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Supplemental information

Antrodiellin B/hypnophilin/coriolin and strained 5/5/5 and 5/6/4 skeletons via [5+2+1]/epoxidation/transannular radical cyclization

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Supplemental Experimental Procedures

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Abbreviations

Å	Angstrom
Ac	Acetyl
Bu	Butyl
atm	Atmosphere
brsm	based on recovered starting materials
CBS	Corey-Bakshi-Shibata reagent
DBB	4,4'-di-tert-butylbiphenyl
DCM	Dichloromethane
DMP	Dess-Martin periodinane
DFT	density functional theory
DIBAL-H	diisobutylaluminum hydride
DMAP	*N,N*-4-dimethylaminopyridine
EA	ethyl acetate
Et	Ethyl
ee	enantiomeric excess
EI	electron impact ion source
ESI	electron spray ionization
HPLC	high performance liquid chromatography
HRMS	high-resolution mass spectroscopy
m-CPBA	m-chloro-peroxybenzoic acid
Me	methyl
MOM	Methoxymethyl
m.p.	melting point
Ms	methanesulfony
NMO	4-methyl-morpholin-4-oxide
PDC	pyridinium dichromate
PE	petroleum ether
Ph	phenyl
r.t.	room temperature
THF	Tetrahydrofuran
TLC	thin layer chromatography
TPAP	tetra-n-propylammonium perruthenate
Ts	Tosyl
TS	transition state
VCP	vinylcyclopropane

S1. General Information

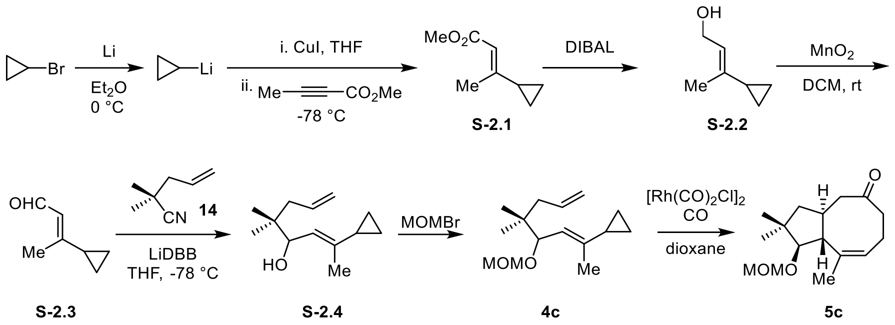
All reactions were carried out in oven-dried glassware with magnetic stirring. Reactions were stirred using Teflon-coated magnetic stir bars. All chemicals were used as received without further purification. Flash column chromatography was performed using silica gel (200−300 mesh). Analytical thin layer chromatography (TLC) was performed with 0.2−0.3 mm silica gel HSGF254 plates. Nuclear magnetic resonance (NMR) spectra were measured on Bruker AVANCE III 400 (^{1}H at 400 MHz, ^{13}C{1H} at 101 MHz), Bruker-600M Hz (1H at 600 MHz; 13C at 151 MHz) NMR spectrometers. Data for ^{1}H NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to tetramethylsilane (TMS, 0.00 ppm), multiplicity (d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddt = doublet of doublet of triplets, m = multiplet), coupling constant *J* (Hz), and integration. Data for ^{13}C{1H} NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to $CDCl_3$ (77.16 ppm) or CD3OD (49.00 ppm), multiplicity (null = singlet, q = quartet), and coupling constant *J* (Hz). Distortionless enhancement by polarization transfer (DEPT) was used to distinguish carbon signals (CH_2, CH, or C). High-resolution mass spectra (HRMS) were recorded on Bruker Solarix XR Fourier transform ion cyclotron resonance (FTICR) mass spectrometer (electrospray ionization, ESI). The enantiomer excesses (e.e.) of the products were determined by chiral HPLC analysis using Agilent Technologies 1200 series. Single crystal X-ray diffractometer was measured on XtaLAB PRO 007HF(Mo). Optical rotations were measured on PerkinElmer model 341LC Polarimeter at 20 °C or 25 °C with visible light (λ = 589 nm) and 100 mm length cuvette.

All DFT calculations were performed with the Gaussian 09 software package.[1] Pruned integration grids with 99 radial shells and 590 angular points per shell were used. Geometry optimizations of all the stationary points were carried out in the gas phase at the BMK[2]/def2-SVP[3,4] level. Unscaled harmonic frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298 K. On the basis of the optimized structures, Gibbs energies of solvation in 1,4-dioxane were computed at the SMD[5]/BMK/def2-SVP level and single-point energy refinements were performed with ORCA 4.2.1[6,7] at the DLPNO-CCSD(T)[8,9]/def2-TZVPP[3,4] level (using the def2- TZVPP/C auxiliary basis set and tight thresholds). All discussed energy differences are based on Gibbs energies in 1,4-dioxane at 298 K.

S2. Synthesis of [5+2+1] Cycloadduct

[5+2+1] cycloadducts **5a**,[10] **5b**,[10] **5d**,[10] **5e**[10] and **5f**[11] were prepared according literature report.

Synthesis of 5c:



Synthesis of S-2.1:

To a **flask A** with Li (778.7 mg, 112.2 mmol) was added Et$_2$O (27.3 mL) under argon atmosphere. Then a solution of cyclopropyl bromide (5.43 g, 44.88 mmol) in Et$_2$O (40 mL) was prepared. Part of the cyclopropyl bromide solution (10 mL) was added to the **flask A** in one portion. After the reaction initiated, **flask A** was cooled at 0 °C. Then the rest of cyclopropyl bromide solution was added to **flask A**. The reaction mixture was stirred at 0 °C for another 2 h, affording the cyclopropyl lithium solution.

To a **flask B** with CuI (4.66 g, 24.5 mmol) was added THF (180 mL) under argon atmosphere at −78 °C. Then all newly prepared cyclopropyl lithium solution in **flask A** was transferred to **flask B**. F**lask B** was stirred at 0 °C for another 15 min, giving cyclopropyl copper lithium solution as a black solution.

Then **flask B** was cooled at −78 °C. A solution of 2-butynoic acid methyl ester (2.00 g, 20.4 mmol) in THF (20 mL) was added to flask B. The reaction mixture was stirred at −78 °C for 1 h, quenched with saturated aqueous NH$_4$Cl solution, and then extracted with Et$_2$O. The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/Et$_2$O) afforded compound **S-2.1** as a colorless oil for next step.

Synthesis of S-2.2:

To a solution of **S-2.1** in DCM (61.2 mL) was added DIBAL-H (1.0 M in hexane, 61.2 mL, 61.2 mmol) under argon atmosphere at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, quenched with saturated aqueous Rochelle salt (potassium sodium tartrate) solution, and extracted with Et$_2$O. The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 5:1 petroleum ether/Et$_2$O) afforded compound **S-2.2** (1.4143 g, 62% for 2 steps) as a colorless oil for next step. The ^{1}H NMR and ^{13}C{^{1}H} NMR matched with the reported data in literature report.[12]

TLC (5:1 petroleum ether/EtOAc, R$_f$): 0.3

^{1}H NMR (400 MHz, CDCl3, *δ*): 5.46 (t, *J* = 7.0, 1H), 4.15 (d, *J* = 7.0 Hz, 2H), 1.57 (s, 3H), 1.45 – 1.36 (m, 1H), 1.28 – 1.20 (m, 1H), 0.64 – 0.56 (m, 2H), 0.52 – 0.44 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 140.7, 121.8, 59.4, 18.8, 14.0, 4.8.

Synthesis of S-2.3[13]:

To a solution of **S-2.2** (1.4370 g, 12.8 mmol) in DCM (64 mL) was added active MnO$_2$ (11.13 g, 128 mmol). The reaction mixture was stirred at room temperature for 24 h, filtrated through silica gel.

The filtrate was concentrated by rotary evaporation to afford product **S-2.3** (1.3474 g, 95%) as a colorless oil.

TLC (5:1 petroleum ether/EtOAc, R*f*): 0.5.

^{1}H NMR (400 MHz, CDCl3, *δ*): 9.97 (d, *J* = 8.1 Hz, 1H), 5.89 (d, *J* = 8.1, 1H), 2.02 (d, *J* = 1.2 Hz, 3H), 1.63 – 1.55 (m, 1H), 0.96 – 0.90 (m, 2H), 0.82 – 0.77 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 190.5, 166.3, 125.2, 20.3, 14.5, 8.3.

HRMS (ESI−FTICR, *m/z*): [M + Na]$^+$ calculated for $C_7H_{10}NaO^+$:133.0624; found: 133.0624.

Synthesis of S-2.4:

To a flask with Li (1.2 g, 165 mmol) was added THF (42 mL) under an argon atmosphere at 0 °C. Then a solution of 4,4'-di-tert-butyl-1,1'-biphenyl (DBB, 9 g, 33 mmol) in THF (42 mL) was added and stirred for 5 h. The reaction mixture turned to dark green color to afford fresh LiDBB solution (*ca.* 0.4 M in THF).

To a flask was added LiDBB (68.1 mL, 27.2 mmol) at −78 °C. Then a solution of **14** (1.4873 g, 13.6 mmol) in THF (1.0 mL) was added and stirred for 30 seconds to afford lithium reagent. After that, a solution of **S-2.3** (500.9 mg, 4.54 mmol) in THF (1.0 mL) was added to the newly prepared lithium reagent. Then the reaction mixture was stirred at 0 °C for another 15 min, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound **S-2.4** (376.8 mg, 43%) as a colorless oil.

TLC (5:1 petroleum ether/EtOAc, R*f*): 0.6.

^{1}H NMR (400 MHz, CDCl3, *δ*): 5.93 – 5.80 (m, 1H), 5.31 (dm, *J* = 9.4Hz, 1H), 5.07 – 5.05 (m, 1H), 5.05 – 5.00 (m, 1H), 4.09 (dd, *J* = 9.4, 3.1 Hz, 1H), 2.16 – 2.07 (m, 1H), 2.02 – 1.91 (m, 1H), 1.57 (d, *J* = 1.3 Hz, 3H), 1.45 – 1.36 (m, 1H), 1.25 (d, *J* = 3.4 Hz, 1H), 0.89 (s, 3H), 0.84 (s, 3H), 0.62 – 0.55 (m, 2H), 0.53 – 0.43 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 140.4, 135.6, 122.5, 117.1, 74.6, 43.3, 38.5, 22.6, 22.4, 19.1, 14.7, 4.8, 4.6.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{13}H_{23}O^+$:195.1743; found: 195.1741.

Synthesis of 4c:

To a flask with **S-2.4** (290.5 mg, 1.495 mmol) was added DCM (15 mL). After that, DIPEA (4.9 mL, 29.6 mmol) and MOMBr (0.49 mL, 6.00 mmol) were added. Then the reaction mixture was stirred at room temperature for 12 h, quenched with water, and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 petroleum ether/EtOAc) afforded chiral compound **4c** (298.3 mg, 84%) as a colorless oil.

TLC (100:1 petroleum ether/EtOAc, R*f*): 0.3

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 5.90 – 5.77 (m, 1H), 5.11 (dm, *J* = 10.0 Hz, 1H), 5.05 – 4.95 (m, 2H), 4.60 (d, *J* = 6.7 Hz, 1H), 4.42 (d, *J* = 6.7 Hz, 1H), 4.03 (d, *J* = 10.0 Hz, 1H), 3.36 (s, 3H), 2.10 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.02 (dd, *J* = 13.5, 7.5 Hz, 1H) 1.57 (d, *J* = 1.3 Hz, 3H), 1.45 – 1.37 (m, 1H), 0.90 (s, 3H), 0.84 (s, 3H), 0.63 – 0.56 (m, 2H), 0.49 – 0.44 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 142.2, 135.6, 119.8, 117.0, 93.3, 77.8, 55.6, 43.4, 38.1, 22.9, 22.9, 19.0, 15.0, 4.8 (2C).

HRMS (ESI−FTICR, *m/z*): [M + Na]$^+$ calculated for $C_{15}H_{26}NaO_2^+$: 261.1825; found: 261.1822.

Synthesis of 5c:

To a flask with **4c** (99.9 mg, 0.419 mmol) and $[Rh(CO)_2Cl]_2$ (16.3 mg, 0.0419 mmol) was added dioxane (8.4 mL) under an argon atmosphere. The reaction mixture was bubbled with balloon pressured (slightly higher than 1 atm) mix gas of CO and N_2 (1:4, V/V) at room temperature for 5 min and then stirred at 95 °C for 144 h under balloon pressured mix gas of CO and N_2 (1:4, V/V). After cooling, the reaction mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 petroleum ether/EtOAc) afforded [5 + 2 + 1] cycloadduct **5c** (55.8 mg, 51%) as a colorless oil.

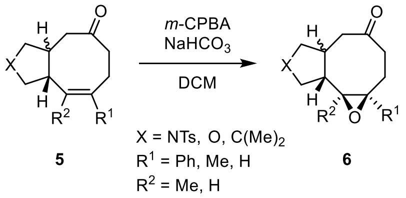
TLC (5:1 petroleum ether/EtOAc, R_f): 0.6

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 5.48 (dd, *J* = 10.8, 6.2 Hz, 1H), 4.63 (d, *J* = 6.72 Hz, 1H), 4.59 (d, *J* = 6.72, 1H), 3.78 (d, *J* = 7.9 Hz, 1H), 3.33 (s, 3H), 3.02 – 2.87 (m, 2H), 2.68 – 2.58 (m, 2H), 2.41 – 2.27 (m, 2H), 2.16 – 2.05 (m, 1H), 1.74 (s, 3H), 1.67 (dd, *J* = 12.6, 7.4 Hz, 1H), 1.39 (dd, *J* = 12.6, 10.2 Hz, 1H), 1.34 – 1.27 (m, 1H), 1.06 (s, 3H), 1.04 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 212.8, 138.1, 126.0, 96.2, 87.0, 55.5, 54.4, 47.8, 47.1, 47.1, 39.9, 36.7, 29.6, 25.0, 21.8, 20.6.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{16}H_{27}O_3^+$: 267.1955; found: 267.1949.

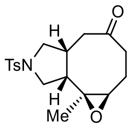
S3. Synthesis of Epoxide of [5+2+1] Cycloadduct



General Procedure: To a solution of [5+2+1] cycloadduct (ca. 0.35 mmol, 1.0 equiv.) in DCM (7.0 mL) was added $NaHCO_3$ (1.5 – 3.0 equiv.) and *m*-CPBA (75% in H_2O, 3.0 – 5.0 equiv.). The reaction mixture was stirred at room temperature for 4 h, quenched with water, and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography afforded corresponding epoxide of [5+2+1] cycloadduct.

Products of epoxidation:

Epoxide 6a:



6a

run 1: Following general procedure. substrate: **5a** (116.7 mg, 0.35 mmol), *m*-CPBA (75%, 120.8 mg, 0.525 mmol), $NaHCO_3$ (88.2 mg, 1.05 mmol); product: **6a** (116.0 mg, 95%).

run 2: Following general procedure. substrate: **5a** (117.2 mg, 0.35 mmol), *m*-CPBA (75%, 121.3 mg, 0.527 mmol), $NaHCO_3$ (88.4 mg, 1.05 mmol); product: **6a** (116.5 mg, 95%).

The average yield of two runs: 95%.

Physical Form: white solid

Melting Point: 221.0 – 222.1 °C

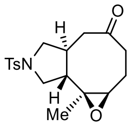
TLC (1:1 petroleum ether/EtOAc, R$_{f}$): 0.26

^{1}**H NMR** (400 MHz, CDCl3, δ): 7.71 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 3.74 (d, *J* = 10.5 Hz, 1H), 3.55 (dd, *J* = 9.7, 9.7 Hz, 1H), 3.25 (dd, *J* = 10.5, 6.7 Hz, 1H), 3.09 (dd, *J* = 10.5, 10.5 Hz, 1H), 2.98 (dd, *J* = 10.2, 4.4 Hz, 1H), 2.72 – 2.56 (m, 2H), 2.44 (s, 3H), 2.42 – 2.25 (m, 4H), 1.98 (dd, *J* = 7.1, 7.1 Hz, 1H), 1.38 – 1.30 (m, 1H), 1.27 (s, 3H).

^{13}**C{^{1}H} NMR** (101 MHz, CDCl3, δ): 212.1, 144.0, 133.8, 130.0, 127.5, 62.6, 59.4, 51.6, 50.0, 43.0, 41.4, 41.0, 39.8, 26.0, 21.7, 20.2.

HRMS (ESI−FTICR, *m/z*): [M + H]$^{+}$ calculated for $C_{18}H_{24}NO_4S^{+}$: 350.1421; found: 350.1415.

Epoxide 6b:



6b

run 1: Following general procedure. substrate: **5b** (116.8 mg, 0.35 mmol), *m*-CPBA (75%, 120.8 mg, 0.525 mmol), $NaHCO_3$ (88.2 mg, 1.05 mmol); product: **6b** (101.7 mg, 83%).

run 2: Following general procedure. substrate: **5b** (116.7 mg, 0.35 mmol), *m*-CPBA (75%, 121.1 mg, 0.526 mmol), $NaHCO_3$ (88.8 mg, 1.05 mmol); product: **6b** (100.9 mg, 82%).

The average yield of two runs: 83%.

Physical Form: white foam

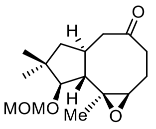
TLC (1:1 petroleum ether/EtOAc, R$_{f}$): 0.50

^{1}**H NMR** (400 MHz, CDCl3, δ): 7.70 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.61 (dd, *J* = 10.1, 7.6 Hz, 1H), 3.54 (dd, *J* = 10.1, 8.2 Hz, 1H), 3.29 (dd, *J* = 10.1, 10.1 Hz, 1H), 2.84 (dd, *J* = 10.1, 10.1 Hz, 1H), 2.69 – 2.57 (m, 2H), 2.44 (s, 3H), 2.50 – 2.36 (m, 2H), 2.31 – 2.16 (m, 3H), 1.92 – 1.75 (m, 2H), 1.05 (s, 3H).

^{13}**C{^{1}H} NMR** (101 MHz, CDCl3, δ): 211.2, 144.0, 133.6, 130.0, 127.6, 63.2, 58.4, 53.0, 48.9, 48.5, 42.4, 42.2, 40.8, 22.9, 21.7, 17.6.

HRMS (ESI−FTICR, *m/z*): [M + H]$^{+}$ calculated for $C_{18}H_{24}NO_4S^{+}$: 350.1421; found: 350.1415.

Epoxide 6c:



6c

run 1: Following general procedure. substrate: **5c** (23.5 mg, 0.0882 mmol), *m*-CPBA (75%, 30.5 mg, 0.132 mmol), NaHCO$_3$ (22.3 mg, 0.265 mmol), DCM (1.8 mL); product: **6c** (21.7 mg, 87%).

run 2: Following general procedure. substrate: **5c** (23.4 mg, 0.088 mmol), *m*-CPBA (75%, 30.3 mg, 0.132 mmol), NaHCO$_3$ (22.2 mg, 0.264 mmol), DCM (1.8 mL); product: **6c** (21.0 mg, 85%).

The average yield of two runs: 86%.

Physical Form: colorless oil

Note: The reaction scale is different from other examples.

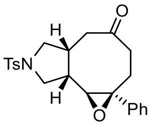
TLC (3:1 petroleum ether/EtOAc, R_f): 0.3

^{1}H NMR (400 MHz, CDCl3, *δ*): 4.75 (d, *J* = 6.9 Hz, 1H), 4.68 (d, *J* = 6.9 Hz, 1H), 3.84 (d, *J* = 8.2 Hz, 1H), 3.43 (s, 3H), 2.73 – 2.62 (m, 2H), 2.53 – 2.40 (m, 2H), 2.33 – 2.23 (m, 2H), 2.15 (ddd, *J* = 10.8, 8.1, 3.1 Hz, 1H), 2.07 – 1.93 (m, 1H), 1.79 (dd, *J* = 11.9, 8.3 Hz, 1H), 1.76 – 1.69 (m, 1H), 1.35 (dd, *J* = 13.0, 10.2 Hz, 1H), 1.26 (s, 3H), 1.08 (s, 3H), 1.03 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 213.1, 95.7, 84.6, 62.7, 59.5, 55.7, 55.7, 46.7, 46.2, 42.4, 39.9, 37.6, 29.5, 25.1, 23.0, 18.3.

HRMS (ESI–FTICR, *m/z*): $[M + NH_4]^+$ calculated for $C_{16}H_{30}NO_4^+$: 300.2169; found: 300.2161.

Epoxide 6d:



6d

run 1: Following general procedure. substrate: **5d** (140.1 mg, 0.354 mmol), *m*-CPBA (75%, 244.6 mg, 1.063 mmol), NaHCO$_3$ (148.8 mg, 1.77 mmol); product: **6d** (108.1 mg, 74%).

run 2: Following general procedure. substrate: **5d** (137.9 mg, 0.349 mmol), *m*-CPBA (75%, 240.7 mg, 1.046 mmol), NaHCO$_3$ (146.6 mg, 1.745 mmol); product: **6d** (109.0 mg, 76%).

The average yield of two runs: 75%.

Physical Form: white solid

Melting Point: 153.5 – 154.5 °C

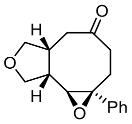
TLC (1:1 petroleum ether/EtOAc, R_f): 0.5

^{1}H NMR (400 MHz, CDCl3, *δ*): 7.74 (d, *J* = 7.9 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.34 – 7.28 (m, 4H), 3.76 (d, *J* = 10.6 Hz, 1H), 3.62 (dd, *J* = 10.1, 8.5 Hz, 1H), 3.37 (dd, *J* = 10.6, 5.3 Hz, 1H), 3.07 (dd, *J* = 10.4 Hz, 1H), 2.79 – 2.62 (m, 4H), 2.58 – 2.50 (m, 1H), 2.50 – 2.37 (m, 2H), 2.33 (s, 3H), 2.01 – 1.92 (m, 1H), 1.77 – 1.68 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 211.8, 144.1, 138.9, 133.4, 130.0, 128.9, 128.9, 127.5, 127.0, 62.6, 61.1, 52.2, 51.6, 42.1, 41.9, 41.5, 39.5, 30.6, 21.6.

HRMS (ESI–FTICR, *m/z*): $[M + H]^+$ calculated for $C_{23}H_{26}NO_4S^+$: 412.1577; found: 412.1572.

Epoxide 6e:


6e

run 1: Following general procedure. substrate: **5e** (87.2 mg, 0.360 mmol), *m*-CPBA (75%, 248.5 mg, 1.08 mmol), $NaHCO_3$ (151.2 mg, 1.8 mmol); product: **6e** (80.0 mg, 86%).

run 2: Following general procedure. substrate: **5e** (86.1 mg, 0.355 mmol), *m*-CPBA (75%, 245.3 mg, 1.066 mmol), $NaHCO_3$ (149.1 mg, 1.775 mmol); product: **6e** (80.7 mg, 88%).

The average yield of two runs: 87%.

Physical Form: colorless oil

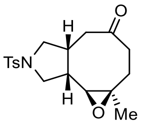
TLC (2:1 petroleum ether/EtOAc, R_f): 0.5

^{1}H NMR (400 MHz, CDCl3, δ): 7.54 – 7.46 (m, 2H), 7.45 – 7.36 (m, 3H), 4.22 – 4.09 (m, 2H), 3.95 (dd, *J* = 9.0, 4.6 Hz, 1H), 3.57 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.37 (d, *J* = 9.8 Hz, 1H), 2.96 – 2.63 (m, 4H), 2.59 – 2.34 (m, 2H), 2.20 – 2.04 (m, 1H), 1.90 – 1.79 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, δ): 212.3, 139.3, 128.9, 128.8, 127.2, 72.6, 71.9, 62.7, 61.9, 42.6, 41.8, 41.5, 40.6, 30.6.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{16}H_{19}O_3{}^+$: 259.1329; found: 259.1322.

Epoxide 6f:


6f

run 1: Following general procedure. substrate: **5f** (116.7 mg, 0.35 mmol), *m*-CPBA (75%, 120.9 mg, 0.525 mmol), $NaHCO_3$ (88.1 mg, 1.05 mmol); product: **6f** (88.4 mg, 72%).

run 2: Following general procedure. substrate: **5f** (117.0 mg, 0.35 mmol), *m*-CPBA (75%, 120.8 mg, 0.525 mmol), $NaHCO_3$ (89.0 mg, 1.05 mmol); product: **6f** (89.0 mg, 73%).

The average yield of two runs: 72%.

Physical Form: white foam

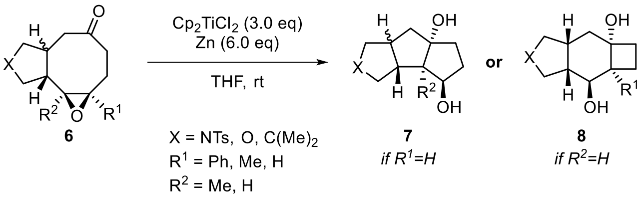
TLC (1:1 petroleum ether/EtOAc, R_f): 0.5

^{1}H NMR (400 MHz, CDCl3, δ): 7.72 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.70 (d, *J* = 10.3 Hz, 1H), 3.53 (dd, *J* = 10.0, 7.9 Hz, 1H), 3.24 (dd, *J* = 10.3, 5.4 Hz, 1H), 3.01 (dd, *J* = 10.0, 10.0 Hz, 1H), 2.61 (ddd, *J* = 14.9, 12.1, 3.2 Hz, 1H), 2.49 – 2.27 (m, 5H), 2.44 (s, 3H), 2.17 (ddd, *J* = 14.4, 6.0, 3.2 Hz, 1H), 1.86 – 1.71 (m, 1H), 1.47 (dd, *J* = 14.4, 2.3 Hz, 1H), 1.41 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, δ): 211.8, 144.0, 133.6, 130.0, 127.6, 61.9, 59.3, 52.0, 51.3, 42.0, 41.9, 41.3, 39.6, 31.0, 21.7, 21.7.

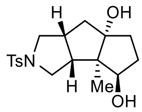
HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{18}H_{24}NO_4S^+$: 350.1421; found: 350.1420.

S4. Ti-Mediated Cyclization of Epoxide to Tricycles



General Procedure: To a flask with Cp$_2$TiCl$_2$ (3.0 equiv.) and Zn powder (6.0 equiv.) was added THF (1.5 mL) under an argon atmosphere. The reaction mixture was stirred at room temperature for 30 min to generate a dark green suspension. A solution of epoxide of [5+2+1] cycloadduct (1.0 mmol, 1.0 equiv.) in THF (1.5 mL) was added and stirred for another 4 h at room temperature. Then the reaction mixture was quenched with water, and extracted with Et$_2$O. The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography afforded cyclization tricyclic product.

Tricycle product 7a:



7a

run 1: Following general procedure. substrate: **6a** (34.8 mg, 0.10 mmol), Cp$_2$TiCl$_2$ (74.7 mg, 0.30 mmol), Zn (39.2 mg, 0.6 mmol); product: **7a** (26.7 mg, 76%).

run 2: Following general procedure. substrate: **6a** (34.9 mg, 0.10 mmol), Cp$_2$TiCl$_2$ (74.6 mg, 0.30 mmol), Zn (39.0 mg, 0.6 mmol); product: **7a** (27.1 mg, 77%).

The average yield of two runs: 76%.

Physical Form: white foam, colorless oil after some time (hours to days).

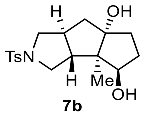
TLC (1:1 petroleum ether/EtOAc, R*f*): 0.2

^{1}H NMR (400 MHz, CDCl3, *δ*): 7.68 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.86 (dd, *J* = 7.3, 7.3 Hz, 1H), 3.31 (dd, *J* = 10.0, 4.9 Hz, 1H), 3.12 (dd, *J* = 9.6, 2.2 Hz, 1H), 2.94 (dd, *J* = 9.6, 7.3 Hz, 1H), 2.87 (dd, *J* = 10.0, 8.6 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.53 – 2.45 (m, 1H), 2.43 (s, 3H), 2.12 – 1.99 (m, 2H), 1.94 – 1.82 (m, 3H), 1.64 (ddd, *J* = 13.9, 8.8, 8.8 Hz, 1H), 1.52 (dd, *J* = 13.2, 8.8 Hz, 1H), 1.48 – 1.37 (m, 1H), 0.98 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 143.8, 132.2, 129.7, 128.1, 89.3, 80.9, 55.6, 53.7, 49.9, 45.8, 45.4, 39.9, 36.0, 31.2, 21.7, 16.7.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{18}H_{26}NO_4S^+$: 352.1577; found: 352.1568.

Tricycle product 7b:



7b

run 1: Following general procedure. substrate: **6b** (34.9 mg, 0.10 mmol), Cp_2TiCl_2 (74.6 mg, 0.30 mmol), Zn (39.2 mg, 0.6 mmol); product: **7b** (33.5 mg, 95%).

run 2: Following general procedure. substrate: **6b** (35.0 mg, 0.10 mmol), Cp_2TiCl_2 (74.7 mg, 0.30 mmol), Zn (39.4 mg, 0.6 mmol); product: **7b** (33.1 mg, 94%).

The average yield of two runs: 94%.

Physical Form: colorless oil.

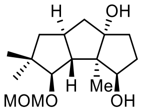
TLC (1:1 petroleum ether/EtOAc, R*f*): 0.2

^{1}H NMR (400 MHz, CDCl3, *δ*): 7.70 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 3.70 (dd, *J* = 10.5, 6.1 Hz, 1H), 3.50 (dd, *J* = 9.2, 6.5 Hz, 1H), 3.40 (dd, *J* = 8.8, 6.9 Hz, 1H), 2.88 (dd, *J* = 11.0, 8.8 Hz, 1H), 2.78 (dd, *J* = 10.5, 9.2 Hz, 1H), 2.43 (s, 3H), 2.06 – 1.93 (m, 1H), 1.90 – 1.76 (m, 4H), 1.66 (s, 1H), 1.62 (s, 1H), 1.54 – 1.30 (m, 3H), 1.30 – 1.23 (m, 1H), 0.89 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 143.4, 135.3, 129.8, 127.3, 94.3, 79.6, 54.1, 52.2, 49.4, 47.1, 44.5, 43.8, 37.4, 29.9, 21.7, 15.7.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{18}H_{26}NO_4S^+$: 352.1577; found: 352.1576.

Tricycle product 7c:



7c

run 1: Following general procedure. substrate: **6c** (21.0 mg, 0.0744 mmol), Cp_2TiCl_2 (55.5 mg, 0.223 mmol), Zn (29.2 mg, 0.446 mmol); product: **7c** (17.1 mg, 81%).

run 2: Following general procedure. substrate: **6c** (21.1 mg, 0.0744 mmol), Cp_2TiCl_2 (55.6 mg, 0.223 mmol), Zn (29.4 mg, 0.446 mmol); product: **7c** (17.7 mg, 83%).

The average yield of two runs: 82%.

Physical Form: white solid.

Melting Point: 76.2 – 78.0 °C

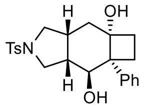
TLC (1:1 petroleum ether/EtOAc, R*f*): 0.4

^{1}H NMR (400 MHz, CDCl3, *δ*): 4.68 (d, *J* = 6.7 Hz, 1H), 4.60 (d, *J* = 6.7 Hz, 1H), 3.66 (dd, *J* = 10.5, 6.0 Hz, 1H), 3.52 (d, *J* = 9.9 Hz, 1H), 3.43 (s, 3H), 2.11 – 2.00 (m, 1H), 2.00 – 1.95 (m, 1H), 1.95 – 1.81 (m, 3H), 1.61 – 1.49 (m, 2H), 1.40 (ddd, *J* = 13.3, 13.3, 6.4 Hz, 1H), 1.31 (dd, *J* = 12.2, 12.2 Hz, 1H), 1.21 (dd, *J* = 11.6, 11.6 Hz, 1H), 1.14 (s, 3H), 1.07 (s, 3H), 1.01 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 96.9, 94.3, 83.1, 79.5, 60.6, 56.6, 52.5, 46.6, 45.4, 44.6, 38.9, 37.9, 31.6, 30.5, 26.4, 15.6.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{16}H_{29}O_4^+$: 285.2060; found: 285.2061.

Tricycle product 8d:



8d

run 1: Following general procedure. substrate: **6d** (41.2 mg, 0.10 mmol), Cp_2TiCl_2 (74.5 mg, 0.30 mmol), Zn (39.4 mg, 0.6 mmol); product: **8d** (34.6 mg, 84%).

run 2: Following general procedure. substrate: **6d** (41.1 mg, 0.10 mmol), Cp_2TiCl_2 (74.4 mg, 0.30 mmol), Zn (39.5 mg, 0.60 mmol); product: **8d** (34.4 mg, 83%).

The average yield of two runs: 84%.

Physical Form: colorless oil.

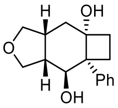
TLC (1:1 petroleum ether/EtOAc, R*f*): 0.5

^{1}H NMR (400 MHz, CDCl3, *δ*): 7.71 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.36 – 7.23 (m, 5H), 3.75 (dd, *J* = 10.7, 2.9 Hz, 1H), 3.38 – 3.27 (m, 2H), 3.23 (dd, *J* = 10.2, 4.2 Hz, 1H), 2.94 (dd, *J* = 9.7, 5.5 Hz, 1H), 2.73 – 2.58 (m, 1H), 2.52 – 2.45 (m, 1H), 2.44 (s, 3H), 2.42 – 2.33 (m, 1H), 2.30 – 2.21 (m, 1H), 2.18 – 2.07 (m, 1H), 1.92 – 1.77 (m, 2H), 1.73 (dd, *J* = 12.8, 12.8 Hz, 1H), 1.60 (s, 1H), 1.15 (d, J = 3.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 143.7, 139.8, 131.9, 129.6, 128.9, 128.1, 128.1, 127.4, 76.8, 76.3, 55.6, 54.7, 52.9, 40.4, 36.8, 33.7, 31.1, 21.6, 17.2.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{23}H_{28}NO_4^+$: 414.1734; found: 414.1733.

Tricycle product 8e:



8e

run 1: Following general procedure. substrate: **6e** (25.7 mg, 0.10 mmol), Cp_2TiCl_2 (74.7mg, 0.30 mmol), Zn (39.2 mg, 0.6 mmol); product: **8e** (20.8 mg, 80%).

run 2: Following general procedure. substrate: **6e** (25.8 mg, 0.10 mmol), Cp_2TiCl_2 (74.5 mg, 0.30 mmol), Zn (39.4 mg, 0.60 mmol); product: **8e** (21.0 mg, 81%).

The average yield of two runs: 80%.

Physical Form: white solid.

Melting Point: 205.7 – 206.9 °C

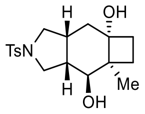
TLC (1:1 petroleum ether/EtOAc, R*f*): 0.5

^{1}H NMR (400 MHz, CDCl3, *δ*): 7.47 – 7.40 (m, 2H), 7.37 – 7.28 (m, 3H), 4.04 – 3.97 (m, 2H), 3.90 (d, *J* = 10.7 Hz, 1H), 3.84 (dd, *J* = 9.3, 4.2 Hz, 1H), 3.57 (dd, *J* = 8.8, 5.0 Hz, 1H), 2.79 – 2.64 (m, 1H), 2.58 – 2.47 (m, 1H), 2.46 – 2.36 (m, 2H), 2.31 – 2.24 (m, 1H), 1.95 – 1.82 (m, 2H), 1.74 (dd, *J* = 13.0 Hz, 1H), 1.63 (s, 1H), 1.13 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 140.2, 128.9, 128.1, 127.3, 77.5, 76.8, 75.0, 73.6, 55.6, 41.7, 36.3, 35.2, 31.0, 17.2.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{16}H_{21}O_3^+$: 261.1485; found: 261.1484.

Tricycle product 8f:



8f

run 1: Following general procedure. substrate: **6f** (34.9 mg, 0.10 mmol), Cp_2TiCl_2 (74.8mg, 0.30 mmol), Zn (39.1 mg, 0.6 mmol); product: **8f** (27.0 mg, 77%).

run 2: Following general procedure. substrate: **6f** (35.0 mg, 0.10 mmol), Cp_2TiCl_2 (74.8 mg, 0.30 mmol), Zn (39.4 mg, 0.60 mmol); product: **8f** (27.4 mg, 78%).

The average yield of two runs: 78%.

Physical Form: white solid.

Melting Point: 164.2 – 165.5 °C

TLC (1:1 petroleum ether/EtOAc, R_f): 0.3

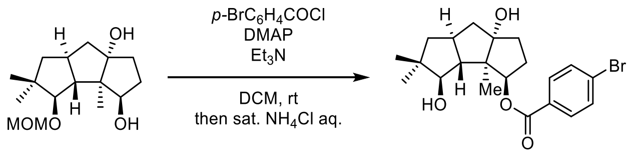
^{1}H NMR (400 MHz, CDCl3, *δ*): 7.70 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.58 (dd, *J* = 11.7, 5.9 Hz, 1H), 3.26 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.21 (dd, *J* = 9.6, 8.3 Hz, 1H), 3.08 (dd, *J* = 10.1, 7.6 Hz, 1H), 2.87 (dd, *J* = 9.6, 5.7 Hz, 1H), 2.62 – 2.50 (m, 1H), 2.44 (s, 3H), 2.12 – 1.92 (m, 3H), 1.77 – 1.66 (m, 3H), 1.59 – 1.48 (m, 3H), 1.06 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 143.8, 131.9, 129.8, 128.2, 76.9, 75.6, 54.2, 51.7, 46.3, 38.8, 35.1, 34.3, 34.0, 28.9, 21.7, 13.0.

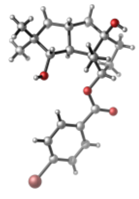
HRMS (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{18}H_{26}NO_4S^+$: 352.1577; found: 352.1576.

S5. Synthesis of Tricyclic Analogs for X-Ray Diffraction

Synthesis of *trans-anti-cis*-configurated 5/5/5 tricyclic analogs (9):



7c **9**



CCDC 2176952

To a flask with **7c** (136.7 mg, 0.481 mmol), *p*-BrC_6H_4COCl (158.4 mg, 0.72 mmol) and DMAP (58.8 mg, 0.481 mmol) were added DCM (10 mL) and TEA (1 mL) under an argon atmosphere. The reaction mixture was stirred at room temperature for 7 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 petroleum ether/EtOAc) afforded compound **9** (80.4 mg, 40%) as a white solid. The relative configuration of **9** was determined by X-ray diffraction (CCDC 2176952).

TLC (1:1 petroleum ether/EtOAc, R_f): 0.6

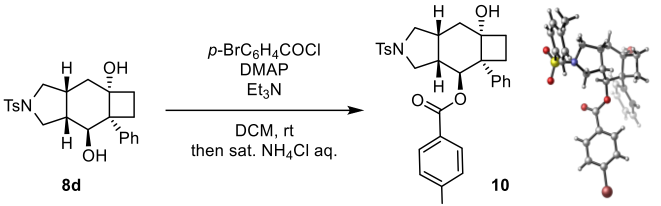
Melting Point: 160.1 – 161.3 °C

^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.99 – 7.93 (m, 2H), 7.61 – 7.55 (m, 2H), 5.02 (dd, J = 10.4, 6.1 Hz, 1H), 3.48 (dd, J = 9.8, 4.8 Hz, 1H), 2.20 (dddd, J = 12.2, 6.2, 6.2, 1.6 Hz, 1H), 2.10 – 1.97 (m, 3H), 1.89 (dd, J = 12.6, 5.7 Hz, 1H), 1.74 (m, 1H), 1.62 – 1.57 (m, 1H), 1.57 – 1.52 (m, 1H), 1.41 (d, J = 4.7 Hz, 1H), 1.39 – 1.31 (m, 1H), 1.26 – 1.18 (m, 1H), 1.13 (s, 3H), 1.07 (s, 3H), 1.00 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ): 166.3, 132.0, 131.2, 129.6, 128.2, 94.3, 82.4, 78.0, 62.5, 50.9, 46.1, 45.4, 42.8, 39.7, 37.4, 30.6, 27.6, 25.9, 16.2.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{21}H_{28}BrO_4^+$: 423.1165; found: 423.1165.

Synthesis of *cis-anti-cis*-configurated 5/6/4 tricyclic analogs (10):



8d **10** **CCDC 2176955**

To a flask with **8d** (103.3 mg, 0.250 mmol), *p*-BrC$_6$H$_4$COCl (82.3 mg, 0.375 mmol) and DMAP (30.6 mg, 0.250 mmol) were added DCM (5 mL) and TEA (0.75 mL). The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was purified by flash column chromatography (silica gel, 1:1 petroleum ether/EtOAc) afforded compound **10** (111.2 mg, 75%) as a white solid. The relative configuration of **10** was determined by X-ray diffraction (CCDC 2176955).

