, 4H), 1.69 (s, 3H), 1.65 (s, 3H), 1.55 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.31, 141.21, 137.01, 132.60, 129.62, 127.18, 123.49, 119.55, 40.68, 31.75, 26.14, 25.68, 23.19, 21.50, 17.60; HRMS (ESI) *m/z* calcd for $C_{17}H_{25}NO_2SNa$ $(M+Na)^+$ 330.1498, found 330.1497.

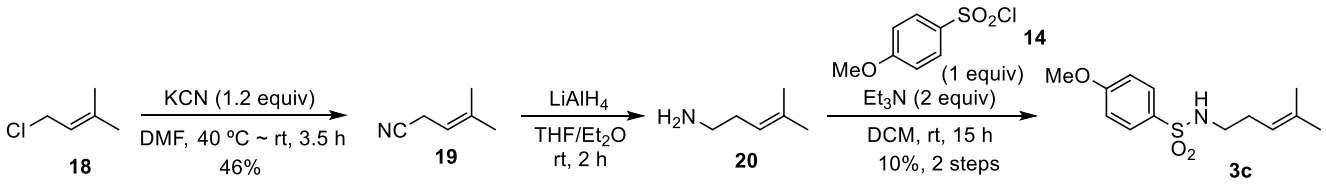


3f; White solid ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H), 5.08 (t, J = 7.2 Hz, 1H), 4.99 (t, J = 7.0 Hz, 1H), 4.39 (t, J = 5.4 Hz, 1H), 3.60 (t, J = 6.3 Hz, 2H), 1.94-2.05 (m, 4H), 1.70 (s, 3H), 1.66 (s, 3H), 1.57 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.87, 146.12, 141.65, 132.54, 128.28, 124.19, 123.30, 118.94, 40.71, 31.71, 26.06, 25.55, 23.09, 17.51; HRMS (ESI) *m/z* calcd for $C_{16}H_{22}N_2O_4SNa$ $(M+Na)^+$ 361.1192, found 361.1196.



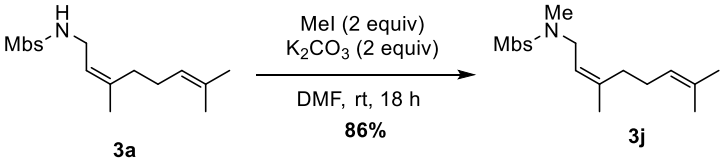
3i; White solid ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.6 Hz, 2H), 8.06 (d, J = 8.6 Hz, 2H), 4.98-5.06 (m, 2H), 4.42 (t, J = 5.5 Hz, 1H), 3.66 (t, J = 6.4 Hz, 2H), 1.91-2.01 (m, 4H), 1.66 (s, 3H), 1.57 (s, 3H), 1.56 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.78, 146.07, 141.34, 131.69, 128.24, 124.11, 123.29, 117.94, 40.93, 39.08, 25.97, 25.41, 17.40, 16.06; HRMS (ESI) *m/z* calcd for $C_{16}H_{22}N_2O_4SNa$ $(M+Na)^+$ 361.1192, found 361.1195.

Preparation of 3c



To a solution of 1-chloro-3-methyl-2-butene (**18**) (337.4 μL, 3 mmol) in DMF (5 mL) was added KCN (234.4 mg, 3.6 mmol, 1.2 equiv) at 0 °C. The reaction mixture was warmed to 40 °C. After being stirred for 1.5 h at 40 °C, the reaction mixture was cooled to rt, and stirred for an additional 2 h. H_2O was added and extracted with hexane. The organic later was washed with H_2O, dried over Na_2SO_4, and concentrated *in vacuo*. 4-methylpent-3-enenitrile (**19**) (132.0 mg, 46%) was obtained and used in the next step without further purification. To a solution of **19** (132.0 mg, 1.39 mmol) in Et_2O (5 mL) was added $LiAlH_4$ (2.5 M in THF, 1.4 mL, 2.5 equiv) at 0 °C. After being stirred for 2 h at rt, H_2O was added at 0 °C and filtered with celite. The organic later was concentrated *in vacuo*. To a solution of crude product and Et_3N (184.5 μL, 1.32 mmol) in DCM (3 mL) was added *p*-methoxybenzenesulfonyl chloride (**14**) (136.4 mg, 0.66 mmol) at 0 °C. After being stirred for 15 h at rt, sat. $NaHCO_3$ was added and extracted with DCM. The organic later was washed with 2NHCl, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **3c** (38.0 g, 10%, 2 steps) as a light yellow oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.77-7.81 (m, 2H), 6.96-7.00 (m, 2H), 4.92 (t, J = 7.2 Hz, 1H), 4.37 (t, J = 5.7 Hz, 1H), 3.87 (s, 3H), 2.93 (q, J = 6.7 Hz, 2H), 2.15 (q, J = 6.7 Hz, 2H), 1.67 (s, 3H), 1.56 (s, 3H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 162.81, 135.68, 131.56, 129.22, 119.71, 114.19, 55.59, 42.87, 28.11, 25.74, 17.85; HRMS (ESI) *m/z* calcd for $C_{13}H_{19}NO_3SNa$ $(M+Na)^+$ 292.0978, found 292.0975.

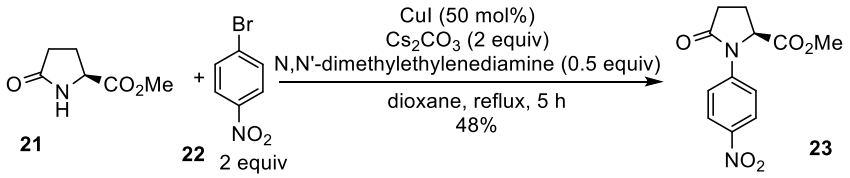
Preparation of 3j



To a solution of **3a** (204.8 mg, 0.63 mmol) and K_2CO_3 (174.1 mg, 1.26 mmol, 2 equiv) in DMF (4 mL) was added MeI (78.4 μL, 1.26 mmol, 2 equiv) at rt. After being stirred for 18 h at rt, H_2O was added and extracted with toluene. The organic later was washed with $Na_2S_2O_3$, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **3j** (183.2 mg, 86%) as a colorless oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.74 (m, 2H), 6.97-7.01 (m, 2H), 5.09 (t, J = 7.0 Hz, 1H), 5.04 (br s, 1H), 3.88 (s, 3H), 3.59 (d, J = 7.0 Hz, 2H), 2.63 (s, 3H), 1.98-2.05 (m, 4H), 1.71 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.76, 141.03, 132.13, 129.60, 129.23, 123.58, 119.31, 114.10, 55.57, 47.43, 34.00, 31.81, 26.34, 25.68, 23.43, 17.60; HRMS (ESI) *m/z* calcd for $C_{18}H_{27}NO_3SNa$ $(M+Na)^+$ 360.1604, found 360.1604.

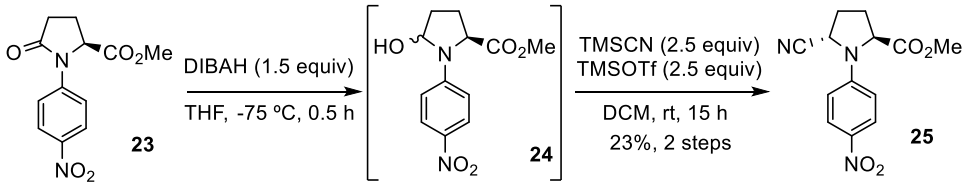
2. 2. Preparation of catalysts

Preparation of methyl (2*S*)-1-(4-nitrophenyl)-5-oxopyrrolidine-2-carboxylate (23)



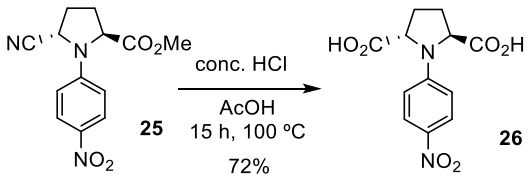
A solution of methyl L-pyroglutamate (**21**) (10 g, 70 mmol), 1-bromo-4-nitrobenzne (**22**) (28 g, 140 mmol, 2 equiv), CuI (6.7 g, 35 mmol, 50 mol%), Cs_2CO_3 (45.6 g, 140 mmol, 2 equiv) and N,N'-dimethylethylenediamine (3.8 mL, 35 mmol, 0.5 equiv) was refluxed for 5 h. After cooling to rt, the reaction mixture was filtered with celite, and concentrated in *vacuo*. 0.5 NHCl was added and extracted with EtOAc. The organic later was washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **23** (9.0 g, 48%) as a yellow solid.; $[\alpha]^{27}_D$ = –43.1 (c 1.50, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22-8.26 (m, 2H), 7.71-7.75 (m, 2H), 4.83 (dd, J = 9.0, 2.6 Hz, 1H), 3.78 (s, 3H), 2.77-2.86 (m, 1H), 2.50-2.68 (m, 2H), 2.22-2.29 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.43, 171.35, 143.82, 143.57, 124.50, 119.50, 60.62, 52.83, 30.79, 22.75; HRMS (ESI) *m*/*z* calcd for $C_{12}H_{12}N_2O_5Na$ (M+Na)$^+$ 287.0638, found 287.0640.

Preparation of methyl (2*S*,5*S*)-5-cyano-1-(4-nitrophenyl)pyrrolidine-2-carboxylate (25)



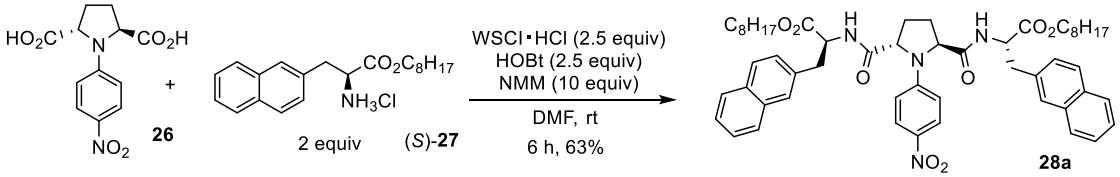
To a solution of **23** (7.8 g, 29.4 mmol) in THF (85 mL) was added DIBAH (1M in hexane, 44.1 mL, 44.1 mmol, 1.5 equiv) at -75 °C. After being stirred for 0.5 h at -75 °C, the reaction mixture was poured to aq. NaK tartrate, and stirred for 2 h. The mixture was extracted with EtOAc. The organic later was dried over Na_2SO_4, and concentrated *in vacuo*. To a solution of crude product in DCM (140 mL) were added TMSCN (9.2 mL, 73.5 mmol, 2.5 equiv) and TMSOTf (13.3 mL, 73.5 mmol, 2.5 equiv) at 0 °C. After being stirred for 15 h at rt, the reaction mixture was quenched by addition of sat. $NaHCO_3$, and stirred for 3 h. The mixture was extracted with $CHCl_3$. The organic later was dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **25** (1.9 g, 23%, 2steps) as a yellow solid.; $[\alpha]^{28}_D$ = –301.1 (c 0.32, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.18-8.22 (m, 2H), 6.62-6.66 (m, 2H), 4.75 (d, J = 7.8 Hz, 1H), 4.51-4.53 (m, 1H), 3.77 (s, 3H), 2.54-2.71 (m, 2H), 2.47-2.51 (m, 1H), 2.36-2.40 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.89, 148.32, 139.90, 126.16, 117.64, 112.25, 77.32, 77.00, 76.67, 60.62, 52.88, 49.42, 29.69, 29.56; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{13}N_3O_4Na$ (M+Na)$^+$ 298.0798, found 298.0798.

Preparation of (2*S*,5*S*)-1-(4-nitrophenyl)pyrrolidine-2,5-dicarboxylic acid (26)



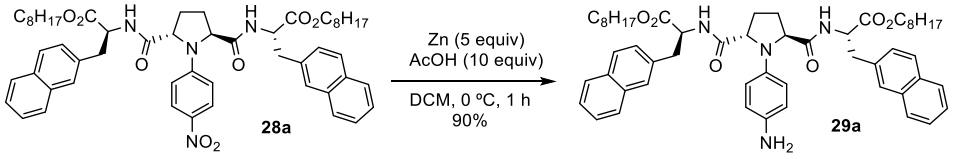
A solution of **25** (1.9 g, 6.8 mmol) and conc. HCl (14 mL) in acetic acid (6 mL) was refluxed for 15 h. After cooling to rt, sat. $NaHCO_3$ (20 mL) was added and stirred for 3 h. The reaction mixture was extracted with EtOAc. The organic later was dried over Na_2SO_4, and concentrated *in vacuo*. **26** (1.4 g) was obtained and used in the next step without further purification.

Preparation of (2*S*,5*S*)-2,5-Bis[(2*S*)-3-(naphthyl-2-yl)-1-octyloxy-1-oxopropan-2-ylaminocarbonyl]- 1-(4-nitrophenyl)pyrrolidine (28a)



To a solution of **26** (750 mg, 2.68 mmol), (*S*)-**27** (2 g, 5.36 mmol, 2 equiv), HOBt (905.4 mg, 6.7 mmol, 2.5 equiv), NMM (3 mL, 26.8 mmol, 10 equiv) in DMF (27 mL) was added WSCI·HCl (1.3 g, 6.7 mmol, 2.5 equiv) at 0 °C. After being stirred for 6 h at rt, aq. citric acid was added and extracted with EtOAc. The organic later was washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **28a** (1.51 g, 63%) as a yellow solid.; $[\alpha]^{26}_D$ = –107.2 (c 0.22, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.80-7.82 (m, 2H), 7.68-7.74 (m, 4H), 7.59 (d, J = 9.1 Hz, 2H), 7.44-7.51 (m, 6H), 7.13 (dd, J = 8.3, 1.3 Hz, 2H), 6.05 (d, J = 9.1 Hz, 2H), 5.93 (d, J = 7.8 Hz, 2H), 4.81 (q, J = 6.8 Hz, 2H), 4.03-4.13 (m, 6H), 3.34 (dd, J = 14.2, 5.7 Hz, 2H), 3.15 (q, J = 6.8 Hz, 2H), 1.85-2.00 (m, 4H), 1.54-1.58 (m, 4H), 1.25-1.30 (m, 20H), 0.88 (t, J = 6.9 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.06, 170.65, 148.89, 139.20, 133.19, 132.97, 132.46, 128.52, 127.77, 127.24, 126.71, 126.62, 126.22, 125.67, 112.06, 77.20, 66.07, 62.99, 52.58, 37.61, 31.73, 29.10, 29.02, 28.43, 25.76, 22.60, 14.07; HRMS (ESI) *m*/*z* calcd for $C_{54}H_{66}N_4O_8Na$ $(M+Na)^+$ 921.4773, found 921.4785.

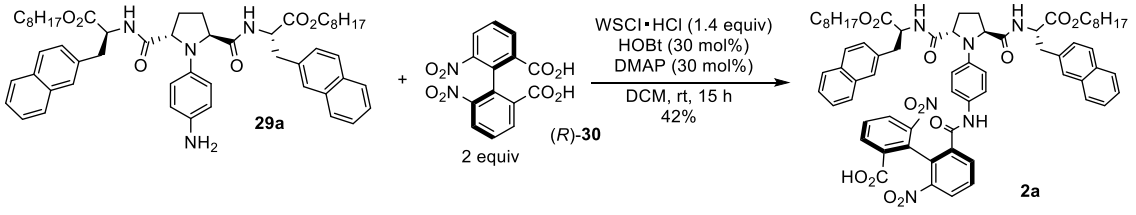
Preparation of (2*S*,5*S*)-2,5-Bis[(2*S*)-3-(naphthyl-2-yl)-1-octyloxy-1-oxopropan-2-ylaminocarbonyl]- 1-(4-aminophenyl)pyrrolidine (29a)



To a solution of **28a** (600 mg, 0.67 mmol) in DCM (30 mL) were added Zn (218.4 mg, 3.34 mmol, 5 equiv) and AcOH (381.5 μL, 6.67 mmol, 10 equiv) at 0 °C. After being stirred for 6 h at 0 °C, the reaction mixture was filtered with celite, and washed with sat. $NaHCO_3$, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **29a** (526.7 mg, 90%) as a brown solid.; $[\alpha]^{27}_D$ = –89.1 (c 0.24, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.78-7.81 (m, 2H), 7.71 (t, J = 8.2 Hz, 4H), 7.45-7.48 (m, 6H), 7.14 (dd, J = 8.5, 1.6 Hz, 2H), 6.33 (d, J = 8.9 Hz, 2H), 6.16-6.19 (m, 4H), 4.77 (q, J = 6.8 Hz, 2H), 3.98-4.02 (m, 6H), 3.30 (dd, J = 14.0, 5.9 Hz, 2H), 3.19 (br s, 1H), 3.11 (q, J = 6.8 Hz, 2H), 1.68-1.83 (m, 4H), 1.48 (t, J = 6.8 Hz, 4H), 1.17-1.31 (m, 20H), 0.88 (t, J = 7.0 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.71, 170.94, 138.31, 136.48,

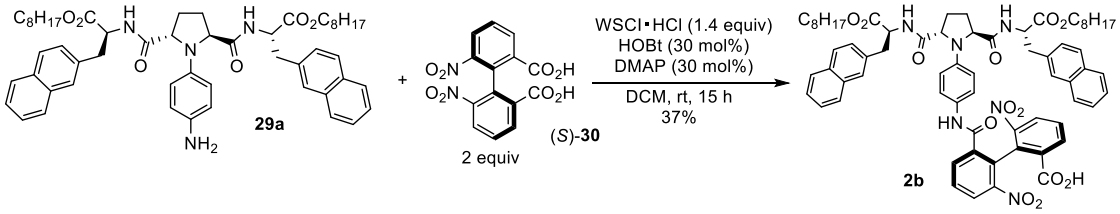
133.39, 133.28, 132.42, 128.27, 127.83, 127.67, 127.37, 126.94, 126.28, 125.79, 116.78, 114.18, 65.70, 62.86, 52.79, 37.77, 31.74, 29.10, 28.90, 28.33, 25.71, 22.60, 14.06; HRMS (ESI) *m/z* calcd for $C_{54}H_{69}N_4O_6$ $(M+H)^+$ 869.5212, found 869.5212.

Preparation of catalyst 2a



To a solution of **29a** (521.5 mg, 0.6 mmol), (*R*)-6,6'-dinitrodiphenic acid (**30**) (398.7 mg, 1.2 mmol, 2 equiv), HOBt (24.3 mg, 0.18 mmol, 30 mol%) and DMAP (22.0 mg, 0.18 mmol, 30 mol%) in DCM (15 mL) was added WSCI·HCl (126.5 mg, 0.66 mmol, 1.1 equiv) at rt. After being stirred for 15 h at rt, aq. citric acid was added and extracted with EtOAc. The organic later was washed with sat. $NaHCO_3$, 0.5 NHCl and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **2a** (300.2 mg, 42%) as a yellow solid.; $[\alpha]^{25}_D$ = +11.1 (c 0.60, MeOH); ^{1}H-NMR (400 MHz, acetone-d6) δ 9.06 (br s, 1H), 8.19-8.28 (m, 3H), 7.93 (d, J = 7.1 Hz, 1H), 7.76-7.79 (m, 2H), 7.64-7.72 (m, 6H), 7.58 (s, 2H), 7.35-7.45 (m, 6H), 7.25 (dd, J = 8.5, 1.6 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 6.00 (d, J = 9.0 Hz, 2H), 4.69 (td, J = 8.7, 5.2 Hz, 2H), 4.09 (d, J = 7.8 Hz, 2H), 3.85-3.99 (m, 4H), 3.23 (dd, J = 14.0, 5.5 Hz, 2H), 3.03 (dd, J = 14.0, 9.0 Hz, 2H), 1.98-2.00 (m, 2H), 1.52-1.57 (m, 2H), 1.41 (t, J = 6.3 Hz, 4H), 1.14-1.21 (m, 20H), 0.79 (t, J = 7.0 Hz, 6H); ^{13}C-NMR (100 MHz, acetone-d6) δ 171.34, 169.27, 164.03, 162.13, 147.72, 147.20, 140.56, 135.87, 132.95, 132.56, 131.62, 130.90, 130.61, 130.24, 129.30, 127.25, 127.18, 126.97, 126.14, 125.86, 125.56, 125.40, 124.24, 123.72, 123.57, 119.81, 110.84, 63.03, 60.96, 51.32, 35.19, 29.80, 27.16, 23.77, 20.57, 11.66; HRMS (ESI) *m/z* calcd for $C_{68}H_{75}N_6O_{13}$ $(M+H)^+$ 1183.5387, found 1183.5392.

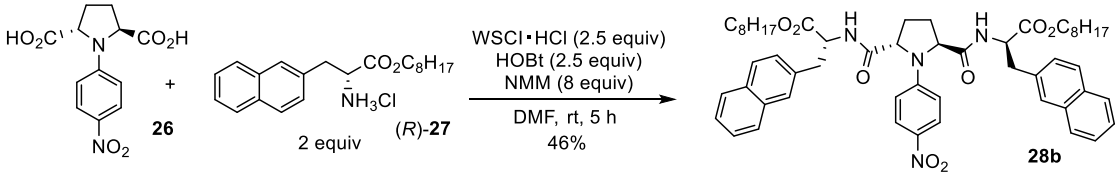
Preparation of catalyst 2b



To a solution of **29a** (521.5 mg, 0.6 mmol), (*S*)-6,6'-dinitrodiphenic acid (**30**) (398.7 mg, 1.2 mmol, 2 equiv), HOBt (24.3 mg, 0.18 mmol, 30 mol%) and DMAP (22.0 mg, 0.18 mmol, 30 mol%) in DCM (15 mL) was added WSCI·HCl (126.5 mg, 0.66 mmol, 1.1 equiv) at rt. After being stirred for 15 h at rt, aq. citric acid was added and extracted with EtOAc. The organic later was washed with sat. $NaHCO_3$, 0.5 NHCl and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **2b** (263.6 mg, 37%) as a yellow solid.; $[\alpha]^{26}_D$ = –97.2 (c 0.26, MeOH); ^{1}H-NMR (400 MHz, acetone-d6) δ 9.69 (br s, 1H), 8.12-8.22 (m, 3H), 7.73-7.88 (m, 7H), 7.65-7.72 (m, 4H), 7.43-7.52 (m, 6H), 7.34 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.5 Hz,

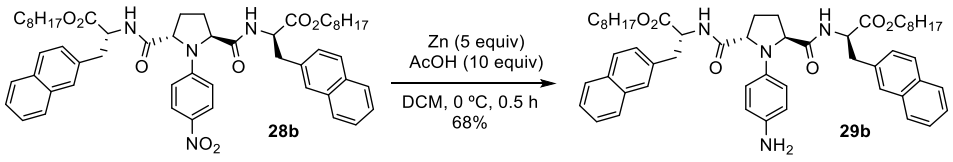
2H), 6.17 (d, J = 8.7 Hz, 2H), 4.85 (dd, J = 14.1, 8.1 Hz, 2H), 4.27 (d, J = 6.6 Hz, 2H), 3.91-4.07 (m, 4H), 3.31 (dd, J = 13.8, 5.4 Hz, 2H), 3.15 (dd, J = 13.8, 8.6 Hz, 2H), 2.16 (brs, 2H), 1.66-1.71 (m, 2H), 1.47 (t, J = 5.9 Hz, 4H), 1.12-1.30 (m, 20H), 0.88 (t, J = 7.0 Hz, 6H); ^{13}C-NMR (100 MHz, acetone-d6) δ 171.03, 169.31, 164.22, 162.27, 147.59, 147.03, 140.69, 136.19, 133.01, 132.54, 131.64, 131.42, 130.63, 130.14, 130.03, 129.11, 127.28, 127.23, 127.11, 126.14, 125.91, 125.87, 125.57, 125.44, 125.27, 124.23, 123.71, 123.52, 119.41, 110.87, 62.99, 61.01, 51.27, 35.24, 29.80, 27.16, 23.77, 20.57, 11.66; HRMS (ESI) *m/z* calcd for $C_{68}H_{75}N_6O_{13}$ $(M+H)^+$ 1183.5387, found 1183.5393.

Preparation of (2*S*,5*S*)-2,5-Bis[(2*R*)-3-(naphthyl-2-yl)-1-octyloxy-1-oxopropan-2-ylaminocarbonyl]- 1-(4-nitrophenyl)pyrrolidine (28b)



To a solution of **26** (750 mg, 2.68 mmol), (*R*)-**27** (2 g, 5.36 mmol, 2 equiv), HOBt (905.4 mg, 6.7 mmol, 2.5 equiv), NMM (2.4 mL, 21.4 mmol, 8 equiv) in DMF (27 mL) was added WSCI·HCl (1.3 g, 6.7 mmol, 2.5 equiv) at 0 °C. After being stirred for 5 h at rt, aq. citric acid was added and extracted with EtOAc. The organic later was washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **28b** (1.1 g, 46%) as a yellow solid.; $[\alpha]^{27}_D$ = –215.8 (c 0.26, $CHCl_3$) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.71-7.74 (m, 2H), 7.50-7.63 (m, 6H), 7.43 (dt, J = 9.5, 3.4 Hz, 4H), 7.25 (d, J = 8.7 Hz, 2H), 6.92 (dd, J = 8.3, 1.7 Hz, 2H), 6.07-6.11 (m, 2H), 5.95 (d, J = 8.0 Hz, 2H), 4.85 (td, J = 7.7, 5.5 Hz, 2H), 4.08-4.19 (m, 6H), 3.21 (dd, J = 14.2, 5.5 Hz, 2H), 3.06 (q, J = 7.2 Hz, 2H), 2.23-2.28 (m, 2H), 1.91-2.00 (m, 2H), 1.58-1.63 (q, J = 6.9 Hz, 4H), 1.25-1.29 (m, 20H), 0.88 (t, J = 6.9 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.35, 170.64, 148.81, 139.13, 133.04, 132.46, 132.30, 128.45, 127.58, 127.18, 126.45, 126.32, 126.14, 125.65, 111.92, 66.08, 63.14, 52.45, 37.55, 31.72, 29.31, 29.08, 28.46, 25.79, 22.58, 14.05; HRMS (ESI) *m/z* calcd for $C_{54}H_{66}N_4O_8Na$ $(M+Na)^+$ 921.4773, found 921.4781.

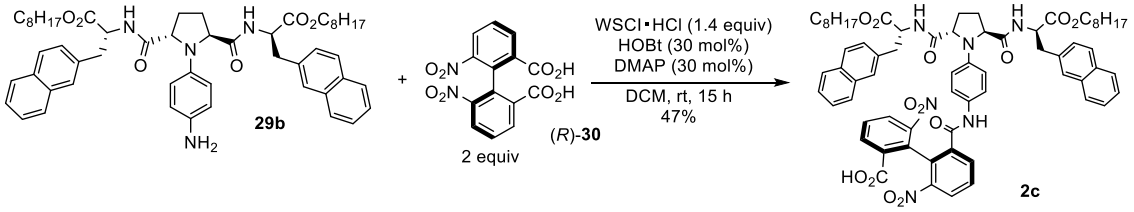
Preparation of (2*S*,5*S*)-2,5-Bis[(2*R*)-3-(naphthyl-2-yl)-1-octyloxy-1-oxopropan-2-ylaminocarbonyl]- 1-(4-aminophenyl)pyrrolidine (29b)



To a solution of **28b** (449.6 mg, 0.5 mmol) in DCM (6 mL) was added Zn (163.5 mg, 2.5 mmol, 5 equiv) AcOH (286.0 μL, 5 mmol, 10 equiv) at 0 °C. After being stirred for 0.5 h at 0 °C, the reaction mixture was filtered with celite, and washed with sat. $NaHCO_3$, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **29b** (294.1 mg, 68%) as a brown solid.; $[\alpha]^{26}_D$ = –121.6 (c 0.29, $CHCl_3$) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75-7.78 (m, 2H), 7.57-7.63 (m, 4H), 7.44 (td, J = 6.5, 3.3 Hz,

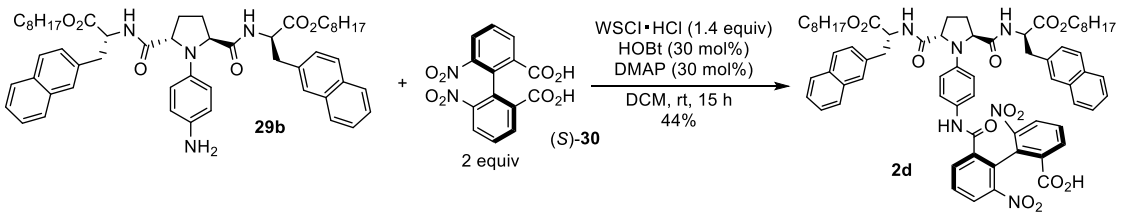
4H), 7.22 (s, 2H), 6.82 (dd, J = 8.5, 1.6 Hz, 2H), 6.39 (d, J = 8.7 Hz, 2H), 6.21-6.25 (m, 4H), 4.90-4.95 (m, 2H), 4.14 (d, J = 7.8 Hz, 2H), 4.01-4.07 (m, 4H), 3.25 (br s, 1H), 3.15 (dd, J = 14.0, 6.2 Hz, 2H), 3.02 (dd, J = 14.0, 5.4 Hz, 2H), 2.17-2.25 (m, 2H), 1.97-2.02 (m, 2H), 1.54 (q, J = 6.6 Hz, 4H), 1.21-1.30 (m, 20H), 0.86-0.89 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.51, 171.21, 138.61, 136.34, 133.35, 132.88, 132.42, 128.31, 127.80, 127.65, 127.62, 126.92, 126.02, 125.71, 117.05, 113.99, 65.77, 62.89, 52.33, 37.87, 31.74, 31.58, 29.34, 29.11, 28.45, 25.80, 22.61, 14.08; HRMS (ESI) *m*/*z* calcd for $C_{54}H_{69}N_4O_6$ (M+H)$^+$ 869.5212, found 869.5212.

Preparation of catalyst 2c



To a solution of **29b** (521.5 mg, 0.6 mmol), (*R*)-6,6'-dinitrodiphenic acid (**30**) (398.7 mg, 1.2 mmol, 2 equiv), HOBt (24.3 mg, 0.18 mmol, 30 mol%) and DMAP (22.0 mg, 0.18 mmol, 30 mol%) in DCM (15 mL) was added WSCI·HCl (126.5 mg, 0.66 mmol, 1.1 equiv) at rt. After being stirred for 15 h at rt, aq. citric acid was added and extracted with EtOAc. The organic later was washed with sat. $NaHCO_3$, 0.5 NHCl and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **2c** (330.7 mg, 47%) as a yellow solid.; $[\alpha]^{27}_D$ = +9.1 (c 0.38, MeOH); ^{1}H-NMR (400 MHz, acetone-d6) δ 10.00 (br s, 1H), 8.16 (d, J = 8.2 Hz, 1H), 7.93-8.03 (m, 2H), 7.80-7.83 (m, 3H), 7.67 (d, J = 7.8 Hz, 4H), 7.42-7.50 (m, 7H), 7.28-7.35 (m, 3H), 7.21 (d, J = 8.7 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 6.32 (d, J = 8.7 Hz, 2H), 4.78 (q, J = 7.2 Hz, 2H), 4.25 (d, J = 7.5 Hz, 2H), 4.05 (ddd, J = 25.1, 10.9, 6.8 Hz, 4H), 3.13-3.18 (m, 4H), 2.10-2.21 (m, 2H), 1.69 (dd, J = 19.9, 14.4 Hz, 2H), 1.53-1.56 (m, 4H), 1.23-1.29 (m, 20H), 0.86 (t, J = 6.9 Hz, 6H); ^{13}C-NMR (100 MHz, acetone-d6) δ 170.91, 170.83, 169.17, 164.11, 162.19, 147.58, 147.09, 140.40, 135.99, 132.64, 132.50, 131.58, 131.00, 130.58, 130.23, 130.07, 129.19, 127.36, 127.28, 127.21, 126.15, 125.80, 125.75, 125.68, 125.60, 125.31, 124.15, 123.66, 123.54, 119.80, 111.03, 63.15, 60.94, 51.31, 51.23, 35.42, 29.80, 27.17, 23.82, 20.56, 11.67; HRMS (ESI) *m*/*z* calcd for $C_{68}H_{75}N_6O_{13}$ (M+H)$^+$ 1183.5387, found 1183.5387.

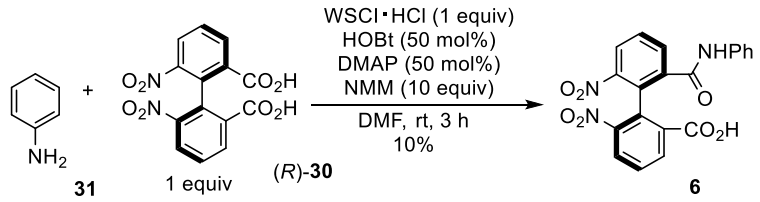
Preparation of catalyst 2d



To a solution of **29b** (521.5 mg, 0.6 mmol), (*S*)-6,6'-dinitrodiphenic acid (**30**) (398.7 mg, 1.2 mmol, 2 equiv), HOBt (24.3 mg, 0.18 mmol, 30 mol%) and DMAP (22.0 mg, 0.18 mmol, 30 mol%) in DCM (15 mL) was added WSCI·HCl (126.5 mg, 0.66 mmol, 1.1 equiv) at rt. After being stirred for 15 h at rt, aq. citric acid was added and extracted with EtOAc. The organic later was washed with sat. $NaHCO_3$, 0.5 NHCl and brine, dried over Na_2SO_4, and

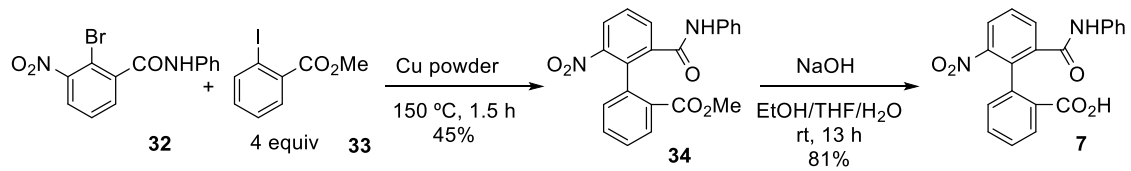
concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **2d** (314.2 mg, 44%).; $[\alpha]^{27}_D$ = –93.6 (c 0.29, MeOH); ^{1}H-NMR (400 MHz, acetone-d6) δ 9.33 (br s, 1H), 8.34 (d, J = 8.2 Hz, 1H), 8.24 (t, J = 7.4 Hz, 2H), 8.00-8.05 (m, 1H), 7.75-7.84 (m, 3H), 7.60-7.70 (m, 5H), 7.42-7.49 (m, 6H), 7.35 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.9 Hz, 2H), 7.11 (dd, J = 8.3, 1.3 Hz, 2H), 6.28 (d, J = 8.9 Hz, 2H), 4.75 (dt, J = 8.2, 5.5 Hz, 2H), 4.19 (d, J = 7.5 Hz, 2H), 3.99-4.09 (m, 4H), 3.10-3.22 (m, 4H), 2.13-2.16 (m, 2H), 1.67 (d, J = 5.5 Hz, 2H), 1.54 (q, J = 6.5 Hz, 4H), 1.24-1.29 (m, 20H), 0.87 (t, J = 6.9 Hz, 6H); ^{13}C-NMR (100 MHz, acetone-d6) δ 170.66, 169.24, 163.96, 162.35, 147.61, 147.08, 140.54, 136.12, 132.71, 132.56, 131.59, 130.96, 130.58, 130.17, 129.12, 127.28, 126.12, 125.81, 125.73, 125.68, 125.61, 125.40, 124.13, 123.64, 123.53, 119.72, 111.03, 63.09, 60.97, 51.26, 35.41, 29.80, 27.17, 26.57, 23.82, 20.56, 11.64; HRMS (ESI) *m/z* calcd for $C_{68}H_{75}N_6O_{13}$ $(M+H)^+$ 1183.5387, found 1183.5393.

Preparation of catalyst 6



To a solution of aniline (**31**) (69.5 μL, 0.76 mmol), (*R*)-6,6'-dinitrodiphenic acid (**30**) (252.5 mg, 0.76 mmol, 1 equiv), HOBt (51.3 mg, 0.38 mmol, 50 mol%), DMAP (46.4 mg, 0.38 mmol, 50 mol%) and NMM (839.2 μL, 7.6 mmol, 10 equiv) in DMF (5 mL) was added WSCI·HCl (145.7 mg, 0.76 mmol, 1 equiv) at rt. After being stirred for 3 h at rt, aq. citric acid was added and extracted with EtOAc. The organic later was washed with sat. $NaHCO_3$, 0.5 NHCl and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **6** (32.2 mg, 10%) as a white solid.; $[\alpha]^{26}_D$ = +261.4 (c 0.11, MeOH); ^{1}H-NMR (400 MHz, acetone-d6) δ 11.18 (br s, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.69 (d, J = 7.3 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.01 (t, J = 7.9 Hz, 2H), 6.83 (t, J = 7.4 Hz, 1H); ^{13}C-NMR (100 MHz, acetone-d6) δ 170.63, 164.56, 147.90, 147.59, 139.21, 138.56, 132.66, 131.49, 130.02, 128.55, 128.38, 128.28, 127.85, 124.59, 124.24, 122.87, 119.05, 118.96; HRMS (ESI) *m/z* calcd for $C_{20}H_{12}N_3O_7$ $(M-H)^-$ 406.0681, found 406.0683.

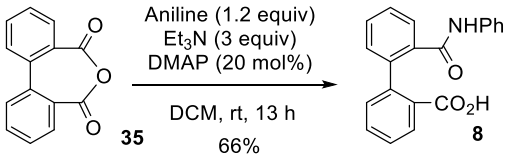
Preparation of catalyst 7



32 (192.7 mg, 0.6 mmol), methyl *o*-iodobenzoate (**33**) (352.9 μL, 2.4 mmol, 4 equiv) and Cu powder (300 mg) were stirred for 1.5 h at 150 °C. After cooling to rt, EtOAc was added and filtered with celite. Purification of the crude product by flash chromatography on silica gel provided **34** (101.9 mg, 45%). To a solution of **34** (101.9 mg, 0.27 mmol) in EtOH (4 mL) and THF (2 mL) was added 1M aq. NaOH (3 mL) at rt. After being stirred for 13 h at

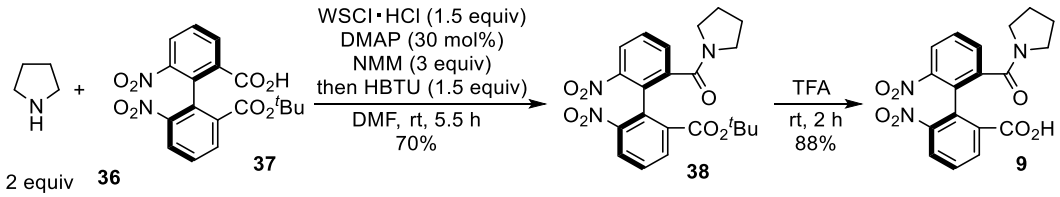
rt, 2NHCl was added and extracted with EtOAc. The organic later was dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **7** (79.3 mg, 81%) as a yellow solid.; ^{1}H-NMR (400 MHz, acetone-d6) δ 9.27 (br s, 1H), 8.10 (d, J = 8.2 Hz, 1H), 8.03 (d, J = 7.5 Hz, 1H), 7.94 (d, J = 7.5 Hz, 1H), 7.72 (t, J = 7.9 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.3 Hz, 1H), 7.21 (t, J = 7.9 Hz, 2H), 7.02 (t, J = 7.3 Hz, 1H); ^{13}C-NMR (100 MHz, acetone-d6) δ 169.42, 166.24, 150.06, 140.49, 139.54, 137.10, 134.99, 132.88, 132.55, 131.86, 131.40, 130.95, 129.82, 129.73, 129.63, 125.85, 125.06, 120.53; HRMS (ESI) *m/z* calcd for $C_{20}H_{13}N_2O_5$ $(M–H)^-$ 361.0830, found 361.0834.

Preparation of catalyst 8



To a solution of diphenic anhydride (**35**) (134.5 mg, 0.6 mmol), aniline 65.8 μL, 0.72 mmol, 1.2 equiv), and Et_3N (251.6 μL, 1.8 mmol, 3 equiv) in DCM (6 mL) was added DMAP (14.7 mg, 0.12 mmol, 20 mol%) at rt.. After being stirred for 13 h at rt, 2NHCl was added and extracted with DCM. The organic later was dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **7** (126.0 mg, 66%) as a white solid.; ^{1}H-NMR (400 MHz, acetone-d6) δ 9.41 (br s, 1H), 7.85-7.88 (m, 1H), 7.71-7.73 (m, 1H), 7.42-7.51 (m, 6H), 7.17-7.23 (m, 4H), 7.01 (t, J = 7.4 Hz, 1H); ^{13}C-NMR (100 MHz, acetone-d6) δ 169.81, 167.72, 140.66, 139.50, 138.63, 136.25, 131.82, 131.14, 130.33, 129.86, 129.69, 128.98, 128.70, 127.88, 127.75, 127.68, 123.90, 119.30; HRMS (ESI) *m/z* calcd for $C_{20}H_{14}NO_3$ $(M–H)^-$ 316.0979, found 316.0982.

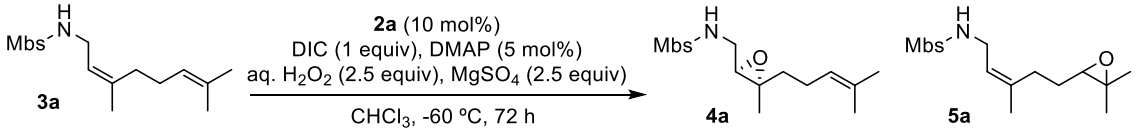
Preparation of catalyst 9



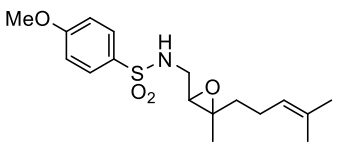
To a solution of pyrolidine (**36**) (21.0 μL, 0.252 mmol, 2 equiv), (*R*)-6,6'-dinitrodiphenic acid mono *tert*-butyl ester (**37**) (48.9 mg, 0.126 mmol), DMAP (4.6 mg, 0.038 mmol, 30 mol%) and NMM (41.7 μL, 0.378 mmol, 3 equiv) in DMF (5 mL) was added WSCI·HCl (36.4 mg,0.19 mmol, 1.5 equiv) at rt. After being stirred for 3 h at rt, HBTU (72.1 mg, 0.19 mmol, 1.5 equiv) was added and stirred additional 2.5 h. aq. Citric acid was added and extracted with EtOAc. The organic later was washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **38** (39.1 mg, 70%). To **38** (39.1 mg, 0.09 mmol) was added TFA (2 mL) at 0 °C. After being stirred for 2 h at rt, the reaction mixture was quenched by addition of sat. $NaHCO_3$, and extracted with EtOAc. The organic later was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **9** (29.9 mg, 88%) as a white solid.; $[\alpha]^{26}_D$ = +111.3 (c 0.17, MeOH) ^{1}H-NMR

(400 MHz, acetone-d6) δ 8.22 (ddd, J = 8.2, 5.3, 1.1 Hz, 2H), 8.12 (dd, J = 7.8, 1.1 Hz, 1H), 7.64-7.76 (m, 3H), 3.18-3.23 (m, 1H), 3.02-3.12 (m, 3H), 1.64-1.70 (m, 4H); ^{13}C-NMR (100 MHz, acetone-d6) δ 166.66, 166.29, 149.87, 138.26, 135.10, 134.35, 132.37, 131.85, 131.04, 130.36, 130.16, 128.11, 125.81, 49.36, 46.23, 26.55, 24.67; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{14}N_3O_7$ $(M-H)^-$ 384.0837, found 384.0843.

