

Supporting Information

Palladium-Catalyzed Asymmetric Sequential Hydroalkylation and Hydroamination of 1,3-Enynes with 3-Hydroxyindoles

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Contents

1. General Information	1
2. General Procedure for the Preparation of Substrates	2
3. Solvent Screening for the Reaction	15
4. General Procedure for the Palladium-Catalyzed Asymmetric Sequential Hydroalkylation and Hydroamination of 1,3-Enynes Reaction	15
5. Mechanistic Studies	56
6. Further Study	66
7. Determination of the Absolute Configurations of 3aa, 8 and 9	82
8. DFT Calculations	85
9. ¹ H, ¹³ C and ¹⁹ F NMR Spectra of Title Compounds	143
10. References	221

1. General Information

Reagents and Solvents: PE refers to petroleum ether b. p. 60-90 °C, EA refers to ethyl acetate, and DCM refers to dichloromethane. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they were listed as volume/volume ratios.

Data collection: ^1H , ^{13}C and ^{19}F NMR Spectrum were collected on BRUKER AV-300 (300 MHz) spectrometer using CDCl_3 as solvent. Chemical shifts of ^1H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane ($\delta = 0.00$ ppm) with the solvent resonance as an internal standard (CDCl_3 : $\delta = 7.26$ ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard (CDCl_3 : $\delta = 77.16$ ppm). High Resolution Mass measurement was performed on Agilent Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus. Optical rotations were measured on an Anton Paar MCP 100 automatic polarimeter with $[\alpha]_D^{25}$ values reported in degrees; concentration (c) is in g/100 mL. The enantiomeric excess values were determined by chiral HPLC using an Agilent 1200 LC instrument with Daicel CHIRALPAK[®] IA-3, IB-3, IC-3, AD-H, OD-H and AS-H columns. X-ray diffraction analyses were carried out on a microcrystalline powder using a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer using Mo radiation ($\lambda = 0.71073$ Å) or Cu radiation ($\lambda = 1.54178$ Å).

2. General Procedure for the Preparation of Substrates

2.1 General Procedure for the Preparation of Substrates 1

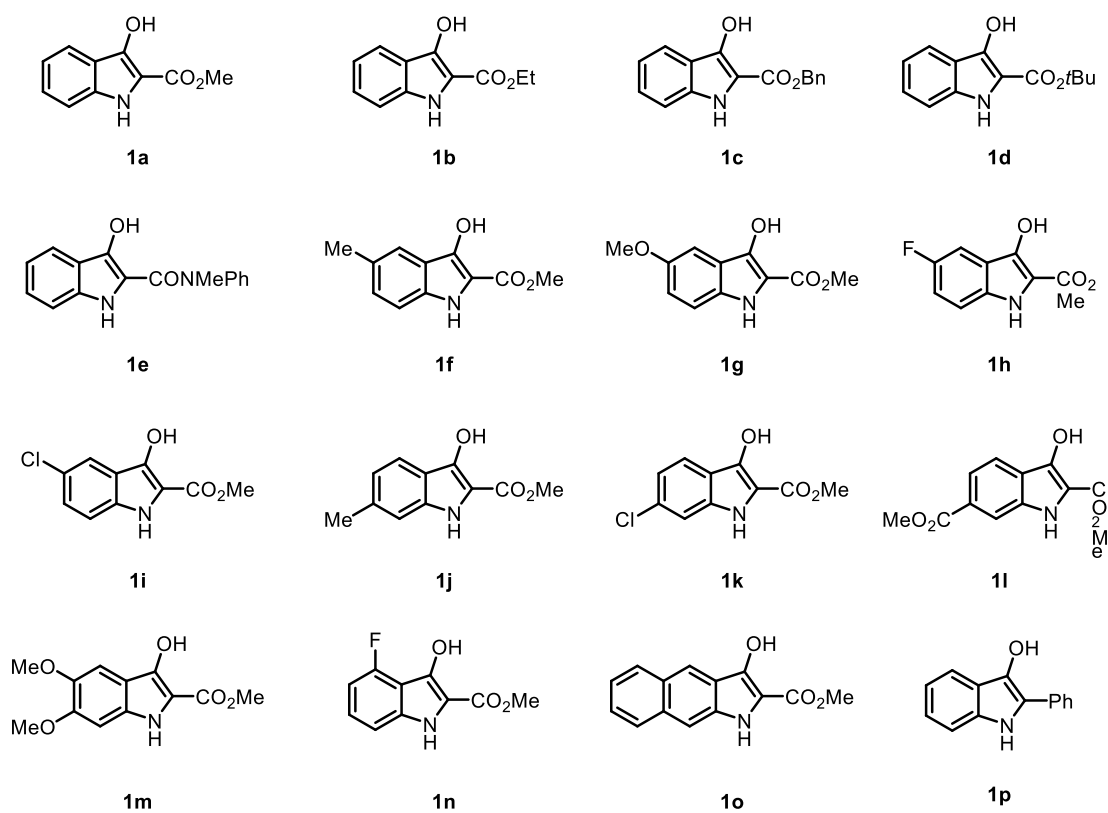
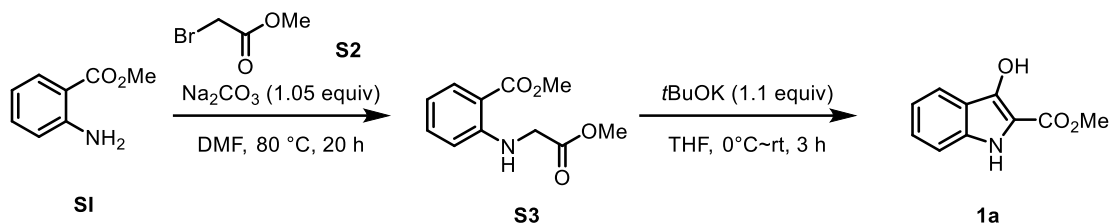


Figure S1. Structures of Substrates 1

1p is known compound and was synthesized according to the reported procedure.¹

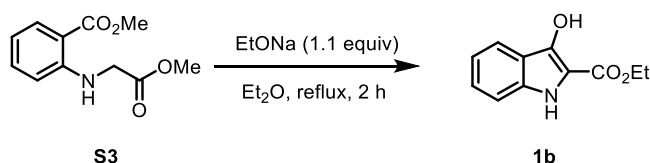
General procedure A: synthesis of **1a**, **1c** and **1f-1o**^{2,3} (synthesis of **1a** is used as an example):



Methyl antranilate **S1** (6.05 g, 40.0 mmol, 1.0 equiv) and anhydrous Na_2CO_3 (4.45 g, 42.0 mmol, 1.05 equiv) was dissolved in anhydrous DMF (40.0 mL). Methylbromoacetate **S2** (8.34 g, 54.4 mmol, 1.36 equiv) was added and the reaction mixture was heated to 80 °C for 20 h. The mixture was then poured into H_2O and extracted with Et_2O . The organic phase was washed with brine and dried with MgSO_4 , filtered and concentrated to yield pure diester **S3** (7.14 g) in 80% yield.

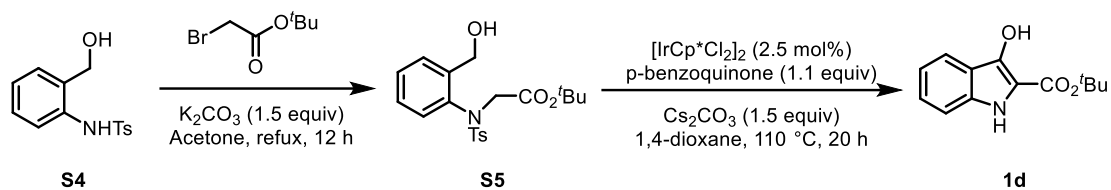
Diester **S3** (5.57 g, 25.0 mmol, 1.0 equiv) was dissolved in anhydrous THF (50.0 mL) and cooled to 0 °C. $t\text{BuOK}$ (3.08 g, 27.5 mmol, 1.1 eq) was dissolved in anhydrous THF (25.0 mL) and added dropwise to the cold solution via canula, the reaction mixture turned dark red. The reaction was monitored by TLC and after 3 hours, the mixture was concentrated to remove most of the THF. $\text{H}_2\text{O}/\text{AcOH}$ (4:1) (50.0 mL) was added and the mixture was extracted with DCM. The organic phase was washed with brine and dried over MgSO_4 , before being filtered and concentrated. Then the residue was purified by flash chromatography (PE/EA = 50/1-15/1) to give **1a** (3.58 g, 75% yield).

General procedure B: synthesis of **1b**⁴



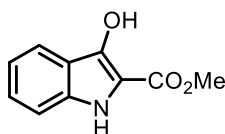
Diester **S3** (2.23 g, 10.0 mmol, 1.0 equiv) was dissolved in anhydrous Et_2O (10.0 mL) and cooled to 0 °C. EtONa (3.74 g, 11.0 mmol, 1.1 equiv, 20 wt% in EtOH) was added dropwise to the solution via canula. Then the mixture was refluxed under Ar for 2 h. After concentrating, the residue was purified by flash chromatography (PE/EA = 30/1) to give **1b** (1.74 g, 85% yield).

General procedure C: synthesis of **1d** and **1e**⁵ (synthesis of **1d** is used as an example):



To a solution of **S4**⁶ (5.55 g, 20.0 mmol, 1.0 equiv) in acetone (0.5 M) were successively added the tert-butyl bromoacetate (4.37 mL, 30.0 mmol, 1.5 equiv) and K_2CO_3 (4.14 g, 30.0 mmol, 1.5 equiv). The reaction mixture was then refluxed under Ar for 12 h. The mixture was then cooled, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (PE/EA = 4/1-2/1) to give **S5** (5.17 g, 66% yield).

To a solution of the product **S5** (5.17 g, 13.2 mmol, 1.0 equiv) in 1,4-dioxane (20.0 mL) were successively added *p*-benzoquinone (1.57 g, 14.5 mmol, 1.1 equiv), $[\text{IrCp}^*\text{Cl}_2]_2$ (262.9 mg, 0.33 mmol, 2.5 mol %) and Cs_2CO_3 (6.4 g, 19.8 mmol, 1.5 equiv). The reaction media was heated in a sealed tube for 20 h at 110 °C, cooled to rt and then concentrated under reduced pressure. The residue was purified by flash chromatography (PE/EA = 10/1-4/1) to give the product **1d** (1.57 g, 51% yield).



methyl 3-hydroxy-1H-indole-2-carboxylate (1a)

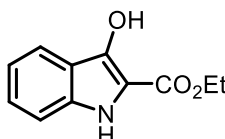
Prepared according to General Procedure A on a 40.0 mmol scale.

3.58 g, 75% yield. White solid, m.p. 158-160 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 10.86 (s, 1H), 9.32 (s, 1H), 7.74 – 7.71 (m, 1H), 7.31 – 7.20 (m, 2H), 6.97 (ddd, *J* = 8.0, 6.6, 1.2 Hz, 1H), 3.84 (s, 3H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 162.2, 143.1, 135.0, 125.8, 119.9, 118.4, 118.3, 112.4, 109.1, 51.1 ppm.

HRMS (ESI) calcd for [C₁₀H₉NO₃+H]⁺ 192.0655, found 192.0657.



ethyl 3-hydroxy-1H-indole-2-carboxylate (1b)

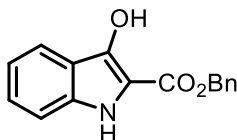
Prepared according to General Procedure B on a 10.0 mmol scale.

1.74 g, 85% yield. White solid, m.p. 116-118 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 10.82 (s, 1H), 9.24 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.21 (m, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 161.8, 143.1, 134.9, 125.8, 119.8, 118.4, 118.3, 112.4, 109.2, 59.6, 14.6 ppm.

HRMS (ESI) calcd for [C₁₁H₁₂NO₃+H]⁺ 206.0812, found 206.0815.



benzyl 3-oxoindoline-2-carboxylate (1c)

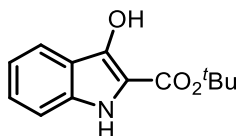
Prepared according to General Procedure A on a 20.0 mmol scale.

0.53 g, 10% yield. White solid, m.p. 158-160 °C.

¹H NMR (300 MHz, CDCl₃) δ 7.86 (br s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.34 (m, 5H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 5.38 (s, 2H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 161.6, 143.8, 136.8, 135.2, 128.5, 127.9, 127.8, 126.0, 120.0, 118.5, 118.4, 112.5, 109.1, 64.9 ppm.

HRMS (ESI) calcd for [C₁₆H₁₃NO₃+H]⁺ 268.0968, found 268.0965.



tert-butyl 3-hydroxy-1H-indole-2-carboxylate (1d)

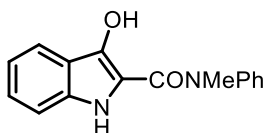
Prepared according to General Procedure C on a 50.0 mmol scale.

1.57 g, 51% yield. White solid, m.p. 98-100 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 10.63 (s, 1H), 8.99 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.00 – 6.95 (m, 1H), 1.59 (s, 9H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 161.5, 143.0, 134.5, 125.6, 119.6, 118.3, 112.3, 110.2, 80.4, 28.2 ppm.

HRMS (ESI) calcd for [C₁₃H₁₅NO₃+H]⁺ 233.1052, found 233.1054.



3-hydroxy-N-methyl-N-phenyl-1H-indole-2-carboxamide (1e)

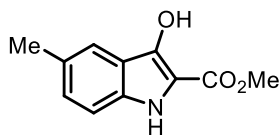
Prepared according to General Procedure C on a 10.0 mmol scale.

0.85 g, 32% yield. White solid, m.p. 142-143 °C.

¹H NMR (300 MHz, CDCl₃) δ 10.91 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.57 (m, 3H), 7.43 (dd, *J* = 6.6, 2.8 Hz, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 5.71 (s, 1H), 3.49 (s, 3H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ 164.5, 150.3, 142.8, 134.8, 130.5, 129.2, 128.3, 126.8, 120.0, 119.4, 117.3, 111.6, 109.3, 38.2 ppm.

HRMS (ESI) calcd for [C₁₆H₁₄N₂O₂+H]⁺ 267.1128, found 267.1130.



methyl 3-hydroxy-5-methyl-1H-indole-2-carboxylate (1f)

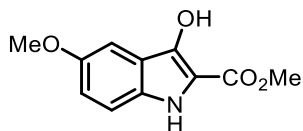
Prepared according to General Procedure A on a 10.0 mmol scale.

1.37 g, 67% yield. Yellow solid, m.p 157-158 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 10.70 (s, 1H), 9.12 (s, 1H), 7.47 (s, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 7.07 – 7.04 (m, 2H), 3.82 (s, 3H), 2.35 (s, 3H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 162.2, 142.7, 133.6, 127.7, 126.9, 118.8, 118.4, 112.1, 109.2, 50.9, 21.1 ppm.

HRMS (ESI) calcd for [C₁₁H₁₂NO₃+H]⁺ 206.0812, found 206.0818.



methyl 3-hydroxy-5-methoxy-1H-indole-2-carboxylate (1g)

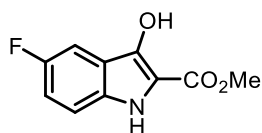
Prepared according to General Procedure A on a 10.0 mmol scale.

1.52 g, 69% yield. Yellow solid, m.p. 142-144 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 10.69 (s, 1H), 9.11 (s, 1H), 7.22 – 7.15 (m, 3H), 6.90 (dd, *J* = 9.0, 2.3 Hz, 1H), 3.84 (s, 3H), 3.77 (s, 3H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 152.7, 142.7, 130.6, 118.0, 117.5, 113.5, 109.8, 99.6, 55.2, 51.0 ppm.

HRMS (ESI) calcd for [C₁₁H₁₁NO₄+H]⁺ 222.0761, found 222.0757.



methyl 5-fluoro-3-hydroxy-1H-indole-2-carboxylate (1h)

Prepared according to General Procedure A on a 10.0 mmol scale.

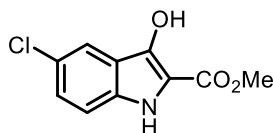
1.35 g, 65% yield. Yellow solid, m.p. 194-196 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 10.83 (s, 1H), 9.25 (s, 1H), 7.32 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.16 (dd, *J* = 9.1, 4.5 Hz, 1H), 6.97 (td, *J* = 9.2, 2.5 Hz, 1H), 3.70 (s, 3H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 161.9, 156.0 (d, ¹*J*_{C-F} = 232.8 Hz), 142.6 (d, ⁴*J*_{C-F} = 5.5 Hz), 131.7, 117.9 (d, ³*J*_{C-F} = 9.8 Hz), 114.7 (d, ²*J*_{C-F} = 26.9 Hz), 113.8 (d, ³*J*_{C-F} = 9.2 Hz), 111.0, 103.9 (d, ²*J*_{C-F} = 23.8 Hz), 51.2 ppm.

¹⁹F NMR (282 MHz, DMSO-*d*₆) δ -124.72 ppm.

HRMS (ESI) calcd for [C₁₀H₈FNO₃+H]⁺ 210.0561, found 210.0556.



methyl 5-chloro-3-hydroxy-1H-indole-2-carboxylate (1i)

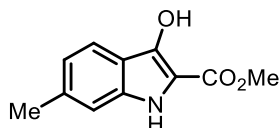
Prepared according to General Procedure A on a 10.0 mmol scale.

1.19 g, 53% yield. White solid, m.p. 173-175 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 11.10 (s, 1H), 9.56 (s, 1H), 7.77 (d, *J* = 1.9 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.83 (s, 3H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 161.8, 141.9, 133.1, 125.8, 122.8, 119.1, 119.0, 114.1, 110.6, 51.2 ppm.

HRMS (ESI) calcd for [C₁₀H₈ClNO₃+H]⁺ 248.0085, found 248.0085.



methyl 3-hydroxy-6-methyl-1H-indole-2-carboxylate (1j)

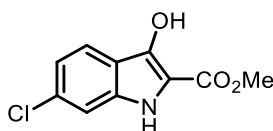
Prepared according to General Procedure A on a 10.0 mmol scale.

1.39 g, 68% yield. Yellow solid, m.p. 158-160 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 10.69 (s, 1H), 9.24 (s, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.06 (s, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 3.82 (s, 3H), 2.36 (s, 3H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 162.2, 143.3, 135.6, 135.4, 120.5, 119.6, 116.3, 111.8, 108.5, 50.9, 21.7 ppm.

HRMS (ESI) calcd for [C₁₁H₁₂NO₃+H]⁺ 206.0812, found 206.0814.



methyl 6-chloro-3-hydroxy-1H-indole-2-carboxylate (1k)

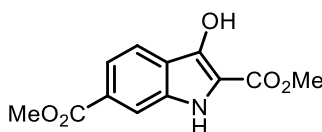
Prepared according to General Procedure A on a 10.0 mmol scale.

0.87 g, 39% yield. White solid, m.p. 182-184 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 11.03 (s, 1H), 9.59 (s, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 1.6 Hz, 1H), 6.98 (dd, *J* = 8.7, 1.8 Hz, 1H), 3.83 (s, 3H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 162.1, 143.0, 135.2, 130.8, 121.9, 119.3, 117.4, 111.9, 110.2, 51.5 ppm.

HRMS (ESI) calcd for [C₁₀H₈ClNO₃+H]⁺ 226.0625, found 226.0626.



dimethyl 3-hydroxy-1H-indole-2,6-dicarboxylate (1l)

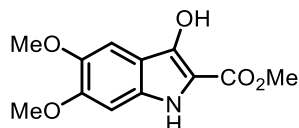
Prepared according to General Procedure A on a 10.0 mmol scale.

0.92 g, 37% yield. Yellow solid, m.p. 206-208 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 11.33 (s, 1H), 9.61 (s, 1H), 7.97 (s, 1H), 7.84 (d, *J* = 8.5) 7.54 (dd, *J* = 8.5, 1.4 Hz, 1H), 3.86 (*app.* s, 6H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 166.8, 161.8, 142.2, 133.7, 126.4, 121.2, 120.2, 118.3, 114.5, 112.3, 52.1, 51.4 ppm.

HRMS (ESI) calcd for [C₁₂H₁₁NO₅+H]⁺ 250.0710, found 250.0704.



methyl 3-hydroxy-5,6-dimethoxy-1H-indole-2-carboxylate (1m)

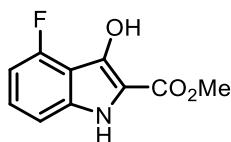
Prepared according to General Procedure A on a 10.0 mmol scale.

1.58 g, 63% yield. Yellow solid, m.p. 98-100 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 10.52 (s, 1H), 9.04 (br s, 1H), 7.10 (s, 1H), 6.71 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 161.9, 150.4, 144.4, 143.5, 130.7, 110.5, 107.7, 100.3, 94.1, 55.6, 55.4, 50.7 ppm.

HRMS (ESI) calcd for [C₁₂H₁₃NO₅+H]⁺ 252.0866, found 250.0863.



methyl 4-fluoro-3-hydroxy-1H-indole-2-carboxylate (1n)

Prepared according to General Procedure A on a 10.0 mmol scale.

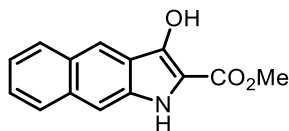
1.46 g, 70% yield. Blue solid, m.p. 210-212 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 11.26 (s, 1H), 8.96 (s, 1H), 7.19 (td, *J* = 7.9, 5.2 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 6.69 (dd, *J* = 11.2, 7.6 Hz, 1H), 3.86 (s, 3H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 162.2, 156.8 (d, ¹*J*_{C-F} = 249.6 Hz), 141.8, 137.4 (d, ³*J*_{C-F} = 9.7 Hz), 126.7 (d, ³*J*_{C-F} = 8.0 Hz), 109.7 (d, ⁴*J*_{C-F} = 1.4 Hz), 109.05 (d, ⁴*J*_{C-F} = 4.1 Hz), 107.9 (d, ²*J*_{C-F} = 18.8 Hz), 103.5 (d, ²*J*_{C-F} = 18.2 Hz), 51.6 ppm.

¹⁹F NMR (282 MHz, DMSO-*d*₆) δ -121.36 ppm.

HRMS (ESI) calcd for [C₁₀H₉FNO₃+H]⁺ 210.0561, found 210.0556.



methyl 3-hydroxy-1H-benzof[1,2-b]indole-2-carboxylate (1o)

Prepared according to General Procedure A on a 10.0 mmol scale.

0.24 g, 10% yield. Yellow solid, m.p. 184-186 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 10.76 (s, 1H), 9.64 (s, 1H), 8.36 (s, 1H), 7.97 – 7.88 (m, 2H), 7.75 (s, 1H), 7.31 (dddd, *J* = 25.5, 8.0, 6.6, 1.3 Hz, 2H), 3.89 (s, 3H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 162.1, 142.6, 134.7, 132.2, 128.7, 127.2, 127.1, 124.9, 122.3, 121.4, 118.3, 111.9, 106.9, 51.3 ppm.

HRMS (ESI) calcd for [C₁₄H₁₁NO₃+H]⁺ 242.0812, found 242.0810.

2.2 General Procedure for the Preparation of Substrates 2

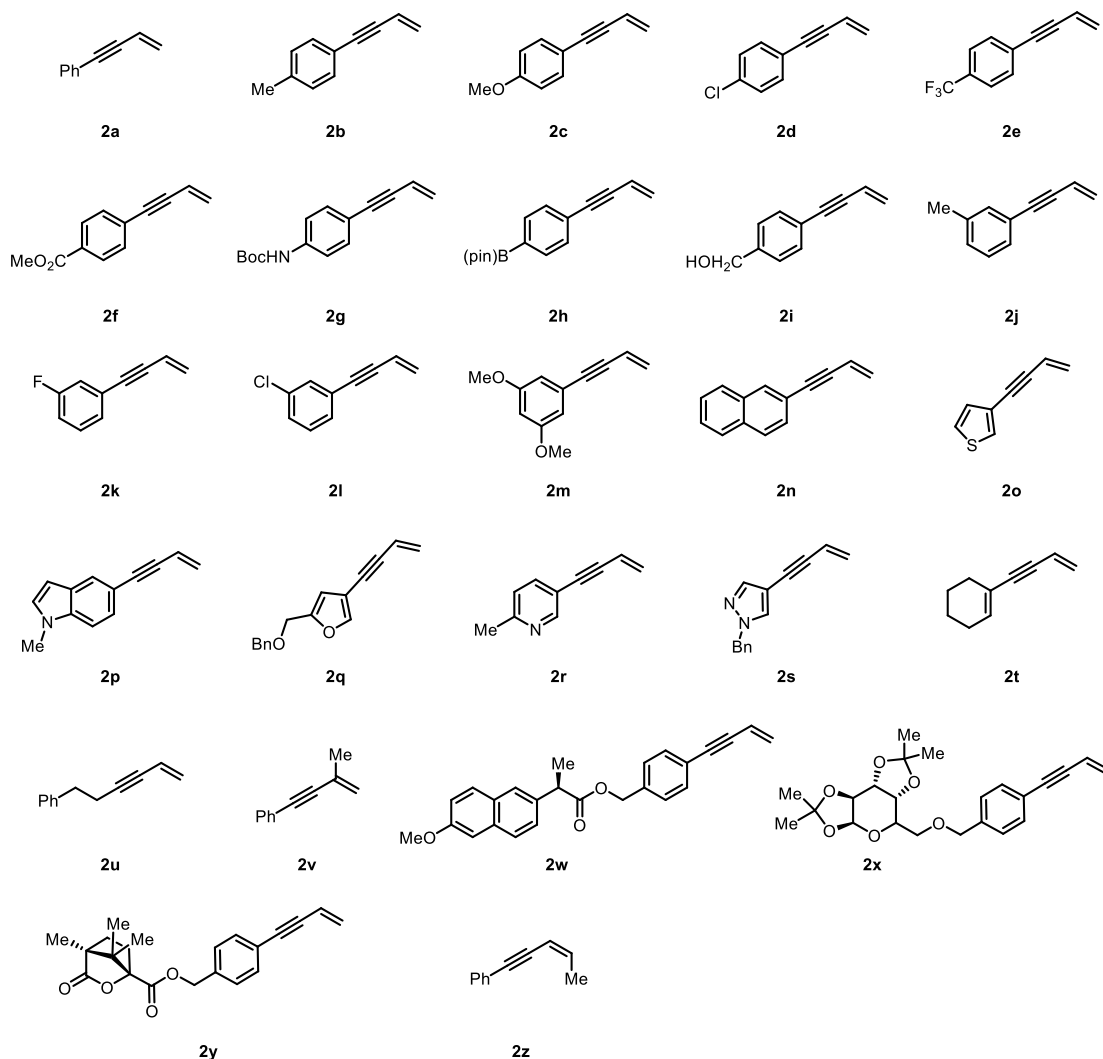
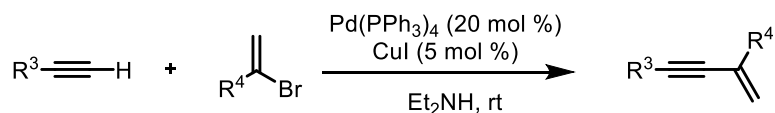


Figure S2. Structures of Substrates 2

General procedure D: synthesis of **2a-2h**, **2j-2p** and **2r-2v** and **2z**⁷

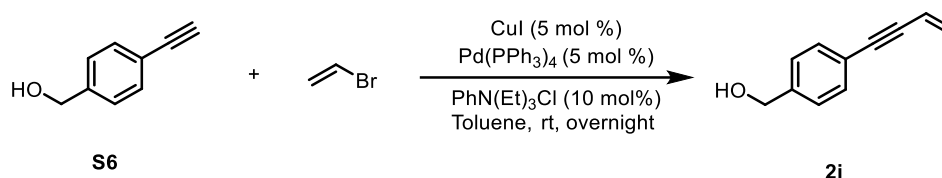


2a-2h, 2j-2p and 2r-2v

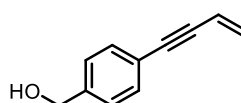
A three-necked flask charged with Pd(PPh₃)₄ (70.2 mg, 0.1 mmol) and CuI (47.6 mg, 0.25 mmol) was evacuated and backfilled with argon (repeated for 3 times), Et₂NH (10.0 mL) was added at room temperature. Then alkyne (5.0 mmol, 1.0 equiv) and 2-bromopropene (6.0 mmol, 1.2 equiv) were added, and the solution was stirred overnight at room temperature. Then saturated aq. NH₄Cl (10.0 mL) was added to the mixture,

and the aqueous layer was extracted with DCM. The combined organic phase was washed with 1M HCl, brine, dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. The crude mixture was purified by flash column chromatography on silica gel with PE as eluent to afford 1,3-enynes.

General procedure E: synthesis of **2i**:



To a three-necked flask equipped with a magnetic stir bar was added Pd(PPh₃)₄ (115.5 mg, 1.0 mmol, 5 mol %), CuI (190.0 mg, 1.0 mmol, 5 mol %), alkyne (2.64 g, 20.0 mmol, 1.0 equiv), PhN(Et)₃Cl (2.0 mmol, 10 mol %) and dry toluene (5.4 mL) under argon at room temperature. Then bromoethane (1M in THF, 26.0 mL, 1.3 equiv) and 10% NaOH aqueous solution (24.0 mL) was added sequentially to the flask. The resulting solution continued to stir at room temperature overnight. The reaction was then quenched with saturated NH₄Cl solution, extracted by EA, concentrated and purified by flash column chromatography to provide the pure product **2i** (2.31 g, 73% yield).



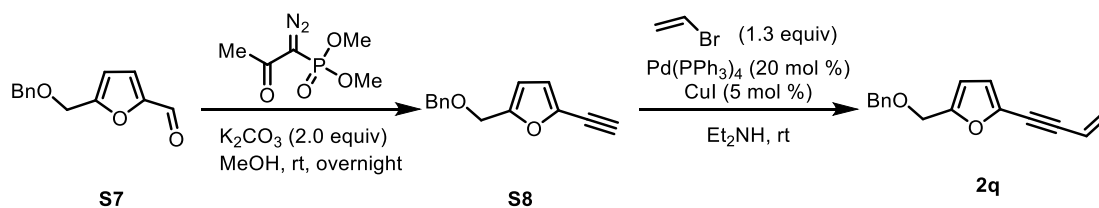
*(4-(but-3-en-1-yn-1-yl)phenyl)methanol (2i)*⁸

2.31 g, 73% yield. Yellow solid.

¹H NMR (300 MHz, DMSO-*d*₆) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 6.13 (dd, *J* = 17.4, 11.3 Hz, 1H), 5.74 (d, *J* = 17.3 Hz, 1H), 5.63 (d, *J* = 10.9 Hz, 1H), 5.28 (s, 1H), 4.52 (s, 2H) ppm.

¹³C NMR (75 MHz, DMSO-*d*₆) δ 143.5, 131.1, 127.7, 126.6, 120.4, 117.2, 90.2, 87.9, 62.5 ppm.

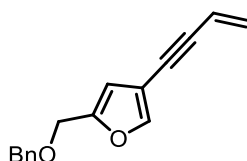
General procedure F: synthesis of **2q-2r**⁹ (synthesis of **2q** is used as an example):



A three-necked flask charged with aldehyde **S7**¹⁰ (5.0 mmol) and K₂CO₃ (1.38 g, 10.0 mmol, 2.0 equiv) was evacuated and backfilled with argon (repeated for 3 times),

methanol (30.0 mL) was added, and the reaction mixture was stirred for 10 min at room temperature. A solution of Ohira-Bestmann reagent (1.15 g, 6.0 mmol in 10.0 mL of MeOH) was added dropwise by syringe. The mixture was stirred at room temperature overnight. After the reaction is completed (TLC control), the reaction mixture was diluted with Et₂O washed with saturated NaHCO₃, brine and dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum, and purified by flash column chromatography to provide the pure product **S8**.

1,3-enyne **2q** was prepared via general procedure D after flash chromatography on silica gel with PE/EA (100/1).



2-((benzyloxy)methyl)-4-(but-3-en-1-yn-1-yl)furan (2q)

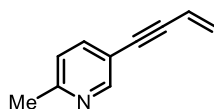
Prepared according to General Procedure F on a 5.0 mmol scale.

0.94 g, 79% yield. Yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 7.34 – 7.30 (m, 5H), 6.54 (d, *J* = 3.3 Hz, 1H), 6.31 (d, *J* = 3.3 Hz, 1H), 6.00 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.74 (dd, *J* = 17.6, 2.0 Hz, 1H), 5.55 (dd, *J* = 11.2, 2.0 Hz, 1H), 4.54 (s, 2H), 4.45 (s, 2H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ 153.2, 137.7, 137.1, 128.5, 128.0, 127.9, 127.7, 116.4, 116.2, 110.7, 92.5, 80.1, 72.3, 63.9 ppm.

HRMS (ESI) calcd for [C₁₆H₁₄O₂+H]⁺ 239.1067, found 239.1066.



5-(but-3-en-1-yn-1-yl)-2-methylpyridine (2r)

Prepared according to General Procedure F on a 5.0 mmol scale.

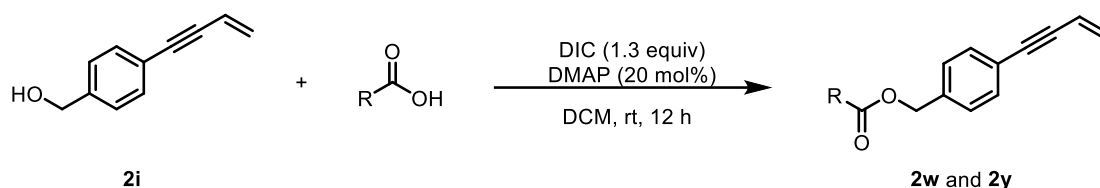
0.5 g, 71% yield. Yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 8.56 (d, *J* = 1.1, 1H), 7.60 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.02 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.76 (dd, *J* = 17.5, 2.0 Hz, 1H), 5.58 (dd, *J* = 11.1, 2.0 Hz, 1H), 2.55 (s, 3H) ppm.

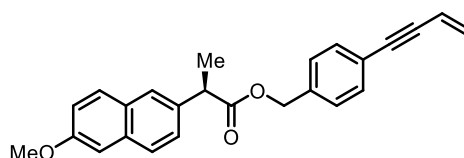
¹³C NMR (75 MHz, CDCl₃) δ 157.7, 151.5, 138.6, 127.6, 122.7, 117.2, 116.8, 90.5, 86.7, 24.4 ppm.

HRMS (ESI) calcd for [C₁₀H₉N+H]⁺ 144.0808, found 144.0811.

General procedure G: synthesis of **2w** and **2y**⁸



To a solution of carboxylic acid (6.0 mmol, 1.2 equiv), alcohol **2i** (791.0 mg, 5.0 mmol, 1.0 equiv) and DMAP (122.0 mg, 1.0 mmol, 20 mol %) in dry DCM (30.0 mL) was added diisopropylcarbodiimide (DIC, 820.3 mg, 6.5 mmol, 1.5 equiv) in DCM (5.0 mL) dropwise. The resulting mixture was stirred at room temperature overnight. After this time, the reaction was quenched with water, extracted by DCM, concentrated and purified by flash column chromatography to provide the pure product.

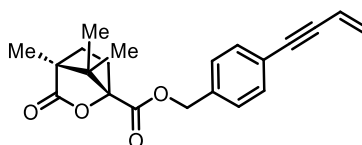


*4-(but-3-en-1-yn-1-yl)benzyl (R)-2-(6-methoxynaphthalen-2-yl)propanoate (2w)*⁸

1.53 g, 83% yield. Yellow solid.

¹H NMR (300 MHz, CDCl₃) δ 7.74 – 7.67 (m, 3H), 7.40 – 7.37 (m, 3H), 7.21 – 7.15 (m, 4H), 6.00 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.73 (dd, *J* = 17.6, 2.1 Hz, 1H), 5.54 (dd, *J* = 11.0, 2.2 Hz, 1H), 5.09 (d, *J* = 2.5 Hz, 3H), 3.94 – 3.84 (m, 4H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ 174.5, 157.8, 136.2, 135.5, 133.8, 131.7, 129.4, 129.0, 127.9, 127.3, 127.2, 126.3, 126.1, 123.0, 119.1, 117.2, 105.6, 89.7, 88.5, 66.1, 55.4, 45.5, 18.6 ppm.



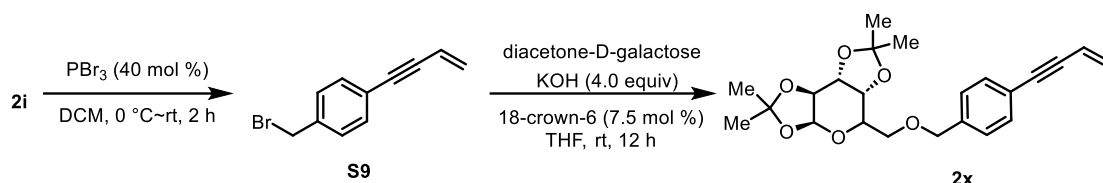
*4-(but-3-en-1-yn-1-yl)benzyl (1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (2y)*⁸

1.34 g, 79% yield. Yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.01 (dd, *J* = 17.6, 11.1 Hz, 1H), 5.74 (dd, *J* = 17.5, 2.1 Hz, 1H), 5.56 (dd, *J* = 11.1, 2.1 Hz, 1H), 5.25 (s, 2H), 2.43 (ddd, *J* = 13.5, 10.6, 4.3 Hz, 1H), 2.08 – 1.87 (m, 2H), 1.68 (ddd, *J* = 13.4, 9.3, 4.3 Hz, 1H), 1.10 (s, 3H), 1.01 (s, 3H), 0.89 (s, 3H) ppm.

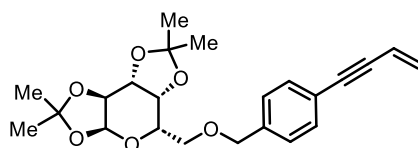
¹³C NMR (75 MHz, CDCl₃) δ 178.1, 167.4, 135.2, 131.8, 128.4, 127.4, 123.5, 117.1, 91.0, 89.4, 88.8, 66.7, 54.8, 54.4, 30.7, 28.9, 16.8, 16.7, 9.7 ppm.

General procedure H: synthesis of **2x**⁸



To a solution of enyne **2i** (791.0 mg, 5.0 mmol) in dry DCM (20.0 mL) was added PBr_3 (188 μL , 2.0 mmol) under 0 $^{\circ}\text{C}$. The reaction was stirred at room temperature for 2 h. The reaction was then quenched with saturated NaHCO_3 aqueous solution, extracted with DCM, condensed and purified by flash column chromatography to provide the pure product **S9**.

To a solution of diacetone-D-galactose (520.6 mg, 2.0 mmol), 18-crown-6 (40.0 mg, 0.15 mmol 7.5 mol %) in dry THF (20.0 mL) was added the KOH (448.0 mg, 8.0 mmol, 4.0 equiv). The reaction was stirred at room temperature for 3 h. Then 1-(bromomethyl)-4-(but-3-en-1-yn-1-yl)benzene **S9** in THF (5.0 mL) was added to above solution dropwise. The resulting mixture continued to stir at room temperature for 12 h. The reaction was then quenched with water, extracted by EA, concentrated and purified by flash column chromatography to provide the pure product **2x** (552.1 mg, 69% yield).



(3a*S*,5*S*,5a*R*,8a*R*,8b*S*)-5-(((4-(but-3-en-1-yn-1-yl)benzyl)oxy)methyl)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran (2x**)⁸**

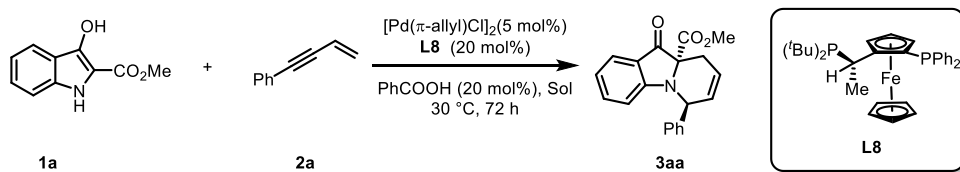
552.1 mg, 69% yield. Yellow solid.

¹H NMR (300 MHz, CDCl_3) δ 7.43 – 7.41 (m, 2H), 7.32 – 7.28 (m, 2H), 6.01 (dd, J = 17.5, 11.1 Hz, 1H), 5.72 (dd, J = 17.5, 2.1 Hz, 1H), 5.55 (s, 1H), 5.53 (dd, J = 8.9, 2.1 Hz, 2H), 4.64 – 4.52 (m, 4H), 4.31 (dd, J = 5.0, 2.4 Hz, 2H), 4.26 (dd, J = 7.9, 1.8 Hz, 1H), 4.02 – 3.99 (m, 1H), 3.69 – 3.63 (m, 2H), 1.54 (s, 3H), 1.44 (s, 3H), 1.33 (s, 6H) ppm.

¹³C NMR (75 MHz, CDCl_3) δ 138.7, 131.6, 127.6, 127.0, 122.3, 117.3, 109.3, 108.7, 96.4, 90.0, 88.1, 73.0, 71.2, 70.7, 70.6, 69.1, 67.0, 26.2, 26.1, 25.0, 24.5 ppm.

3. Solvent Screening for the Reaction

Table S1 Solvent Screening^{a,b,c}

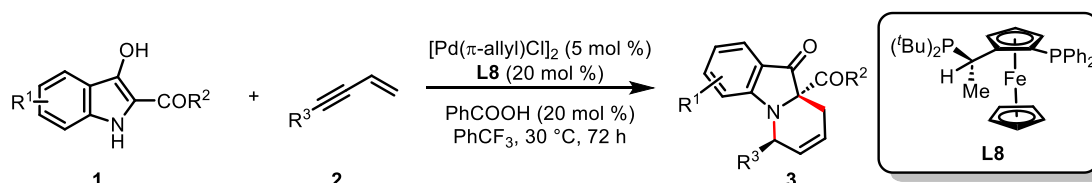


entry	solvent	yield (%)	ee (%)	dr
1	PhCF ₃	86	95	>20:1
1	toluene	80	92	>20:1
2	m-Xylene	75	91	>20:1
3	Mesitylene	78	90	>20:1
4	EA	65	92	15:1
5	Acetone	73	90	>20:1
6	EtOH	trace	/	/

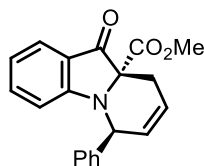
^aReaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Pd] (10 mol %), **L8** (20 mol %) and PhCOOH (20 mol %) in solvent (1.0 mL), under argon atmosphere. ^bYields of **3aa** were determined by GC with dodecane as the internal standard. ^cThe dr and ee values were determined by chiral HPLC analysis.

4. General Procedure for the Palladium-Catalyzed Asymmetric Sequential Hydroalkylation and Hydroamination of 1,3-Enynes

Reaction



A sealed tube was charged with **1** (0.2 mmol, 1.0 equiv), [Pd(π-allyl)Cl]₂ (3.7 mg, 0.01 mmol, 5 mol %), **L8** (21.7 mg, 0.04 mmol, 20 mol %), PhCOOH (4.9 mg, 0.04 mmol, 20 mol %). The vial was thoroughly flushed with Ar, and PhCF₃ (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 30 °C (oil temperature) for 72 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel to afford products **3**.



methyl (6S,9aR)-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3aa)

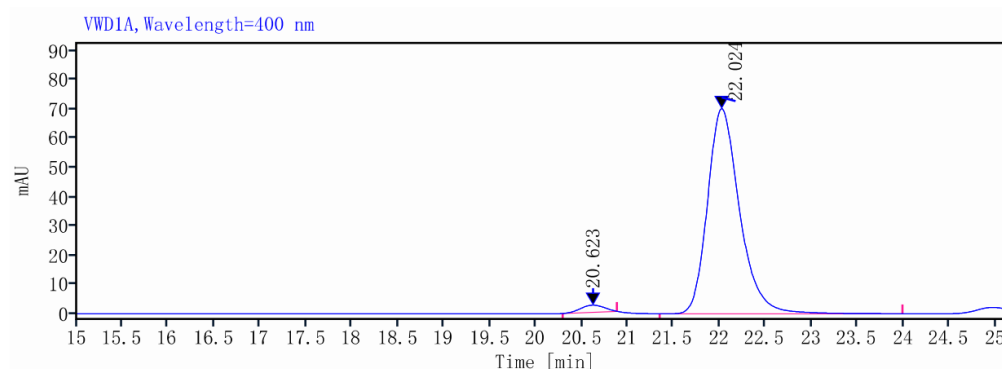
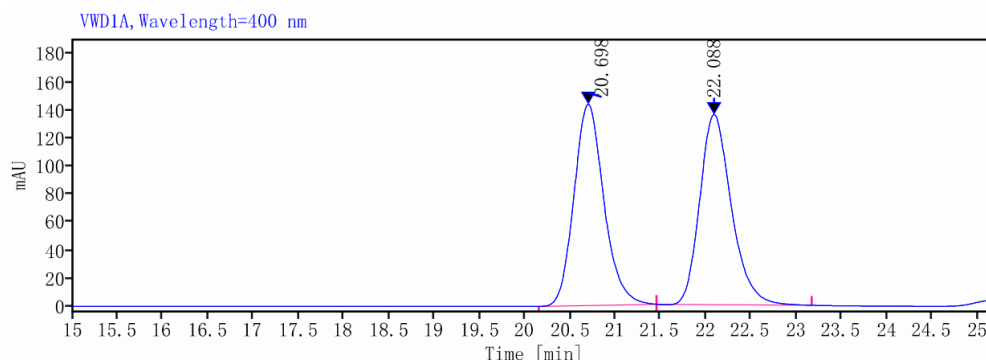
53.6 mg, 84% yield, 95% ee, >20:1 dr. R_f = 0.5 (PE/EA = 10/1); Yellow solid, m.p. 180-182 °C. $[\alpha]_D^{25}$ = -170.7 (c = 0.082, CHCl_3).

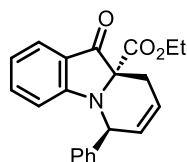
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.66 (d, J = 7.6 Hz, 1H), 7.50 – 7.35 (m, 5H), 7.21 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 6.77 (t, J = 7.4 Hz, 1H), 6.09 (d, J = 8.5 Hz, 1H), 5.96 (ddt, J = 8.2, 6.5, 1.8 Hz, 1H), 5.79 (dt, J = 10.0, 2.8 Hz, 1H), 5.39 – 5.36 (m, 1H), 3.83 (s, 3H), 3.42 (ddd, J = 16.7, 6.4, 2.2 Hz, 1H), 2.62 (dq, J = 16.8, 2.7 Hz, 1H) ppm.

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 194.6, 168.0, 159.6, 140.1, 137.2, 131.7, 129.3, 128.3, 127.6, 125.1, 121.1, 120.1, 118.2, 111.4, 74.8, 59.3, 53.7, 28.8 ppm.

HRMS (ESI) calcd for $[\text{C}_{20}\text{H}_{17}\text{NO}_3 + \text{Na}]^+$ 342.1109, found 342.1101.

HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis λ = 400 nm, t_{R1} = 20.6 min (minor), t_{R2} = 22.1 min (major).





ethyl (6*S*,9*aR*)-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*ba*)

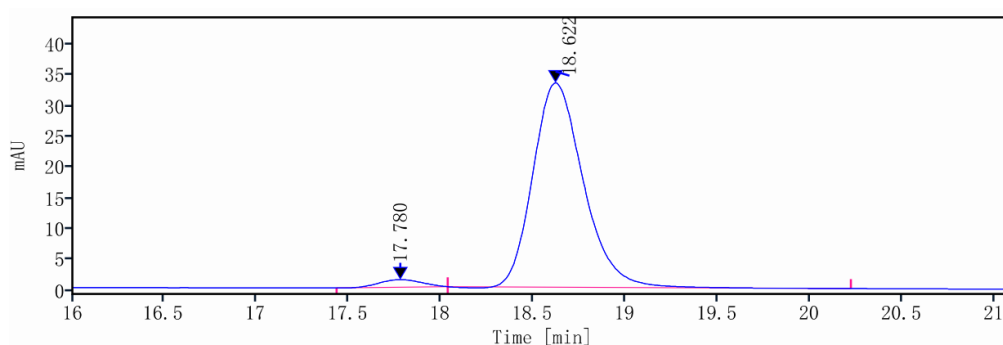
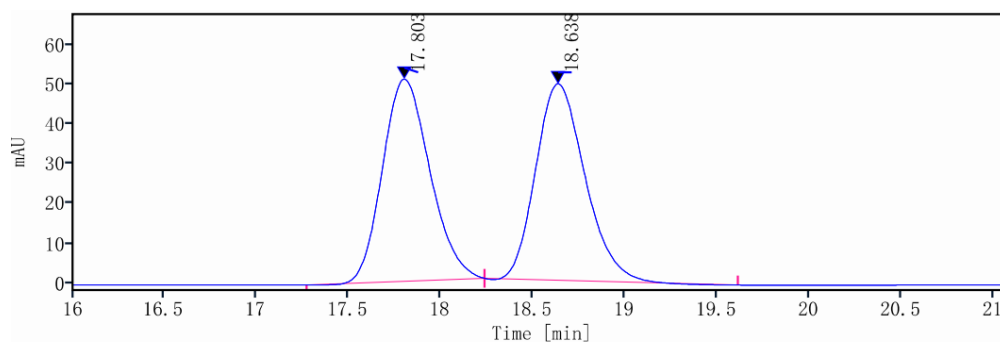
49.3 mg, 74% yield, 94% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 185-187 °C. $[\alpha]_D^{25} = -96.9$ ($c = 0.096$, CHCl₃).

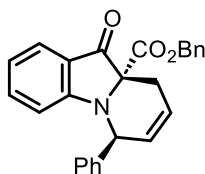
¹H NMR (300 MHz, CDCl₃) δ 7.57 (dt, $J = 7.9, 0.8$ Hz, 1H), 7.37 – 7.31 (m, 5H), 7.12 (ddd, $J = 8.5, 7.1, 1.4$ Hz, 1H), 6.67 (t, $J = 7.4$ Hz, 1H), 6.00 (d, $J = 8.4$ Hz, 1H), 5.87 (ddt, $J = 10.0, 6.4, 1.8$ Hz, 1H), 5.70 (dt, $J = 10.0, 2.7$ Hz, 1H), 5.28 (*app.* t, $J = 2.7$ Hz, 1H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.33 (ddd, $J = 16.7, 6.5, 2.2$ Hz, 1H), 2.52 (dtd, $J = 16.6, 3.1, 1.8$ Hz, 1H), 1.24 (t, $J = 7.1$ Hz, 3H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ 194.8, 167.3, 159.7, 140.1, 137.2, 131.7, 129.3, 128.2, 127.5, 125.1, 121.0, 120.1, 118.2, 111.3, 74.9, 62.7, 59.2, 28.7, 14.2 ppm.

HRMS (ESI) calcd for [C₂₁H₁₉NO₃+Na]⁺ 356.1257, found 356.1260.

HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 17.8$ min (minor), $t_{R2} = 18.6$ min (major).





benzyl (6*S*,9*aR*)-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*ca*)

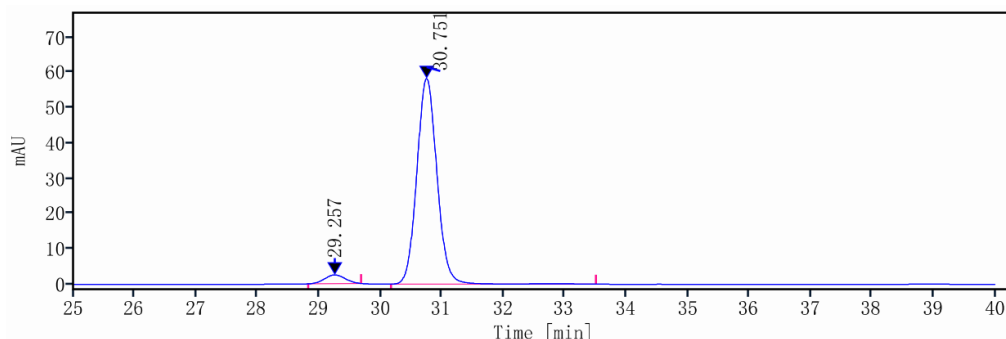
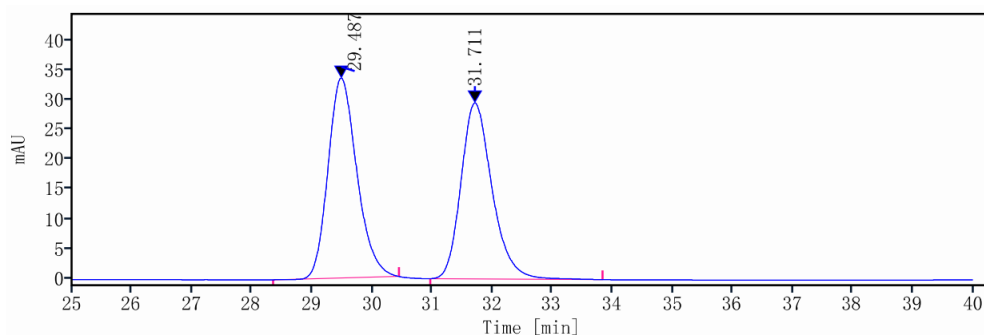
57.7 mg, 73% yield, 92% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 10/1); Yellow solid, m.p. 116–118 °C. $[\alpha]_D^{25} = -125.0$ ($c = 0.068$, CHCl_3).

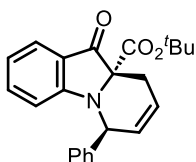
^1H NMR (300 MHz, CDCl_3) δ 7.58 (d, $J = 7.8, 1.5, 0.7$ Hz, 1H), 7.35 – 7.19 (m, 10H), 7.12 (ddd, $J = 8.5, 7.1, 1.5$ Hz, 1H), 6.70 – 6.65 (m, 1H), 5.99 (d, $J = 8.4$ Hz, 1H), 5.84 (ddt, $J = 10.0, 6.4, 1.8$ Hz, 1H), 5.64 (dt, $J = 9.9, 2.7$ Hz, 1H), 5.23 (q, $J = 2.6$ Hz, 1H), 5.16 (s, 2H), 3.36 (ddd, $J = 16.7, 6.5, 2.2$ Hz, 1H), 2.54 (dtd, $J = 16.7, 3.2, 1.8$ Hz, 1H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 194.6, 167.3, 159.7, 140.0, 137.3, 135.4, 131.7, 129.3, 128.6, 128.3, 128.2, 127.7, 127.5, 125.1, 121.1, 120.2, 118.3, 111.3, 75.0, 68.0, 59.2, 28.7 ppm.

HRMS (ESI) calcd for $[\text{C}_{26}\text{H}_{21}\text{NO}_3 + \text{H}]^+$ 396.1594, found 396.1597.

HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 29.3$ min (minor), $t_{R2} = 30.8$ min (major).





tert-butyl (6S,9aR)-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3da)

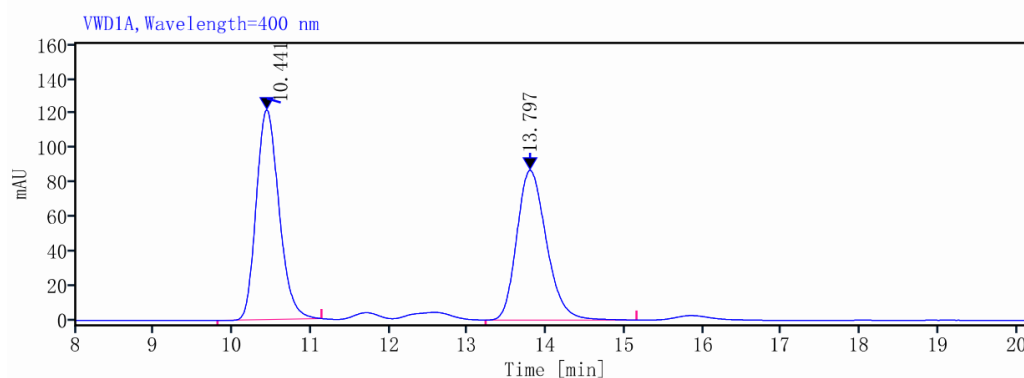
45.5 mg, 63% yield, 91% ee, 14:1 dr. $R_f = 0.5$ (PE/EA = 10/1); Yellow solid, 44-46 °C. $[\alpha]_D^{25} = -215.91$ ($c = 0.088$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.56 (dd, $J = 8.0, 2.8$ Hz, 1H), 7.38 – 7.31 (m, 5H), 7.10 (ddd, $J = 10.0, 5.3, 2.4$ Hz, 1H), 6.66 (td, $J = 7.5, 3.0$ Hz, 1H), 5.99 (dd, $J = 8.5, 2.9$ Hz, 1H), 5.88 (ddt, $J = 10.0, 6.4, 1.8$ Hz, 1H), 5.69 (dt, $J = 9.9, 2.7$ Hz, 1H), 5.25 (p, $J = 2.3$ Hz, 1H), 3.28 (ddd, $J = 16.6, 6.4, 2.2$ Hz, 1H), 2.48 (dtd, $J = 16.6, 3.1, 1.8$ Hz, 1H), 1.41 (s, 9H) ppm.

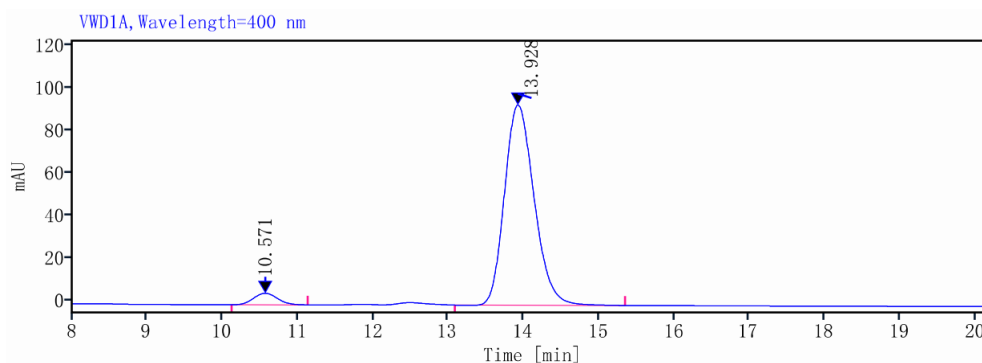
^{13}C NMR (75 MHz, CDCl_3) δ 195.1, 166.0, 159.8, 140.4, 137.0, 131.5, 129.3, 128.2, 127.5, 125.0, 121.3, 120.4, 118.0, 111.1, 83.3, 75.7, 59.3, 28.7, 27.9 ppm.

HRMS (ESI) calcd for $[\text{C}_{23}\text{H}_{23}\text{NO}_3 + \text{H}]^+$ 362.1751, found 362.1759.

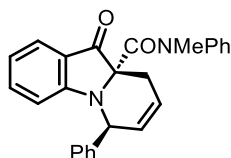
HPLC: Daicel Chiralpak AS-H, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 10.6$ min (minor), $t_{R2} = 13.9$ min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.441	MM m	0.3128	2458.8624	122.1755	51.7440
13.797	MM m	0.4081	2293.1174	87.3872	48.2560



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.571	MM m	0.3460	120.5122	5.4505	4.4559
13.928	MM m	0.4252	2584.0637	94.4455	95.5441



(6S,9aR)-N-methyl-10-oxo-N,6-diphenyl-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxamide (3ea)

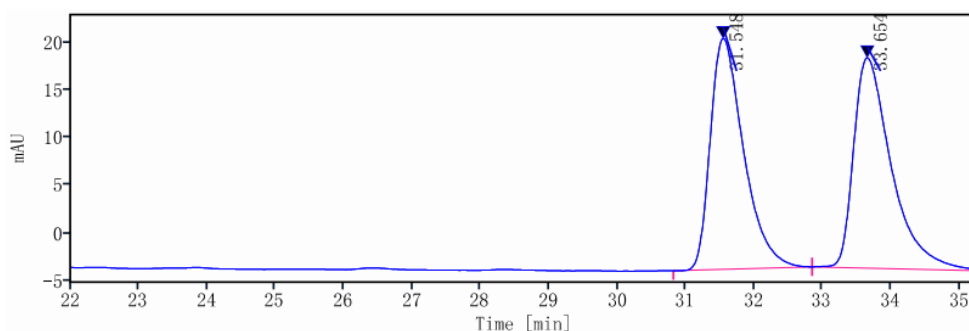
33.9 mg, 43% yield, 79% ee, 6.3:1 dr. $R_f = 0.5$ (PE/EA = 2/1); Yellow solid, m.p. 88–90 °C. $[\alpha]_D^{25} = -23.077$ ($c = 0.052$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.49 – 7.44 (m, 1H), 7.30 – 7.27 (m, 4H), 7.13 – 7.12 (m, 2H), 6.94 – 6.82 (m, 2H), 6.62 (ddd, $J = 8.5, 7.0, 1.4$ Hz, 1H), 6.53 – 6.48 (m, 1H), 6.05 (ddt, $J = 9.9, 6.5, 1.7$ Hz, 1H), 5.77 (dt, $J = 9.7, 2.9$ Hz, 1H), 5.17 – 5.14 (m, 1H), 4.91 (d, $J = 8.5$ Hz, 1H), 3.54 (ddd, $J = 16.0, 6.6, 1.6$ Hz, 1H), 3.25 (s, 3H), 2.15 (dq, $J = 15.9, 3.0$ Hz, 1H) ppm.

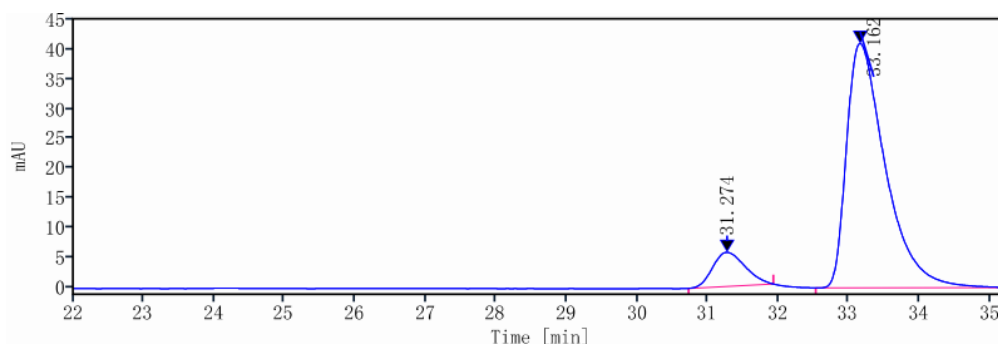
^{13}C NMR (75 MHz, CDCl_3) δ 197.1, 166.3, 157.8, 141.7, 138.8, 135.5, 130.5, 130.1, 129.5, 129.1, 128.7, 128.5, 128.4, 128.3, 127.9, 127.6, 127.0, 124.3, 123.8, 122.9, 122.7, 119.6, 117.6, 112.3, 107.1, 74.9, 60.0, 46.5, 42.6, 41.3, 31.2, 29.8 ppm. (Multiple signals are observed due to the existence of two amide rotamers.)

HRMS (ESI) calcd for $[\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_2 + \text{Na}]^+$ 417.1573, found 417.1583.

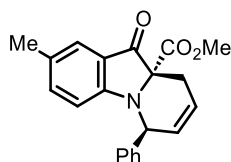
HPLC: Daicel Chiralpak IA-3, n-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 31.3$ min (minor), $t_{R2} = 33.2$ min (major)



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
31.548	MM m	0.5171	822.5907	24.2885	49.2324
33.654	BB	3.1600	848.2413	22.1327	50.7676



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
31.274	MM m	0.4999	182.3025	5.7196	10.4033
33.162	MM m	0.5786	1570.0558	41.0181	89.5967



methyl (6*S*,9*aR*)-2-methyl-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*fa*)

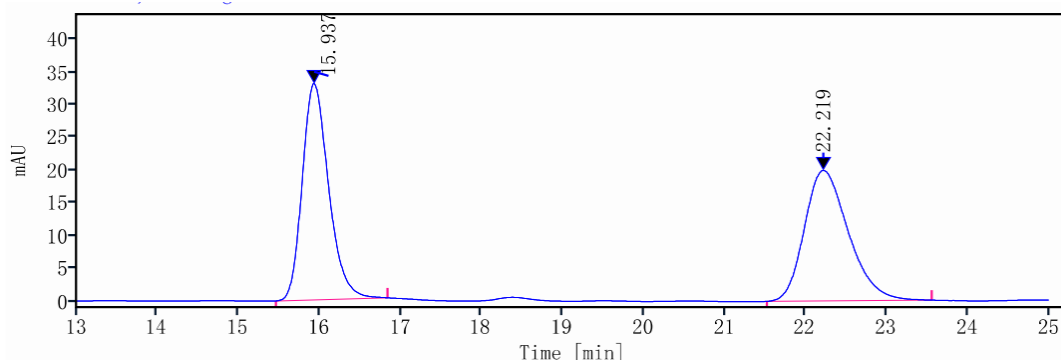
56.7 mg, 85% yield, 94% ee, > 20:1 dr. R_f = 0.5 (PE/EA = 6/1); Yellow solid, m.p. 70-72 °C. $[\alpha]_D^{25}$ = -52.86 (c = 0.070, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.49 – 7.28 (m, 6H), 6.99 (dd, J = 8.5, 1.7 Hz, 1H), 5.93 (d, J = 8.6 Hz, 1H), 5.88 (ddd, J = 6.3, 3.5, 1.8 Hz, 1H), 5.71 (dt, J = 10.0, 2.6 Hz, 1H), 5.28 (p, J = 2.2 Hz, 1H), 3.76 (s, 3H), 3.33 (ddd, J = 16.7, 6.4, 2.0 Hz, 1H), 2.55 (ddd, J = 16.6, 4.9, 3.1 Hz, 1H), 2.20 (s, 3H) ppm.

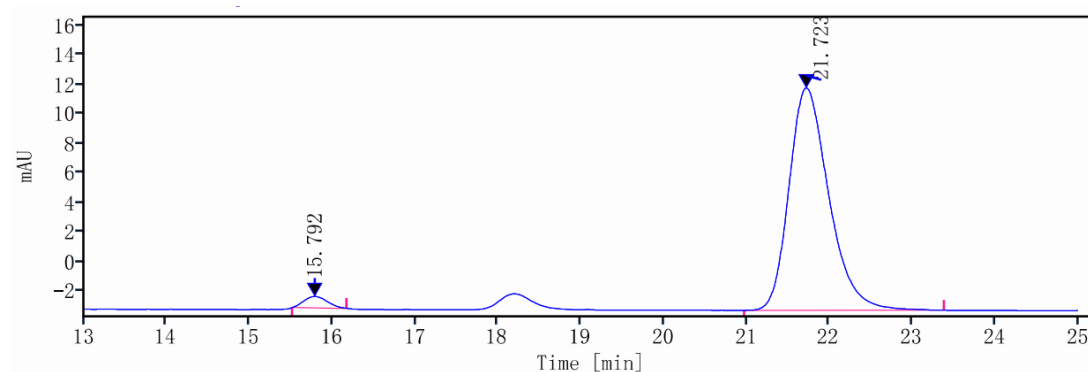
¹³C NMR (75 MHz, CDCl₃) δ 193.9, 168.2, 160.1, 149.0, 140.1, 131.7, 129.3, 128.2, 127.5, 124.8, 121.1, 120.0, 117.8, 111.6, 74.9, 59.2, 53.7, 28.8, 22.8 ppm.

HRMS (ESI) calcd for [C₂₁H₁₉NO₃+H]⁺ 334.1438, found 334.1431.

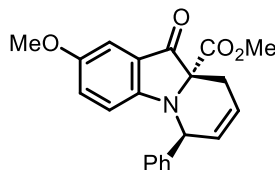
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 15.8 min (minor), t_{R2} = 21.7 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.937	MM m	0.3480	747.2216	33.0264	49.9283
22.219	MM m	0.5787	749.3671	19.9283	50.0717



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.792	MM m	0.3122	15.0592	0.7767	2.9165
21.723	MM m	0.5114	501.2804	15.0199	97.0835



methyl (6*S*,9*aR*)-2-methoxy-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*ga*)

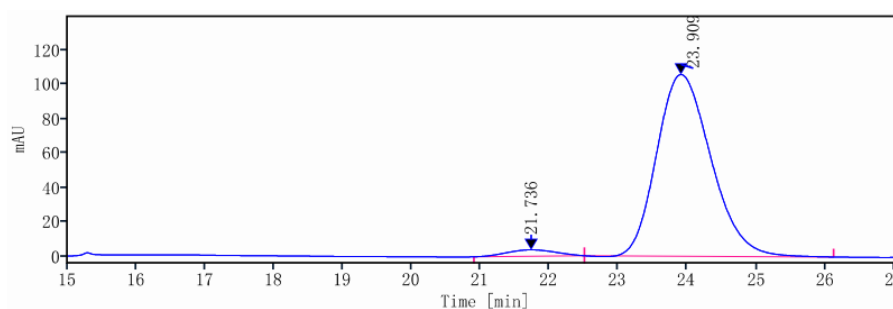
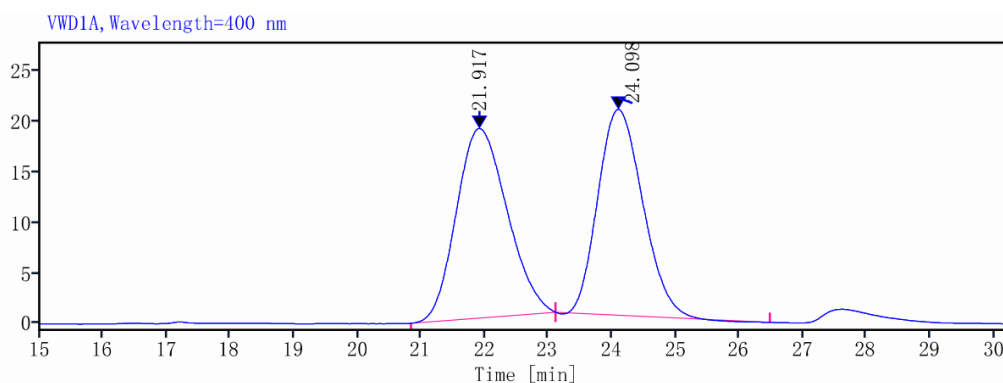
60.1 mg, 86% yield, 94% ee, > 20:1 dr. R_f = 0.3 (PE/EA = 6/1); Yellow solid, m.p. 161–162 °C. $[\alpha]_D^{25}$ = -118.75 (c = 0.064, CHCl₃).

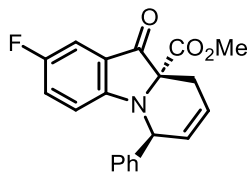
¹H NMR (300 MHz, CDCl₃) δ 7.38–7.33 (m, 7H), 7.04 (d, J = 2.7 Hz, 1H), 6.83 (dd, J = 9.0, 2.7 Hz, 1H), 5.96 (d, J = 9.0 Hz, 1H), 5.88 (ddt, J = 10.0, 6.3, 1.4 Hz, 1H), 5.70 (dt, J = 10.3, 2.7 Hz, 1H), 5.26 (p, J = 2.2 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.33 (ddd, J = 17.0, 6.5, 1.9 Hz, 1H), 2.56 (dt, J = 16.5, 2.5 Hz, 1H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ 194.6, 168.1, 155.7, 152.6, 140.2, 131.8, 129.3, 128.3, 127.6, 121.1, 119.9, 112.4, 105.4, 75.4, 59.2, 55.8, 53.7, 28.8 ppm.

HRMS (ESI) calcd for [C₂₁H₁₉NO₄+Na]⁺ 372.1206, found 372.1211.

HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 21.7 min (minor), t_{R2} = 23.9 min (major).





methyl (6S,9aR)-2-fluoro-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3ha)

48.6 mg, 72% yield, 94% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 150-152 °C. $[\alpha]_D^{25} = -113.8$ ($c = 0.094$, CHCl_3).

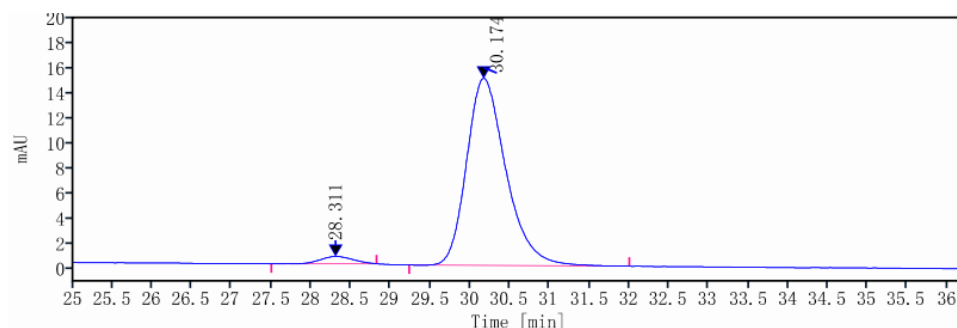
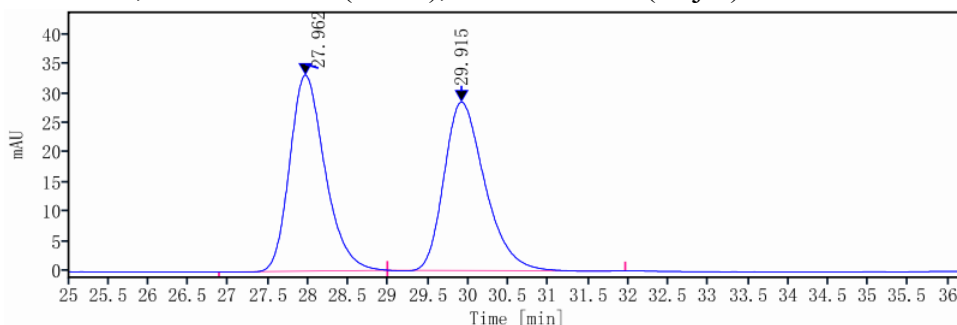
^1H NMR (300 MHz, CDCl_3) δ 7.41 – 7.30 (m, 6H), 7.22 (dd, $J = 7.2, 2.8$ Hz, 1H), 6.89 (td, $J = 8.9, 2.8$ Hz, 1H), 5.95 (dd, $J = 9.0, 3.8$ Hz, 1H), 5.87 (ddt, $J = 10.0, 6.4, 1.8$ Hz, 1H), 5.74 – 5.69 (m, 1H), 5.25 (p, $J = 2.1$ Hz, 1H), 3.76 (s, 3H), 3.32 (ddd, $J = 16.7, 6.4, 2.2$ Hz, 1H), 2.54 (dq, $J = 16.7, 2.8$ Hz, 1H) ppm.

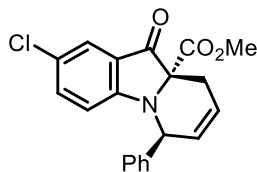
^{13}C NMR (75 MHz, CDCl_3) δ 194.3 (d, $^4J_{\text{C-F}} = 3.4$ Hz), 167.7, 156.5, 155.9 (d, $^1J_{\text{C-F}} = 238.0$ Hz), 139.8, 131.6, 129.4, 128.4, 127.5, 125.1 (d, $^2J_{\text{C-F}} = 24.8$ Hz), 120.9, 120.2 (d, $^3J_{\text{C-F}} = 7.3$ Hz), 112.1 (d, $^3J_{\text{C-F}} = 7.3$ Hz), 110.1 (d, $^2J_{\text{C-F}} = 22.8$ Hz), 75.5, 59.2, 53.8, 28.7 ppm.

^{19}F NMR (282 MHz, CDCl_3) δ -126.08 ppm.

HRMS (ESI) calcd for $[\text{C}_{20}\text{H}_{16}\text{FNO}_3 + \text{Na}]^+$ 360.1006, found 360.1013.

HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis $\lambda = 250$ nm, $t_{R1} = 28.3$ min (minor), $t_{R2} = 30.2$ min (major).





methyl (6*S*,9*aR*)-2-chloro-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*ia*)

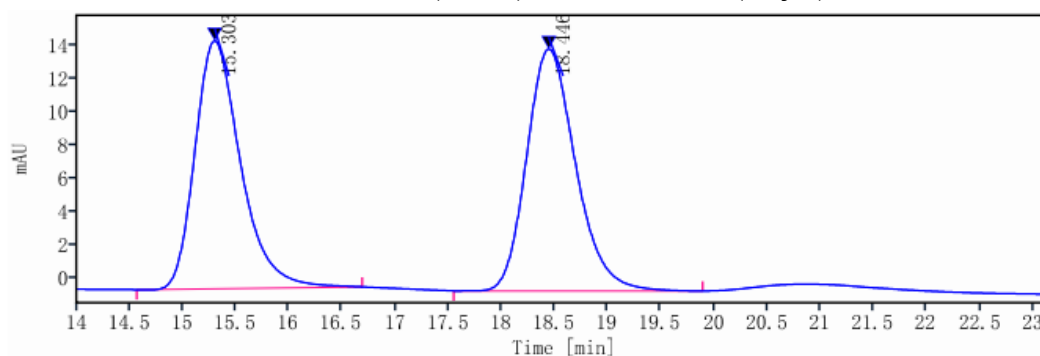
55.2 mg, 78% yield, 94% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 115-117 °C. $[\alpha]_D^{25} = -115.00$ ($c = 0.06$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.54 – 7.53 (m, 1H), 7.39 – 7.28 (m, 1H), 7.07 (d, $J = 8.8$ Hz, 1H), 5.95 (d, $J = 8.8$ Hz, 1H), 5.88 (d, $J = 6.6$ Hz, 1H), 5.71 (d, $J = 9.9$ Hz, 1H), 5.28 (*app.* s, 1H), 3.77 (s, 3H), 3.34 (dd, $J = 17.2, 5.4$ Hz, 1H), 2.56 (d, $J = 16.5$ Hz, 1H) ppm.

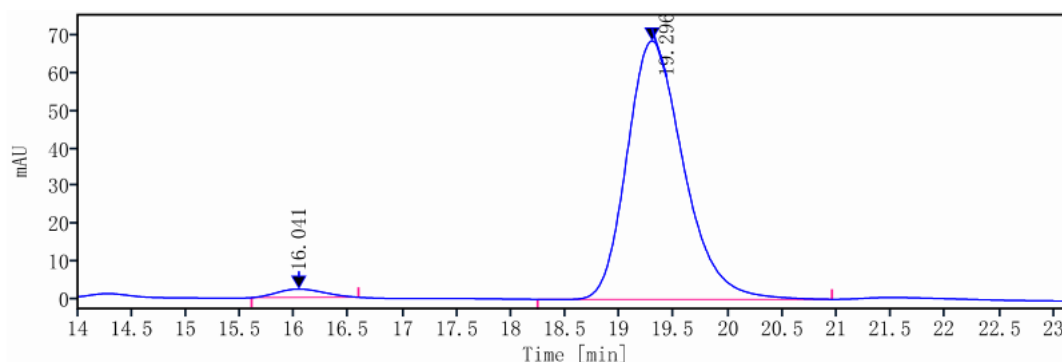
¹³C NMR (75 MHz, CDCl₃) δ 193.5, 167.5, 158.0, 139.5, 137.0, 131.4, 129.5, 128.5, 127.5, 124.4, 123.7, 121.0, 120.9, 112.4, 75.2, 59.2, 53.9, 28.7 ppm.

HRMS (ESI) calcd for [C₂₀H₁₆ClNO₃+H]⁺ 354.0891, found 354.0896.

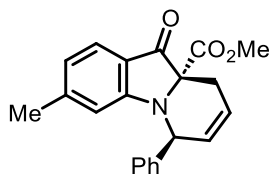
HPLC: Daicel Chiralpak AS-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 16.0$ min (minor), $t_{R2} = 19.3$ min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.303	MM m	0.4559	442.9157	14.8526	48.8214
18.446	MM m	0.4937	464.3013	14.4948	51.1786



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
16.041	MM m	0.4704	66.5584	2.2290	2.6249
19.296	MM m	0.5588	2469.1030	68.1316	97.3751



methyl (6S,9aR)-3-methyl-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3ja)

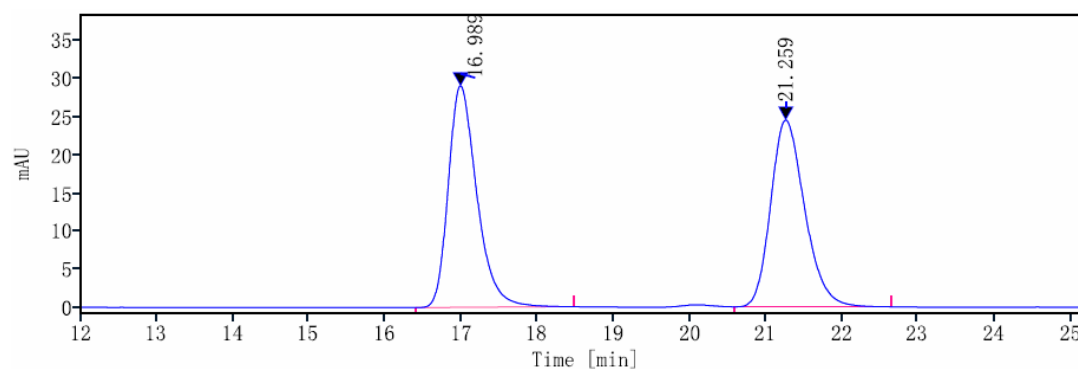
56.0 mg, 84% yield, 94% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 135–137 °C. $[\alpha]_D^{25} = -64.52$ ($c = 0.062$, CHCl_3).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.48 (d, $J = 7.9$ Hz, 1H), 7.43 – 7.31 (m, 5H), 6.53 (dd, $J = 8.0, 1.3$ Hz, 1H), 5.89 (ddt, $J = 10.0, 6.4, 1.8$ Hz, 1H), 5.80 (s, 1H), 5.71 (dt, $J = 10.0, 2.7$ Hz, 1H), 5.30 – 5.27 (m, 1H), 3.77 (s, 3H), 3.33 (ddd, $J = 16.6, 6.5, 2.2$ Hz, 1H), 2.55 (dtd, $J = 16.7, 3.1, 1.8$ Hz, 1H), 2.08 (s, 3H) ppm.

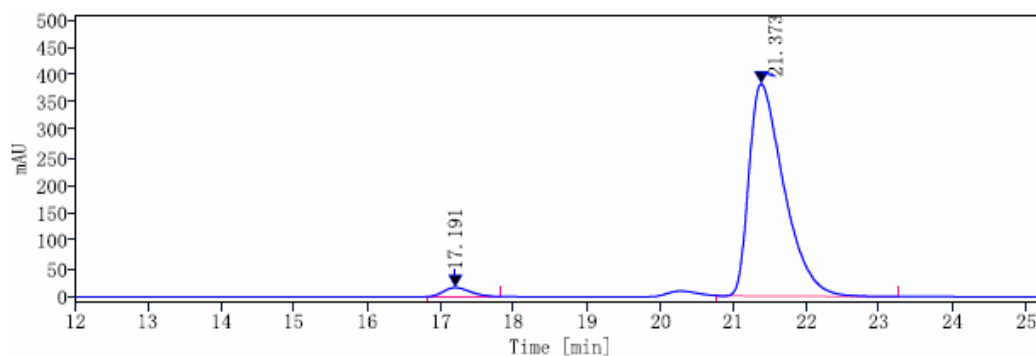
$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 193.9, 168.2, 160.1, 149.0, 140.1, 131.7, 129.3, 128.2, 127.5, 124.8, 121.1, 120.0, 117.8, 111.6, 74.9, 59.2, 53.7, 28.8, 22.8 ppm.

HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{19}\text{NO}_3 + \text{H}]^+$ 334.1438, found 334.1447.

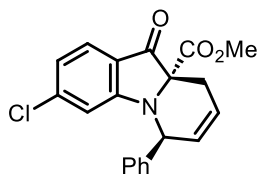
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 17.2$ min (minor), $t_{R2} = 21.4$ min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
16.989	MM m	0.4001	758.7587	29.1106	49.8721
21.259	MM m	0.4785	762.6506	24.5450	50.1279



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
17.191	MM m	0.3927	413.1568	16.3580	3.1570
21.373	MM m	0.5025	12673.7554	382.5373	96.8430



methyl (6*S*,9*aR*)-3-chloro-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*ka*)

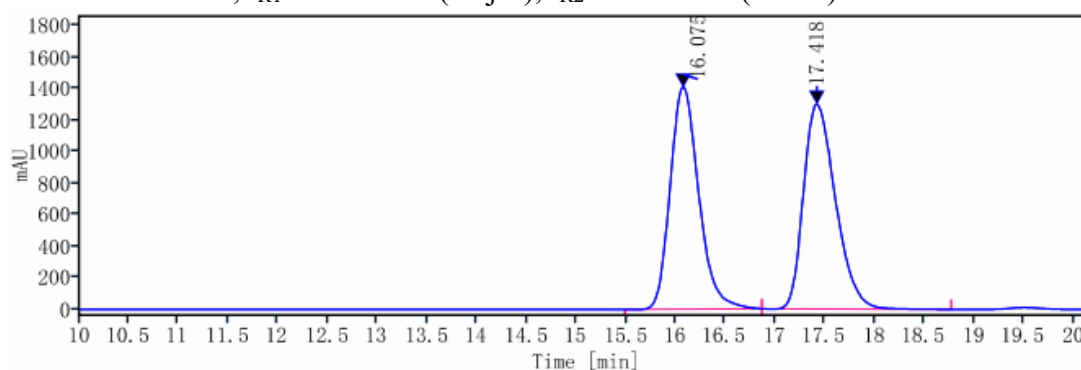
55.9 mg, 79% yield, 94% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 150-152 °C. $[\alpha]_D^{25} = -73.41$ ($c = 0.104$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.47 (d, $J = 8.3$ Hz, 1H), 7.46 – 7.19 (m, 5H), 6.64 (dd, $J = 8.2, 1.7$ Hz, 1H), 5.95 (d, $J = 1.2$ Hz, 1H), 5.91 – 5.84 (ddt, $J = 10.0, 6.4, 1.8$ Hz, 1H), 5.69 (dt, $J = 10.2, 2.7$ Hz, 1H), 5.26 (p, $J = 2.4$ Hz, 1H), 3.75 (s, 3H), 3.32 (ddd, $J = 16.6, 6.5, 2.1$ Hz, 1H), 2.53 (dtd, $J = 16.7, 3.1, 1.8$ Hz, 1H) ppm.

