

Supporting Information

Enantioselective Synthesis of Axially Chiral Vinyl arenes through Palladium-catalyzed C-H Olefination

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General Information

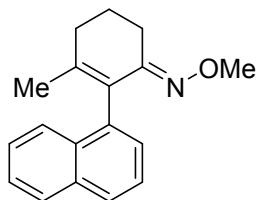
Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, all the aldehydes recrystallized or distilled prior to use. Dichloromethane, toluene, were freshly distilled from CaH₂, tetrahydrofuran (THF) and 1,4-dioxane were dried and distilled from metal sodium and benzophenone. MeOH solvents were not dried. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (300 - 400 mesh). ¹H, ¹³C NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in CDCl₃. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. HPLC was carried out with a Agilent 1260 infinity using a chiralcel AD-H column, a chiralcel OJ-H column, a chiralcel AS-H column, a chiralcel IB column, a chiralcel IC column, or a chiralcel OX-H column.

General procedure for the synthesis of parent enones.

Aryl boronic acid (5 mmol) and 2-iodo-3-methylcyclohex-2-en-1-one (5.5 mmol, 1.1 eq) were dissolved in 1,4-dioxane (40 mL) under nitrogen. To this mixture, Pd(PPh₃)₄ (5 mol%) was added. The resulting mixture was degassed and purged with nitrogen (3 times) then stirred at room temperature for 10 minutes. An aqueous solution of sodium carbonate (2 M, 3.0 eq) was added via syringe and the reaction mixture was then stirred at 100 °C overnight (ca 10 h). The reaction was then cooled to room temperature and concentrated. The residue was diluted with EA (15 mL) and water (20 mL), and neutralized with 2 N HCl (ca 13 mL, until PH=7). The resulting mixture was then extracted with EA (4×15 mL). The combined organic phases were washed with brine (30 mL) and dried over anhydrous sodium sulfate. After removal of the solvent, a short silica gel column filtration of the crude mixture afforded parent enones, which were used directly in the next step without purification^[1].

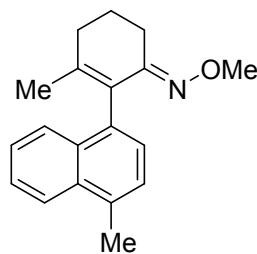
General procedure for the synthesis of substrates 1.

The parent enone (1.95 g, 8.3 mmol) was dissolved in MeOH (20 mL) and methoxylamine hydrochloride (2.08 g, 3.0 equiv) was added. The reaction mixture was stirred at room temperature for 10 min and then NaHCO₃ (2.09 g, 3.0 equiv) was gradually added. Stirring was continued for further 6 h. The solution was then diluted with ethyl acetate (30 mL), washed with brine (10 mL), extracted with EA (3×20 mL), dried over anhydrous Na₂SO₄, filtered, and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel to afford **1a** (87% yield)^[2].



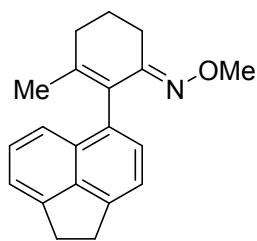
1a

(E)-3-methyl-2-(naphthalen-1-yl)cyclohex-2-en-1-one O-methyl oxime **1 a** (87% yield). **1H NMR** (**400 MHz, CDCl₃**) δ 7.86 – 7.81 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.35 (m, 3H), 7.19 (dd, *J* = 7.0, 1.0 Hz, 1H), 3.53 (s, 3H), 2.77 – 2.67 (m, 2H), 2.36 (dd, *J* = 11.1, 5.4 Hz, 2H), 1.99 – 1.88 (m, 2H), 1.46 (s, 3H). **13C NMR** (**101 MHz, CDCl₃**) δ 156.88 (s), 143.35 (s), 136.51 (s), 133.49 (s), 132.37 (s), 129.82 (s), 128.12 (s), 127.37 (s), 126.78 (s), 125.88 (s), 125.45 (s), 125.32 (s), 125.25 (s), 61.45 (s), 31.79 (s), 22.99 (s), 21.75 (s), 21.21 (s). **HRMS (ESI)** m/z: [M+Na]⁺calculated for C₁₈H₁₉NaNO: 288.1359, found: 288.1361.



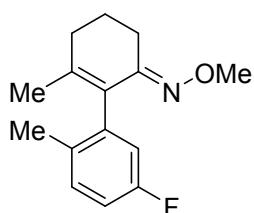
1b

(E)-3-methyl-2-(4-methylnaphthalen-1-yl)cyclohex-2-en-1-one O-methyl oxime **1b** (65% yield). **1H NMR** (**400 MHz, CDCl₃**) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.46 (dd, *J* = 11.1, 4.0 Hz, 1H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.08 (d, *J* = 7.1 Hz, 1H), 3.54 (s, 3H), 2.79 – 2.63 (m, 5H), 2.35 (dd, *J* = 11.1, 5.4 Hz, 2H), 1.92 (d, *J* = 4.0 Hz, 2H), 1.45 (s, 3H). **13C NMR** (**101 MHz, CDCl₃**) δ 157.04 (s), 143.41 (s), 134.72 (s), 132.80 (s), 132.61 (s), 132.39 (s), 129.98 (s), 127.01 (s), 126.48 (s), 126.23 (s), 125.07 (s), 124.25 (s), 61.46 (s), 31.81 (s), 23.05 (s), 21.83 (s), 21.22 (s), 19.50 (s). **HRMS (ESI)** m/z: [M+Na]⁺calculated for C₁₉H₂₁NNaO: 302.1515, found: 302.1525.



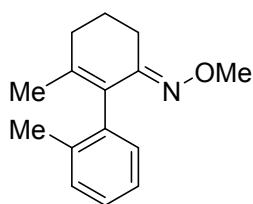
1c

(E)-2-(1,2-dihydroacenaphthylen-5-yl)-3-methylcyclohex-2-en-1-one *O*-methyl oxime **1c** (66% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.38 – 7.30 (m, 2H), 7.28 (d, *J* = 6.4 Hz, 1H), 7.22 (d, *J* = 6.1 Hz, 1H), 7.14 (d, *J* = 7.0 Hz, 1H), 3.56 (s, 3H), 3.45 – 3.35 (m, 4H), 2.72 (td, *J* = 6.3, 2.8 Hz, 2H), 2.42 – 2.28 (m, 2H), 1.96 – 1.87 (m, 2H), 1.48 (s, 3H). **13C NMR (101 MHz, CDCl₃)** δ 156.97 (s), 145.95 (s), 144.47 (s), 143.20 (s), 139.33 (s), 131.65 (s), 130.82 (s), 129.19 (d, *J* = 15.8 Hz), 127.19 (s), 121.10 (s), 118.73 (d, *J* = 17.0 Hz), 61.46 (s), 31.87 (s), 30.55 (s), 30.12 (s), 23.08 (s), 21.86 (s), 21.28 (s). **HRMS (ESI)** m/z: [M+Na]⁺calculated for C₂₀H₂₁NNaO: 314.1515, found: 314.1528.



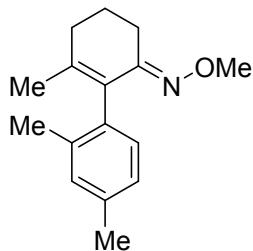
1d

(E)-5'-fluoro-2',6-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one *O*-methyl oxime **1d** (68% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.14 – 7.07 (m, 1H), 6.85 (td, *J* = 8.5, 2.6 Hz, 1H), 6.69 (dd, *J* = 9.5, 2.5 Hz, 1H), 3.68 (s, 3H), 2.71 – 2.53 (m, 2H), 2.25 (t, *J* = 5.9 Hz, 2H), 2.05 (s, 3H), 1.81 (p, *J* = 6.4 Hz, 2H), 1.52 (s, 3H). **13C NMR (101 MHz, CDCl₃)** δ 162.02 (s), 159.61 (s), 155.79 (s), 142.05 (s), 139.93 (d, *J* = 7.8 Hz), 132.10 (d, *J* = 3.0 Hz), 130.36 (d, *J* = 7.8 Hz), 116.57 (d, *J* = 20.6 Hz), 113.15 (d, *J* = 20.7 Hz), 61.60 (s), 31.49 (s), 22.77 (s), 21.31 (s), 21.00 (s), 18.62 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₁₅H₁₉FNO: 248.1445, found: 248.1448.



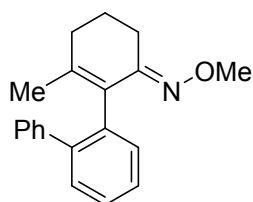
1e

(E)-2',6-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one O-methyl oxime **1e** (68% yield). **1H NMR** (**400 MHz**, **CDCl₃**) δ 7.15 (dt, *J* = 9.2, 4.0 Hz, 3H), 6.95 (d, *J* = 6.3 Hz, 1H), 3.67 (s, 3H), 2.73 – 2.49 (m, 2H), 2.25 (t, *J* = 5.8 Hz, 2H), 2.10 (s, 3H), 1.89 – 1.74 (m, 2H), 1.50 (d, *J* = 0.5 Hz, 3H). **13C NMR** (**101 MHz**, **CDCl₃**) δ 141.72 (s), 136.51 (s), 129.93 (s), 129.31 (s), 126.53 (s), 125.17 (s), 61.54 (s), 31.55 (s), 22.87 (s), 21.38 (s), 21.11 (s), 19.42 (s). **HRMS (ESI)** m/z: [M+Na]⁺calculated for C₁₅H₁₉NNaO: 252.1359, found: 252.1370.



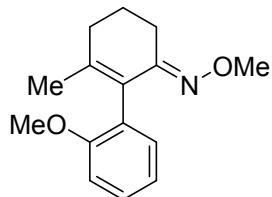
1f

(E)-2',4',6-trimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one O-methyl oxime **1f** (87% yield). **1H NMR** (**400 MHz**, **CDCl₃**) δ 7.02 – 6.92 (m, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 3.68 (s, 3H), 2.72 – 2.52 (m, 2H), 2.32 (s, 3H), 2.24 (t, *J* = 5.9 Hz, 2H), 2.06 (s, 3H), 1.81 (p, *J* = 6.4 Hz, 2H), 1.50 (s, 3H). **13C NMR** (**101 MHz**, **CDCl₃**) δ 156.43 (s), 141.79 (s), 136.23 (s), 135.83 (s), 135.12 (s), 130.99 (s), 130.19 (s), 129.79 (s), 125.95 (s), 61.51 (s), 31.59 (s), 22.93 (s), 21.43 (s), 21.18 (s), 21.12 (s), 19.36 (s). **HRMS (ESI)** m/z: [M+Na]⁺calculated for C₁₆H₂₁NNaO: 266.1515, found: 266.1527.



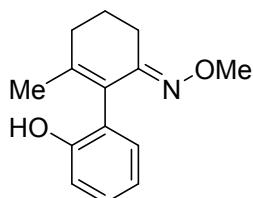
1g

(E)-6-methyl-4,5-dihydro-[1,1':2',1"-terphenyl]-2(3H)-one O-methyl oxime **1g** (51% yield). **¹H NMR** (**400 MHz, CDCl₃**) δ 7.39 – 7.26 (m, 7H), 7.23 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.12 (d, *J* = 6.3 Hz, 1H), 3.69 (s, 3H), 2.55 – 2.34 (m, 2H), 2.16 – 1.89 (m, 2H), 1.77 – 1.54 (m, 2H), 1.40 (s, 3H). **¹³C NMR** (**101 MHz, CDCl₃**) δ 157.15 (s), 142.37 (s), 142.02 (s), 141.85 (s), 136.90 (s), 131.03 (s), 129.28 (s), 128.69 (s), 127.38 (s), 126.84 (s), 126.60 (s), 126.47 (s), 61.53 (s), 31.50 (s), 22.72 (s), 21.74 (s), 20.73 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₀H₂₂NO: 292.1696, found: 292.1685.



1h

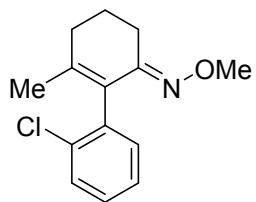
(E)-2'-methoxy-6-methyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one O-methyl oxime **1h** (99% yield). **¹H NMR** (**400 MHz, CDCl₃**) δ 7.28 – 7.22 (m, 1H), 7.01 – 6.87 (m, 3H), 3.76 (d, *J* = 6.4 Hz, 3H), 3.67 (s, 3H), 2.73 – 2.52 (m, 2H), 2.34 – 2.17 (m, 2H), 1.90 – 1.72 (m, 2H), 1.57 (s, 3H). **¹³C NMR** (**101 MHz, CDCl₃**) δ 157.21 (s), 156.46 (s), 142.11 (s), 131.61 (s), 128.05 (s), 127.85 (s), 127.71 (s), 120.19 (s), 111.32 (s), 61.40 (s), 55.93 (s), 31.61 (s), 22.84 (s), 21.63 (s), 21.03 (s). **HRMS (ESI)** m/z: [M+Na]⁺calculated for C₁₅H₁₉NNaO₂: 268.1308, found: 268.1321.



1i

(E)-2'-hydroxy-6-methyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one O-methyl oxime **1i** (53% yield). **¹H NMR** (**400 MHz, CDCl₃**) δ 7.25 – 7.18 (m, 1H), 7.01 – 6.94 (m, 2H), 6.90 (t, *J* = 7.3 Hz, 1H), 3.78 (s, 3H), 2.77 – 2.54 (m, 2H), 2.38 – 2.19 (m, 2H), 1.92 – 1.71 (m, 2H), 1.67 (s, 3H). **¹³C NMR** (**101 MHz, CDCl₃**) δ 157.44 (s), 153.57 (s), 147.22 (s), 131.64 (s), 128.77 (s), 127.52 (s), 125.80 (s), 120.25 (s), 117.37 (s), 61.93 (s), 31.97 (s), 23.41 (s), 22.53 (s), 20.57 (s). **HRMS (ESI)**

m/z: [M+H]⁺calculated for C₁₄H₁₈NO₂: 232.1332, found: 232.1336.



1j

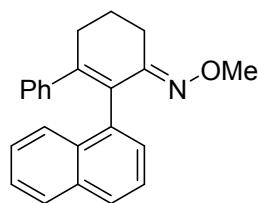
(E)-2'-chloro-6-methyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one O-methyl oxime **1j** (80.7% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.33 (m, 1H), 7.26 – 7.16 (m, 2H), 7.11 – 7.04 (m, 1H),

3.67 (s, 3H), 2.71 – 2.53 (m, 2H), 2.35 – 2.17 (m, 2H), 1.90 – 1.75 (m, 2H), 1.55 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 155.81 (s), 142.85 (s), 137.46 (s), 133.93 (s), 131.74 (s), 129.39 (s),

128.99 (s), 127.88 (s), 126.12 (s), 61.58 (s), 31.53 (s), 22.74 (s), 21.35 (s), 20.91 (s). **HRMS (ESI)**

m/z: [M+H]⁺calculated for C₁₄H₁₇ClNO: 250.0993, found: 250.0994.



1k

(E)-2-(naphthalen-1-yl)-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one O-methyl oxime **1k** (86% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.76 (m, 1H), 7.73 (dd, *J* = 6.2, 2.9 Hz, 1H), 7.60 (d, *J* =

8.2 Hz, 1H), 7.45 – 7.32 (m, 2H), 7.21 (dd, *J* = 12.4, 4.9 Hz, 1H), 7.00 (d, *J* = 6.9 Hz, 1H), 6.97 –

6.87 (m, 3H), 6.87 – 6.73 (m, 2H), 3.53 (s, 3H), 2.95 – 2.72 (m, 3H), 2.66 (dt, *J* = 17.4, 5.7 Hz,

1H), 2.17 – 1.96 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.78 (s), 146.16 (s), 142.33 (s),

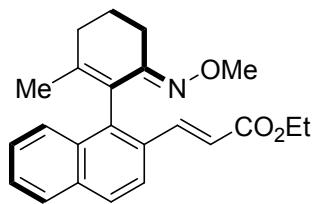
136.23 (s), 133.16 (d, *J* = 19.4 Hz), 131.91 (s), 128.49 (s), 128.06 (s), 127.37 (d, *J* = 11.0 Hz),

126.82 (s), 126.49 (d, *J* = 3.9 Hz), 125.38 – 124.88 (m), 61.74 (s), 32.31 (s), 23.28 (s), 21.57 (s).

HRMS (ESI) m/z: [M+H]⁺calculated for C₂₃H₂₂NO: 328.1696, found: 328.1696.

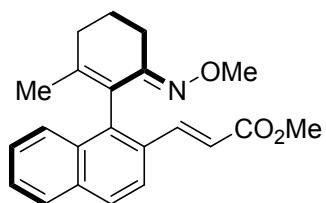
General procedure for the synthesis of products 3.

Under air atmosphere, the racemic substrate **1a-1k** (0.3 mmol), Pd(OAc)₂ (6.7 mg, 10 mol%), N-Acetyl-L-alanine (7.9 mg, 20 mol%) and AgOAc(150 mg, 0.9 mmol, 3 equiv) were added to a tube containing a magnetic stir bar. After which, MeOH (3.0 mL) was added using a syringe. Then ethyl acrylate (96 μ L, 0.9 mmol, 3 equiv) was added with microsyringe. The reaction mixture was stirred at 40 °C in an oil bath for 48 hours. The reaction mixture was cooled to room temperature. The solvent was then evaporated *in vacuo* and the residue was purified by using flash silica gel column chromatography with EA and PE as eluent to afford the final products.



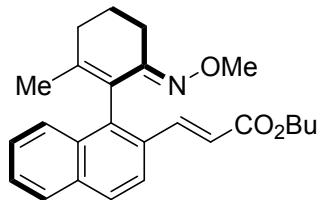
3a

Ethyl (*E*)-3-(1-((*E*)-6(methoxyimino)-2-methylcyclohex-1-en-1-yl)naphthalen-2-yl)acrylate **3a** (77.3 mg, 71% yield). **1H NMR** (400 MHz, CDCl₃) δ 7.75 (d, *J* = 13.0 Hz, 1H), 7.72 (d, *J* = 4.5 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.42 – 7.16 (m, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.43 (d, *J* = 17.2 Hz, 3H), 2.80 – 2.56 (m, 2H), 2.34 (t, *J* = 5.9 Hz, 2H), 1.98 – 1.87 (m, 2H), 1.29 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **13C NMR** (101 MHz, CDCl₃) δ 167.36 (s), 156.20 (s), 144.93 (s), 143.71 (s), 138.54 (s), 134.11 (s), 132.39 (s), 130.02 (s), 127.99 (s), 127.43 (s), 127.21 (s), 126.73 (s), 126.57 (s), 126.31 (s), 122.63 (s), 118.32 (s), 61.55 (s), 60.28 (s), 31.84 (s), 22.90 (s), 21.49 (s), 21.18 (s), 14.33 (s). **HRMS (ESI)** m/z: [M+Na]⁺calculated for C₂₃H₂₅NNaO₃: 386.1727, found: 386.1739. $[\alpha]_{D}^{22}$ = 50 (c = 0.03, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 95:5, 0.8mL/min, 290 nm, 97% ee); major enantiomer t_r = 5.97 min, minor enantiomer t_r = 6.82 min.



3b

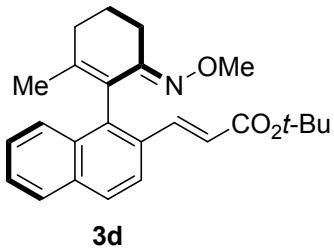
Methyl (E)-3-((E)-6-(methoxyimino)-2-methylcyclohex-1-en-1-yl)naphthalen-2-yl)acrylate **3b** (70.2 mg, 67% yield). **1H NMR** (**400 MHz**, **CDCl₃**) δ 7.83 (d, *J* = 5.7 Hz, 1H), 7.81 – 7.65 (m, 4H), 7.44 (dt, *J* = 15.0, 7.2 Hz, 2H), 6.46 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 3.49 (s, 3H), 2.85 – 2.65 (m, 2H), 2.43 (t, *J* = 6.1 Hz, 2H), 2.04 – 1.95 (m, 2H), 1.37 (s, 3H). **13C NMR** (**101 MHz**, **CDCl₃**) δ 167.78 (s), 156.18 (s), 144.94 (s), 143.95 (s), 138.59 (s), 134.14 (s), 132.37 (s), 129.98 (s), 127.98 (s), 127.44 (s), 127.20 (s), 126.65 (d, *J* = 11.8 Hz), 126.33 (s), 122.63 (s), 117.92 (s), 61.55 (s), 51.55 (s), 31.83 (s), 22.88 (s), 21.46 (s), 21.17 (s). **HRMS (ESI)** m/z: [M+Na]⁺ calculated for C₂₂H₂₃NNaO₃: 372.1570, found: 372.1579. $[\alpha]_{D}^{22} = 58$ (c = 0.02, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 290 nm, 96% ee); major enantiomer *t_r* = 6.21 min, minor enantiomer *t_r* = 7.31 min.



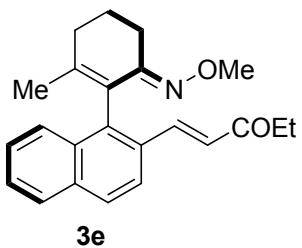
3c

Butyl (E)-3-((E)-6-(methoxyimino)-2-methylcyclohex-1-en-1-yl)naphthalen-2-yl) acrylate **3c** (63.3 mg, 54% yield). **1H NMR** (**400 MHz**, **CDCl₃**) δ 7.82 (d, *J* = 6.7 Hz, 1H), 7.77 (dd, *J* = 14.1, 5.2 Hz, 3H), 7.73 – 7.67 (m, 1H), 7.43 (dt, *J* = 21.7, 6.9 Hz, 2H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.5 Hz, 2H), 3.49 (s, 3H), 2.88 – 2.61 (m, 2H), 2.42 (t, *J* = 6.0 Hz, 2H), 1.99 (p, *J* = 6.4 Hz, 2H), 1.75 – 1.63 (m, 2H), 1.52 – 1.39 (m, 2H), 1.37 (s, 3H), 0.97 (t, *J* = 7.4 Hz, 3H). **13C NMR** (**101 MHz**, **CDCl₃**) δ 167.40 (s), 156.18 (s), 144.91 (s), 143.62 (s), 138.50 (s), 134.11 (s), 132.39 (s), 130.02 (s), 127.98 (s), 127.42 (s), 127.22 (s), 126.64 (d, *J* = 15.6 Hz), 126.30 (s), 122.59 (s), 118.35 (s), 64.19 (s), 61.53 (s), 31.83 (s), 30.81 (s), 22.88 (s), 21.47 (s), 21.16 (s), 19.26 (s), 13.73

(s). **HRMS (ESI)** m/z: [M+Na]⁺calculated for C₂₅H₂₉NNaO₃: 414.2040, found: 414.2052. [α]D= 57 (c = 0.01, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 290 nm, 98% ee); major enantiomer t_r = 5.77 min, minor enantiomer t_r = 6.74 min.



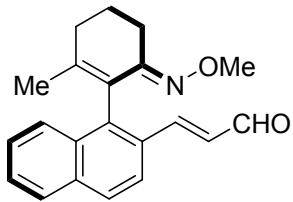
tert-butyl (E)-3-(1-((E)-6-(methoxyimino)-2-methylcyclohex-1-en-1-yl)naphthalen-2-yl)acrylate **3d** (65.4 mg, 56% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.70 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.42 (ddd, *J* = 15.1, 13.7, 6.8 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 3.49 (s, 3H), 2.84 – 2.65 (m, 2H), 2.42 (t, *J* = 6.0 Hz, 2H), 2.08 – 1.90 (m, 2H), 1.53 (s, 9H), 1.37 (s, 3H). **13C NMR (101 MHz, CDCl₃)** δ 166.63 (s), 156.23 (s), 144.89 (s), 142.48 (s), 138.25 (s), 134.00 (s), 132.42 (s), 130.13 (s), 127.96 (s), 127.35 (s), 127.20 (s), 126.72 (s), 126.45 (s), 126.25 (s), 122.65 (s), 120.26 (s), 80.12 (s), 61.54 (s), 31.83 (s), 28.29 (s), 22.90 (s), 21.52 (s), 21.19 (s). **HRMS (ESI)** m/z: [M+Na]⁺calculated for C₂₅H₂₉NNaO₃: 414.2040, found: 414.2050. [α]D= 44 (c = 0.01, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 97:3, 0.8 mL/min, 290 nm, >99% ee); major enantiomer t_r = 5.29 min, minor enantiomer t_r = 6.52 min.



(E)-1-(1-((E)-6-(methoxyimino)-2-methylcyclohex-1-en-1-yl)naphthalen-2-yl)pent-1-en-3-one **3e** (48.9 mg, 47% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.73 (t, *J* = 4.9 Hz, 1H), 7.69 (d, *J* = 3.3 Hz, 1H), 7.51 – 7.37 (m, 2H), 6.76 (d, *J* = 16.2 Hz,

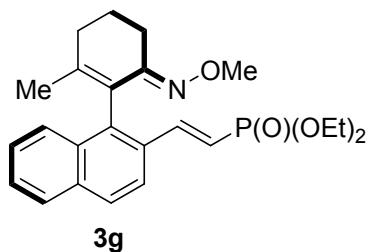
1H), 3.49 (s, 3H), 2.89 – 2.61 (m, 4H), 2.43 (t, J = 6.0 Hz, 2H), 2.05 – 1.93 (m, 2H), 1.37 (s, 3H), 1.17 (t, J = 7.3 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 201.26 (s), 145.09 (s), 141.54 (s), 138.96 (s), 134.18 (s), 132.37 (s), 130.11 (s), 128.05 (s), 127.51 (s), 127.20 (s), 126.68 (s), 126.40 (s), 126.29 (s), 122.50 (s), 61.61 (s), 33.92 (s), 31.85 (s), 22.91 (s), 21.54 (s), 21.25 (s), 8.44 (s).

HRMS (ESI) m/z: [M+Na]⁺calculated for C₂₃H₂₅NNaO₂: 370.1778, found: 370.1789. [α]D₂₂ = 62 (c = 0.009, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (hexanes: 2-propanol = 94:6, 0.8 mL/min, 290 nm, >99% ee); major enantiomer t_r = 8.22 min, minor enantiomer t_r = 10.65 min.

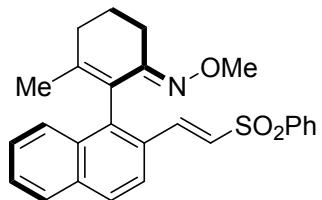


3f

(E)-3-(1-((E)-6-(methoxyimino)-2-methylcyclohex-1-en-1-yl)naphthalen-2-yl)acrylaldehyde **3f** (15.4 mg, 16% yield). **¹H NMR (400 MHz, CDCl₃)** δ 9.66 (d, J = 7.7 Hz, 1H), 7.89 – 7.78 (m, 2H), 7.78 – 7.69 (m, 2H), 7.59 (d, J = 15.9 Hz, 1H), 7.51 (t, J = 7.1 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 6.76 (dd, J = 15.9, 7.7 Hz, 1H), 3.50 (s, 3H), 2.88 – 2.64 (m, 2H), 2.45 (t, J = 5.8 Hz, 2H), 2.00 (dt, J = 12.9, 6.2 Hz, 2H), 1.39 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 194.18 (s), 156.08 (s), 151.96 (s), 145.39 (s), 139.37 (s), 134.58 (s), 132.24 (s), 129.68 (s), 128.90 (s), 128.16 (s), 127.74 (s), 127.20 (s), 127.00 (s), 126.79 (s), 126.63 (s), 122.61 (s), 61.68 (s), 31.85 (s), 22.87 (s), 21.52 (s), 21.18 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₁H₂₂NO₂: 320.1645, found: 320.1647. [α]D₂₂ = 83 (c = 0.006, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak IB column (hexanes: 2-propanol = 98:2, 0.8 mL/min, 290 nm, >99% ee); major enantiomer t_r = 12.03 min, minor enantiomer t_r = 13.66 min.

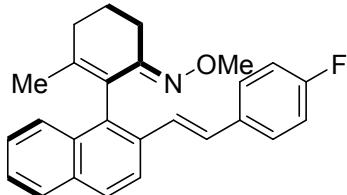


Diethyl ((E)-2-(1-((E)-6-(methoxyimino)-2-methylcyclohex-1-en-1-yl)naphthalen-2-yl)vinyl)phosphonate **3g** (112.8 mg, 88% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.65 – 7.53 (m, 1H), 7.52 – 7.39 (m, 2H), 6.27 (t, *J* = 18.2 Hz, 1H), 4.12 (dd, *J* = 13.7, 6.8 Hz, 4H), 3.48 (s, 3H), 2.73 (d, *J* = 3.3 Hz, 2H), 2.41 (d, *J* = 5.4 Hz, 2H), 2.03 – 1.95 (m, 2H), 1.42 – 1.31 (m, 9H). **13C NMR (101 MHz, CDCl₃)** δ 155.06 (s), 143.97 (s), 133.03 (s), 131.20 (s), 127.00 (s), 126.43 (s), 126.01 (s), 125.57 (d, *J* = 2.7 Hz), 125.36 (s), 121.30 (s), 60.83 (d, *J* = 4.2 Hz), 60.51 (s), 30.79 (s), 21.84 (s), 20.53 (s), 20.10 (s), 15.37 (d, *J* = 6.1 Hz). **HRMS (ESI)** m/z: [M+Na]⁺calculated for C₂₄H₃₀NNaO₄P: 450.1805, found: 450.1819. [α]D₂₂ = 14 (c = 0.005, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 290 nm, >99% ee); major enantiomer *t*_r = 11.03 min, minor enantiomer *t*_r = 12.43 min.



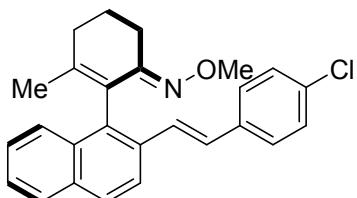
(E)-3-methyl-2-((E)-2-(phenylsulfonyl)vinyl)naphthalen-1-yl)cyclohex-2-en-1-one O-methyl oxime **3h** (112.3 mg, 87% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.92 (s, 1H), 7.90 (s, 1H), 7.85 – 7.68 (m, 4H), 7.66 – 7.38 (m, 6H), 6.83 (d, *J* = 15.5 Hz, 1H), 3.43 (s, 3H), 2.86 – 2.65 (m, 2H), 2.43 (t, *J* = 5.9 Hz, 2H), 2.02 (dt, *J* = 12.8, 6.3 Hz, 2H), 1.35 (s, 3H). **13C NMR (101 MHz, CDCl₃)** δ 156.24 (s), 145.55 (s), 142.30 (s), 141.06 (s), 139.35 (s), 134.39 (s), 133.15 (s), 129.25 (s), 128.27 (s), 128.12 (s), 127.69 (d, *J* = 5.0 Hz), 127.37 (s), 127.13 (s), 126.71 (d, *J* = 8.7 Hz), 122.63 (s), 61.59 (s), 31.82 (s), 22.86 (s), 21.63 (s), 21.11 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₆H₂₆NO₃S: 432.1628, found: 432.1618. [α]D₂₂ = 12 (c = 0.008, CHCl₃).

Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 75:25, 0.8 mL/min, 290 nm, >99% *ee*); major enantiomer t_r = 8.03 min, minor enantiomer t_r = 9.24 min.



3i

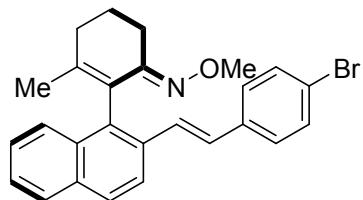
(E)-2-(2-((E)-4-fluorostyryl)naphthalen-1-yl)-3-methylcyclohex-2-en-1-one O-methyl oxime **3i** (81.6 mg, 71% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.83 (d, J = 8.7 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.66 (dd, J = 6.8, 2.8 Hz, 1H), 7.47 – 7.34 (m, 4H), 7.10 (d, J = 2.6 Hz, 2H), 7.05 (dd, J = 12.1, 5.3 Hz, 2H), 3.51 (s, 3H), 2.91 – 2.68 (m, 2H), 2.43 (t, J = 5.7 Hz, 2H), 2.07 – 1.94 (m, 2H), 1.38 (s, 3H). **13C NMR (101 MHz, CDCl₃)** δ 163.43 (s), 160.98 (s), 155.97 (s), 144.54 (s), 135.09 (s), 134.28 (s), 132.99 (s), 132.61 (s), 132.35 (s), 127.99 – 127.83 (m), 127.79 (s), 127.67 (s), 127.52 (s), 127.17 (s), 126.20 (s), 126.02 (s), 125.41 (s), 122.50 (s), 115.70 (s), 115.49 (s), 61.58 (s), 31.89 (s), 23.00 (s), 21.45 (d, J = 4.5 Hz). **HRMS (ESI)** m/z: [M+H]⁺ calculated for C₂₆H₂₅FNO: 386.1915, found: 386.1910. $[\alpha]_{D}^{22}$ = 79 (c = 0.02, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak OX-H column (hexanes: 2-propanol = 98:2, 0.8 mL/min, 290 nm, 96% *ee*); major enantiomer t_r = 8.89 min, minor enantiomer t_r = 9.78 min.



3j

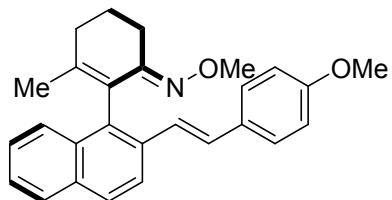
(E)-2-(2-((E)-4-chlorostyryl)naphthalen-1-yl)-3-methylcyclohex-2-en-1-one O-methyl oxime **3j** (88.5 mg, 74% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.83 (d, J = 8.7 Hz, 1H), 7.79 (dd, J = 14.4, 5.5 Hz, 2H), 7.70 – 7.63 (m, 1H), 7.46 – 7.35 (m, 4H), 7.31 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 16.3 Hz, 1H), 7.07 (d, J = 16.3 Hz, 1H), 3.51 (s, 3H), 2.89 – 2.70 (m, 2H), 2.42 (d, J = 5.6 Hz, 2H),

2.00 (qt, $J = 14.3$, 7.3 Hz, 2H), 1.38 (s, 3H). **^{13}C NMR (101 MHz, CDCl₃)** δ 155.97 (s), 144.61 (s), 136.60 (s), 135.34 (s), 133.07 (s), 132.89 (s), 132.59 (s), 132.19 (s), 128.83 (s), 128.39 (s), 127.93 (s), 127.74 (s), 127.59 (d, $J = 4.0$ Hz), 127.21 (s), 126.24 (s), 126.05 (s), 125.51 (s), 122.49 (s), 61.59 (s), 31.89 (s), 29.71 (s), 23.00 (s), 21.45 (d, $J = 5.9$ Hz). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₆H₂₅ClNO: 402.1619, found: 402.1616. $[\alpha]_{D}^{22} = 123$ (c = 0.04, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak OX-H column (hexanes: 2-propanol = 98:2, 0.5 mL/min, 290 nm, 97% ee); major enantiomer t_r = 9.04 min, minor enantiomer t_r = 9.94 min.



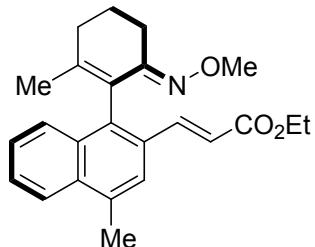
3k

(E)-2-(2-((E)-4-bromostyryl)naphthalen-1-yl)-3-methylcyclohex-2-en-1-one O-methyl oxime **3k** (84.9 mg, 64% yield). **^1H NMR (400 MHz, CDCl₃)** δ 7.83 (d, $J = 8.7$ Hz, 1H), 7.81 – 7.74 (m, 2H), 7.71 – 7.61 (m, 1H), 7.47 (d, $J = 8.5$ Hz, 2H), 7.44 – 7.36 (m, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 16.3$ Hz, 1H), 7.05 (d, $J = 16.3$ Hz, 1H), 3.52 (d, $J = 9.9$ Hz, 3H), 2.88 – 2.68 (m, 2H), 2.42 (d, $J = 5.2$ Hz, 2H), 2.07 – 1.91 (m, 2H), 1.38 (s, 3H). **^{13}C NMR (101 MHz, CDCl₃)** δ 155.97 (s), 144.61 (s), 137.05 (s), 135.38 (s), 133.08 (s), 132.59 (s), 132.17 (s), 131.77 (s), 128.52 (s), 127.94 (s), 127.74 (s), 127.62 (s), 127.23 (s), 126.24 (s), 126.06 (s), 125.53 (s), 122.48 (s), 121.00 (s), 61.59 (s), 31.89 (s), 23.00 (s), 21.45 (d, $J = 6.2$ Hz). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₆H₂₄BrNO: 446.1114, found: 446.1115. $[\alpha]_{D}^{22} = 91$ (c = 0.02, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak OX-H column (hexanes: 2-propanol = 98:2, 0.5 mL/min, 290 nm, 96% ee); major enantiomer t_r = 9.49 min, minor enantiomer t_r = 10.37 min.



3l

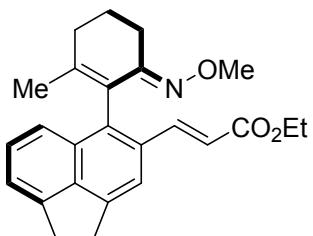
(E)-2-(2-((E)-4-methoxystyryl)naphthalen-1-yl)-3-methylcyclohex-2-en-1-one O-methyl oxime **3l** (58.1 mg, 49% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.85 (d, *J* = 8.7 Hz, 1H), 7.78 (dd, *J* = 14.8, 5.8 Hz, 2H), 7.70 – 7.62 (m, 1H), 7.43 – 7.35 (m, 4H), 7.08 (s, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 3.83 (s, 3H), 3.51 (s, 3H), 2.86 – 2.71 (m, 2H), 2.42 (t, *J* = 5.8 Hz, 2H), 2.07 – 1.96 (m, 2H), 1.38 (s, 3H). **13C NMR (101 MHz, CDCl₃)** δ 159.14 (s), 155.98 (s), 144.45 (s), 134.59 (s), 132.78 (d, *J* = 3.3 Hz), 132.67 (s), 130.91 (s), 128.38 (s), 127.89 (s), 127.67 (s), 127.07 (s), 126.15 (s), 125.92 (s), 125.70 (s), 125.17 (s), 122.56 (s), 114.15 (s), 61.58 (s), 55.37 (s), 31.90 (s), 23.02 (s), 21.47 (d, *J* = 3.7 Hz). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₇H₂₈NO₂: 398.2115, found: 398.2104. [α]D₂₂ D= 126 (c = 0.03, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak OX-H column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 290 nm, 96% ee); major enantiomer t_r = 6.70 min, minor enantiomer t_r = 8.03 min.



3m

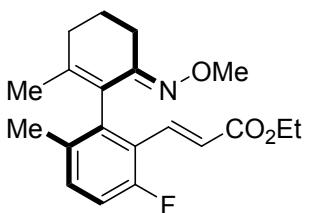
Ethyl (E)-3-((E)-6-(methoxyimino)-2-methylcyclohex-1-en-1-yl)-4-methylnaphthalen-2-yl)acrylate **3m** (57.5 mg, 51% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 16.0 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.58 (s, 1H), 7.54 – 7.46 (m, 1H), 7.42 (dd, *J* = 11.1, 4.1 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.49 (s, 3H), 2.85 – 2.65 (m, 5H), 2.41 (t, *J* = 6.0 Hz, 2H), 2.03 – 1.95 (m, 2H), 1.36 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). **13C NMR (101 MHz, CDCl₃)** δ 167.43 (s), 156.39 (s), 145.02 (s), 143.80 (s), 136.96 (s), 133.46 (d, *J* = 14.1 Hz), 132.47 (s), 129.50 (s), 127.32 (s), 126.43 (s), 125.95 (s), 124.19 (s), 123.27 (s), 118.02 (s), 67.10 (s), 61.52 (s), 60.24 (s), 31.86 (s), 22.94 (s), 21.53 (s), 21.18 (s), 19.63 (s), 14.32 (s). **HRMS**

(ESI) m/z: [M+H]⁺calculated for C₂₄H₂₈NO₃: 378.2064, found: 378.2066. [α]D = 54 (c = 0.009, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak OX-H column (hexanes: 2-propanol = 98:2, 0.5 mL/min, 290 nm, 98% ee); major enantiomer t_r = 12.4 min, minor enantiomer t_r = 13.33 min.



