

# **CHEMISTRY**

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## **AN ASIAN JOURNAL**

### Supporting Information

#### **Chiral Phosphorus–Olefin Ligands for the Rh<sup>I</sup>-Catalyzed Asymmetric Addition of Aryl Boronic Acids to Electron-Deficient Olefins**

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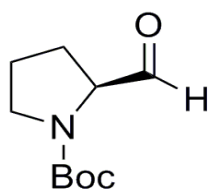
## 1. General information

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR data was acquired on a Bruker AV-400 MHz spectrometer. Commercial reagents were purchased and used without further purification. THF was distilled over benzophenone ketyl under nitrogen.  $\text{CH}_2\text{Cl}_2$  was distilled over  $\text{CaH}_2$  under nitrogen.  $\text{CH}_3\text{OH}$  was distilled over  $\text{CaH}_2$  under nitrogen. THF was distilled over  $\text{CaH}_2$  under nitrogen. Dioxane was distilled over  $\text{LiAlH}_4$  under nitrogen.

## 2. Preparation of Ligands

### Synthesis of *L*-prolinal from (*S*)-(-)-1-Boc-2-pyrrolidinemethanol <sup>1</sup>:

To a solution of *L*-Prolinol (1 mmol) in dry  $\text{CH}_3\text{CN}$  (1 mL) in a 50 mL flask were added the following solutions: (1)  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  (0.05 mmol in 1 mL  $\text{CH}_3\text{CN}$ ) (2) bpy (0.05 mmol in 1 mL  $\text{CH}_3\text{CN}$ ) (3) TEMPO (0.05 mmol in 1 mL  $\text{CH}_3\text{CN}$ ) (4) *N*-methyl imidazole (0.1 mmol in 1 mL  $\text{CH}_3\text{CN}$ ). The dark red/brown reaction mixture was stirred rapidly open to air and monitored by TLC until no starting material remained (often accompanied by a change in reaction color to green/blue). The crude reaction mixture was concentrated and purified by silica column chromatography (gradient elution of EtOAc in Hex).



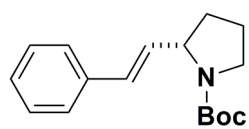
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.64 – 9.41 (m, 1H), 4.20-4.01 (m, 1H), 3.71 – 3.38 (m, 2H), 2.17 – 1.79 (m, 4H), 1.49 – 1.39 (m, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$

200.64, 153.66, 80.62, 79.78, 65.01, 46.71, 28.26, 23.95.

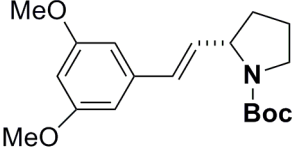
HRMS-ESI( $m/z$ ): Calcd for  $C_{10}H_{17}NO_3$   $[M+H]^+$  200.1287, Found: 200.1292.

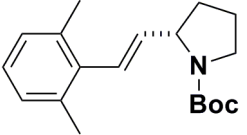
### **General procedure for the synthesis of olefin from *L*-prolinal:**

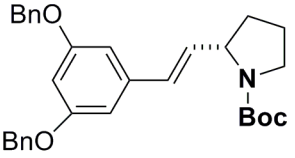
To a solution of diethyl benzylphosphonate (1.5 mmol) in THF (5 mL) was added *n*-BuLi (2.4M in hexane, 0.625 ml, 1.5mmol) at -78 °C over 5 min, and then the whole was stirred at the same temperature for 1 h. A solution of *L*-prolinal (1mmol) in THF was added to the above solution. At this temperature, it was stirred for 1 h and then allowed to warm to rt. After being stirred for overnight, 20 mL of water was added to quench the reaction. The aqueous phase was extracted by AcOEt (3×20 mL) and the combined organic phases were washed with brine and dried over anhydrous  $Na_2SO_4$  and evaporated in vacuum. The desired products were isolated by silica gel column chromatography.

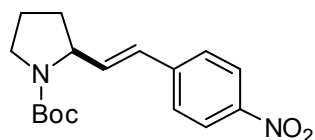


A pale yellow oil, yield 62%,  $[\alpha]_D^{20}$  -62( $c$  0.05  $CHCl_3$ ).  $^1H$  NMR(400 MHz,  $CDCl_3$ ):  $\delta$  7.37-7.22 (m, 5H), 6.42 (d,  $J$ =16 Hz, 1H), 6.13-6.08 (m, 1H), 4.44-4.40 (m, 1H), 3.48 (br, 2H), 2.14-1.83 (m, 4H), 1.45 (s, 9H).  $^{13}C$  NMR(100 MHz,  $CDCl_3$ ):  $\delta$  154.8, 137.1, 130.8, 129.4, 128.6, 1227.3, 126.3, 79.2, 59.0, 46.3, 32.6, 28.5, 23.0. HRMS(ESI)( $m/z$ ): Calcd for  $C_{17}H_{23}NO_2$   $[M+Na]^+$  296.1665, Found: 296.1606.


 A colorless oil, yield 75%,  $[\alpha]_D^{20} -41$  ( $c$  0.05  $\text{CHCl}_3$ ).  $^1\text{H NMR}$ (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.53 (s, 2H), 6.37-6.33 (m, 2H), 6.10-6.06 (m, 1H), 4.43-4.39 (m, 1H), 3.81 (s, 6H), 3.48-3.40 (m, 2H), 2.07-1.79 (m, 4H), 1.62-1.44 (m, 9H);  $\delta$  160.9, 156.1, 139.1, 131.3, 129.6, 104.4, 99.5, 79.2, 58.9, 55.3, 46.3, 32.6, 28.5, 23.1. HRMS(ESI)( $m/z$ ): Calcd for  $\text{C}_{19}\text{H}_{27}\text{NO}_4$   $[\text{M}+\text{H}]^+$  334.1931, Found: 334.1963.


 A pale oil, yield 55%,  $[\alpha]_D^{20} -20$  ( $c$  0.08  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.02 (br, 3H), 6.30 (d,  $J = 15.6$  Hz, 1H ), 5.57 (dd,  $J = 15.6$  and 5.2 Hz, 1H ), 4.49 (br, 1H ), 3.37 (br, 2H ), 2.28 (s, 6H ), 2.15-1.78 (m, 4H ), 1.47 (s, 9H ).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.8, 137.0, 135.9, 135.8, 135.7, 127.6, 126.4, 79.3 , 58.8, 46.2, 32.4, 28.6, 22.7, 20.9. HRMS-ESI( $m/z$ ): Calcd for  $\text{C}_{19}\text{H}_{27}\text{NO}_2$   $[\text{M}+\text{Na}]^+$  324.1934, Found: 324.1930.


 A pale oil, 83% yield,  $[\alpha]_D^{20} -44$  ( $c$  0.04,  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$  ):  $\delta$  7.45 – 7.28 (m, 10H), 6.61 (s, 2H), 6.51 (s, 1H), 6.31 (d,  $J = 14.4$  Hz, 1H), 6.06 (br, 1H), 5.05 (s, 4H), 4.60–4.11 (m, 1H), 3.43 (m, 2H), 2.05–1.57 (m, 4H), 1.53–1.20 (m, 9H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.0, 139.2, 136.9, 131.5, 128.6, 128.0, 127.6, 127.19, 108.3, 105.6, 101.1, 79.3, 70.1, 59.0, 46.3, 32.8, 28.5, 22.9. HRMS-ESI( $m/z$ ): Calcd for  $\text{C}_{31}\text{H}_{35}\text{NO}_4$   $[\text{M}+\text{Na}]^+$  508.2458, Found: 508.2446.

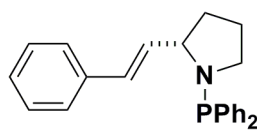


A pale oil, 78% yield,  $[\alpha]_D^{20} -40$  ( $c$  0.50,  $\text{CHCl}_3$ ).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (d,  $J = 7.6$  Hz, 2H), 7.47 (d,  $J = 8.4$  Hz, 2H), 6.47 (d,  $J = 13.2$  Hz 1H), 6.32 (br, 1H), 4.55–4.49 (m, 1H), 3.58–3.48 (m, 2H), 2.14–1.81 (m, 4H), 1.48–1.41 (br, 9H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.5, 154.6, 146.7, 143.6, 136.0, 127.6, 127.0, 124.0, 78.5, 65.0, 59.0, 46.7, 32.4, 28.5. HRMS-ESI( $m/z$ ): Calcd for  $\text{C}_{31}\text{H}_{35}\text{NO}_4$   $[\text{M}+\text{Na}]^+$  508.2458, Found: 508.2446.

### General procedure for the synthesis of the chiral olefin, P-ligands:

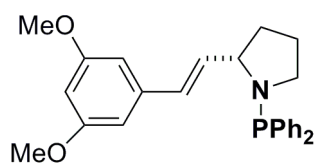
AcCl (10 mmol) was added slowly to an oven-dried 25 mL flask charged with dried methanol (10 ml) at  $0^\circ\text{C}$ . The resulting mixture was stirring for 1 hour at room temperature. A solution of olefin (1 mmol) in dried 1,4-dioxane was added to the reaction mixture. The resulting mixture was stirring for 3 hours at rt. The solvent was removed and then an aqueous solution of 10%NaOH (10 mL) was added. The reaction mixture was extracted by  $\text{CH}_2\text{Cl}_2$  and the organic phases was dried over  $\text{Na}_2\text{SO}_4$  and evaporated under vacuum to give a colourless amorphous. To this amorphous in  $\text{CH}_2\text{Cl}_2$  was added  $\text{Et}_3\text{N}$  (5mmol) and  $\text{PPh}_2\text{Cl}$  (2mmol) in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$ . The mixture was stirred at room temperature for 6-10 h. The residue was purified by silica gel chromatography to give the desired ligand.



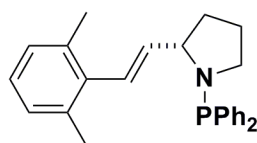
pale yellow oil, yield 65%.  $[\alpha]_D^{20} +39$  ( $c$  0.08  $\text{CHCl}_3$ ).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47–7.16 (m, 15H),

6.47 (d,  $J=10.8$  Hz, 1H), 6.15 (dd,  $J=10.6$  and 4.8 Hz, 1H), 4.20-4.18 (m, 1H), 2.99--2.96 (m, 1H), 2.88-2.87 (m, 1H), 2.12-2.09(m,1H), 1.86-1.85 (m, 1H), 1.76-1.72 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.4 (d,  $J_{\text{CP}}=6.6\text{Hz}$ ), 139.1(d,  $J_{\text{CP}}=10.1\text{Hz}$ ), 137.3, 133.7 (d,  $J_{\text{CP}}=1.8\text{Hz}$ ), 132.5, 132.32, 132.25, 132.12, 129.8, 128.5, 128.2 (d,  $J_{\text{CP}}=4.3\text{Hz}$ ), 128.1(d,  $J_{\text{CP}}=3.8\text{Hz}$ ), 127.1, 126.4, 65.7(d,  $J_{\text{CP}}=20.3\text{Hz}$ ), 46.7(d,  $J_{\text{CP}}=5.7\text{Hz}$ ), 33.9(d,  $J_{\text{CP}}=4.3\text{Hz}$ ), 25.5. HRMS-ESI( $m/z$ ): Calcd for  $\text{C}_{12}\text{H}_{24}\text{FN}$   $[\text{M}+\text{H}]^+$  358.1646, Found: 358.1672.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  43.46.

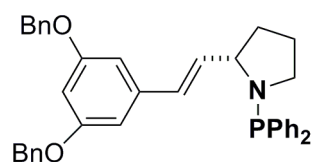


A pale yellow oil, yield 52%,  $[\alpha]_{\text{D}}^{20} +47$  ( $c$  0.20  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ): 7.40–7.21 (m, 10H), 6.40 (s, 2H), 6.31 (d,  $J=10.4$  Hz, 1H), 6.26 (s, 1H), 6.04 (dd,  $J=10.4$  and 3.6 Hz, 1H), 4.11-4.09 (m, 1H), 3.70 (s, 6H), 2.90–2.88 (m, 1H), 2.82 –2.81 (m, 1H), 2.04-2.01 (m, 1H), 1.79-1.75(m, 1H), 1.68-1.63(m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.8, 139.4 (d,  $J_{\text{CP}}=7.8$  Hz), 134.2 (d,  $J_{\text{CP}}=2.9$  Hz), 132.6, 132.4, 132.2, 132.0, 129.8, 128.2 (d,  $J_{\text{CP}}=10.0$  Hz), 128.1 (d,  $J_{\text{CP}}=6.0$  Hz), 104.5, 99.6, 65.6 (d,  $J_{\text{CP}}=30.0$  Hz), 55.3, 46.7 (d,  $J_{\text{CP}}=8.2$  Hz), 33.8 (d,  $J_{\text{CP}}=5.6$  Hz), 25.5. HRMS-ESI ( $m/z$ ): Calcd for  $\text{C}_{26}\text{H}_{28}\text{NO}_2\text{P}$   $[\text{M}+\text{H}]^+$  417.1858, Found: 417.1858.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  43.65.

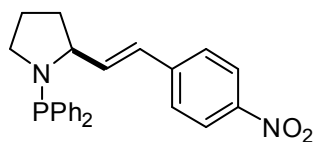


A pale yellow oil, yield 62%.  $[\alpha]_{\text{D}}^{20} -90$  ( $c$  0.12  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45 – 7.22 (m, 10H), 7.00 (br, 3H), 6.46 (d,  $J=16.0$  Hz, 1H), 5.65 (dd,  $J=16.0$  and

7.2 Hz, 1H), 4.21 (br, 1H), 3.03 (br, 1H), 2.83 (br, 1H), 2.26 (s, 6H), 2.10 (br, 1H), 1.86–1.73 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.7 (d,  $J_{\text{CP}} = 24\text{Hz}$ ), 139.5, 139.4, 138.5, 137.3, 136.1, 132.5, 132.4, 132.1, 132.0, 128.3, 128.2, 128.1, 127.7, 127.6, 126.3, 66.2 (d,  $J_{\text{CP}} = 21\text{Hz}$ ), 47.0 (d,  $J_{\text{CP}} = 5.9\text{Hz}$ ), 34.6 (d,  $J_{\text{CP}} = 4.4\text{Hz}$ ), 25.7, 21.1. HRMS-ESI( $m/z$ ): Calcd for  $\text{C}_{26}\text{H}_{28}\text{P}$   $[\text{M}+\text{H}]^+$  386.2032, Found: 386.2034.



A pale yellow oil, yield 80%.  $[\alpha]_{\text{D}}^{20}$  -28 ( $c$  0.13  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49 – 7.30 (m, 20H), 6.56 (s, 2H), 6.49 (s, 1H), 6.38 (d,  $J = 15.6$  Hz, 1H), 6.11 (dd,  $J = 16.0$  and 7.6 Hz, 1H), 5.01 (s, 4H), 4.18 – 4.13 (m, 1H), 2.99–2.96 (m, 1H), 2.90–2.87 (m, 1H), 2.12–2.04 (m, 1H), 1.85 – 1.83 (m, 1H), 1.77 – 1.68 (m, 2H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  160.1, 139.5, 137.0, 134.4 (d,  $J_{\text{CP}} = 8.0$  Hz), 132.5, 132.4, 132.3, 132.2, 129.8, 128.7, 128.6, 128.3, 128.2, 128.1 (d,  $J_{\text{CP}} = 6.8\text{Hz}$ ), 128.0, 127.6, 105.7, 101.2, 70.1, 65.6 (d,  $J_{\text{CP}} = 20.0\text{Hz}$ ), 46.8 (d,  $J_{\text{CP}} = 5.4\text{Hz}$ ), 33.9 (d,  $J_{\text{CP}} = 4.4$  Hz), 25.6. HRMS-ESI( $m/z$ ): Calcd for  $\text{C}_{38}\text{H}_{36}\text{NO}_2\text{P}$   $[\text{M}+\text{H}]^+$  570.2556, Found: 570.2542.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  43.58.



A pale yellow oil, yield 52%,  $[\alpha]_{\text{D}}^{20}$  -64 ( $c$  1.0  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.12 (d,  $J = 8.4$  Hz, 2H), 7.46–7.29 (m, 12H), 6.50 (d,  $J = 16.0$  Hz, 1H), 6.33 (dd,  $J = 16.0$  and 7.6 Hz, 1H), 4.25–4.22 (m, 1H), 3.03–2.99 (m, 1H), 2.92 – 2.91 (m, 1H), 2.16–2.11 (m, 1H), 1.87–1.82 (m, 1H), 1.79–1.72 (m, 2H).  $^{13}\text{C}$

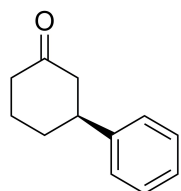


NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  146.6, 143.9, 139.2 (d,  $J_{CP}$  = 6.1 Hz), 139.0 (d,  $J_{CP}$  = 1.5 Hz), 138.7 (d,  $J_{CP}$  = 9.7 Hz), 132.6, 132.4, 132.2, 132.0, 129.8, 128.3, 128.2, 128.1 (d,  $J_{CP}$  = 6.0 Hz), 104.5, 99.6, 65.6 (d,  $J_{CP}$  = 20.0 Hz), 55.3, 46.7 (d,  $J_{CP}$  = 5.2 Hz), 33.8 (d,  $J_{CP}$  = 4.3 Hz), 25.5. HRMS-ESI ( $m/z$ ): Calcd for C<sub>26</sub>H<sub>28</sub>NO<sub>2</sub>P [M+H]<sup>+</sup> 417.1858, Found: 417.1858. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  44.49.

### 3. Asymmetric Catalytic Reactions

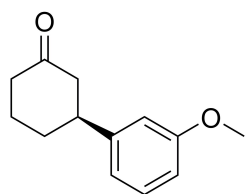
#### General procedure for Rhodium(I)-catalyzed asymmetric 1,4-addition of phenylboronic Acid to cycloalkenones:

Under N<sub>2</sub> atmosphere, a reaction flask was charged with RhCl(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> (2.9 mg, 0.0075 mmol) and PhB(OH)<sub>2</sub> (2.5 mmol). To the flask were added successively 1, 4-dioxane (2.0 mL), ligand (0.018 mmol), cyclohexenone (0.5 mmol), and 4M aq potassium hydroxide (0.5 mmol). The mixture was stirred at room temperature. After dilution with AcOEt, the mixture was washed with 10% aq NaOH and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and purification by silica gel column chromatography.



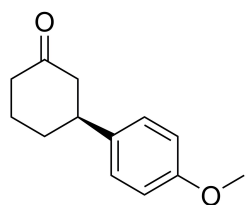
97% yield,  $[\alpha]_D^{20}$  -21 ( $c$  0.10 CHCl<sub>3</sub>), 93% ee, (AD, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 16.0 and 18.9 min for major and minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 – 7.29 (m, 2H), 7.27 – 7.20 (m, 3H), 3.01 (tt,  $J$  = 11.7, 4.0 Hz, 1H), 2.65 – 2.33 (m, 4H), 2.20 – 2.04 (m, 2H), 1.91 – 1.74 (m, 2H). <sup>13</sup>C NMR

(100 MHz, CDCl<sub>3</sub>):  $\delta$  211.1, 144.4, 128.7, 126.7, 48.9, 44.8, 41.2, 32.8, 25.6.



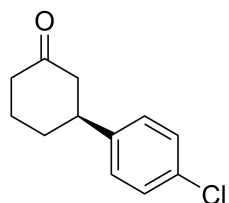
93% yield,  $[\alpha]_D^{20}$  -10 (*c* 0.24 CHCl<sub>3</sub>), 90% ee (OD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 40.4 and 45.1 min for major and minor). <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>):  $\delta$  7.25 (td, *J* = 7.7, 1.3 Hz, 1H), 6.84 – 6.75 (m, 3H), 3.80 (s, 3H), 2.98 (tt, *J* = 11.8, 3.9 Hz, 1H), 2.62 – 2.32 (m, 4H), 2.18 – 2.04 (m, 2H), 1.91 – 1.73 (m, 2H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>):  $\delta$  211.0, 159.8, 146.1, 129.7, 118.9, 112.7, 111.7, 55.2 48.9, 44.8, 41.2, 32.7, 25.5.



99%yield,  $[\alpha]_D^{20}$  -18 (*c* 0.50 CHCl<sub>3</sub>), 90% ee (OJ-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 39.8 and 42.3 min for major and minor). <sup>1</sup>H NMR (400 MHz,

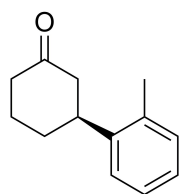
CDCl<sub>3</sub>):  $\delta$  7.14 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 2.97 (tt, *J* = 11.7, 3.9 Hz, 1H), 2.60 – 2.34 (m, 4H), 2.18 – 2.02 (m, 2H), 1.85 – 1.72 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  211.5, 158.5, 136.6, 127.5, 114.0, 55.3, 49.3, 44.0, 41.2, 33.0, 25.0.



70% yield,  $[\alpha]_D^{20}$  -8.0 (*c* 0.24 CHCl<sub>3</sub>), 93% ee (AD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 18.6 and 20.9 min for major and minor). <sup>1</sup>H NMR (400 MHz,

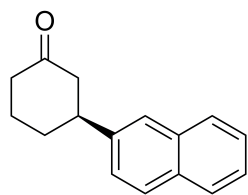
CDCl<sub>3</sub>):  $\delta$  7.30 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 2.99 (tt, *J* = 11.8, 3.9 Hz, 1H), 2.60 – 2.33 (m, 4H), 2.19 – 2.03 (m, 2H), 1.88 – 1.74

(m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  210.6, 142.8, 132.4, 128.8, 128.0, 48.8, 44.1, 32.7, 25.4.



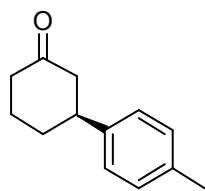
98% yield,  $[\alpha]_{\text{D}}^{20}$  -22 (*c* 0.30  $\text{CHCl}_3$ ), 87% ee (AD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 14.2 and 17.5 min for major and minor).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):

$\delta$  7.27 – 7.11 (m, 4H), 3.27 – 3.14 (m, 1H), 2.56 – 2.35 (m, 4H), 2.32 (s, 3H), 2.17 (ddd,  $J = 12.5, 6.3, 3.4$  Hz, 1H), 2.00 (d,  $J = 10.2$  Hz, 1H), 1.90 – 1.72 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  211.3, 142.3, 135.1, 130.7, 126.5, 125.1, 48.4, 41.3, 40.3, 32.0, 25.8, 19.3.