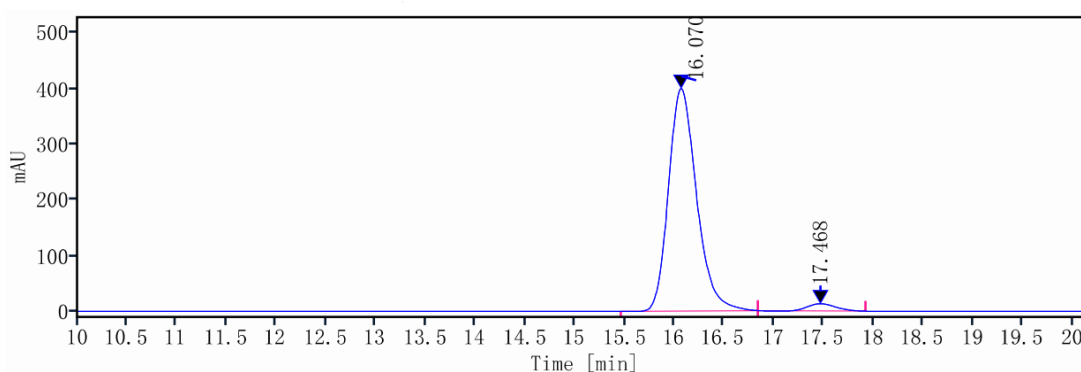
^{13}C NMR (75 MHz, CDCl_3) δ 193.3, 167.5, 159.8, 143.8, 139.2, 131.4, 129.5, 128.6, 127.5, 126.0, 121.0, 119.0, 118.5, 111.4, 75.1, 59.3, 53.8, 28.7 ppm.

HRMS (ESI) calcd for $[\text{C}_{20}\text{H}_{16}\text{ClNO}_3 + \text{H}]^+$ 354.0891, found 354.0885.

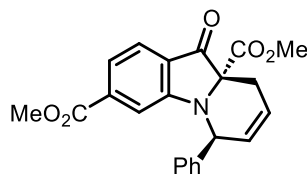
HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 16.1$ min (major), $t_{R2} = 17.5$ min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
16.075	MM m	0.3088	28157.1615	1410.7917	49.2105
17.418	MM m	0.3485	29060.6563	1301.5187	50.7895



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
16.070	MM m	0.3026	7832.3422	399.8030	97.0258
17.468	MM m	0.2953	240.0911	12.8917	2.9742



dimethyl (6*S*,9*aR*)-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-3,9*a*(10*H*)-dicarboxylate (3*la*)

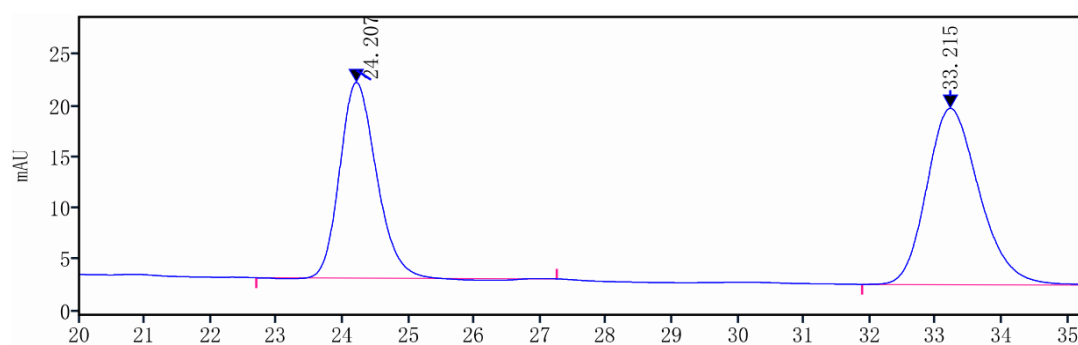
46.1 mg, 61% yield, 93% ee, >20:1 dr, $R_f = 0.5$ (PE/EA = 4/1); Yellow solid, m.p. 142–143 °C. $[\alpha]_D^{25} = -64.52$ ($c = 0.062$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, $J = 8.0$ Hz, 1H), 7.42 – 7.28 (m, 6H), 6.66 (s, 1H), 5.89 (ddt, $J = 10.0, 6.4, 1.8$ Hz, 1H), 5.73 (dt, $J = 10.0, 2.8$ Hz, 1H), 5.32 – 5.30 (m, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.34 (ddd, $J = 16.7, 6.4, 2.2$ Hz, 1H), 2.55 (dq, $J = 16.7, 2.7$ Hz, 1H) ppm.

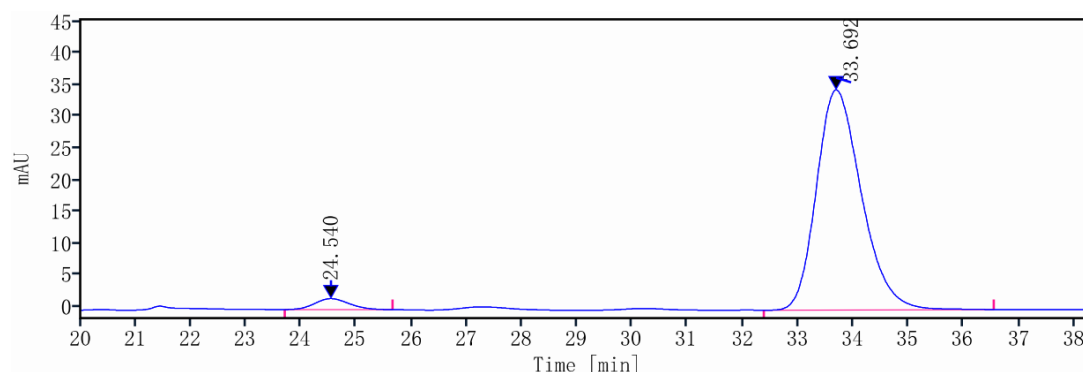
¹³C NMR (75 MHz, CDCl₃) δ 190.7, 163.5, 162.3, 155.2, 135.4, 133.5, 127.5, 125.5, 124.6, 123.7, 120.9, 118.9, 117.0, 115.0, 108.6, 71.2, 55.3, 49.9, 48.5, 24.8 ppm.

HRMS (ESI) calcd for [C₂₂H₁₉NO₅+H]⁺ 378.1336, found 378.1340.

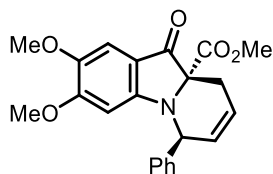
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 24.5$ min (minor), $t_{R2} = 33.7$ min (major) (the racemic sample is a mixture of *R* and *S*-enantiomers).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
24.207	MM m	0.5921	730.5235	19.1035	43.4225
33.215	BB	3.6400	951.8366	17.2084	56.5775



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
24.540	MM m	0.6555	75.3591	1.7323	3.6889
33.692	BB	4.1600	1967.4916	34.7681	96.3111



methyl (6*S*,9*aR*)-2,3-dimethoxy-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*ma*)

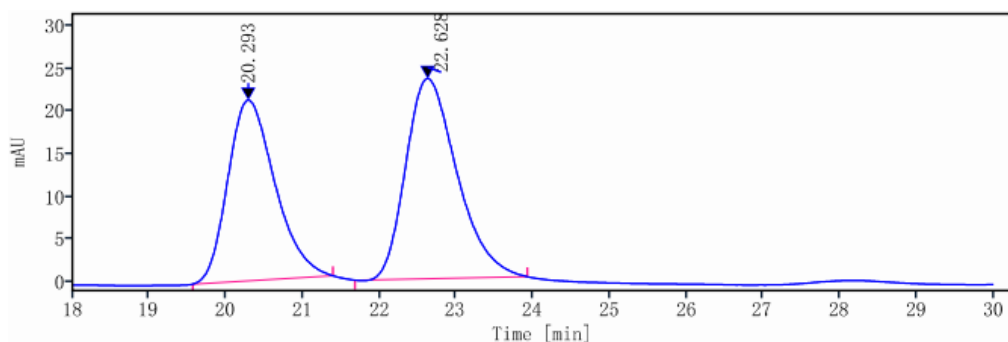
66.8 mg, 88% yield, 96% ee, >20:1 dr, $R_f = 0.5$ (PE/EA = 4/1); Yellow solid, m.p. 150-151 °C. $[\alpha]_D^{25} = -60.64$ ($c = 0.094$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.41 – 7.31 (m, 5H), 6.97 (s, 1H), 5.92 (ddt, $J = 10.0$, 6.4, 1.8 Hz, 1H), 5.71 (dt, $J = 10.1$, 2.7 Hz, 1H), 5.41 (s, 1H), 5.28 (p, $J = 2.3$ Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.38 (s, 3H), 3.35 – 3.28 (m, 1H) 2.53 (dtd, $J = 16.7$, 3.3, 1.8 Hz, 1H) ppm.

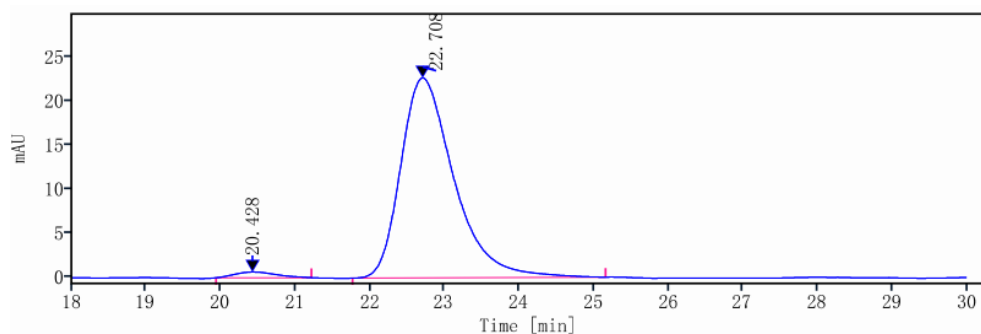
^{13}C NMR (75 MHz, CDCl_3) δ 192.3, 168.4, 157.9, 157.5, 143.3, 140.1, 131.3, 129.3, 128.4, 128.0, 121.6, 110.8, 104.7, 93.9, 74.6, 59.3, 56.2, 55.7, 53.6, 28.9 ppm.

HRMS (ESI) calcd for $[\text{C}_{22}\text{H}_{22}\text{NO}_5 + \text{H}]^+$ 380.1492, found 380.1496.

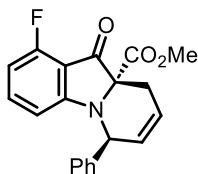
HPLC: Daicel Chiralpak AS-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 20.4$ min (minor), $t_{R2} = 22.6$ min (major) (the racemic sample is a mixture of *R* and *S*-enantiomers).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.293	MM m	0.6573	900.0665	21.1160	45.3813
22.628	MM m	0.7124	1083.2765	23.3860	54.6187



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.428	MM m	0.4865	24.7129	0.6457	2.1565
22.708	MM m	0.7578	1121.2397	22.6386	97.8435



methyl (6S,9aR)-1-fluoro-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3na)

51.3 mg, 76% yield, 96% ee, >20:1 dr. R_f = 0.5 (PE/EA = 10/1); Yellow solid, m.p. 52–54 °C. $[\alpha]_D^{25}$ = -108.8 (c = 0.102, CHCl₃).

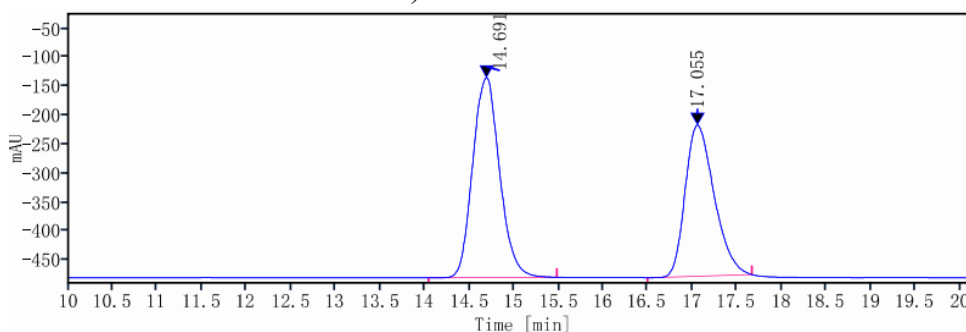
¹H NMR (300 MHz, CDCl₃) δ 8.18 (s, 1H), 7.73 (dd, J = 8.2, 1.2 Hz, 1H), 7.46 – 7.26 (m, 8H), 7.17 (ddd, J = 8.1, 6.3, 1.6 Hz, 1H), 6.22 (s, 1H), 5.91 (ddt, J = 9.9, 6.3, 1.7 Hz, 1H), 5.78 (dt, J = 10.0, 2.7 Hz, 1H), 5.38 (p, J = 1.8 Hz, 1H), 3.76 (s, 3H), 3.44 – 3.35 (m, 1H), 2.68 – 2.59 (m, 1H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ 190.8, 167.5, 160.4 (d, $^3J_{C-F}$ = 5.6 Hz), 159.7 (d, $^1J_{C-F}$ = 261.0 Hz), 139.7, 138.9 (d, $^3J_{C-F}$ = 10.2 Hz), 131.5, 129.4, 128.4, 127.4, 120.9, 108.7 (d, $^2J_{C-F}$ = 17.1 Hz), 107.2 (d, $^4J_{C-F}$ = 3.8 Hz), 104.5 (d, $^2J_{C-F}$ = 18.6 Hz), 75.1, 59.4, 53.8, 28.7 ppm.

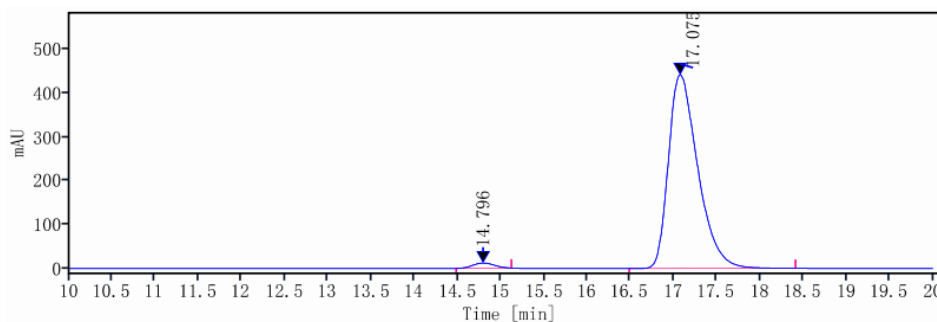
¹⁹F NMR (282 MHz, CDCl₃) δ -111.48 ppm.

HRMS (ESI) calcd for [C₂₀H₁₆FNO₃+H]⁺ 338.1187, found 338.1192.

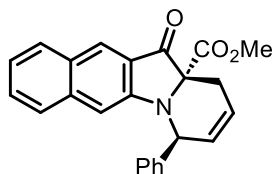
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 400 nm, t_{R1} = 14.8 min (minor), t_{R2} = 17.1 min (major) (the racemic sample is a mixture of *R* and *S*-enantiomers).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.691	MM m	0.3262	7219.7047	344.9312	55.1422
17.055	MM m	0.3465	5873.1739	260.9834	44.8578



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.796	MM m	0.2739	208.1095	12.0255	1.9584
17.075	MM m	0.3612	10418.3213	441.7255	98.0416



methyl (4*S*,12*aR*)-12-oxo-4-phenyl-1,4-dihydrobenzo[*f*]pyrido[1,2-*a*]indole-12*a*(12*H*)-carboxylate (30*a*)

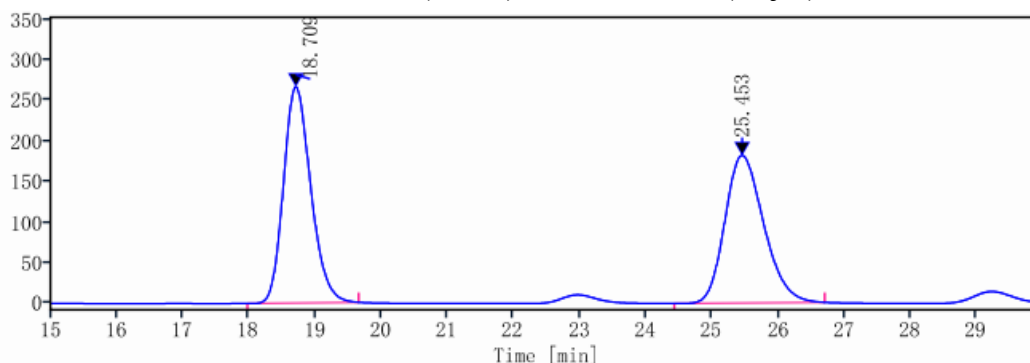
62.1 mg, 84% yield, 94% ee, 19:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 66–68 °C. $[\alpha]_D^{25} = -280.0$ ($c = 0.10$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.92 – 7.82 (m, 4H), 7.62 – 7.49 (m, 3H), 7.37 (d, $J = 8.5$ Hz, 1H), 7.06 (ddd, $J = 8.5, 7.1, 1.4$ Hz, 1H), 6.68 (t, $J = 7.4$ Hz, 1H), 6.08 (d, $J = 8.4$ Hz, 1H), 5.98 – 5.91 (m, 1H), 5.76 (dt, $J = 9.9, 2.8$ Hz, 1H), 5.51 (q, $J = 2.7$ Hz, 1H), 3.80 (s, 3H), 3.41 (ddd, $J = 16.7, 6.5, 2.2$ Hz, 1H), 2.68 – 2.60 (m, 1H) ppm.

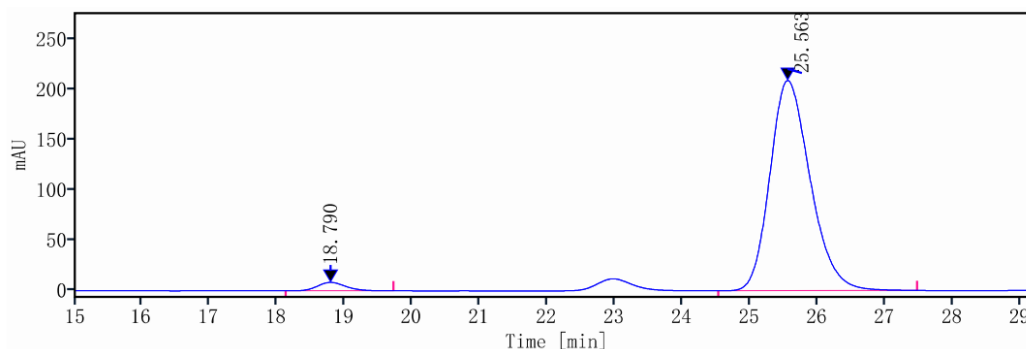
¹³C NMR (75 MHz, CDCl₃) δ 195.5, 168.5, 152.7, 140.0, 139.4, 131.8, 130.6, 129.4, 129.3, 128.2, 127.5, 127.3, 126.9, 126.6, 123.3, 122.6, 121.0, 105.1, 75.0, 59.4, 53.6, 29.0 ppm.

HRMS (ESI) calcd for [C₂₄H₁₉NO₃+H]⁺ 370.1438, found 334.1447.

HPLC: Daicel C hirapak OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 18.8$ min (minor), $t_{R2} = 25.6$ min (major).

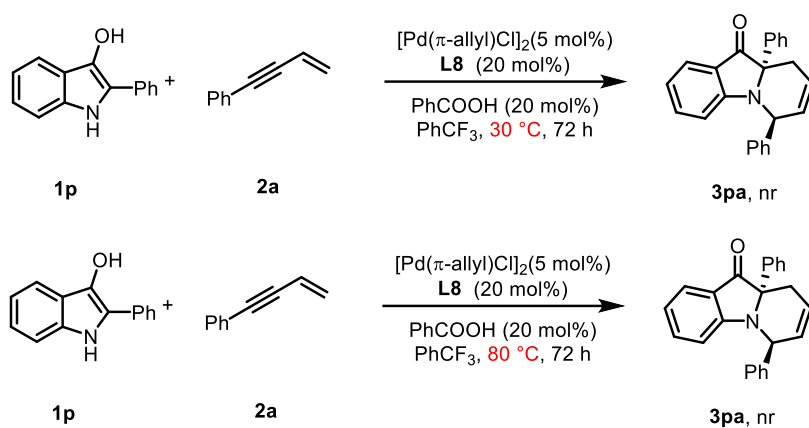


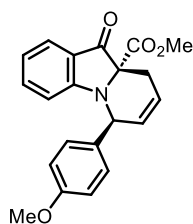
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
18.709	MM m	0.4447	7639.2036	266.3043	50.8268
25.453	MM m	0.6305	7390.6817	181.7306	49.1732



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
18.790	MM m	0.4459	243.6563	8.4126	2.7229
25.563	MM m	0.6382	8704.8310	209.7493	97.2771

In addition, we synthesized substrate 2-phenyl-1H-indol-3-ol (**1p**) and test this substrate under the standard conditions, but no product was formed with **1p** fully recovered. Further raising the reaction temperature to 80 °C did not produce **3pa** either. This outcome suggests that the presence of a carboxylic ester group at C2-position is essential for the efficiency of this reaction.





methyl (6*S*,9*aR*)-6-(4-methoxyphenyl)-10-oxo-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate(3*ab*)

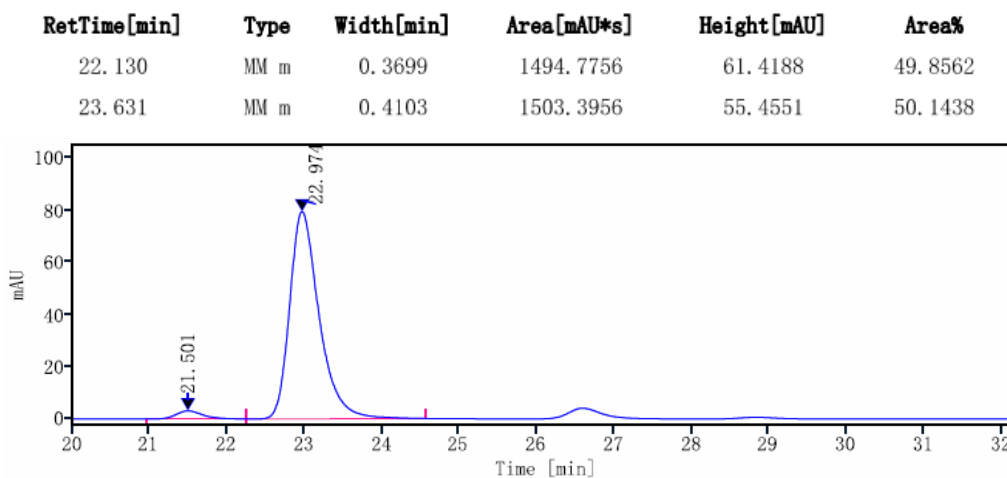
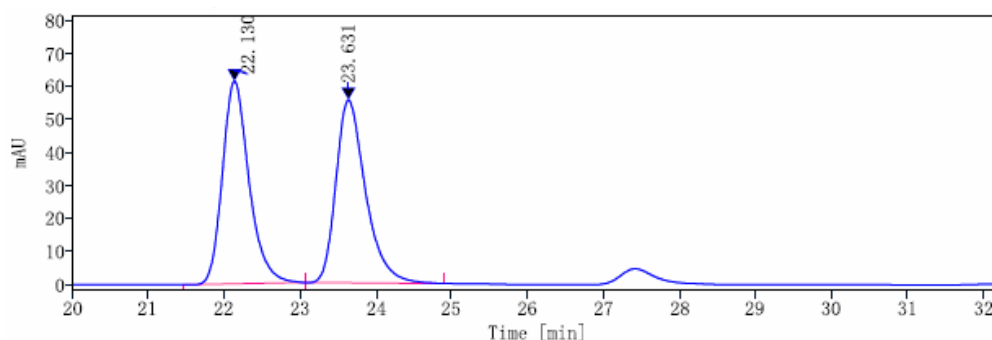
79.4 mg, 88% yield, 94% ee, 18:1 dr. $R_f = 0.3$ (PE/EA = 6/1); Yellow solid, m.p. 177-179 °C. $[\alpha]_D^{25} = -83.56$ ($c = 0.1$, CHCl_3).

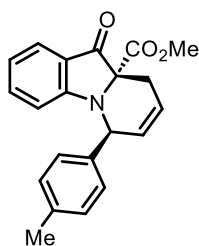
^1H NMR (300 MHz, CDCl_3) δ 7.56 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.16 – 7.10 (m, 1H), 6.89 (d, $J = 8.2$ Hz, 2H), 6.67 (t, $J = 7.4$ Hz, 1H), 6.04 (d, $J = 8.4$ Hz, 1H), 5.88 – 5.82 (m, 1H), 5.68 – 5.64 (m, 1H), 5.24 (q, $J = 2.7$ Hz, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.31 (ddd, $J = 16.7, 6.4, 2.1$ Hz, 1H), 2.51 (dt, $J = 16.7, 2.6$ Hz, 1H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 194.7, 167.9, 159.7, 159.5, 137.3, 132.0, 131.8, 128.7, 125.1, 120.7, 119.9, 118.1, 114.6, 111.4, 74.7, 58.6, 55.4, 53.7, 28.8 ppm.

HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{19}\text{NO}_4 + \text{Na}]^+$ 372.1206, found 372.1211.

HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 21.5$ min (minor), $t_{R2} = 23.0$ min (major).





methyl (6S,9aR)-10-oxo-6-(p-tolyl)-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3ac)

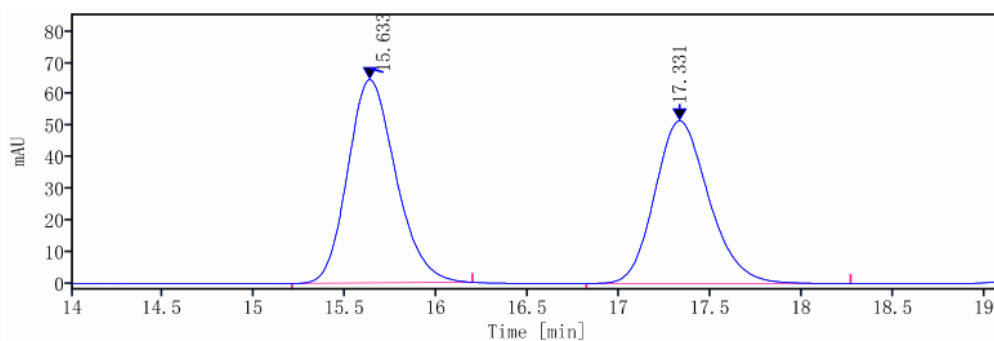
48.1 mg, 72% yield, 93% ee, >20:1 dr. $R_f = 0.4$ (PE/EA = 6/1); Yellow solid, m.p. 177–179 °C. $[\alpha]_D^{25} = -88.97$ ($c = 0.14$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.56 (d, $J = 7.7$ Hz, 1H), 7.22 – 7.10 (m, 5H), 6.67 (t, $J = 7.5$ Hz, 1H), 6.03 (d, $J = 8.4$ Hz, 1H), 5.83 (d, $J = 7.7$ Hz, 1H), 5.66 (dt, $J = 10.0, 2.7$ Hz, 1H), 5.24 (q, $J = 2.8$ Hz, 1H), 3.73 (s, 3H), 3.31 (dd, $J = 16.0, 6.7$ Hz, 1H), 2.51 (d, $J = 16.9$ Hz, 1H), 2.36 (s, 3H) ppm.

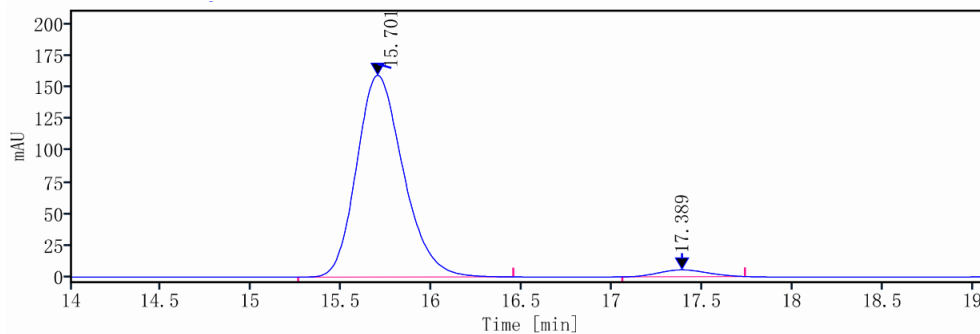
^{13}C NMR (75 MHz, CDCl_3) δ 194.7, 168.0, 159.7, 138.1, 137.2, 137.0, 131.9, 130.0, 127.4, 125.1, 120.9, 120.0, 118.2, 111.4, 74.8, 58.9, 53.7, 28.8, 21.3 ppm.

HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{19}\text{NO}_4 + \text{H}]^+$ 334.1438, found 334.1438.

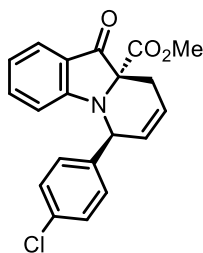
HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 15.7$ min (major), $t_{R2} = 17.4$ min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.633	MM m	0.2816	1181.7554	64.5337	52.7079
17.331	MM m	0.3178	1060.3291	51.5821	47.2921



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.701	MM m	0.2757	2870.0501	159.6973	96.6046
17.389	MM m	0.2928	100.8751	5.4295	3.3954



methyl (6*S*,9*aR*)-6-(4-chlorophenyl)-10-oxo-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*ad*)

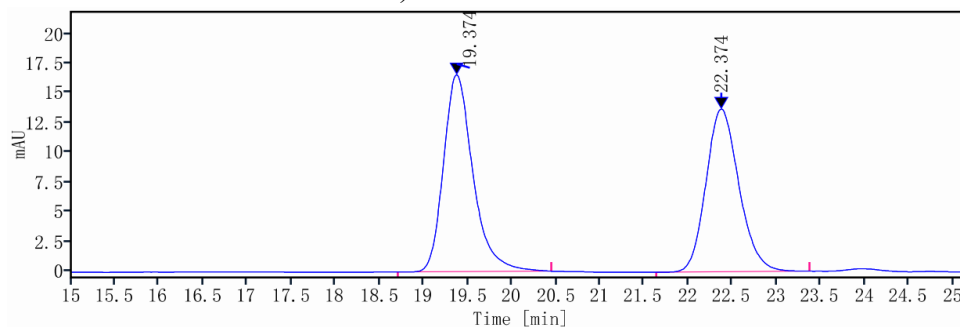
59.3 mg, 84% yield, 94% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 170-173 °C. $[\alpha]_D^{25} = -33.33$ ($c = 0.09$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.58 (d, $J = 7.8$ Hz, 1H), 7.35 – 7.15 (m, 4H), 7.17 (t, $J = 7.8$ Hz, 1H), 6.72 (t, $J = 7.5$ Hz, 1H), 6.01 (d, $J = 8.4$ Hz, 1H), 5.88 (t, $J = 8.3$ Hz, 1H), 5.65 (d, $J = 9.9$ Hz, 1H), 5.27 (s, 1H), 3.74 (s, 3H), 3.32 (dd, $J = 16.5, 6.4$ Hz, 1H), 2.52 (d, $J = 16.8$ Hz, 1H) ppm.

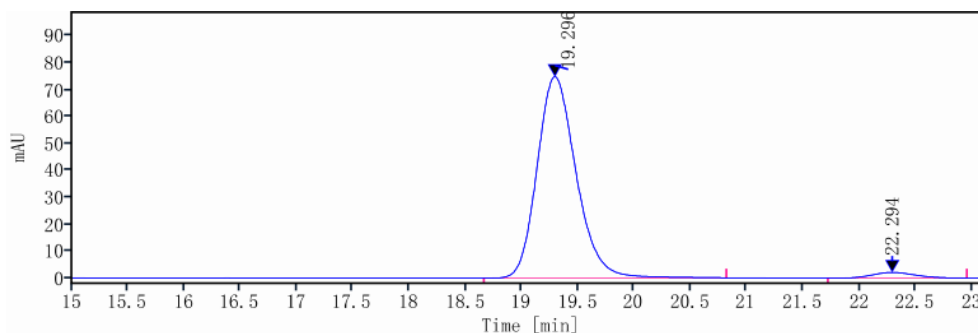
¹³C NMR (75 MHz, CDCl₃) δ 194.4, 167.8, 159.4, 138.7, 137.4, 133.9, 131.3, 129.6, 128.8, 125.3, 121.5, 120.2, 118.5, 111.2, 74.7, 58.5, 53.7, 28.7 ppm.

HRMS (ESI) calcd for [C₂₀H₁₆ClNO₄+Na]⁺ 376.0711, found 376.0713.

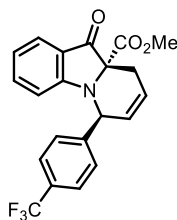
HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 19.3$ min (major), $t_{R2} = 22.3$ min (major) (the racemic sample is a mixture of *R* and *S*-enantiomers).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
19.374	MM m	0.3555	385.8210	16.5793	52.0579
22.374	MM m	0.4005	355.3176	13.7043	47.9421



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
19.296	MM m	0.3706	1800.6627	74.8668	97.0116
22.294	MM m	0.4058	55.4684	2.1023	2.9884



methyl (6*S*,9*aR*)-10-oxo-6-(4-(trifluoromethyl)phenyl)-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*ae*)

46.5 mg, 60% yield, 96% ee, >20:1 dr. R_f = 0.5 (PE/EA = 6/1); Yellow solid, m.p. 163–165 °C. $[\alpha]_D^{25}$ = -115.56 (c = 0.14, CHCl₃).

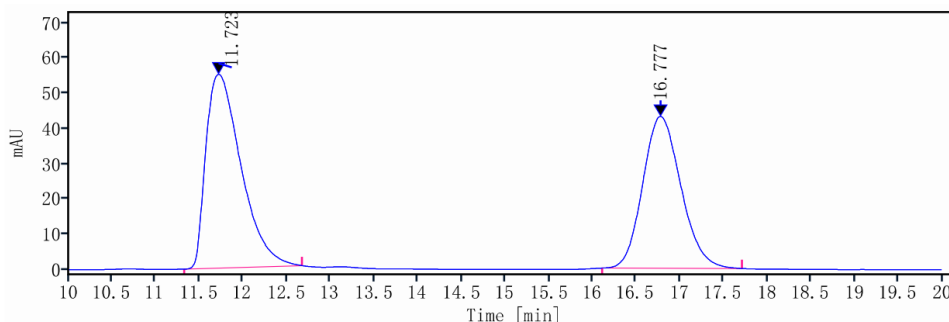
¹H NMR (300 MHz, CDCl₃) δ 7.64 – 7.58 (m, 3H), 7.47 (s, 1H), 7.45 (s, 1H), 7.18 (ddd, J = 8.5, 7.1, 1.4 Hz, 1H), 6.73 (t, J = 7.5 Hz, 1H), 5.97 (d, J = 8.4 Hz, 1H), 5.91 (ddt, J = 8.3, 6.4, 1.8 Hz, 1H), 5.67 (dt, J = 9.9, 2.8 Hz, 1H), 5.39 – 5.35 (m, 1H), 3.75 (s, 3H), 3.35 (ddd, J = 16.9, 6.6, 2.2 Hz, 1H), 2.56 (dtd, J = 16.7, 3.1, 1.8 Hz, 1H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ 194.2, 167.8, 159.2, 144.3 (q, $^4J_{C-F}$ = 1.2 Hz), 137.4, 130.9, 130.5 (q, $^2J_{C-F}$ = 32.4 Hz), 127.7, 126.4 (q, $^3J_{C-F}$ = 3.7 Hz), 125.3, 124.0 (q, $^1J_{C-F}$ = 270.4 Hz), 122.0, 120.3, 118.7, 111.1, 74.8, 58.8, 53.8, 28.7 ppm.

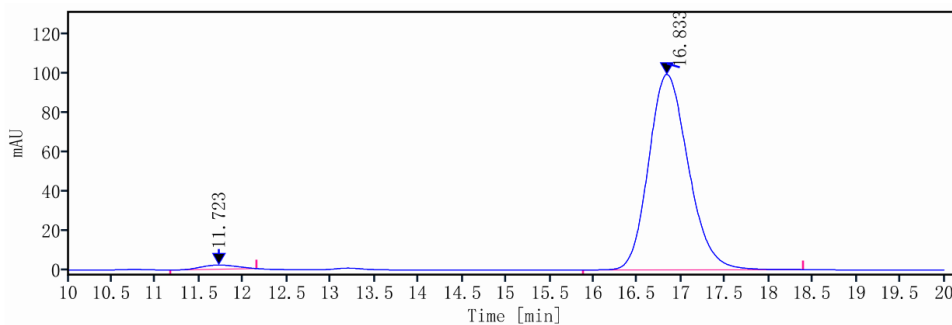
¹⁹F NMR (282 MHz, CDCl₃) δ -62.45 ppm.

HRMS (ESI) calcd for [C₂₁H₁₆F₃NO₄+Na]⁺ 410.0974, found 410.0980.

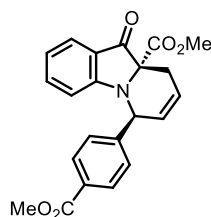
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 400 nm, t_{R1} = 11.7 min (minor), t_{R2} = 16.8 min (major) (the racemic sample is a mixture of *R* and *S*-enantiomers).



RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
11.723	MM m	0.4374	1534.9969	55.0265	54.0044
16.777	MM m	0.4700	1307.3597	43.0876	45.9956



RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
11.723	MM m	0.4487	56.9500	2.0982	1.7878
16.833	MM m	0.4867	3128.5375	99.5400	98.2122



methyl (6*S*,9*aR*)-6-(4-(methoxycarbonyl)phenyl)-10-oxo-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*af*)

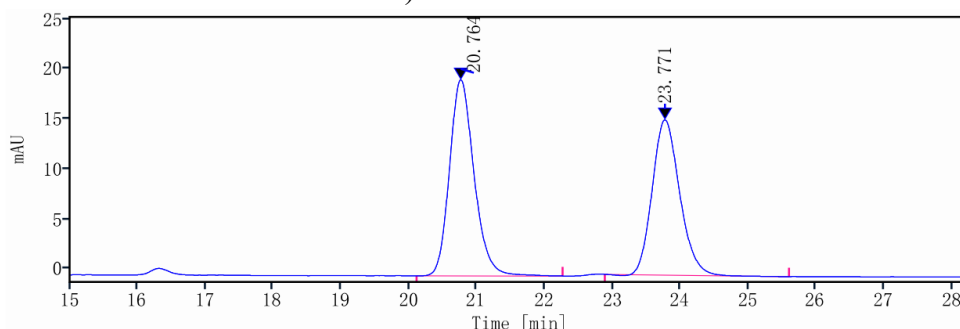
58.9 mg, 78% yield, 96% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 210–212 °C. $[\alpha]_D^{25} = -58.33$ ($c = 0.06$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.9$ Hz, 2H), 7.13 (ddd, $J = 8.5, 7.1, 1.4$ Hz, 1H), 6.71 (t, $J = 7.4$ Hz, 1H), 5.96 (d, $J = 8.4$ Hz, 1H), 5.92 – 5.88 (m, 1H), 5.68 (dt, $J = 10.0, 2.8$ Hz, 1H), 5.35 (q, $J = 2.5$ Hz, 1H), 3.92 (s, 3H), 3.75 (s, 3H), 3.35 (ddd, $J = 16.7, 6.6, 2.2$ Hz, 1H), 2.56 (dq, $J = 16.9, 3.0$ Hz, 1H) ppm.

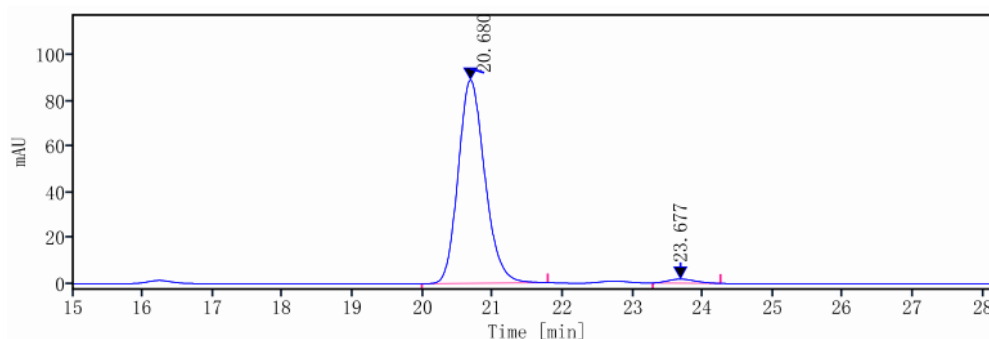
¹³C NMR (75 MHz, CDCl₃) δ 194.3, 167.8, 166.7, 159.3, 145.3, 137.3, 130.8, 130.7, 130.1, 127.5, 125.3, 121.9, 120.2, 118.6, 111.1, 74.6, 58.9, 53.8, 52.3, 28.7 ppm.

HRMS (ESI) calcd for [C₂₂H₁₉NO₅+Na]⁺ 400.1155, found 400.1153.

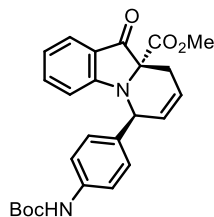
HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 20.7$ min (major), $t_{R2} = 23.7$ min (minor) (the racemic sample is a mixture of *R* and *S*-enantiomers).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.764	MM m	0.3862	494.5404	19.6145	53.1890
23.771	MM m	0.4330	435.2392	15.5273	46.8110



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.680	MM m	0.4086	2347.5975	88.7617	98.0214
23.677	MM m	0.4220	47.3869	1.7836	1.9786



methy (6S,9aR)-6-(4-((tert-butoxycarbonyl)amino)phenyl)-10-oxo-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3ag)

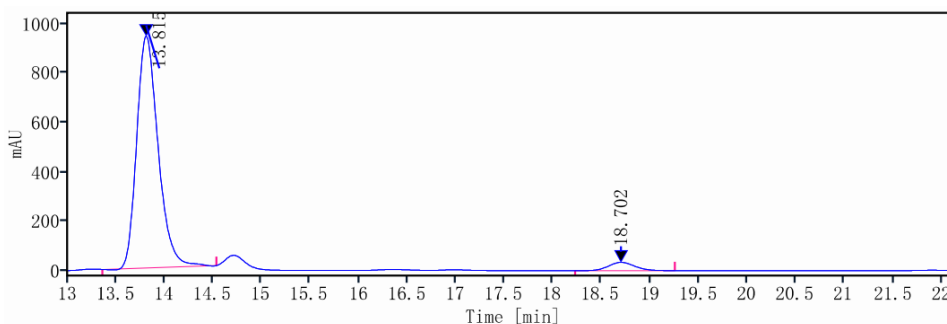
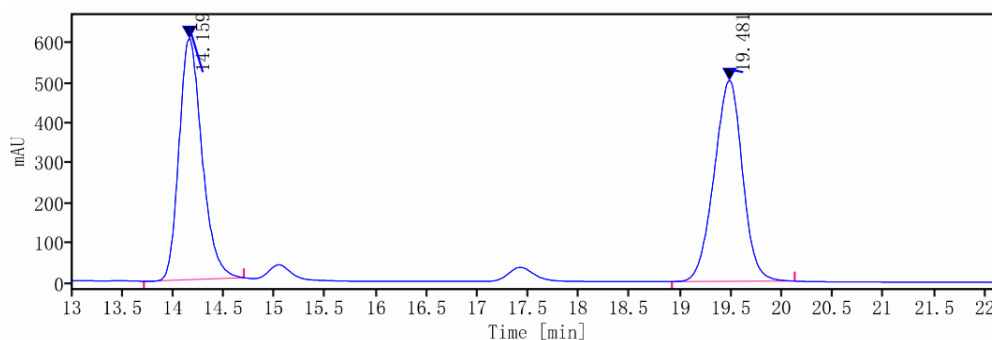
73.9 mg, 85% yield, 92% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 4/1); Yellow solid, m.p. 115–116 °C. $[\alpha]_D^{25} = -35.714$ ($c = 0.07$, CHCl_3).

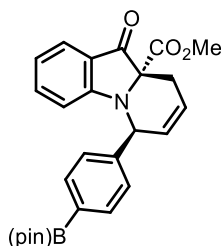
^1H NMR (300 MHz, CDCl_3) δ 7.59 – 7.56 (m, 1H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.3$ Hz, 2H), 7.15 (ddd, $J = 8.4, 7.2, 1.4$ Hz, 1H), 6.71 – 6.66 (m, 2H), 6.08 (d, $J = 8.4$ Hz, 1H), 5.89 – 5.83 (m, 1H), 5.66 (dt, $J = 9.9, 2.6$ Hz, 1H), 5.25 (q, $J = 2.5$ Hz, 1H), 3.75 (s, 3H), 3.32 (ddd, $J = 16.6, 6.4, 1.8$ Hz, 1H), 2.52 (dq, $J = 16.6, 3.0$ Hz, 1H), 1.53 (s, 9H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 194.7, 168.0, 159.7, 152.8, 138.5, 137.4, 134.3, 131.8, 128.2, 125.1, 120.9, 120.0, 119.2, 118.2, 111.5, 80.8, 74.8, 58.7, 53.7, 28.8, 28.4 ppm.

HRMS (ESI) calcd for $[\text{C}_{25}\text{H}_{27}\text{N}_2\text{O}_5 + \text{H}]^+$ 435.1914, found 435.1914.

HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 13.8$ min (minor), $t_{R2} = 18.7$ min (major).





methyl (6S,9aR)-10-oxo-6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate(3ah)

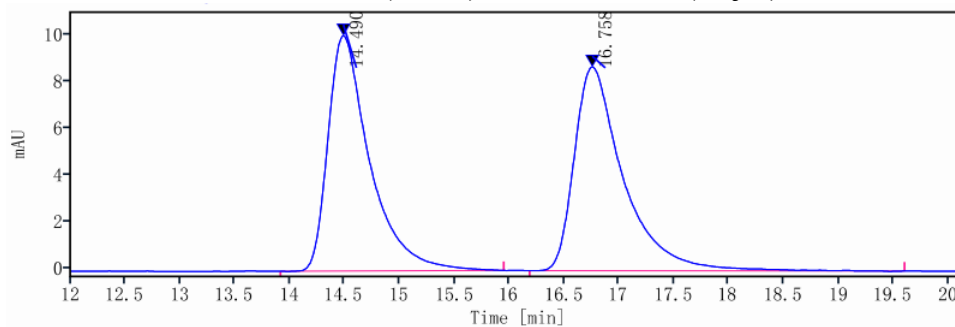
67.7 mg, 76% yield, 94% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 4/1); Yellow solid, m.p. 86-87 °C. $[\alpha]_D^{25} = -76.316$ ($c = 0.076$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.80 (d, $J = 7.9$ Hz, 2H), 7.57 (d, $J = 7.7$ Hz, 1H), 7.32 (d, $J = 7.5$ Hz, 2H), 7.15–7.09 (m, 1H), 6.68 (t, $J = 7.4$ Hz, 1H), 6.00 (d, $J = 8.5$ Hz, 1H), 5.87 (ddt, $J = 10.0, 6.4, 1.6$ Hz, 1H), 5.66 (dt, $J = 10.8, 2.8$ Hz, 2H), 5.29 (*app. s*, 1H), 3.74 (s, 3H), 3.37–3.28 (m, 1H), 2.59–2.50 (m, 1H), 1.35 (s, 12H) ppm.

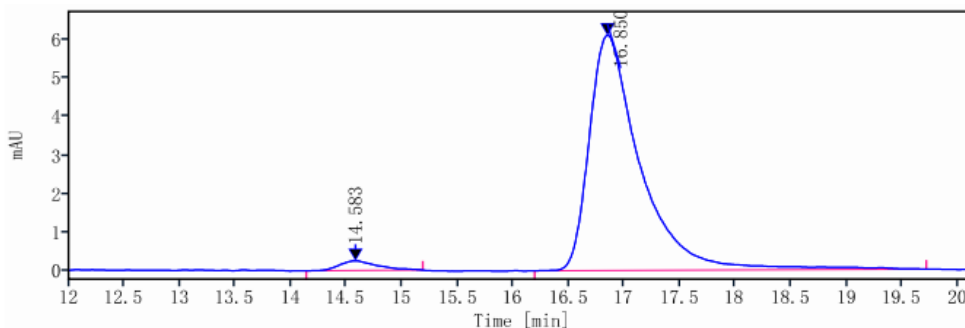
^{13}C NMR (75 MHz, CDCl_3) δ 194.6, 168.0, 159.6, 143.2, 137.3, 135.8, 131.3, 126.9, 125.1, 121.3, 120.0, 118.3, 111.4, 84.0, 74.7, 59.3, 53.7, 28.8, 25.0 ppm.

HRMS (ESI) calcd for $[\text{C}_{26}\text{H}_{29}\text{BNO}_5 + \text{H}]^+$ 446.2133, found 446.2142.

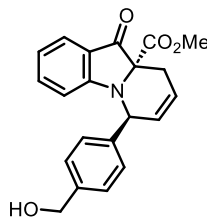
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 14.8$ min (minor), $t_{R2} = 16.9$ min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.490	MM m	0.3883	267.0018	10.1044	49.6022
16.758	MM m	0.4558	271.2844	8.7468	50.3978



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.583	MM m	0.3417	6.0518	0.2543	3.0000
16.850	MM m	0.4672	195.6750	6.1176	97.0000



methyl (6S,9aR)-6-(4-(hydroxymethyl)phenyl)-10-oxo-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3ai)

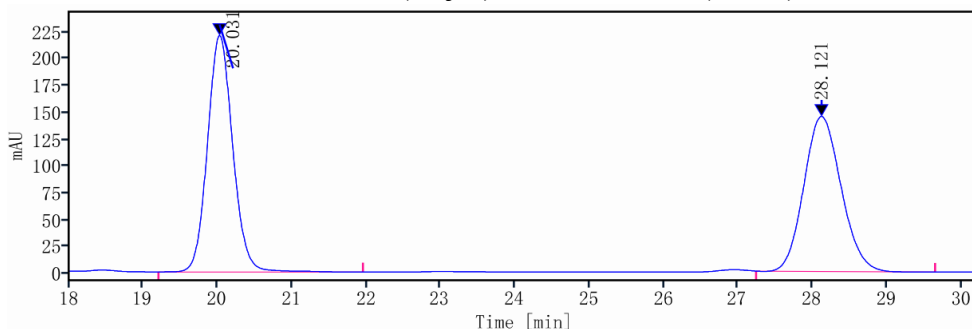
46.2 mg, 64% yield, 90% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 2/1); Yellow solid, m.p. 74–75 °C. $[\alpha]_D^{25} = -87.963$ ($c = 0.108$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.58 (d, $J = 7.7$ Hz, 1H), 7.35 (q, $J = 8.1$ Hz, 2H), 7.13 (ddd, $J = 8.4, 7.0, 1.3$ Hz, 1H), 6.69 (t, $J = 7.4$ Hz, 1H), 6.03 (d, $J = 8.4$ Hz, 1H), 5.87 (ddt, $J = 9.9, 6.4, 1.7$ Hz, 1H), 5.68 (dt, $J = 10.0, 2.6$ Hz, 1H), 5.32 – 5.28 (m, 1H), 4.72 (s, 2H), 3.75 (s, 3H), 3.33 (ddd, $J = 16.6, 6.5, 1.9$ Hz, 1H), 2.54 (dq, $J = 16.6, 3.1$ Hz, 1H), 2.21 (br s, 1H) ppm.

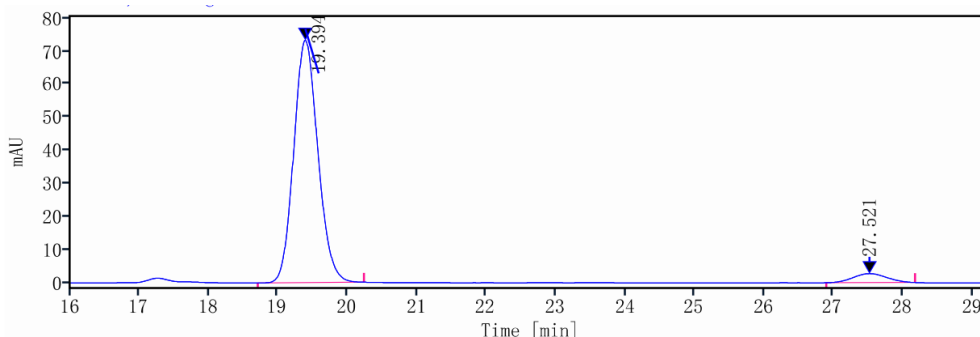
^{13}C NMR (75 MHz, CDCl_3) δ 194.7, 168.0, 159.6, 139.4, 137.3, 131.6, 127.9, 127.7, 125.2, 121.1, 120.0, 118.3, 111.4, 74.8, 64.9, 58.9, 53.7, 28.7 ppm.

HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{19}\text{NO}_4 + \text{H}]^+ 350.1387$, found 350.1390.

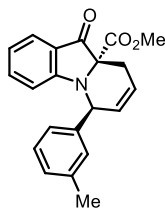
HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 19.4$ min (major), $t_{R2} = 27.5$ min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.031	MM m	0.3631	5189.1987	220.0629	50.8624
28.121	MM m	0.5390	5013.2296	144.4189	49.1376



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
19.394	MM m	0.3743	1773.6878	73.3074	95.0695
27.521	MM m	0.5267	91.9877	2.7328	4.9305



methyl (6S,9aR)-10-oxo-6-(m-tolyl)-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3aj)

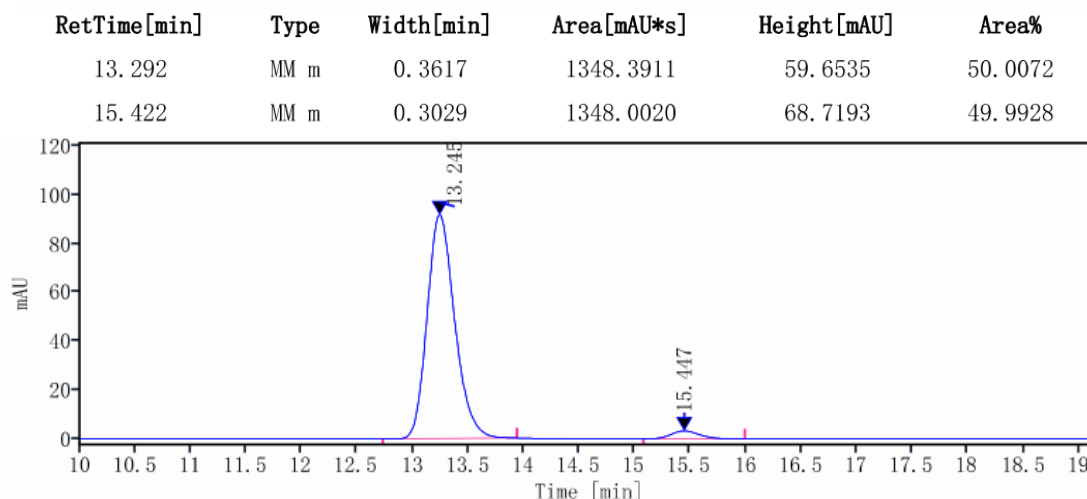
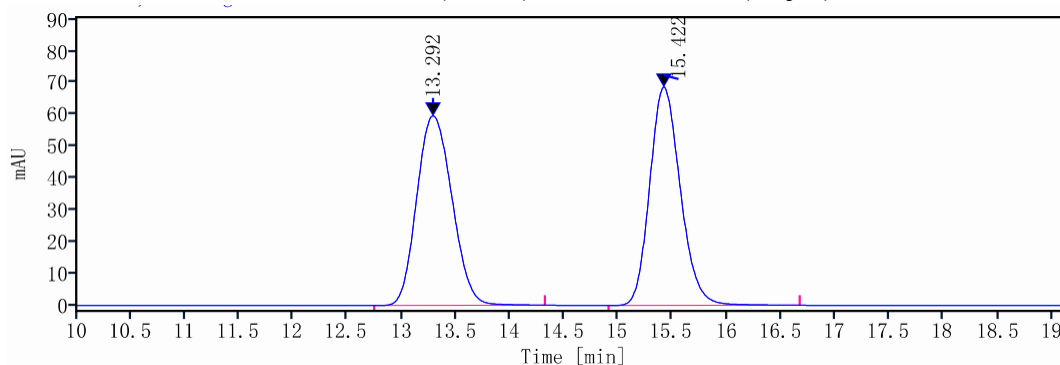
49.3 mg, 74% yield, 93% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 163–165 °C. $[\alpha]_D^{25} -115.56$ ($c = 0.14$, CHCl_3).

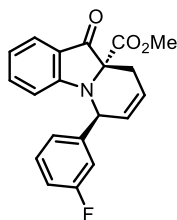
^1H NMR (300 MHz, CDCl_3) δ 7.57 (d, $J = 7.7$ Hz, 1H), 7.23 (d, $J = 7.5$ Hz, 1H), 7.16 – 7.10 (m, 5H), 6.67 (t, $J = 7.5$ Hz, 1H), 6.03 (d, $J = 8.4$ Hz, 1H), 5.86 (t, $J = 8.3$ Hz, 1H), 5.68 (dt, $J = 10.3, 2.8$ Hz, 1H), 5.24 (*app.* s, 1H), 3.74 (s, 3H), 3.32 (dd, $J = 16.6, 6.0$ Hz, 1H), 2.53 (d, $J = 17.0$ Hz, 1H), 2.34 (s, 3H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 194.7, 168.0, 159.7, 139.9, 139.1, 137.3, 131.8, 129.2, 129.0, 128.1, 125.1, 124.6, 121.0, 120.0, 118.2, 111.4, 74.8, 59.2, 53.7, 28.7, 21.6 ppm.

HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{19}\text{NO}_4 + \text{H}]^+$ 334.1438, found 334.1439.

HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 13.2$ min (minor), $t_{R2} = 15.4$ min (major).





methyl (6*S*,9*aR*)-6-(3-fluorophenyl)-10-oxo-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate(3*ak*)

53.3 mg, 79% yield, 93% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 141-143 °C. $[\alpha]_D^{25} = -15.15$ ($c = 0.066$, CHCl₃).

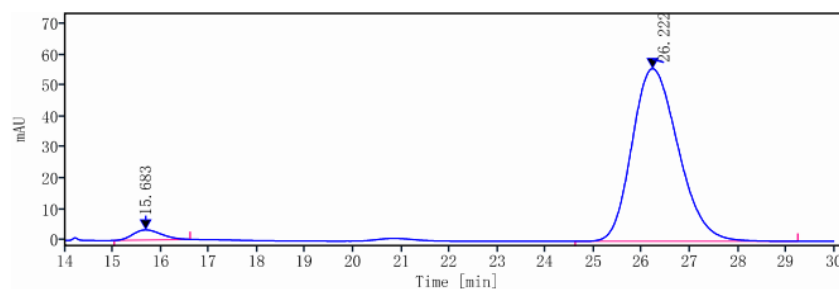
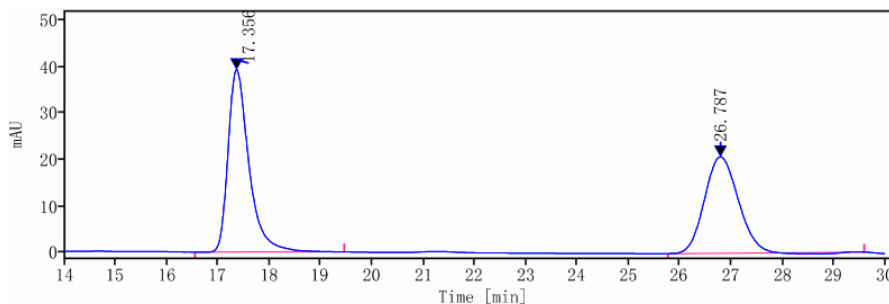
¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, $J = 7.7$ Hz, 1H), 7.35 (q, $J = 7.6$ Hz, 1H), 7.20 – 7.13 (m, 2H), 7.02 (t, $J = 7.8$ Hz, 2H), 6.72 (t, $J = 7.5$ Hz, 1H), 6.04 (d, $J = 8.4$ Hz, 1H), 5.90 (t, $J = 8.3$ Hz, 1H), 5.68 (d, $J = 9.8$ Hz, 1H), 5.29 (*app. s*, 1H), 3.74 (s, 3H), 3.33 (dd, $J = 16.7$ Hz, 1H), 2.53 (d, $J = 16.7$ Hz, 1H) ppm.

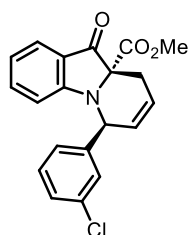
¹³C NMR (75 MHz, CDCl₃) δ 194.4, 167.9, 163.4 (d, $^1J_{C-F} = 247.4$ Hz), 159.4, 142.8 (d, $^3J_{C-F} = 6.7$ Hz), 137.4, 131.1, 130.9 (d, $^3J_{C-F} = 8.3$ Hz), 125.2, 123.1 (d, $^4J_{C-F} = 1.9$ Hz), 121.7, 120.2, 118.6, 115.3 (d, $^2J_{C-F} = 21.3$ Hz), 114.3 (d, $^2J_{C-F} = 22.0$ Hz), 111.2, 74.7, 58.7, 53.8, 28.7 ppm.

¹⁹F NMR (282 MHz, CDCl₃) δ -111.58 ppm.

HRMS (ESI) calcd for [C₂₀H₁₆FN₃O₃+H]⁺ 338.1187, found 338.1190.

HPLC: Daicel Chiralpak AS-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 15.7$ min (minor), $t_{R2} = 26.2$ min (major) (the racemic sample is a mixture of *R* and *S*-enantiomers).





methyl (6*S*,9*aR*)-6-(3-chlorophenyl)-10-oxo-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*a*)

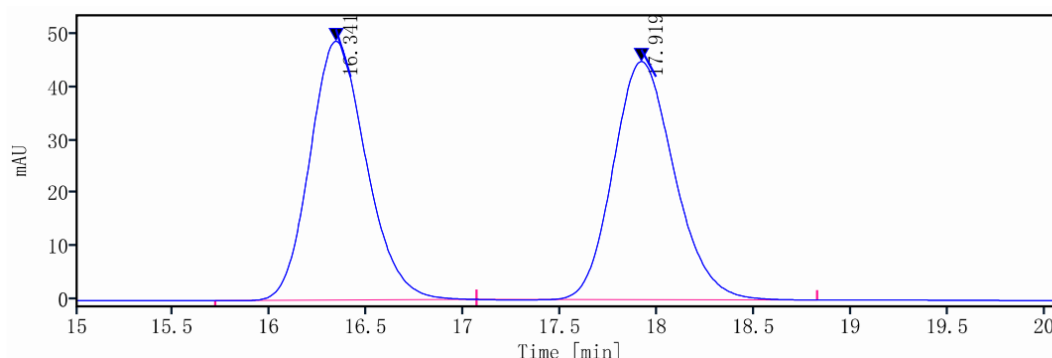
51.6 mg, 76% yield, 93% ee, 19:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 149–150 °C. $[\alpha]_D^{25} = -71.429$ ($c = 0.056$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.61 (ddd, $J = 7.7, 1.4, 0.7$ Hz, 1H), 7.33 (s, 1H), 7.32 (d, $J = 1.6$ Hz, 1H), 7.26 – 7.21 (m, 1H), 7.20 – 7.17 (m, 1H), 6.77 – 6.72 (m, 1H), 6.06 (d, $J = 8.4$ Hz, 1H), 5.92 (ddt, $J = 10.0, 6.4, 1.7$ Hz, 1H), 5.68 (dt, $J = 9.9, 2.5$ Hz, 1H), 5.28 (p, $J = 2.2$ Hz, 1H), 3.76 (s, 3H), 3.35 (ddd, $J = 16.7, 6.6, 1.9$ Hz, 1H), 2.56 (ddd, $J = 16.7, 5.0, 3.1$ Hz, 1H) ppm.

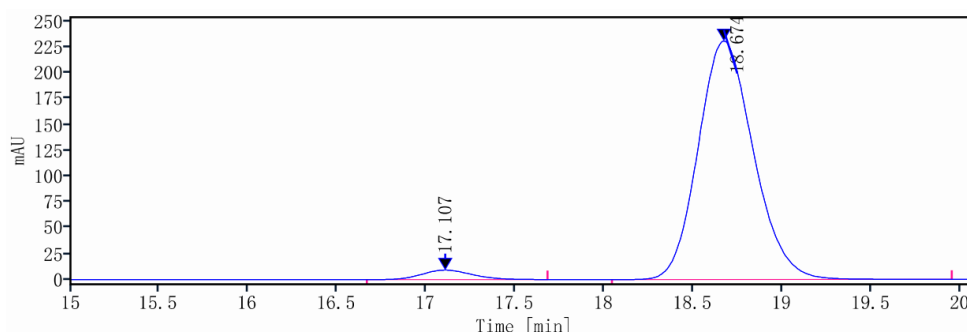
^{13}C NMR (75 MHz, CDCl_3) δ 194.4, 167.8, 159.4, 142.3, 137.4, 135.1, 131.0, 130.7, 128.5, 127.5, 125.7, 125.3, 121.8, 120.2, 118.6, 111.2, 74.8, 58.7, 53.8, 28.7 ppm.

HRMS (ESI) calcd for $[\text{C}_{20}\text{H}_{16}\text{ClNO}_4 + \text{H}]^+$ 354.0891, found 354.0889.

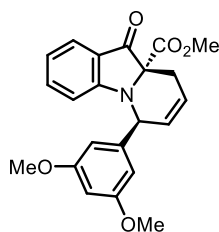
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 17.1$ min (major), $t_{R2} = 18.7$ min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
16.341	MM m	0.3121	989.7593	48.9092	50.0057
17.919	MM m	0.3403	989.5349	45.0391	49.9943



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
17.107	MM m	0.3003	178.1335	9.1820	3.4486
18.674	MM m	0.3339	4987.1909	230.9823	96.5514



methyl (6*S*,9*aR*)-6-(3,5-dimethoxyphenyl)-10-oxo-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*am*)

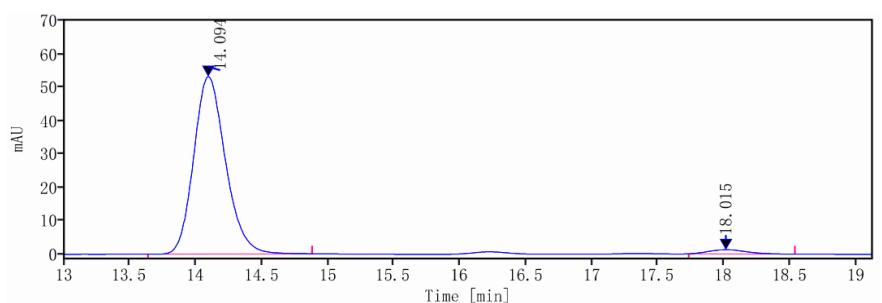
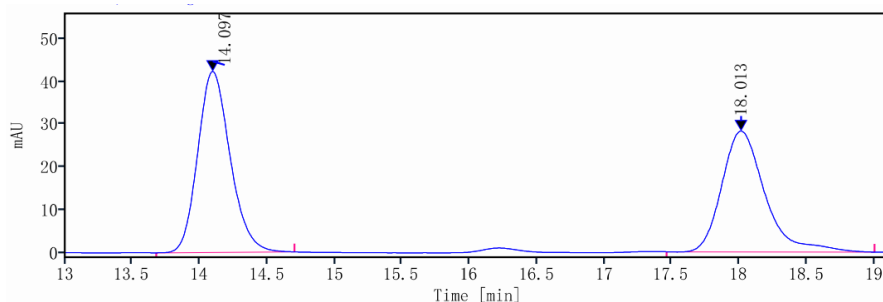
64.5 mg, 85% yield, 95% ee, >20:1 dr. R_f = 0.5 (PE/EA = 6/1); Yellow solid, m.p. 120–122 °C. $[\alpha]_D^{25}$ = -90.566 (c = 0.106, CHCl₃).

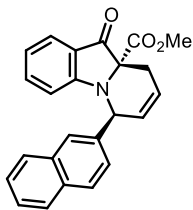
¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, J = 7.6 Hz, 1H), 7.19 (t, J = 7.7 Hz, 1H), 6.70 (t, J = 7.4 Hz, 1H), 6.48 (s, 1H), 6.41 (s, 1H), 6.17 (d, J = 8.4 Hz, 1H), 5.96 – 5.68 (m, 1H), 5.69 (dt, J = 10.1, 2.9 Hz, 1H), 5.18 (*app.* s, 1H), 3.76 (*app.* s, 6H), 3.74 (s, 3H), 3.31 (dd, J = 16.2, 5.7 Hz, 1H), 2.51 (dq, J = 16.8, 3.2 Hz, 1H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ 194.6, 167.9, 161.5, 159.7, 142.5, 137.4, 131.4, 125.0, 121.3, 120.0, 118.3, 111.5, 105.5, 99.6, 74.7, 59.2, 55.4, 53.7, 28.6 ppm.

HRMS (ESI) calcd for [C₂₂H₂₁NO₅+H]⁺ 380.1492, found 380.1493.

HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 400 nm, t_{R1} = 14.1 min (major), t_{R2} = 18.0 min (minor) (the racemic sample is a mixture of *R* and *S*-enantiomers).





methyl (6S,9aR)-6-(naphthalen-2-yl)-10-oxo-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3an)

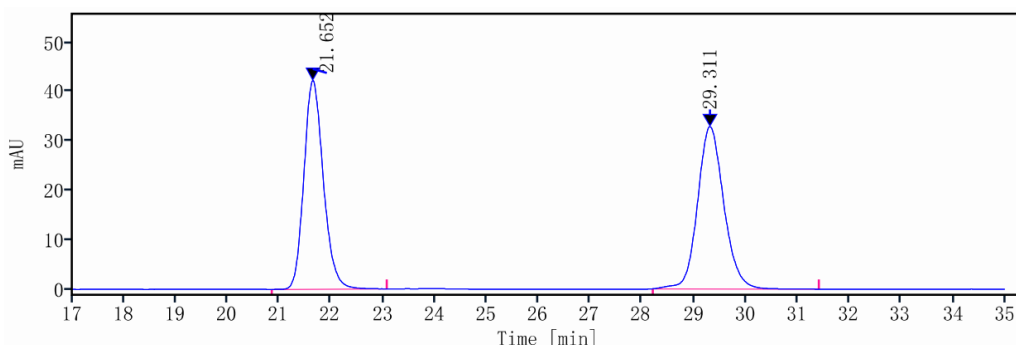
53.9 mg, 73% yield, 94% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 171-172 °C. $[\alpha]_D^{25} = -30.0$ ($c = 0.09$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.88 – 7.78 (m, 4H), 7.59 – 7.49 (m, 3H), 7.33 (d, $J = 8.5$ Hz, 1H), 7.02 (ddd, $J = 8.5, 7.1, 1.4$ Hz, 1H), 6.64 (t, $J = 7.4$ Hz, 1H), 6.04 (d, $J = 8.4$ Hz, 1H), 5.90 (ddt, $J = 8.2, 6.4, 1.9$ Hz, 1H), 5.72 (dt, $J = 9.9, 2.8$ Hz, 1H), 5.48 (q, $J = 2.7$ Hz, 1H), 3.74 (s, 3H), 3.37 (ddd, $J = 16.7, 6.5, 2.2$ Hz, 1H), 2.53 (d, $J = 16.7$ Hz, 1H) ppm.

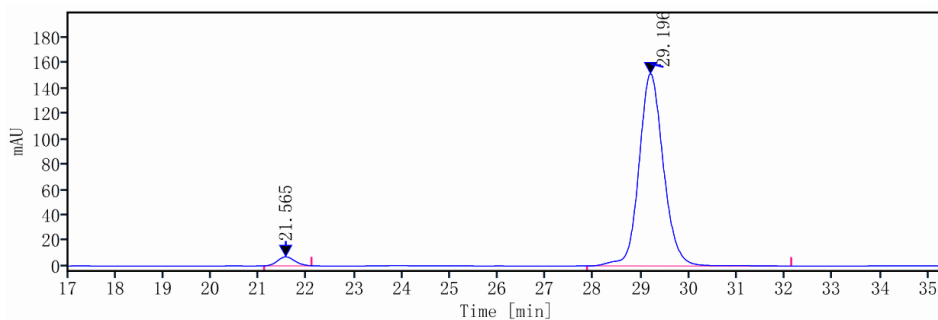
^{13}C NMR (75 MHz, CDCl_3) δ 194.6, 168.0, 159.7, 137.7, 137.4, 133.7, 133.3, 131.6, 129.4, 127.9, 126.61, 126.59, 126.4, 125.1, 124.9, 121.5, 120.0, 118.3, 111.4, 74.7, 59.4, 53.7, 28.9 ppm.

HRMS (ESI) calcd for $[\text{C}_{24}\text{H}_{19}\text{NO}_3 + \text{H}]^+$ 370.1438, found 370.1434.

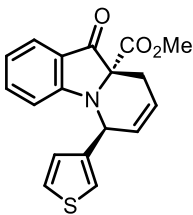
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 21.6$ min (minor), $t_{R2} = 29.2$ min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
21.652	MM m	0.4002	1103.3202	42.3102	48.8198
29.311	MM m	0.5403	1156.6642	32.8865	51.1802



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
21.565	MM m	0.3831	173.4437	7.0481	3.1294
29.196	MM m	0.5445	5369.0267	151.1243	96.8706



methyl (6*S*,9*aR*)-10-oxo-6-(thiophen-3-yl)-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3ao)

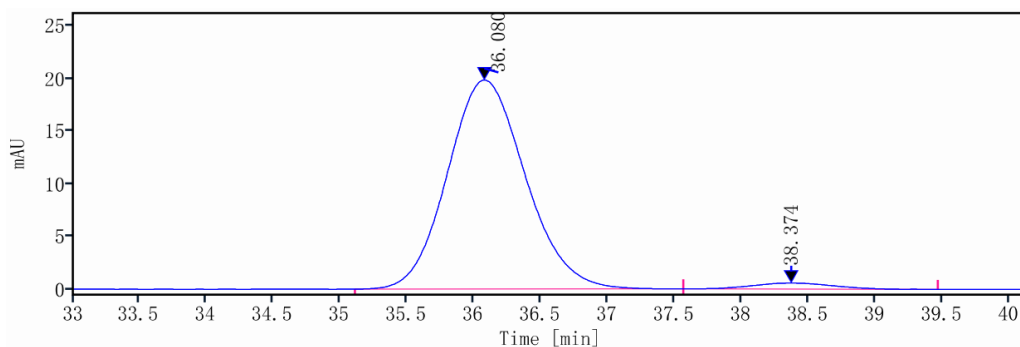
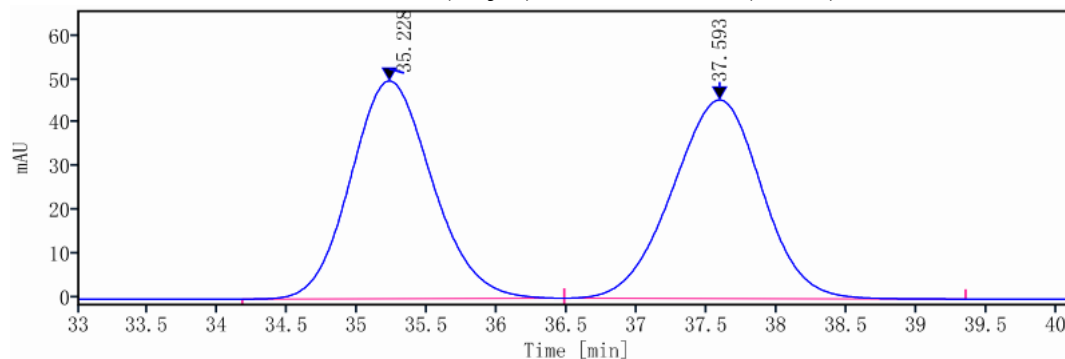
53.4 mg, 82% yield, 94% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 152–154 °C. $[\alpha]_D^{25} = -60.0$ ($c = 0.07$, CHCl_3).

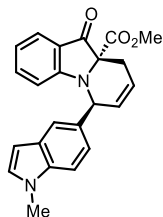
^1H NMR (300 MHz, CDCl_3) δ 7.58 – 7.55 (m, 1H), 7.31 (d, $J = 3.2$ Hz, 2H), 7.21 – 7.15 (m, 1H), 6.93 – 6.91 (m, 1H), 6.69 (t, $J = 7.4$ Hz, 1H), 6.13 (d, $J = 8.4$ Hz, 1H), 5.92 – 5.85 (m, 1H), 5.67 (dt, $J = 10.0, 2.8$ Hz, 1H), 5.47 – 5.44 (m, 1H), 3.73 (s, 3H), 3.30 (ddd, $J = 16.8, 6.6, 2.5$ Hz, 1H), 2.47 (dtd, $J = 16.7, 3.2, 1.8$ Hz, 1H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 194.6, 167.8, 159.8, 141.1, 137.5, 130.9, 127.3, 126.6, 125.1, 122.7, 121.5, 119.8, 118.3, 110.9, 74.6, 54.4, 53.7, 28.8 ppm.

HRMS (ESI) calcd for $[\text{C}_{18}\text{H}_{15}\text{NO}_3\text{S} + \text{H}]^+$ 326.0845, found 326.0847.

HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 36.1$ min (major), $t_{R2} = 38.4$ min (minor).





methyl (6*S*,9*aR*)-6-(1-methyl-1*H*-indol-5-yl)-10-oxo-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*ap*)

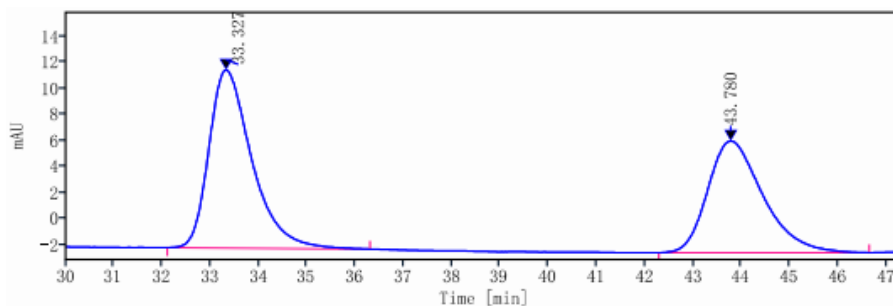
65.5 mg, 88% yield, 93% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 4/1); Yellow solid, m.p. 170–172 °C. $[\alpha]_D^{25} = -26.9$ ($c = 0.104$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.53 (s, 1H), 7.47 – 7.44 (m, 1H), 7.18 (d, $J = 8.6$ Hz, 1H), 7.03 – 6.88 (m, 3H), 6.52 (t, $J = 7.4$ Hz, 1H), 6.38 (d, $J = 3.1$ Hz, 1H), 5.92 (d, $J = 8.5$ Hz, 1H), 5.74 (ddt, $J = 9.8, 6.3, 1.7$ Hz, 1H), 5.63 (dt, $J = 9.9, 2.7$ Hz, 1H), 5.28 (dt, $J = 4.7, 1.7$ Hz, 1H), 3.69 (s, 3H), 3.66 (s, 3H), 3.25 (ddd, $J = 16.7, 6.2, 2.2$ Hz, 1H), 2.48 (dq, $J = 16.7, 2.8$ Hz, 1H) ppm.

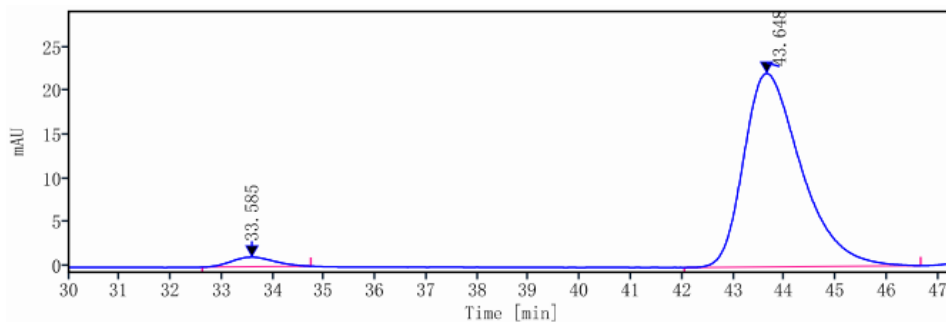
¹³C NMR (75 MHz, CDCl₃) δ 194.9, 168.0, 160.1, 137.2, 136.6, 132.6, 130.7, 129.7, 128.8, 124.9, 120.9, 120.1, 119.8, 117.8, 111.6, 110.2, 101.1, 74.8, 59.6, 53.6, 33.0, 28.8 ppm.

HRMS (ESI) calcd for [C₂₃H₂₀N₂O₃+H]⁺ 373.1547, found 373.1537.

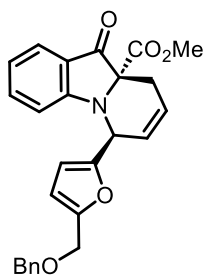
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 33.6$ min (minor), $t_{R2} = 43.6$ min (major). (the racemic sample is a mixture of *R* and *S*-enantiomers).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
33.327	BB	4.2000	844.4930	13.6656	55.3858
43.780	BB	4.3533	680.2524	8.5664	44.6142



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
33.585	MM m	0.8414	63.4710	1.0965	3.5315
43.648	BB	4.6233	1733.8155	22.2399	96.4685



methyl (6S,9aR)-6-(5-((benzyloxy)methyl)furan-2-yl)-10-oxo-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3aq)

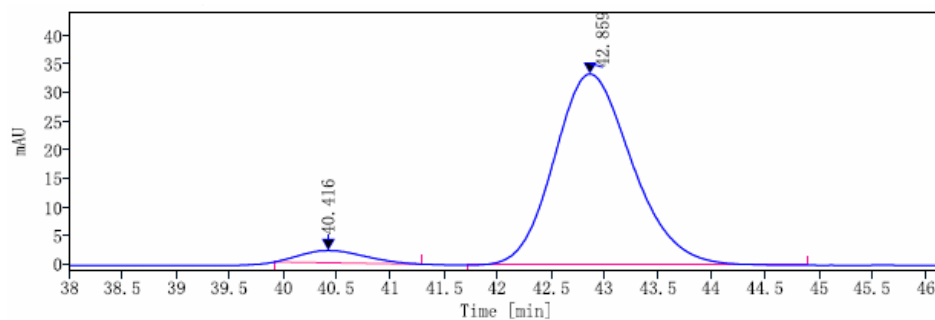
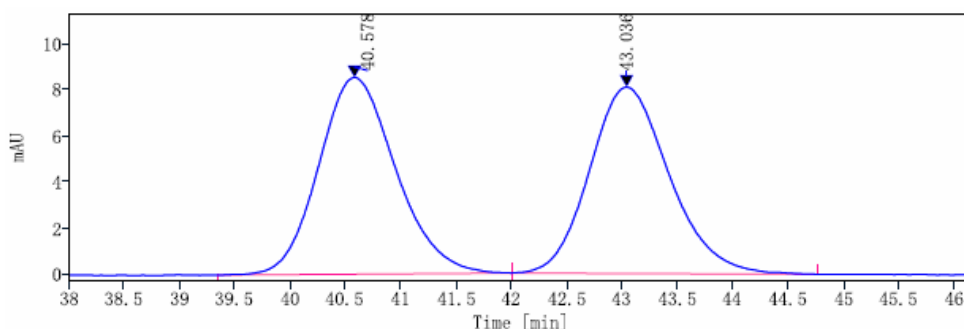
44.7 mg, 52% yield, 90% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 4/1); Yellow solid, m.p. 153-154 °C. $[\alpha]_D^{25} = -70.833$ ($c = 0.072$, CHCl_3).

