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Supporting Information for

Pd-Catalyzed Asymmetric Decarboxylation for the Construction of Spiro[4.5]deca-6,9-dien-8-ones Featuring Vicinal Quaternary Carbon Stereocenters

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1. General Information

Commercially available reagents and solvents were purchased from Energy, *J*&K, TCI, aladdin or Daicel, and used without further purification. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra were recorded at room temperature on a Bruker AV-400 spectrometer and referenced to the residual deuterated solvent signals ($CDCl_3$ ^{1}H NMR, $\delta = 7.26$; ^{13}C NMR, $\delta = 77.16$). All reported NMR values are given in parts per million (ppm). FT-IR measurements were carried out on a Thermo Fisher Nicolet 6700 FT-IR spectrometer or Bruker ALPHA II. High resolution mass spectra (HRMS) were obtained on a WATERS I-Class VION IMS Qtof Spectrometer. The X-ray analysis of **3a** and **7** was collected on Bruker D8 Quest diffractometer. Optical rotations were recorded on a polarimeter with a sodium lamp of wavelength 589 nm. Enantiomeric excesses were determined by chiral High Performance Liquid Chromatography (HPLC) analysis. UV detection was monitored at 250 nm. HPLC samples were dissolved in HPLC grade isopropanol (IPA) unless otherwise stated.

2. Preparation of *para*-Quinone Methides (*p*-QMs).

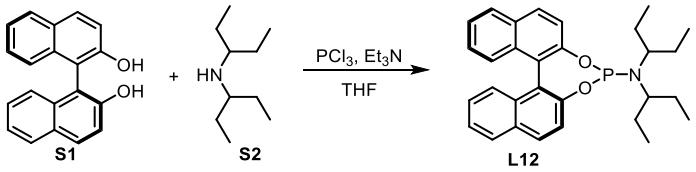
The *para*-quinone methides (**2a**-**2o**) were prepared according to the previously reported procedure. [1]

3. Preparation of Vinyl Methylene Cyclic Carbonates.

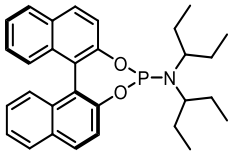
The vinyl methylene cyclic carbonates **1** was prepared according to our previously reported method.[2]

4. Preparation of Chiral Ligands.

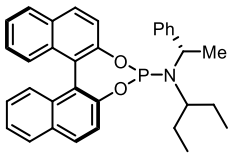
Chiral ligands **L1-L11** were purchased from chemical suppliers. The general procedure for the preparation of ligands **L12-L24** is described as follows with the use **L12** as an example.



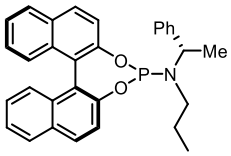
The triethylamine (5.0 eq.) was added dropwise to a stirred ice-cooled solution of PCl_3 (0.087 g, 1.0 eq.) in THF (5 mL). The ice bath was removed and the solution left to warm to room temperature before amine **S1**(0.1 g, 1.0 eq.) was added to the stirring solution. After additional 5 hours of stirring, binaphthol (0.18 g, 1.0 eq.) was added to the suspension and the subsequent mixture was left to stir for an additional 18 h. The solution was then filtered on a small pad of celite and rinsed with DCM. The resulting solution was concentrated under reduced pressure to afford a yellow residue. After flash column chromatography, the ligand **L12** was obtained as a white solid (0.15 g, 50% yield).



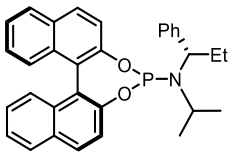
Ligand L12 : purified by column chromatography (petroleum ether/ethyl acetate = 100:1); white solid ; $[\alpha]_D^{20} = +333.9$ (*c* = 0.25, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.88 (dd, *J* = 8.2, 6.7 Hz, 3H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.41 - 7.34 (m, 3H), 7.29 - 7.22 (m, 2H), 7.22 - 7.16 (m, 1H), 2.89 - 2.68 (m, 2H), 1.81 - 1.75 (m, 2H), 1.69 - 1.39 (m, 6H), 0.89 (t, *J* = 7.4 Hz, 6H), 0.81 - 0.74 (m, 6H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 148.53. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 150.5, 150.1, 133.0, 132.9, 131.4, 130.4, 130.3, 129.5, 128.4, 128.2, 127.2, 126.0, 125.9, 124.7, 124.3, 124.2, 124.1, 122.6, 122.5, 122.4, 121.98, 121.95, 57.8, 57.7, 29.5, 11.90, 11.89, 11.8. **IR** ν_{max}/cm^{-1} 2962, 2930, 2872, 1587, 1460, 1230, 1015, 989, 816, 747. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{30}H_{35}O_2NP]^+$: 472.2405, found:472.2415.



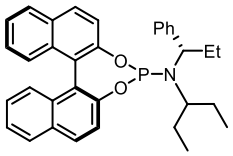
Ligand L14 : purified by column chromatography (petroleum ether/ethyl acetate = 100:1); white solid ; $[\alpha]_D^{20} = +179.3$ (*c* = 0.24, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.41 - 7.31 (m, 5H), 7.30 - 7.24 (m, 3H), 7.23 - 7.13 (m, 2H), 4.54 - 4.38 (m, 1H), 2.95 - 2.76 (m, 1H), 1.66 (d, *J* = 7.0 Hz, 3H), 1.56 - 1.41 (m, 2H), 1.37 - 1.16 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.33 (t, *J* = 7.4 Hz, 3H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 147.60. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.4, 149.9, 145.6, 133.0, 132.8, 131.4, 130.5, 130.4, 129.6, 128.4, 128.3, 128.2, 127.9, 127.6, 127.2, 126.9, 126.1, 125.9, 124.8, 124.4, 124.2, 122.5, 122.4, 121.8, 58.2, 54.0, 53.9, 29.7, 29.6, 11.6, 11.5. **IR** ν_{max}/cm^{-1} 2962, 2932, 2872, 1260, 1089, 1018, 938, 817, 746, 696. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{33}H_{33}O_2NP]^+$: 506.2249, found:506.2252.



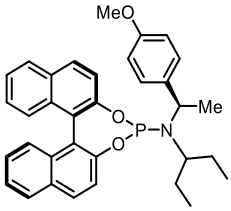
Ligand L15: purified by column chromatography (petroleum ether/ethyl acetate = 100:1); white solid ; $[\alpha]_D^{20} = +203.3$ (*c* = 0.25, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.45 - 7.27 (m, 7H), 7.25 - 7.17 (m, 2H), 7.13 (d, *J* = 8.8 Hz, 1H), 4.61 - 4.47 (m, 1H), 2.66 - 2.48 (m, 1H), 2.38 - 2.21 (m, 1H), 1.74 (dd, *J* = 7.2, 2.4 Hz, 3H), 1.33 - 1.21 (m, 1H), 1.16 - 1.01 (m, 1H), 0.42 (t, *J* = 7.4 Hz, 3H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 147.86. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.65, 150.60, 149.8, 143.8, 143.8, 133.0, 132.7, 131.5, 130.6, 130.3, 129.9, 128.5, 128.4, 128.3, 127.43, 127.42, 127.3, 127.2, 127.1, 126.1, 126.0, 124.8, 124.5, 124.30, 124.25, 122.41, 122.39, 122.19, 122.17, 122.1, 77.5, 77.2, 76.8, 56.6, 56.3, 45.8, 22.7, 22.4, 22.2, 11.2. **IR** ν_{max}/cm^{-1} 2963, 2926, 2868, 1503, 1326, 1229, 1205, 1069, 940. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{31}H_{29}O_2NP]^+$: 478.1936, found:478.1936.



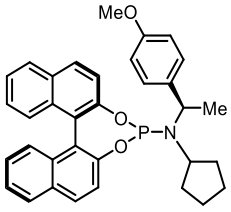
Ligand L17: purified by column chromatography (petroleum ether/ethyl acetate = 100:1); white solid ; $[\alpha]_D^{20} = +199.4$ (*c* = 0.29, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.42-7.36 (m, 5H), 7.32 - 7.25 (m, 2H), 7.25 - 7.21 (m, 3H), 4.15 - 3.95 (m, 1H), 3.52 - 3.27 (m, 1H), 2.35 - 2.13 (m, 1H), 2.12 - 1.85 (m, 1H), 1.07 (t, *J* = 7.2 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 149.43. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.6, 150.2, 146.7, 133.0, 132.8, 131.5, 130.6, 130.3, 129.6, 128.5, 128.4, 127.2, 126.7, 126.1, 126.0, 124.8, 124.4, 124.2, 122.5, 122.3, 122.0, 60.8, 60.6, 46.4, 46.3, 31.9, 31.7, 22.8, 22.1, 12.3, 12.27. **IR** ν_{max}/cm^{-1} 2968, 2926, 2869, 1459, 1327, 1200, 1155, 1023, 943. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{32}H_{31}O_2NP]^+$: 492.2092, found:492.2091.



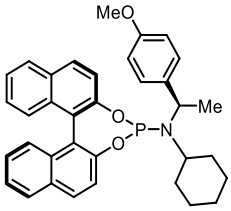
Ligand L18 : purified by column chromatography (petroleum ether/ethyl acetate = 100:1); white solid ; $[\alpha]_D^{20} = +184$ (*c* = 0.25, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.56 - 7.49 (m, 3H), 7.43 - 7.33 (m, 5H), 7.31 - 7.25 (m, 2H), 7.24 - 7.17 (m, 2H), 7.14 (d, *J* = 8.8 Hz, 1H), 4.08 - 3.95 (m, 1H), 2.94 - 2.81 (m, 1H), 2.23 - 2.01 (m, 2H), 1.44 - 1.32 (m, 2H), 1.10 (p, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H), 0.20 (t, *J* = 7.4 Hz, 3H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 146.24. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.3, 150.24, 149.9, 145.5, 133.0, 132.8, 131.5, 130.5, 130.3, 129.6, 128.41, 128.35, 128.2, 128.0, 127.9, 127.23, 127.19, 126.9, 126.1, 125.9, 124.8, 124.4, 124.22, 124.16, 122.51, 122.49, 122.4, 122.0, 61.5, 61.3, 58.54, 58.52, 32.0, 31.8, 29.7, 24.3, 12.52, 12.48, 11.7, 11.6. **IR** ν_{max}/cm^{-1} 2958, 2922, 2871, 1588, 1462, 1326, 1071. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{34}H_{35}O_2NP]^+$: 520.2409, found: 520.2405.



Ligand L22 : purified by column chromatography (petroleum ether/ethyl acetate = 100:1); white solid ; $[\alpha]_D^{20} = -132.8$ (*c* = 0.26, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.51 (dd, *J* = 8.8, 0.6 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.40 - 7.33 (m, 3H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.25 - 7.17 (m, 3H), 6.95 - 6.86 (m, 2H), 4.51 - 4.36 (m, 1H), 3.83 (s, 3H), 2.90 - 2.77 (m, 1H), 1.62 (d, *J* = 7.2 Hz, 3H), 1.52 - 1.44 (m, 2H), 1.38 - 1.25 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.37 (t, *J* = 7.4 Hz, 3H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 148.03. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 150.5, 150.4, 150.0, 137.4, 133.0, 132.9, 131.4, 130.5, 130.4, 129.6, 128.9, 128.8, 128.4, 128.2, 127.3, 126.1, 125.9, 124.8, 124.4, 124.22, 124.17, 122.5, 121.8, 113.6, 113.1, 58.2, 58.1, 55.4, 53.3, 53.2, 29.7, 29.6, 11.6, 11.5. **IR** ν_{max}/cm^{-1} 2962, 2929, 2871, 1588, 1509, 1231, 939. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{34}H_{35}O_3NP]^+$: 536.2355, found: 536.2353.

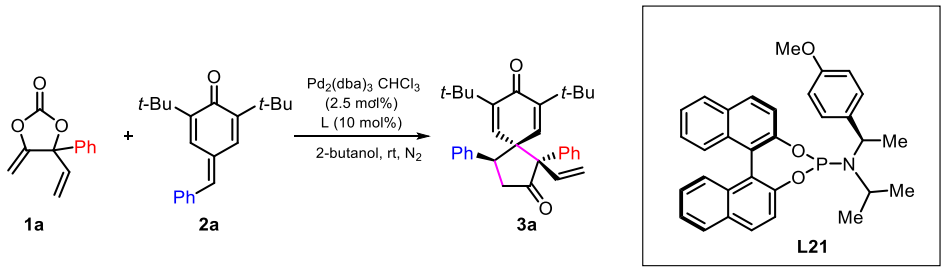


Ligand L23: purified by column chromatography (petroleum ether/ethyl acetate = 100:1); white solid ; $[\alpha]_D^{20} = -100.87$ (*c* = 0.35, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.38 - 7.25 (m, 5H), 7.21 - 7.17 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.45 - 4.38 (m, 1H), 3.81 (s, 3H), 3.33 - 3.22 (m, 1H), 1.86 - 1.73 (m, 2H), 1.68 - 1.52 (m, 5H), 1.57 (d, *J* = 6.8 Hz, 3H), 1.28 - 1.12 (m, 2H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 151.13. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.3, 150.5, 150.4, 150.1, 136.9, 132.9, 132.7, 131.4, 130.5, 130.4, 129.4, 128.4, 128.2, 127.2, 126.1, 125.9, 124.8, 124.4, 124.24, 124.18, 122.5, 122.3, 121.6, 113.6, 57.0, 56.9, 55.3, 53.1, 53.0, 34.4, 32.8, 32.7, 23.8.; **IR** ν_{max}/cm^{-1} 2954, 2865, 1508, 1461, 1229, 1203, 1176, 1035, 945. **HRMS** (ESI): *m/z* $[M+Na]^+$ calculated for $[C_{34}H_{32}O_3NPNa]^+$: 556.2012, found:556.2012.

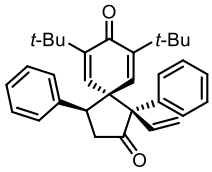


Ligand L24: purified by column chromatography (petroleum ether/ethyl acetate = 100:1); white solid ; $[\alpha]_D^{20} = -127.5$ (*c* = 0.25, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.42 - 7.27 (m, 5H), 7.25 - 7.19 (m, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 4.52 - 4.43 (m, 1H), 3.84 (s, 3H), 2.80 - 2.59 (m, 1H), 1.92 - 1.74 (m, 1H), 1.64 (d, *J* = 7.0 Hz, 3H), 1.59 - 1.46 (m, 4H), 1.39 - 1.27 (m, 2H), 0.93 - 0.80 (m, 2H), 0.59 - 0.49 (m, 1H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 151.43. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.4, 150.64, 150.56, 150.1, 137.5, 133.0, 132.8, 131.4, 130.5, 130.3, 129.6, 128.40, 128.37, 128.2, 127.2, 126.1, 125.9, 124.8, 124.4, 124.3, 124.2, 122.6, 122.2, 121.7, 113.6, 55.5, 55.4, 53.2, 53.0, 35.1, 34.1, 27.1, 26.3, 25.5, 24.5, 24.4. **IR** ν_{max}/cm^{-1} 2923, 2852, 1509, 1232, 1034, 943. **HRMS** (ESI): *m/z* $[M+Na]^+$ calculated for $[C_{35}H_{34}O_3NPNa]^+$: 570.2168, found: 570.2170.

5. General Procedure for the Optimization of the Reaction Conditions.

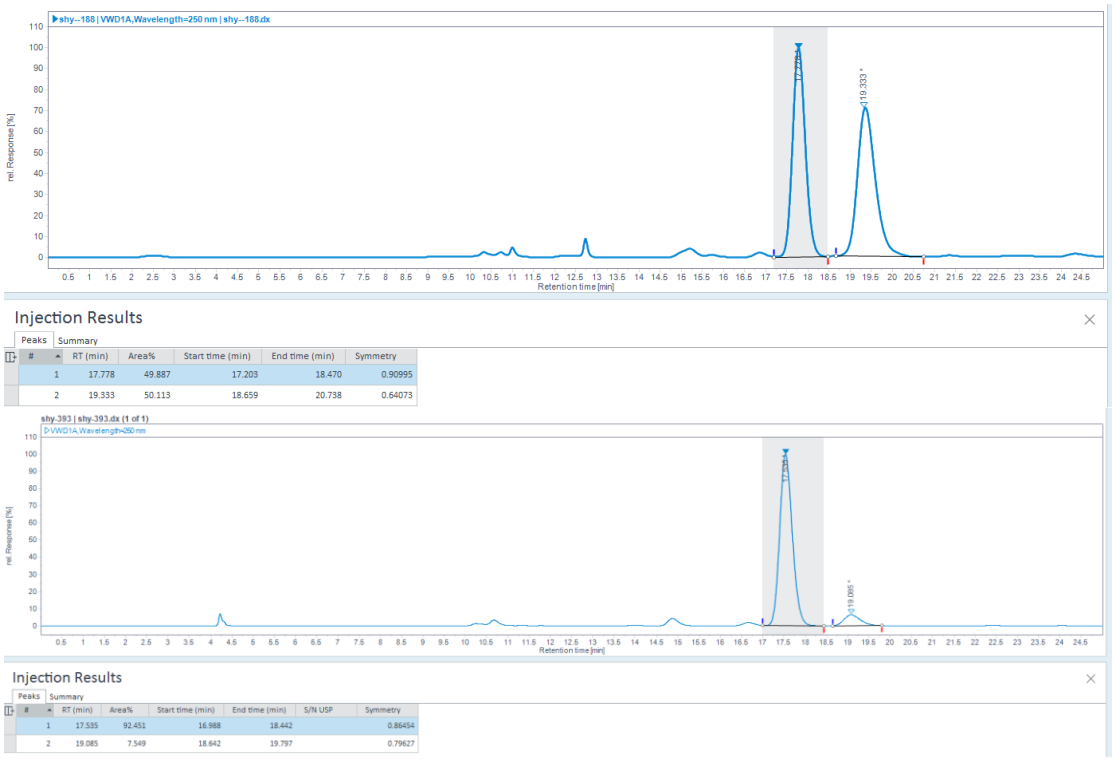


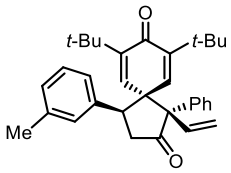
In the glovebox, to a vial equipped with a dried stir bar was added $Pd_2(dba)_3{\cdot}CHCl_3$ (0.0025 mmol), ligand **L21** (0.01 mmol), anhydrous 2-Butanol (0.5 mL). The reaction mixture was then allowed to stir for 1 h at room temperature, followed by the addition of cyclic carbonate **1a** (0.10 mmol) and *para*-quinone methide **2a** (0.15 mmol). Then, the reaction mixture was allowed to stir at room temperature until the starting material disappeared (monitored by TLC) in the glovebox. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (petroleum ether/ethyl acetate = 50:1). The *dr* values were determined by ^{1}H NMR analysis of crude reaction mixture. The enantiopurity of the purified product was analyzed by chiral HPLC.



Compound 3a: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 40 mg, 79% yield, *dr* >20:1, 92.5:7.5 *er*, $[\alpha]_D^{20} = -134.9$ (*c* = 0.33, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 - 7.35 (m, 3H), 7.19 - 7.10 (m, 5H), 6.91 - 6.88 (m, 2H), 6.41 (d, *J* = 3.2 Hz, 1H), 6.24 (d, *J* = 3.2 Hz, 1H), 5.95 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.25 (d, *J* = 11.2 Hz, 1H), 5.13 (d, *J* = 17.6 Hz, 1H), 3.61 (dd, *J* = 12.6, 8.6 Hz, 1H), 3.25 (dd, *J* = 19.6, 12.6 Hz, 1H), 3.09 (dd, *J* = 19.6, 8.6 Hz, 1H), 1.08 (s, 9H), 1.06 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.0, 185.6, 148.7, 148.6, 141.5, 138.8, 138.5, 136.7, 135.0, 129.64, 128.60, 128.4, 128.0, 127.7, 127.5, 118.7, 69.9, 55.9, 47.6, 41.5, 35.3, 35.2, 29.3, 29.0. **IR** ν_{max}/cm^{-1} 2953, 2920, 2865, 1737, 1631, 1453, 1355, 1252, 1201, 1106, 925. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{32}H_{37}O_2]^+$: 453.2794, found:453.2796.

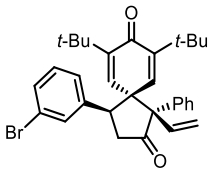
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 19.08 min (minor) and 17.54 min (major).





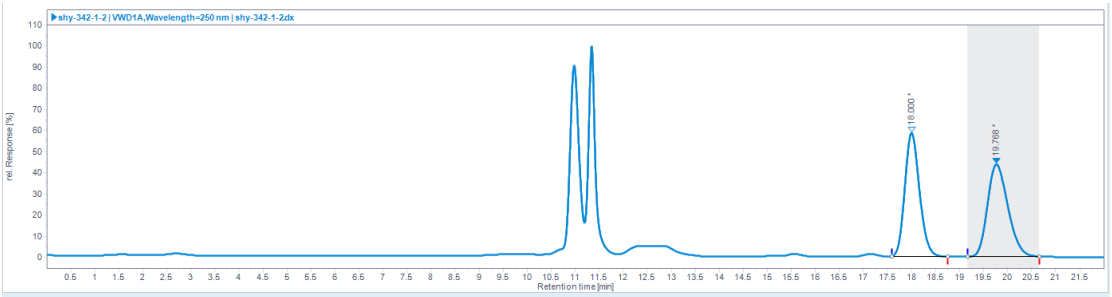
Compound 3b: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 40 mg, 85% yield, 11:1 *dr*, 91.5:8.5 *er*, $[\alpha]_D^{20} = -127.7$ (*c* = 0.23, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 - 7.33 (m, 3H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 3.0 Hz, 1H), 6.23 (d, *J* = 3.0 Hz, 1H), 5.94 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.25 (d, *J* = 11.2 Hz, 1H), 5.13 (d, *J* = 17.6 Hz, 1H), 3.58 (dd, *J* = 12.6, 8.6 Hz, 1H), 3.25 (dd, *J* = 19.6, 12.6 Hz, 1H), 3.07 (dd, *J* = 19.6, 8.6 Hz, 1H), 2.21 (s, 3H), 1.08 (s, 9H), 1.06 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.1, 185.7, 148.7, 148.5, 141.7, 139.0, 138.5, 136.9, 136.7, 134.9, 129.6, 129.4, 128.41, 128.38, 128.0, 127.5, 125.7, 118.7, 69.9, 55.8, 47.6, 41.5, 35.3, 35.2, 29.3, 29.1, 21.5. **IR** ν_{max}/cm^{-1} 2956, 2919, 2866, 1742, 1630, 1367, 1258, 1093, 1013. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{33}H_{39}O_2]^+$: 467.2945, found : 467.2935.

The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 16.63 min (minor) and 15.01 min (major).



Compound 3c: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 46 mg, 81% yield, 13:1 *dr*, 94:6 *er*, $[\alpha]_D^{20} = -96.0$ (*c* = 0.24, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 - 7.34 (m, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.18 - 7.16 (m, 2H), 7.04 - 7.00 (m, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.21 (d, *J* = 3.2 Hz, 1H), 5.93 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.26 (dd, *J* = 11.2, 0.7 Hz, 1H), 5.13 (dd, *J* = 17.6, 0.7 Hz, 1H), 3.56 (dd, *J* = 12.4, 8.8 Hz, 1H), 3.19 (dd, *J* = 19.6, 12.4 Hz, 1H), 3.08 (dd, *J* = 19.6, 8.8 Hz, 1H), 1.08 (s, 9H), 1.06 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.2, 185.5, 149.2, 149.1, 141.0, 138.2, 137.6, 136.4, 131.7, 130.8, 129.6, 129.0, 128.5, 128.2, 127.2, 121.7, 118.9, 69.8, 55.7, 47.2, 41.3, 35.4, 35.3, 29.4, 29.1. **IR** ν_{max}/cm^{-1} 2955, 2910, 2866, 1740, 1637, 1368, 1243, 1044, 928, 783. **HRMS** (ESI): *m/z* $[M+Na]^+$ calculated for $[C_{32}H_{35}BrO_2Na]^+$: 553.1713, found: 553.1721.

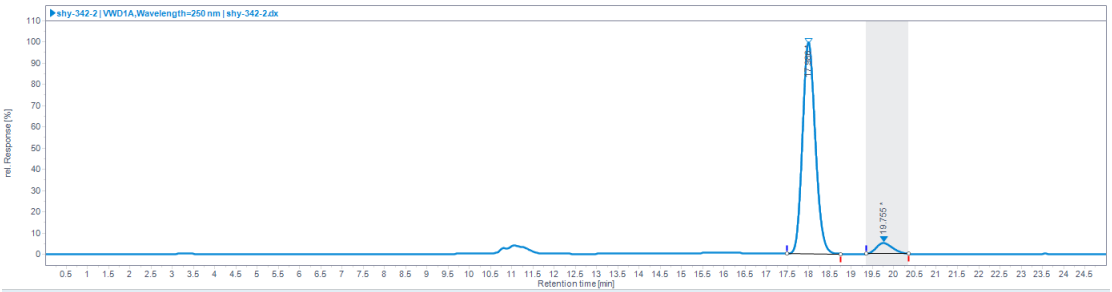
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 19.76 min (minor) and 17.99 min (major).



Injection Results

Peaks | Summary

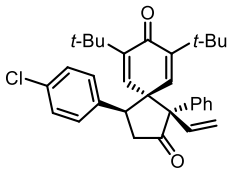
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	18.000	49.213	17.581	18.743	0.86754
2	19.768	50.787	19.158	20.652	0.79296



Injection Results

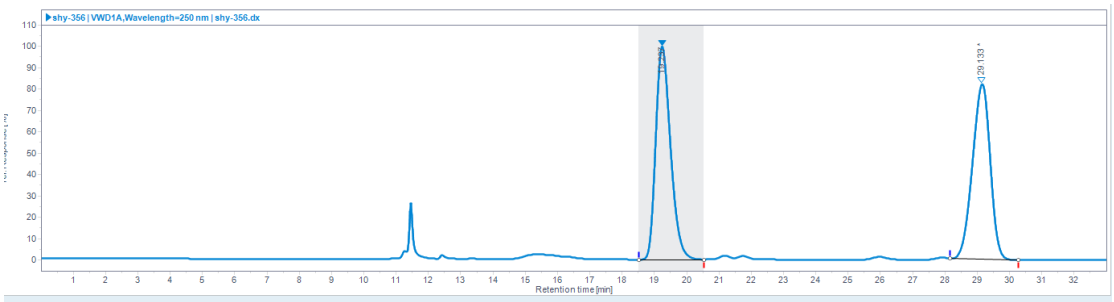
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	17.986	93.970	17.472	18.736	0.88806
2	19.755	6.030	19.354	20.340	0.80610



Compound 3d : purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 40 mg, 77% yield, 11:1 *dr*, 89:11 *er*, $[\alpha]_D^{20} = -68.8$ (*c* = 0.18, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 - 7.35 (m, 3H), 7.18 - 7.16 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.37 (d, *J* = 3.0 Hz, 1H), 6.21 (d, *J* = 3.0 Hz, 1H), 5.93 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 5.13 (d, *J* = 17.6 Hz, 1H), 3.58 (dd, *J* = 12.2, 9.0 Hz, 1H), 3.17 (dd, *J* = 19.6, 12.2 Hz, 1H), 3.08 (dd, *J* = 19.6, 9.0 Hz, 1H), 1.09 (s, 9H), 1.08 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.4, 185.4, 149.09, 149.08, 141.2, 138.4, 138.3, 136.5, 133.8, 133.5, 129.9, 129.6, 128.5, 128.1, 127.7, 118.9, 69.9, 55.7, 47.0, 41.5, 35.4, 35.3, 29.3, 29.1. **IR** ν_{max}/cm^{-1} 2955, 2918, 2865, 1742, 1635, 1492, 1367, 1250, 1091, 1013, 928. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{32}H_{36}ClO_2]^+$: 487.2398, found: 487.2389.

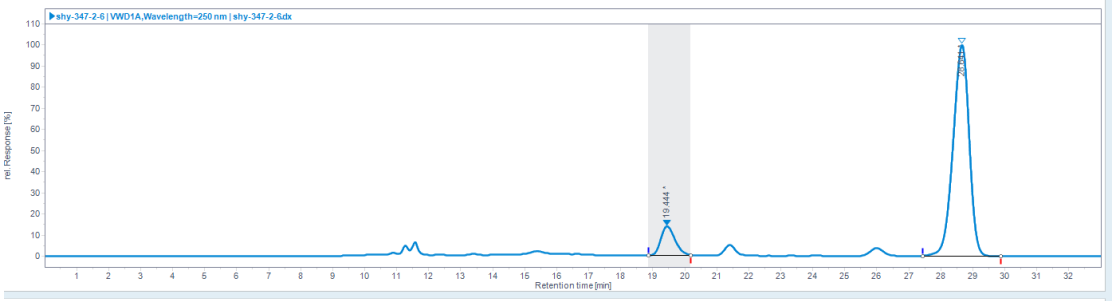
The *ee* was determined by HPLC analysis: CHIRALPAK IG (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 ^oC; 250 nm; retention time: 19.44 min (minor) and 28.64 min (major).



Injection Results

Peaks | Summary

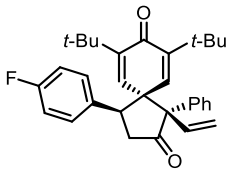
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	19.237	50.481	18.515	20.528	0.75301
2	29.133	49.519	28.161	30.278	1.13297



Injection Results

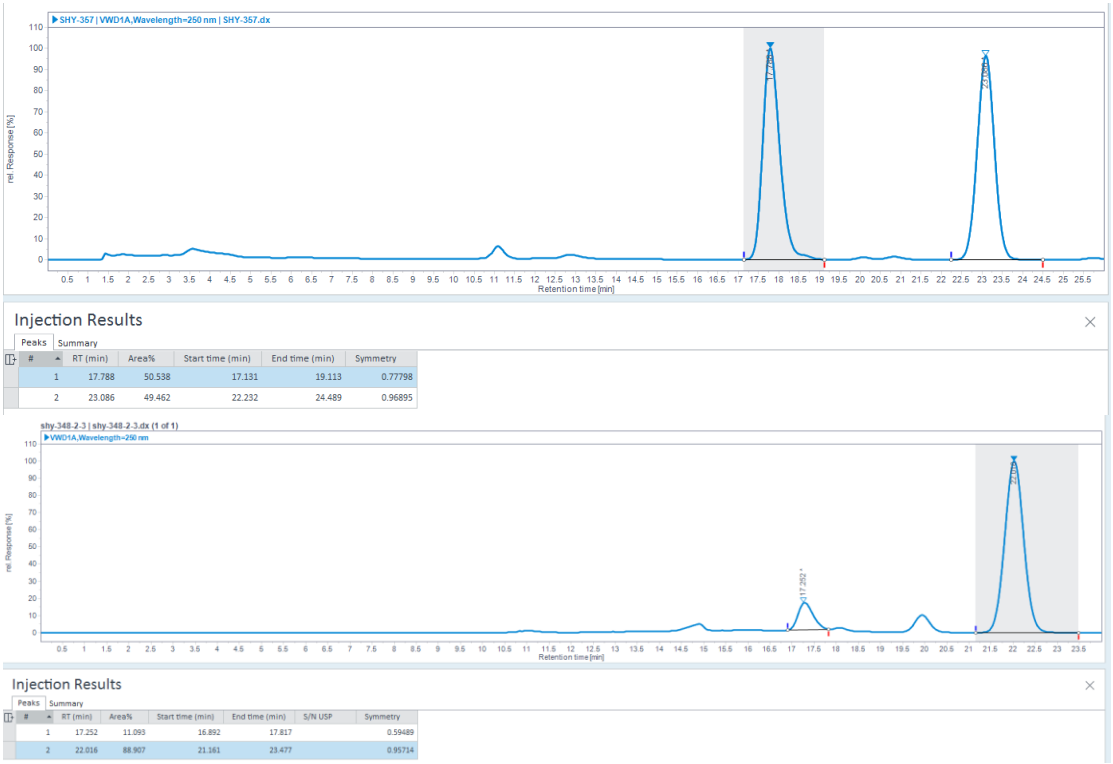
Peaks | Summary

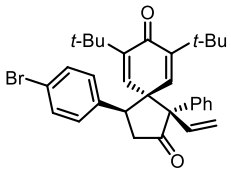
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	19.444	10.717	18.854	20.174	0.80286
2	28.641	89.283	27.420	29.861	1.16294



Compound 3e: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 44 mg, 91% yield, 11:1 *dr*, 89:11 *er* , $[\alpha]_D^{20} = -108.9$ (*c* = 0.27, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 - 7.35 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.90-6.81 (m, 4H), 6.38 (s, 1H), 6.22 (s, 1H), 5.94 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 5.13 (d, *J* = 17.6 Hz, 1H), 3.59 (dd, *J* = 12.0, 9.2 Hz, 1H), 3.17 (dd, *J* = 19.6, 12.0 Hz, 1H), 3.08 (dd, *J* = 19.6, 9.2 Hz, 1H), 1.08 (s, 18H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.55 (s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.6, 185.5, 162.1 (d, J_{CF}= 245 Hz), 149.0 (d, J_{CF} = 3 Hz), 141.3, 138.5, 138.3, 136.6, 130.8 (d, J_{CF} = 3 Hz), 130.1 (d, J_{CF} = 8 Hz), 129.6, 128.4, 128.1, 118.8, 114.6, 114.4, 69.9, 55.8, 46.9, 41.7, 35.33, 35.27, 29.3, 29.1. **IR** ν_{max}/cm^{-1} 2955, 2921, 2855, 1737, 1635, 1509, 1357, 1231, 1160, 1105, 926. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{32}H_{36}O_2F]^+$: 471.2694, found: 471.2692.

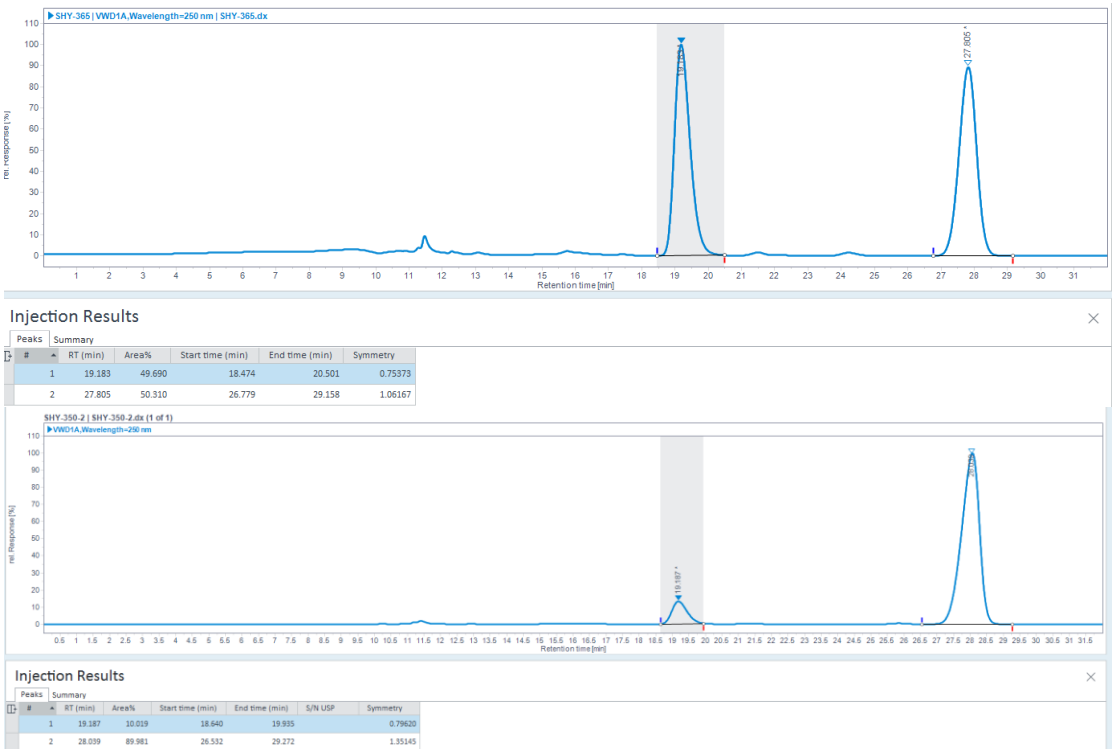
The *ee* was determined by HPLC analysis: CHIRALPAK IG (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 17.25 min (minor) and 22.01 min (major).

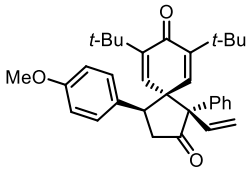




Compound 3f: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 38 mg, 68% yield, 10:1 *dr*, 90:10 *er*, $[\alpha]_D^{20} = -129.8$ (*c* = 0.27, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 - 7.33 (m, 3H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 7.4 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.37 (d, *J* = 2.8 Hz, 1H), 6.21 (d, *J* = 2.8 Hz, 1H), 5.93 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 5.13 (d, *J* = 17.6 Hz, 1H), 3.56 (dd, *J* = 12.2, 9.0 Hz, 1H), 3.17 (dd, *J* = 19.6, 12.2 Hz, 1H), 3.07 (dd, *J* = 19.6, 9.0 Hz, 1H), 1.09 (s, 9H), 1.08 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.3, 185.4, 149.1, 141.2, 138.32, 138.30, 136.4, 134.3, 130.7, 130.2, 129.6, 128.5, 128.1, 121.5, 118.9, 69.8, 55.6, 47.0, 41.5, 35.4, 35.3, 29.3, 29.1. **IR** ν_{max}/cm^{-1} 2936, 2917, 2866, 1740, 1631, 1486, 1368, 1251, 1097, 1073, 1006, 921. **HRMS** (ESI): *m/z* $[M+Na]^+$ calculated for $[C_{32}H_{35}BrO_2Na]^+$: 553.1713, found: 553.1721.

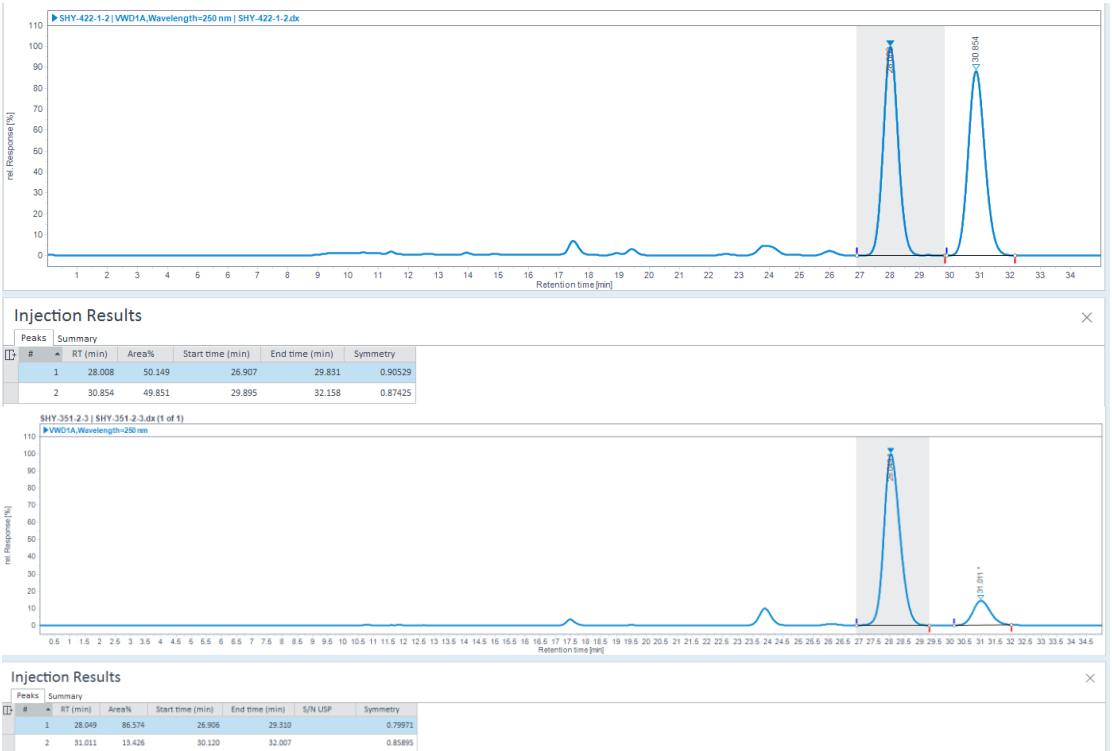
The *ee* was determined by HPLC analysis: CHIRALPAK IG (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 ^oC; 250 nm; retention time: 19.19 min (minor) and 28.04 min (major).

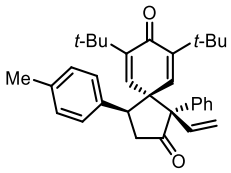




Compound 3g: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 37 mg, 72% yield, 8:1 *dr*, 86.5:13.5 *er*, $[\alpha]_D^{20} = -115.6$ (*c* = 0.25, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 - 7.34 (m, 3H), 7.17 (d, *J* = 6.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 3.0 Hz, 1H), 6.22 (d, *J* = 3.0 Hz, 1H), 5.94 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.24 (d, *J* = 11.2 Hz, 1H), 5.12 (d, *J* = 17.76Hz, 1H), 3.70 (s, 3H), 3.56 (dd, *J* = 12.6, 8.8 Hz, 1H), 3.18 (dd, *J* = 19.6, 12.6 Hz, 1H), 3.06 (dd, *J* = 19.6, 8.8 Hz, 1H), 1.08 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.1, 185.6, 159.0, 148.71, 148.69, 141.7, 139.0, 138.5, 136.8, 129.64, 129.63, 128.4, 128.0, 127.0, 118.7, 113.0, 69.9, 56.0, 55.4, 46.9, 41.9, 35.3, 35.2, 29.3, 29.1. **IR** ν_{max}/cm^{-1} 2954, 2914, 2867, 1738, 1626, 1513, 1366, 1249, 1182, 1105, 1033, 925. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{33}H_{39}O_3]^+$:483.2894, found: 483.2886.

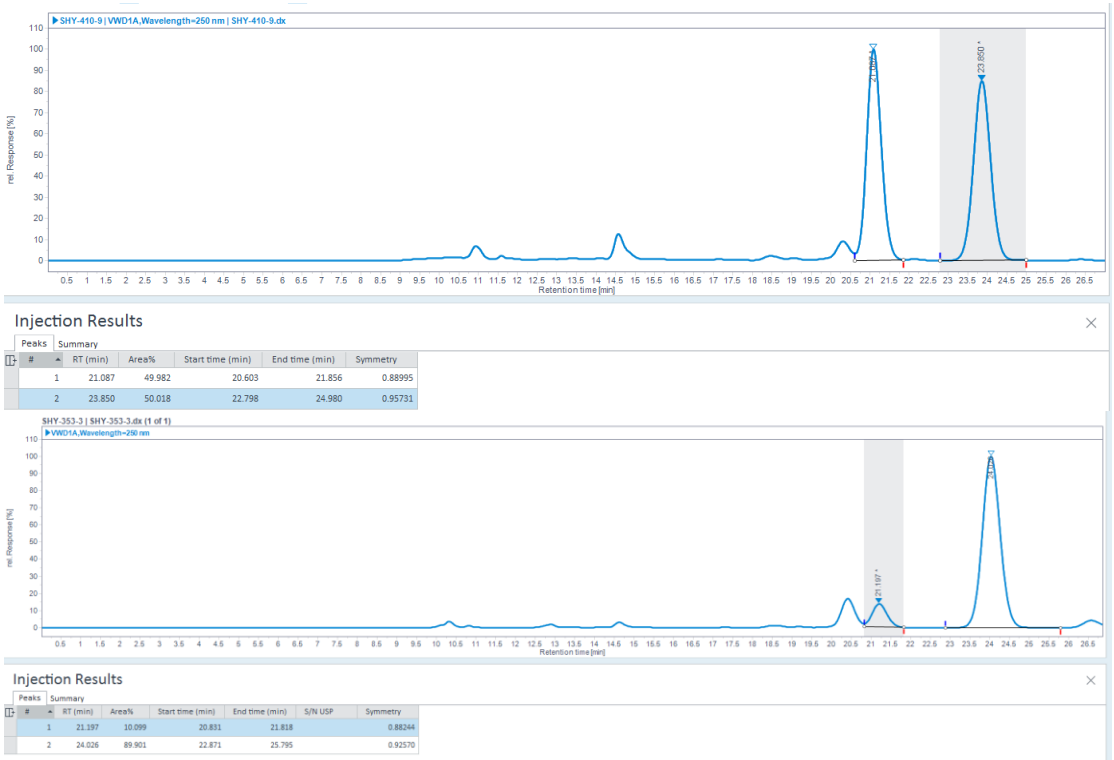
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 ^oC; 250 nm; retention time: 28.05 min (minor) and 31.01 min (major).

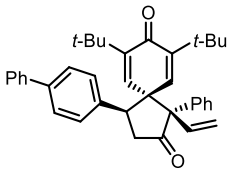




Compound 3h: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 42 mg, 76% yield, 11:1 *dr*, 90:10 *er*, $[\alpha]_D^{20} = -106.4$ (*c* = 0.25, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 - 7.32 (m, 3H), 7.17 (d, *J* = 7.4 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.40 (d, *J* = 3.0 Hz, 1H), 6.22 (d, *J* = 3.0 Hz, 1H), 5.94 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.24 (d, *J* = 11.2 Hz, 1H), 5.13 (d, *J* = 17.6 Hz, 1H), 3.58 (dd, *J* = 12.6, 8.6 Hz, 1H), 3.22 (dd, *J* = 19.7, 12.6 Hz, 1H), 3.06 (dd, *J* = 19.7, 8.6 Hz, 1H), 2.22 (s, 3H), 1.08 (s, 9H), 1.07 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.1, 185.7, 148.63, 148.58, 141.8, 139.0, 138.6, 137.3, 136.7, 132.0, 129.6, 128.43, 128.37, 128.2, 128.0, 118.7, 69.9, 55.9, 47.2, 41.7, 35.3, 35.2, 29.3, 29.1, 21.1. **IR** ν_{max}/cm^{-1} 2953, 2921, 2865, 1740, 1636, 1455, 1367, 1245, 1176, 927. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{33}H_{39}O_2]^+$: 467.2944, found: 467.2936.

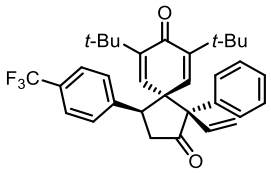
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 ^oC; 250 nm; retention time: 21.20 min (minor) and 24.03 min (major).





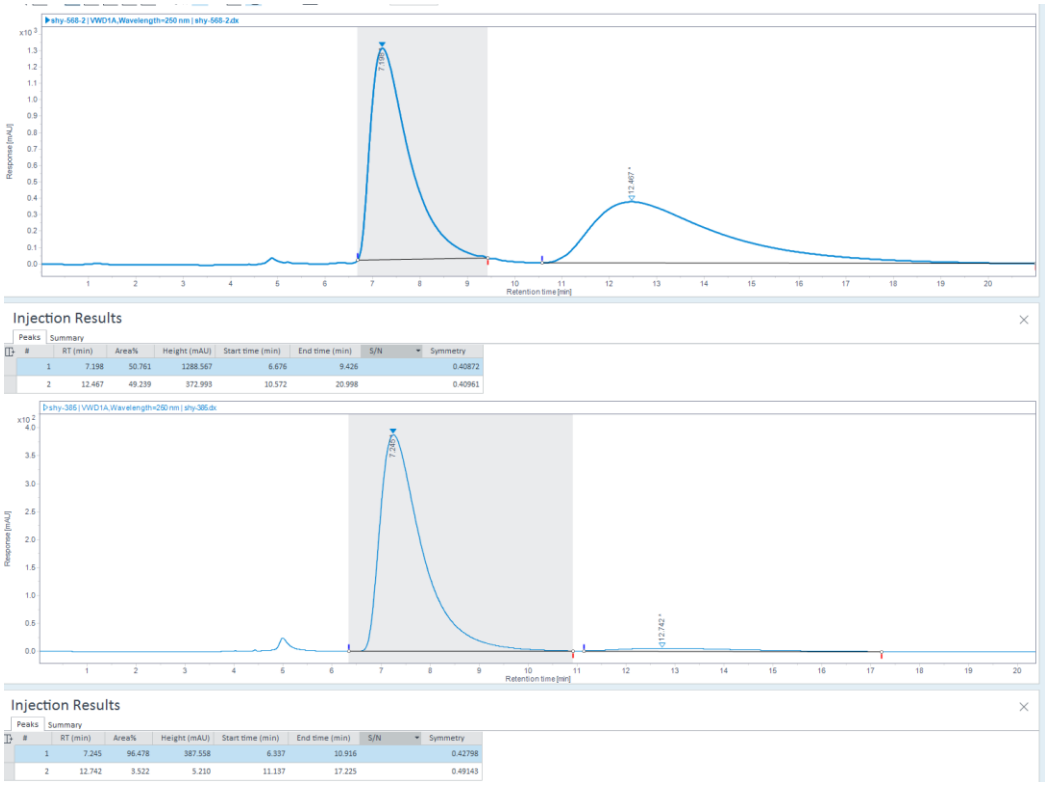
Compound 3i: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 40 mg, 70% yield, > 20:1 *dr*, 90:10 *er*, $[\alpha]_D^{20} = -149.2$ (*c* = 0.20, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 - 7.29 (m, 10H), 7.20 (d, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.43 (d, *J* = 3.0 Hz, 1H), 6.26 (d, *J* = 3.0 Hz, 1H), 5.96 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 5.14 (d, *J* = 17.6 Hz, 1H), 3.66 (dd, *J* = 12.6, 8.6 Hz, 1H), 3.28 (dd, *J* = 19.6, 12.6 Hz, 1H), 3.12 (dd, *J* = 19.6, 8.6 Hz, 1H), 1.10 (s, 9H), 1.07 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.9, 185.5, 148.8, 148.7, 141.5, 140.68, 140.66, 138.8, 138.5, 136.7, 134.2, 129.6, 129.0, 128.9, 128.4, 128.1, 127.5, 127.2, 126.2, 118.8, 69.9, 55.9, 47.3, 41.5, 35.34, 35.26, 29.3, 29.1. **IR** ν_{max}/cm^{-1} 2952, 2906, 2861, 1743, 1633, 1355, 1250, 1175, 837. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{38}H_{41}O_2]^+$: 529.3101, found: 529.3096.