3n

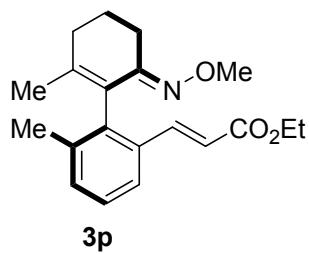
Ethyl (E)-3-((E)-6-(methoxyimino)-2-methylcyclohex-1-en-1-yl)-1,2-dihydroacenaphthylen-4-yl)acrylate **3n** (53.7 mg, 46% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.48 (s, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.19 (d, *J* = 6.8 Hz, 2H), 6.37 (d, *J* = 15.9 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.48 – 3.40 (m, 3H), 3.38 – 3.28 (m, 4H), 2.78 – 2.57 (m, 2H), 2.33 (t, *J* = 5.9 Hz, 2H), 1.98 – 1.85 (m, 2H), 1.31 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **13C NMR (101 MHz, CDCl₃)** δ 167.51 (s), 156.35 (s), 145.71 (s), 144.96 (d, *J* = 11.6 Hz), 144.63 (s), 140.11 (s), 134.64 (s), 131.77 (s), 130.69 (s), 128.04 (s), 126.84 (s), 121.96 (s), 120.30 (s), 117.74 (s), 115.94 (s), 61.51 (s), 60.19 (s), 31.88 (s), 30.50 (s), 30.02 (s), 22.96 (s), 21.52 (s), 21.24 (s), 14.33 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₅H₂₈NO₃: 390.2064, found: 390.2061. [α]D = 43 (c = 0.01, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak OX-H column (hexanes: 2-propanol = 98:2, 0.5 mL/min, 290 nm, 98% ee); major enantiomer t_r = 15.91 min, minor enantiomer t_r = 19.29 min.



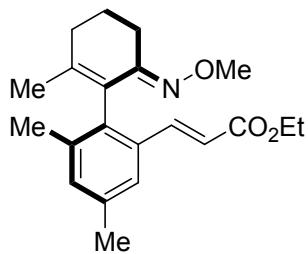
3o

Ethyl (E)-3-((E)-3-fluoro-2'-(methoxyimino)-6,6'-dimethyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-yl)acrylate **3o** (57.7 mg, 56% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.45 (d, *J* = 16.3 Hz, 1H),

7.13 (dd, J = 8.2, 5.5 Hz, 1H), 6.93 (dd, J = 11.1, 8.5 Hz, 1H), 6.56 (d, J = 16.3 Hz, 1H), 4.22 (q, J = 7.0 Hz, 2H), 3.65 (d, J = 10.1 Hz, 3H), 2.78 – 2.68 (m, 1H), 2.57 (ddd, J = 16.9, 8.0, 5.8 Hz, 1H), 2.37 – 2.23 (m, 2H), 2.05 (s, 3H), 1.93 – 1.80 (m, 2H), 1.43 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl₃)** δ 167.63 (s), 161.58 (s), 159.08 (s), 155.23 (s), 143.50 (s), 141.12 (d, J = 2.9 Hz), 138.29 (s), 132.63 (d, J = 3.4 Hz), 131.43 (d, J = 9.4 Hz), 128.18 (s), 122.52 (s), 122.37 (s), 121.17 (s), 121.07 (s), 114.20 (s), 113.98 (s), 61.67 (s), 60.28 (s), 31.56 (s), 22.76 (s), 21.00 (d, J = 7.3 Hz), 19.17 (s), 14.30 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₀H₂₅FNO₃: 346.1813, found: 346.1806. $[\alpha]_{D}^{22} = 40$ (c = 0.03, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 96:4, 0.8mL/min, 290 nm, 98% ee); major enantiomer t_r = 6.00 min, minor enantiomer t_r = 7.70 min.

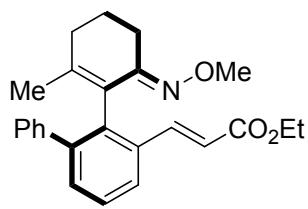


Ethyl (E)-3-((E)-2'-(methoxyimino)-6,6'-dimethyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-yl)acrylate **3p** (41.7 mg, 43% yield). **^1H NMR (400 MHz, CDCl₃)** δ 7.62 (d, J = 16.0 Hz, 1H), 7.47 (dt, J = 7.8, 3.9 Hz, 1H), 7.24 – 7.14 (m, 2H), 6.31 (d, J = 16.0 Hz, 1H), 4.22 (tt, J = 7.2, 3.6 Hz, 2H), 3.64 (d, J = 7.1 Hz, 3H), 2.74 (ddd, J = 16.9, 7.3, 5.5 Hz, 1H), 2.58 (ddd, J = 16.9, 8.1, 5.7 Hz, 1H), 2.39 – 2.21 (m, 2H), 2.10 (s, 3H), 1.96 – 1.79 (m, 2H), 1.40 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl₃)** δ 167.32 (s), 155.57 (s), 144.14 (s), 143.30 (s), 139.25 (s), 137.23 (s), 133.23 (s), 131.13 (s), 128.38 (s), 126.81 (s), 123.14 (s), 118.11 (s), 61.60 (s), 60.19 (s), 31.60 (s), 22.81 (s), 21.07 (s), 19.60 (s), 14.30 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₀H₂₆NO₃: 328.1907, found: 328.1915. $[\alpha]_{D}^{22} = 39$ (c = 0.04, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 290 nm, >99% ee); major enantiomer t_r = 4.95 min, minor enantiomer t_r = 6.55 min.



3q

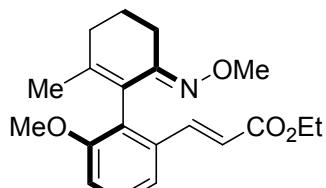
Ethyl (E)-3-((E)-2'-(methoxyimino)-4,6,6'-trimethyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-yl)acrylate **3q** (48.6 mg, 48% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.60 (d, *J* = 16.0 Hz, 1H), 7.30 (s, 1H), 7.04 (s, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 4.21 (tt, *J* = 7.2, 3.6 Hz, 2H), 3.64 (s, 3H), 2.73 (ddd, *J* = 16.8, 7.3, 5.5 Hz, 1H), 2.57 (ddd, *J* = 16.8, 8.1, 5.7 Hz, 1H), 2.33 (s, 3H), 2.31 – 2.20 (m, 2H), 2.06 (s, 3H), 1.93 – 1.79 (m, 2H), 1.40 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **13C NMR (101 MHz, CDCl₃)** δ 167.40 (s), 155.78 (s), 144.28 (s), 143.43 (s), 136.99 (s), 136.42 (s), 136.08 (s), 132.99 (s), 132.29 (s), 128.29 (s), 123.75 (s), 117.77 (s), 61.58 (s), 60.14 (s), 31.63 (s), 22.86 (s), 21.28 – 20.94 (m), 19.52 (s), 14.30 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₁H₂₈NO₃: 342.2064, found: 342.2065. [α]_D = 44 (c = 0.02, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 97:3, 0.8 mL/min, 290 nm, >99% ee); major enantiomer *t*_r = 5.93 min, minor enantiomer *t*_r = 7.33 min.



3r

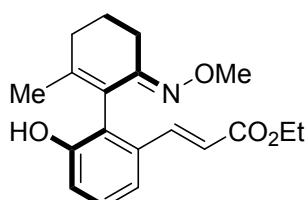
Ethyl (E)-3-((E)-2''-(methoxyimino)-6''-methyl-2",3",4",5"-tetrahydro-[1,1':2',1"-terphenyl]-3'-yl)acrylate **3r** (67.7 mg, 58% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.69 – 7.65 (m, 1H), 7.64 – 7.62 (m, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.29 – 7.25 (m, 3H), 7.25 – 7.22 (m, 2H), 6.37 (d, *J* = 15.9 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 3H), 2.53 (ddd, *J* = 16.7, 8.6, 4.8 Hz, 1H), 2.31 (ddd, *J* = 16.7, 8.2, 4.8 Hz, 1H), 2.23 – 2.07 (m, 1H), 1.99 – 1.84 (m, 1H), 1.78 – 1.63 (m, 1H), 1.52 – 1.41 (m, 1H), 1.32 (dd, *J* = 8.9, 5.3 Hz, 6H). **13C NMR (101 MHz, CDCl₃)** δ 167.24 (s), 156.84 (s), 144.26 (s), 143.79 (s), 142.69 (s), 141.92 (s), 138.07 (s), 133.87 (s), 131.13 (s), 128.62 (s), 128.28 (s), 127.33 (s), 127.09 (s), 126.74 (s), 124.70 (s), 118.52 (s), 61.61 (s),

60.26 (s), 31.44 (s), 22.53 (s), 21.65 (s), 20.60 (s), 14.31 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₅H₂₈NO₃: 390.2064, found: 390.2061. [α]₂₂ D= -20 (c = 0.03, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 96:4, 0.8 mL/min, 290 nm, >99% ee); major enantiomer t_r = 6.20 min, minor enantiomer t_r = 7.11 min.



3s

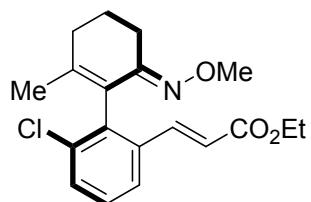
Ethyl (E)-3-((E)-6-methoxy-2'-(methoxyimino)-6'-methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-yl) acrylate **3s** (74.3 mg, 72% yield). **¹H NMR (400 MHz, CDCl₃)** δ 7.59 (d, *J* = 16.0 Hz, 1H), 7.28 – 7.24 (m, 2H), 6.96 – 6.84 (m, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 3.62 (s, 3H), 2.75 (dt, *J* = 16.7, 6.1 Hz, 1H), 2.55 (ddd, *J* = 16.7, 8.3, 5.9 Hz, 1H), 2.29 (d, *J* = 5.7 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.45 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 167.22 (s), 157.35 (s), 156.00 (s), 143.71 (d, *J* = 4.6 Hz), 134.58 (s), 129.09 (s), 127.84 (s), 125.33 (s), 118.58 (s), 118.04 (s), 112.39 (s), 61.46 (s), 60.23 (s), 56.19 (s), 31.62 (s), 22.78 (s), 21.38 (s), 21.04 (s), 14.29 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₀H₂₆NO₄: 344.1856, found: 344.1852. [α]₂₂ D= 59 (c = 0.04, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 290 nm, >99% ee); major enantiomer t_r = 5.86 min, minor enantiomer t_r = 7.30 min.



3t

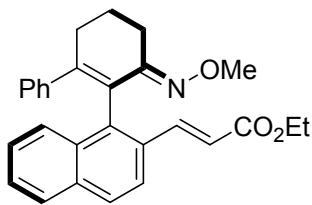
Ethyl (E)-3-((E)-6-hydroxy-2'-(methoxyimino)-6'-methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-yl) acrylate **3t** (68.4 mg, 69% yield). **¹H NMR (400 MHz, CDCl₃)** δ 7.55 (d, *J* = 15.9 Hz, 1H), 7.26 – 7.18 (m, 2H), 6.98 (dd, *J* = 7.0, 2.0 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 5.45 (d, *J* = 82.7 Hz, 1H),

4.22 (dt, $J = 13.4, 6.7$ Hz, 2H), 3.71 (s, 3H), 2.87 – 2.56 (m, 2H), 2.42 – 2.24 (m, 2H), 1.89 (dd, $J = 11.8, 5.8$ Hz, 2H), 1.51 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR (101 MHz, CDCl₃)** δ 167.18 (s), 156.15 (s), 153.41 (s), 148.92 (s), 143.30 (s), 134.46 (s), 128.52 (s), 126.21 (s), 123.85 (s), 118.78 (s), 118.44 (s), 117.59 (s), 61.93 (s), 60.35 (s), 31.86 (s), 23.16 (s), 21.80 (s), 20.77 (s), 14.30 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₁₉H₂₄NO₄: 330.1700, found: 330.1690. [α]D₂₂ D= -24 (c = 0.01, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak OX-H column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 290 nm, 96% ee); major enantiomer t_r = 8.93 min, minor enantiomer t_r = 10.41 min.



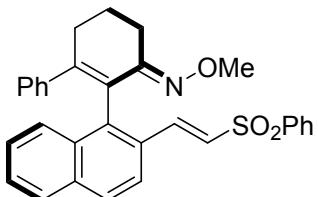
3u

Ethyl (E)-3-((E)-6-chloro-2'-(methoxyimino)-6'-methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-yl) acrylate **3u** (36.5 mg, 35% yield). **^1H NMR (400 MHz, CDCl₃)** δ 7.57 (d, $J = 16.1$ Hz, 1H), 7.53 (d, $J = 8.2$ Hz, 1H), 7.41 (d, $J = 7.9$ Hz, 1H), 7.23 (t, $J = 7.9$ Hz, 1H), 6.34 (d, $J = 16.0$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 3.63 (s, 3H), 2.73 (dt, $J = 16.8, 6.3$ Hz, 1H), 2.58 (ddd, $J = 16.8, 7.8, 6.0$ Hz, 1H), 2.32 (t, $J = 6.0$ Hz, 2H), 1.93 – 1.82 (m, 2H), 1.46 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR (101 MHz, CDCl₃)** δ 166.87 (s), 155.19 (s), 144.40 (s), 142.95 (s), 138.22 (s), 135.57 (s), 134.80 (s), 130.33 (s), 127.95 (s), 126.99 (s), 124.01 (s), 119.61 (s), 61.64 (s), 60.41 (s), 31.59 (s), 22.66 (s), 21.09 (s), 20.86 (s), 14.27 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₁₉H₂₃ClNO₃: 348.1361, found: 348.1357. [α]D₂₂ D= 81 (c = 0.01, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 290 nm, >99% ee); major enantiomer t_r = 5.53 min, minor enantiomer t_r = 6.68 min.



3v

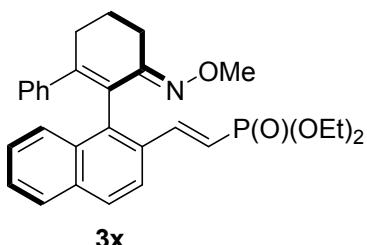
Ethyl (E)-3-(1-((E)-3-(methoxyimino)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)naphthalen-2-yl)acrylate **3v** (79.5 mg, 62% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.89 (d, *J* = 16.0 Hz, 1H), 7.85 (d, *J* = 9.3 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.41 (p, *J* = 6.3 Hz, 2H), 6.87 (q, *J* = 6.0 Hz, 3H), 6.77 (d, *J* = 6.4 Hz, 2H), 6.24 (d, *J* = 15.9 Hz, 1H), 4.35 – 4.17 (m, 2H), 3.49 (d, *J* = 13.9 Hz, 3H), 3.03 – 2.77 (m, 3H), 2.71 (dt, *J* = 11.7, 5.6 Hz, 1H), 2.14 (d, *J* = 4.2 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **13C NMR (101 MHz, CDCl₃)** δ 167.34 (s), 156.32 (s), 147.92 (s), 144.06 (s), 141.78 (s), 138.13 (s), 133.62 (s), 133.24 (s), 130.15 (s), 128.81 (s), 127.89 (s), 127.46 (s), 127.39 (s), 127.26 (s), 126.73 (s), 126.65 (s), 126.29 (s), 126.13 (s), 122.38 (s), 118.13 (s), 61.79 (s), 60.25 (s), 32.39 (s), 23.18 (s), 21.51 (s), 14.39 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₈H₂₈NO₃: 426.2064, found: 426.2066. [α]_D = 21 (c = 0.05, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 290 nm, 96% ee); major enantiomer *t*_r = 6.84 min, minor enantiomer *t*_r = 8.52 min.



3w

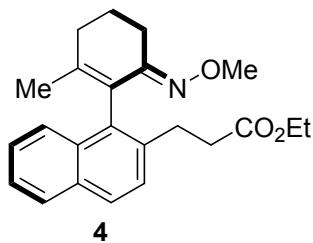
(E)-2-(2-((E)-2-(phenylsulfonyl)vinyl)naphthalen-1-yl)-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one O-methyl oxime **3w** (88.9 mg, 60% yield). **1H NMR (400 MHz, CDCl₃)** δ 7.92 (s, 1H), 7.90 (s, 1H), 7.87 (d, *J* = 9.3 Hz, 1H), 7.82 (d, *J* = 15.4 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.64 – 7.52 (m, 4H), 7.44 (p, *J* = 6.8 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 1H), 6.85 (dt, *J* = 24.1, 7.1 Hz, 3H), 6.73 (d, *J* = 7.2 Hz, 2H), 6.62 (d, *J* = 15.4 Hz, 1H), 3.47 (s, 3H), 2.86 (ddd, *J* = 14.4, 8.1, 5.3 Hz, 3H), 2.71 (dt, *J* = 11.6, 5.5 Hz, 1H), 2.25 – 2.07 (m, 2H). **13C NMR (101 MHz, CDCl₃)** δ 156.35 (s), 148.53 (s),

142.14 (s), 141.50 (s), 141.10 (s), 139.29 (s), 133.21 (d, $J = 6.1$ Hz), 129.25 (s), 128.45 (s), 128.16 (s), 128.02 (s), 127.73 (s), 127.66 (s), 127.52 (s), 127.41 (s), 126.99 – 126.84 (m), 126.67 (s), 126.49 (s), 122.45 (s), 61.83 (s), 32.39 (s), 23.16 (s), 21.48 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₃₁H₂₈NO₃S: 494.1784, found: 494.1780. [α]_D**22** = 37 (c = 0.02, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 80:20, 0.8 mL/min, 290 nm, >99% ee); major enantiomer t_r = 8.28 min, minor enantiomer t_r = 10.78 min.



Diethyl ((E)-2-((E)-3-(methoxyimino)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)naphthalen-2-yl)vinyl)phosphonate **3x** (105.7 mg, 72% yield) **¹H NMR (400 MHz, CDCl₃)** δ 7.88 – 7.82 (m, 1H), 7.73 – 7.69 (m, 1H), 7.63 (dd, $J = 15.9, 7.0$ Hz, 2H), 7.49 (d, $J = 8.7$ Hz, 1H), 7.45 – 7.38 (m, 2H), 6.92 – 6.83 (m, 3H), 6.79 (d, $J = 6.7$ Hz, 2H), 6.07 (t, $J = 18.2$ Hz, 1H), 4.18 – 4.02 (m, 4H), 3.51 (s, 3H), 2.89 – 2.78 (m, 3H), 2.71 (dt, $J = 17.4, 5.5$ Hz, 1H), 2.13 (td, $J = 12.6, 6.5$ Hz, 2H), 1.36 (t, $J = 7.0$ Hz, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 155.25 (s), 146.85 (s), 140.70 (s), 136.57 (s), 132.57 (s), 126.88 (s), 126.44 (s), 126.35 (s), 126.17 (s), 125.71 (s), 125.29 (s), 125.17 (s), 121.05 (s), 60.73 (s), 31.33 (s), 22.14 (s), 20.45 (s), 15.42 (d, $J = 6.5$ Hz). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₉H₃₃NO₄P: 490.2142, found: 490.2157. [α]_D**22** = 58 (c = 0.03, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 290 nm, 98% ee); major enantiomer t_r = 13.11 min, minor enantiomer t_r = 16.16 min.

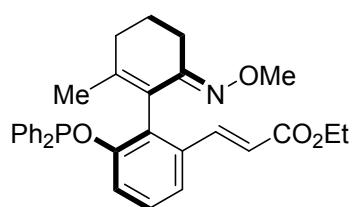
General procedure for the synthesis of 4, 5



4

The **3a** (72.6 mg, 0.2 mmol) and Pd/C (20 wt%) (5 mol%) were added in methanol (2 mL). The resulting mixture were degassed, purged with hydrogen (3 times) and then stirred at room temperature for overnight. The mixture were filtered through Celite plug and the Celite was washed with EA. The combined organic layer were concentrated under reduced pressure to give **4** (32.9 mg, 55% yield, 97% ee). The crude material were purified by silica gel column chromatography (eluent: PE/EA = 10:1).

¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, *J* = 5.2, 3.8 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.37 (dd, *J* = 7.8, 4.2 Hz, 3H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.53 (s, 3H), 2.91 (t, *J* = 8.2 Hz, 2H), 2.80 – 2.69 (m, 2H), 2.69 – 2.50 (m, 2H), 2.39 (d, *J* = 2.3 Hz, 2H), 2.04 – 1.88 (m, 2H), 1.38 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 173.54 (s), 156.19 (s), 143.77 (s), 135.79 (s), 134.34 (s), 132.39 (s), 132.21 (s), 128.09 (s), 127.90 (s), 127.04 (d, *J* = 3.8 Hz), 125.73 (d, *J* = 11.0 Hz), 124.80 (s), 61.48 (s), 60.31 (s), 35.19 (s), 31.74 (s), 29.10 (s), 22.97 (s), 21.59 (s), 21.24 (s), 14.26 (s). **HRMS (ESI)** m/z: [M+H]⁺calculated for C₂₃H₂₈NO₃ : 366.2064 , found: 366.2064. **[α]D₂₂** D= 108.7 (c = 0.01, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak OX-H column (hexanes: 2-propanol = 98:2, 0.8 mL/min, 254 nm, 97% ee); major enantiomer t_r = 7.70 min, minor enantiomer t_r = 8.27 min.

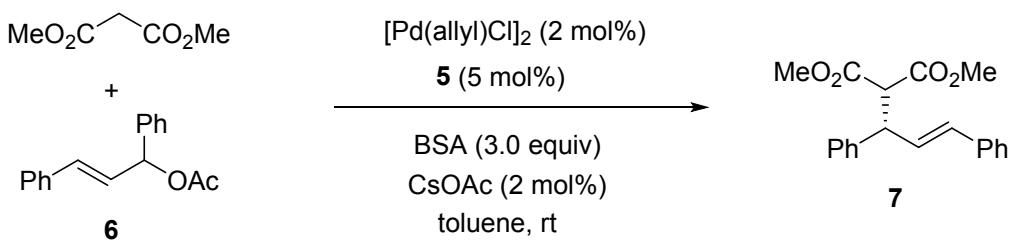


5

3t (32.9 mg, 1 mmol) and Et₃N (0.16 mL, 1.1 eq) were dissolved in THF (6 mL) under nitrogen and then added dropwise to a solution of PPh₂Cl (0.27 mL, 1.5 eq) at 0 °C under argon. The resulting solution was allowed to warm to room temperature and stirred for overnight. The mixture was filtered through Celite plug and the Celite was washed with EA. The combined organic layer was concentrated under reduced pressure to give **5** (265.5 mg, 52% yield). The crude material was purified by silica gel column chromatography (eluent: PE/EA = 2:1).

¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 16.0 Hz, 1H), 7.49 – 7.36 (m, 4H), 7.25 (s, 7H), 7.12 (dd, *J* = 18.4, 10.5 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 4.13 (q, *J* = 6.9 Hz, 2H), 3.57 (s, 3H), 2.66 – 2.51 (m, 1H), 2.22 – 2.10 (m, 2H), 2.02 – 1.92 (m, 1H), 1.77 – 1.52 (m, 2H), 1.34 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 167.19 (s), 155.63 (s), 155.11 (d, *J* = 10.0 Hz), 144.10 (s), 143.34 (s), 141.89 (s), 141.70 (d, *J* = 4.4 Hz), 141.50 (s), 134.78 (s), 131.31 (d, *J* = 3.0 Hz), 130.24 (d, *J* = 3.3 Hz), 130.01 (d, *J* = 2.9 Hz), 129.49 (d, *J* = 8.6 Hz), 128.36 (dd, *J* = 7.0, 5.6 Hz), 127.95 (s), 125.58 (s), 119.95 (s), 119.01 (s), 118.84 (s), 61.60 (s), 60.32 (s), 31.55 (s), 22.74 (s), 21.67 (s), 20.73 (s), 14.33 (s). **HRMS (ESI)** m/z: [M+H]⁺ calculated for C₃₁H₃₃NO₅P: 530.2091, found: 530.2084. [α]_D = 14.8 (c = 0.01, CHCl₃).

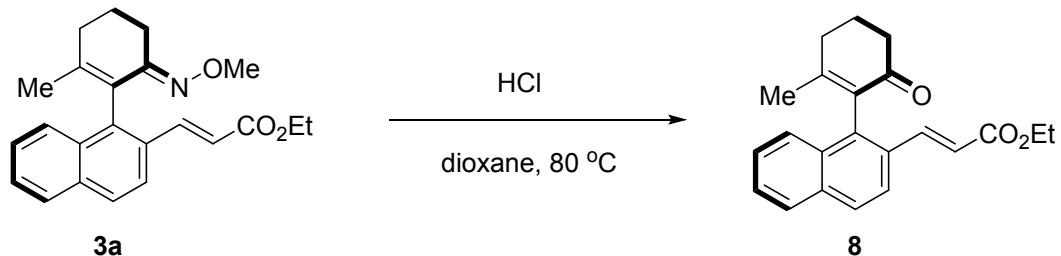
General procedure for the synthesis of **7**



5 (2.6 mg, 5 mol%) and [Pd(C₃H₅)Cl]₂ (0.7 mg, 2 mol%) were dissolved in toluene (0.5 mL) in a Schlenk tube under N₂. The resulting solution was stirred at room temperature for 1 h, then allylic acetate (25.3 mg, 0.1 mmol) in toluene (1 mL) was added to this solution. After stirring for 15 mins, malonate (39.7 mg, 0.3 mmol), BSA (61.1 mg, 0.3 mmol) and CsOAc (3.9 mg, 2 mol%) were added. The mixture was stirred at room temperature for 12h, diluted with diethyl ether and washed with saturated NH₄Cl (aq.). The organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography, eluting with PE

and EA to afford the corresponding product **7** (19.6 mg, 60% yield, 37% ee)^[3].

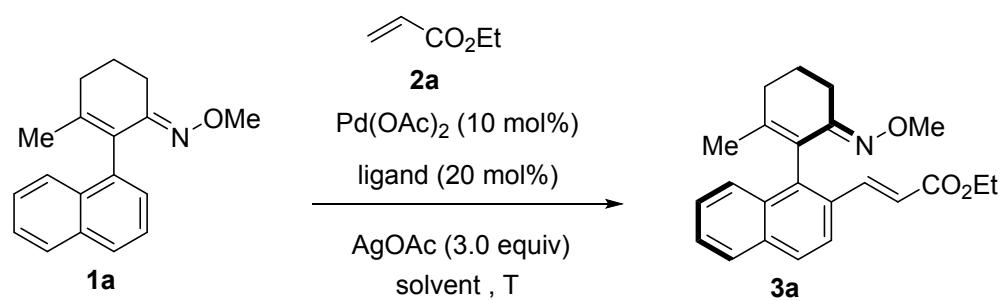
General procedure for the synthesis of 8



To a solution of **3a** (108 mg, 0.3 mmol) in dioxane (3 mL), was added aqueous HCl (6 M, 3 mL) and the mixture was heated at 80 °C (oil bath temperature) for 3 h. The resulting mixture was cooling to room temperature, and was extracted twice with EA. The combine organic extracts were washed three times with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo* after filtration. Purification by silica gel column chromatography (eluent: PE/EA = 5:1) gave product **8** (56 mg, 56% yield, 99% ee)^[4].

¹H NMR (400 MHz, CDCl₃) δ 7.82 (dd, *J* = 8.0, 5.2 Hz, 2H), 7.72 (dd, *J* = 18.6, 12.3 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.37 (m, 2H), 6.47 (d, *J* = 15.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.67 (t, *J* = 6.3 Hz, 4H), 2.33 – 2.19 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 197.51 (s), 167.08 (s), 161.00 (s), 142.48 (s), 135.88 (s), 134.23 (s), 133.75 (s), 132.12 (s), 130.49 (s), 128.36 (s), 126.85 (d, *J* = 11.5 Hz), 125.79 (s), 122.77 (s), 119.28 (s), 60.42 (s), 37.97 (s), 32.62 (s), 29.70 (s), 22.51 (d, *J* = 6.3 Hz), 14.32 (s). **HRMS (ESI) m/z:** [M+H]⁺calculated for C₂₂H₂₃O₃: 335.1642, found: 335.1644. **[α]D₂₅** = 12.5 (c = 0.03, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (hexanes: 2-propanol = 97:3, 1 mL/min, 270 nm, 99% ee); major enantiomer t_r = 25.09 min, minor enantiomer t_r = 34.66 min.

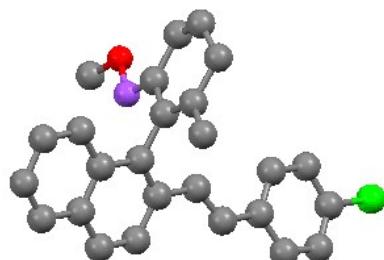
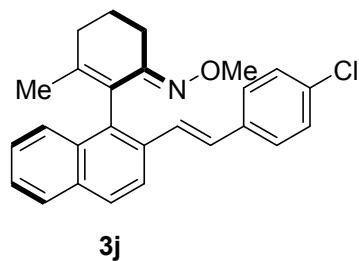
Table S1. Optimization of the Reaction Conditions^a.



| Entry | L | Solvent | T [°C] | Yield [%] ^b | ee [%] ^c |
|-----------------|----|------------------------------------|--------|------------------------|---------------------|
| 1 | L1 | CF ₃ CH ₂ OH | 80 | 81 | 48 |
| 2 | L1 | CF ₃ CH ₂ OH | 60 | 76 | 54 |
| 3 | L1 | CF ₃ CH ₂ OH | 50 | 70 | 60 |
| 4 | L1 | CF ₃ CH ₂ OH | 40 | 66 | 72 |
| 5 | L1 | toluene | 40 | 14 | 66 |
| 6 | L1 | THF | 40 | 38 | 94 |
| 7 | L1 | HFIP | 40 | 10 | 46 |
| 8 | L1 | <i>t</i> -AmOH | 40 | 26 | 96 |
| 9 | L1 | CH ₃ OH | 40 | 41 | 96 |
| 10 | L2 | CH ₃ OH | 40 | 27 | 96 |
| 11 | L3 | CH ₃ OH | 40 | 21 | 90 |
| 12 | L4 | CH ₃ OH | 40 | 31 | 88 |
| 13 | L5 | CH ₃ OH | 40 | 18 | 84 |
| 14 | L6 | CH ₃ OH | 40 | 18 | 94 |
| 15 | L7 | CH ₃ OH | 40 | 45 | 96 |
| 16 | L8 | CH ₃ OH | 40 | 71 | 97 |
| 17 ^d | L8 | CH ₃ OH | 40 | trace | - |
| 18 ^e | L8 | CH ₃ OH | 40 | 9 | 99 |

^{a)} Unless otherwise noted, the reaction was carried out using **1a** (0.3 mmol), **2a** (0.3 mmol), AgOAc (0.9 mmol), Pd(OAc)₂ (10 mol %), and ligand (20 mol %) in solvent (3 mL) under air for 48 hours. ^b yield of isolated product. ^c ee value determined by HPLC analysis using a chiral stationary phase. ^d Benzoquinone was used instead of AgOAc. ^e 0.1 equiv of AgOAc under O₂ balloon was used. **L1** = Boc-L-Phe-OH, **L2** = Boc-L-Tle-OH, **L3** = Boc-Ile-OH, **L4** = Boc-D-Val-OH, **L5** = CBZ-L-Val-OH, **L6** = CBZ-L-Phe-OH, **L7** = Ac-L-Leu-OH, **L8** = Ac-L-Ala-OH, HFIP = hexafluoroisopropanol.

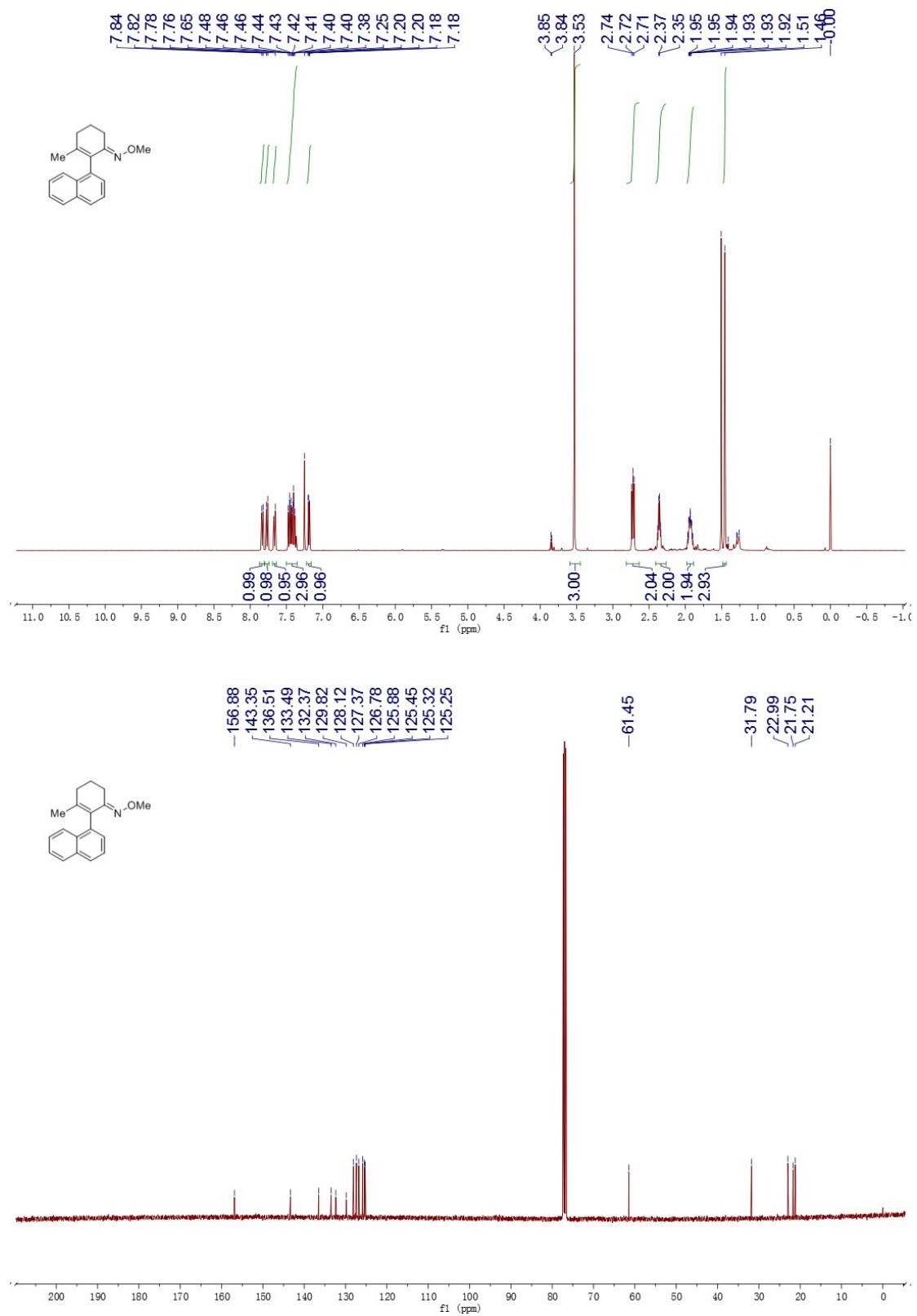
X-ray structures of chiral product **3j** (CCDC 1827731)