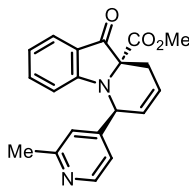
^1H NMR (300 MHz, CDCl_3) δ 7.60 (d, $J = 7.7$ Hz, 1H), 7.37 – 7.20 (m, 6H), 6.72 (t, $J = 7.4$ Hz, 1H), 6.39 – 6.36 (m, 2H), 6.25 (d, $J = 8.5$ Hz, 1H), 6.06 – 5.99 (m, 1H), 5.72 (dt, $J = 10.0, 2.7$ Hz, 1H), 5.45 (p, $J = 2.2$ Hz, 1H), 4.48 (s, 2H), 4.47 (s, 2H), 3.76 (s, 3H), 3.30 (ddd, $J = 16.6, 6.4, 1.8$ Hz, 1H), 2.51 (dq, $J = 16.6, 3.1$ Hz, 1H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 194.5, 167.9, 159.5, 152.2, 151.8, 137.8, 128.5, 128.2, 128.0, 127.9, 125.2, 123.6, 119.7, 118.4, 110.8, 110.3, 109.7, 74.1, 71.7, 63.8, 53.7, 52.2, 28.8 ppm.

HRMS (ESI) calcd for $[\text{C}_{26}\text{H}_{23}\text{NO}_5 + \text{H}]^+$ 430.1649, found 430.1644.

HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 40.4$ min (minor), $t_{R2} = 42.9$ min (major).





methyl (6S,9aR)-6-(2-methylpyridin-4-yl)-10-oxo-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3ar)

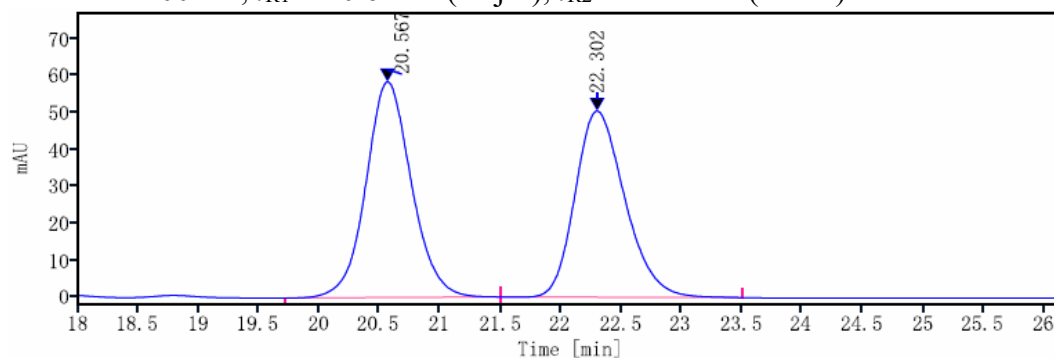
43.4 mg, 65% yield, 90% ee, >20:1 dr. $R_f = 0.2$ (PE/EA = 4/1); Yellow solid, m.p. 82–84 °C. $[\alpha]_D^{25} = -56.82$ ($c = 0.044$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 8.68 (d, $J = 2.3$ Hz, 1H), 7.70 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.58 (dd, $J = 8.1, 2.2$ Hz, 1H), 7.33 – 7.25 (m, 2H), 6.86 (d, $J = 7.4$ Hz, 1H), 6.19 (d, $J = 8.4$ Hz, 1H), 6.08 – 6.01 (m, 1H), 5.78 (dd, $J = 9.9, 2.7$ Hz, 1H), 5.48 – 5.44 (m, 1H), 3.87 (s, 3H), 3.46 (ddd, $J = 16.7, 6.5, 2.1$ Hz, 1H), 2.71 (s, 3H), 2.70 – 2.61 (m, 1H) ppm.

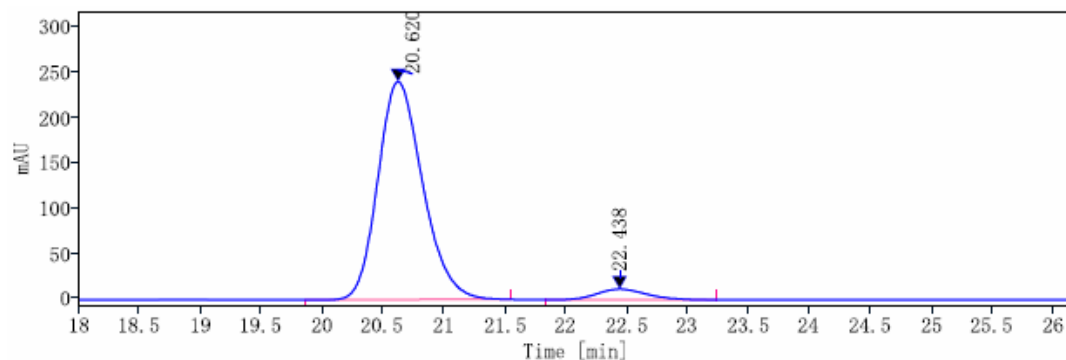
^{13}C NMR (75 MHz, CDCl_3) δ 194.3, 167.8, 159.2, 158.8, 148.3, 137.4, 135.5, 132.8, 131.1, 125.3, 124.0, 121.9, 120.2, 118.6, 111.1, 74.7, 56.4, 53.8, 28.7, 24.3 ppm.

HRMS (ESI) calcd for $[\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_3 + \text{H}]^+$ 335.1390, found 335.1385.

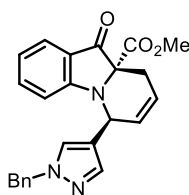
HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 20.6$ min (major), $t_{R2} = 22.4$ min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.567	MM m	0.3992	1527.8614	58.3997	51.5022
22.302	MM m	0.4390	1438.7336	50.4110	48.4978



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.620	MM m	0.3941	6141.1368	240.3778	94.9104
22.438	MM m	0.4368	329.3205	11.6868	5.0896



methyl (6*S*,9*aR*)-6-(1-benzyl-1*H*-pyrazol-4-yl)-10-oxo-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*as*)

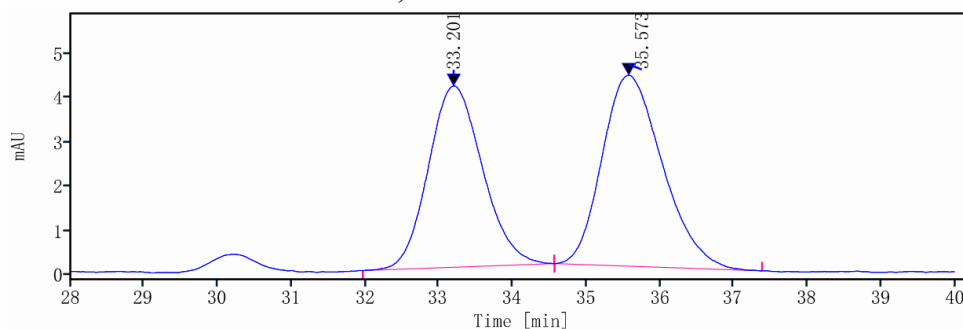
68.3 mg, 85% yield, 97% ee, >20:1 dr. R_f = 0.5 (PE/EA = 6/1); Yellow oil. $[\alpha]_D^{25}$ = -15.0 (c = 0.094, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.57 – 7.49 (m, 2H), 7.36 – 7.29 (m, 4H), 7.20 – 7.14 (m, 3H), 6.70 (t, J = 7.4 Hz, 1H), 6.29 (d, J = 8.5 Hz, 1H), 5.84 (ddt, J = 10.0, 6.4, 1.4 Hz, 1H), 5.66 (dt, J = 10.0, 2.7 Hz, 1H), 5.32 (*app.* d, J = 2.7 Hz, 1H), 5.29 (s, 2H), 3.71 (s, 3H), 3.26 (ddd, J = 16.6, 6.6, 2.1 Hz, 1H), 2.41 (dtd, J = 16.8, 3.2, 1.8 Hz, 1H) ppm.

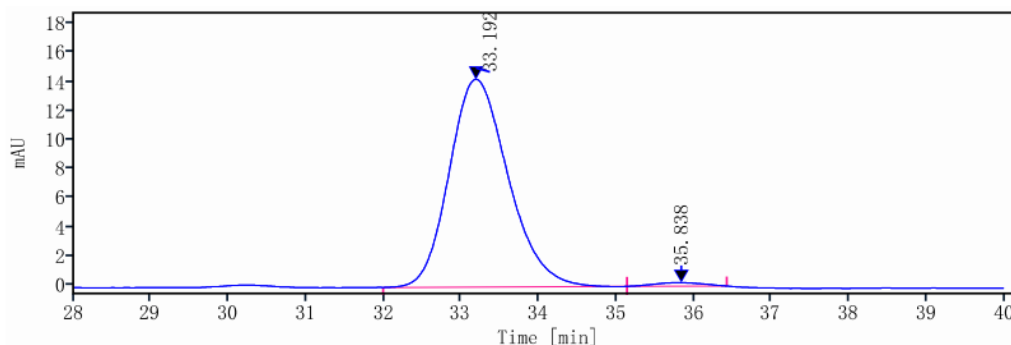
^{13}C NMR (75 MHz, CDCl_3) δ 194.6, 167.8, 159.8, 138.8, 137.1, 136.5, 131.6, 128.9, 128.5, 128.2, 127.5, 125.2, 121.3, 120.8, 120.0, 118.2, 111.3, 74.8, 56.4, 53.6, 50.1, 28.8 ppm.

HRMS (ESI) calcd for $[\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_3 + \text{H}]^+$ 400.1656, found 400.1658.

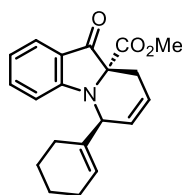
HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 400 nm, t_{R1} = 33.2 min (major), t_{R2} = 35.8 min (minor). (the racemic sample is a mixture of *R* and *S*-enantiomers).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
33.201	BB	2.5956	208.8932	4.0957	45.9866
35.573	BB	2.8133	245.3551	4.3120	54.0134



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
33.192	BM m	0.8112	753.9467	14.2969	98.6205
35.838	MM m	0.5222	10.5463	0.2470	1.3795



methyl (6S,9aR)-6-(cyclohex-1-en-1-yl)-10-oxo-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3at)

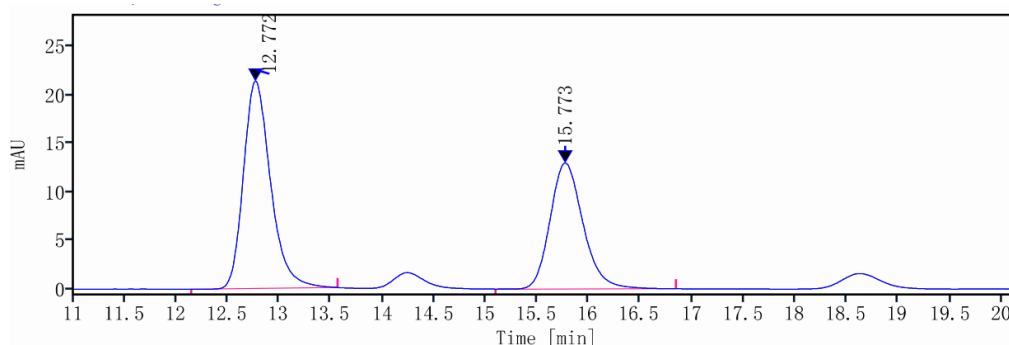
42.7 mg, 66% yield, 90% ee, 10:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 85–87 °C. $[\alpha]_D^{25} = -13.0$ ($c = 0.09$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.57 (ddd, $J = 7.7, 1.5, 0.7$ Hz, 1H), 7.41 (ddd, $J = 8.5, 7.1, 1.5$ Hz, 1H), 7.16 (dt, $J = 8.5, 0.8$ Hz, 1H), 6.74 (td, $J = 7.8, 0.8$ Hz, 1H), 6.08 – 5.99 (m, 1H), 5.96 (ddt, $J = 10.1, 6.5, 1.8$ Hz, 1H), 5.51 (dt, $J = 9.9, 2.9$ Hz, 1H), 4.76 (q, $J = 2.5$ Hz, 1H), 3.69 (s, 3H), 3.21 (ddd, $J = 16.5, 6.7, 2.0$ Hz, 1H), 2.26 (dtd, $J = 16.4, 3.1, 1.8$ Hz, 1H), 2.20 – 2.02 (m, 1H), 1.89 – 1.49 (m, 7H) ppm.

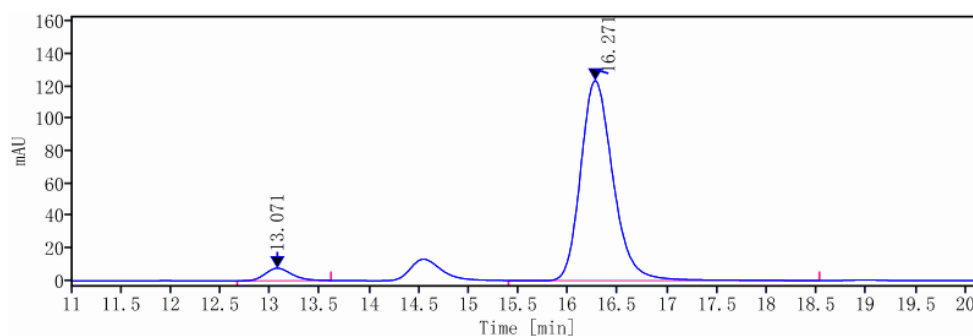
^{13}C NMR (75 MHz, CDCl_3) δ 194.8, 168.1, 160.4, 137.8, 137.2, 130.5, 127.2, 125.2, 123.4, 119.4, 117.9, 110.6, 74.2, 61.7, 53.6, 28.7, 25.7, 22.7, 22.6, 22.5 ppm.

HRMS (ESI) calcd for $[\text{C}_{20}\text{H}_{21}\text{NO}_3 + \text{Na}]^+$ 346.1414, found 346.1410.

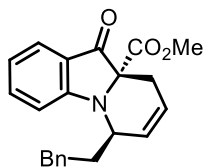
HPLC: Daicel Chiralpak AS-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 400$ nm, $t_{R1} = 13.1$ min (minor), $t_{R2} = 16.3$ min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.772	MM m	0.2797	391.7696	21.3850	57.5867
15.773	MM m	0.3410	288.5435	12.9972	42.4133



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.071	MM m	0.2843	141.9468	7.6555	4.8441
16.271	MM m	0.3475	2788.3860	123.4729	95.1559



methyl (6R,9aR)-10-oxo-6-phenethyl-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate(3au)

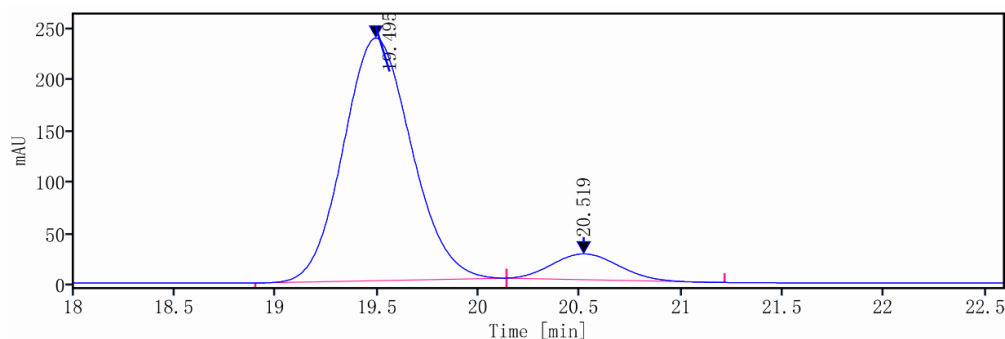
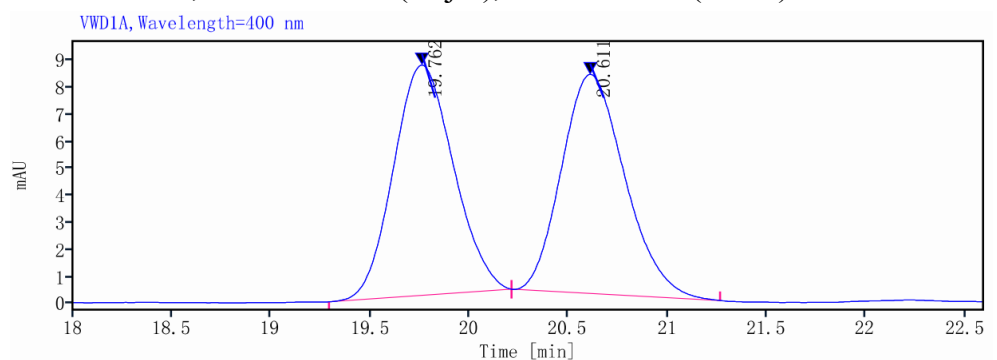
34.7 mg, 50% yield, 81% ee, 15:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellowish oil. $[\alpha]_D^{25} = -63.830$ ($c = 0.094$, CHCl_3).

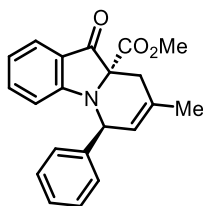
^1H NMR (300 MHz, CDCl_3) δ 7.64 (d, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 7.7$ Hz, 1H), 7.30–7.20 (m, 3H), 7.13 (d, $J = 7.2$ Hz, 2H), 7.04 (d, $J = 8.4$ Hz, 1H), 6.82 (t, $J = 7.2$ Hz, 1H), 6.09 (t, $J = 8.1$ Hz, 1H), 5.82 (d, $J = 9.1$ Hz, 1H), 4.56 (*app.* s, 1H), 3.70 (s, 3H), 3.28 (dd, $J = 16.3, 6.6$ Hz, 1H), 2.60–2.47 (m, 3H), 2.33 (d, $J = 16.3$ Hz, 1H), 2.20–2.12 (m, 1H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 194.6, 168.2, 159.8, 141.7, 137.9, 130.7, 128.6, 128.4, 126.1, 125.6, 124.2, 120.6, 118.1, 110.4, 75.5, 53.6, 53.4, 34.6, 29.4, 28.5 ppm.

HRMS (ESI) calcd for $[\text{C}_{22}\text{H}_{21}\text{NO}_3 + \text{H}]^+$ 348.1594, found 348.1596.

HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 98/2, flow rate = 0.5 mL/min, uv-vis $\lambda = 250$ nm, $t_{R1} = 19.5$ min (major), $t_{R2} = 20.5$ min (minor).





methyl (6*S*,9*aR*)-8-methyl-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3*av*)

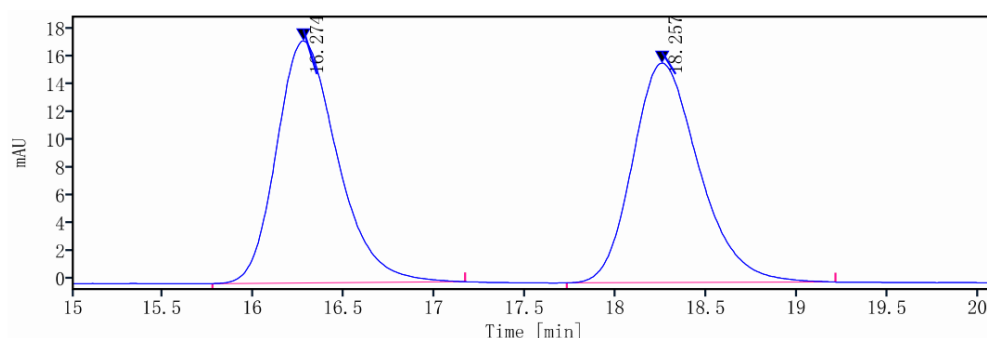
24.0 mg, 36% yield, 94% ee, 16:1 dr. $R_f = 0.4$ (PE/EA = 6/1); Colorless oil. $[\alpha]_D^{25} = -53.0$ ($c = 0.08$, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.55 (m, 1H), 7.37 – 7.27 (m, 5H), 7.11 (ddd, $J = 8.5, 7.2, 1.4$ Hz, 1H), 6.66 (t, $J = 7.4$ Hz, 1H), 5.97 (d, $J = 8.5$ Hz, 1H), 5.40 – 5.38 (m, 1H), 5.18 (*app. s*, 1H), 3.73 (s, 3H), 3.15 (dd, $J = 16.2, 1.7$ Hz, 1H), 2.52 – 2.47 (m, 1H), 1.79 (q, $J = 1.7$ Hz, 3H) ppm.

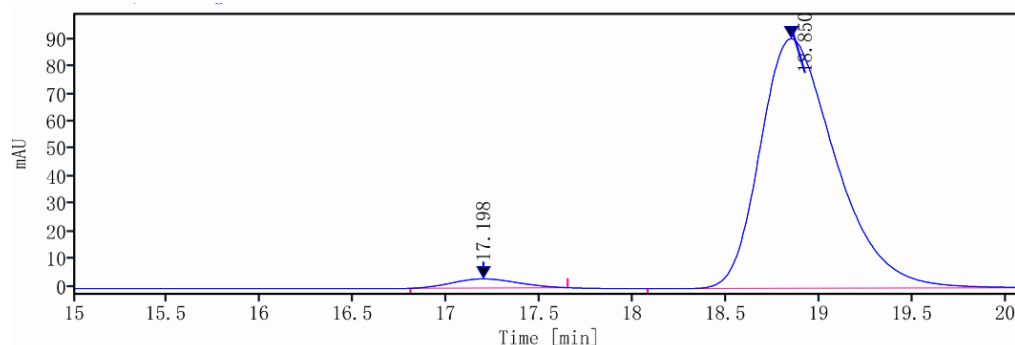
^{13}C NMR (75 MHz, CDCl_3) δ 194.7, 167.9, 159.6, 140.6, 137.2, 129.8, 129.2, 128.1, 127.4, 125.2, 125.1, 120.2, 118.1, 111.3, 75.2, 58.9, 53.6, 33.2, 23.5 ppm.

HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{19}\text{NO}_3 + \text{H}]^+$ 334.1438, found 334.1440.

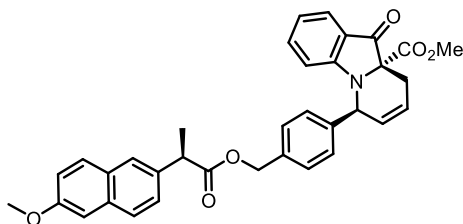
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis $\lambda = 250$ nm, $t_{R1} = 17.2$ min (minor), $t_{R2} = 18.8$ min (major).



16.274	MM m	0.3591	409.6851	17.5043	50.2384
18.257	MM m	0.3922	405.7963	15.8781	49.7616



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
17.198	MM m	0.3834	80.8003	3.3262	3.0708
18.850	MM m	0.4325	2550.4782	90.5792	96.9292



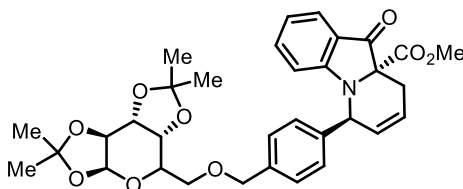
methyl (6S,9aR)-6-(4-(((R)-2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)methyl)phenyl)-10-oxo-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate(3aw)

96.6 mg, 86% yield, >20:1 dr. R_f = 0.3 (PE/EA = 4/1); Yellow solid, m.p. 55-56 °C. $[\alpha]_D^{25}$ = -40.4 (c = 0.052, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.69 – 7.63 (m, 3H), 7.57 (dd, J = 7.8, 1.4 Hz, 1H), 7.39 (dd, J = 8.5, 1.9 Hz, 1H), 7.24 – 7.19 (m, 4H), 7.14 – 7.05 (m, 3H), 6.67 (t, J = 7.4 Hz, 1H), 5.96 (d, J = 8.5 Hz, 1H), 5.85 (ddt, J = 10.0, 6.5, 1.8 Hz, 1H), 5.63 (dt, J = 9.9, 2.7 Hz, 1H), 5.26 (q, J = 2.5 Hz, 1H), 5.12 (s, 2H), 3.95 – 3.87 (m, 4H), 3.73 (s, 3H), 3.32 (ddd, J = 15.6, 6.0, 1.8 Hz, 2H), 2.55 – 2.46 (m, 1H), 1.59 (d, J = 7.3 Hz, 3H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 194.5, 174.5, 167.9, 159.5, 157.7, 139.8, 137.2, 136.1, 135.5, 133.7, 131.5, 129.3, 128.9, 128.7, 127.5, 127.2, 126.3, 126.0, 125.1, 121.1, 120.0, 119.1, 118.3, 111.3, 105.5, 74.7, 66.0, 58.8, 55.3, 53.7, 45.4, 28.7, 18.5 ppm.

HRMS (ESI) calcd for $[\text{C}_{35}\text{H}_{32}\text{NO}_6+\text{H}]^+$ 562.2224, found 562.2226.



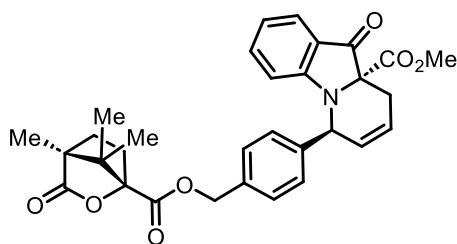
methyl (6S,9aR)-10-oxo-6-(4-(((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)methyl)phenyl)-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (3ax)

106.5 mg, 90% yield, >20:1 dr. R_f = 0.2 (PE/EA = 4/1); Yellow oil. $[\alpha]_D^{25}$ = -68.18 (c = 0.11, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.61 (dd, J = 7.7, 1.4 Hz, 1H), 7.41 – 7.32 (m, 5H), 7.18 (ddd, J = 8.5, 7.1, 1.4 Hz, 1H), 6.73 (t, J = 7.4 Hz, 1H), 6.07 (d, J = 8.4 Hz, 1H), 5.91 (ddt, J = 10.0, 6.5, 1.8 Hz, 1H), 5.72 (dt, J = 10.0, 2.7 Hz, 1H), 5.61 (d, J = 5.0 Hz, 1H), 5.33 (t, J = 2.7 Hz, 1H), 4.71 – 4.59 (m, 3H), 4.40 – 4.30 (m, 2H), 4.08 (td, J = 6.2, 1.9 Hz, 1H), 3.79 – 3.70 (m, 5H), 3.37 (ddd, J = 16.6, 6.5, 2.1 Hz, 1H), 2.57 (dd, J = 16.6, 2.5 Hz, 1H), 1.59 (s, 3H), 1.49 (s, 3H), 1.39 (d, J = 1.8 Hz, 6H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 194.6, 167.9, 159.6, 139.2, 138.5, 137.3, 131.7, 128.5, 127.4, 125.1, 121.0, 120.0, 118.2, 111.4, 109.3, 108.6, 96.4, 74.7, 72.9, 71.3, 70.7, 70.6, 69.2, 67.0, 58.9, 53.7, 28.7, 26.2, 26.1, 25.0, 24.5 ppm.

HRMS (ESI) calcd for $[\text{C}_{33}\text{H}_{37}\text{NO}_9+\text{H}]^+$ 592.2541, found 592.2537.



methyl **(6*S*,9*aR*)-10-oxo-6-(4-((((1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carbonyl)oxy)methyl)phenyl)-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (3ay)**

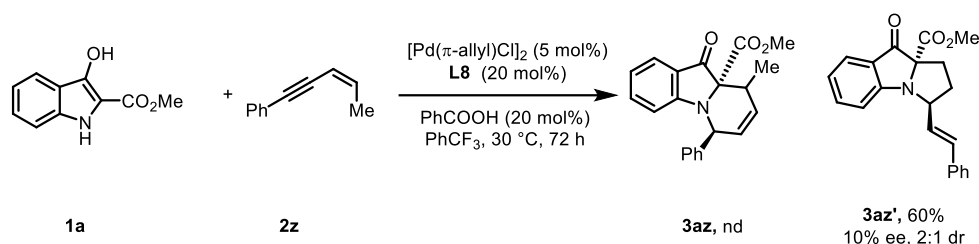
60.4 mg, 57% yield, >20:1 dr. $R_f = 0.2$ (PE/EA = 4/1); Yellow oil. $[\alpha]_D^{25} = +73.33$ ($c = 0.090$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.58 (d, $J = 7.8$ Hz, 1H), 7.39 – 7.32 (m, 4H), 7.12 (t, $J = 7.4$ Hz, 1H), 6.69 (t, $J = 7.4$ Hz, 1H), 5.99 (d, $J = 8.4$ Hz, 1H), 5.91 – 5.86 (m, 1H), 5.67 (dt, $J = 10.0, 2.6$ Hz, 2H), 5.30 (s, 1H), 5.28 (s, 2H), 3.75 (s, 3H), 3.33 (ddd, $J = 16.6, 6.5, 1.9$ Hz, 1H), 2.58 – 2.40 (m, 2H), 2.10 – 1.88 (m, 2H), 1.69 (ddd, $J = 13.4, 9.3, 4.2$ Hz, 1H), 1.11 (s, 3H), 1.03 (s, 3H), 0.90 (s, 3H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 194.5, 178.1, 167.9, 167.5, 159.5, 140.6, 137.2, 135.2, 131.4, 129.4, 127.8, 125.2, 121.3, 120.1, 118.4, 111.2, 91.1, 76.7, 74.7, 66.8, 58.8, 54.9, 54.4, 53.7, 30.7, 29.0, 28.7, 16.9, 16.8, 9.8 ppm.

HRMS (ESI) calcd for $[\text{C}_{31}\text{H}_{31}\text{NO}_7 + \text{H}]^+$ 530.2173, found 530.2176.

Additionally, we synthesis enyne **2z** and test it under the standard conditions. Nevertheless, the desired product **3az** was not detected, with compound **3az'** formed in 60% yield with 10% ee and 2:1 dr.



methyl (E)-9-oxo-3-styryl-2,3-dihydro-1H-pyrrolo[1,2-a]indole-9a(9H)-carboxylate(3az')

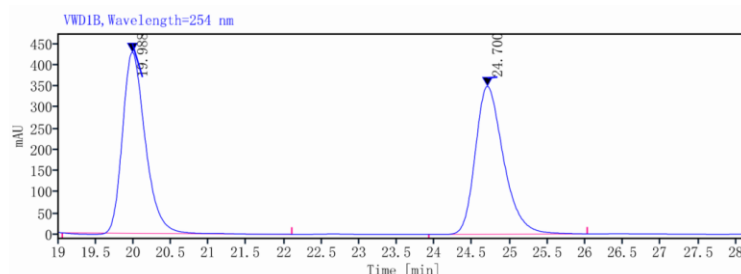
40.0 mg, 60% yield, 11% ee, 2:1 dr. $R_f = 0.4$ (PE/EA = 6/1); Yellow oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 (dt, $J = 7.8, 1.0$ Hz, 1H), 7.52 (ddd, $J = 8.4, 7.1, 1.4$ Hz, 1H), 7.44 – 7.42 (m, 2H), 7.36 – 7.32 (m, 2H), 7.28 – 7.24 (m, 1H), 7.07 (d, $J = 8.2$ Hz, 1H), 7.00 (t, $J = 7.4$ Hz, 1H), 6.77 (dd, $J = 15.7, 1.2$ Hz, 1H), 6.37 (dd, $J = 15.7, 6.5$ Hz, 1H), 4.00 (dt, $J = 8.6, 6.5$ Hz, 1H), 2.80 (ddd, $J = 12.7, 6.1, 1.9$ Hz, 1H), 2.45 (ddd, $J = 11.3, 7.7, 5.8$ Hz, 1H), 2.23 – 2.13 (m, 1H), 1.75 (td, $J = 12.4, 6.8$ Hz, 1H) ppm.

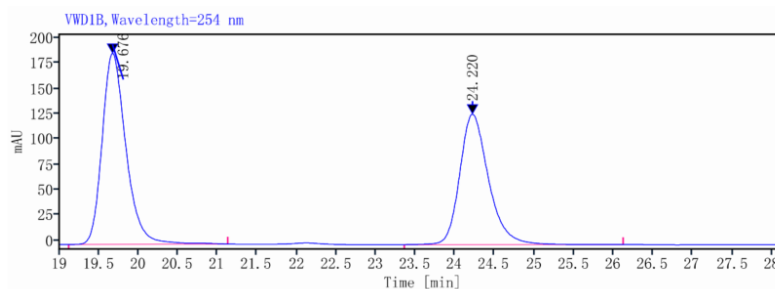
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 198.7, 169.8, 165.6, 137.8, 136.6, 131.0, 130.5, 128.8, 127.9, 126.6, 125.3, 122.8, 121.8, 114.3, 81.1, 67.0, 53.3, 36.6, 29.9 ppm.

HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{19}\text{NO}_3 + \text{H}]^+$ 334.1438, found 334.1436.

HPLC: Daicel Chiralpak IB-3, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis $\lambda = 250$ nm, $t_{R1} = 19.7$ min (major), $t_{R2} = 24.2$ min (minor).



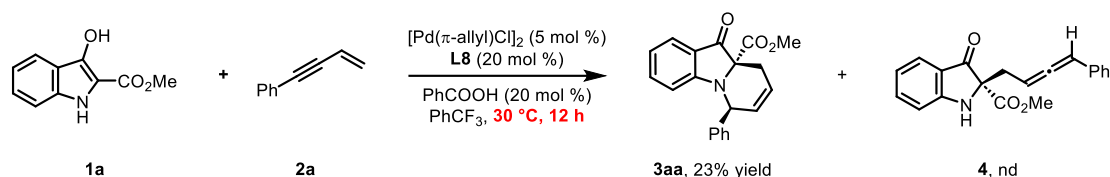
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
19.988	MM m	0.3207	8893.6714	427.4763	49.4489
24.700	MM m	0.3977	9091.8909	349.2656	50.5511



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
19.676	MM m	0.3183	3944.8278	188.3801	54.8028
24.220	MM m	0.3847	3253.3953	128.7891	45.1972

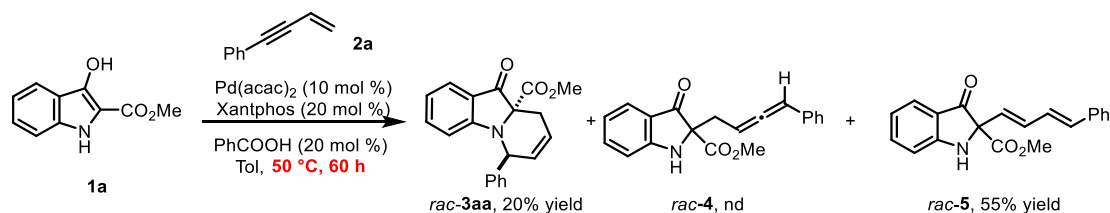
5. Mechanistic Studies

Intermediate Monitoring under Chiral Conditions



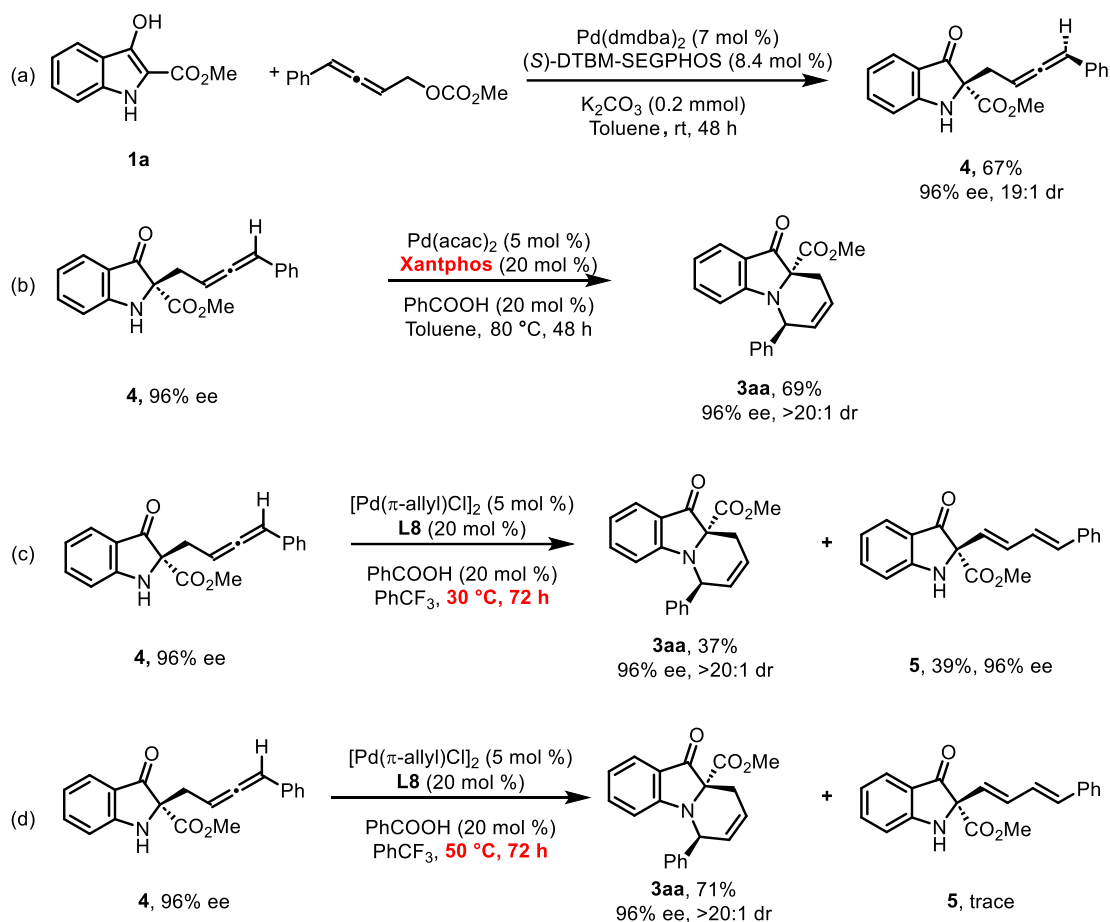
A sealed tube was charged with **1a** (38.2 mg, 0.2 mmol, 1.0 equiv), $[\text{Pd}(\pi\text{-allyl})\text{Cl}]_2$ (3.7 mg, 0.01 mmol, 5 mol %), **L8** (21.7 mg, 0.04 mmol, 20 mol %), PhCOOH (4.9 mg, 0.04 mmol, 20 mol %). The vial was thoroughly flushed with Ar, and PhCF_3 (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was stirred at 30 °C (oil temperature) for 12 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (80/1 to 50/1) to afford product **3aa** (14.6 mg, 23% yield) with considerable amounts **1a** remaining.

Intermediate Monitoring under Non-chiral Conditions

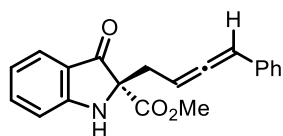


A sealed tube was charged with **1a** (38.2 mg, 0.2 mmol, 1.0 equiv), $\text{Pd}(\text{acac})_2$ (6.2 mg, 0.02 mmol, 10 mol %), Xantphos (23.2 mg, 0.04 mmol, 20 mol %), PhCOOH (4.9 mg, 0.04 mmol, 20 mol %). The vial was thoroughly flushed with Ar, and toluene (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 50 °C (oil temperature) for 60 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (80/1 to 50/1) to afford product **3aa** (12.8 mg, 20% yield) along with diene **5** (35.9 mg, 55% yield). Again, allene **4** was not detected.

Synthesis of Allene 4 and Intramolecular hydroamination of allene intermediate



(a) Allene **4** was synthesized as follows¹¹: A sealed tube was charged with **1a** (38.2 mg, 0.2 mmol, 1.0 equiv), Pd(dmdba)₂ (11.4 mg, 0.014 mmol, 7 mol %), (S)-DTBM-SEGPHOS (19.8 mg, 0.0168 mmol, 8.4 mol %), K₂CO₃ (27.8 mg, 0.2 mmol, 1.0 equiv). The vial was thoroughly flushed with Ar, and toluene (1.5 mL) was added via a syringe under Ar atmosphere. The reaction mixture was stirred at room temperature for 10 mins. Allenyl carbonate (76.9 mg, 0.4 mmol, 2.0 equiv) dissolved in toluene (0.5 mL) was then added to the reaction mixture. The reaction mixture was vigorously stirred at room temperature for 48 h. The reaction mixture was then diluted with EA (10.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (50/1 to 20/1) to afford product **4** (42.7 mg, 67% yield, 96% ee, 19:1 dr).



methyl (2R)-3-oxo-2-(4-phenylbuta-2,3-dien-1-yl)indoline-2-carboxylate (4)

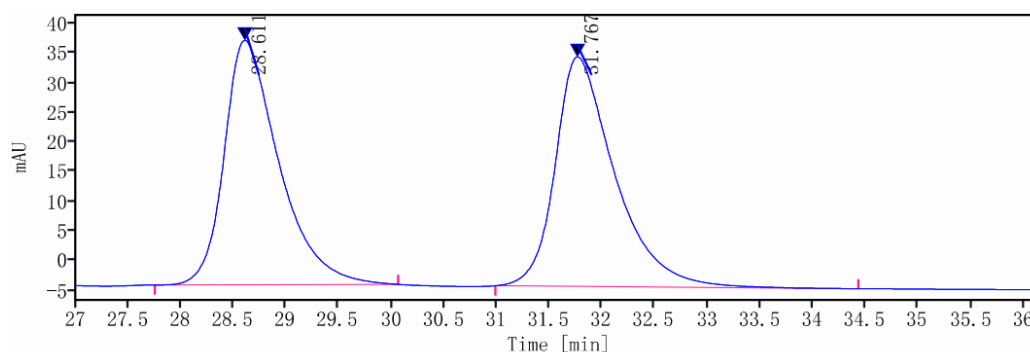
42.7 mg, 67% yield, 96% ee, 19:1 dr. $R_f = 0.4$ (PE/EA = 6/1); Yellow oil. $[\alpha]_D^{25} = -99.2$ ($c = 0.09$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.35 – 7.19 (m, 5H), 6.95 – 6.88 (m, 2H), 6.20 (dt, *J* = 6.0, 2.8 Hz, 1H), 5.56 (q, *J* = 6.6 Hz, 1H), 5.37 (s, 1H), 3.68 (s, 3H), 3.15 (ddd, *J* = 14.8, 6.5, 2.9 Hz, 1H), 2.64 (ddd, *J* = 14.8, 7.1, 2.6 Hz, 1H) ppm.

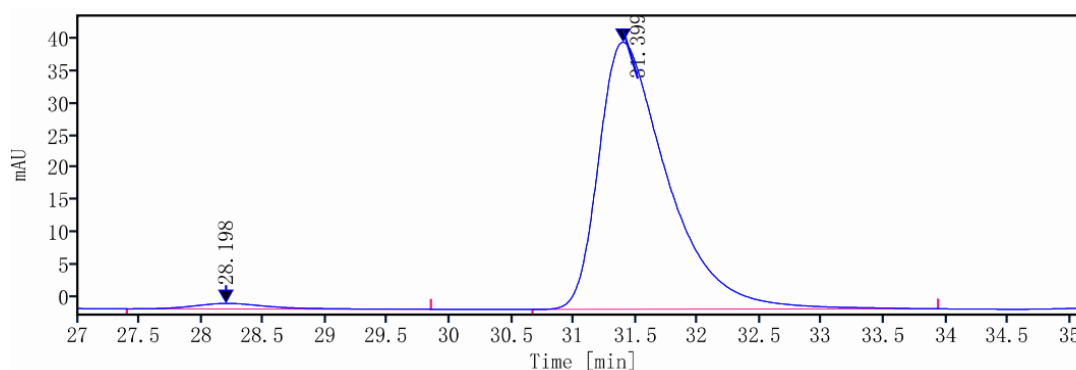
¹³C NMR (75 MHz, CDCl₃) δ 206.5, 195.1, 168.4, 161.6, 137.8, 133.9, 128.7, 127.3, 127.0, 125.2, 120.4, 120.0, 113.6, 96.0, 89.2, 73.9, 53.5, 35.5 ppm.

HRMS (ESI) calcd for [C₂₀H₁₇NO₃+Na]⁺ 342.1109, found 342.1104.

HPLC: Daicel Chiralcel IB-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, *t*_{R1} = 28.2 min (minor), *t*_{R2} = 31.4 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
28.611	MM m	0.5373	1487.3484	41.1914	49.3735
31.767	MM m	0.5797	1525.0957	38.7064	50.6265



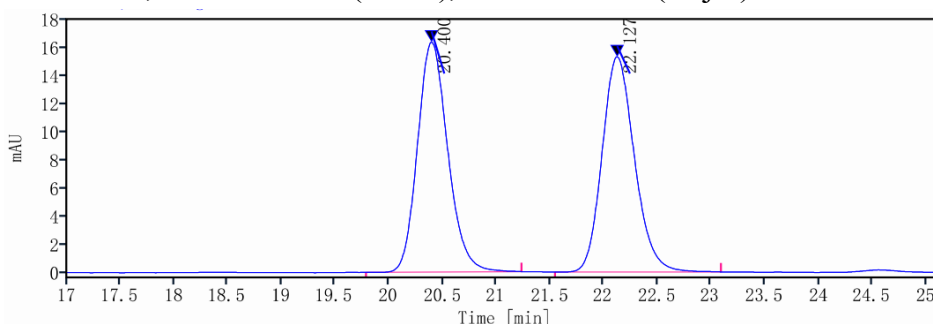
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
28.198	MM m	0.5743	35.9678	0.8700	2.2010
31.399	MM m	0.5733	1598.1763	41.4977	97.7990

(b) A sealed tube was charged with **4** (63.8 mg, 0.2 mmol, 1.0 equiv), Pd(acac)₂ (6.2 mg, 0.02 mmol, 10 mol %), Xantphos (23.2 mg, 0.04 mmol, 20 mol %) and PhCOOH (4.9 mg, 0.04 mmol, 20 mol %). The vial was thoroughly flushed with Ar, and toluene (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 80 °C (oil temperature) for 48 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under vacuum to give dark residue, which was purified by flash

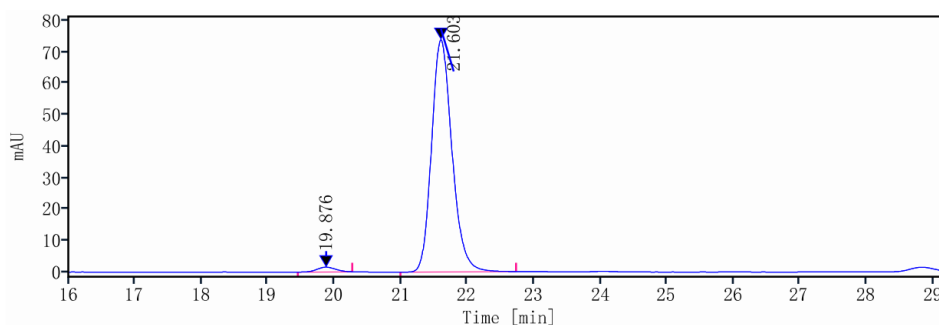
chromatography on silica gel with PE/EA (80/1 to 50/1) to afford product **3aa** (44.0 mg, 69% yield, 96% ee, >20:1 dr).

(c) A sealed tube was charged with **4** (63.8 mg, 0.2 mmol, 1.0 equiv), [Pd(π -allyl)Cl]₂ (3.7 mg, 0.01 mmol, 5 mol %), **L8** (21.7 mg, 0.04 mmol, 20 mol %) and PhCOOH (4.9 mg, 0.04 mmol, 20 mol %). The vial was thoroughly flushed with Ar, and PhCF₃ (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 30 °C (oil temperature) for 72 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (80/1 to 50/1) to afford product **3aa** (23.6 mg, 37% yield) and diene **5** (24.9 mg, 39% yield).

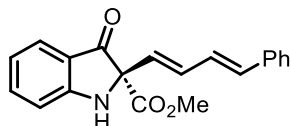
3aa, HPLC: Daicel Chiralcel IA-3, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 19.9 min (minor), t_{R2} = 21.6 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.400	MM m	0.3003	320.6013	16.3821	49.9818
22.127	MM m	0.3242	320.8352	15.3291	50.0182



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
19.876	MM m	0.2942	29.0365	1.5112	1.8097
21.603	MM m	0.3272	1575.4720	73.7552	98.1903



methyl (R)-3-oxo-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)indoline-2-carboxylate (5)

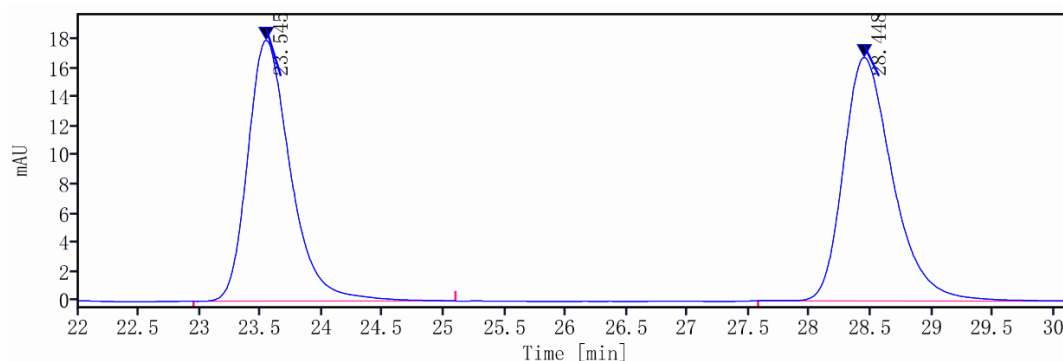
35.1 mg, 55% yield. $R_f = 0.4$ (PE/EA = 6/1); Yellow solid, m.p. 161-162 °C. $[\alpha]_D^{25} = +104.930$ ($c = 0.142$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.60 (d, $J = 7.8$ Hz, 1H), 7.51 (ddd, $J = 8.3, 7.0, 1.2$ Hz, 1H), 7.41 – 7.18 (m, 5H), 7.05 (d, $J = 8.3$ Hz, 1H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.80 (dd, $J = 15.3, 10.5$ Hz, 1H), 6.67 (dd, $J = 14.8, 10.5$ Hz, 1H), 6.56 (d, $J = 15.4$ Hz, 1H), 6.29 (d, $J = 14.7$ Hz, 1H), 5.36 (s, 1H), 3.83 (s, 3H) ppm.

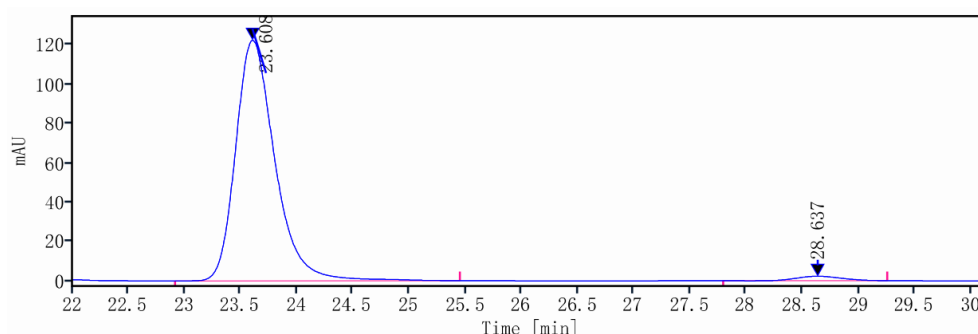
^{13}C NMR (75 MHz, CDCl_3) δ 193.8, 168.1, 161.4, 137.9, 136.9, 134.5, 131.3, 128.8, 128.3, 128.0, 127.4, 126.6, 125.8, 120.7, 119.1, 113.7, 75.4, 54.0 ppm.

HRMS (ESI) calcd for $[\text{C}_{20}\text{H}_{17}\text{NO}_3 + \text{Na}]^+$ 342.1109, found 342.1113.

HPLC: Daicel Chiralcel IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 250$ nm, $t_{R1} = 23.6$ min (major), $t_{R2} = 28.6$ min (minor).



RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
23.545	MM m	0.3728	437.0682	17.9062	48.2439
28.448	MM m	0.4277	468.8872	16.6931	51.7561

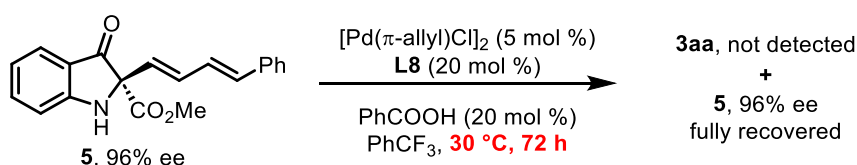


RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
23.608	MM m	0.3695	2972.6552	122.3230	97.9730
28.637	MM m	0.4269	61.5009	2.2639	2.0270

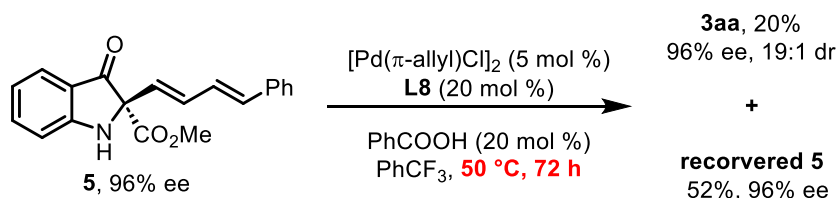
(d) A sealed tube was charged with **4** (63.8 mg, 0.2 mmol, 1.0 equiv), $[\text{Pd}(\pi\text{-allyl})\text{Cl}]_2$ (3.7 mg, 0.01 mmol, 5 mol %), **L8** (21.7 mg, 0.04 mmol, 20 mol %) and PhCOOH (4.9

mg, 0.04 mmol, 20 mol %). The vial was thoroughly flushed with Ar, and PhCF₃ (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 50 °C (oil temperature) for 72 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (80/1 to 50/1) to afford product **3aa** (45.3 mg, 71% yield).

Intramolecular hydroamination of allene intermediate



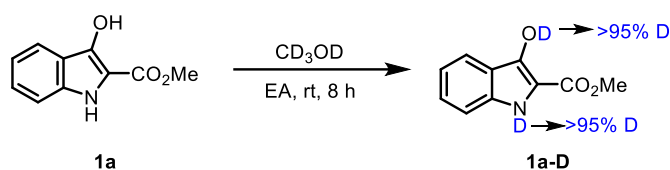
A sealed tube was charged with **5** (63.8 mg, 0.2 mmol, 1.0 equiv), [Pd(π-allyl)Cl]₂ (3.7 mg, 0.01 mmol, 5 mol %), **L8** (21.7 mg, 0.04 mmol, 20 mol %), PhCOOH (4.9 mg, 0.04 mmol, 20 mol %). The vial was thoroughly flushed with Ar, and PhCF₃ (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 30 °C (oil temperature) for 72 h. The reaction was monitored by TLC, and no product was detected with quantity of **5** recovered.



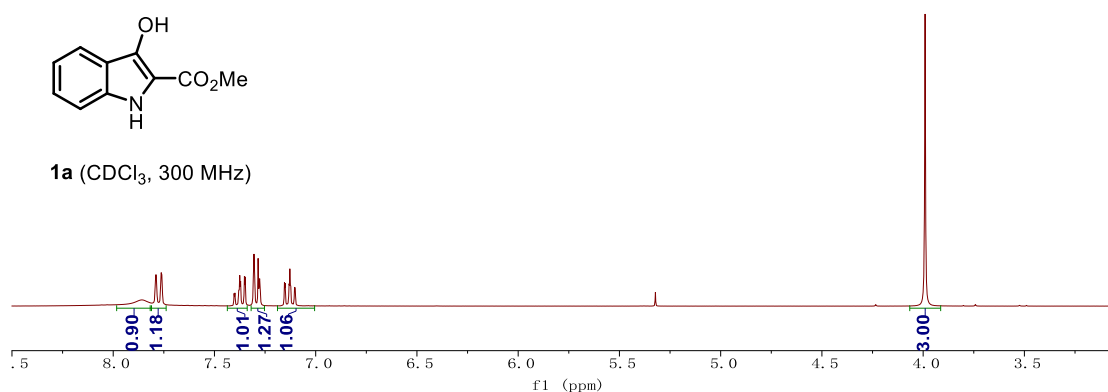
A sealed tube was charged with **5** (63.8 mg, 0.2 mmol, 1.0 equiv), [Pd(π-allyl)Cl]₂ (3.7 mg, 0.01 mmol, 5 mol %), **L8** (21.7 mg, 0.04 mmol, 20 mol %), PhCOOH (4.9 mg, 0.04 mmol, 20 mol %). The vial was thoroughly flushed with Ar, and PhCF₃ (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 50 °C (oil temperature) for 72 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (80/1 to 50/1) to afford product **3aa** (12.8 mg, 20% yield, 96% ee and 19:1 dr) and with diene **5** recovered in 52% yield.

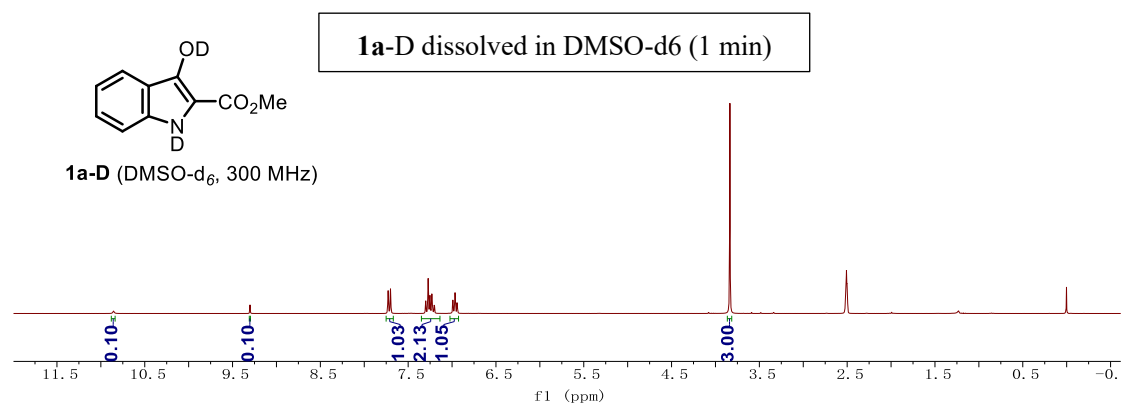
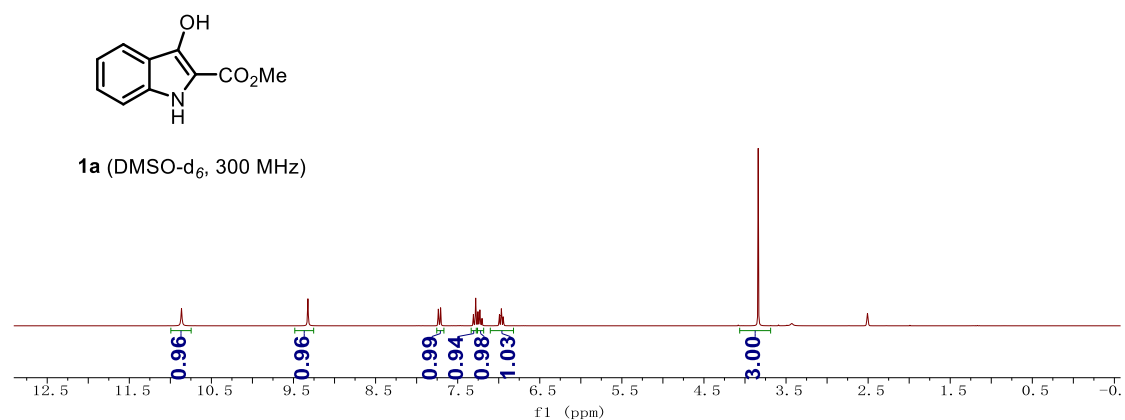
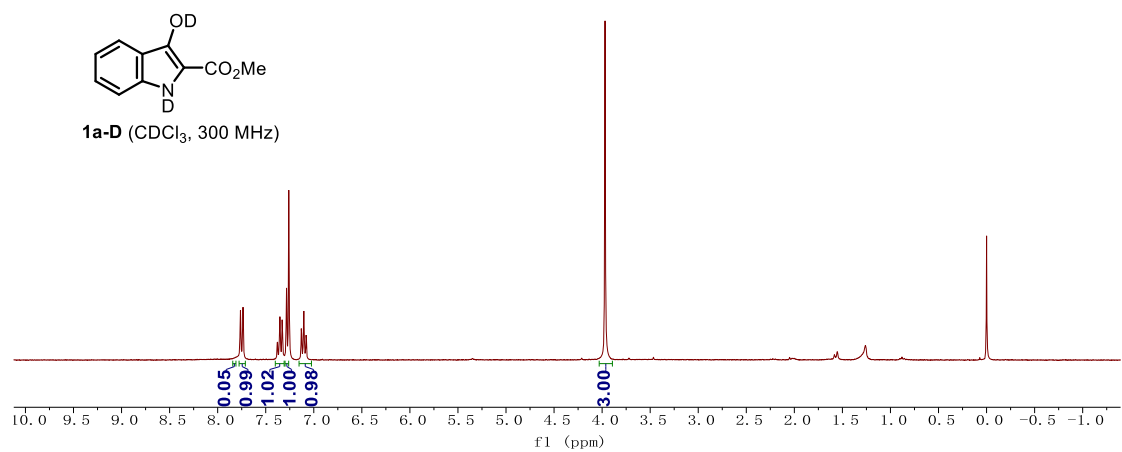
Deuterium Incorporation Experiment and Control Experiment

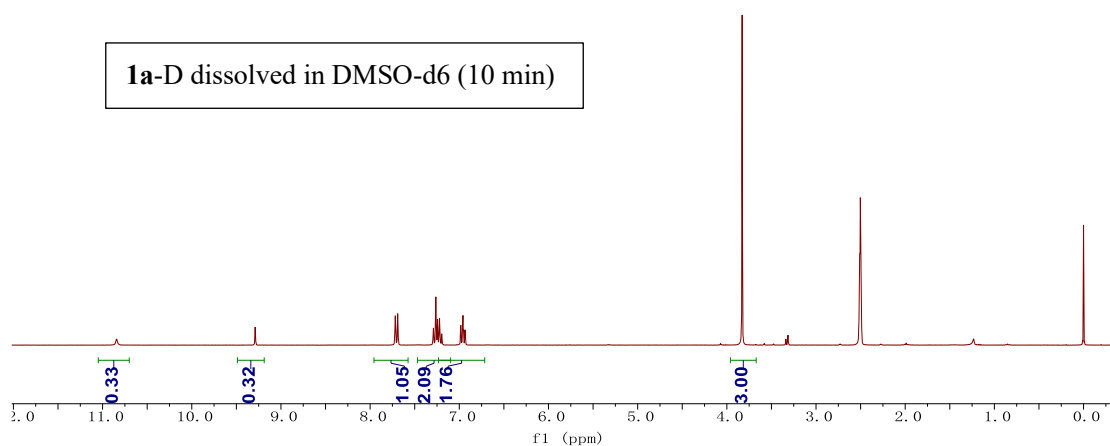
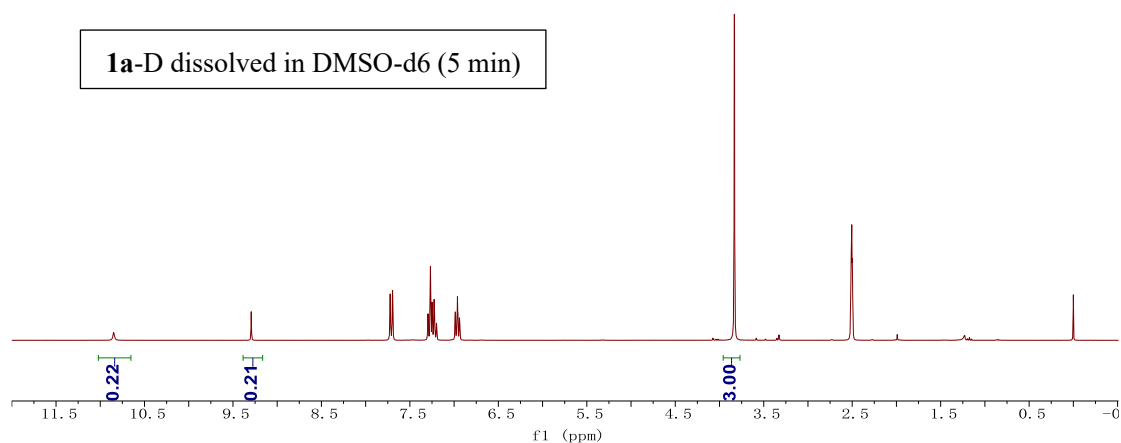
we successfully prepared the deuterated substrate **1a-D**¹² (with deuterium incorporation at both exchangeable O–H and N–H positions, which precluded the isolation of a singly labeled analogue) and PhCOOD¹³ with >95% D content. Then we carried the reaction of **1a-D** in the presence of PhCO₂D under standard condition, and product **3aa** was achieved in 65% yield, exhibiting 69% and 72% deuterium enrichment at the α- and β-positions, respectively.



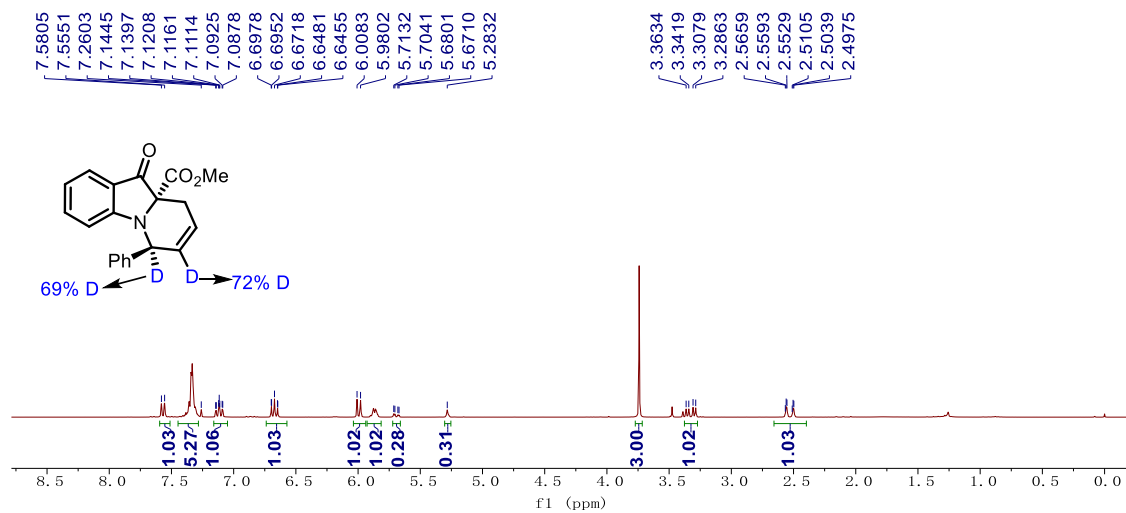
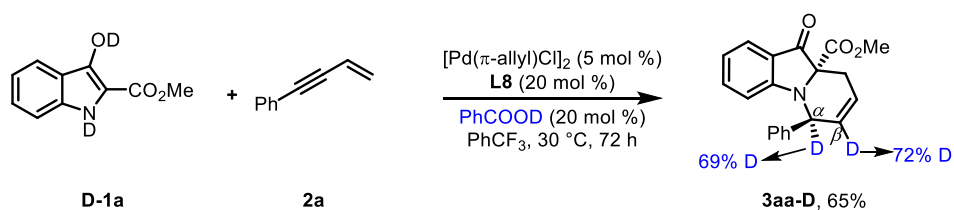
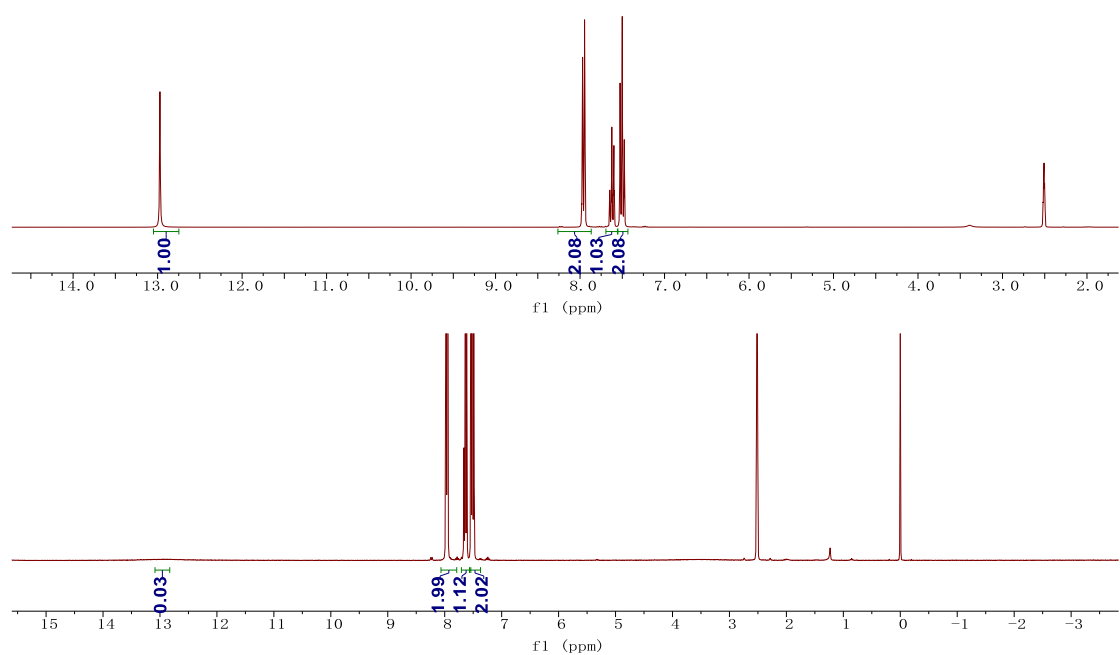
N,O-deuterium labeled indole **1a-D**, was synthesized as following procedure: In a dried 10 mL schlenk tube, indole **1a** (382.0 mg, 2 mmol) was dissolved in CD₃OD:EA (3:1, 4 mL) and the mixture was stirred in room temperature for 4 hours. Then the mixture was concentrated under vacuum to remove the solvent. CD₃OD:EA (3:1, 4 mL) was added into the schlenk tube again and the mixture was stirred in room temperature for another 4 hours. After that, the mixture was concentrated under vacuum to give quantitative yield of the product **1a-D**. The NMR of **1a-D** shows D% >95% in CDCl₃. In DMSO-*d*₆, however, the deuteration level was approximately 90%, likely due to rapid H–D exchange with trace water present in the DMSO-*d*₆.





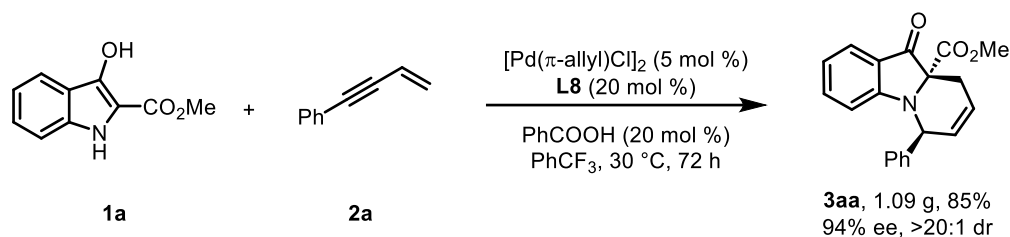


Sodium benzoate (288 mg, 2 mmol, 1 equiv) was taken into a round bottom flask, it was heated by heating gun under reduced pressure for 10 minutes. After cooling, the D₂O (2 mL) was added and dissolved. And then added Deuterium Chloride (20% in D₂O, 0.32 mL, 2 mmol, 1.0 equiv) to the reaction mixture, a white solid precipitated and continue to stir for 10min, to filter under reduced pressure; it was washed with D₂O (3 mL×2), the filter transferred to a dry round bottom bottle, the residual moisture was dried under reduced pressure at the 65°C, obtained white solid benzoic **acid-D1** (316 mg, 86%). The NMR of **acid-D1** shows D%>95% in DMSO-d₆.



6. Further Study

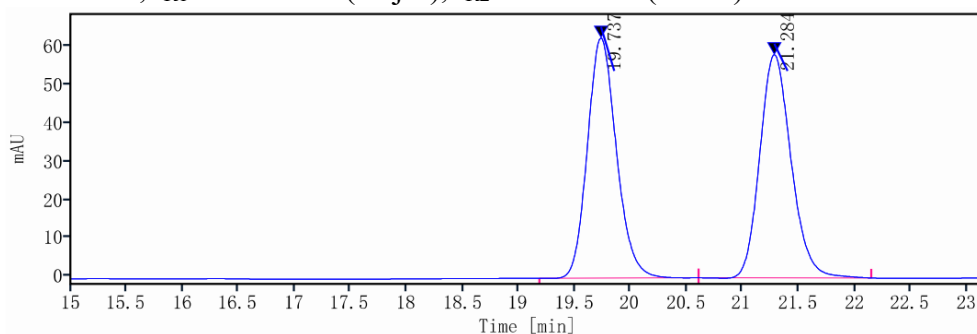
Gram-Scale reaction of **3aa**



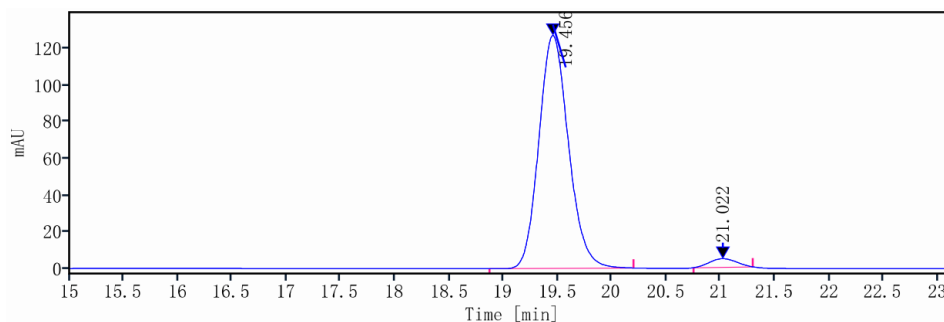
A sealed tube was charged with **1a** (764.0 mg, 4.0 mmol, 1.0 equiv), $[\text{Pd}(\pi\text{-allyl})\text{Cl}]_2$ (74.0 mg, 0.2 mmol, 5 mol %), **L8** (434.0 mg, 0.8 mmol, 20 mol %), and PhCOOH (98.0 mg, 0.8 mmol, 20 mol %). The vial was thoroughly flushed with Ar, and **2a** (1.02 g, 8.0 mmol, 2.0 equiv) in PhCF₃ (20.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 30 °C (oil temperature) for 72 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (80:1 to 50:1) to afford product **3aa** (1.09 g, 85% yield) with 94% ee and >20:1 dr.

ent-**3aa**, 53.4 mg, 84% yield, 94% ee, >20:1 dr. R_f = 0.5 (PE/EA = 10/1); Yellow solid, $[\alpha]_D^{25}$ = +120.34 (c = 0.094, CHCl₃).

HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis λ = 400 nm, t_{R1} = 19.5 min (major), t_{R2} = 21.0 min (minor).

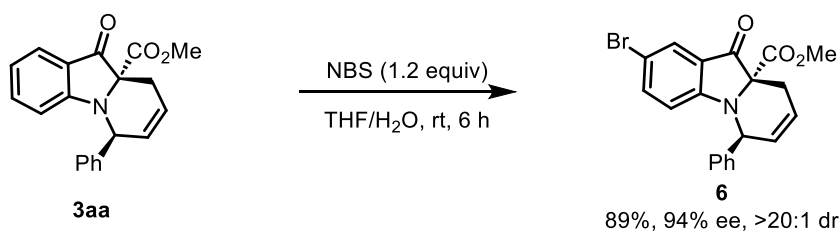


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
19.737	MM m	0.2779	1130.8970	62.8546	49.9153
21.284	MM m	0.3006	1134.7358	58.4118	50.0847



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
19.456	MM m	0.2932	2407.9245	127.0002	96.7759
21.022	MM m	0.2759	80.2196	4.6818	3.2241

Synthetic Transformation



To a stirred solution of **3aa** (63.8 mg, 0.2 mmol, 1.0 equiv) in THF/H₂O (2.0 mL, v/v = 9:1) was added *N*-Bromosuccinimide (NBS, 42.8 mg, 0.24 mmol, 1.2 equiv) at room temperature. After stirring for 6 h at room temperature, the reaction was extracted with EA (2×10.0 mL) and then washed with H₂O and brine, dried over Na₂SO₄ and concentrated in vacuum. The crude product was purified by flash column chromatography on silica gel to yield the pure product **6** (70.5 mg, 89% yield, 94% ee, > 20:1 dr).

methyl (6*S*,9*aR*)-2-bromo-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (6)

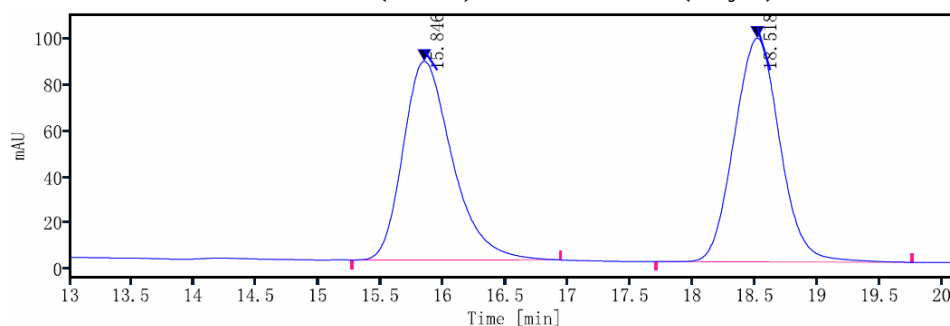
70.5 mg, 89% yield, 94% ee, >20:1 dr. $R_f = 0.5$ (PE/EA = 6/1); Yellow solid, m.p. 192-193 °C. $[\alpha]_D^{25} = -132.3$ ($c = 0.105$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.69 (d, $J = 2.0$ Hz, 1H), 7.45 – 7.24 (m, 5H), 7.19 (dd, $J = 8.8, 2.2$ Hz, 1H), 5.89 (dd, $J = 9.4, 6.8$ Hz, 1H), 5.71 (dt, $J = 10.0, 2.6$ Hz, 1H), 5.27 (*app.* s, 1H), 3.77 (s, 3H), 3.34 (ddd, $J = 16.7, 6.4, 1.8$ Hz, 1H), 2.55 (dq, $J = 16.7, 3.1$ Hz, 1H) ppm.

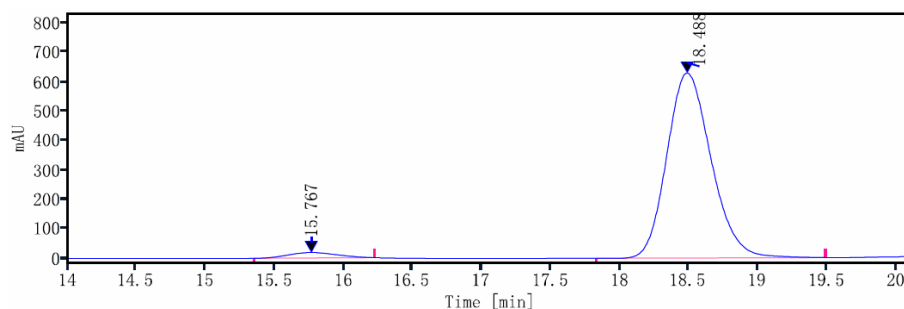
¹³C NMR (75 MHz, CDCl₃) δ 193.3, 167.4, 158.3, 139.6, 139.5, 131.4, 129.5, 128.5, 127.5, 121.6, 120.9, 112.9, 110.6, 75.1, 59.2, 53.9, 28.7 ppm.

HRMS (ESI) calcd for [C₂₀H₁₇BrNO₃+H]⁺ 398.0386, found 398.0389.

HPLC: Daicel Chiralcel AS-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 250$ nm, $t_{R1} = 15.8$ min (minor), $t_{R2} = 18.5$ min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.846	MM m	0.4201	2369.3655	86.3679	48.9201
18.518	MM m	0.4010	2473.9760	97.1702	51.0799



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.767	MM m	0.3841	453.0693	18.6075	3.1284
18.488	MM m	0.3457	14029.2864	630.2837	96.8716



To a stirred solution of **3aa** (63.8 mg, 0.2 mmol, 1.0 equiv) and AuCl₃ (3.0 mg, 0.01 mmol, 5 mol %) in DCE (2.0 mL) was added *N*-Iodosuccinimide (NIS, 67.5 mg, 0.3 mmol, 1.5 equiv) at room temperature. After stirring for 12 h at room temperature, the reaction was quenched with saturated Na₂S₂O₃ and extracted with EA (10.0 mL×2) and then washed with H₂O and brine, dried over Na₂SO₄ and concentrated in vacuum. The crude product was purified by flash column chromatography on silica gel to yield the pure product **7** (83.0 mg, 93% yield, 94% ee, > 20:1 dr).

methyl (6*S*,9*aR*)-2-iodo-10-oxo-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-9*a*(10*H*)-carboxylate (7)

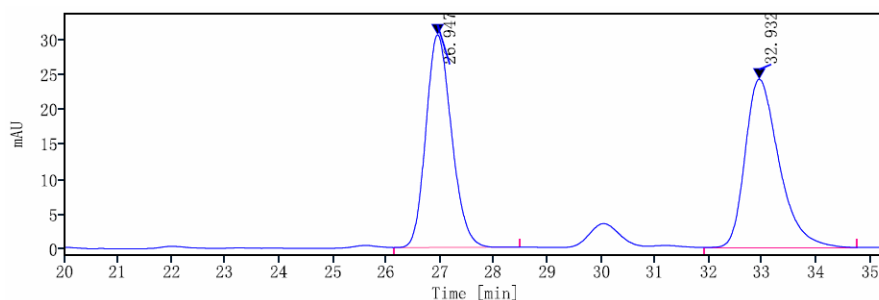
83.0 mg, 93% yield, 94% ee, >20:1 dr. *R*_f = 0.5 (PE/EA = 6/1); Yellow solid, m.p. 195–197 °C. [α]_D²⁵ = -101.389 (*c* = 0.072, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, *J* = 1.6 Hz, 1H), 7.42 – 7.30 (m, 5H), 5.89 (ddt, *J* = 10.0, 6.4, 1.7 Hz, 1H), 5.81 (d, *J* = 8.7 Hz, 1H), 5.71 (dt, *J* = 10.0, 2.5 Hz, 1H), 5.27 (p, *J* = 2.5 Hz, 1H), 3.77 (s, 3H), 3.34 (ddd, *J* = 16.7, 6.4, 1.8 Hz, 1H), 2.54 (dq, *J* = 16.7, 3.1 Hz, 1H) ppm.

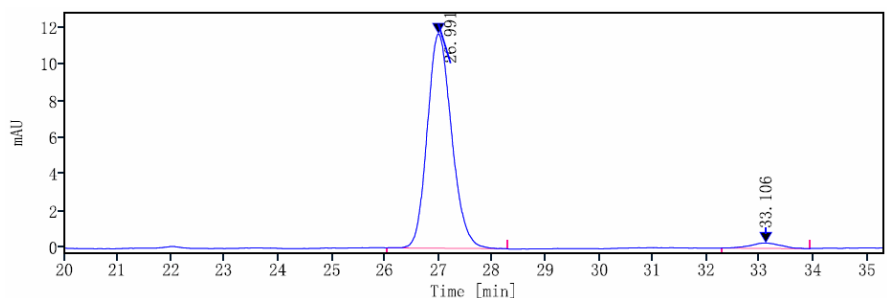
¹³C NMR (75 MHz, CDCl₃) δ 193.0, 167.4, 158.7, 145.0, 139.5, 133.6, 131.4, 129.5, 128.5, 127.5, 122.3, 120.9, 113.5, 79.5, 74.8, 59.2, 53.8, 28.6 ppm.

HRMS (ESI) calcd for [C₂₀H₁₇INO₃+H]⁺ 446.0248, found 446.0254.

