

Supporting Information

A Novel Approach to the Tetracyclic Frameworks of Anislactone-type Sesquiterpenoids

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1. General Information

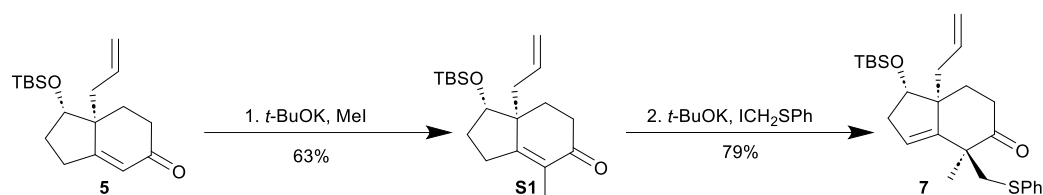
Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Non-aqueous reaction was conducted under an inert atmosphere of argon in flame-dried glassware. Anhydrous solvent was treated as follow: tetrahydrofuran was distilled from sodium under argon atmosphere, dichloromethane and toluene was distilled from calcium hydride under argon atmosphere. The boiling range of petroleum ether was 60 to 90 °C.

Thin layer chromatography was conducted on Merck 60 F254 pre-coated silica gel plates. Column chromatography was carried out by normal silica gel (40-60 μm , 200-400 mesh, Silicycle P60). NMR data including ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz, 500 MHz and 600 MHz. The chemical shifts (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvents. Coupling constants are given in Hz.

High-resolution mass spectra were obtained using Bruker APEXIII 7.0 TESLA FTMS (the ESI). Optical rotations were measured on an Anton Paar MCP 300 polarimeter and are reported as follows: $[\alpha]_D^{25}$ (c g/100 mL, solvent).

The X-ray crystallographic data was collected at 173 K on a Rigaku XtaLAB PRO MM003-DS dual system with a Cu micro-focus source or Bruker D8 quest.

2. Experimental Procedures and Spectroscopic Data of Compounds



A solution of racemic enone **5** (200.0 mg, 0.6 mmol, 1.0 equiv) and *t*-BuOK (97.0 mg, 0.7 mmol, 1.2 equiv) in anhydrous *t*-BuOH (2 mL) was stirred at room temperature for 30 min under argon atmosphere. The reaction mixture was heated to 80 °C and slowly added to MeI (34.0 μL , 0.7 mmol, 1.05 equiv.). The reaction mixture was stirred at 80 °C for 20 min before it was quenched with water (40 mL). The reaction contents were extracted with ethyl acetate (10 mL \times 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/100, v/v) to yield **S1** (120 mg, 0.38 mmol, 63%) as a light yellow liquid.

^1H NMR (500 MHz, CDCl_3) δ 6.07 – 5.91 (m, 1H), 5.05 – 4.93 (m, 2H), 3.79 (dd, J = 10.3, 7.6 Hz, 1H), 2.57 (m, 1H), 2.52 – 2.42 (m, 2H), 2.42 – 2.34 (m, 1H), 2.34 – 2.28 (m, 1H), 2.28 – 2.23 (m, 1H), 2.22 – 2.18 (m, 1H), 2.04 – 1.94 (m, 1H), 1.92 – 1.81 (m, 1H), 1.71 – 1.63 (m, 4H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 198.9, 166.4, 136.7, 129.6, 116.5, 82.5, 48.5, 36.6, 33.3, 33.1, 30.4, 26.3, 25.8, 18.1, 10.7, -4.5, -4.9.

HRMS(ESI), Calculated $\text{C}_{19}\text{H}_{33}\text{O}_2\text{Si}^+$, $[\text{M}+\text{H}]^+$: 321.2244, found: 321.2249.

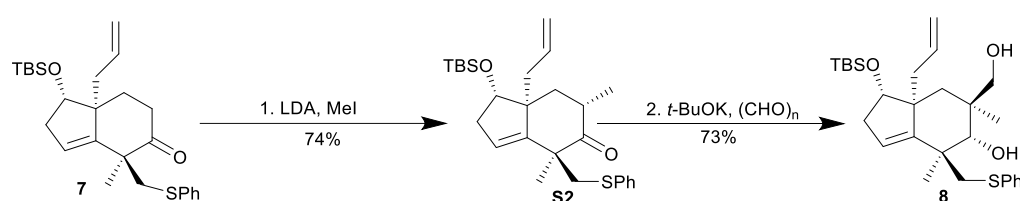
A solution of enone **S1** (400.0 mg, 1.3 mmol, 1.0 equiv) and *t*-BuOK (210.0 mg, 2.0 mmol, 1.5 equiv) in anhydrous THF (5 mL) was stirred at 0 °C for 30 min under argon atmosphere. The reaction mixture was cooled to -78 °C and slowly added to ICH₂SPh (437.0 mg, 1.8 mmol, 1.4 equiv.). The reaction mixture was stirred at -78 °C for 10 min before it was quenched with saturated ammonium

chloride solution (30 mL). The reaction contents were extracted with ethyl acetate (10 mL \times 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/100, v/v) to yield compound **7** (392.0 mg, 0.9 mmol, 79%) as a light yellow liquid.

^1H NMR (500 MHz, CDCl_3) δ 7.43 - 7.39 (m, 2H), 7.32 - 7.31 (m, 1H), 7.30 - 7.28 (m, 1H), 7.23 - 7.19 (m, 1H), 6.15 - 6.03 (m, 1H), 5.59 (dd, J = 3.5, 1.8 Hz, 1H), 5.11 - 5.01 (m, 2H), 4.11 (t, J = 8.3 Hz, 1H), 3.38 (s, 2H), 2.65 - 2.54 (m, 1H), 2.47 - 2.35 (m, 5H), 2.06 - 2.00 (m, 1H), 1.85 - 1.78 (m, 1H), 1.39 (s, 3H), 0.98 (s, 9H), 0.12 (d, J = 4.1 Hz, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 213.4, 148.0, 137.5, 136.2, 130.1, 128.8, 126.3, 123.6, 116.6, 82.6, 52.6, 50.4, 43.9, 39.6, 37.1, 35.5, 32.2, 27.3, 27.3, 25.9, 18.1, -4.5, -4.9.

HRMS(ESI), Calculated $\text{C}_{26}\text{H}_{39}\text{O}_2\text{SSi}^+$, $[\text{M}+\text{H}]^+$: 443.2435, found: 443.2435.



A solution of compound **7** (340.0 mg, 0.8 mmol, 1.0 equiv) in anhydrous THF (8 mL) was stirred at room temperature for 10 min under argon atmosphere. The reaction mixture was cooled to $-78\text{ }^\circ\text{C}$ and slowly added to lithium diisopropylamide (LDA) (1.6 mL, 1.6 mmol, 2.0 equiv, 1 M in THF). The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 10 min and warmed to room temperature for 50 min and slowly added to MeI (239.0 μL , 4.0 mmol, 5.0 equiv). The reaction mixture was stirred at room temperature for 4 h before it was quenched with saturated ammonium chloride solution (30 mL). The reaction contents were extracted with ethyl acetate (10 mL \times 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/100, v/v) to yield compound **S2** (259.0 mg, 0.6 mmol, 74%) as a yellow liquid.

^1H NMR (500 MHz, CDCl_3) δ 7.43 - 7.38 (m, 2H), 7.30 - 7.27 (m, 2H), 7.21-7.16 (m, 1H), 6.15 - 6.05 (m, 1H), 5.50 (dd, J = 3.5, 1.8 Hz, 1H), 5.11-4.96 (m, 2H), 4.05 (t, J = 8.4 Hz, 1H), 3.44 (d, J = 12.1 Hz, 1H), 3.34 (d, J = 12.1 Hz, 1H), 2.76 - 2.66 (m, 1H), 2.60 (d, J = 18.9 Hz, 1H), 2.47 (dd, J = 14.3, 8.2 Hz, 1H), 2.40 - 2.28 (m, 2H), 2.08 (dd, J = 13.0, 5.3 Hz, 1H), 1.46 (t, J = 13.3 Hz, 1H), 1.39 (s, 3H), 1.13 (d, J = 6.6 Hz, 3H), 0.95 (s, 9H), 0.10 (d, J = 7.3 Hz, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 214.5, 148.4, 137.8, 136.4, 130.1, 128.8, 126.2, 123.2, 116.5, 83.3, 53.3, 50.4, 43.5, 42.4, 39.6, 37.4, 37.0, 29.2, 25.9, 18.1, 15.7, -4.5, -4.8.

HRMS(ESI), Calculated $\text{C}_{27}\text{H}_{41}\text{O}_2\text{SSi}^+$, $[\text{M}+\text{H}]^+$: 457.2591, found: 457.2590.

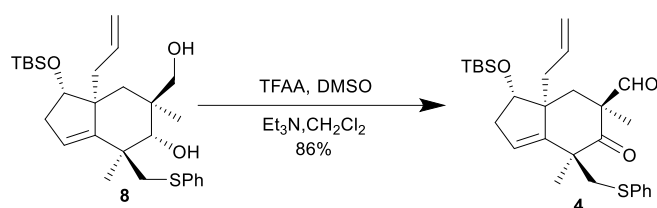
A solution of compound **S2** (456.0 mg, 1.0 mmol, 1.0 equiv) and *t*-BuOK (224.0 mg, 2.0 mmol, 2.0 equiv) in anhydrous THF (5 mL) was stirred at room temperature for 30 min under argon atmosphere. The reaction mixture was added to paraformaldehyde (300.0 mg, 10.0 mmol, 10.0 equiv) and stirred at room temperature for 4 h. The reaction mixture was quenched with water (30 mL). The reaction contents were extracted with ethyl acetate (10 mL \times 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to yield compound **8** (356.2 mg, 0.73 mmol, 73%) as a yellow liquid.

¹H NMR (500 MHz, CDCl₃) δ 7.45 - 7.40 (m, 2H), 7.27-7.25 (m, 2H), 7.16-7.14 (m, 1H), 6.04 - 5.93 (m, 1H), 5.55 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.03 (d, *J* = 15.3 Hz, 1H), 4.94 (d, *J* = 10.0 Hz, 1H), 3.95 (d, *J* = 3.6 Hz, 1H), 3.92 (t, *J* = 8.4 Hz, 1H), 3.33-3.30 (m, 2H), 3.28 (s, 2H), 3.04 (d, *J* = 3.8 Hz, 1H), 2.65 (m, 2H), 2.53 (m, 1H), 2.32 (m, 1H), 2.22 (m, 1H), 1.62 (d, *J* = 13.9 Hz, 1H), 1.30 (s, 3H), 1.26 (s, 3H), 1.03 (d, *J* = 14.0 Hz, 1H), 0.92 (s, 9H), 0.05 (d, *J* = 5.9 Hz, 6H)

¹³C NMR (126 MHz, CDCl₃) δ 147.6, 138.1, 137.0, 129.5, 129.0, 126.0, 123.3, 116.2, 86.5, 77.7, 76.7, 50.7, 44.9, 44.7, 44.0, 39.4, 39.4, 39.3, 25.9, 22.3, 18.1, 18.0, -4.4, -4.8

HRMS(ESI), Calculated C₂₈H₄₅O₃SSi⁺, [M+H]⁺: 489.2853, found: 489.2587.

m.p.: 106.48-107.58 °C;

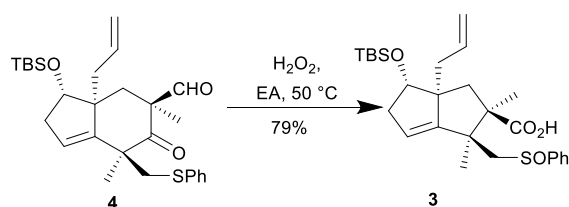


A solution of trifluoroacetic anhydride (TFAA) (340.0 mg, 1.5 mmol, 2.2 equiv) in anhydrous CH₂Cl₂ (5 mL) was stirred at -78 °C for 10 min under argon atmosphere. The reaction mixture was slowly added to DMSO (385.0 μL, 5.5 mmol, 8.0 equiv) and stirred at -78 °C for 30 min. The reaction mixture was added to compound **8** (330.0 mg, 0.7 mmol, 1.0 equiv). The reaction mixture was stirred at -78 °C for 60 min before it was added to Et₃N (1.38 mL, 10.0 mmol, 15.0 equiv). The reaction mixture was stirred at room temperature for 60 min before it was quenched with saturated ammonium chloride solution (30 mL). The reaction contents were extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/80, v/v) to yield compound **4** (300.0 mg, 0.6 mmol, 86%).

¹H NMR (500 MHz, CDCl₃) δ 9.42 (s, 1H), 7.37 - 7.31 (m, 3H), 7.30 (d, *J* = 1.7 Hz, 1H), 7.25 - 7.20 (m, 1H), 6.08 - 5.97 (m, 1H), 5.70 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.05 - 4.99 (m, 2H), 4.28 (t, *J* = 8.3 Hz, 1H), 3.36 (d, *J* = 12.2 Hz, 1H), 3.24 (d, *J* = 12.2 Hz, 1H), 2.65 (d, *J* = 14.8 Hz, 1H), 2.55 - 2.48 (m, 1H), 2.43 - 2.36 (m, 1H), 2.35 - 2.27 (m, 1H), 2.22 - 2.15 (m, 1H), 1.75 (d, *J* = 14.8 Hz, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 0.98 (s, 9H), 0.15 (d, *J* = 20.6 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 211.3, 198.4, 146.4, 136.7, 135.7, 129.7, 129.0, 126.5, 124.9, 116.9, 82.1, 61.2, 52.2, 50.3, 43.7, 40.4, 39.6, 39.6, 25.9, 25.0, 23.0, 18.0, -4.4, -4.8

HRMS(ESI), Calculated C₂₈H₄₁O₃SSi⁺, [M+H]⁺: 485.2540, found: 485.2543.



A solution of compound **4** (500.0 mg, 1.0 mmol, 1.0 equiv) in ethyl acetate (5 mL) was stirred at room temperature for 10 min. The reaction mixture was added to H₂O₂ (30% in H₂O) (1.3 mL, 10.0 mmol, 10.0 equiv) and stirred at 50 °C for 12 h. The reaction mixture was quenched with water (30

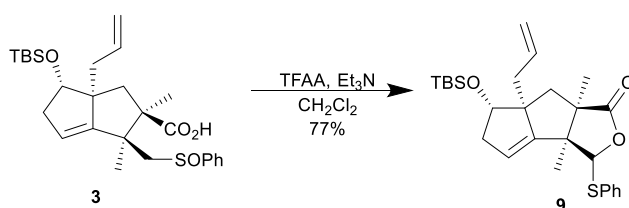
mL). The reaction contents were extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/8, v/v) to yield compound **3** (386.2 mg, 0.79 mmol, 79%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 7.66-7.63 (m, 2H), 7.45 - 7.38 (m, 3H), 6.09 - 5.96 (m, 1H), 5.33 (m, 1H), 5.04 - 4.91 (m, 2H), 4.49 (t, *J* = 8.1 Hz, 1H), 3.12 (d, *J* = 14.1 Hz, 1H), 2.98 (d, *J* = 14.0 Hz, 1H), 2.50 (m, 1H), 2.46 - 2.38 (m, 2H), 2.33 (d, *J* = 14.5 Hz, 1H), 2.23 (m, 1H), 1.55 (d, *J* = 14.2 Hz, 1H), 1.49 (s, 3H), 1.45 (s, 3H), 0.88 (s, 9H), 0.01 (d, *J* = 9.3 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 180.7, 157.1, 145.0, 137.1, 131.1, 129.3, 124.3, 119.3, 116.2, 82.3, 68.0, 58.8, 56.4, 47.2, 44.7, 41.3, 40.3, 25.9, 21.8, 21.7, 18.1, -4.5, -4.6.

HRMS(ESI), Calculated C₂₈H₄₁O₄SSi⁺, [M+H]⁺: 489.2489, found: 489.2491.

m.p.: 73.77-74.60 °C;



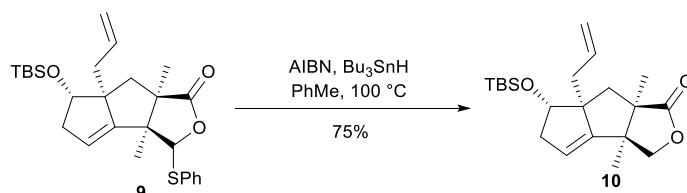
A solution of compound **3** (120.0 mg, 0.2 mmol, 1.0 equiv) in CH₂Cl₂ (8 mL) was stirred at room temperature for 10 min. The reaction mixture was added to Et₃N (96.0 μL, 0.6 mmol, 2.5 equiv) and stirred at room temperature for 10 min. The reaction mixture was added to trifluoroacetic anhydride (42.0 μL, 0.3 mmol, 1.2 equiv) and stirred at room temperature for 20 min. The reaction mixture was quenched with water (30 mL). The reaction contents were extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to yield compound **9** (95.2 mg, 0.15 mmol, 77%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 7.0 Hz, 2H), 7.39 (d, *J* = 7.1 Hz, 2H), 7.31 (s, 1H), 6.14 (s, 1H), 6.11 - 6.00 (m, 1H), 5.39 (s, 1H), 5.05 (t, *J* = 14.5 Hz, 2H), 4.12 - 3.97 (m, 1H), 2.56 - 2.46 (m, 2H), 2.41 - 2.31 (m, 2H), 1.71 - 1.59 (m, 2H), 1.43 (s, 3H), 1.21 (s, 3H), 0.95 (s, 9H), 0.10 (d, *J* = 10.0 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 181.0, 151.1, 136.5, 135.0, 131.9, 129.4, 128.2, 123.6, 116.6, 95.1, 83.6, 58.3, 58.0, 53.7, 44.6, 42.3, 40.8, 25.9, 18.0, 17.5, 17.1, -4.6, -4.8.