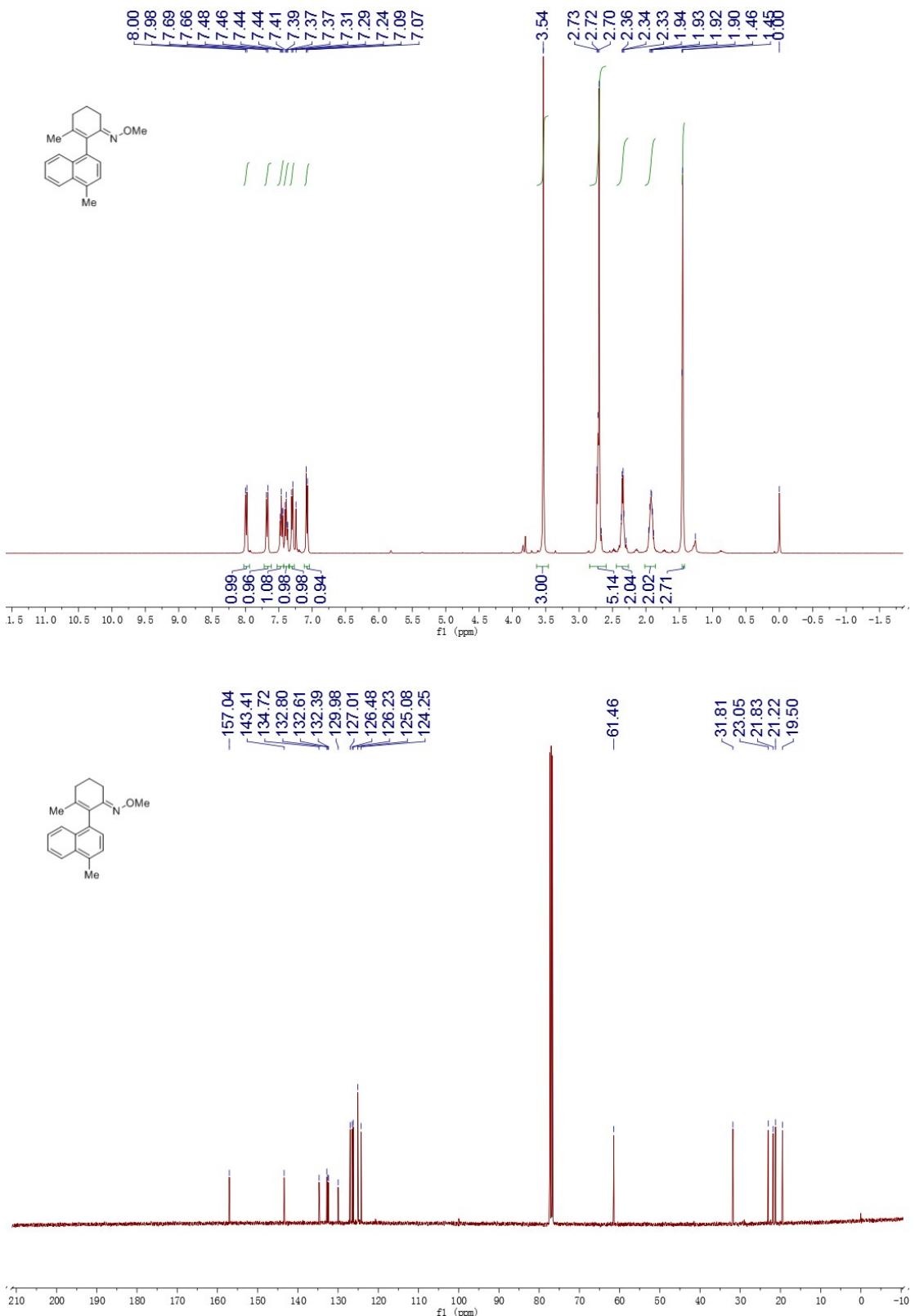


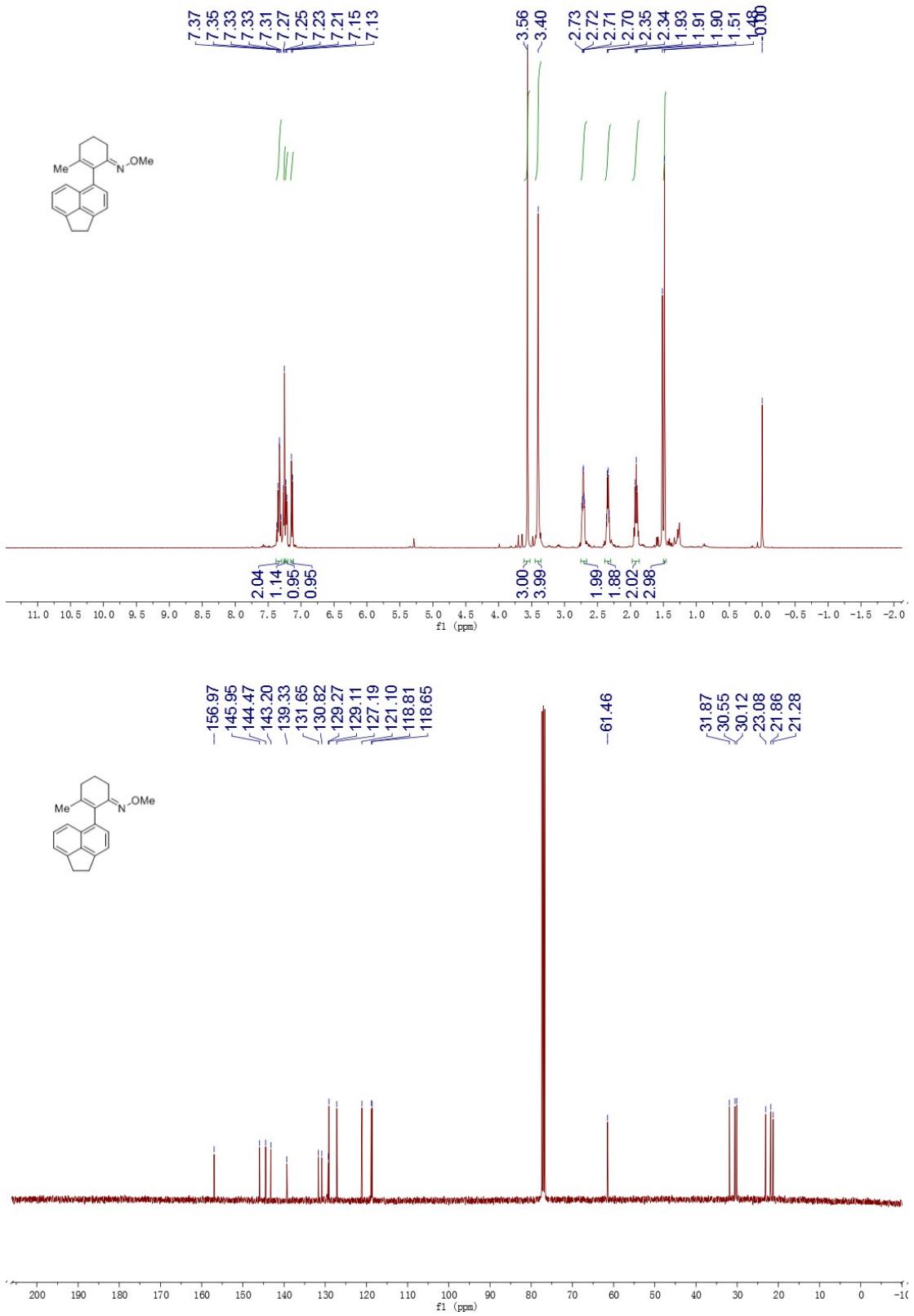
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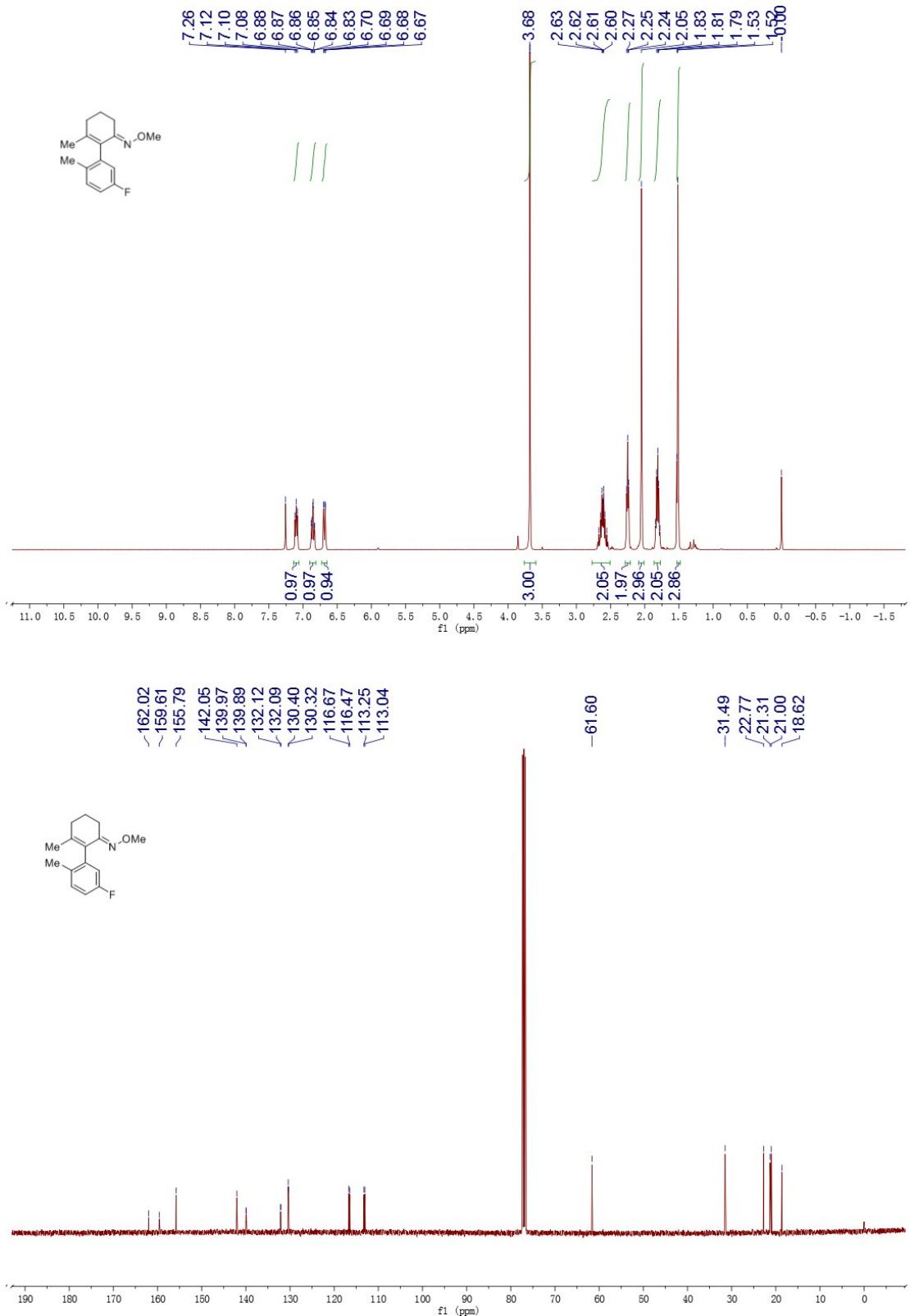
- [1] Q.-L. Li and H.-B. Zhang. *Chem. Eur. J.* **2015**, 21, 16379.
- [2] Liang, Y.-F.; Wang, X.-Y.; Yuan, Y.-Z.; Liang, Y.-J.; Li, X.-Y.; Jiao, N. *ACS Catal.* **2015**, 5, 6148.
- [3] Q.-L. Liu; W.-F. Chen; Q.-Y. Jiang; X.-F. Bai; Z.-F. Li; Z. Xu; and L.-W. Xu. *ChemCatChem* **2016**, 8, 1495.
- [4] Y.-X. Yang; B. Zhou; and Y.-C. Li. *Adv. Synth. Catal.* **2012**, 354, 2916.

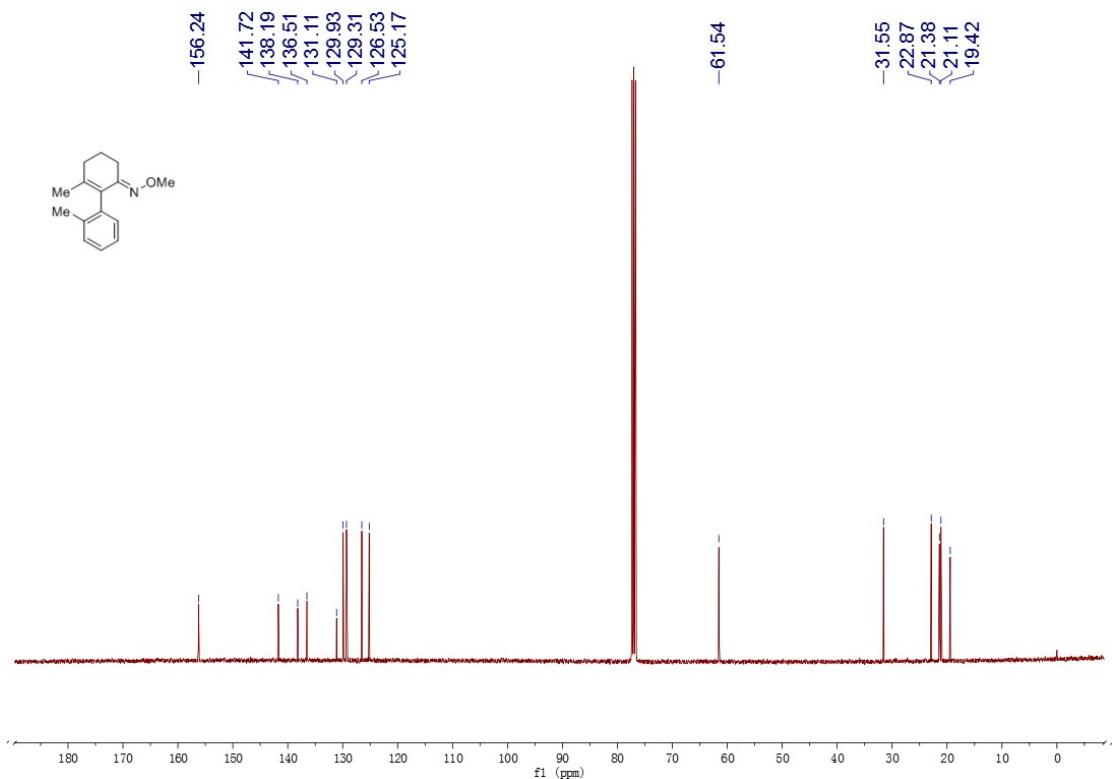
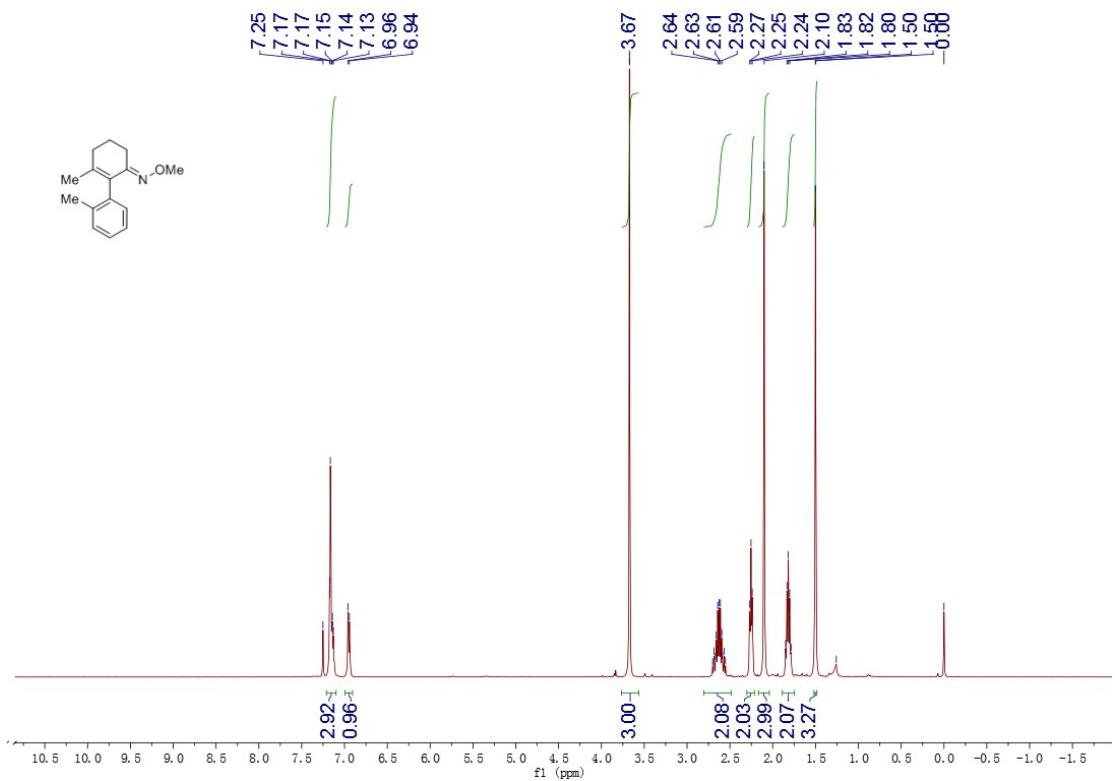
¹H , ¹³C NMR Spectra

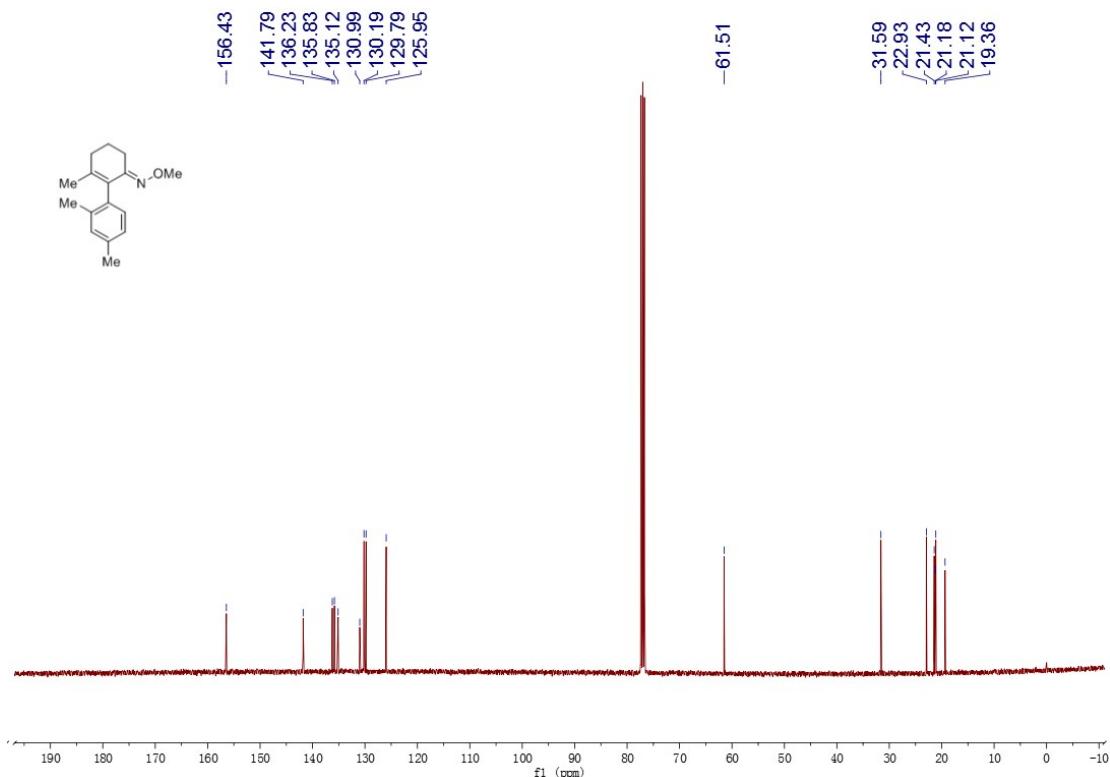
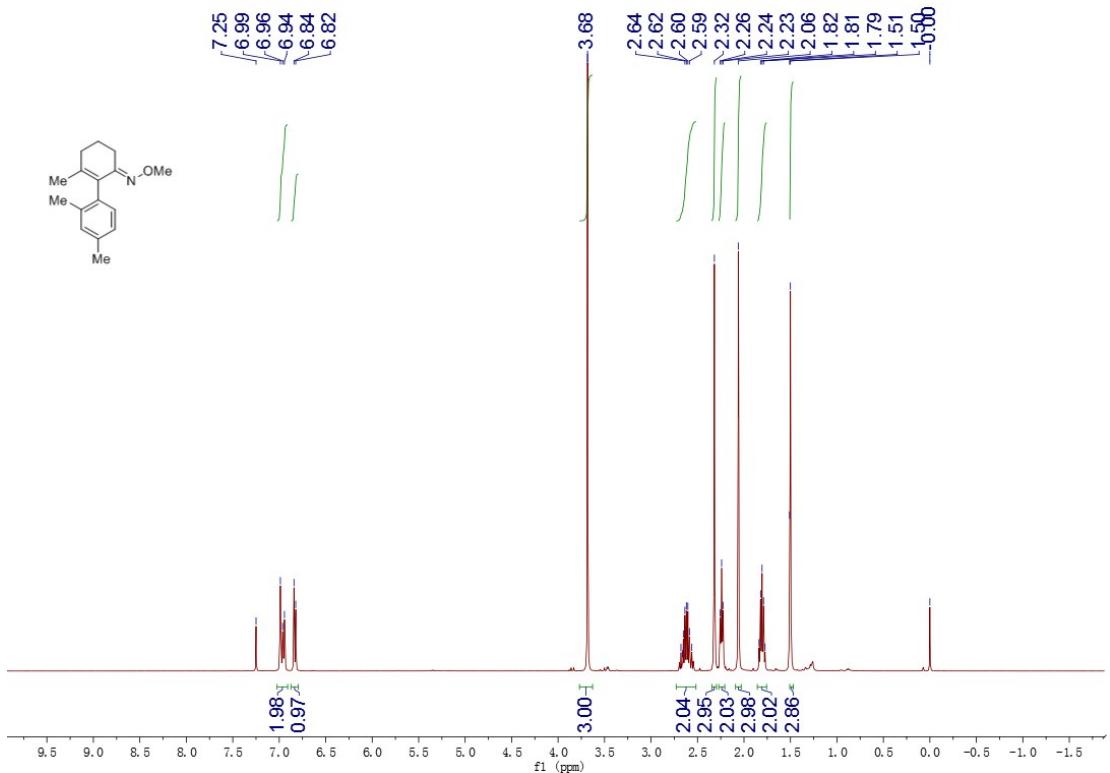


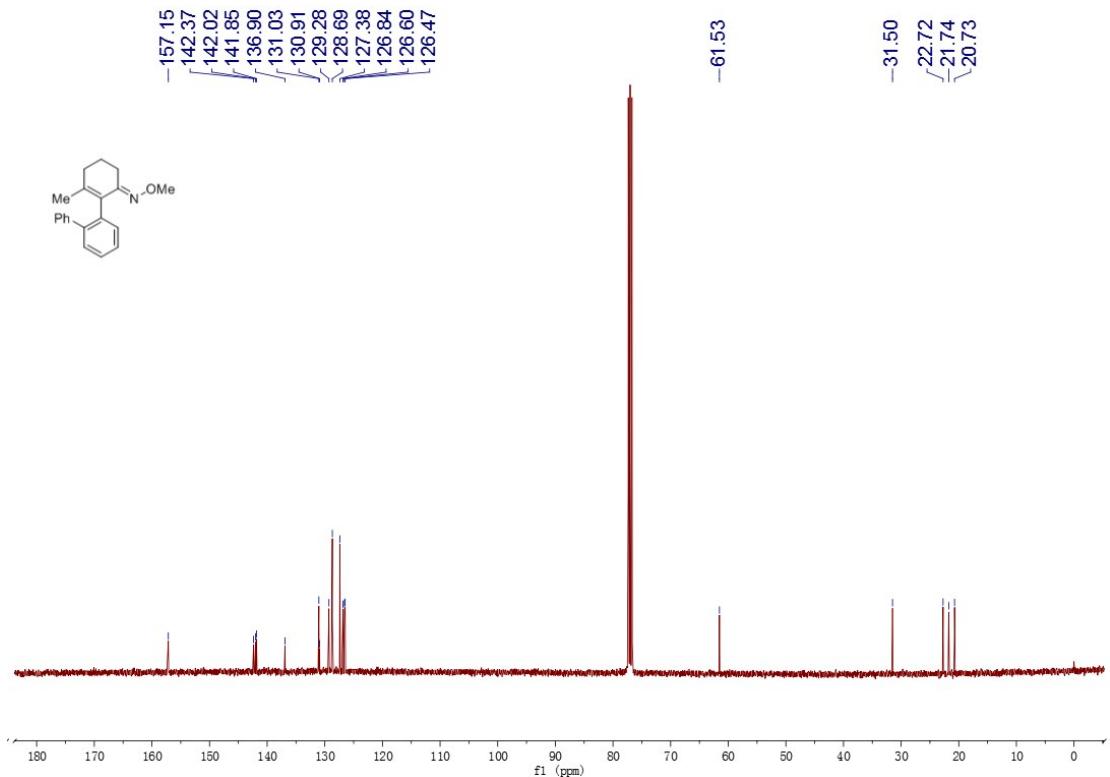
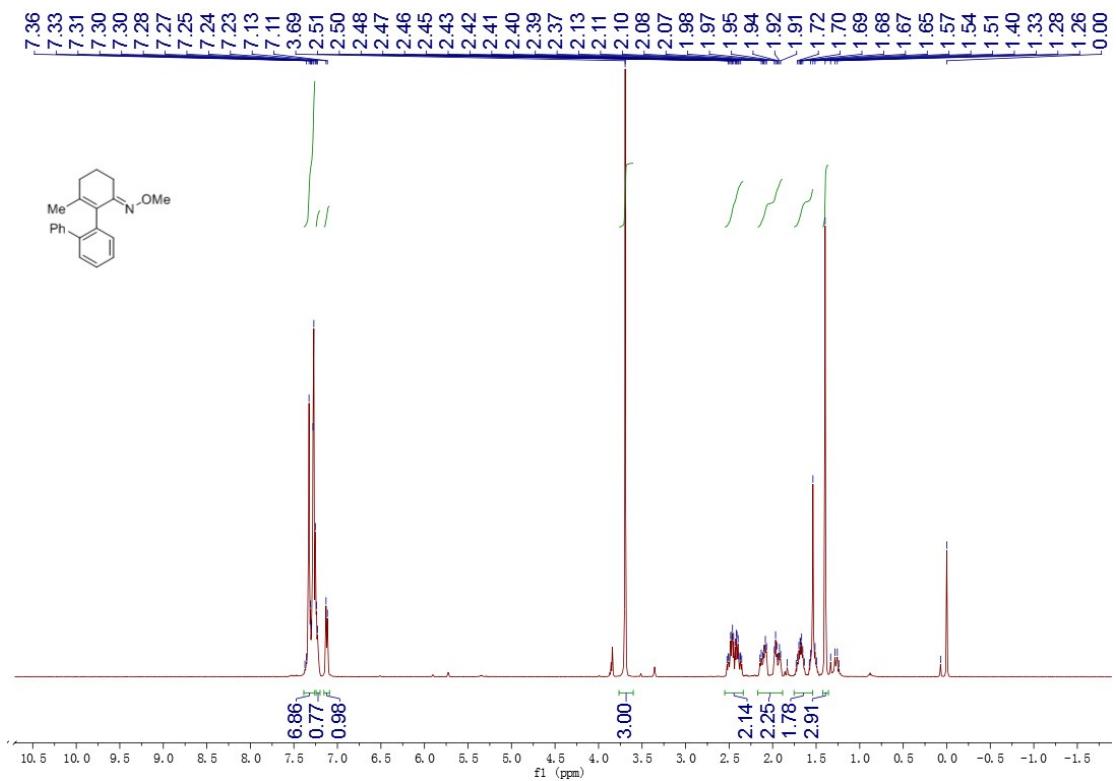


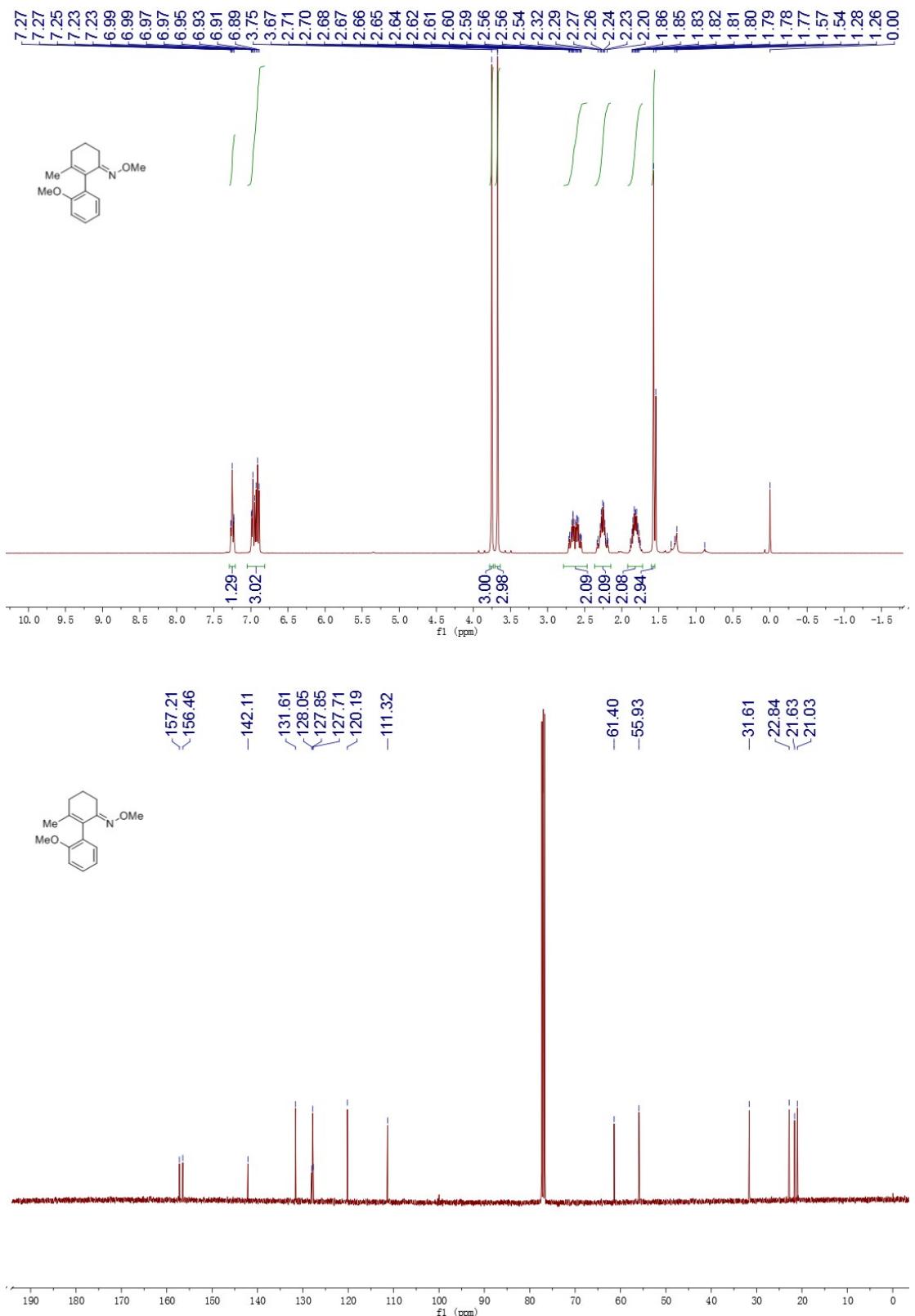


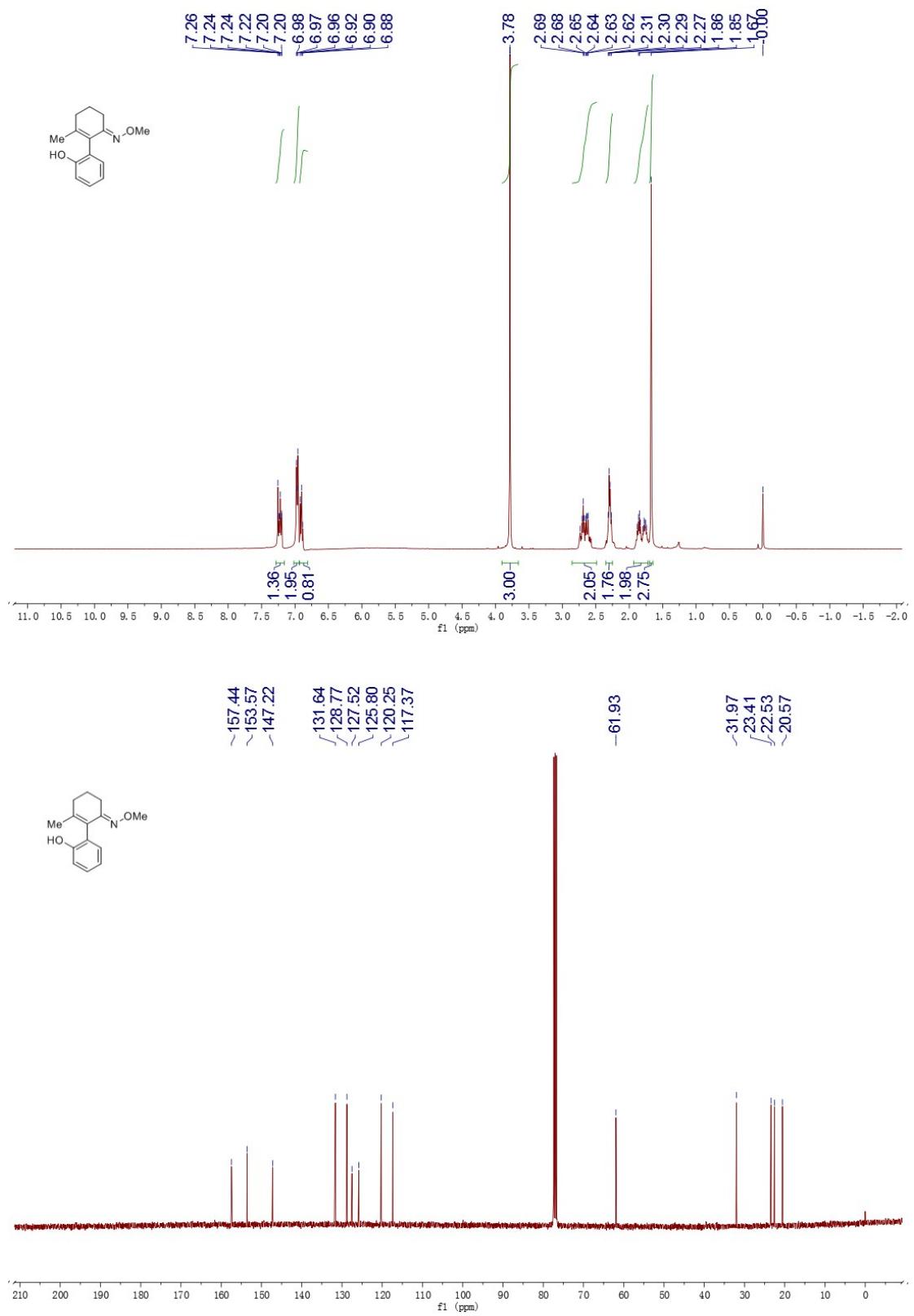


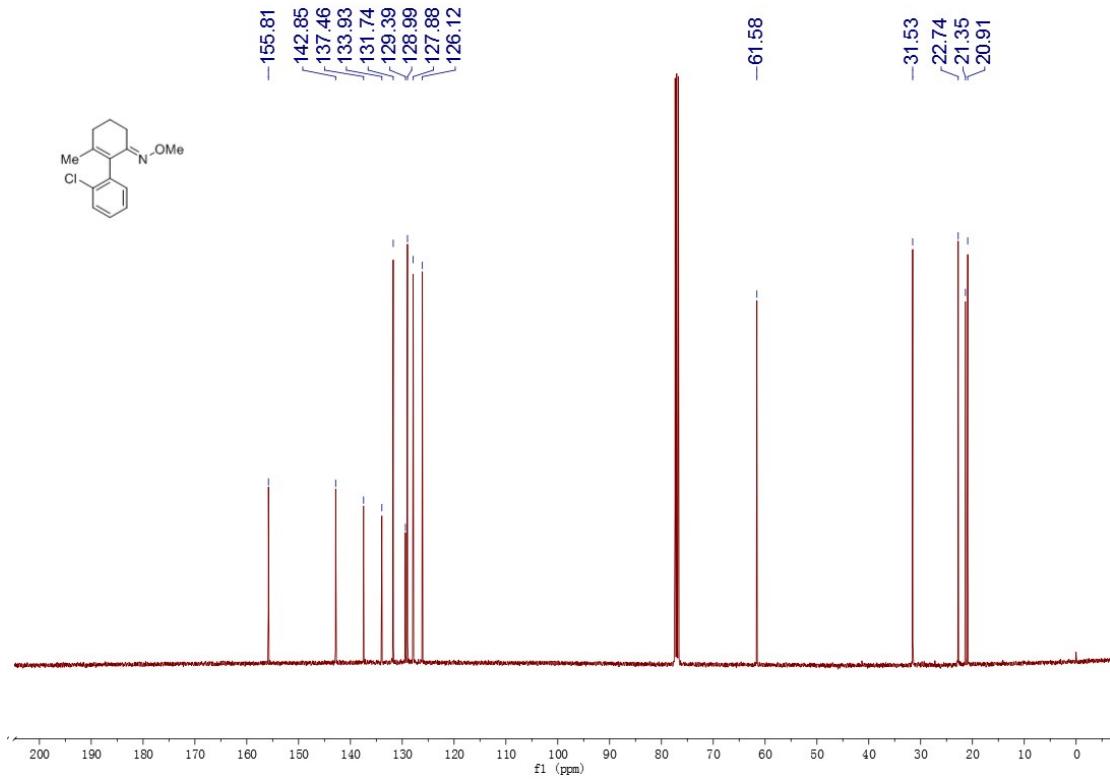
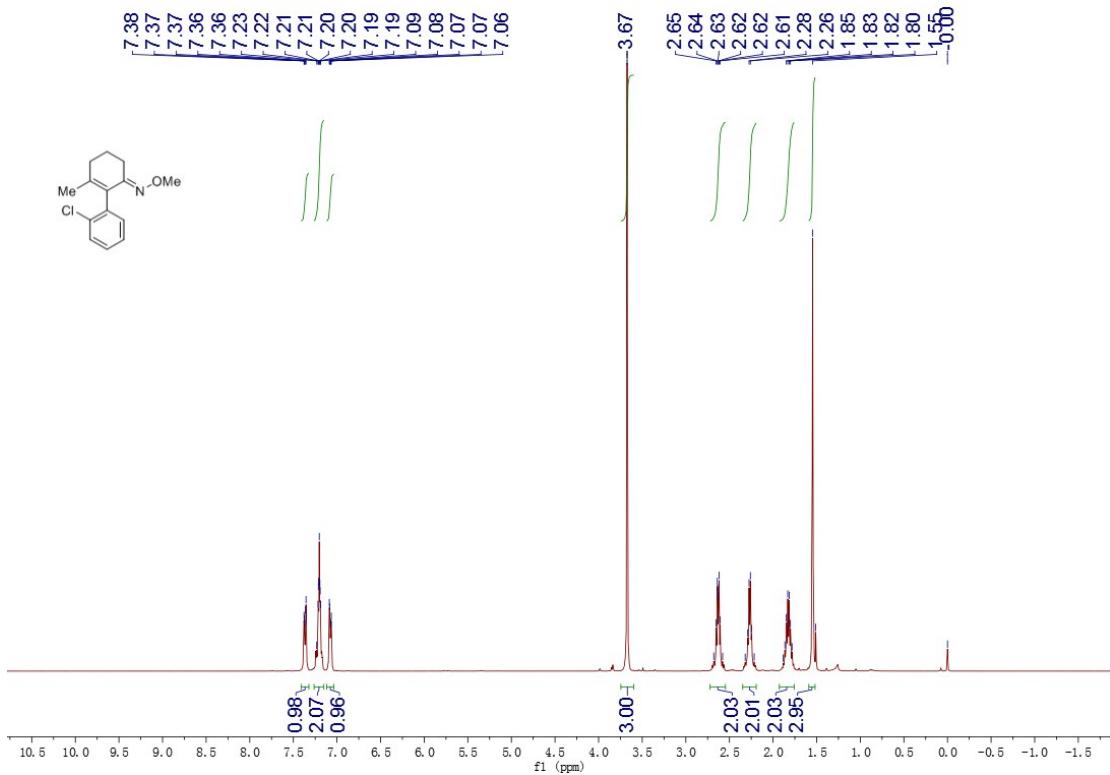