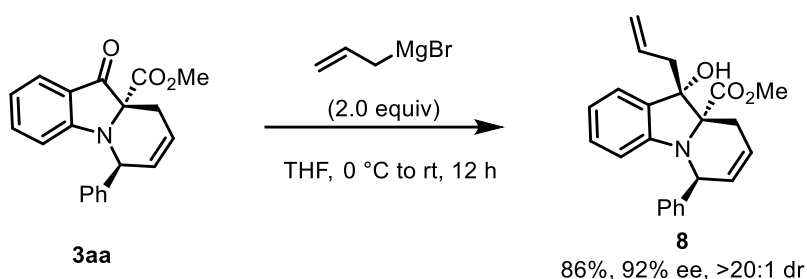
HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, *t*_{R1} = 27.0 min (major), *t*_{R2} = 33.1 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
26.947	MM m	0.5148	1003.8977	30.2817	48.8860
32.932	BB	2.8467	1049.6493	23.9833	51.1140



RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
26.991	MM m	0.4892	370.0105	11.6928	97.0293
33.106	MM m	0.4867	11.3285	0.2894	2.9707



A sealed tube was charged with the substrate **3aa** (63.8 mg, 0.2 mmol, 1.0 equiv) in THF (2.0 mL). Then allylmagnesium bromide (1.3 M in THF, 0.31 mL, 0.4 mmol, 2.0 equiv) was added dropwise at 0 °C under nitrogen atmosphere. After completion of the addition, the reaction mixture was stirred for additional 12 h before it was diluted with cold aqueous saturated NH_4Cl solution (3.0 mL) and extracted with EA. The combined organic layer was dried over Na_2SO_4 , concentrated *in vacuo* after filtration. The residue was purified by flash column chromatography on silica gel (PE/EA = 15:1 to 6:1) to afford the alcohol **8** (62.2 mg, 86% yield) as white solid with 94% ee and >20:1 dr.

methyl (6S,9aR,10S)-10-allyl-10-hydroxy-6-phenyl-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (8)

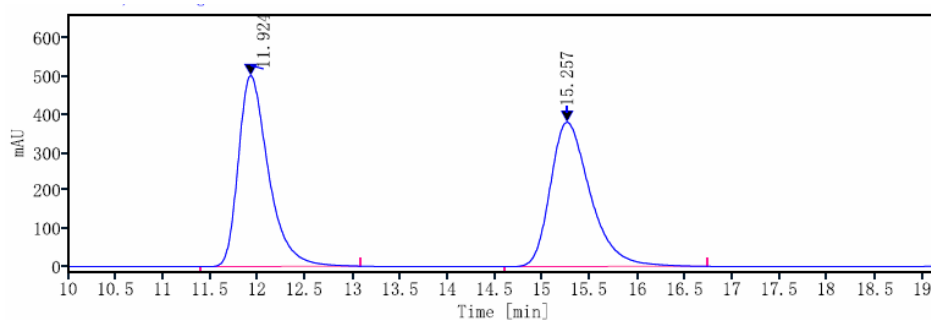
62.2 mg, 86% yield, 92% ee, >20:1 dr. R_f = 0.4 (PE/EA = 6/1); White solid, m.p. 160–162 °C. $[\alpha]_D^{25}$ = -184.09 (c = 0.044, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 7.46 – 7.28 (m, 5H), 7.13 – 7.10 (m, 1H), 6.96 (td, J = 7.7, 1.2 Hz, 1H), 6.74 – 6.69 (m, 1H), 6.04 – 5.80 (m, 3H), 5.67 (dt, J = 9.9, 2.7 Hz, 1H), 5.32 – 5.24 (m, 2H), 4.99 – 4.96 (m, 1H), 3.68 (s, 3H), 3.04 (ddd, J = 15.7, 6.6, 2.0 Hz, 1H), 2.87 – 2.79 (m, 1H), 2.73 (d, J = 7.2 Hz, 2H), 2.64 (s, 1H) ppm.

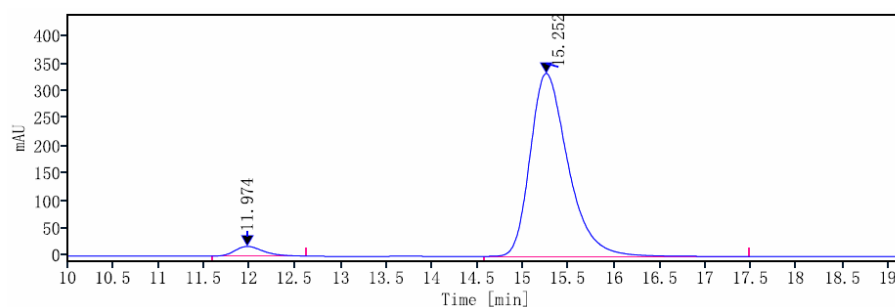
^{13}C NMR (75 MHz, CDCl_3) δ 172.7, 149.5, 142.1, 132.6, 131.5, 130.9, 129.1, 127.5, 126.8, 123.1, 122.1, 120.3, 118.3, 108.5, 81.9, 60.8, 52.2, 42.5, 27.8 ppm.

HRMS (ESI) calcd for $[\text{C}_{23}\text{H}_{23}\text{NO}_3 + \text{H}]^+$ 362.1751, found 362.1753.

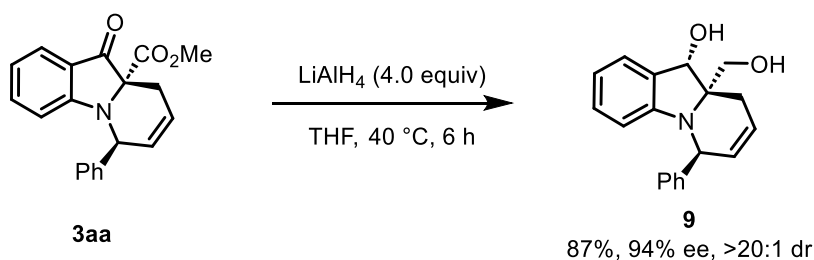
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 12.0 min (minor), t_{R2} = 15.3 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.924	MM m	0.3348	11065.5981	502.8066	49.8918
15.257	MM m	0.4450	11113.6156	380.2545	50.1082



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.974	MM m	0.3325	391.6974	17.9575	3.9115
15.252	MM m	0.4402	9622.4024	333.8913	96.0885



A sealed tube was charged with LiAlH_4 (29.6 mg, 0.8 mmol, 4.0 equiv). Then **3aa** (63.8 mg, 0.2 mmol, 1.0 equiv) in THF (0.1 M) was added dropwise under a nitrogen atmosphere. After completion of the addition, the reaction mixture was stirred at 40 °C for additional 6 h before it was quenched with saturated aqueous Rochelle salt (3.0 mL) and extracted with EA. The combined organic layer was dried over MgSO_4 , concentrated *in vacuo* after filtration. The residue was purified by flash column chromatography on silica gel (PE/EA = 10:1 to 2:1) to afford the alcohol **9** (51.0 mg, 87% yield) as white solid with 94% ee and >20:1 dr.

(6*S*,9*aS*,10*S*)-9*a*-(hydroxymethyl)-6-phenyl-6,9,9*a*,10-tetrahydropyrido[1,2-*a*]indol-10-ol (9)

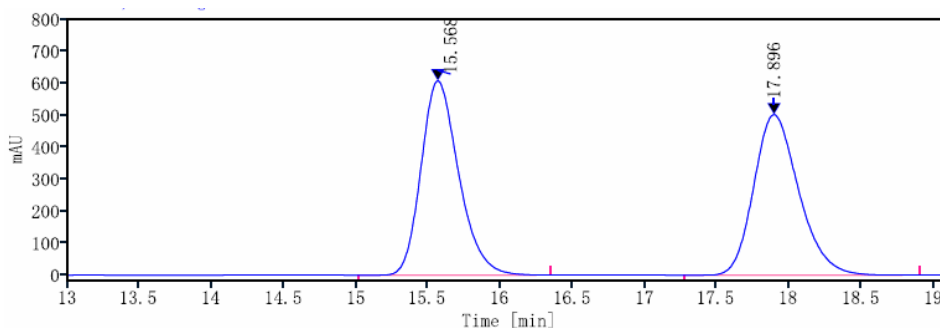
51.0 mg, 87% yield, 94% ee, >20:1 dr. $R_f = 0.3$ (PE/EA = 4/1); White solid, m.p. 134–136 °C. $[\alpha]_D^{25} = -165.625$ ($c = 0.096$, CHCl_3).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.36 – 7.25 (m, 5H), 7.19 (dt, $J = 7.2, 1.4$ Hz, 1H), 6.84 – 6.78 (m, 1H), 6.64 (td, $J = 7.4, 1.0$ Hz, 1H), 5.80 – 5.73 (m, 1H), 5.71 (d, $J = 7.8$ Hz, 1H), 5.65 – 5.60 (m, 1H), 5.37 (s, 1H), 4.80 (p, $J = 2.5$ Hz, 1H), 3.96 – 3.82 (m, 2H), 3.48 (br s, 1H), 2.96 – 2.88 (m, 1H), 2.76 (br s, 1H), 2.48 (dq, $J = 17.0, 2.8$ Hz, 1H) ppm.

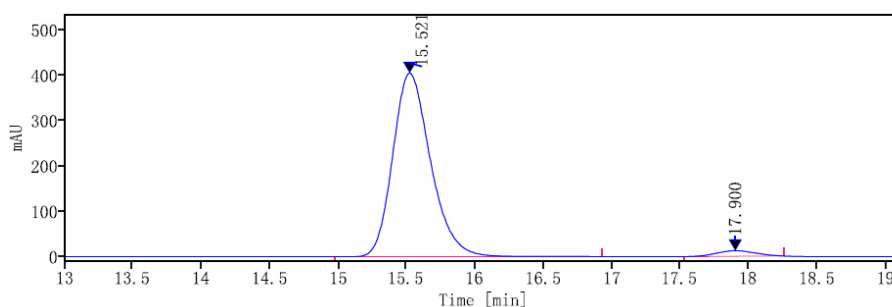
$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 148.1, 141.7, 130.5, 130.0, 129.1, 128.7, 127.6, 126.9, 122.8, 121.4, 117.9, 108.3, 83.0, 68.6, 60.6, 58.4, 31.3 ppm.

HRMS (ESI) calcd for $[\text{C}_{19}\text{H}_{19}\text{NO}_2 + \text{H}]^+$ 294.1489, found 294.1488.

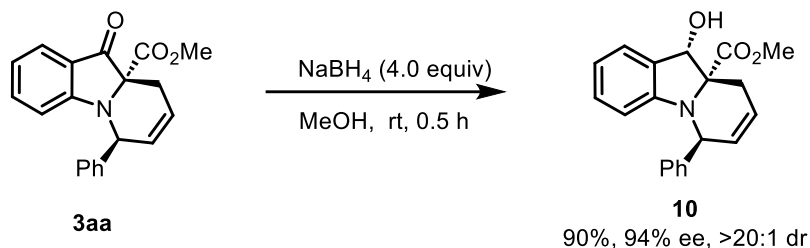
HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis $\lambda = 254$ nm, $t_{R1} = 15.5$ min (major), $t_{R2} = 17.9$ min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.568	MM m	0.2776	11066.8139	610.3181	50.2807
17.896	MM m	0.3331	10943.2429	504.4015	49.7193



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.521	MM m	0.2942	7775.2318	404.6089	96.9811
17.900	MM m	0.3134	242.0339	12.2013	3.0189



To a solution of **3aa** (63.8 mg, 0.2 mmol, 1.0 equiv) in MeOH (2.0 mL) at room temperature was added NaBH₄ (29.6 mg, 0.8 mmol, 4.0 equiv) in portions. The reaction mixture was stirred at room temperature for 0.5 h. After the reaction was completed, the reaction mixture was quenched with saturated aqueous NH₄Cl solution and evaporated under reduced pressure. The mixture was then extracted with DCM, dried over Na₂SO₄, and concentrated under reduced pressure. The concentrated mixture was purified by flash column chromatography on silica gel (PE/EA = 10:1 to 4:1) to obtain the desired product **10** (57.8 mg, 90% yield) with 94% ee and >20:1 dr.

methyl (6S,9aR,10S)-10-hydroxy-6-phenyl-6,9-dihydropyrido[1,2-a]indole-9a(10H)-carboxylate (10)

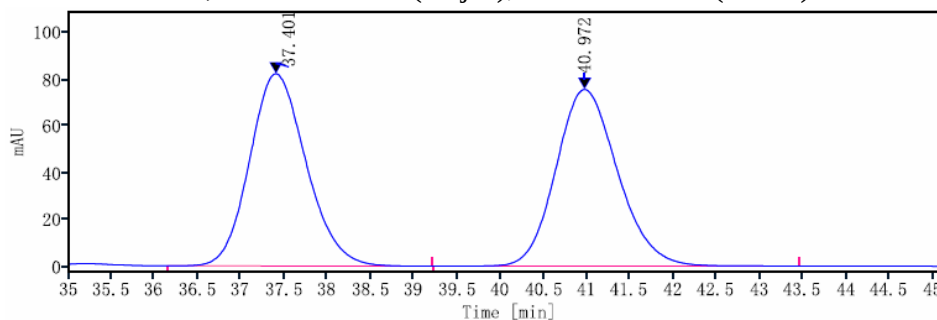
57.8 mg, 90% yield, 94% ee, >20:1 dr. *R*_f = 0.4 (PE/EA = 6/1); White solid, m.p. 192–193 °C. [α]_D²⁵ = -132.3 (*c* = 0.105, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.45 – 7.28 (m, 5H), 7.23 (d, *J* = 7.1 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 5.92 (d, *J* = 7.8 Hz, 1H), 5.85 – 5.80 (m, 1H), 5.70 – 5.65 (m, 1H), 5.47 (d, *J* = 4.3 Hz, 1H), 5.05 (s, 1H), 3.72 (s, 3H), 3.27 (dd, *J* = 16.1, 5.0 Hz, 1H), 2.79 (d, *J* = 6.7 Hz, 1H), 2.69 (d, *J* = 16.0 Hz, 1H) ppm.

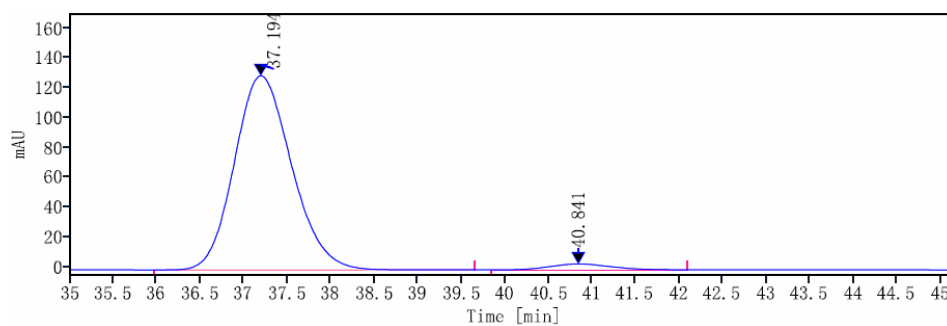
¹³C NMR (75 MHz, CDCl₃) δ 172.6, 149.4, 141.7, 131.4, 129.1, 129.1, 128.9, 127.7, 127.1, 123.0, 121.8, 118.4, 108.6, 80.4, 76.8, 60.3, 52.3, 33.0 ppm.

HRMS (ESI) calcd for [C₂₀H₂₀NO₃+H]⁺ 322.1438, found 322.1439.

HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, *t*_{R1} = 37.2 min (major), *t*_{R2} = 40.8 min (minor).

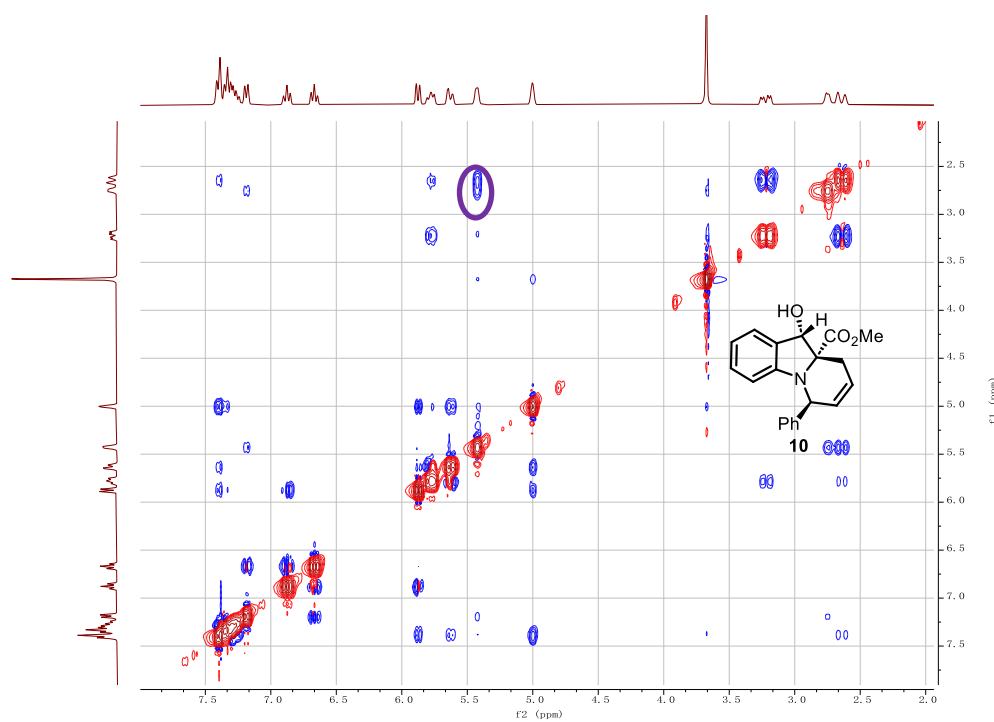


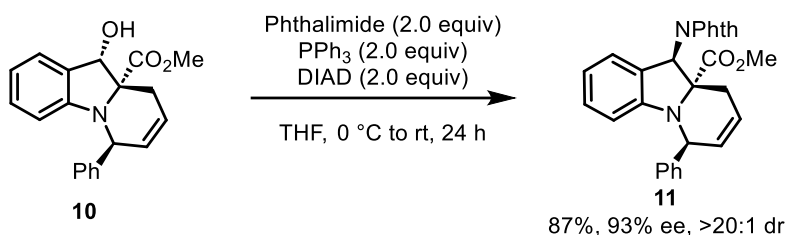
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
37.401	BB	3.0667	3746.6128	82.3392	49.8937
40.972	BB	4.2300	3762.5776	75.6754	50.1063



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
37.194	BB	3.6867	5960.3090	130.3112	96.9633
40.841	BB	2.2567	186.6625	3.8785	3.0367

The NOE spectrum of compound **10**:





A sealed tube charged with **10** (64.3 mg, 0.2 mmol, 1.0 equiv), phthalimide (58.9 mg, 0.4 mmol, 2.0 equiv), and PPh₃ (104.9 mg, 0.4 mmol, 2.0 equiv) was evacuated and backfilled with argon (repeated for 3 times). Then the reaction mixture was then stirred at room temperature for 0.5 h, and DIAD (79 μ L, 0.4 mmol, 2.0 equiv) was added slowly at 0 °C. Then the reaction was stirred for 24 h. After the reaction was completed, the reaction mixture was quenched with saturated aqueous NH₄Cl solution. The mixture was then extracted with EA, dried over Na₂SO₄, and concentrated under reduced pressure. The concentrated mixture was purified by flash column chromatography on silica gel (PE/EA = 30:1 to 10:1) to obtain the desired product **11** (50.9 mg, 87% yield) with 93% ee and >20:1 dr.

methyl (6S,9aR,10R)-10-(1,3-dioxoisindolin-2-yl)-6-phenyl-6,9-dihydropyrido[1,2-*a*]indole-9a(10H)-carboxylate (11)

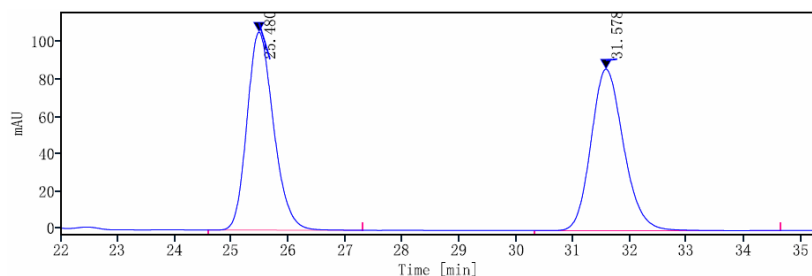
50.9 mg, 87% yield (79% yield over two steps), 93% ee, >20:1 dr. R_f = 0.3 (PE/EA = 6/1); White solid, m.p. 190-191 °C. $[\alpha]_D^{25}$ = -225.758 (c = 0.066, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.94 (dd, J = 6.5, 1.5 Hz, 1H), 7.81 – 7.69 (m, 3H), 7.63 (d, J = 7.3 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 7.05 (d, J = 7.2 Hz, 1H), 7.01 – 6.88 (m, 1H), 6.61 (t, J = 7.4 Hz, 1H), 5.98 (d, J = 8.0 Hz, 1H), 5.90 (s, 1H), 5.72 (dt, J = 10.0, 2.7 Hz, 1H), 5.59 (ddt, J = 10.1, 6.6, 1.9 Hz, 1H), 5.32 (p, J = 2.4 Hz, 1H), 3.75 (s, 3H), 2.77 (ddd, J = 15.9, 6.4, 2.0 Hz, 1H), 2.51 (dq, J = 15.9, 3.1 Hz, 1H) ppm.

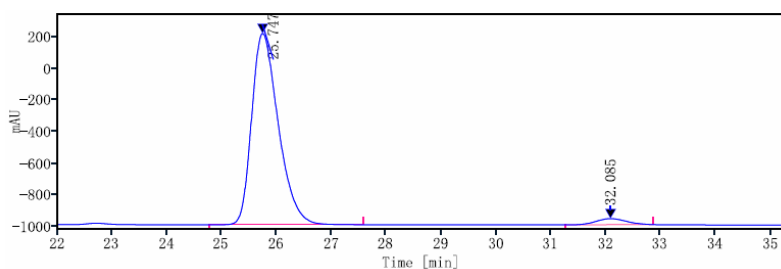
¹³C NMR (75 MHz, CDCl₃) δ 174.0, 168.2, 166.9, 151.5, 141.4, 134.5, 134.2, 132.0, 131.9, 131.5, 129.8, 129.1, 127.4, 127.0, 124.5, 123.7, 122.8, 119.4, 118.0, 108.8, 72.5, 60.1, 55.5, 53.0, 28.7 ppm.

HRMS (ESI) calcd for [C₂₈H₂₂N₂O₄+H]⁺ 451.1652, found 451.1648.

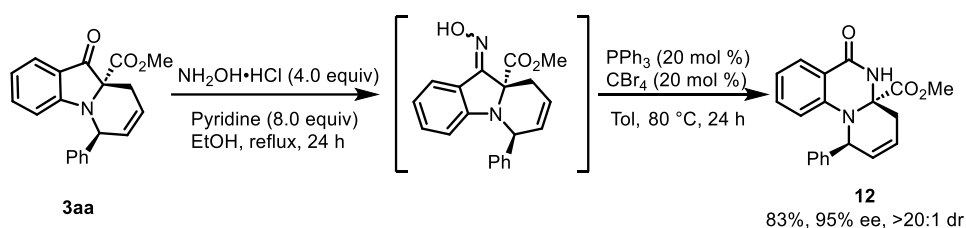
HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 25.7 min (major), t_{R2} = 32.1 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
25.480	MM m	0.4982	3447.9546	106.3738	50.1518
31.578	MM m	0.6114	3427.0877	86.6501	49.8482



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height [mAU]	Area%
25.747	MM m	0.5193	40908.7004	1213.3448	96.5129
32.085	MM m	0.5947	1478.0574	38.7764	3.4871



The synthesis of oxime was performed following a modified literature procedure.¹⁴ To an oven-dried 10 mL schlenk tube equipped with a tefloncoated magnetic stir bar was added **3aa** (63.8 mg, 0.2 mmol, 1.0 equiv), hydroxylamine hydrochloride (55.6 mg, 0.8 mmol, 4.0 equiv) and pyridine (130 μ L, 1.6 mmol, 8.0 equiv). Then the schlenk tube was evacuated and filled with argon for three times. After that, pre-dried EtOH (2.0 mL) was added via a syringe under argon atmosphere. Then the reaction mixture was stirred at 80 $^{\circ}$ C in oil bath for 24 h. After completion of the reaction, it was quenched with H₂O (30.0 mL) and extracted with EA (10.0 mL $\times$ 3). The organic layer was washed with saturated brine, dried over Na₂SO₄, and concentrated under reduced pressure. The oxime could be obtained in quantitative yield without the need of further purification.

The Beckmann rearrangement of oxime was conducted following a reported literature procedure.¹⁵ To an oven-dried 10 mL schlenk tube equipped with a tefloncoated magnetic stir bar was added CBr₄ (13.3 mg, 0.04 mmol, 20 mol %) and PPh₃ (5.3 mg, 0.04 mmol, 20 mol %). Then the schlenk tube was evacuated and filled with argon for three times. After that, the oxime (66.9 mg, 0.2 mmol, 1.0 equiv) was dissolved in toluene (2.0 mL) and then added via a syringe under argon atmosphere. Then the reaction mixture was stirred at 80 $^{\circ}$ C in oil bath for 24 h. After completion of the reaction, the crude product was concentrated in vacuum and purified by flash chromatography on silica gel (PE/EA = 30:1 to 6:1) to obtain the desired product **12** (55.5 mg, 83% yield) with 95% ee and >20:1 dr.

methyl (1S,4aS)-6-oxo-1-phenyl-1,4,5,6-tetrahydro-4aH-pyrido[1,2-a]quinazoline-4a-carboxylate (12)

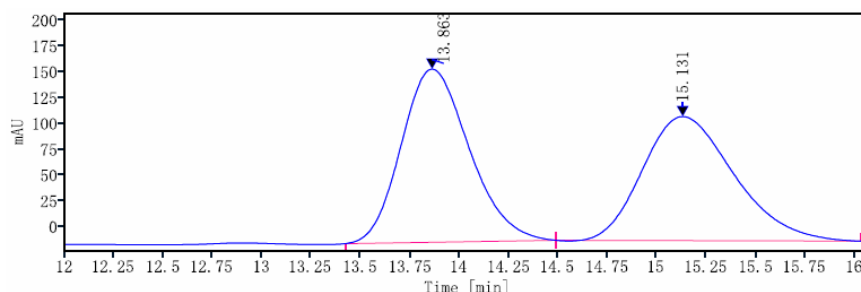
55.5 mg, 83% yield, 95% ee, >20:1 dr. $R_f = 0.4$ (PE/EA = 4/1); Colorless oil. $[\alpha]_D^{25} = -112.30$ ($c = 0.100$, CHCl_3).

^1H NMR (300 MHz, CDCl_3) δ 9.37 (s, 1H), 8.11 (ddd, $J = 7.6, 1.4, 0.6$ Hz, 1H), 7.37 – 7.25 (m, 5H), 6.97 (ddd, $J = 8.2, 7.4, 1.4$ Hz, 1H), 6.66 (td, $J = 7.8, 1.0$ Hz, 1H), 5.92 (d, $J = 8.2$ Hz, 1H), 5.84 – 5.77 (m, 1H), 5.70 (dt, $J = 10.0, 2.7$ Hz, 1H), 5.23 (dq, $J = 4.7, 2.1$ Hz, 1H), 3.75 (s, 3H), 3.28 (ddd, $J = 16.5, 6.5, 2.2$ Hz, 1H), 2.83 – 2.75 (m, 1H) ppm.

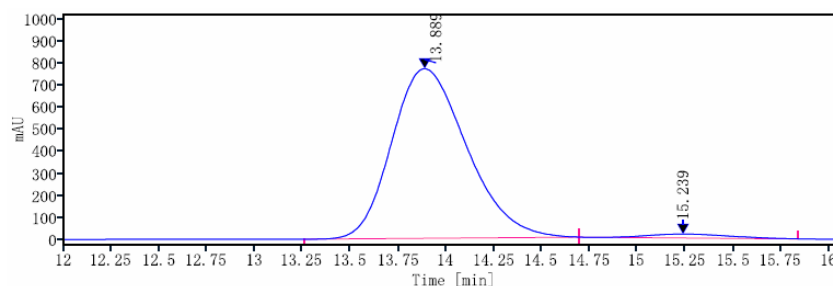
^{13}C NMR (75 MHz, CDCl_3) δ 171.1, 155.2, 153.4, 140.8, 132.8, 131.8, 129.4, 129.2, 127.9, 127.2, 120.9, 118.3, 118.0, 109.4, 77.6, 76.7, 71.3, 59.2, 53.4, 31.5 ppm.

HRMS (ESI) calcd for $[\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_3 + \text{H}]^+$ 335.1390, found 335.1388.

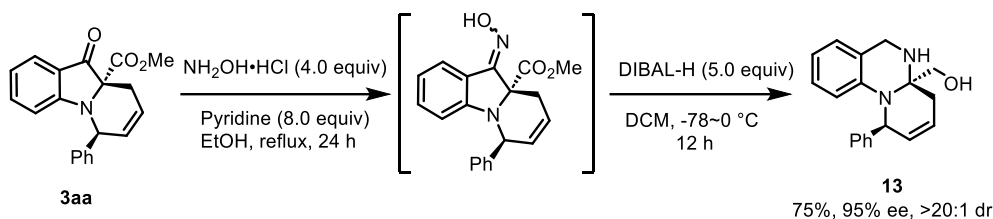
HPLC: Daicel Chiralcel AS-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis $\lambda = 250$ nm, $t_{R1} = 13.9$ min (major), $t_{R2} = 15.2$ min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.863	MM m	0.3711	4020.8796	168.0905	50.9833
15.131	MM m	0.4985	3865.7868	120.4140	49.0167



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.889	MM m	0.4241	20995.2074	770.0059	97.6713
15.239	MM m	0.4717	500.5831	17.1942	2.3287



The synthesis of oxime was performed following a modified literature procedure.¹⁴ To an oven-dried 10 mL schlenk tube equipped with a tefloncoated magnetic stir bar was added **3aa** (63.8 mg, 0.2 mmol, 1.0 equiv), hydroxylamine hydrochloride (55.6 mg, 0.8 mmol, 4.0 equiv) and pyridine (130 μ L, 1.6 mmol, 8.0 equiv). Then the schlenk tube was evacuated and filled with argon for three times. After that, pre-dried EtOH (2.0 mL) was added via a syringe under argon atmosphere. Then the reaction mixture was stirred at 80 $^{\circ}$ C in oil bath for 24 h. After completion of the reaction, it was quenched with H₂O (30.0 mL) and extracted with EA (10.0 mL $\times$ 3). The organic layer was washed with saturated brine, dried over Na₂SO₄, and concentrated under reduced pressure. The oxime could be obtained in quantitative yield without the need of further purification.

The DIBALH-mediated reductive ring-expansion reaction of oxime was performed following the modified literature procedures.¹⁶ To an oven-dried 10 mL reaction tube equipped with a tefloncoated magnetic stir bar and a rubber plug was added oxime (66.9 mg, 0.2 mmol, 1.0 equiv). Then the reaction tube was evacuated and filled with argon for three times. After that, DCM (2.0 mL) was added via a syringe under argon atmosphere. The mixture was stirred at -78 $^{\circ}$ C, while DIBAL-H (1.0 mL, 1 M in hexane, 5.0 equiv) was added via a syringe over a period of 10 min. Then the reaction mixture was warmed to room temperature and stirred for 12 h. After completion of the reaction, it was quenched with saturated aqueous Rochelle salt (5.0 mL) at -78 $^{\circ}$ C, and extracted with DCM (5.0 mL $\times$ 3). The combined organic layer was washed with saturated brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 6:1 to 2:1) to obtain the desired product **13** (43.8 mg, 75% yield) with 95% ee and >20:1 dr.

((1S,4aS)-1-phenyl-1,4,5,6-tetrahydro-4aH-pyrido[1,2-a]quinazolin-4a-yl)methanol (13)

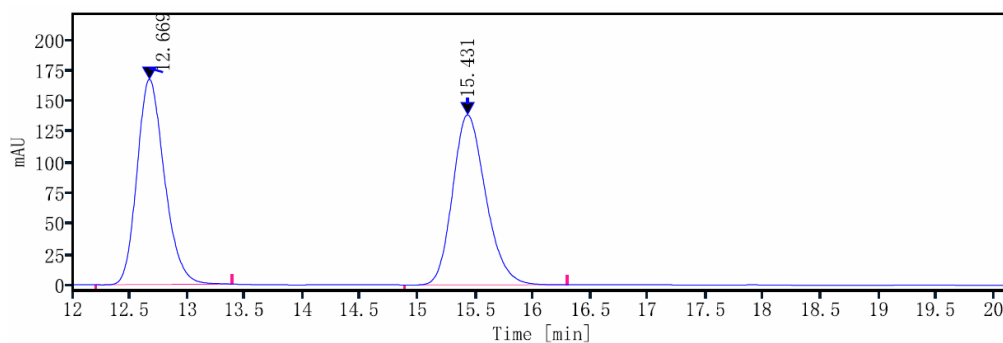
43.8 mg, 75% yield, 95% ee, >20:1 dr. R_f = 0.4 (PE/EA = 2/1); Colorless oil. $[\alpha]_D^{25}$ = -96.3 (c = 0.094, CHCl₃).

¹H NMR (300 MHz, DMSO-*d*₆) δ 11.13 (s, 1H), 7.95 (d, J = 6.7 Hz, 1H), 7.37 – 7.26 (m, 5H), 6.82 – 6.77 (m, 1H), 6.46 (t, J = 7.3 Hz, 1H), 5.76 – 5.74 (m, 1H), 5.65 (d, J = 10.5 Hz, 1H), 5.60 (d, J = 8.1 Hz, 1H), 5.17 (s, 1H), 4.83 (t, J = 6.1 Hz, 1H), 3.80 – 3.41 (m, 2H), 2.56 (s, 1H), 2.48 (s, 2H) ppm.

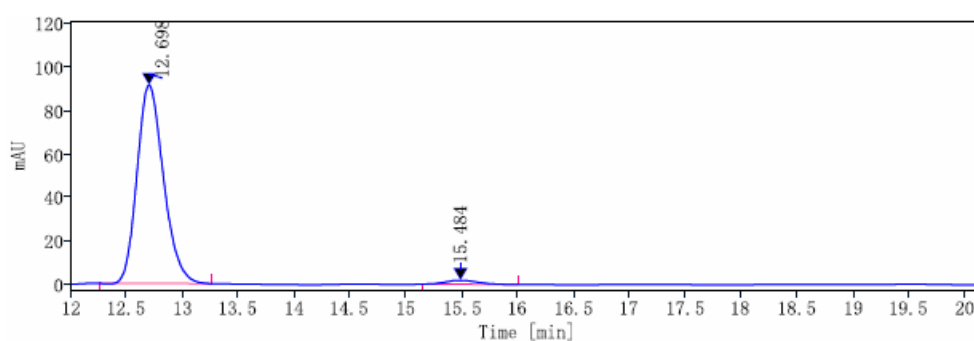
¹³C NMR (75 MHz, DMSO-*d*₆) δ 147.7, 142.2, 131.3, 120.7, 120.3, 118.9, 118.1, 117.5, 117.2, 110.9, 109.8, 105.6, 98.1, 69.2, 56.4, 55.3, 46.9, 19.5 ppm

HRMS (ESI) calcd for [C₁₉H₂₁N₂O+H]⁺ 293.1643, found 293.1651.

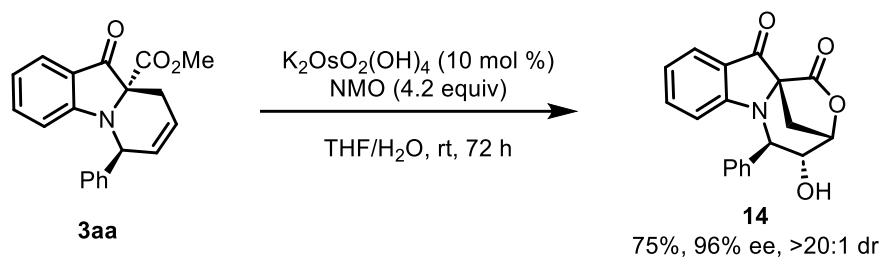
HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 12.7 min (major), t_{R2} = 15.5 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.669	MM m	0.2550	2768.2343	167.2983	50.0419
15.431	MM m	0.3085	2763.6000	138.6838	49.9581



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.698	MM m	0.2538	1502.5076	91.4100	97.6351
15.484	MM m	0.3017	36.3931	1.8808	2.3649



A sealed tube charged with **3aa** (63.8 mg, 0.2 mmol, 1.0 equiv), $\text{K}_2\text{OsO}_2(\text{OH})_2$ (6.2 mg, 0.02 mmol, 10 mol %), and NMO (98.4 mg, 0.84 mmol, 4.2 equiv) was evacuated and backfilled with argon (repeated for 3 times). A mixture of THF (2.0 mL) and H_2O (0.2 mL) was then added, and the reaction mixture was then stirred at room temperature for 72 h. After the reaction was completed, the reaction mixture was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution. The mixture was then extracted with EA, dried over Na_2SO_4 , and concentrated under reduced pressure. The concentrated mixture was purified by flash column chromatography on silica gel

(PE/EA = 6:1 to 2:1) to obtain the desired product **14** (48.2 mg, 75% yield) with 96% ee and >20:1 dr.

(3*S*,4*R*,5*R*,11*aR*)-4-hydroxy-5-phenyl-4,5-dihydro-1*H*,3*H*,11*H*-3,11*a*-methano[1,4]oxazepino[4,3-*a*]indole-1,11-dione (14**)**

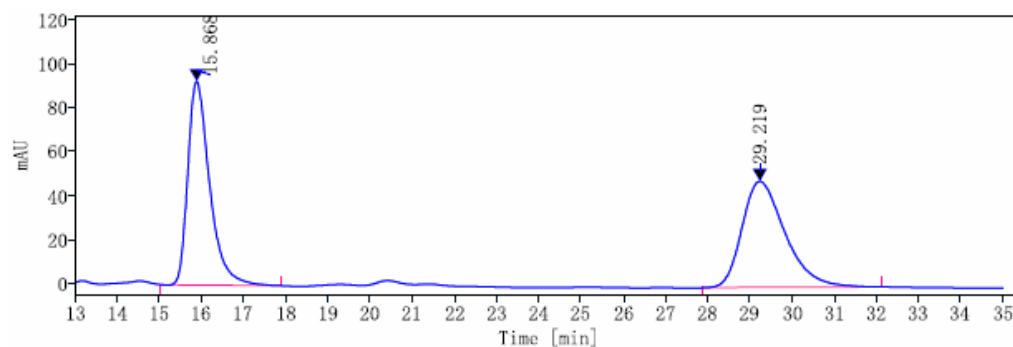
48.2 mg, 75% yield, 96% ee, >20:1 dr. R_f = 0.3 (PE/EA = 2/1); Yellow solid, m.p. 160 °C (Decomposition) $[\alpha]_D^{25}$ = +70.365 (c = 0.126, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ 7.59 – 7.41 (m, 6H), 7.32 (t, J = 7.8 Hz, 1H), 6.85 (t, J = 7.5 Hz, 1H), 6.30 (d, J = 8.2 Hz, 1H), 5.27 (t, J = 7.8 Hz, 1H), 5.09 (dd, J = 9.4, 7.7 Hz, 1H), 4.27 (d, J = 9.6 Hz, 1H), 3.97 (s, 1H), 2.89 (dd, J = 13.5, 8.0 Hz, 1H), 1.84 (dd, J = 13.5, 8.0 Hz, 1H) ppm.

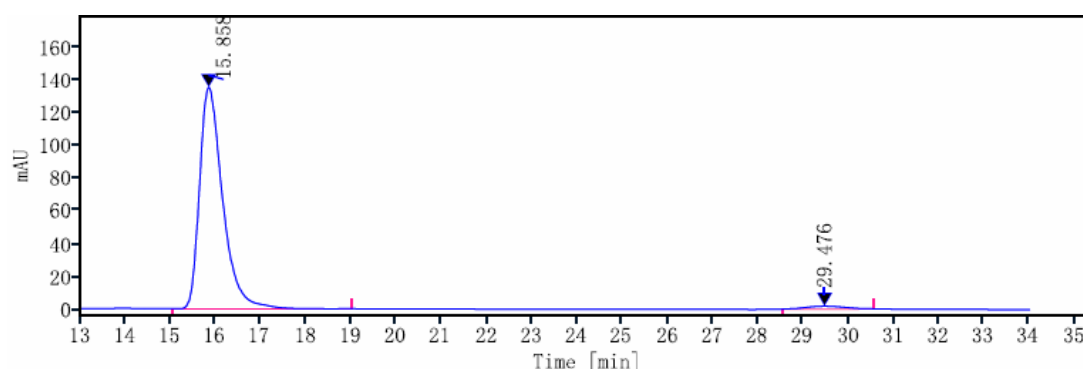
¹³C NMR (75 MHz, CDCl₃) δ 198.6, 159.5, 154.0, 138.9, 138.5, 129.5, 129.1, 127.4, 125.3, 121.4, 119.4, 112.9, 87.4, 79.3, 72.7, 61.2, 33.2 ppm.

HRMS (ESI) calcd for [C₁₉H₁₅NO₄+H]⁺ 360.0633, found 360.0633.

HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 15.9 min (major), t_{R2} = 29.5 min (minor).

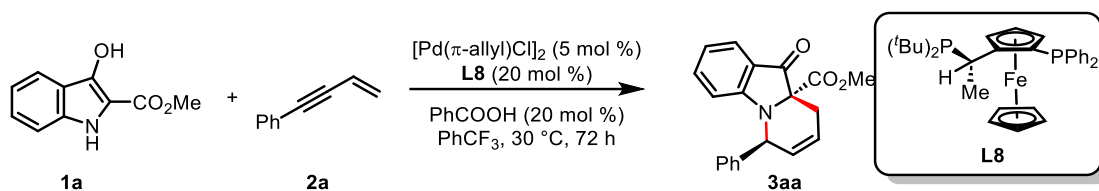


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.868	MM m	0.5470	3313.3832	92.2679	49.3216
29.219	MM m	1.0841	3404.5380	48.0828	50.6784



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.858	MM m	0.5396	4798.9980	135.3776	97.7793
29.476	MM m	0.9386	108.9895	1.7453	2.2207

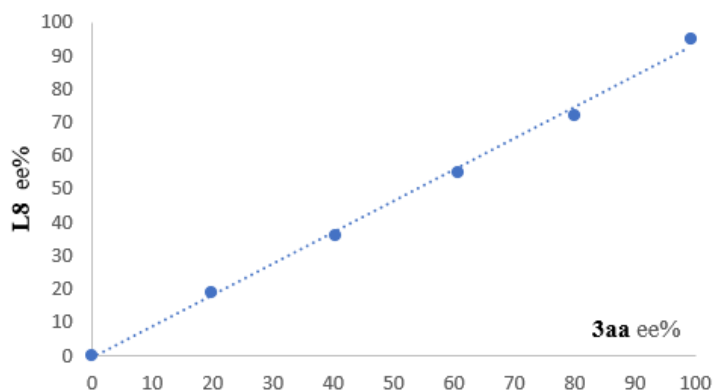
Details of Nonlinear Effect (NLE) Experiments



A sealed tube was charged with **1a** (38.2 mg, 0.2 mmol, 1.0 equiv), $[\text{Pd}(\pi\text{-allyl})\text{Cl}]_2$ (3.7 mg, 0.01 mmol, 5 mol %), **L8** (21.7 mg, 0.04 mmol, 20 mol %, mixtures of two enantiomers determined by weight), PhCOOH (4.9 mg, 0.04 mmol, 20 mol %). The vial was thoroughly flushed with Ar, and **2a** (51.2 mg, 0.4 mmol, 2.0 equiv) as well as PhCF₃ (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 30 °C (oil temperature) for 72 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (80:1 to 30:1) to afford product **3a**. Analysis of the pure samples by chiral-HPLC provided the reported enantiomeric excesses.

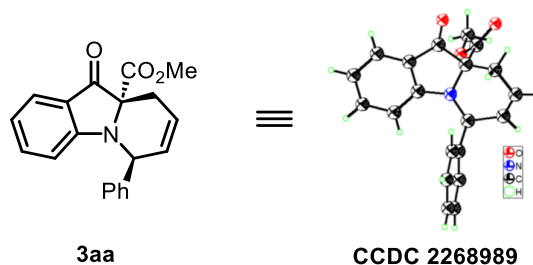
The results were listed as follows:

ee (L8)	ee (3aa)
0.0	0.0
19.8	19.0
40.1	36.0
60.4	55.0
79.7	72.0
>99	95.0



7. Determination of the Absolute Configurations of 3aa, 8 and 9

Experimental: Single Crystal **3aa** was grown by slow evaporation of concentrated solution in the mixed solution of DCM and *n*-hexane in glass vial, which was then sealed by plug with needle on it.

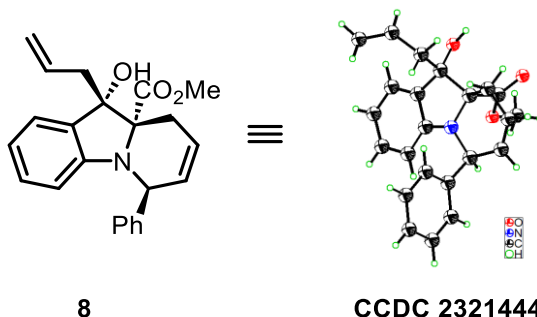


ORTEP plot of the crystal structure of 3aa (50% ellipsoid probability)

X-ray crystallographic data of **3aa**

CCDC number	2268989
Bond precision	C-C = 0.0029 Å
Cell	a=8.4028 (2) b=10.9104 (3) c=17.5842 (4) alpha=90 beta=90 gamma=90
Temperature	100 K
Volume	1612.08 (7)
Space group	P 21 21 21
Sum formula	C ₂₀ H ₁₇ NO ₃
Mr	319.35
Dx, g cm ⁻³	1.316
Z	4
Mu (mm ⁻¹)	0.718
F000	672
h, k, lmax	10,13,21
Tmin, Tmax	0.966, 0.979
Correction method	# Reported T Limits: Tmin=0.507 Tmax=0.754
AbsCorr	MULTI-SCAN
Data completeness	1.73/1.00
Theta(max)	74.470
R(reflections)	0.0337 (3100)
wR2(reflections)	0.0865 (3295)
S	1.035

Experimental: Vapor diffusion crystallization method was used for crystal growth of **8**. The compound **8** was dissolved in DCM to make saturated solution in small via and placed in closed bottle with another solvent as *n*-hexane.

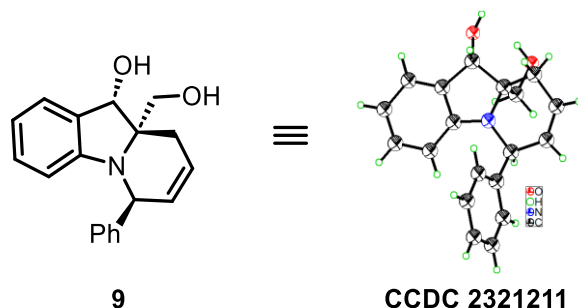


ORTEP plot of the crystal structure of 8 (50% ellipsoid probability)

X-ray crystallographic data of **8**

CCDC number	2321444
Bond precision	C-C = 0.0041 Å
Cell	a=9.4981 (6) b=12.7136 (8) c=15.5146 (10) alpha=90 beta=90 gamma=90
Temperature	150 K
Volume	1873.5 (2)
Space group	P 21 21 21
Sum formula	C ₂₃ H ₂₃ NO ₃
Mr	361.42
Dx, g cm ⁻³	1.281
Z	4
Mu (mm ⁻¹)	0.676
F000	768.0
h, k, lmax	11,15,19
Tmin, Tmax	0.952, 0.973
Correction method	# Reported T Limits: Tmin=0.471 Tmax=0.754
AbsCorr	MULTI-SCAN
Data completeness	1.74/0.99
Theta(max)	74.765
R(reflections)	0.0452 (3415)
wR2(reflections)	0.1090 (3823)
S	1.068

Experimental: Vapor diffusion crystallization method was used for crystal growth of **9**. The compound **9** was dissolved in DCM to make saturated solution in small via and placed in closed bottle with another solvent as *n*-hexane.



ORTEP plot of the crystal structure of 9 (50% ellipsoid probability)

X-ray crystallographic data of **9**

CCDC number	2321211
Bond precision	C-C = 0.0042Å
Cell	a=15.3057 (4) b=6.3268 (1) c=16.4984 (4) alpha=90 beta=91.234(2) gamma=90
Temperature	170 K
Volume	1597.27 (6)
Space group	P 21
Sum formula	2(C ₁₉ H ₁₉ NO ₂)·H ₂ O
Mr	604.72
Dx, g cm ⁻³	1.257
Z	2
Mu (mm ⁻¹)	0.665
F000	644.0
h, k, lmax	19,7,20
Tmin, Tmax	0.938, 0.967
Correction method	# Reported T Limits: Tmin=0.545 Tmax=0.754
AbsCorr	MULTI-SCAN
Data completeness	1.80/0.99
Theta(max)	74.691
R(reflections)	0.0411 (5877)
wR2(reflections)	0.1046 (6435)
S	1.028

8. DFT Calculations

All computations were conducted using Density Functional Theory (DFT) with the Gaussian 09 software package.¹⁷ Geometry optimizations for all intermediates and transition states were carried out at the B3LYP level¹⁸ of theory, incorporating Grimme's D3 dispersion¹⁹ correction with Becke–Johnson damping²⁰. All calculations were performed in the gas phase using a mixed basis set: the SDD basis set²¹ with associated effective core potentials was employed for Pd, while the 6-31G(d) basis set²² was used for other atoms. Vibrational frequency calculations were carried out at the same level to confirm the nature of each stationary point (either a local minimum or a transition state) and to obtain thermal corrections for free energy calculations. To improve energetic accuracy, solvation single-point energies were refined using the B3LYP-D3BJ functional with a larger basis set, 6-311+G(d,p)²³-SDD (for Pd, in trifluorotoluene (SMD model²⁴, $\epsilon = 9.2$). The optimized structures were visualized with CYLview.²⁵

The formation of an η^1 -butadienyl–Pd intermediate **B-1** has two possible pathways (Figure S3). In the first pathway, the Pd(0) intermediate **Pd⁰-L** undergoes oxidative addition with benzoic acid via transition state **TS-A**, which has an energy barrier of 0.8 kcal/mol, yielding Pd-H species **A**. Subsequently, intermediate **A** participates in regioselective migratory insertion with the alkyne moiety of substrate **2a**. The insertion via transition state **TS-B-1** exhibits an energy barrier of 17.8 kcal/mol, which is 8.3 kcal/mol lower than that via **TS-B-1-isomer**. Thus, the formation of the η^1 -butadienyl–Pd intermediate **B-1** is kinetically favored.

Alternatively, the Pd(0) intermediate **Pd⁰-L** may first coordinate with the alkyne moiety of **2a** to generate a more stable intermediate **Pd⁰-L-2a**, followed by ligand-to-ligand hydrogen transfer (LLHT)²⁶ to afford intermediate **B-1**.

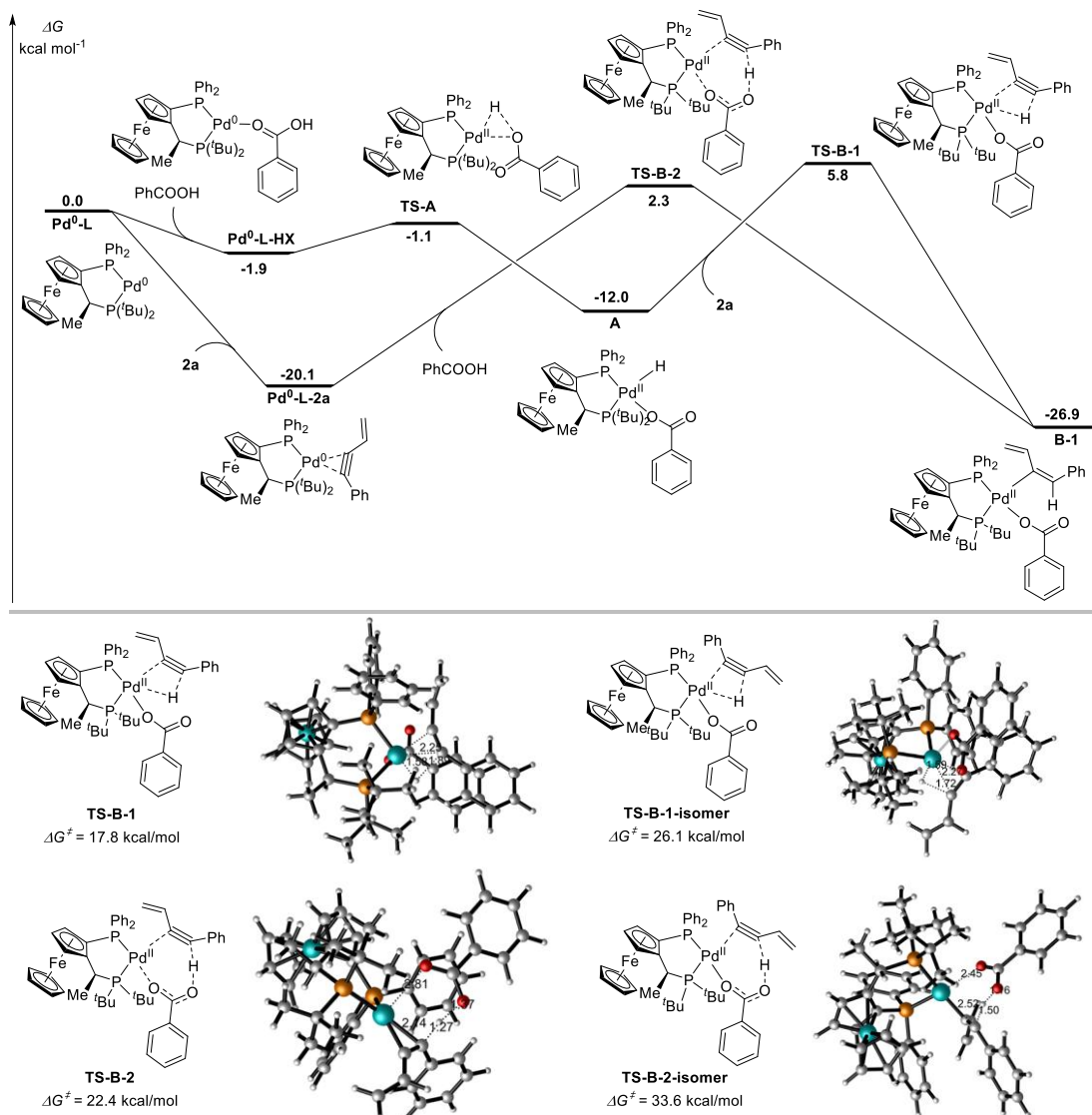


Figure S3. The generation of η^1 -butadienyl-Pd intermediate **B-1.**

Intermediate **B-1** undergoes isomerization via transition state **TS-C-1** with an energy barrier of 11.0 kcal/mol to form the intermediate **B-2** (Figure S4). Owing to the marginally higher energy of **B-2** relative to **B-1**, this transformation is reversible. Alternatively, intermediate **B-1** may undergo ligand exchange with substrate **1a** to form intermediate **C-1**. Subsequent isomerization of **C-1** proceeds via transition state **TS-C-2** with a slightly elevated energy barrier of 13.7 kcal/mol , compared to the former pathway. Under the experimental reaction temperature, both mechanistic routes are thermodynamically accessible. Consequently, the four intermediates—**B-1**, **B-2**, **C-1**, and **C-2**—are likely to coexist within the reaction system, establishing a dynamic kinetic equilibrium. Further transformation of intermediates **C-1** and **C-2** ultimately leads to different types of products.

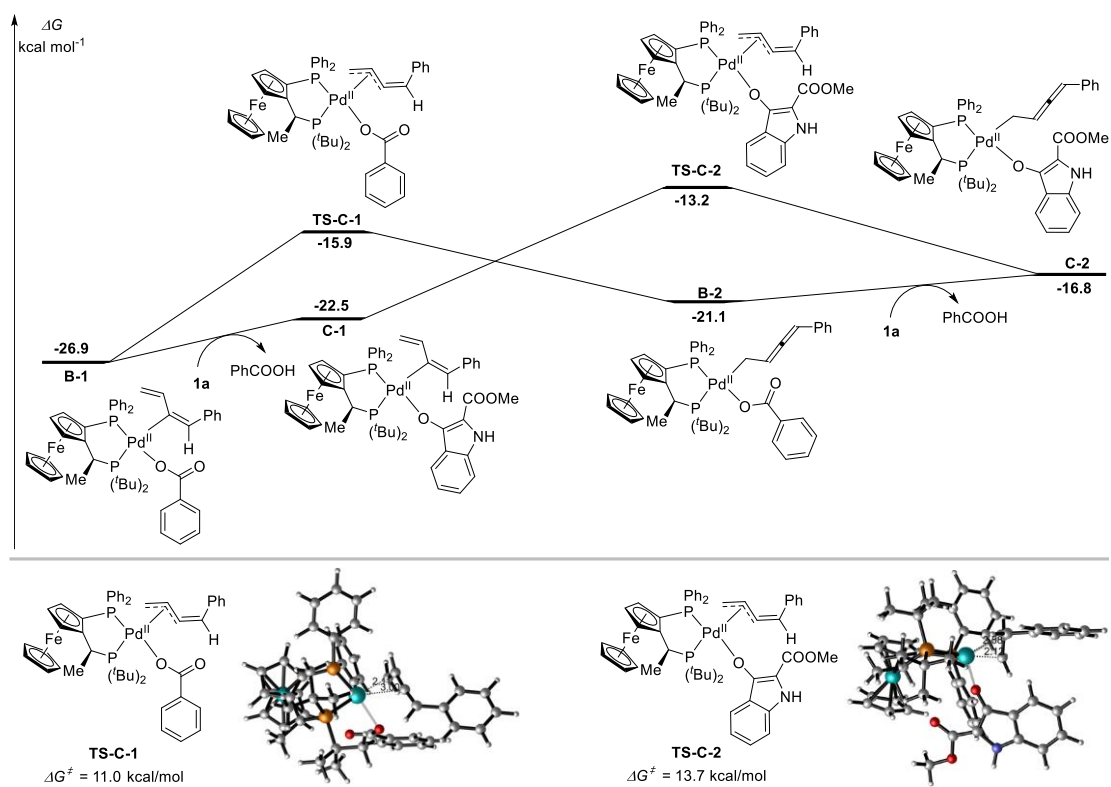


Figure S4. The isomerization of η^1 -butadienyl-Pd intermediate B-1.

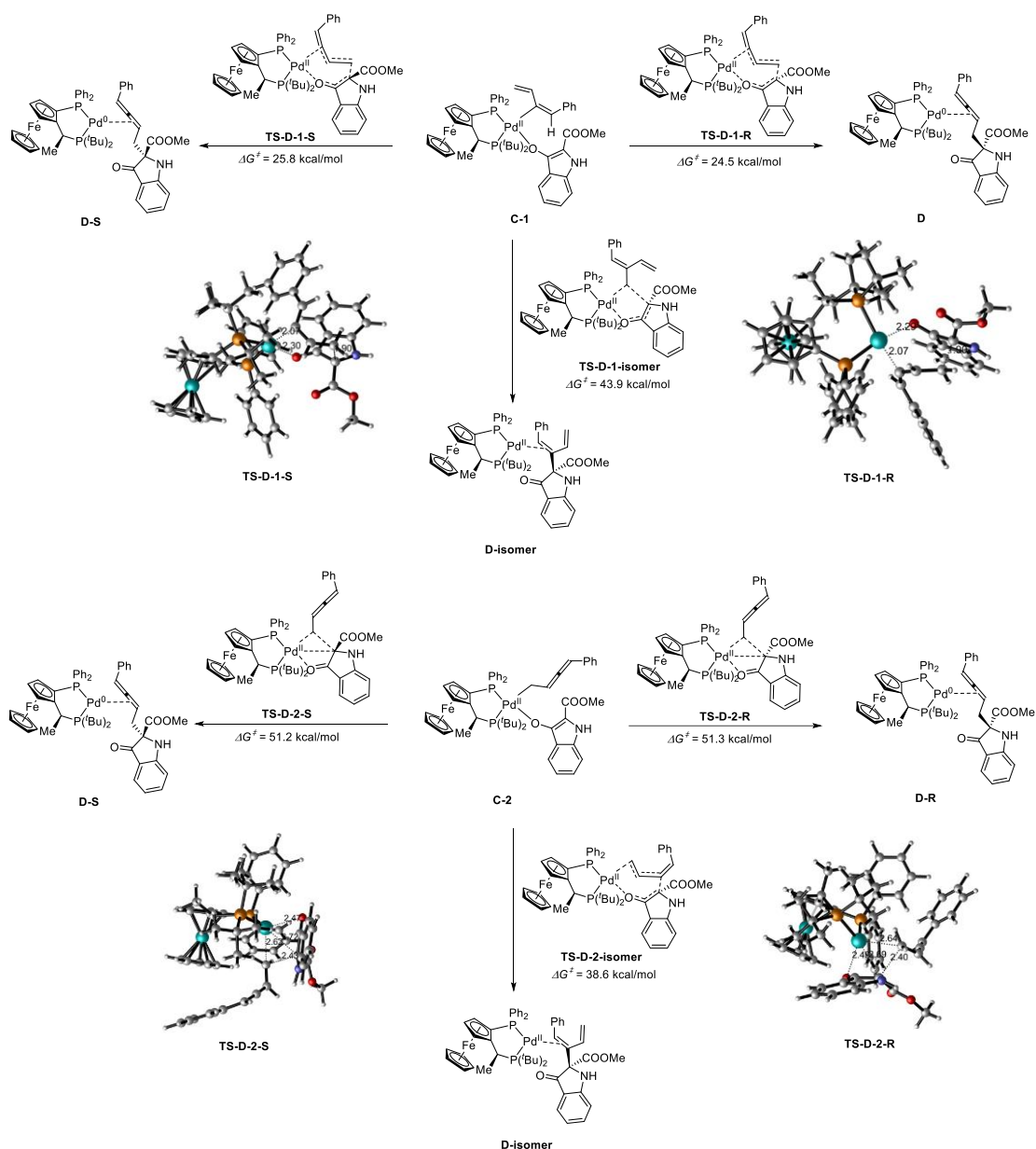


Figure S5. The generation of allene intermediate **4** ($\Delta G^\ddagger$ is calculated relative to **B-1**).

The direct electrophilic attack by the proton of benzoic acid on the palladium-activated allene intermediate **D** governs the stereoselectivity of the product (Figure S6). The pathway proceeding through transition state **TS-E-Z-R** to form intermediate **E** exhibits an energy barrier of 12.8 kcal/mol, representing the kinetically most favorable route. Subsequently, the carboxylate anion in intermediate **E** can selectively abstract a hydrogen atom from either the indole nitrogen atom or the β -carbon atom of the ester group. The energy barrier for transition state **TS-F-1** is 9.9 kcal/mol, leading to the formation of the zwitterionic intermediate **F-1** after the step. The transition state **TS-F-1**, associated with a barrier of 9.9 kcal/mol, leads to the formation of the zwitterionic intermediate **F-1**. Further investigation into the transformation of **F-1** to the polycyclic product revealed two distinct pathways (Figure S7). The outer-sphere nucleophilic

attack via **TS-G-outer** presents an energy barrier of 11.0 kcal/mol, significantly lower than that of the inner-sphere reductive elimination pathway through **TS-G-inner**, indicating a strong kinetic preference for the outer-sphere mechanism.

Alternatively, proton abstraction from the β -carbon of the ester by the carboxylate in **E** may reversibly yield a conjugated diene byproduct (Figure S8). The transition state **TS-F-2-E**, leading to the *E*-configured diene **5**, has an energy barrier of 16.8 kcal/mol, which is 4.9 kcal/mol lower than that for the *Z*-configured pathway. The calculational results suggest the formation of the *E*-isomer is kinetically favorable.

Overall, the energy barrier for transition state **TS-F-2-E** is 2.1 kcal/mol lower than that required for formation of the target product **4**, indicating that the conjugated diene byproduct is kinetically accessible under lower-reaction temperature. At elevated temperatures, however, the thermodynamic product **4** becomes favored.

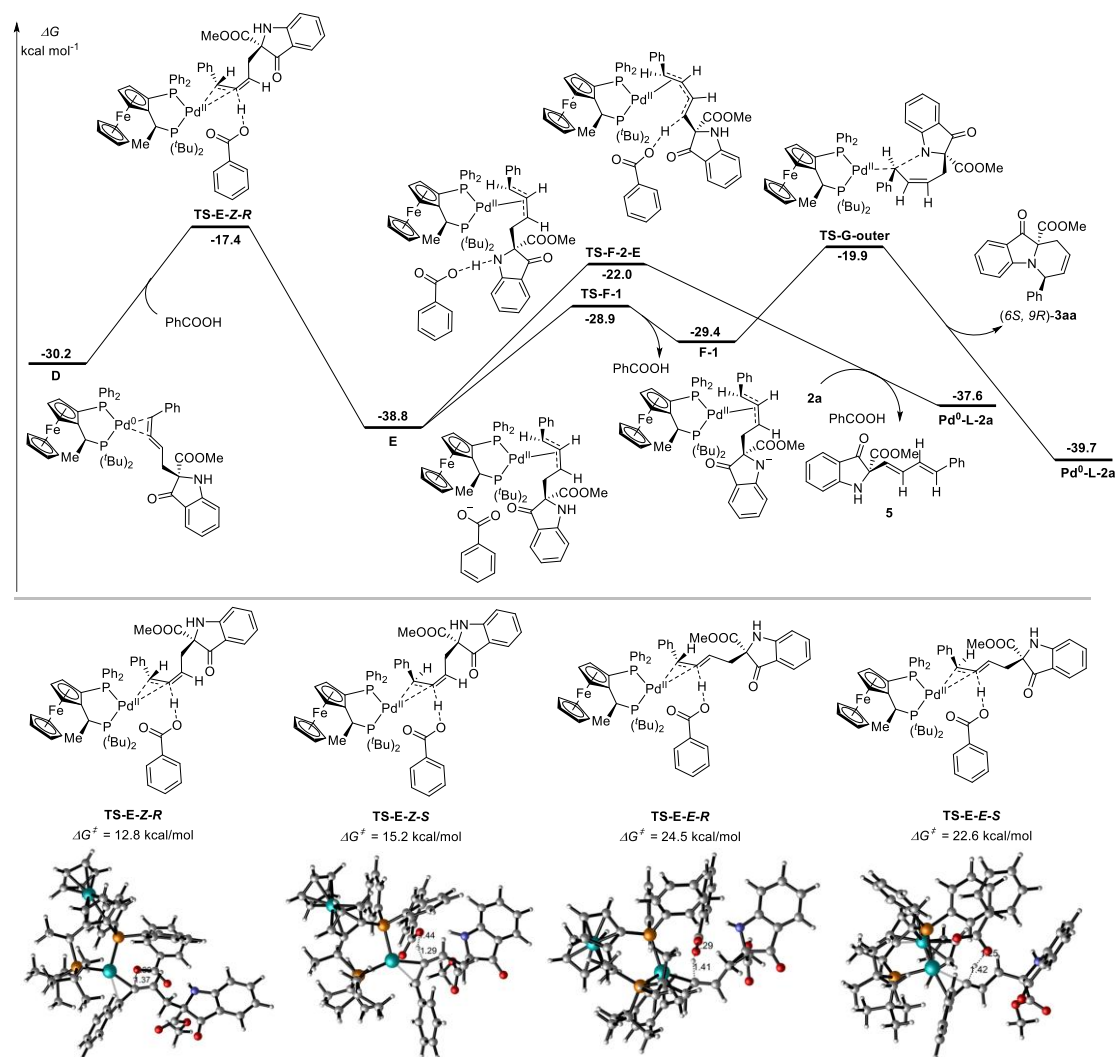


Figure S6. Calculated energy profile for the generation of product (*R*)-4.

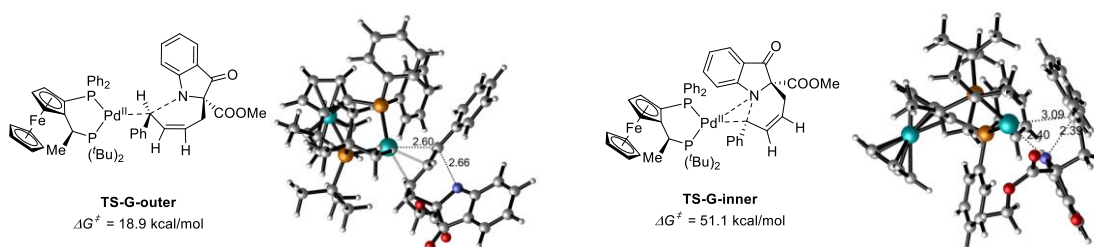


Figure S7. Competitive transition states for the generation of polycyclic product.

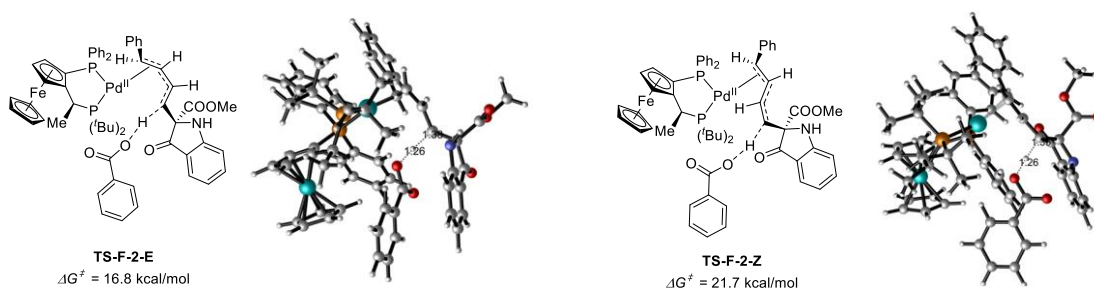


Figure S8. Competitive transition states for the formation of *E/Z* byproducts.

Table S1. The calculated energies of stationary points (in Hartree/Particle).

Structure	ZPE	H _{corr}	G _{corr}	E _{ele}	H _{sol}	G _{sol}
1a	0.177940	0.190872	0.139665	-667.167862	-666.976990	-667.028197
2a	0.143808	0.153645	0.108695	-385.940119	-385.786474	-385.831424
Pd⁰-L	0.641768	0.679799	0.574403	-2178.690261	-2178.010462	-2178.115858
PhCOOH	0.116028	0.124064	0.084026	-420.981327	-420.857263	-420.897301
Pd⁰-L-HX	0.758119	0.804863	0.676150	-2599.692312	-2598.887449	-2599.016162
TS-A	0.753295	0.799687	0.673516	-2599.688401	-2598.888714	-2599.014885
A	0.757162	0.803378	0.679029	-2599.711361	-2598.907983	-2599.032332
TS-B-1	0.901711	0.957447	0.815479	-2985.650884	-2984.693437	-2984.835405
TS-B-1-isomer	0.900573	0.956817	0.810199	-2985.632363	-2984.675546	-2984.822164
Pd⁰-L-2a	0.787716	0.835893	0.706464	-2564.686082	-2563.850189	-2563.979618
TS-B-2	0.900944	0.956295	0.813409	-2985.654579	-2984.698284	-2984.841170
TS-B-2-isomer	0.900925	0.956737	0.811325	-2985.634764	-2984.678027	-2984.823439
B-1	0.907536	0.962969	0.819023	-2985.706453	-2984.743484	-2984.887430
B-1-isomer	0.906833	0.962910	0.816526	-2985.674515	-2984.711605	-2984.857989
B-2	0.907687	0.962950	0.819776	-2985.697983	-2984.735033	-2984.878207
TS-C-1	0.906780	0.961890	0.817615	-2985.687478	-2984.725588	-2984.869863
TS-C-2	0.969069	1.028678	0.877924	-3231.874474	-3230.845796	-3230.996550
C-1	0.969152	1.029427	0.877146	-3231.888467	-3230.859040	-3231.011321
C-2	0.968276	1.029027	0.873273	-3231.875497	-3230.846470	-3231.002224
TS-D-1-R	0.968173	1.027483	0.875971	-3231.855235	-3230.827752	-3230.979264

TS-D-1-S	0.968889	1.027944	0.877583	-3231.854719	-3230.826775	-3230.977136
TS-D-1-isomer	0.967839	1.027766	0.876665	-3231.825099	-3230.797333	-3230.948434
TS-D-2-R	0.967030	1.027194	0.876286	-3231.796904	-3230.769710	-3230.920618
TS-D-2-S	0.965927	1.026464	0.872017	-3231.792795	-3230.766331	-3230.920778
TS-D-2-isomer	0.967749	1.027071	0.875795	-3231.832598	-3230.805527	-3230.956803
D	0.969711	1.029938	0.874999	-3231.898619	-3230.868681	-3231.023620
D-S	0.969851	1.029936	0.876367	-3231.897880	-3230.867944	-3231.021513
TS-E-E-R	1.083362	1.151141	0.982264	-3652.864135	-3651.712994	-3651.881871
TS-E-E-S	1.083241	1.151475	0.979692	-3652.864584	-3651.713109	-3651.884892
TS-E-Z-R	1.082998	1.150929	0.978311	-3652.878774	-3651.727845	-3651.900463
TS-E-Z-S	1.082676	1.150513	0.978752	-3652.875444	-3651.724931	-3651.896692
E	1.091776	1.159563	0.989434	-3652.924064	-3651.764501	-3651.934630
E-Z-S	1.091312	1.159143	0.990320	-3652.909942	-3651.750799	-3651.919622
TS-F-1	1.087683	1.154402	0.988730	-3652.907561	-3651.753159	-3651.918831
F-1	0.971083	1.030578	0.877898	-3231.900255	-3230.869677	-3231.022357
TS-G-outer	0.969976	1.029067	0.877590	-3231.884841	-3230.855774	-3231.007251
TS-G-inner	0.970781	1.029343	0.882721	-3231.838639	-3230.809296	-3230.955918
(6<i>S</i>, 9<i>R</i>)-3aa	0.328360	0.348975	0.279461	-1053.170047	-1052.821072	-1052.890586
(6<i>R</i>, 9<i>R</i>)-3aa	0.328281	0.348934	0.279083	-1053.168933	-1052.819999	-1052.889850
TS-F-2-E	1.085754	1.152800	0.985459	-3652.893320	-3651.740520	-3651.907861
(<i>E</i>)-5	0.325591	0.347680	0.272126	-1053.159316	-1052.811636	-1052.887190
TS-F-2-Z	1.084753	1.152144	0.983193	-3652.883296	-3651.731152	-3651.900103
(<i>Z</i>)-5	0.325967	0.347904	0.272484	-1053.155081	-1052.807177	-1052.882597

Note: ZPE = zero-point vibrational energy; Hcorr = thermal correction to enthalpy; Gcorr = thermal correction to Gibbs free energy; Eele = the electronic energies in solvent; Hsol = ethalpies in solvent; Gsol = Gibbs free energies in solvent.