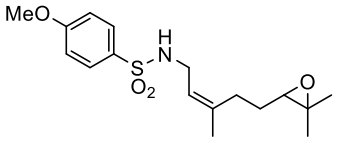
2. 3. General procedure for site- and enantioselective epoxidation



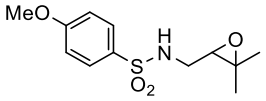
To a solution of **3a** (32.3 mg, 0.1 mmol), **2a** (11.8 mg, 0.01 mmol, 10 mol%), DMAP (0.6 mg, 0.005 mmol, 5 mol%) and $MgSO_4$ (30.1 mg, 0.25 mmol, 2.5 equiv) in $CHCl_3$ (0.5 mL) was added 30% aq. H_2O_2 (25.6 μL,0.25 mmol, 2.5 equiv) at 0 °C. After cooling to -60 °C, DIC (15.4 μL, 0.1 mmol, 1 equiv) was added. After being stirred for 72 h at -60 °C, the reaction mixture was quenched by addition of aq. $Na_2S_2O_3$. The mixture was diluted with sat. $NaHCO_3$, and extracted with EtOAc. The organic later was dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided **4a** (25.1 mg, 74%). Regioselectivity was determined by the integration of ^{1}H NMR.



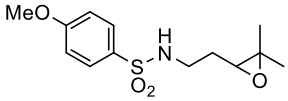
4a; Colorless oil; 89% ee; $[\alpha]^{27}_D$ = +41.8 (c 0.21, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79-7.83 (m, 2H), 6.96-7.00 (m, 2H), 5.00-5.04 (m, 1H), 4.91 (dd, J = 7.7, 4.9 Hz, 1H), 3.87 (s, 3H), 3.25 (ddd, J = 13.5, 7.7, 4.6 Hz, 1H), 2.93 (ddd, J = 13.5, 7.2, 4.9 Hz, 1H), 2.84 (dd, J = 7.2, 4.6 Hz, 1H), 1.99-2.09 (m, 2H), 1.69 (s, 3H), 1.58 (s, 3H), 1.50-1.55 (m, 1H), 1.31-1.39 (m, 1H), 1.27 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.02, 132.74, 131.34, 129.25, 123.05, 114.32, 62.03, 61.51, 55.63, 42.54, 32.81, 25.67, 23.98, 21.88, 17.63; Chiral HPLC (Chiralcel AD-H): flow rate: 1.0 mL/min, eluent: hexane/2-propanol = 90/10, column oven: 35 °C, retention time: 25.0 (major), 28.4 (minor); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{25}NO_4SNa$ $(M+Na)^+$ 362.1397, found 362.1396.



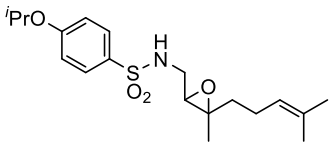
5a; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79-7.83 (m, 2H), 6.96-6.99 (m, 2H), 5.21 (t, J = 7.4 Hz, 1H), 4.68 (t, J = 5.8 Hz, 1H), 3.87 (s, 3H), 3.53 (t, J = 6.6 Hz, 2H), 2.63 (dd, J = 8.1, 4.7 Hz, 1H), 2.06-2.16 (m, 2H), 1.62-1.71 (m, 4H), 1.44-1.53 (m, 1H), 1.31 (s, 3H), 1.24 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.78, 140.10, 131.79, 129.28, 120.66, 114.14, 63.57, 58.97, 55.59, 40.52, 28.30, 26.46, 24.83, 23.11, 18.79; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{25}NO_4SNa$ $(M+Na)^+$ 362.1397, found 362.1400.



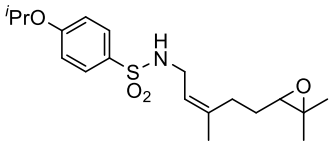
4b [1]; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.80-7.84 (m, 2H), 6.97-7.00 (m, 2H), 5.09 (dd, J = 7.2, 5.1 Hz, 1H), 3.87 (s, 3H), 3.23 (ddd, J = 13.7, 7.6, 5.1 Hz, 1H), 2.98 (qd, J = 6.9, 5.0 Hz, 1H), 2.85 (dd, J = 6.6, 5.0 Hz, 1H), 1.26 (s, 3H), 1.21 (s, 3H); Chiral HPLC (Chiralcel AD-H): flow rate: 1.0 mL/min, eluent: hexane/2-propanol = 90/10, column oven: 35 °C, retention time: 51.0 (minor), 56.3 (major).



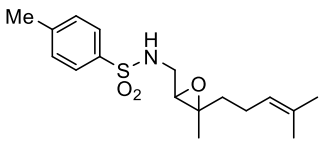
4c; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79-7.83 (m, 2H), 6.96-7.00 (m, 2H), 4.74-4.77 (m, 1H), 3.87 (s, 3H), 3.06-3.23 (m, 2H), 2.71 (q, J = 4.2 Hz, 1H), 1.82-1.90 (m, 1H), 1.51-1.56 m, 1H), 1.28 (s, 3H), 1.23 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.88, 131.43, 129.24, 114.25, 62.15, 58.23, 55.60, 41.25, 28.44, 24.59, 18.81; Chiral HPLC (Chiralcel OD-H): flow rate: 1.0 mL/min, eluent: hexane/2-propanol = 95/5, column oven: 30 °C, retention time: 62.8 (major), 66.3 (minor); HRMS (ESI) *m*/*z* calcd for $C_{13}H_{20}NO_4SNa$ (M+H)$^+$ 286.1108, found 286.1110.



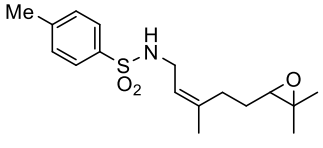
4d; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75-7.79 (m, 2H), 6.93-6.96 (m, 2H), 5.03 (t, J = 7.2 Hz, 1H), 4.56-4.66 (m, 2H), 3.23-3.29 (m, 1H), 2.91-2.97 (m, 1H), 2.84 (dd, J = 7.1, 4.6 Hz, 1H), 1.99-2.10 (m, 2H), 1.69 (s, 3H), 1.58 (s, 3H), 1.51-1.53 (m, 1H), 1.31-1.39 (m, 7H), 1.27 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.53, 132.75, 130.71, 129.25, 123.05, 115.66, 70.43, 62.05, 61.50, 42.54, 32.81, 25.67, 23.99, 21.88, 21.81, 17.62; ; Chiral HPLC (Chiralcel AD-H): flow rate: 1.0 mL/min, eluent: hexane/2-propanol = 93/7, column oven: 35 °C, retention time: 24.8 (major), 28.4 (minor); HRMS (ESI) *m*/*z* calcd for $C_{19}H_{29}NO_4SNa$ (M+Na)$^+$ 390.1710, found 390.1706.



5d; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76-7.79 (m, 2H), 6.94 (d, J = 8.9 Hz, 2H), 5.21 (t, J = 7.4 Hz, 1H), 4.60-4.67 (m, 2H), 3.53 (t, J = 6.6 Hz, 2H), 2.64 (dd, J = 8.0, 4.8 Hz, 1H), 2.05-2.18 (m, 2H), 1.61-1.70 (m, 4H), 1.45-1.54 (m, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.30 (s, 3H), 1.24 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.27, 140.03, 131.20, 129.28, 120.71, 115.50, 70.35, 63.57, 58.92, 40.53, 28.32, 26.50, 24.83, 23.11, 21.84, 18.78; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{29}NO_4SNa$ (M+Na)$^+$ 390.1710, found 390.1709.

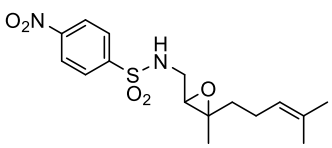


4e; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 5.00-5.04 (m, 1H), 4.89 (dd, J = 7.4, 4.8 Hz, 1H), 3.23-3.30 (m, 1H), 2.94 (ddd, J = 13.5, 7.2, 4.8 Hz, 1H), 2.84 (dd, J = 7.2, 4.6 Hz, 1H), 2.43 (s, 3H), 1.99-2.11 (m, 2H), 1.69 (s, 4H), 1.57 (s, 3H), 1.49-1.55 (m, 1H), 1.31-1.42 (m, 1H), 1.26 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.58, 136.81, 132.65, 129.74, 127.06, 123.04, 62.10, 61.51, 42.54, 32.77, 25.64, 23.93, 21.82, 21.49, 17.58; HPLC (Chiralcel AD-H): flow rate: 1.0 mL/min, eluent: hexane/2-propanol = 95/5, column oven: 35 °C, retention time: 38.2 (major), 42.5 (minor); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{25}NO_3SNa$ (M+Na)$^+$ 346.1447, found 346.1448.

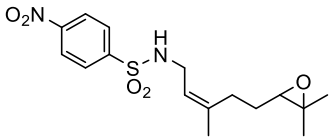


5e; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 5.20 (t, J = 7.5 Hz, 1H), 4.81 (t, J = 5.8 Hz, 1H), 3.53 (t, J = 6.7 Hz, 2H), 2.63 (dd, J = 8.0, 4.8 Hz, 1H), 2.43 (s, 3H), 2.06-2.16 (m, 2H),

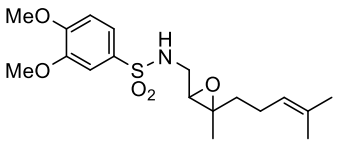
1.61-1.70 (m, 4H), 1.46-1.53 (m, 1H), 1.30 (s, 3H), 1.24 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.20, 140.02, 137.17, 129.58, 127.15, 120.62, 63.57, 58.94, 40.52, 28.27, 26.44, 24.80, 23.06, 21.48, 18.75; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{25}NO_3SNa$ (M+Na)$^+$ 346.1447, found 346.1448.



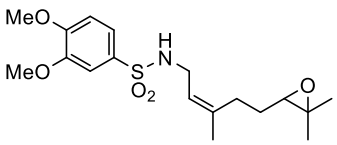
4f; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.37 (dt, J = 9.1, 2.1 Hz, 2H), 8.07 (dt, J = 9.1, 2.1 Hz, 2H), 5.27-5.30 (m, 1H), 5.00-5.04 (m, 1H), 3.41 (dq, J = 13.8, 3.9 Hz, 1H), 2.95-3.01 (m, 1H), 2.86 (q, J = 3.9 Hz, 1H), 1.98-2.13 (m, 2H), 1.69 (s, 3H), 1.53-1.60 (m, 4H), 1.33-1.40 (m, 1H), 1.29 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.10, 145.92, 132.87, 128.27, 124.42, 122.83, 62.09, 61.96, 42.83, 32.88, 25.64, 23.94, 21.84, 17.62; HPLC (Chiralcel AD-H): flow rate: 1.0 mL/min, eluent: hexane/2-propanol = 90/10, column oven: 35 °C, retention time: 29.9 (major), 40.3 (minor); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}N_2O_5SNa$ (M+Na)$^+$ 377.1142, found 377.1147.



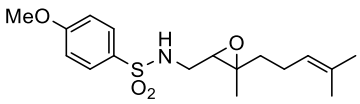
5f; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.34-8.37 (m, 2H), 8.05-8.09 (m, 2H), 5.47 (t, J = 5.7 Hz, 1H), 5.26 (t, J = 7.7 Hz, 1H), 3.56-3.65 (m, 2H), 2.67 (dd, J = 9.1, 3.9 Hz, 1H), 2.17-2.25 (m, 1H), 2.06-2.12 (m, 1H), 1.76-1.84 (m, 1H), 1.70 (s, 3H), 1.38-1.47 (m, 1H), 1.33 (s, 3H), 1.27 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.91, 146.44, 140.71, 128.31, 124.22, 120.40, 63.54, 59.78, 40.51, 28.08, 25.74, 24.83, 22.93, 18.87; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}N_2O_5SNa$ (M+Na)$^+$ 377.1142, found 377.1145.



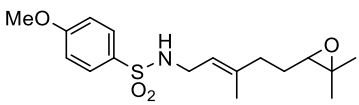
4g; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.5, 2.3 Hz, 1H), 7.35 (d, J = 2.3 Hz, 1H), 6.94 (d, J = 8.5 Hz, 1H), 5.00-5.04 (m, 1H), 4.90 (dd, J = 7.8, 4.7 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.27 (ddd, J = 13.4, 7.8, 4.4 Hz, 1H), 2.91-2.97 (m, 1H), 2.85 (dd, J = 7.3, 4.4 Hz, 1H), 1.99-2.12 (m, 2H), 1.68 (s, 3H), 1.50-1.58 (m, 4H), 1.32-1.40 (m, 1H), 1.27 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.71, 149.24, 132.76, 131.38, 123.03, 121.05, 110.57, 109.56, 61.99, 61.56, 56.23, 56.20, 42.59, 32.85, 25.67, 24.00, 21.89, 17.63; HPLC (Chiralcel AD-H): flow rate: 1.0 mL/min, eluent: hexane/2-propanol = 90/10, column oven: 35 °C, retention time: 27.5 (major), 29.6 (minor); HRMS (ESI) *m*/*z* calcd for $C_{18}H_{27}NO_5SNa$ (M+Na)$^+$ 392.1502, found 392.1503.



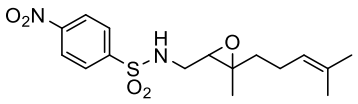
5g; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.6, 2.2 Hz, 1H), 7.36 (d, J = 2.2 Hz, 1H), 6.94 (d, J = 8.6 Hz, 1H), 5.24 (t, J = 7.4 Hz, 1H), 4.78 (t, J = 5.9 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.53 (t, J = 6.7 Hz, 2H), 2.65 (q, J = 4.3 Hz, 1H), 2.06-2.21 (m, 2H), 1.65-1.74 (m, 4H), 1.43-1.52 (m, 1H), 1.31 (s, 3H), 1.24 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.43, 149.11, 140.10, 131.82, 121.07, 120.70, 110.46, 109.71, 63.54, 59.10, 56.22, 56.16, 40.56, 28.27, 26.36, 24.86, 23.08, 18.80; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{27}NO_5SNa$ (M+Na)$^+$ 392.1502, found 392.1502.



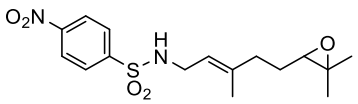
4h; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79-7.83 (m, 2H), 6.97-7.00 (m, 2H), 5.03 (tt, J = 7.1, 1.3 Hz, 1H), 4.78 (dd, J = 7.5, 5.0 Hz, 1H), 3.87 (s, 3H), 3.22 (ddd, J = 13.8, 7.6, 5.0 Hz, 1H), 2.99 (ddd, J = 13.8, 6.7, 5.0 Hz, 1H), 2.83 (dd, J = 6.7, 5.0 Hz, 1H), 2.01 (q, J = 7.6 Hz, 2H), 1.68 (s, 3H), 1.57-1.64 (m, 4H), 1.35-1.43 (m, 1H), 1.20 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.00, 132.27, 131.30, 129.23, 123.15, 114.31, 61.26, 60.66, 55.59, 42.62, 38.08, 25.63, 23.54, 17.63, 16.59; HPLC (Chiralcel AD-H): flow rate: 1.0 mL/min, eluent: hexane/2-propanol = 90/10, column oven: 35 °C, retention time: 25.1 (minor), 29.0 (major); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{25}NO_4SNa$ (M+Na)$^+$ 362.1397, found 362.1396.



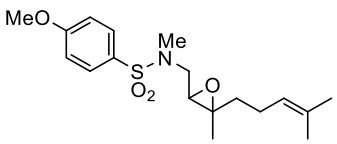
5h; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79-7.82 (m, 2H), 6.96-7.00 (m, 2H), 5.11 (dt, J = 7.0, 1.0 Hz, 1H), 4.45 (t, J = 5.7 Hz, 1H), 3.87 (s, 3H), 3.56 (t, J = 6.4 Hz, 2H), 2.64 (dd, J = 6.7, 5.6 Hz, 1H), 2.00-2.15 (t, 2H), 1.47-1.62 (m, 5H), 1.29 (s, 3H), 1.23 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.81, 140.01, 131.59, 129.25, 119.28, 114.14, 63.80, 58.27, 55.57, 40.84, 36.06, 27.00, 24.78, 18.67, 16.19; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{25}NO_4SNa$ (M+Na)$^+$ 362.1397, found 362.1402.



4i; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.38 (dt, J = 9.1, 2.1 Hz, 2H), 8.08 (dt, J = 9.1, 2.1 Hz, 2H), 5.12 (br s, 1H), 5.03 (tt, J = 7.1, 1.3 Hz, 1H), 3.40 (d, J = 13.6 Hz, 1H), 3.02 (dd, J = 13.6, 7.4 Hz, 1H), 2.86 (dd, J = 7.4, 4.3 Hz, 1H), 2.00-2.05 (m, 2H), 1.59-1.68 (m, 7H), 1.37-1.47 (m, 1H), 1.23 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.14, 145.87, 132.47, 128.30, 124.45, 122.96, 61.63, 60.66, 42.93, 38.06, 25.64, 23.53, 17.63, 16.70; HPLC (Chiralcel AD-H): flow rate: 1.0 mL/min, eluent: hexane/2-propanol = 90/10, column oven: 35 °C, retention time: 32.3 (minor), 58.4 (major); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}N_2O_5SNa$ (M+Na)$^+$ 377.1142, found 377.1144.

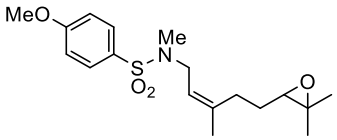


5i; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, J = 7.1, 1.8 Hz, 2H), 8.06 (dd, J = 7.1, 1.8 Hz, 2H), 5.13 (dt, J = 7.1, 1.0 Hz, 1H), 4.59 (t, J = 5.3 Hz, 1H), 3.66 (t, J = 6.2 Hz, 2H), 2.63 (dd, J = 7.3, 4.8 Hz, 1H), 2.03-2.17 (m, 2H), 1.59-1.67 (m, 4H), 1.44-1.53 (m, 1H), 1.29 (s, 3H), 1.24 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.04, 146.23, 141.18, 128.34, 124.32, 118.64, 63.79, 58.27, 41.02, 36.25, 26.97, 24.79, 18.73, 16.26; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}N_2O_5SNa$ (M+Na)$^+$ 377.1142, found 377.1145.



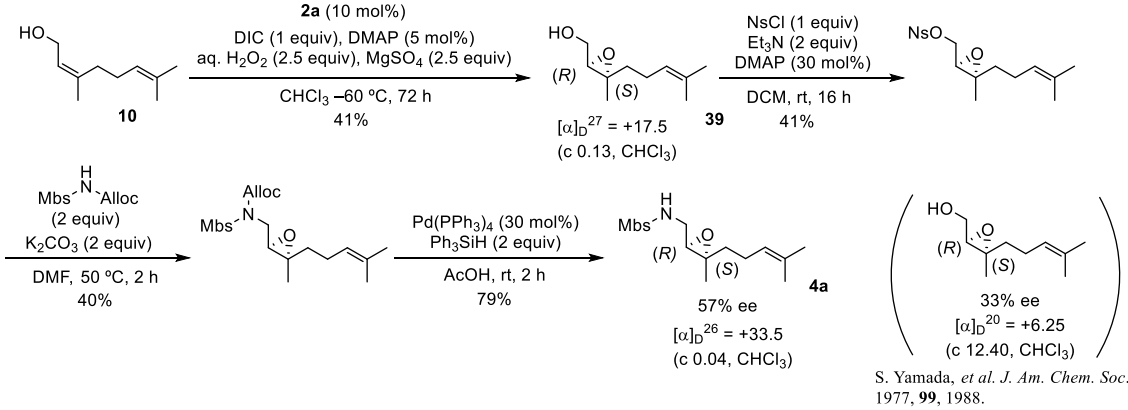
4j; Colorless oil; ^{1}H-NMR (400 MHz, methanol-d4) δ 7.72-7.75 (m, 2H), 7.09-7.13 (m, 2H), 5.10-5.13 (m, 1H), 3.88 (s, 3H), 3.60 (dd, J = 14.2, 3.4 Hz, 1H), 2.88 (dd, J = 7.3, 3.4 Hz, 1H), 2.78 (s, 3H), 2.73 (dd, J = 14.2, 7.3 Hz, 1H), 2.12 (q, J = 7.7 Hz, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.40-1.58 (m, 2H), 1.28 (s, 3H); ^{13}C-NMR (100 MHz, methanol-d4) δ 164.82, 133.17, 130.75, 129.92, 124.60, 115.52, 63.63, 61.49, 56.24, 50.85, 36.13, 33.96, 25.89, 24.98, 22.15, 17.71; HPLC (Chiralcel AD-H): flow rate: 1.0

mL/min, eluent: hexane/2-propanol = 92/8, column oven: 35 °C, retention time: 12.0 (major), 13.8 (minor); HRMS (ESI) *m*/*z* calcd for $C_{18}H_{27}NO_4SNa$ $(M+Na)^+$ 376.1553, found 376.1553.



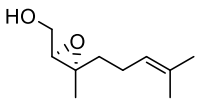
5j; Colorless oil; ^{1}H-NMR (400 MHz, methanol-d4) δ 7.71-7.74 (m, 2H), 7.09-7.12 (m, 2H), 5.16 (t, J = 7.0 Hz, 1H), 3.88 (s, 3H), 3.61 (d, J = 7.0 Hz, 2H), 2.73 (t, J = 6.3 Hz, 1H), 2.62 (s, 3H), 2.19 (t, J = 7.8 Hz, 2H), 1.74 (s, 3H), 1.55-1.65 (m, 2H), 1.27 (s, 3H), 1.23 (s, 3H); ^{13}C-NMR (100 MHz, methanol-d4) δ 164.04, 141.26, 130.18, 129.33, 120.18, 114.77, 64.73, 59.60, 55.58, 47.89, 34.07, 28.68, 27.53, 24.39, 22.88, 18.21; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{27}NO_4SNa$ $(M+Na)^+$ 376.1553, found 376.1558.

2. 4. Determination of absolute configuration of 4a



S. Yamada, *et al. J. Am. Chem. Soc.*, 1977, **99**, 1988.

Nerol (**10**) was oxidize to 2,3-epoxynerol (**39**) by catalytic epoxidation with **2a**. Absolute configuration of **39** was determined to (*R, S*) by comparison of optical rotation between synthetic and literature data.[2] **39** was converted into sulfonamide by nosylation of hydroxy group, S_N2 reaction with protected sulfonamide, and deprotection of Alloc group.[3] Optical rotation of this compound, which has (*R, S*) configuration, was +33.5 (c 0.04, $CHCl_3$). By comparison of optical rotation, absolute configuration of **4a**, which was obtained from catalytic epoxidation of **3a**, was determined to (*R, S*).

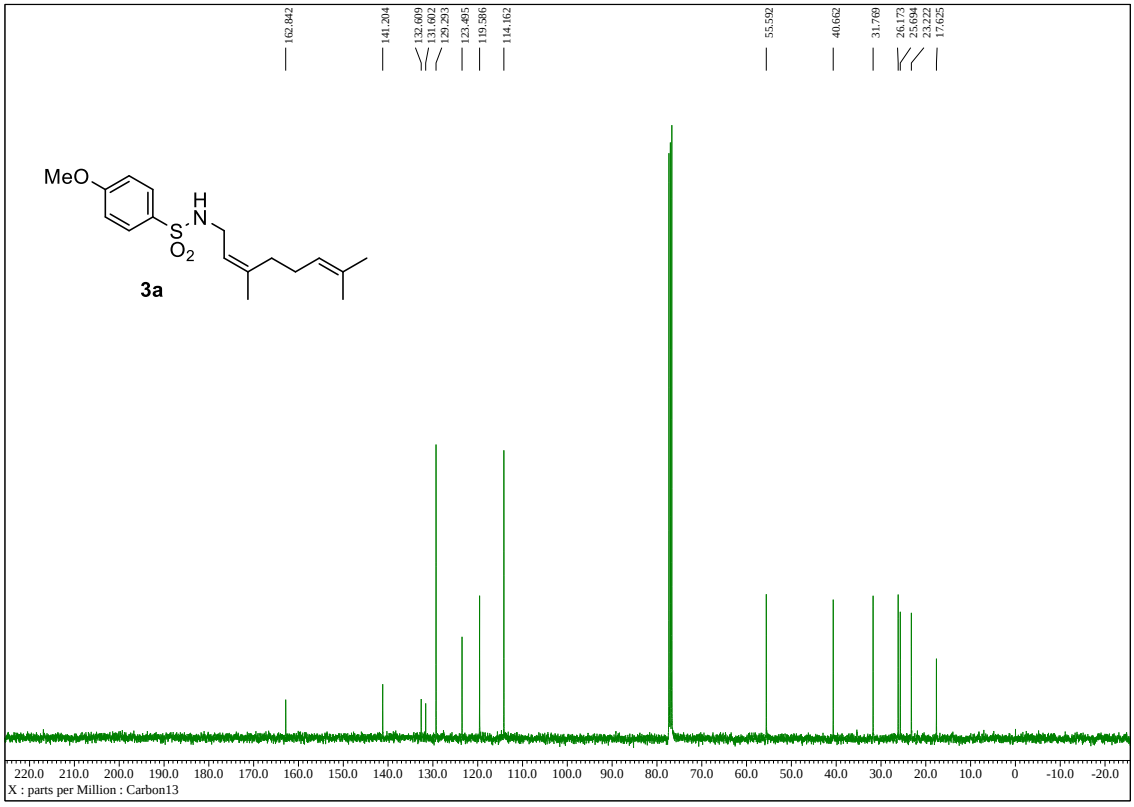


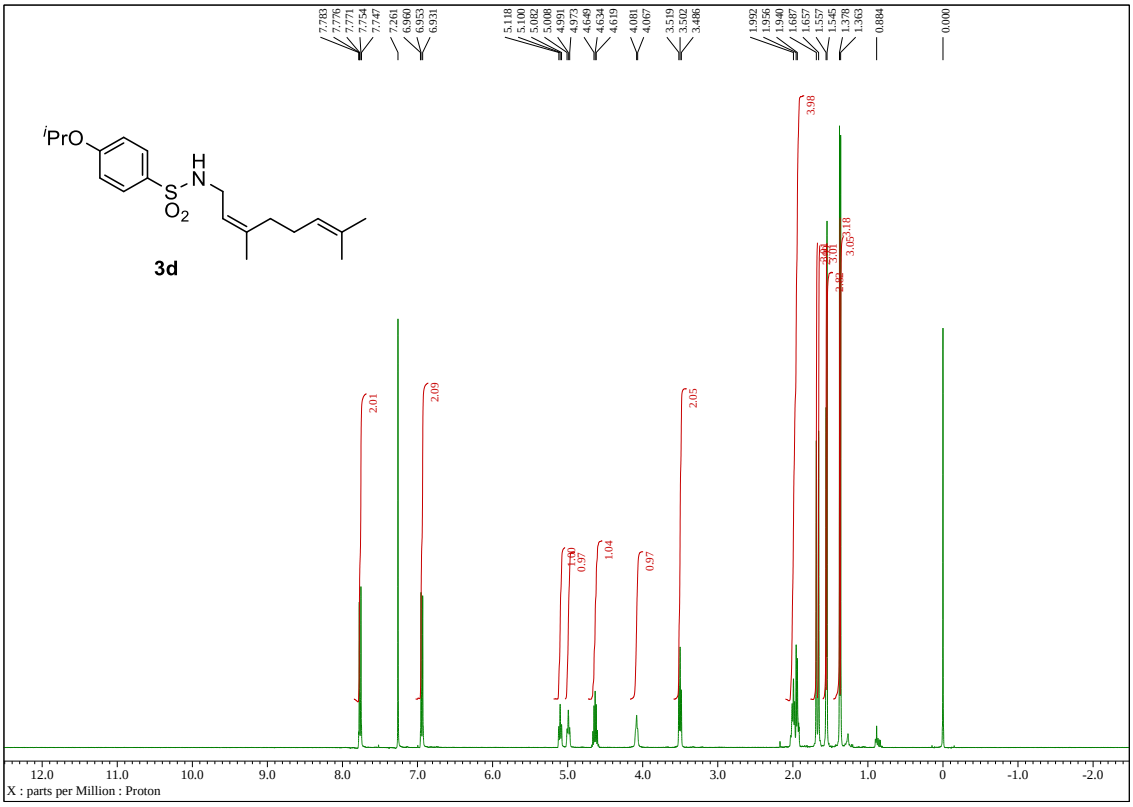
39 [4] ; Colorless oil; $[\alpha]^{27}_D$ = +17.5 (c 0.13, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.08-5.12 (m, 1H), 3.79-3.84 (m, 1H), 3.64-3.69 (m, 1H), 2.97 (dd, J = 6.7, 4.5 Hz, 1H), 2.05-2.17 (m, 2H), 1.93 (br s, 1H), 1.62-1.73 (m, 7H), 1.45-1.52 (m, 1H), 1.35 (s, 3H); Enantio excess was determined by derivatization to sulfonamide **4a**; 57% ee; $[\alpha]^{26}_D$ = +33.5 (c 0.04, $CHCl_3$).

3. References

1. N. Ji, J. Yuan, M. Liu, T. Lan and W. He, *Chem. Commun.*, 2016, **52**, 7731-7734.
2. S. Yamada, T. Mashiko and S. Terashima, *J. Am. Chem. Soc.*, 1977, **99**, 1988-1990.
3. Y. Kitabayashi, S. Yokoshima and T. Fukuyama, *Org. Lett.*, 2014, **16**, 2862−2864.
4. H. Egami, T. Oguma and T. Katsuki, *J. Am. Chem. Soc.*, 2010, **132**, 5886-5895.

