

Supplementary Information

A Flexible and Divergent Strategy to Flavonoids with a Chiral A-Ring Featuring Intramolecular Michael Addition: Stereoselective Synthesis of (+)-Cryptocaryone, (+)-Cryptogione F, and (+)-Cryptocaryanones A and B, as Well as (+)-Cryptochinones A and C

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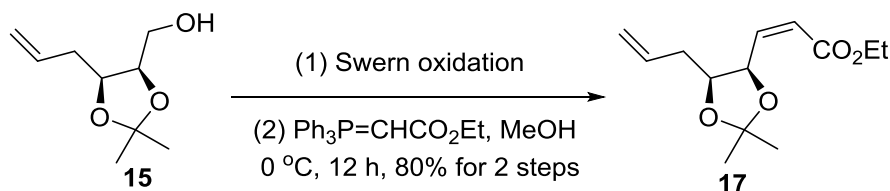
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Experimental procedures and spectroscopic data

General Information: Flash chromatography was performed using silica gel (200-300 mesh). Reactions were monitored by thin layer chromatography (TLC). Visualization was achieved under a UV lamp (254 nm), IR spectra were recorded on a commercial spectrophotometer. Optical rotations were reported as follows: $[\alpha]_D^{25}$ (c : g/100 mL, in solvent). ^1H NMR spectra were recorded on commercial instruments (400 MHz) with TMS as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as the internal standard, and were calibrated using residual undeuterated solvent as an internal reference (CDCl_3 : ^1H NMR = 7.26, ^{13}C NMR = 77.05). HRMS spectra were recorded by using a commercial apparatus and methanol or Dichloromethane was used to dissolve the sample. All air sensitive manipulations were carried out under a dry argon. Solvents for reaction were distilled prior to use: dichloromethane and PhCH_3 from CaH_2 , tetrahydrofuran (THF) from Na and acetone from Potassium carbonate, other reagents were obtained from commercial suppliers unless otherwise stated. Drying of organic extracts during the work-up of reactions was performed over anhydrous Na_2SO_4 .

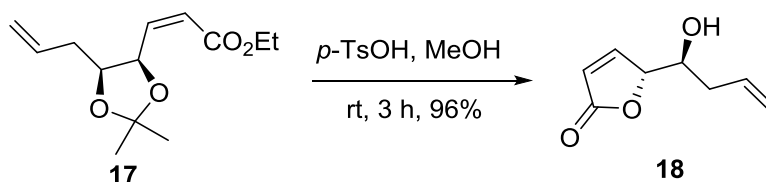
Experimental procedures



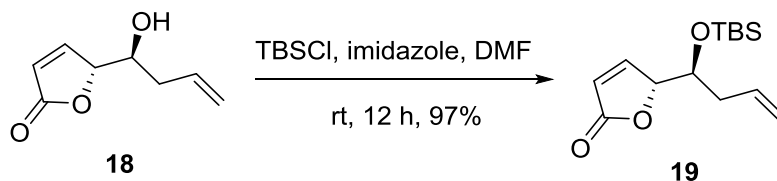
Compound 17: Oxalyl chloride (0.76 mL, 8.7 mmol) was added to a solution of DMSO (1.24 mL, 17.43 mmol) in CH_2Cl_2 (32 mL) at $-78\text{ }^\circ\text{C}$. The mixture was stirred for 30 min, then a solution of **15** (1.0 g, 5.81 mmol) in CH_2Cl_2 (7 mL) was added dropwise, and the resulting mixture was stirred for 2 h. Triethylamine (4.86 mL, 34.86 mmol) was added dropwise, and the mixture was stirred for 30 min and allowed to warm to rt. Water (30 mL) was added, and the mixture was extracted with CH_2Cl_2 (3×30 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The crude product was used in the next step without further purification.

$\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$ (2.5 g, 7.25 mmol) was added to a solution of the crude aldehyde in methanol (28 mL) at $0\text{ }^\circ\text{C}$. The resulting mixture was stirred at $0\text{ }^\circ\text{C}$ for 12 h, and concentrated in vacuo. The residue was purified by flash column chromatography using petroleum ether/ EtOAc (25:1) as eluent to afford compound **17** (1.1 g, 80% for 2 steps) as a colorless oil: $[\alpha]_D^{26} = -154.8^\circ$ ($c = 1.36$, CHCl_3); IR (neat)

ν_{max} : 2986, 2937, 1719, 1645, 1416, 1376, 1219, 1190, 1049, 914, 824 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.23 (dd, $J = 11.6, 7.6$ Hz, 1H), 5.91 (dd, $J = 11.6, 1.2$ Hz, 1H), 5.86 – 5.76 (m, 1H), 5.64 – 5.60 (m, 1H), 5.11 – 5.01 (m, 2H), 4.44 (ddd, $J = 8.7, 6.6, 4.6$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 2.22 – 2.07 (m, 2H), 1.50 (s, 3H), 1.36 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 146.4, 134.8, 121.7, 117.1, 108.7, 77.9, 75.1, 60.5, 35.2, 28.1, 25.3, 14.2; HRMS (ESI-TOF): m/z calcd for $\text{C}_{13}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$: 241.1434, found: 241.1431.

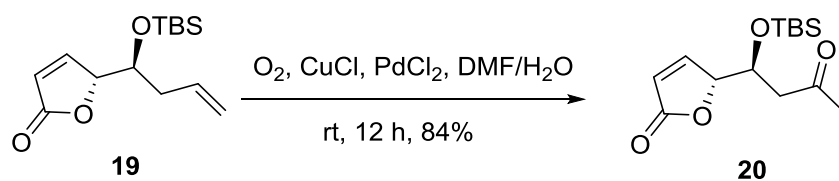


Compound 18: To a stirred solution of **17** (3.3 g, 13.7 mmol) in MeOH (50 mL) was added p -TsOH (474 mg, 2.75 mmol) at rt, and the resulting mixture was stirred for 3 h. The mixture was concentrated in vacuo, and purified by flash chromatography using petroleum ether/ EtOAc (2:1 to 1:1) as eluent to afford compound **18** (2.0 g, 96%) as a colorless oil: $[\alpha]_{\text{D}}^{26} = +169.9^\circ$ ($c = 1.04$, CHCl_3); IR (neat) ν_{max} : 3445, 3082, 2913, 1751, 1642, 1430, 1319, 1167, 1104, 1043, 921, 822 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (dd, $J = 5.6, 1.6$ Hz, 1H), 6.17 (dd, $J = 6.0, 2.0$ Hz, 1H), 5.91 – 5.77 (m, 1H), 5.23 – 5.18 (m, 2H), 4.95 (dt, $J = 5.7, 1.8$ Hz, 1H), 3.83 (td, $J = 9.7, 4.7$ Hz, 1H), 2.63 (d, $J = 4.8$ Hz, 1H), 2.51 – 2.44 (m, 1H), 2.38 – 2.30 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 154.1, 132.9, 122.6, 119.5, 85.3, 70.8, 38.0; HRMS (ESI-TOF): m/z calcd for $\text{C}_8\text{H}_{11}\text{O}_3$ $[\text{M}+\text{H}]^+$: 155.0703, found: 155.0705.

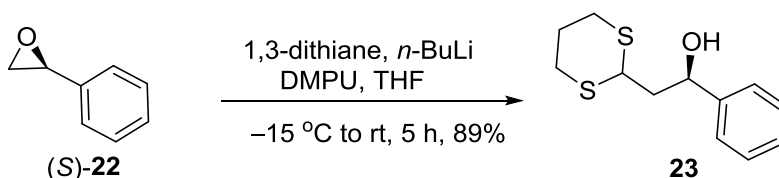


Compound 19: To a stirred solution of **18** (3.3 g, 13.7 mmol) in DMF (7 mL) were added imidazole (1.95 g, 28.6 mmol) and TBSCl (3.66 g, 24.3 mmol) at 0 $^\circ\text{C}$. The mixture was stirred at rt overnight, then it was diluted with water and extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with water and sat. NaCl, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using petroleum ether/ EtOAc (8:1) to afford compound **19** (3.6 g, 97%) as a colorless oil: $[\alpha]_{\text{D}}^{26} = +146.3^\circ$ ($c = 1.32$, CHCl_3); IR (neat) ν_{max} : 3081, 2955, 2932, 2892, 2858, 1760, 1473, 1356, 1256, 1160, 1116, 895, 835, 778 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (dd, $J = 5.6, 1.6$ Hz, 1H), 6.14 (dd, $J = 6.0, 2.0$ Hz, 1H), 5.91 – 5.81 (m, 1H), 5.22 – 5.14 (m, 2H), 4.95 (dt, $J = 5.0, 1.8$ Hz, 1H), 3.93 (dd, $J = 10.8, 5.2$ Hz, 1H), 2.45 – 2.38 (m, 2H), 0.85 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 154.0, 132.9, 122.6, 118.9, 84.9, 71.9,

39.2, 25.7, 18.0, -4.5, -4.9; HRMS (ESI-TOF): m/z calcd for $C_{14}H_{24}NaO_3Si$ $[M+Na]^+$: 291.1387, found: 291.1391.

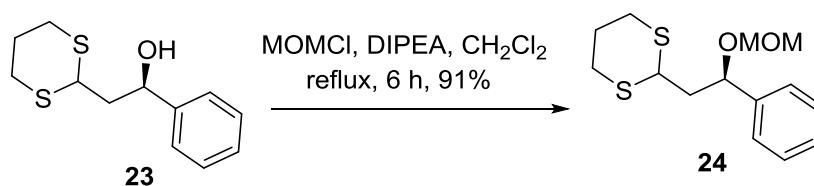


Compound 20: To a stirred solution of **19** (2.0 g, 7.46 mmol) in DMF (20 mL) and water (4 mL) were added PdCl_2 (0.13 g, 0.75 mmol) and CuCl (0.37 g, 3.73 mmol), and the mixture was stirred at room temperature overnight under an oxygen atmosphere. The mixture was diluted with water and extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with water and sat. NaCl , dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using petroleum ether/ EtOAc (6:1) to afford compound **20** (1.8 g, 84%) as a white solid: m.p. $34 - 35$ °C; $[\alpha]_D^{26} = +86.8$ ° ($c = 0.84$, CHCl_3); IR (neat) ν_{max} : 3413, 2932, 2858, 1759, 1718, 1364, 1256, 1161, 1092, 836, 779 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (dd, $J = 5.6, 1.6$ Hz, 1H), 6.14 (dd, $J = 5.6, 2.0$ Hz, 1H), 5.03 – 4.99 (m, 1H), 4.39 (dd, $J = 10.7, 5.6$ Hz, 1H), 2.70 (qd, $J = 16.9, 5.8$ Hz, 2H), 2.18 (s, 3H), 0.82 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 205.6, 172.6, 153.2, 122.9, 85.4, 68.4, 47.4, 31.4, 25.7, 17.9, -4.8, -5.0; HRMS (ESI-TOF): m/z calcd for $C_{14}H_{25}O_4Si$ $[M+H]^+$: 285.1517, found: 285.1516.

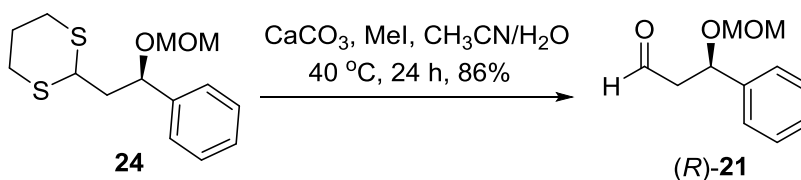


Compound 23: To a solution of 1,3-dithiane (1.2 g, 10 mmol) in THF (30 mL) was added dropwise $n\text{-BuLi}$ (4.4 mL, 2.5 M in pentane, 1.8 mmol) at -15 °C under an argon atmosphere, and the resulting mixture was stirred for 30 min before $(S)\text{-22}$ (1.15 mL, 10 mmol) was added. The reaction mixture was warmed to 0 °C, and DMPU (5 mL) was slowly added. After stirred at rt for 5 h, the reaction mixture was quenched with aqueous NH_4Cl and diluted with EtOAc. The organic layers was separated, and the aqueous layer was extracted with EtOAc (3×30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (2:1) to afford alcohol **23** (2.1 g, 89%) as a colorless oil: $[\alpha]_D^{26} = -16.4$ ° ($c = 1.24$, CHCl_3); IR (neat) ν_{max} : 3418, 2915, 1420, 1264, 1042, 897 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.32 (m, 4H), 7.30 – 7.27 (m, 1H), 5.03 – 4.99 (m, 1H), 4.17 (dd, $J = 8.6, 5.8$ Hz, 1H), 2.92 – 2.79 (m, 4H), 2.36 (br.s, 1H), 2.27 – 2.19 (m, 1H), 2.15 – 2.03 (m, 2H), 1.96 – 1.84

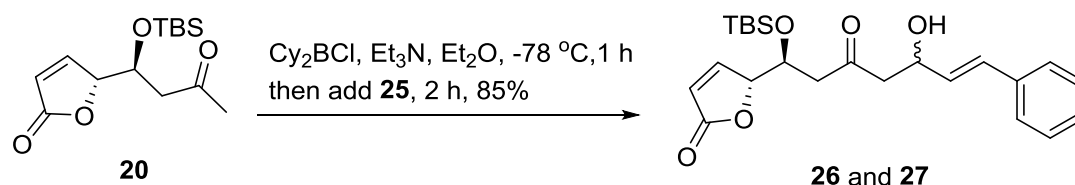
(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 128.6, 127.8, 125.8, 71.1, 44.4, 43.9, 30.0, 29.8, 25.9; HRMS (ESI-TOF): m/z calcd for $\text{C}_{12}\text{H}_{17}\text{OS}_2$ $[\text{M}+\text{H}]^+$: 241.0715, found: 241.0715.



Compound 24: To a solution of **23** (0.96 g, 4.0 mmol) in CH_2Cl_2 (28 mL) were slowly added DIPEA (1.25 mL, 7.1 mmol) and MOMCl (1.3 mL, 16.8 mmol). The resulting mixture was refluxed for 6 h, then it was quenched with sat. NaHCO_3 and extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (10:1) to afford compound **24** (1.03 g, 91%) as a colorless oil: $[\alpha]_D^{26} = -76.9^\circ$ ($c = 1.36$, CHCl_3); IR (neat) ν_{max} : 3060, 2940, 2894, 1493, 1454, 1422, 1148, 1024, 915, 763 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 4.89 (dd, $J = 9.0, 5.0$ Hz, 1H), 4.56 – 4.50 (m, 2H), 4.10 (dd, $J = 9.0, 5.7$ Hz, 1H), 3.37 (s, 3H), 2.91 – 2.77 (m, 4H), 2.33 – 2.26 (m, 1H), 2.13 – 2.02 (m, 2H), 1.96 – 1.85 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.1, 128.5, 127.9, 126.9, 94.3, 74.4, 55.8, 43.6, 43.5, 29.9, 29.6, 26.0; HRMS (ESI-TOF): m/z calcd for $\text{C}_{14}\text{H}_{21}\text{O}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 285.0977, found: 285.0972.



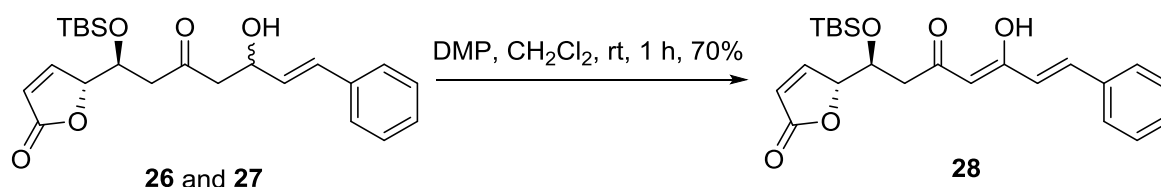
Compound (R)-21: To a stirred mixture of **24** (0.92 g, 3.2 mmol) and CaCO_3 (3.2 g, 32 mmol) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9/1, 32.0 mL) was added MeI (1.8 mL, 28.8 mmol). The reaction mixture was stirred at 40 $^\circ\text{C}$ for 24 h, and was filtered through a pad of Celite. The two phases were separated and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (10:1) to afford aldehyde **21** (535 mg, 86%) as a colorless oil: $[\alpha]_D^{26} = -165.9^\circ$ ($c = 1.08$, CHCl_3); IR (neat) ν_{max} : 3032, 2948, 2892, 1727, 1456, 1400, 1363, 1152, 1029, 920, 762 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 9.82 (dd, $J = 2.5, 1.4$ Hz, 1H), 7.41 – 7.28 (m, 5H), 5.18 (dd, $J = 9.2, 4.0$ Hz, 1H), 4.58 – 4.49 (m, 2H), 3.35 (s, 3H), 2.98 (ddd, $J = 16.5, 9.3, 2.7$ Hz, 1H), 2.69 (ddd, $J = 16.5, 4.0, 1.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.4, 140.1, 128.8, 128.3, 126.8, 94.1, 72.7, 55.8, 51.3; HRMS (ESI-TOF): m/z calcd for $\text{C}_{11}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 195.1016, found: 195.1018.



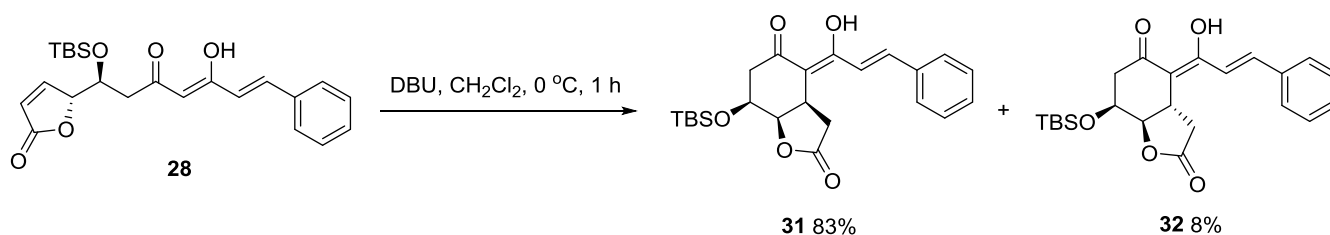
Compound 26 and 27: To a solution of **20** (1.0 g, 3.52 mmol) in dry Et₂O (40 mL) were slowly added triethylamine (0.93 mL, 6.70 mmol) and Cy₂BCl (5.6 mL, 1 M in hexanes, 5.6 mmol) at -78°C under an argon atmosphere successively. The mixture was stirred for 1 h, then a solution of cinnamaldehyde (**25**) of Et₂O (7.0 mL, 1 M in Et₂O, 7.0 mmol) was added at -78°C . The resulting mixture was stirred for 2 h, then quenched by the addition of MeOH (8 mL) and pH ≈ 7 buffer (2 mL), followed by MeOH (8 mL) and 30% H₂O₂ solution (4 mL) at 0°C . The mixture was warmed to rt and stirred for 0.5 h before being diluted with H₂O and EtOAc. The organic layer was separated and the aqueous phase was extracted with EtOAc (3 \times 40 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/EtOAc (10:1) to afford compound **26** and **27** (1.2 g, 85%) .

Compound 26 (more polar isomer): a yellow oil, $[\alpha]_{\text{D}}^{26} = +42.8^\circ$ ($c = 0.43$, CHCl₃); IR (neat) ν_{max} : 3451, 2931, 2858, 1756, 1712, 1636, 1382, 1256, 1091, 1049, 836, 779 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (dd, $J = 5.8, 1.5$ Hz, 1H), 7.39 – 7.35 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.24 (m, 1H), 6.64 (d, $J = 15.3$ Hz, 1H), 6.20 (dd, $J = 15.9, 6.2$ Hz, 1H), 6.16 (dd, $J = 5.8, 2.0$ Hz, 1H), 5.03 (dt, $J = 4.6, 1.8$ Hz, 1H), 4.77 (s, 1H), 4.44 (dd, $J = 10.6, 5.8$ Hz, 1H), 2.86 (d, $J = 3.0$ Hz, 1H), 2.84 – 2.68 (m, 4H), 0.84 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 207.6, 172.6, 153.1, 136.3, 130.7, 129.9, 128.6, 127.9, 126.5, 123.0, 85.4, 68.6, 68.3, 50.6, 47.7, 25.7, 18.0, -4.8 , -4.9 ; HRMS (ESI-TOF): m/z calcd for C₂₃H₃₃O₅Si [M+H]⁺: 417.2092, found: 417.2091.

Compound 27 (less polar isomer): a yellow oil, $[\alpha]_{\text{D}}^{26} = +63.0^\circ$ ($c = 0.33$, CHCl₃); IR (neat) ν_{max} : 3466, 2930, 2857, 1756, 1712, 1367, 1256, 1093, 1042, 837, 780 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (dd, $J = 5.8, 1.5$ Hz, 1H), 7.39 – 7.35 (m, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.24 (m, 1H), 6.64 (dd, $J = 15.9, 0.7$ Hz, 1H), 6.20 (dd, $J = 15.9, 6.2$ Hz, 1H), 6.15 (dd, $J = 5.8, 2.0$ Hz, 1H), 5.02 (dt, $J = 4.9, 1.8$ Hz, 1H), 4.78 (dd, $J = 11.4, 6.1$ Hz, 1H), 4.42 (q, $J = 5.7$ Hz, 1H), 2.93 (s, 1H), 2.80 – 2.74 (m, 4H), 0.84 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 207.6, 172.6, 153.2, 136.3, 130.7, 129.9, 128.6, 127.9, 126.5, 122.9, 85.4, 68.5, 68.2, 50.6, 47.6, 25.7, 18.0, -4.7 , -5.0 ; HRMS (ESI-TOF): m/z calcd for C₂₃H₃₃O₅Si [M+H]⁺: 417.2092, found: 417.2088.



Compound 28: To a solution of **26** and **27** (55 mg, 0.132 mmol) in CH₂Cl₂ (3 mL) was added Dess–Martin periodinane (84 mg, 0.20 mmol) at 0 °C. The reaction mixture was stirred at rt for 1 h, then it was quenched with a mixture of sat. NaHCO₃ (10 mL), sat. Na₂S₂O₃ (10 mL) and H₂O (10 mL) and extracted with CH₂Cl₂ (3 × 25 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (4:1) to afford compound **28** (38 mg, 70%) as a brown oil: [α]_D²⁶ = +49.2 ° (c = 0.64, CHCl₃); IR (neat) ν_{max}: 2954, 2930, 2857, 1787, 1759, 1637, 1586, 1443, 1256, 1157, 1112, 835, 778 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 15.27 (br s, 1H), 7.63 (d, *J* = 15.9 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.43 – 7.36 (m, 3H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 5.8, 2.0 Hz, 1H), 5.69 (s, 1H), 5.08 (dt, *J* = 4.0, 1.8 Hz, 1H), 4.44 (td, *J* = 6.1, 4.4 Hz, 1H), 2.66 (dd, *J* = 6.2, 3.1 Hz, 2H), 0.83 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 177.5, 172.7, 153.0, 140.7, 134.8, 130.2, 129.0, 128.1, 123.1, 122.2, 102.1, 85.5, 69.4, 44.7, 25.7, 18.0, –4.9, –5.0; HRMS (ESI-TOF): *m/z* calcd for C₂₃H₃₁O₅Si [M+H]⁺: 415.1935, found: 415.1939.

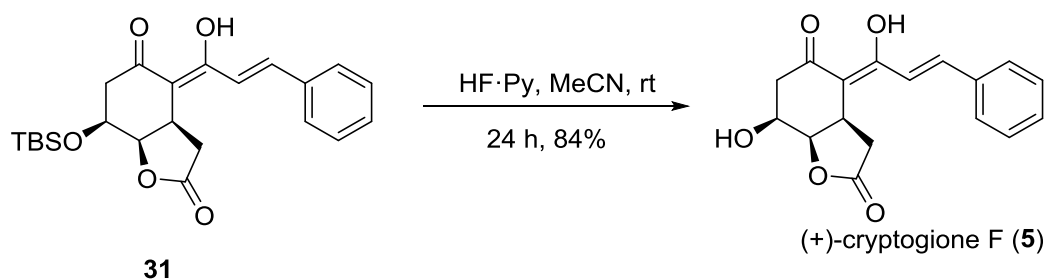


Compound 31 and 32: To a solution of **28** (70 mg, 0.17 mmol) in CH₂Cl₂ (3 mL) was added DBU (28 μL, 0.19 mmol) at 0 °C. The mixture was stirred for 1 h, then it was quenched with solution of sat. NH₄Cl, and extracted with CH₂Cl₂ (3 × 25 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (6:1 to 4:1) to afford compound **31** (59 mg, 83%) and compound **32** (5.6 mg, 8%).

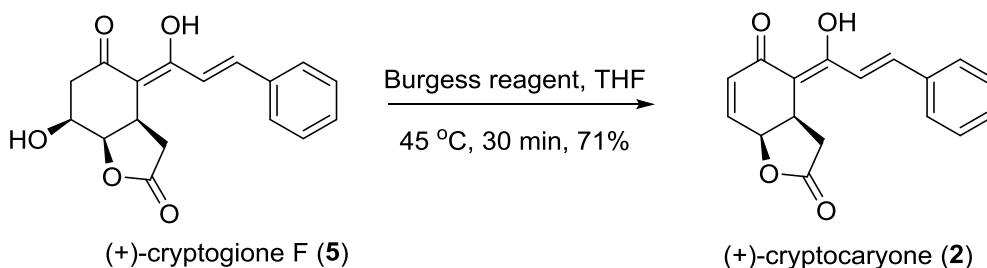
Compound 31: a brown oil, $[\alpha]_D^{26} = +313.8^\circ$ ($c = 0.42$, CHCl_3); IR (neat) ν_{max} : 3381, 2930, 2857, 1781, 1628, 1583, 1410, 1257, 1087, 1050, 839, 781 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 16.82 (d, $J = 0.9$ Hz, 1H), 7.79 (d, $J = 15.6$ Hz, 1H), 7.57 – 7.51 (m, 2H), 7.46 – 7.37 (m, 3H), 6.72 (dd, $J = 15.5, 0.9$ Hz, 1H), 4.70 (dd, $J = 8.4, 2.8$ Hz, 1H), 4.38 (dd, $J = 6.2, 3.1$ Hz, 1H), 3.79 (dt, $J = 11.0, 9.6$ Hz, 1H), 2.82 (dd, $J = 17.1, 9.7$ Hz, 1H), 2.72 (dd, $J = 17.1, 11.2$ Hz, 1H), 2.69 – 2.65 (m, 2H), 0.85 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.6, 179.0, 176.0, 143.0, 134.7, 130.7, 129.1, 128.3, 118.7, 106.0, 78.2, 67.6, 40.6, 38.1, 33.6, 25.7, 17.9, –5.2, –5.2; HRMS (ESI-TOF): m/z calcd for $\text{C}_{23}\text{H}_{31}\text{O}_5\text{Si} [\text{M}+\text{H}]^+$: 415.1935, found: 415.1934.

