

Palladium-Catalyzed Enantioselective β -Hydride Elimination for the Construction of Remote Stereocenters

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Materials and Methods

Unless otherwise noted, all reactions were assembled on a Schlenk vacuum line or in a glovebox using oven-dried glassware and were stirred with Teflon-coated magnetic stirring bars. All the ligands were purchased from Strem Chemicals or Sinocompound Catalysts Co., Ltd. and were used as received. Unless otherwise noted, reagents were obtained from commercial sources (Shanghai Bidepharm, Adamas-beta[®], Energy Chemical, J&K Scientific and others) and used without further purification. All dried solvents (PhMe, MBTE, THF, 1,4-dioxane, DCE, CH₂Cl₂) were purchased from Energy Chemical. TLC analysis of reaction mixtures was performed on huanghai silica gel 60 F254 TLC plates and visualized by UV, KMnO₄, I₂/silica, and/or ceric ammonium molybdate stain. All work-up and purification procedures were carried out with reagent grade solvents in air. Reaction temperatures above 23 °C refer to temperatures of an aluminum heating block or a silicon oil bath, which were controlled by an electronic temperature modulator from IKA. Flash chromatography was carried out with silica gel 200–300 or 300–400 mesh. ¹H and ¹³C NMR spectra were recorded with Bruker AV-400 spectrometers and were referenced to residual ¹H and ¹³C signals of the deuterated solvents respectively (δ H 7.26, δ C 77.16 for chloroform). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). The ee value was determined on Shimadzu LC-20A HPLC workstation (Daicel chiral columns Chiralpak IA, IC, ID, IE, IF, IH, OD-3, C1). HRMS was performed on a Varian QFT-ESI instrumental. GCMS was performed on Thermofisher Trace 1310/Q Exactive GC. Optical rotations were recorded on a Insmark polarimeter (using the sodium D line; 589 nm). Melting points were determined on an X-4B melting point apparatus.

Preparation of Substrates

The substrates in **Figure S1** are known compounds and were prepared according to literature methods¹.

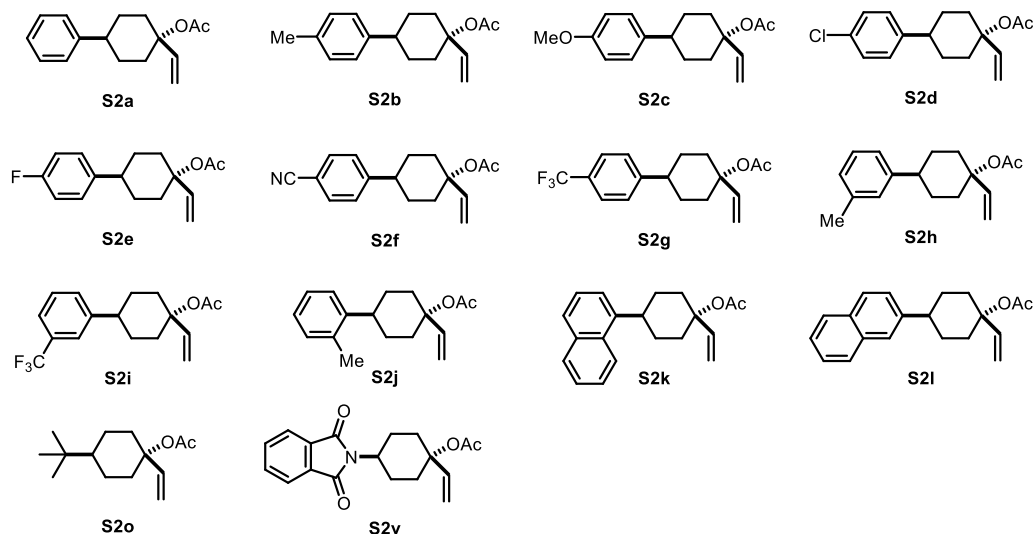


Figure S1 known compounds

The substrates in **Figure 2** are unknown compounds, and their preparation process and characterization were as follows.

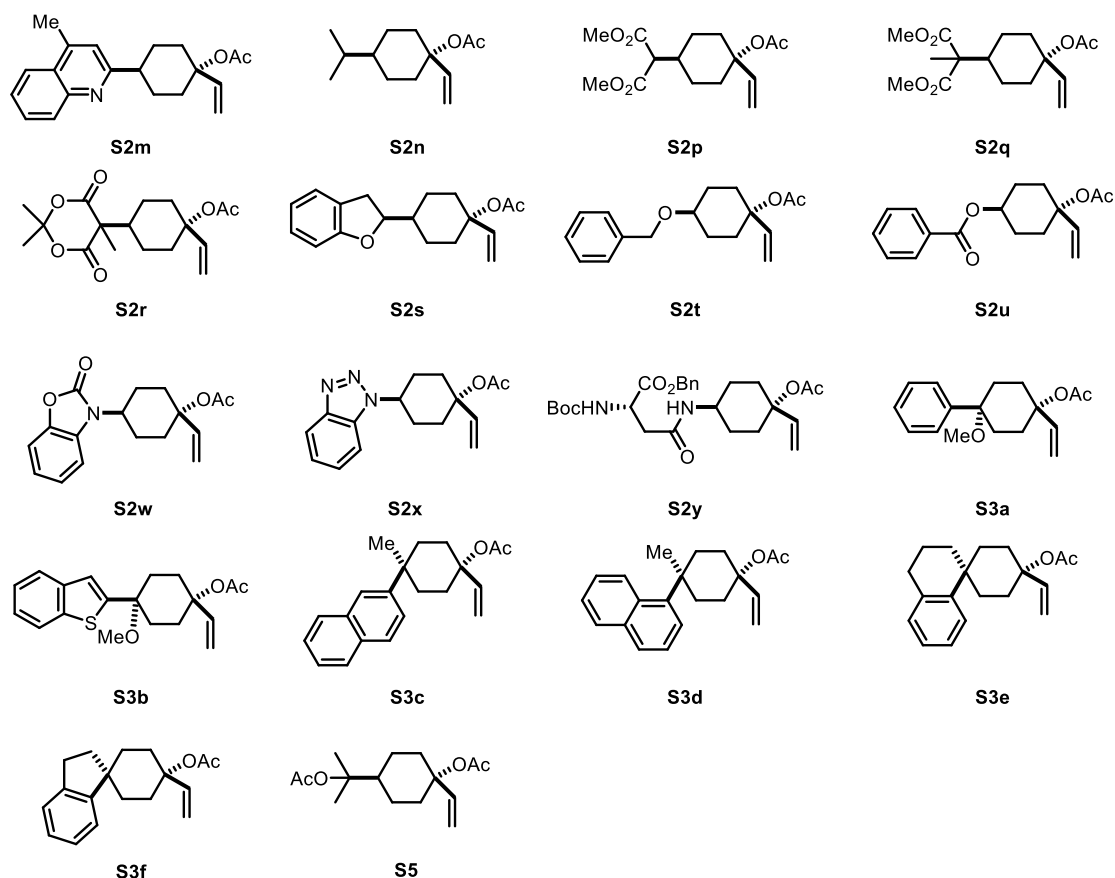
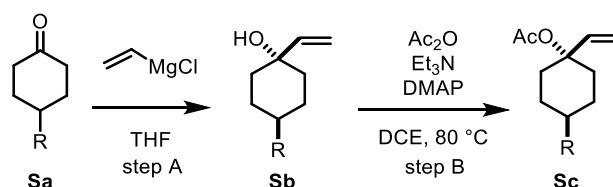


Figure S2 unknown compounds

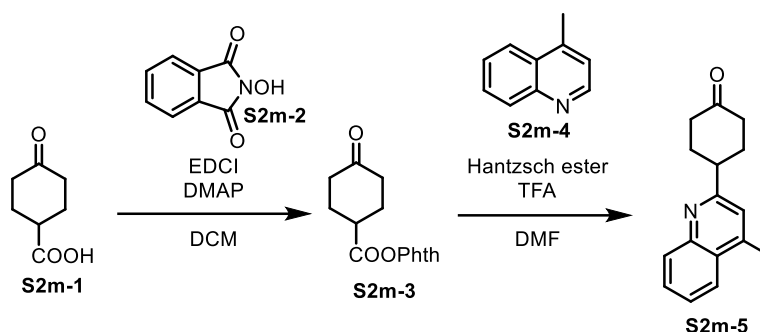
General Procedure:



Step A: In the eggplant shaped bottle, **Sa** (1 equiv) was added, vacuumed, replaced with argon, and dissolved with THF (0.2 M). The reaction was transferred to $-78\text{ }^\circ\text{C}$ for cooling, and added vinyl magnesium chloride drop by drop. Then the reaction was transferred to room temperature to stir. After the reaction was completed, saturated NH_4Cl aqueous solution was added under the ice bath to quench the reaction. The crude product was extracted with EA (3 times). The combined organic layers were washed with brine, dried over MgSO_4 , and concentrated. The residue was purified by silica gel column chromatography to give the target product **Sb** (The *trans* and *cis* isomers can be isolated as pure compounds).

Step B: In the eggplant shaped bottle, **Sb** (1 equiv, R and vinyl *cis* isomer), Ac_2O (4 equiv), Et_3N (4 equiv) and DMAP (0.5 equiv) were added and dissolved with DCE (0.5 M). The reaction mixture was stirred at $80\text{ }^\circ\text{C}$ for 12 h. The residue was concentrated

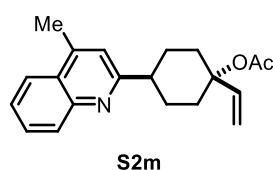
and purified by silica gel column chromatography to give the target product **S2c**.



In the eggplant shaped bottle, **S2m-1** (5 g, 35 mmol, 1 equiv), **S2m-2** (6.9 g, 42 mmol, 1.2 equiv) and DMAP (427 mg, 3.5 mmol, 0.1 equiv) were added and dissolved with THF (0.7 M). Then the solution of EDCI (8.1 g, 42 mmol, 1.2 equiv) in THF (0.4 M) was added drop by drop. After the reaction was completed, HCl aqueous solution was added and extracted with DCM (3 times). The collected organic phase was dried with MgSO_4 , and filtered. The filtrate was concentrated, washed with Et_2O , and filtered. The solid was collected and dried without further purification.

S2m-3 (2.9 g, 10 mmol, 2 equiv), **S2m-4** (0.7 mL, 5 mmol, 1 equiv) and Hantzsch (2.5 g, 10 mmol, 2 equiv) were added to the eggplant shaped bottle. The mixture was vacuumed, replaced with argon, and dissolved with DMF (0.05 M). TFA (0.8 mL, 10 mmol, 2 equiv) was added. The reaction was stirred under blue light irradiation until completion of the reaction. The reaction solvent was evaporated. Saturated NaHCO_3 aqueous solution was added and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO_4 , and concentrated in vacuo to obtain **S2m-5** without further purification.

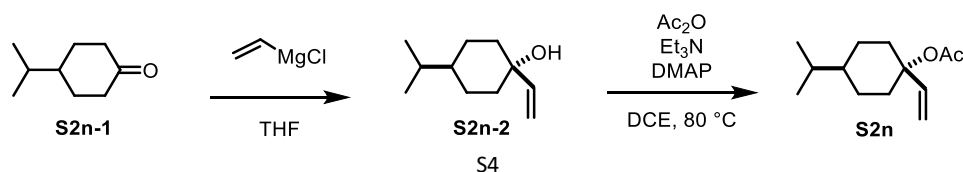
The product **S2m** was synthesized following the general procedure A and B from compound **S2m-5**.



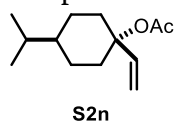
^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.13 (s, 1H), 6.29 (dd, J = 17.7, 10.9 Hz, 1H), 5.46 – 5.32 (m, 2H), 3.10 – 2.92 (m, 1H), 2.68 (s, 3H), 2.58 – 2.46 (m, 2H), 2.08 – 2.03 (m, 2H), 2.00 (s, 3H), 1.95 – 1.76 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.9, 164.9, 139.6, 129.5, 129.3, 127.2, 125.8, 123.7, 120.1, 116.9, 81.7, 60.5, 45.8, 35.3, 29.0, 22.5, 19.0.

HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{24}\text{NO}_2^+$ ($\text{M} + \text{H}$) $^+$: 310.1802, Found: 310.1802.



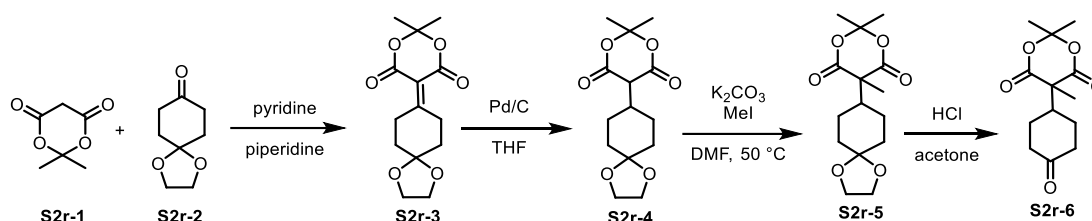
The product **S2n** was synthesized following the general procedure A and B from compound **S2n-1**.



¹H NMR (400 MHz, CDCl₃) δ 6.14 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.37 – 5.18 (m, 2H), 2.40 – 2.24 (m, 2H), 1.95 (s, 3H), 1.72 – 1.57 (m, 4H), 1.48 – 1.36 (m, 1H), 1.18 – 1.09 (m, 3H), 0.85 (s, 3H), 0.83 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.9, 139.7, 116.4, 82.3, 43.2, 35.4, 31.9, 26.3, 22.5, 20.2.

HRMS (ESI) calcd. for C₁₃H₂₂NaO₂⁺ (*M* + Na)⁺: 233.1512, Found: 233.1512.



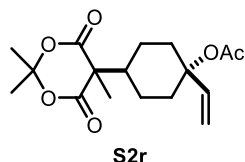
In the eggplant shaped bottle, **S2r-1** (7.2 g, 50 mmol, 1 equiv), **S2r-2** (7.2 g, 50 mmol, 1 equiv), pyridine (5 M) and piperidine (1 mL, 10 mmol, 0.2 equiv) were added and stirred at 50 °C until completion. After then, *n*-hexane was added and filtered. The solid was collected and dried without further purification.

In the eggplant shaped bottle, **S2r-3** (12.8 g, 45 mmol, 1 equiv), THF (1.5 M), 10% Pd/C (55% wet weight, 1.3 g) was added and stirred at room temperature under hydrogen atmosphere. After the reaction was completed and filtered. The filtrate was concentrated and dried without further purification.

In the eggplant shaped bottle, **S2r-4** (3.6 g, 12.7 mmol, 1 equiv), DMF (0.25 M), K₂CO₃ (3.5 g, 25.4 mmol, 2 equiv) and MeI (4 mL, 63.5 mmol, 5 equiv) were added and stirred at 50 °C until completion. The reaction solvent was evaporated. Aqueous solution was added and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, concentrated in vacuo and purified by silica gel column chromatography (PE:EA = 10:1 to 5:1 to 1:1) to obtain **S2r-5**.

In the eggplant shaped bottle, **S2r-5** (3.2 g, 10.7 mmol, 1 equiv) was added and dissolved with acetone. Then HCl aqueous solution (26.7 mL, 26.7 mmol, 2.5 equiv, 1 M) was added. The reaction was stirred at room temperature until completion. The reaction solvent was evaporated. Saturated NaHCO₃ aqueous solution was added and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo to obtain **S2r-6** without further purification.

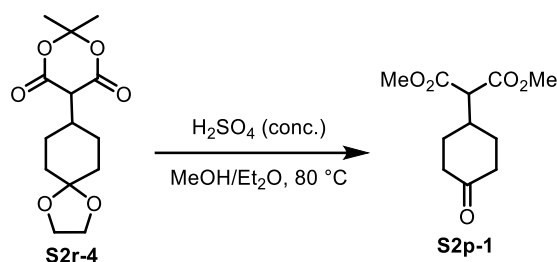
The product **S2r** was synthesized following the general procedure A and B from compound **S2r-6**.



¹H NMR (400 MHz, CDCl₃) δ 6.07 (dd, *J* = 17.8, 10.8 Hz, 1H), 5.37 – 5.23 (m, 2H), 2.54 – 2.40 (m, 2H), 2.11 – 2.01 (m, 1H), 1.92 (s, 3H), 1.76 – 1.69 (m, 2H), 1.70 (s, 3H), 1.66 (s, 3H), 1.65 – 1.55 (m, 2H), 1.54 (s, 3H), 1.41 – 1.26 (m, 2H).

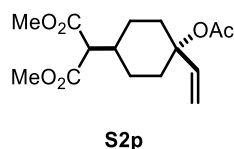
¹³C NMR (101 MHz, CDCl₃) δ 170.1, 169.7, 138.4, 117.6, 104.8, 80.9, 52.8, 47.5, 35.4, 30.6, 28.0, 24.7, 22.3, 20.2.

HRMS (ESI) calcd. for C₁₇H₂₄NaO₆⁺ (*M* + Na)⁺: 347.1465, Found: 347.1464.



In the eggplant shaped bottle, **S2r-4** (2.8 g, 10 mmol, 1 equiv), MeOH (0.2 M), Et₂O (0.2 M), concentrated sulfuric acid (0.5 mL, 10 mmol, 1 equiv) were added and stirred at 80 °C until completion. The reaction solvent was evaporated. Saturated NaHCO₃ aqueous solution was added and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo to obtain **S2p-1** without further purification.

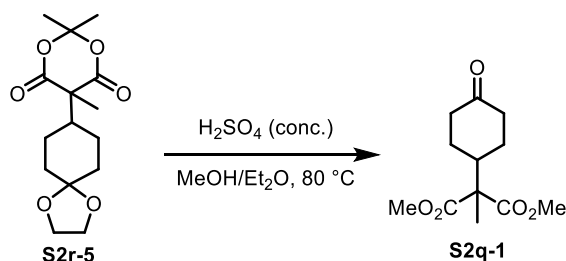
The product **S2p** was synthesized following the general procedure A and B from compound **S2p-1**.



¹H NMR (400 MHz, CDCl₃) δ 6.11 (dd, *J* = 17.8, 10.9 Hz, 1H), 5.36 – 5.20 (m, 2H), 3.72 (s, 6H), 3.21 (d, *J* = 9.6 Hz, 1H), 2.34 – 2.24 (m, 2H), 2.21 – 2.12 (m, 1H), 1.96 (s, 3H), 1.80 – 1.64 (m, 4H), 1.31 – 1.15 (m, 2H).

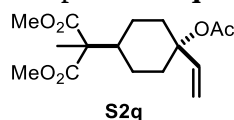
¹³C NMR (101 MHz, CDCl₃) δ 169.9, 169.0, 139.2, 116.8, 81.2, 56.6, 52.6, 36.4, 34.2, 26.7, 22.4.

HRMS (ESI) calcd. for C₁₅H₂₂NaO₆⁺ (*M* + Na)⁺: 321.1309, Found: 321.1308.



In the eggplant shaped bottle, **S2r-5** (1 g, 3.93 mmol, 1 equiv), MeOH (0.2 M), Et₂O (0.2 M), concentrated sulfuric acid (0.2 mL, 3.93 mmol, 1 equiv) were added and stirred at 80 °C until completion. The reaction solvent was evaporated. Saturated NaHCO₃ aqueous solution was added and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo to obtain **S2q-1** without further purification.

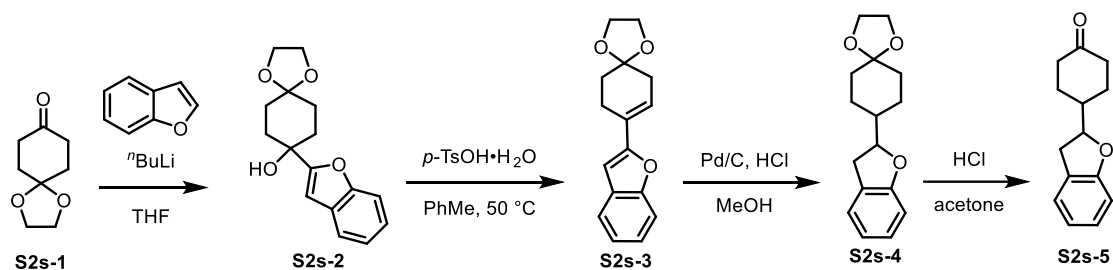
The product **S2q** was synthesized following the general procedure A and B from compound **S2q-1**.



¹H NMR (400 MHz, CDCl₃) δ 6.14 (dd, *J* = 17.8, 10.9 Hz, 1H), 5.39 – 5.26 (m, 2H), 3.72 (s, 6H), 2.52 – 2.38 (m, 2H), 2.24 (s, 3H), 2.23 – 2.16 (m, 1H), 1.76 – 1.65 (m, 2H), 1.62 – 1.54 (m, 2H), 1.34 (s, 3H), 1.31 – 1.20 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 172.2, 169.8, 138.9, 117.2, 81.4, 57.1, 52.5, 41.8, 35.5, 24.6, 22.4, 16.6.

HRMS (ESI) calcd. for C₁₆H₂₄NaO₆⁺ (*M* + Na)⁺: 335.1465, Found: 335.1464.



In the eggplant shaped bottle, benzofuran (4.1 mL, 38.4 mmol, 1.2 equiv) was added, vacuumed, replaced with argon, and dissolved with THF (0.1 M). The mixture was transferred to -78 °C for cooling. ⁿBuLi (17 mL, 41.6 mmol, 1.3 equiv, 2.4 M) was added drop by drop. The reaction was transferred to room temperature to stir for 1 h, then transferred to -78 °C again. The THF solution (0.1 M) of **S2s-1** (5 g, 32 mmol, 1 equiv) was added drop by drop. The reaction was stirred at room temperature until completion. After then, saturated NH₄Cl aqueous solution was added under the ice bath to quench the reaction and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo to obtain **S2s-2** without further purification.

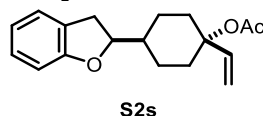
In the eggplant shaped bottle, the crude product **S2s-2** (32 mmol, 1 equiv) and *p*-TsOH·H₂O (0.6 g, 3.2 mmol, 0.1 equiv), and PhMe (0.3 M) were added. The reaction was stirred at 80 °C until completion. After then, saturated NaHCO₃ aqueous solution was added and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, concentrated in vacuo, and purified by silica gel column chromatography (PE:EA = 15:1 to 10:1) to obtain **S2s-3**.

In the eggplant shaped bottle, **S2s-3** (4.27g, 16.7 mmol, 1 equiv), MeOH (0.6 M), 10% Pd/C (55% wet weight, 427mg), and concentrated HCl (10 drops) were added. The

reaction was stirred at room temperature under hydrogen atmosphere until completion. After then, the reaction was filtered. The filtrate was concentrated and dried without further purification.

In the eggplant shaped bottle, **S2s-4** (16.7 mmol, 1 equiv) was added and dissolved with acetone. Then HCl aqueous solution (4.2 mL, 4.17 mmol, 0.25 equiv, 1 M) was added. The reaction was stirred at 50 °C until completion. The reaction solvent was evaporated. Saturated NaHCO₃ aqueous solution was added and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo to obtain **S2s-5** without further purification.

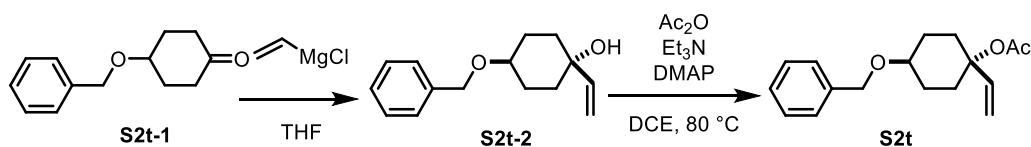
The product **S2s** was synthesized following the general procedure A and B from compound **S2s-5**.



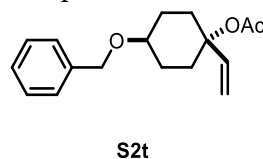
¹H NMR (400 MHz, CDCl₃) δ 7.14 (d, J = 7.3 Hz, 1H), 7.09 (t, J = 7.7 Hz, 1H), 6.81 (t, J = 7.3 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.18 (dd, J = 17.7, 10.9 Hz, 1H), 5.43 – 5.22 (m, 2H), 4.52 (q, J = 8.6 Hz, 1H), 3.27 – 3.10 (m, 1H), 2.93 (dd, J = 15.5, 8.5 Hz, 1H), 2.45 – 2.34 (m, 2H), 1.97 (s, 3H), 1.97 – 1.90 (m, 1H), 1.78 – 1.67 (m, 4H), 1.39 – 1.22 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 169.9, 159.8, 139.4, 128.1, 126.9, 124.9, 120.3, 116.8, 109.2, 86.3, 81.8, 41.9, 34.5, 34.4, 33.5, 25.1, 24.7, 22.4.

HRMS (ESI) calcd. for C₁₈H₂₂NaO₃⁺ (M + Na)⁺: 309.1461, Found: 309.1461.



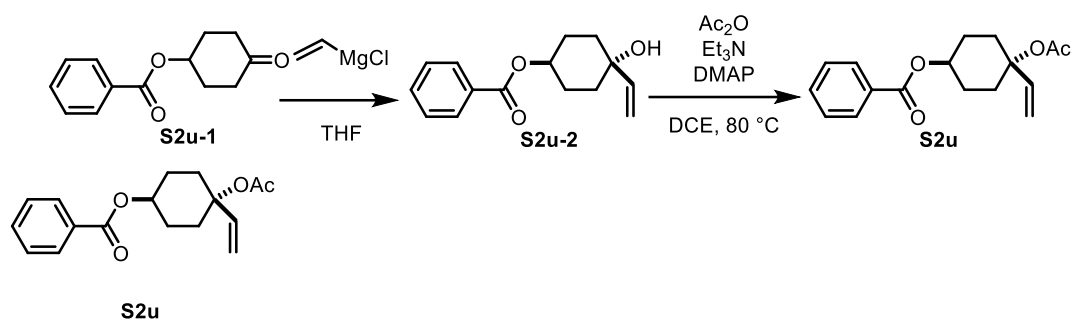
The product **S2t** was synthesized following the general procedure A and B from compound **S2t-1**.



¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.13 (m, 5H), 6.00 (dd, J = 17.7, 11.0 Hz, 1H), 5.11 – 4.94 (m, 2H), 4.47 (s, 2H), 3.37 – 3.24 (m, 1H), 2.32 – 2.23 (m, 2H), 1.94 (s, 3H), 1.88 – 1.78 (m, 2H), 1.60 – 1.47 (m, 2H), 1.45 – 1.34 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 170.1, 141.3, 138.9, 128.5, 127.7, 127.6, 113.9, 80.7, 76.0, 70.2, 32.8, 27.5, 22.2.

HRMS (ESI) calcd. for C₁₇H₂₂NaO₃⁺ (M + Na)⁺: 297.1461, Found: 297.1460.

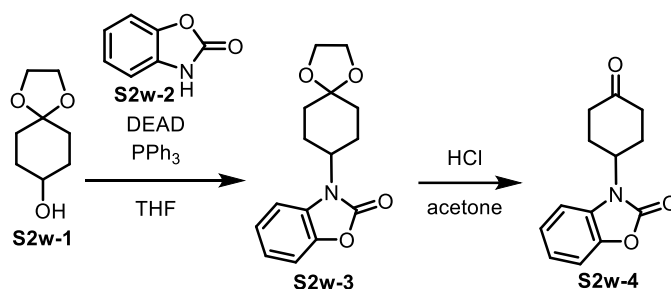


The product **S2u** was synthesized following the general procedure A and B from compound **S2u-1**.

¹H NMR (400 MHz, CDCl₃) δ 8.09 – 7.96 (m, 2H), 7.64 – 7.52 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.17 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.35 – 5.14 (m, 3H), 2.27 – 2.16 (m, 2H), 2.11 (s, 3H), 2.02 – 1.86 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 170.1, 166.0, 141.3, 133.0, 130.8, 129.6, 128.5, 114.4, 81.0, 69.7, 30.1, 26.2, 22.2.

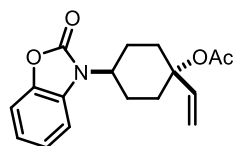
HRMS (ESI) calcd. for C₁₇H₂₀NaO₄⁺ (*M* + Na)⁺: 311.1254, Found: 311.1254.



In the eggplant shaped bottle, **S2w-2** (3.2 g, 24 mmol, 1.2 equiv) and PPh₃ (6.3 g, 24 mmol, 1.2 equiv) were added and dissolved with THF (1 M). Under the ice bath, **S2w-1** (3.2 g, 20 mmol, 1 equiv) and DEAD (3.8 mL, 24 mmol, 1.2 equiv) were added. The reaction was stirred at room temperature until completion. After then, the reaction solvent was evaporated, diluted by PE:EA (10:1), and filtered. The filtrate was concentrated and purified by silica gel column chromatography (PE:EA = 20:1 to 10:1 to 5:1 to 3:1) to give **S2w-3**.

In the eggplant shaped bottle, **S2w-3** (2.86 g, 10.4 mmol, 1 equiv) was added and dissolved with acetone. Then HCl aqueous solution (2.5 mL, 2.5 mmol, 0.25 equiv, 0.25 M) was added. The reaction was stirred at 50 °C until completion. The reaction solvent was evaporated. Saturated NaHCO₃ aqueous solution was added and the aqueous layer was extracted with EA (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo to obtain **S2w-4** without further purification.

The product **S2w** was synthesized following the general procedure A and B from compound **S2w-4**.

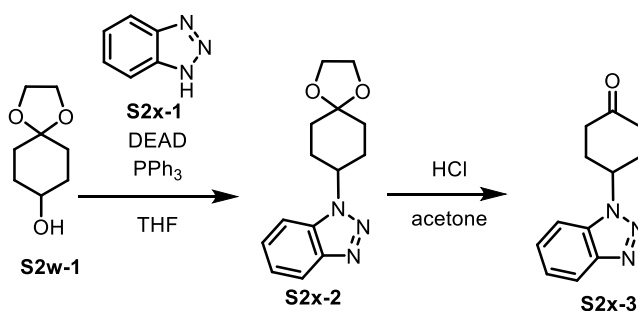


S2w

^1H NMR (400 MHz, CDCl_3) δ 7.19 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.17 – 7.05 (m, 2H), 7.01 (dd, $J = 7.6, 1.1$ Hz, 1H), 6.29 (dd, $J = 17.7, 11.0$ Hz, 1H), 5.60 – 5.44 (m, 2H), 4.25 – 4.20 (m, 1H), 2.65 – 2.57 (m, 2H), 2.59 (s, 3H), 2.32 – 2.17 (m, 2H), 1.92 – 1.78 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.8, 168.7, 154.0, 142.8, 138.3, 130.0, 123.8, 122.3, 118.5, 110.4, 80.2, 64.1, 34.4, 25.9, 22.3.

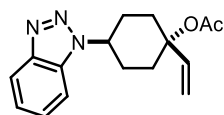
HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{19}\text{NNaO}_4^+$ ($\text{M} + \text{Na}$) $^+$: 324.1206, Found: 324.1206.



In the eggplant shaped bottle, **S2x-1** (2.9 g, 24 mmol, 1.2 equiv) and PPh_3 (6.3 g, 24 mmol, 1.2 equiv) were added and dissolved with THF (1 M). Under the ice bath, **S2w-1** (3.2 g, 20 mmol, 1 equiv) and DEAD (3.8 mL, 24 mmol, 1.2 equiv) were added. The reaction was stirred at room temperature until completion. After then, the reaction solvent was evaporated, diluted by PE:EA (10:1), and filtered. The filtrate was concentrated and purified by silica gel column chromatography (PE:EA = 20:1 to 10:1 to 5:1) to give **S2x-2**.

In the eggplant shaped bottle, **S2x-2** (1.7 g, 6.6 mmol, 1 equiv) was added and dissolved with acetone. Then HCl aqueous solution (1.7 mL, 1.65 mmol, 0.25 equiv, 0.25 M) was added. The reaction was stirred at 50 °C until completion. The reaction solvent was evaporated. Saturated NaHCO_3 aqueous solution was added and the aqueous layer was extracted with EA (3 times). The combined organic layers were washed with saturated brine, dried over MgSO_4 , and concentrated in vacuo to obtain **S2x-3** without further purification.

The product **S2x** was synthesized following the general procedure A and B from compound **S2x-3**.

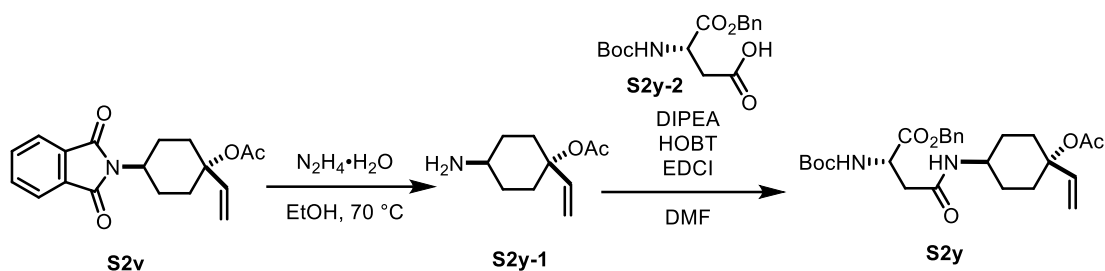


S2x

^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.82 (m, 2H), 7.41 – 7.32 (m, 2H), 6.20 (dd, $J = 17.7, 11.0$ Hz, 1H), 5.38 – 5.23 (m, 2H), 5.01 – 4.85 (m, 1H), 2.51 – 2.38 (m, 2H), 2.36 – 2.22 (m, 4H), 2.15 – 2.06 (m, 2H), 2.04 (s, 3H).

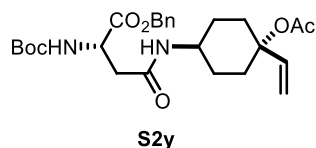
¹³C NMR (101 MHz, CDCl₃) δ 169.9, 144.1, 139.7, 126.3, 118.2, 116.3, 80.7, 62.8, 32.2, 27.8, 22.3.

HRMS (ESI) calcd. for C₁₆H₁₉N₃NaO₂⁺ (M + Na)⁺: 308.1369, Found: 308.1369.



In the eggplant shaped bottle, **S2v** (320 mg, 1.02 mmol, 1 equiv) was added and dissolved with EtOH (0.1 M). Hydrazine monohydrate (0.15 mL, 3.06 mmol, 3 equiv) was added. The reaction was stirred at 70 °C until completion. After then, the reaction solvent was evaporated, diluted by *n*-hexane, and filtered. The solid was collected and dried without further purification.

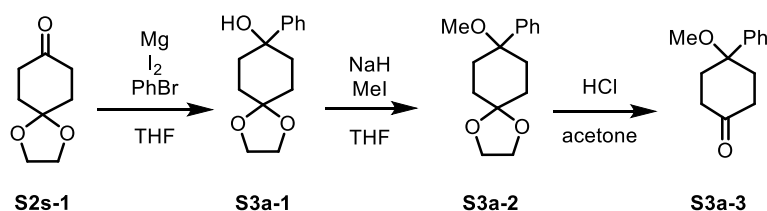
In the eggplant shaped bottle, **S2y-1** (1.02 mmol, 1 equiv) was added and dissolved with DMF (0.1 M). Then **S2y-2** (329 mg, 1.02 mmol, 1 equiv), DIPEA (0.3 mL, 1.73 mmol, 1.7 equiv), HOBT (159 mg, 1.2 mmol, 1.2 equiv) and EDCI (232 mg, 1.2 mmol, 1.2 equiv) were added by sequence under ice bath. The reaction was stirred at room temperature until completion. The reaction solvent was evaporated. Saturated NaHCO₃ aqueous solution was added and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, concentrated in vacuo and purified by silica gel column chromatography (PE:EA = 5:1 to 1:1) to obtain **S2y**.



¹H NMR (400 MHz, CDCl₃) δ 7.30 (s, 5H), 6.08 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.93 (d, *J* = 6.6 Hz, 1H), 5.80 (d, *J* = 7.8 Hz, 1H), 5.28 – 5.20 (m, 2H), 5.18 (d, *J* = 12.4 Hz, 1H), 5.11 (d, *J* = 12.4 Hz, 1H), 4.55 – 4.44 (m, 1H), 3.92 – 3.77 (m, 1H), 2.88 – 2.74 (m, 1H), 2.71 – 2.58 (m, 1H), 2.12 – 2.00 (m, 2H), 1.95 (s, 3H), 1.92 – 1.71 (m, 4H), 1.38 (s, 9H), 1.36 – 1.26 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 171.4, 169.9, 169.2, 155.8, 139.7, 135.4, 128.6, 128.4, 128.2, 116.1, 80.5, 80.0, 67.3, 50.6, 46.4, 38.1, 32.3, 28.3, 27.7, 22.2.

HRMS (ESI) calcd. for C₂₆H₃₆N₂NaO₇⁺ (M + Na)⁺: 511.2415, Found: 511.2413.

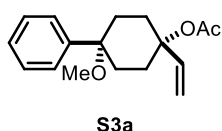


In the eggplant shaped bottle, magnesium chips (1.84 g, 76.8 mmol, 2.4 equiv), and a small amount of iodine and PhBr were added and replaced with argon. A small amount of THF was added. The reaction was heated until the brown red faded. A THF (1.6 M) solution of PhBr (6.7 mL, 64 mmol, 2 equiv) was added. The mixture was reacted at room temperature until a large amount of magnesium chips disappeared. In another eggplant shaped bottle, **S2s-1** (5 g, 32 mmol, 1 equiv) was added and replaced with argon. Then THF (0.8 M) was added. The solution was transferred to -78 °C for cooling. The above prepared Grignard reagent was added to cooled solution drop by drop. The reaction was stirred at this temperature for 30 minutes, and transferred to room temperature until completion. After then, saturated NH₄Cl aqueous solution was added under the ice bath to quench the reaction and the aqueous layer was extracted with EA (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo to obtain **S3a-1** without further purification.

In the eggplant shaped bottle, **S3a-1** (2.34 g, 10 mmol, 1 equiv) was added and dissolved with THF (0.5 M). Then NaH (0.8 g, 20 mmol, 2 equiv, 60%) was added under ice bath. The reaction was stirred at room temperature for 30 min, then MeI (1.6 mL, 25 mmol, 2.5 equiv) was added. After the reaction was completed, ethanol was added to quench reaction. The reaction solvent was evaporated and purified by silica gel column chromatography (PE:EA = 5:1) to give the product **S3a-2**.

In the eggplant shaped bottle, **S3a-2** (2.5 g, 10 mmol, 1 equiv) was added and dissolved with acetone. Then HCl aqueous solution (2.5 mL, 2.5 mmol, 0.25 equiv, 1 M) was added. The reaction was stirred at 50 °C until completion. The reaction solvent was evaporated. Saturated NaHCO₃ aqueous solution was added and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo to obtain **S3a-3** without further purification.

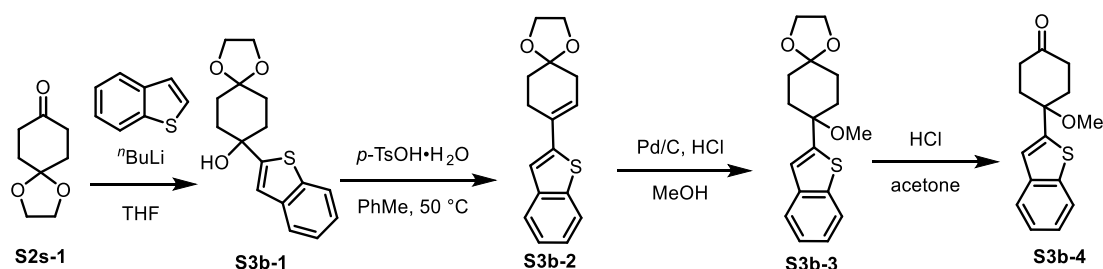
The product **S3a** was synthesized following the general procedure A and B from compound **S3a-3**.



¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.18 (m, 5H), 6.18 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.44 – 5.15 (m, 2H), 2.96 (s, 3H), 2.24 – 2.02 (m, 6H), 2.01 (s, 3H), 1.97 – 1.82 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 170.0, 139.3, 128.4, 127.4, 126.4, 116.6, 81.1, 76.5, 64.2, 49.9, 31.8, 31.2, 22.4.

HRMS (ESI) calcd. for C₁₇H₂₂NaO₃⁺ (*M* + Na)⁺: 297.1461, Found: 297.1461.



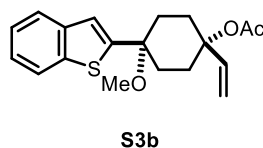
In the eggplant shaped bottle, benzothiophene (5.15 g, 38.4 mmol, 1.2 equiv) was added, vacuumed, replaced with argon, and dissolved with THF (0.1 M). The mixture was transferred to -78 °C for cooling. *n*-BuLi (17 mL, 41.6 mmol, 1.3 equiv, 2.4 M) was added drop by drop. The reaction was transferred to room temperature to stir for 1 h, then transferred to -78 °C again. The THF solution (0.1 M) of **S2s-1** (5 g, 32 mmol, 1 equiv) was added drop by drop. The reaction was stirred at room temperature until completion. After then, saturated NH₄Cl aqueous solution was added under the ice bath to quench the reaction and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo to obtain **S3b-1** without further purification.

In the eggplant shaped bottle, the crude product **S3b-1** (32 mmol, 1 equiv) and *p*-TsOH·H₂O (0.6 g, 3.2 mmol, 0.1 equiv), and PhMe (0.3 M) were added. The reaction was stirred at 80 °C until completion. After then, saturated NaHCO₃ aqueous solution was added and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, concentrated in vacuo, and purified by silica gel column chromatography (PE:EA = 15:1 to 10:1) to obtain **S3b-2**.

In the eggplant shaped bottle, **S3b-2** (3 g, 11 mmol, 1 equiv), MeOH (0.6 M), 10% Pd/C (55% wet weight, 300 mg), and concentrated HCl (10 drops) were added. The reaction was stirred at room temperature under hydrogen atmosphere until completion. After then, the reaction was filtered. The filtrate was concentrated and dried without further purification.

In the eggplant shaped bottle, **S3b-3** (11 mmol, 1 equiv) was added and dissolved with acetone. Then HCl aqueous solution (0.8 mL, 0.75 mmol, 0.25 equiv, 1 M) was added. The reaction was stirred at 50 °C until completion. The reaction solvent was evaporated. Saturated NaHCO₃ aqueous solution was added and the aqueous layer was extracted with DCM (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo to obtain **S3b-4** without further purification.

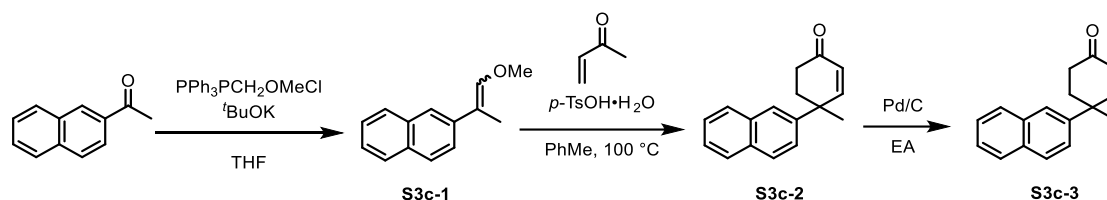
The product **S3b** was synthesized following the general procedure A and B from compound **S3b-4**.



¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.79 (m, 1H), 7.73 (dd, *J* = 6.8, 1.9 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.20 (s, 1H), 6.14 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.35 – 5.11 (m, 2H), 3.10 (s, 3H), 2.31 – 2.23 (m, 2H), 2.20 – 2.08 (m, 4H), 2.06 – 1.94 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 170.0, 139.9, 139.6, 124.6, 124.4, 123.6, 122.5, 122.3, 116.0, 80.9, 75.8, 50.1, 32.7, 31.4, 22.3.

HRMS (ESI) calcd. for C₁₉H₂₂NaO₃S⁺ (*M* + Na)⁺: 353.1182, Found: 353.1182.

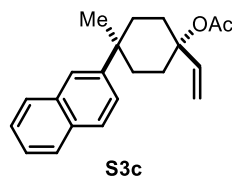


In the eggplant shaped bottle, PPh₃PCH₂OMeCl (15.4 g, 45 mmol, 1.5 equiv) and THF (0.4 M) were added and cooled to -78 °C. Then ^tBuOK (54 mL, 54 mmol, 1.8 equiv, 1 M THF solution) was added. Then the reaction was transferred to room temperature for 1 h and cooled to -78 °C again. 2-Acetonaphthone (5.1 g, 30 mmol, 1 equiv) was added. The reaction was transferred to room temperature until completion. After then, the reaction solvent was evaporated. The concentrate was diluted by PE:EA (10:1) and filtered. The filtrate was concentrated and purified by silica gel column chromatography (PE:EA = 100:0 to 20:1) to give **S3c-1**.

In the eggplant shaped bottle, **S3c-1** (5.8 g, 29 mmol, 1 equiv), methyl vinyl ketone (3.5 mL, 43.5 mmol, 1.5 equiv) and *p*-TsOH·H₂O (5.8 g, 30.5 mmol, 1.05 equiv) were added and dissolved with PhMe (1 M). The reaction was stirred at 100 °C for 12 h, and then transferred to room temperature to stir for another 12 h. Saturated NaHCO₃ aqueous solution was added to quench the reaction and the aqueous layer was extracted with EA (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, concentrated in vacuo and purified by silica gel column chromatography (PE:EA = 10:1) to obtain **S3c-2**.

In the eggplant shaped bottle, **S3c-2** (5.2 g, 22 mmol, 1 equiv), EA (1 M), and 10% Pd/C (55% wet weight, 520 mg) were added. The reaction was stirred at room temperature under hydrogen atmosphere until completion. After then, the reaction was filtered. The filtrate was concentrated and dried without further purification.

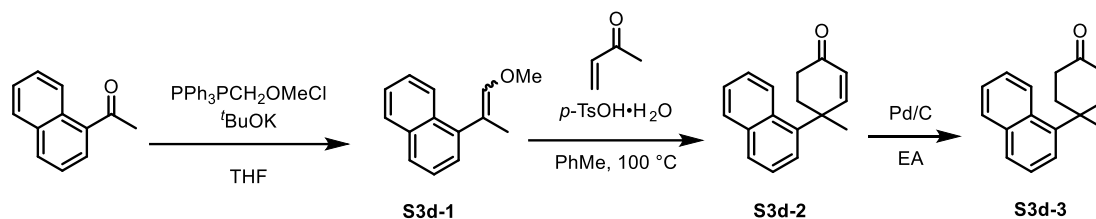
The product **S3c** was synthesized following the general procedure A and B from compound **S3c-3**.



¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.76 (m, 4H), 7.55 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.51 – 7.39 (m, 2H), 6.00 (dd, *J* = 17.8, 10.8 Hz, 1H), 5.09 – 4.95 (m, 2H), 2.39 – 2.22 (m, 4H), 2.10 (s, 3H), 1.83 (td, *J* = 14.2, 2.4 Hz, 2H), 1.57 (t, *J* = 12.7 Hz, 2H), 1.27 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.1, 141.5, 133.7, 131.8, 128.3, 128.0, 127.5, 126.0, 125.6, 124.8, 124.6, 113.9, 81.7, 38.0, 32.9, 31.5, 22.4.

HRMS (ESI) calcd. for $C_{21}H_{24}NaO_2^+$ ($M + Na$) $^+$: 331.1669, Found: 331.1669.

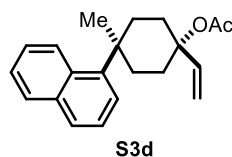


In the eggplant shaped bottle, PPh_3PCH_2OMeCl (15.4 g, 45 mmol, 1.5 equiv) and THF (0.4 M) were added and cooled to $-78\text{ }^\circ\text{C}$. Then $tBuOK$ (54 mL, 54 mmol, 1.8 equiv, 1 M THF solution) was added. Then the reaction was transferred to room temperature for 1 h and cooled to $-78\text{ }^\circ\text{C}$ again. 1-Acetonaphthone (5.1 g, 30 mmol, 1 equiv) was added. The reaction was transferred to room temperature until completion. After then, the reaction solvent was evaporated. The concentrate was diluted by PE:EA (10:1) and filtered. The filtrate was concentrated and purified by silica gel column chromatography (PE:EA = 100:0 to 20:1) to give **S3d-1**.

In the eggplant shaped bottle, **S3d-1** (5.8 g, 29 mmol, 1 equiv), methyl vinyl ketone (3.5 mL, 43.5 mmol, 1.5 equiv) and $p\text{-TsOH}\cdot H_2O$ (5.8 g, 30.5 mmol, 1.05 equiv) were added and dissolved with PhMe (1 M). The reaction was stirred at $100\text{ }^\circ\text{C}$ for 12 h, and then transferred to room temperature to stir for another 12 h. Saturated $NaHCO_3$ aqueous solution was added to quench the reaction and the aqueous layer was extracted with EA (3 times). The combined organic layers were washed with saturated brine, dried over $MgSO_4$, concentrated in vacuo and purified by silica gel column chromatography (PE:EA = 10:1) to obtain **S3d-2**.

In the eggplant shaped bottle, **S3d-2** (4.4 g, 18.6 mmol, 1 equiv), EA (1 M), and 10% Pd/C (55% wet weight, 440 mg) were added. The reaction was stirred at room temperature under hydrogen atmosphere until completion. After then, the reaction was filtered. The filtrate was concentrated and dried without further purification.

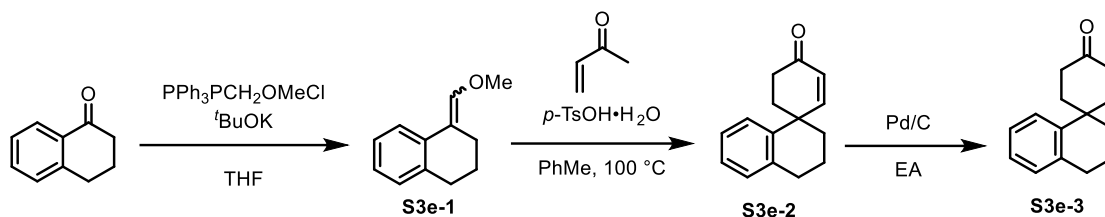
The product **S3d** was synthesized following the general procedure A and B from compound **S3d-3**.



1H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, $J = 7.6$ Hz, 1H), 7.88 (d, $J = 6.7$ Hz, 1H), 7.73 (d, $J = 7.9$ Hz, 1H), 7.57 – 7.37 (m, 4H), 6.05 (dd, $J = 17.4, 11.0$ Hz, 1H), 5.16 – 5.01 (m, 2H), 2.59 – 2.46 (m, 2H), 2.26 – 2.16 (m, 2H), 2.09 (s, 3H), 2.00 (t, $J = 12.6$ Hz, 2H), 1.81 – 1.62 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 141.1, 135.4, 131.6, 129.9, 127.7, 126.5, 125.1, 125.0, 124.7, 124.6, 114.3, 81.5, 39.0, 34.7, 31.6, 22.3.

HRMS (ESI) calcd. for $C_{21}H_{24}NaO_2^+$ ($M + Na$) $^+$: 331.1669, Found: 331.1668.

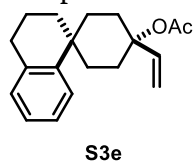


In the eggplant shaped bottle, $\text{PPh}_3\text{PCH}_2\text{OMeCl}$ (10.3 g, 30 mmol, 1.5 equiv) and THF (0.4 M) were added and cooled to $-78\text{ }^\circ\text{C}$. Then $t\text{BuOK}$ (36 mL, 36 mmol, 1.8 equiv, 1 M THF solution) was added. Then the reaction was transferred to room temperature for 1 h and cooled to $-78\text{ }^\circ\text{C}$ again. 1-Tetralone (2.9 g, 20 mmol, 1 equiv) was added. The reaction was transferred to room temperature until completion. After then, the reaction solvent was evaporated. The concentrate was diluted by PE:EA (10:1) and filtered. The filtrate was concentrated and purified by silica gel column chromatography (PE:EA = 100:0 to 20:1) to give **S3e-1**.

In the eggplant shaped bottle, **S3e-1** (3 g, 17.2 mmol, 1 equiv), methyl vinyl ketone (2.1 mL, 25.8 mmol, 1.5 equiv) and $p\text{-TsOH}\cdot\text{H}_2\text{O}$ (3.44 g, 18.1 mmol, 1.05 equiv) were added and dissolved with PhMe (1 M). The reaction was stirred at $100\text{ }^\circ\text{C}$ for 12 h, and then transferred to room temperature to stir for another 12 h. Saturated NaHCO_3 aqueous solution was added to quench the reaction and the aqueous layer was extracted with EA (3 times). The combined organic layers were washed with saturated brine, dried over MgSO_4 , concentrated in vacuo and purified by silica gel column chromatography (PE:EA = 25:1 to 10:1) to obtain **S3e-2**.

In the eggplant shaped bottle, **S3e-2** (2.38 g, 11.2 mmol, 1 equiv), EA (1 M), and 10% Pd/C (55% wet weight, 238 mg) were added. The reaction was stirred at room temperature under hydrogen atmosphere until completion. After then, the reaction was filtered. The filtrate was concentrated and dried without further purification.

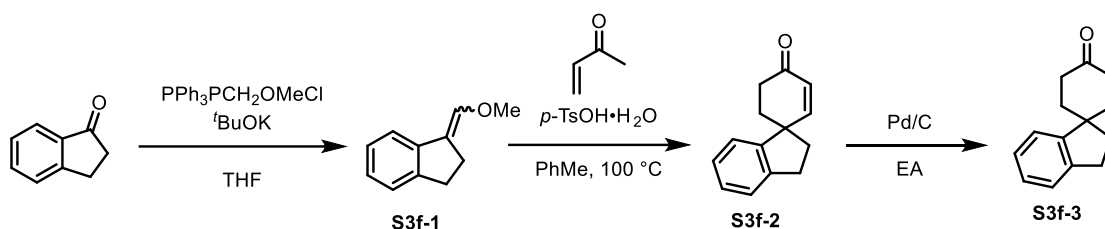
The product **S3e** was synthesized following the general procedure A and B from compound **S3e-3**.



^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, $J = 7.9\text{ Hz}$, 1H), 7.15 (t, $J = 7.4\text{ Hz}$, 1H), 7.11 – 7.02 (m, 2H), 6.32 (dd, $J = 17.7, 10.9\text{ Hz}$, 1H), 5.56 – 5.40 (m, 2H), 2.77 (t, $J = 6.2\text{ Hz}$, 2H), 2.29 (d, $J = 12.6\text{ Hz}$, 2H), 2.05 – 1.84 (m, 9H), 1.80 – 1.70 (m, 2H), 1.67 – 1.58 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.9, 145.0, 139.2, 137.4, 129.2, 126.6, 126.0, 125.6, 117.3, 82.0, 36.5, 35.6, 31.6, 31.2, 31.0, 22.5, 19.3.

HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{24}\text{NaO}_2^+$ ($\text{M} + \text{Na}$) $^+$: 307.1669, Found: 307.1668.

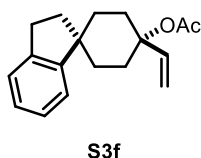


In the eggplant shaped bottle, $\text{PPh}_3\text{PCH}_2\text{OMeCl}$ (10.3 g, 30 mmol, 1.5 equiv) and THF (0.4 M) were added and cooled to $-78\text{ }^\circ\text{C}$. Then $t\text{BuOK}$ (36 mL, 36 mmol, 1.8 equiv, 1 M THF solution) was added. Then the reaction was transferred to room temperature for 1 h and cooled to $-78\text{ }^\circ\text{C}$ again. Indanone (2.6 g, 20 mmol, 1 equiv) was added. The reaction was transferred to room temperature until completion. After then, the reaction solvent was evaporated. The concentrate was diluted by PE:EA (10:1) and filtered. The filtrate was concentrated and purified by silica gel column chromatography (PE:EA = 100:0 to 20:1) to give **S3f-1**.

In the eggplant shaped bottle, **S3f-1** (3.1 g, 19.3 mmol, 1 equiv), methyl vinyl ketone (2.4 mL, 29 mmol, 1.5 equiv) and $p\text{-TsOH}\cdot\text{H}_2\text{O}$ (3.86 g, 20.3 mmol, 1.05 equiv) were added and dissolved with PhMe (1 M). The reaction was stirred at $100\text{ }^\circ\text{C}$ for 12 h, and then transferred to room temperature to stir for another 12 h. Saturated NaHCO_3 aqueous solution was added to quench the reaction and the aqueous layer was extracted with EA (3 times). The combined organic layers were washed with saturated brine, dried over MgSO_4 , concentrated in vacuo and purified by silica gel column chromatography (PE:EA = 25:1 to 10:1) to obtain **S3f-2**.

In the eggplant shaped bottle, **S3f-2** (1.94 g, 9.8 mmol, 1 equiv), EA (1 M), and 10% Pd/C (55% wet weight, 194 mg) were added. The reaction was stirred at room temperature under hydrogen atmosphere until completion. After then, the reaction was filtered. The filtrate was concentrated and dried without further purification.

The product **S3f** was synthesized following the general procedure A and B from compound **S3f-3**.



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.25 – 7.10 (m, 4H), 6.29 (dd, $J = 17.7, 10.9\text{ Hz}$, 1H), 5.48 – 5.34 (m, 2H), 2.91 (t, $J = 7.3\text{ Hz}$, 2H), 2.35 (d, $J = 13.4\text{ Hz}$, 2H), 2.06 (t, $J = 7.3\text{ Hz}$, 2H), 2.01 (s, 3H), 2.00 – 1.91 (m, 2H), 1.79 – 1.68 (m, 2H), 1.64 – 1.54 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.9, 139.3, 126.7, 126.3, 124.7, 122.5, 116.7, 81.7, 47.3, 41.6, 33.6, 32.5, 29.9, 22.4.

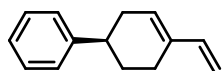
HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{22}\text{NaO}_2^+$ ($\text{M} + \text{Na}$) $^+$: 293.1512, Found: 293.1512.

General Procedure for Pd catalyzed $\beta\text{-H}$ elimination

In an Ar-filled glove box, (*R,R*)-DACH-phenyl Trost ligand **L11** (2.5 mg, 0.0036 mmol,

1.8 mol%) and Pd₂dba₃·CHCl₃ (1.6 mg, 0.0015 mmol, 0.75 mol%) were dissolved in dry 1,4-dioxane (0.4 M, 0.5 mL) to stir at room temperature for 1 h. To the solution, substrate (0.2 mmol) was added. The resulting mixture was stirred at 50 °C for 12 h. The mixture was then purified by silica gel column chromatography to give the desired product.

Characterization of Products



(*R*)-4-vinyl-1,2,3,6-tetrahydro-1,1'-biphenyl (2a)

Prepared according to General Procedure, colorless oil, 90% yield, 90% ee.

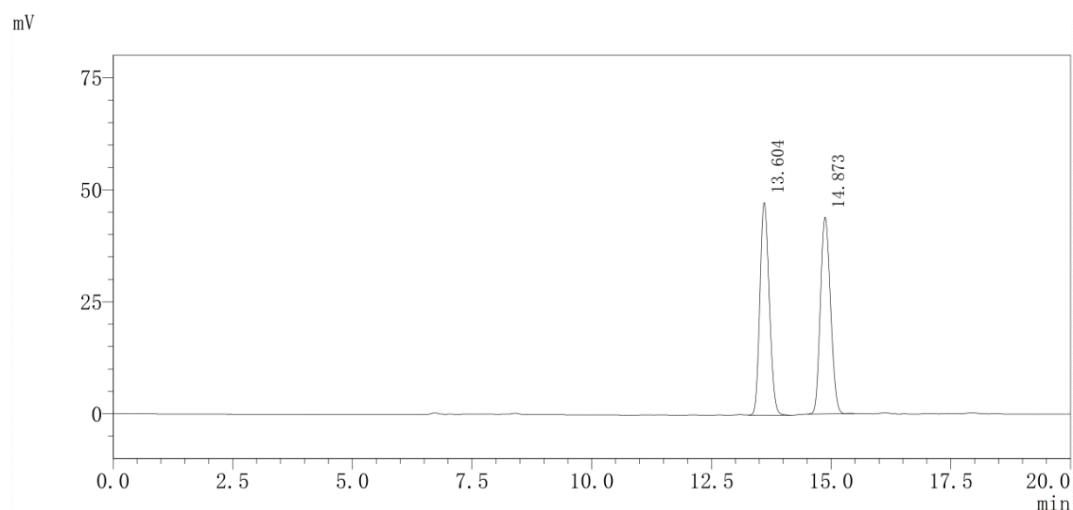
$[\alpha]_D^{25} = +96.2$ (c 1.0, CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.12 (m, 5H), 6.41 (dd, J = 17.5, 10.7 Hz, 1H), 5.84 (d, J = 2.9 Hz, 1H), 5.10 (d, J = 17.5 Hz, 1H), 4.95 (d, J = 10.7 Hz, 1H), 2.80 (q, J = 10.0 Hz, 1H), 2.51 – 2.17 (m, 4H), 2.04 (d, J = 11.3 Hz, 1H), 1.89 – 1.71 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 146.9, 139.8, 136.0, 129.3, 128.5, 127.0, 126.2, 110.5, 40.4, 34.1, 29.7, 24.6.

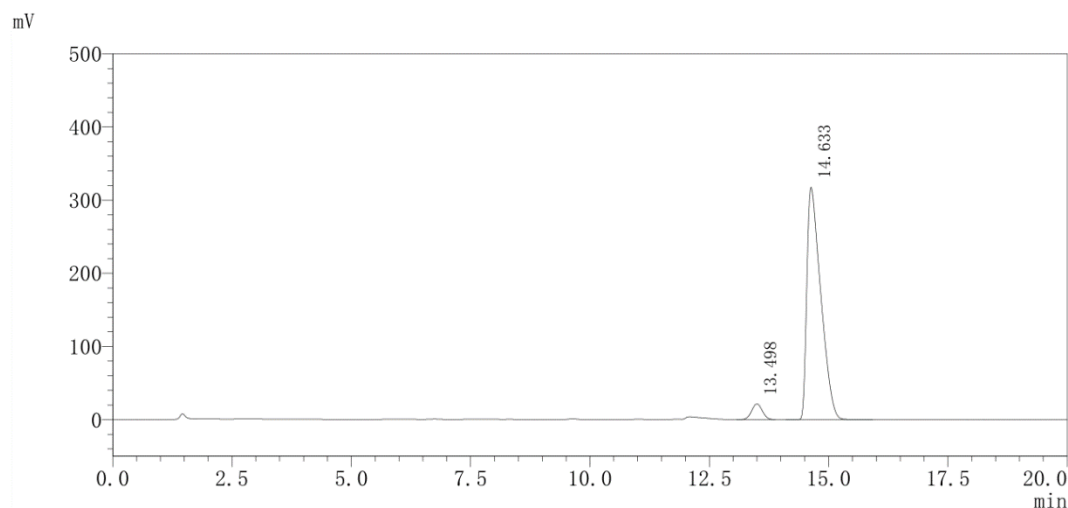
GCMS (EI) calcd. for C₁₄H₁₆⁺ (M^+): 184.1247, Found: 184.1242.

The ee value was 90%, t_r (minor) = 13.498, t_r (major) = 14.633 (Chiralcel OD-3, λ = 254 nm, hexanes:^{*i*}PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



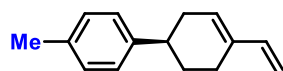
检测器A 254nm

Peak#	Time	Area	Height	Height%	Area%
1	13.604	646822	47426	51.933	50.007
2	14.873	646645	43895	48.067	49.993
总计		1293467	91321	100.000	100.000



检测器A 254nm

Peak#	Time	Area	Height	Height%	Area%
1	13.498	335967	21374	6.307	4.945
2	14.633	6458303	317540	93.693	95.055
总计		6794270	338914	100.000	100.000



(*R*)-4'-methyl-4-vinyl-1,2,3,6-tetrahydro-1,1'-biphenyl (2b)

Prepared according to General Procedure, colorless oil, 83% yield, 93% ee.

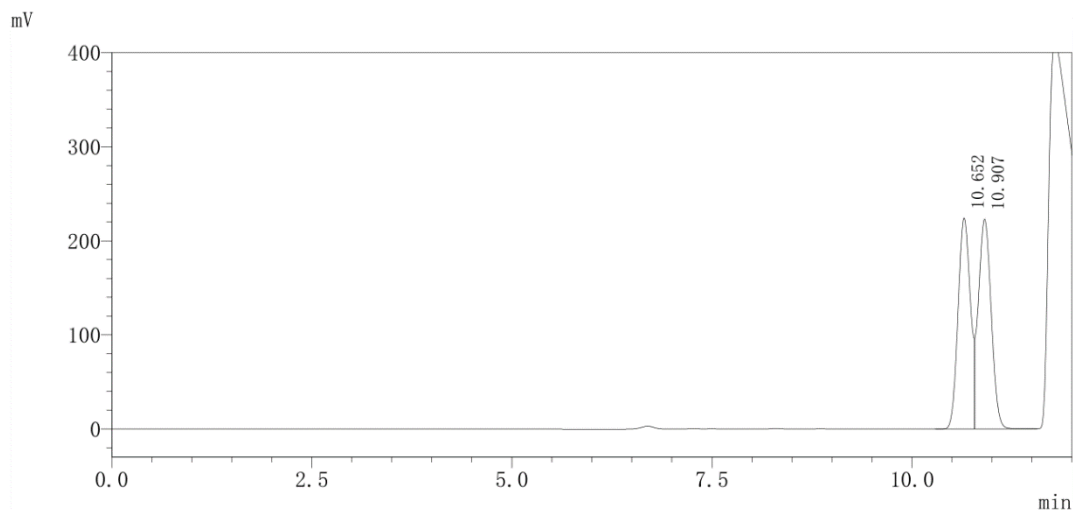
$[\alpha]_D^{25} = +103.2$ (c 1.0, CHCl_3)

^1H NMR (400 MHz, CDCl_3) δ 7.24 (s, 4H), 6.52 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.95 (d, $J = 3$ Hz, 1H), 5.22 (d, $J = 17.5$ Hz, 1H), 5.06 (d, $J = 10.7$ Hz, 1H), 2.98 – 2.81 (m, 1H), 2.60 – 2.30 (m, 7H), 2.21 – 2.08 (m, 1H), 1.95 – 1.82 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 144.0, 139.8, 136.0, 135.7, 129.4, 129.2, 126.9, 110.4, 39.9, 34.2, 29.8, 24.6, 21.1.

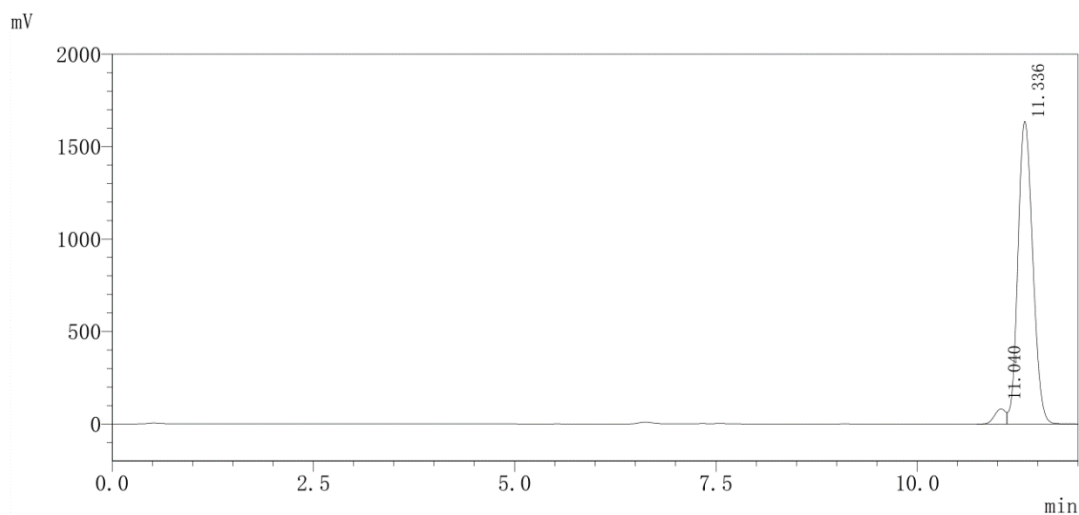
GCMS (EI) calcd. for $\text{C}_{15}\text{H}_{18}^+$ (M^+): 198.1403, Found: 198.1405.

The ee value was 93%, t_r (minor) = 11.040, t_r (major) = 11.336 (Chiralcel OD-3, $\lambda = 220$ nm, hexanes: i PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



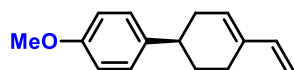
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	10.652	2438499	224247	50.120	49.534
2	10.907	2484346	223175	49.880	50.466
总计		4922845	447421	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	11.040	804137	81697	4.752	3.682
2	11.336	21036341	1637371	95.248	96.318
总计		21840477	1719068	100.000	100.000



(R)-4'-methoxy-4-vinyl-1,2,3,6-tetrahydro-1,1'-biphenyl (2c)

Prepared according to General Procedure, pale yellow solid, 84% yield, m.p. 50-51 °C, 91% ee.

$[\alpha]_D^{25} = +78.2$ (c 1.0, CHCl_3)

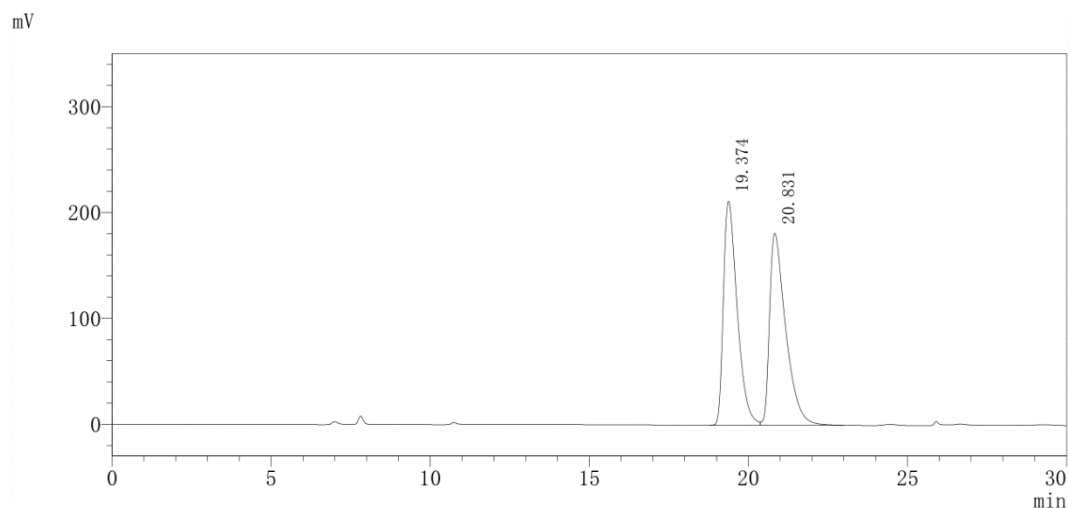
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.18 (d, $J = 8.5$ Hz, 2H), 6.88 (d, $J = 8.5$ Hz, 2H), 6.43 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.85 (d, $J = 3.6$ Hz, 1H), 5.12 (d, $J = 17.5$ Hz, 1H), 4.97 (d,

$J = 10.7$ Hz, 1H), 3.81 (s, 3H), 2.78 (t, $J = 10.7$ Hz, 1H), 2.50 – 2.35 (m, 2H), 2.32 – 2.19 (m, 2H), 2.11 – 1.99 (m, 1H), 1.90 – 1.67 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 158.0, 139.8, 139.1, 136.0, 129.3, 127.8, 113.9, 110.4, 55.4, 39.5, 34.3, 29.9, 24.6.

