

## Supporting Information

### Construction of the highly oxidized bicyclo[3.2.1]octane CD ring system of aconitine via a late stage enyne cycloisomerization

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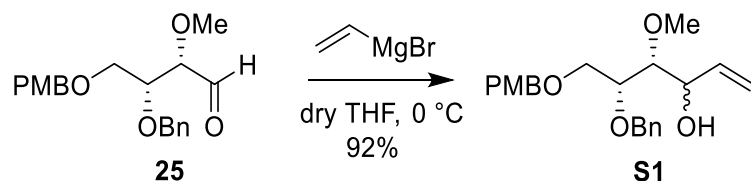
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## 1. General information

All reactions that require anhydrous conditions were performed in flame-dried glassware under Ar atmosphere and all reagents were purchased from commercial suppliers (CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> was purchased from ACROS) without further purification. Solvent purification was conducted according to Purification of Laboratory Chemicals 2nd edn (Perrin, D. D., Armarego, W. L. F. and Perrin, D. R., Pergamon Press: Oxford, 1980). The products were purified by flash column chromatography on silica gel (200 – 300 meshes) from the Anhui Liangchen Silicon Material Company (China). Reactions were monitored by thin layer chromatography (TLC, 0.2 mm, HSGF254) supplied by Yantai Chemicals (China). Visualization was accomplished with UV light, exposure to iodine, stained with ethanolic solution of phosphomolybdic acid or basic solution of KMnO<sub>4</sub>. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Varian INOVA-400/54, Agilent DD2-600/54 and calibrated by using residual undeuterated chloroform ( $\delta$ , <sup>1</sup>H NMR = 7.260, <sup>13</sup>C NMR = 77.00) and residual undeuterated acetone ( $\delta$ , <sup>1</sup>H NMR = 2.050, <sup>13</sup>C NMR = 29.85) The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, dt = double triplet, m = multiplet, and coupling constants (*J*) are reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum Two FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on Bruker Apex IV FTMS or Agilent LC-MSD TOF ESI mass spectrometers. The specific optical rotation was obtained from Rudolph Research Analytical Autopol VI automatic polarimeter. LC-MS analysis was performed on HP Agilent 6420 Triple Quad LC/MS.

## 2. Experimental procedures and characterization data

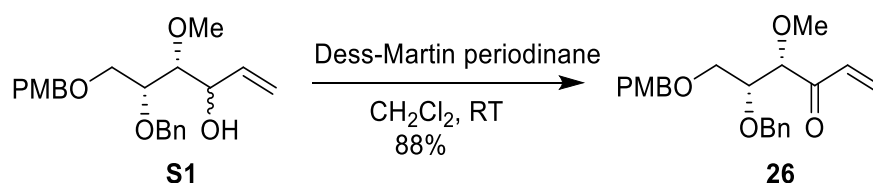


**Experimental:** Under argon atmosphere, to a solution of chiral aldehyde **25** (250 mg, 0.73 mmol, 1.0 equiv.) in dry THF (10.0 mL) was slowly added vinylmagnesium bromide (1.0 M in dry THF, 1.45 mL, 2.0equiv.) at 0 °C via syringe. When TLC indicated the complete consumption of starting material the reaction was quenched with sat. NH<sub>4</sub>Cl aq. (10 mL). The aqueous layer was separated and extracted with ethyl acetate (10 mL × 2). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by silica-gel column chromatography (petroleum ether:ethyl acetate, 4:1 v/v) to afford desired product **S1** (248 mg, 92%, dr ≈ 4 : 1 based on <sup>1</sup>H-NMR analysis) as a colorless oil.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, all observed signals are listed):** δ 7.51 – 7.21 (m, 14H), 6.88 (d, *J* = 8.4 Hz, 2.8H), 5.93 – 5.80 (m, 1.4H), 5.34 (d, *J* = 17.2 Hz, 0.4 H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.22 – 5.11 (m, 1.4 H), 4.75 – 4.67 (m, 1.4 H), 4.56 (d, *J* = 12.0 Hz, 1.4 H), 4.52 – 4.43 (m, 2.8 H), 4.34 (brs, 0.4 H), 4.25 (brs, 1H), 3.89 (brs, 0.6H), 3.81 (s, 3.6H), 3.77 – 3.71 (m, 1.4H), 3.70 – 3.62 (m, 2.6H), 3.50 (s, 3H), 3.43 (brs, 1H), 3.33 – 3.25 (m, 1.4 H), 3.06 (d, *J* = 6.4 Hz, 0.4 H), 2.76 (d, *J* = 4.8 Hz, 1H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, all observed signals are listed):** δ 159.2, 138.2, 137.9, 137.8, 130.0, 129.9, 129.9, 129.4, 128.4, 128.3, 128.3, 128.0, 128.0, 127.9, 127.7, 116.2, 115.9, 113.8, 83.7, 82.1, 78.2, 78.0, 73.1, 72.9, 72.1, 71.5, 69.2, 68.8, 61.1, 59.1, 55.3.

**HRMS (*m/z*):** [M+Na]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>28</sub>O<sub>5</sub>Na, 395.1829; found, 395.1832.



**Experimental:** To a solution of **S1** (240 mg, 0.64 mmol, 1.0 equiv.) in DCM (10.0 mL) was added Dess-Martin periodinane (410 mg, 0.97 mmol, 1.5 equiv.). The reaction mixture was allowed to stir at room temperature for 1 h before being quenched with sat. Na<sub>2</sub>SO<sub>3</sub> aq. (10 mL). The aqueous layer was separated and extracted with dichloromethane (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by silica-gel column chromatography (petroleum ether:ethyl acetate, 9:1 v/v) to afford desired product **26** (210 mg, 88%) as a colorless oil.

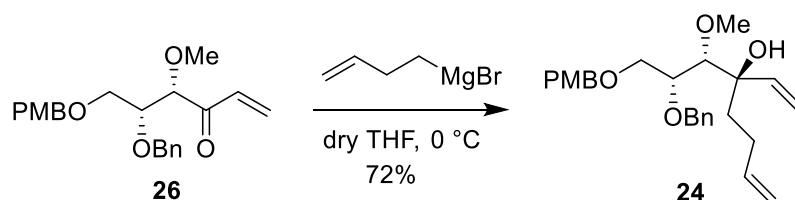
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.32 – 7.19 (m, 7H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.81 (dd, *J* = 17.2 Hz, 10.4 Hz, 1H), 6.36 (dd, *J* = 17.2 Hz, 1.6 Hz, 1H), 5.70 (dd, *J* = 10.4 Hz, 1.6 Hz, 1H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.43 (dd, *J* = 16.4 Hz, 11.6 Hz, 2H), 3.99 – 3.91 (m, 2H), 3.80 (s, 3H), 3.69 – 3.61 (m, 1H), 3.61 – 3.55 (m, 1H), 3.39 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 200.9, 159.1, 137.7, 132.1, 130.0, 129.3, 129.3, 128.7, 128.1, 128.1, 128.0, 128.0, 127.6, 113.7, 113.7, 86.2, 78.6, 73.3, 72.9, 68.3, 59.1, 55.2.

**Optical rotation:**  $[\alpha]_{\text{D}}^{25} = -48.1$  ( $c$  0.94,  $\text{CHCl}_3$ )

**IR** (neat):  $\nu_{\text{max}} = 1698, 1612, 1512, 1400, 1259, 1090, 1029, 764, 749 \text{ cm}^{-1}$

**HRMS** ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{22}\text{H}_{26}\text{O}_5\text{Na}$ , 393.1672; found, 393.1683.



**Experimental:** Under argon atmosphere, to a solution of 3-butenylmagnesium bromide (0.5 M in dry THF, 1.6 mL, 2.0 equiv.) in dry THF (5.0 mL) was slowly added **26** (150 mg in 2.0 mL dry THF, 0.40 mmol, 1.0 equiv.) at  $0\text{ }^\circ\text{C}$  via syringe. When TLC indicated the complete consumption of **26**, the reaction was quenched with sat.  $\text{NH}_4\text{Cl}$  aq. (50 mL). The aqueous layer was separated and extracted with ethyl acetate (8 mL  $\times$  2). The combined organic layers were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was subjected to silica-gel column chromatography (petroleum ether:ethyl acetate, 12:1 v/v) to afford desired product **24** as a colorless oil (124 mg, 72%, single diastereoisomer was observed).

**TLC:**  $R_f = 0.40$  (petroleum ether:ethyl acetate, 8:1 v/v)

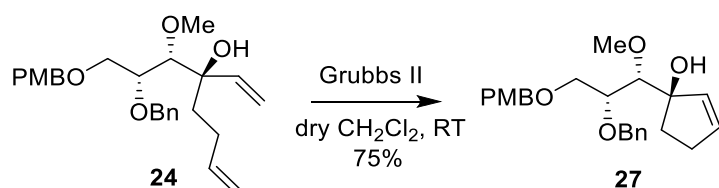
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.35 – 7.20 (m, 7H), 6.89 (d,  $J = 8.4$  Hz, 2H), 5.89 – 5.69 (m, 2H), 5.37 (d,  $J = 17.2$  Hz, 1H), 5.20 (d,  $J = 10.8$  Hz, 1H), 4.99 (d,  $J = 17.2$  Hz, 1H), 4.91 (d,  $J = 10.0$  Hz, 1H), 4.65 (d,  $J = 10.8$  Hz, 1H), 4.50 – 4.38 (m 3H), 4.38 (s, 3H), 3.70 – 3.63 (m, 2H), 3.55 (s, 3H), 3.23 (brs, 1H), 2.21 – 2.15 (m, 1H), 2.03 – 1.86 (m, 1H), 1.45 (t,  $J = 10.8$  Hz, 1H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  159.3, 140.9, 139.2, 137.4, 129.8, 129.5, 129.5, 128.4, 128.4, 128.2, 128.2, 127.9, 114.6, 114.0, 113.8, 113.8, 83.4, 79.3, 79.1, 73.1, 72.8, 68.5, 62.5, 55.3, 36.7, 27.4.

**Optical rotation:**  $[\alpha]_{\text{D}}^{25} = -11.5$  ( $c$  0.34,  $\text{CHCl}_3$ )

**IR** (neat):  $\nu_{\text{max}} = 1513, 1262, 1086, 1028, 803, 754, 733, 700 \text{ cm}^{-1}$

**HRMS** ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{26}\text{H}_{34}\text{O}_5\text{Na}$ , 449.2298; found, 449.2307.



**Experimental:** Under argon atmosphere, Grubbs II (309 mg, 0.36 mmol, 0.05 equiv.) was added to a solution of **24** (3.10 g, 7.27 mmol, 1.0 equiv.) in dry  $\text{CH}_2\text{Cl}_2$  (150 mL) at room temperature. 12 h later the reaction mixture was directly concentrated in vacuo and purified by silica-gel column chromatography (petroleum ether: ethyl acetate, 4:1 v/v to 2:1 v/v) to afford desired product **27** as a colorless oil (2.18 g, 75%).

**TLC:**  $R_f = 0.50$  (petroleum ether:ethyl acetate, 4:1 v/v)

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.38 – 7.25 (m, 7H), 6.90 (d,  $J = 6.0$  Hz, 2H), 5.96 – 5.90 (m, 1H), 5.66 – 5.60 (m, 1H), 4.72 (d,  $J = 7.6$  Hz, 1H), 4.61 (d,  $J = 7.6$  Hz, 1H), 4.52 – 4.46 (m, 2H), 3.95 – 3.89 (m, 1H), 3.83 (s, 3H), 3.71 (d,  $J = 4.0$  Hz, 1H), 3.52 (s, 3H), 3.40 (s, 1H), 3.32 (d,  $J = 2.0$  Hz, 1H), 2.54 – 2.43 (m, 1H), 2.33 – 2.21 (m, 2H), 1.88 – 1.79 (m, 1H).

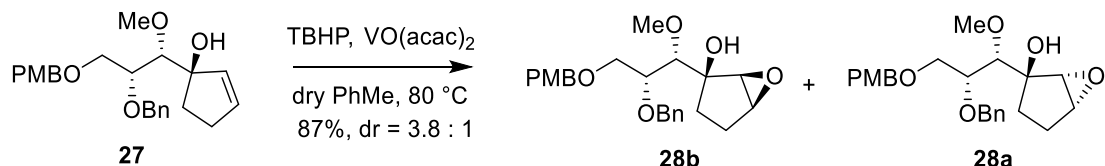
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  159.3, 137.9, 134.8, 134.6, 130.0, 129.4, 129.4, 128.4, 128.4, 128.2,

128.2, 127.8, 113.8, 113.8, 87.5, 83.8, 78.5, 73.1, 73.0, 69.6, 61.3, 55.3, 35.2, 31.0.

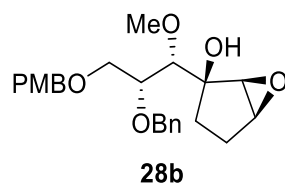
**Optical rotation:**  $[\alpha]_D^{25} = -23.1$  (*c* 0.36, CHCl<sub>3</sub>)

**IR** (neat):  $\nu_{\max} = 3457, 2915, 1612, 1513, 1454, 1302, 1248, 1090, 1032, 820$  cm<sup>-1</sup>

**HRMS** (*m/z*):  $[M+Na]^+$  calcd. for C<sub>24</sub>H<sub>30</sub>O<sub>5</sub>Na, 421.1985; found, 421.1992.



**Experimental:** Under argon atmosphere, VO(acac)<sub>2</sub> (23 mg, 0.09 mmol, 0.1 equiv.) was added to a solution of **27** (350 mg, 0.88 mmol, 1.0 equiv.) in dry PhMe (10.0 mL). Then the mixture was sonicated for 15 min till no obvious solid was observed, after which TBHP (2.3 M in DCM, 1.1 mL, 3.0 equiv.) was added dropwise via syringe at room temperature. Then the mixture was heated to 80 °C till the complete consumption of **27**. The reaction was quenched with sat. Na<sub>2</sub>SO<sub>3</sub> aq. (10 mL). The aqueous layer was separated and extracted with ethyl acetate (10 mL × 2). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was subjected to silica-gel column chromatography (petroleum ether:ethyl acetate, 5:1 v/v to 2:1 v/v) to afford desired product **28b** (250 mg, 69%) and the diastereoisomer **28a** (65 mg, 18%) as colorless oil.



**TLC:**  $R_f = 0.30$  (petroleum ether:ethyl acetate, 3:1 v/v)

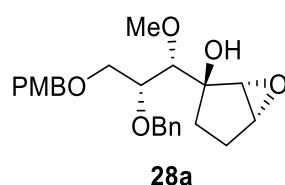
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.37 – 7.23 (m, 7H), 6.89 (d, *J* = 5.6 Hz, 2H), 4.73 (d, *J* = 7.6 Hz, 1H), 4.58 (d, *J* = 7.6 Hz, 1H), 4.50 (dd, *J* = 11.2 Hz, 7.6 Hz, 2H), 3.96 (brs, 1H), 3.82 (s, 3H), 3.74 (d, *J* = 4.0 Hz, 2H), 3.49 (s, 3H), 3.43 (d, *J* = 6.8 Hz, 1H), 3.32 (d, *J* = 2.0 Hz, 1H), 2.89 (s, 1H), 2.14 – 2.04 (m, 2H), 1.71 – 1.62 (m, 1H), 1.40 – 1.31 (m, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  159.1, 137.8, 129.8, 129.3, 129.3, 128.1, 128.1, 127.9, 127.9, 127.6, 113.6, 113.6, 82.1, 82.0, 77.4, 72.9, 72.7, 68.8, 61.2, 61.1, 57.2, 55.1, 30.0, 27.0.

**Optical rotation:**  $[\alpha]_D^{25} = -8.5$  (*c* 0.40, CHCl<sub>3</sub>)

**IR** (neat):  $\nu_{\max} = 2962, 1612, 1258, 1084, 1016, 851, 796, 751$  cm<sup>-1</sup>

**HRMS** (*m/z*):  $[M+Na]^+$  calcd. for C<sub>24</sub>H<sub>30</sub>O<sub>6</sub>Na, 437.1935; found, 437.1938.



**TLC:**  $R_f = 0.20$  (petroleum ether:ethyl acetate, 1:1 v/v)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 – 2.22 (m, 7H), 6.88 (d, *J* = 5.6 Hz, 2H), 4.72 (d, *J* = 8.0 Hz,

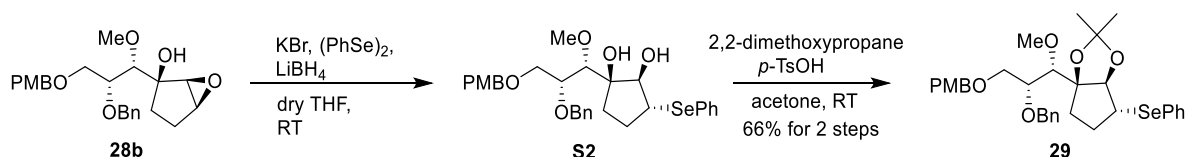
1H), 4.58 (d,  $J = 8.0$  Hz, 1H), 4.46 (dd,  $J = 12.8$  Hz, 8.0 Hz, 2H), 4.16 (q,  $J = 5.6$  Hz, 1H), 3.81 (s, 3H), 3.80 – 3.76 (m, 1H), 3.71 – 3.67 (m, 1H), 3.65 – 3.60 (m, 1H), 3.48 (d,  $J = 4.0$  Hz, 1H), 3.39 (s, 3H), 3.35 (d,  $J = 2.8$  Hz, 1H), 1.96 – 1.86 (m, 2H), 1.67 – 1.59 (m, 1H), 1.31 – 1.20 (m, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.2, 138.2, 130.2, 129.4, 129.4, 128.3, 128.3, 128.2, 128.2, 127.7, 113.8, 113.8, 79.6, 78.2, 73.2, 73.1, 72.9, 69.0, 65.6, 64.1, 59.9, 55.3, 28.4, 24.8.

**Optical rotation:**  $[\alpha]_{\text{D}}^{25} = +7.2$  ( $c$  0.20,  $\text{CHCl}_3$ )

**IR** (neat):  $\nu_{\text{max}} = 2987, 2324, 1612, 1513, 1275, 1260, 1095, 1052, 764$   $\text{cm}^{-1}$

**HRMS** ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{24}\text{H}_{30}\text{O}_6\text{Na}$ , 437.1935; found, 437.1943.



**Experimental:** Under argon atmosphere, KBr (1.12 g, 9.41 mmol, 6.5 equiv.) and  $(\text{PhSe})_2$  (452 mg, 1.44 mmol, 1.0 equiv.) were suspended in dry THF (10.0 mL) at room temperature. Then  $\text{LiBH}_4$  (2.0 M in THF, 1.66 mL, 2.3 equiv.) was added dropwise to the mixture which was kept stirring for 1.5 h at the corresponding temperature. A solution of **28b** (600 mg, 1.44 mmol, 1.0 equiv.) in dry THF (5.0 mL) was injected into the reaction mixture. 10 h later the reaction was quenched with sat.  $\text{NH}_4\text{Cl}$  aq. (20 mL). The aqueous layer was separated and extracted with ethyl acetate (20 mL  $\times$  2). The combined organic layers were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The crude product was directly dissolved into 10.0 mL acetone without further purification. To the solution were added 2,2-dimethoxypropane (2.0 mL) and  $p$ -TsOH (28 mg, 0.14 mmol, 0.1 equiv.). The reaction mixture was then kept stirring for 2 h at room temperature before being quenched with sat.  $\text{NaHCO}_3$  aq. (10 mL). The aqueous layer was separated and extracted with ethyl acetate (10 mL  $\times$  2). The combined organic layers were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The crude product was purified by silica-gel column chromatography (petroleum ether:acetone, 15:1 v/v to 2:1) to afford desired product **29** (585 mg, 66% for 2 steps) and recycled **S2** (163 mg).