Compound 32: a yellow solid, m.p. 106 – 108 °C; $[\alpha]_D^{22} = -140.0^\circ (c = 0.56, \text{CHCl}_3)$; IR (neat) ν_{max} : 3371, 2928, 2852, 1782, 1622, 1580, 1406, 1250, 1109, 1047, 837, 771 cm^{-1} ; ^1H NMR (400 MHz,

CDCl₃) δ 16.89 (d, J = 0.5 Hz, 1H), 7.81 (d, J = 15.6 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.45 – 7.39 (m, 3H), 6.73 (d, J = 15.6 Hz, 1H), 4.61 (t, J = 6.4 Hz, 1H), 4.29 (td, J = 5.9, 4.0 Hz, 1H), 3.82 (ddd, J = 8.6, 7.0, 5.8 Hz, 1H), 3.05 (dd, J = 17.5, 8.8 Hz, 1H), 2.77 (dd, J = 17.8, 3.9 Hz, 1H), 2.55 – 2.44 (m, 2H), 0.87 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 189.9, 180.8, 175.0, 143.4, 134.7, 130.8, 129.1, 128.4, 118.7, 106.2, 80.0, 66.0, 38.6, 38.0, 32.9, 25.6, 18.0, –4.8, –4.9; HRMS (ESI-TOF): m/z calcd for C₂₃H₃₁O₅Si [M+H]⁺: 415.1935, found: 415.1930.

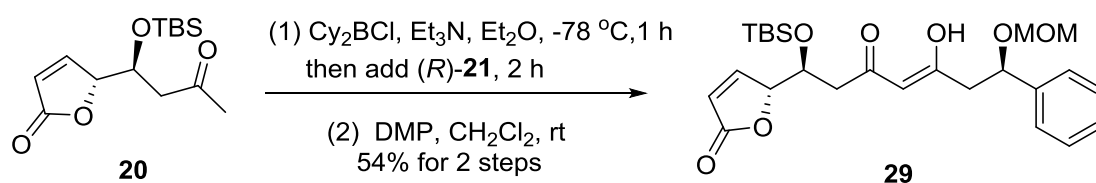


(+)-Cryptogione F (5): To a solution of **31** (50 mg, 0.12 mmol) in CH₃CN (2 mL) at 0 °C was added HF Py complex (70% HF, 0.2 mL) dropwise. The mixture was stirred for 24 h, then it was diluted with water and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with sat. NaHCO₃, dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (1:1) to afford **(+)-5** (30 mg, 84%) as a pale-yellow solid: m.p. 106 – 108 °C; [α]_D²⁶ = +190.1 ° (c = 0.05, MeOH); IR (neat) ν_{\max} : 3426, 2928, 1773, 1628, 1579, 1409, 1190, 1074, 1045, 973, 764 cm⁻¹; ¹H NMR (400 MHz, CDCl₃-CD₃OD) δ 7.77 (d, J = 15.4 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.44 – 7.40 (m, 3H), 6.75 (d, J = 15.5 Hz, 1H), 4.80 (dd, J = 8.0 Hz, 2.8 Hz, 1H), 4.31 – 4.27 (m, 1H), 3.84 (dd, J = 17.4, 8.7 Hz, 1H), 3.41 (s, 1H), 2.91 (dd, J = 17.2, 9.3 Hz, 1H), 2.83 – 2.72 (m, 2H), 2.68 (dd, J = 18.0, 2.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃-CD₃OD) δ 190.6, 179.5, 177.2, 143.1, 134.5, 130.6, 128.9, 128.2, 118.5, 105.9, 79.1, 65.5, 38.9, 38.0, 33.5; HRMS (ESI-TOF): m/z calcd for C₁₇H₁₆O₅Na [M+Na]⁺: 323.0889, found: 323.0890.



(+)-Cryptocaryone (2): To a solution of **5** (20 mg, 0.067 mmol) in dry THF (1.3 mL) was added Burgess reagent (43 mg, 0.17 mmol) at rt. The mixture was stirred for 30 min at 45 °C, then it was diluted with water and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were

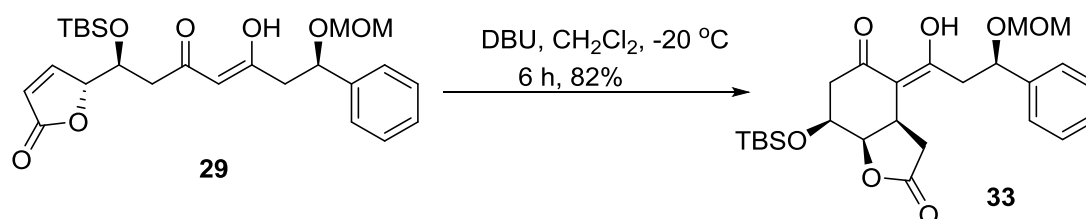
dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (4:1) to afford (+)-**2** (13.4 mg, 71%) as yellow solid: m.p. 152 – 153 °C; $[\alpha]_{\text{D}}^{26} = +775.6^\circ$ ($c = 0.80$, CHCl_3); IR (neat) ν_{max} : 3385, 2925, 1781, 1628, 1577, 1415, 1284, 1148, 1019, 758 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 15.99 (d, $J = 1.3$ Hz, 1H), 7.77 (d, $J = 15.6$ Hz, 1H), 7.58 – 7.55 (m, 2H), 7.43 – 7.41 (m, 3H), 6.78 (dd, $J = 15.6, 1.2$ Hz, 1H), 6.55 (ddd, $J = 10.2, 2.1, 1.1$ Hz, 1H), 6.21 (dd, $J = 10.2, 1.9$ Hz, 1H), 5.48 (dt, $J = 8.8, 2.0$ Hz, 1H), 3.99 (dtd, $J = 12.2, 8.8, 0.9$ Hz, 1H), 2.79 (dd, $J = 17.6, 8.7$ Hz, 1H), 2.62 (dd, $J = 17.2, 12.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.9, 174.5, 174.1, 142.4, 139.8, 134.8, 130.6, 130.1, 129.1, 128.2, 116.7, 103.3, 76.2, 35.3, 33.9; HRMS (ESI-TOF): m/z calcd for $\text{C}_{17}\text{H}_{14}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 305.0784, found: 305.0789.



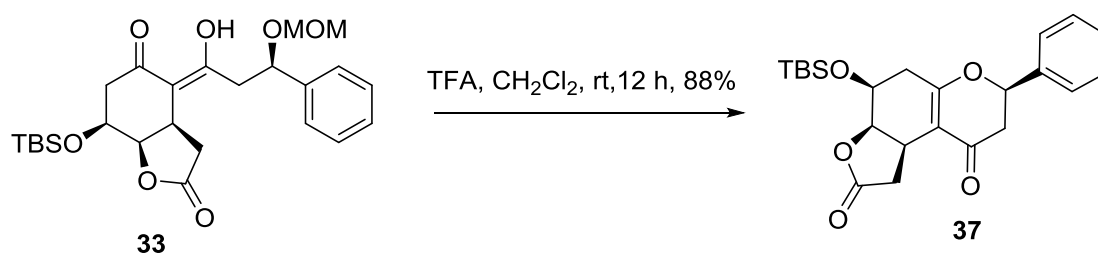
Compound 29: To a solution of **20** (432 mg, 1.52 mmol) in dry Et_2O (15 mL) was slowly added triethylamine and Cy_2BCl (2.6 mL, 1 M in hexanes, 2.6 mmol) at -78°C under an argon atmosphere successively. The mixture was stirred at the same temperature for 1 h, then a solution of aldehyde (R)-**21** (440 mg, 2.28 mmol) of Et_2O (3 mL) was added at -78°C . The mixture was stirred at -78°C for 2 h, then quenched by the addition of MeOH (4 mL) and pH ≈ 7 buffer (1 mL), followed by MeOH (4 mL) and 30% H_2O_2 solution (2 mL) at 0°C . The mixture was warmed to rt and stirred for 0.5 h before being diluted with H_2O and EtOAc. The layers were separated and the aqueous phase was extracted with EtOAc (3×30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (4:1 to 2:1) to afford a mixture of two isomers.

To a solution of the above mixture in CH_2Cl_2 (20 mL) was added DMP (722 mg, 1.7 mmol) at 0°C . The reaction mixture was stirred at rt for 40 min, then it was quenched with sat. NaHCO_3 (15 mL), sat. $\text{Na}_2\text{S}_2\text{O}_3$ (15 mL) and H_2O (15 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (4:1) to afford compound **29** (391 mg, 54% for 2 steps) as a yellowish oil: $[\alpha]_{\text{D}}^{26} = +111.2^\circ$ ($c = 0.44$, CHCl_3); IR (neat) ν_{max} : 3381, 2931, 2857, 1760, 1605, 1464, 1256, 1097, 836, 779 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 15.38 (br s, 1H), 7.46 (dd, $J = 5.8, 1.5$ Hz, 1H), 7.35 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 6.16 (dd, $J = 5.8, 2.0$ Hz, 1H), 5.56 (s, 1H), 5.08 (dd, $J = 9.2, 4.7$ Hz, 1H), 4.99 (dt, $J = 4.2, 1.8$ Hz, 1H), 4.49 (s, 2H), 4.36 – 4.31 (m, 1H), 3.28 (s, 3H), 2.80 (dd, $J = 14.7, 9.2$ Hz, 1H), 2.62 (dd, $J = 14.7, 4.7$ Hz, 1H), 2.54 (d, $J = 6.2$ Hz, 2H), 0.83 (s, 9H), 0.05 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.9, 189.8, 172.6, 152.9, 140.5, 128.7,

128.6, 128.1, 126.8, 123.1, 102.4, 94.1, 85.3, 74.3, 69.3, 55.7, 46.8, 43.2, 25.7, 18.0, -5.0; HRMS (ESI-TOF): m/z calcd for $C_{25}H_{36}O_7SiNa$ $[M+Na]^+$: 499.2123, found: 499.2115.

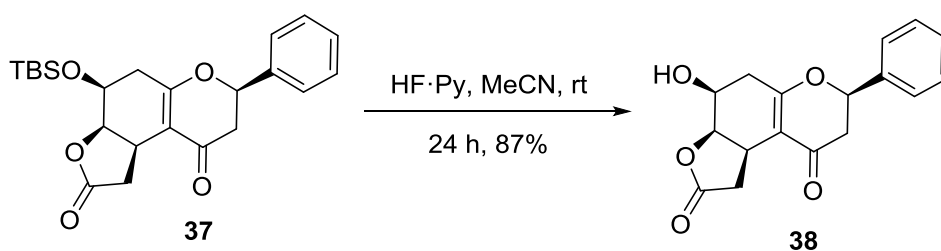


Compound 33: To a solution of **29** (120 mg, 0.25 mmol) in CH_2Cl_2 (5 mL) was added DBU (41 μ L, 0.28 mmol) at $-20\text{ }^\circ\text{C}$. The mixture was stirred for 6 h, and quenched with sat. NH_4Cl , and extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/EtOAc (4:1) to afford compound **33** (98 mg, 82%) as a yellowish oil: $[\alpha]_D^{26} = +246.2^\circ$ ($c = 0.52$, $CHCl_3$); IR (neat) ν_{max} : 3346, 2953, 2931, 2892, 1783, 1596, 1466, 1410, 1257, 1153, 1088, 840, 781 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 16.69 (s, 1H), 7.36 – 7.34 (m, 4H), 7.33 – 7.27 (m, 1H), 5.21 (dd, $J = 9.4, 4.4$ Hz, 1H), 4.55 (dd, $J = 8.2, 2.8$ Hz, 1H), 4.46 (q, $J = 6.9$ Hz, 2H), 4.30 (q, $J = 3.2$ Hz, 1H), 3.45 (dt, $J = 10.8, 9.5$ Hz, 1H), 3.26 (s, 3H), 2.94 (dd, $J = 9.5, 4.4$ Hz, 1H), 2.90 (dd, $J = 9.5, 1.3$ Hz, 1H), 2.80 (dd, $J = 17.4, 11.1$ Hz, 1H), 2.61 – 2.54 (m, 3H), 0.85 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 184.6, 176.3, 140.6, 128.7, 128.2, 126.6, 107.0, 93.9, 78.1, 74.4, 67.1, 55.6, 44.6, 38.7, 37.4, 33.8, 25.6, 17.8, -5.2, -5.3; HRMS (ESI-TOF): m/z calcd for $C_{25}H_{37}O_7Si$ $[M+H]^+$: 477.2303, found: 477.2302.

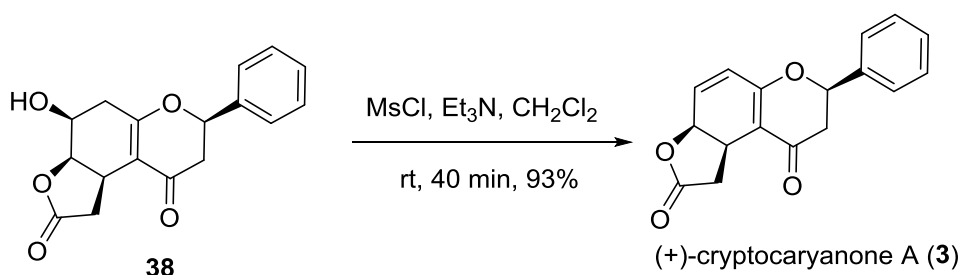


Compound 37: To a solution of **33** (56 mg, 0.12 mmol) in CH_2Cl_2 (3 mL) was slowly added trifluoroacetic acid (0.6 mL) at $0\text{ }^\circ\text{C}$. The mixture was stirred at rt overnight, then it was diluted with water and extracted with CH_2Cl_2 (3×25 mL). The organic phase was washed with sat. $NaHCO_3$ and sat. $NaCl$, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using petroleum ether/EtOAc (4:1 to 2:1) to afford compound **37** (44 mg, 88%) as a pale yellow oil: $[\alpha]_D^{26} = +52.2^\circ$ ($c = 0.74$, $CHCl_3$); IR (neat) ν_{max} : 2953, 2857, 1780, 1668, 1620, 1412, 1368, 1172, 1088, 938, 839, 781 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.34 (m, 5H), 5.40 (dd, $J = 14.1, 3.4$ Hz, 1H), 4.58 (dd, $J = 8.2, 2.8$ Hz, 1H), 4.32 (dd, $J = 6.4, 3.1$ Hz, 1H), 3.55 (dd, $J = 18.9, 9.5$

Hz, 1H), 2.99 (dd, $J = 17.6, 9.6$ Hz, 1H), 2.91 (dd, $J = 16.7, 14.2$ Hz, 1H), 2.67 (dd, $J = 16.7, 3.5$ Hz, 1H), 2.61 (ddd, $J = 18.3, 2.8, 1.5$ Hz, 1H), 2.54 (dd, $J = 18.3, 3.7$ Hz, 1H), 2.38 (dd, $J = 17.6, 10.7$ Hz, 1H), 0.87 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.8, 176.9, 167.4, 137.8, 129.1, 128.9, 126.1, 111.4, 80.8, 78.0, 67.1, 42.9, 35.1, 34.9, 31.9, 25.7, 17.9, $-5.1, -5.3$; HRMS (ESI-TOF): m/z calcd for $\text{C}_{23}\text{H}_{31}\text{O}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 415.1935, found: 415.1941.

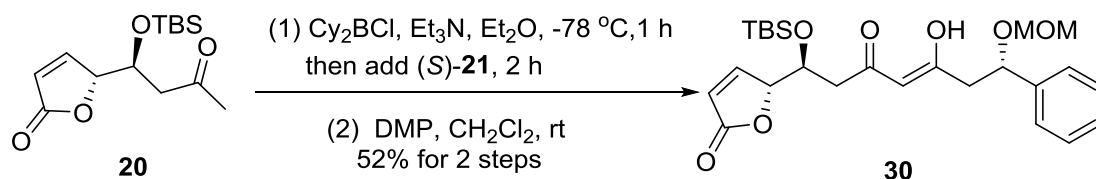


Compound 38: To a solution of **37** (58 mg, 0.14 mmol) in anhydrous CH_3CN (2.3 mL) was added HF Py complex (70%, 0.23 mL) at 0°C . The reaction was slowly warmed to rt and stirred for 24 h, then it was diluted with water and extracted with ethyl acetate. The organic phase was washed with sat. NaHCO_3 , dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using petroleum ether/ EtOAc (1:1) to afford compound **38** (37 mg, 87%) as a colorless oil: $[\alpha]_{\text{D}}^{26} = +62.7^\circ$ ($c = 0.52$, CHCl_3); IR (neat) ν_{max} : 3436, 2920, 1773, 1662, 1612, 1416, 1330, 1173, 1074, 758 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.36 (m, 5H), 5.41 (dd, $J = 14.1, 3.4$ Hz, 1H), 4.70 (dd, $J = 7.8, 2.7$ Hz, 1H), 4.33 (s, 1H), 3.59 (q, $J = 8.7$ Hz, 1H), 3.29 (d, $J = 4.1$ Hz, 1H), 3.04 – 2.93 (m, 2H), 2.74 – 2.59 (m, 3H), 2.49 (dd, $J = 17.9, 8.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.1, 177.6, 167.7, 137.7, 129.0, 128.9, 126.2, 110.8, 81.0, 78.7, 66.1, 42.8, 34.9, 33.6, 32.0; HRMS (ESI-TOF): m/z calcd for $\text{C}_{17}\text{H}_{17}\text{O}_5$ $[\text{M}+\text{H}]^+$: 301.1071, found: 301.1072.



(+)-Cryptocaryanone A (3): To a solution of **38** (30 mg, 0.10 mmol) in CH_2Cl_2 (2 mL) were slowly added Et_3N (0.14 mL, 1.0 mmol) and MsCl (31 μL , 0.4 mmol) at 0°C . The mixture was stirred at rt for 40 min, then it was quenched with water and extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (4:1 to 2:1) to afford (+)-**3** (26 mg, 93%) as a white powder. $[\alpha]_{\text{D}}^{26} = +182.3^\circ$ ($c = 0.44$, CHCl_3); IR (neat) ν_{max} : 2925, 1779, 1655, 1588, 1426, 1377,

1324, 1167, 1012, 758 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.37 (m, 5H), 6.28 (dd, J = 10.0, 2.8 Hz, 1H), 6.09 (dd, J = 10.0, 2.0 Hz, 1H), 5.51 – 5.44 (m, 2H), 3.87 (dt, J = 10.4, 9.2 Hz, 1H), 2.98 (dd, J = 18.0, 9.2 Hz, 1H), 2.92 (dd, J = 14.0, 9.4 Hz, 1H), 2.72 (dd, J = 17.1, 3.6 Hz, 1H), 2.39 (dd, J = 17.9, 10.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.3, 175.4, 162.6, 137.5, 134.7, 129.2, 129.0, 126.2, 124.1, 108.8, 80.9, 76.5, 42.8, 33.2, 30.6; HRMS (ESI-TOF): m/z calcd for $\text{C}_{17}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 283.0965, found: 283.0962.



Compound 30: To a solution of **20** (260 mg, 0.92 mmol) in dry Et_2O (9 mL) was slowly added Et_3N (0.26 mL, 1.84 mmol) and Cy_2BCl (1.56 mL, 1 M in hexanes, 1.56 mmol) at -78°C under an argon atmosphere successively. The resulting mixture was stirred at the same temperature for 1 h, then a solution of aldehyde (S)-**21** (230 mg, 1.2 mmol) of Et_2O (2 mL) was added at -78°C . The mixture was stirred at -78°C for 2 h, then quenched by the addition of MeOH (2 mL) and pH \approx 7 buffer (0.5 mL), followed by MeOH (2 mL) and 30% H_2O_2 solution (1 mL) at 0°C . The reaction mixture was warmed to rt and stirred for 0.5 h before being diluted with H_2O and EtOAc . The layers were separated and the aqueous phase was extracted with EtOAc (3×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (2:1) to afford a mixture of two isomers.

To a solution of the above mixture in CH_2Cl_2 (12 mL) was added Dess–Martin periodinane (434 mg, 1.0 mmol) at 0°C . The mixture was stirred at rt for 40 min, then it was quenched with a mixture of sat. NaHCO_3 (10 mL), sat. $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL) and H_2O (10 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (4:1) to afford compound **30** (228 mg, 52% for 2 steps) as a brown oil: $[\alpha]_{\text{D}}^{26} = -26.7^\circ$ (c = 0.58, CHCl_3); IR (neat) ν_{max} : 3381, 2931, 2857, 1760, 1604, 1465, 1256, 1154, 1097, 1051, 835, 778 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 15.40 (br s, 1H), 7.48 (dd, J = 5.8, 1.4 Hz, 1H), 7.36 – 7.27 (m, 5H), 6.17 (dd, J = 5.6, 2.0 Hz, 1H), 5.56 (s, 1H), 5.09 (dd, J = 9.2, 4.7 Hz, 1H), 5.00 – 4.96 (m, 1H), 4.50 (s, 2H), 4.32 (dd, J = 10.7, 6.1 Hz, 1H), 3.29 (s, 3H), 2.81 (dd, J = 14.7, 9.2 Hz, 1H), 2.62 (dd, J = 14.7, 4.7 Hz, 1H), 2.54 (dd, J = 6.2, 1.9 Hz, 2H), 0.81 (s, 9H), 0.05 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.9, 189.8, 172.6, 153.0, 140.5, 128.6, 128.2, 126.8, 123.1, 102.5, 94.1, 85.3, 74.3, 69.4, 55.6, 46.8, 43.2, 25.6, 18.0, -4.9 , -5.0 ; HRMS (ESI-TOF): m/z calcd for $\text{C}_{25}\text{H}_{37}\text{O}_7\text{Si}$ $[\text{M}+\text{H}]^+$: 477.2303, found: 477.2302.

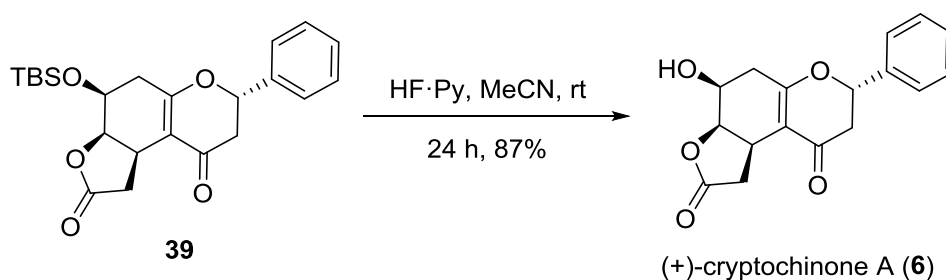


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39

32.2, 25.6, 17.9, -5.0, -5.1. HRMS (ESI-TOF): m/z calcd for $C_{23}H_{31}O_5Si$ $[M+H]^+$: 415.1935, found: 415.1938.

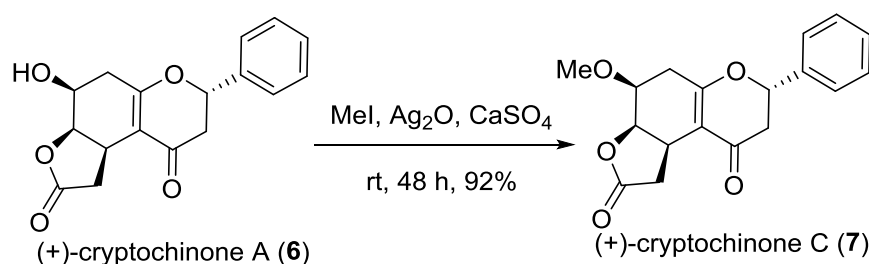


(+)-Cryptochinone A (6): To a solution of **39** (84 mg, 0.20 mmol) in anhydrous CH_3CN (2 mL) was added HF Py complex (70%, 0.2 mL) at 0 °C. The reaction was slowly warmed to rt and stirred for 24 h. The mixture was diluted with water and extracted with ethyl acetate. The organic phase was washed with sat. $NaHCO_3$, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using PE-EtOAc (1:1) to afford (+)-**6** (51 mg, 86%) as a colorless solid: m.p. 194 – 195 °C; $[\alpha]_D^{26} = +196.7^\circ$ ($c = 0.15$, $CHCl_3$); IR (neat) ν_{max} : 3445, 2977, 1774, 1660, 1620, 1417, 1167, 1080, 1048, 757 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 5H), 5.40 (dd, $J = 14.8, 3.6$ Hz, 1H), 4.80 (dd, $J = 6.6, 2.4$ Hz, 1H), 4.17 (br s, 1H), 3.57 – 3.50 (m, 1H), 3.02 (dd, $J = 18.0, 8.8$ Hz, 1H), 2.88 (dd, $J = 17.1, 14.7$ Hz, 1H), 2.71 – 2.63 (m, 3H), 2.56 (dd, $J = 18.0, 4.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 176.8, 168.5, 137.5, 129.1, 128.9, 126.3, 110.7, 80.5, 79.6, 66.6, 42.5, 36.6, 32.6, 32.4; HRMS (ESI-TOF): m/z calcd for $C_{17}H_{16}O_5Na$ $[M+Na]^+$: 323.0895, found: 323.0891.