TLC (1:1 petroleum ether/EtOAc, R$_f$): 0.4

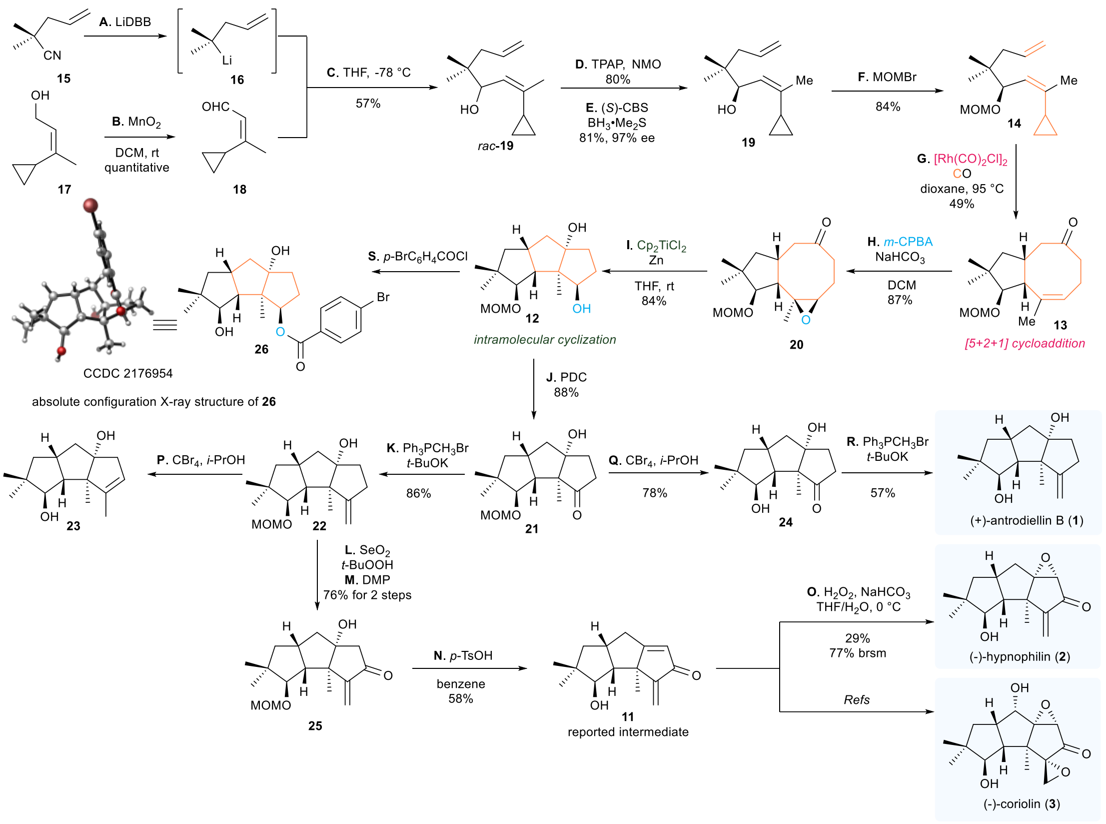
Melting Point: 207 – 208 °C

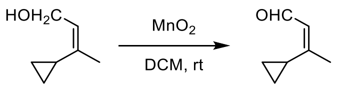
^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.75 – 7.67 (m, 2H), 7.59 – 7.52 (m, 2H), 7.50 – 7.43 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.29 – 7.22 (m, 4H), 7.19 – 7.12 (m, 1H), 5.42 (d, J = 9.6 Hz, 1H), 3.71 (dd, J = 9.6, 7.5 Hz, 1H), 3.59 (dd, J = 10.0, 7.5 Hz, 1H), 2.94 (dd, J = 10.0, 7.5 Hz, 1H), 2.90 – 2.74 (m, 2H), 2.69 (dd, J = 9.6, 6.4 Hz, 1H), 2.55 (ddd, J = 11.2, 11.2, 4.4 Hz, 1H), 2.46 (s, 3H), 2.37 (ddd, J = 12.4, 9.6, 4.4 Hz, 1H), 2.26 (ddd, J = 12.9, 9.6, 7.9 Hz, 1H), 2.00 – 1.85 (m, 2H), 1.71 – 1.61 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ): 164.4, 143.9, 138.1, 131.8, 131.6, 130.9, 129.8, 128.5, 128.5, 128.1, 128.1, 127.9, 127.3, 78.9, 75.9, 55.1, 54.3, 52.7, 40.9, 36.8, 33.9, 32.3, 21.6, 17.7.

HRMS (ESI−FTICR, *m/z*): [M + NH$_4$]$^+$ calculated for $C_{30}H_{34}BrN_2O_5S^+$: 613.1366; found: 613.1362.

S6. Synthesis of (+)-Antrodiellin B, (−)-Hypnophilin and (−)-Coriolin





17 18

(*Z*)-3-cyclopropylbut-2-enal (18)[13]

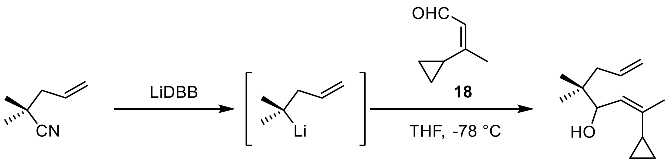
To a solution of **17**[14] (1.9495 g, 17.4 mmol) in DCM (30 mL) was added active MnO$_2$ (7.55 g, 86.9 mmol). The reaction mixture was stirred at room temperature for 14 h, then filtered through neutral Al$_2$O$_3$ (200-300 mesh) and eluted by Et$_2$O quickly. The filtrate was concentrated to afford compound **18** (2.1216 g, quantitative) as a colorless oil.

TLC (5:1 petroleum ether/EtOAc, R$_f$): 0.7

^{1}H NMR (400 MHz, CDCl3, *δ*): 10.15 (d, *J* = 8.1 Hz, 1H), 5.92 (d, *J* = 8.1, Hz, 1H), 2.58 – 2.46 (m, 1H), 1.63 (d, *J* = 1.1 Hz, 3H), 0.97 – 0.91 (m, 2H), 0.89 – 0.83 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3, *δ*): 190.6, 164.8, 129.0, 19.4, 13.6, 7.4 (2C).

HRMS (ESI–FTICR, *m/z*): [M + Na]$^+$ calculated for C$_7$H$_{10}$NaO$^+$: 133.0624; found: 133.0623.



15 16 ***rac*-19**

(*Z*)-2-cyclopropyl-5,5-dimethylocta-2,7-dien-4-ol (*rac*-19)

To a flask with Li (1.2 g, 165 mmol) was added THF (42 mL) under an argon atmosphere at 0 °C.

Then a solution of 4,4'-di-tert-butyl-1,1'-biphenyl (DBB, 9 g, 33 mmol) in THF (42 mL) was added and stirred for 5 h. The reaction mixture turned to dark green color to afford fresh LiDBB solution (*ca.* 0.4 M in THF).

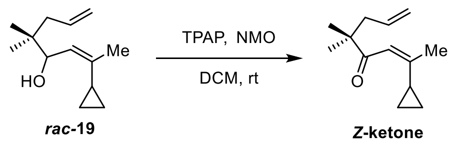
To a flask was added LiDBB (68 mL, 27.2 mmol) at −78 °C. Then a solution of **15** (1.980 g, 18.2 mmol) in THF (1.0 mL) was added and stirred for 30 s to afford **16**. After that, a solution of **18** (501.0 mg, 4.54 mmol) in THF (1.0 mL) was added to **15**. Then the reaction mixture was stirred at 0 °C for another 15 min, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound ***rac*-19** (499.9 mg, 57%) as a colorless oil.

TLC (10:1 petroleum ether/EtOAc, R_f): 0.5

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.95 – 5.81 (m, 1H), 5.35 (d, J = 9.3 Hz, 1H), 5.08 – 5.05 (m, 1H), 5.04 – 5.01 (m, 1H), 4.33 (dd, J = 9.3, 3.8 Hz, 1H), 2.14 (dd, J = 13.4, 7.5 Hz, 1H), 2.02 (dd, J = 13.4, 7.5, 1H), 1.80 – 1.70 (m, 1H), 1.44 (d, J = 1.4 Hz, 3H), 1.34 (d, J = 3.8 Hz, 1H), 0.92 (s, 3H), 0.88 (s, 3H), 0.66 – 0.60 (m, 3H), 0.56 – 0.49 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 139.5, 135.6, 125.4, 117.0, 74.0, 43.4, 38.3, 22.6, 22.4, 18.9, 12.8, 4.5, 4.3.

HRMS (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{13}H_{23}O^+$: 195.1743; found: 195.1741.



(*Z*)-2-cyclopropyl-5,5-dimethylocta-2,7-dien-4-one (*Z*-ketone)

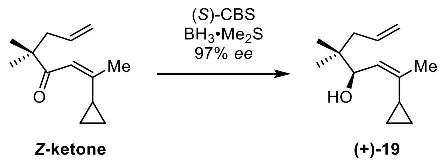
To a flask with ***rac*-19** (490.2 mg, 2.52 mmol), tetrapropylammonium perruthenate (TPAP, 44.3 mg, 0.126 mmol) and N-methylmorpholine oxide (NMO, 443.0 mg, 3.78 mmol) was added DCM (25 mL). The reaction mixture was stirred at room temperature for 24 h, filtrated through silica gel and eluted with DCM and EtOAc. The filtration was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound ***Z*-ketone** (386.5 mg, 80%) as a colorless oil.

TLC (10:1 petroleum ether/EtOAc, R_f): 0.7

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.35 (d, J = 1.5 Hz, 1H), 5.78 – 5.63 (m, 1H), 5.06 – 4.98 (m, 2H), 3.19 (ddd, J = 8.4, 5.5, 3.2 Hz, 1H), 2.29 (ddd, J = 8.0, 1.2, 1.2 Hz, 1H), 2.29 (ddd, J = 8.0, 1.2, 1.2 Hz, 1H), 1.55 (d, J = 1.2 Hz, 3H), 1.15 – 1.11 (s, 6H), 0.87 – 0.80 (m, 2H), 0.78 – 0.72 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 205.5, 160.0, 134.6, 120.7, 117.5, 46.9, 44.3, 24.4, 19.1, 14.4, 7.1.

HRMS (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{13}H_{21}O^+$: 193.1587; found: 193.1582.



(*R*,*Z*)-2-cyclopropyl-5,5-dimethylocta-2,7-dien-4-ol ((+)-19)

To a flask with ***Z*-ketone** (381.5 mg, 1.984 mmol) was added toluene (20 mL) under an argon atmosphere. Then a solution of (*S*)-CBS (1.0 M in toluene, 2.0 mL, 2.0 mmol) was added to the flask. The flask was cooled at −30 °C and a solution of $BH_3 \cdot Me_2S$ (2.0 M in THF, 5.0 mL, 10.0 mmol) was added. The reaction mixture was stirred at −30 °C for 4 h, then quenched with MeOH. After the solution warmed to room temperature, saturated aqueous NH_4Cl solution was added and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded chiral compound **(+)-19** (312.6 mg, 81%) as a colorless oil. The enantiomeric excess value (97% ee) was measured by chiral HPLC.

TLC (5:1 petroleum ether/EtOAc, R*f*): 0.6

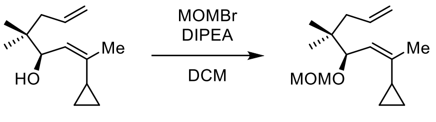
^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 5.95 – 5.81 (m, 1H), 5.35 (dm, *J* = 9.3 Hz, 1H), 5.08 – 5.05 (m, 1H), 5.04 – 5.01 (m, 1H), 4.33 (dd, *J* = 9.3, 3.8 Hz, 1H), 2.14 (dd, J = 13.4, 7.5 Hz, 1H), 2.02 (dd, *J* = 13.4, 7.5, 1H), 1.80 – 1.70 (m, 1H), 1.44 (d, *J* = 1.4 Hz, 3H), 1.34 (d, *J* = 3.8 Hz, 1H), 0.92 (s, 3H), 0.88 (s, 3H), 0.66 – 0.60 (m, 3H), 0.56 – 0.49 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 139.5, 135.6, 125.4, 117.0, 74.0, 43.4, 38.3, 22.6, 22.4, 18.9, 12.8, 4.5, 4.3.

HRMS (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{13}H_{23}O^+$: 195.1743; found: 195.1740.

Specific Rotation: $[\alpha]^{20}_D$ = +43.8 (*c* 0.88 $CHCl_3$).

HPLC: ChiralPak AS-H; 4 mg/ mL; hexane : *i*-propanol = 99.8 : 0.2; 1.0 mL/min; t_R(major) = 7.86 min, t_R(minor) = 8.67 min; ee = 97%.



(+)-19 **(−)-14**

(*R,Z*)-(4-(methoxymethoxy)-5,5-dimethylocta-2,7-dien-2-yl)cyclopropane ((−)-14)

To a flask with **(+)-19** (314.1 mg, 1.616 mmol) was added DCM (16 mL) at 0 °C. After that, DIPEA (5.3 mL, 32.3 mmol) and MOMBr (0.53 mL, 6.47 mmol) was added. Then the reaction mixture was warmed to room temperature and stirred for 12 h, quenched with water, and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 30:1 petroleum ether/EtOAc) afforded chiral compound **(−)-14** (325.1 mg, 84%) as a colorless oil.

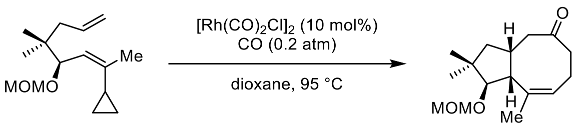
TLC (5:1 petroleum ether/EtOAc, R*f*): 0.8

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 5.93 – 5.79 (m, 1H), 5.16 (dm, *J* = 10.0 Hz, 1H), 5.04 (dd, *J* = 1.2, 1.2 Hz, 1H), 5.02 – 4.99 (m, 1H), 4.72 (d, *J* = 6.6 Hz, 1H), 4.46 (d, *J* = 6.6 Hz, 1H), 4.27 (d, *J* = 10.0 Hz, 1H), 3.38 (s, 3H), 2.16 – 2.01 (m, 2H), 1.80 – 1.70 (m, 1H), 1.46 (d, *J* = 1.2 Hz, 3H), 0.93 (s, 3H), 0.88 (s, 3H), 0.66 – 0.57 (m, 3H), 0.53 – 0.46 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 141.0, 135.6, 122.8, 116.9, 93.5, 77.2, 55.7, 43.5, 38.0, 23.0, 22.9, 18.9, 12.7, 4.4, 4.4.

HRMS (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{15}H_{27}O_2^+$: 239.2006; found: 239.2001.

Specific Rotation: $[\alpha]^{20}_D$ = −81.0 (*c* 0.62 $CHCl_3$).



(-)-14 (-)-13

(*1R,3aR,9aR,Z*)-1-(methoxymethoxy)-2,2,9-trimethyl-1,2,3,3a,4,6,7,9a-octahydro-5H cyclopenta[8]annulen-5-one ((−)-13)

To a flask with **(−)-14** (500.9 mg, 2.1 mmol) and [Rh(CO)$_2$Cl]$_2$ (81.8 mg, 0.21 mmol) was added dioxane (42 mL) under an argon atmosphere. The reaction mixture was bubbled with balloon pressured (slightly higher than 1 atm) mix gas of CO and N_2 (1:4, V/V) at room temperature for 5 min and then stirred at 95 °C for 168 h under balloon pressured mix gas of CO and N_2 (1:4, V/V). After cooling, the reaction mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 petroleum ether/EtOAc) afforded [5 + 2 + 1] cycloadduct **(−)-13** (274.3 mg, 49%) as a light yellow oil.

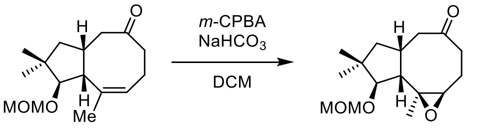
TLC (5:1 petroleum ether/EtOAc, R*f*): 0.6

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 5.77 – 5.69 (m, 1H), 4.61 (s, 2H), 4.05 (d, *J* = 5.9 Hz, 1H), 3.34 (s, 3H), 3.01 (dd, *J* = 10.6, 5.9 Hz, 1H), 2.59 – 2.42 (m, 2H), 2.39 – 2.27 (m, 2H), 2.24 – 2.16 (m, 2H), 2.09 – 2.01 (m, 1H), 1.86 (d, *J* = 1.5 Hz, 3H), 1.64 (dd, *J* = 12.7, 5.9 Hz, 1H), 1.15 (dd, *J* = 12.4, 12.4 Hz, 1H), 1.12 (s, 3H), 1.04 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 213.8, 136.4, 125.8, 95.9, 86.7, 55.3, 48.3, 48.0, 44.5, 44.4, 40.7, 37.1, 28.3, 24.9, 23.1, 22.0.

HRMS (ESI−FTICR, *m/z*): [M + NH$_4$]$^+$ calculated for $C_{16}H_{30}NO_3^+$: 284.2220; found: 284.2213.

Specific Rotation: $[\alpha]^{20}_D$ = −7.0 (*c* 0.50 CHCl$_3$).



(−)-13 (−)-20

(*1aR,5aR,8R,8aS,8bS*)-8-(methoxymethoxy)-7,7,8b-trimethyldecahydro-4H cyclopenta[3,4]cycloocta[1,2-b]oxiren-4-one ((−)-20)

To a flask with **(−)-13** (123.6 mg, 0.464 mmol) was added DCM (9.2 mL). Then NaHCO$_3$ (117.0 mg, 1.392 mmol) and *m*-CPBA (75% in H$_2$O, 160.2 mg, 0.696 mmol) was added. The reaction mixture was stirred at room temperature for 4 h, then quenched with water, and extracted with Et$_2$O. The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 3:1 petroleum ether/EtOAc) afforded compound **(−)-20** (114.0 mg, 87%) as a colorless oil.

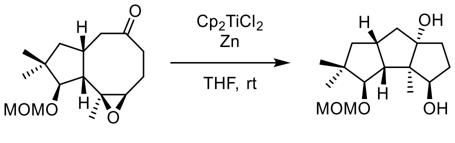
TLC (3:1 petroleum ether/EtOAc, R*f*): 0.25

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 4.80 (d, *J* = 6.7 Hz, 1H), 4.61 (d, *J* = 6.7 Hz, 1H), 4.08 (d, *J* = 5.5 Hz, 1H), 3.40 (s, 3H), 3.03 (dd, *J* = 10.7, 4.1 Hz, 1H), 2.65 – 2.50 (m, 4H), 2.39 – 2.29 (m, 1H), 2.22 (d, *J* = 10.0 Hz, 1H), 1.91 (dd, *J* = 10.0, 5.5 Hz, 1H), 1.67 – 1.62 (m, 1H), 1.50 –1.40 (m, 1H), 1.43 (s, 3H), 1.40 – 1.30 (m, 1H), 1.13 (s, 3H), 0.99 (s, 3H)..

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 212.9, 95.1, 84.0, 64.4, 59.9, 55.3, 49.5, 47.6, 44.3, 40.7, 40.6, 37.2, 27.9, 24.6, 22.4, 21.7.

HRMS (ESI−FTICR, *m/z*): [M + NH$_4$]$^+$ calculated for $C_{16}H_{30}NO_4^+$: 300.2169; found: 300.2164.

Specific Rotation: $[\alpha]^{20}_D = -45.2$ (*c* 0.40 CHCl$_3$).



(−)-20 **(+)-12**

(*3R,3aR,3bR,4R,6aS,7aR*)-3-(methoxymethoxy)-2,2,3b-trimethyldecahydro-6aH-cyclopenta[a]pentalene-4,6a-diol ((+)-12)

To a flask with Cp$_2$TiCl$_2$ (215.4 mg, 0.865 mmol) and Zn powder (113.0 mg, 1.728 mmol) was added THF (4.3 mL) under an argon atmosphere. The reaction mixture was stirred at room temperature for 30 min to generate a dark green suspension. A solution of **(−)-20** (81.4 mg, 0.288 mmol) in THF (4.3 mL) was added and stirred for another 4 h at room temperature. Then the reaction mixture was quenched with water, and extracted with Et$_2$O. The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 1:1 petroleum ether/EtOAc) afforded compound **(+)-12** (68.7 mg, 84%) as a white solid.

TLC (1:1 petroleum ether/EtOAc, R$_f$): 0.3

Melting Point: 82.0 – 82.5 °C

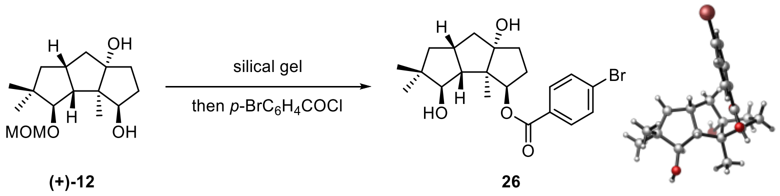
^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 4.70 (s, 2H), 3.96 (dd, *J* = 7.9, 7.9 Hz, 1H), 3.62 (d, *J* = 8.2 Hz, 1H), 3.41 (s, 3H), 2.53 (dd, *J* = 12.0, 8.2 Hz, 1H), 2.49 – 2.38 (m, 1H), 2.26 (d, *J* = 7.0 Hz, 1H), 2.22 – 2.10 (m, 1H), 2.04 (dd, *J* = 12.3, 7.8 Hz, 1H), 2.01 – 1.90 (m, 1H), 1.73 (dd, *J* = 12.8, 7.8 Hz, 1H), 1.70 –1.53 (m, 3H), 1.34 (dd, *J* = 12.4, 8.8 Hz, 1H), 1.16 – 1.11 (m, 1H), 1.10 (s, 3H), 1.09 (s, 3H), 0.97 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 97.6, 90.9, 88.9, 80.7, 55.9, 54.8, 50.7, 47.4, 44.8, 44.6, 35.4, 34.8, 30.7, 27.4, 21.0, 16.8.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{16}H_{29}O_4^+$: 285.2060; found: 285.2054.

Specific Rotation: $[\alpha]^{20}_D = 17.8$ (*c* 0.38 CHCl$_3$).

Note: When **(+)-12** was treated with silica gel during column chromatography, the MOM group would be removed to generate triol if the silica gel was too acid (such as Yinlong®, which was produced by Yantai Huayang New Material Technology Co. Ltd). Using silica gel produced by other suppliers did not have this problem.



(+)-12 **26**

CCDC 2176954

(3R,3aR,3bR,4R,6aR,7aS)-4,7a-dihydroxy-3a,5,5-trimethyldecahydro-1H-cyclopenta[a]pentalen-3-yl 4-bromobenzoate (26)

The compound **(+)-12** was transformed to triol under the acid silica gel (Yinlong®, which was produced by Yantai Huayang New Material Technology Co. Ltd) after column chromatography. To a flask with triol (25.3 mg, 0.105 mmol) and *p*-BrC$_6$H$_4$COCl (48.4 mg, 0.220 mmol) and DMAP (18.0 mg, 0.147 mmol) were added TEA (0.4 mL) and DCM (3.0 mL). The reaction mixture was stirred at room temperature for 12 h and purified by flash column chromatography (silica gel, 2:1 petroleum ether/EtOAc) to afford compound **26** (40.3 mg, 91%) as a white solid. The absolute configuration of **26** was determined by X-ray diffraction (CCDC 2176954).

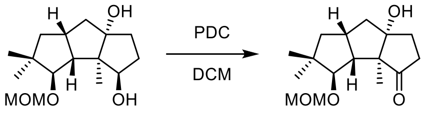
TLC (1:1 petroleum ether/EtOAc, R$_f$): 0.5

Melting Point: 180.4 – 181.6 °C

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): 7.96 – 7.89 (m, 2H), 7.62 – 7.55 (m, 2H), 5.13 (dd, *J* = 7.7, 6.1 Hz, 1H), 3.78 (dd, *J* = 8.6, 5.5 Hz, 1H), 2.57 – 2.36 (m, 3H), 2.13 (dd, *J* = 13.0, 8.2 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.83 – 1.72 (m, 2H), 1.71 – 1.64 (m, 1H), 1.49 (dd, *J* = 13.0, 6.7 Hz, 1H), 1.44 (s, 1H), 1.31 (d, *J* = 5.8 Hz, 1H), 1.28 – 1.23 (m, 1H), 1.19 (s, 3H), 1.03 (s, 3H), 0.89 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 165.8, 131.8, 131.1, 129.5, 128.0, 90.6, 83.5, 81.2, 54.1, 53.2, 45.7, 45.6, 43.9, 36.2, 35.9, 28.3, 26.7, 20.0, 16.2.

HRMS (ESI–FTICR, *m/z*): [M + NH$_4$]$^+$ calculated for C$_{21}$H$_{31}$BrNO$_4$$^+$: 440.1431; found: 440.1434.



(+)-12 **(+)-21**

(3aS,3bR,4R,6aR,7aS)-7a-hydroxy-4-(methoxymethoxy)-3a,5,5-trimethyldecahydro-3H-cyclopenta[a]pentalen-3-one ((+)-21)

To a flask with **(+)-12** (68.7 mg, 0.242 mmol), 4 Å molecular sieves (181.4 mg) and PDC (181.8 mg, 0.483 mmol) was added DCM (5.0 mL). The reaction mixture was stirred at room temperature for 24 h, then filtered and eluted with EtOAc to get the filtrate. The solution was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 1:1 petroleum ether/EtOAc) afforded compound **(+)-21** (60.2 mg, 88%) as a colorless oil.

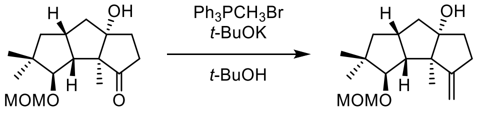
TLC (1:1 petroleum ether/EtOAc, R$_f$): 0.6

^{1}H NMR (400 MHz, CDCl$_3$, *δ*): δ 4.71 (d, *J* = 6.8 Hz, 1H), 4.62 (dd, *J* = 6.8, 1.0 Hz, 1H), 3.74 (d, *J* = 6.9 Hz, 1H), 3.40 (s, 3H), 2.60 – 2.44 (m, 3H), 2.42 – 2.28 (m, 1H), 2.13 –2.03 (m, 1H), 1.97 – 1.86 (m, 2H), 1.72 (dd, *J* = 12.7, 7,7 Hz, 1H), 1.67 – 1.59 (m, 1H), 1.57 – 1.47 (m, 2H), 1.29 – 1.19 (m, 1H), 1.08 (*app*. s, 6H), 0.93 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, *δ*): 220.0, 96.2, 89.7, 86.3, 59.4, 55.7, 53.8, 47.0, 44.1, 43.2, 36.9, 35.0, 31.8, 27.2, 20.9, 12.2.

HRMS (ESI–FTICR, *m/z*): [M + H]$^+$ calculated for C$_{16}$H$_{27}$O$_4$$^+$: 283.1904; found: 283.1899.

Specific Rotation: $[\alpha]^{20}_{D}$ = 4.6 (*c* 0.93 CHCl$_3$).



(+)-21 **(+)-22**

(3R,3aR,3bR,6aS,7aR)-3-(methoxymethoxy)-2,2,3b-trimethyl-4-methylenedecahydro-6aH-cyclopenta[a]pentalen-6a-ol ((+)-22)

To a flask with *t*-BuOK (142.7 mg, 1.272mmol) and Ph_3PCH_3Br (378.2 mg, 1.06 mmol) were added *t*-BuOH (1.5 mL) and toluene (7.5 mL) under an argon atmosphere. The reaction mixture was stirred at 80 °C for 3 h to get the ylide reagent. The prepared ylide solution was transferred to another flask with **(+)-21** (59.8 mg, 0.212 mmol) under an argon atmosphere. The reaction mixture was stirred at 100 °C for 12 h, quenched with water, and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 petroleum ether/EtOAc) afforded compound **(+)-22** (51.0 mg, 86%) as a colorless oil.

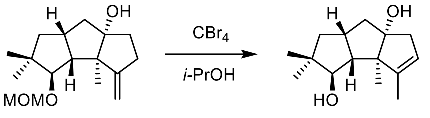
TLC (3:1 petroleum ether/EtOAc, R*f*): 0.7

^{1}**H NMR** (400 MHz, $CDCl_3$, *δ*): 4.89 (dd, *J* = 2.4, 2.4 Hz Hz, 1H), 4.86 (dd, *J* = 2.1, 2.1 Hz, 1H), 4.72 (d, *J* = 6.6 Hz, 1H), 4.66 (d, *J* = 6.6 Hz, 1H), 3.77 (d, *J* = 7.7 Hz, 1H), 3.41 (s, 3H), 2.59 – 2.48 (m, 2H), 2.48 – 2.34 (m, 2H), 1.94 – 1.84 (m, 2H), 1.73 – 1.69 (m, 1H), 1.69 – 1.63 (m, 1H), 1.42 (dd, *J* = 13.6, 4.6 Hz, 1H), 1.37 (s, 1H), 1.28 (dd, *J* = 12.7, 9.9 Hz, 1H), 1.08 (s, 3H), 1.07 (s, 3H), 0.94 (s, 3H).

^{13}**C{^{1}H} NMR** (101 MHz, $CDCl_3$, *δ*): 159.3, 106.3, 96.8, 92.1, 88.3, 57.3, 55.8, 55.6, 47.1, 43.7, 43.0, 36.2, 34.9, 28.5, 27.4, 21.1, 17.0.

HRMS (EI−FTICR, *m/z*): $[M - CH_3OCH_2]^{\cdot+}$ calculated for $C_{15}H_{23}O_2^{\cdot+}$: 235.1693; found: 235.1692.

Specific Rotation: $[\alpha]^{20}_{D}$ = 2.2 (*c* 0.47 $CHCl_3$).



(+)-22 **(−)-23**

(3R,3aR,3bR,6aR,7aR)-2,2,3b,4-tetramethyl-1,2,3,3a,3b,6,7,7a-octahydro-6aH-cyclopenta[a]pentalene-3,6a-diol ((−)-23)

To a flask with **(+)-22** (9.4 mg, 0.0335 mmol) and *i*-PrOH (1.0 mL) was added CBr_4 (5.4 mg, 0.0163 mmol). The reaction mixture was stirred at 80°C for 8 h. Then the solution was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 6:1 petroleum ether/EtOAc) afforded compound **(−)-23** (4.6 mg, 58%) as a white solid.

Melting Point: 150.6 – 152.2 °C

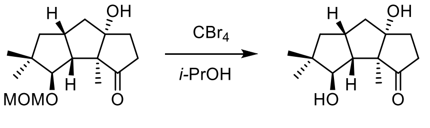
TLC (3:1 petroleum ether/EtOAc, R*f*): 0.3

^{1}**H NMR** (400 MHz, Methanol-d4, *δ*): δ 5.13 – 5.07 (m, 1H), 3.72 (d, *J* = 9.2 Hz, 1H), 2.37 – 2.21 (m, 4H), 2.06 (dd, *J* = 13.4, 9.0 Hz, 1H), 1.71 (dd, *J* = 12.7, 8.6 Hz, 1H), 1.63 (dd, *J* = 4.1 Hz, 2.0 Hz, 3H), 1.53 (dd, *J* = 13.5, 5.6 Hz, 1H), 1.24 (dd, *J* = 12.8, 8.1 Hz, 1H), 1.10 (s, 3H), 0.99 (s, 3H), 0.86 (s, 3H).

^{13}**C{^{1}H} NMR** (101 MHz, Methanol-d4, *δ*): 149.8, 120.8, 92.6, 82.4, 59.8, 56.7, 48.0, 47.0, 45.2, 44.1, 37.3, 27.4, 21.0, 15.2, 13.9.

HRMS (ESI−FTICR, *m/z*): $[M + Na]^{+}$ calculated for $C_{15}H_{24}NaO_2^{+}$: 259.1669; found: 259.1667.

Specific Rotation: $[\alpha]^{25}_{D}$ = -4.6 (*c* 0.74 MeOH).



(+)-21 **(+)-24**

(3aS,3bR,4R,6aR,7aS)-4,7a-dihydroxy-3a,5,5-trimethyldecahydro-3H-cyclopenta[a]pentalen-3-

one ((+)-24)

To a flask with **(+)-21** (19.1 mg, 0.068 mmol) and *i*-PrOH (2.0 mL) was added CBr_4 (25.2 mg, 0.076 mmol). The reaction mixture was stirred at 80°C for 2 h. Then the solution was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 2:1 petroleum ether/EtOAc) afforded compound **(+)-24** (12.6 mg, 78%) as a white solid.

Melting Point: 217.4 – 219.4 °C

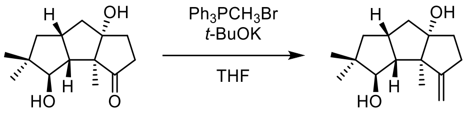
TLC (1:1 petroleum ether/EtOAc, R*f*): 0.4

^{1}H NMR (400 MHz, Methanol-d4, *δ*): δ 3.78 (d, *J* = 8.5 Hz, 1H), 2.55 – 2.36 (m, 3H), 2.26 (ddd, *J* = 19.6, 9.2, 8.0 Hz, 1H), 2.06 (ddd, *J* = 13.2, 9.2, 4.1 Hz, 1H), 1.93 (ddd, *J* = 13.0, 10.4, 7.9 Hz, 1H), 1.74 (dd, *J* = 14.3, 9.2 Hz, 1H), 1.67 (dd, *J* = 12.5, 8.4 Hz, 1H), 1.59 (dd, *J* = 14.3, 3.4 Hz, 1H), 1.31 (dd, *J* = 12.8, 3.4 Hz, 1H), 1.08 (s, 3H), 0.98 (s, 3H), 0.86 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Methanol-d4, *δ*): 223.6, 89.6, 81.8, 61.2, 55.0, 46.7, 44.5, 44.4, 37.6, 35.6, 32.1, 26.9, 20.3, 12.5.

HRMS (ESI−FTICR, *m/z*): $[M + Na]^+$ calculated for $C_{14}H_{22}NaO_3^+$: 261.1461; found: 261.1460.

Specific Rotation: $[\alpha]^{25}_D$ = 32.3 (*c* 0.195 MeOH).



(+)-24 **(+)-antrodiellin B (1)**

(+)-antrodiellin B (1)

To a reaction tube with *t*-BuOK (122 mg, 1.0 mmol) and Ph_3PCH_3Br (356 mg, 1.0 mmol) was added THF (1.0 mL) under an argon atmosphere. The reaction mixture was stirred at room temperature for 30 min, then a solution of **(+)-24** (9.7 mg, 0.041 mmol) in THF (2.0 mL) was added and stirred for another 3 h at room temperature. The solution was quenched with water and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc) afforded compound **(+)-antrodiellin B (1**) (5.5 mg, 57%) as a white solid. The ^{1}H NMR, ^{13}C{^{1}H} NMR and specific rotation matched with the literature report.[15]

Melting Point: 198.4 – 200.5 °C

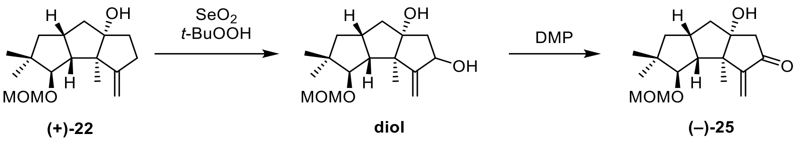
TLC (1:1 petroleum ether/EtOAc, R*f*): 0.6

^{1}H NMR (600 MHz, Methanol-d4, *δ*): δ 4.90 (dd, *J* = 2.5, 2.5 Hz, 1H), 4.79 (ddd, *J* = 2.2, 2.2, 0.7 Hz, 1H), 3.87 (d, *J* = 8.5 Hz, 1H), 2.56 – 2.48 (m, 1H), 2.48 – 2.38 (m, 2H), 2.36 – 2.28 (m, 1H), 1.84 – 1.77 (m, 2H), 1.75 – 1.69 (m, 1H), 1.66 (dd, *J* = 12.5, 8.9 Hz, 1H), 1.44 (dd, *J* = 13.9, 3.1 Hz, 1H), 1.30 (dd, *J* = 13.1, 3.9 Hz, 1H), 1.10 (s, 3H), 0.98 (s, 3H), 0.86 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Methanol-d4, *δ*): 162.1, 106.2, 92.6, 82.4, 59.0, 56.7, 46.9, 44.8, 44.3, 37.2, 35.2, 29.2, 27.1, 20.5, 18.3.

HRMS (ESI−FTICR, *m/z*): $[M + Na]^+$ calculated for $C_{15}H_{24}NaO_2^+$: 259.1669; found: 259.1668.

Specific Rotation: $[\alpha]^{25}_D$ = 45.2 (*c* 0.25 MeOH).



(3aR,3bR,4R,6aR,7aR)-7a-hydroxy-4-(methoxymethoxy)-3a,5,5-trimethyl-3-methylenedecahydro-2H-cyclopenta[a]pentalen-2-one ((–)-25)

To a flask with **(+)-22** (49.9 mg, 0.178 mmol) and SeO_2 (13.8 mg, 0.125 mmol) were added DCM (5 mL) and TBHP (70% in H_2O, 74 µL, 0.534 mmol). The reaction mixture was stirred at room temperature for 1 h, then filtrated. The filtrate was concentrated by rotary evaporation. to afford crude product **diol** (46.6 mg, 89%) as a lightly yellow oil for next step.

TLC (1:1 petroleum ether/EtOAc, R_f): 0.4

To a flask with **diol** (46.6 mg, 0.157 mmol) and $NaHCO_3$ (19.8 mg, 0.236 mmol) were added DCM (10 mL) and Dess-Martin periodinate (100.0 mg, 0.236 mmol). The reaction mixture was stirred at room temperature for 1 h, quenched with aqueous $NaHCO_3$ solution, and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 2:1 petroleum ether/EtOAc) afforded compound **(–)-25** (40.1 mg, 87%) as a colorless oil. The overall yield of two steps is 76%.

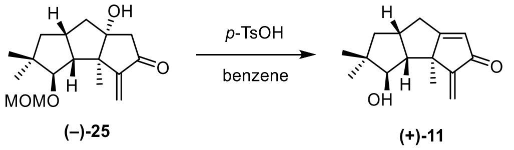
TLC (1:1 petroleum ether/EtOAc, R_f): 0.7

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 6.07 (s, 1H), 5.29 (s, 1H), 4.66 (s, 2H), 3.84 (d, *J* = 7.8 Hz, 1H), 3.40 (s, 3H), 2.63 – 2.51 (m, 2H), 2.49 – 2.38 (m, 2H), 1.94 (dd, *J* = 13.8, 9.0 Hz, 1H), 1.75 (dd, *J* = 12.6, 8.2 Hz, 1H), 1.65 (s, 1H), 1.60 (dd, *J* = 13.9, 5.1 Hz, 1H), 1.32 (dd, *J* = 12.6, 10.5 Hz, 1H), 1.26 (s, 3H), 1.11 (s, 3H), 0.94 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 204.2, 154.7, 117.7, 96.6, 88.1, 86.8, 57.6, 55.8, 54.4, 48.9, 46.9, 44.1, 43.5, 36.4, 27.3, 20.9, 16.9.

HRMS (ESI−FTICR, *m/z*): $[M + NH_4]^+$ calculated for $C_{17}H_{30}NO_4^+$: 312.2169; found: 312.2167.

Specific Rotation: $[\alpha]^{20}_D$ = -16.8 (*c* 0.81 $CHCl_3$).



(3aS,3bR,4R,6aS)-4-hydroxy-3a,5,5-trimethyl-3-methylene-3,3a,3b,4,5,6,6a,7-octahydro-2H-cyclopenta[a]pentalen-2-one ((+)-11)

To a flask with **(–)-25** (17.1 mg, 0.0581 mmol) and *p*-TsOH·H_2O (5.5 mg, 0.0290 mol) was added benzene (6 mL). The reaction mixture was stirred at 50 °C for 2 h, then purified by flash column chromatography (silica gel, 3:1 petroleum ether/EtOAc) afforded compound **(+)-11** (7.8 mg, 58%) as a colorless oil. The ^{1}H NMR, ^{13}C{^{1}H} NMR, HRMS and specific rotation matched with the literature report.[16]

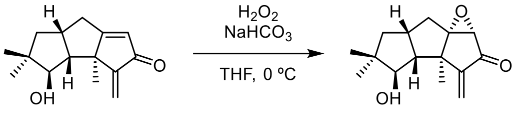
TLC (2:1 petroleum ether/EtOAc, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 5.93 (s, 1H), 5.91 (d, *J* = 1.9 Hz, 1H), 5.36 (s, 1H), 3.87 (d, *J* = 8.5 Hz, 1H), 2.78 (dd, *J* = 14.3, 8.0 Hz, 1H), 2.75 – 2.58 (m, 1H), 2.25 (ddd, *J* = 14.3, 8.5, 2.0 Hz, 1H), 2.15 (dd, *J* = 12.0, 8.5 Hz, 1H), 1.91 (dd, *J* = 12.7, 7.8 Hz, 1H), 1.49 (s, 1H), 1.28 (s, 3H), 1.26 (d, *J* = 2.5 Hz, 1H), 1.09 (s, 3H), 0.93 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 197.8, 188.3, 154.1, 123.5, 114.0, 80.8, 54.5, 51.1, 46.4, 45.4, 40.5, 33.1, 26.6, 24.1, 19.7.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{15}H_{21}O_2^+$: 233.1536; found: 233.1534.

Specific Rotation: $[\alpha]^{20}_D$ = 82.6 (*c* 0.45 $CHCl_3$).