**TLC:**  $R_f = 0.70$  (petroleum ether:acetone, 4:1 v/v)

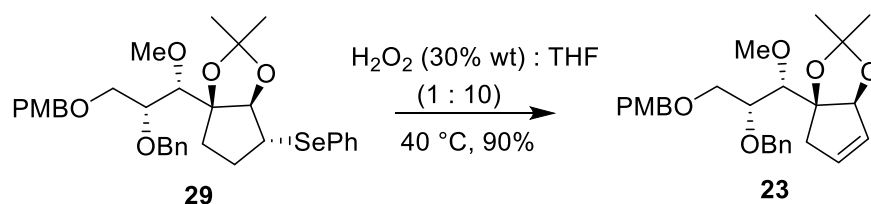
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.54 (d,  $J = 4.8$  Hz, 2H), 7.37 (d,  $J = 4.8$  Hz, 2H), 7.32 (t,  $J = 4.8$  Hz, 2H), 7.29 – 7.19 (m, 6H), 6.86 (d,  $J = 5.6$  Hz, 2H), 4.70 (dd,  $J = 13.2$  Hz, 7.2 Hz, 2H), 4.62 (brs, 1H), 4.49 (d,  $J = 7.6$  Hz, 1H), 4.43 (d,  $J = 8.0$  Hz, 1H), 3.92 – 3.86 (m, 1H), 3.81 (s, 3H), 3.76 – 3.71 (m, 1H), 3.66 (brs, 1H), 3.61 – 3.52 (m, 5H), 2.37 (dd,  $J = 14.4$  Hz, 8.4 Hz, 2H), 1.85 (dd,  $J = 14.0$  Hz, 8.4 Hz, 1H), 1.72 (dd,  $J = 14.4$  Hz, 8.4 Hz, 1H), 1.42 (s, 3H), 1.33 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.1, 138.8, 133.1, 133.1, 130.9, 130.5, 129.2, 129.2, 129.1, 129.1, 128.2, 128.2, 128.0, 128.0, 127.4, 126.9, 113.7, 113.7, 110.7, 93.3, 91.4, 83.1, 79.5, 73.6, 72.9, 69.7, 62.3, 55.3, 48.7, 32.0, 30.9, 28.0, 27.7.

**Optical rotation:**  $[\alpha]_{\text{D}}^{25} = -22.0$  ( $c$  0.20,  $\text{CHCl}_3$ )

**IR** (neat):  $\nu_{\text{max}} = 2925, 1612, 1512, 1454, 1253, 1090, 1029, 8001, 736, 695$   $\text{cm}^{-1}$

**HRMS** ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{33}\text{H}_{40}\text{O}_6\text{SeNa}$ , 635.1882; found, 635.1888.



**Experimental:** Compound **29** (400 mg, 0.65 mmol, 1.0 equiv.) was dissolved into H<sub>2</sub>O<sub>2</sub> (30% wt):THF 1:10 v/v (5.5 mL). Then the reaction mixture was heated to 40 °C for 5 h before being quenched with sat. Na<sub>2</sub>SO<sub>3</sub> aq. (6 mL). The aqueous layer was separated and extracted with ethyl acetate (6 mL × 2). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The desired product **23** (268 mg, 90%) was obtained by silica-gel column chromatographic purification (petroleum ether:acetone, 20:1 v/v).

**TLC:** R<sub>f</sub> = 0.50 (petroleum ether:acetone, 10:1 v/v)

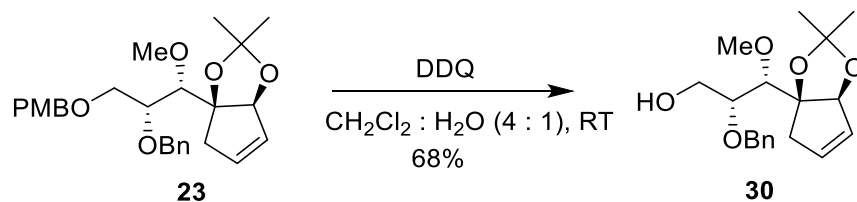
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.39 – 7.19 (m, 7H), 6.87 (d, *J* = 5.2 Hz, 2H), 5.86 (brs, 1H), 5.75 (brs, 1H), 5.13 (brs, 1H), 4.65 (s, 2H), 4.49 (d, *J* = 8.0 Hz, 1H), 4.43 (d, *J* = 7.6 Hz, 1H), 3.98 (brs, 1H), 3.81 (s, 3H), 3.71 (t, *J* = 6.0 Hz, 1H), 3.62 – 3.57 (m, 1H), 3.52 – 3.47 (m, 4H), 3.89 (d, *J* = 12.0 Hz, 1H), 2.44 (d, *J* = 12.0 Hz, 1H), 1.39 (s, 3H), 1.35 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 159.2, 138.6, 134.2, 130.7, 130.4, 129.2, 129.2, 128.2, 128.2, 128.1, 128.1, 127.4, 113.7, 113.7, 110.7, 90.5, 89.8, 82.2, 78.0, 73.5, 72.9, 69.7, 61.3, 55.3, 40.1, 29.2, 28.7.

**Optical rotation:** [α]<sub>D</sub><sup>25</sup> = +13.8 (*c* 0.50, CHCl<sub>3</sub>)

**IR (neat):** ν<sub>max</sub> = 2962, 2931, 1613, 1513, 1455, 1367, 1246, 1174, 1090, 1051, 799 cm<sup>-1</sup>

**HRMS (*m/z*):** [M+Na]<sup>+</sup> calcd. for C<sub>27</sub>H<sub>34</sub>O<sub>6</sub>Na, 477.2248; found, 477.2251.



**Experimental:** To a solution of **23** (240 mg, 0.53 mmol, 1.0 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> : H<sub>2</sub>O (4 : 1 v/v, 10.0 mL) was added DDQ (240 mg, 1.06 mmol, 2.0 equiv.). The reaction mixture was allowed to stir at room temperature for 1.5 h till the complete consumption of **23**. Then the reaction was quenched with sat. NaHCO<sub>3</sub> aq. (10 mL). The aqueous layer was separated and extracted with dichloromethane (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was subjected to silica-gel column chromatography (petroleum ether:acetone, 20:1 v/v) to afford desired product **30** (120 mg, 68%).

**TLC:** R<sub>f</sub> = 0.30 (petroleum ether:acetone, 6:1 v/v)

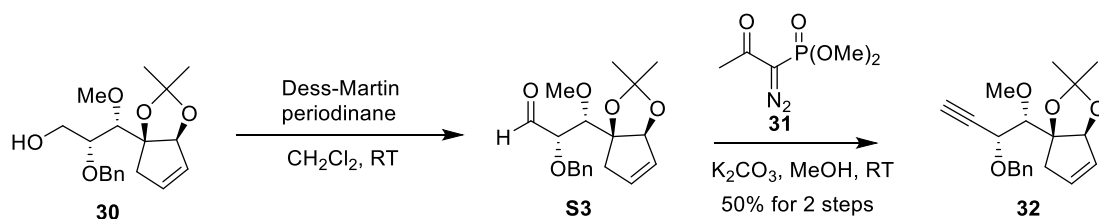
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.42 – 7.27 (m, 5H), 5.89 (brd, *d* = 4.0 Hz, 1H), 5.83 – 5.79 (m, 1H), 5.15 (s, 1H), 4.76 (d, *J* = 7.6 Hz, 1H), 4.66 (d, *J* = 7.6 Hz, 1H), 3.88 – 3.79 (m, 1H), 3.75 – 3.65 (m, 2H), 3.59 (s, 3H), 3.39 (d, *J* = 4.8 Hz, 1H), 2.79 (d, *J* = 12.0 Hz, 1H), 2.67 (t, *J* = 4.4 Hz, 1H), 2.47 (d, *J* = 12.0 Hz, 1H), 1.43 (s, 3H), 1.35 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 138.4, 133.6, 131.2, 128.5, 128.5, 128.0, 128.0, 127.7, 111.4, 90.3, 89.9, 84.2, 82.2, 73.5, 62.6, 61.4, 39.7, 29.2, 28.6.

**Optical rotation:** [α]<sub>D</sub><sup>25</sup> = +19.6 (*c* 0.30, CHCl<sub>3</sub>)

**IR (neat):** ν<sub>max</sub> = 3437, 2923, 2348, 2322, 1368, 1243, 1047, 856 cm<sup>-1</sup>

**HRMS** ( $m/z$ ):  $[M+Na]^+$  calcd. for  $C_{19}H_{26}O_5Na$ , 357.1672; found, 357.1678.



**Experimental:** To a solution of **30** (300 mg, 0.90 mmol, 1.0 equiv.) in  $CH_2Cl_2$  (10.0 mL) was added Dess-Martin periodinane (762 mg, 1.80 mmol, 2.0 equiv.). The reaction mixture was allowed to stir at room temperature for 1 h before being quenched with sat.  $Na_2SO_3$  aq. (10 mL). The aqueous layer was separated and extracted with dichloromethane (10 mL  $\times$  3). The combined organic layers were washed with brine, dried over anhydrous  $Na_2SO_4$  and concentrated in vacuo. The crude product of **S3**, **31** (345 mg, 1.80 mmol, 2.0 equiv.) and  $K_2CO_3$  (241 mg, 1.80 mmol, 2.0 equiv.) were directly dissolved into MeOH (10 mL). The reaction mixture was kept stirring for around 2 h at the corresponding temperature, and then, concentrated in vacuo. The residue was diluted with  $H_2O$  (10 mL) and ethyl acetate (10 mL). The aqueous layer was separated and extracted with ethyl acetate (10 mL  $\times$  2). The combined organic layers were washed with brine, dried over anhydrous  $Na_2SO_4$  and concentrated in vacuo. The desired product **32** (146 mg, 50% for 2 steps) was obtained by silica-gel column chromatographic purification (petroleum ether:ethyl acetate, 20:1 v/v).

**TLC:**  $R_f = 0.60$  (petroleum ether:ethyl acetate, 10:1 v/v)

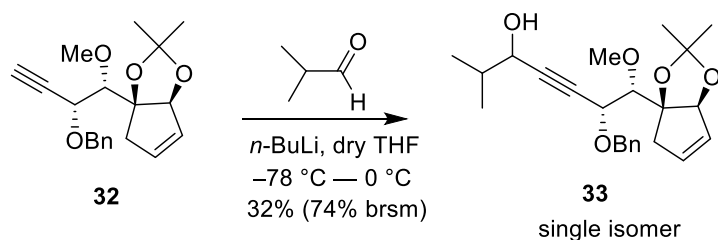
**$^1H$  NMR (400 MHz,  $CDCl_3$ ):**  $\delta$  7.42 – 7.24 (m, 5H), 5.85 (d,  $J = 12.0$  Hz, 1H), 5.77 – 5.71 (m, 1H), 5.11 (s, 1H), 4.88 (d,  $J = 8.0$  Hz, 1H), 4.56 (d,  $J = 9.6$  Hz, 2 H), 3.69 (s, 3H), 3.52 (brs, 1H), 2.91 (d,  $J = 12.4$  Hz, 1H), 2.55 (brs, 1H), 2.43 (d,  $J = 12.4$  Hz, 1H), 1.36 (s, 3H), 1.33 (s, 3H).

**$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):**  $\delta$  137.5, 134.4, 130.4, 128.1, 128.1, 128.1, 128.1, 127.5, 110.9, 90.1, 90.0, 85.0, 81.6, 75.3, 71.2, 67.4, 61.4, 40.1, 29.3, 28.7.

**Optical rotation:**  $[\alpha]_D^{25} = -44.1$  ( $c$  0.20,  $CHCl_3$ )

**IR** (neat):  $\nu_{max} = 2988, 1969, 1275, 1261, 1072$   $cm^{-1}$

**HRMS** ( $m/z$ ):  $[M+Na]^+$  calcd. for  $C_{20}H_{24}O_4Na$ , 351.1567; found, 351.1573.



**Experimental:** Under argon atmosphere, **32** (140 mg, 0.43 mmol, 1.0 equiv.) was dissolved into dry THF (10.0 mL) to which was added  $n-BuLi$  (2.5 M in hexane, 222  $\mu L$ , 0.55 mmol, 1.3 equiv.) via syringe at  $-78$   $^{\circ}C$ . 30 min later, isobutyraldehyde (62 mg, 0.85 mmol, 2.0 equiv.) was added to the reaction mixture which was allowed to stir for additional 1 h. The reaction was quenched with sat.  $NH_4Cl$  aq. (10 mL). The aqueous layer was separated and extracted with ethyl acetate (10 mL  $\times$  2). The combined organic layers were washed with brine, dried over anhydrous  $Na_2SO_4$  and concentrated in vacuo. The crude product was purified by silica-gel column chromatography (petroleum ether:ethyl acetate, 6:1 v/v) to afford desired product **33** as a colorless oil (54 mg, 32%,



74% brsm, single isomer was observed) and recycled **32** (80 mg).

**TLC:**  $R_f = 0.15$  (petroleum ether:ethyl acetate, 10:1 v/v)

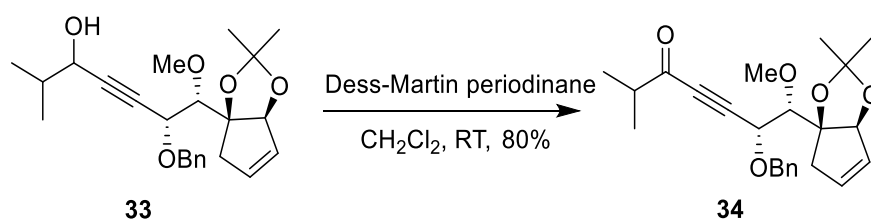
**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.40 – 7.27 (m, 5H), 5.89 – 5.82 (m, 1H), 5.78 – 5.70 (m, 1H), 5.14 (brs, 1H), 5.84 (d,  $J = 11.6$  Hz, 1H), 4.61 – 4.51 (m, 2H), 4.24 (t,  $J = 5.2$  Hz, 1H), 3.67 (s, 3H), 3.48 (d,  $J = 2.8$  Hz, 1H), 2.89 (d,  $J = 18.8$  Hz, 1H), 2.47 (d,  $J = 18.0$  Hz, 1H), 1.99 – 1.82 (m, 2H), 1.37 (s, 3H), 1.33 (s, 3H), 1.03 (dd,  $J = 8.8$  Hz, 6.8 Hz, 6H).

**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  137.7, 134.4, 130.5, 128.2, 128.2, 128.1, 128.1, 127.6, 111.1, 90.3, 89.9, 87.0, 85.4, 83.4, 71.3, 68.2, 68.0, 61.5, 40.4, 34.4, 29.3, 28.7, 18.1, 17.6.

**Optical rotation:**  $[\alpha]_D^{25} = -22.8$  ( $c$  0.12,  $\text{CHCl}_3$ )

**IR** (neat):  $\nu_{\text{max}} = 2962, 1260, 1090, 1075, 1020 \text{ cm}^{-1}$

**HRMS** ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{24}\text{H}_{32}\text{O}_5\text{Na}$ , 423.2142; found, 423.2149.



**Experimental:** To a solution of **33** (50 mg, 0.13 mmol, 1.0 equiv.) in DCM (5.0 mL) was added Dess-Martin periodinane (106 mg, 0.25 mmol, 2.0 equiv.). The reaction mixture was allowed to stir at room temperature for 1 h before being quenched with sat.  $\text{Na}_2\text{SO}_3$  aq. (5 mL). The aqueous layer was separated and extracted with dichloromethane (5 mL  $\times$  3). The combined organic layers were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was subjected to silica-gel column chromatography (petroleum ether:ethyl acetate, 8:1 v/v) to afford desired product **34** (40 mg, 80%) as a colorless oil.

**TLC:**  $R_f = 0.40$  (petroleum ether:ethyl acetate, 10:1 v/v)

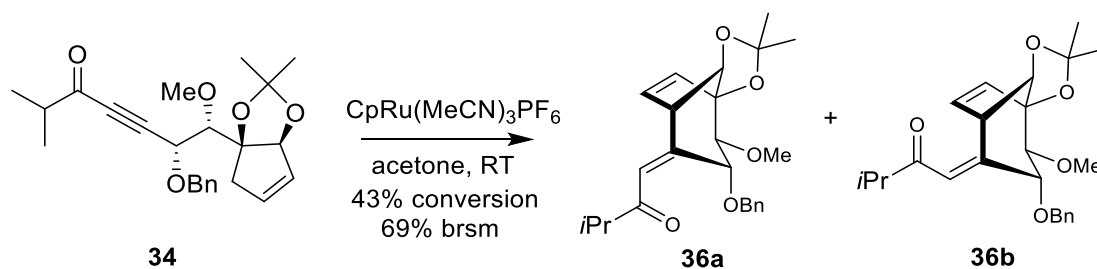
**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.41 – 7.27 (m, 5H), 5.89 – 5.80 (m, 1H), 5.77 – 5.69 (m, 1H), 5.10 (brs, 1H), 4.86 (d,  $J = 11.6$  Hz, 1H), 4.71 (d,  $J = 2.4$  Hz, 1H), 4.59 (d,  $J = 11.6$  Hz, 1H), 3.66 (s, 3H), 3.55 (d,  $J = 2.4$  Hz, 1H), 2.90 (d,  $J = 18.0$  Hz, 1H), 2.73 – 2.61 (m, 1H), 2.43 (d,  $J = 18.0$  Hz, 1H), 1.33 (d,  $J = 10.4$  Hz, 6H), 1.22 (dd,  $J = 6.8$  Hz, 2.0 Hz, 6H).

**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  191.3, 137.0, 134.3, 130.4, 128.3, 128.3, 128.2, 128.2, 127.8, 111.1, 90.4, 90.2, 89.8, 85.0, 85.0, 71.8, 67.9, 61.3, 43.0, 39.9, 29.4, 28.6, 17.8, 17.8.

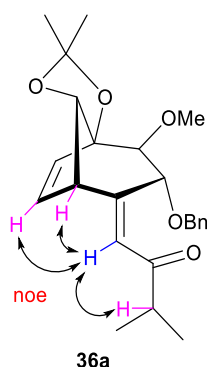
**Optical rotation:**  $[\alpha]_D^{25} = -37.9$  ( $c$  0.38,  $\text{CHCl}_3$ )

**IR** (neat):  $\nu_{\text{max}} = 2963, 1674, 1455, 1260, 1071, 1051, 1016, 798, 764 \text{ cm}^{-1}$

**HRMS** ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{24}\text{H}_{30}\text{O}_5\text{Na}$ , 421.1985; found, 421.1992.



**Experimental:** To a solution of **34** (20 mg, 0.05 mmol, 1.0 equiv.) in acetone (3.0 mL) was added  $\text{CpRu}(\text{MeCN})_3\text{PF}_6$  (11 mg, 0.025 mmol, 0.5 equiv.). The reaction mixture was allowed to stir at room temperature for 2 h, then concentrated in vacuo. The crude product was purified by silica-gel column chromatography (dichloromethane) to afford desired product **36a** (2.4 mg, 28% brsm) and **36b** (3.5 mg, 41% brsm) as colorless oil and recycle 11.4 mg of **34**.



**TLC:**  $R_f = 0.35$  (dichloromethane)

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.39 – 7.27 (m, 5H), 6.16 (brs, 1H), 5.93 – 5.89 (m, 1H), 5.88 – 5.84 (m, 1H), 5.31 (brs, 1H), 4.84 (brs, 1H), 4.65 (q,  $J = 3.6$  Hz, 2H), 3.91 (d,  $J = 3.2$  Hz, 1H), 3.77 (brs, 1H), 3.44 (s, 3H), 2.61 (p,  $J = 4.0$  Hz, 1H), 1.44 (s, 3H), 1.41 (s, 3H), 1.05 (s, 3H), 1.03 (s, 3H).

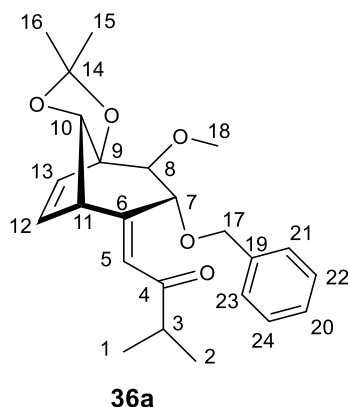
**$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):**  $\delta$  205.3, 153.3, 138.5, 134.2, 132.7, 128.1, 128.1, 127.9, 127.9, 127.5, 124.8, 111.6, 95.7, 90.2, 84.5, 80.2, 72.3, 59.6, 59.1, 41.4, 27.8, 27.1, 18.2, 17.8.