HRMS(ESI), Calculated C₂₇H₃₉O₃SSi⁺, [M+H]⁺: 471.2384, found: 471.2384.

m.p.: 123.72-125.38 °C;



A solution of compound **9** (150.0 mg, 0.3 mmol, 1.0 equiv) and Bu₃SnH (931.0 mg, 3.2 mmol, 10.0 equiv) in PhMe (15 mL) was stirred at room temperature for 10 min. The reaction mixture was

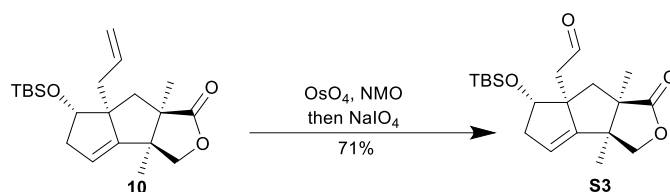
added to AIBN (524.0 mg, 3.2 mmol, 10.0 equiv, added to the bottle in 4 batches at intervals of 1 h) and stirred at 100 °C for 5 h. The reaction mixture was quenched with water (30 mL). The reaction contents were extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/80, v/v) to yield compound **10** (87.0 mg, 0.24 mmol, 75%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 6.08 - 5.93 (m, 1H), 5.50 (dd, *J* = 4.0, 1.7 Hz, 1H), 5.04 - 4.91 (m, 2H), 4.37 (d, *J* = 9.1 Hz, 1H), 4.02 - 3.94 (m, 1H), 3.89 (d, *J* = 9.1 Hz, 1H), 2.50 (dd, *J* = 13.9, 7.6 Hz, 1H), 2.44 (dd, *J* = 16.8, 8.8 Hz, 1H), 2.38 - 2.31 (m, 1H), 2.28 - 2.21 (m, 1H), 2.18 (d, *J* = 14.2 Hz, 1H), 1.58 (d, *J* = 14.3 Hz, 1H), 1.19 (s, 3H), 1.18 (s, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 183.4, 154.7, 136.5, 119.8, 116.4, 84.1, 73.6, 58.2, 55.4, 48.2, 45.7, 41.9, 40.9, 25.8, 18.2, 18.0, 17.5, -4.7, -4.8.

HRMS(ESI), Calculated C₂₁H₃₈NO₃Si⁺, [M+NH₄]⁺: 380.2615, found: 380.2612.

m.p.:133.74-135.56 °C;



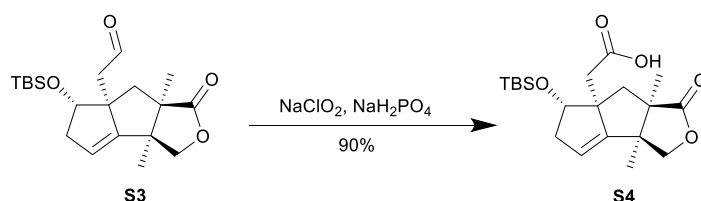
A solution of compound **10** (500.0 mg, 1.4 mmol, 1.0 equiv) in acetone (14 mL) was stirred at room temperature for 10 min. The reaction mixture was added to OsO₄ (0.7 mL, 0.055 mmol, 0.04 equiv, 2% in H₂O) and stirred at room temperature for 50 min. The reaction mixture was added to water (14 mL) and NaIO₄ (882.0 mg, 4.1 mmol, 3.0 equiv). Then, the reaction mixture was stirred at room temperature for 50 min. The reaction mixture was quenched with saturated NaS₂O₃ (30 mL). The reaction contents were extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/8, v/v) to yield compound **S3** (360.0 mg, 1.0 mmol, 71%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 9.81 (dd, *J* = 3.7, 1.5 Hz, 1H), 5.51 - 5.52 (m, 1H), 4.36 (d, *J* = 9.3 Hz, 1H), 4.03 (dd, *J* = 8.7, 7.1 Hz, 1H), 3.92 (d, *J* = 9.3 Hz, 1H), 2.70 (dd, *J* = 15.1, 3.7 Hz, 1H), 2.52 - 2.37 (m, 3H), 2.34 (dd, *J* = 15.1, 1.6 Hz, 1H), 1.85 (d, *J* = 9.3 Hz, 1H), 1.19 (d, *J* = 20.6 Hz, 6H), 0.86 (s, 9H), 0.04 (d, *J* = 8.3 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 202.0, 182.6, 154.7, 120.2, 83.6, 73.1, 57.4, 56.2, 48.2, 47.8, 44.0, 41.2, 25.8, 18.0, 17.9, 17.0, -4.7, -4.9.

HRMS(ESI), Calculated C₂₀H₃₃O₄Si⁺, [M+H]⁺: 365.2143, found: 365.2135.

m.p.:122.85-123.73 °C;



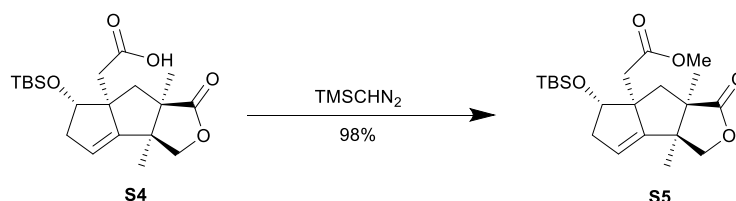
A solution of compound **S3** (2.0 g, 5.6 mmol, 1.0 equiv) in acetone (112 mL) and water (28 mL) was stirred at room temperature for 10 min. The reaction mixture was added to 2-methyl-2-butene (10.8 mL, 140.0 mmol, 25.0 equiv) and stirred at room temperature for 5 min. The reaction mixture was added to NaClO₂ (5.1 g, 56.0 mmol, 10.0 equiv) and NaH₂PO₄ (4.7 g, 38.2 mmol, 6.8 equiv). The reaction mixture was stirred at room temperature for 50 min. The reaction mixture was quenched with water (30 mL). The reaction contents were concentrated in vacuo to remove acetone and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/4, v/v) to yield compound **S4** (1.9 g, 5.1 mmol, 90%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 5.52 - 5.51 (m, 1H), 4.35 (d, *J* = 9.3 Hz, 1H), 4.05 (dd, *J* = 8.7, 7.0 Hz, 1H), 3.91 (d, *J* = 9.3 Hz, 1H), 2.84 (d, *J* = 15.0 Hz, 1H), 2.60 - 2.53 (m, 1H), 2.51 - 2.37 (m, 3H), 1.94 (d, *J* = 15.2 Hz, 1H), 1.19 (d, *J* = 3.3 Hz, 6H), 0.89 (s, 9H), 0.10 (d, *J* = 4.8 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 182.6, 174.4, 154.9, 120.5, 84.0, 73.2, 55.9, 55.8, 48.3, 42.7, 40.5, 38.9, 25.8, 18.1, 17.7, 16.8, -4.8, -4.9.

HRMS(ESI), Calculated C₂₀H₃₃O₅Si⁺, [M+H]⁺: 381.2092, found: 381.2094.

m.p.: 139.24-140.72 °C;

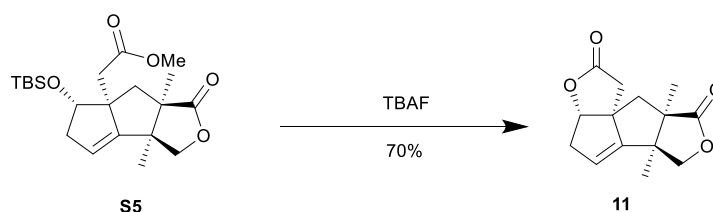


A solution of compound **S4** (950.0 mg, 2.5 mmol, 1.0 equiv) in CH₂Cl₂ (50 mL) and MeOH (10 mL) was stirred at room temperature for 10 min. The reaction mixture was added to TMSCHN₂ (2.5 mL, 5.0 mmol, 2.0 equiv, 2 M in CH₂Cl₂) and stirred at 30 °C for 30 min. The reaction mixture was quenched with water (30 mL). The reaction contents were extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to yield compound **S5** (975 mg, 2.47 mmol, 98%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 5.52 (dd, *J* = 4.1, 1.8 Hz, 1H), 4.34 (d, *J* = 9.2 Hz, 1H), 3.95 (dd, *J* = 8.7, 7.1 Hz, 1H), 3.89 (d, *J* = 9.2 Hz, 1H), 3.62 (s, 3H), 2.61 (d, *J* = 15.3 Hz, 1H), 2.48 - 2.34 (m, 4H), 2.19 (d, *J* = 15.0 Hz, 1H), 1.18 (s, 3H), 1.12 (s, 3H), 0.85 (s, 9H), 0.02 (d, *J* = 1.9 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 182.9, 172.3, 155.1, 120.8, 83.9, 73.2, 56.4, 55.7, 51.1, 48.3, 42.8, 40.8, 37.1, 25.8, 18.2, 17.8, 16.7, -4.8, -4.9.

HRMS(ESI), Calculated C₂₁H₃₅O₅Si⁺, [M+H]⁺: 395.2248, found: 395.2251.



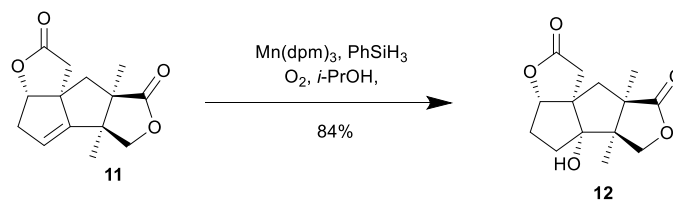
A solution of compound **S5** (975.0 mg, 2.5 mmol, 1.0 equiv) in THF (25 mL) was stirred at room temperature for 10 min. The reaction mixture was added to TBAF (7.4 mL, 7.4 mmol, 3.0 equiv, 1 M in THF) and stirred at room temperature for 40 min. The reaction mixture was quenched with water (30 mL). The reaction contents were extracted with ethyl acetate (10 mL \times 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/8, v/v) to yield compound **11** (428.0 mg, 1.73 mmol, 70%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 5.47 (dd, J = 3.5, 1.7 Hz, 1H), 4.92 (dd, J = 8.3, 6.1 Hz, 1H), 4.41 (d, J = 9.5 Hz, 1H), 3.99 (d, J = 9.4 Hz, 1H), 2.99 -2.98 (m, 1H), 2.89 (d, J = 18.1 Hz, 1H), 2.65 - 2.64 (m, 1H), 2.59 (d, J = 14.6 Hz, 1H), 2.56 (d, J = 11.1 Hz, 1H), 1.78 (d, J = 14.6 Hz, 1H), 1.22 (s, 3H), 1.15 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 182.1, 176.4, 153.8, 119.8, 91.1, 72.5, 58.2, 55.5, 48.2, 47.4, 43.4, 42.0, 18.1, 16.1.

HRMS(ESI), Calculated C₁₄H₁₆O₄Na⁺, [M+Na]⁺: 271.0941, found: 271.0939.

m.p.:171.30-172.81 °C;



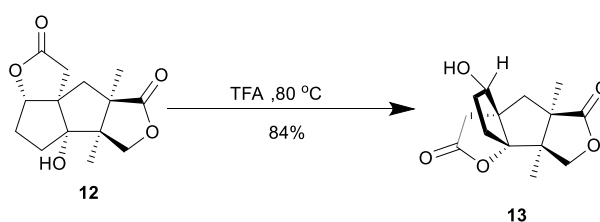
A solution of compound **11** (100.0 mg, 0.4 mmol, 1.0 equiv) in *i*-PrOH (8 mL) and CH₂Cl₂ (2 mL) was stirred at room temperature under O₂ for 10 min. The reaction mixture was added to Mn(dpm)₃ (41.0 mg, 0.16 mmol, 0.4 equiv) and stirred at room temperature for 3 min. The reaction mixture was added to PhSiH₃ (96.0 μ L, 0.8 mmol, 2.0 equiv) and stirred at room temperature for 1 h. The reaction mixture was quenched with water (30 mL). The reaction contents were extracted with ethyl acetate (10 mL \times 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/8, v/v) to yield compound **12** (89.0 mg, 0.34 mmol, 84%) as a white solid.

¹H NMR (500 MHz, Methanol-d₄) δ 4.67 (dd, J = 6.4, 3.9 Hz, 1H), 4.34 (d, J = 9.8 Hz, 1H), 3.89 (d, J = 9.9 Hz, 1H), 3.27 (s, 1H), 3.13 (d, J = 17.8 Hz, 1H), 2.49 (d, J = 17.8 Hz, 1H), 2.24 (d, J = 14.9 Hz, 1H), 2.18 -2.17 (m, 1H), 2.08 - 1.99 (m, 1H), 1.90 - 1.75 (m, 3H), 1.16 (s, 3H), 1.06 (s, 3H).

¹³C NMR (126 MHz, Methanol-d₄) δ 183.7, 178.1, 81.0, 80.2, 58.4, 54.7, 50.8, 44.4, 38.4, 35.3, 30.5, 18.5, 15.2.

HRMS(ESI), Calculated C₁₄H₁₉O₅⁺, [M+H]⁺: 267.1227, found: 267.1226.

m.p.:201.48-203.74 °C;



A solution of compound **12** (152.0 mg, 0.6 mmol, 1.0 equiv) in CF₃COOH (6 mL) was stirred at 80 °C for 18 h. The reaction mixture was quenched with saturated NaHCO₃ aqueous solution (80 mL). The reaction contents were extracted with ethyl acetate (10 mL × 5). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/8, v/v) to yield compound **13** (138.0 mg, 0.52 mmol, 84%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 4.33 (d, *J* = 10.0 Hz, 1H), 3.99 (d, *J* = 10.0 Hz, 1H), 3.97-3.93 (m, 1H), 3.34 (d, *J* = 19.6 Hz, 1H), 2.55 (d, *J* = 14.4 Hz, 1H), 2.31 (d, *J* = 19.6 Hz, 1H), 1.98 (q, *J* = 5.5, 4.2 Hz, 2H), 1.75 - 1.56 (m, 3H), 1.21 (s, 3H), 1.07 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 181.2, 176.7, 105.0, 79.1, 72.8, 58.6, 55.3, 54.5, 46.0, 37.9, 32.5, 30.8, 18.8, 15.2.

HRMS(ESI), Calculated C₁₄H₁₉O₅⁺, [M+H]⁺: 267.1227, found: 267.1231.

m.p.: 177.81-179.34 °C;



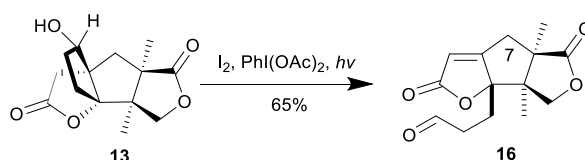
A solution of compound **13** (67.0 mg, 250.0 μmol, 1.0 equiv) in CH₂Cl₂ (3 mL) was stirred at room temperature for 10 min. The reaction mixture was added to NaHCO₃ (28.0 mg, 0.3 mmol, 1.3 equiv) and DMP (128.0 mg, 0.3 mmol, 1.2 equiv) stirred at room temperature for 20 min. The reaction mixture was quenched with water (30 mL). The reaction contents were extracted with CH₂Cl₂ (10 mL × 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to yield compound **14** (60.0 mg, 0.22 mmol, 89%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 4.15 (d, *J* = 9.9 Hz, 1H), 3.99 (d, *J* = 10.0 Hz, 1H), 2.92 (d, *J* = 19.1 Hz, 1H), 2.83-2.70 (m, 3H), 2.58-2.52 (m, 1H), 2.39 - 2.27 (m, 1H), 2.21 - 2.09 (m, 1H), 1.87 (d, *J* = 15.1 Hz, 1H), 1.25 (s, 3H), 1.20 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 213.9, 179.5, 173.5, 101.7, 71.6, 60.8, 56.3, 54.6, 42.6, 41.6, 37.3, 28.3, 18.9, 15.4.

HRMS(ESI), Calculated C₁₄H₁₆O₅Na⁺, [M+H]⁺: 287.0890, found: 287.0884.

m.p.: 196.77-199.85 °C;



A solution of compound **13** (27.0 mg, 0.1 mmol, 1.0 equiv) in CH₂Cl₂ (3 mL) was stirred at room temperature for 10 min. The reaction mixture was added to PhI(OAc)₂ (97.0 mg, 0.3 mmol, 3.0 equiv) and I₂ (26.0 mg, 0.1 mmol, 1.0 equiv) stirred at room temperature under blue light for 20 min. The reaction mixture was quenched with saturated Na₂S₂O₃ aqueous solution water (30 mL).

