SUPPORTING INFORMATION

Collective Asymmetric Total Synthesis of (+)-Sinensilactam A, (+)-Lingzhilactone B and (-)-Lingzhiol: Divergent reactivity of styrene

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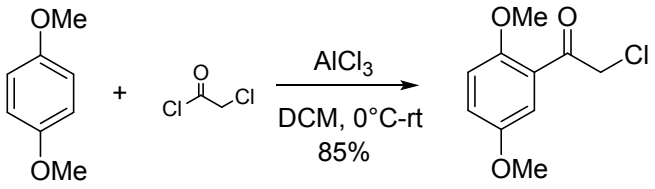
I. General Information

All reactions were performed with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF) was distilled over sodium. Dry dichloro−methane (DCM) was distilled over calcium hydride. N, N-Dimethylformamide (DMF)

and methanol (MeOH) were dried with 4Å molecular sieve without distillation. Reagents were used as received without further purification, unless otherwise stated. Silica gel (200-300 mesh, Qingdao Marine Chemical Ltd., China), light petroleum ether (bp 60–90 ºC) and ethyl acetate were used for product purification by flash column chromatography. Melting Point (MP) was determined with a X-4 Taike micro melting point apparatus and was uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker Avance 400 and 600 spectrometer at 400 MHz and 600 MHz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) was recorded on Bruker Avance 400 and 600 spectrometer at 100 and 150 MHz. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Mass spectra were recorded on a VG-Auto-Spec-3000 spectrometer. High-resolution mass spectral analysis (HRMS) data were recorded via electron impact mass spectrometry using a time of flight analyzer.

II. General Experimental Procedures

Synthesis of Compound 1

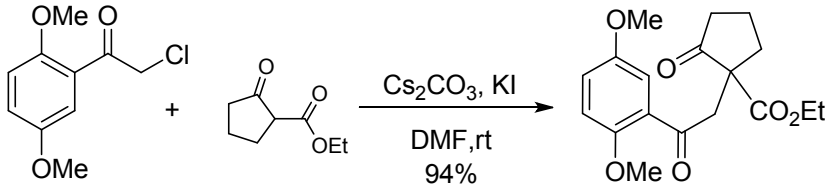


1

To a solution of 1,4-dimethoxybenzene (10.00 g, 72.46 mmol, 1.0 equiv.) and $AlCl_3$ (10.60 g, 79.71 mmol, 1.1 equiv.) in DCM (50 mL) at 0 °C were added chloroacetyl chloride (7.50 mL, 94.20 mmol, 1.3 equiv.) dropwise and stirred for 30 min at 0℃ and then for 12 h at room temperature. The reaction was poured into a mixture of crushed ice and 21 mL Conc. HCl and stirred for 20 minutes again, the mixture was extracted with DCM (3 × 80 mL). The combined organic layers were washed with H_2O (2 × 100 mL), brine (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was crystallized from methanol to afford **1** (13.18 g, 85% yield) as white solid (mp: 84-86℃). R_f = 0.3 (petroleum ether/EtOAc = 7/1); ^{1}H NMR (400

MHz, $CDCl_3$): δ 7.40 (d, *J* = 3.2 Hz, 1H), 7.09 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 4.78 (s, 2H), 3.90 (s, 3H), 3.79 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ191.8, 153.7, 153.5, 124.9, 121.8, 114.2, 113.1, 56.1, 55.8, 51.1; IR (neat):ν_{max} (cm^{-1}) = 3100, 2918,1687, 1496, 1457, 1013, 816, 718, 630; HRMS (EIMS) calcd. for $C_{10}H_{11}ClO_3$ $[M]^+$:214.0397, found 214.0396;

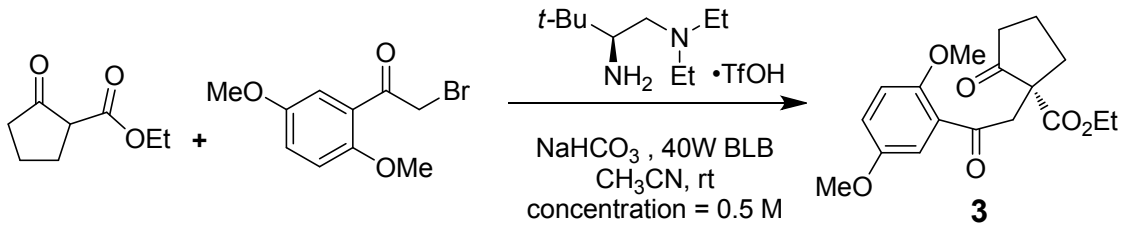
Synthesis of Compound 2



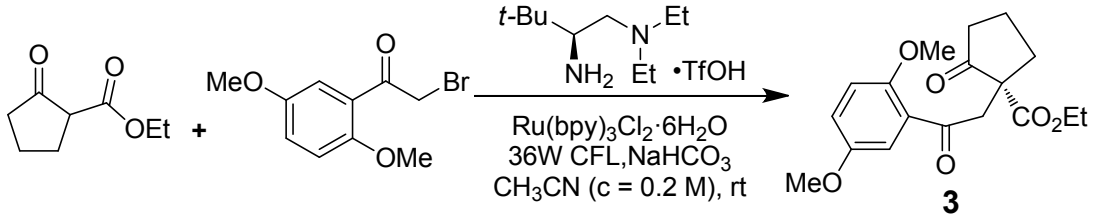
1 **2**

To a solution of **1** (6.00 g, 28.03 mmol, 1.0 equiv.) and ethyl 2-oxocyclopentane carboxylate (6.56 g, 42.05 mmol, 1.5 equiv.) in DMF (65 mL) were added Cs_2CO_3 (12.79 g, 39.24 mmol, 1.4 equiv.) and KI (4.65 g, 28.03 mmol, 1.0 equiv.). The mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of H_2O (100 mL), and the mixture was extracted with ethyl acetate (3 × 80 mL). The combined organic layers were washed with H_2O (2 × 100 mL), brine (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (petroleum ether/EtOAc = 6/1) to afford **2** (8.80 g, 94% yield) as pale yellow oil. R_f = 0.3 (Petroleum ether/EtOAc = 4/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 3.2 Hz, 1H), 7.03 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.86 – 3.81 (m, 4H), 3.78 (s, 3H), 3.51 (d, *J* = 19.3 Hz, 1H). 2.68 – 2.44 (m, 3H), 2.09 (m, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.2, 197.7, 170.8, 153.6, 153.4, 127.0, 121.1, 113.5, 113.1, 61.4, 58.0, 56.0, 55.8, 48.7, 37.8, 33.4, 19.8, 14.0. IR (neat): ν_{max} (cm^{-1}) = 2961, 2906, 2836, 1751, 1722, 1671, 1496, 1224, 865, 815. HRMS (EIMS) calcd. for $C_{18}H_{22}O_6$ $[M]^+$: 334.1416, found 334.1424;

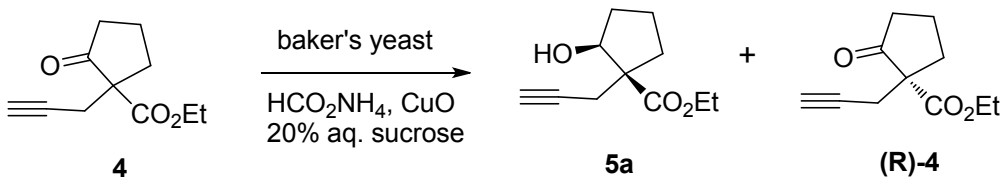
Photoalkylation: synthesis of chiral-3



Model reaction: An oven-dried 25 mL schlenk tube was charged with primary- tertiary diamine (257 mg, 0.80 mmol, 0.2 equiv.), phenacyl bromide (1.02 g, 4.00 mmol, 1 equiv.) and $NaHCO_3$ (336 mg, 4.00 mmol, 1 equiv.). The tube was purged with a stream of nitrogen, 8 mL of dry CH_3CN (with cyclic *β*-keto-ester, 16 mmol, 4 equiv.) was added via syringe. The resultant mixture was degassed three times. Then the tube was placed approximately 3 cm to 40W black light bulb (main wavelength: 365 nm) and stirred at room temperature. After the reaction was completed (TLC analysis, about 3 days). Solvent was removed and the residue was purified directly by silica gel column to give the target product (31% yield, 96% *ee*).



An oven-dried 10 mL schlenk tube was charged with primary-tertiary diamine (257 mg, 0.80 mmol, 0.2 equiv.), phenacyl bromide (1.02 g, 4.00 mmol, 1 equiv.), Ru $(bpy)_3Cl_2·6H_2O$ (171 mg, 0.20 mmol, 0.05 equiv.) and $NaHCO_3$ (336 mg, 4.00 mmol, 1 equiv.) . The tube was purged with a stream of nitrogen, 2 mL of dry CH_3CN (with cyclic *β*-keto-ester, 1.6 mmol, 4 equiv.) was added via syringe. The resultant mixture was degassed three times. Then the tube was placed approximately 3 cm to 36W CFL and stirred at room temperature. After the reaction was complete (TLC analysis, about 2 days). Solvent was removed and the residue was purified directly by silica gel column to give the target products (71% yield, 99% *ee*). HPLC analysis: Daicel Chiralpak OJ-H, iso-propanol/hexane = 5/95, flow rate = 1.0 mL/min, λ = 254 nm, retention time = 37. 62 min (major) and 40.27 min (minor).



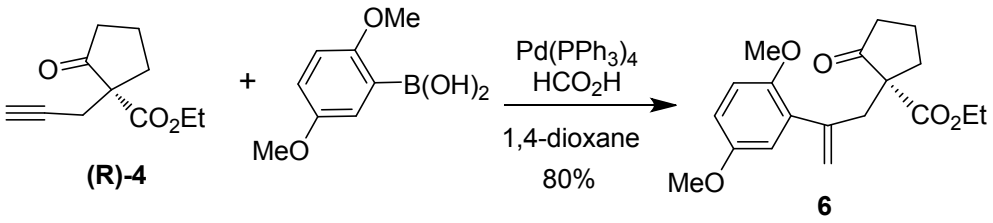
4 **5a** **(R)-4**

A round-bottomed 2000 mL flask with a magnetic stirring bar was charged with an aqueous solution of 20 % sucrose (260 g) in water (1300 mL) followed by Baker's yeast (56 g) and CuO (4.12 g , 51.49 mmol, 1 equiv.), $HCOONH_4$ (6.48 g, 102.98 mmol, 2 equiv.). To this resulting grayish solution was added *β*-keto-ester **4** (10.00 g, 51.49 mmol, 1 equiv.) dropwise. The reaction was vigorously stirred at 30 °C under air for 21 h. The suspension was then filtered through Celite pad. The solid (Baker's yeast, CuO and Celite) were then stirred vigorously with EtOAc for 30 minutes to recover product. The process was repeated until no more product in EtOAc by TLC. The aqueous layer was extracted with EtOAc four times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford crude product. It was purified by flash column chromatography (Petroleum ether/EtOAc = 40/1) to afford **(R)-4** (4.3 g, 43% yield) as light yellow oil, together with **5a** (4.5 g, 45% yield) as light yellow oil

5a: R_f = 0.3 (petroleum ether/EtOAc = 5/1); $[\alpha]_D^{25}$ = -50.48 (c = 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (q, *J* = 7.1 Hz, 2H), 2.72 (t, *J* = 2.5 Hz, 2H), 2.55 – 2.43 (m, 2H), 2.36 – 2.23 (m, 2H), 2.13 – 1.92 (m, 2H), 1.69 (s, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 213.71, 170.35, 79.85, 70.70, 61.76, 58.74, 38.30, 32.55, 23.11, 19.74;

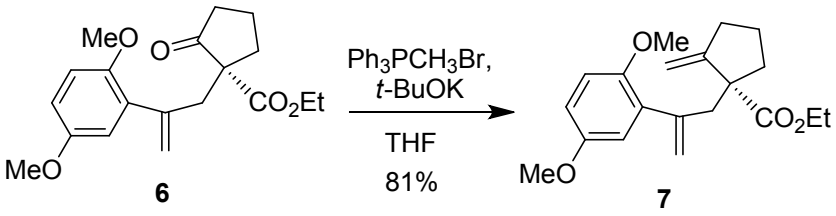
(R)-4: R_f = 0.2 (Petroleum ether/EtOAc=3/1); $[\alpha]_D^{25}$ = +24.41 (c = 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 – 4.15 (m, 2H), 3.00 (d, *J* = 5.2 Hz, 1H), 2.56 – 2.41 (m, 2H), 2.25 (ddd, *J* = 13.2, 9.3, 7.0 Hz, 1H), 2.07 – 1.95 (m, 2H), 1.93 – 1.61 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9, 80.2, 78.3, 70.6, 61.1, 57.0, 32.5, 31.6, 25.3, 20.6, 14.2;

Synthesis of Compound 6



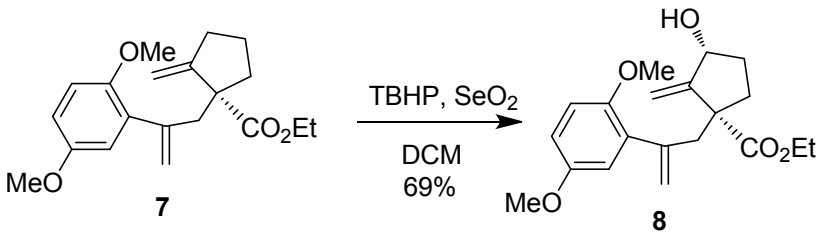
To a solution of **(R)-4** (3.44 g, 17.73 mmol, 1.0 equiv.) and aryl boronic acid (3.87 g, 21.28 mmol, 1.2 equiv.) in 1,4-dioxane (60 mL) were added $Pd(PPh_3)_4$ (616 mg, 0.53 mmol, 0.03 equiv.) and HCOOH (0.417 mL), the mixture was stirred for 10 minutes at room temperature and for 2 h at 30 °C . The suspension was then filtered through Celite and the mixture was extracted with ethyl acetate (3 × 80 mL). The combined organic layers were washed with H_2O (2 × 100 mL), brine (100 mL), dried over Na_2SO_4 and concentrated at reduced pressure to afford crude product. It was purified by flash chromatography (petroleum ether/EtOAc = 15/1) to afford **6** (4.7 g, 80% yield) as pale yellow oil. R_f= 0.3 (petroleum ether/EtOAc = 5/1); 100 % *ee*. $[\alpha]_D^{25}$ = -46.88 (c = 0.21, $CHCl_3$); HPLC analysis: Daicel Chiralpak AD-H, *iso*- propanol/hexane = 5/95, flow rate = 1.0 mL/min, λ = 254 nm, retention time = 9.45 min (major) and 10.23 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, *J* = 2.2 Hz, 2H), 6.65 (d, *J* = 1.8 Hz, 1H), 5.17 (s, 1H), 5.10 (d, *J* = 1.4 Hz, 1H), 3.95 (d, *J* = 7.2 Hz, 2H), 3.77 (d, *J* = 8.9 Hz, 6H), 3.30 (d, *J* = 14.2 Hz, 1H), 2.81 (d, *J* = 14.2 Hz, 1H), 2.40 (dd, *J* = 8.9, 4.2 Hz, 1H), 2.32 – 2.23 (m, 1H), 2.07 (dd, *J* = 15.5, 5.6 Hz, 1H), 1.85 (dd, *J* = 11.8, 7.2 Hz, 2H), 1.67 (s, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.1, 169.8, 153.3, 151.0, 144.4, 132.3, 119.1, 116.6, 113.0, 111.5, 61.3, 60.8, 56.0, 55.8, 40.1, 37.5, 31.8, 19.4, 14.0; IR (neat):v_{max} (cm^{-1}) = 2957, 2833, 1750, 1720, 1630, 1495, 1218, 1047, 809. HRMS (EIMS) calcd. for $C_{19}H_{24}O_5$ $[M]^+$: 332.1624, found 332.1626;

Synthesis of Compound 7



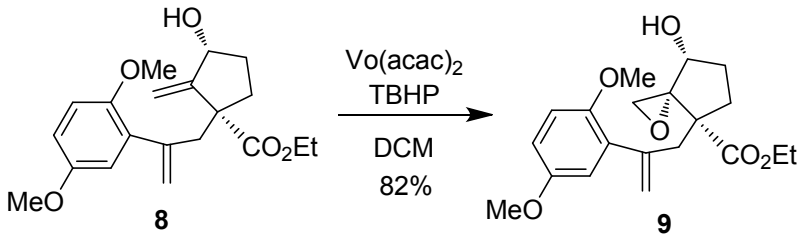
To a solution of methyltriphenylphosphonium bromide (25.21 g, 71.82 mmol, 6.0 equiv.) in THF (70 mL) at 0℃ was added anhydrous *t*-BuOK (7.64 g, 68.22 mmol , 5.7 equiv.) under Ar and stirred for 30 min at 0℃ and then for 1 h at room temperature. Then, the mixture was re-cooled to 0℃ and a solution of **6** (4.00 g, 11.97 mmol, 1.0 equiv.) in THF (40 mL) was added dropwise, the resulted mixture was stirred for another 3 h. The reaction was quenched by addition of cold H_2O (100 mL), and the mixture was extracted with ethyl acetate (3 × 80 mL), washed sequentially with H_2O (2 × 100 mL), brine (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 30/1) to afford **7** (3.19 g, 81% yield) as colorless oil. R_f= 0.4 (petroleum ether/EtOAc = 10/1); $[\alpha]_D^{25}$= +18.22 (c = 0.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 1.0 Hz, 2H), 6.65 (s, 1H), 5.14 (d, *J* = 16.1 Hz, 2H), 5.04 – 4.99 (m, 2H), 3.89 – 3.84 (m, 1H), 3.77 (d, *J* = 10.9 Hz, 6H), 3.70 – 3.64 (m, 1H), 3.32 (d, *J* = 14.2 Hz, 1H), 2.58 (d, *J* = 14.2 Hz, 1H), 2.34 – 2.25 (m, 3H), 1.68 – 1.58 (m, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 155.3, 153.3, 150.9, 145.9, 133.1, 117.8, 116.4, 112.6, 111.4, 107.8, 60.3, 56.1, 56.0, 55.7, 45.0, 34.4, 33.4, 23.9, 13.8. IR (neat):ν_{max} (cm^{-1}) = 2978, 2953, 2832, 1723, 1645, 1495, 1219, 1047, 806. HRMS (EIMS) calcd. for $C_{20}H_{26}O_4$ $[M]^+$: 330.1 831, found 330.1832;

Synthesis of Compound 8



To a solution of SeO_2 (2.69 g, 24.24 mmol, 5.0 equiv.) in DCM (50 mL) at 0℃ was added *t*-BuOOH (15.15 mL, 4 M in DCM, 60.60 mmol, 5.0 equiv.) and stirred for 30 min at 0℃, and a solution of **7** (4.00 g, 12.12 mmol, 1.0 equiv.) in DCM (35 mL) was added. After being warmed to room temperature, the mixture was stirred for 5 h. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ (100 mL), and the mixture was extracted with DCM (3 × 80 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 3/1) to afford **8** (2.89 g, 69% yield) as colorless oil. R_f = 0.3 (petroleum ether/EtOAc = 2/1); $[\alpha]_D^{25}$ = -20.98 (c = 0.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 1.5 Hz, 2H), 6.63 (s, 1H), 5.33 (dd, *J* = 42.4, 1.8 Hz, 2H), 5.12–5.05 (m, 2 H), 4.38 (s, 1H), 3.90 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.78 – 3.69 (m, 7H), 3.30 (d, *J* = 14. 1 Hz, 1H), 2.63 (d, *J* = 14.1 Hz, 1H), 2.34 (ddd, *J* = 12.9, 6.6, 4.1 Hz, 1H), 2.02 – 1.95 (m, 1H), 1.68 – 1.59 (m, 2H), 1.50 (ddd, *J* = 13.1, 10.3, 6.5 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 157.1, 153.3, 150.8, 145.3, 132.8, 118.3, 116.4, 112.7, 111.5, 75.2, 60.7, 56.0, 55.7, 54.5, 45.7, 34.0, 30.0, 13.8. IR (neat):ν_{max} (cm^{-1}) = 3436, 2940, 2833, 1723, 1580, 1496, 1218, 884, 807. HRMS (EIMS) calcd. for $C_{20}H_{26}O_5$ $[M]^+$: 346.1780, found 346.1774;

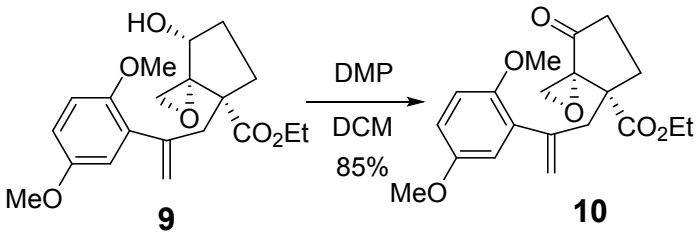
Synthesis of Compound 9



To a solution of **8** (3.40 g, 9.82 mmol, 1.0 equiv.) in DCM (45 mL) at 0℃ were added $VO(acac)_2$ (779 mg, 2.94 mmol, 0.3 equiv.) and TBHP (7.36 mL, 4 M in hexane, 29.46

mmol, 3.0 equiv.) and stirred for 30 min at 0℃. After being warmed to room temperature, the mixture was stirred for 4 h. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ (80 mL) and the mixture was extracted with DCM (3 × 60 mL). The combined organic layers were washed sequentially with saturated aqueous Na_2CO_3 (80 mL), brine (80 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 3/1) to afford **9** (2.91 g, 82% yield) as colorless oil. R_f = 0.3 (Petroleum ether/EtOAc = 2/1); $[\alpha]_D^{25}$ = -61.40 (c = 0.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 1.3 Hz, 2H), 6.61 (s, 1H), 5.08 (d, *J* = 9.7Hz, 2H), 4.14 – 4.04 (m, 1H), 3.93 – 3.85 (m, 1H), 3.77 – 3.69 (m, 7H), 3.21 (d, *J* = 14.2 Hz, 1H), 3.09 (d, *J* = 4.4 Hz, 1H), 2.77 (d, *J* = 4.4 Hz, 1H), 2.61 (d, *J* = 14.2 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.14 – 2.04 (m, 1H), 1.91 (d, *J* = 9.7 Hz, 1H), 1.67 – 1.58 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 153.3, 150.7, 144.3, 132.4, 118.4, 116.4, 112.8, 111.6, 70.0, 68.2, 60.6, 56.0, 55.7, 51.8, 47.3, 42.0, 32.7, 27.3, 13.9. IR (neat):ν_{max} (cm^{-1}) = 3474, 2939, 2833, 1727, 1580, 1492, 1216, 1069, 884, 807. HRMS (EIMS) calcd. for $C_{20}H_{26}O_6$ $[M]^+$: 362.1729, found 362.1730;

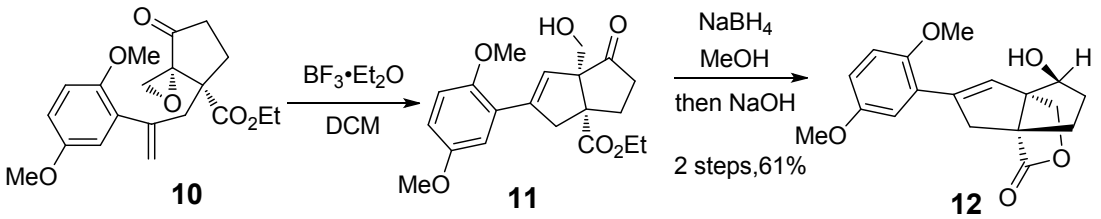
Synthesis of Compound 10



To a solution of **9** (2.10 g, 5.80 mmol, 1.0 equiv.) in DCM (45 mL) at 0℃ was added Dess-Martin reagent (4.91 g, 11.60 mmol, 2.0 equiv.) under Ar and stirred for 30 min at 0℃. After being warmed to room temperature, the mixture was stirred for 4 h. The

reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ (60 mL) and the mixture was extracted with DCM (3 × 50 mL). The combined organic layers were washed with brine (60 mL), and dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 6/1) to afford **10** (1.77 g, 85% yield) as colorless oil. R_f= 0.3 (petroleum ether/EtOAc = 3/1); $[\alpha]_D^{25}$ = +3.07 (c = 0.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 2H), 6.67 (s, 1H), 5.15 (d, *J* = 19.3 Hz, 2H), 3.94 – 3.88 (m, 1H), 3.82 – 3.74 (m, 7H), 3.14 (dd, *J* = 14.3, 10.3 Hz, 2H), 3.01 (d, *J* = 6.3 Hz, 1H), 2.76 (d, *J* = 14.3 Hz, 1H), 2.55 – 2.47 (m, 2H), 2.39 – 2.30 (m, 1H), 2.14 – 2.07 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 212.4, 170.9, 153.4, 150.7, 143.6, 132.0, 119.0, 116.4, 113.0, 111.6, 64.1, 61.1, 56.0, 55.7, 50.0, 40.1, 34.4, 26.4, 13.9. IR (neat):v_{max} (cm^{-1}) = 2938, 2833, 1752, 1727, 1580, 1492, 1217, 1045, 875, 805. HRMS (EIMS) calcd. for $C_{20}H_{24}O_6$ $[M]^+$: 360.1573, found 360.1582;

Synthesis of Compound 12

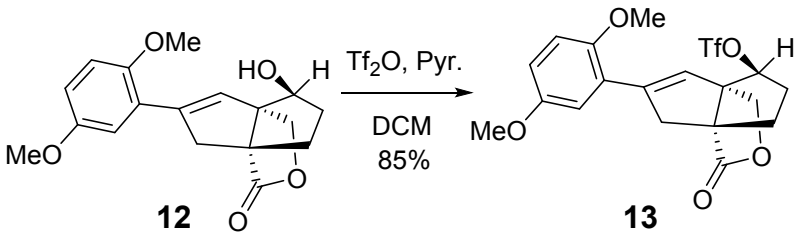


To a solution of **10** (2.60 g, 7.22 mmol, 1.0 equiv.) in DCM (27 mL) at 0℃ was added $BF_3{\cdot}Et_2O$ (1.78 mL, 14.44 mmol, 2.0 equiv.) under Ar, the mixture was stirred at 0℃ for 1 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (60 mL), and the mixture was extracted with DCM (3 × 50 mL). The combined organic layers were washed with brine (60 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product which was used in next step without further purification. R_f= 0.4 (Petroleum ether/EtOAc = 1/1);

To a solution of the crude **11** in MeOH (27 mL) at 0℃ was added $NaBH_4$ (301 mg, 7.94 mmol, 1.1 equiv.), the mixture was stirred at 0℃ for 10 min. To a solution were added NaOH (346 mg, 8.66 mmol, 1.2 equiv.), the mixture was stirred at 0℃ for 30 min. The

reaction was quenched by addition of saturated aqueous NH_4Cl (60 mL), and the mixture was extracted with ethyl acetate (3 × 50mL). The combined organic layers were washed with H_2O (2 × 60 mL), brine (60 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 3/2) to afford **12** (1.58 g, 61% yield) as colorless oil. R_f = 0.3 (Petroleum ether/EtOAc = 1/2); 99.96 % *ee*. $[\alpha]_D^{25}$ = -9.82 (c = 0.17, $CHCl_3$); HPLC analysis: Daicel Chiralpak AD-H, *iso*-propanol/hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time = 26.89 min (major) and 13.98 (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.80 (m, 3H), 6.30 (s, 1H), 4.36 (d, *J* = 9.6 Hz, 1H), 4.21 (s, 1H), 4.07 (d, *J* = 9.6 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.37 (dd, *J* = 17.1, 1.0 Hz, 1H), 2.98 (dd, *J* = 17.1, 1.4 Hz, 1H), 2.36 – 2.30 (m, 1H), 2.18 – 2.11 (m, 1H), 2.04 – 1.92 (m, 2H), 1.72 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ 182.6, 153.3, 152.1, 143.2, 126.6, 124.2, 115.0, 113.8, 112.0, 78.3, 76.0, 71.3, 58.8, 55.8, 47.1, 35.6, 35.5. IR (neat):ν_{max} (cm^{-1}) = 3445, 2938, 2833, 1747, 1580, 1497, 1216, 1145, 890. HRMS (EIMS) calcd. for $C_{18}H_{20}O_5$ $[M]^+$:316.1311, found 316.1302;

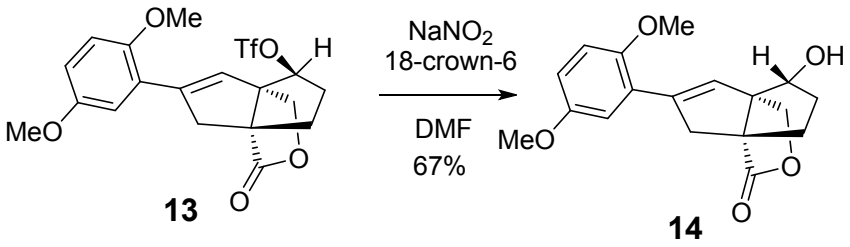
Synthesis of Compound 13



To a solution of **12** (272 mg, 0.860 mmol, 1.0 equiv.) in DCM (4 mL) at 0℃ were added pyridine (345 μL, 4.300 mmol, 5.0 equiv.) and Tf_2O (289 μL, 1.720 mmol, 2.0 equiv.) under Ar, the mixture was stirred at 0℃ for 15min. The reaction was quenched by addition of H_2O (20 mL) and the mixture was extracted with DCM (3 × 15 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 6/1) to afford **13** (327 mg, 85% yield) as white solid (mp: 129-131℃). R_f = 0.4 (Petroleum ether/EtOAc = 4/1); $[\alpha]_D^{25}$ = -46.58

(c = 0.23, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.81 (m, 3H), 6.29 (s, 1H), 5.26 (s, 1H), 4.41 (d, *J* = 10.0 Hz, 1H), 4.17 (d, *J* = 10.0 Hz, 1H), 3.79 (d, *J* = 16.9 Hz, 6H), 3.51 (dd, *J* = 17.3, 1.7 Hz, 1H), 2.97 (dd, *J* = 17.3, 1.7 Hz, 1H), 2.47 – 2.43 (m, 1H), 2.34 – 2.26 (m, 1H), 2.20 – 2.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.8, 153.3, 152.2, 142.7, 125.6, 123.9, 115.0, 114.3, 112.2, 94.4, 75.5, 69.8, 59.0, 55.8, 55.7, 46.3, 34.7, 34.0. IR (neat):v_{max} (cm^{-1}) = 2947, 2838, 1778, 1580, 1503, 1409, 1209, 1155, 882, 821. HRMS (EIMS) calcd. for $C_{19}H_{19}F_3O_7S$ $[M]^+$: 448.0804, found 448.0807;

Synthesis of Compound 14

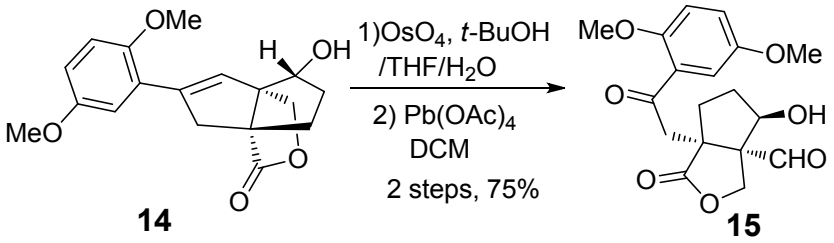


To a solution of **13** (327 mg, 0.729 mmol, 1.0 equiv.) in DMF (4 mL) at 0℃ were added 18-crown-6 (192 mg, 0.729 mmol, 1.0 equiv.) and $NaNO_2$ (309 mg, 3.645 mmol, 5.0 equiv.). After being warmed to room temperature, the mixture was stirred for 5 h. The reaction was quenched by addition of H_2O (20 mL) and the mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with H_2O (2 × 20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 3/2) to afford **14** (154 mg, 67% yield) as pale yellow oil.