4. ^{1}H-NMR and ^{13}C-NMR spectra

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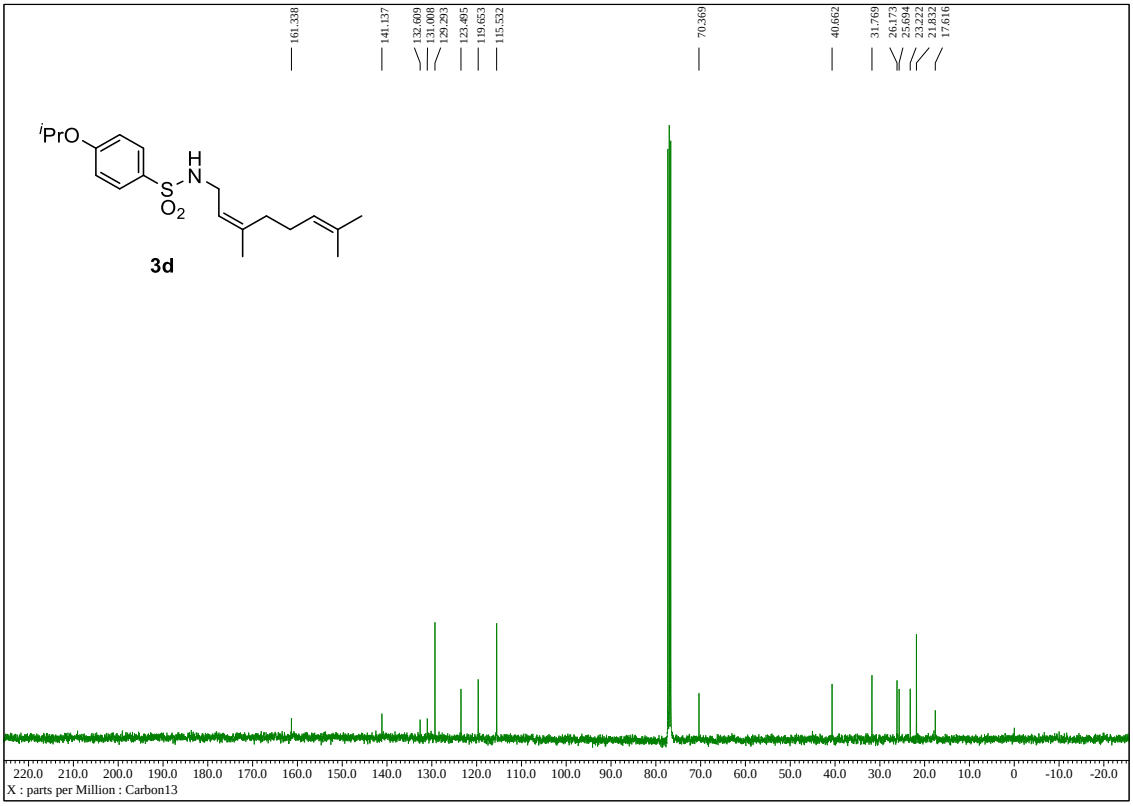
7.754
7.747
7.261
6.960
6.953
6.931
5.118
5.100
5.082
5.008
4.991
4.973
4.649
4.634
4.619
4.081
4.067
3.519
3.502
3.486
1.992
1.956
1.940
1.687
1.657
1.557
1.545
1.378
1.363
0.884
0.000
iPrO
H
N
S
O2
3d
3.98
3.65
2.01
2.09
2.05
1.04
0.97
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton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131.008
129.293
123.495
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115.532
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40.662
31.769
26.173
25.694
23.222
21.832
17.616
iPrO
H
N
S
O2
3d
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
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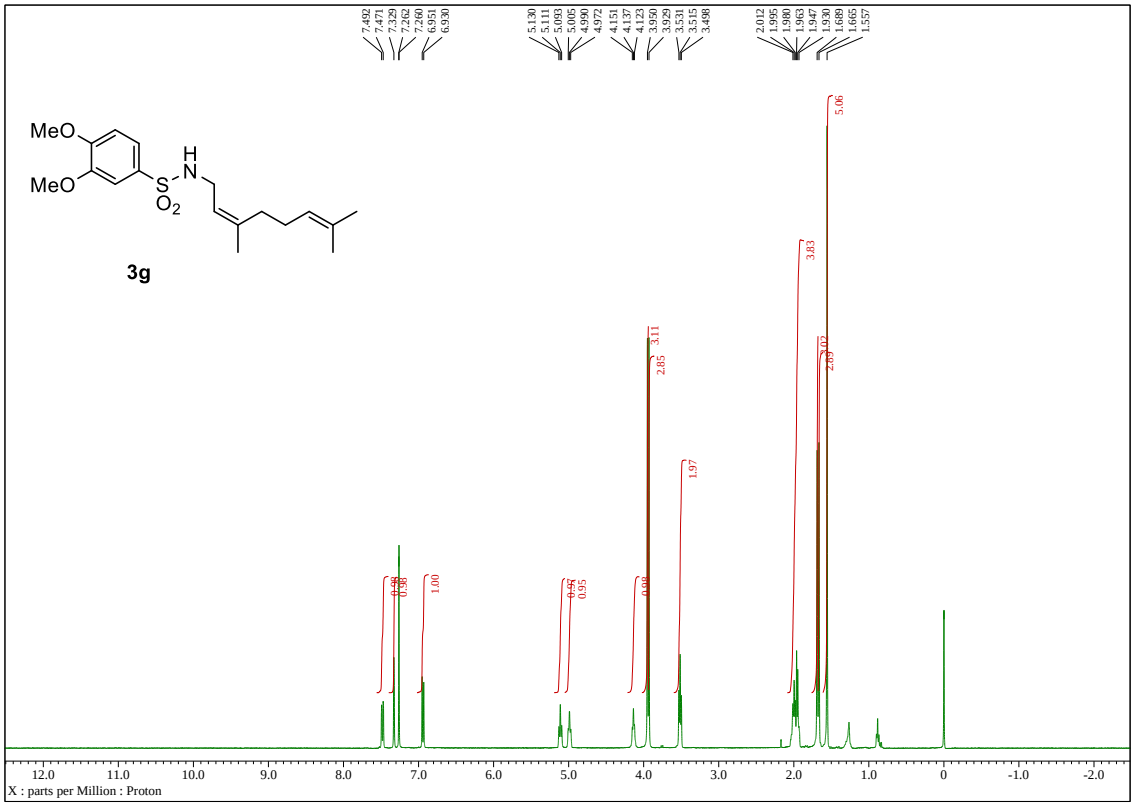
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6.930
5.130
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5.098
5.005
4.990
4.972
4.151
4.137
4.123
3.950
3.929
3.531
3.515
3.498
2.012
1.995
1.980
1.963
1.947
1.930
1.689
1.665
1.557
MeO
MeO
H
N
S
O2
3g
5.06
3.83
3.11
2.85
2.69
2.03
1.97
1.00
0.98
0.98
0.95
0.88
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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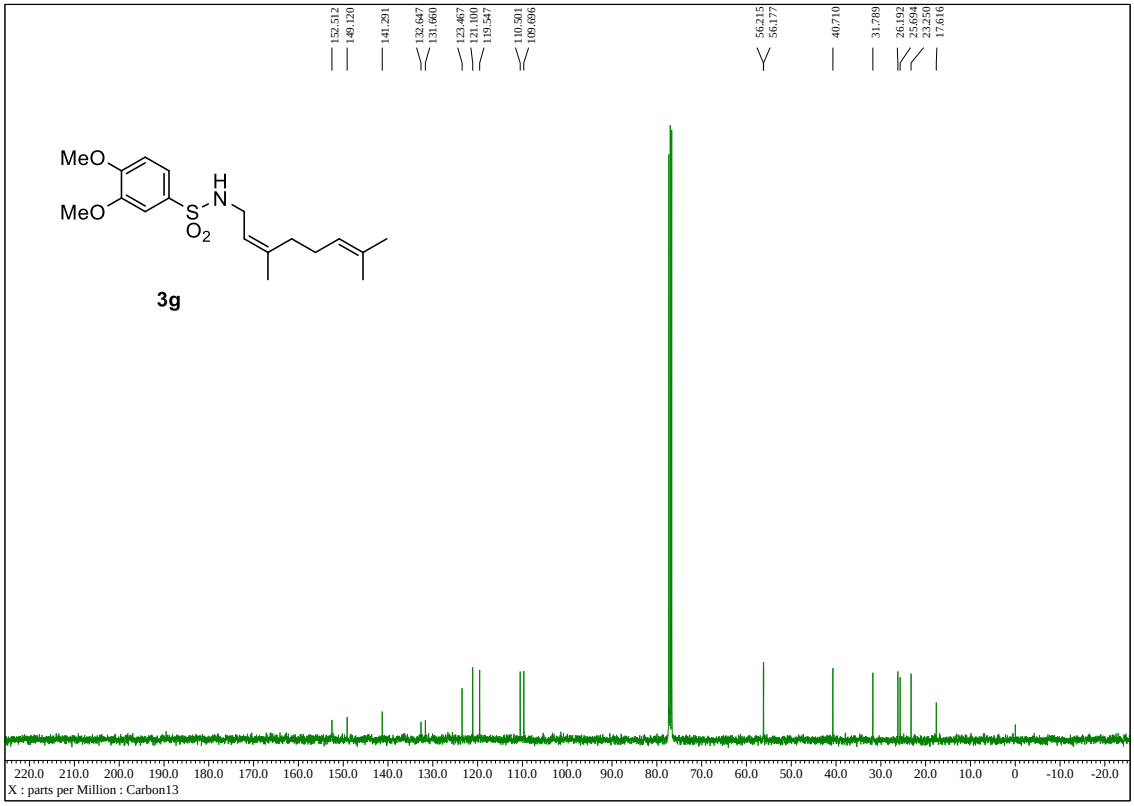
0
-1.0
-2.0
X : parts per Million : Proton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31.789
26.192
25.694
23.250
17.616
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MeO
H
N
S
O2
3g
220.0
210.0
200.0
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180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
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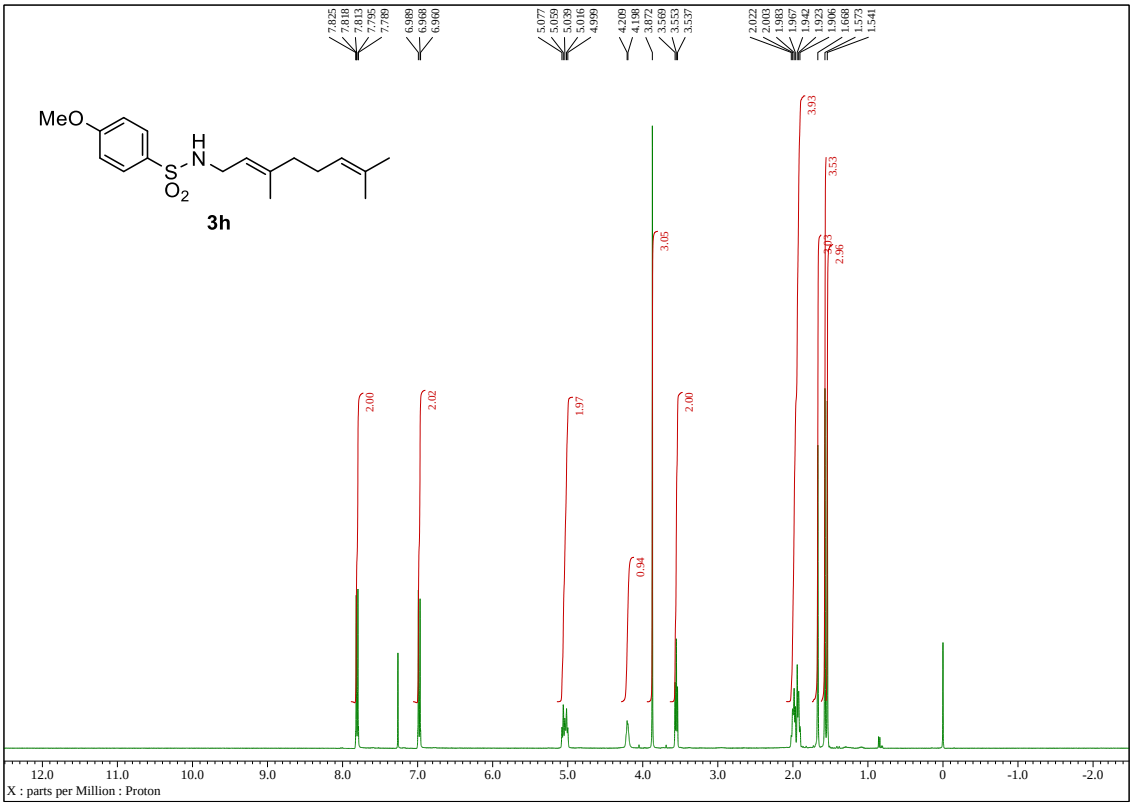
X : parts per Million : Carbon13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5.016
4.999
4.209
4.198
3.872
3.569
3.553
3.537
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2.003
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1.967
1.942
1.923
1.906
1.668
1.573
1.541
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H
N
S
O2
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3.53
3.05
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2.36
2.00
2.02
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2.00
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11.0
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9.0
8.0
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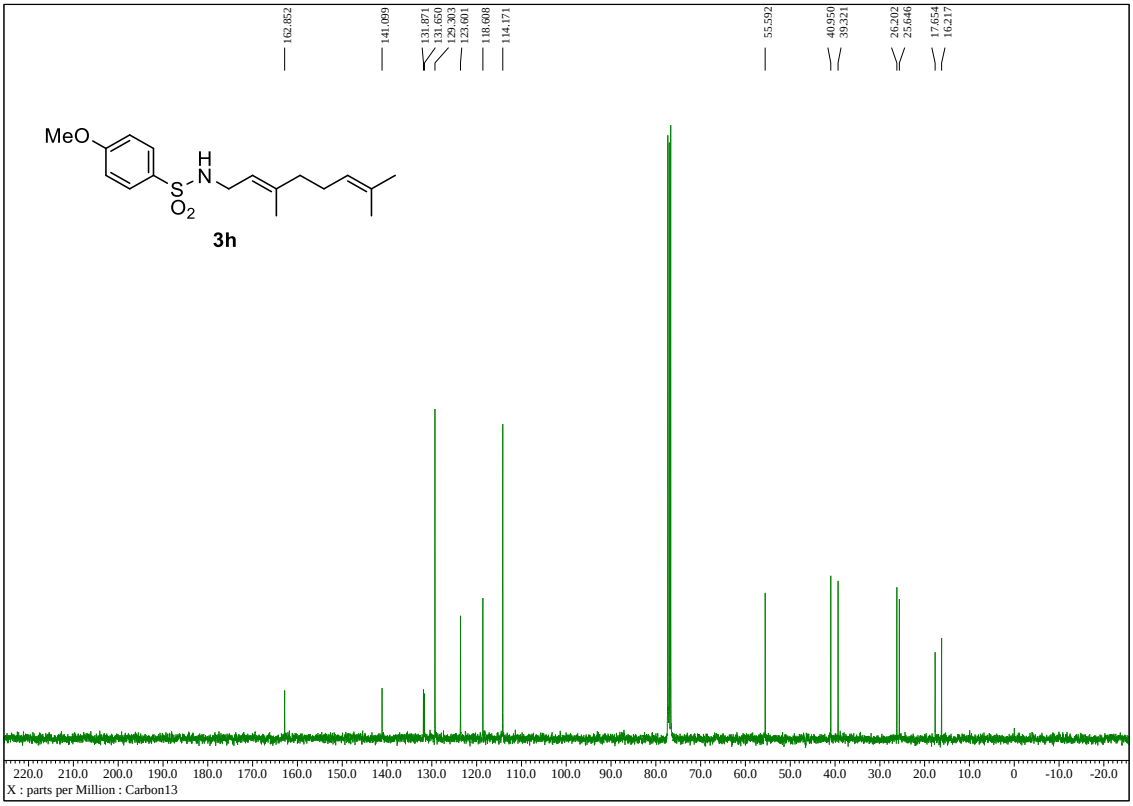
0
-1.0
-2.0
X : parts per Million : Proton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39.321
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25.646
17.654
16.217
MeO
H
N
S
O2
3h
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
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130.0
120.0
110.0
100.0
90.0
80.0
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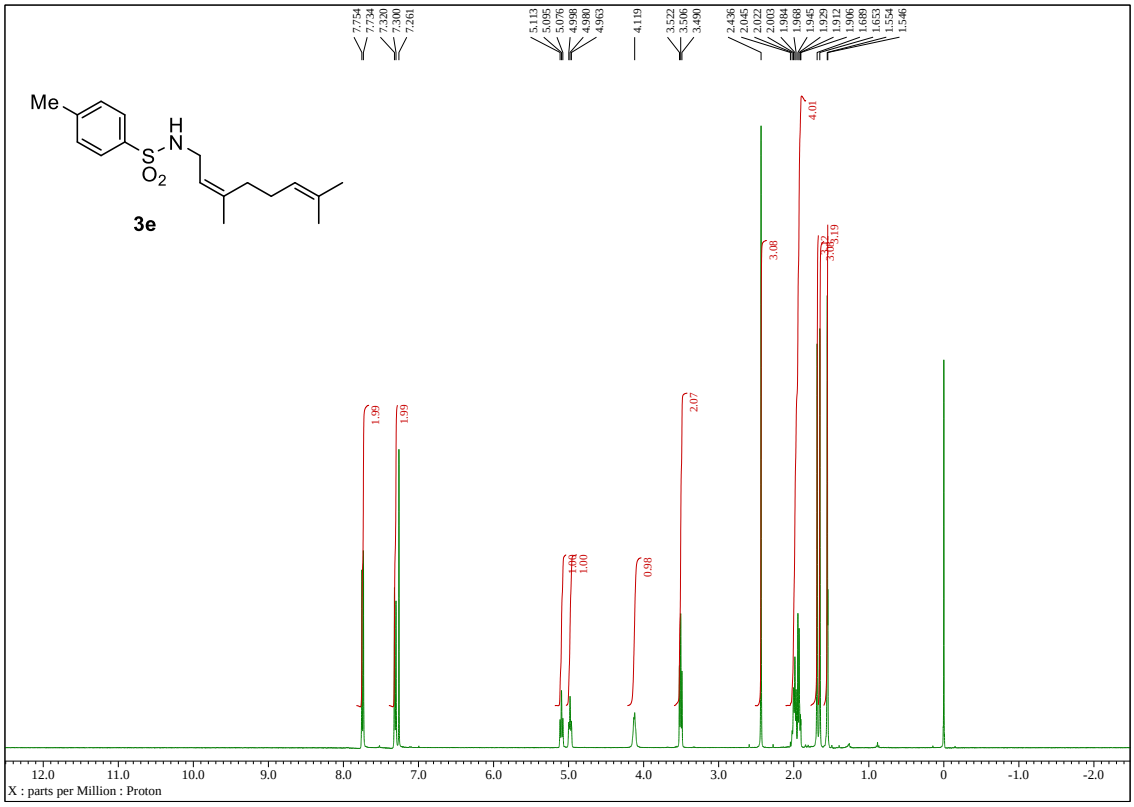
X : parts per Million : Carbon13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1.929
1.912
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N
S
O2
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3.08
3.07
3.06
3.19
1.99
1.99
2.07
1.00
1.00
0.98
12.0
11.0
10.0
9.0
8.0
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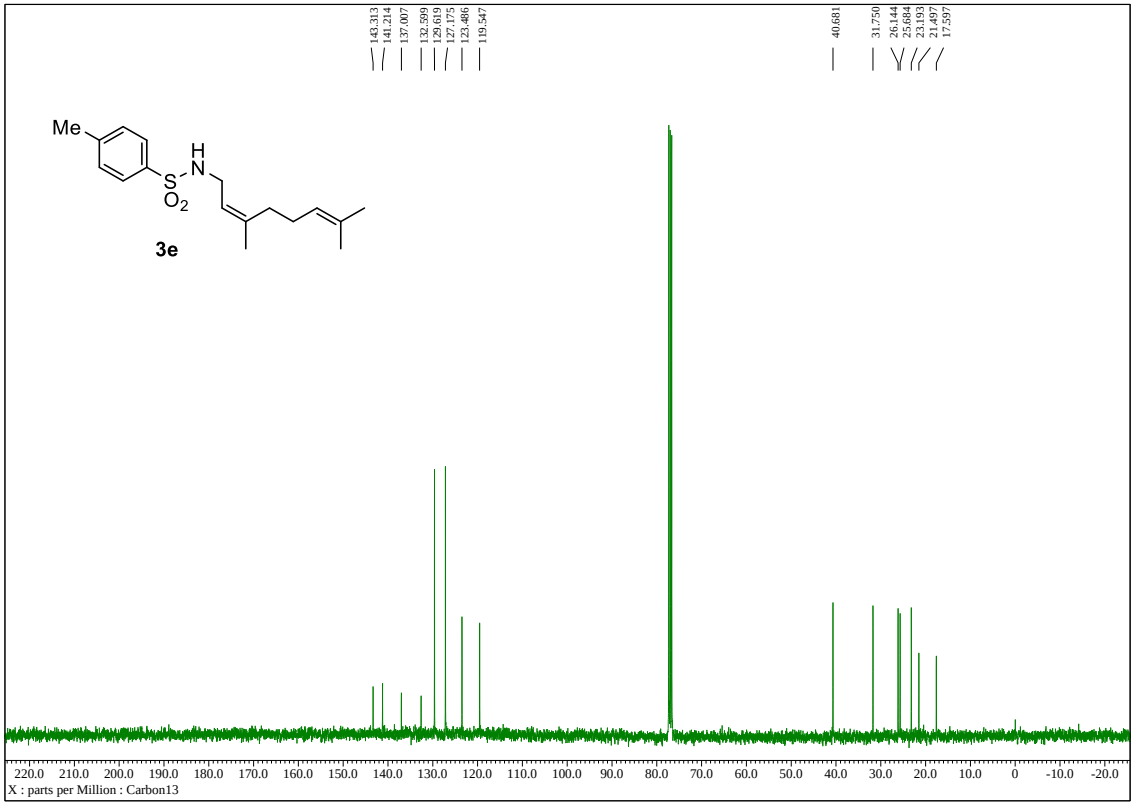
0
-1.0
-2.0
X : parts per Million : Proton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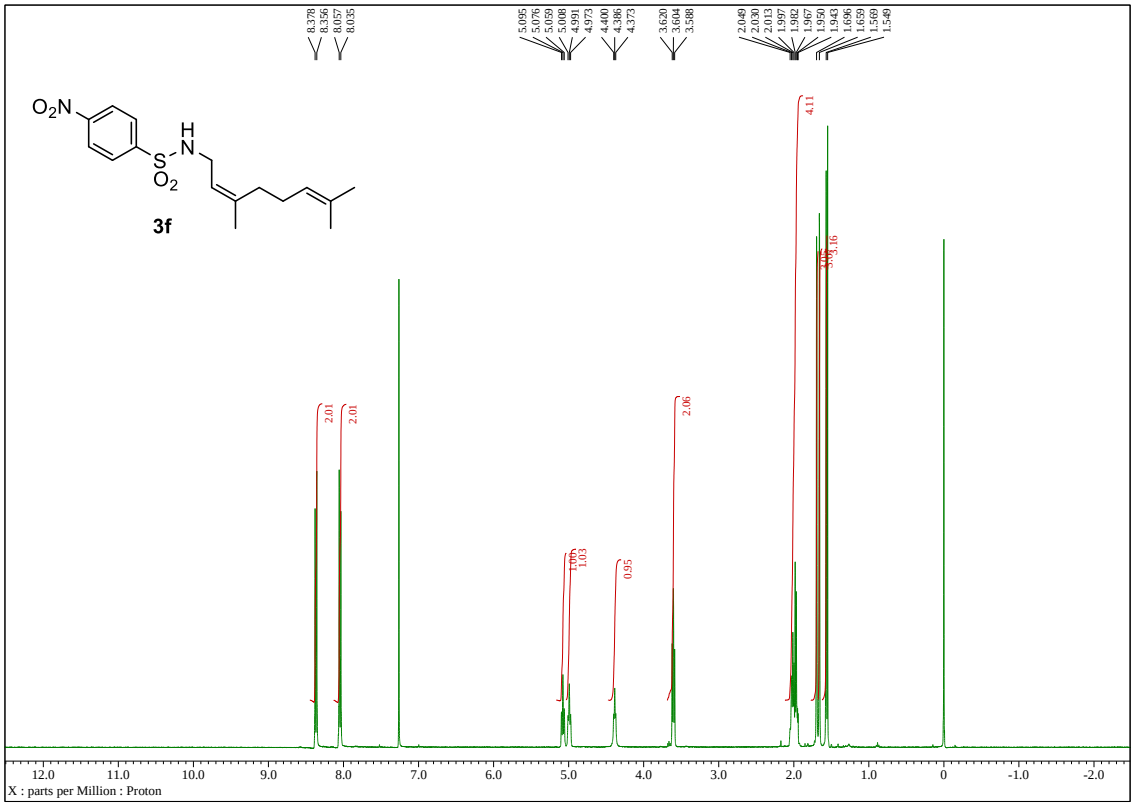
X : parts per Million : Carbon13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1.659
1.569
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3.00
3.16
2.01
2.01
2.06
1.00
1.03
0.95
O2N
H
N
S
O2
3f
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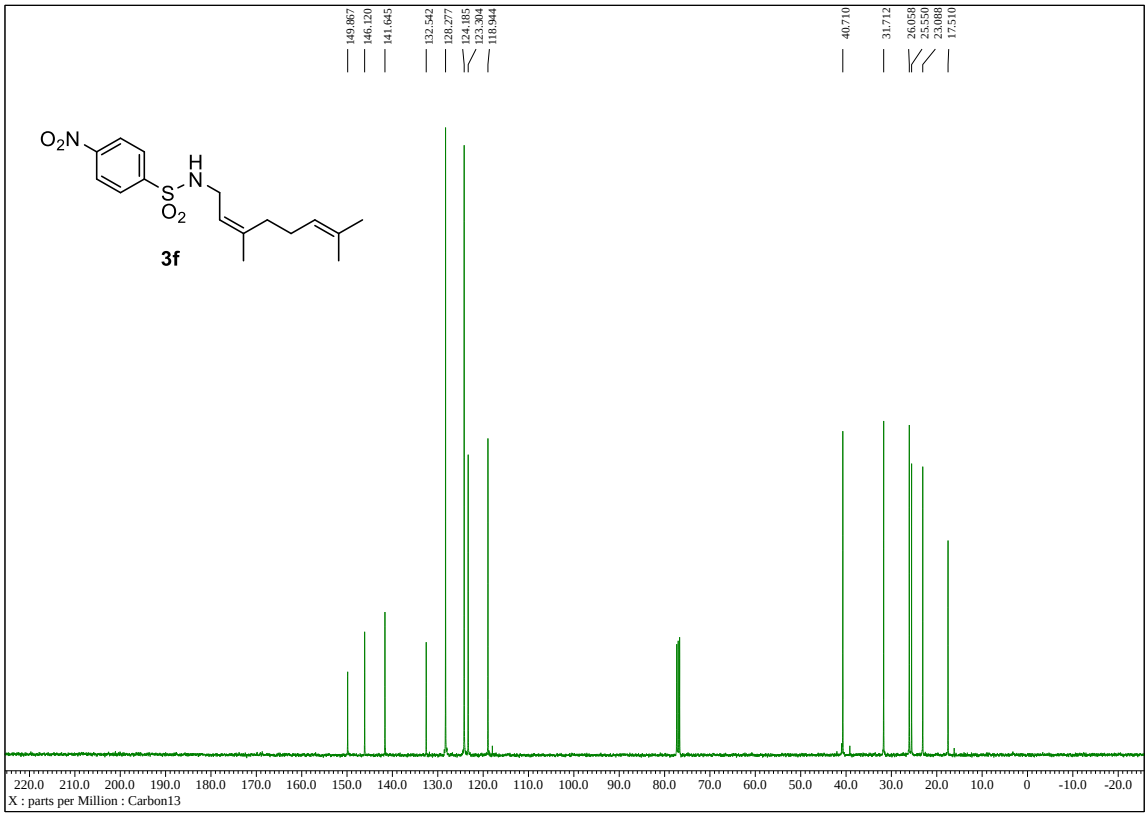
X : parts per Million : Proton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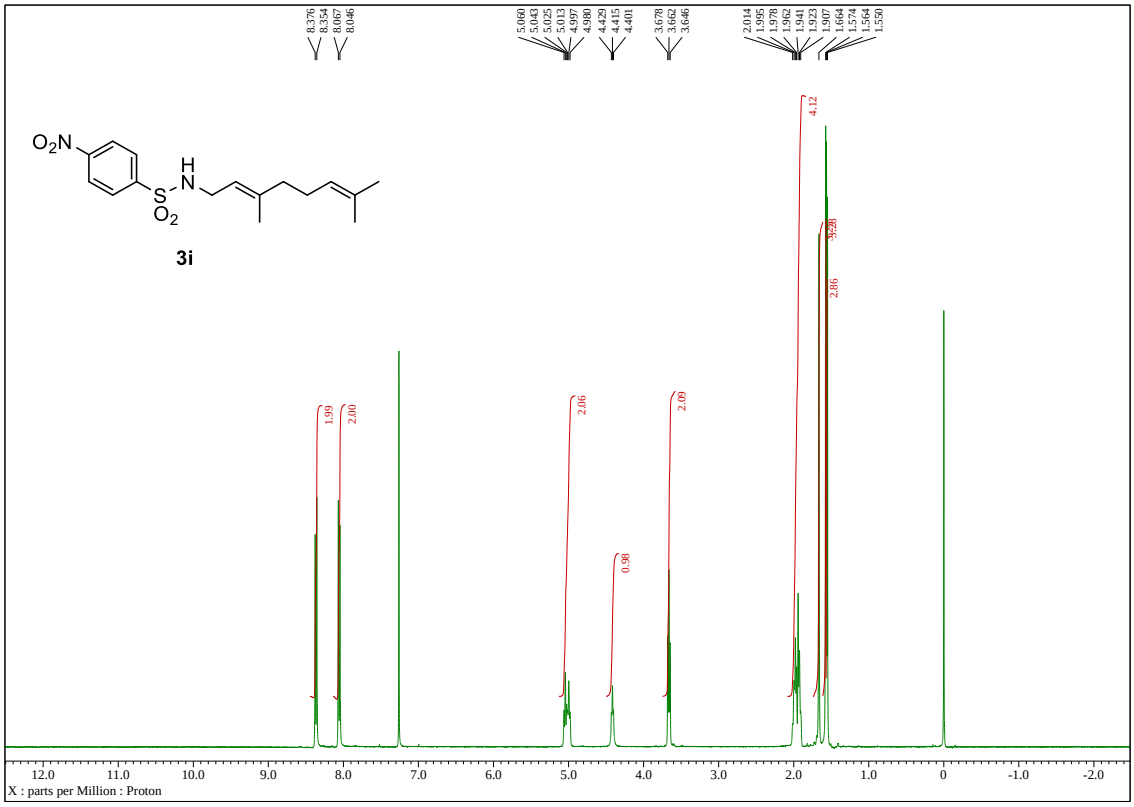
H
N
S
O2
3f
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13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5.013
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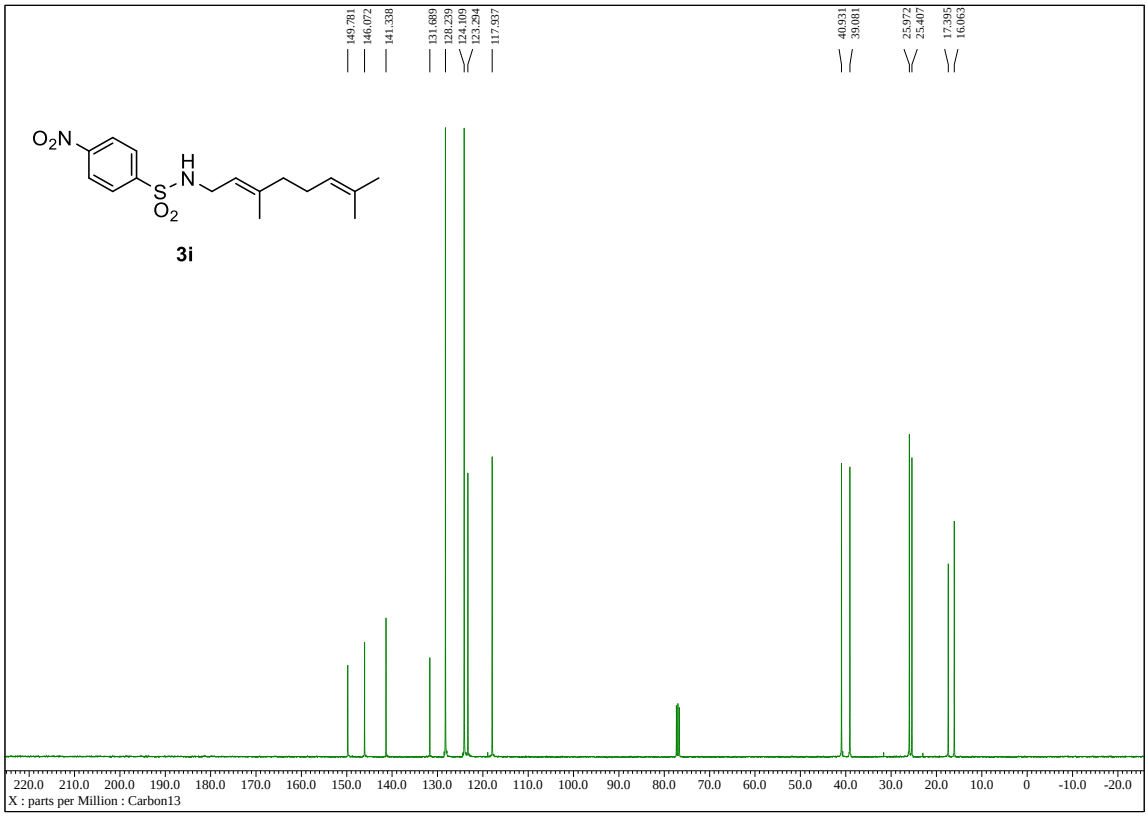
4.415
4.401
3.678
3.662
3.646
2.014
1.995
1.978
1.962
1.941
1.923
1.907
1.664
1.574
1.564
1.550
4.12
3.28
2.86
1.99
2.00
2.06
0.98
2.09
O2N
H
N
S
O2
3i
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton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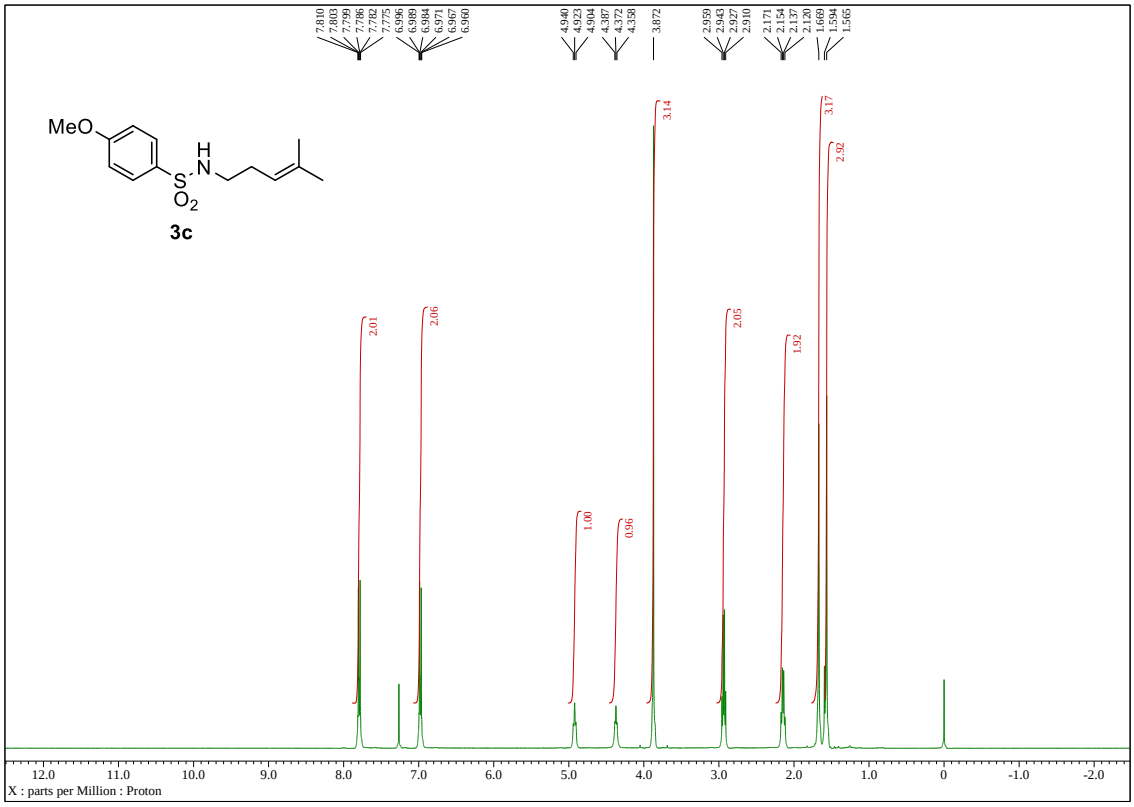
146.072
141.338
131.689
128.259
124.109
123.294
117.937
40.931
39.081
25.972
25.407
17.395
16.063
O2N
H
N
S
O2
3i
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13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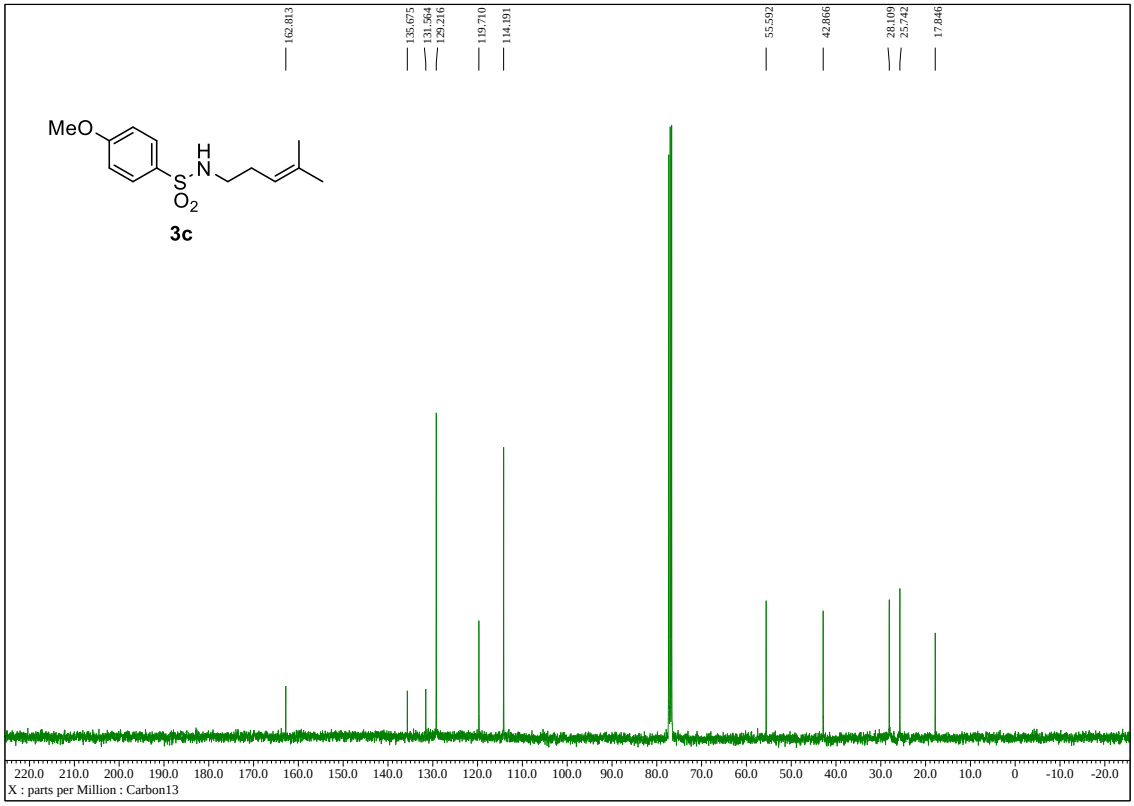
7.803
7.799
7.786
7.782
7.775
6.996
6.989
6.984
6.971
6.967
6.960
4.940
4.923
4.904
4.387
4.372
4.338
3.872
2.959
2.943
2.927
2.910
2.171
2.154
2.137
2.120
1.669
1.594
1.565
MeO
H
N
S
O2
3c
2.01
2.06
1.00
0.96
3.14
2.05
1.92
3.17
2.92
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton


162.813
135.675
131.564
129.216
119.710
114.191
55.592
42.866
28.109
25.742
17.846
MeO
H
N
S
O2
3c
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
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40.0
30.0
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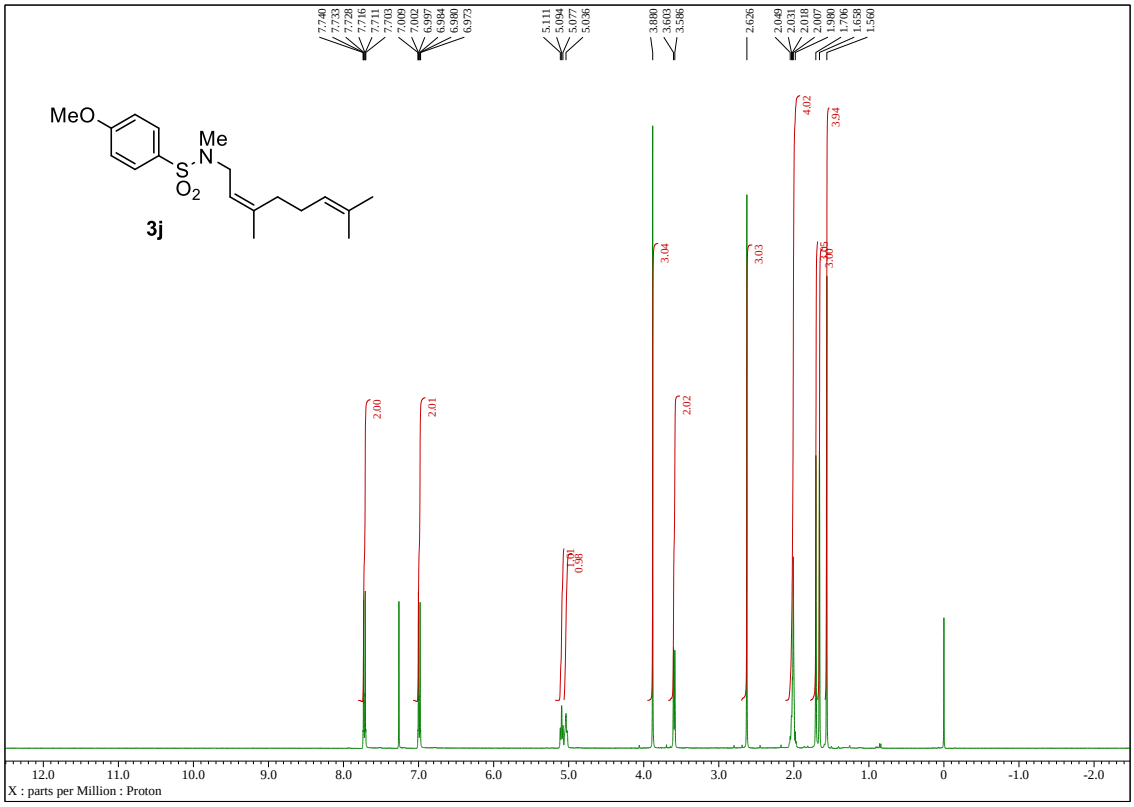
0
-10.0
-20.0
X : parts per Million : Carbon13


7.740
7.733
7.726
7.716
7.711
7.703
7.009
7.002
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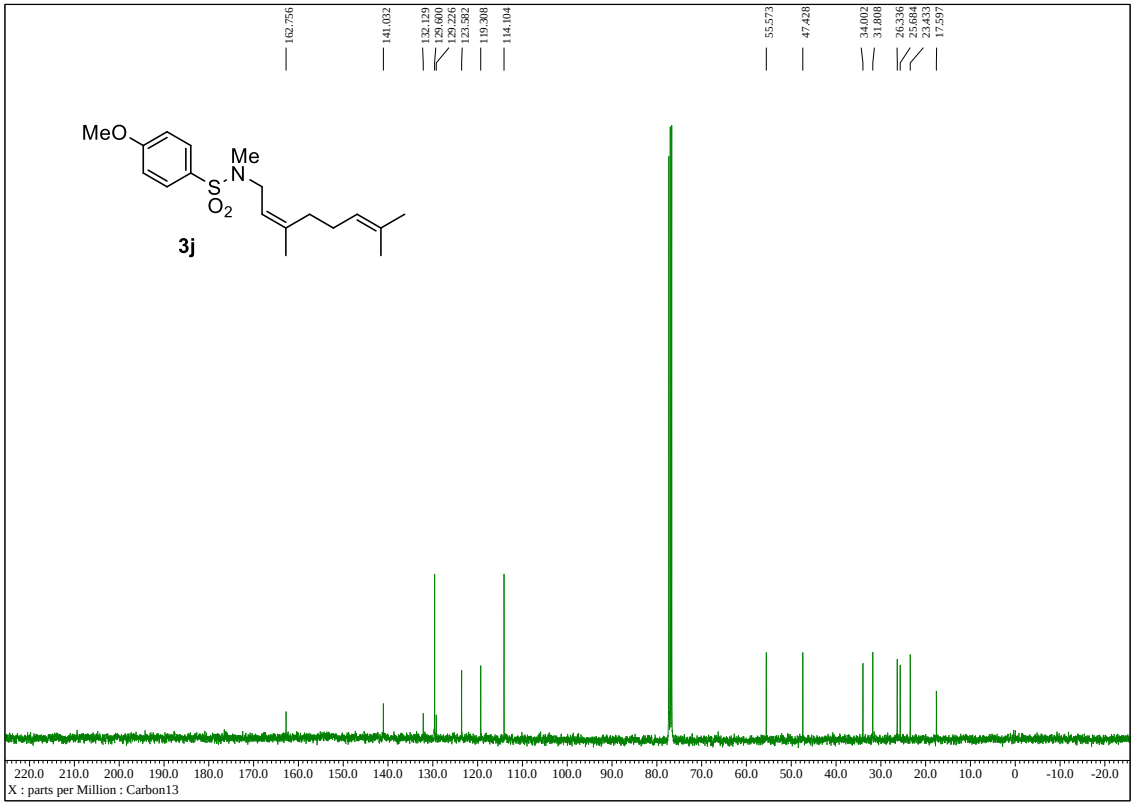
6.984
6.980
6.973
5.111
5.094
5.077
5.036
3.880
3.603
3.586
2.626
2.049
2.031
2.018
2.007
1.980
1.706
1.658
1.560
MeO
Me
N
S
O2
3j
4.02
3.94
3.04
3.03
3.00
2.00
2.01
2.02
1.70
0.98
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton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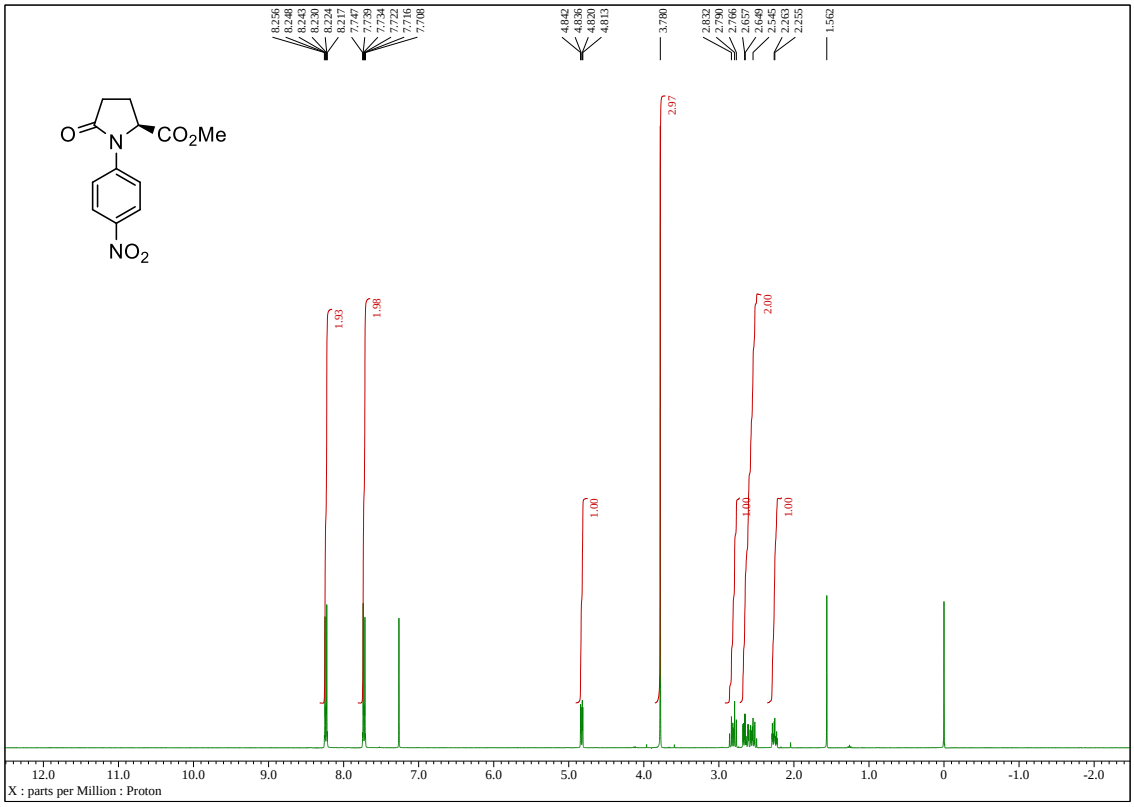
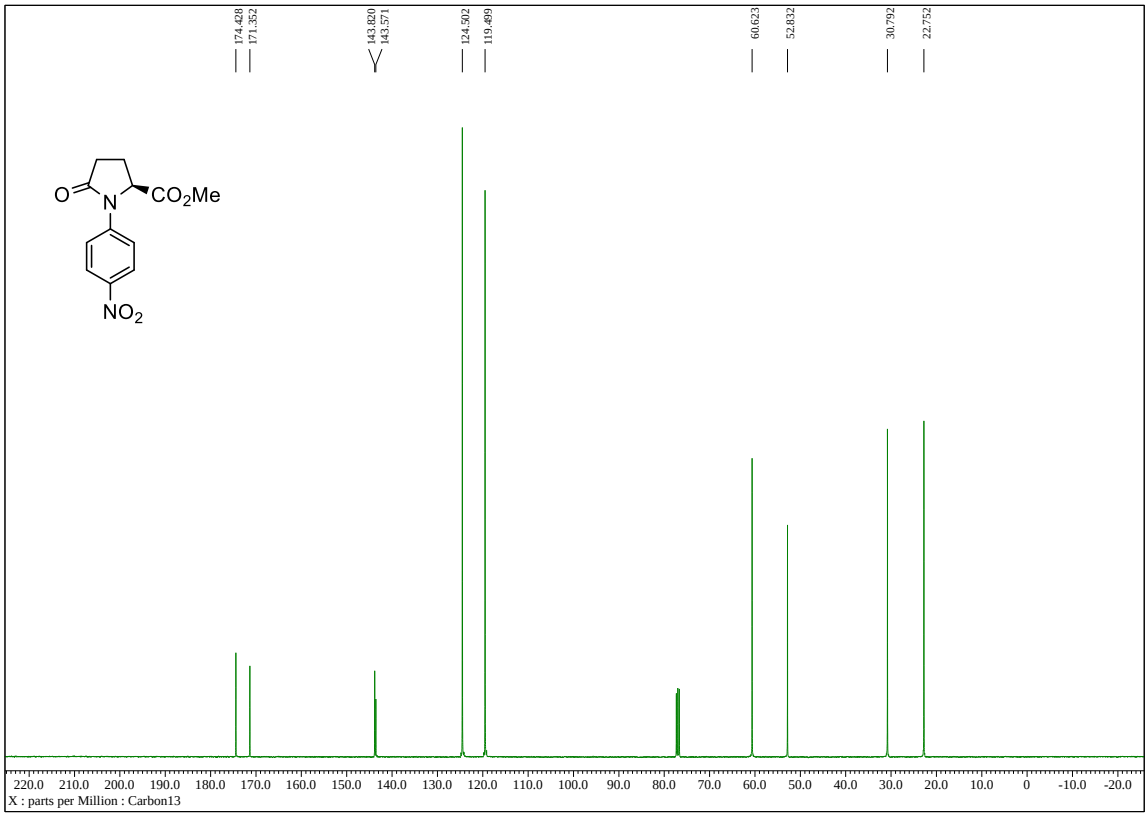
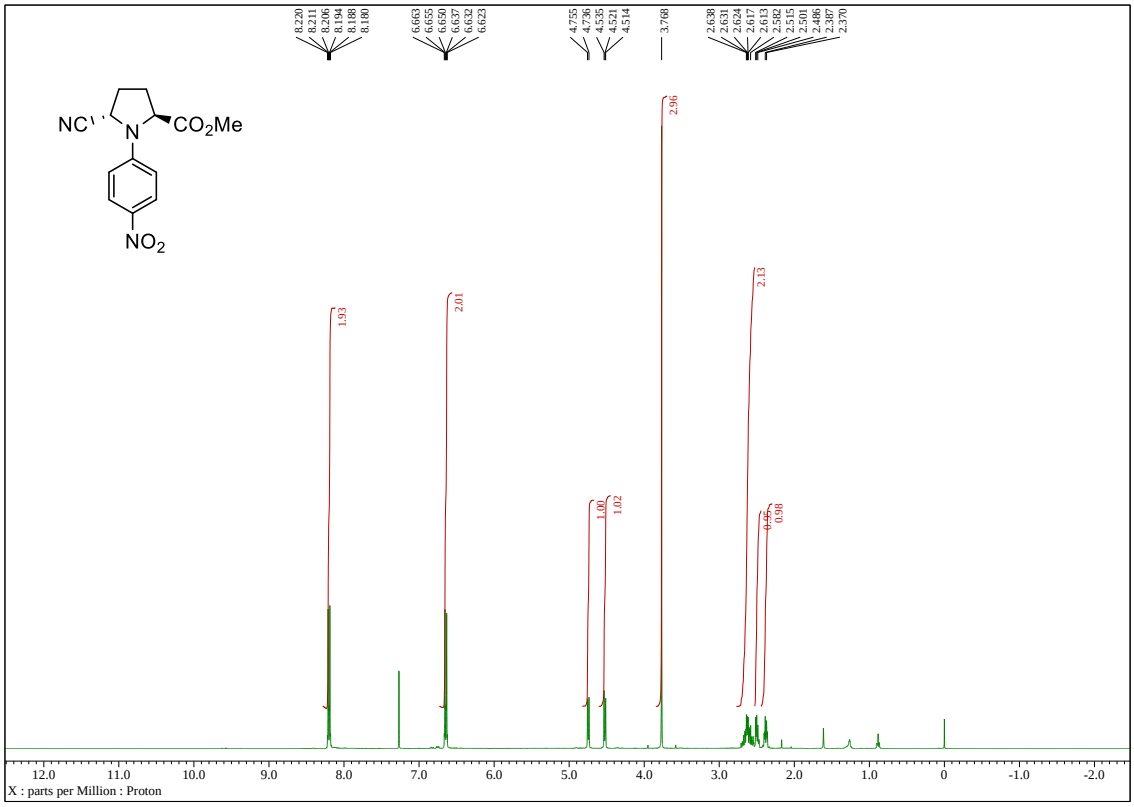
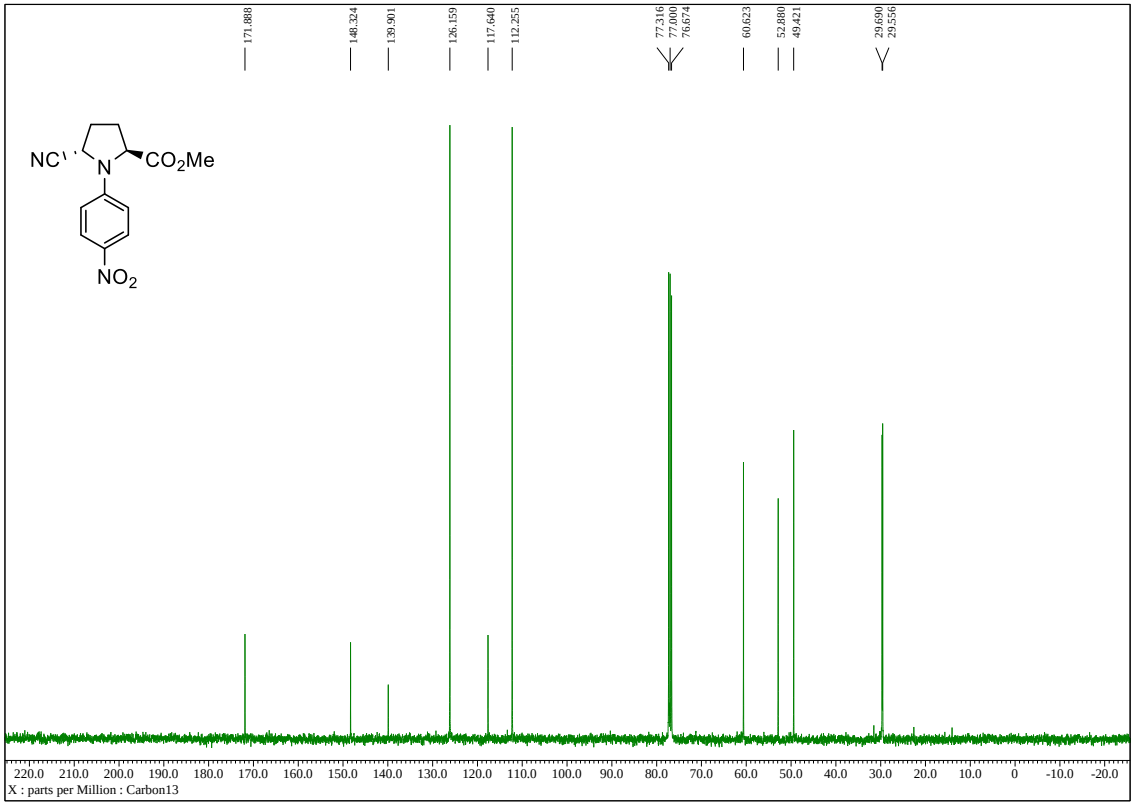
141.032
132.129
129.600
129.226
123.582
119.308
114.104
55.573
47.428
34.002
31.808
26.336
25.684
23.433
17.597
MeO
Me
N
S
O2
3j
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13