(+)-11 **(−)-hypnophilin (2)**

(−)-hypnophilin (2)

To a flask with **(+)-11** (7.5 mg, 0.0323 mmol) and $NaHCO_3$ (47.7 mg, 0.568 mmol) were added THF (1.0 mL) and H_2O (1.0 mL). The suspension was cooled to 0 °C. Then a solution of H_2O_2 (30% in H_2O, 84 µL, 0.827 mmol) was added. The reaction mixture was stirred at 0 °C for 80 min (reaction time, 80 min here, was crucial for this reaction. Longer reaction time led to other unidentified products), diluted with with Et_2O. After extraction with Et_2O, the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 4:1 petroleum ether/EtOAc) afforded compound **(−)-hypnophilin (2**) (2.3 mg, 29%) as a colorless oil and substrate **(+)-11** (4.7 mg). The yield based on recovered starting material was 77%. The ^{1}H NMR, ^{13}C{^{1}H} NMR and specific rotation matched with the literature report.[16]

TLC (2:1 petroleum ether/EtOAc, R*f*): 0.5

^{1}H NMR (600 MHz, $CDCl_3$, *δ*): 6.13 (s, 1H), 5.46 (s, 1H), 3.87 (d, *J* = 9.0 Hz, 1H), 3.44 (s, 1H), 2.70 – 2.58 (m, 1H), 2.14 (dd, *J* = 12.0, 9.0 Hz, 1H), 1.99 – 1.87 (m, 3H), 1.30 (s, 3H), 1.20 (dd, *J* = 12.8, 10.2 Hz, 1H), 1.07 (s, 3H), 0.89 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, *δ*): 197.6, 153.7, 121.7, 81.2, 76.0, 61.1, 56.1, 46.1, 45.5, 44.1, 34.5, 30.7, 26.4, 19.7, 17.8.

HRMS (ESI−FTICR, *m/z*): [M + H]$^+$ calculated for $C_{15}H_{21}O_3^+$: 249.1485; found: 249.1486.

Specific Rotation: $[\alpha]^{20}_D$ = −80.5 (*c* 0.18 $CHCl_3$).

S7. DFT Study of Stereochemistry Rationalization

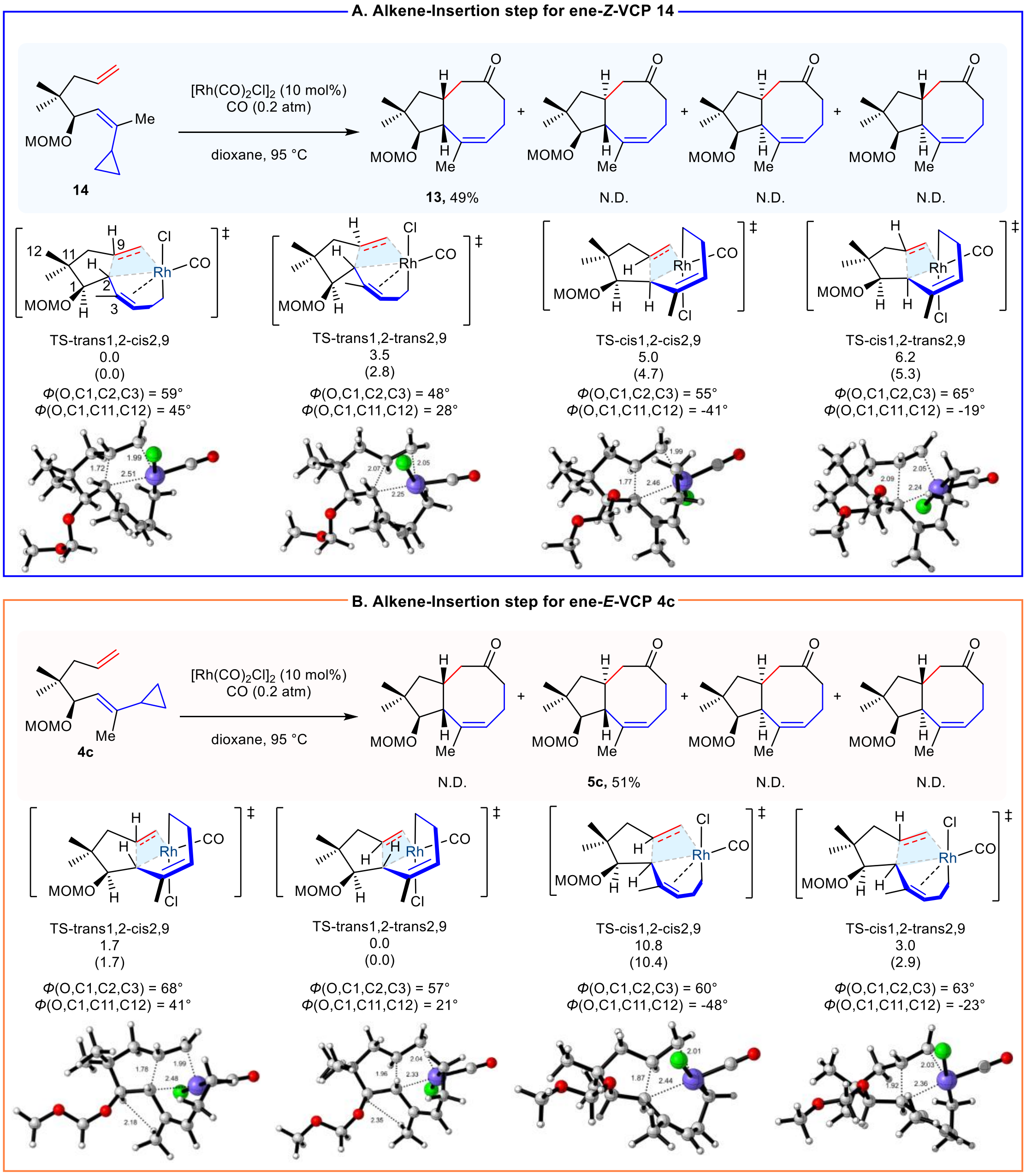


Figure S1. Computational study of diastereoselectivities of [5+2+1] cycloaddition for substrates **14** and **4c**. Reported are relative Gibbs energies in 1,4-dioxane for the alkene insertion steps (corresponding relative Gibbs free energies in the gas phase are shown in brackets). All were computed at the SMD(1,4-dioxane)/DLPNO-CCSD(T)/def2-TZVPP//BMK/def2-SVP level (see SI). Color scheme: H, white; C, gray; O, red; Cl, green; Rh, purple. Energy values are reported in kcal/mol. Bond lengths are reported in Å. N.D.=not detected.

We used DFT study to understand the diastereoselectivity of [5+2+1] cycloaddition of ene-*Z*-VCP substrate **14** (Figure S1A) and ene-*E*-VCP substrate **4c** (Figure S1B). Previous mechanistic investigation of [5+2+1] cycloaddition shows that the alkene-insertion step is irreversible and the stereoselectivity is determined by this step.[17] Based on this, we calculated the Gibbs energy of alkene-insertion transition states forming four isomers. For ene-*Z*-VCP, the most favored alkene-insertion transition state is **TS-trans$_{1,2}$-cis$_{2,9}$**, which will lead to cis$_{1,2}$-cis$_{2,9}$ product **13**. The calculation results agreed with our experiment. The other three transition states are 3-5 kcal/mol higher than TS-trans$_{1,2}$-cis$_{2,9}$. Therefore, the other three diastereoisomers would not be observed in the experiment. Through analyzing the structure of transition state in **TS-trans$_{1,2}$-cis$_{2,9}$**, we found that the dihedral angles Φ(O,C1,C2,C3) and Φ(O,C1,C11,C12) are 59° and 45°, respectively. The corresponding values of Φ(O,C1,C11,C12) in **TS-trans$_{1,2}$-trans$_{2,9}$** and **TS-cis$_{1,2}$-trans$_{2,9}$** are 28° and -19°. The much smaller angle values mean a larger torsional strain in the *trans*-configurated alkene-insertion transition states. In another disfavored transition state, **TS-cis$_{1,2}$-cis$_{2,9}$**, the MOM group, which occupied the position of *endo* face of five-membered ring, experiences obvious repulsion from the carbon bonding with Rh atom. For ene-*E*-VCP substrate, the most favored transition state is **TS-trans$_{1,2}$-trans$_{2,9}$**. The calculation results nicely accord with the experiment result. **TS-cis$_{1,2}$-cis$_{2,9}$** and **TS-cis$_{1,2}$-trans$_{2,9}$** are disfavored due to the same reason of ene-*Z*-VCP substrate. Compared with the most favored transition state TS-trans$_{1,2}$-trans$_{2,9}$, the nonbonding H···H distance in **TS-trans$_{1,2}$-cis$_{2,9}$** is 2.18 Å in, suggesting that a transannular repulsion exists in the *cis*-alkene insertion transition states.

Computed Energies of the Stationary Points:

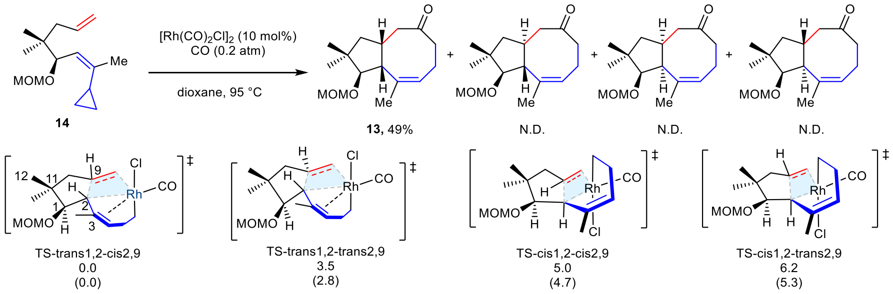


Table S1. Thermal Corrections to Gibbs Energies (TCGs) and Single-Point Energies (SPEs)

	TCG[a] (a.u.)	SPE[a] (a.u.)	SPE[b] (a.u.)	SPE[c] (a.u.)
TS-trans1,2-cis2,9	0.35133	-1419.78827	-1419.799775	-1419.709413
TS-trans1,2-trans2,9	0.348958	-1419.778533	-1419.788941	-1419.702512
TS-cis1,2-cis2,9	0.351108	-1419.780269	-1419.791222	-1419.701749
TS-cis1,2-trans2,9	0.347904	-1419.775056	-1419.78515	-1419.697541

[a] Computed at the BMK/def2-SVP level.

[b] Computed at the SMD(1,4-dioxane)/BMK/def2-SVP//BMK/def2-SVP level.

[c] Computed at the DLPNO-CCSD(T)/def2-TZVPP//BMK/def2-SVP level.

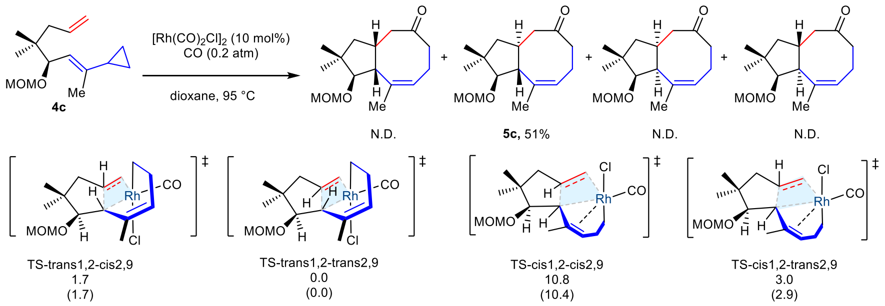


Table S2. Thermal Corrections to Gibbs Energies (TCGs) and Single-Point Energies (SPEs)

	TCG^a (a.u.)	SPE^a (a.u.)	SPE^b (a.u.)	SPE^c (a.u.)
TS-trans1,2-cis2,9	0.350075	-1419.785232	-1419.795959	-1419.704876
TS-trans1,2-trans2,9	0.350242	-1419.785966	-1419.796662	-1419.707735
TS-cis1,2-cis2,9	0.350093	-1419.771384	-1419.782578	-1419.69045
TS-cis1,2-trans2,9	0.348655	-1419.780083	-1419.790987	-1419.701345

^{a}Computed at the BMK/def2-SVP level.

^{b}Computed at the SMD(1,4-dioxane)/BMK/def2-SVP//BMK/def2-SVP level.

^{c}Computed at the DLPNO-CCSD(T)/def2-TZVPP//BMK/def2-SVP level.

Cartesian Coordinates of the Stationary Points:

Ene insertion of *Z*-substrate

TS-trans1,2-cis2,9

C	0.26097400	1.73312200	0.15759900
C	-0.41354800	0.25200000	0.70832300
C	0.12526600	-1.19444300	0.89228500
C	0.20310500	-1.61555200	2.34606400
C	1.59291300	1.81188800	-0.56909600
C	-0.91180700	2.32096500	-0.65774800
C	-2.22765700	1.71040300	-0.15448200
C	-1.80491800	0.23390900	0.02273500
C	-2.67000000	2.33187100	1.18308100
C	-3.35472800	1.85377700	-1.18657400
C	0.34411900	-2.13028700	-0.08671700
C	0.25216300	-1.96327800	-1.59868900
C	0.91826500	-0.62842700	-1.97707100
O	-2.69991300	-0.50723400	0.80995800
C	-3.23979100	-1.65565800	0.23796200
O	-4.22372400	-1.38988700	-0.69374600
C	-5.44615900	-0.98735400	-0.14151300
H	0.37783600	2.25322400	1.11681700
H	-0.59973100	0.54743300	1.74707800
H	-0.81098000	-1.56357100	2.78059600
H	0.58297600	-2.64331200	2.44841300
H	0.86711500	-0.93741200	2.90491800
H	2.33621300	2.42893400	-0.04881600
H	1.51410200	2.06594500	-1.63571700
H	-0.90174000	3.42242300	-0.58737900
H	-0.77635100	2.06544000	-1.72368500
H	-1.72579700	-0.21714500	-0.98255700
H	-3.51736600	1.76787300	1.60427500
H	-2.98737500	3.37641700	1.02474700
H	-1.86517600	2.34056500	1.93663700
H	-3.57724700	2.91861000	-1.37271400
H	-3.08026500	1.38564600	-2.14740800
H	-4.27644500	1.36889100	-0.82804700
H	0.61018100	-3.13023800	0.28029500
H	0.79724300	-2.80578900	-2.05389200
H	-0.79614800	-2.06249300	-1.94617100
H	0.17802700	0.15129900	-2.22339700
H	1.56976500	-0.73731500	-2.85808000
H	-2.45974600	-2.23509300	-0.28676800
H	-3.64116900	-2.24927000	1.08195100
H	-5.33169200	-0.09667100	0.50390100
H	-6.12576100	-0.74319500	-0.97106300

H	-5.89866000	-1.79967800	0.46172500
Rh	1.89568600	-0.12649400	-0.21023200
Cl	2.93489000	0.37145200	1.95987900
C	3.55449100	-0.18382800	-1.01120100
O	4.57901600	-0.20645900	-1.50032600

TS-trans1,2-trans2,9

C	-0.35324600	0.08795000	0.45996000
C	0.13649900	-1.25002500	0.96049300
C	0.20116000	-1.40428300	2.46549400
C	-1.79847100	0.19636200	-0.06152700
C	0.50060400	-2.28023800	0.12582700
C	0.35762800	-2.25774700	-1.38883300
C	1.42928200	-1.27604000	-1.89038400
O	-2.67892900	-0.39454100	0.86288000
C	-3.22381300	-1.61920900	0.48720800
O	-4.16846700	-1.50452400	-0.51420800
C	-5.37596800	-0.92317100	-0.10651700
H	-0.24208600	0.79467900	1.29315000
H	-0.82574400	-1.34357500	2.86649500
H	0.63903000	-2.37410600	2.74952100
H	0.79645900	-0.59164000	2.91132100
H	-1.91072700	-0.31093100	-1.03465700
H	0.88849200	-3.19008000	0.60122700
H	0.46791200	-3.27517800	-1.79971500
H	-0.65663000	-1.91619000	-1.65866300
H	1.10224000	-0.68512100	-2.76375500
H	2.33424800	-1.82895600	-2.18919100
H	-2.44489300	-2.30139300	0.10139600
H	-3.66746000	-2.04234500	1.40908900
H	-5.22905200	0.10445300	0.27490200
H	-6.04299900	-0.88948900	-0.98018100
H	-5.86022600	-1.52418400	0.68893600
Rh	1.79173600	-0.11649400	-0.19180200
Cl	2.34583700	1.18589600	1.84875100
C	3.66606900	-0.35271000	-0.39190700
O	4.78870900	-0.44964600	-0.51355000
C	0.22265300	1.34684400	-1.08007300
H	-0.21319200	0.78340900	-1.91451600
C	1.64120000	1.63047600	-1.25203200
H	2.03928300	1.50759900	-2.26617100
H	2.04400600	2.48548200	-0.69551700
C	-2.11201500	1.71563000	-0.24257400
C	-0.73449900	2.37791700	-0.51168500
H	-0.29762800	2.81344800	0.40279000
H	-0.82512100	3.19735500	-1.24736200
C	-3.06178900	1.90226300	-1.43850900
H	-2.57712100	1.60964200	-2.38690400
H	-3.95987900	1.27290800	-1.31733400
H	-3.38347700	2.95374900	-1.52948200
C	-2.74527800	2.30966600	1.02605400
H	-3.75264100	1.90054200	1.19816000
H	-2.13720200	2.09398800	1.92013300
H	-2.82356500	3.40553700	0.92169500

TS-cis1,2-cis2,9

C	0.37869400	0.50007900	0.71944900
C	-0.07094600	-0.88773900	1.25831900
C	-0.16968100	-0.88951800	2.77544100
C	-0.26431500	-2.07505900	0.59617500
C	-0.23336300	-2.40285000	-0.89052800
C	-0.77845500	-1.20249700	-1.67220500
H	0.32377200	1.10919700	1.62671600
H	-0.94145000	-0.17112900	3.09769500
H	-0.42835200	-1.88667000	3.16198200
H	0.79790700	-0.58600600	3.21475300
H	-0.48863800	-2.92187000	1.25885800
H	0.77724700	-2.72806900	-1.20186200
H	-0.88939800	-3.27860900	-1.03192000
H	-1.38178300	-1.51393000	-2.53930600
H	0.03764200	-0.56199100	-2.03964000
Rh	-1.80381300	-0.19639400	-0.17572600
Cl	-2.85697500	0.96999600	1.72398400
C	-3.43748900	-0.63947800	-0.91156300
O	-4.44481300	-0.88960400	-1.37315300
C	-0.30047900	1.72280800	-0.35984800
H	-0.52450100	2.48060400	0.40083200
C	-1.55971200	1.51319000	-1.17264700
H	-2.35081100	2.23816500	-0.94359900
H	-1.39638300	1.39079300	-2.25264600
C	2.18593700	1.87162800	-0.31462400
C	0.93799900	2.09853600	-1.18223000
H	0.99700900	1.45484600	-2.07698900
H	0.84749900	3.14317800	-1.52834600
C	2.30315300	2.93076900	0.80027400
H	1.40280200	3.00452500	1.43159400
H	3.16041600	2.70618000	1.45800600
H	2.47542700	3.92578400	0.35610700

C	3.47631500	1.87583900	-1.14627000
H	3.63156000	2.87414800	-1.59018400
H	4.34800900	1.62867400	-0.51896200
H	3.42815600	1.13140300	-1.95435100
C	1.87791800	0.48083600	0.29785200
H	2.48913700	0.31858300	1.20505300
O	2.14545300	-0.53742000	-0.63111500
C	3.01178100	-1.52082500	-0.22181300
H	3.01513300	-2.29544900	-1.01535900
H	2.66785700	-1.98807200	0.73263900
O	4.28680400	-0.99283000	-0.04610000
C	5.21111100	-1.91938400	0.43324200
H	5.33651300	-2.77409900	-0.26249200
H	6.17927800	-1.40865300	0.53623700
H	4.91576100	-2.32289700	1.42392900

TS-cis1,2-trans2,9

C	0.33065000	0.22108100	0.58536400
C	-0.13313200	-1.03993600	1.28034000
C	-0.29857400	-0.91588200	2.78380200
C	-0.43142600	-2.22354400	0.64691400
C	-0.24741200	-2.53154500	-0.83284500
C	-1.22174200	-1.62050400	-1.60023100
H	0.08754000	1.04903700	1.26572900
H	-0.96597700	-0.07327500	3.02705600
H	-0.70893400	-1.84068200	3.21862500
H	0.68602500	-0.72304300	3.24711500
H	-0.81566200	-3.02520300	1.29101300
H	0.79148400	-2.32221900	-1.12579200
H	-0.43608000	-3.60315500	-1.01008700
H	-2.10502800	-2.19298800	-1.92595200
H	-0.76746200	-1.17793100	-2.50300500
Rh	-1.73766800	-0.18948300	-0.17635900
Cl	-2.47408000	1.44041100	1.55339300
C	-3.58391100	-0.54680500	-0.45263700
O	-4.69080500	-0.71438000	-0.63046400
C	-1.57373400	1.32125000	-1.55092800
H	-2.07041200	2.23864300	-1.21184800
H	-1.87066400	0.97482300	-2.54785100
C	2.03429100	1.86280100	-0.22954100
C	2.50880200	2.70522600	0.96790500
H	1.82765000	2.59980900	1.83074600
H	3.52139200	2.40113600	1.28367200
H	2.54086000	3.77481800	0.69853700
C	3.07537400	1.93954500	-1.35934900
H	4.01200100	1.44355600	-1.06009400
H	2.71536100	1.44136700	-2.27365600
H	3.28690000	2.99604500	-1.59694000
C	1.81436700	0.38054000	0.23465800
H	2.38176900	0.22713700	1.17135300
O	2.25460700	-0.56152900	-0.71342900
C	3.19487900	-1.46177500	-0.27516200
H	3.32244700	-2.21176100	-1.08222700
H	2.84921500	-1.98745200	0.64838500
O	4.39442600	-0.80789700	-0.01312300
C	5.38869300	-1.64629900	0.48940600
H	5.64356800	-2.45622000	-0.22415200
H	6.28765100	-1.03761500	0.66268900
H	5.08677300	-2.11449500	1.44895900
C	0.64866100	2.35748200	-0.72334000
H	0.76552700	3.05603200	-1.57135300
H	0.08510300	2.89124700	0.06155000
C	-0.16616200	1.17763500	-1.20942800
H	0.39981500	0.50697000	-1.86743500

Ene insertion of *E*-substrate

TS-trans1,2-cis2,9

C	3.79799000	-0.27312800	0.40061300
O	4.89155000	-0.48279600	0.62484200
Rh	2.01525600	0.04203300	0.03632300
C	-0.37182000	0.35053700	-0.57105900
C	-1.73193800	-0.06733700	0.04651500
O	-2.59821400	1.01602100	-0.18754600
C	1.66417000	-1.71363700	-0.83977500
C	0.25705200	-1.22328200	-1.10582800
C	-0.81611900	-2.15940400	-0.54413000
C	-2.16285300	-1.42747000	-0.55181100
C	-2.73648000	-1.25966000	-1.96977600
C	0.25357300	1.51943000	0.23543600
C	1.64496000	2.20663500	-1.79711700
C	2.49094300	0.91597200	-1.80066700
Cl	1.39289700	-0.94648700	2.21568000
C	-3.17508000	-2.16884600	0.33758600
H	2.24351000	0.24493900	-2.64147300
H	0.78309600	2.13911800	-2.48583000
H	3.56259200	1.15774600	-1.87754000
H	2.22164700	3.09512700	-2.09936800
H	-1.59712600	-0.21520900	1.13414100

H	-0.53599000	-2.41644400	0.49301300
H	-0.84226900	-3.09436200	-1.13095400
H	0.13167400	-1.07132600	-2.18525400
H	2.25631400	-1.90211000	-1.74484700
H	1.71947600	-2.53693800	-0.11588300
H	-0.58520200	0.78003400	-1.55871800
H	-2.03912900	-0.74115200	-2.64938900
H	-3.66574700	-0.67023800	-1.93018800
H	-2.96099100	-2.24809400	-2.40617400
H	-3.34727200	-3.18636200	-0.05442800
H	-4.14177300	-1.64396900	0.35752000
H	-2.79573100	-2.26774300	1.36983800
C	-3.71886400	1.15924800	0.58990100
H	-3.90241400	2.24759200	0.71612800
H	-3.56638800	0.70423300	1.59776900
O	-4.82190000	0.57836400	-0.03240600
C	-6.01484400	0.78826500	0.65785300
H	-6.23830100	1.86927300	0.76984200
H	-6.82572700	0.32071900	0.08113600
H	-5.99308200	0.33451700	1.67055000
C	-0.25622500	1.86374200	1.62244300
H	-1.29081700	2.23522900	1.55045800
H	-0.21790500	0.99937100	2.29960900
H	0.36591900	2.66170700	2.05544300
C	1.14671700	2.36931000	-0.37173000
H	1.49729800	3.22817400	0.21365000

TS-trans1,2-trans2,9

C	3.78738900	-0.01458000	-0.18234600
Rh	1.92320700	0.01898600	0.00066500
Cl	1.79659600	-0.58188700	-2.40442400
O	4.91482400	-0.01258700	-0.31048400
C	-0.35503400	-0.04313900	0.50644200
C	0.23174800	-1.42583600	0.45744000
C	1.60267400	-0.94608200	2.58835400
C	2.07332000	0.41661800	2.03324800
C	1.60758900	1.97283800	-0.49284900
C	0.20172500	1.52895500	-0.51470900
C	-0.86707600	2.36713700	0.17115700
C	-2.21317500	1.60202000	0.11941200
C	-3.02729300	2.03924800	-1.11218900
C	-1.79716100	0.09461800	-0.01526800
O	-2.58957400	-0.78693600	0.74166500
C	-3.02527300	1.84417100	1.40137600
H	-1.83777300	-0.20737500	-1.07878800
H	1.41928500	1.25657000	2.32509100
H	0.75831000	-0.87172700	3.30010800
H	3.09178200	0.66510800	2.36948300
H	2.41571800	-1.46354600	3.12105200
H	-0.93552500	3.33783000	-0.35037900
H	-0.55886700	2.58422300	1.20893600
H	-0.08617200	1.18400100	-1.51673700
H	1.87618900	2.70608900	0.27970400
H	2.03451000	2.17403700	-1.48192300
H	-0.32957600	0.35412200	1.52810700
H	-2.49416100	1.46709100	2.29170000
H	-4.00006600	1.33747200	1.34721900
H	-3.18965800	2.92768200	1.53388500
H	-3.35832600	3.08661400	-1.00721400
H	-3.91739000	1.40045100	-1.22130300
H	-2.42479900	1.96447300	-2.03506100
C	-3.61625000	-1.43985500	0.11130000
H	-3.90988600	-2.28307400	0.76938800
H	-3.28385200	-1.85096100	-0.87248500
O	-4.70074700	-0.58856500	-0.08866900
C	-5.80148800	-1.22589900	-0.66186200
H	-6.17553200	-2.05012200	-0.02081500
H	-6.60138600	-0.48067400	-0.77707100
H	-5.56192400	-1.64624000	-1.66014600
C	-0.25088300	-2.41504500	-0.57907800
H	-1.23124600	-2.80946900	-0.26268500
H	-0.33910400	-1.95246100	-1.57234800
H	0.45321200	-3.25591400	-0.66600400
C	1.19989900	-1.79211600	1.37941700
H	1.59948700	-2.81009400	1.29439100

TS-cis1,2-cis2,9

C	-3.37198100	-0.87173400	-0.78274900
Rh	-1.78722200	-0.15553100	-0.12613200
C	-2.24254500	1.44456000	2.19115200
C	-2.79991900	1.45089300	0.75282100
O	-4.33160500	-1.30611200	-1.20572100
Cl	-0.78904400	-2.19867500	-1.09911300
C	-1.33081600	0.93521500	-1.74625900
C	-0.24520600	1.53435600	-0.90653000
C	1.12676600	1.62796800	-1.57309100
C	2.21733300	1.76405500	-0.50212400
C	3.61357700	1.57652000	-1.11116800

C	-0.36580100	-0.22421300	1.67051100
C	0.28682300	0.80616600	0.73599500
C	1.80503100	0.61361600	0.45878000
O	2.04988600	-0.62509600	-0.14048100
C	2.18201700	3.13260400	0.20997100
H	-2.63359000	2.40619600	0.22589800
H	-1.53328000	2.27446400	2.36684100
H	-3.88666200	1.27192700	0.76639700
H	-3.02785900	1.53736800	2.95839000
H	2.34986400	0.68850700	1.42313600
H	1.30832900	0.70670700	-2.15018500
H	1.11967400	2.47996900	-2.27632300
H	-0.57223400	2.50621700	-0.51959400
H	-2.11453500	1.64382100	-2.04468900
H	-0.98136100	0.29684000	-2.56835300
H	0.17898400	1.76118600	1.26041500
H	1.19091200	3.41478300	0.59922500
H	2.89240600	3.14677200	1.05521900
H	2.49089400	3.92431800	-0.49324100
H	3.81843400	2.40146600	-1.81507900
H	4.39342500	1.58349600	-0.33188100
H	3.69250100	0.62084700	-1.64560600
C	2.99914200	-1.46994500	0.37102900
H	2.72104000	-2.49145400	0.03927000
H	3.00894100	-1.44498300	1.48465600
O	4.26998600	-1.13894100	-0.09206600
C	5.25486400	-2.02115500	0.34500500
H	5.05870200	-3.05878300	0.00519600
H	6.21616600	-1.69078600	-0.07432300
H	5.33857800	-2.03385500	1.45222600
C	0.30175400	-1.54116200	2.01029200
H	0.50366000	-2.13699600	1.11028800
H	1.24234600	-1.35253900	2.55428200
H	-0.35653000	-2.12119900	2.67483600
C	-1.52439700	0.11366100	2.33775600
H	-1.92604000	-0.62516500	3.04163600

TS-cis1,2-trans2,9

C	-3.66833400	-0.27490800	-0.40589700
Rh	-1.84841200	-0.02808700	-0.06495800
Cl	-1.47022000	-1.99607400	-1.51982100
O	-4.76955000	-0.41865000	-0.64043100
C	0.37114600	0.38116000	0.60811700
C	-0.24513800	-0.76346400	1.37342600
C	-1.83580200	0.88536600	2.56960500
C	-2.23704700	1.54900300	1.23309800
C	-1.41365100	1.18974400	-1.62980200
C	-0.02078400	0.96661300	-1.17578800
C	0.88094900	2.18323500	-1.00858100
C	2.21403200	1.74564800	-0.34103100
C	3.32343900	1.64145200	-1.40059700
C	1.89149600	0.35504500	0.31577600
O	2.25552700	-0.72238900	-0.50434300
C	2.63944100	2.74184900	0.75292600
H	-1.62566100	2.43425600	0.98515400
H	-1.07368500	1.45178800	3.13892600
H	-3.28875700	1.87449400	1.24102800
H	-2.70281400	0.77451600	3.23937400
H	2.42030400	0.27268900	1.28472700
H	1.05921900	2.62038300	-2.00573400
H	0.35401200	2.95148600	-0.41451200
H	0.45330500	0.13359600	-1.71089400
H	-1.79044600	2.21822400	-1.54497000
H	-1.66721200	0.69087300	-2.57205200
H	0.19451500	1.31103700	1.16034600
H	1.90127400	2.79105600	1.57338600
H	3.61455800	2.45719600	1.18370700
H	2.73684200	3.75760900	0.33291600
H	3.53290100	2.64478700	-1.80915400
H	4.24603400	1.22740400	-0.96964000
H	3.01898600	0.98202000	-2.22825500
C	3.24911800	-1.56105700	-0.06235200
H	3.28110700	-2.40914200	-0.77496200
H	3.02366100	-1.95861000	0.95373800
O	4.47385400	-0.90036600	-0.01836100
C	5.50967000	-1.69528700	0.46978400
H	5.67377100	-2.59150200	-0.16245700
H	6.42905500	-1.09233800	0.46687300
H	5.31333700	-2.03769700	1.50711000
C	0.29334000	-2.17230100	1.26114000
H	0.53620600	-2.43163400	0.22326500
H	1.19581700	-2.26324500	1.89103300
H	-0.45181100	-2.89184400	1.63218100
C	-1.31241800	-0.50840700	2.22138300
H	-1.72763500	-1.37111500	2.75676800

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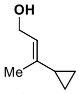
S9. NMR Spectra of New Compounds



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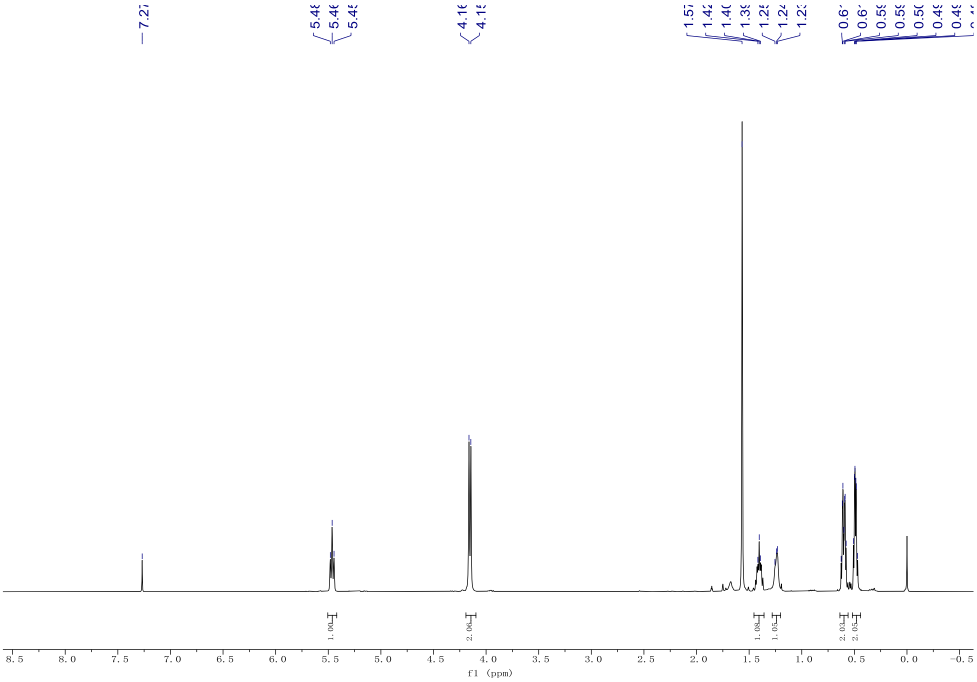

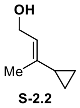

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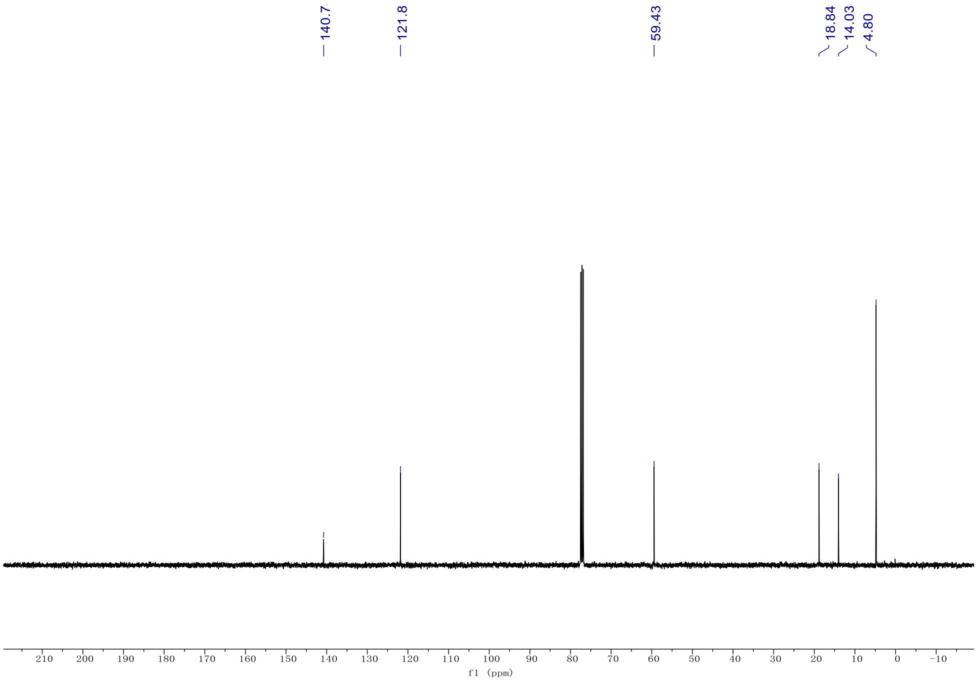

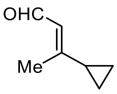
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Me

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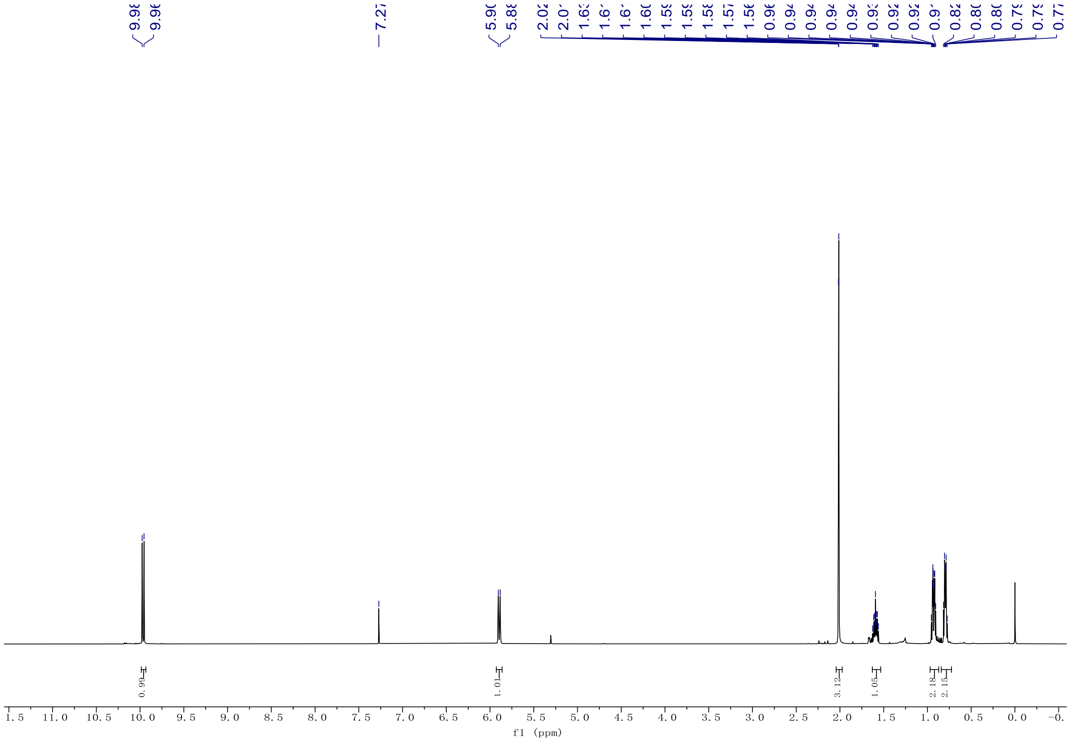
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1.63
1.61
1.61
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1.59
1.58
1.57
1.56
0.96
0.94
0.94
0.94
0.94
0.93
0.92
0.92
0.91
0.82
0.80
0.80
0.79
0.79
0.77
0.99
1.01
3.12
1.05
2.18
2.15
1.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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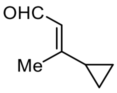
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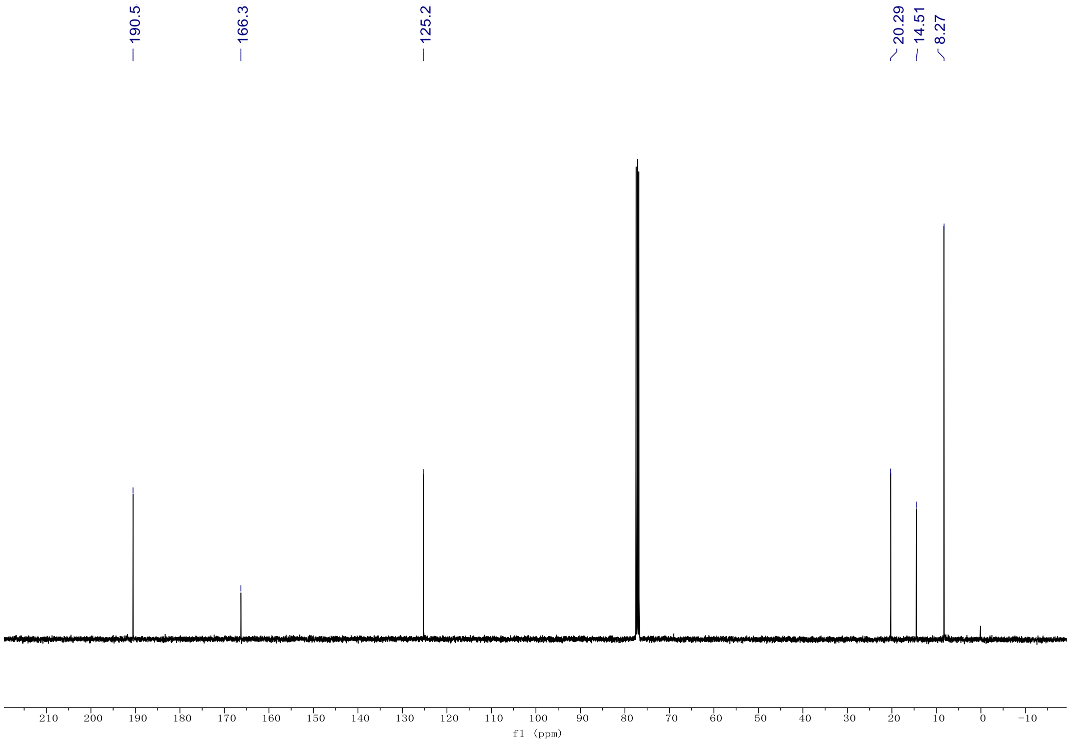
S-2.3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20.29
14.51
8.27
210
200
190
180
170
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110
100
90
80
70
60
50
40
30
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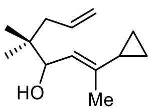
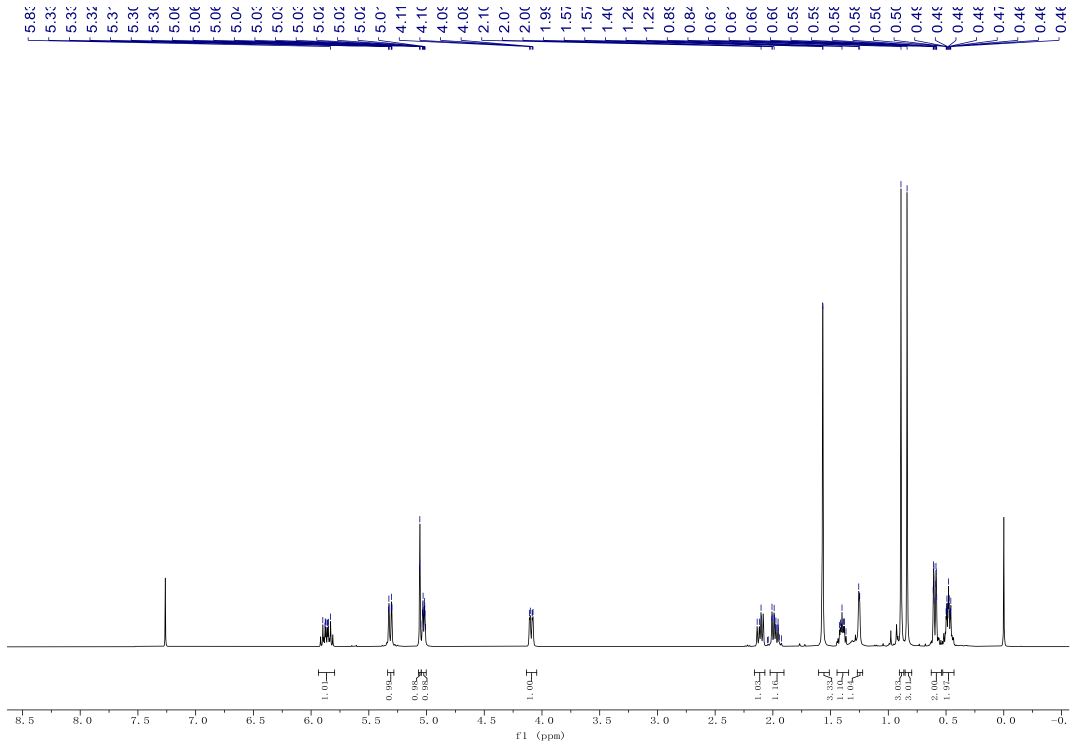
f1 (ppm)