R_f = 0.4 (petroleum ether/EtOAc = 2/3); $[\alpha]_D^{25}$ = -81.48 (c = 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.82 – 6.78 (m, 3H), 6.44 (s, 1H), 4.87 (d, *J* = 9.5 Hz, 1H), 4.24 (t, *J* = 6.0 Hz, 1H), 4.13 (d, *J* = 9.5 Hz, 1H), 3.79 (d, *J* = 18.8 Hz, 6H), 3.38 (dd, *J* = 17.1, 1.7 Hz, 1H), 2.94 (dd, *J* = 17.1, 1.4 Hz, 1H), 2.45 – 2.39 (m, 1H), 2.11 – 2.03 (m, 2H), 1.88 – 1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.8, 153.3, 152.1, 139.4, 131.3, 124.5, 115.1, 113.4, 112.0, 78.6, 71.8, 68.7, 58.7, 55.8, 46.8, 35.3, 34.7. IR (neat):v_{max} (cm^{-1}) = 3436, 2935, 2833, 1738, 1579, 1499, 1216, 1151, 878. HRMS (EIMS) calcd.

for $C_{18}H_{20}O_5$ $[M]^+$: 316.1311, found 316.1319;

Synthesis of Compound 15

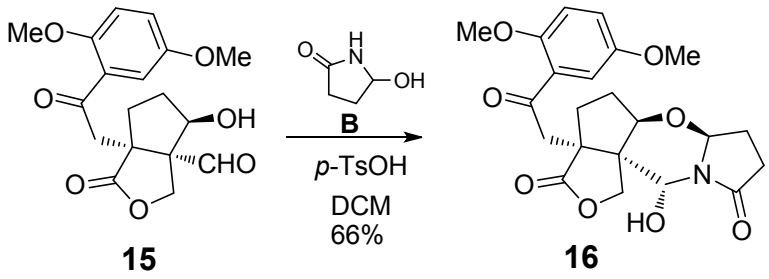


To a solution of **14** (154 mg, 0.487 mmol, 1.0 equiv.) in *t*-BuOH (2.5 mL) and THF (1 mL) at room temperature were added NMO (50% in H_2O, 113 mg , 0.974 mmol, 2.0 equiv.) and OsO_4 (2% in H_2O, 607 μL, 0.048 mmol, 0.1 equiv.), the mixture was stirred at room temperature for 13 h. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ (15 mL), and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product which was used in next step without further purification.

To a solution of the product made above in DCM (3.5 mL) at 0℃ was added Pb(O Ac)$_4$ (215 mg, 0.487 mmol, 1.0 equiv.) under Ar, the mixture was stirred at 0℃ for 10 min. The reaction was quenched by addition of H_2O (15 mL) and the mixture was extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 1/1) to afford **15** (127 mg, 75% yield) as colorless oil. R_f= 0.4 (petroleum ether/EtOAc = 1/2); 99.2 % *ee*. $[\alpha]_D^{25}$ = +156.66 (c = 0.1, $CHCl_3$); HPLC analysis: Daicel Chiralpak OJ-H, *iso*-propanol/hexane = 20/80, flow rate = 1.0 mL/min, λ =254 nm, retention time = 42.16 min (major) and 29.15 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.29 (d, *J* = 3.2 Hz, 1H), 7.06 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.89 (d, *J* = 9.1 Hz, 1H), 4.99 (s, 2H), 4.69 (dd, *J* = 10.1, 4.9 Hz, 1H), 3.88 (s, 3H), 3.75 (d, *J* = 13.3 Hz, 4H), 3.43 (d, *J* = 19.7 Hz, 1H), 2.16 – 2.12 (m, 2H), 2.06 – 2.00 (m, 1H), 1.84 – 1.76 (m, 1H), 1.70

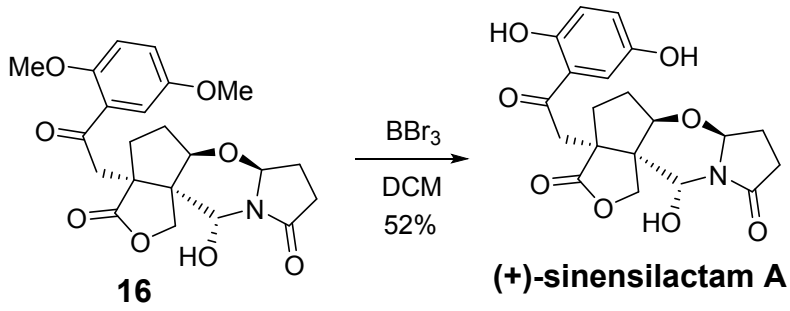
– 1.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.0, 199.0, 181.1, 154.3, 153.4, 125.3, 122.4, 113.3, 113.2, 66.8, 63.1, 56.0, 55.8, 55.0, 49.5, 34.6, 30.8. IR (neat):ν_{max} (cm^{-1}) = 3435, 2942, 2840, 1745, 1715, 1653, 1578, 1493, 1279, 1225, 1167, 1047, 883, 817. HRMS (EIMS) calcd. for $C_{18}H_{20}O_7$ $[M]^+$: 348.1209, found 348.1205;

Synthesis of Compound 16



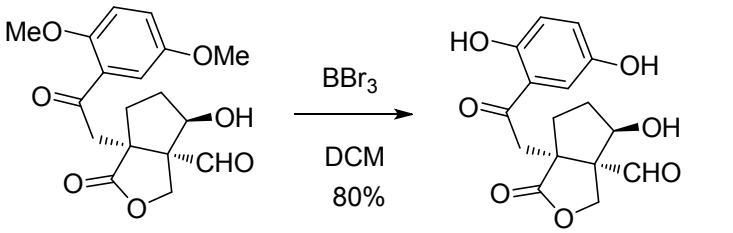
To a solution of **15** (124 mg, 0.356 mmol, 1.0 equiv.) and γ-lactam-hemiaminal **B** (180 mg, 1.780 mmol, 5.0 equiv.) in DCM (11 mL) was added *p*-TsOH (6 mg, 0.036 mmol, 0.1 equiv.), and the resultant mixture was stirred at 40℃ for 5 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (10 mL), and the mixture was extracted with DCM (3 × 7 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatogramphy (Petroleum ether/EtOAc = 1/2) to afford **16** (101 mg, 66% yield) as white solid (mp: 236-238℃). R_f = 0.4 (petroleum ether/EtOAc = 1/2); $[\alpha]_D^{25}$ = +18.72 (c = 0.1, DMSO); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.26 (d, *J* = 2.8 Hz, 1H), 7.20 – 7.14 (m, 2H), 6.44 (d, *J* = 3.3 Hz, 1H), 5.45 (d, *J* = 3.2 Hz, 1H), 5.25 (dd, *J* = 6.2, 3.3 Hz, 1H), 4.31 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.23 (d, *J* = 10.1 Hz, 1H), 3.87 (s, 3H), 3.79 – 3.74 (m, 5H), 3.38 (d, *J* = 19.4 Hz, 1H), 2.44 – 2.36 (m, 1H), 2.31 – 2.22 (m, 2H), 1.90 – 1.82 (m, 2H), 1.79 – 1.71 (m, 2H), 1.53 (dd, *J* = 11.7, 7.7 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.1, 182.0, 173.0, 154.1, 153.3, 126.1, 121.2, 114.8, 114.1, 84.9, 77.5, 76.4, 69.5, 56.8, 56.0, 51.8, 49.2, 49.0, 34.4, 29.7, 25.4, 23.9. IR (neat):ν_{max} (cm^{-1}) = 3425, 2954, 1766, 1668, 1657, 1497, 1279, 1199, 1165, 1051, 885, 820. HRMS (EIMS) calcd. for $C_{22}H_{25}NO_8$ $[M]^+$: 431.1580, found 431.1587;

Synthesis of Compound sinensilactam A



To a solution of **16** (28 mg, 0.064 mmol, 1.0 equiv.) in DCM (2 mL) at 0℃ was added BBr_3 (1M in DCM, 384 μL, 0.384 mmol) under Ar, the mixture was stirred at 0℃ for 5h. The reaction was quenched by addition of cold H_2O (7 mL) and the mixture was extracted with ethyl acetate (3 × 5mL). The combined organic layers were washed with brine (7 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography ($MeOH/CHCl_3$ = 1/10) to afford **(+)-sinensilactam A** (13 mg, 52% yield) as pale yellow solid. R_f = 0.4 ($MeOH/CHCl_3$ = 1/9); $[\alpha]_D^{25}$ = +50.3 (c = 0.07, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.81 (s, 1H), 9.21 (s, 1H), 7.22 (d, *J* = 2.9 Hz, 1H), 6.98 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 5.45 (s, 1H), 5.25 (dd, *J* = 6.2, 3.4 Hz, 1H), 4.32 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.24 (d, *J* = 10.1 Hz, 1H), 3.85 (d, *J* = 19.2 Hz, 1H), 3.77 (d, *J* = 10.1 Hz, 1H), 3.41 (d, *J* = 19.1 Hz, 1H), 2.39 (dd, *J* = 21.4, 11.2 Hz, 1H), 2.32 – 2.23 (m, 2H), 1.93 – 1.80 (m, 2H), 1.73 (ddd, *J* = 12.0, 8.6, 4.4 Hz, 1H), 1.62 – 1.47 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 201.6, 181.4, 172.5, 153.3, 149.5, 124.3, 120.0, 118.5, 114.6, 84.4, 77.0, 75.9, 69.2, 51.3, 48.2, 45.4, 33.9, 29.3, 25.0, 23.5. IR (neat):ν_{max} (cm^{-1}) = 3371, 3331, 2920, 1737, 1667, 1618, 1489, 1281, 1197, 1172, 1054, 881, 815.HRMS (EIMS) calcd. for $C_{20}H_{21}NO_8$ $[M]^+$: 403.1267, found 403.1272;

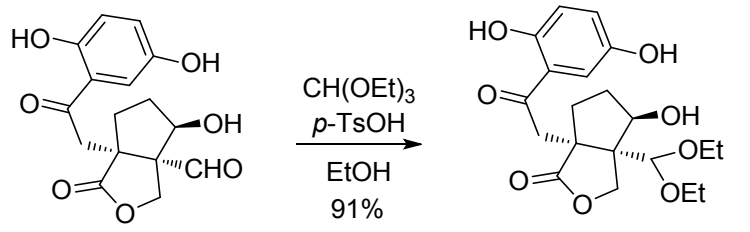
Synthesis of Compound lingzhilactone B



15 **(+)-lingzhilactone B**

To a solution of **15** (30 mg, 0.086 mmol, 1.0 equiv.) in DCM (3 mL) at 0℃ was added BBr_3 (1M in DCM, 430 μL, 0.430 mmol, 5.0 equiv.) under Ar, the mixture was stirred at 0℃ for 5h. The reaction was quenched by addition of cold H_2O (7 mL) and the mixture was extracted with ethyl acetate (3 × 5mL). The combined organic layers were washed with brine (7 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (petroleum ether/EtOAc = 1/2) to afford **lingzshilactone B** (22 mg, 80% yield) as pale yellow solid. R_f = 0.4 (petroleum ether/EtOAc = 1/2); $[\alpha]_D^{25}$ = +154.75 (c = 0.08, Acetone); ^{1}H NMR (400 MHz, acetone-d6) δ 10.99 (s, 1H), 9.68 (s, 1H), 8.22 (s, 1H), 7.33 (d, *J* = 2.9 Hz, 1H), 7.13 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.81 (t, *J* = 8.2 Hz, 1H), 4.96 – 4.88 (q, 2H), 4.75 (d, *J* = 4.8 Hz, 1H), 4.66 (dd, *J* = 10.9, 5.4 Hz, 1H), 3.78 (s, 2H), 2.06 (s, 1H), 2.01 (dd, *J* = 16.8, 11.3 Hz, 2H), 1.65 – 1.56 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6): δ 205.2, 203.2, 181.2, 156.4, 150.4, 126.8, 119.7, 119.4, 115.4, 77.9, 66.9, 63.7, 54.4, 44.5, 35.5, 32.0. IR (neat):ν_{max} (cm^{-1}) = 3375, 2922, 1741, 1640, 1621, 1485, 1390, 1277, 1170, 1026, 874, 808. HRMS (EIMS) calcd. for $C_{16}H_{16}O_7$ $[M]^+$: 320.0896, found 320.0901;

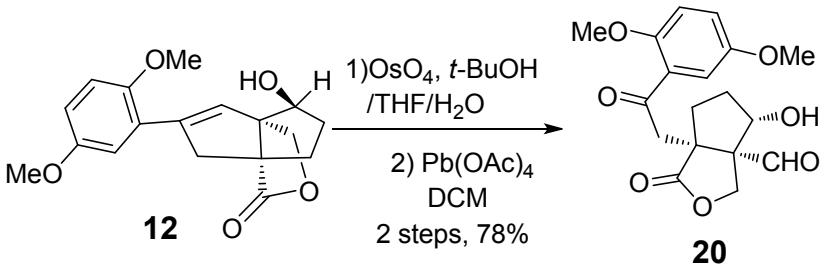
Synthesis of Compound lingzhilactone C



(+)-lingzhilactone B **(+)-lingzhilactone C**

To a solution of **lingzhilactone B** (24 mg, 0.08 mmol, 1.0 equiv.) in EtOH (4 mL) at room temperature were added $CH(OEt)_3$ (31.26 μL, 0.19 mmol, 2.5 equiv.) and *p*-Ts OH (1.3 mg , 0.008 mmol, 0.1 equiv.) under Ar, the mixture was stirred at 35℃ for 5 h. The reaction was quenched by addition of cold H_2O (7 mL) and the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with brine (7 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 1/2) to afford **lingzhilactone C** (26 mg, 91% yield) as yellow oil. R_f = 0.4 (Petroleum ether/EtOAc = 1/1); $[\alpha]_D^{20}$ = +114.27 (c = 0.06, DMSO); ^{1}H NMR (400 MHz, CD_3OD) δ 7.22 (d, J = 2. 9 Hz, 1H), 7.02 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.80 (d, *J* = 8.9 Hz, 1H), 4.81 (d, *J* = 8.8 Hz, 1H), 4.59 (dd, *J* = 10.7, 6.7 Hz, 1H), 4.41 (s, 1H), 4.27 (d, *J* = 8.8 Hz, 1H), 3. 99 (d, *J* = 18.9 Hz, 1H), 3.77 – 3.73 (m, 1H), 3.65 (dq, *J* = 14.1, 7.0 Hz, 1H), 3.51 (dq, *J* = 9.2, 7.0 Hz, 1H), 3.40 (d, *J* = 18.9 Hz, 1H), 3.24 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.98 (ddd, *J* = 24.2, 12.4, 6.3 Hz, 2H), 1.77 (td, *J* = 13.1, 6.0 Hz, 1H), 1.35 (ddd, *J* = 12.9, 11.8, 6.3 Hz, 1H), 1.14 (t, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, CD_3O D): *δ* 203.6, 184.1, 155.0, 149.4, 124.8, 118.9, 118.5, 113.8, 105.9, 74. 4, 68.1, 67.1, 65.2, 56.7, 52.8, 43.7, 34.8, 30.6, 14.5, 13.9. IR (neat): ν_{max} (cm^{-1}) = 3439, 2976, 1756, 1635, 1616, 1482, 1376, 1279, 1165, 1053, 870, 807. HRMS (EIMS) calcd. for $C_{20}H_{26}O_8$ $[M]^+$: 394.1628, found 394.1627.

Synthesis of Compound **20**

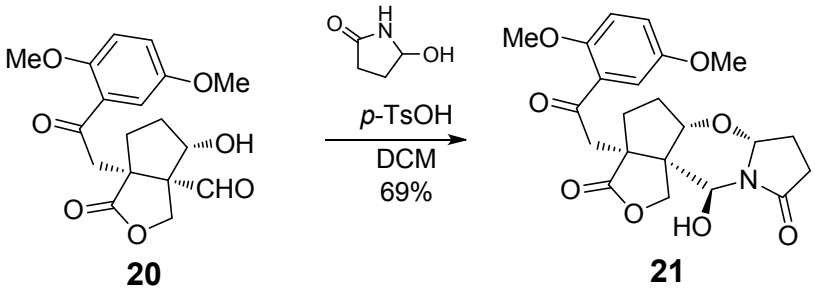


To a solution of **12** (120 mg, 0.379 mmol, 1.0 equiv.) in *t*-BuOH (2 mL) and THF (0.8 mL) at room temperature were added NMO (50% in H_2O, 88 mg, 0.758 mmol, 2.0 equiv.) and OsO_4 (2% in H_2O, 460 μL, 0.037 mmol, 0.1 equiv.), the mixture was stirred

at room temperature for 12 h. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ (10 mL), and the mixture was extracted with ethyl acetate (3 × 7 mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product which was used in next step without further purification.

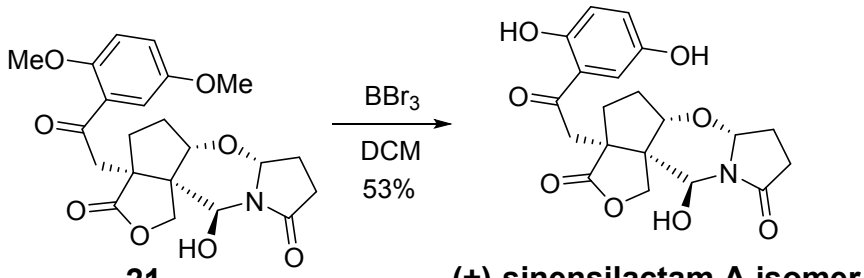
To a solution of the product made above in DCM (2.4 mL) at 0℃ was added Pb(OA c)$_4$ (167 mg, 0.379 mmol, 1.0 equiv.) under Ar, the mixture was stirred at 0℃ for 10 min. The reaction was quenched by addition of H_2O (10 mL) and the mixture was extracted with DCM (3 × 7 mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 1/1) to afford **20** (102 mg, 78% yield) as white solid (mp: 60-62℃). R_f = 0.5 (petroleum ether/EtOAc = 1/2); 99.9% *ee*. $[\alpha]_D^{25}$ = +142.18 (c = 0.31, $CHCl_3$); HPLC analysis: Daicel Chiralpak OJ-H, *iso*-propanol/hexane = 20/80, flow rate =1.0 mL/min, λ = 254 nm, retention time = 44.39 min (major) and 32.89 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.28 (t, *J* = 6.6 Hz, 1H), 7.07 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.91 (d, *J* = 9.1 Hz, 1H), 5.07 (d, *J* = 9.9 Hz, 1H), 4.39 (s, 1H), 4.01 (d, *J* = 10.0 Hz, 1H), 3.96 (d, *J* = 19.9 Hz, 1H), 3.90 (s, 3H), 3.81 – 3.74 (m, 4H), 3.12 (d, *J* = 3.1 Hz, 1H), 2.50 – 2.42 (m, 1H), 2.24 (dd, *J* = 13.0, 6.8 Hz, 1H), 1.92 (dd, *J* = 13.7, 6.4 Hz, 1H), 1.79 – 1.70 (m, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ 203.2, 199.3, 181.1, 154.4, 153.4, 125.3, 122.5, 113.4, 113.2, 83.1, 71.2, 62.6, 56.0, 55.8, 54.4, 49.3, 37.3, 32.4. IR (neat):ν_{max} (cm^{-1}) = 3456, 2939, 2838, 1761, 1716, 1609, 1581, 1494, 1277, 1223, 1158, 1017, 820. HRMS (EIMS) calcd. for $C_{18}H_{20}O_7$ $[M]^+$: 348.1209, found 348.1218;

Synthesis of Compound 21



To a solution of **20** (60 mg, 0.172 mmol, 1.0 equiv.) and γ-lactam-hemiaminal (52 mg, 0.516 mmol, 3.0 equiv.) in DCM (1.5 mL) was added *p*- (6 mg, 0.034 mmol, 0.2 equiv.), and the resultant mixture was stirred at 28℃ for 9 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (7 mL), and the mixture was extracted with DCM (3 × 5mL). The combined organic layers were washed with brine (7 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 1/2) to afford **21** (51 mg, 69% yield) as white solid (mp: 220-222℃). R_f = 0.3 (petroleum ether/EtOAc = 1/2); $[\alpha]_D^{25}$= +94.32 (c = 0.133, DMSO); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 3.3 Hz, 1H), 7.05 (dd, *J* = 9.0, 3.3 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 5.3 6 (d, *J* = 4.1 Hz, 1H), 5.21 (dd, *J* = 6.6, 4.2 Hz, 1H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.26 (d, *J* = 3.8 Hz, 2H), 3.84 (s, 3H), 3.81 – 3.78 (m, 4H), 3.71 (d, *J* = 19.9 Hz, 1H), 3.28 (d, *J* =19.9 Hz, 1H), 2.37 (ddd, *J* = 7.6, 5.1, 2.7 Hz, 2H), 2.31 (ddd, *J* = 8.3, 6.1, 1.7 Hz, 1 H), 2.22 (td, *J* = 13.2, 5.9 Hz, 1H), 2.07 (dd, *J* = 12.5, 6.4 Hz, 1H), 1.83 – 1.77 (m, 2 H), 1.61 (ddd, *J* = 13.7, 6.8, 3.7 Hz, 1H).^{13}C NMR (125 MHz, $CDCl_3$): δ 199.7, 182.4, 172.3, 154.4, 153.4, 126.4, 121.8, 114.0, 113.7, 84.1, 80.4, 72.2, 71.5, 56.3, 56.0, 52.6, 52.3, 48.7, 38.7, 29.9, 29.2, 24.8. IR (neat):ν_{max} (cm^{-1}) = 3296, 2954, 1757, 1685, 1654, 1492, 1300, 1190, 1176, 1030, 869, 816. HRMS (EIMS) calcd. for $C_{22}H_{25}NO_8$ $[M]^+$: 4 31.1580, found 431.1576;

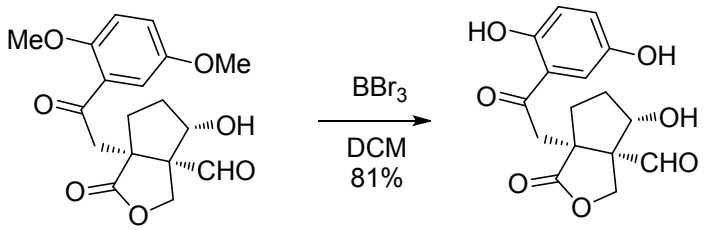
Synthesis of Compound sinensilactam A isomer



21 **(+)-sinensilactam A isomer**

To a solution of **21** (32 mg, 0.074 mmol, 1.0 equiv.) in DCM (2.4 mL) at 0℃ was added BBr_3 (1M in DCM, 444 μL, 0.444 mmol, 6.0 equiv.) under Ar, the mixture was stirred at 0℃ for 5h. The reaction was quenched by addition of cold H_2O (7 mL) and the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with brine (7 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (MeOH/ $CHCl_3$ = 1/10) to afford **sinesilactam A isomer** (16 mg, 53% yield) as pale yellow solid. R_f = 0.4 (MeOH/$CHCl_3$ = 1/9); $[\alpha]_D^{25}$= +45.04 (c = 0.1, DMSO); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.63 (s, 1H), 9.20 (s, 1H), 7.16 (d, *J* = 2.9 Hz, 1H), 6.99 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.81 (d, *J* = 8.8Hz, 1H), 6.61 (s, 1H), 5.29 (s, 1H), 5.27 – 5.24 (m, 1H), 4.53 (d, *J* = 10.5 Hz, 1H), 4.33(s, 1H), 3.94 (d, *J* = 10.5 Hz, 1H), 3.74 (d, *J* = 19.9 Hz, 1H), 3.24 (d, *J* = 19.9 Hz, 1H), 2.38 – 2.16 (m, 4H), 1.87 (dd, *J* = 12.4, 6.2 Hz, 1H), 1.72 (ddd, *J* = 19.1, 13.1, 7.6 Hz, 2H), 1.56 – 1.48 (m, 1H).^{13}C NMR (100 MHz, DMSO-d_6): δ 202.8, 182.0, 171.4, 153.7, 149.8, 124.8, 120.8, 118.8, 115.2, 83.6, 80.1, 72.0, 70.6, 52.2, 51.9, 45.4, 38.8, 29.5,29.0, 24.6. IR (neat):ν_{max} (cm^{-1}) = 3415, 3194, 2917, 1730, 1668, 1622, 1486, 1282, 1179, 1170, 1059, 877, 800. HRMS (EIMS) calcd. for $C_{20}H_{21}NO_8$ $[M]^+$: 403.1267, found 403.1269;

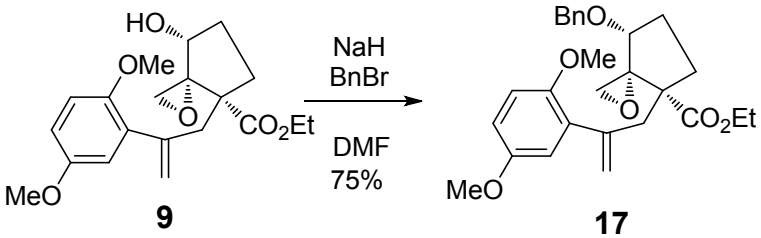
Synthesis of (+)-epi-lingzhilactone B



20 **(+)-epi-lingzhilactone B**

To a solution of **20** (29 mg, 0.083 mmol, 1.0 equiv.) in DCM (3 mL) at 0℃ was added BBr_3 (1M in DCM, 415 μL, 0.415 mmol, 5.0 equiv.) under Ar, the mixture was stirred at 0℃ for 5h. The reaction was quenched by addition of cold H_2O (7 mL) and the mixture was extracted with ethyl acetate (3 × 5mL). The combined organic layers were washed with brine (7 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 1/2) to afford **(+)-epi-lingzhilactone B** (21 mg, 81% yield) as pale yellow solid. R_f = 0.4 (petroleum ether/EtOAc = 1/2); $[\alpha]_D^{25}$ = +85.27 (c = 0.14, DMSO); ^{1}H NMR (400 MHz, acetone-d6) δ 10.99 (s, 1H), 9.74 (s, 1H), 8.21 (s, 1H), 7.43 (d, *J* = 2.9 Hz, 1H), 7.13 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.82 (d, *J* = 8.9 Hz, 1H), 4.94 (d, *J* = 9.7 Hz, 1H), 4.57 (d, *J* = 3.9 Hz, 1H), 4.51 (s, 1H), 4.15 (d, *J* = 19.4 Hz, 1H), 4.10 (d, *J* = 9.7 Hz, 1H), 4.00 (d, *J* = 19.4 Hz, 1H), 2.60 (dd, *J* = 11.8, 7.5 Hz, 2H), 2.18 (dd, *J* = 13.0, 6.9 Hz, 1H), 1.92 (dd, *J* = 13.5, 6.6 Hz, 1H), 1.85 – 1.77 (m, 1H). ^{13}C NMR (100 MHz, acetone-d6): δ 205.6, 202.2, 181.1, 156.1, 150.1, 126.3, 119.3, 115.3, 84.6, 70.9, 62.7, 53.0, 44.2, 38.1, 32.9. IR (neat):V_{max} (cm^{-1}) = 3356, 3346, 2920, 1758, 1710, 1619, 1485, 1388, 1284, 1159, 1042, 886,824. HRMS (EIMS) calcd. for $C_{16}H_{16}O_7$ $[M]^+$: 320.0896, found 320.0900;

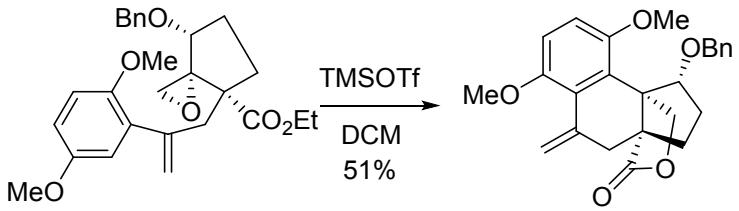
Synthesis of Compound 17



9 **17**

To a solution of **9** (1.00 g, 2.762 mmol, 1.0 equiv.) in DMF (10 mL) at 0℃ was added NaH (60%, 132 mg, 3.314 mmol, 1.2 equiv.) and BnBr (655 μL, 5.524 mmol, 2.0 equiv.) under Ar, the mixture was stirred at 0℃ for 1h. The reaction was quenched by addition of saturated aqueous NH_4Cl (30 mL) and the mixture was extracted with ethyl acetate (3 × 20mL). The combined organic layers were washed with H_2O (2 × 30 mL), and brine (30 mL), and dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 6/1) to afford **17** (936 mg, 75% yield) as colorless oil. R_f = 0.4 (petroleum ether/EtOAc = 5/1); 99.4% *ee*. $[\alpha]_D^{25}$ = -43.59 (c = 0.23, $CHCl_3$); HPLC analysis: Daicel Chiralpak AD-H, *iso*-propanol/hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time = 17.97 min (major) and 19.39 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 5H), 6.73 (s, 2H), 6.61 (s, 1H), 5.06 (d, *J* = 9.5 Hz, 2H), 4.55 (q, *J* = 12.3 Hz, 2H), 3.92 – 3.83 (m, 2H), 3.79 – 3.71 (m, 7H), 3.13 (d, *J* = 14.1 Hz, 1H), 2.96 (d, *J* = 5.0 Hz, 1H), 2.71 (d, *J* = 4.9 Hz, 1H), 2.55 – 2.46 (m, 2H), 2.04 – 1.97 (m, 1H), 1.90 – 1.80 (m, 1H), 1.56 – 1.49 (m, 1H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 153.3, 150.7, 144.6, 138.4, 132.6, 128.3, 127.6, 127.5, 118.2, 116.4, 112.8, 111.6, 71.6, 67.5, 60.6, 56.1, 55.7, 51.7, 46.4, 42.0, 28.7, 27.6, 14.0. IR (neat):ν_{max} (cm^{-1}) = 2940, 2833, 1729, 1581, 1496, 1218, 1046, 886, 808. HRMS (EIMS) calcd. for $C_{27}H_{32}O_6$ $[M]^+$: 452.2199, found 452.2195;

Synthesis of Compound 18

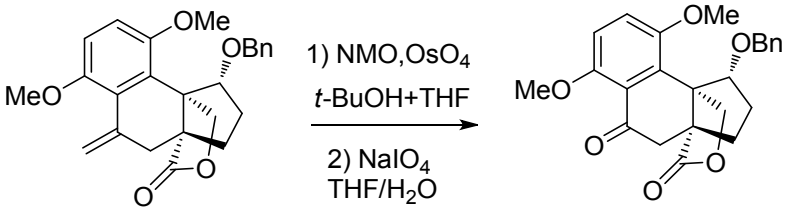


17 **18**

To a solution of **17** (100 mg, 0.221 mmol, 1.0 equiv.) in anhydrous DCM (1 mL) at 0℃ was added TMSOTf (100 μL, 0.552 mmol, 2.5 equiv.) under Ar, the mixture was stirred at 0℃ for 1h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (10 mL), and the mixture was extracted with DCM (3 × 7 mL). The combined organic layers

were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 6/1) to afford **18** (45 mg, 51% yield) as colorless oil. R_f= 0.4 (Petroleum ether/EtOAc = 5/1); $[\alpha]_D^{25}$ = -23.04 (c = 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 4H), 7.29 (dd, *J* = 8.3, 4.1 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.69 (d, *J* = 9.0 Hz, 1H), 5.92 (d, *J* = 1.1 Hz, 1H), 5.51 (s, 1H), 5.22 (d, *J* = 9.6 Hz, 1H), 4.69 (d, *J* = 12.4 Hz, 1H), 4.43 (d, *J* = 12.5 Hz, 1H), 4.09 (d, *J* = 9.6 Hz, 1H), 3.99 (d, *J* = 1.6 Hz, 1H), 3.79 (s, 3H), 3.58 (s, 3H), 2.51 (dd, *J* = 32.7, 12.4 Hz, 2H), 2.35 (td, *J* = 12.5, 7.6 Hz, 1H), 1.89 (ddd, *J* = 21.0, 13.3, 8.2 Hz, 2H), 1.25 – 1.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.2, 151.1, 150.7, 138.6, 134.1, 128.3, 127.4, 127.3,127.0, 126.5, 119.6, 110.6, 109.9, 85.8, 72.4, 70.3, 57.1, 56.0, 55.2, 52.2, 40.4, 32.0, 30.1. IR (neat):vmax (cm^{-1}) = 2926, 2851, 1760, 1631, 1496, 1475, 1261, 1062, 888, 802. HRMS (EIMS) calcd. for $C_{25}H_{26}O_5$ $[M]^+$: 406.1780, found 406.1773;

Synthesis of Compound 19

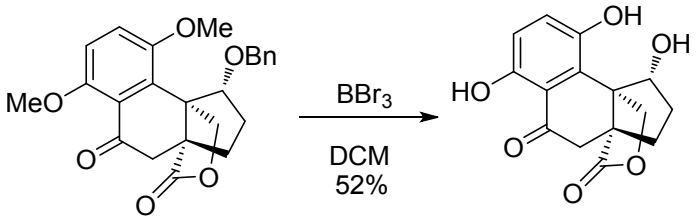


To a solution of **18** (71 mg, 0.174 mmol, 1.0 equiv.) in *t*-BuOH (1 mL) and THF (0.4 mL) at room temperature were added NMO (50% in H_2O, 40 mg, 0.348 mmol, 2.0 equiv.) and OsO_4 (2% in H_2O, 212 μL, 0.017 mmol, 0.1 equiv.), the mixture was stirred at room temperature for 7 h. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ (10 mL), and the mixture was extracted with ethyl acetate (3 × 7 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude was used in next step without further purification.