Cartesian coordinates (unit: angstrom)

1a				H	4.802054	0.776481	-0.000901
C	1.419795	0.561893	0.000084	H	2.785667	2.238995	-0.000387
C	1.297484	-0.861335	0.000362	H	-0.435237	-2.106834	-0.001606
C	2.431509	-1.685292	0.000238	O	-0.257341	2.376307	0.000188
C	3.674365	-1.069184	-0.000189	H	-1.242706	2.389601	0.000252
C	3.808774	0.338238	-0.000520	N	-0.035267	-1.182756	0.000929
C	2.692350	1.157614	-0.000245	C	-2.213118	0.123710	0.000036
C	0.087835	1.079309	0.000059	O	-2.785815	1.216125	0.000139
C	-0.785228	-0.002581	0.000103	O	-2.867529	-1.059734	-0.000368
H	2.338976	-2.767473	0.000464	C	-4.301202	-0.967858	-0.000369
H	4.568881	-1.685564	-0.000286	H	-4.658689	-1.997676	-0.001097

H	-4.651009	-0.439109	0.889855	H	-1.313161	-1.826696	0.421258
H	-4.650966	-0.437800	-0.889820	C	-2.465111	-2.334303	-1.309973
2a				H	-1.876765	-3.239795	-1.495822
C	2.474666	1.307736	-0.000309	H	-3.372076	-2.629335	-0.791474
C	1.088634	1.187030	-0.000566	H	-2.759588	-1.925674	-2.279769
C	0.485417	-0.085979	-0.000138	P	-2.640402	0.103755	0.297357
C	1.307509	-1.229764	0.000421	P	1.067139	1.037043	0.482613
C	2.692743	-1.099389	0.000660	C	-3.626562	0.936622	-1.105103
C	3.281218	0.167334	0.000241	C	-3.811322	-0.757607	1.559205
H	2.928182	2.294849	-0.000698	C	-4.698162	-1.940796	1.128633
H	0.456576	2.069203	-0.001120	C	-4.721753	0.350883	2.123376
H	0.844844	-2.211457	0.000783	C	-2.895309	-1.246097	2.700629
H	3.316229	-1.988957	0.001150	C	-2.645349	1.124384	-2.278151
H	4.362974	0.265314	0.000302	C	-4.880494	0.193332	-1.588823
C	-0.931516	-0.213432	-0.000391	C	-4.027876	2.343317	-0.616115
C	-2.144603	-0.302805	-0.000599	H	-4.115832	-2.854036	0.981037
C	-3.554684	-0.452849	-0.001045	H	-5.416398	-2.153541	1.931894
H	-3.929349	-1.476403	-0.003616	H	-5.272202	-1.743323	0.221516
C	-4.429568	0.566286	0.001432	H	-5.487208	0.655646	1.403848
H	-5.499115	0.382029	0.000907	H	-5.239948	-0.024618	3.015318
H	-4.099235	1.600413	0.004050	H	-4.145133	1.236367	2.410749
Pd⁰-L				H	-2.281520	-0.429837	3.096587
C	0.788437	-3.852701	-0.102127	H	-3.511489	-1.651318	3.514361
C	1.552653	-4.187382	-1.261230	H	-2.218878	-2.042410	2.371364
H	1.210850	-4.779574	-2.100000	H	-4.662252	-0.823623	-1.923303
C	2.827900	-3.556597	-1.142144	H	-5.646019	0.140084	-0.809299
H	3.620735	-3.586456	-1.878072	H	-5.319425	0.735295	-2.437454
C	2.851949	-2.829597	0.084563	H	-4.513214	2.887562	-1.437477
H	3.661052	-2.213014	0.447115	H	-4.728555	2.310154	0.221485
C	1.589640	-3.013406	0.727040	H	-3.147156	2.909159	-0.296107
H	1.283319	-2.553657	1.655599	H	-1.719273	1.603999	-1.945900
C	-0.366837	-0.947324	-1.258820	H	-2.380898	0.181480	-2.761553
C	-0.063446	-1.531757	-2.535890	H	-3.109131	1.770619	-3.034732
C	1.241108	-1.144492	-2.948121	C	2.635850	0.443126	1.255655
H	1.748368	-1.475881	-3.844718	C	2.537475	-0.216186	2.487923
C	1.773959	-0.305840	-1.939966	C	3.902030	0.602080	0.673613
H	2.751693	0.153013	-1.943190	C	3.671975	-0.740027	3.109748
C	0.801708	-0.154175	-0.892287	H	1.560068	-0.312138	2.954734
Fe	1.317203	-2.135007	-1.124920	C	5.039377	0.092154	1.299741
H	-0.235381	-4.145610	0.090274	H	4.001357	1.139435	-0.264065
H	-0.693798	-2.216652	-3.081297	C	4.926020	-0.588456	2.515400
C	-1.644062	-1.321791	-0.492251	H	3.578353	-1.256626	4.061005
				H	6.014697	0.224649	0.838986
				H	5.811852	-0.988211	3.000859

C	1.632059	2.527704	-0.442888	C	3.527172	-1.053688	-0.024326
C	2.426702	3.484413	0.209673	H	3.626808	-2.099878	0.223065
C	1.162806	2.813288	-1.733855	C	2.309307	-0.295151	0.094209
C	2.762995	4.680831	-0.420688	Fe	2.922155	-0.381634	-1.862963
H	2.787193	3.287423	1.215370	H	1.484532	1.185325	-3.720439
C	1.492891	4.015842	-2.360543	H	4.480235	1.884611	-1.254914
H	0.543276	2.090770	-2.254023	C	1.743226	2.322794	-0.633278
C	2.296576	4.952509	-1.709489	H	1.460493	2.288783	-1.689365
H	3.387831	5.403873	0.096783	C	2.630687	3.576267	-0.461197
H	1.123576	4.217144	-3.362721	H	3.363309	3.649559	-1.271913
H	2.556315	5.886486	-2.199735	H	2.043580	4.491130	-0.483981
Pd	-0.989794	1.284464	1.333011	H	3.184737	3.550995	0.480102
PhCOOH				P	0.014732	2.423453	0.132440
C	0.511634	1.222731	-0.000367	P	0.772449	-1.022832	0.777830
C	-0.219946	0.028308	-0.000327	C	0.167359	3.263860	1.840684
C	0.448339	-1.202980	-0.000025	C	-0.913476	3.550375	-1.107081
C	1.841008	-1.234341	0.000211	C	-0.223879	4.834555	-1.594449
C	2.568195	-0.042098	0.000218	C	-2.274642	3.903084	-0.478682
C	1.902623	1.186416	-0.000134	C	-1.194199	2.655684	-2.333935
H	-0.029386	2.162817	-0.000659	C	1.317542	2.563102	2.586447
H	-0.124457	-2.123158	0.000388	C	0.389246	4.784125	1.860931
H	2.359842	-2.188447	0.000533	C	-1.131611	2.937677	2.610299
H	3.654279	-0.070150	0.000336	H	0.683409	4.618749	-2.166548
H	2.468973	2.113055	-0.000240	H	-0.905188	5.375752	-2.265199
C	-1.701085	0.121866	0.000002	H	0.036176	5.512465	-0.777819
O	-2.311014	-1.092352	-0.000376	H	-2.178874	4.628140	0.334337
H	-3.267228	-0.903068	0.000105	H	-2.918882	4.354310	-1.244968
O	-2.334815	1.158545	0.000635	H	-2.776755	3.008616	-0.097021
Pd ⁰ -L-HX				H	-1.746476	1.755946	-2.048253
C	1.940309	0.214032	-3.582910	H	-1.791840	3.217683	-3.064032
C	3.292822	-0.126356	-3.885967	H	-0.274142	2.341835	-2.838254
H	4.042297	0.541949	-4.289280	H	1.324576	5.077971	1.380483
C	3.493827	-1.490638	-3.516938	H	-0.429607	5.326559	1.380721
H	4.425693	-2.036261	-3.586480	H	0.435816	5.125313	2.904151
C	2.268832	-1.991009	-2.983322	H	-1.037251	3.293608	3.645204
H	2.109152	-2.977731	-2.573328	H	-2.009828	3.416184	2.170786
C	1.306859	-0.934619	-3.022373	H	-1.310824	1.857546	2.629581
H	0.298296	-0.970841	-2.633546	H	2.291967	2.728326	2.121420
C	2.581836	1.050964	-0.401835	H	1.369153	2.951285	3.612225
C	3.962361	1.052639	-0.801516	H	1.150649	1.487501	2.651602
C	4.537204	-0.226736	-0.573530	C	0.967901	-2.819249	0.361937
H	5.547228	-0.524883	-0.822692	C	0.196376	-3.332542	-0.688793
				C	1.802663	-3.694153	1.072583
				C	0.286988	-4.675556	-1.054546

H	-0.483236	-2.668207	-1.215306	H	0.287003	-0.959458	-2.582633
C	1.889705	-5.040396	0.714860	C	2.508448	1.256898	-0.450705
H	2.376806	-3.324944	1.916983	C	3.860309	1.369186	-0.923523
C	1.139312	-5.532910	-0.355202	C	4.549881	0.143929	-0.717371
H	-0.315211	-5.053794	-1.876199	H	5.566373	-0.073684	-1.017718
H	2.539431	-5.706546	1.276371	C	3.641305	-0.758814	-0.113002
H	1.205640	-6.581700	-0.630925	H	3.839874	-1.791840	0.129314
C	1.126196	-1.058895	2.589992	C	2.372527	-0.100665	0.064168
C	0.043118	-1.293346	3.451407	Fe	2.889811	-0.154421	-1.920969
C	2.395152	-0.842908	3.143554	H	1.257593	1.271159	-3.734765
C	0.225673	-1.322026	4.832673	H	4.280646	2.238270	-1.407885
H	-0.946741	-1.437286	3.026134	C	1.563072	2.458271	-0.616314
C	2.576267	-0.861768	4.528261	H	1.292327	2.466157	-1.676543
H	3.240075	-0.643701	2.493154	C	2.332258	3.774224	-0.361486
C	1.494267	-1.102822	5.375554	H	3.086851	3.938116	-1.137601
H	-0.623206	-1.504425	5.486103	H	1.669023	4.636633	-0.378529
H	3.564823	-0.685270	4.943924	H	2.850986	3.759428	0.599447
H	1.636473	-1.114300	6.452659	P	-0.164203	2.342555	0.145693
Pd	-0.936424	0.275185	0.266536	P	0.929086	-0.954313	0.787123
C	-5.990369	0.142604	-0.804950	C	-0.135892	3.163220	1.868896
C	-5.194865	-0.955752	-0.451417	C	-1.214824	3.366556	-1.078130
C	-5.762178	-2.234889	-0.368492	C	-0.646477	4.716431	-1.543972
C	-7.117305	-2.410203	-0.639297	C	-2.608124	3.580435	-0.457185
C	-7.908244	-1.313906	-0.991536	C	-1.398422	2.460405	-2.314679
C	-7.343975	-0.037956	-1.073828	C	1.071799	2.586834	2.629172
H	-5.530776	1.123229	-0.861802	C	-0.089205	4.698453	1.917495
H	-5.137291	-3.076709	-0.093237	C	-1.403832	2.675756	2.605401
H	-7.557176	-3.401099	-0.575579	H	0.287724	4.598477	-2.101564
H	-8.964938	-1.453714	-1.201860	H	-1.366864	5.193241	-2.222302
H	-7.960123	0.813455	-1.347475	H	-0.469157	5.408647	-0.717347
C	-3.757567	-0.732512	-0.171129	H	-2.588153	4.300468	0.365177
O	-3.072268	-1.814813	0.165731	H	-3.280692	3.983180	-1.226092
H	-2.103035	-1.487121	0.318480	H	-3.032607	2.638899	-0.097945
O	-3.231177	0.385506	-0.249721	H	-1.872480	1.513050	-2.044695
TS-A				H	-2.035544	2.973332	-3.047133
C	1.793384	0.341216	-3.603611	H	-0.447708	2.238114	-2.809694
C	3.154853	0.104071	-3.959456	H	0.815643	5.105475	1.461870
H	3.832715	0.824136	-4.398720	H	-0.954776	5.154151	1.429964
C	3.477336	-1.235564	-3.586831	H	-0.100993	5.021821	2.967161
H	4.445839	-1.707154	-3.689006	H	-1.370138	3.023618	3.646593
C	2.318002	-1.823553	-2.998758	H	-2.323290	3.055493	2.155093
H	2.251931	-2.814655	-2.574217	H	-1.458795	1.582055	2.608233
C	1.274838	-0.846987	-3.008461	H	1.028812	1.499013	2.675045
				H	2.030231	2.871335	2.190224

H	1.056388	2.959641	3.661600	C	-2.294006	-3.184326	2.891751
C	1.221562	-2.726125	0.356008	H	-3.260736	-3.656094	3.010839
C	0.421756	-3.304187	-0.637456	C	-1.498829	-3.193084	1.708619
C	2.177850	-3.521202	1.004182	H	-1.755147	-3.679603	0.779762
C	0.603337	-4.635690	-1.011934	C	-0.329960	-2.405207	1.947287
H	-0.353286	-2.704322	-1.104114	H	0.465227	-2.196199	1.240589
C	2.358279	-4.854199	0.633843	C	-1.865496	0.779656	1.810009
H	2.771912	-3.103597	1.811364	C	-2.857402	0.537015	2.817805
C	1.577910	-5.411945	-0.381682	C	-3.881543	-0.296891	2.291183
H	-0.024466	-5.068252	-1.785896	H	-4.734490	-0.680024	2.835461
H	3.101804	-5.459895	1.144845	C	-3.541547	-0.599482	0.949479
H	1.716147	-6.451322	-0.666091	H	-4.088344	-1.252044	0.286031
C	1.304984	-0.964017	2.590212	C	-2.301010	0.059838	0.628070
C	0.253980	-1.272791	3.467444	Fe	-2.045401	-1.251757	2.192784
C	2.567466	-0.663505	3.117950	H	0.309261	-1.273513	3.770824
C	0.464461	-1.287259	4.845068	H	-2.808531	0.891761	3.837954
H	-0.730414	-1.484785	3.058619	C	-0.656610	1.653001	2.143255
C	2.774400	-0.670376	4.498801	H	-0.113579	1.094391	2.911271
H	3.383702	-0.405786	2.451349	C	-1.122408	2.960192	2.820712
C	1.725398	-0.982868	5.364278	H	-1.691409	2.731824	3.726448
H	-0.357698	-1.526098	5.514023	H	-0.275622	3.576671	3.118245
H	3.755805	-0.427695	4.897371	H	-1.770188	3.551494	2.171059
H	1.887280	-0.984008	6.438604	P	0.700286	1.836720	0.838071
Pd	-0.963419	0.065942	0.280246	P	-1.504561	-0.107187	-0.986771
C	-5.890022	-0.060373	-0.740962	C	0.519775	3.521096	-0.049849
C	-5.090413	-1.162489	-0.411124	C	2.270963	1.809668	1.923184
C	-5.657820	-2.442022	-0.349865	C	2.218883	2.680307	3.191960
C	-7.013869	-2.616024	-0.617879	C	3.489333	2.227892	1.078999
C	-7.808490	-1.515278	-0.947225	C	2.457458	0.342819	2.362800
C	-7.245327	-0.237897	-1.008148	C	-0.925503	3.618252	-0.574733
H	-5.432754	0.921966	-0.782180	C	0.863248	4.774447	0.771685
H	-5.025077	-3.283698	-0.091901	C	1.439176	3.486236	-1.292301
H	-7.451846	-3.608952	-0.570067	H	1.437140	2.359117	3.887080
H	-8.866006	-1.652601	-1.156031	H	3.176090	2.578915	3.719325
H	-7.863774	0.617832	-1.263826	H	2.075428	3.741268	2.976262
C	-3.642343	-0.963768	-0.128095	H	3.483315	3.298862	0.857708
O	-2.945125	-2.005013	0.169920	H	4.399509	2.021554	1.656474
H	-1.781273	-1.485215	0.342586	H	3.542938	1.664394	0.145565
O	-3.148111	0.195961	-0.191513	H	2.442413	-0.360878	1.529290
				H	3.421771	0.247019	2.877424
A				H	1.683926	0.039499	3.073717
C	-0.411056	-1.915323	3.284822	H	0.214117	4.910895	1.637696
C	-1.623022	-2.390340	3.868356	H	1.900591	4.767970	1.113486
H	-1.986773	-2.157483	4.860640	H	0.740466	5.655962	0.128946

H	1.260132	4.393278	-1.884500	TS-B-1		
H	2.498372	3.455592	-1.034753	C	2.999441	0.432406 -3.377418
H	1.223058	2.617263	-1.922161	C	4.408544	0.204230 -3.405480
H	-1.117108	2.858838	-1.331872	H	5.166722	0.921356 -3.692654
H	-1.684245	3.515272	0.203456	C	4.640902	-1.124183 -2.938994
H	-1.067430	4.597652	-1.049125	H	5.608712	-1.589777 -2.804678
C	-1.938329	-1.801980	-1.546446	C	3.377847	-1.705719 -2.621053
C	-0.955949	-2.801604	-1.522148	H	3.220072	-2.689034 -2.202631
C	-3.226712	-2.109828	-2.004395	C	2.356143	-0.743866 -2.891247
C	-1.272502	-4.100111	-1.922838	H	1.287709	-0.864627 -2.727299
H	0.052473	-2.559949	-1.198687	C	3.008255	1.429910 -0.155581
C	-3.539337	-3.409936	-2.402296	C	4.418455	1.584973 -0.379721
H	-3.980235	-1.330686	-2.071461	C	5.093814	0.391829 0.002089
C	-2.563803	-4.408407	-2.356447	H	6.154147	0.202770 -0.100269
H	-0.504561	-4.867881	-1.900161	C	4.119300	-0.526021 0.466283
H	-4.539251	-3.638987	-2.760119	H	4.290463	-1.541398 0.793478
H	-2.805865	-5.419139	-2.672836	C	2.826414	0.103004 0.388222
C	-2.499449	0.942068	-2.112989	Fe	3.698793	-0.005926 -1.476110
C	-2.036150	1.117494	-3.426153	H	2.505965	1.354460 -3.654484
C	-3.679709	1.576320	-1.708281	H	4.897767	2.448446 -0.816991
C	-2.749547	1.911995	-4.320648	C	2.027101	2.530213 -0.553182
H	-1.109429	0.640503	-3.732512	H	1.915755	2.443314 -1.635841
C	-4.387728	2.378278	-2.606017	C	2.677892	3.908529 -0.293318
H	-4.040286	1.452156	-0.692571	H	3.524490	4.042477 -0.973075
C	-3.925693	2.546847	-3.911432	H	1.998591	4.736702 -0.473025
H	-2.383216	2.043365	-5.334819	H	3.061755	3.988747 0.725332
H	-5.300124	2.871415	-2.282363	P	0.204386	2.385875 -0.056878
H	-4.476358	3.173365	-4.607314	P	1.329420	-0.705571 0.977755
Pd	0.686236	0.244458	-0.969441	C	-0.065474	3.360869 1.569754
C	5.208208	-2.461004	-0.390845	C	-0.627064	3.237200 -1.560856
C	4.666264	-1.281925	-0.915964	C	-0.020036	4.586886 -1.989337
C	5.508458	-0.355543	-1.543455	C	-2.123914	3.452198 -1.283570
C	6.876136	-0.607080	-1.644268	C	-0.477475	2.257855 -2.744735
C	7.412131	-1.784551	-1.117142	C	1.026266	2.911662 2.558460
C	6.575418	-2.711373	-0.490112	C	-0.057319	4.894483 1.446722
H	4.537458	-3.163926	0.091145	C	-1.423507	2.946053 2.168854
H	5.075005	0.552163	-1.948336	H	1.013536	4.484572 -2.327308
H	7.525020	0.113894	-2.134600	H	-0.596840	4.960119 -2.844446
H	8.478563	-1.979631	-1.195290	H	-0.060368	5.350229 -1.209627
H	6.990375	-3.628060	-0.079375	H	-2.301559	4.148674 -0.458682
C	3.189645	-1.027102	-0.778375	H	-2.587995	3.879242 -2.180592
O	2.788599	0.129059	-1.197463	H	-2.636272	2.513487 -1.067716
H	0.606685	-0.604301	-2.298950	H	-0.757452	1.228256 -2.503635
O	2.456462	-1.889094	-0.254981	H	-1.107634	2.611288 -3.571054

H	0.550522	2.237767	-3.120111	C	-1.581240	-1.813662	-2.290812
H	0.897290	5.292772	1.102803	O	-0.752407	-0.842579	-2.202540
H	-0.846370	5.259633	0.784454	H	-2.060852	0.941091	-0.094568
H	-0.246758	5.319618	2.440473	O	-1.291452	-3.031028	-2.285773
H	-1.540028	3.431293	3.146427	C	-6.392620	-0.788984	1.276425
H	-2.262666	3.257019	1.543190	C	-5.052037	-1.137100	1.154851
H	-1.486494	1.864426	2.308483	C	-4.078813	-0.143334	0.939564
H	0.979970	1.839084	2.743059	C	-4.479824	1.195145	0.859056
H	2.035827	3.155739	2.224278	C	-5.823307	1.538911	0.983419
H	0.862218	3.417426	3.518311	C	-6.784830	0.549105	1.190033
C	1.654214	-2.476470	0.671603	H	-7.135599	-1.566670	1.427940
C	1.198162	-3.025445	-0.531339	H	-4.743603	-2.175966	1.199381
C	2.295318	-3.292387	1.613103	H	-3.733542	1.959687	0.689780
C	1.387927	-4.381215	-0.795557	H	-6.119074	2.581879	0.913451
H	0.643356	-2.426074	-1.244693	H	-7.833408	0.817204	1.281957
C	2.495367	-4.645911	1.338082	C	-2.711944	-0.591953	0.804052
H	2.622439	-2.880480	2.562377	C	-1.896301	-1.545482	0.853062
C	2.042858	-5.191826	0.133331	C	-1.514810	-2.927362	0.916548
H	0.985344	-4.788675	-1.717505	H	-1.385784	-3.395609	-0.058358
H	2.991893	-5.276237	2.070933	C	-1.334953	-3.613211	2.052959
H	2.185985	-6.249937	-0.069135	H	-1.060677	-4.662479	2.018919
C	1.437992	-0.558689	2.810156	H	-1.426655	-3.153194	3.032192
C	0.256188	-0.682030	3.557342				
C	2.641922	-0.303663	3.480335	TS-B-1-isomer			
C	0.280818	-0.564973	4.945880	C	-4.243232	-0.660132	-1.888557
H	-0.686542	-0.843116	3.045533	C	-5.498909	-0.619003	-1.210696
C	2.663441	-0.180400	4.870853	H	-6.178358	-1.450507	-1.077550
H	3.559855	-0.184401	2.915257	C	-5.671153	0.698367	-0.687685
C	1.485147	-0.312903	5.606697	H	-6.504619	1.037833	-0.086896
H	-0.642729	-0.659159	5.510322	C	-4.521828	1.468304	-1.036843
H	3.602634	0.023250	5.377670	H	-4.327006	2.492729	-0.752602
H	1.503705	-0.212769	6.688211	C	-3.641100	0.627984	-1.783082
Pd	-0.691331	0.235075	0.256499	H	-2.674946	0.902292	-2.176570
C	-4.020692	-2.453467	-2.168060	C	-2.591968	-1.490458	0.908590
C	-3.060106	-1.449900	-2.338026	C	-3.899691	-1.717592	1.462283
C	-3.487729	-0.128297	-2.500421	C	-4.367991	-0.536432	2.100077
C	-4.845520	0.190505	-2.473664	H	-5.341104	-0.404156	2.554576
C	-5.796000	-0.813675	-2.283797	C	-3.359216	0.448210	1.965569
C	-5.378776	-2.138912	-2.135106	H	-3.410646	1.473822	2.302869
H	-3.670655	-3.474543	-2.059939	C	-2.247708	-0.116561	1.250337
H	-2.742596	0.644266	-2.639168	Fe	-3.969222	-0.171839	0.103140
H	-5.162882	1.224014	-2.588909	H	-3.808200	-1.528839	-2.366014
H	-6.852958	-0.564997	-2.244025	H	-4.475595	-2.624630	1.363741
H	-6.114976	-2.925790	-1.989258	C	-1.902453	-2.605227	0.092848

H	-2.199429	-2.451439	-0.949987	C	0.066718	0.832953	2.671243
C	-2.470752	-3.973757	0.528948	C	1.463626	0.959713	2.714684
H	-3.506225	-4.078336	0.187985	C	-0.644080	0.714615	3.875088
H	-1.914195	-4.805737	0.111328	C	2.132693	0.985660	3.938666
H	-2.467996	-4.078942	1.616112	H	2.022607	0.982075	1.786194
P	-0.022078	-2.532239	-0.119274	C	0.028866	0.733225	5.096883
P	-0.698713	0.808749	0.994429	H	-1.721042	0.586526	3.857876
C	0.740075	-3.202967	1.505202	C	1.418247	0.873314	5.132120
C	0.392591	-3.731908	-1.567632	H	3.215357	1.078383	3.956608
C	-0.228009	-5.143059	-1.560646	H	-0.532241	0.634429	6.022295
C	1.928977	-3.850419	-1.630302	H	1.940238	0.883573	6.084947
C	-0.068860	-3.052183	-2.867388	Pd	0.498123	-0.314456	-0.860000
C	-0.060562	-2.628708	2.686716	C	5.972109	-0.503090	-1.144767
C	0.733400	-4.737022	1.625272	C	4.870792	-0.319167	-0.300799
C	2.191151	-2.702515	1.631936	C	5.084533	-0.002544	1.046400
H	-1.302097	-5.117709	-1.766609	C	6.381138	0.131197	1.541706
H	0.236213	-5.716119	-2.373288	C	7.475811	-0.046097	0.692466
H	-0.060095	-5.699335	-0.638525	C	7.268354	-0.363679	-0.652467
H	2.337696	-4.430678	-0.799072	H	5.783023	-0.754533	-2.182802
H	2.193542	-4.379058	-2.555310	H	4.226427	0.125842	1.696360
H	2.414004	-2.870891	-1.664250	H	6.539724	0.372668	2.589784
H	0.460359	-2.115735	-3.039034	H	8.486667	0.060417	1.077502
H	0.136659	-3.724051	-3.710239	H	8.118417	-0.503656	-1.315127
H	-1.146286	-2.853844	-2.864382	C	3.477330	-0.476098	-0.862443
H	-0.270617	-5.160842	1.560741	O	2.528292	-0.169936	-0.038707
H	1.365736	-5.218110	0.876643	H	-0.764287	-0.364033	-1.821308
H	1.138941	-5.002561	2.610047	O	3.325123	-0.876183	-2.026340
H	2.606204	-3.081232	2.575328	C	1.625468	5.010901	-2.367559
H	2.828774	-3.056082	0.819314	C	1.098756	3.751684	-2.630404
H	2.245862	-1.615297	1.633670	C	1.428307	2.656115	-1.806482
H	-0.069588	-1.541843	2.685177	C	2.298834	2.850472	-0.721943
H	-1.094032	-2.980625	2.712751	C	2.824855	4.114449	-0.468612
H	0.422886	-2.944447	3.619825	C	2.488411	5.197223	-1.283256
C	-1.292440	2.547053	0.834559	H	1.358822	5.850647	-3.003261
C	-1.559999	3.039685	-0.450788	H	0.411134	3.604605	-3.458257
C	-1.440790	3.411353	1.929172	H	2.558779	1.995538	-0.111238
C	-1.987879	4.352459	-0.638318	H	3.500819	4.253561	0.370258
H	-1.413844	2.395767	-1.307949	H	2.895851	6.182839	-1.076609
C	-1.870573	4.726169	1.742318	C	0.818430	1.381681	-2.079601
H	-1.210837	3.061224	2.929451	C	0.123071	0.669021	-2.876846
C	-2.149100	5.200031	0.459438	C	-0.370998	0.446681	-4.202993
H	-2.177790	4.717041	-1.643909	H	0.123516	1.051368	-4.964997
H	-1.980111	5.382238	2.601644	C	-1.362587	-0.381050	-4.563499
H	-2.474508	6.226356	0.314751	H	-1.682387	-0.455436	-5.597319

H	-1.873502	-1.002101	-3.836706	H	2.299221	-0.969544	-1.999884
				H	2.937731	-2.540345	-2.542606
Pd⁰-L-2a				H	1.221522	-2.362887	-2.149007
C	-1.688695	-2.408500	-2.847659	H	1.782265	-3.649867	3.088507
C	-3.034261	-2.878121	-2.920933	H	3.350489	-3.093164	2.483262
H	-3.347565	-3.913888	-2.923587	H	2.795634	-2.611341	4.085509
C	-3.894611	-1.739756	-2.938180	H	3.021851	-0.237485	3.754845
H	-4.976383	-1.762075	-2.951179	H	3.731949	-0.500789	2.154267
C	-3.082718	-0.569021	-2.872508	H	2.351499	0.587633	2.327373
H	-3.437906	0.449759	-2.824105	H	0.150184	-0.217723	3.065599
C	-1.715693	-0.982220	-2.815164	H	-0.242475	-1.930914	3.230937
H	-0.854103	-0.337322	-2.704181	H	0.828682	-1.150609	4.400951
C	-1.638514	-2.121815	0.497092	C	-2.365973	1.950193	-0.413970
C	-2.770326	-3.004932	0.429679	C	-1.941024	2.346840	-1.687793
C	-3.972709	-2.245733	0.399269	C	-3.566455	2.467707	0.094418
H	-4.974192	-2.644035	0.303315	C	-2.717514	3.213427	-2.457746
C	-3.614242	-0.875642	0.445206	H	-0.989389	1.984252	-2.060720
H	-4.289620	-0.035083	0.389469	C	-4.345453	3.331587	-0.675438
C	-2.180783	-0.773736	0.508899	H	-3.884015	2.208547	1.100109
Fe	-2.757813	-1.749935	-1.204119	C	-3.925719	3.700748	-1.956345
H	-0.805223	-3.029898	-2.792160	H	-2.370262	3.516326	-3.441429
H	-2.722539	-4.081912	0.360916	H	-5.274314	3.725418	-0.271882
C	-0.218951	-2.703402	0.491167	H	-4.529548	4.379849	-2.551826
H	-0.054507	-3.042489	-0.536025	C	-1.559461	1.421904	2.254241
C	-0.186105	-3.968816	1.376125	C	-0.799614	2.531343	2.658372
H	-0.834527	-4.744787	0.957897	C	-2.446676	0.834897	3.164222
H	0.811923	-4.393808	1.440722	C	-0.935383	3.050232	3.944219
H	-0.538422	-3.760393	2.388803	H	-0.088496	2.968162	1.961672
P	1.269934	-1.531379	0.671513	C	-2.573454	1.349621	4.456484
P	-1.284556	0.803550	0.543061	H	-3.027323	-0.032655	2.868434
C	1.807263	-1.524509	2.506875	C	-1.821524	2.457674	4.848254
C	2.569727	-2.441064	-0.407023	H	-0.341517	3.908743	4.245645
C	2.607893	-3.975595	-0.312650	H	-3.259965	0.882014	5.157192
C	3.970672	-1.893006	-0.089066	H	-1.919882	2.854933	5.854629
C	2.230727	-2.050735	-1.860484	Pd	0.918000	0.685537	-0.059451
C	0.554928	-1.192021	3.338702	C	5.833736	0.774471	-2.450454
C	2.466619	-2.801397	3.055196	C	4.480324	1.058255	-2.280918
C	2.791416	-0.347468	2.686589	C	3.990134	1.497402	-1.036882
H	1.671642	-4.440643	-0.635149	C	4.900693	1.650913	0.026823
H	3.397168	-4.347253	-0.979207	C	6.253041	1.370473	-0.150715
H	2.841654	-4.328932	0.694720	C	6.727164	0.924774	-1.387472
H	4.345318	-2.250891	0.873570	H	6.192567	0.432744	-3.417897
H	4.672361	-2.231628	-0.861544	H	3.784394	0.932597	-3.105097
H	3.989767	-0.804182	-0.089198	H	4.526213	1.976604	0.992503

H	6.940352	1.495479	0.681975	C	-2.167235	3.679470	-3.233404
H	7.781138	0.698779	-1.521319	C	0.218939	3.598794	-2.457620
C	2.580092	1.718165	-0.832445	H	-4.649967	3.043576	-0.067171
C	1.556212	2.490685	-0.842370	H	-4.253739	4.704552	0.351620
C	0.989843	3.776133	-1.168174	H	-4.005808	4.146683	-1.303158
H	0.199715	4.138451	-0.511577	H	-1.699247	5.265440	-0.775177
C	1.332585	4.506867	-2.241280	H	-2.015451	5.418591	0.954064
H	0.855622	5.460860	-2.447970	H	-0.595962	4.517407	0.393861
H	2.092496	4.165511	-2.939022	H	-1.596500	2.675990	1.995605
TS-B-2				H	-3.064480	3.653520	2.259014
				H	-3.194160	1.994231	1.660537
C	-4.843899	-1.861240	0.201510	H	-3.131984	3.176803	-3.326924
C	-5.108170	-2.847061	-0.797545	H	-2.319137	4.619291	-2.695950
H	-5.755008	-2.726554	-1.656635	H	-1.829341	3.936552	-4.245712
C	-4.325633	-4.000966	-0.492776	H	0.505680	3.934342	-3.463342
H	-4.275049	-4.906927	-1.082282	H	0.117490	4.485451	-1.828229
C	-3.577157	-3.726407	0.691103	H	1.021182	2.972040	-2.063674
H	-2.867570	-4.389987	1.163573	H	-0.079894	0.905520	-2.989249
C	-3.899769	-2.403565	1.120974	H	-1.722440	0.995624	-3.674373
H	-3.473954	-1.891091	1.970365	H	-0.399659	1.910353	-4.406413
C	-2.257423	-0.604884	-1.489741	C	-0.772651	-1.359433	2.065107
C	-2.745394	-1.397192	-2.580713	C	-1.249000	-0.396680	2.960377
C	-2.086167	-2.658785	-2.576088	C	-0.843754	-2.715423	2.416255
H	-2.279721	-3.478110	-3.255461	C	-1.813172	-0.779374	4.179831
C	-1.181298	-2.670967	-1.483813	H	-1.165112	0.650586	2.691126
H	-0.529140	-3.483131	-1.198498	C	-1.395665	-3.097991	3.636556
C	-1.256742	-1.402060	-0.816138	H	-0.461661	-3.468099	1.734277
Fe	-3.098936	-2.362759	-0.795302	C	-1.888502	-2.130475	4.518481
H	-5.259301	-0.862319	0.234035	H	-2.183127	-0.022395	4.865912
H	-3.529388	-1.117342	-3.267827	H	-1.445648	-4.150485	3.901455
C	-2.828770	0.748957	-1.092087	H	-2.322490	-2.431788	5.467620
H	-3.199006	0.642096	-0.065613	C	1.380156	-1.866133	0.241520
C	-4.038449	1.068738	-1.988174	C	2.133373	-2.241899	1.364210
H	-4.791366	0.281392	-1.872451	C	1.858083	-2.188388	-1.038054
H	-4.503126	2.017166	-1.739741	C	3.315587	-2.964734	1.207606
H	-3.757924	1.105152	-3.042397	H	1.811390	-1.960012	2.360271
P	-1.551565	2.141001	-0.842921	C	3.037964	-2.913208	-1.188977
P	-0.100284	-0.808137	0.448745	H	1.327028	-1.844614	-1.916804
C	-1.095961	2.798979	-2.569289	C	3.766372	-3.310246	-0.066166
C	-2.506135	3.461190	0.170906	H	3.888727	-3.238434	2.088199
C	-3.933762	3.847634	-0.255757	H	3.402907	-3.136502	-2.186415
C	-1.643030	4.736112	0.179258	H	4.691535	-3.866601	-0.187410
C	-2.590600	2.907546	1.607182	Pd	0.343569	1.464522	0.394420
C	-0.817302	1.564548	-3.451824	C	5.210779	-0.484196	-2.293981

C	3.897048	-0.126965	-2.613959	C	-3.625377	-2.082037	-1.930074
C	3.330463	-0.579526	-3.810214	C	-4.653377	-1.294426	-1.341083
C	4.063159	-1.394897	-4.671094	H	-5.682314	-1.241133	-1.671573
C	5.370652	-1.763032	-4.340138	C	-4.065967	-0.536818	-0.298116
C	5.943885	-1.302603	-3.151899	H	-4.562332	0.185066	0.334185
H	5.633644	-0.126676	-1.362088	C	-2.665435	-0.859946	-0.222813
H	2.309080	-0.292961	-4.037616	Fe	-3.144657	-0.092091	-2.088400
H	3.617542	-1.746145	-5.598155	H	-1.191469	-0.200515	-4.130751
H	5.941421	-2.403149	-5.007836	H	-3.756554	-2.722350	-2.790418
H	6.960951	-1.585971	-2.893936	C	-1.102462	-2.521933	-1.743009
C	3.060453	0.684243	-1.656949	H	-0.866751	-2.046575	-2.699370
O	1.846843	0.844789	-1.897747	C	-1.409086	-4.000924	-2.064368
H	2.786681	1.467130	0.357405	H	-2.152640	-4.066182	-2.864209
O	3.681282	1.146556	-0.627127	H	-0.526127	-4.533289	-2.408951
C	0.540728	4.695191	2.829375	H	-1.814731	-4.528131	-1.198571
C	1.552502	4.056812	2.212841	P	0.515233	-2.183199	-0.812893
H	-0.476496	4.325379	2.788323	P	-1.604498	-0.161855	1.075712
C	1.442810	2.821816	1.486282	C	0.827918	-3.638250	0.390615
C	2.182295	1.701773	1.453688	C	1.776372	-2.238025	-2.254931
H	0.723332	5.581911	3.429277	C	1.539948	-3.305555	-3.337390
H	2.561480	4.462458	2.309433	C	3.198436	-2.418616	-1.695390
C	2.774664	0.944669	2.571628	C	1.691066	-0.847514	-2.917339
C	2.099975	0.845658	3.802556	C	-0.435965	-3.799043	1.255370
C	3.981582	0.247025	2.405677	C	1.193133	-4.995664	-0.235595
C	2.617386	0.070413	4.836713	C	1.966726	-3.223895	1.347048
H	1.151503	1.359482	3.924307	H	0.591069	-3.167575	-3.864250
C	4.505912	-0.513102	3.450431	H	2.337730	-3.222942	-4.086945
H	4.483943	0.292073	1.445817	H	1.570640	-4.323261	-2.940916
C	3.825940	-0.611805	4.665596	H	3.397071	-3.453447	-1.404219
H	2.075764	-0.006021	5.775986	H	3.926508	-2.149314	-2.470469
H	5.442338	-1.045785	3.306841	H	3.379389	-1.784941	-0.830197
H	4.229736	-1.217659	5.472190	H	2.002376	-0.058295	-2.231697
TS-B-2-isomer				H	2.352094	-0.822319	-3.793401
C	-1.973792	0.420923	-3.717826	H	0.678144	-0.615768	-3.259635
C	-3.349929	0.380575	-4.091014	H	0.376528	-5.433505	-0.810375
H	-3.791875	-0.285362	-4.820529	H	2.075466	-4.938541	-0.876629
C	-4.047261	1.333548	-3.290642	H	1.429294	-5.696898	0.575619
H	-5.113550	1.516998	-3.305276	H	2.042905	-3.977496	2.142330
C	-3.103564	1.957844	-2.423566	H	2.935353	-3.165970	0.848367
H	-3.333015	2.696906	-1.671163	H	1.773169	-2.252101	1.806968
C	-1.817480	1.391830	-2.684846	H	-0.590056	-2.926185	1.886727
H	-0.891649	1.620998	-2.172843	H	-1.348113	-3.959388	0.676502
C	-2.379025	-1.830394	-1.260229	H	-0.307170	-4.664848	1.917597
				C	-2.424085	1.451969	1.404014

C	-2.092081	2.549235	0.597217	H	0.114217	4.522747	1.175272
C	-3.338065	1.633020	2.450602	H	2.851195	3.239910	-1.875948
C	-2.669148	3.798467	0.823234	H	3.059300	5.569599	-2.669674
H	-1.359693	2.431164	-0.187554	H	1.791616	7.395091	-1.548972
C	-3.917470	2.883087	2.676226	C	1.303629	2.317721	0.148306
H	-3.595692	0.799041	3.094038	C	0.843318	1.799313	1.256013
C	-3.584600	3.969190	1.864516	C	0.737701	1.995871	2.687162
H	-2.382625	4.638273	0.196781	H	1.447445	1.387618	3.252845
H	-4.624261	3.007836	3.491931	C	-0.111046	2.784320	3.363586
H	-4.028707	4.943692	2.047236	H	-0.073695	2.827409	4.448750
C	-2.082111	-1.127647	2.567233	H	-0.862937	3.390658	2.873316
C	-1.300730	-0.955116	3.721010				
C	-3.143618	-2.040535	2.591023	B-1			
C	-1.581425	-1.679217	4.877450	C	4.229073	-1.803555	1.558453
H	-0.473555	-0.252433	3.702238	C	5.380663	-1.013934	1.852480
C	-3.413735	-2.775213	3.747393	H	6.377973	-1.172957	1.463860
H	-3.750476	-2.187190	1.704246	C	4.971958	0.052007	2.708457
C	-2.635780	-2.596671	4.891757	H	5.606527	0.845884	3.080161
H	-0.971076	-1.535784	5.764821	C	3.570892	-0.074808	2.937512
H	-4.233763	-3.488227	3.751908	H	2.959263	0.599445	3.517693
H	-2.846683	-3.170963	5.789475	C	3.108633	-1.223158	2.223690
Pd	0.588896	-0.083282	0.452327	H	2.086660	-1.571470	2.165747
C	6.187916	0.696502	-0.404889	C	3.186911	0.111383	-1.018464
C	5.246150	0.017159	0.377271	C	4.571795	0.491961	-1.022458
C	5.666559	-0.968600	1.279005	C	4.746564	1.669551	-0.244632
C	7.020159	-1.274072	1.396056	H	5.687771	2.159969	-0.034814
C	7.958916	-0.594916	0.614537	C	3.478332	2.038166	0.263501
C	7.541946	0.390010	-0.284385	H	3.269187	2.876307	0.910703
H	5.845101	1.458337	-1.095916	C	2.499348	1.092277	-0.203630
H	4.918526	-1.479730	1.875531	Fe	3.946558	0.143709	0.909059
H	7.345543	-2.039624	2.094857	H	4.206442	-2.671174	0.912199
H	9.015219	-0.832705	0.706780	H	5.372457	-0.055877	-1.496986
H	8.272965	0.918989	-0.889273	C	2.736597	-1.160913	-1.732577
C	3.789153	0.316703	0.255512	H	3.075392	-1.981521	-1.095486
O	2.969921	-0.236582	1.014387	C	3.506180	-1.309298	-3.062601
H	2.365593	1.479016	-0.491628	H	4.579313	-1.390393	-2.867740
O	3.455234	1.140354	-0.697536	H	3.217001	-2.208207	-3.601540
C	0.878426	6.066150	-0.111065	H	3.356472	-0.447520	-3.716622
C	0.760117	4.753450	0.336925	P	0.887220	-1.552183	-1.798926
C	1.469866	3.704022	-0.286498	P	0.742746	1.316016	0.187930
C	2.294841	4.029660	-1.381826	C	0.195883	-0.995345	-3.492223
C	2.413044	5.344665	-1.824957	C	0.920620	-3.453762	-1.635535
C	1.704581	6.371244	-1.195881	C	2.007904	-4.177465	-2.450208
H	0.322809	6.855927	0.389173	C	-0.447070	-4.044632	-2.024224

C	1.174503	-3.724336	-0.137711	Pd	-0.622616	-0.391891	-0.330458
C	0.559587	0.494286	-3.639827	C	-3.145575	-4.241726	2.323711
C	0.669402	-1.780426	-4.727338	C	-3.139342	-3.509901	1.130512
C	-1.346082	-1.087490	-3.437158	C	-4.162612	-3.706698	0.194801
H	3.021159	-3.897892	-2.147153	C	-5.179242	-4.625612	0.450750
H	1.907431	-5.255521	-2.271593	C	-5.180063	-5.354807	1.642357
H	1.907962	-4.015550	-3.526484	C	-4.161173	-5.161052	2.578816
H	-0.605580	-4.018991	-3.106588	H	-2.346027	-4.069105	3.035899
H	-0.469575	-5.098460	-1.718432	H	-4.148185	-3.128183	-0.722150
H	-1.269615	-3.526666	-1.530279	H	-5.972808	-4.772634	-0.277146
H	0.412790	-3.273879	0.501334	H	-5.973142	-6.070886	1.841471
H	1.176029	-4.808678	0.032131	H	-4.160902	-5.726621	3.506917
H	2.150721	-3.346347	0.184912	C	-2.036864	-2.520822	0.878687
H	1.738221	-1.683029	-4.915320	O	-2.059876	-1.955964	-0.285306
H	0.423888	-2.843099	-4.655417	H	-2.068827	1.749811	-1.533786
H	0.147204	-1.387933	-5.609646	O	-1.172561	-2.315374	1.753176
H	-1.749828	-0.688276	-4.376874	C	-5.196710	4.196565	0.678993
H	-1.701700	-2.112200	-3.325292	C	-4.284571	3.144438	0.677520
H	-1.762894	-0.503209	-2.613186	C	-3.676643	2.717501	-0.517940
H	0.126142	1.082225	-2.827732	C	-4.014594	3.399688	-1.701495
H	1.637734	0.673888	-3.651089	C	-4.933222	4.446902	-1.702175
H	0.148543	0.875085	-4.583541	C	-5.531284	4.853330	-0.508567
C	0.697411	1.559968	2.004369	H	-5.649315	4.508321	1.616962
C	0.273323	0.488142	2.803560	H	-4.040290	2.644507	1.606210
C	1.103014	2.756623	2.611495	H	-3.535189	3.102548	-2.631369
C	0.275432	0.610689	4.193697	H	-5.176210	4.950403	-2.634363
H	-0.074542	-0.434069	2.342894	H	-6.245228	5.672281	-0.501542
C	1.104008	2.873710	4.001561	C	-2.622236	1.690017	-0.596308
H	1.398840	3.604273	2.001789	C	-2.192858	0.795003	0.315962
C	0.693084	1.799331	4.795517	C	-2.823721	0.449669	1.585344
H	-0.056589	-0.225980	4.801223	H	-2.238196	0.614928	2.488793
H	1.416418	3.806025	4.463573	C	-4.015065	-0.157915	1.688925
H	0.690456	1.893750	5.877768	H	-4.414766	-0.460831	2.652649
C	0.411942	2.974138	-0.512344	H	-4.605547	-0.393241	0.808745
C	-0.600961	3.782404	0.025588				
C	1.085594	3.400932	-1.665830	B-1-isomer			
C	-0.946863	4.983899	-0.589683	C	3.477798	-3.662724	-0.794837
H	-1.132800	3.465436	0.913503	C	4.678593	-3.125825	-1.351008
C	0.740965	4.606810	-2.277105	H	4.982735	-3.184171	-2.387831
H	1.880658	2.792576	-2.083782	C	5.381299	-2.451756	-0.307750
C	-0.280235	5.396221	-1.744682	H	6.309926	-1.907387	-0.417181
H	-1.752750	5.581644	-0.175563	C	4.612080	-2.567526	0.888834
H	1.271139	4.927700	-3.169436	H	4.859392	-2.137552	1.848894
H	-0.555243	6.329419	-2.227932	C	3.435867	-3.318481	0.586765

H	2.640929	-3.557421	1.277031	H	-0.546739	1.623450	-4.157856
C	1.770197	-0.817927	-1.374288	C	1.117129	-1.542738	2.391743
C	2.894204	-0.468178	-2.190990	C	0.203775	-2.593563	2.514129
C	3.826012	0.271281	-1.408752	C	2.289358	-1.560486	3.163431
H	4.785744	0.639071	-1.745530	C	0.471632	-3.670207	3.365213
C	3.296874	0.392334	-0.097831	H	-0.717791	-2.560619	1.945912
H	3.763605	0.891774	0.737832	C	2.553403	-2.627414	4.017743
C	2.019474	-0.255544	-0.068573	H	2.991173	-0.735704	3.091269
Fe	3.517646	-1.597605	-0.579252	C	1.648260	-3.690469	4.113434
H	2.717800	-4.213239	-1.333166	H	-0.242617	-4.484722	3.447785
H	3.051134	-0.762296	-3.217562	H	3.464710	-2.634757	4.609103
C	0.642932	-1.750228	-1.795340	H	1.858311	-4.524296	4.777051
H	0.620147	-2.565184	-1.061770	C	1.148236	1.291822	2.266868
C	0.997790	-2.367076	-3.163260	C	0.671496	1.297889	3.588678
H	1.962050	-2.877385	-3.078890	C	1.739440	2.451237	1.750856
H	0.267144	-3.090088	-3.508175	C	0.796836	2.440290	4.377352
H	1.097612	-1.603476	-3.935030	H	0.199904	0.411025	4.001464
P	-1.146081	-1.096582	-1.620704	C	1.859765	3.592464	2.541166
P	0.772439	-0.166990	1.228862	H	2.070697	2.481535	0.724602
C	-1.506456	-0.019002	-3.153035	C	1.391166	3.591093	3.855433
C	-2.214650	-2.694538	-1.627238	H	0.422605	2.432092	5.397189
C	-1.852555	-3.796379	-2.638941	H	2.300752	4.486945	2.111552
C	-3.684946	-2.303266	-1.853559	H	1.478467	4.484216	4.467593
C	-2.081266	-3.307636	-0.222234	Pd	-1.405609	0.112725	0.356014
C	-0.282394	0.887845	-3.387380	C	1.179334	5.522637	-0.883315
C	-1.796717	-0.825423	-4.433144	C	1.062970	4.138812	-1.053487
C	-2.706999	0.895774	-2.843868	C	2.092300	3.441628	-1.697646
H	-0.898150	-4.275423	-2.405065	C	3.220248	4.116647	-2.164867
H	-2.623171	-4.575315	-2.575639	C	3.333176	5.497451	-1.985600
H	-1.832580	-3.444002	-3.671482	C	2.309216	6.199138	-1.342589
H	-3.881058	-2.027755	-2.891732	H	0.366868	6.041604	-0.385716
H	-4.320052	-3.165088	-1.614845	H	1.998276	2.368630	-1.813828
H	-3.997369	-1.483697	-1.214041	H	4.012011	3.565574	-2.667387
H	-2.406817	-2.604930	0.545253	H	4.213008	6.024843	-2.345663
H	-2.710073	-4.204901	-0.159782	H	2.393620	7.274064	-1.202595
H	-1.051487	-3.610410	-0.005065	C	-0.159262	3.409784	-0.511736
H	-0.986563	-1.506650	-4.699508	O	-0.112303	2.133911	-0.573934
H	-2.724108	-1.399146	-4.372272	H	-2.372380	2.615283	0.344070
H	-1.909987	-0.114538	-5.261183	O	-1.089601	4.102350	-0.050120
H	-2.929877	1.487952	-3.740631	C	-5.612527	-2.056003	1.623454
H	-3.608727	0.340325	-2.574892	C	-4.490725	-1.243517	1.489397
H	-2.468287	1.581683	-2.030353	C	-4.499950	-0.135131	0.621164
H	-0.014396	1.429602	-2.476813	C	-5.682959	0.145631	-0.089736
H	0.587115	0.335436	-3.749165	C	-6.801358	-0.676374	0.034778

C	-6.769091	-1.782773	0.886931	C	1.632182	-1.086740	-4.378239
H	-5.588535	-2.902990	2.303937	C	3.320960	0.080861	-2.964768
H	-3.590476	-1.444133	2.062602	C	0.951850	0.885553	-3.008659
H	-5.700295	1.005640	-0.752335	C	1.991320	-3.653947	-0.040592
H	-7.701664	-0.451357	-0.530412	C	3.273715	-3.460815	-2.196272
H	-7.641866	-2.422080	0.984729	C	3.819885	-1.977454	-0.250840
C	-3.312087	0.694512	0.435347	H	0.583084	-1.336522	-4.560979
C	-3.216078	2.020212	0.712255	H	1.944430	-0.405867	-5.180214
C	-4.145388	2.766094	1.554782	H	2.232052	-1.995344	-4.474815
H	-5.008307	2.237165	1.957480	H	4.012752	-0.757141	-3.083878
C	-3.941870	4.065343	1.830850	H	3.507634	0.776125	-3.793927
H	-4.631871	4.628749	2.453400	H	3.532936	0.600070	-2.030988
H	-3.072901	4.581474	1.431000	H	1.167882	1.518238	-2.145111
B-2				H	1.131567	1.471544	-3.919514
C	-3.224858	-0.540989	-2.733708	H	-0.115110	0.631919	-2.986700
C	-4.361336	-1.401968	-2.659339	H	2.534527	-4.071766	-2.715972
H	-4.622912	-2.174226	-3.370633	H	3.758327	-2.808150	-2.926141
C	-5.061573	-1.098519	-1.452815	H	4.043326	-4.140272	-1.808063
H	-5.946654	-1.603960	-1.089494	H	4.527575	-2.742290	0.095308
C	-4.357718	-0.056305	-0.780811	H	4.371618	-1.275486	-0.879858
H	-4.609640	0.370832	0.178661	H	3.458992	-1.427943	0.620464
C	-3.218928	0.286152	-1.572176	H	1.611255	-3.136401	0.840946
H	-2.458720	1.008213	-1.316294	H	1.164410	-4.202569	-0.499686
C	-1.252657	-2.581912	-0.984889	H	2.729776	-4.389520	0.302326
C	-2.265728	-3.570615	-1.227500	C	-1.926845	0.045500	2.239193
C	-3.192363	-3.578513	-0.147804	C	-2.524707	1.194860	1.703130
H	-4.084388	-4.187200	-0.081582	C	-2.370031	-0.438810	3.477223
C	-2.772907	-2.599387	0.786633	C	-3.569341	1.829884	2.373093
H	-3.273234	-2.327193	1.704723	H	-2.162081	1.606631	0.769489
C	-1.568536	-1.983706	0.293937	C	-3.416025	0.197904	4.148621
Fe	-3.124103	-1.701949	-1.026485	H	-1.898882	-1.309317	3.920881
H	-2.478453	-0.542491	-3.517640	C	-4.021486	1.327049	3.595568
H	-2.353072	-4.179849	-2.114038	H	-4.014982	2.720255	1.941188
C	-0.188925	-2.244981	-2.029966	H	-3.751531	-0.187764	5.107309
H	-0.615896	-1.447302	-2.644090	H	-4.832590	1.822832	4.121509
C	0.009380	-3.461611	-2.958222	C	0.233993	-1.873159	2.520900
H	-0.897974	-3.630513	-3.547827	C	1.459998	-1.427509	3.042603
H	0.823071	-3.320598	-3.662269	C	-0.274349	-3.116777	2.925220
H	0.207037	-4.370531	-2.385228	C	2.154674	-2.214975	3.961432
P	1.382753	-1.360880	-1.455280	H	1.905934	-0.500073	2.693525
P	-0.611540	-0.808324	1.279455	C	0.425962	-3.898051	3.844328
C	2.678103	-2.677209	-1.014596	H	-1.204962	-3.486683	2.509275
C	1.851027	-0.371039	-3.033827	C	1.640762	-3.447824	4.365630
				H	3.108471	-1.863803	4.343816

H	0.025870	-4.862320	4.145519	P	-0.103830	-1.969958	-1.487523
H	2.188721	-4.062192	5.074774	P	-1.203137	-0.160412	1.336278
Pd	1.032096	0.321461	0.263810	C	-0.280678	-3.756127	-0.848266
C	6.108009	1.978910	1.248702	C	0.977170	-1.964505	-3.072109
C	5.006112	2.077978	0.390976	C	0.809632	-3.180405	-4.001562
C	5.085068	2.901769	-0.738956	C	2.448496	-1.890032	-2.610917
C	6.252536	3.615524	-1.007487	C	0.682199	-0.682090	-3.880686
C	7.350469	3.509143	-0.150619	C	-0.921388	-3.685561	0.546168
C	7.276049	2.688958	0.978342	C	-1.160242	-4.671189	-1.717475
H	6.022426	1.339408	2.120494	C	1.121877	-4.364802	-0.665483
H	4.223383	2.974848	-1.393187	H	-0.218669	-3.319178	-4.343318
H	6.306832	4.255852	-1.884040	H	1.429957	-3.015411	-4.892044
H	8.260674	4.064804	-0.360686	H	1.146406	-4.113383	-3.543639
H	8.128846	2.605628	1.646924	H	2.732421	-2.731528	-1.974646
C	3.757976	1.292288	0.704699	H	3.093226	-1.916006	-3.499465
O	2.841073	1.352971	-0.209320	H	2.635143	-0.955716	-2.079824
H	-1.385462	2.912533	-2.120013	H	0.576976	0.197547	-3.247556
O	3.682638	0.649326	1.764127	H	1.520496	-0.510758	-4.567468
C	-4.164681	5.283775	0.697628	H	-0.218957	-0.775183	-4.491913
C	-2.918343	4.755167	0.374070	H	-2.203309	-4.343217	-1.696336
C	-2.743871	3.999029	-0.797608	H	-0.836511	-4.724175	-2.756645
C	-3.850798	3.797439	-1.636626	H	-1.130667	-5.688826	-1.306078
C	-5.100619	4.321871	-1.308745	H	1.025351	-5.318535	-0.131058
C	-5.264336	5.065900	-0.139529	H	1.626713	-4.569407	-1.611495
H	-4.280571	5.869327	1.605875	H	1.761513	-3.709082	-0.064629
H	-2.064767	4.914882	1.026694	H	-0.319111	-3.086988	1.232296
H	-3.729472	3.210477	-2.543329	H	-1.925848	-3.262536	0.505199
H	-5.946834	4.147235	-1.967505	H	-1.001218	-4.699992	0.958344
H	-6.236609	5.477271	0.116201	C	-1.543387	1.562344	1.878637
C	-1.452071	3.370105	-1.130110	C	-0.996323	2.619706	1.141438
C	-0.425473	3.268299	-0.312279	C	-2.361273	1.842827	2.982107
C	0.578922	3.108320	0.518376	C	-1.265854	3.940796	1.496891
H	1.400948	3.824125	0.461618	H	-0.388092	2.405629	0.272873
C	0.723307	1.985775	1.495103	C	-2.632764	3.165521	3.334537
H	1.626346	2.085912	2.096064	H	-2.776396	1.033472	3.574122
H	-0.146041	1.888285	2.141848	C	-2.084589	4.216631	2.594005
TS-C-1				H	-0.829602	4.745708	0.912555
				H	-3.266404	3.374761	4.192026
C	-1.790352	-1.315190	-2.009707	H	-2.292884	5.245109	2.875232
H	-1.495121	-0.282055	-2.229197	C	-1.292469	-1.079626	2.935835
C	-2.426742	-1.906063	-3.277919	C	-0.430716	-0.691543	3.976873
H	-3.283799	-1.291668	-3.573606	C	-2.133192	-2.180641	3.145652
H	-1.730593	-1.910696	-4.113124	C	-0.403996	-1.389114	5.182168
H	-2.780351	-2.928182	-3.130812	H	0.211669	0.172326	3.854484

C	-2.105210	-2.880669	4.353271	H	-6.273358	1.984311	0.000222
H	-2.816287	-2.496013	2.368302	C	-4.092593	2.414481	-0.282281
C	-1.239513	-2.491804	5.374272	H	-3.808866	2.852591	0.663169
H	0.267549	-1.067225	5.973079	C	-3.213721	2.139051	-1.375038
H	-2.766755	-3.731243	4.492180	H	-2.144586	2.303441	-1.412308
H	-1.218826	-3.037407	6.313209	C	-2.811070	-1.250868	-0.882578
Pd	0.703930	-0.419837	0.154501	C	-4.177819	-1.656972	-1.024962
C	0.919728	4.426556	-1.745122	C	-4.898907	-1.326595	0.158088
C	1.739966	3.316886	-1.504058	H	-5.960616	-1.465311	0.313069
C	3.073042	3.516211	-1.125268	C	-3.992037	-0.717196	1.061779
C	3.577549	4.808930	-0.984219	H	-4.223809	-0.335034	2.045547
C	2.752813	5.911910	-1.217838	C	-2.690294	-0.681971	0.447381
C	1.422266	5.718714	-1.600337	Fe	-4.053827	0.380624	-0.664583
H	-0.108678	4.250524	-2.041839	H	-3.589936	1.146743	-3.340421
H	3.695062	2.646501	-0.942723	H	-4.618175	-2.080995	-1.914738
H	4.613094	4.957083	-0.689375				
H	3.145433	6.919019	-1.103810	TS-C-2			
H	0.780171	6.575680	-1.787389	C	-1.954326	-1.172607	-1.919369
C	1.158936	1.924092	-1.588262	H	-1.696510	-0.107211	-1.942132
O	1.947046	0.962735	-1.284774	C	-2.670512	-1.505377	-3.239075
H	4.403347	-1.775118	-0.658416	H	-3.607321	-0.940050	-3.283552
O	-0.055454	1.807743	-1.888510	H	-2.076533	-1.216632	-4.102161
C	7.671905	0.233289	1.895045	H	-2.910948	-2.565794	-3.336581
C	6.342266	-0.110493	1.674933	P	-0.231236	-1.895202	-1.626023
C	5.971747	-0.834205	0.529340	P	-1.239851	-0.315123	1.397126
C	6.969930	-1.202894	-0.384730	C	-0.399810	-3.756900	-1.243771
C	8.302673	-0.857873	-0.163734	C	0.701000	-1.650171	-3.284014
C	8.659531	-0.138764	0.977208	C	0.345389	-2.670410	-4.381323
H	7.941864	0.794346	2.785672	C	2.213388	-1.740553	-3.003641
H	5.574832	0.179180	2.387319	C	0.434162	-0.217642	-3.791229
H	6.692650	-1.761244	-1.275524	C	-0.880932	-3.884366	0.211643
H	9.061758	-1.150653	-0.883932	C	-1.400068	-4.511528	-2.135866
H	9.697169	0.131335	1.151466	C	0.990052	-4.415274	-1.315320
C	4.571781	-1.209209	0.257031	H	-0.719699	-2.701905	-4.617797
C	3.539485	-0.892225	1.002911	H	0.876087	-2.381006	-5.297440
C	2.588064	-0.480819	1.836519	H	0.669315	-3.683372	-4.128521
H	2.308289	-1.129636	2.669693	H	2.509352	-2.721308	-2.626163
C	1.761011	0.703727	1.592600	H	2.748787	-1.579063	-3.948659
H	1.231703	1.092496	2.457149	H	2.517229	-0.962664	-2.302445
H	2.218931	1.485542	0.991939	H	0.655158	0.512378	-3.014520
C	-3.979887	1.510057	-2.398656	H	1.103011	-0.035298	-4.642640
C	-5.328560	1.390879	-1.943118	H	-0.586985	-0.059047	-4.140046
H	-6.144282	0.921084	-2.477155	H	-2.419454	-4.151601	-1.972664
C	-5.396749	1.956166	-0.633966	H	-1.171150	-4.435789	-3.199422

H	-1.384071	-5.576165	-1.867176	C	2.397575	-1.107276	1.755236
H	0.920475	-5.432694	-0.909451	H	2.128001	-1.845973	2.512941
H	1.369210	-4.495321	-2.336237	C	1.778107	0.194569	1.814968
H	1.720224	-3.864136	-0.712818	H	1.270525	0.440471	2.740657
H	-0.198487	-3.379036	0.899873	H	2.287440	1.026911	1.338213
H	-1.879273	-3.464055	0.341119	C	-5.491042	0.859095	-1.726852
H	-0.924288	-4.947437	0.483194	C	-6.152077	0.971737	-0.465241
C	-1.575263	1.427293	1.846762	H	-7.121555	0.560263	-0.216556
C	-0.777566	2.423001	1.280926	C	-5.284264	1.677527	0.423436
C	-2.629983	1.786249	2.700354	H	-5.479131	1.899690	1.463331
C	-1.044989	3.772034	1.528301	C	-4.093025	1.999709	-0.291410
H	0.038246	2.145054	0.627927	H	-3.221119	2.492713	0.106797
C	-2.889668	3.129814	2.958818	C	-4.215399	1.491620	-1.616310
H	-3.246906	1.018779	3.156353	H	-3.440665	1.552414	-2.367824
C	-2.103708	4.125029	2.364597	C	-2.891835	-1.395162	-0.750271
H	-0.426995	4.528101	1.054833	C	-4.174442	-2.025251	-0.843910
H	-3.707525	3.404830	3.619285	C	-4.822074	-1.966798	0.423759
H	-2.318156	5.171812	2.561150	H	-5.820703	-2.320240	0.643563
C	-1.235152	-1.126005	3.053606	C	-3.948464	-1.308741	1.327802
C	-0.720142	-0.437200	4.164691	H	-4.140611	-1.109711	2.372299
C	-1.638868	-2.459275	3.224000	C	-2.743312	-0.962207	0.623734
C	-0.596050	-1.068780	5.402273	Fe	-4.373304	-0.056776	-0.253375
H	-0.437331	0.605406	4.070380	H	-5.874850	0.343506	-2.597610
C	-1.519893	-3.087220	4.463202	H	-4.614948	-2.423860	-1.745630
H	-2.062968	-3.006114	2.392631	C	3.220005	2.632842	-0.558382
C	-0.990990	-2.398007	5.555908	C	3.035720	4.039113	-0.530949
H	-0.196930	-0.515510	6.247702	C	4.064753	4.890373	-0.102759
H	-1.845960	-4.117738	4.573740	C	5.259357	4.306698	0.307778
H	-0.896823	-2.889522	6.519892	C	5.446899	2.907447	0.297966
Pd	0.684677	-0.682244	0.219406	C	4.430247	2.067075	-0.138743
H	3.928906	-2.215706	-1.103133	C	1.997704	2.023480	-1.076581
C	7.259157	-0.765802	1.717754	C	1.116754	3.108718	-1.332323
C	5.912242	-0.970863	1.435419	H	3.934100	5.969321	-0.088614
C	5.521734	-1.630307	0.257724	H	6.069776	4.948254	0.644575
C	6.517688	-2.072298	-0.626540	H	6.392734	2.486498	0.627026
C	7.866944	-1.869499	-0.341474	H	4.561774	0.990722	-0.169781
C	8.243529	-1.215285	0.832029	H	1.452194	5.210797	-1.303433
H	7.543639	-0.248216	2.629764	O	1.816861	0.764544	-1.238563
H	5.150087	-0.605052	2.116627	N	1.756794	4.319169	-0.945234
H	6.225037	-2.573439	-1.545951	C	-0.242019	3.104725	-1.768045
H	8.623518	-2.217758	-1.039181	O	-0.960481	2.133162	-2.013253
H	9.294154	-1.050561	1.053254	O	-0.723713	4.394824	-1.874935
C	4.104793	-1.830349	-0.103893	C	-2.081119	4.514521	-2.294412
C	3.081063	-1.517027	0.662970	H	-2.252883	5.583127	-2.438163

H	-2.252740	3.974889	-3.230317	H	1.161708	3.803035	0.232346
H	-2.764923	4.125999	-1.535052	H	-0.306202	2.524871	1.945736
C-1				H	-1.090574	4.029966	2.469869
C	-5.365377	0.862174	1.478225	H	-2.070463	2.682689	1.885702
C	-6.405372	-0.015729	1.044768	H	-2.165155	4.143075	-3.246758
H	-7.308268	0.276247	0.524941	H	-0.717634	4.916493	-2.581971
C	-6.014977	-1.350179	1.367535	H	-0.683941	4.214279	-4.199855
H	-6.571443	-2.247665	1.131264	H	1.244531	2.890019	-3.768876
C	-4.735104	-1.299873	1.992932	H	1.422211	3.462686	-2.097073
H	-4.153128	-2.147302	2.320910	H	1.358749	1.738846	-2.418067
C	-4.333019	0.069394	2.061022	H	-0.714538	0.615014	-3.180115
H	-3.388581	0.430382	2.443731	H	-2.203960	1.511862	-3.528358
C	-3.432910	0.561717	-1.229216	H	-0.776183	1.730467	-4.551443
C	-4.706356	0.277315	-1.829559	C	-1.469934	-2.089666	1.199980
C	-4.913615	-1.129826	-1.862372	C	-1.267454	-1.427019	2.419721
H	-5.803958	-1.632244	-2.216253	C	-1.916624	-3.417273	1.200198
C	-3.774864	-1.744237	-1.288587	C	-1.531315	-2.083336	3.622020
H	-3.614177	-2.804533	-1.161519	H	-0.858705	-0.420843	2.431523
C	-2.841689	-0.717531	-0.908736	C	-2.167982	-4.073670	2.405918
Fe	-4.632016	-0.479851	0.089649	H	-2.053340	-3.945095	0.262065
H	-5.343619	1.935795	1.341032	C	-1.981127	-3.405670	3.619027
H	-5.430767	1.009290	-2.151481	H	-1.369843	-1.561718	4.560886
C	-2.978774	1.981275	-0.903651	H	-2.507028	-5.105739	2.397504
H	-3.204938	2.139734	0.155326	H	-2.177024	-3.917745	4.556830
C	-3.850633	2.973872	-1.700518	C	-0.681873	-2.391585	-1.597333
H	-4.883608	2.925000	-1.338054	C	0.223247	-3.412100	-1.273843
H	-3.523683	4.002372	-1.596415	C	-1.083877	-2.237238	-2.931756
H	-3.861371	2.727565	-2.765025	C	0.710940	-4.264052	-2.263028
P	-1.117587	2.316074	-0.860822	H	0.554208	-3.537578	-0.250062
P	-1.173973	-1.148018	-0.343321	C	-0.589896	-3.087532	-3.921016
C	-0.584589	2.728122	-2.639735	H	-1.785711	-1.455471	-3.200142
C	-1.022971	3.822564	0.318198	C	0.309387	-4.102024	-3.589744
C	-2.120059	4.891941	0.177245	H	1.421997	-5.040274	-1.998171
C	0.342565	4.519432	0.171086	H	-0.910477	-2.955831	-4.950657
C	-1.122731	3.216407	1.733111	H	0.697938	-4.760674	-4.360993
C	-1.112631	1.576509	-3.518194	Pd	0.327321	0.499939	-0.109141
C	-1.078961	4.079404	-3.184493	H	2.496665	-0.282714	-1.723842
C	0.954633	2.704774	-2.725989	C	4.897687	-4.079343	-1.048096
H	-3.117729	4.507190	0.406749	C	3.798684	-3.271407	-0.770660
H	-1.908152	5.685457	0.905012	C	3.773815	-1.923345	-1.168607
H	-2.137050	5.357551	-0.811996	C	4.884564	-1.422742	-1.869021
H	0.415904	5.072510	-0.770827	C	5.989843	-2.228099	-2.138576
H	0.446836	5.248437	0.985291	C	6.002526	-3.562519	-1.731034
				H	4.892781	-5.119611	-0.731493

H	2.954521	-3.679370	-0.228841	C	-2.378233	-2.169659	-1.135268
H	4.887733	-0.380492	-2.173600	C	-3.687863	-2.728931	-1.319509
H	6.842926	-1.809634	-2.666358	C	-4.452347	-2.553463	-0.132264
H	6.860727	-4.194344	-1.943555	H	-5.487874	-2.835804	0.004325
C	2.627019	-1.021356	-0.932994	C	-3.635445	-1.881028	0.809986
C	1.775068	-0.978282	0.110005	H	-3.919796	-1.570643	1.804751
C	1.900260	-1.751363	1.343744	C	-2.346630	-1.644766	0.211270
H	1.003690	-2.234347	1.722234	Fe	-3.834902	-0.717993	-0.867852
C	3.014345	-1.835243	2.087321	H	-3.084449	0.462077	-3.321328
H	3.028378	-2.399960	3.016079	H	-4.062562	-3.168884	-2.231303
H	3.935931	-1.347463	1.788495	C	-1.369547	-2.106267	-2.281065
C	4.288110	1.843409	0.274001	H	-1.620133	-1.198491	-2.834890
C	5.190007	1.550837	1.333433	C	-1.613086	-3.289150	-3.240554
C	6.576527	1.554257	1.122585	H	-2.591169	-3.186590	-3.721570
C	7.035067	1.859538	-0.153163	H	-0.874449	-3.333427	-4.034888
C	6.148594	2.168576	-1.208859	H	-1.602634	-4.242768	-2.707154
C	4.775571	2.162545	-0.999493	P	0.443830	-1.722456	-1.885667
C	2.941952	1.710672	0.791161	P	-0.960327	-0.985946	1.164561
C	3.080211	1.368372	2.148874	C	1.400516	-3.356173	-1.730750
H	7.268699	1.322033	1.927364	C	0.934579	-0.738129	-3.464343
H	8.105232	1.862290	-0.342389	C	0.305859	-1.225767	-4.782567
H	6.550544	2.408481	-2.189151	C	2.462398	-0.718335	-3.654610
H	4.076879	2.389638	-1.799930	C	0.454482	0.706176	-3.197720
H	4.793583	0.882264	3.312286	C	0.656661	-4.194798	-0.673845
O	1.867238	1.906921	0.081094	C	1.567733	-4.178022	-3.021030
N	4.455030	1.303964	2.462855	C	2.798060	-3.027350	-1.164957
C	2.075112	0.968537	3.082920	H	-0.786752	-1.176266	-4.785950
O	0.857098	0.967663	2.906714	H	0.658639	-0.568944	-5.587671
O	2.625270	0.535224	4.264481	H	0.609915	-2.243644	-5.040610
C	1.696145	-0.027914	5.188214	H	2.848569	-1.696443	-3.954013
H	2.278989	-0.289247	6.073196	H	2.698239	-0.014201	-4.463736
H	0.913149	0.690711	5.446995	H	2.966157	-0.384237	-2.748925
H	1.230702	-0.923440	4.763522	H	1.000025	1.149553	-2.362510
C-2				H	0.629472	1.314315	-4.095184
C	-3.707629	0.609476	-2.448775	H	-0.617533	0.753925	-2.970849
C	-5.052529	0.155586	-2.295713	H	0.627362	-4.590480	-3.389008
H	-5.624157	-0.400751	-3.026741	H	2.031219	-3.601397	-3.825040
C	-5.491238	0.521445	-0.987325	H	2.231823	-5.024976	-2.805523
H	-6.453689	0.286349	-0.552306	H	3.306483	-3.973998	-0.937571
C	-4.419156	1.195401	-0.331863	H	3.415358	-2.478692	-1.878516
H	-4.420616	1.563547	0.683445	H	2.748869	-2.437474	-0.248007
C	-3.314386	1.247283	-1.235382	H	0.659567	-3.697767	0.296649
H	-2.337512	1.654714	-1.022700	H	-0.381001	-4.408345	-0.946542
				H	1.174006	-5.155176	-0.554462

C	-1.819939	0.092045	2.381772	C	6.272777	3.505289	-0.403199
C	-2.084885	1.426750	2.047041	C	5.893671	4.288599	-1.485982
C	-2.252906	-0.400753	3.620139	C	4.756605	3.980997	-2.267105
C	-2.796689	2.248361	2.919759	C	3.979952	2.868916	-1.972483
H	-1.718512	1.829041	1.110748	C	3.739610	0.862902	-0.328635
C	-2.963430	0.423367	4.495458	C	4.544649	0.512865	0.778093
H	-2.037282	-1.425821	3.902122	H	7.147483	3.753773	0.191722
C	-3.241938	1.744997	4.144613	H	6.487535	5.163383	-1.737640
H	-2.988921	3.279564	2.642008	H	4.494294	4.624398	-3.101921
H	-3.294521	0.030549	5.452820	H	3.102144	2.616066	-2.559839
H	-3.792560	2.385387	4.828065	H	6.298431	1.404415	1.604284
C	-0.433836	-2.426301	2.178220	O	2.692027	0.287463	-0.833820
C	0.854671	-2.390824	2.730565	N	5.590293	1.454368	0.891327
C	-1.236840	-3.558293	2.378115	C	4.423766	-0.572618	1.702037
C	1.332297	-3.472602	3.468700	O	3.567902	-1.453791	1.711391
H	1.511325	-1.552620	2.533324	O	5.419553	-0.534613	2.651937
C	-0.755214	-4.636856	3.120807	C	5.370553	-1.582932	3.618933
H	-2.226690	-3.608993	1.938955	H	6.236875	-1.430503	4.264897
C	0.529528	-4.596947	3.666906	H	4.448430	-1.529254	4.206721
H	2.343835	-3.437995	3.861594	H	5.422660	-2.563459	3.136592
H	-1.381770	-5.513057	3.263517				
H	0.905590	-5.444627	4.233187				
Pd	0.831509	-0.258022	0.032701	TS-D-1-R			
H	-0.804512	3.293952	-1.705382	C	5.703438	-0.649130	1.457156
C	-2.555868	5.904838	1.671703	C	6.625131	0.332931	0.982315
C	-1.554132	5.089821	1.152062	H	7.520568	0.139078	0.406536
C	-1.702409	4.488349	-0.109438	C	6.129037	1.617779	1.357402
C	-2.876752	4.737753	-0.836497	H	6.582181	2.568926	1.110429
C	-3.882698	5.549283	-0.312845	C	4.901507	1.432814	2.056745
C	-3.728578	6.135077	0.944442	H	4.260389	2.212874	2.437446
H	-2.421755	6.365466	2.647017	C	4.637836	0.030588	2.117104
H	-0.644998	4.904500	1.716969	H	3.760621	-0.426323	2.553389
H	-3.004286	4.277280	-1.812717	C	3.502402	-0.450196	-1.083655
H	-4.787874	5.722733	-0.888326	C	4.730416	-0.148109	-1.763297
H	-4.509750	6.770137	1.352446	C	4.902729	1.263022	-1.831005
C	-0.681636	3.576086	-0.657141	H	5.759488	1.778143	-2.244736
C	0.310067	3.049387	0.030277	C	3.785657	1.862416	-1.199377
C	1.285671	2.491072	0.705796	H	3.605362	2.920969	-1.079006
H	2.262661	2.974732	0.653211	C	2.899696	0.823327	-0.750520
C	1.206567	1.209055	1.476174	Fe	4.758903	0.639499	0.142339
H	2.174579	0.959236	1.911252	H	5.779131	-1.717696	1.303243
H	0.451182	1.249826	2.259426	H	5.452641	-0.868876	-2.114168
C	4.342134	2.060424	-0.886872	C	3.086280	-1.870046	-0.708034
C	5.483469	2.384468	-0.102809	H	3.170325	-1.941382	0.382314
				C	4.095306	-2.867319	-1.308397

H	5.086302	-2.696687	-0.872871	C	0.978546	2.490645	-2.565555
H	3.823770	-3.899578	-1.115768	C	-0.752168	4.457321	-1.606168
H	4.185655	-2.743879	-2.389953	H	-0.432171	3.592392	0.330373
P	1.246966	-2.288193	-0.907245	C	0.404309	3.404364	-3.446015
P	1.242046	1.189374	-0.103200	H	1.643876	1.723246	-2.948165
C	0.976184	-2.721838	-2.736688	C	-0.465051	4.390449	-2.968145
C	1.013894	-3.786833	0.256193	H	-1.445997	5.200656	-1.226344
C	2.091016	-4.884020	0.252483	H	0.634134	3.345823	-4.506400
C	-0.347130	-4.435853	-0.057831	H	-0.918933	5.097224	-3.657029
C	0.949560	-3.181699	1.676015	Pd	-0.231370	-0.522710	-0.135330
C	1.627275	-1.579906	-3.543091	H	-2.028743	1.456161	-1.317206
C	1.538044	-4.077886	-3.192144	C	-4.489285	4.156635	1.425663
C	-0.537025	-2.684034	-3.027529	C	-3.532008	3.161143	1.255717
H	3.046335	-4.531745	0.651852	C	-3.290247	2.599715	-0.013913
H	1.751643	-5.696780	0.907695	C	-4.037313	3.090455	-1.102861
H	2.257575	-5.314024	-0.738788	C	-5.002116	4.079116	-0.928846
H	-0.318507	-4.992874	-0.999769	C	-5.235383	4.620493	0.337272
H	-0.587185	-5.147279	0.741957	H	-4.654054	4.577667	2.414616
H	-1.146970	-3.696506	-0.094160	H	-2.954072	2.805812	2.102972
H	0.092774	-2.514432	1.784760	H	-3.860300	2.670227	-2.088742
H	0.831962	-3.993456	2.404993	H	-5.573260	4.429582	-1.784935
H	1.866059	-2.635811	1.934122	H	-5.985204	5.394665	0.475025
H	2.614554	-4.163647	-3.036347	C	-2.279015	1.575749	-0.264668
H	1.049522	-4.909895	-2.677938	C	-1.614302	0.806229	0.632572
H	1.348090	-4.201808	-4.266631	C	-1.961159	0.335817	1.911086
H	-0.692285	-2.862027	-4.100196	H	-1.189648	0.057021	2.622546
H	-1.091941	-3.440677	-2.471682	C	-3.304330	-0.070550	2.147719
H	-0.970215	-1.715810	-2.766685	H	-3.550036	-0.347720	3.174837
H	1.249294	-0.604896	-3.217740	H	-4.074349	0.554285	1.697120
H	2.716391	-1.564768	-3.458293	C	-4.313123	-0.961737	-0.966580
H	1.374392	-1.700890	-4.604290	C	-5.502734	-0.928110	-0.201074
C	1.528890	1.949724	1.538336	C	-6.686098	-0.406537	-0.734716
C	1.403512	1.129867	2.667521	C	-6.660779	0.047346	-2.050537
C	1.907186	3.288616	1.704347	C	-5.488418	-0.012791	-2.831720
C	1.658427	1.636194	3.941688	C	-4.311885	-0.520364	-2.295302
H	1.101013	0.094434	2.538381	C	-3.266486	-1.513163	-0.126852
C	2.144059	3.800223	2.980675	C	-3.855596	-1.636657	1.223842
H	2.008700	3.933361	0.837920	H	-7.596406	-0.361801	-0.143438
C	2.023512	2.974612	4.101483	H	-7.568018	0.458261	-2.484737
H	1.560423	0.989753	4.809149	H	-5.509169	0.349232	-3.855463
H	2.426368	4.842607	3.099538	H	-3.392954	-0.557564	-2.873191
H	2.210669	3.373693	5.094179	H	-5.854425	-1.277442	1.831651
C	0.702481	2.555037	-1.188952	O	-2.088592	-1.824850	-0.452323
C	-0.178979	3.542218	-0.720920	N	-5.272401	-1.503075	1.036977

C	-3.385879	-2.689148	2.150211	H	-3.353524	-1.605928	-3.955430
O	-2.234025	-3.053441	2.282753	H	-2.238842	-2.120345	-5.212848
O	-4.399083	-3.146572	2.934485	H	-2.748108	-3.279150	-3.986119
C	-4.008083	-4.108184	3.921088	H	-0.227003	-3.614747	-3.967953
H	-4.921860	-4.366116	4.457797	H	0.160030	-2.184739	-4.928077
H	-3.579572	-4.995186	3.446719	H	0.875921	-2.388585	-3.323480
H	-3.267547	-3.682544	4.604552	H	-0.230401	0.156779	-3.054098
TS-D-1-S				H	-0.975780	-0.081441	-4.648734
C	-5.315233	1.262503	-0.882567	H	-1.979419	0.285353	-3.242155
C	-6.359290	0.921993	0.030522	H	-3.081090	-4.559727	-1.825612
H	-7.102035	0.147669	-0.110274	H	-1.657916	-4.844381	-2.839034
C	-6.216677	1.747843	1.185934	H	-1.928039	-5.826026	-1.400516
H	-6.833745	1.708691	2.073952	H	0.327135	-5.376418	-0.673799
C	-5.085126	2.595157	0.985794	H	0.708438	-4.274334	-2.005043
H	-4.692650	3.314738	1.689548	H	0.923833	-3.744751	-0.340256
C	-4.529811	2.296419	-0.293985	H	-1.053423	-3.233194	1.150103
H	-3.644176	2.745163	-0.719705	H	-2.692566	-3.684727	0.653390
C	-3.257697	-0.984187	0.482006	H	-1.466183	-4.936424	0.908336
C	-4.370852	-1.423298	1.274477	C	-1.198118	2.490150	0.465566
C	-4.381581	-0.708742	2.506518	C	-0.796292	2.939134	-0.796944
H	-5.127685	-0.800140	3.284760	C	-1.775144	3.390206	1.373189
C	-3.280647	0.185360	2.498366	C	-1.001790	4.272317	-1.161914
H	-3.000187	0.868270	3.287328	H	-0.286574	2.263331	-1.472837
C	-2.569150	0.018223	1.261899	C	-1.982536	4.717561	1.005564
Fe	-4.516382	0.604154	0.910714	H	-2.061439	3.049650	2.363469
H	-5.131578	0.796325	-1.841841	C	-1.603320	5.157963	-0.267725
H	-5.123852	-2.136822	0.976956	H	-0.672529	4.611847	-2.139406
C	-3.008564	-1.405397	-0.959638	H	-2.434832	5.411322	1.709225
H	-3.032754	-0.487273	-1.555791	H	-1.764835	6.194408	-0.551339
C	-4.185858	-2.288757	-1.412919	C	-0.131433	0.763729	2.500553
H	-5.114844	-1.712859	-1.339314	C	0.813143	1.762000	2.783517
H	-4.089092	-2.638070	-2.434100	C	-0.334856	-0.262972	3.434767
H	-4.291641	-3.166227	-0.772495	C	1.525068	1.739326	3.981822
P	-1.255692	-2.020013	-1.427749	H	1.002026	2.544032	2.058736
P	-0.954060	0.724059	0.860988	C	0.370927	-0.275122	4.637576
C	-1.176528	-3.857684	-0.945464	H	-1.047711	-1.053696	3.224054
C	-1.248362	-1.785556	-3.336600	C	1.305039	0.724323	4.914628
C	-2.479529	-2.233000	-4.147712	H	2.260383	2.513439	4.181198
C	-0.031331	-2.539826	-3.907437	H	0.193687	-1.070989	5.356047
C	-1.091917	-0.266481	-3.572844	H	1.860221	0.709627	5.848145
C	-1.633433	-3.921686	0.526374	Pd	0.402949	-0.573407	-0.601719
C	-2.020745	-4.810993	-1.808318	H	3.863719	-2.451994	-1.414378
C	0.286840	-4.328896	-1.000504	C	2.167453	-2.762015	2.822187
				C	2.028313	-2.333949	1.505103

C	3.028223	-2.590211	0.541865	H	2.662378	-4.241085	-3.819147
C	4.173511	-3.291928	0.979341	C	1.741337	-2.246234	-3.388795
C	4.317859	-3.709256	2.297132	H	0.693192	-2.421949	-3.576329
C	3.311358	-3.450181	3.231752	C	2.311934	-1.027815	-2.908980
H	1.382021	-2.539122	3.536207	H	1.771499	-0.118959	-2.678074
H	1.135436	-1.783066	1.213846	C	2.769183	-2.054169	0.463256
H	4.966166	-3.492139	0.262368	C	3.643900	-3.150860	0.150432
H	5.218672	-4.238204	2.597844	C	2.882240	-4.238914	-0.359500
H	3.418158	-3.776443	4.262613	H	3.277187	-5.180466	-0.718084
C	2.989223	-2.140273	-0.837489	C	1.525866	-3.829982	-0.395167
C	2.088675	-1.362953	-1.508282	H	0.691919	-4.403460	-0.772507
C	2.424871	-0.555043	-2.611811	C	1.437151	-2.484895	0.106979
H	1.692167	-0.299284	-3.367599	Fe	2.659408	-2.572070	-1.556477
C	3.652221	0.162014	-2.609862	H	4.436068	-0.524741	-2.392622
H	3.947357	0.617930	-3.557682	H	4.721097	-3.136149	0.248503
H	4.485315	-0.314237	-2.094171	C	3.361622	-0.798449	1.098643
C	4.151763	0.921723	0.650142	H	4.088599	-0.445815	0.363159
C	5.338630	1.351280	0.007732	C	4.189685	-1.202622	2.336192
C	6.587819	1.142782	0.597034	H	4.897070	-1.994081	2.074357
C	6.619716	0.512734	1.841855	H	4.768570	-0.361114	2.714876
C	5.442762	0.101767	2.495921	H	3.561049	-1.585083	3.143149
C	4.199343	0.311395	1.909933	P	2.297687	0.779188	1.323680
C	3.044892	1.237445	-0.226320	P	-0.136323	-1.607576	0.283717
C	3.644189	1.699146	-1.494787	C	1.939666	1.048174	3.199461
H	7.503125	1.462264	0.106193	C	3.577457	2.071657	0.729453
H	7.581220	0.335955	2.316761	C	5.018005	1.918389	1.250160
H	5.508463	-0.397961	3.457435	C	3.080902	3.479551	1.092876
H	3.285018	-0.014071	2.390655	C	3.605691	1.912357	-0.802956
H	5.687750	2.051683	-1.935178	C	1.111696	-0.167300	3.658811
O	1.810529	1.139180	0.009589	C	3.121072	1.266112	4.160836
N	5.014825	1.983961	-1.184434	C	1.036231	2.296424	3.329494
C	2.911033	2.659952	-2.351180	H	5.474977	0.968907	0.956690
O	1.724294	2.607647	-2.614567	H	5.633943	2.716002	0.813794
O	3.747435	3.576313	-2.905681	H	5.088075	2.010375	2.336000
C	3.118457	4.499154	-3.802193	H	3.244510	3.695893	2.151905
H	3.916771	5.149396	-4.161782	H	3.639309	4.223882	0.514437
H	2.647206	3.970221	-4.635643	H	2.021842	3.616896	0.865784
H	2.355904	5.083471	-3.279692	H	2.609027	1.927841	-1.245863
TS-D-1-isomer				H	4.201060	2.721510	-1.244157
				H	4.073276	0.968926	-1.092651
C	3.714272	-1.244126	-2.751376	H	3.755260	0.389597	4.280881
C	4.007778	-2.589785	-3.124222	H	3.744962	2.111429	3.860188
H	4.977326	-3.068107	-3.073598	H	2.712817	1.507002	5.151480
C	2.784918	-3.207897	-3.521176	H	0.535325	2.265035	4.305849

H	1.606004	3.225333	3.281566	O	-2.547390	1.577480	-2.901505
H	0.265121	2.322525	2.561126	O	-3.683409	3.017236	-1.578882
H	0.167875	-0.227350	3.115098	C	-4.870672	2.712348	-2.327484
H	1.635508	-1.116351	3.527215	H	-5.641569	3.375491	-1.934737
H	0.879705	-0.063270	4.726911	H	-4.710036	2.891039	-3.393087
C	-1.129640	-2.202430	-1.143487	H	-5.148034	1.667239	-2.167871
C	-1.232569	-1.365789	-2.264269	C	-3.060435	0.314164	-0.188570
C	-1.805792	-3.430357	-1.139439	H	-2.862333	-0.061113	-1.184479
C	-1.997764	-1.753963	-3.364271	C	-4.370286	-0.105879	0.301714
H	-0.736643	-0.398675	-2.273592	C	-4.967930	-1.210800	-0.346759
C	-2.562391	-3.821699	-2.245220	C	-5.103725	0.520652	1.331086
H	-1.755860	-4.073424	-0.266711	C	-6.218401	-1.687827	0.037556
C	-2.661144	-2.983059	-3.358853	H	-4.425765	-1.699060	-1.152497
H	-2.088165	-1.077474	-4.208111	C	-6.357693	0.048351	1.702647
H	-3.083024	-4.775429	-2.231535	H	-4.682531	1.378848	1.839005
H	-3.263473	-3.282193	-4.212373	C	-6.922674	-1.063859	1.068638
C	-0.887785	-2.495668	1.703214	H	-6.644691	-2.547086	-0.473668
C	-2.272132	-2.409914	1.923225	H	-6.903031	0.553755	2.495836
C	-0.098385	-3.188780	2.632246	H	-7.898840	-1.432002	1.371239
C	-2.849909	-2.991286	3.050443	C	-2.087514	1.108014	0.343409
H	-2.901787	-1.897158	1.208748	C	-2.038039	1.685825	1.689403
C	-0.677896	-3.767061	3.762101	C	-2.277359	1.024483	2.836058
H	0.970071	-3.280666	2.467610	H	-1.725067	2.726273	1.738545
C	-2.053801	-3.667253	3.978037	H	-2.164413	1.522945	3.794604
H	-3.923768	-2.913584	3.196696	H	-2.575290	-0.017714	2.852584
H	-0.052574	-4.303188	4.471041				
H	-2.502720	-4.120783	4.857292	TS-D-2-R			
Pd	0.074450	0.709301	0.341051	C	3.181874	-2.775869	-2.528098
C	0.494528	3.805421	-1.314305	C	2.447998	-3.692009	-3.341154
C	-0.414302	4.532075	-0.519519	H	2.704956	-4.727142	-3.525614
C	-0.136763	5.839689	-0.117243	C	1.282026	-3.018297	-3.818047
C	1.037569	6.428714	-0.588886	H	0.497936	-3.457320	-4.421124
C	1.916641	5.737161	-1.439452	C	1.298875	-1.690193	-3.302204
C	1.648240	4.420567	-1.805588	H	0.541537	-0.934102	-3.437940
C	-0.087135	2.483239	-1.599862	C	2.468535	-1.540804	-2.504817
C	-1.472279	2.517030	-0.953746	H	2.707397	-0.640495	-1.965886
H	-0.828160	6.391457	0.513331	C	1.008247	-3.042573	0.331817
H	1.263675	7.453347	-0.306970	C	1.299686	-4.365211	-0.137491
H	2.806900	6.234820	-1.811840	C	0.309047	-4.759872	-1.081422
H	2.308440	3.874804	-2.469817	H	0.292616	-5.686774	-1.639936
H	-2.445710	4.197210	-0.156920	C	-0.601325	-3.676923	-1.228667
O	0.355465	1.608727	-2.359653	H	-1.437766	-3.626170	-1.910899
N	-1.537842	3.763141	-0.248951	C	-0.176310	-2.610536	-0.365188
C	-2.583560	2.306842	-1.935607	Fe	1.281221	-3.073499	-1.753372

H	4.101899	-2.994963	-2.004175	H	-2.115637	1.155022	-4.390604
H	2.150107	-4.957386	0.177627	H	-4.875262	-1.906660	-3.134857
C	1.707353	-2.510823	1.570617	H	-4.181336	-0.187149	-4.791286
H	2.712318	-2.929655	1.509966	C	-2.237485	-1.474890	1.175531
C	1.045920	-3.192095	2.786886	C	-3.032274	-0.471013	1.748675
H	1.106731	-4.279020	2.660782	C	-2.388406	-2.793591	1.630776
H	1.544259	-2.935509	3.723358	C	-3.954983	-0.775492	2.747108
H	-0.010919	-2.935294	2.868185	H	-2.939366	0.551000	1.403997
P	2.052739	-0.623975	1.703264	C	-3.306204	-3.096525	2.638083
P	-0.996639	-1.022518	-0.112203	H	-1.791788	-3.586465	1.194613
C	1.487860	0.075271	3.419827	C	-4.090926	-2.088975	3.199497
C	3.977688	-0.734910	1.774560	H	-4.576195	0.012938	3.157831
C	4.576939	-1.759689	2.759320	H	-3.409584	-4.123606	2.978112
C	4.583173	0.642440	2.088424	H	-4.808363	-2.325590	3.980355
C	4.402508	-1.141065	0.353960	Pd	0.673619	0.590813	0.123823
C	-0.013848	-0.198189	3.617034	H	-4.099786	1.428975	-1.757519
C	2.241841	-0.387304	4.677421	C	-6.662691	1.602409	2.076897
C	1.654699	1.609558	3.315223	C	-5.587813	2.024188	1.299735
H	4.259585	-2.787403	2.559103	C	-5.280205	1.374643	0.093165
H	5.669822	-1.742043	2.650971	C	-6.086209	0.305448	-0.322704
H	4.350175	-1.535542	3.801319	C	-7.157949	-0.120950	0.460289
H	4.509618	0.884186	3.152199	C	-7.449438	0.522693	1.663710
H	5.648706	0.636564	1.828886	H	-6.891006	2.117826	3.006151
H	4.113177	1.443154	1.517444	H	-4.971688	2.860083	1.619255
H	4.058419	-0.413950	-0.379037	H	-5.849285	-0.200685	-1.253170
H	5.498090	-1.189918	0.297728	H	-7.765529	-0.959292	0.130643
H	4.007204	-2.119329	0.069279	H	-8.286190	0.191973	2.272387
H	2.249509	-1.471995	4.803212	C	-4.114805	1.768942	-0.722008
H	3.274740	-0.032493	4.690874	C	-3.084980	2.432341	-0.255829
H	1.745307	0.038662	5.559776	C	-2.079355	3.122384	0.252720
H	1.232426	2.072959	4.217036	H	-2.136738	4.208235	0.168098
H	2.697445	1.918067	3.240495	C	-0.874985	2.598209	0.866661
H	1.132579	2.008912	2.445539	H	-0.293939	3.309481	1.440906
H	-0.586987	0.026088	2.718337	H	-0.965031	1.633139	1.353228
H	-0.225408	-1.229615	3.897995	C	3.163947	2.454277	-0.808692
H	-0.389842	0.444733	4.423455	C	3.086967	3.569864	0.049276
C	-2.035801	-0.800481	-1.608773	C	4.233048	4.149769	0.589458
C	-1.648448	0.172087	-2.541290	C	5.470195	3.629924	0.195994
C	-3.208156	-1.539318	-1.822477	C	5.559893	2.558598	-0.705092
C	-2.419542	0.387899	-3.684802	C	4.403634	1.963961	-1.213089
H	-0.759784	0.773060	-2.368525	C	1.789698	2.109917	-1.233865
C	-3.971421	-1.325321	-2.970852	C	0.924877	3.167125	-0.623218
H	-3.531780	-2.268402	-1.085583	H	4.170159	4.998021	1.265318
C	-3.579086	-0.359556	-3.903311	H	6.379435	4.078668	0.585850