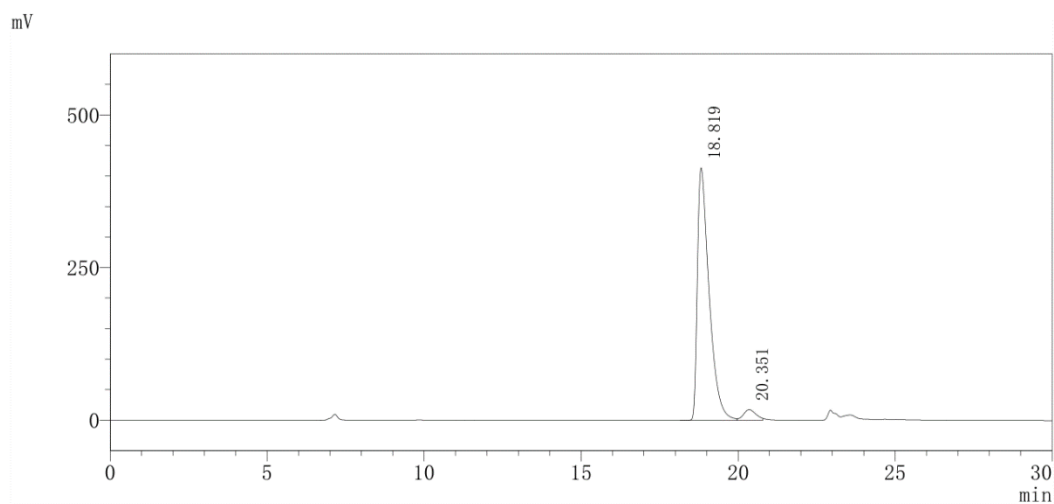
GCMS (EI) calcd. for $\text{C}_{15}\text{H}_{18}\text{O}^+$ (M^+): 214.1352, Found: 214.1348.

The ee value was 91%, t_r (minor) = 20.351, t_r (major) = 18.819 (Chiralcel IE, $\lambda = 220$ nm, hexanes:*i*PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



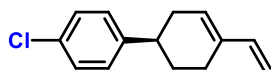
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	19.374	6385138	211597	53.846	49.916
2	20.831	6406683	181370	46.154	50.084
总计		12791821	392967	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	18.819	10819453	414075	95.855	95.520
2	20.351	507440	17907	4.145	4.480
总计		11326892	431982	100.000	100.000



(*R*)-4'-chloro-4-vinyl-1,2,3,6-tetrahydro-1,1'-biphenyl (2d)

Prepared according to General Procedure, white solid, 81% yield, m.p. 51-52 °C, 93% ee.

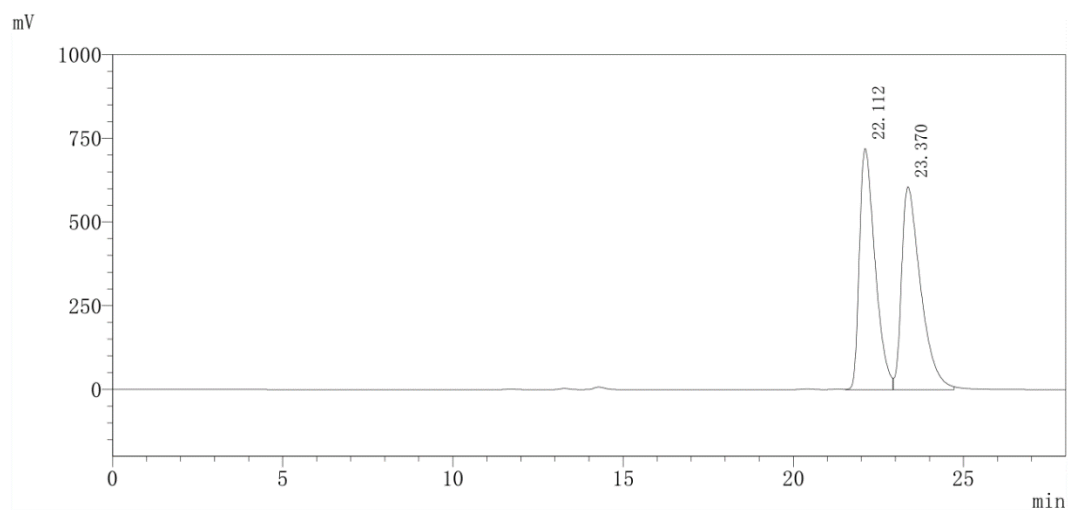
$[\alpha]_D^{25} = +92.8$ (c 1.0, CHCl_3)

^1H NMR (400 MHz, CDCl_3) δ 7.26 (d, $J = 8.4$ Hz, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 6.40 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.82 (d, $J = 3.8$ Hz, 1H), 5.10 (d, $J = 17.5$ Hz, 1H), 4.95 (d, $J = 10.7$ Hz, 1H), 2.93 – 2.67 (m, 1H), 2.49 – 2.11 (m, 4H), 2.09 – 1.94 (m, 1H), 1.85 – 1.65 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 145.3, 139.6, 136.1, 131.8, 128.8, 128.6, 128.4, 110.7, 39.7, 34.0, 29.6, 24.4.

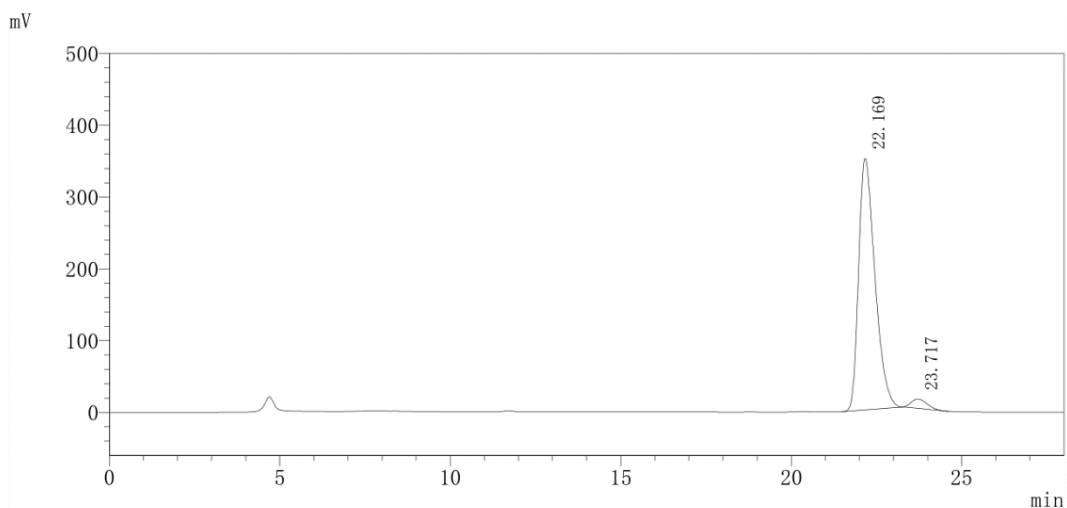
GCMS (EI) calcd. for $\text{C}_{14}\text{H}_{15}\text{Cl}^+$ (M^+): 218.0857, Found: 218.0856.

The ee value was 93%, t_r (minor) = 23.717, t_r (major) = 22.169 (Chiralcel IE, $\lambda = 220$ nm, hexanes:*i*PrOH = 100:0, flow rate = 0.3 mL/min).



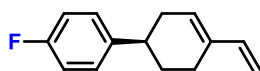
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	22.112	23030626	720482	54.309	49.336
2	23.370	23650410	606163	45.691	50.664
总计		46681036	1326645	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	22.169	11665704	350239	96.447	96.571
2	23.717	414248	12901	3.553	3.429
总计		12079952	363139	100.000	100.000



(R)-4'-fluoro-4-vinyl-1,2,3,6-tetrahydro-1,1'-biphenyl (2e)

Prepared according to General Procedure, white solid, 94% yield, m.p. 30-31 °C, 90% ee.

$[\alpha]_D^{11} = +82.0$ (c 1.0, CHCl_3)

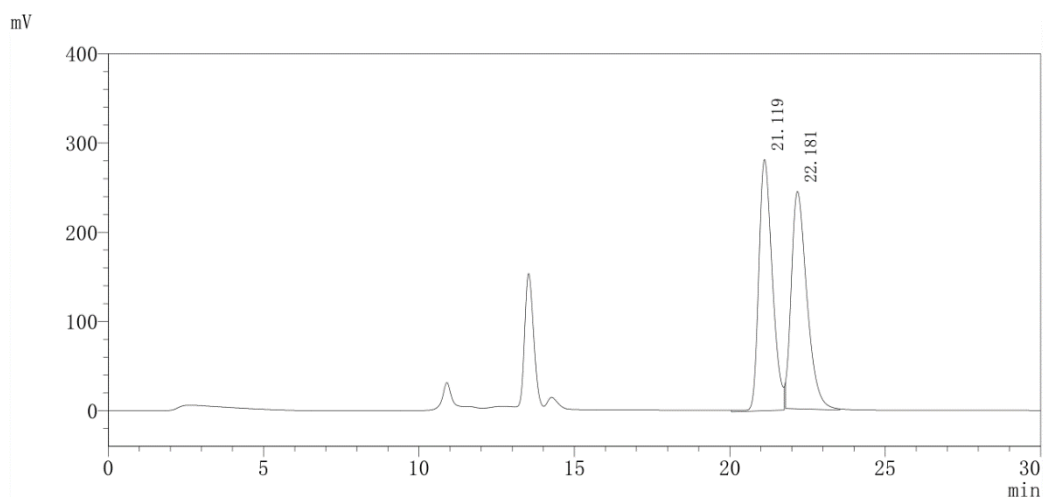
^1H NMR (400 MHz, CDCl_3) δ 7.44 (dd, $J = 8.2, 5.6$ Hz, 2H), 7.24 (t, $J = 8.6$ Hz, 2H), 6.66 (dd, $J = 17.5, 10.7$ Hz, 1H), 6.08 (d, $J = 3.9$ Hz, 1H), 5.36 (d, $J = 17.5$ Hz, 1H), 5.21 (d, $J = 10.7$ Hz, 1H), 3.05 (td, $J = 12.9, 12.5, 3.6$ Hz, 1H), 2.78 – 2.39 (m, 4H), 2.35 – 2.20 (m, 1H), 2.11 – 1.90 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.45 (d, $J = 243.6$ Hz), 142.5 (d, $J = 3.1$ Hz), 139.7, 136.1, 129.0, 128.29 (d, $J = 7.7$ Hz), 115.21 (d, $J = 20.9$ Hz), 110.6, 39.6, 34.2, 29.8, 24.5.

^{19}F NMR (376 MHz, CDCl_3) δ -117.39.

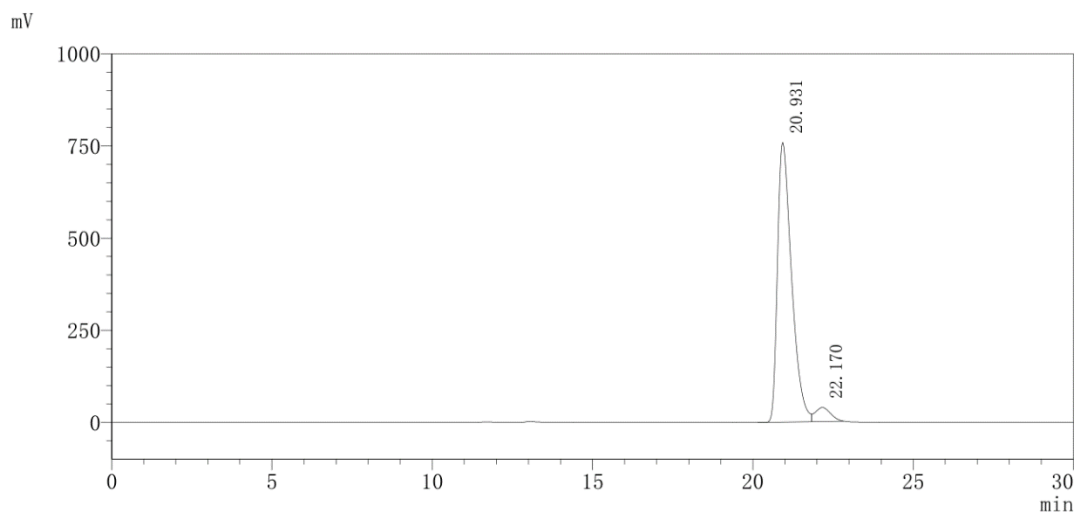
GCMS (EI) calcd. for $\text{C}_{14}\text{H}_{15}\text{F}^+$ (M^+): 202.1152, Found: 202.1148.

The ee value was 90%, t_r (minor) = 22.170, t_r (major) = 20.931 (Chiralcel IE, $\lambda = 220$ nm, hexanes: $i\text{-PrOH} = 100:0$, flow rate = 0.3 mL/min).



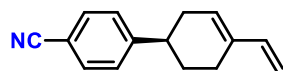
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	21.119	8528900	281521	53.607	49.979
2	22.181	8535959	243640	46.393	50.021
总计		17064859	525162	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	20.931	23172818	758298	95.252	94.864
2	22.170	1254655	37798	4.748	5.136
总计		24427473	796096	100.000	100.000



(R)-4'-vinyl-1',2',3',6'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (2f)

Prepared according to General Procedure, white solid, 92% yield, m.p. 103-104 °C, 88% ee.

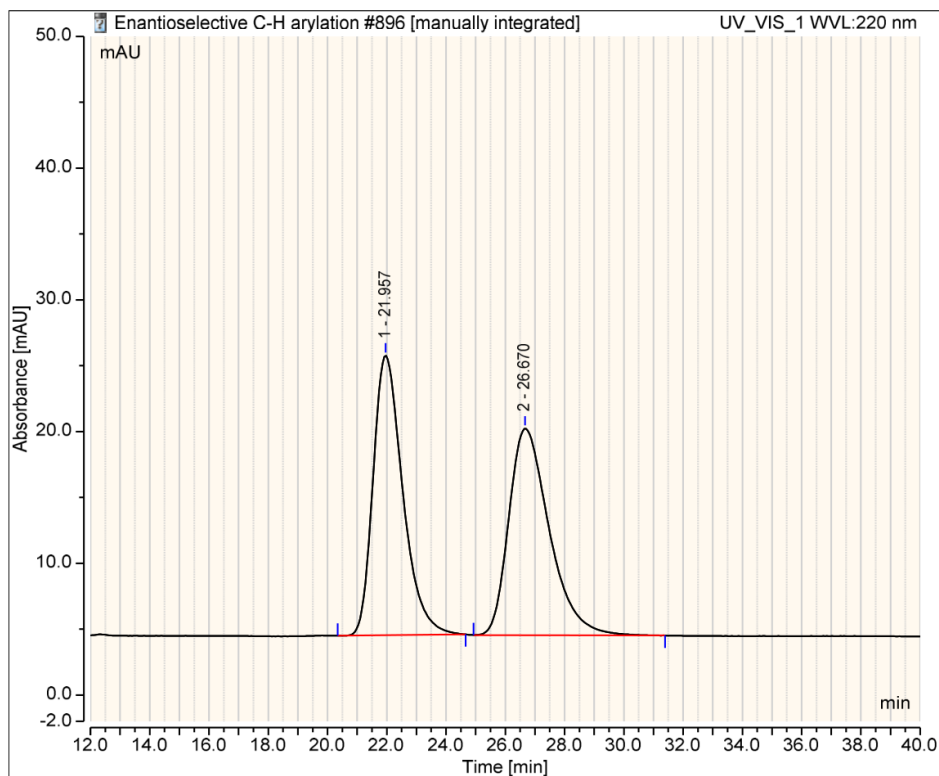
$[\alpha]_D^{11} = +109.8$ (c 1.0, CHCl_3)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 6.40 (dd, $J = 17.5, 10.8$ Hz, 1H), 5.83 (d, $J = 3.6$ Hz, 1H), 5.11 (d, $J = 17.5$ Hz, 1H), 4.97 (d, $J = 10.7$ Hz, 1H), 2.95 – 2.79 (m, 1H), 2.52 – 2.17 (m, 4H), 2.11 – 1.98 (m, 1H), 1.87 – 1.71 (m, 1H).

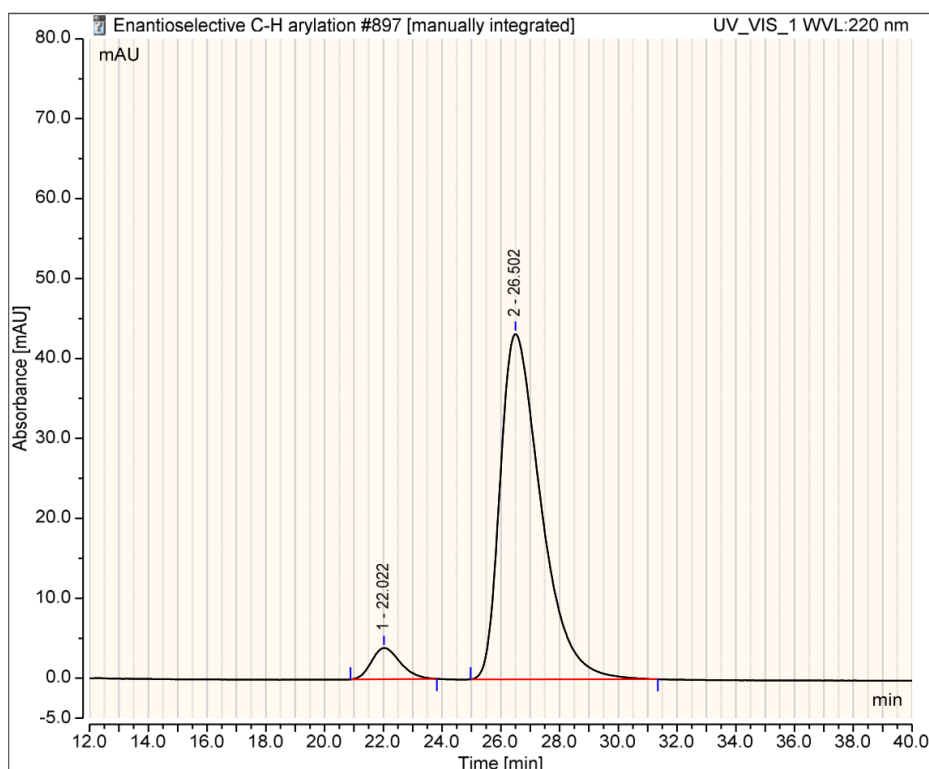
^{13}C NMR (101 MHz, CDCl_3) δ 152.4, 139.4, 136.1, 132.4, 128.2, 127.9, 119.2, 110.9, 110.0, 40.4, 33.5, 29.2, 24.1.

GCMS (EI) calcd. for $\text{C}_{15}\text{H}_{15}\text{N}^+$ (M^+): 209.1199, Found: 209.1200.

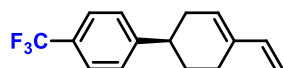
The ee value was 88%, t_r (minor) = 22.022, t_r (major) = 26.502 (Chiralcel IH, λ = 220 nm, hexanes: i PrOH = 99:1, flow rate = 1.0 mL/min).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	ee %
1		21.957	24.652	21.231	49.85	57.51	0.29
2		26.670	24.796	15.687	50.15	42.49	
Total:			49.449	36.918	100.00	100.00	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	ee %
1		22.022	4.445	3.907	6.02	8.29	87.96
2		26.502	69.417	43.234	93.98	91.71	
Total:			73.862	47.141	100.00	100.00	



(*R*)-4'-(trifluoromethyl)-4-vinyl-1,2,3,6-tetrahydro-1,1'-biphenyl (2g)

Prepared according to General Procedure, colorless solid, 89% yield, m.p. 76-77 °C.

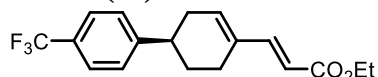
$[\alpha]_D^{25} = +69.2$ (*c* 1.0, CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 6.43 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.86 (d, *J* = 2.7 Hz, 1H), 5.13 (d, *J* = 17.5 Hz, 1H), 4.99 (d, *J* = 10.7 Hz, 1H), 3.00 – 2.83 (m, 1H), 2.59 – 2.19 (m, 4H), 2.13 – 2.01 (m, 1H), 1.93 – 1.73 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 150.9, 139.6, 136.1, 128.6 (q, *J* = 32.1 Hz), 127.4, 125.5 (q, *J* = 3.5 Hz), 124.5 (q, *J* = 271.8 Hz), 110.8, 40.3, 33.8, 29.4, 24.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.27.

GCMS (EI) calcd. for C₁₅H₁₅F₃⁺ (M⁺): 252.1120, Found: 252.1121.



ethyl (*R,E*)-3-(4'-(trifluoromethyl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)acrylate (2g')

$[\alpha]_D^{25} = +62.2$ (*c* 1.0, CHCl₃), white solid, m.p. 111-112 °C, 90% ee.

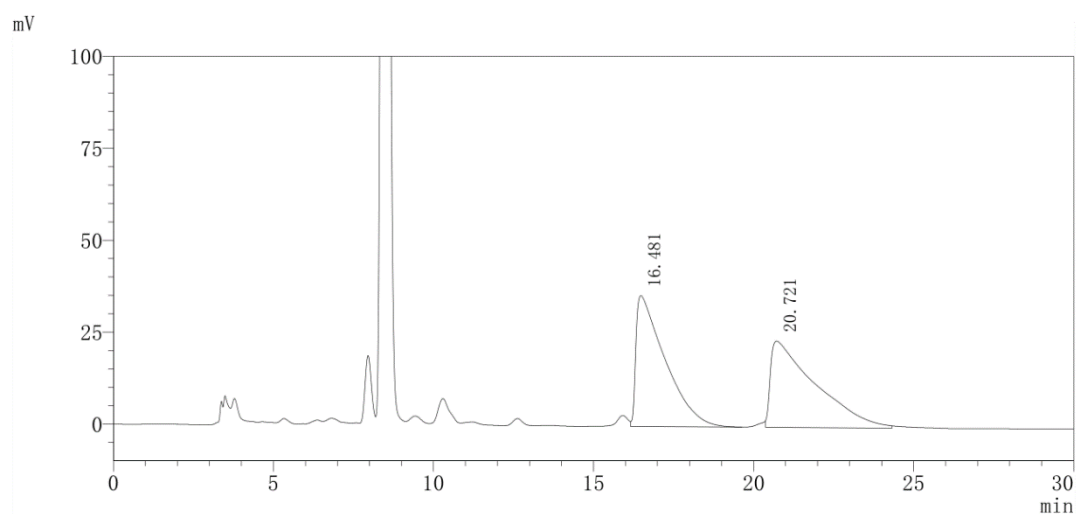
¹H NMR (600 MHz, CDCl₃) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.39 – 7.28 (m, 3H), 6.24 (s, 1H), 5.81 (d, *J* = 15.8 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 2.99 – 2.84 (m, 1H), 2.64 – 2.49 (m, 1H), 2.40 – 2.22 (m, 3H), 2.12 – 2.00 (m, 1H), 1.90 – 1.78 (m, 1H), 1.31 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 167.6, 150.2, 147.1, 137.1, 134.9, 128.7 (q, *J* = 32.3 Hz), 127.3, 125.6 (q, *J* = 3.6 Hz), 124.4 (q, *J* = 271.8 Hz), 115.8, 60.4, 39.7, 34.2, 29.1, 24.6, 14.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.32.

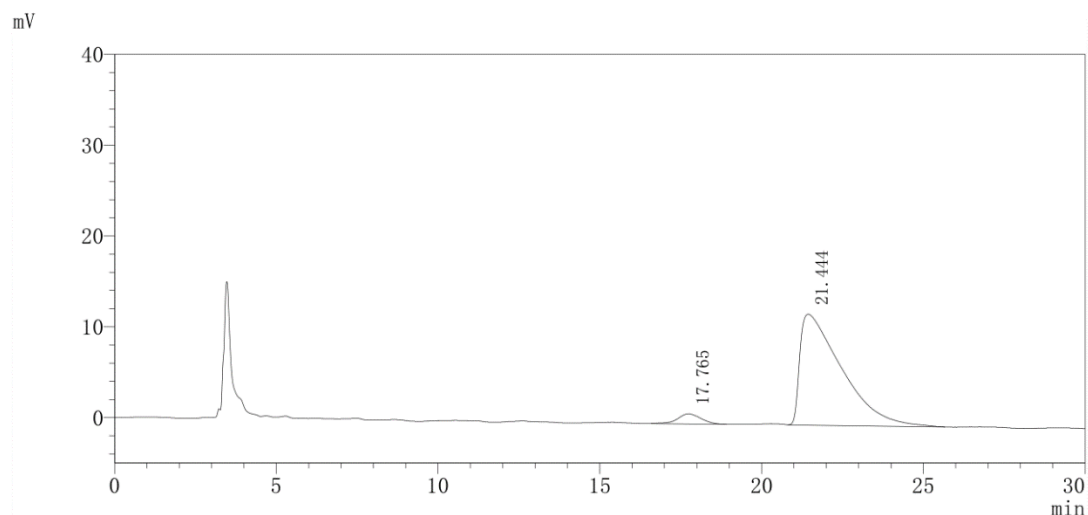
GCMS (EI) calcd. for C₁₈H₁₉F₃O₂⁺ (M⁺): 324.1332, Found: 324.1332.

The ee value was 90%, *t_r* (minor) = 17.765, *t_r* (major) = 21.444 (Chiralcel IF, λ = 220 nm, hexanes:PrOH = 98:2, flow rate = 1.0 mL/min).



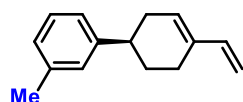
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	16.481	2250607	35584	60.278	49.683
2	20.721	2279281	23449	39.722	50.317
总计		4529888	59033	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	17.765	54820	1099	8.259	4.763
2	21.444	1096113	12210	91.741	95.237
总计		1150933	13309	100.000	100.000



(*R*)-3'-methyl-4-vinyl-1,2,3,6-tetrahydro-1,1'-biphenyl (2h)

Prepared according to General Procedure, colorless oil, 80% yield, 91% ee.

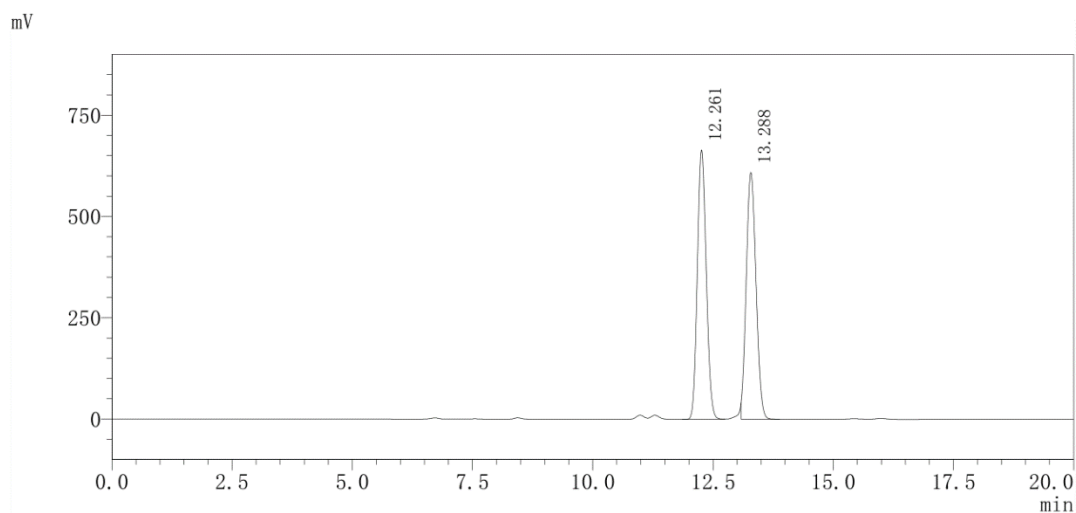
$[\alpha]_D^{25} = +96.2$ (c 1.0, CHCl_3)

^1H NMR (400 MHz, CDCl_3) δ 7.34 (t, $J = 7.7$ Hz, 1H), 7.22 – 7.12 (m, 3H), 6.54 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.97 (d, $J = 4.6$ Hz, 1H), 5.24 (d, $J = 17.5$ Hz, 1H), 5.08 (d, $J = 10.7$ Hz, 1H), 2.97 – 2.80 (m, 1H), 2.62 – 2.46 (m, 5H), 2.46 – 2.30 (m, 2H), 2.23 – 2.11 (m, 1H), 1.99 – 1.84 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.9, 139.8, 138.0, 136.0, 129.4, 128.4, 127.8, 127.0, 124.0, 110.5, 40.4, 34.2, 29.7, 24.6, 21.6.

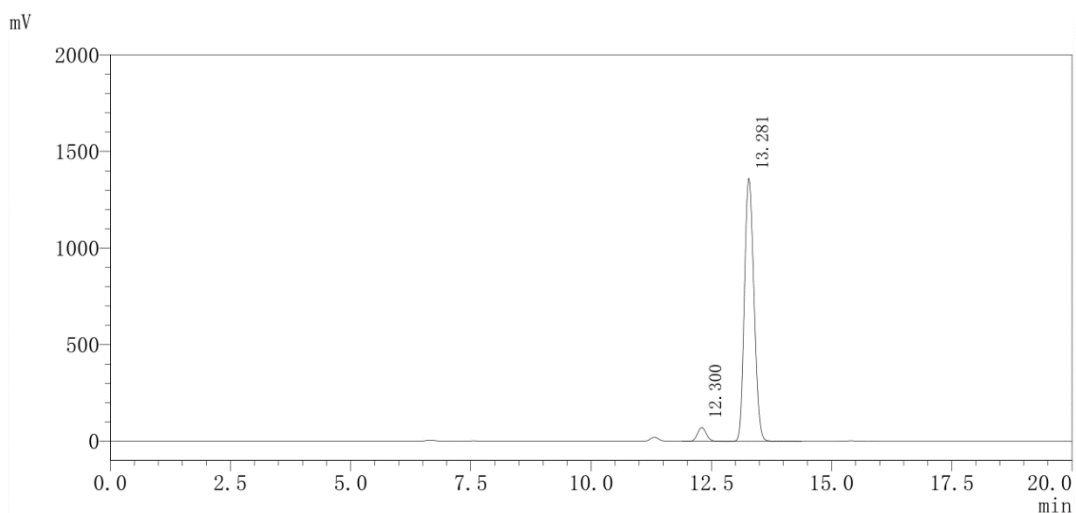
GCMS (EI) calcd. for $\text{C}_{15}\text{H}_{18}^+$ (M^+): 198.1403, Found: 198.1399.

The ee value was 91%, t_r (minor) = 12.300, t_r (major) = 13.281 (Chiralcel OD-3, $\lambda = 220$ nm, hexanes:*i*PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



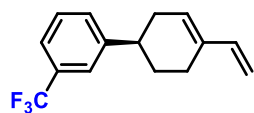
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	12.261	8619368	664876	52.170	50.007
2	13.288	8617107	609563	47.830	49.993
总计		17236475	1274439	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	12.300	889335	70725	4.939	4.518
2	13.281	18795400	1361207	95.061	95.482
总计		19684735	1431932	100.000	100.000



(*R*)-3'-(trifluoromethyl)-4-vinyl-1,2,3,6-tetrahydro-1,1'-biphenyl (2i)

Prepared according to General Procedure, colorless oil, 82% yield, 89% ee.

$[\alpha]_D^{25} = +78.2$ (c 1.0, CHCl_3)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 – 7.37 (m, 4H), 6.42 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.85 (d, $J = 4.3$ Hz, 1H), 5.13 (d, $J = 17.5$ Hz, 1H), 4.98 (d, $J = 10.7$ Hz, 1H), 2.99 –

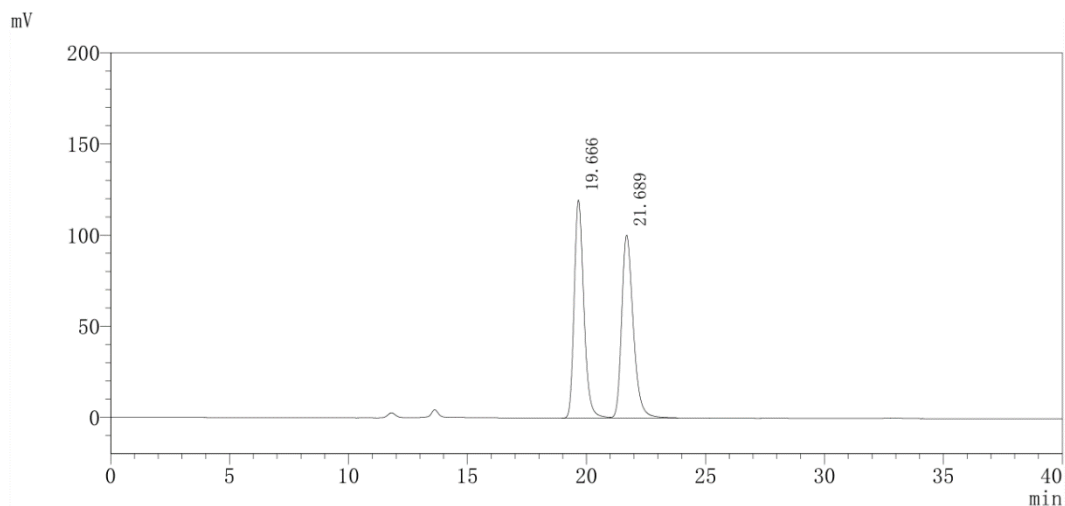
2.80 (m, 1H), 2.54 – 2.35 (m, 2H), 2.34 – 2.19 (m, 2H), 2.12 – 2.02 (m, 1H), 1.91 – 1.72 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.8, 139.6, 136.1, 130.8 (q, $J = 31.8$ Hz), 130.4, 129.0, 128.6, 124.4 (q, $J = 272.7$ Hz), 123.8 (q, $J = 3.5$ Hz), 123.1 (q, $J = 4.0$ Hz), 110.8, 40.2, 33.9, 29.5, 24.34.

^{19}F NMR (376 MHz, CDCl_3) δ -62.45.

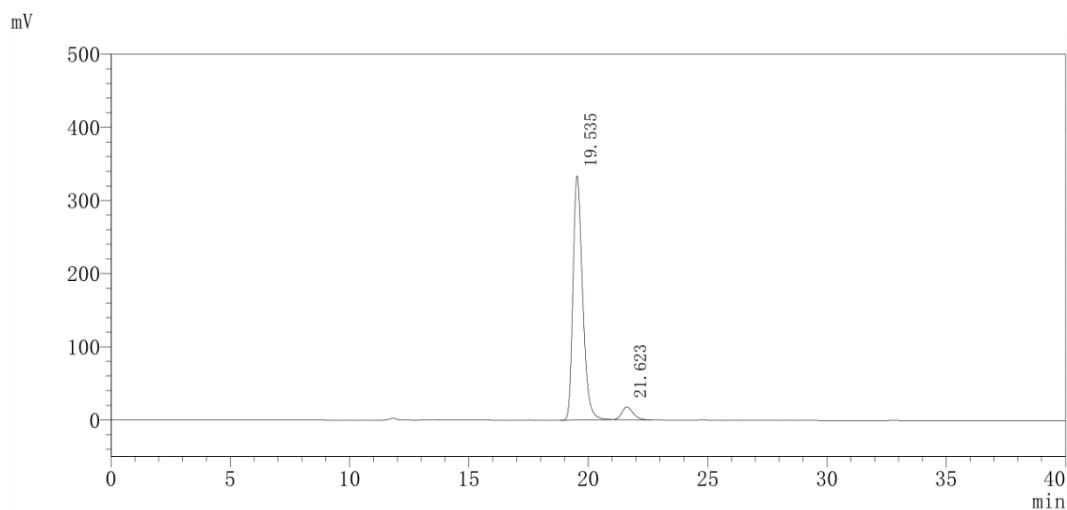
GCMS (EI) calcd. for $\text{C}_{15}\text{H}_{15}\text{F}_3^+$ (M^+): 252.1120, Found: 252.1115.

The ee value was 89%, t_r (minor) = 21.623, t_r (major) = 19.535 (Chiralcel IE, $\lambda = 220$ nm, hexanes:PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



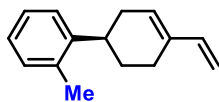
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	19.666	3374982	119604	54.378	49.953
2	21.689	3381349	100344	45.622	50.047
总计		6756331	219948	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	19.535	9393412	333836	95.046	94.263
2	21.623	571668	17400	4.954	5.737
总计		9965079	351236	100.000	100.000



(*R*)-2'-methyl-4-vinyl-1,2,3,6-tetrahydro-1,1'-biphenyl (2j)

Prepared according to General Procedure, colorless oil, 82% yield, 91% ee.

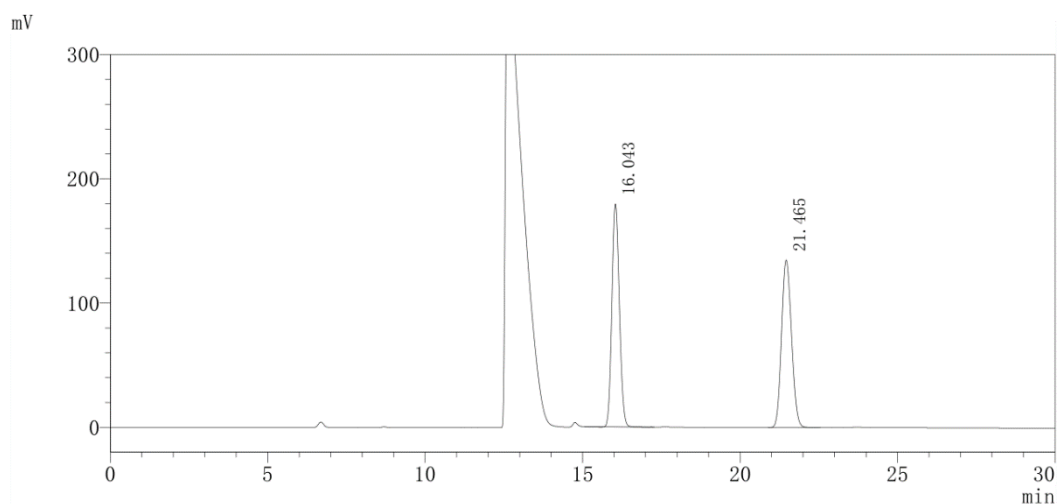
$[\alpha]_D^{25} = +79.4$ (c 1.0, CHCl_3)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.10 (m, 4H), 6.48 (dd, $J = 17.5, 10.8$ Hz, 1H), 5.92 (d, $J = 2.2$ Hz, 1H), 5.17 (d, $J = 17.5$ Hz, 1H), 5.01 (d, $J = 10.7$ Hz, 1H), 3.16 – 2.99 (m, 1H), 2.54 – 2.22 (m, 7H), 2.13 – 1.98 (m, 1H), 1.96 – 1.79 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.9, 139.8, 136.0, 135.5, 130.4, 129.6, 126.4, 125.9, 125.5, 110.5, 35.9, 33.2, 29.1, 24.9, 19.5.

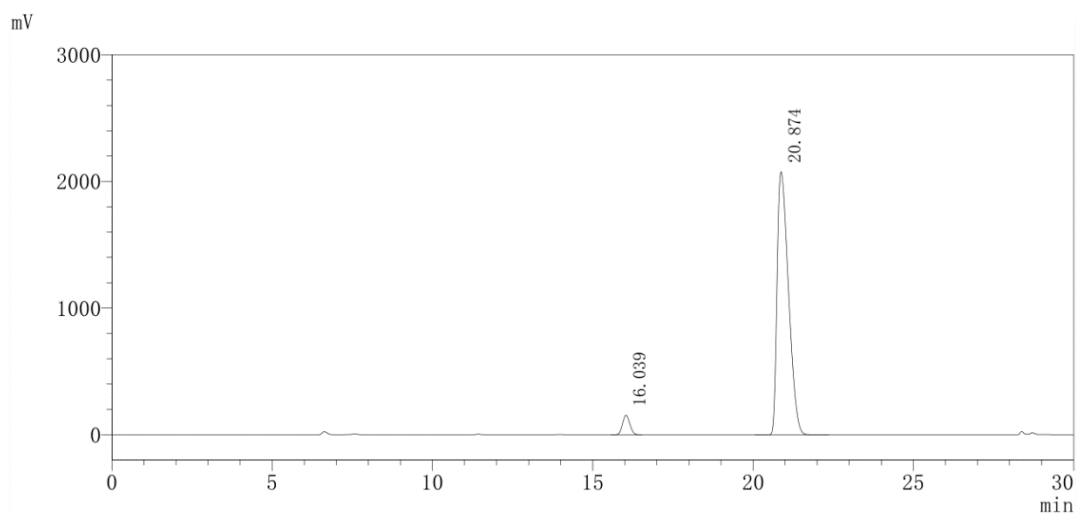
GCMS (EI) calcd. for $\text{C}_{15}\text{H}_{18}^+$ (M^+): 198.1403, Found: 198.1403.

The ee value was 91%, t_r (minor) = 16.039, t_r (major) = 20.874 (Chiralcel OD-3, $\lambda = 220$ nm, hexanes: i PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



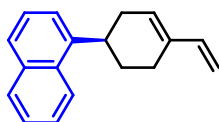
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	16.043	2961974	179501	57.101	49.899
2	21.465	2973954	134855	42.899	50.101
总计		5935928	314356	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	16.039	2466112	154358	6.916	4.581
2	20.874	51369181	2077616	93.084	95.419
总计		53835293	2231974	100.000	100.000



(*R*)-1-(4-vinylcyclohex-3-en-1-yl)naphthalene (2k)

Prepared according to General Procedure, white solid, 89% yield, m.p. 28-29 °C, 94% ee.

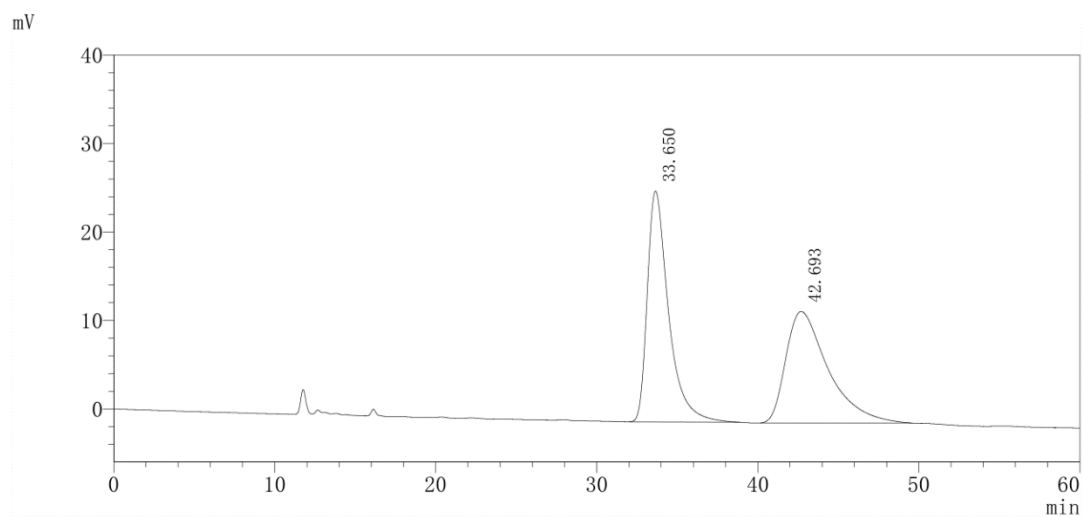
$[\alpha]_D^{25} = -19.8$ (c 1.0, CHCl_3)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 7.5$ Hz, 1H), 7.76 (d, $J = 7.8$ Hz, 1H), 7.64 – 7.34 (m, 4H), 6.51 (dd, $J = 17.4, 10.8$ Hz, 1H), 5.96 (s, 1H), 5.20 (d, $J = 17.5$ Hz, 1H), 5.04 (d, $J = 10.7$ Hz, 1H), 3.84 – 3.52 (m, 1H), 2.76 – 2.56 (m, 1H), 2.51 – 2.35 (m, 3H), 2.26 – 2.16 (m, 1H), 2.11 – 1.96 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.6, 139.7, 136.1, 134.0, 131.6, 129.5, 129.1, 126.7, 125.9, 125.8, 125.5, 123.3, 122.5, 110.6, 35.1, 33.9, 29.3, 24.8.

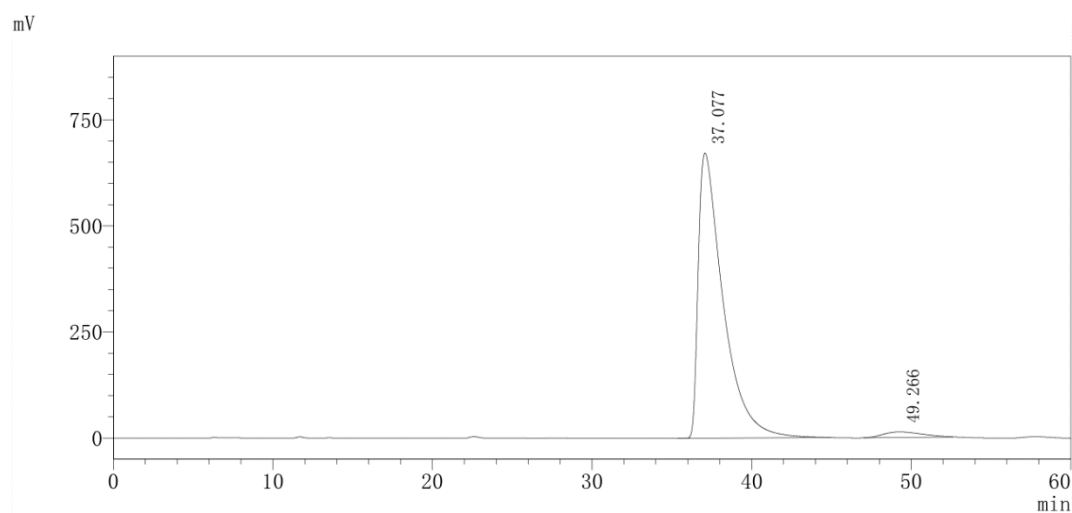
GCMS (EI) calcd. for $\text{C}_{18}\text{H}_{18}^+$ (M^+): 234.1403, Found: 234.1400.

The ee value was 94%, t_r (minor) = 49.266, t_r (major) = 37.077 (Chiralcel IE, $\lambda = 220$ nm, hexanes: i PrOH = 99.8:0.2, flow rate = 0.3 mL/min).



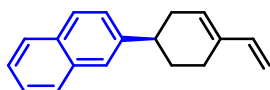
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	33.650	2398631	26103	67.438	51.052
2	42.693	2299732	12604	32.562	48.948
总计		4698363	38707	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	37.077	72963906	672436	98.081	97.058
2	49.266	2211411	13160	1.919	2.942
总计		75175317	685596	100.000	100.000



(R)-2-(4-vinylcyclohex-3-en-1-yl)naphthalene (2l)

Prepared according to General Procedure, white solid, 75% yield, m.p. 50-51 °C, 94% ee.

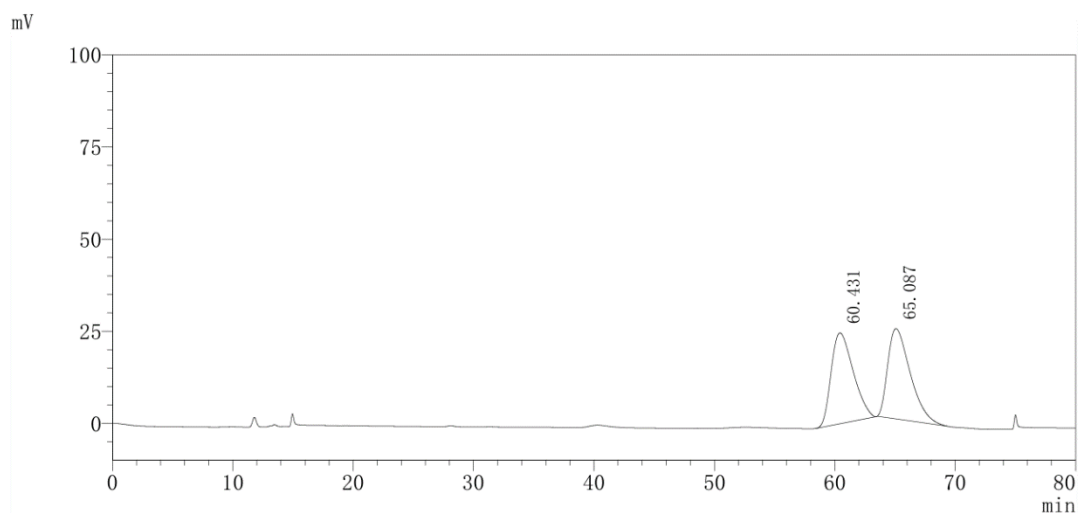
$[\alpha]_D^{11} = +103.6$ (c 1.0, CHCl_3)

¹H NMR (400 MHz, CDCl₃) δ 7.82 (t, *J* = 6.6 Hz, 3H), 7.68 (s, 1H), 7.53 – 7.35 (m, 3H), 6.46 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.90 (d, *J* = 2.6 Hz, 1H), 5.15 (d, *J* = 17.5 Hz, 1H), 5.00 (d, *J* = 10.7 Hz, 1H), 3.11 – 2.87 (m, 1H), 2.63 – 2.07 (m, 5H), 2.01 – 1.84 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 144.4, 139.8, 136.1, 133.8, 132.4, 129.2, 128.1, 127.8, 127.7, 126.1, 126.0, 125.4, 124.9, 110.6, 40.5, 34.0, 29.7, 24.6.

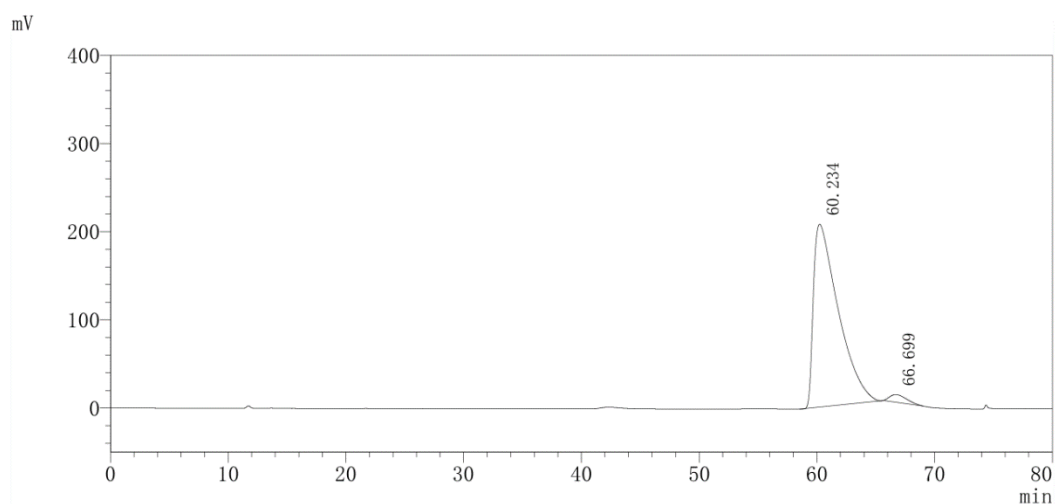
GCMS (EI) calcd. for C₁₈H₁₈⁺ (M⁺): 234.1403, Found: 234.1406.

The ee value was 94%, *t_r* (minor) = 66.699, *t_r* (major) = 60.234 (Chiralcel IE, λ = 220 nm, hexanes:PrOH = 99.8:0.2, flow rate = 0.3 mL/min).



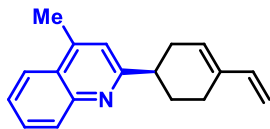
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	60.431	3133797	24651	50.176	49.618
2	65.087	3182013	24478	49.824	50.382
总计		6315810	49129	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	60.234	30417048	207160	95.996	97.159
2	66.699	889375	8642	4.004	2.841
总计		31306422	215801	100.000	100.000



(*R*)-4-methyl-2-(4-vinylcyclohex-3-en-1-yl)quinoline (2m)

Prepared according to General Procedure, white solid, 94% yield, m.p. 38-39 °C, 89% ee.

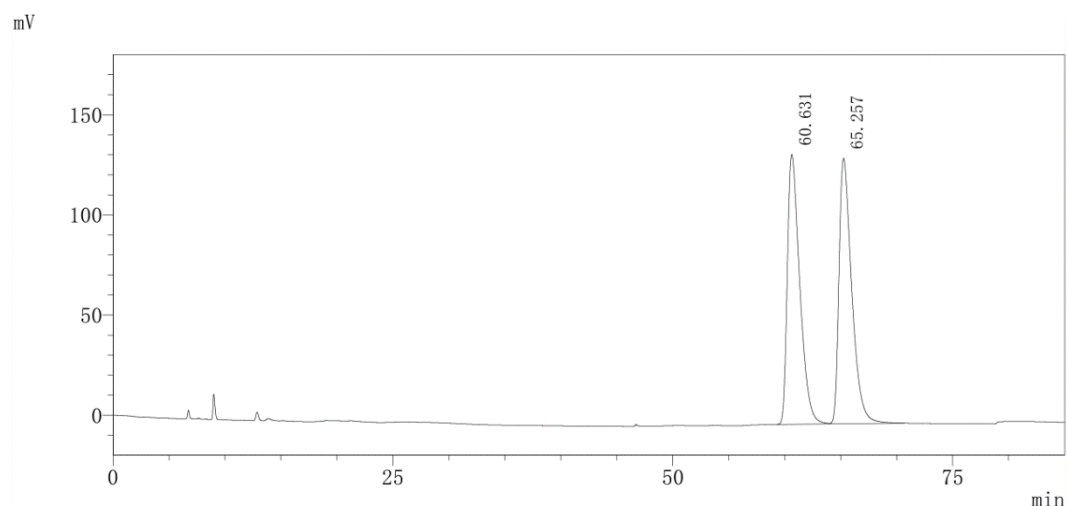
$[\alpha]_{\text{D}}^{25} = +39.9$ (c 1.0, CHCl_3)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 8.2$ Hz, 1H), 7.68 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.18 (s, 1H), 6.44 (dd, $J = 17.4, 10.8$ Hz, 1H), 5.89 (s, 1H), 5.13 (d, $J = 17.5$ Hz, 1H), 4.97 (d, $J = 10.6$ Hz, 1H), 3.22 – 3.03 (m, 1H), 2.69 (s, 3H), 2.63 – 2.14 (m, 5H), 2.04 – 1.89 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.6, 147.8, 144.5, 139.8, 135.9, 129.7, 129.2, 129.0, 127.2, 125.7, 123.7, 120.5, 110.4, 43.3, 32.1, 28.6, 24.4, 19.0.

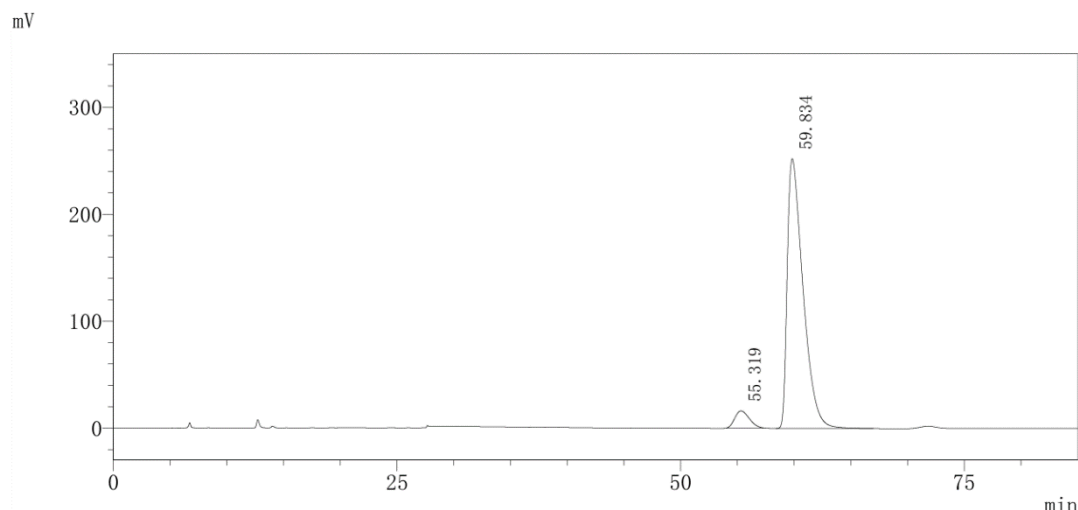
HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{20}\text{N}^+$ ($\text{M} + \text{H}$) $^+$: 250.1590, Found: 250.1590.

The ee value was 89%, t_{r} (minor) = 55.319, t_{r} (major) = 59.834 (Chiralcel OD-3, $\lambda = 220$ nm, hexanes:*i*PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



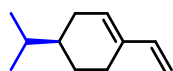
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	60.631	10356383	134693	50.376	49.684
2	65.257	10488103	132682	49.624	50.316
总计		20844486	267375	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	55.319	1405248	16021	5.970	5.444
2	59.834	24405539	252338	94.030	94.556
总计		25810787	268358	100.000	100.000



(*R*)-4-isopropyl-1-vinylcyclohex-1-ene (2n)

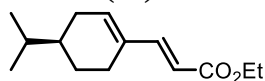
Prepared according to General Procedure, colorless oil, 74% yield.

$[\alpha]_D^{11} = +89.4$ (c 1.0, CHCl_3)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.36 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.81 – 5.71 (m, 1H), 5.06 (d, $J = 17.5$ Hz, 1H), 4.90 (d, $J = 10.7$ Hz, 1H), 2.35 – 2.26 (m, 1H), 2.22 – 2.01 (m, 2H), 1.95 – 1.78 (m, 2H), 1.59 – 1.43 (m, 1H), 1.40 – 1.17 (m, 2H), 0.91 (d, $J = 6.6$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.0, 136.1, 129.9, 109.9, 40.4, 32.4, 29.6, 26.0, 24.6, 20.1, 19.8.

GCMS (EI) calcd. for $\text{C}_{11}\text{H}_{18}^+$ (M^+): 150.1403, Found: 150.1404.



ethyl (*R,E*)-3-(4-isopropylcyclohex-1-en-1-yl)acrylate (2n')

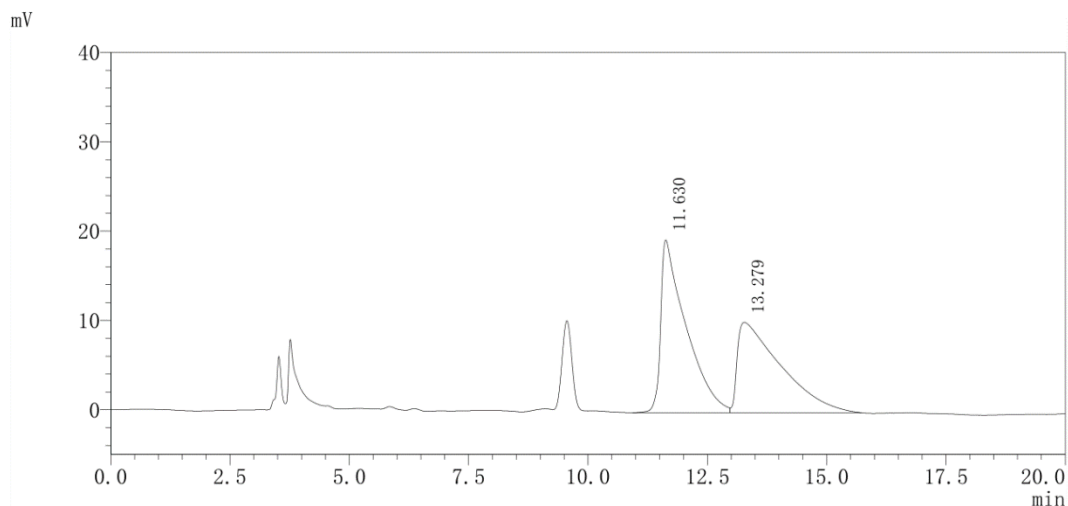
$[\alpha]_D^{11} = +77.8$ (c 1.0, CHCl_3), colorless oil, 92% ee.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.29 (d, $J = 15.7$ Hz, 1H), 6.15 (s, 1H), 5.80 – 5.69 (m, 1H), 4.20 (q, $J = 6.8$ Hz, 2H), 2.26 (t, $J = 14.5$ Hz, 2H), 2.09 (s, 1H), 1.98 – 1.82 (m, 2H), 1.54 – 1.46 (m, 1H), 1.32 – 1.24 (m, 5H), 0.91 (d, $J = 7.2$ Hz, 3H), 0.89 (d, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 167.8, 147.8, 138.9, 135.0, 114.9, 60.3, 40.0, 32.2, 30.3, 25.7, 24.9, 20.0, 19.7, 14.5.

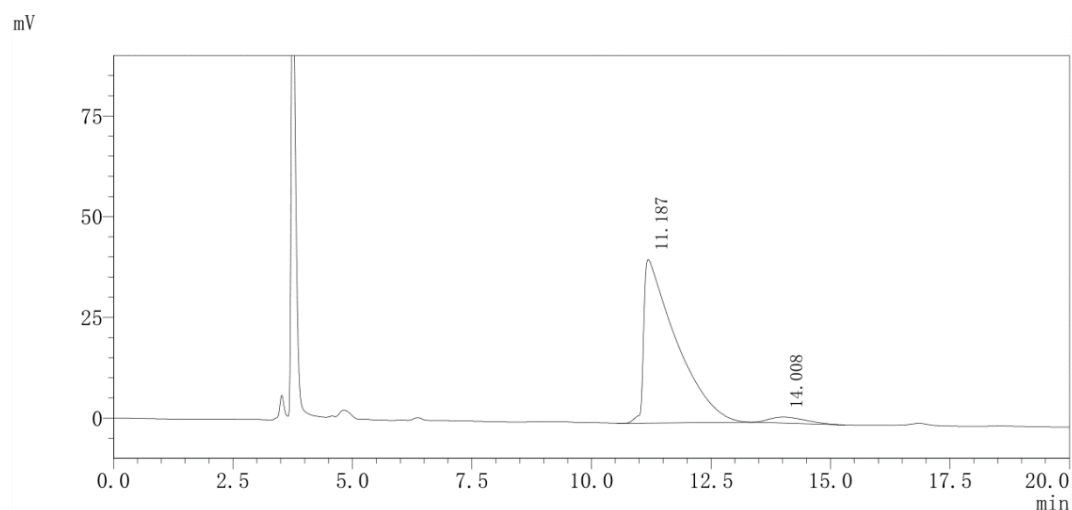
HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{23}\text{O}_2^+$ ($M + H$) $^+$: 223.1693, Found: 223.1694.

The ee value was 92%, t_r (minor) = 14.008, t_r (major) = 11.187 (Chiralcel IE, $\lambda = 220$ nm, hexanes: i -PrOH = 98:2, flow rate = 1.0 mL/min).



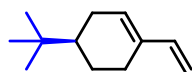
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	11.630	713653	19345	65.655	52.651
2	13.279	641796	10119	34.345	47.349
总计		1355449	29464	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	11.187	1919182	40595	96.449	96.059
2	14.008	78734	1495	3.551	3.941
总计		1997915	42090	100.000	100.000



(R)-4-(tert-butyl)-1-vinylcyclohex-1-ene (2o)

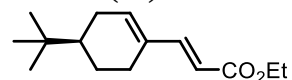
Prepared according to General Procedure, colorless oil, 89% yield.

$[\alpha]_D^{11} = +63.8$ (c 1.0, CHCl_3)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.36 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.84 – 5.68 (m, 1H), 5.05 (d, $J = 17.5$ Hz, 1H), 4.89 (d, $J = 10.7$ Hz, 1H), 2.42 – 2.28 (m, 1H), 2.22 – 2.00 (m, 2H), 1.99 – 1.82 (m, 2H), 1.32 – 1.14 (m, 2H), 0.88 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.9, 136.1, 130.2, 109.9, 44.4, 32.4, 27.5, 27.4, 25.3, 23.8.

GCMS (EI) calcd. for $\text{C}_{12}\text{H}_{20}^+$ (M^+): 164.1560, Found: 164.1559.



(*R,E*)-3-(4-(tert-butyl)cyclohex-1-en-1-yl)acrylate (2o')

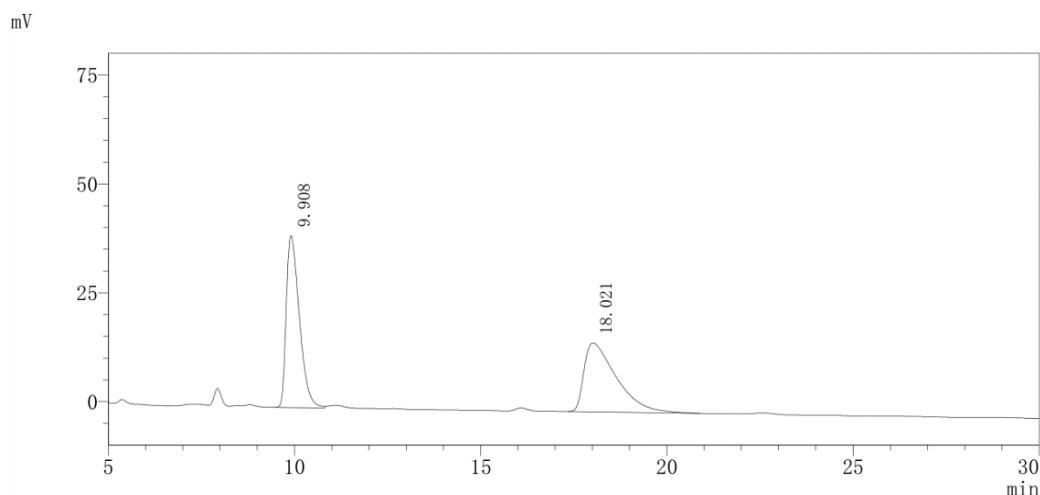
$[\alpha]_{\text{D}}^{25} = +44.0$ (c 1.0, CHCl_3), colorless oil, 92% ee.

^1H NMR (600 MHz, CDCl_3) δ 7.30 (d, $J = 15.7$ Hz, 1H), 6.17 (s, 1H), 5.75 (d, $J = 15.7$ Hz, 1H), 4.20 (q, $J = 6.8$ Hz, 2H), 2.36 – 2.19 (m, 2H), 2.13 – 1.87 (m, 3H), 1.30 (t, $J = 7.0$ Hz, 3H), 1.25 – 1.12 (m, 2H), 0.88 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 167.9, 147.7, 139.3, 134.9, 114.9, 60.3, 44.0, 32.4, 29.9, 28.3, 27.3, 25.6, 23.6, 14.5.

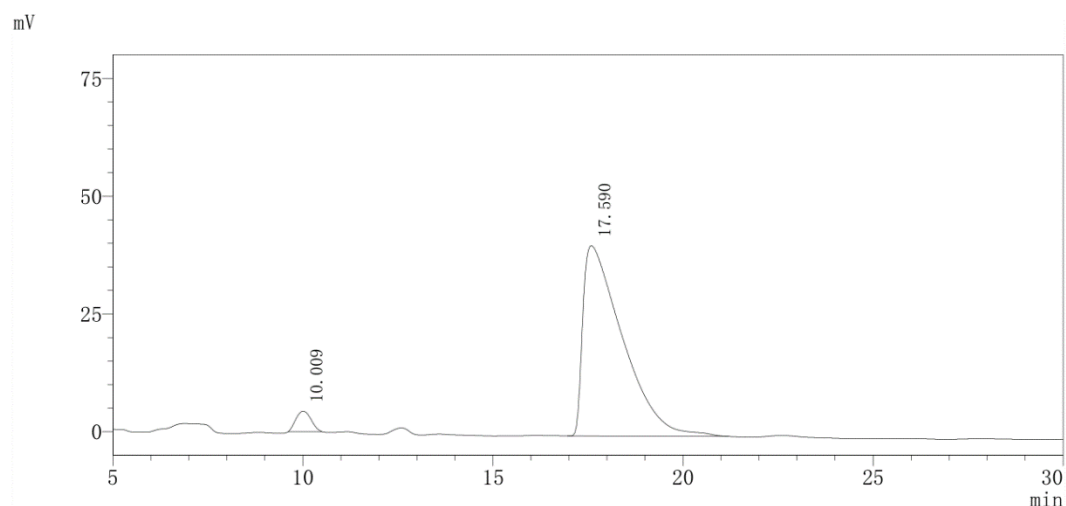
GCMS (EI) calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_2^+$ (M^+): 236.1771, Found: 2236.1771.

The ee value was 92%, t_{r} (minor) = 10.009, t_{r} (major) = 17.590 (Chiralcel IF, $\lambda = 220$ nm, hexanes: i PrOH = 98:2, flow rate = 1.0 mL/min).



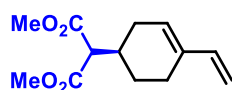
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	9.908	965469	39466	71.361	50.182
2	18.021	958464	15838	28.639	49.818
总计		1923934	55304	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	10.009	119220	4306	9.633	3.905
2	17.590	2933998	40396	90.367	96.095
总计		3053218	44702	100.000	100.000



dimethyl (*R*)-2-(4-vinylcyclohex-3-en-1-yl)malonate (**2p**)

Prepared according to General Procedure, colorless oil, 91% yield, 89% ee.

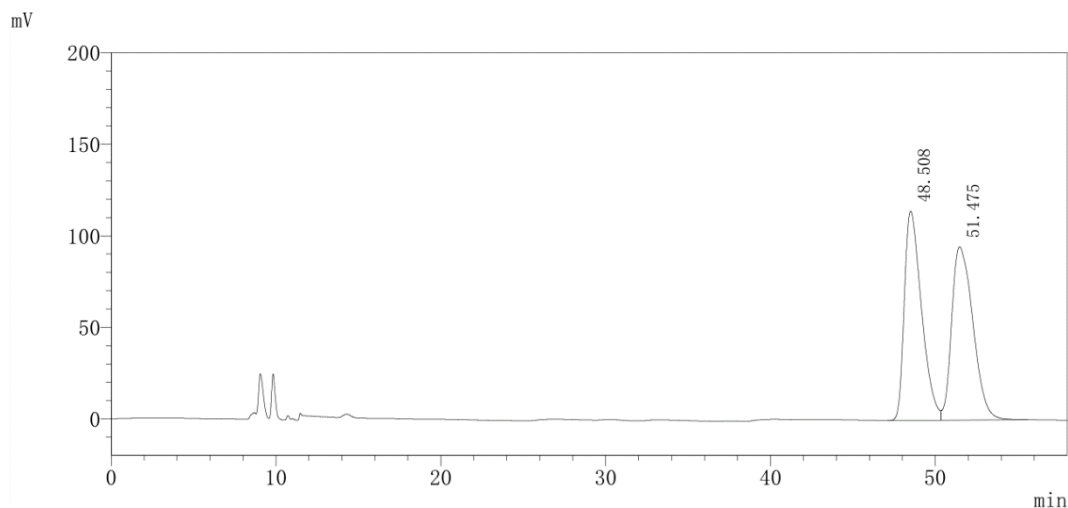
$[\alpha]_D^{25} = +50.6$ (c 1.0, CHCl_3)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.26 (dd, $J = 17.5, 10.8$ Hz, 1H), 5.61 (s, 1H), 4.99 (d, $J = 17.5$ Hz, 1H), 4.85 (d, $J = 10.7$ Hz, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 3.24 (d, $J = 9.2$ Hz, 1H), 2.40 – 2.02 (m, 4H), 1.97 – 1.85 (m, 1H), 1.84 – 1.74 (m, 1H), 1.38 – 1.27 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.1, 139.4, 135.8, 127.5, 110.7, 56.8, 52.5, 34.1, 29.8, 26.4, 23.4.

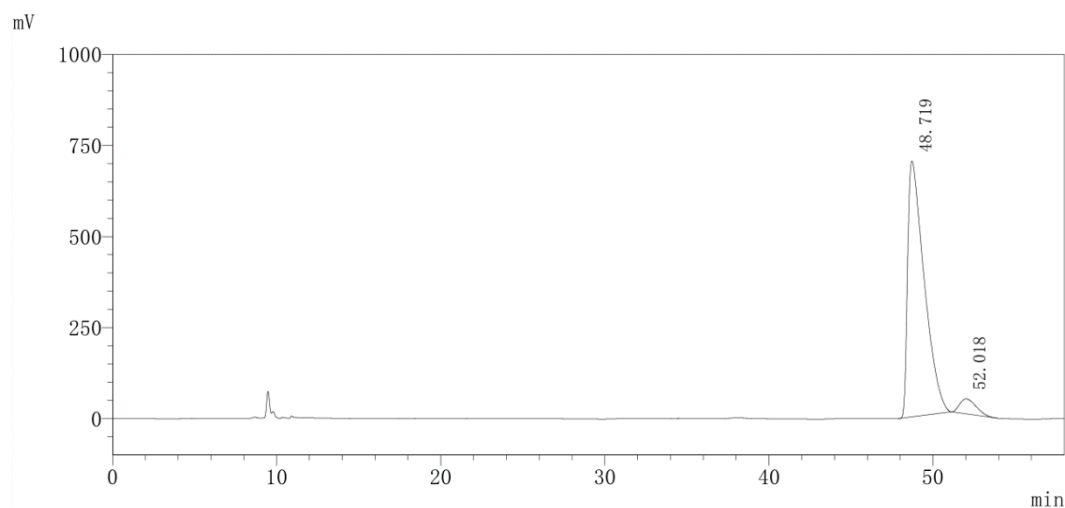
HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{18}\text{NaO}_4^+$ ($\text{M} + \text{Na}$) $^+$: 261.1097, Found: 261.1098.