To a solution of the crude in THF (1.2 mL) and H_2O (0.6 mL) at room temperature was

added $NaIO_4$ (93 mg, 0.435 mmol, 2.5 equiv.), the mixture was stirred at room temperature for 3h. The reaction was quenched by addition of H_2O (10 mL) and the mixture was extracted with ethyl acetate (3 × 7mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4 and concentrated under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 3/2) to afford **19** (52 mg, 74% yield) as colorless oil. R_f= 0.4 (Petroleum ether/EtOAc = 1/1); 99.6% *ee*. $[\alpha]_D^{25}$ = -212.47 (c = 0.23, $CHCl_3$); HPLC analysis: Daicel Chiralpak AD-H, *iso*-propanol/hexane = 5/95, flow rate = 1.0 mL/min, λ = 254 nm, retention time = 19.46 min (major) and 30.46 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 7.00 (d, *J* = 9.1 Hz, 1H), 6.87 (d, *J* = 9.1 Hz, 1H), 5.25 (d, *J* = 9.7 Hz, 1H), 4.71 (d, *J* = 12.5 Hz, 1H), 4.42 (d, *J* = 12.5 Hz, 1H), 4.23 (d, *J* = 9.7 Hz, 1H), 4.08 (d, *J* = 1.9 Hz, 1H), 3.83 (s, 3H), 3.60 (s, 3H), 2.82 (dd, *J* = 34.1, 12.6 Hz, 2H), 2.55 – 2.47 (m, 1H), 1.92 (dd, *J* = 13.7, 8.5 Hz, 2H), 1.40 – 1.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 179.9, 152.0, 150.1, 138.1, 131.3, 128.4, 127.5, 123.3, 116.6, 111.9, 85.3, 71.3, 70.5, 56.5, 56.3, 55.5, 52.5, 44.8, 31.9, 29.4. IR (neat):vmax (cm^{-1}) = 2959, 2865, 1769, 1698, 1478, 1465, 1272, 1012, 870, 821. HRMS (EIMS) calcd. for $C_{24}H_{24}O_6$ $[M]^+$: 408.1573, found 408.1574;

Synthesis of Compound (-)-lingzhiol



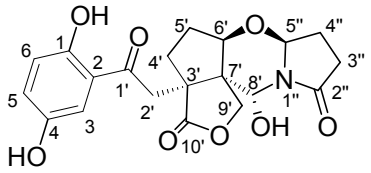
19 **(-)-lingzhiol**

The mixture of **19** (52 mg, 0.127 mmol, 1.0 equiv.) and BBr_3 (1M in DCM, 1.27 mL, 1.2 70 mmol, 10.0 equiv.) under Ar was stirred at 0℃ for 30 min, and then for 4 h at room temperature. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (7 mL) and the mixture was extracted with DCM (3 × 5mL). The combined organic layers were washed with brine (7 mL), dried over Na_2SO_4 and concentrated

under reduced pressure to afford crude product. It was purified by flash chromatography (Petroleum ether/EtOAc = 1/1) to afford **(-)-lingzhiol** (19 mg, 52% yield) as pale yellow solid. R_f = 0.2 (Petroleum ether/EtOAc = 1/1); $[\alpha]_D^{25}$ = -60.7 (c = 0.12, MeOH); ^{1}H NMR (400 MHz, acetone-d6) δ 11.58 (s, 1H), 7.23 (d, *J* = 8.9 Hz, 1H), 6.77 (d, *J* = 8.9 Hz, 1H), 5.22 (d, *J* = 9.6 Hz, 1H), 4.64 (t, *J* = 4.6 Hz, 1H), 4.46 (d, *J* = 9.6 Hz, 1H), 3.10 (d, *J* = 16.0 Hz, 1H), 2.79 (d, *J* = 16.0 Hz, 1H), 2.49 – 2.42 (m, 1H), 1.87 – 1.67 (m, 3H). ^{13}C NMR (100 MHz, acetone-d6): δ 202.3, 180.1, 156.3, 148.0, 129.1, 127.6, 117.9, 116.4, 80.7, 70.9, 56.1, 52.5, 42.3, 33.8, 33.3. IR (neat):vm ax (cm^{-1}) = 3404, 3212, 2979, 1722, 1642, 1463, 1176, 1016, 887, 803. HRMS (EIMS) calcd. for $C_{15}H_{14}O_6$ $[M]^+$: 290.0790, found 290.0789;

III Comparison of the Spectra of Natural and Synthetic Compounds

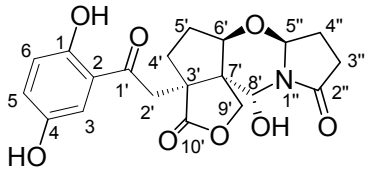
Table S1. Comparison of ^{1}H NMR data for (+)-**sinensilactam A** in DMSO-d_6



(+)-sinensilactam A

	Natural δ[ppm, mult, *J*(Hz)] 400 MHz	Synthetic δ[ppm, mult, *J*(Hz)] 400 MHz	**Err** (Natural-Synthetic) Δδ(ppm)
3	7.22(d, 3.0)	7.22(d, 2.9)	
5	6.99(dd, 8.9, 3.0)	6.98(dd, 8.8, 2.9)	0.01
6	6.83(d, 8.9)	6.83(d, 8.8)	-
2’	a 3.85(d, 19.1)	a 3.85(d, 19.2)	-
	b 3.41(d, 19.1)	b 3.41(d, 19.1)	-
4’	a 1.85(dd, 13.7, 6.1)	1.86-1.80(m)	-0.01
	b 1.80(dd, 13.7, 6.2)		
5’	a 1.90(m)	a 1.89(m)	0.01
	b 1.55(m)	b 1.55(m)	-
6’	4.32(dd, 12.1, 5.7)	4.32(dd, 12.0, 5.6)	-
8’	5.45(brs)	5.45(s)	-
9’	a 4.24(d, 10.2)	a 4.24(d, 10.1)	-
	b 3.76(d, 10.2)	b 3.77(d, 10.1)	-0.01
3’’	a 2.39(d, 17.7)	2.39-2.29(m)	-
	b 2.29(d, 17.7)		
4’’	a 2.25(overlap)	a 2.26(overlap)	-0.01
	b 1.73(m)	b 1.73(m)	-
5’’	5.25(dd, 6.3, 3.7)	5.25(dd, 6.2, 3.4)	-
1-OH	10.7(s)	10.81(s)	-0.11
4-OH	9.20(s)	9.21(s)	-0.01
8’-OH	6.53(brs)	-	-

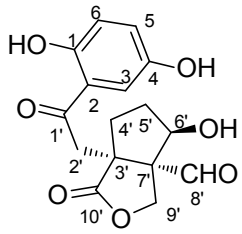
Table S2. Comparison of ^{13}C NMR data for **(+)-sinensilactam A** in DMSO-*d6*



(+)-sinensilactam A

	Natural δC (ppm) 100 MHz	Synthetic δC (ppm) 100 MHz	**Err** (Natural-Synthetic) Δδ(ppm)
1	153.3	153.3	-
2	120.0	120.0	-
3	114.6	114.6	-
4	149.5	149.5	-
5	124.3	124.3	-
6	118.5	118.5	-
1’	201.6	201.6	-
2’	45.4	45.4	-
3’	51.3	51.3	-
4’	33.9	33.9	-
5’	25.0	25.0	-
6’	77.1	77.0	0.1
7’	48.2	48.2	-
8’	75.9	75.9	-
9’	69.2	69.2	-
10’	181.4	181.4	-
2’’	172.6	172.5	0.1
3’’	29.3	29.3	-
4’’	23.5	23.5	-
5’’	84.5	84.4	0.1

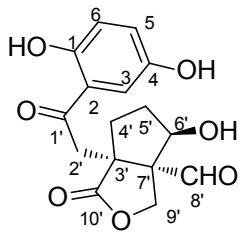
Table S3. Comparison of ^{1}H NMR data for (+)-**lingzhilactone B** in acetone-*d6*



(+)-lingzhilactone B

	Natural δ[ppm, mult, *J*(Hz)] 600 MHz	Synthetic δ[ppm, mult, *J*(Hz)] 400 MHz	**Err** (Natural-Synthetic) Δδ(ppm)
3	7.33(d, 2.9)	7.33(d, 2.9)	-
5	7.12(dd, 8.9, 2.9)	7.13(dd, 8.9, 2.9)	-0.01
6	6.81(d, 8.9)	6.81(t, 8.2)	-
2’	3.77(s)	3.78(s)	-0.01
4’	2.03(m)	2.01(dd, 16.8, 11.3)	0.02
5’	a 2.06(overlap)	a 2.06(s)	-
	b 1.58(m)	b 1.59(m)	-0.01
6’	4.66(dd, 11.0, 5.4)	4.66(dd, 11.0, 5.4)	-
8’	9.68(s)	9.68(s)	-
9’	a 4.94(d, 9.7)	a 4.94(d, 9.7)	-
	b 4.88(d, 9.7)	b 4.88(d, 9.7)	-
1-OH	11.00(s)	10.99(s)	0.01
4-OH	8.35(brs)	8.22 (s)	0.13
6’-OH	-	4.75(d, 4.8)	-

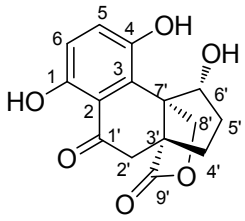
Table S4. Comparison of ^{13}C NMR data for **(+)-lingzhilactone B** in acetone-d_6



(+)-lingzhilactone B

	Natural δ(ppm) 100 MHz	Synthetic δ(ppm) 100 MHz	**Err** (Natural-Synthetic) Δδ (ppm)
1	156.3	156.4	-0.1
2	119.4	119.4	-
3	115.3	115.4	-0.1
4	150.4	150.4	-
5	126.7	126.8	-0.1
6	119.7	119.7	-
1’	205.2	205.2	-
2’	44.4	44.5	-0.1
3’	54.3	54.4	-0.1
4’	35.4	35.5	-0.1
5’	31.9	32.0	-0.1
6’	77.8	77.9	-0.1
7’	63.6	63.7	-0.1
8’	203.3	203.2	0.1
9’	66.9	66.9	-
10’	181.2	181.2	-

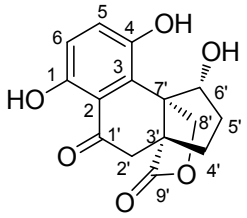
Table S5. Comparison of ^{1}H NMR data for (-)-**lingzhiol** in acetone-d_6



(-)-lingzhiol

	Natural δ[ppm, mult, *J*(Hz)] 400 MHz	Synthetic δ[ppm, mult, *J*(Hz)] 400 MHz	**Err** (Natural-Synthetic) Δδ (ppm)
5	7.22(d, 8.9)	7.23(d, 8.9)	-0.01
6	6.77(d, 8.9)	6.77(d, 8.9)	-
2'a	3.09(d, 16.0)	3.10(d, 16.0)	-0.01
2'b	2.79(d, 16.0)	2.79(d, 16.0)	-0.01
4'a	2.44(m)	2.45(m)	-
4'b	1.78(m)	1.78(m)	-
5'a	1.83(m)	1.84(m)	-0.01
5'b	1.70(m)	1.70(m)	-
6'	4.63(t, 4.8)	4.64(t, 4.6)	-0.01
8'a	5.22(d, 9.6)	5.22(d, 9.6)	-
8'b	4.45(d, 9.6)	4.46(d, 9.6)	-0.01

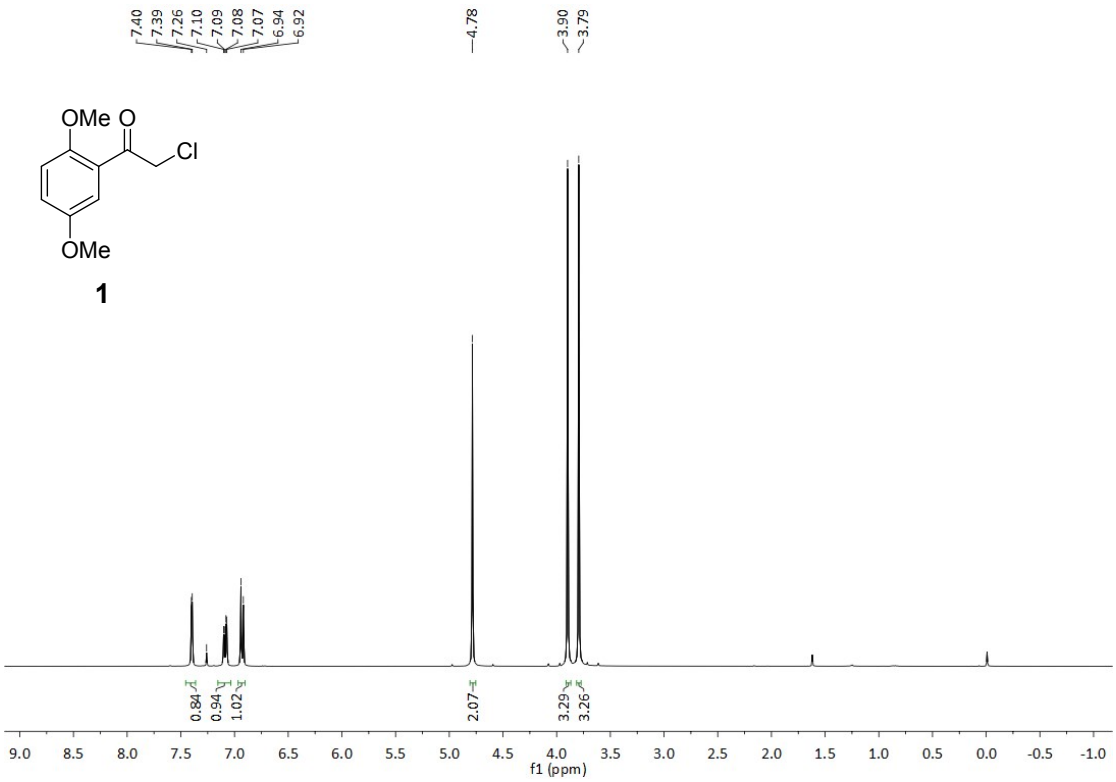
Table S6. Comparison of ^{13}C NMR data for (-)-**lingzhiol** in acetone-*d6*



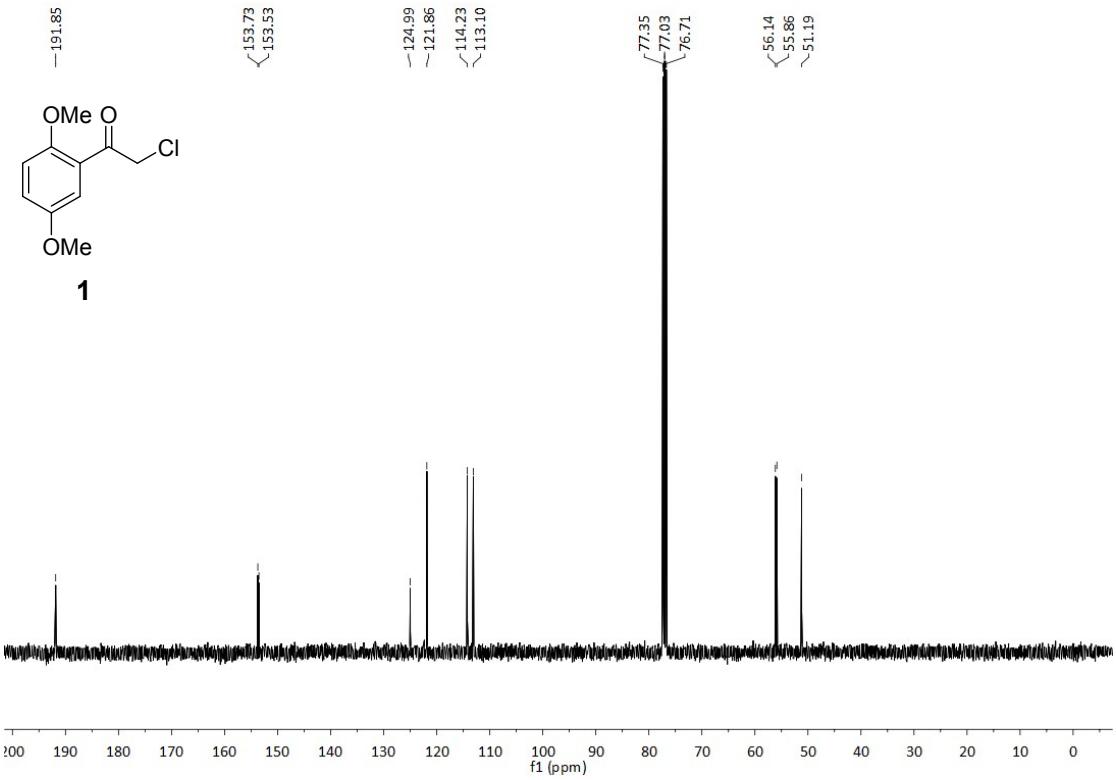
(-)-lingzhiol

	Natural δ[ppm] 100 MHz	Synthetic δ[ppm] 100 MHz	**Err** (Natural-Synthetic) Δδ(ppm)
1	156.3	156.3	-
2	116.4	116.4	-
3	129.1	129.1	-
4	147.9	148.0	-0.1
5	127.5	127.6	-0.1
6	117.9	117.9	-
1’	202.3	202.3	-
2’	42.3	42.3	-
3’	52.5	52.5	-
4’	33.3	33.3	-
5’	33.7	33.8	-0.1
6’	80.6	80.7	-0.1
7’	56.1	56.1	-
8’	70.9	70.9	-
9	180.1	180.1	-

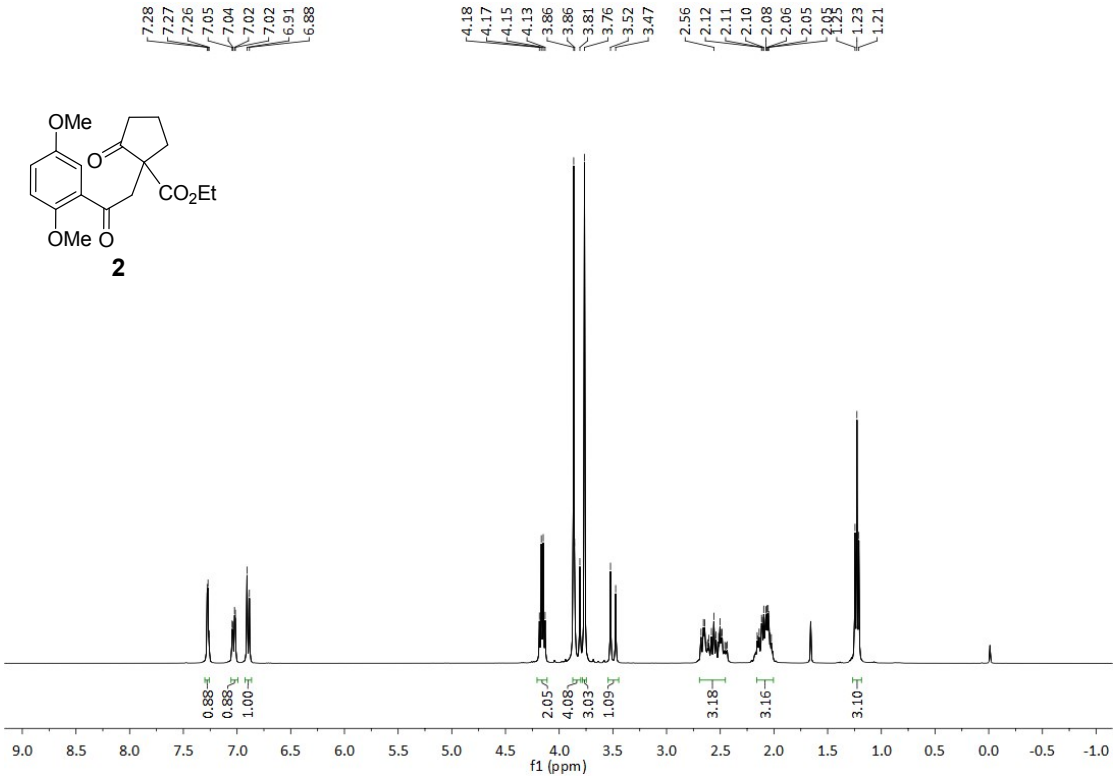
IV NMR Spectra for the Synthesized Compounds



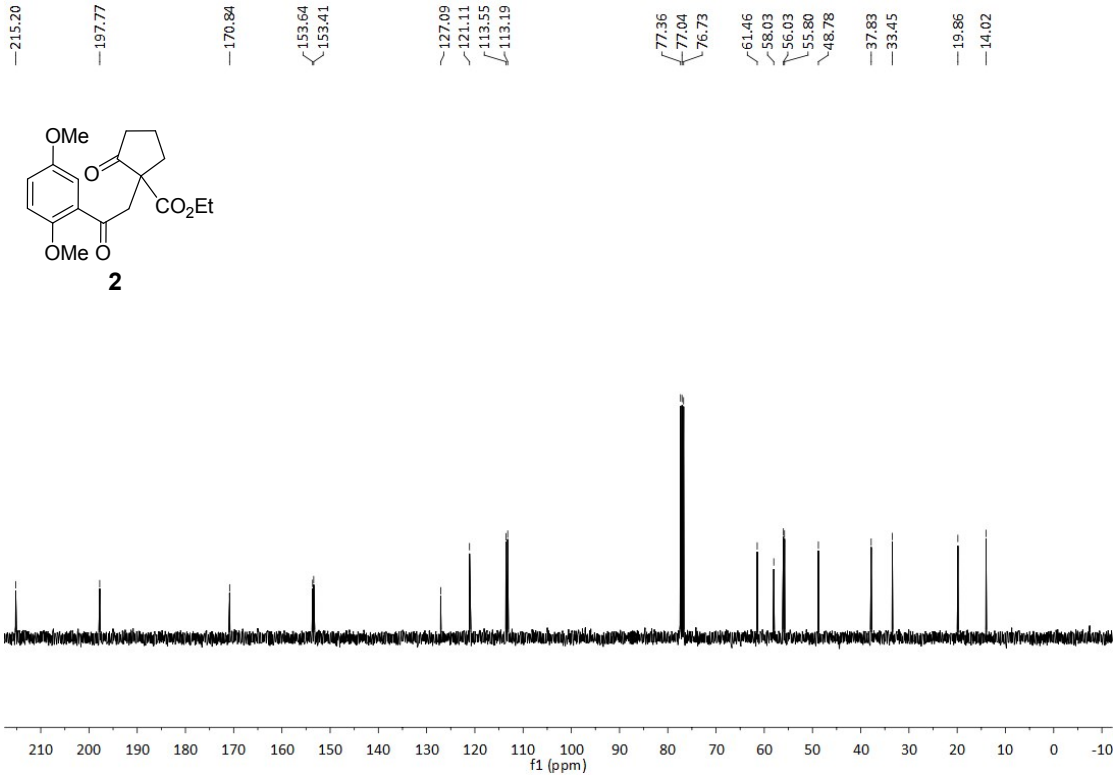
^{1}H NMR (400 MHz, $CDCl_3$) of compound 1



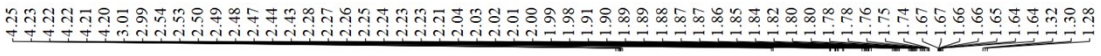
^{13}C NMR (100 MHz, $CDCl_3$) of compound 1