HO
Me

S-2.4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5.33
5.32
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5.30
5.06
5.06
5.04
5.03
5.03
5.02
5.02
5.02
5.01
4.11
4.09
4.08
2.10
2.01
2.00
1.99
1.57
1.57
1.40
1.26
1.25
0.89
0.84
0.61
0.61
0.60
0.60
0.59
0.58
0.58
0.50
0.50
0.49
0.49
0.48
0.48
0.47
0.46
0.46
1.01
0.99
0.98
0.98
1.00
1.03
1.16
3.33
1.10
1.04
3.03
3.01
2.00
1.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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0.5
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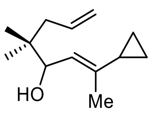
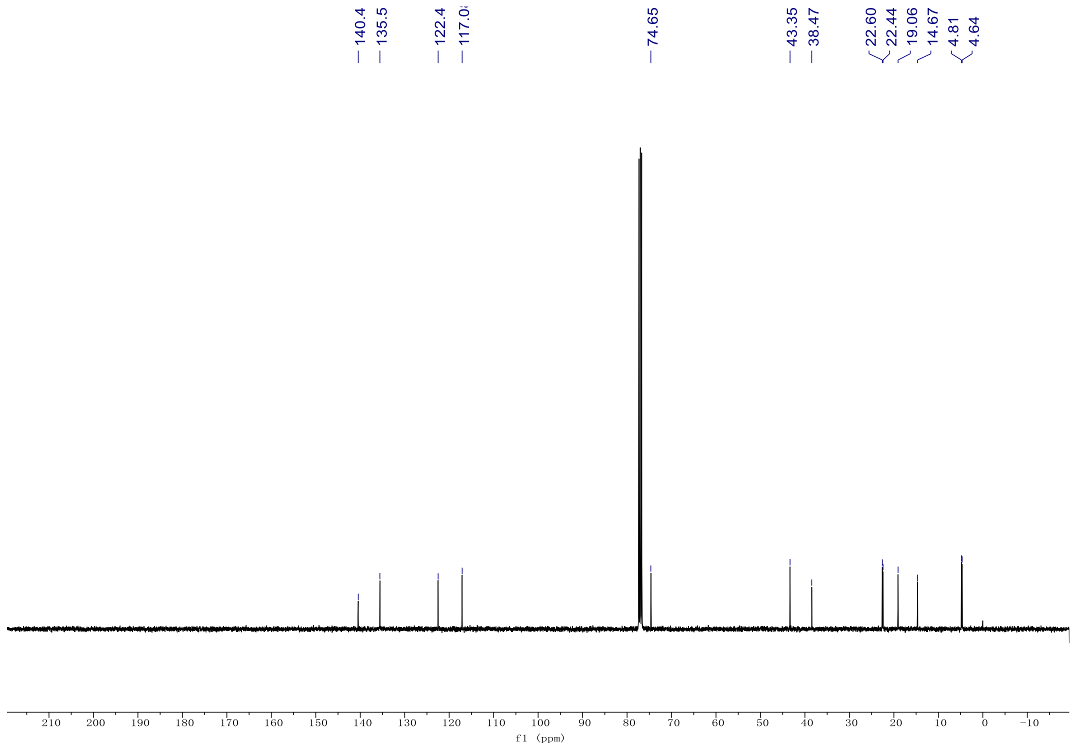
f1 (ppm)


HO
Me

S-2.4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117.0
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38.47
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19.06
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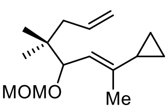
4.81
4.64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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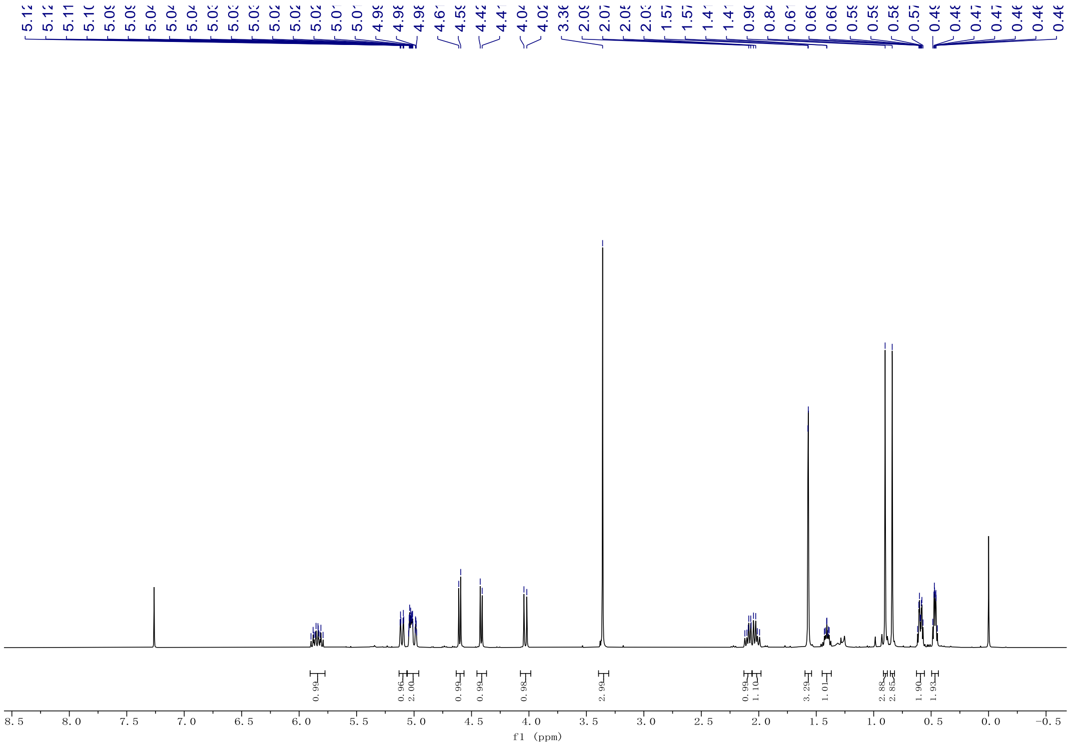
Me

4c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5.04
5.04
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5.03
5.03
5.03
5.02
5.02
5.02
5.01
5.01
4.99
4.98
4.98
4.61
4.59
4.42
4.41
4.04
4.02
3.36
2.09
2.07
2.05
2.03
1.57
1.57
1.41
1.41
0.90
0.84
0.61
0.60
0.60
0.59
0.59
0.58
0.57
0.49
0.48
0.47
0.47
0.46
0.46
0.46
0.99
0.96
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0.99
0.99
0.98
2.99
0.99
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3.29
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1.90
1.93
8.5
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7.5
7.0
6.5
6.0
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5.0
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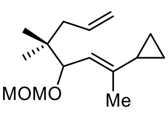
f1 (ppm)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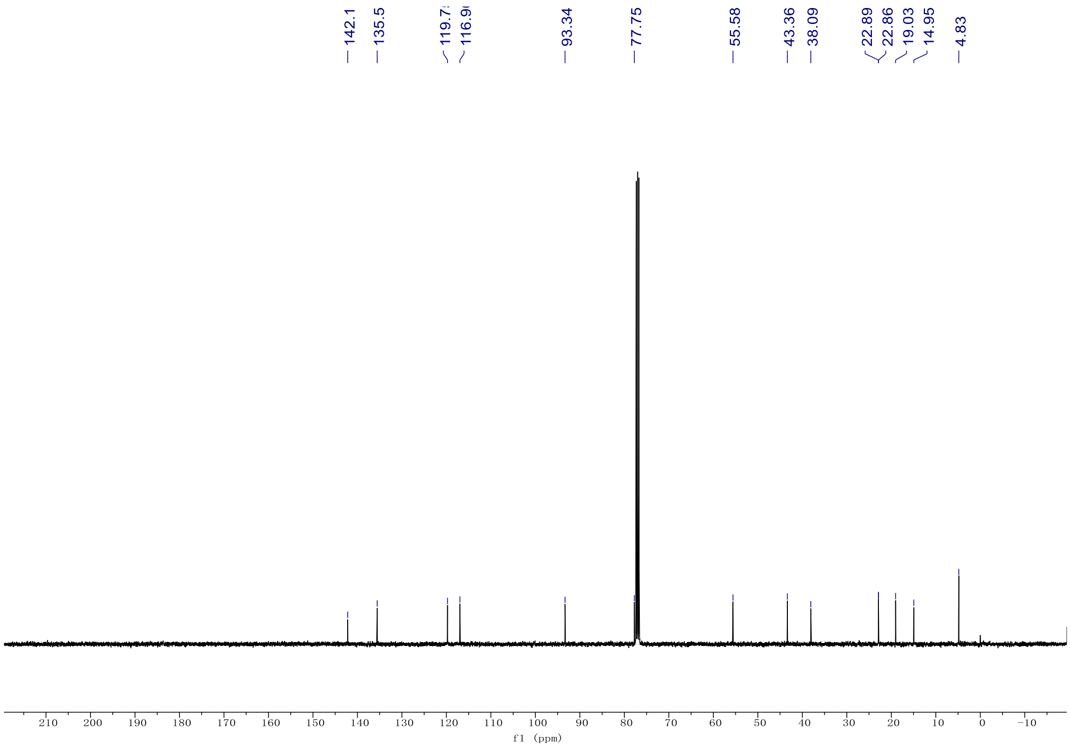
Me

4c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14.95
4.83
210
200
190
180
170
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140
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120
110
100
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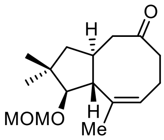
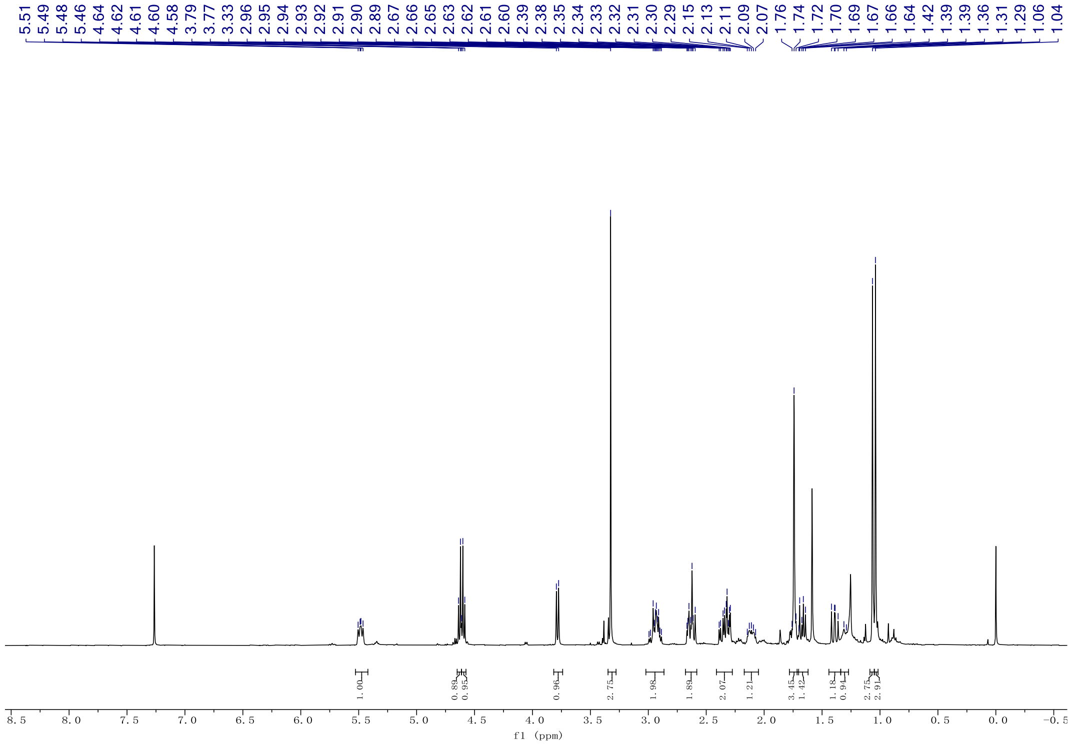
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



H
O
MOMO
H
Me

5c



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2.94
2.93
2.92
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2.90
2.89
2.67
2.66
2.65
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2.62
2.61
2.60
2.39
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2.35
2.34
2.33
2.32
2.31
2.30
2.29
2.15
2.13
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2.09
2.07
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1.72
1.70
1.69
1.67
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1.64
1.42
1.39
1.39
1.36
1.31
1.29
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1.04
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0.95
0.96
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2.07
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1.18
0.94
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7.0
6.5
6.0
5.5
5.0
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2.0
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0.5
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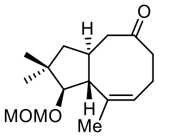
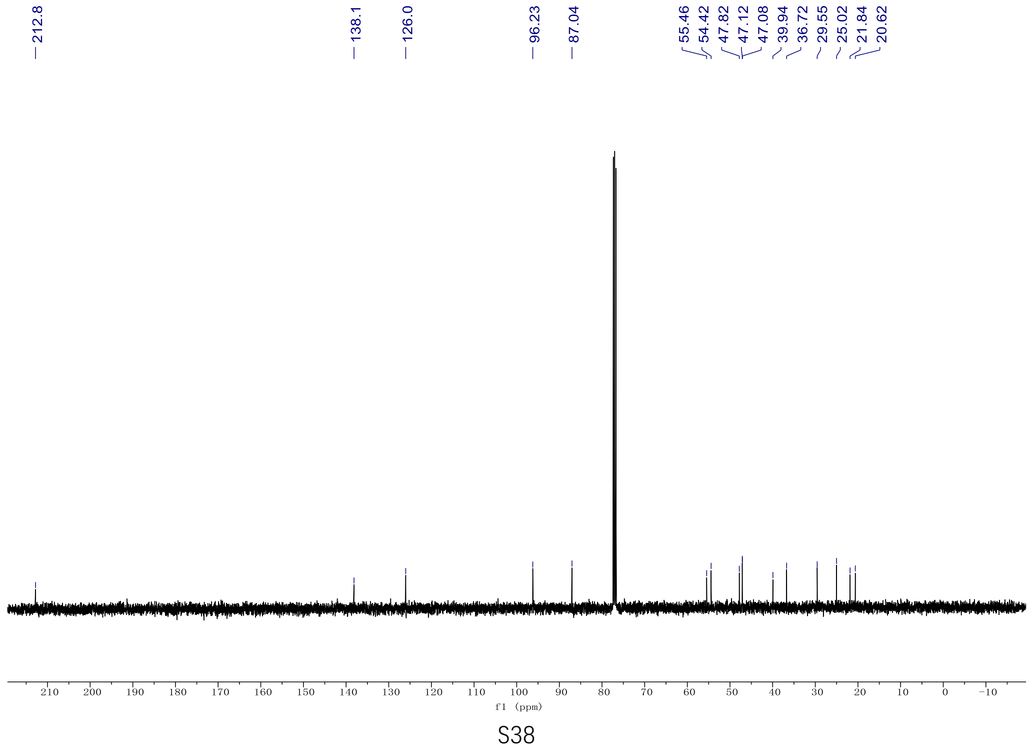
-0.5
f1 (ppm)



H
O
MOMO
H
Me

5c



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55.46
54.42
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47.08
39.94
36.72
29.55
25.02
21.84
20.62
210
200
190
180
170
160
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140
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120
110
100
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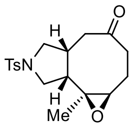
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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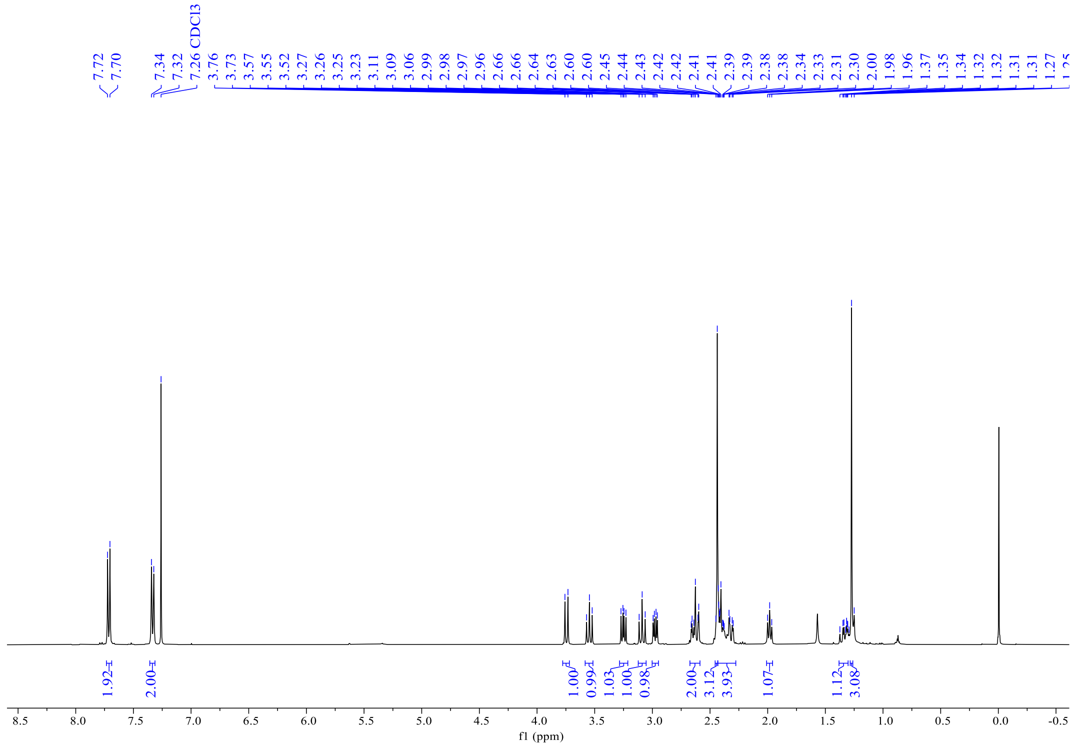
H
TsN
H
Me
O

6a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3.26
3.25
3.23
3.11
3.09
3.06
2.99
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2.97
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2.63
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2.33
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1.31
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1.00
0.99
1.03
1.00
0.98
2.00
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3.93
1.07
1.12
3.08
8.5
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7.5
7.0
6.5
6.0
5.5
5.0
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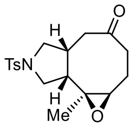
f1 (ppm)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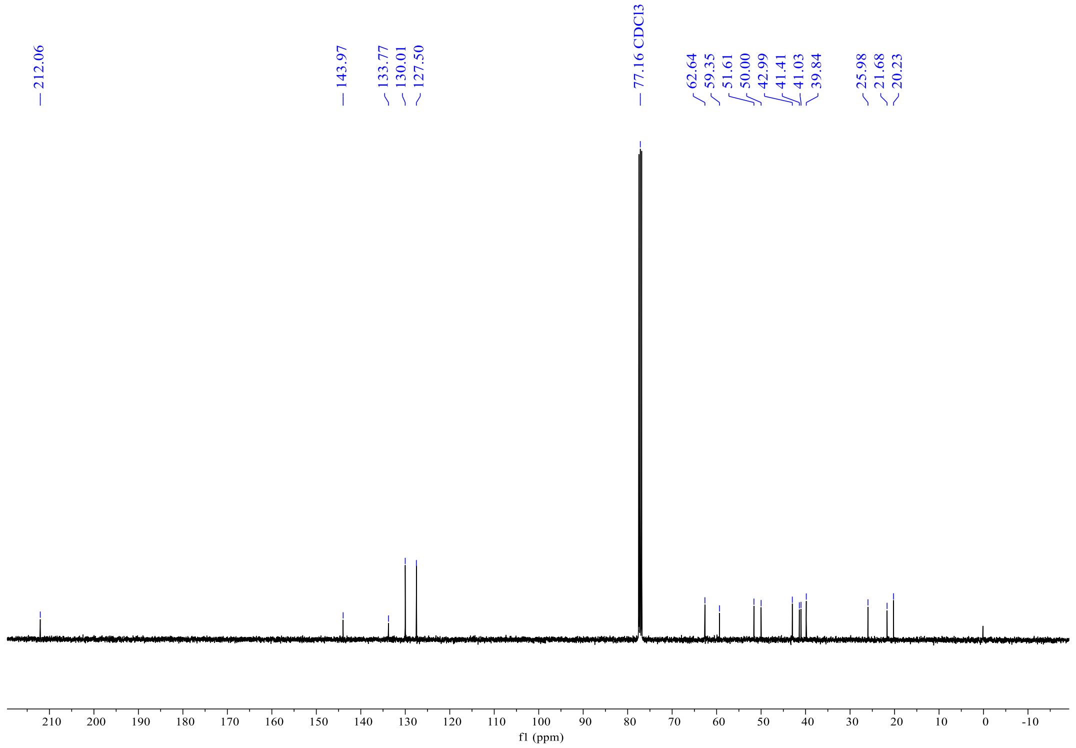
H
TsN
H
Me
O

6a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41.41
41.03
39.84
25.98
21.68
20.23
210
200
190
180
170
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80
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60
50
40
30
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0
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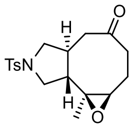
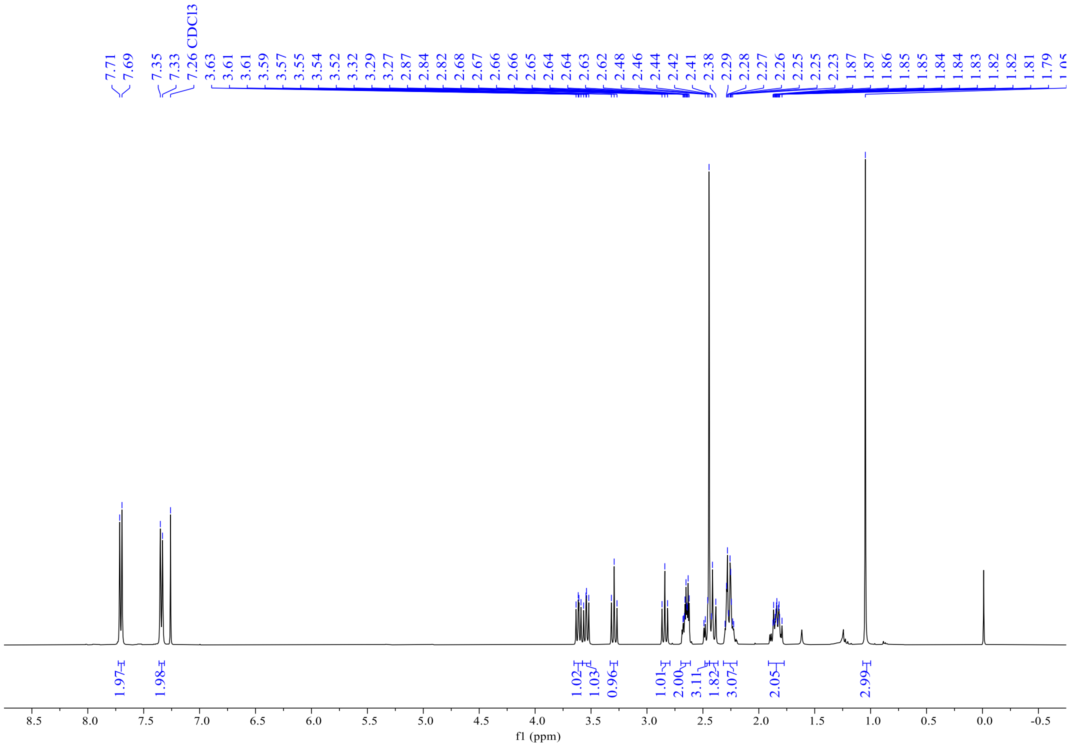
f1 (ppm)


TsN
H
H
O
O

6b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3.61
3.61
3.59
3.57
3.55
3.54
3.52
3.32
3.29
3.27
2.87
2.84
2.82
2.68
2.67
2.66
2.66
2.65
2.64
2.64
2.63
2.62
2.48
2.46
2.44
2.42
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2.28
2.27
2.26
2.25
2.25
2.23
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1.87
1.86
1.85
1.85
1.84
1.84
1.83
1.82
1.82
1.81
1.79
1.97
1.98
1.02
1.03
0.96
1.01
2.00
3.11
1.82
3.07
2.05
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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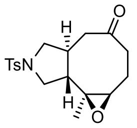
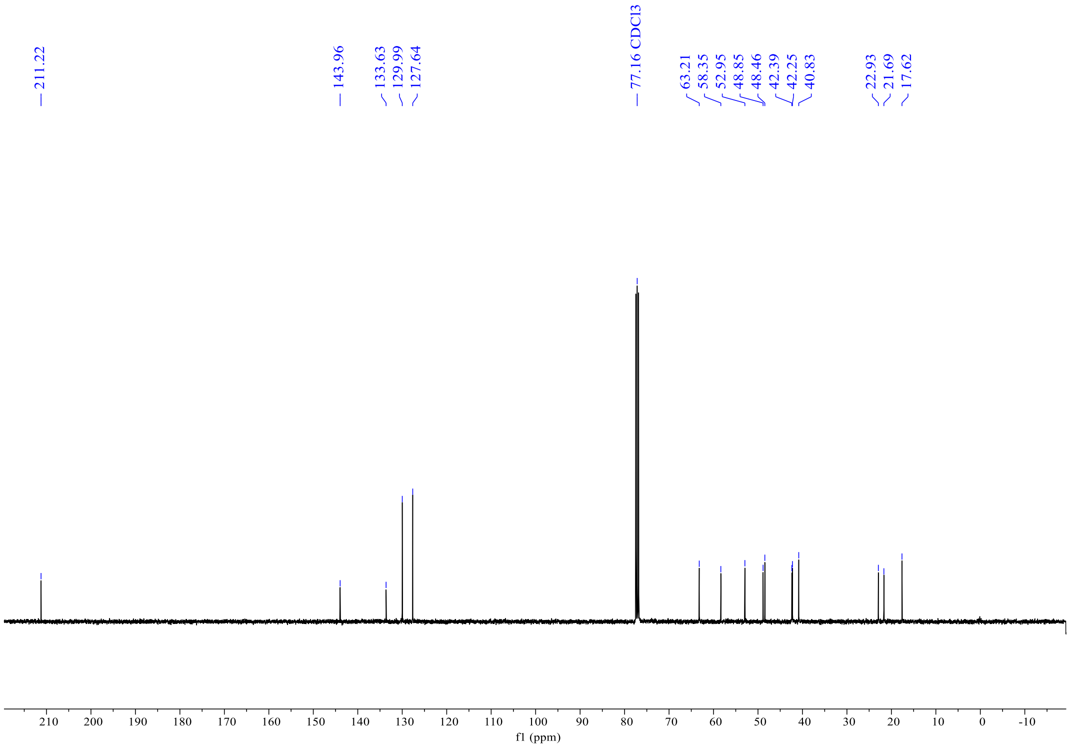
f1 (ppm)


TsN
H
H
O
O

6b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42.39
42.25
40.83
22.93
21.69
17.62
210
200
190
180
170
160
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120
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100
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80
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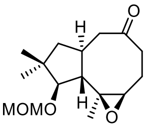
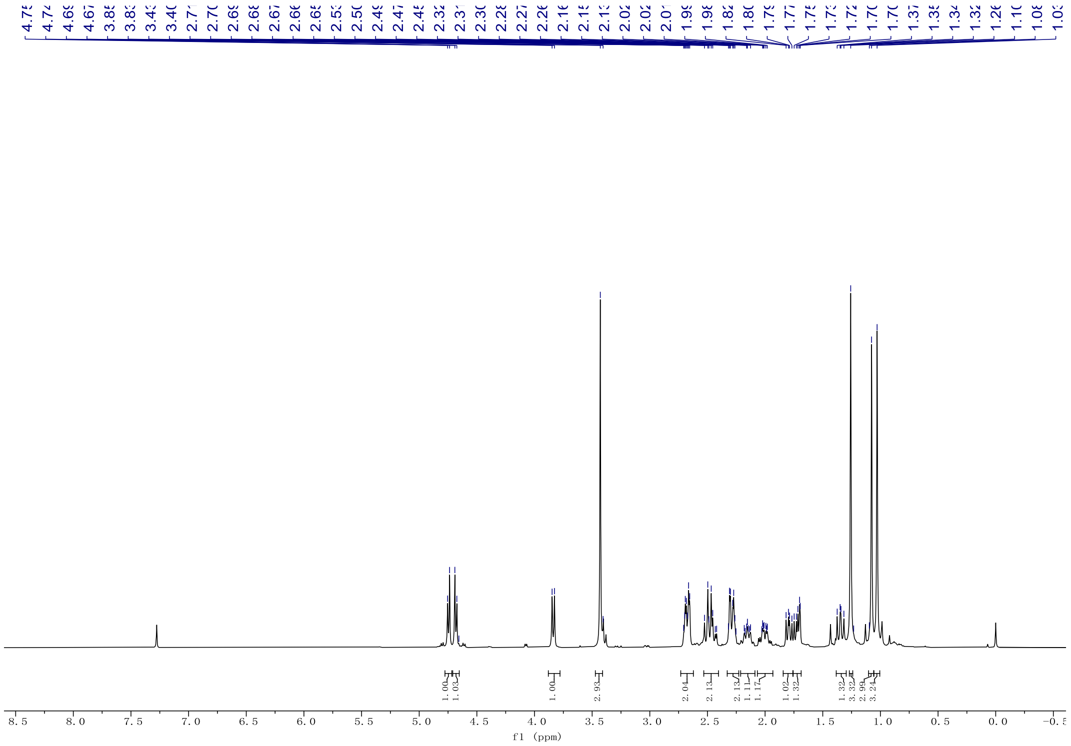
50
40
30
20
10
0
-10
f1 (ppm)



O
H
H
MOMO
O

6c



1.00
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1.00
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2.04
2.13
2.13
1.11
1.17
1.02
1.32
1.32
3.32
2.99
3.24
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.5
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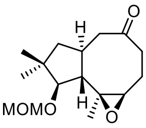
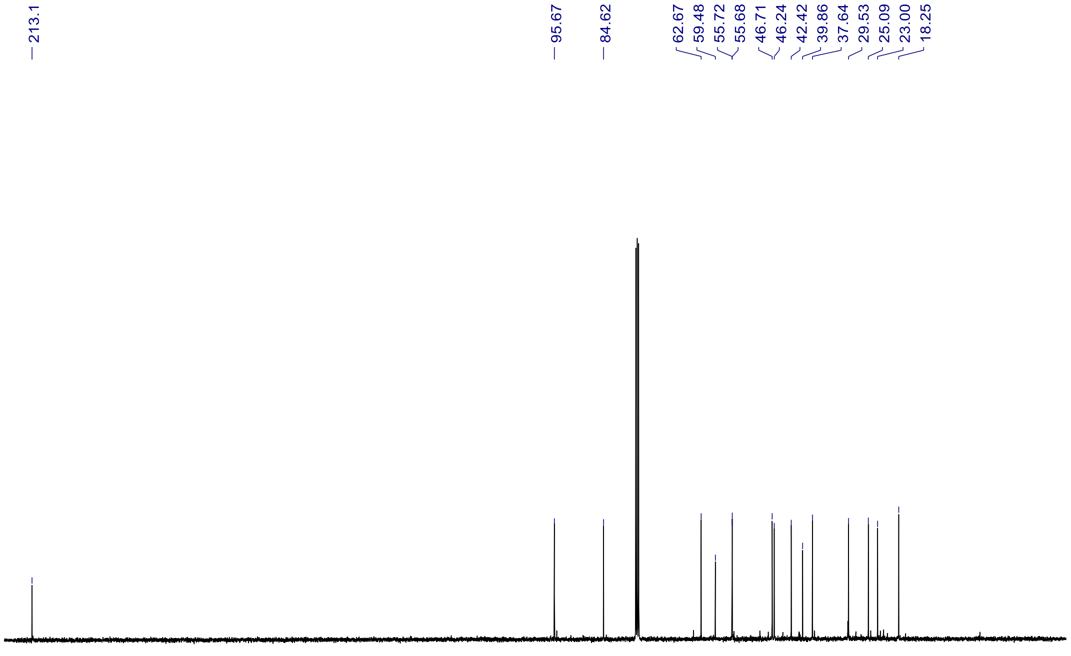
-0.5
f1 (ppm)



O
H
H
MOMO
O

6c



213.1
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84.62
62.67
59.48
55.72
55.68
46.71
46.24
42.42
39.86
37.64
29.53
25.09
23.00
18.25
210
200
190
180
170
160
150
140
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120
110
100
90
80
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60
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30
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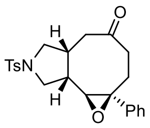
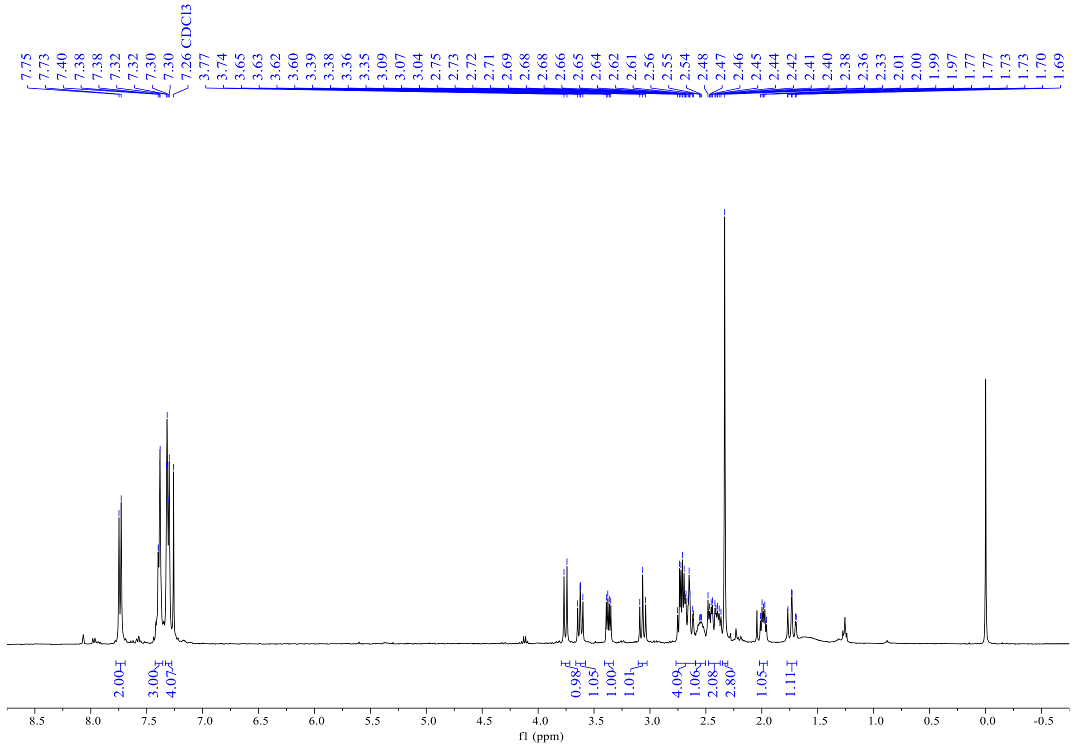
0
-10
f1 (ppm)


O
H
TsN
H
O
Ph

6d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7.32
7.32
7.30
7.30
7.26 CDCl3
3.77
3.74
3.65
3.63
3.62
3.60
3.39
3.38
3.36
3.35
3.09
3.07
3.04
2.75
2.73
2.72
2.71
2.69
2.68
2.68
2.66
2.65
2.64
2.62
2.61
2.56
2.55
2.54
2.48
2.47
2.46
2.45
2.44
2.42
2.41
2.40
2.38
2.36
2.33
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2.00
1.99
1.97
1.77
1.77
1.73
1.73
1.70
1.69
2.00
3.00
4.07
0.98
1.05
1.00
1.01
4.09
1.06
2.08
2.80
1.05
1.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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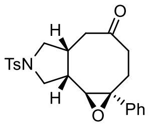
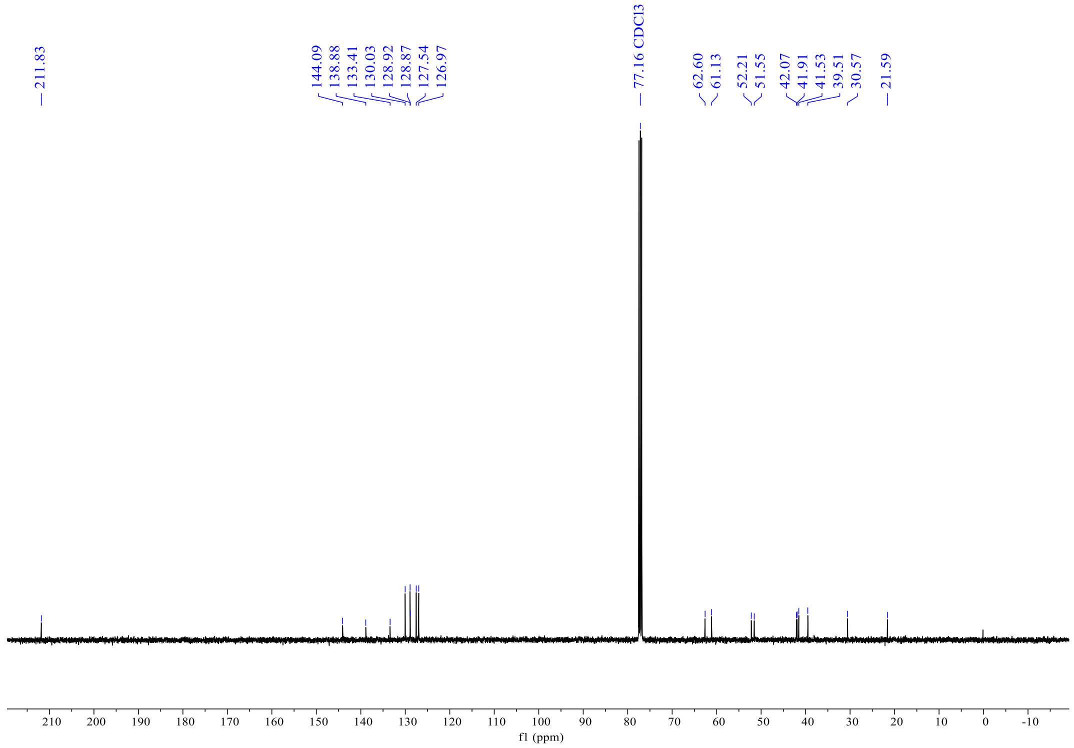
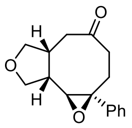
0.5
0.0
-0.5
f1 (ppm)