**Optical rotation:**  $[\alpha]_D^{25} = +122.5$  ( $c$  0.04,  $\text{CHCl}_3$ )

**IR (neat):**  $\nu_{\text{max}} = 2002, 1261, 1672, 1379, 1178, 1108, 751$   $\text{cm}^{-1}$

**HRMS ( $m/z$ ):**  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{24}\text{H}_{30}\text{O}_5\text{Na}$ , 421.1985; found, 437.1988.

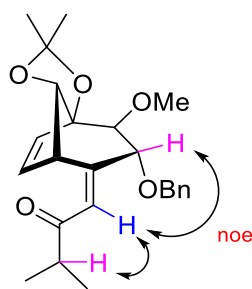
**NOTE:** The structure of **36a** was confirmed by 2D NMR experiments and NOE experiments.



**Table S1. Assignment of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) spectroscopic data of **36a**.**

$\delta_{\text{H}}$ mult. ( $J$ in Hz)	$\delta_{\text{C}}$	No.	HMBC	COSY
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7.39 – 7.27 (m, 5H)	128.1, 128.1, 127.9, 127.9, 127.5	C20, C21, C22, C23, C24	C19, C21/C22 or C23/C24, C17	H17
6.16 (brs, 1H)	124.8	C5	C11, C7, C4, C6	H11, H7
5.93 – 5.89 (m, 1H)	132.7	C13	C11, C10, C9, C12	H11, H10
5.88 – 5.84 (m, 1H)	134.2	C12	C11, C9	H11
5.31 (brs, 1H)	84.5	C10	C8, C14, C12	H11, H12, H13
4.84 (brs, 1H)	80.2	C7	C11, C17, C8	H8, H5, C11
4.65 (q, 3.6, 2H)	72.3	C17	C7, C21/22 or C23/24, C19	H21/22 or H23/24
3.91 (d, 3.2, 1H)	90.2	C8	C18, C7, C9, C6	H7
3.77 (brs, 1H)	59.6	C11	C8	H5, H13, H12, H10, H7
3.44 (s, 3H)	59.1	C18	C8	
2.61 (p, 4.0, 1H)	41.4	C3	C1/2, C4	H1/H2
1.44 (s, 3H)/1.41 (s, 3H)	27.8, 27.1	C15/C16	C16/C15, C14	—
1.05 (s, 3H), 1.03 (s, 3H)	18.2, 17.8	C1/C2	C2/C1, C3, C4	H3
—	205.3	C4	—	—
—	153.3	C6	—	—
—	95.7	C9	—	—
—	111.6	C14	—	—
—	138.5	C19	—	—



**36b**

**TLC:**  $R_f = 0.30$  (dichloromethane)

**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.39 – 7.28 (m, 5H), 6.53 (d,  $J = 4.8$  Hz, 1H), 6.03 – 5.98 (m, 1H), 5.71 (d,  $J = 4.0$  Hz, 1H), 4.56 (dd,  $J = 19.2$  Hz, 8.0 Hz, 2H), 4.38 (brs, 1H), 4.19 (dd,  $J = 4.8$  Hz, 1.6 Hz, 1H), 4.09 (d,  $J = 2.0$  Hz, 1H), 3.84 (d,  $J = 1.6$  Hz, 1H), 3.49 (s, 3H), 3.17 (p,  $J = 4.4$  Hz, 1H), 1.43 (s, 3H), 1.41 (s, 3H), 1.07 (t,  $J = 4.4$  Hz, 6H).

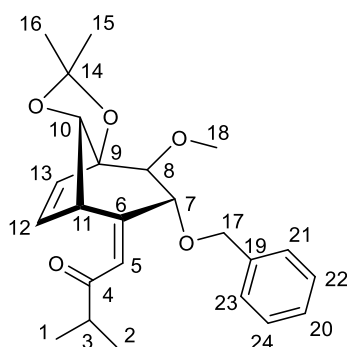
**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  204.8, 145.1, 137.8, 136.2, 136.0, 132.9, 128.5, 128.5, 128.0, 127.8, 127.8, 111.3, 96.6, 83.5, 82.4, 75.6, 72.3, 60.3, 45.5, 34.2, 28.0, 26.6, 19.5, 19.3.

**Optical rotation:**  $[\alpha]_D^{25} = -136.7$  ( $c$  0.06,  $\text{CHCl}_3$ )

**IR** (neat):  $\nu_{\text{max}} = 2931, 2029, 1672, 1456, 1175, 1260, 800, 699$   $\text{cm}^{-1}$

**HRMS** ( $m/z$ ):  $[M+Na]^+$  calcd. for  $C_{24}H_{30}O_5Na$ , 421.1985; found, 437.1985.

*NOTE: The structure of 36b was confirmed by 2D NMR experiments and NOE experiments.*



**36b**

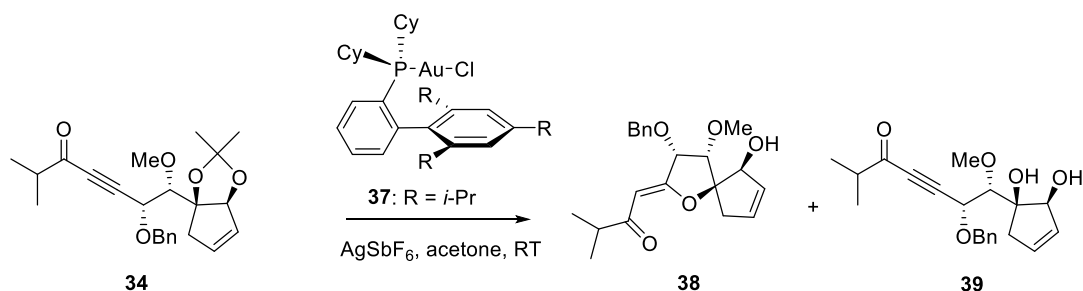
**Table S2. Assignment of the  $^1H$  and  $^{13}C$  NMR ( $CDCl_3$ ) spectroscopic data of 36b.**

$\delta_H$ mult. ( $J$ in Hz)	$\delta_C$	No.	HMBC	COSY
7.39 – 7.28 (m, 5H)	128.5, 128.5, 128.0, 127.8, 127.8	C20, C21, C22, C23, C24	C17, C19	H17
6.53 (d, 4.8, 1H)	136.2	C5	C11, C8, C4, C7, C6	H7
6.03 – 5.98 (m, 1H)	136.0	C13	—	H11, H12, H10
5.71 (d, 4.0, 1H)	132.9	C12	C11, C10, C9, C13, C6	H13, H10
4.56 (dd, 19.2, 8.0, 2H)	72.3	C17	C7, C21/22 or C23/24, C19	—
4.38 (brs, 1H)	82.4	C10	C11, C12, C13, C6	H12, H13
4.19 (dd, 4.8, 1.6, 1H)	75.6	C7	C17, C8, C9, C5, C6	H8, H5
4.09 (d, 2.0, 1H)	45.5	C11	C5	H13, H5
3.84 (d, 1.6, 1H)	83.4	C8	C18, C7, C10, C9, C5	H7
3.49 (s, 3H)	60.3	C18	C8	—
3.17 (p, 4.4, 1H)	34.2	C3	C1/2, C4	H1/2
1.43 (s, 3H), 1.41 (s, 3H)	28.0, 26.6	C15/ C16	C16/C15, C14	H16/H15
1.07 (t, 4.4, 6H)	19.5, 19.3	C1/ C2	C2/C1, C3, C4	H2/H1, H3
—	111.3	C14	—	—
—	145.1	C6	—	—
—	96.7	C9	—	—
—	204.8	C4	—	—
—	137.8	C19	—	—

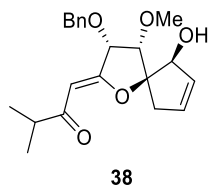
**Table S3. Screening of conditions for enyne cycloisomerization of 34**

Entry	catalyst	solvent	T (°C)	results
1	AuCl <sub>3</sub> , AgSbF <sub>6</sub> , PPh <sub>3</sub>	dioxane/H <sub>2</sub> O <sup>a</sup>	25	decomposed
2	AuCl <sub>3</sub> , AgOTf, PPh <sub>3</sub>	dioxane/H <sub>2</sub> O <sup>a</sup>	25	decomposed
3	<b>37</b>	acetone	25	<b>38</b> (58%), <b>39</b> (25%)
4	PtCl <sub>2</sub> , ( <i>R</i> )-BINAP	dioxane/H <sub>2</sub> O <sup>a</sup>	80	decomposed
5	(Ph <sub>3</sub> P) <sub>2</sub> CpRuCl, CSA, In(OTf) <sub>3</sub>	acetone	45	N.R
6	Hg(OTf) <sub>2</sub> , H <sub>2</sub> O	MeNO <sub>2</sub> /MeCN <sup>b</sup>	25	decomposed

<sup>a</sup> The ratio of dioxane and H<sub>2</sub>O is 6:1. <sup>b</sup> The ratio of MeNO<sub>2</sub> and MeCN is 9:1.



**Experimental:** Under Argon atmosphere, **34** (10 mg, 0.03 mmol, 1.0 equiv.), **37** (1.8 mg, 0.003 mmol, 0.1 equiv.) and AgSbF<sub>6</sub> (1 mg, 0.003 mmol, 0.1 equiv.) were dissolved into acetone (1.0 mL). After kept stirring for 8 h, the reaction mixture was filtered through a pad of silica gel and then concentrated in vacuo. The residue was subjected to silica-gel column chromatography (petroleum ether:ethyl acetate, 8:1 v/v to 3:1) to afford **38** (5.2 mg, 58%) and **39** (2.2 mg, 25%) as colorless oil.



**TLC:** R<sub>f</sub> = 0.5 (petroleum ether:ethyl acetate, 5:1, v/v)

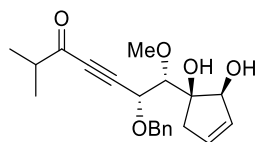
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.46 – 7.30 (m, 5H), 6.07 (brs, 1H), 5.93 – 5.86 (m, 1H), 5.78 – 5.71 (m, 1H), 5.34 (brs, 1H), 4.98 (d, *J* = 11.2 Hz, 1H), 4.88 (d, *J* = 11.2 Hz, 1H), 4.73 (brs, 1H), 3.52 (brs, 1H), 3.41 (brs, 1H), 3.26 (s, 3H), 2.82 (d, *J* = 18.4 Hz, 1H), 2.66 – 2.55 (m, 2H), 1.14 (d, *J* = 3.2 Hz, 3H), 1.12(d, *J* = 2.8 Hz, 3H).

**<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):** δ 203.8, 170.8, 137.1, 131.3, 130.3, 128.7, 128.7, 128.7, 128.7, 128.5, 100.5, 96.8, 86.5, 80.2, 78.8, 74.5, 57.7, 41.7, 38.3, 18.6, 18.4.

**Optical rotation:** [α]<sub>D</sub><sup>25</sup> = -24.3 (*c* 0.07, CHCl<sub>3</sub>)

**IR (neat):** ν<sub>max</sub> = 2961, 1646, 1372, 1259, 1084, 1050, 794, 741 cm<sup>-1</sup>

**HRMS (*m/z*):** [M+Na]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>26</sub>O<sub>5</sub>Na, 381.1672; found, 381.1674.



**39**

**TLC:**  $R_f = 0.1$  (petroleum ether:ethyl acetate, 5:1, v/v)

**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.44 – 7.29 (m, 5H), 5.92 – 5.84 (m, 1H), 5.81 – 5.75 (m, 1H), 5.36 (brs, 1H), 4.81 – 4.68 (m, 3H), 4.41 (d,  $J = 4.8$  Hz, 1H), 3.90 (d,  $J = 5.2$  Hz, 1H), 3.43 (s, 3H), 2.93 – 2.83 (m, 2H), 2.49 (d,  $J = 17.6$  Hz, 1H), 1.07 (dd,  $J = 11.2$  Hz, 6.8 Hz, 6H).

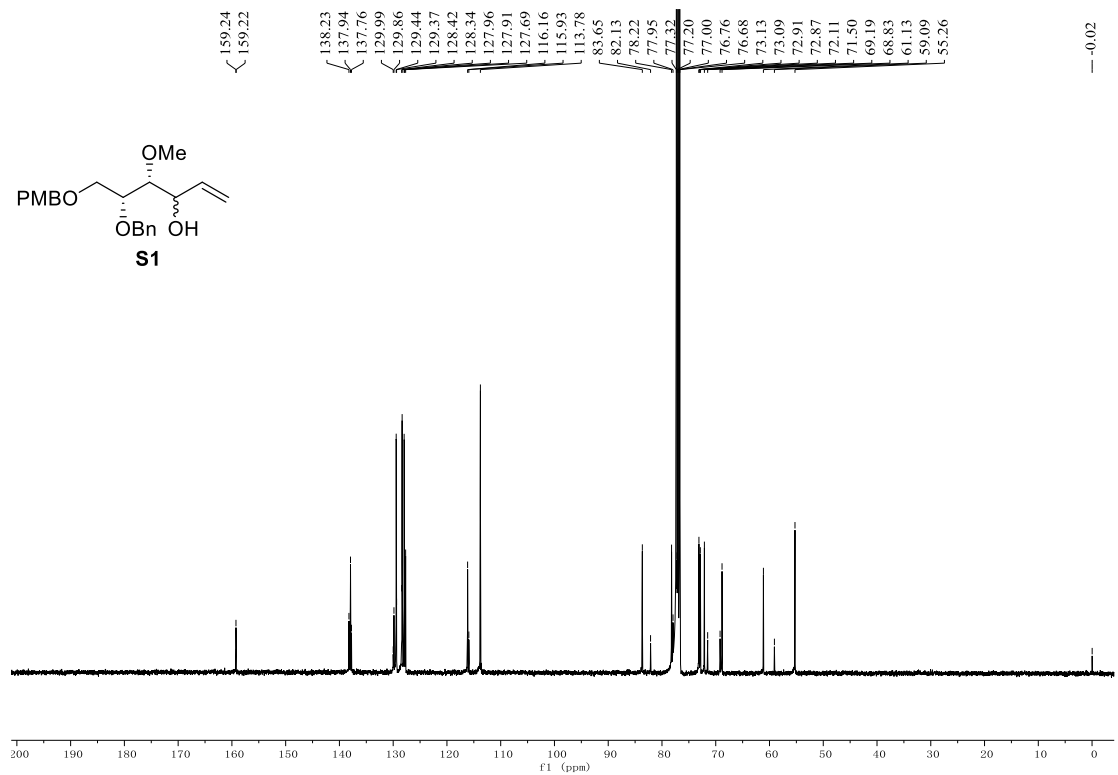
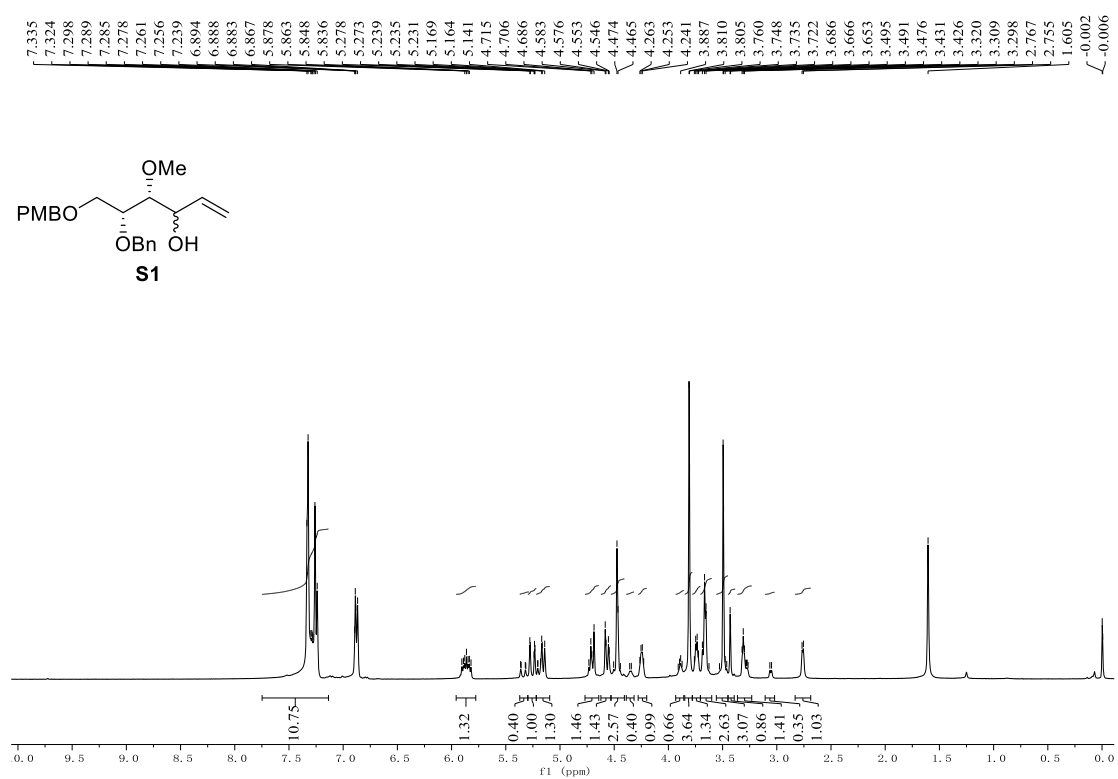
**$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ):**  $\delta$  203.2, 164.7, 136.8, 131.7, 130.3, 128.7, 128.7, 128.3, 128.0, 128.0, 100.9, 96.1, 84.6, 82.4, 80.4, 72.4, 58.6, 40.3, 37.3, 18.6, 18.3.