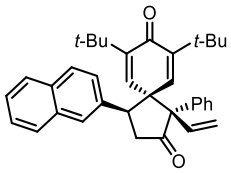
The *ee* was determined by HPLC analysis: CHIRALPAK IG (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 25.48 min (minor) and 20.88 min (major).



Compound 3j : purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 42 mg, 76% yield, > 20:1 *dr*, 96.5:3.5 *er*, $[\alpha]_D^{20} = -115.2$ (*c* = 0.24, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 - 7.35 (m, 5H), 7.18 (d, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.38 (s, 1H), 6.24 (s, 1H), 5.93 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.27 (d, *J* = 11.2 Hz, 1H), 5.14 (d, *J* = 17.6 Hz, 1H), 3.66 (dd, *J* = 12.0, 8.8 Hz, 1H), 3.24 (dd, *J* = 19.6, 12.0 Hz, 1H), 3.12 (dd, *J* = 19.6, 8.8Hz, 1H), 1.09 (s, 9H), 1.05 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.69(s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.1, 185.3, 149.24, 149.81, 141.0, 139.5, 138.2, 138.1, 136.3, 130.0 (q, J_{CF} = 33 Hz), 129.6, 128.9, 128.5, 128.2, 124.5 (q, J_{CF} = 3 Hz), 124.0 (q, J_{CF} = 270 Hz), 119.0, 69.8, 55.7, 47.3, 41.2, 35.4, 35.3, 29.3, 29.0. **IR** ν_{max}/cm^{-1} 2956, 2915, 2867, 1743, 1637, 1368, 1325, 1249, 1165, 1124, 1070. **HRMS** (ESI): *m/z* $[M+Na]^+$ calculated for $[C_{33}H_{35}F_3O_2Na]^+$: 543.2481, found: 543.2482.

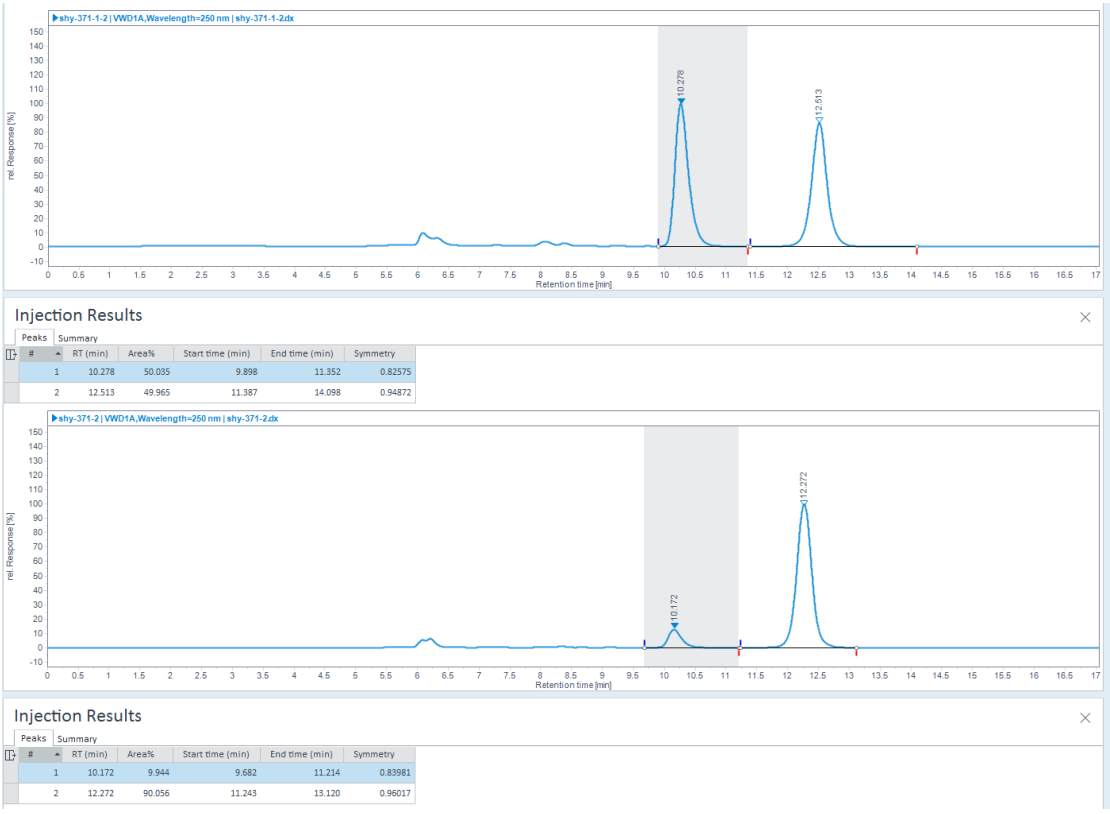
The *ee* was determined by HPLC analysis: CHIRALPAK O*J*H (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.8 mL/min; 35 °C; 250 nm; retention time: 12.74 min (minor) and 7.25 min (major).

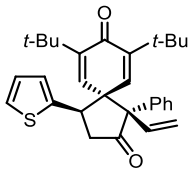




Compound 3k: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 45 mg, 80% yield, 15:1 *dr*, 90:10 *er*, $[\alpha]_D^{20} = -132.6$ (*c* = 0.27, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 - 7.70 (m, 1H), 7.65 - 7.61 (m, 2H), 7.44 - 7.35 (m, 6H), 7.22 (d, *J* = 7.0 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 1H), 6.50 (d, *J* = 3.0 Hz, 1H), 6.32 (d, *J* = 3.0 Hz, 1H), 5.96 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 5.15 (d, *J* = 17.6, 1H), 3.79 (dd, *J* = 12.6, 8.6 Hz, 1H), 3.39 (dd, *J* = 19.6, 12.6 Hz, 1H), 3.17 (dd, *J* = 19.6, 8.6 Hz, 1H), 1.06 (s, 9H), 0.99 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.7, 185.4, 148.6, 141.5, 138.7, 138.4, 136.5, 132.64, 132.59, 132.4, 129.5, 128.3, 127.9, 127.5, 127.4, 127.3, 126.9, 126.5, 126.2, 125.9, 118.7, 69.8, 55.9, 47.5, 41.6, 35.1, 35.0, 29.2, 28.9. **IR** ν_{max}/cm^{-1} 2950, 2909, 2864, 1740, 1630, 1483, 1367, 1250, 1000, 923. **HRMS** (ESI): *m/z* $[M+Na]^+$ calculated for $[C_{36}H_{38}O_2Na]^+$: 525.2764, found: 525.2764.

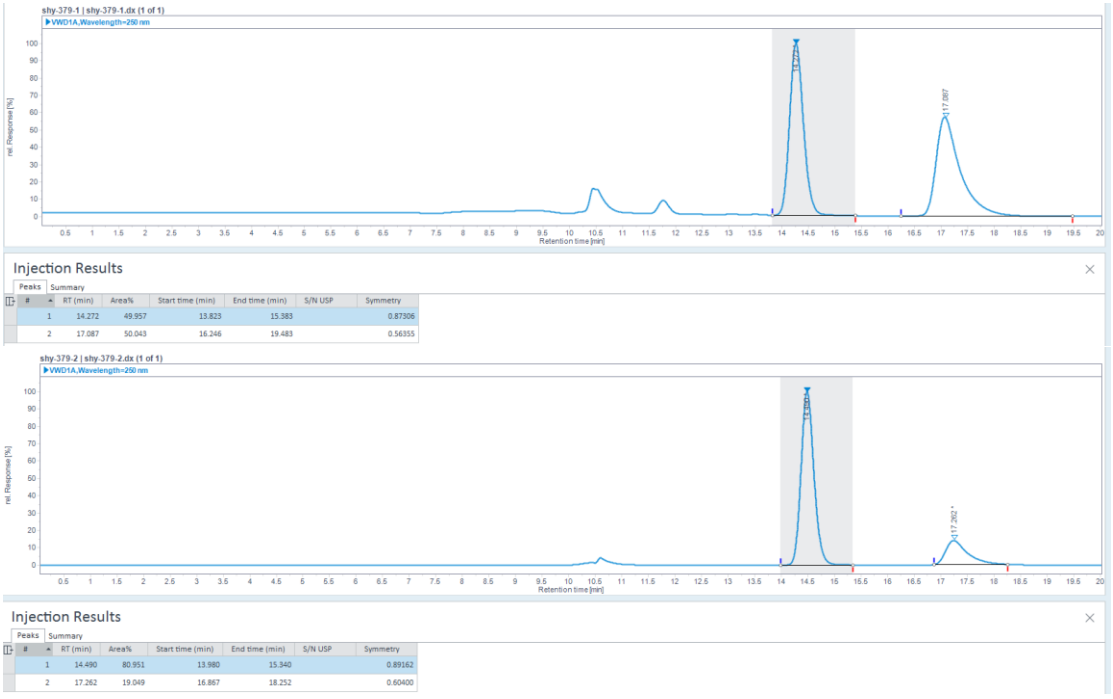
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 10.17 min (minor) and 12.27 min (major).

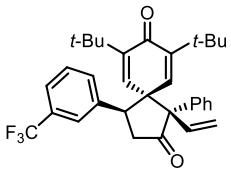




Compound 3l: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 32 mg, 65% yield, > 20:1 *dr*, 81:19 *er*, $[\alpha]_D^{20} = -75.4$ (*c* = 0.18, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 - 7.34 (m, 3H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 5.2 Hz, 1H), 6.83 - 6.79 (m, 1H), 6.60 (d, *J* = 3.4 Hz, 1H), 6.33 (d, *J* = 3.0 Hz, 1H), 6.20 (d, *J* = 3.0 Hz, 1H), 5.90 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 5.14 (d, *J* = 17.6 Hz, 1H), 3.85 (dd, *J* = 12.4, 8.6 Hz, 1H), 3.26 (dd, *J* = 19.6, 8.6 Hz, 1H), 3.16 (dd, *J* = 19.6, 12.4 Hz, 1H), 1.16 (s, 9H), 1.07 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.9, 185.9, 149.6, 149.3, 141.3, 139.6, 138.49, 138.46, 136.3, 129.6, 128.5, 128.1, 126.3, 125.6, 123.8, 119.0, 69.8, 55.7, 43.6, 42.7, 35.5, 35.2, 29.3, 29.0. **IR** ν_{max}/cm^{-1} 2952, 2917, 2865, 1741, 1634, 1367, 1251, 1109, 1000, 932. **HRMS** (ESI): *m/z* $[M+Na]^+$ calculated for $[C_{30}H_{34}O_2SNa]^+$: 481.2172, found: 481.2177.

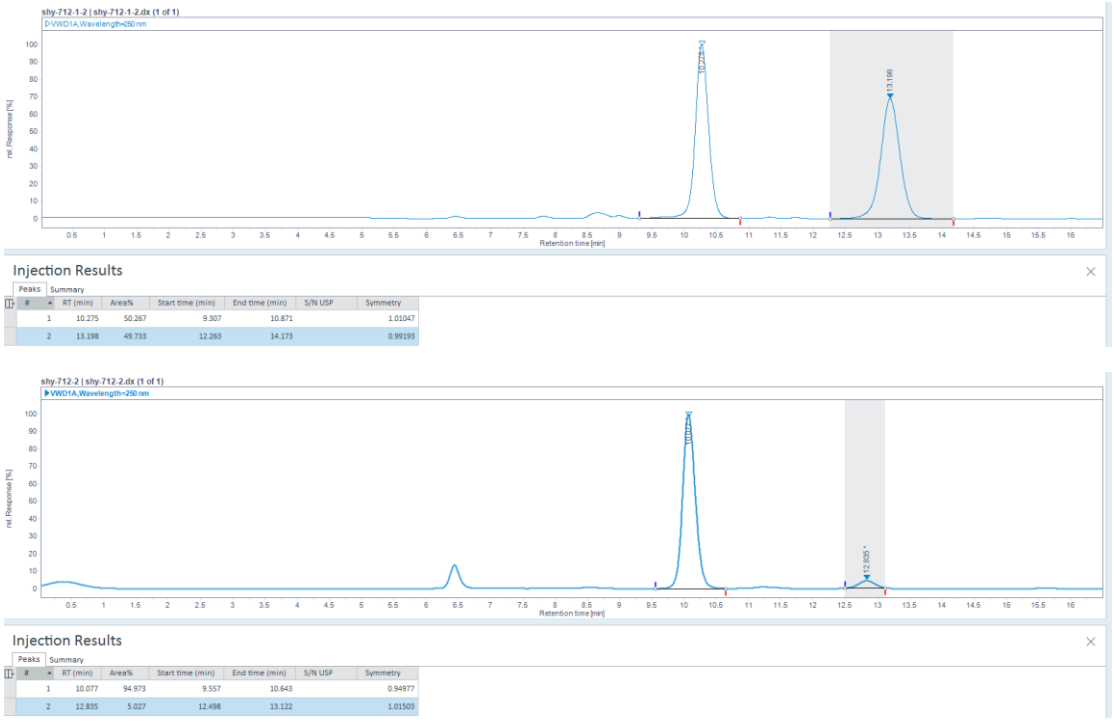
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 17.26 min (minor) and 14.49 min (major).

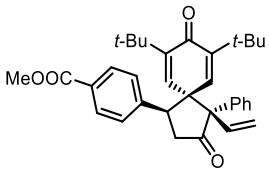




Compound 3m: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 40 mg, 72% yield, >20:1 *dr*, 95:5 *er*, $[\alpha]_D^{20} = -95.5$ (*c* = 0.19, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 - 7.42 (m, 4H), 7.31 - 7.27 (m, 1H), 7.19 - 7.17 (m, 3H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 2.8 Hz, 1H), 6.24 (d, *J* = 2.8 Hz, 1H), 5.92 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.27 (d, *J* = 11.2 Hz, 1H), 5.14 (d, *J* = 17.6Hz, 1H), 3.66 (dd, *J* = 12.4, 8.8 Hz, 1H), 3.26 (dd, *J* = 19.6, 12.4 Hz, 1H), 3.12 (dd, *J* = 19.6, 8.8 Hz, 1H), 1.08 (s, 9H), 1.06 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.5 (s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.1, 185.4, 149.4, 149.3, 141.0, 138.2, 137.9, 136.4, 136.3, 131.8, 130.1 (q, J_{CF} = 32 Hz), 129.5, 128.5, 128.2, 128.1, 125.1 (q, J_{CF} = 4 Hz), 124.6 (q, J_{CF} = 4 Hz), 124.0 (q, J_{CF} = 271 Hz), 119.0, 69.8, 55.7, 47.3, 41.2, 35.34, 35.26, 29.2, 29.0. **IR** ν_{max}/cm^{-1} 2958, 2913, 2868, 1744, 1657, 1638, 1368, 1327, 1165, 1127, 1076. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{33}H_{36}O_2F_3]^+$: 521.2667, found: 521.2668.

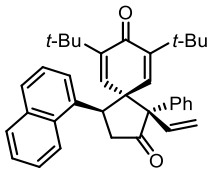
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 12.84 min (minor) and 10.08 min (major).





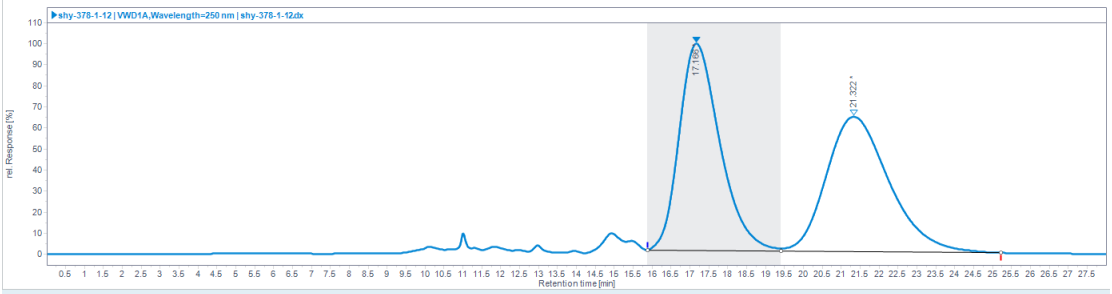
Compound 3n: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 35 mg, 70% yield, >20:1 *dr*, 94.5:5.5 *er*, $[\alpha]_D^{20} = -81.69$ (*c* = 0.31, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.43 - 7.37 (m, 3H), 7.18 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.40 (d, *J* = 2.8 Hz, 1H), 6.24 (d, *J* = 2.8 Hz, 1H), 5.93 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.27 (d, *J* = 11.2 Hz, 1H), 5.14 (d, *J* = 17.6Hz, 1H), 3.86 (s, 3H), 3.66 (dd, *J* = 12.4, 8.8 Hz, 1H), 3.26 (dd, *J* = 19.6, 12.4 Hz, 1H), 3.12 (dd, *J* = 19.6, 8.8 Hz, 1H), 1.08 (s, 9H), 1.06 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.3, 185.4, 166.7, 149.09, 149.05, 141.1, 140.6, 138.2, 136.4, 129.6, 129.4, 128.8, 128.6, 128.5, 128.2, 119.0, 69.8, 55.7, 52.3, 47.5, 41.4, 35.4, 35.3, 29.3, 29.1. **IR** ν_{max}/cm^{-1} 2953, 2910, 2866, 1744, 1720, 1657, 1635, 1368, 1279, 1250, 1186, 1112. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{34}H_{38}O_4Na]^+$: 533.2668, found: 533.2669.

The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.4 mL/min; 35 °C; 250 nm; retention time: 20.77 min (minor) and 16.63 min (major).



Compound 3o: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 35 mg, 66% yield, *dr* > 20:1, 88:12 *er*, $[\alpha]_D^{20} = +60.9$ (*c* = 0.19, $CHCl_3$); **^{1}H NMR** (400 MHz, CDCl3) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.48 - 7.42 (m, 4H), 7.37 - 7.21 (m, 6H), 6.53 (d, *J* = 3.0 Hz, 1H), 6.31 (d, *J* = 3.0 Hz, 1H), 6.04 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.28 (d, *J* = 11.2 Hz, 1H), 5.16 (d, *J* = 17.6 Hz, 1H), 4.75 (dd, *J* = 12.2, 8.6 Hz, 1H), 3.36 (dd, *J* = 19.6, 12.2 Hz, 1H), 3.20 (dd, *J* = 19.6, 8.6 Hz, 1H), 1.11 (s, 9H), 0.65 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.1, 184.9, 148.7, 147.5, 141.1, 139.4, 138.6, 136.9, 133.7, 132.5, 131.3, 129.6, 129.3, 128.5, 128.4, 128.2, 126.3, 126.2, 125.4, 124.2, 122.9, 118.8, 70.2, 56.1, 43.1, 41.3, 35.3, 34.8, 29.1, 28.5. **IR** ν_{max}/cm^{-1} 2955, 2913, 2866, 1740, 1632, 1447, 1366, 1254, 1095, 936. **HRMS** (ESI): *m/z* $[M+Na]^+$ calculated for $[C_{36}H_{38}O_2Na]^+$: 525.2764, found: 525.2764.

The *ee* was determined by HPLC analysis: CHIRALPAK ASH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 21.29 min (minor) and 17.10 min (major).



Injection Results

Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
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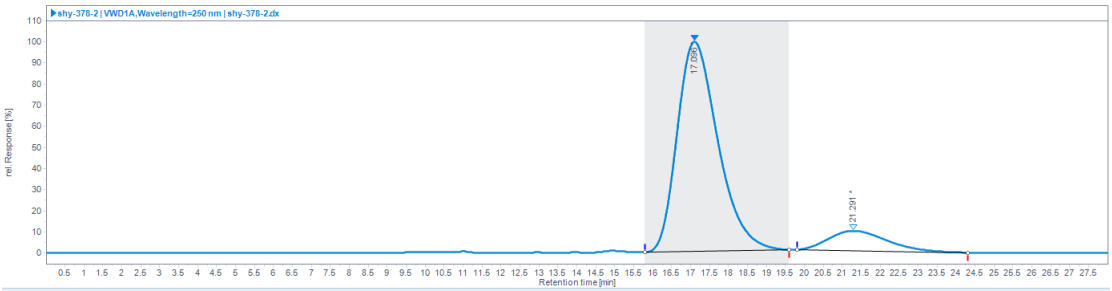
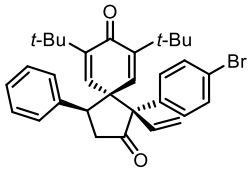
2	21.322	50.158	19.400	25.209	0.74066



Injection Results

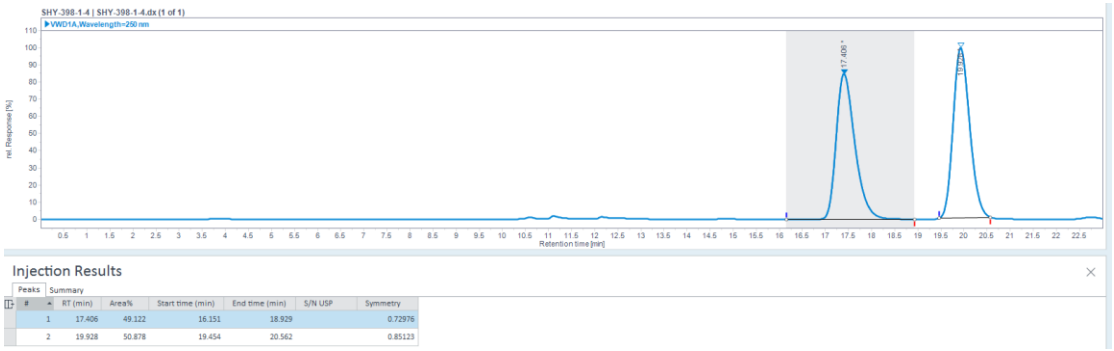
Peaks | Summary

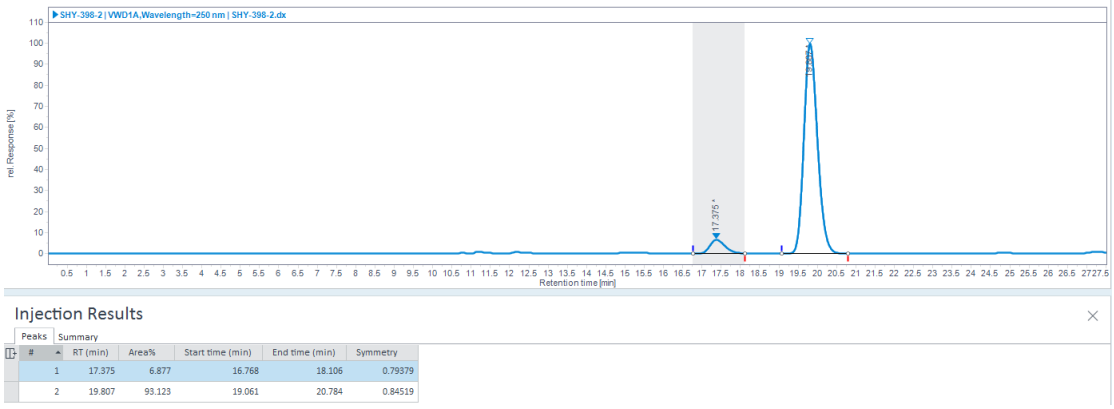
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	17.096	88.155	15.802	19.593	0.70171
2	21.291	11.845	19.813	24.309	0.71003

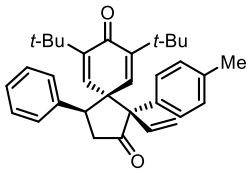


Compound 3p: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); white solid, 38 mg, 71% yield, 11:1 *dr*, 93:7 *er*, $[\alpha]_D^{20} = -134.4$ (c = 0.26, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 4.4 Hz, 3H), 7.05 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 4.4 Hz, 2H), 6.38 (s, 1H), 6.21 (s, 1H), 5.90 (dd, J = 17.6, 11.2 Hz, 1H), 5.26 (d, J = 11.2 Hz, 1H), 5.11 (d, J = 17.6 Hz, 1H), 3.55 (dd, J = 12.6, 8.6 Hz, 1H), 3.25 (dd, J = 19.8, 12.6 Hz, 1H), 3.06 (dd, J = 19.8, 8.6 Hz, 1H), 1.09 (s, 9H), 1.06 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.4, 185.4, 149.2, 148.9, 140.9, 138.4, 137.6, 136.4, 134.8, 131.5, 131.4, 128.6, 127.8, 127.6, 122.2, 119.3, 69.4, 55.7, 47.7, 41.3, 35.4, 35.2, 29.3, 29.0. **IR** ν_{max}/cm^{-1} 2954, 2922, 2865, 1742, 1658, 1637, 1487, 1368, 1249, 1177, 1008. **HRMS** (ESI): *m/z* $[M+Na]^+$ calculated for $[C_{32}H_{35}BrO_2Na]^+$: 553.1713, found: 553.1721.

The *ee* was determined by HPLC analysis: CHIRALPAK IG (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 17.38 min (minor) and 19.81 min (major).

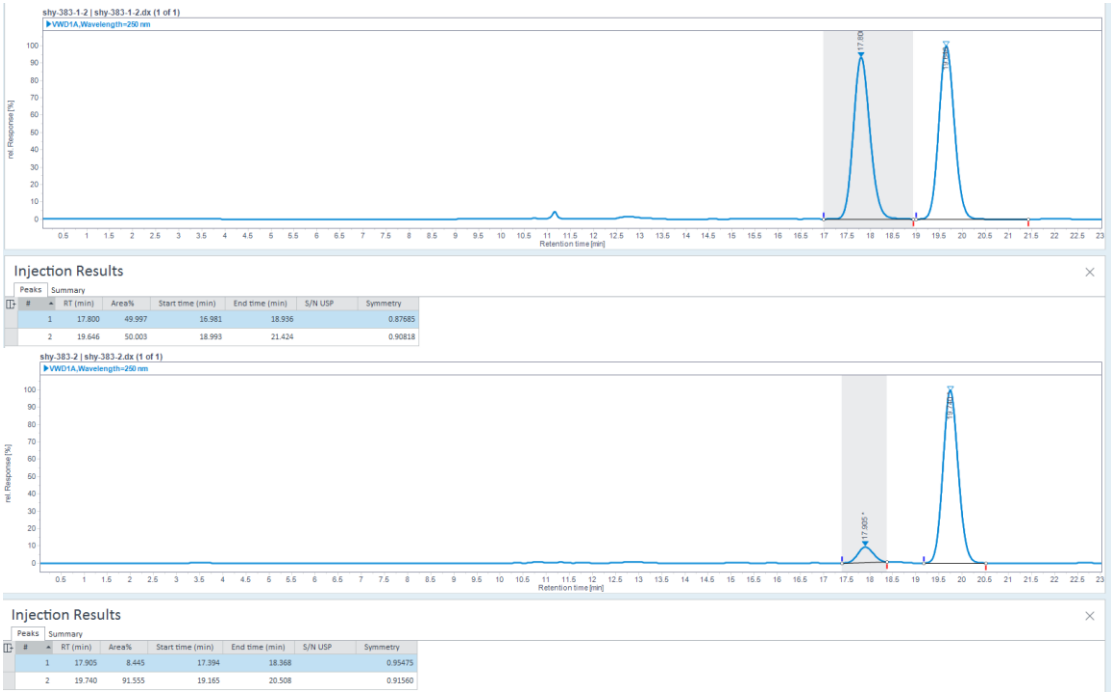


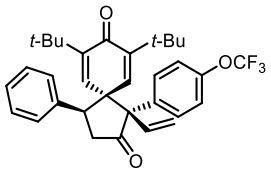




Compound 3q: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 50 mg, 96% yield, > 20:1 *dr*, 91.5:8.5 *er*, $[\alpha]_D^{20} = -140.2$ (*c* = 0.29, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.14 - 7.12 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.91- 6.88 (m, 2H), 6.40 (d, *J* = 3.0 Hz, 1H), 6.29 (d, *J* = 3.0 Hz, 1H), 5.92 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.22 (d, *J* = 11.2 Hz, 1H), 5.10 (d, *J* = 17.6 Hz, 1H), 3.60 (dd, *J* = 12.6, 8.8 Hz, 1H), 3.22 (dd, *J* = 19.8, 12.6 Hz, 1H), 3.07 (dd, *J* = 19.8, 8.8 Hz, 1H), 2.39 (s, 3H), 1.09 (s, 9H), 1.06 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.1, 185.6, 148.7, 148.6, 141.7, 138.9, 137.9, 136.8, 135.2, 135.1, 129.5, 129.1, 128.6, 127.7, 127.5, 118.5, 69.7, 55.9, 47.6, 41.4, 35.3, 35.2, 29.3, 29.0, 21.2. **IR** ν_{max}/cm^{-1} 2954, 2920, 2865, 1742, 1635, 1454, 1367, 1251, 927. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{33}H_{39}O_2]^+$: 467.2945, found:467.2936.

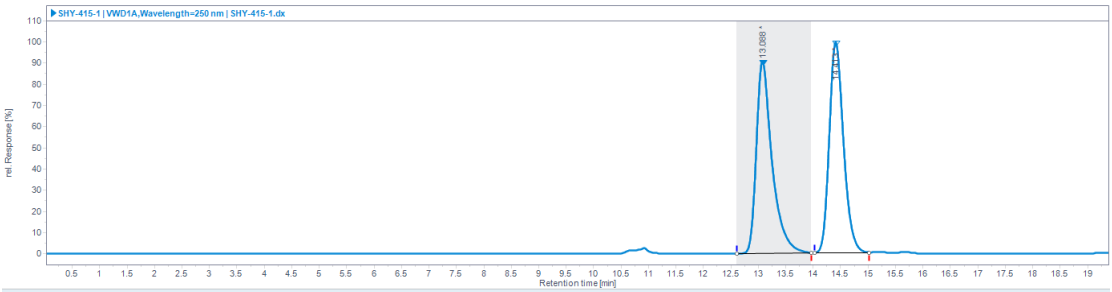
The *ee* was determined by HPLC analysis: CHIRALPAK IG (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 ^oC; 250 nm; retention time: 17.91 min (minor) and 19.74 min (major).





Compound 3r: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 34 mg, 69% yield, >20:1 *dr*, 93:7 *er*, $[\alpha]_D^{20} = -114.6$ (*c* = 0.23, $CHCl_3$); **^{1}H NMR** (400 MHz, CDCl3) δ 7.26 - 7.15 (m, 7H), 6.92 - 7.91 (m, 2H), 6.39 (s, 1H), 6.14 (s, 1H), 5.93 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.28 (dd, *J* = 11.2, 0.8 Hz, 1H), 5.14 (dd, *J* = 17.6, 0.8 Hz, 1H), 3.57 (dd, *J* = 12.4, 8.6 Hz, 1H), 3.27 (dd, *J* = 19.8, 12.4 Hz, 1H), 3.08 (dd, *J* = 19.8, 8.6 Hz, 1H), 1.08 (s, 9H), 1.06 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.83 (s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.4, 185.4, 149.1, 148.9, 148.7, 140.9, 138.4, 137.4, 136.4, 134.7, 131.1, 128.6, 127.9, 127.7, 121.3 (q, J_{CF} = 256 Hz), 119.2, 116.7, 69.1, 55.7, 47.6, 41.4, 35.32, 35.25, 29.3, 29.0. **IR** ν_{max}/cm^{-1} 2957, 2913, 2867, 1744, 1658, 1637, 1506, 1256, 1215, 1170. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{33}H_{36}F_3O_3]^+$: 537.2611, found: 537.2603.

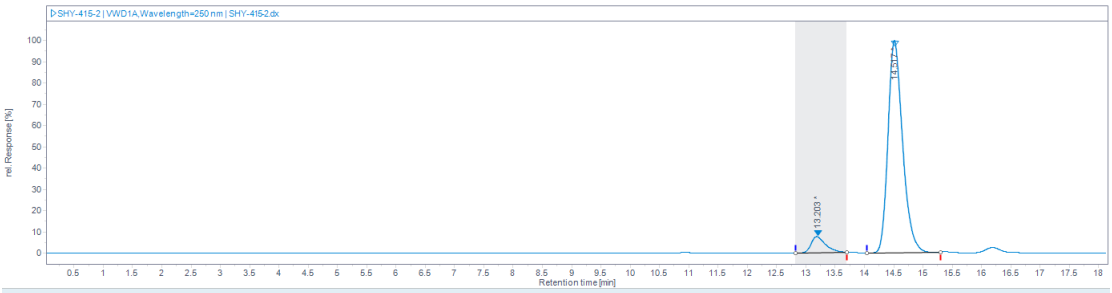
The *ee* was determined by HPLC analysis: CHIRALPAK IG (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 ^{o}C; 250 nm; retention time: 13.20 min (minor) and 14.52 min (major).



Injection Results

Peaks | Summary

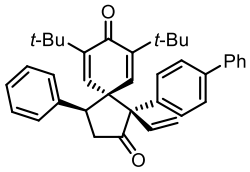
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	13.088	50.193	12.611	13.960	0.71304
2	14.413	49.807	14.030	15.024	0.86714



Injection Results

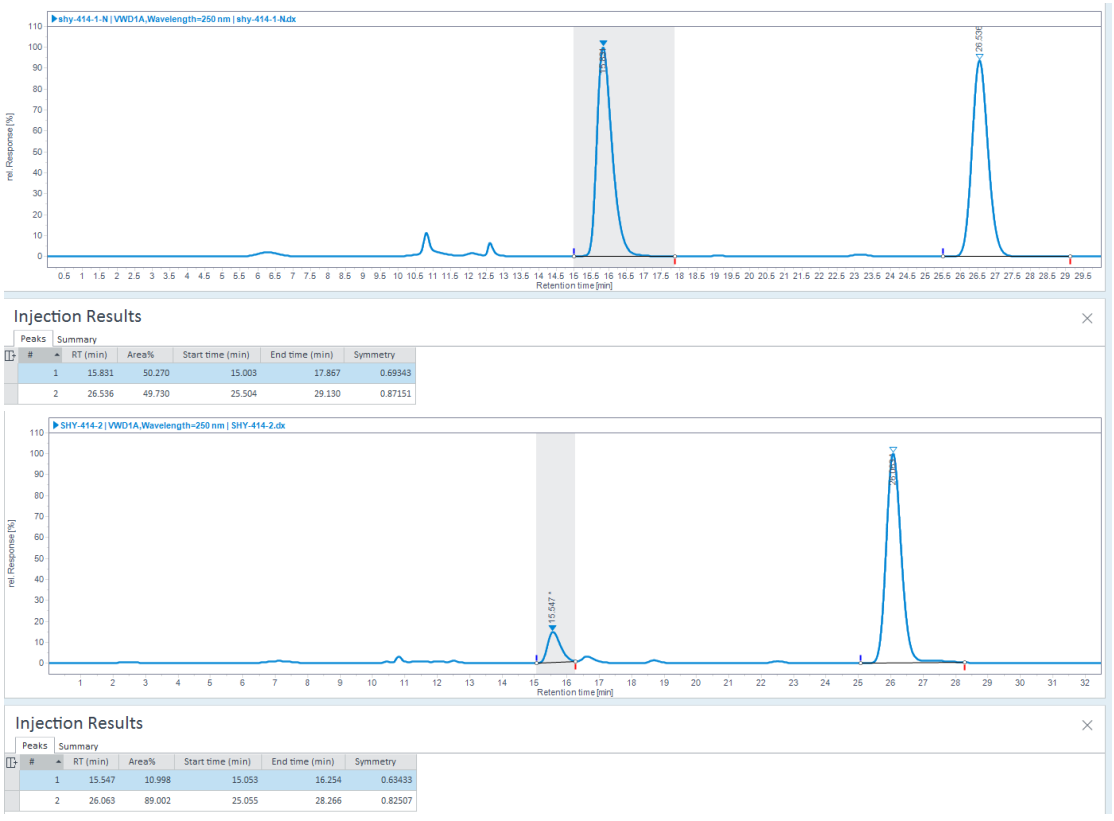
Peaks | Summary

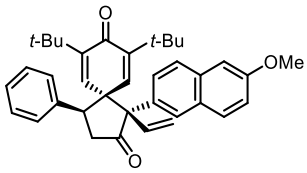
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	13.203	7.046	12.820	13.697	0.76651
2	14.517	92.954	14.047	15.304	0.85640



Compound 3s: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 42 mg, 76% yield, 10:1 *dr*, 89:11 *er*, $[\alpha]_D^{20} = -141.5$ (*c* = 0.26, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 4H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.14 (m, 3H), 6.93 (m, 2H), 6.42 (d, *J* = 2.4 Hz, 1H), 6.32 (d, *J* = 2.4 Hz, 1H), 5.97 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.28 (d, *J* = 11.2 Hz, 1H), 5.17 (d, *J* = 17.6 Hz, 1H), 3.66 (dd, *J* = 12.6, 8.8 Hz, 1H), 3.27 (dd, *J* = 19.8, 12.6 Hz, 1H), 3.12 (dd, *J* = 19.8, 8.8 Hz, 1H), 1.10 (s, 9H), 1.08 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.9, 185.6, 148.9, 148.7, 141.5, 140.8, 140.2, 138.8, 137.4, 136.6, 135.0, 130.1, 129.1, 128.6, 127.9, 127.7, 127.6, 127.2, 126.9, 118.8, 69.7, 56.0, 47.7, 41.4, 35.4, 35.2, 29.3, 29.0. **IR** ν_{max}/cm^{-1} 2955, 2912, 2866, 1742, 1658, 1636, 1454, 1368, 1249, 1178, 1113. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{38}H_{41}O_2]^+$: 529.3101, found: 529.3096.

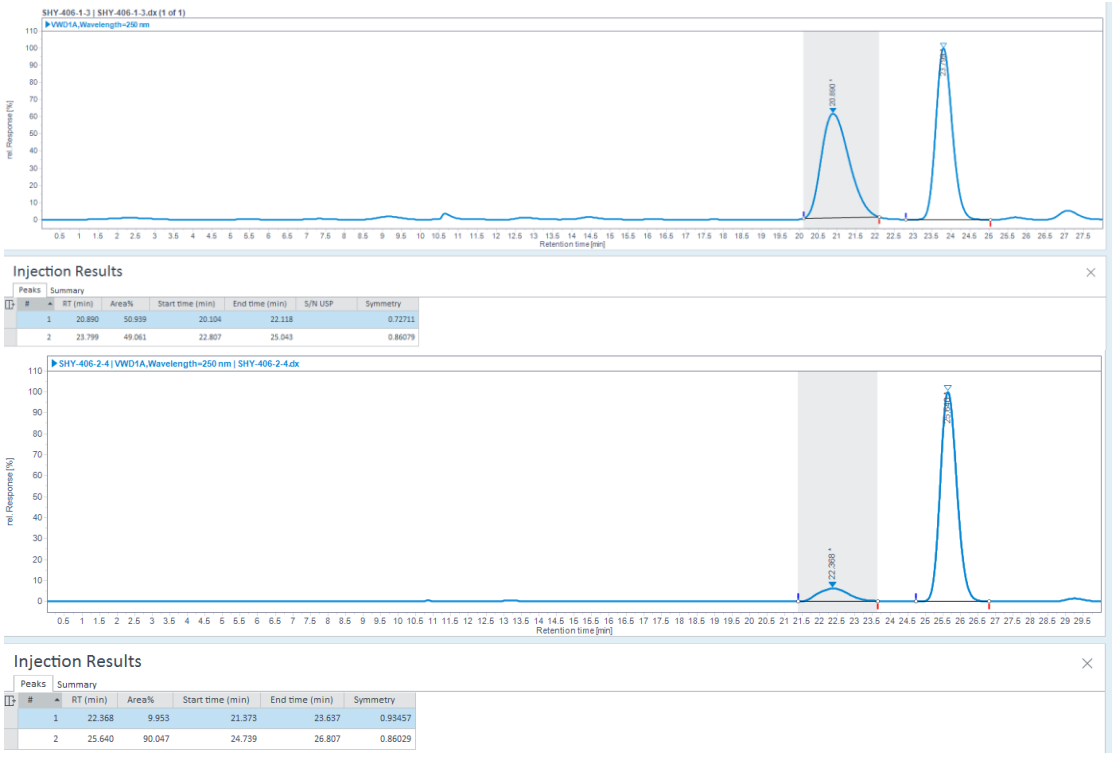
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 15.55 min (minor) and 26.06 min (major).

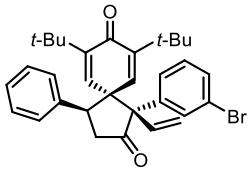




Compound 3t: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 41 mg, 74% yield, 15:1 *dr*, 90:10 *er*, $[\alpha]_D^{20} = -166.8$ (*c* = 0.24, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.50 (s, 1H), 7.27 - 7.13 (m, 6H), 6.89 (d, *J* = 4.4 Hz, 2H), 6.46 (s, 1H), 6.34 (s, 1H), 5.99 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.29 (d, *J* = 11.2 Hz, 1H), 5.14 (d, *J* = 17.6 Hz, 1H), 3.95 (s, 3H), 3.70 - 3.58 (m, 1H), 3.29 (dd, *J* = 19.8, 12.4 Hz, 1H), 3.18 (dd, *J* = 19.8, 8.8 Hz, 1H), 1.09 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.0, 185.7, 158.6, 148.9, 148.7, 141.7, 138.7, 136.8, 135.1, 133.9, 133.3, 129.8, 128.7, 128.6, 128.3, 127.9, 127.7, 127.5, 126.5, 119.6, 119.3, 105.7, 70.4, 56.2, 55.5, 47.7, 41.4, 35.33, 35.25, 29.3, 29.1. **IR** ν_{max}/cm^{-1} 2954, 2908, 2865, 1738, 1657, 1633, 1601, 1482, 1454, 1243, 1221, 1164, 1032. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{37}H_{41}O_3]^+$: 533.3050, found: 533.3054.

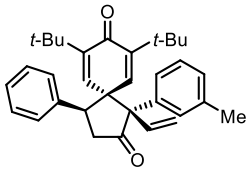
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 22.37 min (minor) and 25.64 min (major).





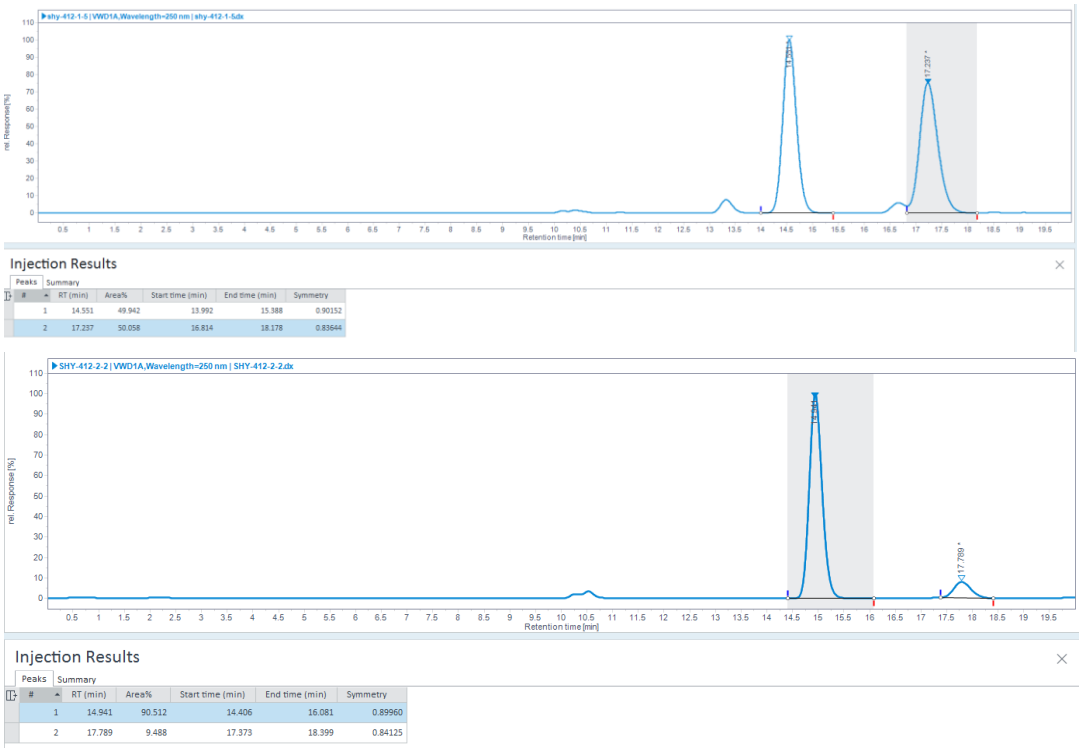
Compound 3u: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 40 mg, 68% yield, *dr* >20:1, 95:5 *er*, $[\alpha]_D^{20}$ = -119.2 (*c* = 0.12, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.32-7.26 (m, 2H), 7.19 - 7.12 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.96 - 6.83 (m, 2H), 6.38 (d, *J* = 2.8 Hz, 1H), 6.20 (d, *J* = 2.8 Hz, 1H), 5.90 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.28 (d, *J* = 11.2 Hz, 1H), 5.15 (d, *J* = 17.6 Hz, 1H), 3.56 (dd, *J* = 12.6, 8.6 Hz, 1H), 3.26 (dd, *J* = 19.8, 12.6 Hz, 1H), 3.08 (dd, *J* = 19.8, 8.6 Hz, 1H), 1.11 (s, 9H), 1.06 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.2, 185.5, 149.1, 149.0, 141.0, 138.2, 136.2, 134.8, 133.1, 131.2, 129.8, 128.5, 127.84, 127.81, 127.6, 122.6, 119.4, 69.4, 55.7, 47.6, 41.3, 35.4, 35.3, 29.3, 29.0. **IR** ν_{max}/cm^{-1} 2955, 2919, 2865, 1743, 1658, 1637, 1454, 1367, 1250, 698. **HRMS** (ESI): *m/z* $[M+Na]^+$ calculated for $[C_{32}H_{35}BrO_2Na]^+$: 553.1713, found: 553.1721.

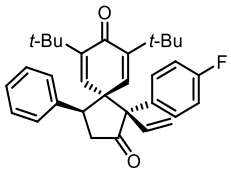
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 20.48 min (minor) and 15.10 min (major).



Compound 3v: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 40 mg, 84% yield, 14:1 *dr* , 90.5:9.5 *er*, $[\alpha]_D^{20} = -111.2$ (*c* = 0.25, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 - 7.26 (m, 1H), 7.17 -7.14 (m, 4H), 6.97 - 6.91 (m, 4H), 6.40 (s, 1H), 6.27 (s, 1H), 5.93 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.24 (d, *J* = 11.2 Hz, 1H), 5.13 (d, *J* = 17.6 Hz, 1H), 3.65 - 3.55 (m, 1H), 3.24 (dd, *J* = 19.6, 12.6 Hz, 1H), 3.08 (dd, *J* = 19.6, 8.6 Hz, 1H), 2.38 (s, 3H), 1.09 (s, 9H), 1.06 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.1, 185.6, 148.64, 148.55, 141.8, 138.9, 138.3, 138.0, 136.7, 135.1, 130.5, 128.8, 128.6, 128.2, 127.7, 127.6, 126.6, 118.5, 69.9, 55.8, 47.6, 41.5, 35.3, 35.2, 29.3, 29.0, 21.8. **IR** ν_{max}/cm^{-1} 2955, 2919, 2865, 1743, 1658, 1637, 1454, 1367, 1250, 698. **HRMS** (ESI): *m/z* $[M+K]^+$ calculated for $[C_{33}H_{38}O_2K]^+$: 505.2503, found: 505.2502.

The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 ^oC; 250 nm; retention time: 17.79 min (minor) and 14.94 min (major).