(+)-Cryptocaryanone B (4): To a solution of **6** (33 mg, 0.11 mmol) in CH_2Cl_2 (2 mL) were added Et_3N (0.15 mL, 1.1 mmol) and $MsCl$ (34 μL , 0.44 mmol) at 0 °C successively. The mixture was stirred at rt for 40 min, then it was quenched with water and extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ EtOAc (4:1 to 2:1) to afford (+)-**4** (28 mg, 90%) as a white powder: $[\alpha]_D^{26} = +265.2^\circ$ ($c = 0.40$, $CHCl_3$); IR (neat) ν_{max} : 2923, 1773, 1654, 1586, 1426, 1378, 1309, 1169, 1005, 760 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 5H), 6.35 (dd, $J = 10.0, 3.6$ Hz, 1H), 6.14 (dd, $J = 10.0, 1.6$ Hz, 1H), 5.46 – 5.38 (m, 2H), 3.76 (td, $J = 9.5, 7.9$ Hz, 1H), 3.01 (dd, $J = 18.0, 9.2$ Hz, 1H), 2.90 (dd, $J = 17.2, 14.4$ Hz, 1H), 2.69 (dd, $J = 17.2, 3.6$ Hz, 1H), 2.63 (dd, $J = 18.0,$

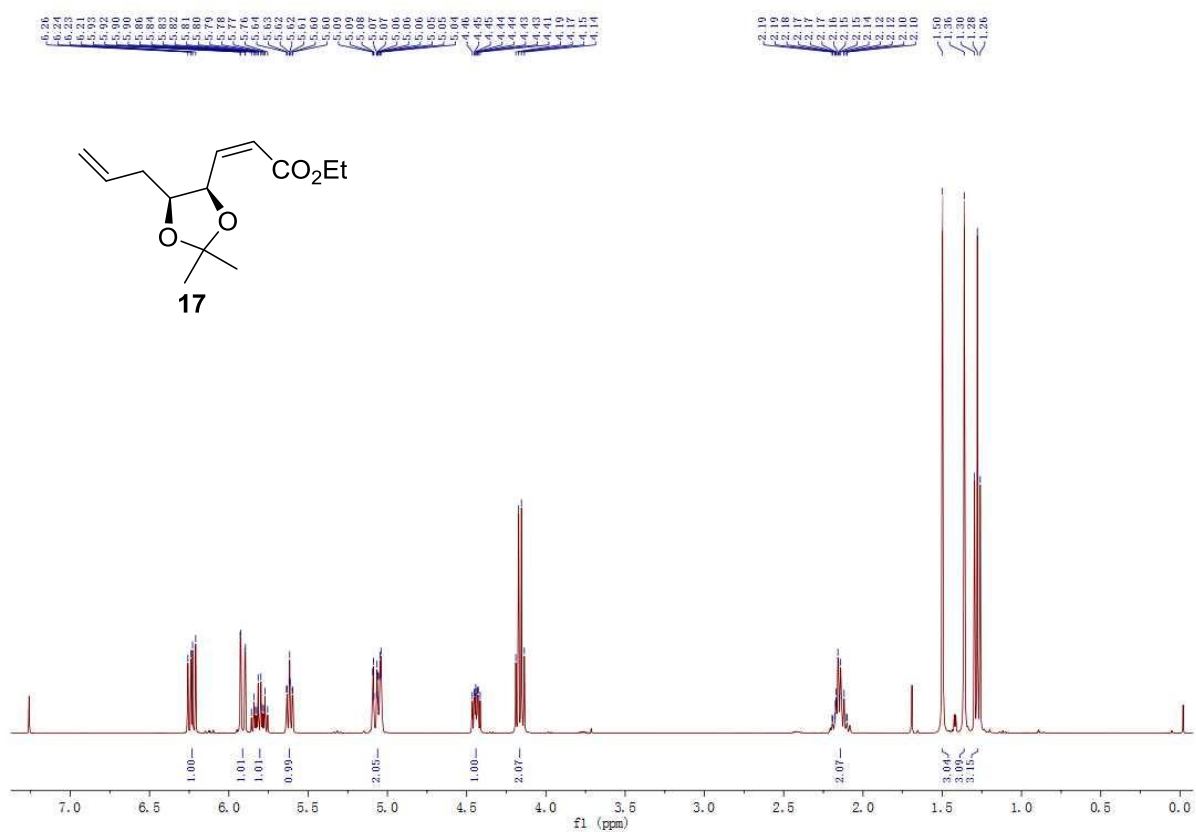
8.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.3, 175.5, 162.8, 137.4, 134.1, 129.1, 128.9, 126.2, 125.2, 109.3, 80.6, 76.1, 42.4, 34.5, 30.8; HRMS (ESI-TOF): m/z calcd for $\text{C}_{17}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 283.0965, found: 283.0963.



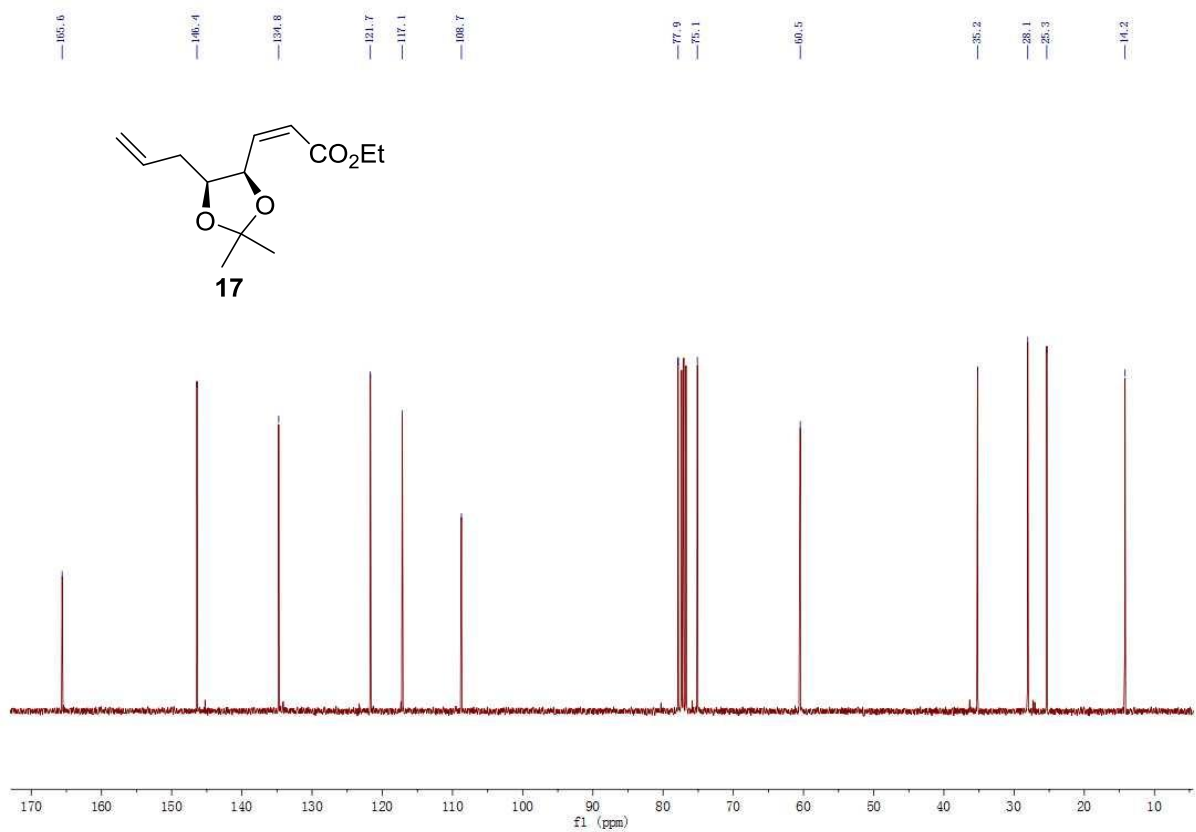
(+)-Cryptochinone C (7): To a solution of **6** (17 mg, 0.057 mmol) in iodomethane (2 mL) were slowly added silver oxide (33 mg, 0.14 mmol) and calcium sulfate at rt. The mixture was stirred in the dark for 48 h, diluted with EtOAc, and filtered through a plug of Celite. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography using petroleum ether/ EtOAc (1:1) to afford (+)-**7** (16.5 mg, 92%) as a colorless oil: $[\alpha]_{\text{D}}^{26} = +176.7^\circ$ ($c = 0.13$, CHCl_3); IR (neat) ν_{max} : 2925, 1778, 1665, 1614, 1413, 1372, 1315, 1167, 1101, 1020, 964, 761 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.37 (m, 5H), 5.40 (dd, $J = 14.6, 3.4$ Hz, 1H), 4.81 (dd, $J = 6.4, 2.4$ Hz, 1H), 3.72 (ddd, $J = 7.6, 5.2, 2.5$ Hz, 1H), 3.52 – 3.45 (m, 1H), 3.44 (s, 3H), 2.97 (dd, $J = 17.6, 8.8$ Hz, 1H), 2.87 (dd, $J = 17.1, 14.6$ Hz, 1H), 2.75 – 2.63 (m, 3H), 2.53 (dd, $J = 17.6, 4.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.7, 176.5, 168.4, 137.5, 129.1, 128.9, 126.3, 110.9, 80.5, 77.2, 75.4, 57.6, 42.6, 36.2, 32.9, 29.6; HRMS (ESI-TOF): m/z calcd for $\text{C}_{18}\text{H}_{19}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 337.1052, found: 337.1050.

Copies of ^1H and ^{13}C NMR spectra for compounds

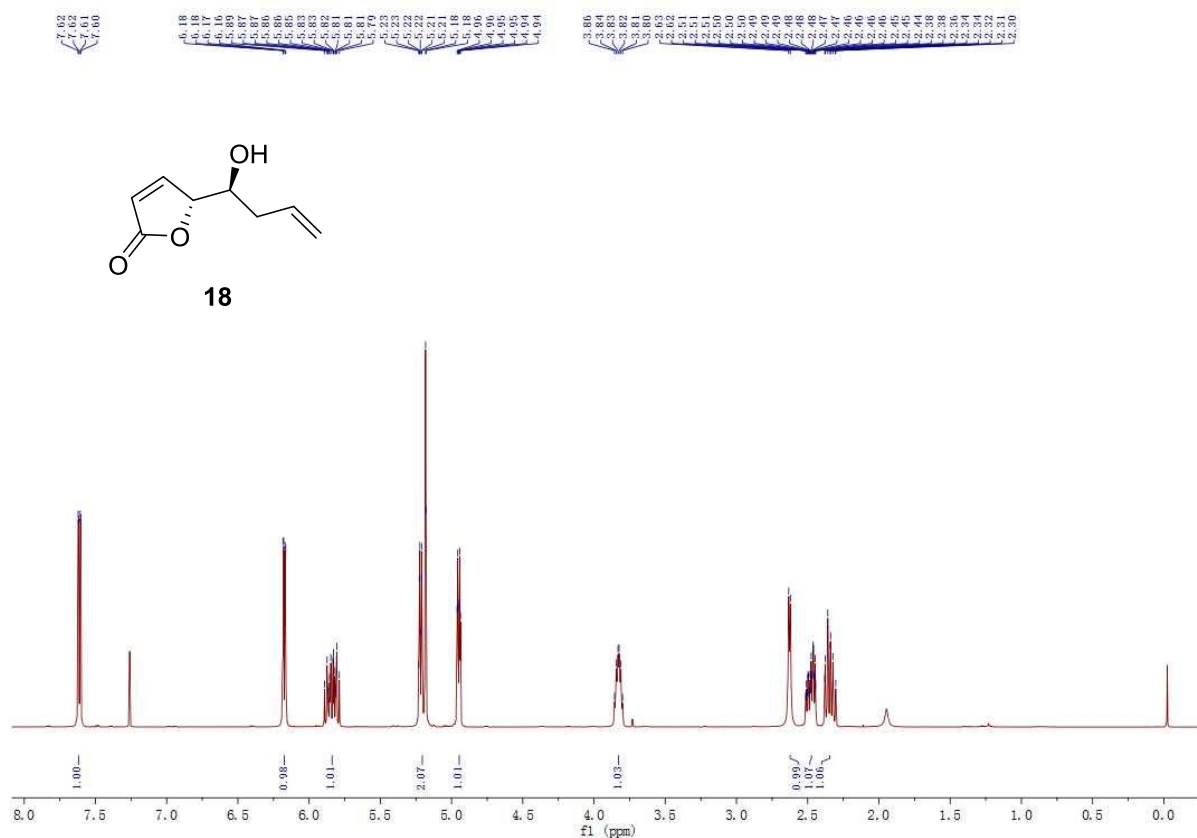
^1H NMR spectrum of compound 17 (400 MHz, CDCl_3)



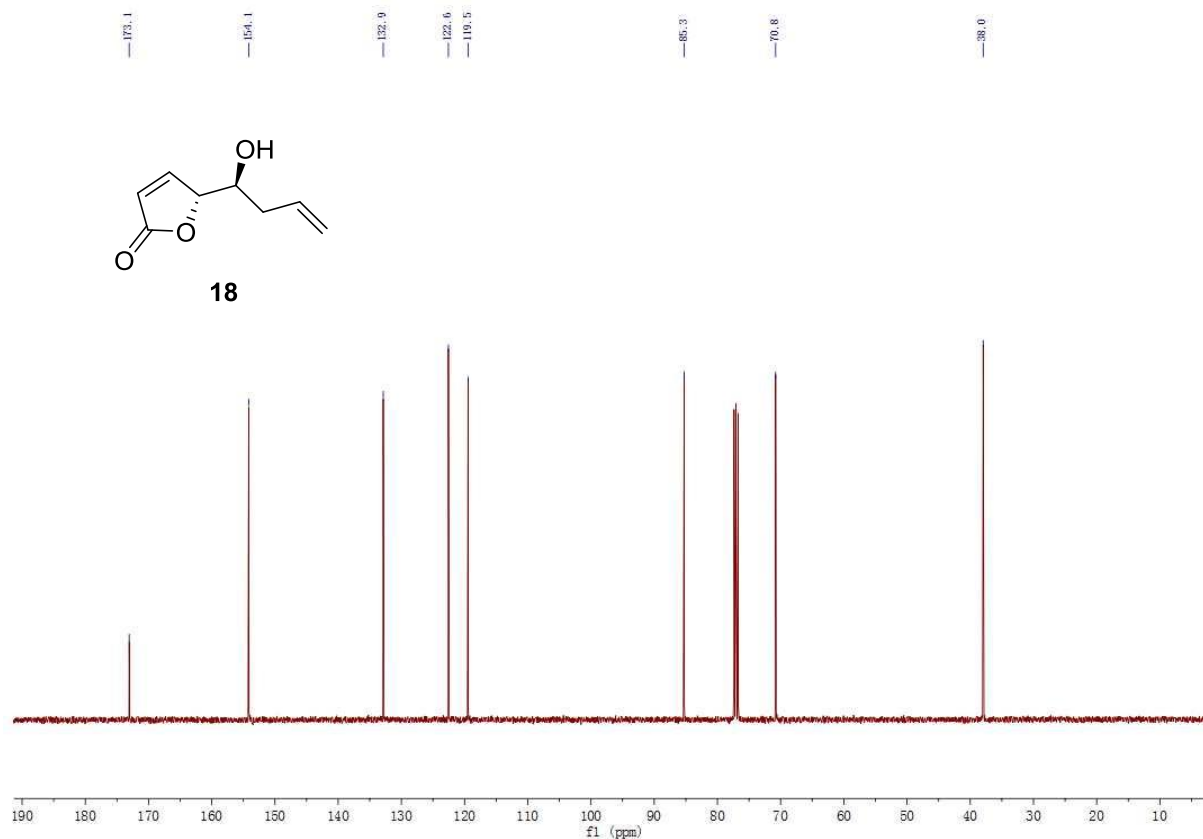
^{13}C NMR spectrum of compound 17 (100 MHz, CDCl_3)



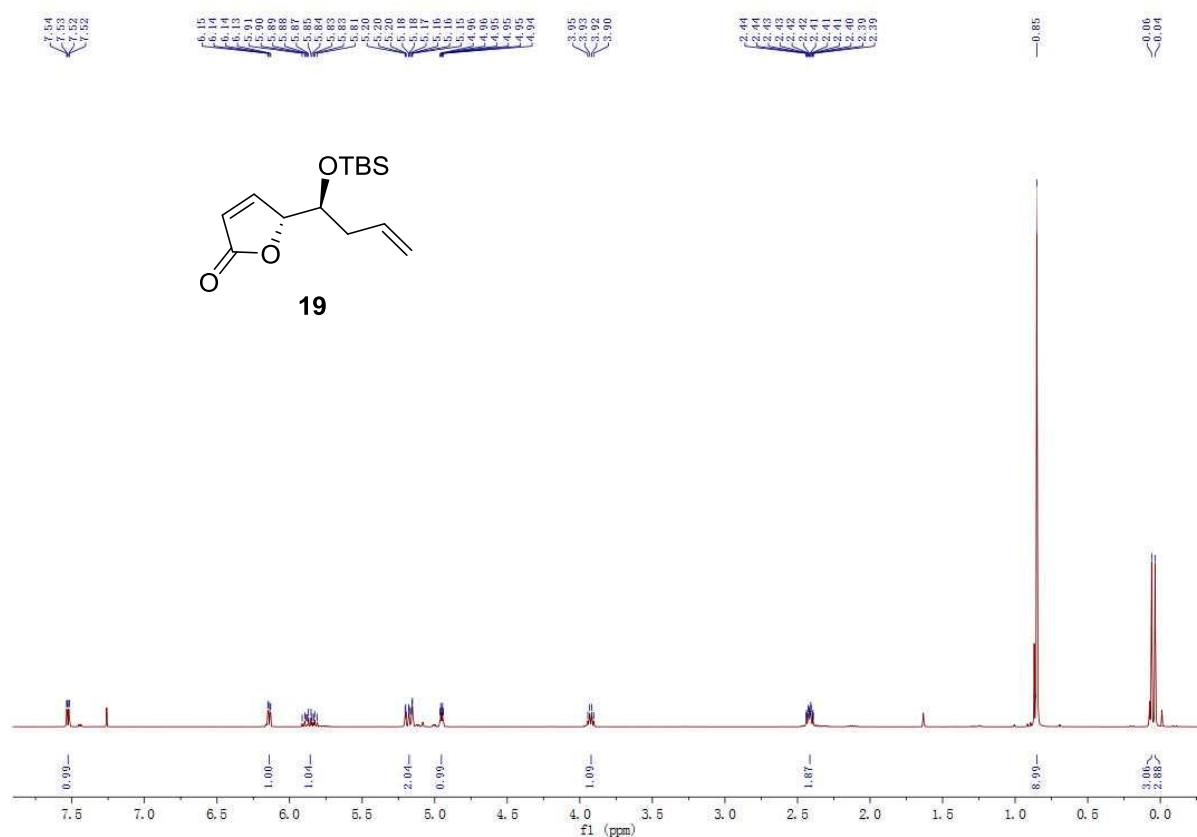
^1H NMR spectrum of compound 18 (400 MHz, CDCl_3)



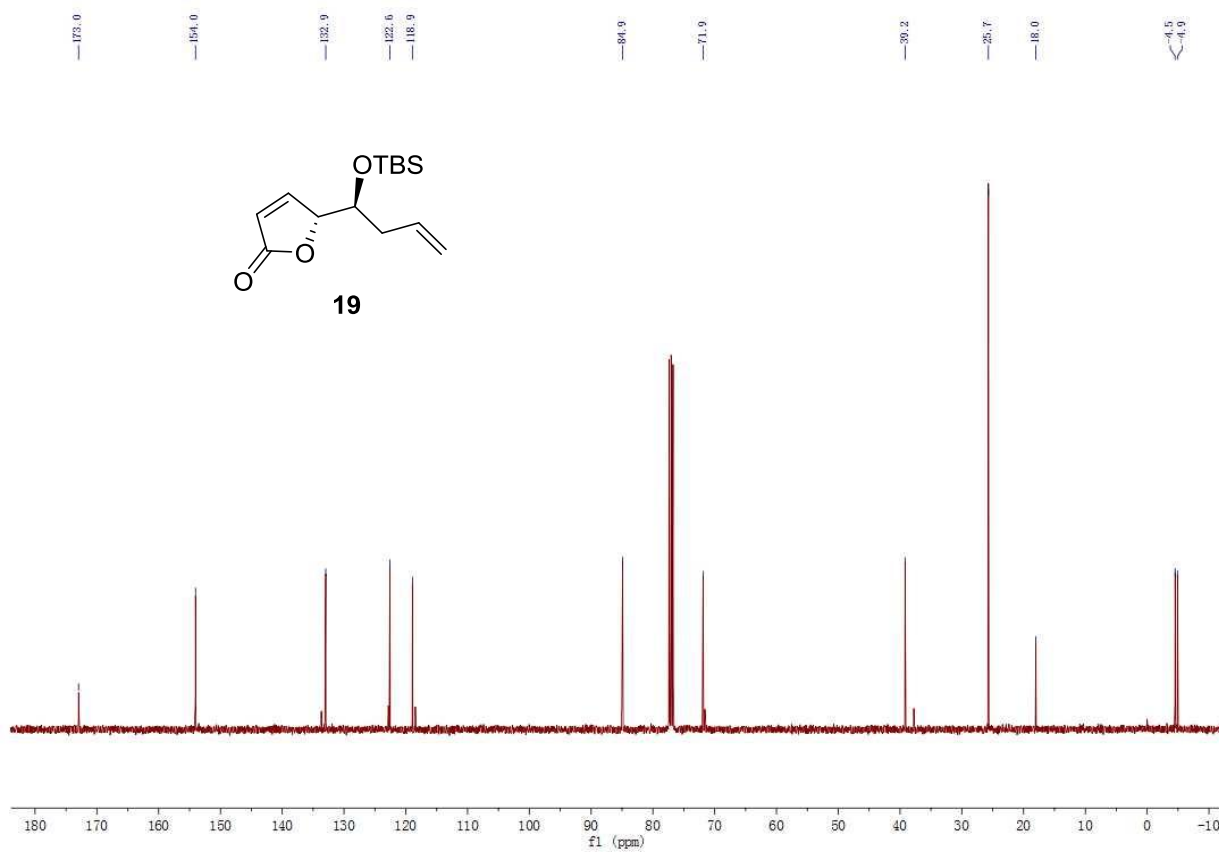
^{13}C NMR spectrum of compound 18 (100 MHz, CDCl_3)



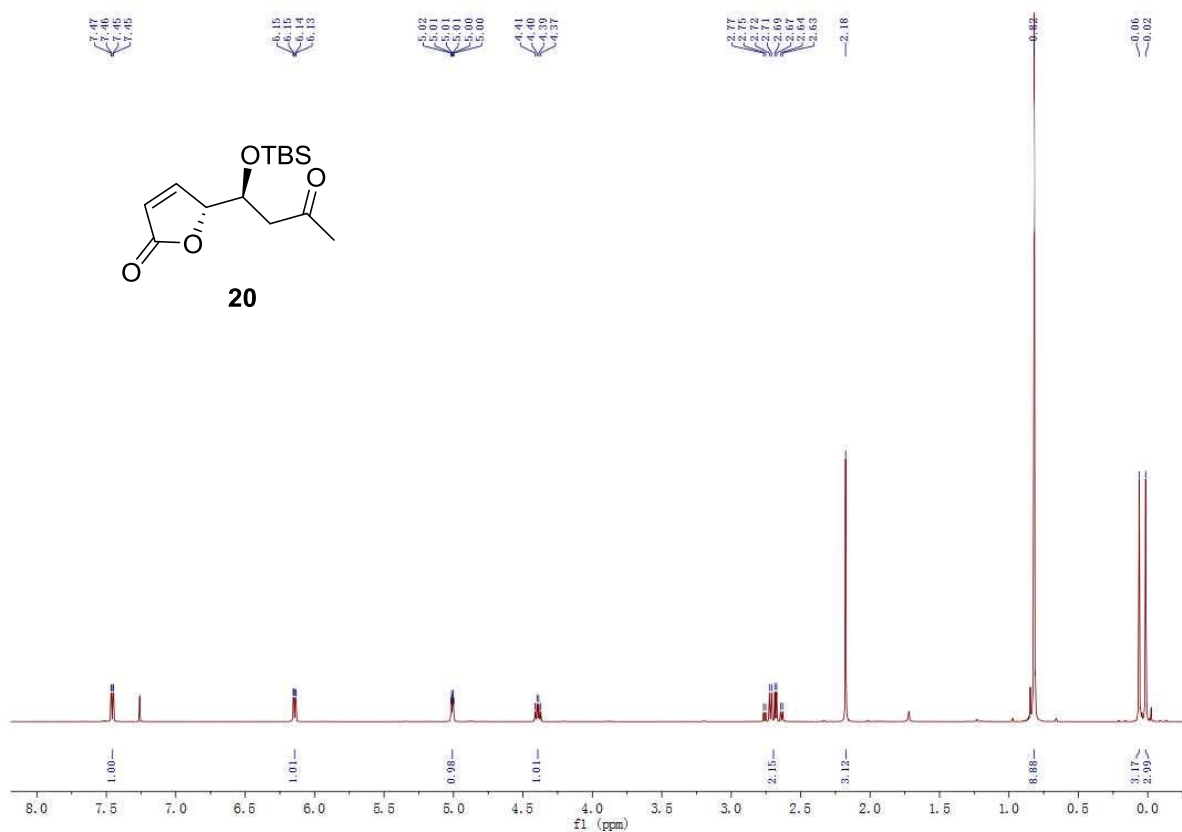
^1H NMR spectrum of compound 19 (400 MHz, CDCl_3)



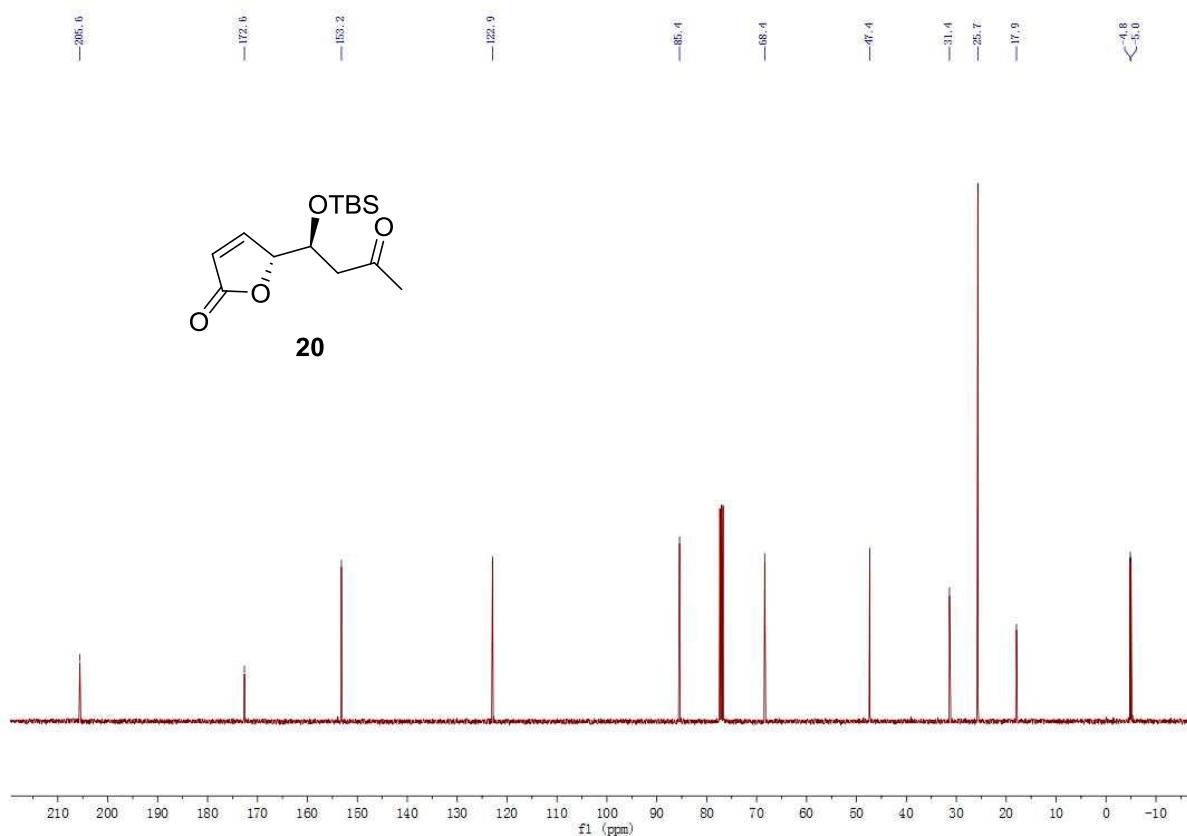
^{13}C NMR spectrum of compound 19 (100 MHz, CDCl_3)