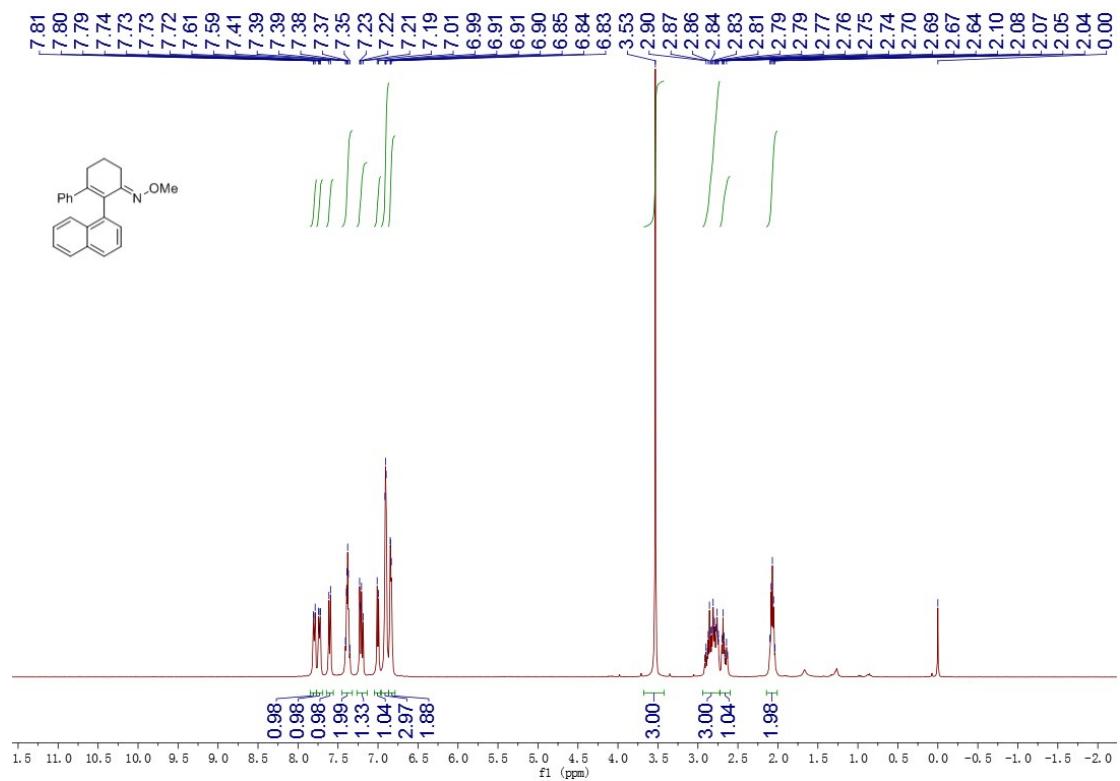


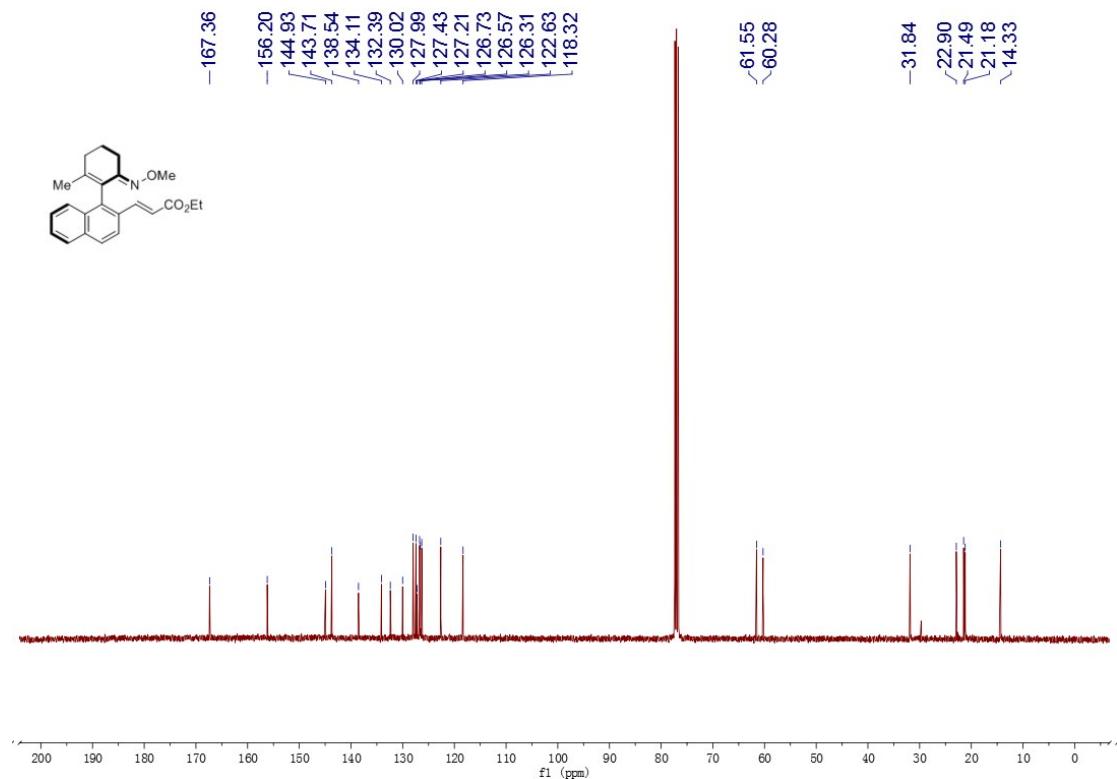
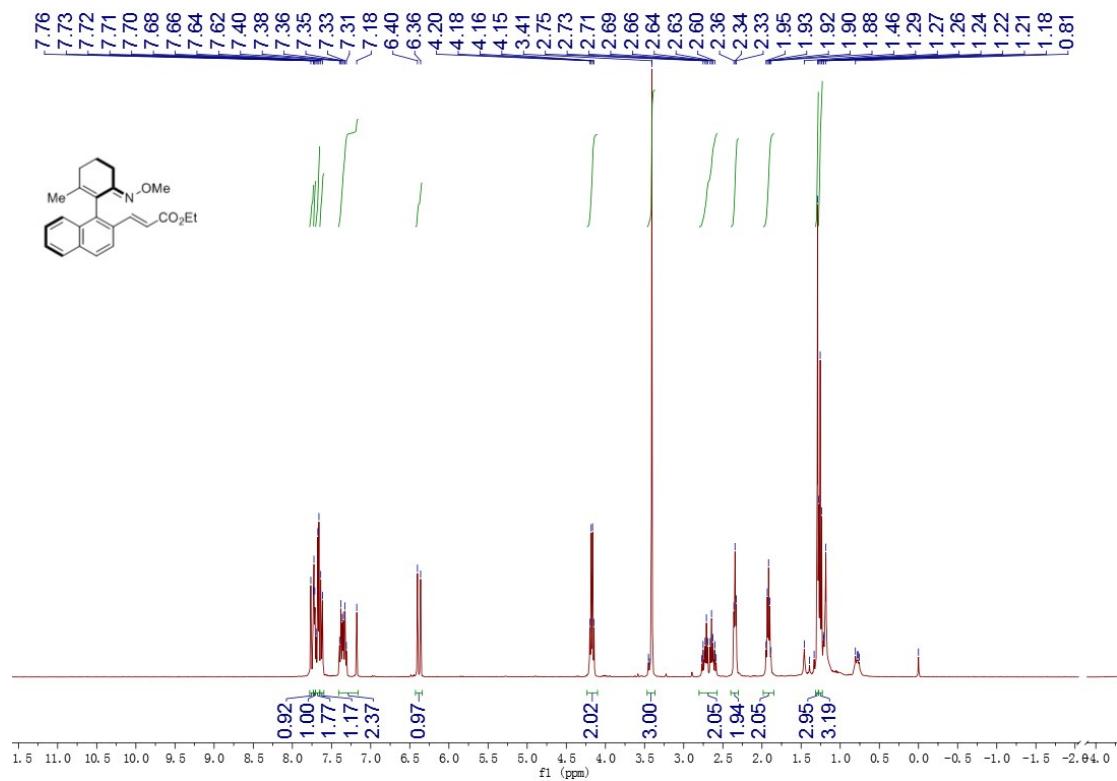


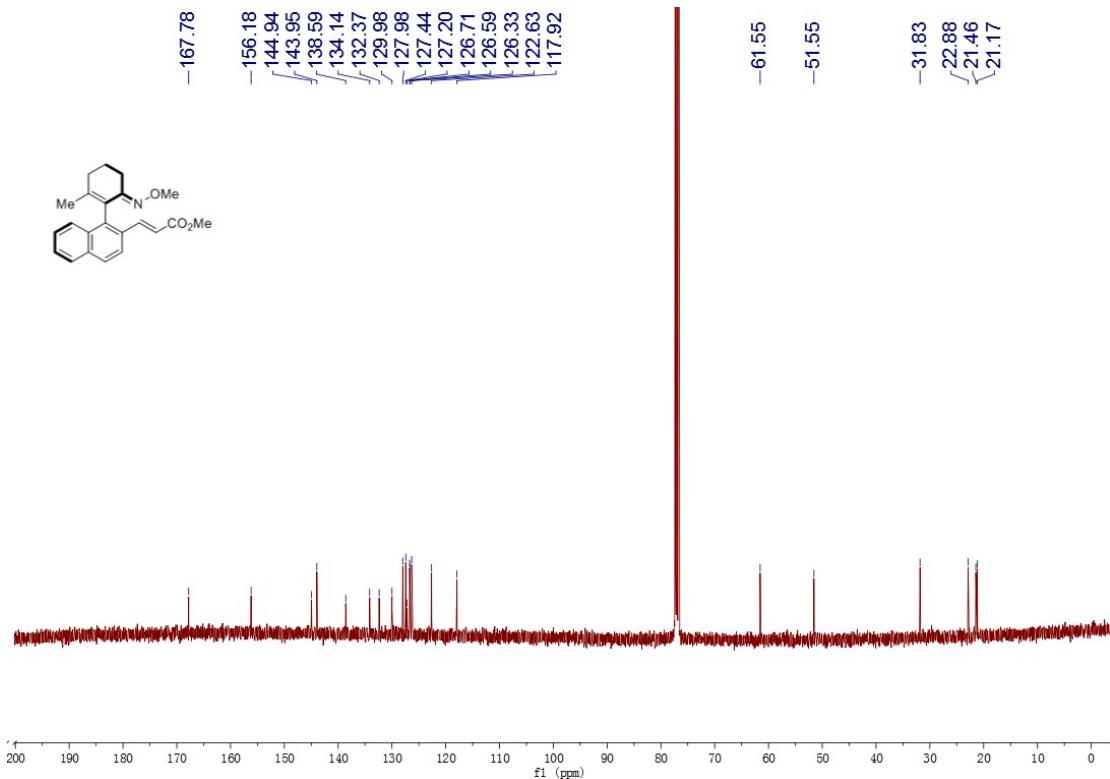
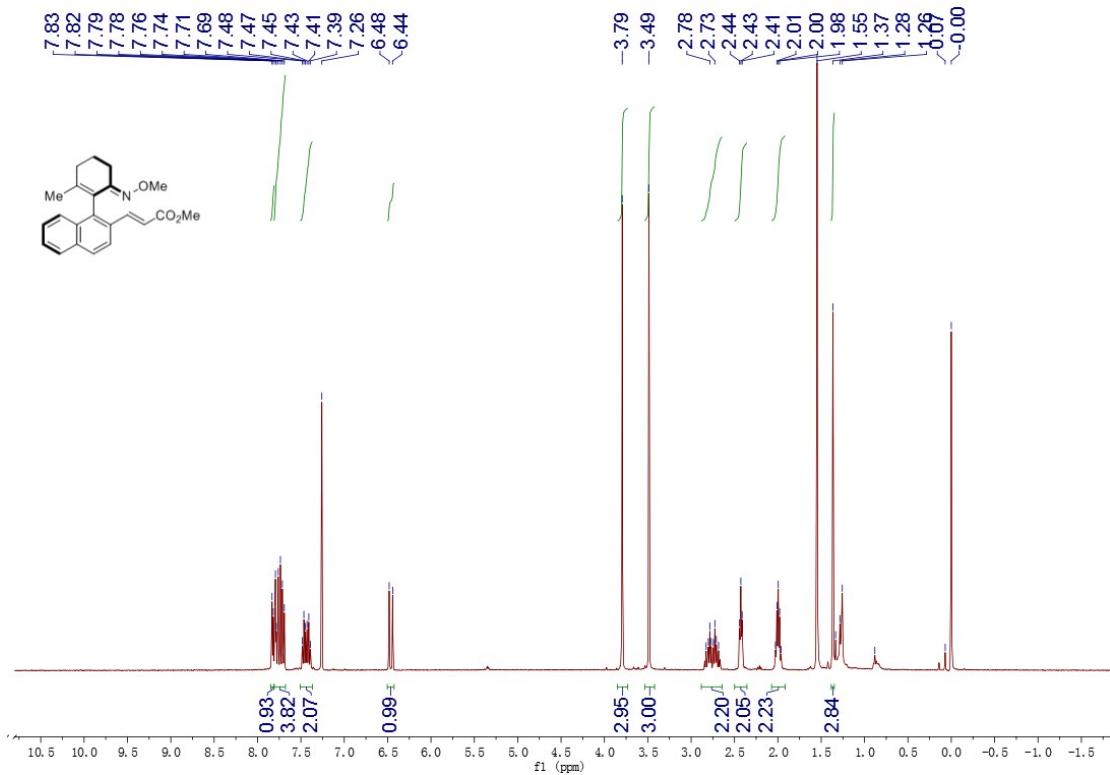


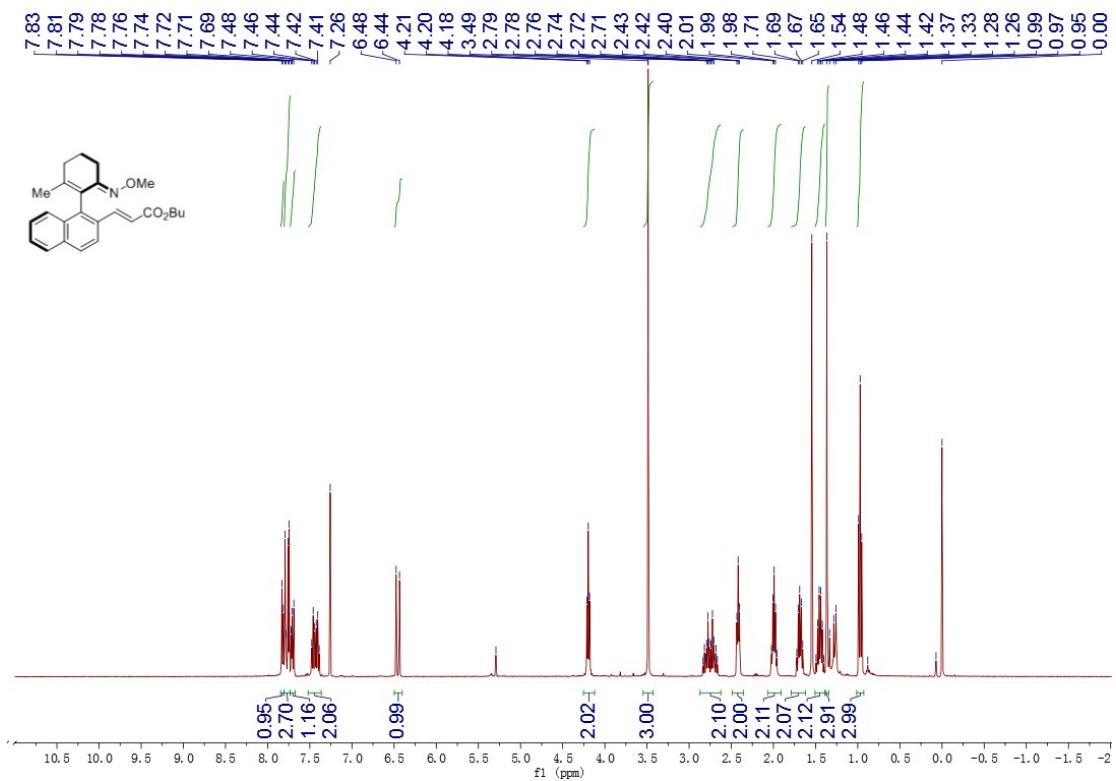


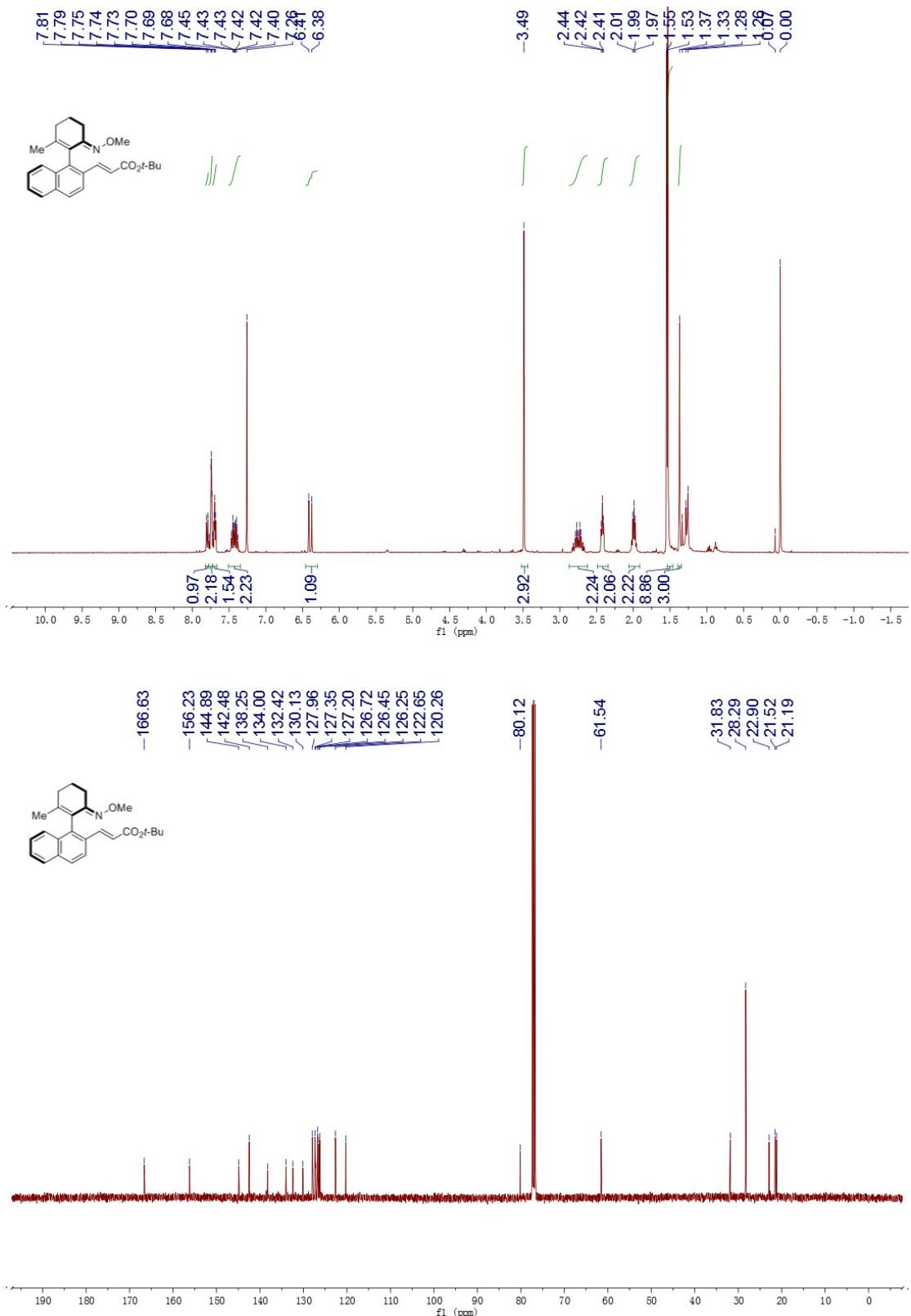


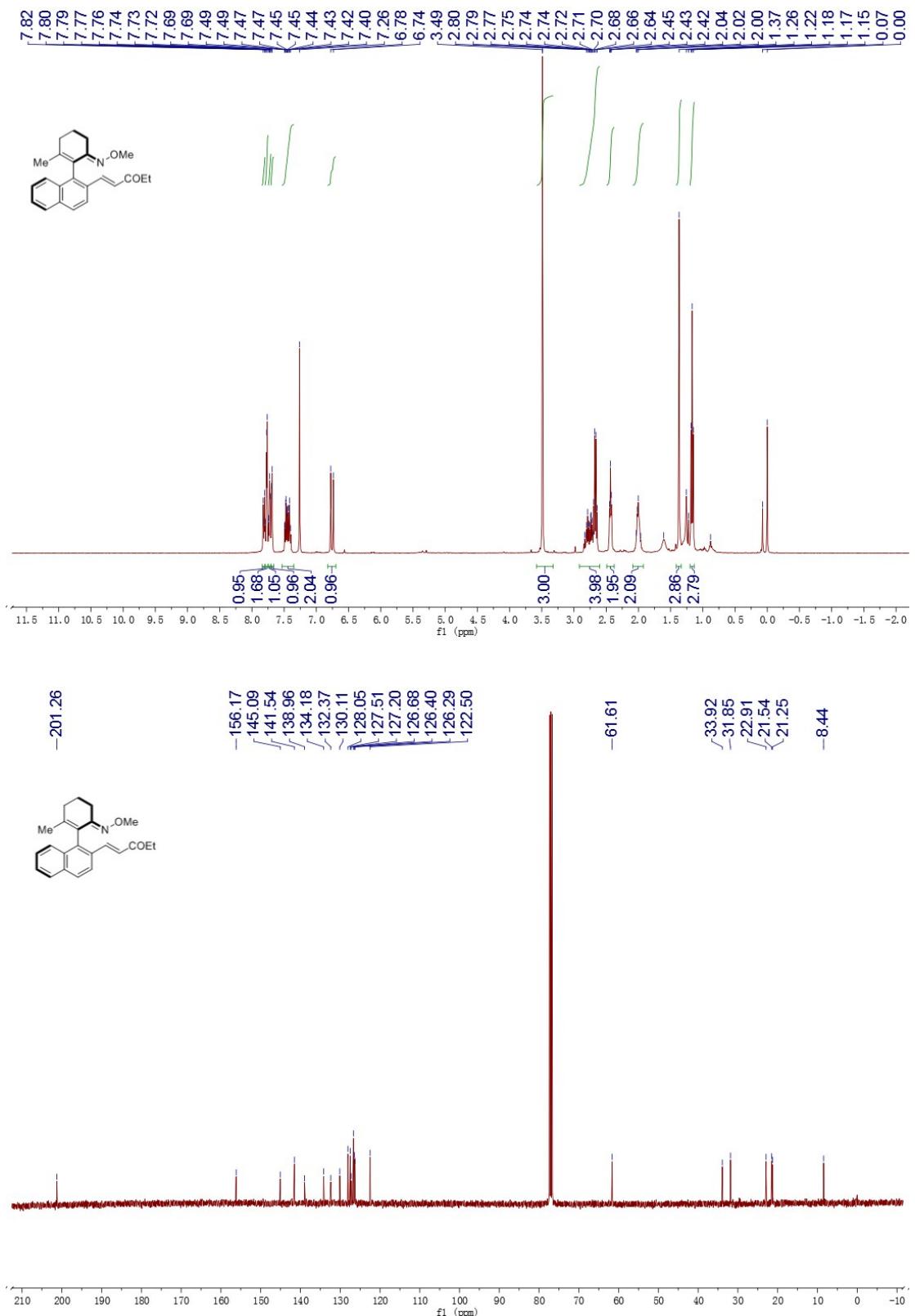


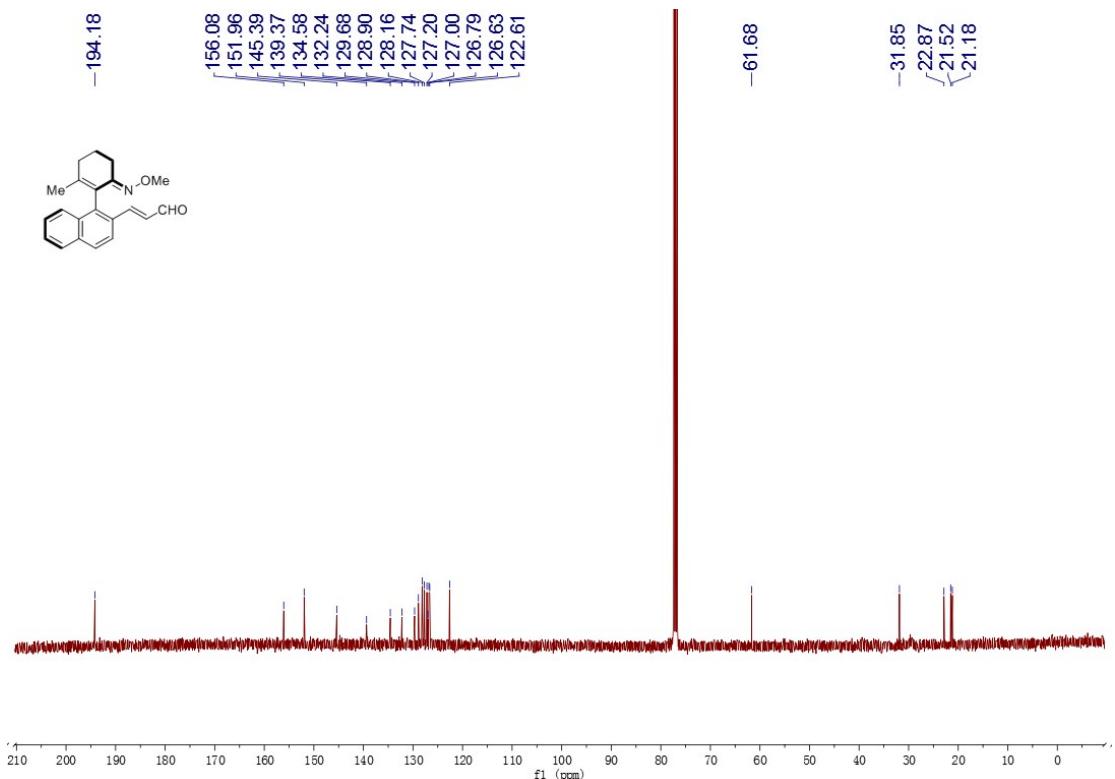
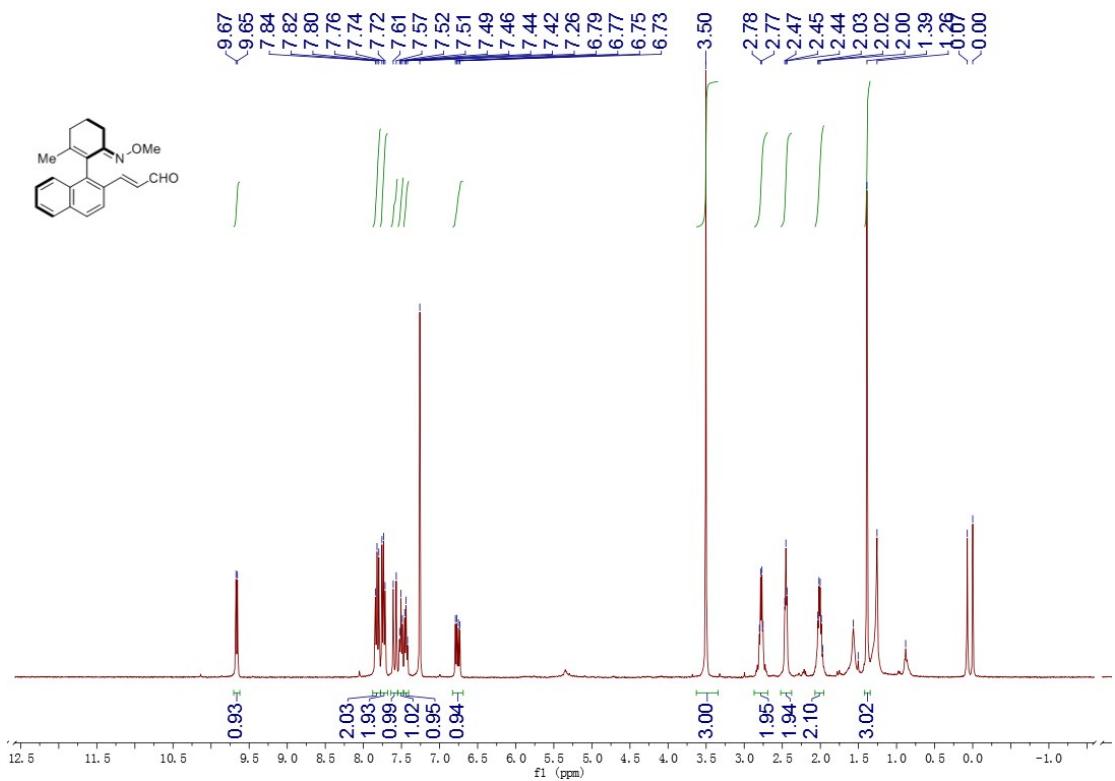


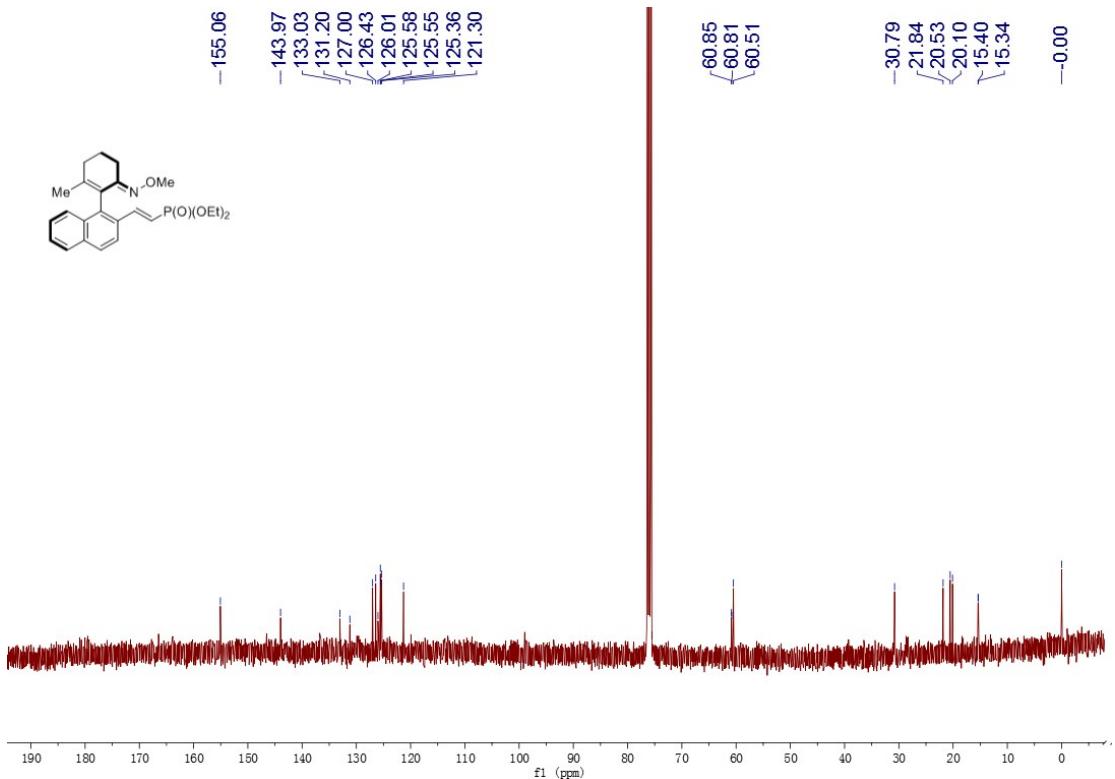
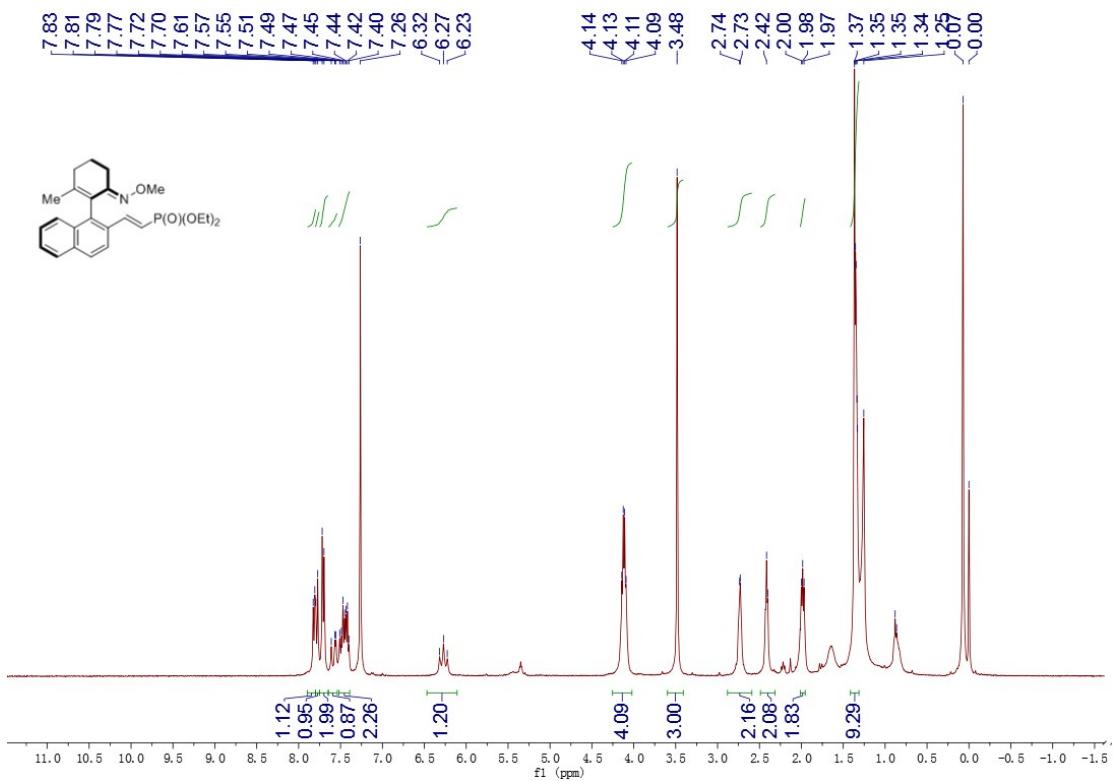


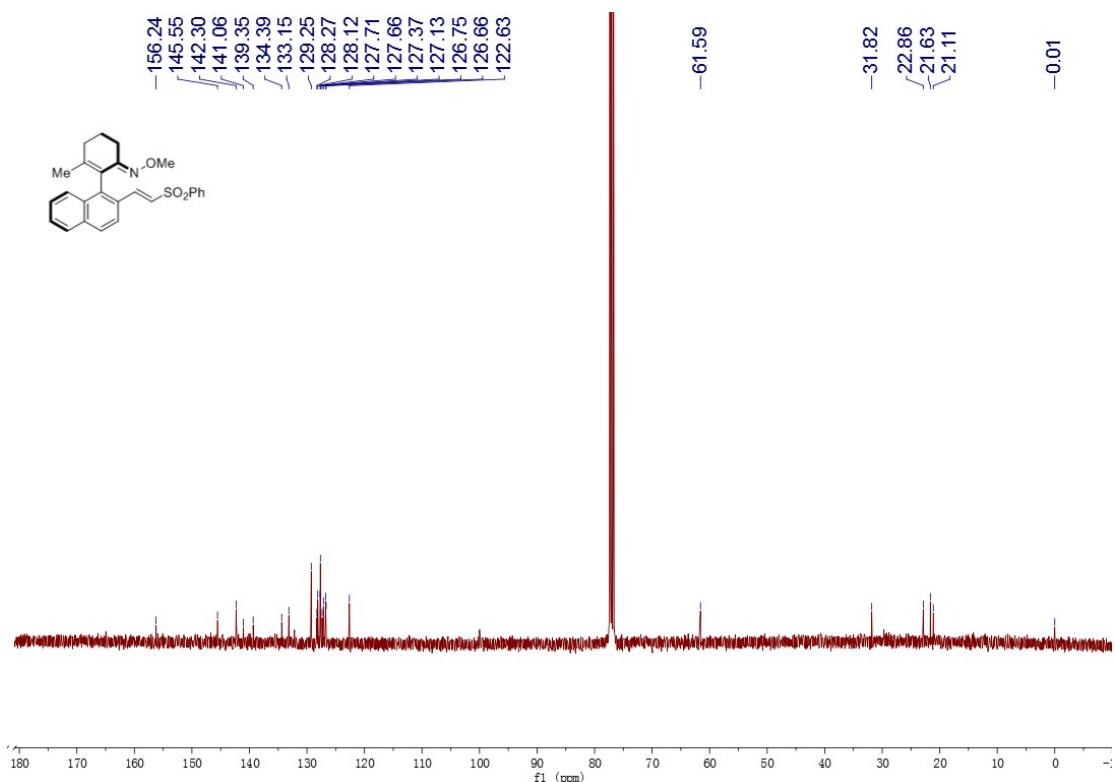
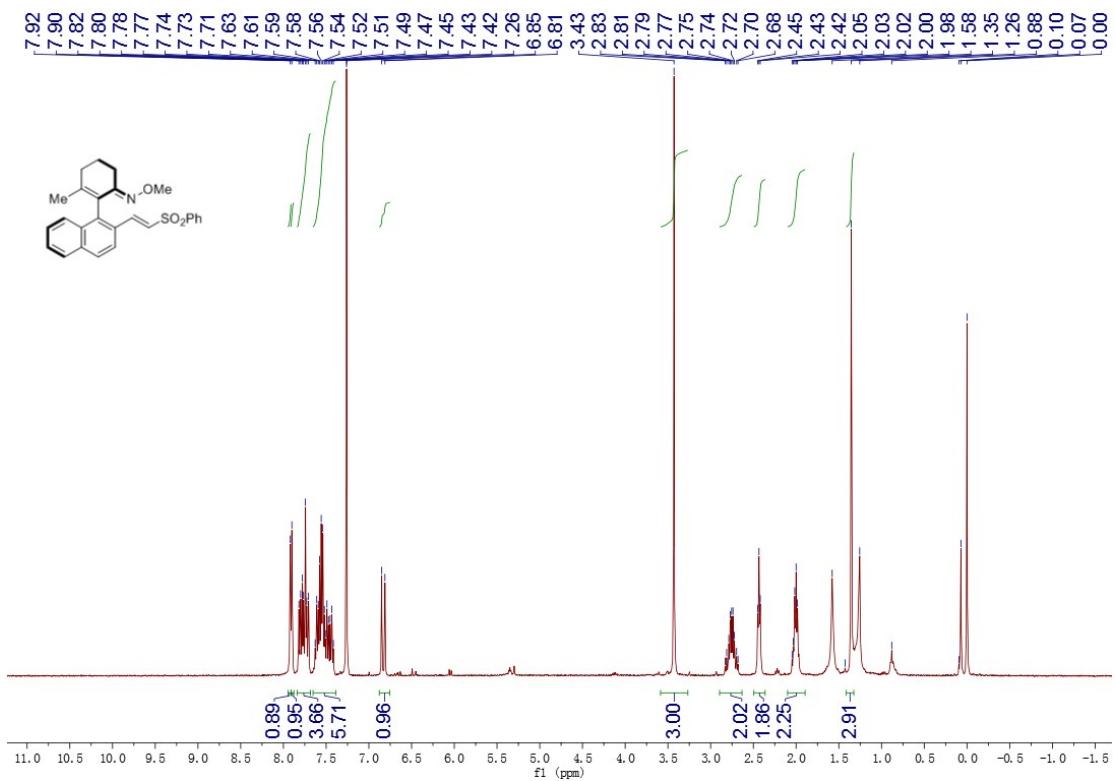