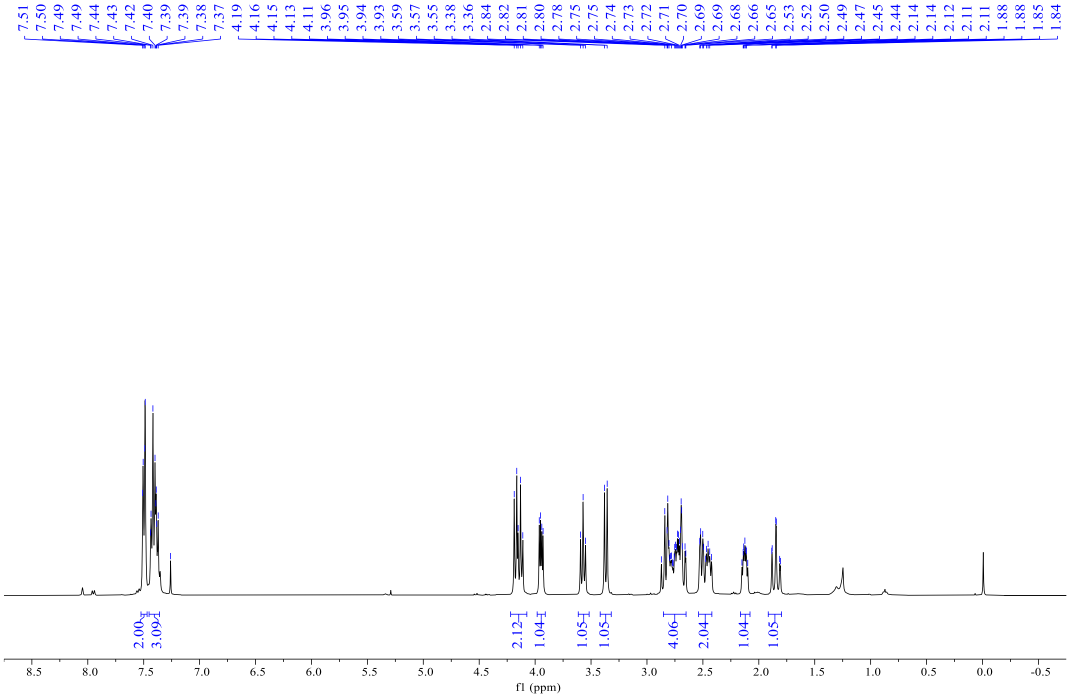

O
H
TsN
H
O
Ph

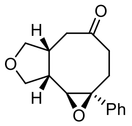
6d


211.83
144.09
138.88
133.41
130.03
128.92
128.87
127.54
126.97
77.16 CDCl3
62.60
61.13
52.21
51.55
42.07
41.91
41.53
39.51
30.57
21.59
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

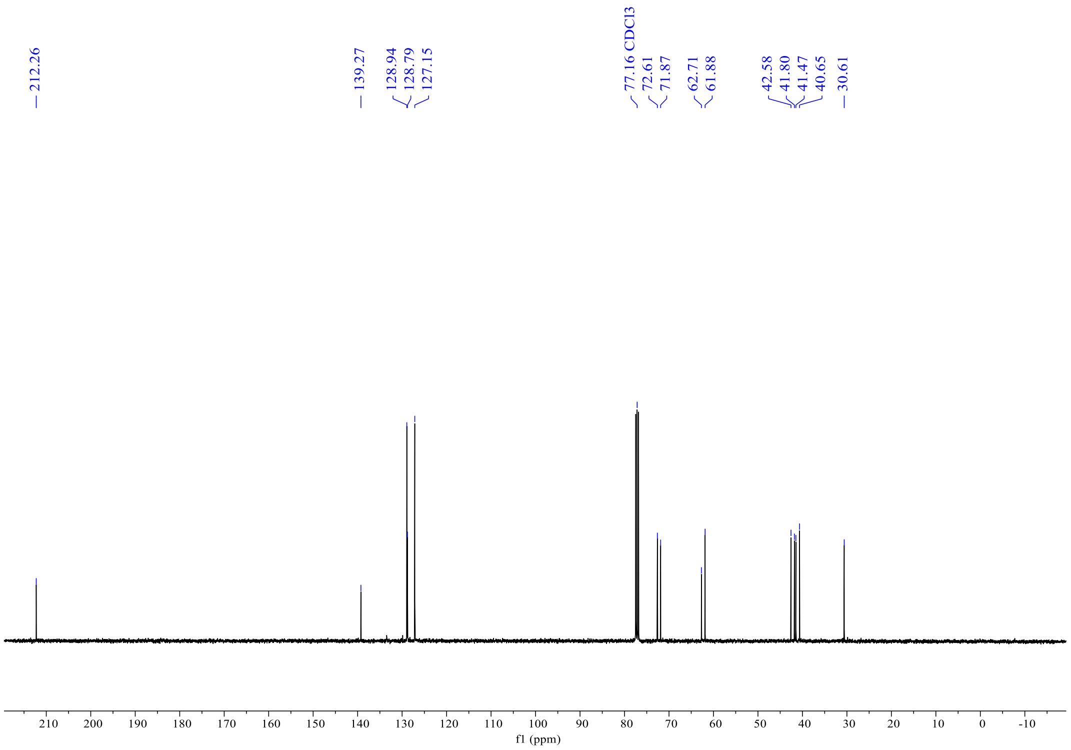

O
H
O
H
O
Ph

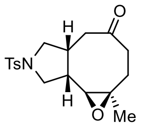
6e


7.51
7.50
7.49
7.49
7.44
7.43
7.42
7.40
7.39
7.39
7.38
7.37
4.19
4.16
4.15
4.13
4.11
3.96
3.95
3.94
3.93
3.59
3.57
3.55
3.38
3.36
2.84
2.82
2.81
2.80
2.78
2.75
2.75
2.74
2.73
2.72
2.71
2.70
2.69
2.69
2.68
2.66
2.65
2.53
2.52
2.50
2.49
2.47
2.45
2.44
2.14
2.14
2.12
2.11
2.11
1.88
1.85
1.84
2.00
3.09
2.12
1.04
1.05
1.05
4.06
2.04
1.04
1.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

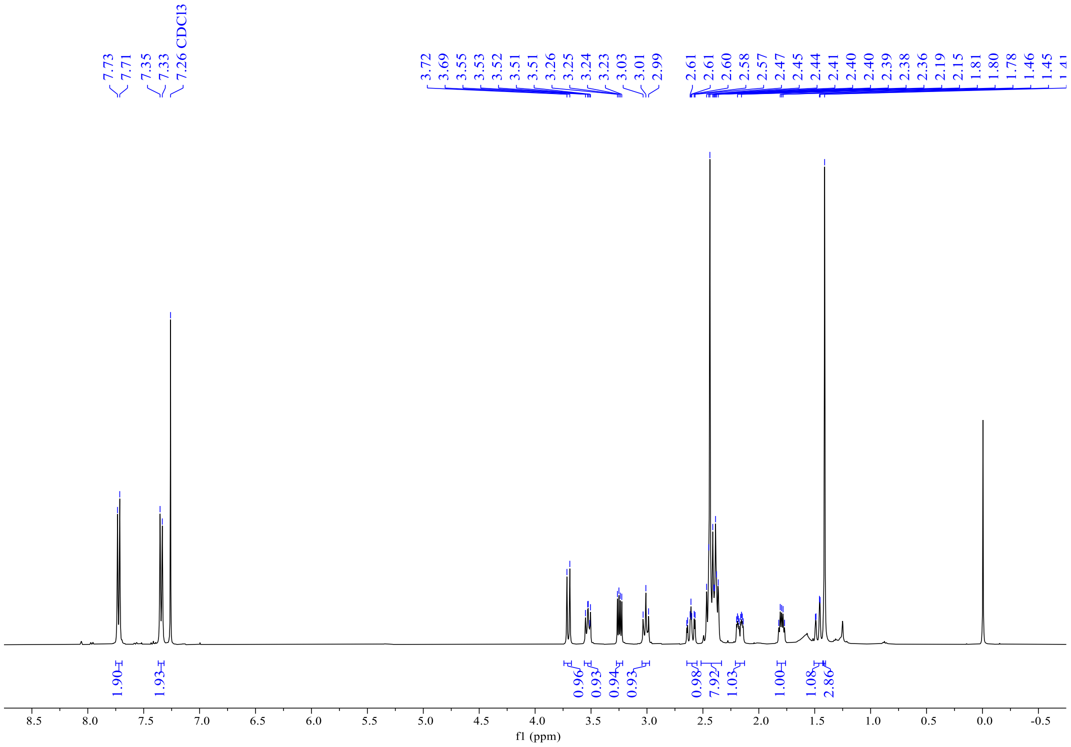

O
H
O
H
O
Ph

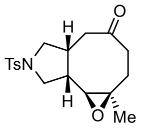
6e


212.26
139.27
128.94
128.79
127.15
77.16 CDCl3
72.61
71.87
62.71
61.88
42.58
41.80
41.47
40.65
30.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

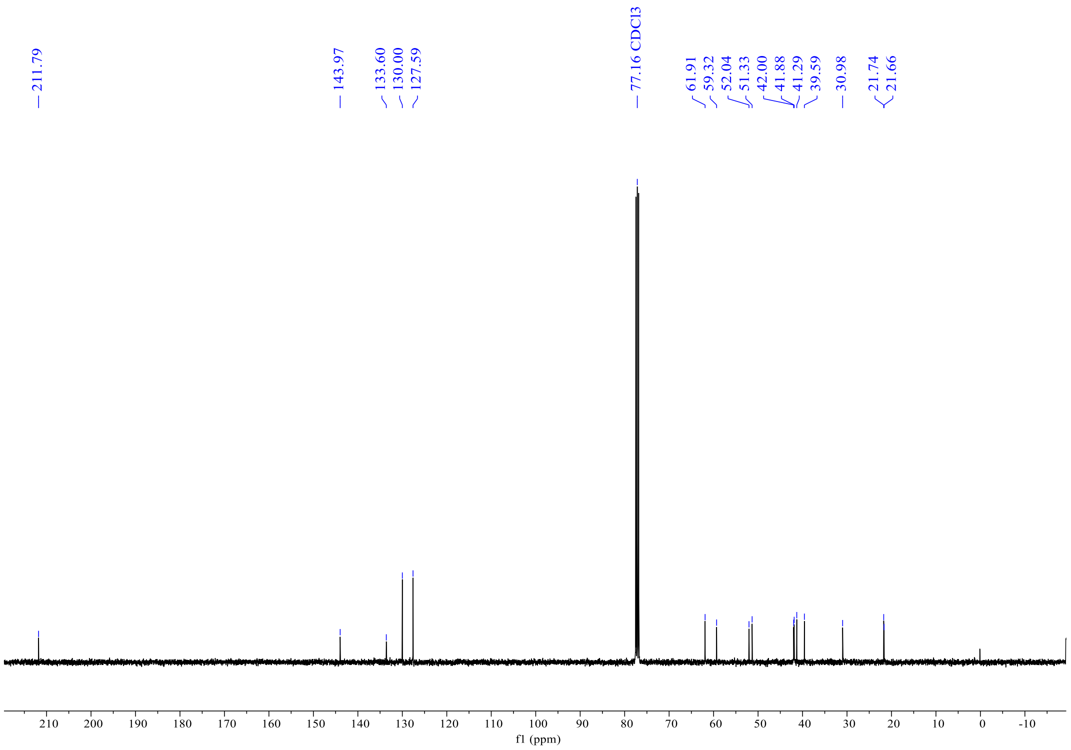

O
H
TsN
H
O
Me

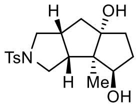
6f


7.73
7.71
7.35
7.33
7.26 CDCl3
3.72
3.69
3.55
3.53
3.52
3.51
3.51
3.26
3.25
3.24
3.23
3.03
3.01
2.99
2.61
2.61
2.60
2.58
2.57
2.47
2.45
2.44
2.41
2.40
2.40
2.39
2.38
2.36
2.19
2.15
1.81
1.80
1.78
1.46
1.45
1.41
1.90
1.93
0.96
0.93
0.94
0.93
0.98
7.92
1.03
1.00
1.08
2.86
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

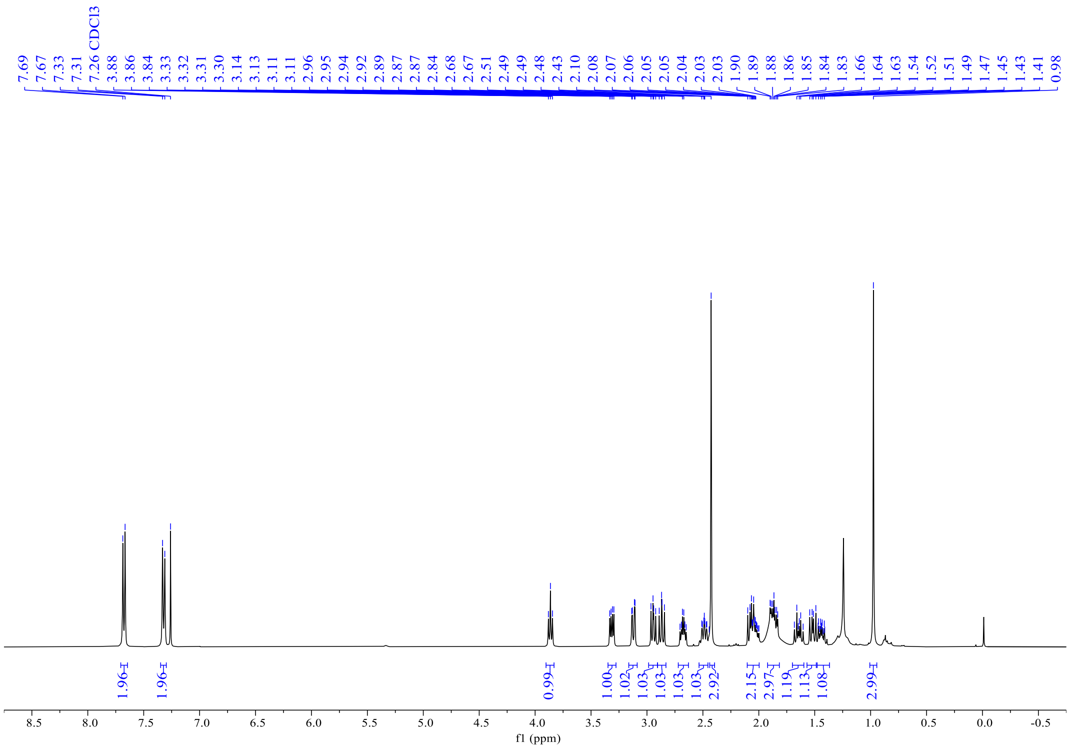

O
H
TsN
H
O
Me

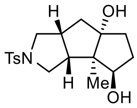
6f


211.79
143.97
133.60
130.00
127.59
77.16 CDCl3
61.91
59.32
52.04
51.33
42.00
41.88
41.29
39.59
30.98
21.74
21.66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

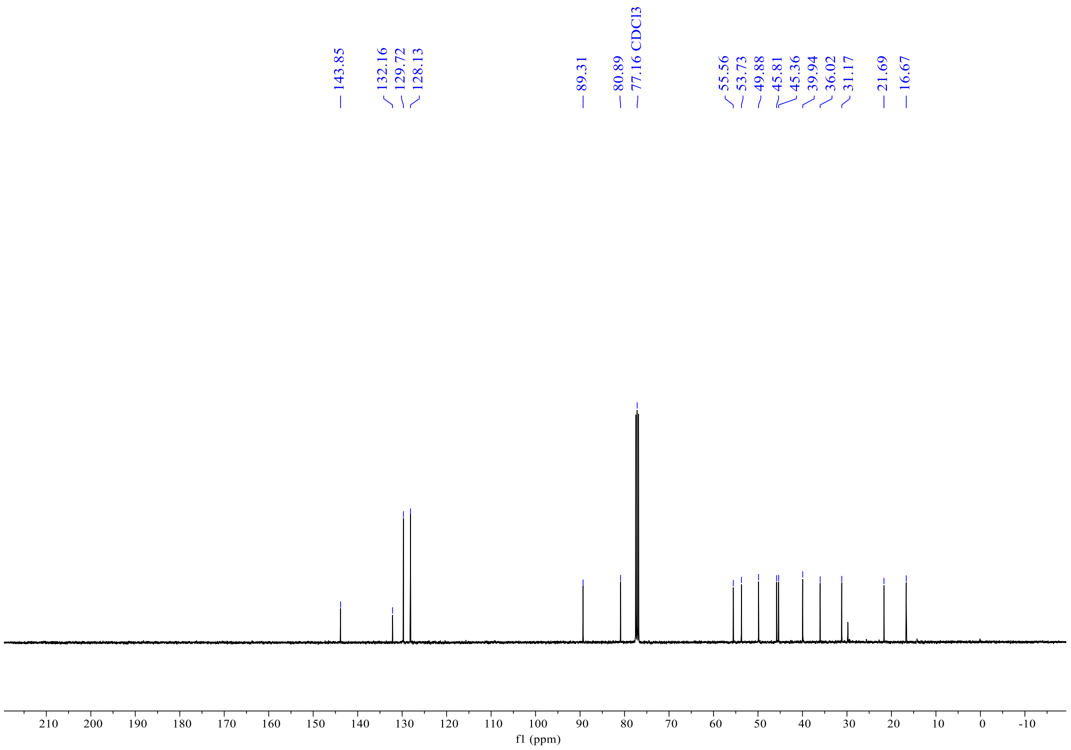

H
OH
TsN
H
Me
OH

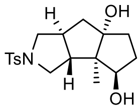
7a


7.69
7.67
7.33
7.31
7.26 CDCl3
3.88
3.86
3.84
3.33
3.32
3.31
3.30
3.14
3.13
3.11
3.11
2.96
2.95
2.94
2.92
2.89
2.87
2.87
2.84
2.68
2.67
2.51
2.49
2.49
2.48
2.43
2.10
2.08
2.07
2.06
2.05
2.05
2.04
2.03
2.03
1.90
1.89
1.88
1.86
1.85
1.84
1.83
1.66
1.64
1.63
1.54
1.52
1.51
1.49
1.47
1.45
1.43
1.41
0.98
1.96
1.96
0.99
1.00
1.02
1.03
1.03
1.03
1.03
2.92
2.15
2.97
1.19
1.13
1.08
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

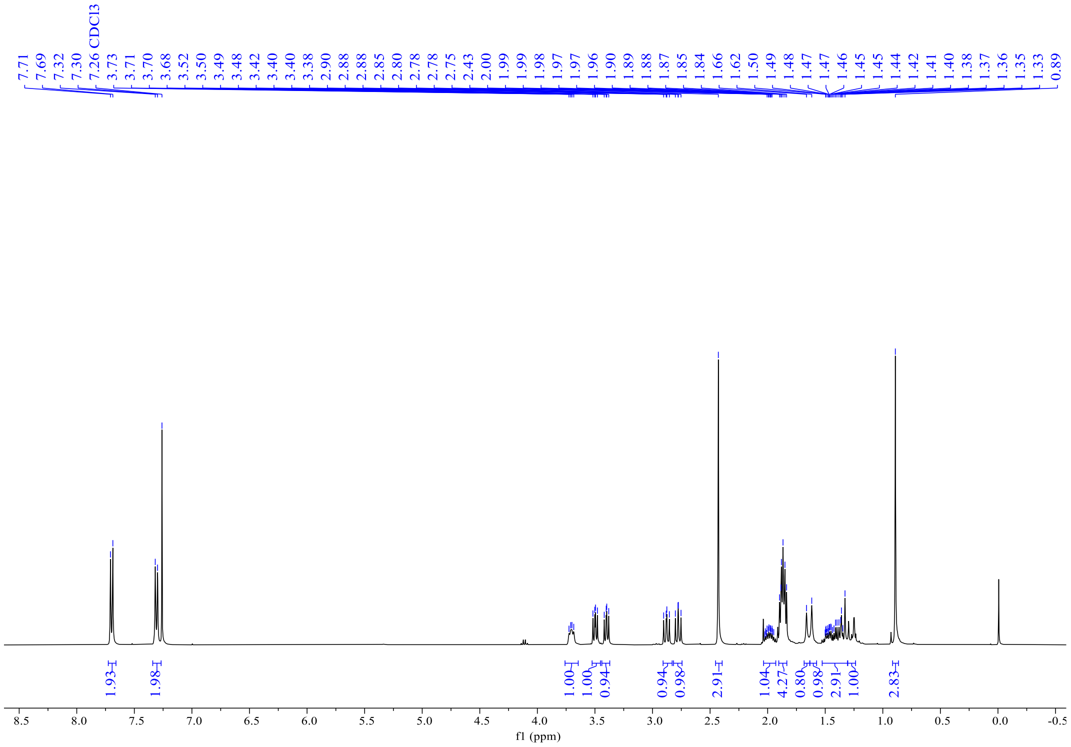

H
OH
TsN
H
Me
OH

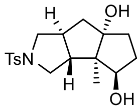
7a


143.85
132.16
129.72
128.13
89.31
80.89
77.16 CDCl3
55.56
53.73
49.88
45.81
45.36
39.94
36.02
31.17
21.69
16.67
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

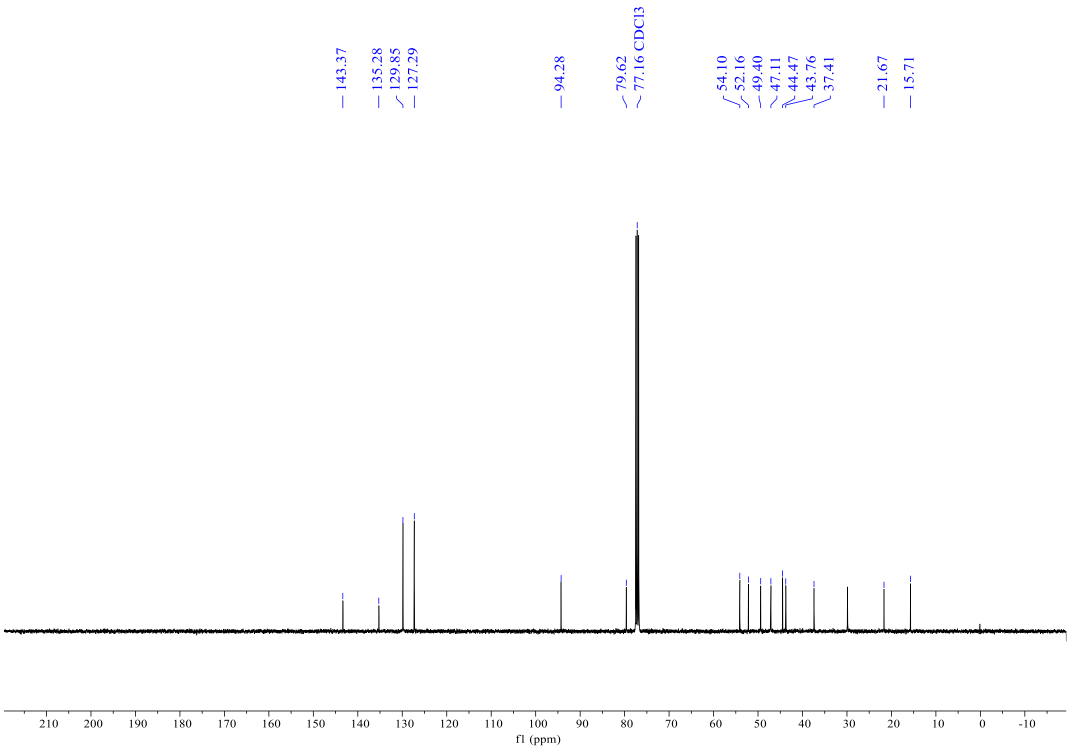

H
OH
TsN
H
OH

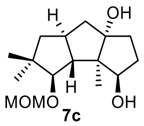
7b

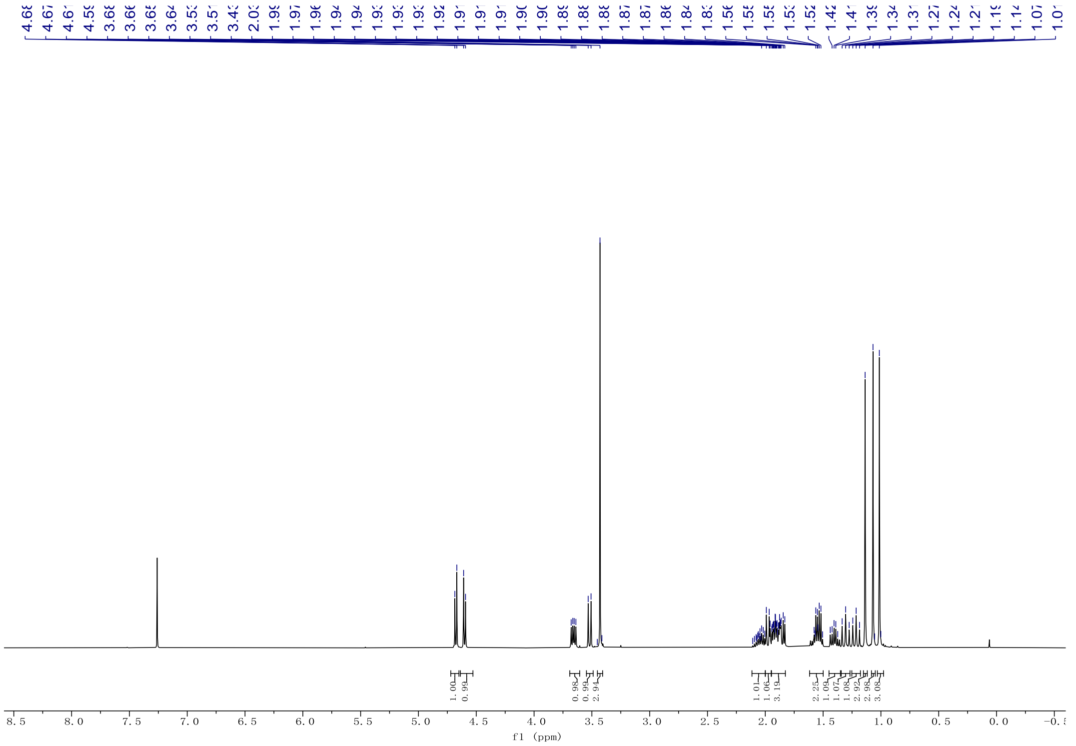

7.71
7.69
7.32
7.30
7.26 CDCl3
3.73
3.71
3.70
3.68
3.52
3.50
3.49
3.48
3.42
3.40
3.40
3.38
2.90
2.88
2.88
2.85
2.80
2.78
2.78
2.75
2.43
2.00
1.99
1.99
1.98
1.97
1.97
1.96
1.90
1.89
1.88
1.87
1.85
1.84
1.66
1.62
1.50
1.49
1.48
1.47
1.47
1.46
1.45
1.45
1.44
1.42
1.41
1.40
1.38
1.37
1.36
1.35
1.33
0.89
1.93
1.98
1.00
1.00
0.94
0.94
0.98
2.91
1.04
4.27
0.80
0.98
2.91
1.00
2.83
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


H
OH
TsN
H
OH

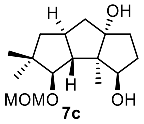
7b

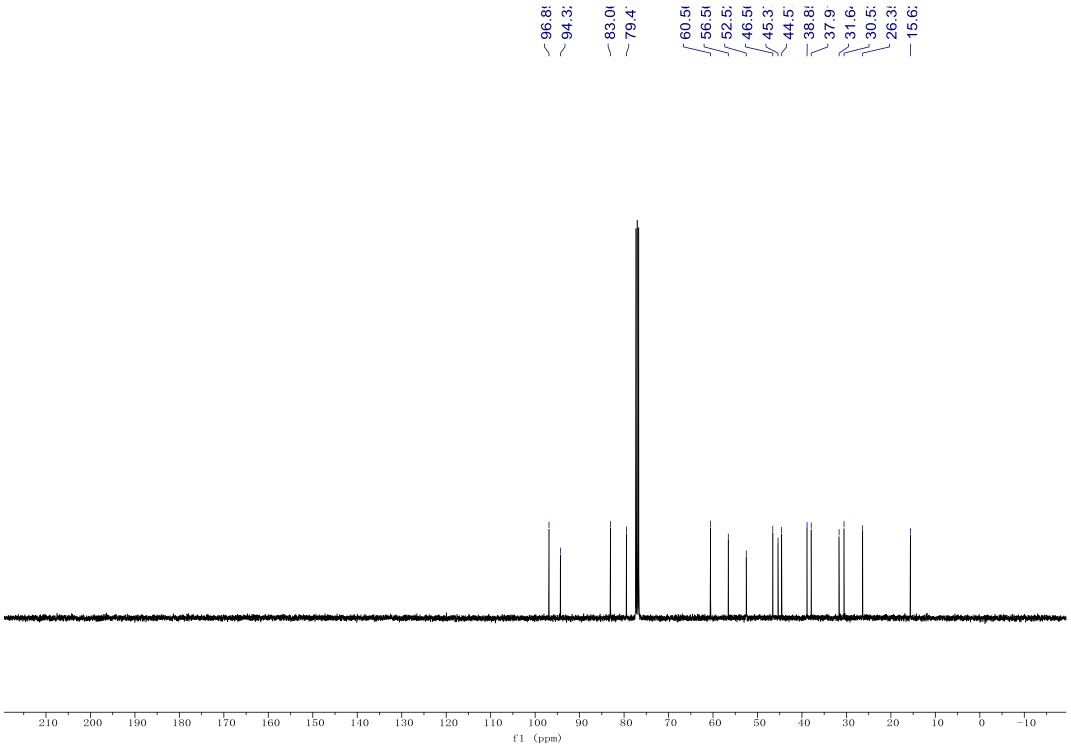

143.37
135.28
129.85
127.29
94.28
79.62
77.16 CDCl3
54.10
52.16
49.40
47.11
44.47
43.76
37.41
21.67
15.71
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7c

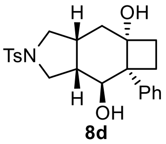


4.68
4.67
4.61
4.59
3.68
3.66
3.65
3.64
3.53
3.51
3.43
2.03
1.99
1.97
1.96
1.94
1.93
1.93
1.93
1.92
1.91
1.91
1.91
1.90
1.90
1.89
1.88
1.88
1.87
1.87
1.86
1.84
1.83
1.56
1.55
1.53
1.52
1.42
1.41
1.39
1.34
1.31
1.27
1.24
1.21
1.19
1.14
1.07
1.01
1.00
0.99
0.98
0.99
2.94
1.01
1.06
3.19
2.25
1.09
1.07
1.08
2.92
2.98
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

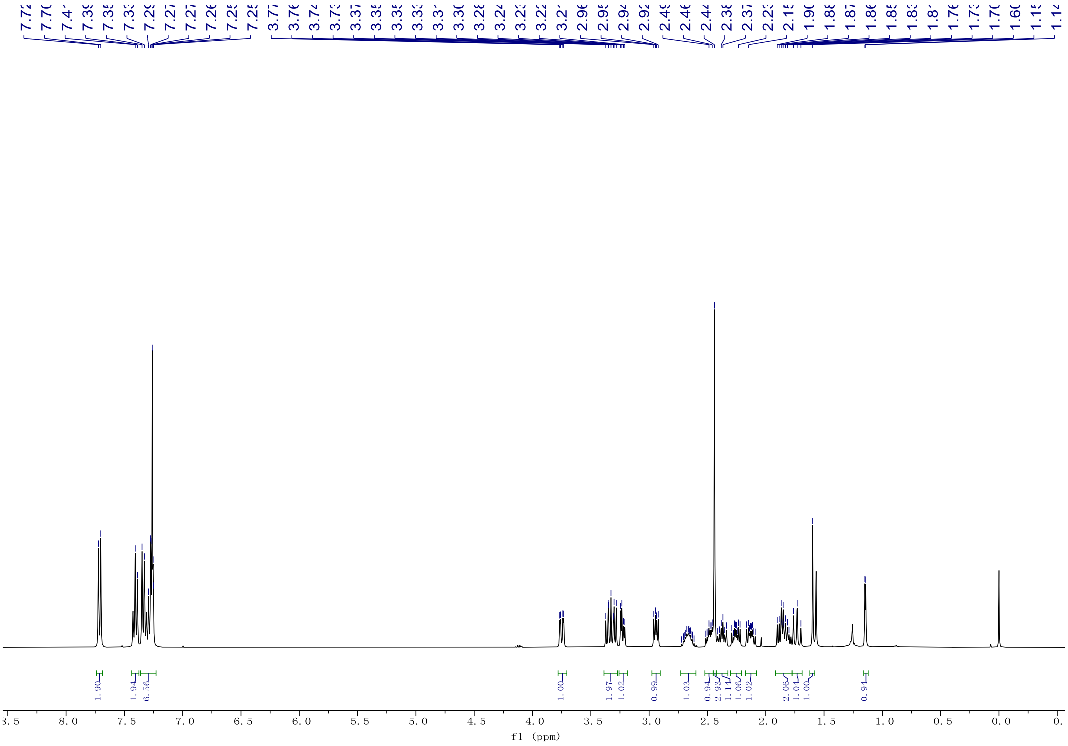

7c



96.85
94.32
83.06
79.41
60.50
56.50
52.52
46.50
45.31
44.57
38.85
37.9
31.64
30.53
26.38
15.63
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


H
OH
TsN
H
OH
Ph

8d


7.72
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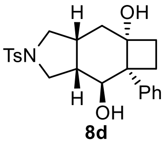
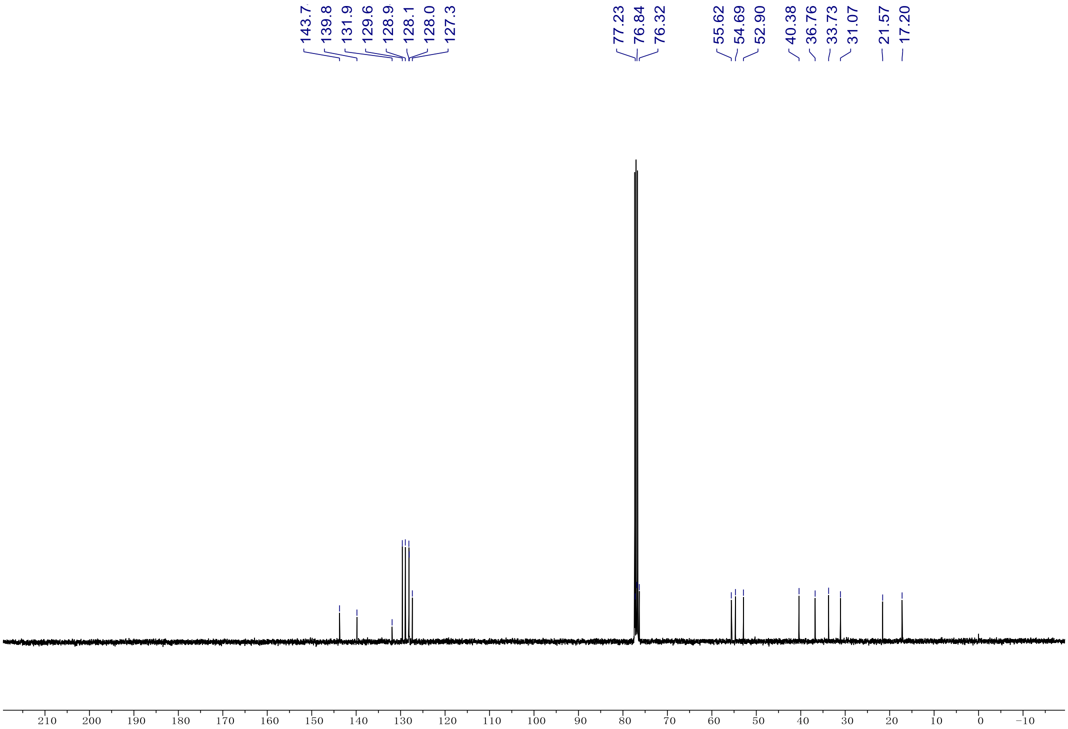
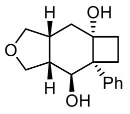
7.33
7.29
7.27
7.27
7.26
7.25
7.25
3.77
3.76
3.74
3.73
3.37
3.35
3.35
3.33
3.31
3.30
3.28
3.24
3.23
3.22
3.21
2.96
2.95
2.94
2.92
2.49
2.46
2.44
2.38
2.37
2.23
2.15
1.90
1.88
1.87
1.86
1.85
1.83
1.81
1.76
1.73
1.70
1.60
1.15
1.14
1.90
1.94
6.56
1.00
1.97
1.02
0.99
1.03
0.94
2.93
1.14
1.06
1.02
2.06
1.04
1.06
0.94
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

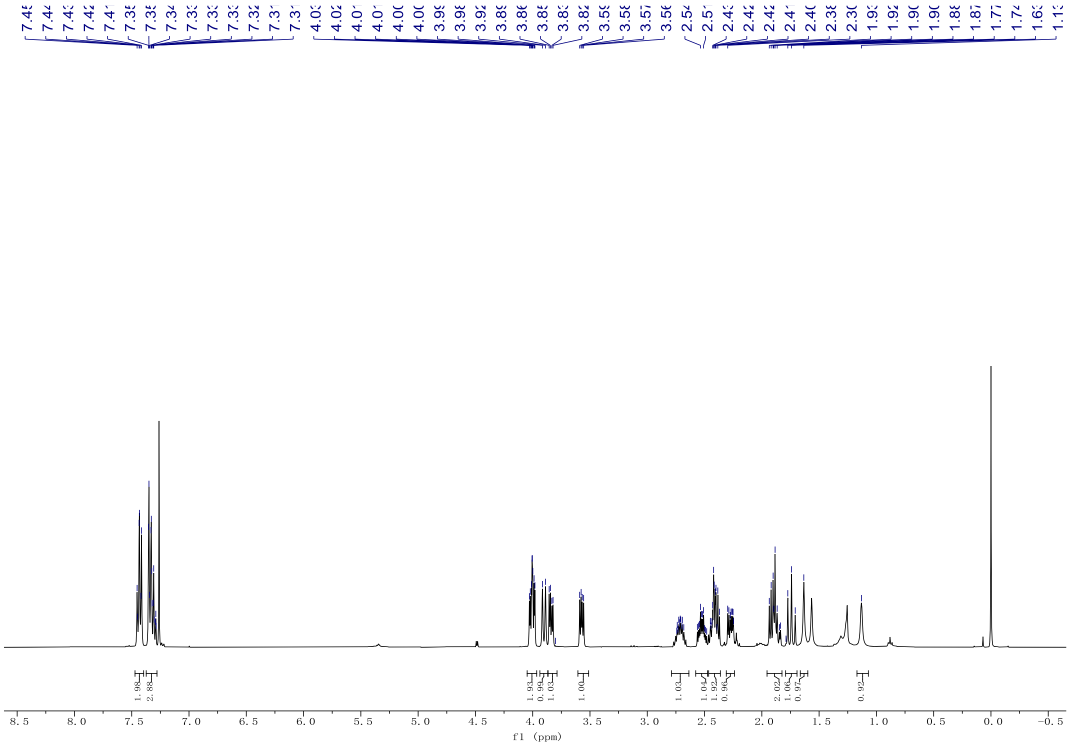

H
OH
TsN
H
OH
Ph

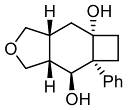
8d


143.7
139.8
131.9
129.6
128.9
128.1
128.0
127.3
77.23
76.84
76.32
55.62
54.69
52.90
40.38
36.76
33.73
31.07
21.57
17.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

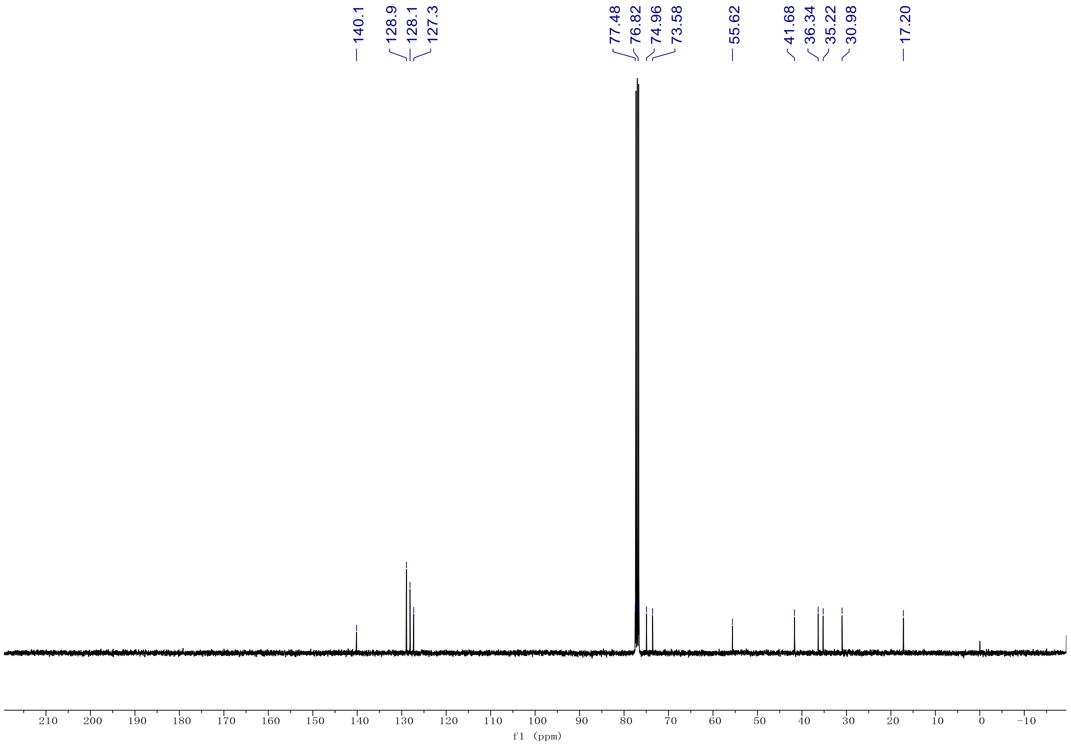

H
OH
O
H
OH
Ph

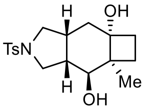
8e


1.98
2.88
1.93
0.99
1.03
1.00
1.03
1.04
1.92
0.96
2.02
1.06
0.97
0.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