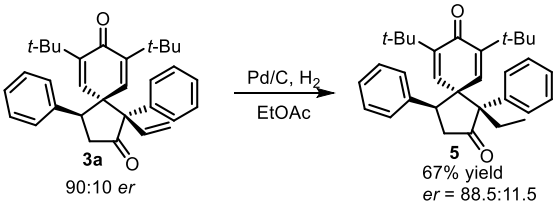




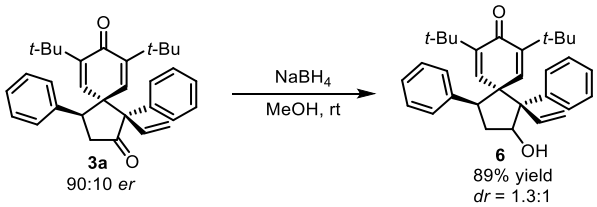
Compound 3w: purified by column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid, 35 mg, 69% yield, 11:1 *dr*, 93:7 *er*, $[\alpha]_D^{20} = -134.4$ (*c* = 0.28, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 - 7.08 (m, 7H), 6.90 (d, *J* = 4.4 Hz, 2H), 6.39 (d, *J* = 2.4 Hz, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 5.92 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 5.11 (d, *J* = 17.6 Hz, 1H), 3.56 (dd, *J* = 12.6, 8.6 Hz, 1H), 3.25 (dd, *J* = 19.6, 12.6 Hz, 1H), 3.07 (dd, *J* = 19.6, 8.6 Hz, 1H), 1.08 (s, 9H), 1.06 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.49 (s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.7, 185.5, 162.1 (d, J_{CF} = 248 Hz), 149.02, 148.8, 141.1, 138.6, 136.7, 134.8, 134.3 (d, J_{CF} = 4 Hz), 131.4 (d, J_{CF} = 8 Hz), 128.6, 127.8, 127.6, 119.0, 115.4 (d, *J* = 22 Hz), 69.2, 55.8, 47.6, 41.3, 35.3, 35.2, 29.3, 29.0. **IR** ν_{max}/cm^{-1} 2954, 2921, 2865, 1745, 1633, 1507, 1366, 1229, 1170, 928. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{32}H_{36}FO_2]^+$: 471.2694, found: 471.2692.

The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.2 mL/min; 35 ^oC; 250 nm; retention time: 22.40 min (minor) and 24.16 min (major).

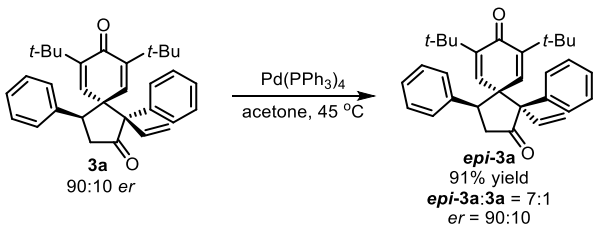
6. Synthetic Transformations and Gram-Scale Synthesis of Product 3a.



To a solution of product **3a** (45 mg, 0.1 mmol, 1.0 eq) in EtOAc (2 mL) was carefully added Pd/C (4.5 mg, 10%). The reaction mixture was degassed and purged with hydrogen. The reaction was allowed to stir for 4h at room temperature. After the completion of the reaction, the mixture was filtered through a celite pad and washed with EtOAc. The solvents were removed and concentrated under reduced pressure and purified by column chromatography to afford the desired product **5** as a colorless oil (67 % yield, *er* = 88.5:11.5).

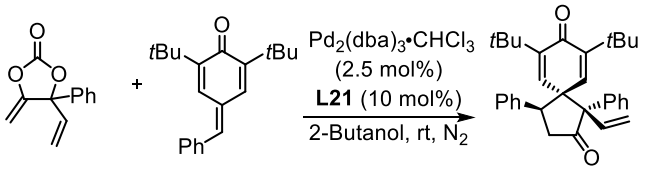


To a well-stirred solution of product **3a** (45 mg, 0.1 mmol, 1.0 eq) in MeOH (2 mL) was added $NaBH_4$ (14.8 mg, 0.5 mmol, 4.0 eq.). The reaction mixture was stirred for 2h at room temperature. After the completion of the reaction (monitored by TLC), water (2 mL) was added. The mixture was extracted with ethyl acetate (3 × 2 mL). The combined organic layers were washed with brine, dried over Na_2SO_4. After concentration in vacuo, the resulting residue was purified by column chromatography to give the corresponding alcohol **6** (89% yield, *dr* = 1.3:1, 69:31 *er* (major); 58.5:41.5 *er* (mino)).

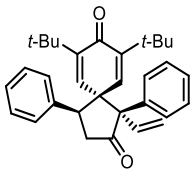


To a solution of product **3a** (45 mg, 0.1 mmol, 1.0 eq) in acetone (2 mL) was added $Pd(PPh_3)_4$ (5.8 mg, 5 mol%) under N_2. The reaction was allowed to stir for 20 h at 45

^{o}C. After the completion of the reaction, the solvents were removed and concentrated under reduced pressure, and then purified by column chromatography to afford the desired product ***epi*-3a** as a yellow solid (91 % yield, ***epi*-3a**:**3a** = 7:1, *er* = 90:10).

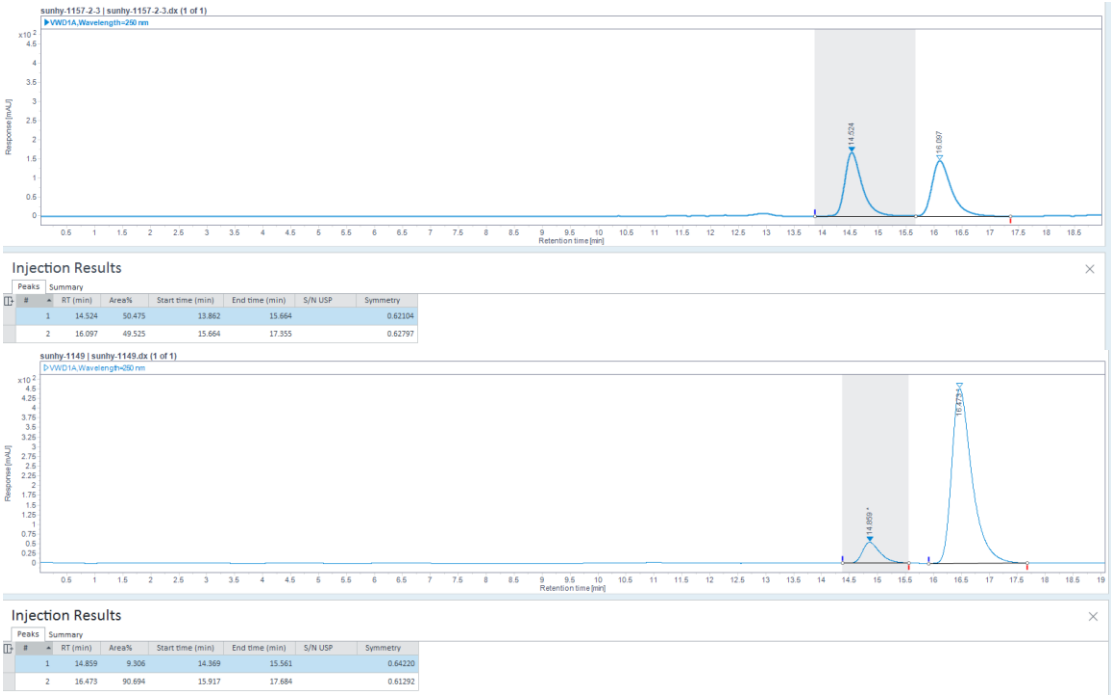


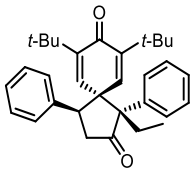
In the glovebox, to a round-bottomed flask with a dried stir bar was added $Pd_2(dba)_3 \cdot CHCl_3$ (0.13g, 0.12 mmol), ligand **L21** (0.25g, 0.5 mmol), anhydrous 2-Butanol (5 mL). The reaction mixture was then allowed to stir for 1 h at room temperature, followed by the addition of cyclic carbonate **1a** (1.00 g, 4.95 mmol) and *para*-quinone methide **2a** (2.2 g, 7.43 mmol). Then, the reaction mixture was allowed to stir at room temperature until the starting material disappeared (monitored by TLC) in the glovebox. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel (chromatography petroleum ether/ethyl acetate = 50:1) to give **3a** (1.70 g, 3.76 mmol, 76%, >20:1 *dr*, 90:10 *er*) as a yellow solid. The *dr* value was determined by ^{1}H NMR spectrum of the crude reaction mixture. The enantiopurity of the product was analyzed by HPLC.



Compound *epi*-3a: yellow solid, $[\alpha]_D^{20} = -86.2$ (c = 0.33, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 - 7.12 (m, 8H), 7.03 - 7.01 (m, 3H), 6.57 (dd, J = 17.2, 10.8 Hz, 1H), 6.15 (s, 1H), 5.52 (d, J = 10.8 Hz, 1H), 5.19 (d, J = 17.2 Hz, 1H), 3.91 (dd, J = 12.4, 8.8 Hz, 1H), 3.21 (dd, J = 19.6, 12.4 Hz, 1H), 3.09 (dd, J = 19.6, 8.6 Hz, 1H), 1.23 (s, 9H), 0.69 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.3, 185.1, 151.0, 147.8, 139.1, 138.4, 138.1, 135.7, 135.3, 128.2, 127.9, 127.73, 127.70, 127.34, 127.25, 120.7, 70.7, 57.0, 47.0, 40.8, 35.4, 34.6, 29.4, 28.5. **IR** ν_{max}/cm^{-1} 2954, 2911, 2865, 1737, 1659, 1636, 1454, 1358, 1251, 1112, 930. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{32}H_{37}O_2]^+$: 453.2794, found:453.2794.

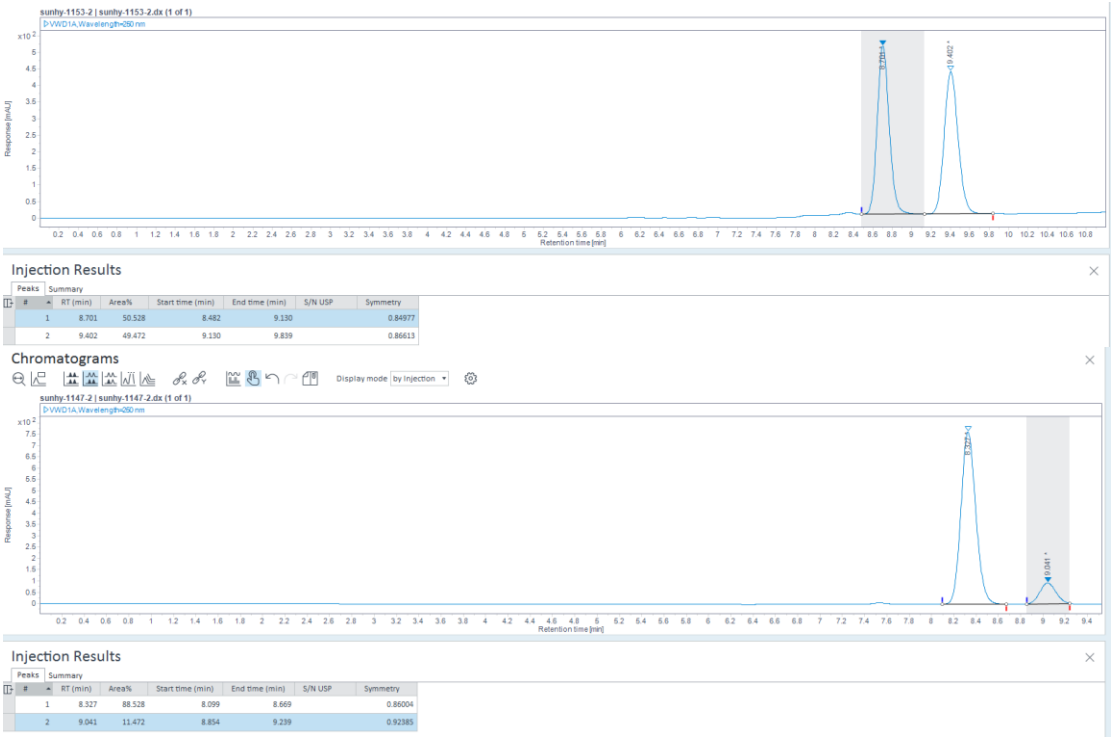
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 ^{o}C; 250 nm; retention time: 14.85 min (minor) and 16.47 min (major).

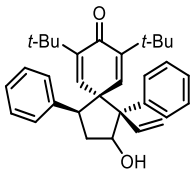




Compound 5: colorless oil; $[\alpha]_D^{20} = -171.1$ (*c* = 0.09, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 - 7.34 (m, 3H), 7.13 - 7.06 (m, 5H), 6.98 - 6.90 (m, 2H), 6.44 (s, 1H), 6.21 (s, 1H), 3.56 (dd, *J* = 12.0, 8.8 Hz, 1H), 3.20 (dd, *J* = 19.6, 12.0 Hz, 1H), 3.09 (dd, *J* = 19.6, 8.8 Hz, 1H), 1.73 – 1.71 (m, 1H), 1.49 – 1.43 (m, 1H), 1.12 (s, 9H), 1.08 (s, 9H), 0.79 (t, *J* = 7.2 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.7, 186.1, 148.8, 148.7, 141.7, 137.8, 136.7, 136.0, 129.4, 128.3, 128.0, 127.8, 127.6, 67.9, 56.8, 47.6, 35.4, 35.3, 29.3, 29.2, 27.0, 9.6.; **IR** ν_{max}/cm^{-1} 2954, 2922, 2863, 1739, 1658, 1636, 1454, 1357, 1275, 1259, 764, 749, 698. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{32}H_{39}O_2]^+$: 455.2950, found:455.2951.

The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.5 mL/min; 35 ^{o}C; 250 nm; retention time: 9.04 min (minor) and 8.32 min (major).





Compound 6: white solid; $[\alpha]_D^{20} = -134.5$ (c = 0.29, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) (major diastereomer) δ 7.38 – 6.97 (m, 10H), 6.86 (s, 1H), 6.29 (dd, J = 17.6, 11.2 Hz, 1H), 6.00 (s, 1H), 5.26 (d, J = 11.2 Hz, 1H), 5.04 – 4.99 (m, 1H), 4.84 (d, J = 17.6 Hz, 1H), 3.45 (dd, J = 11.2, 9.2 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.71 – 2.65 (m, 1H), 0.99 (s, 9H), 0.95 (s, 9H).; **^{1}H NMR** (400 MHz, $CDCl_3$) (minor diastereomer) δ 7.38 – 6.97 (m, 10H), 6.49 (s, 1H), 6.18 (s,1H), 6.11 (dd, J = 17.2, 10.8 Hz, 1H), 5.14 (d, J = 10.8 Hz, 1H), 5.17 – 5.10 (m, 1H), 4.99 (d, J = 17.2 Hz, 1H), 3.90 (t, J = 10.0 Hz, 1H), 3.18 – 3.10 (m, 1H), 2.60 – 2.54 (m, 1H), 1.04 (s, 9H), 0.97 (s, 9H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.3, 186.2, 147.2, 147.0, 146.6, 145.3, 145.2, 145.1, 142.7, 142.2, 141.5, 141.3, 140.0, 139.3, 138.4, 138.3, 130.2, 129.1, 128.3, 128.2, 128.0, 127.9, 127.8, 127.3, 127.23, 127.17, 127.1, 121.4, 115.1, 78.1, 76.0, 66.1, 65.3, 57.2, 55.3, 51.6, 50.7, 37.8, 37.6, 35.1, 35.0, 34.9, 34.6, 29.3, 29.24, 29.16, 29.08. **IR** ν_{max}/cm^{-1} 3498, 3462, 2951, 2920, 1616, 1454, 1367, 1262, 1104, 908, 879, 755, 696. **HRMS** (ESI): *m/z* $[M+H]^+$ calculated for $[C_{32}H_{39}O_2]^+$: 455.2950, found: 455.2955.

The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.5 mL/min; 35 ^{o}C; 250 nm; retention time: 16.76 min, 24.28 min (minor) and 13.56, 15.23 min (major).

7. Methods for the Crystallization of Products 3a and *epi*-3a.

Method for the crystallization of 3a: Suitable crystals were obtained by slowly evaporation of a clear solution of **3a** in a mixture of petroleum ether and ethyl acetate at ambient temperature.

Method for the crystallization of *epi*-3a: Suitable crystals were obtained by slowly evaporation of a solution of compound ***epi*-3a** in a mixture of dichloromethane and petroleum ether at ambient temperature.

8. Crystal Data of 3a.

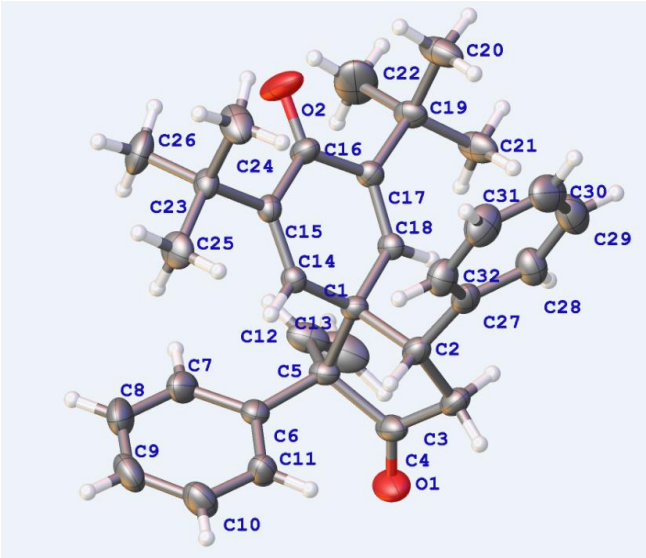


Table 1 Crystal data and structure refinement for 3a.

Identification code	pqm
Empirical formula	$C_{32}H_{36}O_2$
Formula weight	452.61
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.42205(16)
b/Å	10.89247(16)
c/Å	12.9779(2)
α/°	90
β/°	94.5745(14)
γ/°	90
Volume/Å^3	1327.67(4)
Z	2
ρ_{calc}g/cm^3	1.132
μ/mm^{-1}	0.529
F(000)	488.0

Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.832 to 147.53
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	10014
Independent reflections	4960 [R_{int} = 0.0207, R_{sigma} = 0.0220]
Data/restraints/parameters	4960/1/322
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0318, wR_2 = 0.0860
Final R indexes [all data]	R_1 = 0.0323, wR_2 = 0.0866
Largest diff. peak/hole / e Å^{-3}	0.20/-0.14
Flack/Hooft parameter	0.02(10)/0.06(9)

Crystal structure determination of 3a

Crystal Data for $C_{32}H_{36}O_2$ (*M* =452.61 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 9.42205(16) Å, *b* = 10.89247(16) Å, *c* = 12.9779(2) Å, *β* = 94.5745(14) °, *V* = 1327.67(4) Å^3, *Z* = 2, *T* = 149.99(10) K, μ(Cu Kα) = 0.529 mm^{-1}, *Dcalc* = 1.132 g/cm^3, 10014 reflections measured (6.832° ≤ 2Θ ≤ 147.53°), 4960 unique (R_{int} = 0.0207, R_{sigma} = 0.0220) which were used in all calculations. The final R_1 was 0.0318 (I > 2σ(I)) and wR_2 was 0.0866 (all data).

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	3130(2)	1328.1(13)	4139.9(13)	54.4(4)
O2	2344(2)	6958.7(15)	740.1(12)	64.8(5)
C1	3608.7(17)	4279.0(14)	2885.7(12)	24.6(3)
C2	5129.7(19)	3854.2(16)	3352.7(13)	29.6(3)
C3	5005(2)	2456.5(17)	3396.4(14)	35.0(4)
C4	3521(2)	2232.5(16)	3706.8(14)	35.3(4)
C5	2555.0(18)	3353.4(15)	3427.1(13)	28.2(3)
C6	2034.5(18)	3920.4(15)	4408.0(13)	28.5(3)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C7	781(2)	4602(2)	4380.9(16)	42.3(4)
C8	406(2)	5241(2)	5241(2)	52.6(6)
C9	1273(3)	5214(2)	6148.9(18)	49.9(5)
C10	2496(2)	4523(2)	6201.1(16)	46.7(5)
C11	2871(2)	3877(2)	5344.0(14)	38.4(4)
C12	1326(2)	3016(2)	2659.4(15)	42.4(5)
C13	1007(4)	1930(3)	2273(2)	64.9(8)
C14	3350.5(16)	5582.2(14)	3158.7(12)	23.7(3)
C15	2960.3(16)	6475.5(14)	2494.1(12)	24.2(3)
C16	2765.2(19)	6176.1(15)	1371.8(13)	31.6(4)
C17	3112.3(17)	4912.8(14)	1032.3(12)	25.9(3)
C18	3487.3(16)	4070.5(14)	1747.0(12)	24.4(3)
C19	3010(2)	4618.8(16)	-126.1(13)	32.5(4)
C20	4011(3)	5467(2)	-675.7(16)	51.8(6)
C21	3468(3)	3302.5(18)	-333.3(14)	44.3(5)
C22	1467(3)	4766(3)	-573.3(18)	66.0(8)
C23	2721.1(17)	7801.2(14)	2841.6(13)	28.5(3)
C24	3755(3)	8656.3(18)	2343.5(19)	49.3(5)
C25	2987(2)	7929.8(17)	4015.0(15)	40.9(4)
C26	1178(2)	8187(2)	2545(2)	48.3(5)
C27	6324.8(17)	4391.6(17)	2792.7(13)	32.0(4)
C28	6860(2)	3830(2)	1944.2(16)	42.1(4)
C29	7896(2)	4404(3)	1404.4(18)	51.3(5)
C30	8412(2)	5541(3)	1709.9(19)	53.4(6)
C31	7904(2)	6101(2)	2558(2)	51.3(6)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C32	6874.8(19)	5530.8(19)	3097.0(16)	39.3(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	78.1(11)	30.5(7)	57.8(10)	13.2(7)	25.9(8)	6.8(7)
O2	119.0(15)	43.0(9)	30.2(7)	4.4(6)	-7.0(8)	38.1(9)
C1	30.2(7)	22.6(7)	20.7(7)	0.6(6)	0.6(5)	1.4(6)
C2	34.7(8)	28.6(8)	24.8(8)	-1.1(6)	-1.8(6)	6.0(6)
C3	43.3(9)	30.1(9)	31.0(8)	3.4(7)	0.4(7)	11.2(7)
C4	54.0(11)	25.8(8)	26.9(8)	1.7(7)	8.4(7)	3.9(7)
C5	35.8(8)	25.2(7)	23.6(8)	2.6(6)	2.9(6)	-1.8(6)
C6	31.2(8)	28.1(8)	26.7(8)	4.8(6)	6.5(6)	0.3(6)
C7	31.9(9)	54.9(11)	40.9(10)	10.8(9)	7.4(7)	7.7(8)
C8	43.5(11)	59.3(14)	58.3(14)	8.1(11)	24.4(9)	17.6(10)
C9	56.6(13)	51.9(12)	44.7(12)	-4.4(9)	26.9(10)	2.6(10)
C10	49.2(11)	61.2(13)	30.6(10)	-4.4(9)	8.4(8)	2.0(10)
C11	37.1(9)	49.2(11)	28.8(9)	0.2(8)	2.8(7)	11.1(8)
C12	45.4(10)	49.2(11)	31.9(9)	4.2(8)	-1.8(7)	-17.2(9)
C13	79.1(18)	63.4(16)	51.4(14)	-4.3(12)	0.4(13)	-38.5(14)
C14	25.6(7)	24.8(7)	20.6(7)	-3.4(6)	2.1(5)	-0.2(6)
C15	24.1(7)	22.6(7)	26.3(8)	-2.2(6)	4.7(5)	0.5(6)
C16	41.5(9)	27.9(8)	24.8(8)	1.4(7)	-0.6(7)	8.5(7)
C17	29.0(8)	27.7(8)	20.7(7)	-2.1(6)	0.1(6)	0.4(6)
C18	29.6(7)	21.4(7)	22.1(7)	-3.8(6)	1.8(6)	-0.1(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C19	44.5(10)	33.4(9)	19.1(8)	-2.2(7)	-1.3(6)	-0.5(7)
C20	89.0(17)	40.1(11)	28.2(10)	-0.6(8)	16.1(10)	-10.0(11)
C21	74.4(14)	34.6(9)	24.2(9)	-7.5(8)	7.0(8)	-5.6(9)
C22	58.1(14)	101(2)	35.0(11)	-11.7(13)	-19.4(10)	13.3(14)
C23	29.9(8)	21.6(7)	34.7(9)	-3.2(6)	6.8(6)	1.6(6)
C24	59.3(13)	28.4(9)	63.8(14)	-2.7(9)	26.4(11)	-6.8(8)
C25	53.7(11)	29.9(9)	39.6(10)	-12.7(8)	7.3(8)	-0.5(8)
C26	40.3(10)	39.4(11)	64.9(14)	-9.7(10)	1.0(9)	16.3(8)
C27	28.7(8)	37.1(9)	29.3(8)	0.2(7)	-3.4(6)	6.9(7)
C28	38.4(9)	50.3(11)	37.8(10)	-8.6(9)	5.0(8)	2.1(8)
C29	37.9(10)	72.8(15)	44.0(11)	-2.0(11)	8.5(8)	4.5(10)
C30	30.9(10)	70.1(15)	59.8(14)	15.8(12)	7.2(9)	1.5(10)
C31	34.0(10)	47.3(12)	72.0(16)	0.8(11)	0.2(9)	-2.5(8)
C32	31.4(9)	40.1(9)	45.7(11)	-5.3(8)	-1.7(7)	2.8(7)

Table 4 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C4	1.206(2)	C14	C15	1.332(2)
O2	C16	1.227(2)	C15	C16	1.490(2)
C1	C2	1.580(2)	C15	C23	1.535(2)
C1	C5	1.615(2)	C16	C17	1.489(2)
C1	C14	1.488(2)	C17	C18	1.332(2)
C1	C18	1.491(2)	C17	C19	1.533(2)
C2	C3	1.528(2)	C19	C20	1.536(3)
C2	C27	1.506(3)	C19	C21	1.527(3)

Table 4 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C3	C4	1.505(3)	C19	C22	1.531(3)
C4	C5	1.549(2)	C23	C24	1.528(2)
C5	C6	1.530(2)	C23	C25	1.530(3)
C5	C12	1.512(2)	C23	C26	1.533(2)
C6	C7	1.393(2)	C27	C28	1.389(3)
C6	C11	1.395(2)	C27	C32	1.390(3)
C7	C8	1.386(3)	C28	C29	1.394(3)
C8	C9	1.379(4)	C29	C30	1.377(4)
C9	C10	1.373(3)	C30	C31	1.378(4)
C10	C11	1.386(3)	C31	C32	1.387(3)
C12	C13	1.310(3)			

Table 5 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C5	102.75(12)	C14	C15	C23	122.43(14)
C14	C1	C2	110.40(13)	C16	C15	C23	118.93(14)
C14	C1	C5	111.98(13)	O2	C16	C15	120.63(15)
C14	C1	C18	112.36(13)	O2	C16	C17	120.76(16)
C18	C1	C2	109.34(13)	C17	C16	C15	118.61(14)
C18	C1	C5	109.58(12)	C16	C17	C19	119.03(14)
C3	C2	C1	103.63(14)	C18	C17	C16	118.86(14)
C27	C2	C1	113.02(13)	C18	C17	C19	122.11(14)
C27	C2	C3	117.89(15)	C17	C18	C1	125.49(14)
C4	C3	C2	104.32(15)	C17	C19	C20	109.70(14)
O1	C4	C3	125.56(18)	C21	C19	C17	111.86(14)
O1	C4	C5	123.89(18)	C21	C19	C20	106.91(16)

Table 5 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	C4	C5	110.52(15)	C21	C19	C22	107.75(19)
C4	C5	C1	102.95(13)	C22	C19	C17	109.47(16)
C6	C5	C1	111.03(13)	C22	C19	C20	111.14(19)
C6	C5	C4	110.15(13)	C24	C23	C15	109.62(13)
C12	C5	C1	109.30(13)	C24	C23	C25	107.81(16)
C12	C5	C4	111.58(16)	C24	C23	C26	110.51(17)
C12	C5	C6	111.53(15)	C25	C23	C15	111.25(14)
C7	C6	C5	121.42(16)	C25	C23	C26	107.58(15)
C7	C6	C11	117.32(17)	C26	C23	C15	110.04(14)
C11	C6	C5	120.96(15)	C28	C27	C2	122.98(17)
C8	C7	C6	121.17(19)	C28	C27	C32	117.86(18)
C9	C8	C7	120.4(2)	C32	C27	C2	119.08(16)
C10	C9	C8	119.4(2)	C27	C28	C29	121.0(2)
C9	C10	C11	120.4(2)	C30	C29	C28	120.2(2)
C10	C11	C6	121.29(18)	C29	C30	C31	119.4(2)
C13	C12	C5	127.8(2)	C30	C31	C32	120.4(2)
C15	C14	C1	125.77(14)	C31	C32	C27	121.10(19)
C14	C15	C16	118.64(14)				

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C4	C5	C1	179.27(18)	C11	C6	C7	C8	2.0(3)
O1	C4	C5	C6	60.8(2)	C12	C5	C6	C7	-30.8(2)
O1	C4	C5	C12	-63.6(2)	C12	C5	C6	C11	155.66(18)
O2	C16	C17	C18	-176.2(2)	C14	C1	C2	C3	158.05(14)
O2	C16	C17	C19	3.1(3)	C14	C1	C2	C27	-73.19(17)

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-38.06(18)	C14	C1	C5	C4	-142.48(14)
C1	C2	C27	C28	-89.1(2)	C14	C1	C5	C6	-24.63(18)
C1	C2	C27	C32	87.41(18)	C14	C1	C5	C12	98.82(17)
C1	C5	C6	C7	91.36(19)	C14	C1	C18	C17	-3.7(2)
C1	C5	C6	C11	-82.18(19)	C14	C15	C16	O2	176.65(19)
C1	C5	C12	C13	115.8(2)	C14	C15	C16	C17	-4.2(2)
C1	C14	C15	C16	-0.4(2)	C14	C15	C23	C24	119.11(18)
C1	C14	C15	C23	-179.76(14)	C14	C15	C23	C25	0.0(2)
C2	C1	C5	C4	-24.01(15)	C14	C15	C23	C26	-119.16(19)
C2	C1	C5	C6	93.84(15)	C15	C16	C17	C18	4.7(2)
C2	C1	C5	C12	-142.71(15)	C15	C16	C17	C19	-175.99(15)
C2	C1	C14	C15	126.60(17)	C16	C15	C23	C24	-60.2(2)
C2	C1	C18	C17	-126.64(17)	C16	C15	C23	C25	-179.35(15)
C2	C3	C4	O1	-155.0(2)	C16	C15	C23	C26	61.5(2)
C2	C3	C4	C5	23.0(2)	C16	C17	C18	C1	-0.6(2)
C2	C27	C28	C29	175.32(18)	C16	C17	C19	C20	58.9(2)
C2	C27	C32	C31	-175.37(18)	C16	C17	C19	C21	177.38(16)
C3	C2	C27	C28	31.9(2)	C16	C17	C19	C22	-63.3(2)
C3	C2	C27	C32	-151.61(17)	C18	C1	C2	C3	-77.84(16)
C3	C4	C5	C1	1.22(18)	C18	C1	C2	C27	50.91(18)
C3	C4	C5	C6	-117.24(16)	C18	C1	C5	C4	92.15(15)
C3	C4	C5	C12	118.33(17)	C18	C1	C5	C6	-150.01(13)
C4	C5	C6	C7	-155.26(17)	C18	C1	C5	C12	-26.56(19)
C4	C5	C6	C11	31.2(2)	C18	C1	C14	C15	4.2(2)
C4	C5	C12	C13	2.6(3)	C18	C17	C19	C20	-121.80(19)
C5	C1	C2	C3	38.48(16)	C18	C17	C19	C21	-3.3(2)

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C5	C1	C2	C27	167.24(13)	C18	C17	C19	C22	116.0(2)
C5	C1	C14	C15	-119.58(16)	C19	C17	C18	C1	-179.86(15)
C5	C1	C18	C17	121.46(17)	C23	C15	C16	O2	-4.0(3)
C5	C6	C7	C8	-171.75(18)	C23	C15	C16	C17	175.12(14)
C5	C6	C11	C10	171.46(18)	C27	C2	C3	C4	-163.76(14)
C6	C5	C12	C13	-121.0(2)	C27	C28	C29	C30	0.3(3)
C6	C7	C8	C9	-0.1(3)	C28	C27	C32	C31	1.3(3)
C7	C6	C11	C10	-2.3(3)	C28	C29	C30	C31	0.5(3)
C7	C8	C9	C10	-1.6(4)	C29	C30	C31	C32	-0.5(3)
C8	C9	C10	C11	1.2(3)	C30	C31	C32	C27	-0.5(3)
C9	C10	C11	C6	0.7(3)	C32	C27	C28	C29	-1.2(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	*x*	*y*	*z*	U(eq)
H2	5246.71	4150.81	4067.36	36
H3A	5130.96	2094.3	2726.98	42
H3B	5709.22	2114.87	3902.49	42
H7	184.75	4627.47	3774.61	51
H8	-434.84	5691.87	5206.78	63
H9	1031.76	5659.81	6720.69	60
H10	3075.15	4488.39	6815.05	56
H11	3696.31	3405.61	5393.66	46
H12	724.08	3655.03	2434.6	51
H13A	180(40)	1830(40)	1710(30)	89(11)
H13B	1620(50)	1150(50)	2510(40)	113(15)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	*x*	*y*	*z*	U(eq)
H14	3472.23	5791.89	3854.83	28
H18	3690.4	3286.5	1516.03	29
H20A	3710.19	6303.88	-609.29	78
H20B	3981.64	5252.14	-1394.41	78
H20C	4965.04	5376.61	-367.03	78
H21A	4434.54	3184.04	-57.48	66
H21B	3399.82	3155.22	-1064.94	66
H21C	2858.47	2740.85	-7.84	66
H22B	1171.66	5602.11	-494.57	99
H22A	863.27	4233.68	-212.05	99
H22C	1396.66	4554.5	-1293.66	99
H24A	4707.59	8349.52	2471.74	74
H24B	3695.74	9463.48	2634.04	74
H24C	3510.26	8693.22	1611.76	74
H25A	2337.25	7411.74	4347.2	61
H25B	2844.29	8768.4	4209.37	61
H25C	3947.57	7689.95	4224.74	61
H26A	1012.53	8210.25	1805.51	73
H26B	1012.5	8986.49	2822.71	73
H26C	541.89	7605.98	2820.34	73
H28	6522.84	3060.9	1733.3	50
H29	8240.22	4017.33	835.83	62
H30	9097.52	5927.48	1346.68	64
H31	8253.44	6866.34	2771.12	62
H32	6547.18	5917.14	3671.44	47

9. Crystal Data of *epi*-3a.

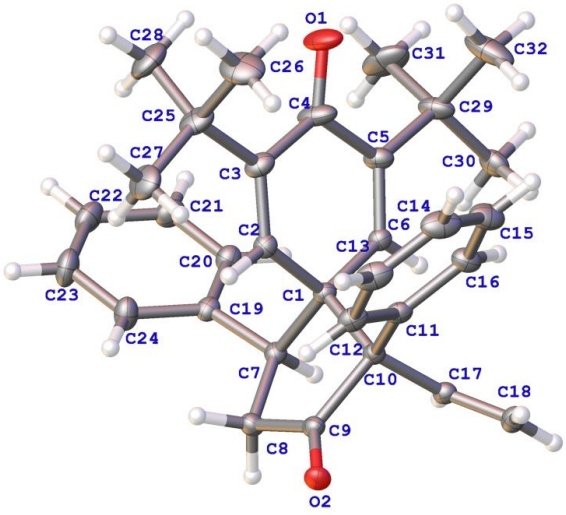


Table 1 Crystal data and structure refinement for *epi*-3a.

Identification code	SHY-11
Empirical formula	$C_{32}H_{36}O_2$
Formula weight	452.61
Temperature/K	149.99(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.38580(10)
b/Å	10.82370(10)
c/Å	26.4399(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2686.01(5)
Z	4
ρ_{calc}g/cm^3	1.119
μ/mm^{-1}	0.522
F(000)	976.0

Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.686 to 143.474
Index ranges	-10 ≤ h ≤ 11, -10 ≤ k ≤ 13, -30 ≤ l ≤ 32
Reflections collected	15182
Independent reflections	5140 [R_{int} = 0.0198, R_{sigma} = 0.0200]
Data/restraints/parameters	5140/6/333
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0361, wR_2 = 0.0937
Final R indexes [all data]	R_1 = 0.0369, wR_2 = 0.0944
Largest diff. peak/hole / e Å^{-3}	0.16/-0.21
Flack/Hooft parameter	0.02(7)/0.02(7)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for *epi*-3a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7179(12)	5111(7)	4817.5(16)	70.7(18)
O1B	7790(20)	4740(30)	4739(7)	86(6)
O2	5945.1(14)	7132.9(12)	2185.1(5)	38.2(3)
C1	6313.5(18)	5195.8(15)	3282.4(6)	27.4(3)
C2	7532.7(19)	5875.0(15)	3510.4(7)	30.8(4)
C3	7898(2)	5846.0(18)	3996.0(7)	40.0(4)
C4	7028(3)	5089(2)	4351.9(8)	57.2(6)
C5	5786(2)	4382.6(17)	4147.6(7)	37.4(4)
C6	5497.9(18)	4465.5(15)	3657.5(6)	28.8(3)
C7	6896.4(18)	4329.8(16)	2842.6(6)	28.9(3)
C8	7126(2)	5216.4(17)	2399.0(6)	33.9(4)
C9	6128.0(18)	6290.3(17)	2477.8(6)	30.1(4)
C10	5327.4(17)	6141.0(15)	2988.7(6)	27.7(3)

C11	5113(2)	7321.0(15)	3289.7(6)	31.9(4)
C12	5951(2)	8368.7(17)	3215.2(7)	38.9(4)
C13	5800(3)	9395.3(19)	3522.1(9)	53.1(6)
C14	4824(3)	9399(2)	3913.7(9)	58.9(6)
C15	3998(3)	8367(2)	3995.6(8)	53.3(6)
C16	4136(2)	7333.8(18)	3688.7(7)	40.7(4)
C17	3942.0(18)	5533.9(16)	2821.9(6)	30.3(4)
C18	2721(2)	6108.0(18)	2751.9(7)	38.0(4)
C19	8153.1(18)	3559.6(16)	3018.0(7)	31.9(4)
C20	7903(2)	2545.5(18)	3327.0(7)	38.6(4)
C21	9015(2)	1852(2)	3523.5(8)	46.6(5)
C22	10407(2)	2155(2)	3407.8(9)	50.3(5)
C23	10674(2)	3135(2)	3096.0(11)	55.8(6)
C24	9558(2)	3834(2)	2899.1(9)	46.2(5)
C25	9171(3)	6584(2)	4203.3(9)	53.2(6)
C26	8628(4)	7528(3)	4593.8(11)	84.1(10)
C27	9898(3)	7327(3)	3785.0(10)	66.1(7)
C28	10135(11)	5742(6)	4500(5)	70(2)
C28B	10552(19)	5630(14)	4289(9)	60(4)
C29	4910(3)	3561(2)	4503.7(7)	49.6(5)
C30	3695(2)	2938(2)	4226.6(8)	45.8(5)
C31	5867(4)	2536(3)	4711.7(12)	86.4(11)
C32	4249(5)	4342(3)	4932.2(10)	91.8(13)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for *epi*-3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	79(4)	99(3)	33.7(14)	10.6(17)	-22.2(19)	-41(3)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for *epi*-3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1B	76(7)	138(12)	44(5)	41(6)	-30(5)	-62(7)
O2	41.2(7)	40.4(7)	32.9(6)	11.1(6)	1.2(5)	-0.4(6)
C1	30.5(8)	25.2(8)	26.5(8)	0.4(6)	-2.8(6)	-1.8(6)
C2	32.3(8)	25.1(8)	35.1(8)	-0.2(7)	-2.0(7)	-3.3(6)
C3	46.1(10)	31.9(9)	41.8(10)	-2.2(8)	-13.4(8)	-8.6(8)
C4	81.2(16)	55.8(13)	34.6(10)	8.8(9)	-22.5(11)	-28.4(13)
C5	51.5(11)	30.9(9)	30.0(9)	2.9(7)	-5.0(8)	-8.7(8)
C6	31.7(8)	24.2(8)	30.3(8)	1.6(6)	-2.3(7)	-1.8(6)
C7	29.3(8)	27.9(8)	29.6(8)	-2.9(7)	-0.5(6)	-1.9(7)
C8	35.2(9)	36.4(9)	30.0(8)	1.2(7)	2.7(7)	-1.4(8)
C9	29.0(8)	34.0(9)	27.3(8)	2.4(7)	-2.3(6)	-5.3(7)
C10	29.6(8)	26.4(8)	27.0(8)	3.4(6)	-1.0(6)	-2.3(7)
C11	40.7(9)	25.1(8)	29.7(8)	2.7(7)	-6.5(7)	0.4(7)
C12	48.7(10)	27.6(9)	40.4(10)	5.7(7)	-9.9(8)	-4.8(8)
C13	77.5(16)	27.2(9)	54.8(12)	1.1(9)	-20.2(12)	-5.4(10)
C14	92.8(19)	35.8(11)	48.0(12)	-12.0(9)	-14.7(13)	10.4(12)
C15	75.6(15)	46.2(12)	38.1(10)	-7.2(9)	2.9(11)	11.2(12)
C16	53.0(11)	35.2(9)	34.0(9)	0.2(8)	2.5(8)	2.5(9)
C17	32.9(8)	29.4(8)	28.6(8)	2.9(6)	-1.3(7)	-4.1(7)
C18	33.0(9)	38.8(10)	42.3(10)	8.1(8)	-2.6(7)	-3.8(8)
C19	32.3(8)	27.0(8)	36.2(9)	-6.1(7)	-4.1(7)	-0.4(7)
C20	36.7(9)	33.6(9)	45.3(10)	1.2(8)	-2.6(8)	0.5(8)
C21	49.9(11)	39.7(10)	50.4(11)	4.1(9)	-8.1(9)	6.7(9)
C22	41.1(10)	45.2(12)	64.7(14)	-6.0(10)	-13.8(10)	12.1(9)
C23	30.4(10)	49.9(12)	87.3(17)	0.7(12)	-1.4(10)	3.3(9)
C24	34.3(9)	39.3(10)	65.1(13)	5.4(10)	3.7(9)	0.6(9)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for *epi*-3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C25	58.4(13)	45.9(12)	55.2(13)	-2.7(10)	-23.7(11)	-17.1(10)
C26	112(2)	79.1(19)	61.0(16)	-25.8(15)	-12.5(16)	-39.7(19)
C27	49.7(13)	75.2(17)	73.5(16)	-6.7(14)	-11.1(12)	-31.8(13)
C28	54(3)	74(3)	82(5)	-12(3)	-37(3)	-4(3)
C28B	53(5)	59(6)	67(9)	16(6)	-33(5)	-17(3)
C29	76.2(15)	45.0(11)	27.8(9)	5.6(8)	-2.4(9)	-20.7(11)
C30	54.5(12)	43.6(11)	39.4(10)	3.3(9)	11.2(9)	-15.3(9)
C31	107(2)	76.9(19)	74.8(18)	49.0(16)	-40.2(17)	-33.6(19)
C32	149(3)	83(2)	42.6(13)	-19.2(13)	34.8(17)	-56(2)

Table 4 Bond Lengths for *epi*-3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C4	1.239(4)	C11	C16	1.398(3)
O1B	C4	1.305(12)	C12	C13	1.383(3)
O2	C9	1.208(2)	C13	C14	1.383(4)
C1	C2	1.488(2)	C14	C15	1.377(4)
C1	C6	1.481(2)	C15	C16	1.388(3)
C1	C7	1.591(2)	C17	C18	1.317(3)
C1	C10	1.583(2)	C19	C20	1.388(3)
C2	C3	1.329(3)	C19	C24	1.387(3)
C3	C4	1.491(3)	C20	C21	1.386(3)
C3	C25	1.539(3)	C21	C22	1.382(3)
C4	C5	1.495(3)	C22	C23	1.366(4)
C5	C6	1.327(2)	C23	C24	1.393(3)
C5	C29	1.534(3)	C25	C26	1.539(4)

Table 4 Bond Lengths for *epi*-3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C7	C8	1.531(2)	C25	C27	1.528(4)
C7	C19	1.517(2)	C25	C28	1.504(6)
C8	C9	1.507(3)	C25	C28B	1.672(17)
C9	C10	1.554(2)	C29	C30	1.514(3)
C10	C11	1.518(2)	C29	C31	1.529(4)
C10	C17	1.522(2)	C29	C32	1.544(4)
C11	C12	1.394(3)			

Table 5 Bond Angles for *epi*-3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C7	108.84(13)	C12	C11	C10	122.37(16)
C2	C1	C10	109.21(13)	C12	C11	C16	117.95(17)
C6	C1	C2	112.95(14)	C16	C11	C10	119.40(16)
C6	C1	C7	110.66(13)	C13	C12	C11	120.8(2)
C6	C1	C10	111.78(14)	C14	C13	C12	120.6(2)
C10	C1	C7	102.90(12)	C15	C14	C13	119.3(2)
C3	C2	C1	125.32(16)	C14	C15	C16	120.6(2)
C2	C3	C4	118.77(17)	C15	C16	C11	120.7(2)
C2	C3	C25	122.16(19)	C18	C17	C10	125.49(16)
C4	C3	C25	119.06(17)	C20	C19	C7	118.87(16)
O1	C4	C3	123.6(4)	C24	C19	C7	123.51(17)
O1	C4	C5	117.3(4)	C24	C19	C20	117.59(17)
O1B	C4	C3	110.6(7)	C21	C20	C19	121.42(18)
O1B	C4	C5	124.4(7)	C22	C21	C20	120.0(2)
C3	C4	C5	118.67(16)	C23	C22	C21	119.5(2)
C4	C5	C29	119.53(16)	C22	C23	C24	120.6(2)

Table 5 Bond Angles for *epi*-3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C5	C4	118.52(17)	C19	C24	C23	120.9(2)
C6	C5	C29	121.94(17)	C3	C25	C26	109.0(2)
C5	C6	C1	125.76(16)	C3	C25	C28B	109.2(5)
C8	C7	C1	103.84(13)	C26	C25	C28B	125.1(8)
C19	C7	C1	111.58(14)	C27	C25	C3	111.22(18)
C19	C7	C8	117.98(15)	C27	C25	C26	106.5(2)
C9	C8	C7	106.86(14)	C27	C25	C28B	94.5(8)
O2	C9	C8	125.58(16)	C28	C25	C3	109.8(3)
O2	C9	C10	124.50(16)	C28	C25	C26	104.6(5)
C8	C9	C10	109.90(14)	C28	C25	C27	115.3(6)
C9	C10	C1	102.17(13)	C5	C29	C32	110.38(18)
C11	C10	C1	111.35(13)	C30	C29	C5	111.41(16)
C11	C10	C9	115.61(14)	C30	C29	C31	107.04(19)
C11	C10	C17	113.69(14)	C30	C29	C32	107.2(2)
C17	C10	C1	111.26(13)	C31	C29	C5	109.0(2)
C17	C10	C9	101.90(13)	C31	C29	C32	111.7(2)

Table 6 Torsion Angles for *epi*-3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C4	C5	C6	171.9(6)	C6	C5	C29	C31	115.7(2)
O1	C4	C5	C29	-9.7(7)	C6	C5	C29	C32	-121.3(3)
O1B	C4	C5	C6	-149.9(19)	C7	C1	C2	C3	-122.7(2)
O1B	C4	C5	C29	28.5(19)	C7	C1	C6	C5	121.59(19)
O2	C9	C10	C1	-161.85(16)	C7	C1	C10	C9	-34.26(15)
O2	C9	C10	C11	-40.8(2)	C7	C1	C10	C11	-158.25(13)
O2	C9	C10	C17	83.0(2)	C7	C1	C10	C17	73.81(16)

Table 6 Torsion Angles for *epi*-3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-0.6(3)	C7	C8	C9	O2	-174.79(17)
C1	C2	C3	C25	-179.58(18)	C7	C8	C9	C10	3.70(18)
C1	C7	C8	C9	-25.53(17)	C7	C19	C20	C21	-176.10(18)
C1	C7	C19	C20	75.77(19)	C7	C19	C24	C23	176.1(2)
C1	C7	C19	C24	-102.2(2)	C8	C7	C19	C20	-164.14(16)
C1	C10	C11	C12	95.11(19)	C8	C7	C19	C24	17.9(3)
C1	C10	C11	C16	-78.68(19)	C8	C9	C10	C1	19.64(17)
C1	C10	C17	C18	152.37(17)	C8	C9	C10	C11	140.72(15)
C2	C1	C6	C5	-0.7(3)	C8	C9	C10	C17	-95.48(15)
C2	C1	C7	C8	-78.39(16)	C9	C10	C11	C12	-20.9(2)
C2	C1	C7	C19	49.71(18)	C9	C10	C11	C16	165.32(15)
C2	C1	C10	C9	81.24(16)	C9	C10	C17	C18	-99.4(2)
C2	C1	C10	C11	-42.74(18)	C10	C1	C2	C3	125.70(19)
C2	C1	C10	C17	-170.68(14)	C10	C1	C6	C5	-124.36(19)
C2	C3	C4	O1	-171.5(7)	C10	C1	C7	C8	37.39(16)
C2	C3	C4	O1B	153.8(17)	C10	C1	C7	C19	165.49(13)
C2	C3	C4	C5	0.6(3)	C10	C11	C12	C13	-174.99(17)
C2	C3	C25	C26	117.8(3)	C10	C11	C16	C15	174.92(19)
C2	C3	C25	C27	0.6(3)	C11	C10	C17	C18	25.7(2)
C2	C3	C25	C28	-128.2(6)	C11	C12	C13	C14	0.8(3)
C2	C3	C25	C28B	-102.3(9)	C12	C11	C16	C15	0.9(3)
C3	C4	C5	C6	-0.6(3)	C12	C13	C14	C15	-0.1(4)
C3	C4	C5	C29	177.8(2)	C13	C14	C15	C16	-0.2(4)
C4	C3	C25	C26	-61.2(3)	C14	C15	C16	C11	-0.2(3)
C4	C3	C25	C27	-178.3(2)	C16	C11	C12	C13	-1.1(3)
C4	C3	C25	C28	52.9(7)	C17	C10	C11	C12	-138.28(17)

Table 6 Torsion Angles for *epi*-3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C4	C3	C25	C28B	78.7(10)	C17	C10	C11	C16	47.9(2)
C4	C5	C6	C1	0.7(3)	C19	C7	C8	C9	-149.57(15)
C4	C5	C29	C30	179.4(2)	C19	C20	C21	C22	-0.8(3)
C4	C5	C29	C31	-62.7(3)	C20	C19	C24	C23	-1.8(3)
C4	C5	C29	C32	60.3(3)	C20	C21	C22	C23	-0.5(4)
C6	C1	C2	C3	0.6(3)	C21	C22	C23	C24	0.7(4)
C6	C1	C7	C8	156.94(14)	C22	C23	C24	C19	0.6(4)
C6	C1	C7	C19	-74.96(17)	C24	C19	C20	C21	2.0(3)
C6	C1	C10	C9	-153.03(13)	C25	C3	C4	O1	7.5(7)
C6	C1	C10	C11	82.98(17)	C25	C3	C4	O1B	-27.2(17)
C6	C1	C10	C17	-44.95(18)	C25	C3	C4	C5	179.6(2)
C6	C5	C29	C30	-2.3(3)	C29	C5	C6	C1	-177.63(18)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for *epi*-3a.