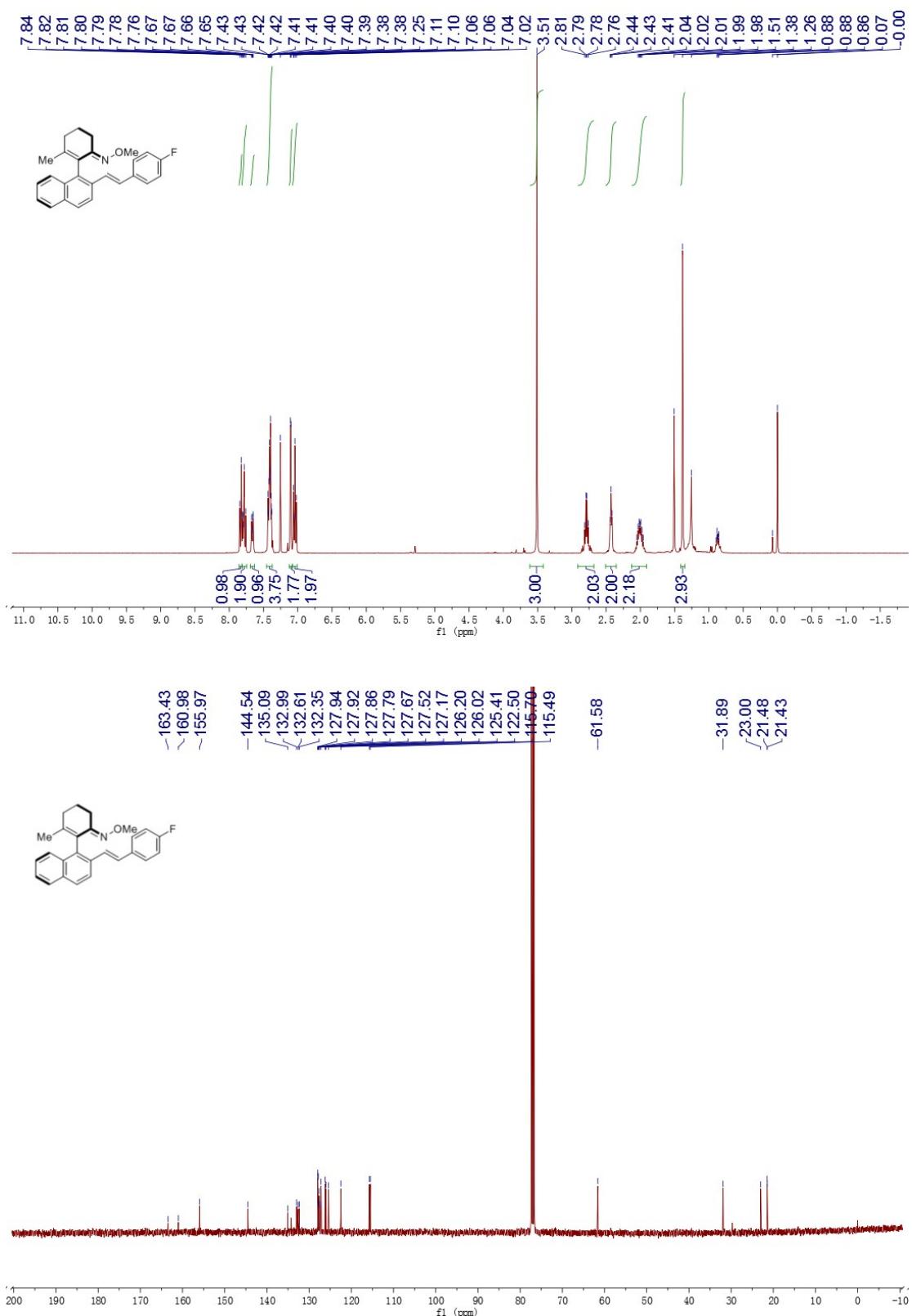


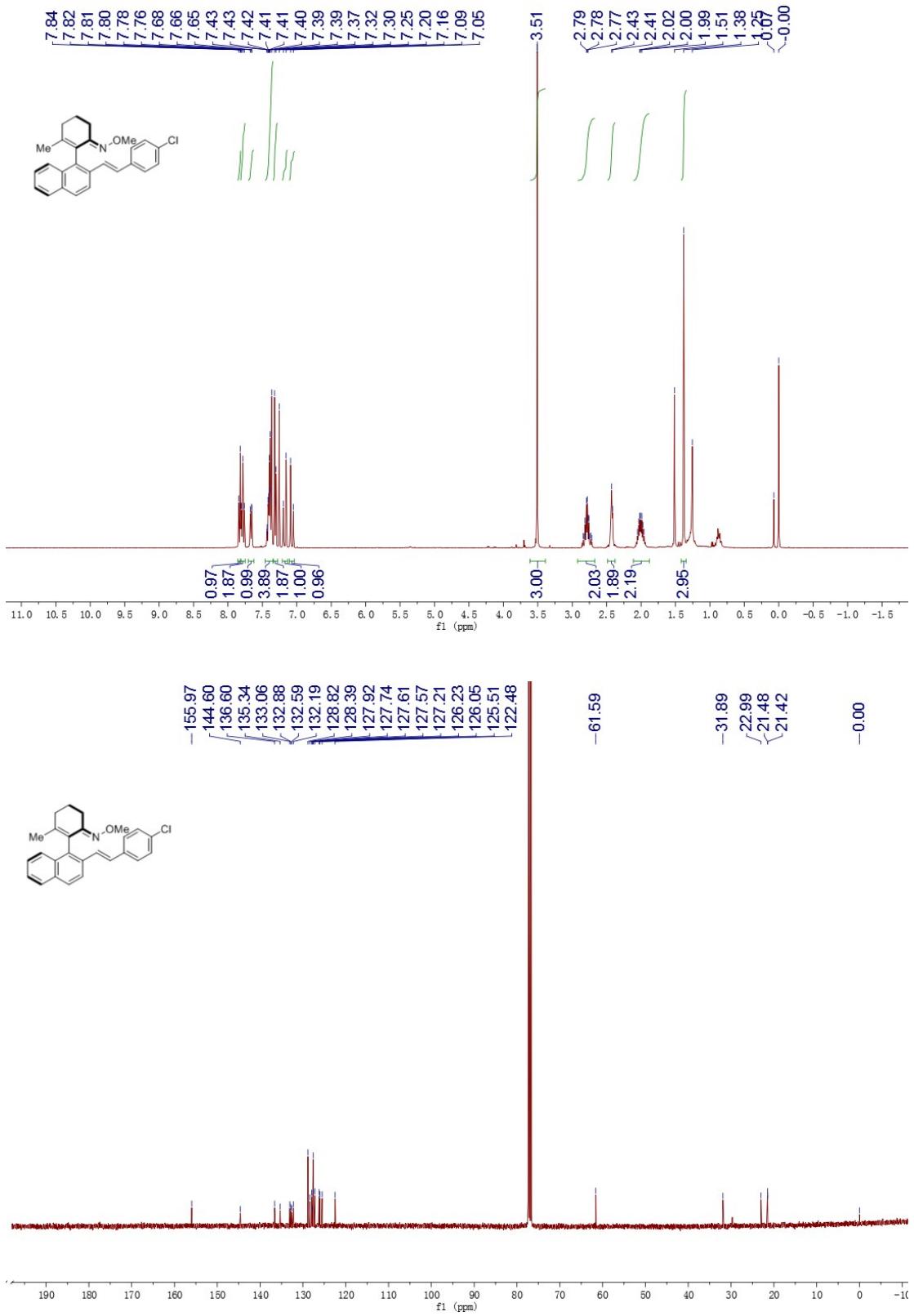


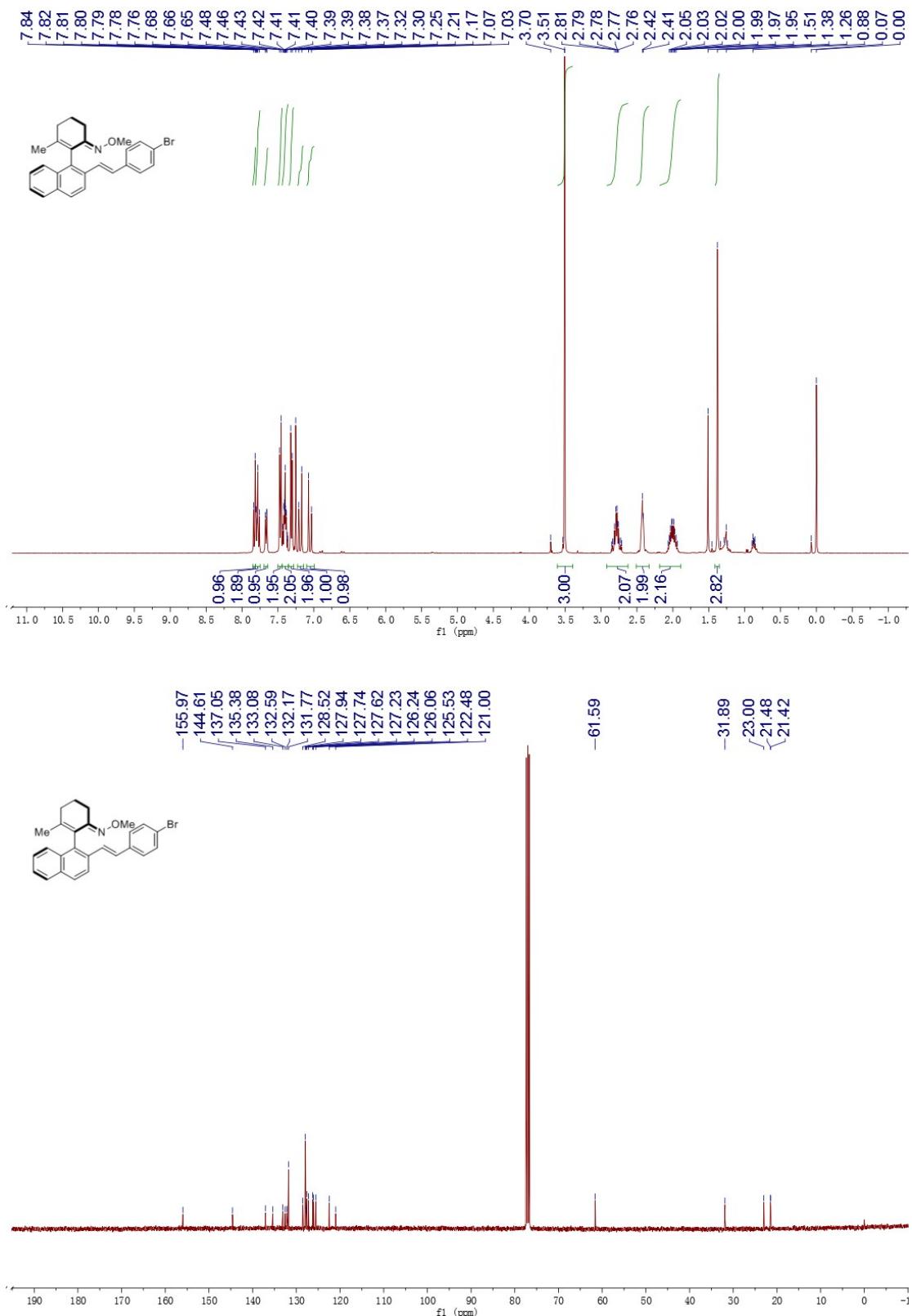


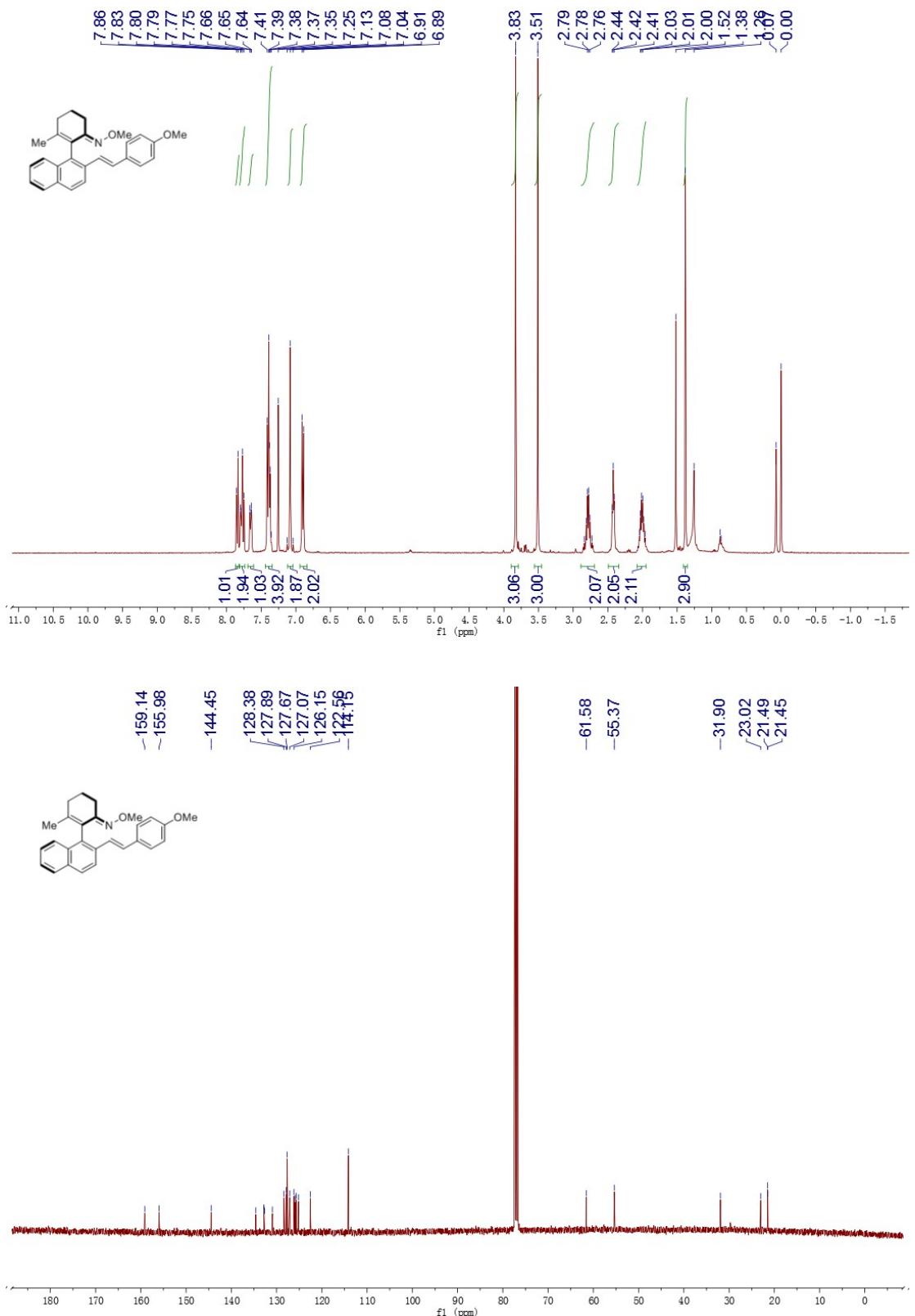


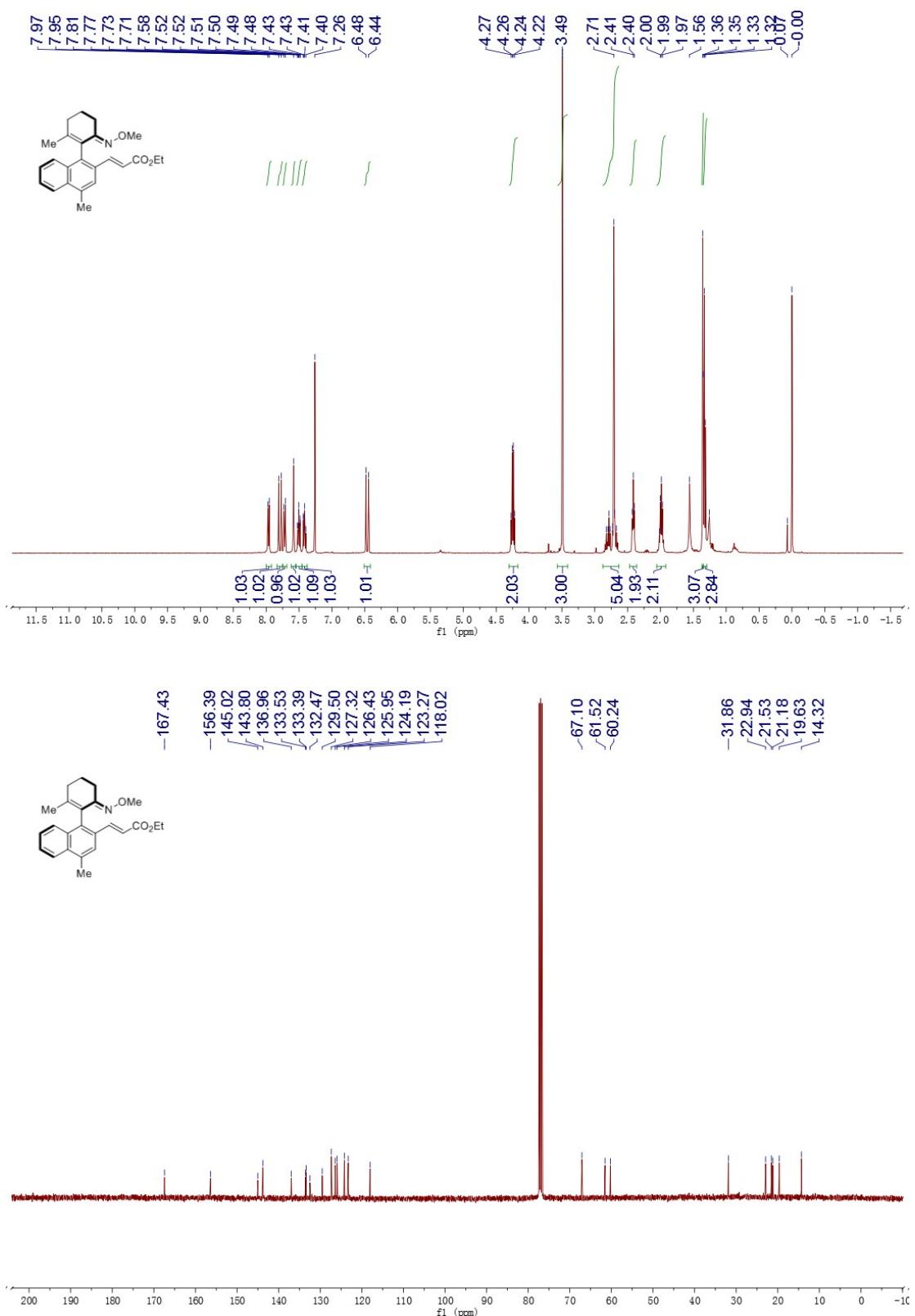


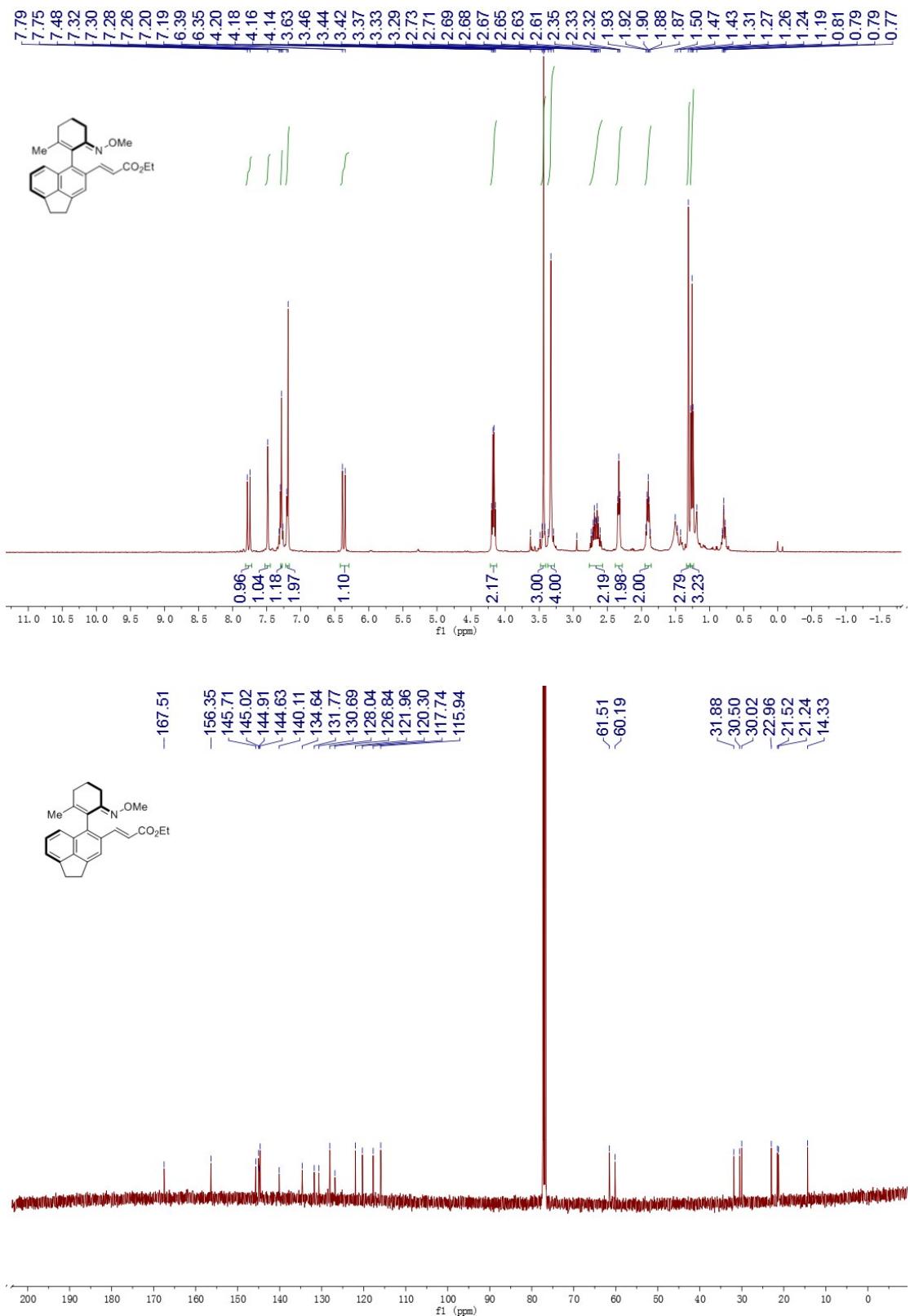


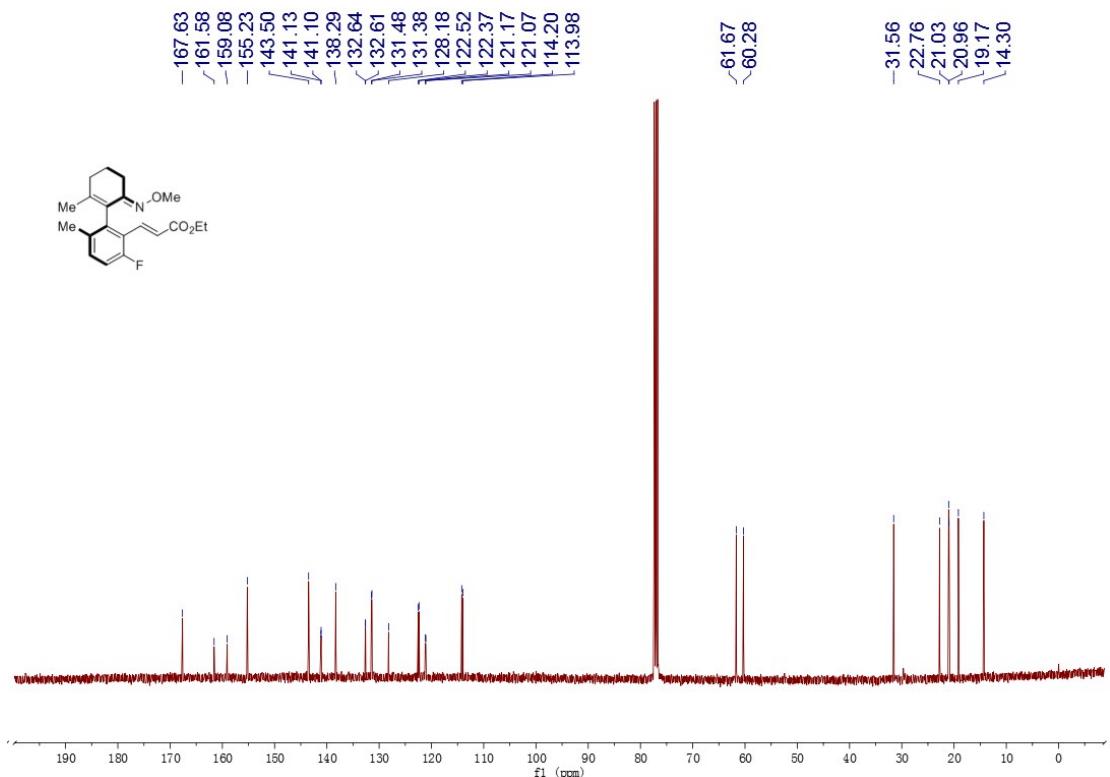
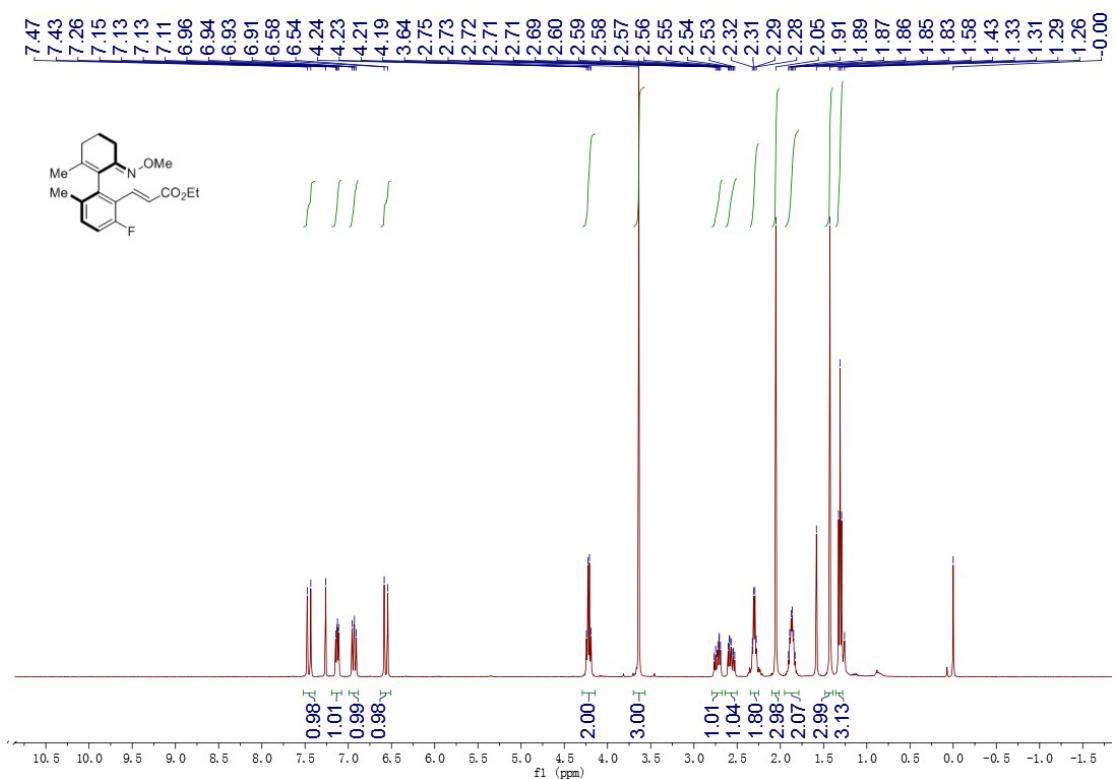


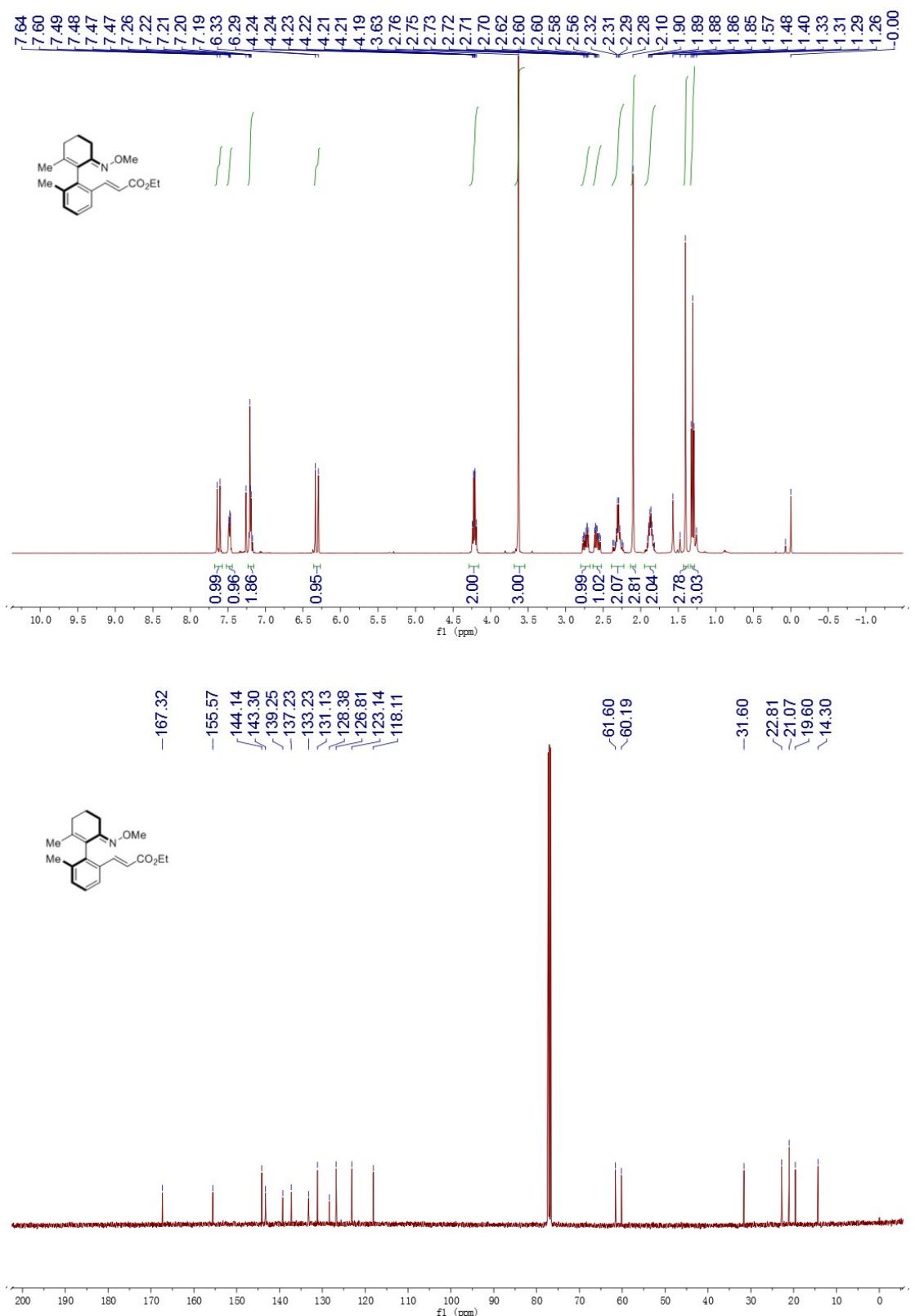


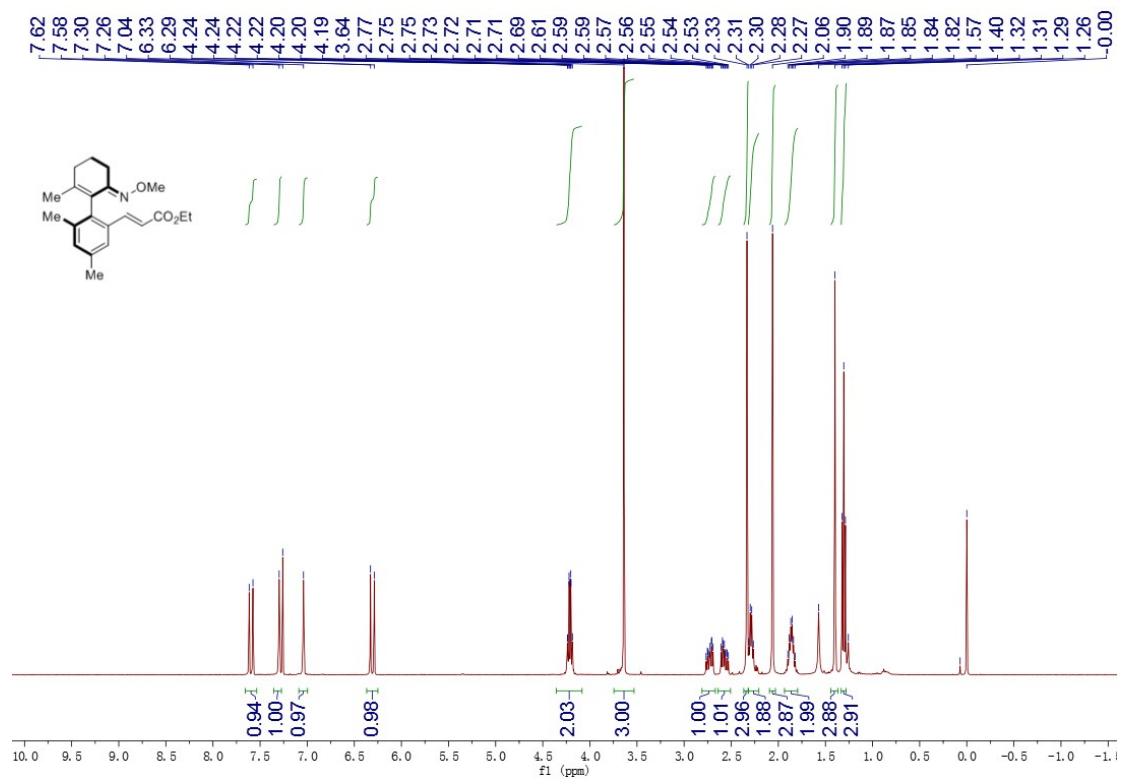


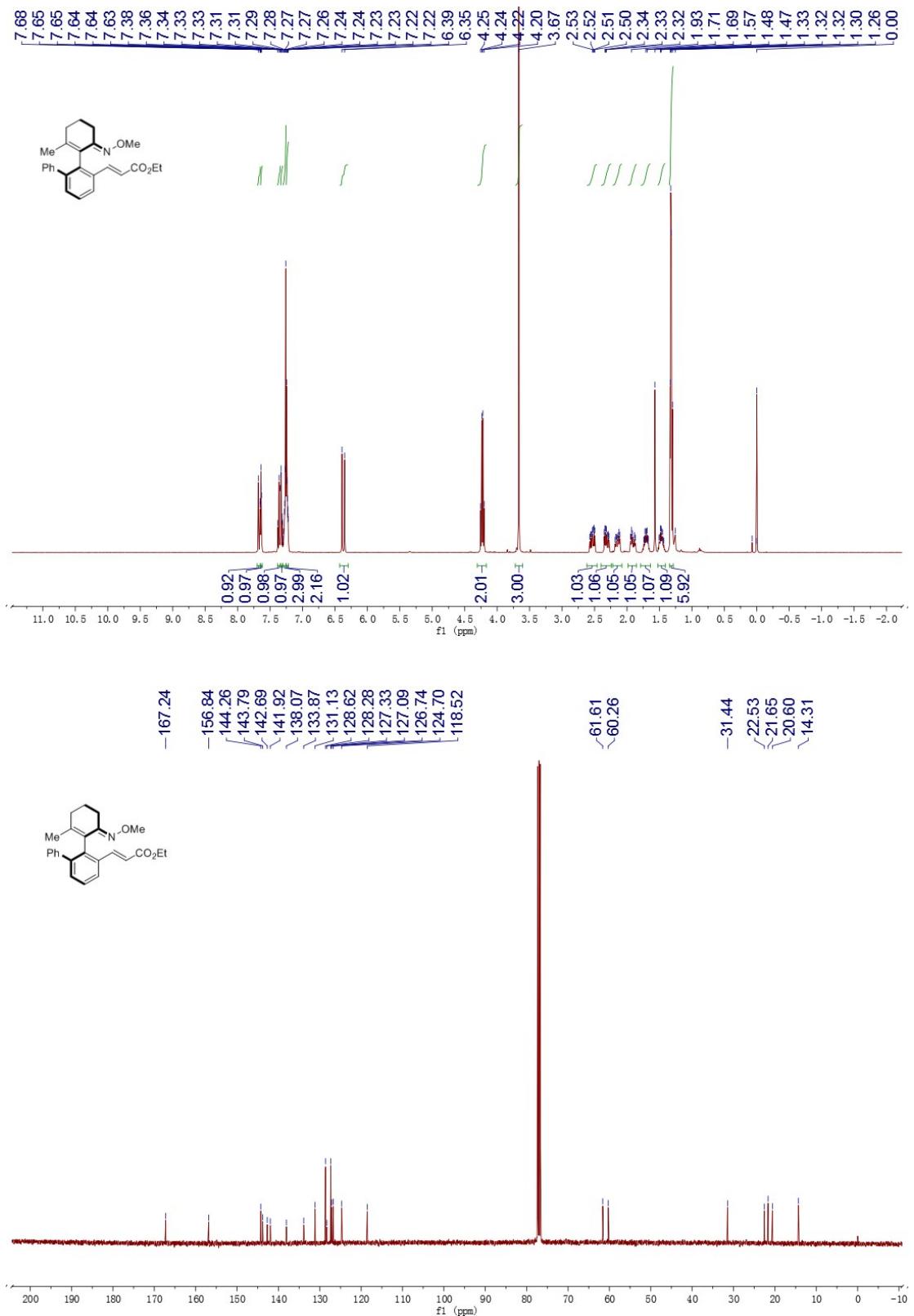


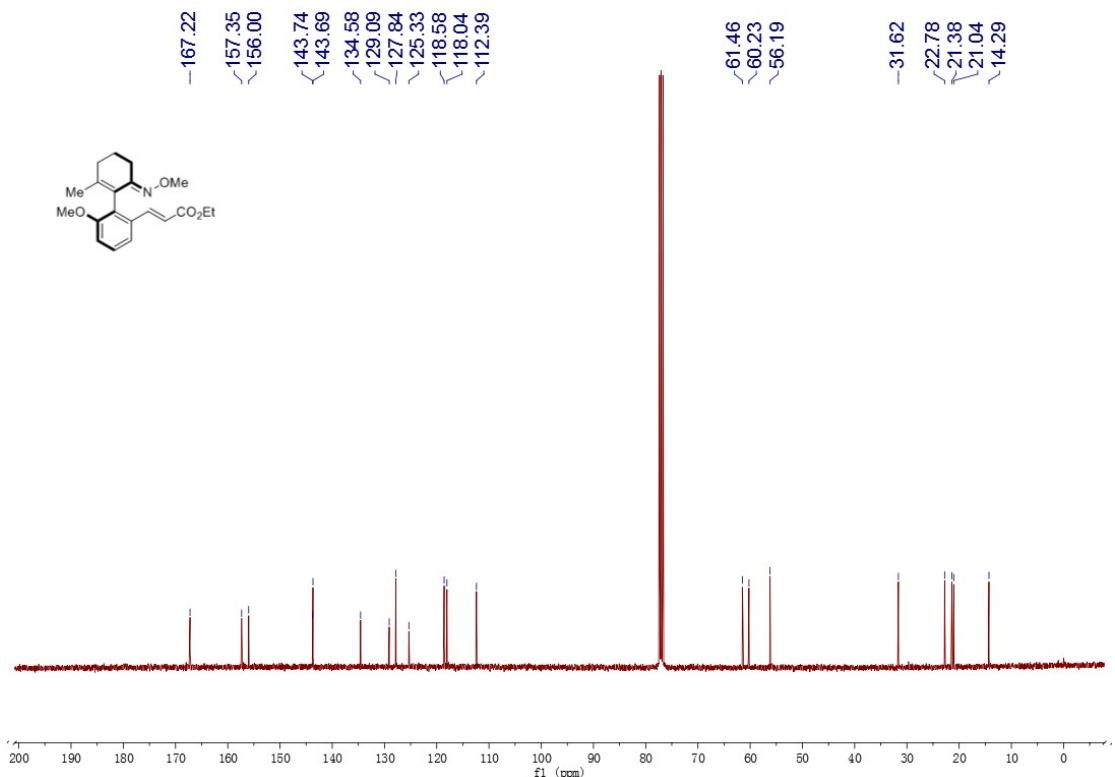
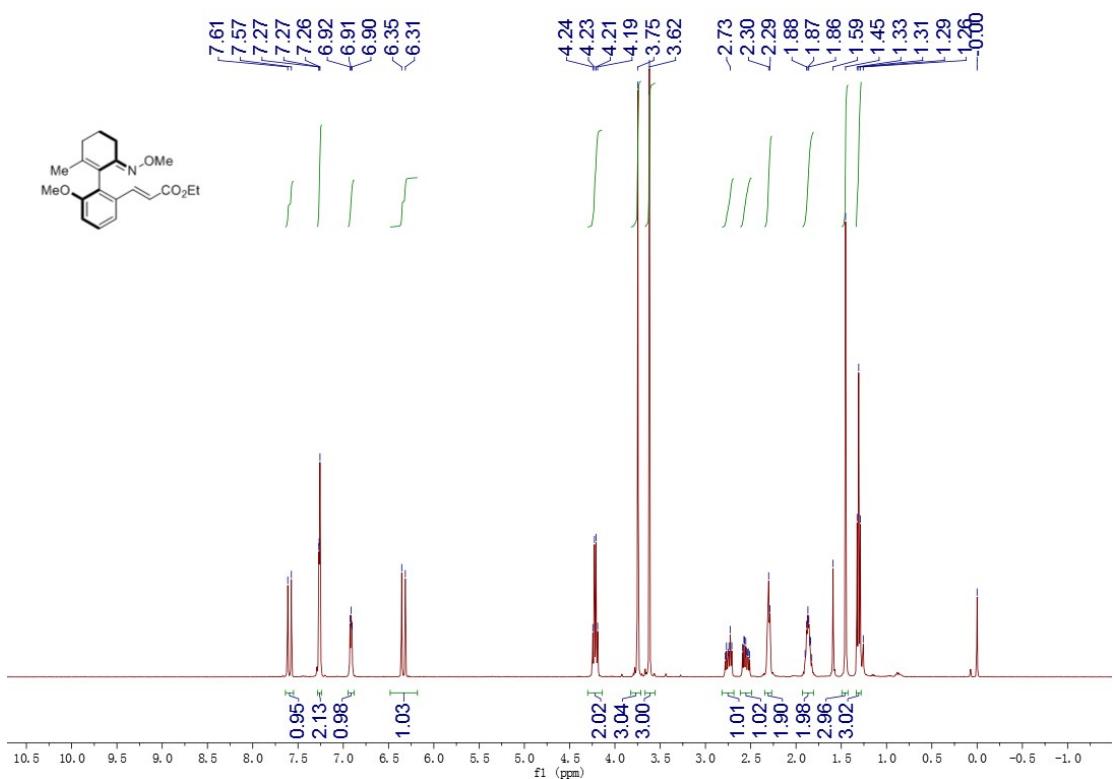