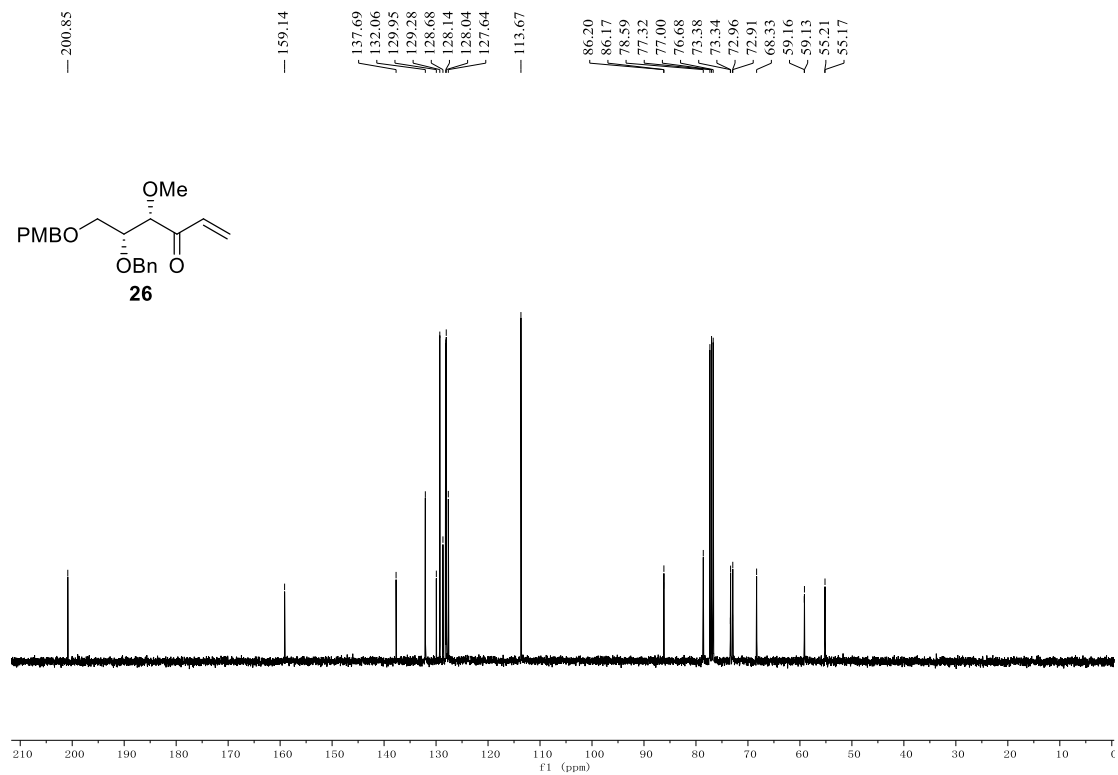
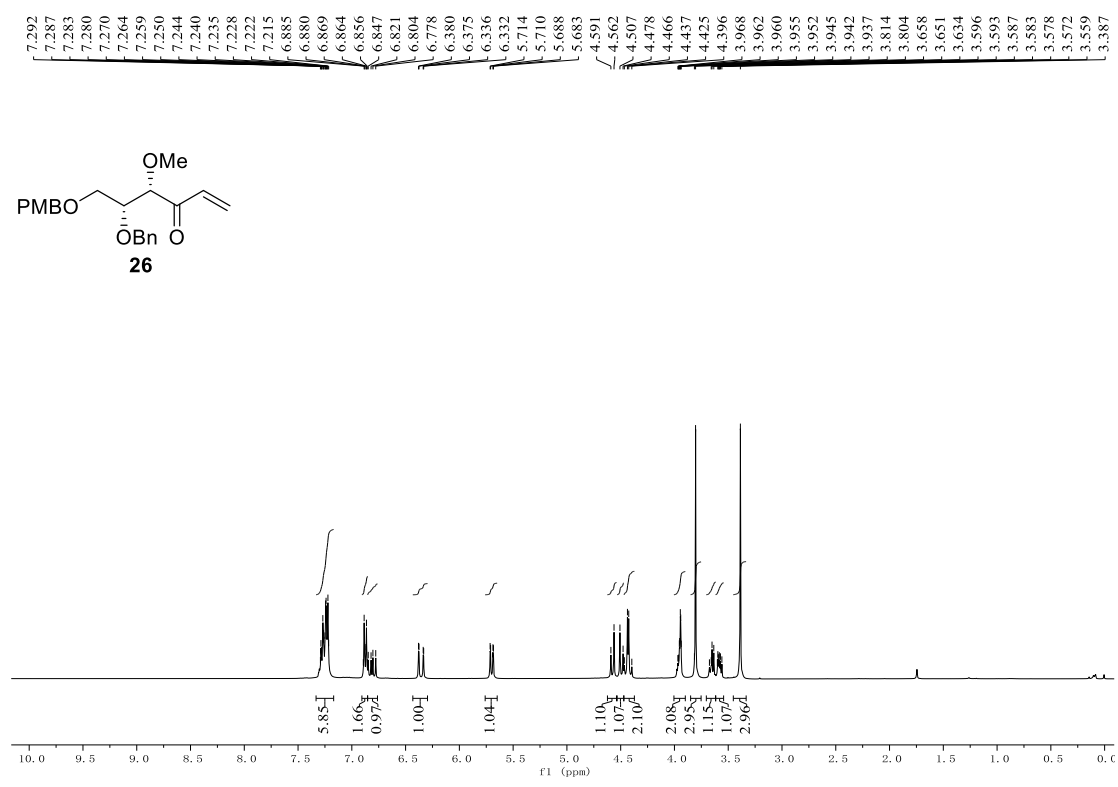
**Optical rotation:**  $[\alpha]_D^{25} = 91.7$  ( $c$  0.06,  $\text{CHCl}_3$ )

**IR** (neat):  $\nu_{\text{max}} = 2925, 1681, 1372, 1263, 795, 741$   $\text{cm}^{-1}$

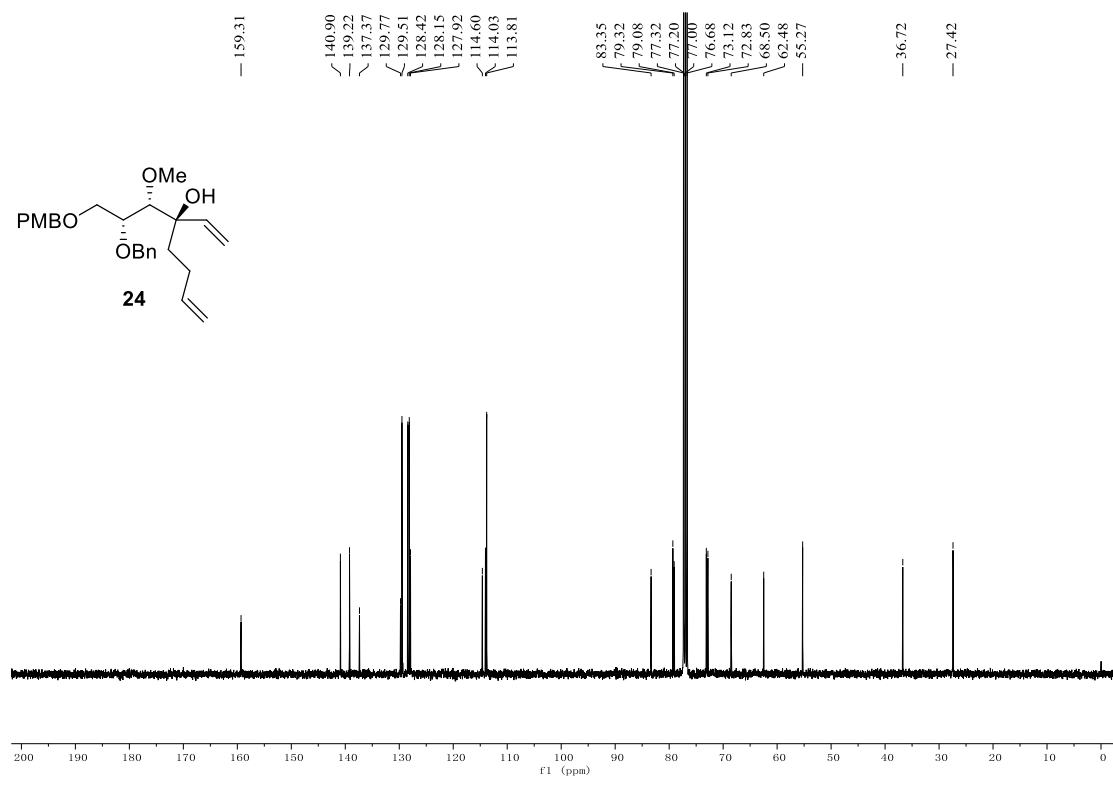
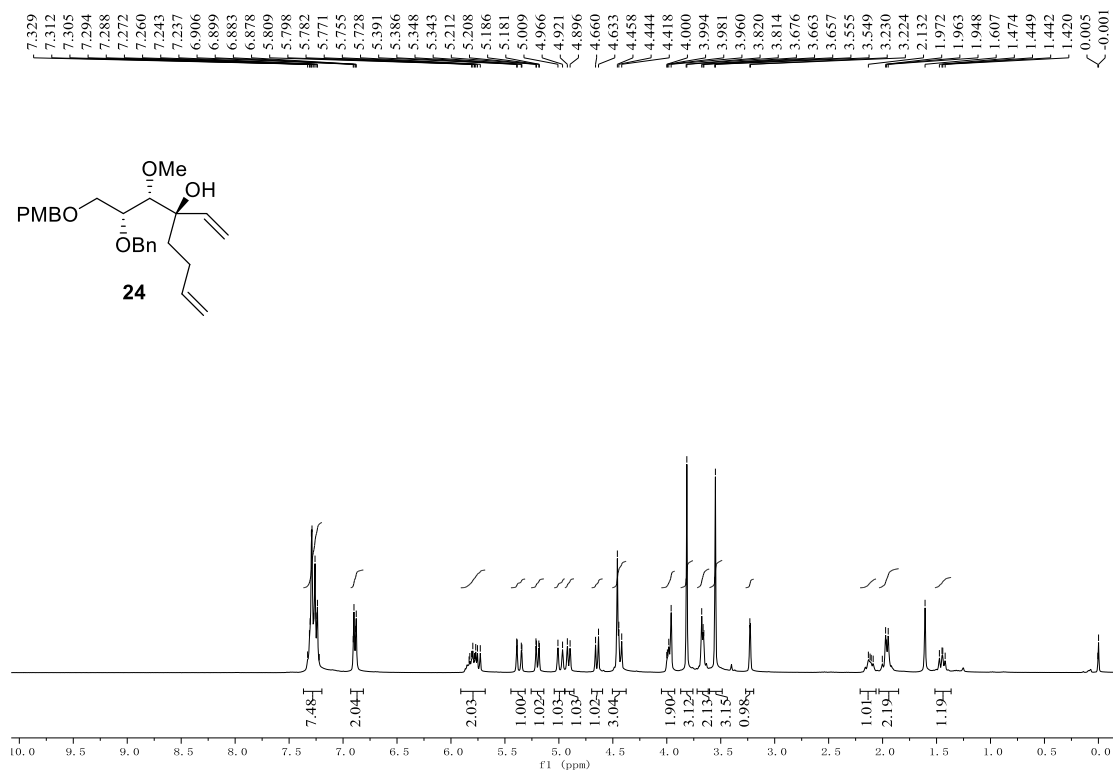
**HRMS** ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{21}\text{H}_{26}\text{O}_5\text{Na}$ , 381.1672; found, 381.1675.

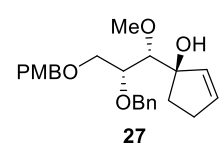
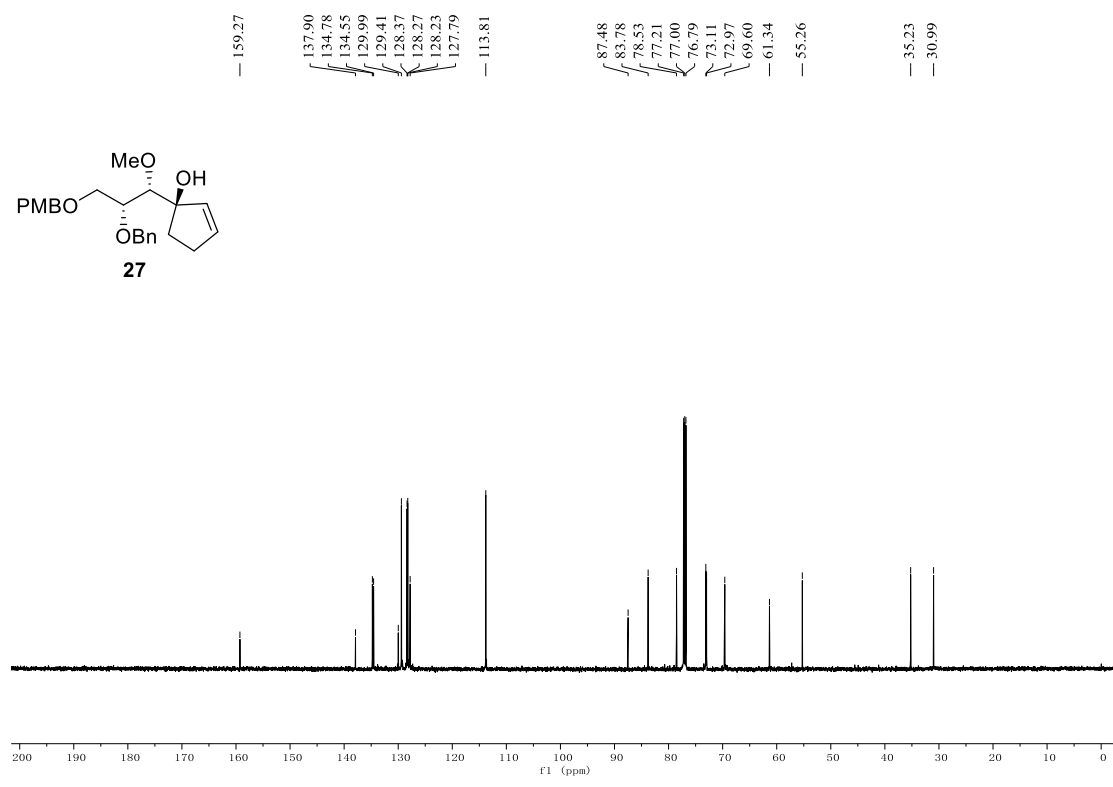
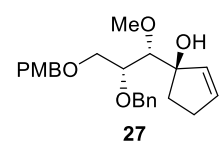
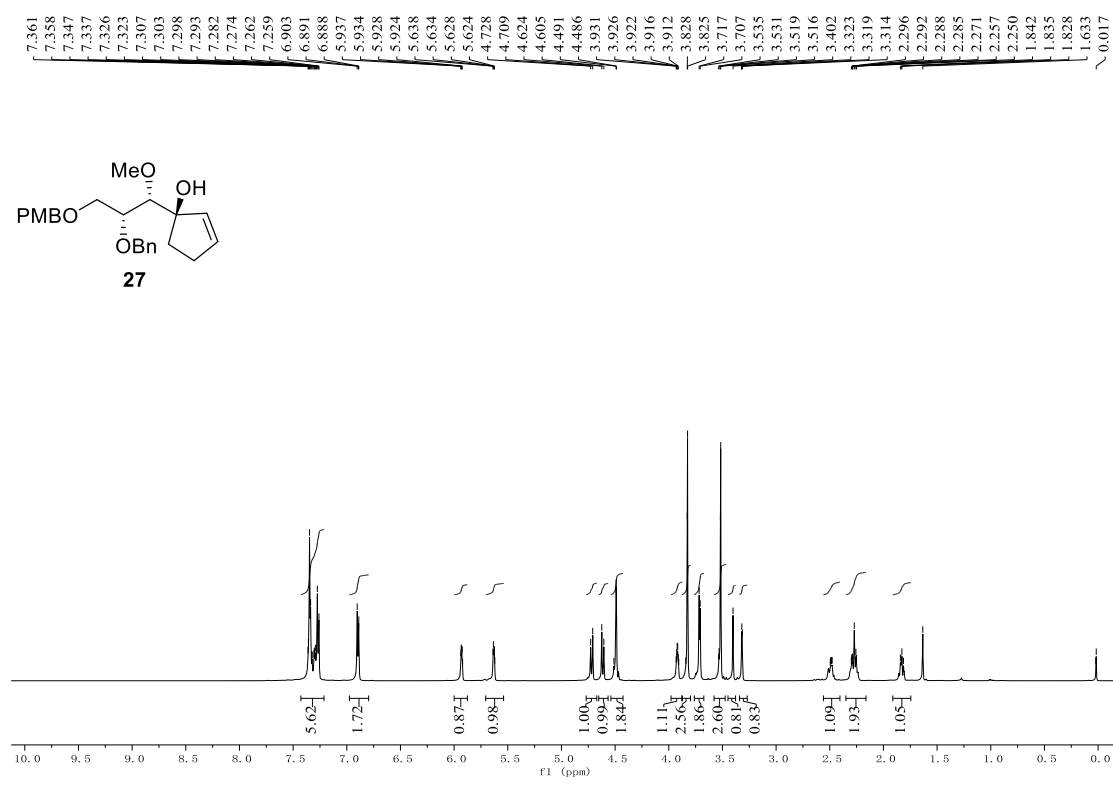
### 3. NMR spectra

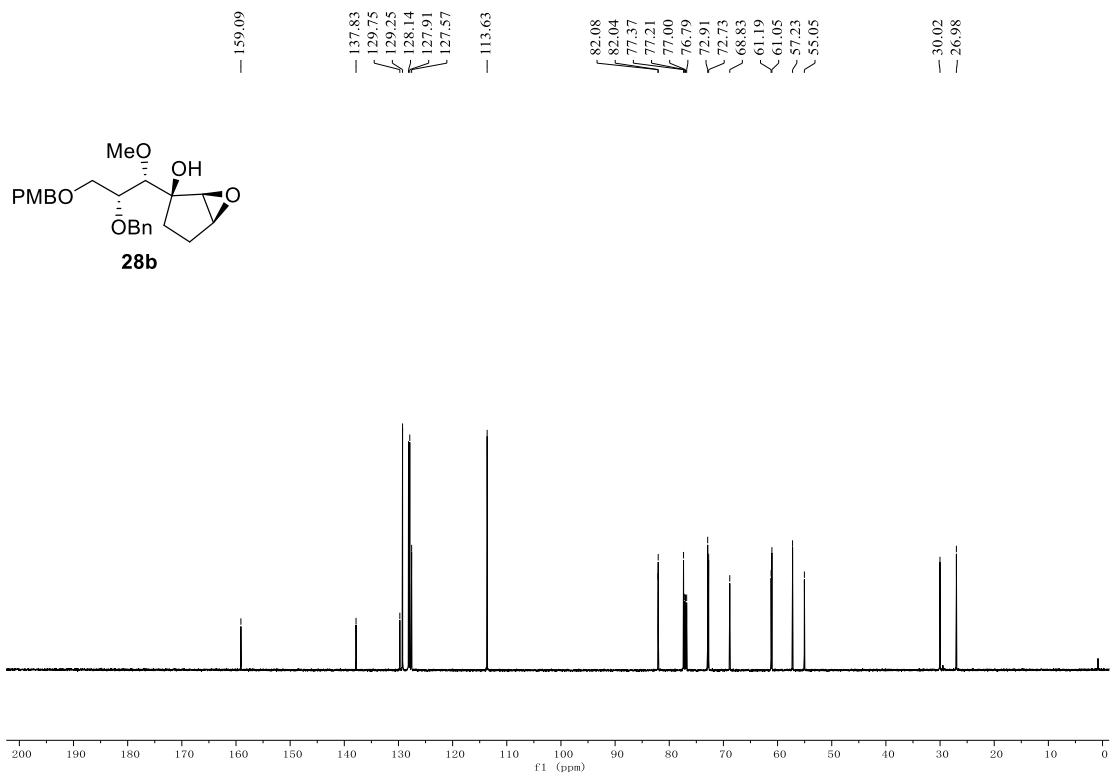
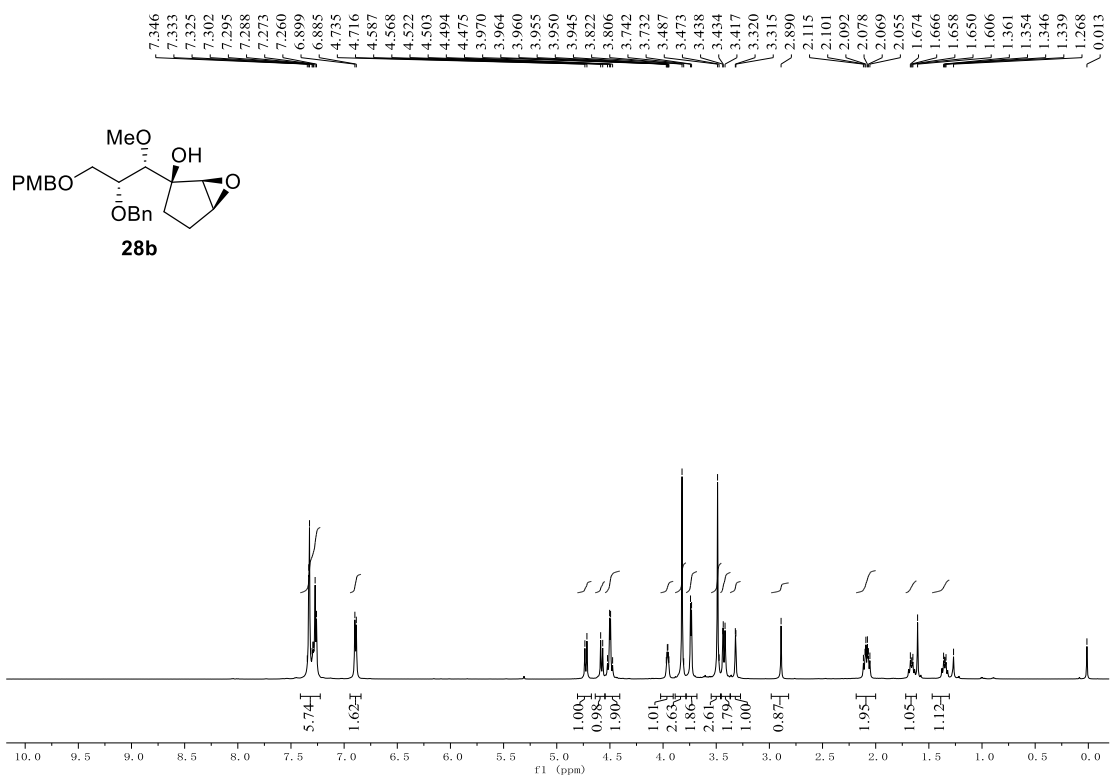