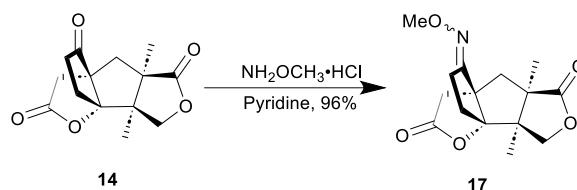
The reaction contents were extracted with CH₂Cl₂ (10 mL × 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/8, v/v) to yield compound **16** (17.0 mg, 65.0 μmol, 65%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 9.67 (s, 1H), 5.84 (d, *J* = 2.3 Hz, 1H), 4.62 (d, *J* = 10.8 Hz, 1H), 4.05 (d, *J* = 10.8 Hz, 1H), 3.23 (dd, *J* = 17.6, 2.4 Hz, 1H), 2.51 (d, *J* = 17.6 Hz, 1H), 2.47 - 2.26 (m, 3H), 2.01 - 1.99 (m, 1H), 1.30 (s, 3H), 0.91 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 199.3, 181.2, 174.4, 172.8, 114.5, 93.3, 70.4, 53.0, 51.2, 36.8, 33.5, 22.9, 20.2, 13.5.

HRMS(ESI), Calculated C₁₄H₁₇O₅⁺, [M+H]⁺: 265.1071, found: 265.1091.

m.p.: 174.48-175.12 °C;



A solution of compound **14** (13.0 mg, 0.05 mmol, 1.0 equiv) in pyridine (1 mL) was stirred at 80 °C for 5 min. The reaction mixture was added to NH₂OCH₃·HCl (9.0 mg, 0.1 mmol, 2.0 equiv) and stirred at 80 °C for 2 h. The reaction mixture was quenched with HCl (30 mL, 2 M in water). The reaction contents were extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/6, v/v) to yield compound **17** (14.0 mg, 48.0 μmol, 96%) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 4.24 (d, *J* = 9.8 Hz, 1H), 3.95 (d, *J* = 9.8 Hz, 1H), 3.84 (s, 3H), 2.99 (d, *J* = 19.4 Hz, 1H), 2.84 (d, *J* = 19.4 Hz, 1H), 2.81 - 2.61 (m, 3H), 2.22 - 2.13 (m, 2H), 2.08 (m, 1H), 1.23 (s, 3H), 1.18 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 180.2, 174.8, 164.5, 104.9, 72.0, 62.2, 57.7, 55.3, 54.2, 45.3, 43.0, 30.8, 30.1, 18.8, 15.9.

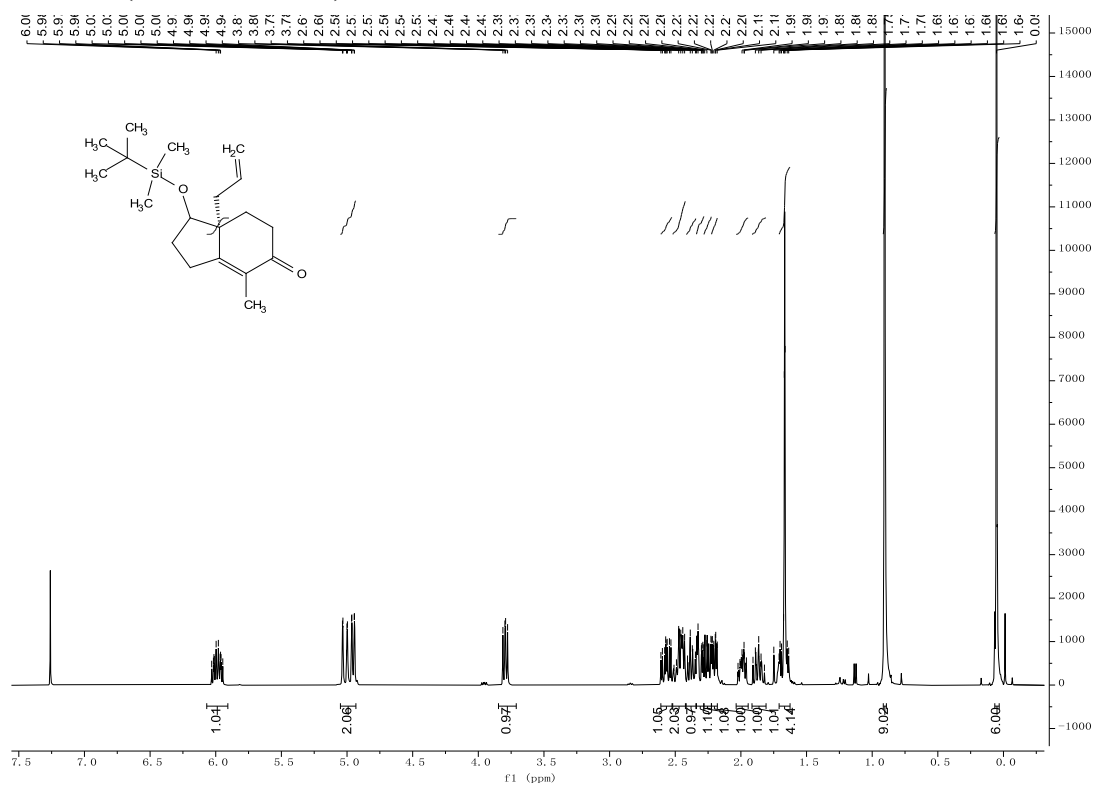
HRMS(ESI), Calculated C₁₅H₂₀O₅⁺, [M+H]⁺: 294.1336, found: 294.1337.

m.p.: 205.47-207.46 °C;

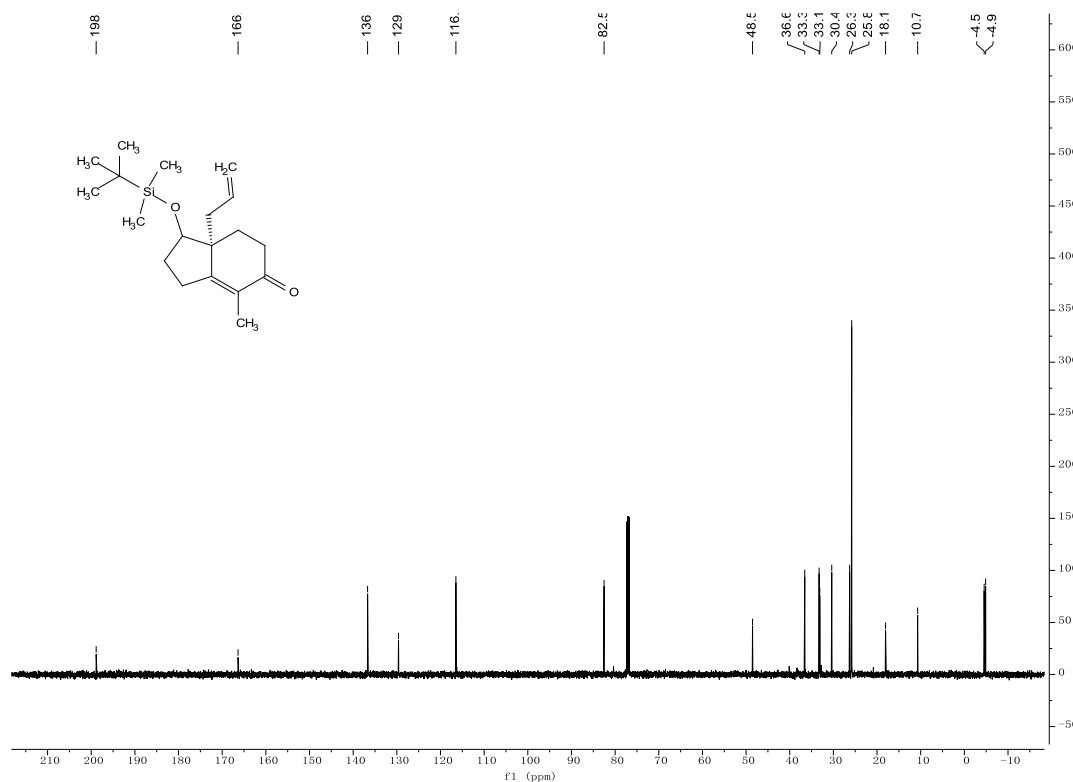
3. ¹H and ¹³C NMR Spectra of Selected Compounds

Compounds S1

¹H NMR (500 MHz, CDCl₃)

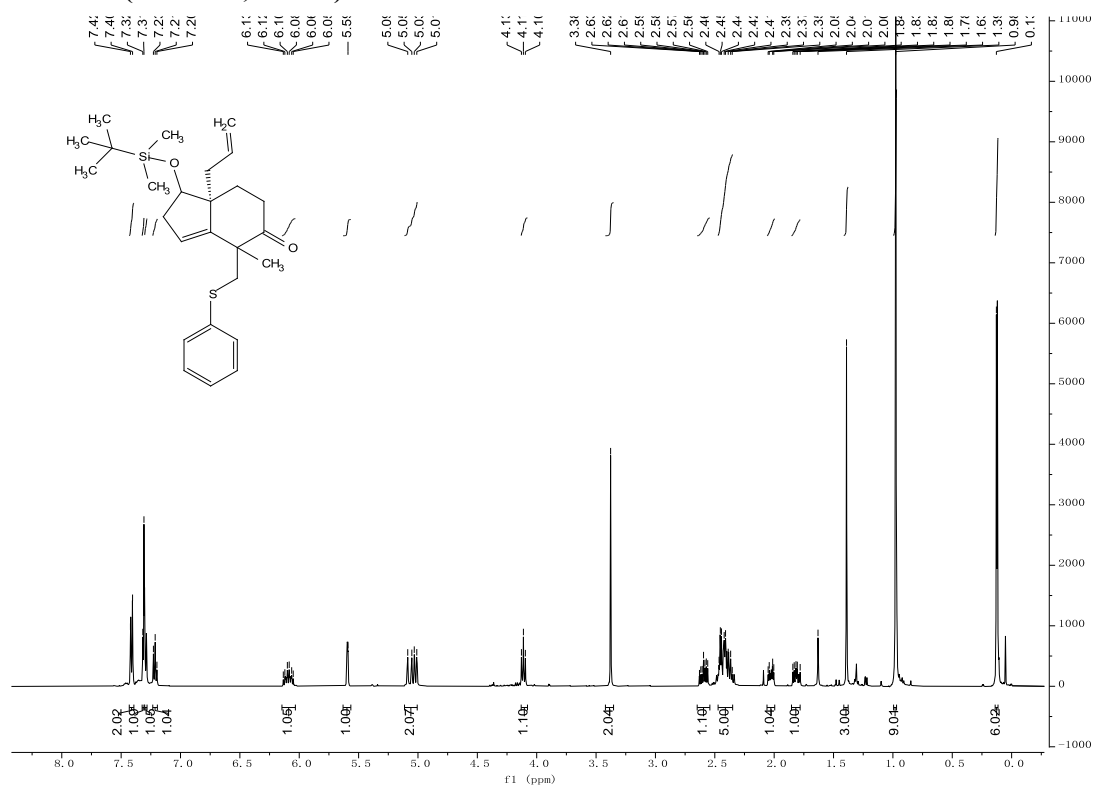


¹³C NMR (126 MHz, CDCl₃)

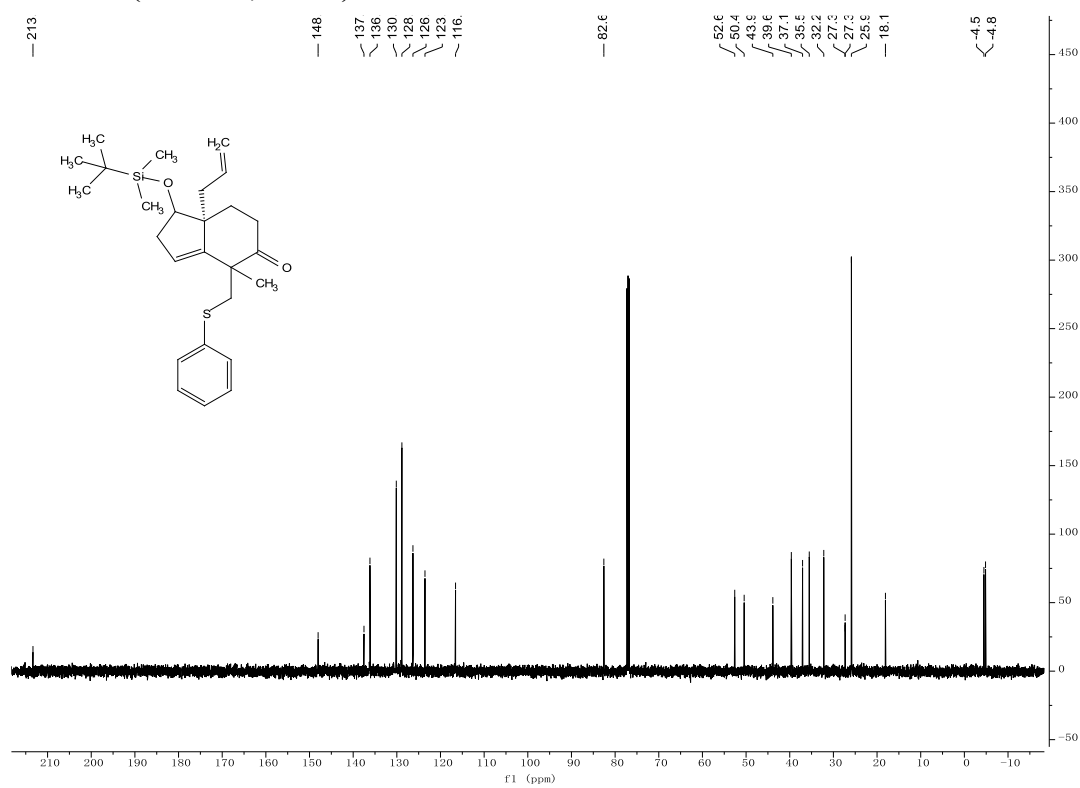


Compounds 7

¹H NMR (500 MHz, CDCl₃)

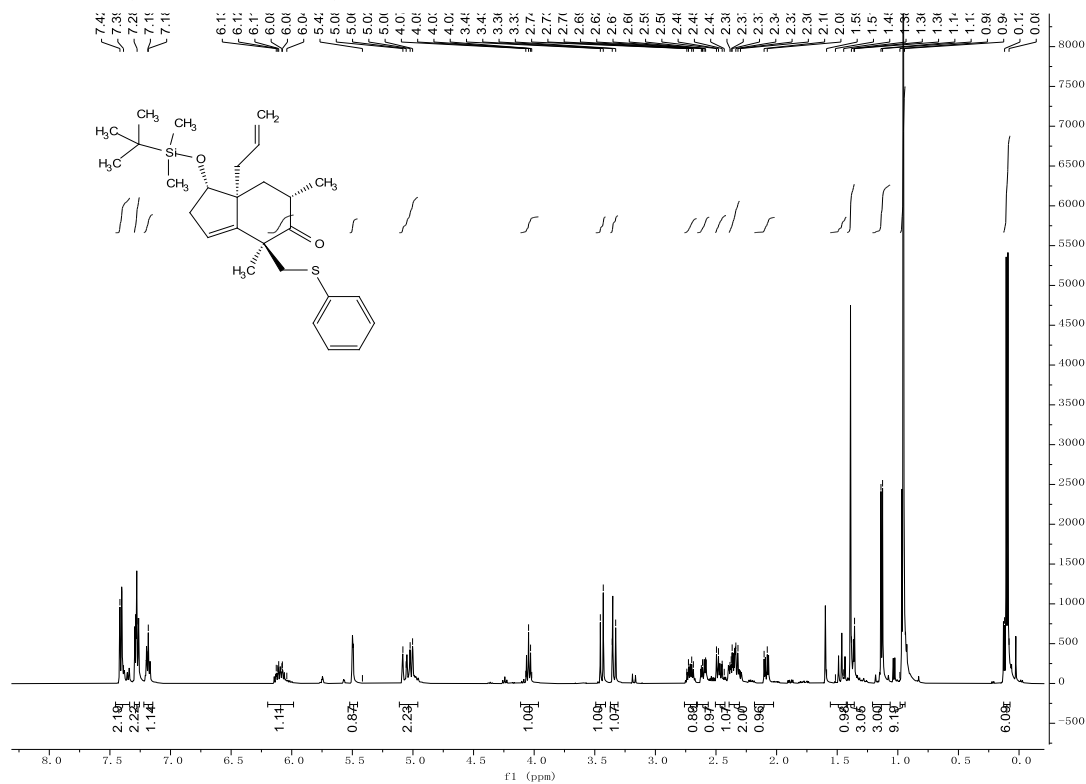


¹³C NMR (126 MHz, CDCl₃)