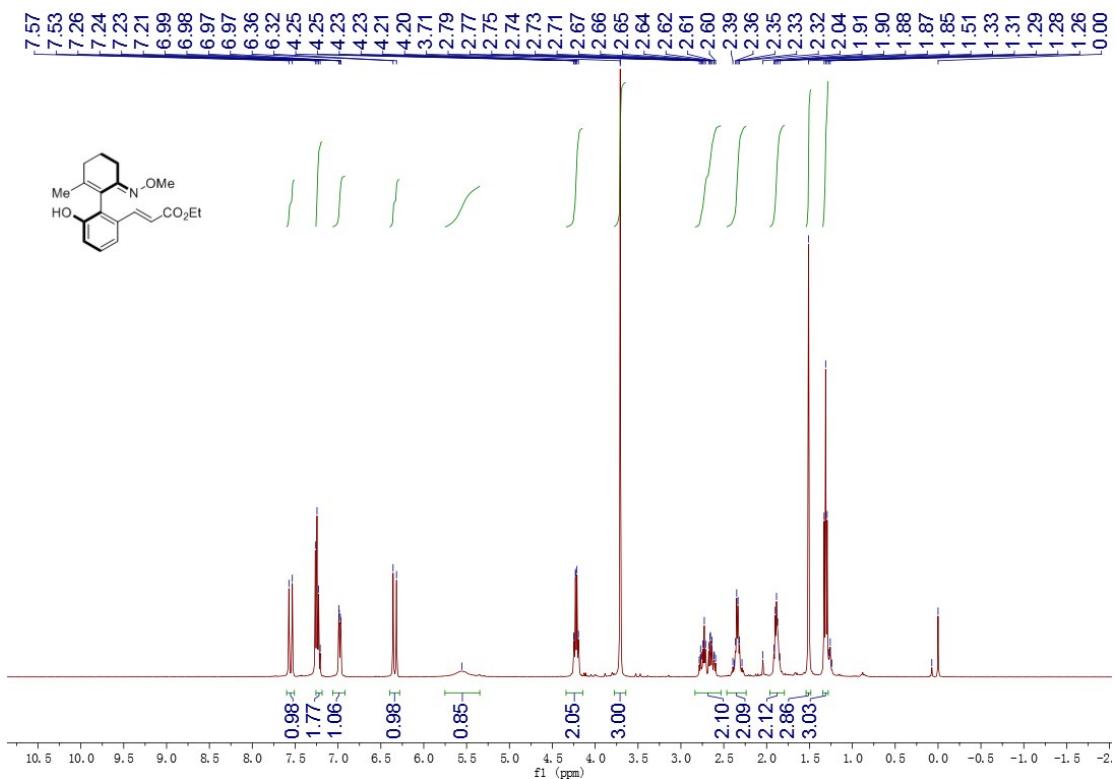


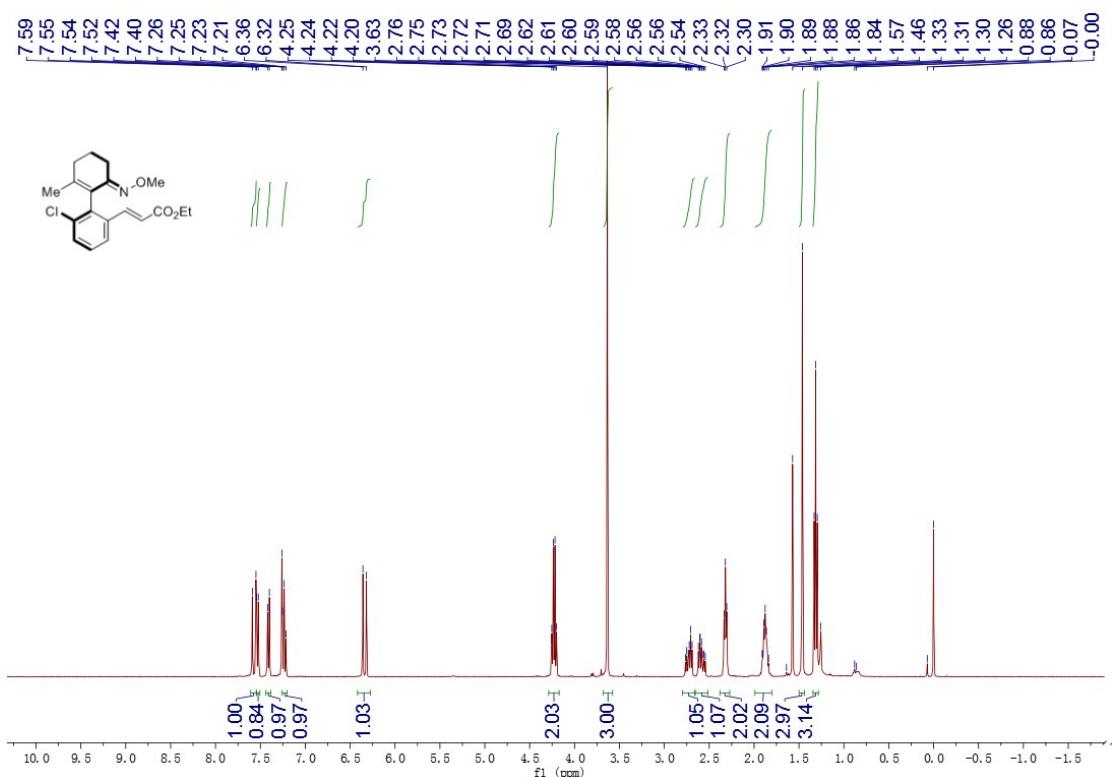


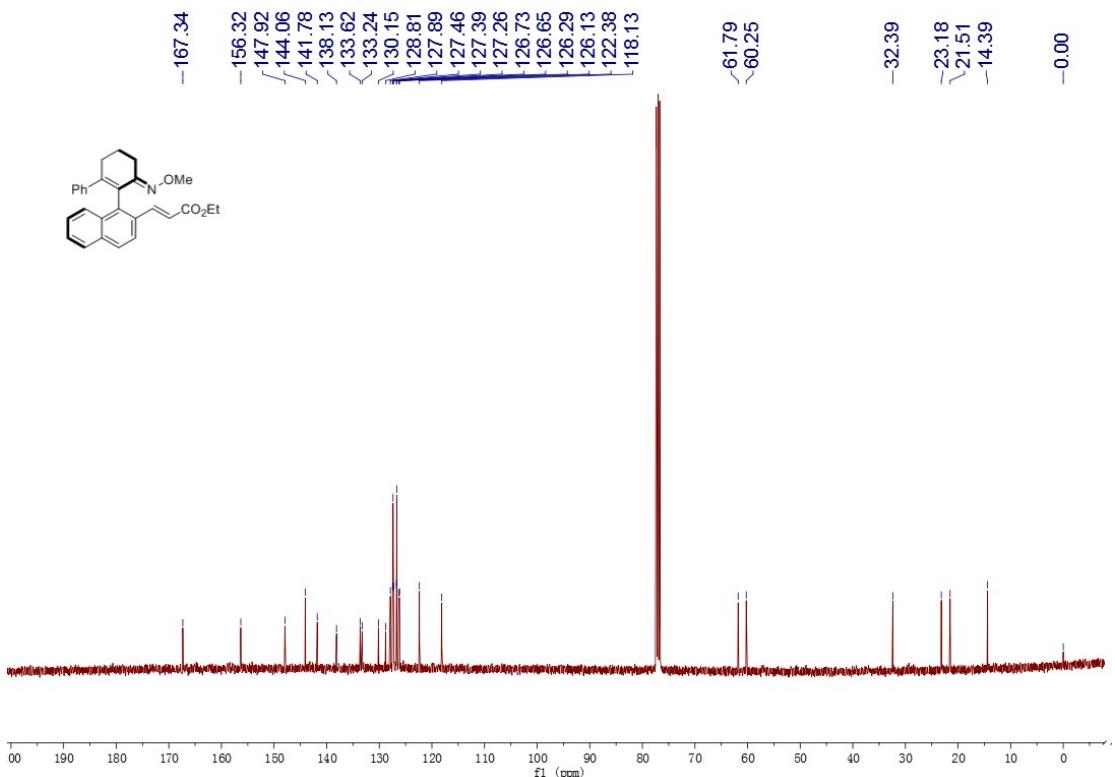
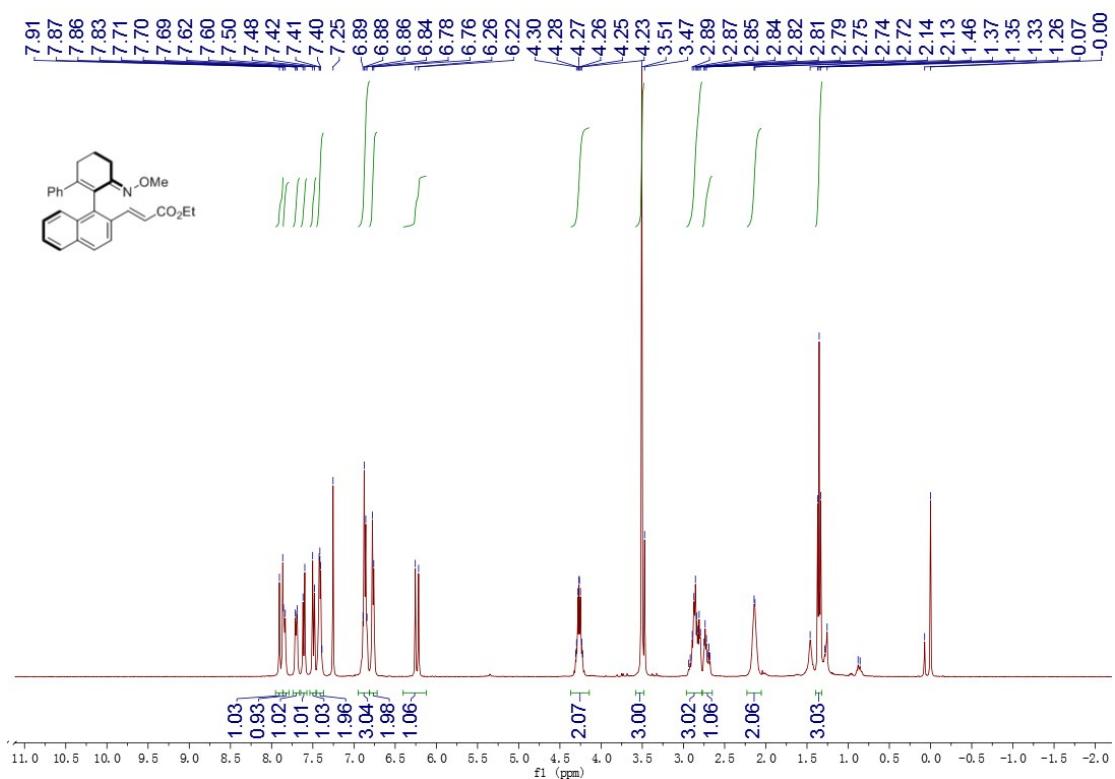


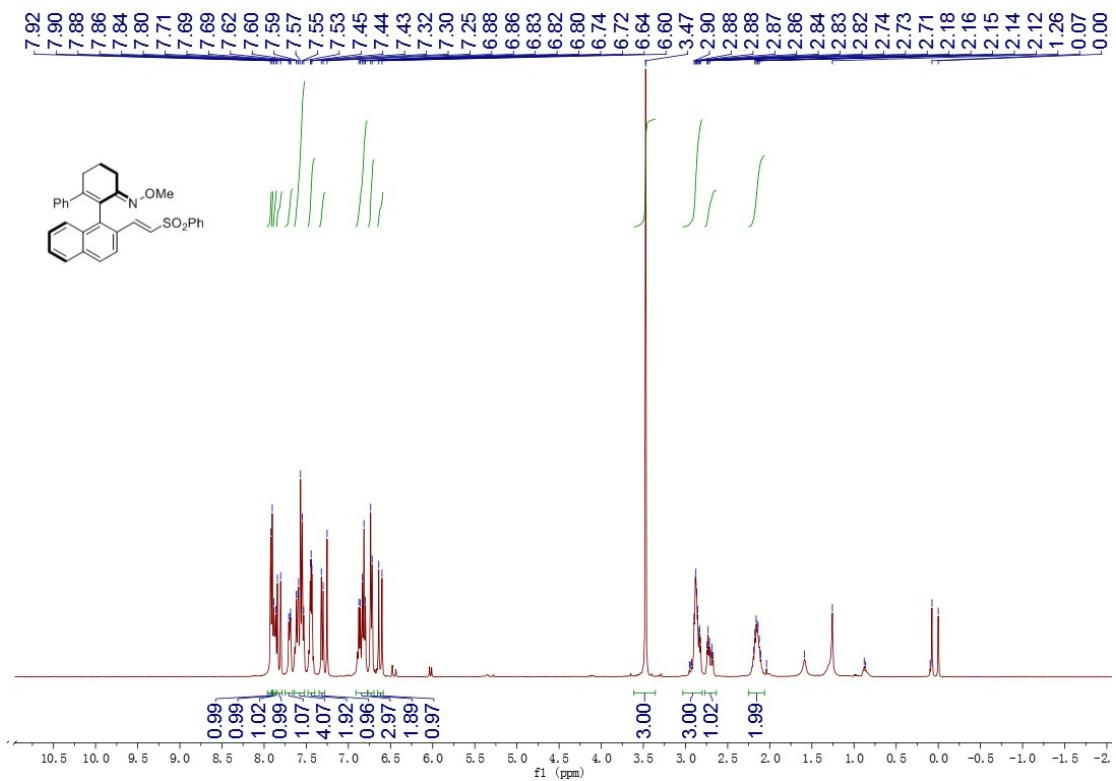


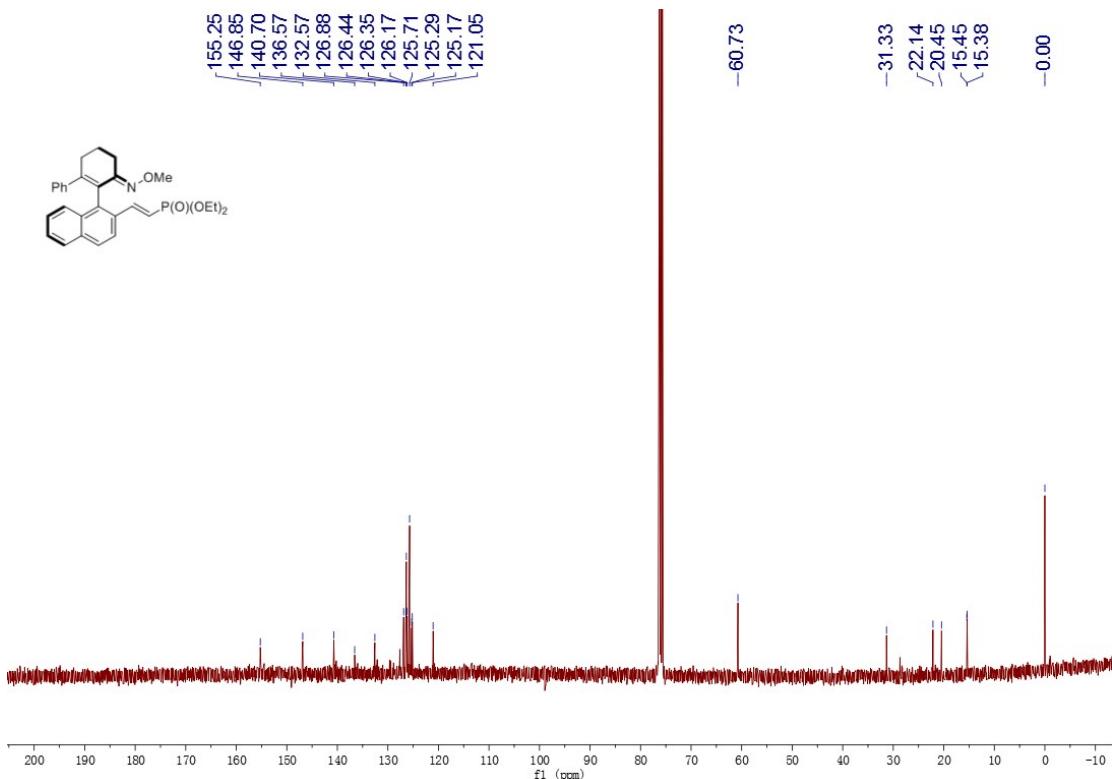
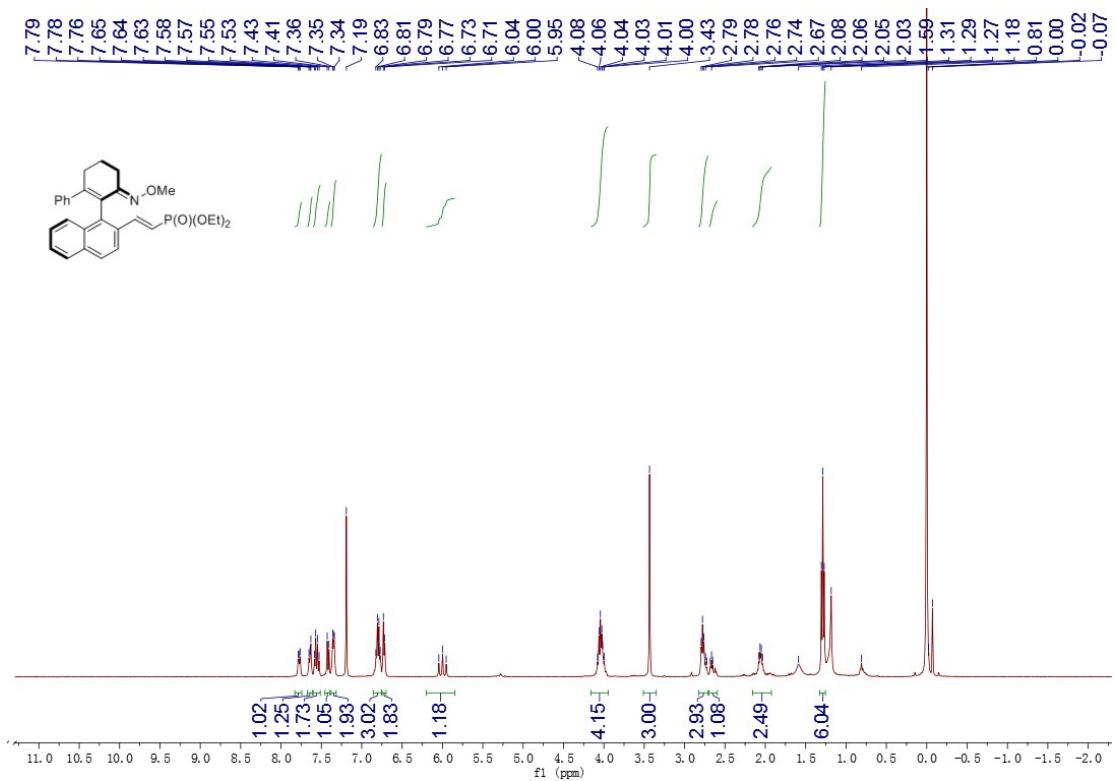


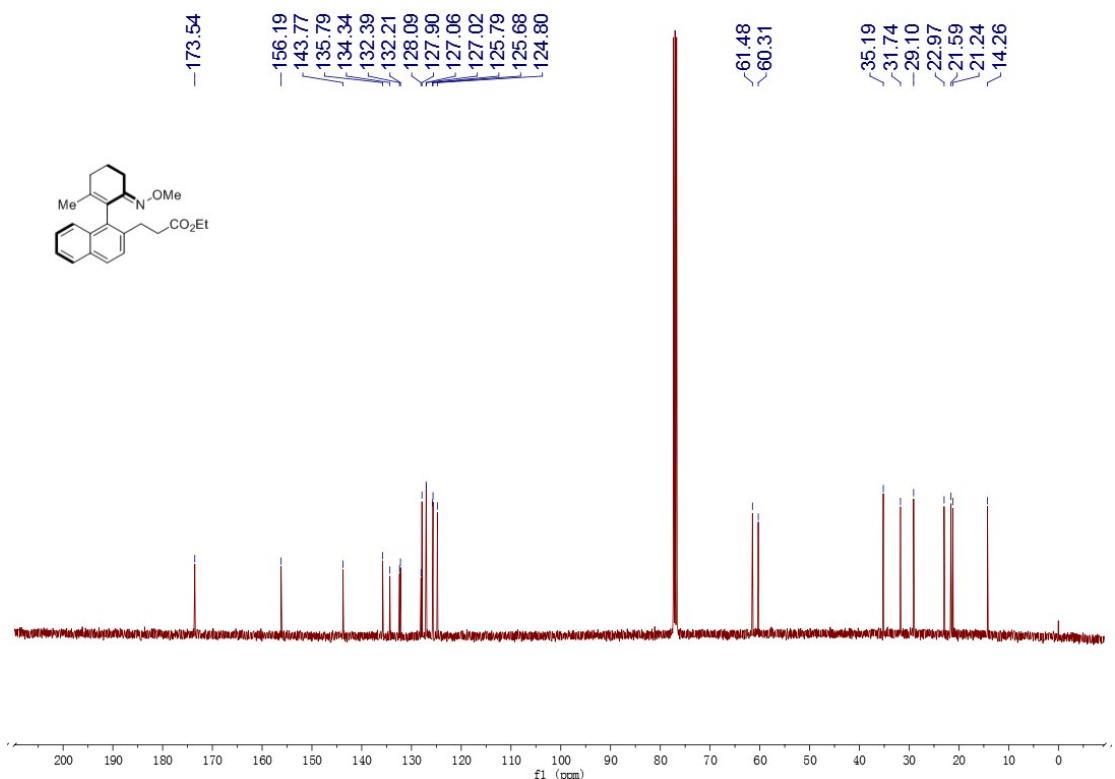
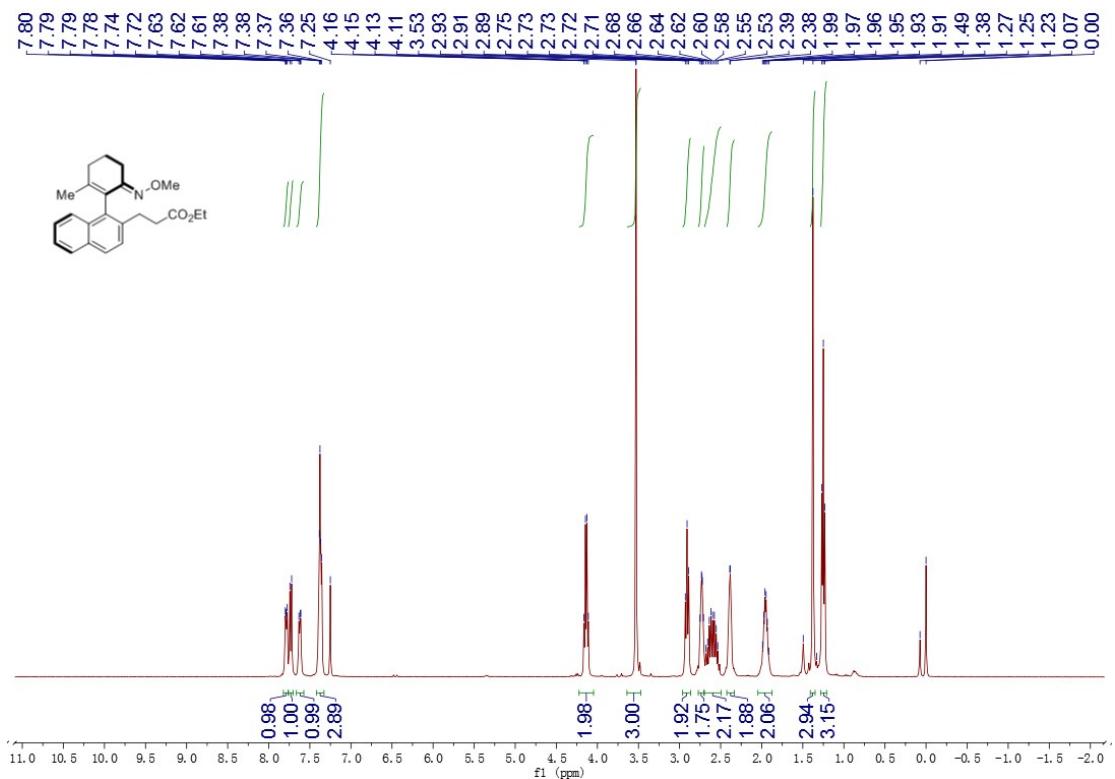


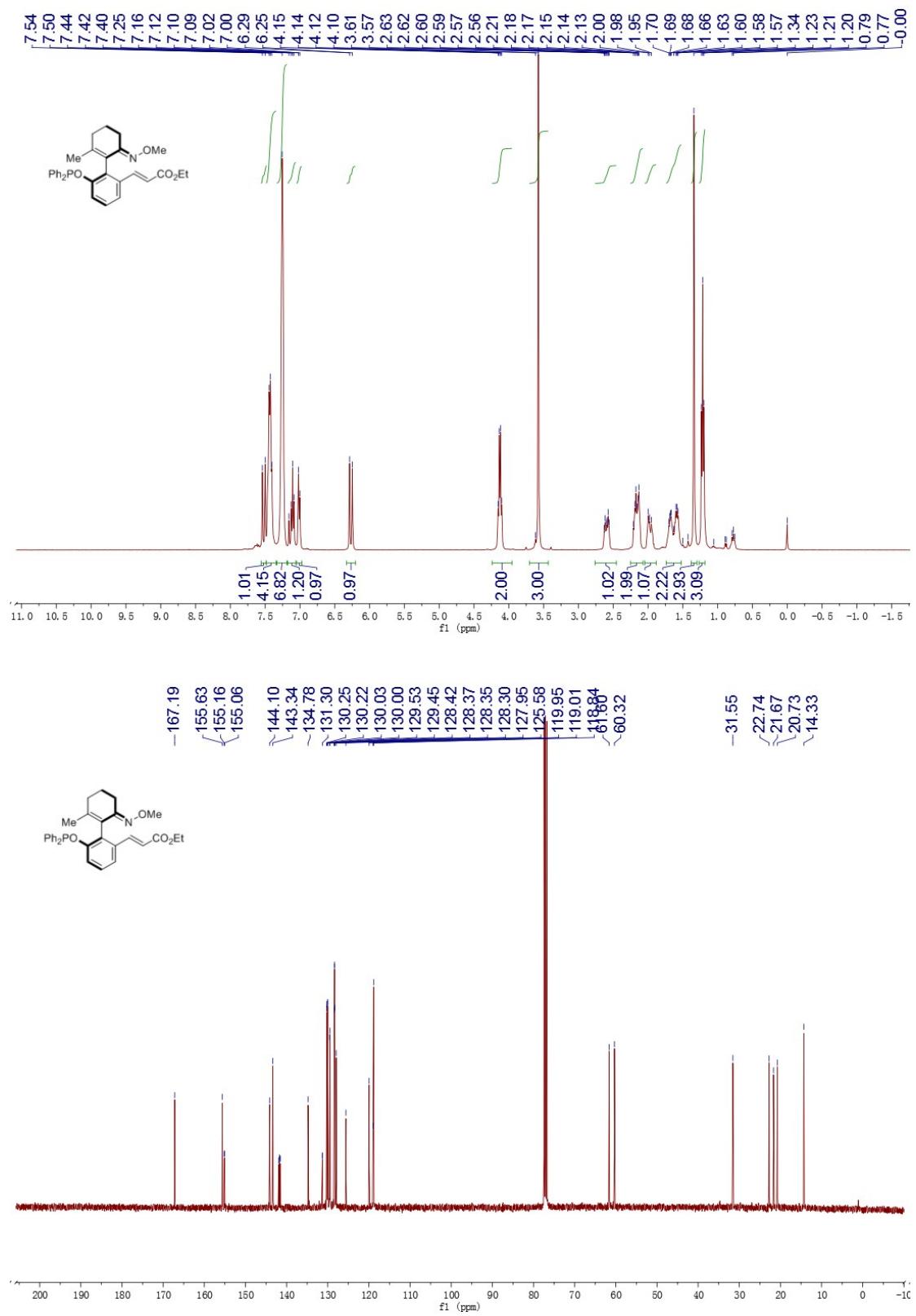


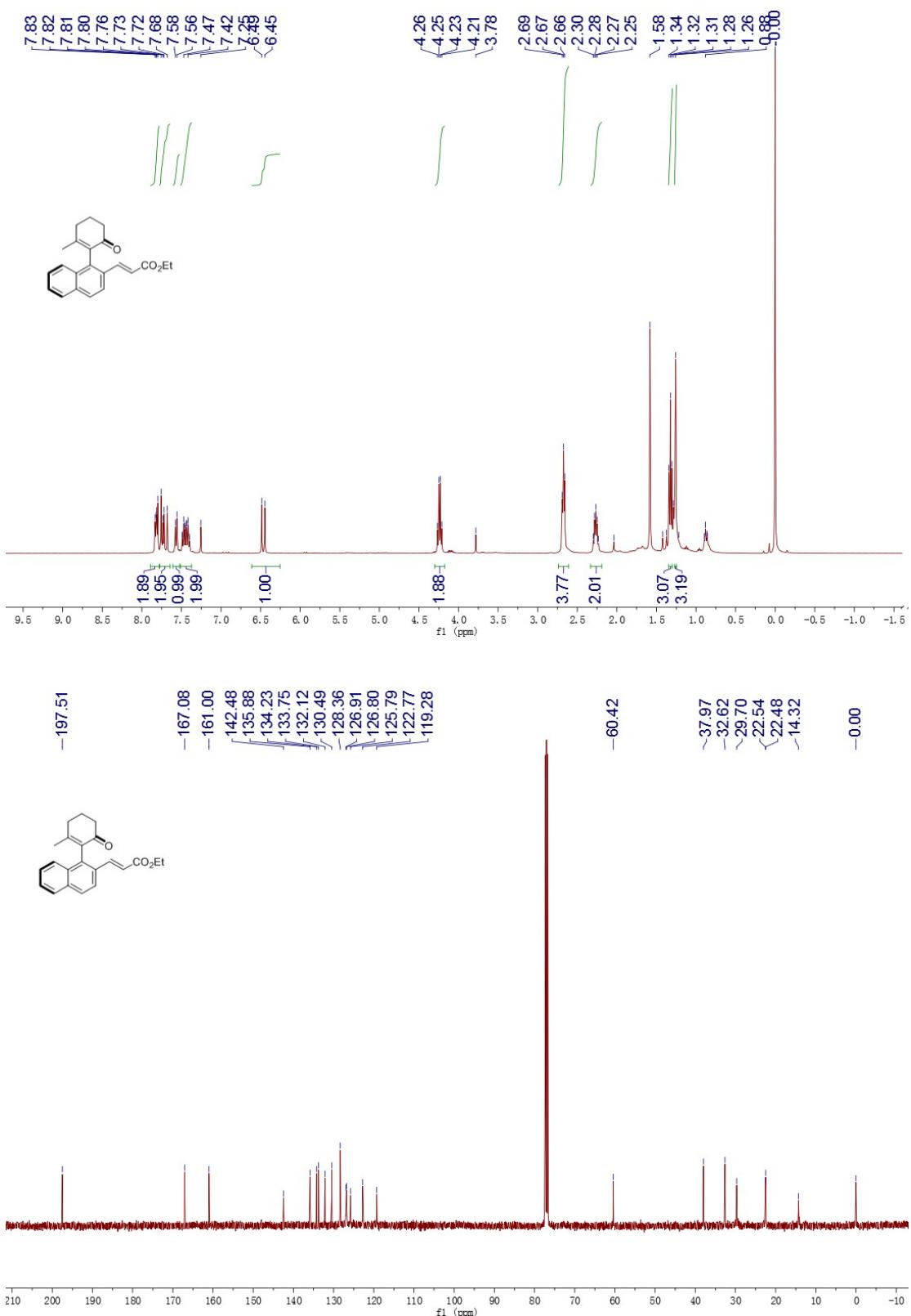




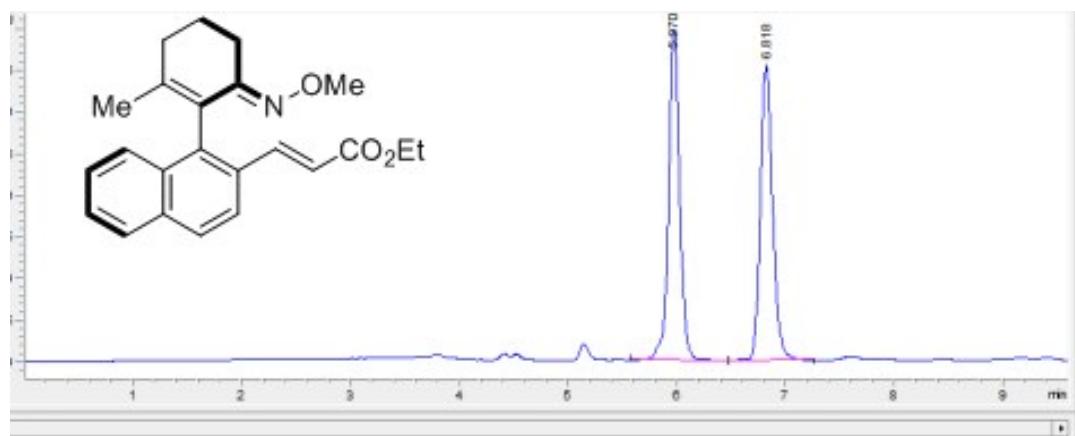




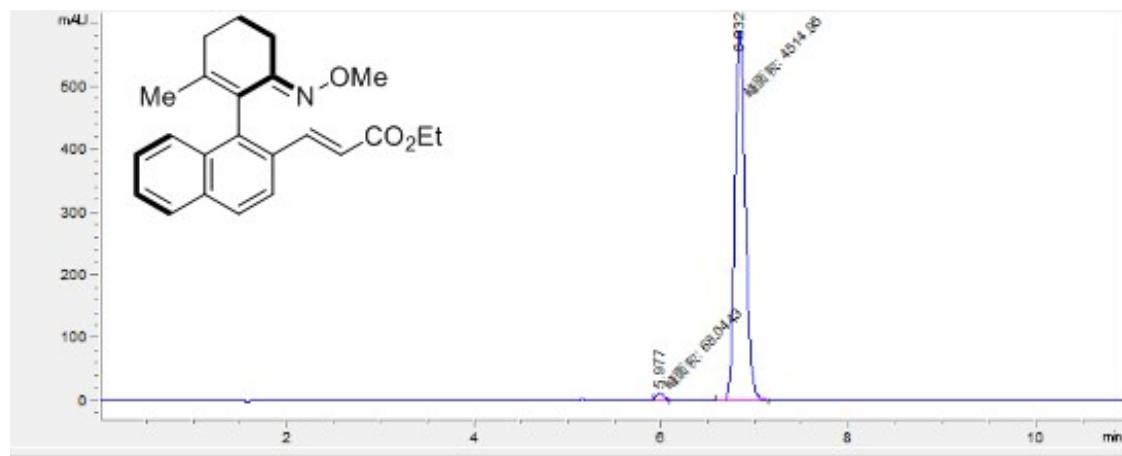




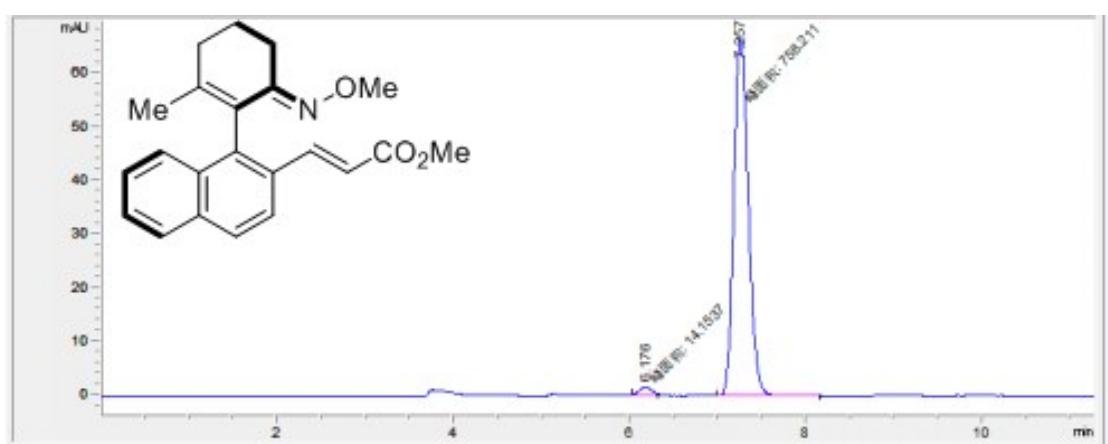
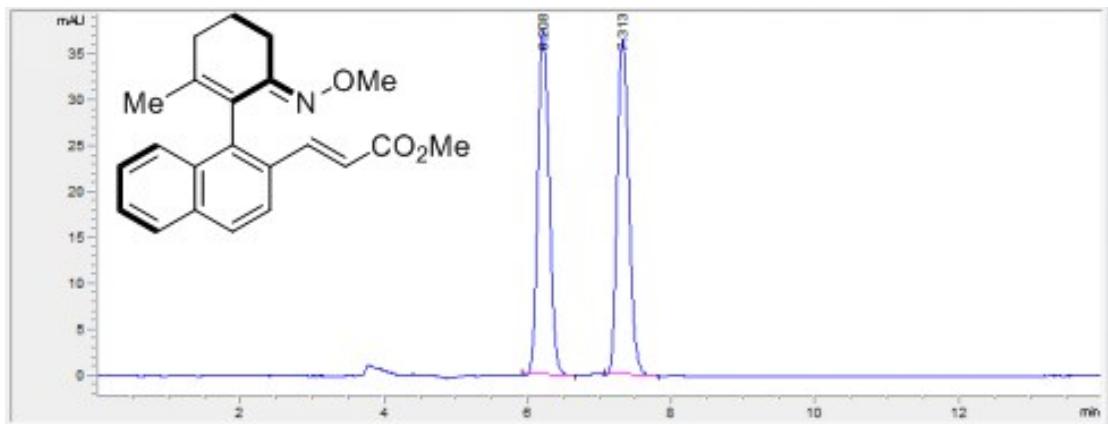
HPLC spectrum of product 3.