8.256
8.248
8.243
8.230
8.224
8.217
7.747
7.739
7.734
7.722
7.716
7.708
4.842
4.836
4.820
4.813
3.780
2.832
2.790
2.766
2.657
2.649
2.545
2.263
2.255
1.562
2.97
1.93
1.90
2.00
1.00
1.00
1.00
O
N
CO2Me
NO2
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton


174.428
171.352
143.820
143.571
124.502
119.499
60.623
52.832
30.792
22.752
O
N
CO2Me
NO2
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13


8.220
8.211
8.206
8.194
8.188
8.180
6.663
6.655
6.650
6.637
6.632
6.623
4.755
4.736
4.535
4.521
4.514
3.768
2.638
2.631
2.624
2.617
2.613
2.582
2.515
2.501
2.486
2.387
2.370
NC
N
CO2Me
NO2
2.96
2.13
2.01
1.93
1.00
1.02
0.95
0.98
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton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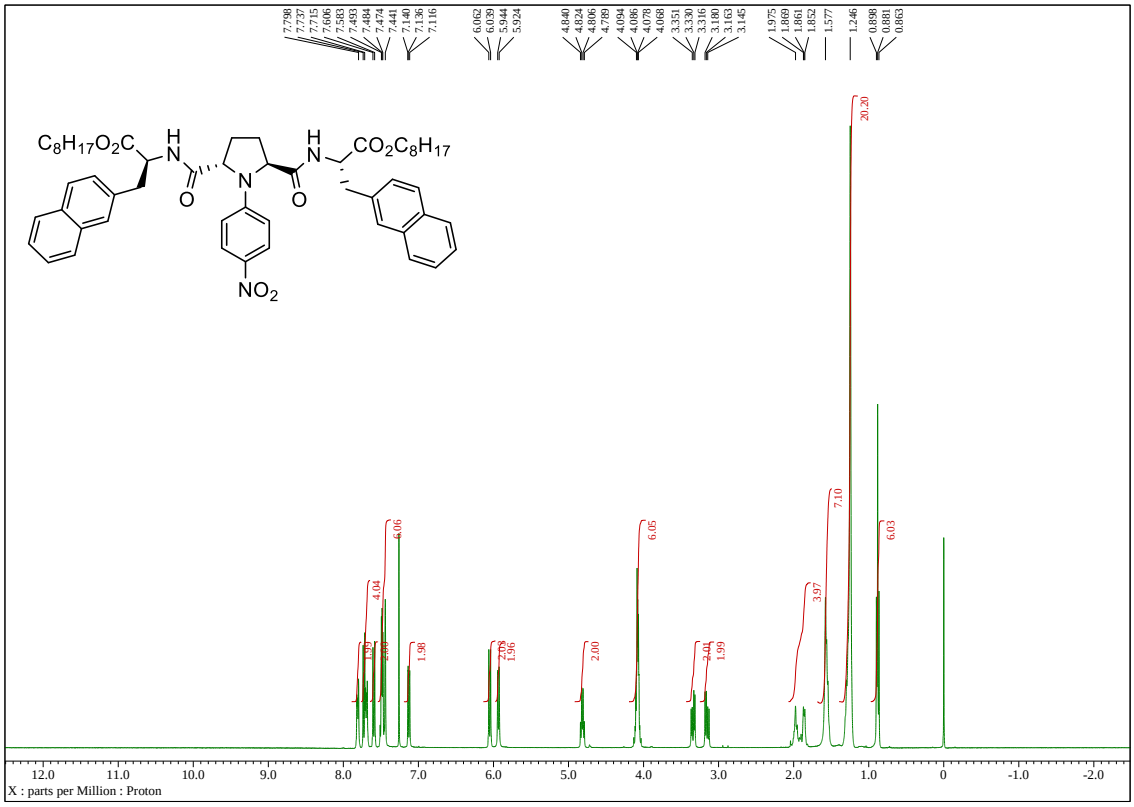
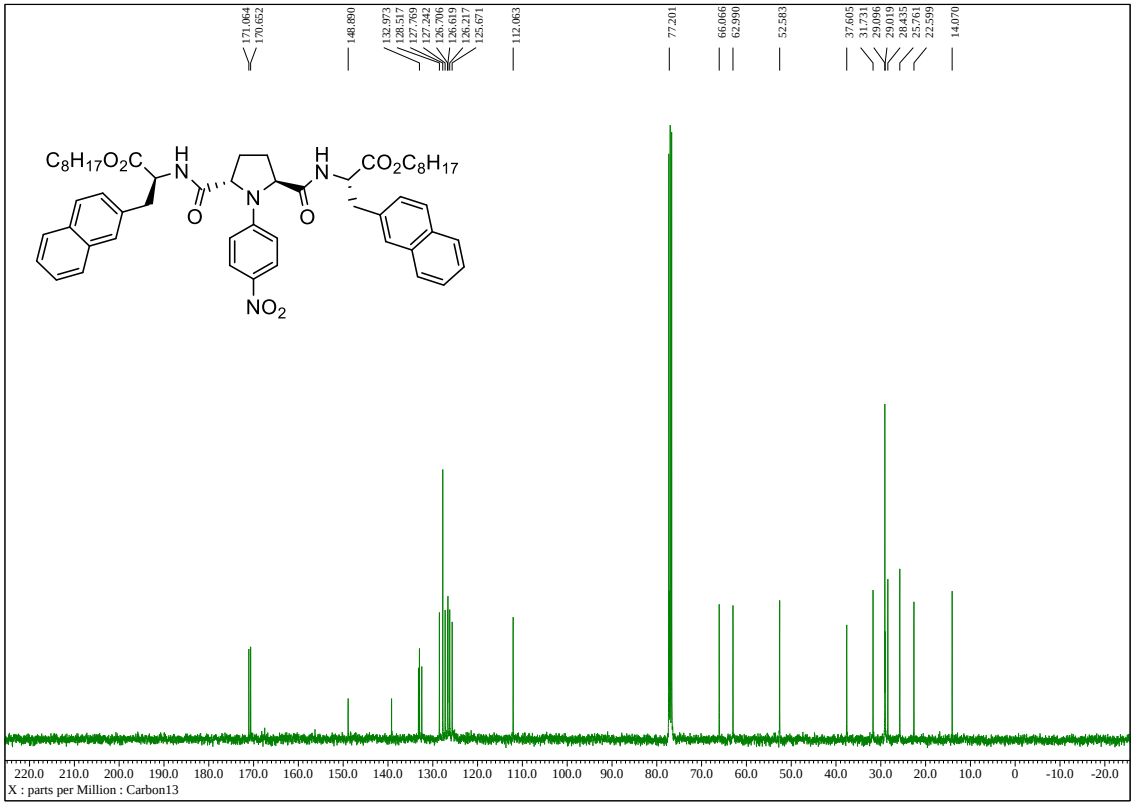
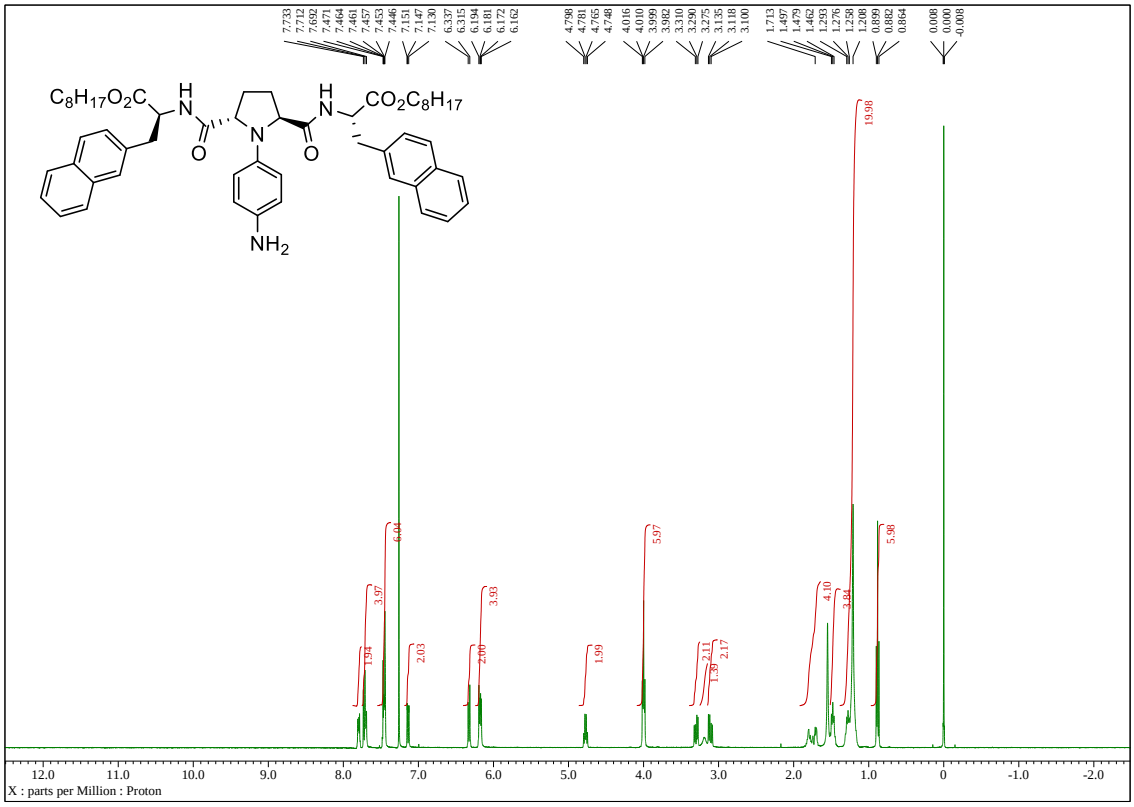
126.159
117.640
112.255
77.316
77.000
76.674
60.623
52.880
49.421
29.690
29.556
NC
N
CO2Me
NO2
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13


X : parts per Million : Proton


X : parts per Million : Carbon13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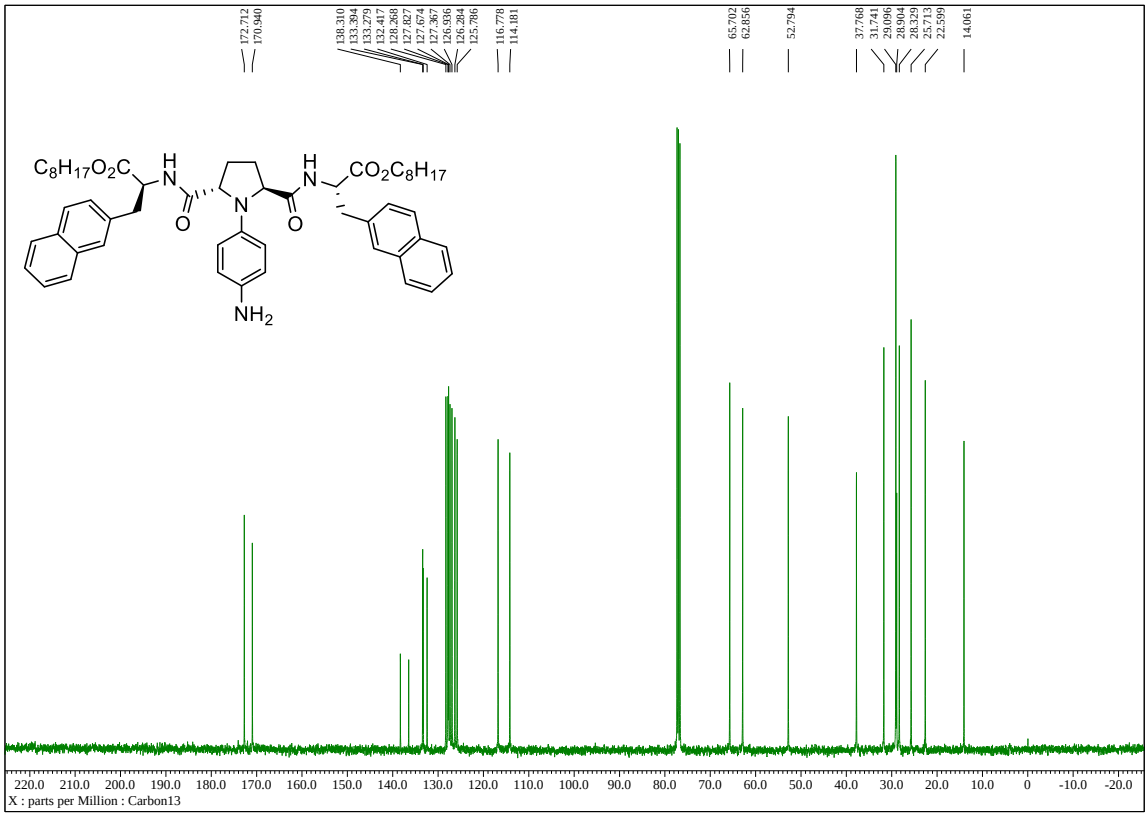
7.471
7.464
7.461
7.457
7.453
7.446
7.151
7.147
7.130
6.337
6.335
6.194
6.181
6.172
6.162
4.798
4.781
4.765
4.748
4.016
4.010
3.999
3.982
3.310
3.290
3.275
3.135
3.118
3.100
1.713
1.497
1.479
1.462
1.293
1.276
1.258
1.208
0.899
0.882
0.864
0.008
0.000
-0.008
C8H17O2C
H
N
O
N
O
H
N
CO2C8H17
NH2
19.98
6.04
5.97
5.98
3.97
3.93
4.10
3.84
1.94
2.03
2.00
1.99
2.11
2.17
1.39
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton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132.417
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127.827
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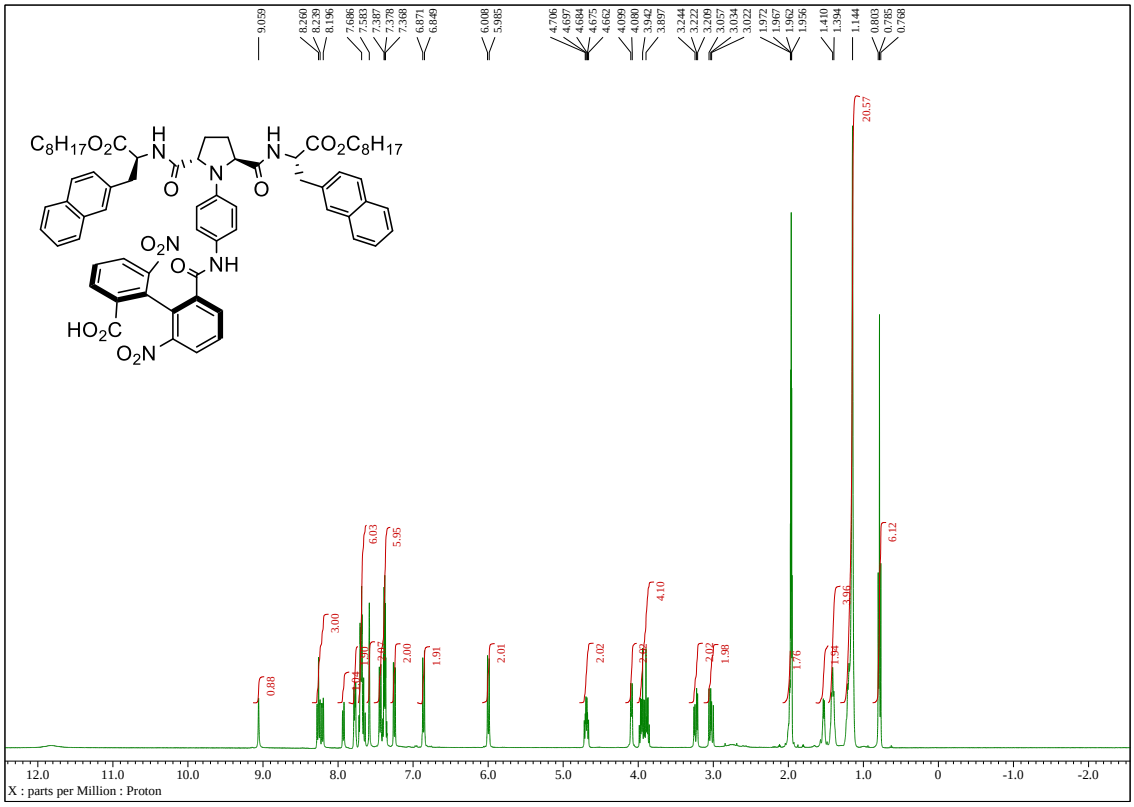
127.367
126.956
126.804
125.786
116.778
114.181
65.702
62.856
52.794
37.768
31.741
29.096
28.904
28.329
25.713
22.599
14.061
C8H17O2C
H
N
O
N
O
H
N
CO2C8H17
NH2
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13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8.239
8.196
7.686
7.583
7.387
7.378
7.368
6.871
6.849
6.008
5.985
4.706
4.697
4.684
4.675
4.662
4.099
4.080
3.942
3.897
3.244
3.222
3.209
3.057
3.034
3.022
1.972
1.967
1.962
1.956
1.410
1.394
1.144
0.803
0.785
0.768
20.57
6.12
6.03
5.95
4.10
3.96
3.00
2.02
2.01
2.00
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1.98
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0.88
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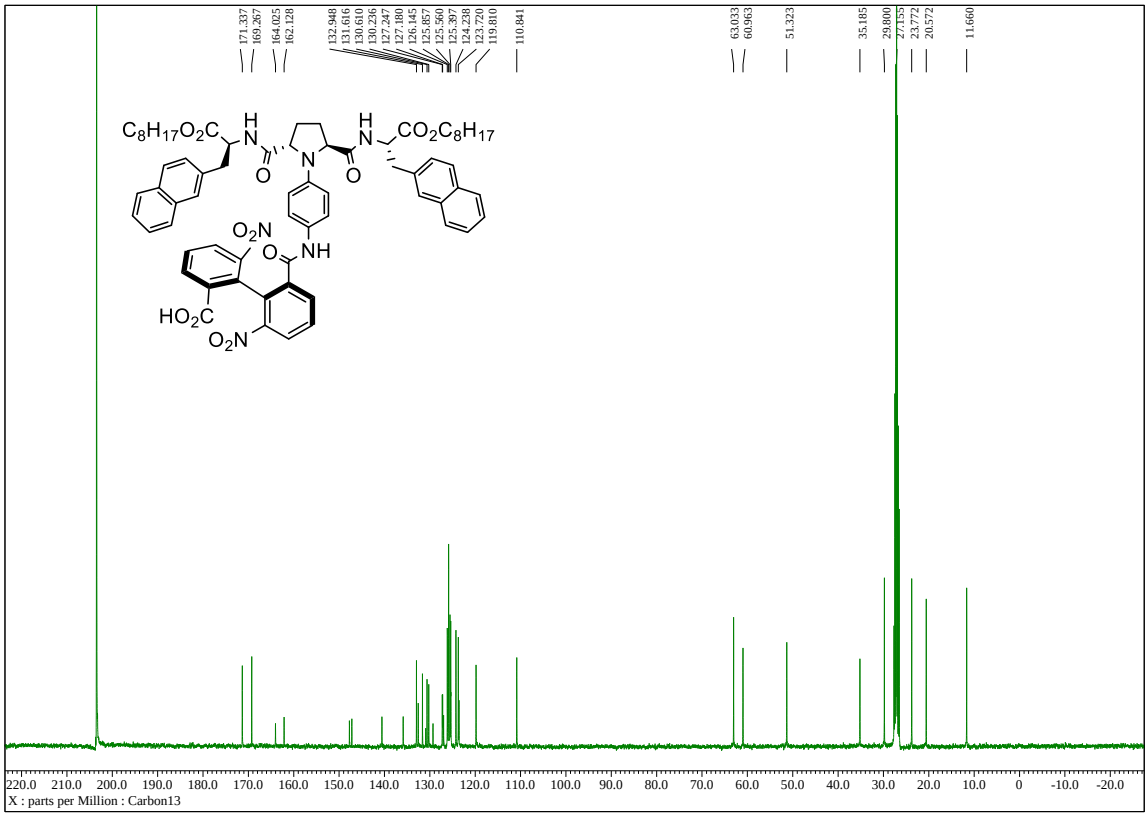
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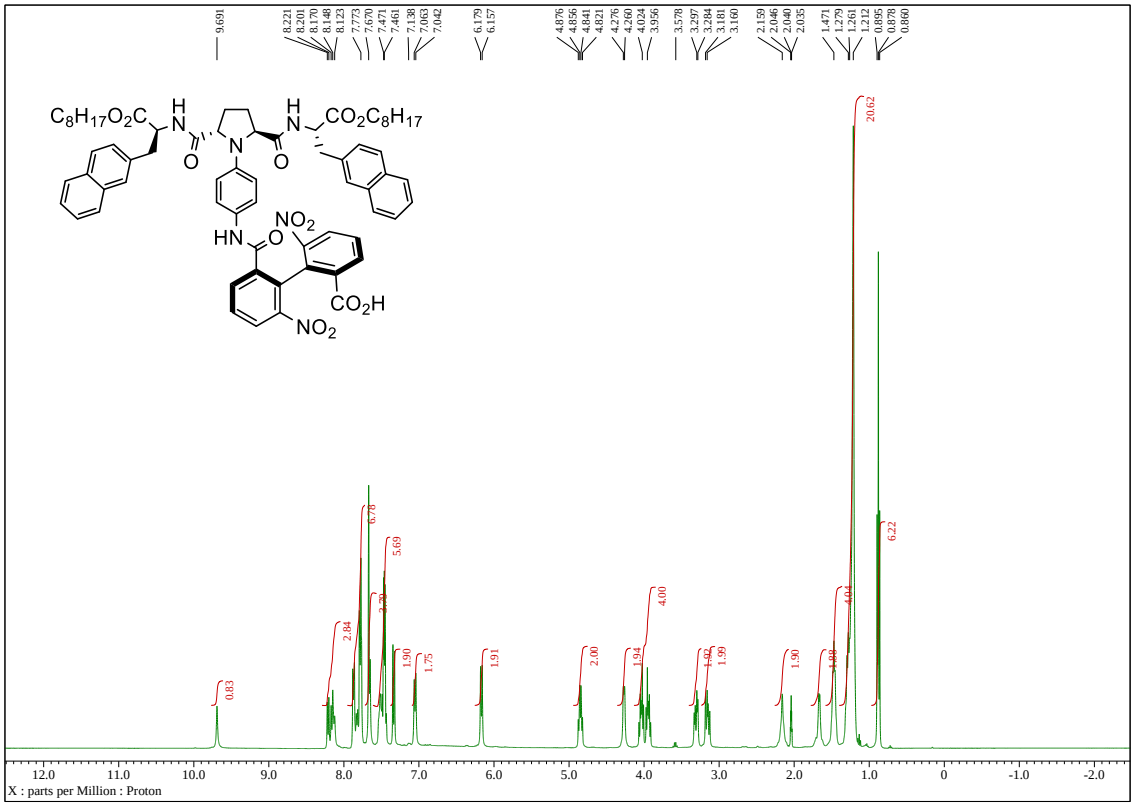
164.025
162.128
132.948
131.616
130.610
130.236
127.247
127.180
126.145
125.857
125.560
125.397
124.238
123.720
119.810
110.841
63.033
60.963
51.323
35.185
29.800
27.155
23.772
20.572
11.660
X : parts per Million : Carbon13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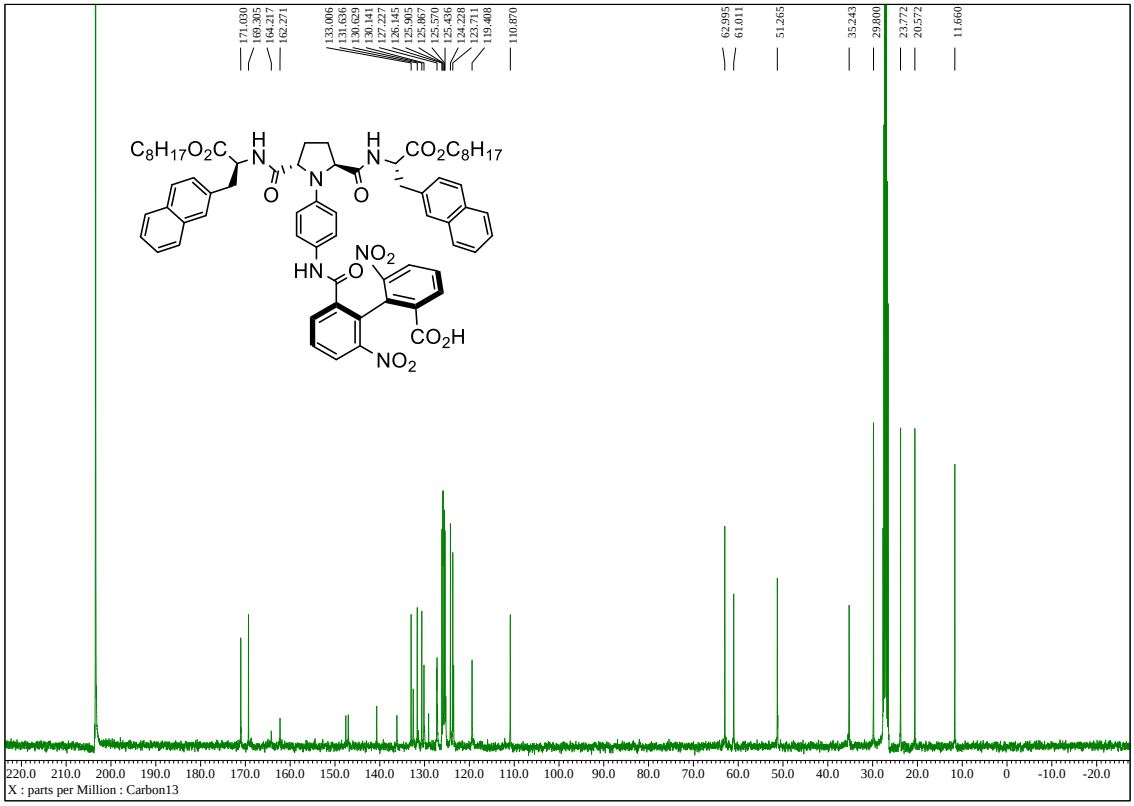
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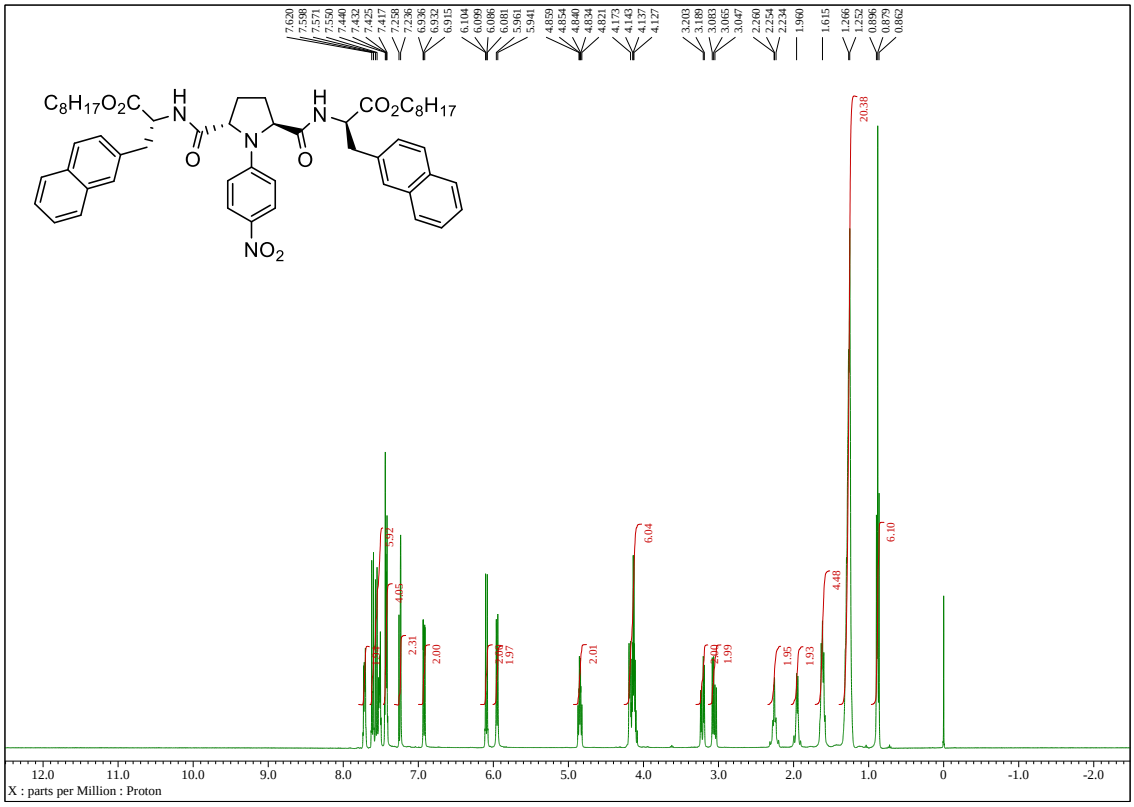
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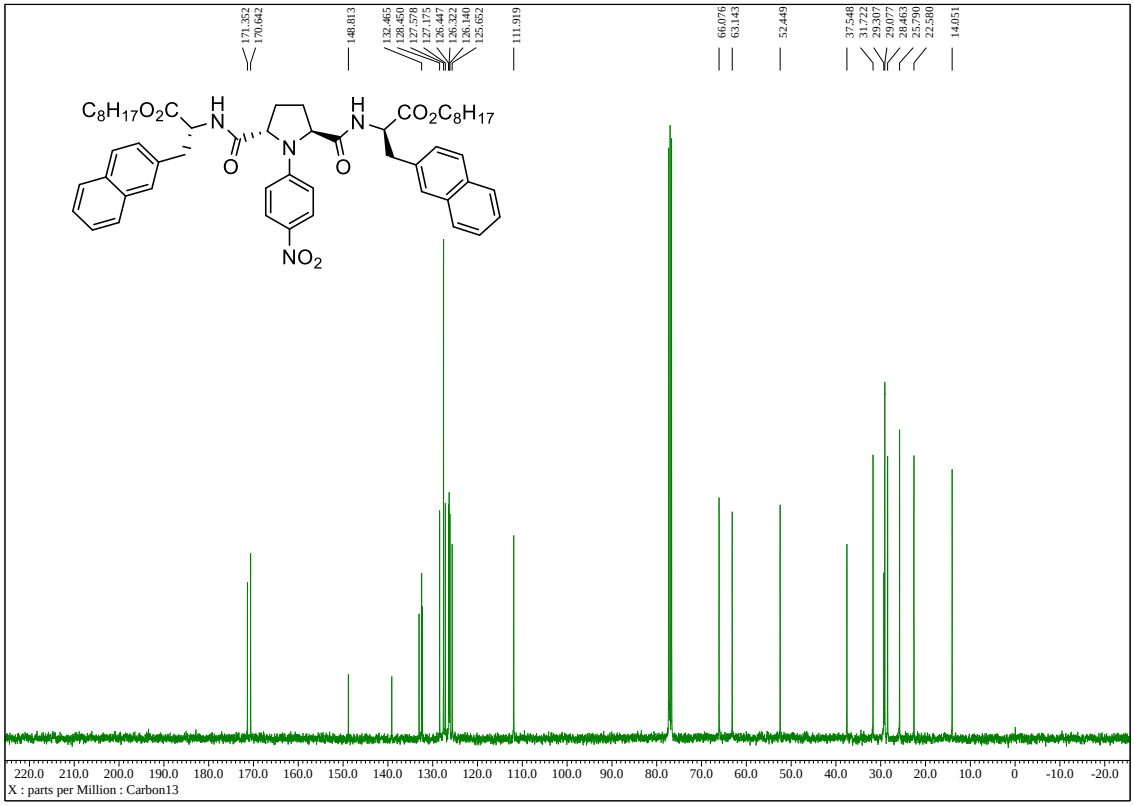
7.550
7.440
7.432
7.425
7.417
7.238
7.236
6.936
6.932
6.915
6.104
6.099
6.086
6.081
5.961
5.941
4.859
4.854
4.840
4.834
4.621
4.173
4.145
4.137
4.127
3.203
3.189
3.085
3.065
3.047
2.260
2.254
2.234
1.960
1.615
1.266
1.252
0.896
0.879
0.862
20.38
6.10
6.04
4.48
4.05
3.92
2.31
2.00
2.01
1.97
1.99
1.95
1.93
C8H17O2C
CO2C8H17
NO2
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton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132.465
128.450
127.578
127.175
126.447
126.322
126.140
125.652
111.919
66.076
63.143
52.449
37.548
31.722
29.307
29.077
28.463
25.790
22.580
14.051
C8H17O2C
CO2C8H17
NO2
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
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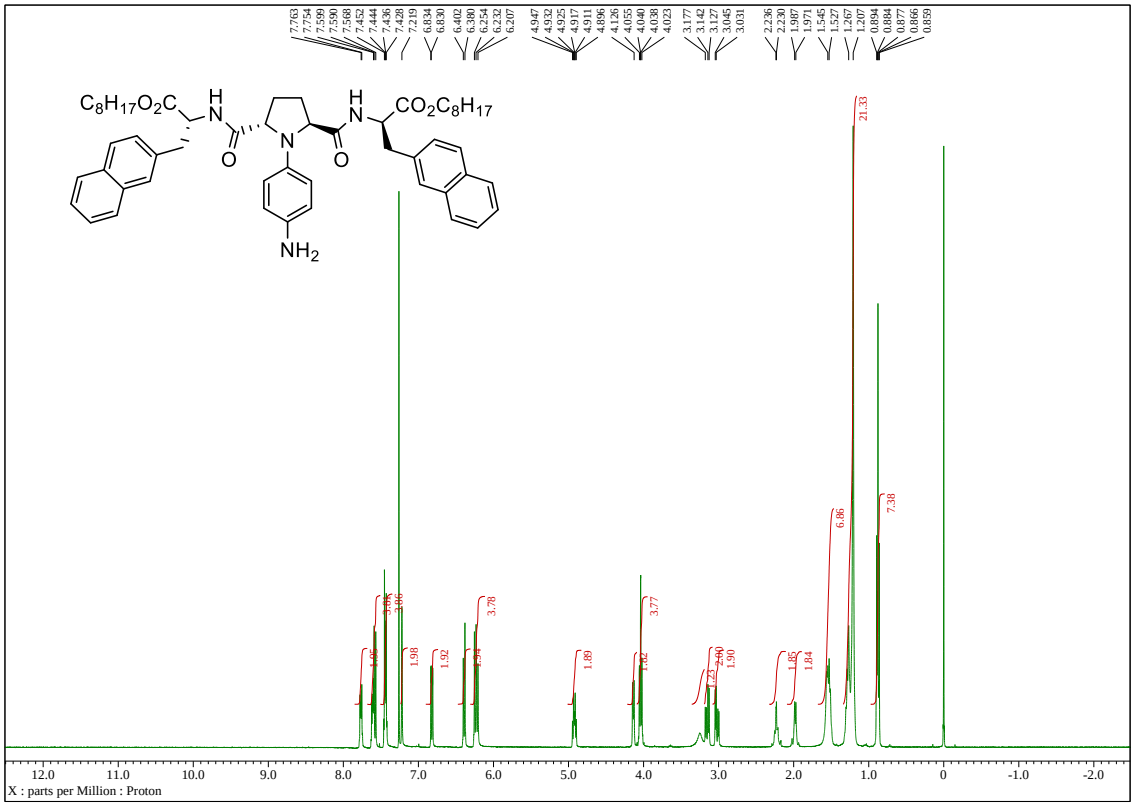
-10.0
-20.0
X : parts per Million : Carbon13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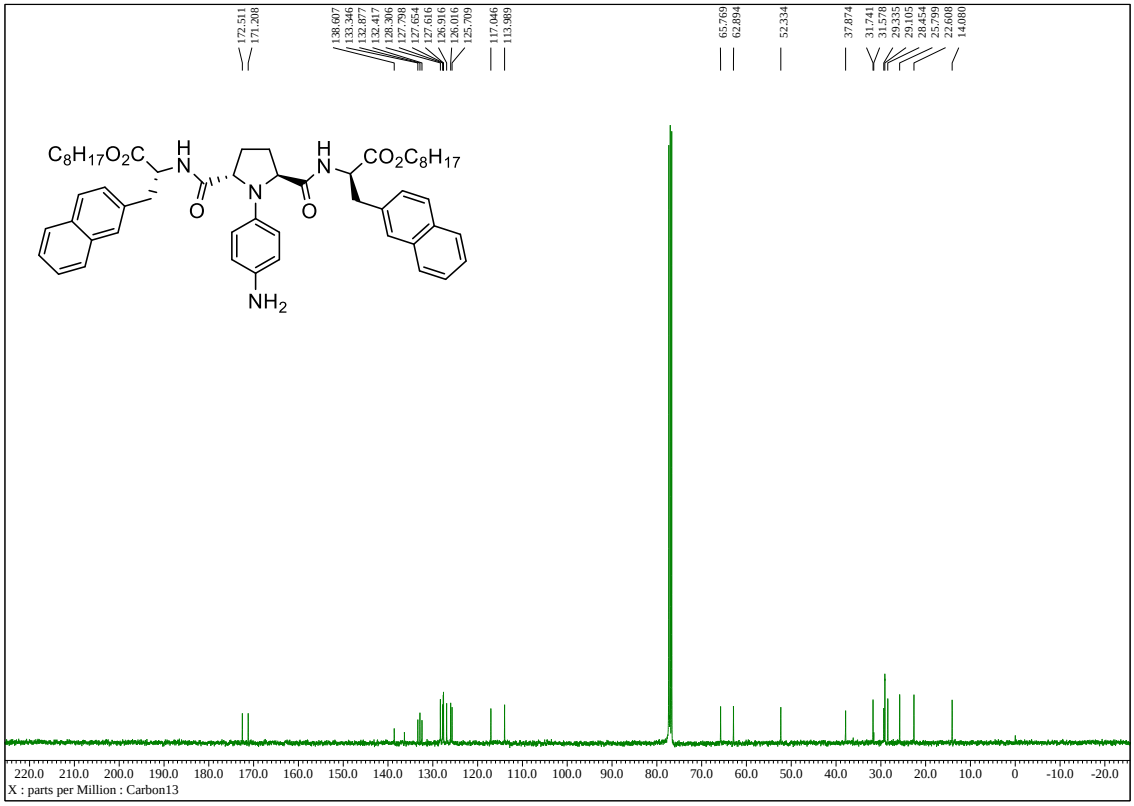
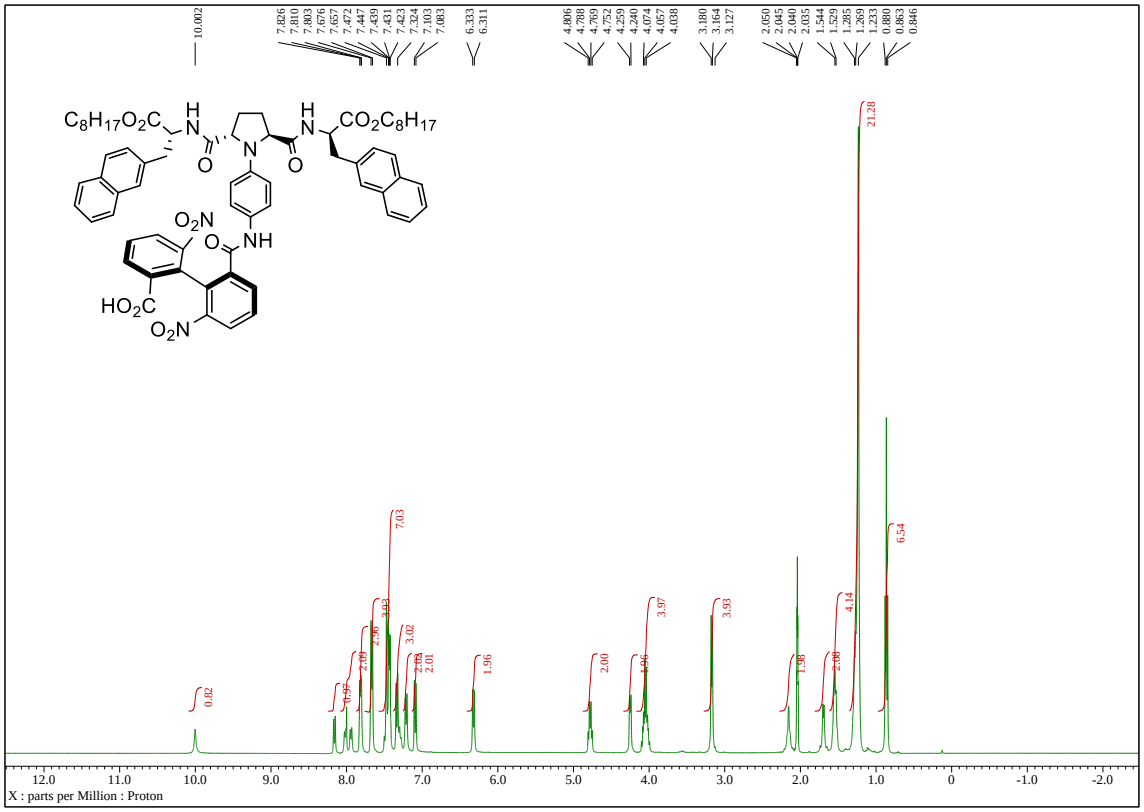
4.947 4.932 4.925 4.917 4.911 4.896 4.135 4.055 4.040 4.038 4.023
3.177 3.142 3.127 3.045 3.031
2.236 2.230 1.987 1.971 1.545 1.527 1.267 1.207 0.894 0.884 0.877 0.866 0.859
C8H17O2C
H
N
O
N
O
H
N
CO2C8H17
NH2
21.33
6.86
7.38
3.78
3.77
1.89
1.98
1.92
1.84
1.90
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton


172.511 171.208
138.607 134.346 132.877 132.417 128.306 127.798 127.654 127.616 126.916 126.016 125.709
117.046 113.989
65.769 62.894
52.334
37.874 31.741 31.570 29.535 29.155 28.454 25.799 22.608 14.080
C8H17O2C
H
N
O
N
O
H
N
CO2C8H17
NH2
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13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7.803
7.676
7.657
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7.447
7.439
7.431
7.423
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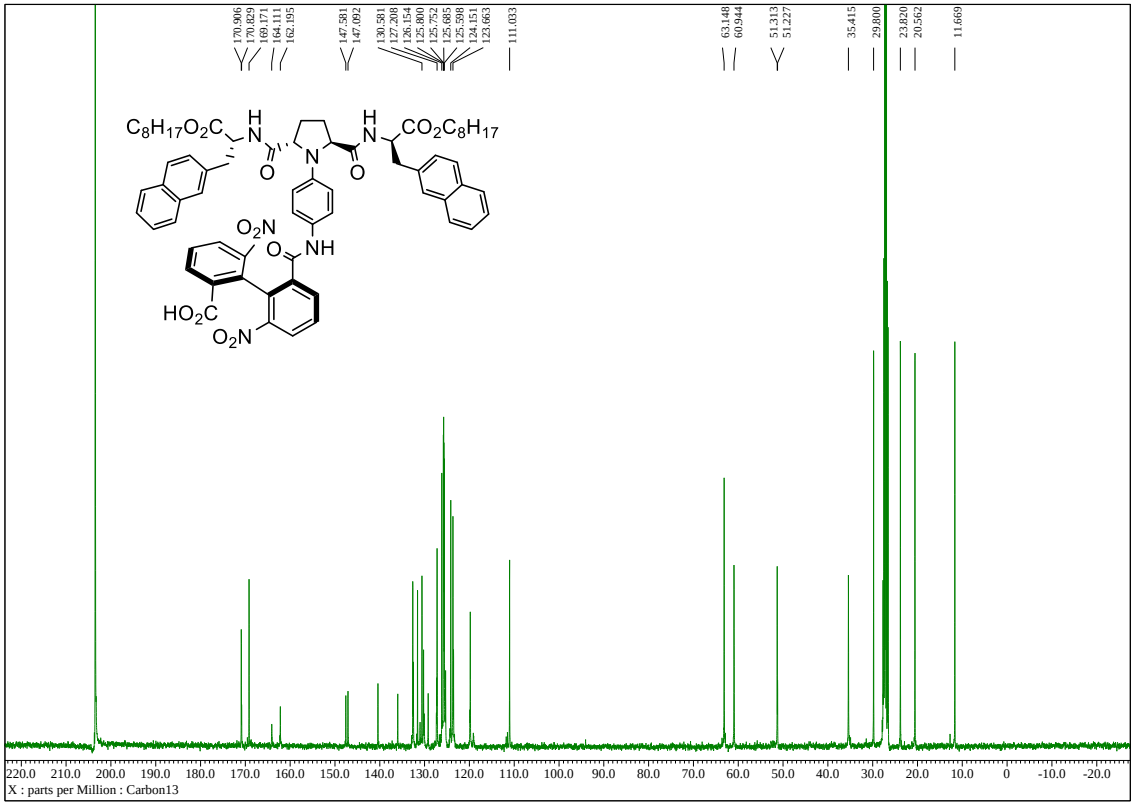
7.103
7.083
6.333
6.311
4.806
4.788
4.769
4.752
4.259
4.240
4.074
4.057
4.038
3.180
3.164
3.127
2.050
2.045
2.040
2.035
1.544
1.529
1.285
1.269
1.233
0.880
0.863
0.846
21.28
7.03
6.54
4.14
3.97
3.93
3.02
2.09
2.06
2.01
1.96
2.00
1.98
2.18
0.82
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton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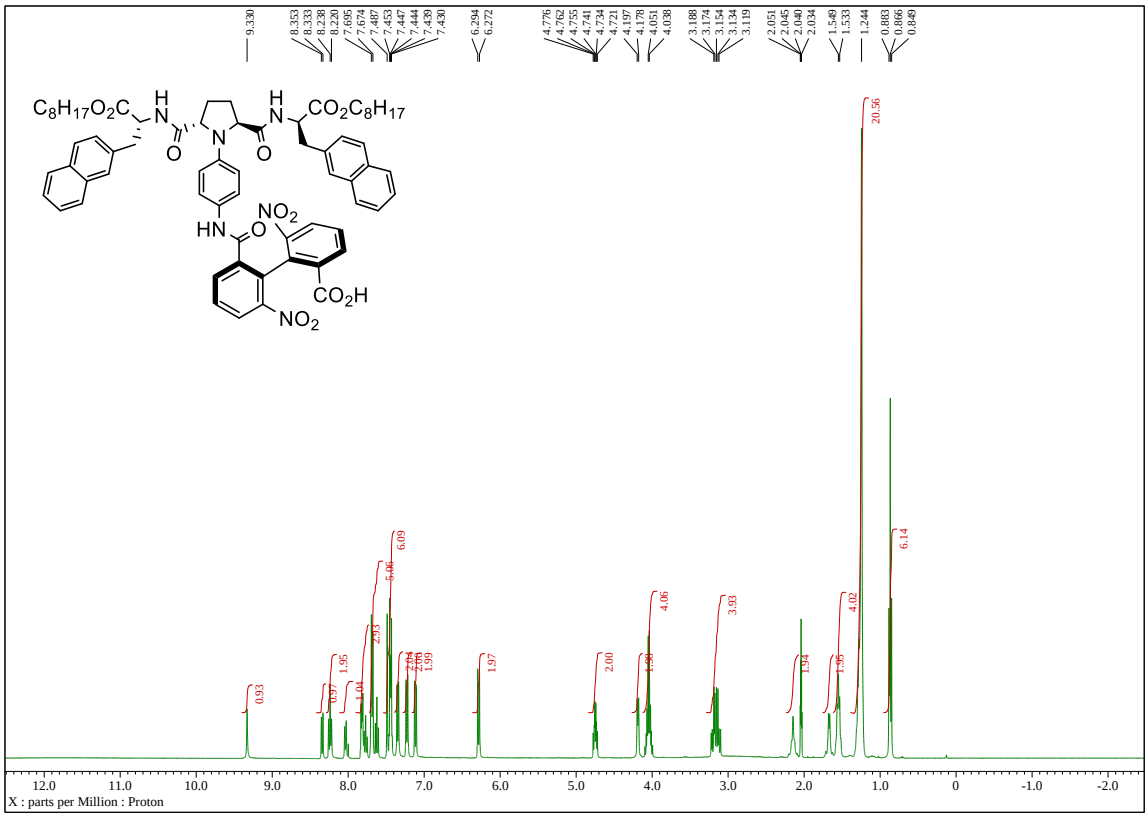
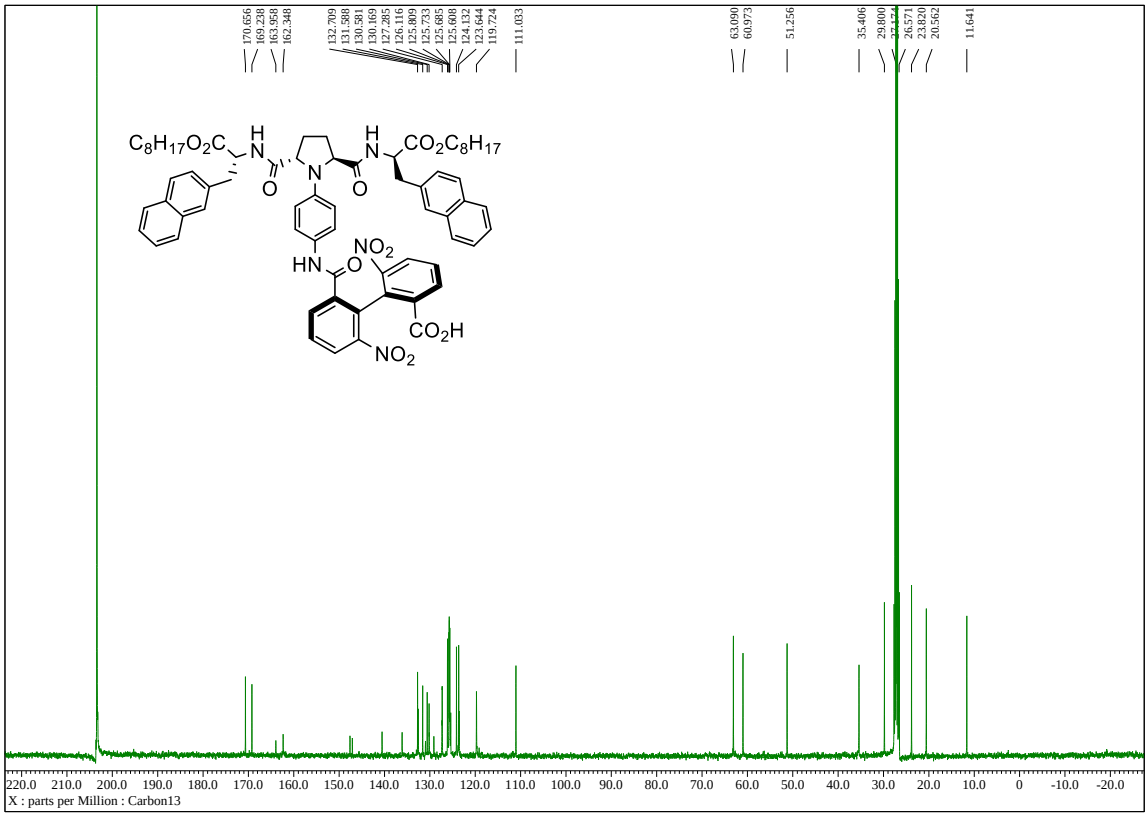
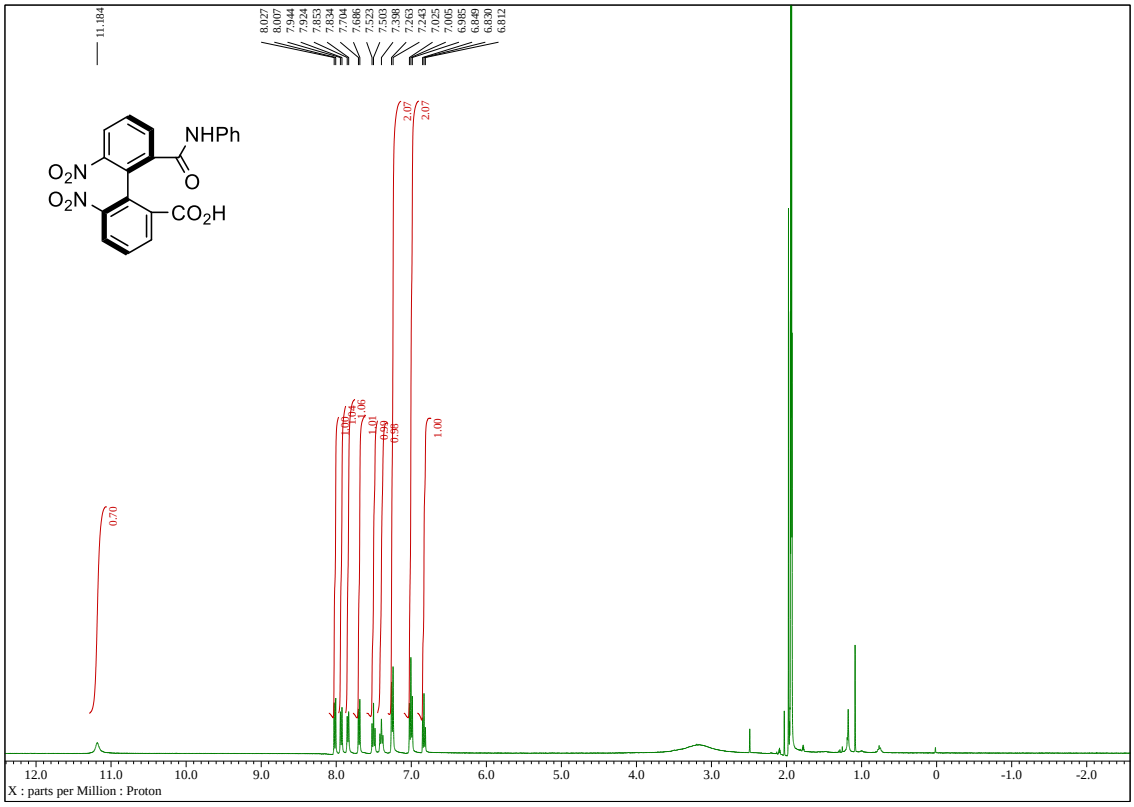
170.809
169.171
164.111
162.195
147.581
147.092
130.581
127.208
126.154
125.800
125.752
125.695
125.598
124.151
123.663
111.033
63.148
60.944
51.313
51.227
35.415
29.800
23.820
20.562
11.669
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13


X : parts per Million : Proton


X : parts per Million : Carbon13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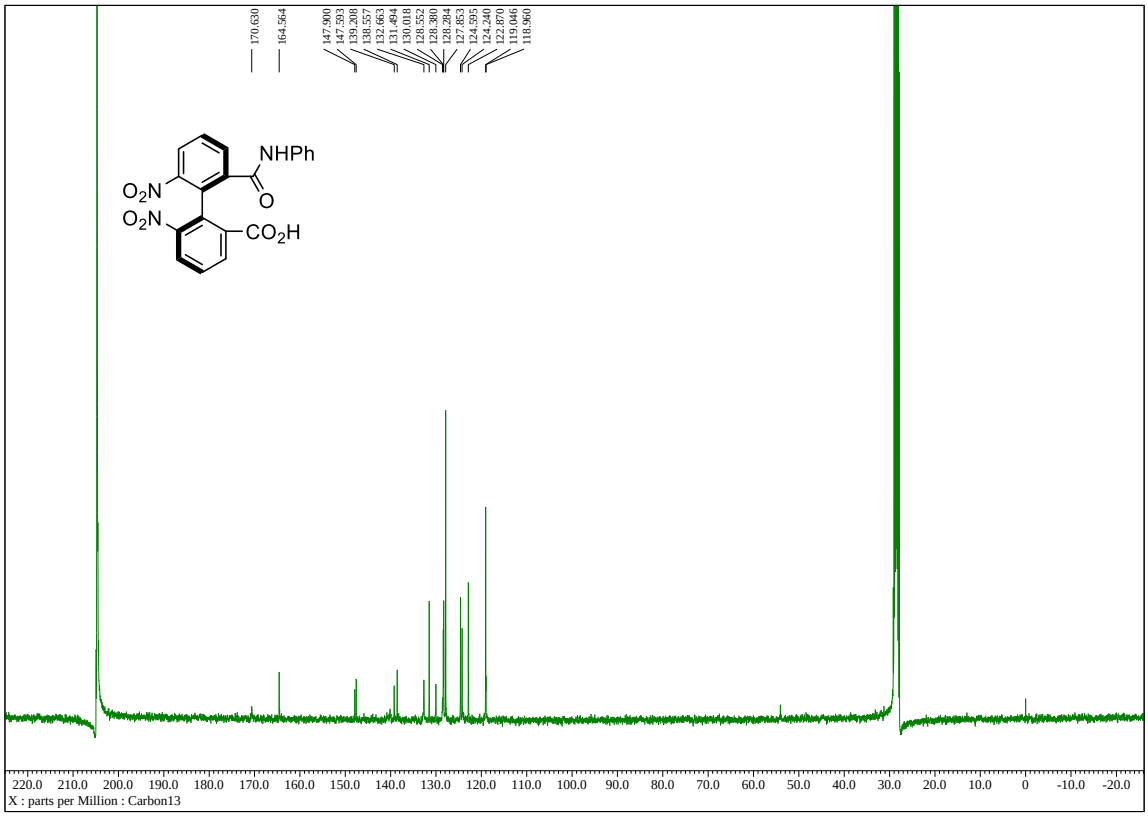
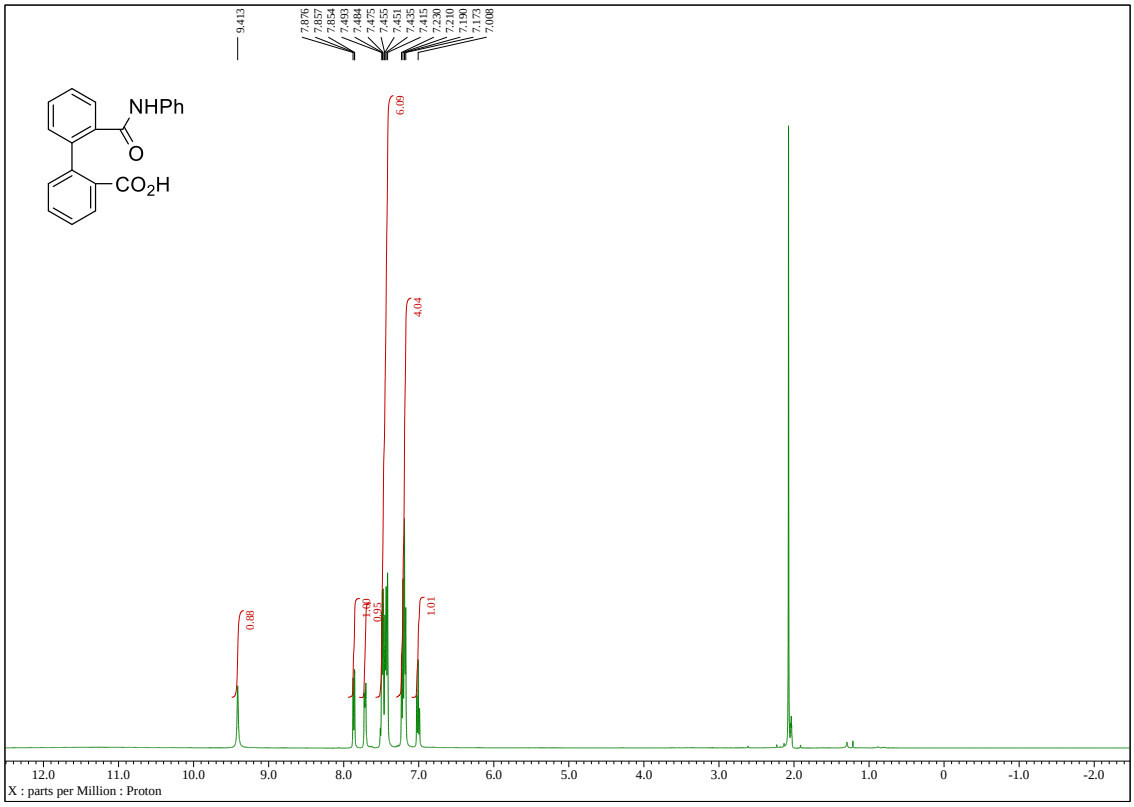
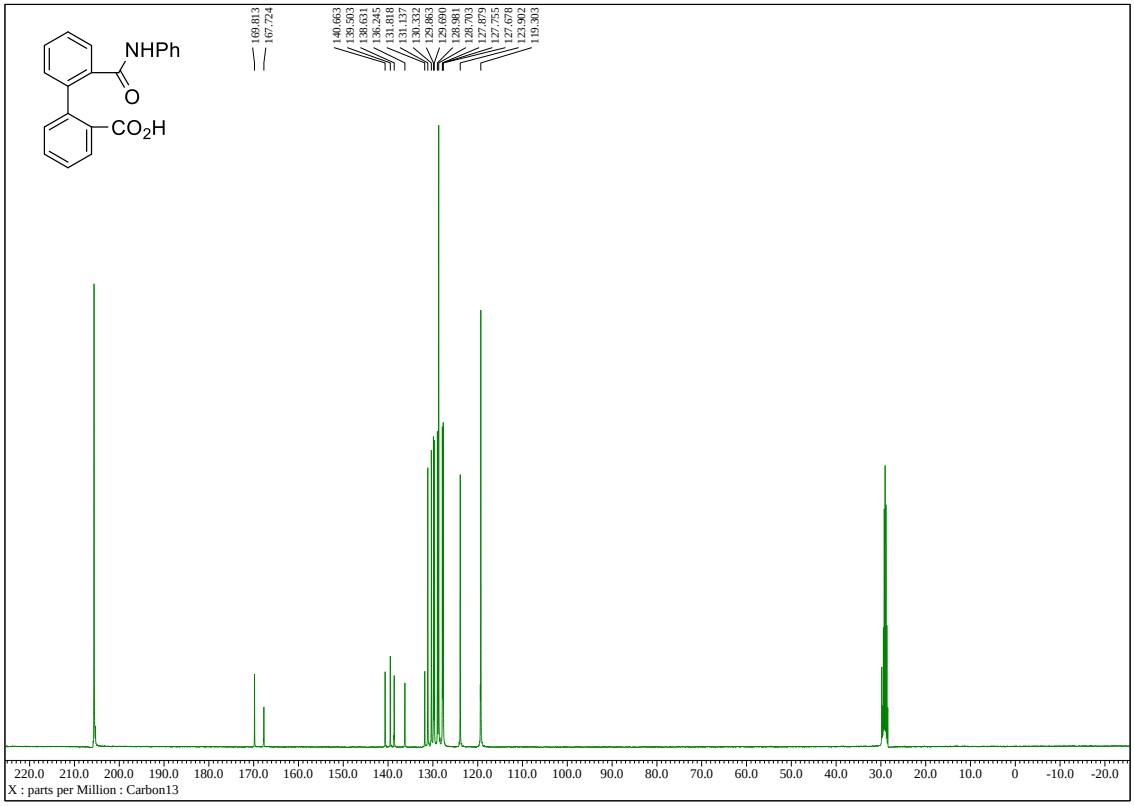
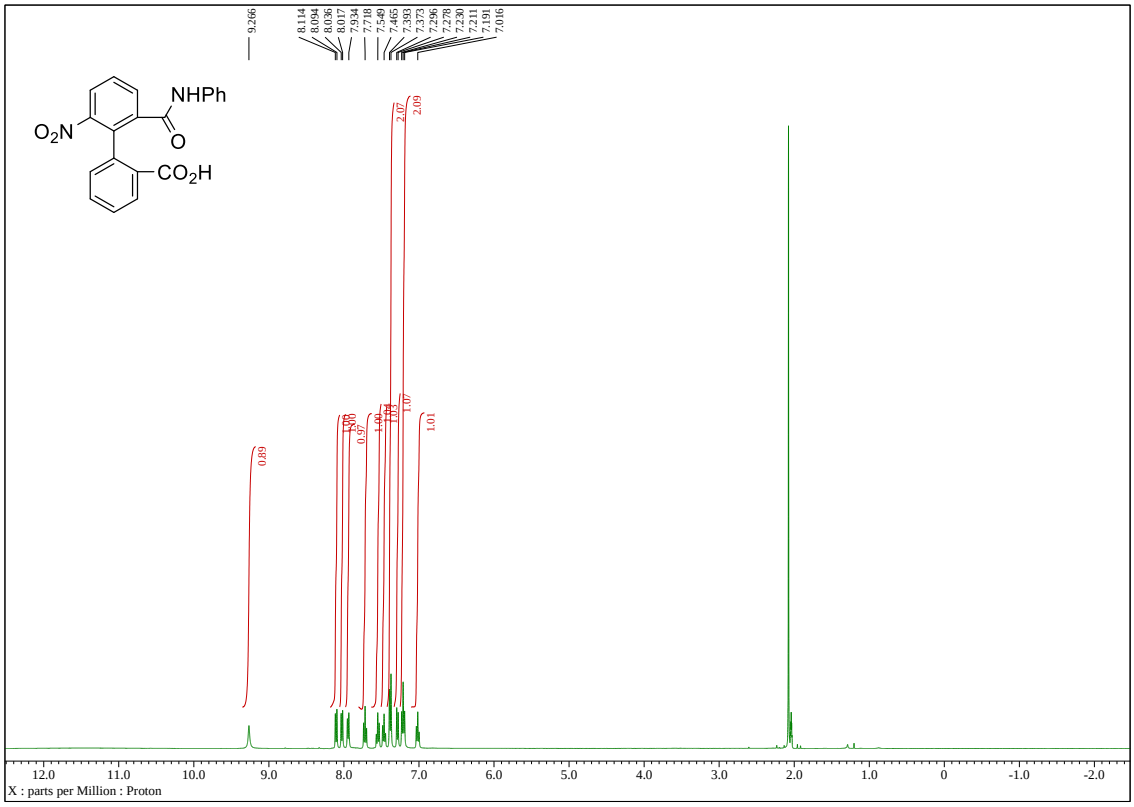
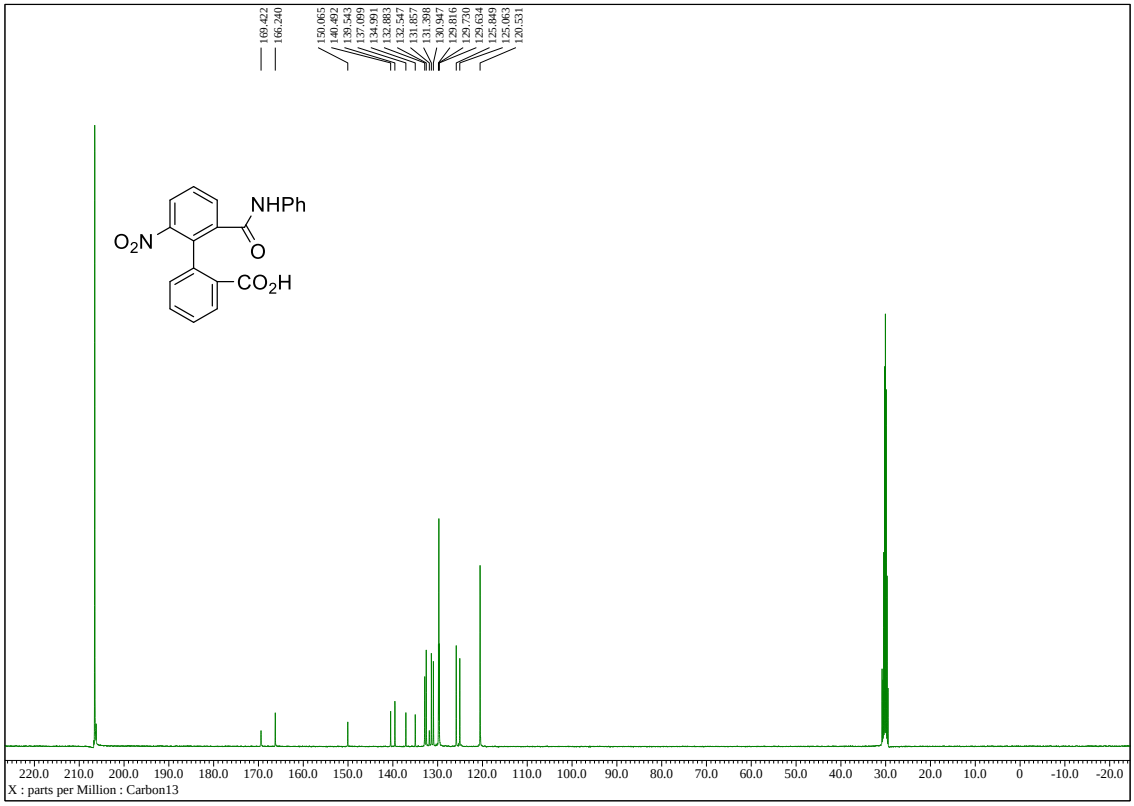
8.027
8.007
7.944
7.924
7.853
7.834
7.704
7.686
7.523
7.503
7.398
7.263
7.243
7.025
7.005
6.985
6.849
6.830
6.812
NHPh
O
O2N
O2N
CO2H
2.07
2.07
1.00
1.07
1.04
1.08
1.0
0.99
0.98
1.00
0.70
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton

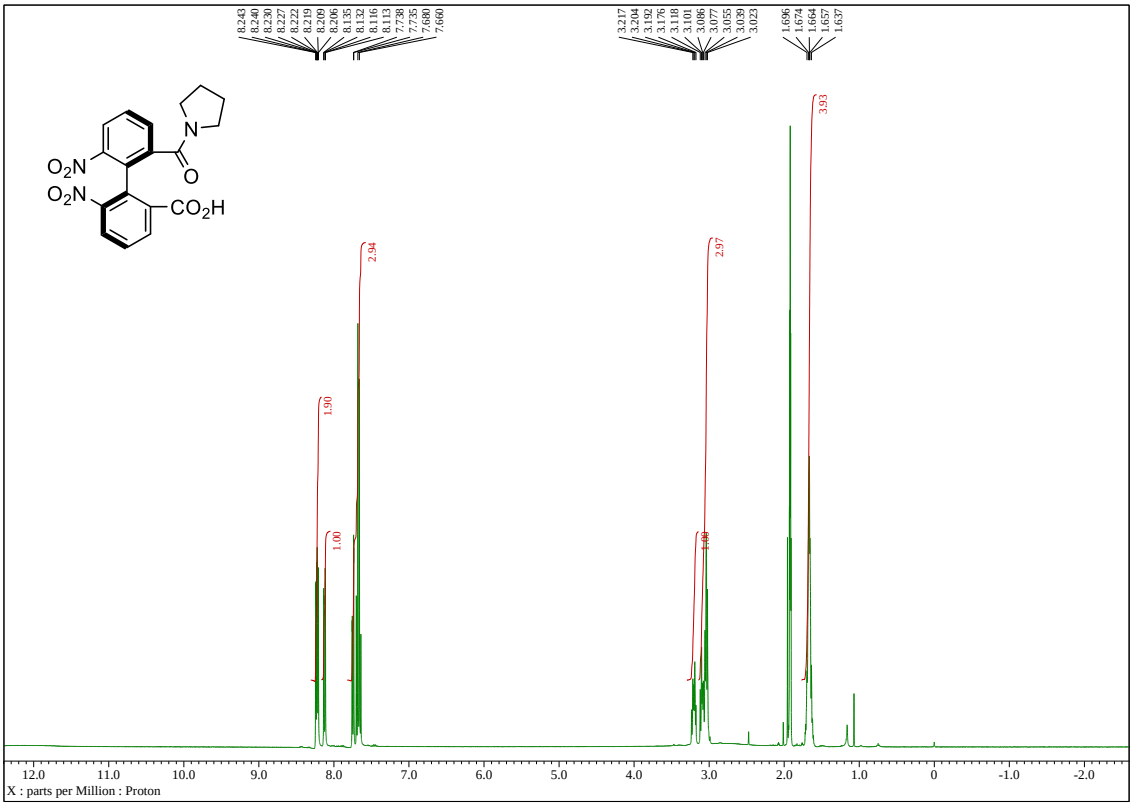

170.630
164.564
147.900
147.593
139.208
138.557
132.663
131.494
130.018
128.552
128.300
128.204
127.853
124.595
124.240
122.870
119.046
118.960
NHPh
O
O2N
O2N
CO2H
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13

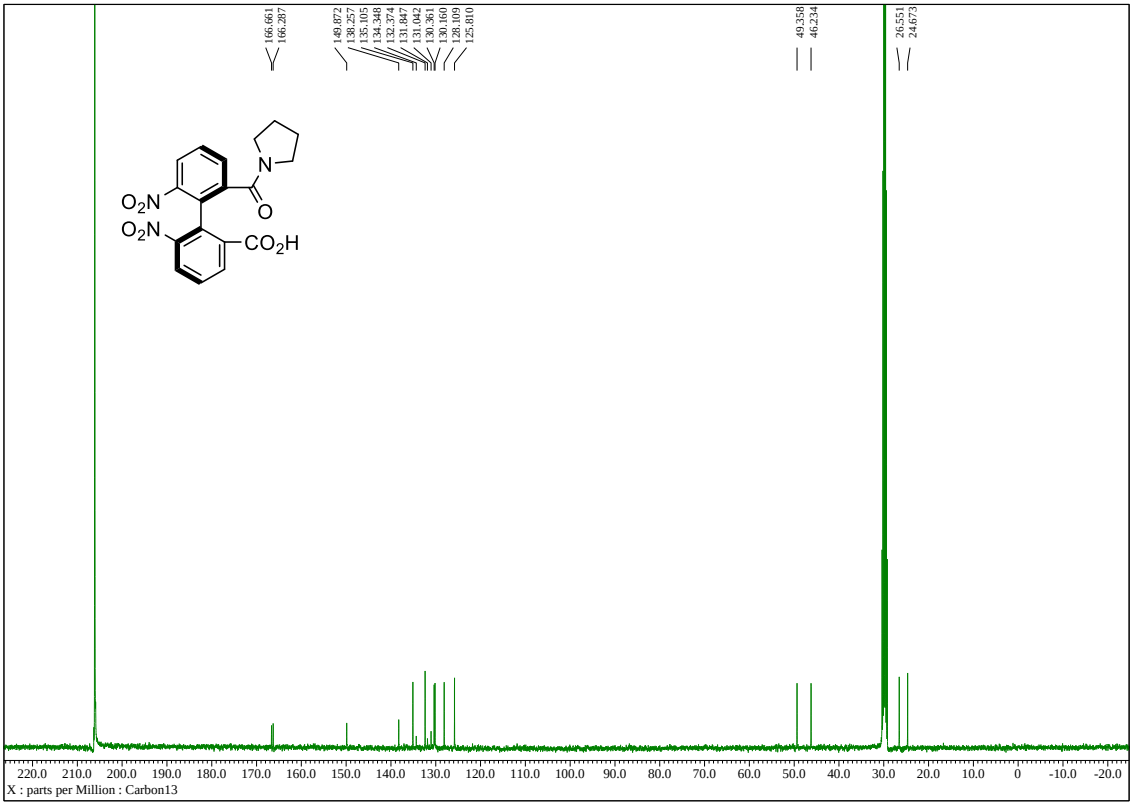

9.413
7.876
7.857
7.854
7.493
7.484
7.475
7.455
7.451
7.435
7.415
7.230
7.210
7.190
7.173
7.008
NHPh
O
CO2H
6.09
4.04
0.88
1.40
0.85
1.01
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton

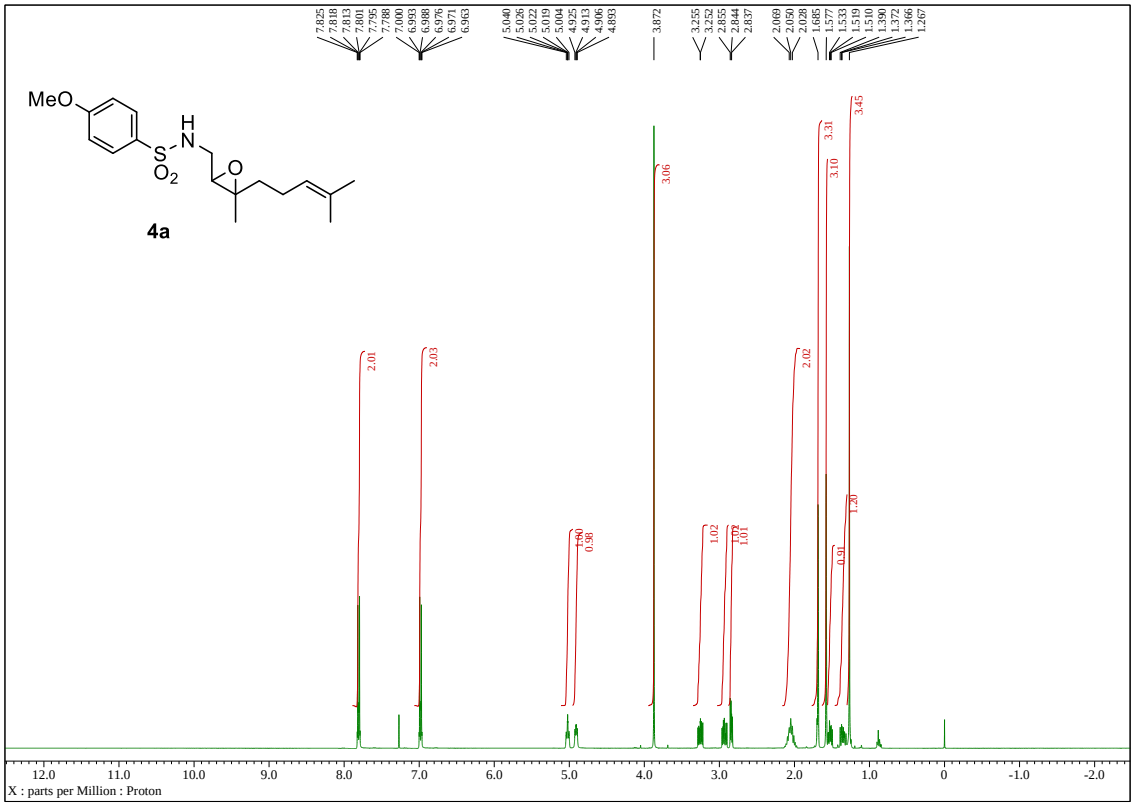

169.813
167.724
140.663
139.593
138.631
136.215
131.818
131.137
130.332
129.863
129.690
128.981
128.703
127.879
127.755
127.678
123.902
119.303
NHPh
O
CO2H
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

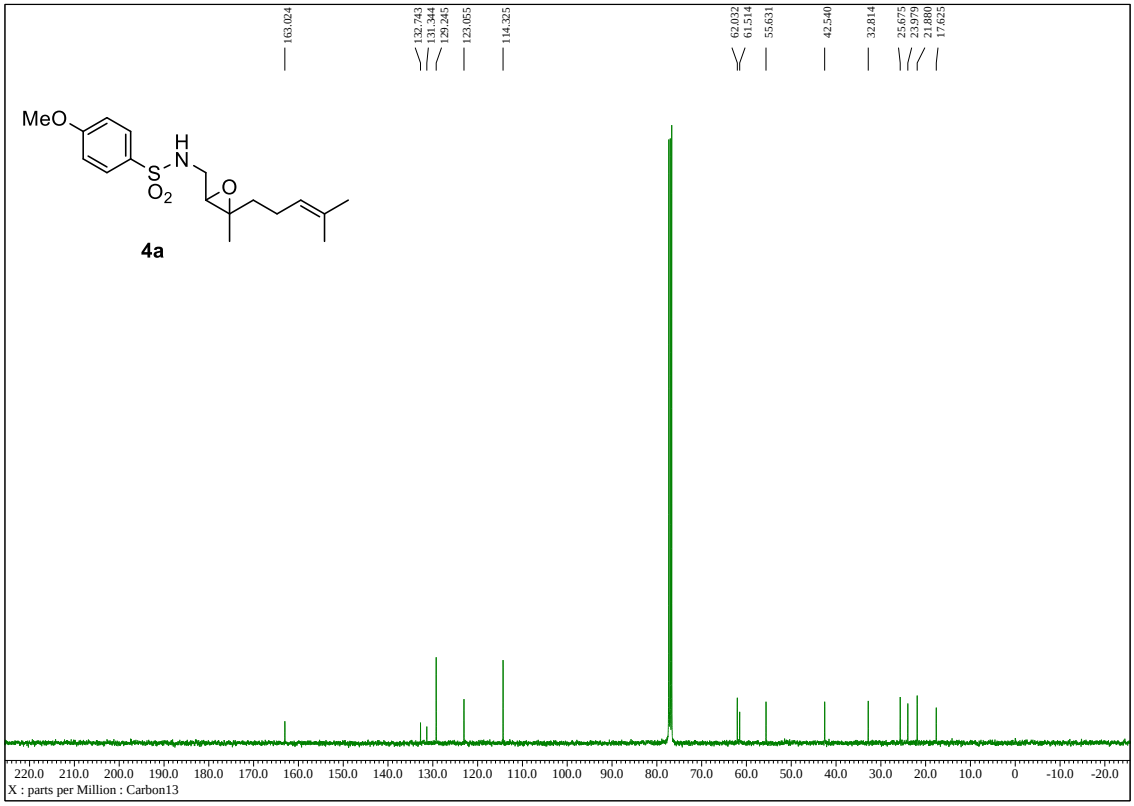

9.266
8.114
8.094
8.036
8.017
7.934
7.718
7.549
7.465
7.393
7.373
7.296
7.270
7.239
7.211
7.191
7.016
2.07
2.09
0.89
0.97
1.00
1.00
1.01
1.07
1.01
NHPh
O2N
O
CO2H
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton

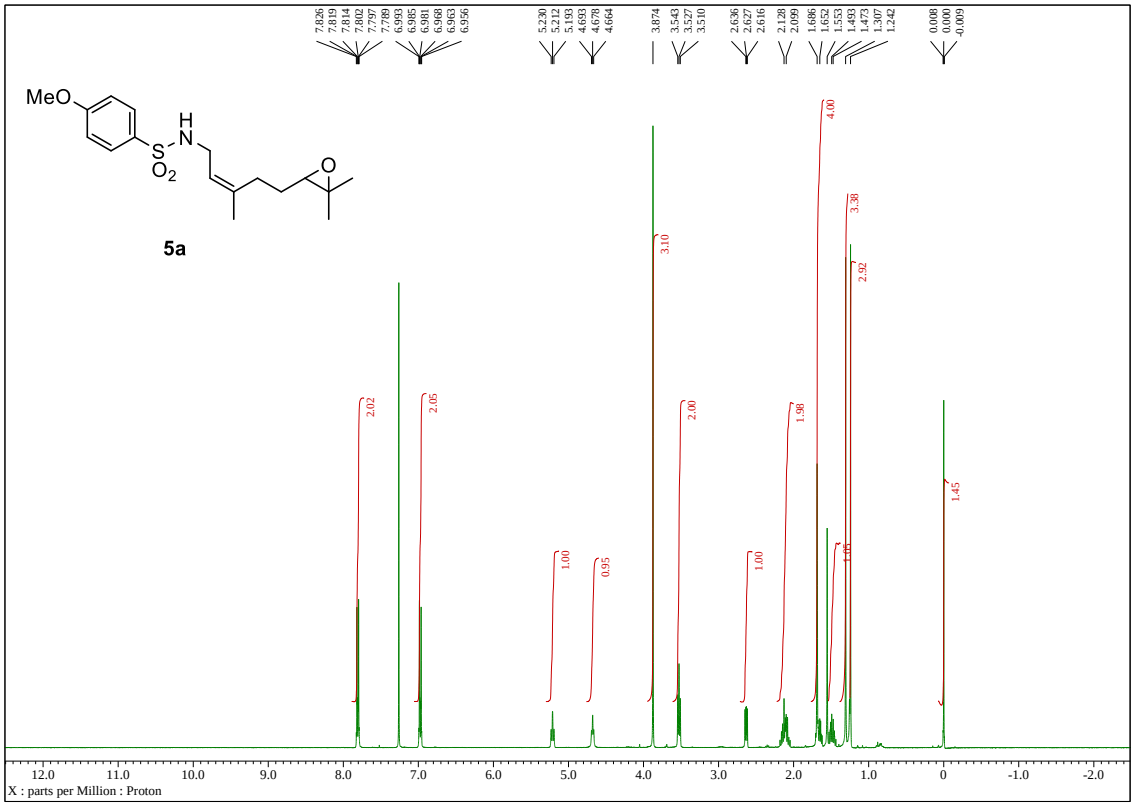

169.422
166.240
150.065
140.462
139.543
137.099
134.991
132.883
132.547
131.857
131.398
130.947
129.816
129.730
129.634
125.849
125.063
120.531
NHPh
O2N
O
CO2H
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