Atom	*x*	*y*	*z*	U(eq)
H2	8084.1	6359.29	3295.71	37
H6	4714.33	4026.3	3539.04	35
H7	6129.04	3760.37	2748.53	35
H8A	8106.15	5500.41	2391.58	41
H8B	6918.05	4805.8	2081.37	41
H12	6620.7	8377.38	2955.91	47
H13	6360.78	10089.71	3464.46	64
H14	4726.53	10090.52	4119.47	71
H15	3340.83	8362.55	4258.88	64
H16	3573.61	6642.3	3749.33	49

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for *epi*-3a.

Atom	*x*	*y*	*z*	U(eq)
H17	3959.42	4686.25	2764.74	36
H18A	2657.67	6955.58	2804.93	46
H18B	1922.08	5665.82	2649.33	46
H20	6969.44	2326.8	3403.94	46
H21	8823.21	1182.23	3733.16	56
H22	11155.7	1696.81	3541.15	60
H23	11609.51	3336.69	3014.42	67
H24	9756.97	4493.31	2685.02	55
H26A	8035.72	8126.48	4427.89	126
H26B	9424.2	7936.87	4748.19	126
H26C	8084.51	7107.64	4848.96	126
H27A	10236.03	6774.76	3527.49	99
H27B	10686.86	7777	3924.48	99
H27C	9227.3	7895.76	3640.34	99
H28A	9628.61	5420.28	4786.4	105
H28B	10952.28	6196.39	4613.72	105
H28C	10438.87	5070.95	4288.03	105
H28D	10308.45	5021.09	4538.89	89
H28E	11362.43	6094.28	4402.67	89
H28F	10776.04	5226.75	3975.93	89
H30A	3038.88	3552.41	4107.53	69
H30B	3211.96	2383.71	4452.32	69
H30C	4065.16	2481.63	3944.18	69
H31A	6227.49	2048.43	4436.75	130
H31B	5324.96	2019.02	4935.51	130
H31C	6648.12	2896.95	4893.48	130

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for *epi*-3a.

Atom	*x*	*y*	*z*	U(eq)
H32A	4994.56	4718.29	5127.14	138
H32B	3685.93	3819.6	5147.21	138
H32C	3654.75	4973.13	4788.82	138

Table 8 Atomic Occupancy for *epi*-3a.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O1	0.69(3)	O1B	0.31(3)	C28	0.69(3)
H28A	0.69(3)	H28B	0.69(3)	H28C	0.69(3)
C28B	0.31(3)	H28D	0.31(3)	H28E	0.31(3)
H28F	0.31(3)				

Crystal structure determination of *epi*-3a

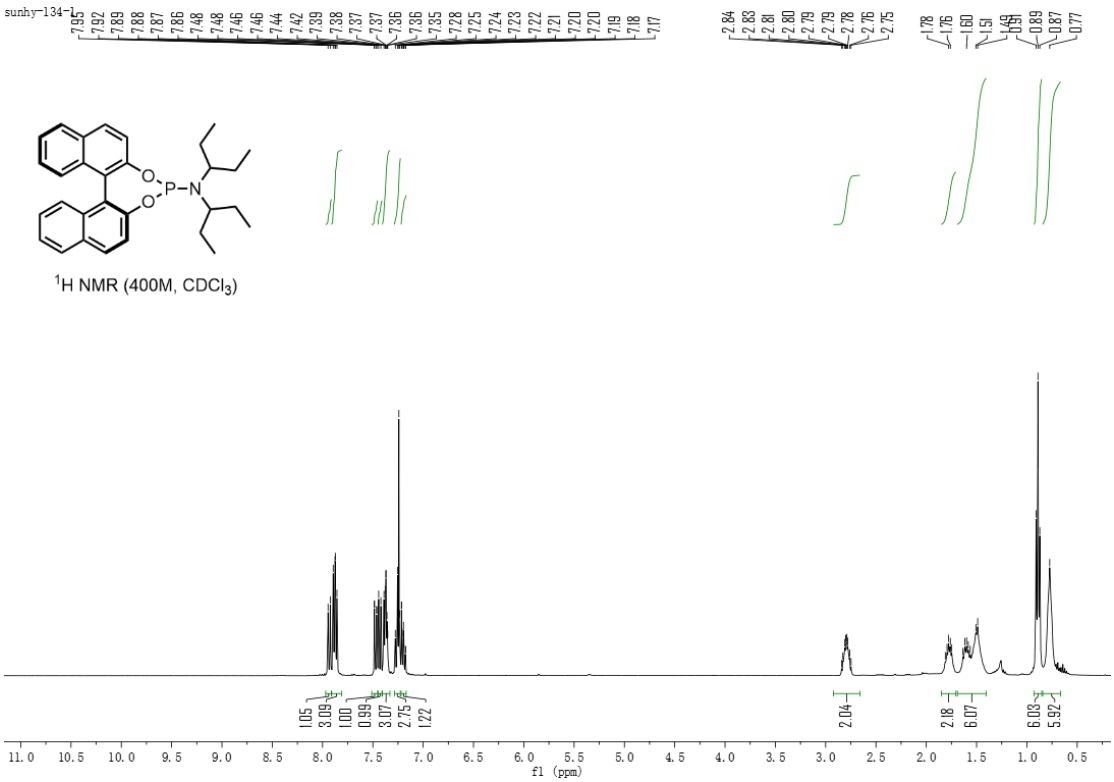
Crystal Data for $C_{32}H_{36}O_2$ (*M* =452.61 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 9.38580(10) Å, *b* = 10.82370(10) Å, *c* = 26.4399(3) Å, *V* = 2686.01(5) Å^3, *Z* = 4, *T* = 149.99(10) K, μ(Cu Kα) = 0.522 mm^{-1}, *Dcalc* = 1.119 g/cm^3, 15182 reflections measured (6.686° ≤ 2Θ ≤ 143.474°), 5140 unique (R_{int} = 0.0198, R_{sigma} = 0.0200) which were used in all calculations. The final R_1 was 0.0361 (I > 2σ(I)) and wR_2 was 0.0944 (all data).

10. References

(1) Chu, W.-D.; Zhang, L.-F.; Bao, X.; Zhao, X.-H.; Zeng, C.; Du, *J*.-Y.; Zhang, G.-B.; Wang, F.-X.; Ma, X.-Y.; Fan, C.-A. *Angew. Chem., Int. Ed*. **2013**, *52*, 9229.

(2) Yan, B.; Zuo, L.; Chang, X.; Liu, T.; Cui, M.; Liu, Y.; Sun, H.; Chen, W.; Guo, W. *Org. Lett.* **2021**, *23*, 351.

11. NMR Spectra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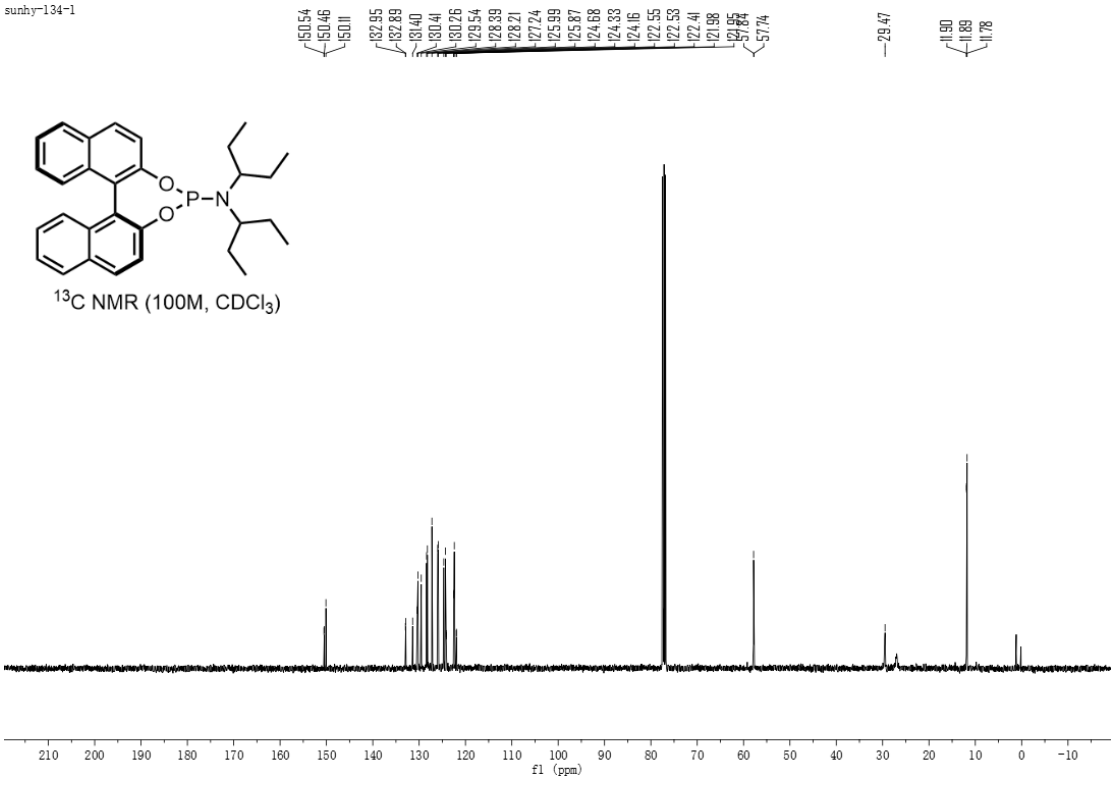
7.95 7.92 7.89 7.88 7.87 7.86 7.48 7.48 7.46 7.46 7.44 7.42 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.28 7.25 7.24 7.23 7.22 7.21 7.20 7.20 7.19 7.18 7.17
2.84 2.83 2.81 2.80 2.79 2.79 2.78 2.76 2.75
1.78 1.76 1.60 1.51 1.49 0.91 0.89 0.87 0.77
1H NMR (400M, CDCl3)
1.05 3.09 1.00 0.99 3.07 2.75 1.22 2.04 2.18 6.07 6.03 5.92
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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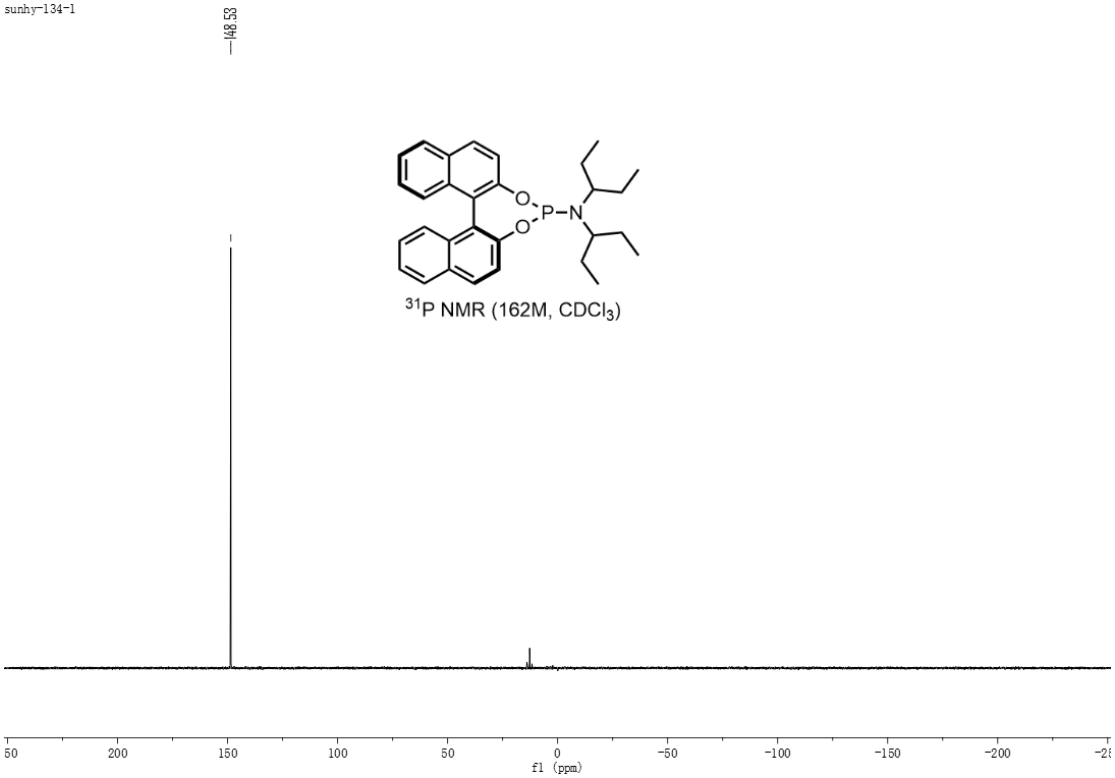
150.54 150.46 150.11 132.95 132.89 131.40 130.41 130.26 129.54 128.39 128.21 127.24 125.99 125.87 124.68 124.33 124.16 122.55 122.53 122.41 121.98 77.85 77.84 77.74
29.47
11.90 11.89 11.78
13C NMR (100M, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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148.53
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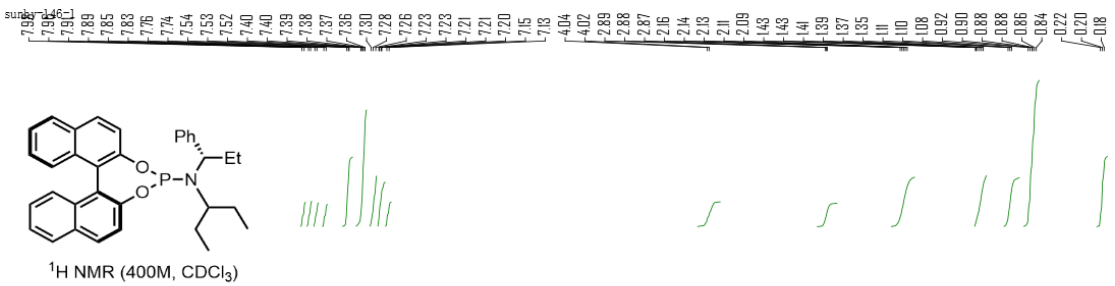
f1 (ppm)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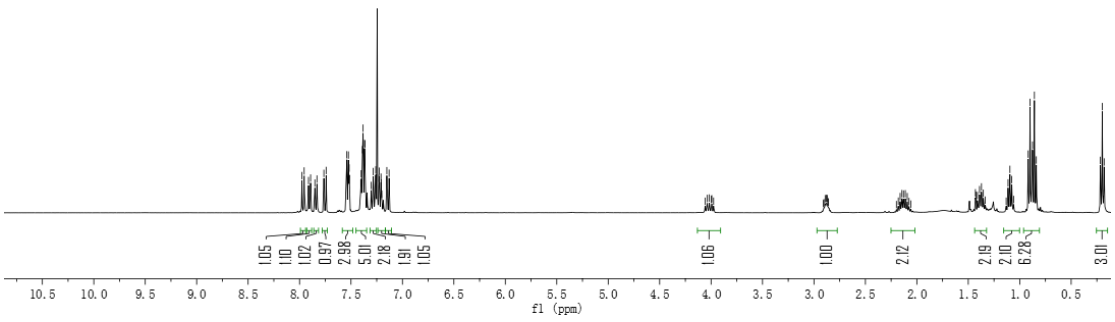
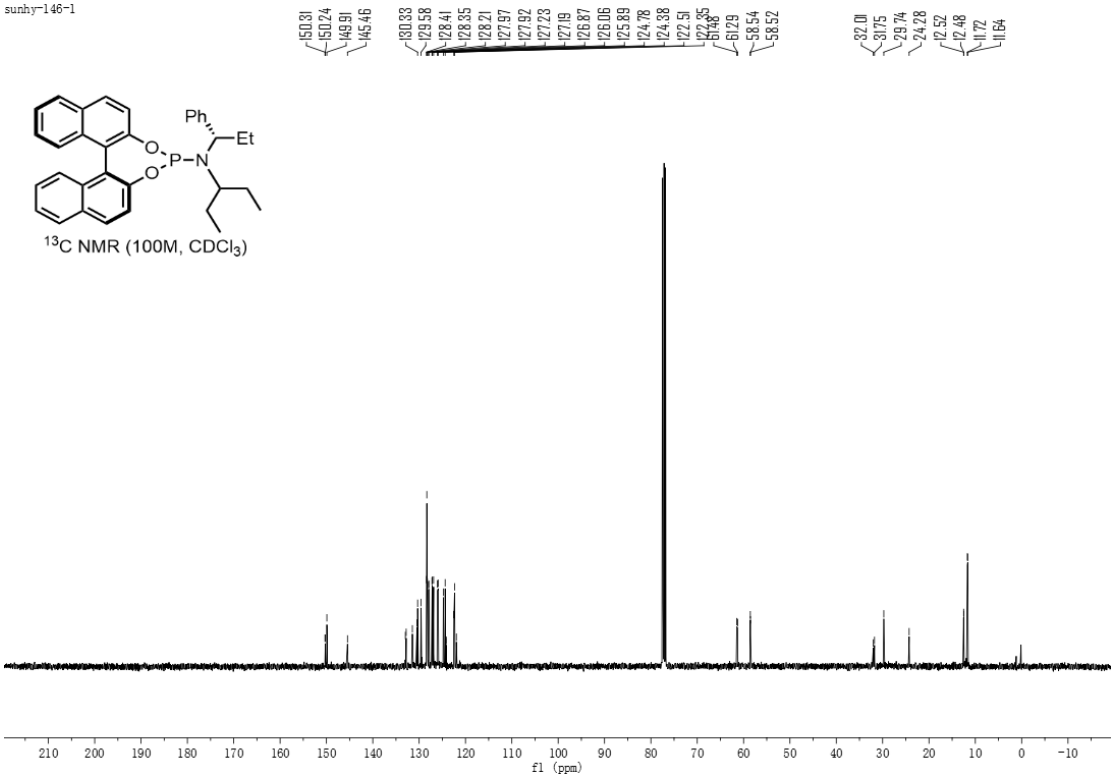
Ph
Et
^{1}H NMR (400M, $CDCl_3$)


f1 (ppm)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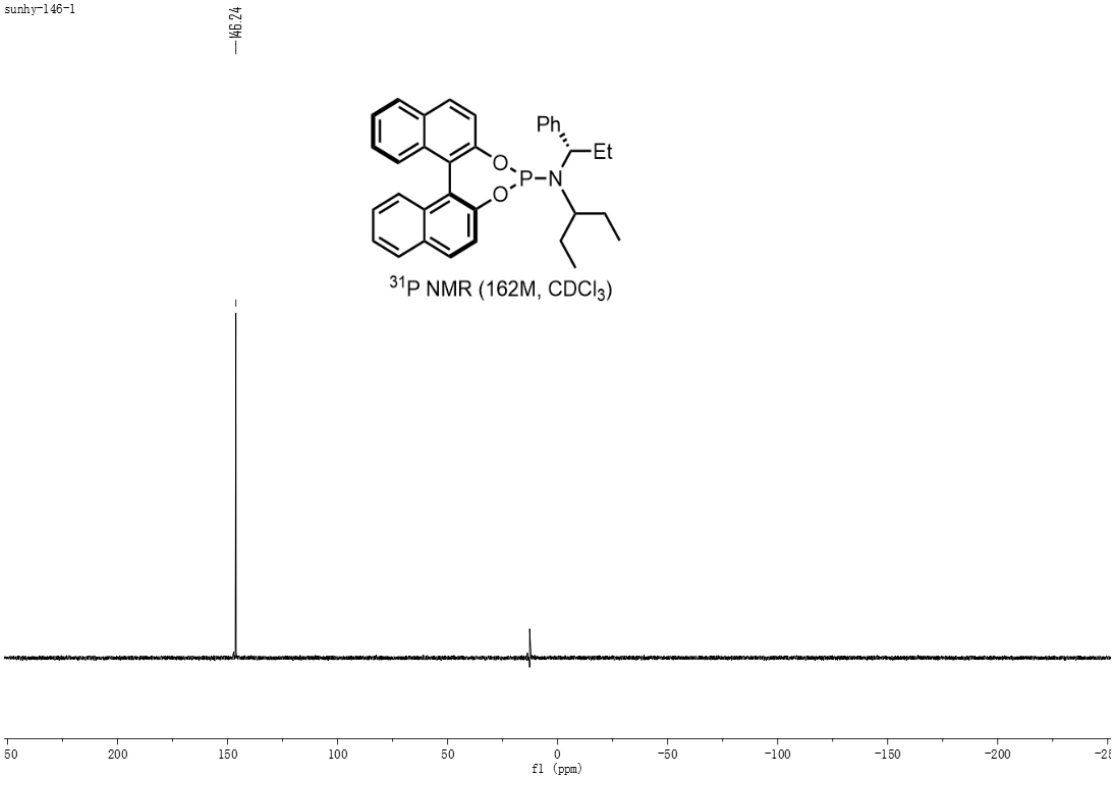
150.31
150.24
149.91
145.46
130.33
129.58
128.41
128.35
128.21
127.97
127.92
127.23
127.19
126.87
126.06
125.89
124.78
124.38
122.51
122.35
61.48
61.29
58.54
58.52
32.01
31.75
29.74
24.28
12.52
12.48
11.72
11.64
Ph
Et
O
P
N
O
^{13}C NMR (100M, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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Ph
Et
O
P
N
O
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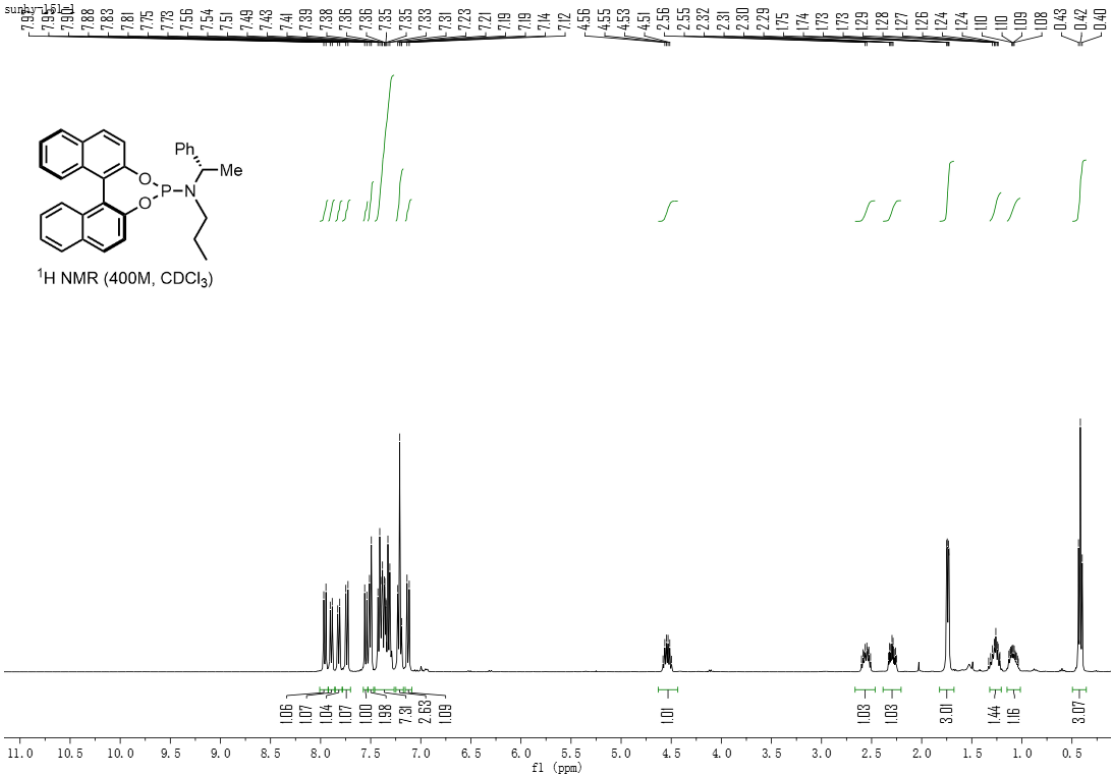
f1 (ppm)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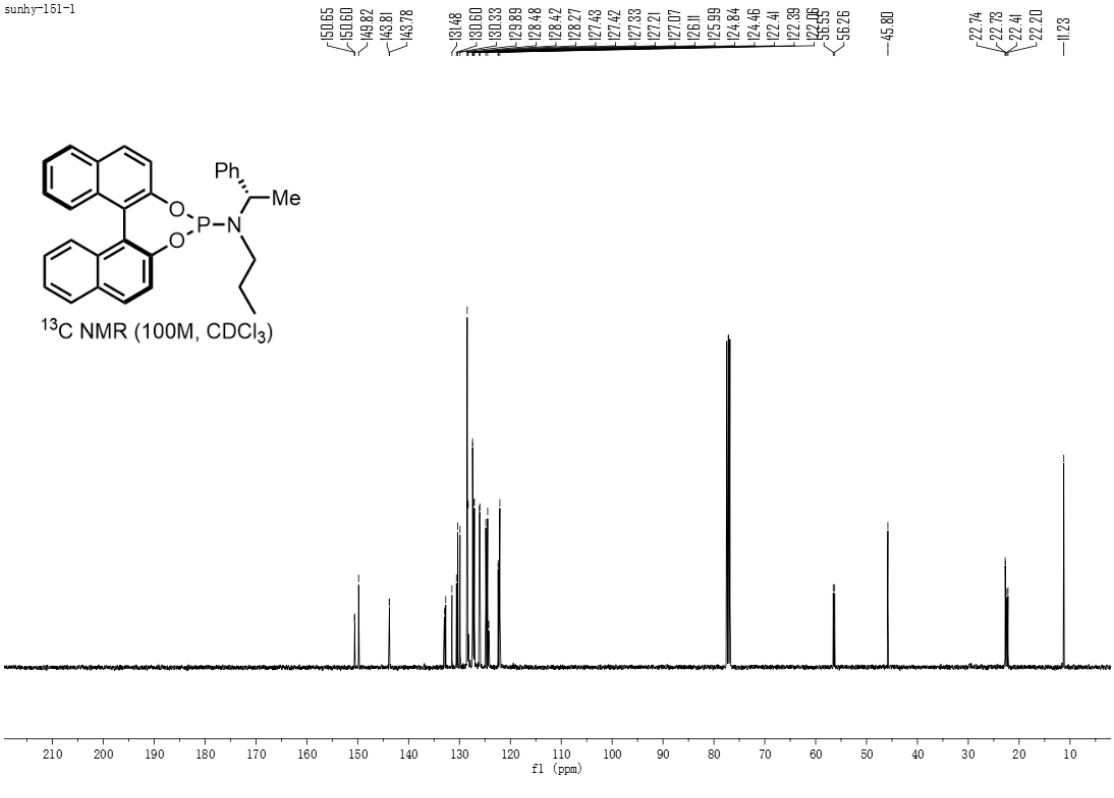
Me
P
N
O
O
1H NMR (400M, CDCl3)
f1 (ppm)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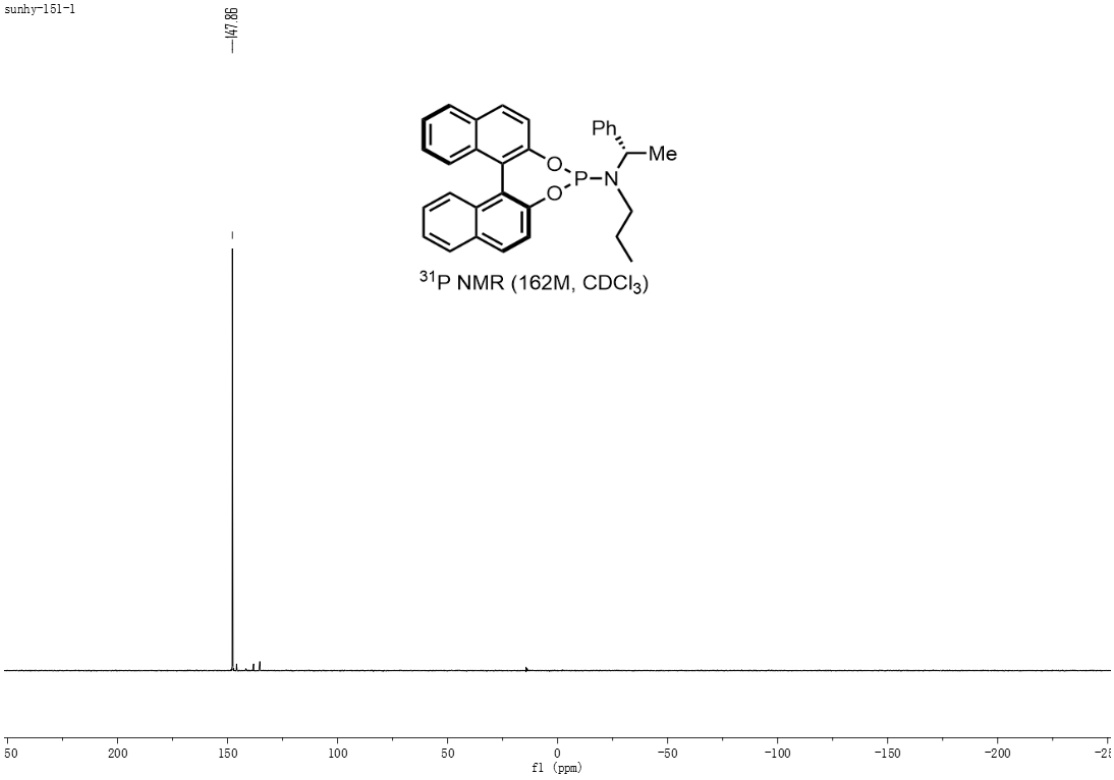
Me
P
N
O
O
13C NMR (100M, CDCl3)
f1 (ppm)

sunhy-151-1



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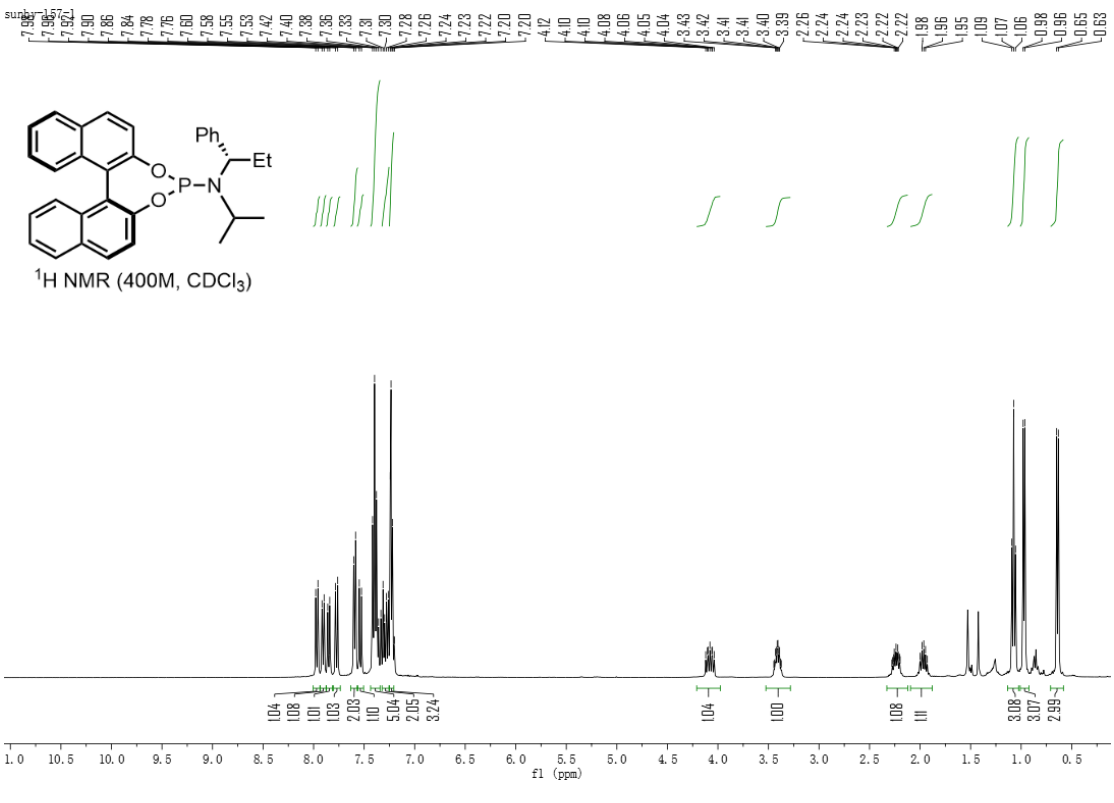

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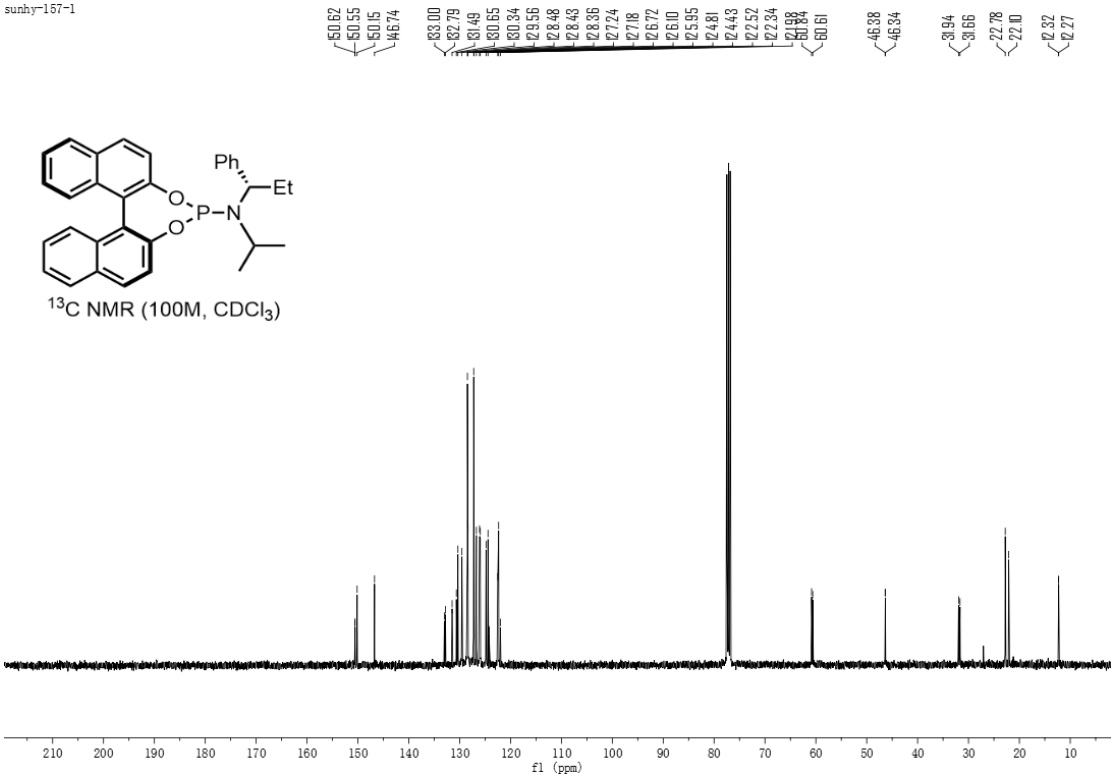

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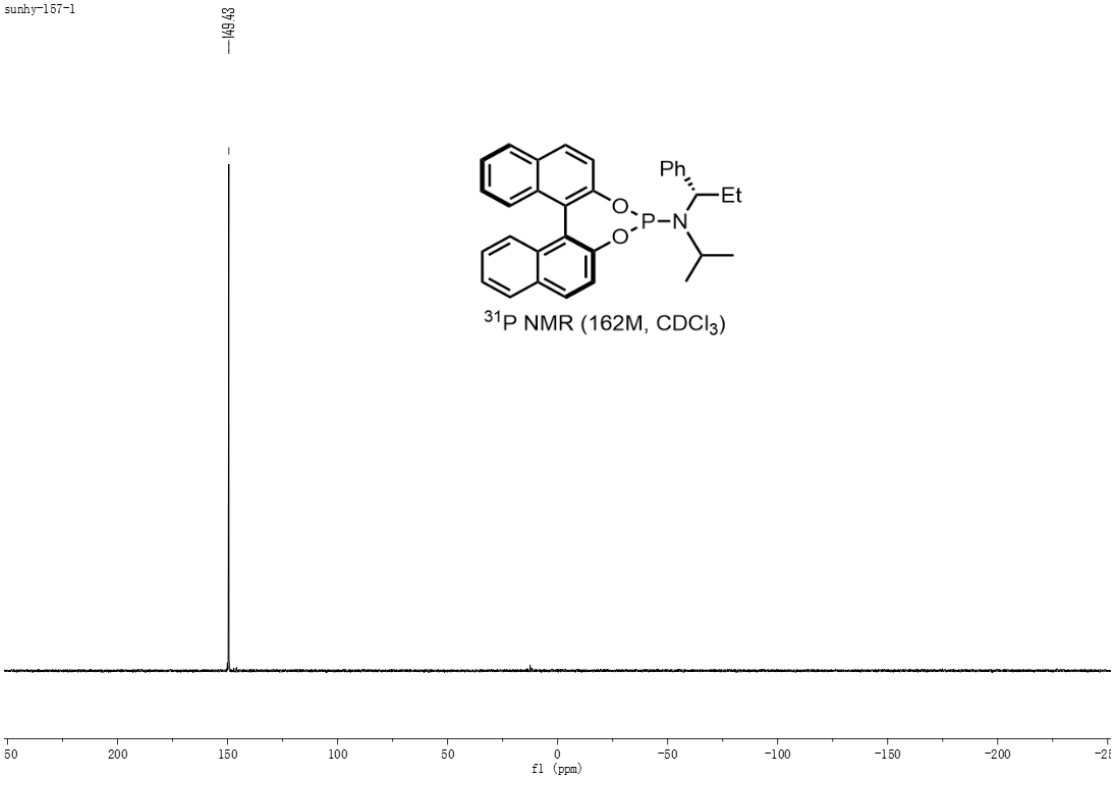

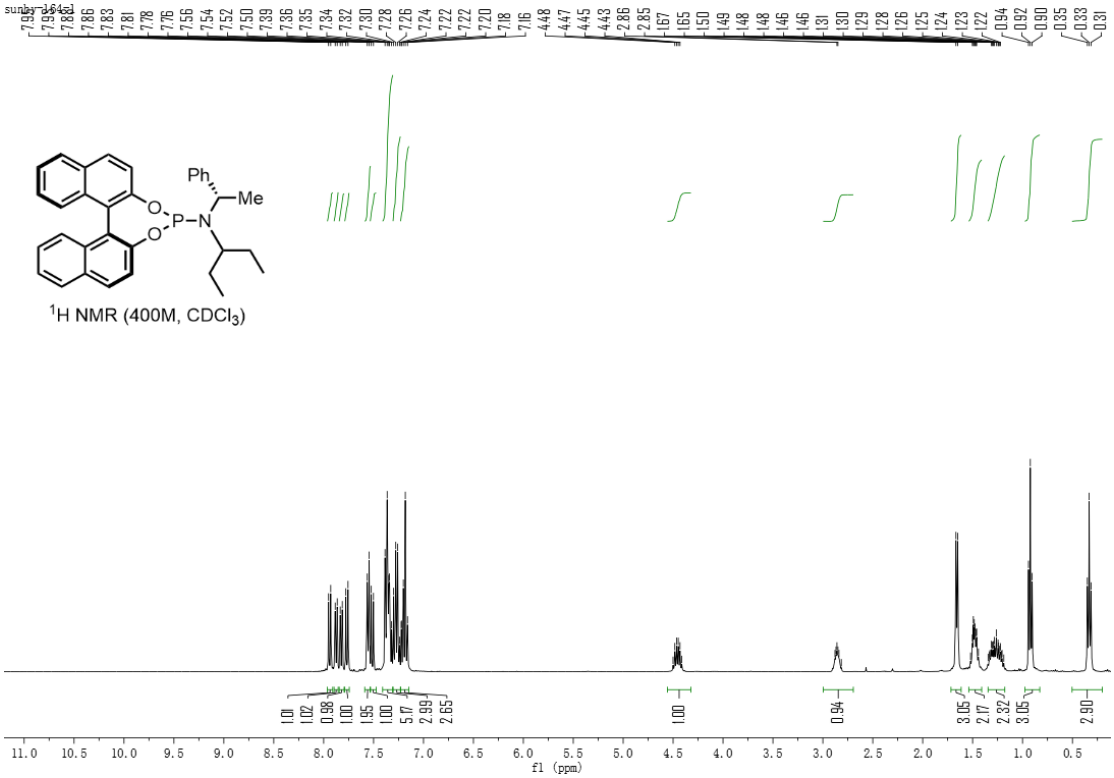
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N
O
O
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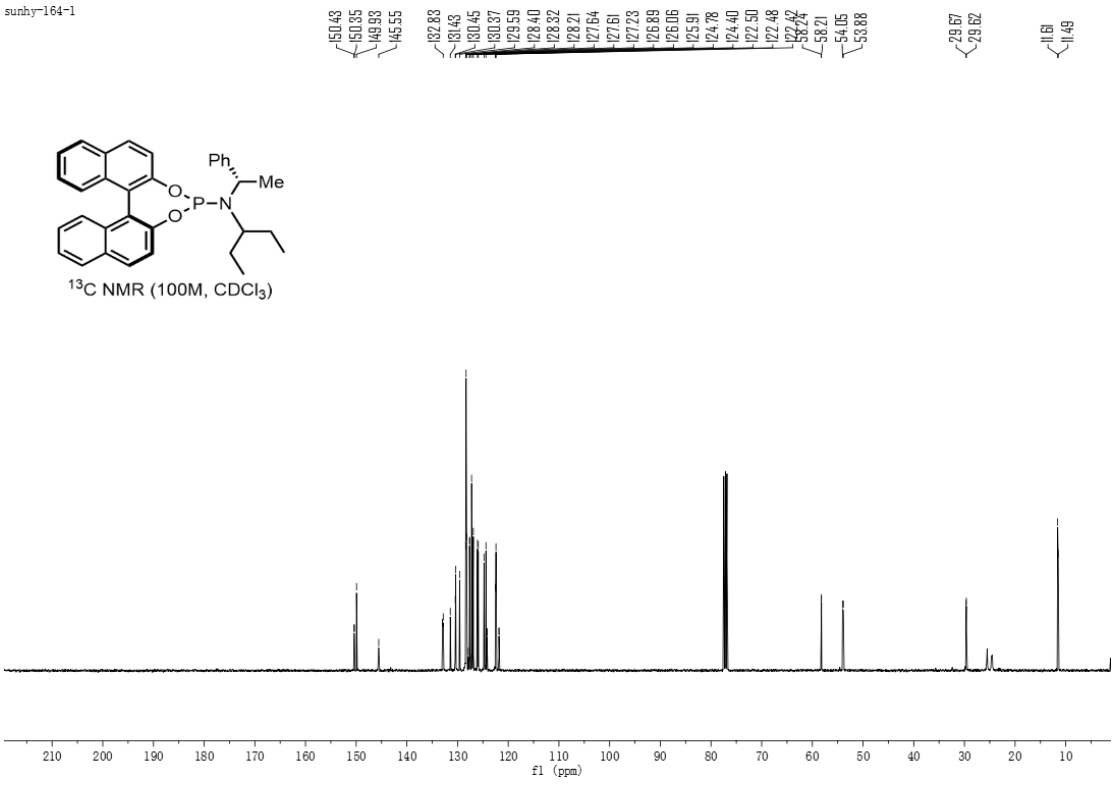
f1 (ppm)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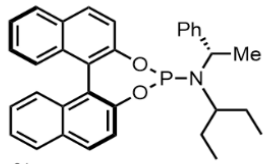
Me
P
N
O
O
^{13}C NMR (100M, CDCl$_3$)
f1 (ppm)

sunhy-164-1

147.60



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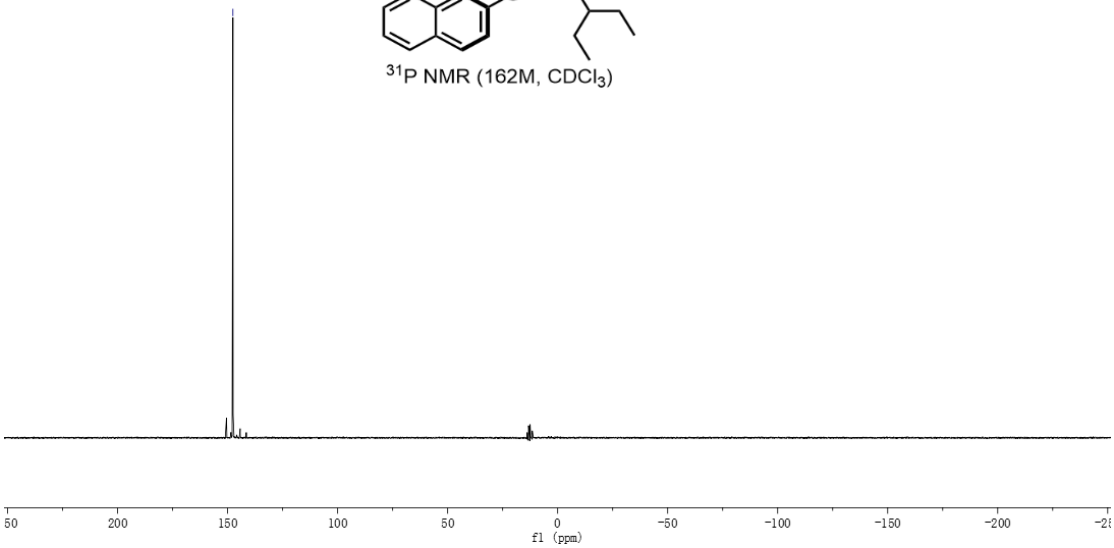

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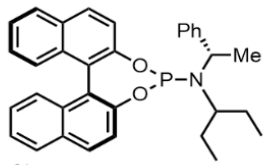
147.60



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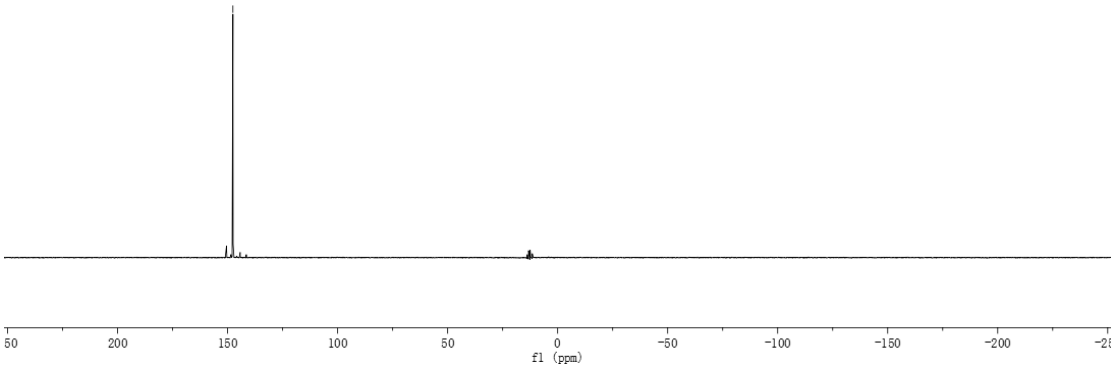