The ee value was 89%, t_r (minor) = 52.018, t_r (major) = 48.719 (Chiralcel IE, $\lambda = 220$ nm, hexanes: i PrOH = 99:1, flow rate = 0.4 mL/min).



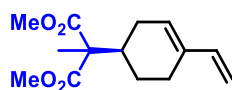
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	48.508	8317591	114288	54.688	49.372
2	51.475	8529251	94693	45.312	50.628
总计		16846842	208980	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	48.719	49234667	702587	94.478	94.487
2	52.018	2872587	41064	5.522	5.513
总计		52107254	743651	100.000	100.000



dimethyl (*R*)-2-methyl-2-(4-vinylcyclohex-3-en-1-yl)malonate (**2q**)

Prepared according to General Procedure, colorless oil, 95% yield, 91% ee.

$[\alpha]_D^{11} = +63.8$ (c 1.0, CHCl_3)

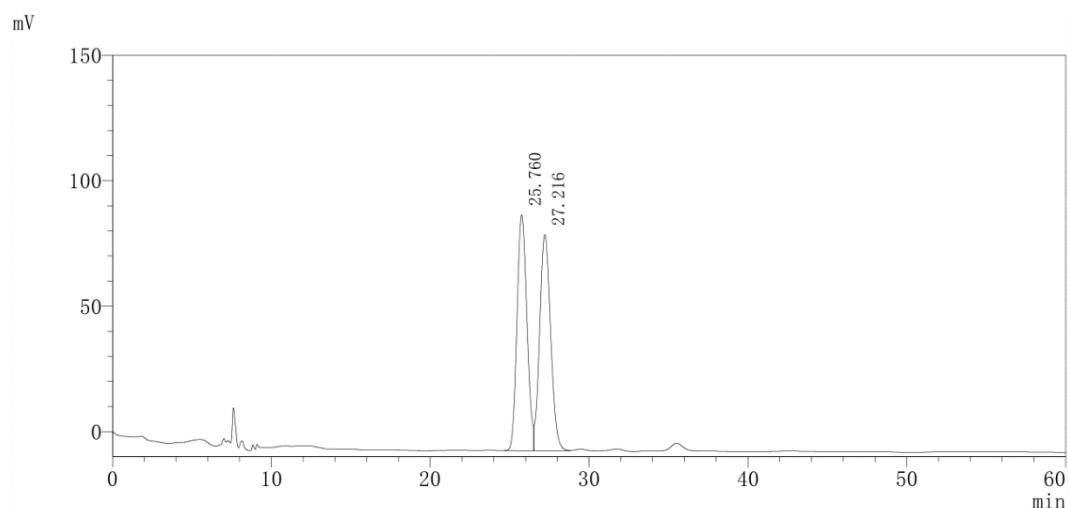
^1H NMR (400 MHz, CDCl_3) δ 6.33 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.69 (s, 1H), 5.05 (d, $J = 17.5$ Hz, 1H), 4.90 (d, $J = 10.7$ Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 2.46 – 2.27 (m,

2H), 2.24 – 2.09 (m, 1H), 2.05 – 1.96 (m, 2H), 1.91 – 1.79 (m, 1H), 1.38 (s, 3H), 1.35 – 1.25 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.2, 139.4, 136.1, 128.2, 110.6, 57.1, 52.5, 38.9, 27.4, 24.8, 24.6, 16.6.

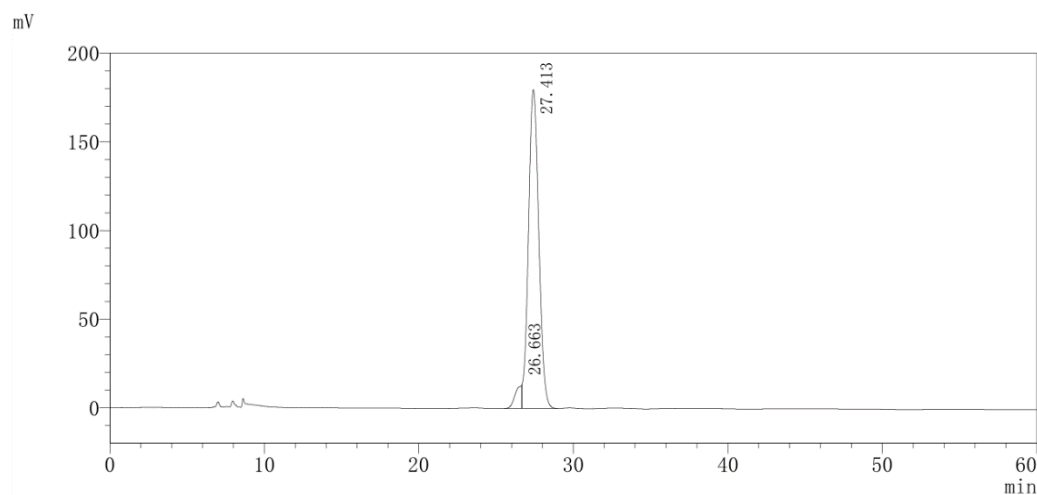
HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{20}\text{NaO}_4^+$ ($\text{M} + \text{Na}$) $^+$: 275.1254, Found: 275.1254.

The ee value was 91%, t_r (minor) = 26.663, t_r (major) = 27.413 (Chiralcel IC, λ = 220 nm, hexanes:*i*PrOH = 99:1, flow rate = 0.5 mL/min).



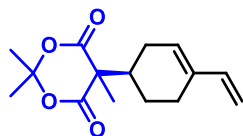
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	25.760	4082957	93986	52.190	49.527
2	27.216	4160927	86097	47.810	50.473
总计		8243885	180082	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	26.663	382276	13112	6.793	4.354
2	27.413	8397730	179908	93.207	95.646
总计		8780006	193020	100.000	100.000



(*R*)-2,2,5-trimethyl-5-(4-vinylcyclohex-3-en-1-yl)-1,3-dioxane-4,6-dione (2r)

Prepared according to General Procedure, colorless oil, 96% yield, 89% ee.

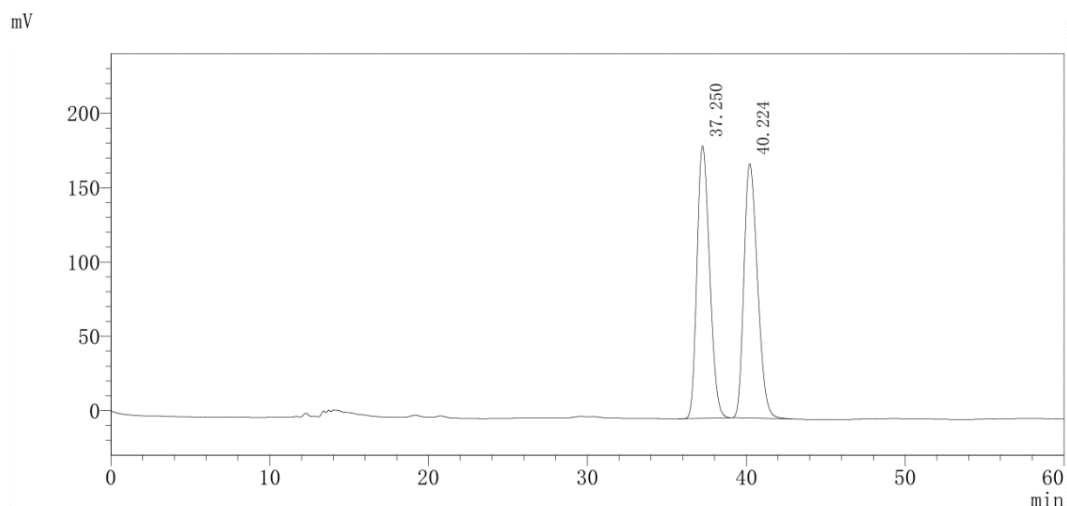
$[\alpha]_D^{25} = +57.0$ (c 1.0, CHCl_3)

^1H NMR (400 MHz, CDCl_3) δ 6.29 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.65 (s, 1H), 5.02 (d, $J = 17.5$ Hz, 1H), 4.90 (d, $J = 10.7$ Hz, 1H), 2.34 (dd, $J = 17.0, 4.7$ Hz, 1H), 2.29 – 2.17 (m, 3H), 2.15 – 2.02 (m, 1H), 1.94 (dd, $J = 12.5, 4.7$ Hz, 1H), 1.73 (s, 3H), 1.69 (s, 3H), 1.58 (s, 3H), 1.44 – 1.31 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.1, 170.0, 139.0, 135.7, 127.2, 110.9, 104.8, 67.2, 52.8, 44.8, 30.6, 28.0, 27.4, 24.7, 24.4, 19.7.

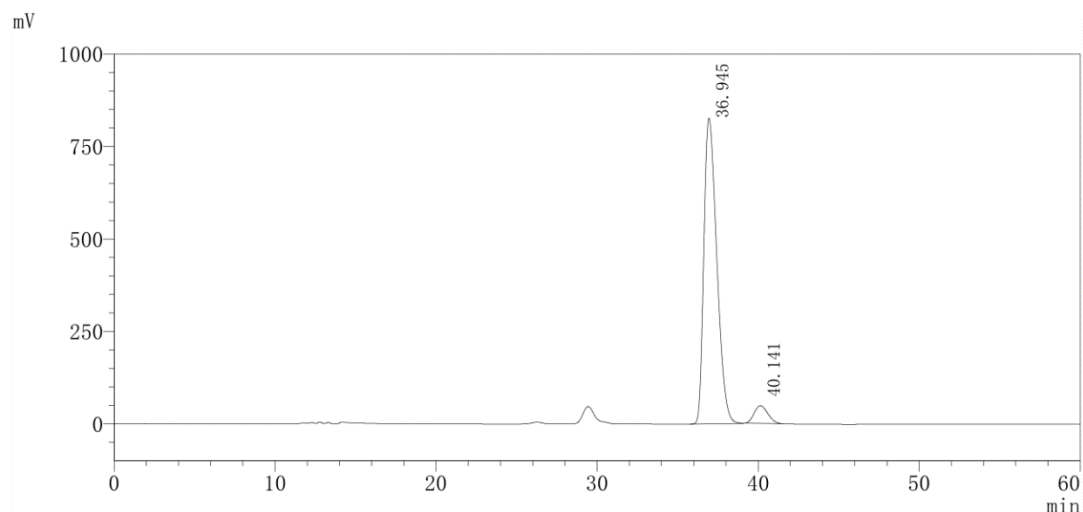
GCMS (EI) calcd. for $\text{C}_{12}\text{H}_{13}\text{O}_2^{2+}$ ($\text{M} - \text{C}_3\text{H}_7\text{O}_2$) $^+$: 189.0910, Found: 189.0910.

The ee value was 89%, t_r (minor) = 40.141, t_r (major) = 36.945 (Chiralcel OD-3, $\lambda = 220$ nm, hexanes:*i*PrOH = 99:1, flow rate = 0.3 mL/min).



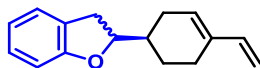
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	37.250	10115580	183069	51.733	49.895
2	40.224	10158037	170805	48.267	50.105
总计		20273617	353874	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	36.945	46089371	826685	94.550	94.259
2	40.141	2807221	47649	5.450	5.741
总计		48896592	874334	100.000	100.000



(*R*)-2-(4-vinylcyclohex-3-en-1-yl)-2,3-dihydrobenzofuran (2s)

Prepared according to General Procedure, colorless oil, 96% yield, dr = 1:1, 84% ee, 91% ee.

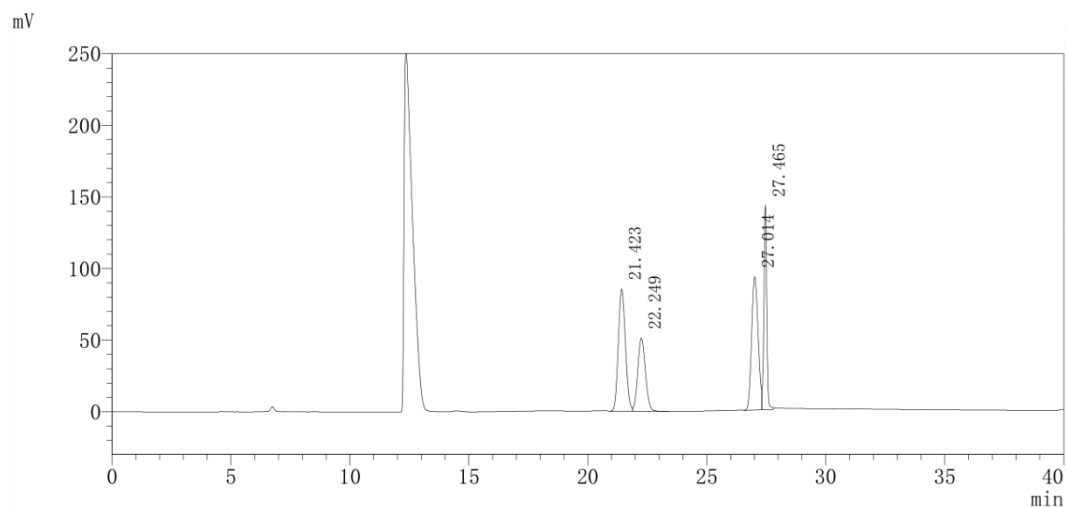
$[\alpha]_D^{25} = +55.3$ (*c* 1.0, CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.06 (m, 4H), 6.91 – 6.72 (m, 4H), 6.39 (dd, *J* = 16.8, 10.4 Hz, 2H), 5.86 – 5.70 (m, 2H), 5.13 (d, *J* = 8.3 Hz, 1H), 5.09 (d, *J* = 8.3 Hz, 1H), 4.97 (d, *J* = 3.7 Hz, 1H), 4.94 (d, *J* = 3.6 Hz, 1H), 4.72 – 4.54 (m, 2H), 3.35 – 3.16 (m, 2H), 3.07 – 2.90 (m, 2H), 2.50 – 2.33 (m, 3H), 2.28 – 2.09 (m, 5H), 2.06 – 1.86 (m, 4H), 1.55 – 1.41 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 159.8, 139.7, 136.5, 136.0, 128.5, 128.1, 127.9, 127.0, 126.9, 125.0, 120.2, 110.5, 110.3, 109.2, 39.4, 39.3, 33.4, 28.3, 27.8, 24.5, 23.6, 23.4.

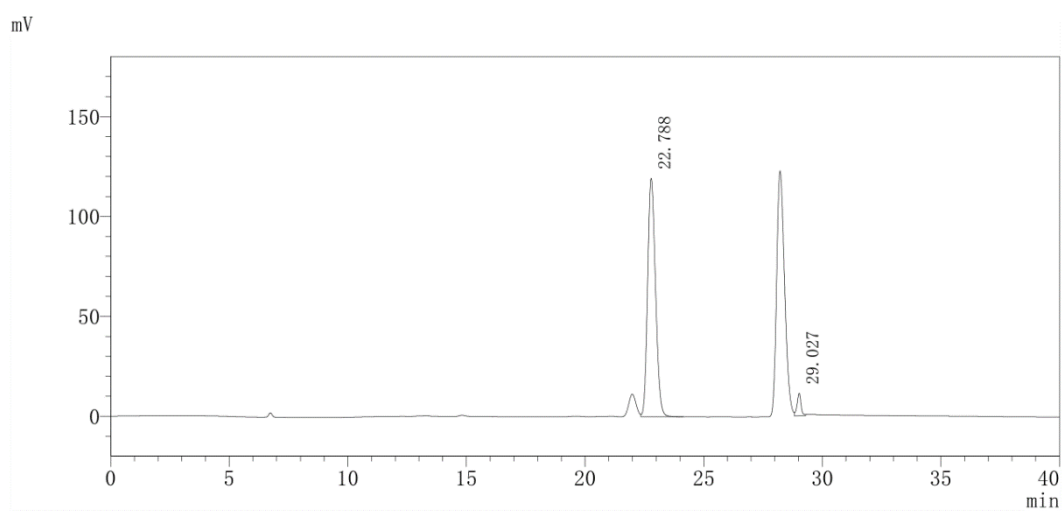
GCMS (EI) calcd. for C₁₆H₁₈O⁺ (*M*⁺): 226.1352, Found: 226.1352.

The ee value was 91%, *t_r* (minor) = 29.027, *t_r* (major) = 22.788 (Chiralcel OD-3, λ = 220 nm, hexanes:*i*PrOH = 99.8:0.2, flow rate = 0.5 mL/min); The ee value was 84%, *t_r* (minor) = 21.990, *t_r* (major) = 28.220 (Chiralcel OD-3, λ = 220 nm, hexanes:*i*PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



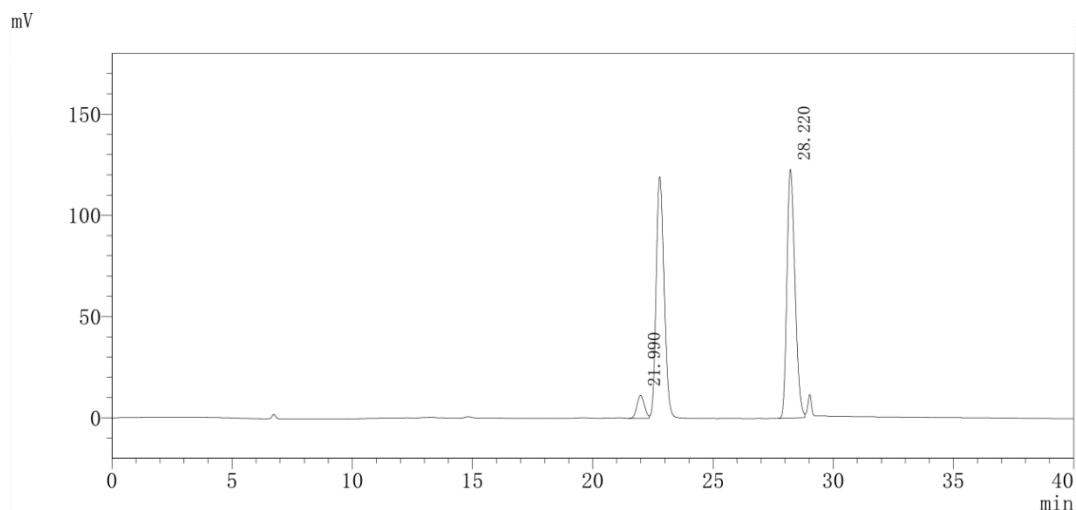
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	21.423	1783948	85415	22.961	30.355
2	22.249	1135831	51140	13.748	19.327
3	27.014	1763393	93103	25.028	30.005
4	27.465	1193844	142336	38.263	20.314
总计		5877016	371994	100.000	100.000



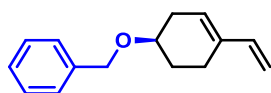
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	22.788	2761561	119416	91.296	95.442
2	29.027	131898	11386	8.704	4.558
总计		2893459	130802	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	21.990	243316	11317	8.428	7.801
2	28.220	2875835	122964	91.572	92.199
总计		3119152	134281	100.000	100.000



(*R*)-(((4-vinylcyclohex-3-en-1-yl)oxy)methyl)benzene (2t)

Prepared according to General Procedure, colorless oil, 74% yield, 72% ee.

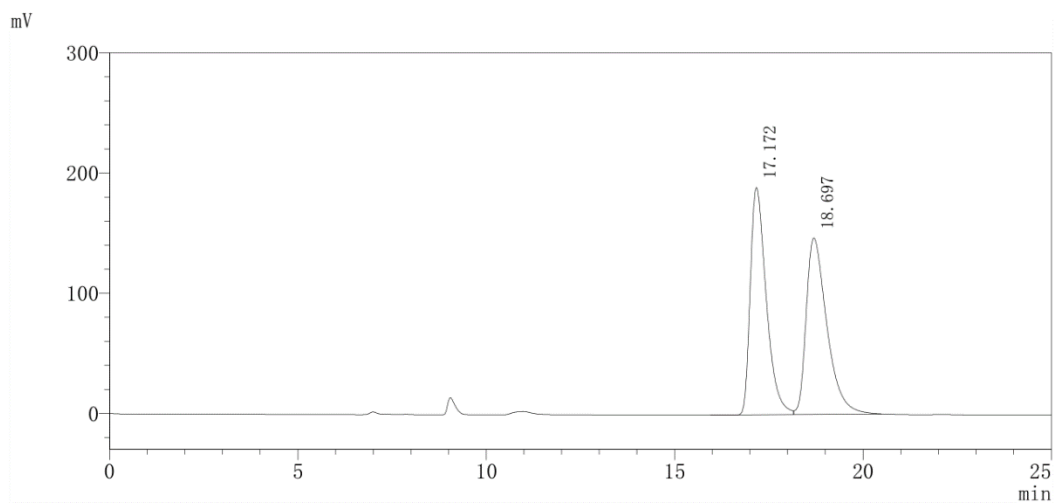
$[\alpha]_D^{25} = -23.8$ (c 1.0, CHCl_3)

^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.19 (m, 4H), 7.19 – 7.12 (m, 1H), 6.23 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.54 (s, 1H), 4.95 (d, $J = 17.5$ Hz, 1H), 4.82 (d, $J = 10.7$ Hz, 1H), 4.50 (d, $J = 12.0$ Hz, 1H), 4.46 (d, $J = 12.0$ Hz, 1H), 3.62 – 3.50 (m, 1H), 2.48 – 2.20 (m, 2H), 2.48 – 2.20 (m, 2H), 2.16 – 2.00 (m, 1H), 1.72 – 1.56 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.3, 139.1, 135.9, 128.5, 127.7, 127.6, 126.7, 110.8, 73.8, 70.2, 32.3, 27.6, 22.5.

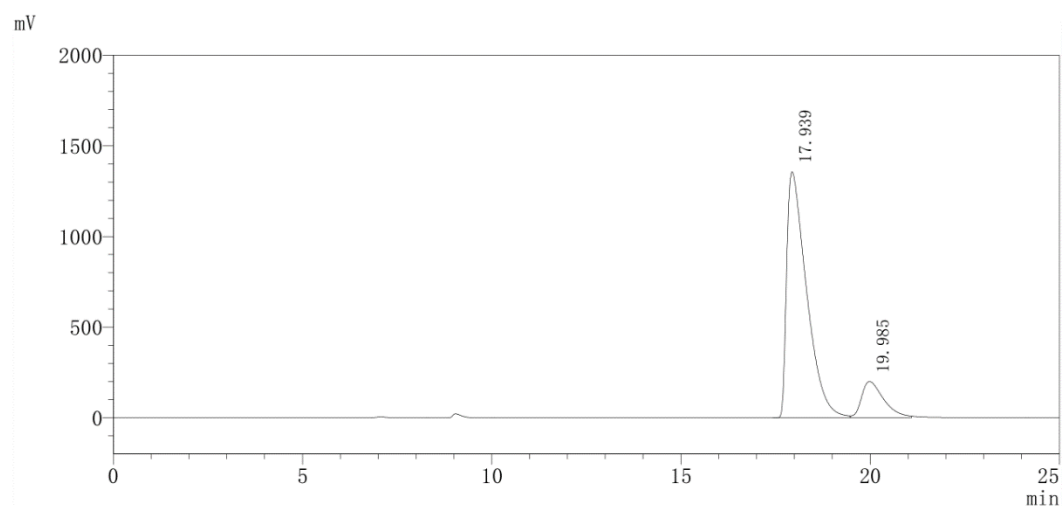
HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{18}\text{NaO}^+$ ($\text{M} + \text{Na}$) $^+$: 237.1250, Found: 237.1250.

The ee value was 72%, t_r (minor) = 19.985, t_r (major) = 17.939 (Chiralcel ID, $\lambda = 220$ nm, hexanes: i PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



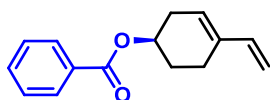
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	17.172	5567120	189028	56.298	49.823
2	18.697	5606688	146733	43.702	50.177
总计		11173807	335760	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	17.939	49503269	1357013	87.183	85.885
2	19.985	8135917	199503	12.817	14.115
总计		57639185	1556516	100.000	100.000



(R)-4-vinylcyclohex-3-en-1-yl benzoate (2u)

Prepared according to General Procedure, white solid, 85% yield, m.p. 27-28 °C, 82% ee.

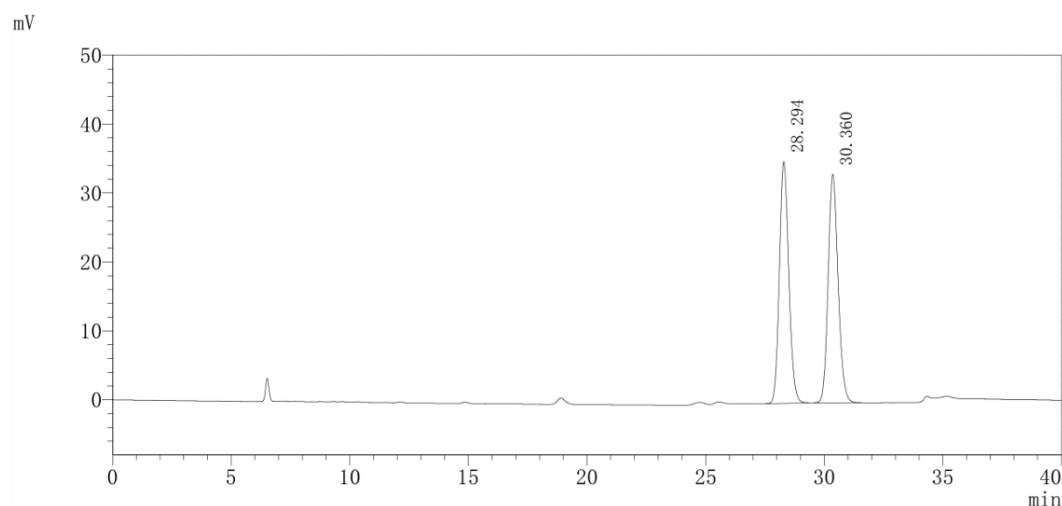
$[\alpha]_D^{11} = +114.0$ (c 1.0, CHCl_3)

¹H NMR (600 MHz, CDCl₃) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 6.39 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.69 (s, 1H), 5.35 – 5.23 (m, 1H), 5.13 (d, *J* = 17.5 Hz, 1H), 4.99 (d, *J* = 10.7 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.48 – 2.27 (m, 3H), 2.10 – 1.93 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 166.3, 139.2, 135.8, 133.0, 130.8, 129.7, 128.4, 125.8, 111.2, 70.1, 31.4, 27.2, 21.6.

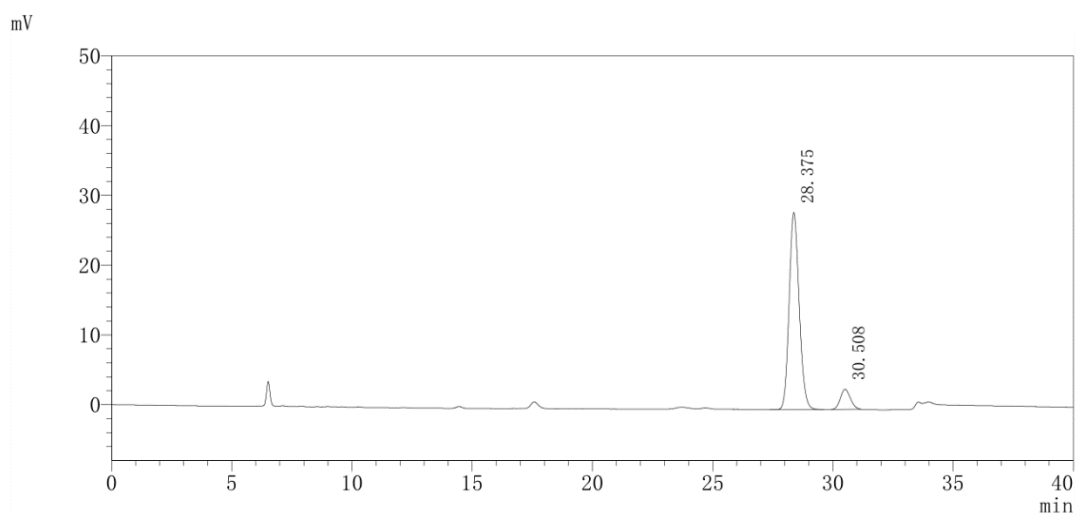
HRMS (ESI) calcd. for C₁₅H₁₆NaO₂⁺: 251.1043, Found: 251.1043.

The ee value was 82%, *t_r* (minor) = 30.508, *t_r* (major) = 28.375 (Chiralcel C1, λ = 220 nm, hexanes:PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



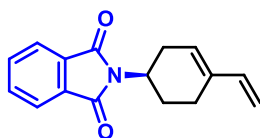
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	28.294	967866	35039	51.376	50.008
2	30.360	967556	33162	48.624	49.992
总计		1935421	68202	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	28.375	820699	28245	90.781	90.839
2	30.508	82768	2868	9.219	9.161
总计		903466	31113	100.000	100.000



(*R*)-2-(4-vinylcyclohex-3-en-1-yl)isoindoline-1,3-dione (2v)

Prepared according to General Procedure, white solid, 89% yield, m.p. 177-178 °C, 99% ee.

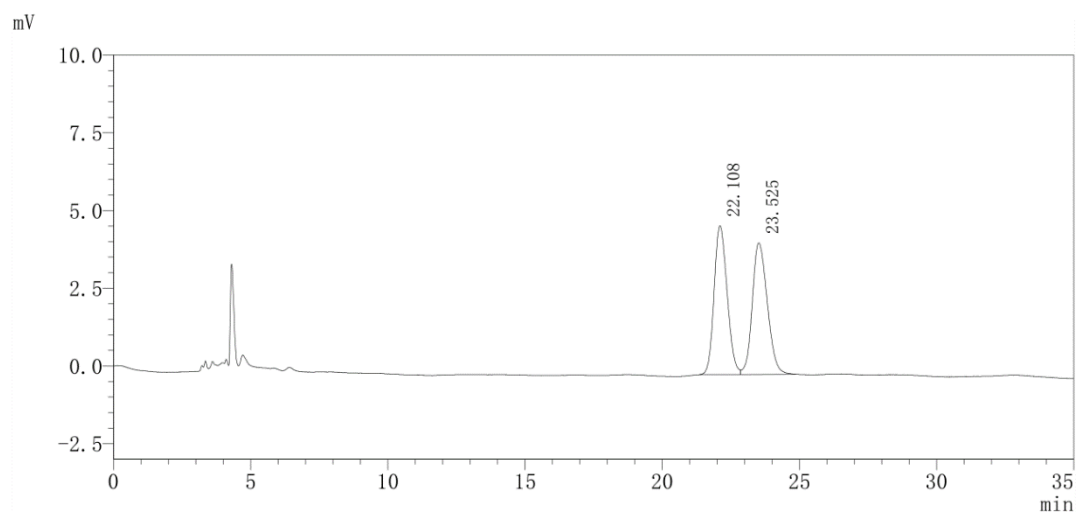
$[\alpha]_D^{25} = -3.9$ (*c* 1.0, CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 6.37 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.74 (d, *J* = 2.0 Hz, 1H), 5.09 (d, *J* = 17.5 Hz, 1H), 4.96 (d, *J* = 10.7 Hz, 1H), 4.49 – 4.28 (m, 1H), 3.10 – 2.90 (m, 1H), 2.65 – 2.38 (m, 2H), 2.36 – 2.18 (m, 2H), 1.98 – 1.83 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 168.5, 139.1, 135.6, 134.0, 132.1, 127.2, 123.2, 111.1, 47.6, 29.1, 26.1, 24.4.

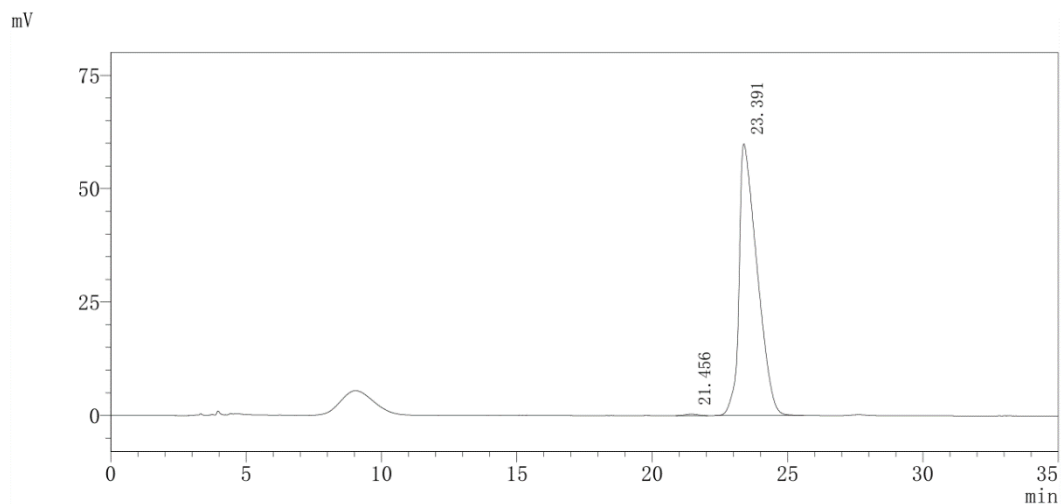
GCMS (EI) calcd. for C₁₆H₁₅NO₂⁺ (*M*⁺): 253.1097, Found: 253.1098.

The ee value was 99%, *t_r* (minor) = 21.456, *t_r* (major) = 23.391 (Chiralcel IA, λ = 220 nm, hexanes:^{*i*}PrOH = 99:1, flow rate = 1.0 mL/min).



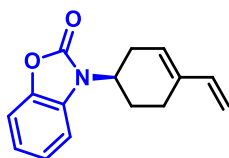
检测器A 254nm

Peak#	Time	Area	Height	Height%	Area%
1	22.108	158398	4788	53.077	49.551
2	23.525	161267	4233	46.923	50.449
总计		319665	9021	100.000	100.000



检测器A 254nm

Peak#	Time	Area	Height	Height%	Area%
1	21.456	10602	333	0.553	0.380
2	23.391	2779174	59898	99.447	99.620
总计		2789776	60231	100.000	100.000



(*R*)-3-(4-vinylcyclohex-3-en-1-yl)benzo[*d*]oxazol-2(3H)-one (2w)

Prepared according to General Procedure, white solid, 74% yield, m.p. 96-97 °C, 87% ee.

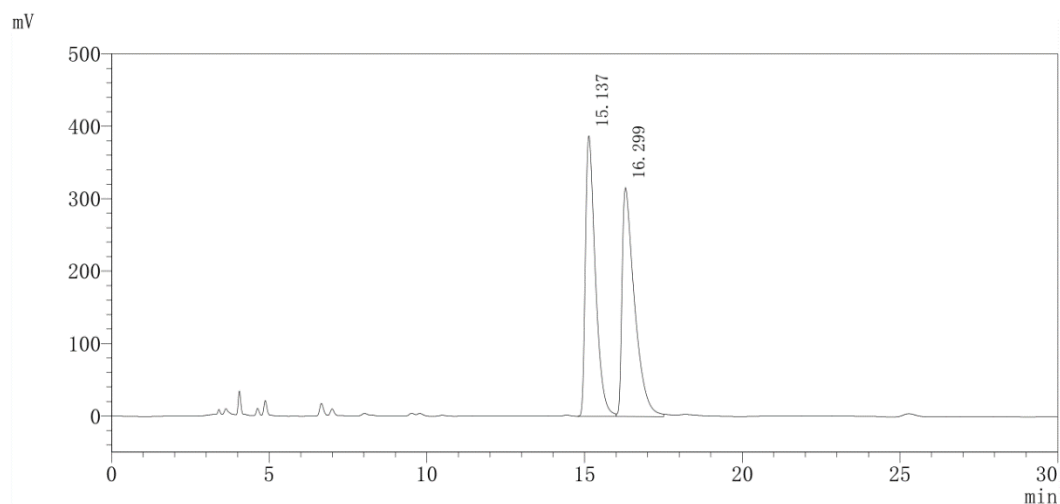
$[\alpha]_D^{25} = +35.6$ (*c* 1.0, CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.19 (m, 4H), 6.55 (dd, *J* = 17.5, 10.8 Hz, 1H), 6.03 – 5.83 (m, 1H), 5.29 (d, *J* = 17.5 Hz, 1H), 5.17 (d, *J* = 10.8 Hz, 1H), 4.65 – 4.49 (m, 1H), 3.16 – 2.99 (m, 1H), 2.74 – 2.42 (m, 4H), 2.32 – 2.17 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 154.0, 142.8, 138.8, 136.0, 130.3, 126.2, 123.7, 122.2, 111.7, 110.3, 109.5, 51.1, 28.5, 26.0, 24.1.

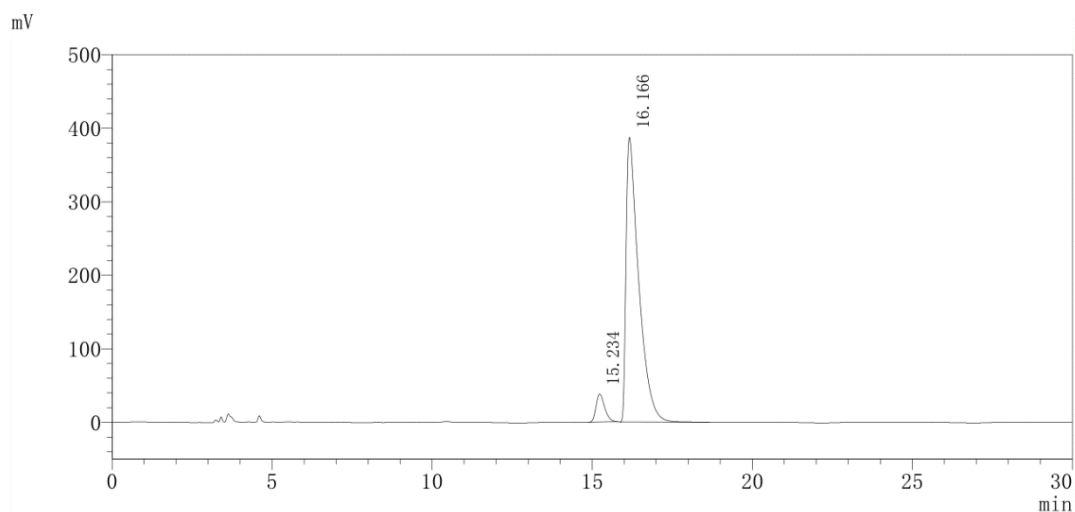
HRMS (ESI) calcd. for C₁₅H₁₅NNaO₂⁺ (*M* + Na)⁺: 264.0995, Found: 264.0995.

The ee value was 87%, *t_r* (minor) = 15.234, *t_r* (major) = 16.166 (Chiralcel OD-3, λ = 220 nm, hexanes:*i*PrOH = 99:1, flow rate = 1.0 mL/min).



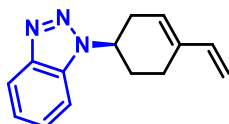
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	15.137	8510198	387381	55.105	49.451
2	16.299	8699084	315608	44.895	50.549
总计		17209282	702990	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	15.234	714338	38033	8.944	6.295
2	16.166	10633839	387205	91.056	93.705
总计		11348177	425237	100.000	100.000



(R)-1-(4-vinylcyclohex-3-en-1-yl)-1H-benzo[d][1,2,3]triazole (2x)

Prepared according to General Procedure, white solid, 92% yield, m.p. 95-96 °C, 89% ee.

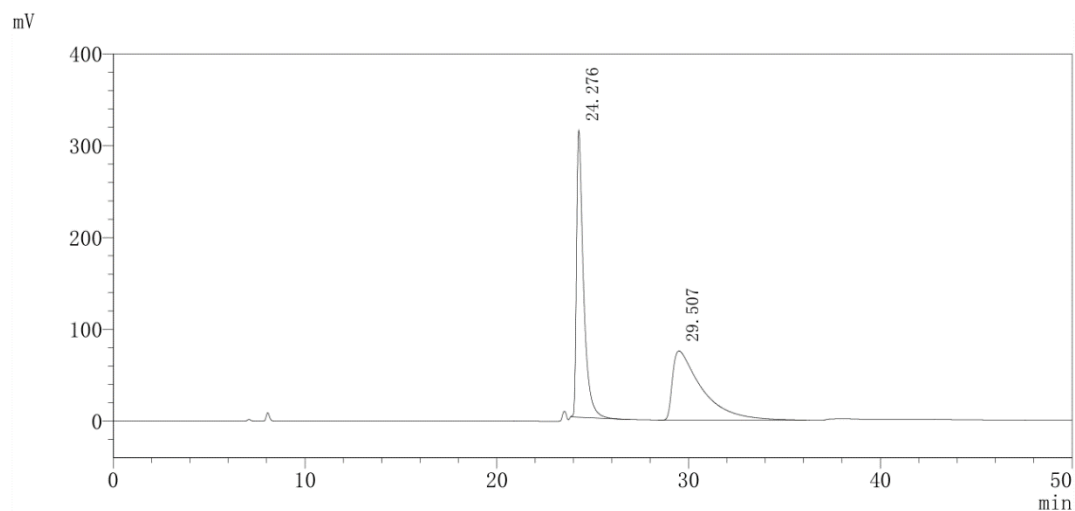
$[\alpha]_D^{11} = +103.6$ (c 1.0, CHCl_3)

¹H NMR (400 MHz, CDCl₃) δ 7.87 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.37 (dd, *J* = 6.5, 3.1 Hz, 2H), 6.42 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.81 (s, 1H), 5.14 (d, *J* = 17.5 Hz, 1H), 5.09 – 4.97 (m, 2H), 3.04 (dd, *J* = 17.4, 10.1 Hz, 1H), 2.93 – 2.77 (m, 1H), 2.58 – 2.29 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 144.1, 138.8, 135.8, 126.3, 125.9, 118.1, 111.7, 62.6, 32.2, 29.0, 23.5.

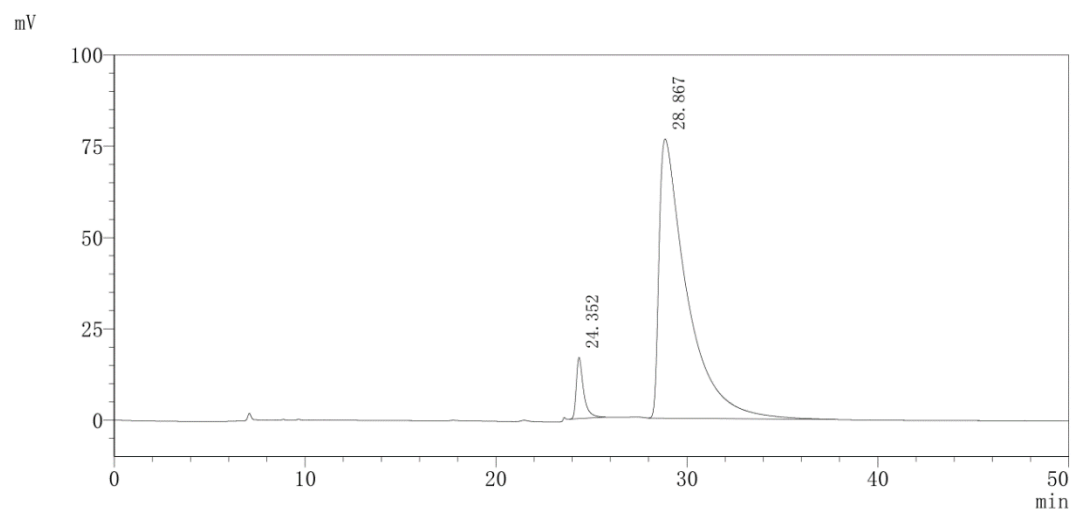
HRMS (ESI) calcd. for C₁₄H₁₆N₃⁺ (M + H)⁺: 226.1339, Found: 226.1339.

The ee value was 89%, *t_r* (minor) = 24.352, *t_r* (major) = 28.867 (Chiralcel IC, λ = 220 nm, hexanes:PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	24.276	7972046	312652	80.560	49.925
2	29.507	7995862	75449	19.440	50.075
总计		15967907	388101	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	24.352	444510	16759	17.976	5.418
2	28.867	7760258	76475	82.024	94.582
总计		8204768	93234	100.000	100.000



(*R*)-benzyl *N*²-(*tert*-butoxycarbonyl)-*N*⁴-((*R*)-4-vinylcyclohex-3-en-1-yl)-*L*-asparaginate (2y)

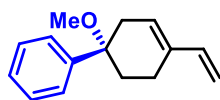
Prepared according to General Procedure, white solid, 98% yield, m.p. 95-96 °C, > 20:1 dr.

$[\alpha]_D^{25} = +5.6$ (*c* 1.0, CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.24 (s, 5H), 6.23 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.73 (d, *J* = 6.7 Hz, 1H), 5.65 (d, *J* = 6.7 Hz, 1H), 5.53 (s, 1H), 5.11 (d, *J* = 12.3 Hz, 1H), 5.05 (d, *J* = 12.4 Hz, 1H), 4.99 (d, *J* = 17.5 Hz, 1H), 4.86 (d, *J* = 10.7 Hz, 1H), 4.44 (s, 1H), 3.96 (s, 1H), 2.76 (d, *J* = 12.9 Hz, 1H), 2.59 (d, *J* = 13.9 Hz, 1H), 2.33 (d, *J* = 17.1 Hz, 1H), 2.14 (s, 2H), 1.93 – 1.71 (m, 2H), 1.61 – 1.44 (m, 1H), 1.32 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 171.5, 169.3, 155.8, 139.1, 135.8, 135.6, 128.6, 128.4, 128.2, 126.3, 111.3, 80.0, 67.4, 50.7, 44.8, 38.2, 32.0, 28.4, 27.6, 22.0.

HRMS (ESI) calcd. for C₂₄H₃₂N₂NaO₅⁺ (*M* + Na)⁺: 451.2203, Found: 451.2203.



(*S*)-1-methoxy-4-vinyl-1,2,3,6-tetrahydro-1,1'-biphenyl (3a)

Prepared according to General Procedure, colorless oil, 89% yield, 86% ee.

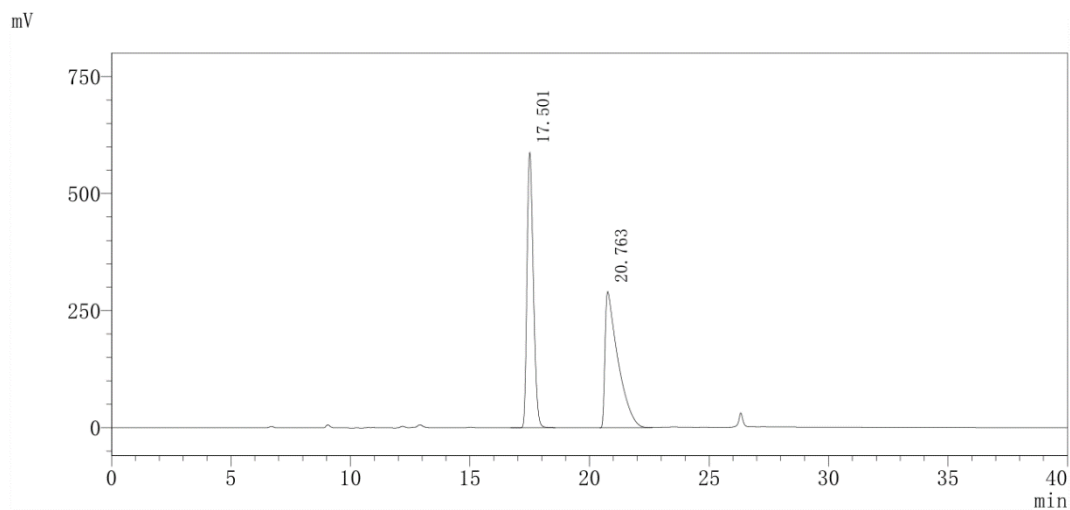
$[\alpha]_D^{25} = +39.3$ (*c* 1.0, CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.22 (m, 1H), 6.39 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.76 (s, 1H), 5.06 (d, *J* = 17.5 Hz, 1H), 4.93 (d, *J* = 10.7 Hz, 1H), 3.02 (s, 3H), 2.62 (d, *J* = 18.4 Hz, 1H), 2.53 (d, *J* = 18.4 Hz, 1H), 2.36 – 2.18 (m, 2H), 2.13 – 1.93 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 144.0, 139.2, 136.2, 128.4, 127.3, 126.3, 110.8, 77.0, 50.3, 37.5, 31.5, 21.6.

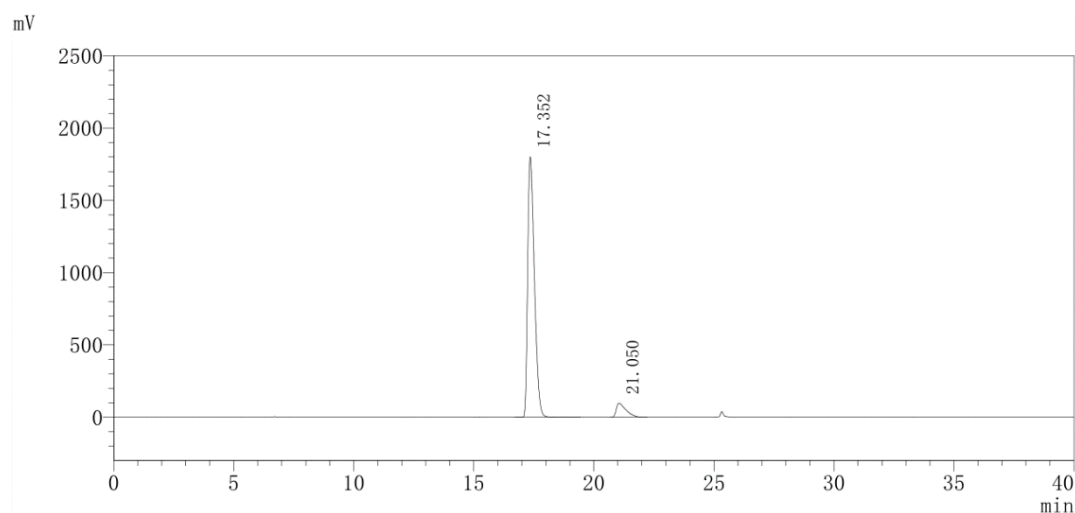
GCMS (EI) calcd. for C₁₅H₁₈O⁺ (*M*⁺): 214.1352, Found: 214.1352.

The ee value was 86%, *t*_r (minor) = 21.050, *t*_r (major) = 17.352 (Chiralcel OD-3, λ = 220 nm, hexanes:^{*i*}PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



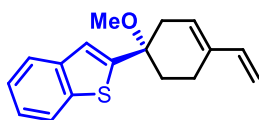
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	17.501	10893338	588501	66.926	49.909
2	20.763	10933264	290831	33.074	50.091
总计		21826602	879332	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	17.352	35118496	1801856	94.888	92.804
2	21.050	2722938	97082	5.112	7.196
总计		37841434	1898938	100.000	100.000



(S)-2-(1-methoxy-4-vinylcyclohex-3-en-1-yl)benzo[b]thiophene (3b)

Prepared according to General Procedure, pale yellow solid, 92% yield, m.p. 67-68 °C, 90% ee.

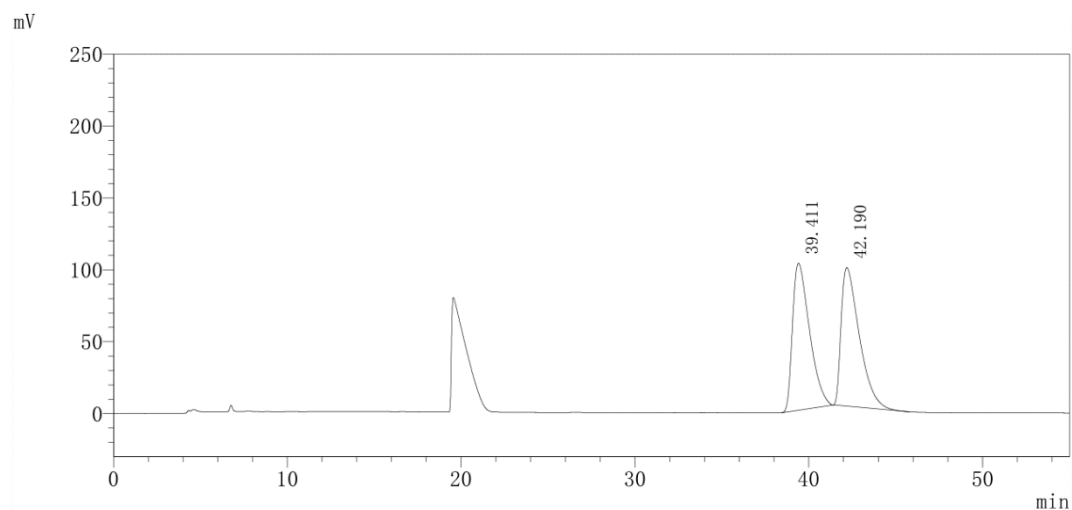
$[\alpha]_D^{25} = +109.0$ (c 1.0, CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 7.1 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.17 (s, 1H), 6.42 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.78 (s, 1H), 5.09 (d, *J* = 17.5 Hz, 1H), 4.98 (d, *J* = 10.7 Hz, 1H), 3.20 (s, 3H), 2.83 (d, *J* = 17.8 Hz, 1H), 2.70 (d, *J* = 18.3 Hz, 1H), 2.44 – 2.31 (m, 2H), 2.24 – 2.05 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 150.1, 139.8, 139.5, 138.9, 136.0, 125.3, 124.2, 124.1, 123.5, 122.4, 121.6, 111.2, 76.1, 50.6, 37.2, 33.0, 21.7.

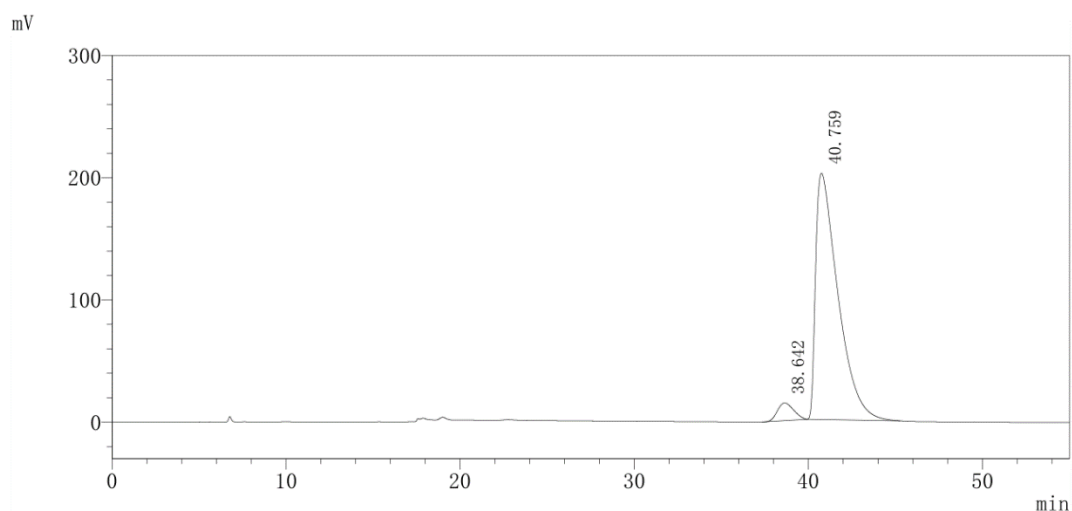
GCMS (EI) calcd. for C₁₇H₁₈OS⁺ (M⁺): 270.1073, Found: 270.1075.

The ee value was 90%, *t_r* (minor) = 38.642, *t_r* (major) = 40.759 (Chiralcel IF, λ = 220 nm, hexanes:PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



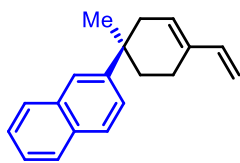
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	39.411	6947655	102201	51.471	49.761
2	42.190	7014422	96359	48.529	50.239
总计		13962077	198561	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	38.642	930005	14463	6.695	4.926
2	40.759	17950345	201547	93.305	95.074
总计		18880349	216010	100.000	100.000



(*R*)-2-(1-methyl-4-vinylcyclohex-3-en-1-yl)naphthalene (3c)

Prepared according to General Procedure, colorless oil, 95% yield, 90% ee.

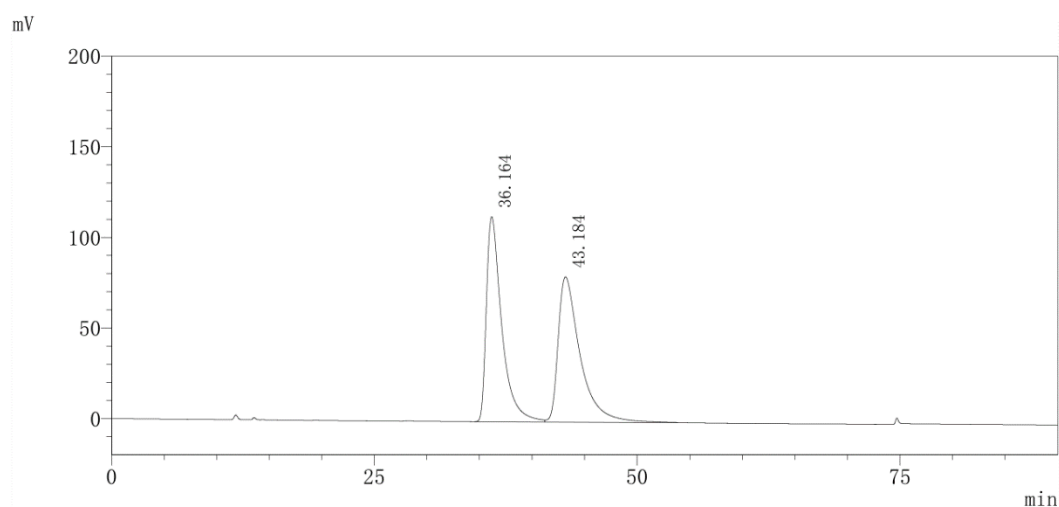
$[\alpha]_D^{25} = +104.2$ (c 1.0, CHCl_3)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.5$ Hz, 3H), 7.77 (s, 1H), 7.59 (dd, $J = 8.7$, 1.6 Hz, 1H), 7.55 – 7.42 (m, 2H), 6.42 (dd, $J = 17.5$, 10.7 Hz, 1H), 5.92 (s, 1H), 5.05 (d, $J = 17.5$ Hz, 1H), 4.93 (d, $J = 10.7$ Hz, 1H), 2.79 (d, $J = 18.9$ Hz, 1H), 2.40 (d, $J = 18.4$ Hz, 1H), 2.34 – 2.12 (m, 2H), 2.06 – 1.89 (m, 2H), 1.41 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.5, 139.6, 135.6, 133.5, 131.9, 128.3, 128.1, 127.8, 127.4, 125.9, 125.4, 124.9, 124.0, 38.2, 36.9, 34.7, 28.6, 21.9.

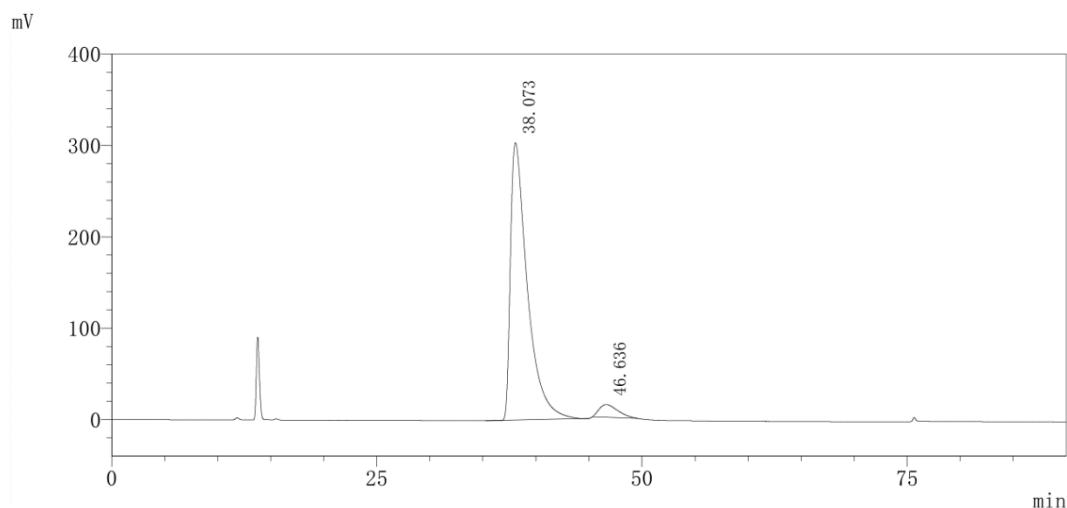
GCMS (EI) calcd. for $\text{C}_{19}\text{H}_{20}^+$ (M^+): 248.1560, Found: 248.1560.

The ee value was 90%, t_r (minor) = 46.636, t_r (major) = 38.073 (Chiralcel IE, $\lambda = 220$ nm, hexanes: i PrOH = 100:0, flow rate = 0.3 mL/min).



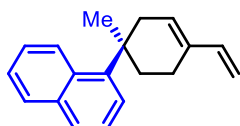
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	36.164	11476904	113232	58.569	49.638
2	43.184	11644093	80097	41.431	50.362
总计		23120998	193329	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	38.073	33610954	303618	95.656	95.191
2	46.636	1697840	13787	4.344	4.809
总计		35308794	317405	100.000	100.000



(*R*)-1-(1-methyl-4-vinylcyclohex-3-en-1-yl)naphthalene (**3d**)

Prepared according to General Procedure, colorless oil, 99% yield, 94% ee.

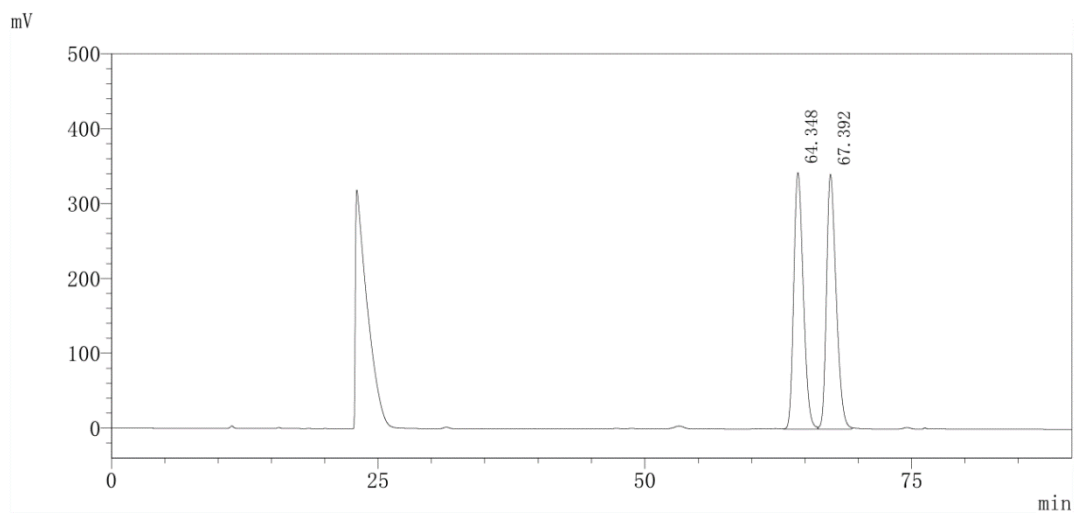
$[\alpha]_{\text{D}}^{25} = -65.4$ (c 1.0, CHCl_3)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.48 (d, $J = 7.9$ Hz, 1H), 7.91 (d, $J = 7.1$ Hz, 1H), 7.75 (d, $J = 7.8$ Hz, 1H), 7.57 – 7.45 (m, 3H), 7.41 (t, $J = 7.5$ Hz, 1H), 6.44 (dd, $J = 17.3$, 10.9 Hz, 1H), 5.91 (s, 1H), 5.04 (d, $J = 17.5$ Hz, 1H), 4.94 (d, $J = 10.7$ Hz, 1H), 2.94 (d, $J = 18.7$ Hz, 1H), 2.73 – 2.63 (m, 1H), 2.58 (d, $J = 18.9$ Hz, 1H), 2.36 – 2.24 (m, 1H), 2.13 – 2.03 (m, 1H), 2.00 – 1.90 (m, 1H), 1.67 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.7, 139.5, 135.4, 135.3, 131.5, 130.0, 128.2, 127.7, 126.6, 125.3, 124.7, 110.4, 40.3, 38.5, 34.5, 27.4, 22.2.

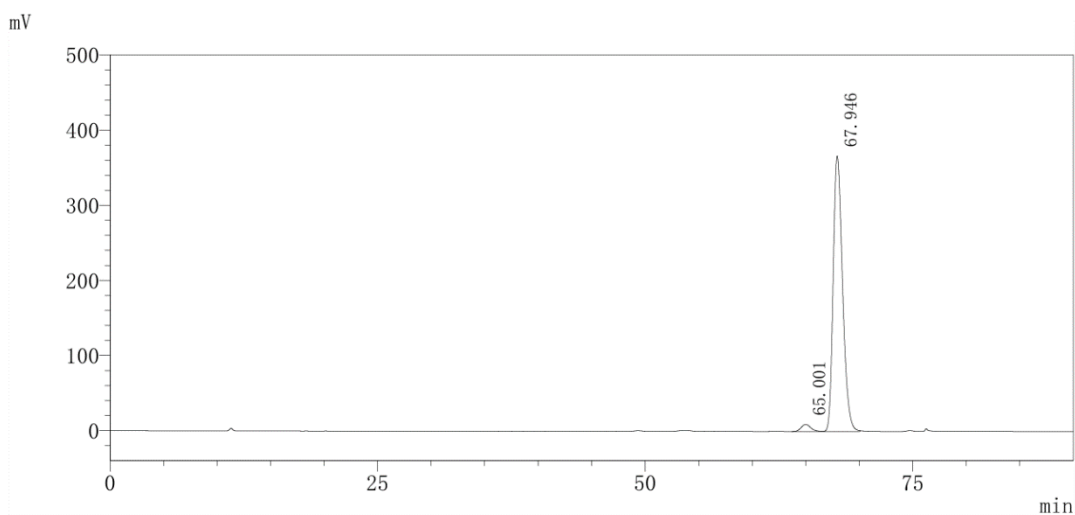
GCMS (EI) calcd. for $\text{C}_{19}\text{H}_{20}^+$ (M^+): 248.1560, Found: 248.1560.

The ee value was 94%, t_{r} (minor) = 65.001, t_{r} (major) = 67.946 (Chiralcel OD-3, $\lambda = 220$ nm, hexanes: i PrOH = 100:0, flow rate = 0.3 mL/min).



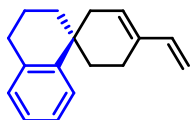
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	64.348	21355603	342755	50.160	49.832
2	67.392	21499305	340568	49.840	50.168
总计		42854908	683323	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	65.001	610310	9525	2.530	2.652
2	67.946	22401717	366913	97.470	97.348
总计		23012027	376439	100.000	100.000



(*R*)-4-vinyl-3',4'-dihydro-2'*H*-spiro[cyclohexane-1,1'-naphthalen]-3-ene (3e)

Prepared according to General Procedure, colorless oil, 99% yield, 90% ee.

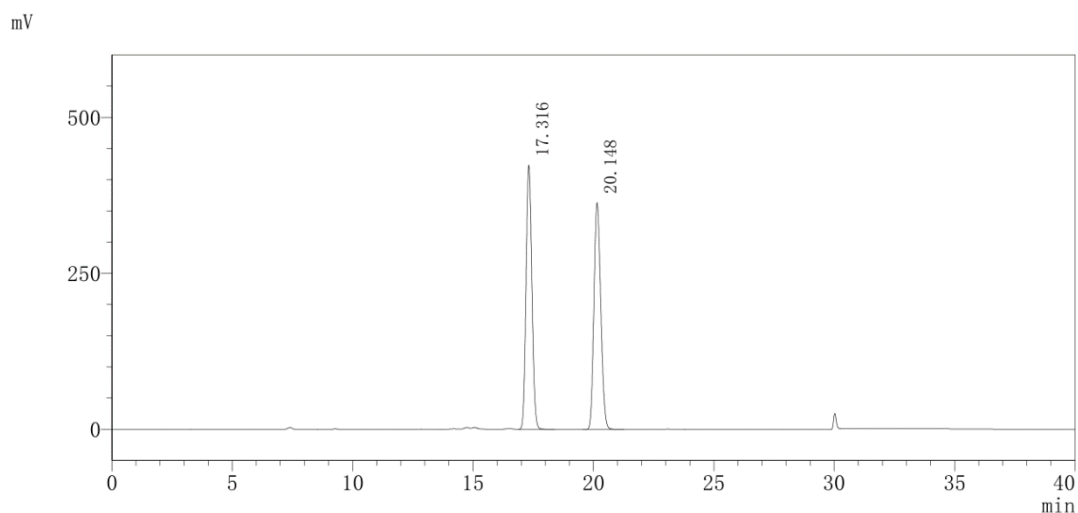
$[\alpha]_{\text{D}}^{25} = +20.9$ (c 1.0, CHCl_3)

^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, J = 7.8 Hz, 1H), 7.24 – 7.07 (m, 3H), 6.46 (dd, J = 17.5, 10.7 Hz, 1H), 5.82 (s, 1H), 5.15 (d, J = 17.5 Hz, 1H), 4.99 (d, J = 10.7 Hz, 1H), 2.82 (t, J = 6.0 Hz, 2H), 2.52 (d, J = 18.6 Hz, 1H), 2.38 – 2.06 (m, 4H), 1.91 – 1.67 (m, 4H), 1.66 – 1.55 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 145.4, 139.7, 137.3, 135.1, 129.2, 129.1, 126.9, 126.1, 125.6, 110.3, 39.5, 35.7, 35.0, 32.4, 30.9, 21.6, 19.3.

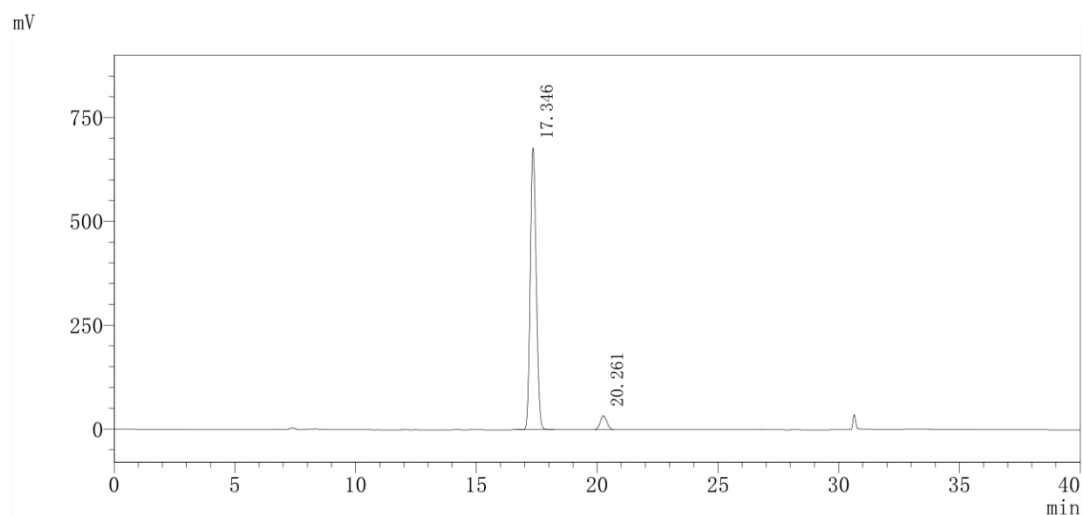
GCMS (EI) calcd. for $\text{C}_{17}\text{H}_{20}^+$ (M^+): 224.1560, Found: 224.1560.

The ee value was 90%, t_r (minor) = 20.261, t_r (major) = 17.346 (Chiralcel OD-3, λ = 220 nm, hexanes: i PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



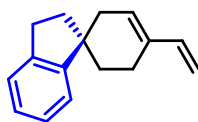
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	17.316	7204379	423190	53.797	50.034
2	20.148	7194678	363447	46.203	49.966
总计		14399057	786637	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	17.346	11670147	677848	95.333	94.831
2	20.261	636165	33183	4.667	5.169
总计		12306312	711031	100.000	100.000



(*R*)-4-vinyl-2',3'-dihydrospiro[cyclohexane-1,1'-inden]-3-ene (3f)

Prepared according to General Procedure, colorless oil, 85% yield, 92% ee.