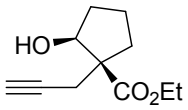


^{1}H NMR (400 MHz, $CDCl_3$) of compound 2

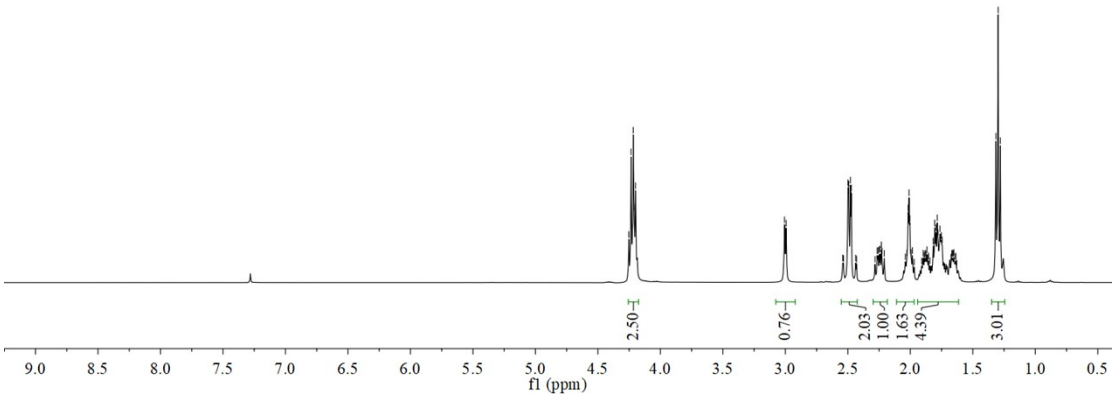


^{13}C NMR (100 MHz, $CDCl_3$) of compound 2

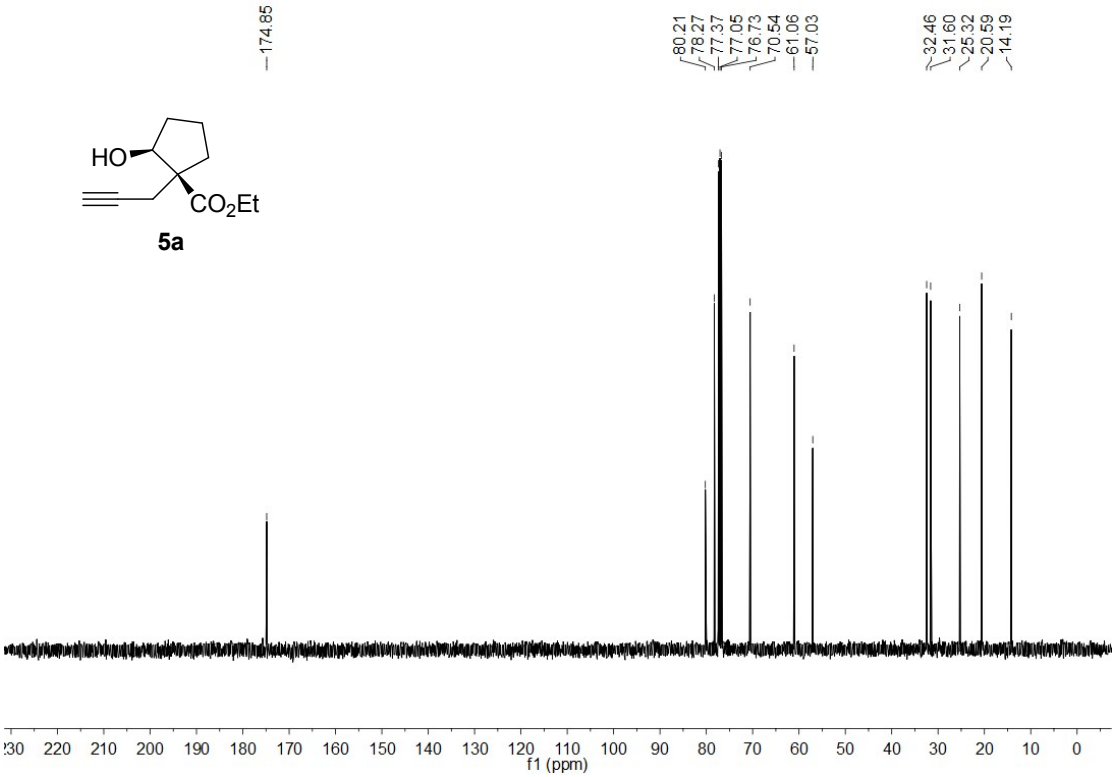




5a

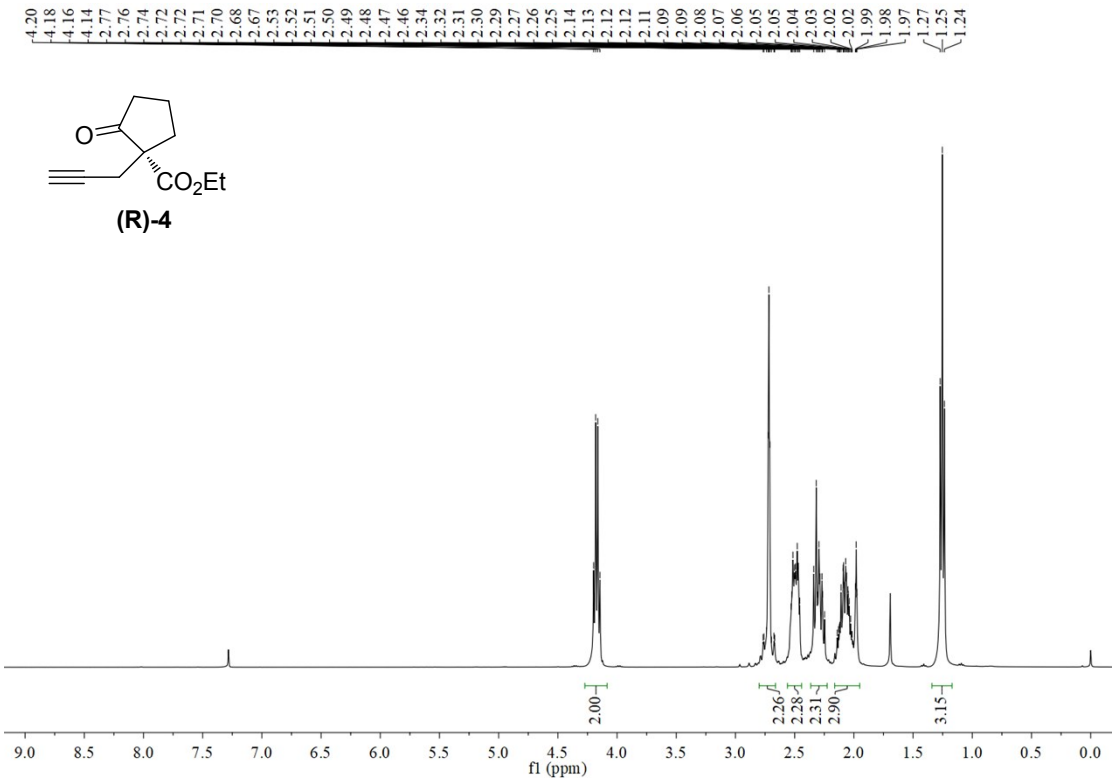


^{1}H NMR (400 MHz, $CDCl_3$) of compound 5a

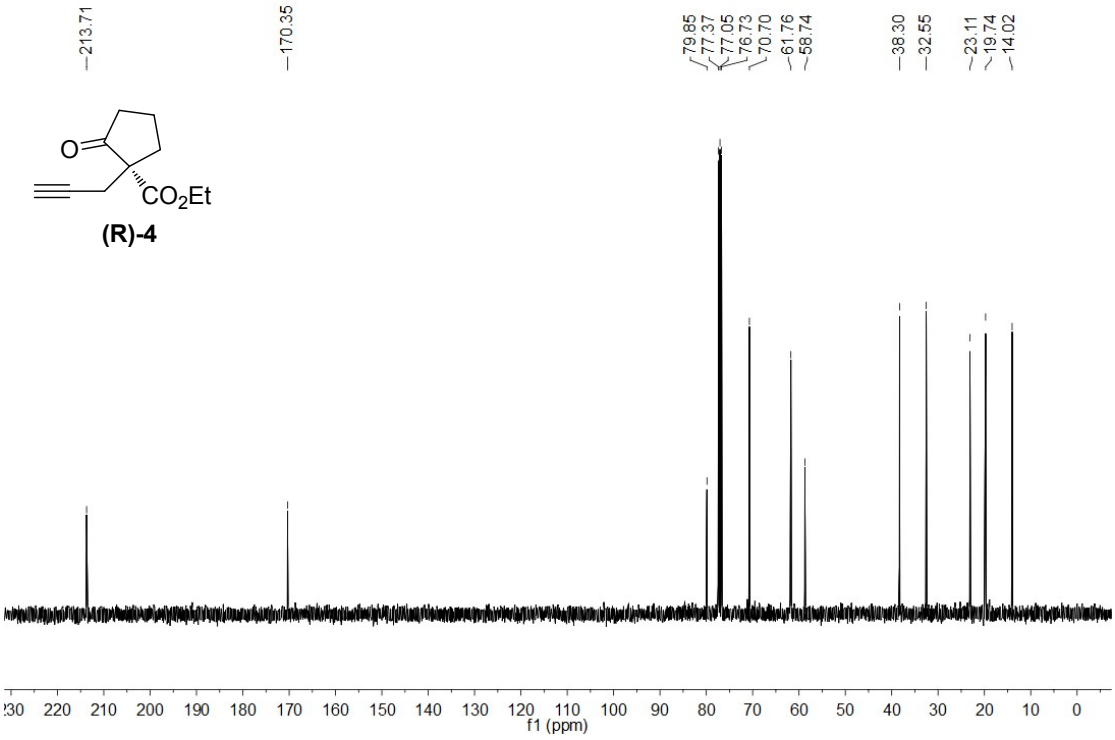


5a

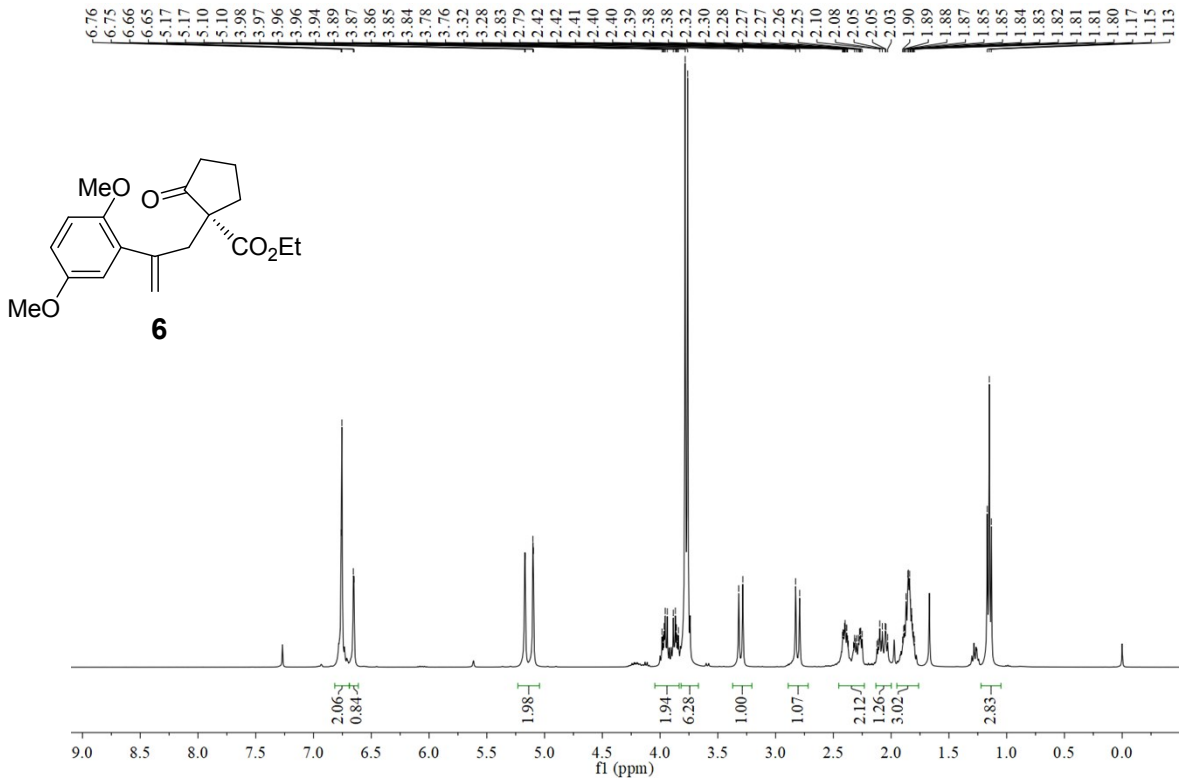
^{13}C NMR (100 MHz, $CDCl_3$) of compound 5a



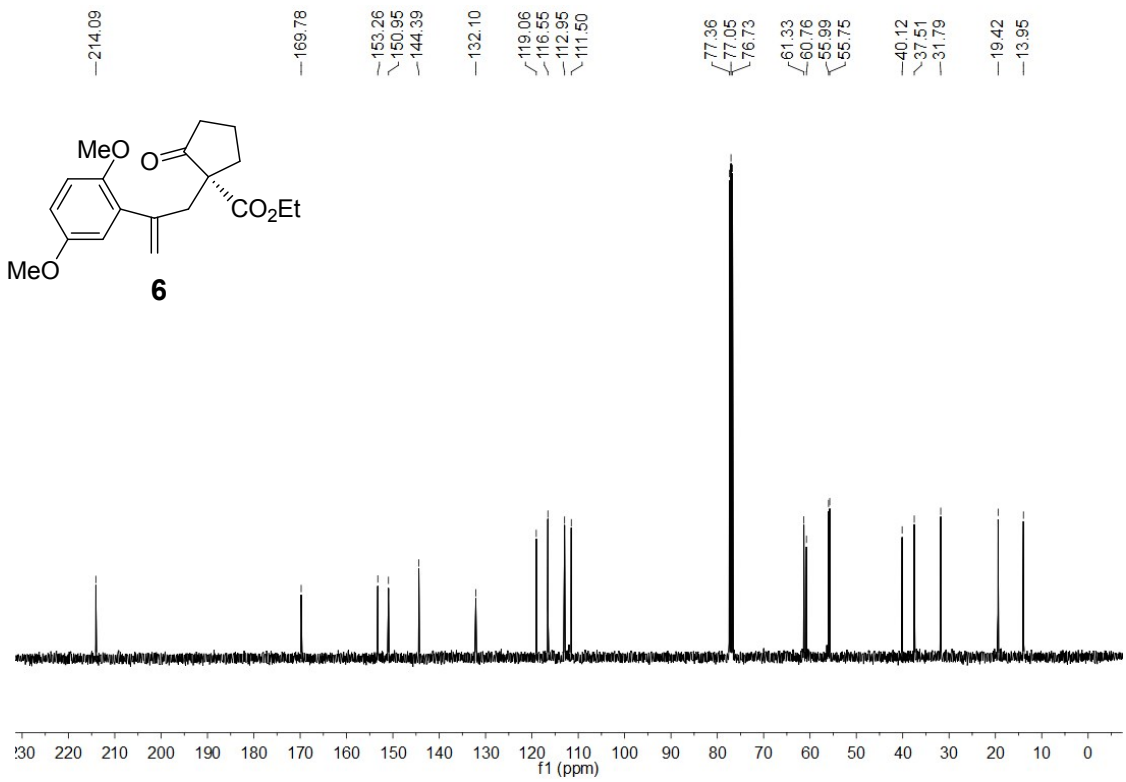
^{1}H NMR (400 MHz, $CDCl_3$) of compound (R)-4



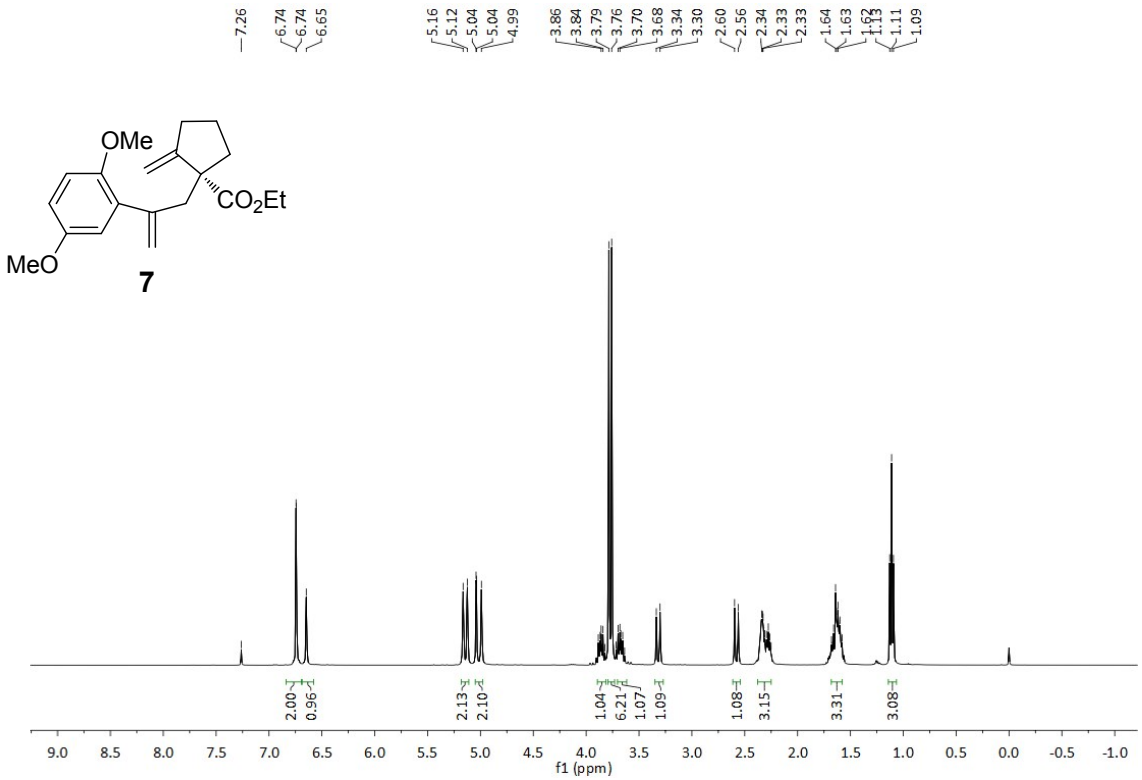
^{13}C NMR (100 MHz, $CDCl_3$) of compound (R)-4



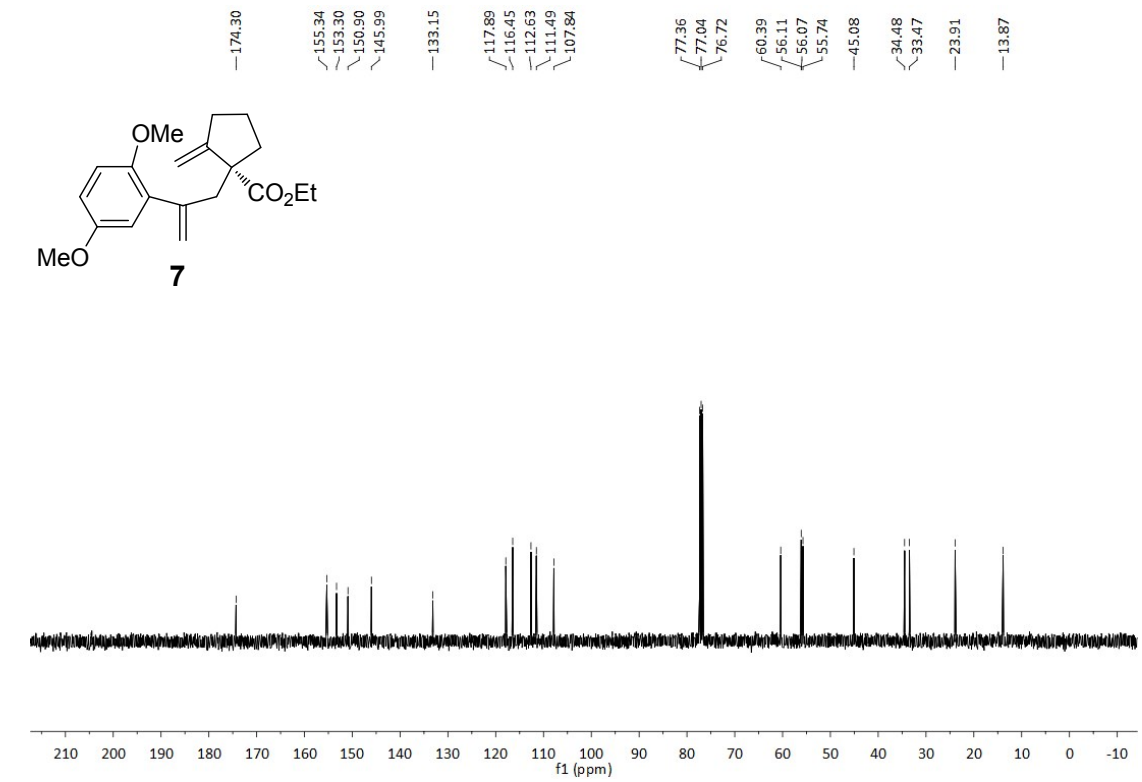
^{1}H NMR (400 MHz, $CDCl_3$) of compound 6



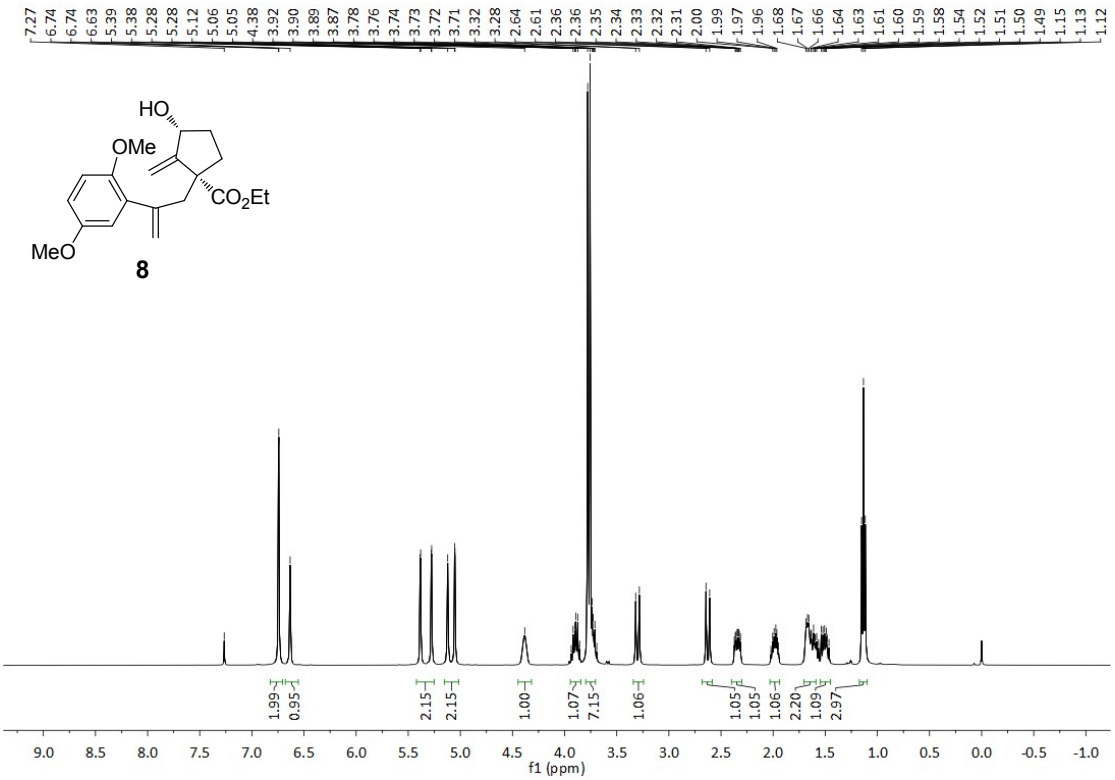
^{13}C NMR (100 MHz, $CDCl_3$) of compound 6



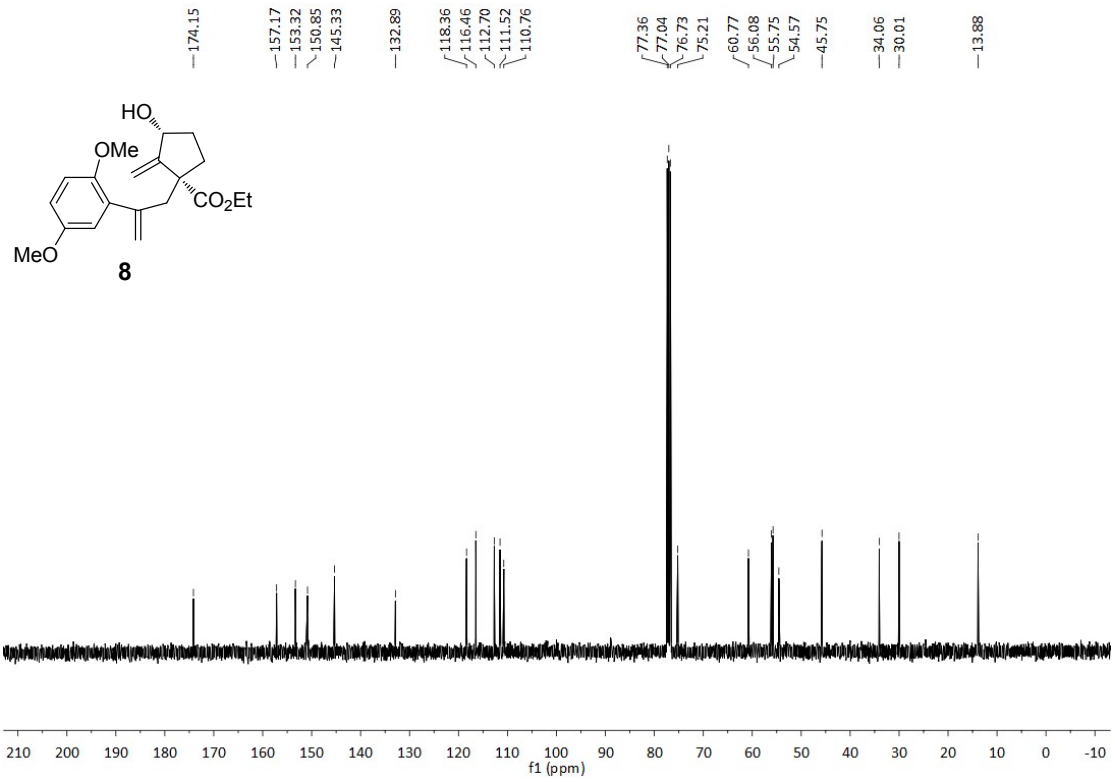
^{1}H NMR (400 MHz, $CDCl_3$) of compound 7



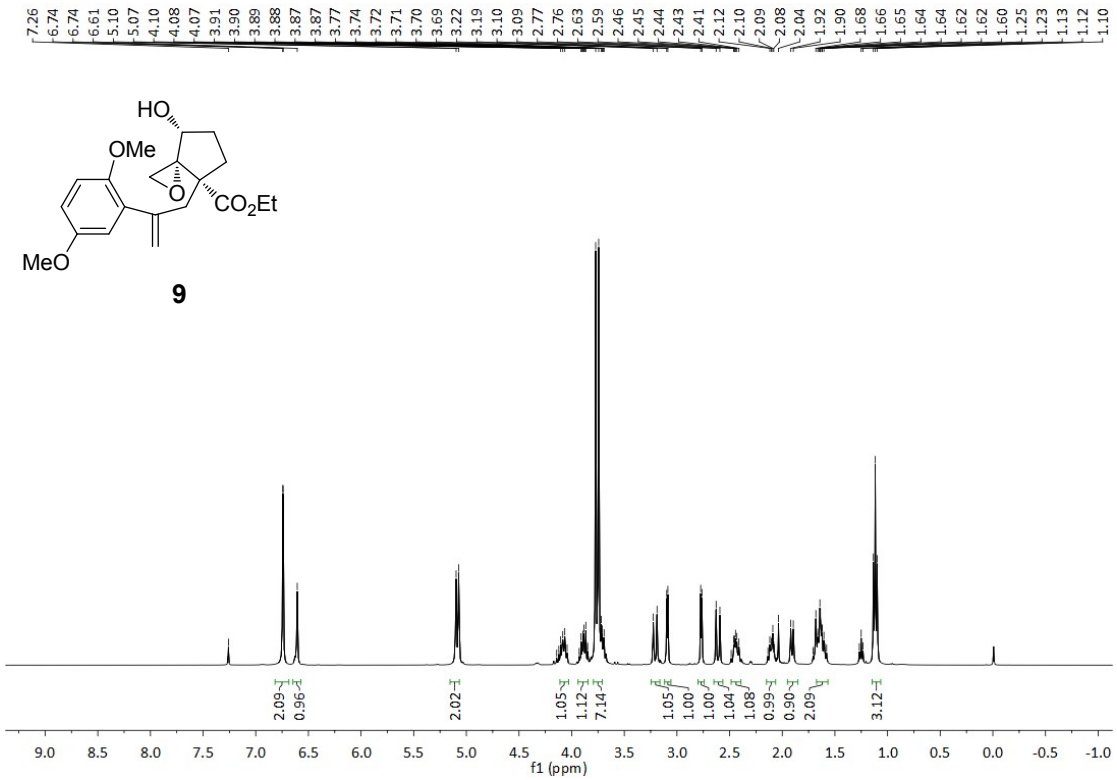
^{13}C NMR (100 MHz, $CDCl_3$) of compound 7



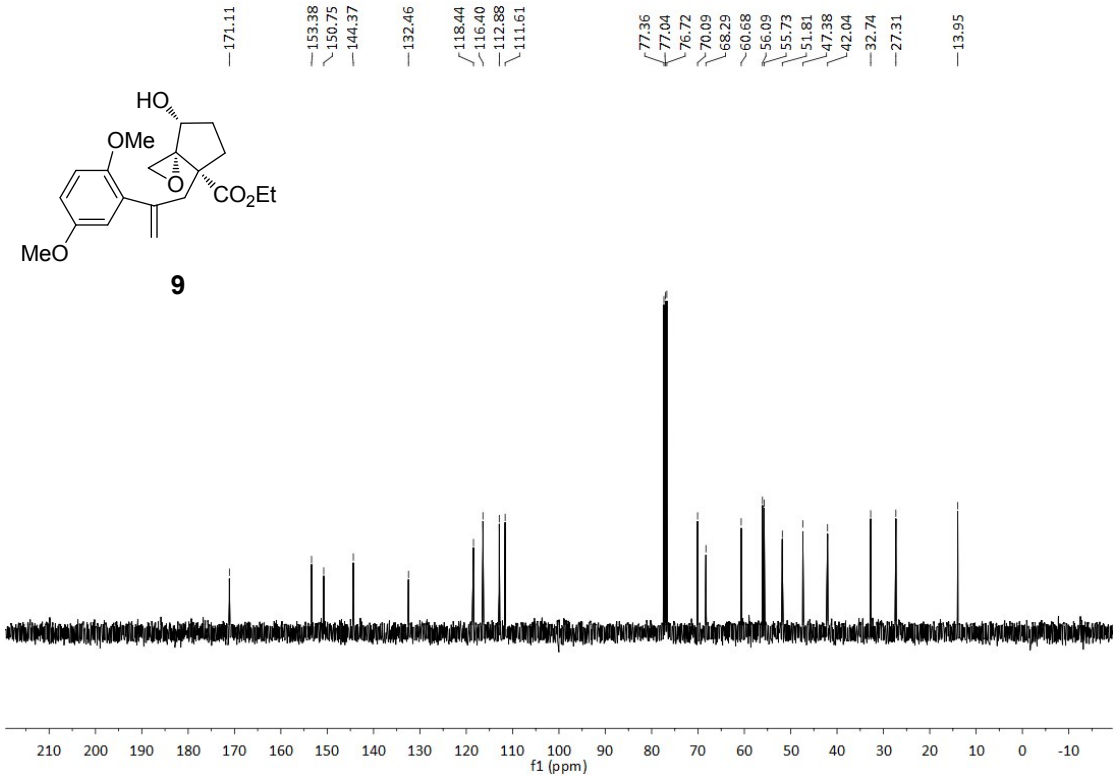
^{1}H NMR (400 MHz, $CDCl_3$) of compound 8



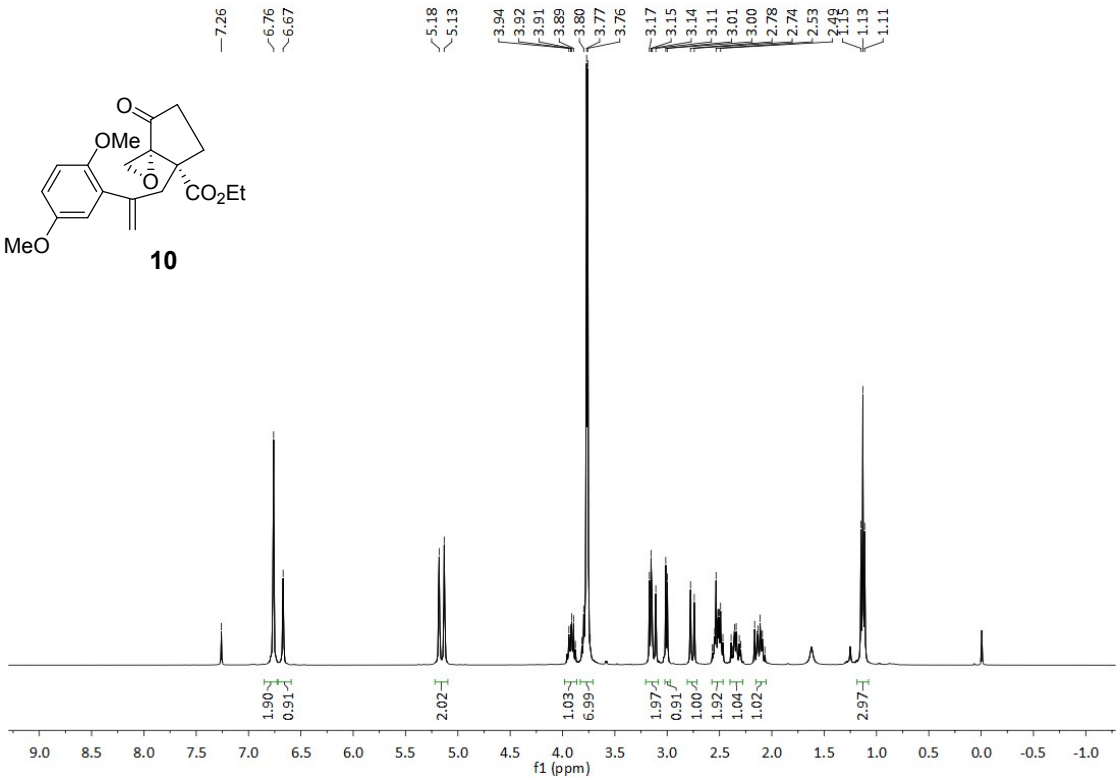
^{13}C NMR (100 MHz, $CDCl_3$) of compound 8