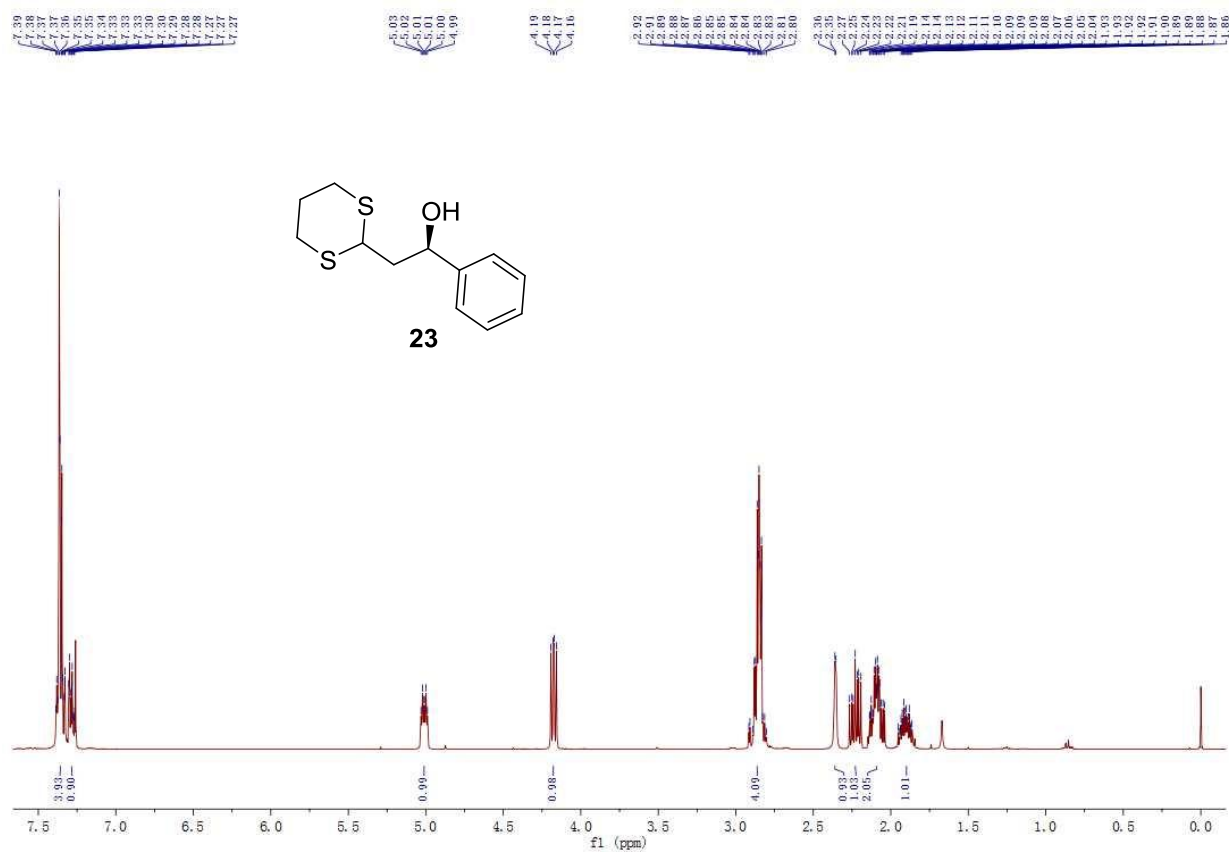
^1H NMR spectrum of compound 20 (400 MHz, CDCl_3)



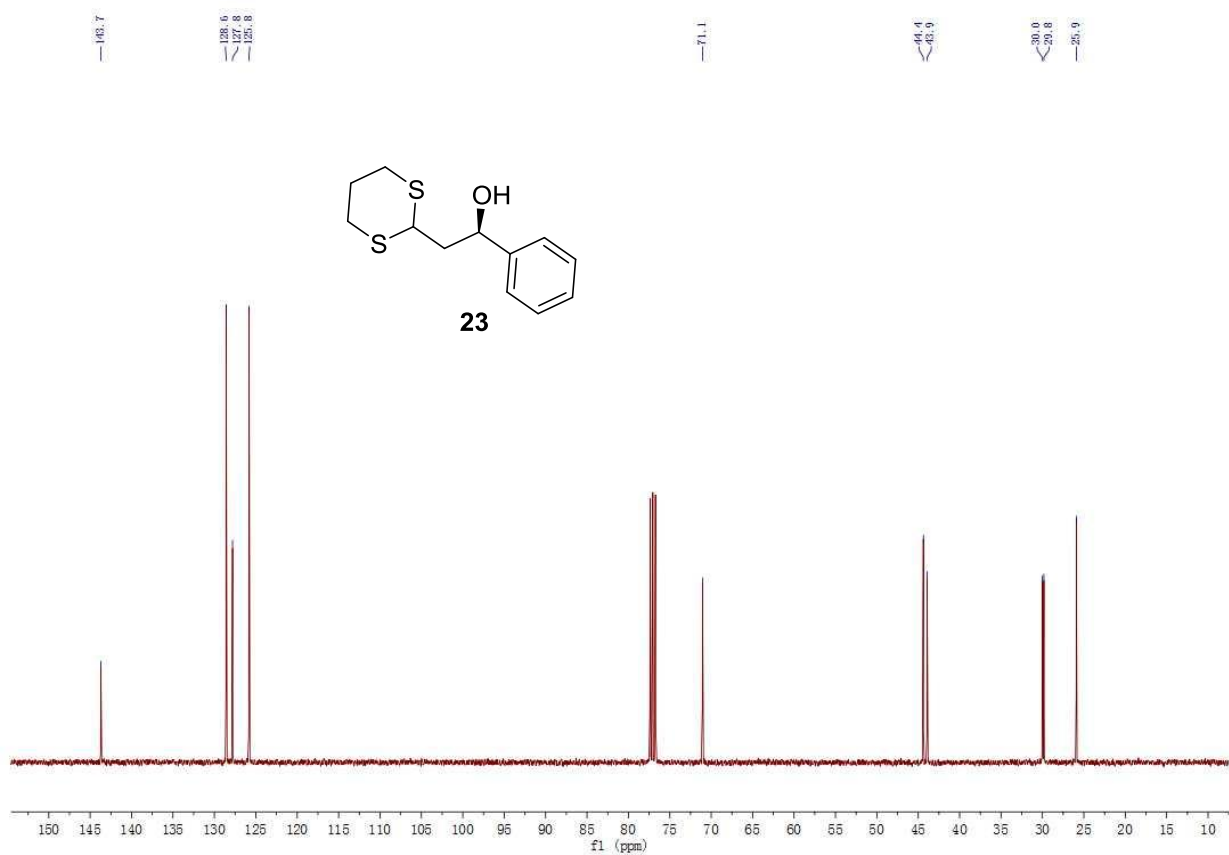
^{13}C NMR spectrum of compound 20 (100 MHz, CDCl_3)



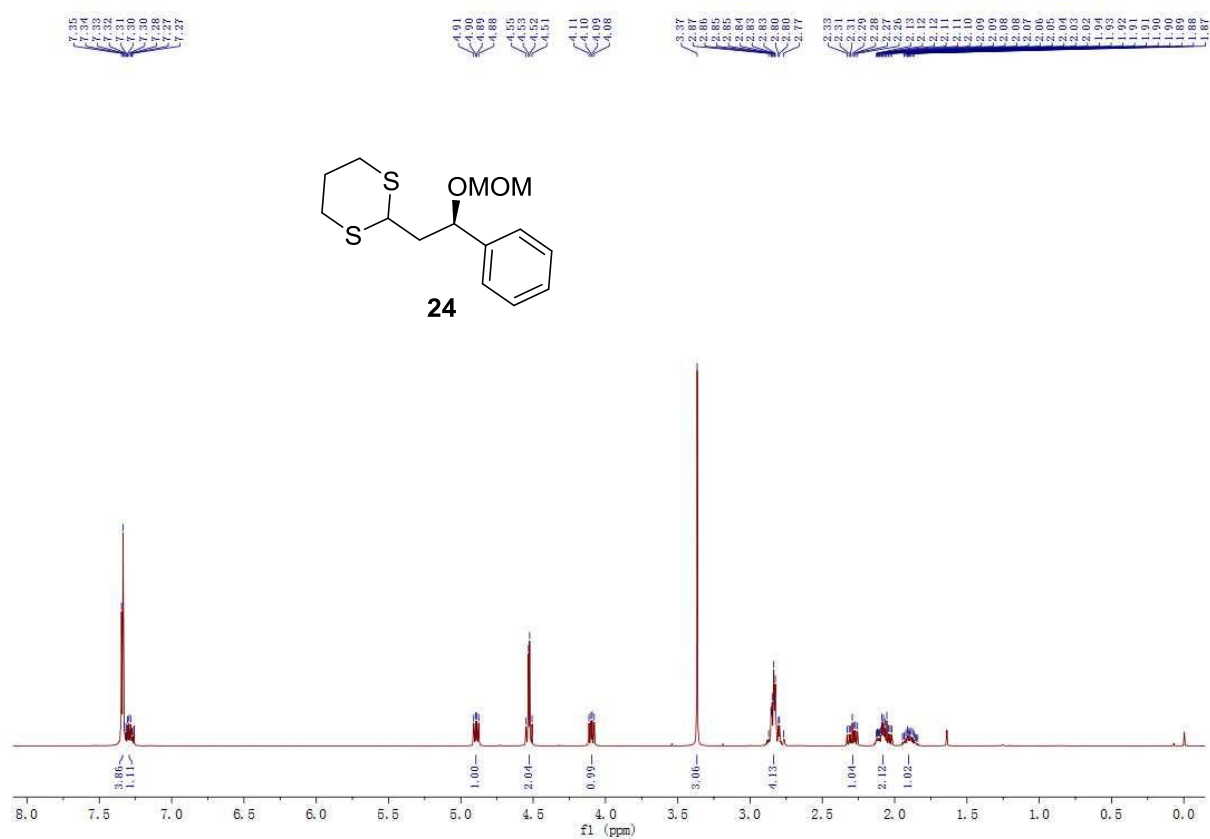
^1H NMR spectrum of compound 23 (400 MHz, CDCl_3)



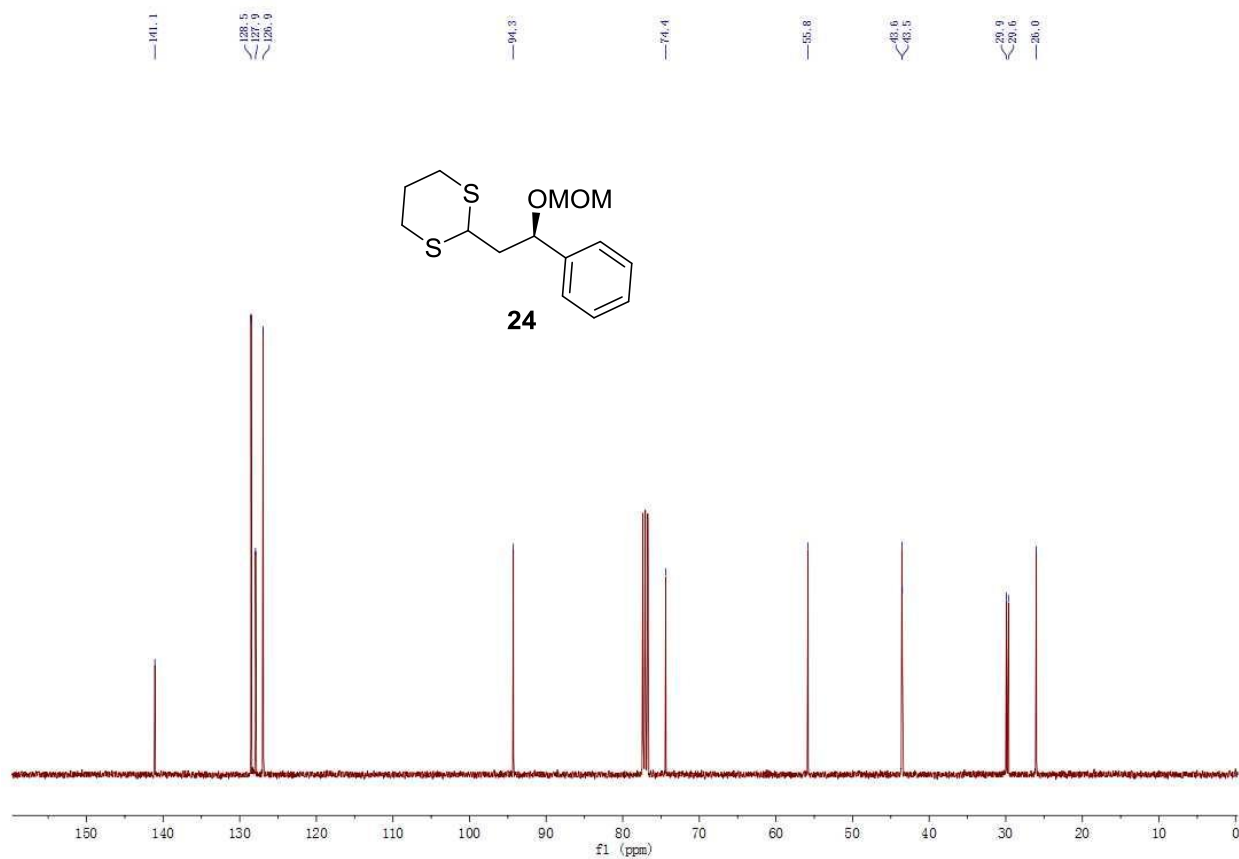
^{13}C NMR spectrum of compound 23 (100 MHz, CDCl_3)



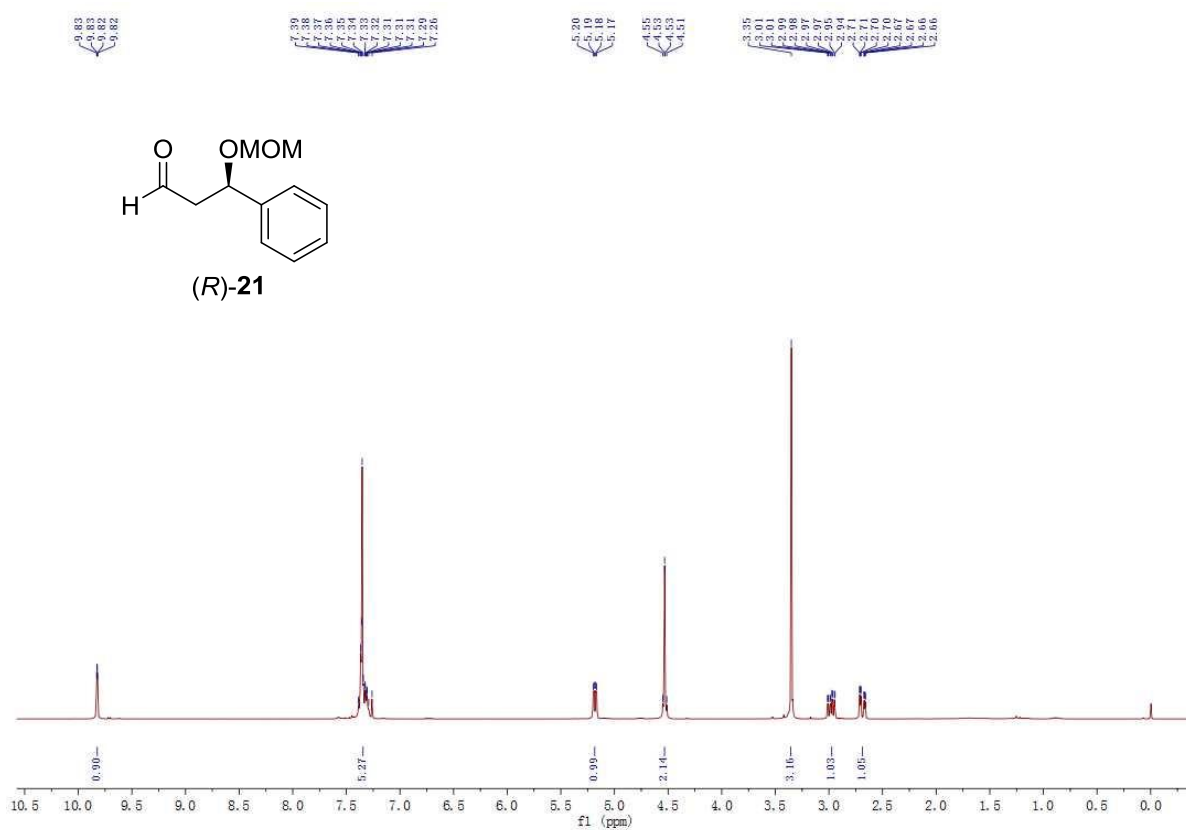
^1H NMR spectrum of compound 24 (400 MHz, CDCl_3)



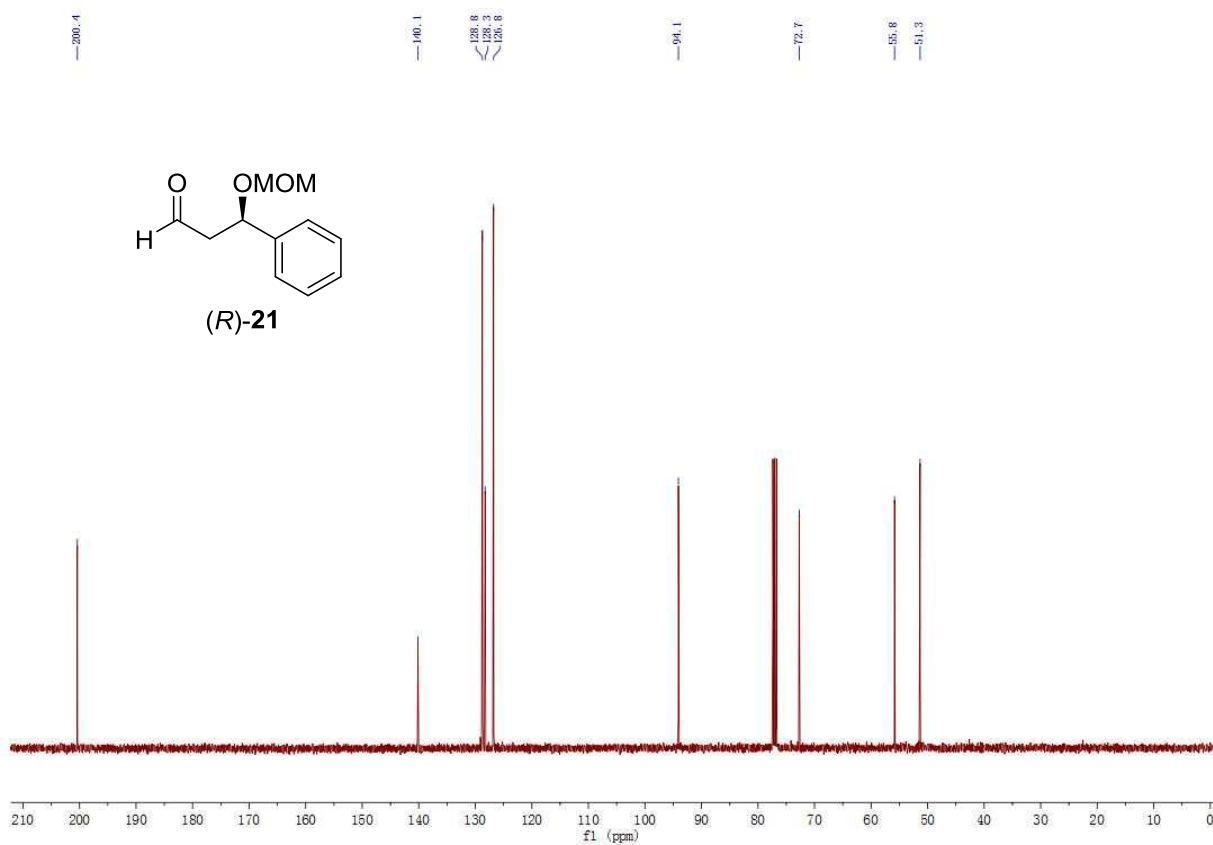
^{13}C NMR spectrum of compound 24 (100 MHz, CDCl_3)



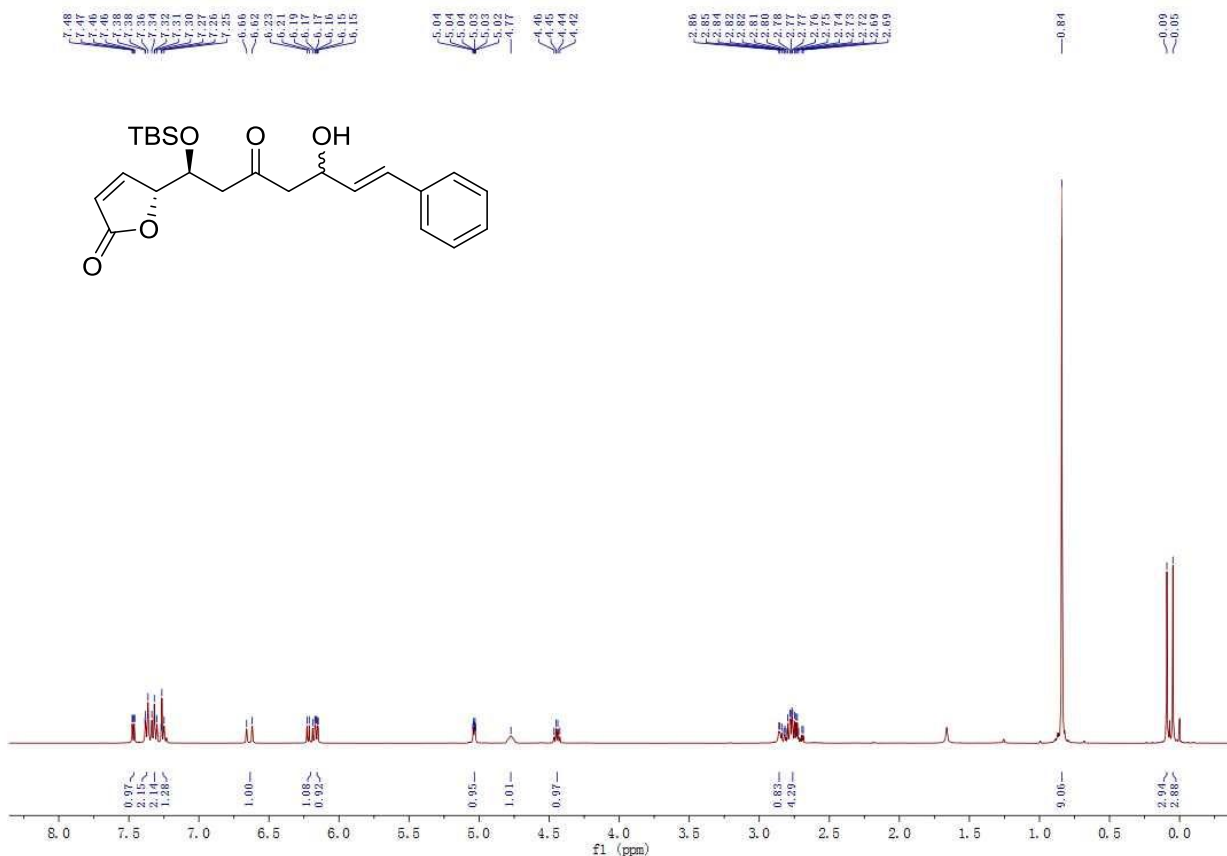
^1H NMR spectrum of compound (R)-21 (400 MHz, CDCl_3)



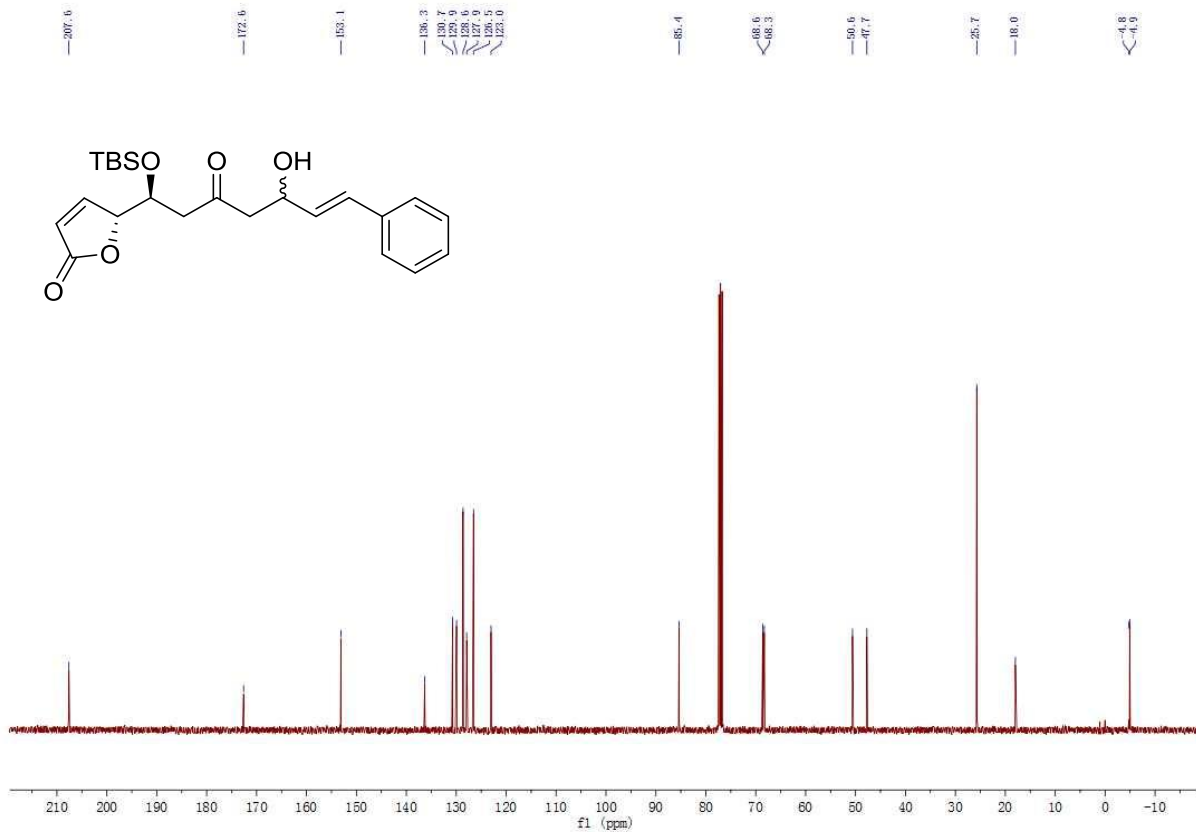
^{13}C NMR spectrum of compound (R)-21 (100 MHz, CDCl_3)