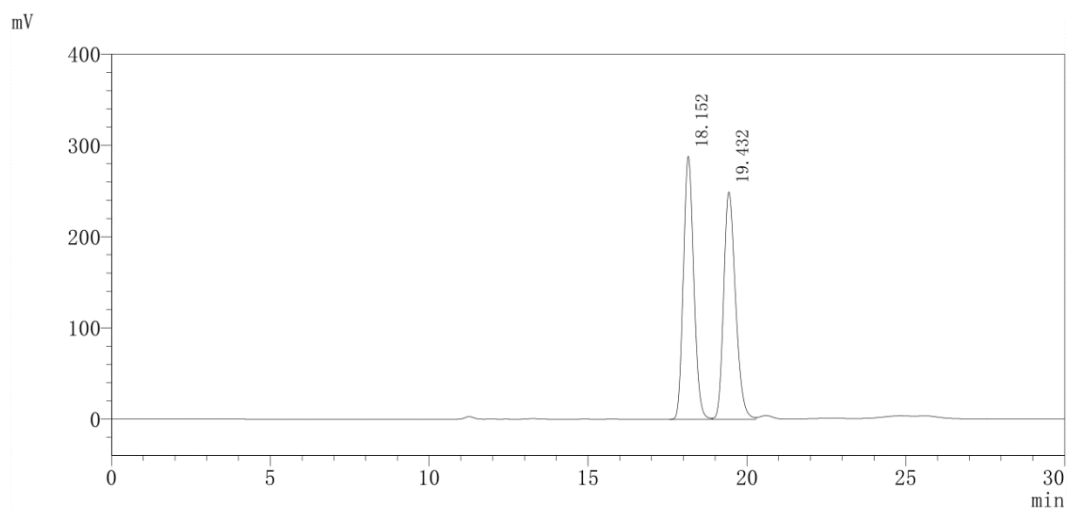
$[\alpha]_D^{11} = +51.4$ (c 1.0, CHCl_3)

^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.16 (m, 4H), 6.52 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.91 (s, 1H), 5.22 (d, $J = 17.5$ Hz, 1H), 5.05 (d, $J = 10.7$ Hz, 1H), 3.09 – 2.91 (m, 2H), 2.50 – 2.26 (m, 4H), 2.09 – 1.96 (m, 3H), 1.85 – 1.71 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 151.3, 143.5, 139.8, 136.1, 129.0, 126.7, 126.5, 124.6, 122.8, 110.4, 46.3, 37.8, 37.6, 32.4, 30.0, 22.0.

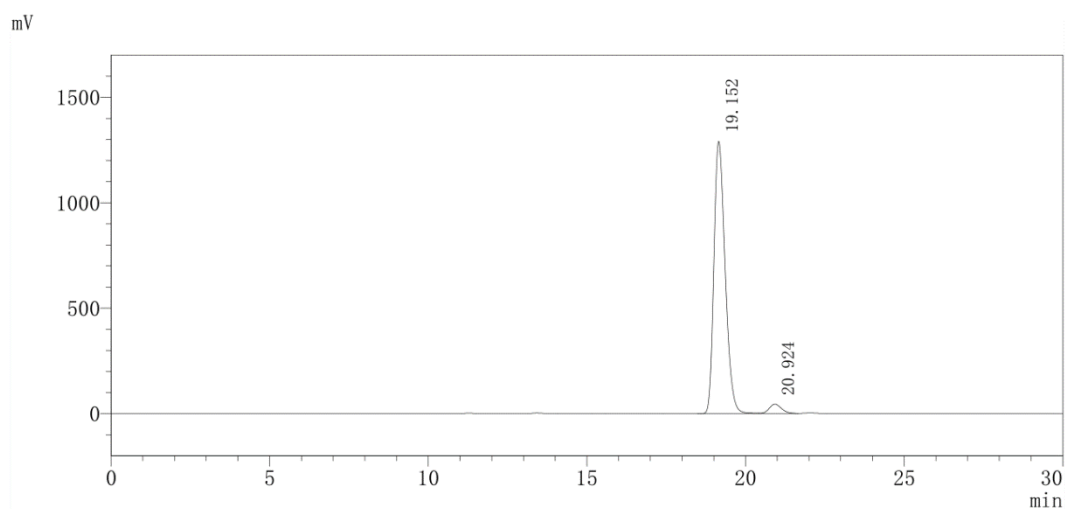
GCMS (EI) calcd. for $\text{C}_{16}\text{H}_{18}^+$ (M^+): 210.1403, Found: 210.1404.

The ee value was 92%, t_r (minor) = 20.924, t_r (major) = 19.152 (Chiralcel IF, $\lambda = 220$ nm, hexanes:*i*PrOH = 100:0, flow rate = 0.3 mL/min).



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	18.152	6506335	288377	53.627	50.016
2	19.432	6502106	249369	46.373	49.984
总计		13008441	537746	100.000	100.000

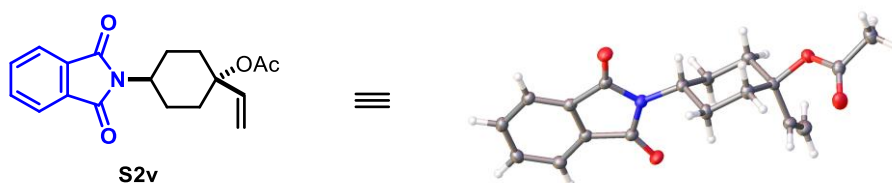


检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	19.152	31835786	1291964	96.658	96.229
2	20.924	1247630	44675	3.342	3.771
总计		33083416	1336639	100.000	100.000

X-ray of substate and product

X-ray of substrate:



Identification code	2297061
Empirical formula	C ₁₈ H ₁₉ NO ₄
Formula weight	313.34
Temperature/K	113.15
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	5.62030(10)
b/Å	9.2003(2)
c/Å	30.1539(8)
α/°	90
β/°	90.534(2)
γ/°	90

Volume/Å ³	1559.14(6)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.335
μ/mm^{-1}	0.095
F(000)	664.0
Crystal size/mm ³	0.32 × 0.24 × 0.16
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	6.988 to 56.564
Index ranges	-7 ≤ h ≤ 7, -12 ≤ k ≤ 12, -38 ≤ l ≤ 40
Reflections collected	20115
Independent reflections	3888 [R_{int} = 0.0649, R_{sigma} = 0.0414]
Data/restraints/parameters	3888/0/209
Goodness-of-fit on F^2	1.047
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0504, wR_2 = 0.1197
Final R indexes [all data]	R_1 = 0.0637, wR_2 = 0.1287
Largest diff. peak/hole / e Å ⁻³	0.30/-0.25

X-ray of product:

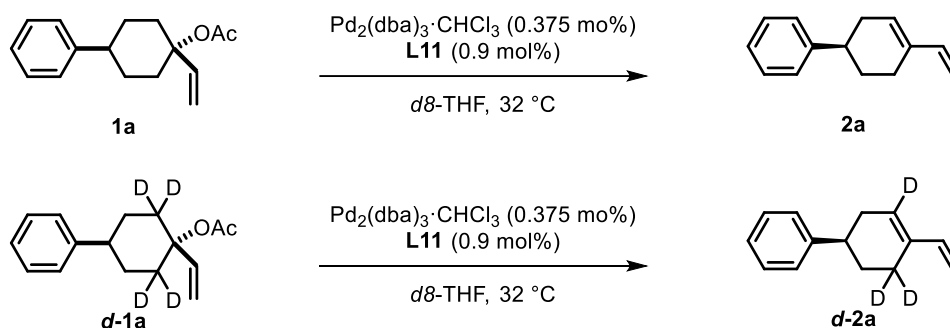


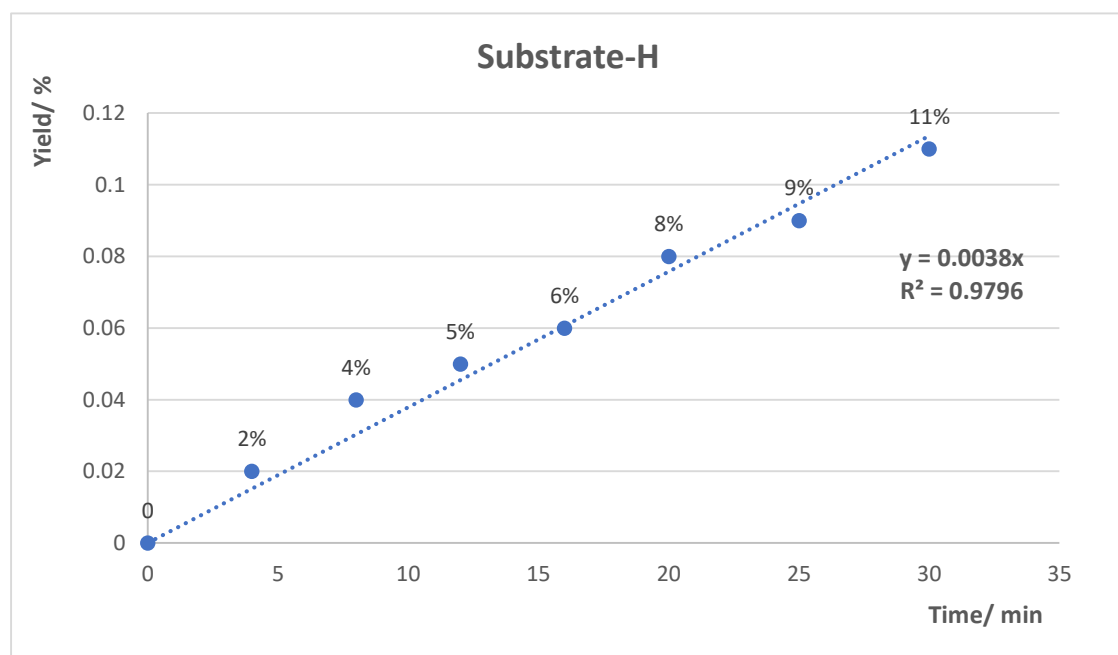
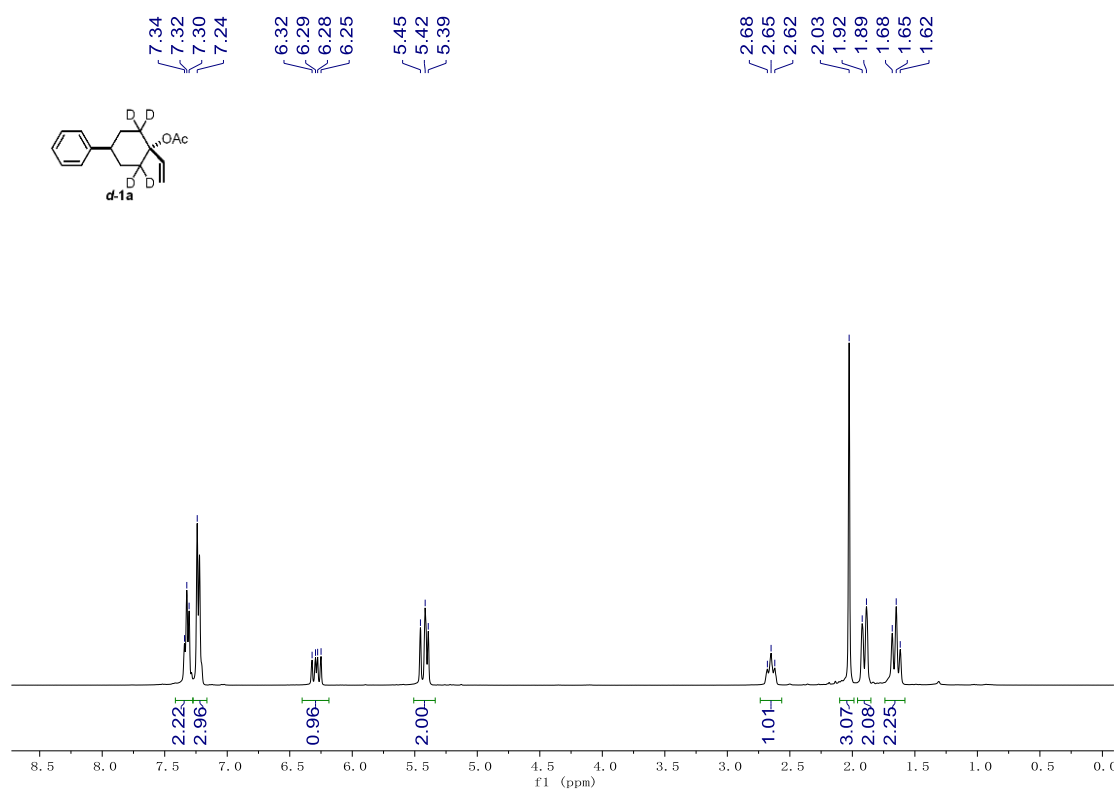
Identification code	2306164
Empirical formula	C ₁₄ H ₁₅ Cl
Formula weight	218.71
Temperature/K	113.15
Crystal system	monoclinic
Space group	P2 ₁
a/Å	12.74654(17)
b/Å	14.6333(2)
c/Å	12.86588(19)
α /°	90
β /°	97.5620(13)
γ /°	90
Volume/Å ³	2378.93(6)

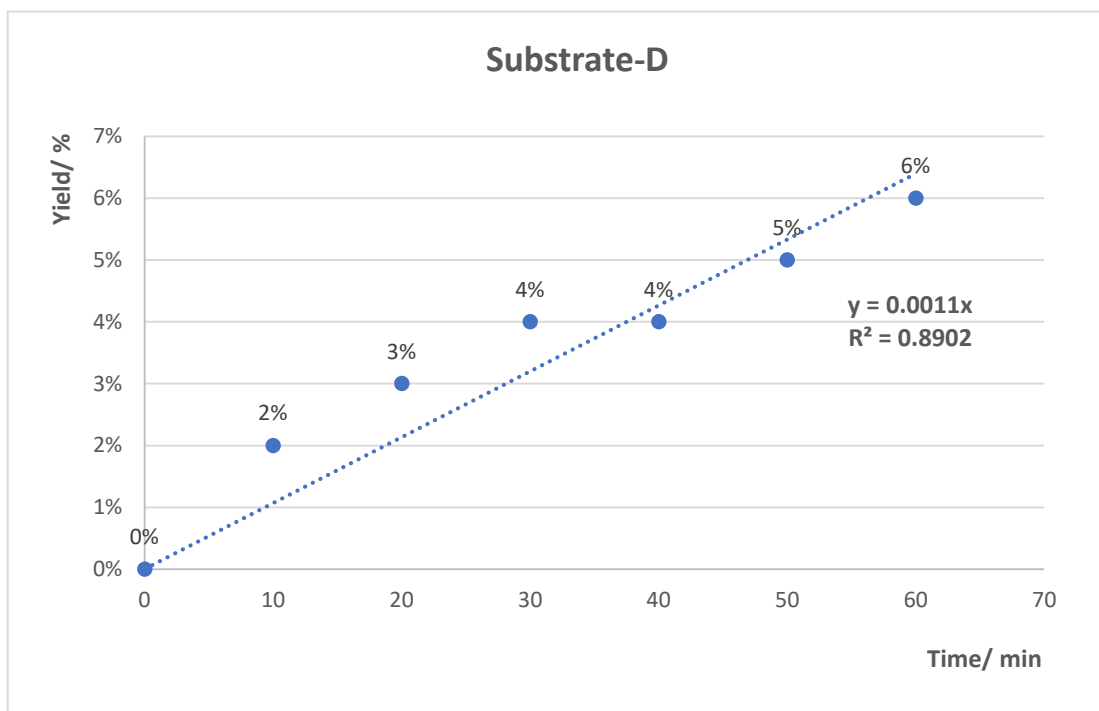
Z	8
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.221
μ/mm^{-1}	0.285
F(000)	928.0
Crystal size/ mm^3	$0.36 \times 0.24 \times 0.18$
Radiation	Mo K α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	3.194 to 56.564
Index ranges	$-16 \leq h \leq 16, -19 \leq k \leq 19, -17 \leq l \leq 17$
Reflections collected	62378
Independent reflections	11769 [$R_{\text{int}} = 0.0693, R_{\text{sigma}} = 0.0369$]
Data/restraints/parameters	11769/421/748
Goodness-of-fit on F^2	1.119
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0929, wR_2 = 0.2396$
Final R indexes [all data]	$R_1 = 0.0966, wR_2 = 0.2444$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.81/-0.32
Flack parameter	0.010(18)

KIE experiment

In an Ar-filled glove box, (*R,R*)-DACH-phenyl Trost ligand **L11** (1.9 mg, 0.0027 mmol, 0.9 mol%) and $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (1.2 mg, 0.001125 mmol, 0.375 mol%) were dissolved in dry *d*8-THF (0.2 M, 1.5 mL) to stir at 32 °C for 1 h. To the solution, 1,1,2,2-tetrachloroethane (16 μL , 0.15 mmol, 0.5 equiv) and substrate (0.3 mmol, 1.0 equiv) were added at the same temperature. Because the reaction was halted at 0 °C, aliquots (50 μL) were taken every time and placed at -20 °C. The amount of **2a** and **d-2a** were monitored by crude ^1H NMR analysis, respectively.

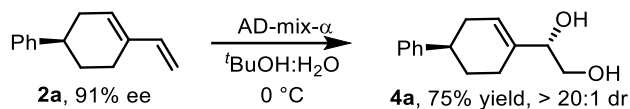




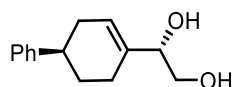


Calculation of KIE: $k_H/k_D = 0.0038/0.0011 = 3.5$

Synthetic Transformations



In an Ar-filled glovebox, (DHQ)₂PHAL (5.0 mg, 0.0064 mmol, 0.04 equiv), K₂OsO₆H₄ (1.2 mg, 0.0032 mmol, 0.02 equiv), K₃Fe(CN)₆ (158 mg, 0.48 mmol, 3 equiv) and K₂CO₃ (66 mg, 0.48 mmol, 3 equiv) were added to 10 mL reaction bottle and sealed with rubber plugs. The resulting mixture was removed from glovebox and dissolved in ^tBuOH:H₂O (0.1 M, 0.8 mL:0.8 mL) to stir at room temperature for 30 min. To the solution, MeSO₂NH₂ (0.16 mmol, 15.2 mg, 1 equiv) and **2a** (30 mg, 0.16 mmol, 1 equiv) were added at 0 °C and stirred at 0 °C for 3 h. After then, aqueous solution was added and the aqueous layer was extracted with EA (8 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo. The mixture was purified by silica gel column chromatography (PE:EA = 1:1) to give the desired product **4a** (26.3 mg, 75% yield).



1-((*R*)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)ethane-1,2-diol (**4a**)

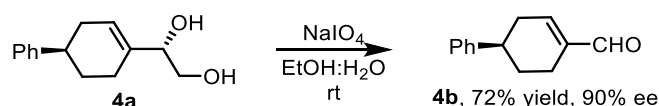
Prepared according to General Procedure, white solid, 75% yield, m.p. 78-79 °C, > 20:1 dr.

$[\alpha]_D^{25} = +60.2$ (c 1.0, CHCl_3)

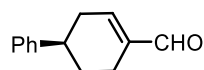
^1H NMR (400 MHz, CDCl_3) δ 7.32 (t, $J = 7.5$ Hz, 2H), 7.28 – 7.18 (m, 3H), 5.89 (s, 1H), 4.20 (s, 1H), 3.74 (s, 1H), 3.62 (s, 1H), 2.89 – 2.76 (m, 1H), 2.72 – 1.95 (m, 7H), 1.87 – 1.71 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 136.6, 128.5, 126.9, 126.2, 123.2, 76.0, 65.6, 40.2, 33.2, 29.7, 26.0.

HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{18}\text{NaO}_2^+$ ($\text{M} + \text{Na}$) $^+$: 241.1199, Found: 241.1199.



In the eggplant shaped bottle, **4a** (17 mg, 0.078 mmol, 1 equiv) and NaIO_4 (20.3 mg, 0.094 mmol, 1.2 equiv) were dissolved in $\text{EtOH:H}_2\text{O}$ (0.06 M, 0.7 mL:0.7 mL) to stir at room temperature until completion. After then, aqueous solution was added and the aqueous layer was extracted with EA (3 times). The combined organic layers were washed with saturated brine, dried over MgSO_4 , and concentrated in vacuo. The mixture was purified by silica gel column chromatography ($\text{PE:EA} = 1:1$) to give the desired product **4b** (10.5 mg, 72% yield).



(R)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde (4b)

Prepared according to General Procedure, colorless oil, 72% yield, 90% ee.

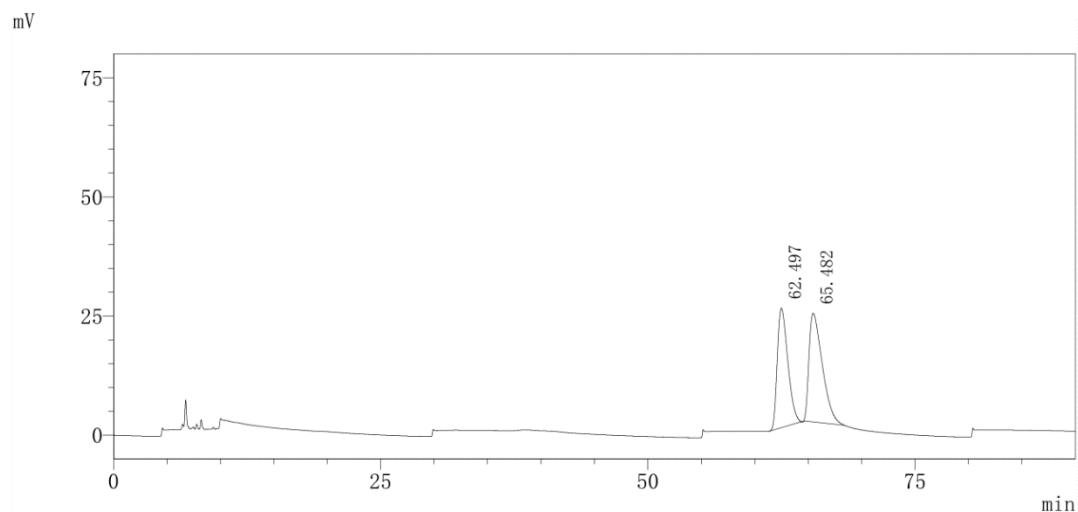
$[\alpha]_D^{25} = +82.5$ (c 1.0, CHCl_3)

^1H NMR (400 MHz, CDCl_3) δ 9.42 (s, 1H), 7.26 (t, $J = 7.4$ Hz, 2H), 7.16 (d, $J = 7.5$ Hz, 3H), 6.83 (s, 1H), 2.84 – 2.74 (m, 1H), 2.67 – 2.53 (m, 1H), 2.50 – 2.33 (m, 2H), 2.24 – 2.10 (m, 1H), 2.06 – 1.90 (m, 1H), 1.75 – 1.60 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 194.0, 150.6, 145.7, 141.5, 128.7, 126.9, 126.6, 39.9, 34.5, 28.8, 22.0.

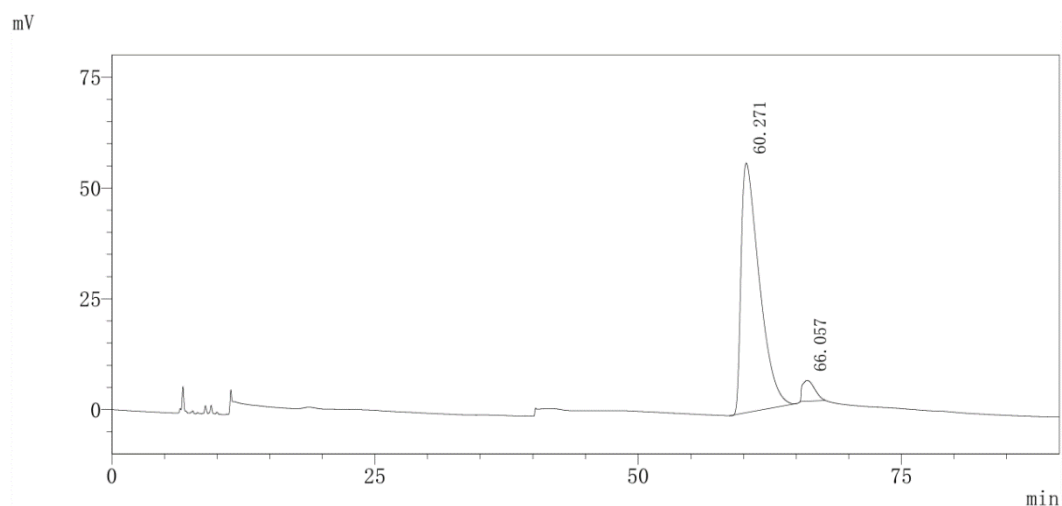
GCMS (EI) calcd. for $\text{C}_{13}\text{H}_{14}\text{O}^+$ (M^+): 186.1039, Found: 186.1039.

The ee value was 90%, t_r (minor) = 66.057, t_r (major) = 60.271 (Chiralcel OD-3, $\lambda = 220$ nm, hexanes: i PrOH = 99.5:0.5, flow rate = 0.5 mL/min).



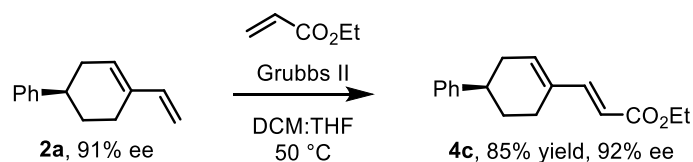
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	62.497	1719879	25081	52.364	46.511
2	65.482	1977885	22817	47.636	53.489
总计		3697764	47898	100.000	100.000

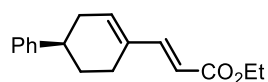


检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	60.271	6775048	56293	92.348	94.759
2	66.057	374733	4665	7.652	5.241
总计		7149781	60958	100.000	100.000



In an Ar-filled glovebox, Grubbs II (13.6 mg, 0.016 mmol, 0.1 equiv), **2a** (30 mg, 0.16 mmol, 1 equiv), ethyl acrylate (0.17 mL, 1.6 mmol, 10 equiv) were dissolved in dry DCM:THF (0.16 M, 0.8 mL:0.2 mL) to stir at 50 °C until completion. The mixture was concentrated in vacuo and then purified by silica gel column chromatography (PE:EA = 15:1) to give the desired product **4c** (35 mg, 85% yield).



ethyl (*R,E*)-3-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)acrylate (4c)

Prepared according to General Procedure, white solid, 85% yield, m.p. 76-77 °C, 92% ee.

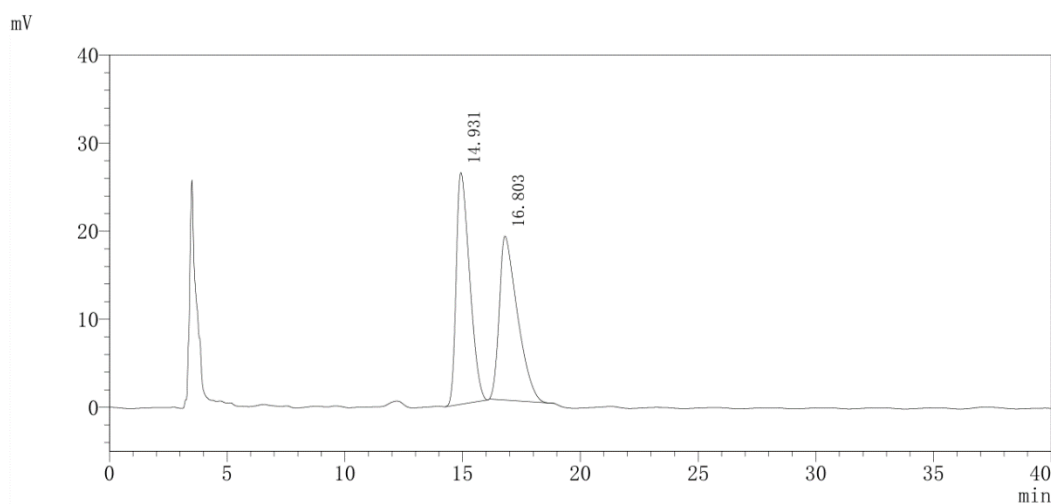
$[\alpha]_D^{25} = +60.8$ (c 1.0, CHCl_3)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 – 7.29 (m, 3H), 7.29 – 7.18 (m, 3H), 6.26 (s, 1H), 5.81 (d, $J = 15.8$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 2.91 – 2.73 (m, 1H), 2.59 – 2.22 (m, 4H), 2.14 – 1.98 (m, 1H), 1.92 – 1.73 (m, 1H), 1.31 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.7, 147.4, 146.2, 137.9, 134.8, 128.6, 126.9, 126.4, 115.5, 60.3, 39.8, 34.5, 29.4, 24.8, 14.5.

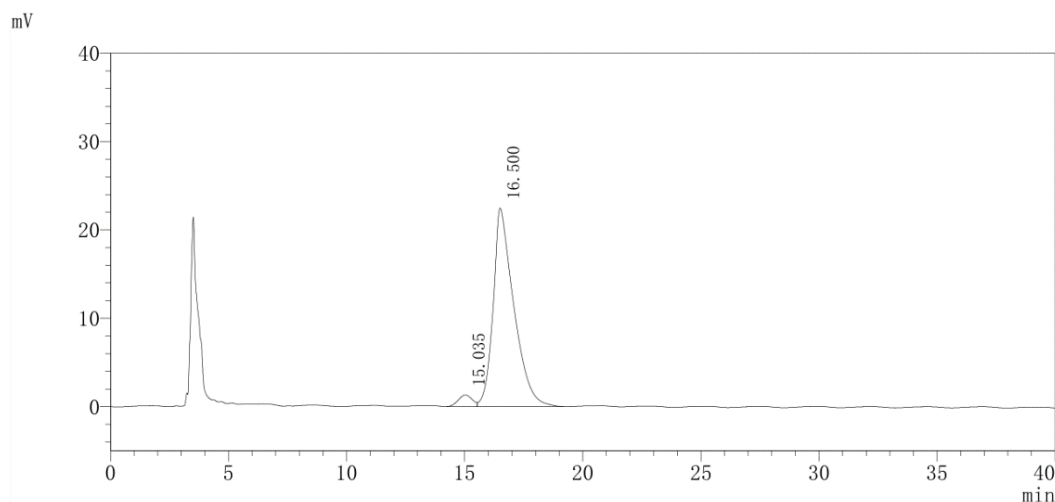
GCMS (EI) calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_2$ (M^+): 256.1458, Found: 256.1458.

The ee value was 92%, t_r (minor) = 15.035, t_r (major) = 16.500 (Chiralcel IF, $\lambda = 220$ nm, hexanes: i PrOH = 98:2, flow rate = 1.0 mL/min).



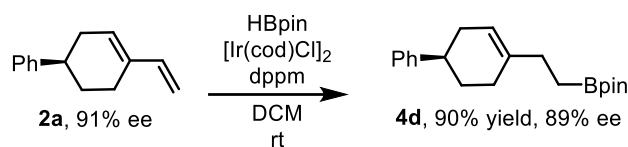
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	14.931	1040147	26299	58.555	50.863
2	16.803	1004850	18615	41.445	49.137
总计		2044997	44914	100.000	100.000

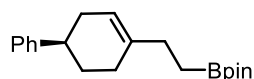


检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	15.035	53840	1308	5.501	3.794
2	16.500	1365373	22466	94.499	96.206
总计		1419213	23774	100.000	100.000



In an Ar-filled glovebox, dppm (7.7 mg, 0.02 mmol, 0.1 equiv) and $[\text{Ir}(\text{cod})\text{Cl}]_2$ (6.7 mg, 0.01 mmol, 0.05 equiv) were dissolved in dry DCM (0.08 M, 2.5 mL) to stir at room temperature for 30 min. To the solution, **2a** (0.2 mmol, 37 mg, 1 equiv) and HBpin (145 μL , 1.0 mmol, 5 equiv) was added. The resulting mixture was removed from glovebox and stirred at room temperature for 24 h. The mixture was concentrated in vacuo and then purified by silica gel column chromatography (PE:EA = 15:1) to give the desired product **4d** (56.4 mg, 90% yield).



(R)-4,4,5,5-tetramethyl-2-(2-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)ethyl)-1,3,2-dioxaborolane (4d)

Prepared according to General Procedure, white solid, 90% yield, m.p. 35-36 $^{\circ}\text{C}$, 89% ee.

$[\alpha]_{\text{D}}^{25} = +28.4$ (c 1.0, CHCl_3)

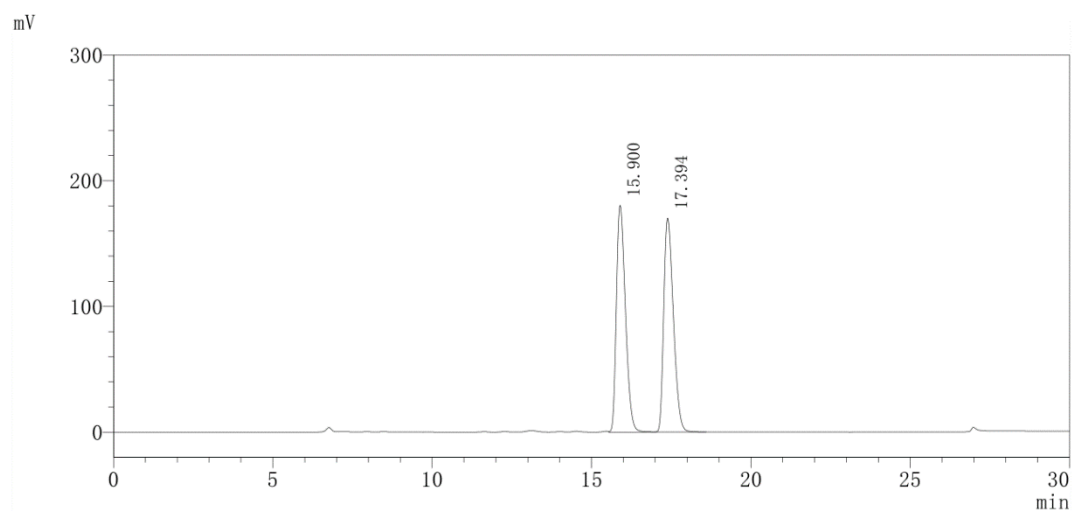
^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.16 (m, 5H), 5.50 (s, 1H), 2.82 – 2.67 (m, 1H), 2.33 – 2.24 (m, 1H), 2.21 – 2.02 (m, 5H), 2.00 – 1.91 (m, 1H), 1.82 – 1.71 (m, 1H), 1.27 (s, 12H), 0.96 (t, $J = 7.1$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.5, 139.6, 128.4, 127.0, 126.0, 119.2, 83.1, 40.4, 33.6, 31.6, 30.2, 29.1, 25.0.

GCMS (EI) calcd. for $\text{C}_{20}\text{H}_{29}\text{NBO}_2^{+}$ (M^{+}): 312.2255, Found: 312.2255.

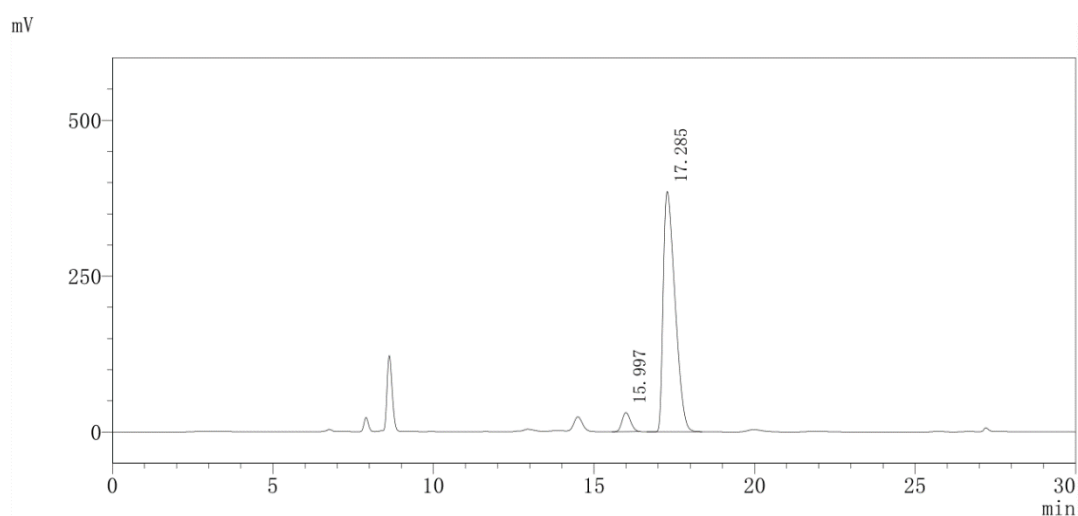
The ee value was 89%, t_{r} (minor) = 15.997, t_{r} (major) = 17.285 (Chiralcel OD-3, $\lambda =$

220 nm, hexanes:*i*PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



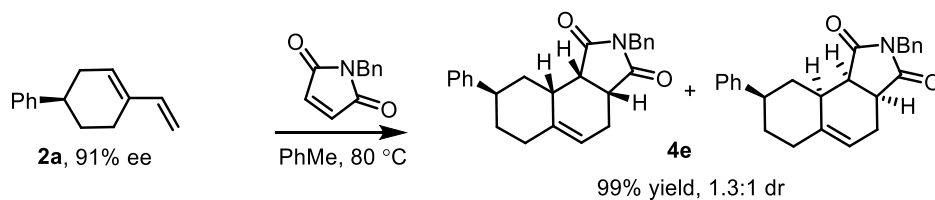
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	15.900	3560082	180450	51.474	49.890
2	17.394	3575720	170116	48.526	50.110
总计		7135801	350566	100.000	100.000



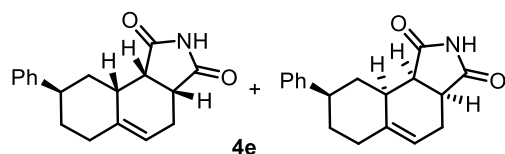
检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	15.997	562123	30603	7.356	5.388
2	17.285	9870800	385435	92.644	94.612
总计		10432923	416037	100.000	100.000



In the eggplant shaped bottle, **2a** (28 mg, 0.15 mmol, 1.5 equiv) and *N*-benzylmaleimide (18.7 mg, 0.10 mmol, 1 equiv) were dissolved in PhMe (0.2 M, 0.5 mL) to stir at 80 °C

until completion. After then, The mixture was concentrated in vacuo and purified by silica gel column chromatography (PE:EA = 20:1 to 5:1) to give the desired product **4e** (36.8 mg, 99% yield, dr = 1.3:1).



Prepared according to General Procedure, white solid, 99% yield, m.p. 90-91 °C.

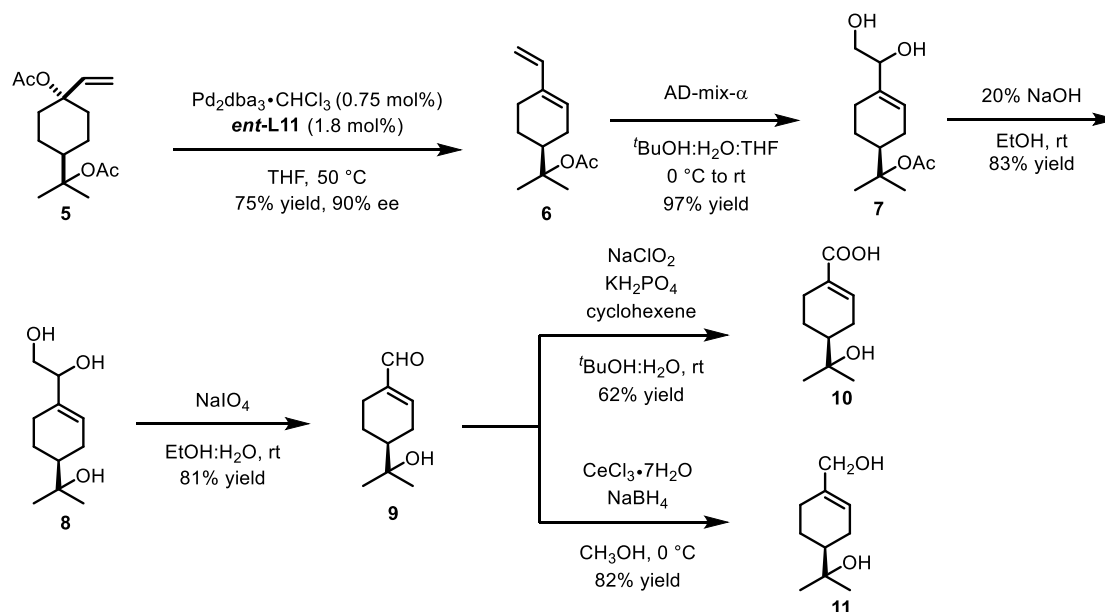
$[\alpha]_D^{25} = -12.8$ (c 1.0, CHCl_3)

^1H NMR (400 MHz, CDCl_3) δ 7.25 – 6.91 (m, 23H), 5.52 – 5.45 (m, 1.3H), 5.40 (s, 1H), 4.64 – 4.43 (m, 4.6H), 3.08 – 1.33 (m, 27.6H).

^{13}C NMR (101 MHz, CDCl_3) δ 179.7, 179.6, 178.3, 178.2, 147.3, 146.4, 141.3, 139.4, 136.1, 135.9, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.2, 126.9, 126.1, 126.0, 119.5, 117.2, 77.4, 44.7, 44.0, 42.3, 40.8, 38.5, 36.3, 35.8, 34.1, 33.7, 33.1, 32.4, 29.4, 28.8, 24.5, 22.0.

HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{25}\text{NNaO}_2^+$ ($M + \text{Na}$) $^+$: 394.1778, Found: 394.1777.

Total synthesis of (-)-oleuropeic acid and (-)-7-hydroxyterpineol.



(S)-2-(4-vinylcyclohex-3-en-1-yl)propan-2-yl acetate (**6**)

In an Ar-filled glove box, (*R,R*)-DACH-phenyl Trost ligand **ent-L11** (83 mg, 0.12 mmol, 1.8 mol%) and $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (52 mg, 0.05 mmol, 0.75 mol%) were dissolved in dry 1,4-dioxane (0.4 M, 17 mL) to stir at room temperature for 1 h. To the solution, **5** (6.7 mmol, 1.8 g, 1 equiv) was added. The resulting mixture was stirred at 50 °C for 48 h. The mixture was then purified by silica gel column chromatography (PE to PE:EA = 50:1) to give the desired product **6**.

Colorless oil, 75% yield, 90% ee.

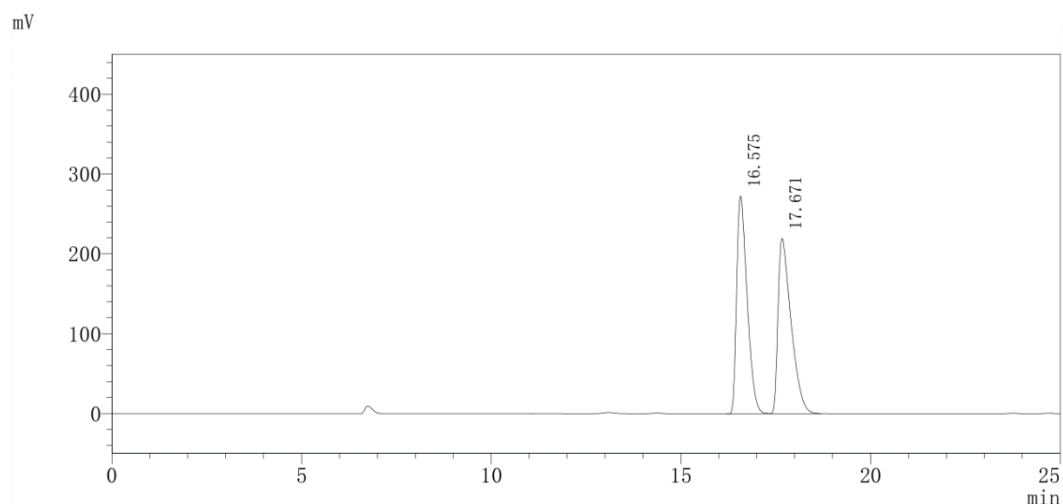
$[\alpha]_D^{24} = -62.4$ (c 0.7, CHCl_3)

^1H NMR (400 MHz, CDCl_3) δ 6.27 (dd, $J = 17.0, 11.1$ Hz, 1H), 5.66 (s, 1H), 4.98 (d, $J = 17.4$ Hz, 1H), 4.83 (d, $J = 10.7$ Hz, 1H), 2.27 (d, $J = 15.8$ Hz, 1H), 2.14 – 1.76 (m, 8H), 1.39 (s, 3H), 1.36 (s, 3H), 1.29 – 1.16 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.5, 139.5, 136.1, 128.8, 110.3, 84.6, 43.0, 27.0, 24.7, 23.4, 23.2, 22.5.

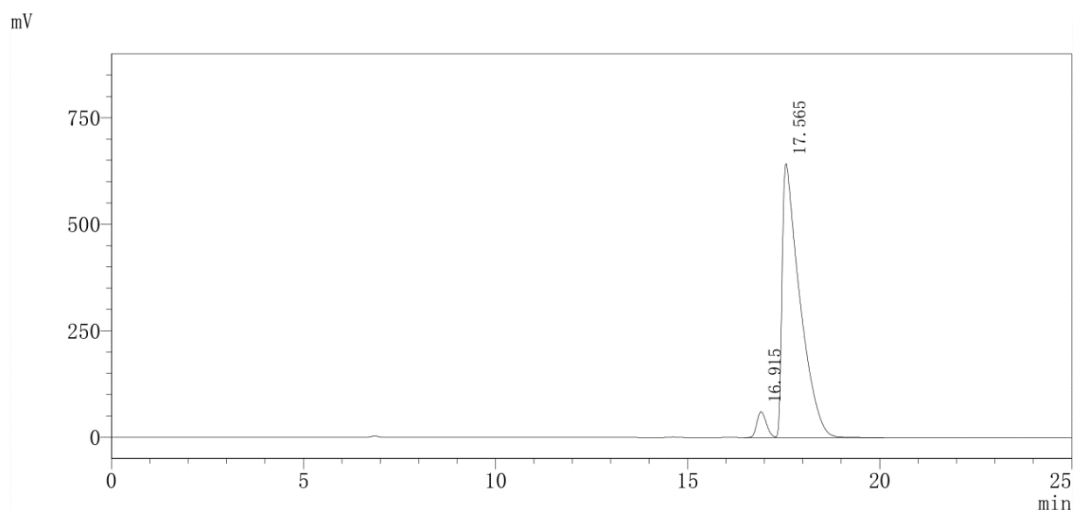
HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{20}\text{NaO}_2^+$ ($\text{M} + \text{Na}$) $^+$: 231.1356, Found: 231.1357.

The ee value was 90%, t_r (minor) = 16.915, t_r (major) = 17.565 (Chiralcel OD-3, $\lambda = 220$ nm, hexanes: i PrOH = 99.8:0.2, flow rate = 0.5 mL/min).



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	16.575	5251828	272788	55.393	49.925
2	17.671	5267652	219669	44.607	50.075
总计		10519481	492458	100.000	100.000



检测器A 220nm

Peak#	Time	Area	Height	Height%	Area%
1	16.915	1028197	60312	8.576	4.752
2	17.565	20606907	642983	91.424	95.248
总计		21635104	703295	100.000	100.000

2-((1*S*)-4-(1,2-dihydroxyethyl)cyclohex-3-en-1-yl)propan-2-yl acetate (7)

In an Ar-filled glovebox, (DHQ)₂PHAL (31.2 mg, 0.04 mmol, 0.04 equiv), K₂OsO₆H₄ (7.4 mg, 0.02 mmol, 0.02 equiv), K₃Fe(CN)₆ (988 mg, 3.0 mmol, 3 equiv) and K₂CO₃ (415 mg, 3.0 mmol, 3 equiv) were added to 50 mL reaction bottle and sealed with rubber plugs. The resulting mixture was removed from glovebox and dissolved in ^tBuOH:H₂O (0.1 M, 3.0 mL:3.0 mL:3.0 mL) to stir at room temperature for 30 min. To the solution, MeSO₂NH₂ (95 mg, 1.0 mmol, 1 equiv) and **6** (208 mg, 1.0 mmol, 1 equiv) in THF (3.0 mL) were added at 0 °C and stirred at 0 °C for 3 h. After then, aqueous solution was added and the aqueous layer was extracted with EA (8 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo. The mixture was purified by silica gel column chromatography (DCM:MeOH = 40:1) to give the desired product **7** (235 mg, 97% yield).

Colorless oil, 97% yield.

$[\alpha]_D^{24} = -20.4$ (*c* 1.0, CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 5.73 (s, 1H), 4.09 (s, 1H), 3.70 – 3.42 (m, 2H), 2.68 (s, 2H), 2.18 (d, *J* = 15.7 Hz, 1H), 2.12 – 1.99 (m, 2H), 1.95 (s, 3H), 1.92 – 1.78 (m, 2H), 1.42 (s, 3H), 1.38 (s, 3H), 1.30 – 1.19 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 170.8, 137.0, 123.9, 84.8, 76.0, 65.5, 42.7, 26.2, 25.2, 23.6, 23.4, 22.6.

HRMS (ESI) calcd. for C₁₃H₂₂NaO₄⁺ (*M* + Na)⁺: 265.1410, Found: 265.1413.

1-((*S*)-4-(2-hydroxypropan-2-yl)cyclohex-1-en-1-yl)ethane-1,2-diol (8)

In the eggplant shaped bottle, **7** (17 mg, 0.078 mmol, 1 equiv) and 20% NaOH:EtOH (0.1 M, 1:2) were added to stir at room temperature until completion. After then, aqueous solution was added and the aqueous layer was extracted with EA (10 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo. The mixture was not purified to give the desired product **8** (110 mg, 83% yield).

White solid, 83% yield, m.p. 80-81 °C.

$[\alpha]_D^{24} = -31.2$ (*c* 1.0, CH₃OH)

¹H NMR (400 MHz, CD₃OD) δ 5.80 – 5.69 (m, 1H), 4.89 (s, 3H), 4.09 – 3.96 (m, 1H), 3.57 – 3.49 (m, 2H), 2.34 – 2.12 (m, 2H), 2.04 – 1.84 (m, 3H), 1.66 – 1.50 (m, 1H), 1.30 – 1.21 (m, 1H), 1.19 (s, 3H), 1.18 (s, 3H).

¹³C NMR (101 MHz, CD₃OD) δ 137.4, 123.7, 76.1, 71.7, 64.5, 45.1, 26.4, 25.8, 24.8, 24.5, 23.6.

HRMS (ESI) calcd. for C₁₁H₂₀NaO₃⁺ (*M* + Na)⁺: 223.1305, Found: 223.1305.

(*S*)-4-(2-hydroxypropan-2-yl)cyclohex-1-ene-1-carbaldehyde (9)

In the eggplant shaped bottle, **8** (110 mg, 0.55 mmol, 1 equiv) and NaIO₄ (143 mg, 0.66 mmol, 1.2 equiv) were dissolved in EtOH:H₂O (0.06 M, 4.5 mL:4.5 mL) to stir at room temperature until completion. After then, aqueous solution was added and the aqueous layer was extracted with EA (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo. The mixture was purified

by silica gel column chromatography (PE:EA = 2:1) to give the desired product **9** (75 mg, 81% yield).

Colorless oil, 81% yield.

$[\alpha]_D^{24} = -96.4$ (*c* 1.0, CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 9.40 (s, 1H), 6.80 (s, 1H), 2.48 (d, *J* = 20.1 Hz, 2H), 2.25 – 1.88 (m, 3H), 1.68 – 1.50 (m, 2H), 1.20 (s, 7H).

¹³C NMR (101 MHz, CDCl₃) δ 194.1, 151.4, 141.5, 72.3, 44.8, 28.2, 27.2, 26.9, 22.7, 22.2.

HRMS (ESI) calcd. for C₁₀H₁₆NaO₂⁺ (*M* + Na)⁺: 191.1043, Found: 191.1044.

(S)-4-(2-hydroxypropan-2-yl)cyclohex-1-ene-1-carboxylic acid (10)

In the eggplant shaped bottle, **9** (16.8 mg, 0.1 mmol, 1 equiv), cyclohexene (140 μ L, 1.4 mmol, 14 equiv), KH₂PO₄ (91 mg, 0.67 mmol, 6.7 equiv), and NaClO₂ (90.4 mg, 1.0 mmol, 10 equiv) were dissolved in *t*BuOH:H₂O (0.12 M, 500 μ L:350 μ L) to stir at room temperature until completion. After then, the mixture was concentrated in vacuo. HCl aqueous solution was added (pH $\approx$ 2) and the aqueous layer was extracted with EA (3 times). The combined organic layers were washed with saturated brine, dried over MgSO₄, and concentrated in vacuo. The mixture was purified by silica gel column chromatography (DCM:MeOH = 10:1) to give the desired product **10** (10.4 mg, 62% yield).

White solid, 62% yield, m.p. 157-158 °C.

$[\alpha]_D^{24} = -33.8$ (*c* 1.0, CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.06 (m, 1H), 2.62 – 2.48 (m, 1H), 2.44 – 2.33 (m, 1H), 2.27 – 1.95 (m, 4H), 1.63 – 1.52 (m, 1H), 1.28 – 1.26 (m, 2H), 1.22 (s, 3H), 1.22 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.0, 142.1, 129.8, 72.6, 44.2, 29.8, 27.8, 27.4, 26.8, 25.0.

HRMS (ESI) calcd. for C₁₀H₁₅O₃⁻ (*M*-H)⁻: 183.1027, Found: 183.1016.

(S)-2-(4-(hydroxymethyl)cyclohex-3-en-1-yl)propan-2-ol (11)

In the eggplant shaped bottle, **9** (16.8 mg, 0.1 mmol, 1 equiv) and CeCl₃·7H₂O (45 mg, 0.12 mmol, 1.2 equiv) were dissolved in MeOH (0.2 M, 0.5 mL) to stir at 0 °C for 30 min. Then NaBH₄ (5.7 mg, 0.15 mmol, 1.5 equiv) was added until completion. The mixture was concentrated in vacuo and purified by silica gel column chromatography (PE:EA = 2:1 to 1:1) to give the desired product **11** (14.0 mg, 82% yield).

Colorless oil, 82% yield.

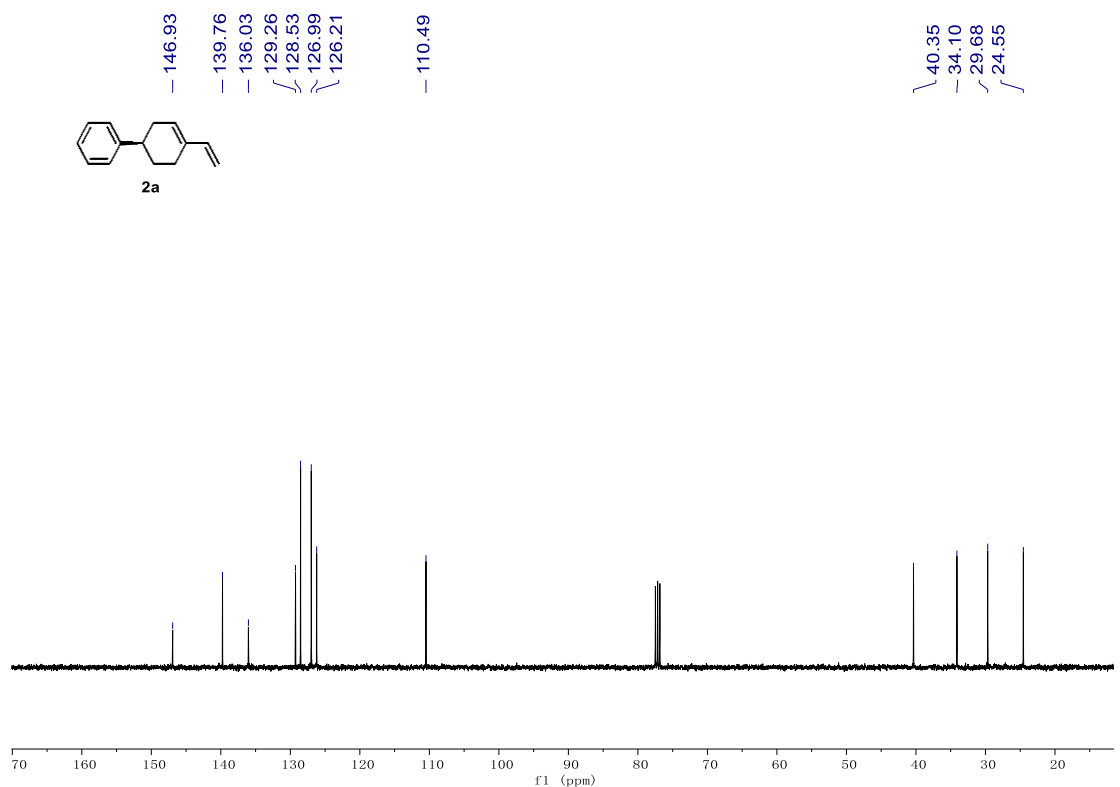
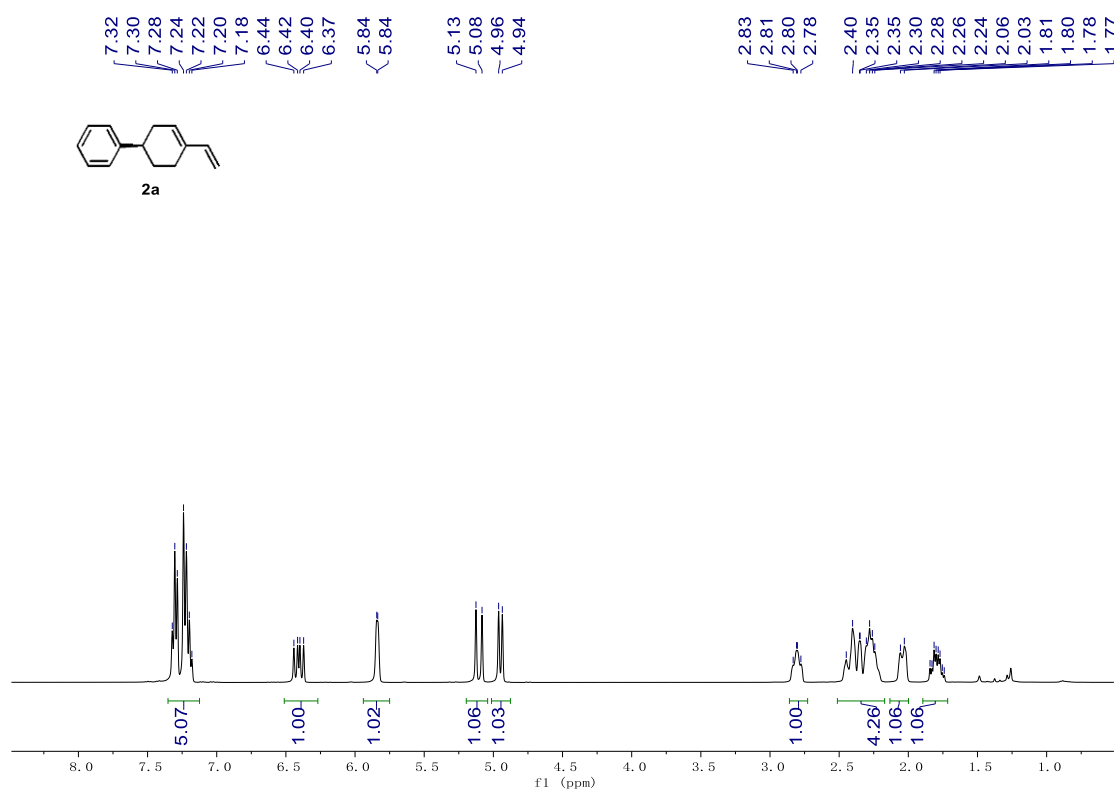
$[\alpha]_D^{24} = -48.0$ (*c* 1.0, CHCl₃)

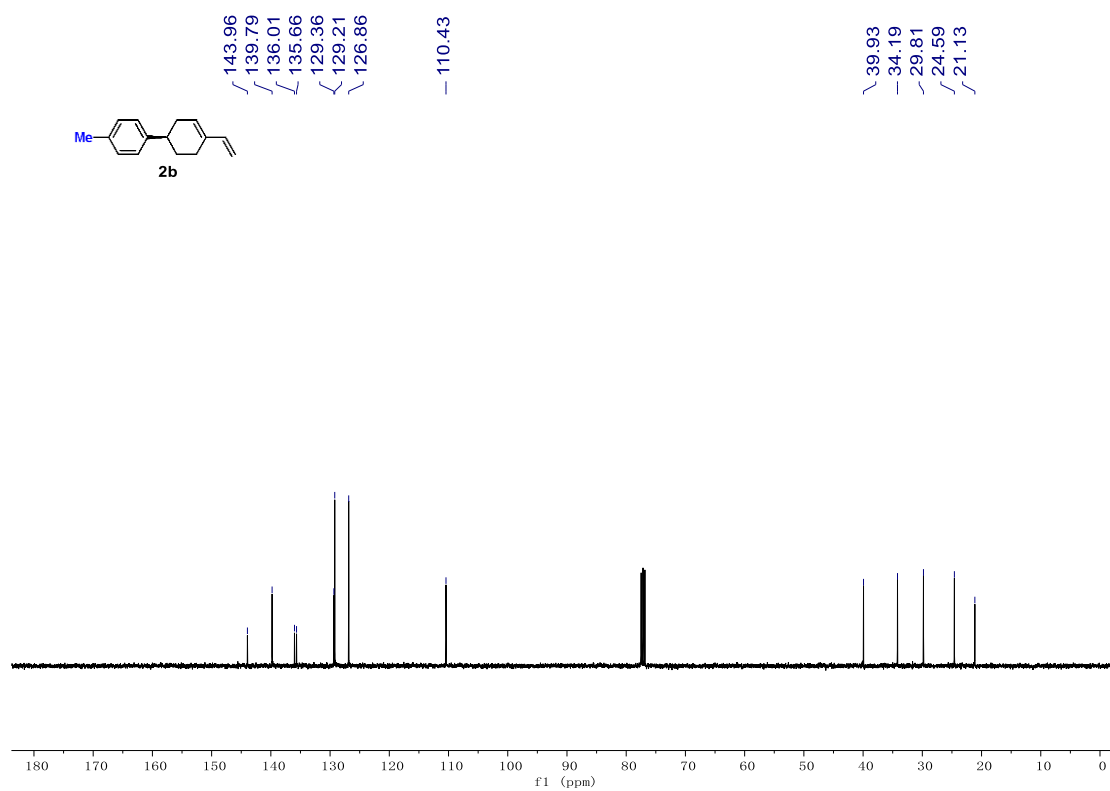
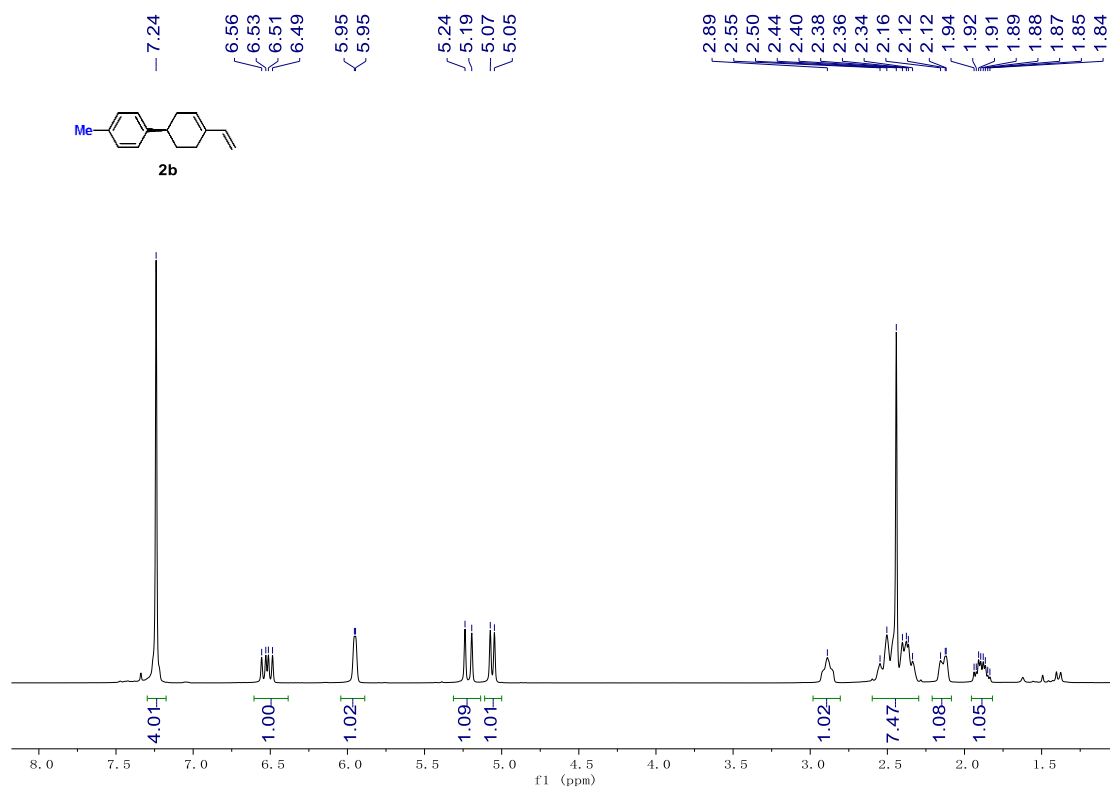
¹H NMR (400 MHz, CDCl₃) δ 5.78 – 5.59 (m, 1H), 4.02 (t, *J* = 13.9 Hz, 2H), 2.21 – 2.01 (m, 3H), 2.00 – 1.93 (m, 1H), 1.92 – 1.80 (m, 1H), 1.60 – 1.50 (m, 1H), 1.32 – 1.23 (m, 3H), 1.20 (s, 3H), 1.19 (s, 3H).

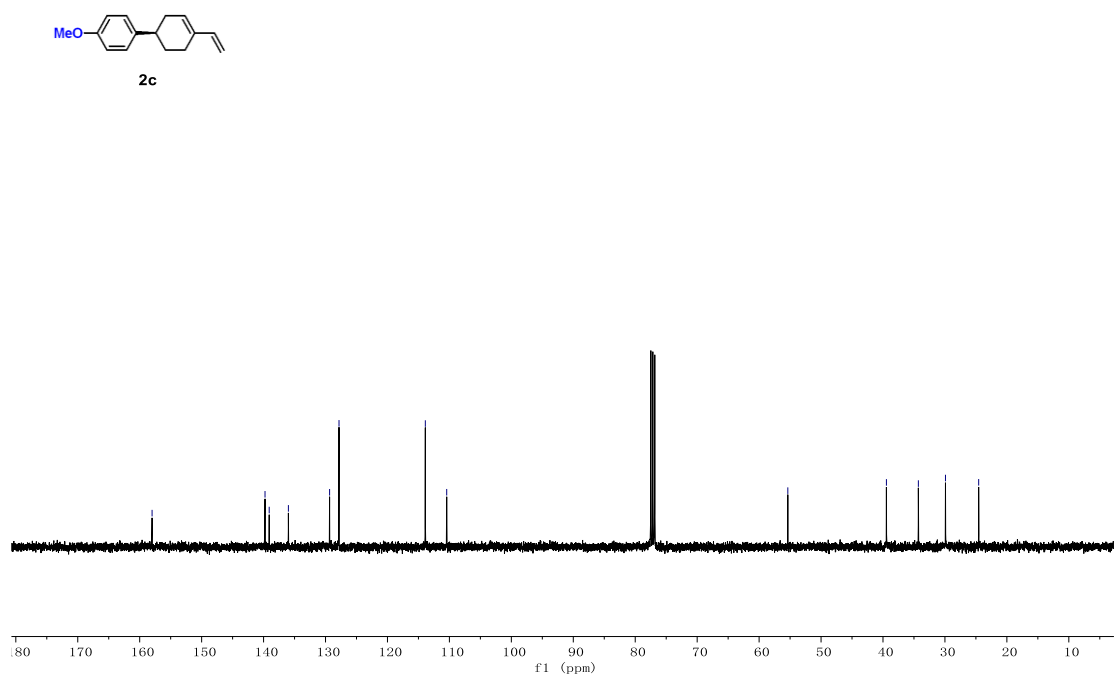
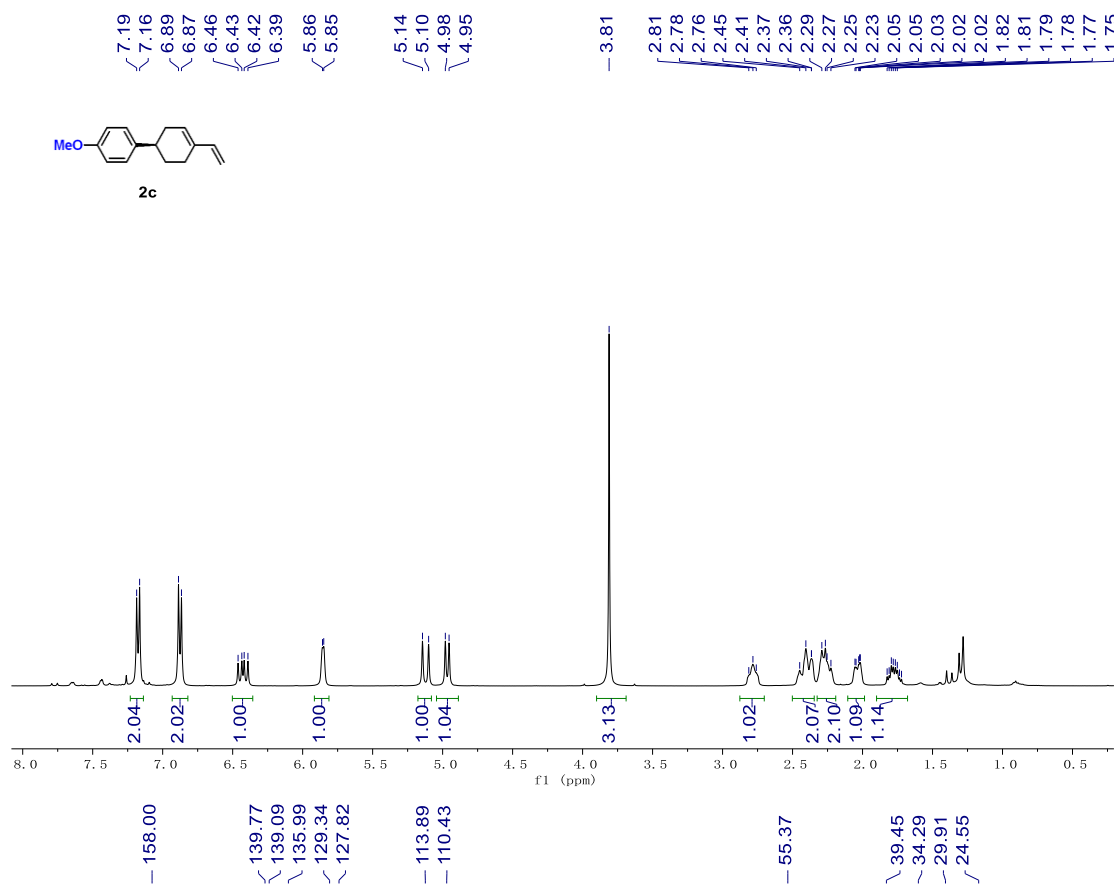
¹³C NMR (101 MHz, CDCl₃) δ 137.6, 122.6, 72.8, 67.3, 45.3, 27.6, 26.7, 26.5, 23.7.