95% yield,  $[\alpha]_{\text{D}}^{20}$  -8.0 (*c* 0.08  $\text{CHCl}_3$ ), 88% ee (AD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 21.3 and 23.6 min for major and minor).  $^1\text{H}$  NMR (400 MHz,

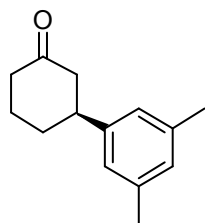
$\text{CDCl}_3$ ):  $\delta$  7.80 (dd,  $J = 8.7, 4.2$  Hz, 3H), 7.63 (s, 1H), 7.50 – 7.41 (m, 2H), 7.35 (dd,  $J = 8.5, 1.7$  Hz, 1H), 3.22 – 3.10 (m, 1H), 2.72 – 2.57 (m, 2H), 2.45 (dddd,  $J = 26.8, 19.6, 8.5, 3.8$  Hz, 2H), 2.17 (tdd,  $J = 9.8, 6.9, 3.3$  Hz, 2H), 2.01 – 1.73 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  211.0, 141.8, 133.6, 132.4, 128.4, 127.7, 126.2, 125.7, 125.4, 124.8, 48.9, 44.8, 41.3, 32.7, 25.6.



90% yield, a colorless oil,  $[\alpha]_{\text{D}}^{20}$  -16 (*c* 0.03,  $\text{CHCl}_3$ ), 84% ee (AD, hexane/2-propanol = 99.2/0.8, 0.4 mL/min, 254 nm, 14.4 and 17.7 min for major and minor).  $^1\text{H}$  NMR

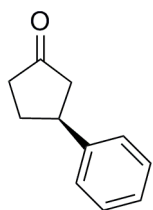
(400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.20 – 7.15 (m, 4H), 3.04 – 2.98 (m, 1H), 2.63 –

2.39 (m, 4H), 2.38 (s, 3H), 2.19 – 2.08 (m, 2H), 1.92 – 1.78 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 211.0, 141.5, 136.2, 129.4, 126.5, 49.1, 44.4, 41.2, 32.9, 25.6, 21.1.



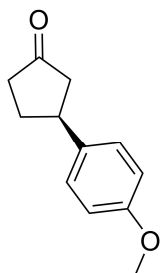
90% yield, a colorless oil,  $[\alpha]_D^{20}$  -57 (c 0.04, CHCl<sub>3</sub>), 88% ee (OD-H, hexane/2-propanol = 99.2/0.8, 0.4 mL/min, 254 nm, 21.9 and 17.3 min for major and minor). <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>): δ 6.92 (s, 1H), 6.89 (s, 2H), 3.00 – 2.94 (m, 1H), 2.63 – 2.39 (m, 4H), 2.36 (s, 6H), 2.21 – 2.08 (m, 2H), 1.91 – 1.80 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 211.2, 144.5, 138.2, 128.4, 124.5, 49.1, 44.8, 41.3, 32.9, 25.7, 21.4.



95% yield,  $[\alpha]_D^{20}$  -82 (c 0.10 CHCl<sub>3</sub>), 86% ee (AS-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 41.9 and 45.2 min for major and minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ

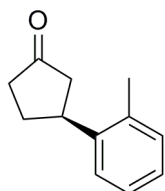
7.38 (dd, *J* = 9.8, 5.3 Hz, 2H), 7.34 – 7.23 (m, 3H), 3.45 (tt, *J* = 11.1, 7.0 Hz, 1H), 2.70 (dd, *J* = 18.2, 7.6 Hz, 1H), 2.57 – 2.43 (m, 2H), 2.43 – 2.26 (m, 2H), 2.11 – 1.92 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 218.39, 143.08, 128.70, 126.75, 45.81, 42.23, 38.89, 31.21.



99% yield,  $[\alpha]_D^{20}$  -86 (c 0.21 CHCl<sub>3</sub>), 91% ee (OD-H, hexane/2-propanol = 99/1, 0.5 mL/min, 254 nm, 32.4 and 34.0 min for minor and major). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.18 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.80 (s,

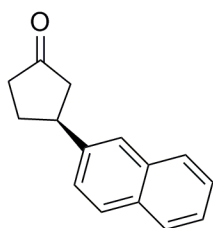
3H), 3.43 – 3.31 (m, 1H), 2.65 (dd, *J* = 18.1, 7.5 Hz, 1H), 2.42 (dddd, *J* =

10.0, 8.0, 6.0, 5.0 Hz, 2H), 2.35 – 2.23 (m, 2H), 2.01 – 1.89 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  218.7, 158.4, 135.1, 127.7, 114.1, 55.3, 46.1, 41.5, 38.9, 31.4.



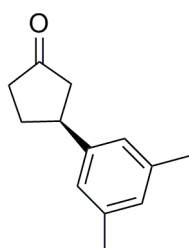
96% yield,  $[\alpha]_{\text{D}}^{20}$  -46 (*c* 0.24  $\text{CHCl}_3$ ), 93% ee (AS-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 62.6 and 78.8 min for major and minor).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.29 – 7.15 (m, 4H), 3.82 – 3.45 (m, 1H), 2.72 – 2.44 (m, 2H), 2.41 (s, 3H), 2.40 – 1.92 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  218.66, 140.97, 135.97, 130.64, 126.48, 124.75, 45.33, 38.56, 38.33, 30.08, 19.66. HRMS-ESI(*m/z*): Calcd for  $\text{C}_{12}\text{H}_{14}\text{O}$   $[\text{M}+\text{Na}]^+$  197.0937, Found: 197.0922.



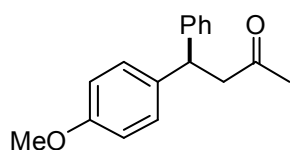
95% yield,  $[\alpha]_{\text{D}}$  -38 (*c* 0.14  $\text{CHCl}_3$ ), 84% ee (AS-H, hexane/2-propanol = 99/1, 0.5 mL/min, 254 nm, 112.0 and 121.5 min for major and minor).  $^1\text{H}$  NMR (400 MHz,

$\text{CDCl}_3$ )  $\delta$  7.94 – 7.76 (m, 3H), 7.67 (s, 1H), 7.53 – 7.37 (m, 3H), 3.60 (ddd, *J* = 13.6, 10.7, 6.9 Hz, 1H), 2.75 (dd, *J* = 18.3, 7.6 Hz, 1H), 2.61 – 2.30 (m, 4H), 2.22 – 1.99 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  218.32, 140.44, 133.48, 132.40, 128.43, 127.63, 126.29, 125.70, 125.35, 124.87, 45.73, 42.34, 38.82, 31.11.

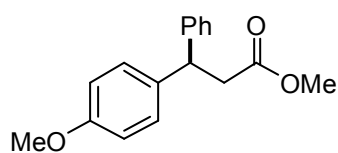


98% yield,  $[\alpha]_{\text{D}}^{20}$  -62 (*c* 0.46  $\text{CHCl}_3$ ), 90% ee (AS-H, hexane/2-propanol = 99/1, 0.5 mL/min, 254 nm, 32.9 and 38.0 min for major and minor).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

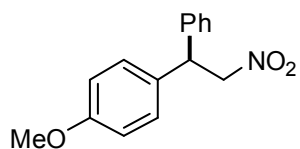
$\delta$  6.89 (s, 1H), 6.87 (s, 2H), 3.43 – 3.22 (m, 1H), 2.64 (dd,  $J = 18.3, 7.3$  Hz, 2H), 2.43 (ddd,  $J = 12.3, 8.2, 5.3$  Hz, 2H), 2.31 (s, 6H), 2.30 – 2.10 (m, 2H), 2.06 – 1.88 (m, 1H).  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  219.01, 143.05, 138.24, 128.40, 124.59, 113.11, 45.93, 42.16, 38.95, 31.37, 31.26, 21.38. HRMS-ESI( $m/z$ ): Calcd for  $\text{C}_{13}\text{H}_{16}\text{O}$   $[\text{M}+\text{Na}]^+$  211.1093, Found: 211.1073.



73% yield,  $[\alpha]_{\text{D}}^{20} -1.2$  ( $c$  0.43  $\text{CHCl}_3$ ), 87% ee (OD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 22.4 and 25.9 min for major and minor).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.10 (m, 7H), 6.81 (d,  $J = 8.7$  Hz, 2H), 4.53 (t,  $J = 7.6$  Hz, 1H), 3.75 (s, 3H), 3.14 (d,  $J = 7.6$  Hz, 2H), 2.06 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) : $\delta$  207.06, 158.13, 144.25, 135.99, 128.63, 127.62, 126.39, 113.98, 55.23, 49.91, 45.31, 30.68. HRMS-ESI( $m/z$ ): Calcd for  $\text{C}_{17}\text{H}_{18}\text{O}_2$   $[\text{M}+\text{Na}]^+$  277.1199, Found: 277.1194.

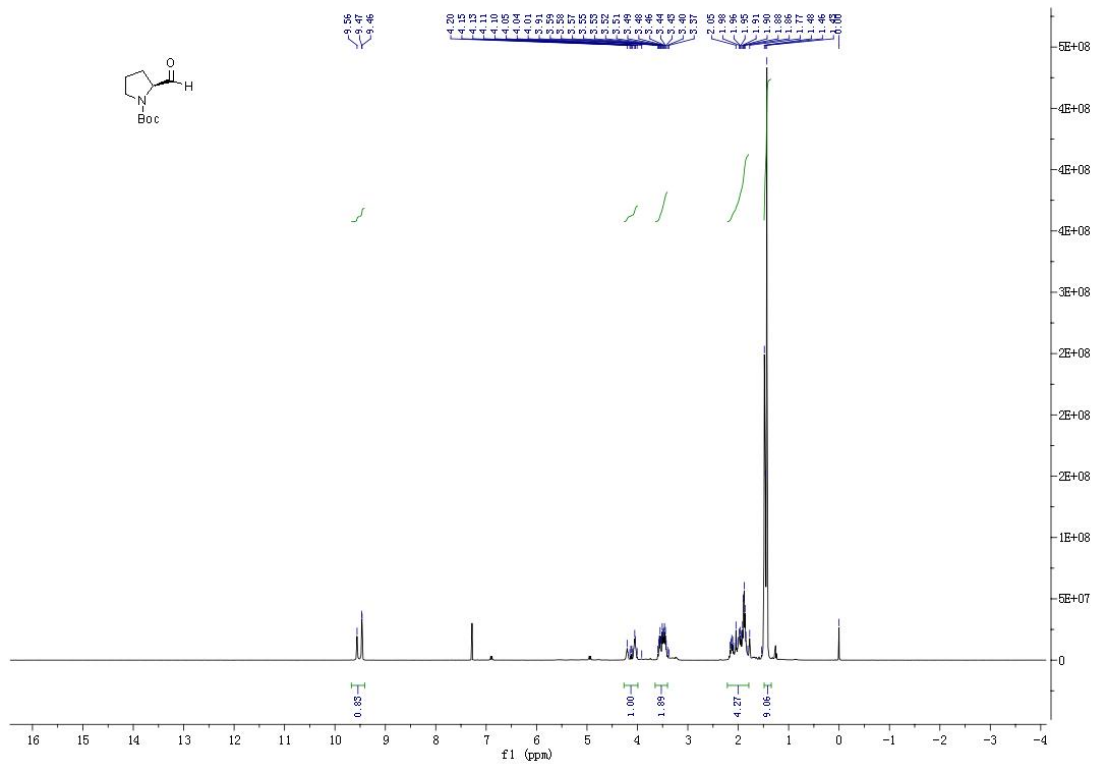


95% yield,  $[\alpha]_{\text{D}}^{20} +17$  ( $c$  0.02  $\text{CHCl}_3$ ), 92% ee (OD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 6.5 and 9.0 min for minor and major).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27–7.13(m, 7H), 6.81(d,  $J = 8.8$  Hz, 2H), 4.51(t,  $J = 8$  Hz, 1H), 3.76(s, 3H), 3.57(s, 3H), 3.02 (d,  $J = 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) : $\delta$  172.4, 158.2, 143.3, 135.6, 128.63, 128.58, 127.6, 113.9, 55.2, 51.7, 46.2, 40.8.

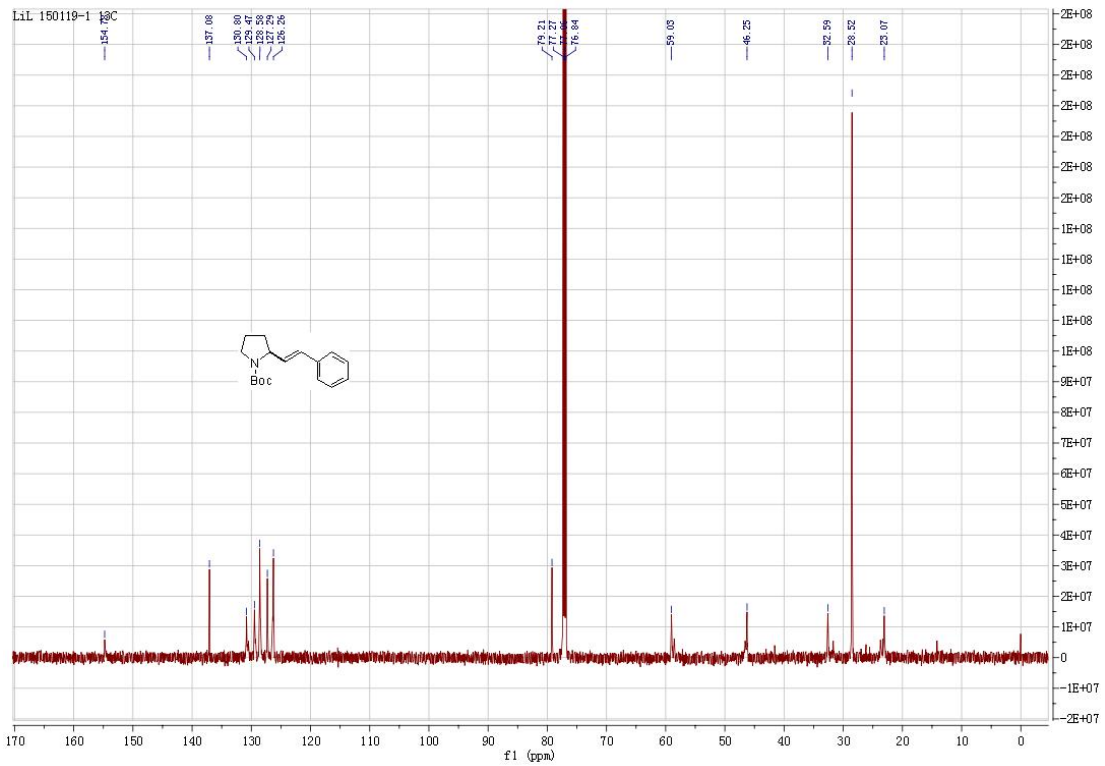
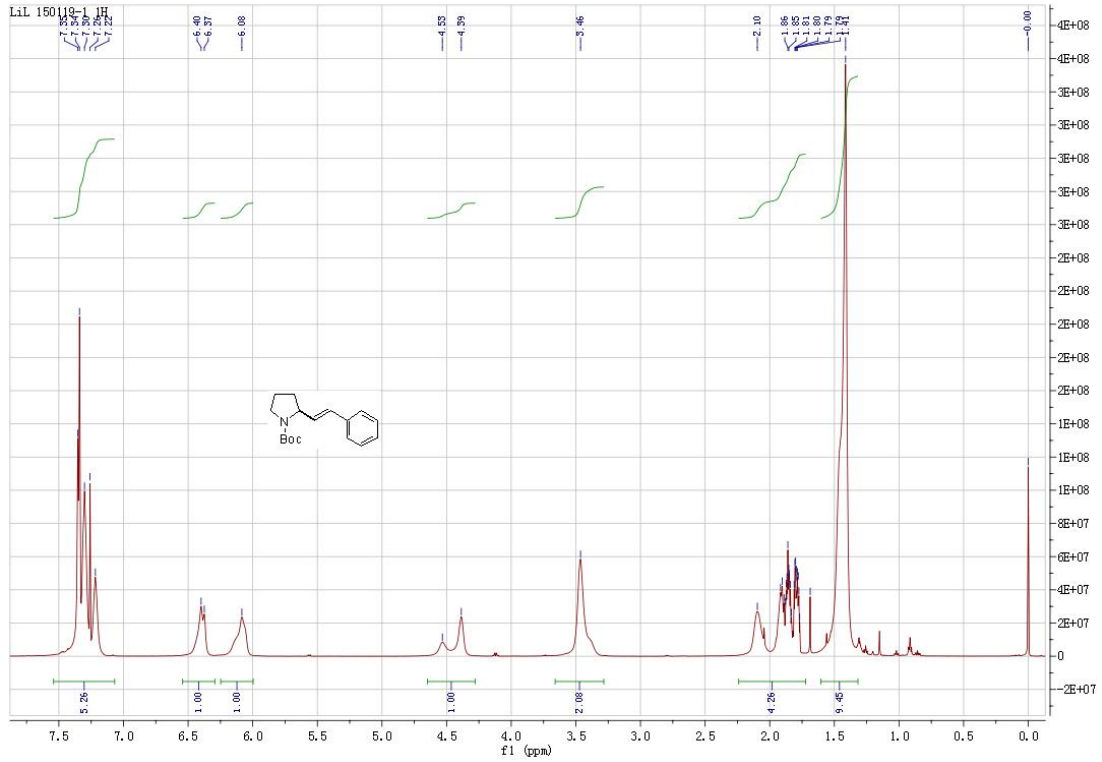


79% yield,  $[\alpha]_D^{20}$  -6.8 ( $c$  0.10  $\text{CHCl}_3$ ), 70% ee  
(OD-H, hexane/2-propanol = 95/5, 0.5 mL/min, 254  
nm, 45.7 and 49.2 min for major and minor) <sup>2</sup>. <sup>1</sup>H NMR (400 MHz,  
 $\text{CDCl}_3$ )  $\delta$  7.33–7.20(m, 5H), 7.14(d,  $J$  = 8.0 Hz, 2H), 6.84(d,  $J$  = 8.0 Hz,  
2H), 4.94-4.92 (m, 2H), 4.84-4.86 (m, 1H), 3.76 (s, 3H). <sup>13</sup>C NMR (100  
MHz,  $\text{CDCl}_3$ ) : $\delta$  203.3, 157.3, 143.5, 135.0, 127.6, 126.6, 125.4, 113.0,  
56.3, 48.7, 44.3.

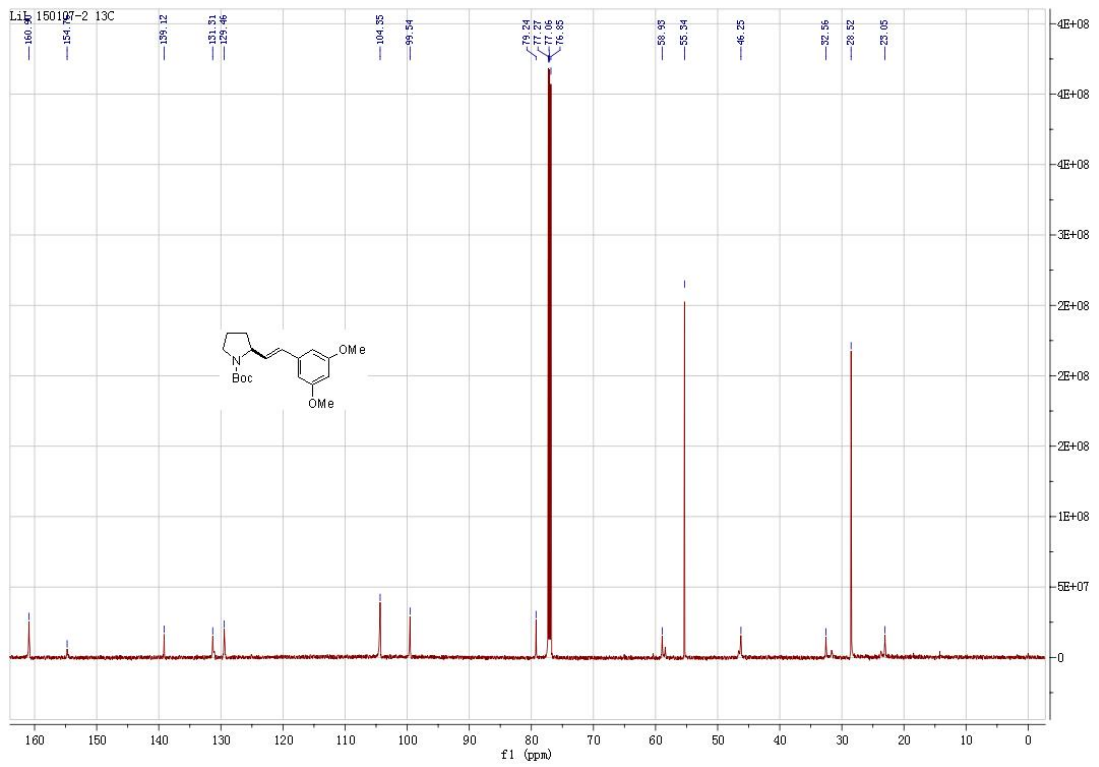
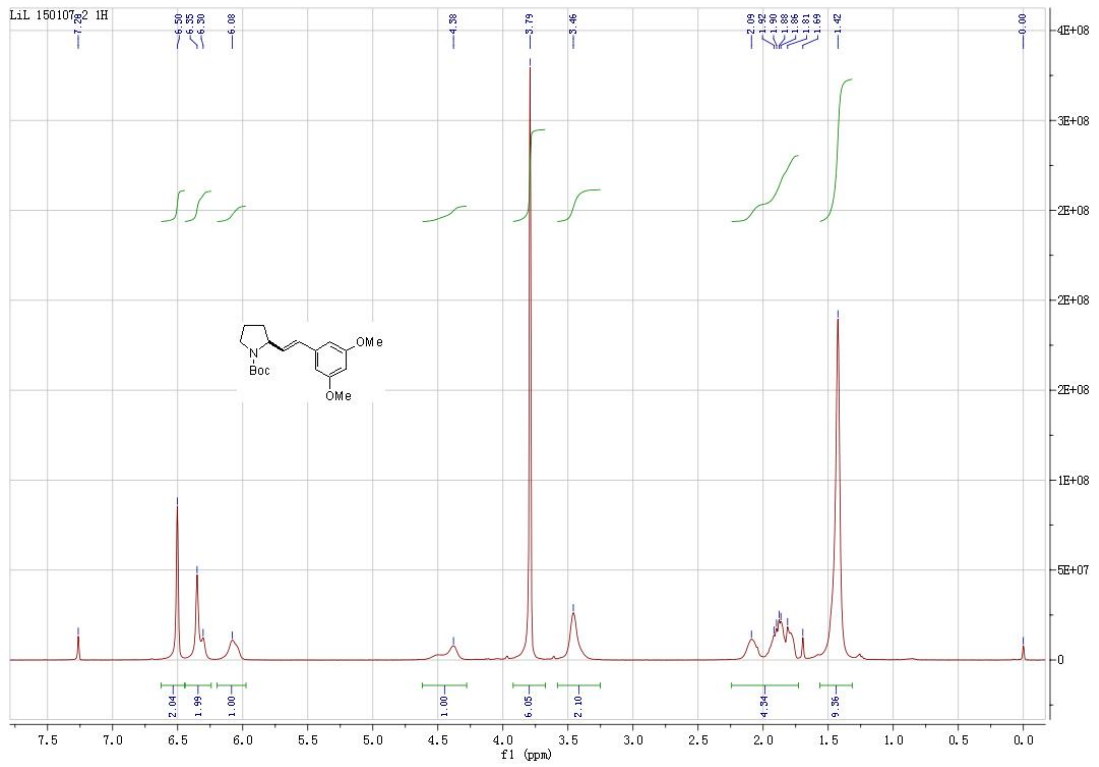
# 4. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra

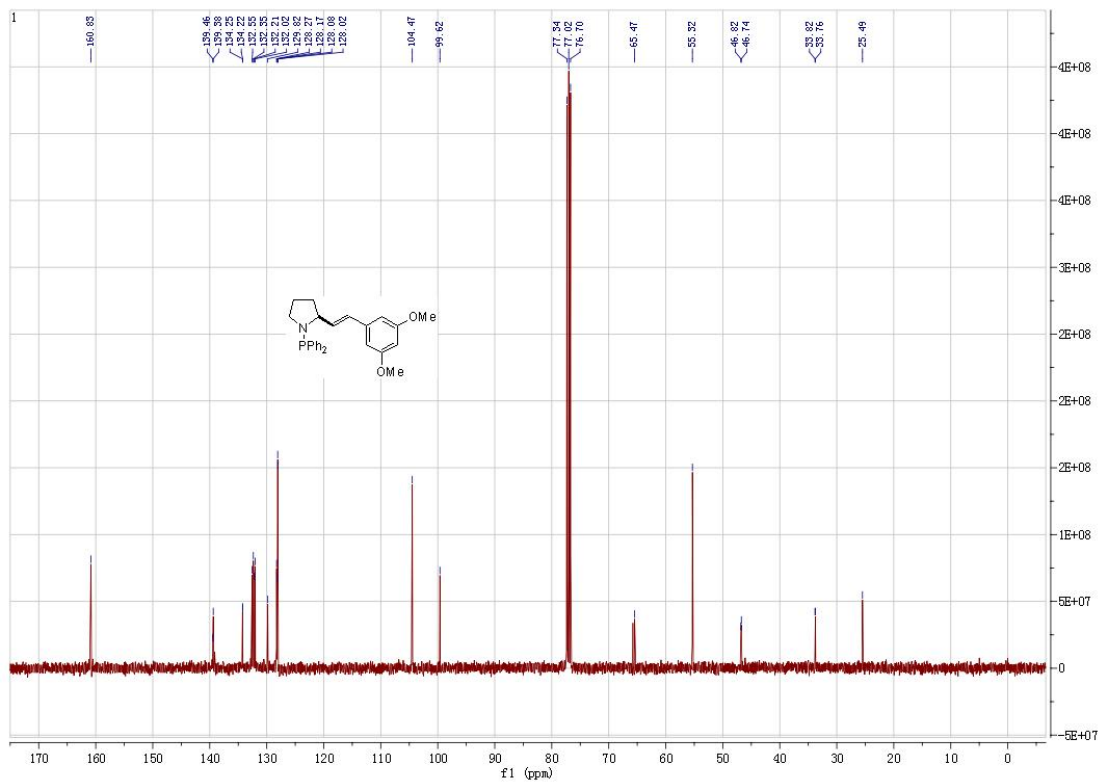
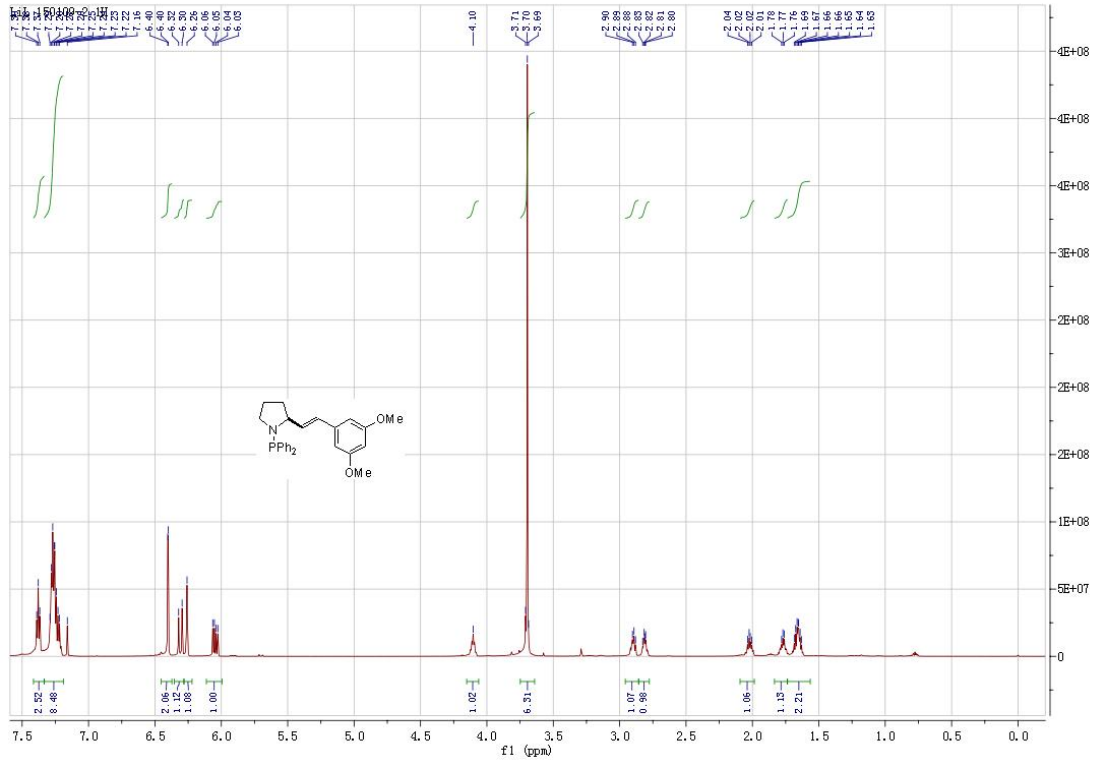


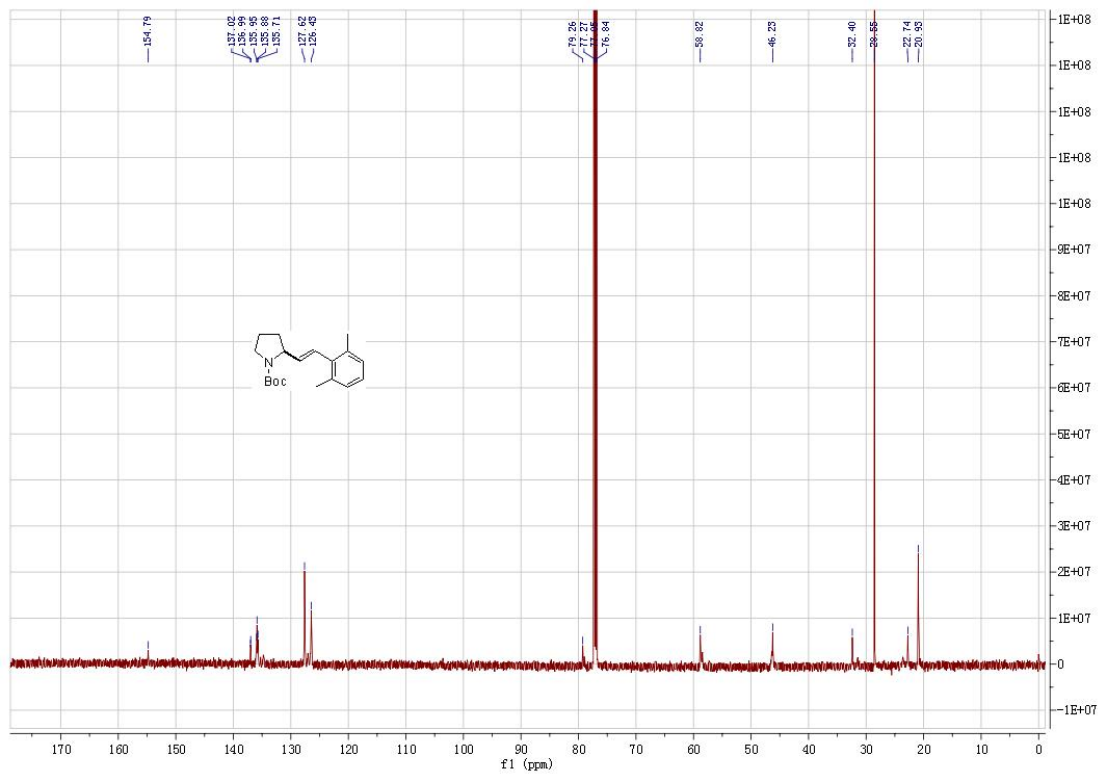
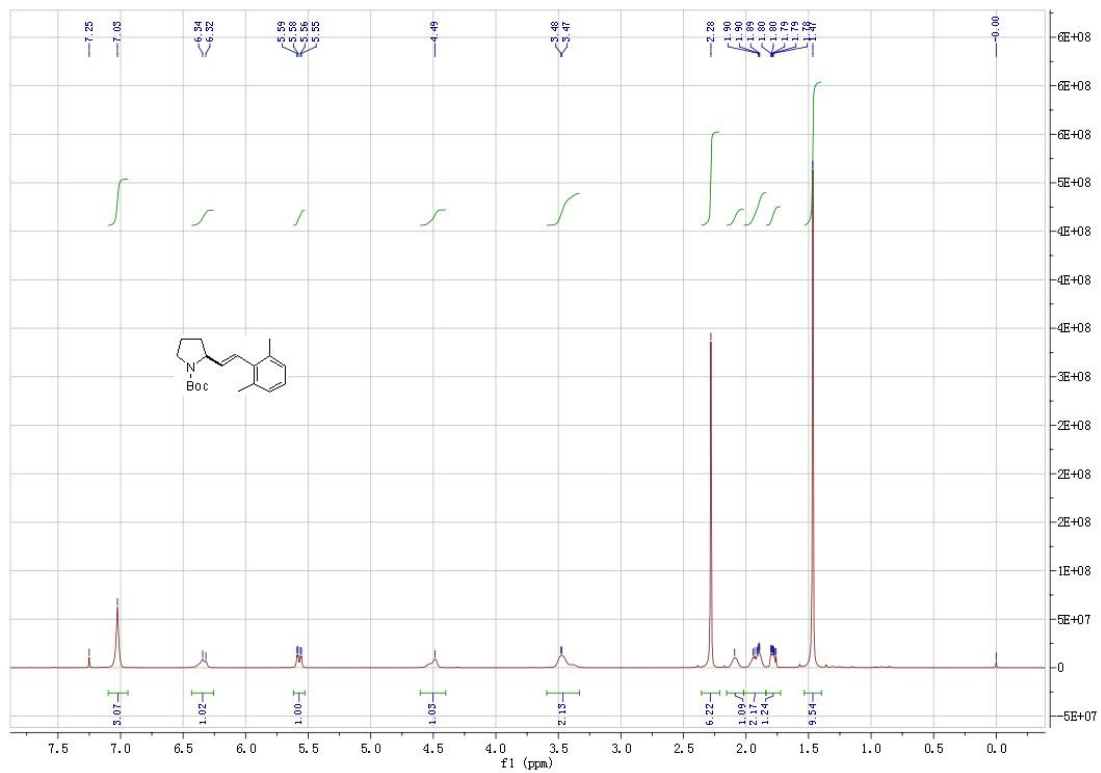


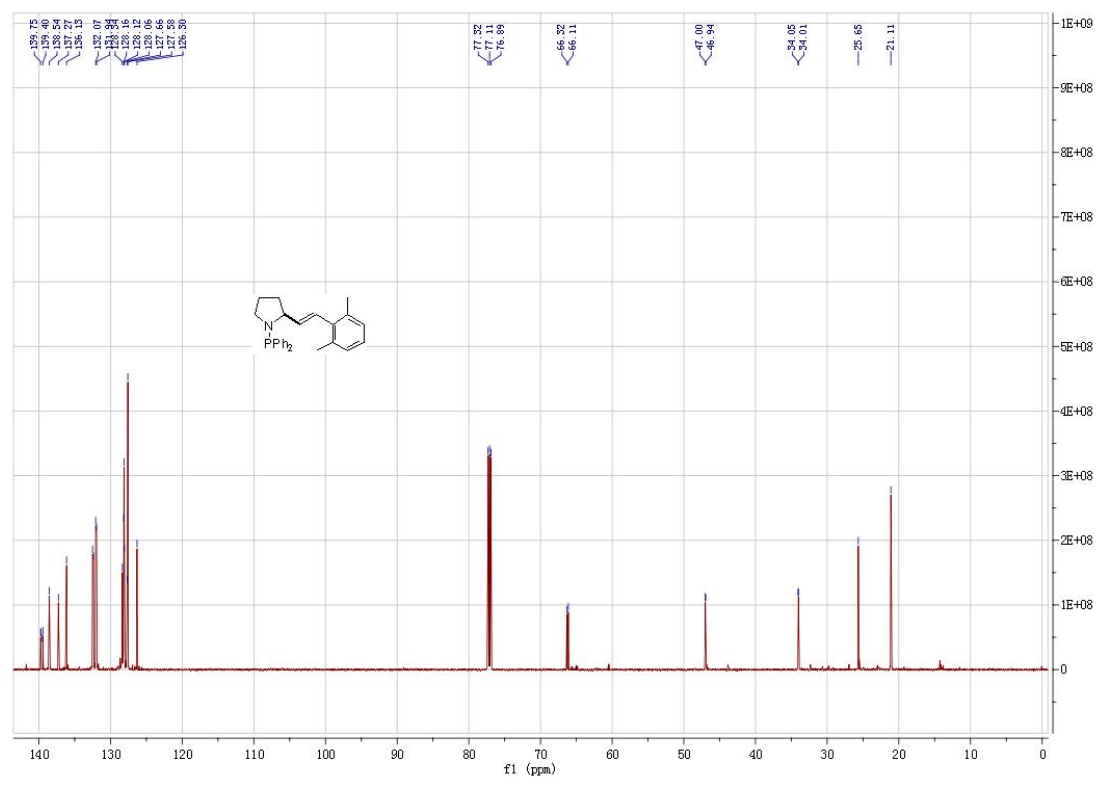
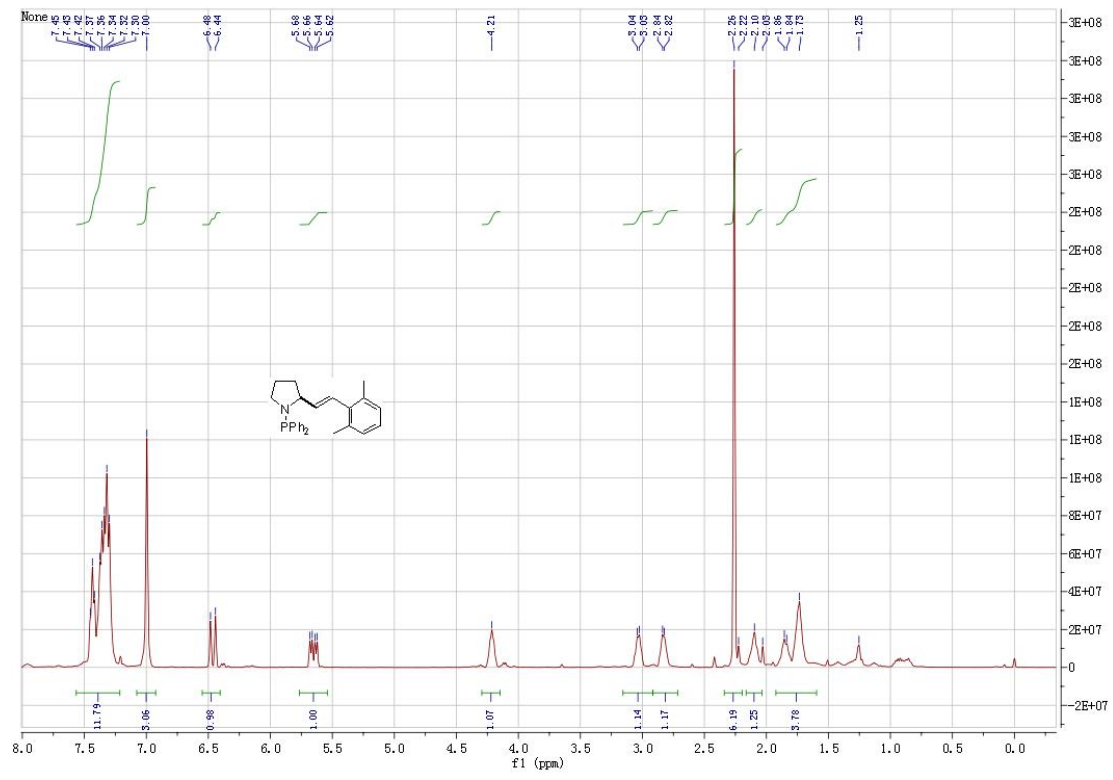


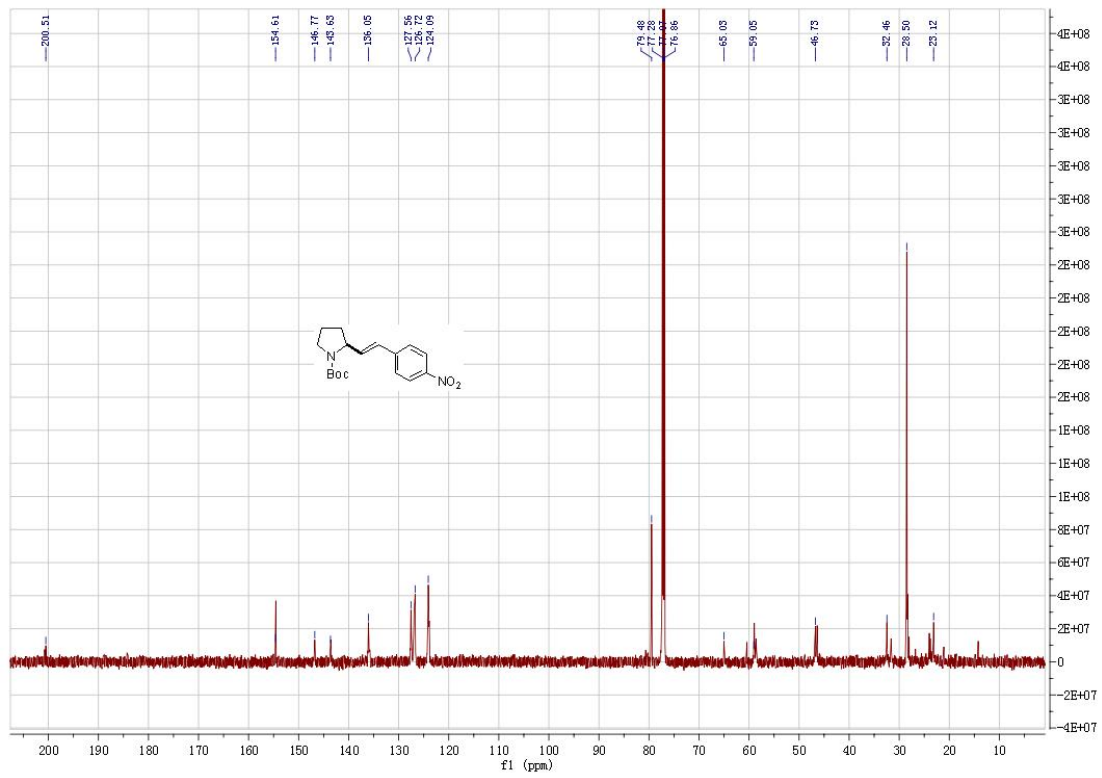
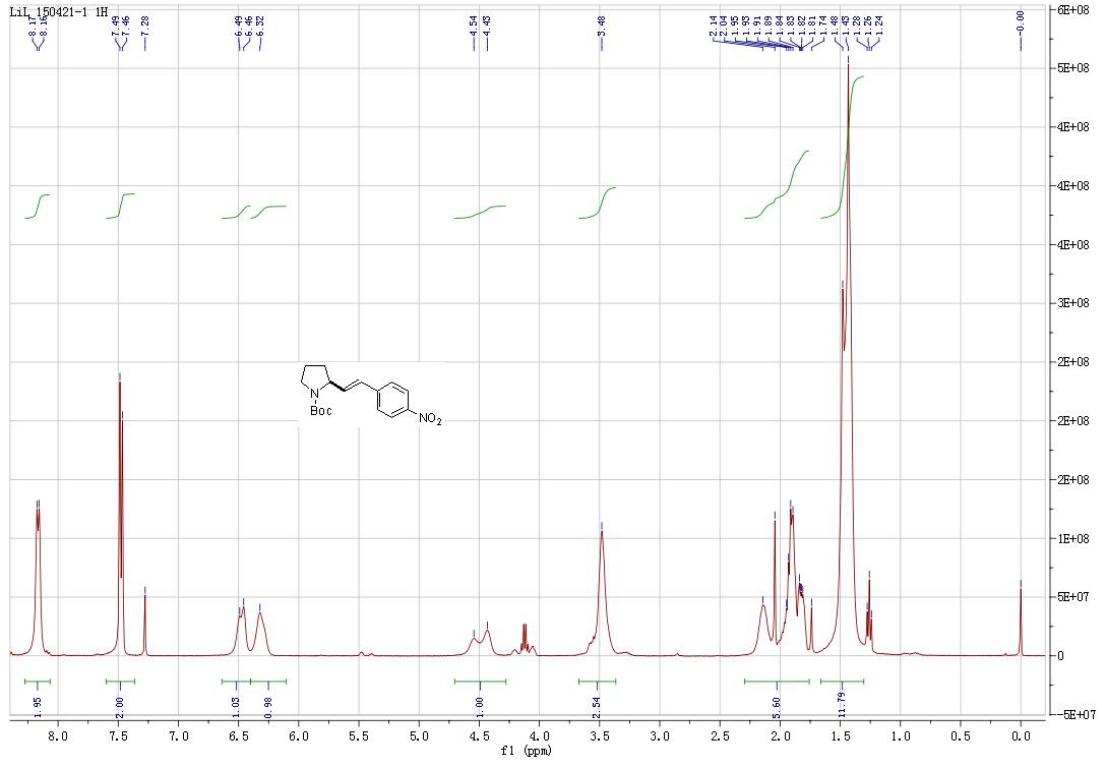