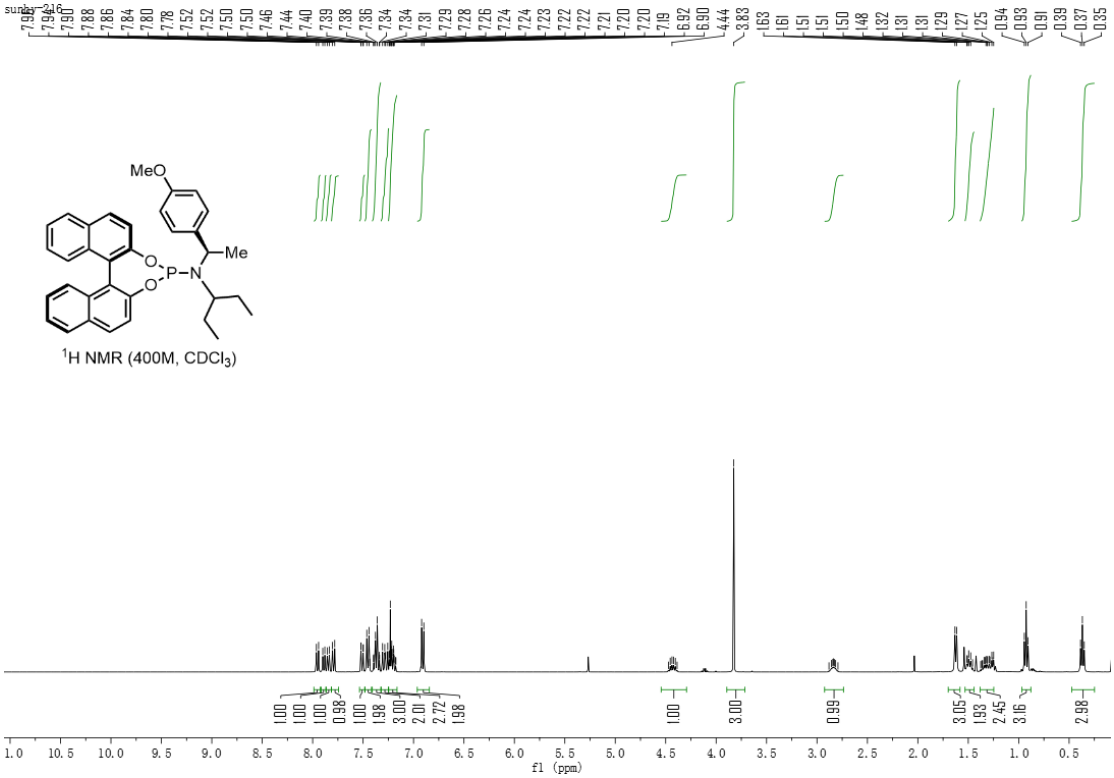
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P–N
O
O
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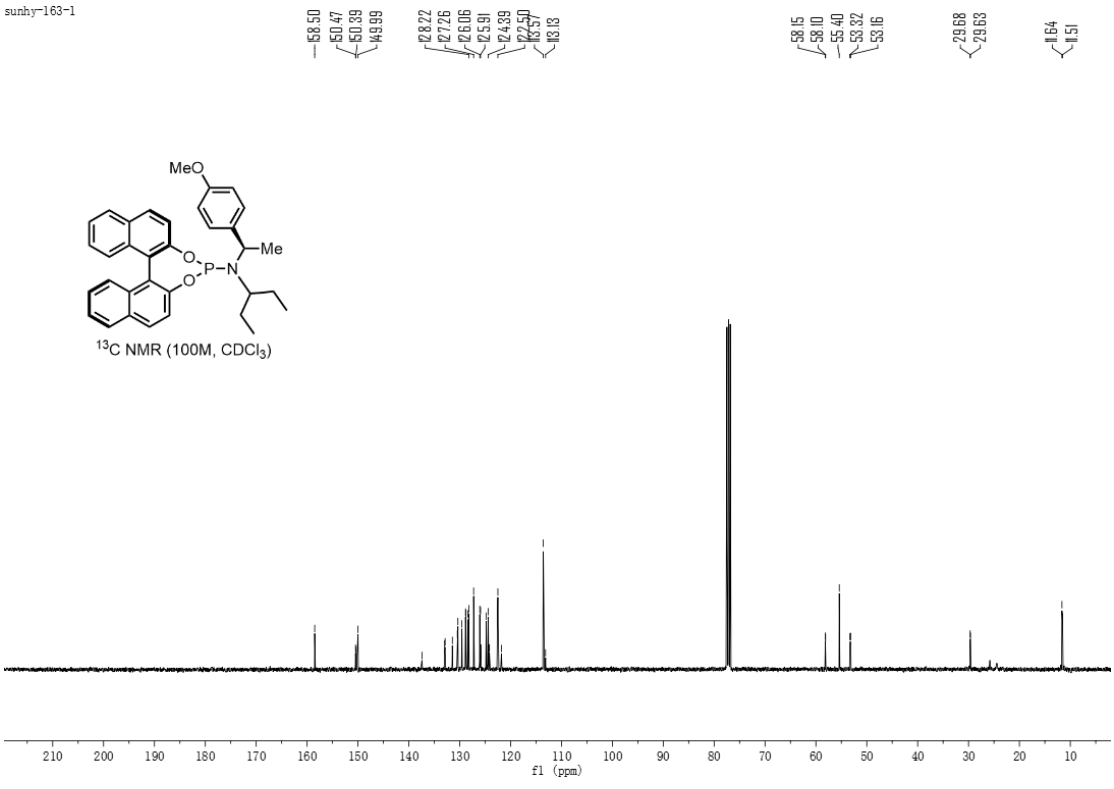
f1 (ppm)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Me
P–N
O
O
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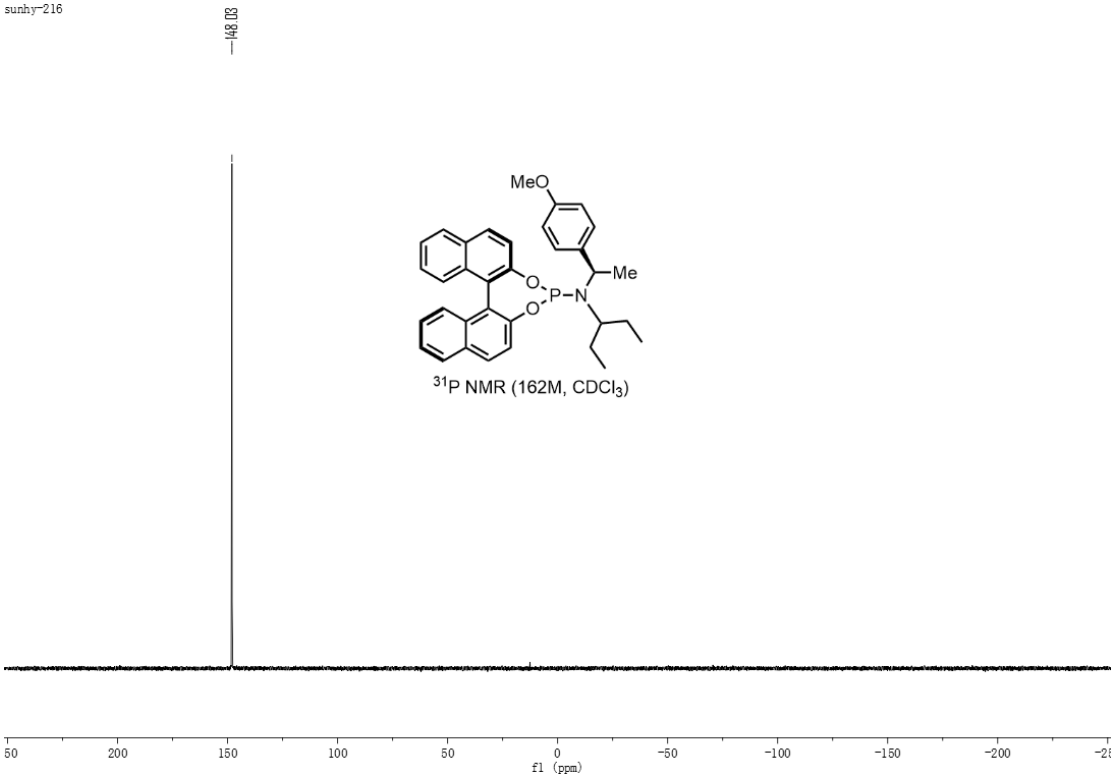
f1 (ppm)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Me
O
P
N
O
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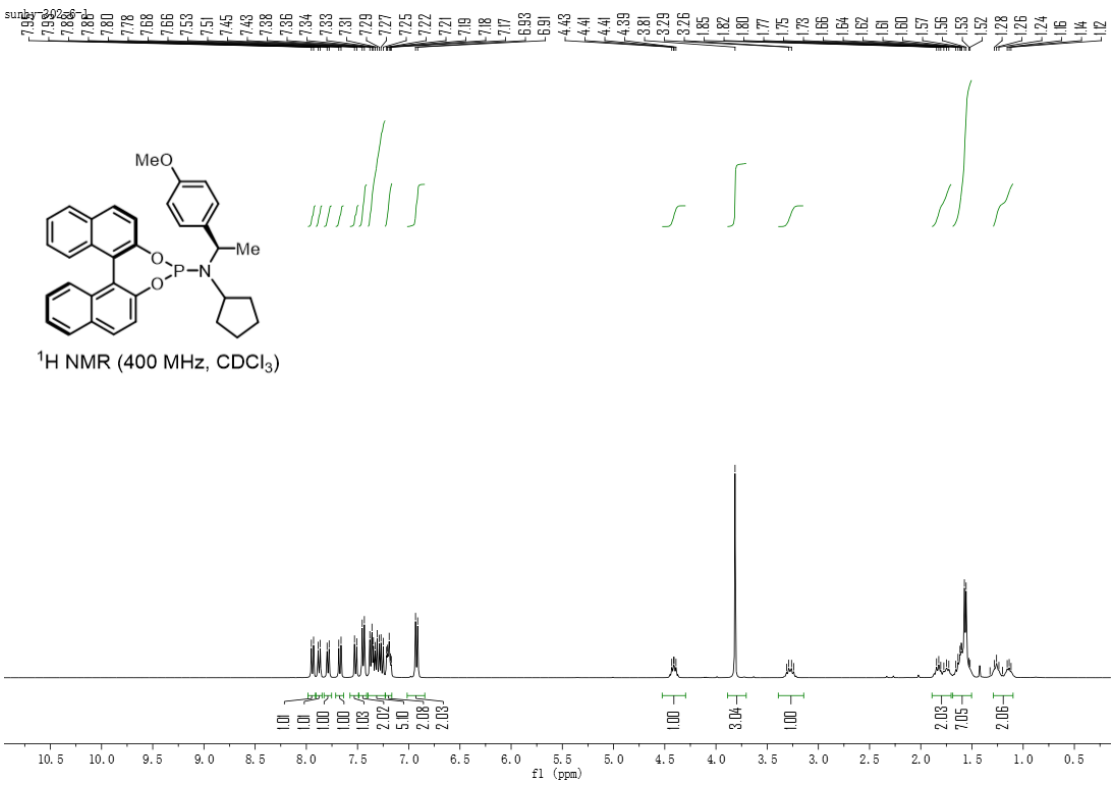
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Me
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P
N
O
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f1 (ppm)

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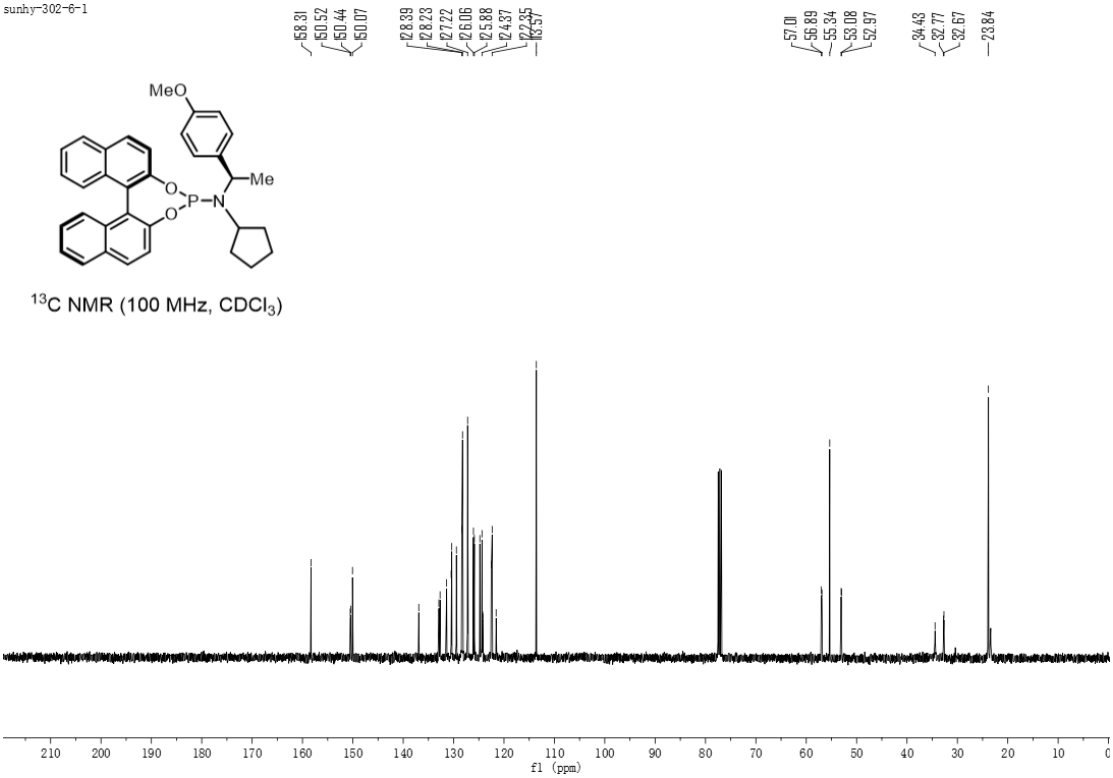

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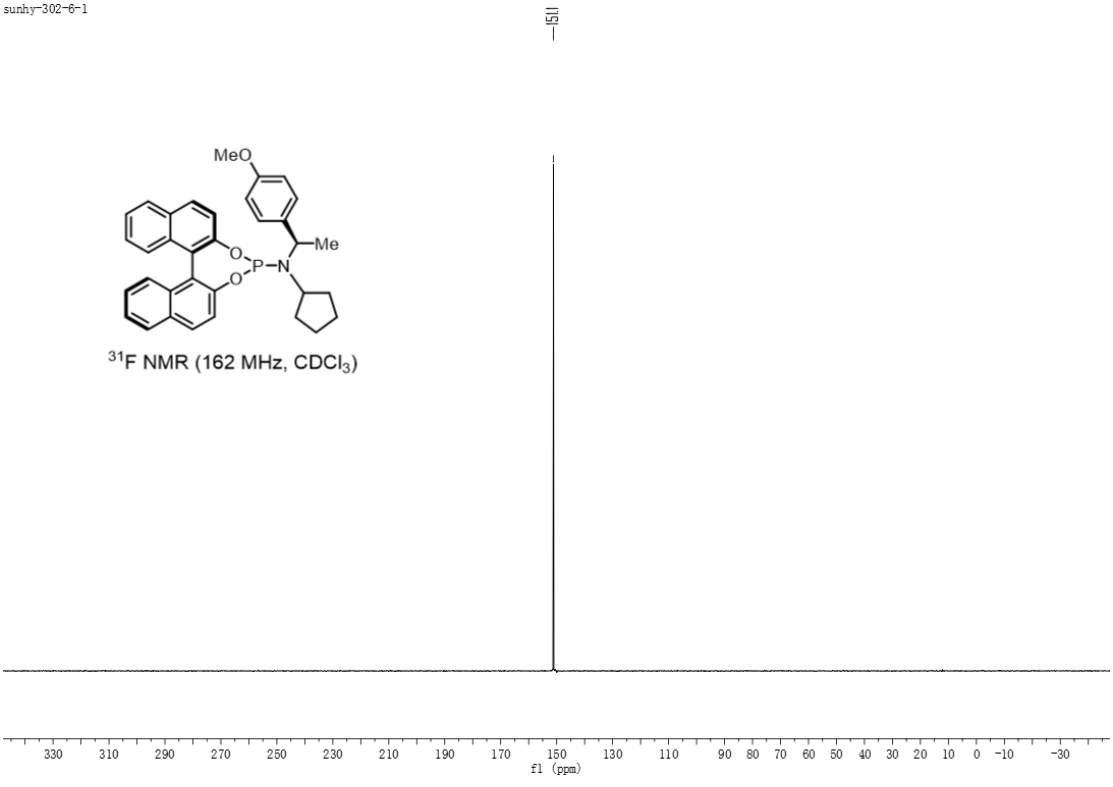
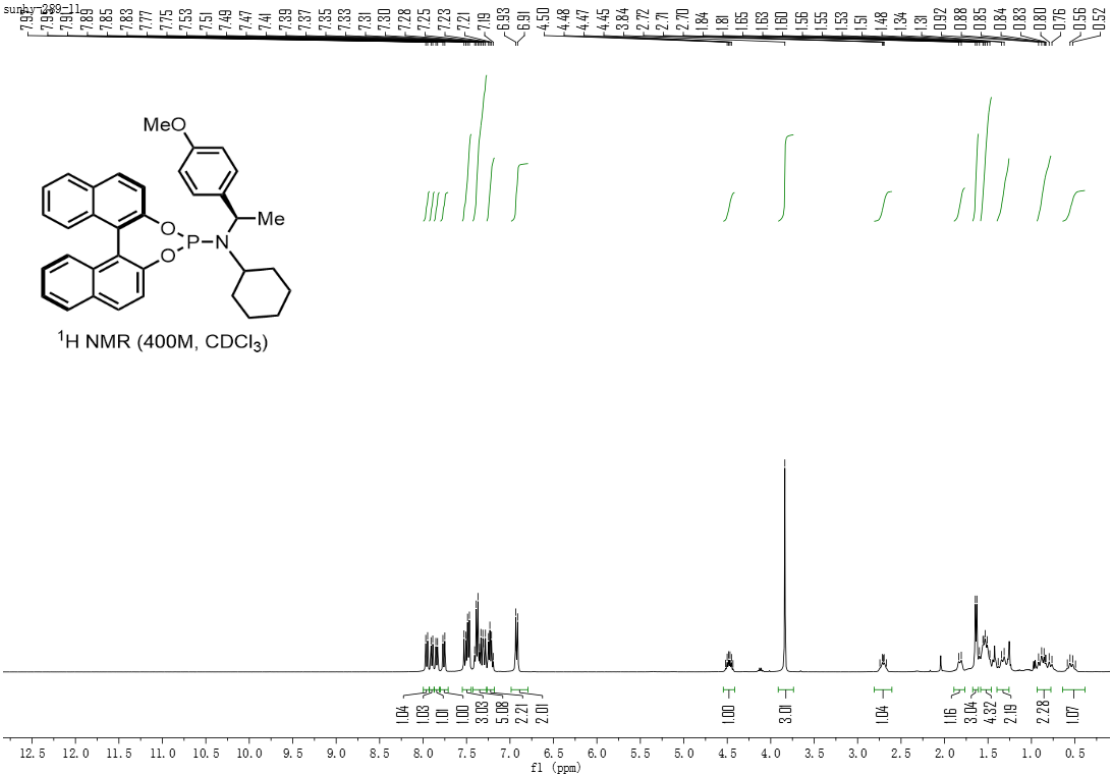


^{31}F NMR (162 MHz, $CDCl_3$)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Me
O
P
N
O
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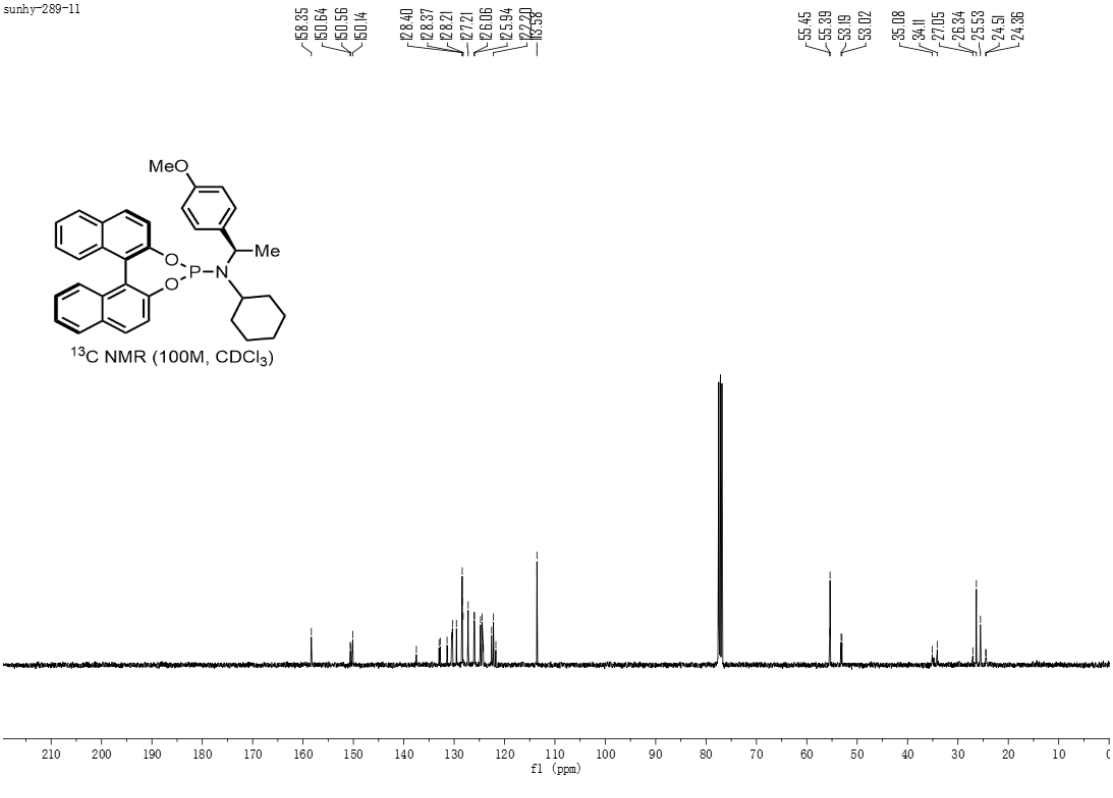
f1 (ppm)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Me
O
P
N
O
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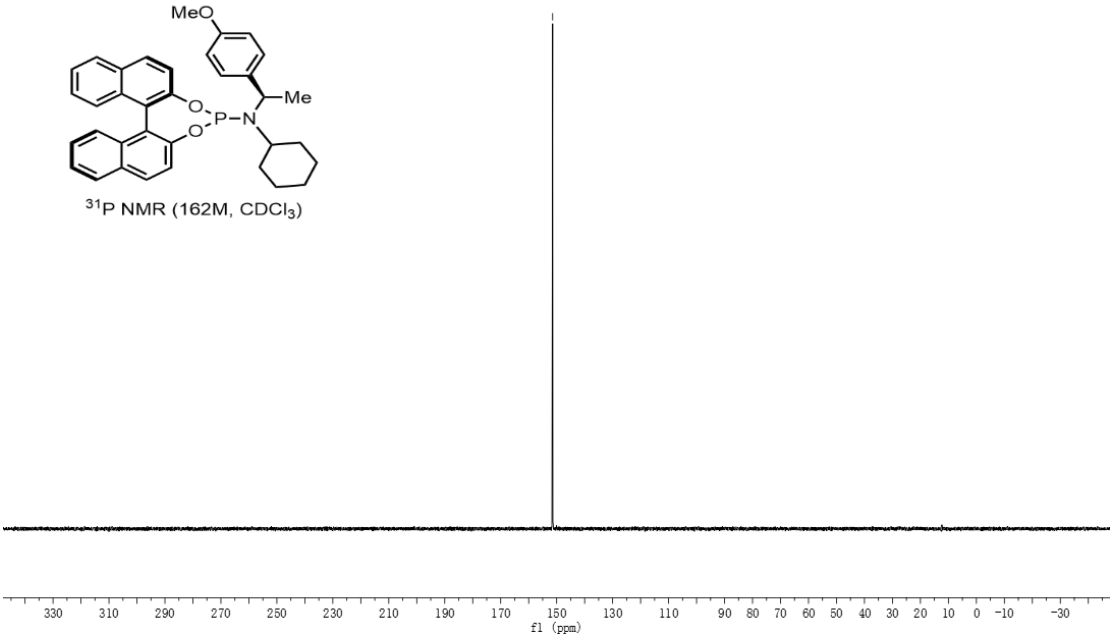
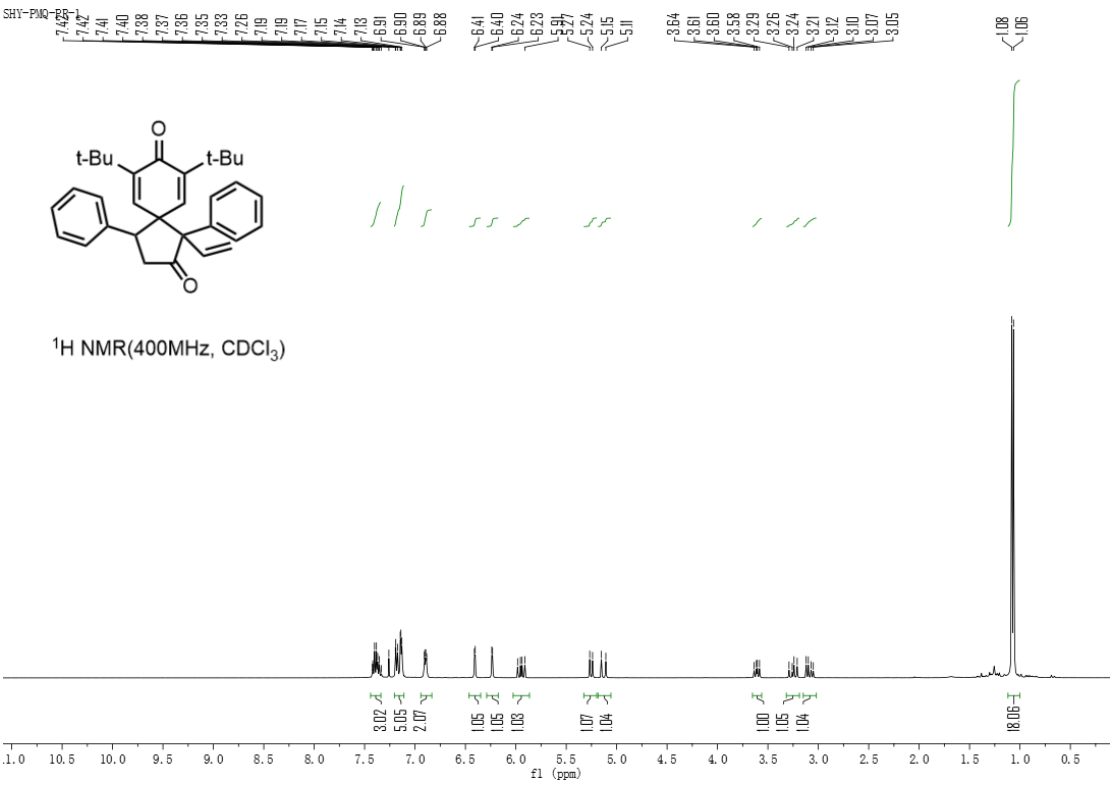
f1 (ppm)

sunhy-289-11

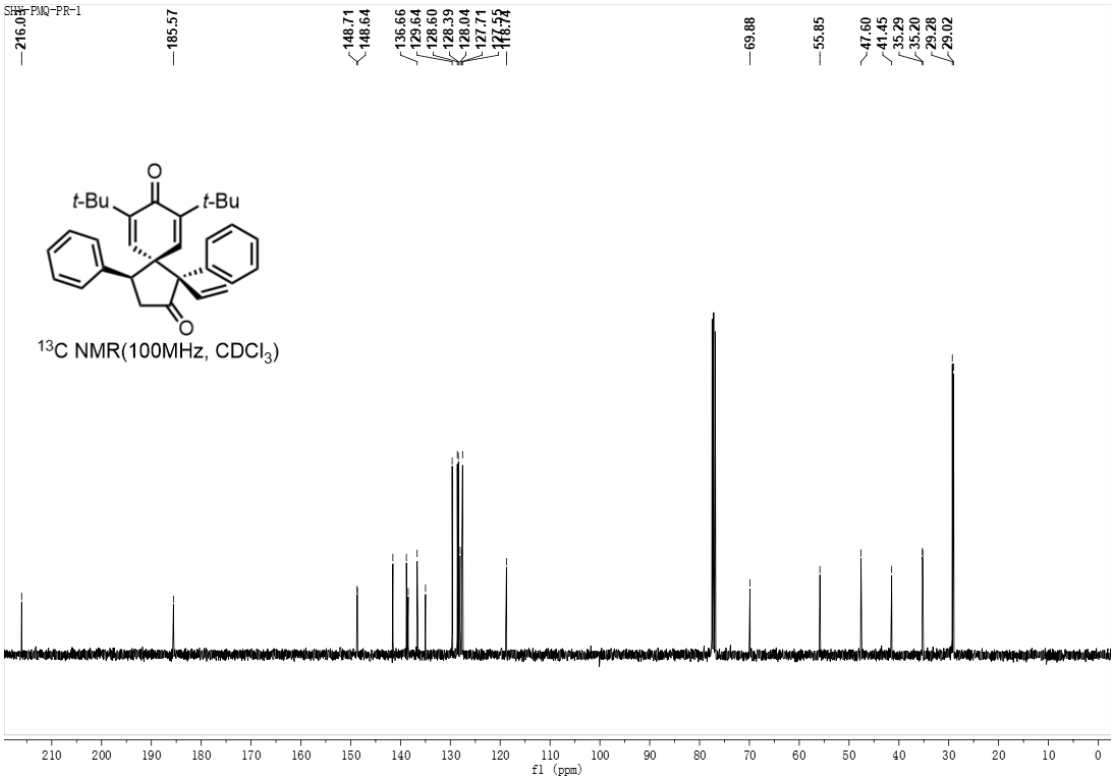


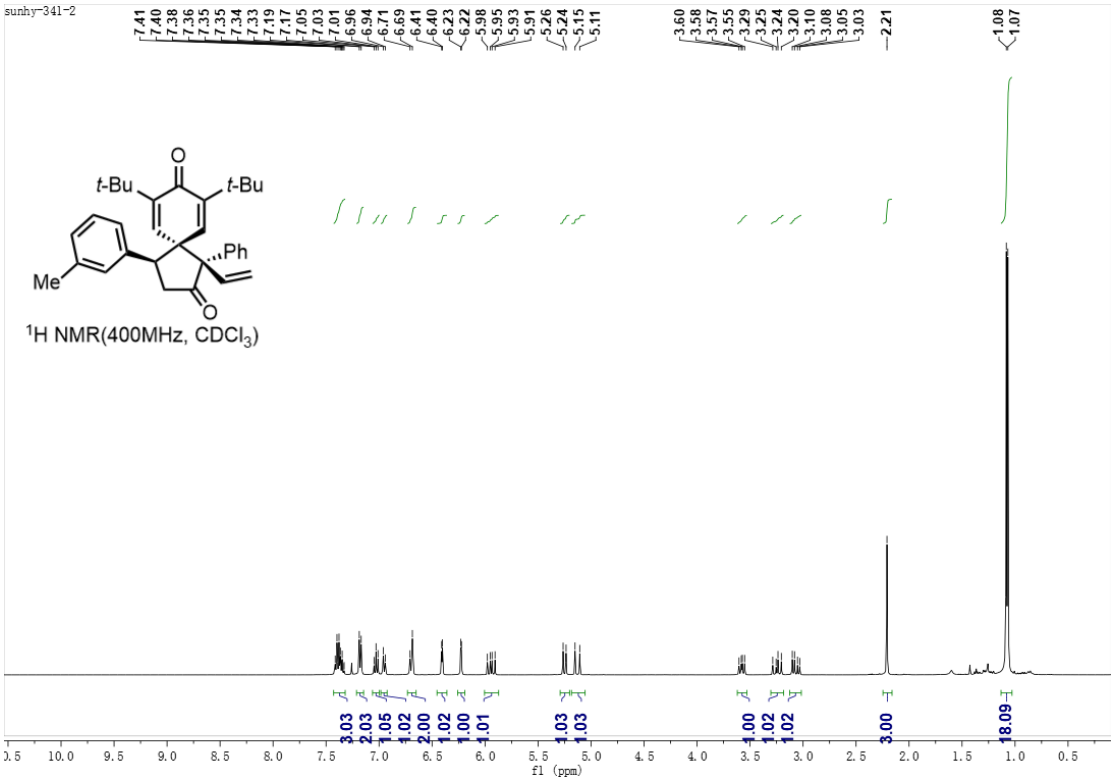
^{31}P NMR (162M, $CDCl_3$)

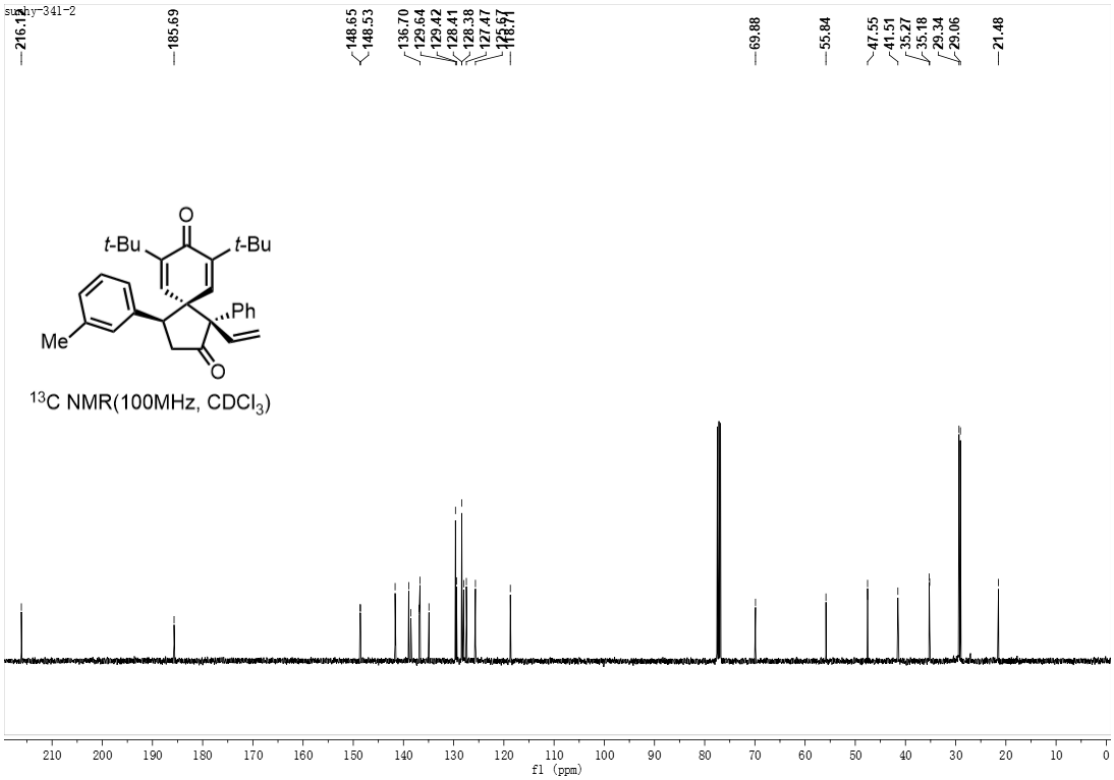
SHY-PMQ-PR-1

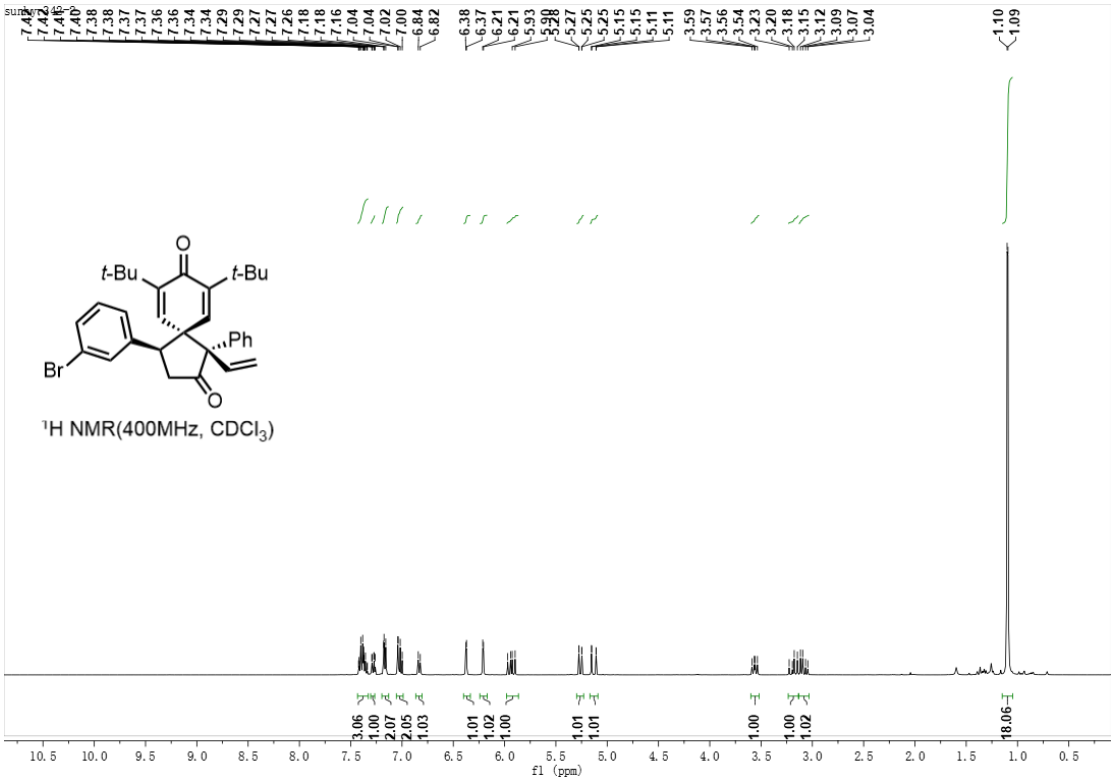


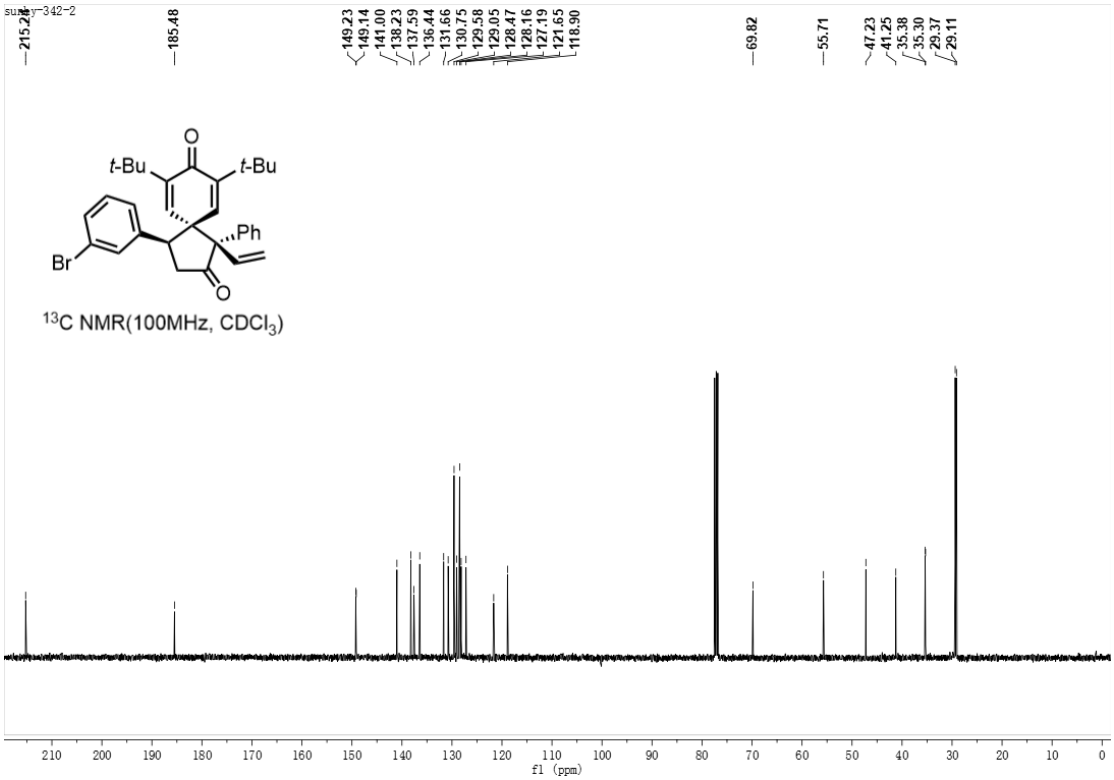
^{1}H NMR(400MHz, $CDCl_3$)

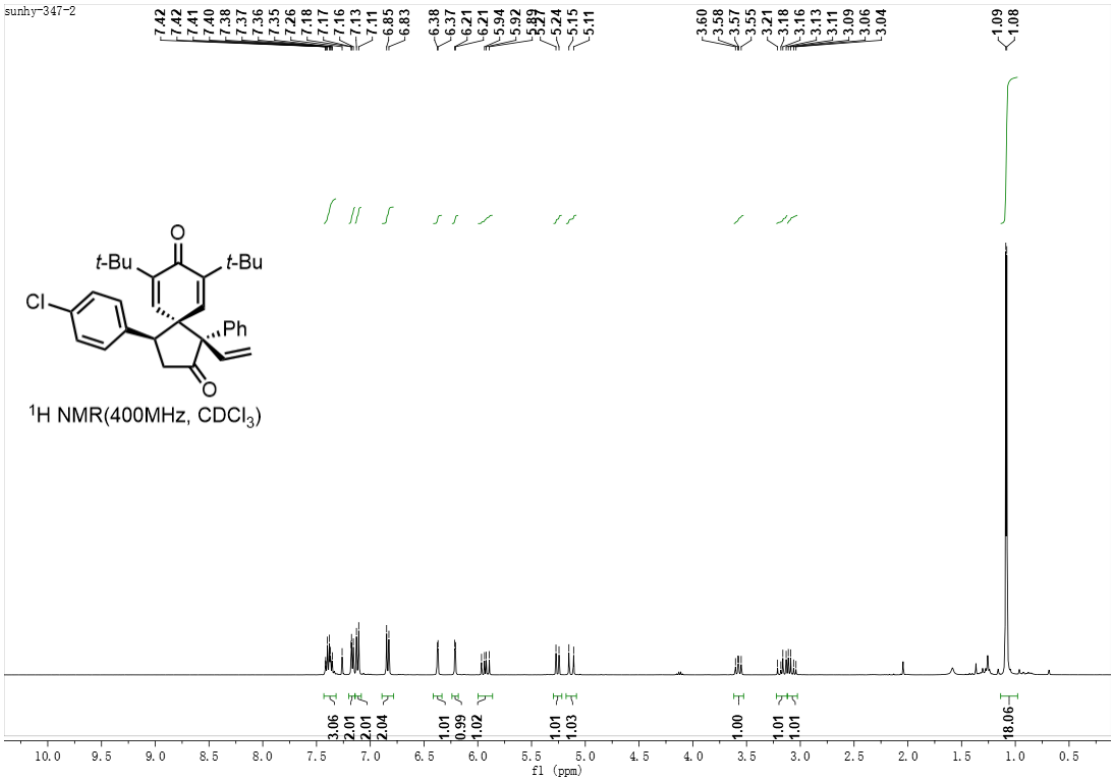

SHW-PMQ-PR-1
216.03
185.57
148.71
148.64
136.66
129.64
128.60
128.39
128.04
127.71
69.88
55.85
47.60
41.45
35.29
35.20
29.28
29.02
t-Bu
t-Bu
13C NMR(100MHz, CDCl3)
f1 (ppm)

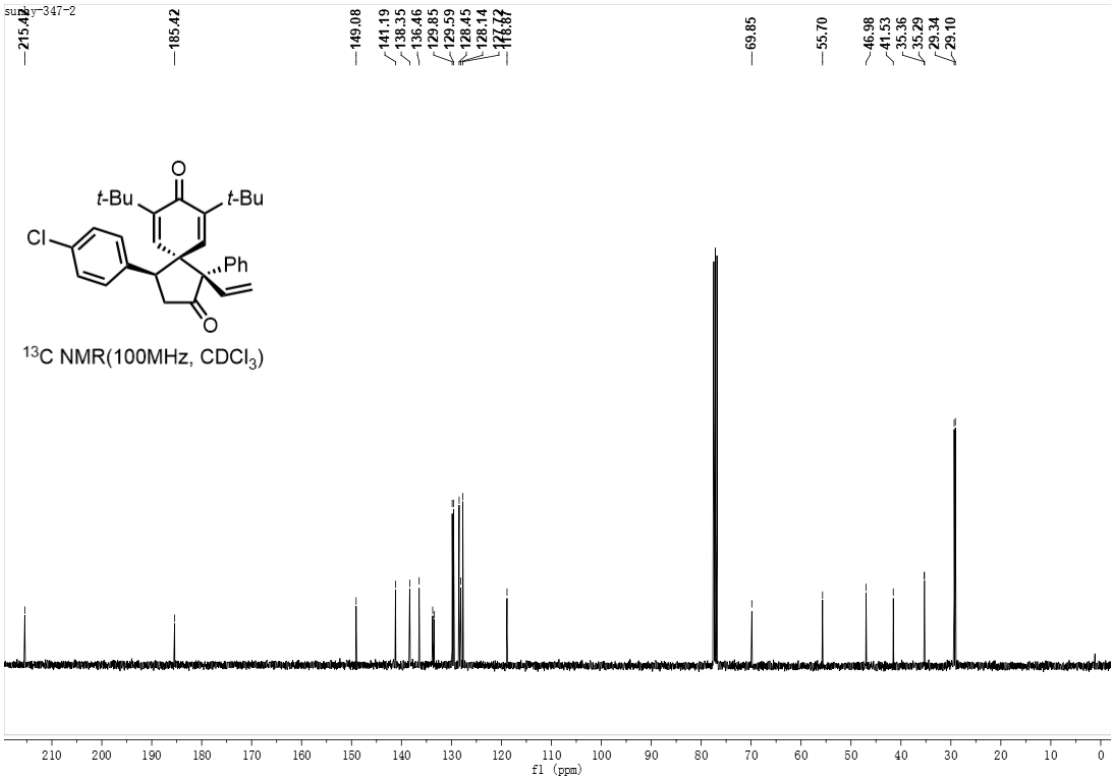

sunhy-341-2
7.41
7.40
7.38
7.36
7.35
7.34
7.33
7.19
7.17
7.05
7.03
7.01
6.96
6.94
6.71
6.69
6.41
6.40
6.23
6.22
5.98
5.95
5.93
5.91
5.26
5.24
5.15
5.11
3.60
3.58
3.57
3.55
3.29
3.25
3.24
3.20
3.10
3.08
3.05
3.03
2.21
1.08
1.07
t-Bu
t-Bu
Ph
Me
1H NMR(400MHz, CDCl3)
3.03
2.03
1.05
1.02
2.00
1.02
1.00
1.01
1.03
1.03
1.00
1.02
1.02
3.00
18.09
f1 (ppm)

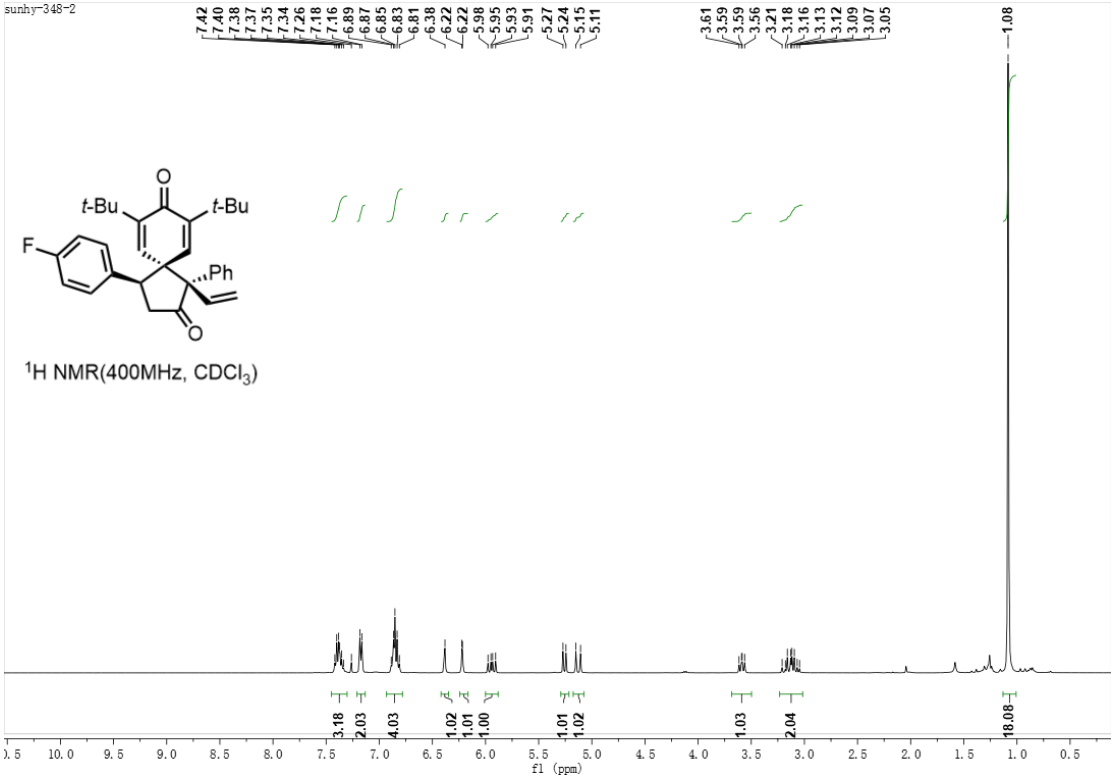

sunby-341-2
216.12
185.69
148.65
148.53
136.70
129.64
129.42
128.41
128.38
127.47
125.67
118.71
69.88
55.84
47.55
41.51
35.27
35.18
29.34
29.06
21.48
t-Bu
t-Bu
Ph
Me
O
O
13C NMR(100MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