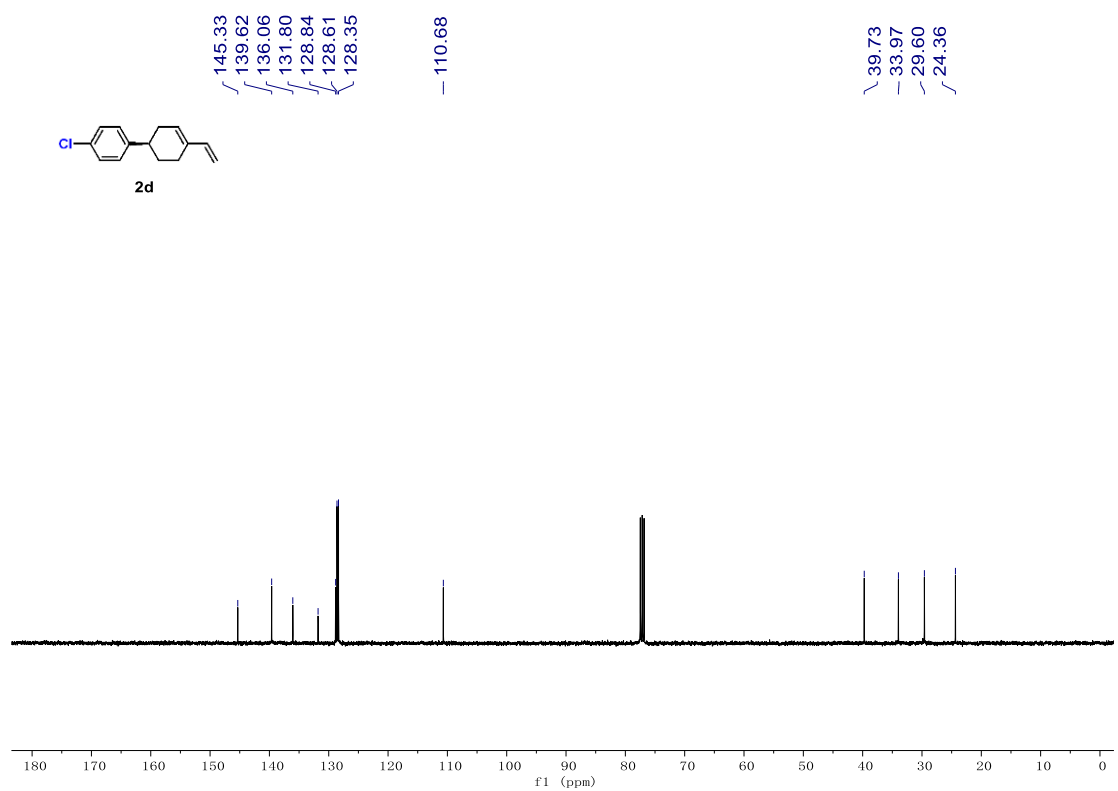
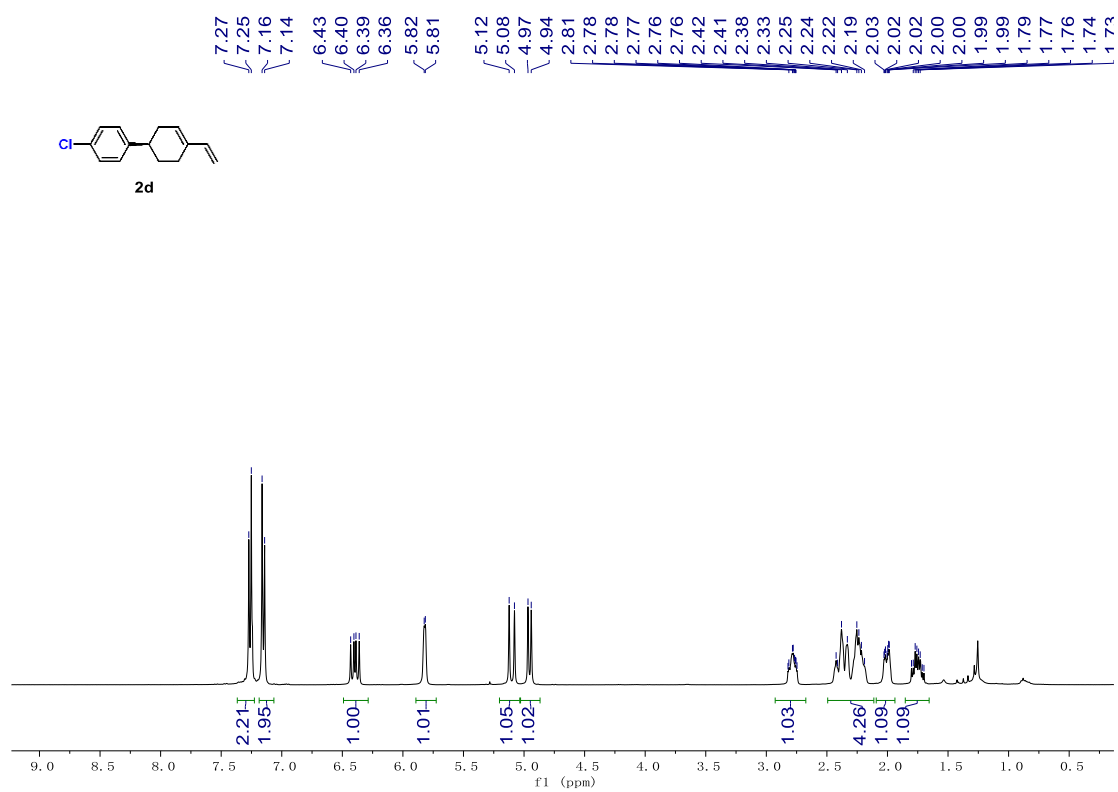
HRMS (ESI) calcd. for C₁₀H₁₈NaO₂⁺ (*M* + Na)⁺: 193.1199, Found: 193.1201.

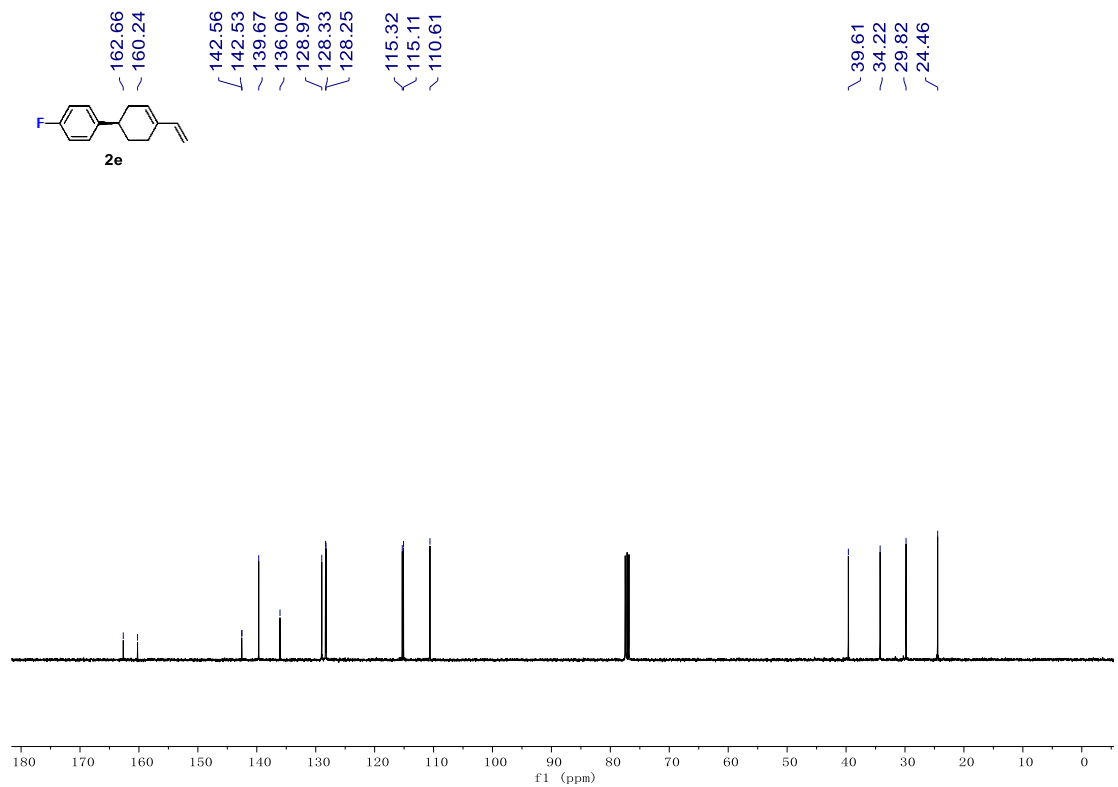
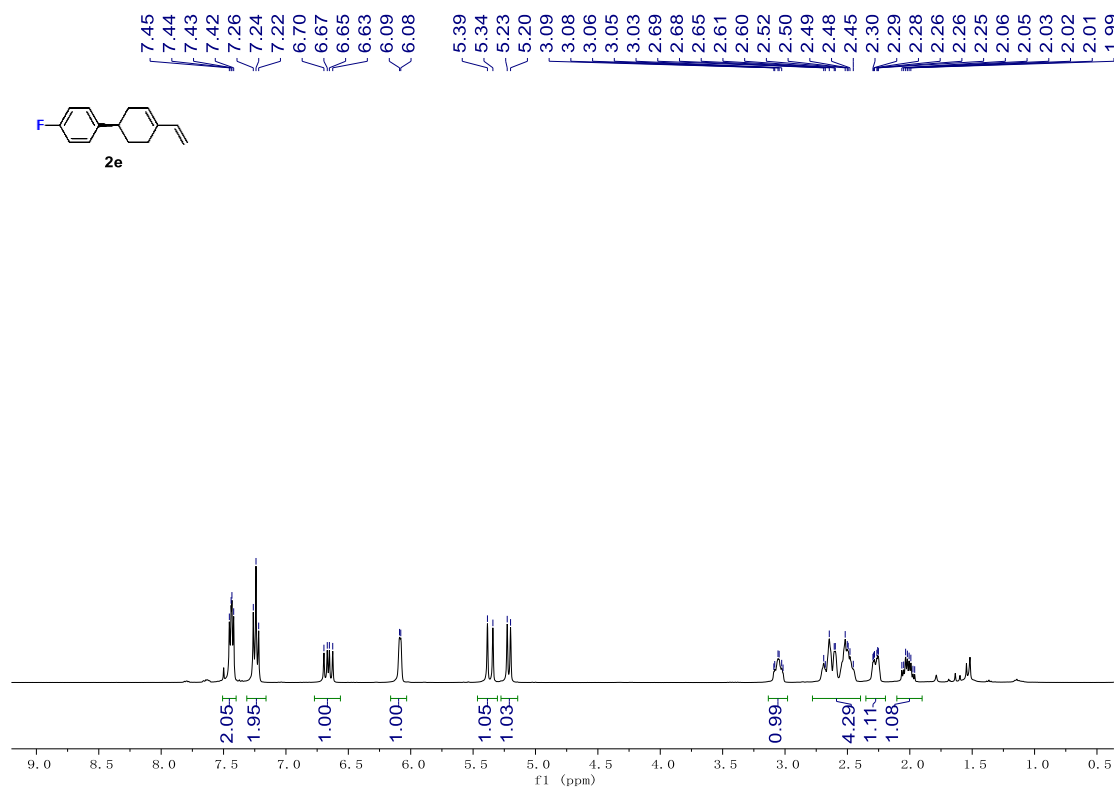
NMR of products

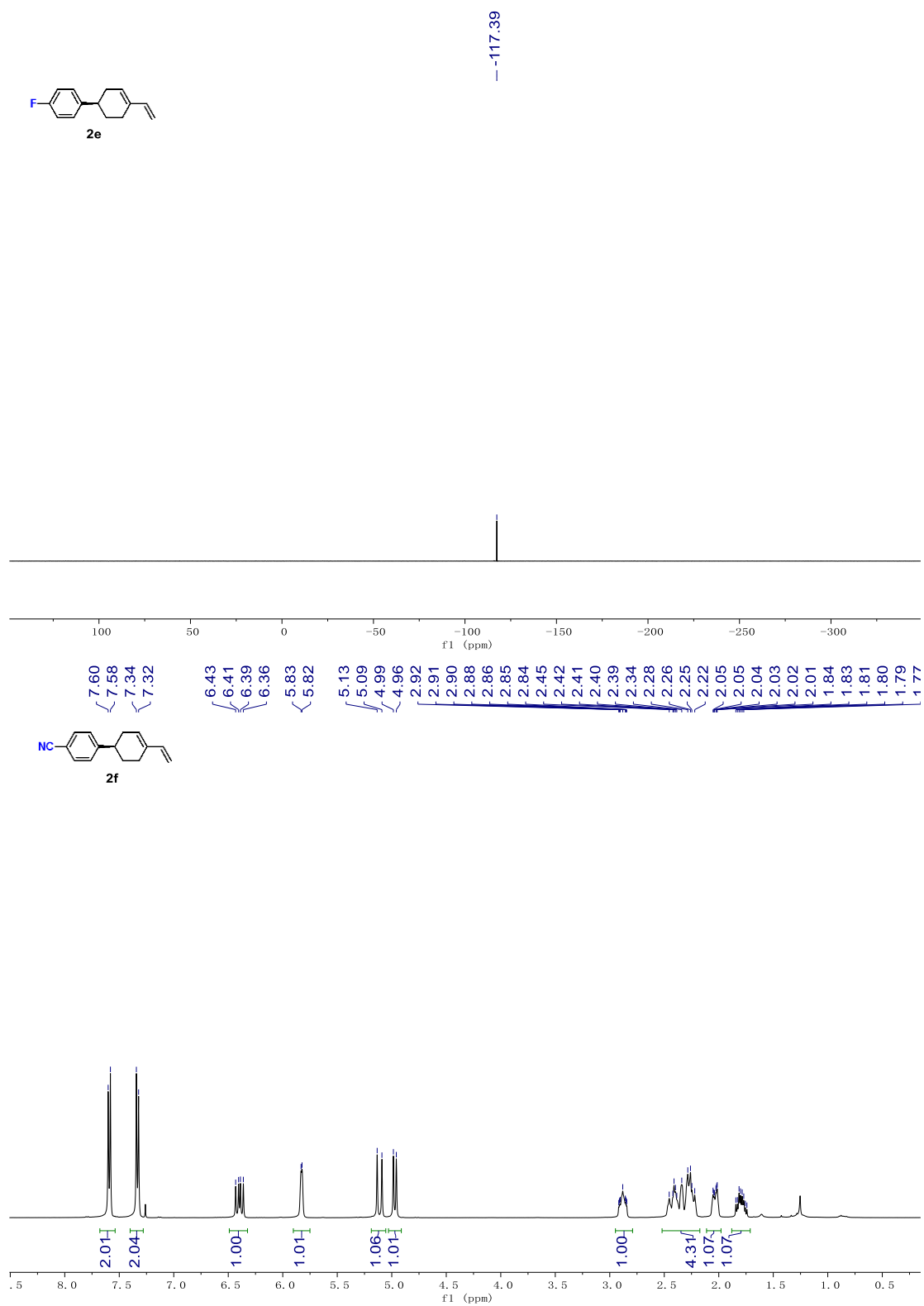


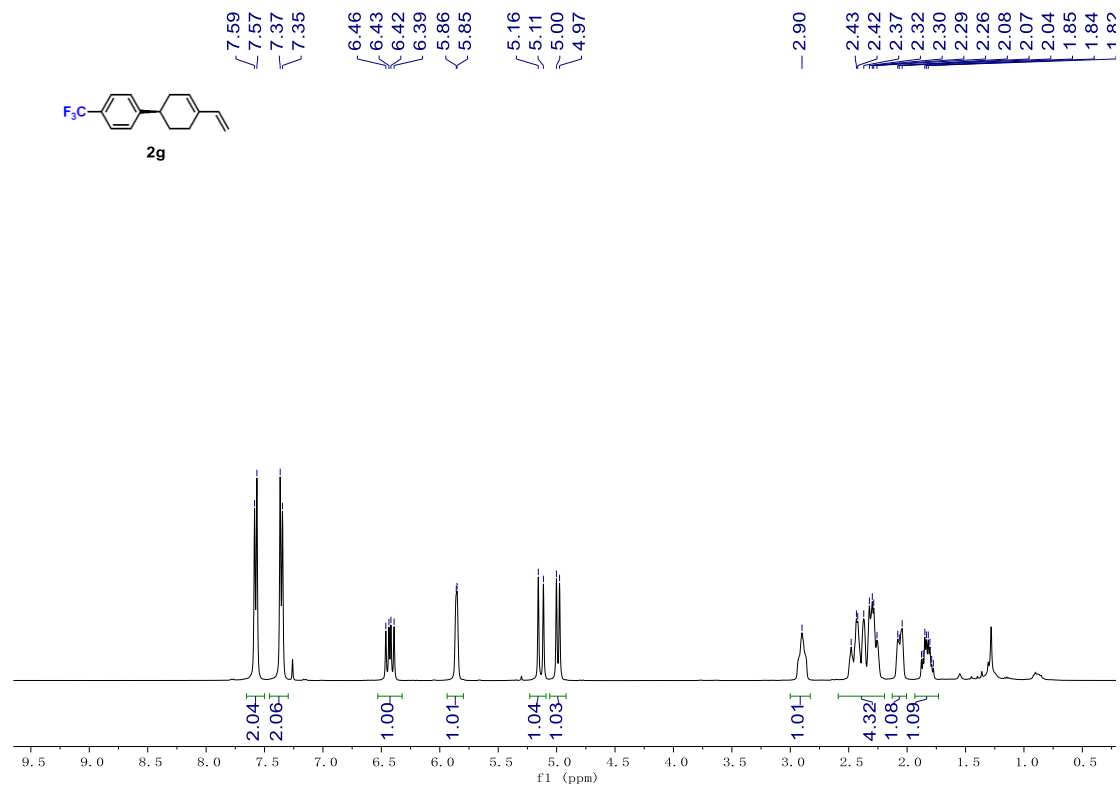
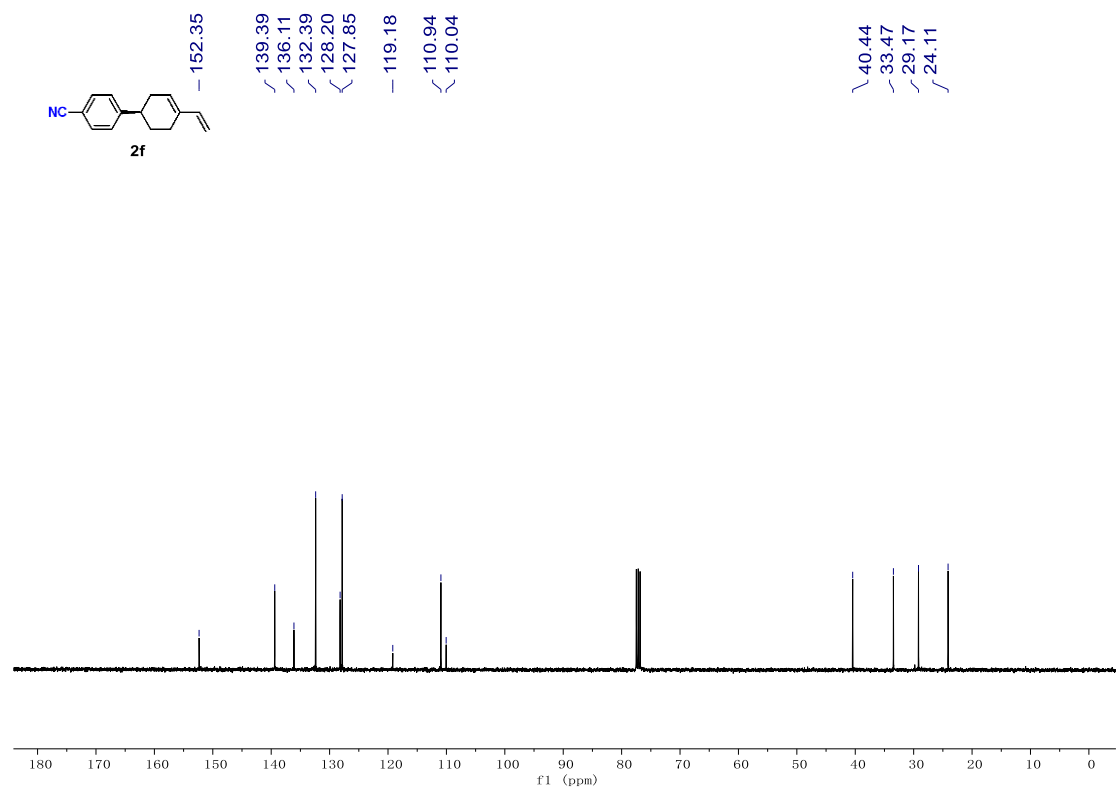


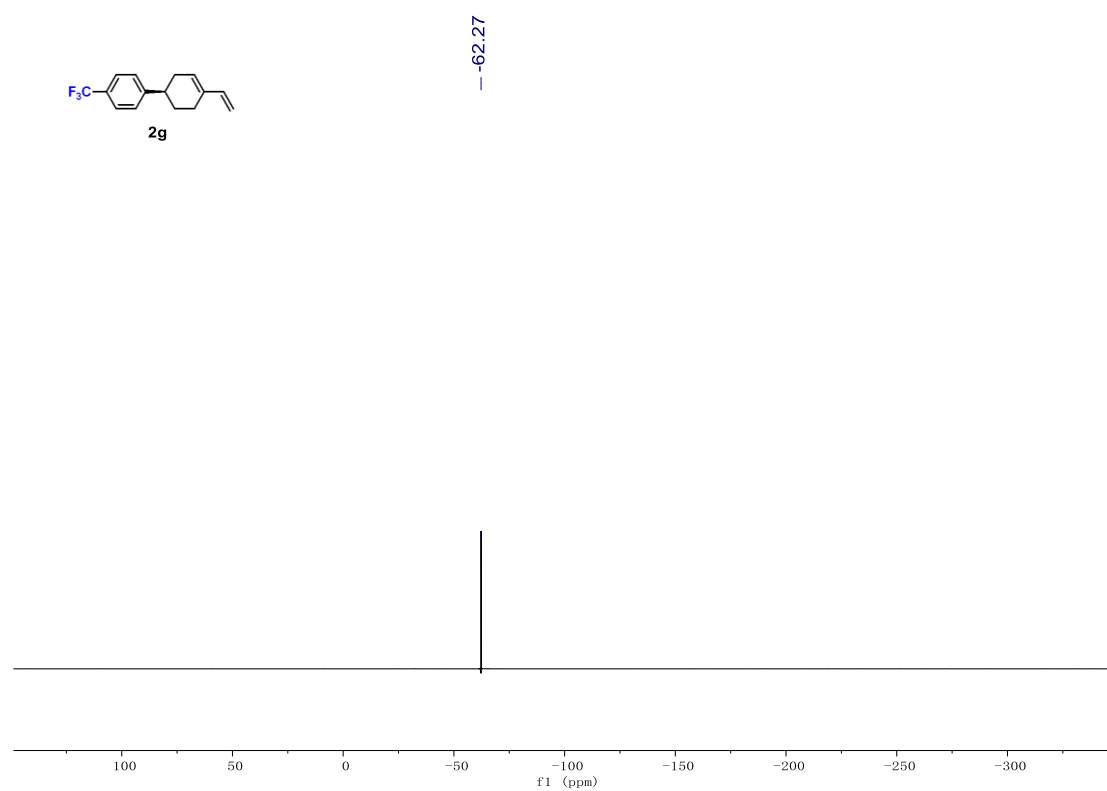
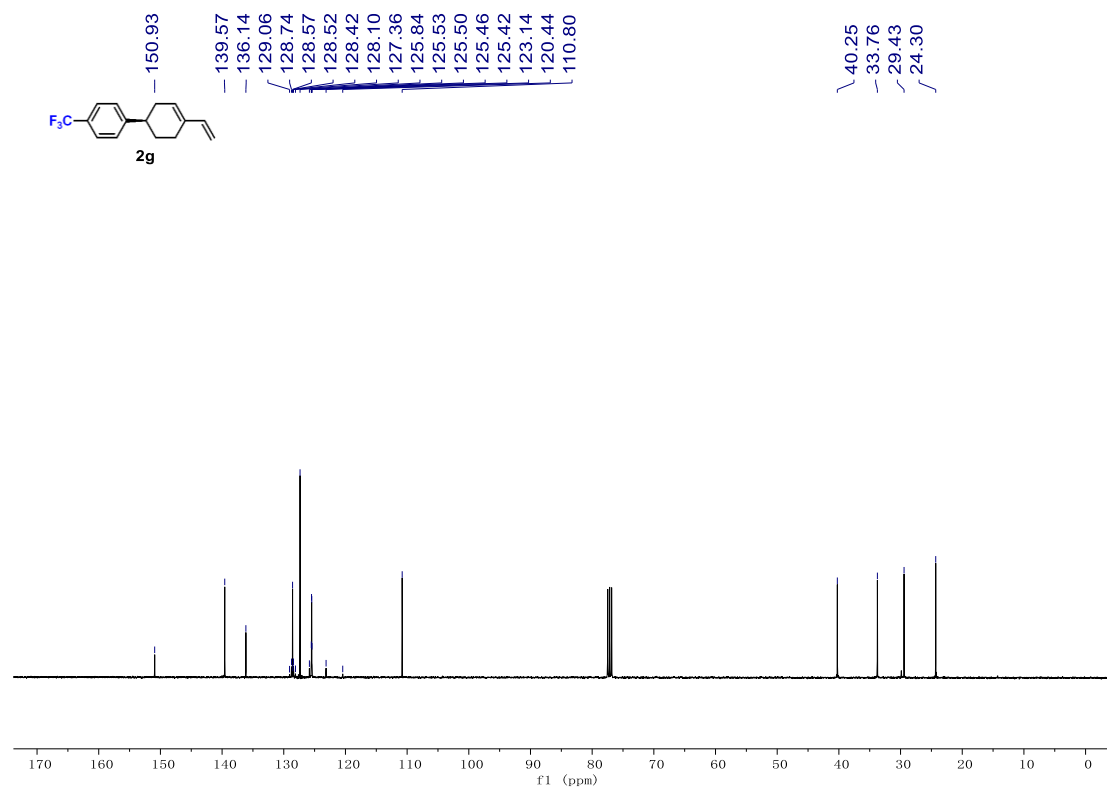


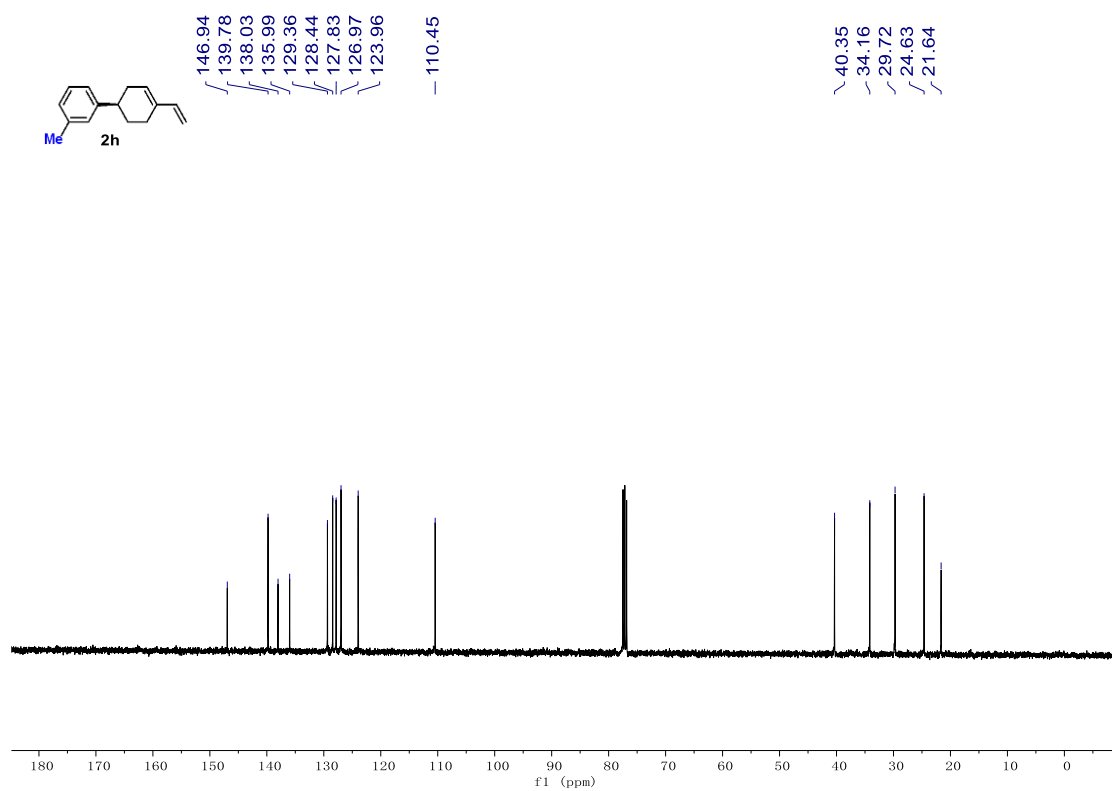
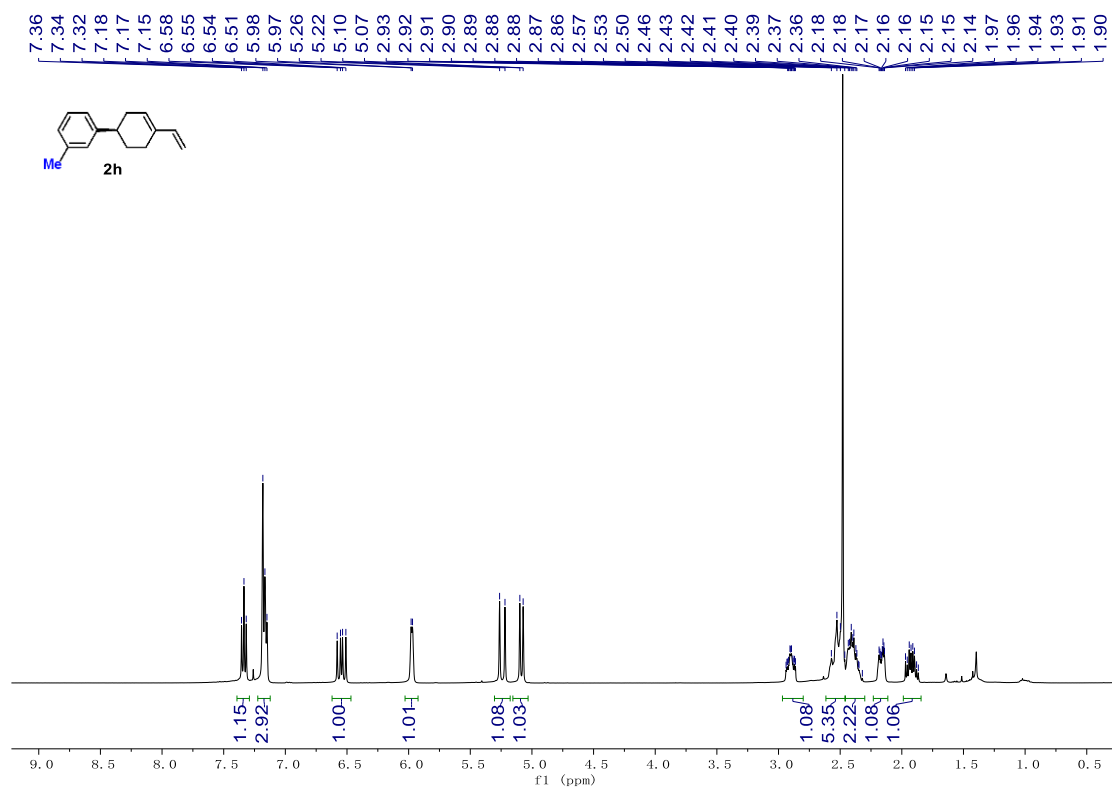


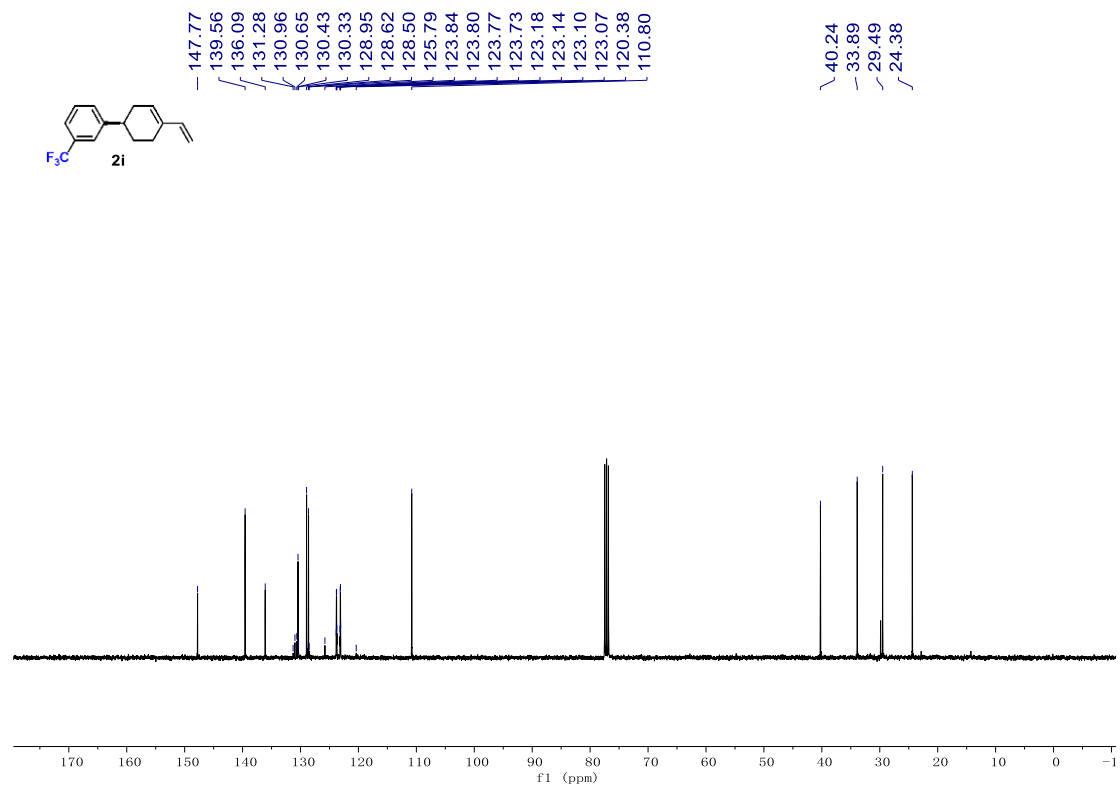
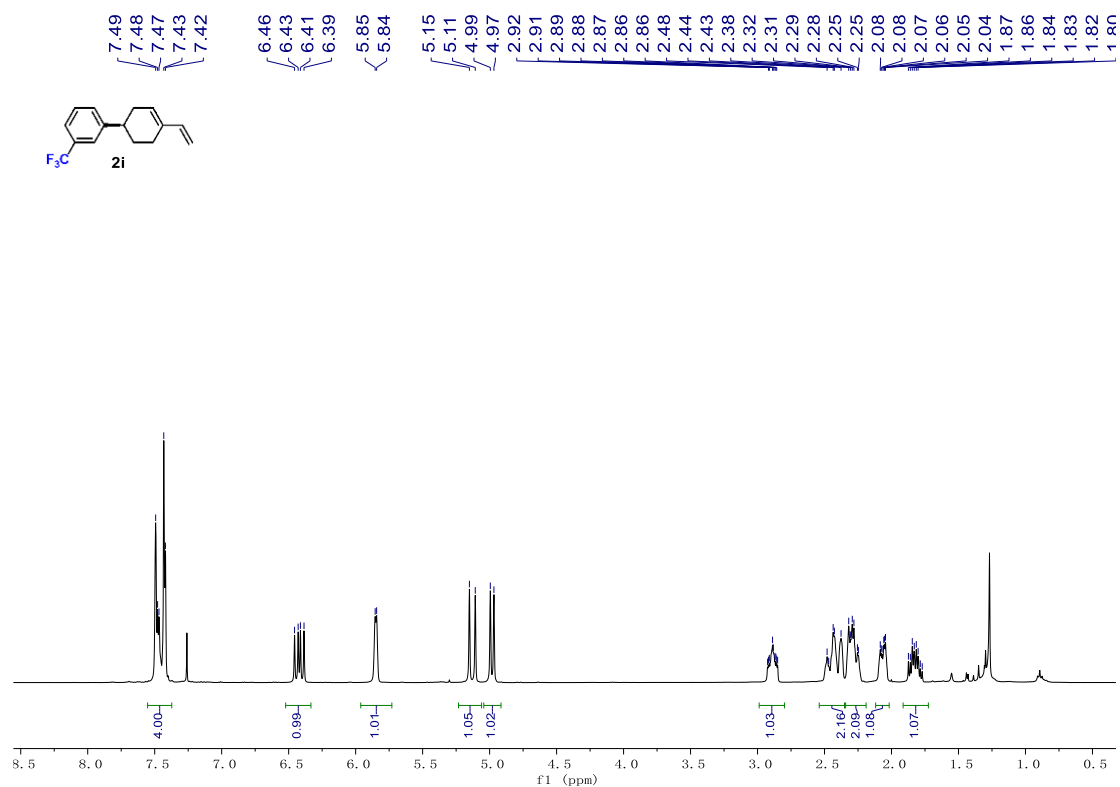


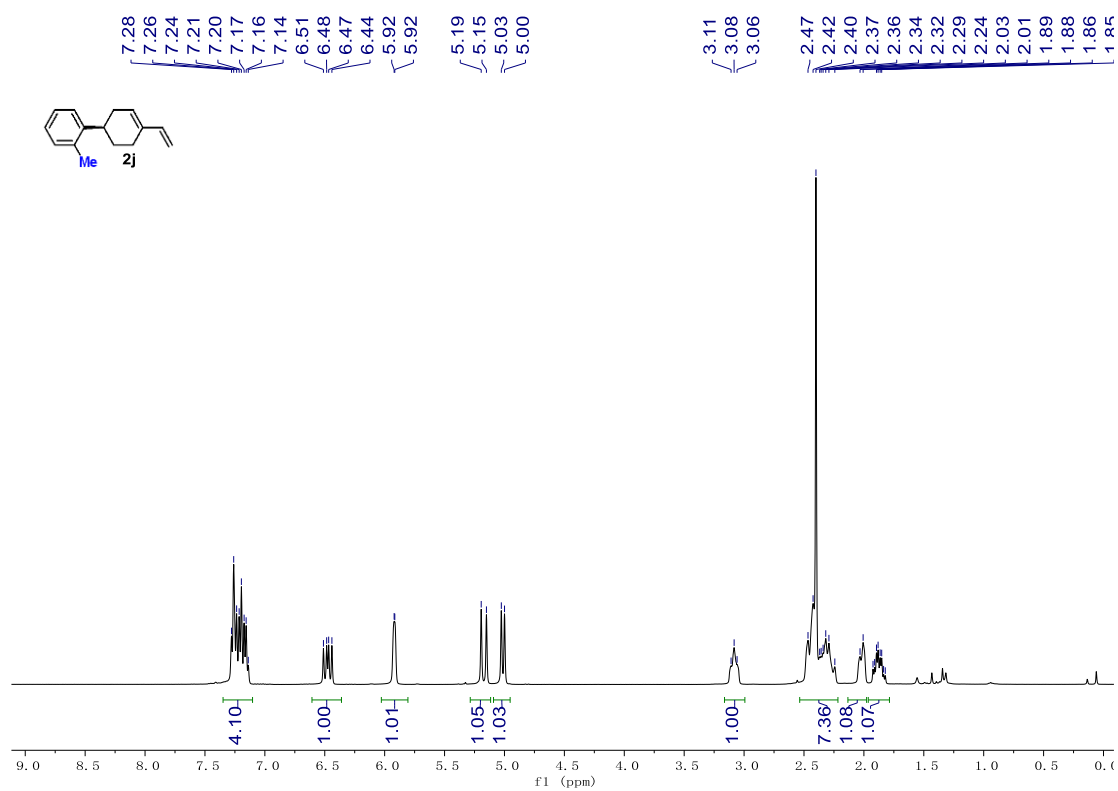
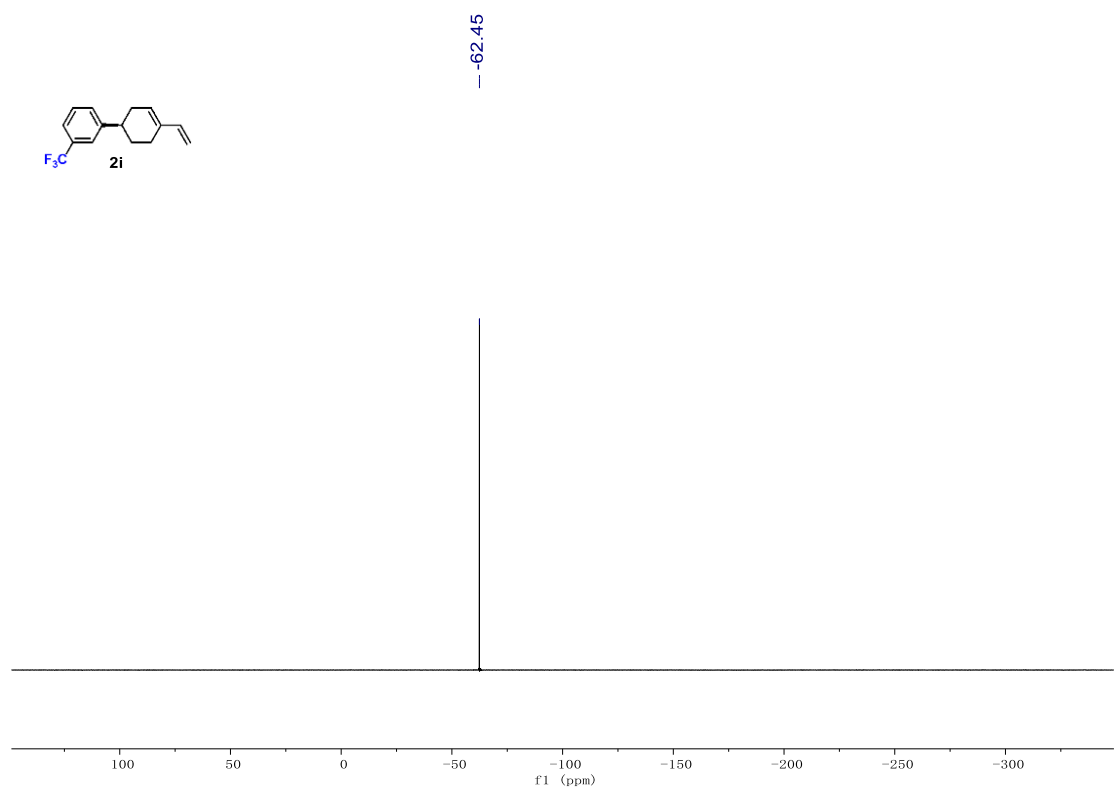


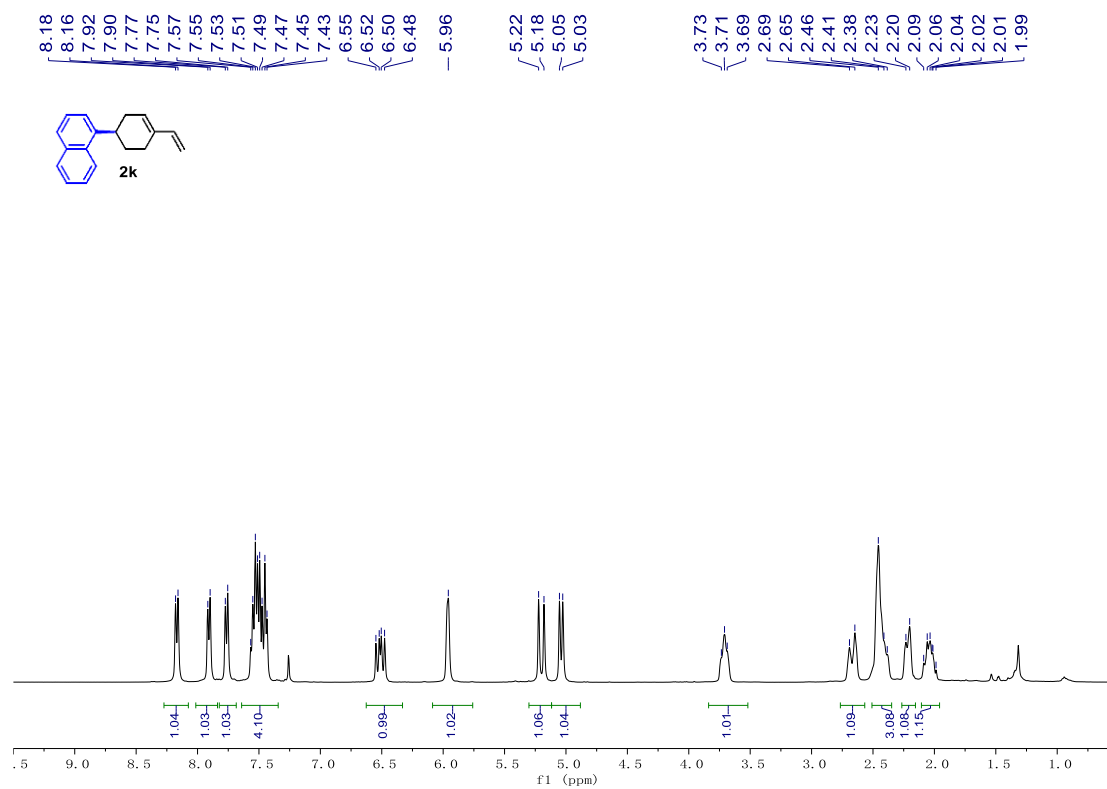
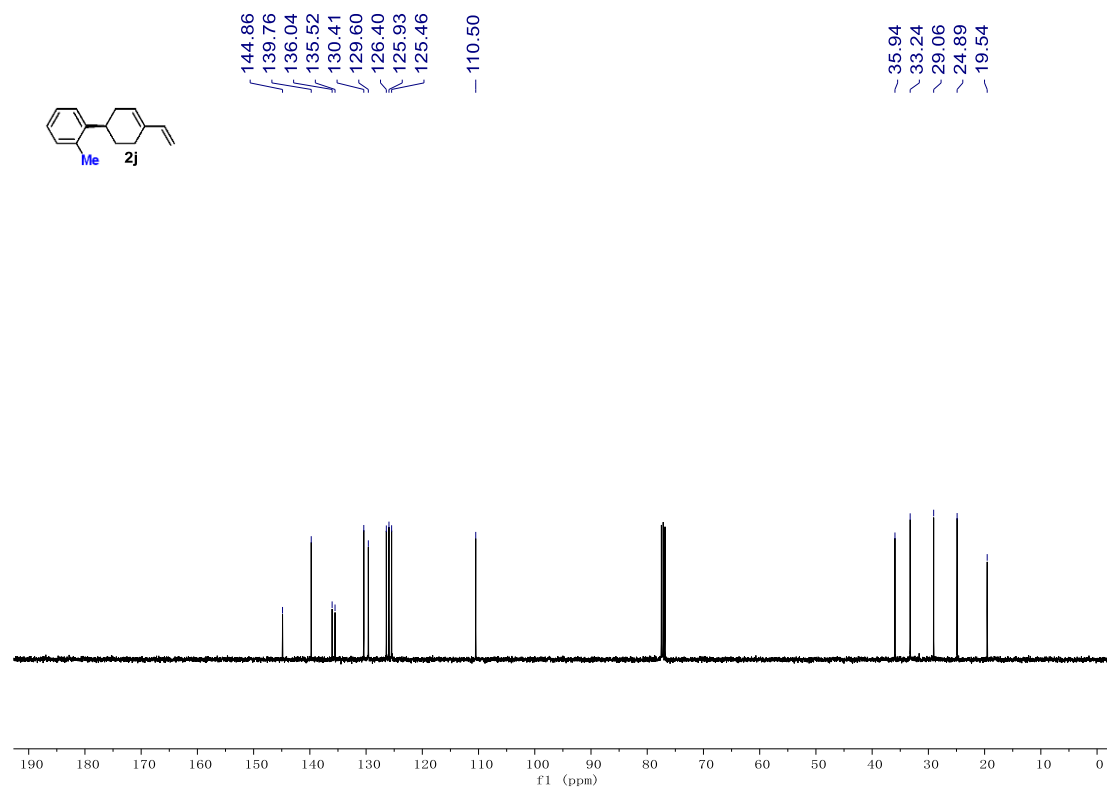


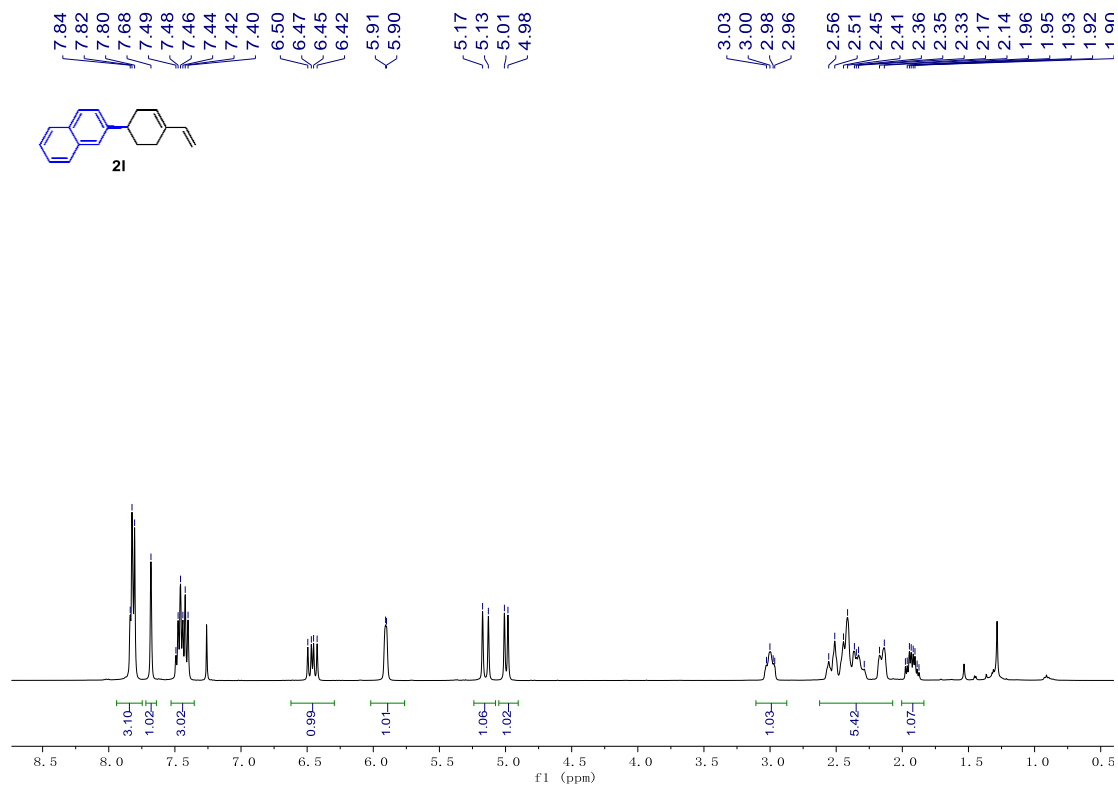
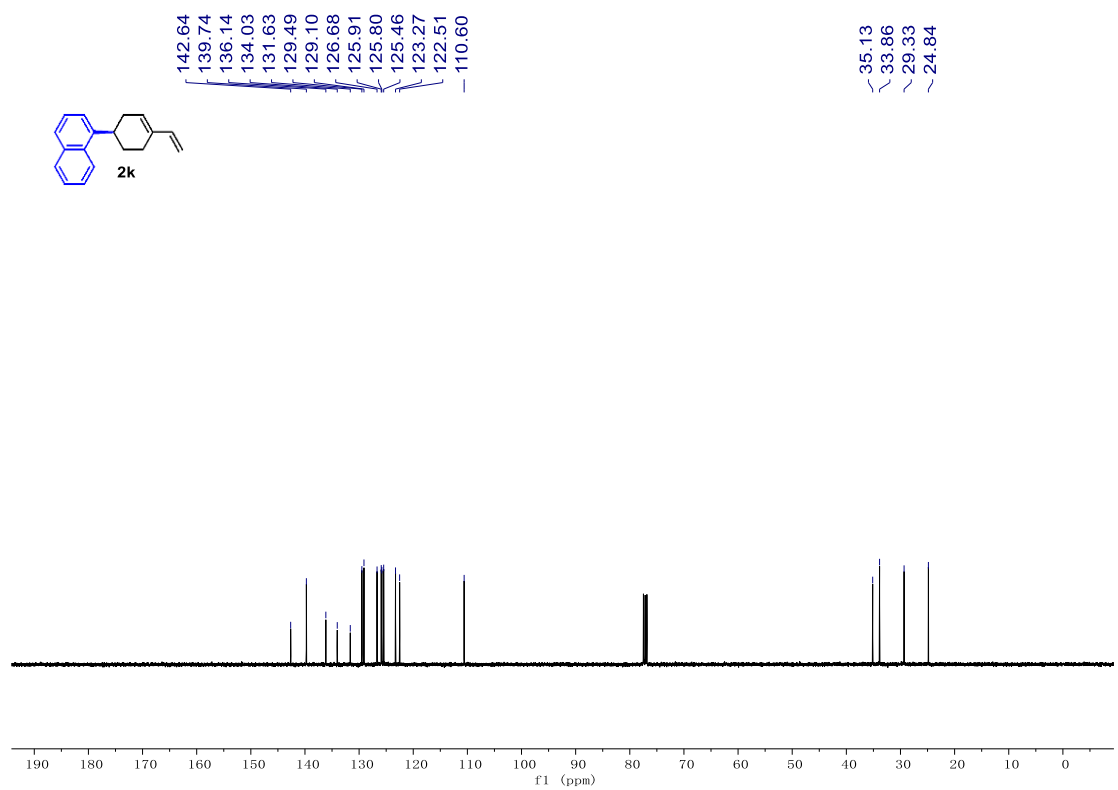


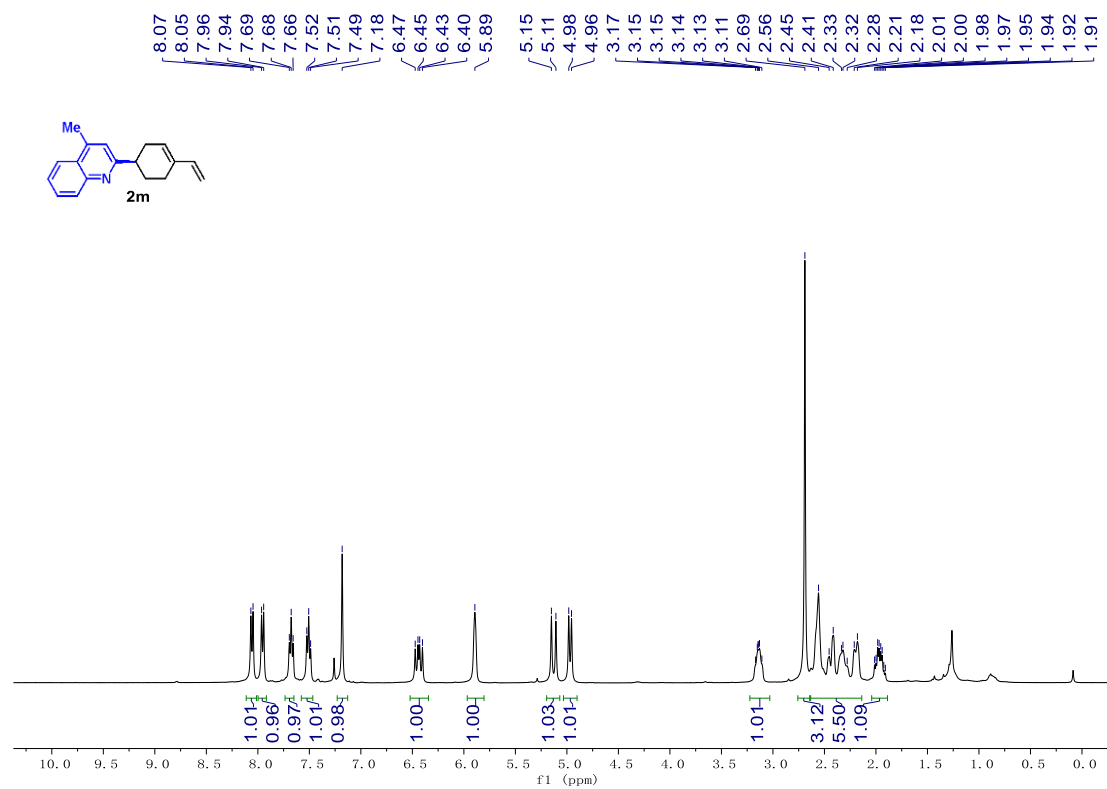
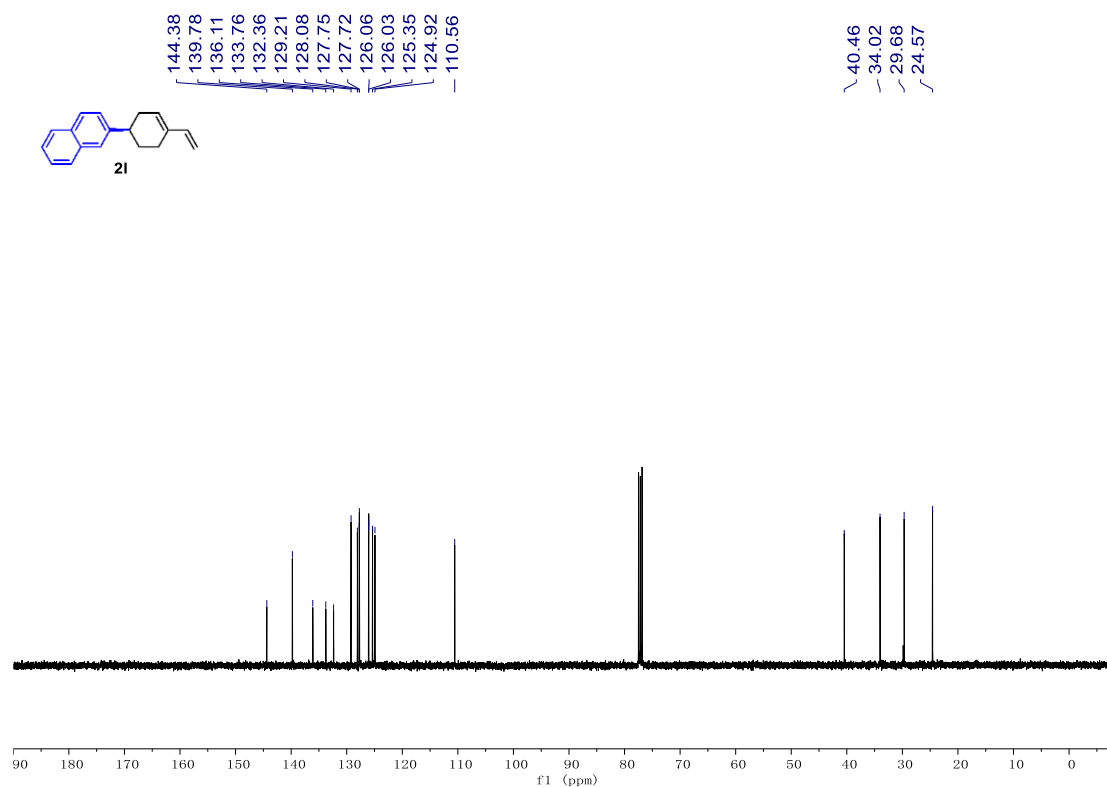


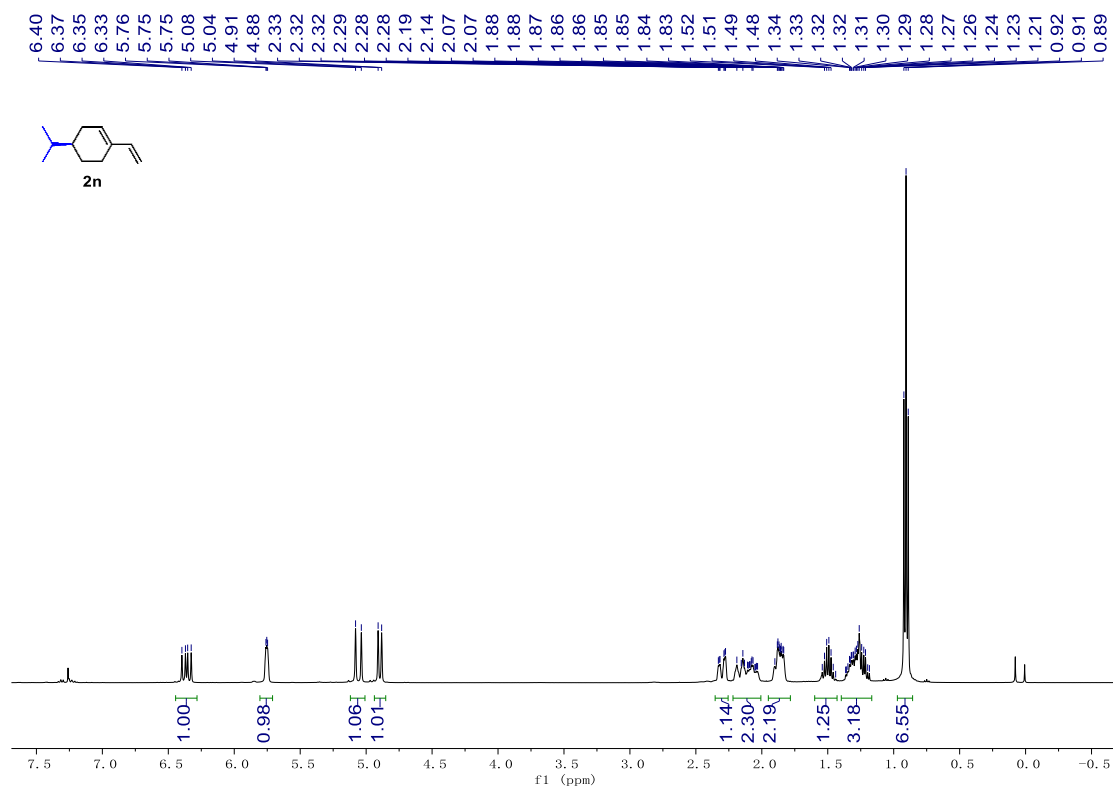
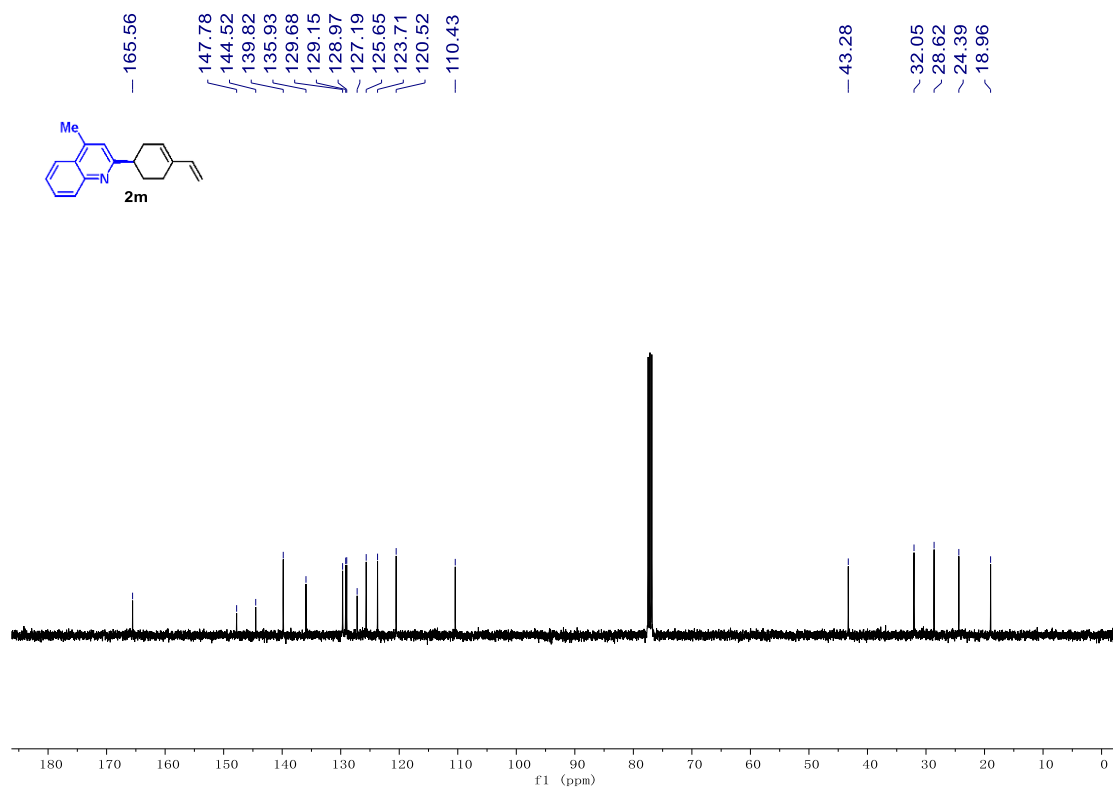


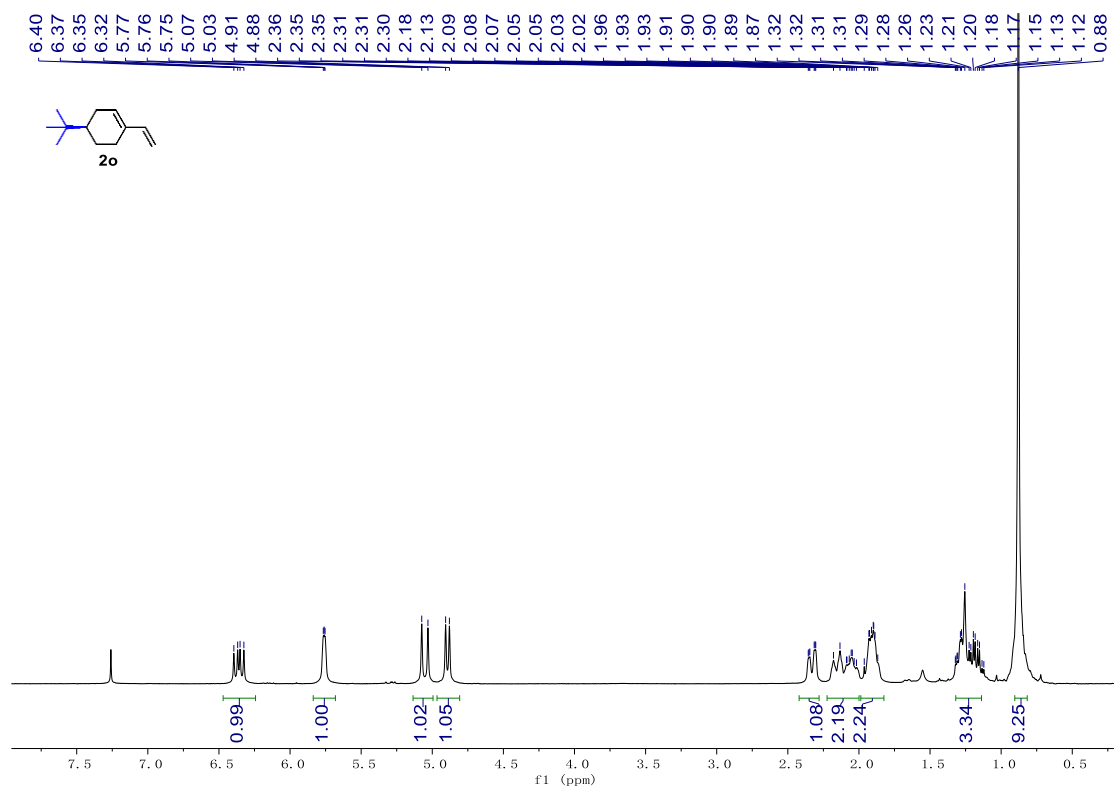
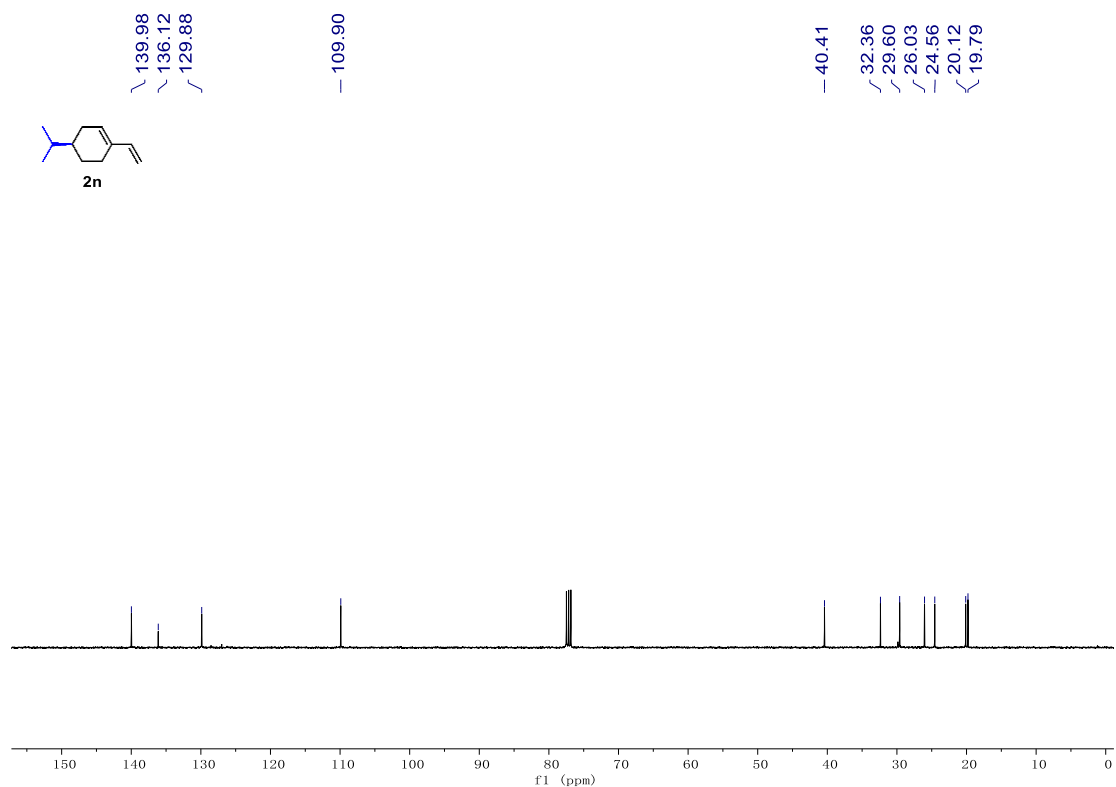