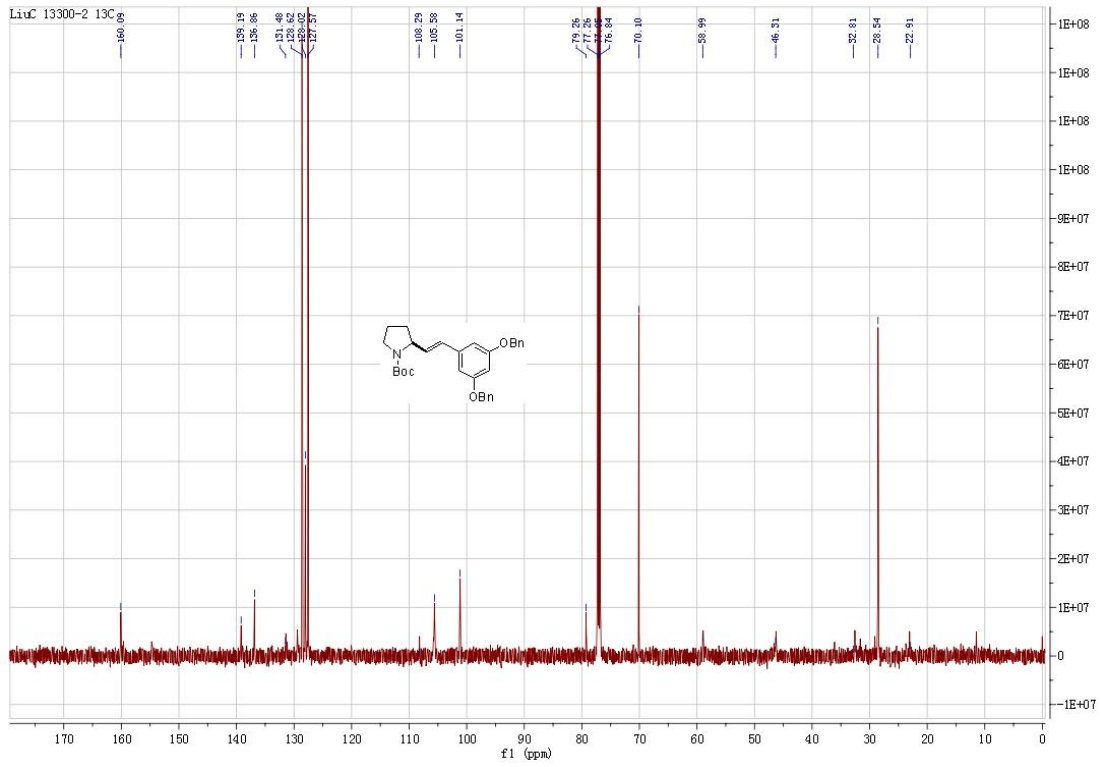
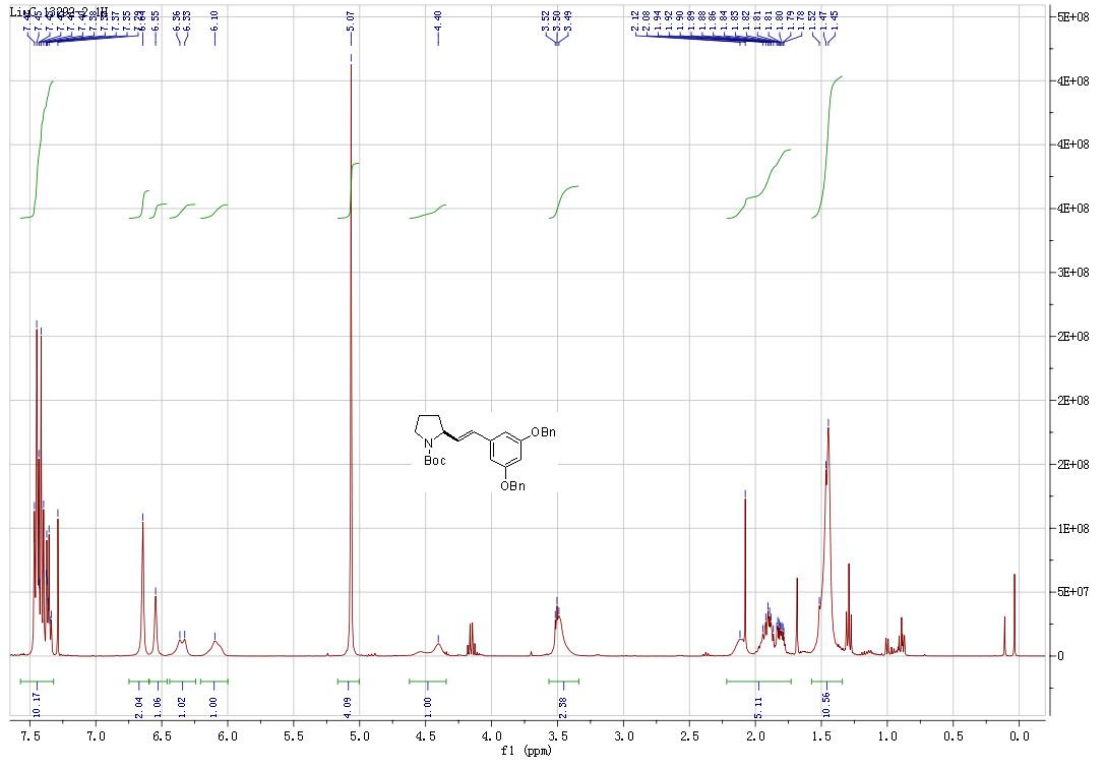






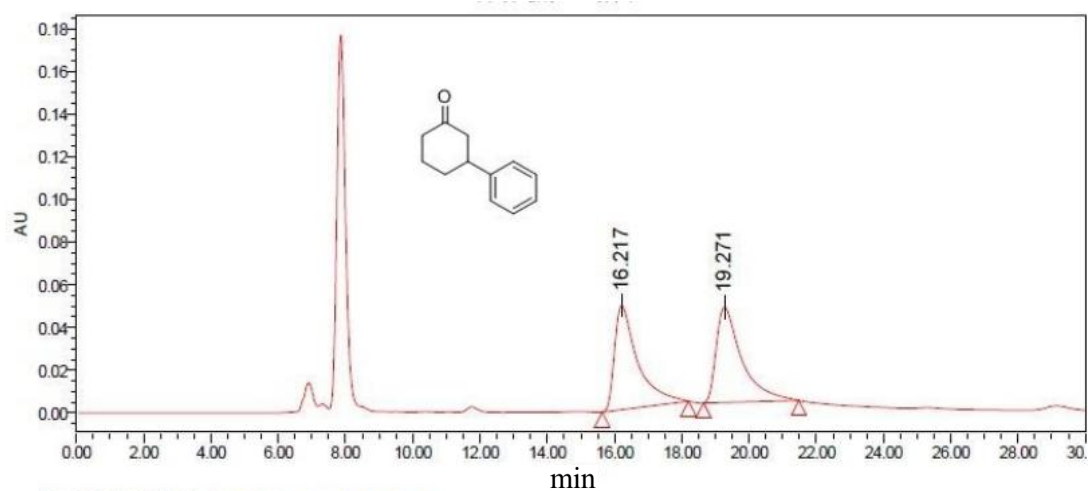






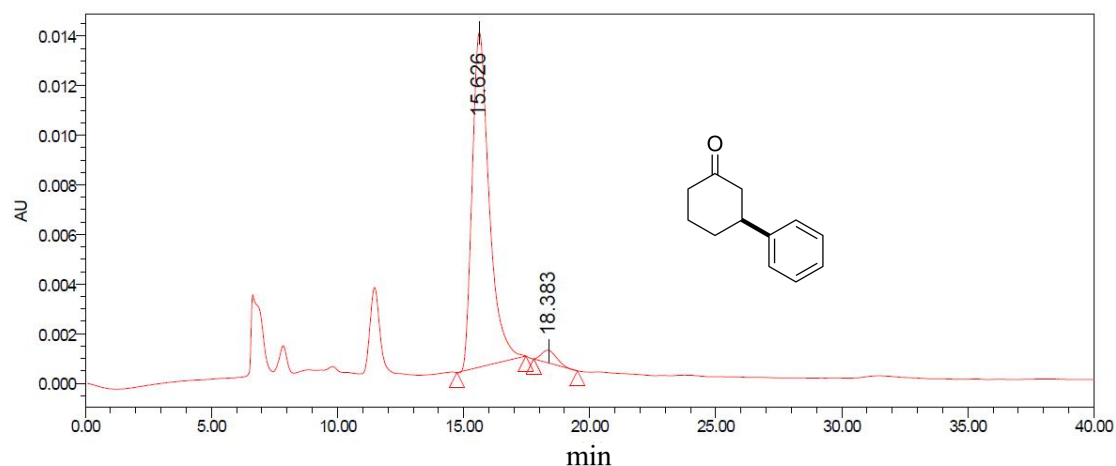


## 5. HPLC Chromatograms



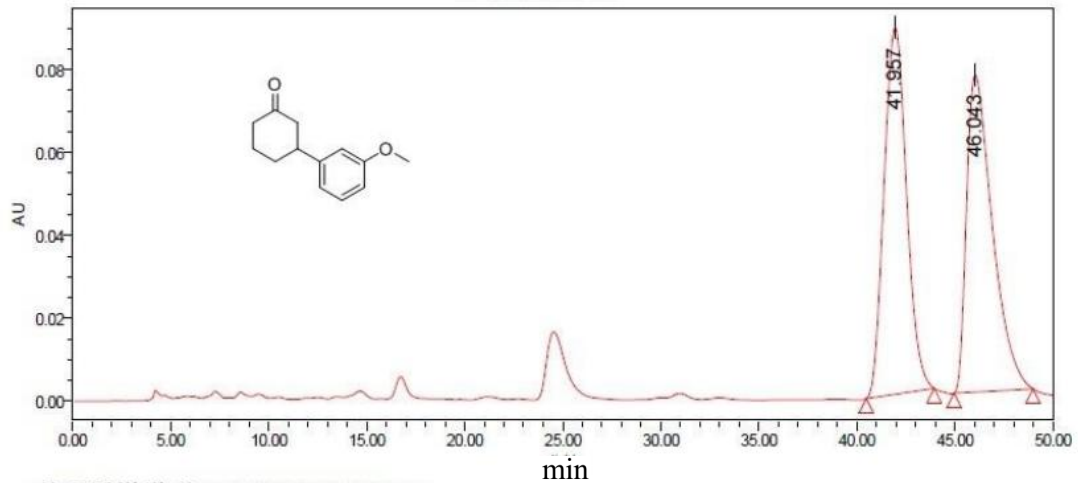
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 16.217               | 2343250           | 49.93         | 48706             |
| 2 | W2489 ChA 254nm                | 19.271               | 2349419           | 50.07         | 44601             |



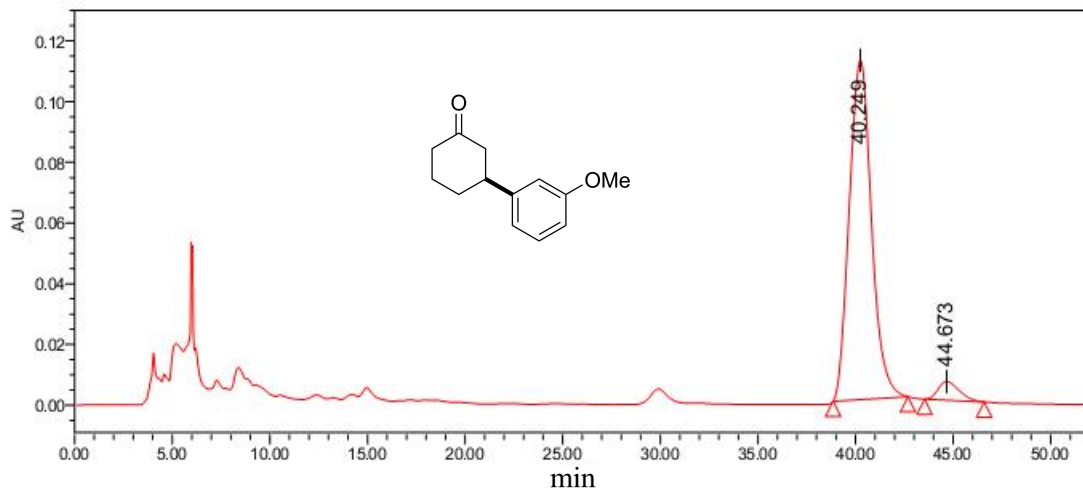
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 15.626               | 632356            | 96.77         | 13499             |
| 2 | W2489 ChA 254nm                | 18.383               | 21078             | 3.23          | 510               |



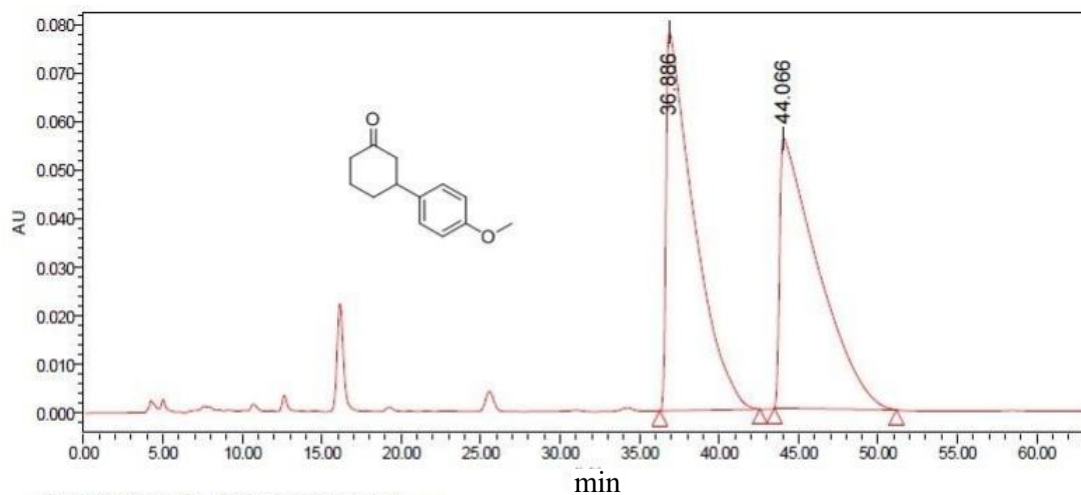
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 41.957               | 7049581           | 50.15         | 88438             |
| 2 | W2489 ChA 254nm                | 46.043               | 7007276           | 49.85         | 76473             |



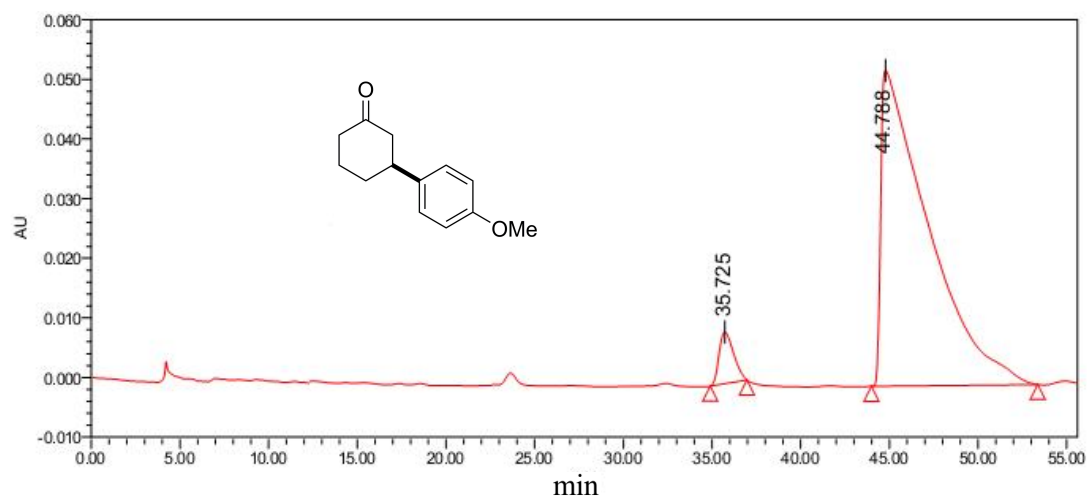
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 40.249               | 8829162           | 94.99         | 111724            |
| 2 | W2489 ChA 254nm                | 44.673               | 465582            | 5.01          | 6187              |



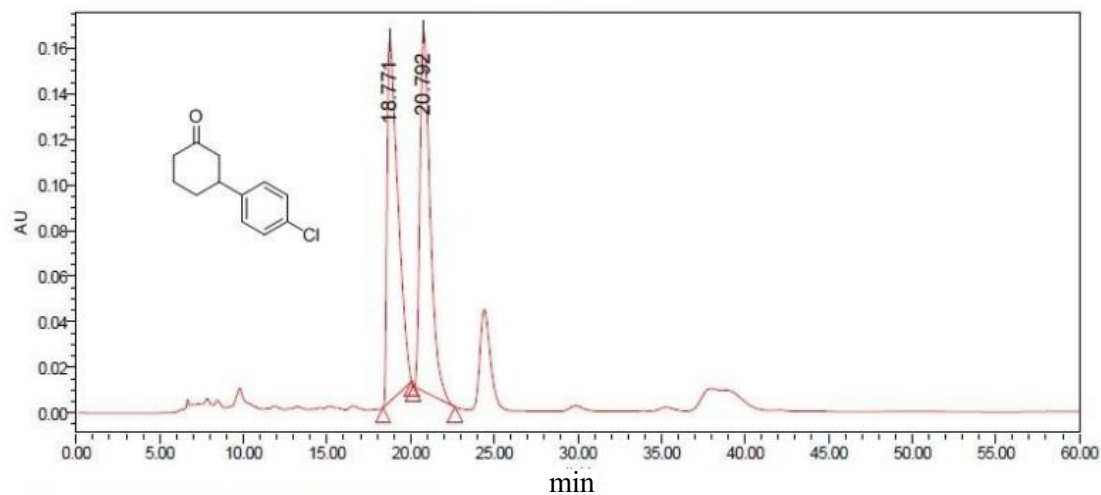
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 36.886               | 9517607           | 50.49         | 77935             |
| 2 | W2489 ChA 254nm                | 44.066               | 9333339           | 49.51         | 55563             |



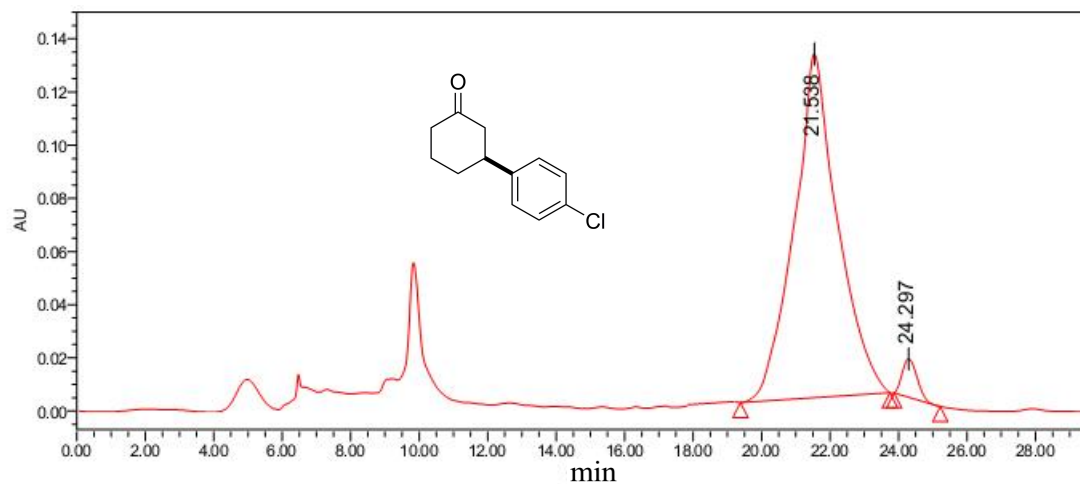
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 35.725               | 493372            | 4.77          | 8668              |
| 2 | W2489 ChA 254nm                | 44.788               | 9845801           | 95.23         | 52949             |