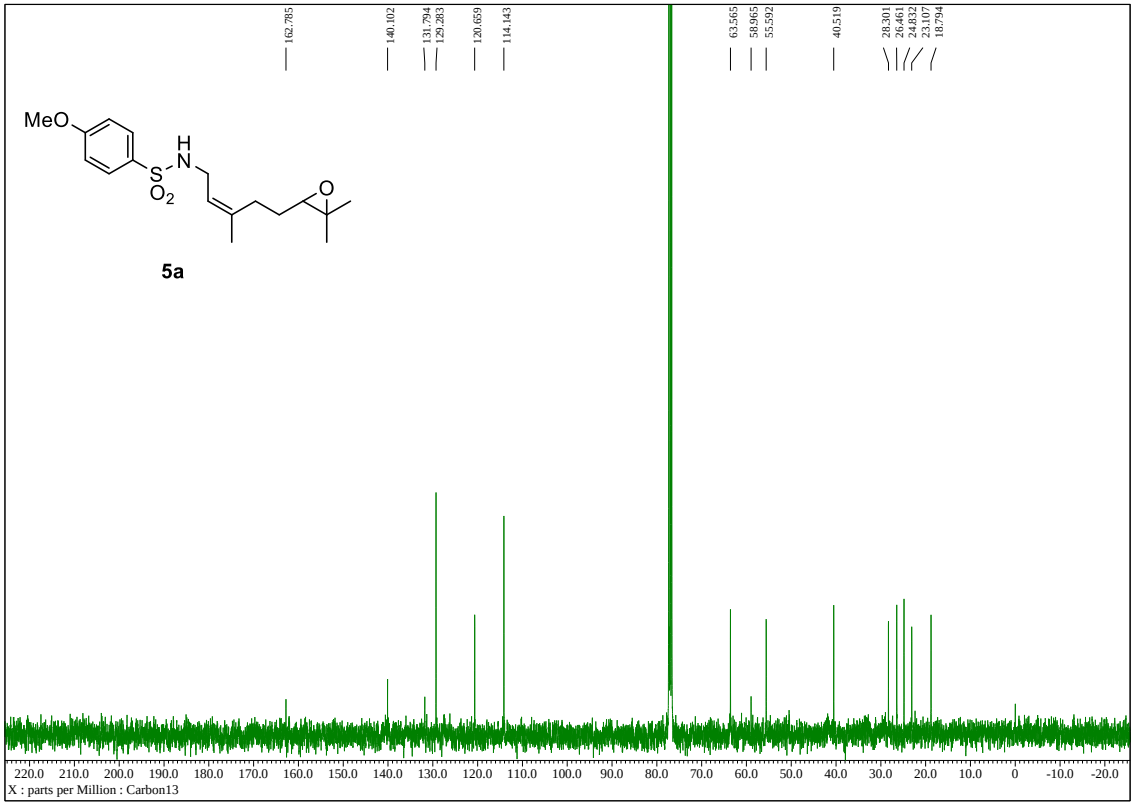

8.243
8.240
8.230
8.227
8.222
8.219
8.209
8.206
8.135
8.132
8.116
8.113
7.738
7.735
7.680
7.660
3.217
3.204
3.192
3.176
3.118
3.101
3.086
3.077
3.055
3.039
3.023
1.696
1.674
1.664
1.657
1.637
3.93
2.97
2.94
1.90
1.00
1.08
O2N
O2N
N
O
CO2H
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton


166.661
166.287
140.872
138.257
135.105
134.348
132.374
131.847
131.042
130.361
130.160
128.109
125.810
49.358
46.234
26.551
24.673
O2N
O2N
N
O
CO2H
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13


MeO
H
N
S
O2
O
4a
7.825
7.818
7.813
7.801
7.795
7.788
7.000
6.993
6.988
6.976
6.971
6.963
5.040
5.026
5.022
5.019
5.004
4.955
4.913
4.906
4.893
3.872
3.255
3.252
3.855
2.844
2.837
2.069
2.050
2.028
1.685
1.577
1.533
1.519
1.510
1.390
1.372
1.366
1.267
2.01
2.03
2.02
3.31
3.45
3.06
3.10
1.20
1.02
1.02
1.01
0.91
1.00
0.98
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton


MeO
H
N
S
O2
O
4a
163.024
132.743
131.344
129.245
123.055
114.325
62.032
61.514
55.631
42.540
32.814
25.675
23.979
21.880
17.625
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13


7.826
7.819
7.814
7.802
7.797
7.789
6.993
6.985
6.981
6.968
6.963
6.956
5.230
5.212
5.193
4.693
4.678
4.664
3.874
3.543
3.527
3.510
2.636
2.627
2.616
2.128
2.099
1.686
1.652
1.555
1.493
1.473
1.307
1.242
0.008
0.000
-0.009
MeO
H
N
S
O2
O
5a
4.00
3.38
3.10
2.92
2.02
2.05
2.00
1.98
1.45
1.00
0.95
1.00
1.05
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton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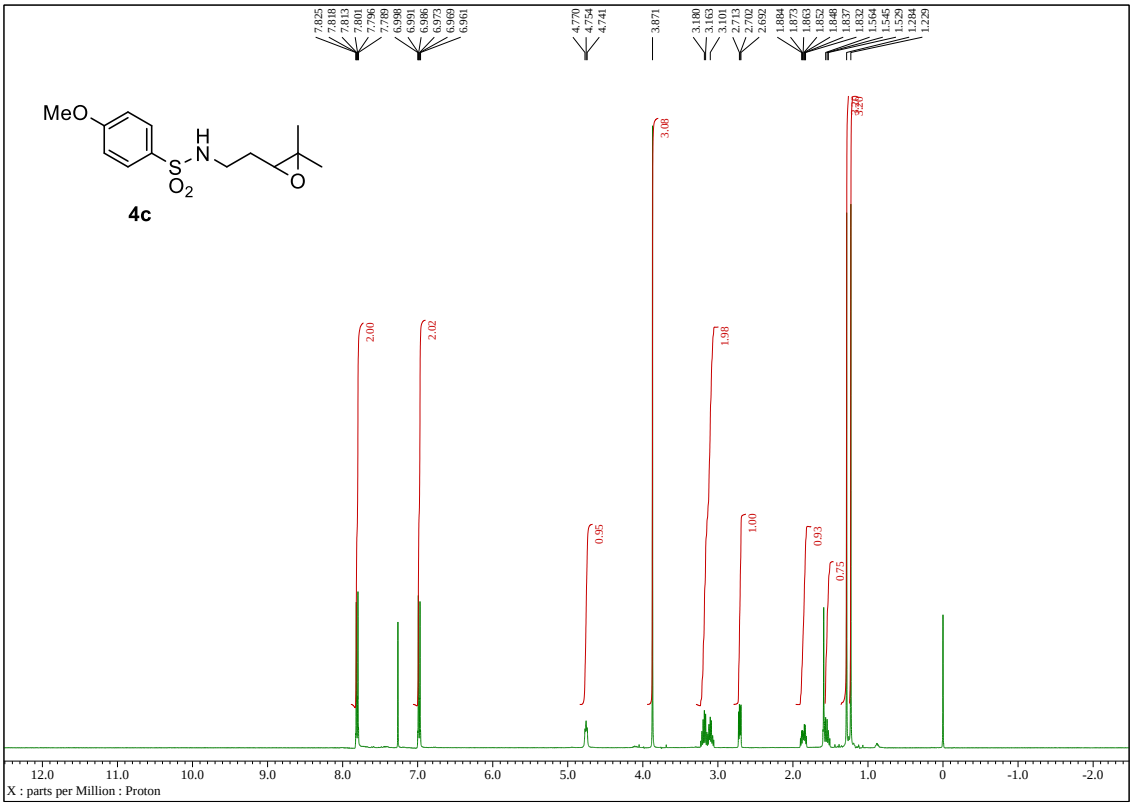
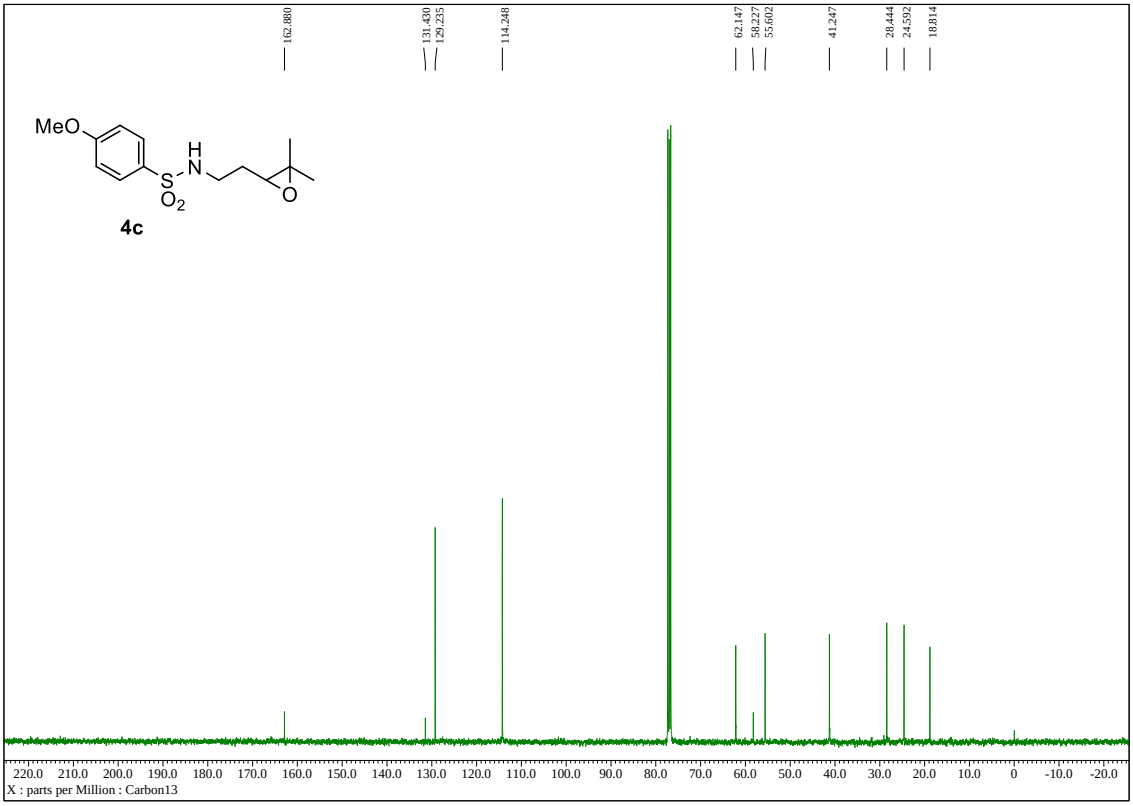
129.283
120.659
114.143
63.565
58.965
55.592
40.519
28.301
26.461
24.832
23.107
18.794
MeO
H
N
S
O2
O
5a
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13


7.825
7.818
7.813
7.801
7.796
7.789
6.998
6.991
6.986
6.973
6.969
6.961
4.770
4.754
4.741
3.871
3.180
3.163
3.101
2.713
2.702
2.692
1.884
1.873
1.863
1.852
1.848
1.837
1.832
1.564
1.545
1.529
1.284
1.229
MeO
H
N
S
O2
O
4c
2.00
2.02
0.95
3.08
1.98
1.00
0.93
0.75
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton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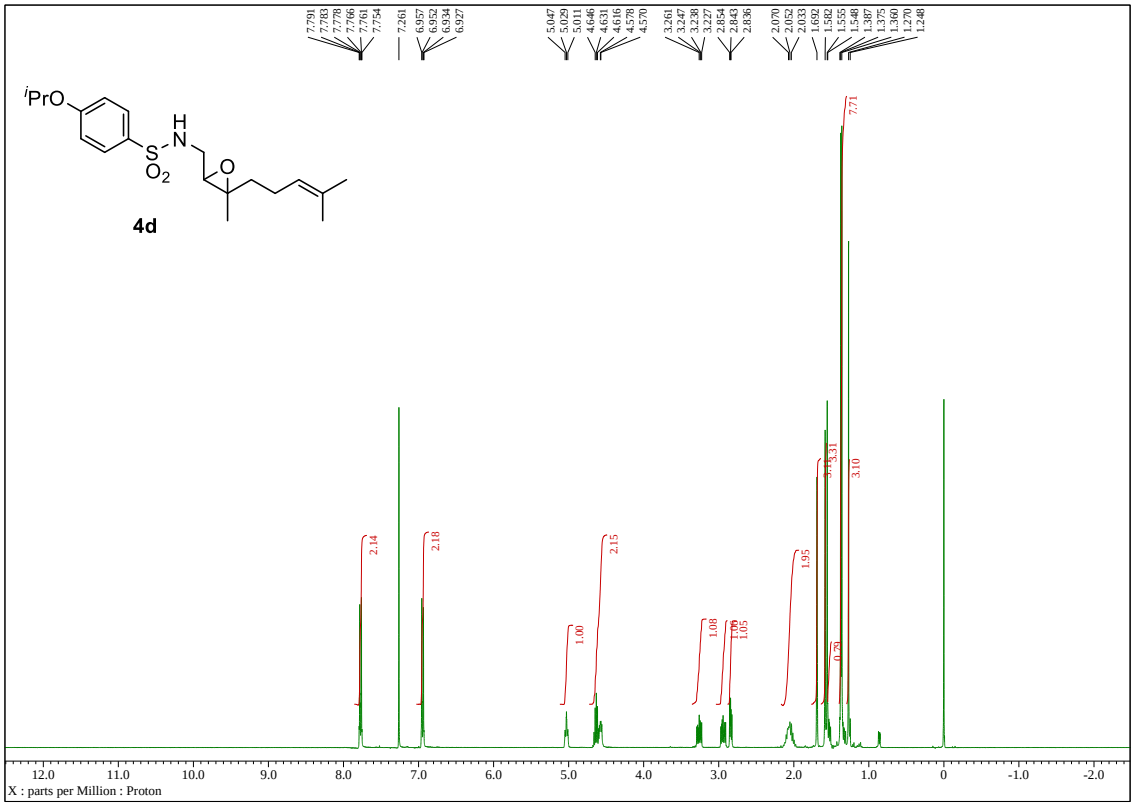
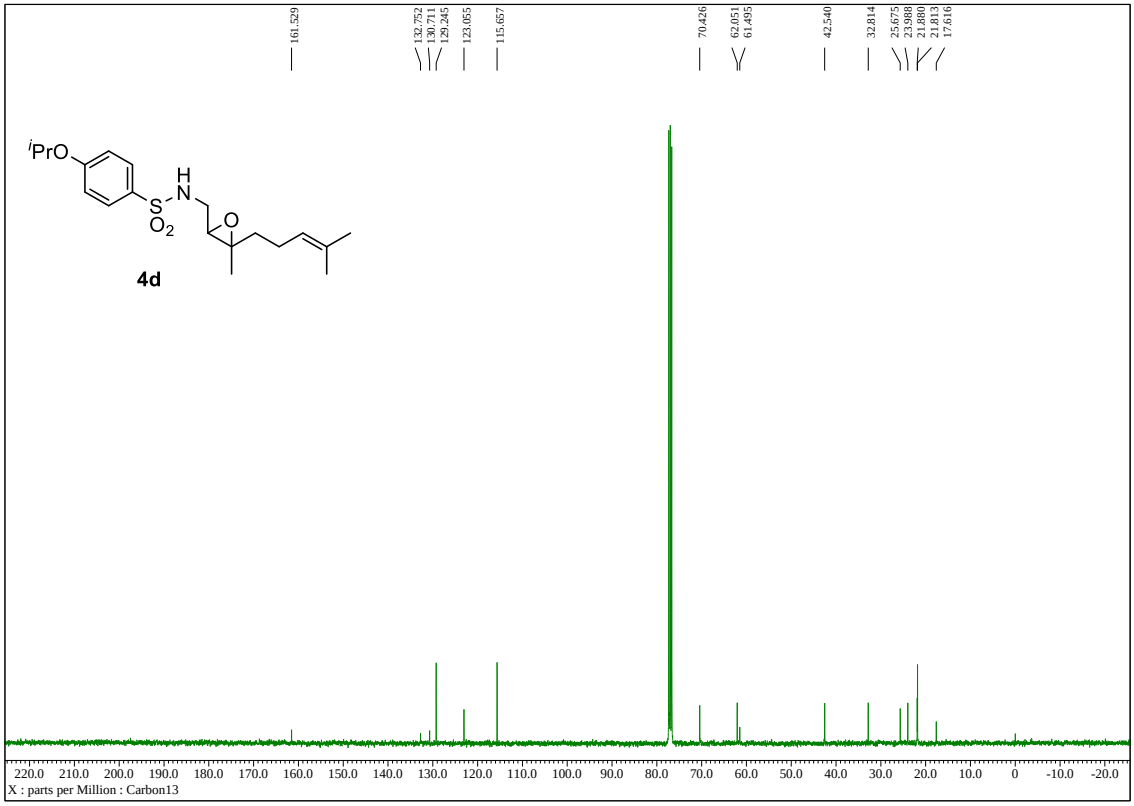
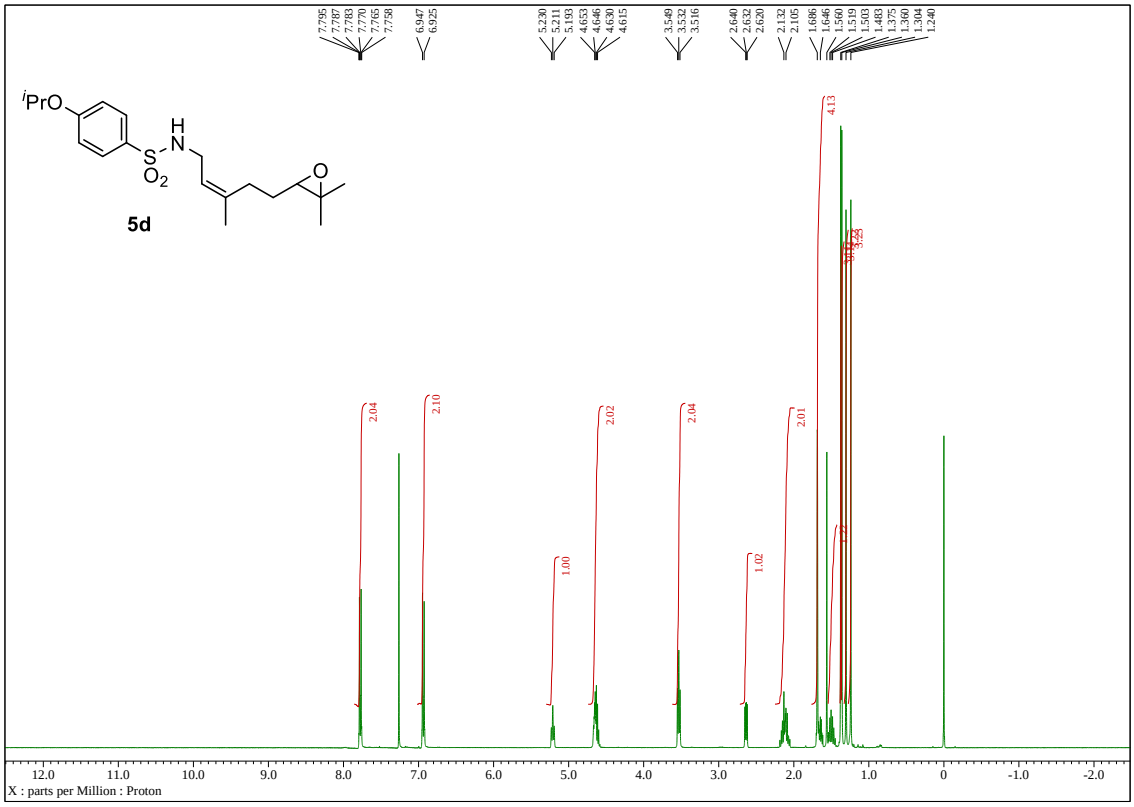
129.235
114.248
62.147
58.227
55.602
41.247
28.444
24.592
18.814
MeO
H
N
S
O2
O
4c
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13


4d
X : parts per Million : Proton


4d
X : parts per Million : Carbon13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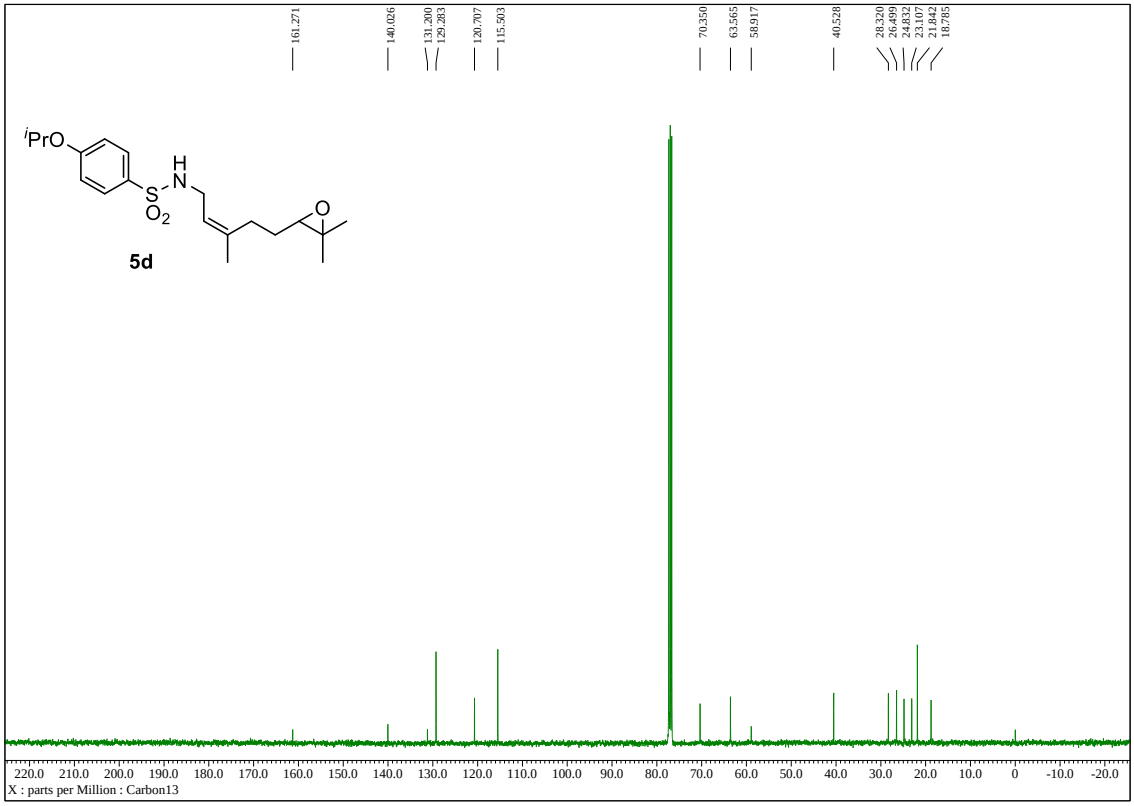
7.780
7.770
7.765
7.758
6.947
6.925
5.230
5.211
5.193
4.653
4.646
4.630
4.615
3.549
3.532
3.516
2.640
2.632
2.620
2.132
2.105
1.686
1.646
1.560
1.519
1.503
1.483
1.375
1.360
1.304
1.240
iPrO
H
N
S
O2
O
5d
4.13
2.04
2.10
2.02
2.04
2.01
1.00
1.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton


161.271
140.026
131.200
129.283
120.707
115.503
70.350
63.565
58.917
40.528
28.320
26.499
24.832
23.107
21.842
18.785
iPrO
H
N
S
O2
O
5d
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
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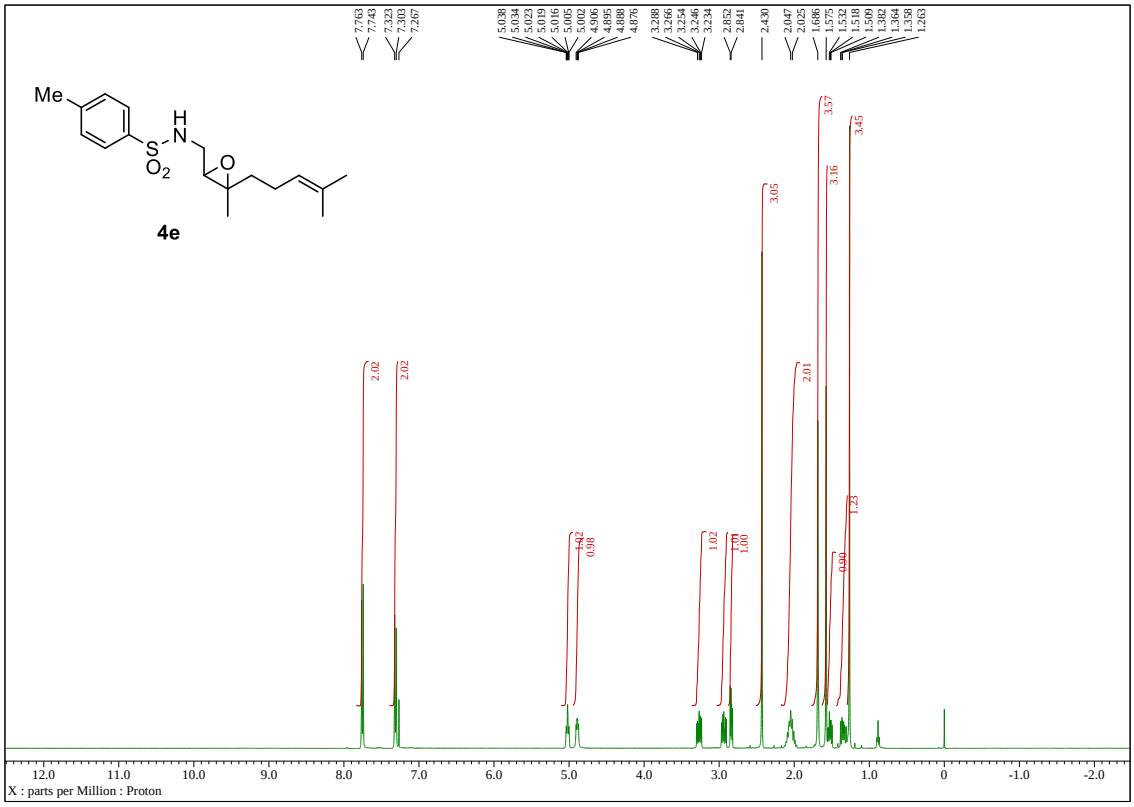
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13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7.303
7.267
5.038
5.034
5.023
5.019
5.016
5.005
5.002
4.906
4.895
4.888
4.876
3.288
3.266
3.254
3.246
3.234
2.852
2.841
2.430
2.047
2.025
1.686
1.575
1.532
1.518
1.509
1.382
1.364
1.338
1.263
Me
H
N
S
O2
O
4e
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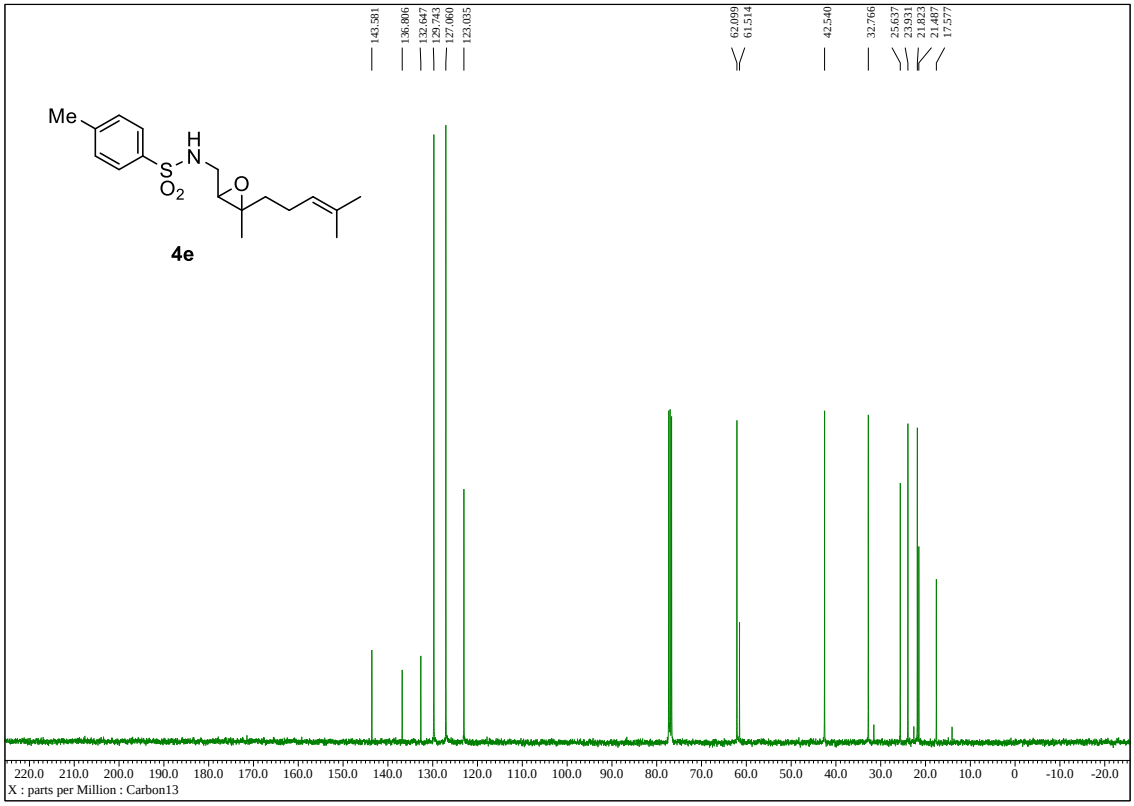
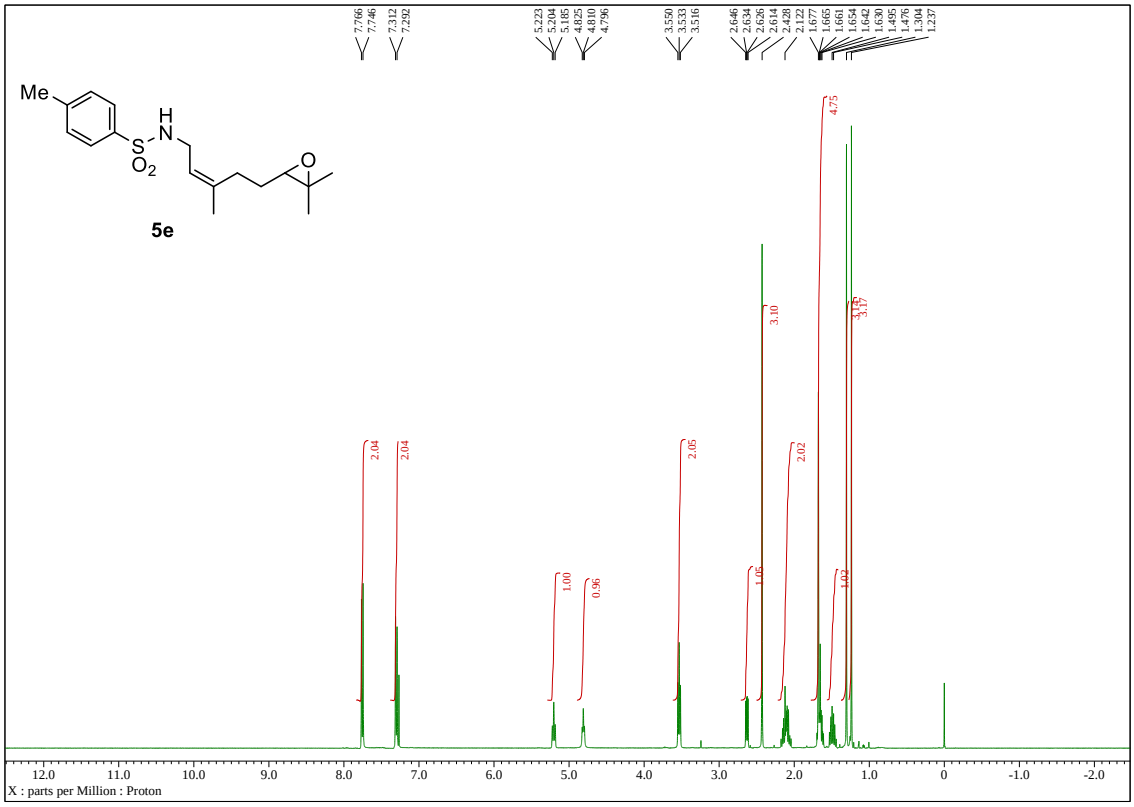
2.02
1.02
1.00
3.05
2.01
3.57
3.16
3.45
1.23
X : parts per Million : Proton


143.581
136.806
132.647
129.743
127.060
123.035
62.099
61.514
42.540
32.766
25.637
23.931
21.823
21.487
17.577
Me
H
N
S
O2
O
4e
X : parts per Million : Carbon13


Me
S
O2
H
N
O
5e
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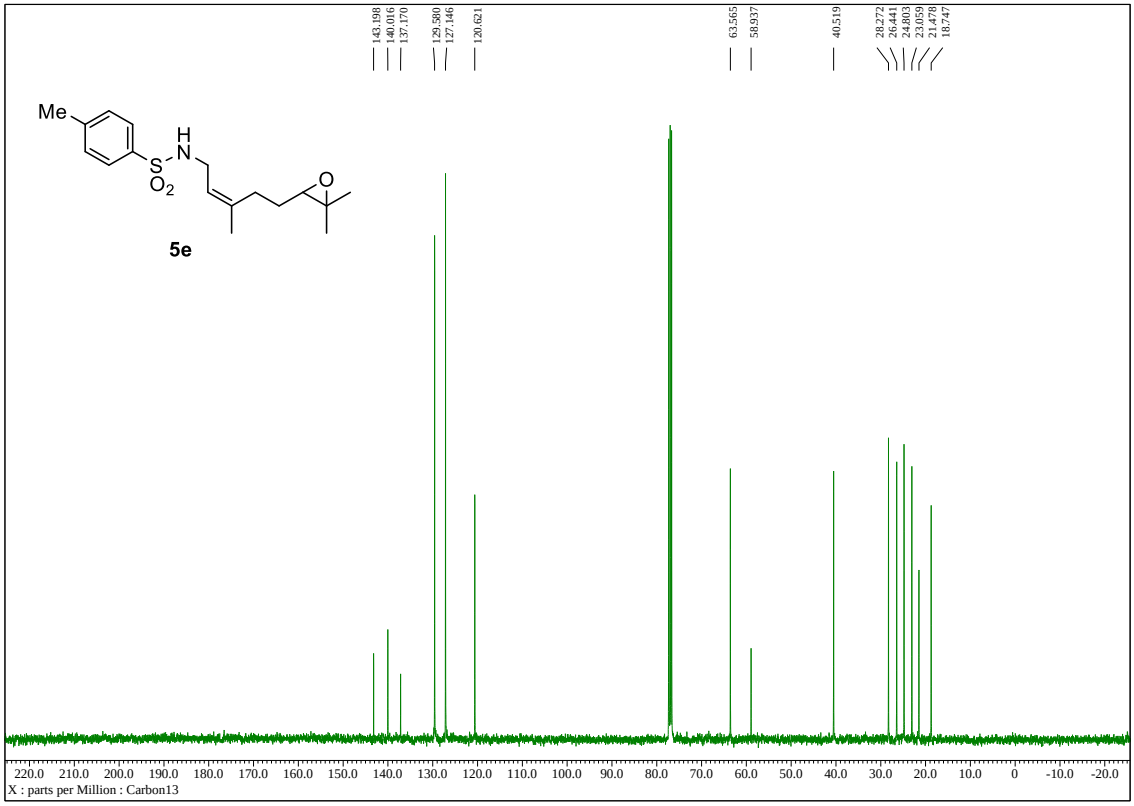
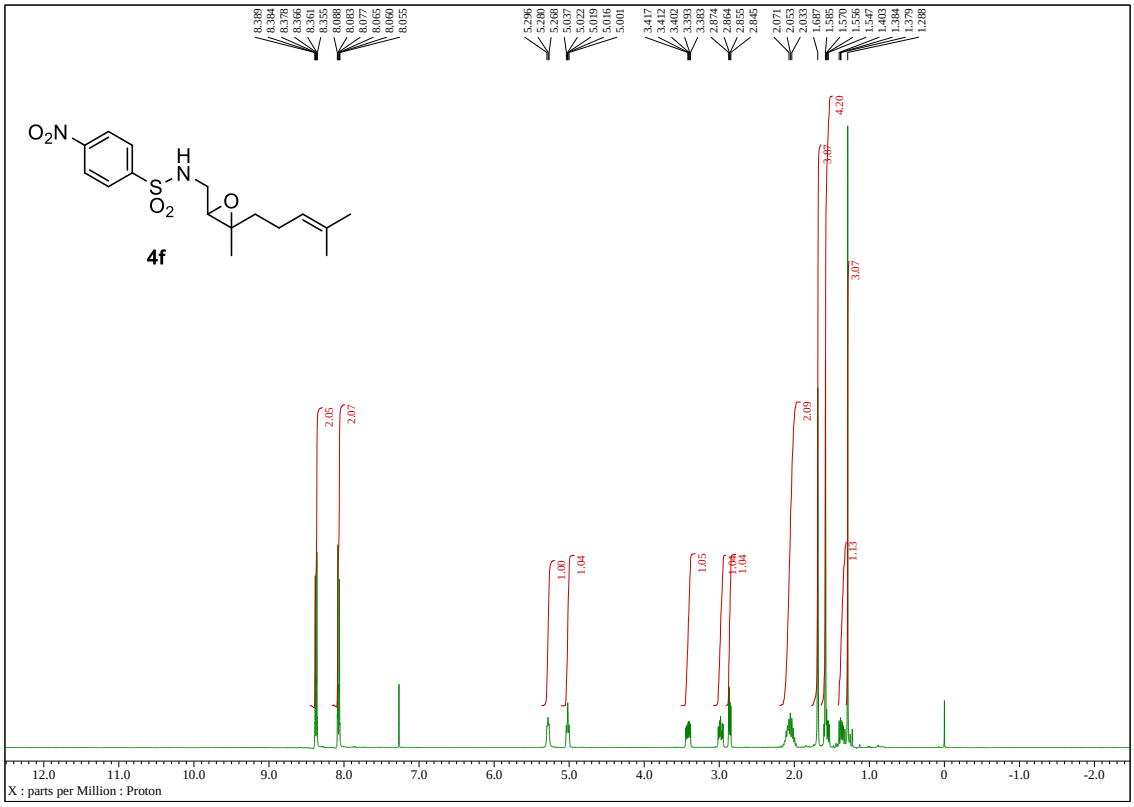
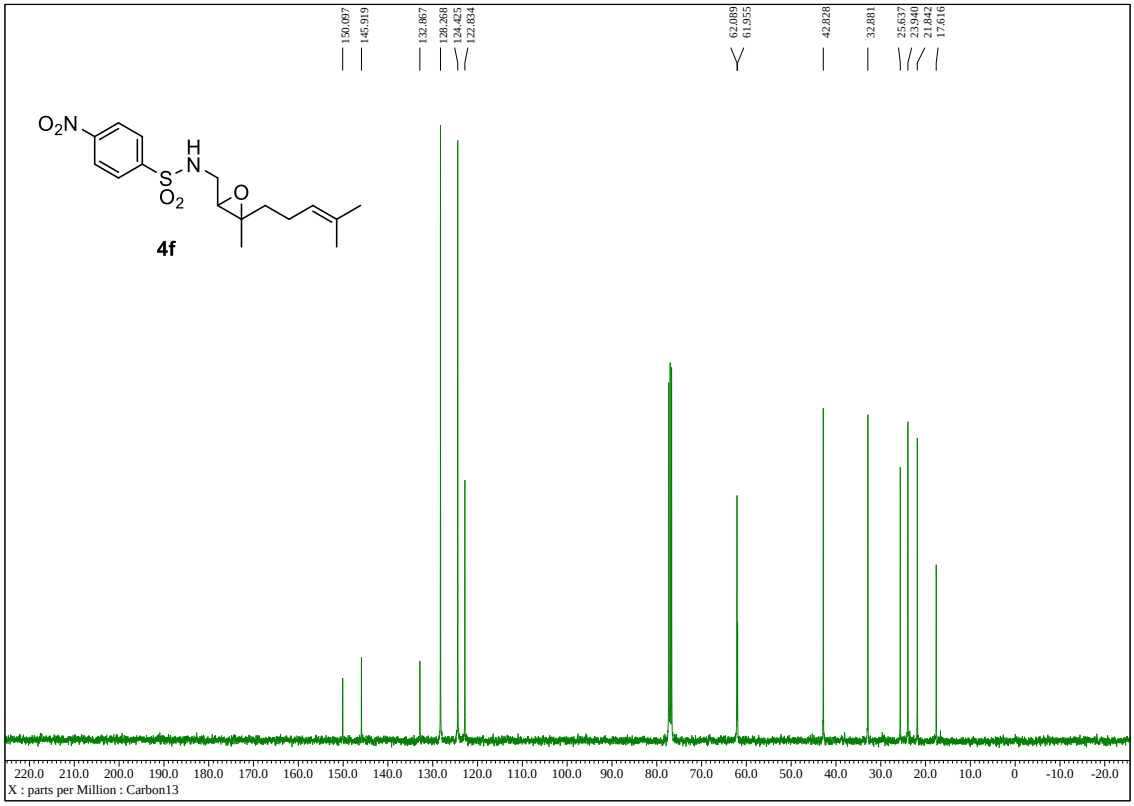
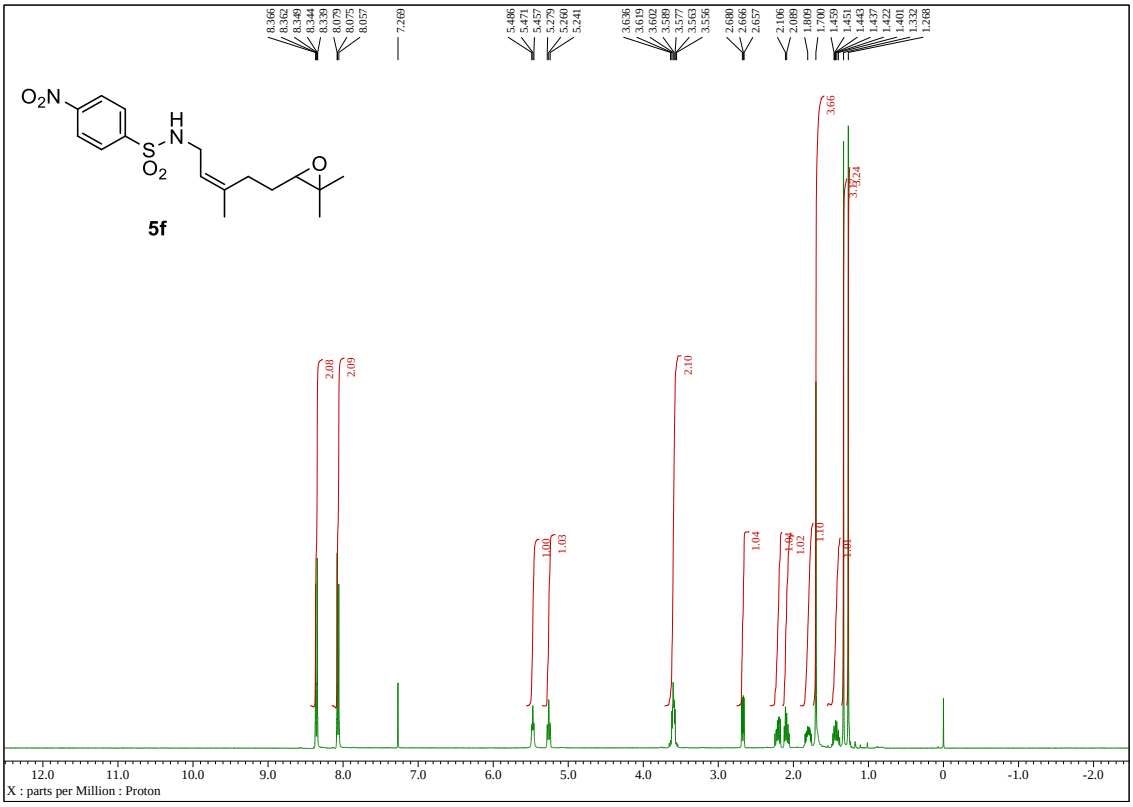
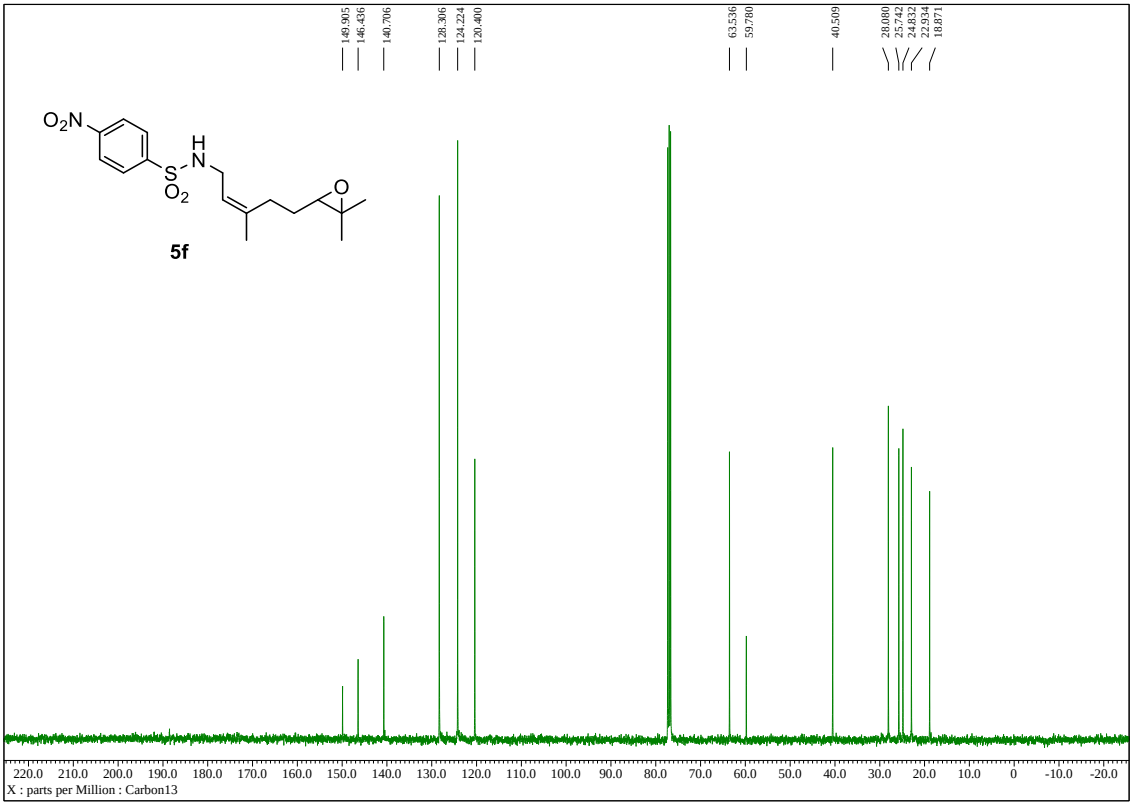
7.746
7.312
7.292
5.223
5.204
5.185
4.825
4.810
4.796
3.550
3.533
3.516
2.646
2.634
2.626
2.614
2.428
2.122
1.677
1.665
1.651
1.634
1.622
1.630
1.495
1.476
1.304
1.237
4.75
3.10
2.04
2.04
2.05
2.02
1.00
0.96
1.05
1.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton