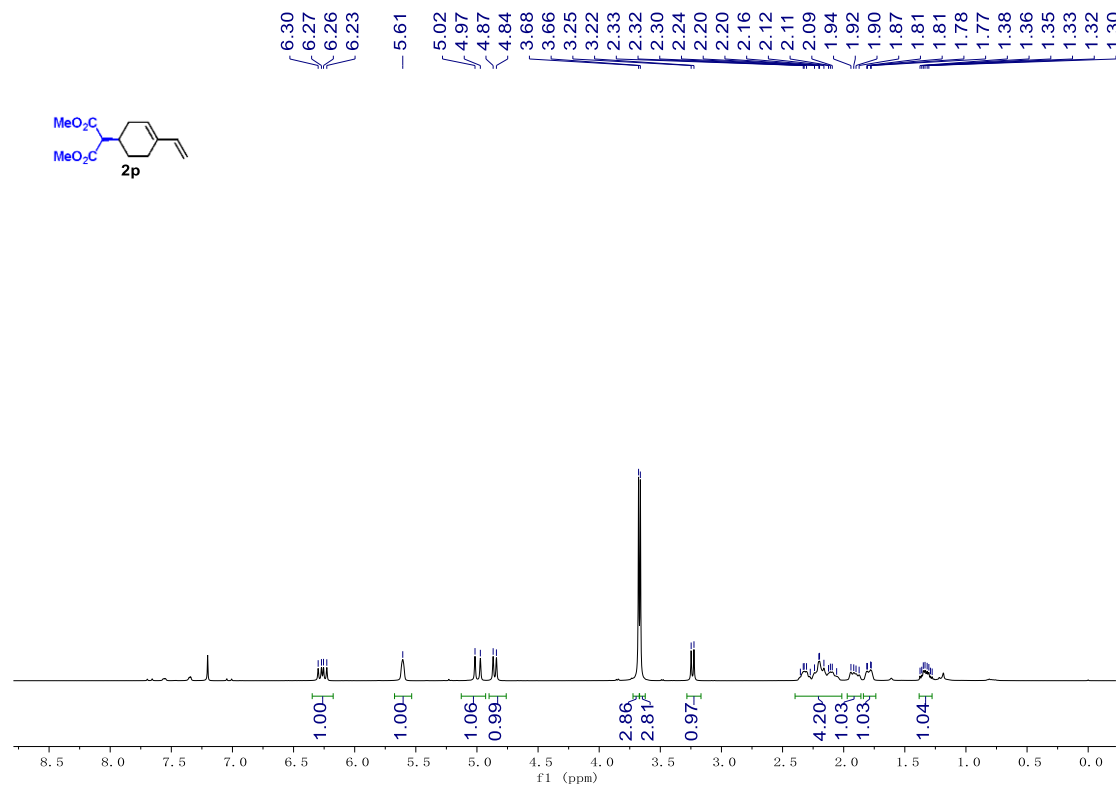
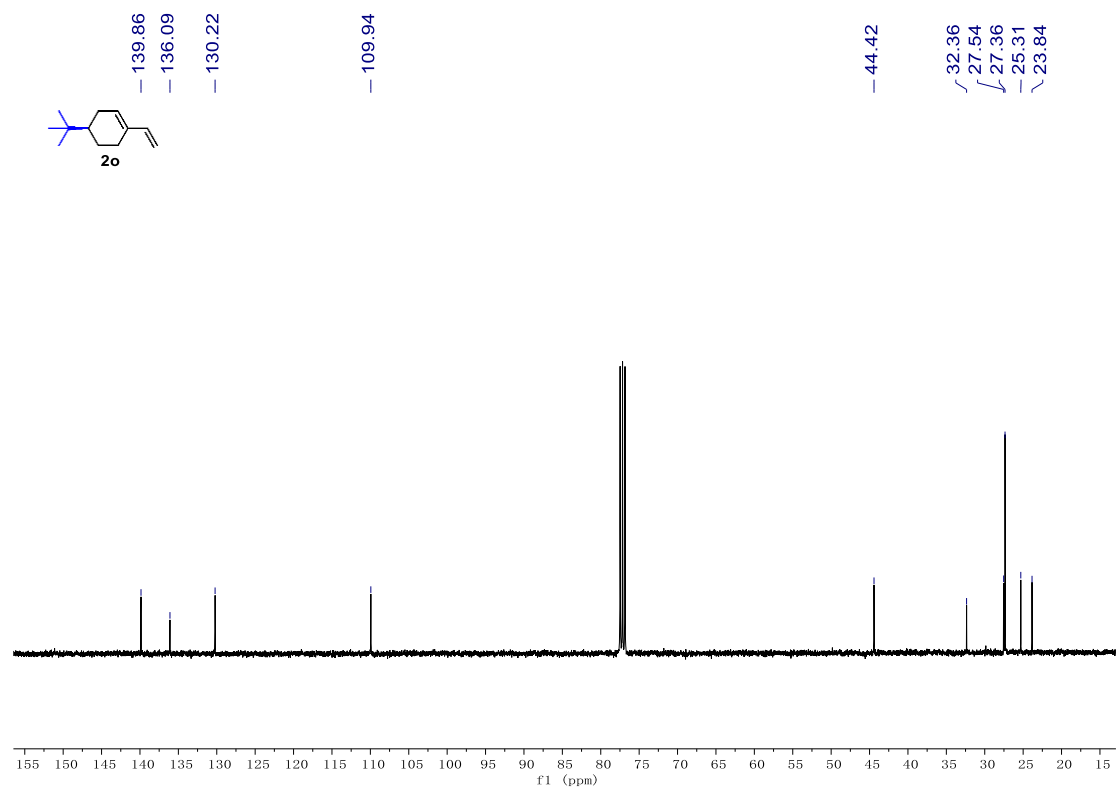


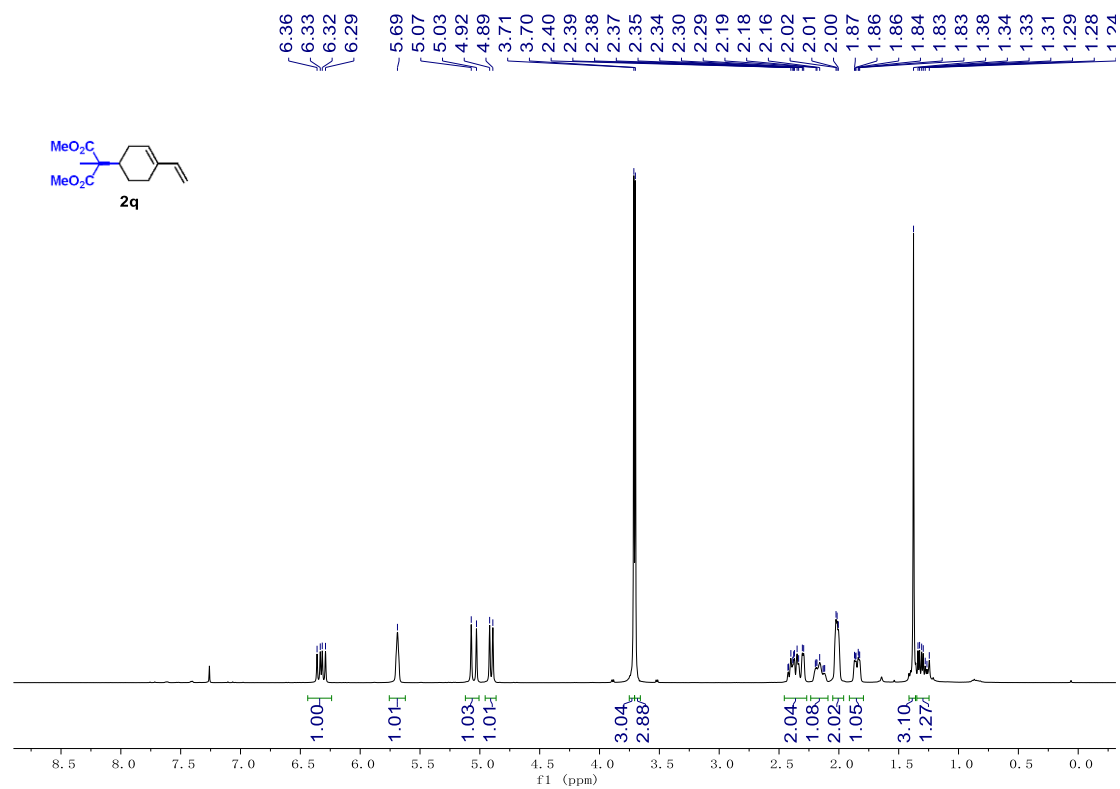
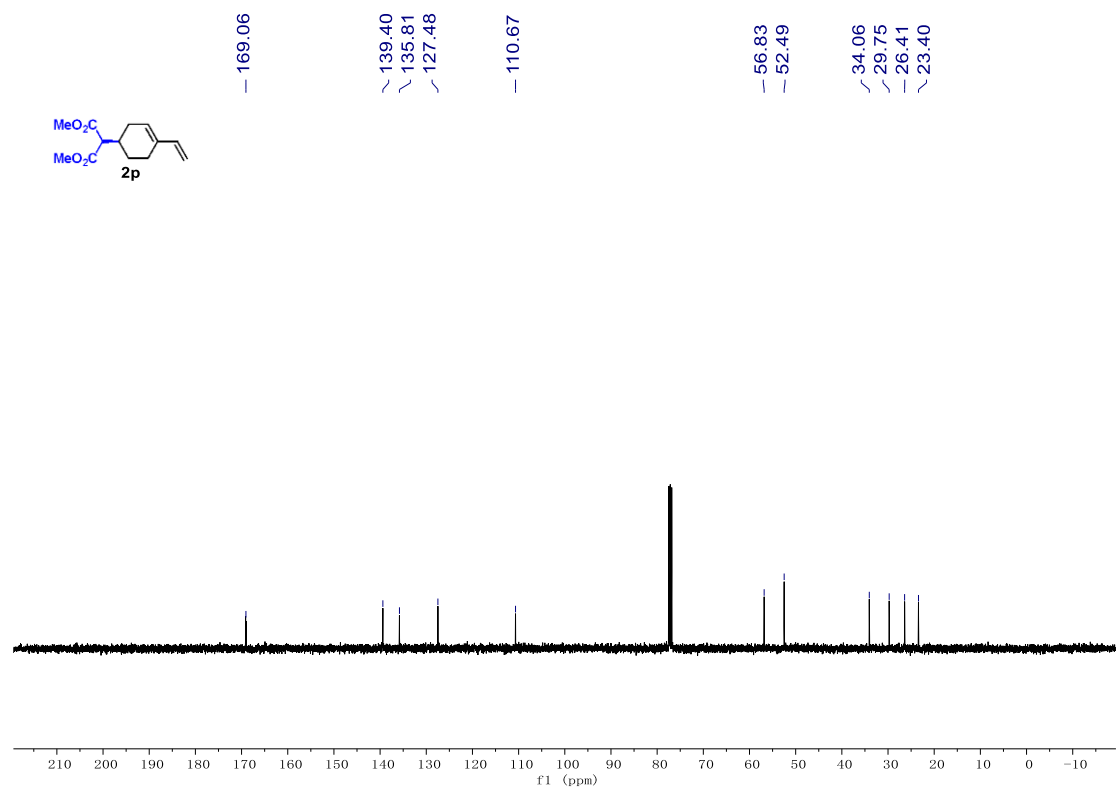


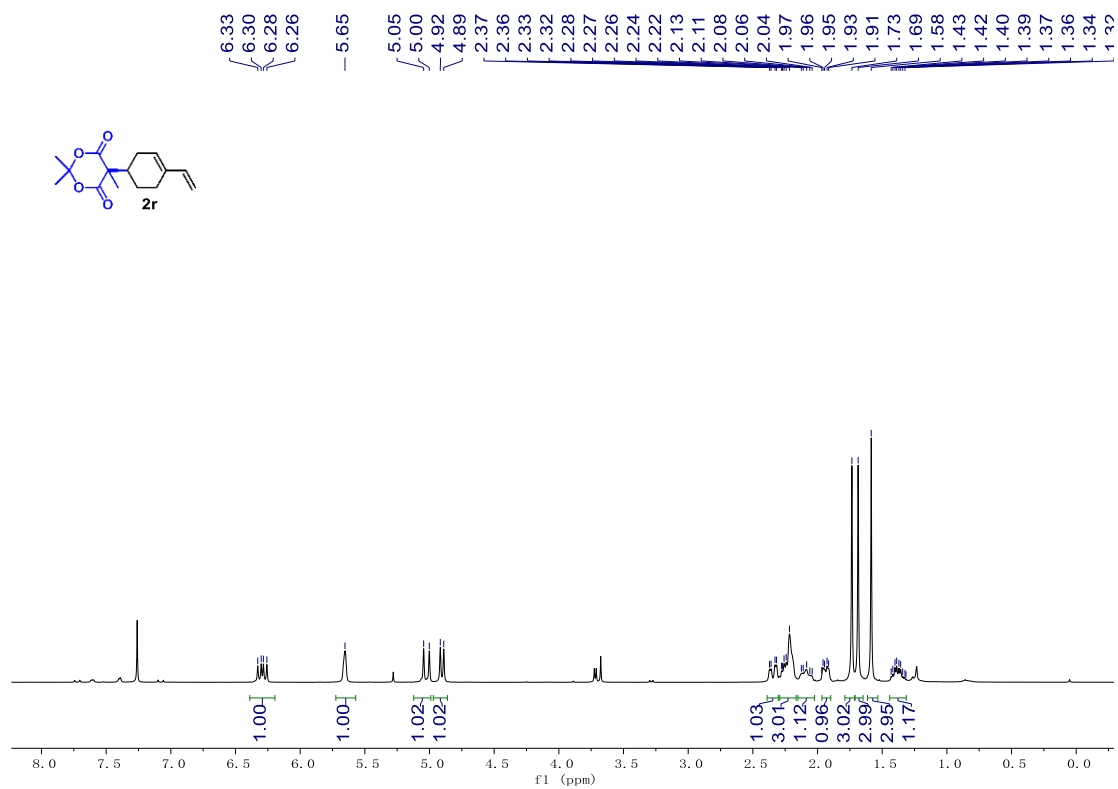
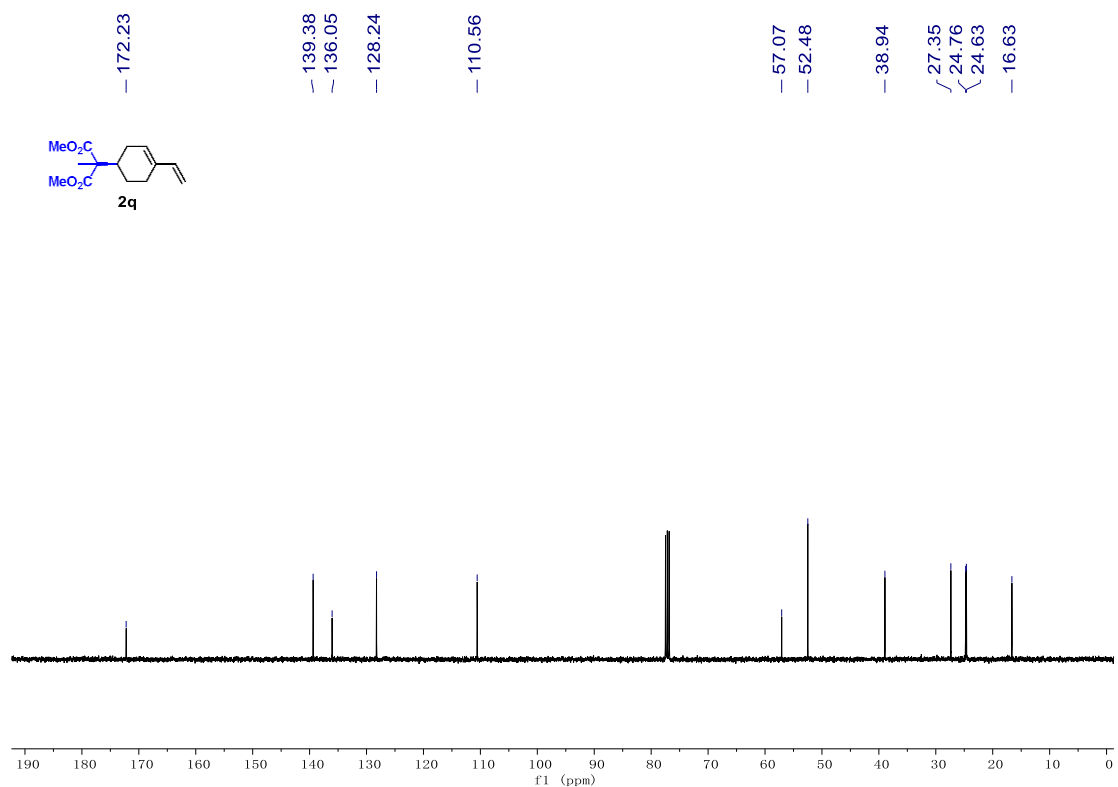


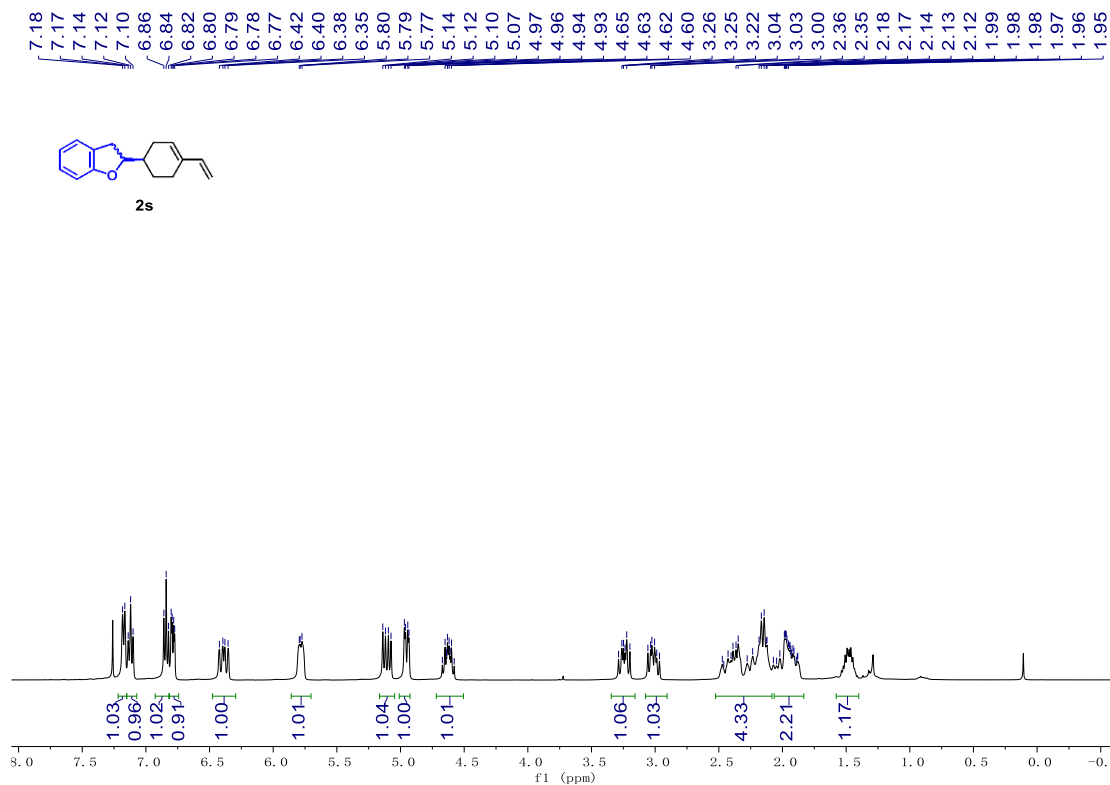
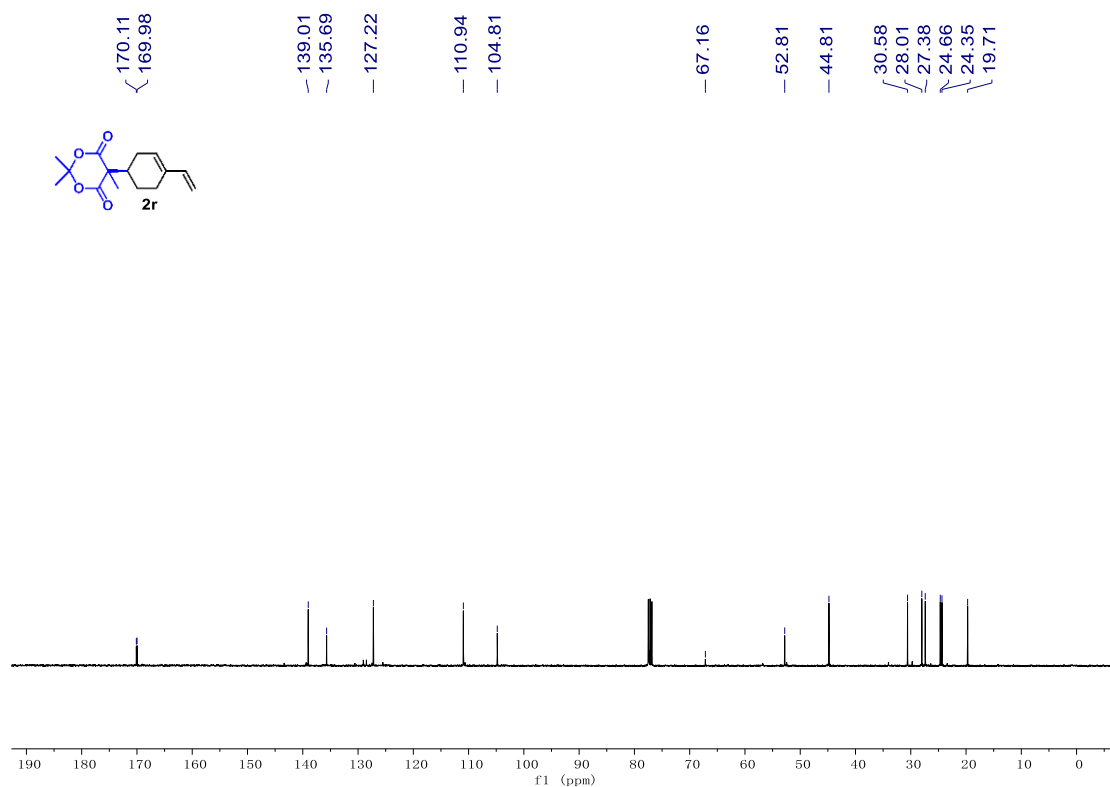


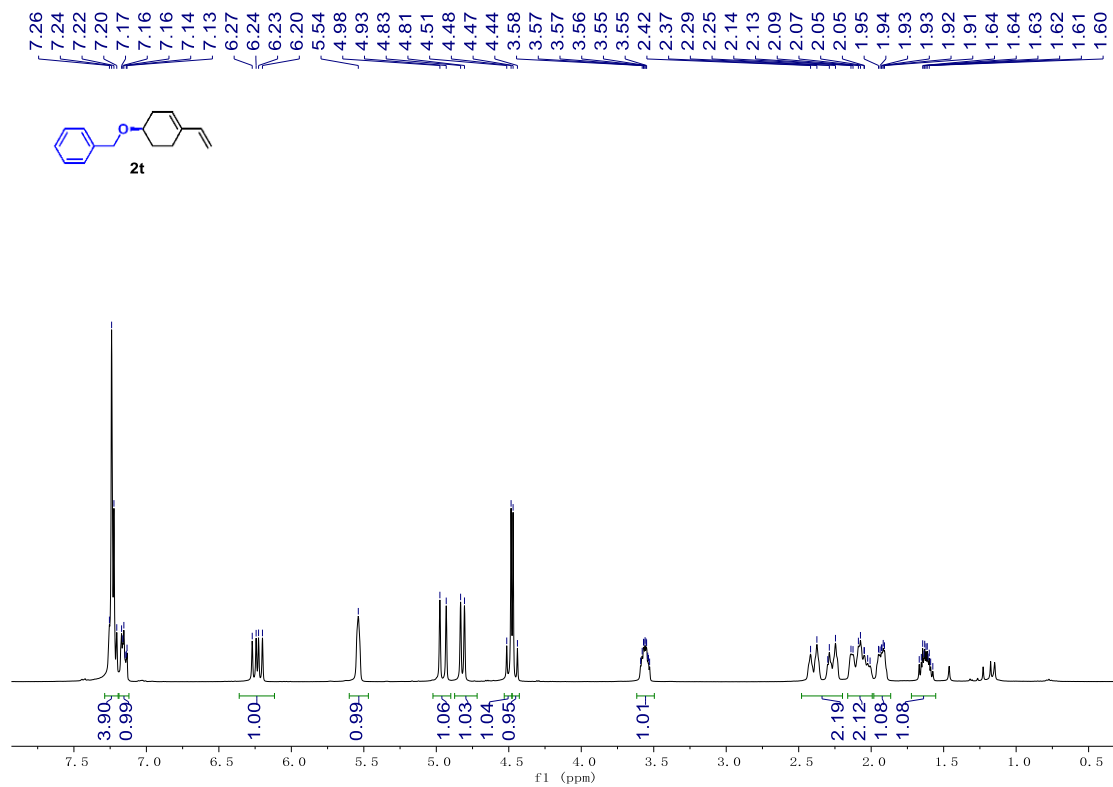
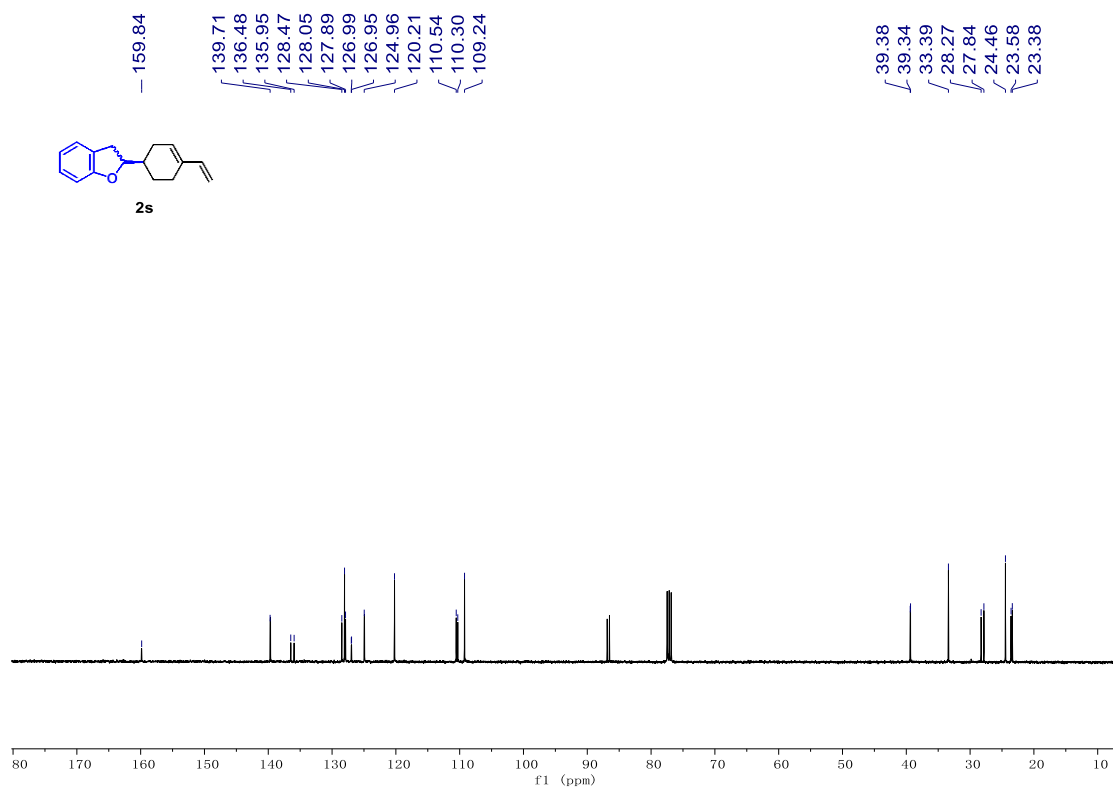


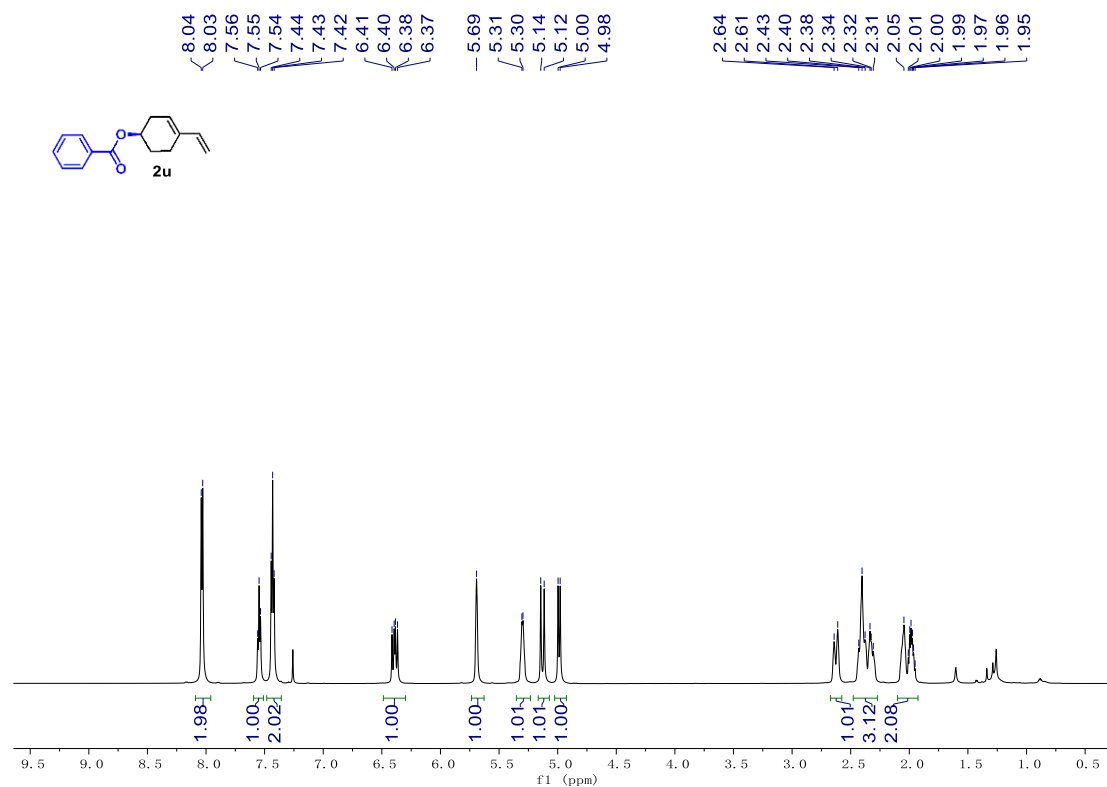
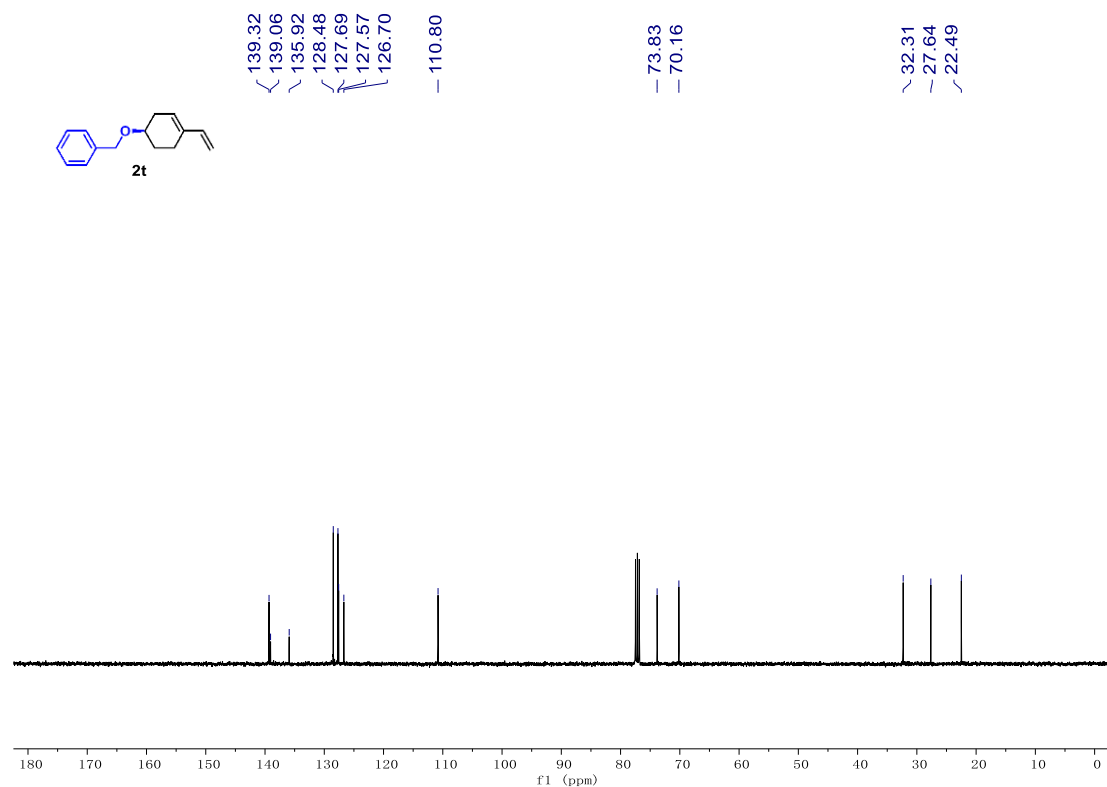


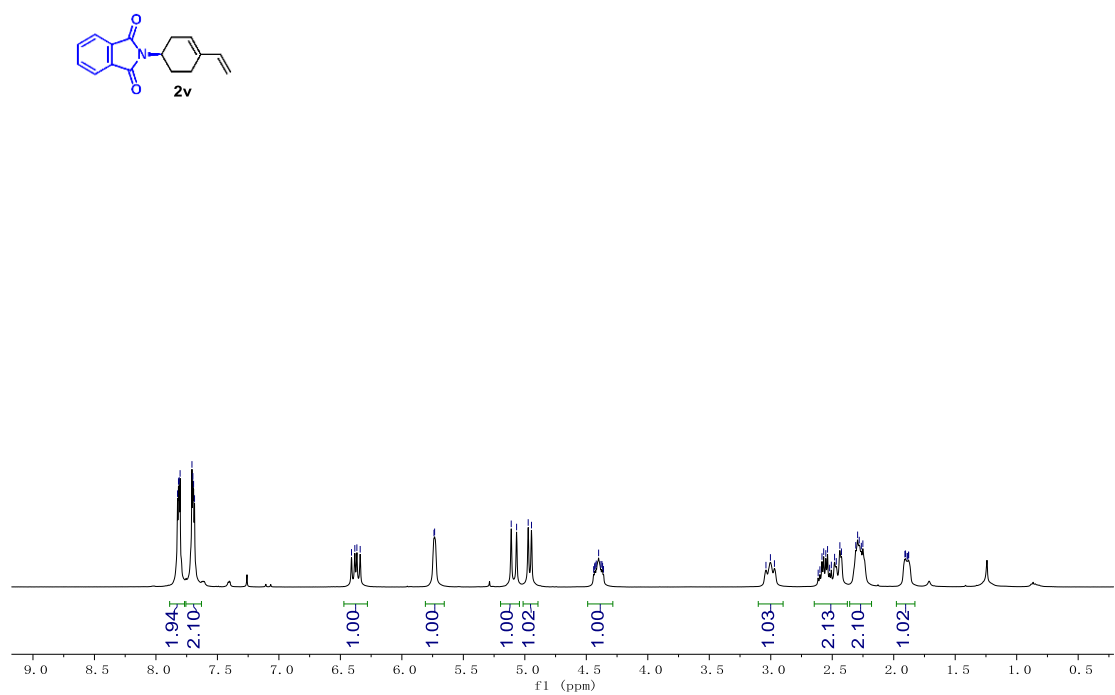
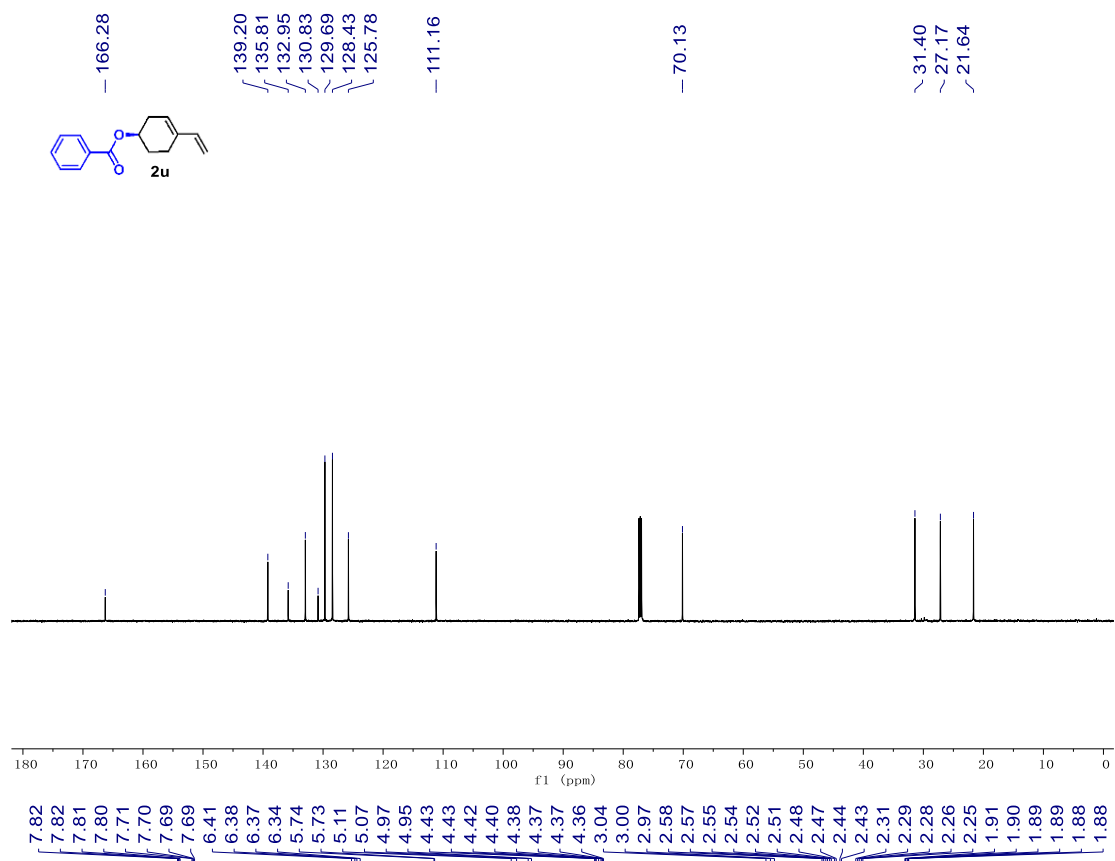


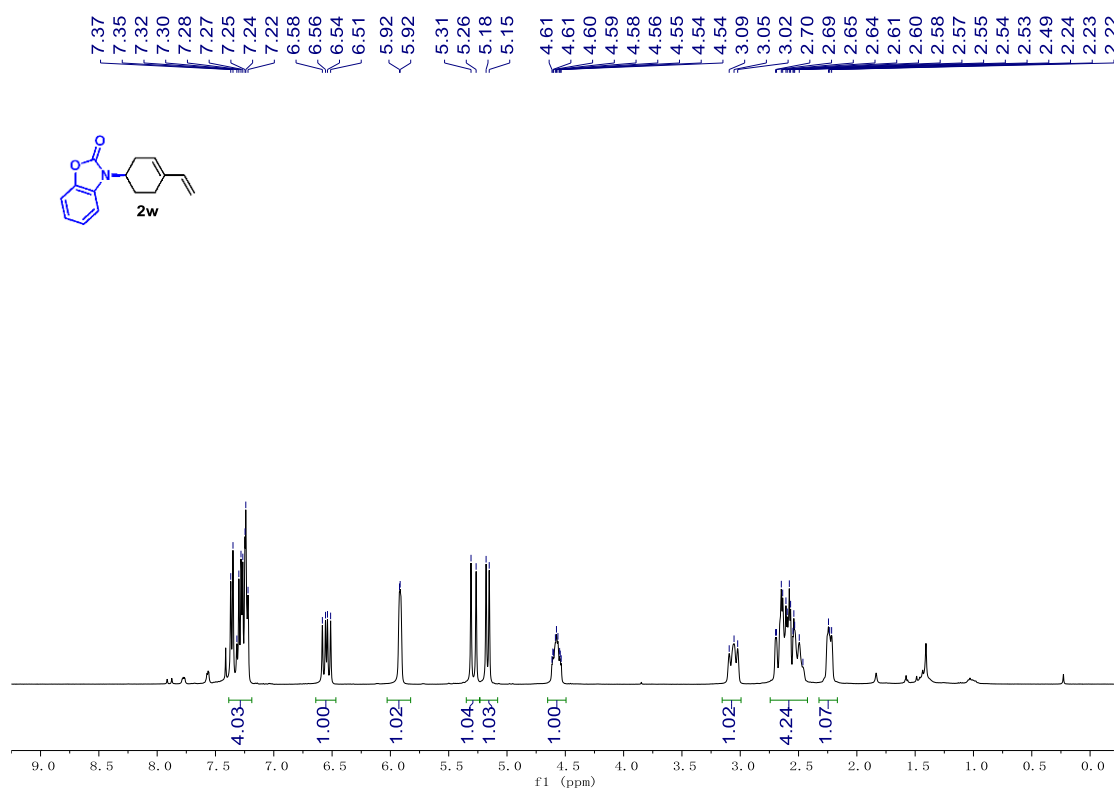
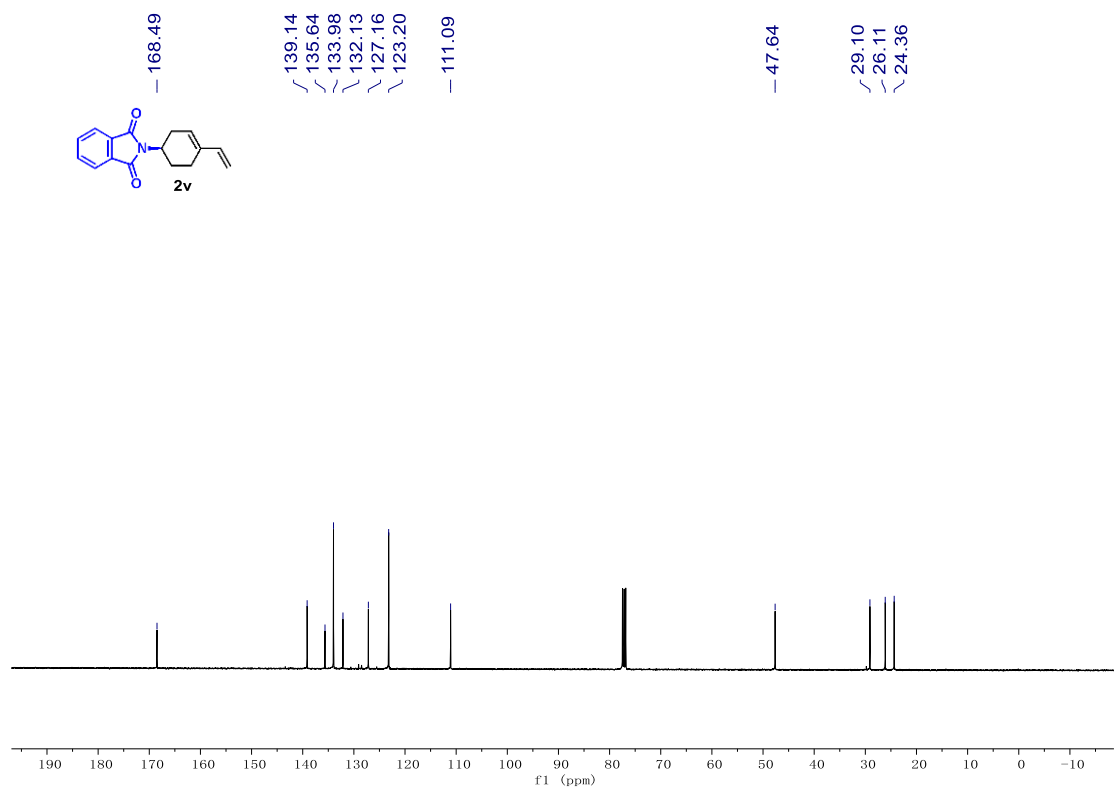


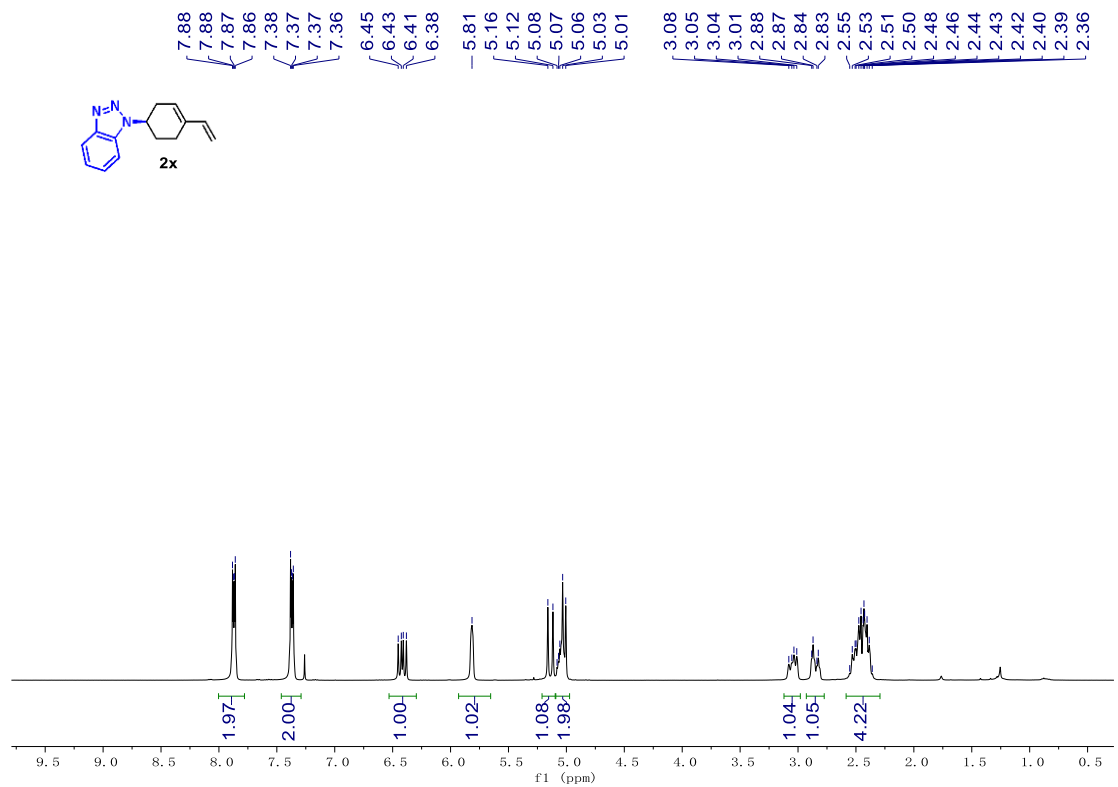
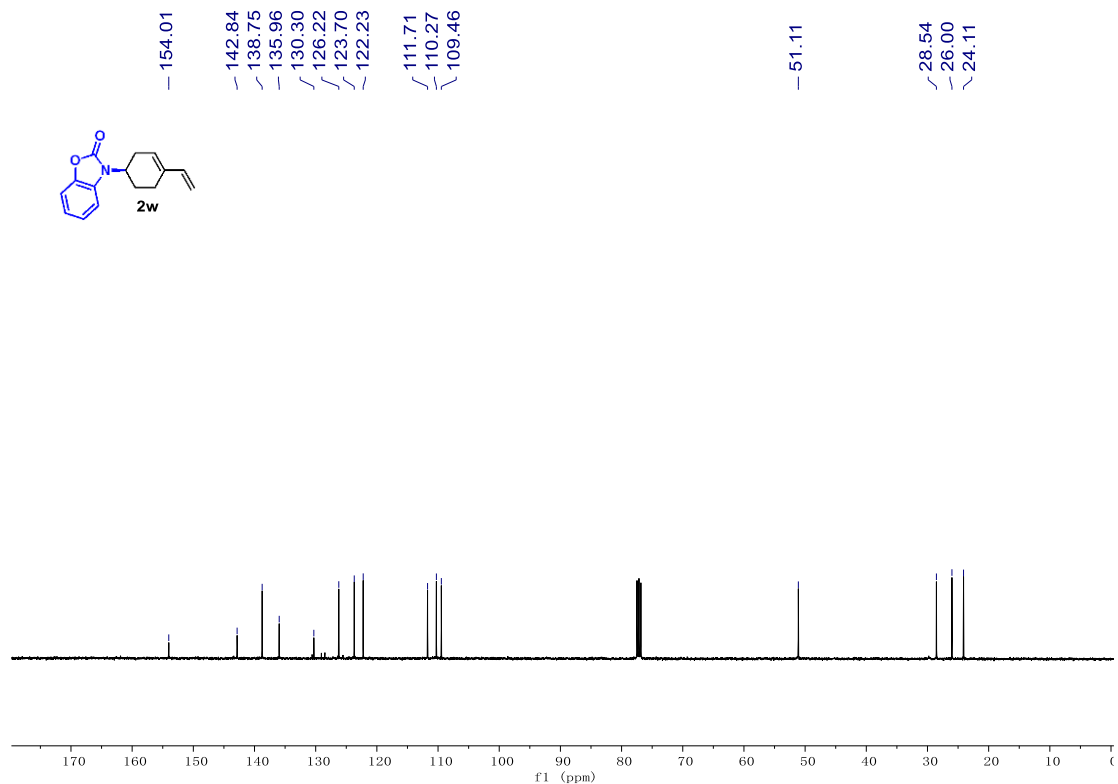


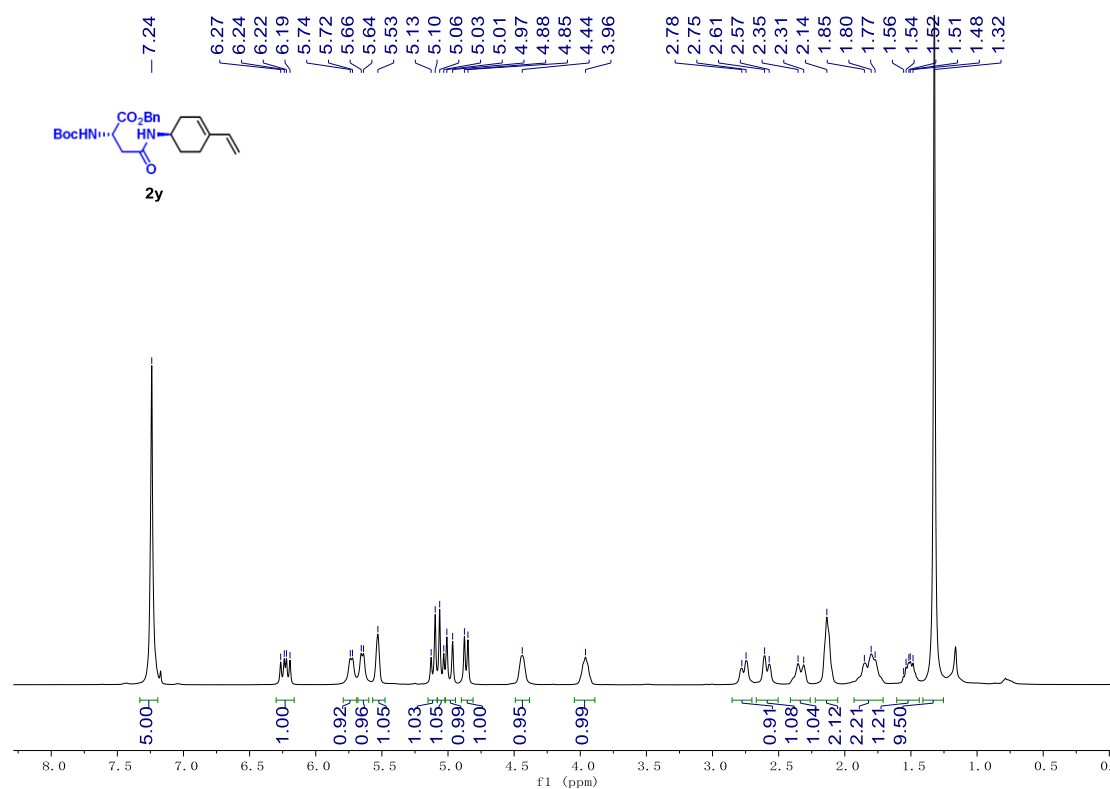


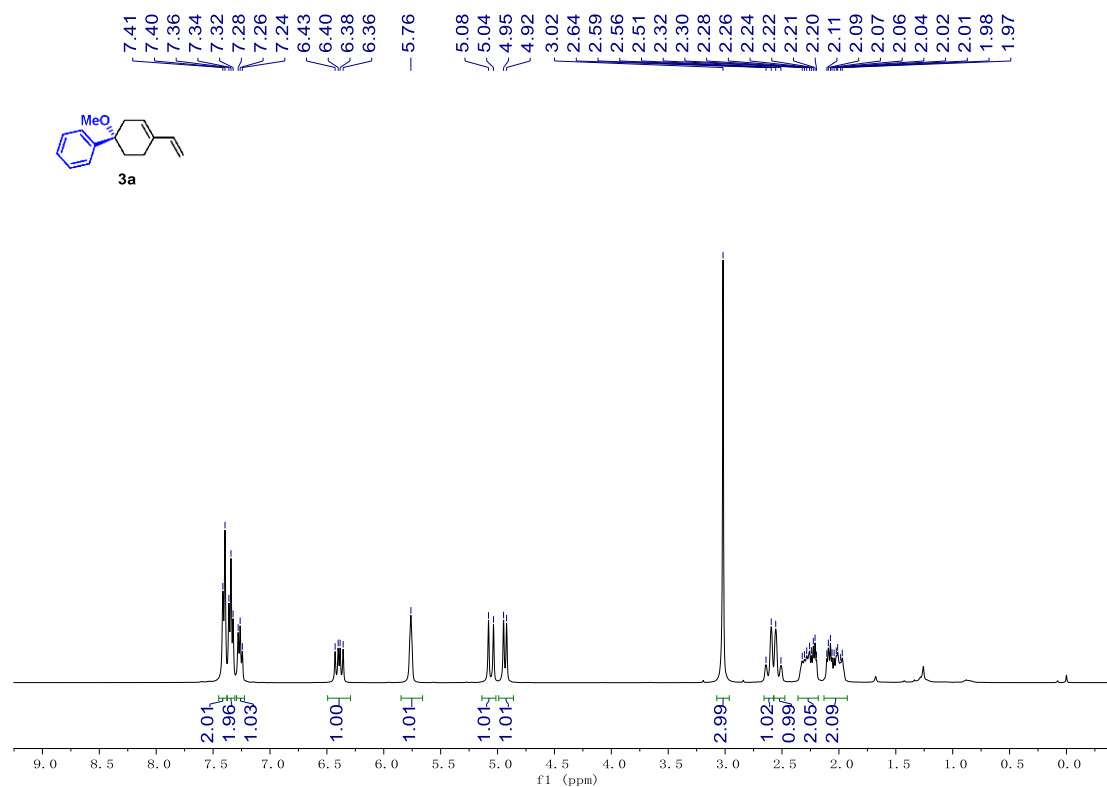
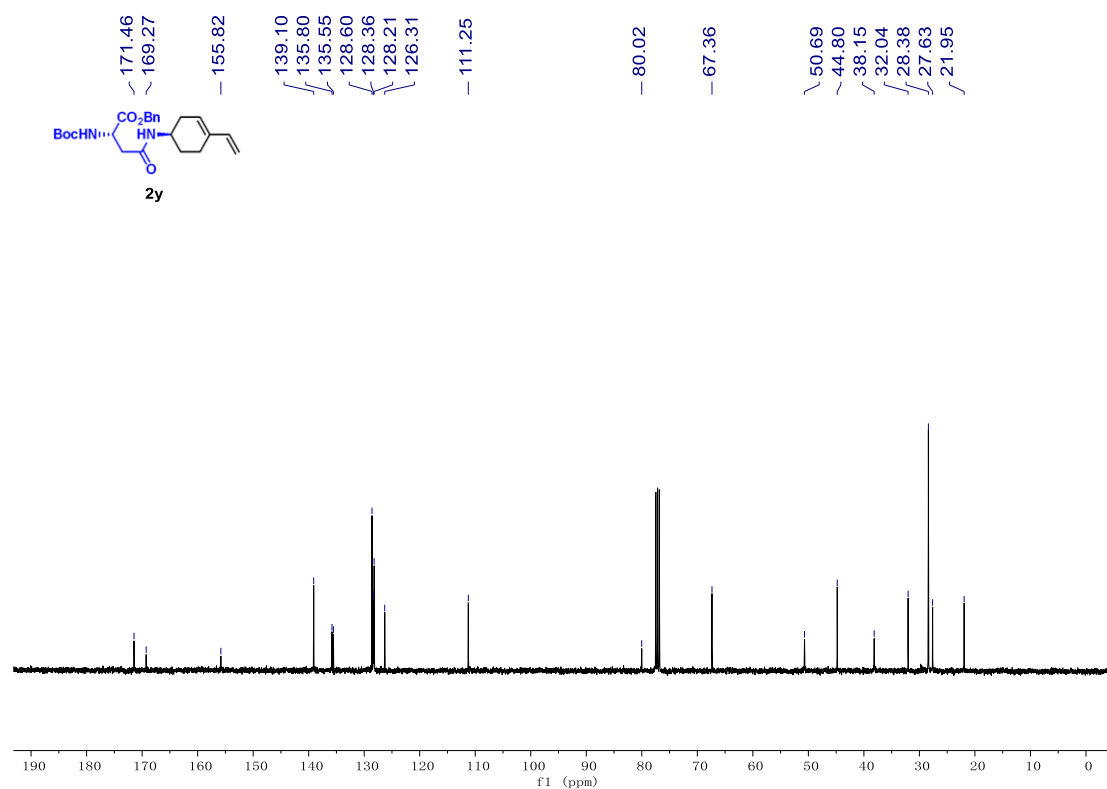


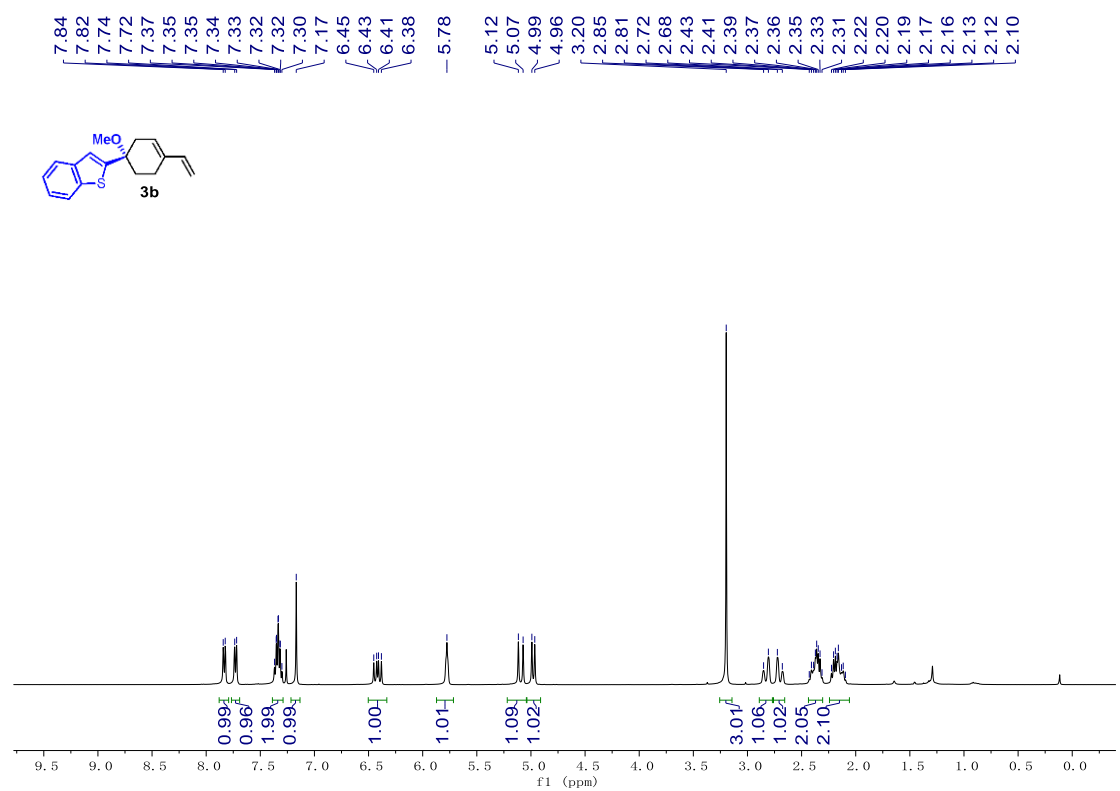
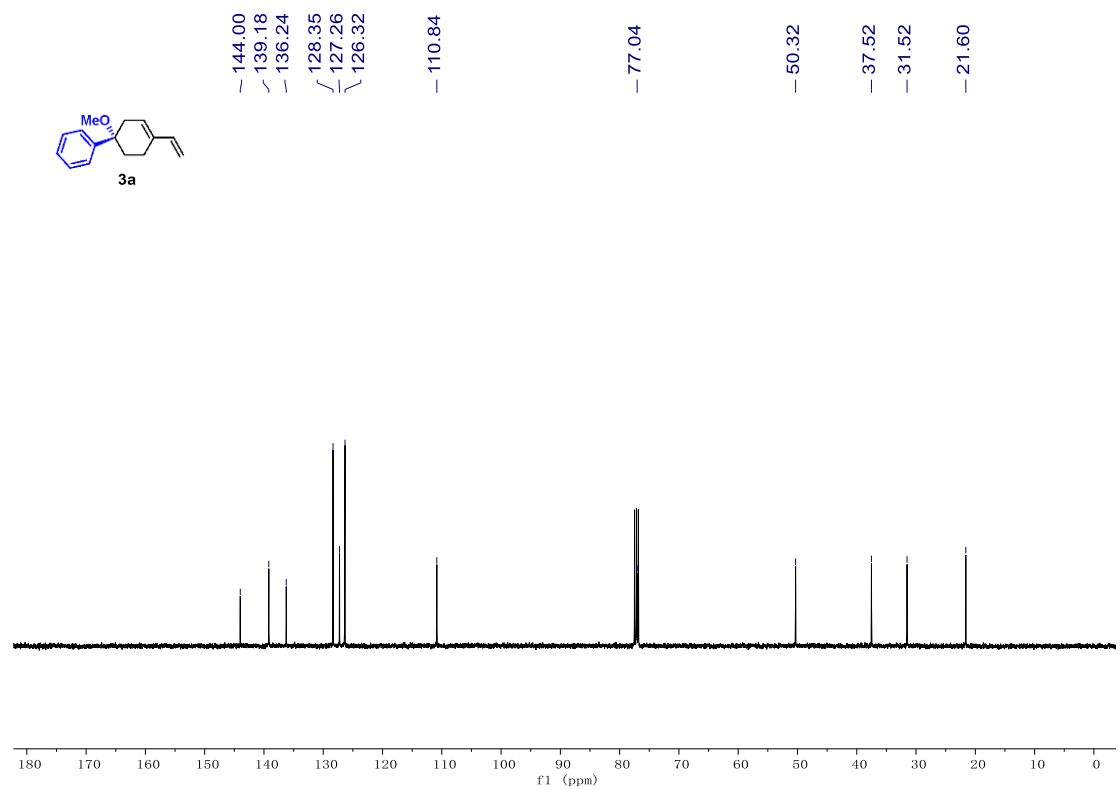


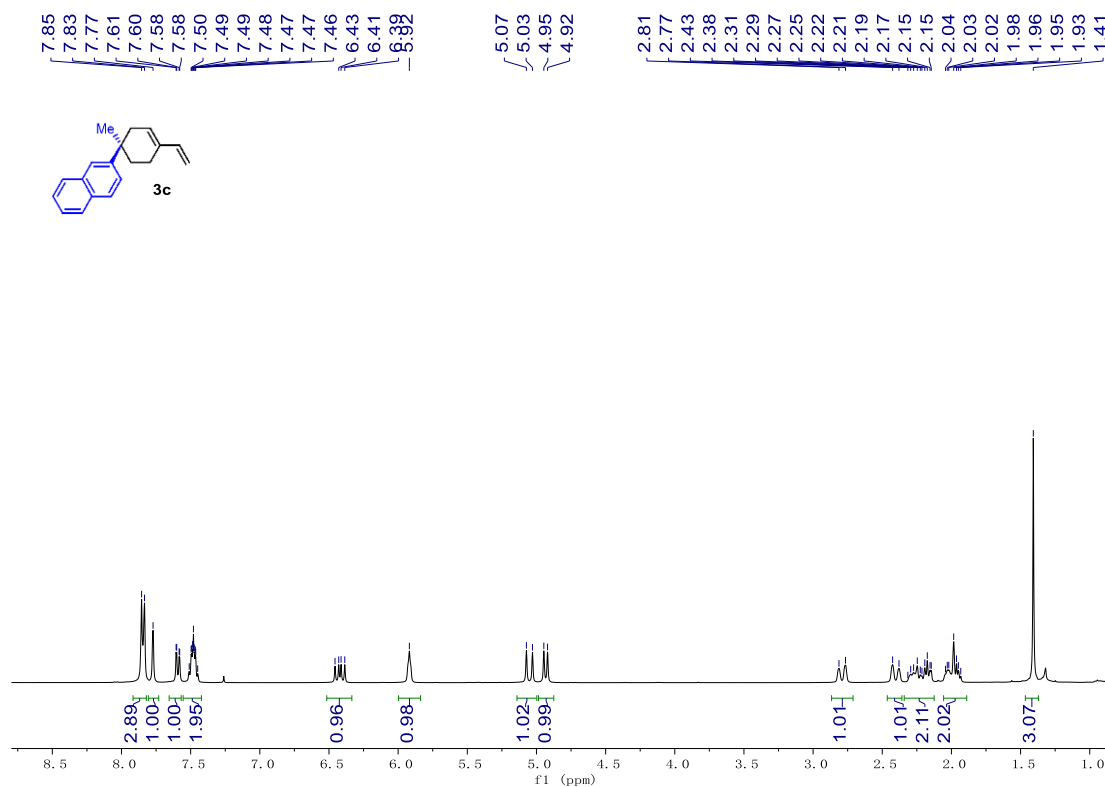
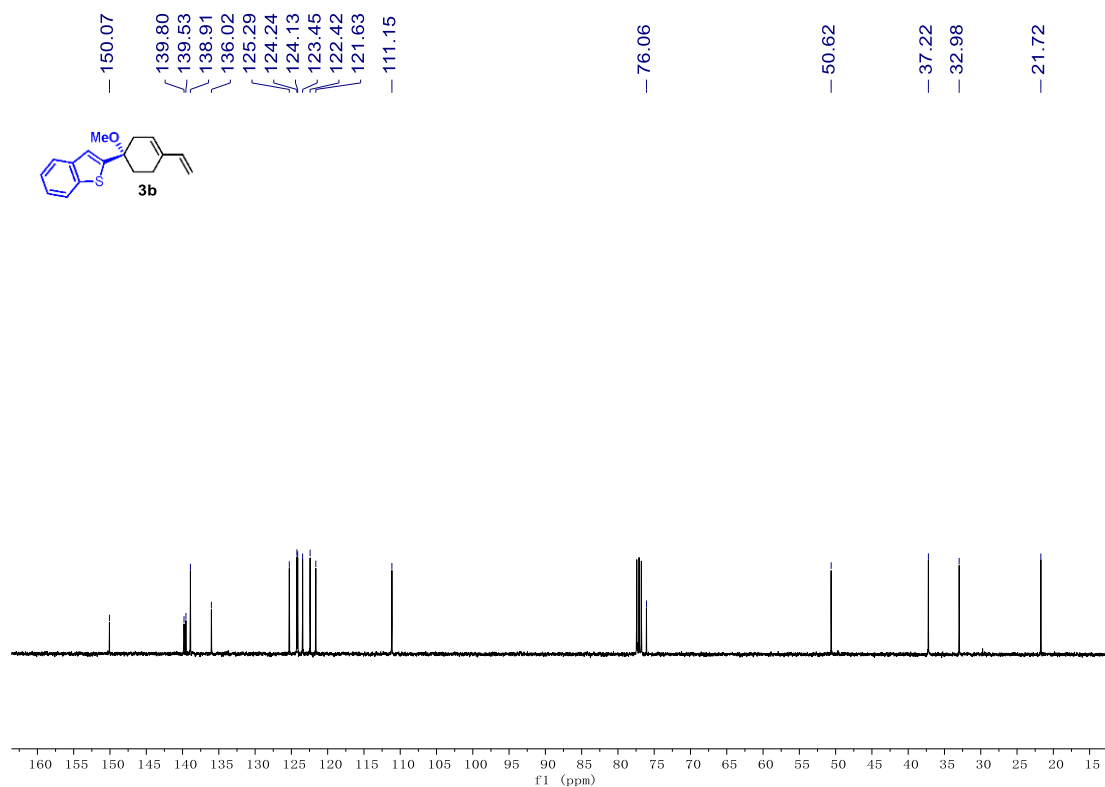


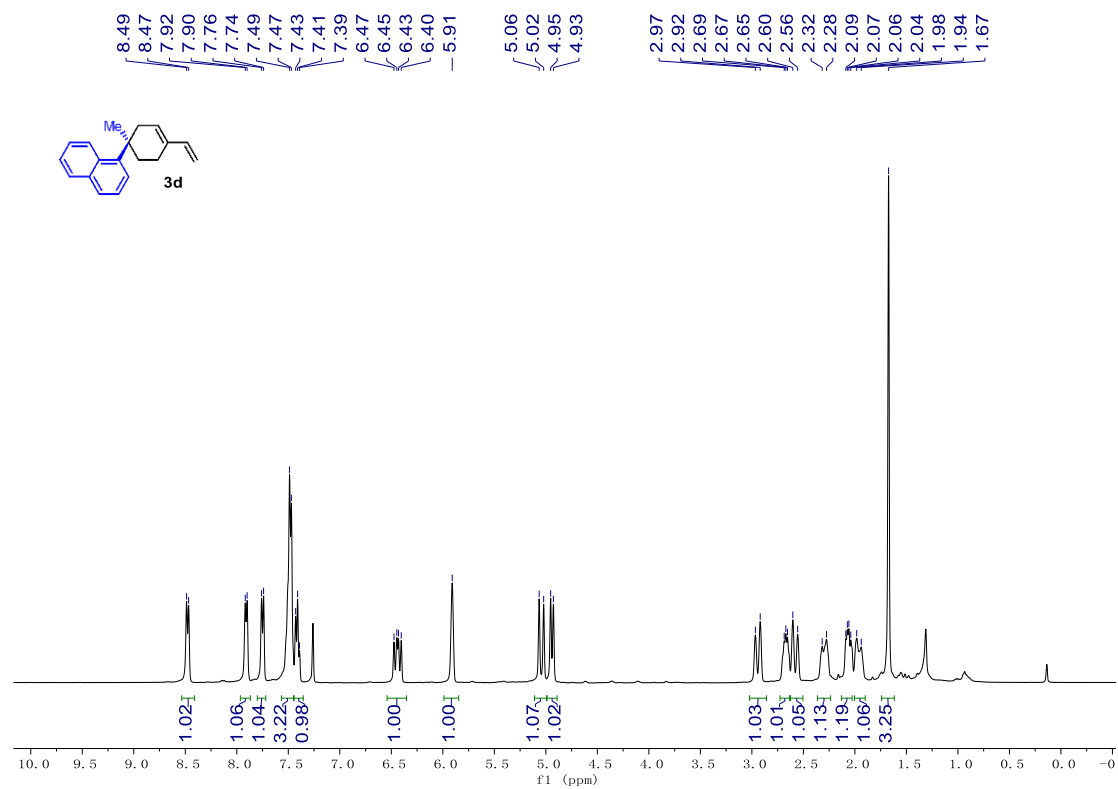
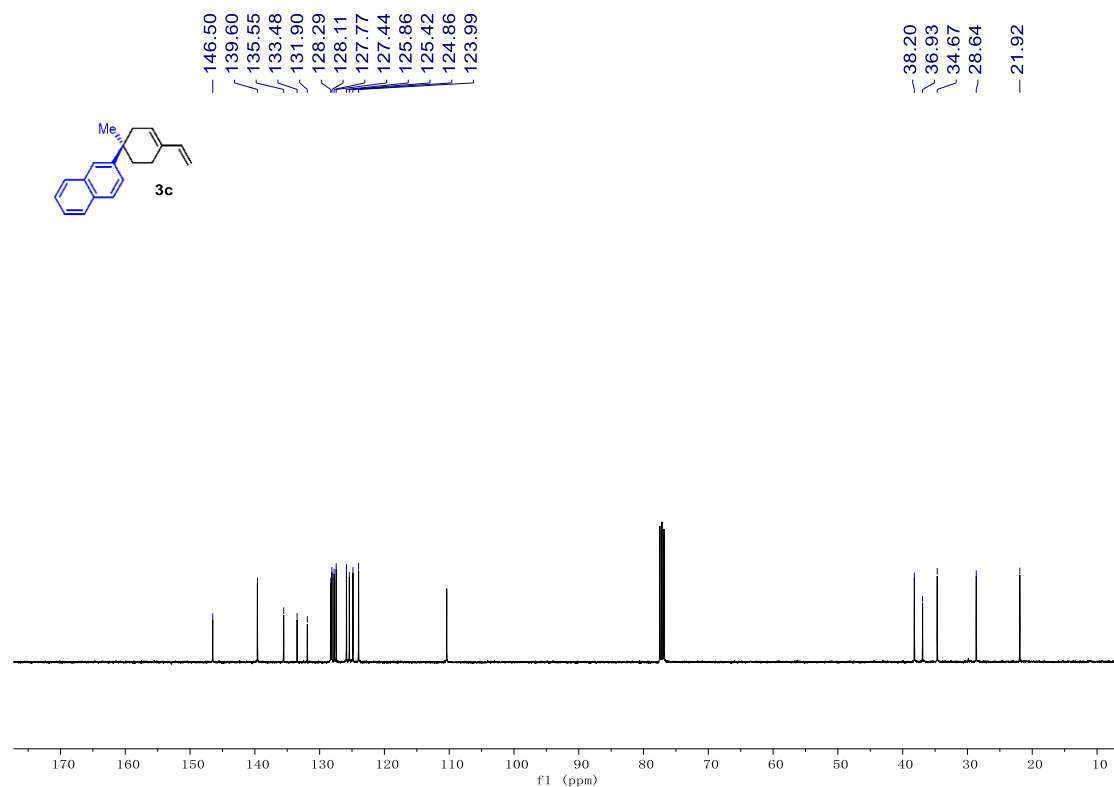