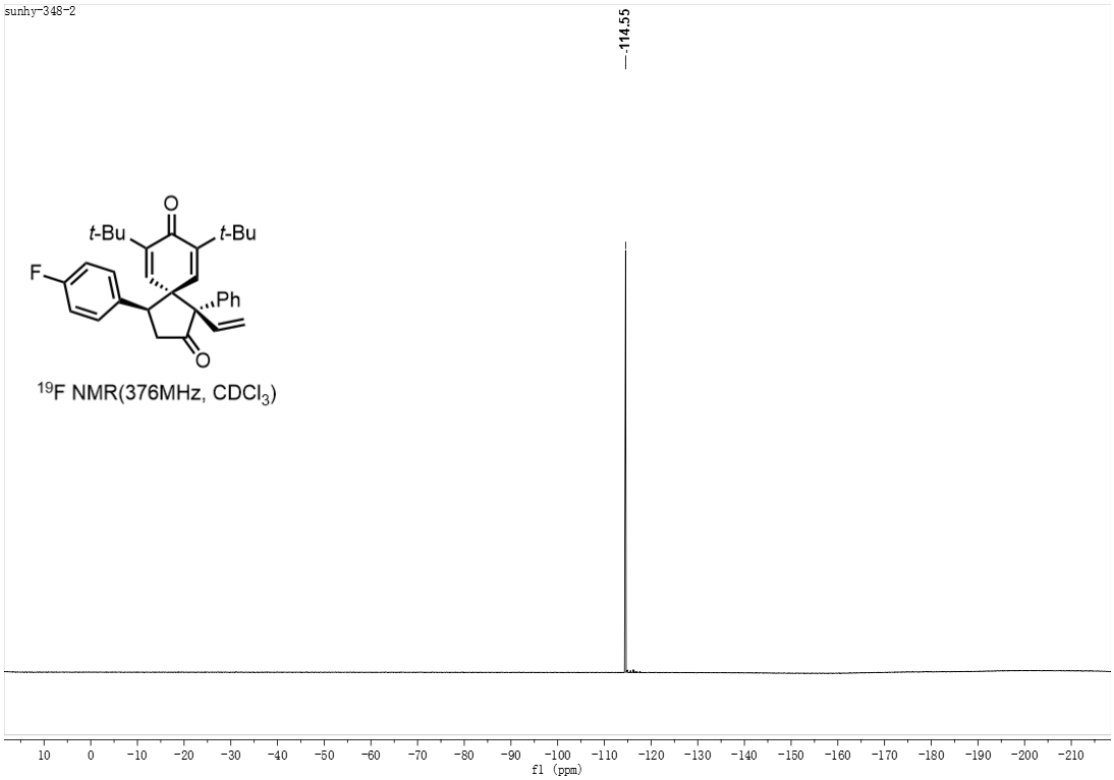

sunby-342-2
7.42
7.42
7.40
7.40
7.38
7.38
7.37
7.37
7.36
7.36
7.34
7.34
7.29
7.29
7.27
7.27
7.26
7.18
7.18
7.16
7.04
7.04
7.02
7.00
6.84
6.82
6.38
6.37
6.21
6.21
5.93
5.90
5.28
5.27
5.25
5.25
5.15
5.15
5.11
5.11
3.59
3.57
3.56
3.54
3.23
3.20
3.18
3.15
3.12
3.09
3.07
3.04
1.10
1.09
t-Bu
t-Bu
Ph
Br
O
O
1H NMR(400MHz, CDCl3)
3.06
1.00
2.07
2.05
1.03
1.01
1.02
1.00
1.01
1.01
1.00
1.00
1.02
18.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

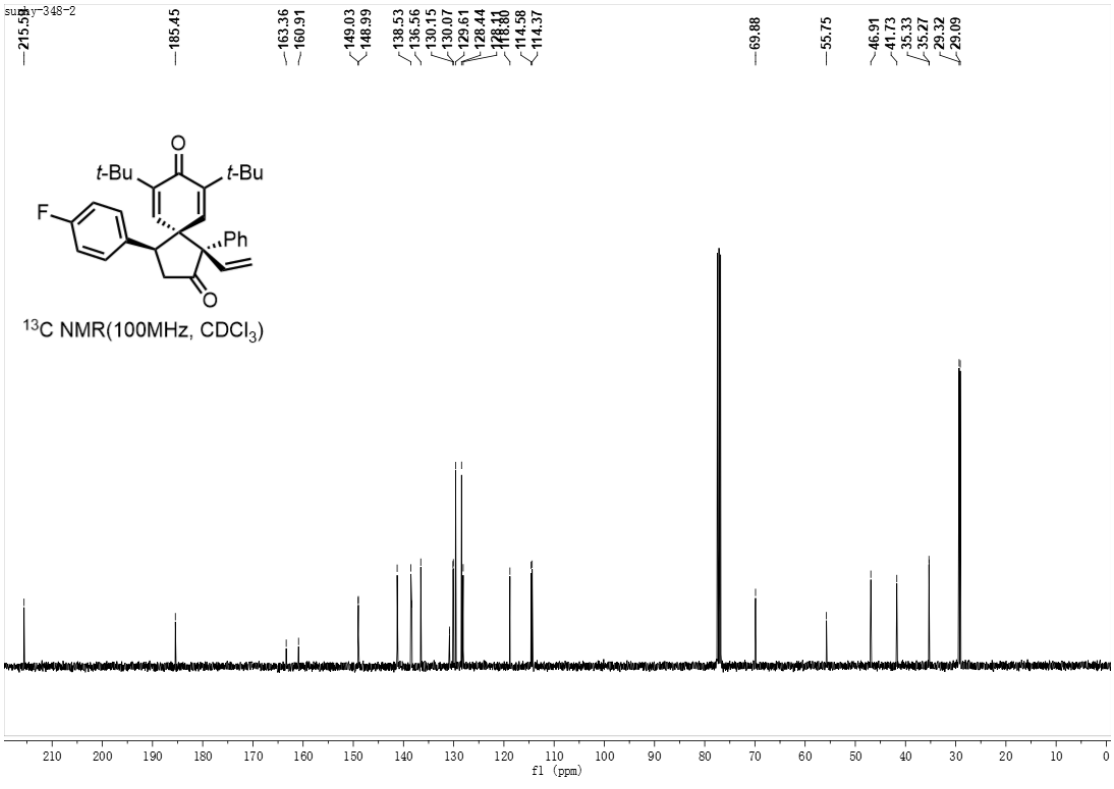

sunhy-342-2
215.24
185.48
149.23
149.14
141.00
138.23
137.59
136.44
131.66
130.75
129.58
129.05
128.47
128.16
127.19
121.65
118.90
69.82
55.71
47.23
41.25
35.38
35.30
29.37
29.11
t-Bu
t-Bu
Ph
Br
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)

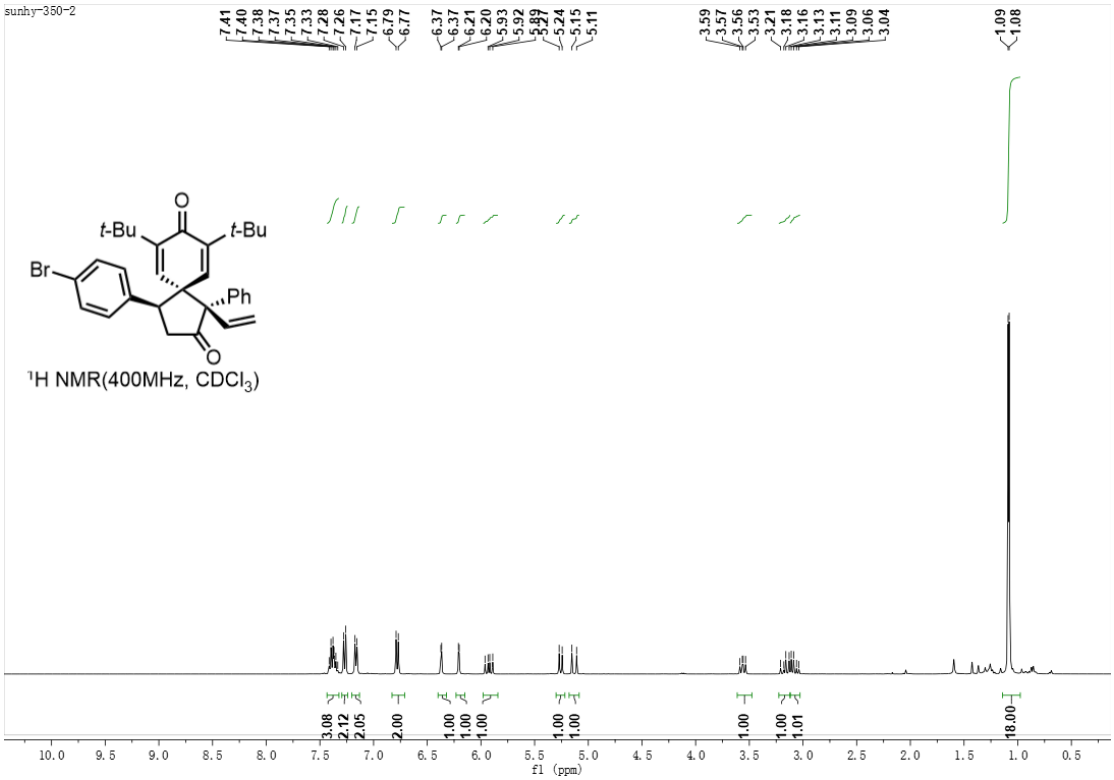

sunhy-347-2
7.42
7.42
7.41
7.40
7.38
7.37
7.36
7.35
7.26
7.18
7.17
7.16
7.13
7.11
6.85
6.83
6.38
6.37
6.21
6.21
5.94
5.92
5.89
5.27
5.24
5.15
5.11
3.60
3.58
3.57
3.55
3.21
3.18
3.16
3.13
3.11
3.09
3.06
3.04
1.09
1.08
t-Bu
t-Bu
Cl
Ph
O
O
1H NMR(400MHz, CDCl3)
3.06
2.01
2.01
2.04
1.01
0.99
1.02
1.01
1.03
1.00
1.01
1.01
18.06
f1 (ppm)

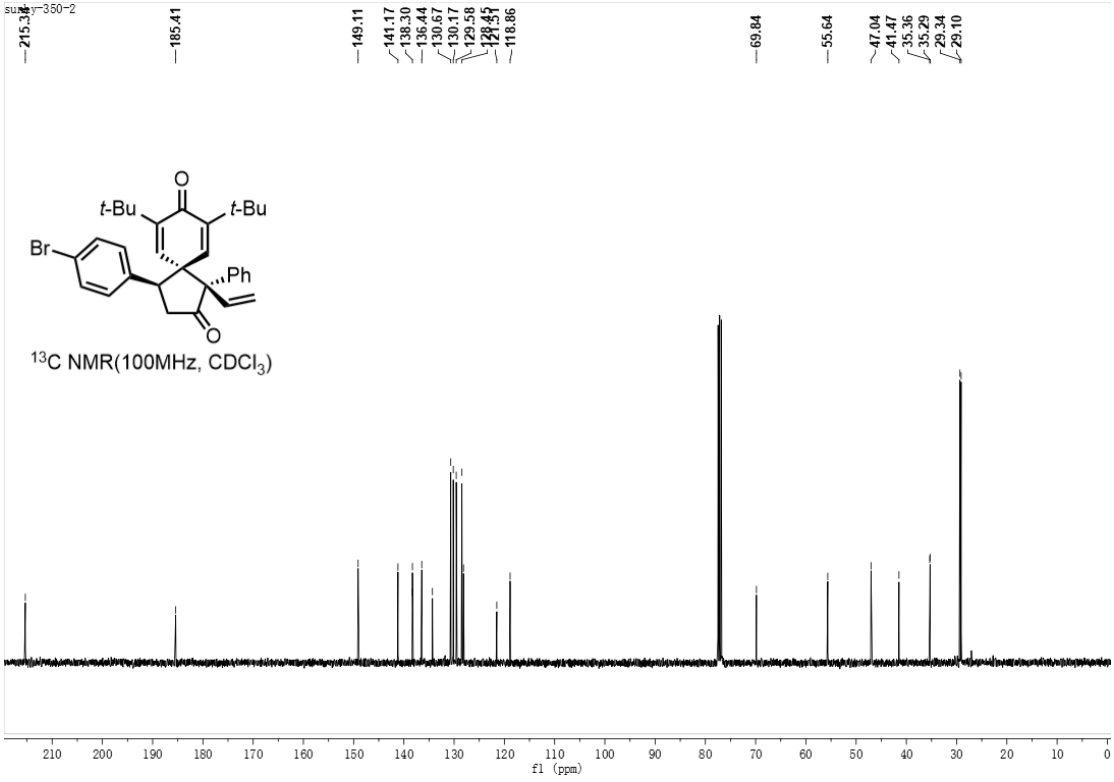

sunhy-347-2
215.42
185.42
149.08
141.19
138.35
136.46
129.85
129.59
128.45
128.14
69.85
55.70
46.98
41.53
35.36
35.29
29.34
29.10
t-Bu
t-Bu
Cl
Ph
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)

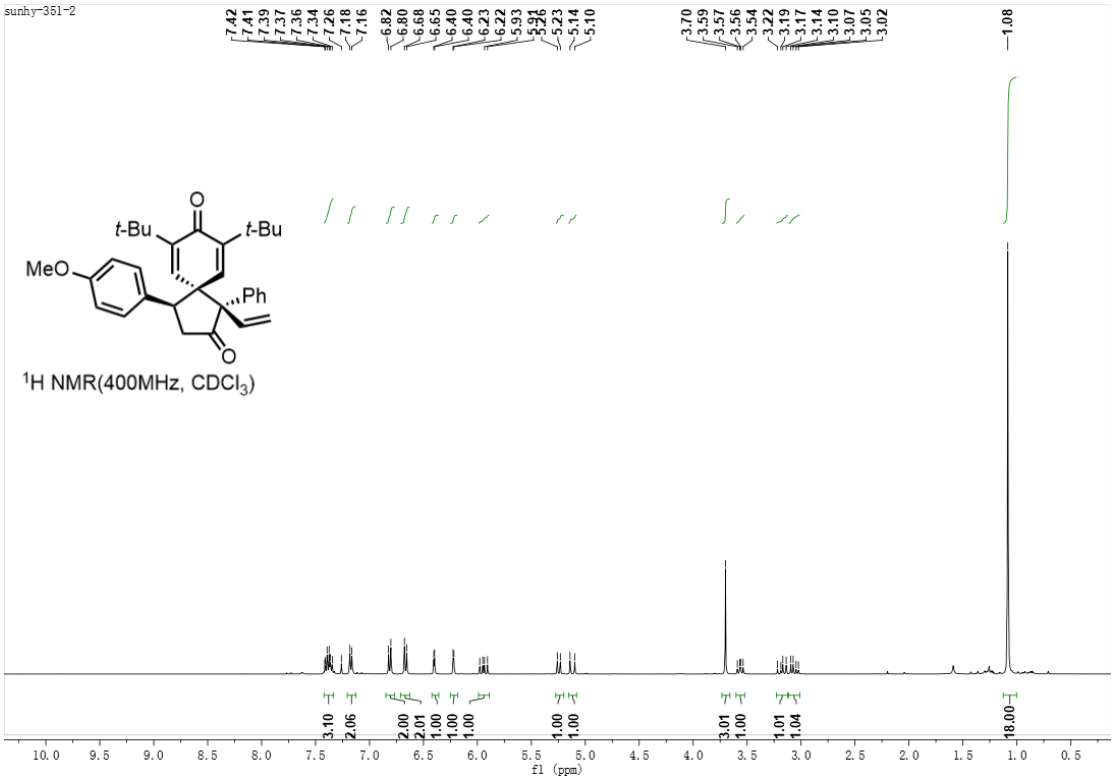

sunhy-348-2
7.42
7.40
7.38
7.37
7.35
7.34
7.26
7.18
7.16
6.89
6.87
6.85
6.83
6.81
6.38
6.22
6.22
5.98
5.95
5.93
5.91
5.27
5.24
5.15
5.11
3.61
3.59
3.59
3.56
3.21
3.18
3.16
3.13
3.12
3.09
3.07
3.05
1.08
t-Bu
t-Bu
F
Ph
O
O
1H NMR(400MHz, CDCl3)
3.18
2.03
4.03
1.02
1.01
1.00
1.01
1.02
1.03
2.04
18.08
f1 (ppm)

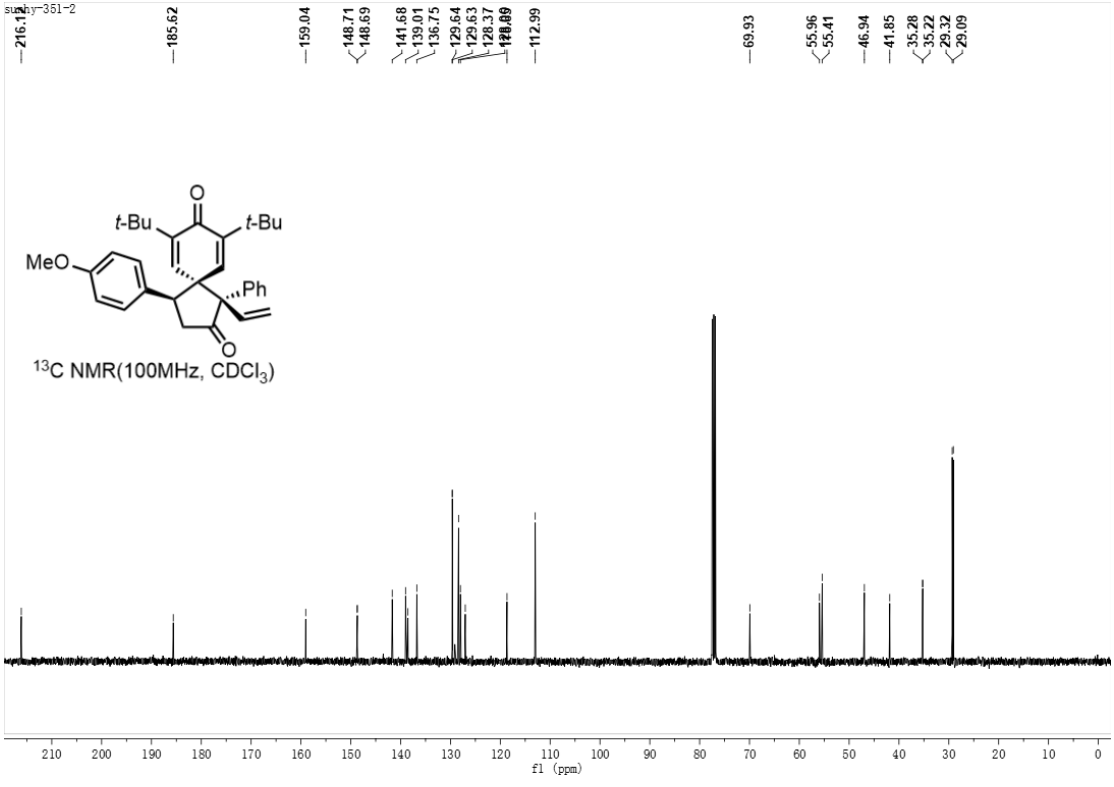

sunhy-348-2
-114.55
t-Bu
t-Bu
F
Ph
O
O
19F NMR(376MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

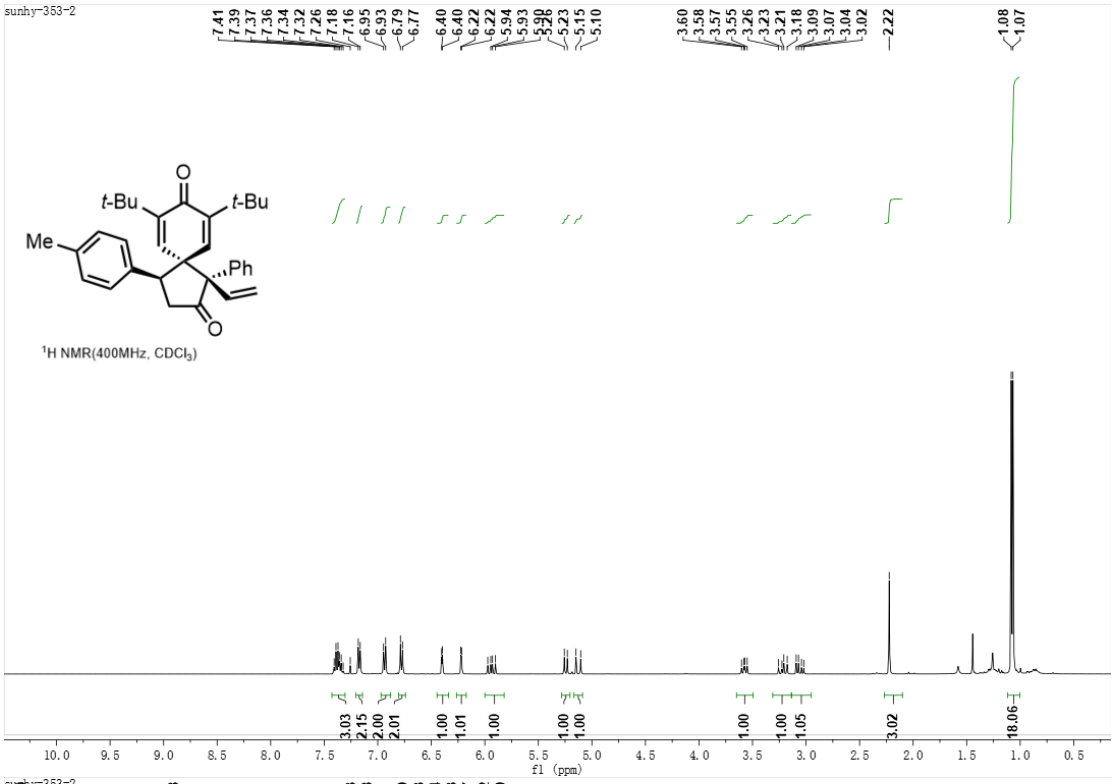

sunhy-348-2
215.58
185.45
163.36
160.91
149.03
148.99
138.53
136.56
130.15
130.07
129.61
128.44
114.58
114.37
69.88
55.75
46.91
41.73
35.33
35.27
29.32
29.09
t-Bu
t-Bu
F
Ph
O
O
13C NMR(100MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

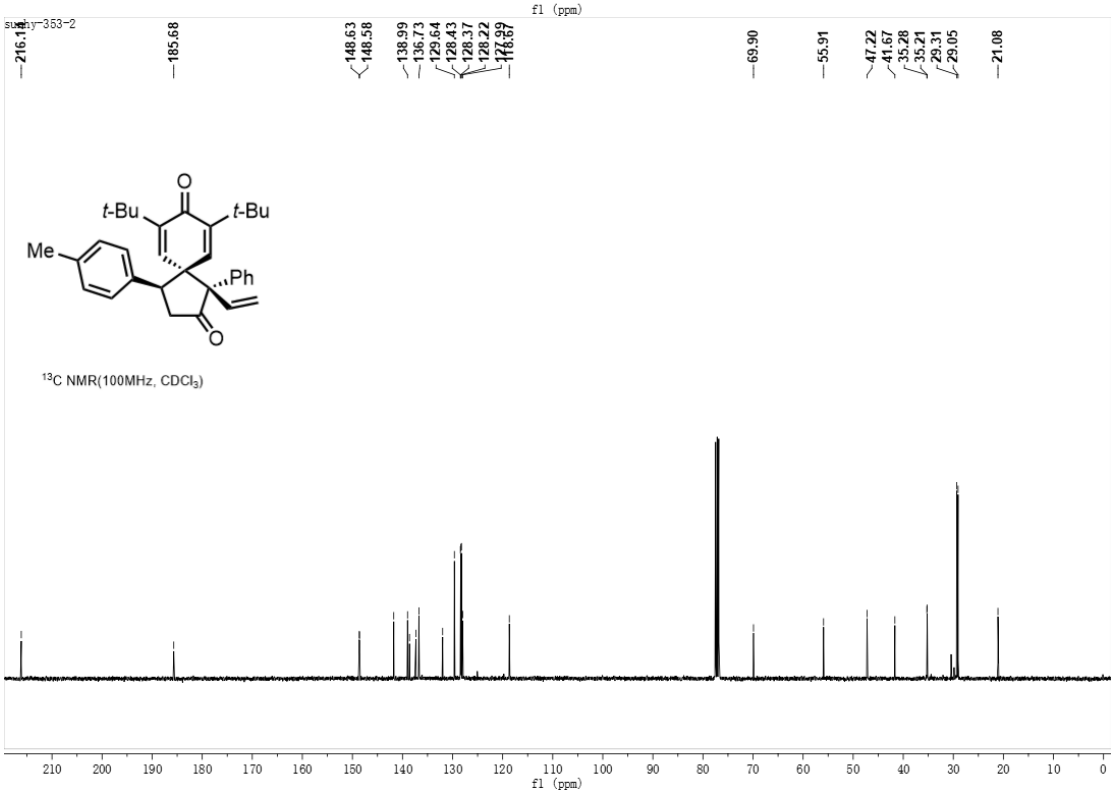

sunhy-350-2
t-Bu
t-Bu
Br
Ph
O
O
1H NMR(400MHz, CDCl3)
f1 (ppm)

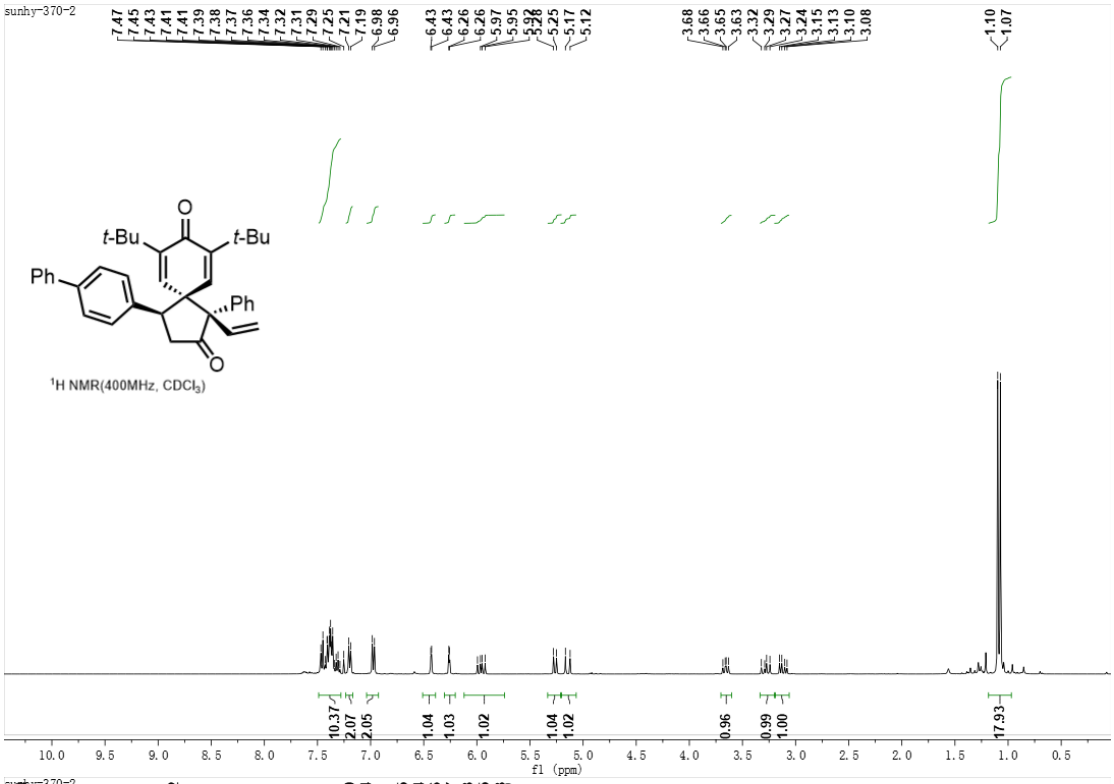

sunhy-350-2
t-Bu
t-Bu
Br
Ph
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)

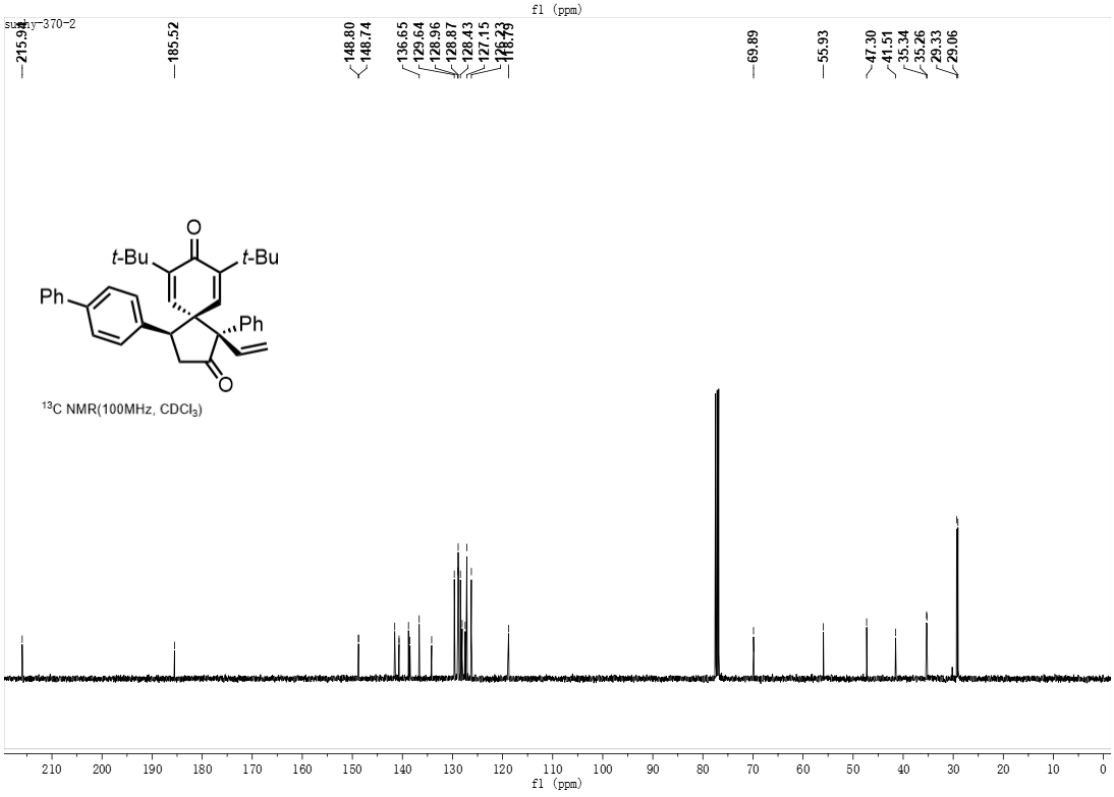

sunhy-351-2
7.42
7.41
7.39
7.37
7.36
7.34
7.26
7.18
7.16
6.82
6.80
6.68
6.65
6.40
6.40
6.23
6.22
5.93
5.91
5.26
5.23
5.14
5.10
3.70
3.59
3.57
3.56
3.54
3.22
3.19
3.17
3.14
3.10
3.07
3.05
3.02
1.08
t-Bu
t-Bu
MeO
Ph
O
O
1H NMR(400MHz, CDCl3)
3.10
2.06
2.00
2.01
1.00
1.00
1.00
1.00
1.00
3.01
1.00
1.01
1.04
18.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

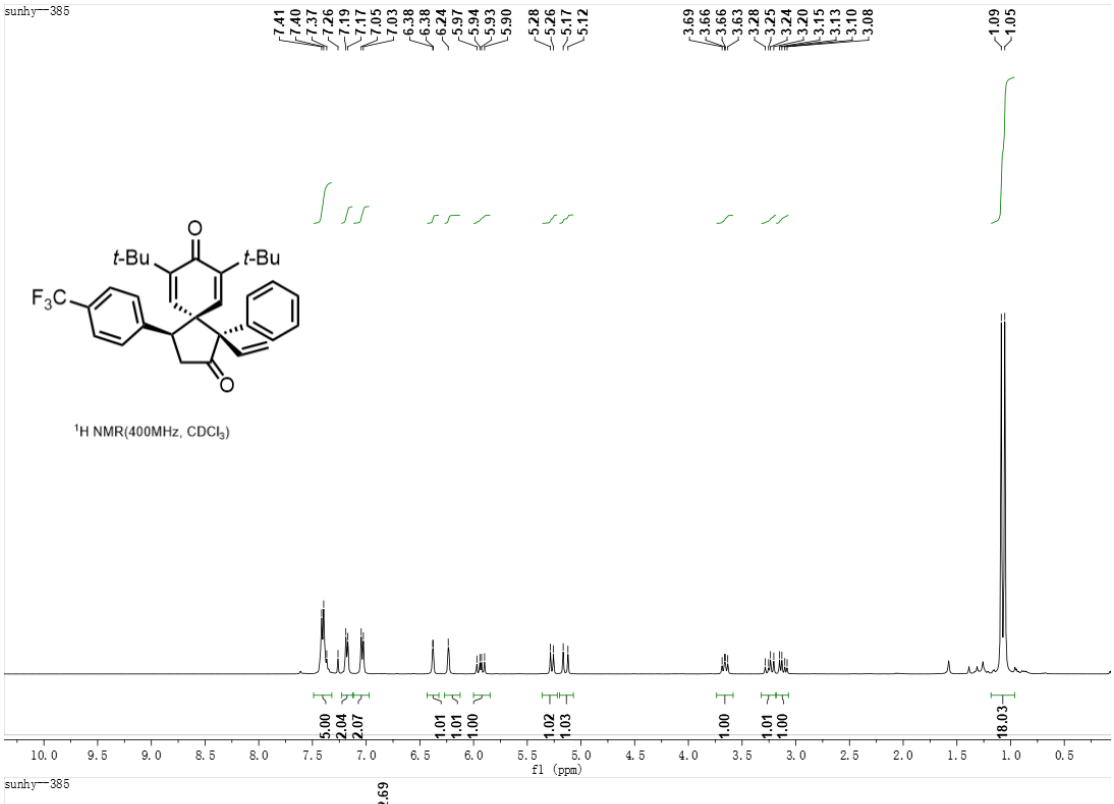

sunhy-351-2
216.12
185.62
159.04
148.71
148.69
141.68
139.01
136.75
129.64
129.63
128.37
112.99
69.93
55.96
55.41
46.94
41.85
35.28
35.22
29.32
29.09
t-Bu
t-Bu
MeO
Ph
O
O
13C NMR(100MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


sunhy-353-2
t-Bu
t-Bu
Me
Ph
O
O
1H NMR(400MHz, CDCl3)
f1 (ppm)

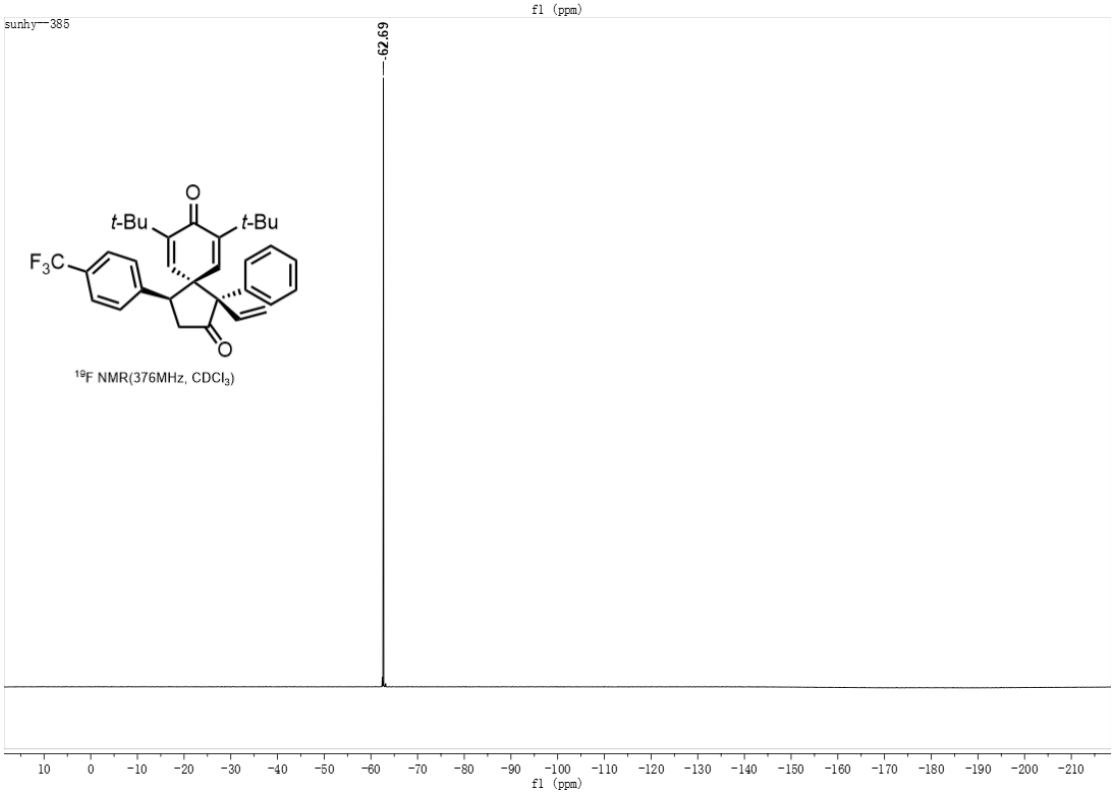

sunhy-353-2
t-Bu
t-Bu
Me
Ph
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)


sunhy-370-2
7.47 7.45 7.43 7.41 7.41 7.39 7.38 7.37 7.36 7.34 7.32 7.31 7.29 7.25 7.21 7.19 6.98 6.96
6.43 6.43 6.26 6.26 5.97 5.95 5.28 5.25 5.17 5.12
3.68 3.66 3.65 3.63 3.32 3.29 3.27 3.24 3.15 3.13 3.10 3.08
1.10 1.07
t-Bu
t-Bu
Ph
Ph
O
O
1H NMR(400MHz, CDCl3)
10.37 2.07 2.05 1.04 1.03 1.02 1.04 1.02 0.96 0.99 1.00 17.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

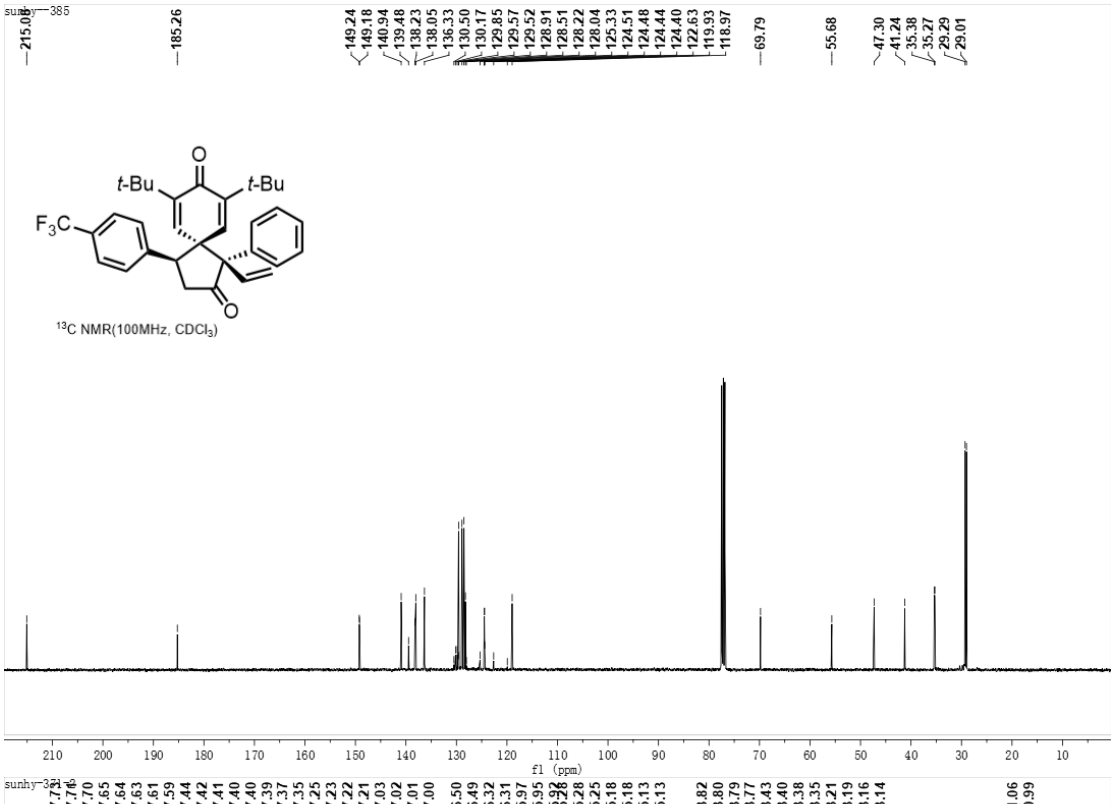

sunhy-370-2
215.94
185.52
148.80 148.74
136.65 129.64 128.96 128.87 128.43 127.15 126.23 118.79
69.89
55.93
47.30 41.51 35.34 35.26 29.33 29.06
t-Bu
t-Bu
Ph
Ph
O
O
13C NMR(100MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

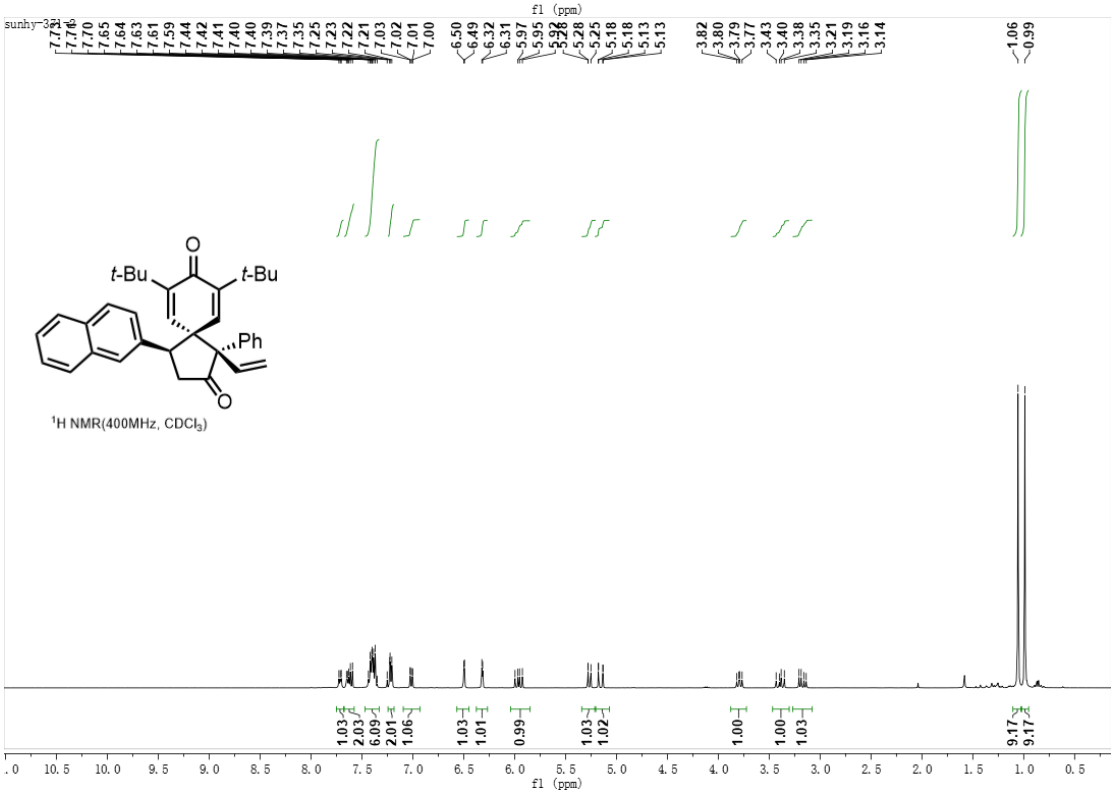


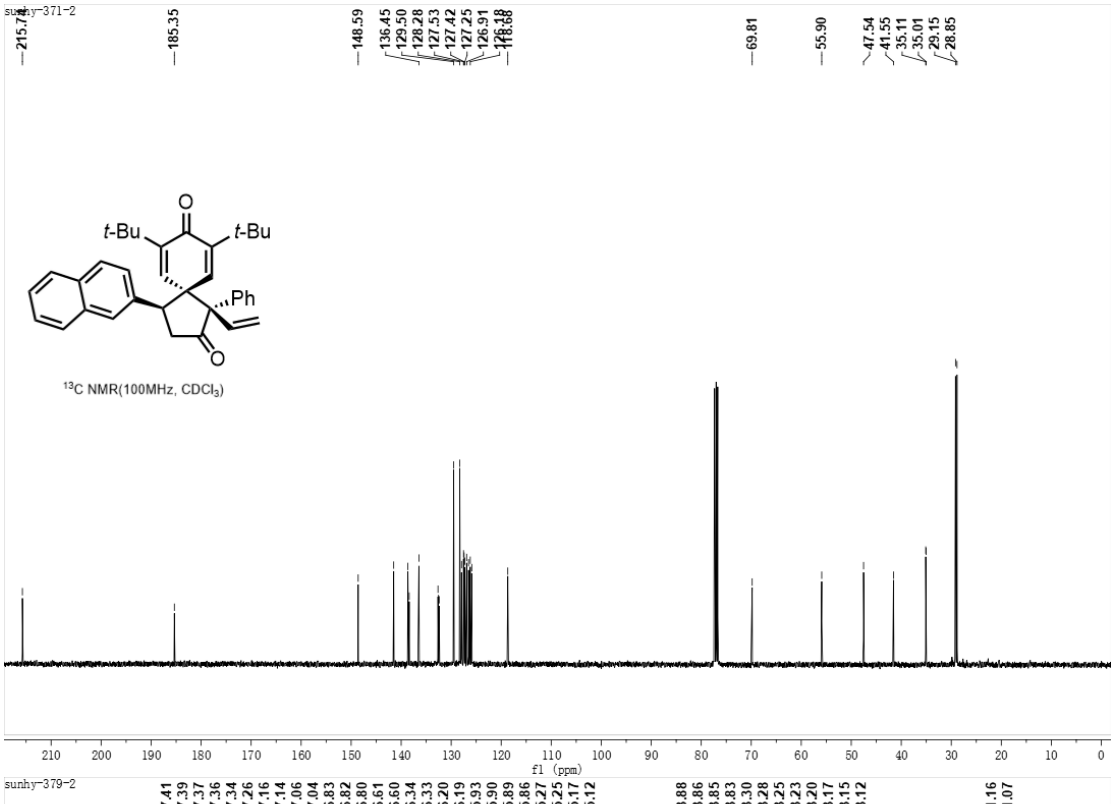
^{1}H NMR(400MHz, $CDCl_3$)