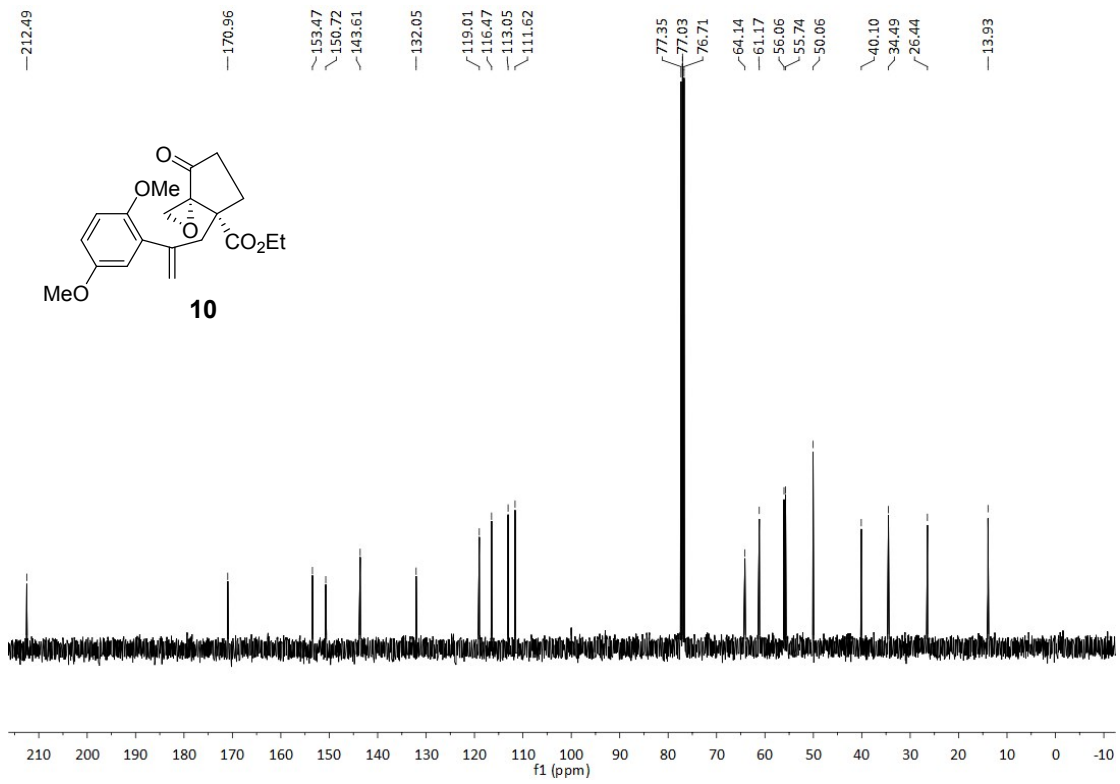
^{1}H NMR (400 MHz, $CDCl_3$) of compound 9



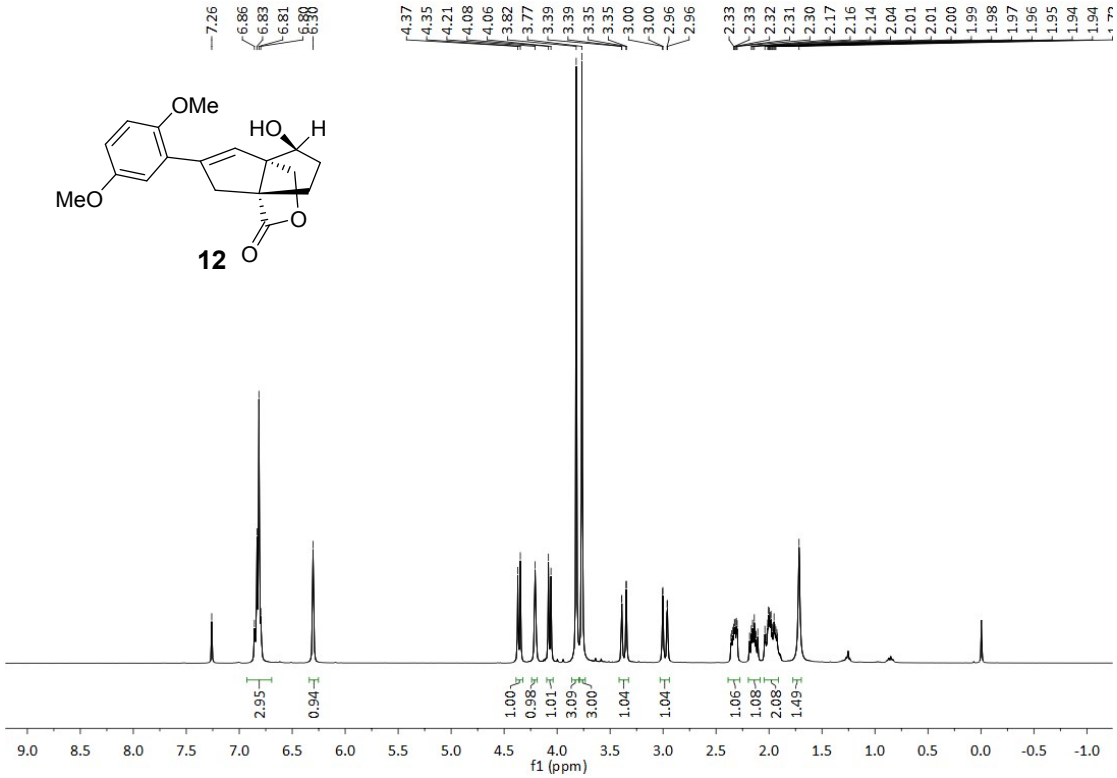
^{13}C NMR (100 MHz, $CDCl_3$) of compound 9



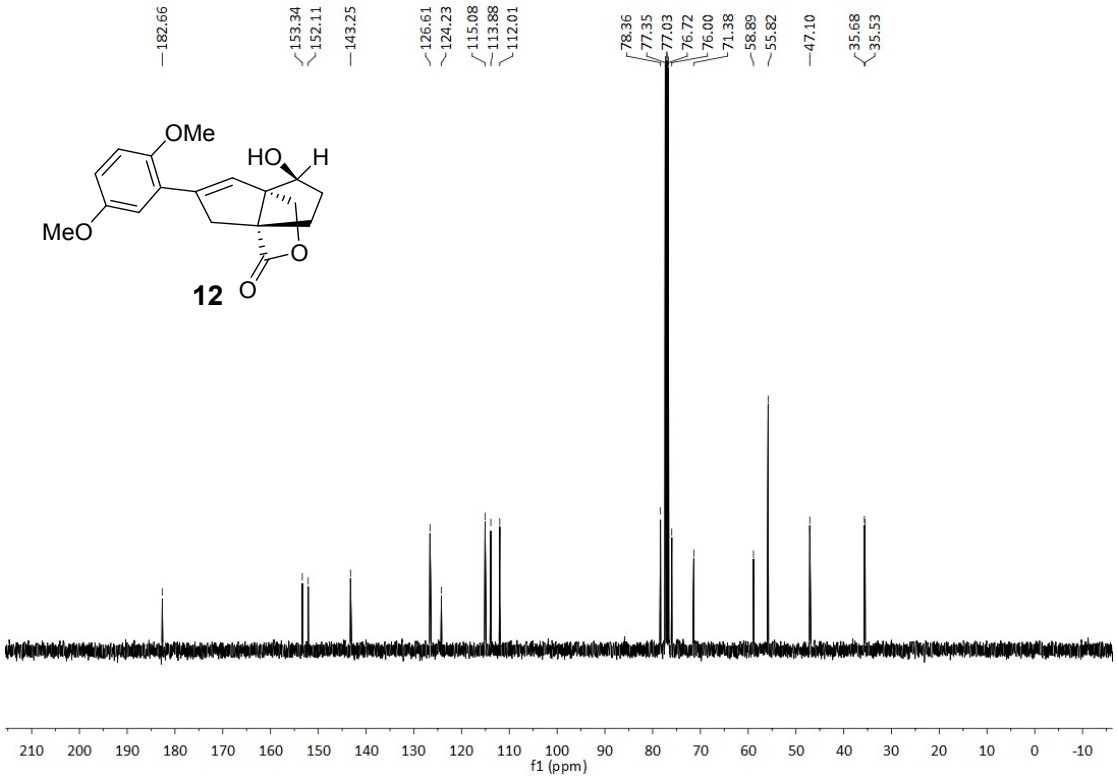
^{1}H NMR (400 MHz, $CDCl_3$) of compound 10



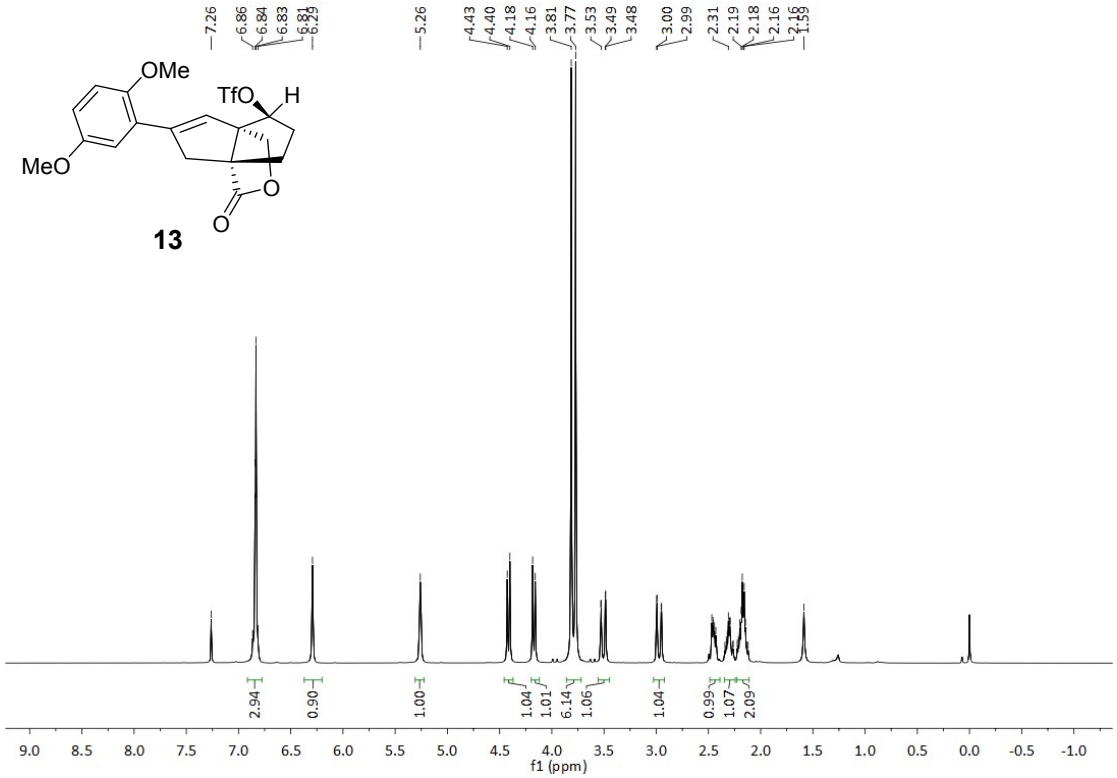
^{13}C NMR (100 MHz, $CDCl_3$) of compound 10



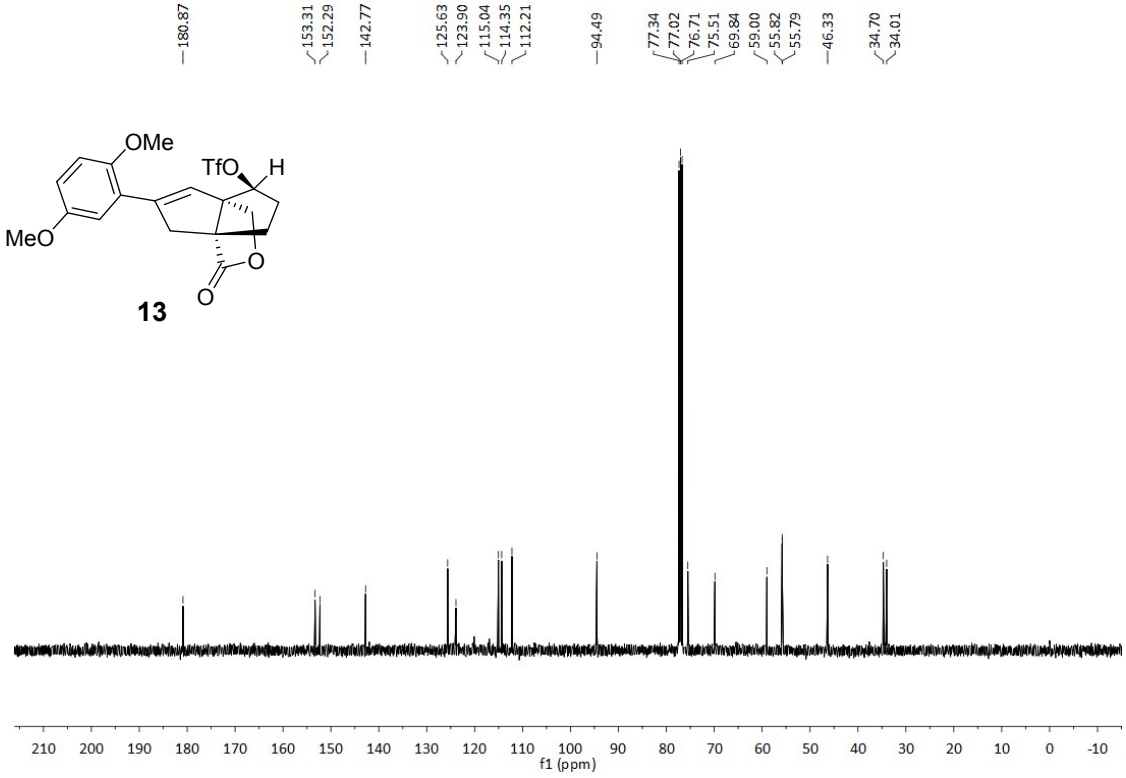
^{1}H NMR (400 MHz, $CDCl_3$) of compound 12



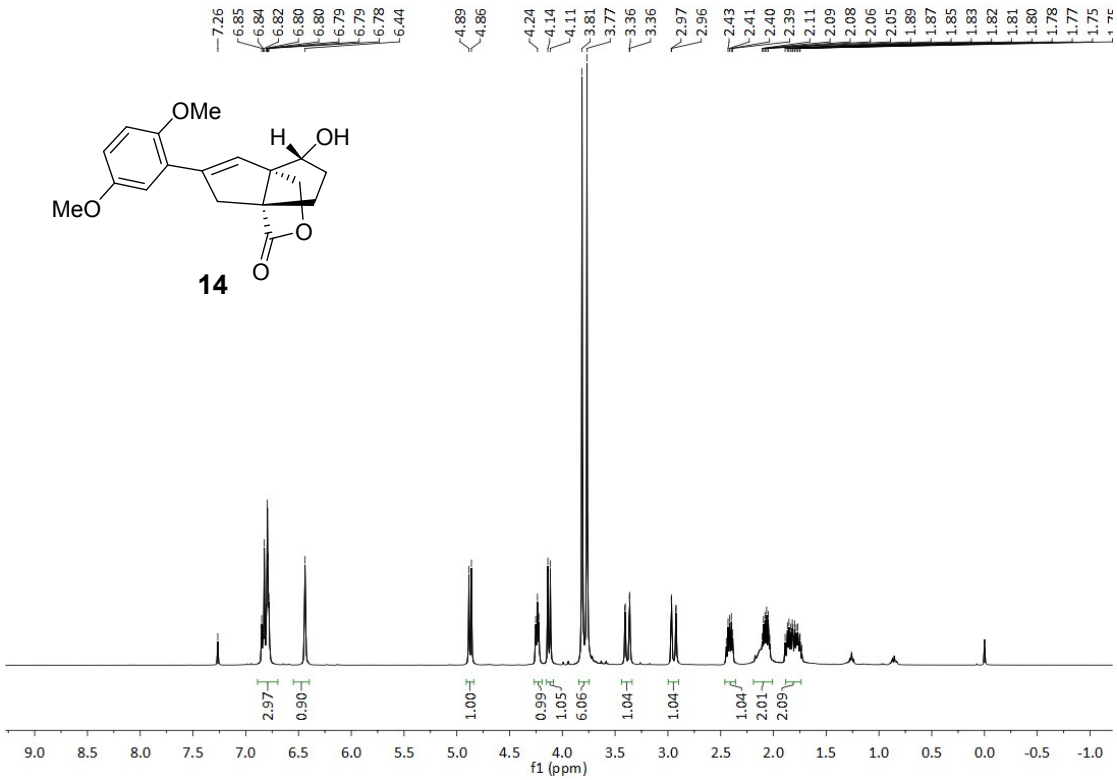
^{13}C NMR (100 MHz, $CDCl_3$) of compound 12



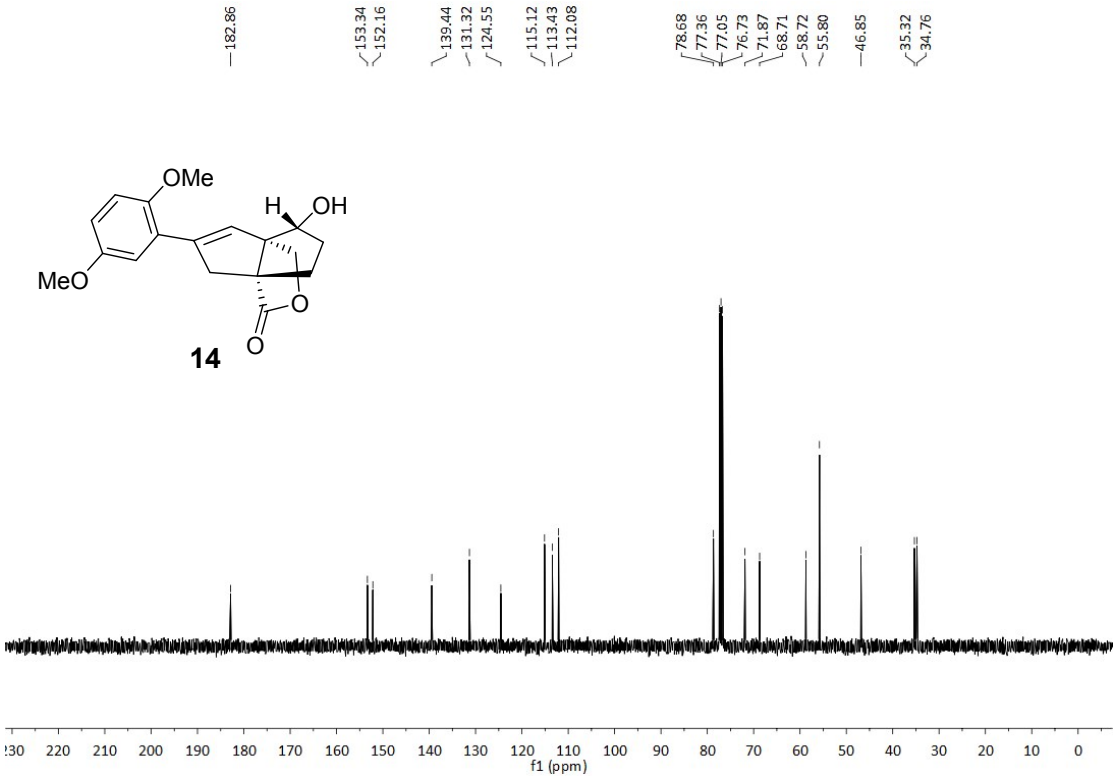
^{1}H NMR (400 MHz, $CDCl_3$) of compound 13



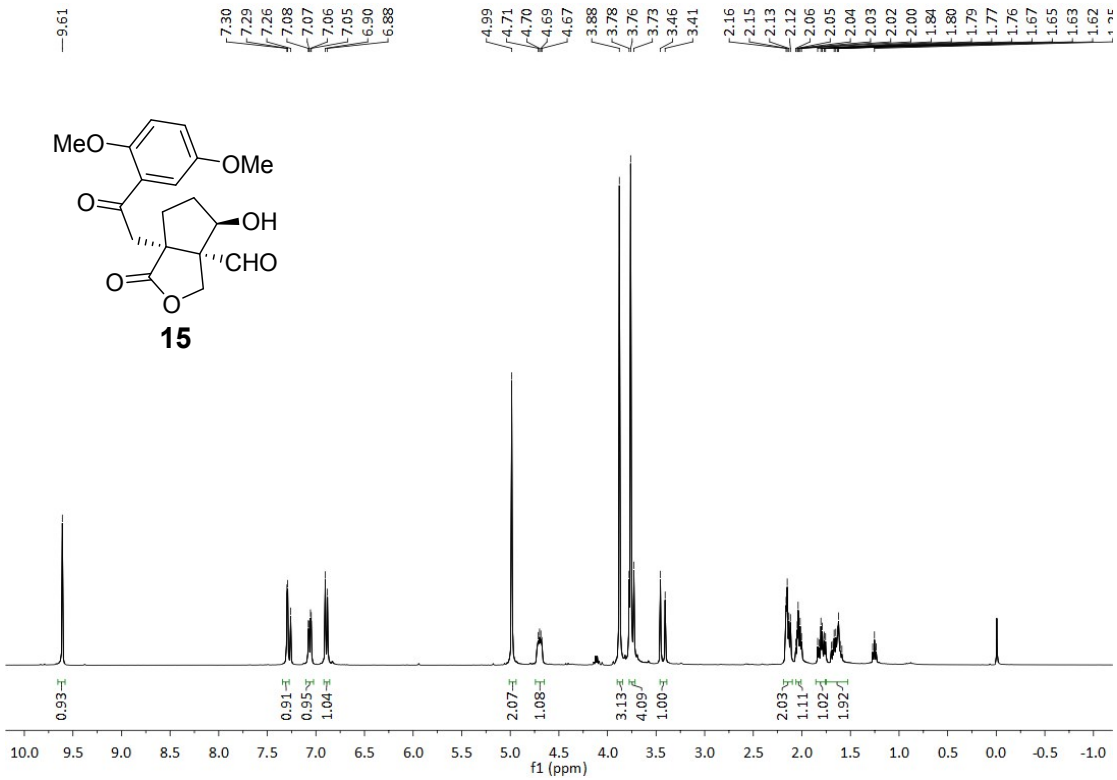
^{13}C NMR (100 MHz, $CDCl_3$) of compound 13



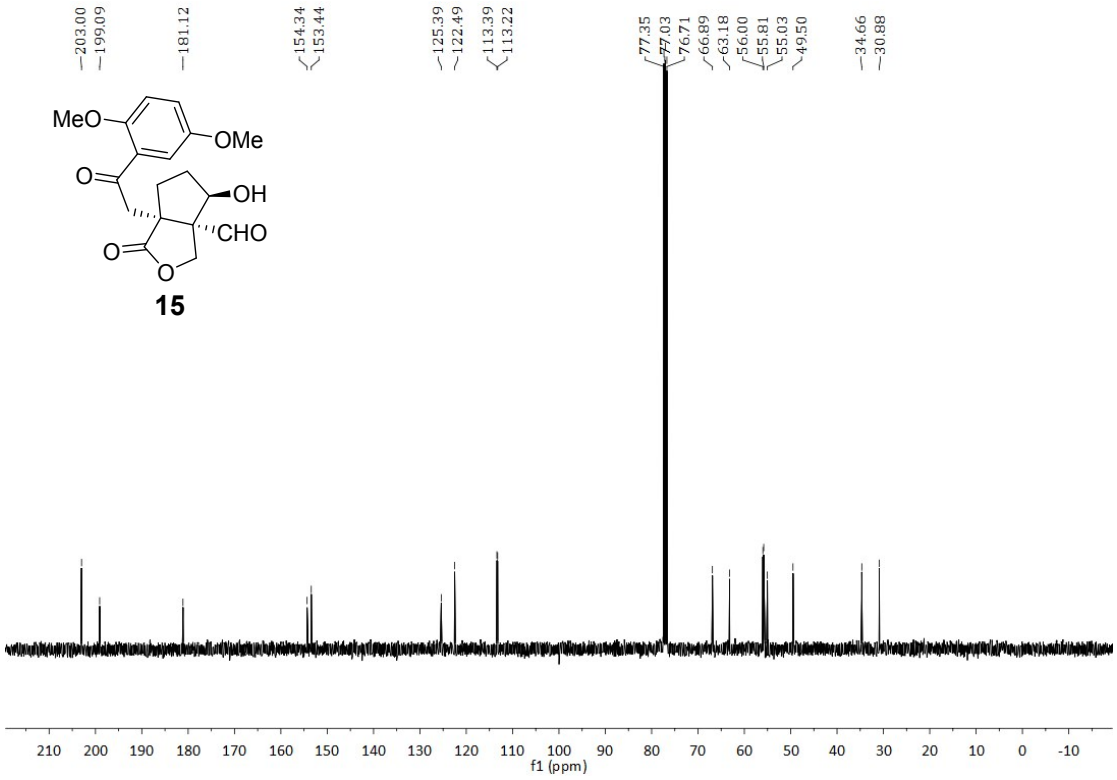
^{1}H NMR (400 MHz, $CDCl_3$) of compound 14



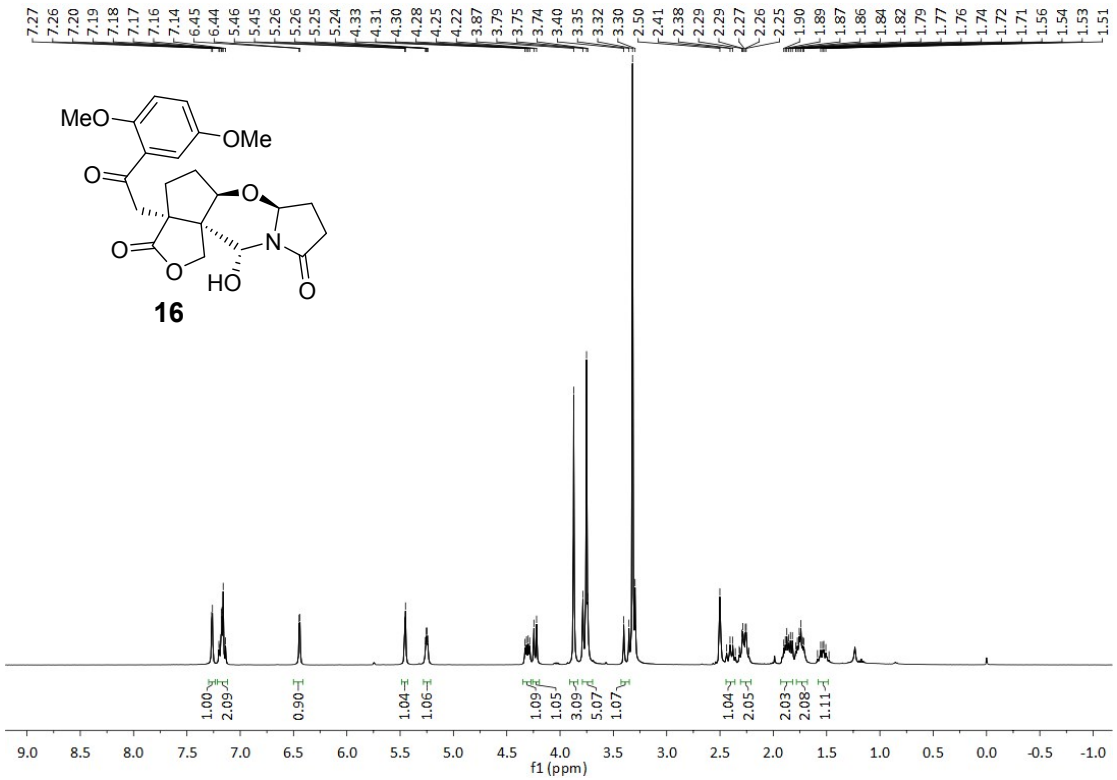
^{13}C NMR (100 MHz, $CDCl_3$) of compound 14



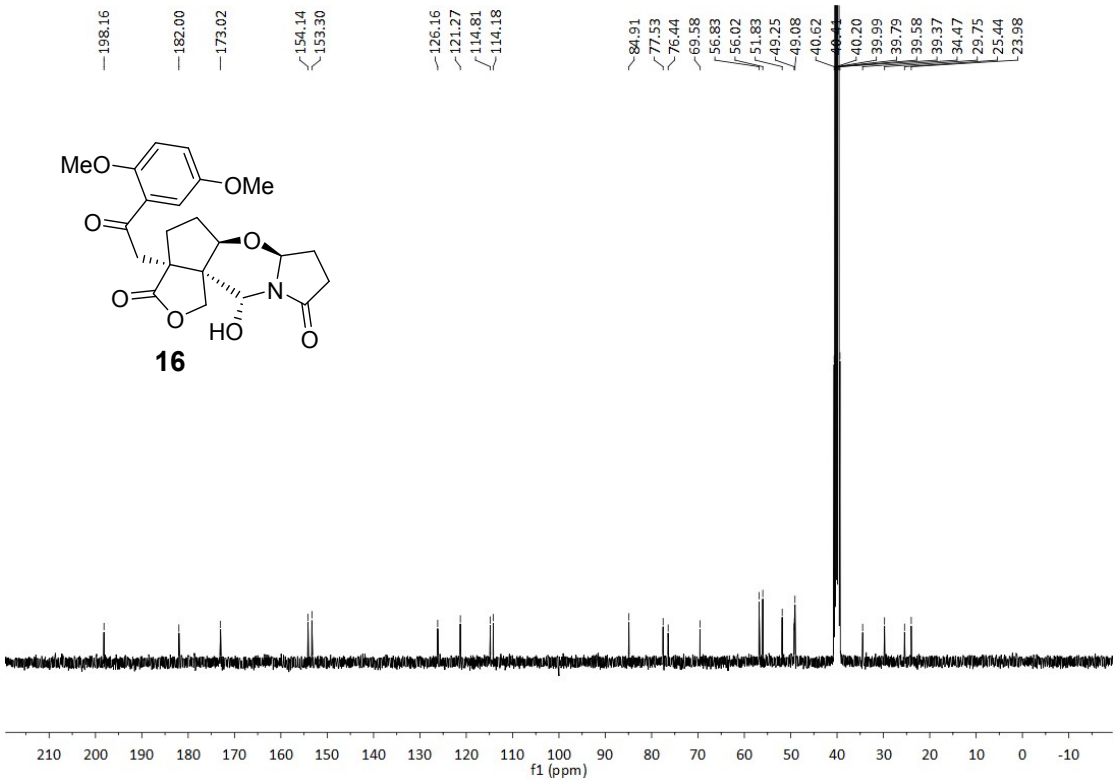
^{1}H NMR (400 MHz, $CDCl_3$) of compound 15