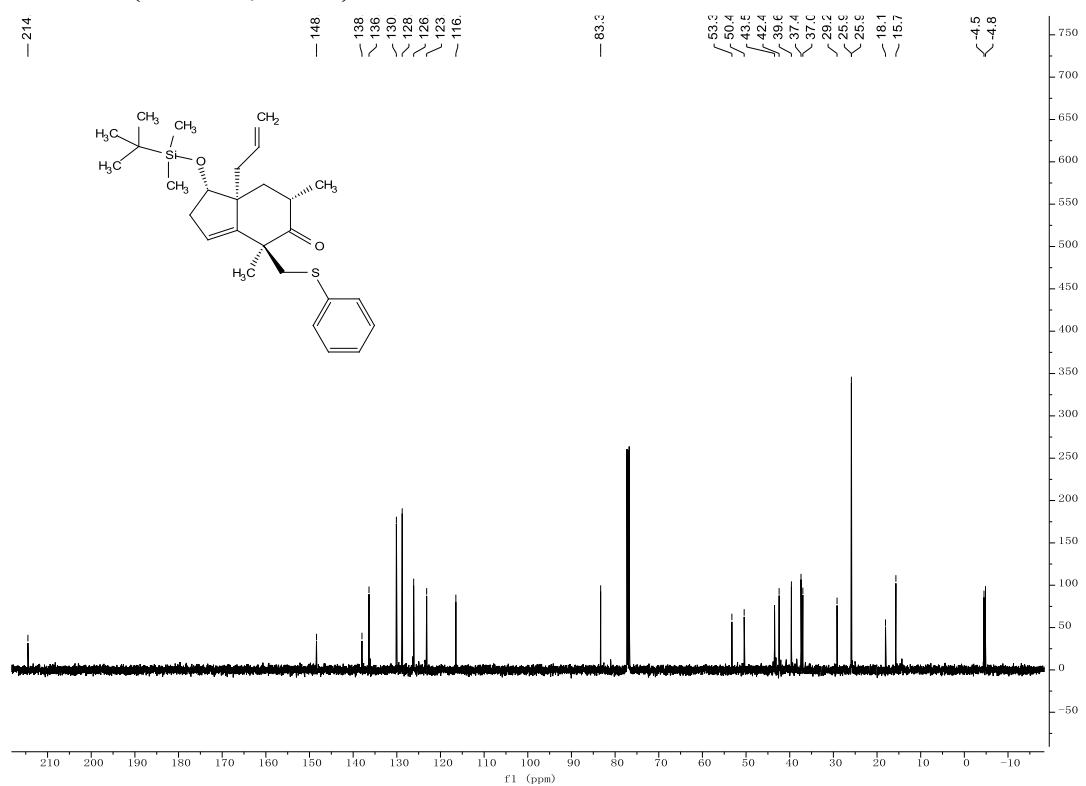


Compounds S2

¹H NMR (500 MHz, CDCl₃)

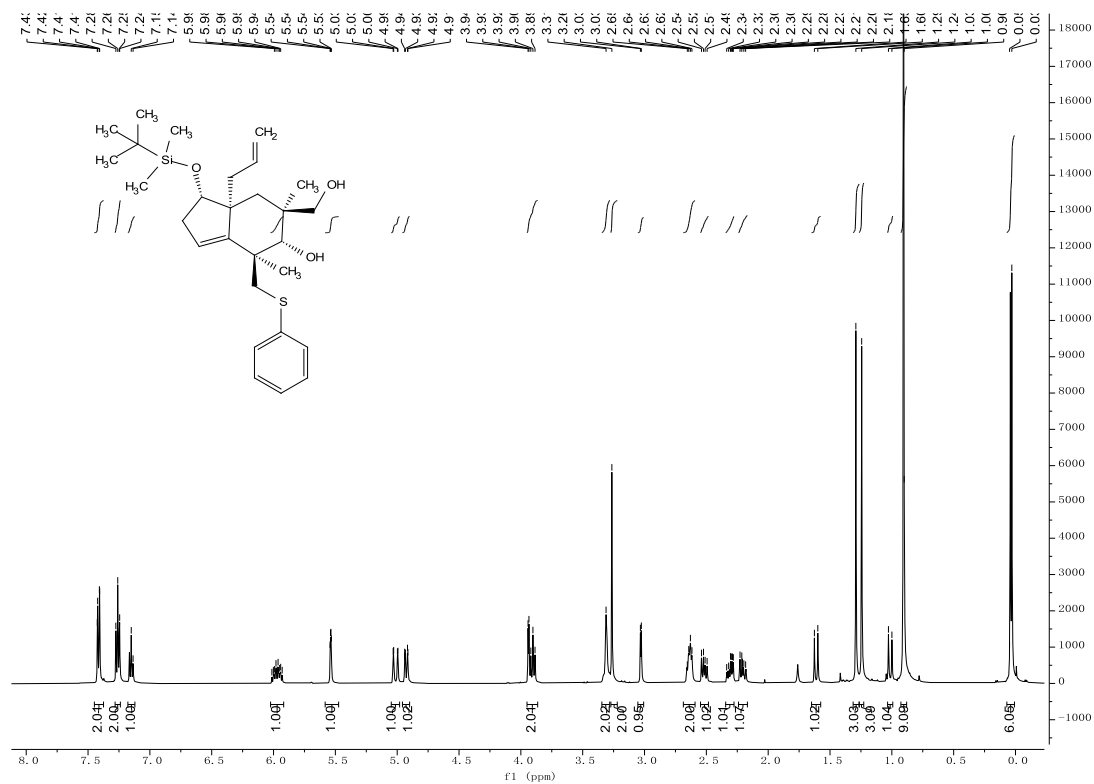


¹³C NMR (126 MHz, CDCl₃)

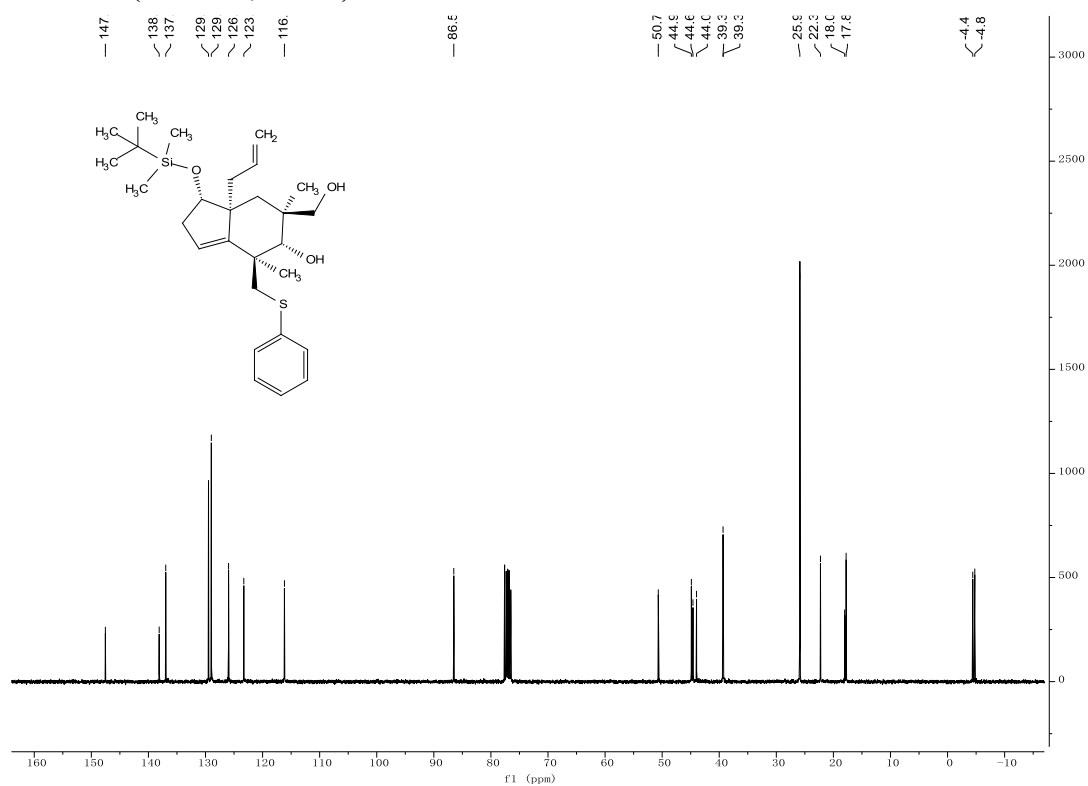


Compounds 8

¹H NMR (500 MHz, CDCl₃)

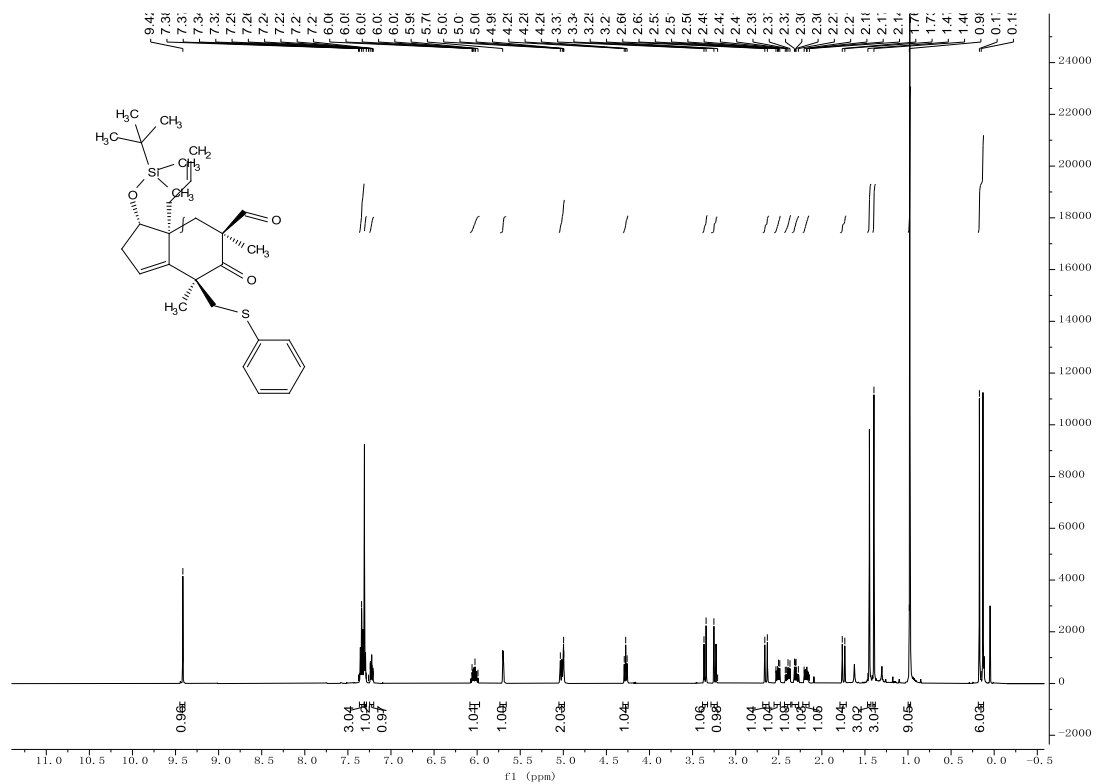


¹³C NMR (126 MHz, CDCl₃)

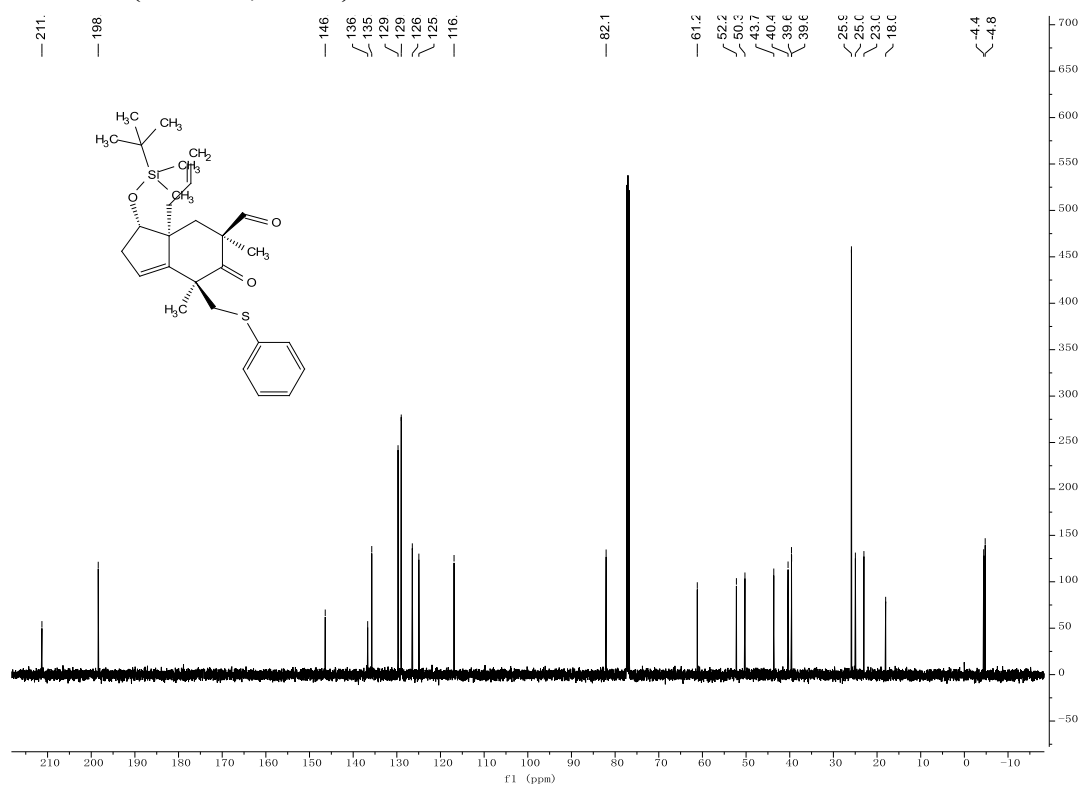


Compounds 4

¹H NMR (500 MHz, CDCl₃)

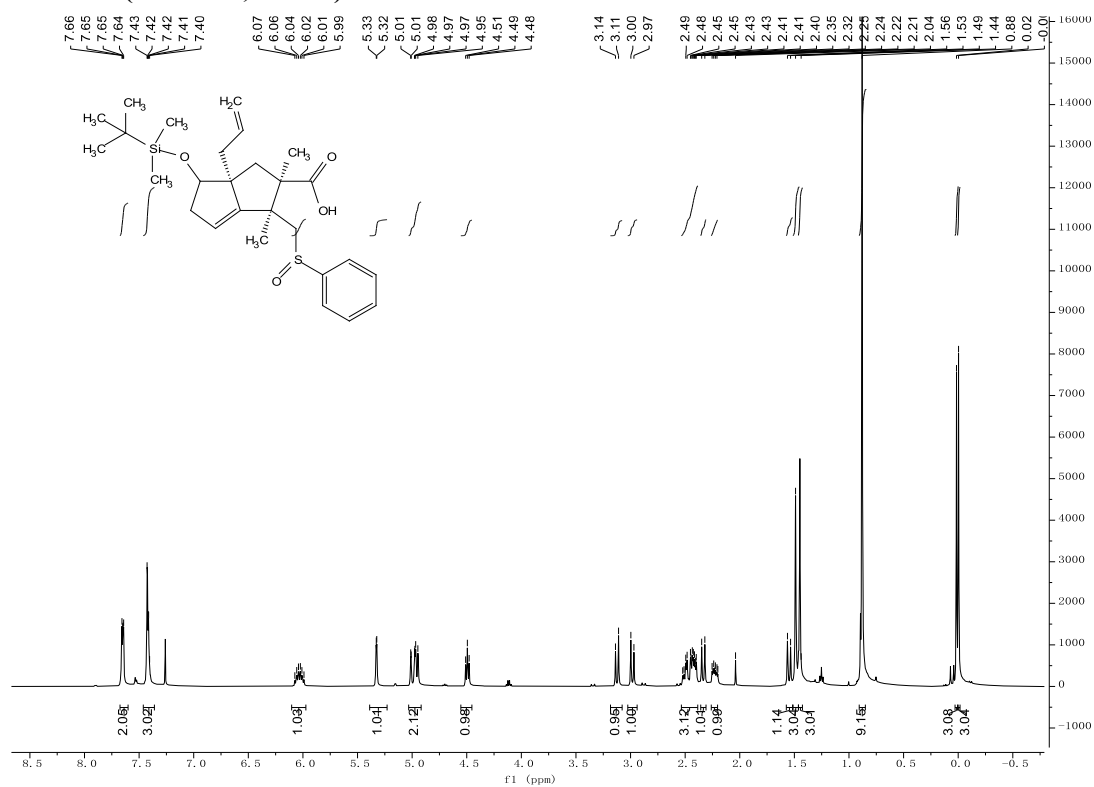


¹³C NMR (126 MHz, CDCl₃)

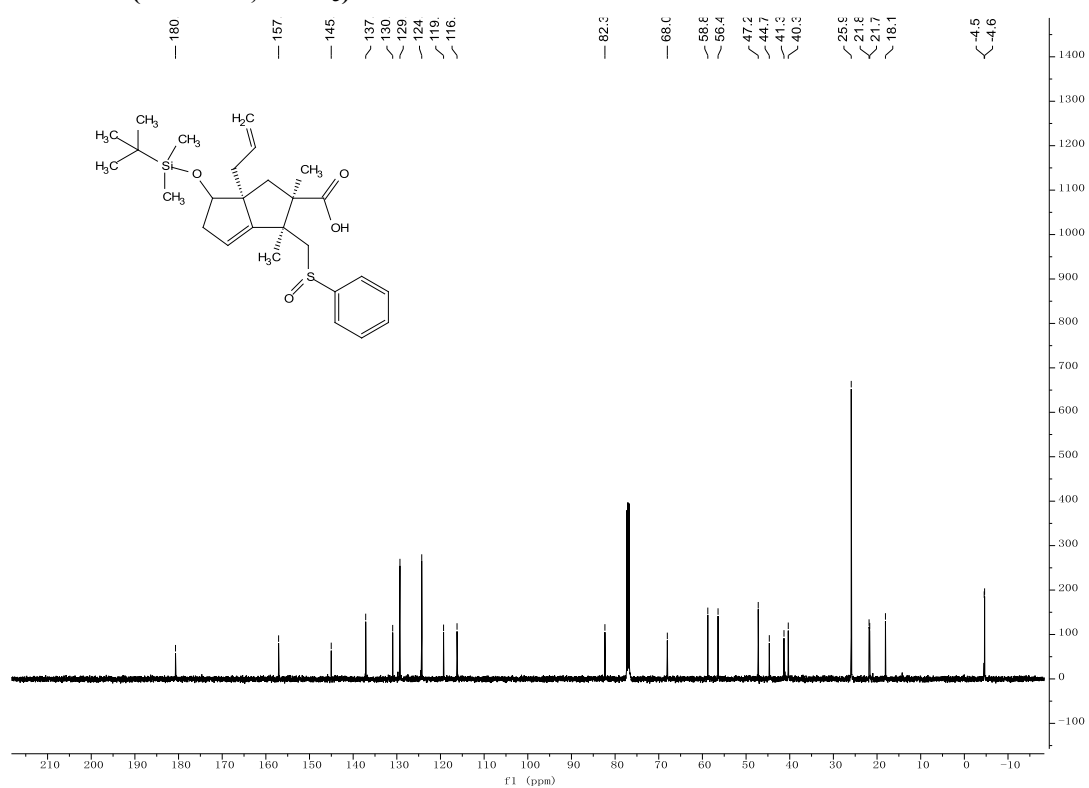


Compounds 3

¹H NMR (500 MHz, CDCl₃)