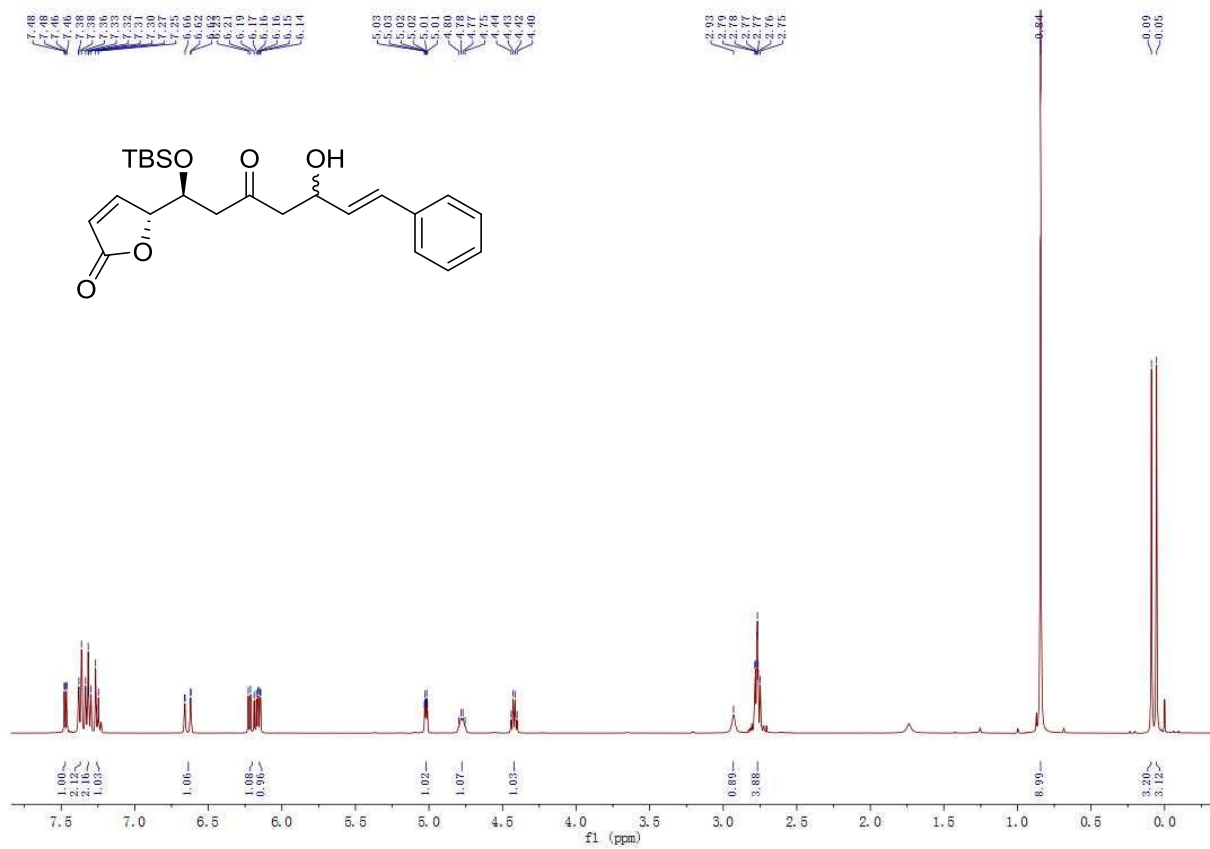
¹H NMR spectrum of compound 26 (more polar isomer) (400 MHz, CDCl₃)



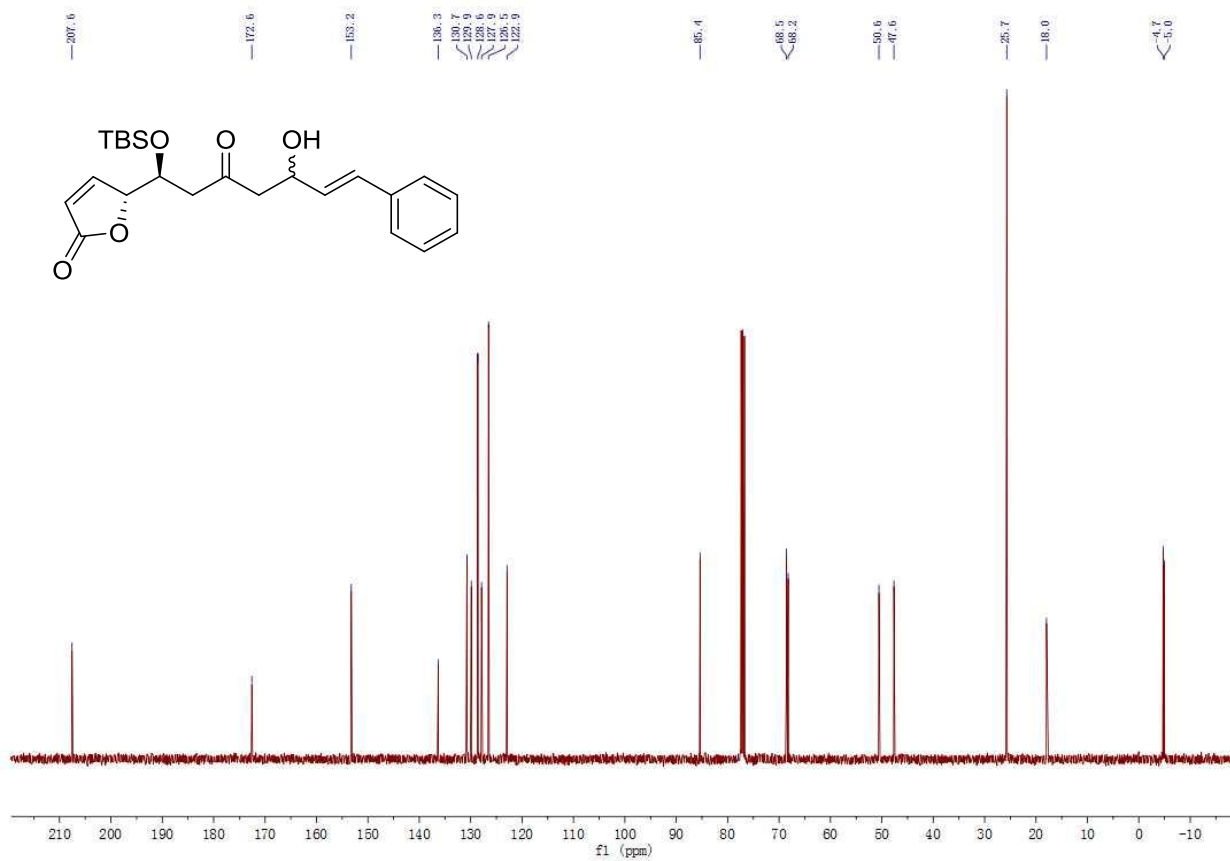
¹³C NMR spectrum of compound 26 (more polar isomer) (100 MHz, CDCl₃)



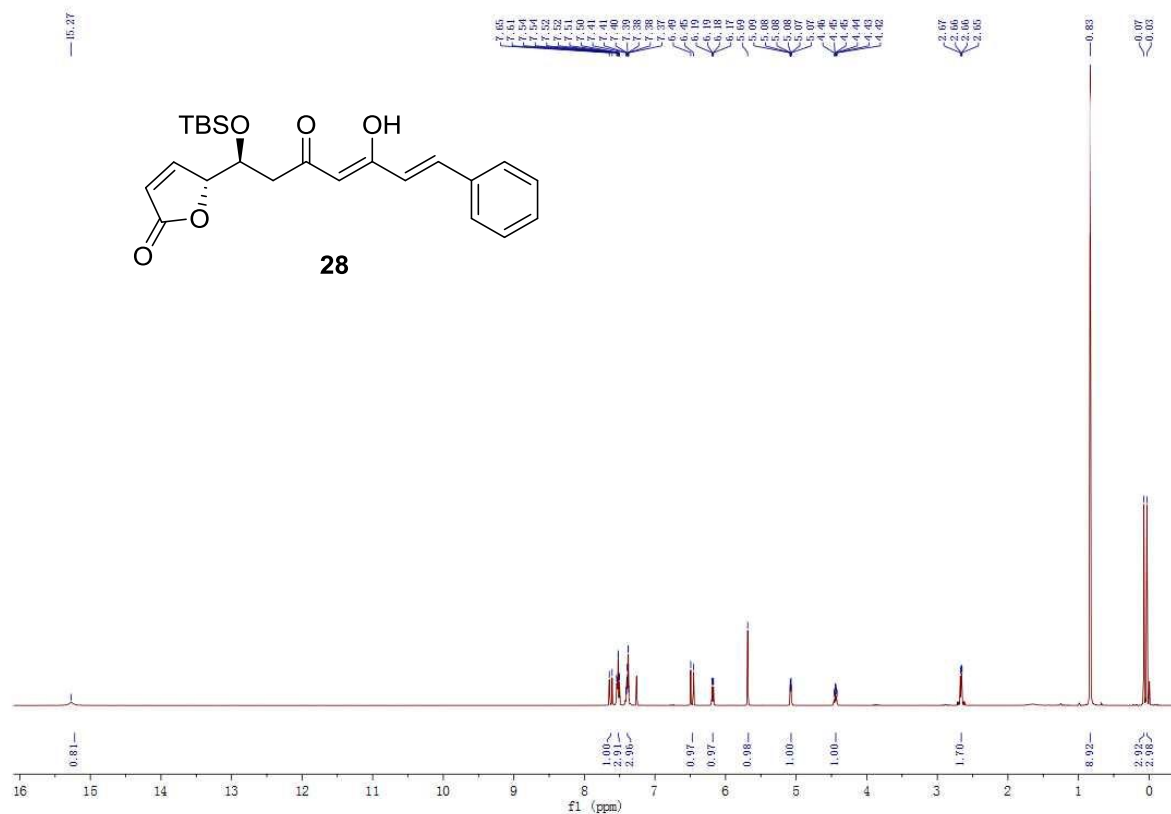
¹H NMR spectrum of compound 27 (less polar isomer) (400 MHz, CDCl₃)



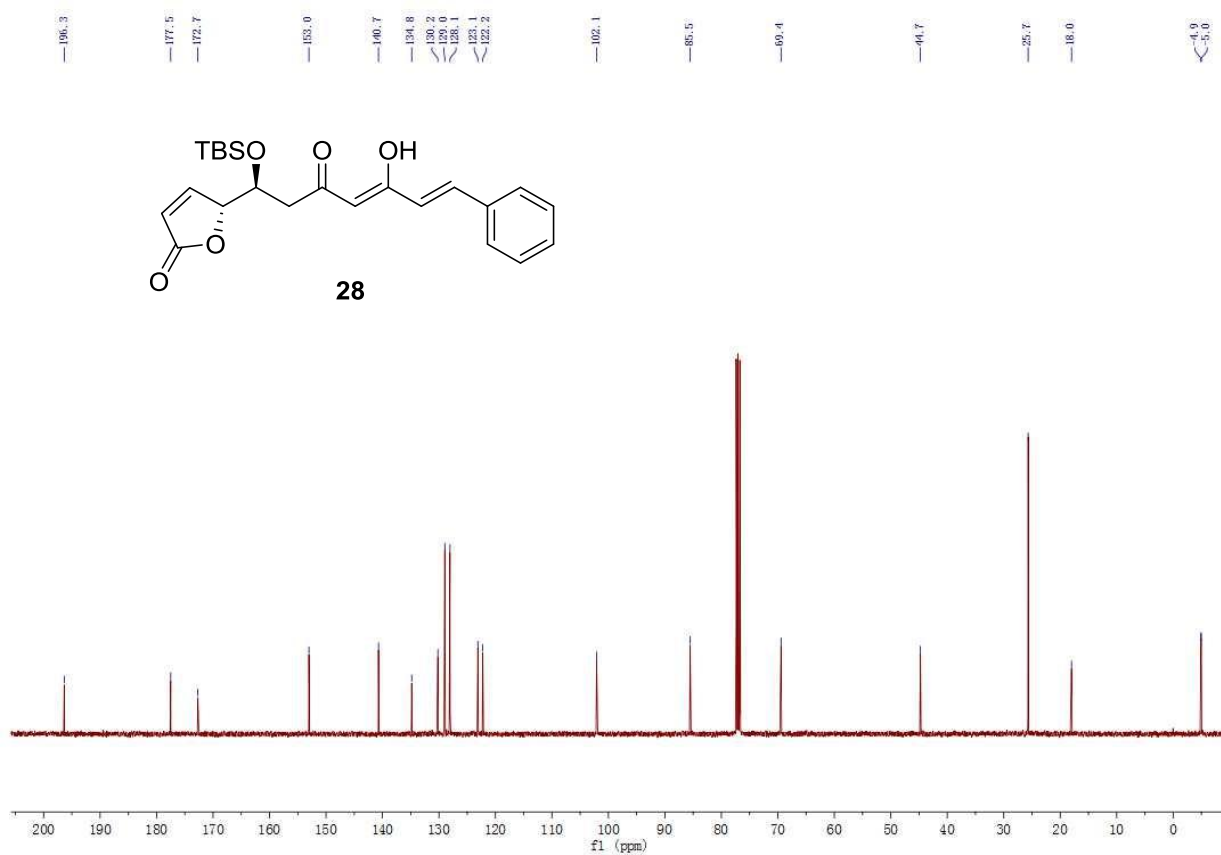
¹³C NMR spectrum of compound 27 (less polar isomer) (100 MHz, CDCl₃)



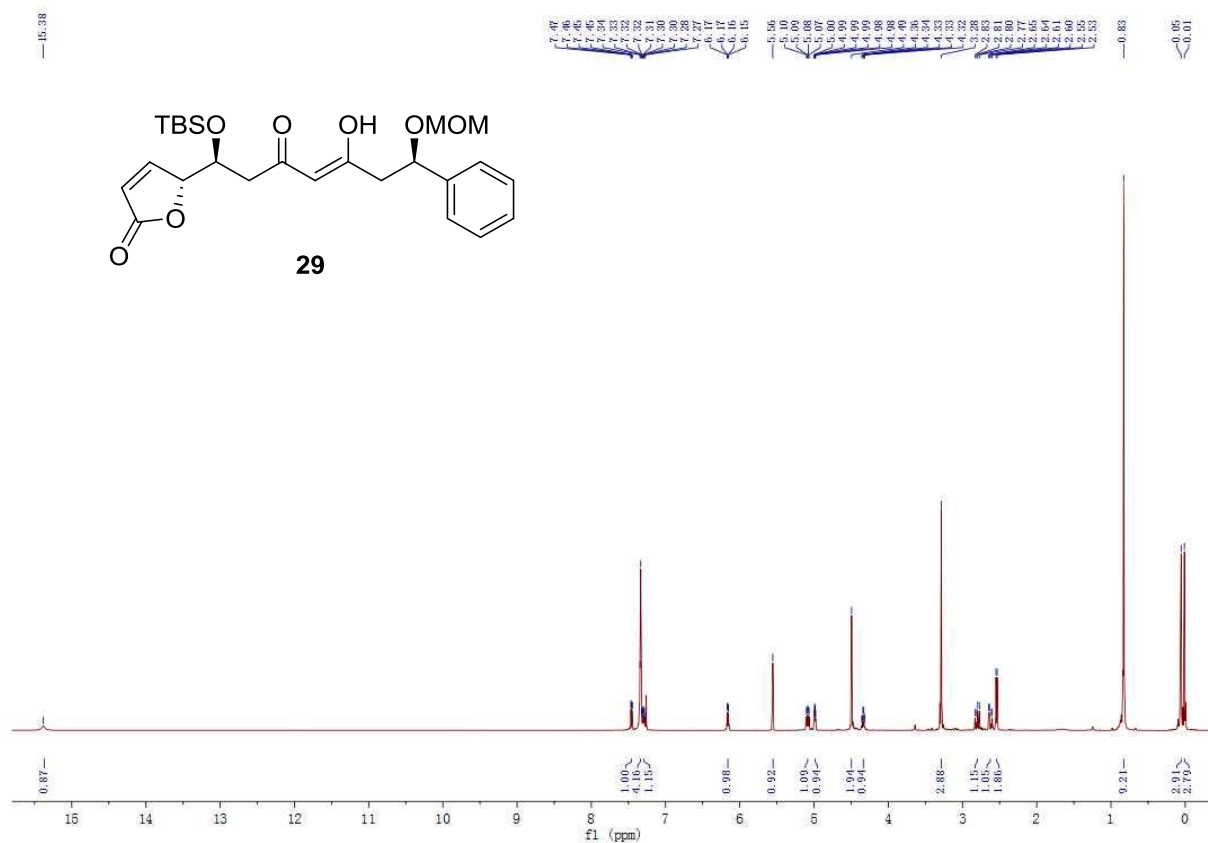
^1H NMR spectrum of compound 28 (400 MHz, CDCl_3)



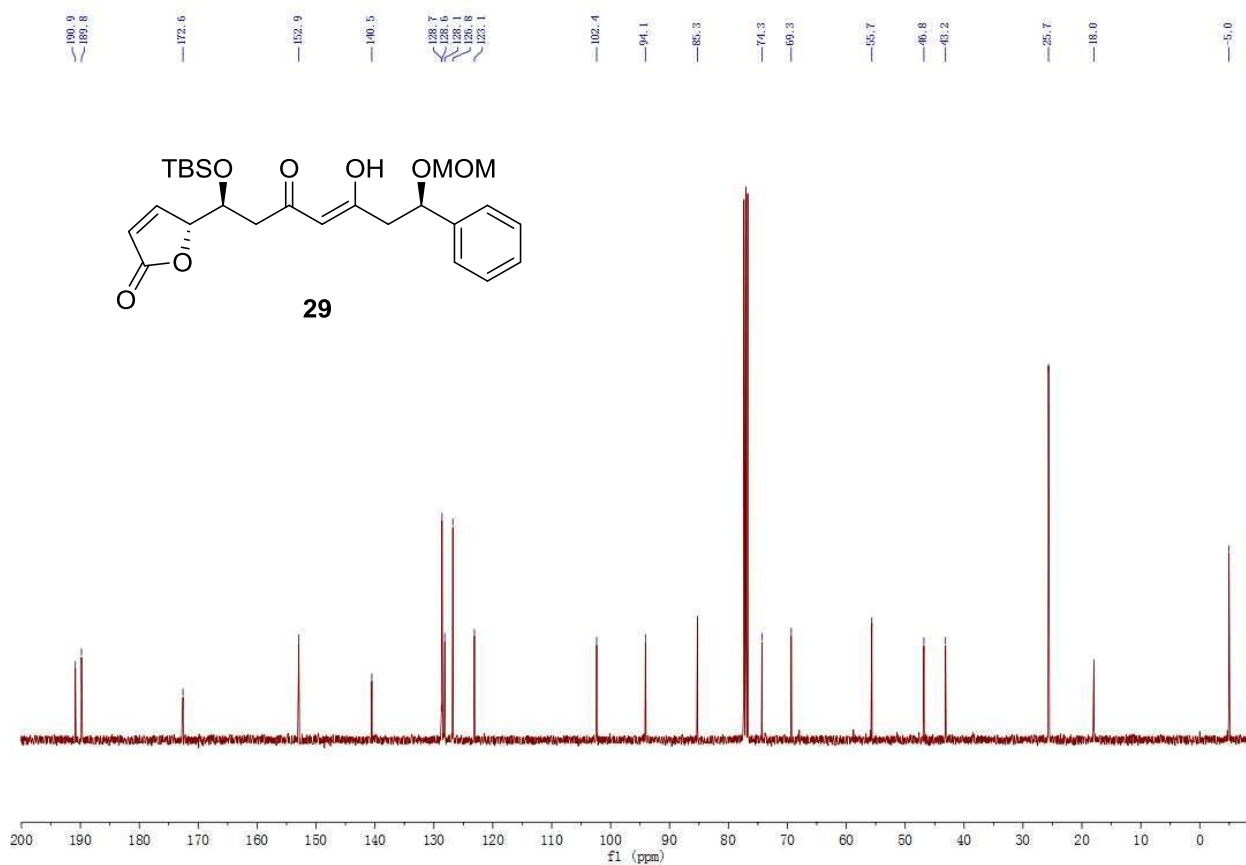
^{13}C NMR spectrum of compound 28 (100 MHz, CDCl_3)



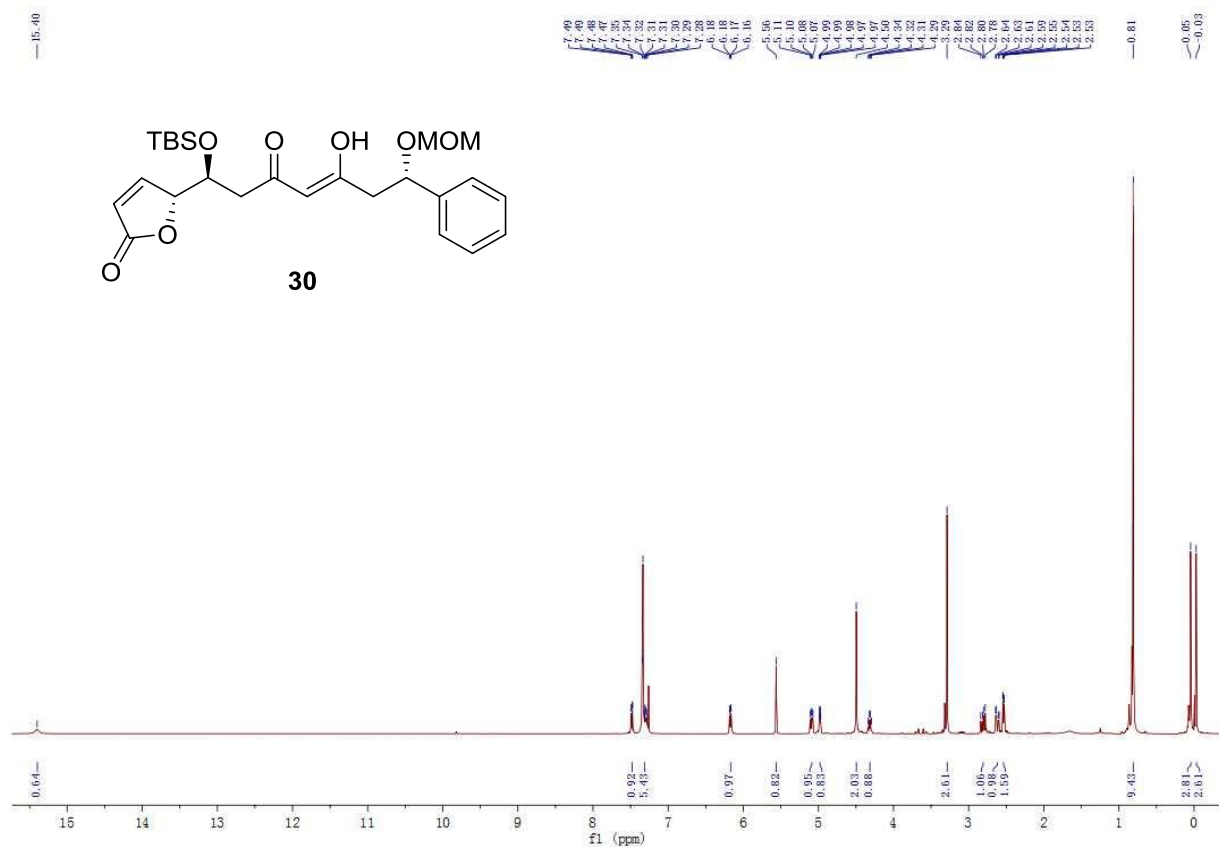
^1H NMR spectrum of compound 29 (400 MHz, CDCl_3)



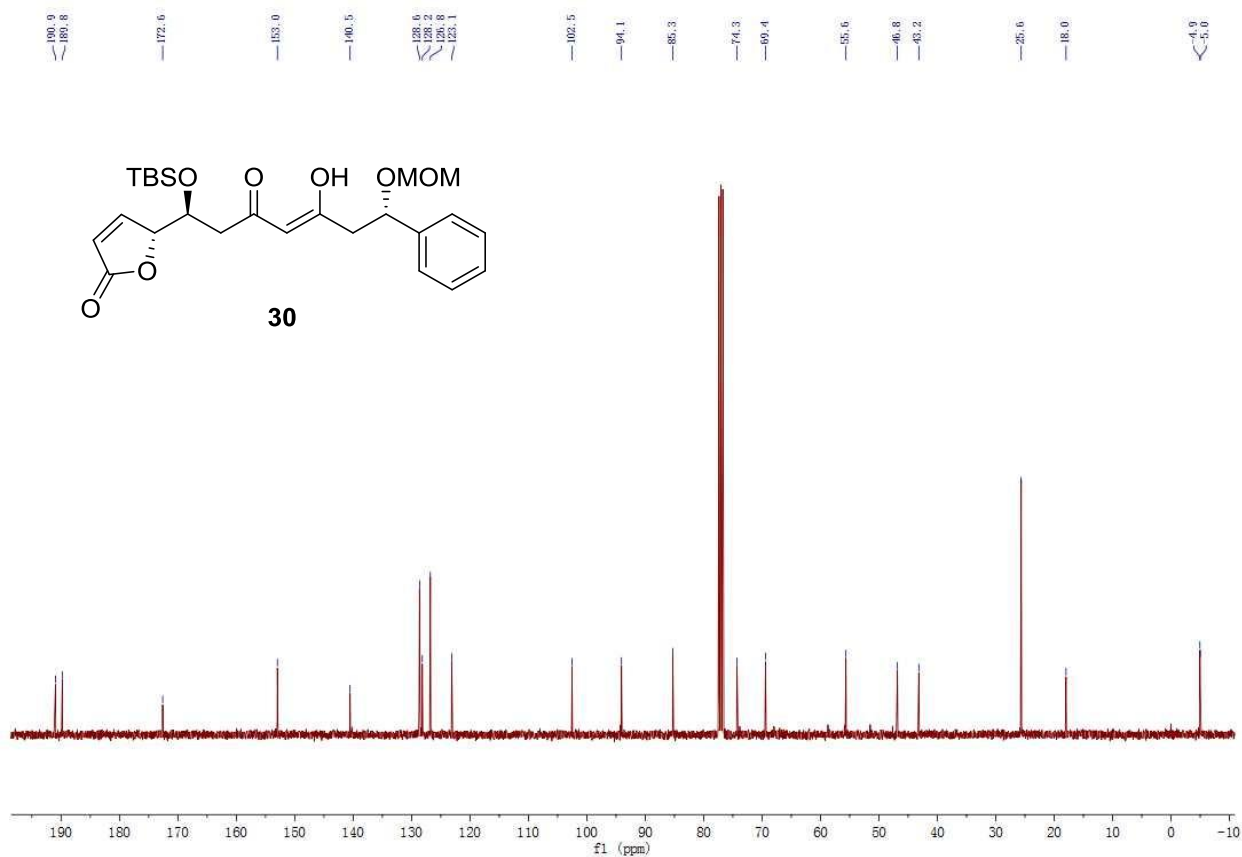
^{13}C NMR spectrum of compound 29 (100 MHz, CDCl_3)