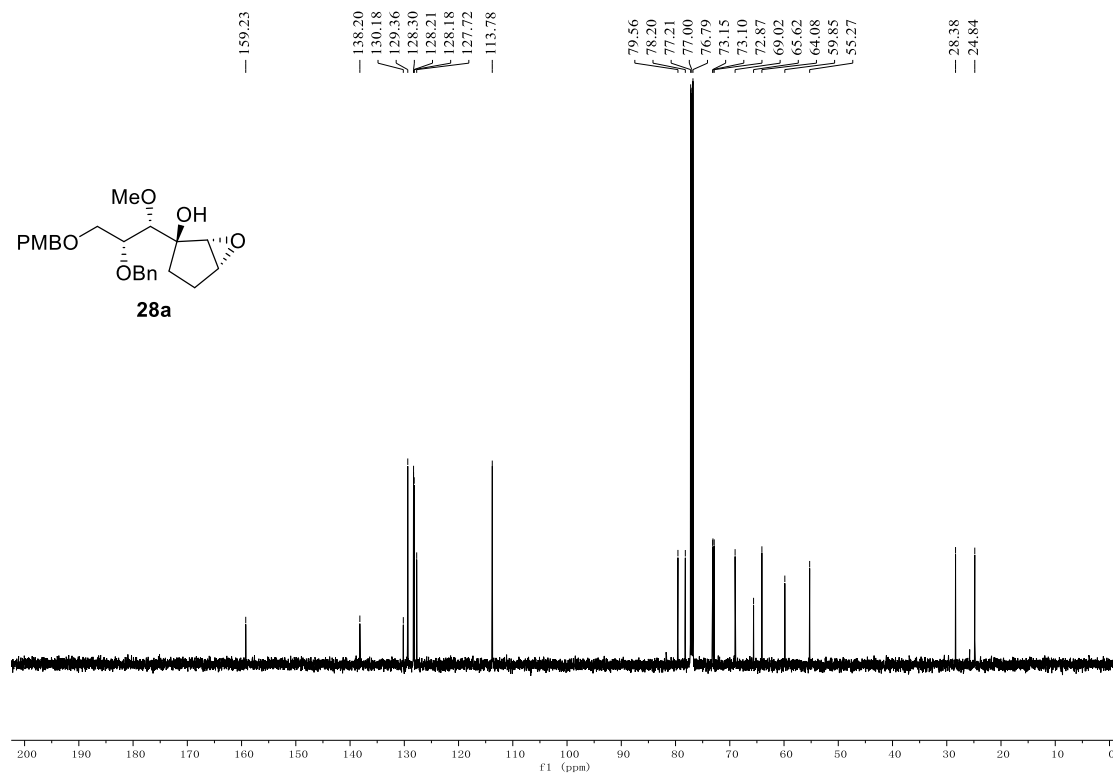
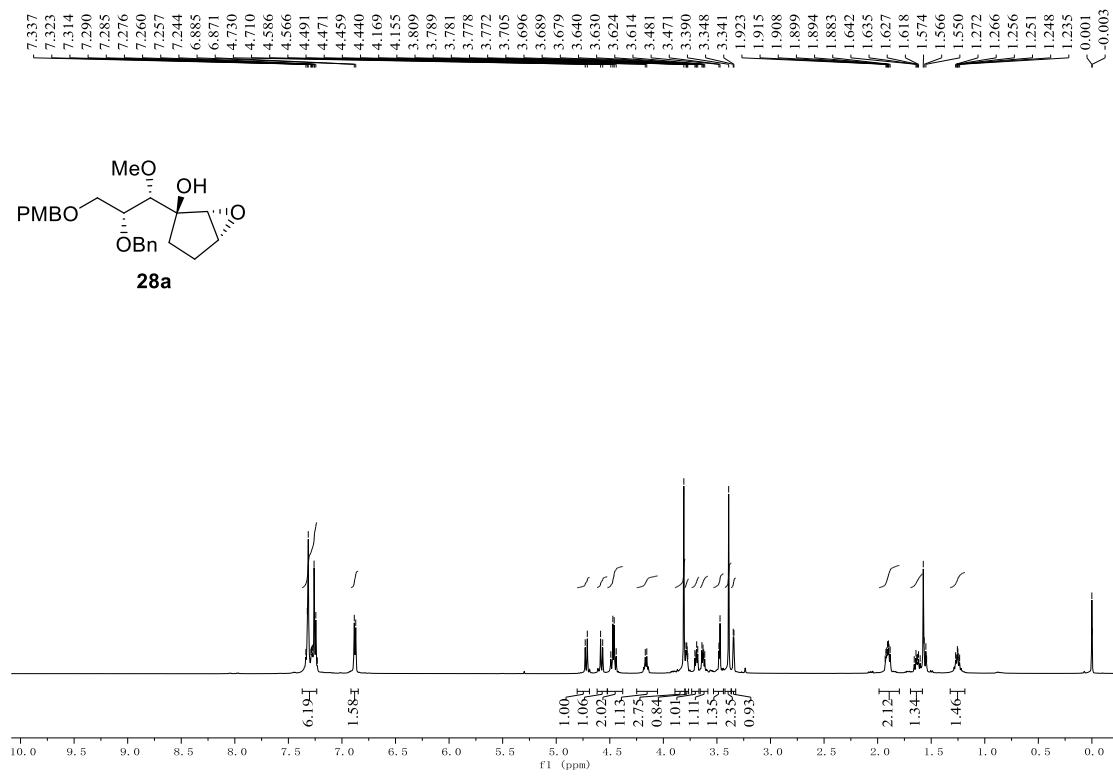


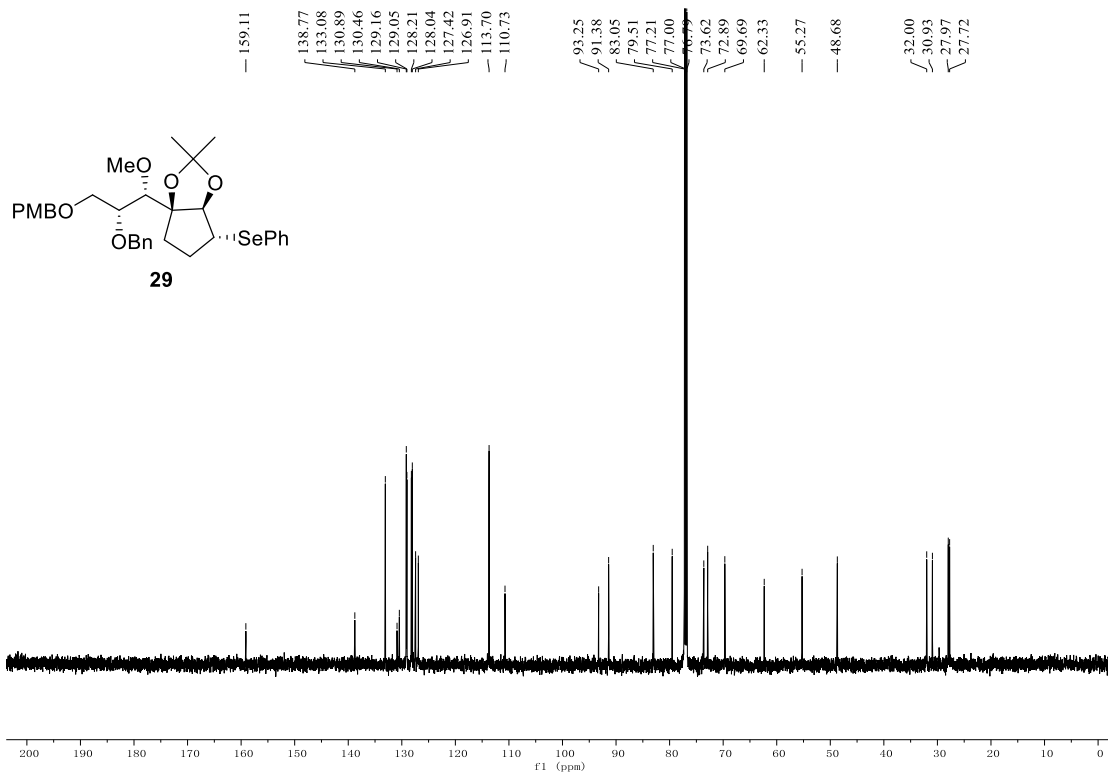
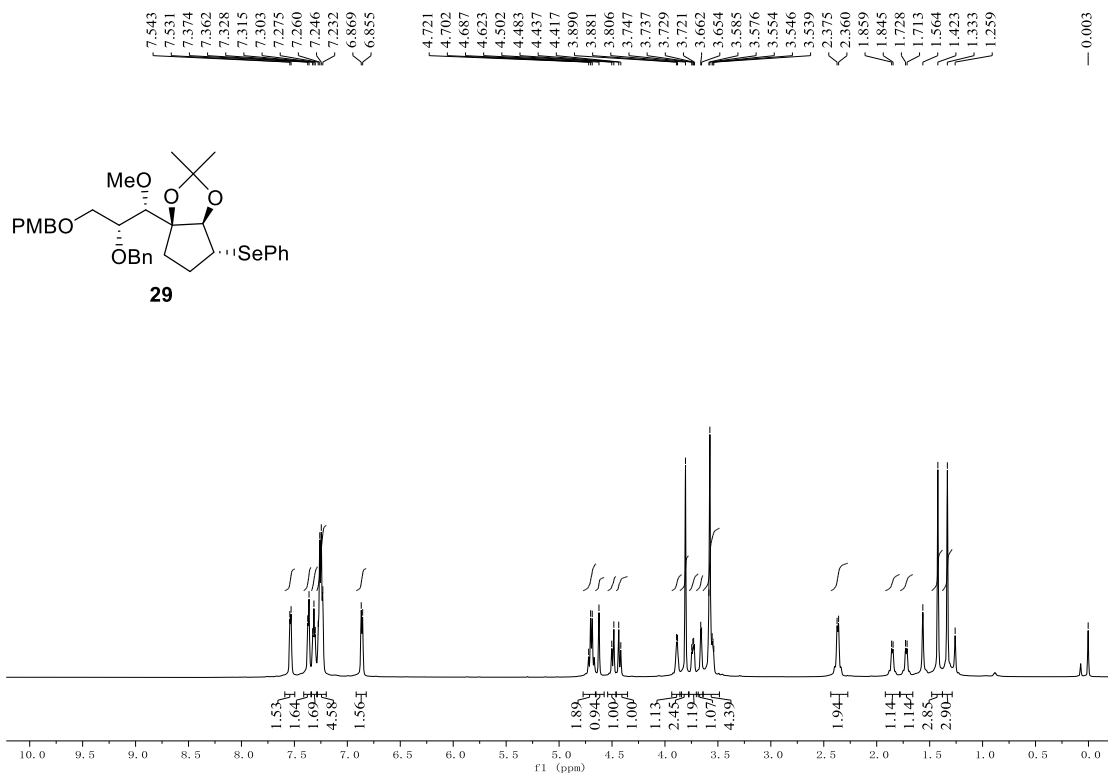


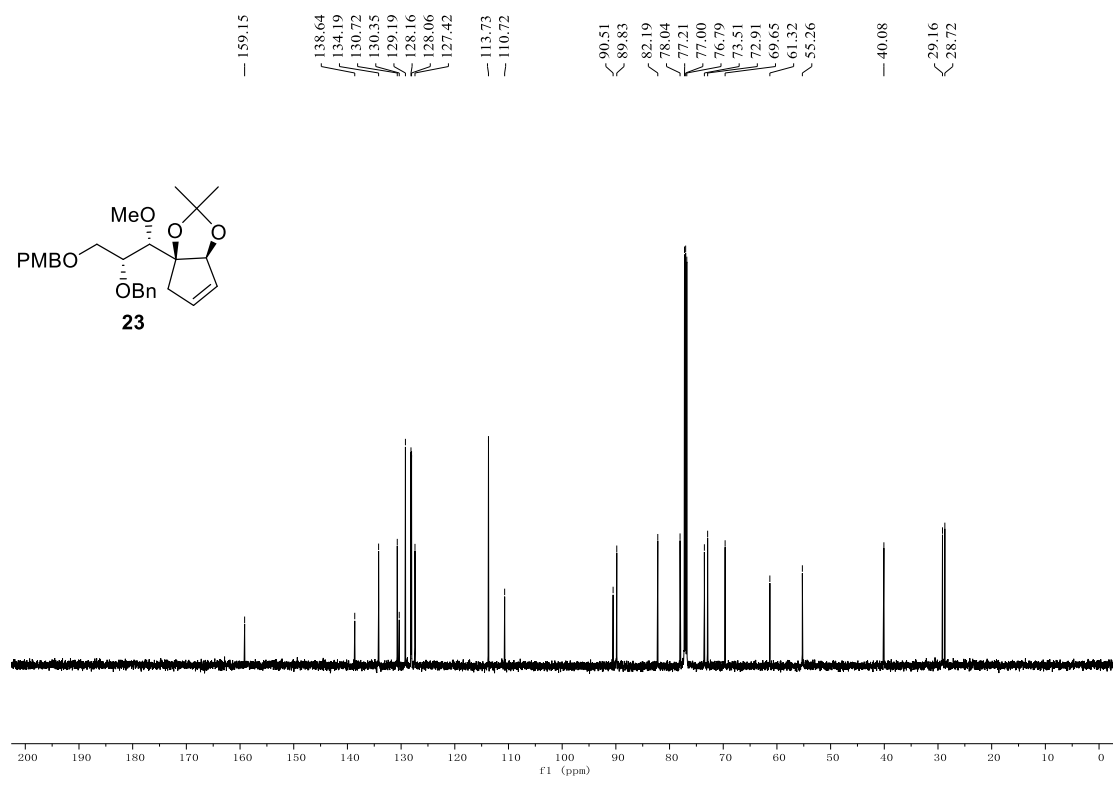
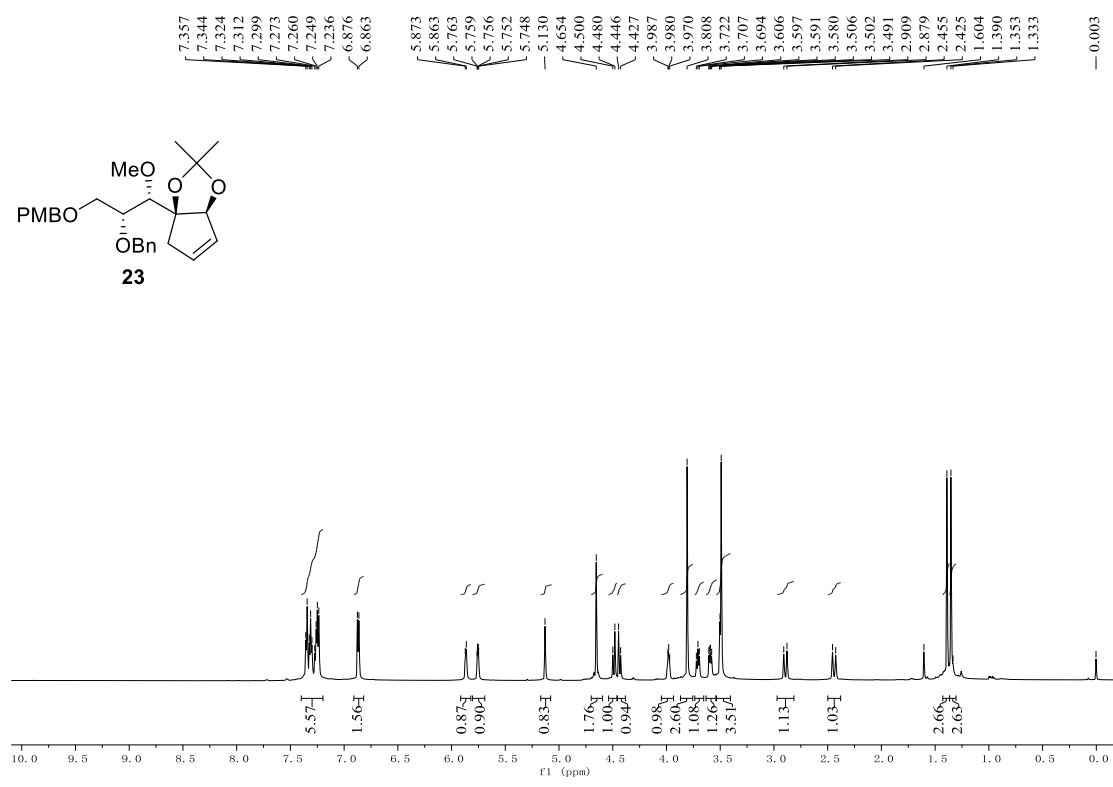
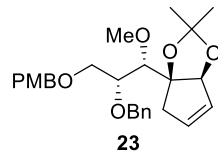


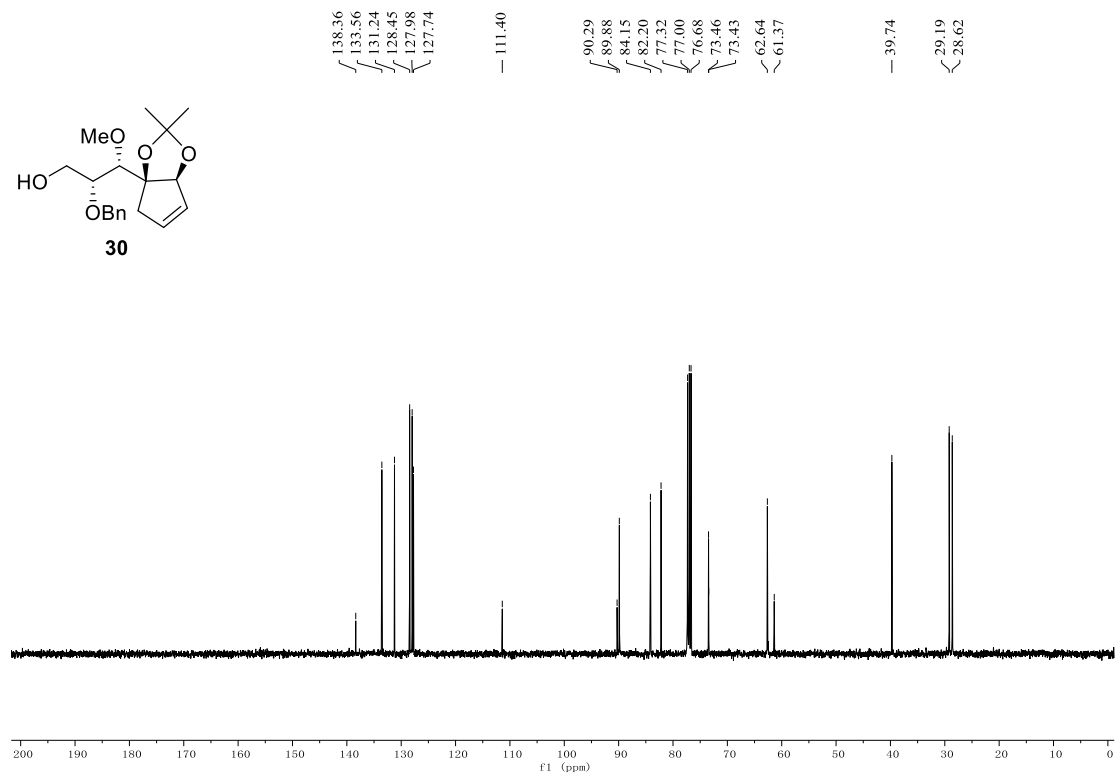
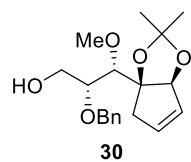
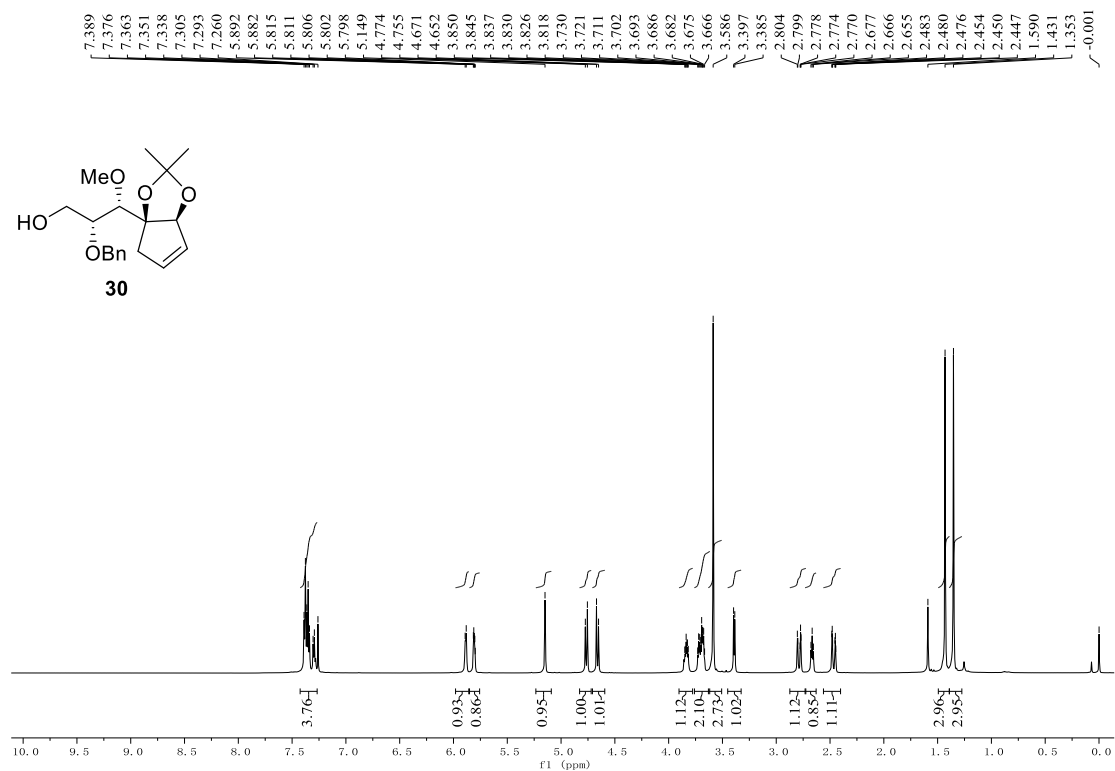
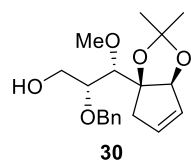