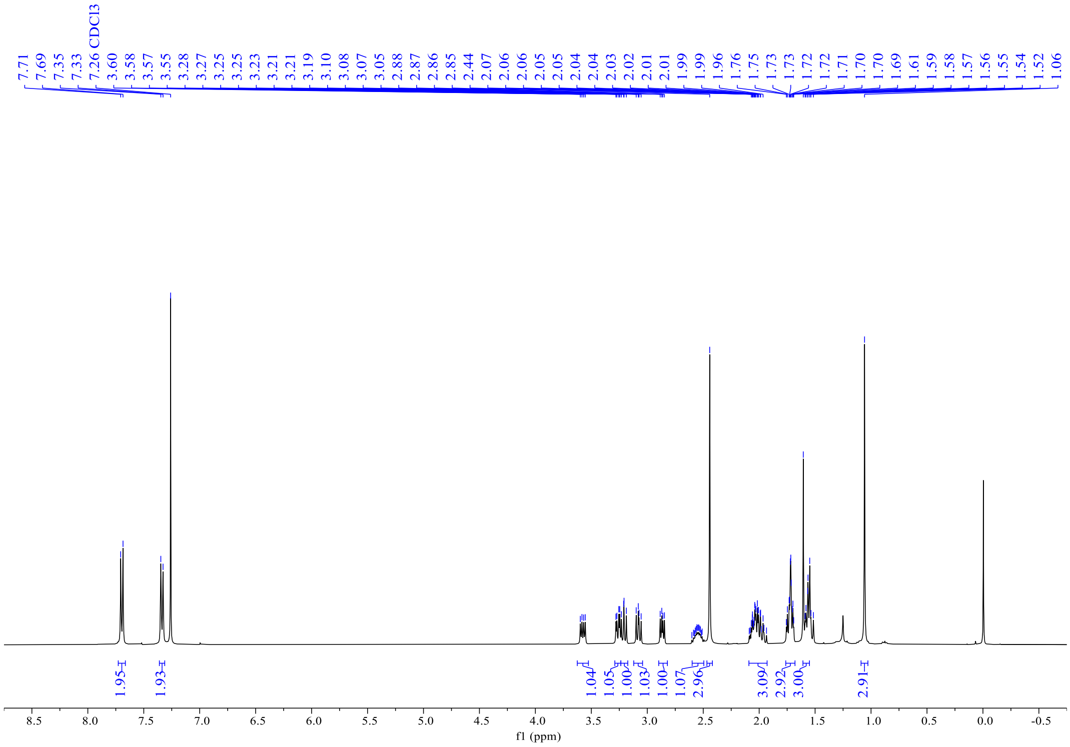

H
OH
O
H
OH
Ph

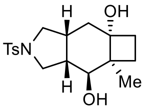
8e


140.1
128.9
128.1
127.3
77.48
76.82
74.96
73.58
55.62
41.68
36.34
35.22
30.98
17.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

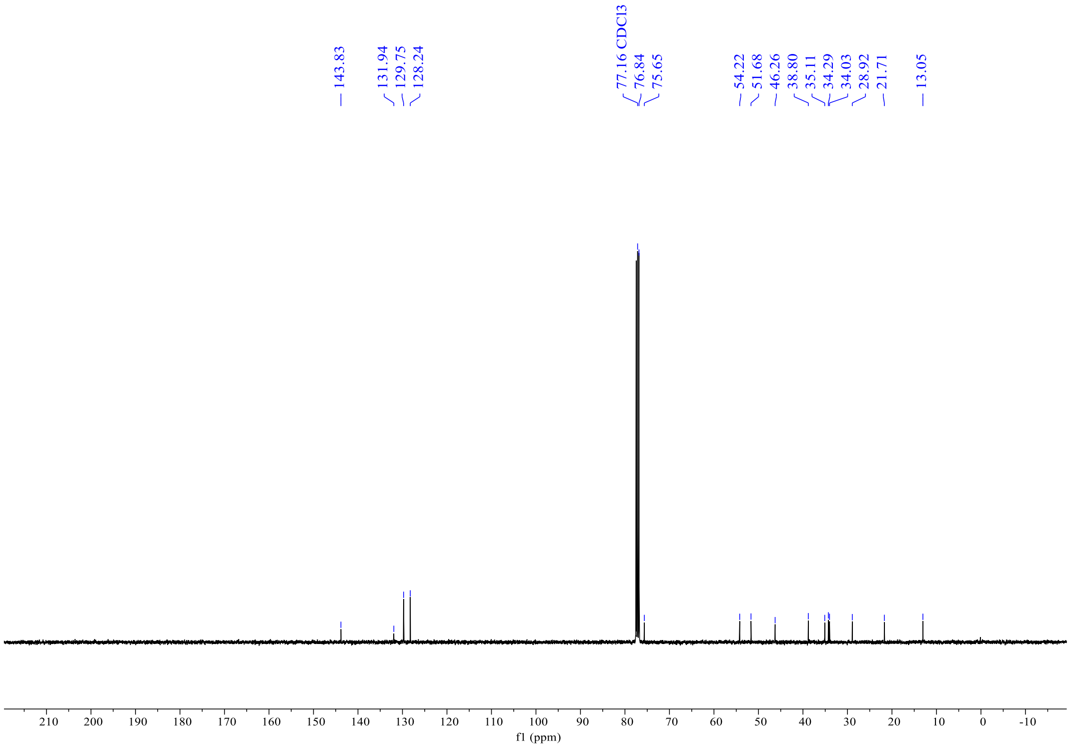

H
OH
TsN
Me
H
OH

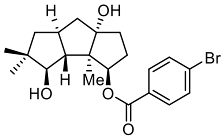
8f


7.71
7.69
7.35
7.33
7.26 CDCl3
3.60
3.58
3.57
3.55
3.28
3.27
3.25
3.25
3.23
3.21
3.21
3.19
3.10
3.08
3.07
3.05
2.88
2.87
2.86
2.85
2.44
2.07
2.06
2.06
2.05
2.05
2.04
2.04
2.03
2.02
2.01
2.01
1.99
1.99
1.96
1.76
1.75
1.73
1.73
1.72
1.72
1.71
1.70
1.70
1.69
1.61
1.59
1.58
1.57
1.56
1.55
1.54
1.52
1.06
1.95
1.93
1.04
1.05
1.00
1.03
1.00
1.07
2.96
3.09
2.92
3.00
2.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

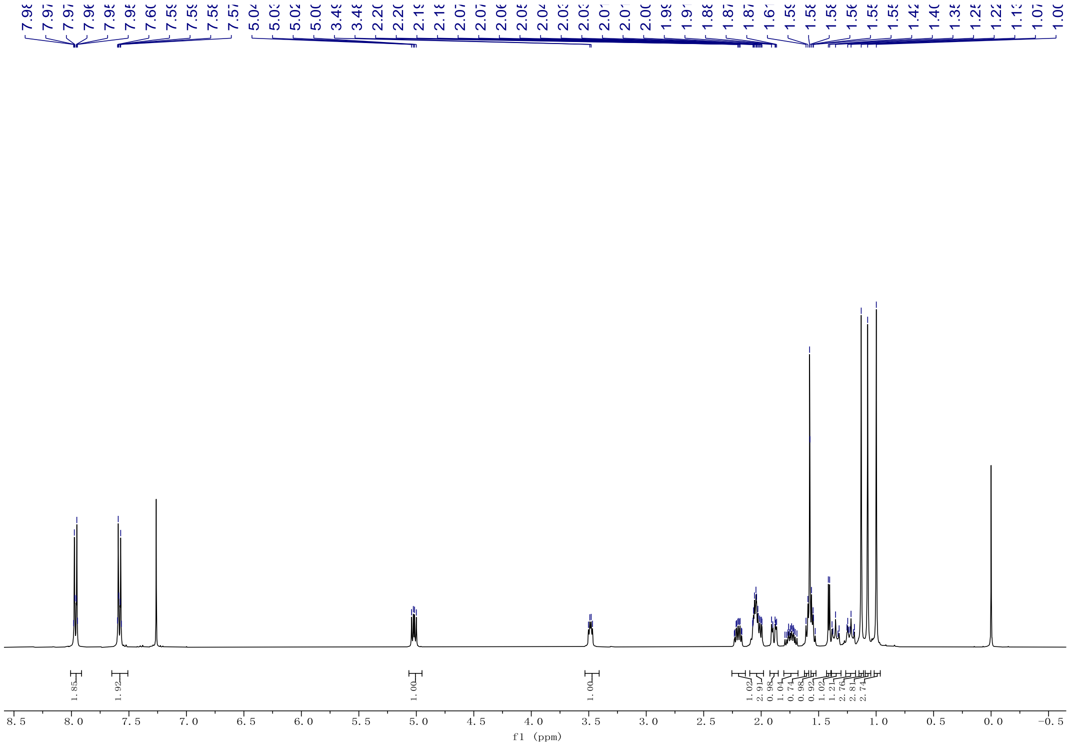

H
OH
TsN
Me
H
OH

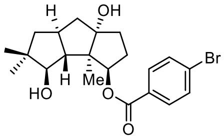
8f


143.83
131.94
129.75
128.24
77.16 CDCl3
76.84
75.65
54.22
51.68
46.26
38.80
35.11
34.29
34.03
28.92
21.71
13.05
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

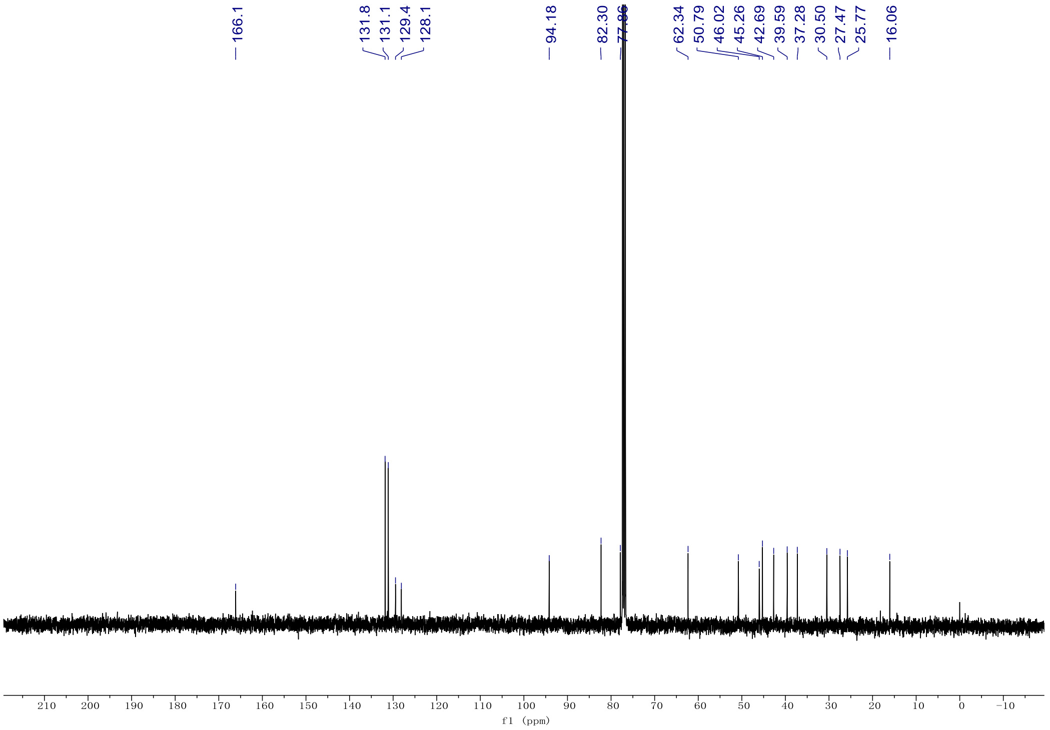

H
OH
Br
H
Me
HO
O
O

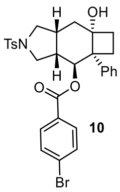
9


7.98 7.97 7.97 7.96 7.95 7.95 7.60 7.59 7.59 7.58 7.57 5.04 5.03 5.02 5.00 3.49 3.48 2.20 2.20 2.19 2.18 2.07 2.07 2.06 2.05 2.04 2.03 2.03 2.01 2.01 2.00 1.99 1.91 1.88 1.87 1.87 1.61 1.59 1.58 1.58 1.56 1.55 1.55 1.42 1.40 1.35 1.25 1.22 1.13 1.07 1.00
1.85
1.92
1.00
1.00
1.02
2.91
0.98
1.04
0.74
0.98
0.92
1.02
1.21
2.76
2.81
2.74
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


H
OH
Br
H
Me
HO
O
O

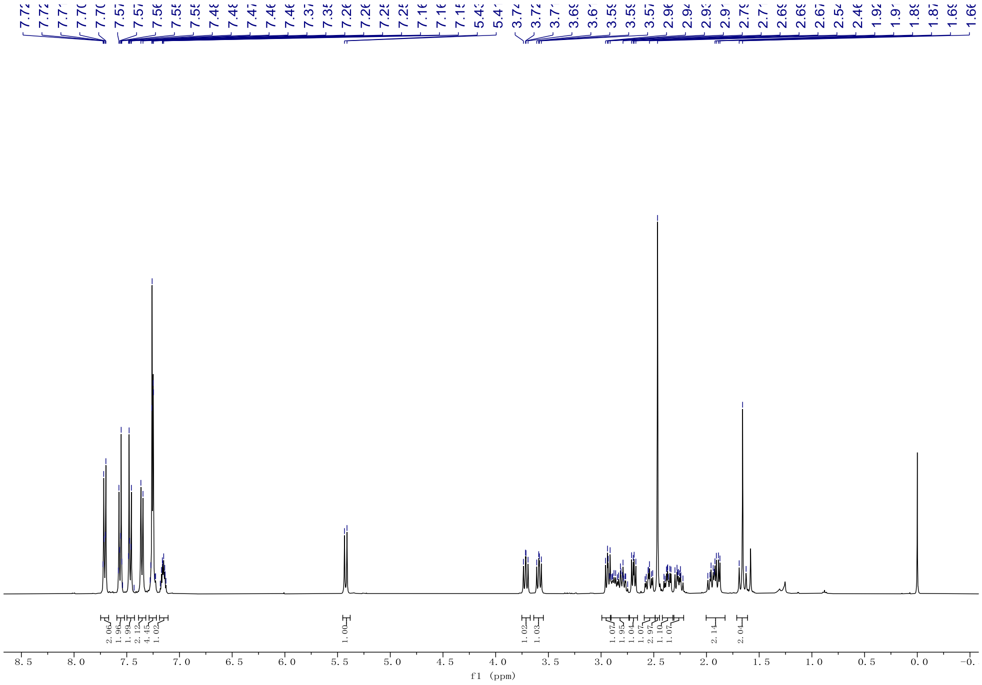
9


166.1
131.8
131.1
129.4
128.1
94.18
82.30
77.06
62.34
50.79
46.02
45.26
42.69
39.59
37.28
30.50
27.47
25.77
16.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

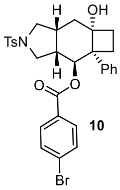


H
OH
TsN
H
Ph
O
O
Br

10

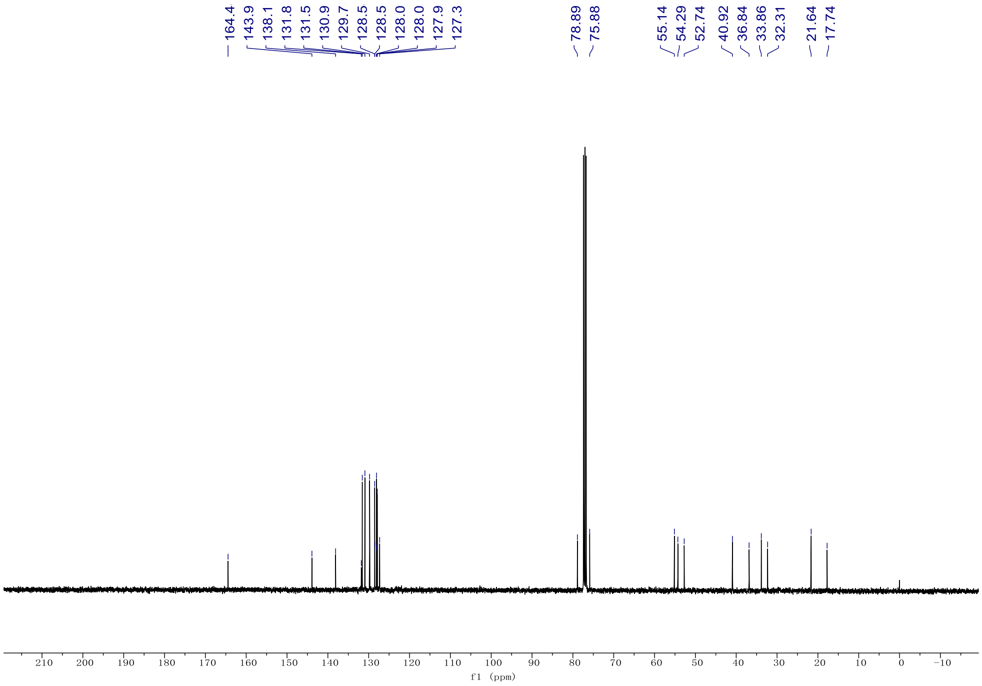


7.72
7.72
7.71
7.70
7.70
7.57
7.57
7.56
7.55
7.55
7.48
7.48
7.47
7.46
7.46
7.37
7.35
7.26
7.26
7.25
7.25
7.16
7.16
7.15
5.43
5.41
3.74
3.72
3.71
3.69
3.61
3.59
3.59
3.57
2.96
2.94
2.93
2.91
2.79
2.77
2.69
2.69
2.67
2.54
2.46
1.92
1.91
1.89
1.87
1.69
1.66
2.06
1.96
1.99
2.12
4.15
1.02
1.00
1.02
1.03
1.07
1.95
1.04
1.07
2.97
1.10
1.07
2.14
2.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

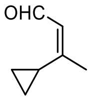


H
OH
TsN
H
Ph
O
O
Br

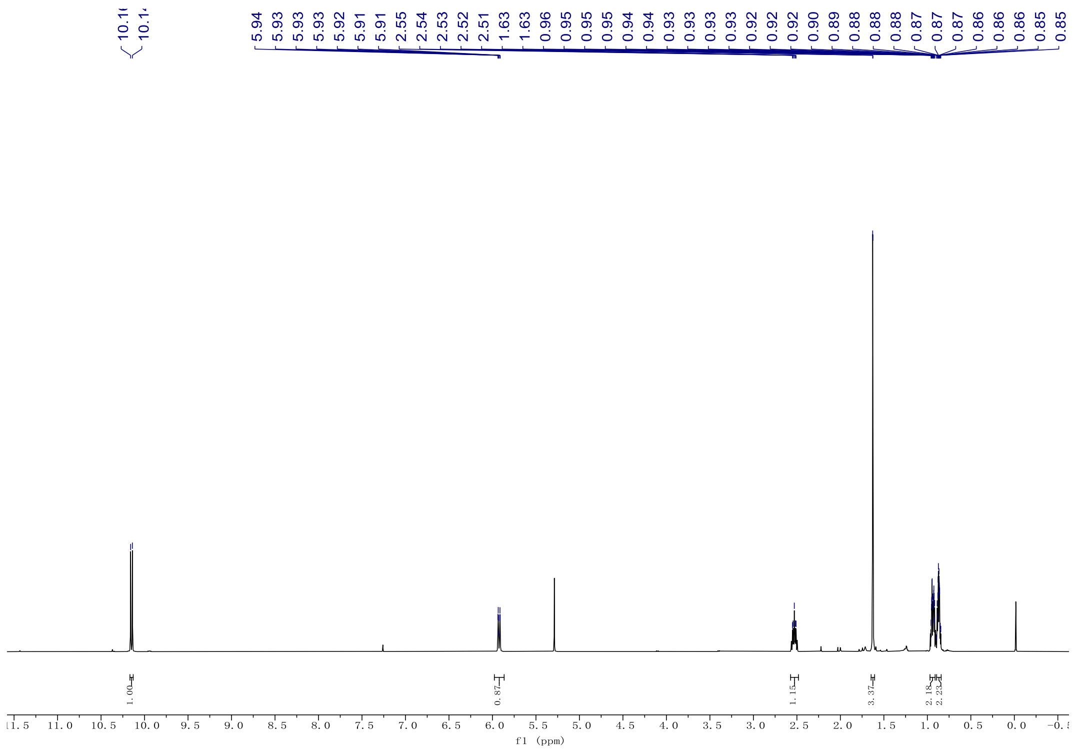
10



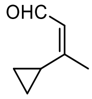
164.4
143.9
138.1
131.8
131.5
130.9
129.7
128.5
128.5
128.0
128.0
127.9
127.3
78.89
75.88
55.14
54.29
52.74
40.92
36.84
33.86
32.31
21.64
17.74
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



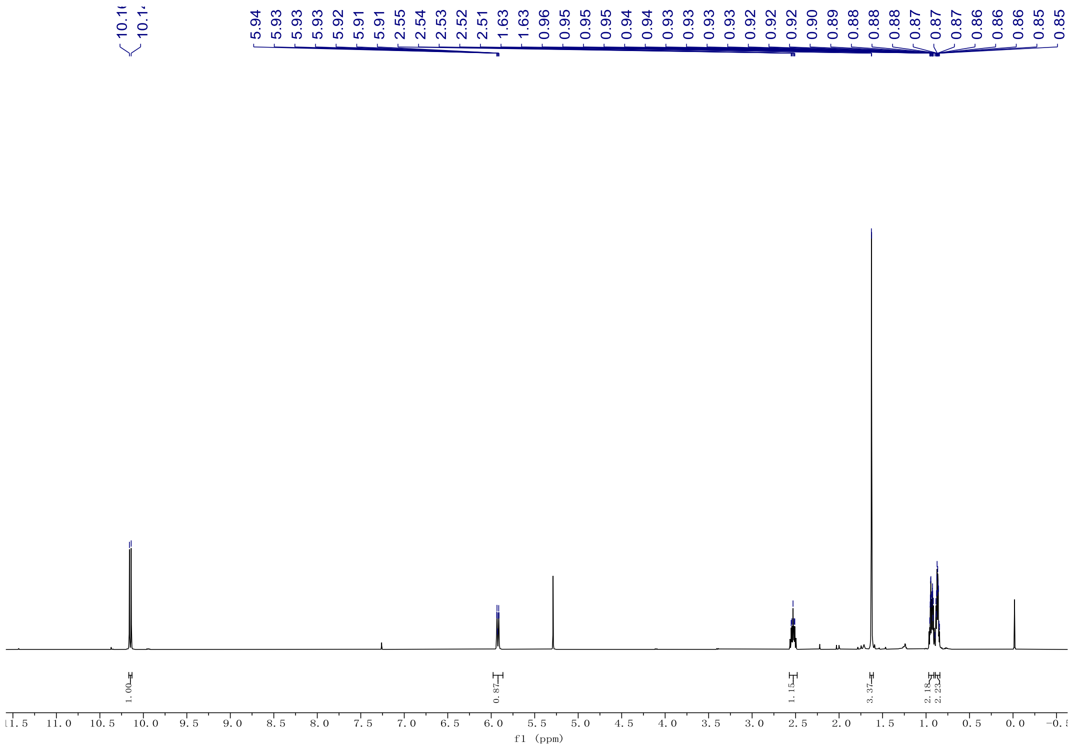
18



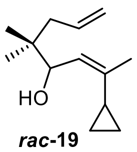
10.1
10.1
5.94
5.93
5.93
5.93
5.92
5.91
5.91
2.55
2.54
2.53
2.52
2.51
1.63
1.63
0.96
0.95
0.95
0.95
0.94
0.94
0.93
0.93
0.93
0.93
0.92
0.92
0.92
0.90
0.89
0.88
0.88
0.88
0.87
0.87
0.87
0.86
0.86
0.85
0.85
1.00
0.87
1.15
3.37
2.18
2.23
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



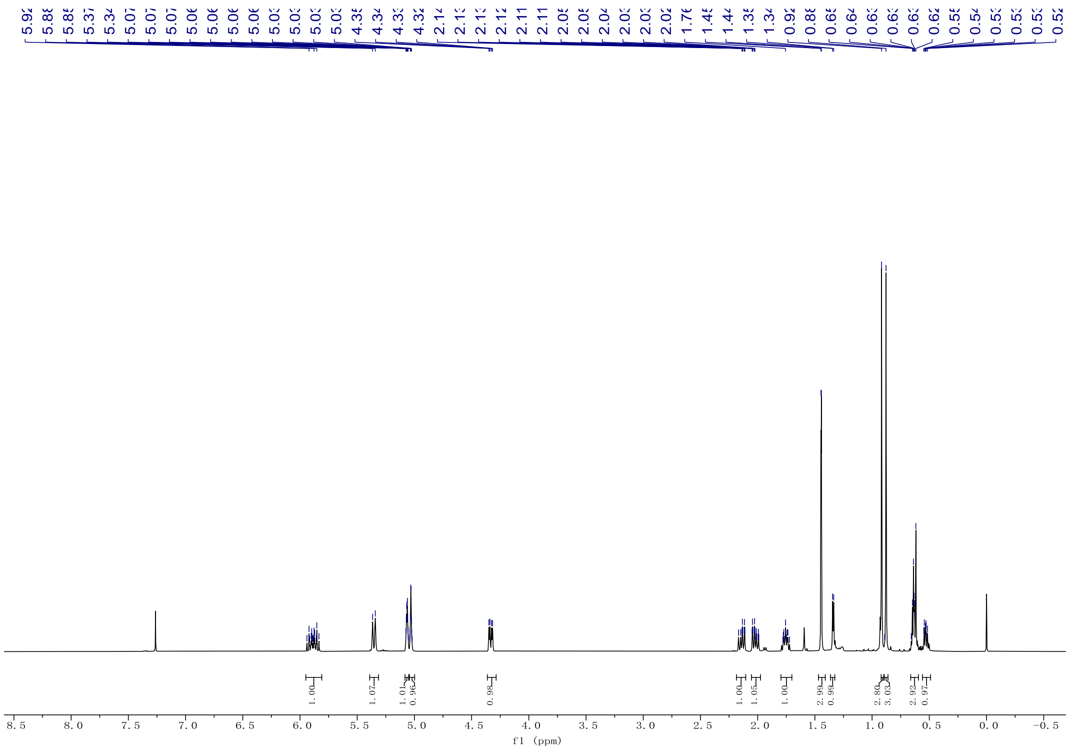
18

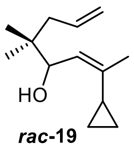


10.1
10.1
5.94
5.93
5.93
5.92
5.91
5.91
2.55
2.54
2.53
2.52
2.51
1.63
1.63
0.96
0.95
0.95
0.94
0.94
0.93
0.93
0.93
0.93
0.92
0.92
0.92
0.90
0.89
0.88
0.88
0.88
0.87
0.87
0.87
0.86
0.86
0.85
0.85
1.00
0.87
1.15
3.37
2.18
2.23
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

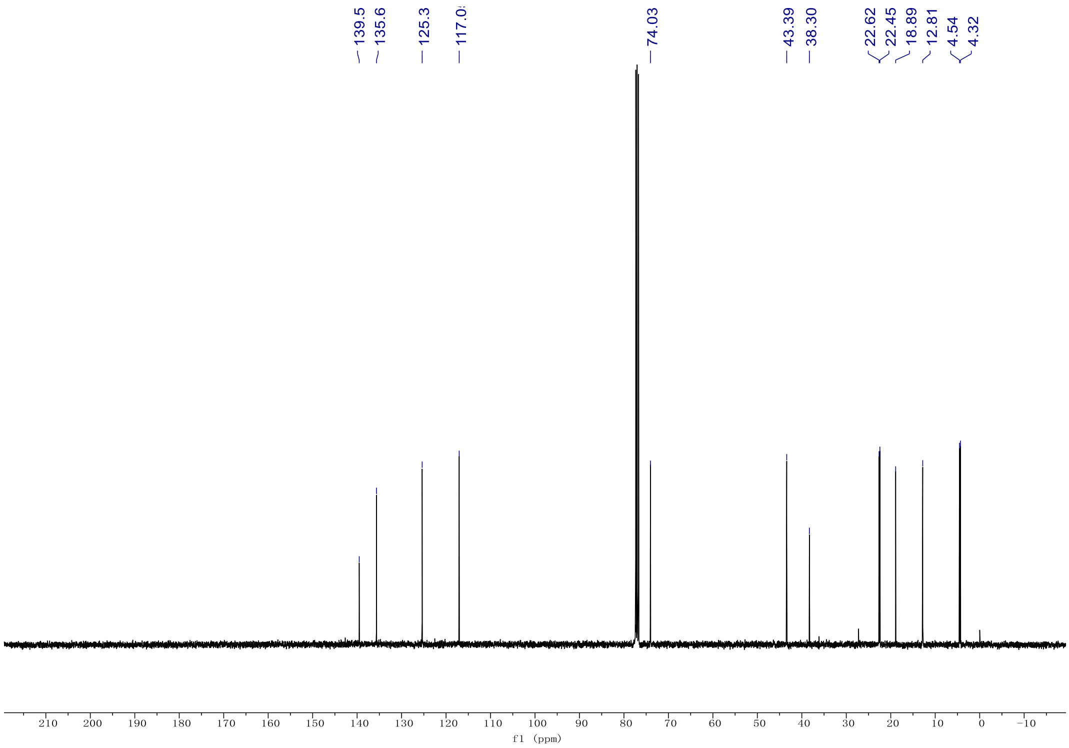


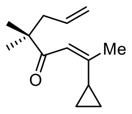
***rac*-19**


5.92
5.88
5.85
5.37
5.34
5.07
5.07
5.06
5.06
5.06
5.03
5.03
5.03
5.03
4.35
4.34
4.33
4.32
2.14
2.13
2.13
2.12
2.11
2.11
2.05
2.04
2.03
2.03
2.02
1.76
1.45
1.44
1.35
1.34
0.92
0.88
0.65
0.64
0.63
0.63
0.63
0.62
0.55
0.54
0.53
0.53
0.52
1.00
1.07
1.01
0.96
0.98
1.00
1.05
1.00
2.99
0.99
2.80
3.03
2.92
0.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

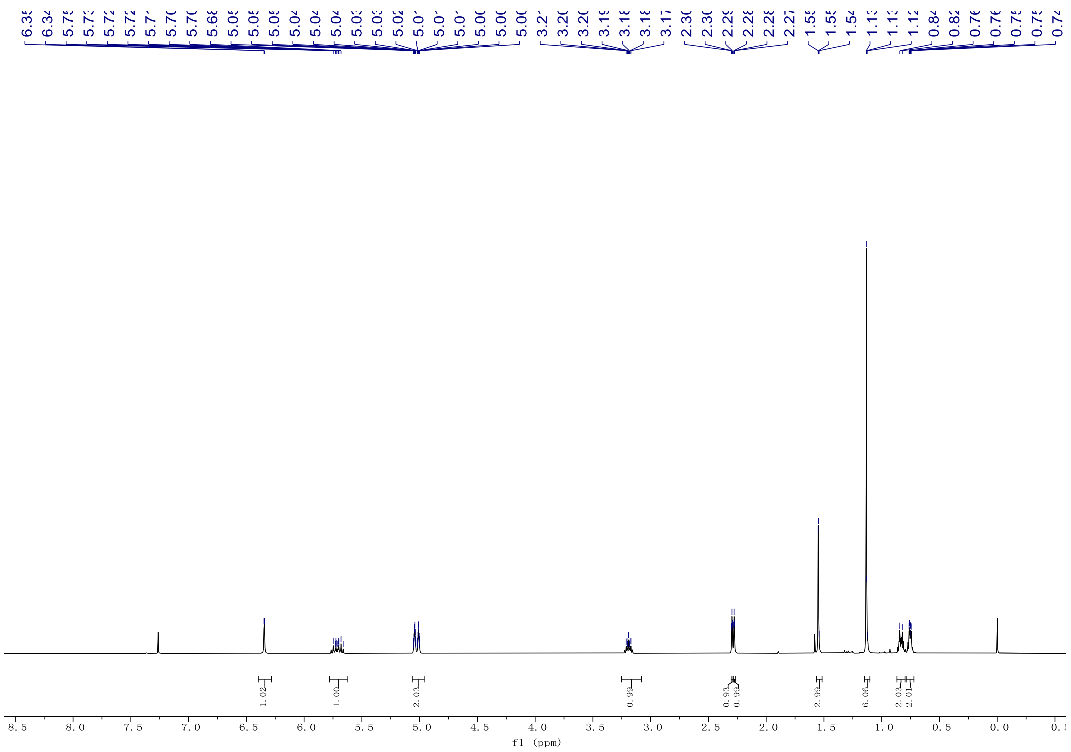


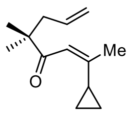
***rac*-19**


139.5
135.6
125.3
117.0
74.03
43.39
38.30
22.62
22.45
18.89
12.81
4.54
4.32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

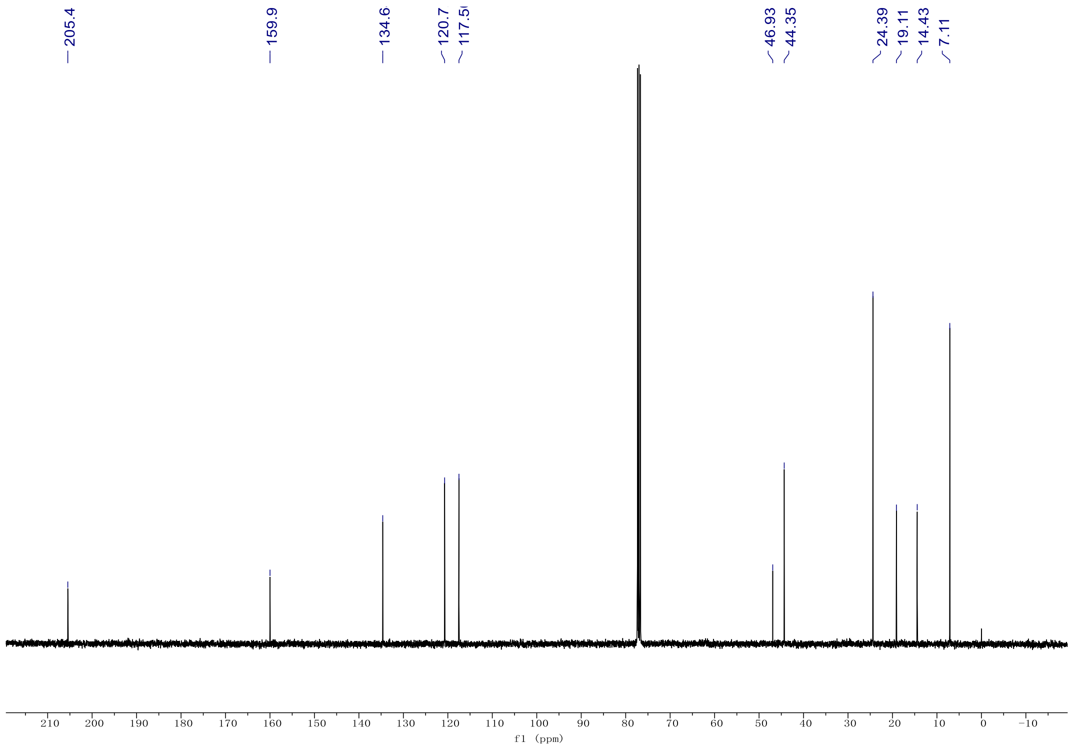


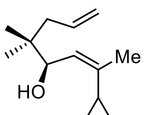
***Z*-ketone**



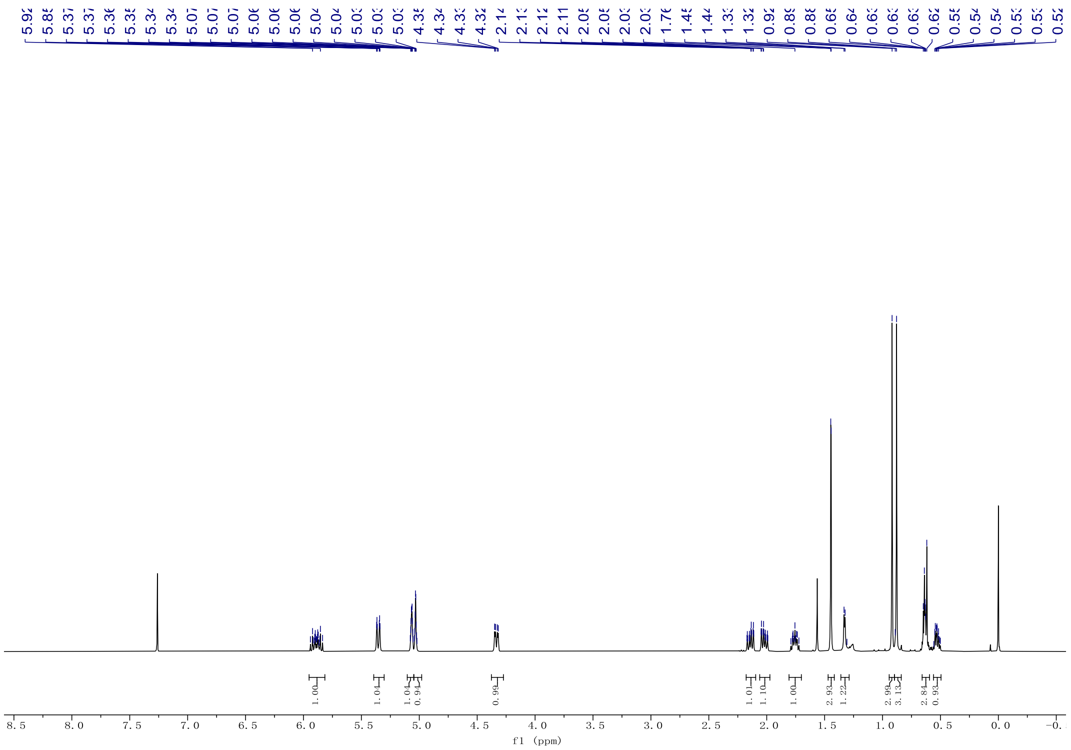


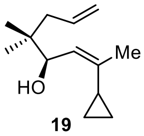
***Z*-ketone**



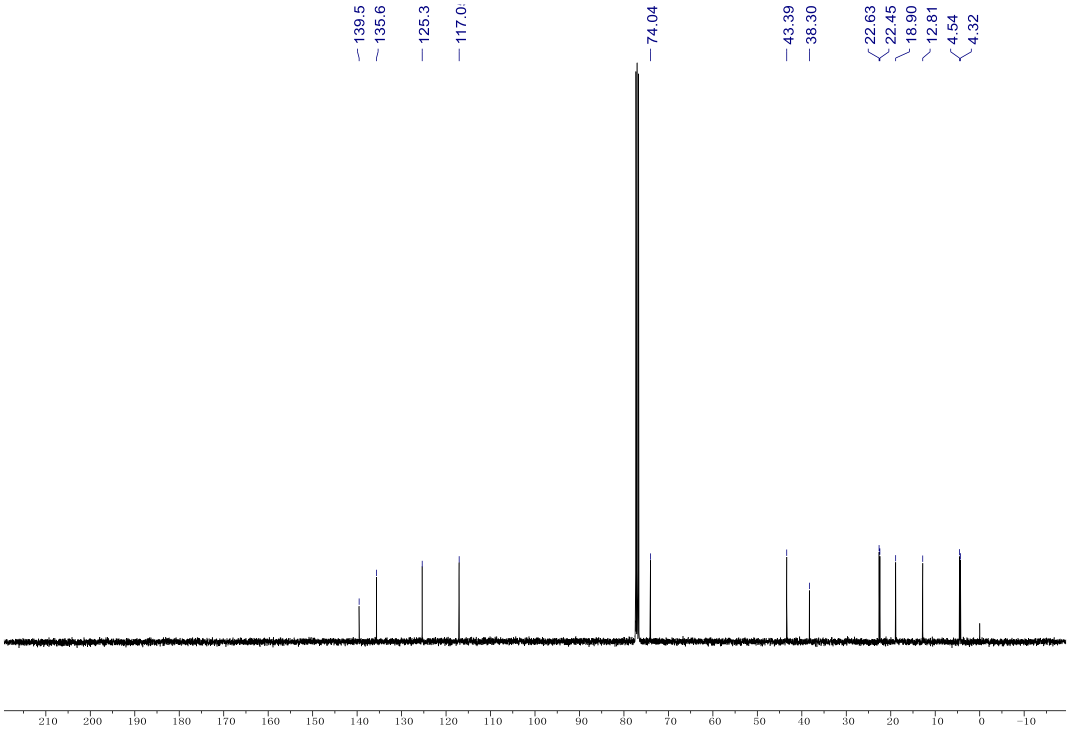

Me
HO

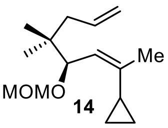
19


1.00
1.04
1.04
0.94
0.99
1.01
1.10
1.00
2.93
1.22
2.99
3.13
2.84
0.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