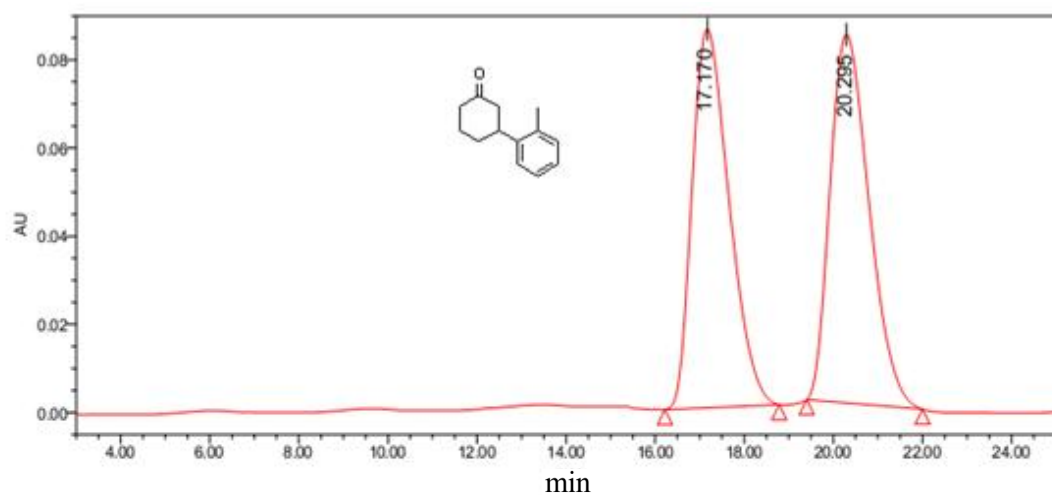
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 18.771               | 7109362           | 51.12         | 158953            |
| 2 | W2489 ChA 254nm                | 20.792               | 6797895           | 48.88         | 157808            |



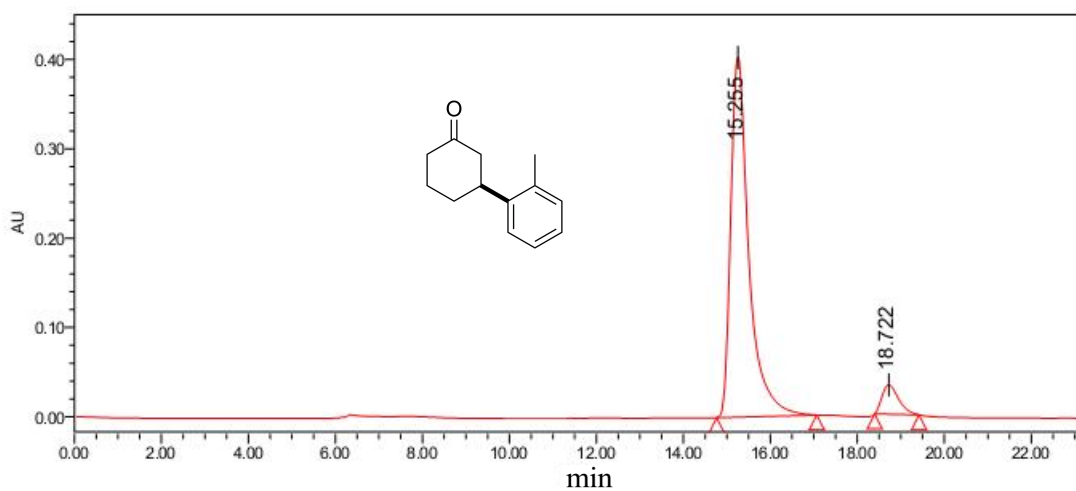
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 21.538               | 11435440          | 96.30         | 129257            |
| 2 | W2489 ChA 254nm                | 24.297               | 438908            | 3.70          | 14454             |



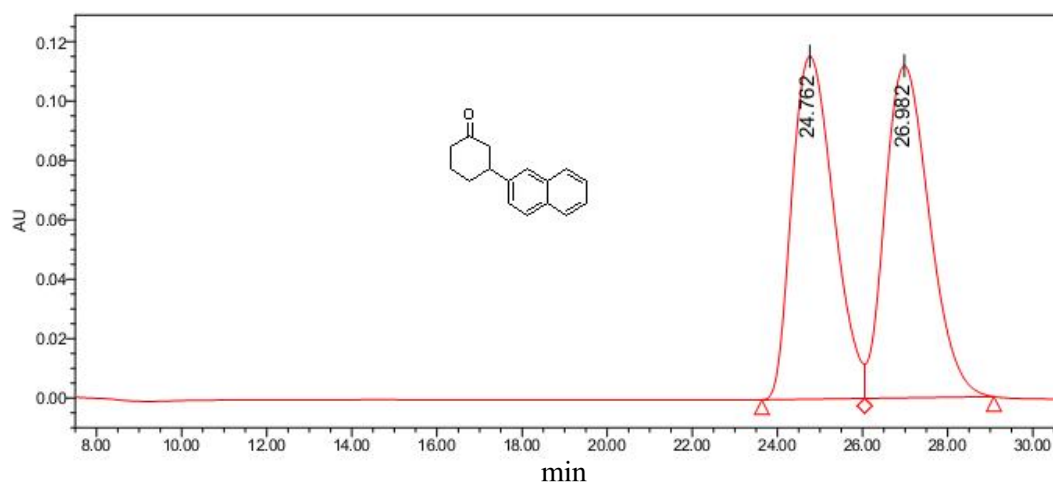
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 17.170               | 4956070           | 49.39         | 85938             |
| 2 | W2489 ChA 254nm                | 20.295               | 5077628           | 50.61         | 83622             |



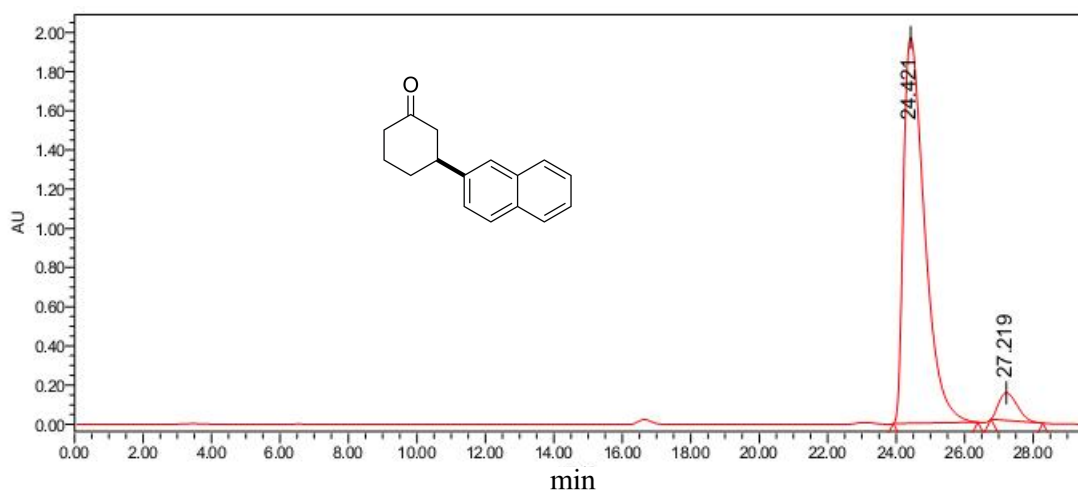
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 15.255               | 11628261          | 93.07         | 402990            |
| 2 | W2489 ChA 254nm                | 18.722               | 866004            | 6.93          | 32767             |



Processing channel description: W2489 ChA 254nm

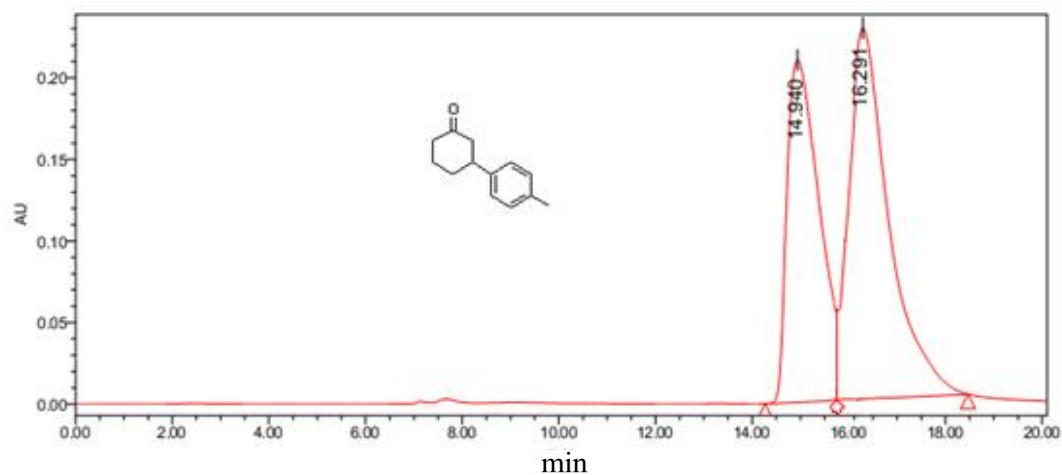
|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 24.762               | 7871785           | 49.17         | 115491            |
| 2 | W2489 ChA 254nm                | 26.982               | 8137551           | 50.83         | 111860            |



Processing channel description: W2489 ChA 254nm

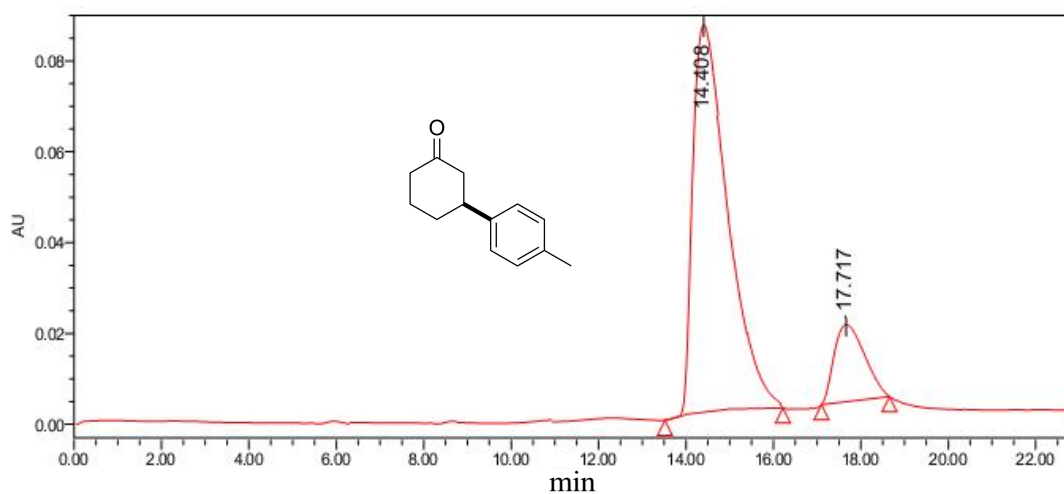
|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 24.421               | 84172432          | 94.05         | 1968660           |
| 2 | W2489 ChA 254nm                | 27.219               | 5328647           | 5.95          | 140772            |





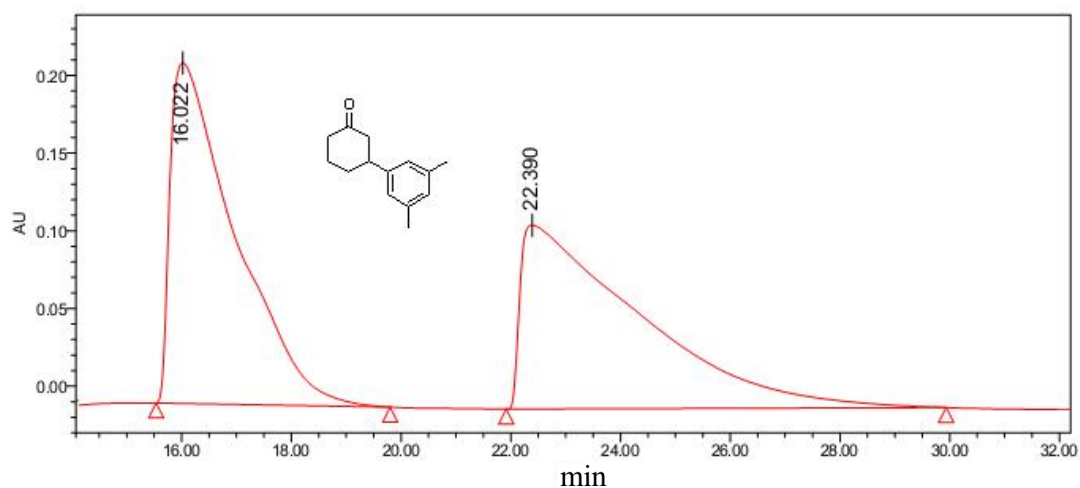
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 14.940               | 11411482          | 50.06         | 209896            |
| 2 | W2489 ChA 254nm                | 16.291               | 11382017          | 49.94         | 227611            |



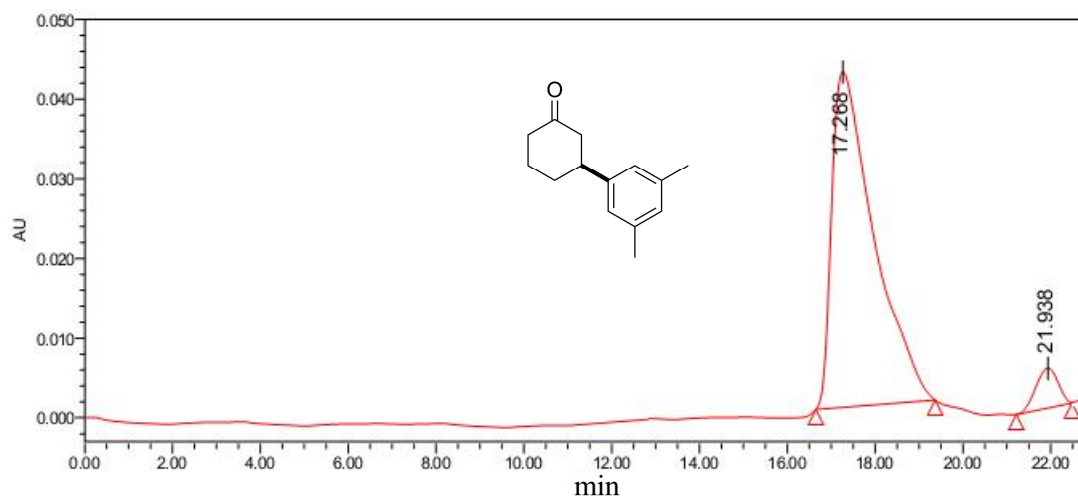
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 14.408               | 5341659           | 91.82         | 84797             |
| 2 | W2489 ChA 254nm                | 17.717               | 475619            | 8.18          | 9305              |



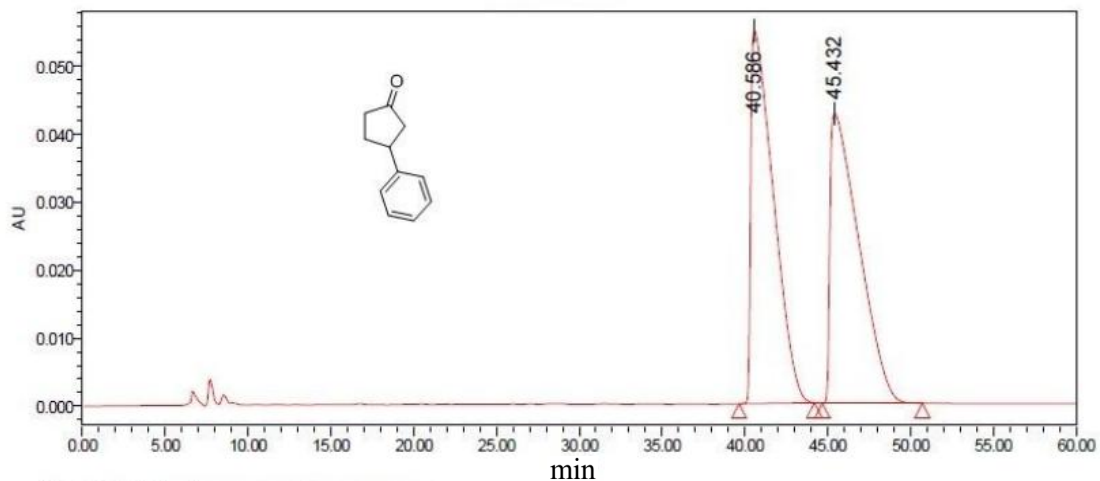
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 16.022               | 26852997          | 50.21         | 327910            |
| 2 | W2489 ChA 254nm                | 22.390               | 26630957          | 49.79         | 176983            |



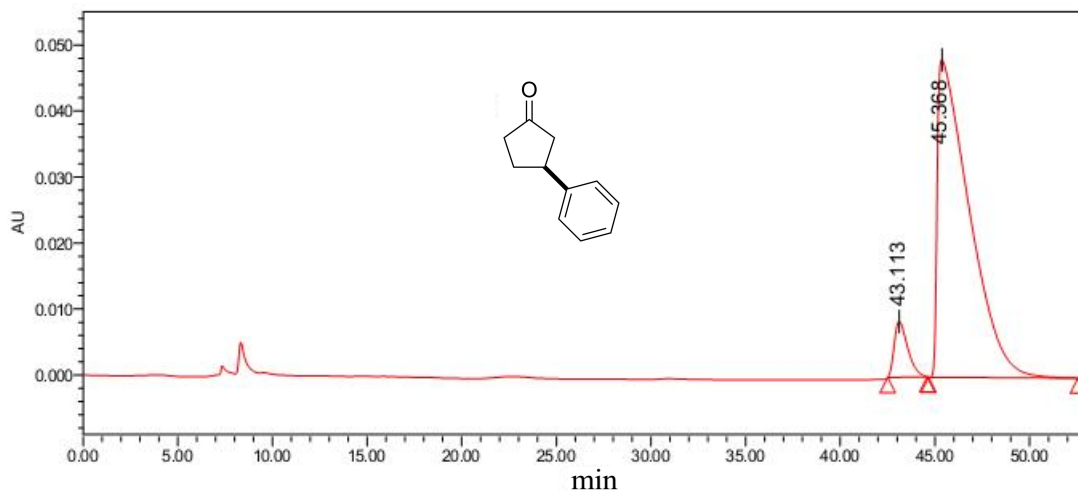
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 17.268               | 2802313           | 94.08         | 42107             |
| 2 | W2489 ChA 254nm                | 21.938               | 176464            | 5.92          | 4991              |



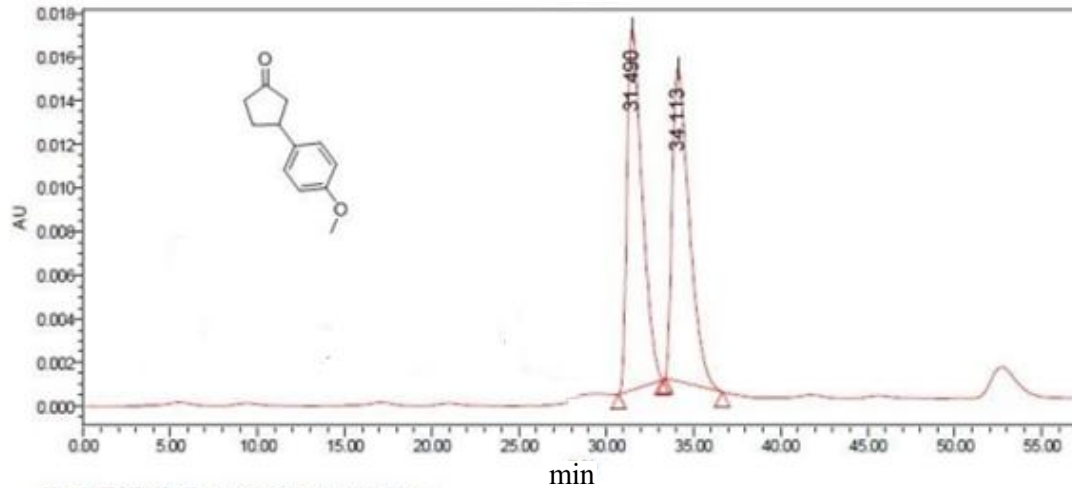
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 40.586               | 5203829           | 50.26         | 54896             |
| 2 | W2489 ChA 254nm                | 45.432               | 5149785           | 49.74         | 42624             |



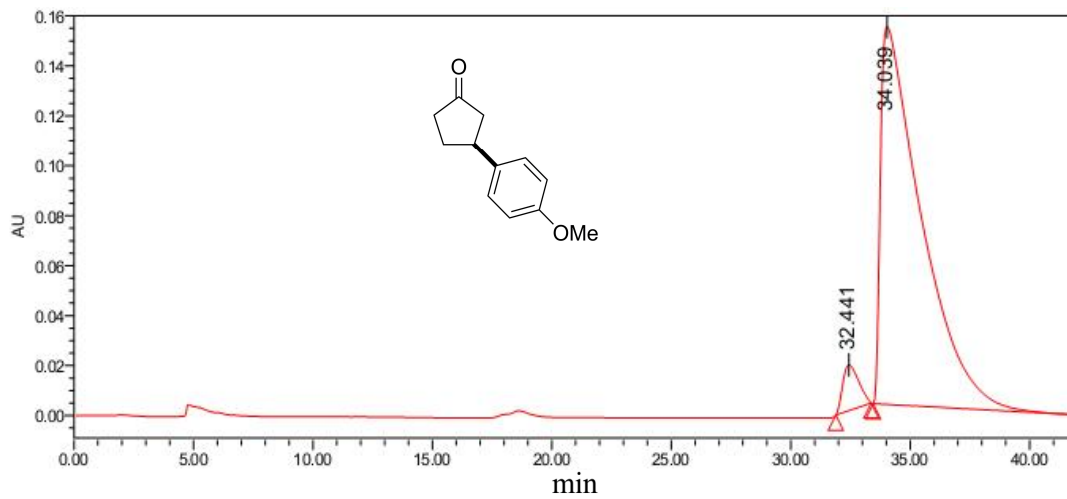
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 43.113               | 419931            | 6.92          | 8457              |
| 2 | W2489 ChA 254nm                | 45.368               | 5644163           | 93.08         | 48060             |