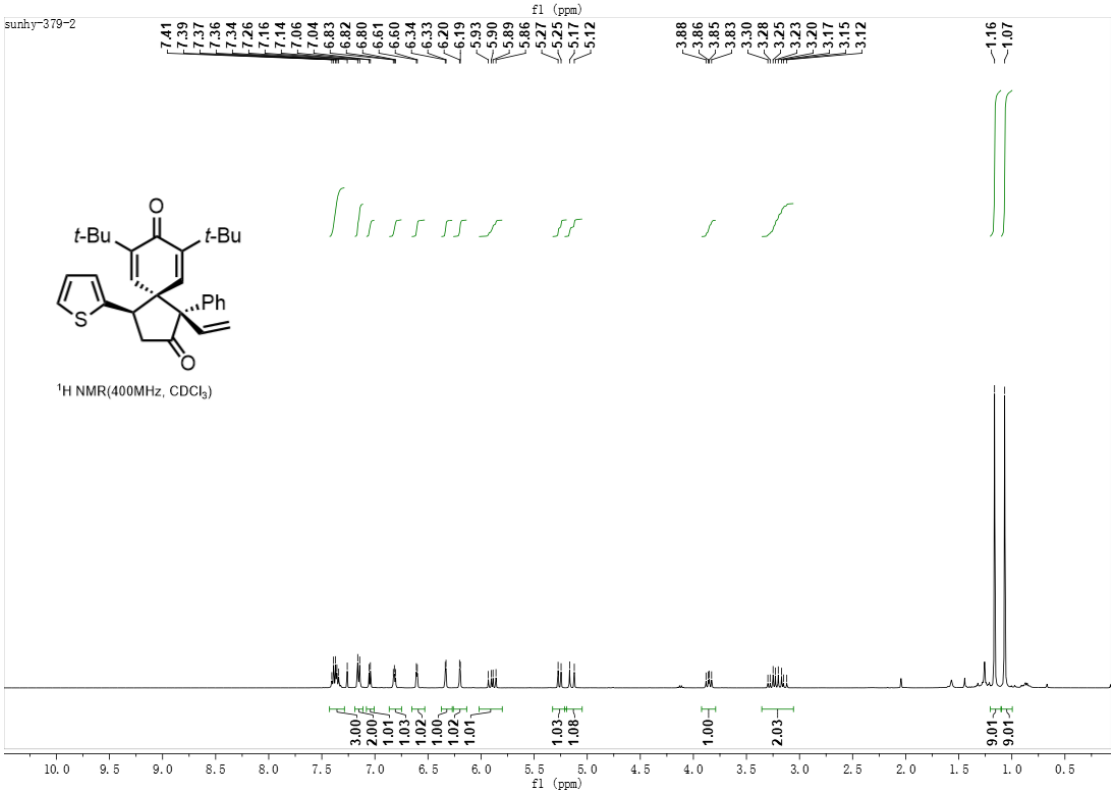


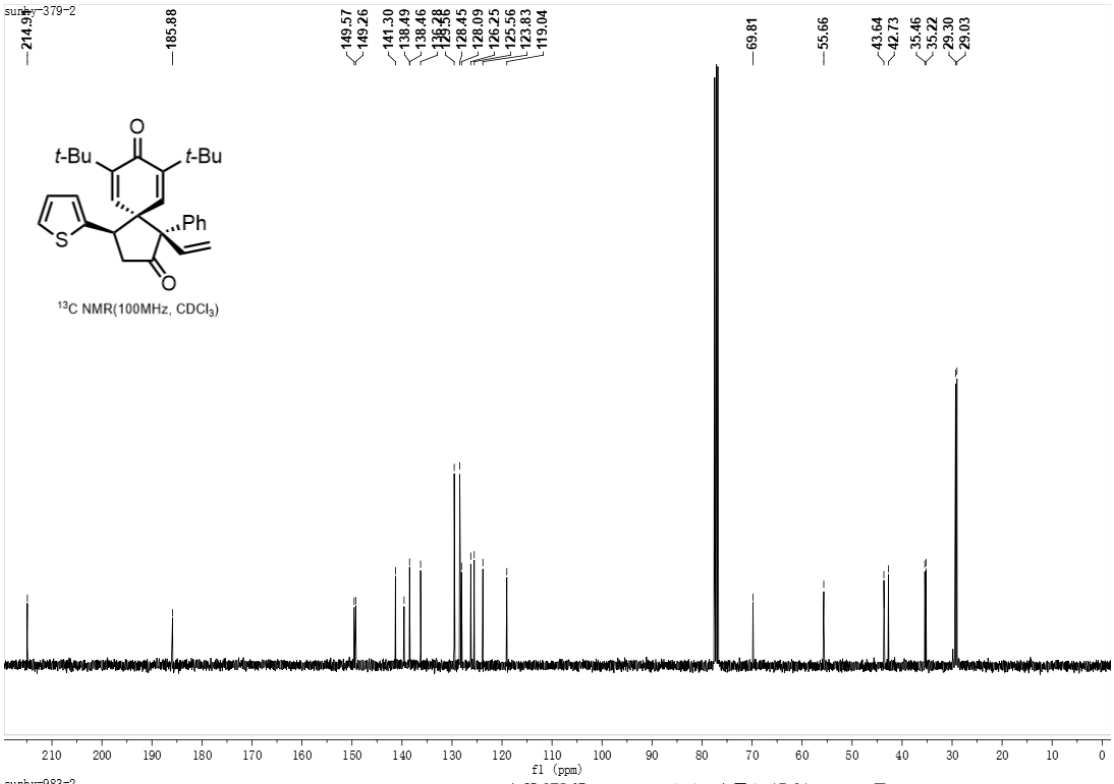
^{19}F NMR(376MHz, $CDCl_3$)

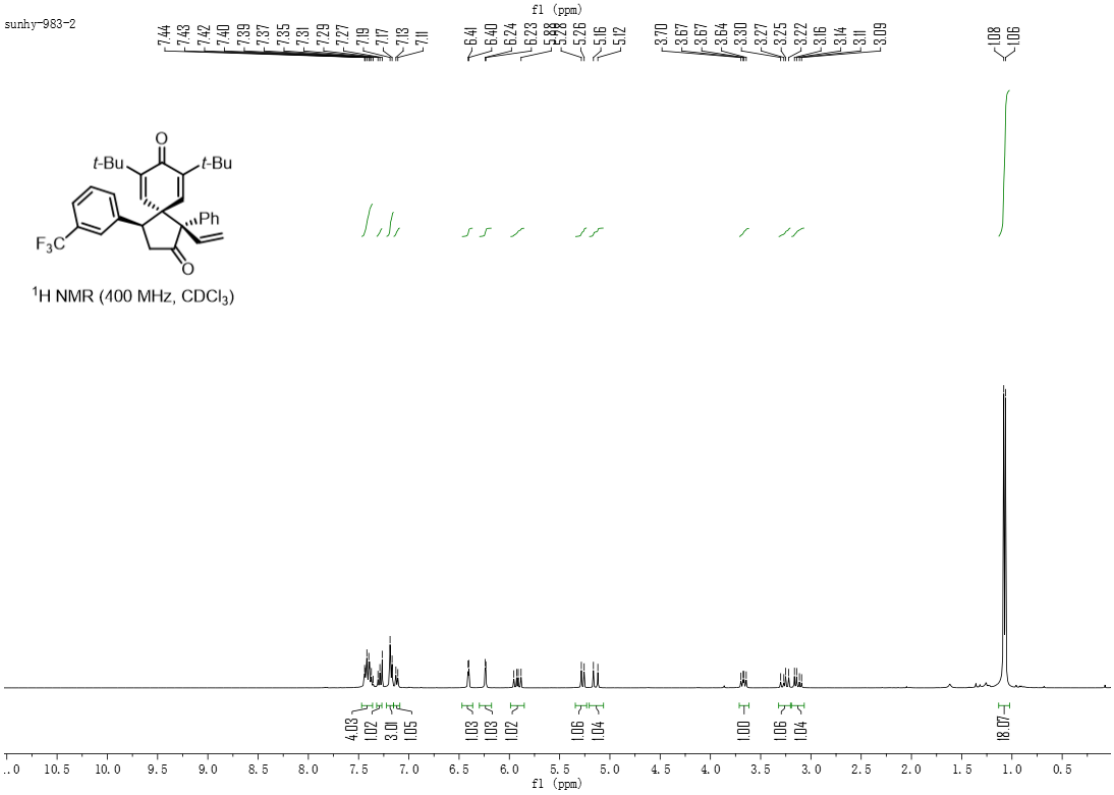

sunhy-385
215.08
185.26
149.24
149.18
140.94
139.48
138.23
138.05
136.33
130.50
130.17
129.85
129.57
129.52
128.91
128.51
128.22
128.04
125.33
124.51
124.48
124.44
124.40
122.63
119.93
118.97
69.79
55.68
47.30
41.24
35.38
35.27
29.29
29.01
t-Bu
t-Bu
F3C
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)

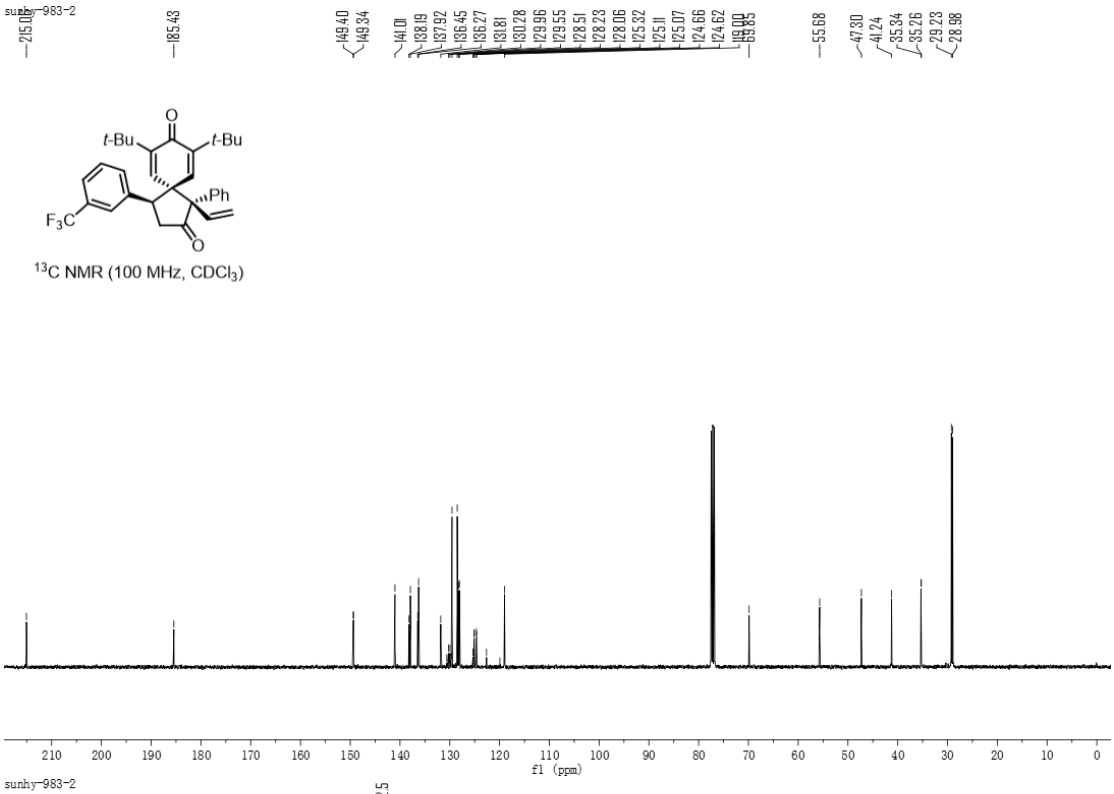

sunhy-321
7.76
7.70
7.65
7.64
7.63
7.61
7.59
7.44
7.42
7.41
7.40
7.40
7.39
7.37
7.35
7.25
7.23
7.22
7.21
7.03
7.02
7.01
7.00
6.50
6.49
6.32
6.31
5.97
5.95
5.28
5.25
5.18
5.13
5.13
3.82
3.80
3.79
3.77
3.43
3.40
3.38
3.35
3.21
3.19
3.16
3.14
1.06
0.99
t-Bu
t-Bu
Ph
O
O
1H NMR(400MHz, CDCl3)
1.03
2.03
6.09
2.01
1.06
1.03
1.01
0.99
1.03
1.02
1.00
1.00
1.03
9.17
9.17
f1 (ppm)

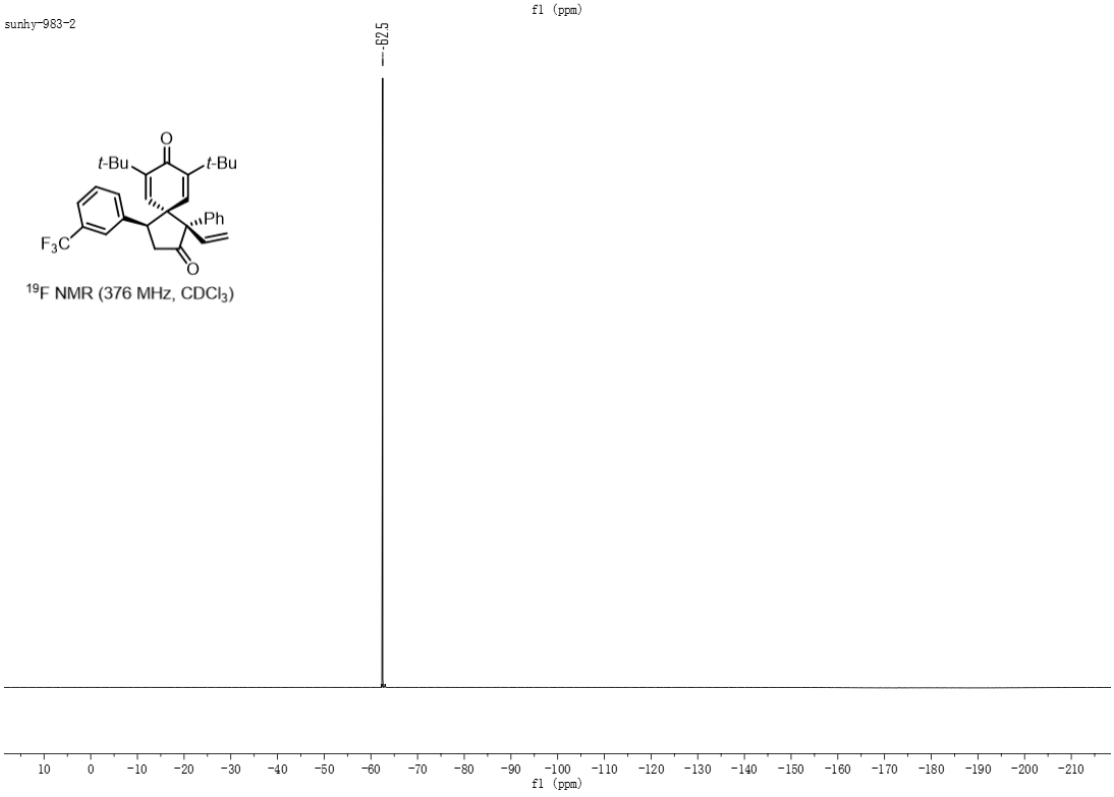

sunhy-371-2
215.74
185.35
148.59
136.45
129.50
128.28
127.53
127.42
127.25
126.91
126.18
118.88
69.81
55.90
47.54
41.55
35.11
35.01
29.15
28.85
t-Bu
t-Bu
Ph
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)

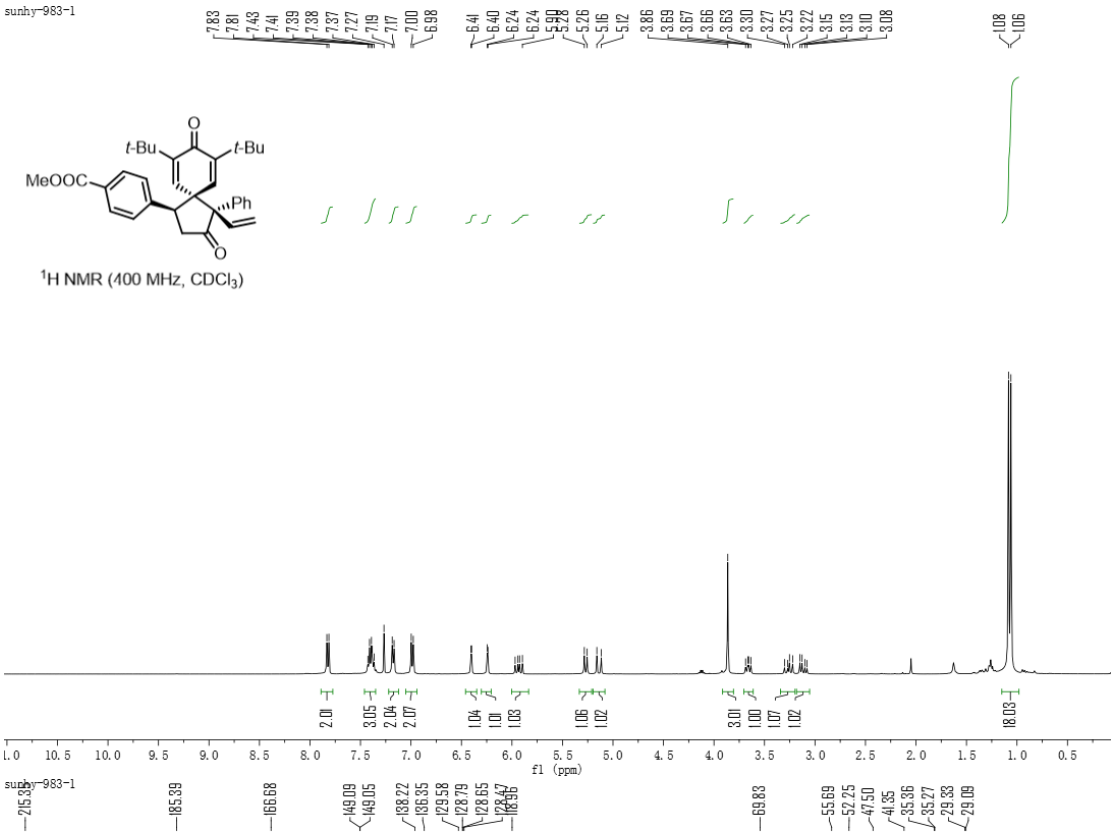

sunhy-379-2
7.41
7.39
7.37
7.36
7.34
7.26
7.16
7.14
7.06
7.04
6.83
6.82
6.80
6.61
6.60
6.34
6.33
6.20
6.19
5.93
5.90
5.89
5.86
5.27
5.25
5.17
5.12
3.88
3.86
3.85
3.83
3.30
3.28
3.25
3.23
3.20
3.17
3.15
3.12
1.16
1.07
t-Bu
t-Bu
Ph
S
O
O
1H NMR(400MHz, CDCl3)
3.00
2.00
1.01
1.03
1.02
1.00
1.02
1.01
1.03
1.08
1.00
2.03
9.01
9.01
f1 (ppm)


sunhy-379-2
214.97
185.88
149.57
149.26
141.30
138.49
138.46
128.45
128.09
126.25
125.56
123.83
119.04
69.81
55.66
43.64
42.73
35.46
35.22
29.30
29.03
t-Bu
t-Bu
Ph
S
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)

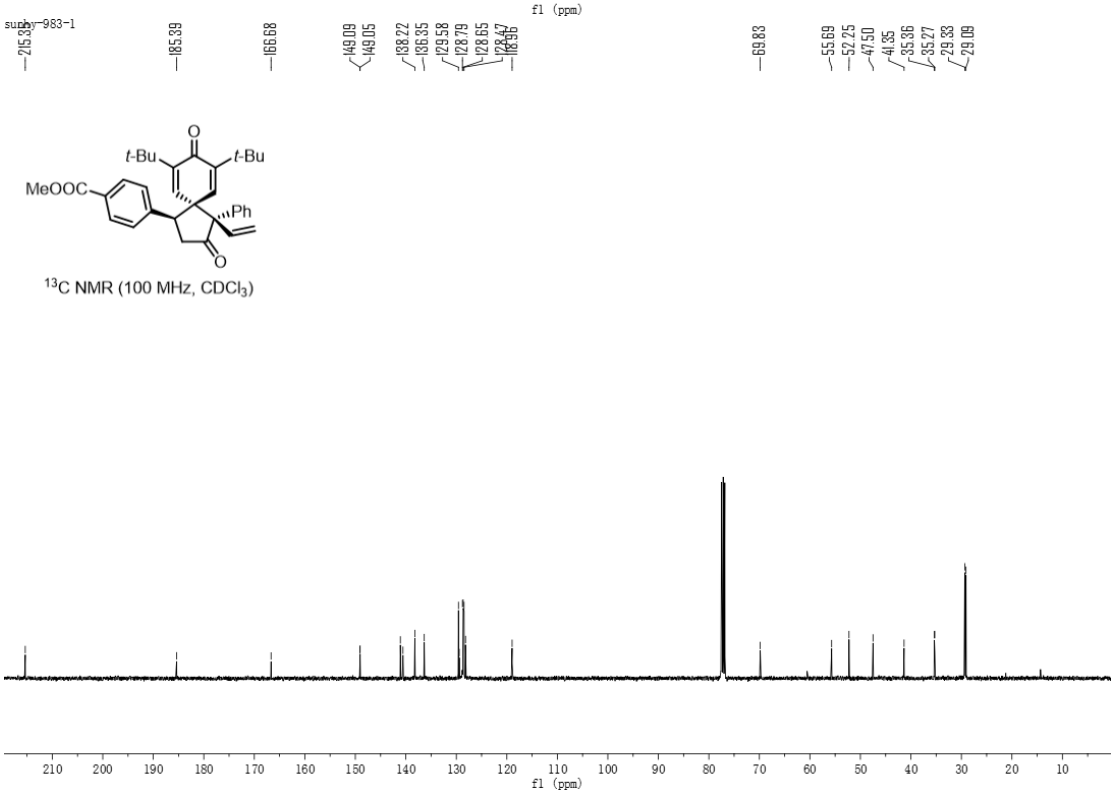

sunhy-983-2
7.44
7.43
7.42
7.40
7.39
7.37
7.35
7.31
7.29
7.27
7.19
7.17
7.13
7.11
6.41
6.40
6.24
6.23
5.88
5.26
5.16
5.12
3.70
3.67
3.67
3.64
3.30
3.27
3.25
3.22
3.16
3.14
3.11
3.09
1.08
1.06
t-Bu
t-Bu
Ph
F3C
O
O
1H NMR (400 MHz, CDCl3)
4.03
1.02
3.01
1.05
1.03
1.03
1.02
1.06
1.04
1.00
1.06
1.04
18.07
f1 (ppm)


sunhy-983-2
215.08
185.43
149.40
149.34
141.01
138.19
137.92
136.45
136.27
131.81
130.28
129.96
129.55
128.51
128.23
128.06
125.32
125.11
125.07
124.66
124.62
119.00
69.85
55.68
47.30
41.24
35.34
35.26
29.23
28.98
t-Bu
t-Bu
Ph
F3C
O
O
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

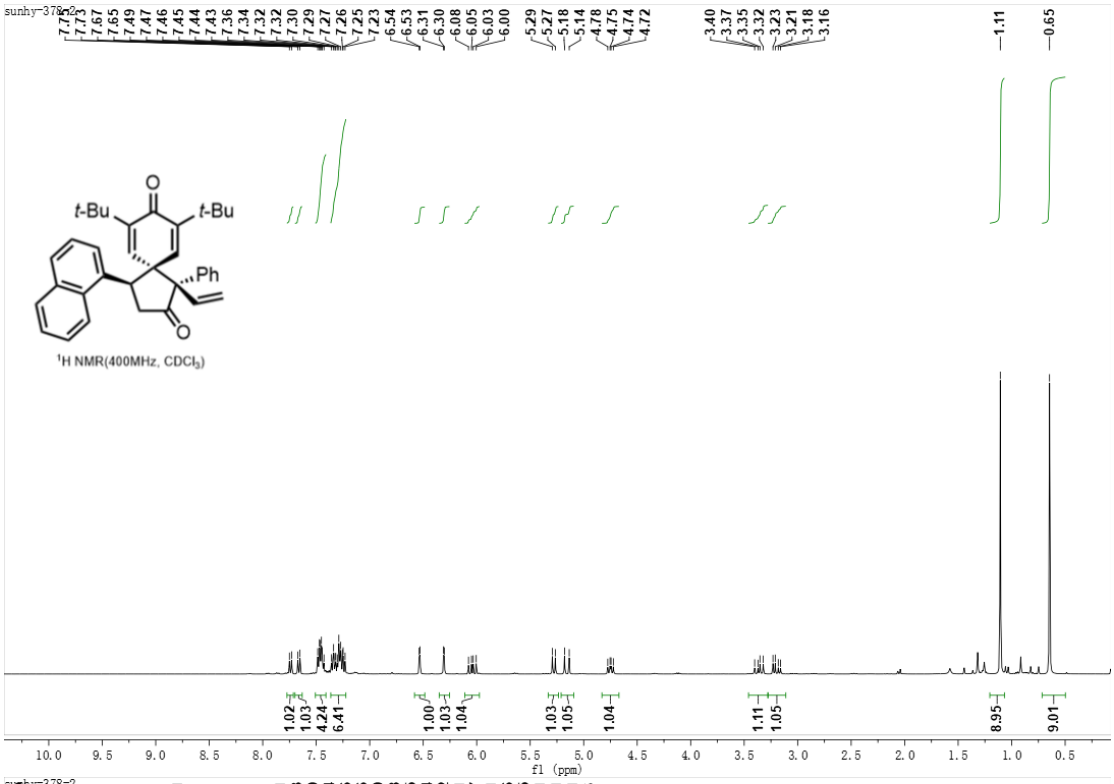

sunhy-983-2
-62.5
t-Bu
t-Bu
Ph
F3C
O
O
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

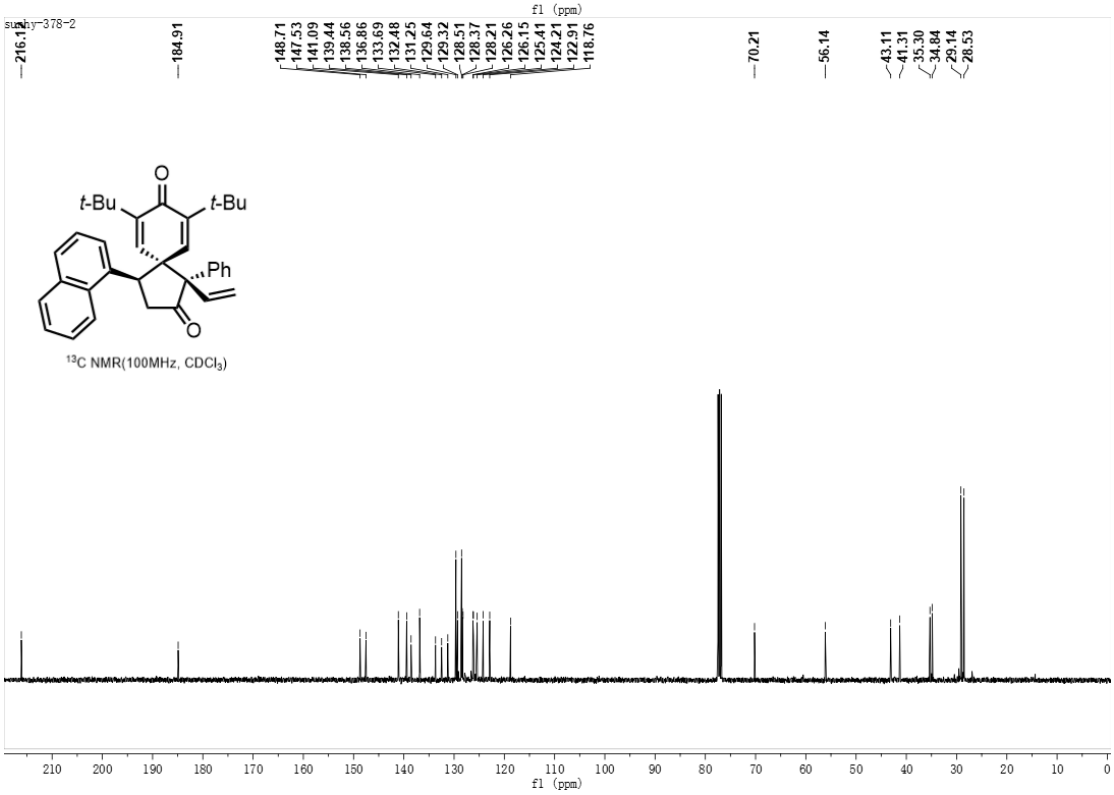


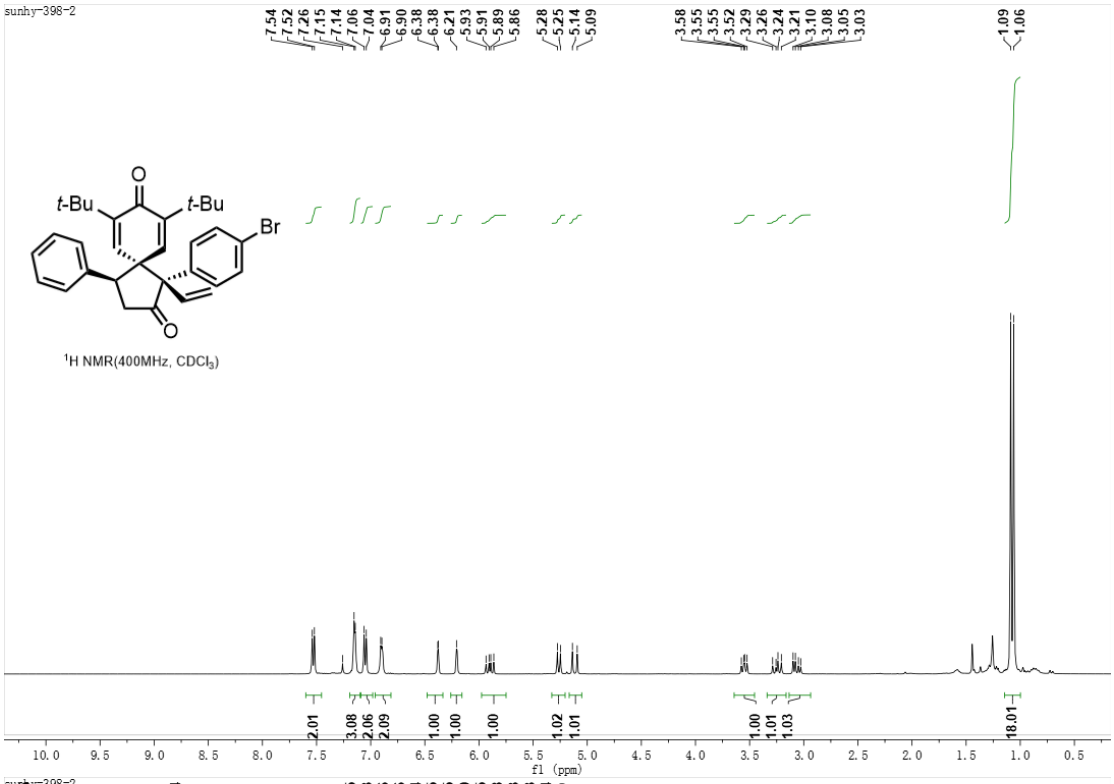
^{1}H NMR (400 MHz, $CDCl_3$)



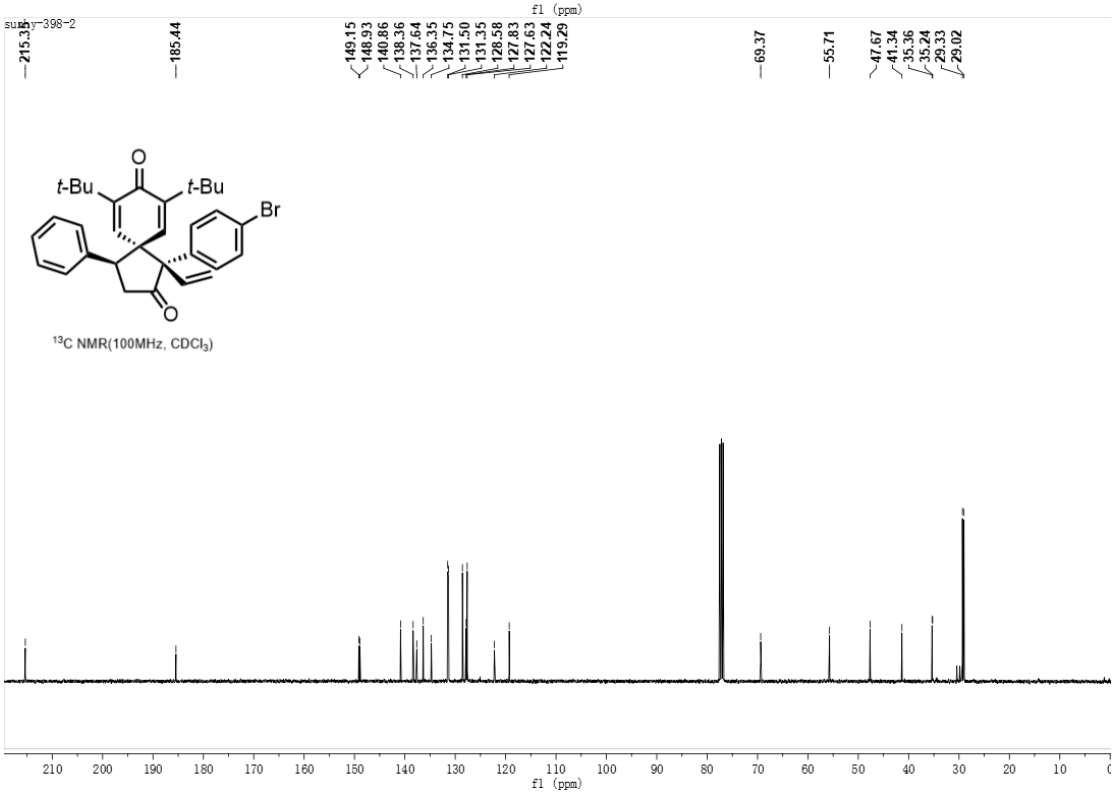
^{13}C NMR (100 MHz, $CDCl_3$)


sunhy-378-2
t-Bu
t-Bu
Ph
O
O
1H NMR(400MHz, CDCl3)
f1 (ppm)

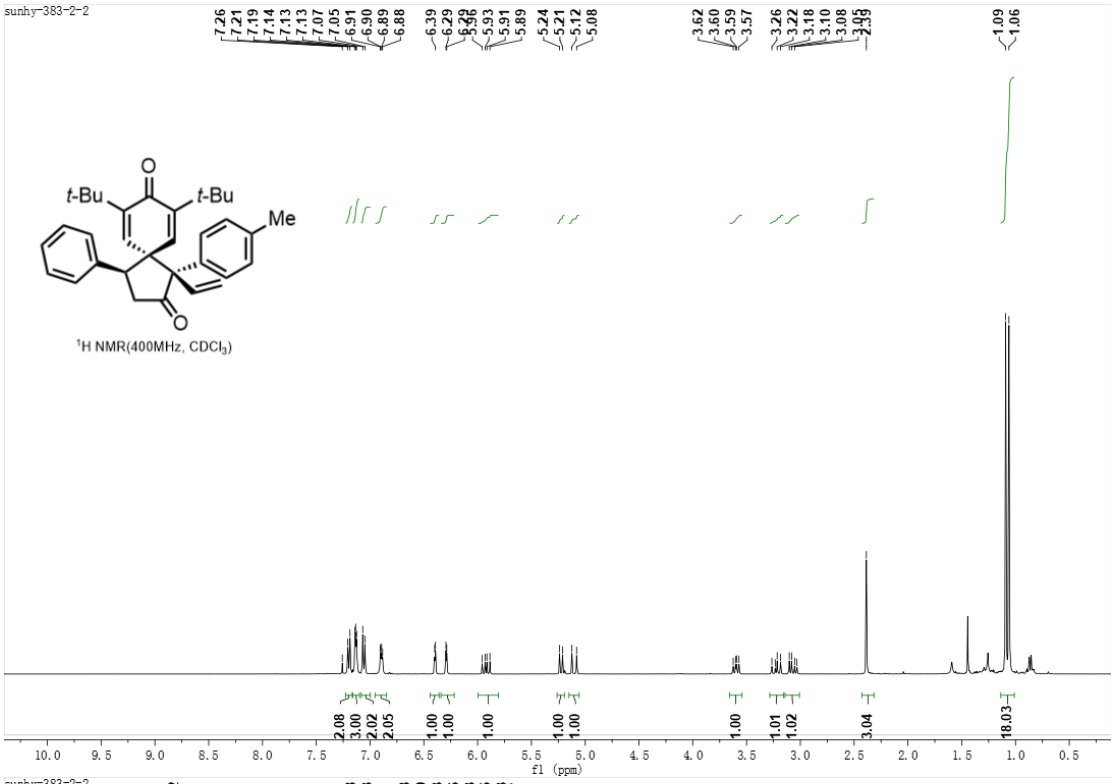

sunhy-378-2
t-Bu
t-Bu
Ph
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)

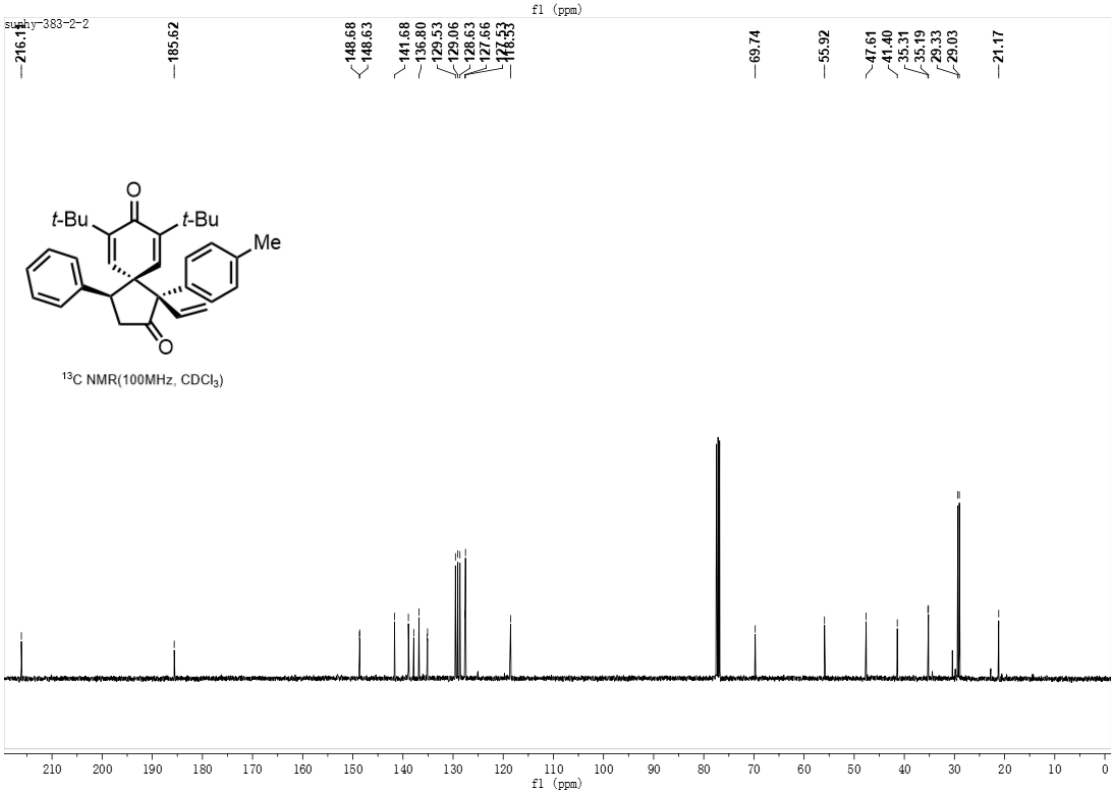


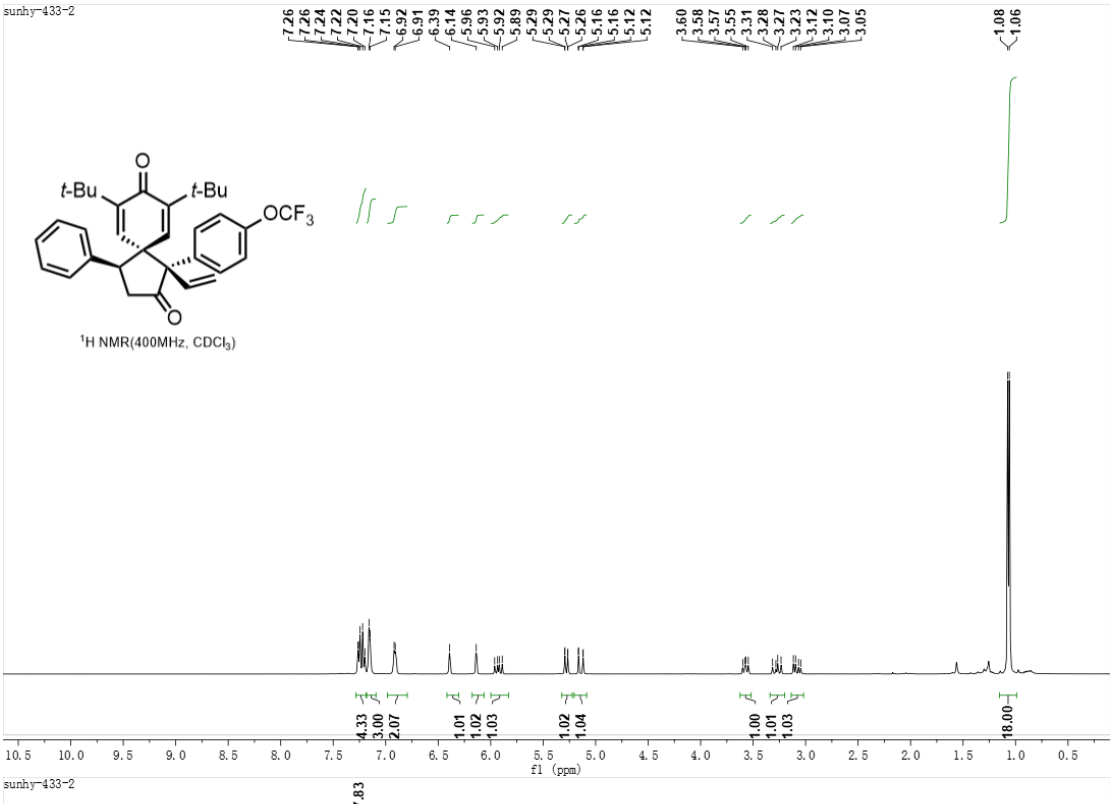
^{1}H NMR(400MHz, $CDCl_3$)

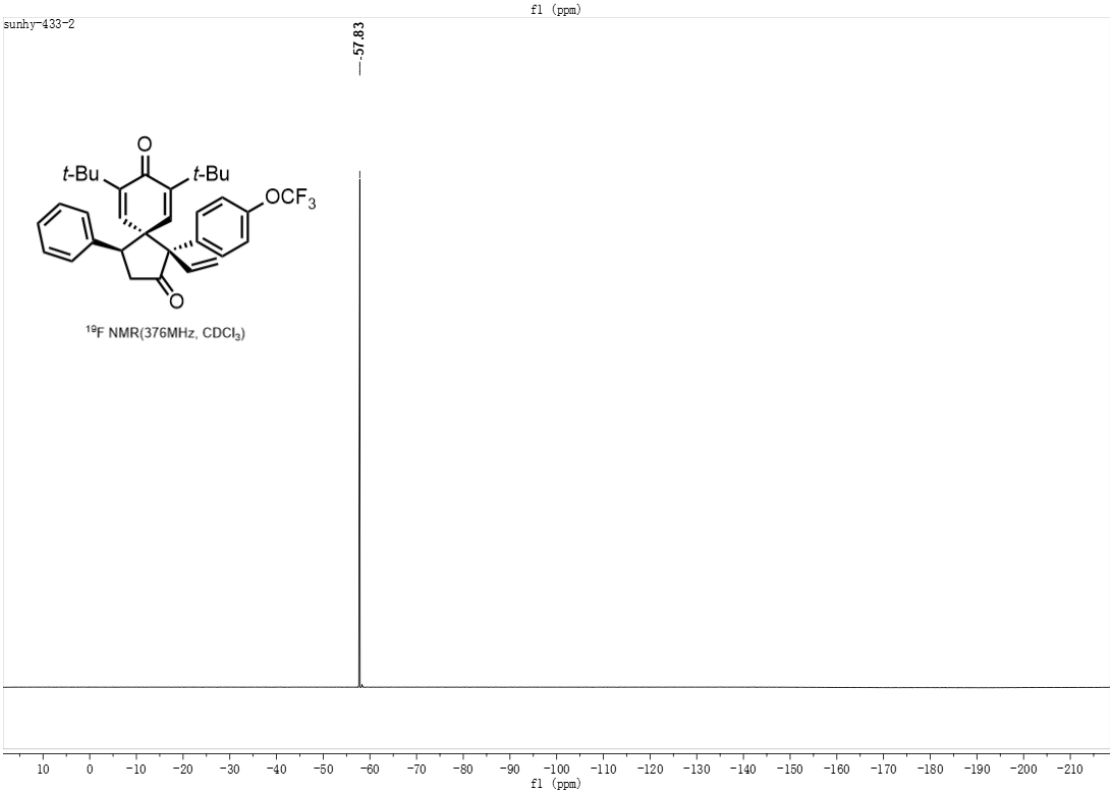


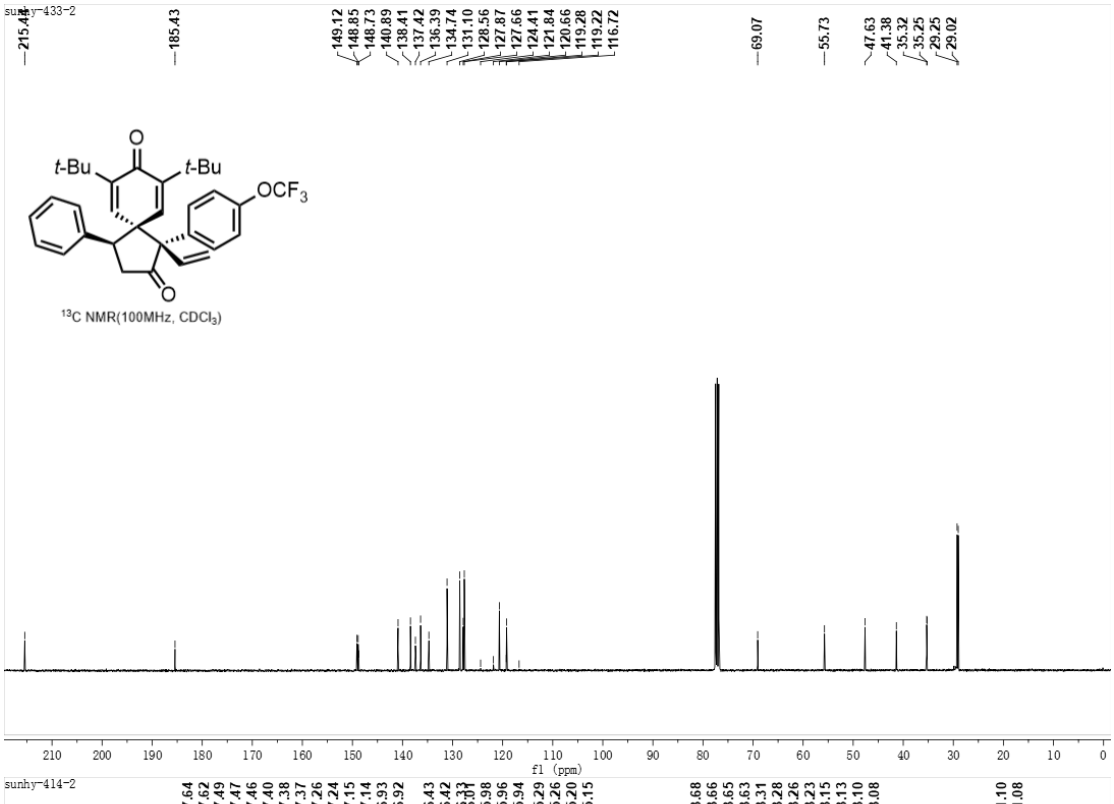
^{13}C NMR(100MHz, $CDCl_3$)

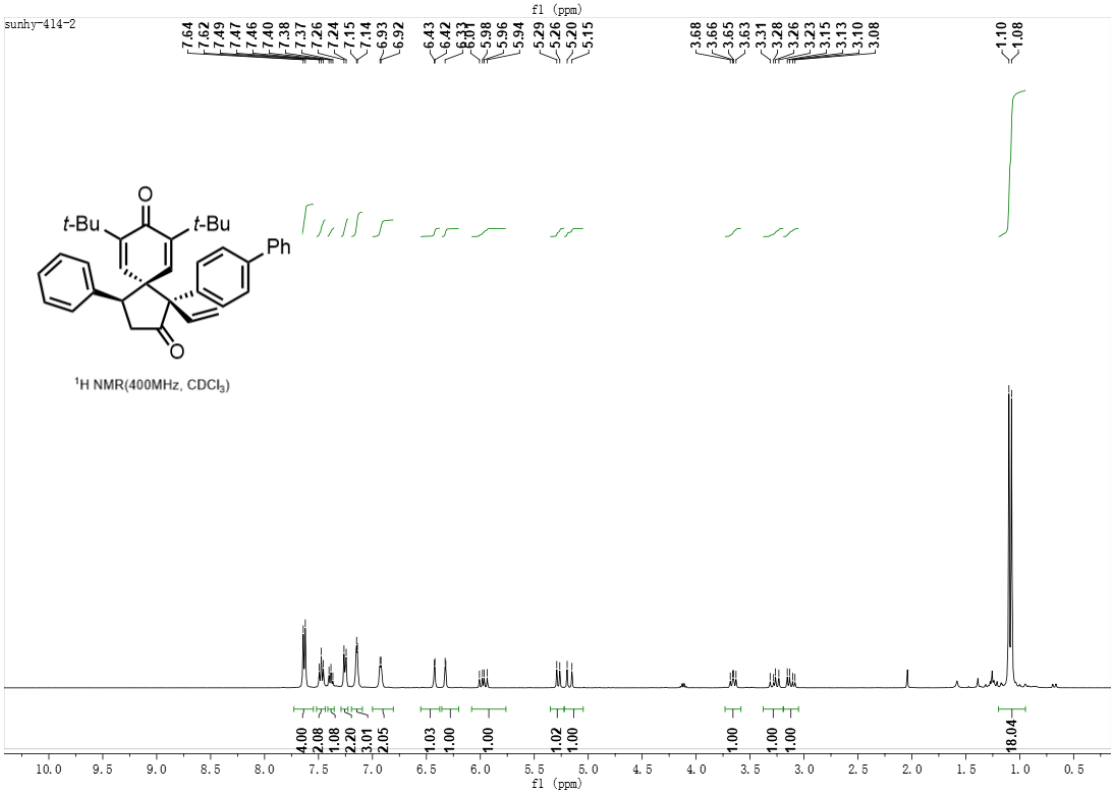

sunhy-383-2-2
t-Bu
t-Bu
Me
O
O
1H NMR(400MHz, CDCl3)
f1 (ppm)