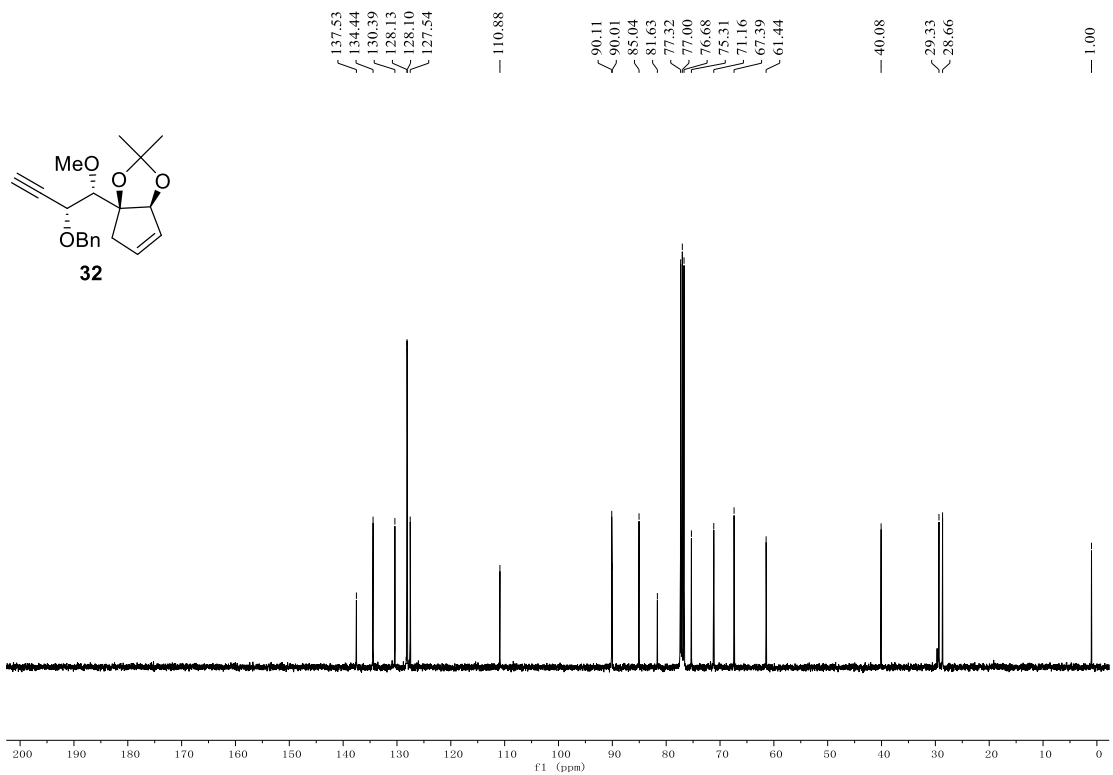
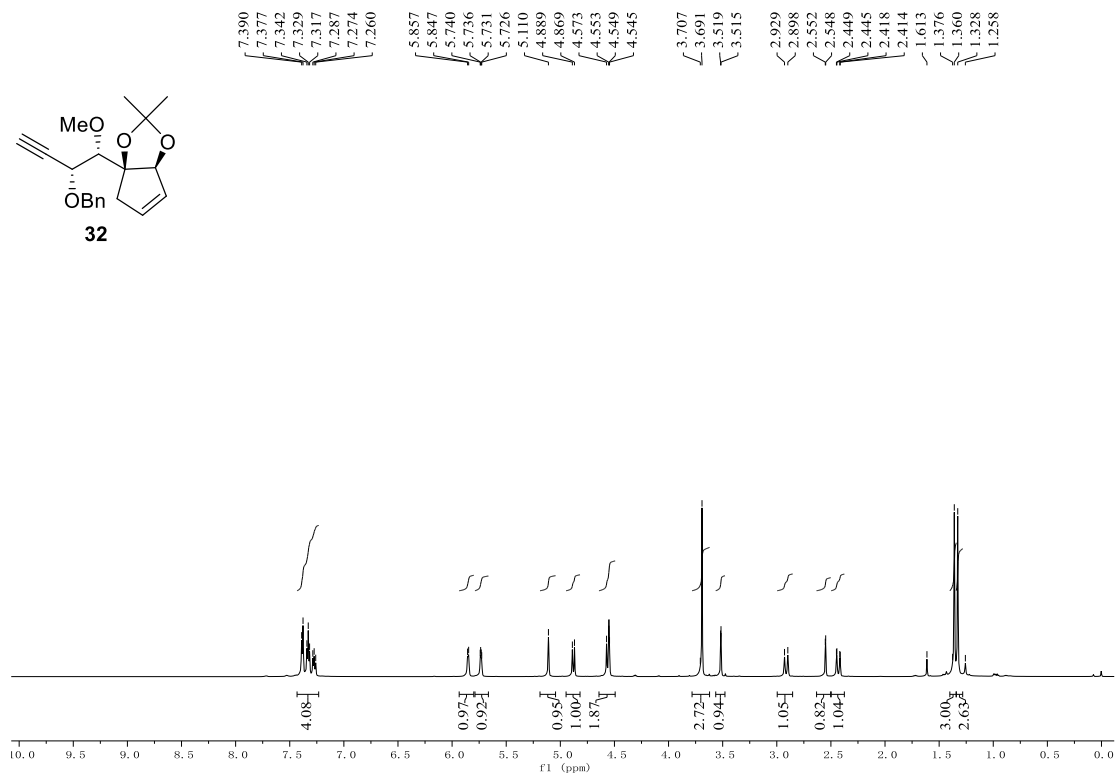
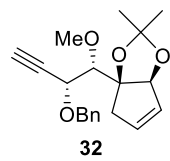




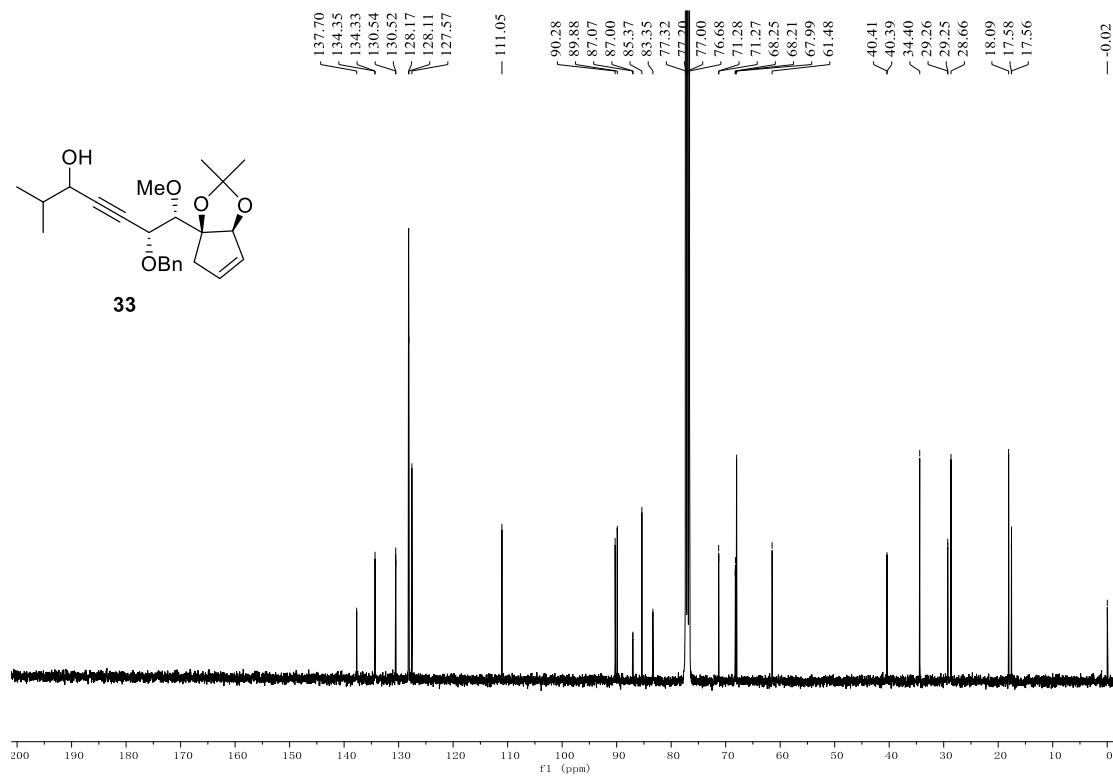
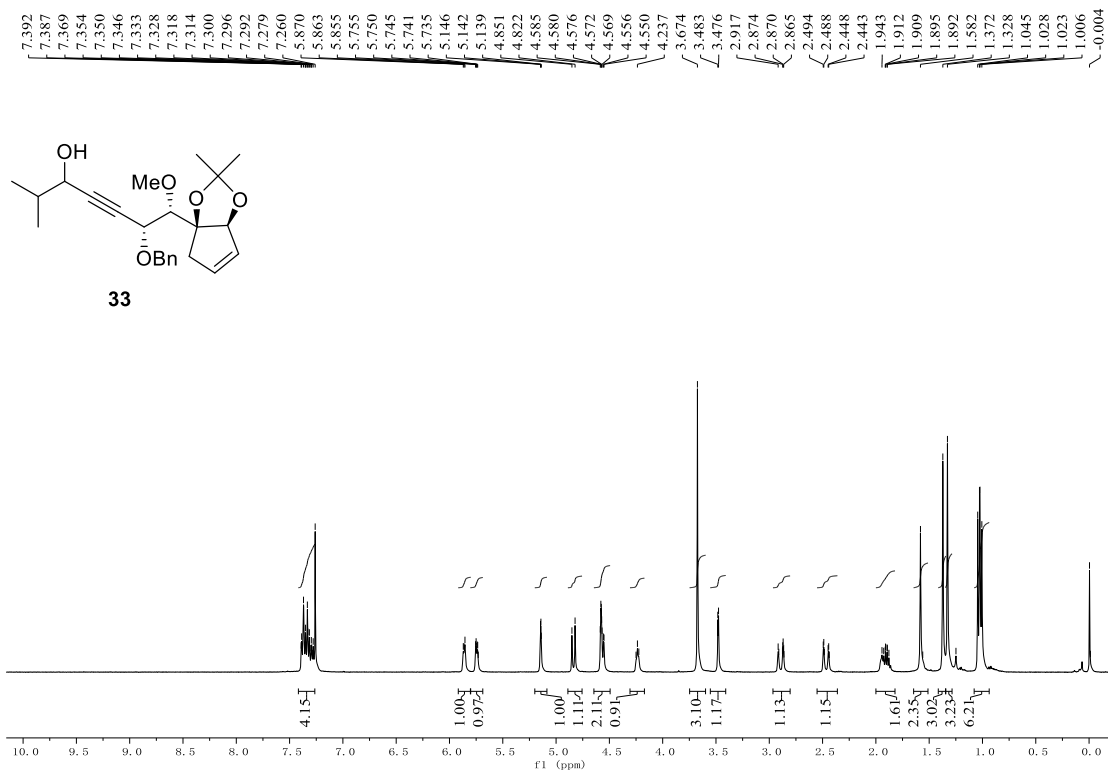


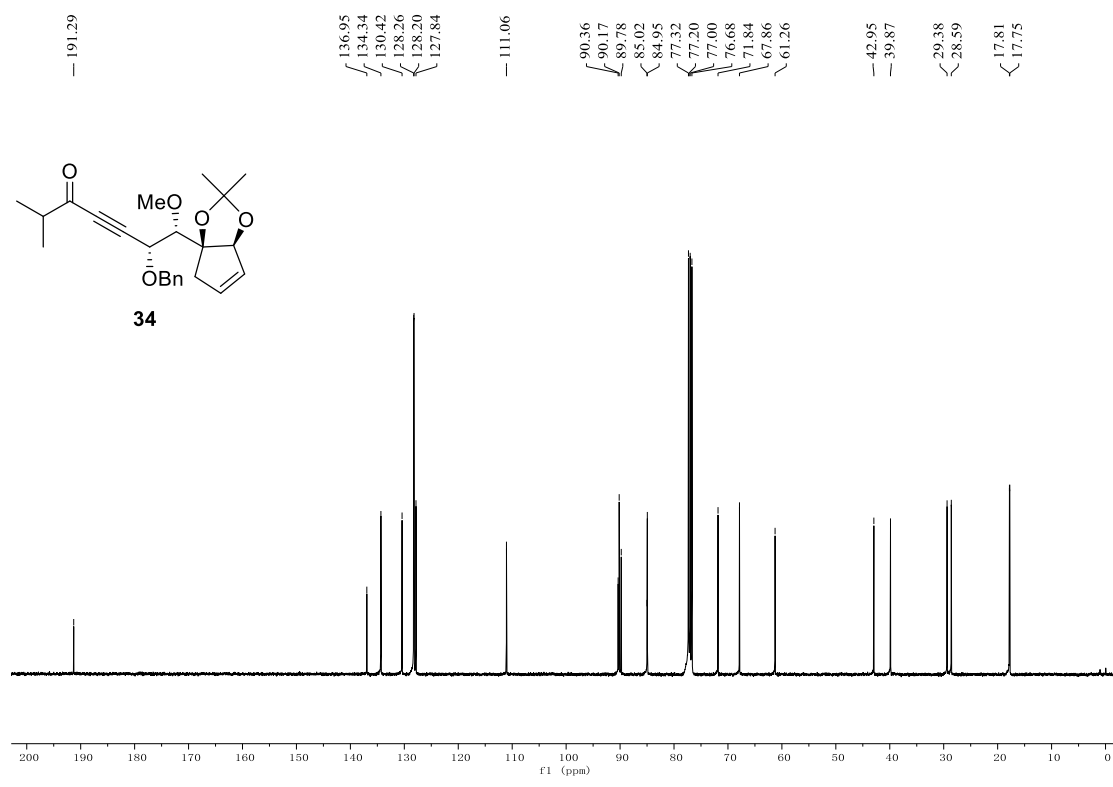
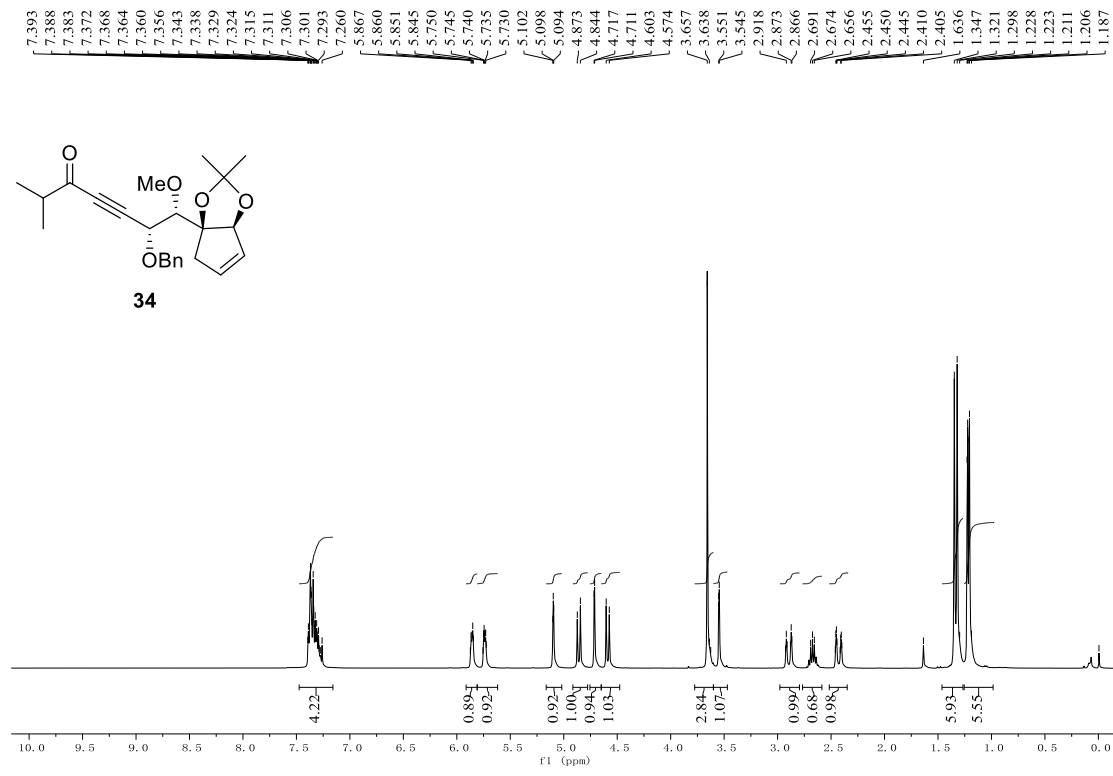