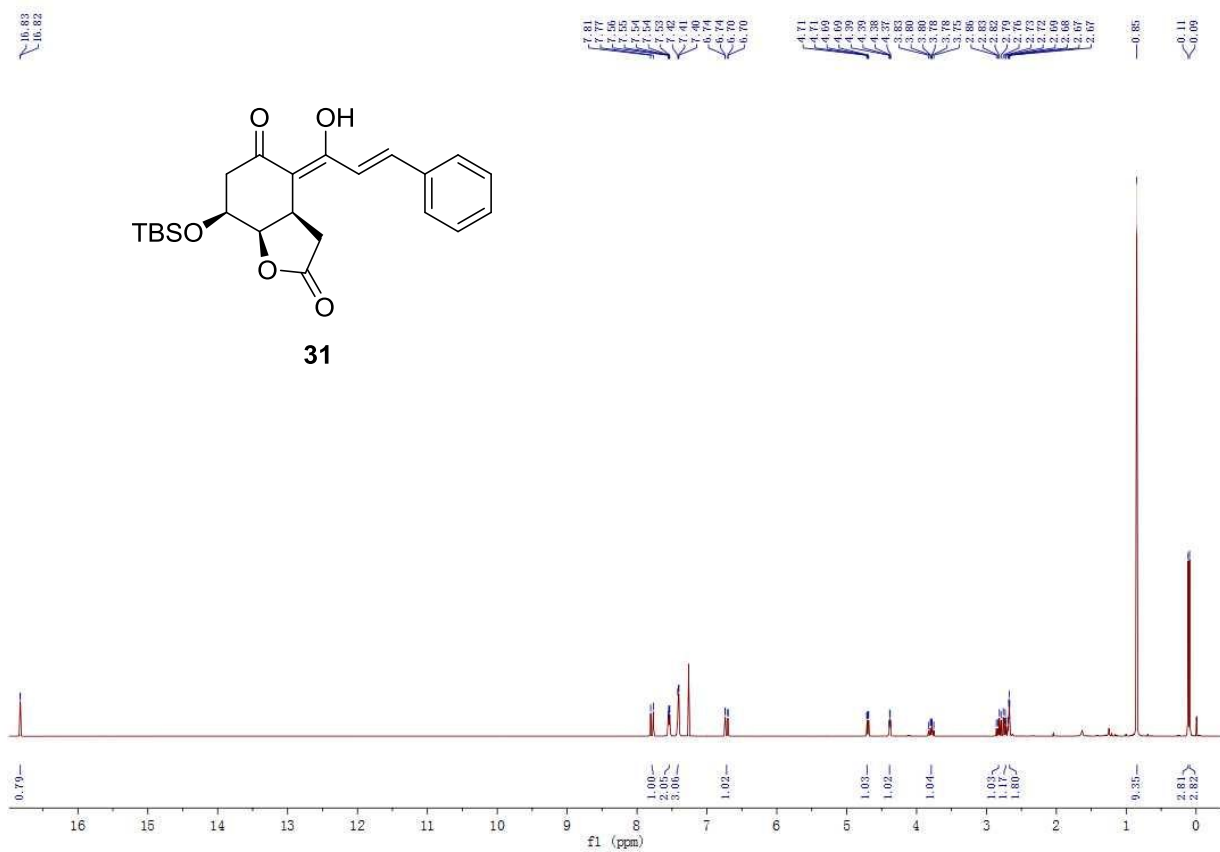
^1H NMR spectrum of compound 30 (400 MHz, CDCl_3)



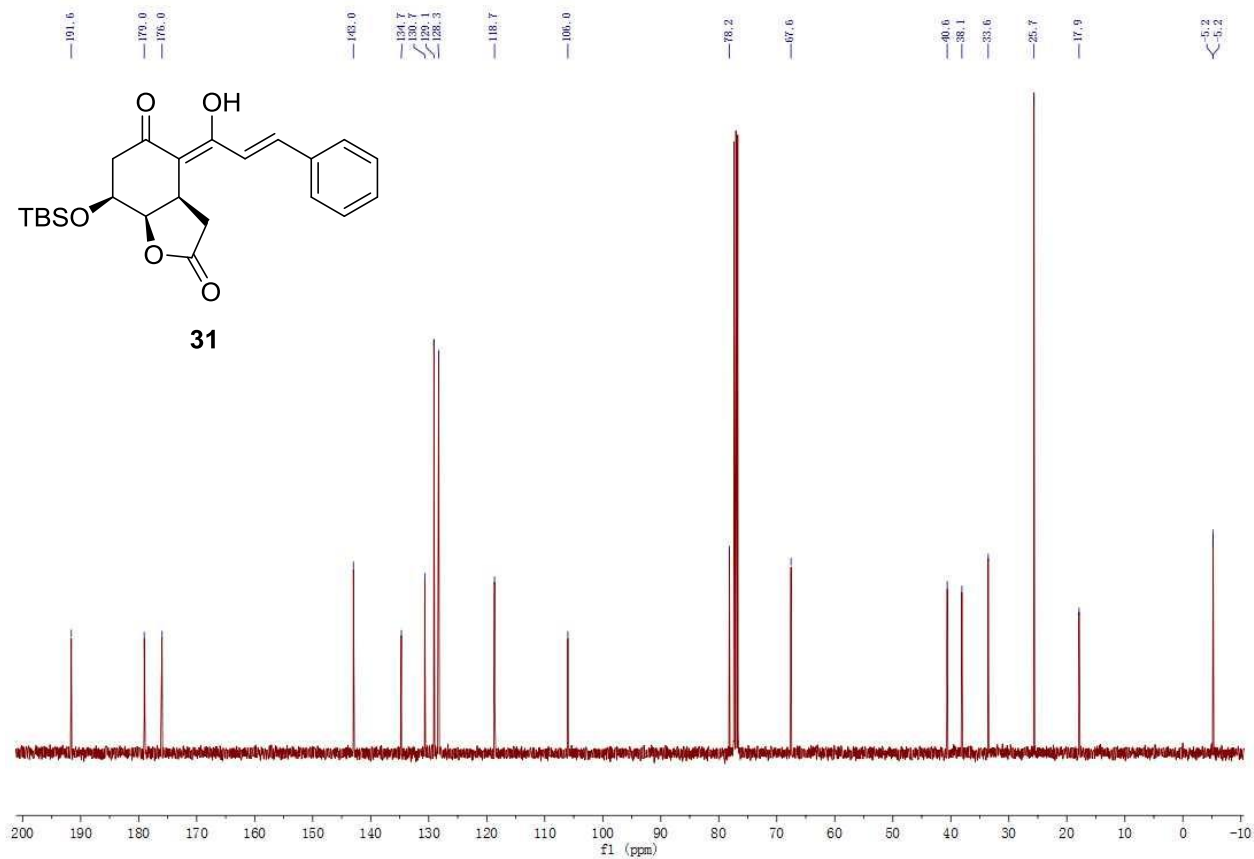
^{13}C NMR spectrum of compound 30 (100 MHz, CDCl_3)



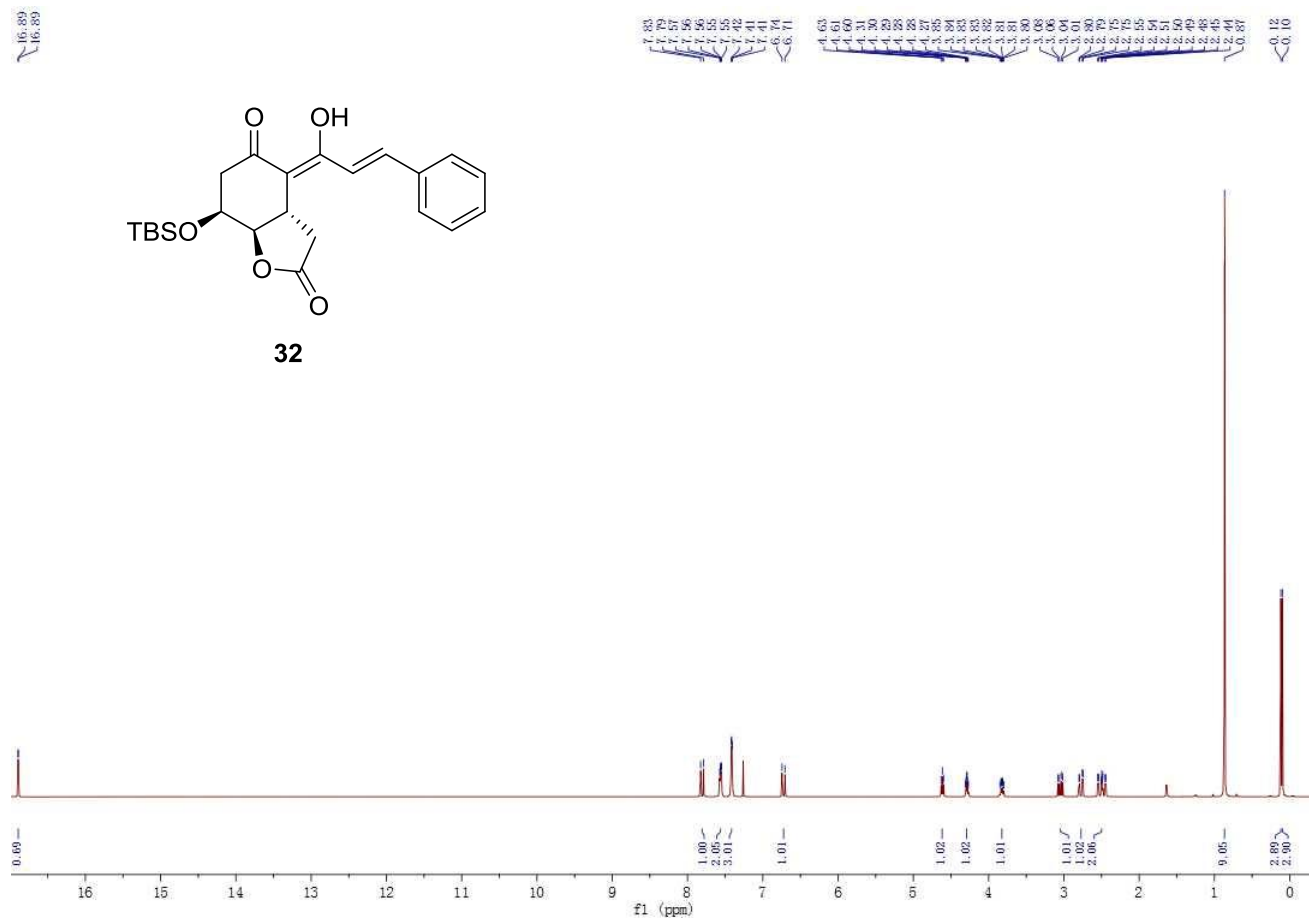
¹H NMR spectrum of compound 31 (400 MHz, CDCl₃)



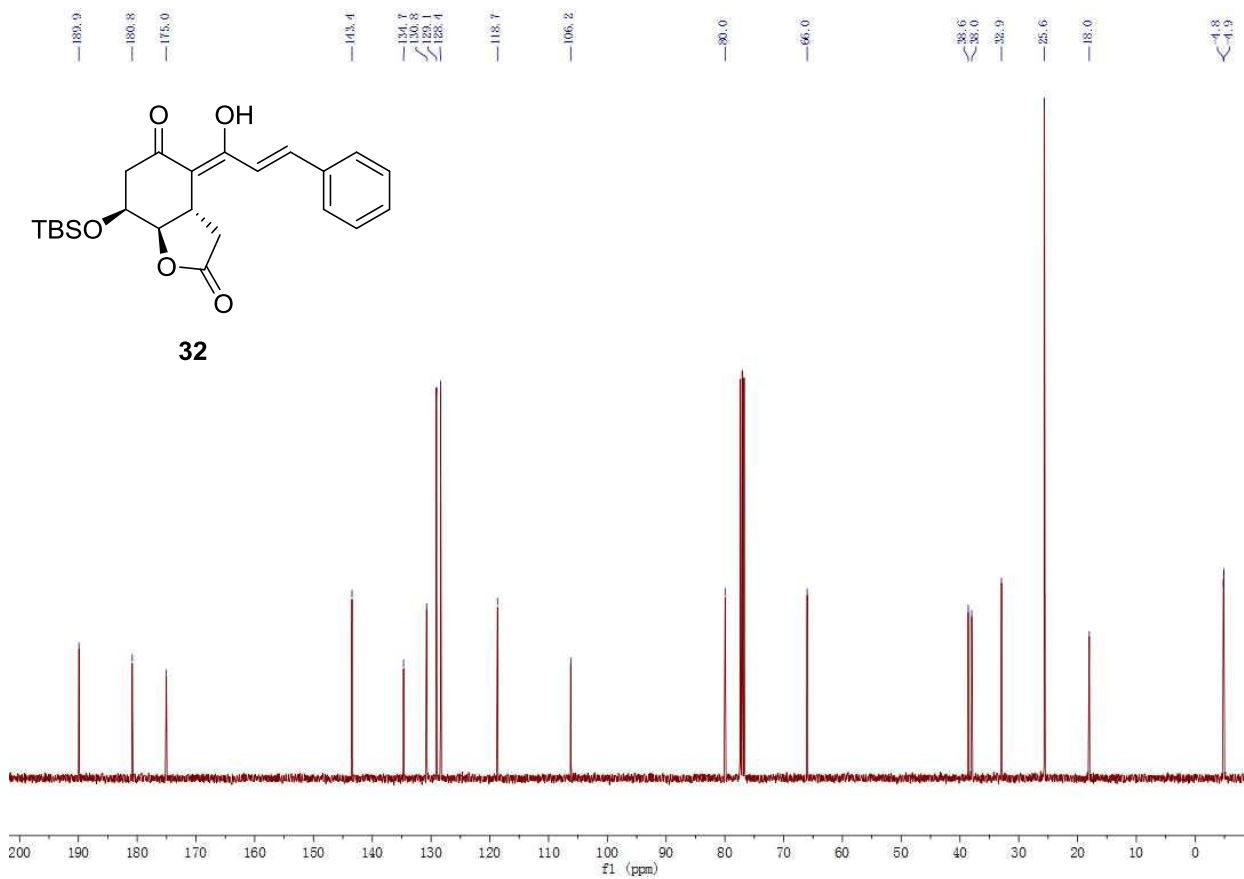
^{13}C NMR spectrum of compound 31 (100 MHz, CDCl_3)



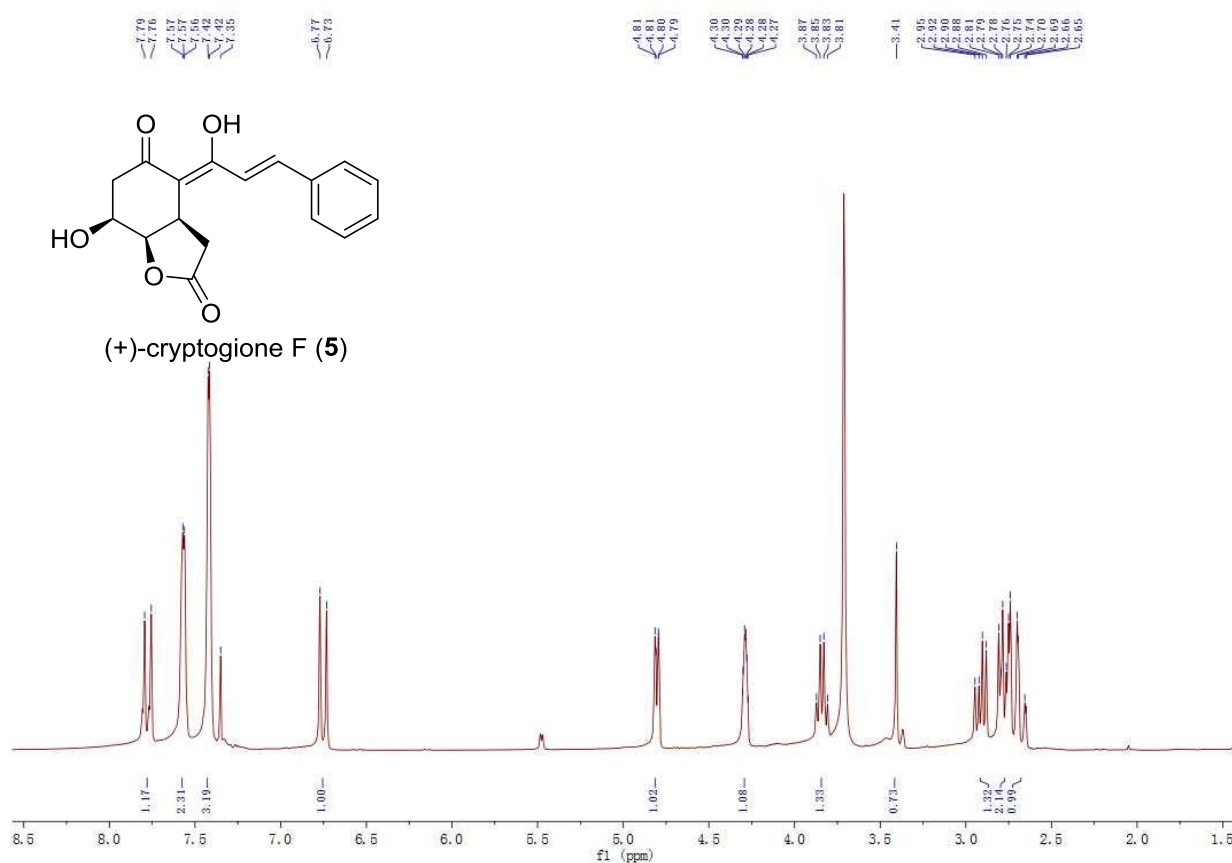
¹H NMR spectrum of compound 32 (400 MHz, CDCl₃)



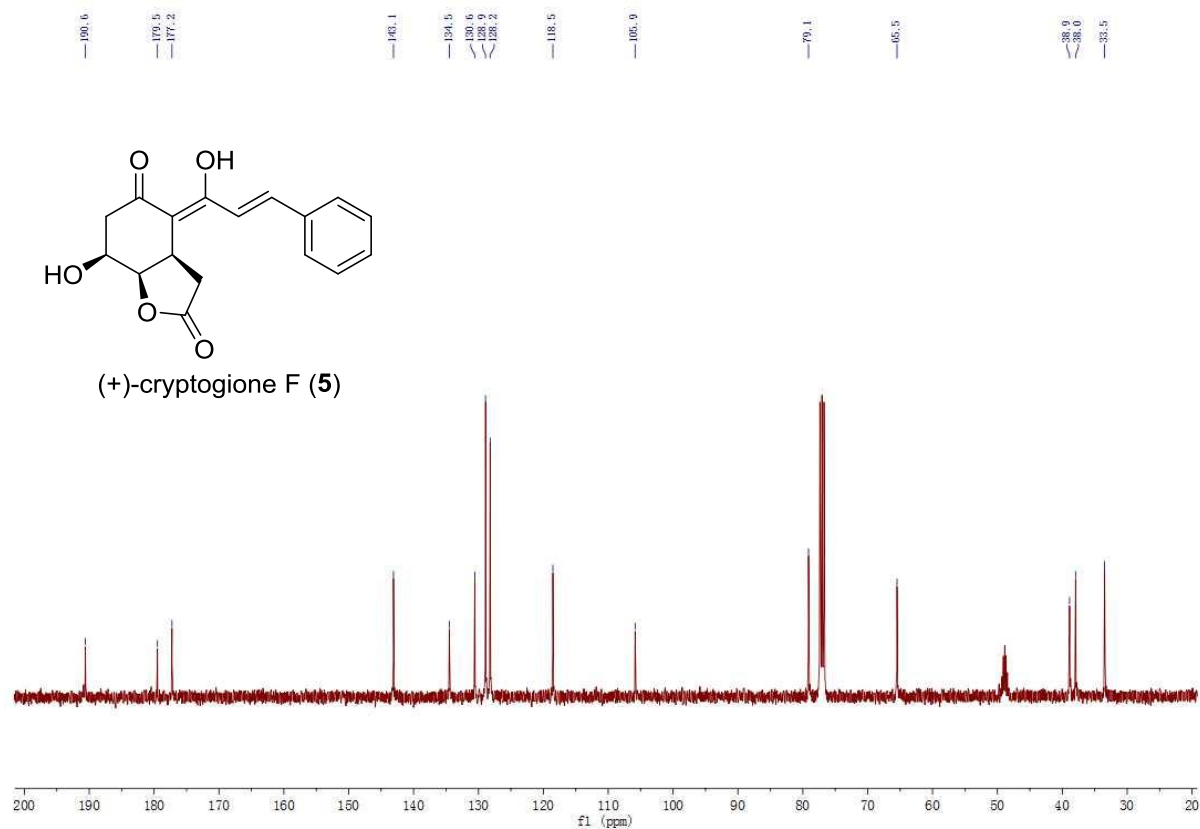
^{13}C NMR spectrum of compound 32 (100 MHz, CDCl_3)



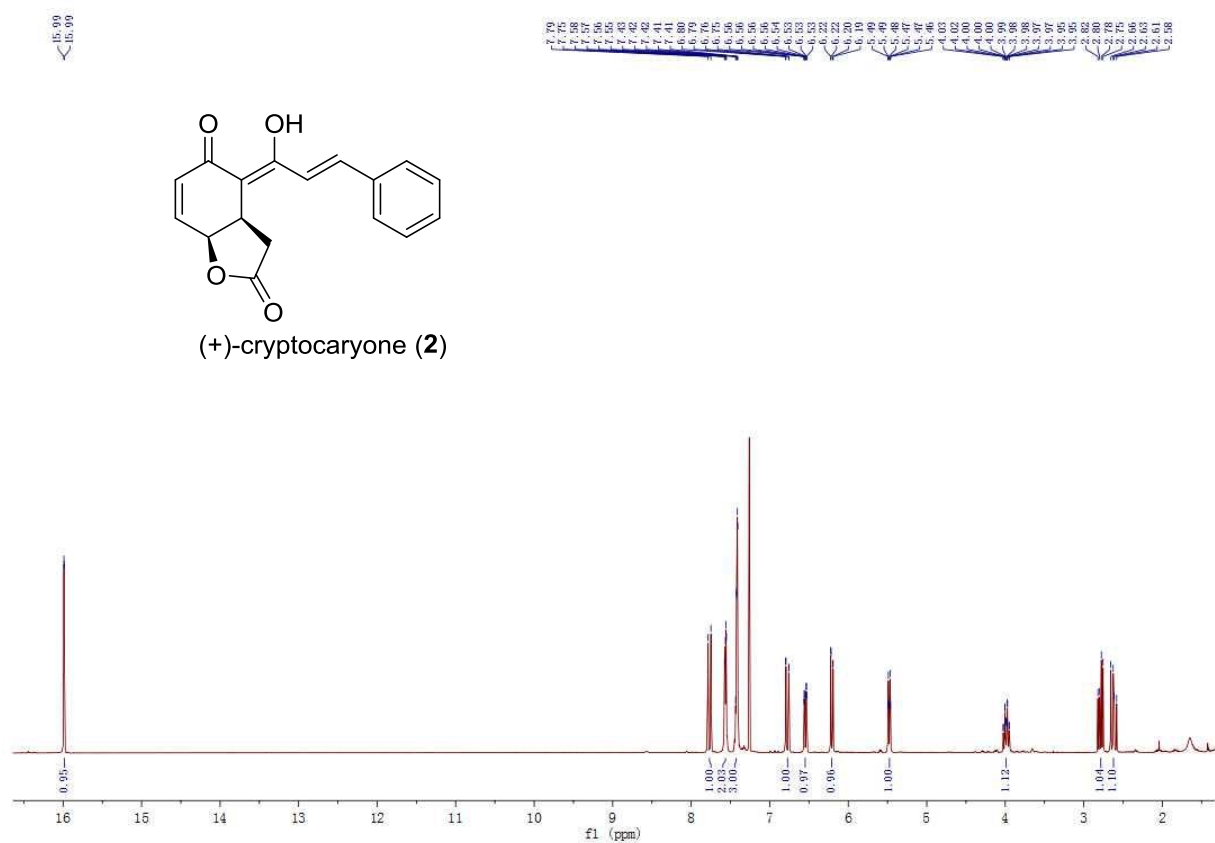
^1H NMR spectrum of compound 5 (400 MHz, $\text{CDCl}_3\text{-CD}_3\text{OD}$)