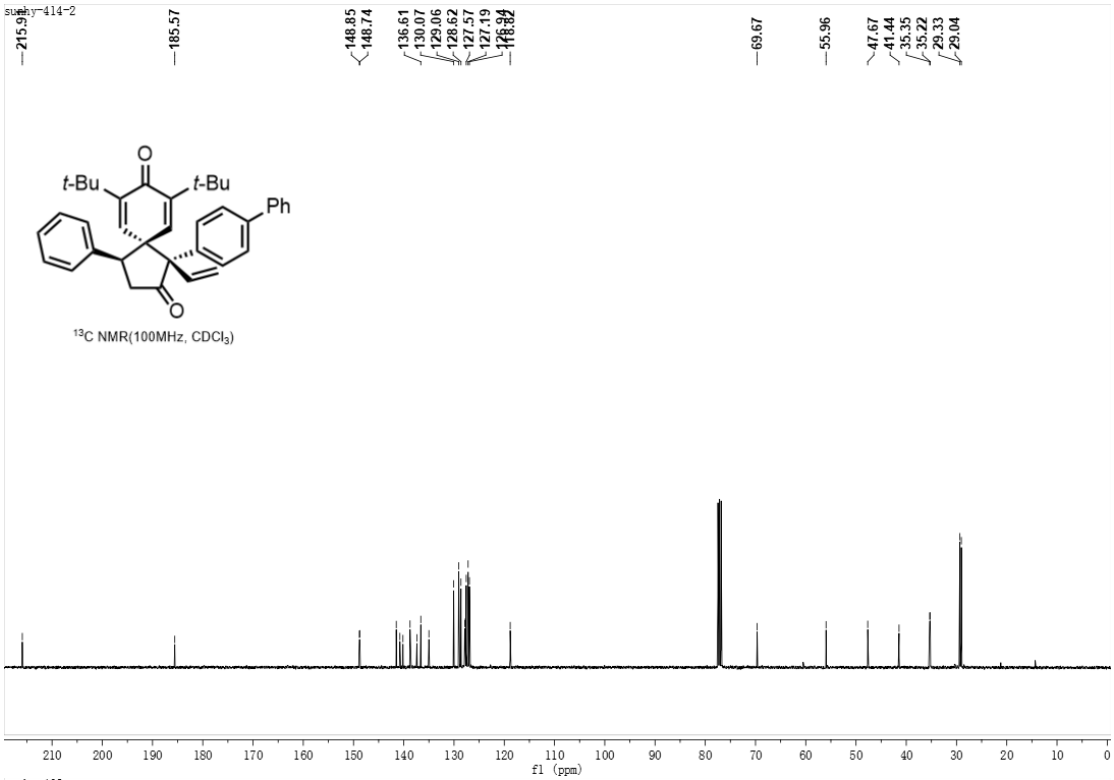

sunhy-383-2-2
t-Bu
t-Bu
Me
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)

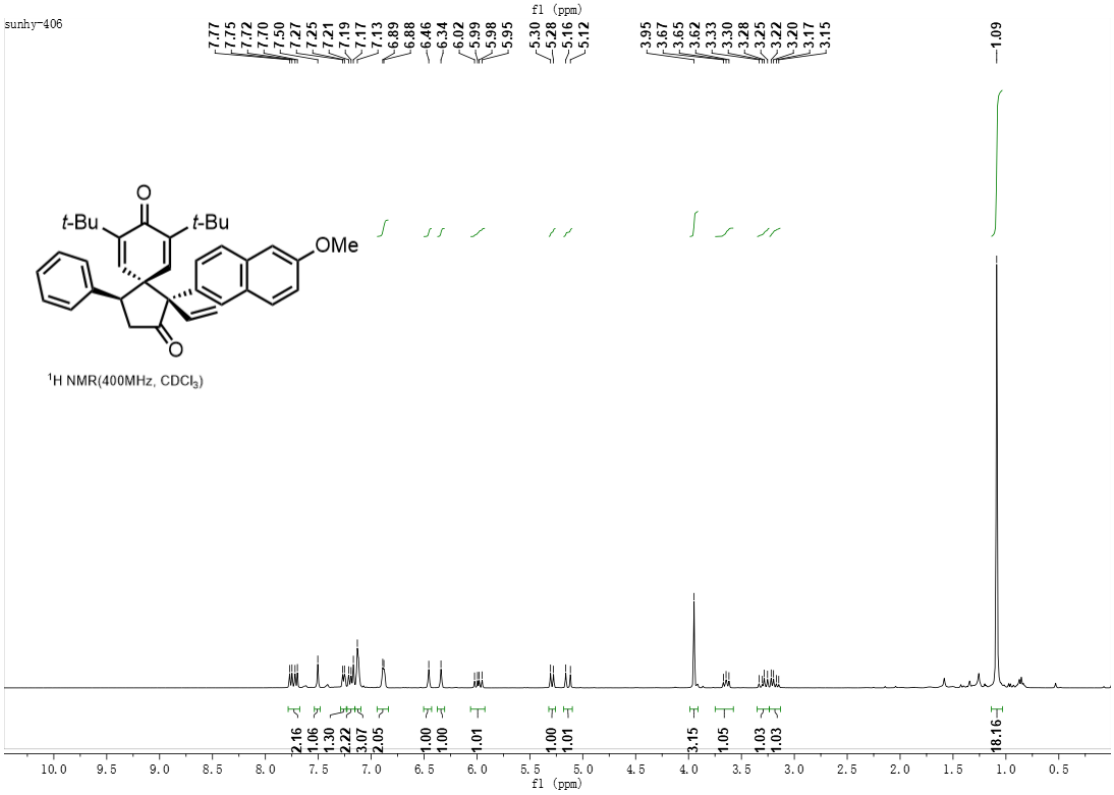

sunhy-433-2
7.26 7.26 7.24 7.22 7.20 7.16 7.15 6.92 6.91 6.39 6.14 5.96 5.93 5.92 5.89 5.29 5.29 5.27 5.26 5.16 5.16 5.12 5.12 3.60 3.58 3.57 3.55 3.31 3.28 3.27 3.23 3.12 3.10 3.07 3.05 1.08 1.06
t-Bu
t-Bu
OCF3
O
O
1H NMR(400MHz, CDCl3)
4.33 3.00 2.07 1.01 1.02 1.03 1.02 1.04 1.00 1.01 1.03 18.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

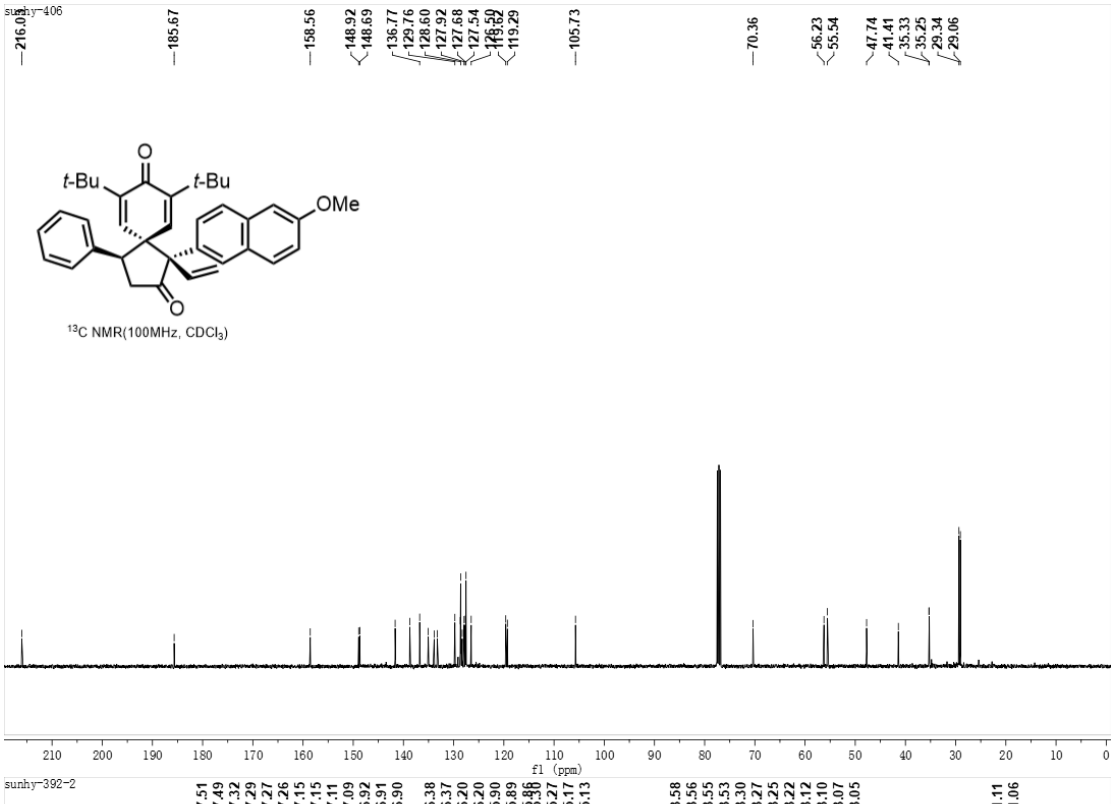

sunhy-433-2
-57.83
t-Bu
t-Bu
OCF3
O
O
19F NMR(376MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

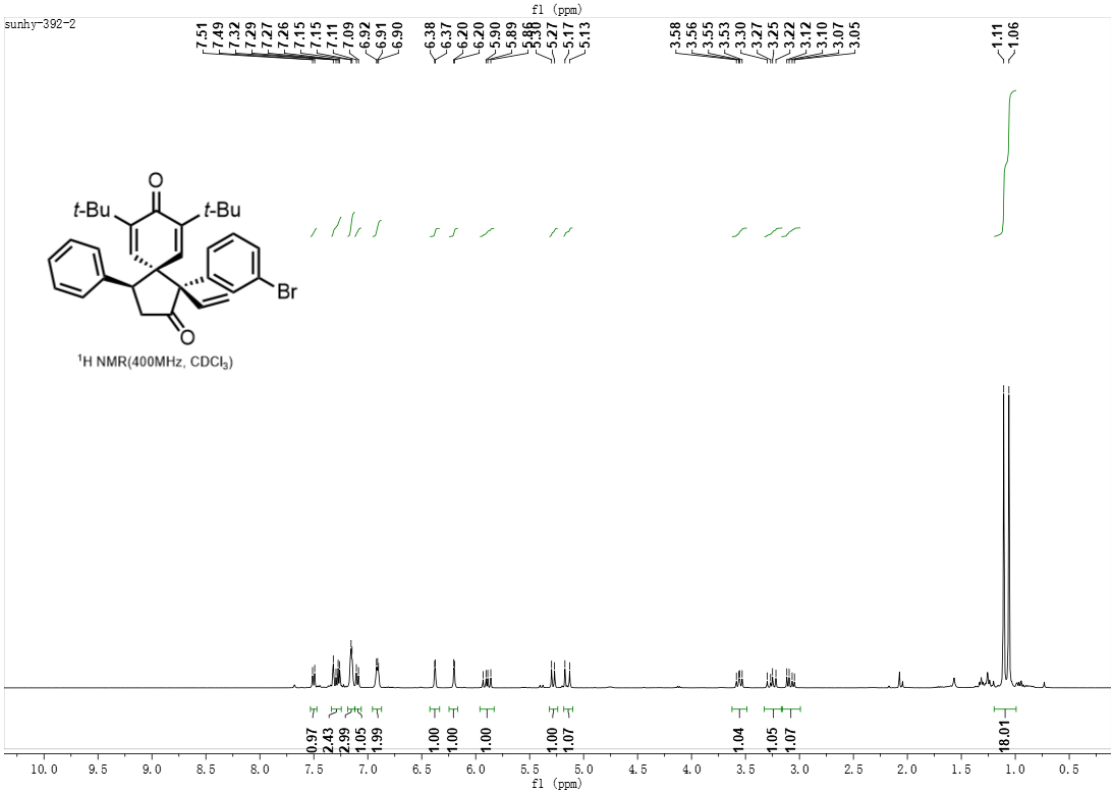

sunhy-433-2
215.48
185.43
149.12
148.85
148.73
140.89
138.41
137.42
136.39
134.74
131.10
128.56
127.87
127.66
124.41
121.84
120.66
119.28
119.22
116.72
69.07
55.73
47.63
41.38
35.32
35.25
29.25
29.02
t-Bu
t-Bu
OCF3
13C NMR(100MHz, CDCl3)
f1 (ppm)

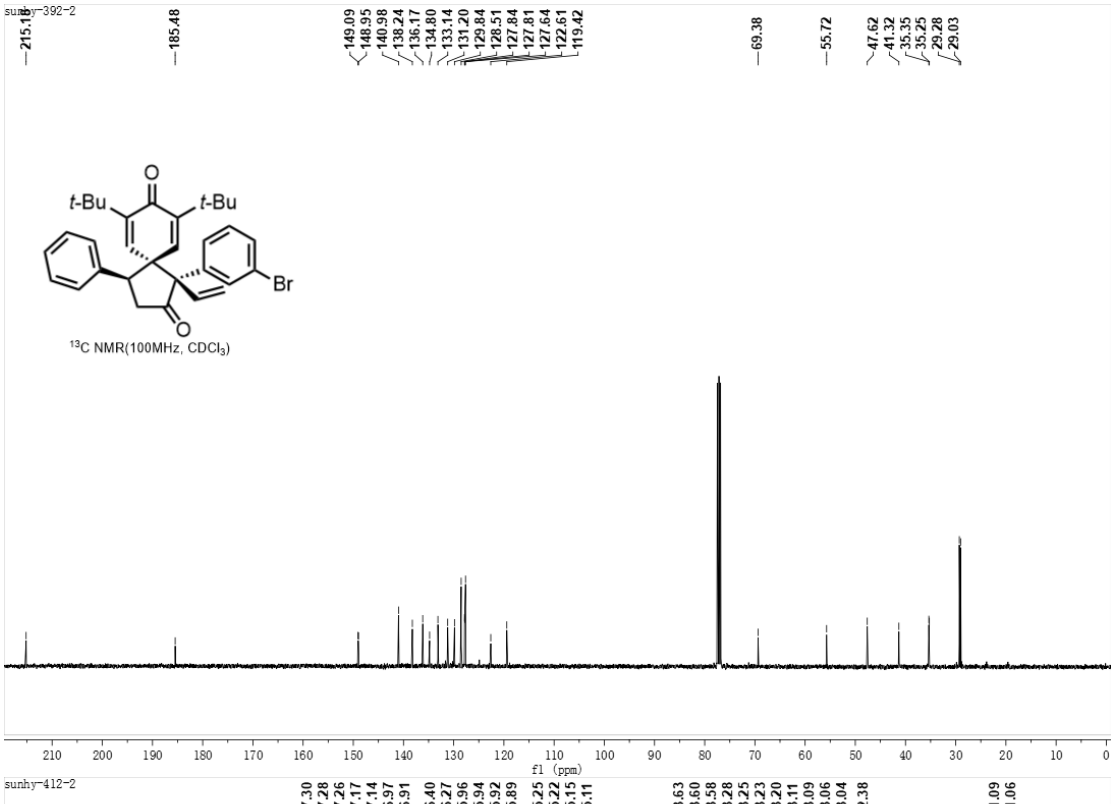

sunhy-414-2
7.64
7.62
7.49
7.47
7.46
7.40
7.38
7.37
7.26
7.24
7.15
7.14
6.93
6.92
6.43
6.42
6.33
6.01
5.98
5.96
5.94
5.29
5.26
5.20
5.15
3.68
3.66
3.65
3.63
3.31
3.28
3.26
3.23
3.15
3.13
3.10
3.08
1.10
1.08
t-Bu
t-Bu
Ph
1H NMR(400MHz, CDCl3)
4.00
2.08
1.08
2.20
3.01
2.05
1.03
1.00
1.00
1.02
1.00
1.00
1.00
1.00
18.04
f1 (ppm)

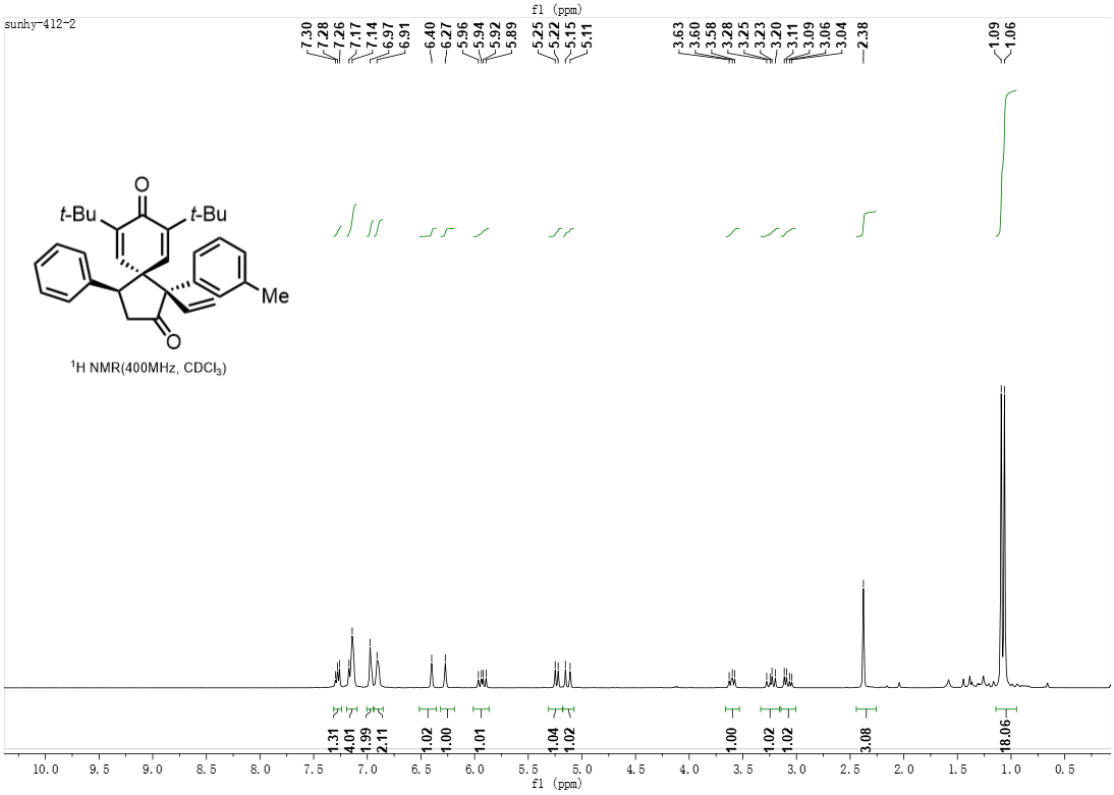

sunhy-414-2
215.93
185.57
148.85
148.74
136.61
130.07
129.06
128.62
127.57
127.19
69.67
55.96
47.67
41.44
35.35
35.22
29.33
29.04
t-Bu
t-Bu
Ph
^{13}C NMR(100MHz, CDCl$_3$)
f1 (ppm)

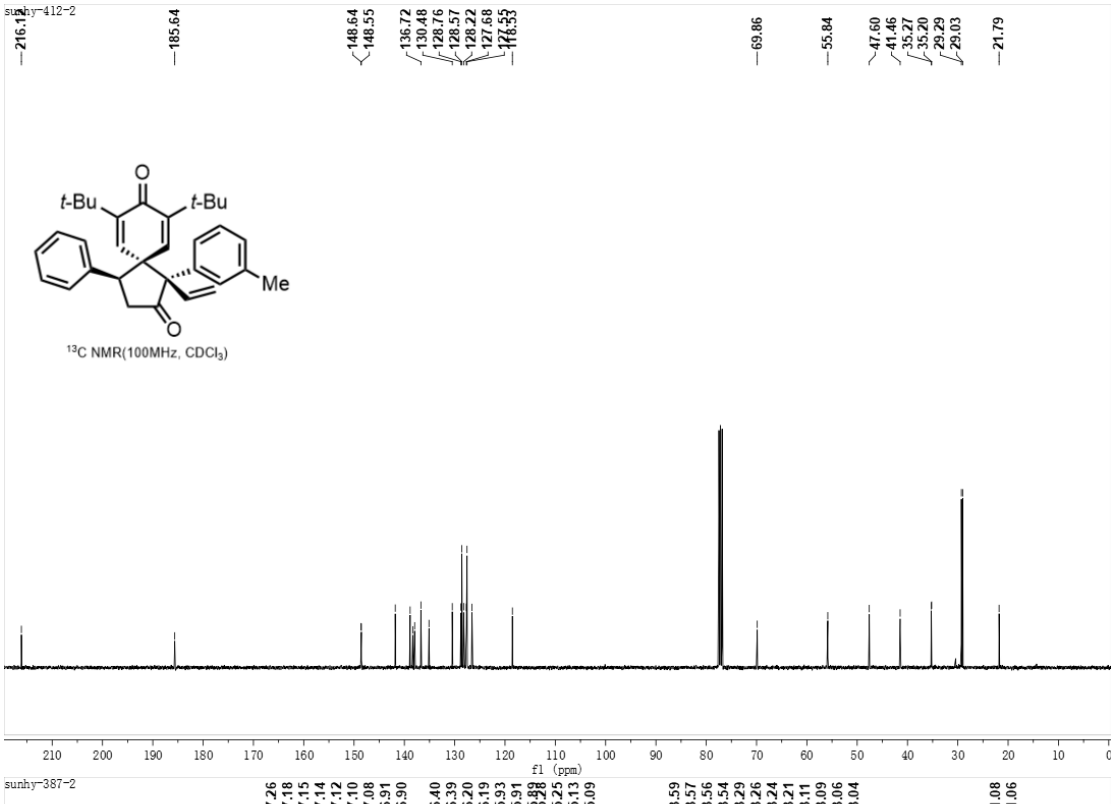

sunhy-406
7.77
7.75
7.72
7.70
7.50
7.27
7.25
7.21
7.19
7.17
7.13
6.89
6.88
6.46
6.34
6.02
5.99
5.98
5.95
5.30
5.28
5.16
5.12
3.95
3.67
3.65
3.62
3.33
3.30
3.28
3.25
3.22
3.20
3.17
3.15
1.09
t-Bu
t-Bu
OMe
^{1}H NMR(400MHz, CDCl$_3$)
2.16
1.06
1.30
2.22
3.07
2.05
1.00
1.00
1.01
1.00
1.01
3.15
1.05
1.03
1.03
18.16
f1 (ppm)

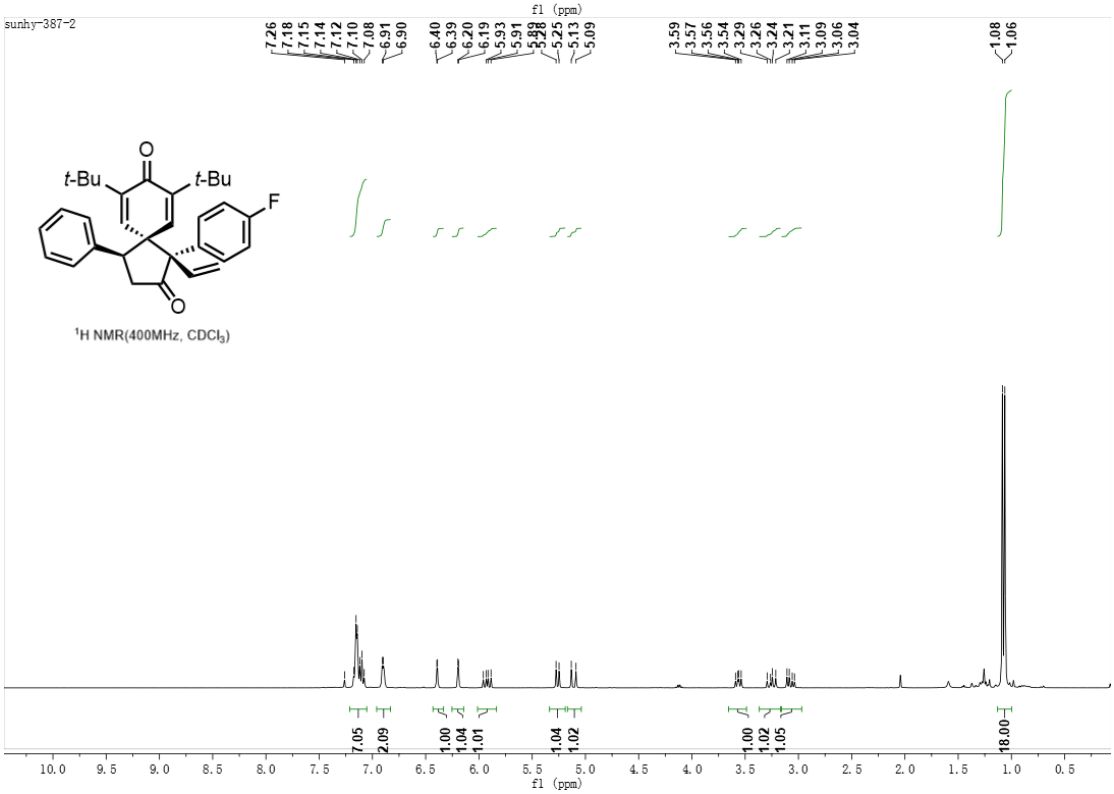

sunhy-406
216.03
185.67
158.56
148.92
148.69
136.77
129.76
128.60
127.92
127.68
127.54
126.50
119.29
105.73
70.36
56.23
55.54
47.74
41.41
35.33
35.25
29.34
29.06
t-Bu
t-Bu
OMe
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)

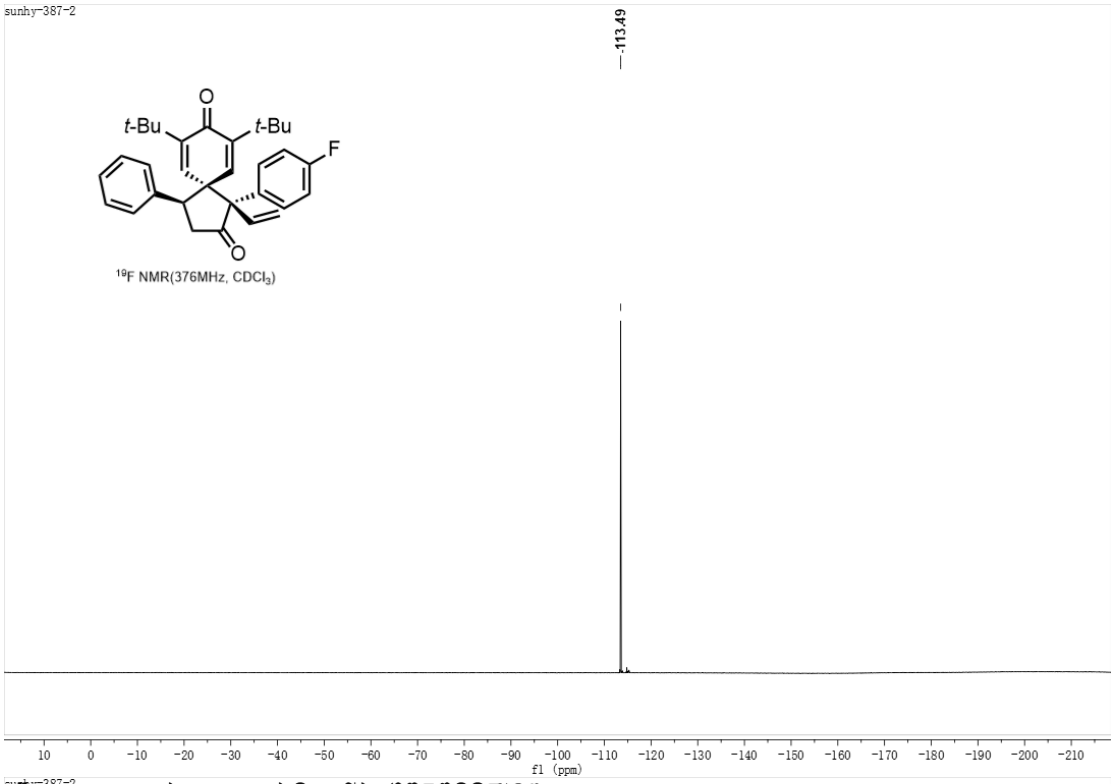

sunhy-392-2
7.51
7.49
7.32
7.29
7.27
7.26
7.15
7.15
7.11
7.09
6.92
6.91
6.90
6.38
6.37
6.20
6.20
5.90
5.89
5.86
5.30
5.27
5.17
5.13
3.58
3.56
3.55
3.53
3.30
3.27
3.25
3.22
3.12
3.10
3.07
3.05
1.11
1.06
t-Bu
t-Bu
Br
O
O
1H NMR(400MHz, CDCl3)
0.97
2.43
2.99
1.05
1.99
1.00
1.00
1.00
1.00
1.07
1.04
1.05
1.07
18.01
f1 (ppm)


sunhy-392-2
215.18
185.48
149.09
148.95
140.98
138.24
136.17
134.80
133.14
131.20
129.84
128.51
127.84
127.81
127.64
122.61
119.42
69.38
55.72
47.62
41.32
35.35
35.25
29.28
29.03
t-Bu
t-Bu
Br
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)

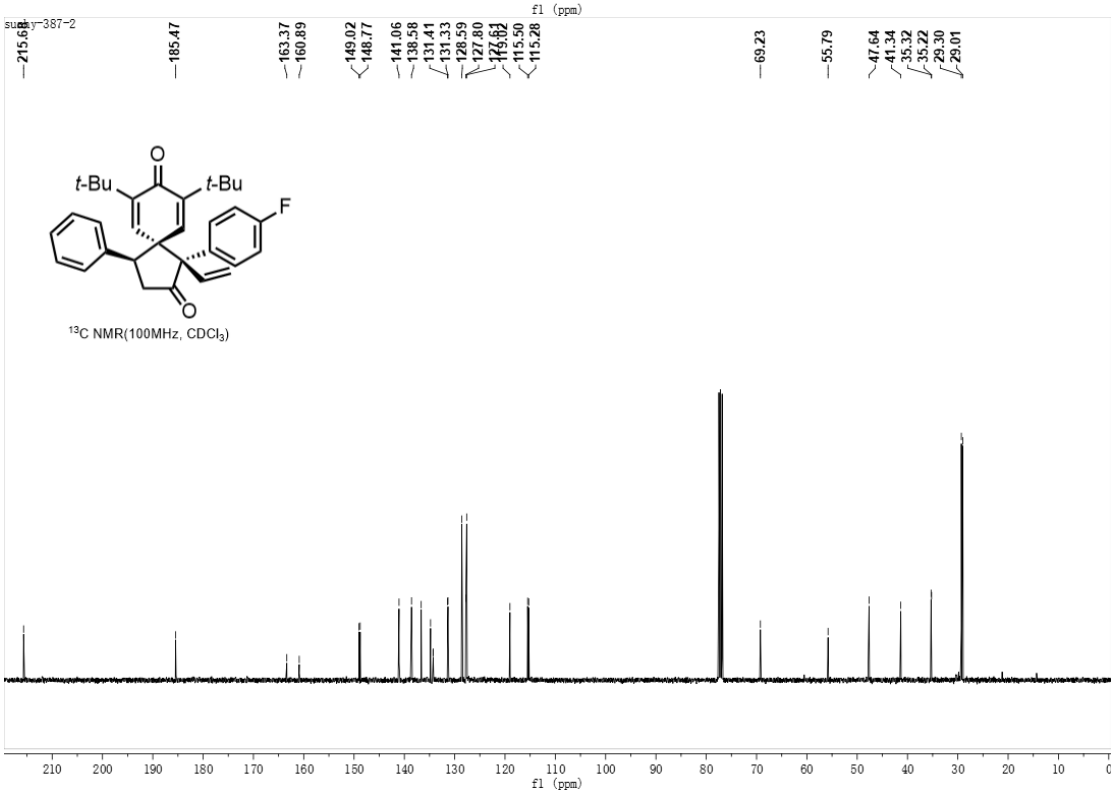

sunhy-412-2
7.30
7.28
7.26
7.17
7.14
6.97
6.91
6.40
6.27
5.96
5.94
5.92
5.89
5.25
5.22
5.15
5.11
3.63
3.60
3.58
3.28
3.25
3.23
3.20
3.11
3.09
3.06
3.04
2.38
1.09
1.06
t-Bu
t-Bu
Me
O
O
1H NMR(400MHz, CDCl3)
1.31
4.01
1.99
2.11
1.02
1.00
1.01
1.04
1.02
1.00
1.02
1.02
3.08
18.06
f1 (ppm)


sunhy-412-2
216.12
185.64
148.64
148.55
136.72
130.48
128.76
128.57
128.22
127.68
127.55
118.53
69.86
55.84
47.60
41.46
35.27
35.20
29.29
29.03
21.79
t-Bu
t-Bu
Me
O
O
13C NMR(100MHz, CDCl3)
f1 (ppm)

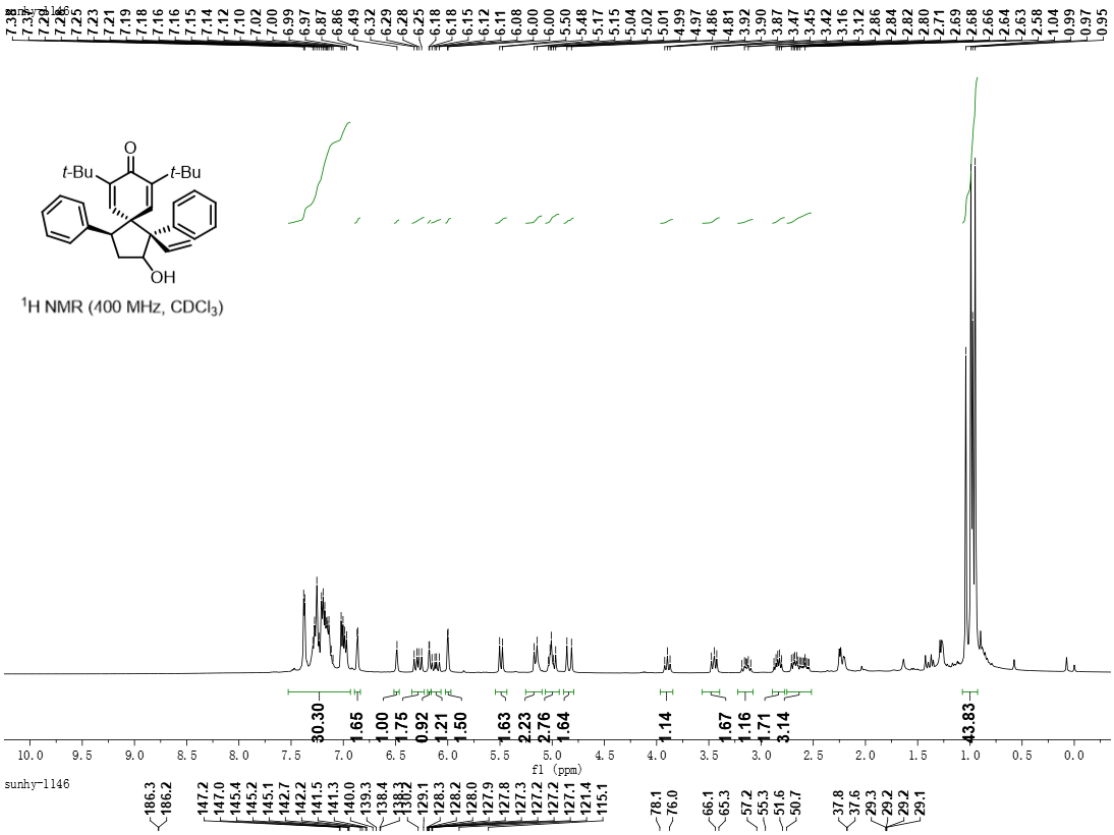

sunhy-387-2
7.26
7.18
7.15
7.14
7.12
7.10
7.08
6.91
6.90
6.40
6.39
6.20
6.19
5.93
5.91
5.25
5.13
5.09
3.59
3.57
3.56
3.54
3.29
3.26
3.24
3.21
3.11
3.09
3.06
3.04
1.08
1.06
t-Bu
t-Bu
F
O
O
1H NMR(400MHz, CDCl3)
7.05
2.09
1.00
1.04
1.01
1.04
1.02
1.00
1.02
1.05
18.00
f1 (ppm)

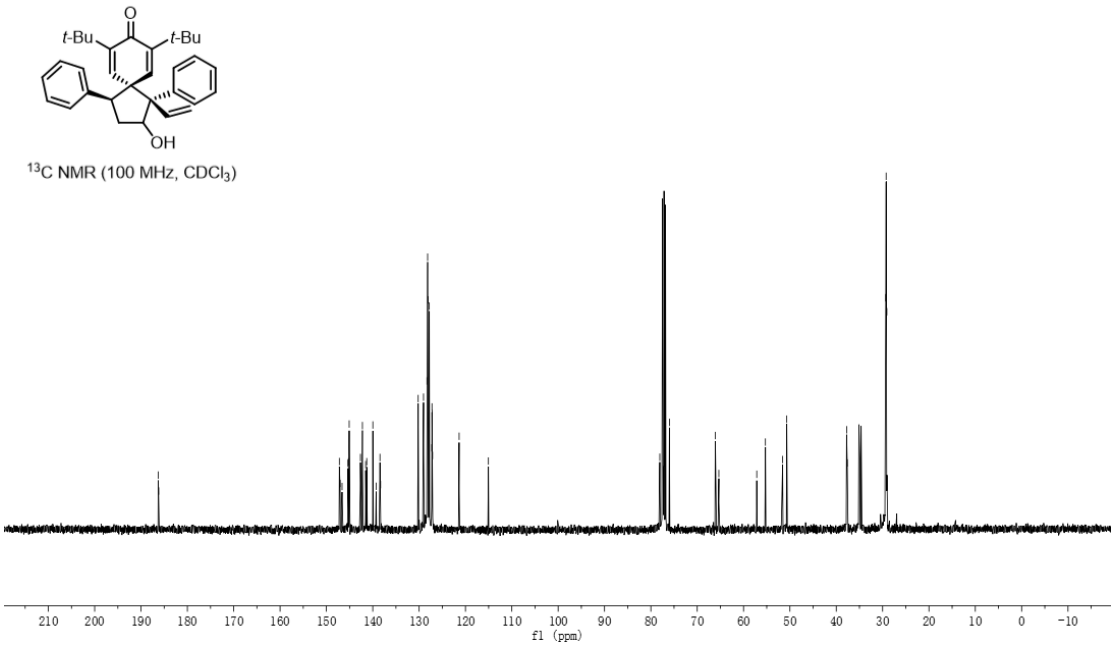


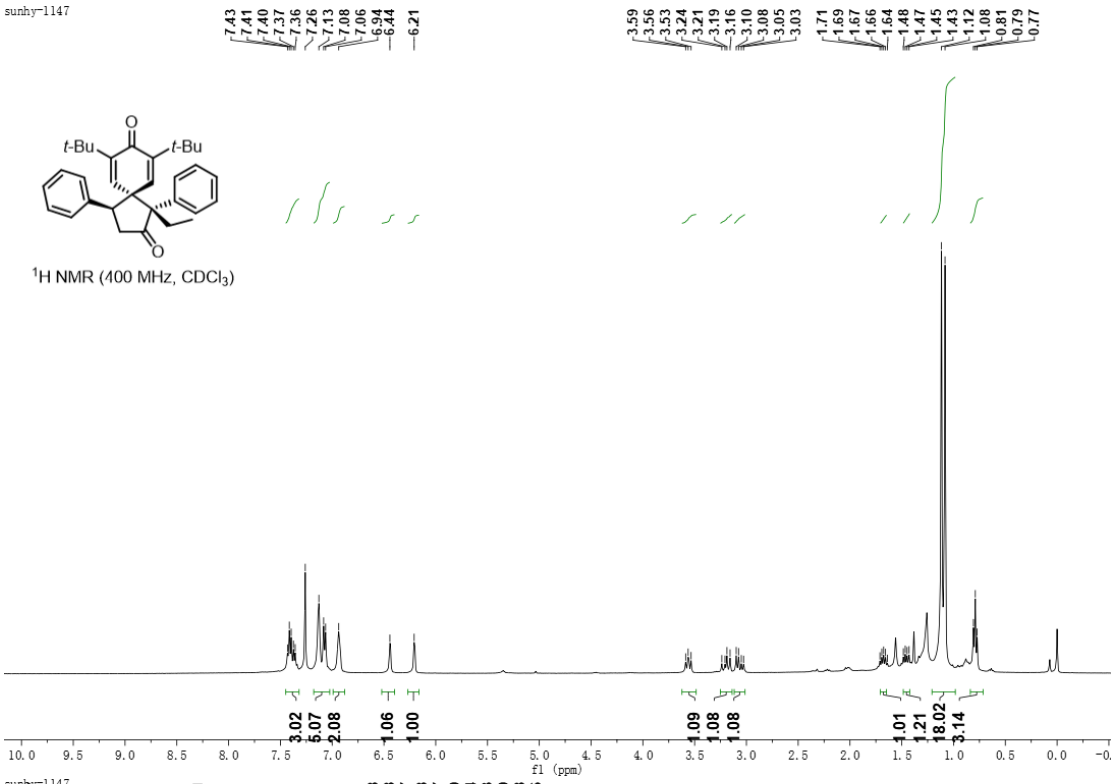
^{19}F NMR(376MHz, $CDCl_3$)



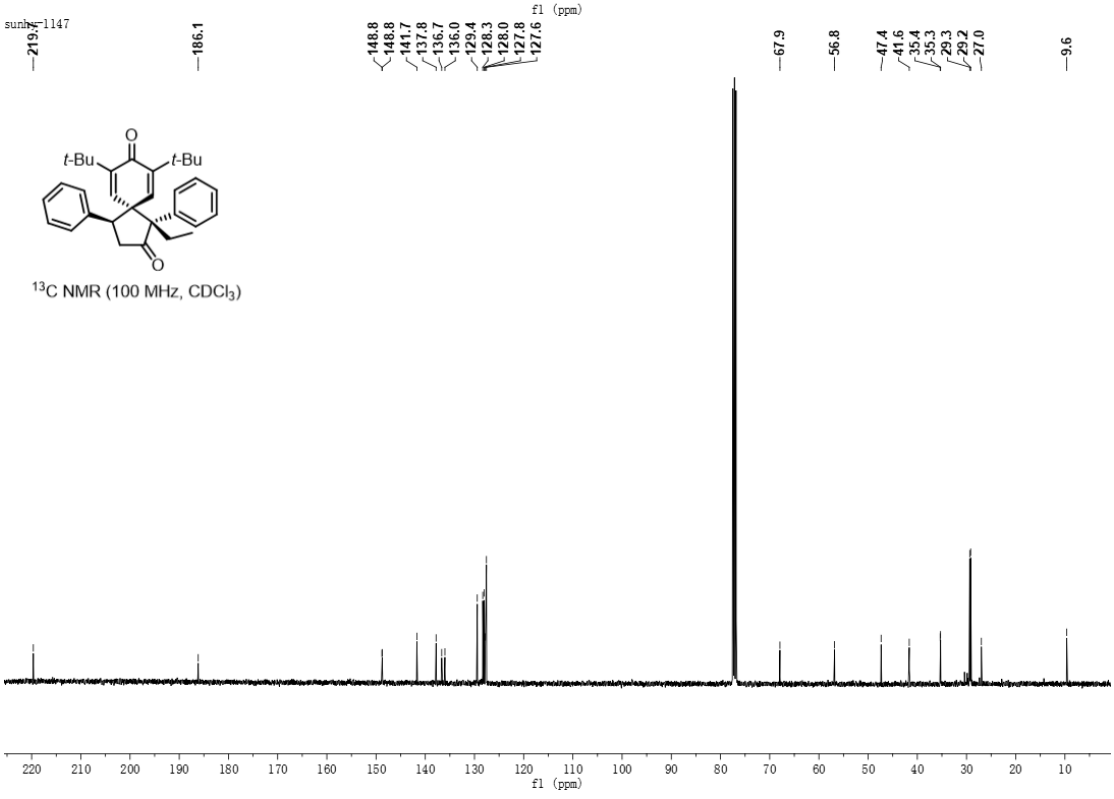
^{13}C NMR(100MHz, $CDCl_3$)


t-Bu
t-Bu
OH
1H NMR (400 MHz, CDCl3)
f1 (ppm)

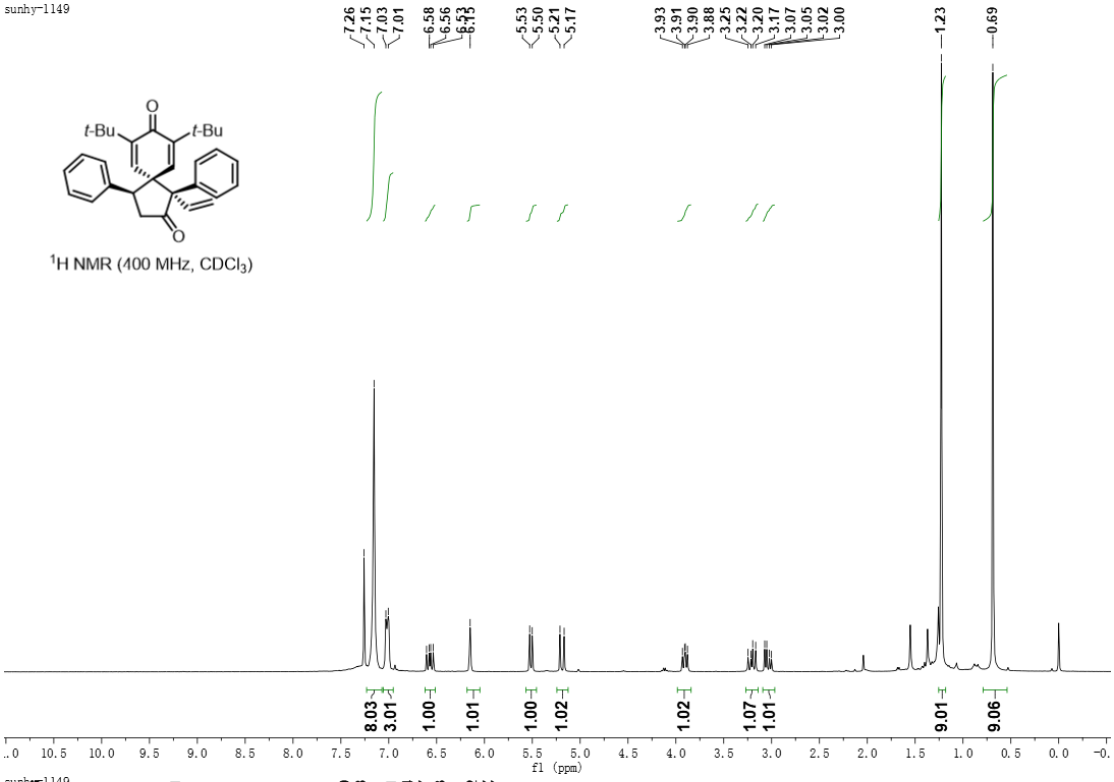

t-Bu
t-Bu
OH
13C NMR (100 MHz, CDCl3)
f1 (ppm)



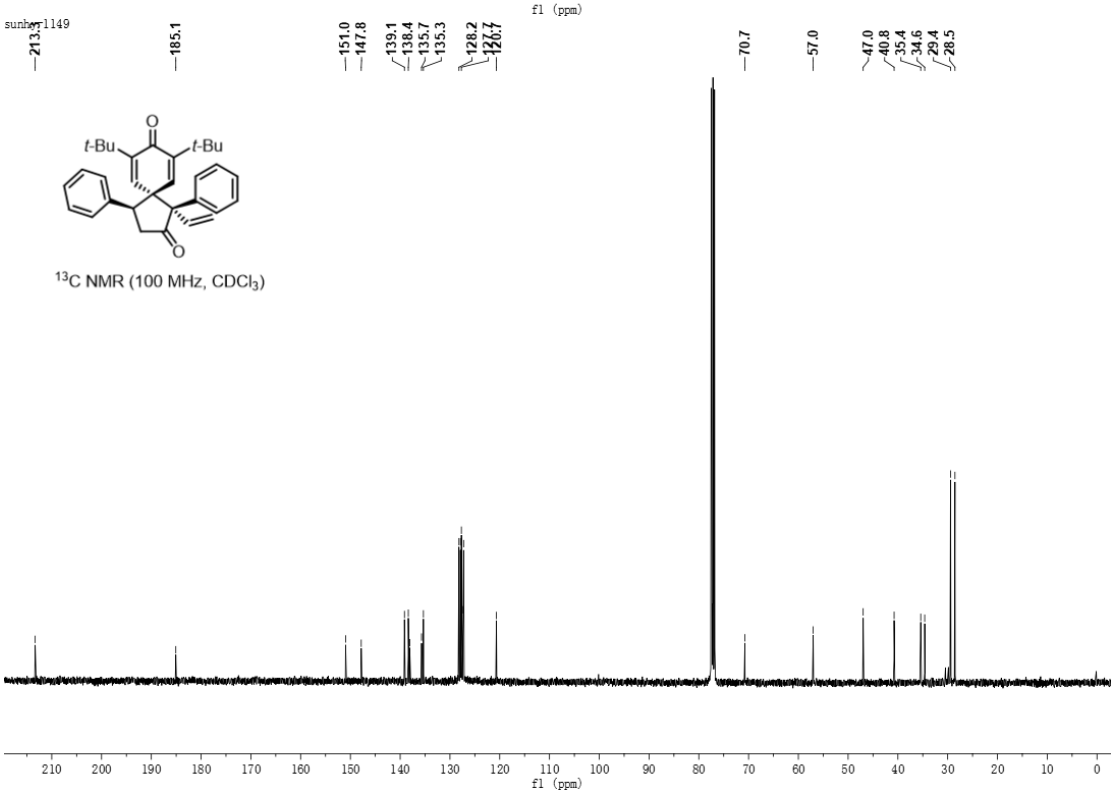
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)