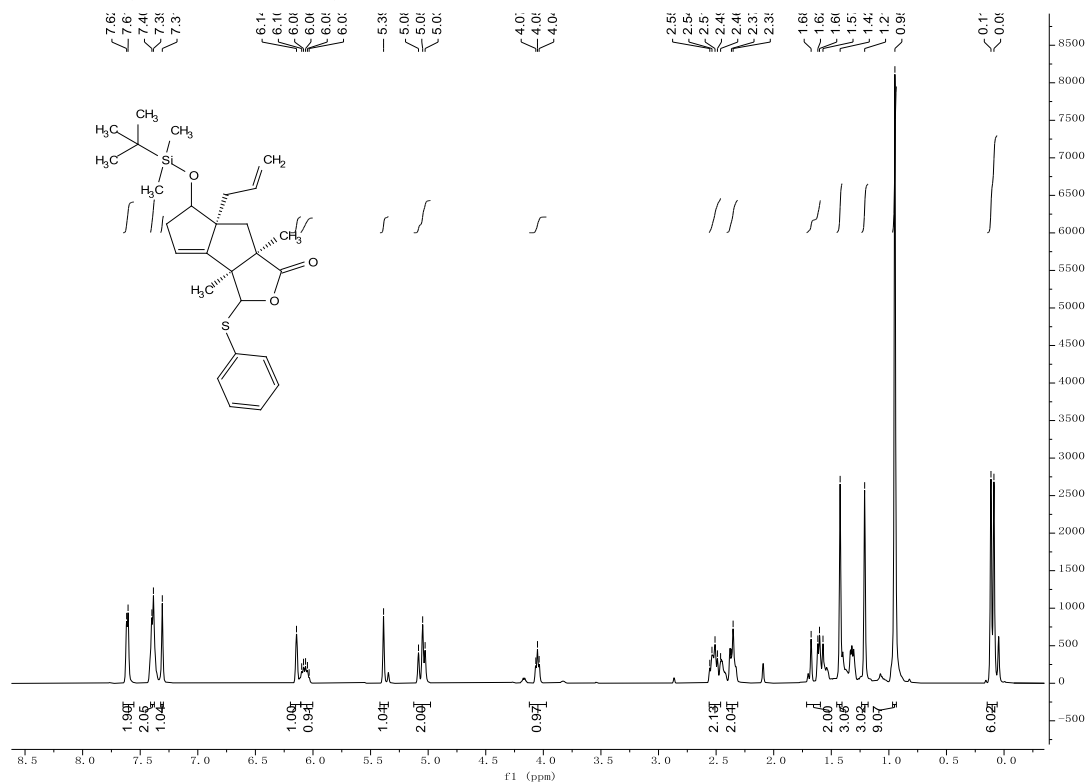


¹³C NMR (126 MHz, CDCl₃)

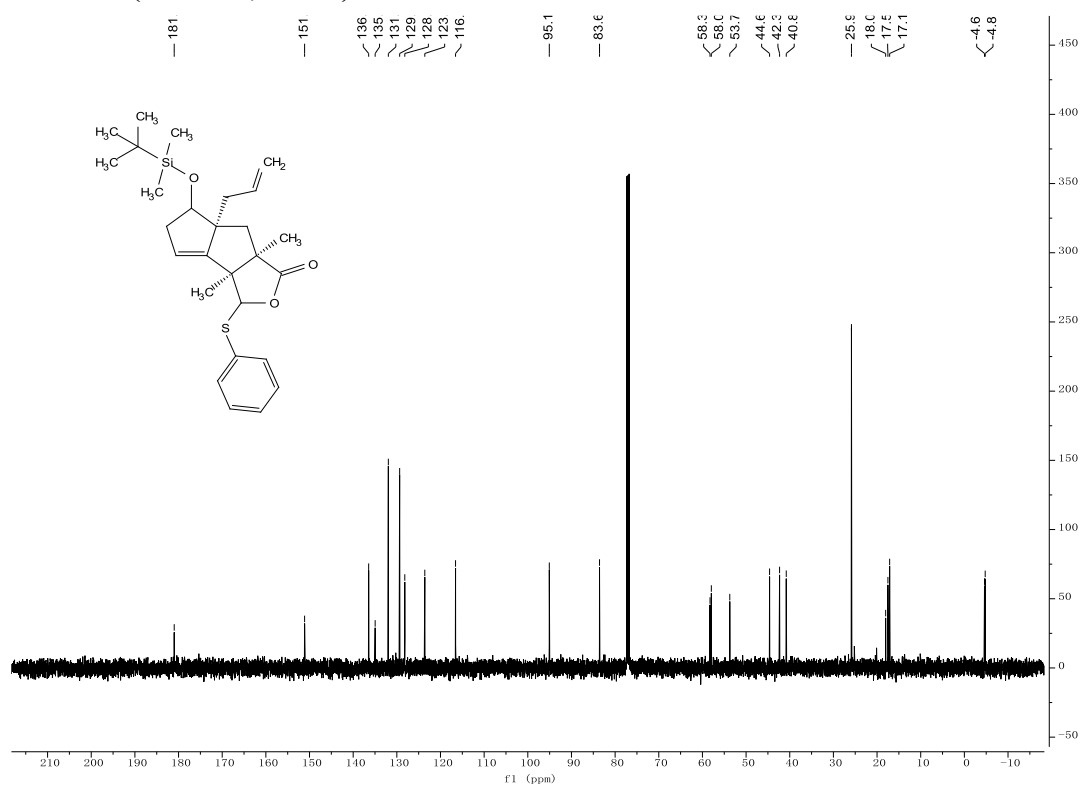


Compounds 9

¹H NMR (500 MHz, CDCl₃)

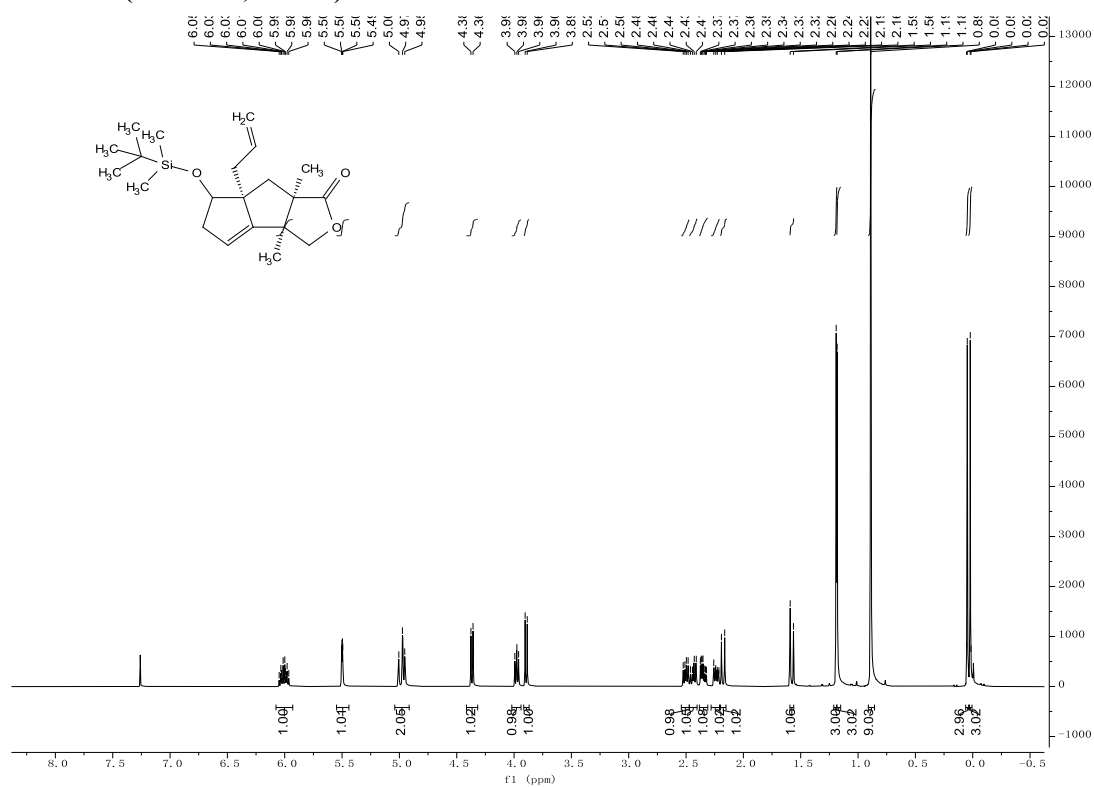


¹³C NMR (126 MHz, CDCl₃)

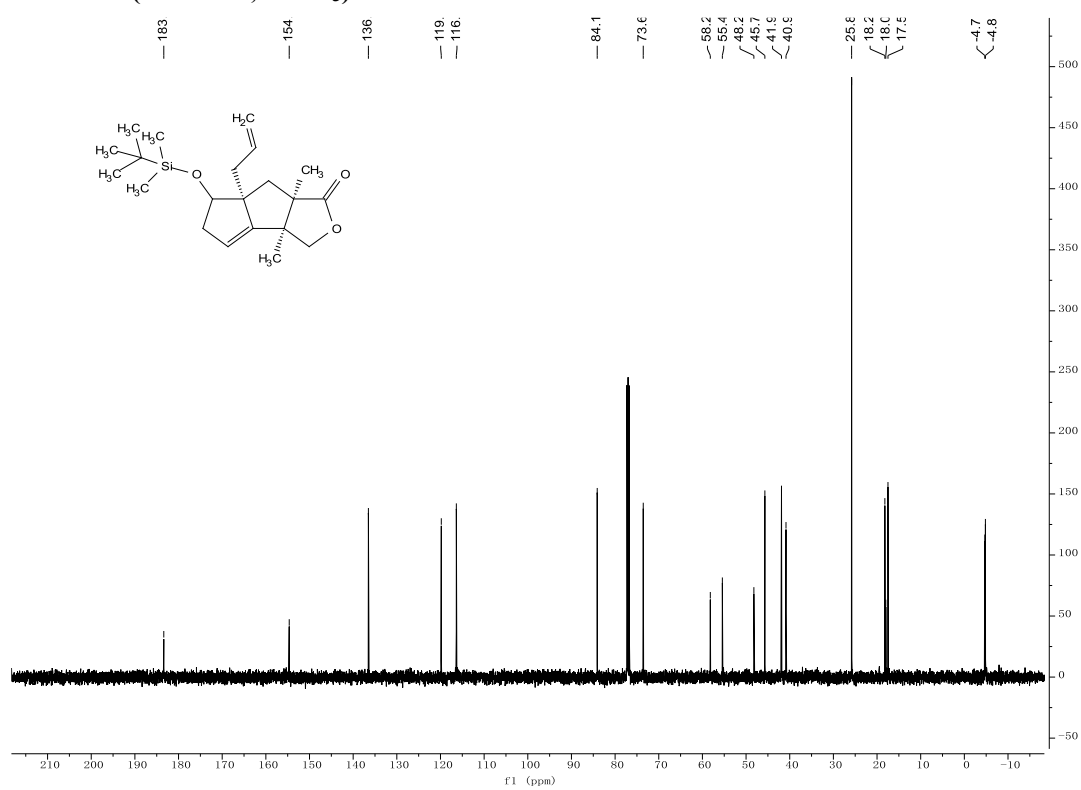


Compounds 10

¹H NMR (500 MHz, CDCl₃)

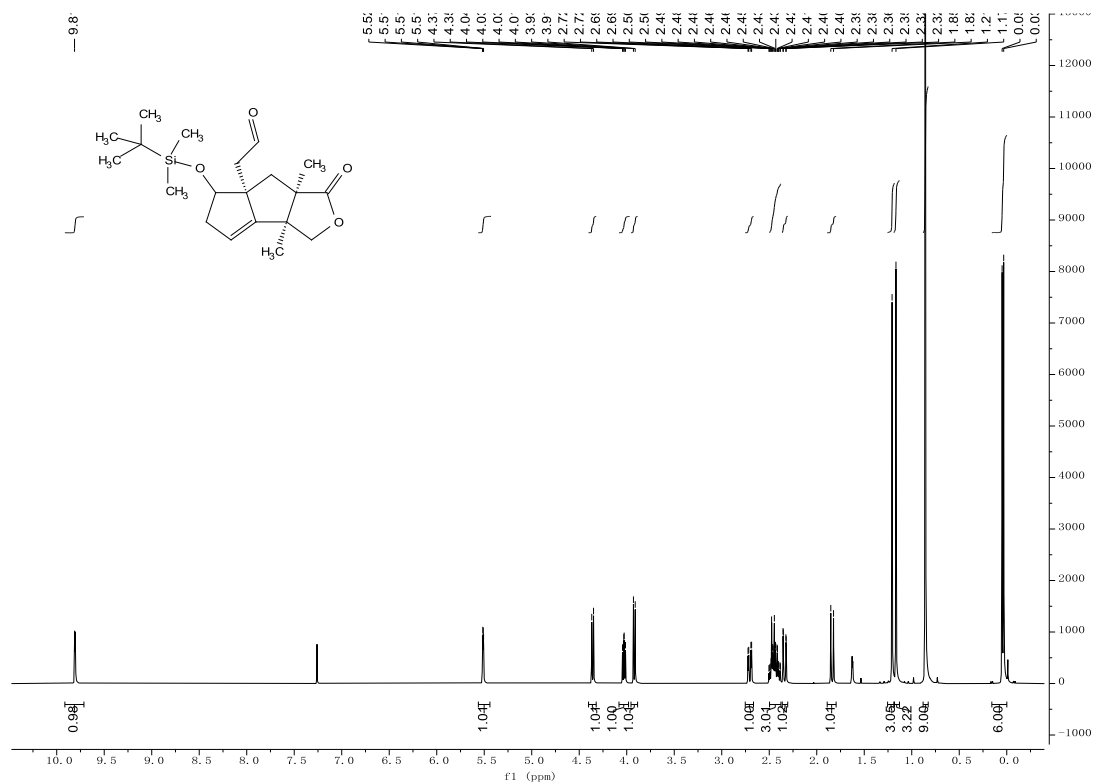


¹³C NMR (126 MHz, CDCl₃)

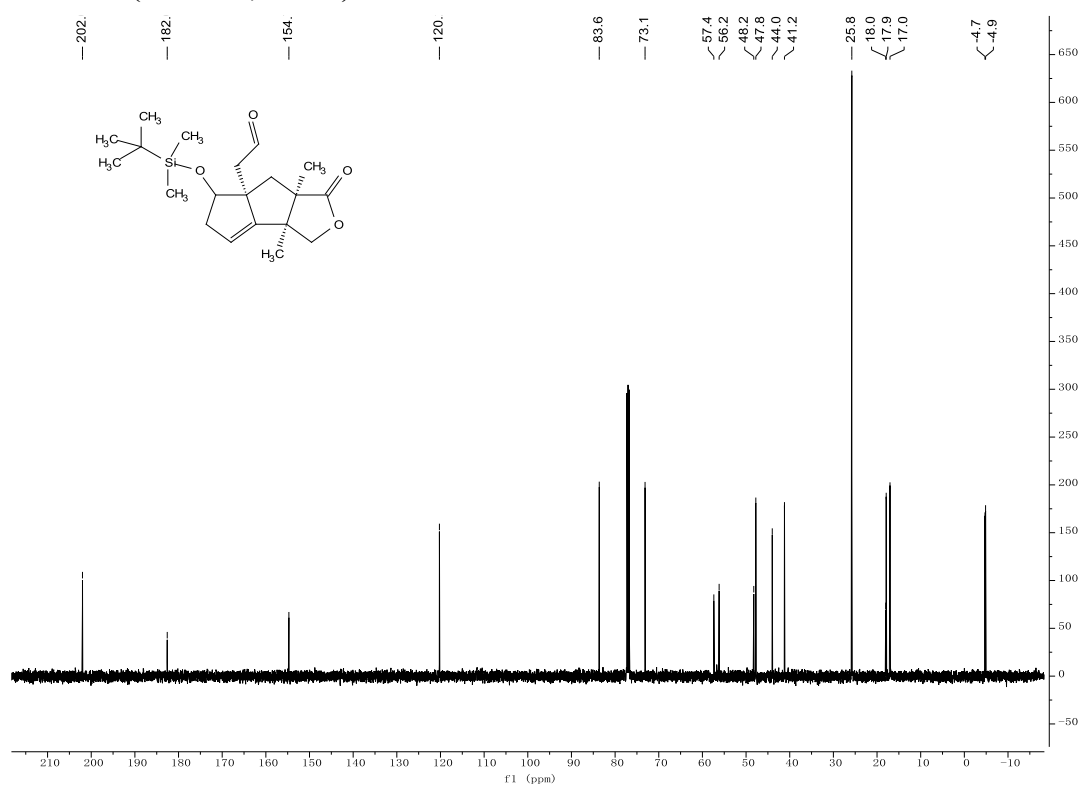


Compounds S3

¹H NMR (500 MHz, CDCl₃)