H	6.535694	2.193743	-1.011009	C	0.024054	3.220198	-2.912456
H	4.456320	1.150156	-1.929026	C	-1.765188	2.041572	-1.679482
H	1.496258	4.912282	0.375210	C	2.651019	-0.898103	-3.265925
O	1.439792	1.306395	-2.137090	C	1.810763	0.824571	-4.881251
N	1.752728	3.951011	0.202029	C	3.005667	1.514436	-2.794104
C	-0.057475	3.839235	-1.485478	H	-2.221261	0.848165	-4.092842
O	-0.679356	3.344097	-2.400877	H	-2.168150	2.597228	-4.297750
O	-0.201718	5.154848	-1.122046	H	-0.899503	1.601567	-5.010212
C	-1.131294	5.895451	-1.924003	H	0.693949	3.259922	-3.774677
H	-1.158432	6.897290	-1.493861	H	-0.682497	4.054182	-3.005364
H	-0.794897	5.932561	-2.963394	H	0.611336	3.385290	-2.011928
H	-2.121133	5.432401	-1.890787	H	-1.259501	2.236229	-0.731761
				H	-2.442604	2.879885	-1.889673
				H	-2.388976	1.150961	-1.552277
TS-D-2-S				H	1.216009	0.073537	-5.403100
C	-2.930804	-1.536923	0.020772	H	1.347451	1.801410	-5.037037
C	-3.623794	-2.458245	-0.816730	H	2.794864	0.852597	-5.367950
H	-4.049387	-2.238607	-1.786938	H	3.963538	1.435083	-3.325958
C	-3.614864	-3.733111	-0.172811	H	2.651416	2.541974	-2.895923
H	-4.029048	-4.650145	-0.570688	H	3.182607	1.323980	-1.731539
C	-2.919507	-3.593735	1.066581	H	2.919519	-1.125078	-2.235078
H	-2.717510	-4.387112	1.774104	H	2.005718	-1.698454	-3.635431
C	-2.500396	-2.235843	1.185402	H	3.576844	-0.919862	-3.855566
H	-1.923344	-1.814605	1.994546	C	1.239150	-2.244505	2.114660
C	-0.338738	-2.342006	-1.909458	C	2.080684	-1.568462	3.016409
C	-0.959577	-3.541238	-2.399568	C	0.318800	-3.169520	2.624796
C	-0.685037	-4.624938	-1.523896	C	2.010745	-1.822144	4.383363
H	-1.059323	-5.635353	-1.622655	H	2.754775	-0.798546	2.658989
C	0.119255	-4.127040	-0.472054	C	0.250142	-3.421816	3.997826
H	0.505009	-4.699798	0.358185	H	-0.361438	-3.682209	1.961359
C	0.346827	-2.720937	-0.680669	C	1.095681	-2.753544	4.881733
Fe	-1.680570	-3.093845	-0.527257	H	2.657418	-1.267778	5.056133
H	-2.742761	-0.495246	-0.192376	H	-0.472948	-4.142382	4.371729
H	-1.589314	-3.606857	-3.273320	H	1.035828	-2.947001	5.949282
C	-0.555286	-1.030065	-2.681871	C	3.109926	-2.191110	-0.037379
H	-1.545538	-0.675284	-2.378797	C	4.131151	-1.251251	0.176391
C	-0.651866	-1.361492	-4.190992	C	3.431256	-3.450018	-0.560310
H	-1.589053	-1.882833	-4.412229	C	5.454990	-1.579667	-0.115844
H	-0.636979	-0.471328	-4.810025	H	3.880691	-0.259640	0.542200
H	0.168093	-2.009476	-4.508216	C	4.755401	-3.767662	-0.863197
P	0.463051	0.524406	-2.261956	H	2.649232	-4.177531	-0.747851
P	1.388530	-1.674212	0.364909	C	5.770120	-2.835078	-0.638858
C	2.012407	0.497034	-3.391269	H	6.237466	-0.845037	0.052962
C	-0.755521	1.900660	-2.831027	H	4.993804	-4.744359	-1.275949
C	-1.545395	1.707197	-4.135341				

H	6.800486	-3.084330	-0.877551	C	-4.963497	-1.050391	-2.310290
Pd	1.041203	0.590895	0.036058	C	-6.245125	-0.459694	-2.098076
H	-3.540659	3.335751	0.465047	H	-7.131544	-0.972252	-1.748688
C	-6.324208	-0.307989	0.909662	C	-6.137191	0.935017	-2.379394
C	-5.202511	0.419864	1.292761	H	-6.926908	1.667082	-2.274729
C	-4.862208	1.609107	0.628143	C	-4.790058	1.208042	-2.759756
C	-5.683686	2.055830	-0.417581	H	-4.382702	2.181511	-2.989820
C	-6.809323	1.327022	-0.799945	C	-4.062431	-0.022295	-2.715816
C	-7.132548	0.140771	-0.139352	H	-3.006311	-0.156513	-2.907631
H	-6.566401	-1.231394	1.427932	C	-3.910301	-0.424620	0.799953
H	-4.569265	0.065443	2.099924	C	-5.296880	-0.170101	1.077200
H	-5.427786	2.975685	-0.937916	C	-5.571499	1.216671	0.914123
H	-7.432603	1.685545	-1.614543	H	-6.540984	1.687415	1.010115
H	-8.008058	-0.429313	-0.436703	C	-4.361526	1.852249	0.539686
C	-3.645506	2.371978	0.967349	H	-4.221981	2.899741	0.312584
C	-2.678568	1.952083	1.749007	C	-3.323201	0.859279	0.475448
C	-1.733107	1.433876	2.519308	Fe	-4.841375	0.411674	-0.849120
H	-1.747115	1.686057	3.579647	H	-4.711509	-2.091643	-2.156672
C	-0.638252	0.614209	2.050361	H	-6.038746	-0.916593	1.316163
H	-0.100776	0.033495	2.789726	C	-3.351169	-1.850151	0.770878
H	-0.843834	0.090424	1.119498	H	-3.485391	-2.200036	-0.256465
C	1.776946	3.738559	0.170442	C	-4.227447	-2.756848	1.661593
C	0.591509	4.335908	0.648174	H	-5.222736	-2.869694	1.217893
C	0.090235	5.507369	0.083513	H	-3.814150	-3.754449	1.769485
C	0.851286	6.119358	-0.916863	H	-4.355914	-2.331687	2.659623
C	2.075115	5.577721	-1.341062	P	-1.475570	-2.087864	0.913541
C	2.545011	4.379572	-0.799476	P	-1.585160	1.296975	0.218779
C	2.004686	2.503706	0.946072	C	-1.049417	-2.320463	2.753773
C	0.910355	2.486032	1.976653	C	-1.235834	-3.720230	-0.074282
H	-0.836506	5.952233	0.435231	C	-2.300762	-4.814828	0.114306
H	0.494355	7.044967	-1.359533	C	0.144314	-4.324462	0.247800
H	2.656478	6.094651	-2.098587	C	-1.244017	-3.302899	-1.561674
H	3.482903	3.940051	-1.121588	C	-1.725654	-1.170918	3.525393
H	-0.784968	3.729099	2.155309	C	-1.454599	-3.659740	3.391429
O	3.018662	1.757317	0.937494	C	0.476511	-2.139014	2.881937
N	0.129650	3.614696	1.741466	H	-3.294680	-4.497679	-0.215004
C	1.225677	2.103828	3.367966	H	-2.017993	-5.677216	-0.503417
O	2.111271	1.353999	3.723718	H	-2.369068	-5.165848	1.147075
O	0.384126	2.713929	4.252955	H	0.178904	-4.752141	1.253037
C	0.603344	2.354785	5.623739	H	0.339375	-5.141057	-0.460066
H	-0.158504	2.889891	6.191825	H	0.939422	-3.586821	0.140125
H	0.500090	1.274305	5.759075	H	-0.412807	-2.630602	-1.786000
H	1.603600	2.656186	5.945098	H	-1.142147	-4.199923	-2.186725
TS-D-2-isomer				H	-2.177099	-2.804805	-1.851357

H	-2.535900	-3.802345	3.423006	C	4.385725	2.078782	-0.932940
H	-1.006804	-4.516409	2.883525	C	3.267945	1.336917	-0.749683
H	-1.094639	-3.673328	4.428860	C	1.947895	1.628180	-1.004303
H	0.746142	-2.157767	3.946731	H	1.612577	2.594033	-0.619728
H	1.033238	-2.933480	2.380439	C	0.945809	0.860975	-1.685086
H	0.815678	-1.191215	2.462321	H	0.197501	1.488276	-2.162258
H	-1.402946	-0.195546	3.163324	H	1.307695	0.086767	-2.363251
H	-2.816813	-1.209785	3.475619	C	3.295932	-1.784815	-2.186025
H	-1.438627	-1.239196	4.582458	C	4.661098	-1.406632	-2.149039
C	-1.694838	2.843189	-0.768064	C	5.500267	-1.641582	-3.242926
C	-1.889470	2.740209	-2.154237	C	4.953548	-2.286346	-4.350352
C	-1.535074	4.115319	-0.202220	C	3.604263	-2.695119	-4.383475
C	-1.952998	3.879997	-2.952803	C	2.768853	-2.451517	-3.299341
H	-1.984144	1.759649	-2.606165	C	2.706266	-1.374215	-0.932811
C	-1.595982	5.257927	-1.003133	C	3.718455	-0.557045	-0.252718
H	-1.363798	4.215536	0.863805	H	6.542945	-1.337833	-3.225468
C	-1.809098	5.145051	-2.377196	H	5.586838	-2.482598	-5.211411
H	-2.100520	3.780173	-4.024638	H	3.220164	-3.198228	-5.265914
H	-1.472699	6.237357	-0.549477	H	1.725490	-2.754446	-3.306057
H	-1.850195	6.034854	-2.998734	H	5.730632	-0.230510	-0.799230
C	-1.063106	1.894479	1.880297	O	1.561656	-1.706639	-0.482239
C	0.281292	1.719456	2.242467	N	4.944166	-0.854678	-0.919933
C	-1.955818	2.454168	2.806341	C	3.710597	-0.567282	1.231798
C	0.721118	2.089442	3.513049	O	2.821803	-0.110243	1.929846
H	0.983294	1.256047	1.558671	O	4.801648	-1.176414	1.748807
C	-1.509947	2.828464	4.074168	C	4.868289	-1.183469	3.177392
H	-3.002200	2.576030	2.548147	H	5.800011	-1.693818	3.423013
C	-0.171667	2.644023	4.430962	H	4.879299	-0.161199	3.567619
H	1.759708	1.917739	3.778269	H	4.012554	-1.714692	3.602754
H	-2.211248	3.253263	4.787259				
H	0.168603	2.924149	5.424221	D			
Pd	-0.160251	-0.371850	-0.321139	C	3.161285	-1.763809	-3.005023
H	4.353955	2.823927	-1.729160	C	3.242893	-3.172375	-3.214994
C	6.947411	1.644627	1.823376	H	4.152464	-3.745164	-3.340020
C	5.723612	1.746184	1.164451	C	1.917079	-3.697427	-3.178872
C	5.662281	1.995023	-0.220373	H	1.644055	-4.740950	-3.265602
C	6.880040	2.187719	-0.906579	C	1.019045	-2.616063	-2.942530
C	8.102074	2.091871	-0.246480	H	-0.050121	-2.698481	-2.819358
C	8.143330	1.809727	1.122742	C	1.788320	-1.416325	-2.830158
H	6.967470	1.450946	2.892897	H	1.410060	-0.426180	-2.612634
H	4.794844	1.665953	1.718709	C	3.137759	-1.966212	0.370815
H	6.851726	2.398392	-1.973114	C	3.732097	-3.243913	0.092195
H	9.026647	2.234121	-0.800014	C	2.720379	-4.241835	0.037624
H	9.096839	1.732559	1.637431	H	2.868831	-5.286650	-0.201434

C	1.477659	-3.603455	0.275547	H	-0.918538	-0.407758	-1.638113
H	0.503759	-4.070188	0.257327	C	-2.890091	-3.387625	-0.149856
C	1.710256	-2.199598	0.491465	H	-1.555555	-3.230800	1.530570
Fe	2.371262	-2.774232	-1.378609	C	-3.242777	-2.881303	-1.401965
H	4.001832	-1.086071	-2.957981	H	-2.823733	-1.387888	-2.897313
H	4.781392	-3.416546	-0.100801	H	-3.466382	-4.195682	0.291769
C	4.027543	-0.721514	0.439271	H	-4.099078	-3.285581	-1.931379
H	4.366999	-0.564108	-0.588403	C	-0.014508	-1.340181	2.616527
C	5.298458	-1.039500	1.258833	C	-0.755229	-0.363523	3.299845
H	5.888444	-1.811740	0.755560	C	0.411570	-2.481207	3.308975
H	5.943200	-0.169644	1.366778	C	-1.083594	-0.535869	4.642879
H	5.057045	-1.415633	2.254566	H	-1.052913	0.538507	2.775905
P	3.206953	0.960772	0.761473	C	0.092864	-2.645805	4.658168
P	0.370411	-1.022693	0.846149	H	1.002557	-3.234368	2.798540
C	3.437091	1.418896	2.609655	C	-0.658517	-1.677576	5.325998
C	4.284639	2.092472	-0.342207	H	-1.664125	0.224664	5.157156
C	5.807312	1.888466	-0.274289	H	0.433102	-3.531927	5.187204
C	3.949813	3.555439	-0.010005	H	-0.906659	-1.808824	6.375455
C	3.827175	1.814697	-1.788230	Pd	0.863659	1.156377	0.306316
C	2.979091	0.215021	3.452435	C	-5.289314	-0.152811	-1.393780
C	4.846260	1.846361	3.052350	C	-5.672476	-0.823601	-0.218240
C	2.460635	2.576285	2.916507	C	-6.471032	-1.967698	-0.256492
H	6.104093	0.889246	-0.607081	C	-6.917182	-2.426229	-1.491630
H	6.288879	2.606758	-0.950737	C	-6.559256	-1.734222	-2.665197
H	6.217079	2.054758	0.724309	C	-5.747135	-0.602824	-2.639072
H	4.376246	3.870310	0.946311	C	-4.362393	1.128514	0.311635
H	4.363039	4.207729	-0.789205	H	-6.736149	-2.466885	0.670736
H	2.870001	3.708586	0.018196	H	-7.547039	-3.307793	-1.557319
H	2.753944	1.960990	-1.910465	H	-6.924510	-2.095177	-3.623130
H	4.341355	2.502105	-2.470807	H	-5.472105	-0.088234	-3.554960
H	4.072930	0.797176	-2.103550	H	-4.502912	1.722738	-1.696154
H	5.589174	1.057000	2.928925	N	-4.411706	0.886292	-1.130574
H	5.195032	2.735041	2.521248	C	-5.097156	-0.112214	0.922619
H	4.815443	2.099105	4.120497	O	-5.122819	-0.391476	2.105477
H	2.495612	2.793919	3.992315	C	-2.930838	1.211425	0.878921
H	2.716310	3.492484	2.380482	H	-3.047491	1.336626	1.961977
H	1.434116	2.306448	2.649587	H	-2.442617	0.251057	0.712554
H	1.944934	-0.050073	3.238647	C	-2.119244	2.321009	0.271172
H	3.593836	-0.674047	3.304906	C	-0.817498	2.278929	0.003097
H	3.034979	0.482508	4.515690	C	0.230656	3.120137	-0.430143
C	-1.072381	-1.787980	-0.001834	H	0.546600	3.932580	0.225775
C	-1.454583	-1.264453	-1.243400	H	-2.661776	3.246161	0.048541
C	-1.811117	-2.844683	0.548807	C	0.577669	3.291014	-1.851936
C	-2.525582	-1.813734	-1.944571	C	0.154776	2.373333	-2.836209

C	1.375530	4.371258	-2.268930	P	-0.751155	-1.351106	-0.402080
C	0.552048	2.507782	-4.162477	C	-3.581831	1.029225	-2.670098
H	-0.482501	1.547161	-2.537722	C	-3.379605	3.021051	-0.230734
C	1.771077	4.507106	-3.598848	C	-4.853476	3.315694	0.094406
H	1.695610	5.105006	-1.533908	C	-2.873932	4.054262	-1.250454
C	1.373173	3.570625	-4.554107	C	-2.556407	3.182536	1.065008
H	0.220809	1.778054	-4.897335	C	-3.640316	-0.487637	-2.932418
H	2.393222	5.350089	-3.889209	C	-4.937789	1.661918	-3.025483
H	1.686964	3.671134	-5.589080	C	-2.511284	1.611265	-3.619177
C	-5.147451	2.406838	0.620844	H	-5.234964	2.679727	0.898657
O	-5.673797	3.103602	-0.223487	H	-4.935994	4.354118	0.441414
O	-5.161299	2.674252	1.933150	H	-5.511045	3.209003	-0.771971
C	-5.865366	3.868107	2.311702	H	-3.508734	4.100534	-2.139549
H	-6.912598	3.805314	2.005720	H	-2.876405	5.049017	-0.788095
H	-5.782641	3.921139	3.396903	H	-1.851791	3.832541	-1.559827
H	-5.407397	4.743522	1.844088	H	-1.487826	3.062097	0.881826
				H	-2.719588	4.186552	1.476251
				H	-2.854156	2.461022	1.832789
D-S				H	-5.768652	1.222179	-2.472506
C	-2.883231	0.187289	3.698557	H	-4.947245	2.742011	-2.861763
C	-3.369375	-0.944644	4.417716	H	-5.133372	1.494075	-4.092858
H	-4.386767	-1.095066	4.754029	H	-2.786244	1.370136	-4.654489
C	-2.290948	-1.866649	4.565024	H	-2.429595	2.697516	-3.540204
H	-2.347510	-2.841663	5.030764	H	-1.525135	1.184313	-3.413165
C	-1.141460	-1.307225	3.934633	H	-2.665149	-0.954433	-2.797573
H	-0.177935	-1.784834	3.843915	H	-4.355514	-1.006927	-2.291389
C	-1.507846	-0.034791	3.394669	H	-3.944541	-0.657774	-3.973345
H	-0.876327	0.634892	2.826030	C	0.596358	-2.164481	0.558584
C	-3.501096	-1.172380	0.689868	C	1.161518	-1.447843	1.622908
C	-4.332286	-2.055852	1.460262	C	1.082703	-3.445518	0.271871
C	-3.598516	-3.223370	1.809699	C	2.153842	-2.020571	2.418375
H	-3.954422	-4.036627	2.428447	H	0.824389	-0.434323	1.813379
C	-2.297855	-3.089113	1.263842	C	2.099110	-4.008225	1.048569
H	-1.479095	-3.786237	1.372371	H	0.678009	-4.001919	-0.566814
C	-2.218137	-1.838644	0.556648	C	2.628377	-3.304922	2.130039
Fe	-2.674008	-1.530440	2.556835	H	2.565287	-1.463923	3.257523
H	-3.467435	1.049929	3.408725	H	2.475901	-4.996241	0.801642
H	-5.340681	-1.845740	1.785064	H	3.412990	-3.743996	2.738885
C	-4.028753	0.203450	0.266275	C	-0.860833	-2.403546	-1.907183
H	-3.985273	0.816284	1.170512	C	-0.140123	-1.980970	-3.036058
C	-5.526819	0.096442	-0.094386	C	-1.642601	-3.563476	-1.992433
H	-6.109958	-0.177992	0.790380	C	-0.186096	-2.715784	-4.219459
H	-5.926797	1.041666	-0.452385	H	0.433900	-1.061208	-2.985304
H	-5.709422	-0.665646	-0.855028	C	-1.695764	-4.291048	-3.182505
P	-2.954482	1.271512	-0.877084				

H	-2.221416	-3.891688	-1.135803	H	6.504194	-3.832583	-0.311166
C	-0.965518	-3.871983	-4.295922	H	6.552371	-3.517267	1.456283
H	0.378526	-2.378365	-5.083909	H	5.115767	-4.289247	0.703191
H	-2.310547	-5.185221	-3.239313				
H	-1.009234	-4.439897	-5.220988	TS-E-E-R			
Pd	-0.593398	0.877461	-0.900058	C	5.018042	1.659201	1.031570
C	4.808420	0.980702	0.773656	C	5.678203	2.702816	0.318986
C	5.684336	1.168284	-0.314352	H	6.700106	2.684220	-0.036627
C	6.676007	2.151632	-0.288680	C	4.736296	3.754751	0.114418
C	6.799882	2.943155	0.847473	H	4.916100	4.671546	-0.431587
C	5.933453	2.740490	1.939642	C	3.495914	3.357416	0.694585
C	4.936302	1.769863	1.925132	H	2.575552	3.920786	0.670704
C	4.120748	-0.620344	-0.785991	C	3.668519	2.057824	1.261320
H	7.329809	2.275129	-1.146896	H	2.914821	1.469553	1.766846
H	7.558985	3.717001	0.899450	C	3.763190	0.259903	-1.862783
H	6.040981	3.366876	2.821309	C	4.794199	1.065482	-2.453352
H	4.268623	1.638072	2.771431	C	4.258458	2.331837	-2.815638
H	3.430057	-0.517516	1.234610	H	4.810323	3.160145	-3.240081
N	3.870425	0.015908	0.500354	C	2.891653	2.342250	-2.438467
C	5.341827	0.198778	-1.350750	H	2.212844	3.177708	-2.520813
O	5.828816	0.022149	-2.451679	C	2.565707	1.070289	-1.848932
C	2.924063	-0.513212	-1.755900	Fe	4.062736	2.018006	-0.783244
H	3.266518	-0.921046	-2.713755	H	5.461051	0.723665	1.333594
H	2.119409	-1.149899	-1.386661	H	5.826232	0.762920	-2.572586
C	2.466751	0.909126	-1.884153	C	4.084797	-1.182665	-1.493390
C	1.291694	1.403855	-1.512983	H	4.949292	-1.103313	-0.828707
C	0.611635	2.633728	-1.412902	C	4.595848	-1.920067	-2.751070
H	0.242509	3.121204	-2.315494	H	5.410830	-1.349357	-3.205215
H	3.217201	1.608452	-2.263802	H	4.985659	-2.906984	-2.504419
C	0.823699	3.515116	-0.247687	H	3.818890	-2.032303	-3.509119
C	1.450505	3.042559	0.924992	P	2.880492	-2.160111	-0.385546
C	0.403024	4.855962	-0.269288	P	0.942402	0.670216	-1.153172
C	1.612292	3.869000	2.031816	C	1.971641	-3.498255	-1.436239
H	1.816847	2.020895	0.943362	C	4.154696	-3.018346	0.764011
C	0.563042	5.681727	0.842979	C	5.374536	-3.659962	0.074680
H	-0.056217	5.251615	-1.171141	C	3.448855	-4.090909	1.608144
C	1.159509	5.192632	2.005863	C	4.678957	-1.914918	1.701153
H	2.103428	3.481796	2.921515	C	1.237722	-2.768263	-2.577109
H	0.224444	6.713866	0.797318	C	2.828493	-4.641582	-2.006563
H	1.284202	5.834729	2.873209	C	0.874635	-4.140592	-0.558750
C	4.559888	-2.075857	-0.641942	H	5.973664	-2.929683	-0.476297
O	4.250038	-2.969985	-1.395546	H	6.025891	-4.085493	0.849452
O	5.377463	-2.239792	0.421388	H	5.107773	-4.469264	-0.606847
C	5.918273	-3.559683	0.570355	H	3.197867	-4.975407	1.017917

H	4.120241	-4.414036	2.413690	H	-2.821975	1.843812	-1.161179
H	2.534280	-3.709270	2.063626	H	-4.225019	3.560656	-2.263677
H	3.874247	-1.334482	2.154671	H	-5.427430	5.250519	-0.889890
H	5.269447	-2.370287	2.506420	H	-5.207396	5.214400	1.585574
H	5.339881	-1.227578	1.168106	C	-2.401391	1.502880	1.536155
H	3.599013	-4.308091	-2.700470	O	-1.976035	0.539583	0.764693
H	3.300844	-5.230952	-1.217381	H	-1.186802	-0.354760	1.267156
H	2.165982	-5.320359	-2.558832	O	-2.166142	1.612417	2.742404
H	0.270875	-4.802795	-1.192801	C	-5.477023	-0.862715	-0.996405
H	1.279042	-4.743819	0.255563	C	-6.083404	-2.098047	-0.693560
H	0.212328	-3.388331	-0.128534	C	-7.321677	-2.452387	-1.234240
H	0.783532	-3.512222	-3.243628	C	-7.972041	-1.540117	-2.058082
H	0.434560	-2.145311	-2.184493	C	-7.376002	-0.293054	-2.331725
H	1.882051	-2.131143	-3.185140	C	-6.133223	0.065719	-1.816372
C	0.307546	2.314520	-0.629906	C	-4.016361	-1.836477	0.534753
C	0.306662	2.643234	0.728513	H	-7.757380	-3.417259	-0.992289
C	-0.191967	3.240192	-1.556422	H	-8.940987	-1.778557	-2.485202
C	-0.167752	3.881194	1.158781	H	-7.903357	0.414379	-2.966662
H	0.652909	1.917302	1.454054	H	-5.689186	1.033732	-2.025689
C	-0.653993	4.485168	-1.127917	H	-3.838574	0.133033	-0.194254
H	-0.240411	2.979396	-2.609289	N	-4.218669	-0.770858	-0.441065
C	-0.642588	4.808415	0.229891	C	-5.188209	-2.834609	0.196149
H	-0.194166	4.102165	2.221129	O	-5.254328	-3.977757	0.603317
H	-1.050542	5.190697	-1.852232	C	-2.625240	-2.532135	0.387735
H	-1.032854	5.764847	0.564412	H	-2.821750	-3.588779	0.172618
C	-0.096641	0.319749	-2.623532	H	-2.160156	-2.090509	-0.494782
C	-1.423758	-0.073500	-2.389281	C	-1.660609	-2.499731	1.541234
C	0.379463	0.386357	-3.937243	C	-0.674180	-1.586950	1.730579
C	-2.266549	-0.386419	-3.453261	C	0.530523	-1.817603	2.465183
H	-1.788431	-0.127772	-1.371042	H	0.822833	-2.855380	2.617173
C	-0.465387	0.063885	-5.002929	H	-1.787074	-3.296121	2.273793
H	1.405324	0.685744	-4.127716	C	1.159337	-0.857812	3.383521
C	-1.785917	-0.321127	-4.764687	C	2.316281	-1.225001	4.099741
H	-3.290545	-0.686131	-3.249511	C	0.651473	0.445143	3.563504
H	-0.089297	0.115613	-6.021205	C	2.982496	-0.308849	4.907274
H	-2.437262	-0.571953	-5.597257	H	2.694442	-2.239340	4.007934
Pd	1.058619	-0.951197	0.541210	C	1.325219	1.360158	4.371360
C	-3.908188	3.498420	1.599441	H	-0.297424	0.726936	3.119976
C	-3.247627	2.531787	0.832627	C	2.501525	0.998682	5.031599
C	-3.367838	2.561436	-0.561390	H	3.877596	-0.613496	5.443132
C	-4.149414	3.537821	-1.179617	H	0.913702	2.358331	4.495826
C	-4.816911	4.490938	-0.409093	H	3.024507	1.716816	5.656634
C	-4.692600	4.470548	0.983506	C	-4.276281	-1.373002	1.976660
H	-3.781748	3.469765	2.676381	O	-3.992975	-2.032133	2.950598

O	-4.885789	-0.176751	2.018870	H	6.029935	-2.933425	-0.781179
C	-5.124436	0.346080	3.339661	H	4.101384	-3.690280	-2.289065
H	-4.169603	0.540740	3.830268	H	3.577351	-4.887857	-1.106082
H	-5.668388	1.276726	3.179593	H	2.442445	-3.667791	-1.698634
H	-5.717036	-0.361138	3.924396	H	2.018772	-3.199797	0.879520
				H	3.254103	-4.441472	1.195935
TS-E-E-S				H	3.413378	-2.829538	1.900370
C	1.558087	-1.732749	3.731214	H	6.313315	-0.991248	-1.887769
C	1.879465	-1.092657	4.963261	H	5.483661	-2.316323	-2.721535
H	2.687467	-1.363128	5.630247	H	5.849212	-0.824529	-3.578507
C	0.976594	-0.002147	5.137230	H	3.539169	-0.812680	-4.315547
H	0.986216	0.707846	5.953777	H	2.878936	-2.093834	-3.291661
C	0.102780	0.033108	4.010226	H	2.201531	-0.473608	-3.203770
H	-0.657552	0.777623	3.825261	H	3.369359	1.421578	-2.121445
C	0.465710	-1.035983	3.135614	H	5.100482	1.332029	-1.766848
H	0.032071	-1.260928	2.171355	H	4.521918	1.162098	-3.422103
C	3.510087	0.558782	1.903524	C	-0.155998	2.428039	0.913895
C	4.046393	0.808519	3.210748	C	-1.198578	1.643128	1.415899
C	3.303073	1.852699	3.831685	C	-0.297501	3.821250	0.899729
H	3.447901	2.227277	4.836565	C	-2.360188	2.232298	1.905857
C	2.279989	2.248654	2.927913	H	-1.095432	0.567702	1.389779
H	1.505083	2.981110	3.105437	C	-1.465992	4.412338	1.382721
C	2.396010	1.455500	1.737848	H	0.493541	4.442777	0.494549
Fe	2.064781	0.264378	3.401836	C	-2.498171	3.621425	1.887034
H	2.059507	-2.592132	3.318171	H	-3.173721	1.606327	2.262455
H	4.880057	0.274959	3.649960	H	-1.577675	5.491632	1.343527
C	4.288175	-0.308418	0.927730	H	-3.416815	4.083116	2.235362
H	4.576100	-1.186718	1.506895	C	2.163954	2.910810	-0.674036
C	5.599987	0.437235	0.599694	C	1.671360	3.244940	-1.946511
H	6.173446	0.578981	1.521616	C	3.293545	3.576442	-0.178826
H	6.226923	-0.114939	-0.102404	C	2.306586	4.227452	-2.704491
H	5.396363	1.426851	0.187990	H	0.806153	2.715958	-2.334849
P	3.391826	-1.113170	-0.564745	C	3.931167	4.551432	-0.948473
P	1.336678	1.570432	0.277114	H	3.680231	3.334830	0.804976
C	4.169201	-0.607604	-2.259511	C	3.441036	4.878231	-2.213142
C	3.890521	-2.940220	-0.230900	H	1.919987	4.475705	-3.689300
C	5.386643	-3.173355	0.064867	H	4.809777	5.056486	-0.556100
C	3.475731	-3.836922	-1.406624	H	3.939736	5.635244	-2.812123
C	3.089859	-3.372527	1.009559	Pd	1.084695	-0.646692	-0.575781
C	4.297931	0.918247	-2.375830	C	-2.131237	3.849788	-2.118181
C	5.530243	-1.232130	-2.610729	C	-2.650158	2.636072	-1.653177
C	3.131624	-1.034084	-3.320665	C	-3.912096	2.613678	-1.049842
H	5.745110	-2.612294	0.933098	C	-4.645979	3.790504	-0.914899
H	5.529813	-4.237196	0.294474	C	-4.120452	5.000543	-1.371904

C	-2.859755	5.028355	-1.973978	H	-0.540160	-0.643864	-3.142183
H	-1.152539	3.855494	-2.583476	C	0.478404	-4.072756	-4.641798
H	-4.303937	1.672999	-0.687628	H	0.732046	-4.723496	-2.609420
H	-5.626763	3.758560	-0.449635	C	0.119043	-3.020710	-5.485985
H	-4.691517	5.919122	-1.262772	H	-0.551492	-0.971930	-5.576955
H	-2.447051	5.968013	-2.331587	H	0.758144	-5.037027	-5.058044
C	-1.836735	1.379753	-1.784518	H	0.126493	-3.156427	-6.563976
O	-2.363211	0.319404	-1.255061				
H	-1.517571	-0.572182	-1.034049	TS-E-Z-R			
O	-0.730875	1.399549	-2.353249	C	-6.658556	-2.468294	-1.008246
C	-5.780184	-0.330354	0.739362	C	-5.920131	-3.644063	-1.338340
C	-5.550975	-0.824582	-0.555996	H	-6.071252	-4.264035	-2.212147
C	-6.156921	-0.248581	-1.672073	C	-4.910660	-3.824392	-0.345524
C	-6.998413	0.843800	-1.482884	H	-4.170341	-4.611333	-0.325956
C	-7.215121	1.344234	-0.187191	C	-5.026888	-2.762107	0.600500
C	-6.612861	0.776573	0.935825	H	-4.390364	-2.601629	1.457089
C	-4.180698	-2.010997	1.037850	C	-6.104215	-1.925251	0.190601
H	-5.947490	-0.648231	-2.659148	H	-6.425020	-1.019673	0.687718
H	-7.478348	1.320778	-2.331079	C	-3.861877	-0.101196	-1.512485
H	-7.870620	2.200810	-0.053450	C	-4.646312	-0.453461	-2.660002
H	-6.794264	1.174333	1.930104	C	-4.103542	-1.626716	-3.257747
H	-4.767488	-0.606418	2.522374	H	-4.510826	-2.149030	-4.113222
N	-5.116731	-1.087341	1.701783	C	-2.979537	-2.025448	-2.488276
C	-4.600972	-1.935139	-0.464996	H	-2.344811	-2.881003	-2.668886
O	-4.170979	-2.667199	-1.331378	C	-2.807109	-1.086111	-1.417289
C	-2.725281	-1.512174	1.193565	Fe	-4.667543	-1.999910	-1.302778
H	-2.725272	-0.470778	0.874705	H	-7.467079	-2.041885	-1.587311
H	-2.475298	-1.558629	2.263306	H	-5.541209	0.049313	-2.995586
C	-1.711501	-2.282165	0.399402	C	-4.186925	1.034703	-0.555475
C	-0.897420	-1.751077	-0.544067	H	-4.225381	0.600661	0.451436
C	0.133841	-2.499426	-1.219709	C	-5.586981	1.584503	-0.881799
H	-1.720419	-3.363165	0.557717	H	-6.319140	0.773980	-0.806042
C	-4.452438	-3.421901	1.565392	H	-5.894112	2.379199	-0.209322
O	-5.427303	-4.075426	1.278313	H	-5.640157	1.974146	-1.899869
O	-3.495849	-3.839022	2.423466	P	-2.781451	2.307904	-0.314942
C	-3.705976	-5.149349	2.974008	P	-1.362105	-0.977910	-0.325215
H	-3.752558	-5.892655	2.174273	C	-2.863540	3.499344	-1.798607
H	-2.851528	-5.332873	3.625541	C	-3.233975	3.200316	1.321965
H	-4.640170	-5.178789	3.540590	C	-4.707640	3.573396	1.553887
H	0.525152	-3.371443	-0.692187	C	-2.381968	4.474489	1.435204
C	0.110312	-2.658853	-2.688352	C	-2.805788	2.241836	2.451210
C	-0.271956	-1.612385	-3.550660	C	-2.940368	2.622567	-3.064617
C	0.471105	-3.892602	-3.259980	C	-4.034642	4.495849	-1.781523
C	-0.261832	-1.796086	-4.930386	C	-1.538919	4.282432	-1.873923

H	-5.339019	2.691474	1.692716	C	1.264171	-4.310351	3.700243
H	-4.771833	4.159520	2.479731	C	2.428533	-5.081597	3.705972
H	-5.125585	4.185873	0.751750	C	3.606505	-4.570350	3.153499
H	-2.722932	5.260677	0.756200	H	4.518562	-2.871284	2.164223
H	-2.462474	4.865753	2.457017	H	0.377480	-2.427418	3.125540
H	-1.326897	4.280637	1.249400	H	0.345197	-4.701950	4.126645
H	-1.731771	2.038818	2.414586	H	2.420049	-6.077838	4.140295
H	-3.031226	2.706091	3.419939	H	4.514266	-5.167712	3.160203
H	-3.347231	1.290279	2.407895	C	2.479894	-1.163156	1.927635
H	-5.007286	4.005369	-1.720490	O	1.343367	-0.538067	1.892232
H	-3.956756	5.202982	-0.951874	H	1.311212	0.399251	0.988239
H	-4.017421	5.081559	-2.710020	O	3.545785	-0.741061	1.449410
H	-1.580174	4.965292	-2.732519	C	5.938700	-0.949737	-1.678804
H	-1.342526	4.876463	-0.979952	C	6.577891	0.100608	-2.369961
H	-0.697605	3.601579	-2.014979	C	7.724087	-0.121662	-3.136195
H	-2.789470	3.257426	-3.946876	C	8.249394	-1.408182	-3.191944
H	-2.159577	1.854107	-3.065951	C	7.622435	-2.451064	-2.481634
H	-3.903864	2.122901	-3.175803	C	6.472389	-2.246537	-1.724530
C	-1.723806	-2.042799	1.117875	C	4.681509	0.928380	-1.132189
C	-1.951364	-1.428966	2.353771	H	8.188361	0.709226	-3.659391
C	-1.810828	-3.438059	1.016484	H	9.143075	-1.613531	-3.772744
C	-2.303520	-2.194200	3.468281	H	8.049428	-3.449863	-2.526455
H	-1.827634	-0.356164	2.439665	H	5.999935	-3.062024	-1.184597
C	-2.139819	-4.204123	2.132786	H	4.473790	-0.950770	-0.185351
H	-1.616925	-3.922917	0.065130	N	4.789036	-0.526265	-1.056970
C	-2.400722	-3.582498	3.357975	C	5.840295	1.335065	-2.105465
H	-2.481513	-1.707983	4.423110	O	6.014081	2.459592	-2.538267
H	-2.198082	-5.285495	2.048381	C	3.317678	1.384893	-1.699887
H	-2.667408	-4.180605	4.224615	H	3.276040	2.474440	-1.661863
C	-0.042309	-1.870523	-1.233150	H	3.273524	1.052804	-2.745052
C	0.893699	-2.647556	-0.536989	C	2.208439	0.738521	-0.935853
C	0.197633	-1.567234	-2.583628	C	1.392181	1.316672	-0.024092
C	2.054844	-3.095083	-1.169688	C	0.974204	2.672190	0.135967
H	0.742525	-2.874522	0.509686	H	2.163482	-0.339900	-1.041570
C	1.351313	-2.026818	-3.215690	C	4.923152	1.592363	0.230982
H	-0.503149	-0.943248	-3.130163	O	4.332241	2.570848	0.626209
C	2.292213	-2.781050	-2.507425	O	5.902718	0.967711	0.902804
H	2.779123	-3.668857	-0.598559	C	6.075933	1.400383	2.259620
H	1.528260	-1.776801	-4.258015	H	6.247297	2.478471	2.303405
H	3.209646	-3.103274	-2.990635	H	5.181966	1.144240	2.833643
Pd	-0.702460	1.243207	-0.054040	H	6.942321	0.853249	2.632141
C	3.616820	-3.293812	2.594782	C	1.032702	3.396409	1.412549
C	2.449886	-2.519918	2.581657	C	1.085869	4.801851	1.401258
C	1.274143	-3.033208	3.141240	C	1.026409	2.744536	2.661945

C	1.107338	5.534175	2.586095	C	-4.189002	4.474039	0.770403
H	1.110675	5.319066	0.444874	C	-1.941397	4.471799	-0.341439
C	1.046237	3.478818	3.844108	H	-4.206587	1.608076	3.686959
H	1.013228	1.660675	2.702834	H	-3.270088	2.783972	4.597500
C	1.079013	4.876563	3.817057	H	-4.240499	3.324646	3.226625
H	1.149555	6.619551	2.547571	H	-1.875116	4.427802	2.696460
H	1.040837	2.954985	4.796744	H	-1.050547	3.484610	3.942758
H	1.093371	5.443829	4.743482	H	-0.520219	3.375695	2.256717
H	1.027248	3.316690	-0.739651	H	-0.686913	0.835961	2.749424
TS-E-Z-S				H	-1.480293	1.111022	4.307921
C	-6.572782	-2.639747	-0.082621	H	-2.275692	0.114992	3.088121
C	-6.052430	-3.514684	-1.083234	H	-5.092336	3.924326	1.043178
H	-6.549905	-3.793675	-2.002710	H	-3.745085	4.879216	1.683488
C	-4.738723	-3.907216	-0.685819	H	-4.495596	5.328597	0.153144
H	-4.066034	-4.543356	-1.243341	H	-2.254340	5.385308	-0.863298
C	-4.448558	-3.279007	0.561983	H	-1.380790	4.768806	0.545001
H	-3.523278	-3.355383	1.111766	H	-1.254586	3.927263	-0.989998
C	-5.578931	-2.495645	0.932964	H	-3.963942	4.112300	-1.978939
H	-5.654476	-1.874023	1.815436	H	-3.137882	2.545852	-1.934426
C	-4.146019	0.091216	-0.665410	H	-4.765791	2.707923	-1.263645
C	-5.326643	0.068683	-1.477523	C	-1.226504	-2.386387	0.067870
C	-5.090464	-0.740490	-2.625799	C	-1.024652	-2.306822	1.449330
H	-5.813682	-0.975106	-3.395495	C	-1.297729	-3.643831	-0.547622
C	-3.764152	-1.240394	-2.540263	C	-0.898639	-3.469831	2.211355
H	-3.275998	-1.895151	-3.247643	H	-0.916597	-1.337009	1.918697
C	-3.162157	-0.720588	-1.345408	C	-1.167104	-4.804192	0.213432
Fe	-4.848161	-1.846678	-0.896631	H	-1.448093	-3.713262	-1.620454
H	-7.532987	-2.141810	-0.110816	C	-0.968685	-4.719146	1.594927
H	-6.267535	0.543373	-1.242086	H	-0.709102	-3.395409	3.277426
C	-4.031613	0.772490	0.689613	H	-1.216291	-5.775716	-0.270612
H	-3.691332	0.009684	1.400090	H	-0.853204	-5.623792	2.184358
C	-5.422234	1.249633	1.141408	C	-0.519613	-1.142523	-2.449722
H	-6.106986	0.395482	1.169349	C	0.659776	-1.904277	-2.439838
H	-5.407981	1.700307	2.129118	C	-0.862118	-0.431808	-3.611492
H	-5.841558	1.982702	0.449648	C	1.466487	-1.968114	-3.576713
P	-2.602429	2.031292	0.833789	H	0.971239	-2.402203	-1.529746
P	-1.416312	-0.836619	-0.882260	C	-0.054827	-0.502213	-4.745154
C	-3.184023	3.624304	-0.025002	H	-1.753246	0.187683	-3.624741
C	-2.357472	2.281393	2.715155	C	1.112472	-1.270714	-4.732300
C	-3.603546	2.514590	3.587029	H	2.384705	-2.547744	-3.548083
C	-1.394421	3.467210	2.900934	H	-0.334201	0.049760	-5.638296
C	-1.654793	1.007448	3.228873	H	1.745073	-1.316891	-5.613961
C	-3.804086	3.210689	-1.374371	Pd	-0.587990	1.151136	-0.002595
				C	2.468682	-2.561691	3.678170

C	2.335862	-2.451450	2.289951	C	1.581915	6.579117	-0.452832
C	2.653432	-3.546124	1.478339	H	1.799366	6.822248	1.679135
C	3.100533	-4.736928	2.047513	H	1.366020	6.002207	-2.520421
C	3.236470	-4.840776	3.434216	H	1.676317	7.639189	-0.670244
C	2.920415	-3.750464	4.249212	C	4.464980	1.291494	0.675012
H	2.204430	-1.704095	4.287800	O	4.304000	2.438516	1.025184
H	2.526820	-3.454531	0.405438	O	4.613669	0.253839	1.513767
H	3.340705	-5.585583	1.412557	C	4.525623	0.572633	2.914782
H	3.586644	-5.768659	3.878493	H	5.259708	1.338952	3.174566
H	3.024714	-3.829988	5.328015	H	3.516070	0.914231	3.146932
C	1.812372	-1.170354	1.696290	H	4.733098	-0.364466	3.430724
O	1.785069	-1.136747	0.401479				
H	1.303519	0.143643	-0.048719	E			
O	1.429468	-0.253387	2.442190	C	-3.030074	0.458426	-1.615838
C	5.510332	-1.255090	-1.088035	H	-3.006708	0.610004	-0.525212
C	6.591155	-0.371815	-1.291701	C	-4.423518	0.907304	-2.081760
C	7.885311	-0.844128	-1.521692	H	-5.164473	0.208802	-1.680216
C	8.103361	-2.217420	-1.515854	H	-4.668524	1.891013	-1.684811
C	7.027270	-3.095759	-1.278736	H	-4.535487	0.935919	-3.168468
C	5.729829	-2.640015	-1.064341	P	-1.530523	1.486528	-2.121605
C	4.574174	0.851136	-0.798870	P	-0.356288	-1.424748	-0.378345
H	8.693238	-0.136503	-1.683067	C	-1.089590	1.071376	-3.930325
H	9.098803	-2.617564	-1.680544	C	-2.047502	3.325050	-2.009015
H	7.215785	-4.166257	-1.260329	C	-3.063828	3.808431	-3.060065
H	4.913774	-3.329840	-0.871687	C	-0.788739	4.206347	-2.137408
H	3.545108	-0.981923	-0.438480	C	-2.612545	3.517404	-0.587792
N	4.318927	-0.578542	-0.968728	C	-0.335993	-0.267789	-3.936431
C	6.085253	0.996851	-1.200287	C	-2.321154	0.931366	-4.842562
O	6.649190	2.057558	-1.389083	C	-0.135062	2.132969	-4.503312
C	3.648021	1.740301	-1.671928	H	-3.999893	3.250877	-3.053526
H	3.719994	2.764823	-1.304456	H	-3.303459	4.857187	-2.841146
H	3.998012	1.699561	-2.707737	H	-2.653182	3.778649	-4.073018
C	2.267917	1.162761	-1.546965	H	-0.535571	4.425544	-3.176166
C	1.449939	1.352944	-0.485426	H	-0.962520	5.161331	-1.629718
C	1.201911	2.400575	0.442833	H	0.073217	3.742642	-1.665188
H	1.348352	2.149392	1.491242	H	-1.902756	3.192146	0.174733
H	2.060759	0.313828	-2.193124	H	-2.823536	4.584548	-0.441648
C	1.334324	3.823615	0.108798	H	-3.533440	2.960720	-0.409811
C	1.527717	4.759505	1.139449	H	-2.943826	0.086190	-4.539966
C	1.284287	4.300340	-1.213688	H	-2.940298	1.829939	-4.860051
C	1.645564	6.120111	0.863982	H	-1.983958	0.739966	-5.870058
H	1.606253	4.405156	2.163501	H	0.261601	1.768095	-5.459098
C	1.409028	5.658222	-1.490255	H	-0.635125	3.083016	-4.698202
H	1.130883	3.593480	-2.023757	H	0.715125	2.316784	-3.837754

H	0.547323	-0.232704	-3.291539	C	-5.697527	-2.393542	-0.181923
H	-0.979080	-1.082407	-3.604998	H	-6.492287	-2.084986	-0.848879
H	-0.004793	-0.493294	-4.958887	C	-5.208106	-3.727135	-0.029237
C	-0.564500	-2.069446	1.326905	H	-5.571481	-4.601963	-0.552728
C	-0.562352	-1.205384	2.424391	C	-4.118257	-3.690366	0.893909
C	-0.747141	-3.447375	1.531995	H	-3.514267	-4.532797	1.199837
C	-0.770081	-1.705817	3.714323	C	-3.939502	-2.336645	1.307813
H	-0.444596	-0.139632	2.270361	H	-3.175345	-1.958381	1.968606
C	-0.943914	-3.944129	2.816561	C	-2.825253	-1.015547	-1.879757
H	-0.735807	-4.129621	0.688925	C	-3.667933	-1.825356	-2.705416
C	-0.961917	-3.071672	3.910531	C	-3.227041	-3.179382	-2.648437
H	-0.802668	-1.017959	4.552644	H	-3.699528	-4.023136	-3.133560
H	-1.088062	-5.010743	2.966210	C	-2.098389	-3.232930	-1.790241
H	-1.129617	-3.459381	4.911349	H	-1.524471	-4.114366	-1.543813
C	0.950493	-2.564106	-1.009912	C	-1.827619	-1.901376	-1.314877
C	1.960245	-3.005952	-0.137292	Fe	-3.716246	-2.498055	-0.752329
C	1.030559	-2.928045	-2.362150	H	-4.964763	-0.459707	0.733220
C	3.020417	-3.781000	-0.606634	H	-4.543119	-1.478807	-3.235414
H	1.929342	-2.734079	0.910893	C	1.954625	0.437559	0.606318
C	2.094214	-3.699641	-2.830699	H	1.850976	-0.294581	1.401849
H	0.255498	-2.624041	-3.051511	C	5.388169	-1.984762	1.042391
C	3.095880	-4.123644	-1.956821	C	5.944826	-1.789490	-0.233379
H	3.792888	-4.105245	0.082208	C	6.832147	-2.712283	-0.792203
H	2.134739	-3.970079	-3.882100	C	7.181249	-3.832131	-0.045513
H	3.929335	-4.716514	-2.321721	C	6.651490	-4.005665	1.247943
Pd	0.164530	0.829167	-0.535764	C	5.755831	-3.097331	1.808820
C	-3.675326	0.448523	4.124451	C	4.435870	0.008585	0.304366
C	-2.573441	1.170977	3.654033	H	7.233567	-2.536567	-1.785679
C	-1.634846	1.656449	4.571592	H	7.866756	-4.570484	-0.448999
C	-1.786755	1.413791	5.937050	H	6.944217	-4.878337	1.825535
C	-2.881113	0.676000	6.397667	H	5.343161	-3.254469	2.800775
C	-3.826856	0.196580	5.487478	H	4.469324	-0.627083	2.293827
H	-4.394722	0.081064	3.401017	N	4.445123	-1.012174	1.354302
H	-0.782758	2.210647	4.192388	C	5.436254	-0.527769	-0.773407
H	-1.052521	1.795320	6.642390	O	5.648618	-0.003404	-1.848856
H	-2.997343	0.478939	7.460358	C	3.046786	0.116188	-0.385448
H	-4.680079	-0.376356	5.841788	H	3.133771	0.856819	-1.181318
C	-2.359896	1.350586	2.159028	H	2.857131	-0.847455	-0.858091
O	-1.246746	1.854561	1.807520	C	4.839591	1.348634	0.907996
O	-3.266894	0.936234	1.396675	O	5.036013	1.514241	2.095738
C	1.597032	1.773238	0.949317	O	4.906758	2.313559	-0.013647
H	1.056316	1.926236	1.877480	C	5.192051	3.633022	0.489098
C	1.704749	2.838261	0.062989	H	6.099460	3.620352	1.096002
C	-4.912259	-1.535206	0.645763	H	5.323844	4.254955	-0.395598

H	4.351408	3.992089	1.087244	H	0.350254	5.891160	-0.472259
C	1.307928	4.212200	0.373547	H	-0.922688	4.804925	0.097898
C	1.928198	5.266339	-0.321919	H	-0.236155	2.959066	1.906243
C	0.321841	4.519805	1.330549	H	1.475219	2.810683	2.337177
C	1.588950	6.591935	-0.064568	H	0.583425	4.272396	2.778558
H	2.677339	5.035268	-1.075882	C	1.213376	-2.000715	0.969301
C	-0.016902	5.846672	1.579286	C	1.061212	-2.557451	-0.304035
H	-0.215121	3.715295	1.824502	C	1.667349	-2.806606	2.027321
C	0.613074	6.887356	0.889665	C	1.364929	-3.906789	-0.519762
H	2.079913	7.392368	-0.611145	H	0.765430	-1.929717	-1.138833
H	-0.790971	6.069900	2.308350	C	1.961943	-4.149648	1.810933
H	0.338833	7.919624	1.088292	H	1.787925	-2.385708	3.020128
H	2.344165	2.724904	-0.808115	C	1.811907	-4.702324	0.534019
E-Z-S				H	1.272964	-4.316777	-1.519743
C	2.892271	1.961731	-0.496626	H	2.315008	-4.763998	2.634828
H	2.731238	1.069713	-1.117405	H	2.055072	-5.747201	0.362187
C	4.123854	2.645675	-1.107818	C	-0.048918	-0.304345	2.853012
H	4.993785	2.012082	-0.914078	C	-0.958042	-1.356501	3.051789
H	4.025895	2.717279	-2.189363	C	0.049288	0.685191	3.841077
H	4.324568	3.639234	-0.700188	C	-1.753208	-1.417061	4.195322
P	1.204017	2.810736	-0.655022	H	-1.038759	-2.136085	2.304616
P	0.876096	-0.218082	1.261039	C	-0.741480	0.623291	4.989404
C	1.112827	4.181829	0.680847	H	0.755467	1.496324	3.728337
C	1.139166	3.635248	-2.382823	C	-1.647893	-0.422692	5.169017
C	2.113080	4.812700	-2.584117	H	-2.458860	-2.233991	4.308339
C	-0.281705	4.175747	-2.664397	H	-0.643058	1.395959	5.746826
C	1.439225	2.527982	-3.413182	H	-2.263577	-0.465376	6.062826
C	0.707020	3.506414	2.001618	Pd	-0.283077	0.919828	-0.420668
C	2.455546	4.903482	0.898867	C	3.710340	-2.902045	-3.252322
C	0.046120	5.240407	0.349194	C	2.467099	-2.269737	-3.361680
H	3.159119	4.534189	-2.470983	C	1.384292	-2.984567	-3.887532
H	1.982013	5.188640	-3.606995	C	1.537338	-4.311703	-4.289541
H	1.902151	5.644322	-1.907163	C	2.776163	-4.944862	-4.150617
H	-0.445084	5.164516	-2.233808	C	3.862262	-4.235993	-3.630806
H	-0.404850	4.270372	-3.750215	H	4.544434	-2.334187	-2.855432
H	-1.067263	3.519325	-2.296955	H	0.424233	-2.484615	-3.962538
H	0.721836	1.708739	-3.351817	H	0.691926	-4.854793	-4.704922
H	1.390110	2.971679	-4.416367	H	2.895411	-5.982628	-4.451628
H	2.419058	2.064750	-3.289244	H	4.827943	-4.723726	-3.523451
H	3.222562	4.222315	1.267319	C	2.281180	-0.847411	-2.852665
H	2.824941	5.386806	-0.007713	O	1.083331	-0.484112	-2.641823
H	2.316074	5.684922	1.657949	O	3.317783	-0.168103	-2.639605
H	-0.095314	5.876063	1.232621	C	-1.683661	-0.114204	-1.723219
				H	-1.038669	-0.633656	-2.426030

C	-1.943159	1.246635	-1.985219	H	-7.745724	0.015159	2.065160
H	-1.580579	1.597023	-2.949200	H	-5.233133	-1.258734	2.373537
C	5.254924	-0.809042	-0.317854	N	-5.144190	-0.869913	1.440946
C	6.267101	-0.355955	0.580807	C	-4.679539	-1.640049	-0.775910
H	6.964347	0.451829	0.399694	O	-4.087700	-2.061208	-1.751921
C	6.156643	-1.105474	1.792089	C	-2.895795	-0.386903	0.568292
H	6.758478	-0.969672	2.681407	H	-3.384656	0.561013	0.368959
C	5.072542	-2.023702	1.640979	H	-2.478055	-0.316786	1.574471
H	4.711279	-2.714389	2.390144	C	-3.591700	-2.739347	1.295975
C	4.522112	-1.838823	0.337977	O	-4.004111	-3.136987	2.369932
H	3.675710	-2.360500	-0.080228	O	-2.645842	-3.356468	0.581712
C	3.173279	1.515318	0.920071	C	-2.087143	-4.555665	1.152544
C	4.265298	1.963731	1.729626	H	-2.854577	-5.329783	1.222341
C	4.234267	1.284933	2.983172	H	-1.287748	-4.847255	0.473780
H	4.958930	1.387959	3.779913	H	-1.684611	-4.350504	2.147226
C	3.126949	0.396030	2.969642				
H	2.828250	-0.268050	3.767859	TS-F-1			
C	2.454204	0.536659	1.705805	C	-2.356548	0.538795	-2.058141
Fe	4.410953	-0.071356	1.433740	H	-2.510441	1.366550	-1.359382
H	5.011491	-0.424376	-1.299773	C	-3.132778	0.891111	-3.336654
H	5.031408	2.658569	1.417496	H	-4.203537	0.806245	-3.129759
C	-3.126040	1.984143	-1.438103	H	-2.936471	1.917111	-3.649702
C	-4.401940	1.640633	-1.913552	H	-2.903132	0.235662	-4.176009
C	-3.027882	2.961965	-0.441365	P	-0.446257	0.442043	-2.120522
C	-5.544841	2.244616	-1.389773	P	-1.663949	-0.093960	1.126478
H	-4.493464	0.861955	-2.664807	C	-0.009542	-1.120211	-3.125346
C	-4.167910	3.575251	0.077881	C	0.063421	2.056049	-3.013135
H	-2.048852	3.191628	-0.039568	C	-0.188583	2.095702	-4.529092
C	-5.431614	3.214389	-0.392114	C	1.561462	2.292412	-2.763674
H	-6.524069	1.935911	-1.742821	C	-0.685009	3.203894	-2.304210
H	-4.067463	4.321446	0.861465	C	-0.176364	-2.315593	-2.161372
H	-6.322686	3.676591	0.022762	C	-0.860936	-1.372674	-4.380143
C	-1.824894	-0.700480	-0.444740	C	1.469810	-1.051394	-3.537215
H	-1.403414	-1.692784	-0.355618	H	-1.231579	1.930960	-4.801209
C	-6.287435	-0.763231	0.660642	H	0.100355	3.084592	-4.908580
C	-6.052630	-1.152333	-0.669513	H	0.421263	1.357628	-5.057295
C	-7.045497	-1.055436	-1.647163	H	2.185197	1.577824	-3.298900
C	-8.294478	-0.569803	-1.277010	H	1.832188	3.297905	-3.107580
C	-8.533398	-0.199498	0.061275	H	1.806818	2.230740	-1.702374
C	-7.548265	-0.287740	1.041531	H	-0.486408	3.183052	-1.228344
C	-4.056828	-1.441049	0.645979	H	-0.308387	4.162800	-2.677963
H	-6.827010	-1.362002	-2.665828	H	-1.766073	3.184354	-2.465531
H	-9.089469	-0.479549	-2.010370	H	-1.901867	-1.583820	-4.130148
H	-9.516692	0.171172	0.338230	H	-0.829528	-0.542428	-5.089881

H	-0.467343	-2.260482	-4.891575	C	0.795676	2.720933	1.628861
H	1.736093	-1.996926	-4.025371	H	-0.128009	3.293023	1.686282
H	1.671742	-0.244614	-4.246331	C	1.834441	3.272559	0.945476
H	2.118234	-0.955496	-2.667633	C	-6.138903	0.417446	-1.106305
H	0.319365	-2.127540	-1.209051	C	-6.694011	-0.896403	-1.154991
H	-1.224303	-2.542613	-1.967520	H	-7.044686	-1.408159	-2.041473
H	0.286457	-3.203063	-2.608623	C	-6.654589	-1.437608	0.164298
C	-2.737092	1.243082	1.778671	H	-6.968762	-2.432063	0.452348
C	-2.620971	2.516125	1.204748	C	-6.069262	-0.461866	1.023707
C	-3.695865	1.034165	2.779774	H	-5.875780	-0.583013	2.079196
C	-3.443812	3.563096	1.622782	C	-5.748320	0.685212	0.236367
H	-1.876466	2.680756	0.433707	H	-5.270391	1.585908	0.588383
C	-4.503490	2.084901	3.213502	C	-2.892117	-0.700242	-1.396700
H	-3.816316	0.049039	3.215551	C	-3.612133	-1.770637	-2.010055
C	-4.380751	3.351322	2.635732	C	-3.859481	-2.774244	-1.026268
H	-3.344694	4.543053	1.164612	H	-4.415709	-3.689308	-1.179147
H	-5.237518	1.912607	3.995296	C	-3.312399	-2.326439	0.207527
H	-5.014455	4.166503	2.972116	H	-3.348015	-2.845520	1.154212
C	-1.319751	-1.241468	2.504845	C	-2.704169	-1.047107	-0.013216
C	-1.400130	-0.874930	3.857530	Fe	-4.738892	-0.992282	-0.479113
C	-0.724813	-2.467248	2.166232	H	-6.012034	1.084930	-1.947356
C	-0.935903	-1.739942	4.848929	H	-3.945452	-1.800038	-3.037776
H	-1.800531	0.089693	4.145070	C	0.668404	1.371891	2.176076
C	-0.255660	-3.322721	3.158661	H	-0.220639	1.333412	2.806711
H	-0.568179	-2.734276	1.128356	C	3.772469	0.734230	-0.068614
C	-0.369786	-2.967196	4.503129	C	4.627614	1.381135	0.855777
H	-1.003429	-1.442415	5.891378	C	5.727564	2.146124	0.460341
H	0.239379	-4.241185	2.864838	C	6.017311	2.245014	-0.894812
H	0.004451	-3.630898	5.277350	C	5.210661	1.553539	-1.822601
Pd	0.300003	0.594906	0.211946	C	4.110031	0.800993	-1.433794
C	2.081137	-5.657122	-0.659679	C	2.933748	0.115588	1.973053
C	2.592201	-4.426049	-1.084384	H	6.335368	2.635468	1.216216
C	3.258554	-4.339274	-2.312920	H	6.870404	2.820891	-1.240178
C	3.406771	-5.474414	-3.108662	H	5.461333	1.604384	-2.879679
C	2.890658	-6.700799	-2.682459	H	3.524819	0.267929	-2.168035
C	2.228248	-6.791159	-1.455412	H	2.677614	-1.208275	-0.107630
H	1.572123	-5.698678	0.297355	N	2.684946	0.083752	0.501670
H	3.656979	-3.381030	-2.625323	C	4.114503	1.115057	2.189773
H	3.927545	-5.404918	-4.059865	O	4.473342	1.547574	3.272836
H	3.006776	-7.584804	-3.303874	C	1.727943	0.501579	2.824529
H	1.829011	-7.745166	-1.121750	H	1.218088	-0.405262	3.147833
C	2.387043	-3.218236	-0.219373	H	2.106231	0.983808	3.738653
O	2.808465	-2.103884	-0.756439	C	3.532207	-1.255388	2.362316
O	1.829280	-3.305309	0.878027	O	4.458743	-1.763290	1.769394

O	2.940293	-1.806467	3.434641	H	-4.271281	0.764982	-3.053483
C	3.387442	-3.132581	3.752154	H	-4.335875	2.538684	-3.099952
H	4.463168	-3.138563	3.944456	H	-3.751826	1.632092	-4.499366
H	2.831929	-3.417212	4.646468	H	-1.479059	2.686575	-4.633140
H	3.153789	-3.797327	2.918285	H	-2.106027	3.830157	-3.445996
C	1.815764	4.530450	0.209534	H	-0.555162	3.012484	-3.159823
C	0.728745	5.426995	0.211675	H	-0.552342	0.394177	-2.982521
C	2.926171	4.835483	-0.602684	H	-2.100254	-0.472337	-2.953888
C	0.746088	6.569791	-0.580749	H	-1.584110	0.359654	-4.424651
H	-0.134631	5.228076	0.840120	C	-0.469964	-1.878698	1.697419
C	2.939774	5.978443	-1.397776	C	-0.477805	-0.978885	2.769655
H	3.772189	4.153286	-0.616106	C	-0.427735	-3.256083	1.954548
C	1.848733	6.850073	-1.394945	C	-0.452922	-1.446262	4.084759
H	-0.101986	7.249311	-0.563526	H	-0.500664	0.087958	2.564606
H	3.804497	6.189089	-2.021041	C	-0.394450	-3.721849	3.267401
H	1.857907	7.742941	-2.013570	H	-0.409347	-3.959596	1.128875
H	2.765407	2.731286	0.875327	C	-0.409659	-2.818733	4.334332
F-1				H	-0.455537	-0.740769	4.910431
				H	-0.351089	-4.789828	3.459819
				H	-0.379500	-3.185142	5.356044
C	-3.448374	0.700192	-0.215041	C	0.503385	-2.314255	-1.002734
H	-3.084147	0.675189	0.817964	C	1.664032	-2.878773	-0.446930
C	-4.912595	1.166946	-0.171629	C	0.258685	-2.468260	-2.378650
H	-5.525680	0.372040	0.263186	C	2.543464	-3.606022	-1.252719
H	-5.030911	2.049448	0.456260	H	1.922870	-2.719577	0.593034
H	-5.313942	1.398150	-1.159828	C	1.146393	-3.184950	-3.177331
P	-2.146152	1.847210	-1.006737	H	-0.627216	-2.037672	-2.826821
P	-0.577628	-1.228183	-0.007703	C	2.290420	-3.754837	-2.614697
C	-2.305353	1.709677	-2.897931	H	3.437185	-4.030707	-0.812805
C	-2.583359	3.612585	-0.420756	H	0.943532	-3.293518	-4.239106
C	-3.887744	4.228637	-0.956461	H	2.994276	-4.301181	-3.234975
C	-1.433643	4.564407	-0.811692	Pd	-0.079198	1.041505	-0.098465
C	-2.619519	3.522580	1.120126	C	1.608262	1.768448	1.218576
C	-1.590397	0.415288	-3.328719	H	1.318881	1.801484	2.267058
C	-3.757017	1.663100	-3.402187	C	1.559085	2.937957	0.467447
C	-1.567053	2.887500	-3.558653	C	-4.883145	-1.800532	2.041902
H	-4.783826	3.666367	-0.697514	C	-5.760665	-2.613644	1.261719
H	-3.994823	5.234349	-0.529796	H	-6.712649	-2.309686	0.846782
H	-3.858655	4.343867	-2.043183	C	-5.136974	-3.884683	1.082845
H	-1.550097	4.950014	-1.825443	H	-5.532534	-4.709389	0.504983
H	-1.424318	5.422513	-0.130823	C	-3.875117	-3.854852	1.750013
H	-0.463025	4.080129	-0.738279	H	-3.146253	-4.652514	1.774387
H	-1.691410	3.089840	1.506103	C	-3.722416	-2.567951	2.345688
H	-2.712428	4.531023	1.539150	H	-2.864148	-2.223676	2.900708
H	-3.457836	2.928045	1.493636				

C	-3.349402	-0.709870	-0.749490	H	1.755592	7.536255	0.125750
C	-4.374654	-1.398004	-1.472957	H	-0.142422	5.918629	3.631292
C	-3.930072	-2.721951	-1.758076	H	0.571935	7.886586	2.287852
H	-4.506387	-3.491974	-2.253023	H	2.017050	2.919212	-0.516390
C	-2.626584	-2.871195	-1.215576				
H	-2.010866	-3.757660	-1.256498	TS-G-outer			
C	-2.245180	-1.628985	-0.603810	C	1.963377	-1.971178	2.521942
Fe	-3.953950	-2.392761	0.284491	C	3.057652	-2.839539	2.231053
H	-5.055508	-0.772823	2.332786	H	3.073883	-3.620850	1.483872
H	-5.349245	-1.000578	-1.717485	C	4.151198	-2.474556	3.070549
C	1.897686	0.496794	0.655472	H	5.137461	-2.919411	3.058857
H	1.930283	-0.327997	1.359836	C	3.731093	-1.383751	3.887417
C	4.874362	-2.168735	0.464526	H	4.344619	-0.852651	4.603101
C	5.443510	-1.936802	-0.839545	C	2.382314	-1.072242	3.551435
C	6.142013	-2.929125	-1.539216	H	1.797456	-0.269093	3.972186
C	6.325640	-4.171530	-0.951377	C	3.740926	-0.550171	-0.163940
C	5.808722	-4.406066	0.354596	C	5.041368	-0.658348	0.437963
C	5.102378	-3.452573	1.059247	C	5.199490	0.355204	1.424286
C	4.213370	-0.096419	0.006617	H	6.058461	0.486470	2.068915
H	6.528714	-2.708351	-2.531970	C	3.998767	1.106430	1.461845
H	6.875604	-4.955854	-1.463104	H	3.771123	1.928500	2.125702
H	5.976361	-5.380450	0.811235	C	3.089592	0.568560	0.486428
H	4.712038	-3.654481	2.053326	Fe	3.597500	-0.871844	1.880906
N	4.137694	-1.180231	0.969961	H	1.004468	-1.975678	2.021721
C	5.062180	-0.606105	-1.237486	H	5.770403	-1.425840	0.219390
O	5.253857	0.036856	-2.266065	C	3.330506	-1.547852	-1.250126
C	2.799522	0.273262	-0.524298	H	3.294063	-2.511901	-0.734383
H	2.870931	1.126371	-1.199592	C	4.469021	-1.664993	-2.288173
H	2.457074	-0.584450	-1.105860	H	5.398809	-1.957700	-1.792919
C	4.952204	1.102336	0.589758	H	4.256710	-2.423566	-3.038931
O	5.828179	1.058118	1.422005	H	4.657286	-0.717171	-2.795857
O	4.550940	2.279606	0.022170	P	1.568671	-1.490957	-1.972941
C	5.260498	3.434483	0.476552	P	1.461831	1.288542	0.170423
H	6.314152	3.375828	0.189807	C	1.627084	-0.621185	-3.680967
H	4.779825	4.287516	-0.006058	C	1.218954	-3.360167	-2.175486
H	5.196579	3.525930	1.564478	C	2.383463	-4.217564	-2.702968
C	1.280441	4.267997	1.004334	C	-0.000727	-3.575524	-3.087485
C	1.682641	5.392402	0.259961	C	0.848512	-3.853374	-0.763108
C	0.622723	4.483864	2.229356	C	2.283081	0.758333	-3.471784
C	1.433635	6.683636	0.716594	C	2.338014	-1.377078	-4.816968
H	2.192909	5.240478	-0.687765	C	0.172242	-0.354267	-4.128044
C	0.370925	5.773799	2.684862	H	3.249802	-4.205197	-2.035262
H	0.292636	3.635616	2.820826	H	2.045662	-5.259591	-2.769072
C	0.771758	6.880860	1.930248	H	2.711595	-3.917277	-3.700542

H	0.226753	-3.381316	-4.138896	C	-5.725148	1.120043	0.087181
H	-0.322754	-4.620885	-3.009233	C	-3.713606	-1.811142	0.840253
H	-0.842749	-2.949022	-2.791223	H	-6.527726	-1.800541	-2.424092
H	-0.032400	-3.335396	-0.381677	H	-7.664233	0.428144	-2.651219
H	0.629205	-4.927651	-0.797480	H	-7.131401	2.246705	-1.052884
H	1.661250	-3.704667	-0.047314	H	-5.497173	1.926019	0.778414
H	3.407029	-1.498920	-4.646595	N	-4.122042	-0.442302	1.143687
H	1.900241	-2.362044	-4.994135	C	-4.584905	-2.323306	-0.354873
H	2.220441	-0.800312	-5.743372	O	-4.484442	-3.431652	-0.871795
H	0.193107	0.245192	-5.047153	C	-2.218159	-1.951413	0.384005
H	-0.381142	-1.270499	-4.339694	H	-1.583937	-1.561598	1.184428
H	-0.375583	0.207378	-3.366373	H	-2.015556	-3.020533	0.281578
H	1.653696	1.400631	-2.855128	C	-1.997584	-1.261453	-0.933042
H	3.267752	0.710879	-3.002255	C	-2.217936	0.126780	-1.049816
H	2.403338	1.249390	-4.445782	C	-2.165363	0.993272	0.045600
C	0.904528	1.878628	1.819186	H	-2.027925	0.590455	1.033529
C	0.103183	1.028114	2.593952	H	-2.188983	-1.855670	-1.818574
C	1.193929	3.161973	2.299864	C	-2.414583	2.427738	-0.024136
C	-0.387003	1.439951	3.831546	C	-2.837877	3.073816	-1.202524
H	-0.149244	0.042733	2.216557	C	-2.211353	3.210051	1.128645
C	0.701443	3.578077	3.538590	C	-2.997759	4.455977	-1.236320
H	1.787647	3.843163	1.698962	H	-3.046079	2.494392	-2.094905
C	-0.087297	2.719885	4.307312	C	-2.367570	4.591765	1.091955
H	-1.018470	0.770956	4.408665	H	-1.913403	2.722489	2.048718
H	0.928206	4.577715	3.898448	C	-2.750727	5.223210	-0.093804
H	-0.479177	3.050226	5.264795	H	-3.324170	4.936362	-2.154354
C	1.849712	2.848839	-0.711336	H	-2.187282	5.175597	1.989818
C	0.773150	3.668586	-1.087128	H	-2.872222	6.302240	-0.124713
C	3.151815	3.218935	-1.069936	C	-3.970006	-2.617486	2.104530
C	0.998829	4.844116	-1.798489	O	-4.991259	-3.212938	2.360576
H	-0.238611	3.388523	-0.821446	O	-2.917706	-2.554776	2.965794
C	3.372586	4.392182	-1.794740	C	-3.134417	-3.210349	4.220357
H	3.990576	2.591399	-0.788400	H	-3.360293	-4.269468	4.068906
C	2.299577	5.207004	-2.158650	H	-2.205352	-3.092298	4.780507
H	0.154088	5.469383	-2.072346	H	-3.967945	-2.747048	4.755779
H	4.385936	4.669712	-2.071611				
H	2.475618	6.119840	-2.720653	TS-G-inner			
Pd	-0.013652	-0.211762	-0.781237	C	3.973661	0.020888	-3.045284
H	-2.410174	0.532432	-2.038803	C	5.328723	0.131843	-2.607292
C	-5.065873	-0.136074	0.228158	H	5.936216	1.027012	-2.632937
C	-5.386932	-1.171348	-0.708231	C	5.722358	-1.132756	-2.074553
C	-6.313604	-0.982054	-1.740920	H	6.681012	-1.362265	-1.628301
C	-6.938040	0.249772	-1.863548	C	4.610076	-2.021843	-2.182554
C	-6.631556	1.286361	-0.941988	H	4.574834	-3.046145	-1.839796

C	3.532799	-1.308645	-2.786379	H	2.518429	1.454265	2.422913
H	2.545269	-1.695605	-2.981438	H	1.939537	2.318617	3.854599
C	2.938726	0.998146	-0.016323	C	0.890432	-2.281542	-0.949429
C	4.319867	1.161579	0.330834	C	1.681465	-3.438530	-0.962159
C	4.804327	-0.050073	0.903323	C	0.071351	-2.009637	-2.048862
H	5.821370	-0.242691	1.218741	C	1.643905	-4.305485	-2.053594
C	3.730433	-0.979387	0.914758	H	2.326498	-3.661863	-0.118601
H	3.770653	-1.994088	1.283017	C	0.035823	-2.870006	-3.147169
C	2.561650	-0.343734	0.372761	H	-0.532279	-1.110100	-2.017124
Fe	4.117459	-0.378635	-1.014663	C	0.821228	-4.023670	-3.149160
H	3.371660	0.815492	-3.465843	H	2.259525	-5.201170	-2.054231
H	4.919118	2.038277	0.132760	H	-0.609587	-2.648051	-3.992735
C	2.106316	2.049662	-0.717713	H	0.794865	-4.701314	-3.997768
H	1.582995	1.546482	-1.537238	C	1.005870	-2.145008	1.897687
C	3.013685	3.121300	-1.347101	C	0.402001	-3.414466	1.926911
H	3.807035	2.630945	-1.920336	C	1.631827	-1.689451	3.070494
H	2.462640	3.758729	-2.035457	C	0.454789	-4.210474	3.071134
H	3.488393	3.765591	-0.606060	H	-0.083476	-3.801244	1.038005
P	0.600117	2.602353	0.331535	C	1.699205	-2.492390	4.207896
P	0.864885	-1.043393	0.418325	H	2.093536	-0.709953	3.085097
C	1.330641	3.239668	1.988516	C	1.114501	-3.760246	4.215591
C	-0.133995	4.086263	-0.640870	H	-0.006629	-5.194678	3.058817
C	0.620843	5.425652	-0.613862	H	2.211764	-2.122744	5.092462
C	-1.552345	4.322275	-0.084927	H	1.170964	-4.387351	5.100903
C	-0.293127	3.594422	-2.093855	Pd	-0.726255	0.659152	0.296778
C	1.669838	2.000005	2.837681	C	-2.675185	-0.075446	2.694201
C	2.600459	4.099743	1.879542	C	-1.736729	0.697534	3.410562
C	0.253176	4.049064	2.733069	C	-2.867616	-1.419774	3.073400
H	1.653477	5.350180	-0.958022	C	-1.041312	0.150682	4.477040
H	0.105171	6.135109	-1.275282	H	-1.558053	1.722571	3.114638
H	0.628969	5.869188	0.385806	C	-2.144951	-1.974903	4.124852
H	-1.540111	4.703998	0.938463	H	-3.592720	-2.019900	2.533850
H	-2.066110	5.060246	-0.713118	C	-1.238627	-1.188795	4.834579
H	-2.138263	3.404364	-0.106614	H	-0.324567	0.757831	5.020882
H	-0.685173	2.575155	-2.125240	H	-2.289485	-3.016095	4.393421
H	-1.012701	4.229420	-2.621130	H	-0.677009	-1.618572	5.656362
H	0.645709	3.616985	-2.652301	H	-4.238700	-0.229577	1.272216
H	3.442657	3.517538	1.500303	C	-3.759061	1.846818	1.416197
H	2.464593	4.975917	1.243029	C	-4.545599	2.231054	0.374040
H	2.879380	4.457698	2.880598	C	-5.016678	1.231548	-0.611583
H	0.576860	4.213106	3.769361	C	-3.822966	0.547037	-1.402442
H	0.089499	5.030566	2.281874	H	-4.722081	3.281828	0.178480
H	-0.708732	3.528900	2.760893	H	-5.561252	0.411407	-0.125124
H	0.824449	1.313605	2.897872	C	-4.099939	-1.820100	-1.571862

C	-4.458380	-3.149056	-1.810432	C	2.283918	-0.828137	-0.665862
C	-3.812575	-4.150252	-1.093443	O	3.446690	-1.368880	-0.270873
C	-2.817670	-3.806315	-0.154288	C	4.322962	-1.782543	-1.333162
C	-2.444905	-2.489803	0.081994	O	1.948616	-0.700115	-1.822813
C	-3.083187	-1.465469	-0.646265	H	4.573314	-0.930856	-1.970040
H	-5.222686	-3.376350	-2.548250	H	5.213326	-2.171552	-0.840010
H	-4.065462	-5.193473	-1.254740	H	3.845007	-2.555995	-1.939692
H	-2.320937	-4.598159	0.401277	H	-0.545647	-1.263697	-1.516717
H	-1.678969	-2.237618	0.800614	H	-0.880657	-3.326429	-0.067229
N	-2.819738	-0.118127	-0.569682	C	-2.202870	-0.934668	-0.196574
C	-4.560187	-0.588127	-2.193760	C	-3.119273	-1.158069	-1.225814
O	-5.348079	-0.397064	-3.105719	C	-2.668180	-0.535382	1.060467
C	-3.215499	1.632659	-2.311509	C	-4.486981	-0.979636	-1.006805
O	-2.377253	1.294360	-3.311616	H	-2.759326	-1.461642	-2.206034
C	-2.234465	-0.035093	-3.820296	C	-4.030673	-0.349480	1.279161
O	-3.450555	2.808783	-2.144431	H	-1.951437	-0.358229	1.856431
H	-3.038562	-0.244493	-4.530085	C	-4.944807	-0.571881	0.245607
H	-1.269208	-0.051162	-4.328785	H	-5.190670	-1.151918	-1.816365
H	-2.234806	-0.782647	-3.030289	H	-4.381881	-0.029607	2.256212
H	-3.284613	2.589155	2.050084	H	-6.007387	-0.424564	0.416552
H	-5.678538	1.664312	-1.361932	H	2.457438	-1.679661	1.908282
C	-3.502036	0.469328	1.642392				

(6*S*, 9*R*)-3aa

C	-0.315216	-2.454764	0.251112
C	0.600303	-2.551521	1.219153
C	1.435420	-1.378565	1.668907
C	1.449532	-0.351736	0.540316
C	-0.714898	-1.161879	-0.433087
H	0.777287	-3.512997	1.695798
H	1.017040	-0.914728	2.571629
C	1.041828	2.000277	0.363072
C	1.094299	3.393360	0.304378
C	0.046265	4.075508	-0.302196
C	-1.035658	3.351694	-0.834520
C	-1.112913	1.962135	-0.772062
C	-0.059070	1.274839	-0.151696
H	1.953808	3.911696	0.718936
H	0.061779	5.158113	-0.376201
H	-1.846245	3.893026	-1.315457
H	-1.962688	1.436607	-1.186826
N	0.088591	-0.074172	0.101188
C	2.005253	1.056590	0.920522
O	3.038614	1.249593	1.533300

(6*R*, 9*R*)-3aa

C	-0.738455	-1.501330	1.932113
C	0.495581	-1.902788	2.242258
C	1.701049	-1.108417	1.810701
C	1.407025	-0.499913	0.433327
C	-1.021368	-0.202694	1.205254
H	0.649504	-2.822896	2.800061
H	1.902903	-0.290068	2.515705
C	1.724232	1.824813	-0.123964
C	2.169613	3.107073	-0.450397
C	1.243360	4.143006	-0.491240
C	-0.108529	3.883173	-0.199248
C	-0.570254	2.610345	0.128099
C	0.365680	1.566470	0.156196
H	3.222623	3.270460	-0.659075
H	1.555648	5.150413	-0.746785
H	-0.821932	4.702298	-0.234664
H	-1.619903	2.428803	0.328601
N	0.148452	0.238950	0.450710
C	2.471927	0.584221	0.037586
O	3.660319	0.355547	-0.084651
C	1.411326	-1.541371	-0.693679

O	2.271616	-2.539475	-0.440500	H	1.982386	0.634893	2.039720
C	2.426081	-3.497785	-1.501156	H	2.813849	0.683248	3.594512
O	0.774704	-1.445681	-1.720076	H	2.333289	-0.858060	2.894228
H	2.791917	-3.004071	-2.404451	H	-2.205472	-2.723127	3.887261
H	3.153508	-4.221500	-1.134438	H	-1.373175	-1.904043	5.222527
H	1.470375	-3.981400	-1.717418	H	-3.137817	-1.927904	5.156589
H	-1.210641	0.555261	1.986042	H	-3.505344	0.541443	5.133954
H	-1.613305	-2.072028	2.229069	H	-1.785845	0.709934	5.480263
C	-2.288626	-0.282506	0.359396	H	-2.508614	1.597174	4.121517
C	-3.527417	-0.101136	0.983949	H	-3.590704	0.275674	2.183505
C	-2.242509	-0.549771	-1.010730	H	-3.453832	-1.490539	2.155006
C	-4.711058	-0.197054	0.253003	H	-4.411586	-0.704049	3.413021
H	-3.565176	0.121585	2.048693	C	-1.716679	-0.364978	-2.343146
C	-3.427859	-0.640400	-1.741936	C	-0.434624	0.079257	-2.676500
H	-1.280567	-0.678824	-1.494345	C	-2.542325	-0.899468	-3.345362
C	-4.662837	-0.467716	-1.115539	C	0.030517	-0.015002	-3.990578
H	-5.666899	-0.051453	0.748787	H	0.220305	0.467931	-1.907911
H	-3.383312	-0.845675	-2.808038	C	-2.084622	-0.980476	-4.658670
H	-5.582301	-0.536600	-1.690236	H	-3.544448	-1.237686	-3.101919
H	2.603513	-1.717403	1.755379	C	-0.796400	-0.539634	-4.982702
TS-F-2-E				H	1.043869	0.302586	-4.207268
C	-0.239137	-1.881688	1.831839	H	-2.732090	-1.388258	-5.430563
H	0.467406	-1.508431	1.081575	H	-0.441608	-0.609707	-6.007261
C	0.499912	-2.928527	2.680474	C	-4.047362	0.110186	-0.792800
H	0.770588	-3.777632	2.044625	C	-4.384774	1.143475	-1.682040
H	1.425392	-2.529308	3.091236	C	-5.074840	-0.502280	-0.061844
H	-0.102045	-3.302312	3.511535	C	-5.705679	1.556895	-1.829992
P	-0.734307	-0.234533	2.646922	H	-3.611730	1.627772	-2.264187
P	-2.256875	-0.277200	-0.593616	C	-6.399448	-0.087859	-0.211693
C	-2.280201	-0.546500	3.733340	H	-4.853150	-1.314591	0.616410
C	0.702801	0.297571	3.807479	C	-6.720106	0.945257	-1.091866
C	0.830711	-0.490563	5.122876	H	-5.934646	2.366150	-2.515399
C	0.521310	1.793352	4.146277	H	-7.180465	-0.581678	0.360166
C	2.022536	0.178422	3.026133	H	-7.751260	1.267969	-1.205079
C	-3.501470	-0.619337	2.804584	Pd	-1.077379	1.189018	0.754217
C	-2.227751	-1.852012	4.546306	C	3.757774	-2.782366	-1.887858
C	-2.516064	0.650060	4.671739	C	3.283040	-1.985839	-0.840681
H	0.934788	-1.565082	4.961204	C	3.502204	-2.380587	0.481939
H	1.731594	-0.147778	5.648777	C	4.178016	-3.568783	0.757575
H	-0.014928	-0.325330	5.794035	C	4.635715	-4.370085	-0.291147
H	-0.332033	1.986169	4.796274	C	4.426089	-3.973315	-1.615366
H	1.419776	2.145336	4.669084	H	3.586861	-2.446432	-2.904711
H	0.397405	2.389963	3.241639	H	3.153685	-1.737712	1.278119
				H	4.351318	-3.868025	1.788008