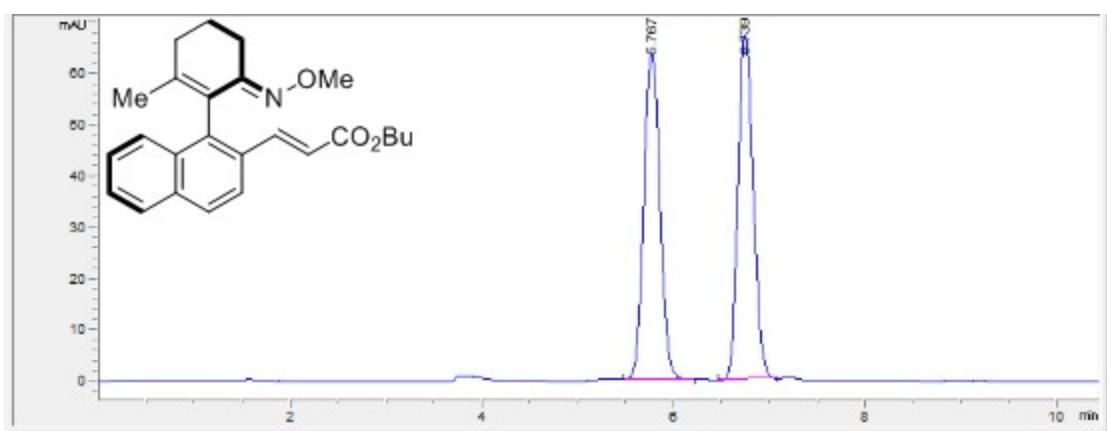


| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 5.97 | 281.8 | 39.7 | 50.360 |
| 2 | 6.818 | 277.8 | 35.5 | 49.640 |

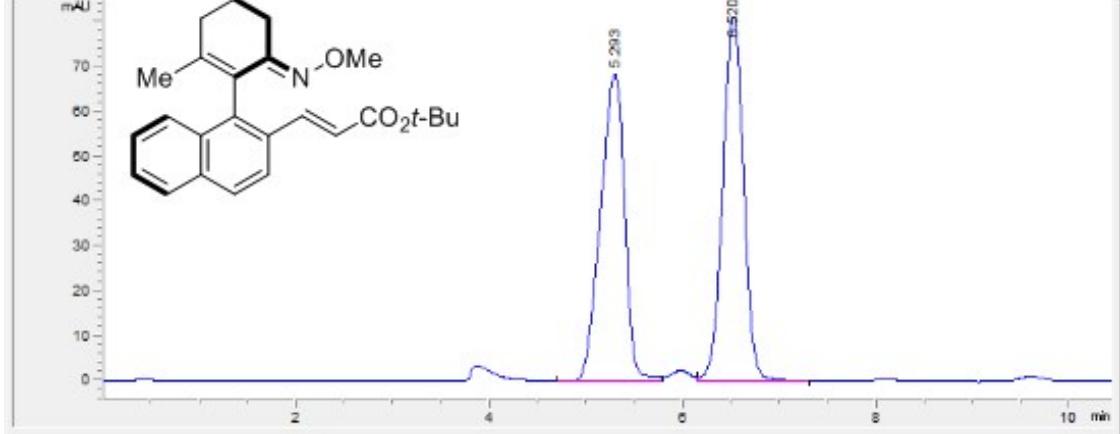
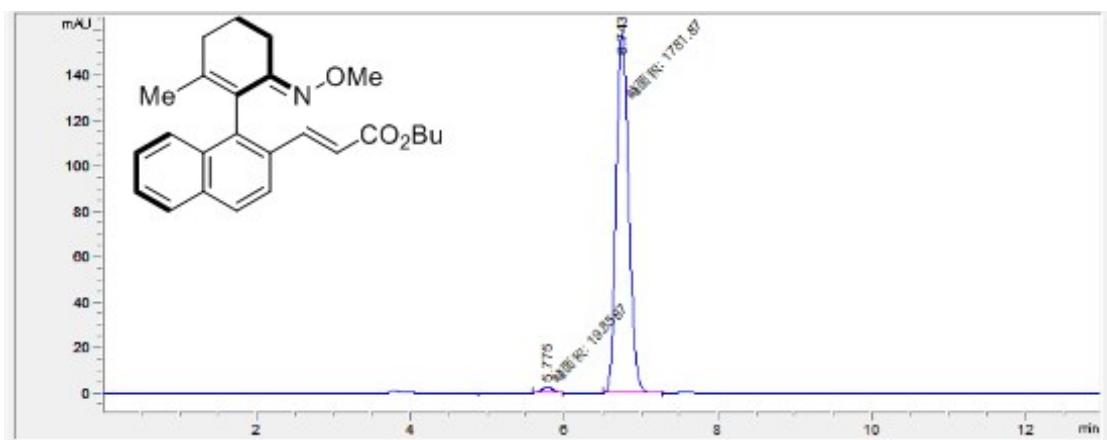


| | Time/min | Area | Height | Area% |
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| 1 | 5.977 | 68 | 11.3 | 1.485 |
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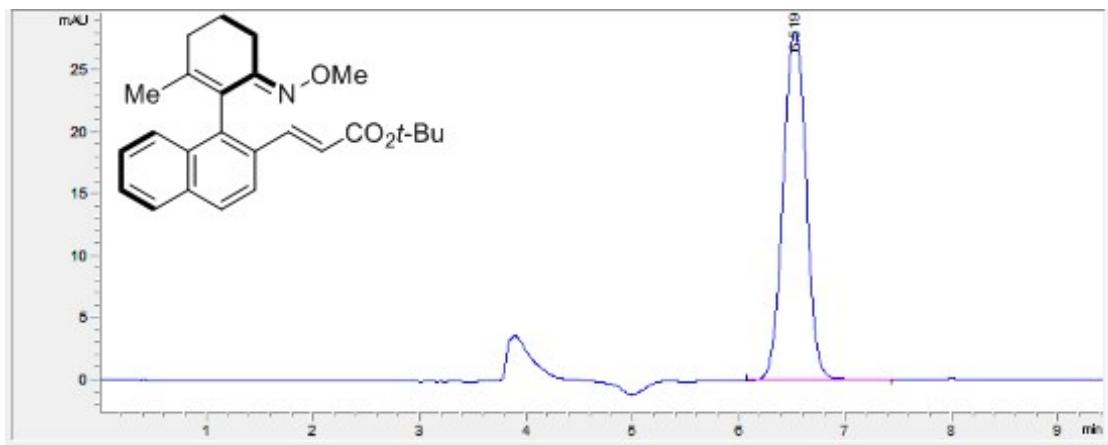




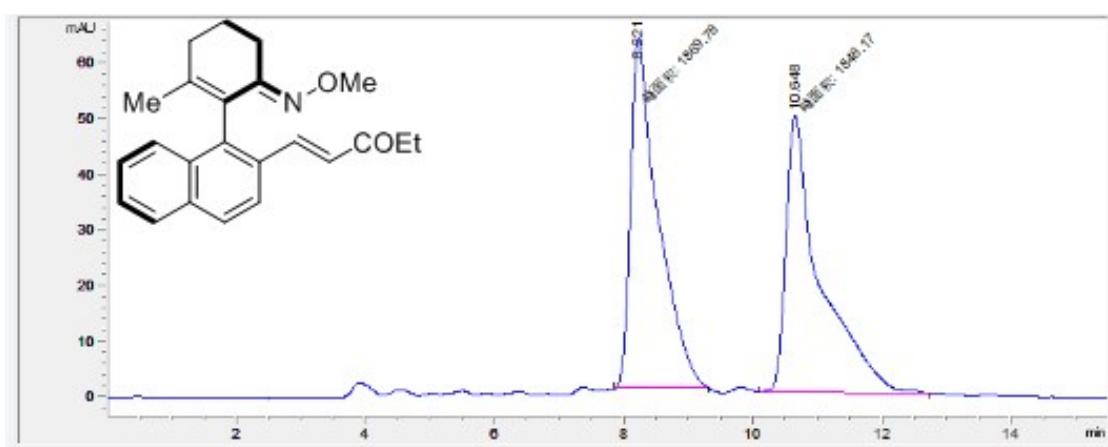
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 5.767 | 752.3 | 63.7 | 50.327 |
| 2 | 6.739 | 742.5 | 67.3 | 49.673 |



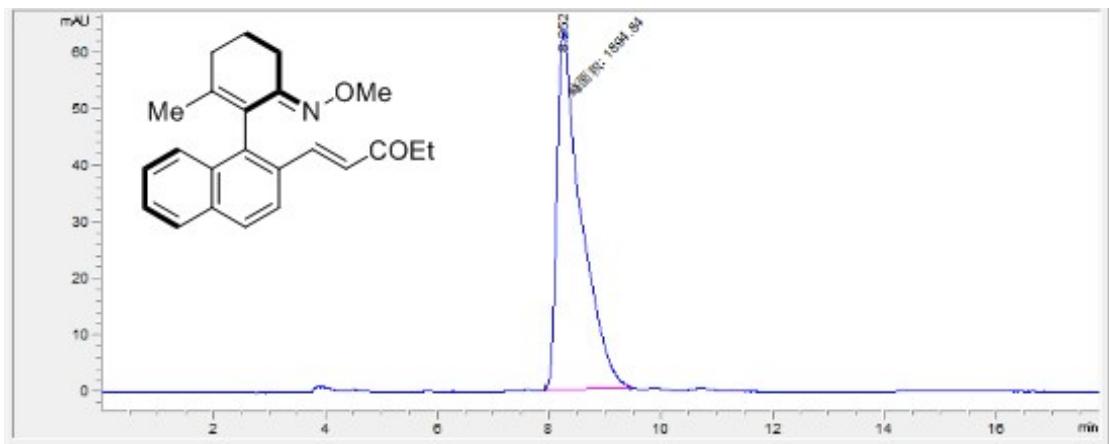
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 5.293 | 1186.9 | 68.4 | 49.269 |
| 2 | 6.52 | 1222.1 | 81.2 | 50.731 |



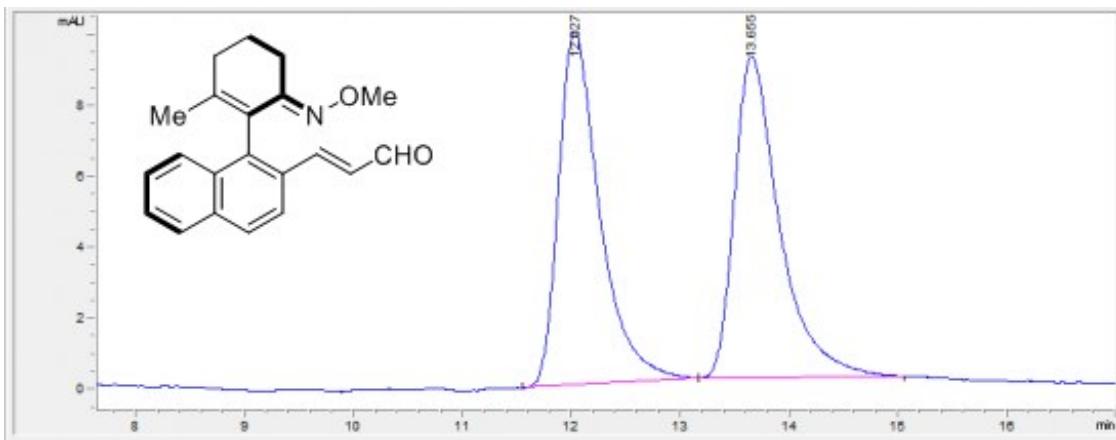
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|---------|
| 1 | 6.519 | 424.8 | 28.2 | 100.000 |



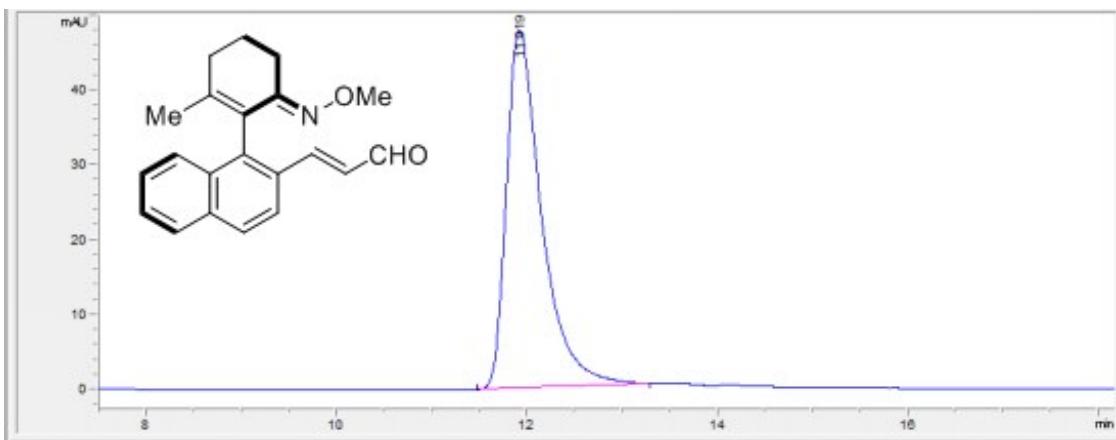
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 8.221 | 1869.8 | 62.9 | 50.291 |
| 2 | 10.648 | 1848.2 | 49.8 | 49.709 |



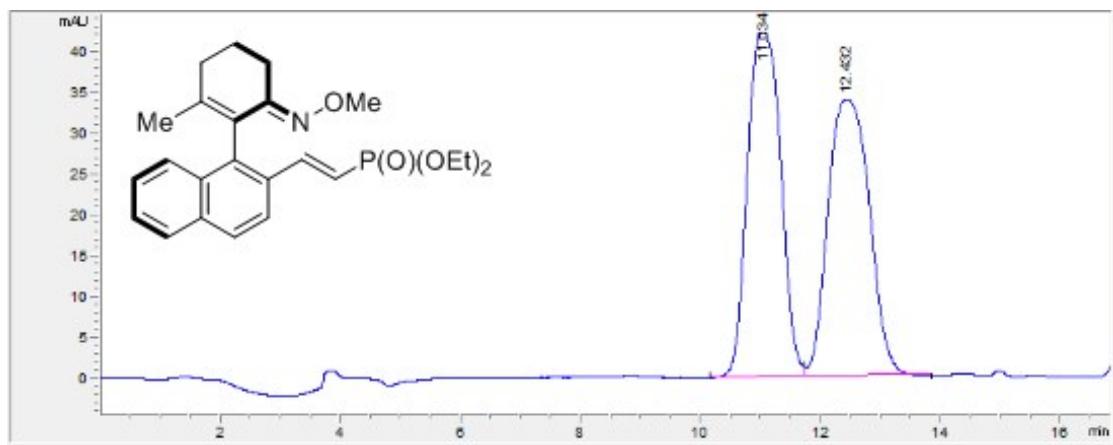
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|---------|
| 1 | 8.252 | 1894.8 | 63.3 | 100.000 |



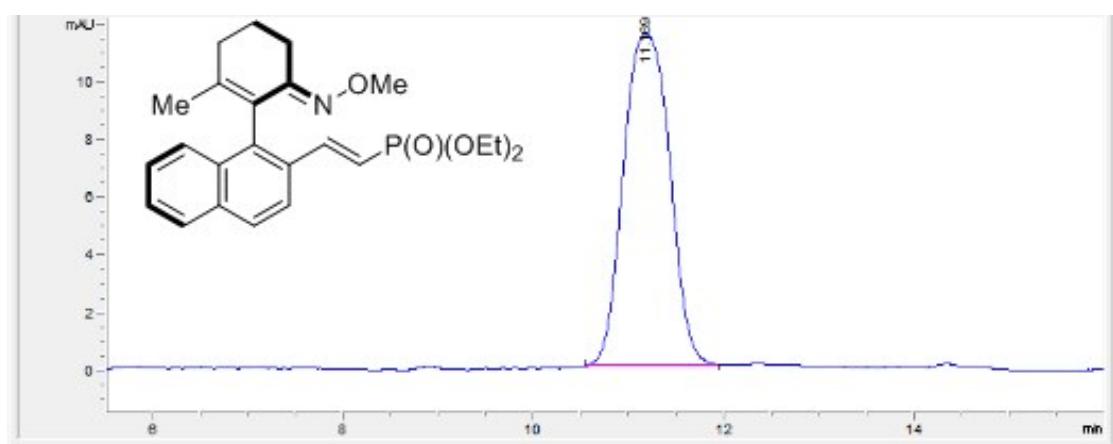
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 12.027 | 262.1 | 9.9 | 50.014 |
| 2 | 13.655 | 262 | 9.1 | 49.986 |



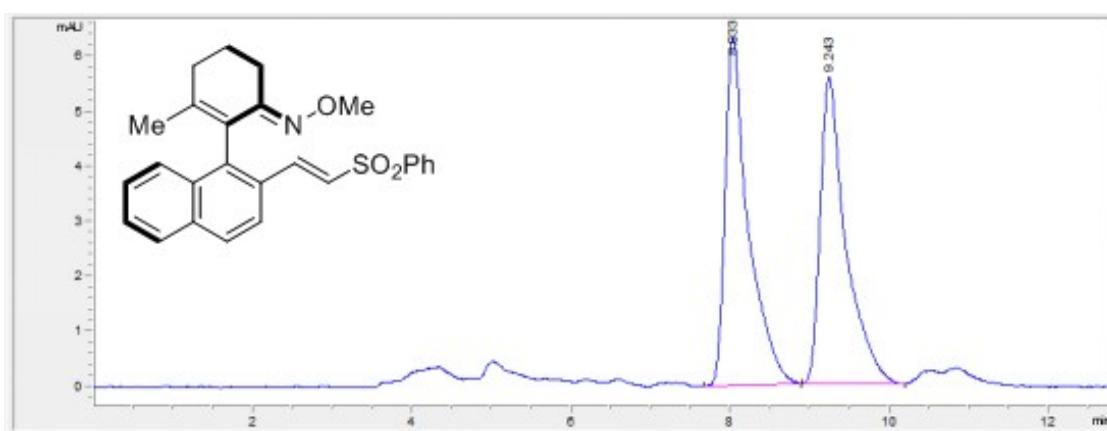
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|---------|
| 1 | 11.919 | 1233.7 | 47.8 | 100.000 |



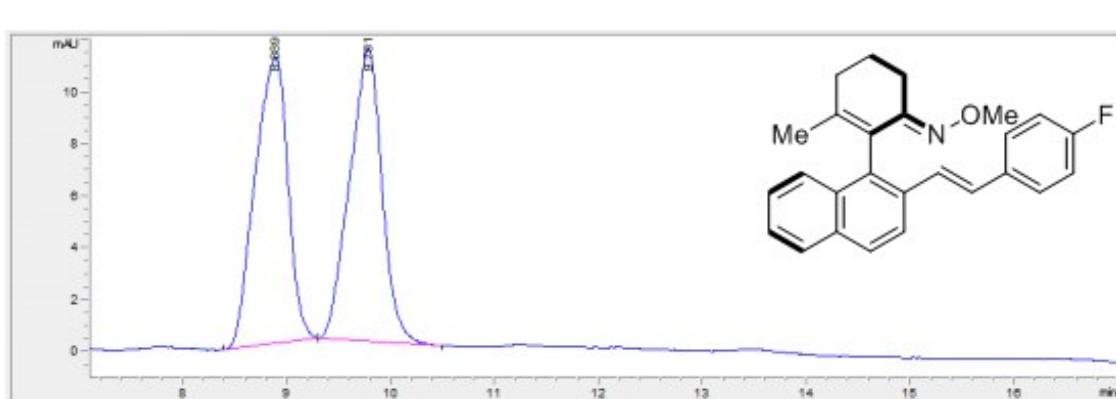
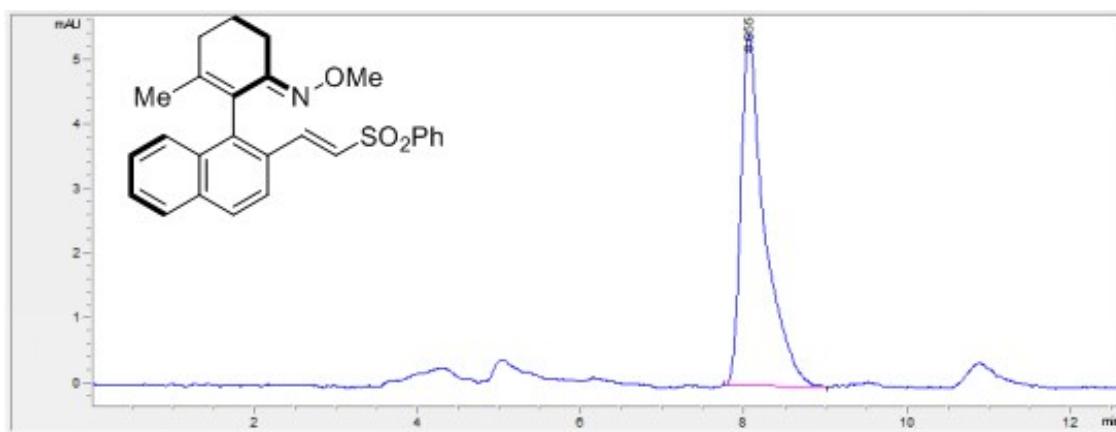
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 11.034 | 1630.2 | 42.3 | 50.051 |
| 2 | 12.432 | 1626.9 | 33.9 | 49.949 |



| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|---------|
| 1 | 11.169 | 388.9 | 11.5 | 100.000 |



| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 8.033 | 129.2 | 6.3 | 50.971 |
| 2 | 9.243 | 124.3 | 5.6 | 49.029 |



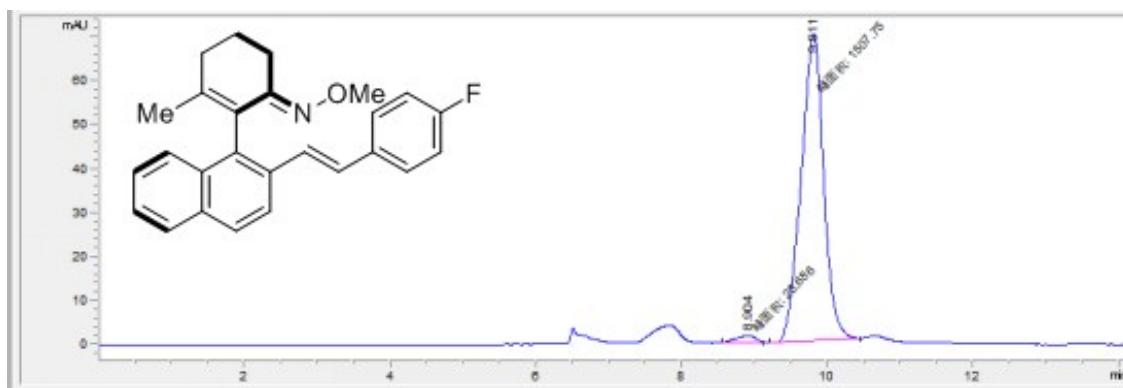
2

9.781

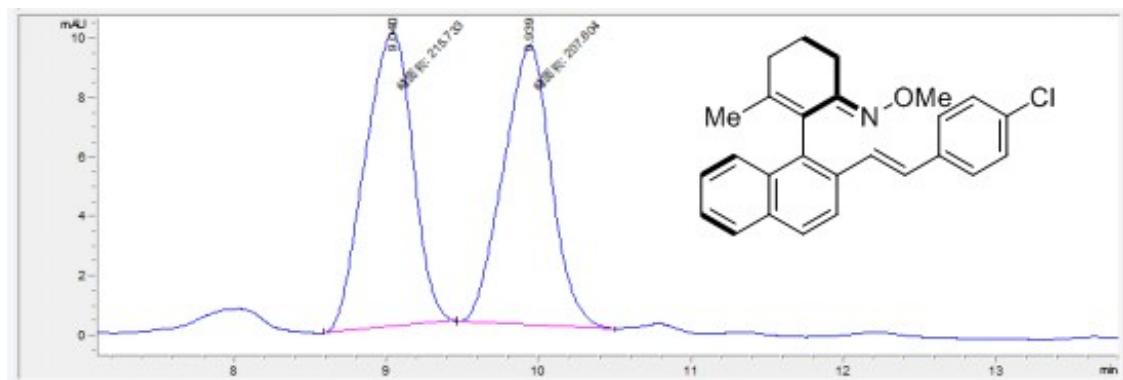
244

11.3

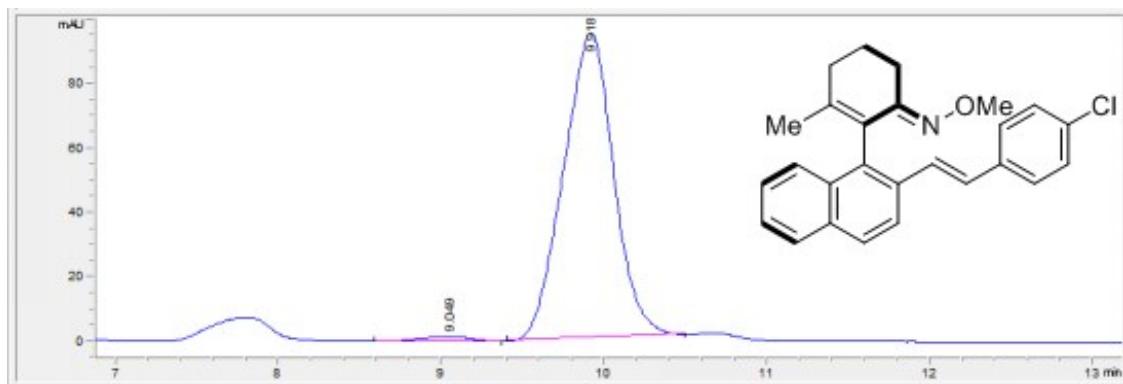
50.116



| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 8.904 | 28.7 | 1.5 | 1.867 |
| 2 | 9.811 | 1507.7 | 69.9 | 98.133 |

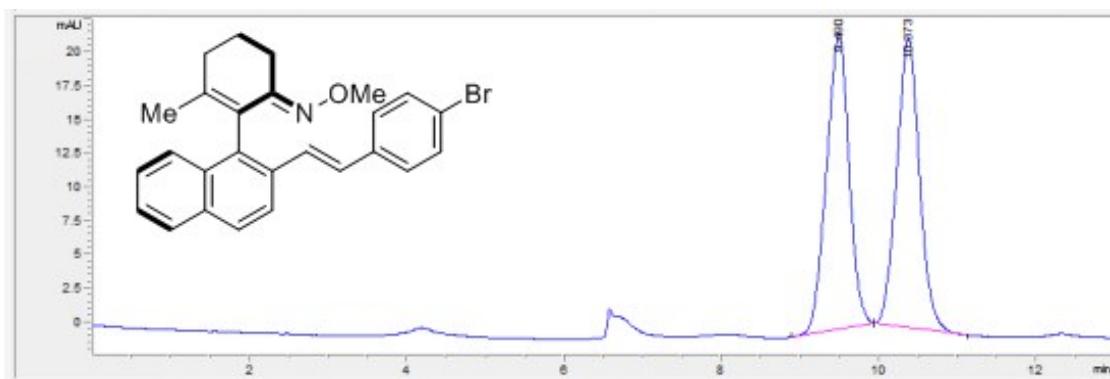


| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 9.04 | 215.7 | 9.9 | 50.960 |
| 2 | 9.939 | 207.6 | 9.5 | 49.040 |

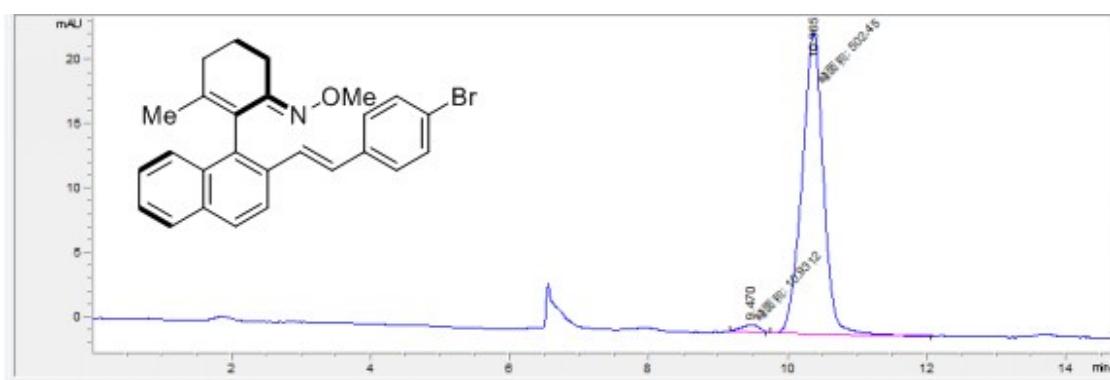


| | Time/min | Area | Height | Area% |
|--|----------|------|--------|-------|
| | | | | |

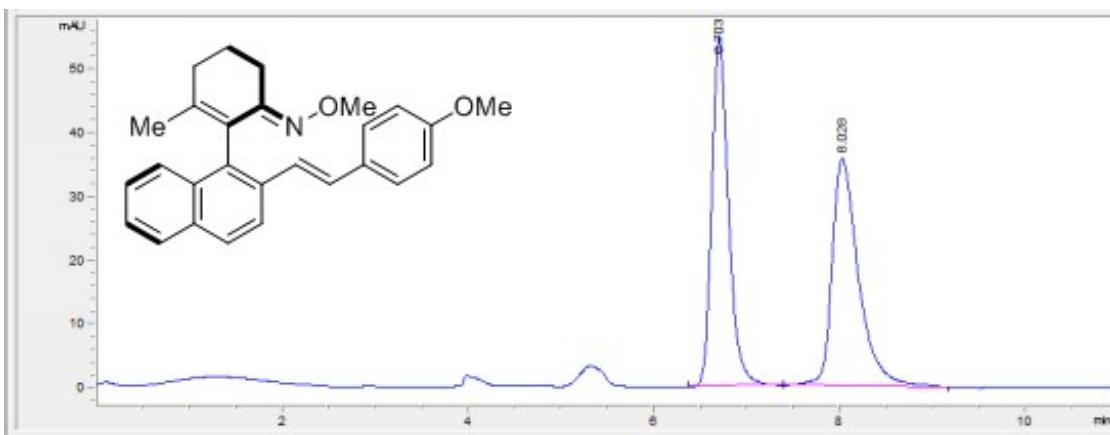
| | | | | |
|---|-------|--------|------|--------|
| 1 | 9.049 | 30.4 | 1.4 | 1.478 |
| 2 | 9.918 | 2028.4 | 94.7 | 98.522 |



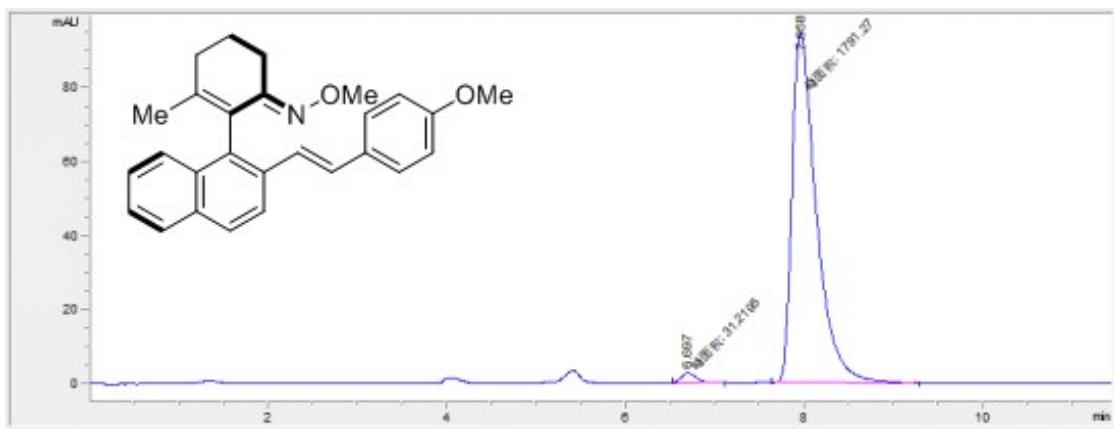
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 9.49 | 436.4 | 21.9 | 50.341 |
| 2 | 10.373 | 430.5 | 21.4 | 49.659 |



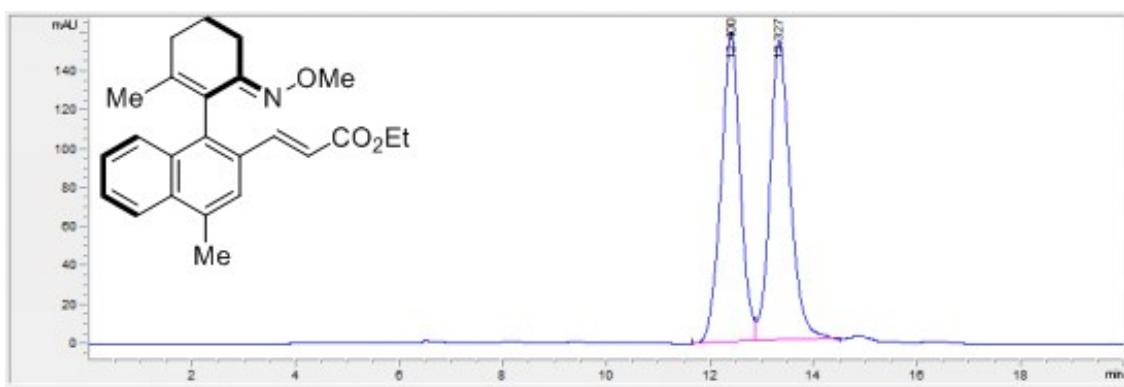
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 9.47 | 10.9 | 6E-1 | 2.129 |
| 2 | 10.365 | 502.4 | 23.5 | 97.871 |



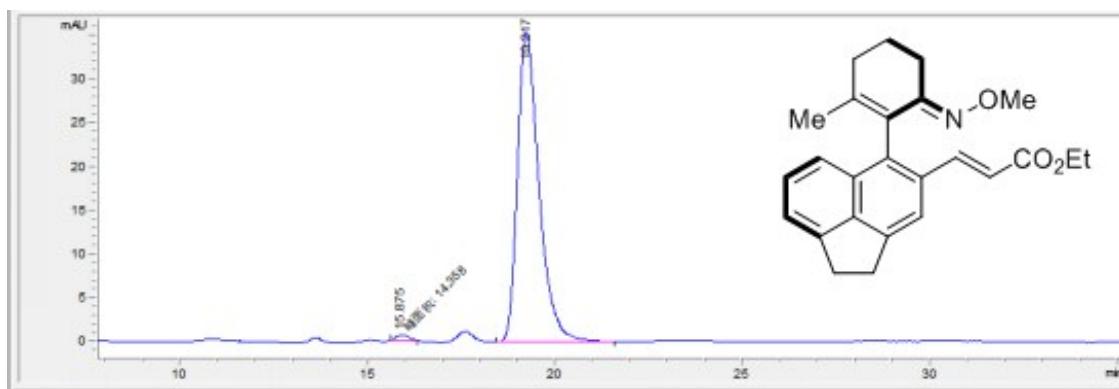
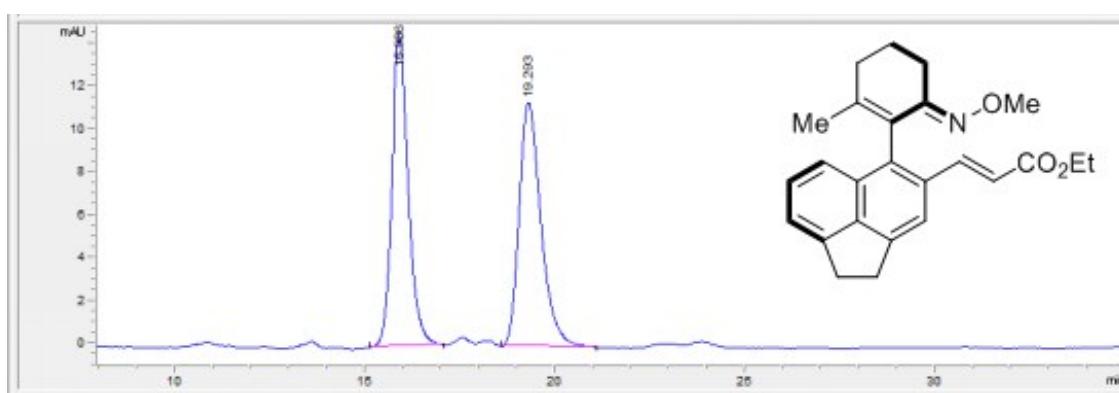
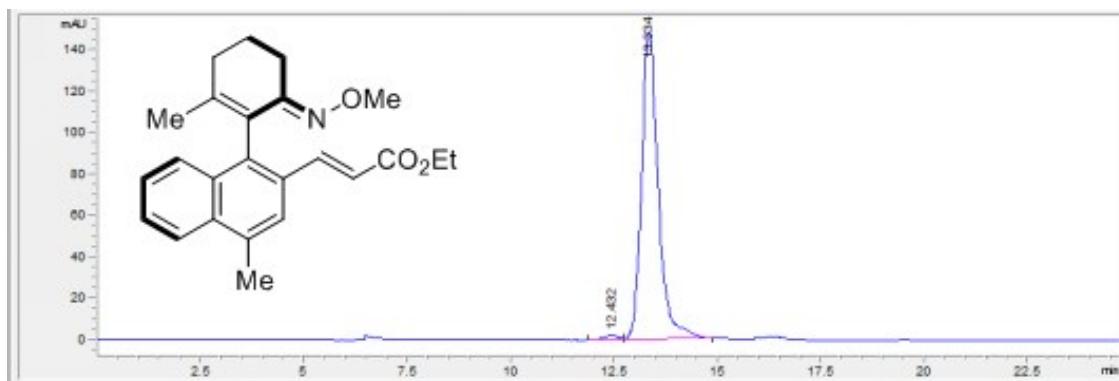
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 6.703 | 689.8 | 54.9 | 49.314 |
| 2 | 8.028 | 709 | 35.7 | 50.686 |

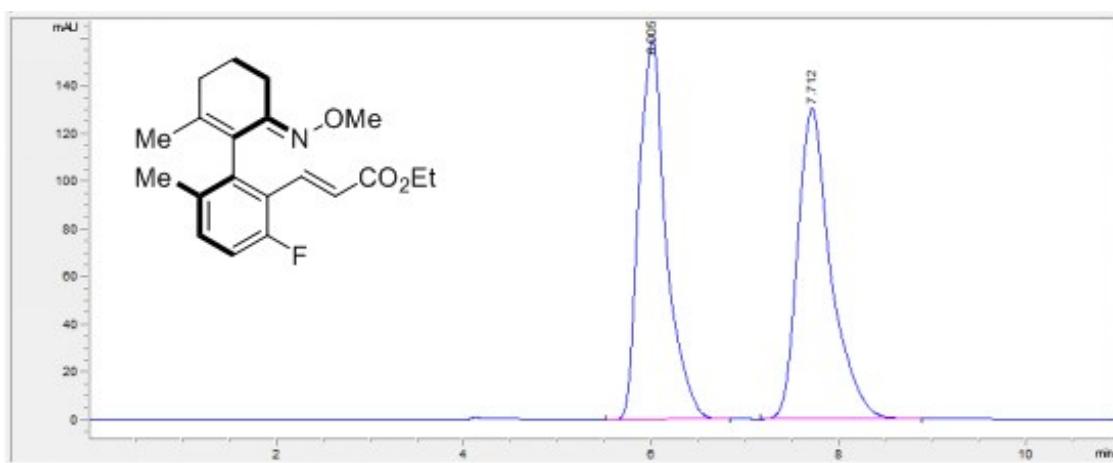


| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 6.697 | 31.2 | 2.7 | 1.713 |
| 2 | 7.958 | 1791.3 | 94.6 | 98.287 |

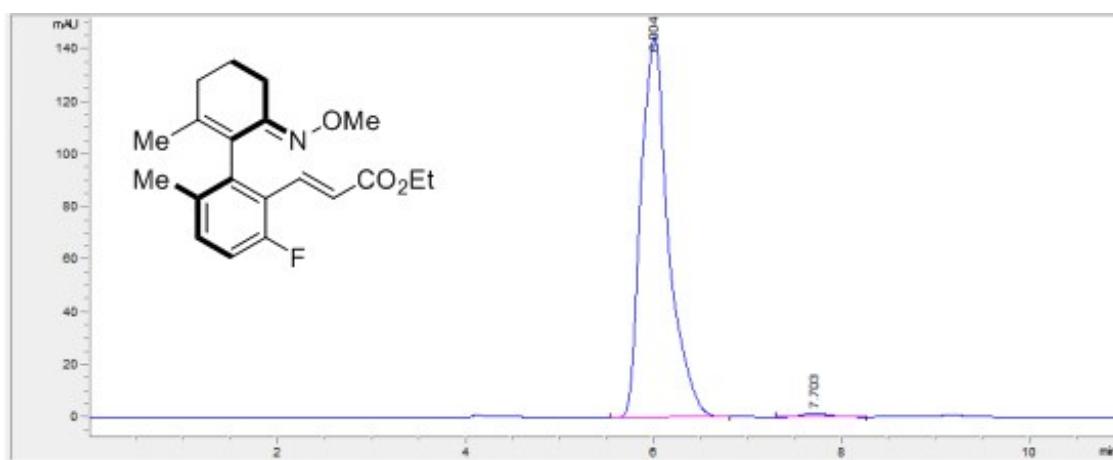


| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 12.4 | 4121.7 | 158.7 | 49.337 |
| 2 | 13.327 | 4232.4 | 154.4 | 50.663 |