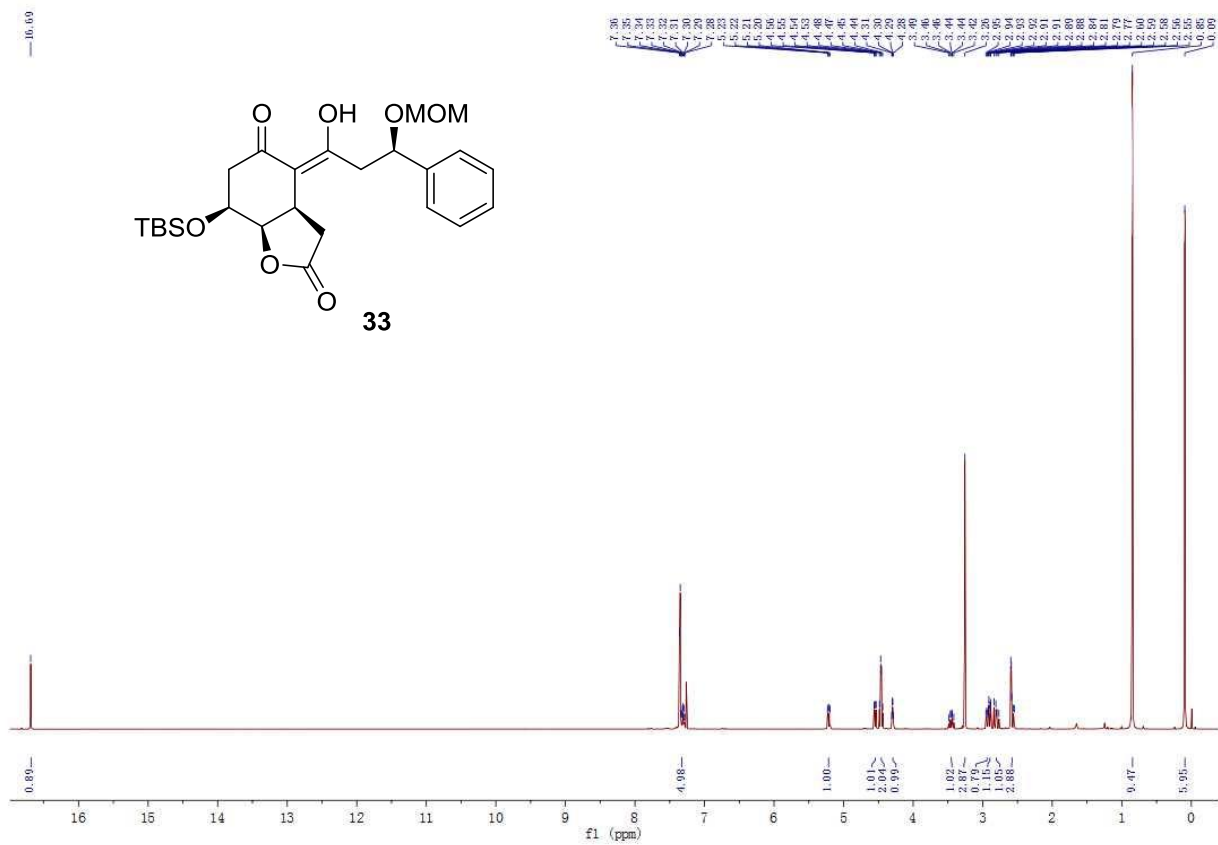
^{13}C NMR spectrum of compound 5 (100 MHz, $\text{CDCl}_3\text{-CD}_3\text{OD}$)



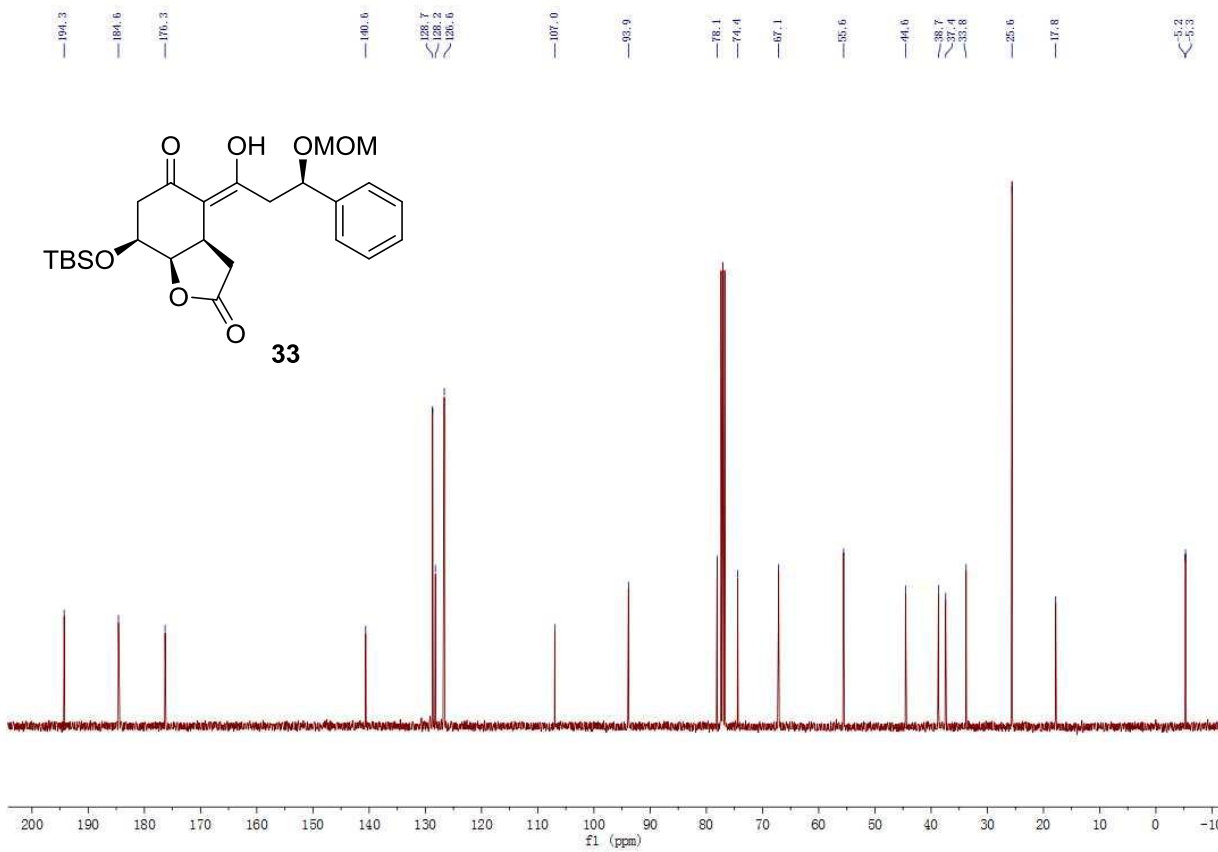
^1H NMR spectrum of compound 2 (400 MHz, CDCl_3)



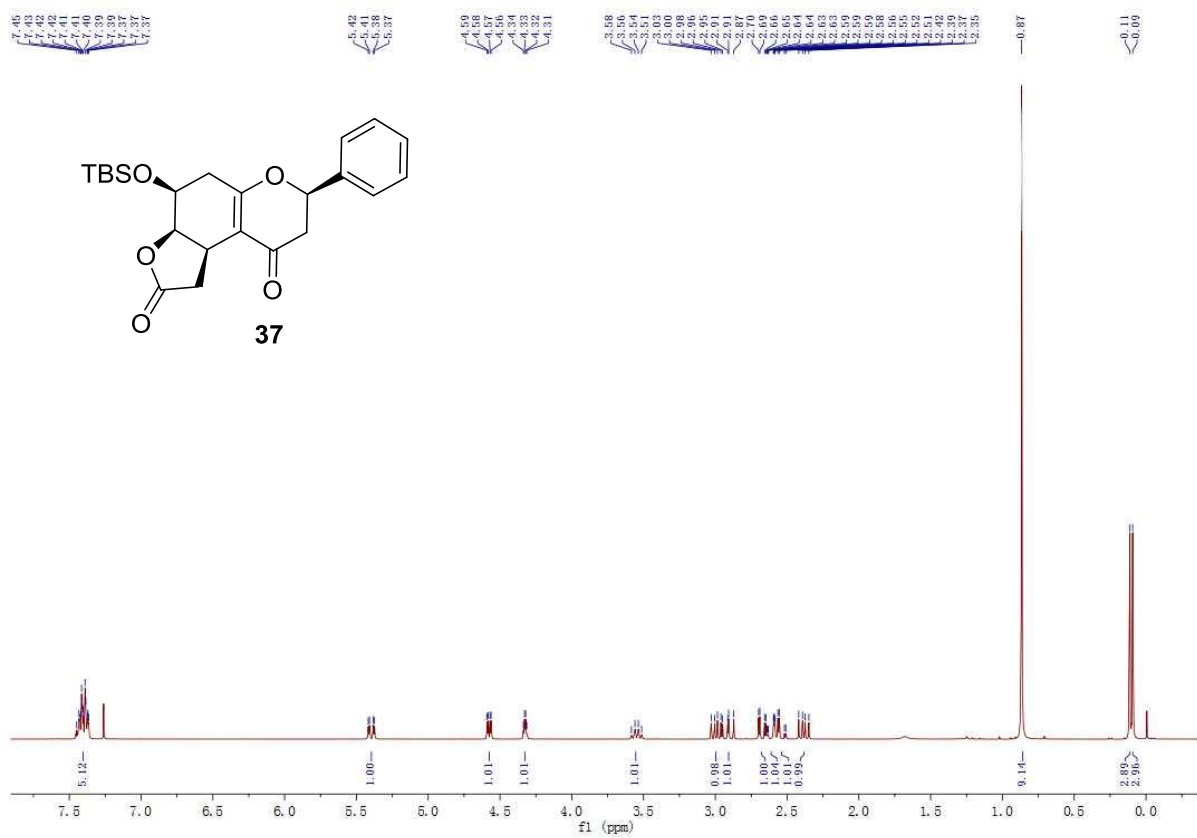
¹H NMR spectrum of compound 33 (400 MHz, CDCl₃)



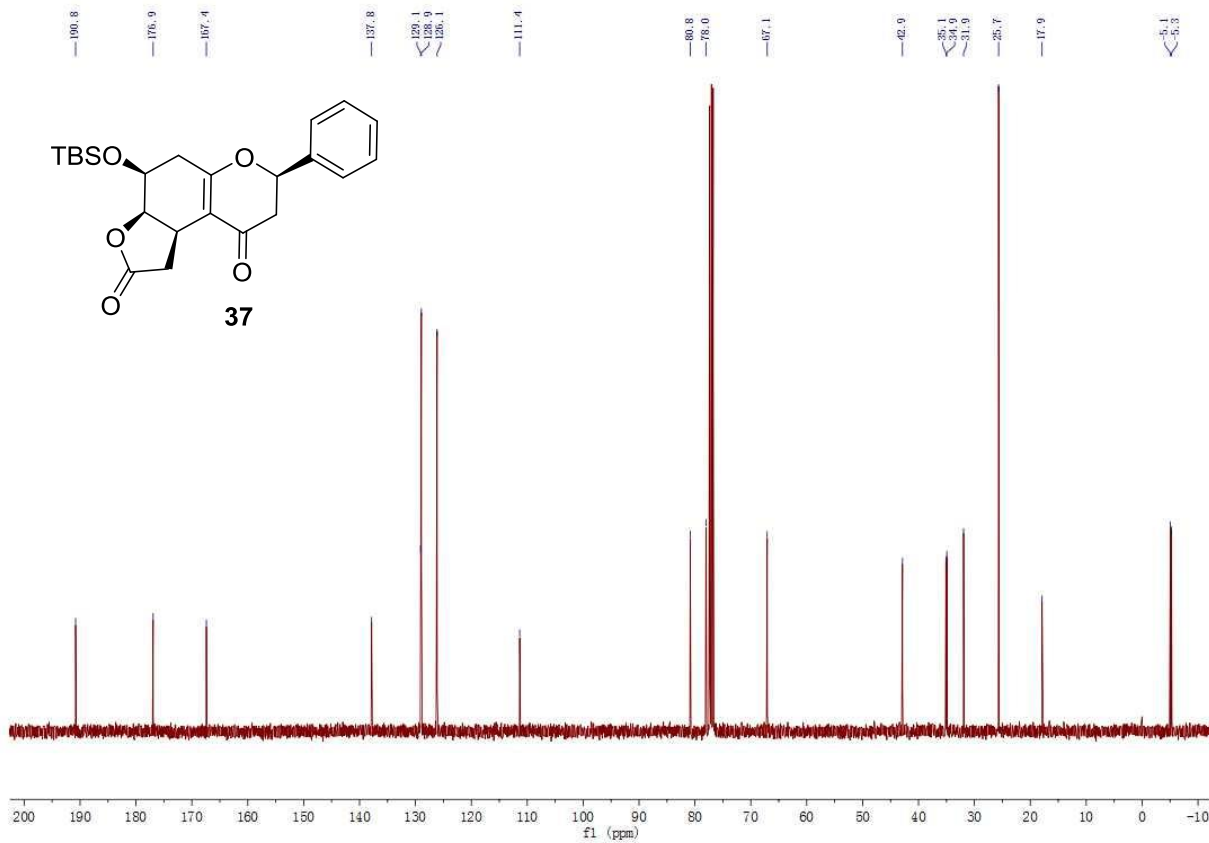
¹³C NMR spectrum of compound 33 (100 MHz, CDCl₃)



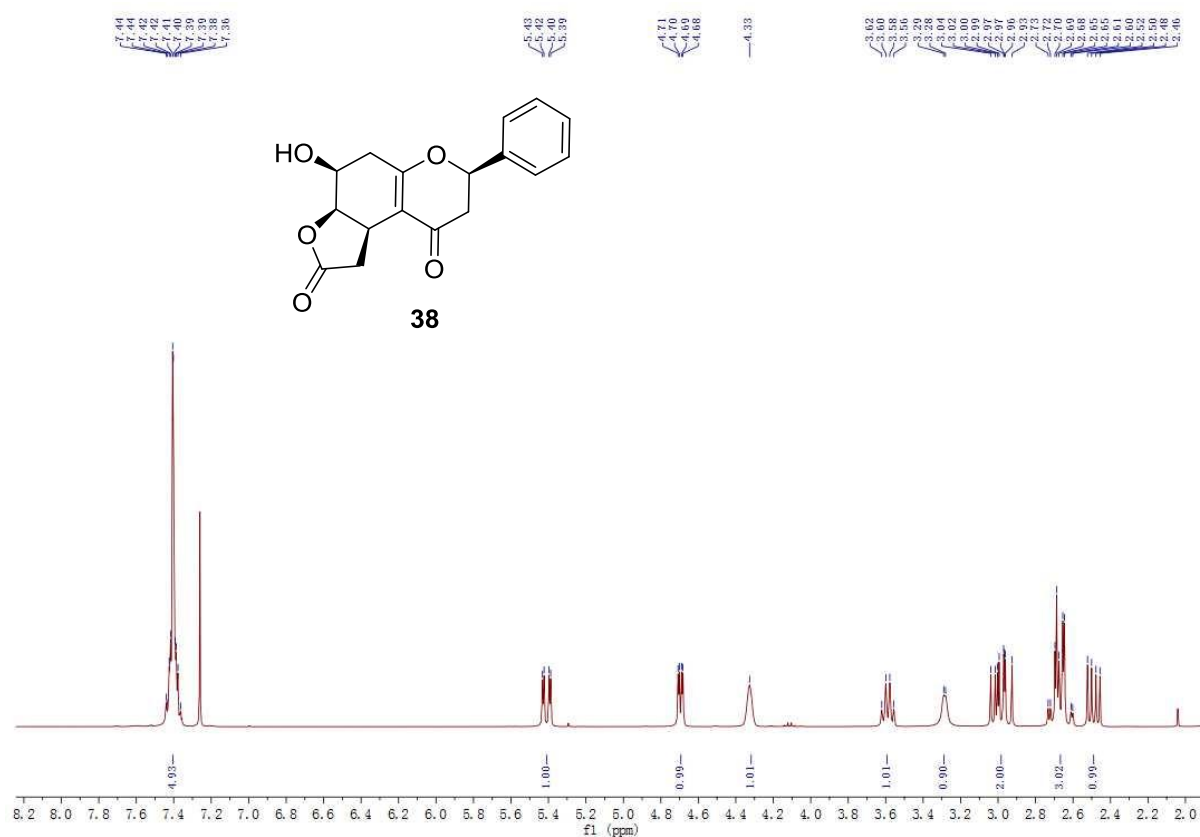
¹H NMR spectrum of compound 37 (400 MHz, CDCl₃)



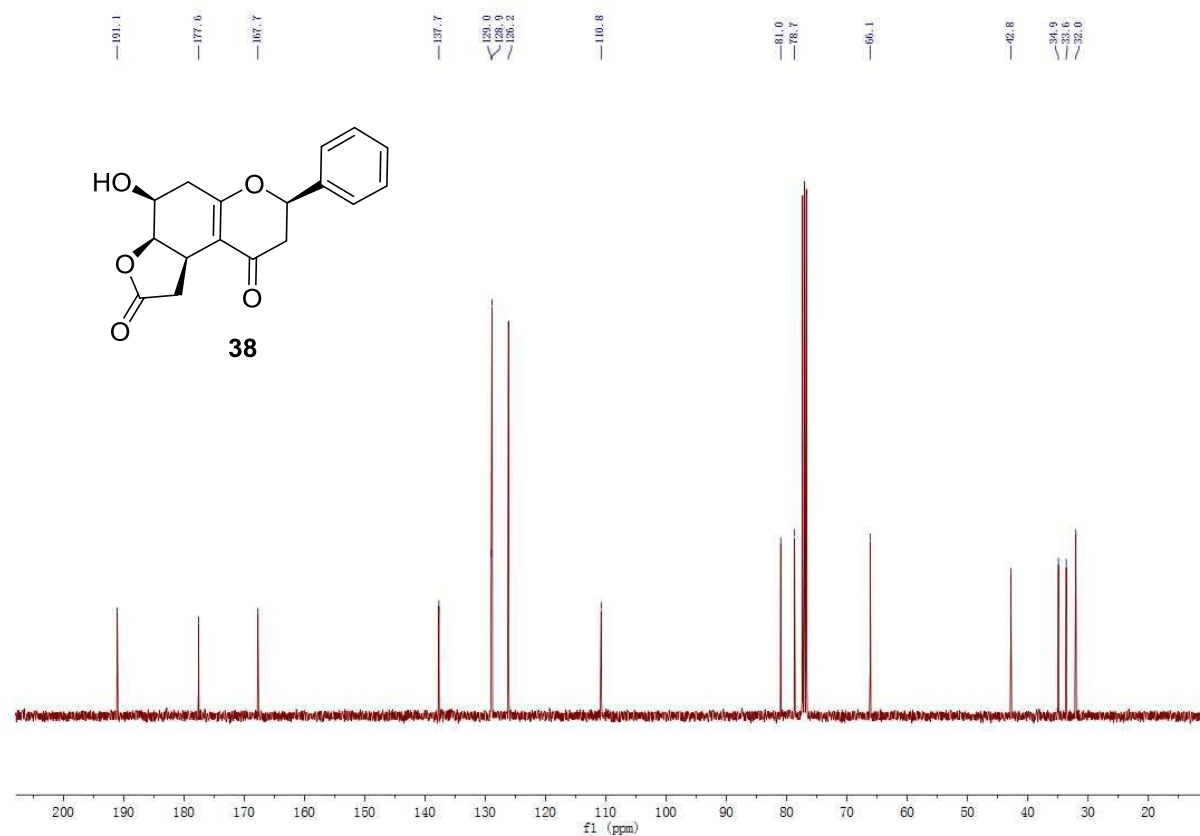
^{13}C NMR spectrum of compound 37 (100 MHz, CDCl_3)



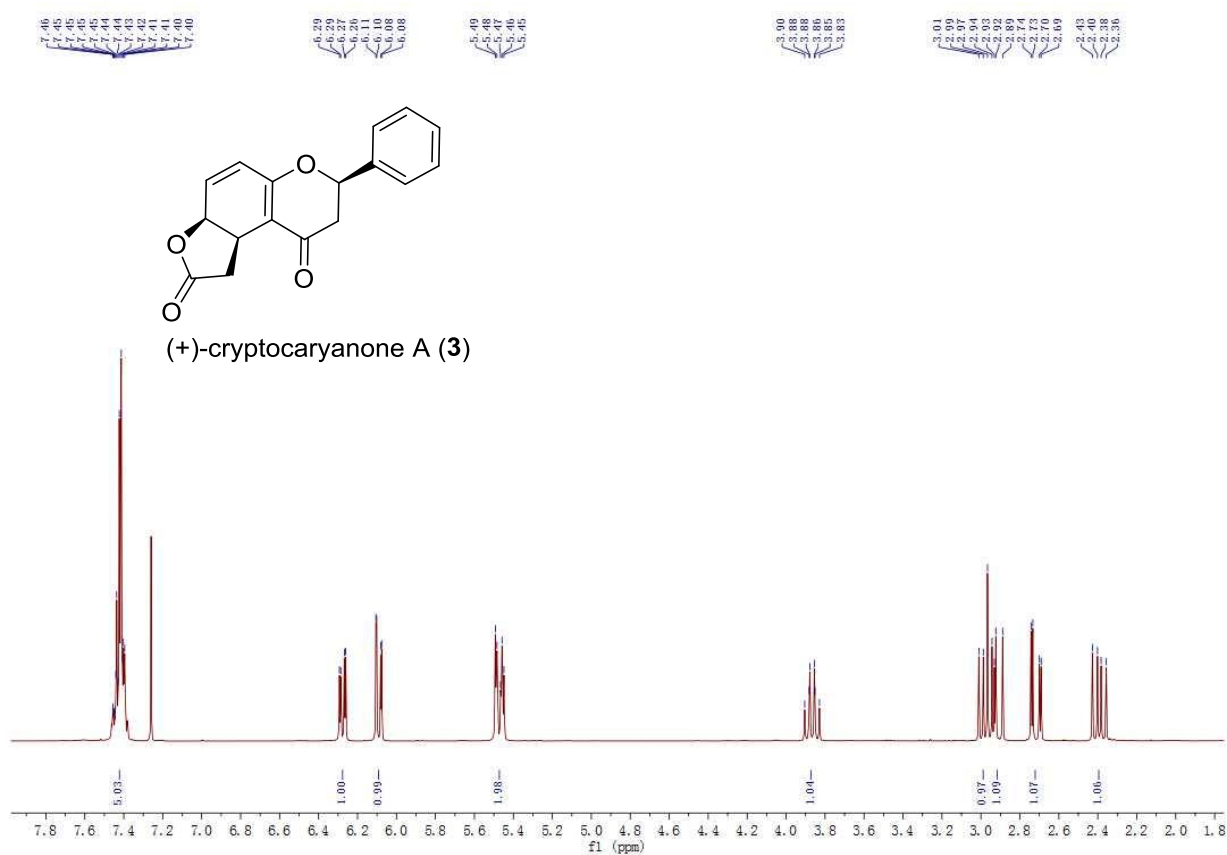
^1H NMR spectrum of compound 38 (400 MHz, CDCl_3)



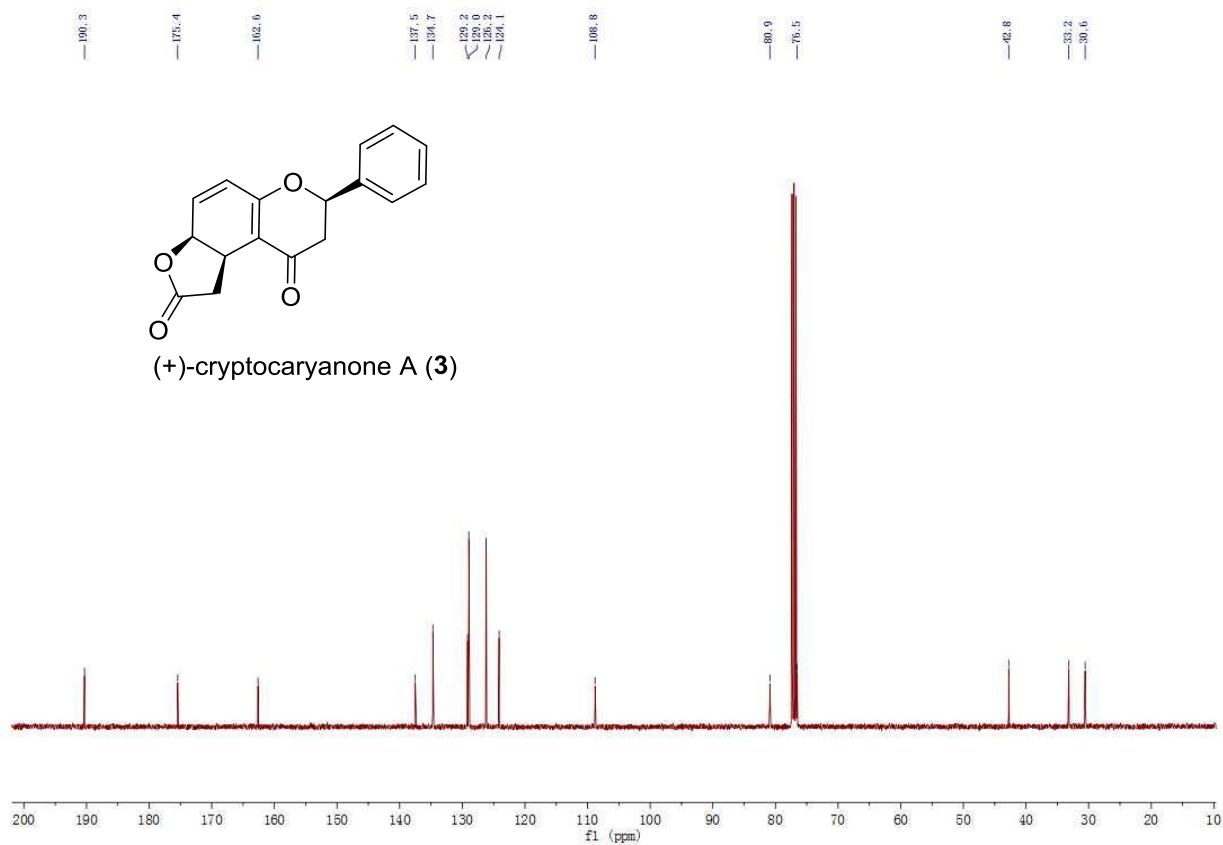
^{13}C NMR spectrum of compound 38 (100 MHz, CDCl_3)