H	5.157675	-5.299241	-0.078254	C	1.961988	2.487906	-0.379144
H	4.783389	-4.594739	-2.431787	H	1.626032	2.657607	-1.402679
C	2.562857	-0.709766	-1.169301	H	1.890469	1.112585	-0.294321
O	1.971734	-0.135198	-0.147531	C	3.733764	4.253674	-0.078885
O	2.556709	-0.276218	-2.321570	O	4.230685	4.769849	0.906467
C	-0.254680	3.237090	0.620713	O	3.306742	4.932474	-1.147005
H	-0.674204	3.788418	1.459834	C	3.482012	6.356460	-1.086638
C	-1.086223	2.941312	-0.509674	H	4.539152	6.606373	-0.966678
C	0.716165	-4.212531	-0.955178	H	3.101412	6.734531	-2.034966
C	-0.104912	-5.379362	-0.956847	H	2.917583	6.773814	-0.248482
H	-0.025103	-6.214210	-0.272765	C	-2.401270	3.591608	-0.674621
C	-1.087358	-5.226019	-1.981578	C	-2.773418	4.099003	-1.930603
H	-1.884498	-5.922814	-2.206318	C	-3.307708	3.732577	0.391941
C	-0.875167	-3.961445	-2.607841	C	-3.999837	4.736727	-2.113473
H	-1.473301	-3.525132	-3.394675	H	-2.085696	3.993544	-2.766369
C	0.240857	-3.337330	-1.973676	C	-4.533696	4.365692	0.209275
H	0.640308	-2.364582	-2.218147	H	-3.054215	3.312294	1.361614
C	-1.410892	-2.517874	1.101637	C	-4.885898	4.874310	-1.043452
C	-1.906695	-3.833940	1.373387	H	-4.262359	5.127274	-3.093120
C	-2.983282	-4.126359	0.487251	H	-5.223139	4.452830	1.044589
H	-3.516345	-5.065782	0.424414	H	-5.843812	5.366698	-1.184531
C	-3.173214	-2.996705	-0.350486	H	-0.579299	2.724037	-1.447614
H	-3.902938	-2.900896	-1.141429				
C	-2.224425	-1.984319	0.024482	(E)-5			
Fe	-1.269940	-3.713227	-0.589550	C	-2.889045	-1.298866	-0.584810
H	1.540970	-4.015312	-0.287161	C	-3.182639	-1.013036	0.758693
H	-1.492261	-4.525568	2.091868	C	-4.069727	-1.800781	1.497011
C	1.127452	2.961986	0.660053	C	-4.681939	-2.876683	0.865702
H	1.612606	3.137578	1.619618	C	-4.403820	-3.146039	-0.487497
C	4.956035	1.132562	0.558306	C	-3.511555	-2.373967	-1.227607
C	5.076477	1.077815	-0.839686	C	-1.668516	0.636535	-0.152627
C	5.891120	0.133503	-1.466438	H	-4.271413	-1.553092	2.534734
C	6.613518	-0.749846	-0.672284	H	-5.377809	-3.508767	1.408006
C	6.517301	-0.671614	0.728356	H	-4.896789	-3.985248	-0.970803
C	5.696712	0.260175	1.361917	H	-3.300666	-2.601619	-2.268049
C	3.471372	2.758117	-0.207516	H	-2.111424	-0.094925	-2.052250
H	5.929786	0.098086	-2.550364	N	-1.932016	-0.433499	-1.111736
H	7.235802	-1.513877	-1.126455	C	-2.467825	0.201230	1.144142
H	7.084160	-1.371596	1.336100	O	-2.430032	0.783147	2.207220
H	5.613393	0.292481	2.444210	C	-2.240734	1.951960	-0.698028
H	4.320433	2.727623	1.694825	O	-2.806258	2.046674	-1.767992
N	4.016725	2.079792	0.973628	O	-2.023430	2.969555	0.139935
C	4.232568	2.122531	-1.425374	C	-2.531054	4.245627	-0.290068
O	4.089978	2.448997	-2.584082	H	-3.614510	4.196578	-0.422011

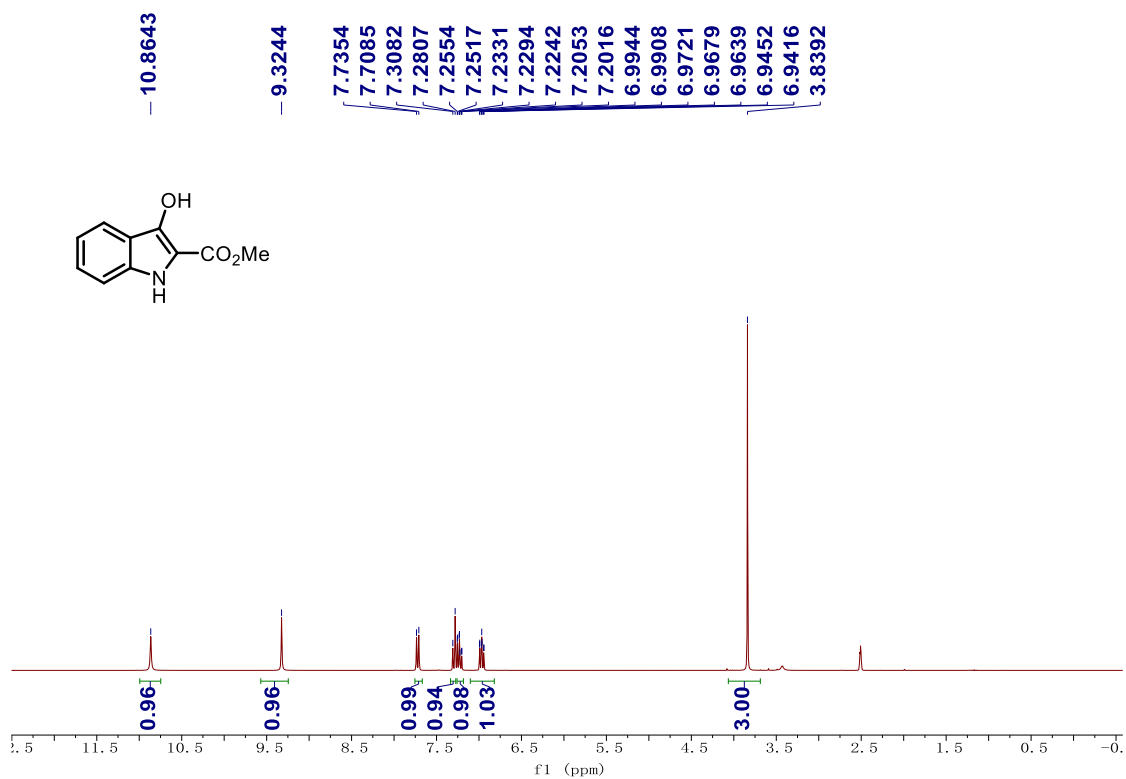
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C	-0.213917	0.795970	0.213915	H	0.359768	-2.399962	4.425511
H	-0.028827	1.533311	0.989999	H	-0.715766	-2.903659	3.127048
C	0.786459	0.078561	-0.322272	H	-5.056687	-0.478730	2.436927
H	0.550144	-0.661361	-1.084326	H	-4.476605	-0.525337	4.113786
C	2.173464	0.223269	0.061943	H	-5.449681	0.835474	3.544665
H	2.388874	0.958640	0.835472	H	-3.824789	2.662686	4.019591
C	3.172762	-0.499185	-0.488405	H	-2.896322	1.440125	4.891260
H	2.906301	-1.221407	-1.260477	H	-2.101582	2.446272	3.665437
C	4.597831	-0.432215	-0.171632	H	-2.944346	2.325961	1.206024
C	5.489441	-1.259947	-0.877605	H	-4.118227	1.084255	0.741995
C	5.131559	0.422928	0.811871	H	-4.610820	2.405400	1.811085
C	6.857318	-1.237243	-0.617354	C	-0.043943	-0.577158	-2.038815
H	5.095573	-1.927938	-1.639785	C	0.984201	-1.257557	-1.382676
C	6.496932	0.445996	1.072162	C	-0.264575	-0.809966	-3.405117
H	4.472000	1.072640	1.378738	C	1.770648	-2.182474	-2.073243
C	7.368655	-0.383031	0.359645	H	1.180523	-1.066796	-0.334168
H	7.523801	-1.887174	-1.177557	C	0.535493	-1.716410	-4.097896
H	6.885988	1.113487	1.836185	H	-1.061633	-0.288043	-3.923918
H	8.434727	-0.362170	0.566576	C	1.548525	-2.412160	-3.430163
TS-F-2-Z				H	2.566667	-2.701507	-1.551111
C	-2.485281	-1.632714	1.381825	H	0.362561	-1.888758	-5.156921
H	-1.526091	-2.043114	1.047582	H	2.171496	-3.119269	-3.969851
C	-3.246786	-2.762940	2.095673	C	-1.520530	1.889370	-2.195965
H	-3.529611	-3.524016	1.362537	C	-0.573460	2.303736	-3.144566
H	-2.629044	-3.247665	2.850658	C	-2.712626	2.618430	-2.064493
H	-4.158387	-2.415521	2.583705	C	-0.855258	3.368623	-4.000839
P	-1.883599	-0.152926	2.406199	H	0.385228	1.800977	-3.208555
P	-1.140297	0.508780	-1.051349	C	-2.984344	3.687924	-2.914502
C	-3.416643	0.911585	2.818795	H	-3.435762	2.341138	-1.305372
C	-1.149926	-0.912313	4.000372	C	-2.065871	4.053087	-3.900670
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C	-0.262203	0.149437	4.680315	H	-3.913464	4.239190	-2.802375
C	-0.198568	-2.040903	3.551471	H	-2.283503	4.881273	-4.569186
C	-3.786010	1.724996	1.559613	Pd	-0.425643	1.157385	1.052525
C	-4.662800	0.125214	3.257552	C	3.666778	-4.655635	1.481575
C	-3.026409	1.916789	3.917130	C	2.734959	-3.619416	1.353784
H	-2.853002	-2.171836	4.633020	C	1.445493	-3.905543	0.885188
H	-1.603682	-1.920760	5.853752	C	1.096119	-5.210766	0.543754
H	-2.742459	-0.626716	5.484939	C	2.031076	-6.240646	0.671784
H	-0.823540	1.014420	5.038353	C	3.316742	-5.961103	1.142721
H	0.234643	-0.307691	5.545523	H	4.658520	-4.410548	1.846020
				H	0.730890	-3.099362	0.777155

H	0.099440	-5.424392	0.166829	O	2.534549	1.773149	-1.494872
H	1.759489	-7.257825	0.402545	C	3.135359	1.127600	1.797393
H	4.045246	-6.761131	1.241668	H	3.847333	0.901710	2.596932
C	3.158347	-2.217260	1.697635	H	2.638802	-0.126462	1.675887
O	2.248235	-1.310172	1.460434	C	4.645042	2.713534	0.591205
O	4.287693	-1.992951	2.150869	O	5.799354	2.944776	0.859798
C	1.036821	2.721484	1.883408	O	3.716393	3.659061	0.358440
H	0.484456	3.240634	2.664842	C	4.159731	5.016923	0.469560
C	0.712506	2.989828	0.524263	H	4.951138	5.221405	-0.256508
C	-2.518335	-4.167114	-1.170185	H	3.278060	5.624116	0.263734
C	-3.858646	-4.314416	-1.641143	H	4.539840	5.213929	1.475726
H	-4.684484	-4.746439	-1.091317	C	-0.185423	4.098553	0.169283
C	-3.927645	-3.744849	-2.948042	C	0.032725	4.786211	-1.036361
H	-4.816133	-3.669609	-3.561065	C	-1.244852	4.525567	0.993165
C	-2.633571	-3.241471	-3.278194	C	-0.772678	5.860643	-1.403914
H	-2.362357	-2.724160	-4.186925	H	0.844098	4.462803	-1.679760
C	-1.762951	-3.505751	-2.179022	C	-2.055025	5.594678	0.621594
H	-0.723076	-3.229353	-2.107782	H	-1.440804	4.005894	1.925570
C	-3.228606	-1.177941	0.143808	C	-1.821952	6.270009	-0.579317
C	-4.595620	-1.493726	-0.146241	H	-0.587297	6.372761	-2.343558
C	-4.928775	-0.972637	-1.429465	H	-2.870048	5.903523	1.271194
H	-5.874949	-1.096308	-1.939413	H	-2.453411	7.105271	-0.869055
C	-3.776276	-0.322839	-1.946183	H	1.437919	2.728085	-0.232874
H	-3.695652	0.167564	-2.905072				
C	-2.721799	-0.413996	-0.977028	(Z)-5			
Fe	-3.358864	-2.311734	-1.570423	C	-1.502489	1.538765	0.370877
H	-2.145537	-4.471130	-0.201179	C	-2.502233	1.470346	-0.611964
H	-5.252129	-2.084271	0.476111	C	-3.179647	2.613057	-1.046340
C	2.074814	1.896085	2.351701	C	-2.855768	3.833800	-0.467268
H	2.044324	1.778270	3.434771	C	-1.869330	3.895079	0.535137
C	5.096983	-0.428545	-0.583185	C	-1.181028	2.763441	0.965268
C	4.247574	0.106911	-1.565353	C	-1.646504	-0.737220	-0.111238
C	4.213086	-0.405862	-2.865964	H	-3.945085	2.525183	-1.811346
C	5.020509	-1.493381	-3.167019	H	-3.362010	4.741559	-0.779567
C	5.818689	-2.075093	-2.158209	H	-1.632804	4.855518	0.985024
C	5.868627	-1.567368	-0.864968	H	-0.415920	2.829122	1.732966
C	3.992304	1.311993	0.520156	H	-0.759009	0.067890	1.586473
H	3.540549	0.030291	-3.597362	N	-0.907159	0.300183	0.608061
H	5.023585	-1.917017	-4.166435	C	-2.687244	0.072700	-0.992263
H	6.417530	-2.949300	-2.400613	O	-3.433431	-0.422623	-1.809494
H	6.480924	-2.025845	-0.096170	C	-2.403244	-1.595948	0.916196
H	5.047366	-0.291066	1.435824	O	-2.325486	-1.425983	2.115955
N	5.037885	0.281955	0.591368	O	-3.133631	-2.547222	0.329911
C	3.422878	1.132809	-0.951187	C	-3.876076	-3.397378	1.222917

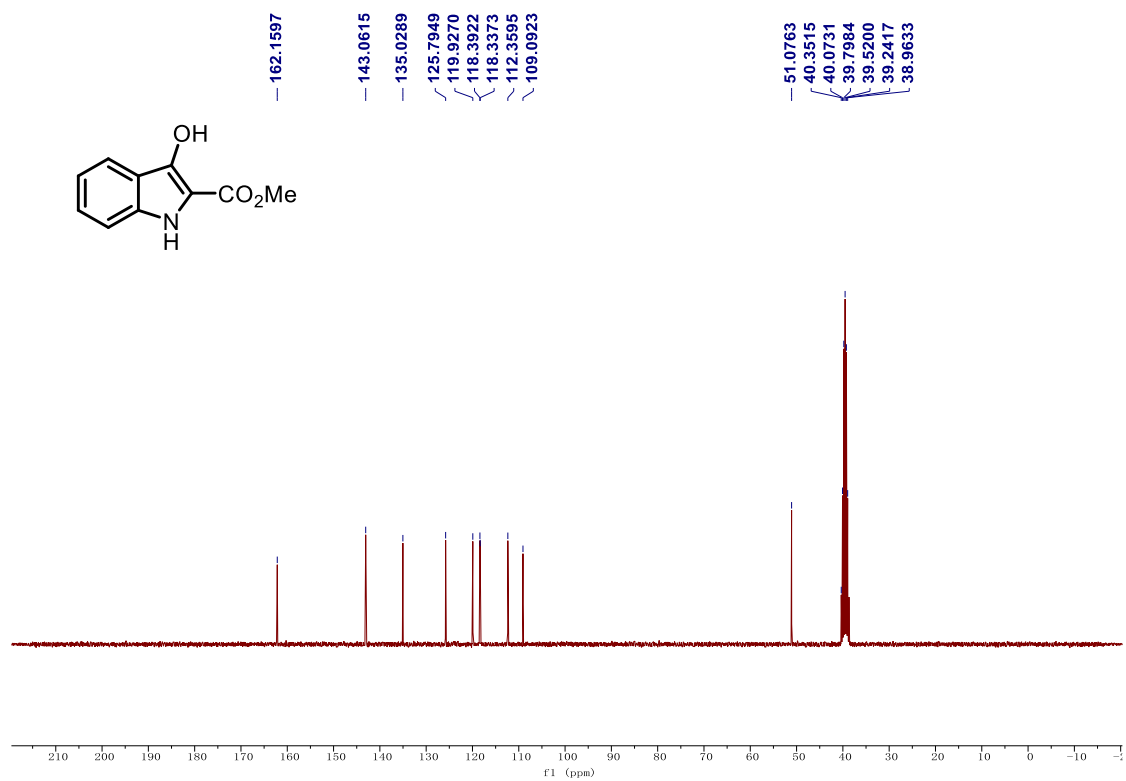
H	-4.575835	-2.803465	1.815529	C	5.302605	-0.942008	-0.715467
H	-4.409922	-4.094834	0.578583	C	3.911231	0.567552	0.549491
H	-3.195831	-3.928301	1.893296	C	6.442670	-0.326448	-0.204364
C	-0.851583	-1.624941	-1.040587	H	5.402284	-1.772654	-1.409984
H	-1.502611	-2.262904	-1.630417	C	5.048675	1.182357	1.059772
C	0.477986	-1.703985	-1.240681	H	2.931637	0.931677	0.843385
H	0.796687	-2.430108	-1.989608	C	6.321521	0.739112	0.687550
C	1.554445	-0.967256	-0.612318	H	7.425931	-0.678830	-0.503502
H	1.277555	-0.206733	0.107022	H	4.944848	2.015000	1.750248
C	2.851688	-1.197041	-0.910005	H	7.207853	1.222882	1.087773
H	3.080881	-1.974193	-1.640236				
C	4.014632	-0.512561	-0.348554				

9. ^1H , ^{13}C and ^{19}F NMR Spectra of Title Compounds

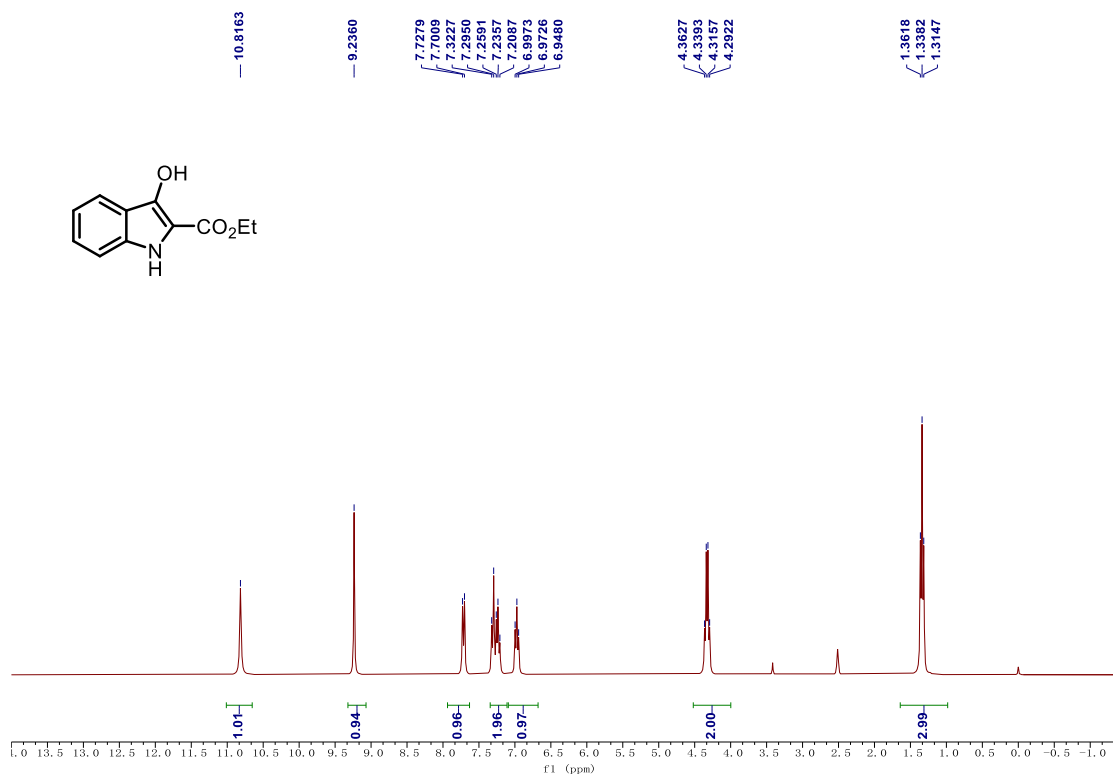
^1H NMR Spectrum of 1a (300 MHz, $\text{DMSO}-d_6$)



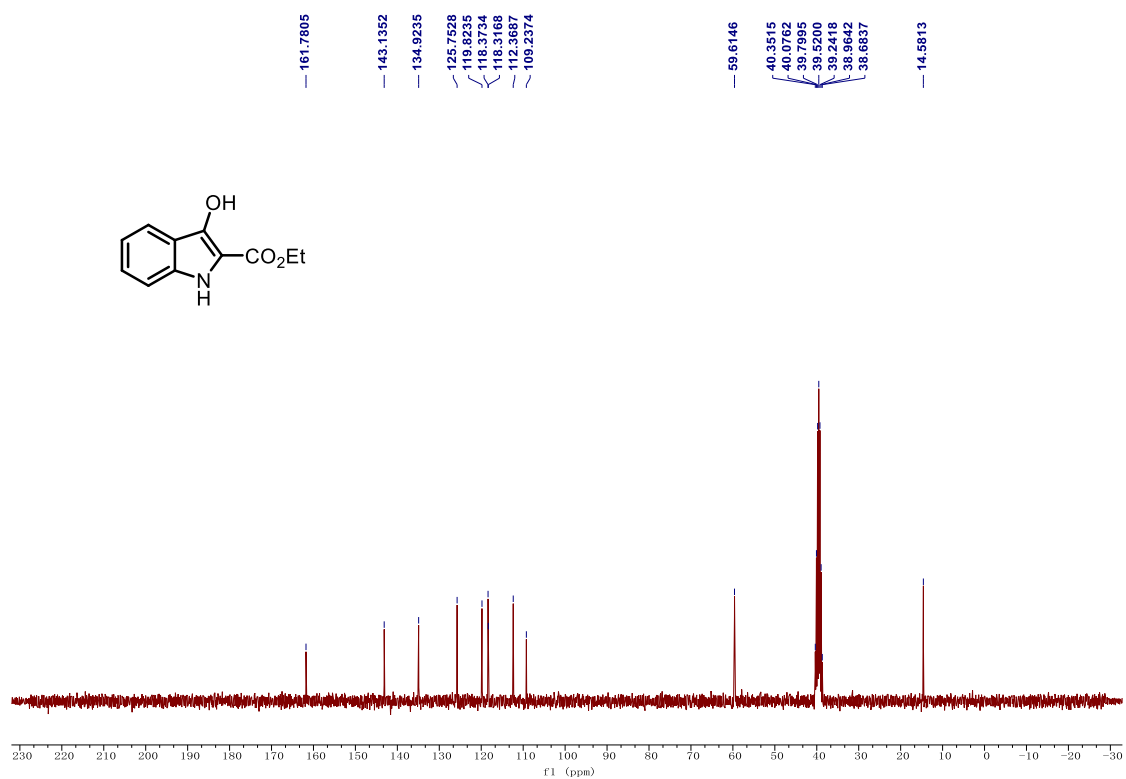
^{13}C NMR Spectrum of 1a (75 MHz, $\text{DMSO}-d_6$)



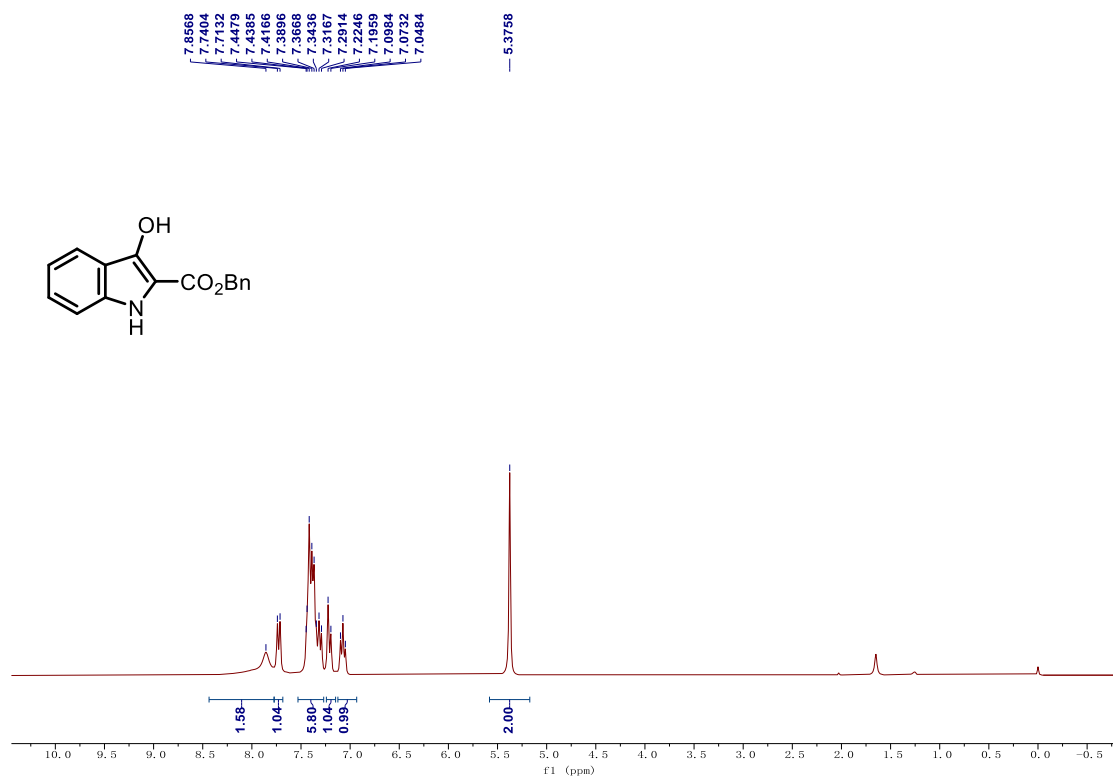
¹H NMR Spectrum of 1b (300 MHz, DMSO-*d*₆)



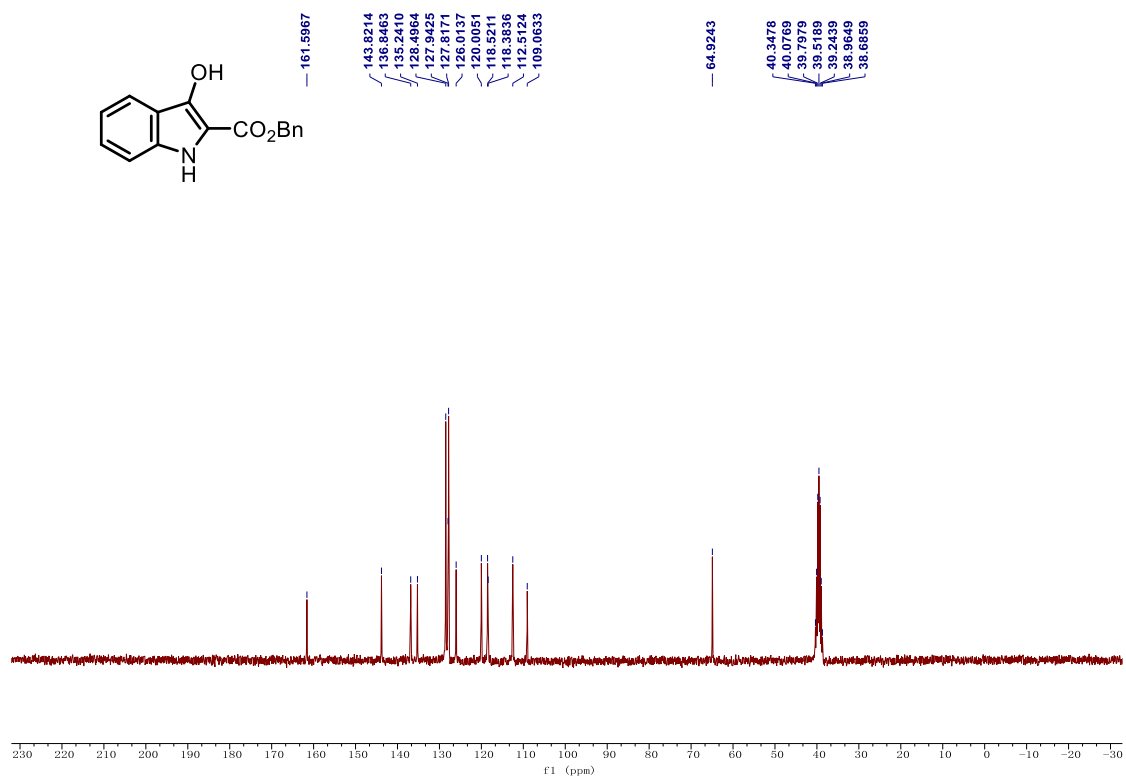
¹³C NMR Spectrum of 1b (75 MHz, DMSO-*d*₆)



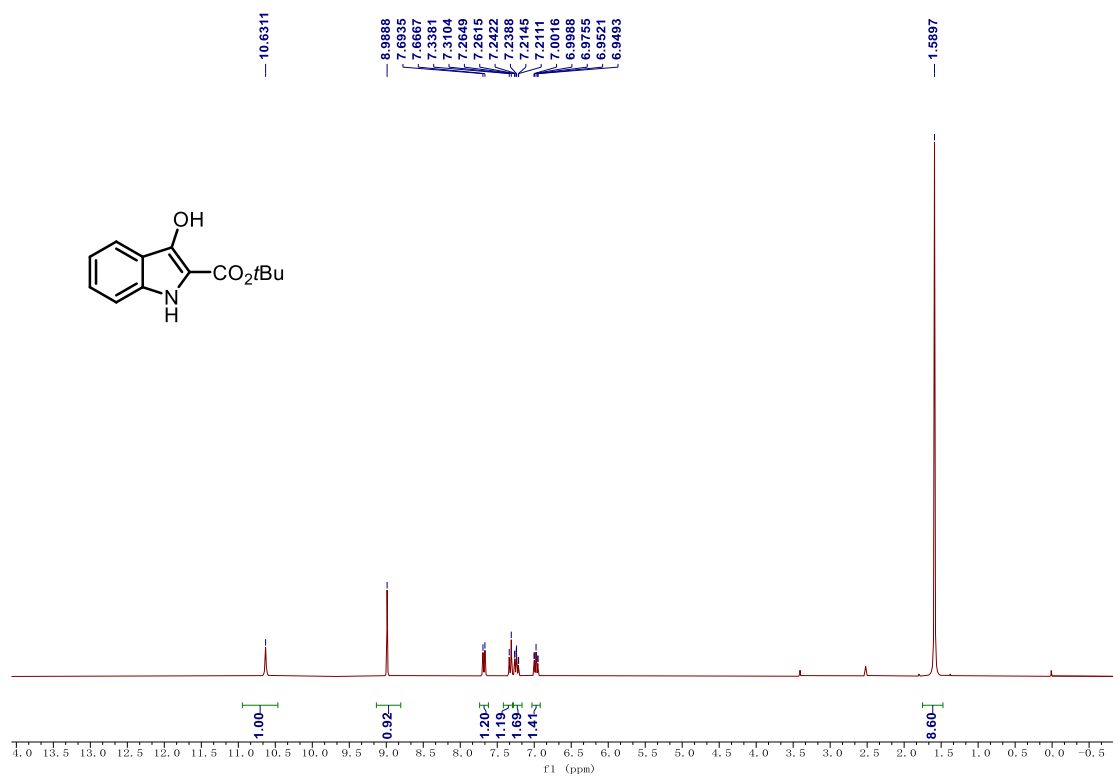
¹H NMR Spectrum of 1c (300 MHz, DMSO-*d*₆)



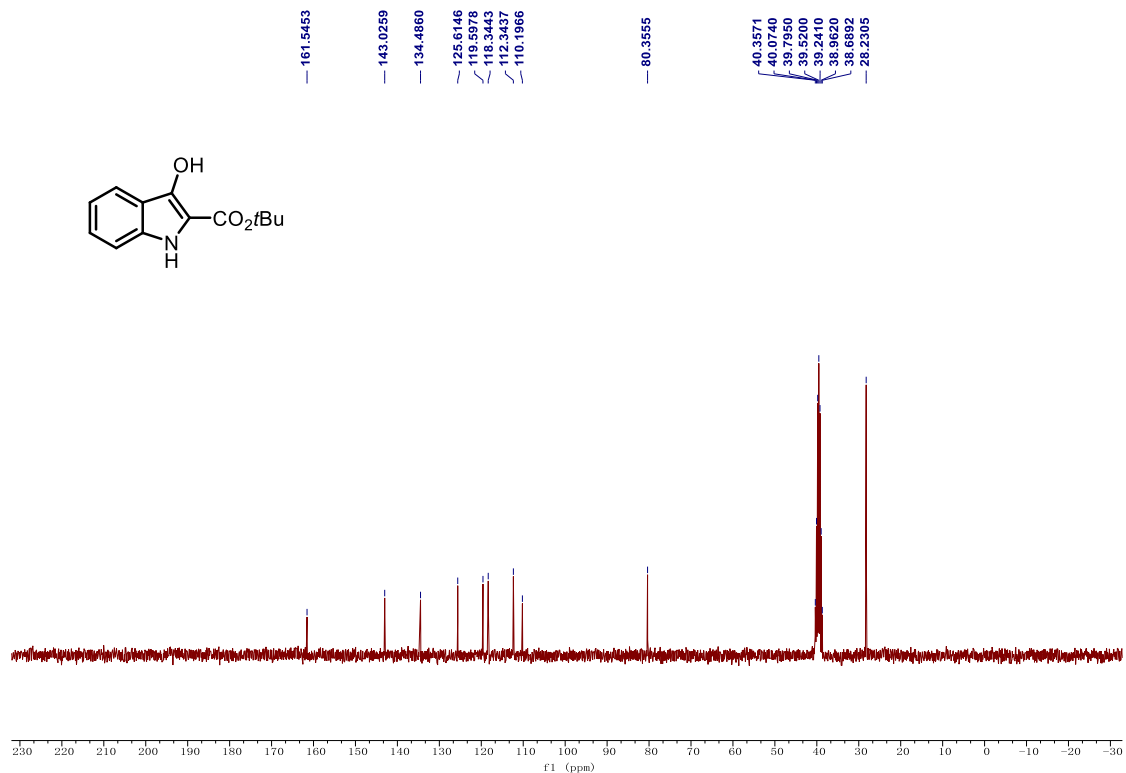
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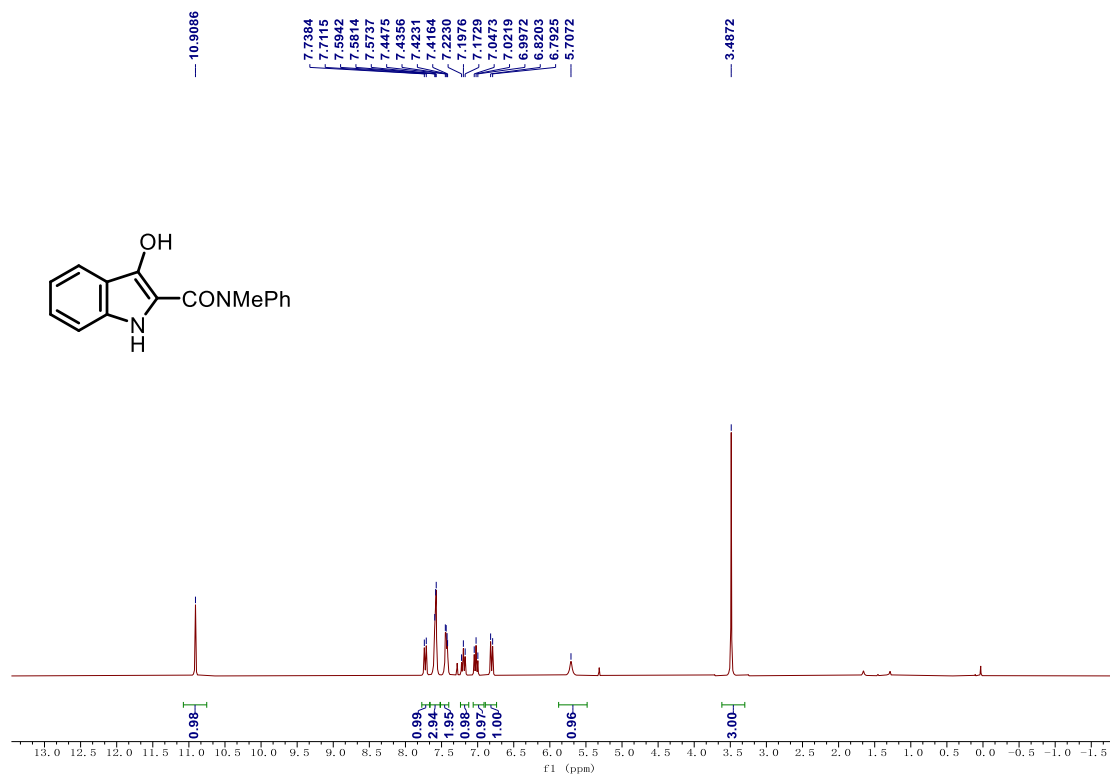
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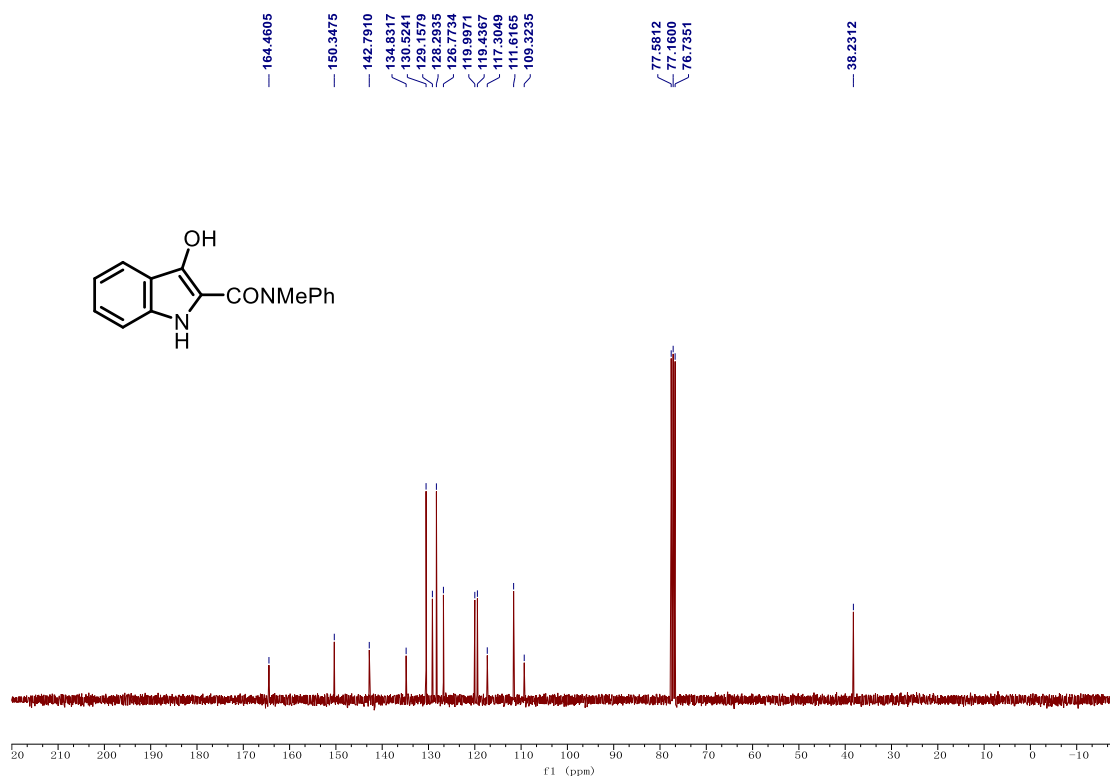
¹³C NMR Spectrum of 1d (75 MHz, DMSO-*d*₆)



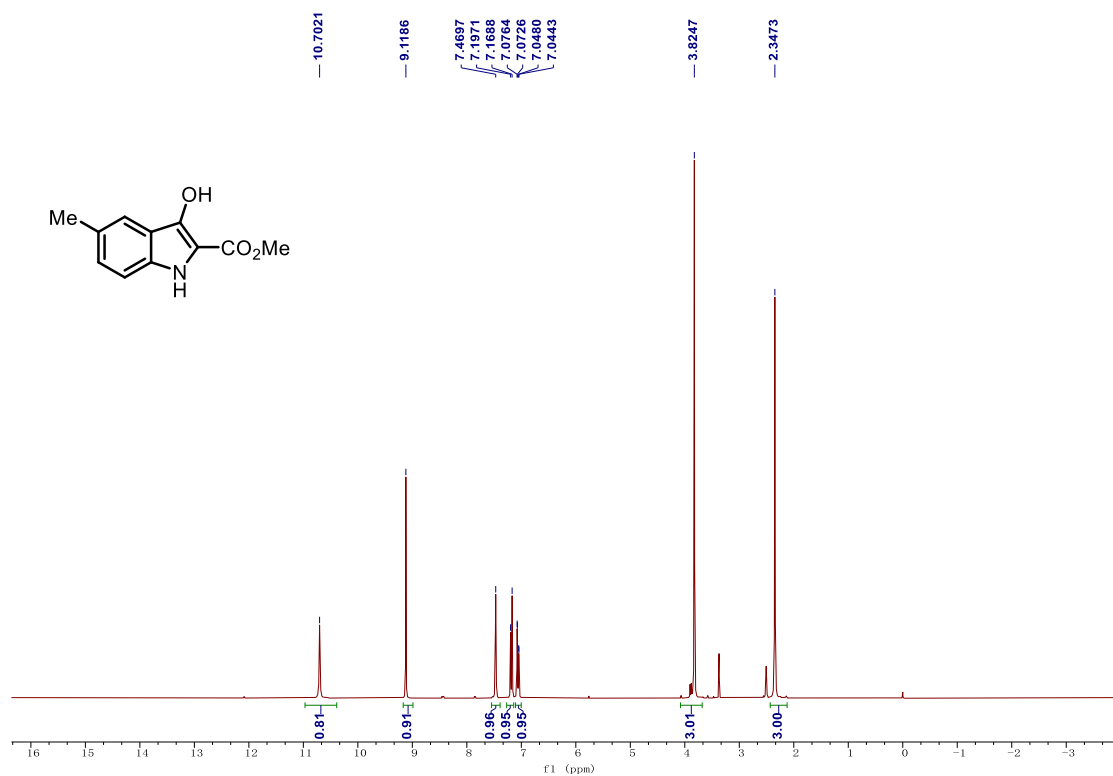
¹H NMR Spectrum of 1e (300 MHz, CDCl₃)



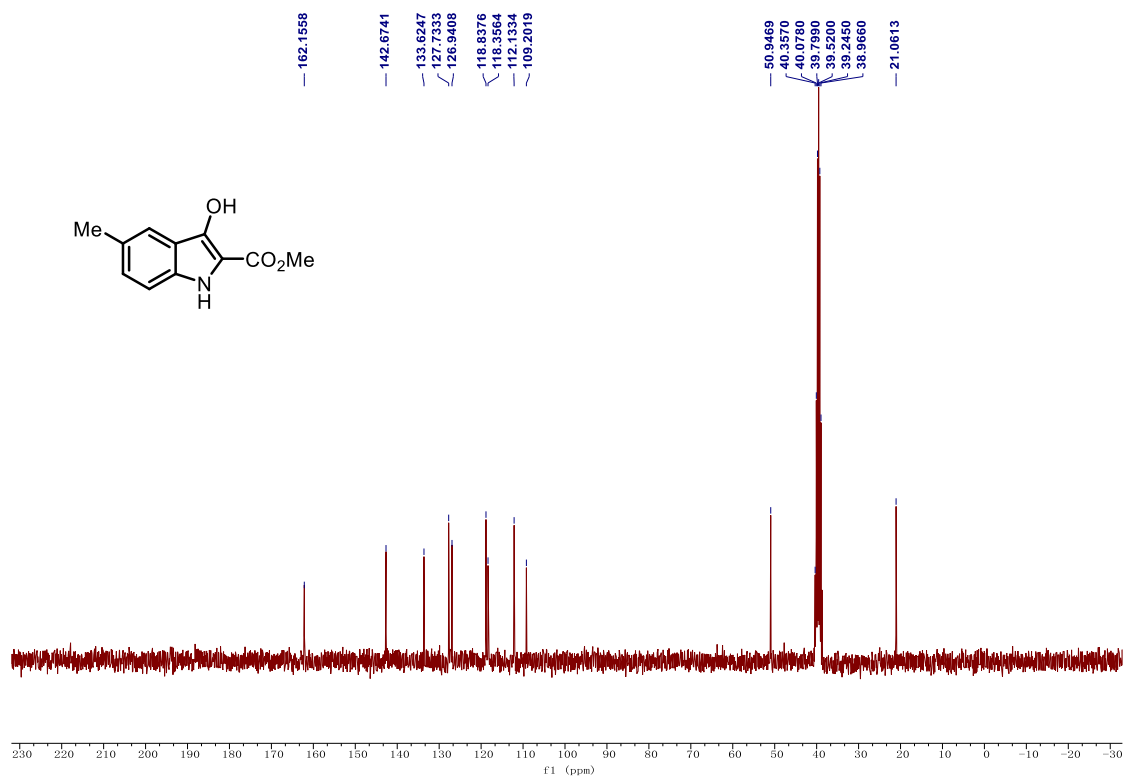
¹³C NMR Spectrum of 1e (75 MHz, CDCl₃)



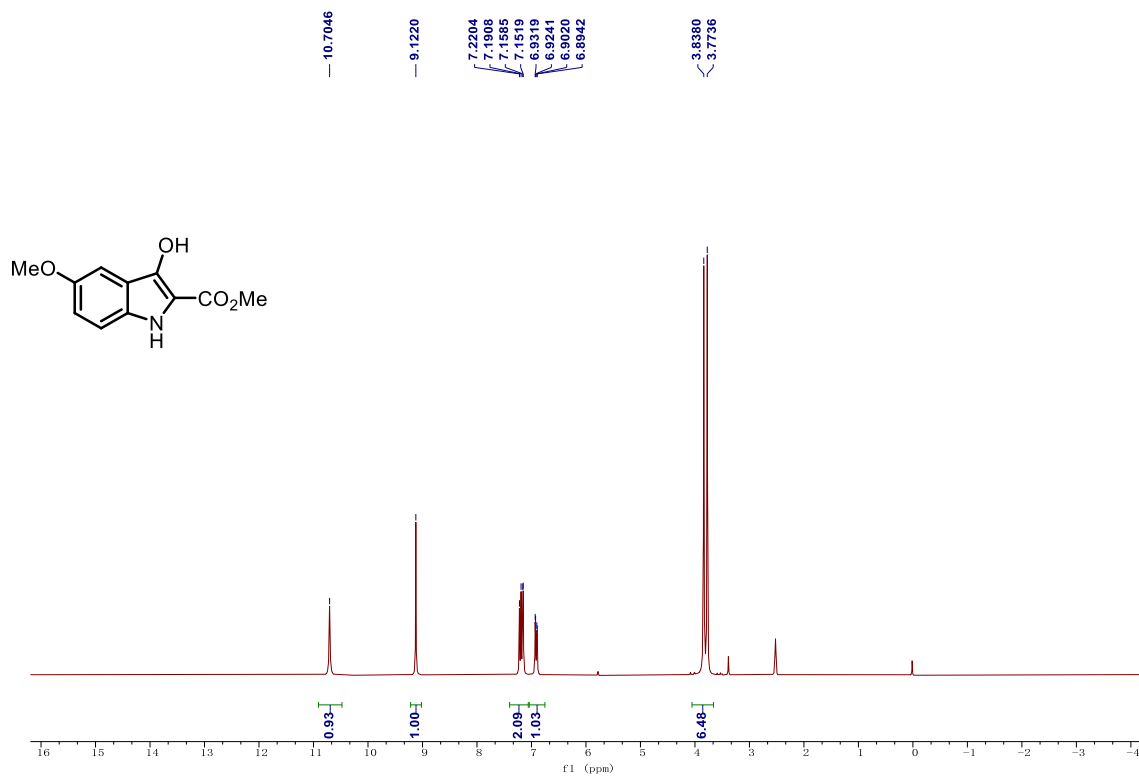
¹H NMR Spectrum of 1f (300 MHz, DMSO-*d*₆)



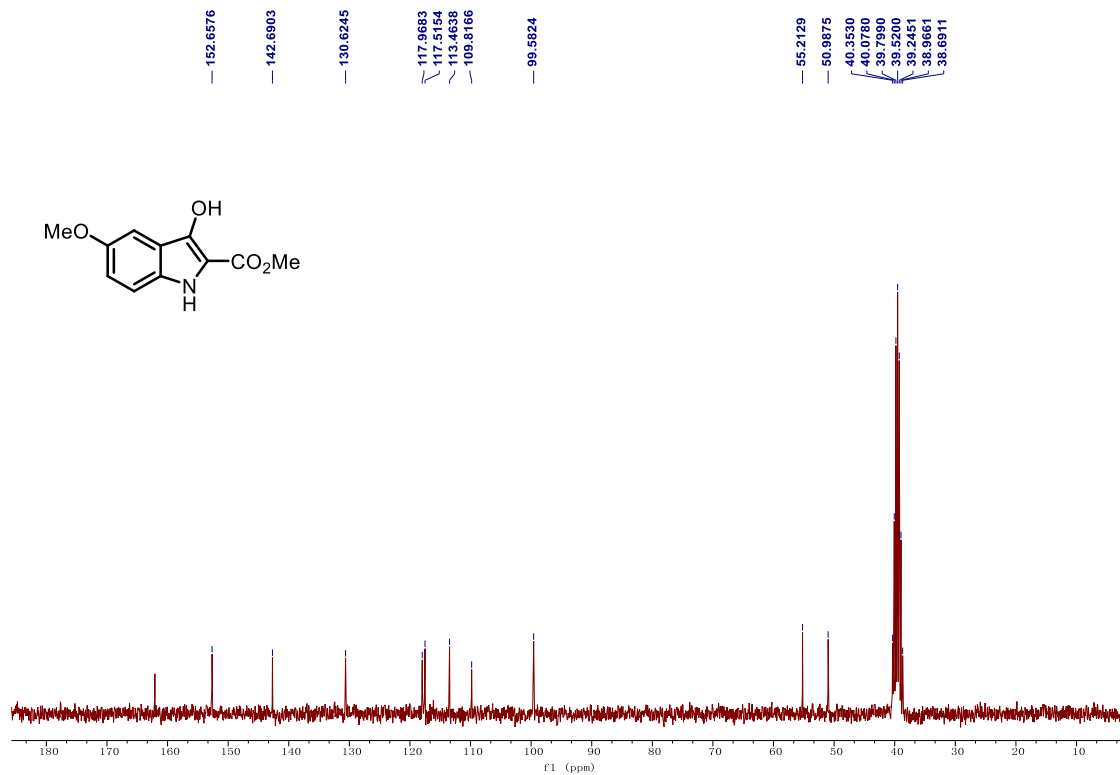
¹³C NMR Spectrum of 1f (75 MHz, DMSO-*d*₆)



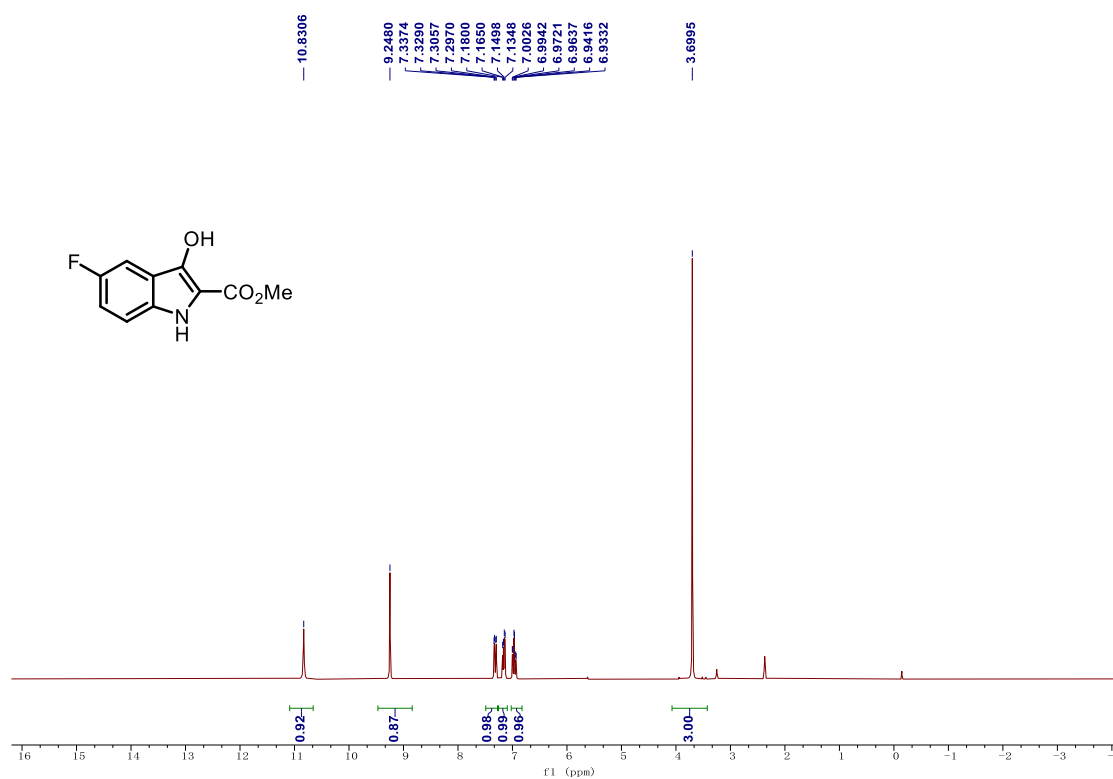
¹H NMR Spectrum of 1g (300 MHz, DMSO-*d*₆)



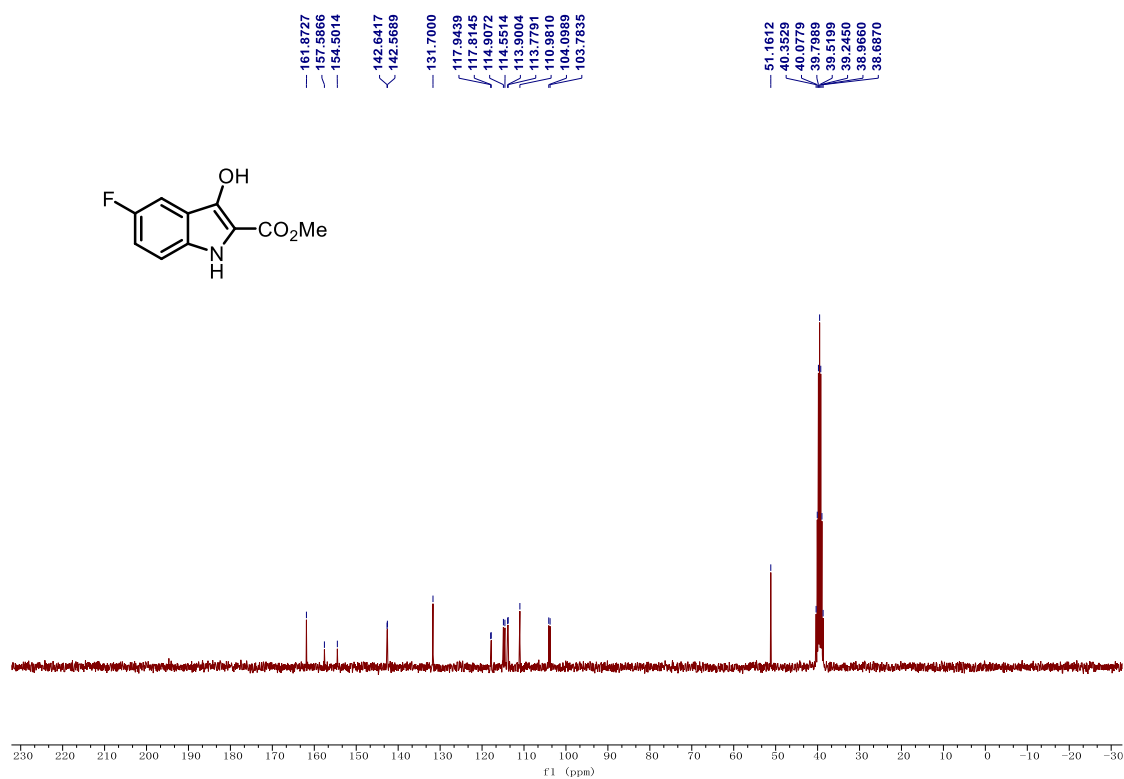
¹³C NMR Spectrum of 1g (75 MHz, DMSO-*d*₆)



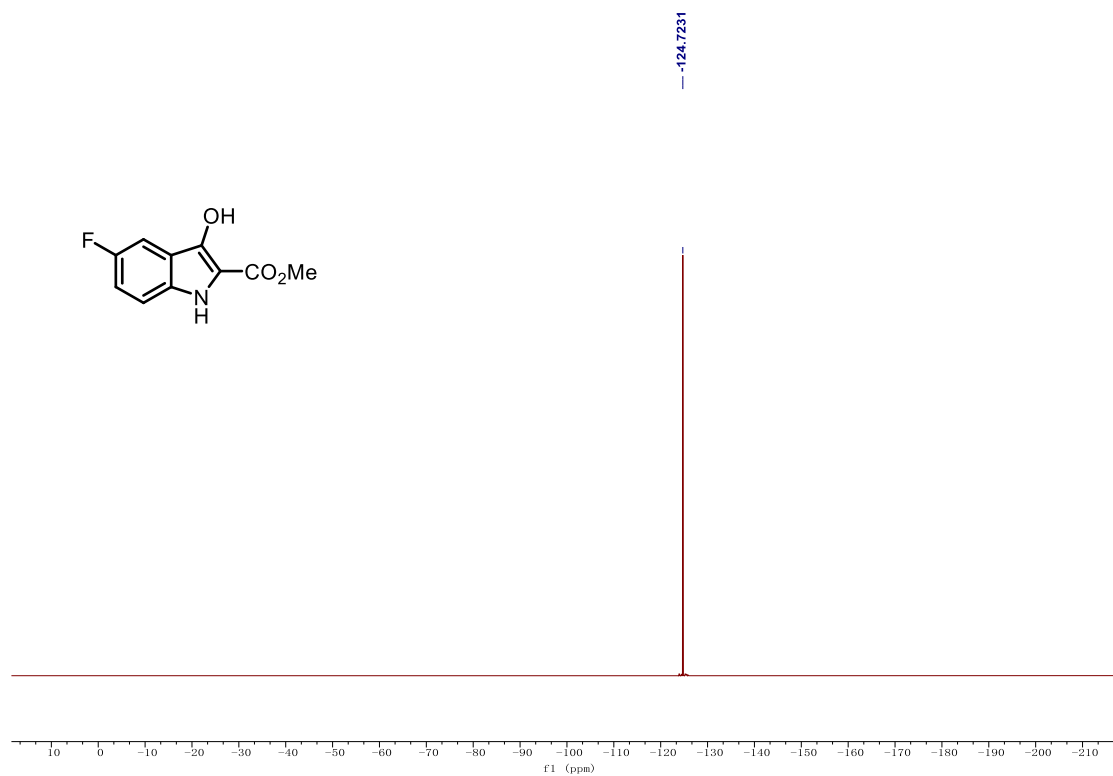
¹H NMR Spectrum of 1h (300 MHz, DMSO-*d*₆)



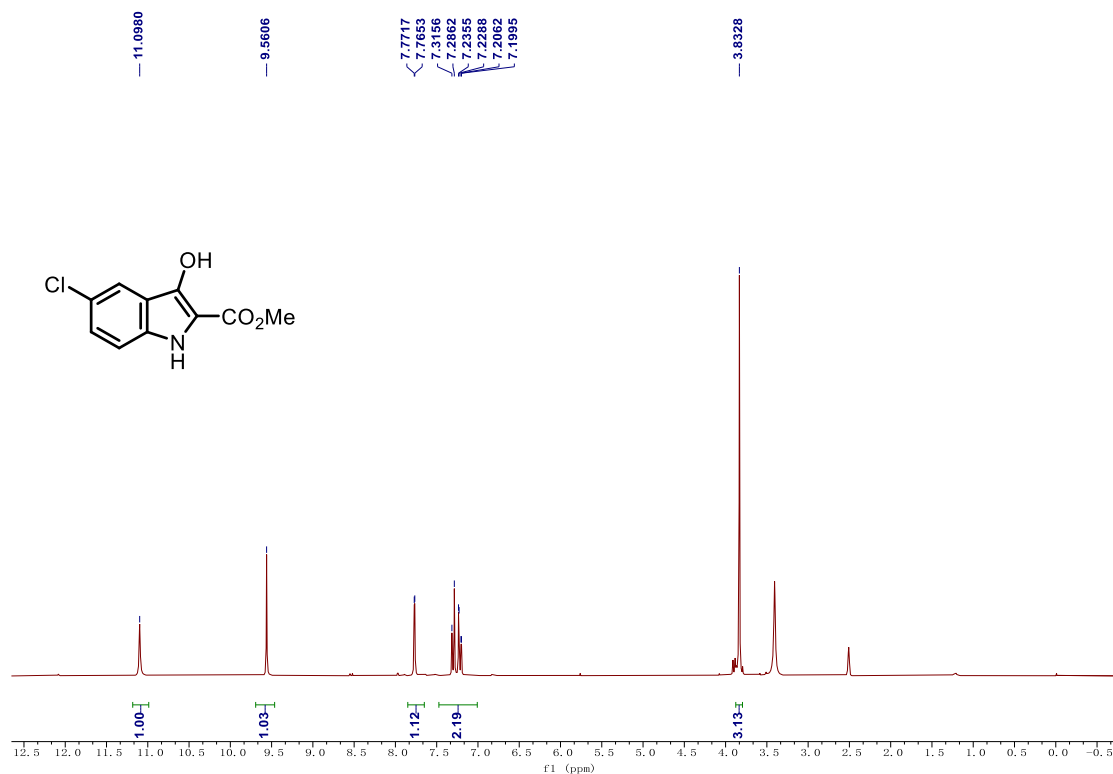
¹³C NMR Spectrum of 1h (75 MHz, DMSO-*d*₆)



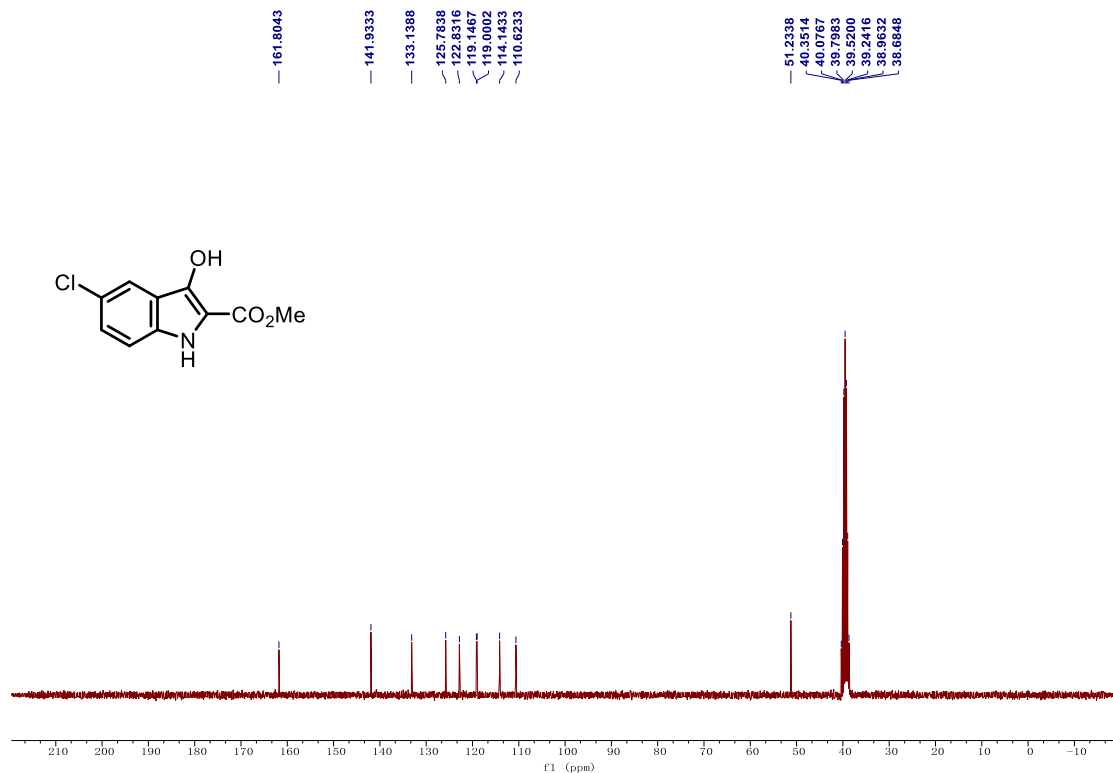
^{19}F NMR Spectrum of 1h (282 MHz, $\text{DMSO-}d_6$)



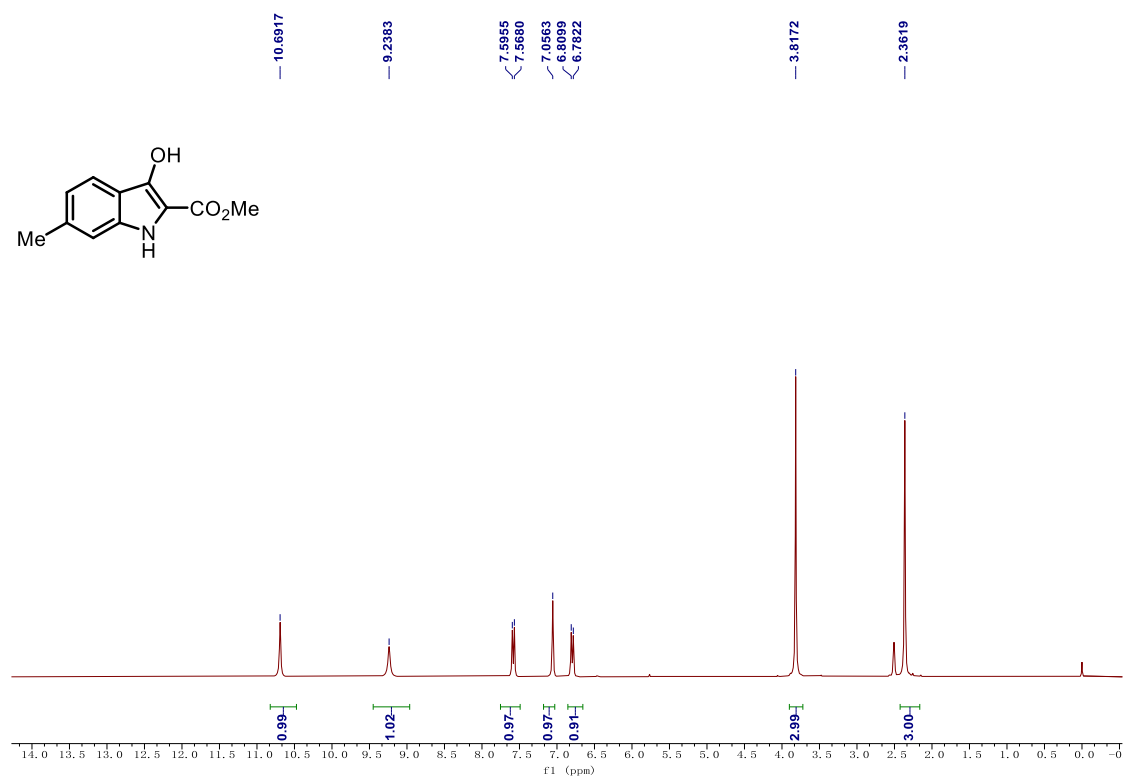
¹H NMR Spectrum of 1i (300 MHz, DMSO-*d*₆)



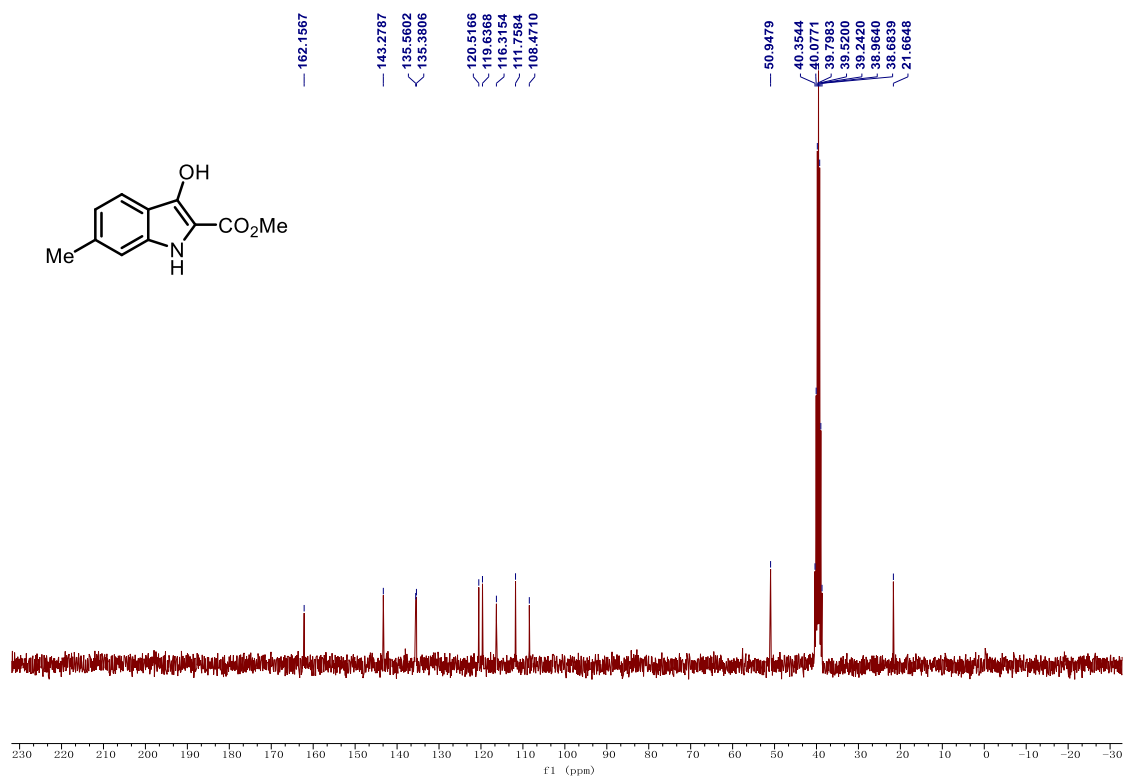
¹³C NMR Spectrum of 1h (75 MHz, DMSO-*d*₆)



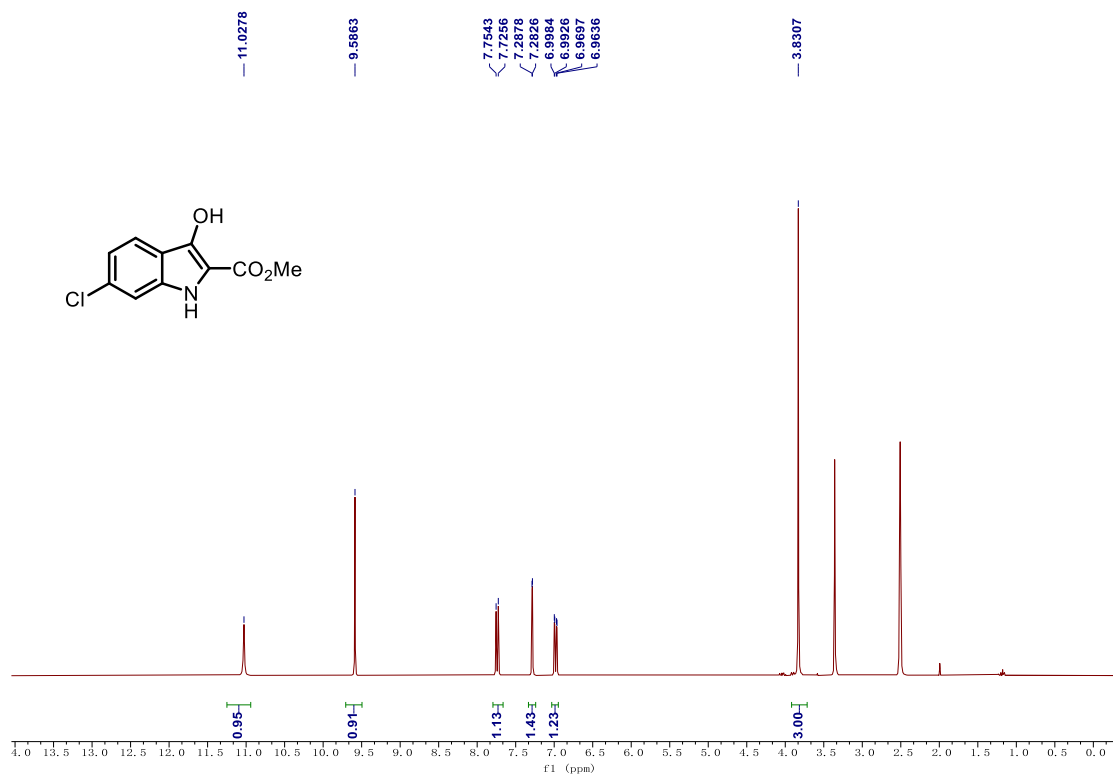
¹H NMR Spectrum of 1j (300 MHz, DMSO-*d*₆)



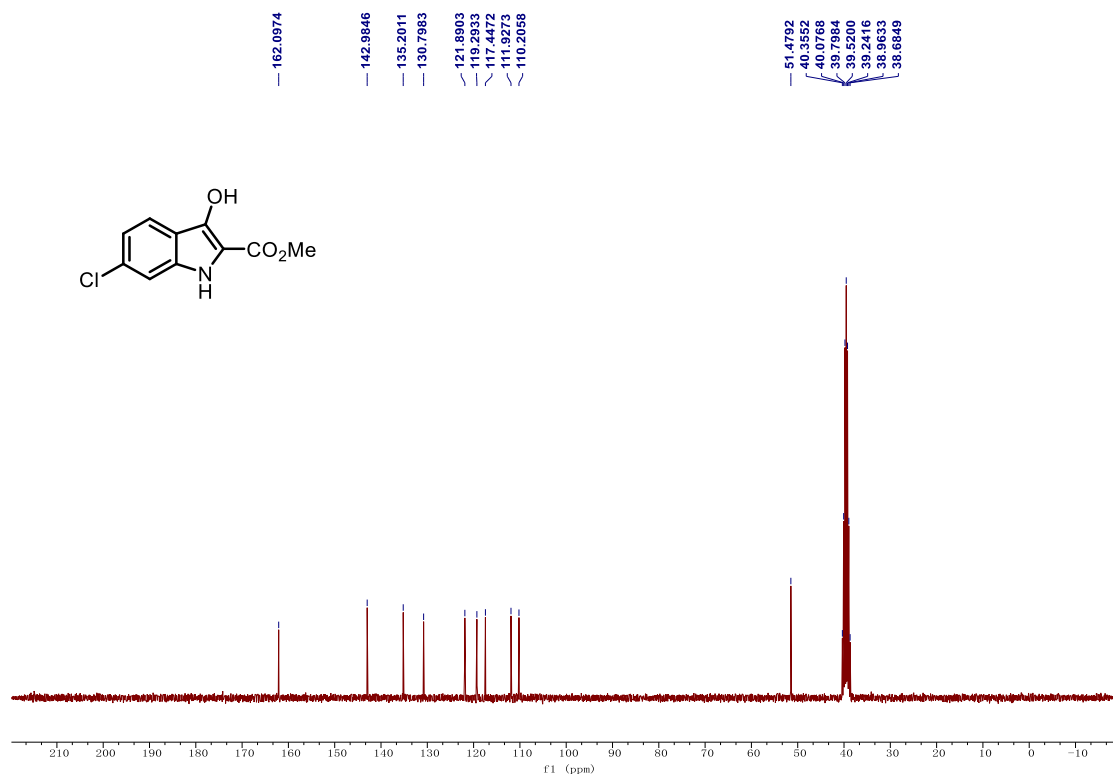
¹³C NMR Spectrum of 1j (75 MHz, DMSO-*d*₆)



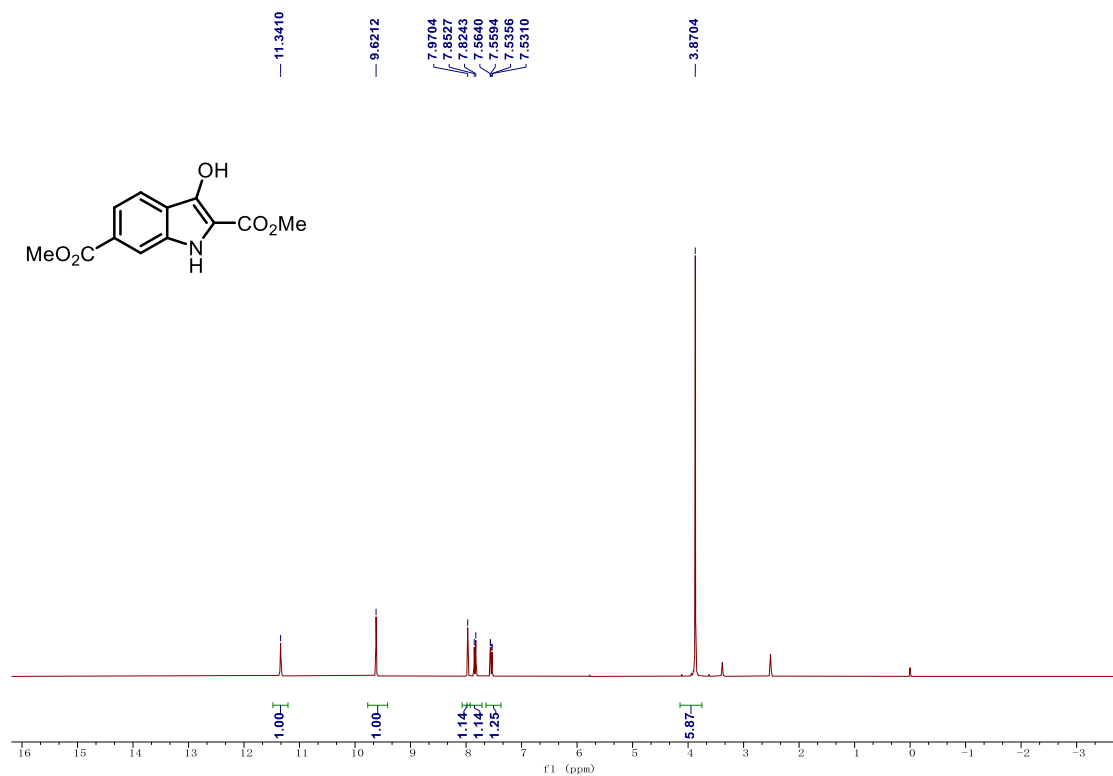
¹H NMR Spectrum of 1k (300 MHz, DMSO-*d*₆)



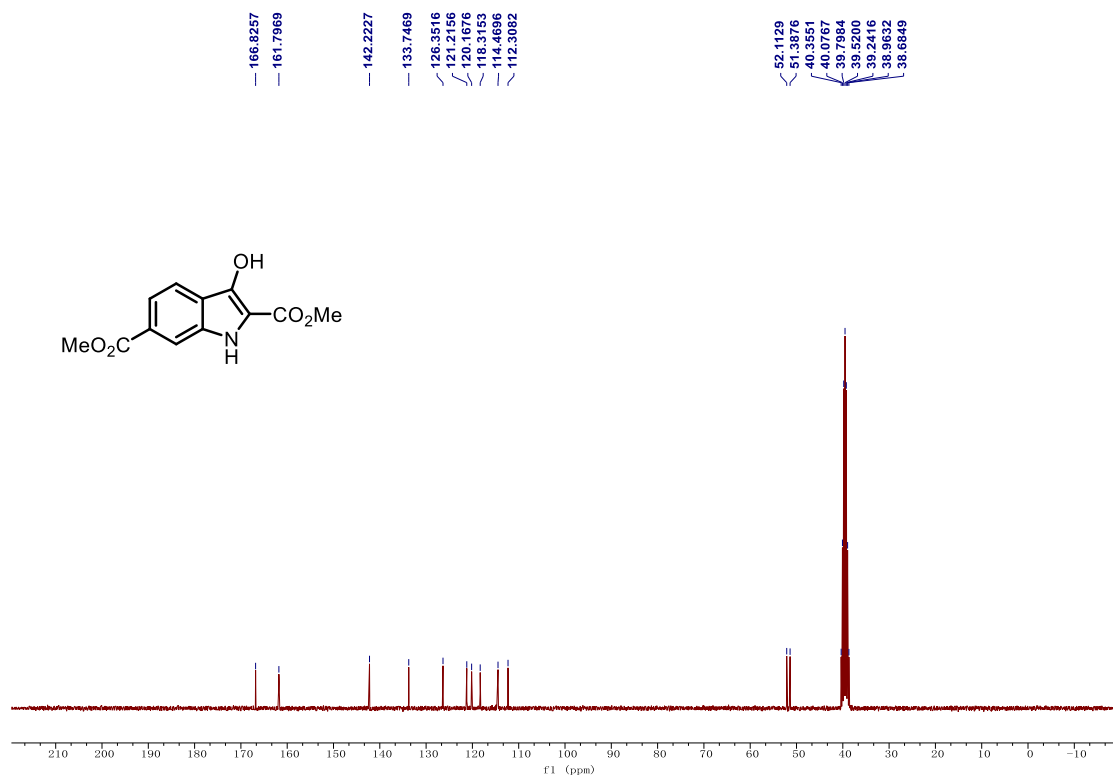
¹³C NMR Spectrum of 1k (75 MHz, DMSO-*d*₆)