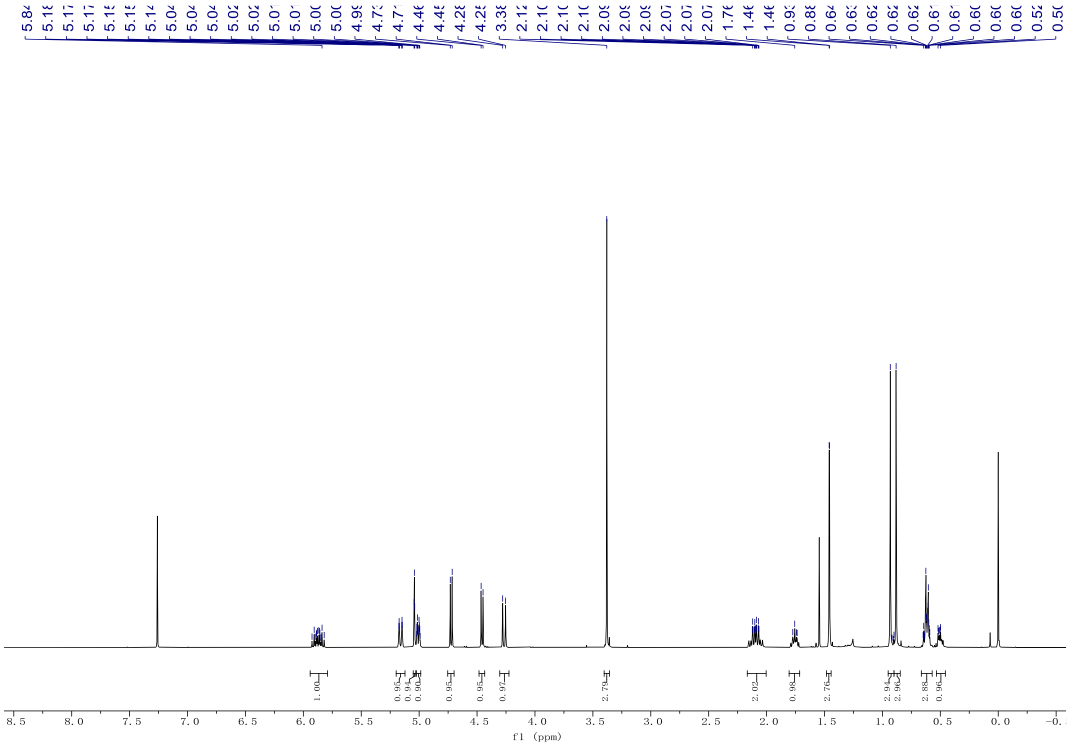

Me
HO

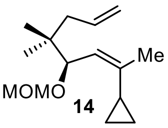
19


139.5
135.6
125.3
117.0
74.04
43.39
38.30
22.63
22.45
18.90
12.81
4.54
4.32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

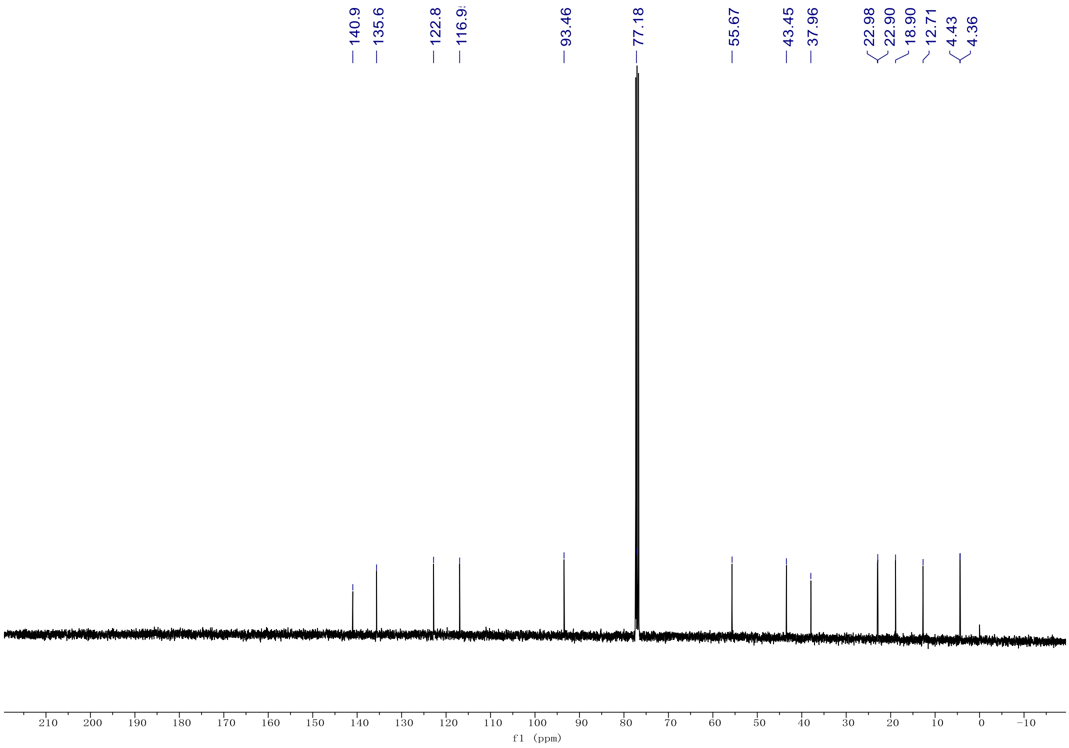

Me
MOMO

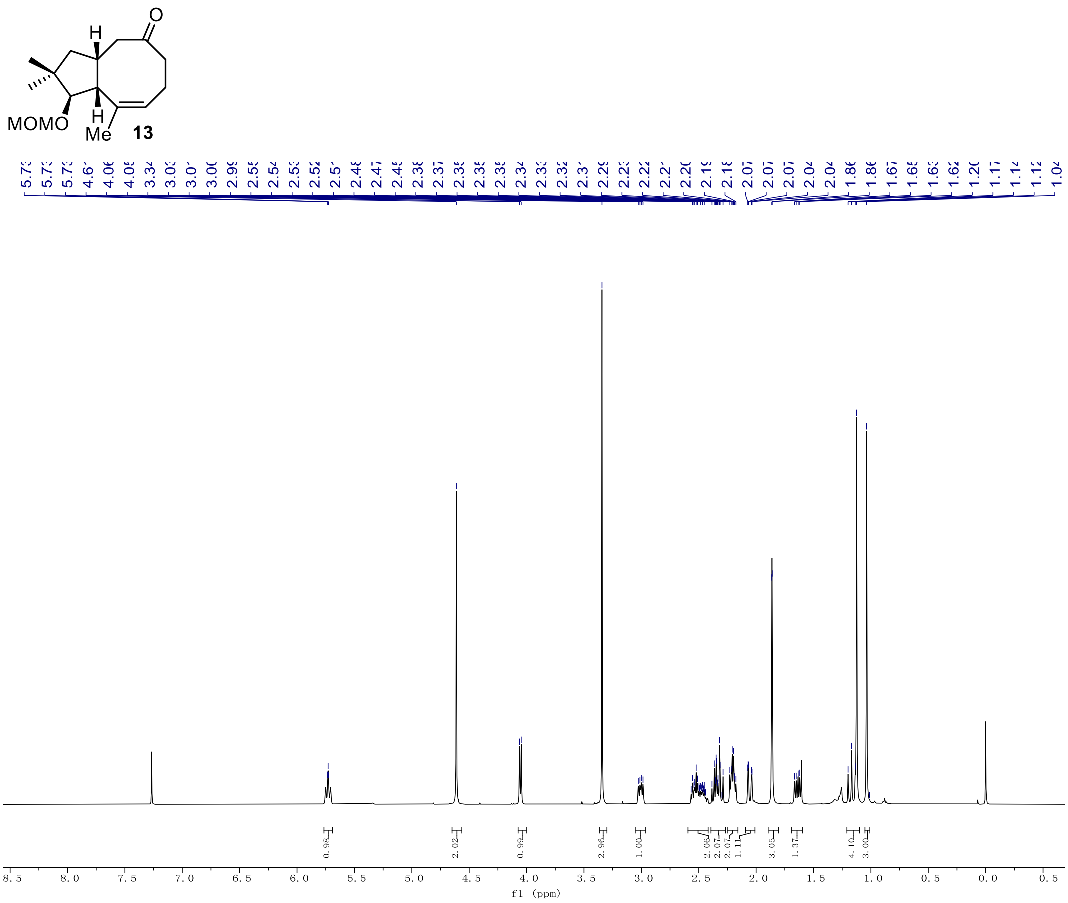
14

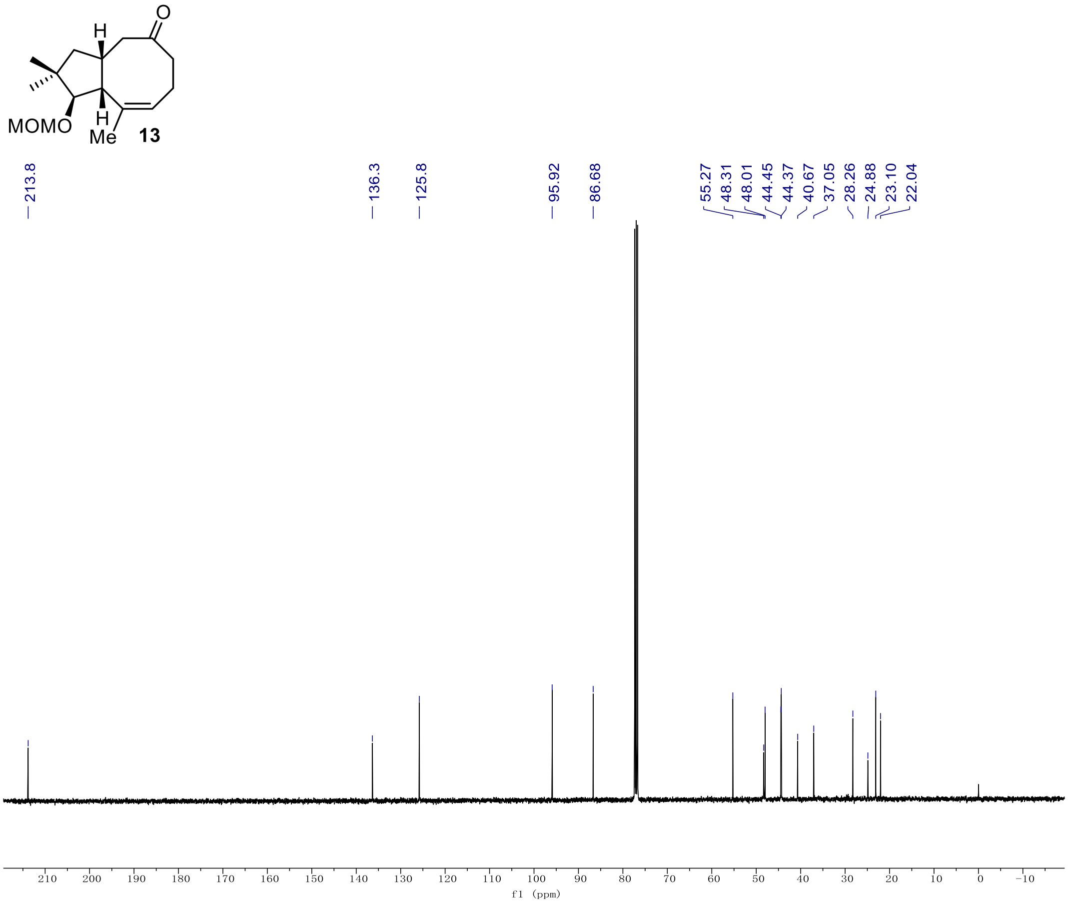

5.84
5.18
5.17
5.17
5.15
5.15
5.14
5.04
5.04
5.04
5.02
5.02
5.01
5.01
5.00
5.00
4.99
4.73
4.71
4.46
4.45
4.28
4.25
3.38
2.12
2.10
2.10
2.10
2.09
2.09
2.09
2.07
2.07
2.07
1.76
1.46
1.46
0.93
0.88
0.64
0.63
0.62
0.62
0.62
0.61
0.61
0.60
0.60
0.60
0.52
0.50
1.00
0.95
0.94
0.90
0.95
0.95
0.97
2.79
2.02
0.98
2.76
2.94
2.96
2.88
0.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

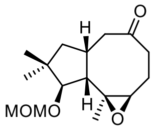

Me
MOMO

14

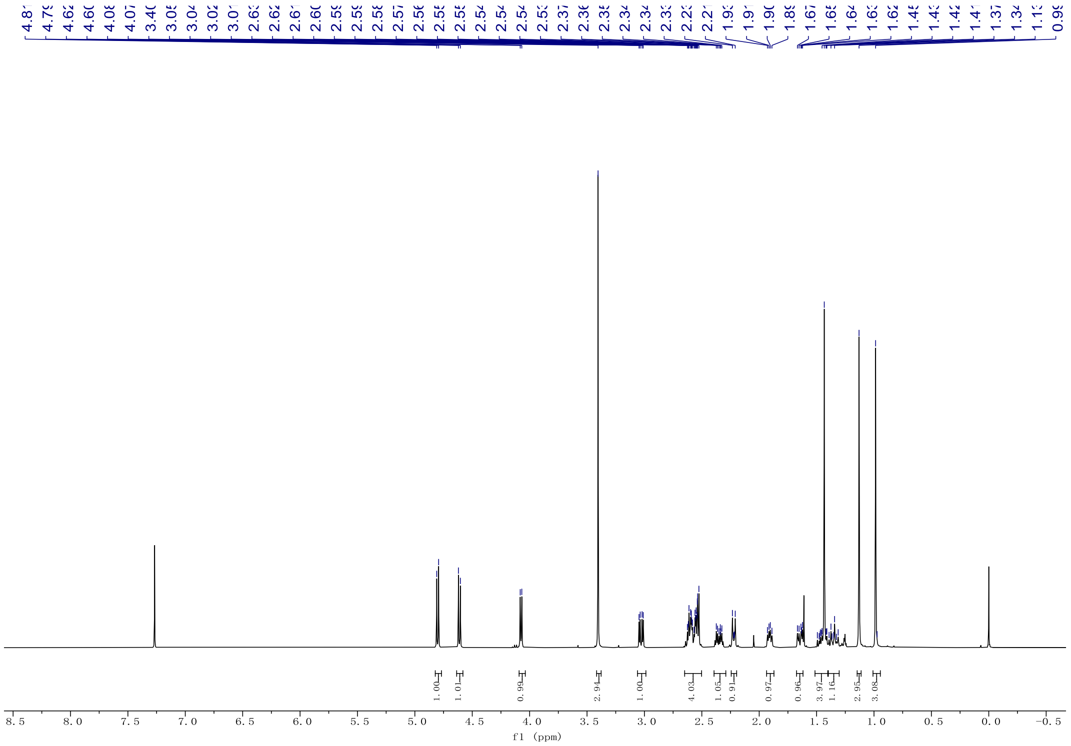

140.9
135.6
122.8
116.9
93.46
77.18
55.67
43.45
37.96
22.98
22.90
18.90
12.71
4.43
4.36
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

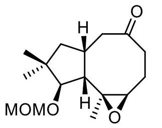

O
H
MOMO
H
Me
13
5.73
5.73
5.73
4.61
4.06
4.05
3.34
3.03
3.01
3.00
2.99
2.55
2.54
2.53
2.52
2.51
2.48
2.47
2.45
2.38
2.37
2.35
2.35
2.35
2.34
2.33
2.32
2.31
2.29
2.23
2.22
2.21
2.20
2.19
2.18
2.07
2.07
2.07
2.04
2.04
1.86
1.86
1.67
1.65
1.63
1.62
1.20
1.17
1.14
1.12
1.04
0.98
2.02
0.99
2.96
1.00
2.06
2.07
2.07
1.11
3.05
1.37
4.10
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


O
H
MOMO
H
Me
13
213.8
136.3
125.8
95.92
86.68
55.27
48.31
48.01
44.45
44.37
40.67
37.05
28.26
24.88
23.10
22.04
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

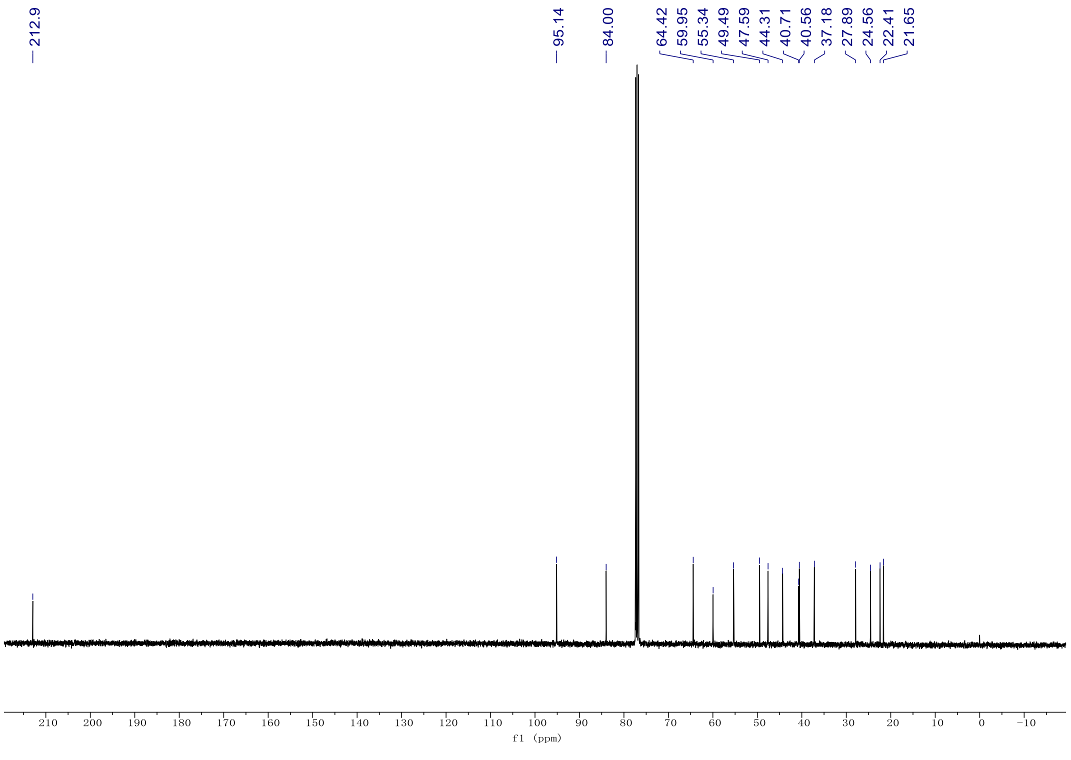


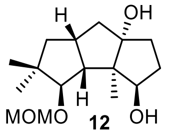
20


4.81
4.79
4.62
4.60
4.08
4.07
3.40
3.05
3.04
3.02
3.01
2.63
2.62
2.61
2.60
2.59
2.59
2.58
2.57
2.56
2.55
2.55
2.54
2.54
2.54
2.53
2.37
2.36
2.35
2.34
2.34
2.33
2.23
2.21
1.93
1.91
1.90
1.89
1.67
1.65
1.64
1.63
1.62
1.45
1.43
1.42
1.41
1.37
1.34
1.13
0.99
1.00
1.01
0.99
2.94
1.00
4.03
1.05
0.91
0.97
0.96
3.97
1.16
2.95
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

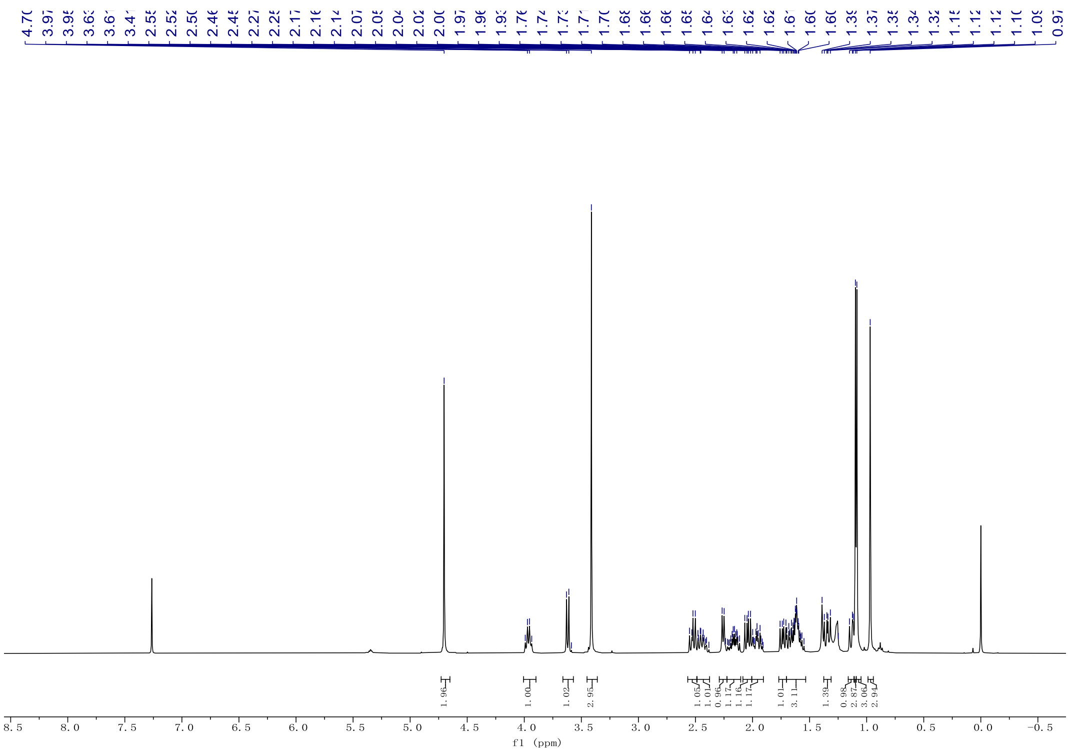


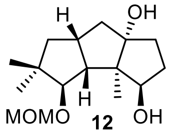
20


212.9
95.14
84.00
64.42
59.95
55.34
49.49
47.59
44.31
40.71
40.56
37.18
27.89
24.56
22.41
21.65
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

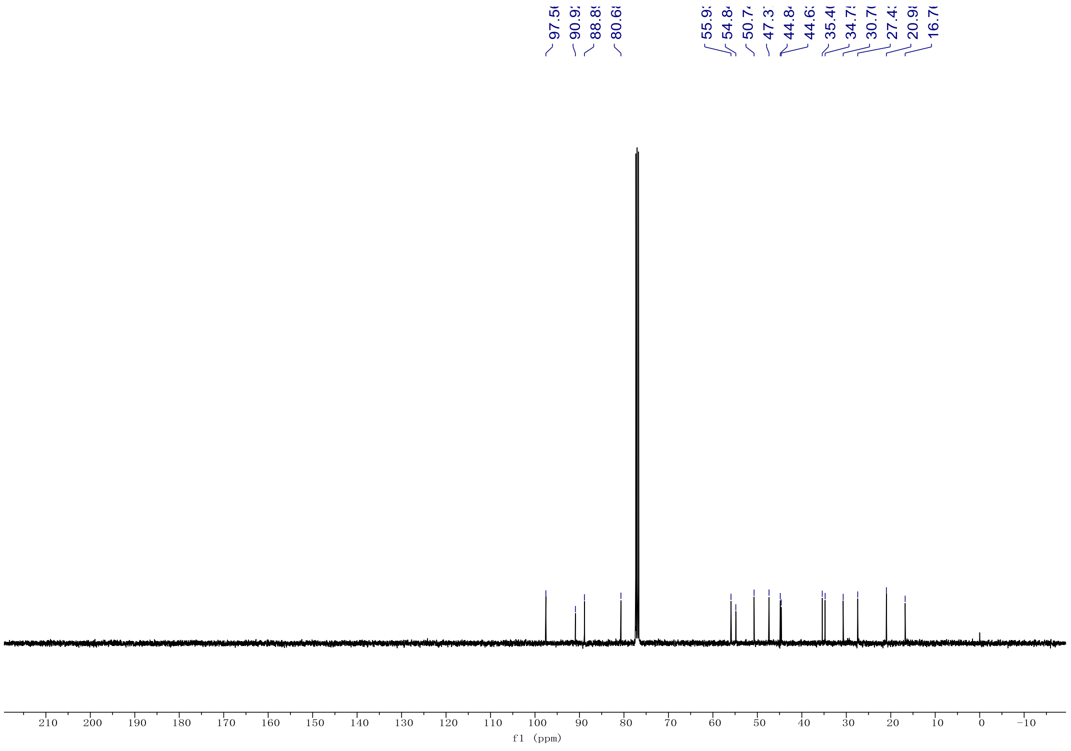

H
OH
MOMO
H
OH

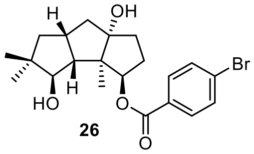
12


4.70
3.97
3.95
3.63
3.61
3.41
2.55
2.52
2.50
2.46
2.45
2.27
2.25
2.17
2.16
2.14
2.07
2.05
2.04
2.02
2.00
1.97
1.96
1.93
1.76
1.74
1.73
1.71
1.70
1.68
1.66
1.66
1.65
1.64
1.63
1.62
1.62
1.61
1.60
1.60
1.39
1.37
1.35
1.34
1.32
1.15
1.12
1.12
1.10
1.09
0.97
1.96
1.00
1.02
2.95
1.05
1.01
0.96
1.17
1.16
1.17
1.01
3.11
1.39
0.98
2.87
3.06
2.94
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

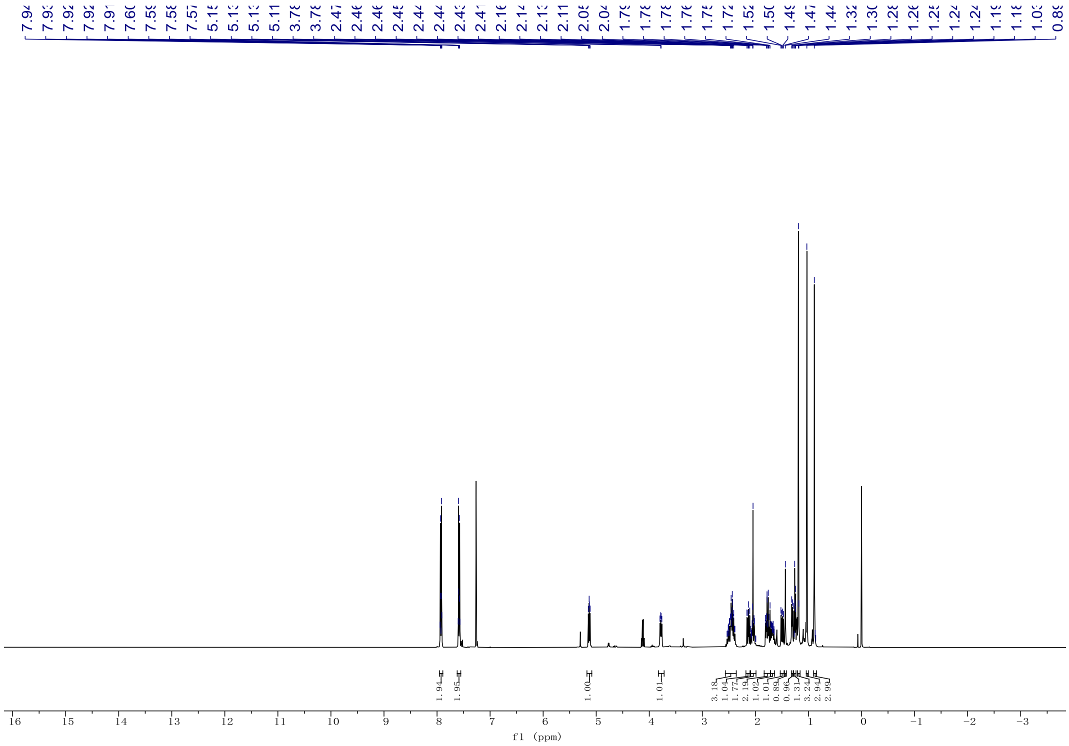

H
OH
MOMO
H
OH

12

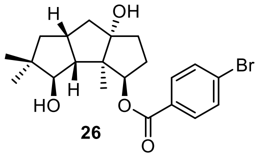

97.50
90.93
88.89
80.68
55.93
54.84
50.74
47.31
44.84
44.63
35.40
34.75
30.70
27.43
20.98
16.70
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



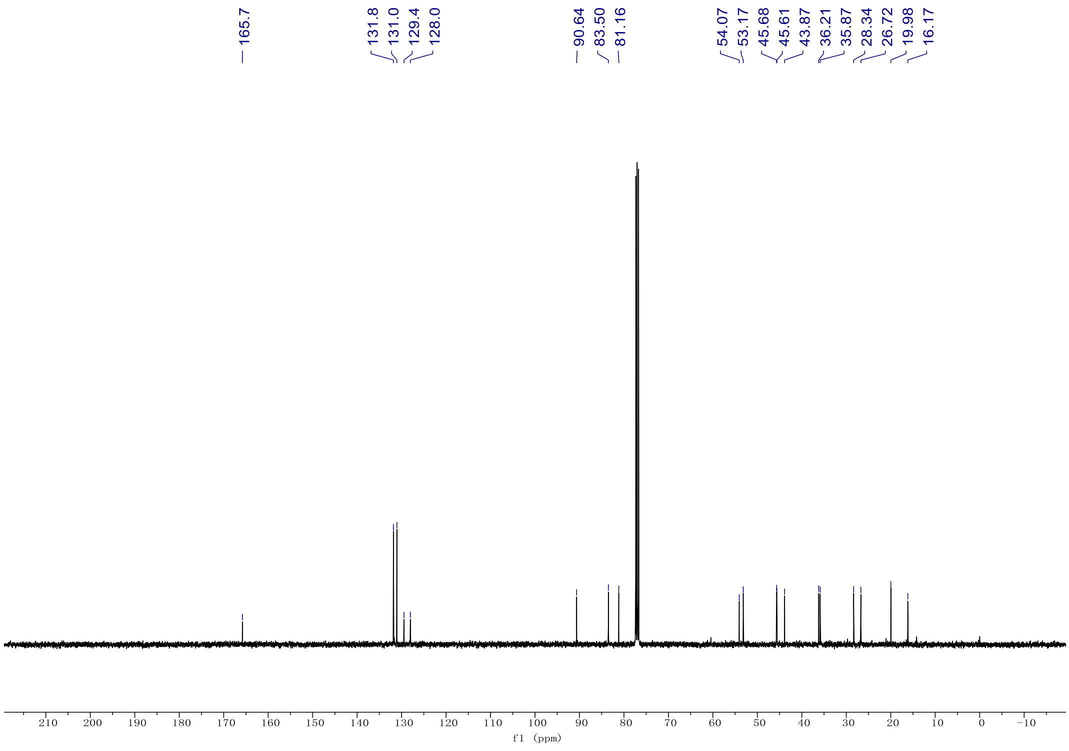
26



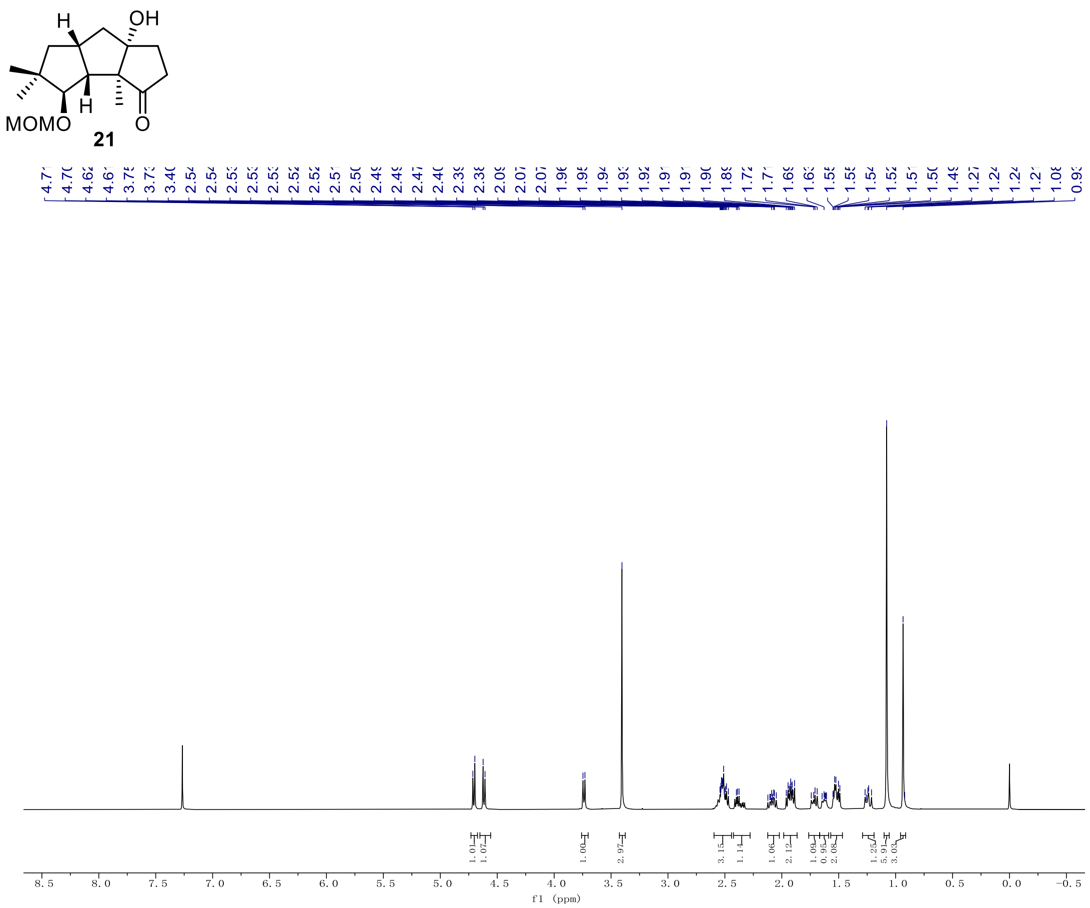
7.94
7.93
7.92
7.92
7.91
7.60
7.59
7.58
7.57
5.15
5.13
5.13
5.11
3.78
3.78
2.47
2.46
2.46
2.45
2.44
2.44
2.43
2.41
2.16
2.14
2.13
2.11
2.05
2.04
1.79
1.78
1.78
1.76
1.75
1.72
1.52
1.50
1.49
1.47
1.44
1.32
1.30
1.28
1.26
1.25
1.24
1.24
1.19
1.18
1.03
0.89
1.94
1.95
1.00
1.01
3.18
1.04
1.72
2.19
1.02
1.01
0.89
0.96
1.31
3.24
2.94
2.99
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

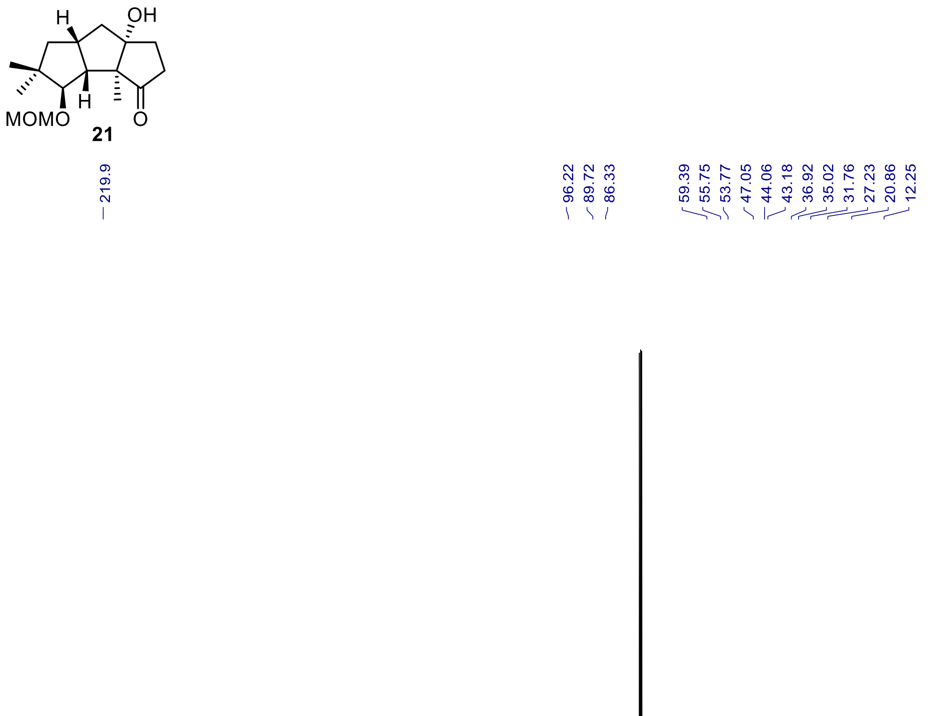


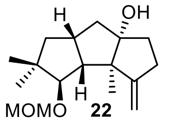
26



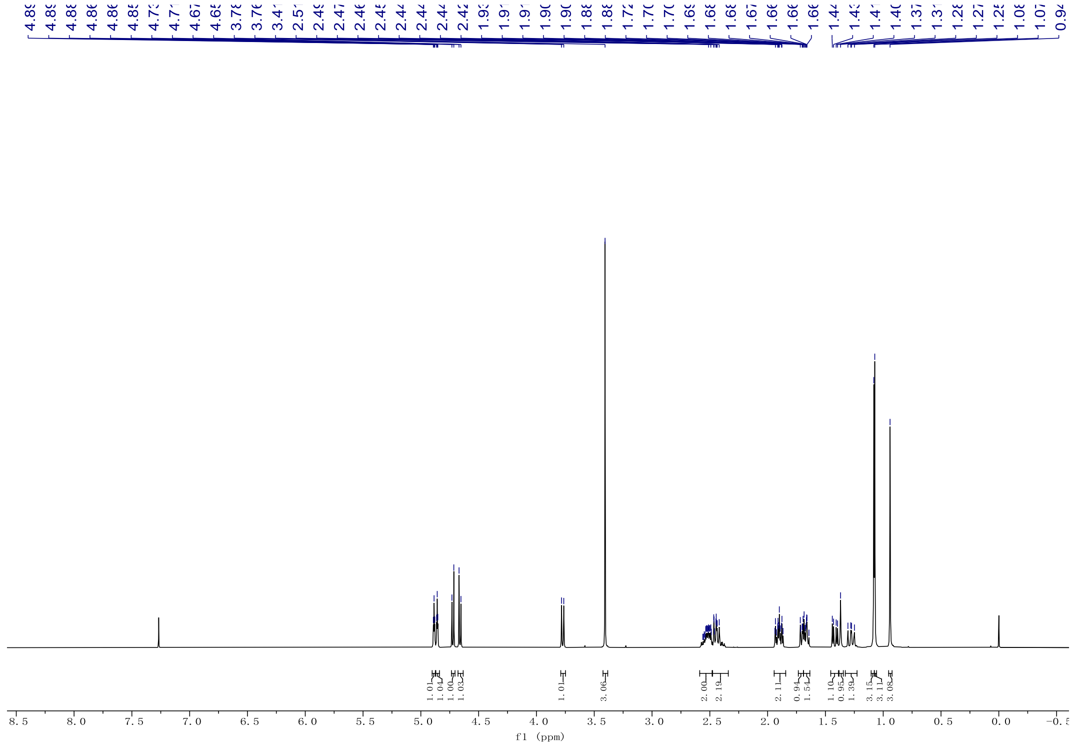
165.7
131.8
131.0
129.4
128.0
90.64
83.50
81.16
54.07
53.17
45.68
45.61
43.87
36.21
35.87
28.34
26.72
19.98
16.17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

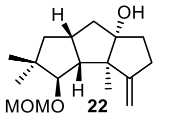

H
OH
MOMO
H
O
21
4.71
4.70
4.62
4.61
3.75
3.73
3.40
2.54
2.54
2.53
2.53
2.52
2.52
2.51
2.50
2.49
2.49
2.47
2.40
2.39
2.38
2.09
2.07
2.07
1.96
1.95
1.94
1.93
1.92
1.91
1.91
1.90
1.89
1.72
1.71
1.69
1.63
1.59
1.55
1.54
1.52
1.51
1.50
1.49
1.27
1.24
1.21
1.08
0.93
1.01
1.07
1.00
2.97
3.15
1.14
1.06
2.12
1.09
0.95
2.08
1.23
5.91
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


H
OH
MOMO
H
O
21
219.9
96.22
89.72
86.33
59.39
55.75
53.77
47.05
44.06
43.18
36.92
35.02
31.76
27.23
20.86
12.25
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−4
f1 (ppm)