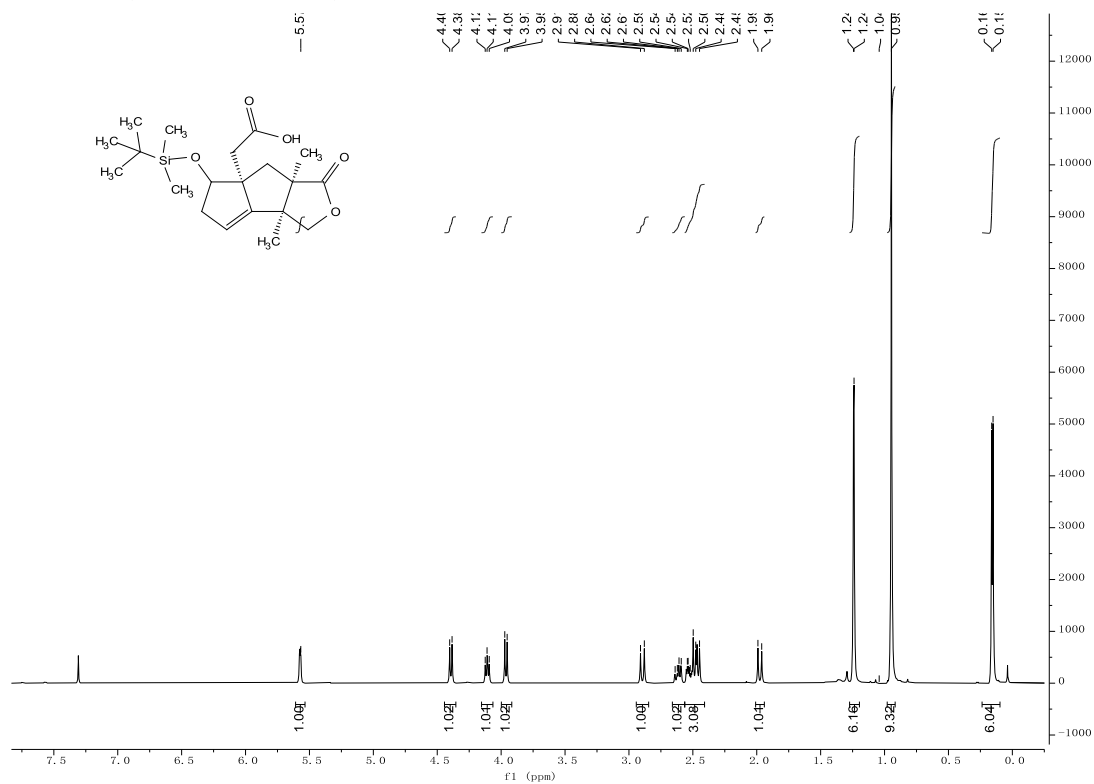


¹³C NMR (126 MHz, CDCl₃)

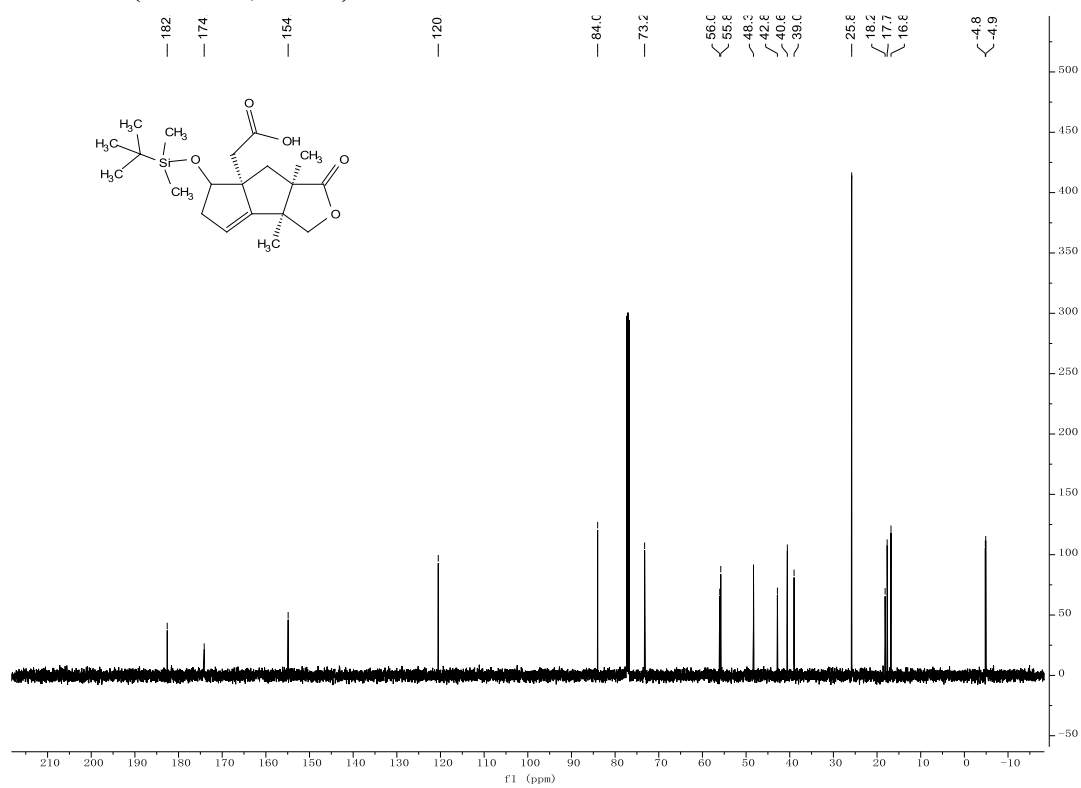


Compounds S4

¹H NMR (500 MHz, CDCl₃)

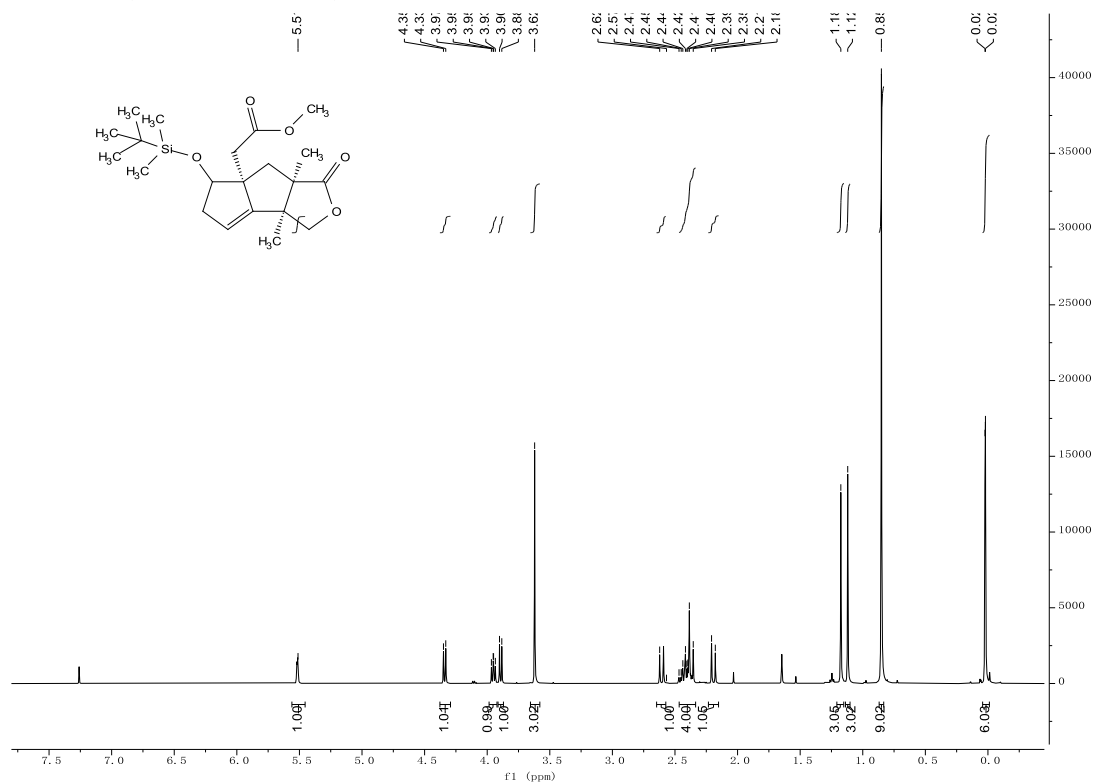


¹³C NMR (126 MHz, CDCl₃)

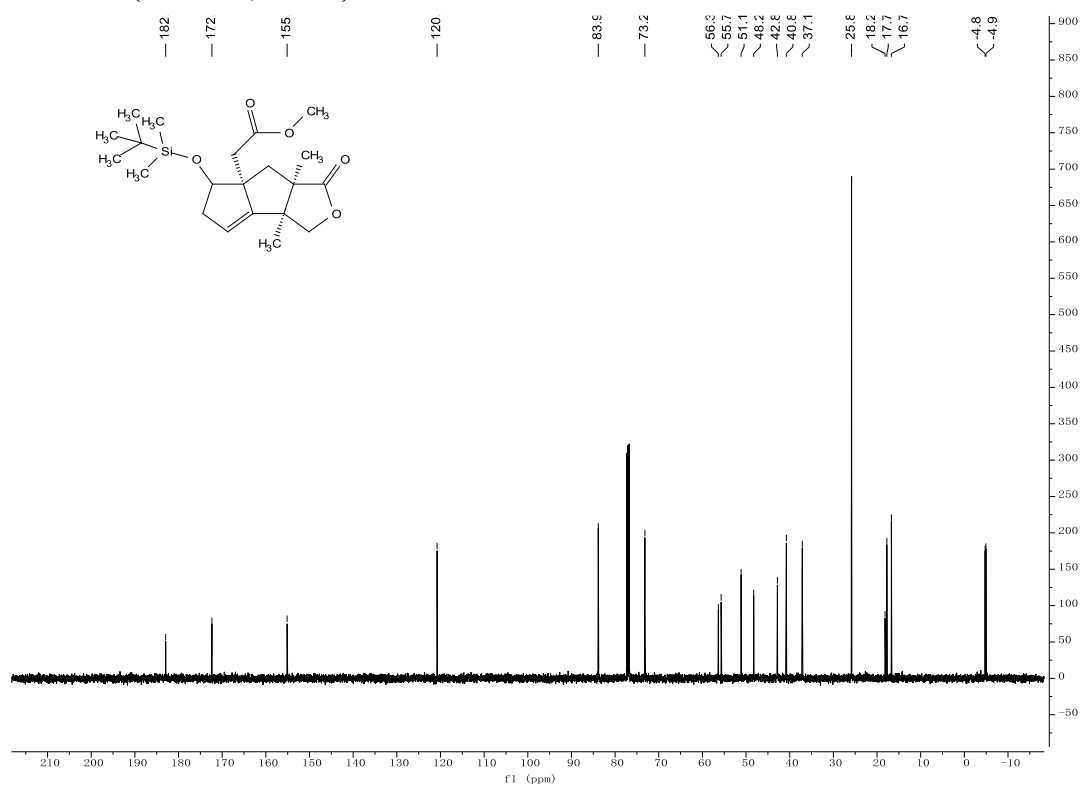


Compounds S5

¹H NMR (500 MHz, CDCl₃)

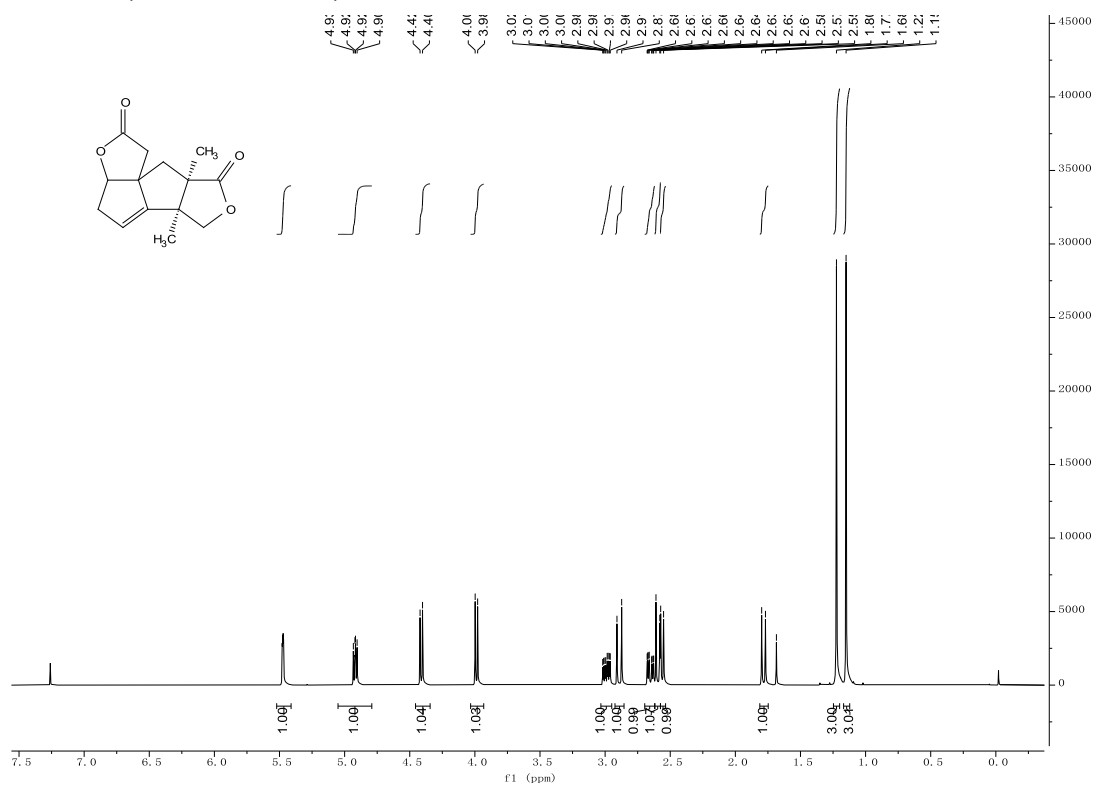


¹³C NMR (126 MHz, CDCl₃)

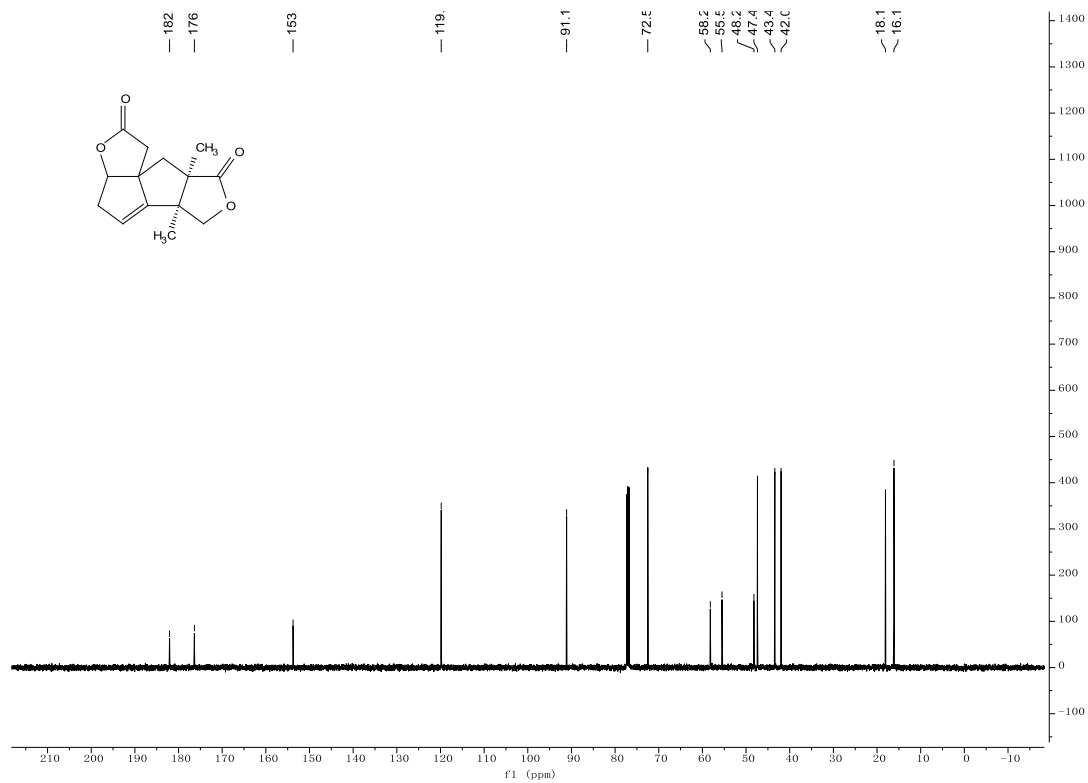


Compounds 11

¹H NMR (500 MHz, CDCl₃)