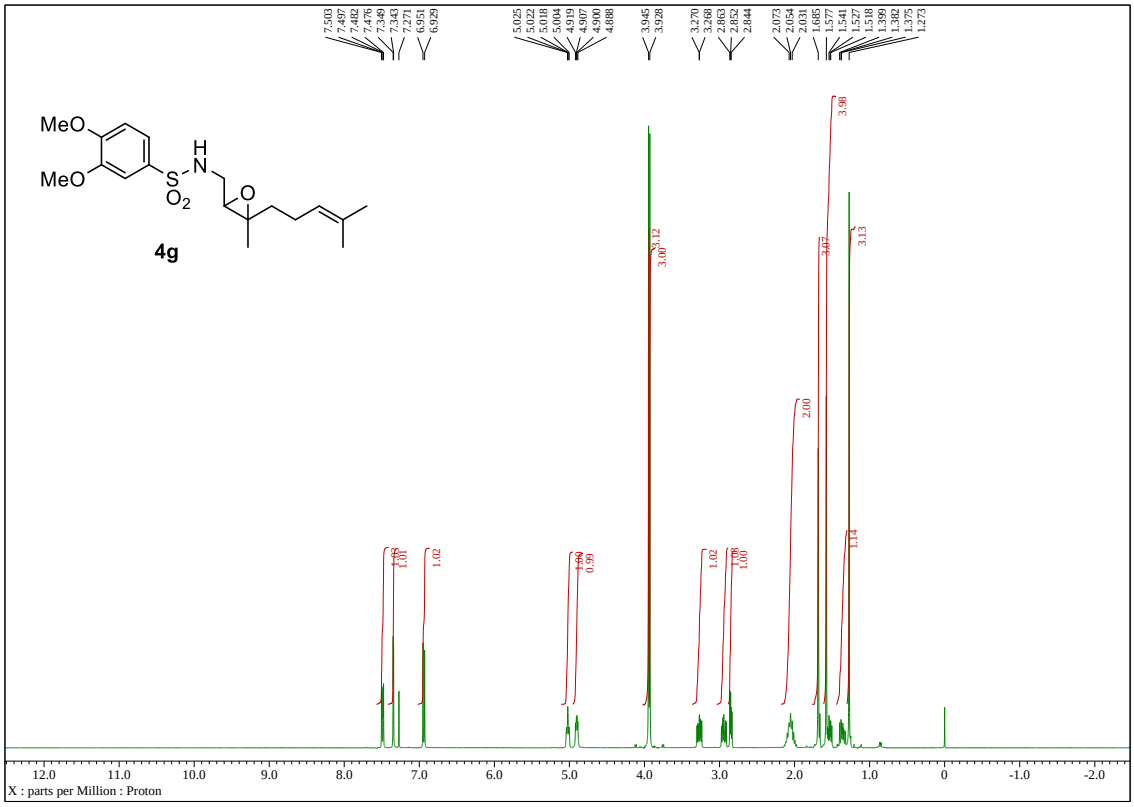

Me
S
O2
H
N
O
5e
142.198
140.016
137.170
129.580
127.146
120.621
63.565
58.937
40.519
28.272
26.441
24.803
23.059
21.478
18.747
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13

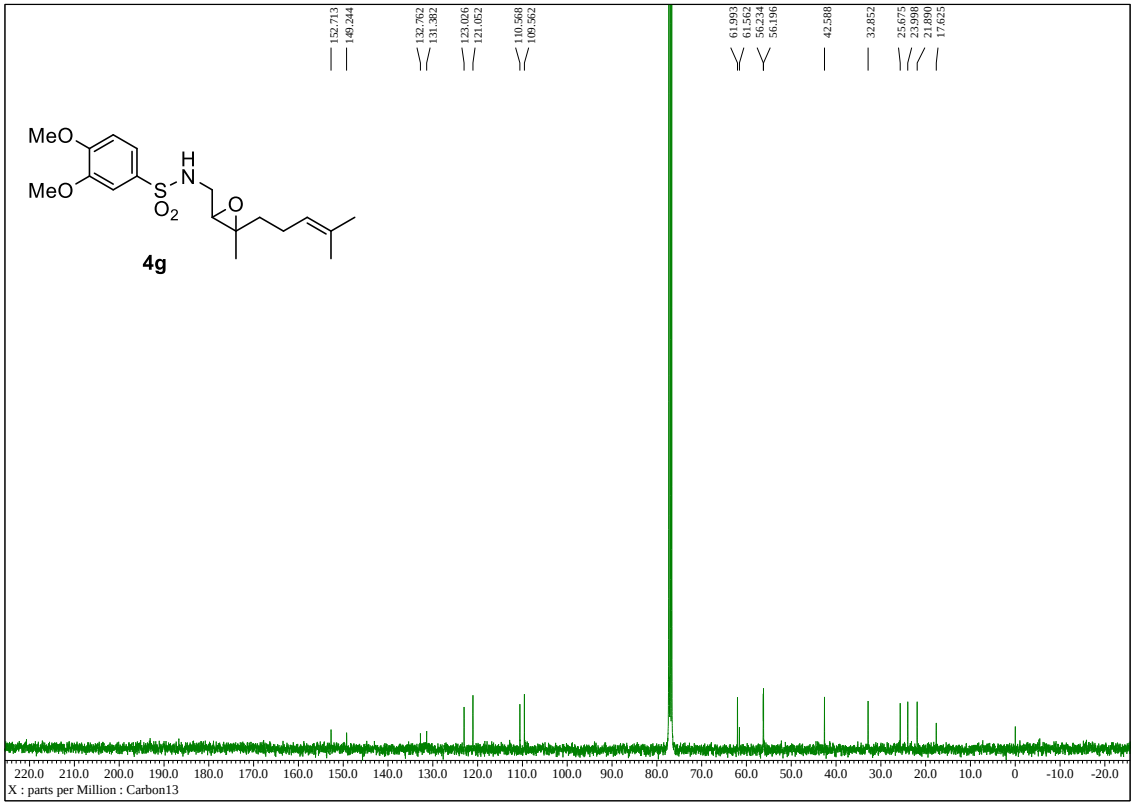

4f
X : parts per Million : Proton

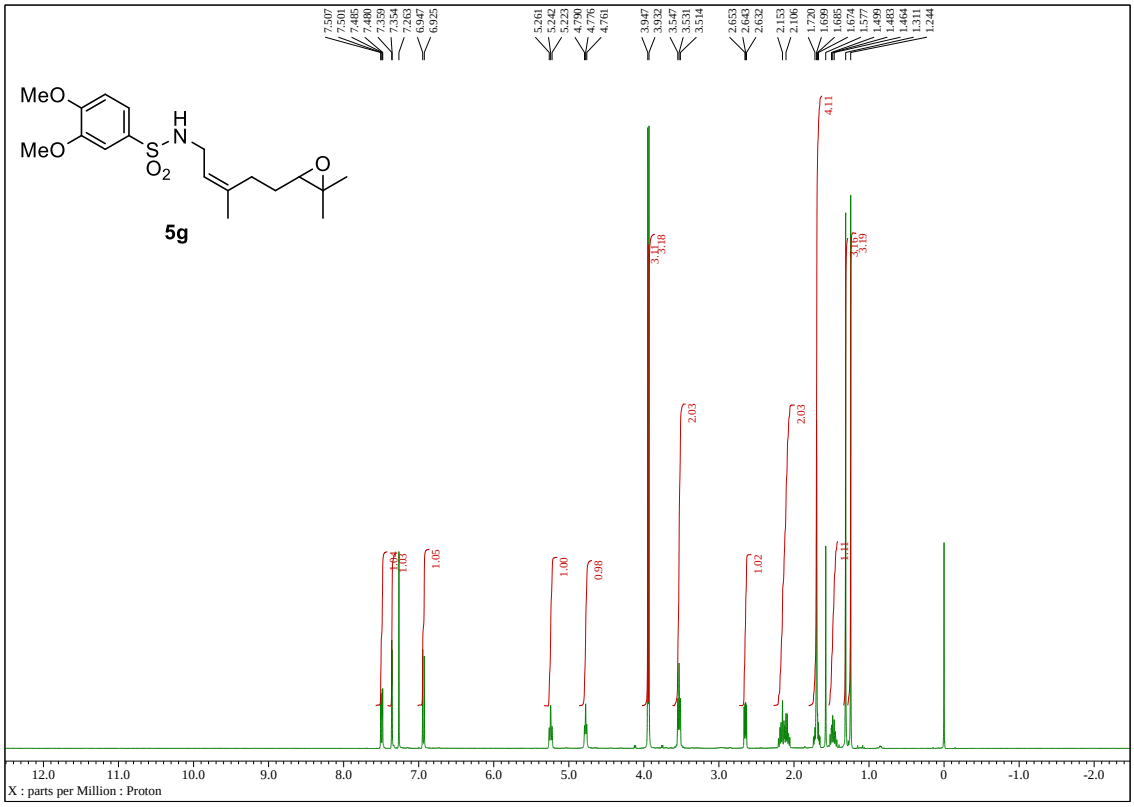

4f
X : parts per Million : Carbon13

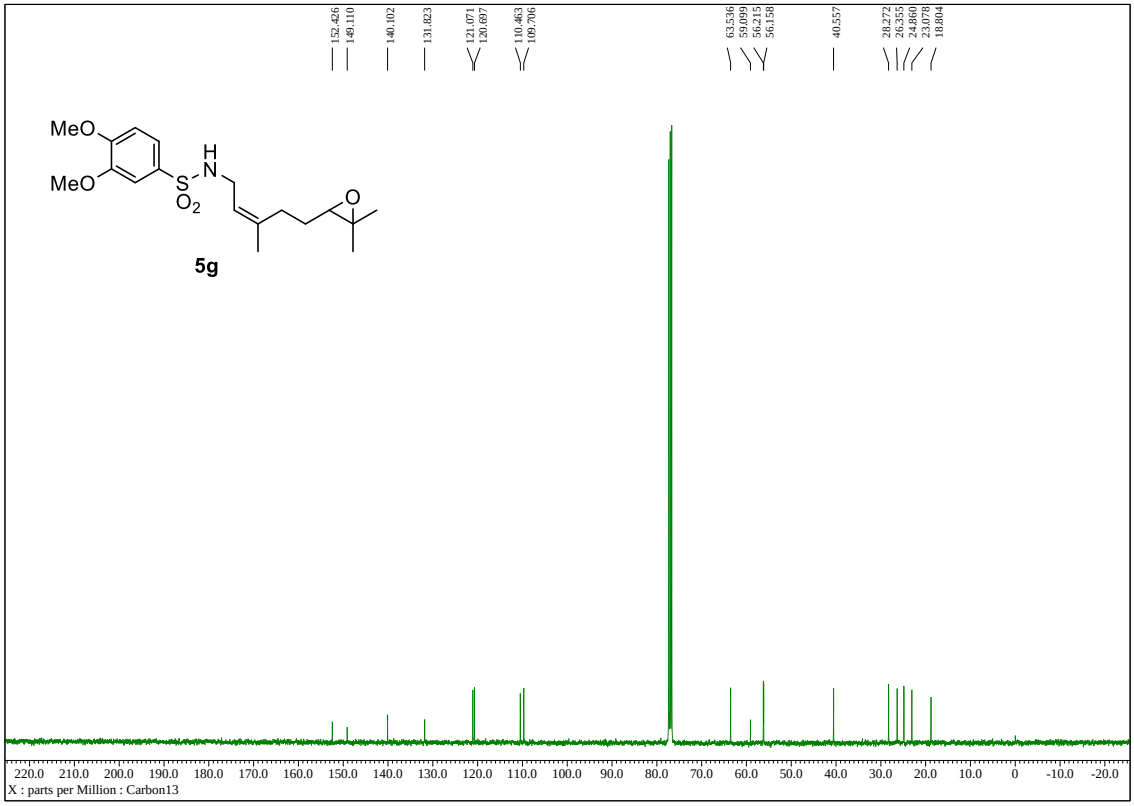

5f
X : parts per Million : Proton

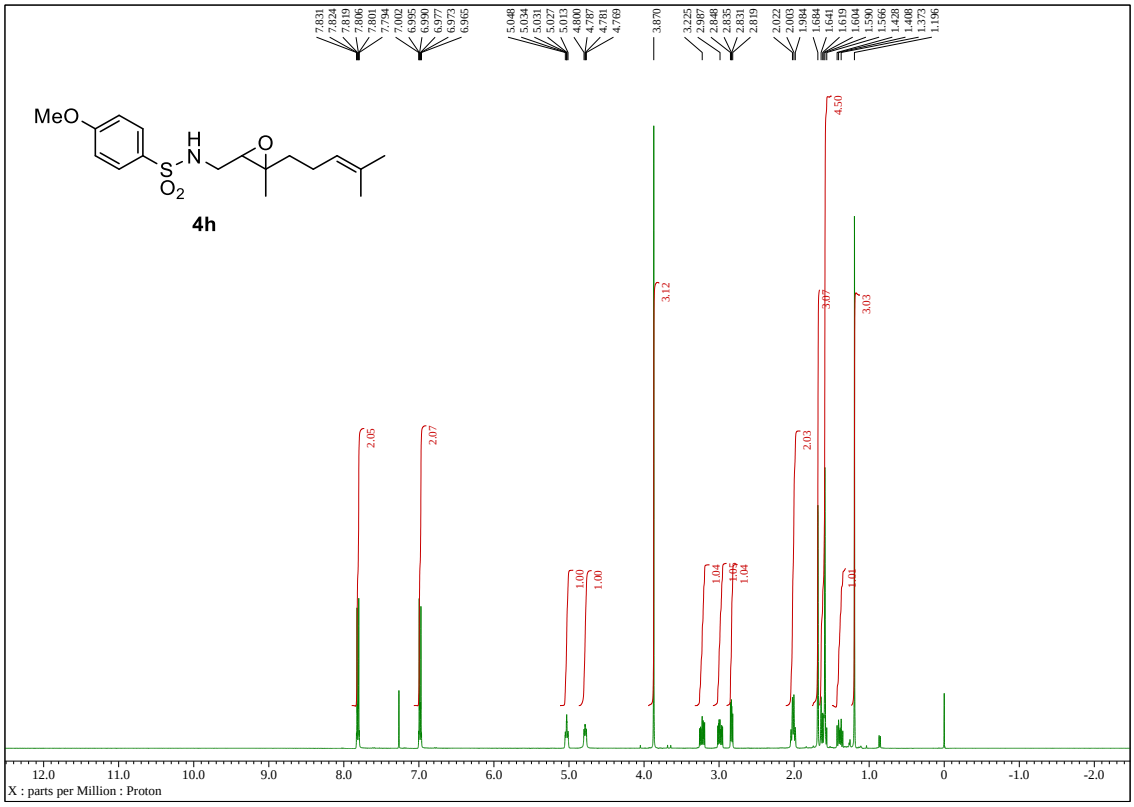

5f
X : parts per Million : Carbon13

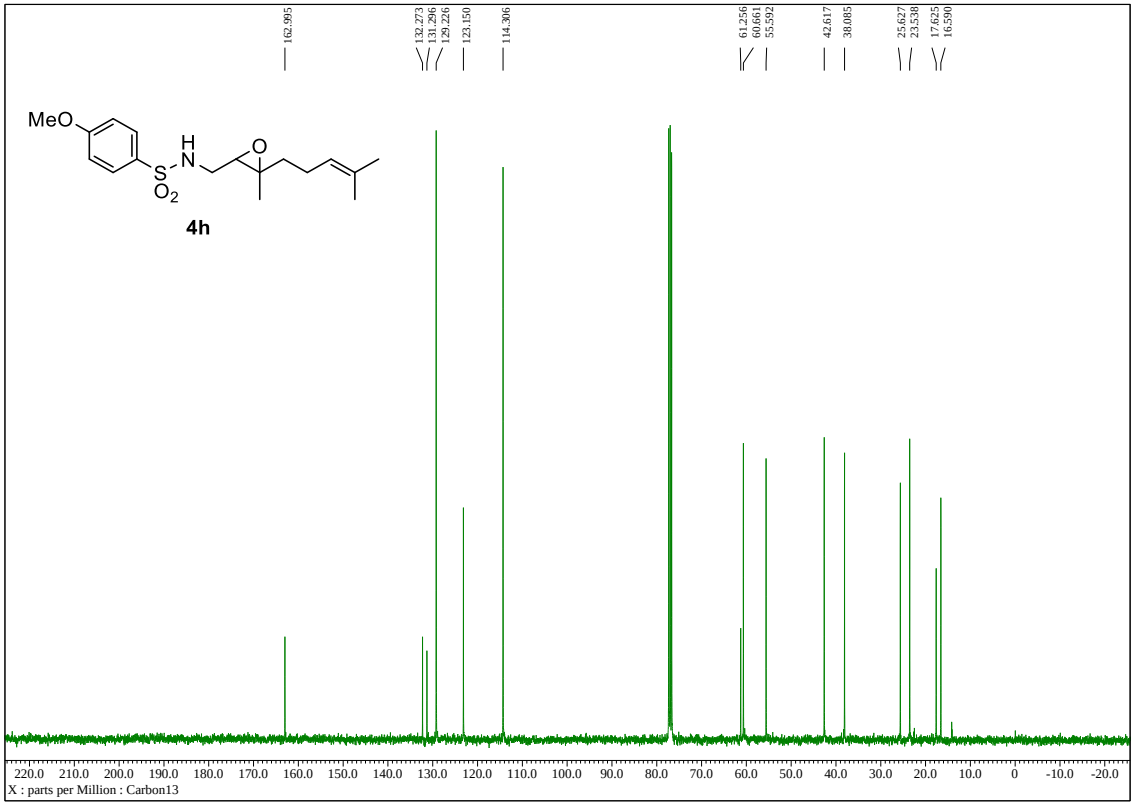

MeO
MeO
H
N
S
O2
O
4g
X : parts per Million : Proton

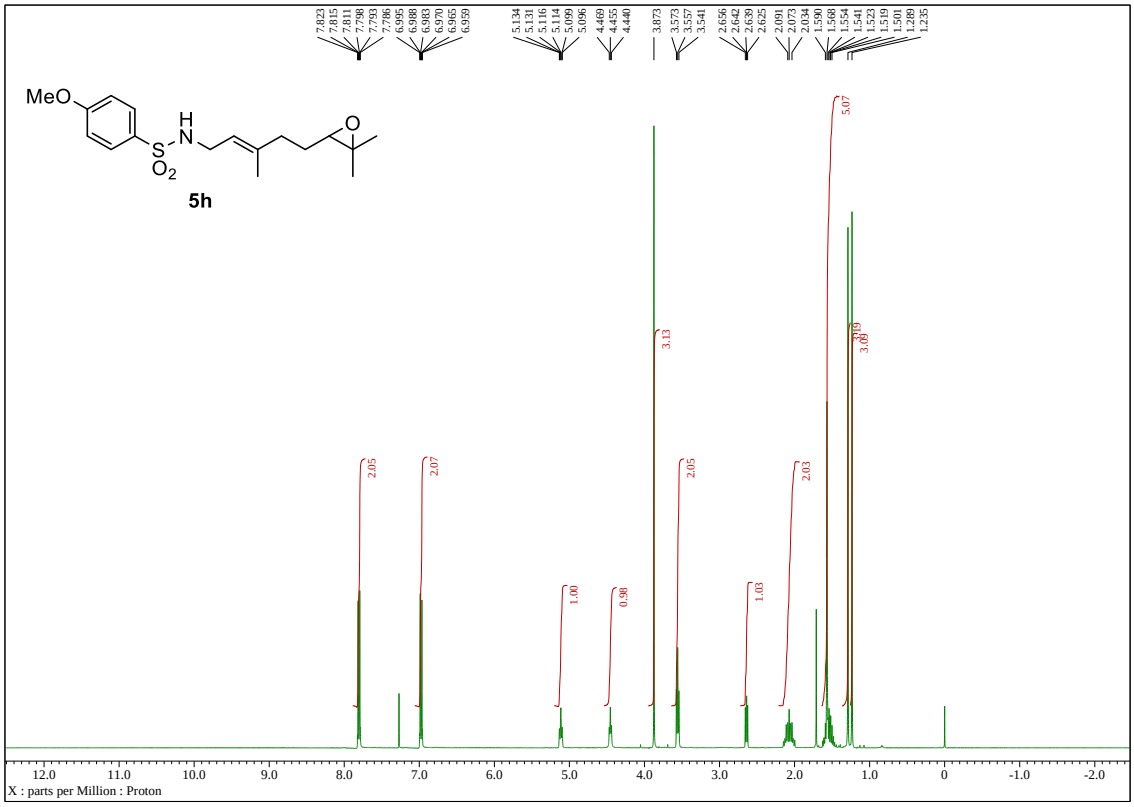

MeO
MeO
H
N
S
O2
O
4g
X : parts per Million : Carbon13

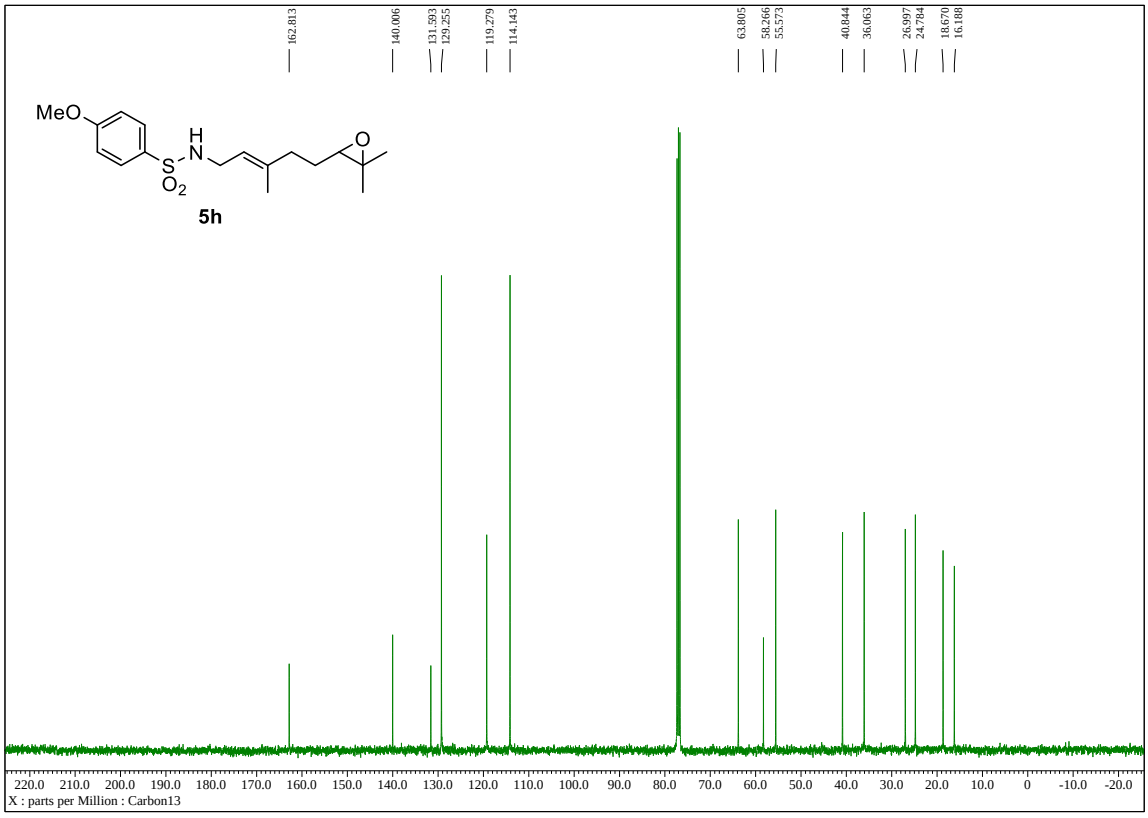

MeO
MeO
H
N
S
O2
O
5g
X : parts per Million : Proton

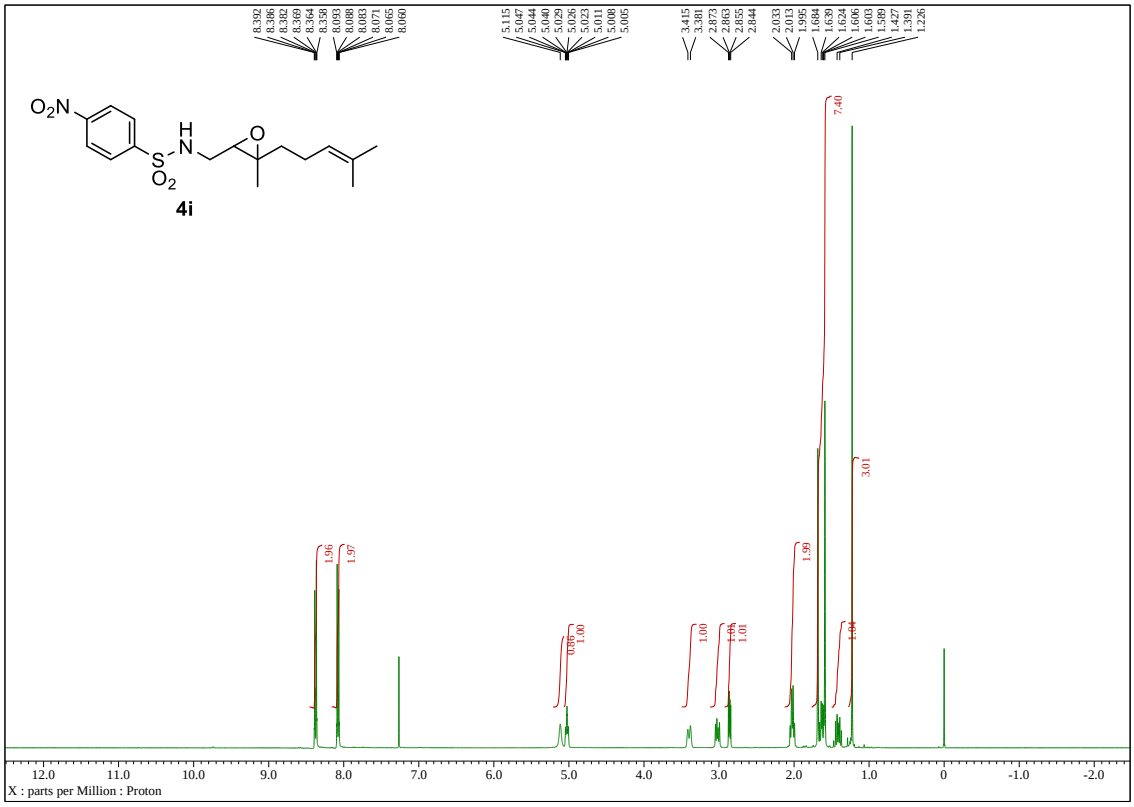

MeO
MeO
H
N
S
O2
O
5g
X : parts per Million : Carbon13

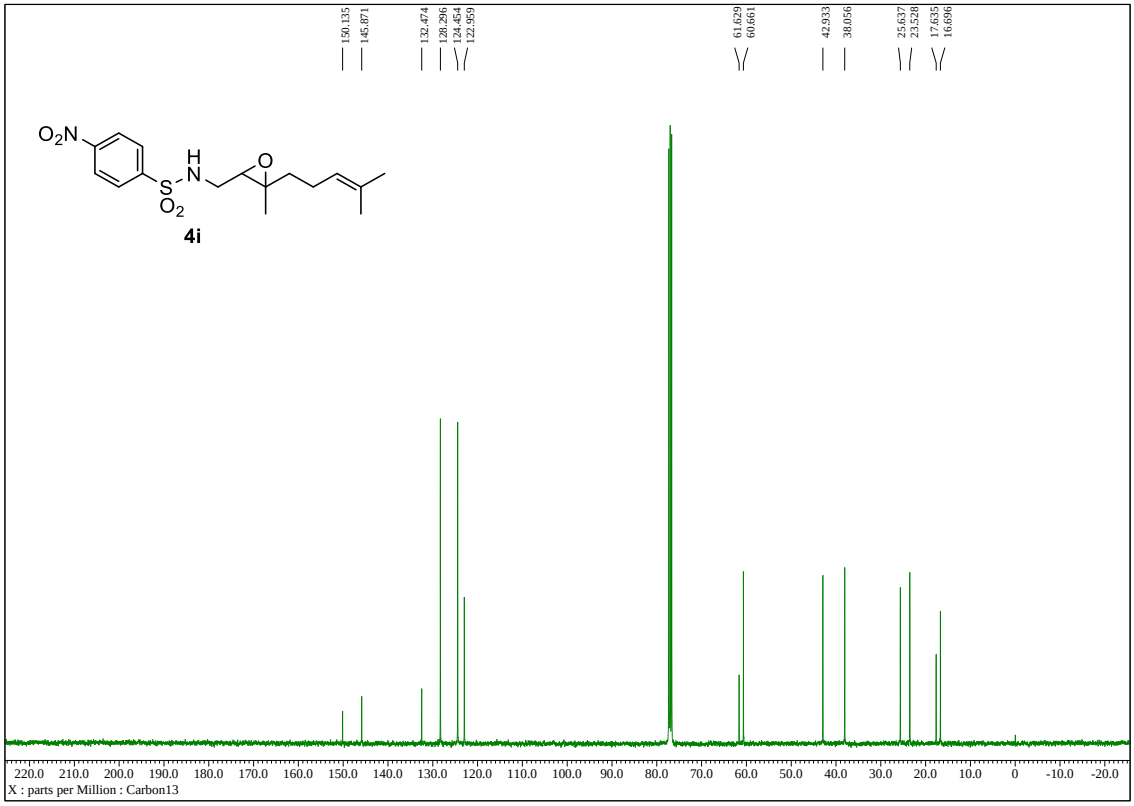

4h
X : parts per Million : Proton

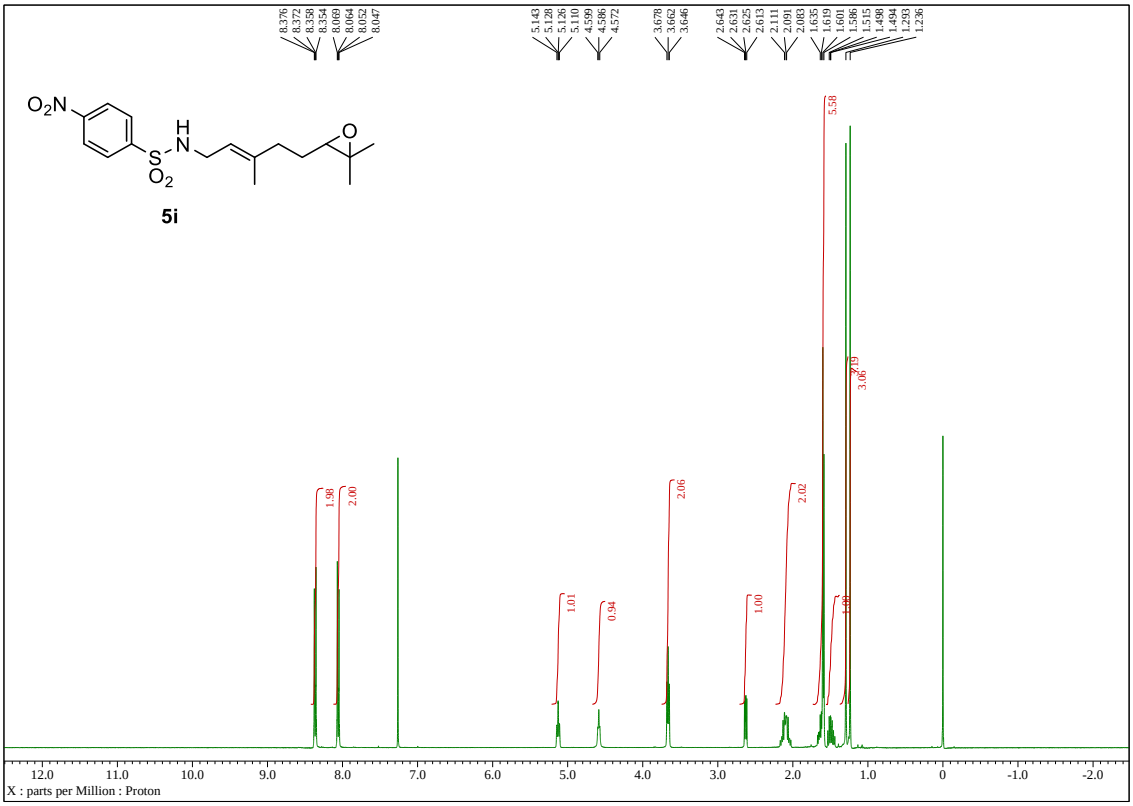

4h
X : parts per Million : Carbon13

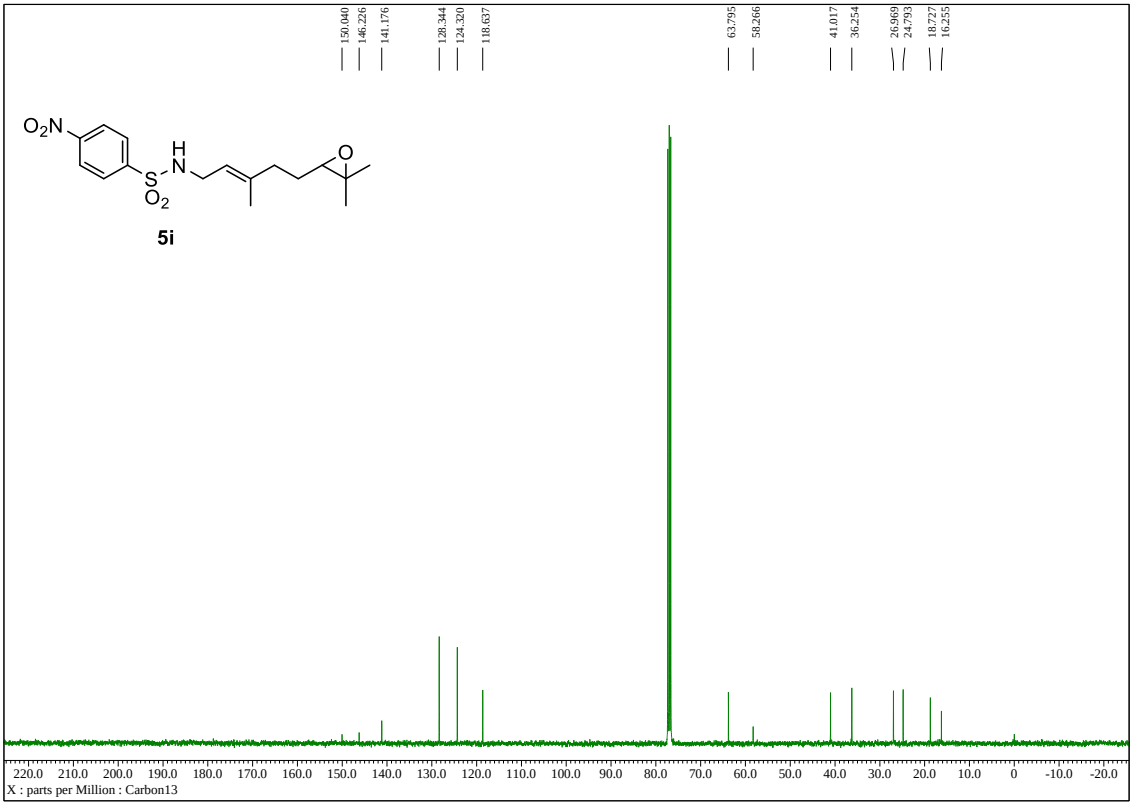

7.823
7.815
7.811
7.798
7.793
7.786
6.995
6.988
6.983
6.970
6.965
6.959
5.134
5.131
5.116
5.114
5.099
5.096
4.469
4.455
4.440
3.873
3.573
3.557
3.541
2.656
2.642
2.639
2.625
2.091
2.073
2.034
1.590
1.568
1.554
1.541
1.523
1.519
1.501
1.289
1.235
MeO
H
N
S
O2
O
5h
5.07
3.13
3.09
3.00
2.05
2.07
2.05
2.03
1.00
0.98
1.03
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton

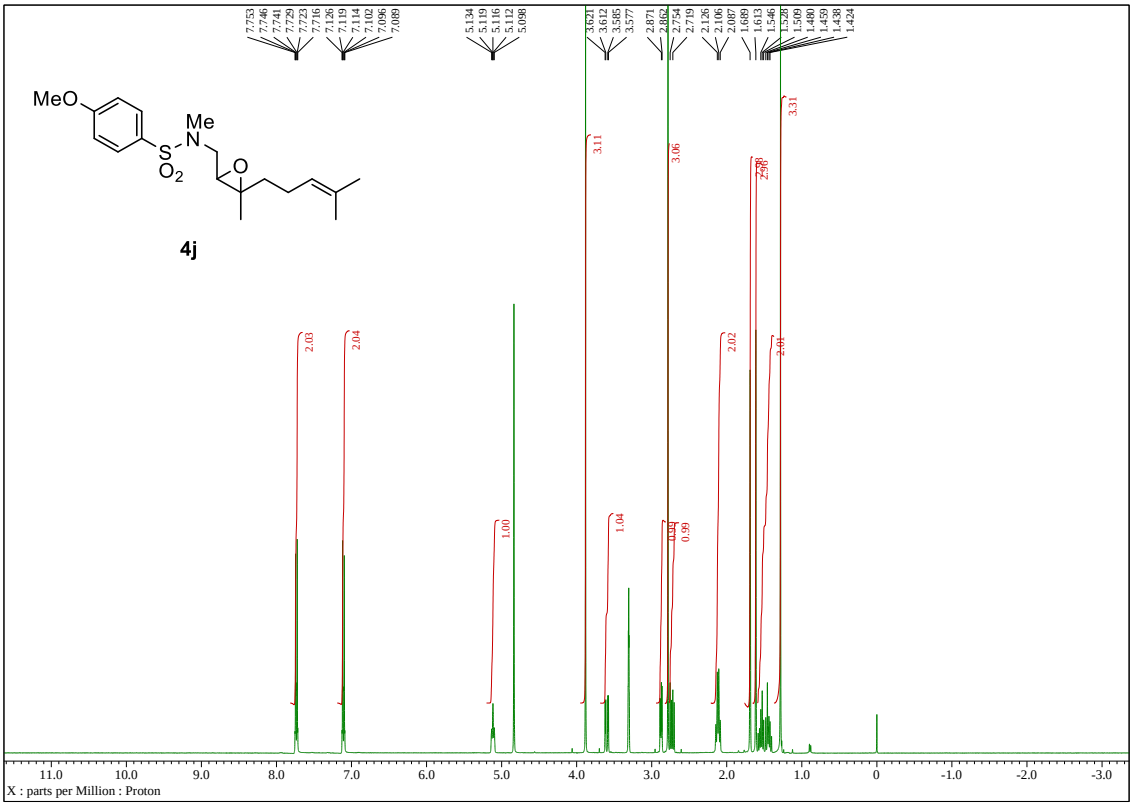

162.813
140.006
131.893
129.255
119.279
114.143
63.805
58.266
55.573
40.844
36.063
26.997
24.784
18.670
16.188
MeO
H
N
S
O2
O
5h
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13