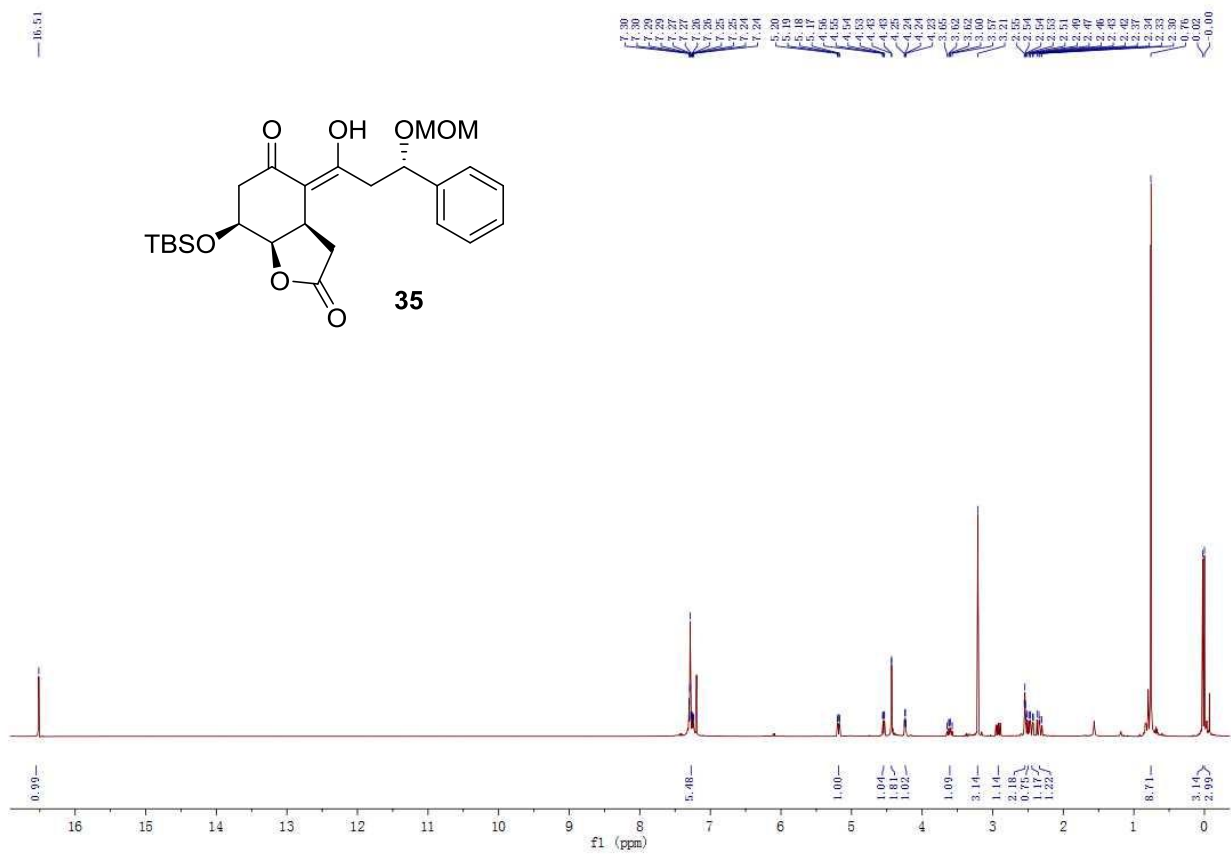
^1H NMR spectrum of compound 3 (400 MHz, CDCl_3)



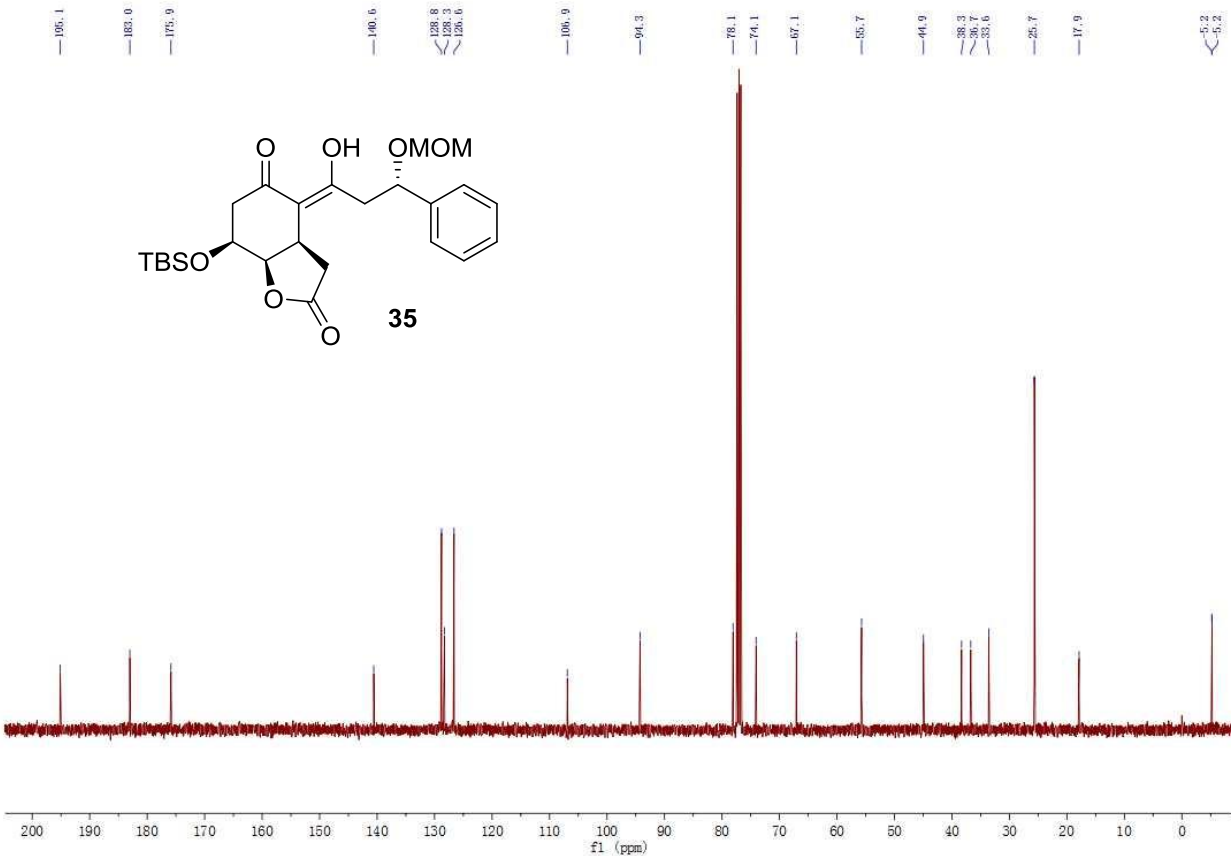
^{13}C NMR spectrum of compound 3 (100 MHz, CDCl_3)



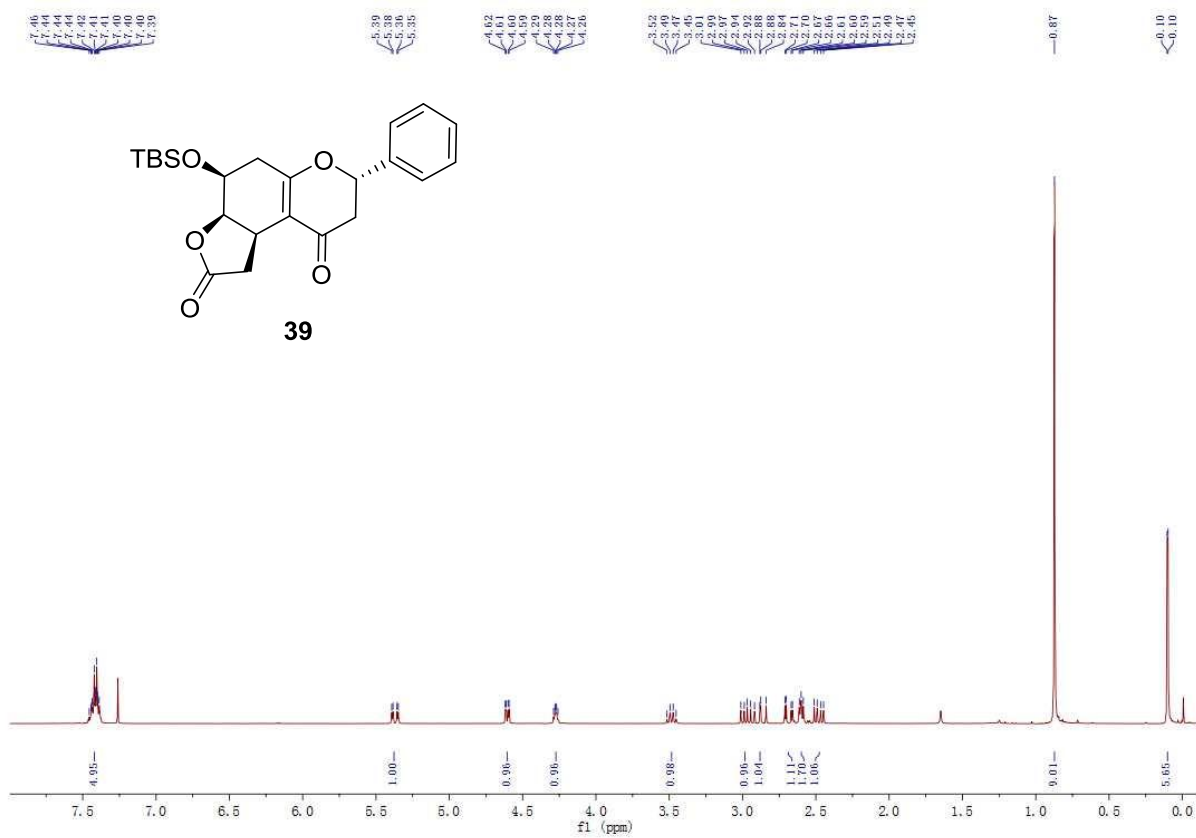
¹H NMR spectrum of compound 35 (400 MHz, CDCl₃)



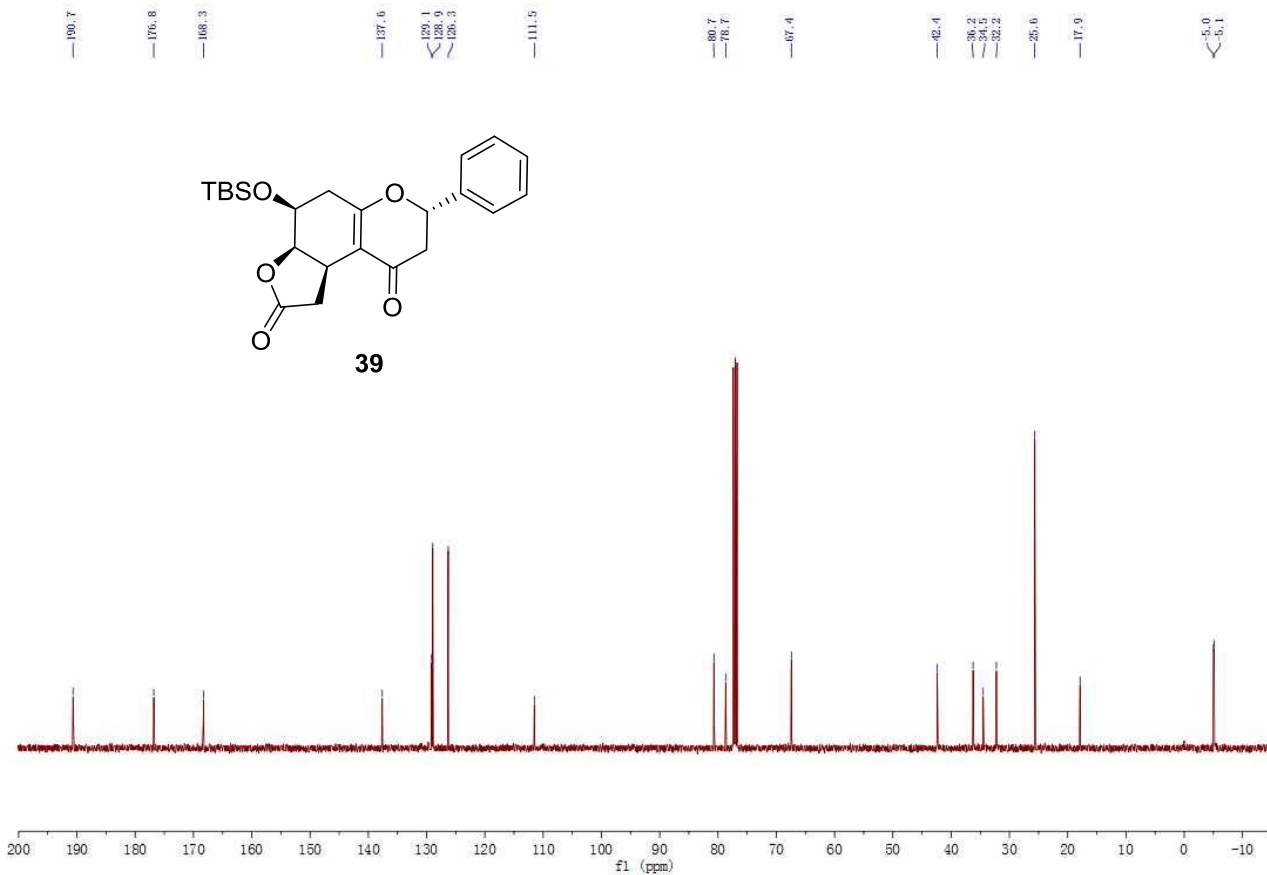
^{13}C NMR spectrum of compound 35 (100 MHz, CDCl_3)



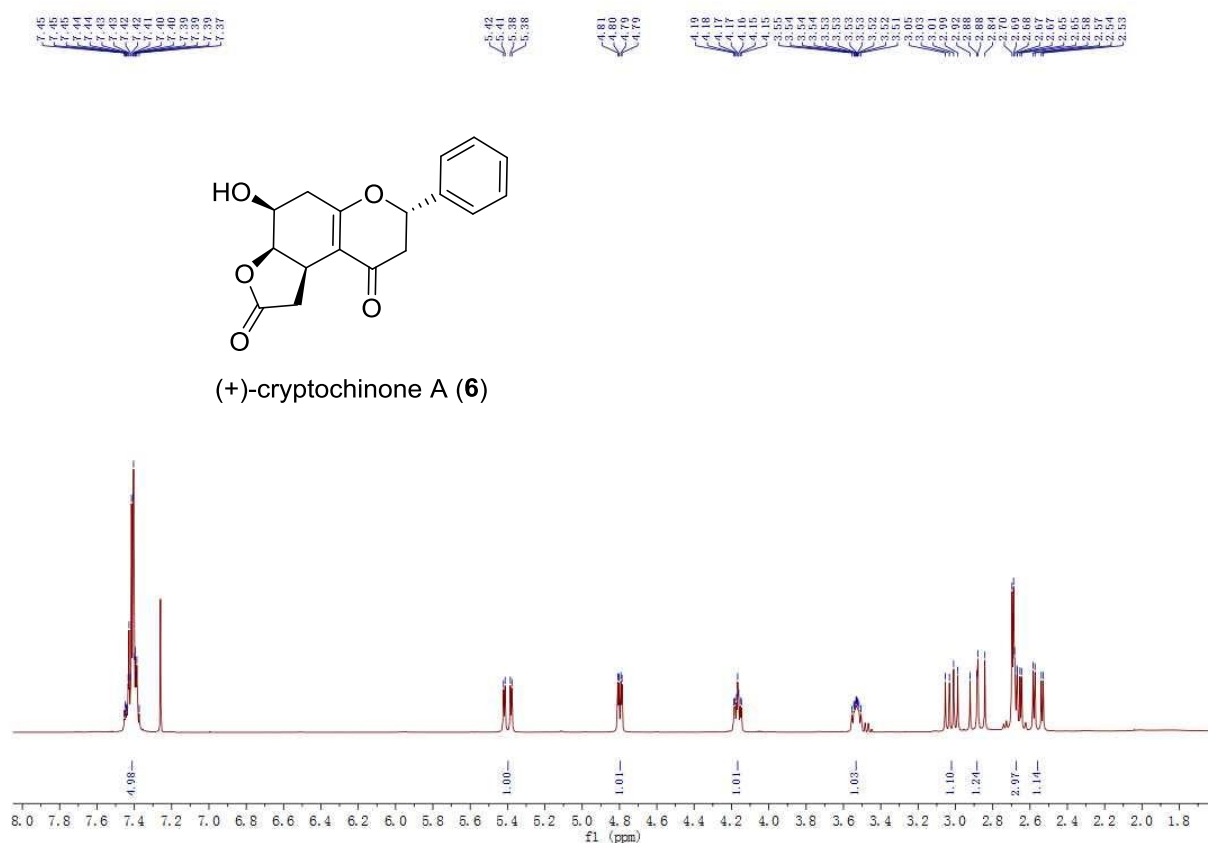
¹H NMR spectrum of compound 39 (400 MHz, CDCl₃)



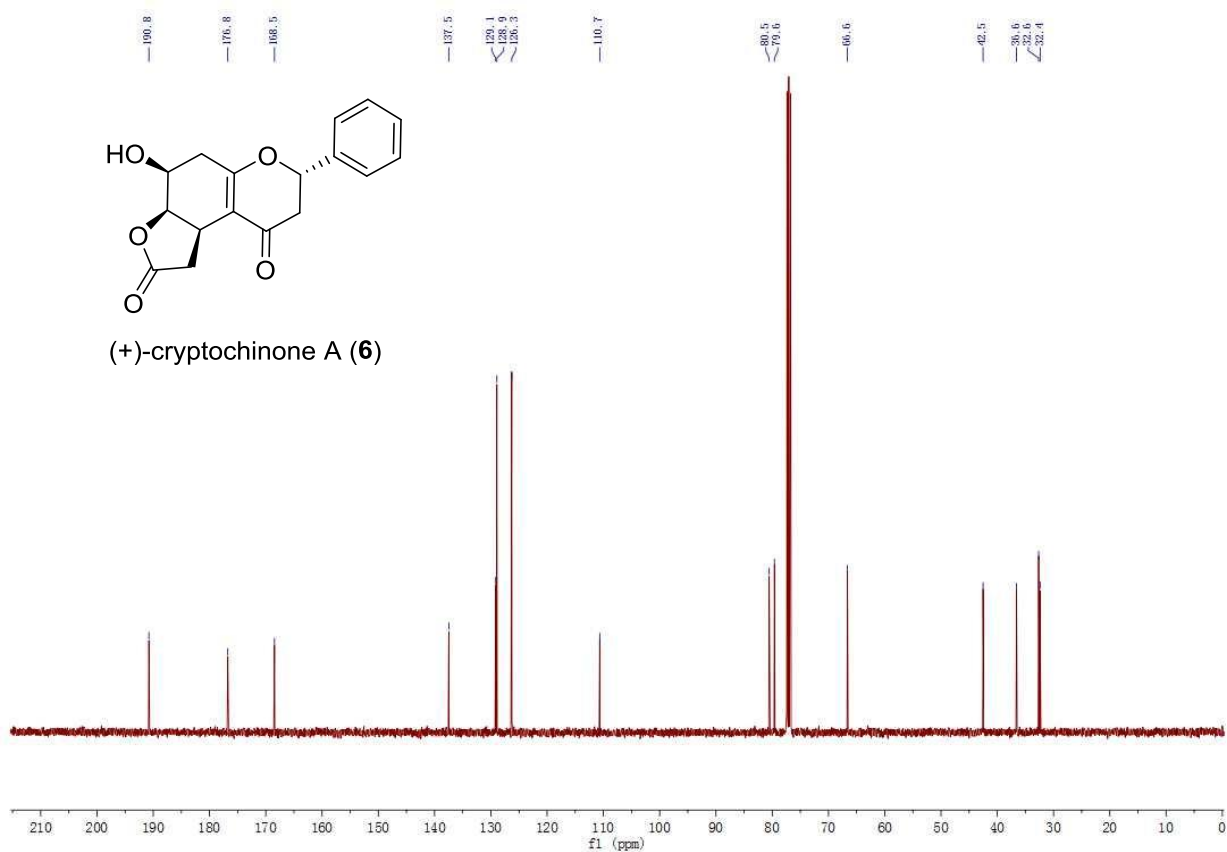
^{13}C NMR spectrum of compound 39 (100 MHz, CDCl_3)



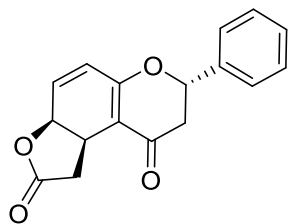
^1H NMR spectrum of compound 6 (400 MHz, CDCl_3)



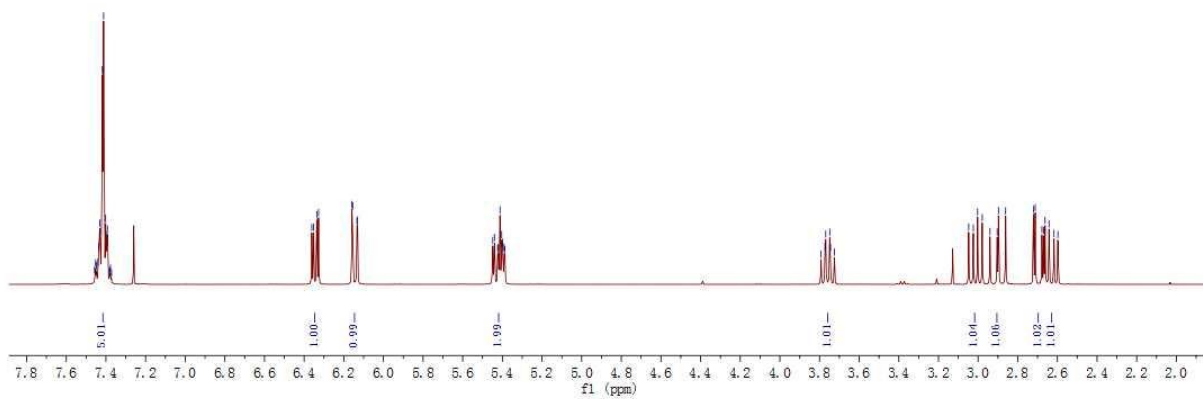
^{13}C NMR spectrum of compound 6 (100 MHz, CDCl_3)



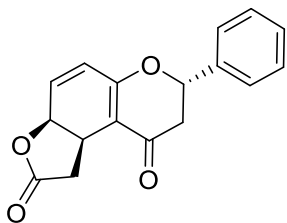
¹H NMR spectrum of compound 4 (400 MHz, CDCl₃)



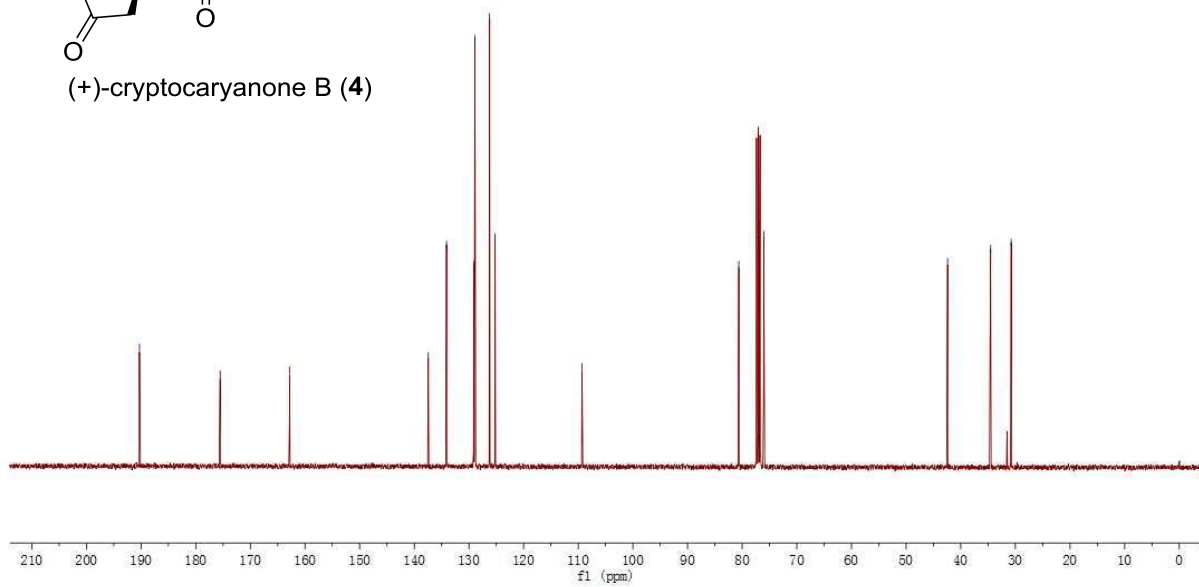
(+)-cryptocaryanone B (**4**)



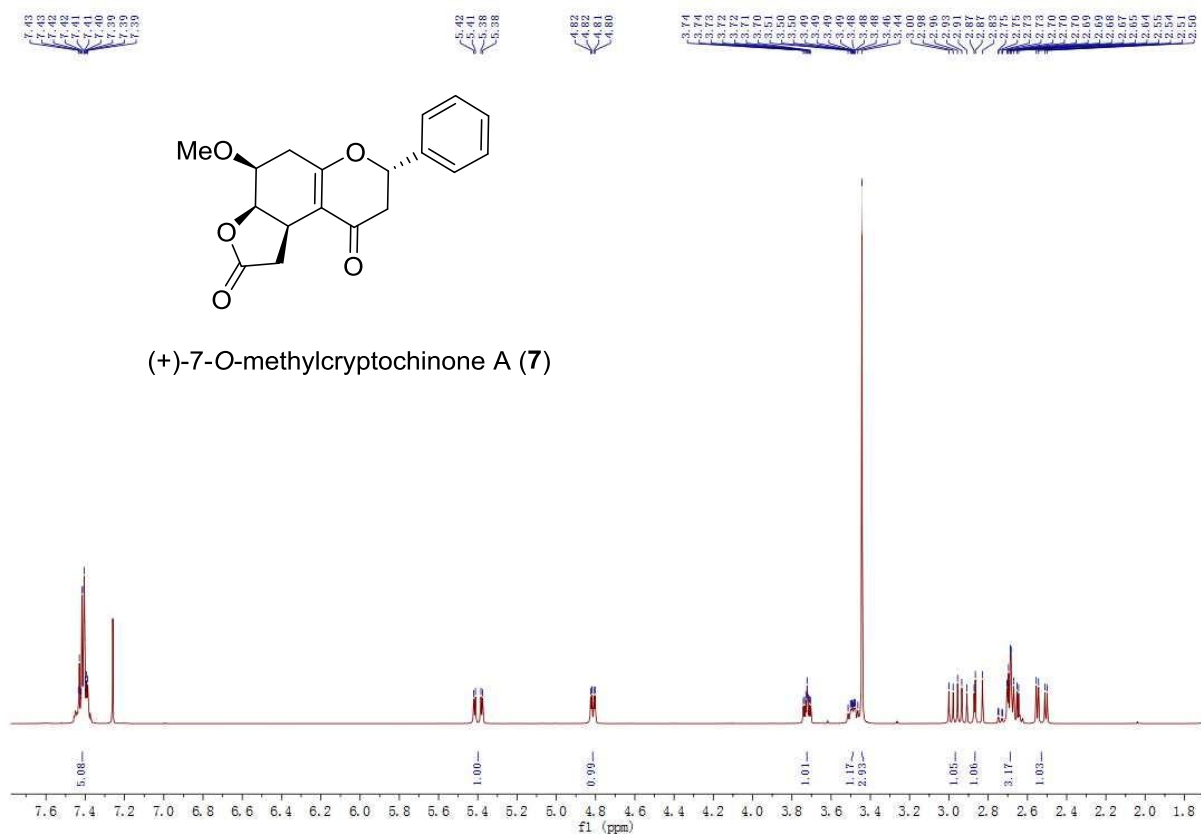
^{13}C NMR spectrum of compound 4 (100 MHz, CDCl_3)



(+)-cryptocaryanone B (**4**)



^1H NMR spectrum of compound 7 (400 MHz, CDCl_3)



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