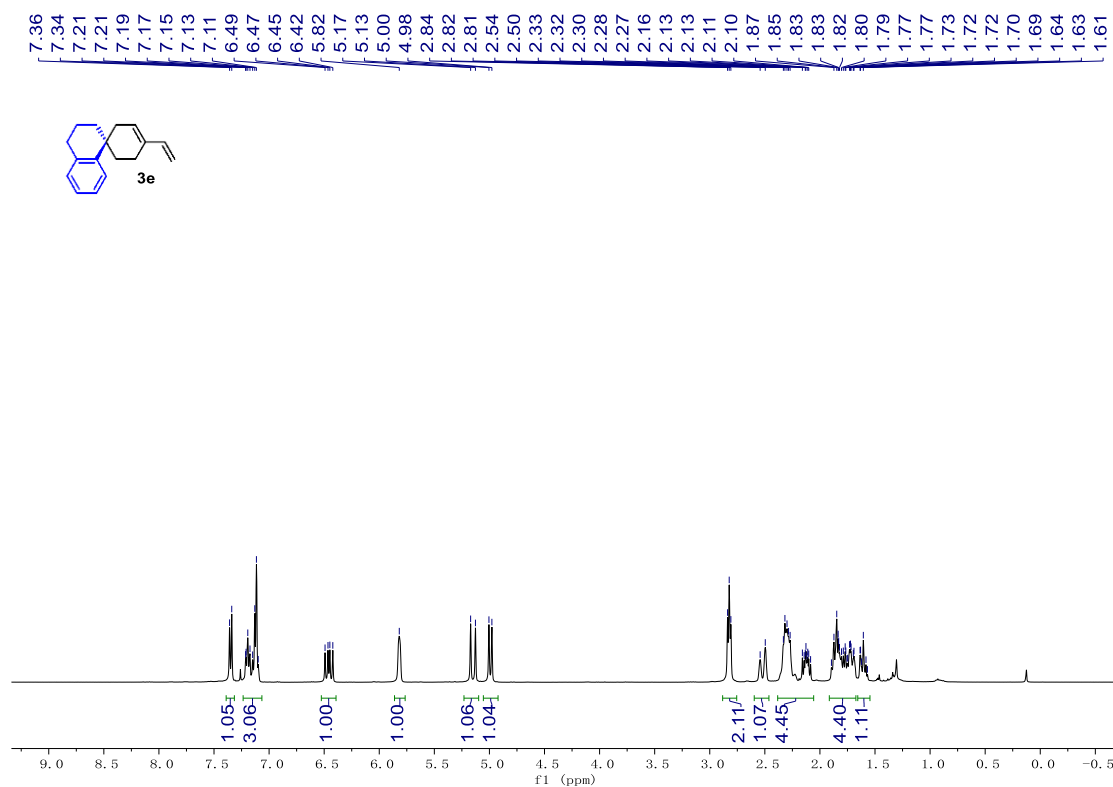
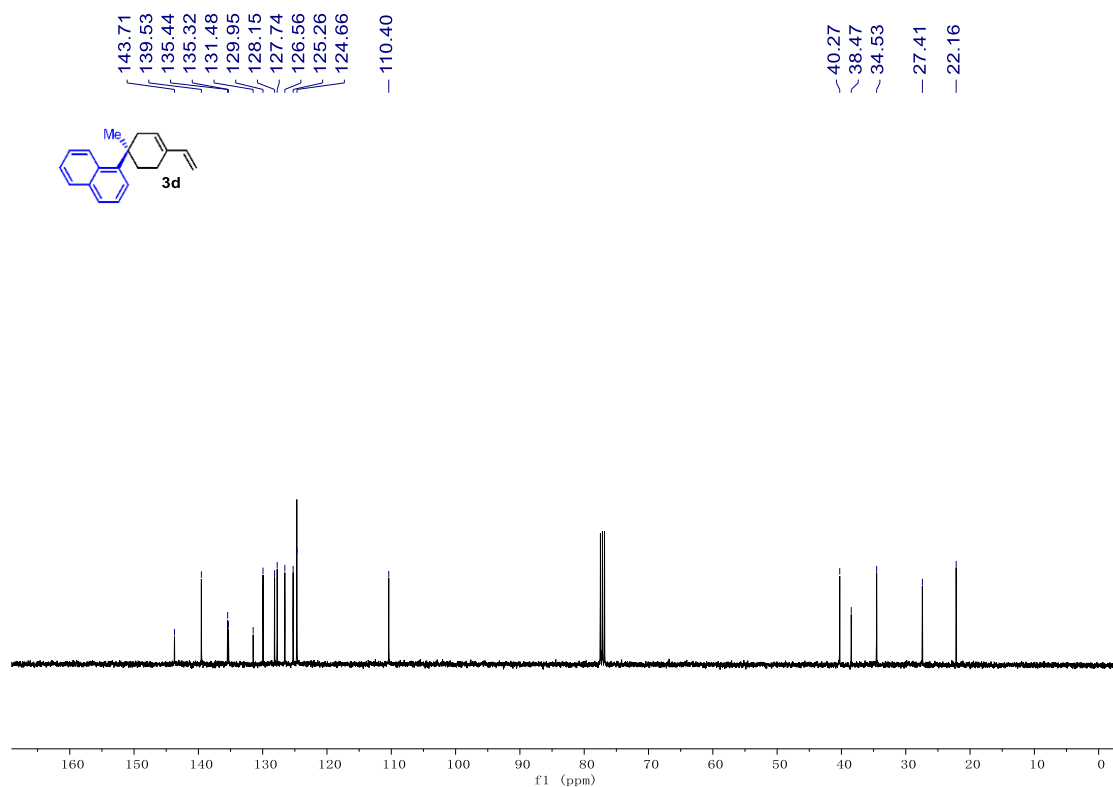


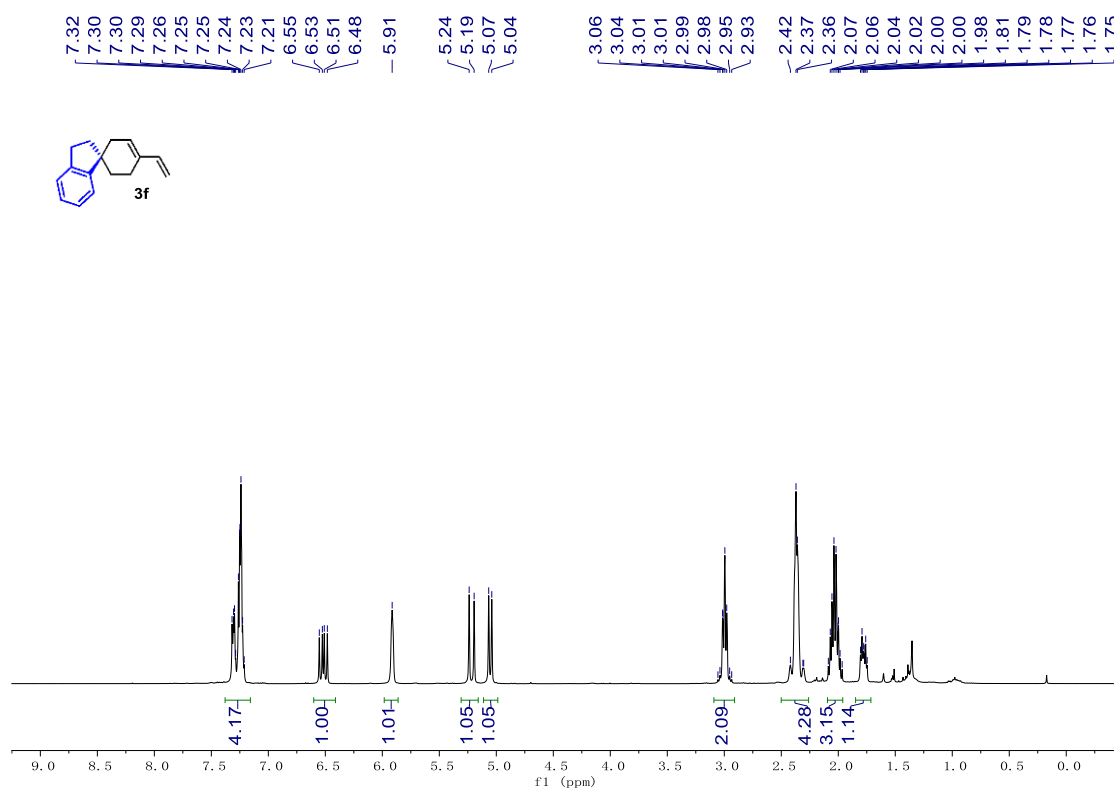
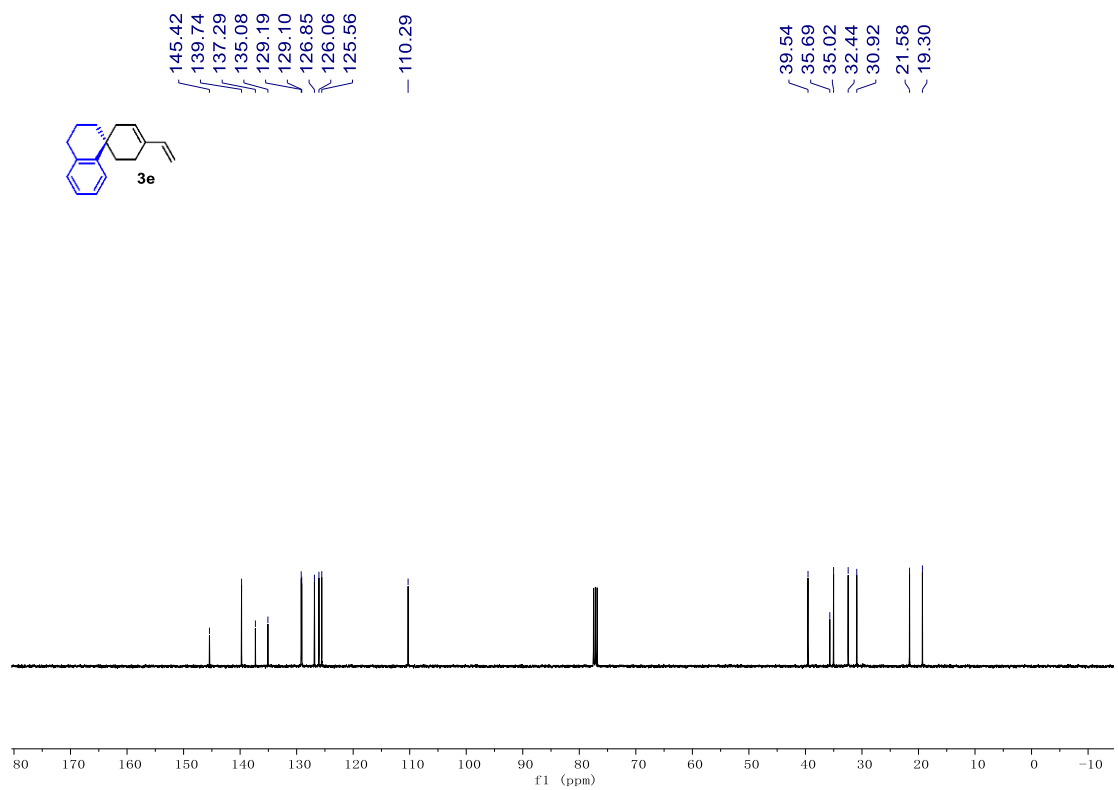


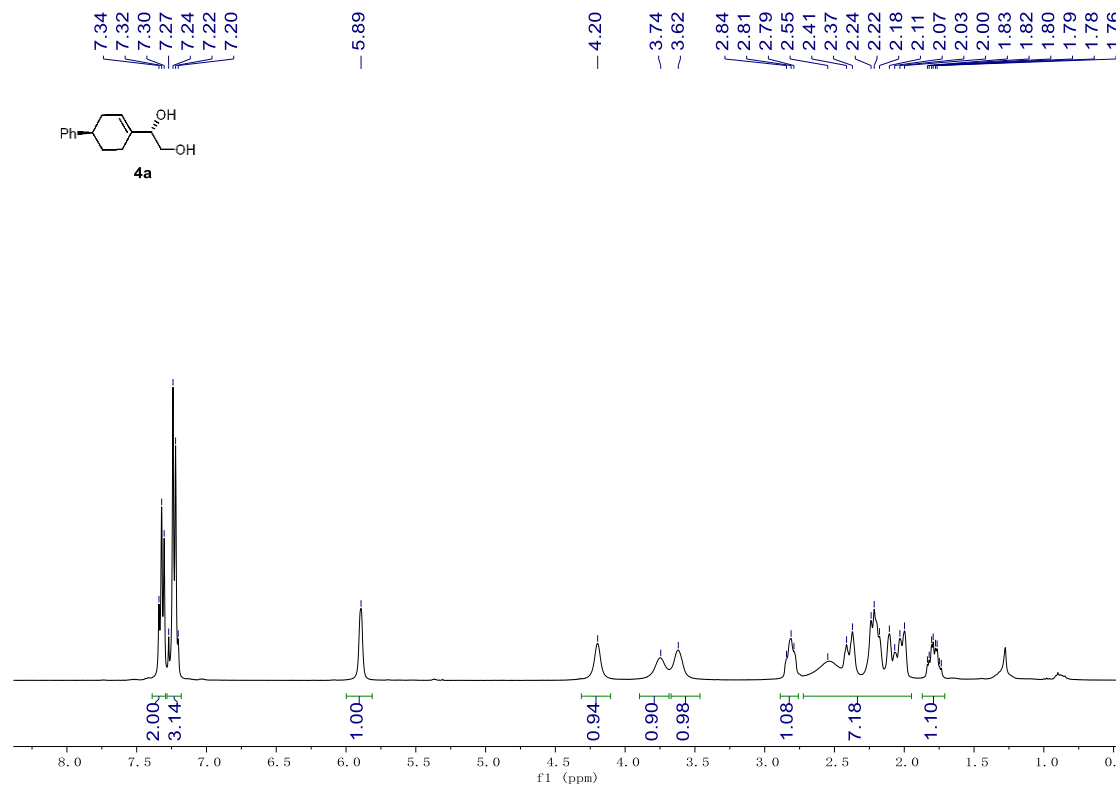
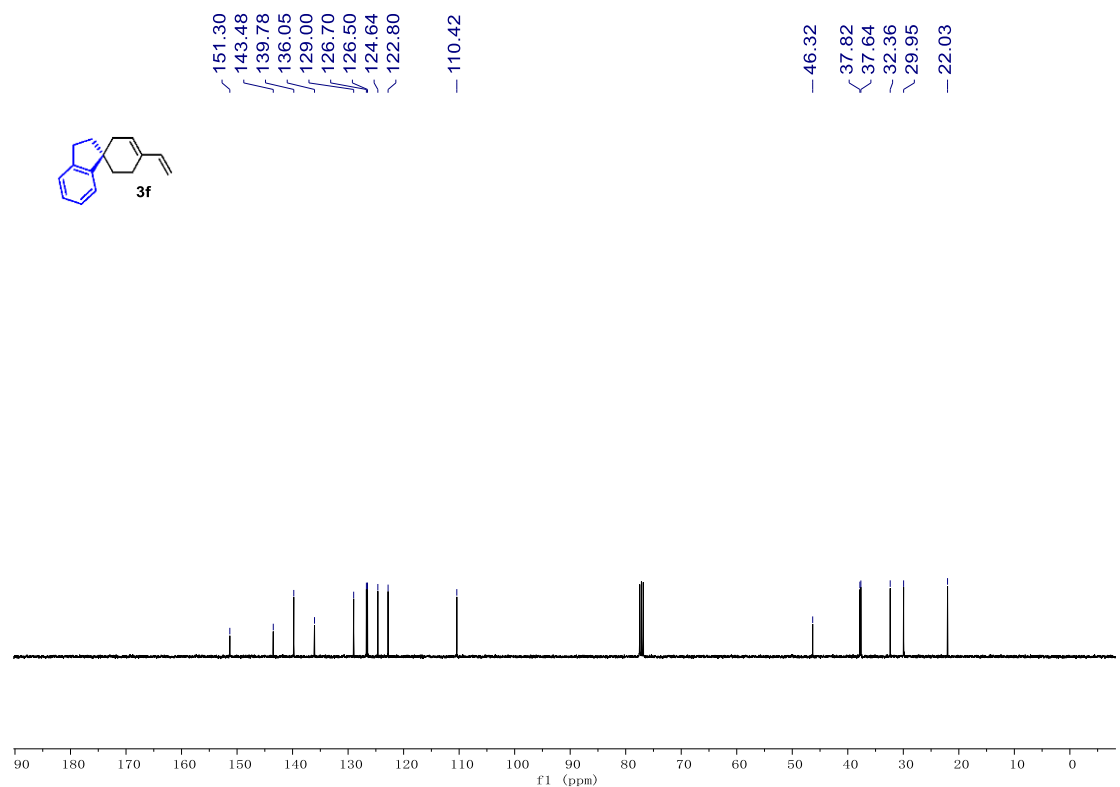


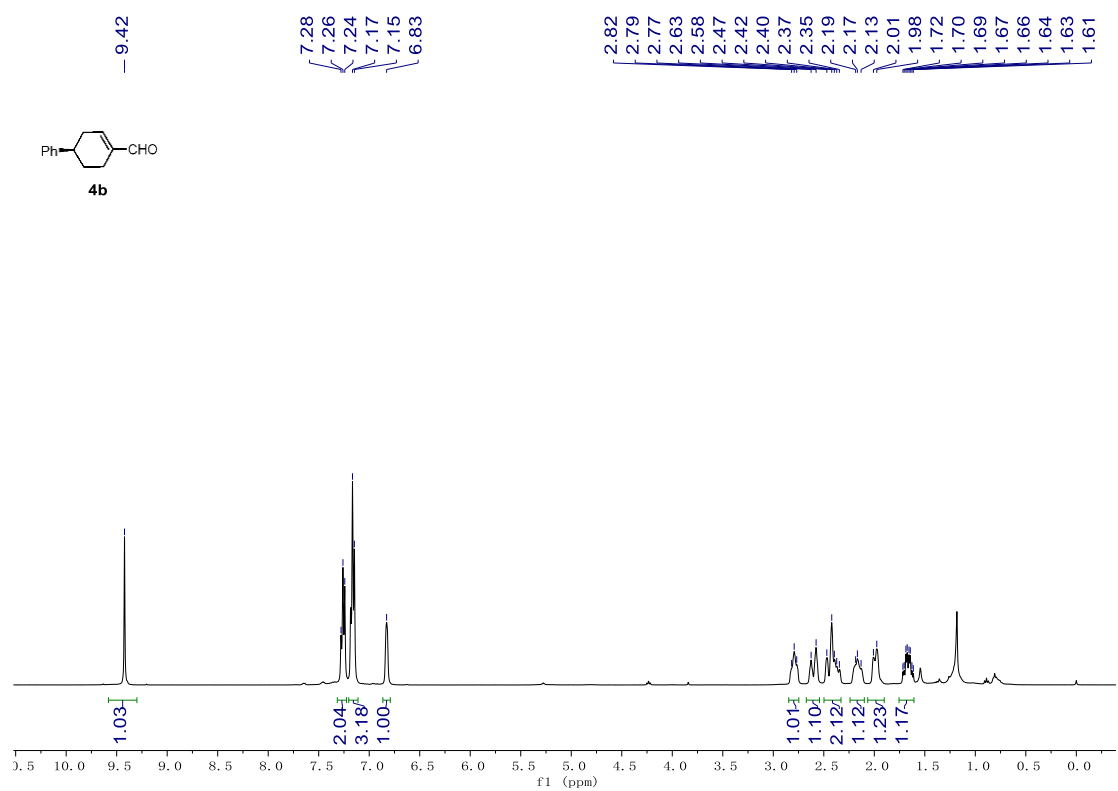
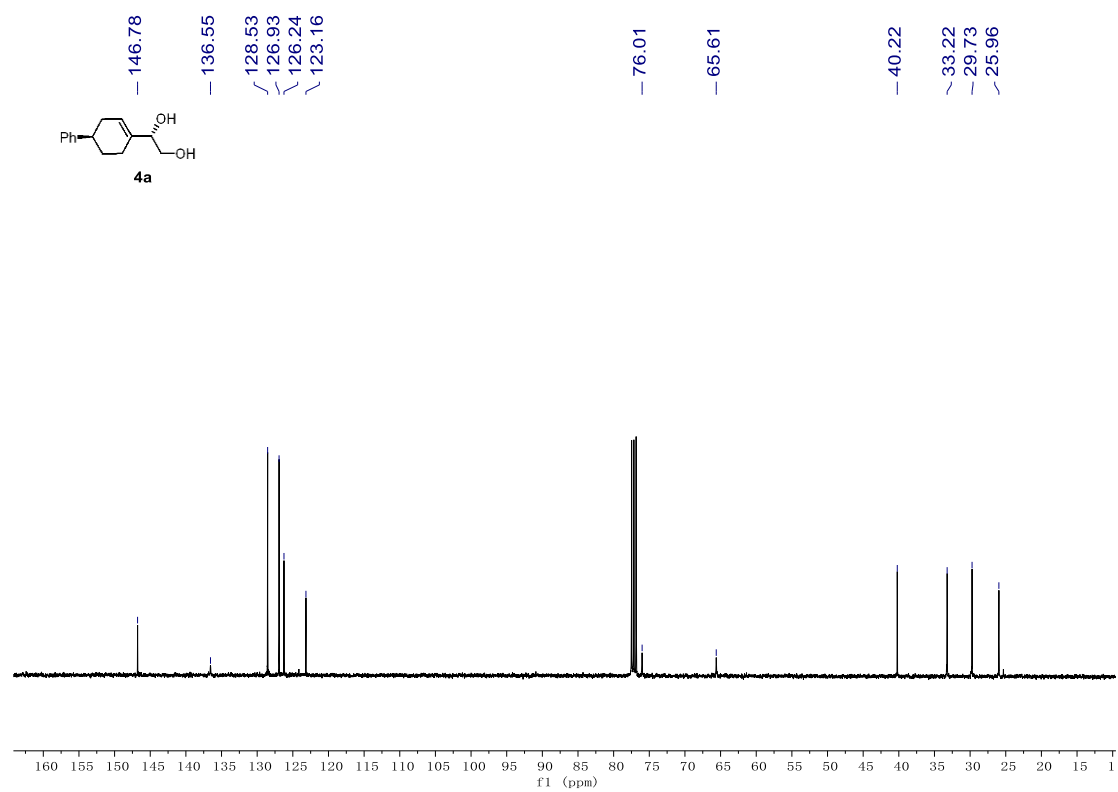


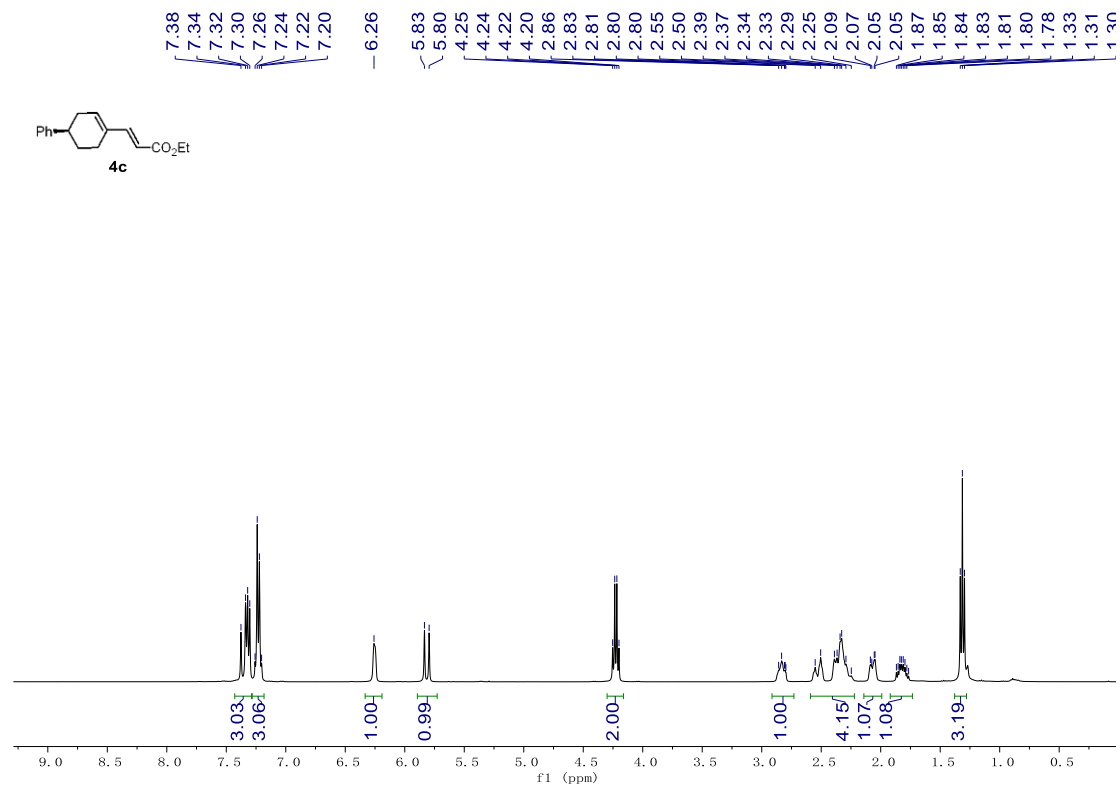
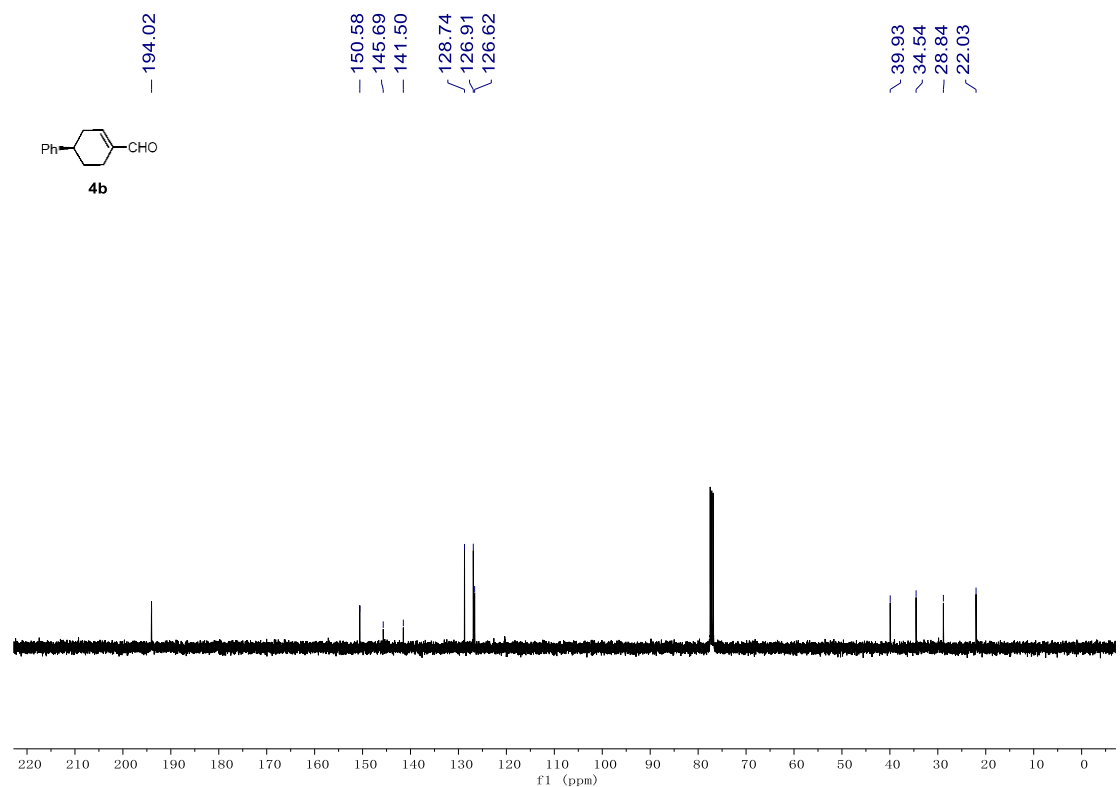


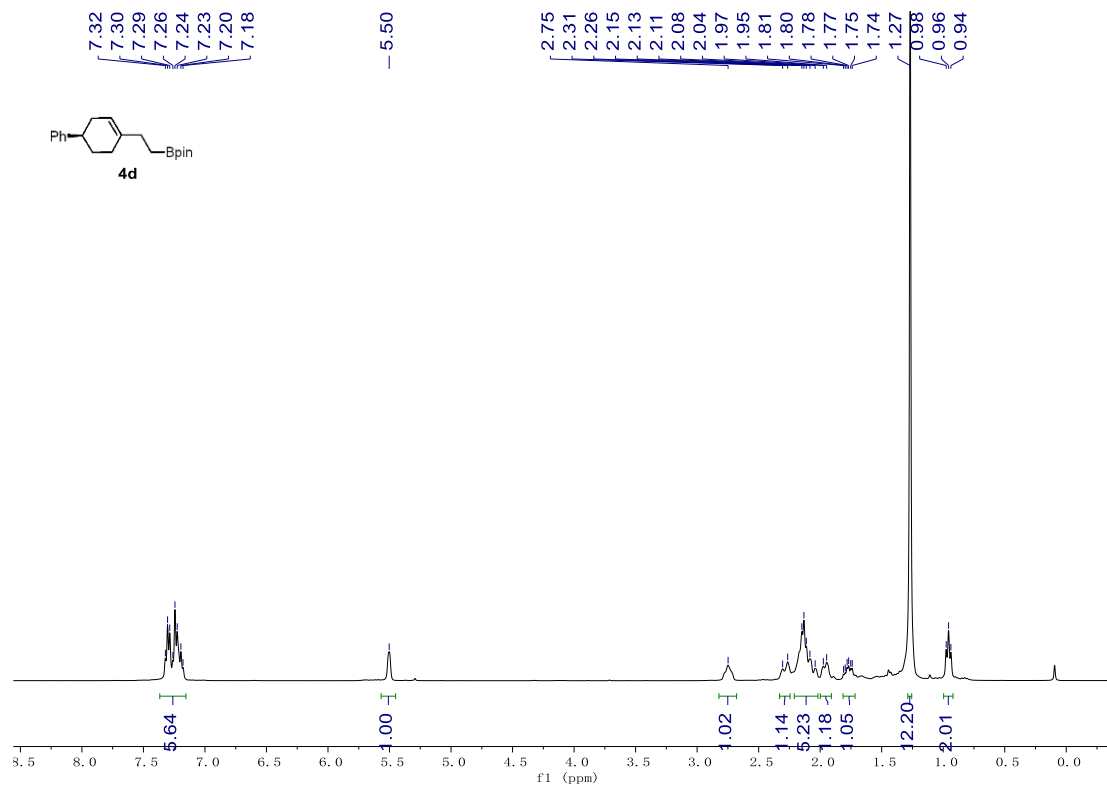
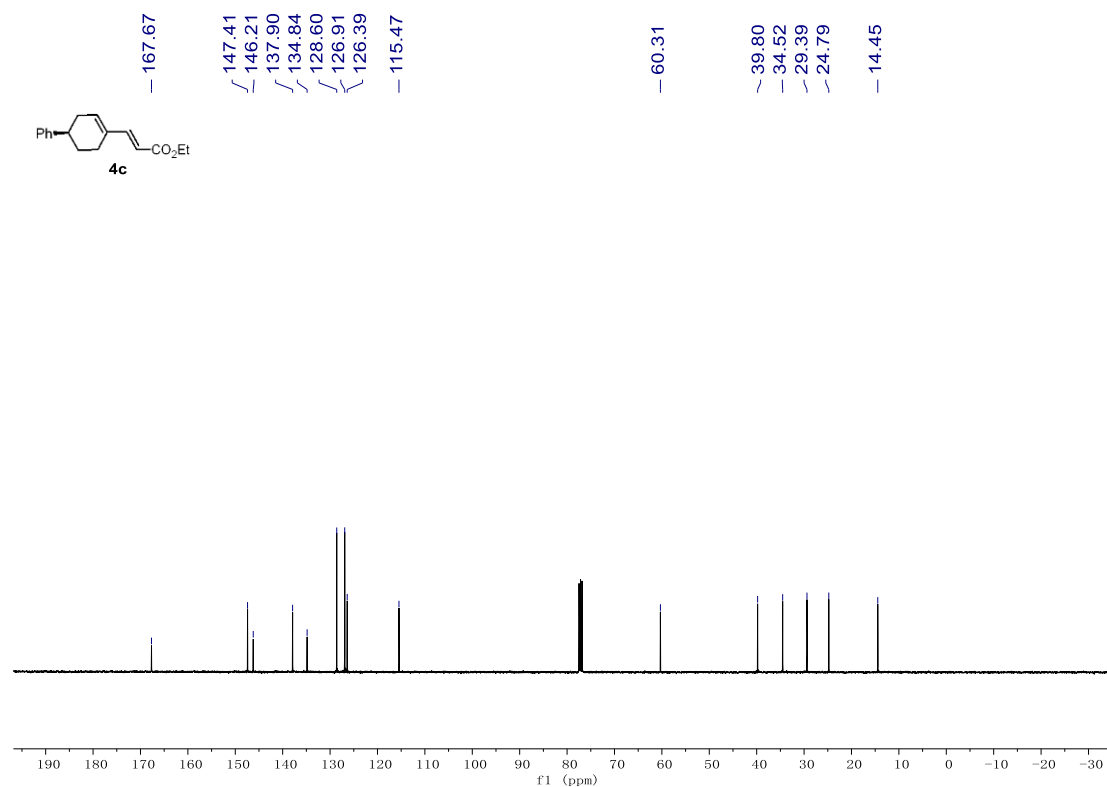


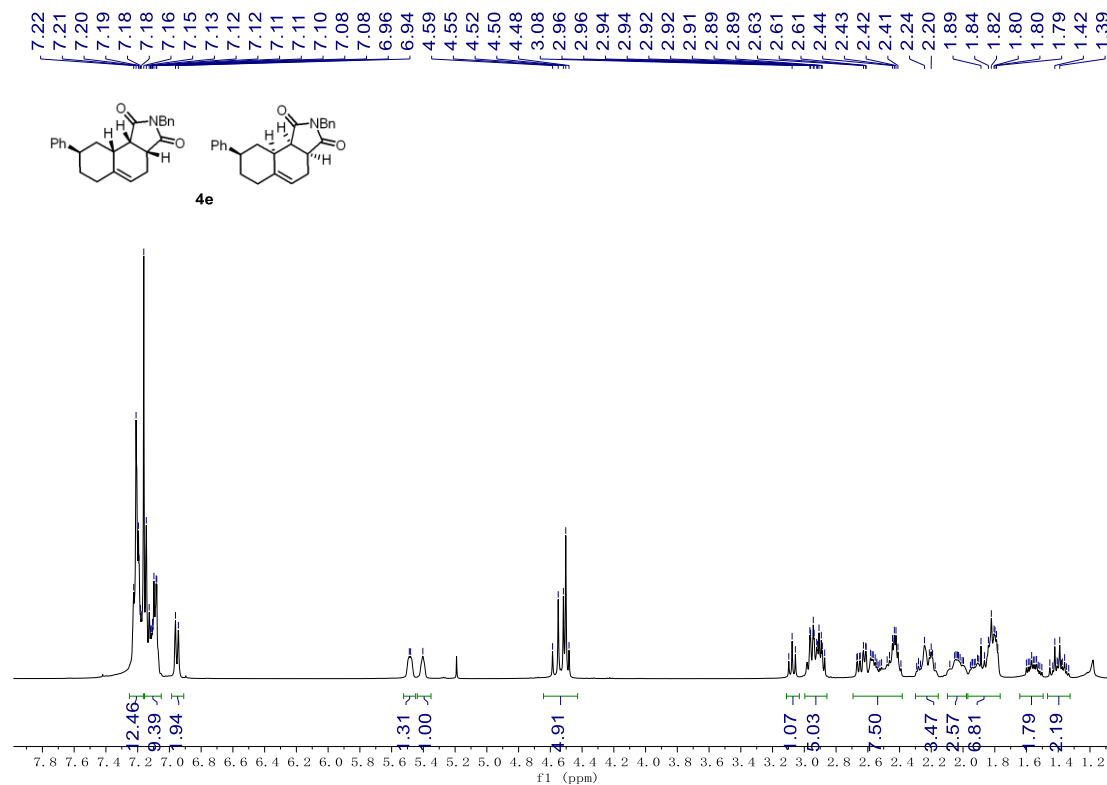
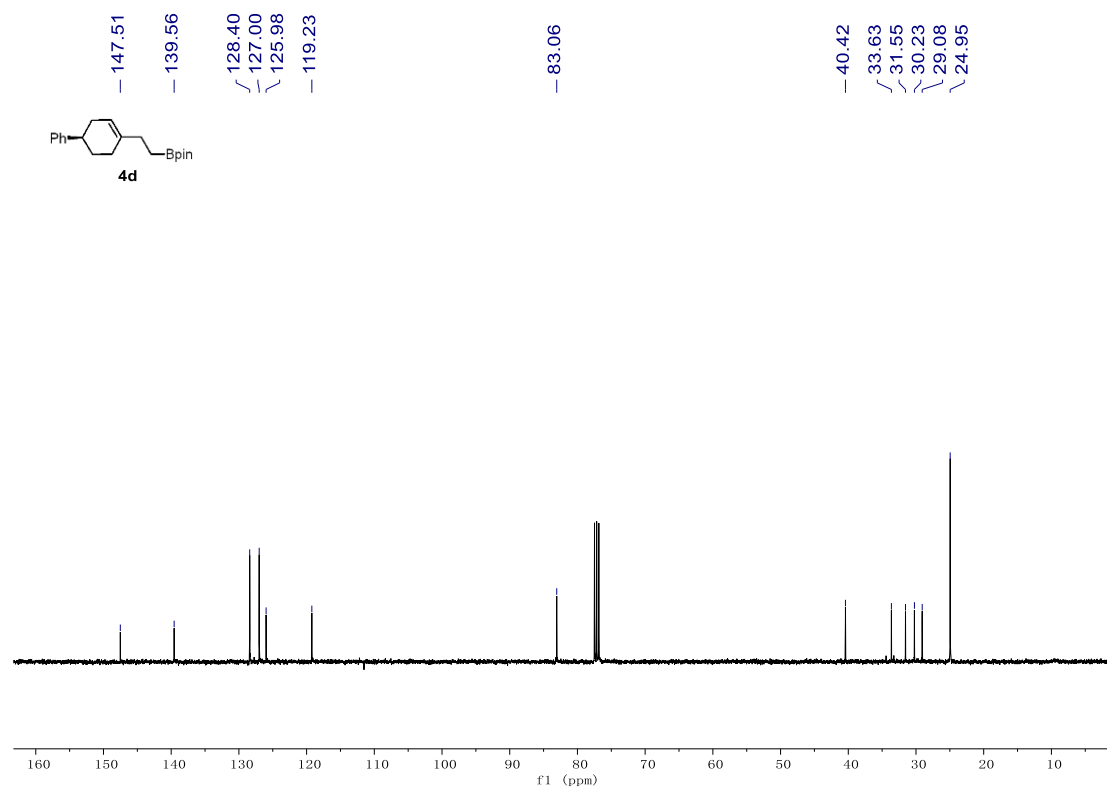


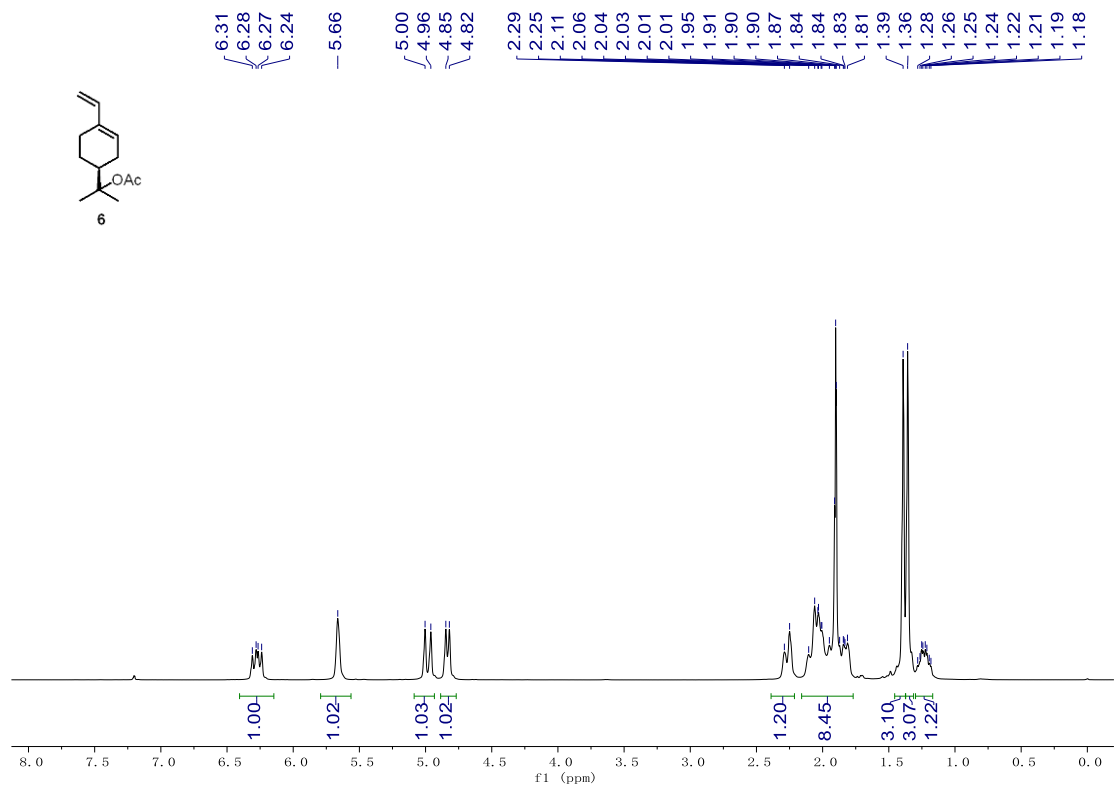
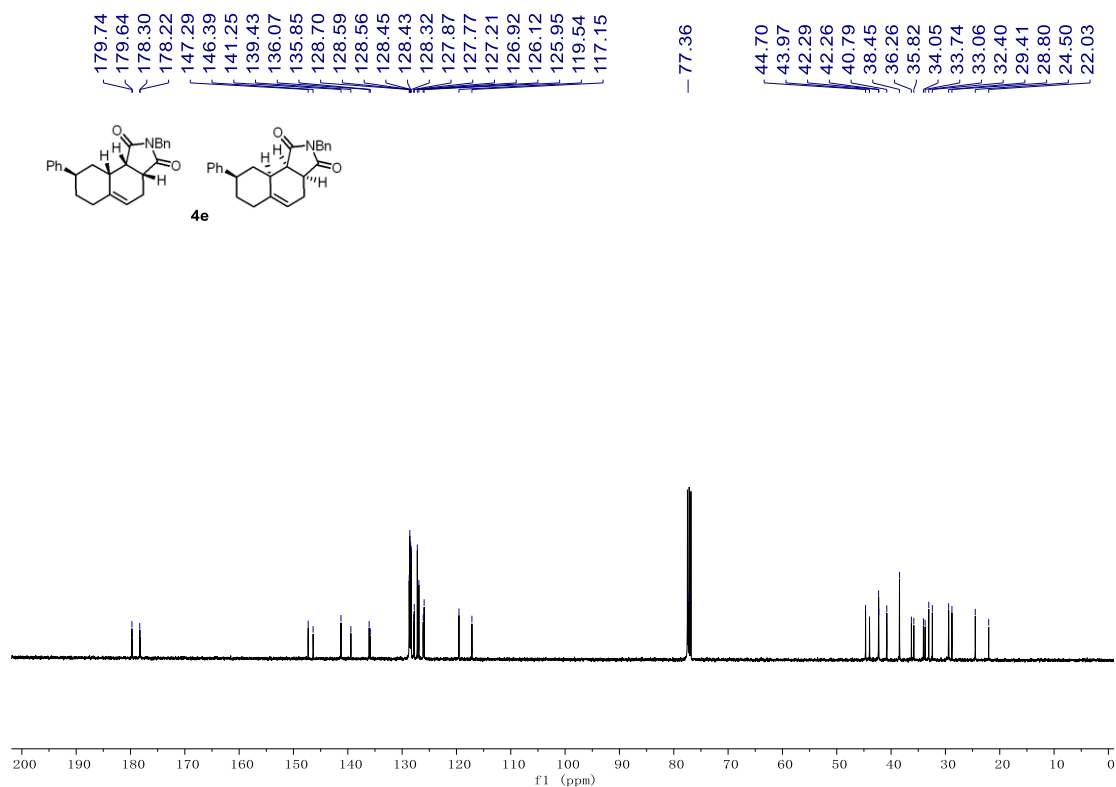


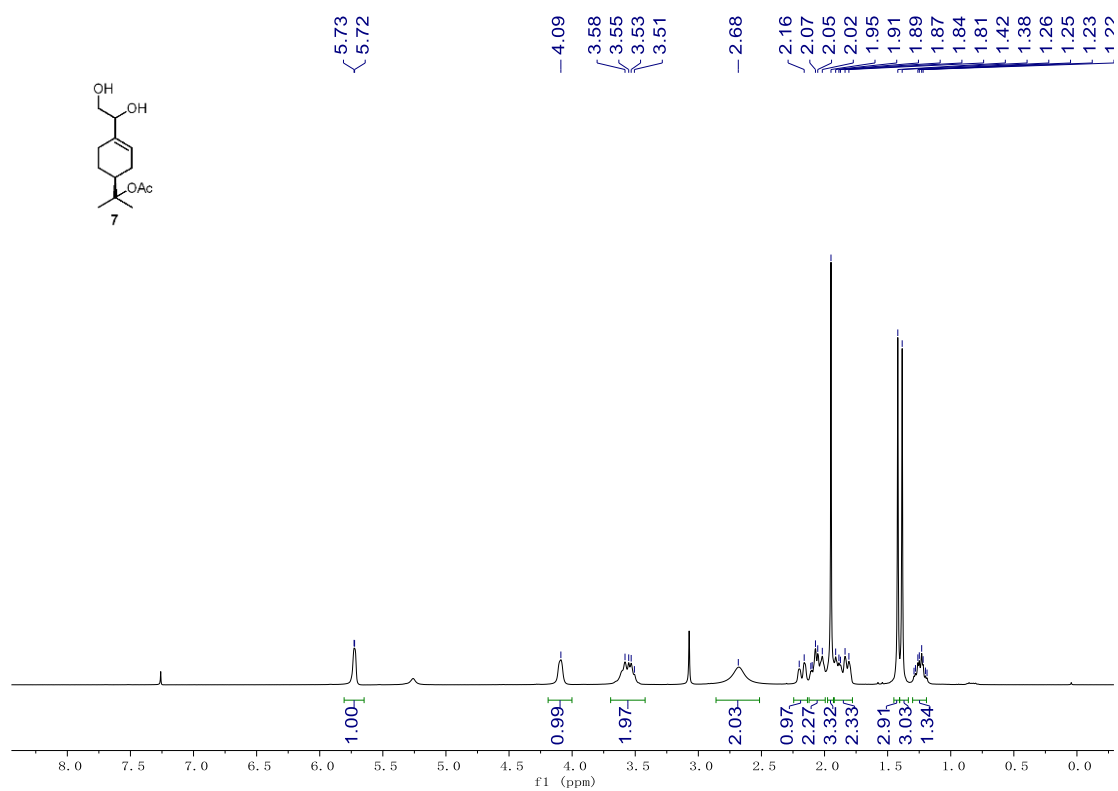
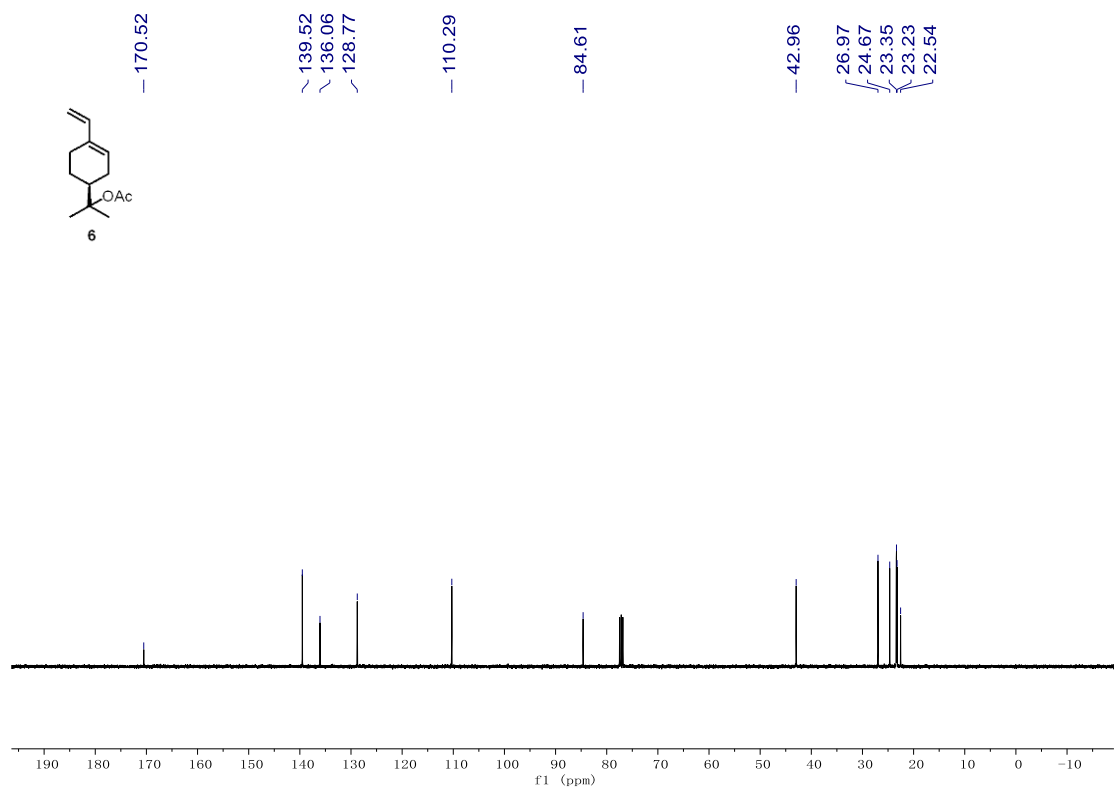


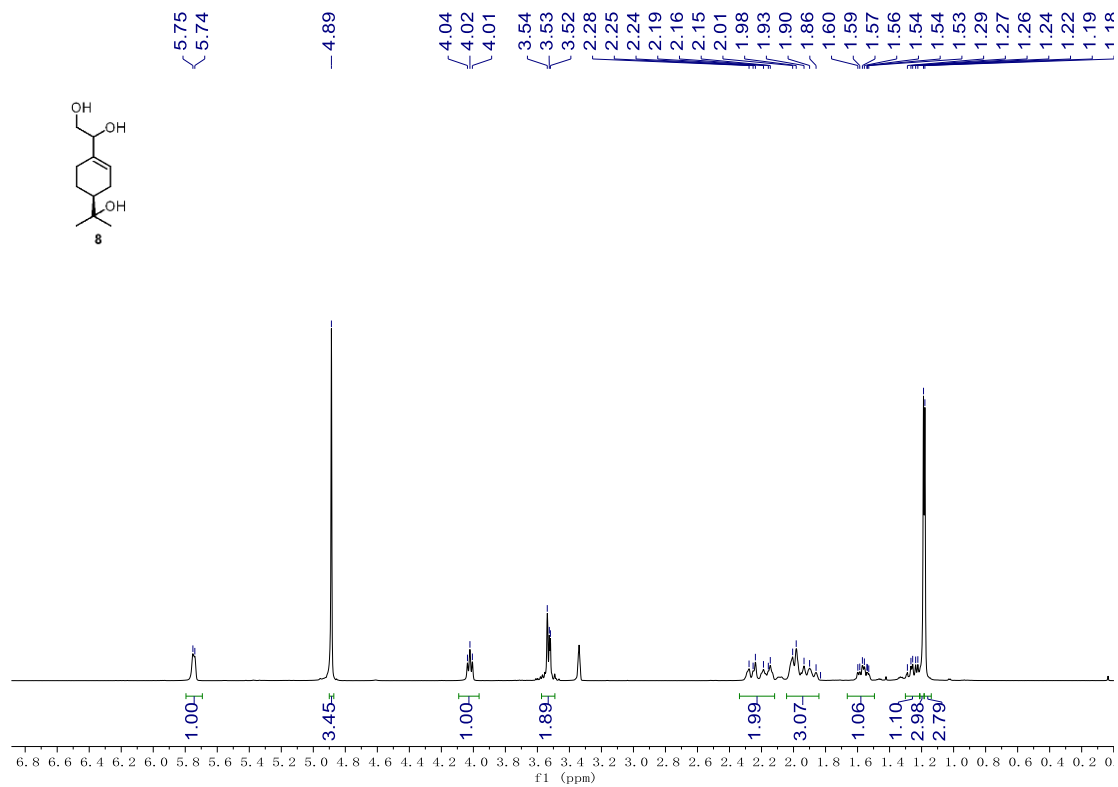
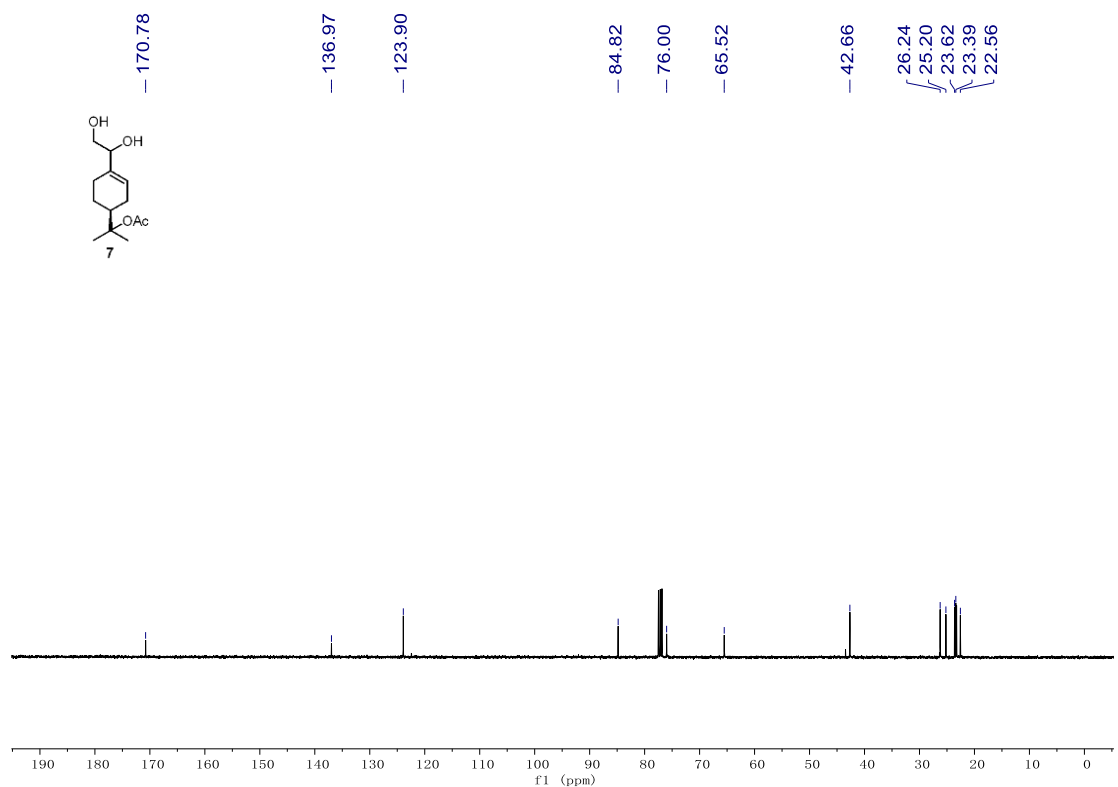


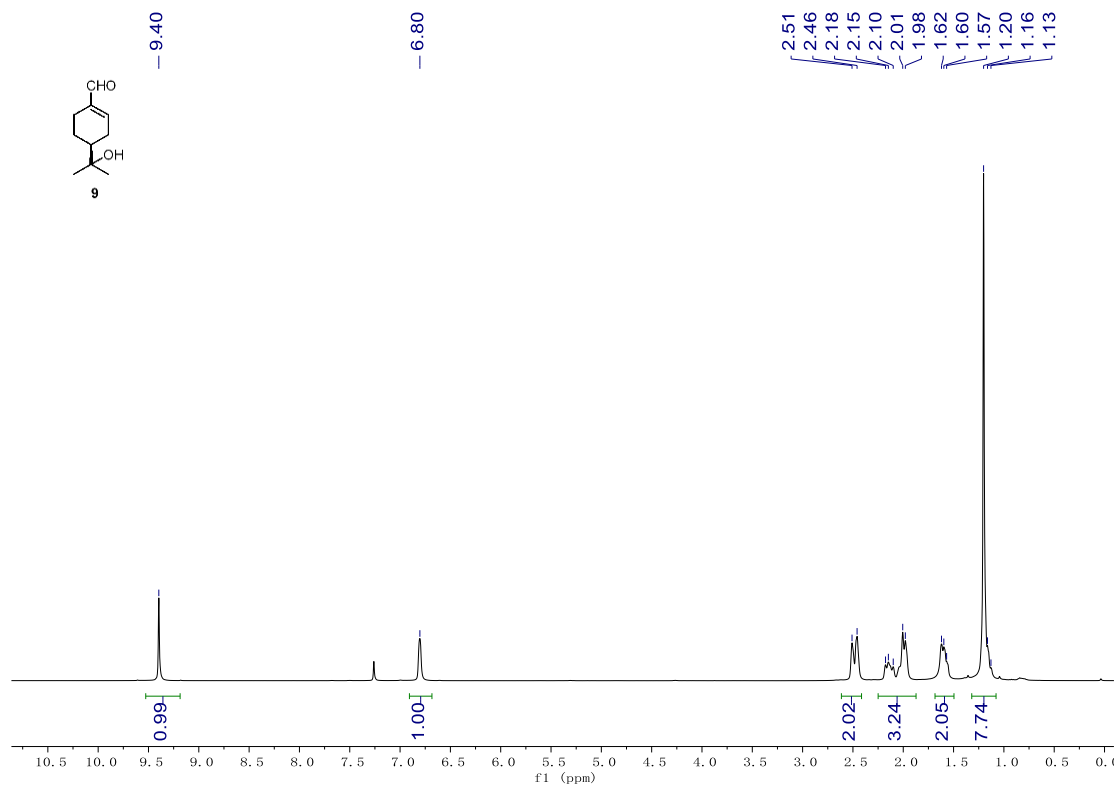
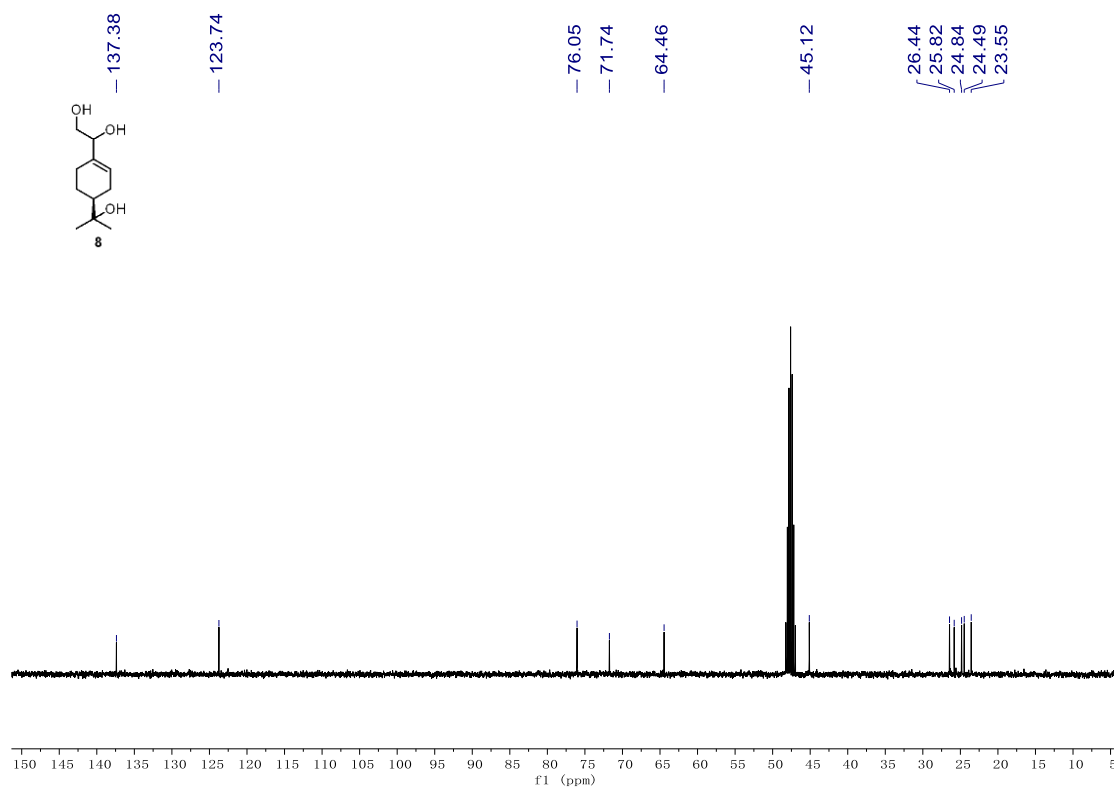


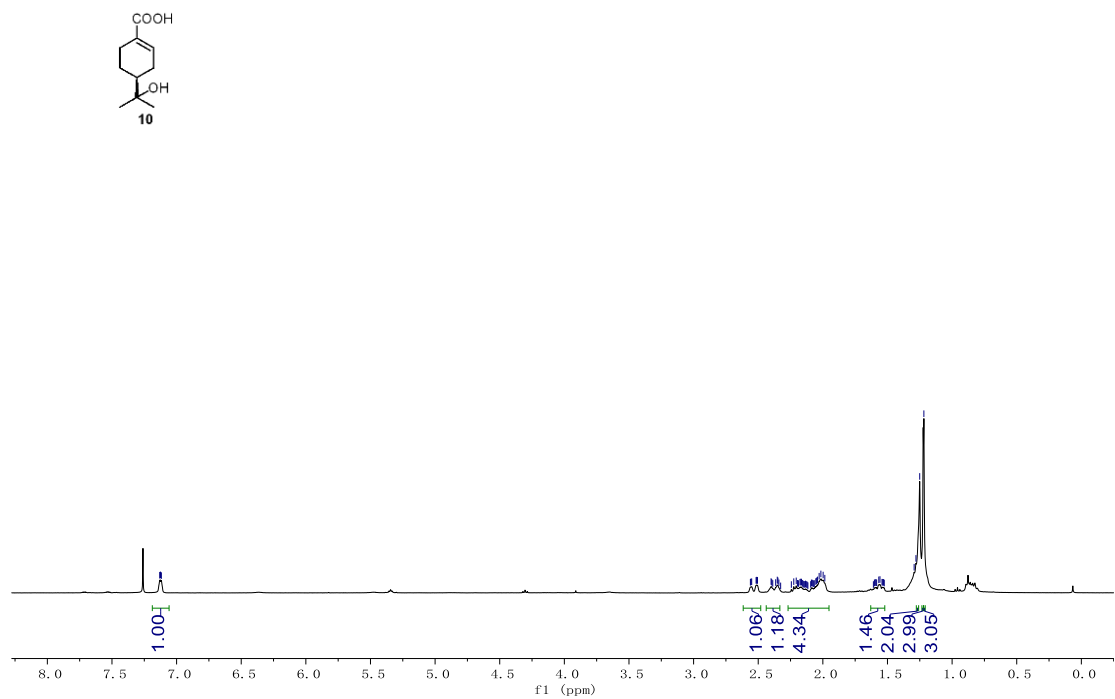
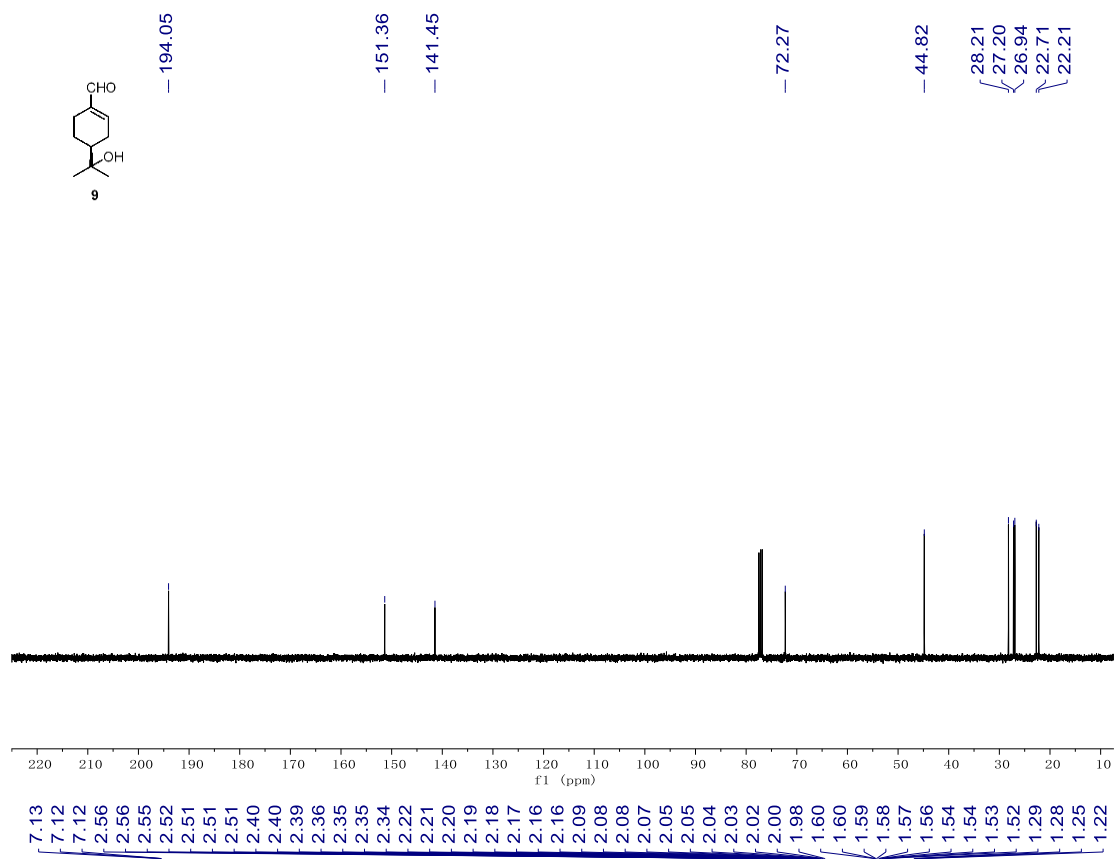


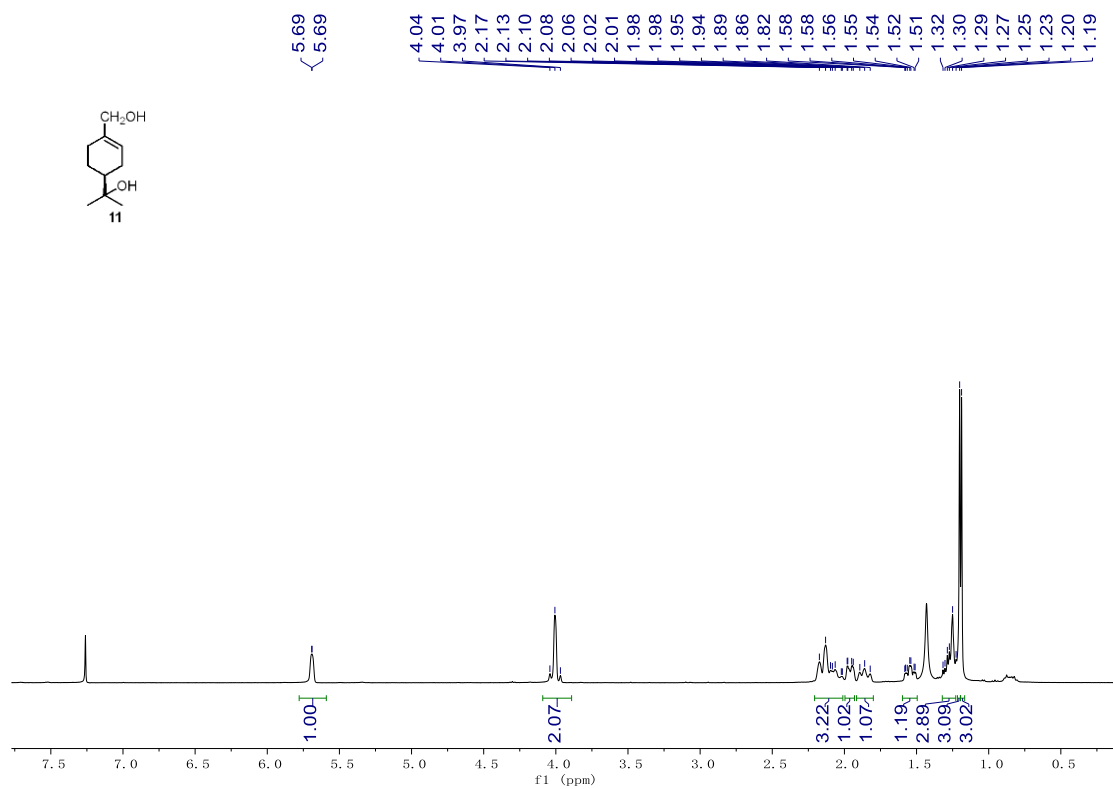
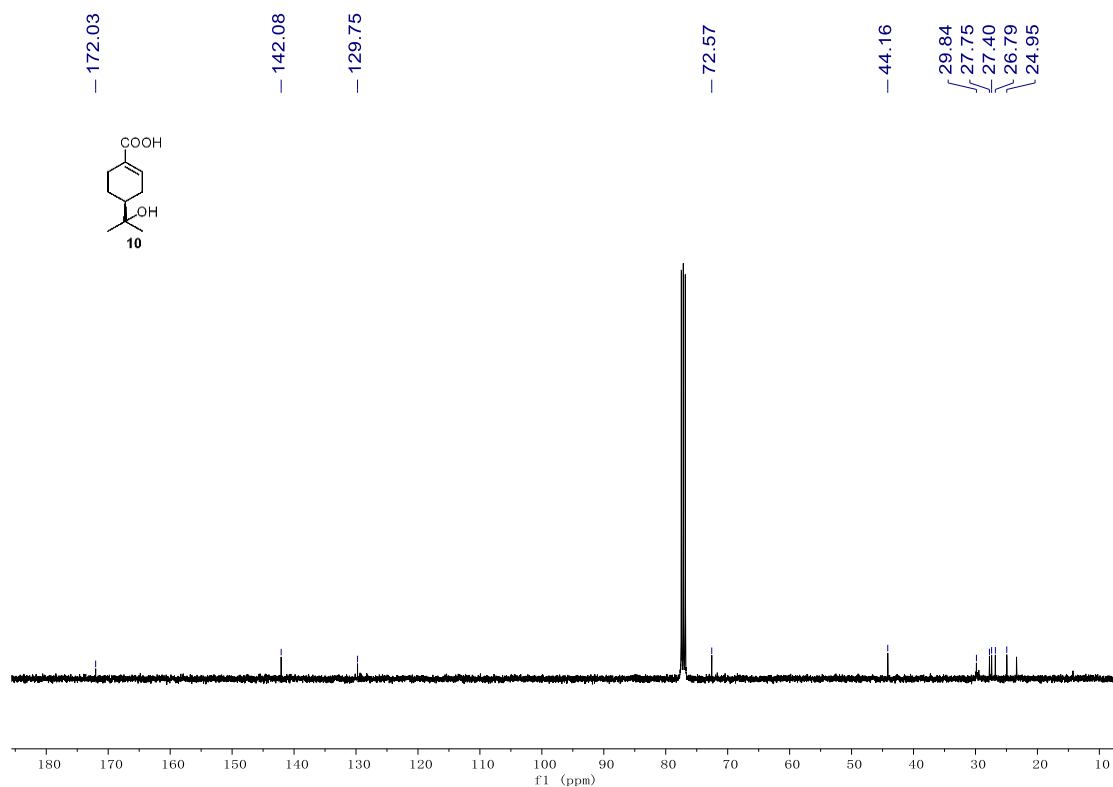


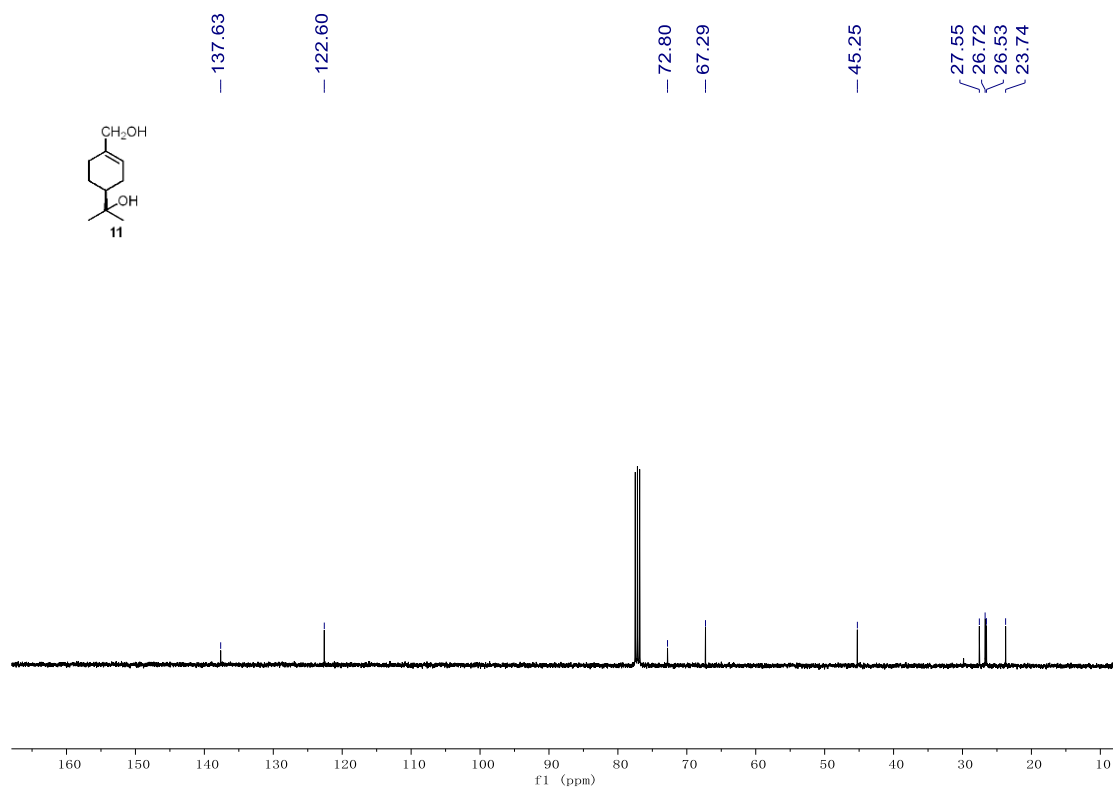








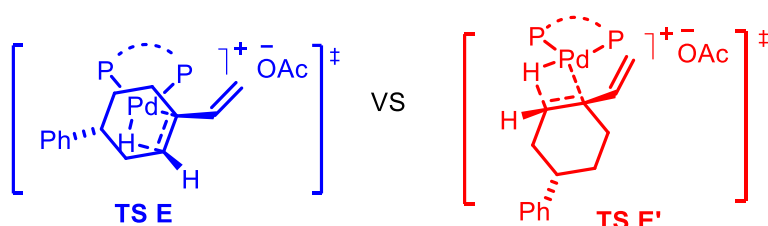




DFT Method

The calculations were performed with the Gaussian 16 program.² Geometry optimizations and frequency analysis were conducted with the Gaussian 16 software package, ω b97xd functional, and SDD basis set for Pd and def2SVP basis set for all other atoms at 323 K. Single-point energy calculations were conducted with the wb97xd functional and SDD basis set for Pd and def2-TZVP basis set for all other atoms, along with the SMD 1,4-dioxane as solvent for correction. Concentration was corrected from 1 atm to 1 mol/L by addition 1.89 kcal/mol to the Gibbs energy of each species. The intrinsic reaction coordinate (IRC) method was performed to confirm the transition states. All energetics reported throughout the text are in kcal/mol.