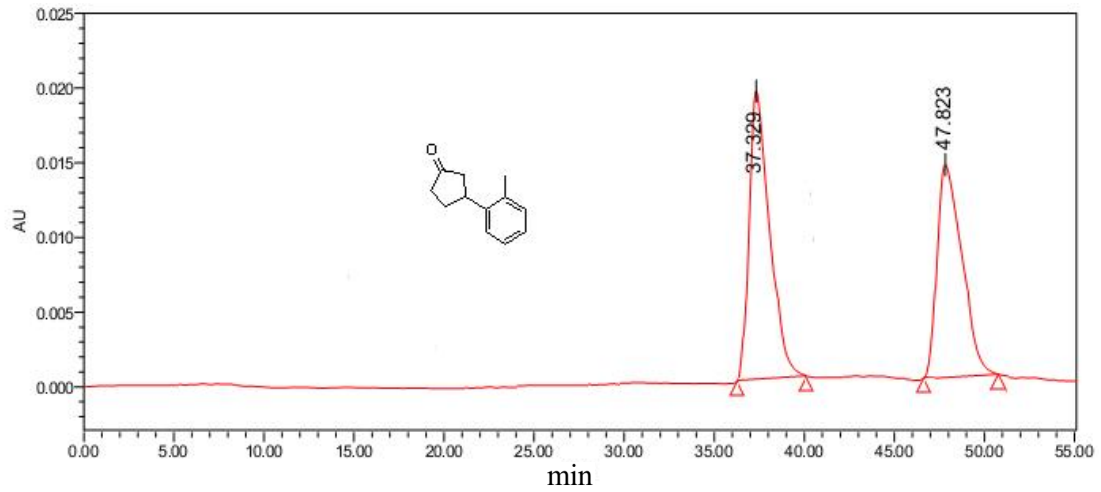
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 31.490               | 994322            | 50.35         | 16543             |
| 2 | W2489 ChA 254nm                | 34.112               | 960623            | 49.65         | 14344             |



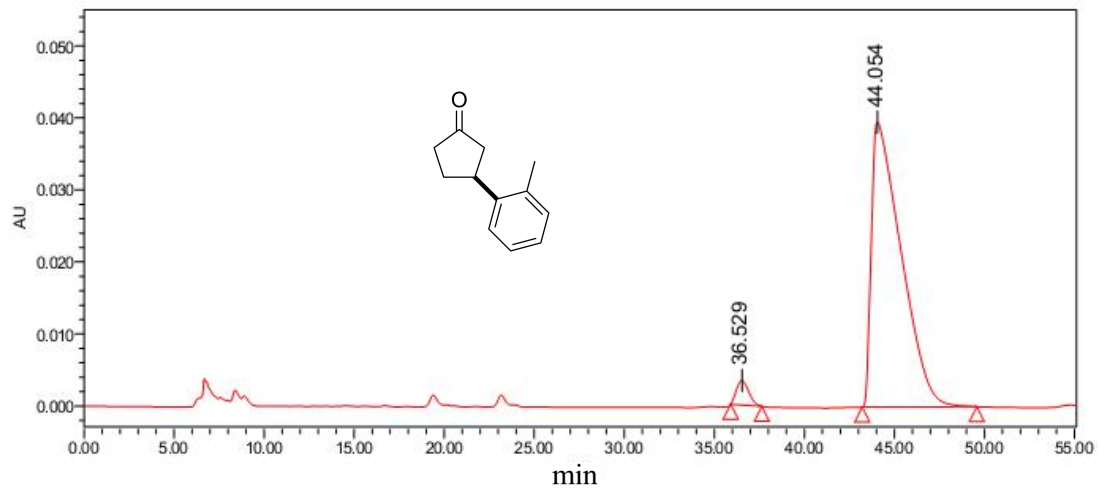
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 32.441               | 844277            | 4.49          | 18270             |
| 2 | W2489 ChA 254nm                | 34.039               | 17972653          | 95.51         | 151221            |



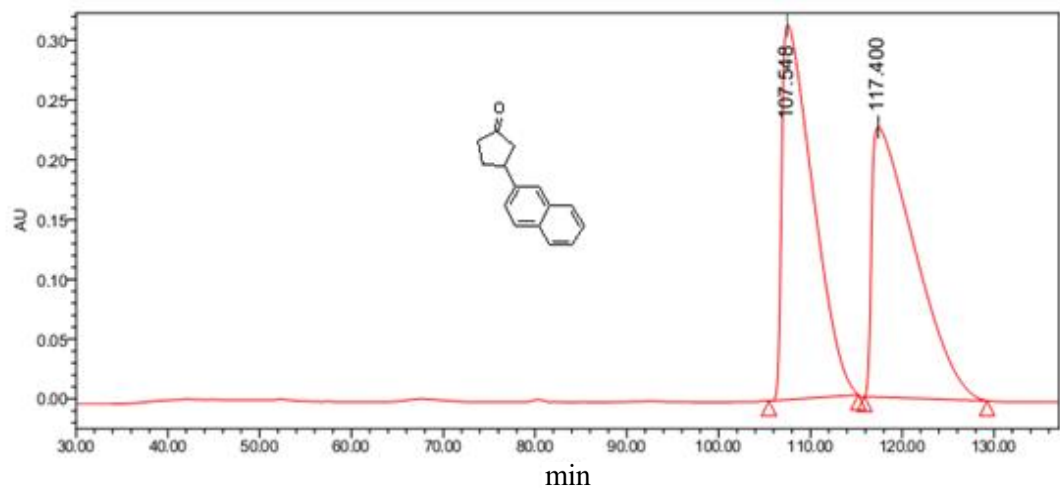
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 37.329               | 1236446           | 50.27         | 18043             |
| 2 | W2489 ChA 254nm                | 47.823               | 1223120           | 49.73         | 13342             |



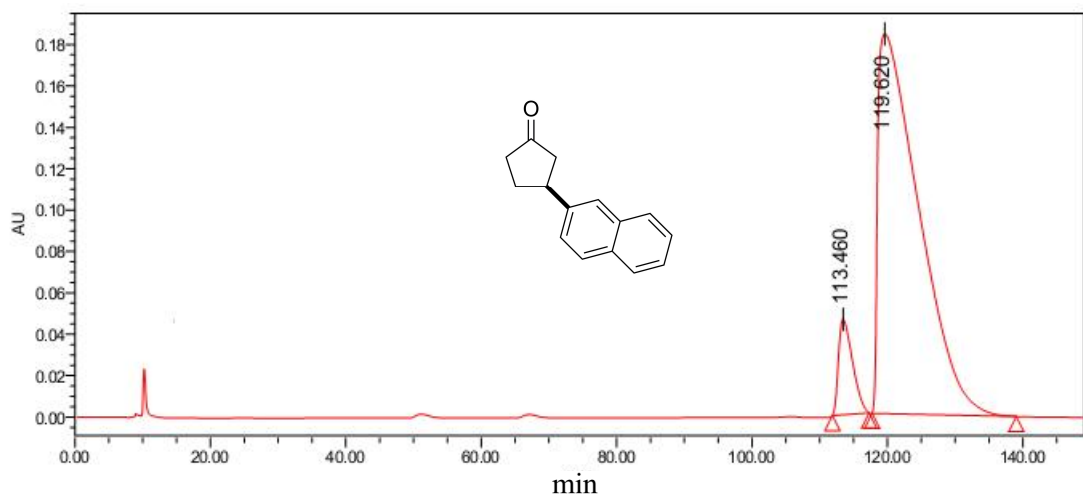
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 36.529               | 162179            | 3.45          | 3394              |
| 2 | W2489 ChA 254nm                | 44.054               | 4538878           | 96.55         | 39579             |



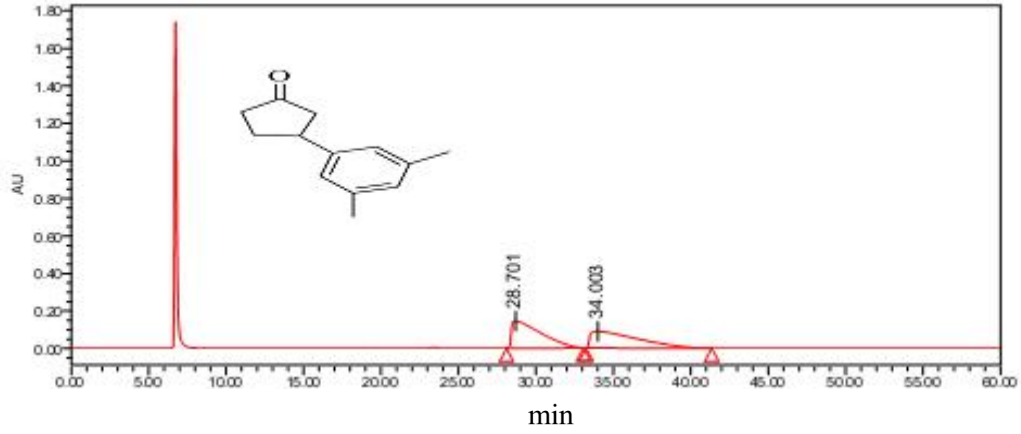
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 107.548              | 73618514          | 49.90         | 313379            |
| 2 | W2489 ChA 254nm                | 117.400              | 73908719          | 50.10         | 225990            |



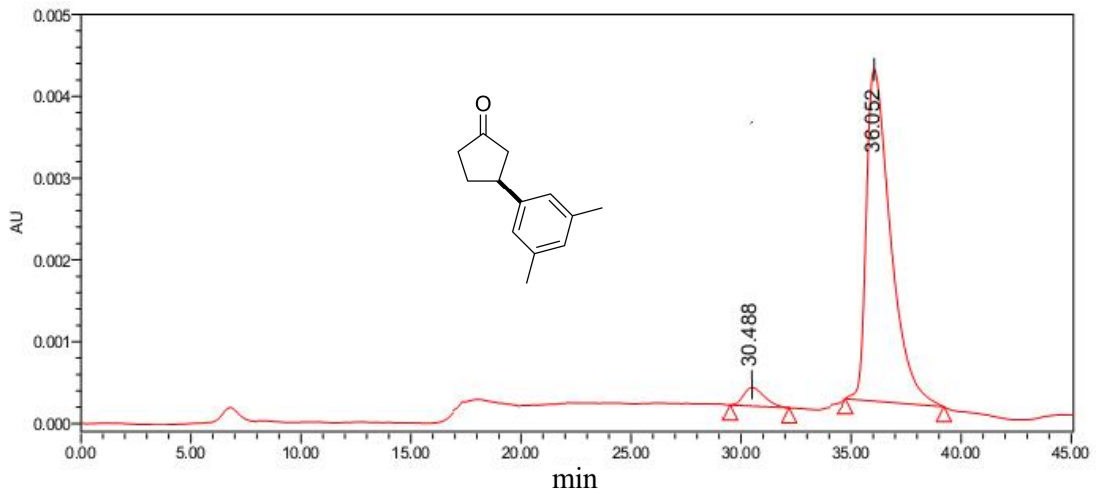
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 113.460              | 6645904           | 7.93          | 46085             |
| 2 | W2489 ChA 254nm                | 119.620              | 77112165          | 92.07         | 183440            |



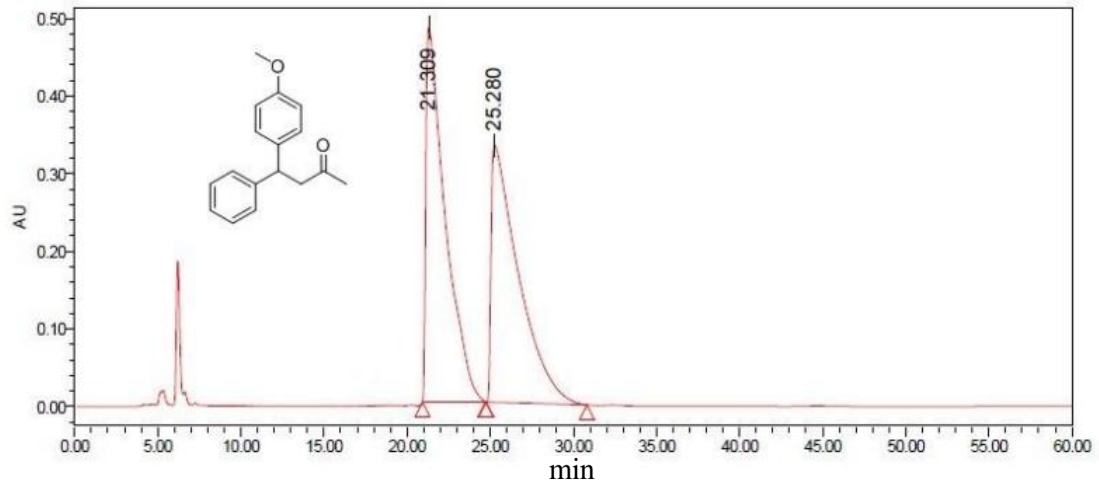
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 28.701               | 19301306          | 50.37         | 145569            |
| 2 | W2489 ChA 254nm                | 34.003               | 19017006          | 49.63         | 88236             |



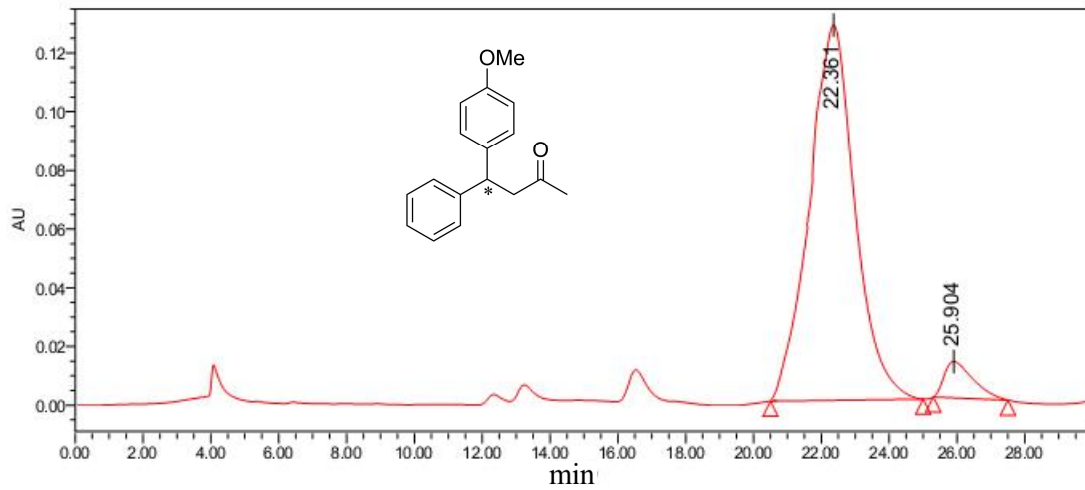
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 30.488               | 15617             | 4.79          | 677               |
| 2 | W2489 ChA 254nm                | 36.052               | 310650            | 95.21         | 4055              |



Processing channel description: W2489 ChA 254nm

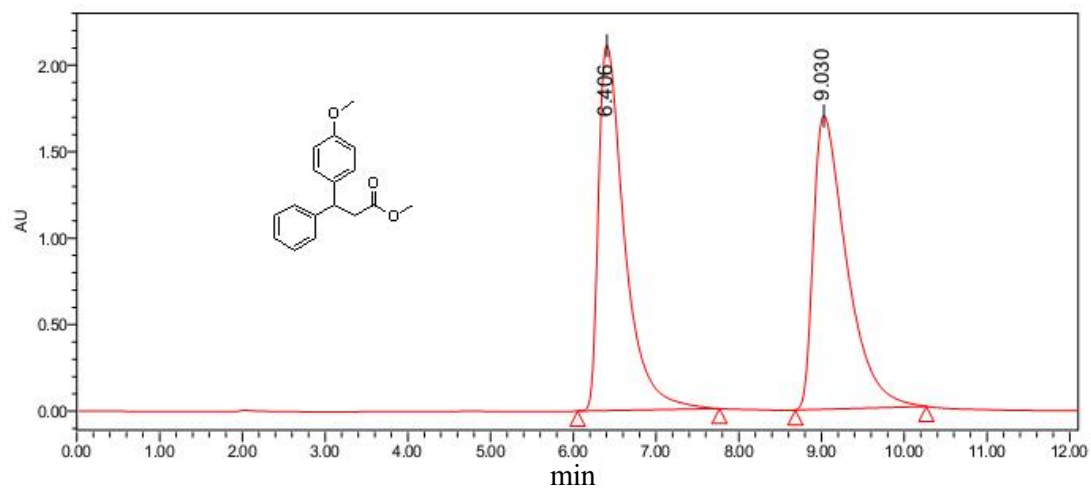
|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 21.309               | 39040087          | 50.73         | 482751            |
| 2 | W2489 ChA 254nm                | 25.280               | 37922434          | 49.27         | 330750            |



Processing channel description: W2489 ChA 254nm

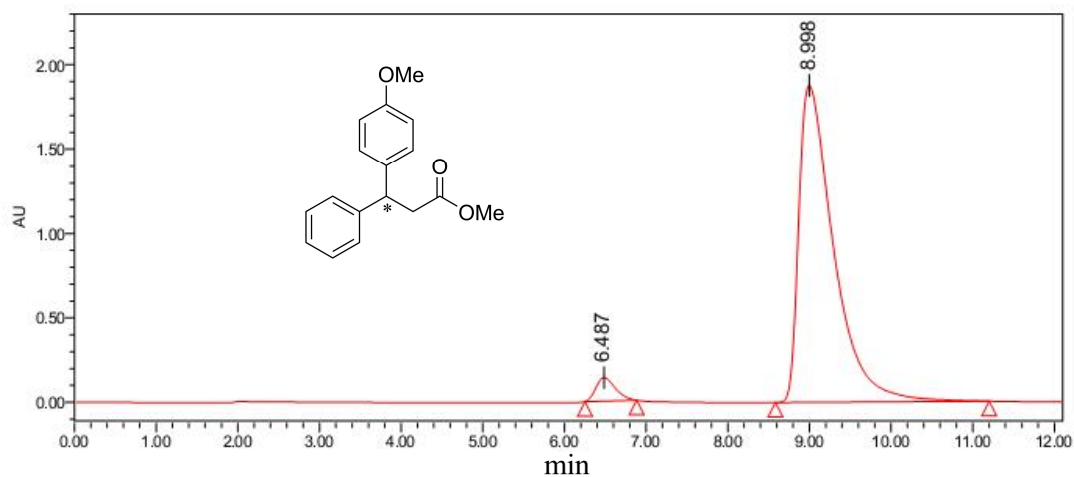
|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 22.361               | 10837909          | 93.66         | 127959            |
| 2 | W2489 ChA 254nm                | 25.904               | 733146            | 6.34          | 12362             |





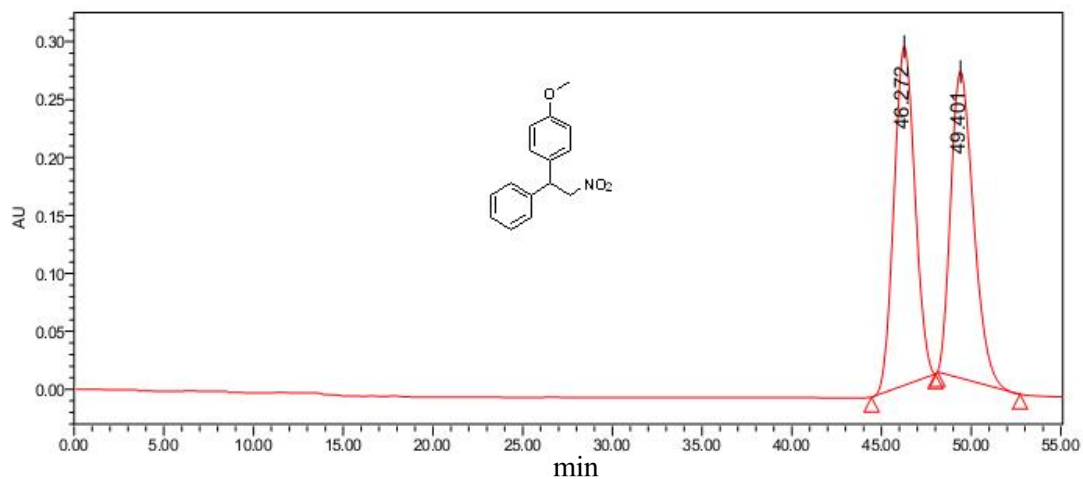
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 6.406                | 46376414          | 49.43         | 2115166           |
| 2 | W2489 ChA 254nm                | 9.030                | 47447740          | 50.57         | 1696895           |



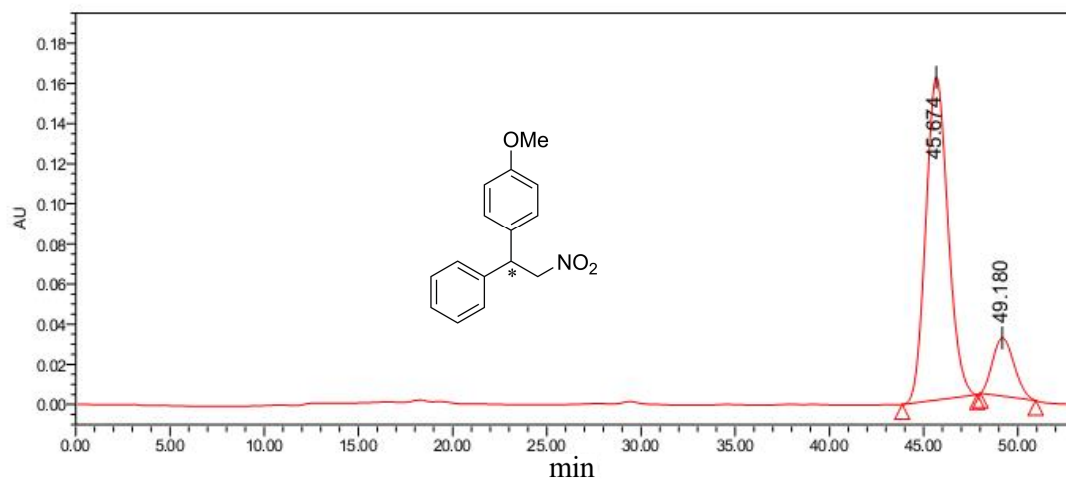
Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 6.487                | 2308872           | 3.98          | 139452            |
| 2 | W2489 ChA 254nm                | 8.998                | 55746656          | 96.02         | 1878035           |



Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 46.272               | 23671274          | 50.29         | 292156            |
| 2 | W2489 ChA 254nm                | 49.401               | 23402266          | 49.71         | 264516            |

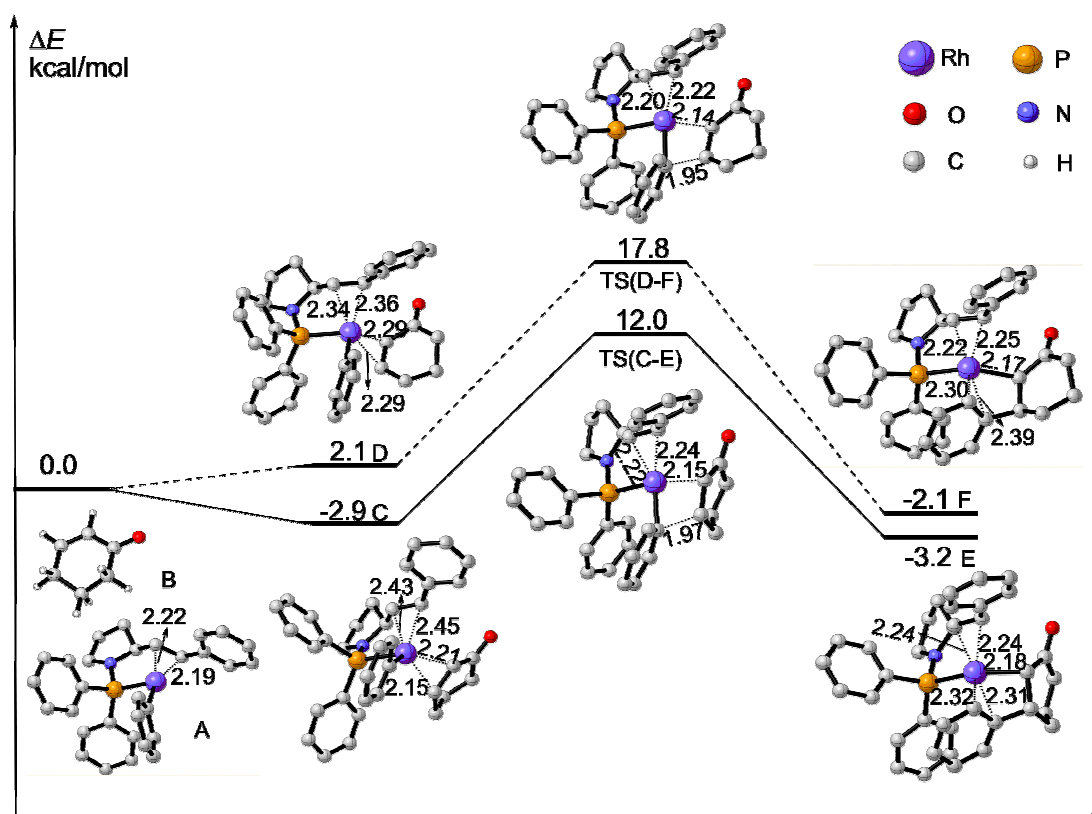


Processing channel description: W2489 ChA 254nm

|   | Processing channel description | Retention time (min) | Peak area (uAU*s) | Peak area (%) | Peak height (uAU) |
|---|--------------------------------|----------------------|-------------------|---------------|-------------------|
| 1 | W2489 ChA 254nm                | 45.674               | 13194880          | 85.08         | 160900            |
| 2 | W2489 ChA 254nm                | 49.180               | 2313883           | 14.92         | 29039             |

## 6. Computational Details

The B3PW91 functional<sup>3</sup> planted in Gaussian 09 software package<sup>4</sup> was used for geometrical optimization and subsequent frequency calculations without any symmetry or geometrical constraints. In these calculations, the 6-31G(d) basis set was used for C, H, N, O, and P atoms, and LanL2DZ basis set together with associated effective core potential (ECP) was applied for Rh atom. To obtain more accurate energies, single-point energy calculations were performed with larger basis sets, viz., 6-311+G(d, p) for C, H, N, O, and P atoms, and the Stuttgart/Dresden ECP and associated basis set (8s7p6d)/[6s5p3d] for Rh atom. The energy profiles were described by these single-point energies including zero-point energy corrections. The stationary points reported are their lowest conformations in energy along the reaction pathway.



**Figure S1.** Computed energy profiles (energies in kcal/mol) for the different stereochemical pathway and optimized geometric structures (Distances are shown in Å, H atom is omitted for clarity) in the arylation of cyclohexenone and the arylrhodium species. Solid line denotes the *si*-face insertion to give (*S*)-configuration, whereas dashed line denotes the *re*-face insertion to get (*R*)-configuration.

**7. Table S1.** Optimized Cartesian Coordinates (Å) and Electronic Energy (a.u., including zero-point energy correction) of Cationic Species **A**, **B**, **C**, **TS(C-E)**, **E**, **D**, **TS(D-F)** and **F**.

| Atom                    | X            | Y            | Z            |
|-------------------------|--------------|--------------|--------------|
| <b>A</b> , -1666.696524 |              |              |              |
| C                       | 1.204188000  | -2.077088000 | -0.743583000 |
| C                       | -0.059647000 | -2.846866000 | -0.451639000 |
| C                       | 2.164594000  | -1.894029000 | 0.250514000  |
| P                       | -1.107646000 | -0.395318000 | -0.062628000 |
| C                       | -2.116957000 | 0.564167000  | -1.252820000 |
| Rh                      | 1.040933000  | -0.025486000 | 0.082295000  |
| C                       | -2.091275000 | -0.335390000 | 1.493773000  |
| C                       | -1.399530000 | -0.410912000 | 2.709713000  |
| C                       | -2.090829000 | -0.463306000 | 3.918662000  |
| C                       | -3.485194000 | -0.441518000 | 3.925265000  |
| C                       | -4.184970000 | -0.367938000 | 2.720817000  |
| C                       | -3.493723000 | -0.315692000 | 1.511267000  |
| C                       | -2.249607000 | 0.119801000  | -2.574424000 |
| C                       | -2.952012000 | 0.879147000  | -3.508406000 |
| C                       | -3.519934000 | 2.096742000  | -3.135646000 |
| C                       | -3.374314000 | 2.555848000  | -1.826542000 |
| C                       | -2.674128000 | 1.798171000  | -0.890513000 |
| N                       | -1.234276000 | -1.990167000 | -0.661170000 |
| C                       | -0.402270000 | -4.032651000 | -1.357632000 |
| C                       | -1.908432000 | -4.221994000 | -1.114062000 |
| C                       | -2.443003000 | -2.805605000 | -0.777554000 |
| C                       | 3.470748000  | -1.247351000 | 0.067732000  |
| C                       | 0.548463000  | 2.594814000  | 1.473879000  |
| C                       | 0.615024000  | 3.985307000  | 1.600362000  |
| C                       | 0.818752000  | 4.783094000  | 0.475589000  |
| C                       | 0.955360000  | 4.180096000  | -0.775801000 |
| C                       | 0.897196000  | 2.791133000  | -0.896901000 |
| C                       | 0.715806000  | 1.964814000  | 0.227610000  |
| C                       | 4.344121000  | -1.138811000 | 1.169002000  |
| C                       | 5.562775000  | -0.480731000 | 1.058113000  |
| C                       | 5.941335000  | 0.098127000  | -0.154798000 |
| C                       | 5.088036000  | 0.008801000  | -1.253724000 |
| C                       | 3.868405000  | -0.655475000 | -1.150092000 |
| H                       | 1.443670000  | -1.944689000 | -1.798486000 |
| H                       | -0.015280000 | -3.201986000 | 0.594814000  |
| H                       | 2.000132000  | -2.358330000 | 1.223037000  |
| H                       | -0.310767000 | -0.419545000 | 2.687909000  |
| H                       | -1.541256000 | -0.513732000 | 4.855413000  |
| H                       | -4.026585000 | -0.477559000 | 4.867448000  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | -5.272102000 | -0.347905000 | 2.722590000  |
| H | -4.047709000 | -0.243258000 | 0.578822000  |
| H | -1.791703000 | -0.821976000 | -2.864625000 |
| H | -3.053241000 | 0.519397000  | -4.529569000 |
| H | -4.066944000 | 2.690000000  | -3.864184000 |
| H | -3.800925000 | 3.511452000  | -1.532547000 |
| H | -2.551658000 | 2.173409000  | 0.121683000  |
| H | 0.185433000  | -4.926115000 | -1.124014000 |
| H | -0.207524000 | -3.756566000 | -2.401391000 |
| H | -2.421882000 | -4.664088000 | -1.973663000 |
| H | -2.069444000 | -4.891808000 | -0.261979000 |
| H | -3.026625000 | -2.818630000 | 0.154923000  |
| H | -3.092452000 | -2.403871000 | -1.564618000 |
| H | 0.367201000  | 1.996830000  | 2.365176000  |
| H | 0.496719000  | 4.445282000  | 2.580117000  |
| H | 0.861027000  | 5.865934000  | 0.570704000  |
| H | 1.104119000  | 4.794767000  | -1.662017000 |
| H | 0.994636000  | 2.343976000  | -1.884835000 |
| H | 4.052592000  | -1.585144000 | 2.117422000  |
| H | 6.220028000  | -0.415326000 | 1.921629000  |
| H | 6.892656000  | 0.616334000  | -0.240958000 |
| H | 5.372943000  | 0.457439000  | -2.202003000 |
| H | 3.223684000  | -0.724724000 | -2.021430000 |

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**B, -308.5050468**

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -1.814503000 | 0.089813000  | 0.132657000  |
| C | -0.962219000 | 1.320405000  | 0.026578000  |
| C | 0.378584000  | 1.286493000  | -0.054130000 |
| C | 1.140809000  | 0.022544000  | 0.017537000  |
| C | 0.327251000  | -1.237605000 | 0.271835000  |
| C | -1.070338000 | -1.159075000 | -0.344397000 |
| H | -2.740827000 | 0.231110000  | -0.439229000 |
| H | -2.132290000 | -0.031528000 | 1.181639000  |
| H | -1.473694000 | 2.283030000  | 0.018004000  |
| H | 0.969370000  | 2.194285000  | -0.150523000 |
| O | 2.357317000  | 0.002310000  | -0.079034000 |
| H | 0.898680000  | -2.094958000 | -0.097490000 |
| H | 0.247516000  | -1.354673000 | 1.364170000  |
| H | -1.645553000 | -2.061548000 | -0.106611000 |
| H | -0.979243000 | -1.119659000 | -1.438167000 |

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**C, -1975.206249**

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.996027000  | 0.048308000  | -1.903299000 |
| C | -0.028783000 | -0.817850000 | -2.581287000 |
| C | 2.212408000  | -0.383521000 | -1.427635000 |
| P | -1.402685000 | 0.164780000  | -0.467434000 |

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -1.668147000 | 1.981948000  | -0.689887000 |
| Rh | 0.606013000  | -0.585940000 | 0.404880000  |
| C  | -3.010631000 | -0.445126000 | 0.184594000  |
| C  | -3.278024000 | -1.819696000 | 0.082326000  |
| C  | -4.459350000 | -2.354807000 | 0.588099000  |
| C  | -5.391193000 | -1.526481000 | 1.215255000  |
| C  | -5.135883000 | -0.161405000 | 1.321482000  |
| C  | -3.956748000 | 0.378239000  | 0.806705000  |
| C  | -1.713306000 | 2.536915000  | -1.976387000 |
| C  | -1.840038000 | 3.913262000  | -2.160390000 |
| C  | -1.918588000 | 4.761696000  | -1.058144000 |
| C  | -1.854998000 | 4.224554000  | 0.226928000  |
| C  | -1.723048000 | 2.849526000  | 0.413444000  |
| N  | -1.361586000 | -0.534399000 | -2.012495000 |
| C  | -0.257800000 | -0.572617000 | -4.079516000 |
| C  | -1.686113000 | -1.091118000 | -4.287548000 |
| C  | -2.432607000 | -0.683692000 | -3.001378000 |
| C  | 3.332423000  | 0.498457000  | -1.036878000 |
| C  | -0.707085000 | 0.590602000  | 2.911495000  |
| C  | -0.767377000 | 1.529612000  | 3.945933000  |
| C  | 0.206617000  | 2.520643000  | 4.058351000  |
| C  | 1.246283000  | 2.559883000  | 3.128711000  |
| C  | 1.308692000  | 1.625885000  | 2.091659000  |
| C  | 0.326065000  | 0.633636000  | 1.963202000  |
| C  | 4.487173000  | -0.074098000 | -0.475873000 |
| C  | 5.573136000  | 0.720548000  | -0.119545000 |
| C  | 5.535661000  | 2.100395000  | -0.318484000 |
| C  | 4.397565000  | 2.680039000  | -0.880524000 |
| C  | 3.309657000  | 1.889453000  | -1.238419000 |
| H  | 0.805528000  | 1.117905000  | -1.985392000 |
| H  | 0.238211000  | -1.878558000 | -2.436203000 |
| H  | 2.467031000  | -1.439048000 | -1.514309000 |
| H  | -2.557271000 | -2.469061000 | -0.407486000 |
| H  | -4.652548000 | -3.420483000 | 0.493138000  |
| H  | -6.312232000 | -1.943748000 | 1.614105000  |
| H  | -5.859471000 | 0.493514000  | 1.800430000  |
| H  | -3.785755000 | 1.447511000  | 0.878618000  |
| H  | -1.638593000 | 1.889619000  | -2.844184000 |
| H  | -1.875925000 | 4.320464000  | -3.168015000 |
| H  | -2.017276000 | 5.835033000  | -1.199158000 |
| H  | -1.893777000 | 4.877924000  | 1.094801000  |
| H  | -1.641392000 | 2.457855000  | 1.422707000  |
| H  | 0.484482000  | -1.081575000 | -4.702000000 |
| H  | -0.197277000 | 0.502698000  | -4.291516000 |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | -2.164507000 | -0.690662000 | -5.186855000 |
| H | -1.673091000 | -2.183595000 | -4.381747000 |
| H | -3.160308000 | -1.445424000 | -2.694741000 |
| H | -2.988427000 | 0.253874000  | -3.133772000 |
| H | -1.479382000 | -0.172260000 | 2.845819000  |
| H | -1.581369000 | 1.479326000  | 4.666932000  |
| H | 0.162475000  | 3.248216000  | 4.865114000  |
| H | 2.020241000  | 3.320850000  | 3.206638000  |
| H | 2.128794000  | 1.676217000  | 1.378505000  |
| H | 4.508902000  | -1.147474000 | -0.298747000 |
| H | 6.454368000  | 0.256142000  | 0.316393000  |
| H | 6.386127000  | 2.719237000  | -0.043367000 |
| H | 4.358265000  | 3.753599000  | -1.048912000 |
| H | 2.441768000  | 2.364304000  | -1.687491000 |
| C | -0.290578000 | -3.277472000 | 1.666118000  |
| C | 0.614580000  | -2.098554000 | 1.937482000  |
| C | 1.930002000  | -2.052653000 | 1.393294000  |
| C | 2.424456000  | -3.108277000 | 0.500878000  |
| C | 1.475201000  | -4.259205000 | 0.176642000  |
| C | -0.006676000 | -3.915190000 | 0.308727000  |
| H | -1.340828000 | -2.972488000 | 1.745834000  |
| H | -0.128615000 | -4.027760000 | 2.459313000  |
| H | 0.466719000  | -1.635867000 | 2.910458000  |
| H | 2.702323000  | -1.453153000 | 1.873504000  |
| O | 3.572848000  | -3.137970000 | 0.058359000  |
| H | 1.730617000  | -4.638353000 | -0.819123000 |
| H | 1.727390000  | -5.064486000 | 0.884341000  |
| H | -0.619080000 | -4.814832000 | 0.164932000  |
| H | -0.291926000 | -3.206360000 | -0.482877000 |

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**TS(C-E), -1975.182372, Imaginary frequency = 286.62i**

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|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 1.135127000  | 1.051891000  | -1.488841000 |
| C  | 0.247593000  | 0.769944000  | -2.670411000 |
| C  | 2.344655000  | 0.403178000  | -1.235727000 |
| P  | -1.315287000 | 0.479841000  | -0.524912000 |
| C  | -1.712878000 | 2.092231000  | 0.280525000  |
| Rh | 0.739277000  | -0.502100000 | 0.040929000  |
| C  | -2.907371000 | -0.445255000 | -0.478512000 |
| C  | -3.018911000 | -1.561105000 | -1.322917000 |
| C  | -4.177463000 | -2.333167000 | -1.334869000 |
| C  | -5.245587000 | -2.003974000 | -0.499326000 |
| C  | -5.147609000 | -0.894469000 | 0.337770000  |
| C  | -3.988175000 | -0.118365000 | 0.348062000  |
| C  | -1.703079000 | 3.291685000  | -0.442683000 |
| C  | -1.904901000 | 4.513731000  | 0.198817000  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -2.115692000 | 4.555321000  | 1.575516000  |
| C | -2.107738000 | 3.368551000  | 2.308853000  |
| C | -1.898411000 | 2.147656000  | 1.671007000  |
| N | -1.139292000 | 0.748809000  | -2.185296000 |
| C | 0.181658000  | 1.827798000  | -3.779579000 |
| C | -1.201372000 | 1.573866000  | -4.397056000 |
| C | -2.096600000 | 1.190187000  | -3.197783000 |
| C | 3.442834000  | 0.970275000  | -0.424871000 |
| C | -1.242490000 | -1.567417000 | 2.261155000  |
| C | -1.890147000 | -1.226432000 | 3.451698000  |
| C | -1.256608000 | -0.420203000 | 4.395459000  |
| C | 0.036693000  | 0.048350000  | 4.135820000  |
| C | 0.684235000  | -0.297216000 | 2.955394000  |
| C | 0.052397000  | -1.101389000 | 1.979599000  |
| C | 4.707163000  | 0.360363000  | -0.496088000 |
| C | 5.788532000  | 0.867477000  | 0.220607000  |
| C | 5.631624000  | 1.993344000  | 1.027685000  |
| C | 4.379653000  | 2.605801000  | 1.111774000  |
| C | 3.298067000  | 2.102335000  | 0.395666000  |
| H | 0.973615000  | 2.038828000  | -1.050467000 |
| H | 0.524305000  | -0.202263000 | -3.109403000 |
| H | 2.648729000  | -0.401256000 | -1.902328000 |
| H | -2.192770000 | -1.812256000 | -1.983607000 |
| H | -4.247391000 | -3.191405000 | -1.998711000 |
| H | -6.150671000 | -2.606060000 | -0.506344000 |
| H | -5.979334000 | -0.623617000 | 0.983590000  |
| H | -3.935017000 | 0.752205000  | 0.994140000  |
| H | -1.523969000 | 3.273203000  | -1.513152000 |
| H | -1.895554000 | 5.434129000  | -0.380231000 |
| H | -2.273241000 | 5.507212000  | 2.076371000  |
| H | -2.250959000 | 3.391250000  | 3.386382000  |
| H | -1.861973000 | 1.237720000  | 2.264043000  |
| H | 0.999964000  | 1.734559000  | -4.500347000 |
| H | 0.231715000  | 2.831055000  | -3.336262000 |
| H | -1.594013000 | 2.435468000  | -4.946503000 |
| H | -1.143890000 | 0.735997000  | -5.102099000 |
| H | -2.805230000 | 0.393292000  | -3.459540000 |
| H | -2.691234000 | 2.042311000  | -2.843627000 |
| H | -1.766867000 | -2.183753000 | 1.536435000  |
| H | -2.898707000 | -1.591618000 | 3.633177000  |
| H | -1.755654000 | -0.167239000 | 5.327593000  |
| H | 0.546597000  | 0.673675000  | 4.865445000  |
| H | 1.702562000  | 0.045518000  | 2.780615000  |
| H | 4.822364000  | -0.528923000 | -1.111363000 |



|   |              |              |              |
|---|--------------|--------------|--------------|
| H | 6.757612000  | 0.379564000  | 0.146751000  |
| H | 6.474796000  | 2.391083000  | 1.586972000  |
| H | 4.244491000  | 3.483359000  | 1.739873000  |
| H | 2.331084000  | 2.590063000  | 0.485230000  |
| C | 0.499158000  | -3.745170000 | 1.026014000  |
| C | 1.284354000  | -2.480096000 | 1.311223000  |
| C | 2.220039000  | -2.034711000 | 0.296445000  |
| C | 2.318774000  | -2.735967000 | -0.995380000 |
| C | 1.267931000  | -3.783929000 | -1.349393000 |
| C | 0.052178000  | -3.815402000 | -0.427197000 |
| H | -0.342592000 | -3.846408000 | 1.717537000  |
| H | 1.178908000  | -4.585512000 | 1.240462000  |
| H | 1.714357000  | -2.479464000 | 2.309771000  |
| H | 3.157049000  | -1.591609000 | 0.630764000  |
| O | 3.255866000  | -2.545034000 | -1.771243000 |
| H | 0.988217000  | -3.638726000 | -2.399251000 |
| H | 1.791525000  | -4.751212000 | -1.309773000 |
| H | -0.541294000 | -4.720461000 | -0.608342000 |
| H | -0.593386000 | -2.951518000 | -0.635660000 |