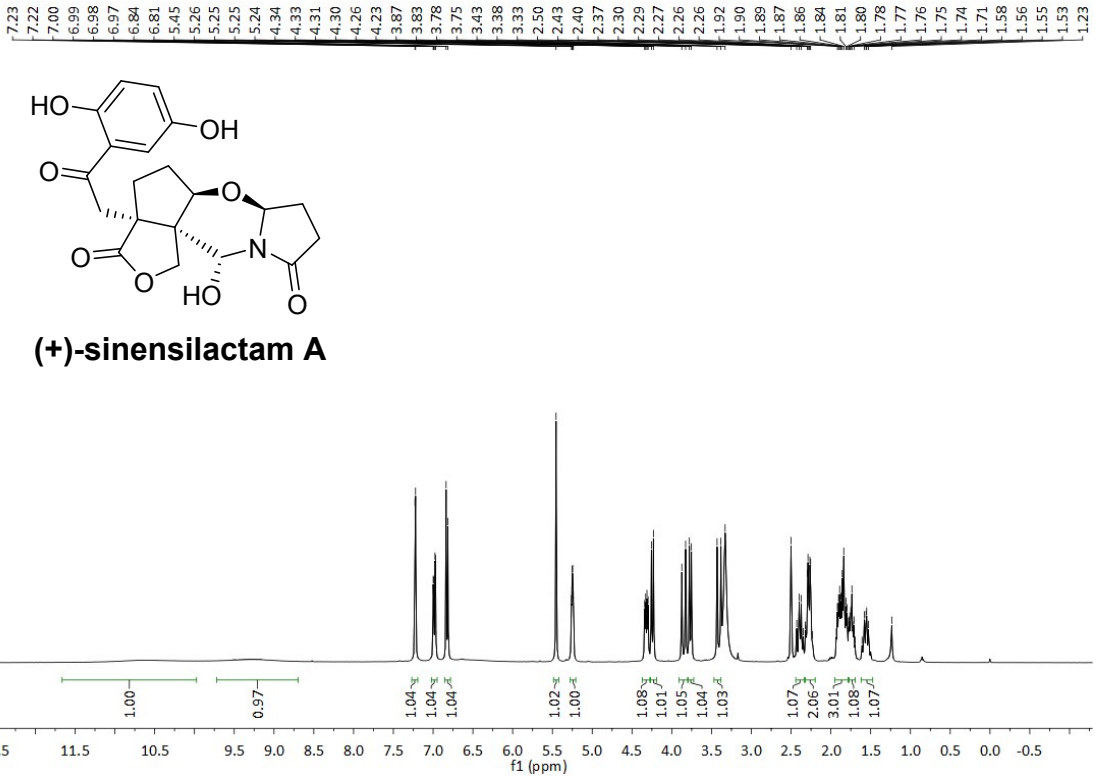
^{13}C NMR (100 MHz, $CDCl_3$) of compound 15



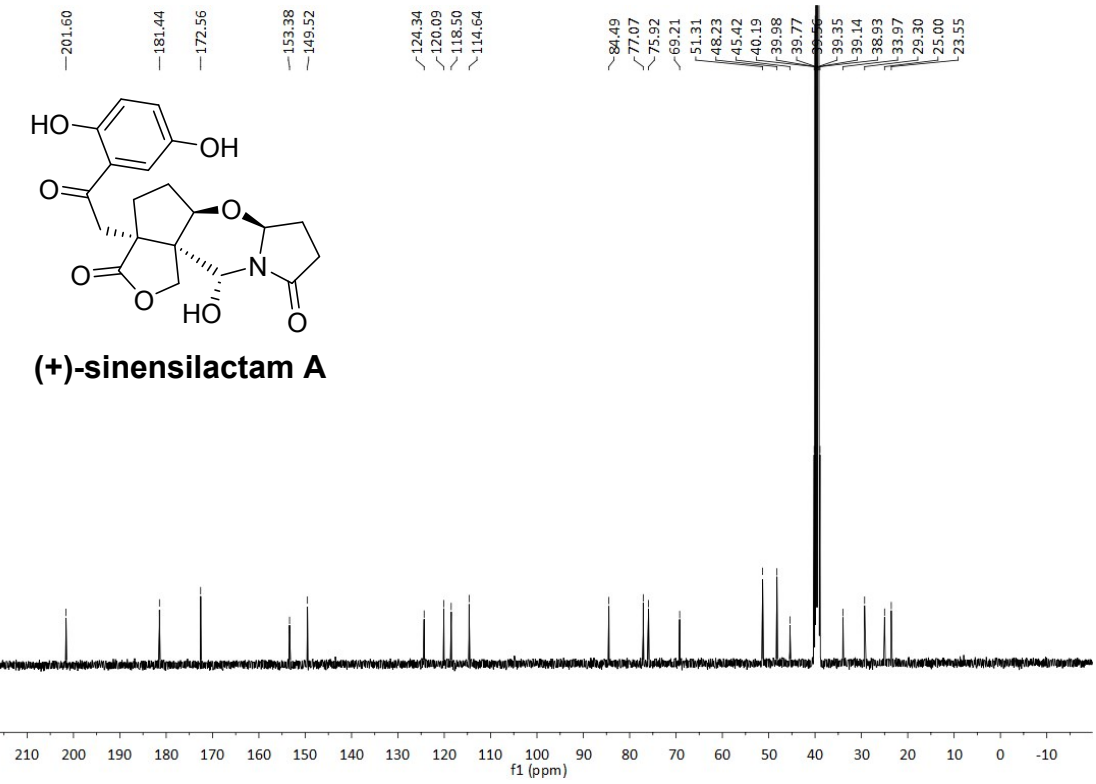
^{1}H NMR (400 MHz, DMSO-d6) of compound 16



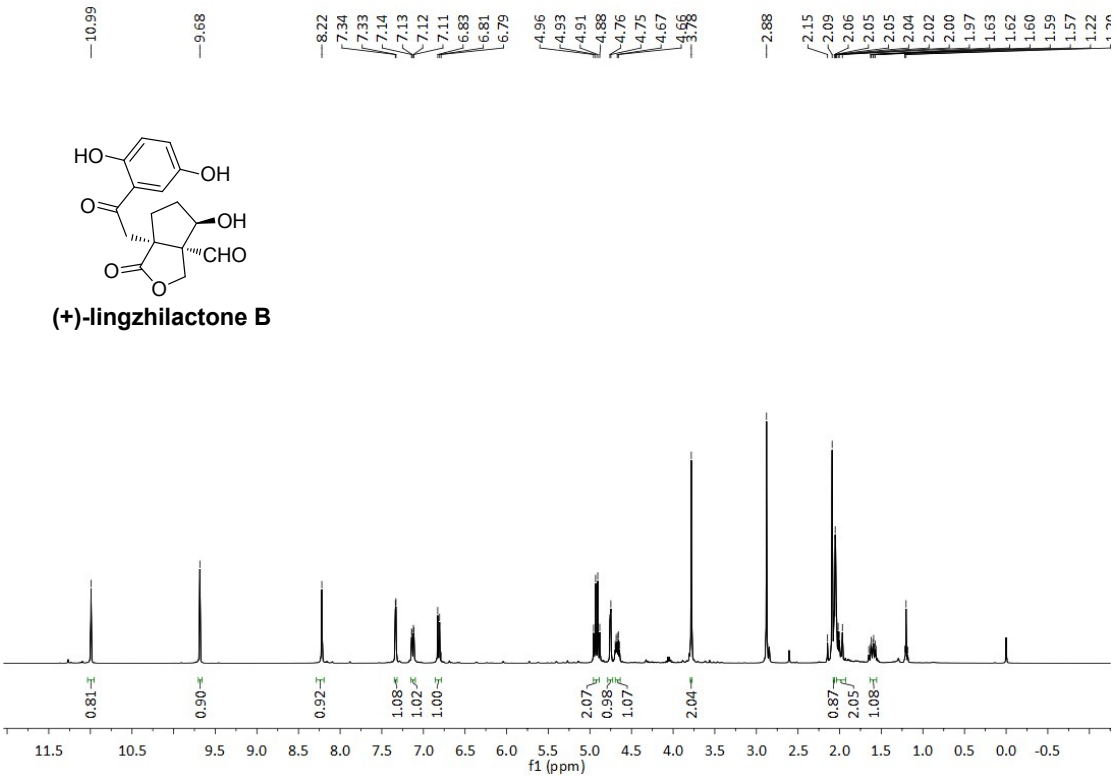
^{13}C NMR (100 MHz, DMSO-d_6) of compound 16



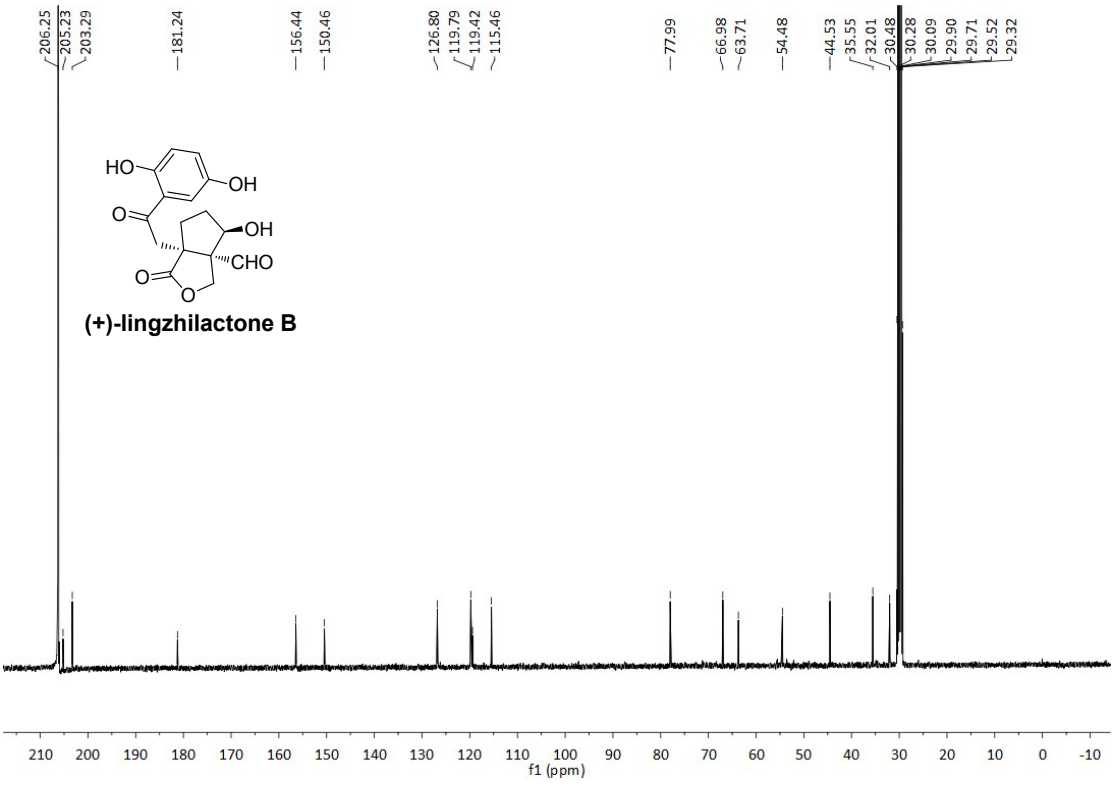
^{1}H NMR (400 MHz, DMSO-d$_6$) of sinensilactam A



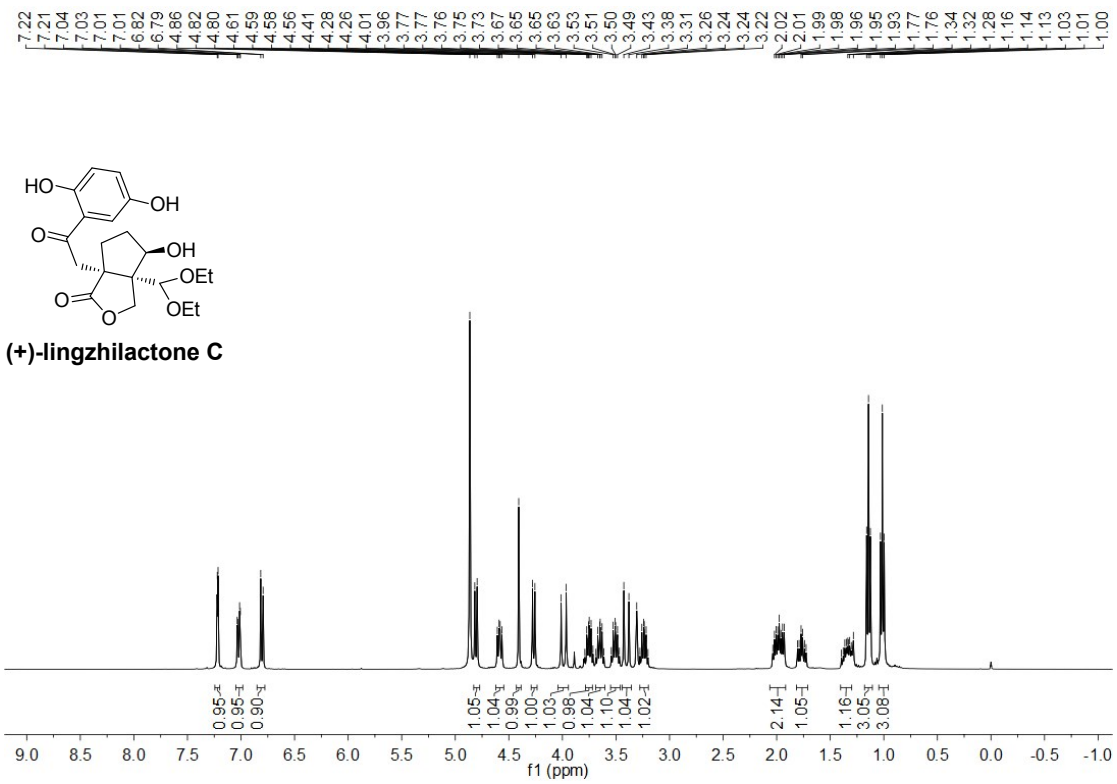
^{13}C NMR (100 MHz, DMSO-d$_6$) of sinensilactam A



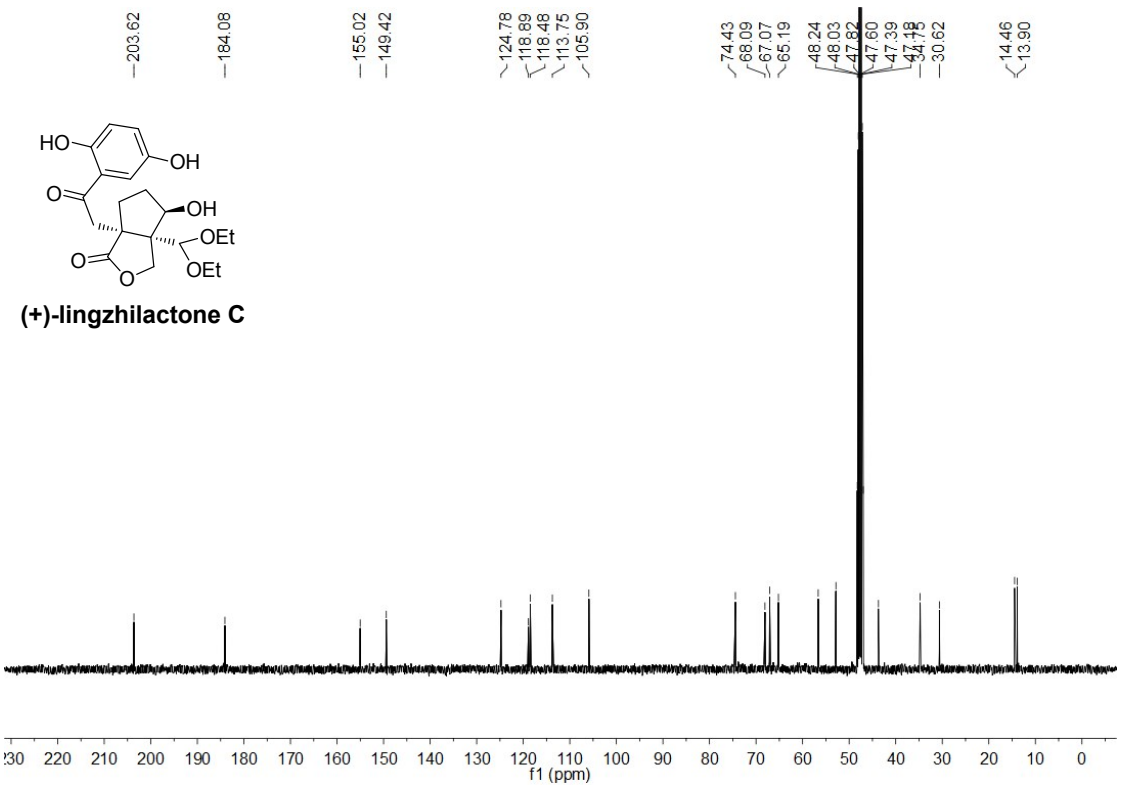
^{1}H NMR (400 MHz, acetone-d$_6$) of lingzhilactone B



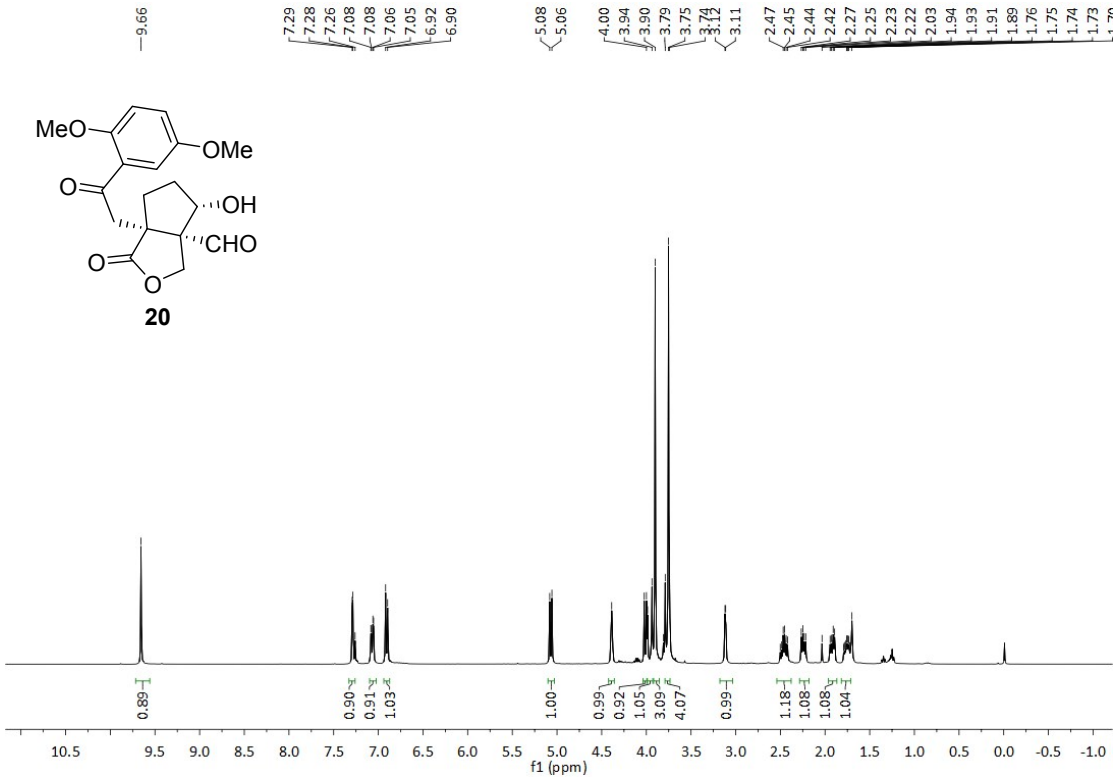
^{13}C NMR (100 MHz, acetone-d$_6$) of lingzhilactone B



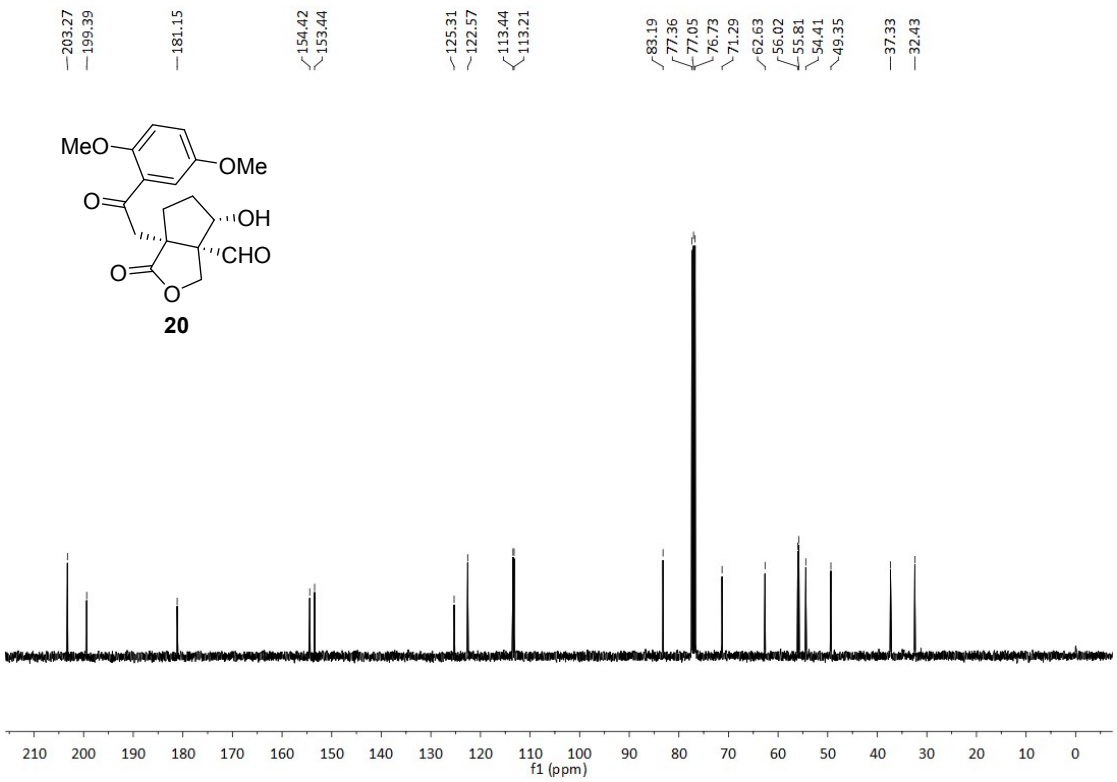
^{1}H NMR (400 MHz, CD_3OD) of lingzhilactone C



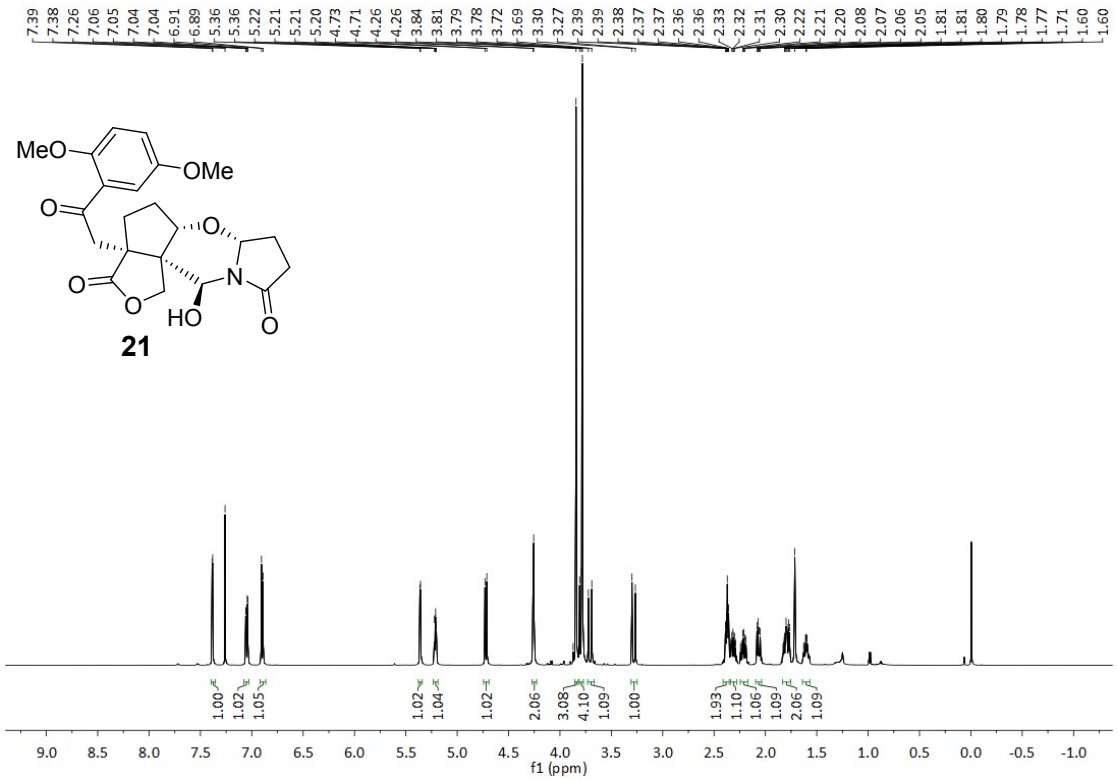
^{13}C NMR (100 MHz, CD_3OD) of lingzhilactone C



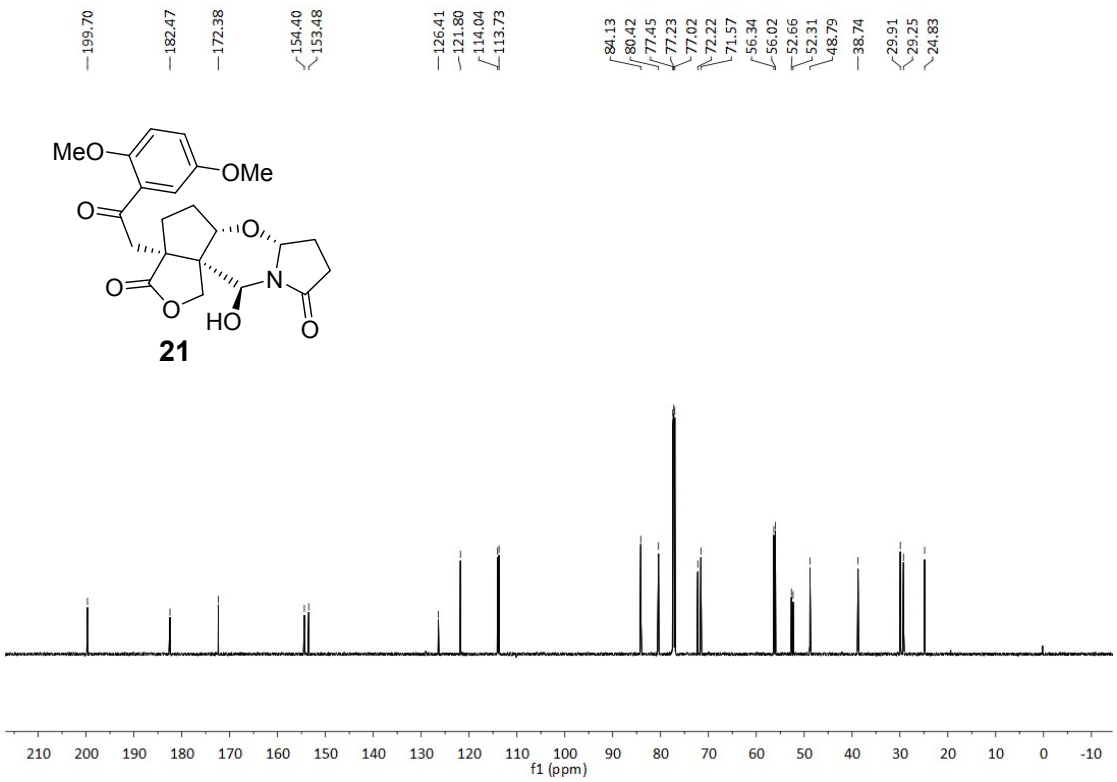
^{1}H NMR (400 MHz, $CDCl_3$) of compound 20



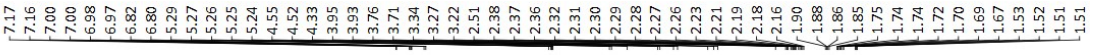
^{13}C NMR (100 MHz, $CDCl_3$) of compound 20