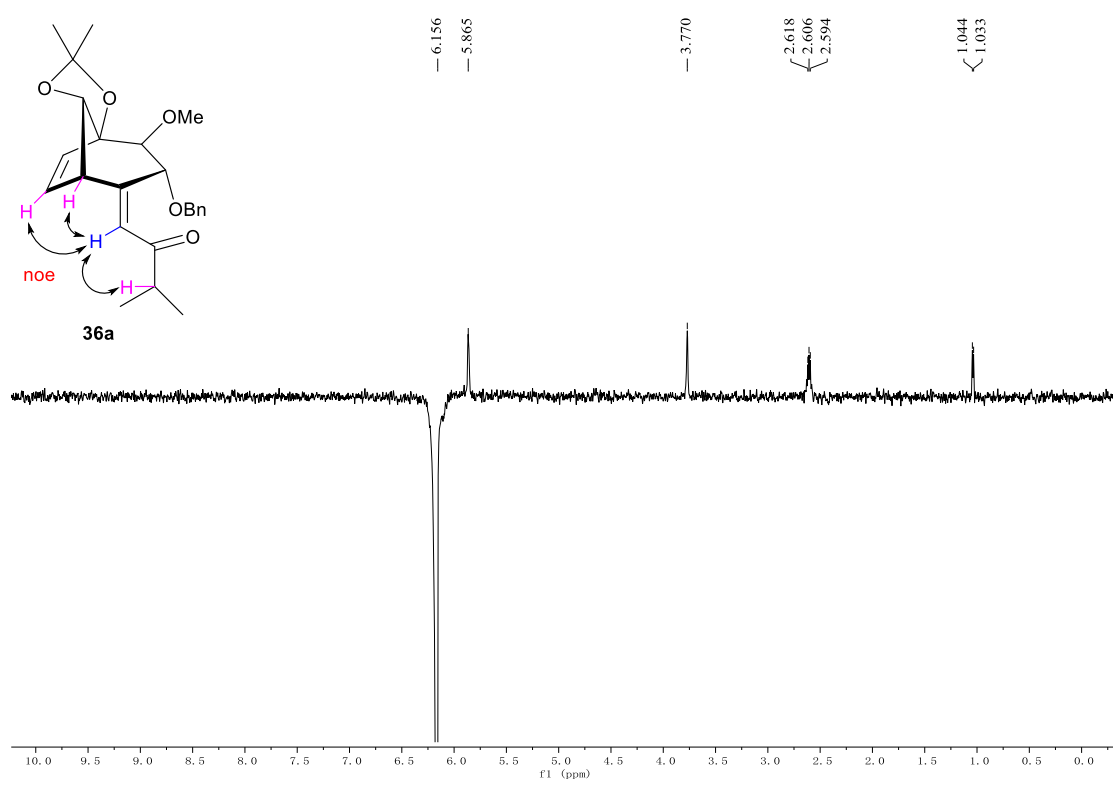
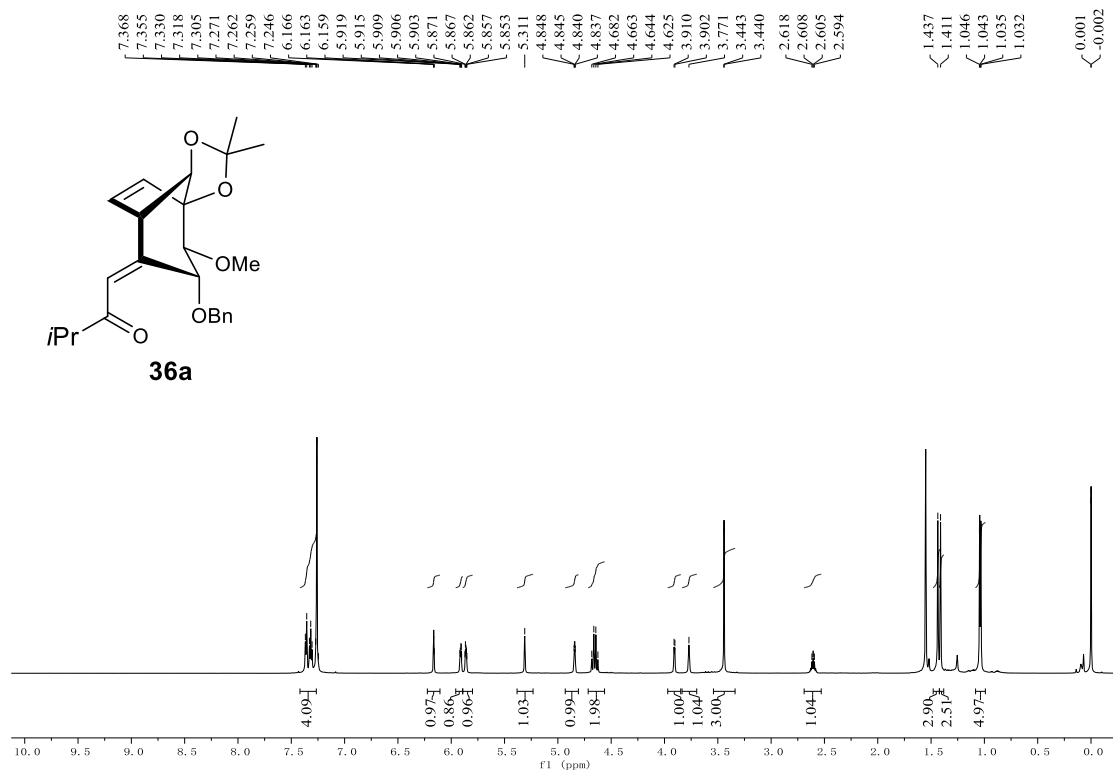


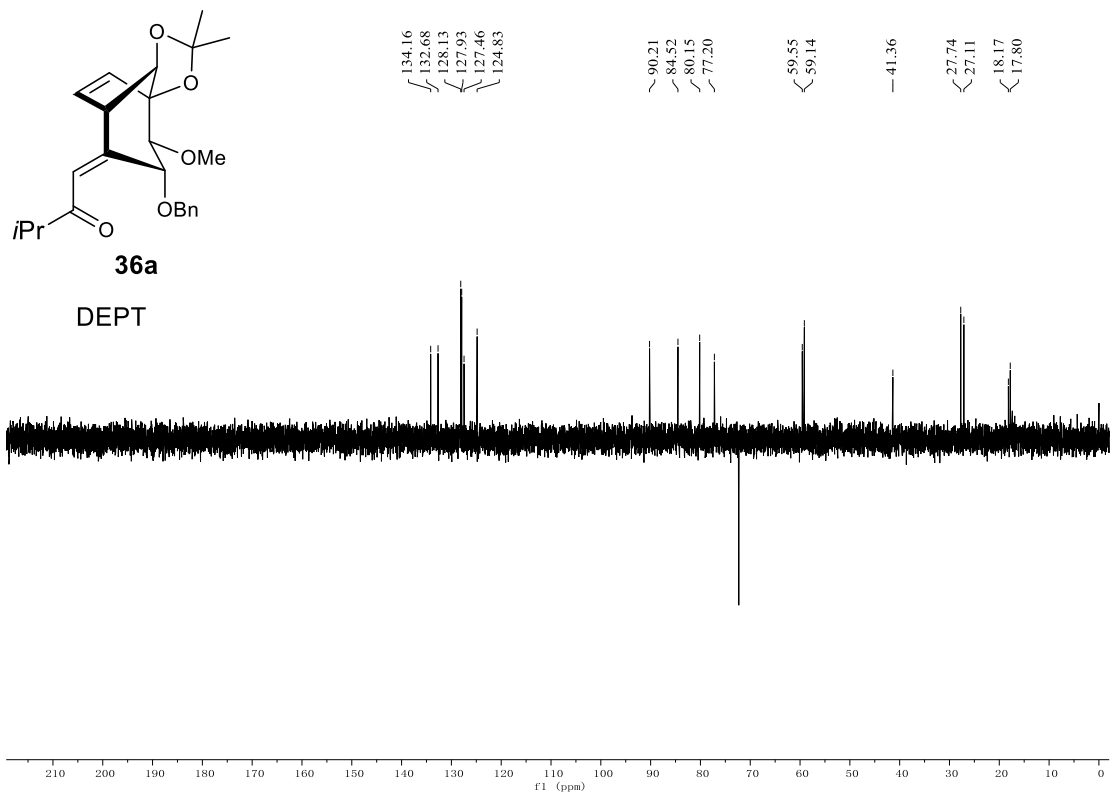
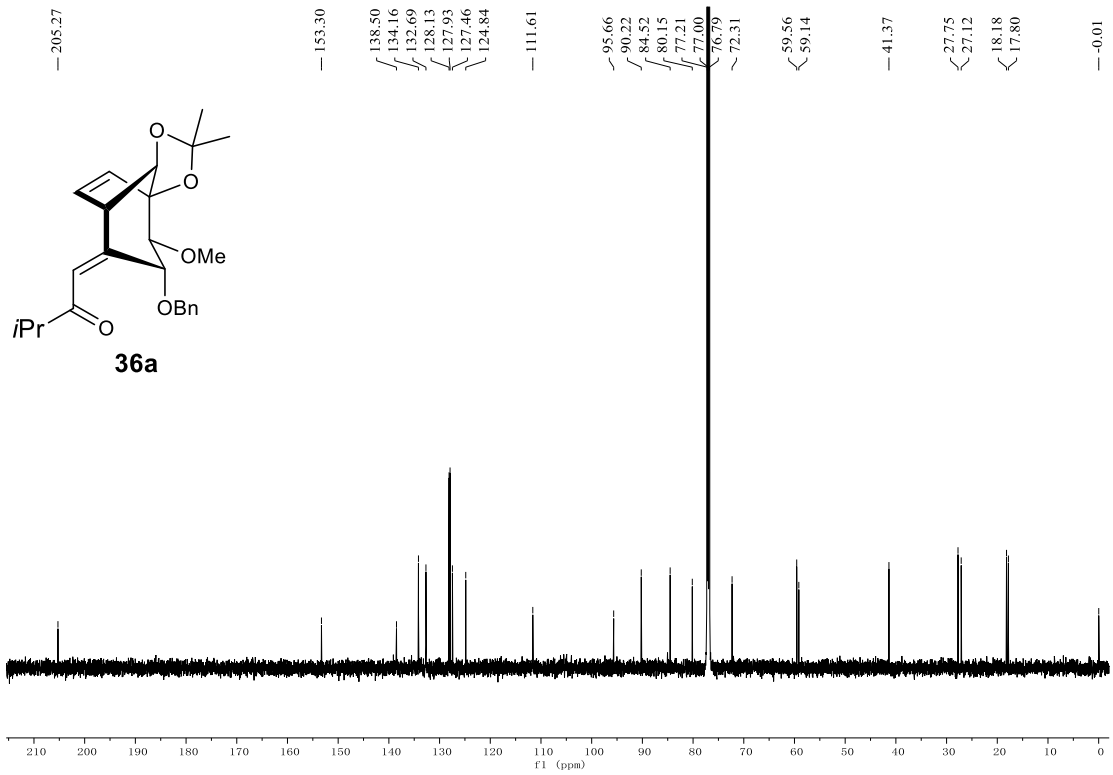


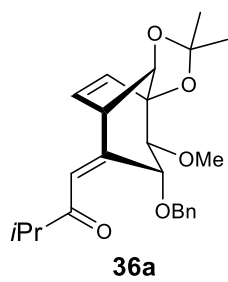




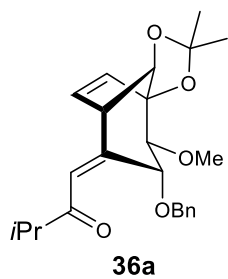
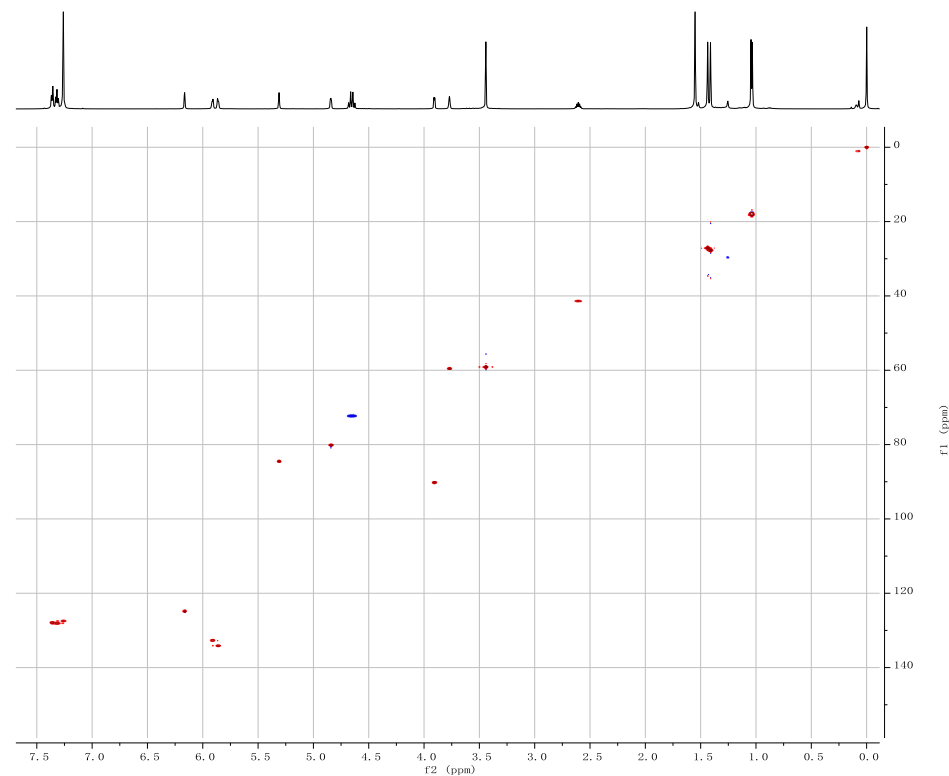




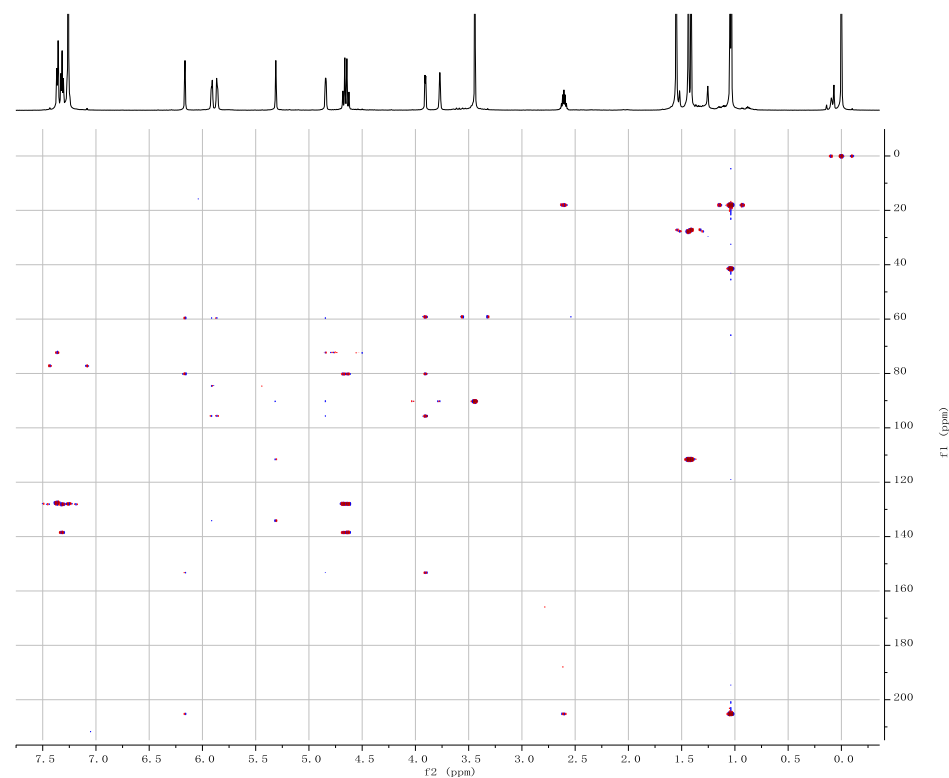


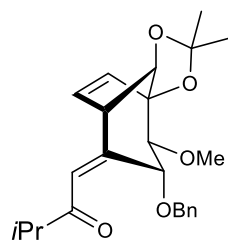


HSQC



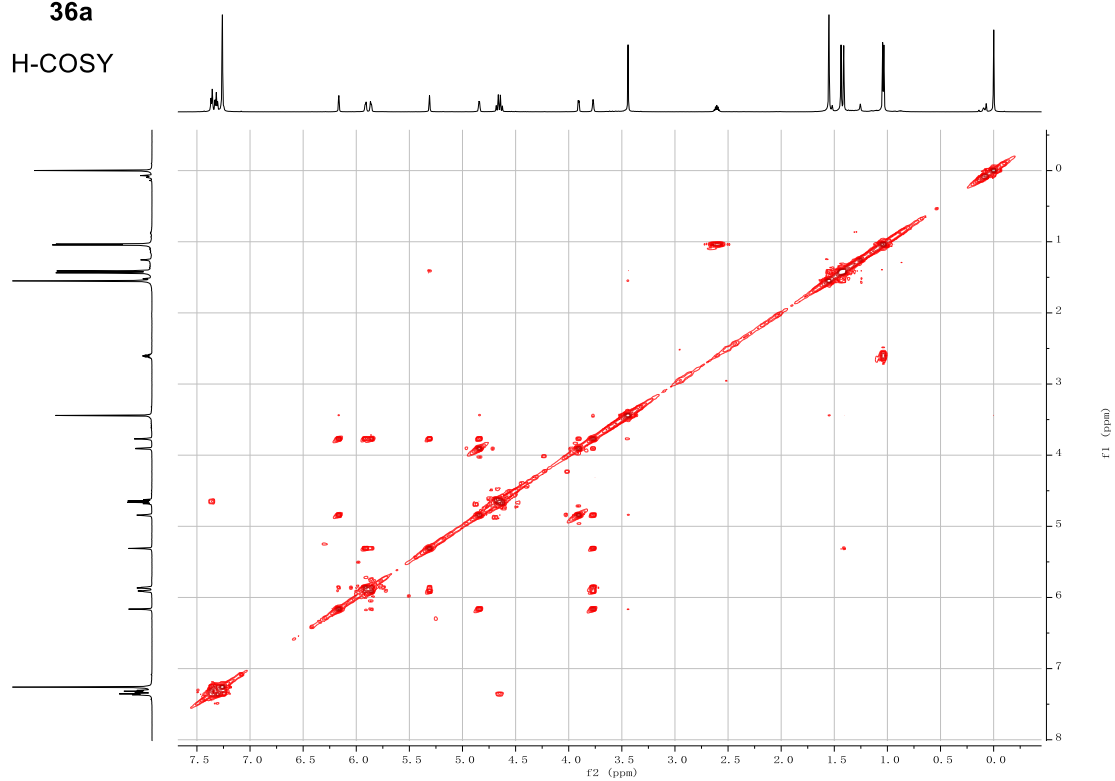
HMBC

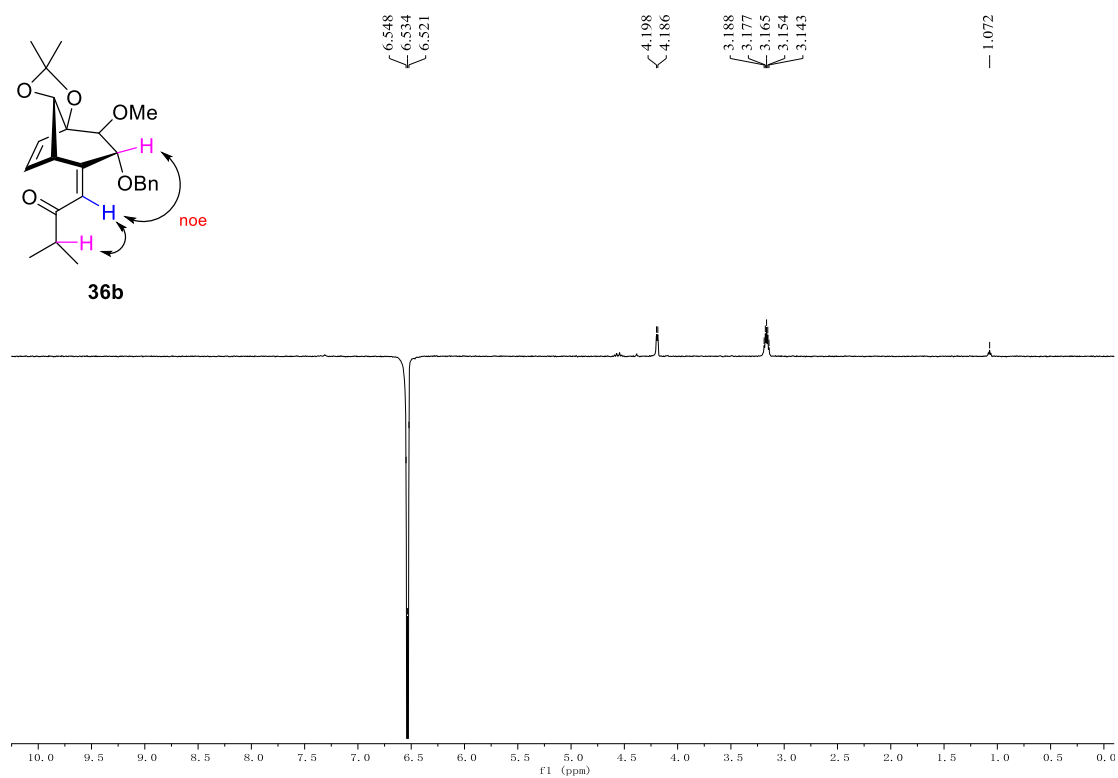
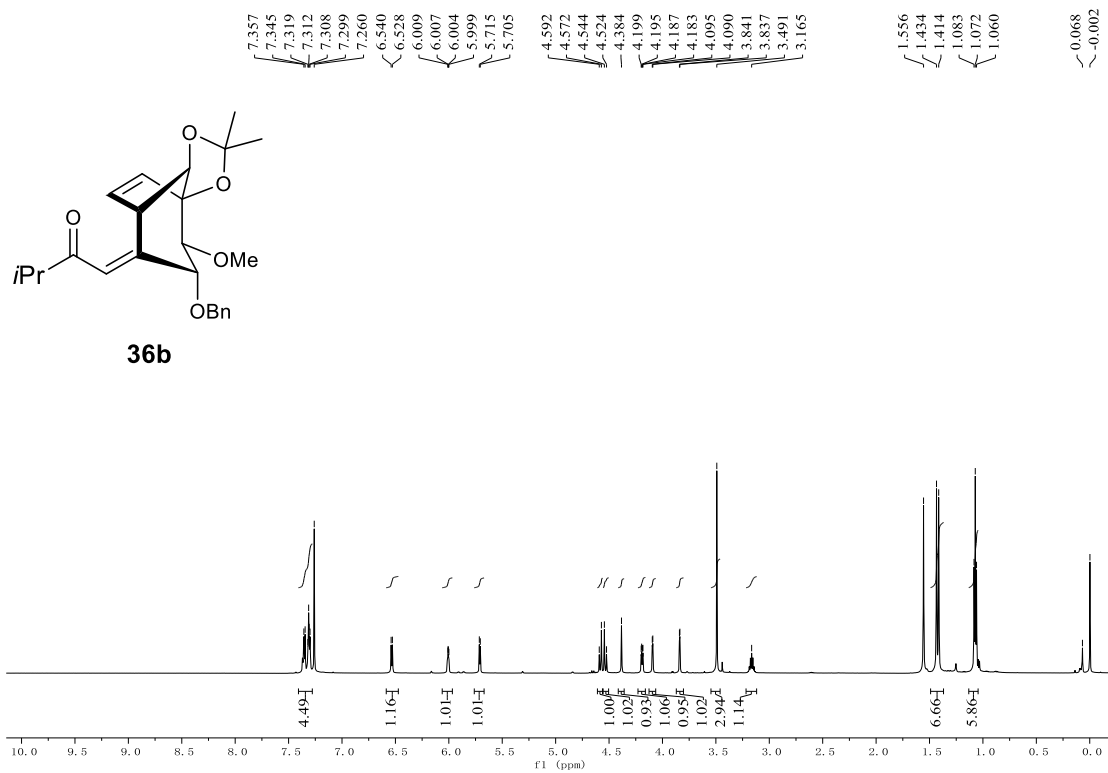