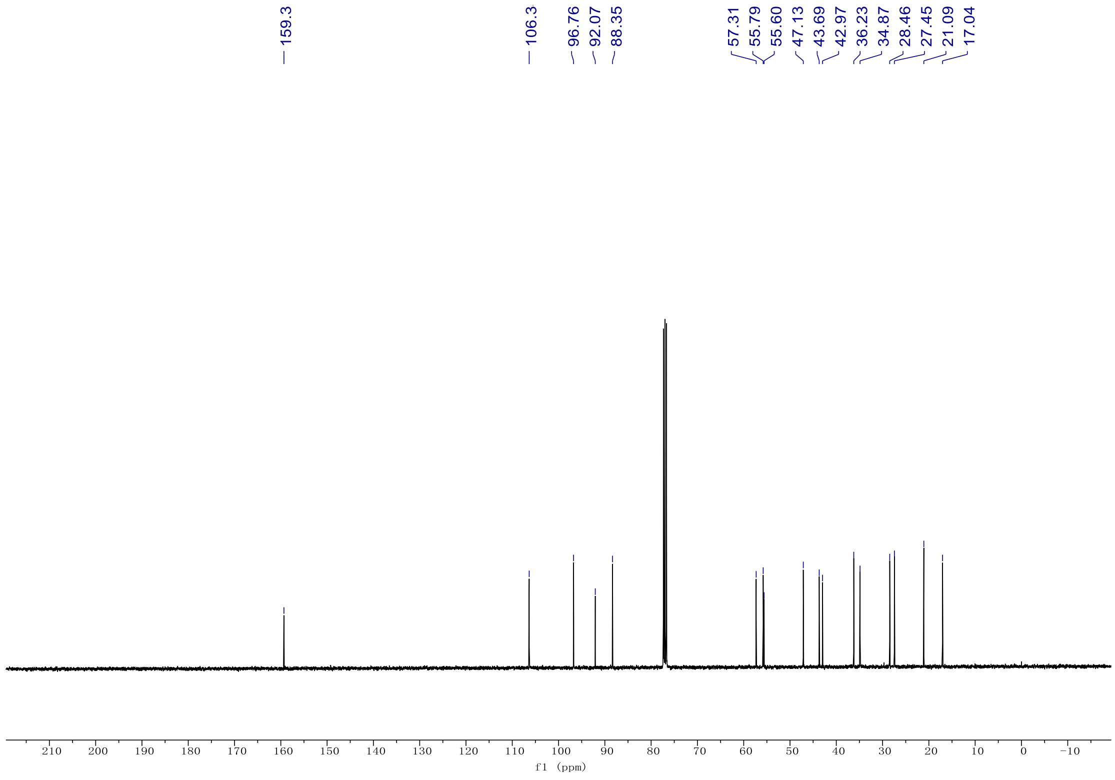

OH
H
H
MOMO

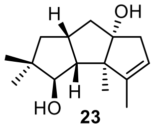
22


4.89
4.89
4.88
4.86
4.85
4.73
4.67
4.65
3.78
3.76
3.41
2.51
2.49
2.47
2.46
2.45
2.44
2.44
2.44
2.42
1.93
1.91
1.91
1.90
1.90
1.88
1.88
1.72
1.70
1.70
1.69
1.68
1.68
1.67
1.66
1.66
1.66
1.44
1.43
1.41
1.40
1.37
1.31
1.28
1.27
1.25
1.08
1.07
0.94
1.01
1.04
1.00
1.03
1.01
3.06
2.00
2.19
2.11
0.94
1.54
1.10
0.95
1.39
3.15
3.11
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

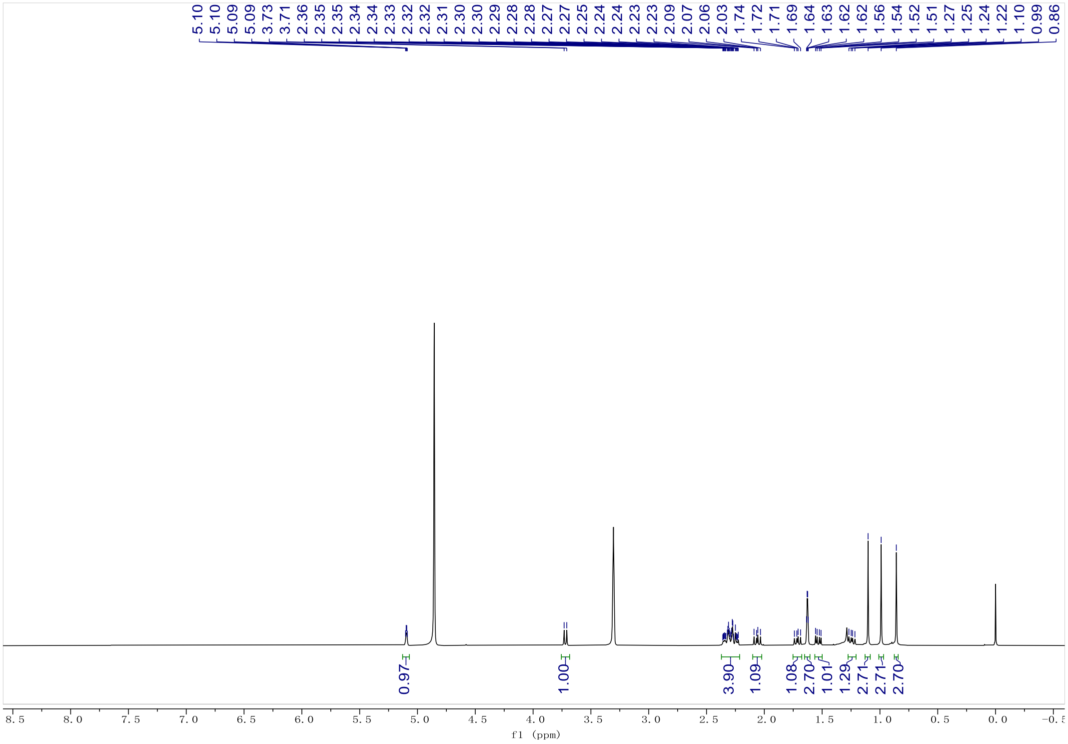

OH
H
H
MOMO

22

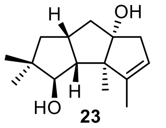

159.3
106.3
96.76
92.07
88.35
57.31
55.79
55.60
47.13
43.69
42.97
36.23
34.87
28.46
27.45
21.09
17.04
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



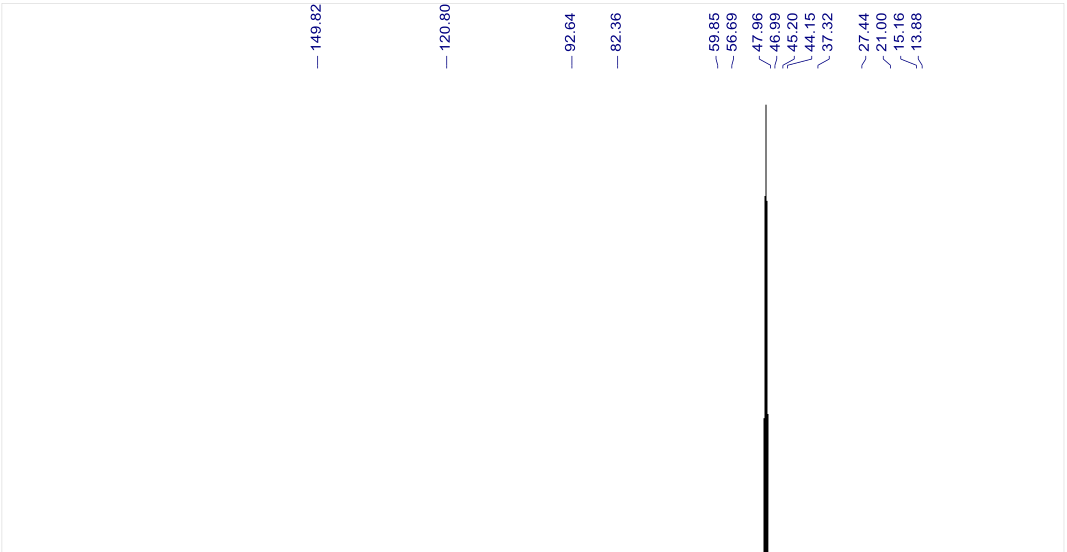
23



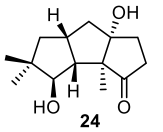
5.10
5.10
5.09
5.09
3.73
3.71
2.36
2.35
2.35
2.34
2.34
2.33
2.32
2.32
2.31
2.30
2.30
2.29
2.28
2.28
2.27
2.27
2.25
2.24
2.24
2.23
2.23
2.23
2.09
2.07
2.06
2.03
1.74
1.72
1.71
1.69
1.64
1.63
1.62
1.62
1.56
1.54
1.52
1.51
1.27
1.25
1.24
1.22
1.10
0.99
0.86
0.97
1.00
3.90
1.09
1.08
2.70
1.01
1.29
2.71
2.71
2.70
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



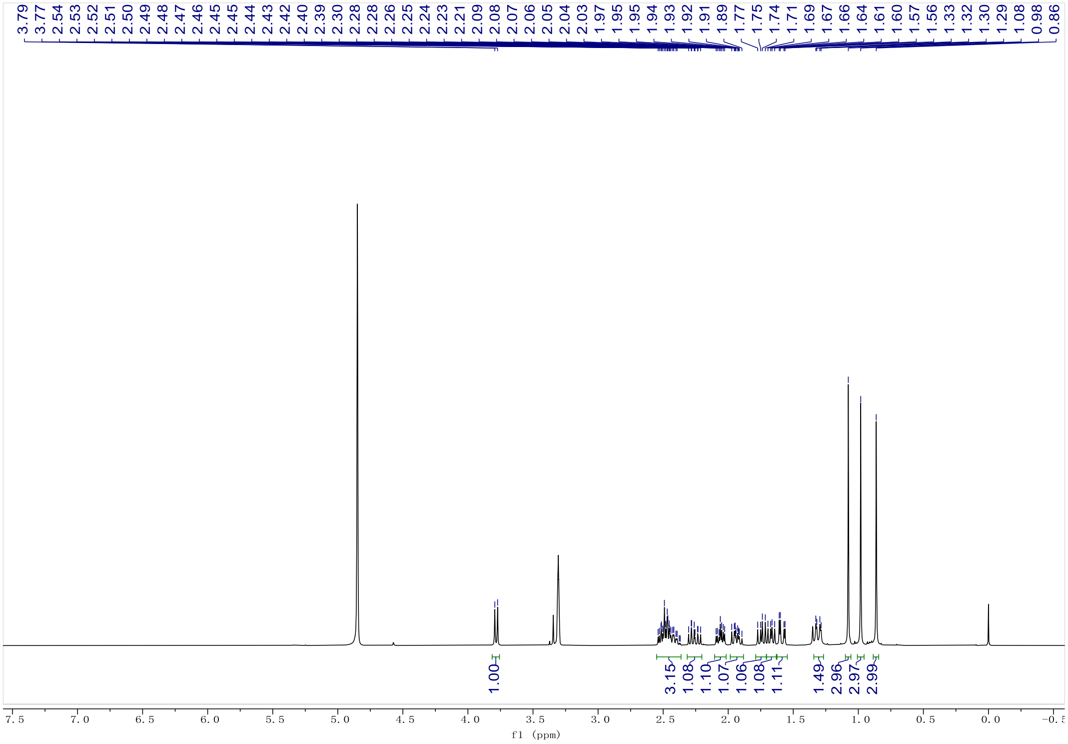
23

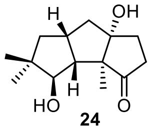


149.82
120.80
92.64
82.36
59.85
56.69
47.96
46.99
45.20
44.15
37.32
27.44
21.00
15.16
13.88
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

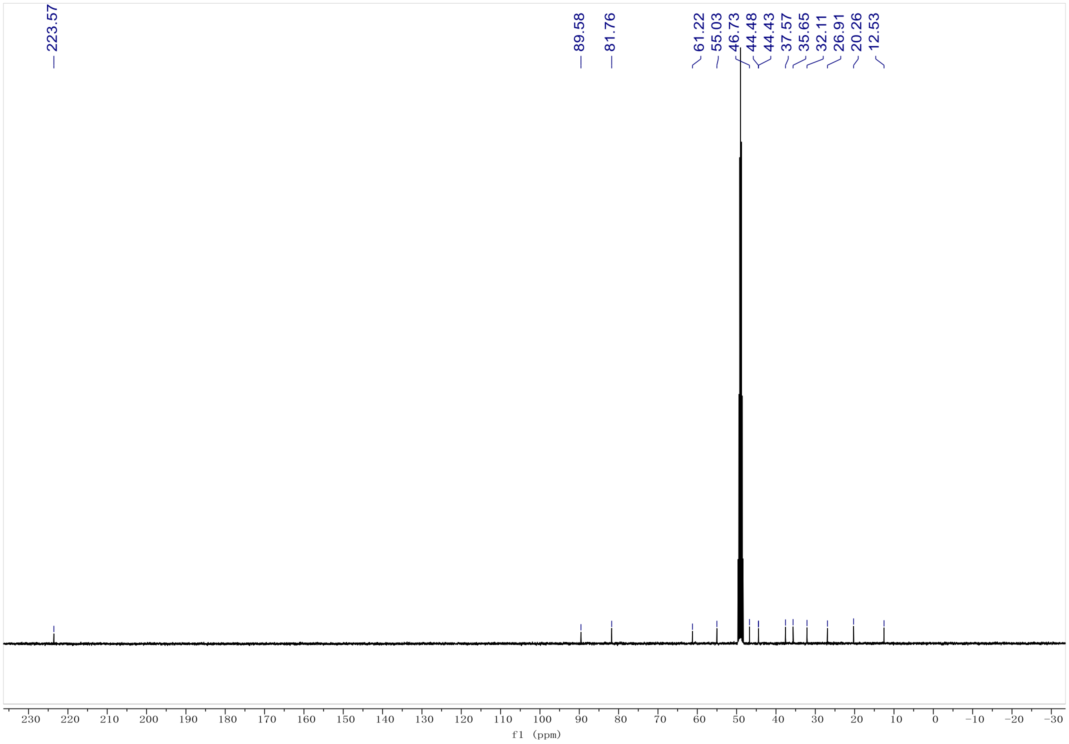

H
OH
H
HO
O

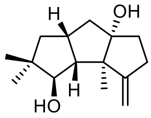
24


3.79
3.77
2.54
2.53
2.52
2.51
2.50
2.49
2.48
2.47
2.46
2.45
2.45
2.44
2.43
2.42
2.40
2.39
2.30
2.28
2.28
2.26
2.25
2.24
2.23
2.21
2.09
2.08
2.07
2.06
2.05
2.04
2.03
1.97
1.95
1.95
1.94
1.93
1.92
1.91
1.89
1.77
1.75
1.74
1.71
1.69
1.67
1.66
1.64
1.61
1.60
1.57
1.56
1.33
1.32
1.30
1.29
1.08
0.98
0.86
1.00
3.15
1.08
1.10
1.07
1.06
1.08
1.11
1.49
2.96
2.97
2.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

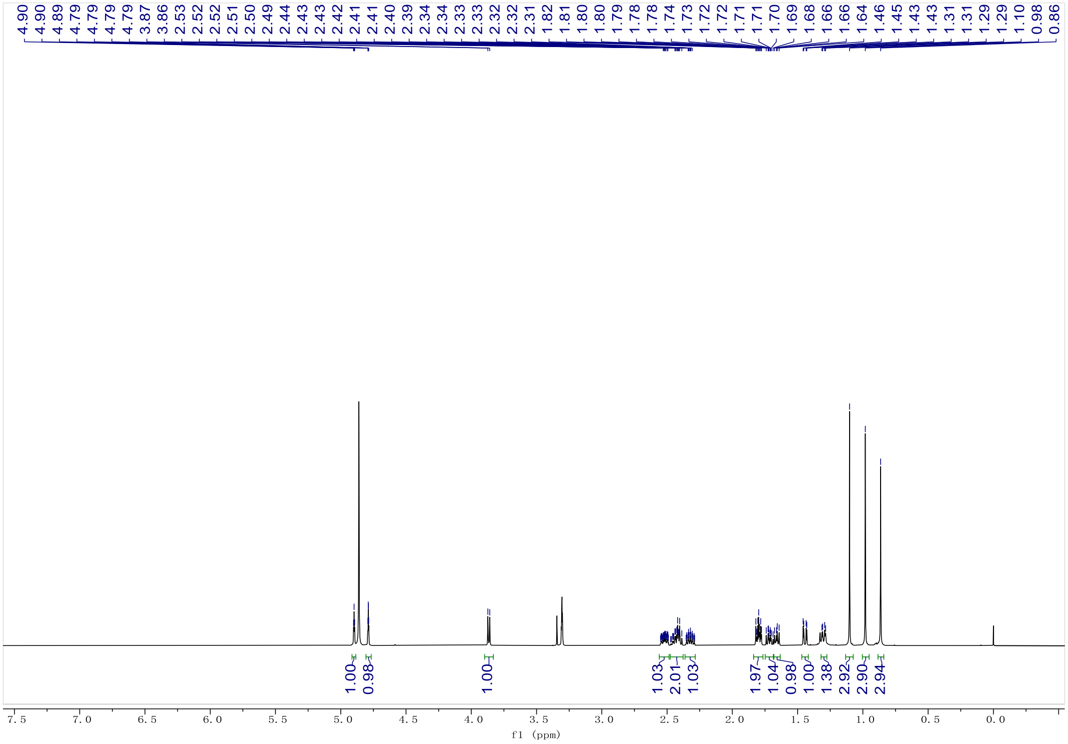

H
OH
H
HO
O

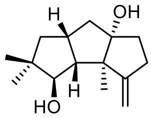
24


223.57
89.58
81.76
61.22
55.03
46.73
44.48
44.43
37.57
35.65
32.11
26.91
20.26
12.53
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)

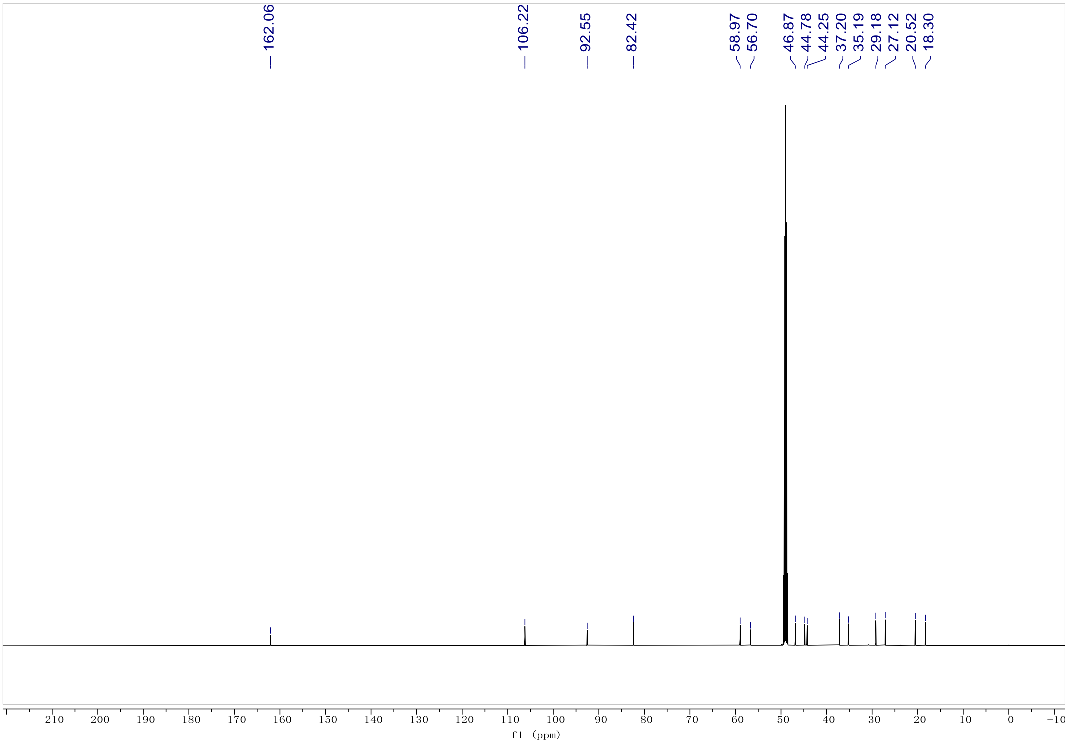


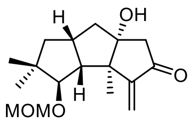
(+)-antrodiellin B (1)



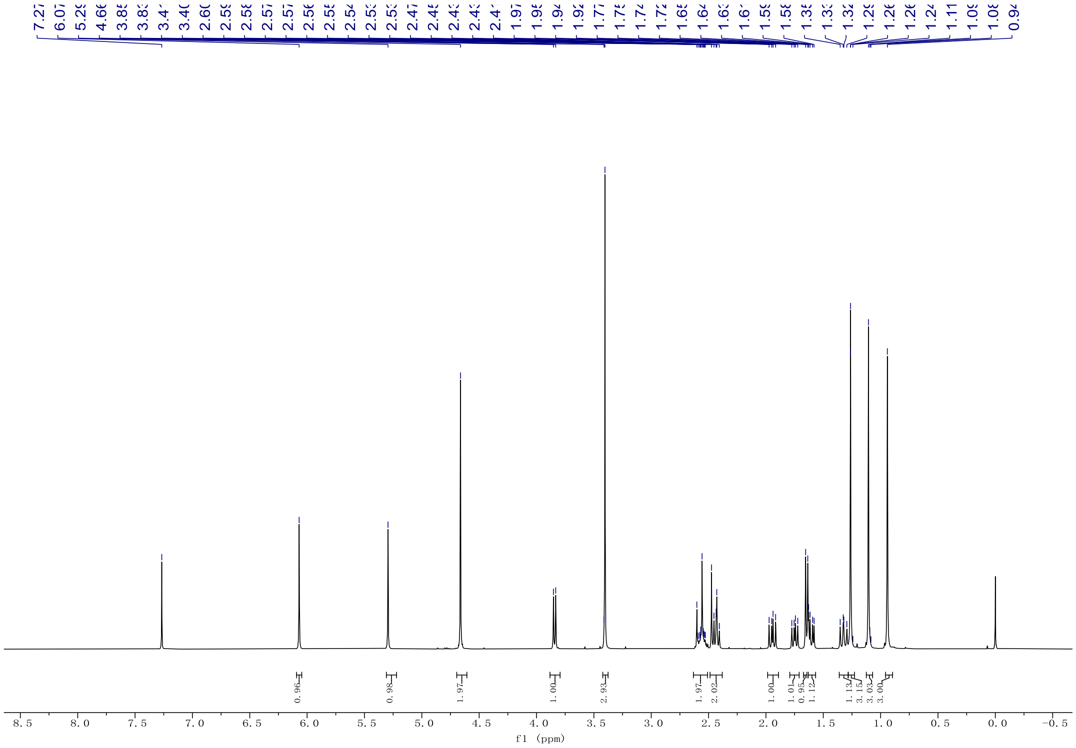


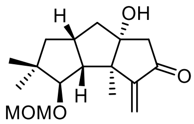
(+)-antrodiellin B (1)



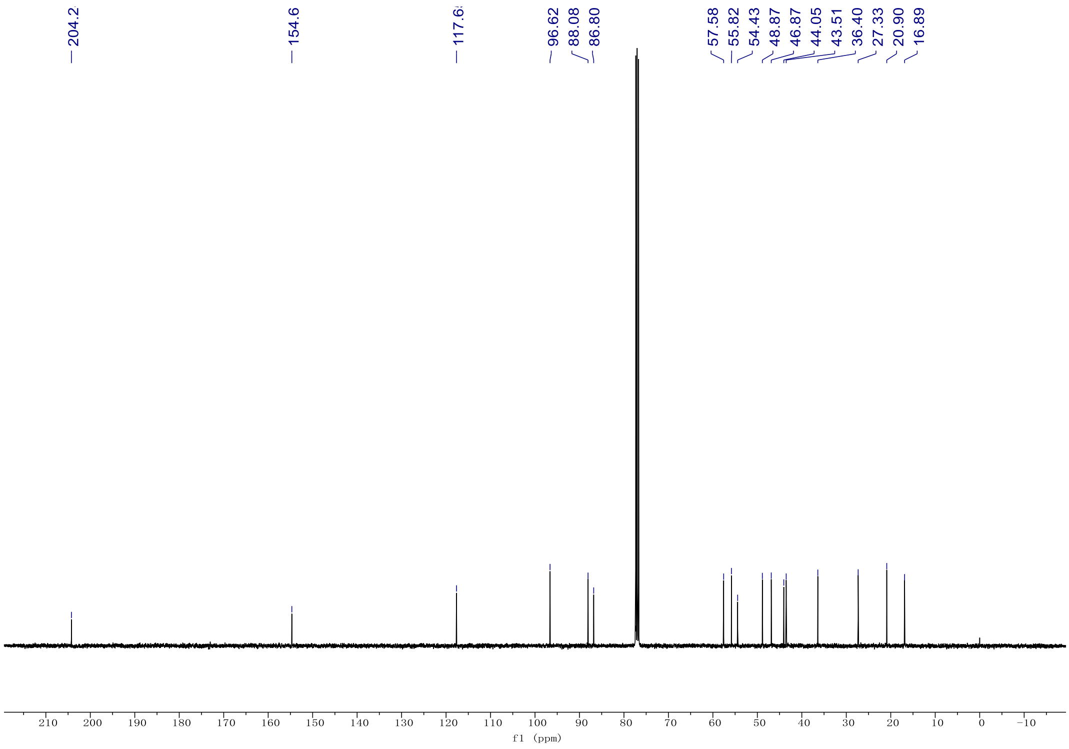

H
OH
O
H
MOMO

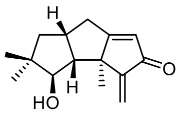
25


7.27
6.07
5.29
4.66
3.85
3.83
3.41
3.40
2.60
2.59
2.58
2.57
2.57
2.56
2.55
2.54
2.53
2.53
2.47
2.45
2.43
2.41
1.97
1.95
1.94
1.92
1.77
1.75
1.74
1.72
1.65
1.64
1.63
1.61
1.59
1.58
1.35
1.33
1.32
1.29
1.26
1.26
1.24
1.11
1.09
1.08
0.94
0.96
0.98
1.97
1.00
2.93
1.97
2.02
1.00
1.01
0.95
1.12
1.13
3.15
3.03
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

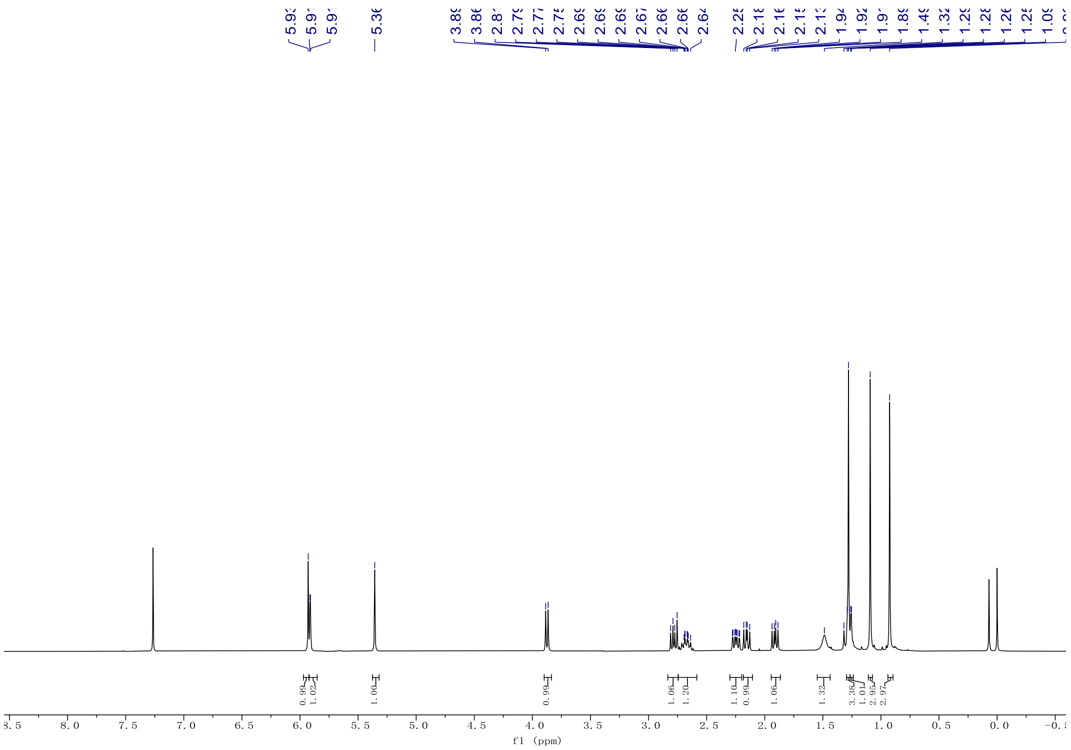

H
OH
O
H
MOMO

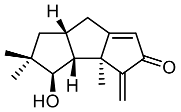
25


204.2
154.6
117.63
96.62
88.08
86.80
57.58
55.82
54.43
48.87
46.87
44.05
43.51
36.40
27.33
20.90
16.89
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

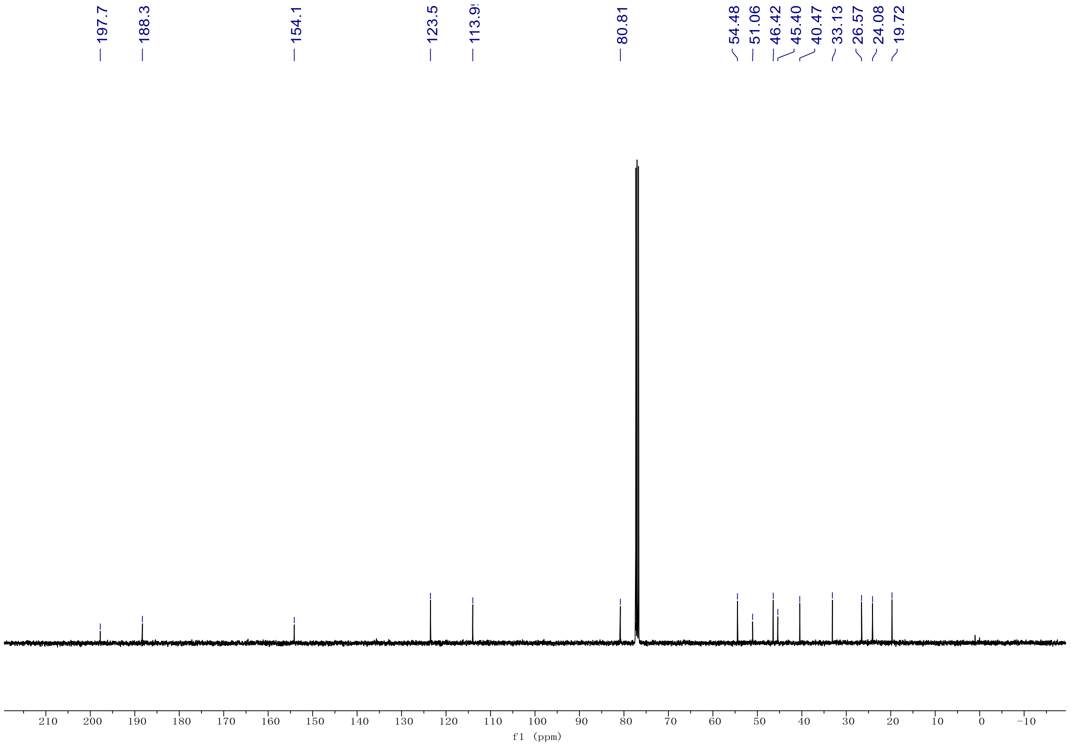


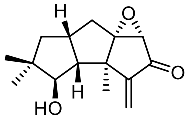
11


5.93
5.91
5.91
5.36
3.89
3.86
2.81
2.79
2.77
2.75
2.69
2.69
2.69
2.67
2.66
2.66
2.64
2.25
2.18
2.16
2.15
2.13
1.94
1.92
1.91
1.89
1.49
1.32
1.29
1.28
1.26
1.25
1.09
0.99
1.02
1.00
0.99
1.06
1.20
1.10
0.99
1.06
1.32
3.38
1.01
2.95
2.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

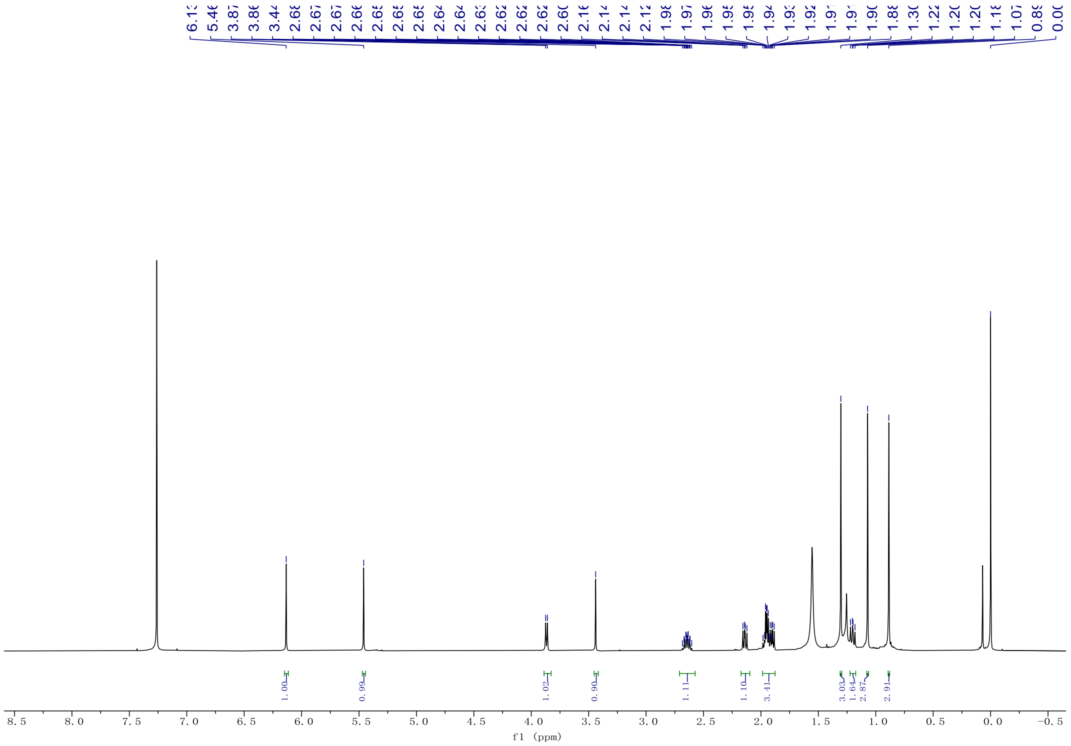


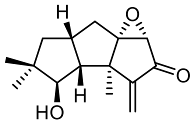
11


197.7
188.3
154.1
123.5
113.9
80.81
54.48
51.06
46.42
45.40
40.47
33.13
26.57
24.08
19.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

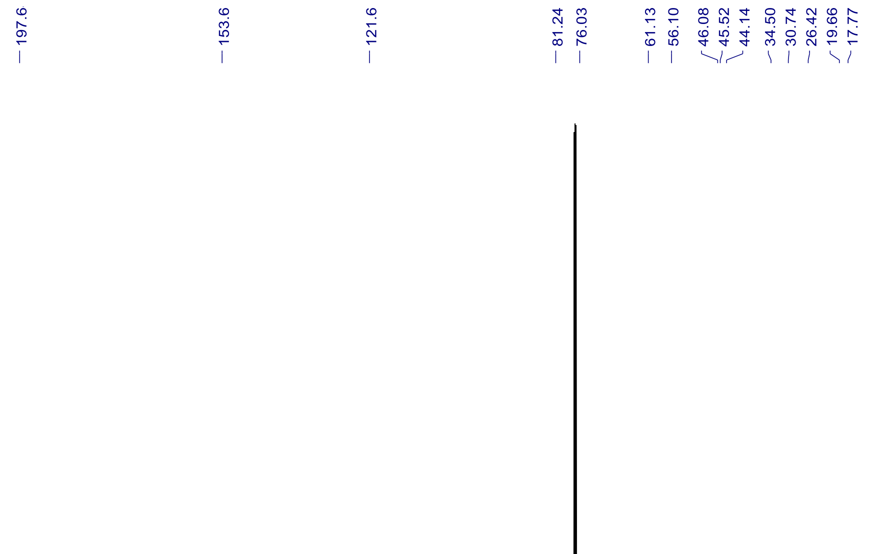


(-)-hypnophilin (**2**)





(-)-hypnophilin (**2**)



S10. HPLC Spectra

HPLC spectra of *rac*-19

Column: ChiralPak AS-H

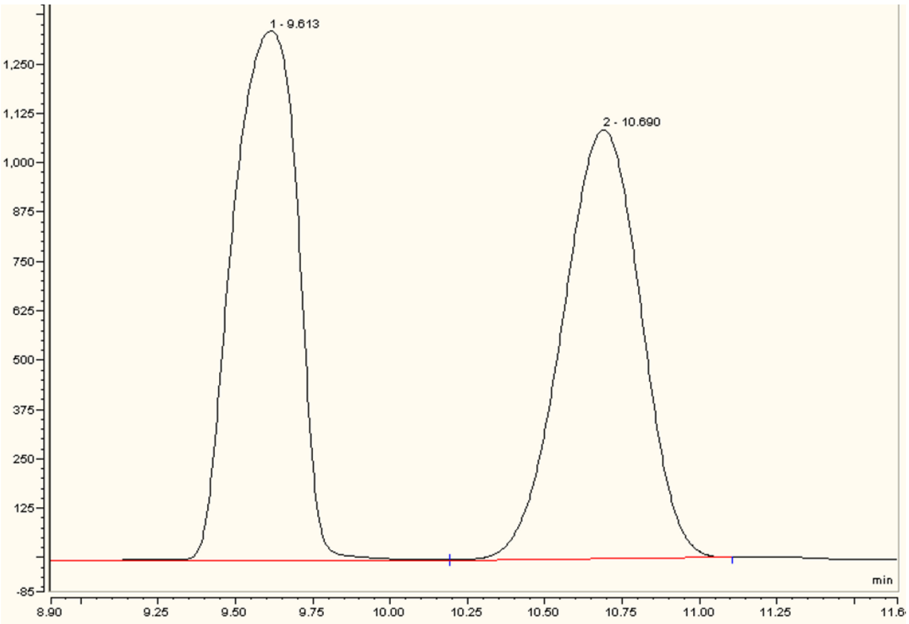
Concertration: 4 mg/ mL

Mobile phase: hexane : *i*-propanol = 99.8 : 0.2

Flow rate: 1.0 mL/min

Measure wave length: 210 nm

ee = 0%



No.	Ret.Time	Area	Height	Rel.Area
	min	mAU*min	mAU	%
1	9.613	325.7656	1340.036	**50.48**
2	10.69	319.5231	1085.899	**49.52**
Total:		645.2887	2425.935	100

HPLC spectra of 19

Column: ChiralPak AS-H

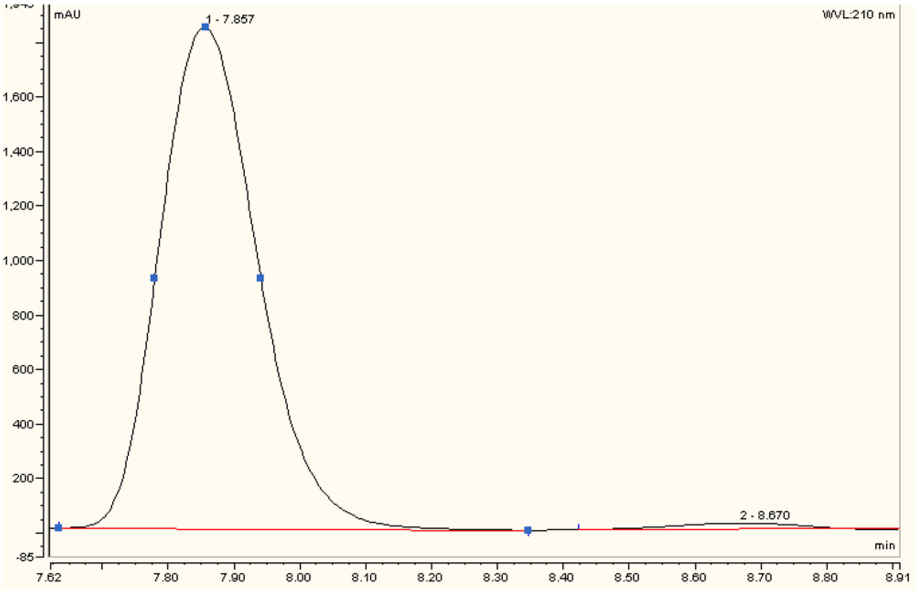
Concertration: 4 mg/ mL

Mobile phase: hexane : *i*-propanol = 99.8 : 0.2

Flow rate: 1.0 mL/min

Measure wave length: 210 nm

ee = 97%



No.	Ret.Time	Area	Height	Rel.Area
	min	mAU*min	mAU	%
1	7.857	316.6319	1839.948	**98.52**
2	8.67	4.7718	22.958	**1.48**
Total:		321.4037	1862.905	100