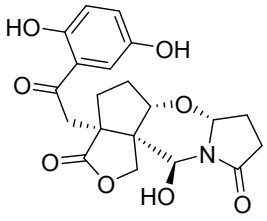


^{1}H NMR (600 MHz, $CDCl_3$) of compound 21

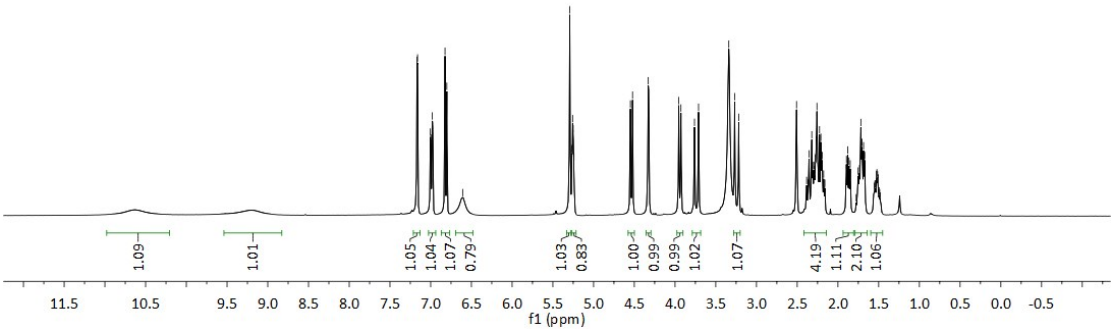


^{13}C NMR (125 MHz, $CDCl_3$) of compound 21

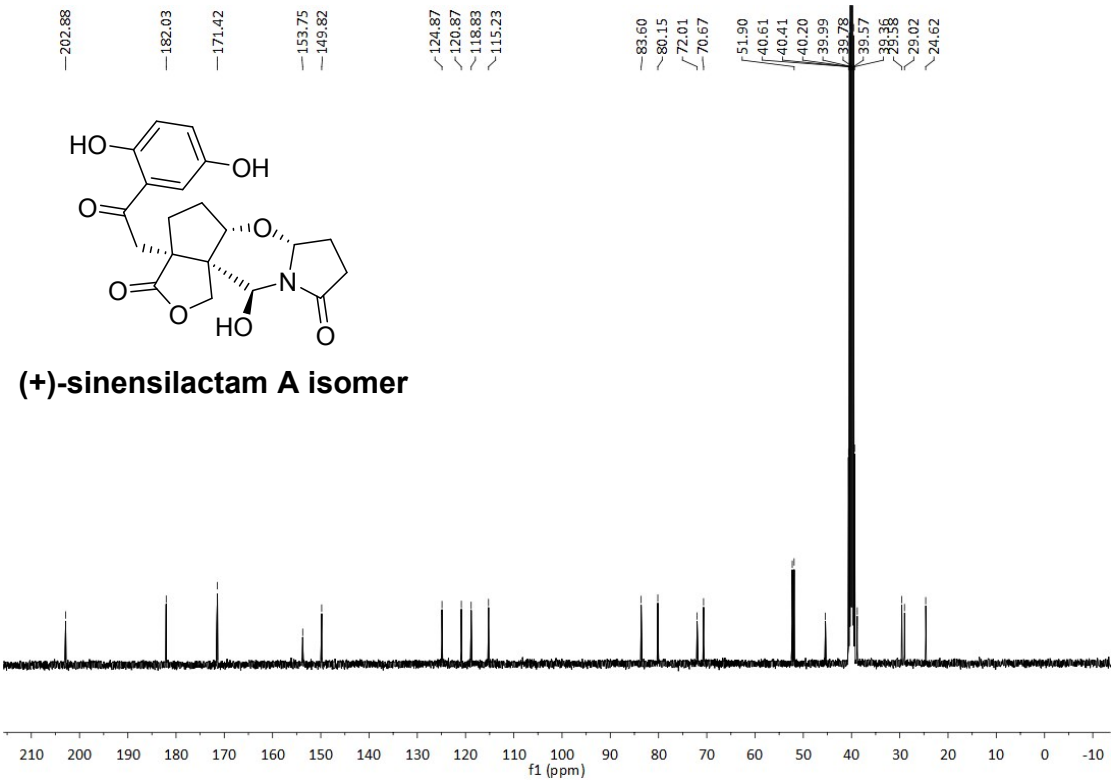




(+)-sinensilactam A isomer

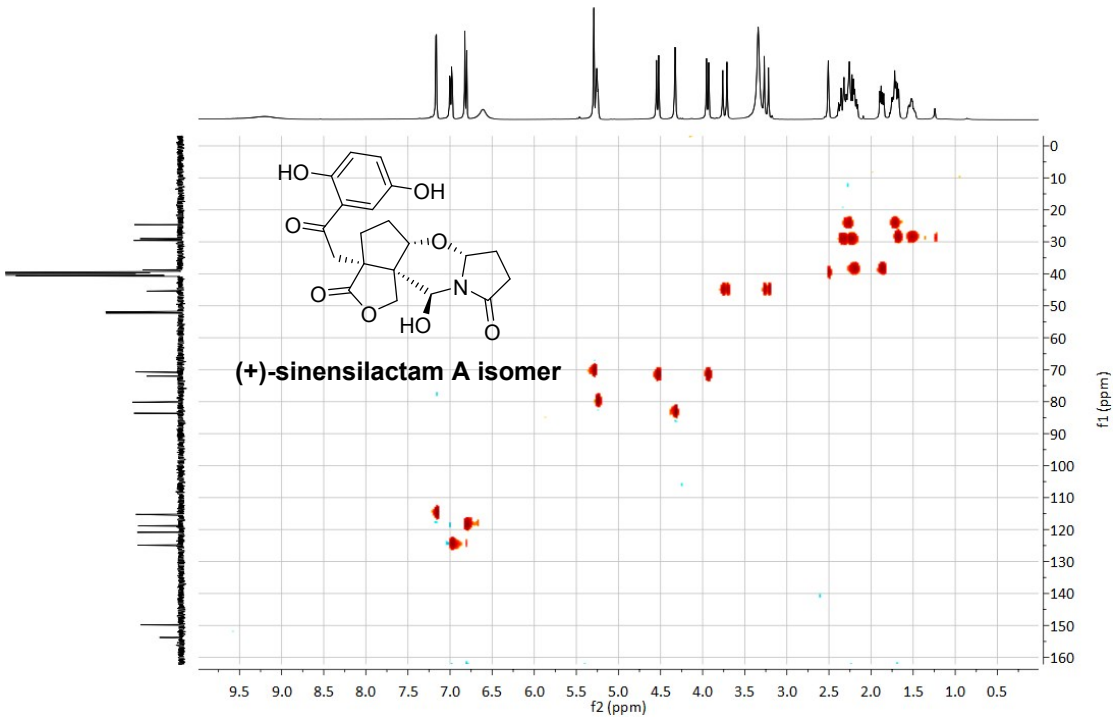


^{1}H NMR (400 MHz, DMSO-d$_6$) of (+)-sinensilactam A isomer

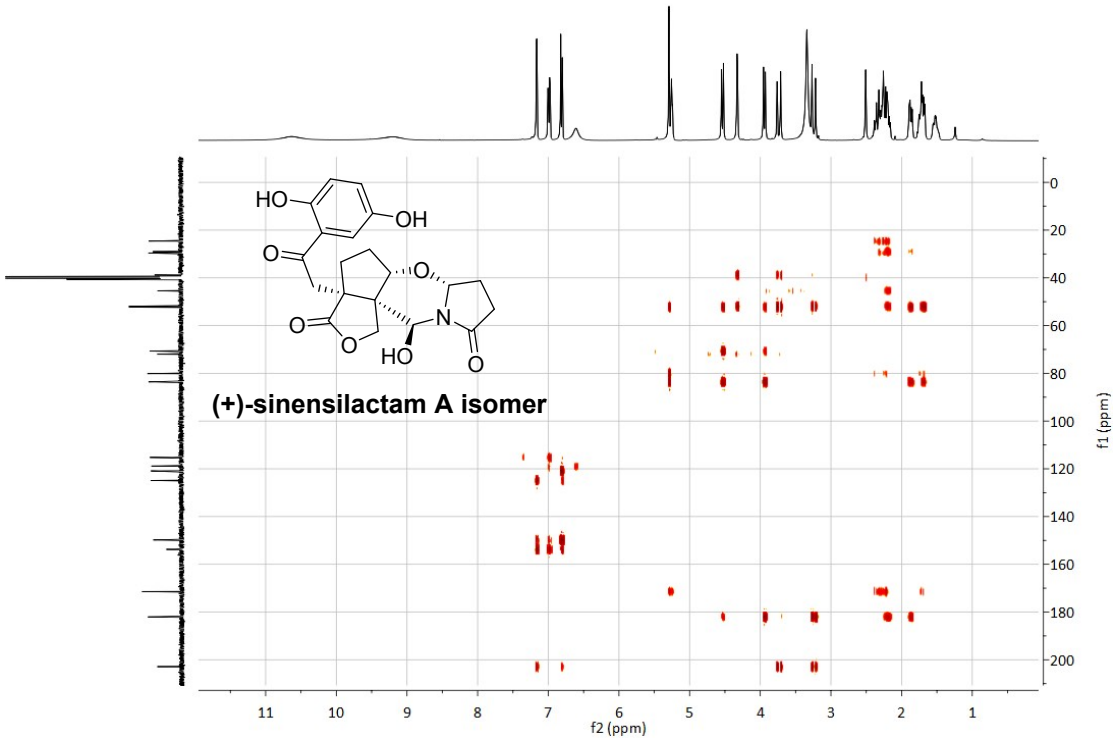


(+)-sinensilactam A isomer

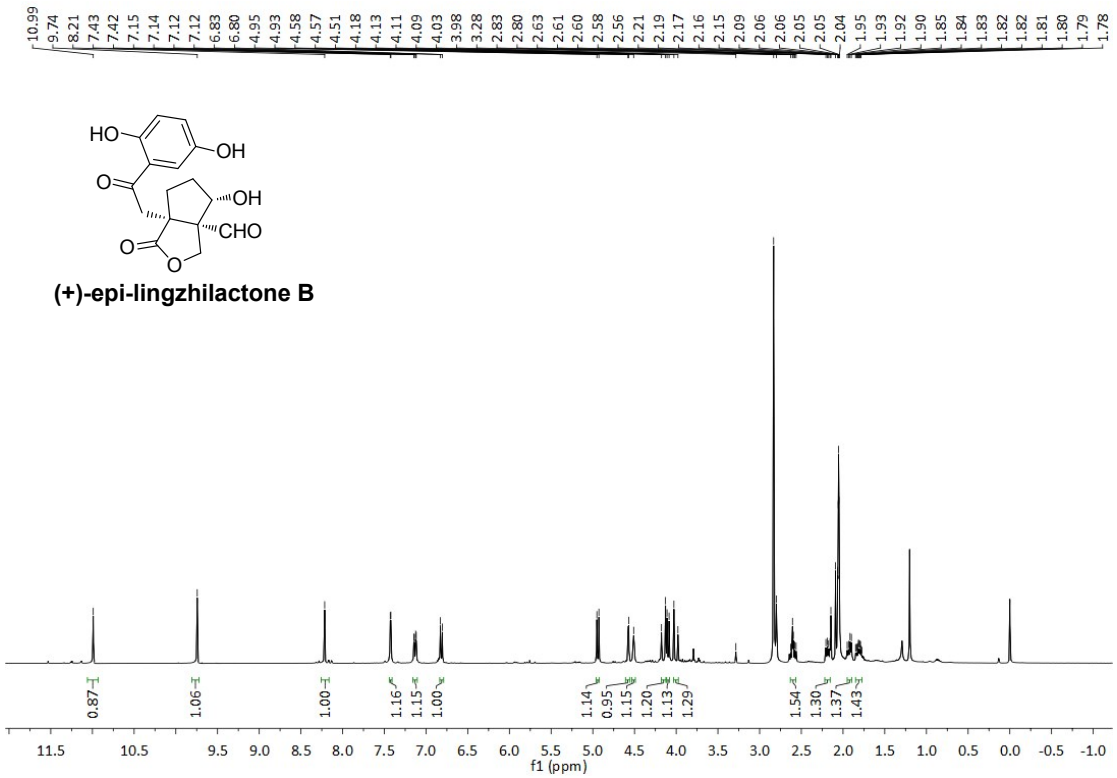
^{13}C NMR (100 MHz, DMSO-d$_6$) of (+)-sinensilactam A isomer



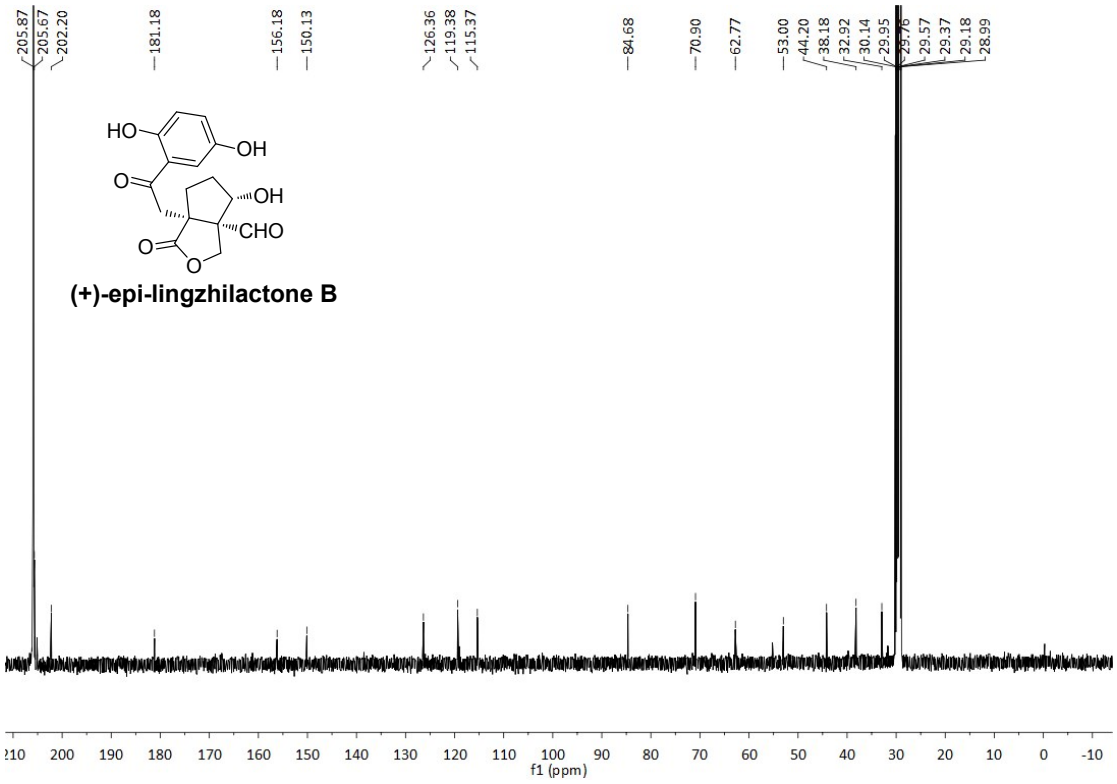
HSQC NMR (DMSO-d_6) of (+)-sinensilactam A isomer



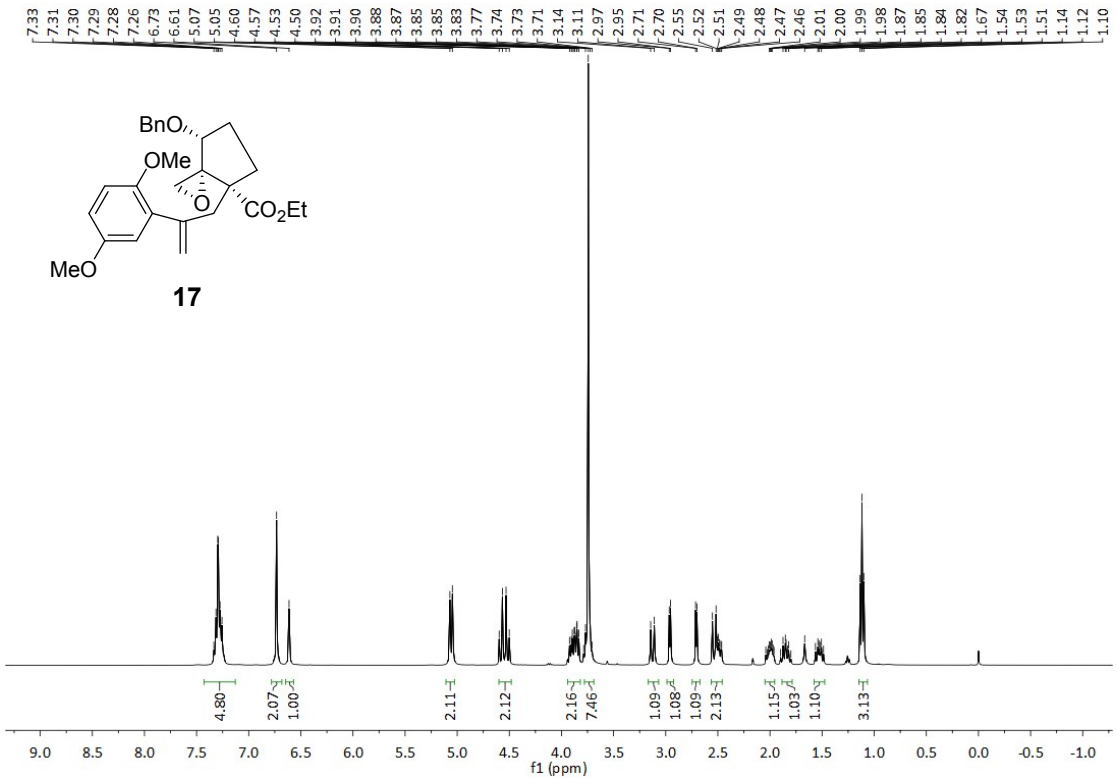
HMBC NMR (DMSO-d_6) of (+)-sinensilactam A isomer



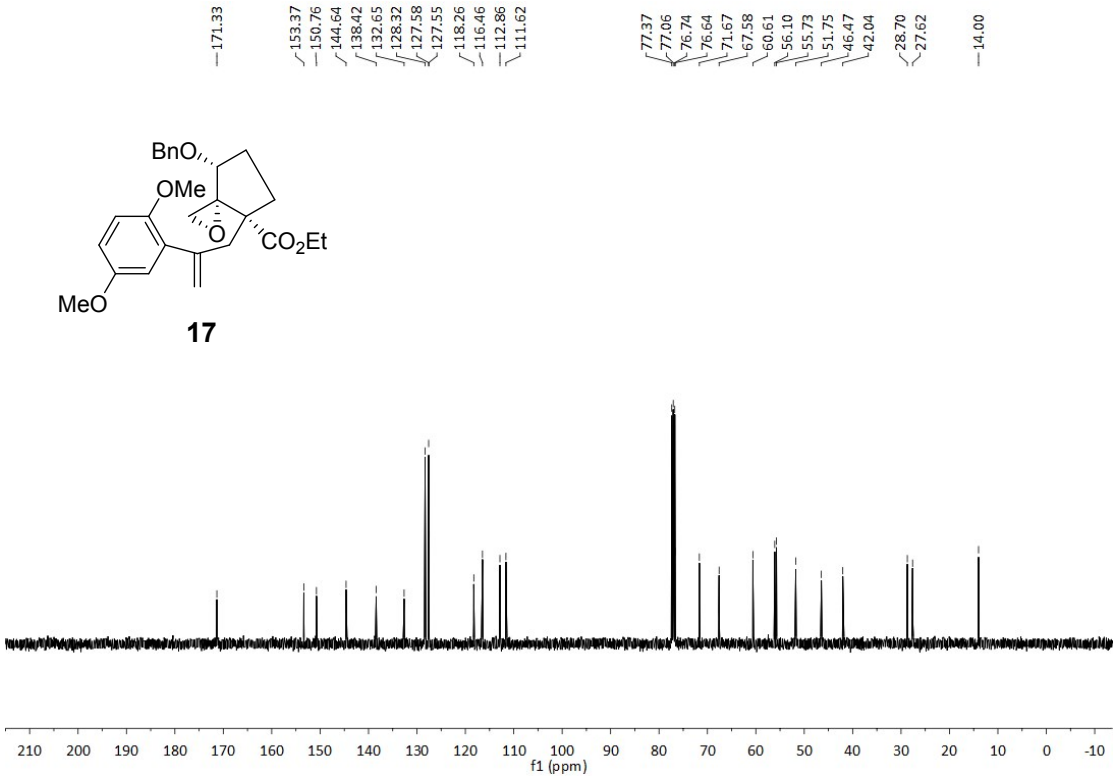
^{1}H NMR (400 MHz, acetone-d$_6$) of (+)-epi-lingzhilactone B



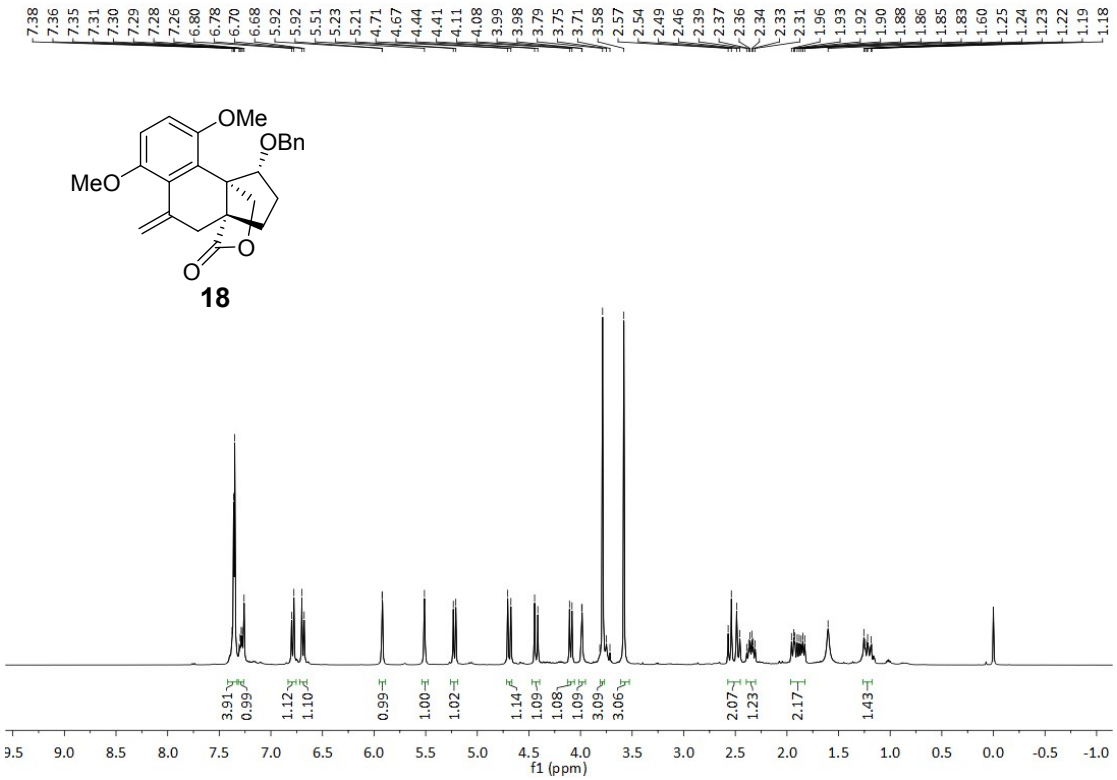
^{13}C NMR (100 MHz, acetone-d$_6$) of (+)-epi-lingzhilactone B



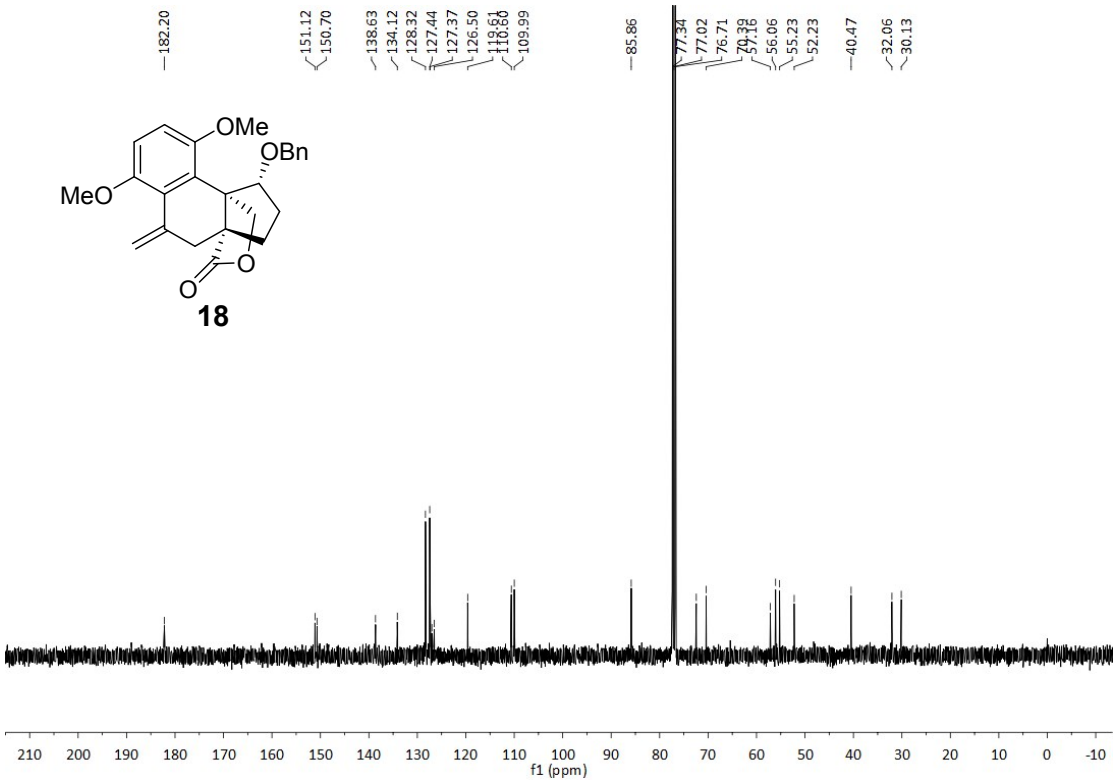
^{1}H NMR (400 MHz, $CDCl_3$) of compound 17



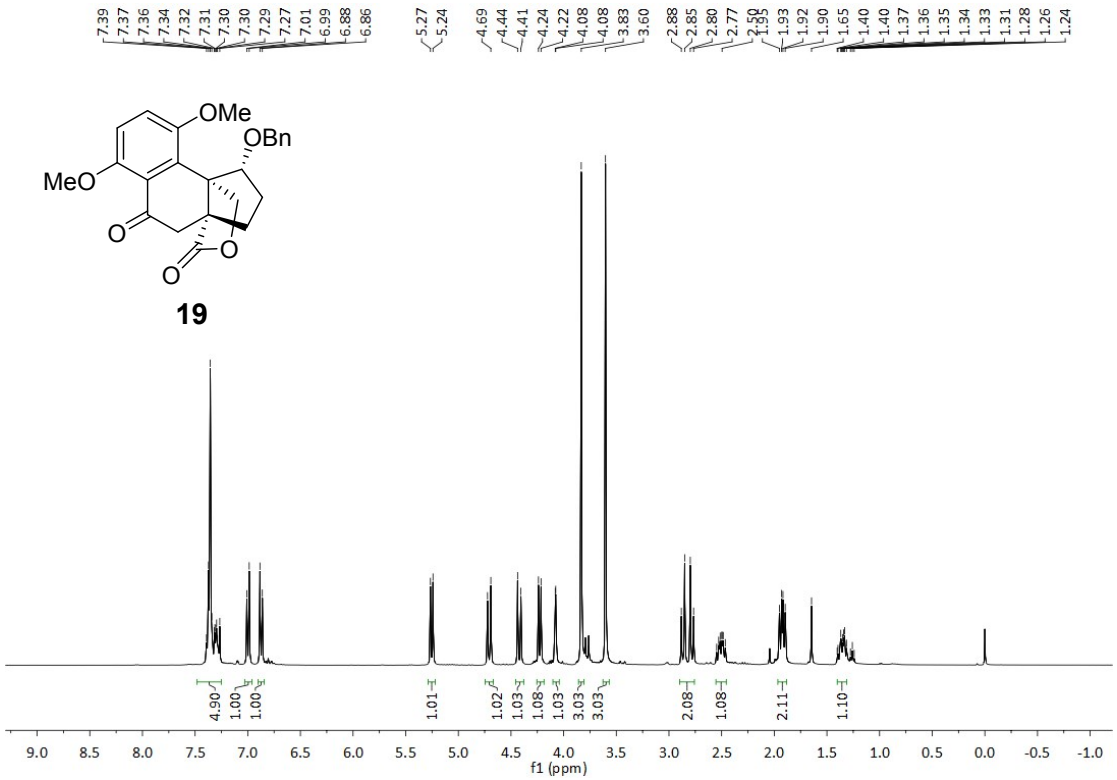
^{13}C NMR (100 MHz, $CDCl_3$) of compound 17



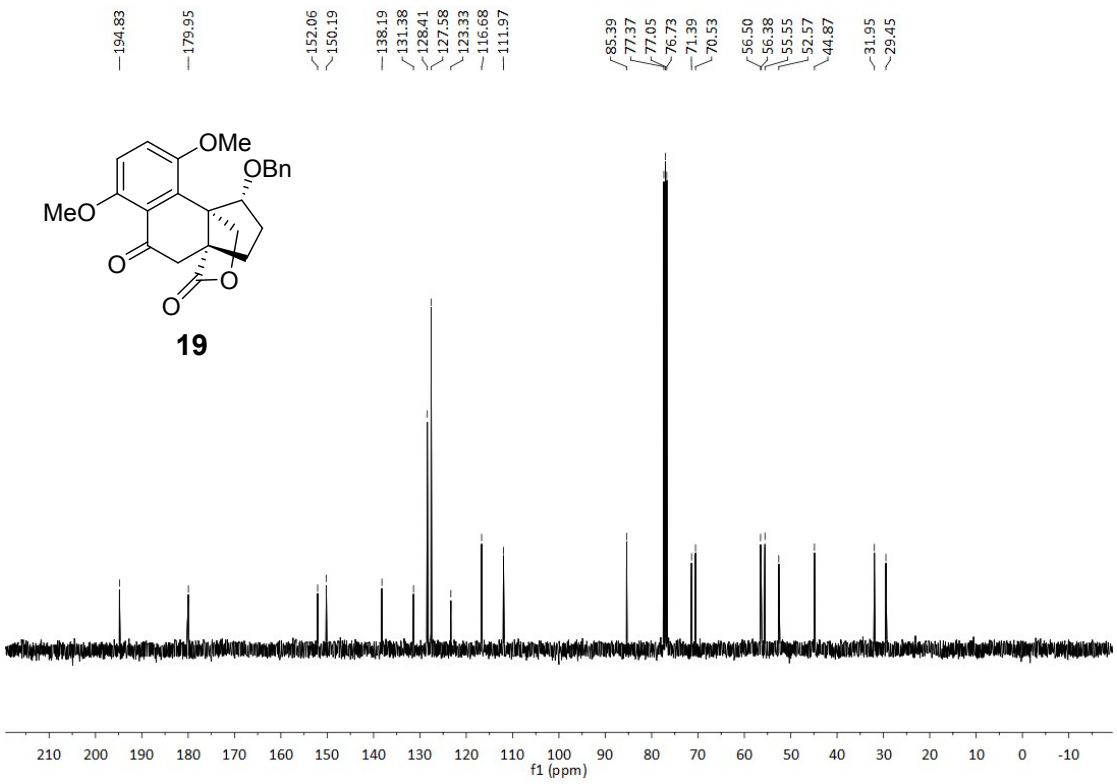
^{1}H NMR (400 MHz, $CDCl_3$) of compound 18



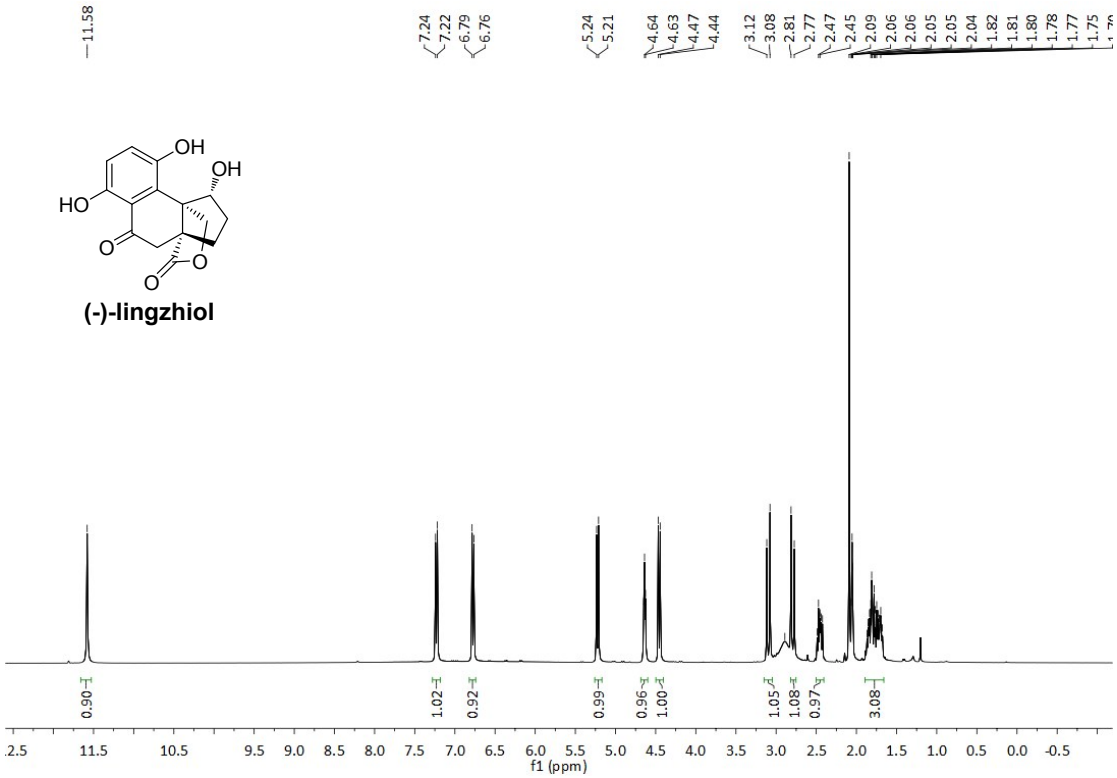
^{13}C NMR (100 MHz, $CDCl_3$) of compound 18