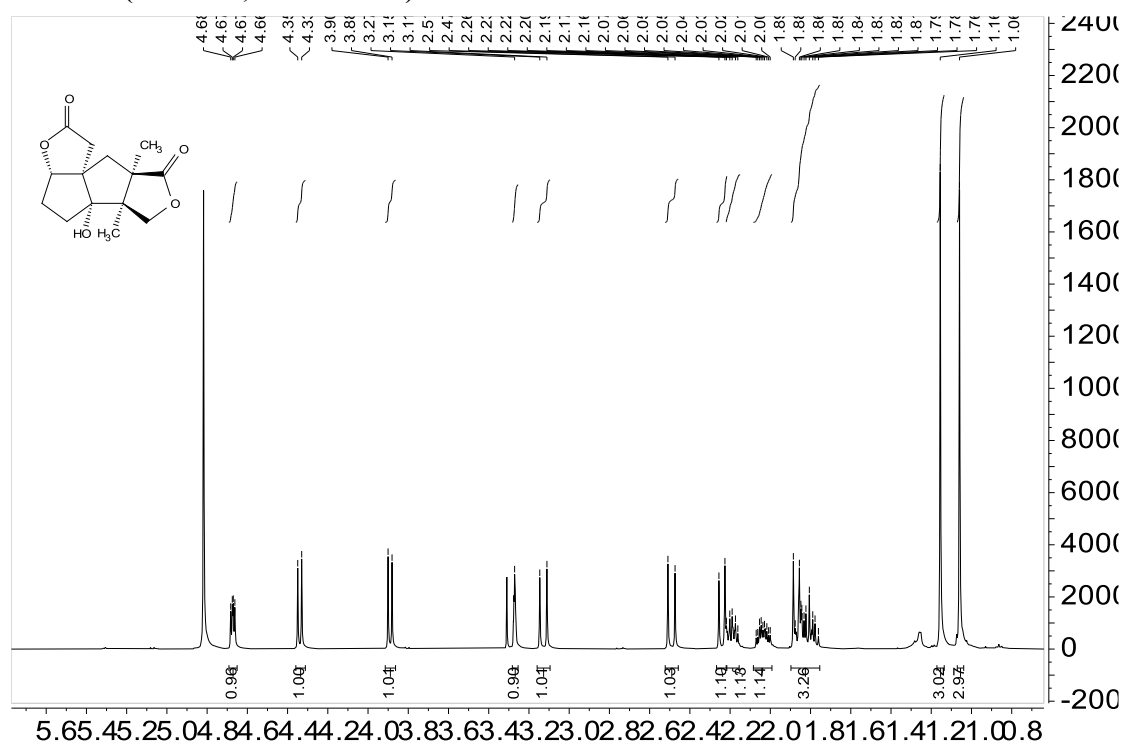


¹³C NMR (126 MHz, CDCl₃)

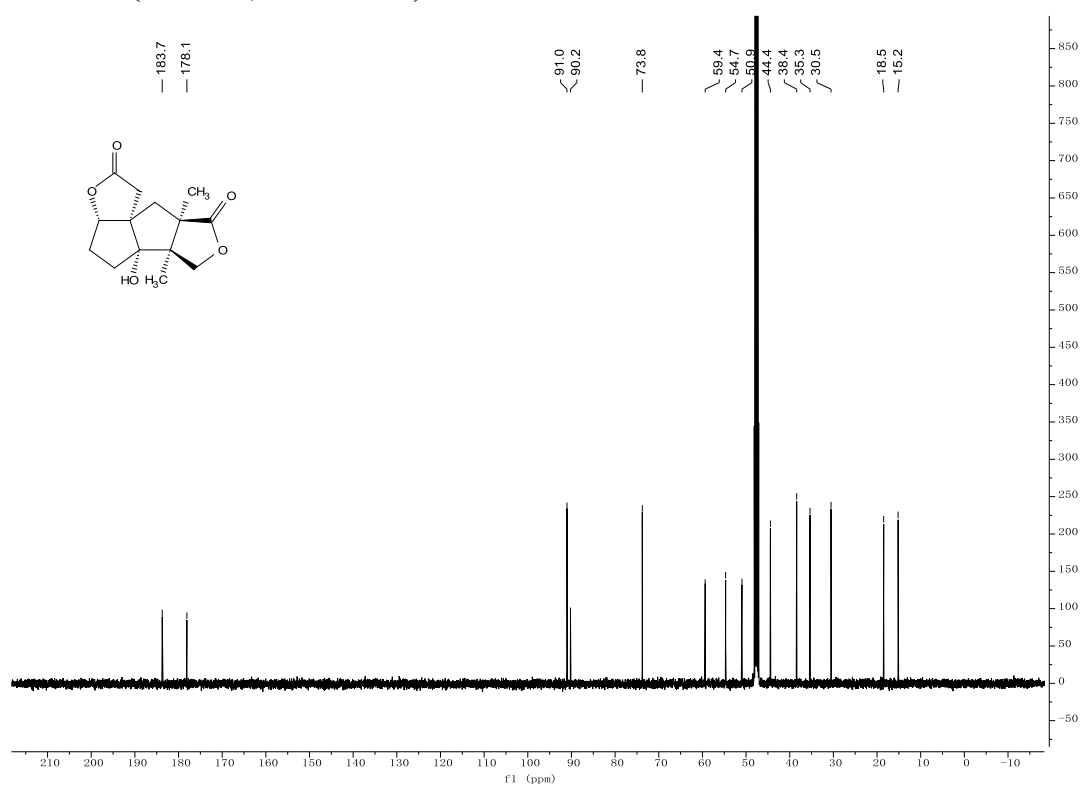


Compounds 12

¹H NMR (500 MHz, Methanol-d₄)

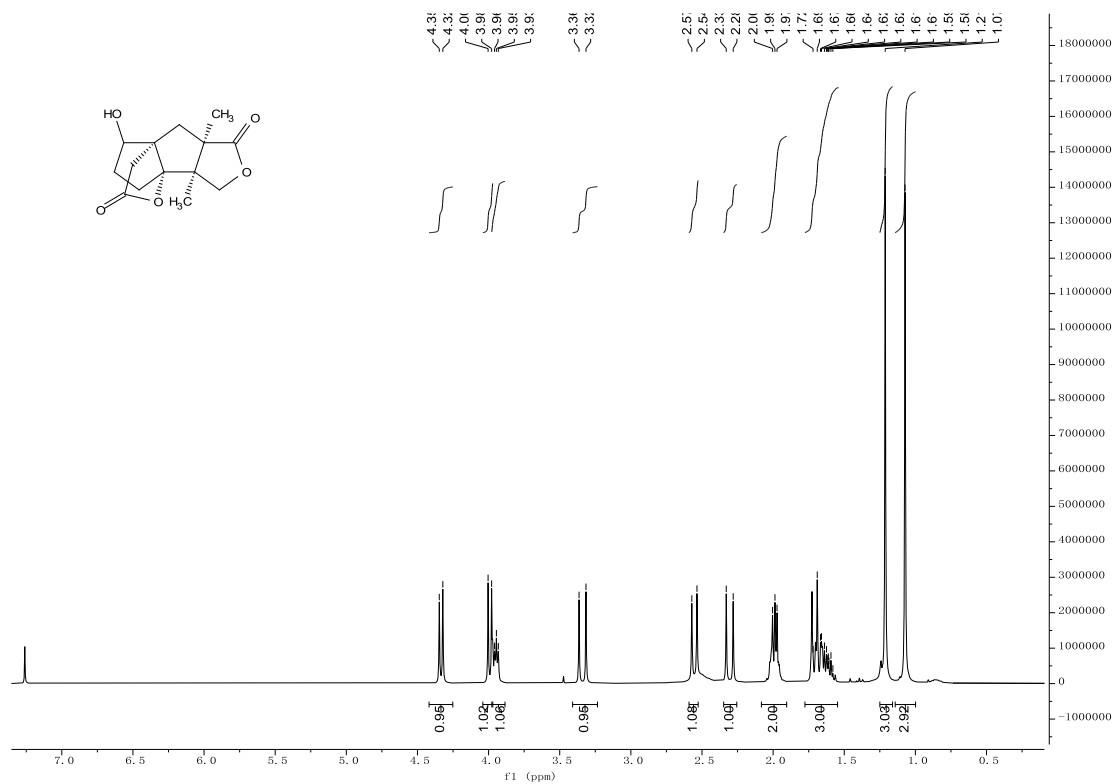


¹³C NMR (126 MHz, Methanol-d₄)

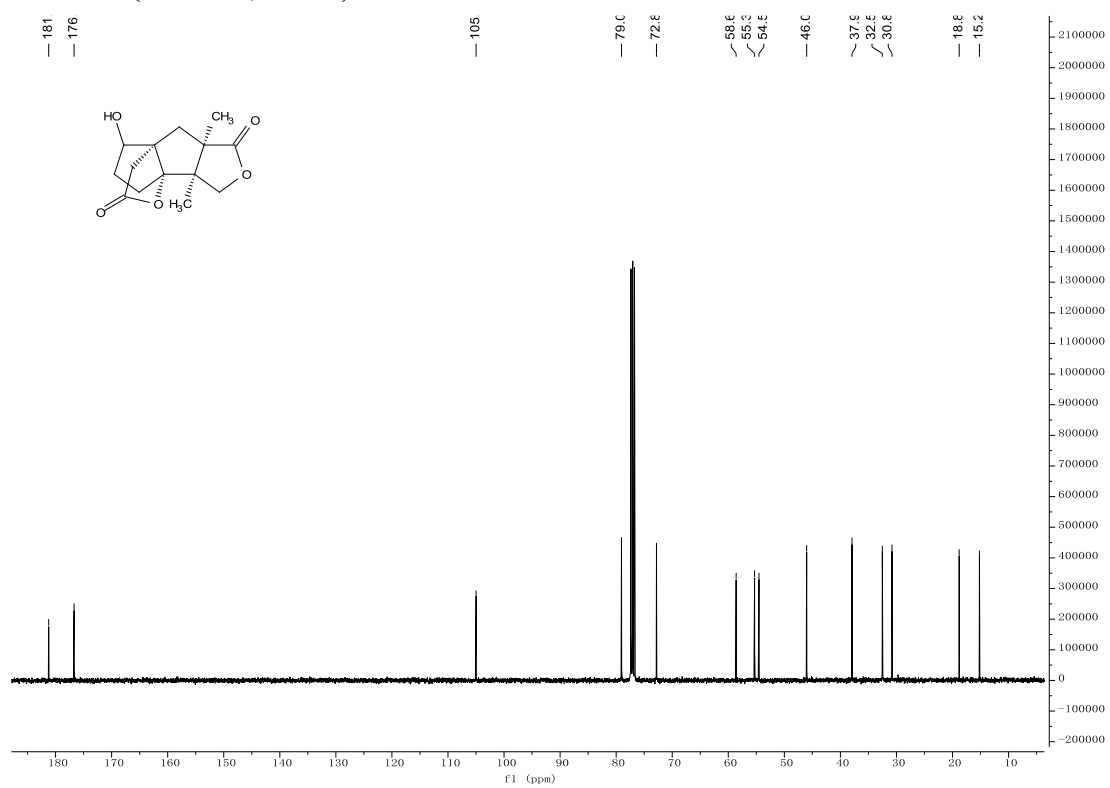


Compounds 13

¹H NMR (500 MHz, CDCl₃)

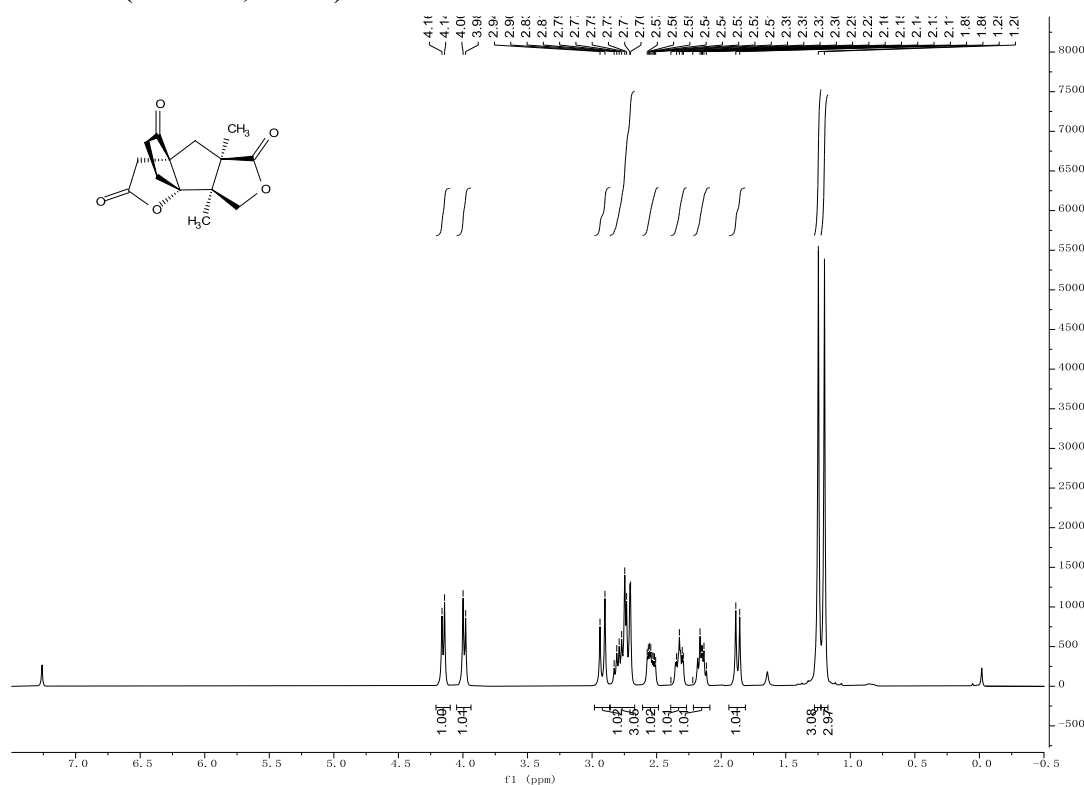


¹³C NMR (126 MHz, CDCl₃)

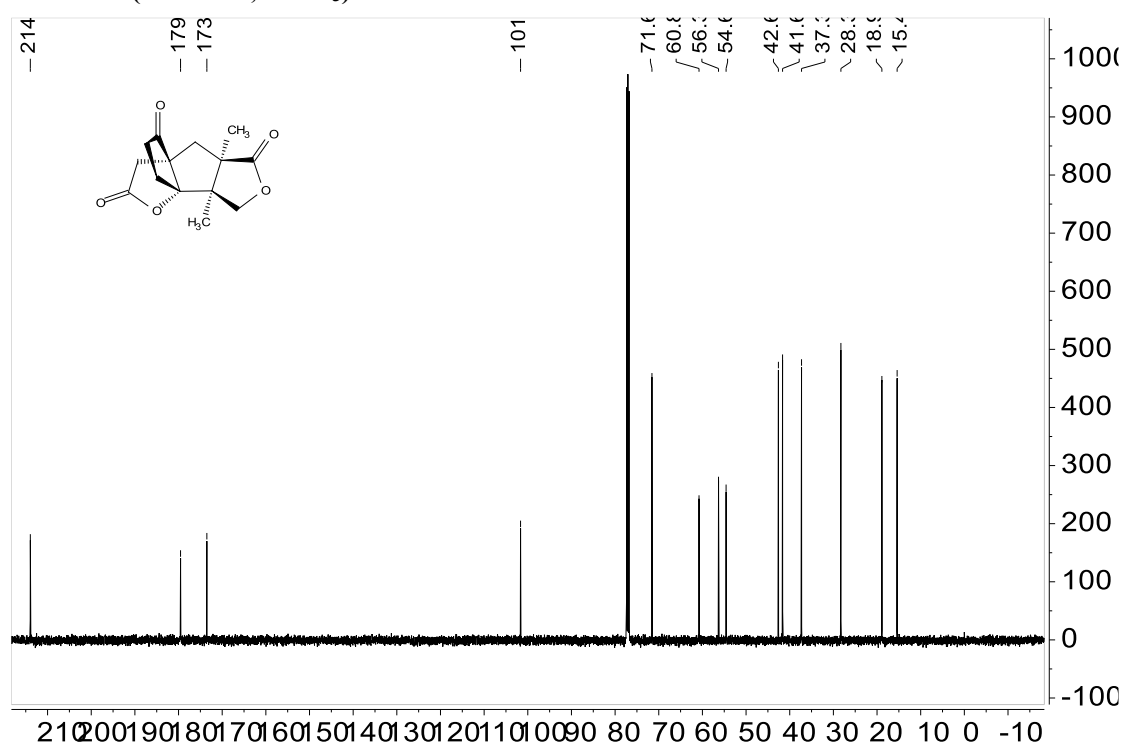


Compounds 14

^1H NMR (500 MHz, CDCl_3)