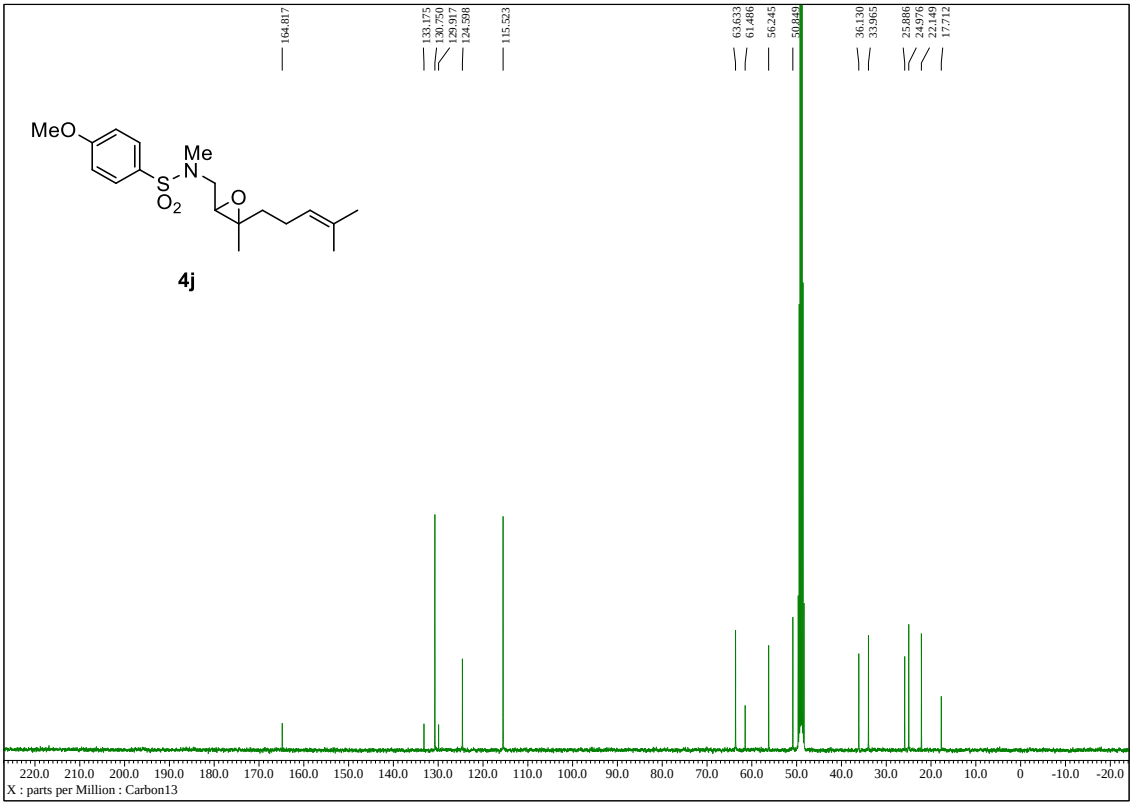

8.392
8.386
8.382
8.369
8.364
8.338
8.093
8.088
8.081
8.071
8.065
8.060
5.115
5.047
5.044
5.040
5.029
5.026
5.023
5.011
5.008
5.005
3.415
3.381
2.873
2.865
2.855
2.844
2.033
2.013
1.995
1.684
1.639
1.624
1.606
1.603
1.589
1.457
1.391
1.226
O2N
H
N
O
S
O2
4i
7.40
3.01
1.96
1.97
1.99
0.98
1.00
1.00
1.06
1.01
1.04
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton

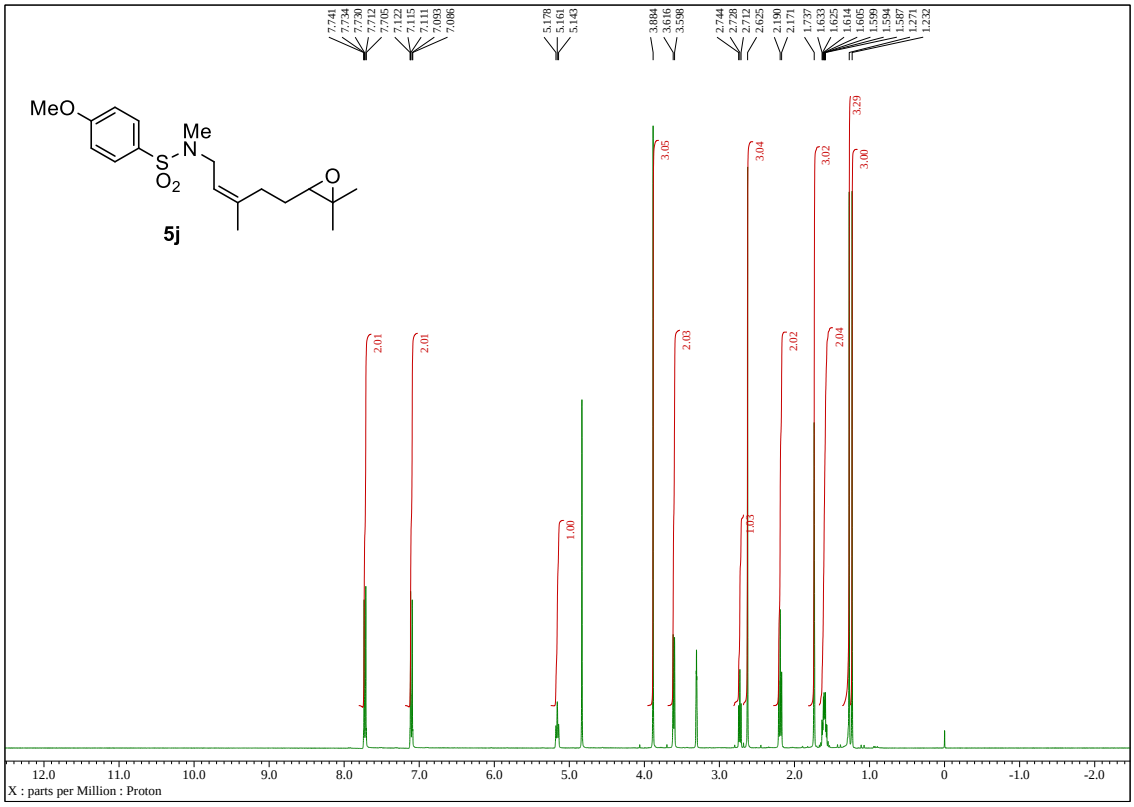

150.135
145.871
132.474
128.296
124.454
122.959
61.629
60.661
42.933
38.056
25.637
23.528
17.635
16.696
O2N
H
N
O
S
O2
4i
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13

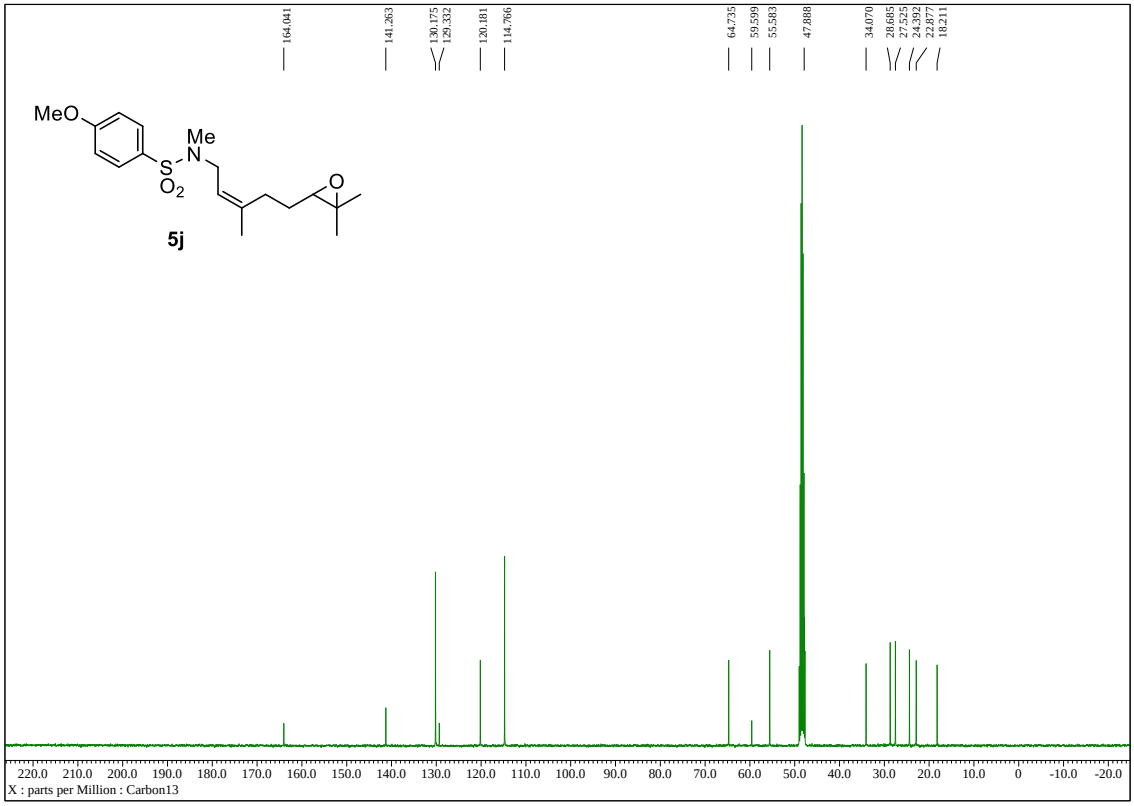

8.376
8.372
8.358
8.354
8.069
8.064
8.052
8.047
5.143
5.128
5.126
5.110
4.599
4.586
4.572
3.678
3.662
3.646
2.643
2.631
2.625
2.613
2.111
2.091
2.083
1.635
1.619
1.601
1.586
1.515
1.490
1.494
1.293
1.236
O2N
H
N
S
O2
O
5i
5.58
3.09
3.08
1.98
2.00
2.06
2.02
1.01
0.94
1.00
1.08
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton


150.040
146.226
141.176
128.344
124.320
118.637
63.795
58.266
41.017
36.254
26.969
24.793
18.727
16.255
O2N
H
N
S
O2
O
5i
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : Carbon13

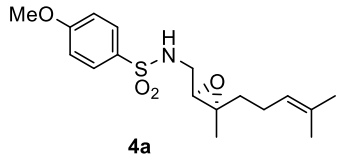

MeO
Me
N
S
O2
O
4j
X : parts per Million : Proton


MeO
Me
N
S
O2
O
4j
X : parts per Million : Carbon13

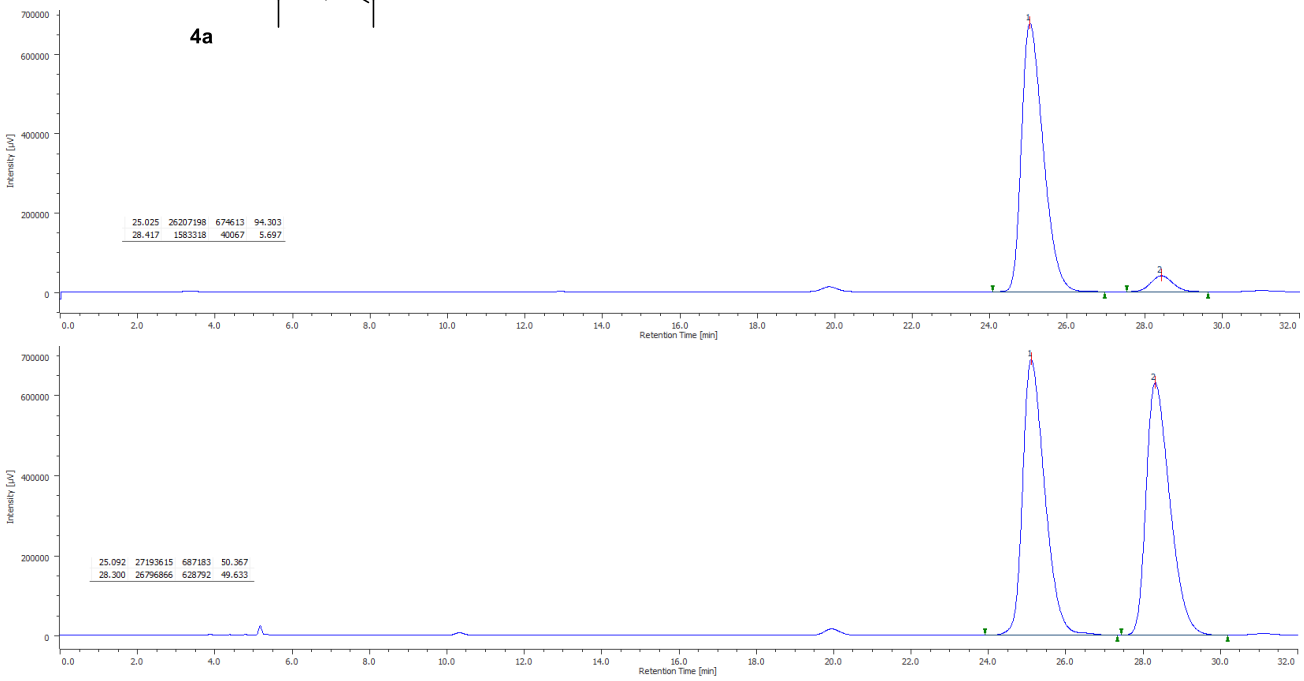

7.741
7.734
7.730
7.712
7.705
7.122
7.115
7.111
7.093
7.086
5.178
5.161
5.143
3.884
3.616
3.598
2.744
2.728
2.712
2.625
2.190
2.171
1.737
1.633
1.625
1.614
1.605
1.599
1.594
1.587
1.271
1.232
MeO
Me
N
S
O2
O
5j
2.01
2.01
1.00
2.03
3.05
1.03
3.04
2.02
3.02
2.04
3.29
3.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton

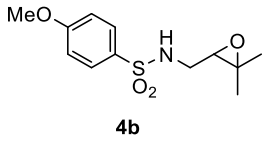

164.041
141.263
130.175
129.352
120.181
114.766
64.735
59.599
55.583
47.888
34.070
28.685
27.525
24.392
22.877
18.211
MeO
Me
N
S
O2
O
5j
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

5. HPLC data

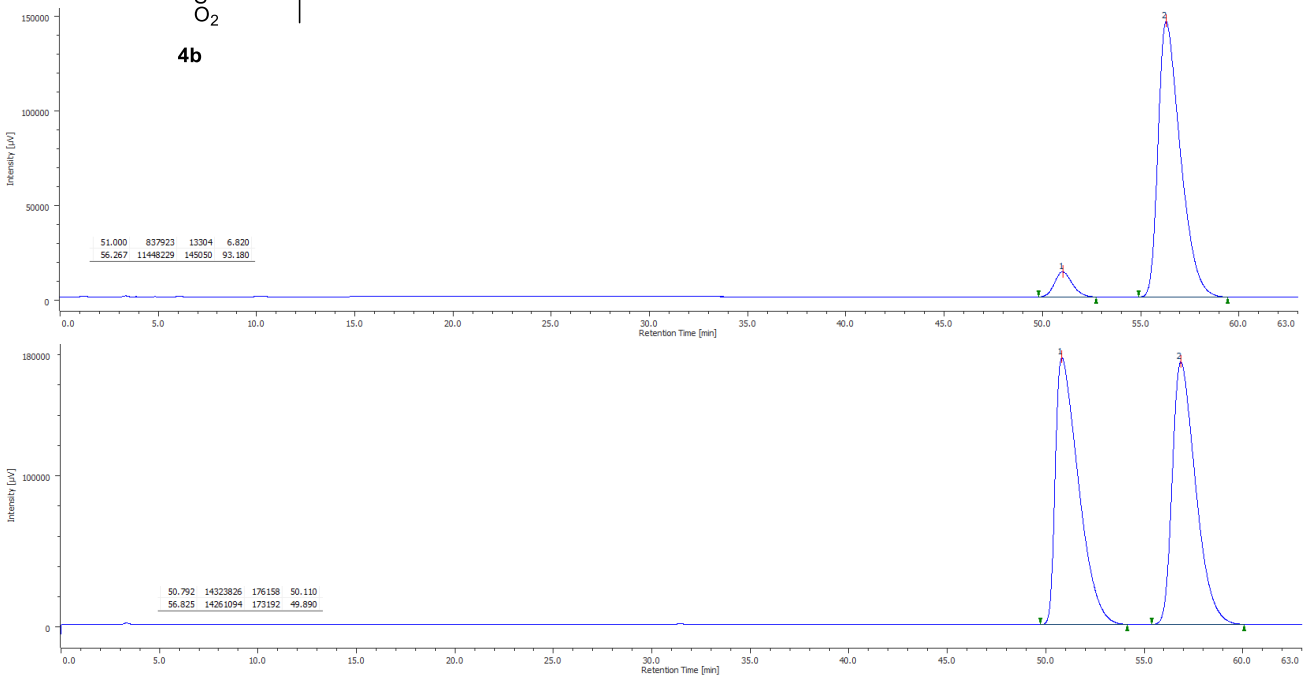


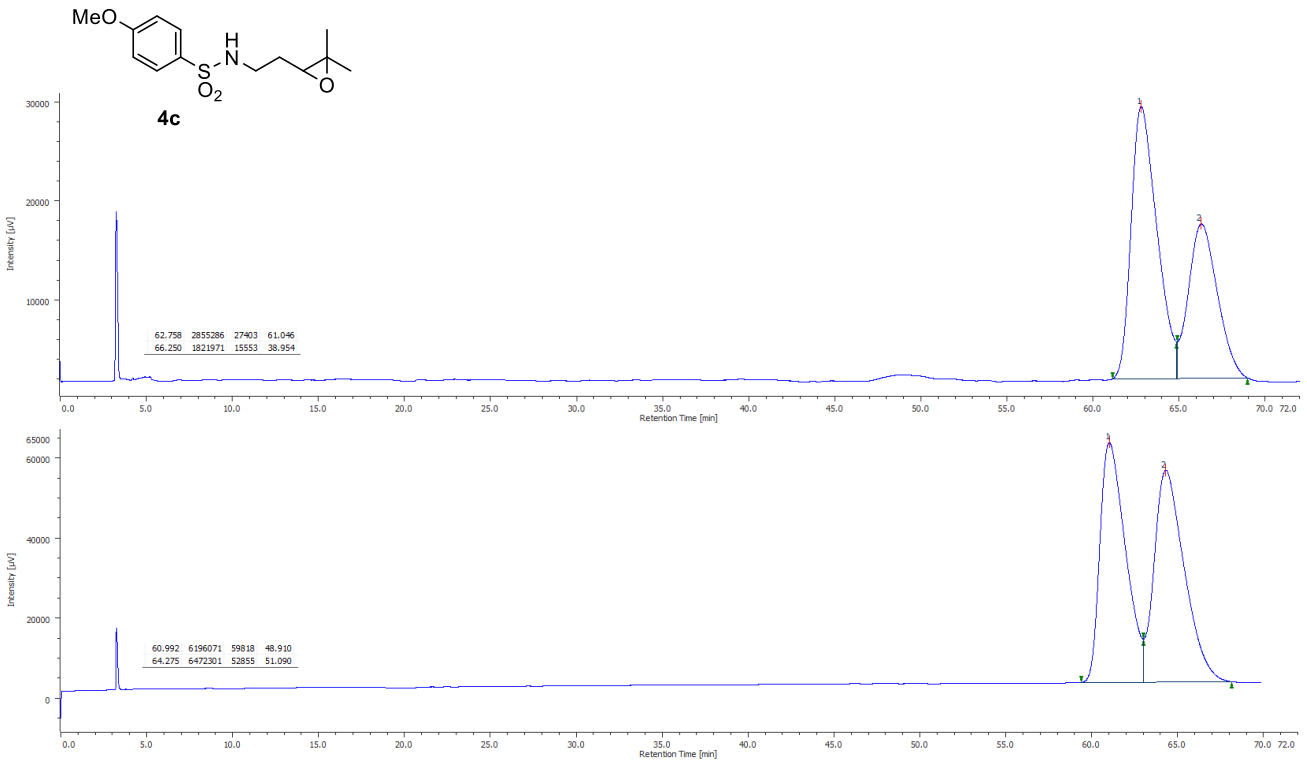
4a

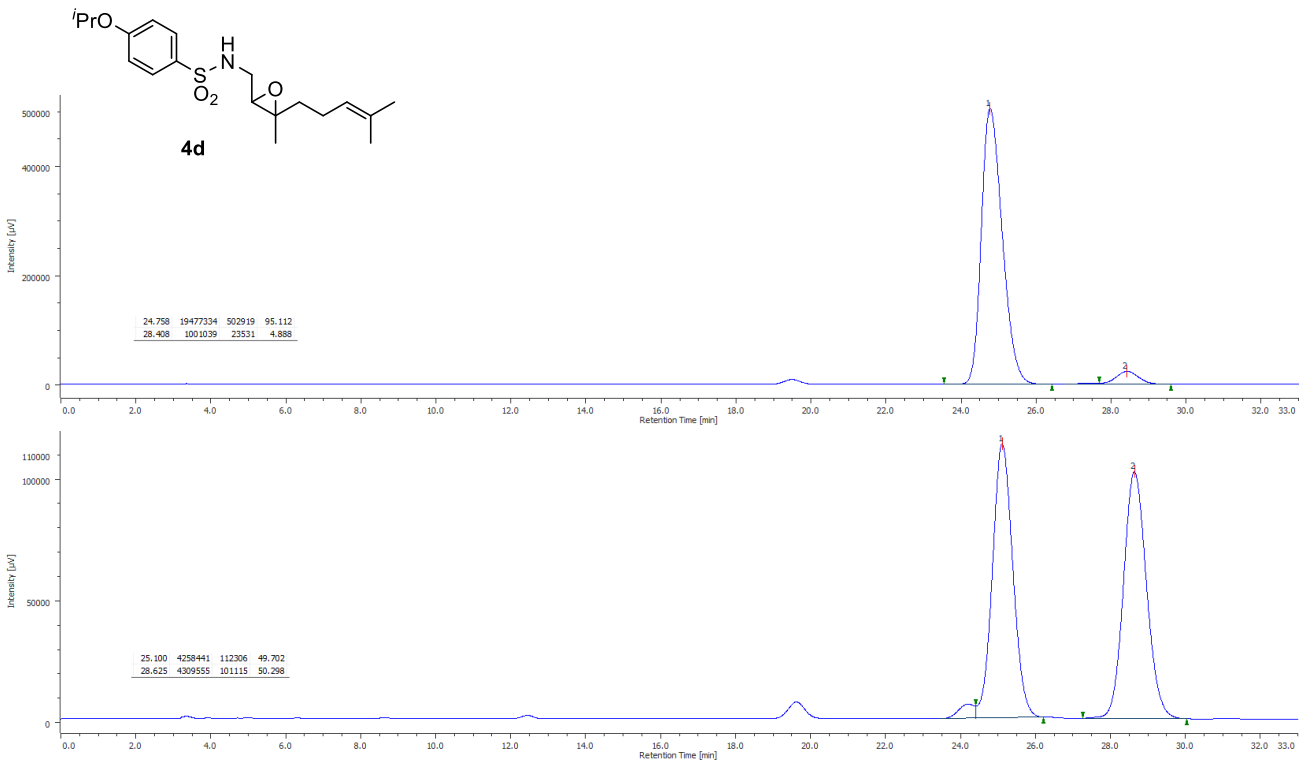


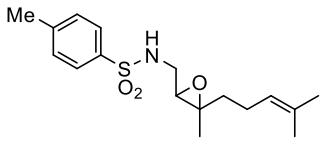


4b

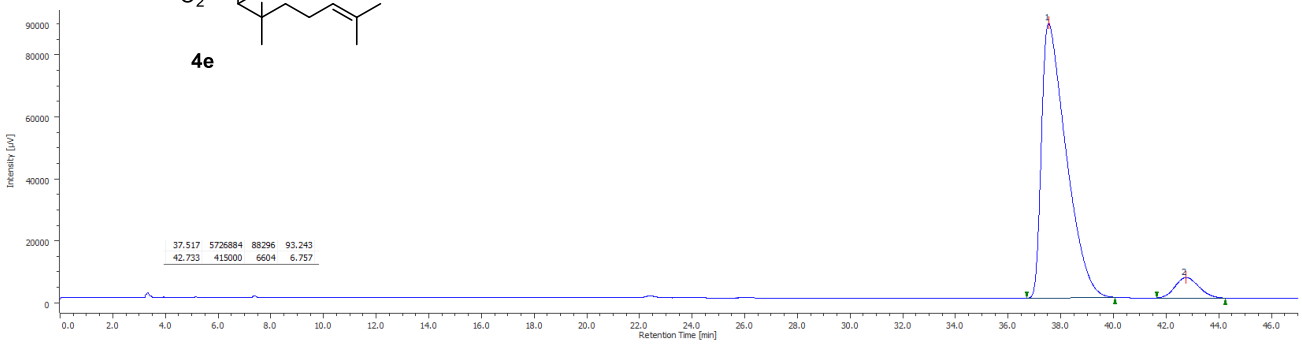


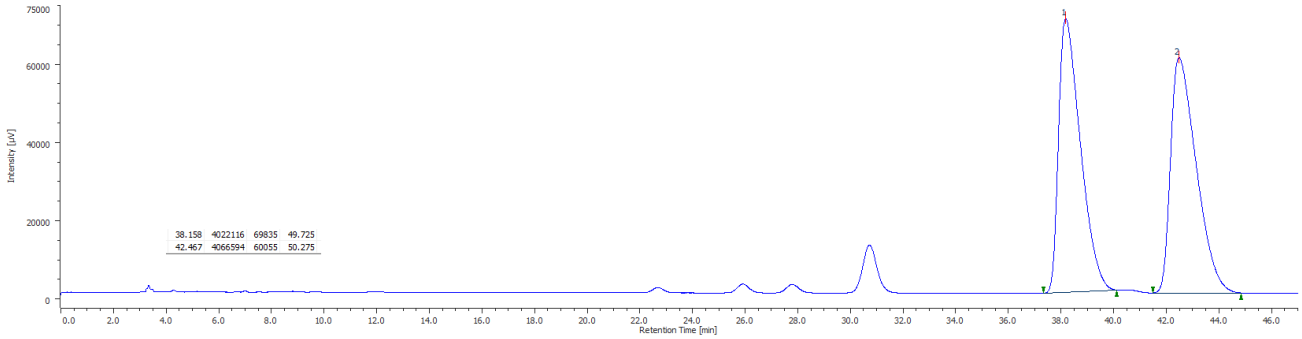

MeO
H
N
S
O2
O
4c
Intensity [μV]
Retention Time [min]
62.758 2855286 27403 61.046
66.250 1821971 15553 38.954
60.992 6196071 59818 48.910
64.275 6472301 52855 51.090

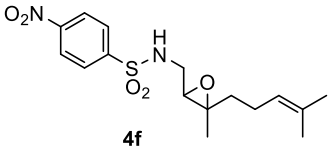

iPrO
H
N
S
O2
O
4d
Intensity [μV]
Retention Time [min]
24.758 19477334 502919 95.112
28.408 1001039 23531 4.888
25.100 4258441 112306 49.702
28.625 4309555 101115 50.298


Me
H
N
S
O2
O

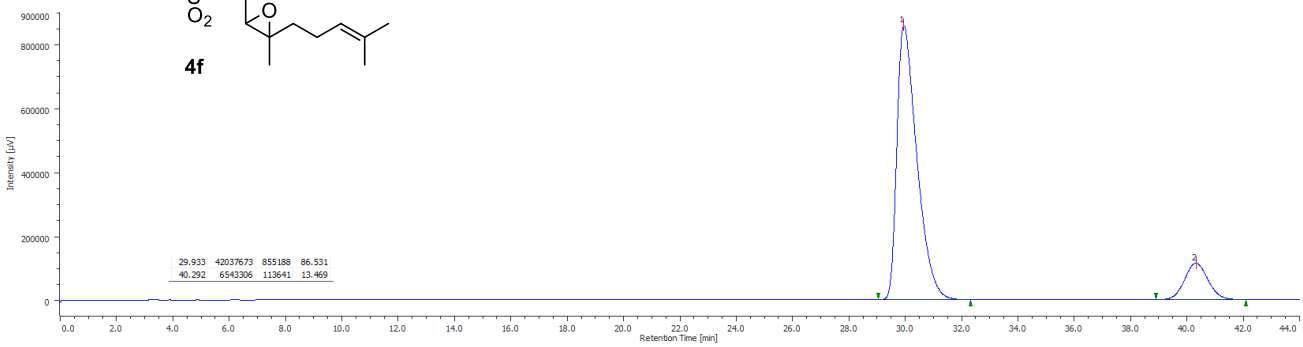
4e

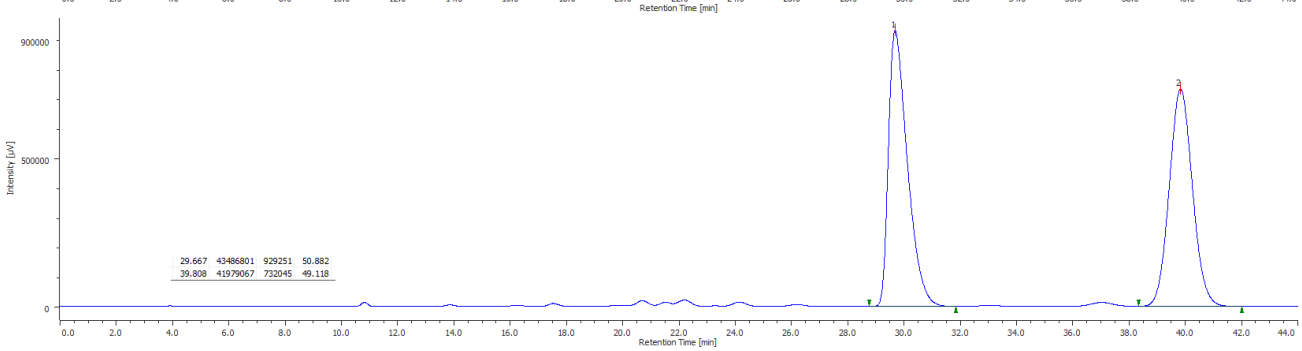

Intensity [μV]
Retention Time [min]
37.517 5726884 88296 93.243
42.733 415000 6604 6.757

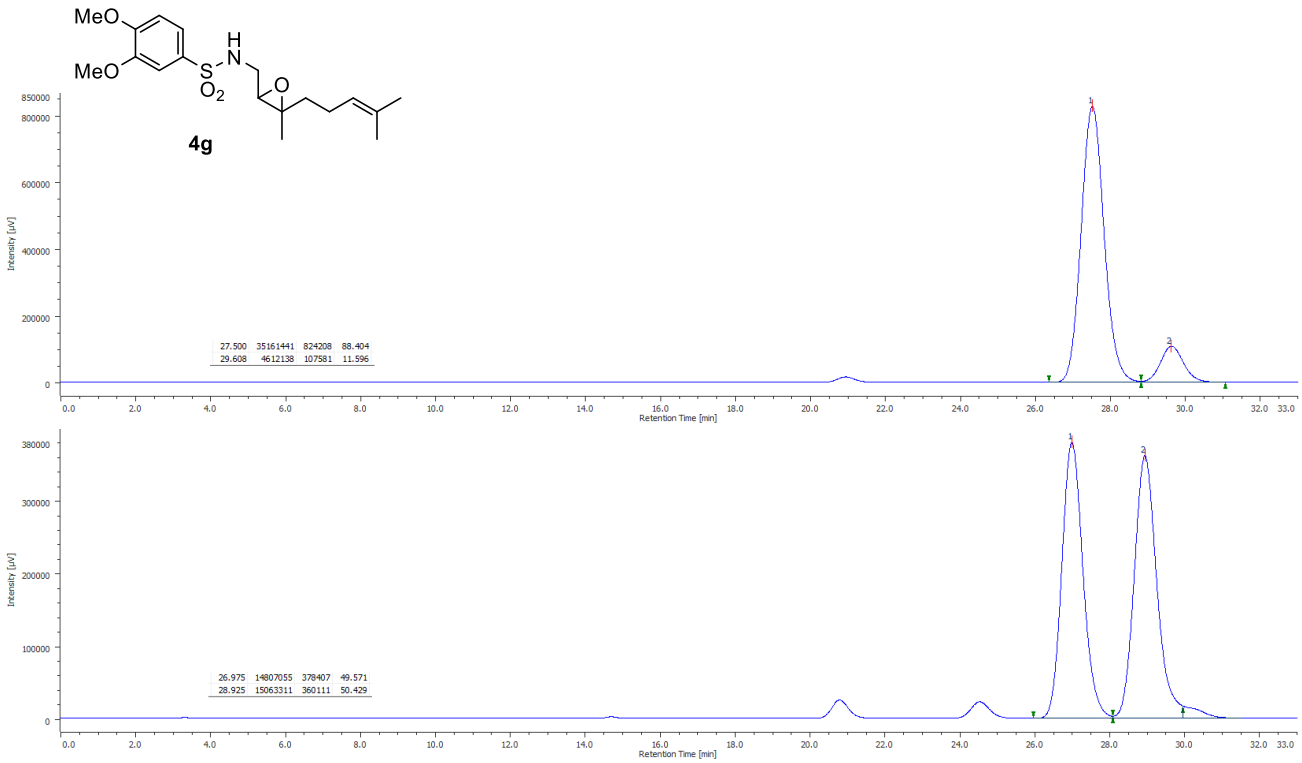

Intensity [μV]
Retention Time [min]
38.158 4022116 69835 49.725
42.467 4066594 60055 50.275

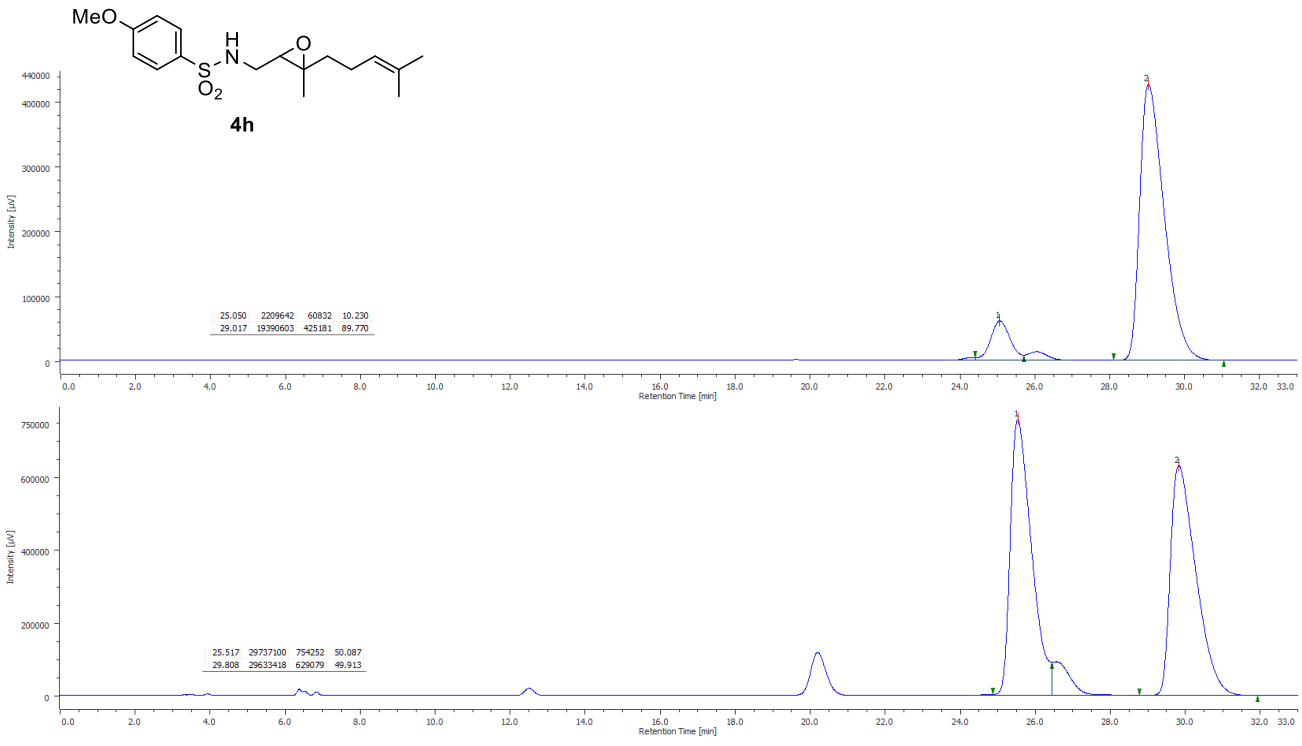

O2N
H
N
S
O2
O

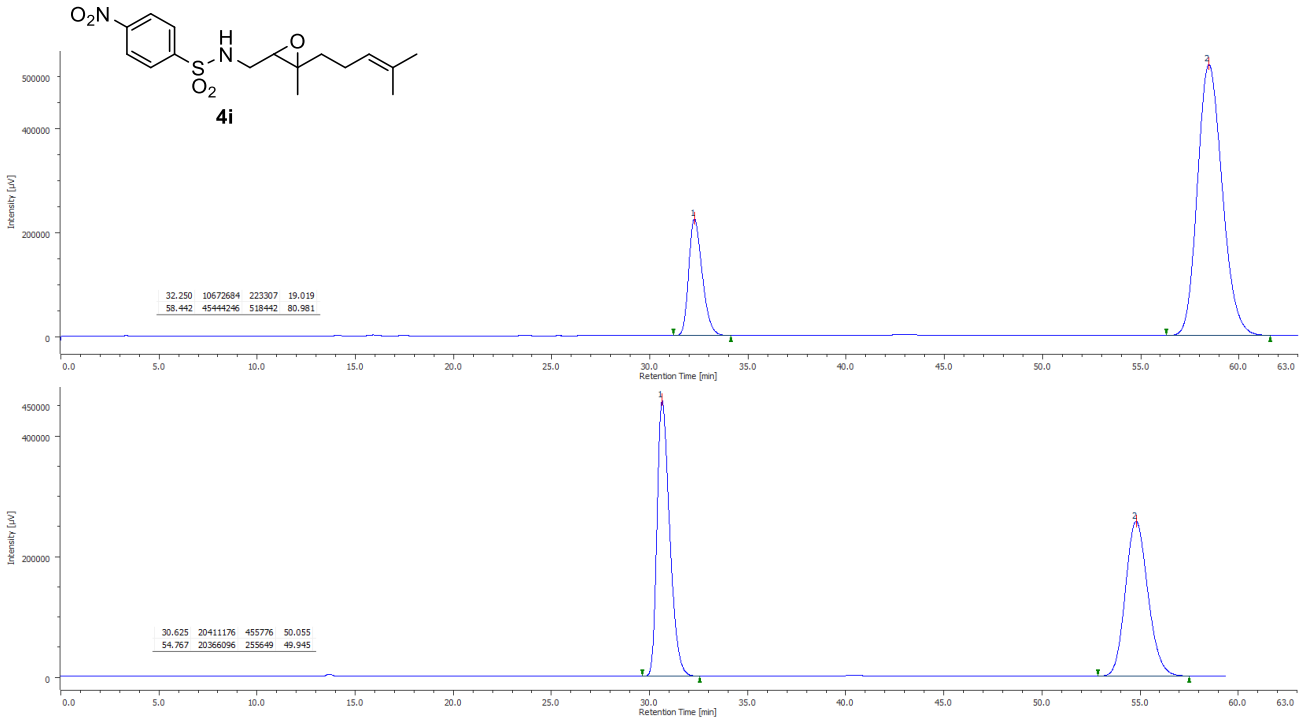
4f

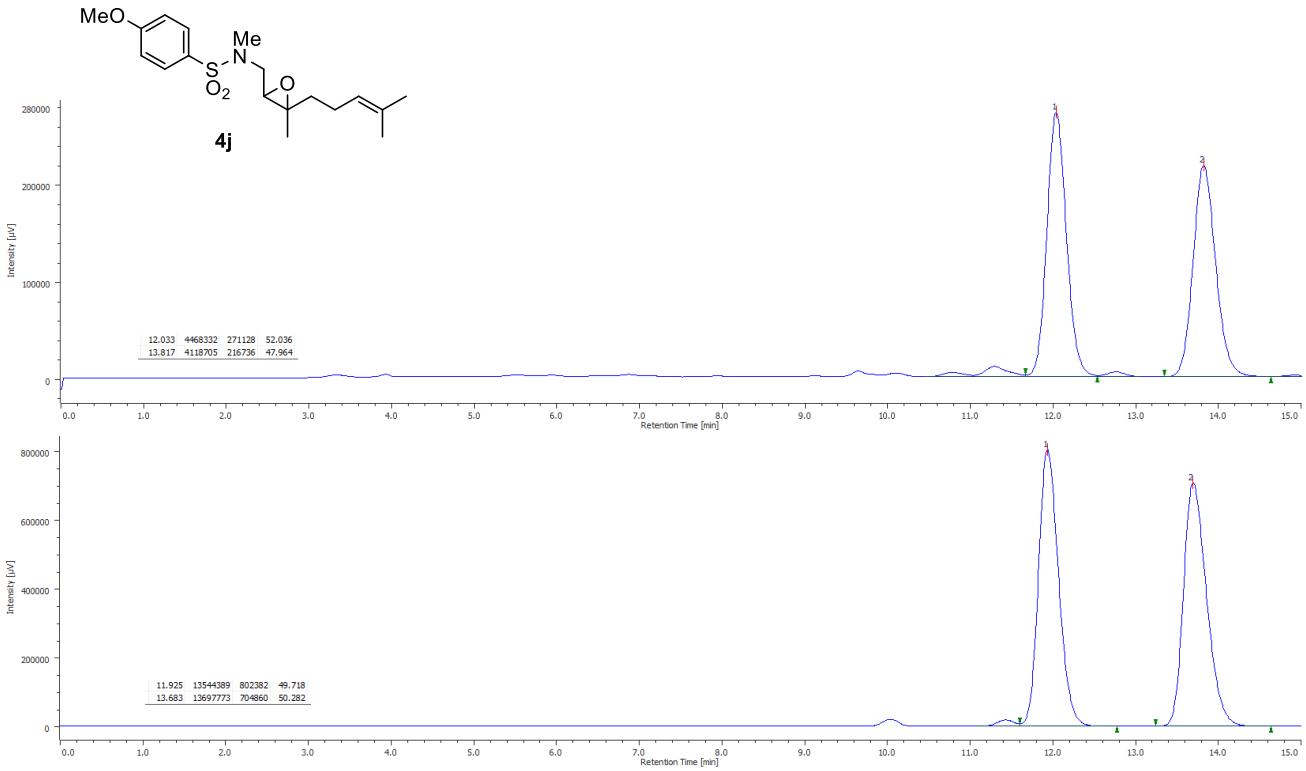

Intensity [μV]
Retention Time [min]
29.933 42037673 855188 86.531
40.292 6543306 113641 13.469


Intensity [μV]
Retention Time [min]
29.667 43486801 929251 50.882
39.808 41979067 732045 49.118


MeO
MeO
H
N
S
O2
O
4g
Intensity [μV]
Retention Time [min]
27.500 35161441 824208 88.404
29.608 4612138 107581 11.596
26.975 14807055 378407 49.571
28.925 15063311 360111 50.429


MeO
H
N
S
O2
O
4h
Intensity [μV]
Retention Time [min]
25.050 2209642 60832 10.230
29.017 19390603 425181 89.770
25.517 29737100 754252 50.087
29.808 29633418 629079 49.913


4i
Intensity [μV]
Retention Time [min]
32.250 10672684 223307 19.019
58.442 45444246 518442 80.981
30.625 20411176 455776 50.055
54.767 20366096 255649 49.945


4j
Intensity [μV]
Retention Time [min]
12.033 4468332 271128 52.036
13.817 4118705 216736 47.964
11.925 13544389 802382 49.718
13.683 13697773 704860 50.282