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**E, -1975.206664**

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|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -0.955650000 | 1.223631000  | 1.381680000  |
| C  | -0.094232000 | 0.782905000  | 2.532490000  |
| C  | -2.235376000 | 0.755161000  | 1.096572000  |
| P  | 1.395476000  | 0.460775000  | 0.316254000  |
| C  | 1.954610000  | 2.102913000  | -0.330547000 |
| Rh | -0.766602000 | -0.411204000 | -0.133942000 |
| C  | 2.895086000  | -0.601346000 | 0.178801000  |
| C  | 2.837779000  | -1.844493000 | 0.828156000  |
| C  | 3.916753000  | -2.721665000 | 0.784151000  |
| C  | 5.072898000  | -2.373717000 | 0.082729000  |
| C  | 5.142692000  | -1.139651000 | -0.558902000 |
| C  | 4.063000000  | -0.255845000 | -0.508382000 |
| C  | 1.955717000  | 3.238685000  | 0.489650000  |
| C  | 2.285226000  | 4.493915000  | -0.022260000 |
| C  | 2.619235000  | 4.636934000  | -1.366874000 |
| C  | 2.609908000  | 3.516930000  | -2.198653000 |
| C  | 2.273221000  | 2.265375000  | -1.687825000 |
| N  | 1.269964000  | 0.607823000  | 2.003046000  |
| C  | 0.127939000  | 1.769163000  | 3.686977000  |
| C  | 1.485622000  | 1.319770000  | 4.245600000  |
| C  | 2.298397000  | 0.906749000  | 2.999482000  |
| C  | -3.209718000 | 1.462776000  | 0.242273000  |
| C  | 0.687849000  | -2.526035000 | -2.012061000 |
| C  | 1.607864000  | -1.898542000 | -2.830905000 |

|   |               |               |               |
|---|---------------|---------------|---------------|
| C | 1. 270712000  | -0. 698285000 | -3. 483051000 |
| C | 0. 033922000  | -0. 116965000 | -3. 272383000 |
| C | -0. 913060000 | -0. 741032000 | -2. 427601000 |
| C | -0. 610810000 | -1. 990825000 | -1. 813210000 |
| C | -4. 557945000 | 1. 072713000  | 0. 312269000  |
| C | -5. 529964000 | 1. 718559000  | -0. 448333000 |
| C | -5. 176064000 | 2. 765025000  | -1. 298804000 |
| C | -3. 838366000 | 3. 157473000  | -1. 383118000 |
| C | -2. 865802000 | 2. 515154000  | -0. 623748000 |
| H | -0. 648598000 | 2. 177443000  | 0. 949204000  |
| H | -0. 480605000 | -0. 164604000 | 2. 939980000  |
| H | -2. 674520000 | 0. 007539000  | 1. 753007000  |
| H | 1. 940258000  | -2. 114113000 | 1. 379229000  |
| H | 3. 856330000  | -3. 678559000 | 1. 296966000  |
| H | 5. 916002000  | -3. 058964000 | 0. 044472000  |
| H | 6. 044162000  | -0. 854223000 | -1. 095755000 |
| H | 4. 144037000  | 0. 710721000  | -0. 995540000 |
| H | 1. 689798000  | 3. 144219000  | 1. 537590000  |
| H | 2. 280091000  | 5. 360674000  | 0. 634260000  |
| H | 2. 877722000  | 5. 614084000  | -1. 766671000 |
| H | 2. 857800000  | 3. 618915000  | -3. 252556000 |
| H | 2. 241149000  | 1. 407343000  | -2. 351867000 |
| H | -0. 676950000 | 1. 733753000  | 4. 427622000  |
| H | 0. 183551000  | 2. 794230000  | 3. 297669000  |
| H | 1. 991276000  | 2. 094347000  | 4. 831179000  |
| H | 1. 344804000  | 0. 452890000  | 4. 902193000  |
| H | 2. 931830000  | 0. 032577000  | 3. 198123000  |
| H | 2. 961415000  | 1. 714776000  | 2. 661818000  |
| H | 0. 957519000  | -3. 466359000 | -1. 541612000 |
| H | 2. 590471000  | -2. 338577000 | -2. 976330000 |
| H | 1. 983705000  | -0. 235318000 | -4. 162264000 |
| H | -0. 238266000 | 0. 803052000  | -3. 783344000 |
| H | -1. 943623000 | -0. 394401000 | -2. 467198000 |
| H | -4. 826359000 | 0. 246875000  | 0. 967034000  |
| H | -6. 567772000 | 1. 402005000  | -0. 375092000 |
| H | -5. 933299000 | 3. 270671000  | -1. 892896000 |
| H | -3. 551268000 | 3. 970347000  | -2. 046344000 |
| H | -1. 828219000 | 2. 825128000  | -0. 716829000 |
| C | -1. 432894000 | -4. 154008000 | -0. 671376000 |
| C | -1. 793352000 | -2. 773074000 | -1. 226818000 |
| C | -2. 413928000 | -1. 833870000 | -0. 181564000 |
| C | -2. 626137000 | -2. 345456000 | 1. 181282000  |
| C | -1. 768891000 | -3. 497916000 | 1. 700911000  |
| C | -0. 764038000 | -4. 053988000 | 0. 697028000  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | -0.809918000 | -4.700949000 | -1.390518000 |
| H | -2.360129000 | -4.735480000 | -0.568185000 |
| H | -2.507300000 | -2.929423000 | -2.050115000 |
| H | -3.303690000 | -1.305928000 | -0.530095000 |
| O | -3.478750000 | -1.877788000 | 1.943816000  |
| H | -1.284831000 | -3.161051000 | 2.626287000  |
| H | -2.475518000 | -4.282969000 | 2.004202000  |
| H | -0.396098000 | -5.033754000 | 1.028039000  |
| H | 0.107000000  | -3.389484000 | 0.634252000  |

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**D, -1975.198152**

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|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.705968000  | 1.963495000  | -0.859300000 |
| C  | -0.262290000 | 2.084576000  | -2.001493000 |
| C  | 1.994597000  | 1.474312000  | -0.975475000 |
| P  | -1.538734000 | 0.412163000  | -0.319846000 |
| C  | -2.258962000 | 1.225659000  | 1.166802000  |
| Rh | 0.604109000  | -0.307493000 | -0.295826000 |
| C  | -2.840029000 | -0.762162000 | -0.879308000 |
| C  | -2.530231000 | -1.566669000 | -1.986892000 |
| C  | -3.471232000 | -2.448458000 | -2.510524000 |
| C  | -4.737626000 | -2.542845000 | -1.930404000 |
| C  | -5.056786000 | -1.744120000 | -0.834768000 |
| C  | -4.115659000 | -0.855274000 | -0.312683000 |
| C  | -2.372095000 | 2.622199000  | 1.208584000  |
| C  | -2.825060000 | 3.268700000  | 2.357919000  |
| C  | -3.170378000 | 2.527725000  | 3.486308000  |
| C  | -3.051573000 | 1.138067000  | 3.460115000  |
| C  | -2.595366000 | 0.489156000  | 2.314669000  |
| N  | -1.560011000 | 1.572839000  | -1.551334000 |
| C  | -0.630940000 | 3.496026000  | -2.476797000 |
| C  | -2.007663000 | 3.274686000  | -3.120401000 |
| C  | -2.685785000 | 2.211407000  | -2.228577000 |
| C  | 3.026739000  | 1.663090000  | 0.064574000  |
| C  | -0.956653000 | -2.531567000 | 1.273688000  |
| C  | -1.227543000 | -3.234186000 | 2.452377000  |
| C  | -0.588839000 | -2.891348000 | 3.642640000  |
| C  | 0.327525000  | -1.838728000 | 3.639367000  |
| C  | 0.590882000  | -1.133020000 | 2.463590000  |
| C  | -0.044514000 | -1.467669000 | 1.254907000  |
| C  | 4.384274000  | 1.544362000  | -0.279949000 |
| C  | 5.382944000  | 1.759144000  | 0.667742000  |
| C  | 5.051232000  | 2.096998000  | 1.978536000  |
| C  | 3.706768000  | 2.215739000  | 2.335854000  |
| C  | 2.707093000  | 2.002738000  | 1.392541000  |
| H  | 0.436015000  | 2.543111000  | 0.023486000  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | 0.118050000  | 1.505299000  | -2.860047000 |
| H | 2.363216000  | 1.169197000  | -1.953107000 |
| H | -1.541788000 | -1.492966000 | -2.435178000 |
| H | -3.216096000 | -3.065431000 | -3.368593000 |
| H | -5.471974000 | -3.235543000 | -2.333736000 |
| H | -6.043369000 | -1.807971000 | -0.382412000 |
| H | -4.379830000 | -0.232369000 | 0.536486000  |
| H | -2.099080000 | 3.206353000  | 0.334500000  |
| H | -2.909116000 | 4.352792000  | 2.368613000  |
| H | -3.524958000 | 3.029680000  | 4.383034000  |
| H | -3.306948000 | 0.551847000  | 4.339281000  |
| H | -2.489513000 | -0.591576000 | 2.319746000  |
| H | 0.107989000  | 3.912941000  | -3.168015000 |
| H | -0.707643000 | 4.168936000  | -1.612872000 |
| H | -2.601185000 | 4.191357000  | -3.195055000 |
| H | -1.881641000 | 2.882632000  | -4.136602000 |
| H | -3.266058000 | 1.492852000  | -2.822178000 |
| H | -3.373806000 | 2.667274000  | -1.503454000 |
| H | -1.469522000 | -2.825034000 | 0.361067000  |
| H | -1.940561000 | -4.056600000 | 2.433328000  |
| H | -0.796764000 | -3.438309000 | 4.559098000  |
| H | 0.838805000  | -1.557577000 | 4.558180000  |
| H | 1.307109000  | -0.314091000 | 2.491114000  |
| H | 4.648988000  | 1.269853000  | -1.297069000 |
| H | 6.426158000  | 1.663878000  | 0.376366000  |
| H | 5.831121000  | 2.266981000  | 2.716534000  |
| H | 3.435032000  | 2.476028000  | 3.356082000  |
| H | 1.666387000  | 2.087594000  | 1.694057000  |
| C | 2.042431000  | -3.270920000 | -0.081248000 |
| C | 1.206595000  | -2.396701000 | -1.003068000 |
| C | 1.822257000  | -1.470628000 | -1.850694000 |
| C | 3.277375000  | -1.273931000 | -1.885030000 |
| C | 4.107188000  | -2.085716000 | -0.905312000 |
| C | 3.466813000  | -3.444200000 | -0.615953000 |
| H | 1.554303000  | -4.246031000 | 0.028895000  |
| H | 2.085852000  | -2.845809000 | 0.928431000  |
| H | 0.234005000  | -2.786567000 | -1.292255000 |
| H | 1.300861000  | -1.092808000 | -2.729914000 |
| O | 3.802580000  | -0.509931000 | -2.693740000 |
| H | 5.115596000  | -2.178506000 | -1.322378000 |
| H | 4.198655000  | -1.504933000 | 0.025255000  |
| H | 4.073380000  | -4.005075000 | 0.106042000  |
| H | 3.445132000  | -4.036722000 | -1.541600000 |

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**TS(D-F)**, -1975.173234, Imaginary frequency = 292.49i

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|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.609471000  | 2.011742000  | -0.635328000 |
| C  | -0.380962000 | 2.333844000  | -1.719606000 |
| C  | 1.920111000  | 1.565131000  | -0.841330000 |
| P  | -1.624673000 | 0.473849000  | -0.248994000 |
| C  | -2.381219000 | 1.003034000  | 1.341258000  |
| Rh | 0.611378000  | -0.171296000 | -0.379473000 |
| C  | -2.880872000 | -0.650824000 | -0.991973000 |
| C  | -2.519097000 | -1.295037000 | -2.185659000 |
| C  | -3.424191000 | -2.114264000 | -2.854704000 |
| C  | -4.706122000 | -2.307585000 | -2.336144000 |
| C  | -5.075766000 | -1.670956000 | -1.153453000 |
| C  | -4.170757000 | -0.844087000 | -0.485797000 |
| C  | -2.563796000 | 2.360771000  | 1.633601000  |
| C  | -3.027495000 | 2.762709000  | 2.885896000  |
| C  | -3.309201000 | 1.812876000  | 3.865958000  |
| C  | -3.112429000 | 0.458927000  | 3.590568000  |
| C  | -2.645836000 | 0.055256000  | 2.341977000  |
| N  | -1.678111000 | 1.818301000  | -1.273739000 |
| C  | -0.715481000 | 3.805947000  | -1.988777000 |
| C  | -2.121210000 | 3.713820000  | -2.604133000 |
| C  | -2.801873000 | 2.543910000  | -1.855362000 |
| C  | 2.973366000  | 1.723994000  | 0.187383000  |
| C  | -0.848710000 | -2.871998000 | 0.608512000  |
| C  | -1.406500000 | -3.483219000 | 1.732475000  |
| C  | -0.877875000 | -3.241639000 | 2.999814000  |
| C  | 0.217067000  | -2.381750000 | 3.129666000  |
| C  | 0.781782000  | -1.787305000 | 2.005881000  |
| C  | 0.247125000  | -1.998677000 | 0.716883000  |
| C  | 4.319519000  | 1.817939000  | -0.204232000 |
| C  | 5.328730000  | 2.004846000  | 0.739323000  |
| C  | 5.019826000  | 2.102380000  | 2.094743000  |
| C  | 3.686663000  | 2.007923000  | 2.499199000  |
| C  | 2.677447000  | 1.822045000  | 1.560170000  |
| H  | 0.381399000  | 2.496480000  | 0.316127000  |
| H  | -0.060087000 | 1.855004000  | -2.660224000 |
| H  | 2.280296000  | 1.409259000  | -1.856728000 |
| H  | -1.516214000 | -1.146330000 | -2.582977000 |
| H  | -3.129063000 | -2.605849000 | -3.778585000 |
| H  | -5.412978000 | -2.950882000 | -2.854258000 |
| H  | -6.074546000 | -1.812466000 | -0.747518000 |
| H  | -4.473989000 | -0.347642000 | 0.431390000  |
| H  | -2.331104000 | 3.105323000  | 0.877649000  |
| H  | -3.167929000 | 3.820693000  | 3.094531000  |
| H  | -3.670989000 | 2.125361000  | 4.842341000  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | -3.313804000 | -0.288016000 | 4.354604000  |
| H | -2.472932000 | -1.000629000 | 2.149931000  |
| H | 0.011185000  | 4.291847000  | -2.647397000 |
| H | -0.739637000 | 4.356725000  | -1.039508000 |
| H | -2.689202000 | 4.645824000  | -2.520358000 |
| H | -2.041240000 | 3.475251000  | -3.671263000 |
| H | -3.389237000 | 1.913629000  | -2.537219000 |
| H | -3.485262000 | 2.900111000  | -1.072893000 |
| H | -1.275219000 | -3.080431000 | -0.369907000 |
| H | -2.254223000 | -4.154237000 | 1.611834000  |
| H | -1.302489000 | -3.726293000 | 3.875459000  |
| H | 0.639452000  | -2.182040000 | 4.111980000  |
| H | 1.644192000  | -1.133596000 | 2.125691000  |
| H | 4.570832000  | 1.730832000  | -1.257085000 |
| H | 6.362367000  | 2.077046000  | 0.409000000  |
| H | 5.807350000  | 2.249979000  | 2.829557000  |
| H | 3.431107000  | 2.078262000  | 3.554074000  |
| H | 1.647588000  | 1.728786000  | 1.895593000  |
| C | 2.547320000  | -3.174962000 | 0.033582000  |
| C | 1.490023000  | -2.379056000 | -0.742337000 |
| C | 1.973433000  | -1.300900000 | -1.585542000 |
| C | 3.406811000  | -1.025377000 | -1.777804000 |
| C | 4.400795000  | -1.849229000 | -0.977460000 |
| C | 3.864069000  | -3.261369000 | -0.738157000 |
| H | 2.144270000  | -4.166617000 | 0.268491000  |
| H | 2.762474000  | -2.696635000 | 0.992737000  |
| H | 0.767277000  | -3.012886000 | -1.253522000 |
| H | 1.417825000  | -1.109995000 | -2.508165000 |
| O | 3.792438000  | -0.220702000 | -2.623356000 |
| H | 5.349457000  | -1.842714000 | -1.523774000 |
| H | 4.577157000  | -1.347090000 | -0.014324000 |
| H | 4.586082000  | -3.857328000 | -0.165904000 |
| H | 3.720206000  | -3.773763000 | -1.699710000 |

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**F, -1975.204948**

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|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -0.532165000 | -1.777549000 | -0.997025000 |
| C  | 0.459076000  | -1.772792000 | -2.125988000 |
| C  | -1.854497000 | -1.343348000 | -1.071277000 |
| P  | 1.701810000  | -0.314548000 | -0.235262000 |
| C  | 2.650120000  | -1.196229000 | 1.076861000  |
| Rh | -0.582736000 | 0.277363000  | -0.169430000 |
| C  | 2.840780000  | 1.040870000  | -0.761525000 |
| C  | 2.284365000  | 2.111855000  | -1.475065000 |
| C  | 3.095181000  | 3.107000000  | -2.015218000 |
| C  | 4.479172000  | 3.047293000  | -1.849756000 |

|   |               |               |               |
|---|---------------|---------------|---------------|
| C | 5. 045837000  | 1. 981816000  | -1. 152740000 |
| C | 4. 233638000  | 0. 981794000  | -0. 617159000 |
| C | 2. 584528000  | -2. 595536000 | 1. 139619000  |
| C | 3. 188329000  | -3. 294465000 | 2. 182998000  |
| C | 3. 869433000  | -2. 605597000 | 3. 185778000  |
| C | 3. 941514000  | -1. 213893000 | 3. 136146000  |
| C | 3. 335538000  | -0. 514730000 | 2. 093628000  |
| N | 1. 747976000  | -1. 375190000 | -1. 556197000 |
| C | 0. 809093000  | -3. 121651000 | -2. 768836000 |
| C | 2. 222043000  | -2. 868735000 | -3. 315134000 |
| C | 2. 884819000  | -1. 959573000 | -2. 257643000 |
| C | -2. 898200000 | -1. 844451000 | -0. 149206000 |
| C | 0. 330336000  | 3. 196372000  | 1. 127160000  |
| C | 1. 278471000  | 2. 997994000  | 2. 111864000  |
| C | 1. 144590000  | 1. 919025000  | 3. 007516000  |
| C | 0. 079850000  | 1. 046929000  | 2. 892698000  |
| C | -0. 902204000 | 1. 239237000  | 1. 890753000  |
| C | -0. 794358000 | 2. 344990000  | 1. 001591000  |
| C | -4. 223926000 | -1. 948193000 | -0. 602197000 |
| C | -5. 221568000 | -2. 472907000 | 0. 218518000  |
| C | -4. 919919000 | -2. 903963000 | 1. 508684000  |
| C | -3. 607259000 | -2. 800426000 | 1. 974614000  |
| C | -2. 610296000 | -2. 277142000 | 1. 158099000  |
| H | -0. 272497000 | -2. 479237000 | -0. 202092000 |
| H | 0. 125814000  | -1. 072802000 | -2. 910435000 |
| H | -2. 219822000 | -0. 908781000 | -1. 999932000 |
| H | 1. 205205000  | 2. 154338000  | -1. 603941000 |
| H | 2. 646374000  | 3. 930996000  | -2. 564686000 |
| H | 5. 113385000  | 3. 825340000  | -2. 267462000 |
| H | 6. 124457000  | 1. 922989000  | -1. 028241000 |
| H | 4. 690627000  | 0. 152501000  | -0. 084471000 |
| H | 2. 059034000  | -3. 138122000 | 0. 358141000  |
| H | 3. 129745000  | -4. 379917000 | 2. 209601000  |
| H | 4. 343355000  | -3. 149560000 | 3. 998888000  |
| H | 4. 474586000  | -0. 668216000 | 3. 911224000  |
| H | 3. 400980000  | 0. 568534000  | 2. 067467000  |
| H | 0. 092985000  | -3. 418653000 | -3. 541203000 |
| H | 0. 825117000  | -3. 903879000 | -1. 998417000 |
| H | 2. 790066000  | -3. 788848000 | -3. 486000000 |
| H | 2. 158658000  | -2. 339555000 | -4. 273386000 |
| H | 3. 521228000  | -1. 192961000 | -2. 720290000 |
| H | 3. 514922000  | -2. 534711000 | -1. 563916000 |
| H | 0. 416347000  | 4. 048745000  | 0. 456140000  |
| H | 2. 118257000  | 3. 681750000  | 2. 204209000  |

|   |               |               |               |
|---|---------------|---------------|---------------|
| H | 1. 875852000  | 1. 779302000  | 3. 799735000  |
| H | -0. 032684000 | 0. 223422000  | 3. 592887000  |
| H | -1. 841901000 | 0. 697117000  | 1. 981452000  |
| H | -4. 466913000 | -1. 602006000 | -1. 602607000 |
| H | -6. 239704000 | -2. 545555000 | -0. 156683000 |
| H | -5. 697895000 | -3. 314049000 | 2. 147835000  |
| H | -3. 360430000 | -3. 126223000 | 2. 982600000  |
| H | -1. 597628000 | -2. 178159000 | 1. 541522000  |
| C | -3. 236436000 | 3. 021482000  | 0. 968303000  |
| C | -1. 985021000 | 2. 725087000  | 0. 121983000  |
| C | -2. 143936000 | 1. 602088000  | -0. 898810000 |
| C | -3. 491137000 | 1. 233377000  | -1. 362227000 |
| C | -4. 683992000 | 1. 619677000  | -0. 501439000 |
| C | -4. 507117000 | 3. 004430000  | 0. 125217000  |
| H | -3. 103243000 | 3. 985205000  | 1. 476666000  |
| H | -3. 341348000 | 2. 266927000  | 1. 758702000  |
| H | -1. 722158000 | 3. 653922000  | -0. 408869000 |
| H | -1. 518790000 | 1. 764645000  | -1. 789383000 |
| O | -3. 677948000 | 0. 655240000  | -2. 435692000 |
| H | -5. 578344000 | 1. 554113000  | -1. 129306000 |
| H | -4. 789885000 | 0. 867183000  | 0. 294495000  |
| H | -5. 378205000 | 3. 257936000  | 0. 742549000  |
| H | -4. 449917000 | 3. 766735000  | -0. 665295000 |

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