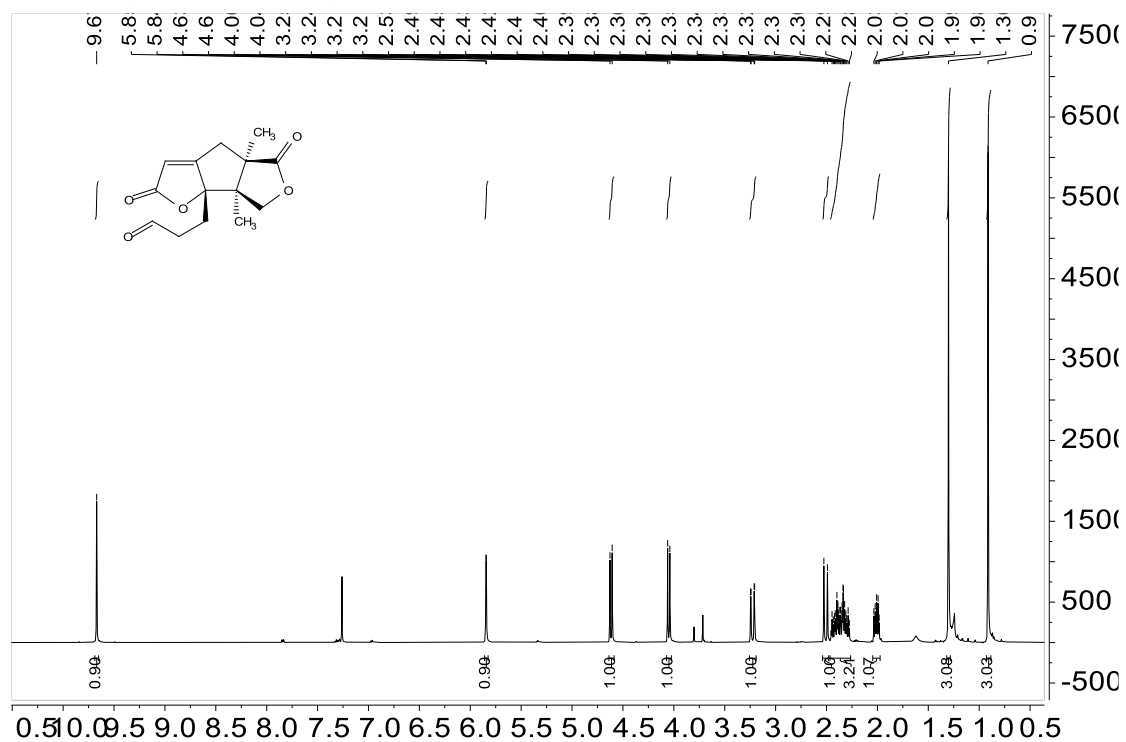


^{13}C NMR (126 MHz, CDCl_3)

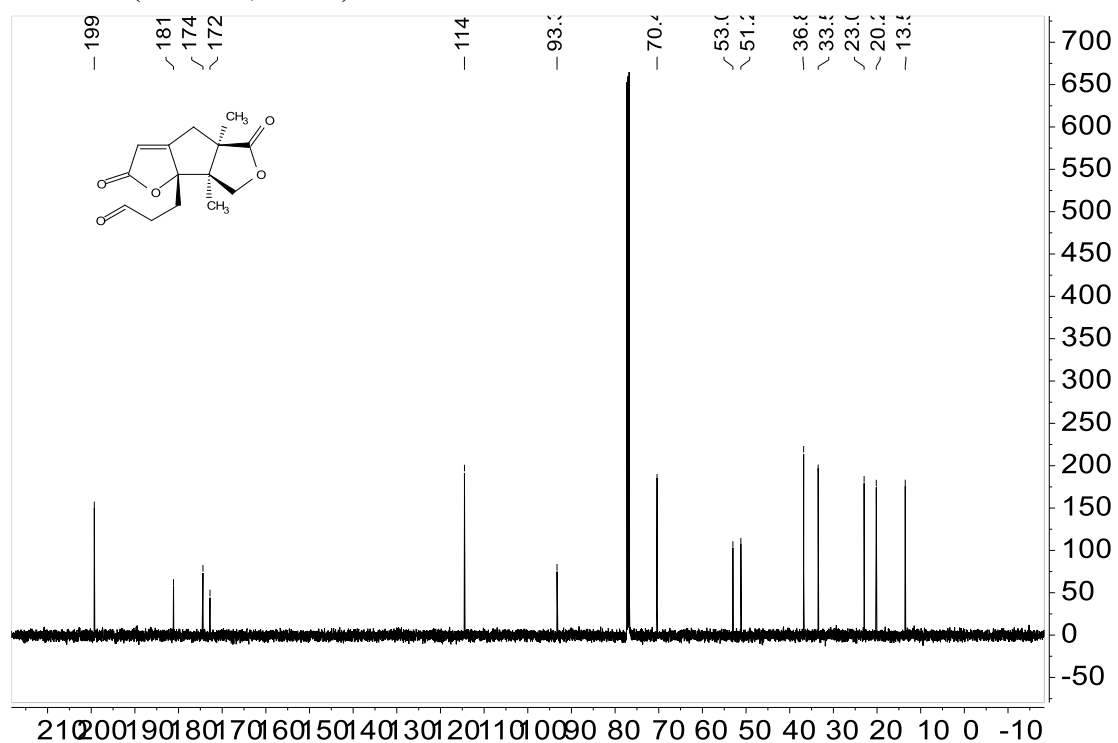


Compounds 16

¹H NMR (500 MHz, CDCl₃)

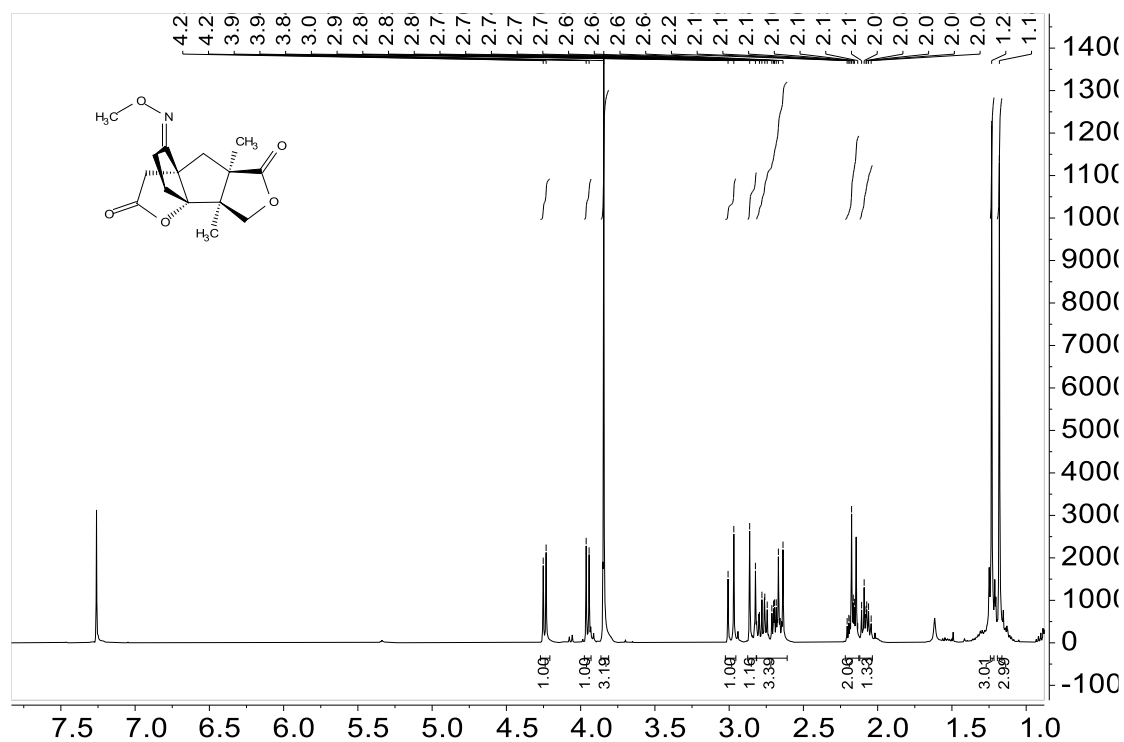


¹³C NMR (126 MHz, CDCl₃)

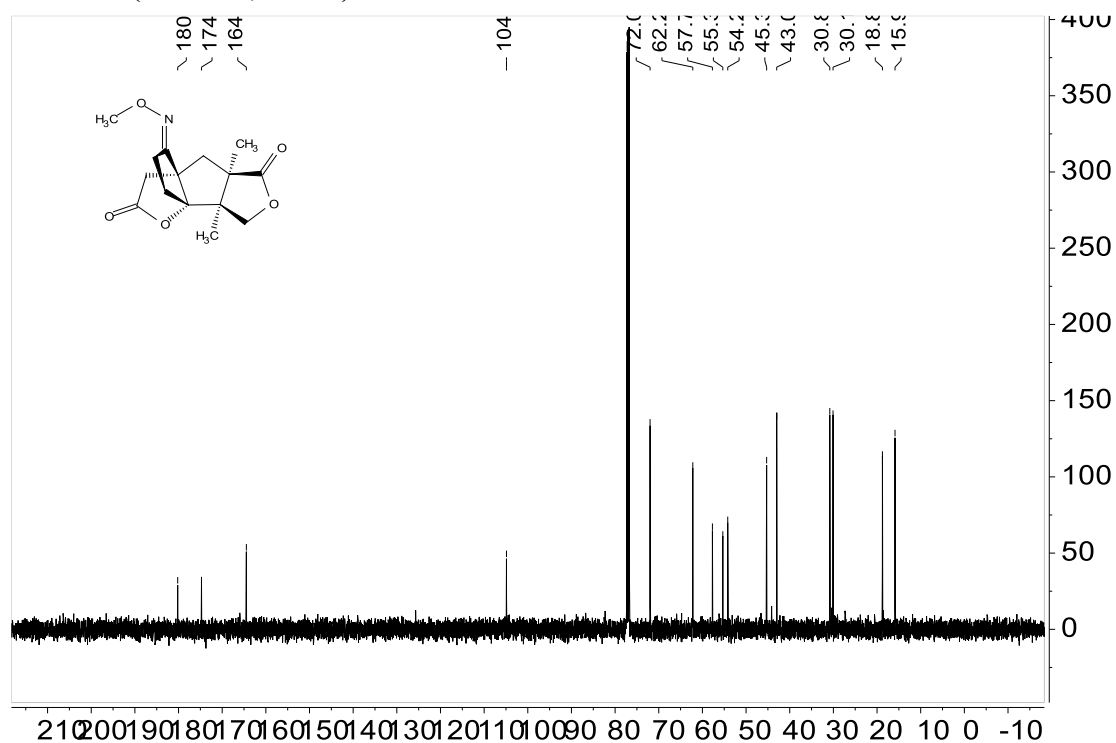


Compounds 17

¹H NMR (500 MHz, CDCl₃)

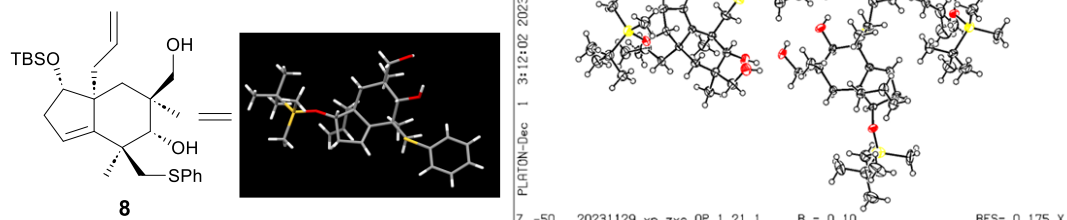


¹³C NMR (126 MHz, CDCl₃)



4. X-ray Crystallographic Data.

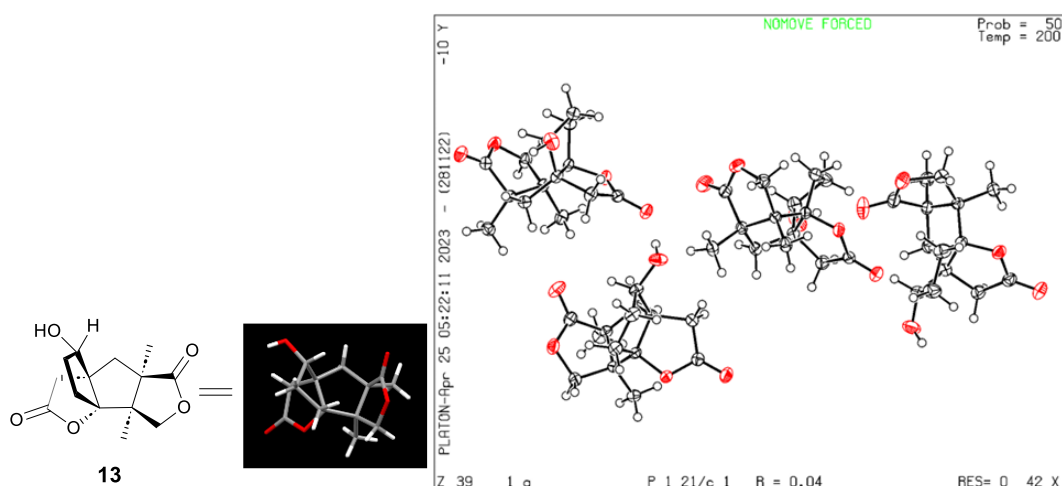
Table S1: Data collection details for compound **8**



Bond precision	C-C = 0.0126 Å
Wavelength	13.34139
Cell:	a = 10.2419 (8) b = 40.802 (3) c = 13.3467 (11) alpha = 90 beta = 90.910 (4) gamma = 90
Volume	5576.7 (8)
Space group	P 1 21 1
Hall group	P 2yb
Sum formula	C ₂₈ H ₄₄ O ₃ S ₂
Mr	492.75
Dx, g cm ⁻³	1.174
Z	8
Mu (mm ⁻¹)	1.262
F000	2144.0
h,k,lmax	12,50,16
Nref	21637
Reported T Limits:	Tmin = 0.590 Tmax = 0.751
Theta(max)	57.101
R(reflections)	0.1021(18023)
wR2(reflections)	0.2861(21637)
S	1.037
Npar	1278

The crystal of compound **8** was grown in the solution of CHCl₃ and MeOH as the solution slowly volatilized at room temperature.

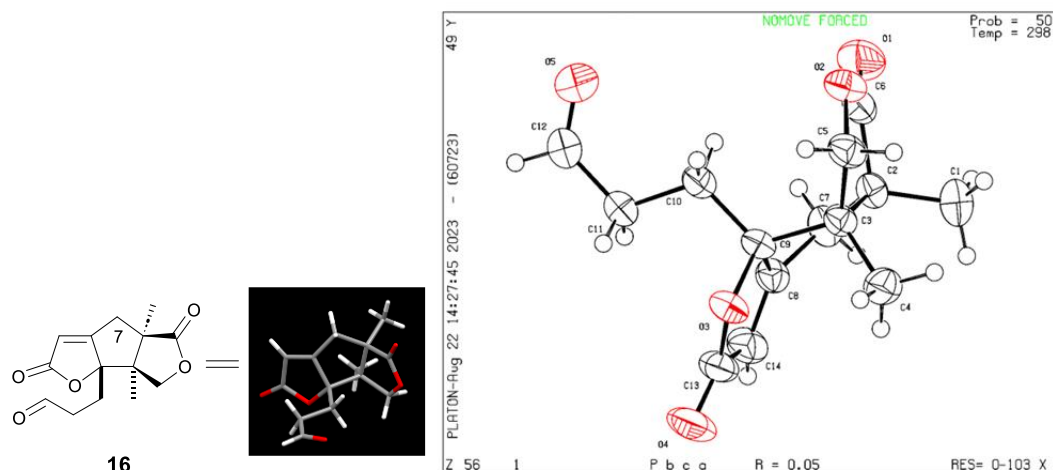
Table S2: Data collection details for compound 13



Bond precision	C-C = 0.0019 Å
Wavelength	1.34139
Cell:	a=11.6821(8)
	b=16.1543(12)
	c=26.457(2)
	alpha=90
	beta=90.330
	gamma=90
Volume	4962.3(6)
Space group	P 1 21/C 1
Hall group	-P 2ybc
Sum formula	C ₁₄ H ₁₈ O ₅
Mr	266.28
Dx, g cm ⁻³	1.426
Z	16
Mu (mm ⁻¹)	0.573
F000	2272.0
h,k,lmax	14,20,33
Nref	10166
Reported T Limits:	Tmin=0.625 Tmax=0.751
Data completeness	0.991
Theta(max)	57.299
R(reflections)	0.0376(7899)
wR2(reflections)	0.1009(10166)
S	1.049
Npar	697

The crystal of compound **13** was grown in the solution of CHCl₃ and MeOH as the solution slowly volatilized at room temperature.

Table S3: Data collection details for compound 16



Bond precision	C-C = 0.0030 Å
Wavelength	1.34137
Cell:	a=1.11397(7)
	b=14.2090(9)
	c=16.1659(11)
	alpha=90
	beta=90
	gamma=90
Volume	2558.8(3)
Space group	P b c a
Hall group	-P 2ac 2ab
Sum formula	C14 H16 O5
Mr	264.27
Dx, g cm ⁻³	1.372
Z	8
Mu (mm ⁻¹)	0.555
F000	1120.0
h,k,lmax	13,17,20
Nref	2608
Reported T Limits:	Tmin=0.414 Tmax=0.751
Data completeness	0.996
Theta(max)	56.976
R(reflections)	0.0494(1724)
wR2(reflections)	0.1315(2608)
S	1.015
Npar	174

The crystal of compound **16** was grown in the solution of CHCl₃ and MeOH as the solution slowly volatilized at room temperature.