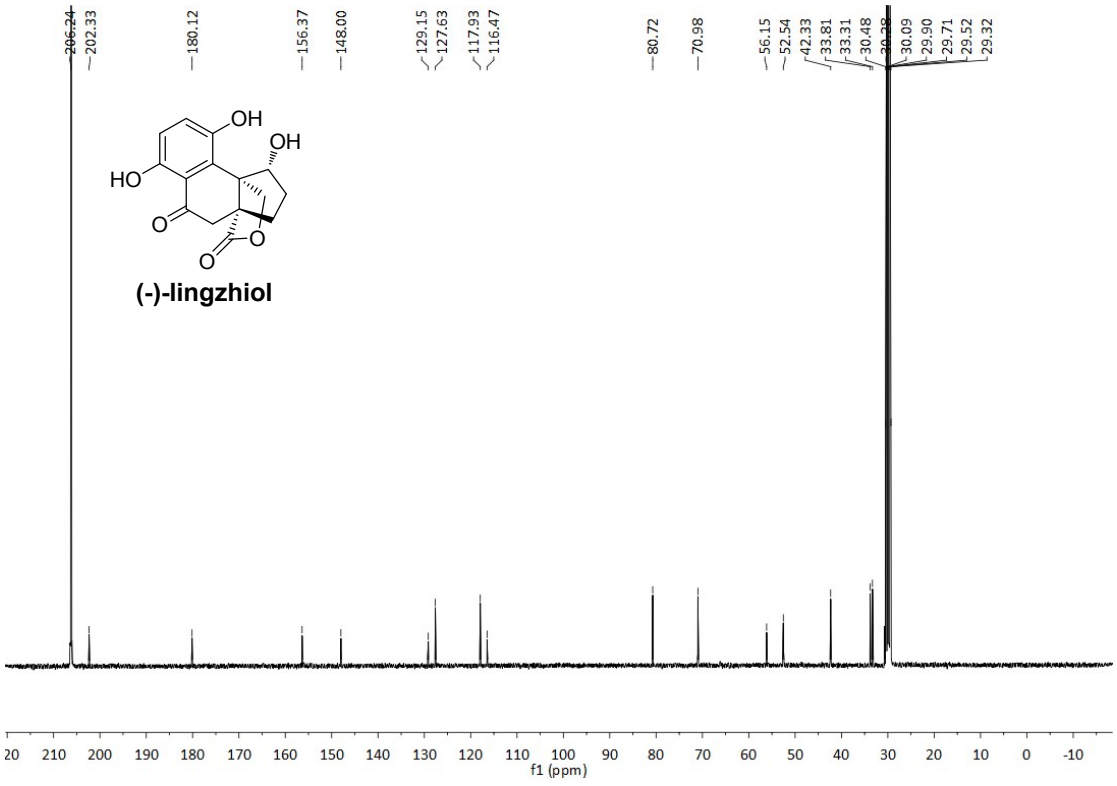
^{1}H NMR (400 MHz, $CDCl_3$) of compound 19



^{13}C NMR (100 MHz, $CDCl_3$) of compound 19

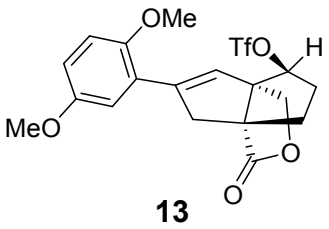


^{1}H NMR (400 MHz, acetone-d$_6$) of (-)-lingzhiol

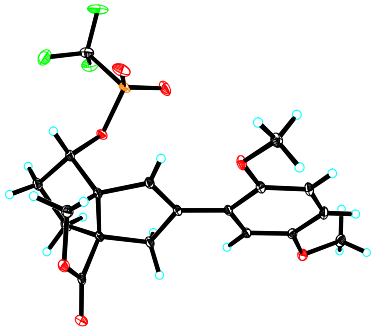


^{13}C NMR (100 MHz, acetone-d$_6$) of (-)-lingzhiol

V X-ray for the Synthesized Compounds

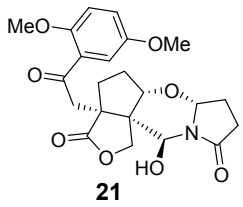


13

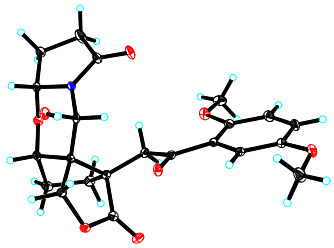


Crystal data and structure refinement for 13

Empirical formula	C19 H19 F3 O7 S	
Formula weight	448.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.1889(12) Å	□= 90°.
	b = 15.6583(16) Å	□= 103.564(2)°.
	c = 11.3387(12) Å	□ = 90°.
Volume	1931.1(4) $Å^3$	
Z	4	
Density (calculated)	1.542 Mg/m^3	
Absorption coefficient	0.237 mm^{-1}	
F(000)	928	
Crystal size	0.730 x 0.250 x 0.200 mm^3	
Theta range for data collection	2.260 to 31.139°.	
Index ranges	-15<=h<=16, -20<=k<=22, -16<=l<=14	
Reflections collected	21253	
Independent reflections	5730 [R(int) = 0.0323]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equiv.alents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5730 / 0 / 273	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0385, wR2 = 0.1050	
R indices (all data)	R1 = 0.0498, wR2 = 0.112	



21



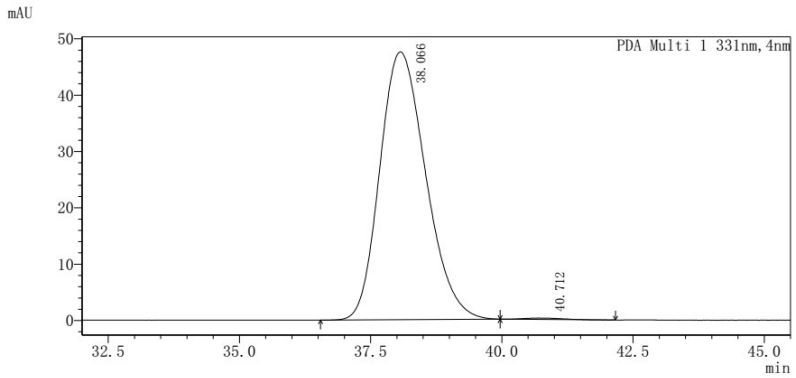
Crystal data and structure refinement for 21

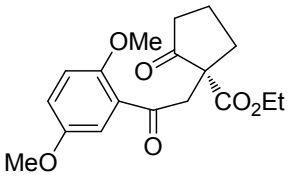
Empirical formula	C22 H25 N O8	
Formula weight	431.43	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 18.9306(14) Å	α= 90°.
	b = 11.0428(8) Å	β= 114.6950(10)°.
	c = 21.1989(16) Å	γ = 90°.
Volume	4026.3(5) $Å^3$	
Z	8	
Density (calculated)	1.423 Mg/m^3	
Absorption coefficient	0.109 mm^{-1}	
F(000)	1824	
Crystal size	0.290 x 0.250 x 0.180 mm^3	
Theta range for data collection	1.214 to 31.214°.	
Index ranges	-27<=h<=26, -14<=k<=16, -30<=l<=30	
Reflections collected	44978	
Independent reflections	12107 [R(int) = 0.0530]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equiv.alents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12107 / 0 / 569	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0488, wR2 = 0.1096	
R indices (all data)	R1 = 0.0842, wR2 = 0.1259	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.416 and -0.290 $e.Å^{-3}$	

VI Chiral HPLC chromatograms of Compounds

Chiral HPLC chromatograms of *rac* 2 and 2

<Chromatogram>





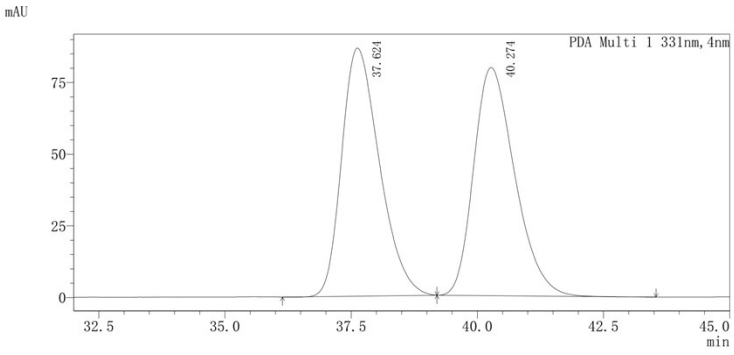
chiral-3

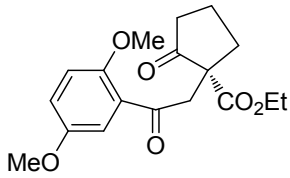
<Peak Results>

PDA Ch1 331nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	38.066	47549	2889592	99.594
2	40.712	248	11790	0.406

<Chromatogram>





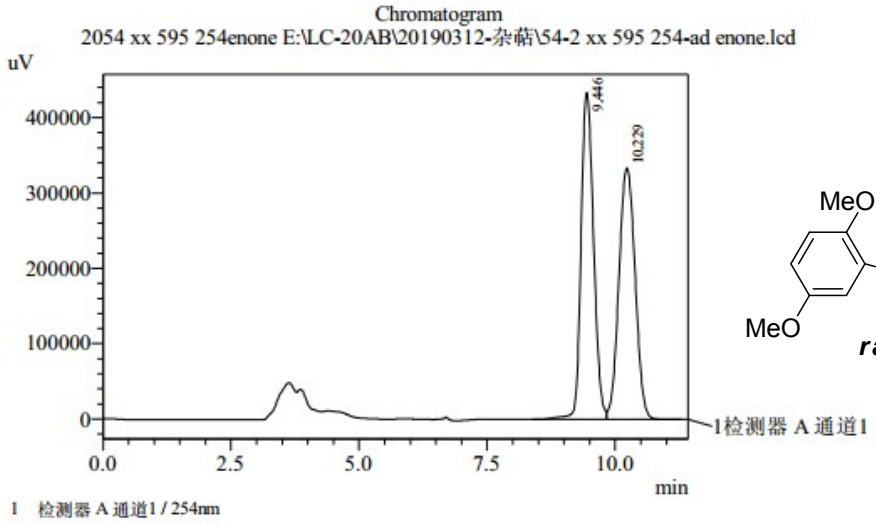
chiral-3

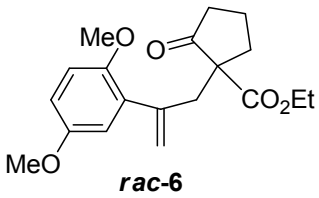
<Peak Results>

PDA Ch1 331nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	37.624	86535	4509854	50.016
2	40.274	79571	4506979	49.984

Chiral HPLC chromatograms of *rac* 6 and 6



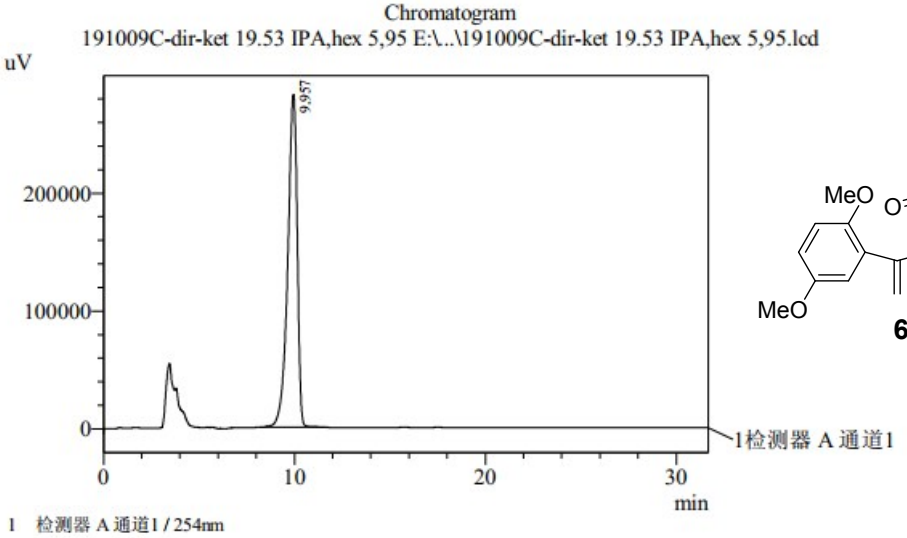


***rac*-6**

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.446	7396312	433907	50.097	56.513
2	10.229	7367647	333896	49.903	43.487
总计		14763959	767803	100.000	100.000



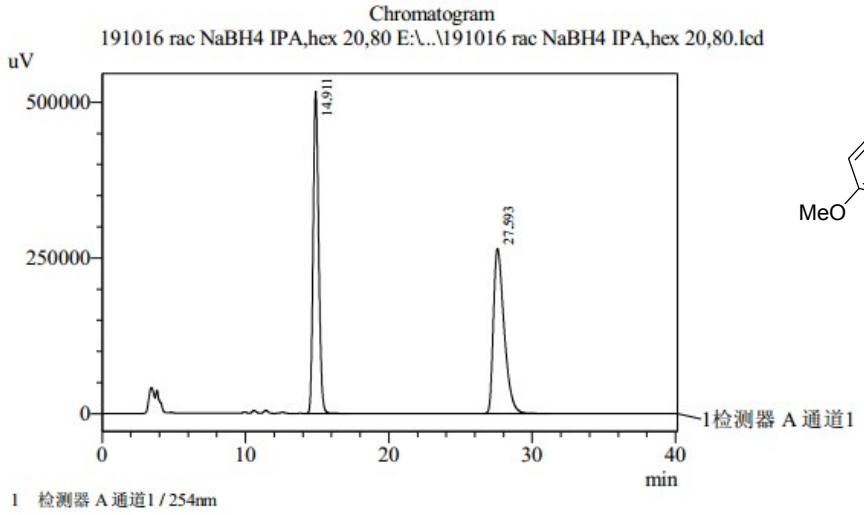
6

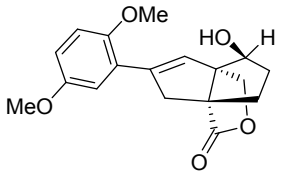
PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.957	9817544	282456	100.000	100.000
总计		9817544	282456	100.000	100.000

Chiral HPLC chromatograms of *rac* 12 and 12



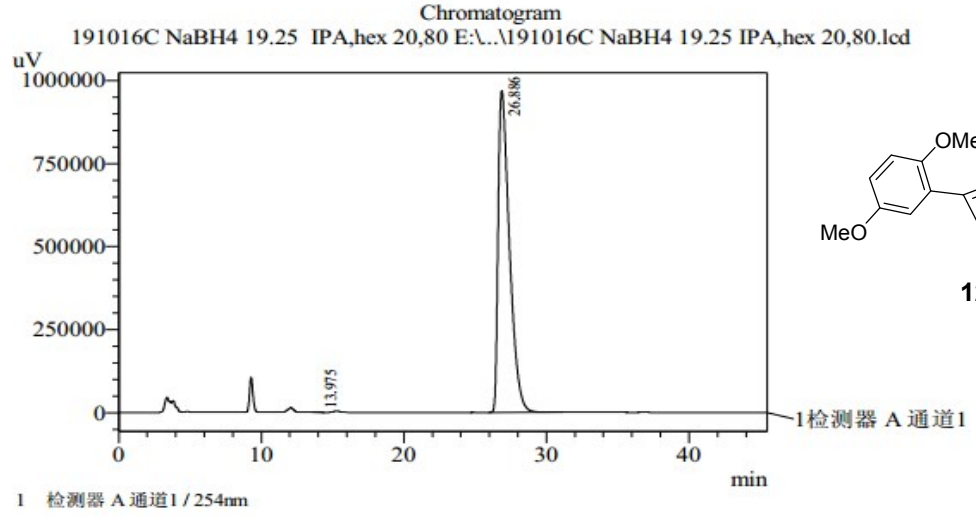


rac-12

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.911	13723741	516868	49.948	66.137
2	27.593	13752110	264648	50.052	33.863
总计		27475851	781516	100.000	100.000



12

PeakTable

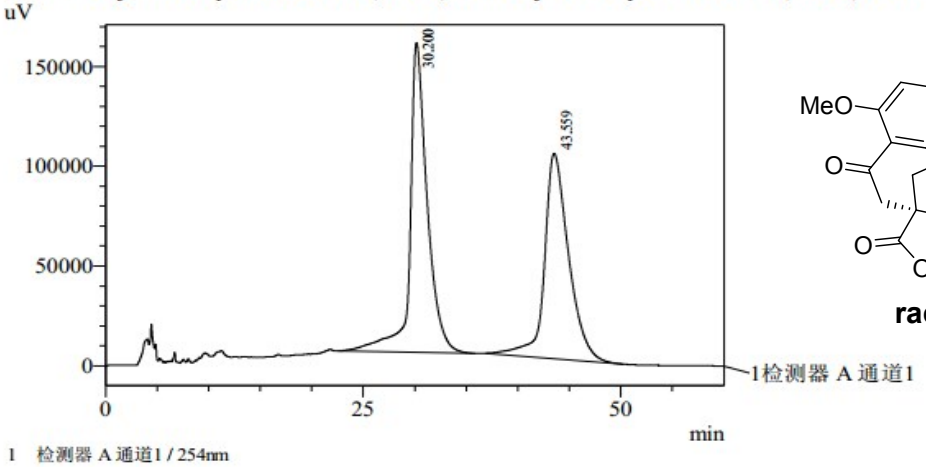
检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.975	9118	375	0.017	0.039
2	26.886	53358912	968604	99.983	99.961
总计		53368030	968979	100.000	100.000

Chiral HPLC chromatograms of *rac* 15 and 15

Chromatogram

191014rac ojh 254nm yichun 19.22 IPA,hex 20,80 ...rac 0jh 254nm yichun 19.22 IPA,hex 20,80.lcd



rac-15

1 检测器 A 通道1 / 254nm

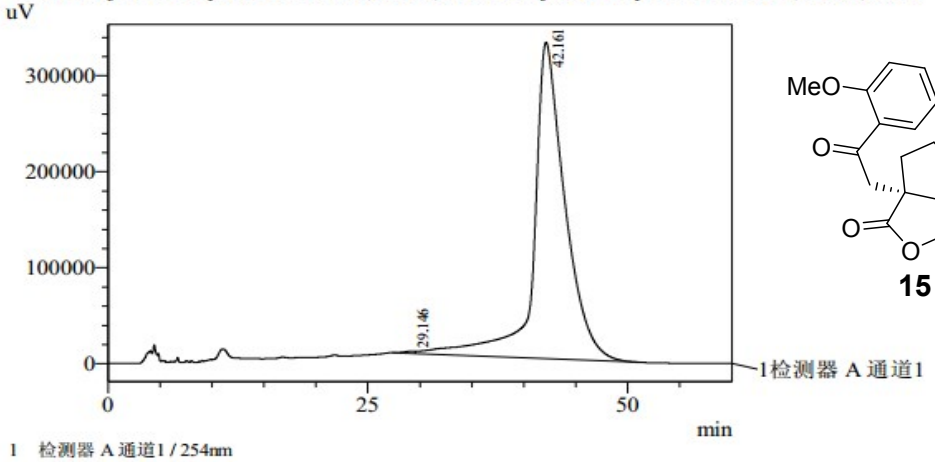
PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.200	18258278	155110	51.963	60.110
2	43.559	16878857	102935	48.037	39.890
总计		35137135	258044	100.000	100.000

Chromatogram

191014C ojh 254nm yichun 21.31 IPA,hex 20,80 ...14C 0jh 254nm yichun 21.31 IPA,hex 20,80.lcd



15

1 检测器 A 通道1 / 254nm

PeakTable

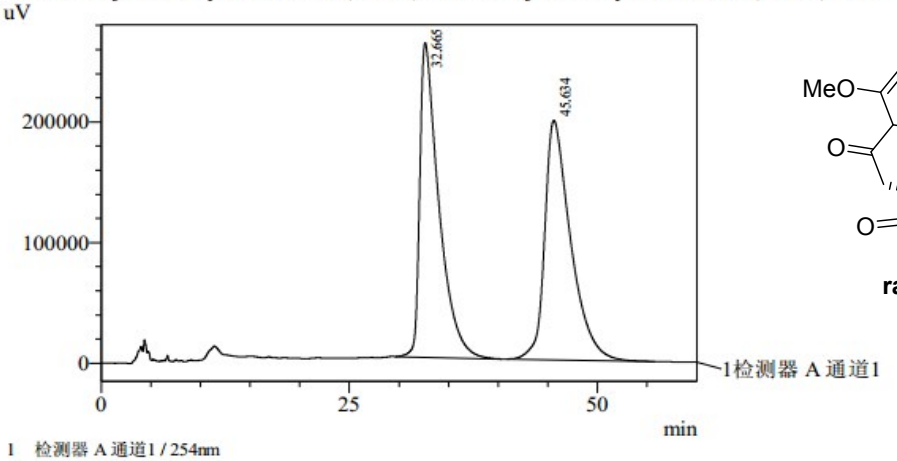
检测器 A Ch1 254nm

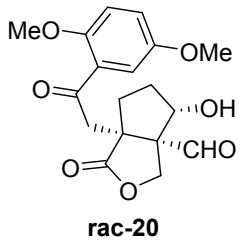
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.146	174460	2500	0.249	0.753
2	42.161	69944442	329605	99.751	99.247
总计		70118901	332105	100.000	100.000

Chiral HPLC chromatograms of *rac* 20 and 20

Chromatogram

191017rac ojh 254nm yichun 14.0 IPA,hex 20,80 ...17rac 0jh 254nm yichun 14.0 IPA,hex 20,80.lcd





rac-20

1 检测器 A 通道1 / 254nm

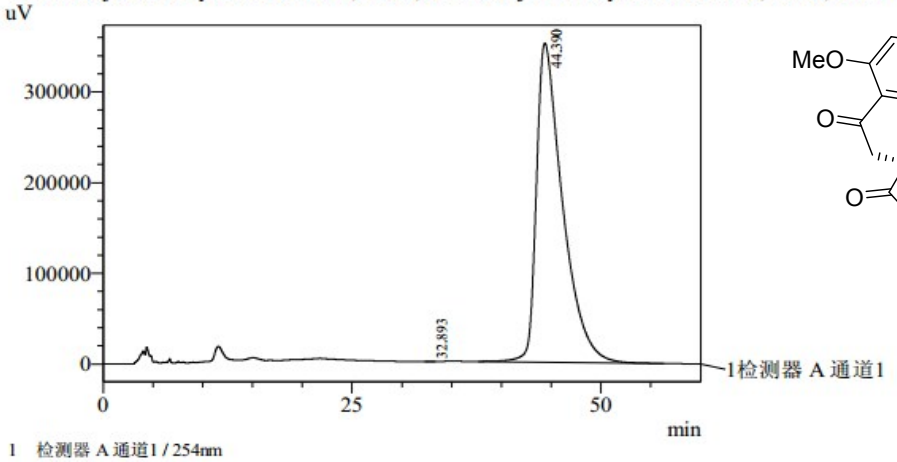
PeakTable

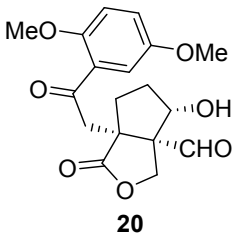
检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.665	34839830	260768	49.059	56.789
2	45.634	36176915	198420	50.941	43.211
总计		71016745	459188	100.000	100.000

Chromatogram

191017C ojh 254nm yichun 15.11 IPA,hex 20,80 ...17C 0jh 254nm yichun 15.11 IPA,hex 20,80.lcd





20

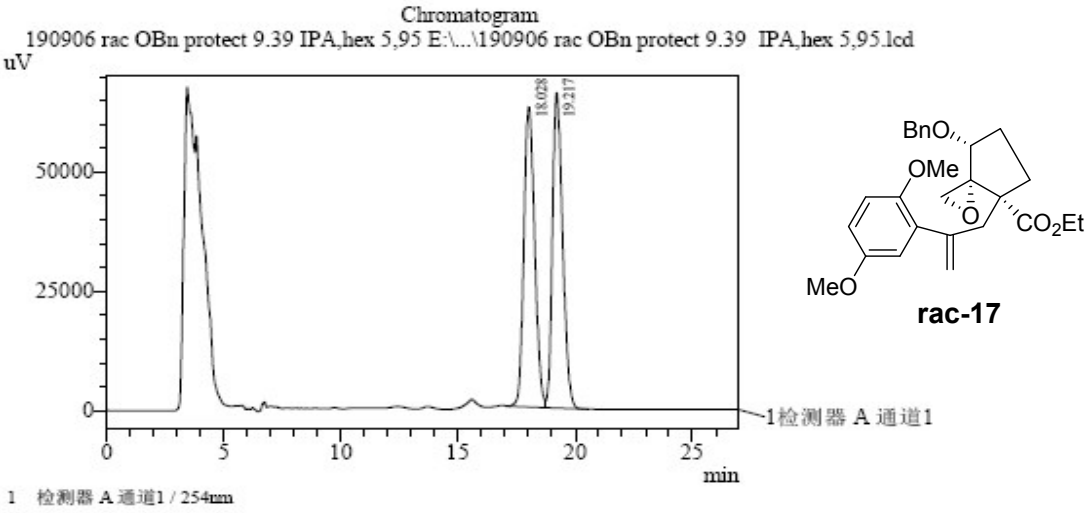
1 检测器 A 通道1 / 254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.893	3431	98	0.005	0.028
2	44.390	64380506	351845	99.995	99.972
总计		64383937	351943	100.000	100.000

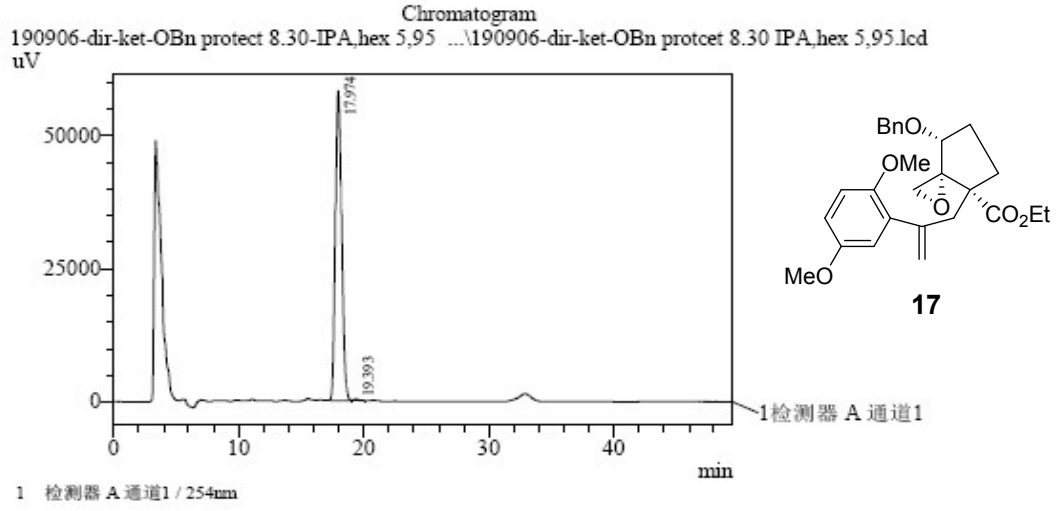
Chiral HPLC chromatograms of *rac* 17 and 17



PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.028	2012177	62991	50.154	48.803
2	19.217	1999810	66080	49.846	51.197
总计		4011987	129071	100.000	100.000

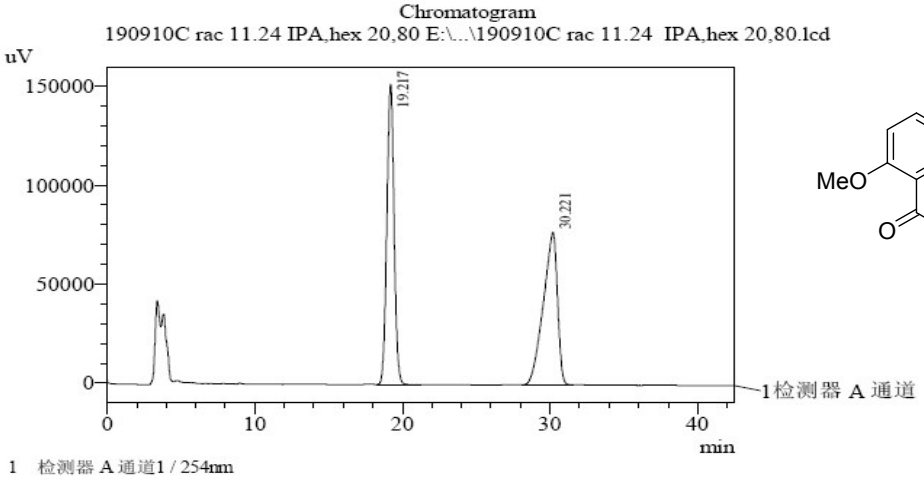


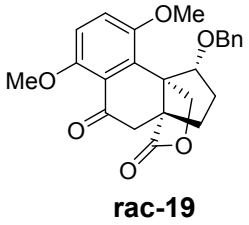
PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.974	2066330	58223	99.506	99.425
2	19.393	10262	337	0.494	0.575
总计		2076592	58560	100.000	100.000

Chiral HPLC chromatograms of *rac* 19 and 19





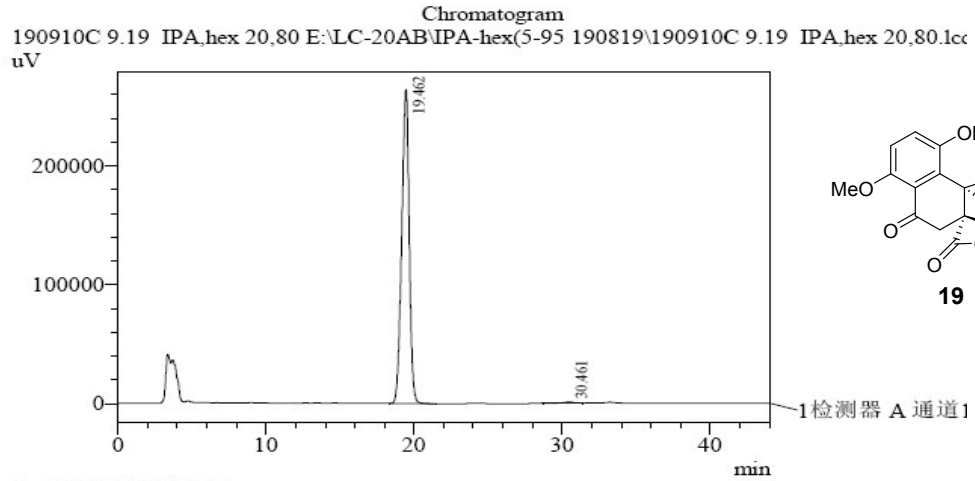
rac-19

1 检测器 A 通道1 / 254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.217	5136587	151809	50.056	66.330
2	30.221	5125056	77059	49.944	33.670
总计		10261643	228867	100.000	100.000



19

1 检测器 A 通道1 / 254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.462	9305247	264204	99.333	99.597
2	30.461	62496	1069	0.667	0.403
总计		9367743	265273	100.000	100.000