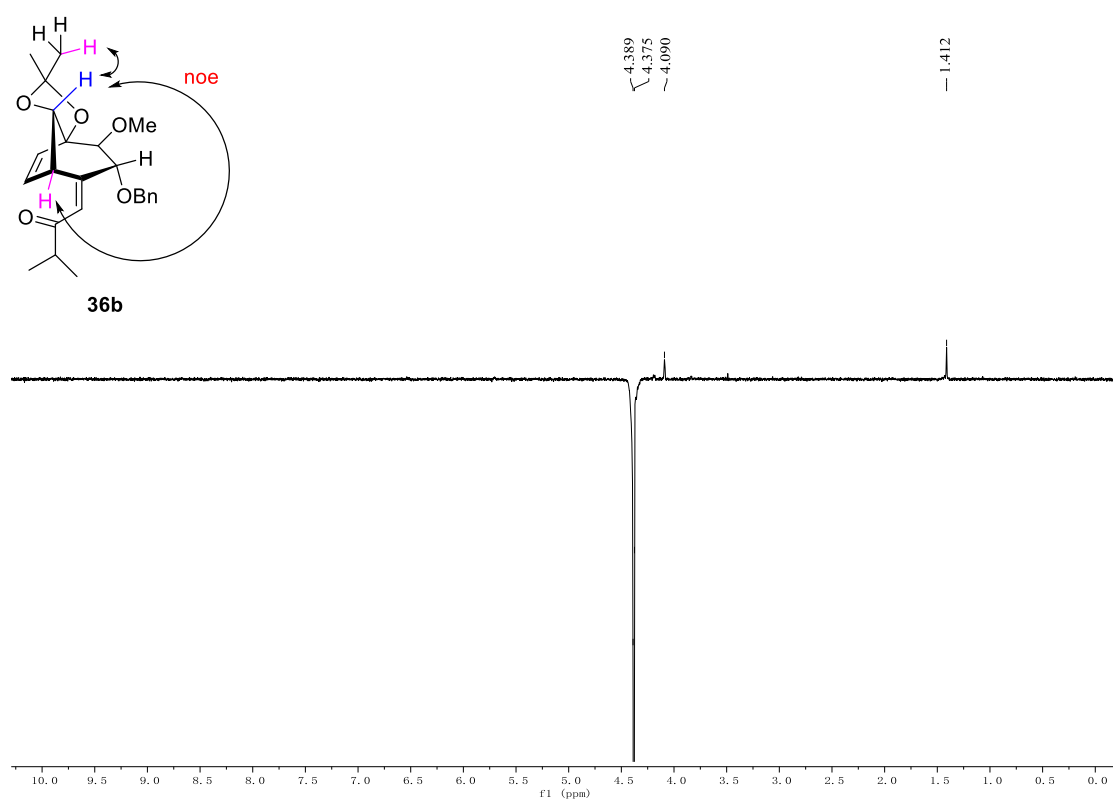
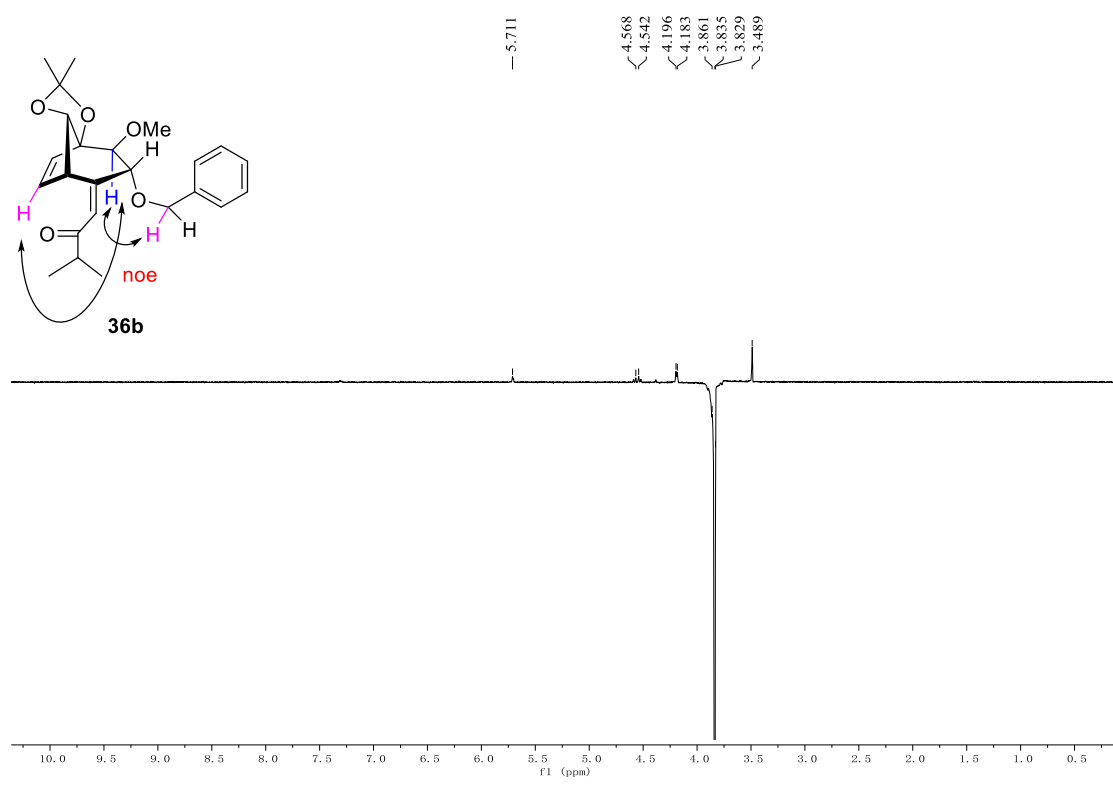


**36a**

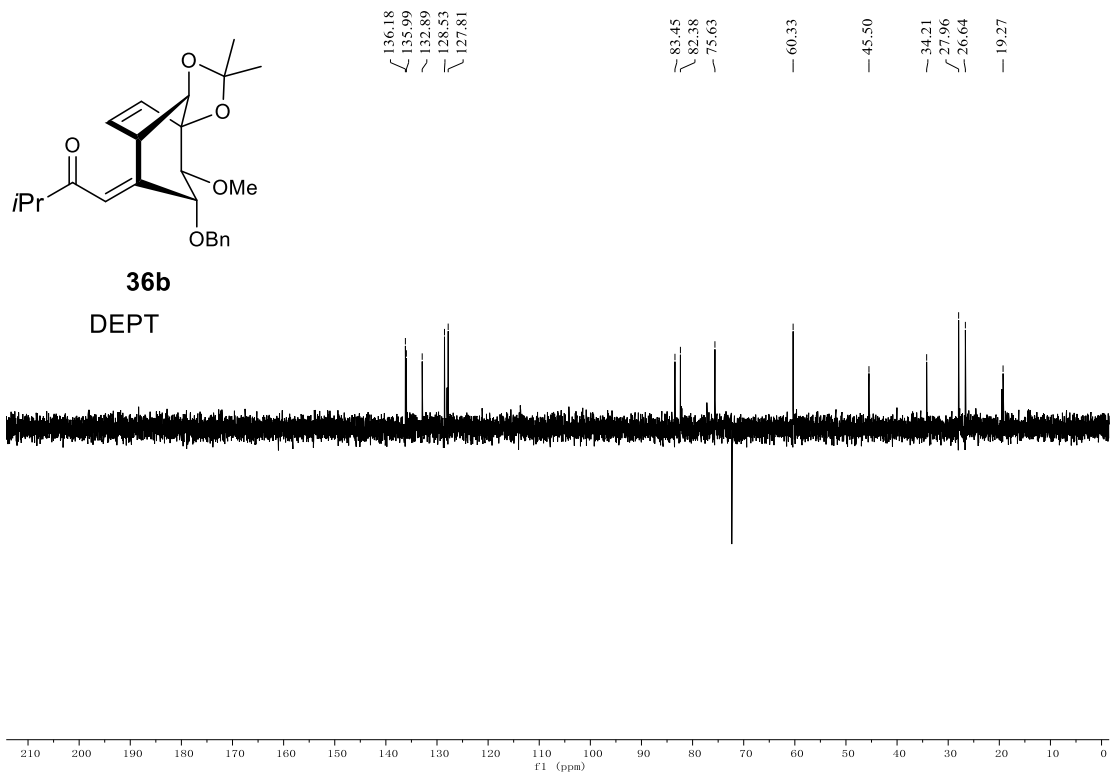
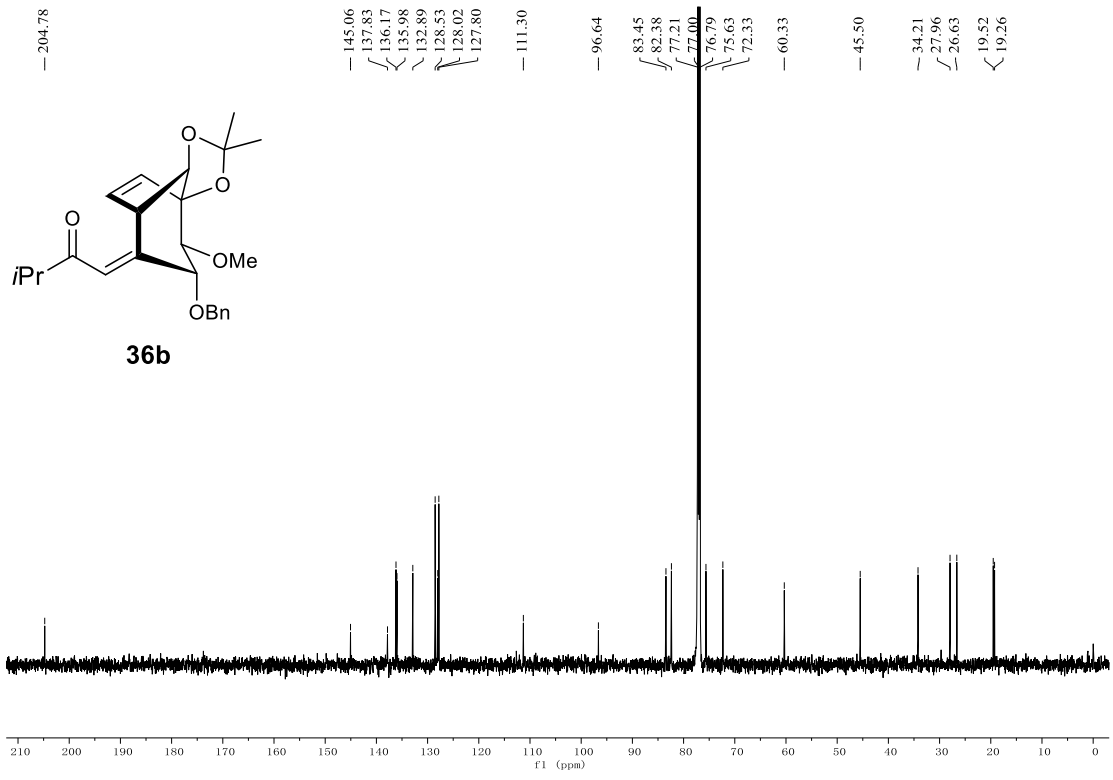
H-COSY

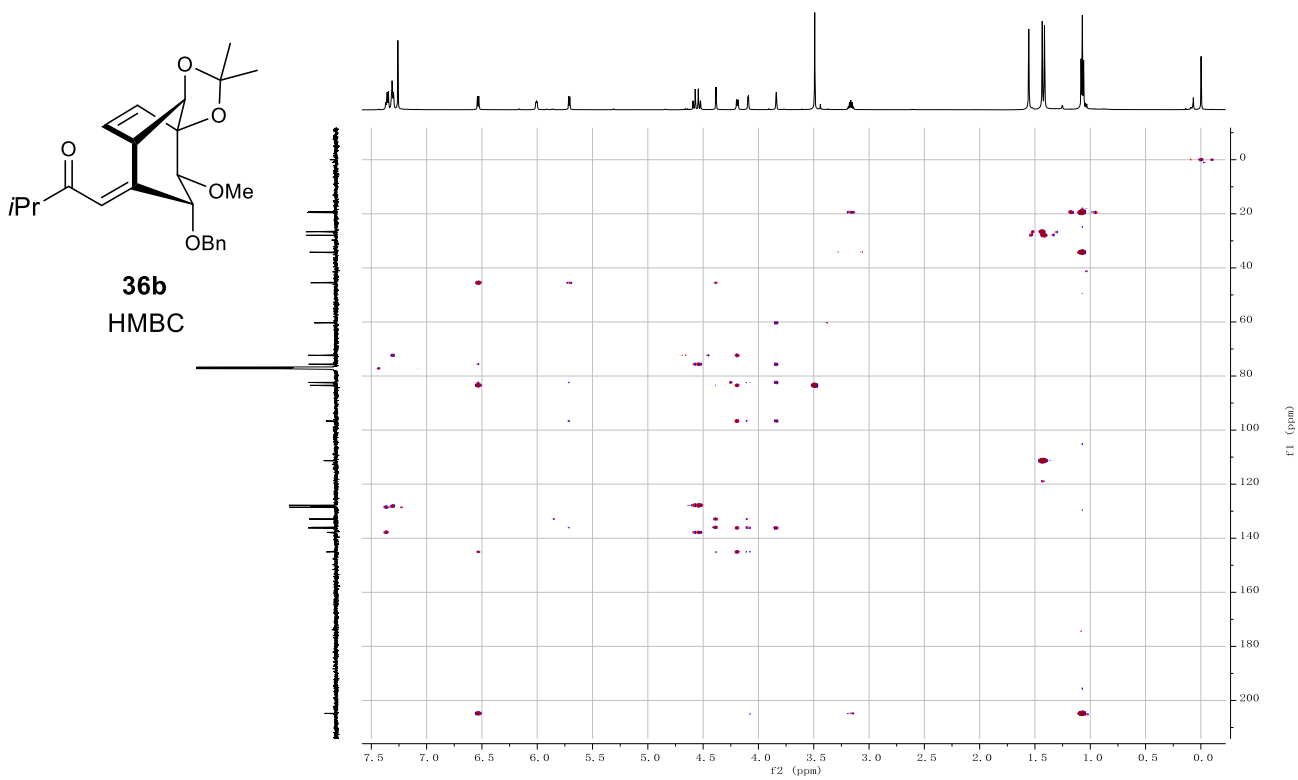
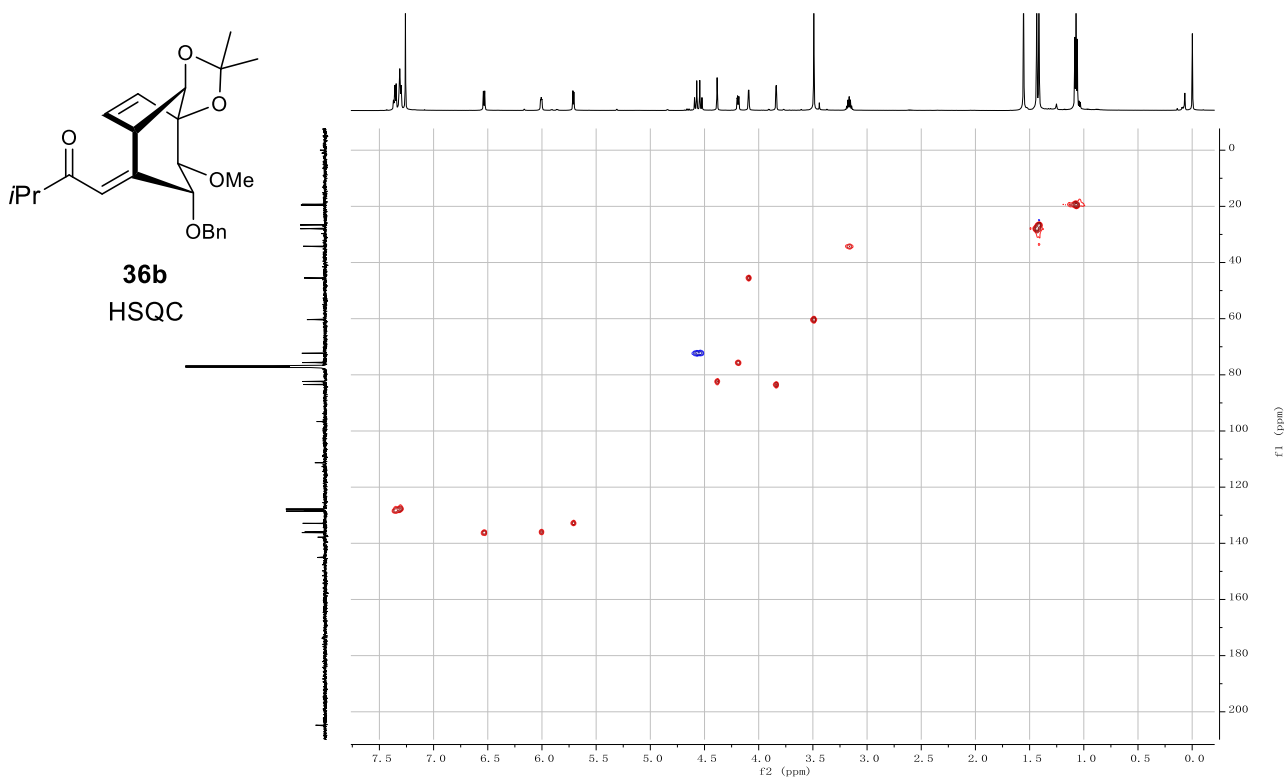


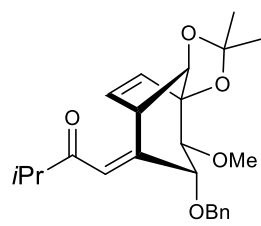












**36b**  
H-COSY