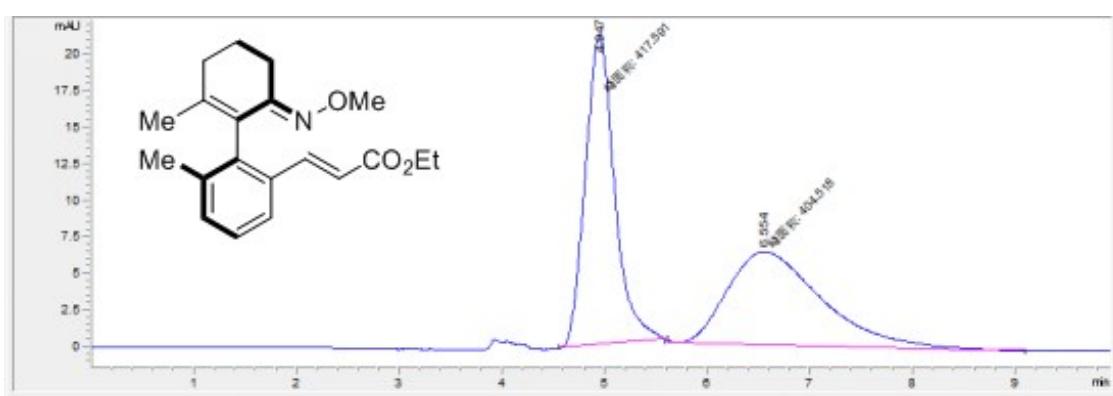




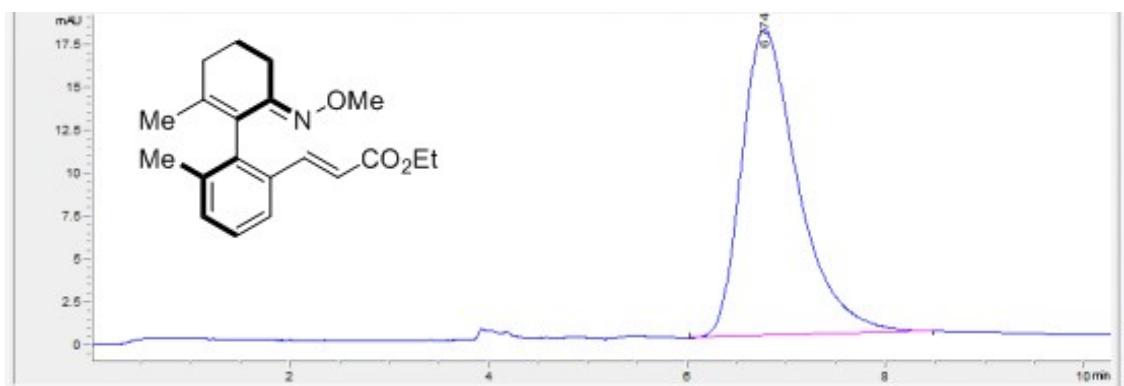
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 6.005 | 3227.3 | 159.5 | 50.109 |
| 2 | 7.712 | 3212.3 | 130.4 | 49.891 |



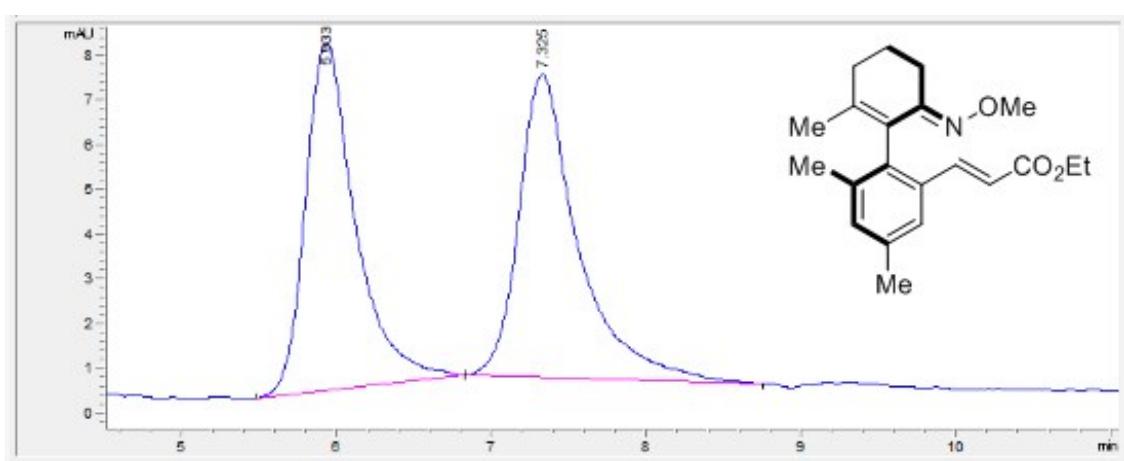
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 6.004 | 2936.5 | 144.9 | 98.880 |
| 2 | 7.703 | 33.3 | 1.5 | 1.120 |



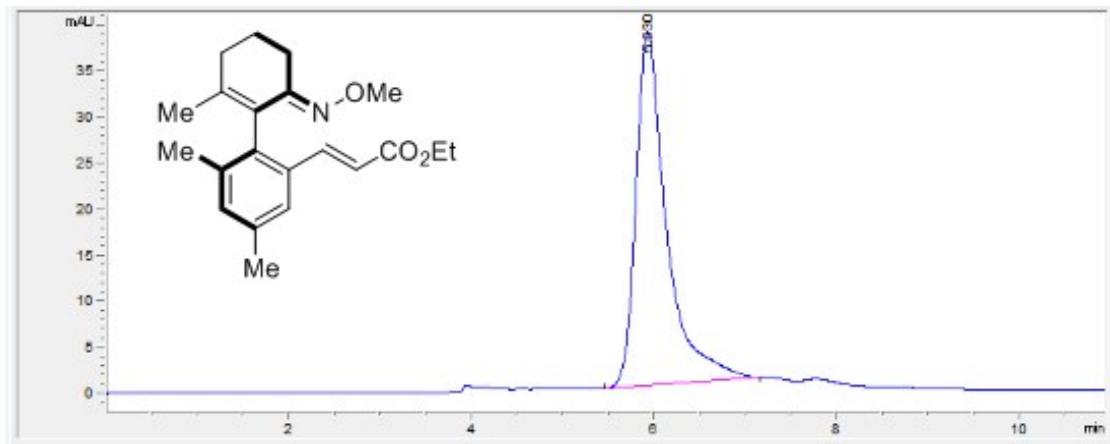
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 4.947 | 417.6 | 21.2 | 50.795 |
| 2 | 6.554 | 404.5 | 6.4 | 49.205 |



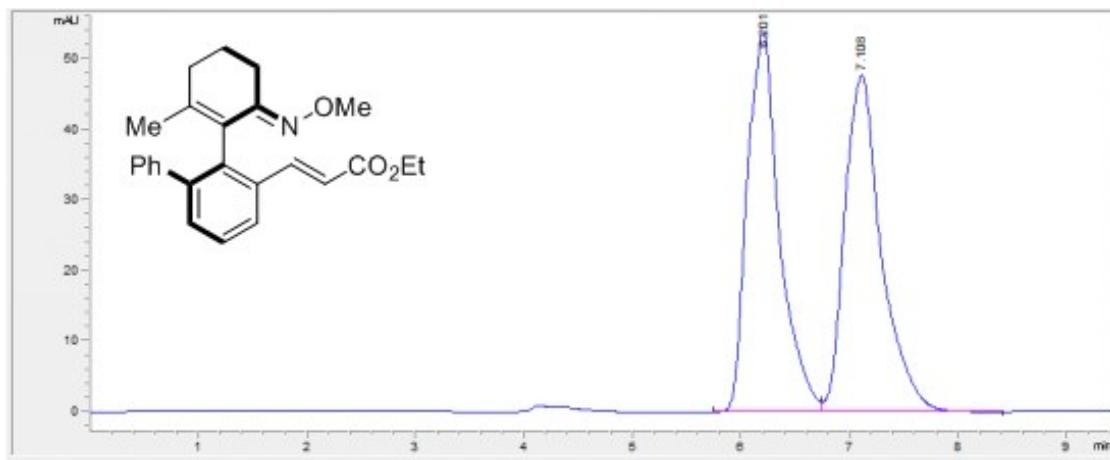
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|---------|
| 1 | 6.774 | 707.6 | 17.8 | 100.000 |



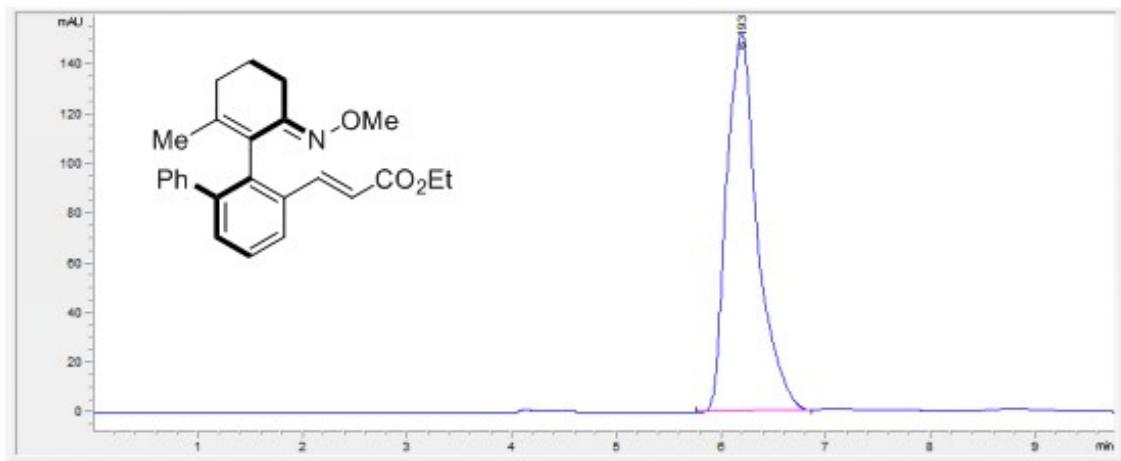
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 5.933 | 174.8 | 7.8 | 49.091 |
| 2 | 7.325 | 181.3 | 6.8 | 50.909 |



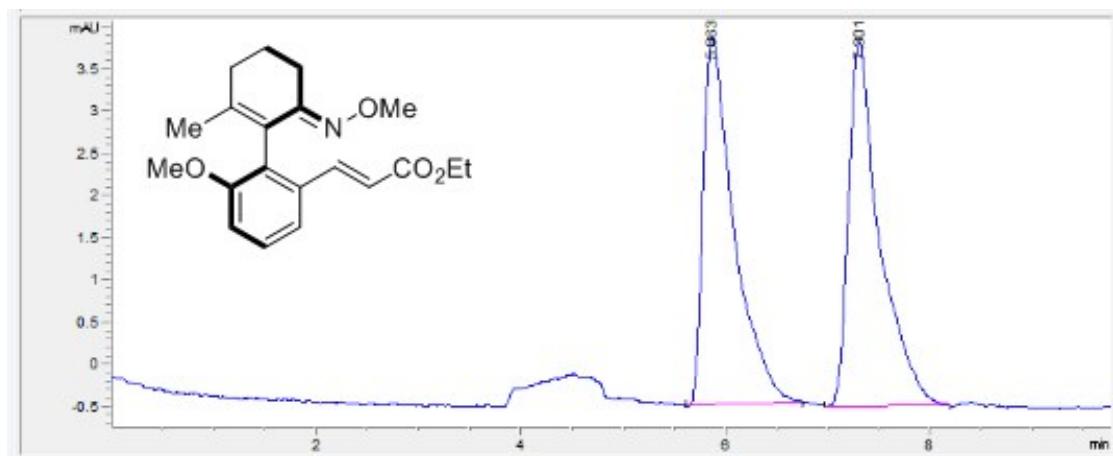
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|---------|
| 1 | 5.93 | 895.6 | 38.4 | 100.000 |



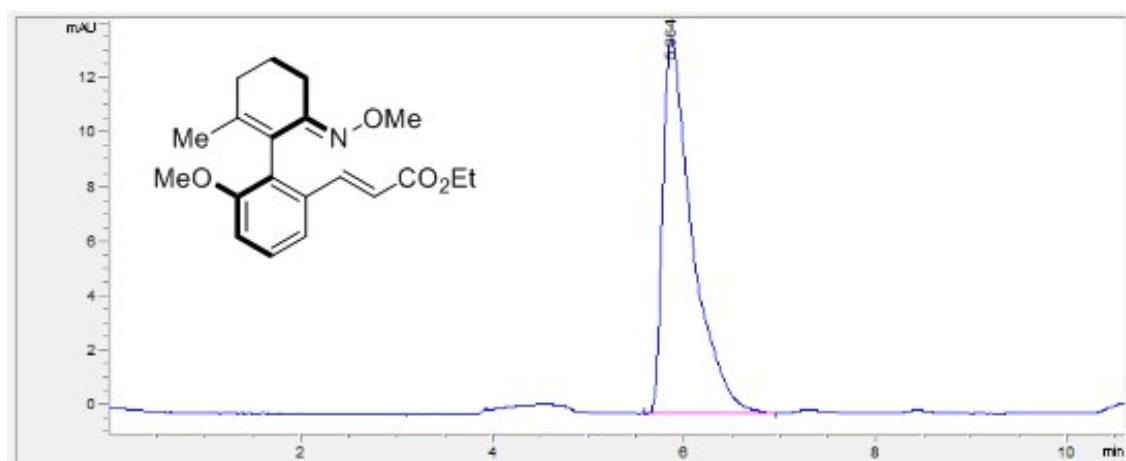
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 6.201 | 1110.2 | 53.7 | 49.768 |
| 2 | 7.108 | 1120.6 | 47.7 | 50.232 |



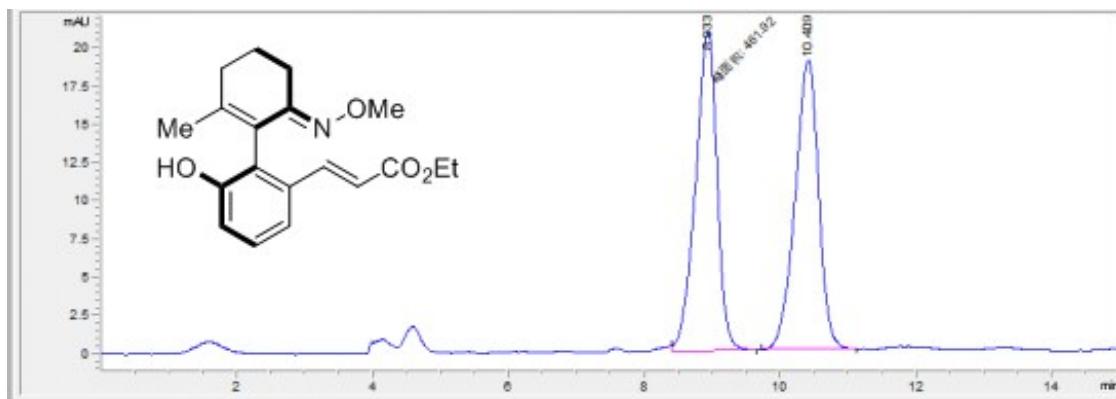
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|---------|
| 1 | 6.193 | 3100.8 | 151.8 | 100.000 |



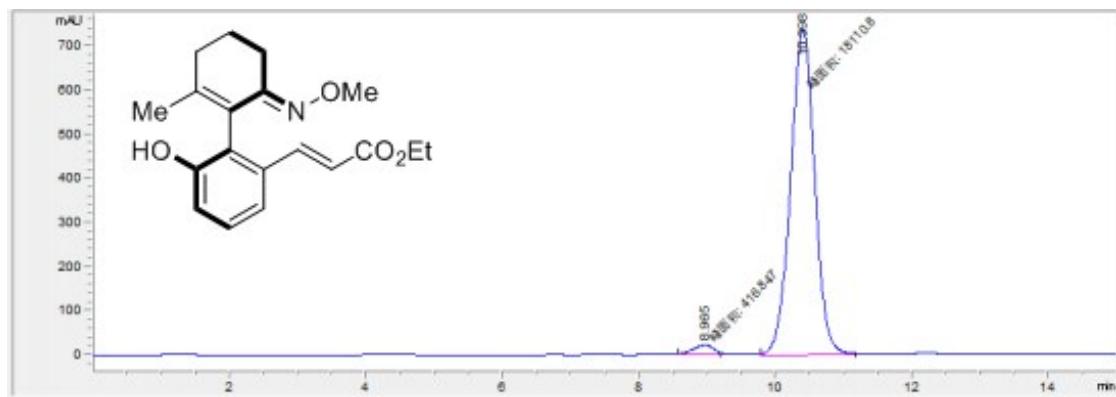
| | Time/min | Area | Height | Area% |
|---|----------|------|--------|--------|
| 1 | 5.863 | 91.7 | 4.4 | 49.922 |
| 2 | 7.301 | 92 | 4.3 | 50.078 |



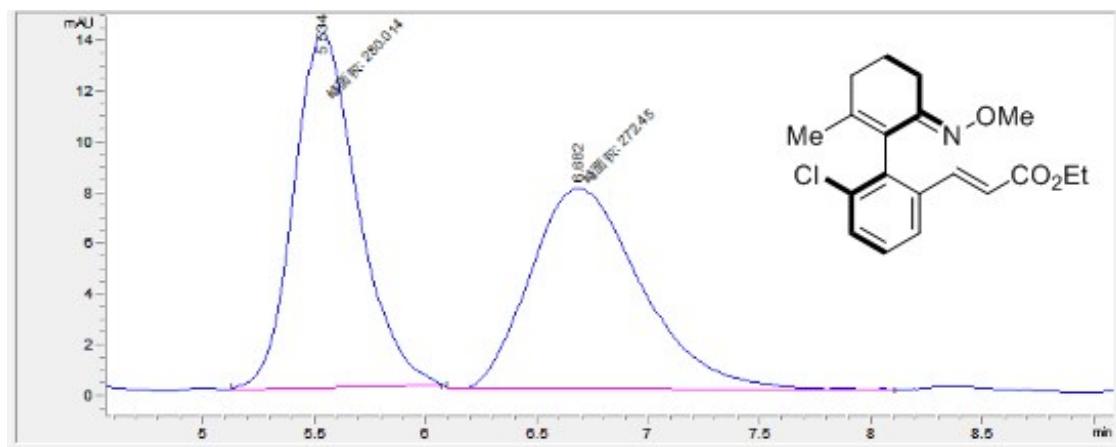
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|---------|
| 1 | 5.864 | 293.8 | 13.8 | 100.000 |



| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 8.933 | 461.9 | 20.9 | 50.291 |
| 2 | 10.409 | 456.6 | 19 | 49.709 |

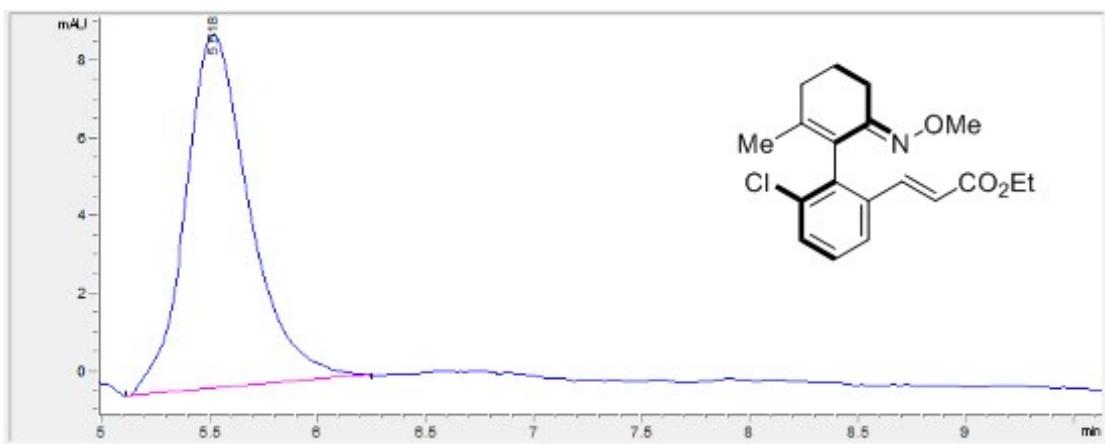


| | Time/min | Area | Height | Area% |
|---|----------|---------|--------|--------|
| 1 | 8.965 | 416.8 | 20.5 | 2.250 |
| 2 | 10.398 | 18110.8 | 736.9 | 97.750 |

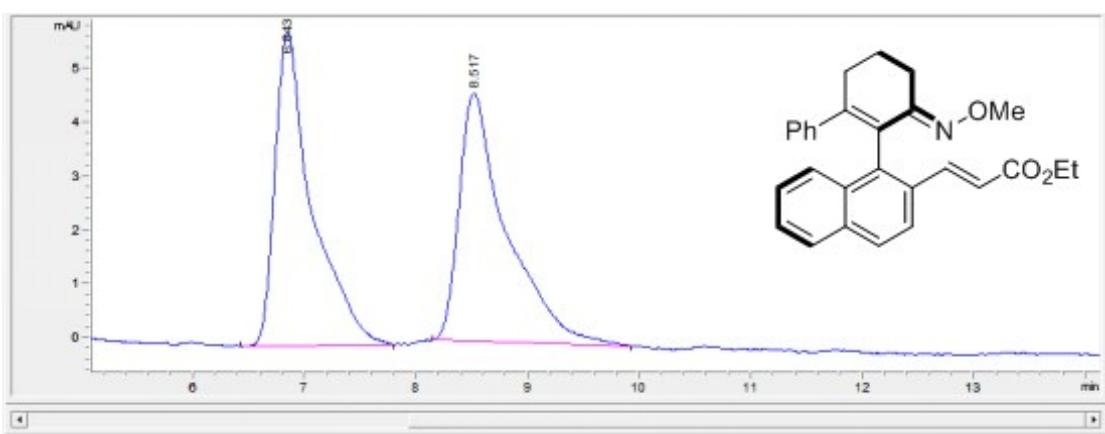


| | Time/min | Area | Height | Area% |
|---|----------|------|--------|--------|
| 1 | 5.534 | 280 | 14 | 50.685 |

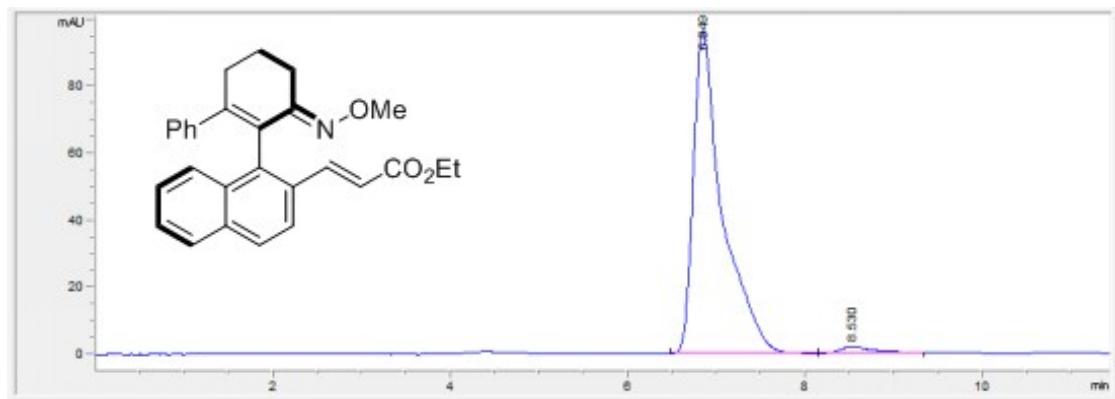
| | | | | |
|---|-------|-------|-----|--------|
| 2 | 6.682 | 272.4 | 7.9 | 49.315 |
|---|-------|-------|-----|--------|



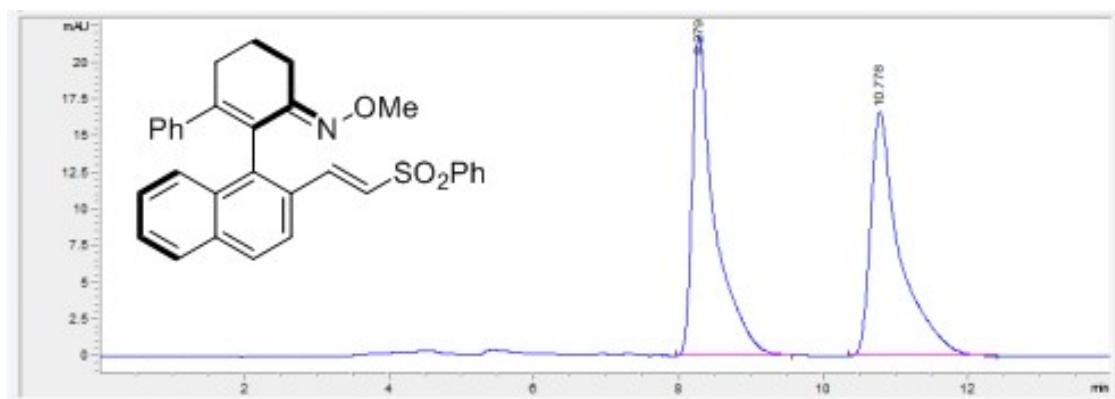
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|---------|
| 1 | 5.518 | 190.2 | 9.1 | 100.000 |



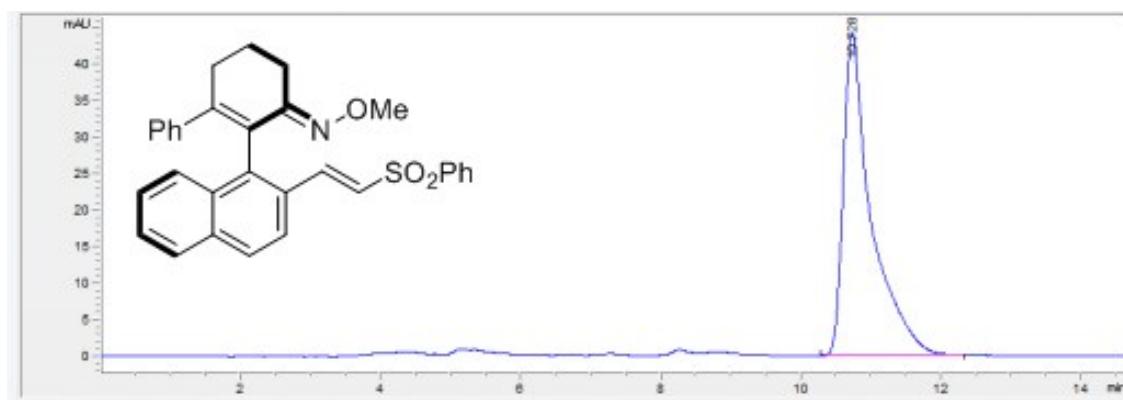
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 6.843 | 135.2 | 5.8 | 49.890 |
| 2 | 8.517 | 135.8 | 4.6 | 50.110 |



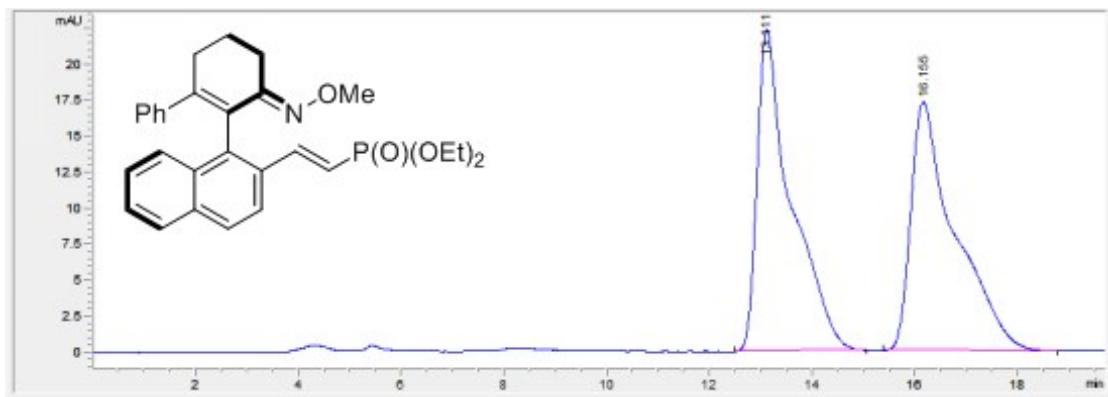
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 6.849 | 2195.5 | 96.2 | 97.781 |
| 2 | 8.53 | 49.8 | 1.9 | 2.219 |



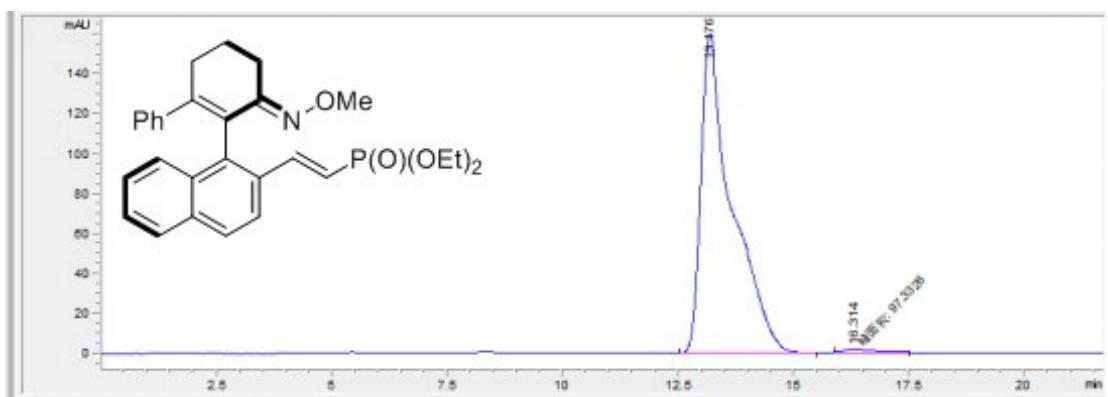
| | Time/min | Area | Height | Area% |
|---|----------|-------|--------|--------|
| 1 | 8.279 | 473 | 21.8 | 50.358 |
| 2 | 10.778 | 466.3 | 16.7 | 49.672 |



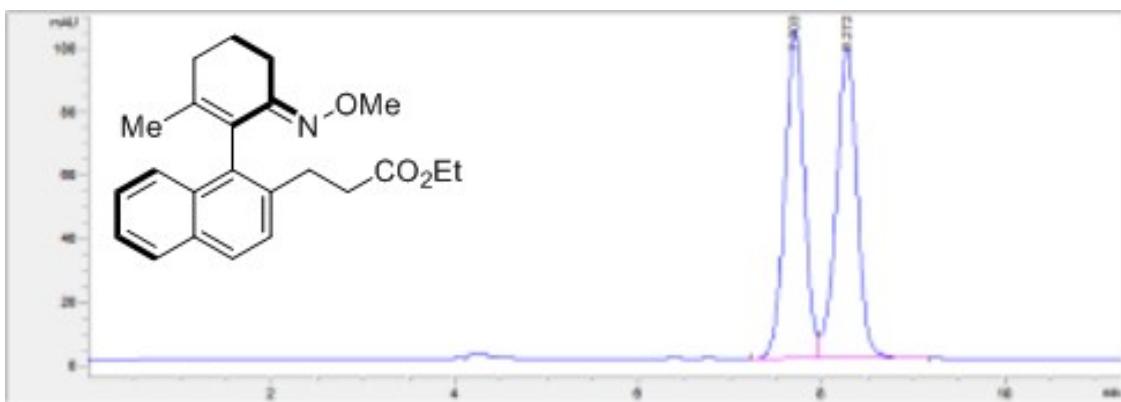
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|---------|
| 1 | 10.728 | 1225.9 | 44.3 | 100.000 |



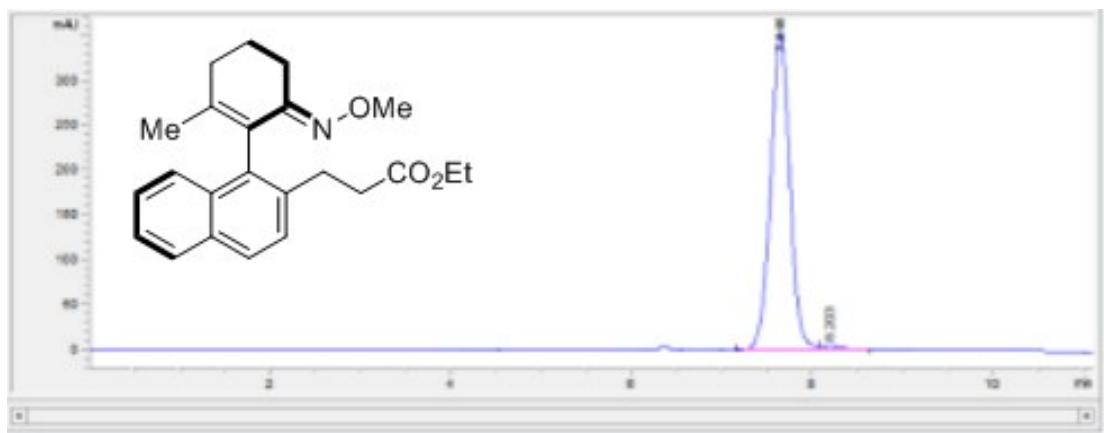
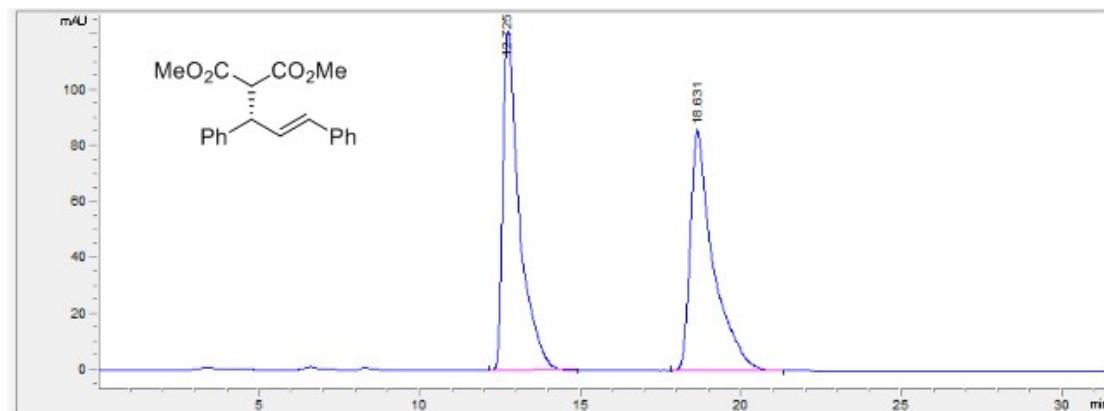
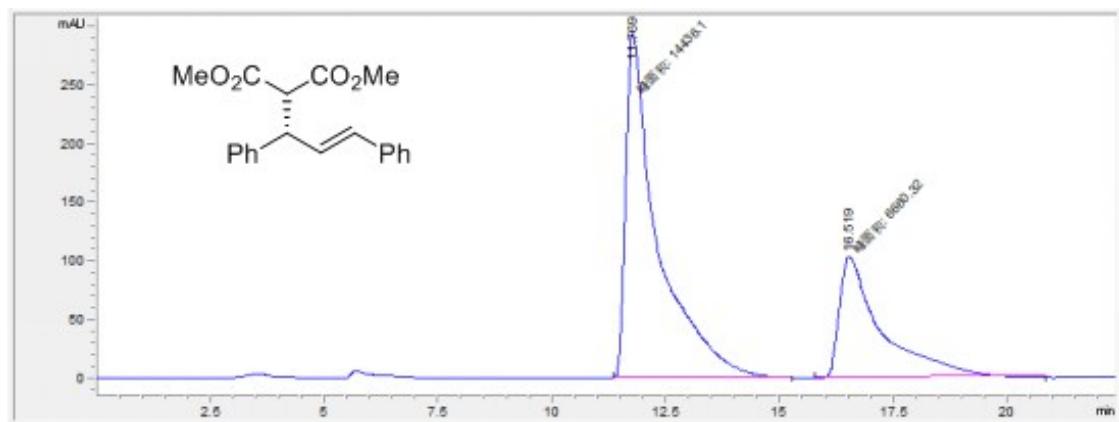
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 13.111 | 1031.4 | 22.3 | 50.062 |
| 2 | 16.155 | 1028.8 | 17.3 | 49.938 |



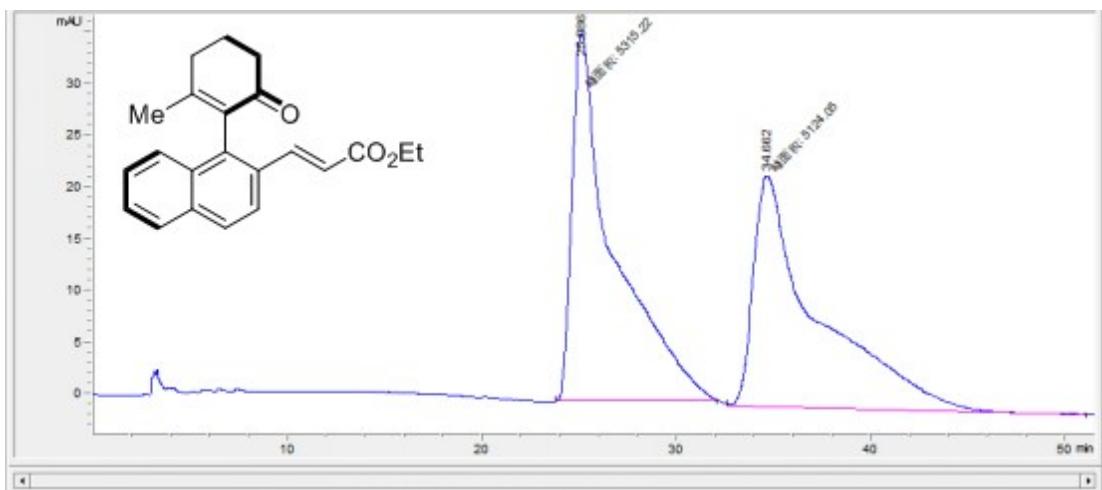
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 13.176 | 7483.4 | 159.9 | 98.716 |
| 2 | 16.314 | 97.3 | 1.9 | 1.284 |



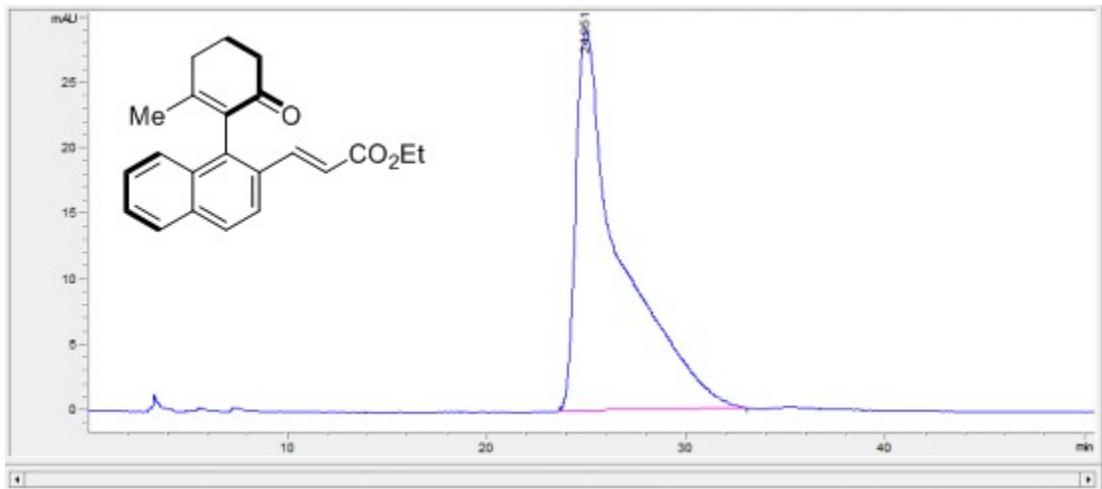
| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 7.703 | 1515.7 | 103.1 | 49.603 |
| 2 | 8.272 | 1540 | 97.9 | 50.397 |

| | Time/min | Area | Height | Area% |
|---|----------|---------|--------|--------|
| 1 | 11.769 | 14436.1 | 294 | 68.429 |
| 2 | 16.519 | 6660.3 | 103.7 | 31.571 |



| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|--------|
| 1 | 25.086 | 5315.2 | 35.6 | 50.916 |
| 2 | 34.662 | 5124 | 22.3 | 49.084 |



| | Time/min | Area | Height | Area% |
|---|----------|--------|--------|-------|
| 1 | 24.951 | 4536.2 | 29 | 100 |