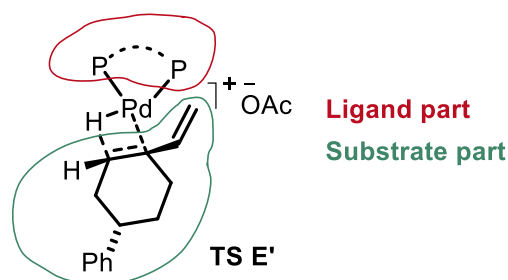
The $\Delta\Delta G^\ddagger$ between **TS E** and **TS E'** was examined by different calculation methods. These results consistently suggest that **TS E** is more energetically favored than **TS E'**.



Calculation methods	$\Delta\Delta G^\ddagger = \Delta G^\ddagger(\text{TS E}) - \Delta G^\ddagger(\text{TS E}')$
M06(SMD)/SDD(Pd)/6-311+G(d,p)//B3LYP(D3)/SDD(Pd)/6-311G(d)	-5.22 kcal/mol
wB97XD(SMD)/SDD(Pd)/6-311+G(d,p)//B3LYP(D3)/SDD(Pd)/6-311G(d)	-5.23 kcal/mol
B3LYP(D3)(SMD)/SDD(Pd)/6-311+G(d,p)//B3LYP(D3)/SDD(Pd)/6-311G(d)	-4.45 kcal/mol
B3LYP(D3)(SMD)/def2-TZVPP //B3LYP(D3)/SDD(Pd)/6-311G(d)	-4.10 kcal/mol
M06(SMD)/def2-TZVPP //B3LYP(D3)/SDD(Pd)/6-311G(d)	-4.99 kcal/mol

IGMH analysis was performed using Multiwfn software based on the calculated structures obtained from Gaussian 16 program.

The weak interactions between the ligand part and substrate part were analyzed by the energy decomposition analysis (EDA), which was performed with density-fitted sSAPT0 using SAPT module^{3,4} in the PSI4 package⁵. The jun-cc-pVDZ basis set was used⁶, which was optimal with the sSAPT0 level due to the good performance in error cancellation⁵. Using **TS E'** as an illustration, the ligand part and substrate part were defined as shown in the figure below. The analysis results are shown below (kcal/mol)



Ligand-Substrate interaction	TS E	TS E'	$\Delta\Delta E$ (TS E-TS E')
Electrostatics	-12.84	-9.81	$\Delta\Delta E_{\text{elstat}} = -3.03$
Exchange	32.57	31.62	$\Delta\Delta E_{\text{exchange}} = 0.95$
Induction	-5.31	-3.76	$\Delta\Delta E_{\text{indu}} = -1.55$
Dispersion	-30.68	-31.66	$\Delta\Delta E_{\text{disp}} = 0.98$
Total sSAPT0	-16.25	-13.61	$\Delta\Delta E_{\text{total}} = -2.64$

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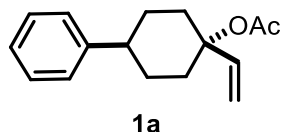
[3] Hohenstein, E. G.; Sherrill, C. D. Density fitting and Cholesky decomposition approximations in symmetry-adapted perturbation theory: Implementation and application to probe the nature of π - π interactions in linear acenes. *J. Chem. Phys.* **2010**, *132*, 184111.

[4] Hohenstein, E. G.; Parrish, R. M.; Sherrill, C. D.; Turney, J. M.; Schaefer III, H. F. Large-scale symmetry-adapted perturbation theory computations via density fitting and Laplace transformation techniques: Investigating the fundamental forces of DNA-intercalator interactions. *J. Chem. Phys.* **2011**, *135*, 174107.

[5] Turney, J. M.; Simmonett, A. C.; Parrish, R. M.; Hohenstein, E. G.; Evangelista, F. A.; Fermann, J. T.; Mintz, B. J.; Burns, L. A.; Wilke, J. J.; Abrams, M. L.; Russ, N. J.; Leininger, M. L.; Janssen, C. L.; Seidl, E. T.; Allen, W. D.; Schaefer, H. F.; King, R. A.; Valeev, E. F.; Sherrill, C. D.; Crawford, T. D. Psi4: an open-source *ab initio* electronic structure program. *WIREs Comp. Mol. Sci.* **2012**, *2*, 556-565.

[6] Kendall, R. A.; Dunning, T. H.; Harrison, R. J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992**, *96*, 6796-6806.

Coordinates and Energies of Stationary Points



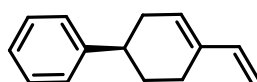
Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -771.852837 a.u.

Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.274447 a.u.

Gibbs free energy at 323 K ((ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -771.578390 a.u.

C	-1.11949500	-0.24099100	-1.04829900
C	-1.72486900	-0.03818600	0.34612300
C	-0.91603200	-0.83855000	1.37677000
C	0.56609300	-0.46526000	1.36143200
C	1.18228900	-0.69186300	-0.03055900
C	0.37982200	0.07988300	-1.09287900
H	-1.03821600	-1.90096400	1.14228900
H	-1.66372200	0.34421500	-1.78644700
H	0.68780900	0.58373100	1.65019500
H	1.10713200	-1.05630300	2.10580100
H	1.08573600	-1.76164200	-0.25778200
H	0.53518000	1.15213100	-0.94888700
H	0.76977100	-0.15562500	-2.08748600
C	2.65549700	-0.34826700	-0.06938900
C	3.60737300	-1.32354100	-0.37491000
C	3.10301200	0.95117900	0.19667000
C	4.96605800	-1.01694900	-0.41476600

H	3.27921400	-2.33753300	-0.58480800
C	4.45821300	1.26320300	0.15862300
H	2.38555700	1.72959900	0.43607100
C	5.39654500	0.27916400	-0.14759200
H	5.68718000	-1.79170500	-0.65473500
H	4.78346500	2.27719100	0.36833700
H	6.45353200	0.52209000	-0.17749800
C	-1.86360200	1.39595200	0.80294200
C	-1.73808200	2.48879000	0.06171600
H	-1.87009400	3.47531800	0.49310900
H	-1.52127900	2.45047900	-0.99901500
H	-2.10850300	1.49527200	1.85940300
H	-1.27468600	-1.29352900	-1.31069300
H	-1.35006500	-0.68478600	2.36903200
O	-3.05823300	-0.66608300	0.43611000
C	-4.06728100	-0.26962100	-0.37188300
O	-3.97225800	0.53324500	-1.26371200
C	-5.34233200	-0.98014400	0.01735600
H	-5.17173100	-2.05353000	0.11552700
H	-5.68220000	-0.61437100	0.98981100
H	-6.10939500	-0.78612900	-0.72954200



2a

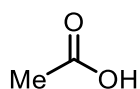
Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -542.799220 a.u.

Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.216024 a.u

Gibbs free energy at 323 K (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -542.583206 a.u.

C	-2.08787300	-0.80173100	-0.70832900
C	-2.73945500	0.17121100	-0.05617300
C	-1.99293000	1.26394000	0.67983600
C	-0.50665100	1.31833100	0.32204100
C	0.10773900	-0.09114000	0.33495100
C	-0.59385700	-0.96025000	-0.72373100
H	-2.11515100	1.11511200	1.76125700
H	-2.66282200	-1.52576900	-1.28073000
H	-0.38676900	1.75608900	-0.67518000
H	0.03021600	1.96914200	1.01771400
H	-0.11275200	-0.53084500	1.31552100
H	-0.20698600	-0.71541000	-1.72220000
H	-0.32952900	-2.01270600	-0.56686700
C	1.61049200	-0.08289800	0.16331900
C	2.44118800	-0.63710800	1.13987900

C	2.20840100	0.47633600	-0.97208200
C	3.82678200	-0.63606400	0.99274100
H	1.99545900	-1.07564500	2.02806100
C	3.59129500	0.48137900	-1.12423100
H	1.58816800	0.91519100	-1.74721100
C	4.40721900	-0.07585400	-0.14126200
H	4.45167200	-1.07295000	1.76506700
H	4.03392200	0.92143600	-2.01213900
H	5.48570500	-0.07258900	-0.25954300
C	-4.20914000	0.24769000	-0.02436800
C	-5.04296100	-0.78939800	0.07233000
H	-6.11904400	-0.65331400	0.07112500
H	-4.67754100	-1.80736000	0.16467200
H	-4.63100700	1.25257800	-0.05510700
H	-2.46505000	2.23037000	0.46602900

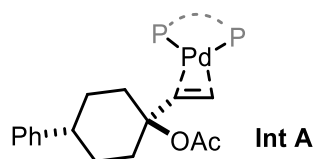


Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -229.036680 a.u.

Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.032005 a.u

Gibbs free energy at 323 K ((ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane))): -229.004675 a.u.

C	0.09187000	0.12875500	0.00001600
O	0.63863700	1.20048500	-0.00000300
C	-1.39285400	-0.11458900	-0.00001300
H	-1.67658100	-0.69764600	-0.87888800
H	-1.67667200	-0.69662000	0.87952100
H	-1.91870600	0.83715600	-0.00058200
O	0.78078300	-1.04013000	0.00000100
H	1.72250700	-0.81072800	-0.00005200



Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3542.384601 a.u.

Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.952408 a.u

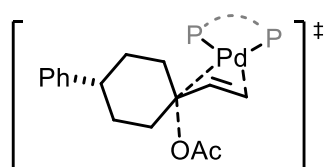
Gibbs free energy at 323 K ((ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane))): -3541.432193 a.u.

Pd	-0.42369100	0.11701000	0.39727800
P	1.10519600	-1.00731700	-1.02969900
P	-2.14567600	-1.41166000	0.93593300
O	-0.06629500	0.66874300	-3.49940100
O	-3.87668400	1.24007200	-0.28428500
N	0.16714200	2.66634500	-2.45715600
N	-2.48707800	1.31118000	-2.08220500

C	-3.47142800	4.98982500	-2.41397100
C	-2.28428300	5.46387900	-3.25406300
C	-0.99746000	4.75606100	-2.82689300
C	-1.12092500	3.22663300	-2.86187900
C	-2.31673900	2.76161800	-2.01050900
C	-3.60150100	3.46826200	-2.47432000
C	-3.54194100	-0.79333100	-1.44942600
C	-3.26584100	-1.78742300	-0.48961300
C	-3.71966300	-3.08803800	-0.72596600
C	-4.40612100	-3.41164200	-1.89441100
C	-4.63914100	-2.43495000	-2.85565000
C	-4.20994400	-1.13010400	-2.62659800
C	2.06250400	1.17335000	-2.51537200
C	2.43816900	0.03287600	-1.77562000
C	3.79406300	-0.19497500	-1.54464000
C	4.76638100	0.67784800	-2.03116000
C	4.39138200	1.80104800	-2.75558200
C	3.03918100	2.04672800	-2.99111900
C	0.65158400	-2.00263000	-2.52502000
C	-0.65513800	-2.46140100	-2.68084400
C	-1.01528600	-3.23307400	-3.78266400
C	-0.06866000	-3.54745000	-4.75244500
C	1.23534000	-3.07364000	-4.61920700
C	1.59194500	-2.30383000	-3.51719300
C	2.00382100	-2.26838200	-0.01470800
C	1.75451200	-2.27913300	1.36178400
C	2.34280200	-3.22922000	2.18964700
C	3.18901400	-4.19241400	1.64909100
C	3.43292300	-4.20452900	0.27640200
C	2.84061200	-3.25377300	-0.55000200
C	-3.28930600	-0.90895000	2.27802800
C	-2.73570400	-0.50720700	3.50022100
C	-3.55150400	-0.08076200	4.54157500
C	-4.93409400	-0.03804900	4.36858100
C	-5.49065900	-0.42645200	3.15323400
C	-4.67423900	-0.86072200	2.11176200
C	-1.60902400	-3.09833600	1.47117900
C	-1.86529700	-3.60526000	2.74875700
C	-1.34628100	-4.84014200	3.13822200
C	-0.57887200	-5.59241800	2.25475600
C	-0.33241600	-5.10323200	0.97316600
C	-0.83351200	-3.86657000	0.59147000
C	0.62437800	1.45633600	-2.85677400
C	-3.28485200	0.66985100	-1.19610700

H	-3.33346300	5.30360600	-1.37187300
H	-4.39690300	5.46043800	-2.75869500
H	-2.47975100	5.25375300	-4.31281600
H	-2.15380800	6.54702900	-3.17084500
H	-0.74093600	5.06248600	-1.80368900
H	-0.16001000	5.05333400	-3.46513000
H	-1.29114900	2.89803500	-3.89263400
H	-3.81841800	3.15149200	-3.50220700
H	-4.42432500	3.12168300	-1.84876200
H	-1.87767000	0.78592300	-2.70222200
H	-3.51186600	-3.86395700	-0.00049600
H	-4.74551500	-4.42980700	-2.05320700
H	-5.15586700	-2.68167500	-3.77699300
H	-4.40368800	-0.35598600	-3.36092600
H	4.10412100	-1.04356300	-0.95288400
H	5.80950000	0.48087800	-1.81546700
H	5.14065500	2.48909700	-3.13203400
H	2.73788000	2.91743400	-3.56457500
H	-1.40769200	-2.18886600	-1.95885300
H	-2.04039000	-3.57174000	-3.88049800
H	-0.34655300	-4.14369100	-5.61553200
H	1.97527600	-3.29375800	-5.38221800
H	2.59879300	-1.90911000	-3.44987300
H	1.06525400	-1.55045800	1.77311500
H	2.11984200	-3.22841000	3.25082600
H	3.64310600	-4.94139800	2.28950000
H	4.08028900	-4.96154700	-0.15448700
H	3.01907900	-3.29568900	-1.61694400
H	-1.65910600	-0.52154500	3.63297700
H	-3.10573800	0.23960500	5.47699800
H	-5.57236400	0.30851400	5.17466400
H	-6.56522500	-0.38323000	3.00850600
H	-5.11486100	-1.14206200	1.16401300
H	-2.47469800	-3.04238900	3.44369700
H	-1.55304900	-5.21430800	4.13584500
H	-0.17402000	-6.55130600	2.56119200
H	0.27509500	-5.66924700	0.27569000
H	-0.61249300	-3.50035300	-0.40074700
H	0.74325500	3.20095000	-1.82613400
H	-2.13178100	3.03124300	-0.96664200
C	1.47029800	2.08307700	3.05847000
C	0.93669500	2.94533400	1.90548100
C	2.09958100	3.53523900	1.09406400
C	3.15802600	2.51759100	0.68541500

C	3.71785400	1.79355400	1.92351700
C	2.54850100	1.09085700	2.61592300
H	2.56488600	4.30844800	1.71308200
H	0.65247900	1.56024200	3.54746500
H	2.73363900	1.77691200	0.00977300
H	3.95662100	3.02103900	0.13485500
H	4.09970100	2.56451400	2.60916100
H	2.10425700	0.36970200	1.92625600
H	2.89254200	0.52871400	3.48991700
C	4.89043100	0.89996000	1.56898700
C	6.08889000	1.48510300	1.14156400
C	4.82762200	-0.49256500	1.62775300
C	7.17788800	0.70807200	0.76381000
H	6.16635600	2.56800900	1.10211800
C	5.91423600	-1.27939700	1.24651900
H	3.92224900	-0.98265500	1.95459600
C	7.09203700	-0.68405700	0.80654000
H	8.09592000	1.18679400	0.43722400
H	5.82700800	-2.35974600	1.29237700
H	7.93932500	-1.29412100	0.51054100
C	-0.14240000	2.33605700	1.03365100
C	-1.27288200	1.71006300	1.55913800
H	-2.24363200	1.83310300	1.09246300
H	-1.31545600	1.47682000	2.61252600
H	-0.27136600	2.88776500	0.10820300
H	1.89295400	2.76002400	3.80845200
H	1.69252100	4.05460800	0.21893300
O	0.33489400	4.22084200	2.44535600
C	-0.57307600	4.24842800	3.43228200
O	-0.91728600	3.31438300	4.11551400
C	-1.14271700	5.64332400	3.57070500
H	-0.37563600	6.40343300	3.41993800
H	-1.90872800	5.78616600	2.80276000
H	-1.60554300	5.75453300	4.54983600



TS B

Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3542.359577 a.u.

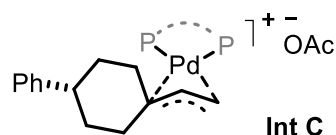
Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.950131 a.u

Gibbs free energy at 323 K (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3541.409446 a.u.

Pd	0.52706100	0.21720700	-0.25609400
P	-0.95955700	-1.19215600	1.00360700
P	2.33020200	-1.07412500	-0.95350800
O	0.00952100	0.44311000	3.55323600
O	3.85709300	1.49313900	0.54894300
N	-0.31554900	2.49471400	2.64454000
N	2.42309100	1.35306000	2.30747300
C	3.15141800	5.04942700	2.95926800
C	1.89639600	5.38199000	3.76851700
C	0.68005900	4.62944400	3.22534200
C	0.90771700	3.11370100	3.15683900
C	2.16924100	2.79221100	2.33687400
C	3.38216300	3.53897600	2.91484500
C	3.59134500	-0.64112200	1.53564700
C	3.38897100	-1.54974000	0.47897100
C	3.89610500	-2.84623700	0.59878300
C	4.56089000	-3.25191800	1.75397100
C	4.71727200	-2.36459100	2.81293600
C	4.23707400	-1.06242400	2.69751300
C	-2.10828400	0.88278100	2.52662000
C	-2.37504200	-0.23424500	1.70923600
C	-3.70187200	-0.53787200	1.40644700
C	-4.75213400	0.23166000	1.90565400
C	-4.48445000	1.32345900	2.71999700
C	-3.16274300	1.64997800	3.02077900
C	-0.50895500	-2.23753300	2.45283200
C	0.81624900	-2.62984400	2.63932400
C	1.17213100	-3.43800200	3.71567600
C	0.20506300	-3.85436600	4.62537800
C	-1.11768400	-3.44773900	4.45984700
C	-1.47268700	-2.64137900	3.38369200
C	-1.75735200	-2.39355600	-0.14490500
C	-1.58265000	-2.19269000	-1.51850100
C	-2.15363600	-3.05911000	-2.44307200
C	-2.89636400	-4.15185500	-2.00465600
C	-3.05621600	-4.37714200	-0.63850300
C	-2.48874200	-3.50523900	0.28669600
C	3.48294200	-0.41783100	-2.20915400
C	2.96336800	0.14822100	-3.37920700
C	3.81303200	0.70742600	-4.32710700
C	5.19029200	0.68819000	-4.12302800
C	5.71363000	0.11843200	-2.96352000
C	4.86598200	-0.42634500	-2.00419900
C	1.77760600	-2.68962900	-1.64764900

C	1.87904700	-2.96610400	-3.01436500
C	1.35834400	-4.15016500	-3.53440800
C	0.74370900	-5.07687700	-2.69860000
C	0.64805300	-4.81386300	-1.33384700
C	1.14908500	-3.62727700	-0.81681000
C	-0.70759400	1.23514900	2.94513000
C	3.27685100	0.82638400	1.39812600
H	3.04330800	5.43266300	1.93742000
H	4.02506200	5.55031300	3.38601300
H	2.05438600	5.10582600	4.81830900
H	1.69794700	6.45756900	3.75613700
H	0.45163700	4.99677300	2.21572300
H	-0.20355300	4.82425400	3.84052700
H	1.05232400	2.72125700	4.16906200
H	3.57446500	3.15809200	3.92572700
H	4.25316800	3.29503100	2.30594500
H	1.83941300	0.74915800	2.87841600
H	3.75133800	-3.55320100	-0.20782400
H	4.94558400	-4.26361300	1.82462600
H	5.21864000	-2.67796900	3.72231500
H	4.37643600	-0.35600300	3.50828100
H	-3.92669500	-1.37059600	0.75557200
H	-5.77019100	-0.01431000	1.62765900
H	-5.29471200	1.93102200	3.10723000
H	-2.94587100	2.50149700	3.65740300
H	1.58332800	-2.27820500	1.96698900
H	2.20961900	-3.72510800	3.84303400
H	0.48102000	-4.47909200	5.46843500
H	-1.87400700	-3.74941400	5.17712700
H	-2.49728000	-2.30168000	3.28806600
H	-0.97096700	-1.36709600	-1.86083600
H	-1.99549100	-2.89122400	-3.50220000
H	-3.33538100	-4.83545200	-2.72364600
H	-3.61989200	-5.23660100	-0.29062700
H	-2.60467200	-3.70324000	1.34489300
H	1.89876700	0.20733100	-3.56089000
H	3.37086700	1.18857000	-5.19086500
H	5.85502300	1.13339300	-4.85619600
H	6.78536500	0.11496100	-2.79364100
H	5.27974800	-0.83391300	-1.09052100
H	2.36906000	-2.26420200	-3.67602500
H	1.44267700	-4.34593100	-4.59820100
H	0.33701600	-5.99597600	-3.10675400
H	0.15708400	-5.51808600	-0.67173100

H	1.04564300	-3.43756200	0.24210800
H	-0.91608000	3.04511200	2.05059100
H	2.01807000	3.12812000	1.30695500
C	-1.56518500	1.53432200	-2.52400700
C	-1.13412300	2.44494100	-1.41588700
C	-2.22153900	3.35157400	-0.93345700
C	-3.52896300	2.61117100	-0.61146600
C	-3.99402300	1.71281900	-1.77473400
C	-2.84790600	0.77707800	-2.16047700
H	-2.37729700	4.06372300	-1.75371500
H	-0.76752000	0.85988200	-2.82393900
H	-3.38306400	1.98786600	0.27151800
H	-4.29957100	3.34131100	-0.35215100
H	-4.20672800	2.36380600	-2.63407800
H	-2.65539200	0.10533000	-1.32230700
H	-3.13196400	0.14702800	-3.00783200
C	-5.27761000	0.97617500	-1.41867200
C	-6.41386300	1.70256000	-1.04099300
C	-5.37228000	-0.41886900	-1.43044600
C	-7.58941600	1.06422600	-0.66048600
H	-6.37895500	2.78742500	-1.04490400
C	-6.54785000	-1.06508300	-1.05061700
H	-4.52274300	-1.02117000	-1.72579700
C	-7.66004200	-0.32841100	-0.65535100
H	-8.45365800	1.65381900	-0.37141800
H	-6.58819700	-2.14970700	-1.06513800
H	-8.57519500	-0.83025400	-0.35881700
C	0.11581500	2.49396000	-0.82609000
C	1.27503300	1.85065100	-1.34704200
H	2.24136200	2.14885400	-0.95603700
H	1.25702100	1.65811100	-2.41376800
H	0.22945600	3.17385900	0.01250300
H	-1.74475000	2.17793600	-3.38603400
H	-1.89106700	3.93949300	-0.07081900
O	-0.29863400	3.96806700	-3.44905900
C	0.49832300	3.43798900	-4.26663800
O	0.83613800	2.22252900	-4.32439000
C	1.16448200	4.37432400	-5.29132700
H	0.64094000	5.32915300	-5.35997300
H	2.19677200	4.56475700	-4.97784000
H	1.20723000	3.89690100	-6.27347700



Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3542.384477 a.u.

Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.949042 a.u.

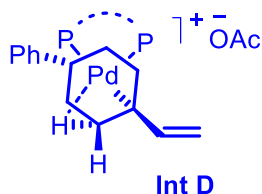
Gibbs free energy at 323 K ((ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3541.435435 a.u.

Pd	0.44602700	-0.14366100	-0.62834300
P	-0.68321200	-0.64421700	1.47707600
P	1.99953200	-1.82752500	-0.98162900
O	0.86783700	1.51242500	2.38969700
O	3.98549000	0.96124000	-1.25951900
N	0.50669400	3.40661600	1.17705100
N	2.95490500	1.74260000	0.62488500
C	4.15793400	5.29197000	-0.10750300
C	3.29145500	5.99227100	0.93971100
C	1.88830100	5.38866200	0.95034800
C	1.89548600	3.87683300	1.21400400
C	2.81808400	3.14696500	0.21544800
C	4.21389900	3.79170400	0.17395300
C	3.89610200	-0.48416200	0.61210600
C	3.41087800	-1.73565100	0.19181300
C	3.91715600	-2.89782500	0.78259600
C	4.86684100	-2.82597700	1.79778100
C	5.31070600	-1.58567500	2.24442500
C	4.82859500	-0.42390000	1.64825100
C	-1.37763600	2.05442700	1.91402300
C	-1.84304300	0.72067600	1.92239200
C	-3.19522300	0.47495500	2.16476600
C	-4.08288800	1.52576200	2.39038600
C	-3.62930800	2.83714500	2.33952900
C	-2.28190200	3.10015500	2.09986600
C	0.10796900	-1.06084900	3.08671400
C	1.43039600	-1.50151800	3.13166500
C	2.02447400	-1.83863400	4.34443300
C	1.30470400	-1.72593600	5.53033400
C	-0.00706600	-1.25722200	5.49690500
C	-0.60121600	-0.92204300	4.28411200
C	-1.78574000	-2.10179900	1.19359900
C	-1.93579300	-2.54780400	-0.12318700
C	-2.73208400	-3.64658400	-0.42521200
C	-3.38091000	-4.33291200	0.59614600
C	-3.21844600	-3.91864400	1.91736700
C	-2.42505200	-2.81398100	2.21528000

C	2.74448600	-1.92001500	-2.64847300
C	1.90453100	-2.05894100	-3.76170400
C	2.43665200	-2.10993300	-5.04446700
C	3.81450000	-2.00317200	-5.23040800
C	4.65096200	-1.84772500	-4.12956700
C	4.12156500	-1.80670100	-2.84178600
C	1.31805600	-3.51992800	-0.70742300
C	1.22709800	-4.47041400	-1.72916400
C	0.63495500	-5.70986600	-1.48987900
C	0.14039500	-6.02286900	-0.22796300
C	0.24937700	-5.09145400	0.80189700
C	0.82542300	-3.85207000	0.56145500
C	0.09936500	2.32057300	1.82847600
C	3.58000200	0.80797400	-0.10835400
H	3.73474400	5.46500300	-1.10366800
H	5.17159700	5.70537100	-0.11799300
H	3.75927700	5.89261000	1.92854600
H	3.22488800	7.06475600	0.73261800
H	1.41787400	5.55530300	-0.02016200
H	1.25533400	5.86858500	1.70128300
H	2.28283800	3.68185600	2.22242100
H	4.69525300	3.61981100	1.14569300
H	4.81051000	3.26957600	-0.57574400
H	2.46914300	1.47010800	1.47958100
H	3.54792500	-3.86503400	0.46730000
H	5.24555900	-3.73875300	2.24473200
H	6.03388300	-1.51984100	3.05016300
H	5.18262700	0.54646500	1.97738900
H	-3.57338500	-0.53817200	2.15109500
H	-5.13108900	1.31046400	2.56688300
H	-4.31851800	3.66250500	2.47944400
H	-1.93741500	4.12285700	2.03014000
H	2.01920200	-1.54303200	2.22809200
H	3.05619900	-2.17202200	4.35507800
H	1.76787900	-1.98187600	6.47747900
H	-0.56658800	-1.13828200	6.41904300
H	-1.60569500	-0.51510500	4.27654700
H	-1.38795600	-2.04364400	-0.91093300
H	-2.83168800	-3.97267100	-1.45436200
H	-3.99975000	-5.19389500	0.36731900
H	-3.70832600	-4.45911800	2.72073600
H	-2.29279800	-2.51948500	3.24853200
H	0.83030200	-2.13070900	-3.62361800
H	1.77669400	-2.22050300	-5.89828000

H	4.23089800	-2.03008200	-6.23161200
H	5.72173800	-1.74737700	-4.26955100
H	4.77697100	-1.65939800	-1.99434300
H	1.62743200	-4.25815700	-2.71086400
H	0.57055000	-6.43310400	-2.29607900
H	-0.32470300	-6.98583100	-0.04643100
H	-0.13670600	-5.31440700	1.78986600
H	0.89271200	-3.14743600	1.37625600
H	-0.19148700	4.02137500	0.68236900
H	2.36344700	3.20205000	-0.77680300
C	-1.90806400	0.41301300	-3.09585800
C	-1.35973900	1.47095800	-2.17456400
C	-2.38159100	2.43306500	-1.65529500
C	-3.64068400	1.74222500	-1.12725800
C	-4.25420200	0.75636500	-2.13289400
C	-3.18891300	-0.25494400	-2.58010800
H	-2.65181800	3.08253900	-2.50327800
H	-1.16219700	-0.34504600	-3.33556700
H	-3.38694800	1.20118200	-0.21649600
H	-4.37799600	2.49536600	-0.83971300
H	-4.57709000	1.32447200	-3.01522600
H	-2.93385900	-0.89142100	-1.73378500
H	-3.59750700	-0.91393100	-3.35239800
C	-5.47086700	0.07179900	-1.54443300
C	-6.75461300	0.37257300	-2.00384800
C	-5.34255200	-0.85405600	-0.50133600
C	-7.87986200	-0.22891100	-1.44251300
H	-6.87514300	1.08976000	-2.81069000
C	-6.46146900	-1.45984300	0.06028500
H	-4.36154700	-1.11207200	-0.12299800
C	-7.73730400	-1.14846400	-0.40741700
H	-8.86761800	0.02104600	-1.81640300
H	-6.33297400	-2.17969500	0.86252400
H	-8.61137900	-1.61995800	0.02976700
C	-0.01082900	1.71771200	-2.00146800
C	1.01866300	0.82448200	-2.43477400
H	2.04847300	1.15774400	-2.37835500
H	0.82949500	0.15662600	-3.26488700
H	0.25604800	2.63756100	-1.48873800
H	-2.13529600	0.93010700	-4.04066800
H	-1.96231300	3.09492100	-0.90079800
O	0.10088700	4.82550700	-1.77074700
C	-0.87179600	5.34517100	-1.18593400
O	-1.27372900	5.04832000	-0.01369900

C	-1.69500100	6.40633400	-1.91928100
H	-1.19457700	6.73283900	-2.83108300
H	-2.67234100	5.98672500	-2.18057200
H	-1.88118800	7.26046100	-1.26410400



Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3542.345226 a.u.

Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.945924 a.u

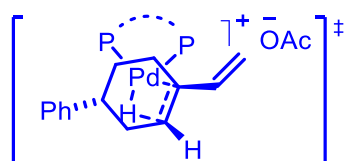
Gibbs free energy at 323 K (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3541.399302 a.u.

Pd	-0.64223300	0.01965600	-0.97122800
P	-1.30620700	1.98249200	0.11632400
P	-1.89441500	-1.88650900	-0.12253800
O	0.74307400	1.73342600	2.64973400
O	0.72619200	-2.23228700	0.83643200
N	2.71321200	1.57028200	1.50560700
N	1.38267900	-0.89867800	2.56422800
C	5.07706500	-1.82402700	2.67411700
C	5.61528700	-0.42121600	2.96286900
C	4.85932000	0.63273900	2.15413100
C	3.34219500	0.58277500	2.38574900
C	2.79357700	-0.84133600	2.17536900
C	3.58106000	-1.88630700	2.97885800
C	-0.87578800	-1.77902200	2.51070800
C	-1.99191000	-2.08715800	1.70615400
C	-3.20770500	-2.38858000	2.32379500
C	-3.32621700	-2.38390300	3.71119400
C	-2.23247800	-2.05323300	4.50148700
C	-1.01369500	-1.75929400	3.89907500
C	1.13861800	3.26480900	0.86065100
C	-0.09455100	3.35996300	0.17292000
C	-0.34828700	4.50612900	-0.58891100
C	0.56486100	5.55695700	-0.63909100
C	1.76754800	5.46047900	0.03911700
C	2.04957200	4.31499300	0.77541700
C	-2.08253600	1.95128600	1.78449100
C	-3.07090900	1.00413600	2.05074800
C	-3.77109700	1.02822900	3.25229800
C	-3.49160100	2.00731300	4.20075900
C	-2.51217300	2.96259300	3.93702000
C	-1.81002100	2.93733600	2.73689200
C	-2.73787600	2.67462500	-0.82886500

C	-3.06085000	2.17809700	-2.09261300
C	-4.16109000	2.66767500	-2.79251800
C	-4.95339200	3.66516100	-2.23226800
C	-4.64453800	4.16373500	-0.96684300
C	-3.54909000	3.66966500	-0.26770900
C	-1.32303900	-3.48868400	-0.81448800
C	-1.29667100	-3.62670300	-2.20621300
C	-0.84976000	-4.80789200	-2.78955800
C	-0.43350600	-5.86700200	-1.98551400
C	-0.47431300	-5.73887100	-0.59930300
C	-0.91207200	-4.55384100	-0.01385100
C	-3.66238100	-1.93387000	-0.64884300
C	-4.35716600	-3.14164300	-0.80313800
C	-5.69277900	-3.14109300	-1.19258200
C	-6.35268500	-1.93715900	-1.43899900
C	-5.66830800	-0.73342600	-1.29838200
C	-4.33157000	-0.73531000	-0.90833700
C	1.51016700	2.10255900	1.74597000
C	0.48054800	-1.62968300	1.88532700
H	5.24371200	-2.07706500	1.62066700
H	5.61189200	-2.57469800	3.26483000
H	5.51982400	-0.21007900	4.03632700
H	6.68268400	-0.36074000	2.72940000
H	5.05985500	0.50149800	1.08798300
H	5.21338100	1.63954300	2.38763700
H	3.12739800	0.87183300	3.42382100
H	3.40942500	-1.71345500	4.04906200
H	3.17252900	-2.87344000	2.74509900
H	1.03061500	-0.09681600	3.08367300
H	-4.07870000	-2.60945700	1.72081500
H	-4.27898600	-2.62930000	4.16849900
H	-2.32043800	-2.03511400	5.58213100
H	-0.14592300	-1.54225300	4.50959400
H	-1.26677600	4.58552400	-1.15191400
H	0.34023700	6.43035600	-1.24174500
H	2.50693000	6.24868200	-0.03135100
H	3.00695400	4.21682100	1.26921500
H	-3.31152900	0.24758600	1.31992000
H	-4.52947500	0.27825500	3.44324500
H	-4.03482100	2.02810700	5.13990300
H	-2.28561700	3.72833400	4.67146300
H	-1.04166100	3.67311300	2.54853300
H	-2.46072700	1.38302200	-2.51398900
H	-4.40031500	2.26258000	-3.77003900

H	-5.81150700	4.04894300	-2.77393600
H	-5.26282600	4.93489400	-0.51978300
H	-3.32722200	4.05223400	0.72112100
H	-1.63296200	-2.81117700	-2.83872700
H	-0.82378300	-4.89977700	-3.87010200
H	-0.07477800	-6.78514000	-2.43758000
H	-0.15190200	-6.56063700	0.03152000
H	-0.91393900	-4.44877500	1.06330100
H	-3.84987100	-4.08240300	-0.62465000
H	-6.21856300	-4.08305000	-1.30878600
H	-7.39304300	-1.94091000	-1.74668000
H	-6.16285900	0.21087500	-1.49908900
H	-3.80836100	0.20505300	-0.82194900
H	3.30372300	1.96801200	0.73588000
H	2.86698800	-1.09612800	1.12057500
C	2.06011800	1.15138600	-1.87937200
C	0.71157200	0.88208600	-2.48647200
C	0.51215600	-0.50943000	-2.99274600
C	1.79920600	-1.25512900	-3.41443800
C	2.99462800	-1.12759700	-2.43090400
C	2.69662600	-0.10479500	-1.31933800
H	-0.23566800	-0.55205100	-3.78614400
H	2.00399100	1.94333200	-1.13870900
H	1.55408400	-2.30251800	-3.59982700
H	2.08611600	-0.82921200	-4.37974100
H	3.83572900	-0.72621700	-3.00451700
H	2.03970800	-0.56487000	-0.57851500
H	3.62437700	0.15949200	-0.81522600
H	0.07136400	-1.20312700	-2.17442900
C	3.45785600	-2.42270600	-1.79808800
C	4.82468800	-2.62781700	-1.58288200
C	2.55886400	-3.37226800	-1.30739900
C	5.28467200	-3.74743100	-0.89541100
H	5.53453600	-1.89169500	-1.94945900
C	3.01393100	-4.49224700	-0.61771000
H	1.49262700	-3.22899500	-1.42123300
C	4.37681000	-4.68526800	-0.40778300
H	6.34983700	-3.88583800	-0.73942400
H	2.29304800	-5.20430400	-0.23303700
H	4.72975900	-5.55719900	0.13362000
C	0.09369500	1.97512100	-3.22986600
C	0.57171500	3.22848500	-3.26071000
H	0.06382900	3.98805300	-3.84621500
H	1.47534400	3.52925300	-2.73814600

H	-0.79292600	1.72980000	-3.80949600
H	2.70680400	1.58124800	-2.65327900
C	4.49885100	3.30154400	-1.30350600
O	3.52334800	3.84786500	-1.85188100
O	4.47122100	2.50398400	-0.31026100
C	5.90040200	3.57361600	-1.87077900
H	6.59420500	3.82591400	-1.06475400
H	6.28210600	2.66306000	-2.34435200
H	5.87838600	4.37466700	-2.61045500



TS E

Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3542.326331 a.u.

Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.941004 a.u

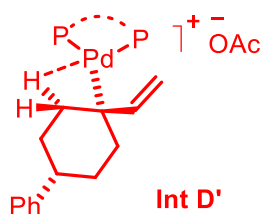
Gibbs free energy at 323 K (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3541.385327 a.u.

Pd	0.72330000	0.15395900	-1.04416700
P	1.47303900	-1.87548000	0.12318700
P	1.80066700	2.02088400	-0.18043700
O	-0.51980300	-1.81789100	2.62377600
O	-0.75641900	2.19137700	0.94797300
N	-2.54492600	-1.74807200	1.56627400
N	-1.29294200	0.74636300	2.62897400
C	-5.01740000	1.51092200	2.89346200
C	-5.48261700	0.07890400	3.16653200
C	-4.71075000	-0.92231100	2.30720700
C	-3.19062400	-0.81103500	2.49029100
C	-2.71444500	0.64135100	2.29375600
C	-3.51578400	1.63238800	3.14862800
C	0.94552100	1.65790600	2.49437300
C	2.00428600	2.04402500	1.64895100
C	3.24745800	2.34284900	2.21077700
C	3.44927400	2.25502400	3.58519500
C	2.41562500	1.83812900	4.41407700
C	1.17015700	1.54859300	3.86728000
C	-0.88827300	-3.33198000	0.82939300
C	0.35763900	-3.34327100	0.16023600
C	0.69273800	-4.46623500	-0.60231600
C	-0.15997000	-5.56535100	-0.68349800
C	-1.38316300	-5.54326700	-0.03500300
C	-1.74230900	-4.42632100	0.71113500

C	2.35468900	-1.88212700	1.73869300
C	3.38482000	-0.96004200	1.93046000
C	4.16647700	-1.00136700	3.07974300
C	3.92554100	-1.96826000	4.05177800
C	2.90291700	-2.89515900	3.86261100
C	2.12198500	-2.85677700	2.71139500
C	2.87946300	-2.45050700	-0.93965000
C	2.98291900	-2.00753900	-2.26034900
C	4.04204800	-2.40979300	-3.06975900
C	5.01670100	-3.26567200	-2.56438300
C	4.92581100	-3.71316900	-1.24695200
C	3.86777300	-3.30790200	-0.43975300
C	1.12926500	3.66514900	-0.64566800
C	0.93744200	3.95458700	-1.99832300
C	0.44168000	5.19349200	-2.39045500
C	0.13544000	6.15632500	-1.43099600
C	0.33694500	5.87551000	-0.08213800
C	0.83304700	4.63539600	0.31110100
C	3.52692500	2.16267200	-0.80571600
C	4.16706100	3.40319900	-0.92461500
C	5.48320500	3.47310100	-1.37190700
C	6.17412600	2.30966700	-1.70859400
C	5.54110500	1.07402900	-1.60219000
C	4.22444800	1.00412200	-1.15632700
C	-1.30551100	-2.21524000	1.74540700
C	-0.44494600	1.52898200	1.94366400
H	-5.23359500	1.78017900	1.85303800
H	-5.56339900	2.22285900	3.52062900
H	-5.34065200	-0.15162500	4.23084200
H	-6.55361600	-0.02326900	2.96758500
H	-4.95295700	-0.77362300	1.25228100
H	-5.01394100	-1.94869400	2.52510000
H	-2.92829500	-1.11165300	3.51414500
H	-3.29863800	1.44351400	4.20760600
H	-3.15774500	2.64183900	2.92638900
H	-0.88890200	-0.06863200	3.09058500
H	4.07322000	2.62976600	1.57320300
H	4.42090500	2.49976600	4.00081900
H	2.57029500	1.74971600	5.48357400
H	0.34810200	1.26787500	4.51381300
H	1.62335400	-4.48829300	-1.15064600
H	0.12805600	-6.41967400	-1.28686200
H	-2.07853700	-6.36737300	-0.13472200
H	-2.71138000	-4.38807600	1.18956400

H	3.59765500	-0.21640800	1.17515500
H	4.96103500	-0.27614100	3.21291100
H	4.53352700	-2.00226700	4.95000100
H	2.70853900	-3.65313500	4.61421700
H	1.32481400	-3.57281800	2.57673300
H	2.23986600	-1.32306100	-2.64744300
H	4.10715400	-2.04752800	-4.09032200
H	5.84463800	-3.58047500	-3.19092900
H	5.68322600	-4.37750300	-0.84445700
H	3.81207900	-3.65508000	0.58453300
H	1.17458900	3.20986900	-2.75140300
H	0.28677800	5.40300200	-3.44336500
H	-0.26364700	7.11826800	-1.73386200
H	0.09632100	6.61917300	0.67016100
H	0.96748200	4.41563300	1.36239600
H	3.63554800	4.31306300	-0.67261000
H	5.96844700	4.43926600	-1.46205300
H	7.19867400	2.36913900	-2.06035900
H	6.06016900	0.16104200	-1.87316800
H	3.73619300	0.04254100	-1.09902800
H	-3.14872300	-2.16947900	0.81807600
H	-2.84255600	0.91155800	1.24799200
C	-2.13292800	-1.23650500	-1.87327300
C	-0.93597500	-0.89085900	-2.71216600
C	-0.73987500	0.43026300	-3.12124900
C	-1.79193000	1.52459400	-2.96269800
C	-3.09786400	1.03837800	-2.30190700
C	-2.77993600	-0.02003200	-1.23979900
H	-0.02056400	0.58482200	-3.92283800
H	-1.87595700	-1.98386500	-1.12767500
H	-1.39059500	2.37061600	-2.40392400
H	-2.01121800	1.91316000	-3.96385900
H	-3.70120700	0.54495700	-3.07309100
H	-2.11002100	0.41347800	-0.49323200
H	-3.69087700	-0.33406400	-0.73243800
H	0.44470900	1.28974900	-2.08199400
C	-3.91641000	2.17316500	-1.72491600
C	-5.24130900	2.36805000	-2.12020000
C	-3.38588100	3.00695400	-0.73251500
C	-6.02363200	3.36700800	-1.54286500
H	-5.66971300	1.72277000	-2.88171400
C	-4.16559600	4.00368800	-0.15389900
H	-2.37197000	2.86235100	-0.38108100
C	-5.48775000	4.18908600	-0.55558700

H	-7.05240700	3.49872700	-1.86284800
H	-3.73615900	4.63354200	0.61894500
H	-6.09537700	4.96487100	-0.10084400
C	-0.21714300	-1.98223800	-3.36952900
C	-0.56246000	-3.27165900	-3.26816100
H	-0.01200100	-4.02551500	-3.82104000
H	-1.40324700	-3.61359200	-2.67120500
H	0.60527800	-1.69464500	-4.02123500
H	-2.85139700	-1.75936000	-2.51170000
C	-4.39552300	-3.56009300	-1.14451600
O	-3.43047200	-4.04094200	-1.76739800
O	-4.34507000	-2.76491000	-0.15011400
C	-5.81516800	-3.92100200	-1.60674200
H	-6.42071500	-4.24296400	-0.75548800
H	-6.29883900	-3.02997000	-2.02002500
H	-5.79614600	-4.70136600	-2.36822800



Int D'

Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3542.341379 a.u.

Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.947038 a.u

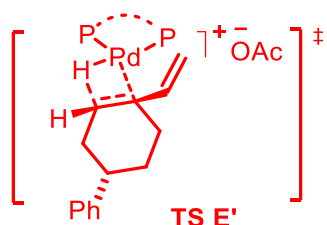
Gibbs free energy at 323 K ((ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3541.394341 a.u.

Pd	0.41391100	-0.16027300	-0.57219600
P	-0.55414900	-1.85552800	0.75030200
P	2.04608400	1.17114500	0.68246100
O	-2.79458000	-0.00604800	1.78018200
O	-0.14968400	2.95577400	0.02176200
N	-4.02180500	0.60947500	-0.04406200
N	-2.02660800	2.49381400	1.23946700
C	-4.47234500	4.84570300	-0.48424200
C	-5.72061300	4.01065400	-0.19523800
C	-5.44476500	2.53078100	-0.44830300
C	-4.26451200	1.99324100	0.37275500
C	-3.00686300	2.87370200	0.22123000
C	-3.31521500	4.37105500	0.39212900
C	0.11767600	2.39513100	2.32264100
C	1.42640400	1.88014100	2.26015800
C	2.19690600	1.82801400	3.42339500
C	1.68630400	2.27645300	4.63841000
C	0.38762800	2.76645700	4.70597600

C	-0.38632500	2.82645800	3.55168200
C	-3.36382000	-1.69725800	0.21501700
C	-2.20141700	-2.50375600	0.23306600
C	-2.30384600	-3.83105500	-0.19835300
C	-3.52395600	-4.36236200	-0.61025600
C	-4.66641600	-3.57318500	-0.59025000
C	-4.58642700	-2.24694000	-0.17816900
C	-0.67834500	-1.65230400	2.57023700
C	0.35775800	-1.03446500	3.26526900
C	0.34182000	-0.97529400	4.65631200
C	-0.71334500	-1.54184100	5.36346000
C	-1.74773200	-2.17236200	4.67241900
C	-1.73257300	-2.22925500	3.28438800
C	0.57221800	-3.33541600	0.69664400
C	0.97985500	-3.86008200	-0.53526000
C	1.89536400	-4.90271000	-0.61017700
C	2.42752400	-5.44892200	0.55626400
C	2.01612200	-4.95317700	1.78906000
C	1.09411800	-3.90986400	1.86199100
C	2.80789400	2.60625700	-0.17802800
C	3.50995900	2.38249300	-1.36490700
C	4.10219600	3.44377900	-2.04284600
C	4.00087600	4.73817200	-1.53926700
C	3.30655700	4.96416500	-0.35285100
C	2.70959300	3.90542600	0.32472600
C	3.53897900	0.20651300	1.15906200
C	4.76976100	0.81901700	1.42674100
C	5.87308500	0.05077400	1.78475100
C	5.76391900	-1.33731300	1.87211100
C	4.54854200	-1.95586600	1.58942400
C	3.44553200	-1.18608200	1.22966500
C	-3.36714000	-0.27666300	0.70960800
C	-0.69842600	2.61587300	1.07378400
H	-4.20451200	4.74610000	-1.54361100
H	-4.66014600	5.90973500	-0.30803200
H	-6.03031200	4.16757600	0.84649100
H	-6.55851500	4.33563300	-0.81919600
H	-5.23260900	2.37300900	-1.50924600
H	-6.31661300	1.91145500	-0.22944600
H	-4.54316600	1.98991800	1.43532800
H	-3.56451200	4.54572200	1.44595400
H	-2.39939300	4.93354900	0.18926300
H	-2.33715900	1.78343800	1.90146700
H	3.19741100	1.41627900	3.38856800

H	2.30401700	2.23381600	5.52937300
H	-0.02168400	3.10963800	5.64971200
H	-1.38815200	3.23555300	3.59081800
H	-1.43356400	-4.47233900	-0.19050700
H	-3.57321100	-5.39845700	-0.92948000
H	-5.62562500	-3.97626500	-0.89629300
H	-5.48271700	-1.62958100	-0.17416800
H	1.19421500	-0.61485700	2.72982500
H	1.15305800	-0.48243900	5.17831800
H	-0.73190200	-1.49446500	6.44730300
H	-2.57639300	-2.61365300	5.21593400
H	-2.54740500	-2.70587100	2.75631200
H	0.56598500	-3.46118400	-1.44551300
H	2.19252400	-5.28652100	-1.58036000
H	3.14780700	-6.25825600	0.50280300
H	2.40907100	-5.37829800	2.70667100
H	0.79399700	-3.54289800	2.83259900
H	3.61480800	1.38041000	-1.75591300
H	4.64489400	3.24866400	-2.96042700
H	4.46048500	5.56685900	-2.06771400
H	3.21994700	5.97002900	0.04452500
H	2.15630400	4.09463000	1.23476200
H	4.86529700	1.89519400	1.34210100
H	6.82188500	0.53541600	1.98964900
H	6.62736700	-1.93340600	2.14829000
H	4.45106600	-3.03475000	1.63723700
H	2.51240600	-1.67628300	0.98867000
H	-4.56090200	0.29376900	-0.88801900
H	-2.57642000	2.70195200	-0.76971100
C	0.36669500	0.68384500	-2.79305700
C	-0.50275900	-0.50817500	-2.54699100
C	-0.01101200	-1.77250300	-3.22330600
C	1.50781000	-1.88766800	-3.15478500
C	2.21284600	-0.76472400	-3.93088000
C	1.33402200	0.52183000	-3.97312200
H	-0.49980900	-2.64361900	-2.78598600
H	-0.21600500	1.60176400	-2.86697500
H	1.78356600	-1.83573800	-2.10170000
H	1.85093400	-2.86147000	-3.51458200
H	2.30295400	-1.09328100	-4.97214900
H	1.95966300	1.41169700	-4.05093700
H	0.71422500	0.49630100	-4.87446700
H	1.05369300	0.94806600	-1.89397200
C	3.63383700	-0.49248600	-3.45200200

C	4.44570100	0.35452900	-4.22042700
C	4.17867400	-1.02928200	-2.28265400
C	5.73749100	0.67583500	-3.82280100
H	4.05381000	0.77129600	-5.14384300
C	5.47261100	-0.70465500	-1.87478300
H	3.60358600	-1.69577200	-1.65546500
C	6.25454200	0.15354700	-2.63711600
H	6.34193000	1.33627200	-4.43623000
H	5.85299100	-1.11542700	-0.94736400
H	7.25712000	0.41391700	-2.31541100
C	-1.93996400	-0.28939200	-2.52110500
C	-2.86287000	-1.19529000	-2.87319100
H	-3.91671700	-0.93956300	-2.85555600
H	-2.59231100	-2.20126500	-3.17495400
H	-2.27283600	0.69625000	-2.20880800
H	-0.34542500	-1.75173600	-4.26994000
C	-6.71623400	-0.26689300	-1.94706800
O	-5.51501000	0.03834400	-2.25607600
O	-7.12429400	-0.53562900	-0.80240700
C	-7.70886200	-0.28828900	-3.11421900
H	-8.71041100	-0.55057300	-2.77270100
H	-7.73120900	0.69160500	-3.59981200
H	-7.37912100	-1.00769600	-3.86975400



Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -3542.321752 a.u.

Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.944748 a.u

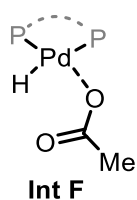
Gibbs free energy at 323 K ((ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane))): -3541.377004 a.u.

Pd	0.40083300	0.00878900	-0.54672200
P	-0.72821400	-1.94105200	0.49102700
P	2.00532400	0.87643200	0.91795000
O	-2.96658900	-0.18608400	1.88503600
O	0.01770800	2.91322600	0.85760200
N	-3.88926000	0.86427700	0.07223300
N	-1.94800300	2.28615700	1.83135600
C	-4.10561300	5.13304800	0.49688500
C	-5.40906600	4.33465200	0.42293400
C	-5.15513300	2.92933500	-0.11912500
C	-4.11921900	2.16169700	0.71138000

C	-2.81821800	2.96712300	0.87273800
C	-3.08284700	4.39870400	1.36350600
C	0.13579800	1.65564800	2.86628700
C	1.39987100	1.08247500	2.63803100
C	2.15433600	0.62993500	3.72111400
C	1.66323400	0.73221800	5.01930500
C	0.39894200	1.26313300	5.24371400
C	-0.35657000	1.72412500	4.17016400
C	-3.51177300	-1.50776800	-0.00766600
C	-2.41702800	-2.39071700	-0.10915400
C	-2.60603900	-3.61559800	-0.75815100
C	-3.85166600	-3.97217000	-1.26963900
C	-4.92835800	-3.10358100	-1.14713800
C	-4.75732600	-1.87275400	-0.52186300
C	-0.78260800	-2.17333100	2.31236200
C	0.40409700	-2.02831800	3.03179000
C	0.44684700	-2.32207300	4.39068000
C	-0.70078300	-2.76038300	5.04477800
C	-1.88762000	-2.90913600	4.33008900
C	-1.93045900	-2.62151900	2.96968000
C	0.26448400	-3.44332100	0.04412000
C	0.82184600	-3.51965700	-1.23410700
C	1.60395900	-4.60306700	-1.61831500
C	1.84121200	-5.63926000	-0.71713000
C	1.27883000	-5.58328300	0.55583200
C	0.49309200	-4.49676100	0.93554600
C	2.88761700	2.44863000	0.56175400
C	3.60017500	2.56990100	-0.63227000
C	4.31597700	3.73091800	-0.90778900
C	4.32925400	4.77798900	0.01047400
C	3.62576100	4.65603900	1.20624200
C	2.90609600	3.49718900	1.48267000
C	3.42643400	-0.28787000	1.03973500
C	4.68522300	0.13677500	1.48423800
C	5.74204500	-0.76484400	1.56022700
C	5.55997100	-2.09591800	1.18436200
C	4.31586400	-2.52185000	0.72622800
C	3.25850500	-1.61919600	0.65300300
C	-3.42421400	-0.20073700	0.72654400
C	-0.61018400	2.32590100	1.74303600
H	-3.70374600	5.26768100	-0.51530500
H	-4.28216500	6.13630100	0.89793500
H	-5.85706000	4.27611900	1.42362900
H	-6.13934200	4.84452100	-0.21253300

H	-4.79612900	2.99180500	-1.15113500
H	-6.06963200	2.33528100	-0.16038300
H	-4.52860700	1.98040900	1.71465200
H	-3.45013600	4.34265800	2.39567100
H	-2.12939000	4.93327000	1.39680600
H	-2.35218400	1.46279900	2.28279500
H	3.12300500	0.17650300	3.55385000
H	2.26584400	0.38187500	5.85046200
H	0.00304000	1.32981300	6.25096500
H	-1.32750100	2.17258500	4.34099900
H	-1.78095400	-4.30615400	-0.86541800
H	-3.97039600	-4.93213100	-1.76186000
H	-5.90203100	-3.36648000	-1.54616600
H	-5.58996500	-1.17620700	-0.46261600
H	1.30838900	-1.71379500	2.52929600
H	1.37671700	-2.20501700	4.93501600
H	-0.67080700	-2.98738700	6.10547300
H	-2.78742500	-3.24847100	4.83218100
H	-2.85662900	-2.73142500	2.42487300
H	0.63925000	-2.71827000	-1.93008700
H	2.02915300	-4.63428900	-2.61602400
H	2.45512100	-6.48560200	-1.00649200
H	1.44982300	-6.38959100	1.26130500
H	0.06478700	-4.47137700	1.92826100
H	3.61786700	1.75545900	-1.34283200
H	4.86350900	3.80590100	-1.83964200
H	4.88464500	5.68488000	-0.20461800
H	3.62652800	5.46888200	1.92479300
H	2.34711900	3.42018100	2.40542200
H	4.84148300	1.17392600	1.75572900
H	6.71299500	-0.42516300	1.90495200
H	6.38859500	-2.79398900	1.24040900
H	4.15918500	-3.54992900	0.41874400
H	2.30303700	-1.95212400	0.27484600
H	-4.32872600	0.73500100	-0.87878500
H	-2.30873700	3.00344100	-0.09512100
C	0.09956900	1.13088800	-2.77959800
C	-0.57610600	-0.06354000	-2.99390000
C	0.14766200	-1.11704700	-3.80023600
C	1.65268100	-1.05922200	-3.56138500
C	2.25056400	0.27967100	-3.99577500
C	1.34494700	1.48648300	-3.56865300
H	-0.24704500	-2.10913300	-3.57804500
H	-0.47407900	1.97568700	-2.40772500

H	1.82684500	-1.19915700	-2.49235500
H	2.16439900	-1.87696300	-4.07664000
H	2.26582400	0.27735200	-5.09117100
H	1.92771000	2.23635100	-3.03382100
H	0.98246800	1.98974800	-4.47341500
H	1.12776100	1.19832500	-1.24118500
C	3.69120000	0.46593400	-3.54475400
C	4.43193500	1.53223000	-4.07248400
C	4.31220100	-0.35975000	-2.60410100
C	5.73716600	1.77609000	-3.66182800
H	3.97394200	2.18258000	-4.81229700
C	5.61870200	-0.11438200	-2.18242000
H	3.78341900	-1.19496400	-2.16666400
C	6.33483300	0.95572400	-2.70493700
H	6.28940200	2.60823300	-4.08664600
H	6.06161400	-0.75764100	-1.43096000
H	7.34862600	1.15211700	-2.37296900
C	-2.01780500	-0.15250000	-2.81907900
C	-2.78910700	-1.13605100	-3.29261100
H	-3.86026100	-1.04667600	-3.18185300
H	-2.39111500	-2.01203000	-3.79264600
H	-2.50855300	0.68704000	-2.33797100
H	-0.07762700	-0.94631900	-4.86178300
C	-6.28078800	0.52659600	-2.30154400
O	-6.92471900	0.26076100	-1.26969500
O	-5.01766700	0.70179400	-2.37020100
C	-7.03155100	0.63097500	-3.63395500
H	-6.68217700	1.49464700	-4.20454200
H	-6.82094200	-0.25863200	-4.23742700
H	-8.10783900	0.69542600	-3.47152700



Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -2999.538030 a.u.

Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.696861 a.u

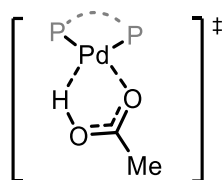
Gibbs free energy at 323 K (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -2998.841169 a.u.

Pd	-0.11382500	0.01222000	-1.14481100
P	0.71002700	-1.78258700	0.34668600
P	1.05696800	1.82518000	-0.42885000
O	-2.22519000	-1.01681100	2.18253000
O	-1.67664300	3.25899300	-0.00147300

N	-3.40453900	-1.00617200	0.22276500
N	-2.64098100	1.61490200	1.24031900
C	-6.06291500	2.33163500	-0.30405100
C	-6.65720100	0.93654400	-0.09076200
C	-5.60771100	-0.15299700	-0.32440600
C	-4.35942000	0.05081100	0.54312300
C	-3.77934600	1.45522000	0.34397700
C	-4.83623400	2.53946200	0.58579100
C	-0.46495500	2.39322500	1.86496700
C	0.83336400	2.18229200	1.36430300
C	1.89710100	2.12495900	2.26603500
C	1.68831000	2.29916200	3.63165500
C	0.40735000	2.51748000	4.11919900
C	-0.66605100	2.55537400	3.23393600
C	-1.92612600	-2.84206200	0.68556900
C	-0.55523900	-3.12097000	0.54600500
C	-0.16214200	-4.45205200	0.36418800
C	-1.09315900	-5.48422100	0.31143700
C	-2.44913700	-5.19833200	0.41002600
C	-2.85539200	-3.88218500	0.59453200
C	1.41815900	-1.46441700	2.00847100
C	2.72726900	-0.97376900	2.11713700
C	3.28777800	-0.73567600	3.36653400
C	2.53881500	-0.94778500	4.52147900
C	1.22413600	-1.39214500	4.41659400
C	0.66384800	-1.65779000	3.16918600
C	2.05767900	-2.70534900	-0.52085000
C	1.97681000	-2.81103200	-1.91630000
C	2.96281300	-3.48995100	-2.62560100
C	4.03643200	-4.07598400	-1.95712000
C	4.10807300	-3.99555200	-0.56910000
C	3.12207300	-3.31955500	0.14648500
C	0.92191200	3.44087600	-1.28314200
C	0.83879200	3.45915700	-2.67535700
C	0.85632100	4.67086400	-3.35921900
C	0.95594100	5.86923400	-2.65636900
C	1.03530600	5.85152400	-1.26582000
C	1.01938900	4.64179900	-0.57916900
C	2.86391800	1.53289400	-0.64468300
C	3.80786800	2.50776500	-0.29340600
C	5.16498900	2.26508700	-0.47154700
C	5.59826300	1.05655300	-1.01991200
C	4.66521500	0.10208600	-1.41125500
C	3.30561100	0.34679000	-1.23038100

C	-2.50015700	-1.50418900	1.07655300
C	-1.64462500	2.47027600	0.93634100
H	-5.77416000	2.44827800	-1.35569600
H	-6.81189800	3.10296900	-0.09981400
H	-7.04404700	0.86039200	0.93372600
H	-7.51014000	0.77423600	-0.75685000
H	-5.30071100	-0.15708700	-1.37582800
H	-6.02172300	-1.14432500	-0.11788300
H	-4.62463600	-0.06189700	1.60131100
H	-5.13076300	2.51132700	1.64255900
H	-4.37705500	3.51347500	0.40586800
H	-2.44049900	0.84536800	1.87680500
H	2.89673000	1.92278500	1.91230400
H	2.53103700	2.24085600	4.31057100
H	0.23858200	2.64495600	5.18301500
H	-1.67372900	2.71332300	3.60133900
H	0.88468900	-4.68945500	0.23506000
H	-0.75378600	-6.50527200	0.17310200
H	-3.18740100	-5.99017300	0.34352000
H	-3.90933000	-3.64490500	0.67972900
H	3.31602600	-0.78690600	1.22770600
H	4.30799500	-0.37153100	3.43373300
H	2.97466900	-0.75744400	5.49685700
H	0.62646300	-1.54127600	5.30960200
H	-0.36632100	-1.97960300	3.09765800
H	1.12879500	-2.37725500	-2.43372400
H	2.88948900	-3.56017200	-3.70584800
H	4.80662000	-4.59998500	-2.51355200
H	4.93055100	-4.46217700	-0.03692200
H	3.18714000	-3.27548500	1.22559000
H	0.74441200	2.52802100	-3.22282300
H	0.78237600	4.67775600	-4.44158000
H	0.96182700	6.81406500	-3.18969900
H	1.09516100	6.78249800	-0.71171700
H	1.05050700	4.63495000	0.50365100
H	3.48248900	3.46032500	0.10779800
H	5.88719600	3.02426400	-0.19007000
H	6.65870900	0.87215300	-1.15635700
H	4.98111900	-0.83497600	-1.85657700
H	2.58447400	-0.38683400	-1.55627200
H	-3.34412500	-1.28542400	-0.76758600
H	-3.41083900	1.53902200	-0.68403500
H	-0.68088900	1.04149700	-2.17929200
C	-1.98747200	-1.98924300	-2.76793700

C	-1.91441600	-3.13732400	-3.76735200
H	-2.88843200	-3.31513000	-4.22059900
H	-1.17392500	-2.92533700	-4.54130300
H	-1.59150500	-4.04158200	-3.24340000
O	-0.84098600	-1.63356300	-2.31489000
O	-3.08874700	-1.52504100	-2.44498800



TS G

Total SCF energy (ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane)): -2999.528371 a.u.

Thermal correction to Gibbs Free Energy at 323 K (ω b97xd/def2SVP/SDD): 0.692960 a.u

Gibbs free energy at 323 K ((ω b97xd/def2-TZVP/SDD/SMD(1,4-dioxane))): -2998.835411 a.u.

Pd	-0.19522100	0.17941200	-0.90886900
P	0.42560000	-2.01858200	-0.01636100
P	1.25950600	1.72030100	-0.12350500
O	-2.43968800	-1.52591100	2.21195500
O	-1.34285800	3.14699900	0.77342900
N	-3.36152600	-1.08214800	0.17378500
N	-2.35117900	1.28293400	1.58644800
C	-5.61763900	2.60023800	0.09359400
C	-6.35569700	1.26229500	-0.00272600
C	-5.39782800	0.12674300	-0.37246700
C	-4.20438100	0.03922900	0.58642900
C	-3.47215000	1.38567100	0.66125500
C	-4.44082300	2.50485100	1.06587100
C	-0.11733700	1.81019100	2.32505200
C	1.15084700	1.68203100	1.72200600
C	2.24155100	1.36129900	2.53002000
C	2.09182300	1.19592900	3.90564700
C	0.84253200	1.33389400	4.49402100
C	-0.26086200	1.63387500	3.69863200
C	-2.13414400	-3.13684700	0.48946400
C	-0.80625300	-3.39795100	0.12711100
C	-0.45821900	-4.70857100	-0.22514900
C	-1.39844300	-5.73162700	-0.21940500
C	-2.71973900	-5.45968300	0.12451200
C	-3.08152600	-4.16544000	0.47485900
C	1.37872400	-2.14180900	1.54811500
C	2.73192500	-1.78036100	1.58923600
C	3.43754900	-1.82597300	2.78669200

C	2.79569800	-2.19612100	3.96545200
C	1.43936100	-2.50927400	3.93920800
C	0.73232200	-2.48846000	2.74022500
C	1.53847400	-2.72604200	-1.30656500
C	1.20357200	-2.43823100	-2.63689500
C	1.98477000	-2.91967700	-3.68217800
C	3.11525800	-3.69019300	-3.41389100
C	3.44849400	-3.98962400	-2.09530900
C	2.66153400	-3.51640300	-1.04707600
C	1.23918200	3.50285200	-0.56309500
C	1.03177600	3.84808800	-1.89936100
C	1.08150000	5.18195400	-2.29325800
C	1.33272100	6.17944600	-1.35415900
C	1.53091100	5.83771600	-0.01799300
C	1.48432900	4.50468700	0.37747700
C	3.02371100	1.34121600	-0.50517800
C	4.07377600	2.15805800	-0.06582600
C	5.39074200	1.83961500	-0.37930100
C	5.67666800	0.71308900	-1.15202800
C	4.63739100	-0.08343800	-1.62294500
C	3.31886400	0.23485100	-1.30300700
C	-2.61970100	-1.81586800	1.02723700
C	-1.31807000	2.15239200	1.48838400
H	-5.24550100	2.88721800	-0.89781900
H	-6.30391900	3.39259200	0.40696000
H	-6.82679100	1.03749800	0.96230300
H	-7.16515700	1.31619400	-0.73733600
H	-5.01738000	0.28660600	-1.38909800
H	-5.91663600	-0.83617200	-0.37991800
H	-4.56381000	-0.20492300	1.59184200
H	-4.80488100	2.30390200	2.08131000
H	-3.88266800	3.44087100	1.10071100
H	-2.22190900	0.40369600	2.07818000
H	3.21595900	1.21299400	2.08674600
H	2.95474700	0.93672600	4.50831000
H	0.71986000	1.19571600	5.56285700
H	-1.24476400	1.73309300	4.14419300
H	0.55777600	-4.92939200	-0.52474800
H	-1.09987700	-6.73777000	-0.49441200
H	-3.46402200	-6.24879000	0.11783100
H	-4.10638200	-3.94159500	0.75141800
H	3.23957500	-1.45981500	0.68878600
H	4.48884000	-1.55624500	2.79641400
H	3.34521300	-2.22603400	4.90069000

H	0.92374500	-2.77568900	4.85591200
H	-0.32621300	-2.71732400	2.73984100
H	0.33432000	-1.82283800	-2.84586300
H	1.71596500	-2.68383200	-4.70639800
H	3.73140100	-4.05622600	-4.22846100
H	4.32246100	-4.59530900	-1.87857400
H	2.92835600	-3.76064900	-0.02658300
H	0.81292500	3.07668200	-2.62953200
H	0.91082400	5.44180800	-3.33284500
H	1.36305500	7.22020300	-1.65996100
H	1.71021800	6.61213000	0.72099800
H	1.61019600	4.24599100	1.42246100
H	3.86076300	3.05073600	0.51079300
H	6.19610500	2.47673700	-0.02848000
H	6.70546700	0.47028300	-1.39743400
H	4.84093300	-0.95238900	-2.23940100
H	2.51028600	-0.37472800	-1.68042300
H	-3.19283900	-1.20731200	-0.81915000
H	-3.06115500	1.62594300	-0.32583800
H	-0.71794800	1.43253200	-1.92107500
C	-2.23537500	0.54387400	-2.97937900
C	-3.36722400	0.44613900	-3.97560400
H	-4.11762900	1.20707900	-3.74987500
H	-2.99089500	0.65757100	-4.97844200
H	-3.82422200	-0.54178300	-3.95654100
O	-1.95967300	-0.44935400	-2.25174500
O	-1.61720700	1.65176800	-2.92141800