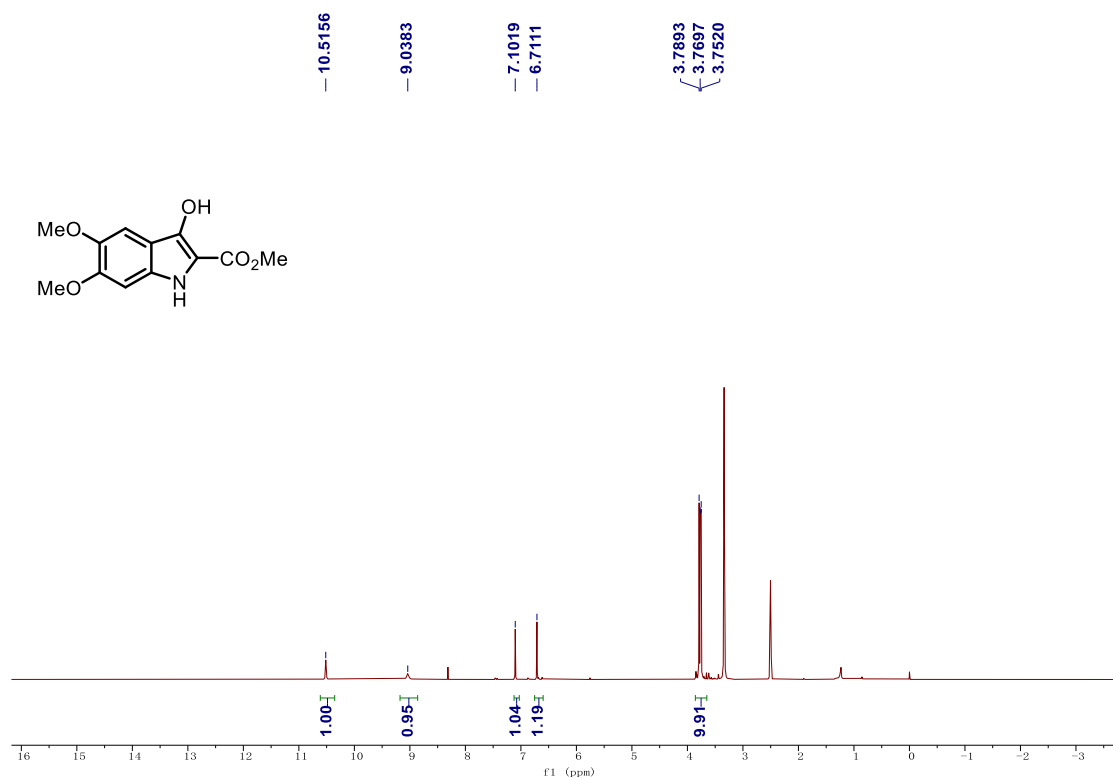
¹H NMR Spectrum of 1l (300 MHz, DMSO-*d*₆)



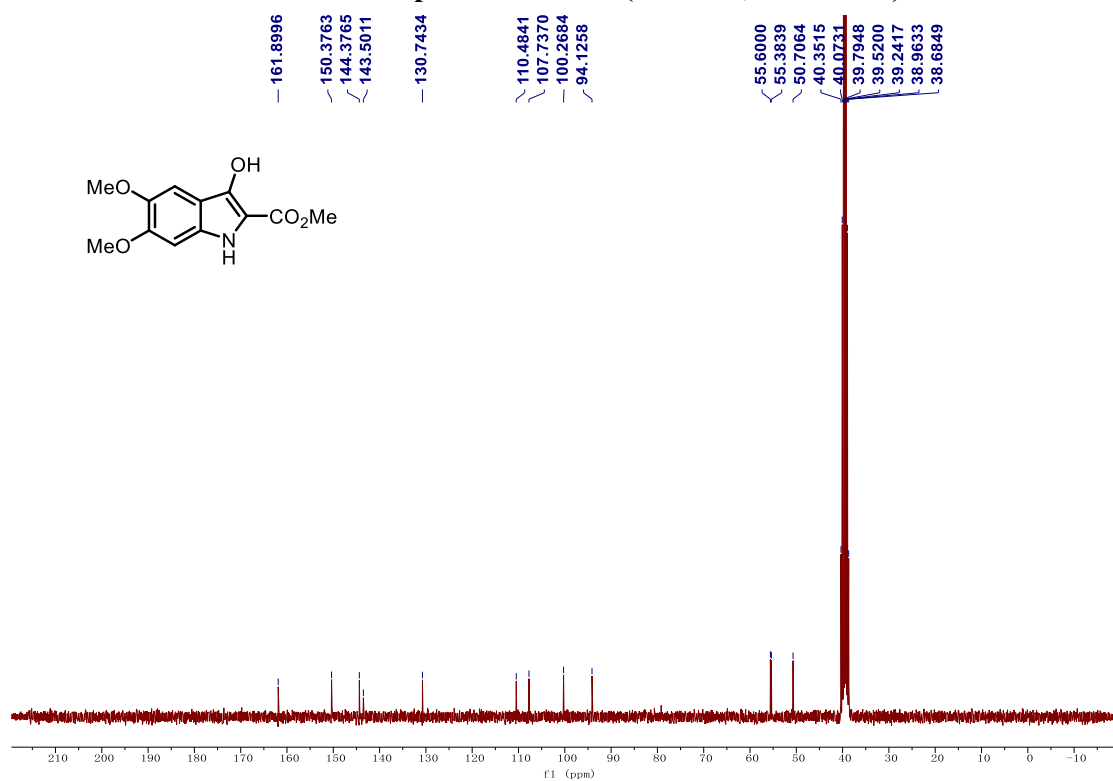
¹³C NMR Spectrum of 1l (75 MHz, DMSO-*d*₆)



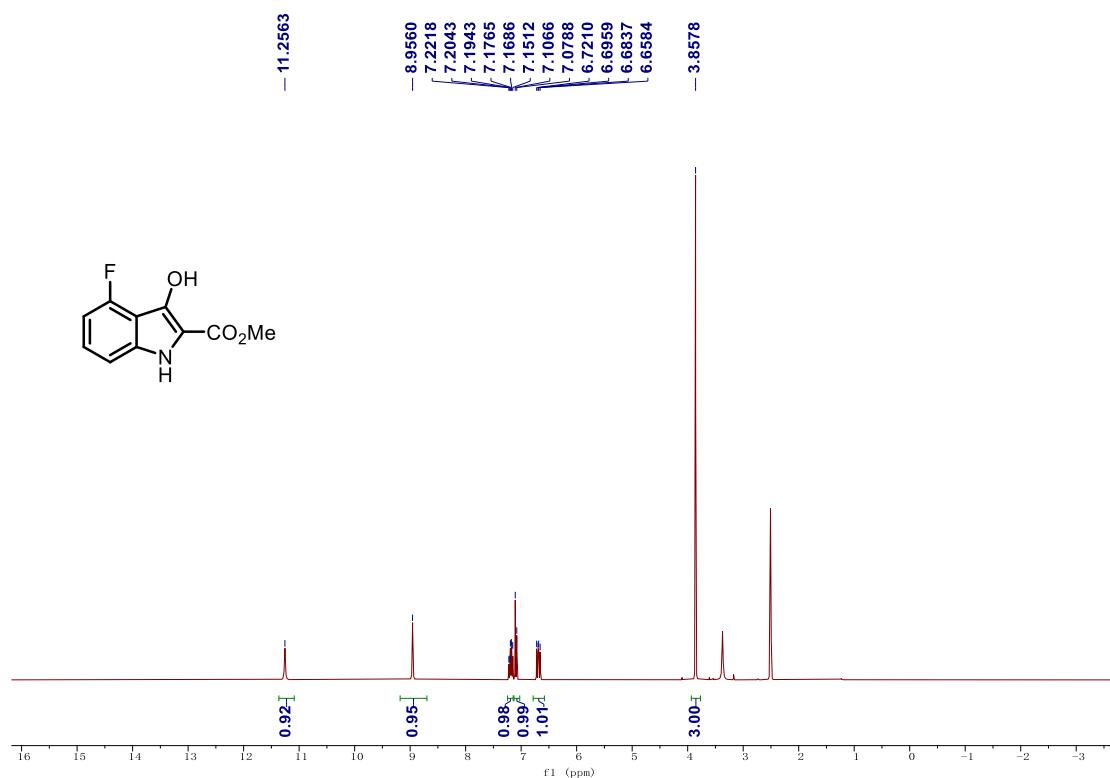
¹H NMR Spectrum of 1m (300 MHz, DMSO-*d*₆)



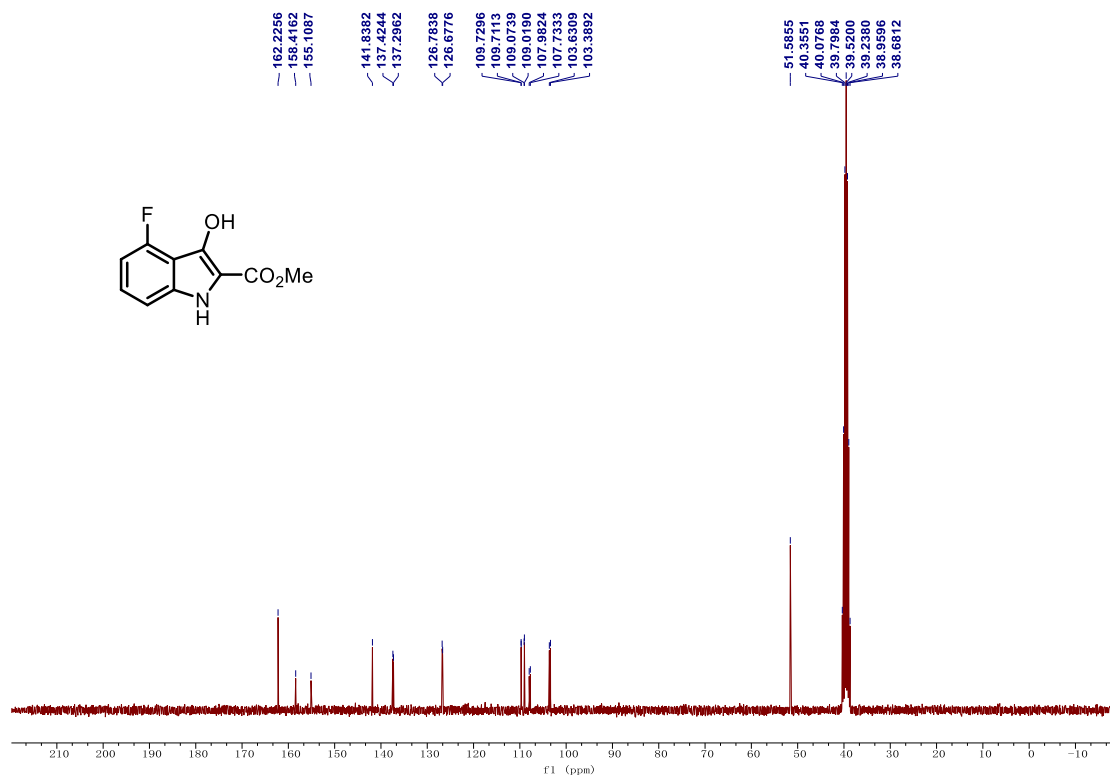
¹³C NMR Spectrum of 1m (75 MHz, DMSO-*d*₆)



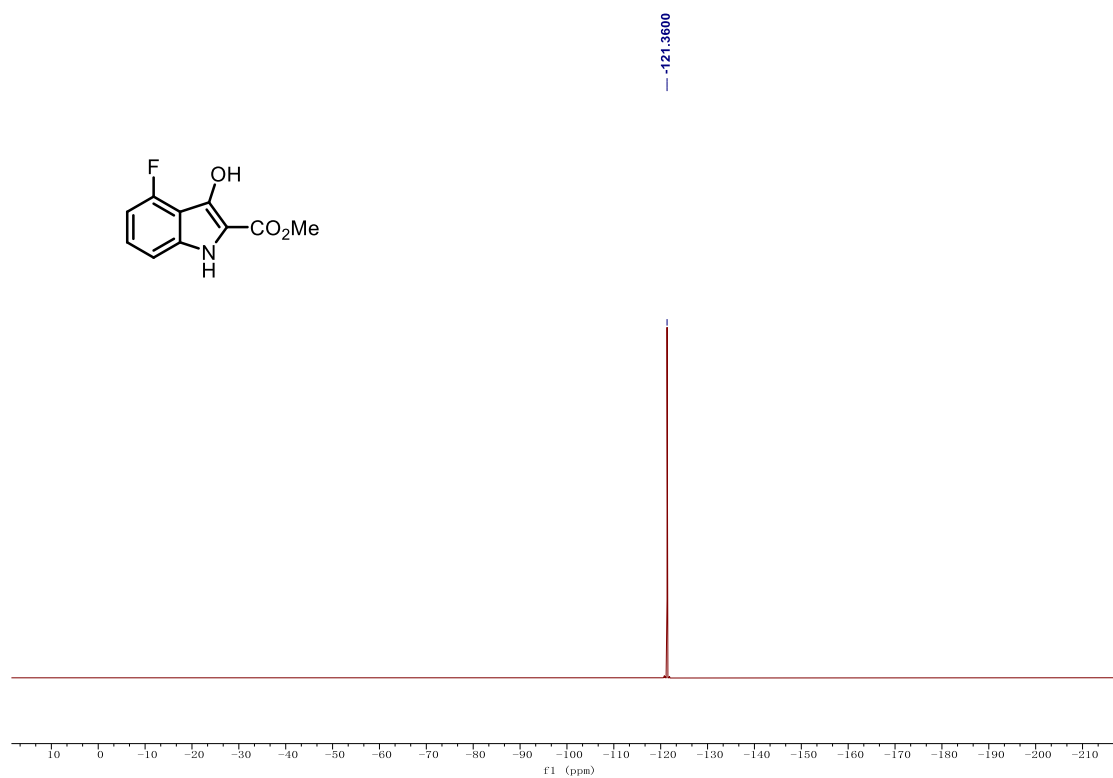
¹H NMR Spectrum of 1n (300 MHz, DMSO-*d*₆)



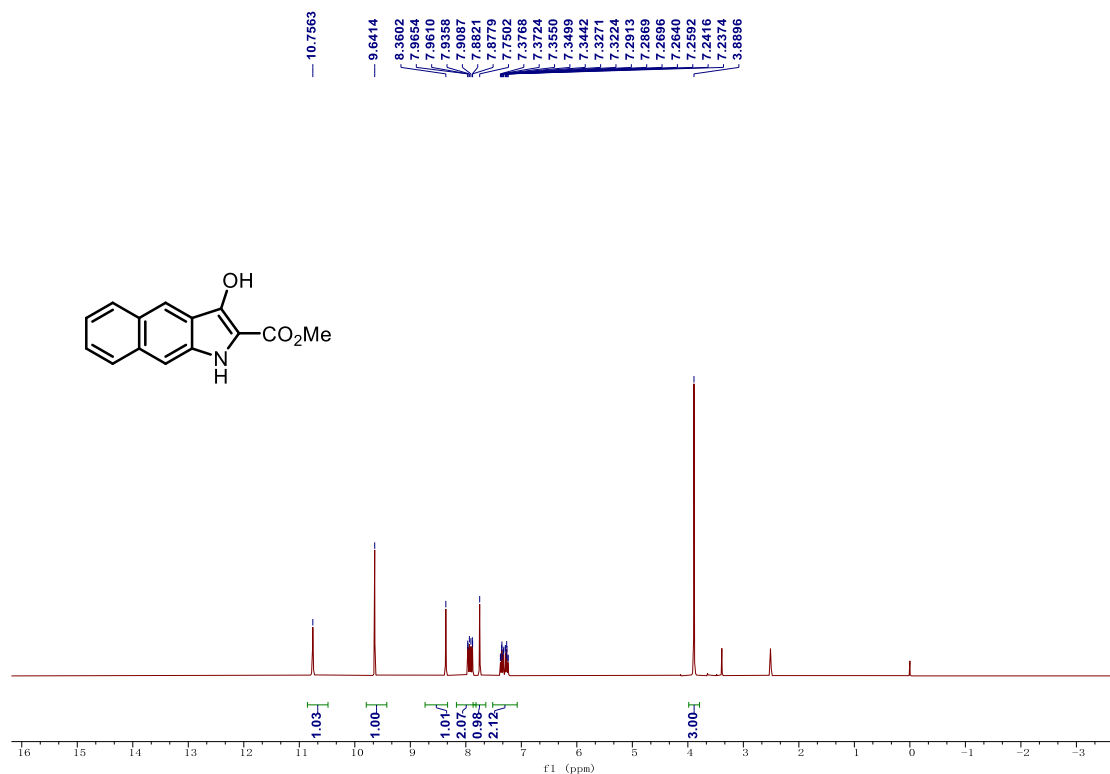
¹³C NMR Spectrum of 1n (75 MHz, DMSO-*d*₆)



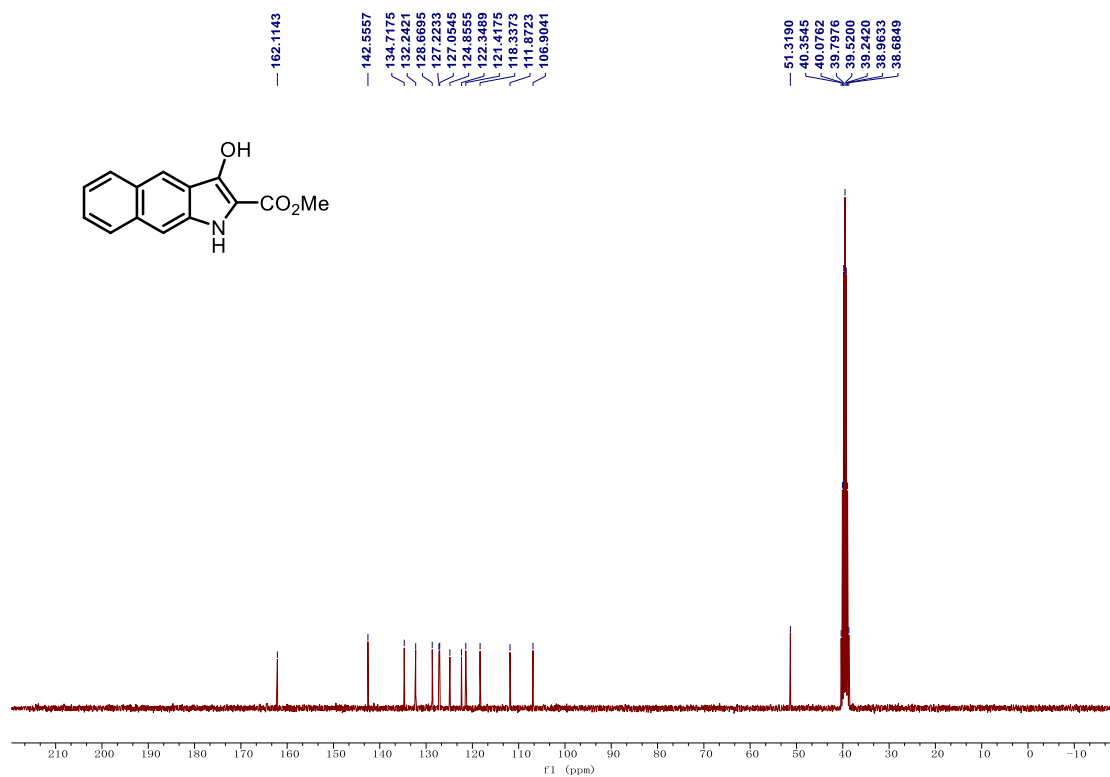
^{19}F NMR Spectrum of 1n (282 MHz, DMSO- d_6)



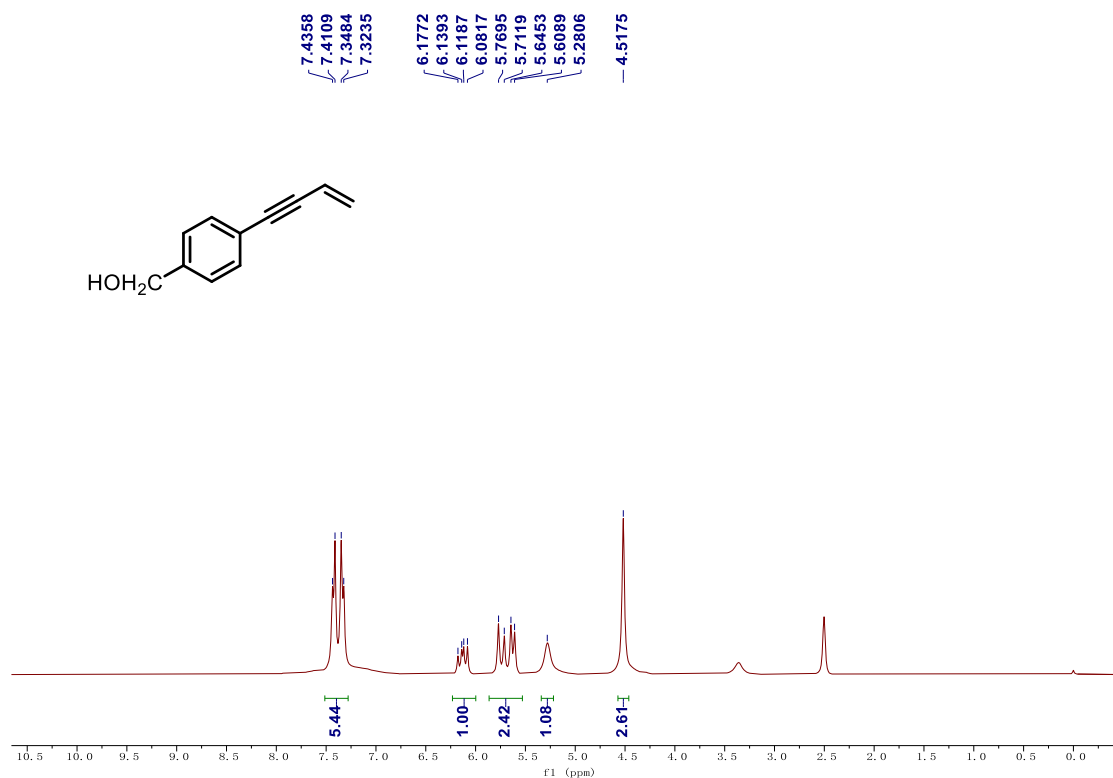
¹H NMR Spectrum of 1o (300 MHz, DMSO-*d*₆)



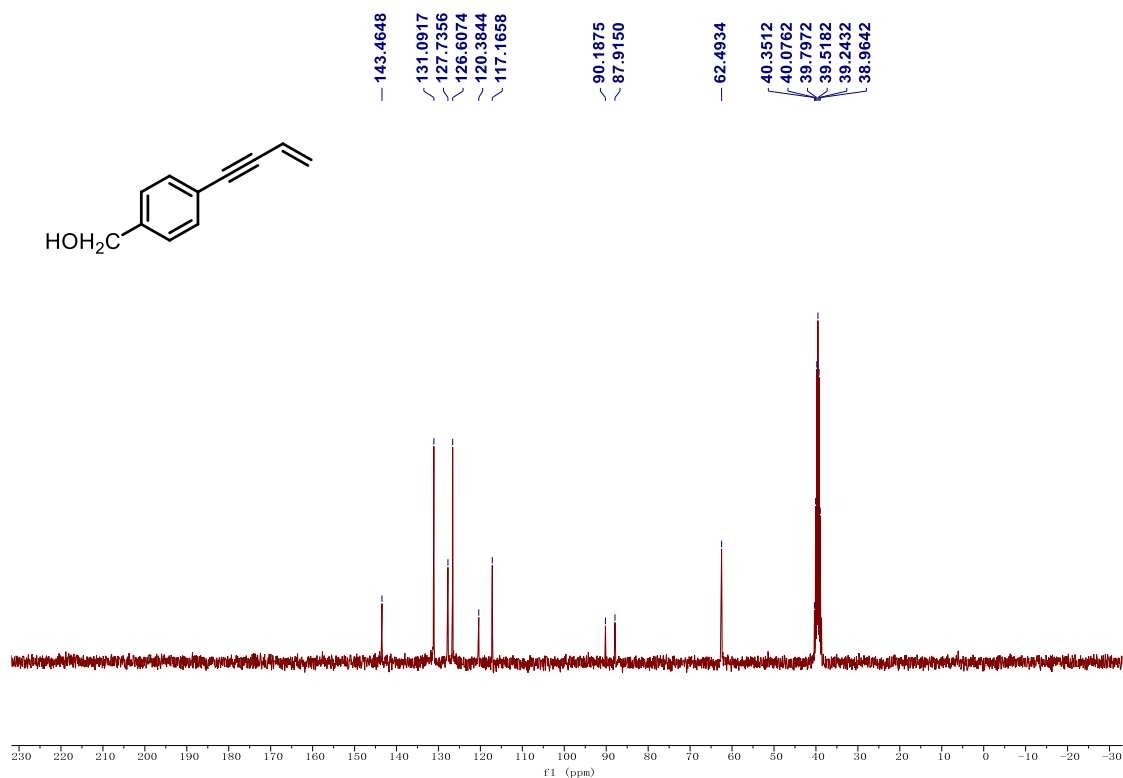
¹³C NMR Spectrum of 1o (75 MHz, DMSO-*d*₆)



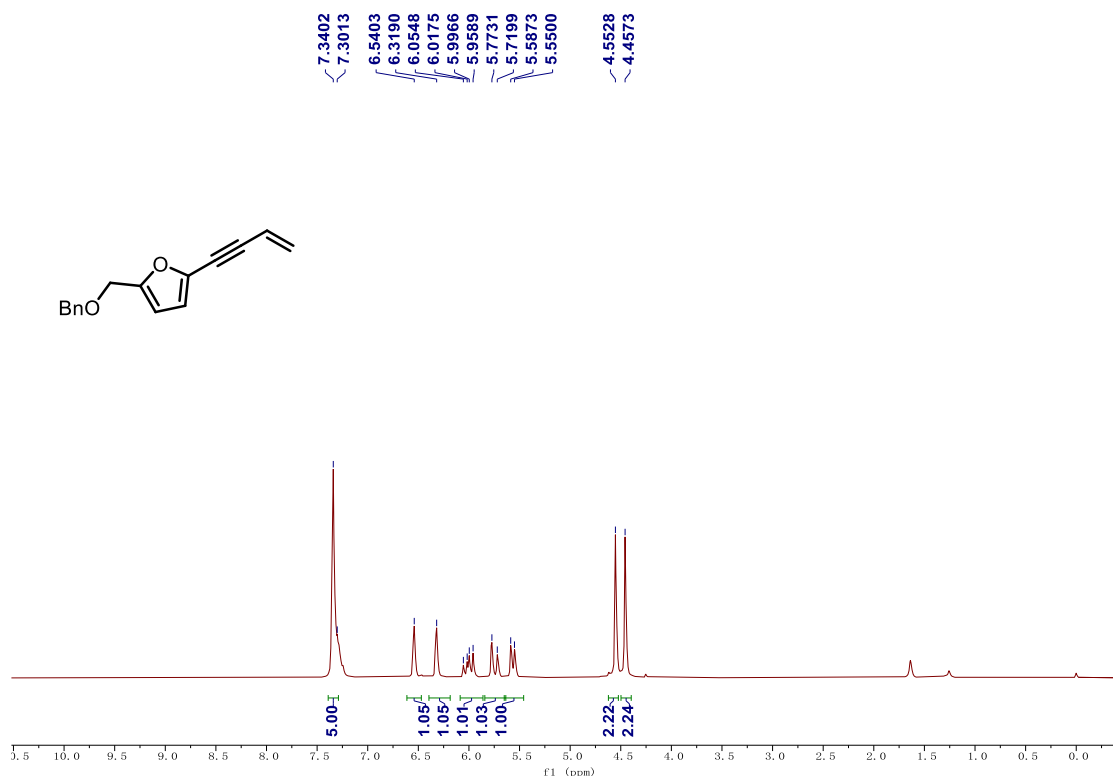
¹H NMR Spectrum of 2i (300 MHz, CDCl₃)



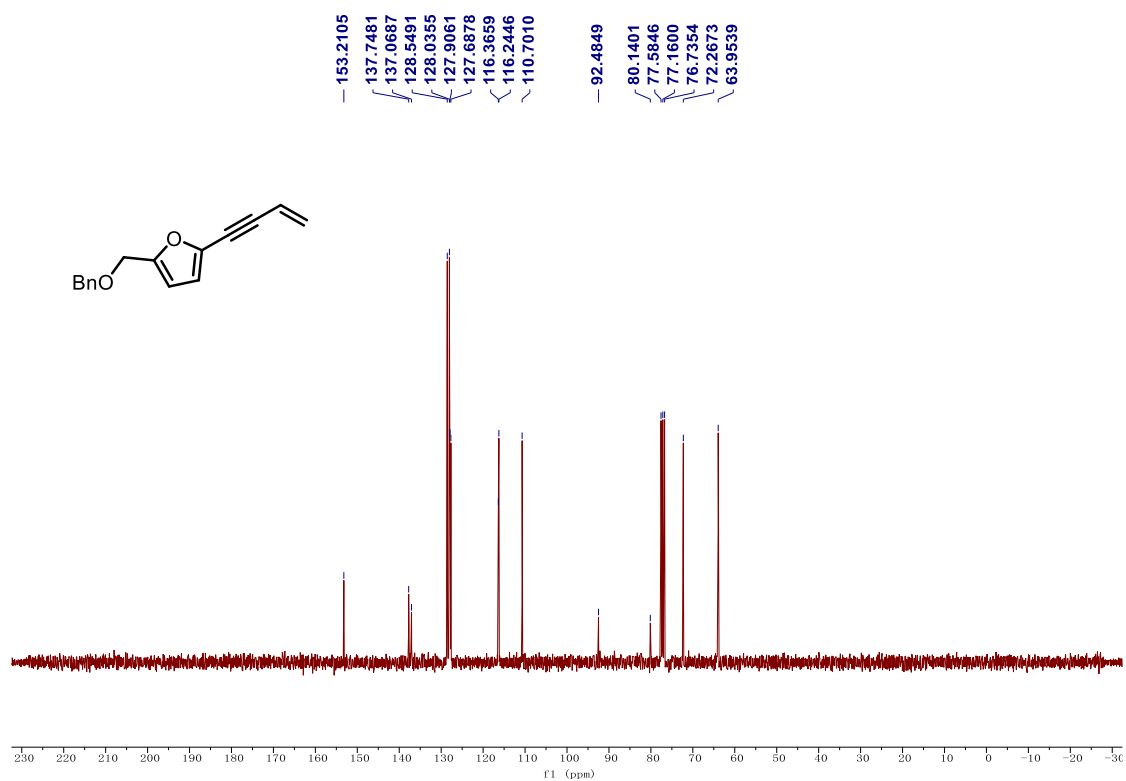
¹³C NMR Spectrum of 2i (75 MHz, CDCl₃)



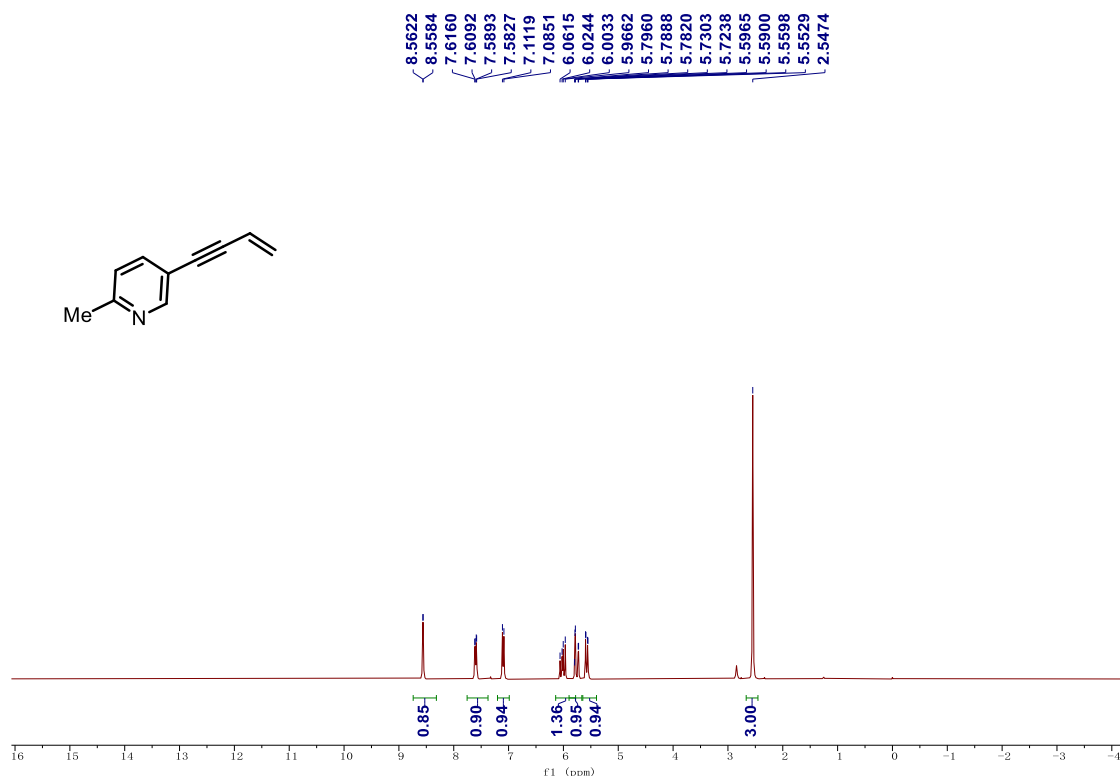
¹H NMR Spectrum of 2q (300 MHz, CDCl₃)



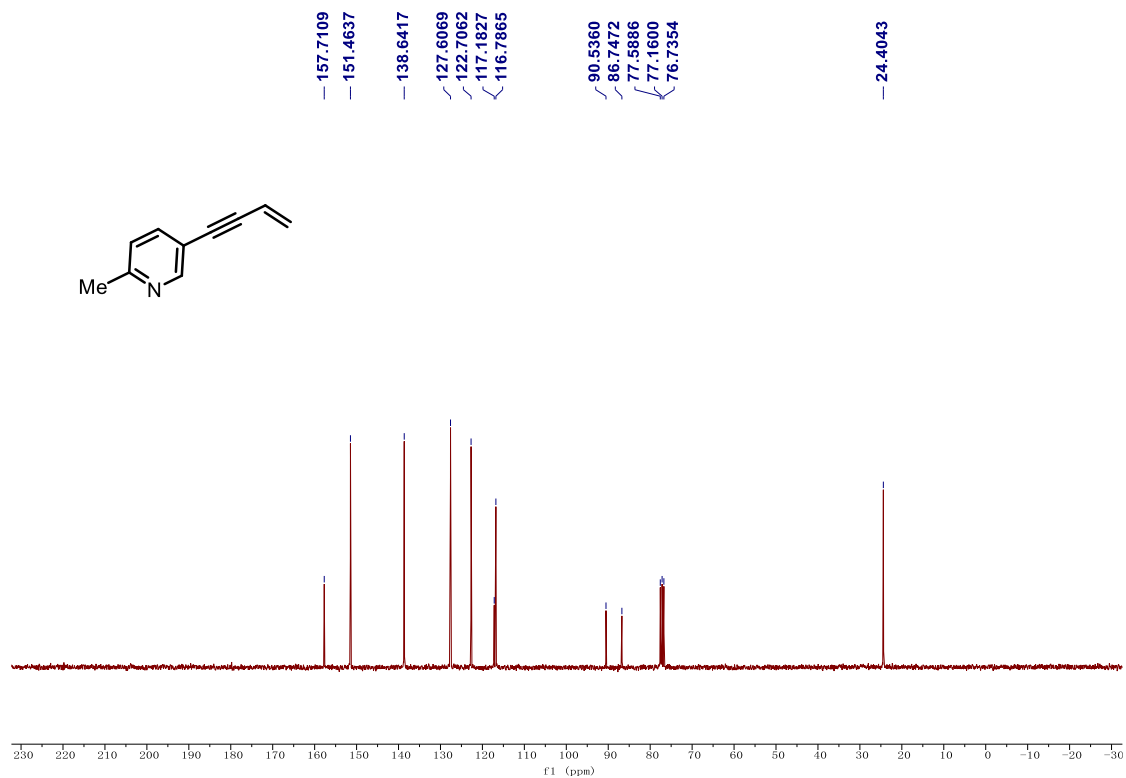
¹³C NMR Spectrum of 2q (75 MHz, CDCl₃)



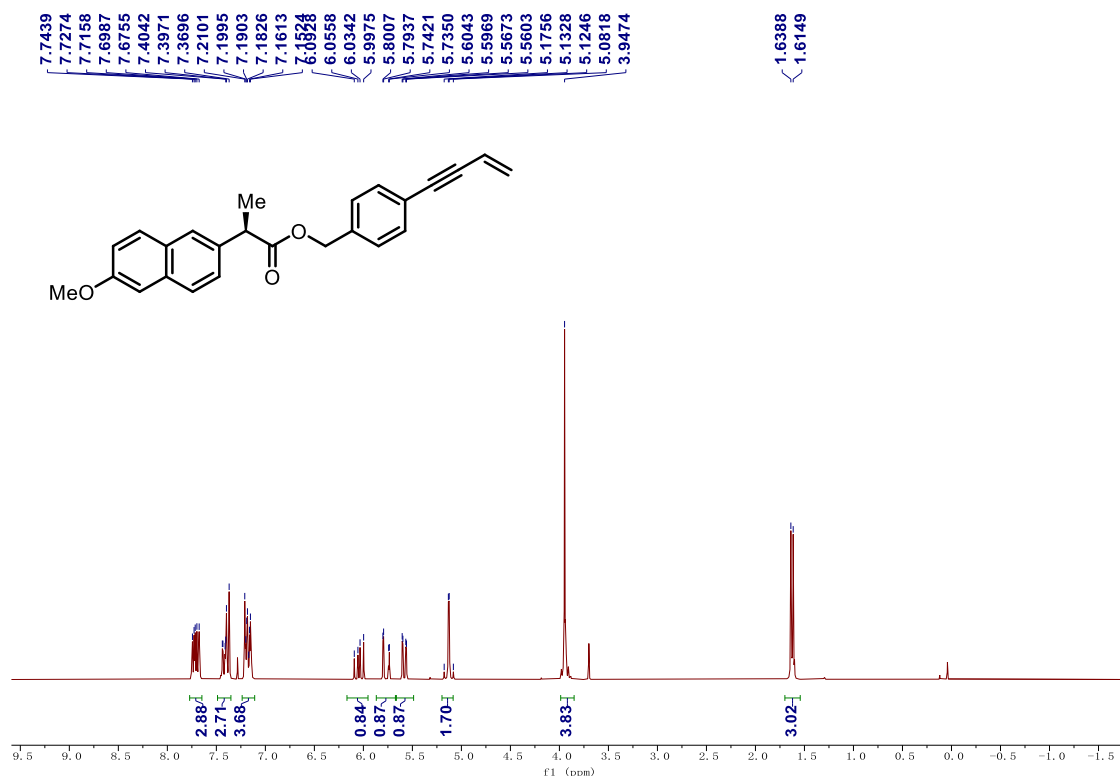
¹H NMR Spectrum of 2r (300 MHz, CDCl₃)



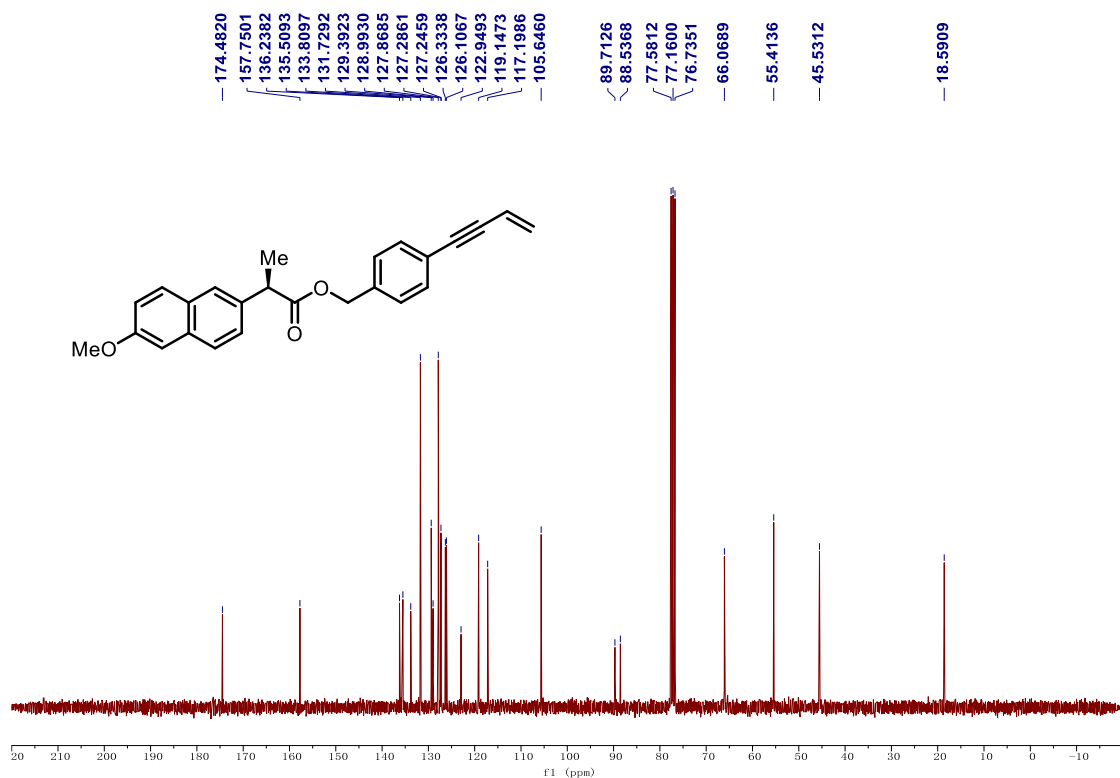
¹³C NMR Spectrum of 2r (75 MHz, CDCl₃)



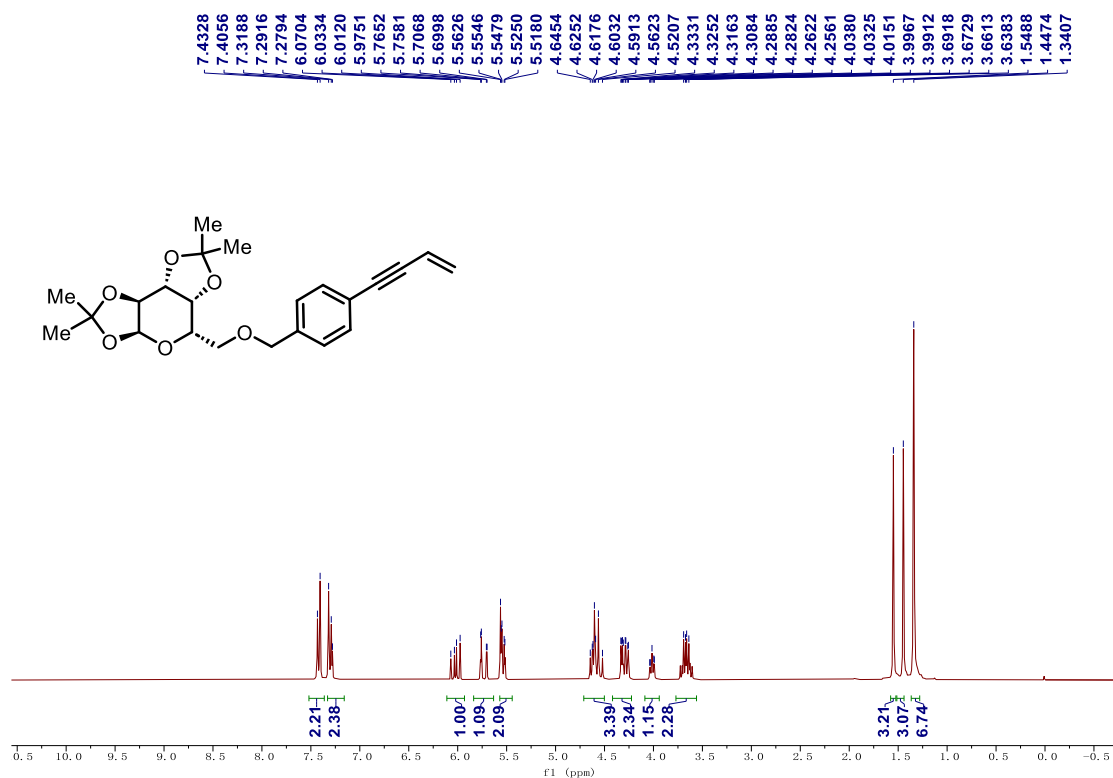
¹H NMR Spectrum of 2w (300 MHz, CDCl₃)



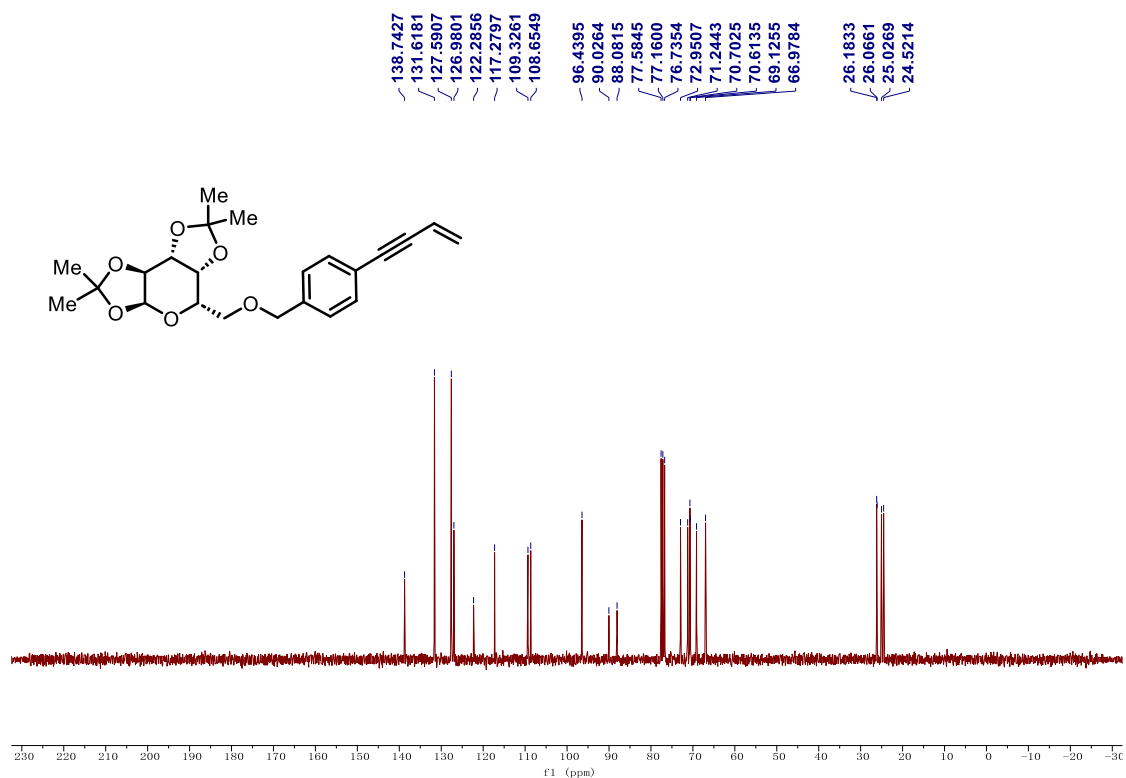
¹³C NMR Spectrum of 2w (75 MHz, CDCl₃)



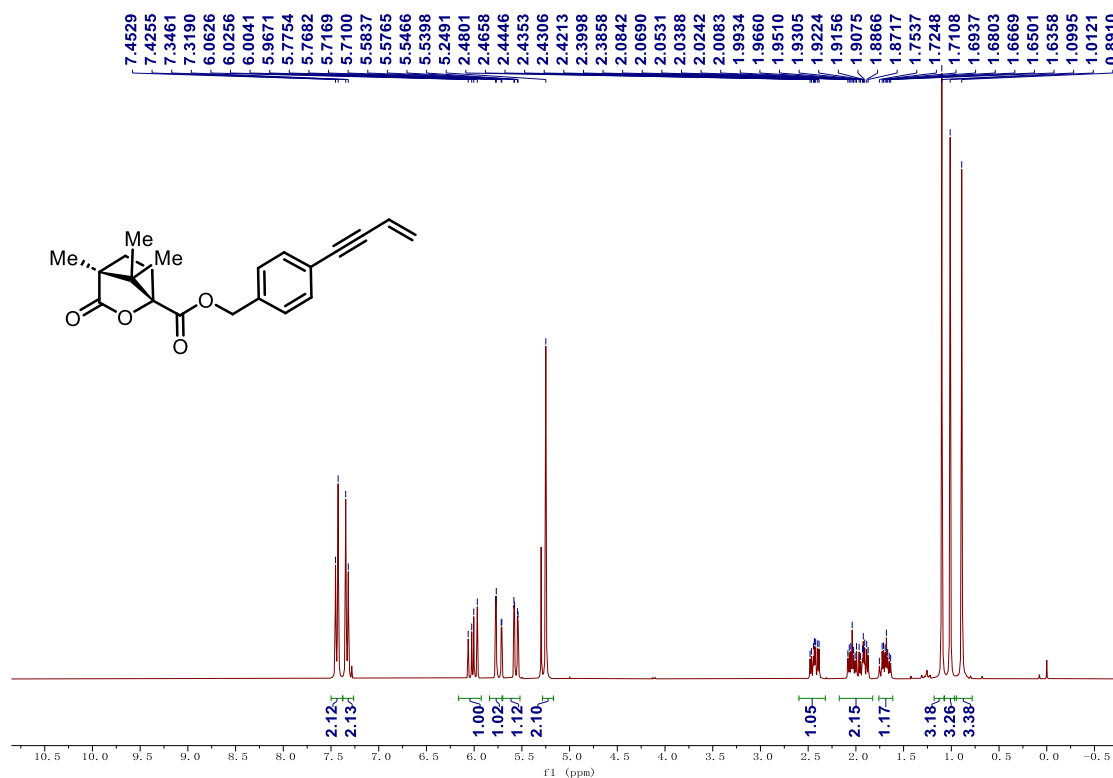
¹H NMR Spectrum of 2x (300 MHz, CDCl₃)



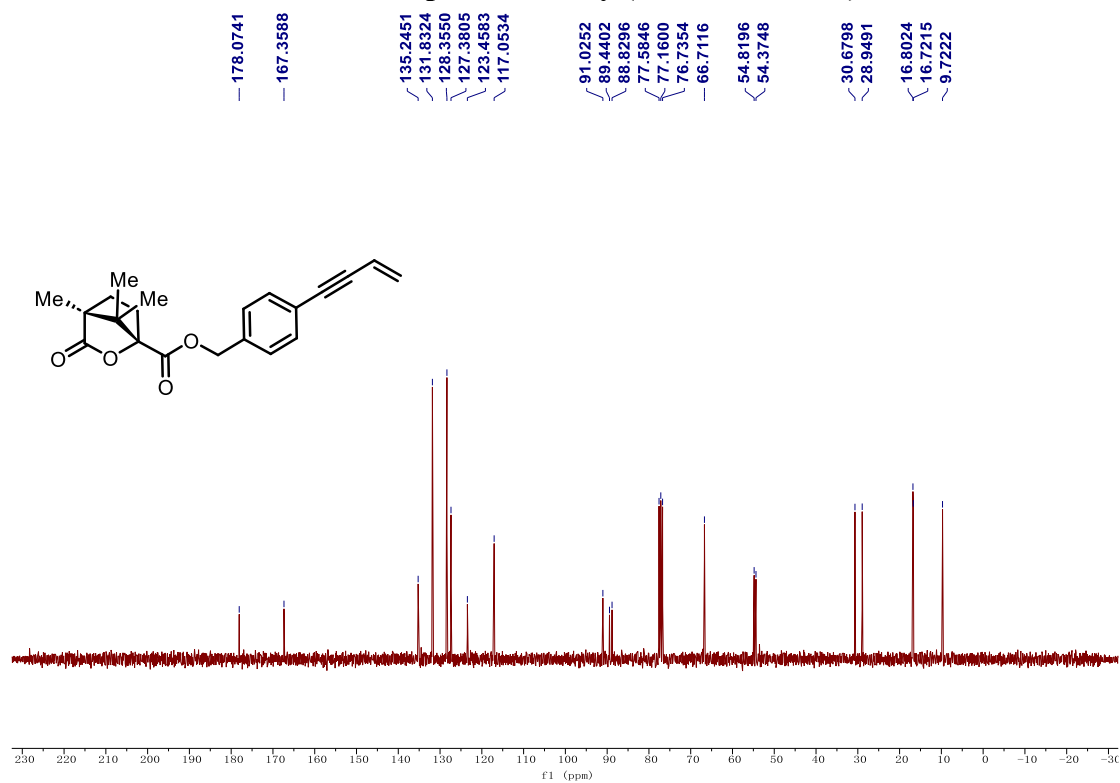
¹³C NMR Spectrum of 2x (75 MHz, CDCl₃)



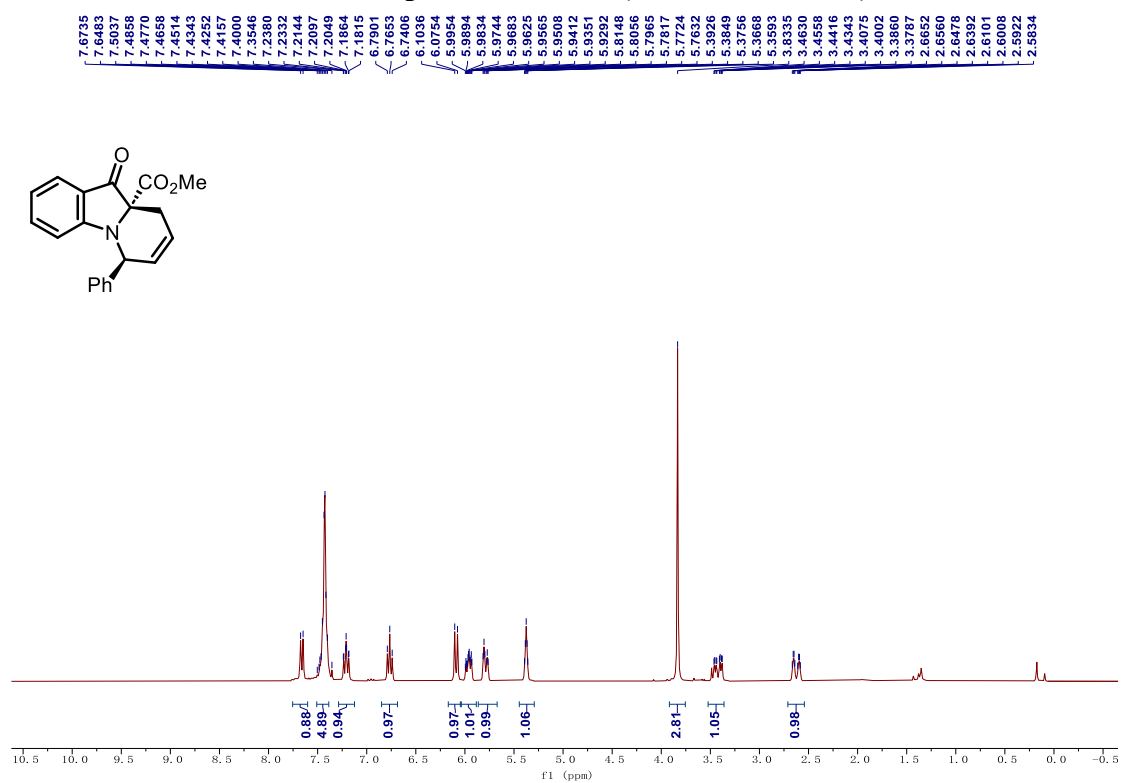
¹H NMR Spectrum of 2y (300 MHz, CDCl₃)



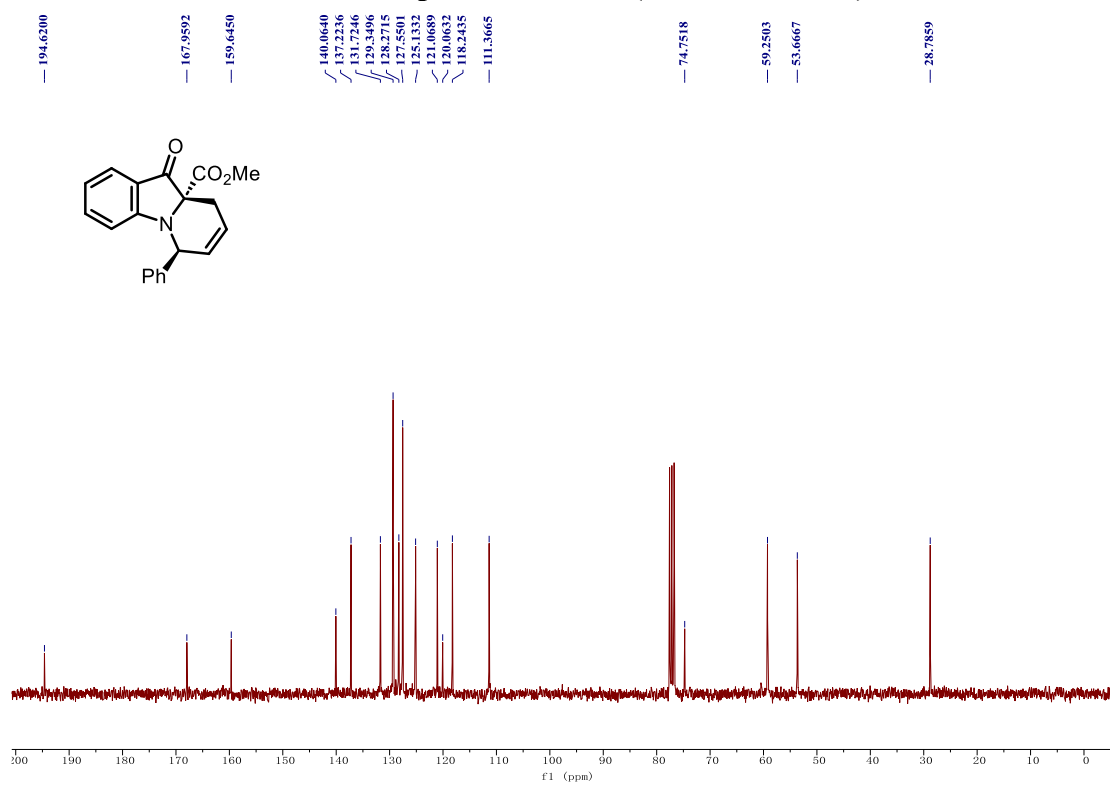
¹³C NMR Spectrum of 2y (75 MHz, CDCl₃)



¹H NMR Spectrum of 3aa (300 MHz, CDCl₃)



¹³C NMR Spectrum of 3aa (75 MHz, CDCl₃)



Chemical structure: CCOC(=O)[C@H]1C=CC[C@@H]1c2ccccc2

¹H NMR spectrum (CDCl₃) showing chemical shifts (ppm) and integration values:

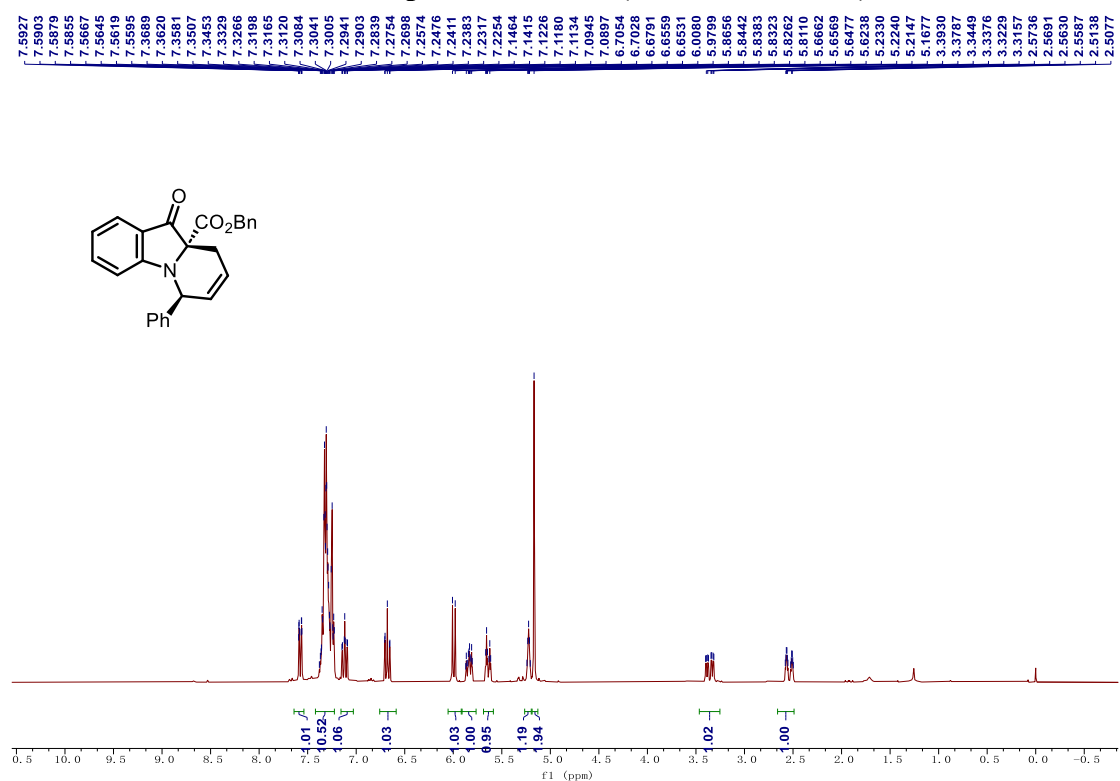
Chemical Shift (ppm)	Integration
7.5656	1.04
7.5628	8.45
7.5790	1.02
7.5595	1.21
7.5555	1.00
7.5527	0.98
7.3687	1.04
7.3603	1.85
7.3600	1.00
7.3588	1.00
7.3563	3.37
7.3584	
7.3435	
7.3351	
7.3208	
7.3133	
7.3085	
7.1469	
7.1421	
7.1232	
7.1186	
7.1139	
7.0950	
7.0902	
6.6966	
6.6719	
6.6475	
6.0129	
5.9849	
5.9010	
5.8738	
5.8679	
5.8639	
5.8529	
5.8467	
5.8405	
5.7221	
5.7131	
5.7040	
5.6889	
5.6798	
5.6706	
5.2967	
5.2888	
5.2796	
5.2706	
4.2324	
4.2088	
4.1851	
4.1615	
3.3736	
3.3664	
3.3521	
3.3448	
3.3182	
3.3109	
3.2966	
3.2822	
2.5650	
2.5601	
2.5556	
2.5495	
2.5452	
2.5390	
2.5048	
2.5006	
2.4943	
2.4899	
1.2681	
1.2444	
1.2208	

Chemical structure of **1-ethyl 2-phenyl-2,3-dihydro-1H-indole-1-carboxylate** is shown. The ¹³C NMR spectrum (CDCl₃) displays peaks corresponding to the structure, with the following chemical shifts (ppm) labeled above the spectrum:

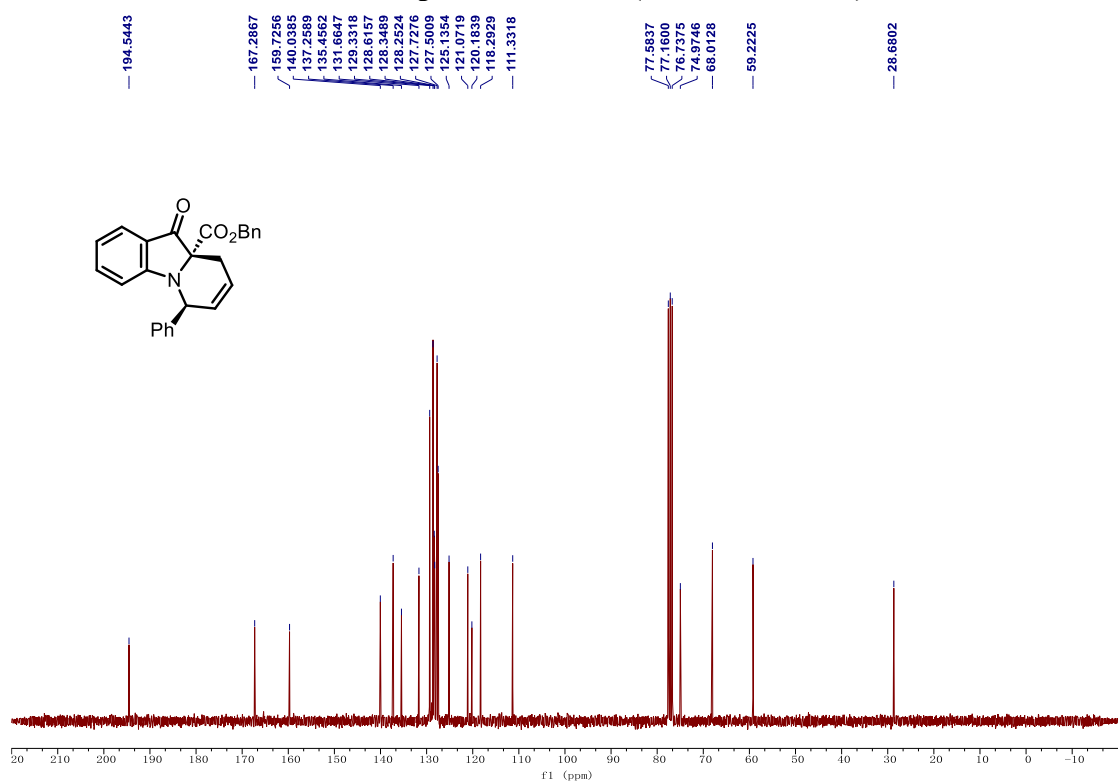
194.7538, 167.2949, 159.6636, 140.0898, 137.1857, 131.6542, 129.3130, 128.2188, 127.4974, 125.0552, 121.0408, 120.0816, 118.1569, 111.2640, 77.5843, 77.1597, 76.7362, 74.8640, 62.7132, 59.2226, 28.6840, 14.1900.

¹³C NMR spectrum (CDCl₃) showing peaks corresponding to the structure. The x-axis is labeled f1 (ppm) and ranges from 230 to -30.

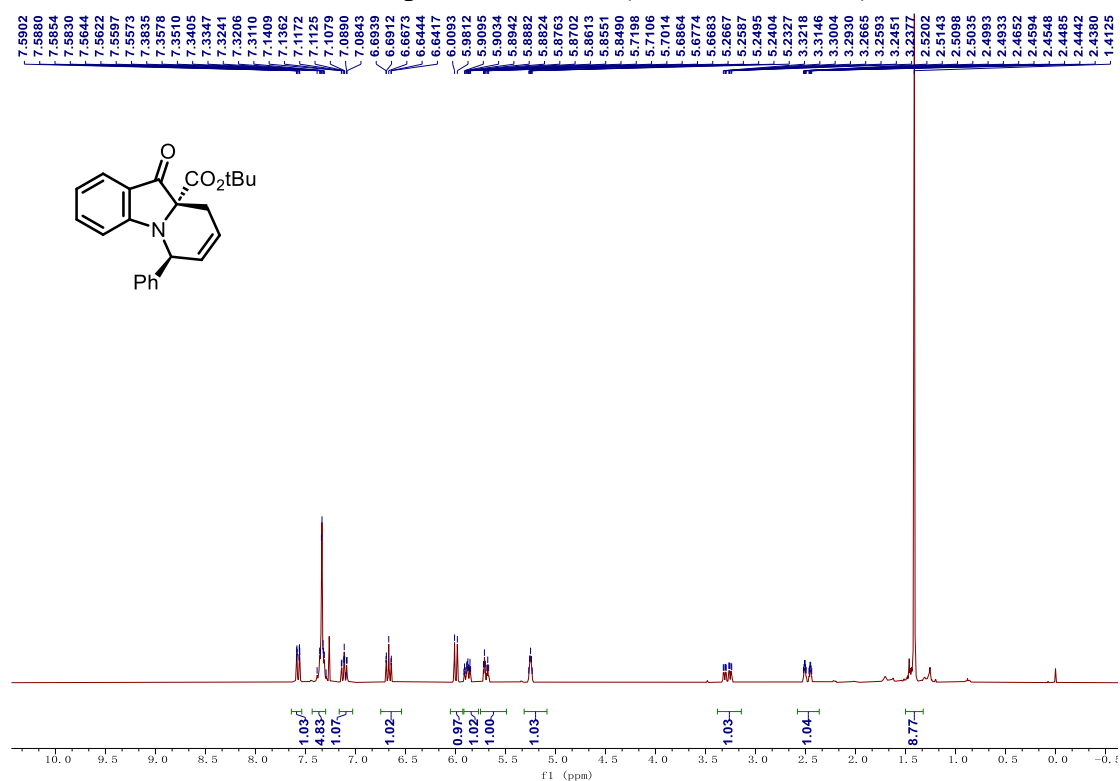
¹H NMR Spectrum of 3a (300 MHz, CDCl₃)



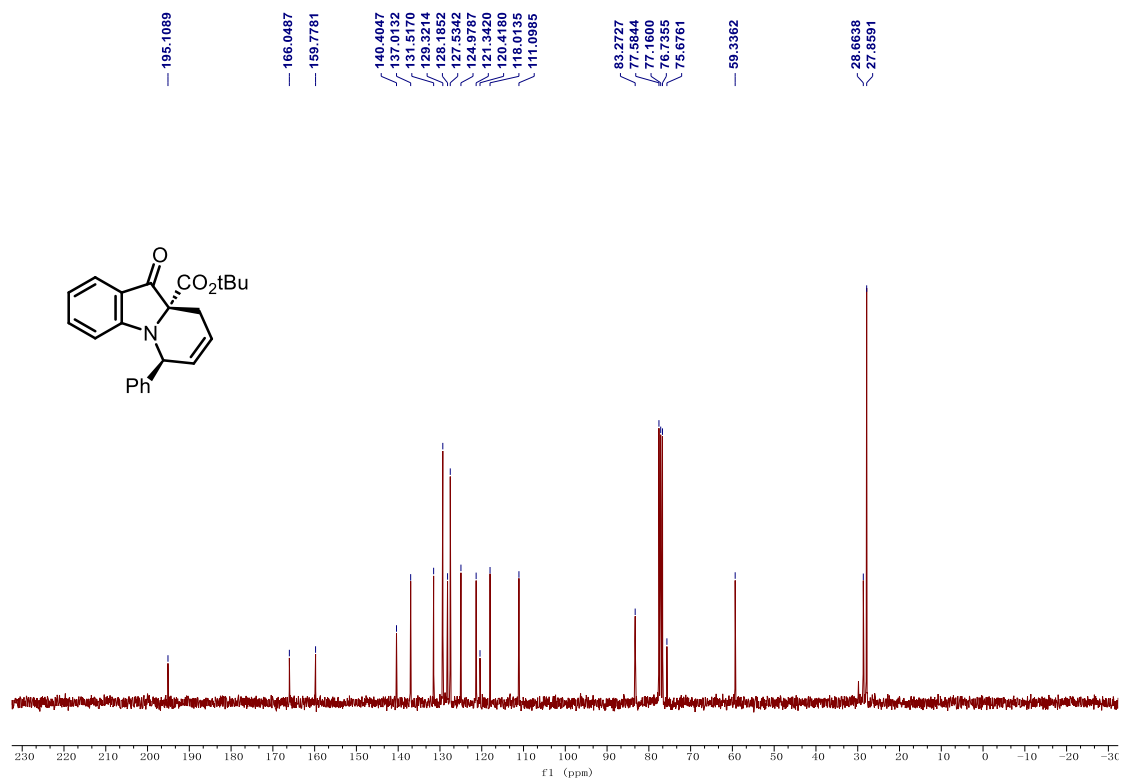
¹³C NMR Spectrum of 3a (75 MHz, CDCl₃)



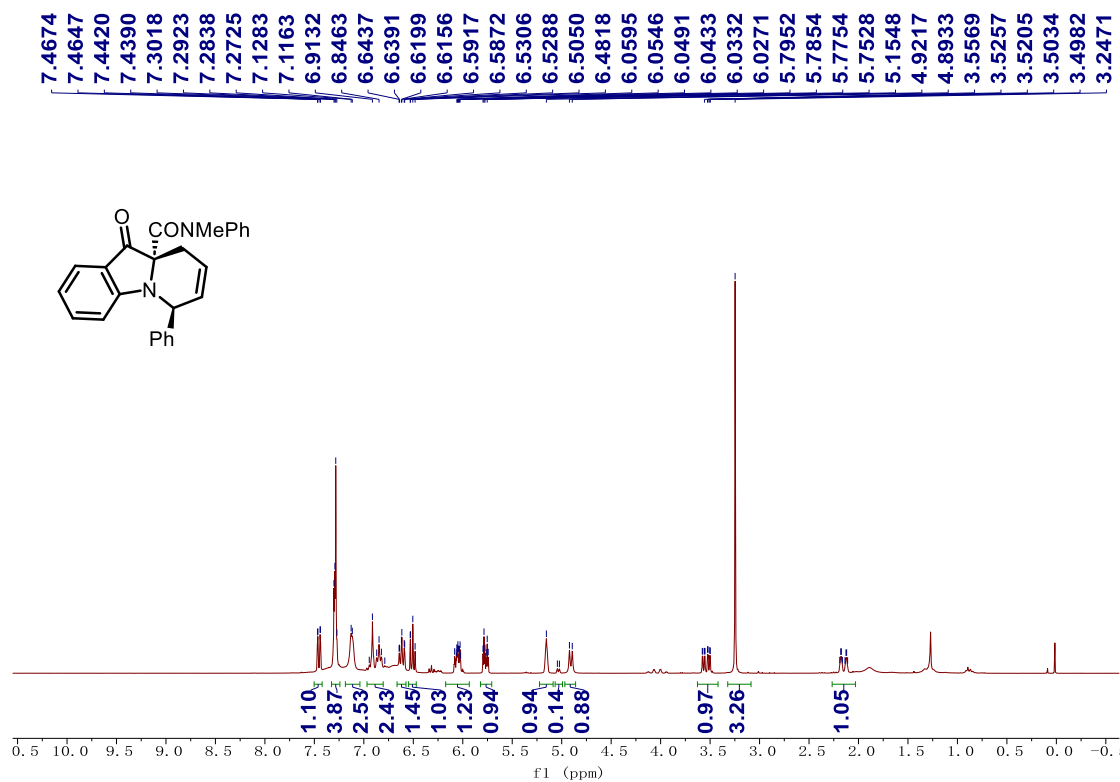
¹H NMR Spectrum of 3da (300 MHz, CDCl₃)



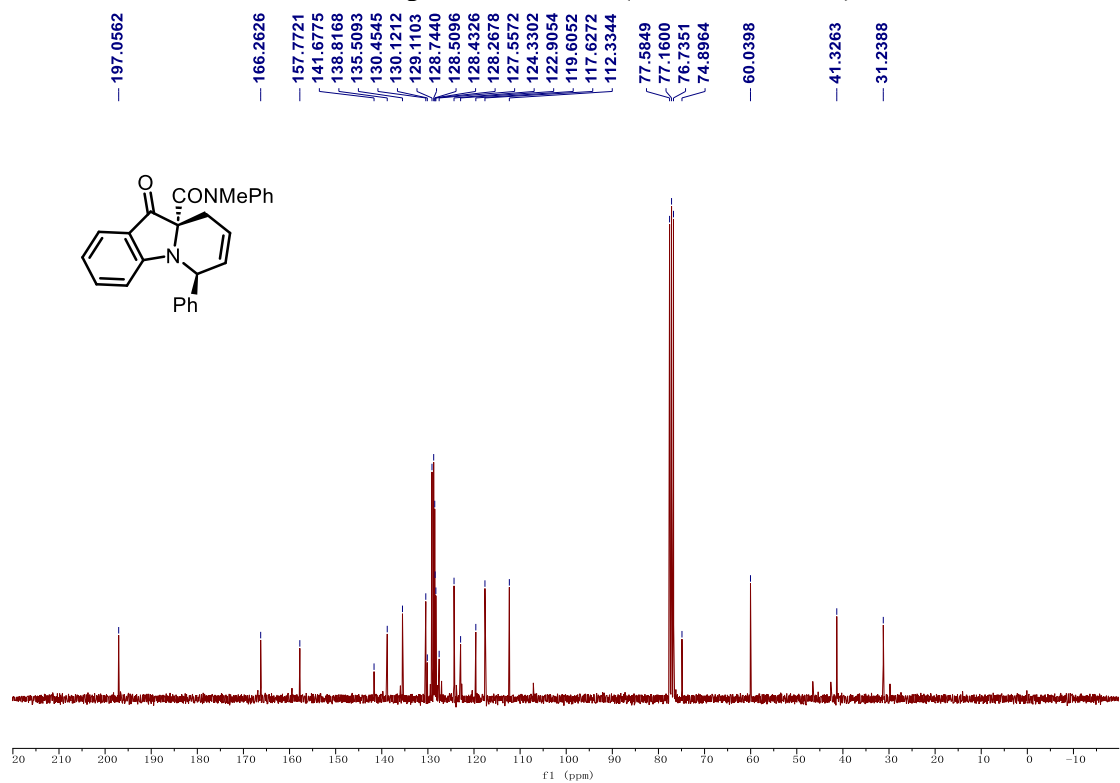
¹³C NMR Spectrum of 3da (75 MHz, CDCl₃)



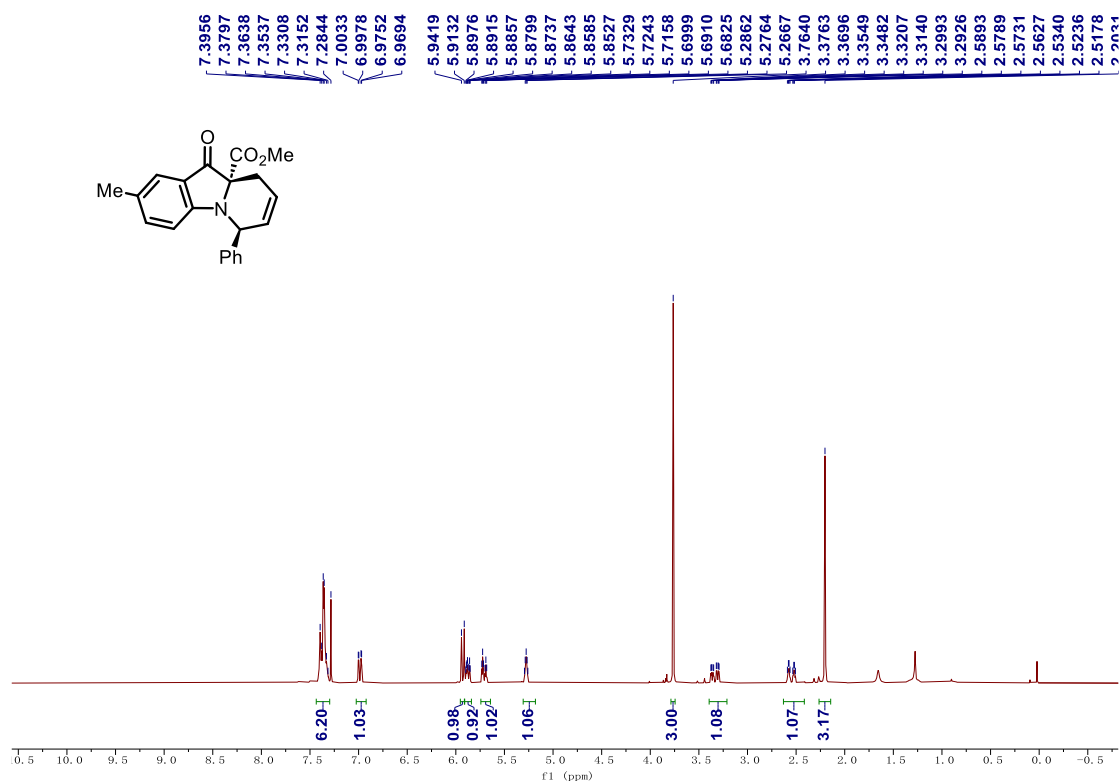
¹H NMR Spectrum of 3ea (300 MHz, CDCl₃)



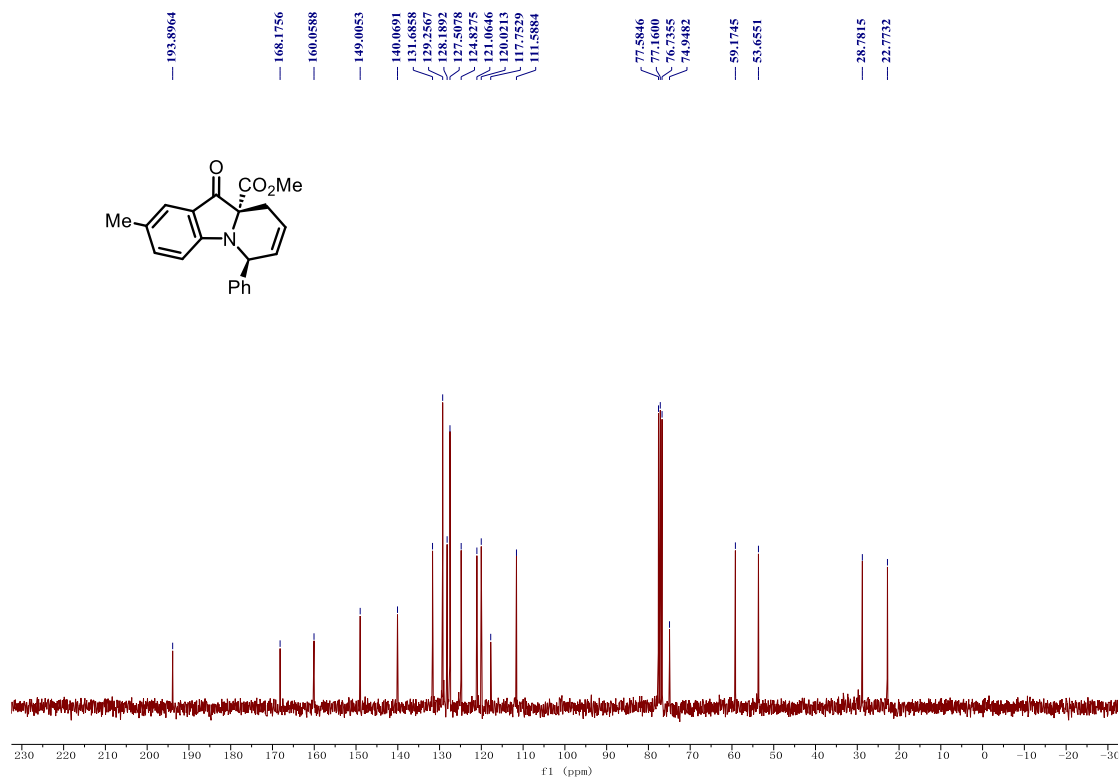
¹³C NMR Spectrum of 3ea (75 MHz, CDCl₃)



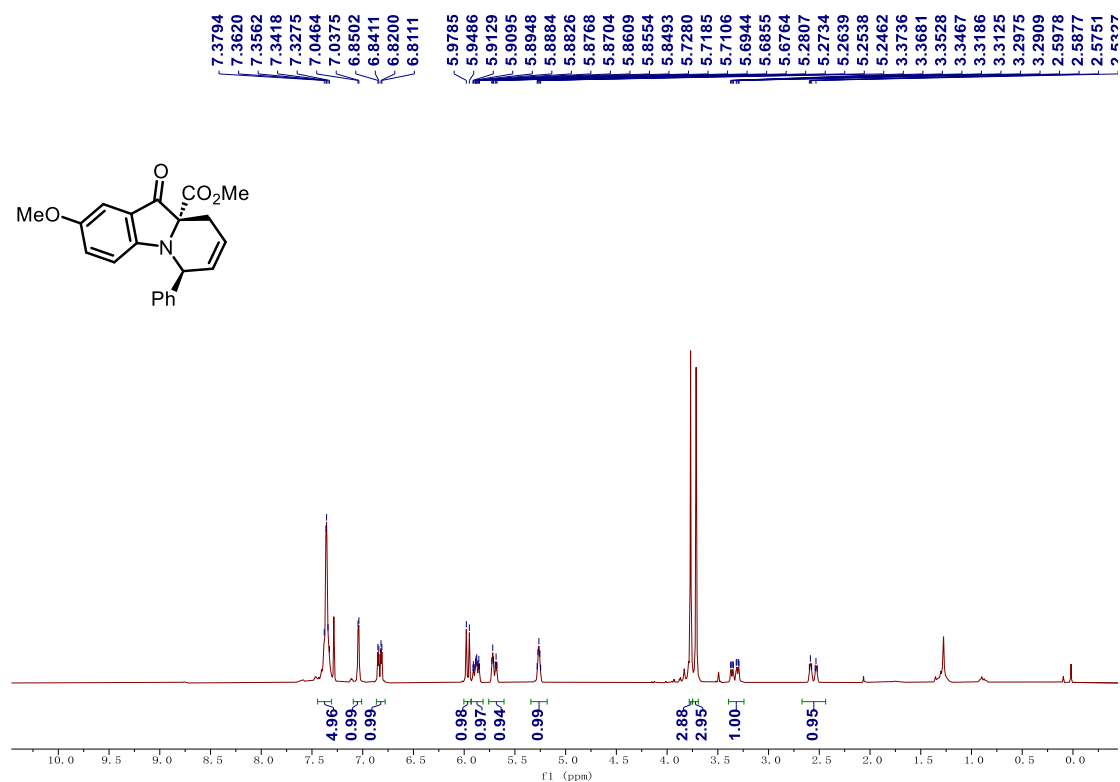
¹H NMR Spectrum of 3fa (300 MHz, CDCl₃)



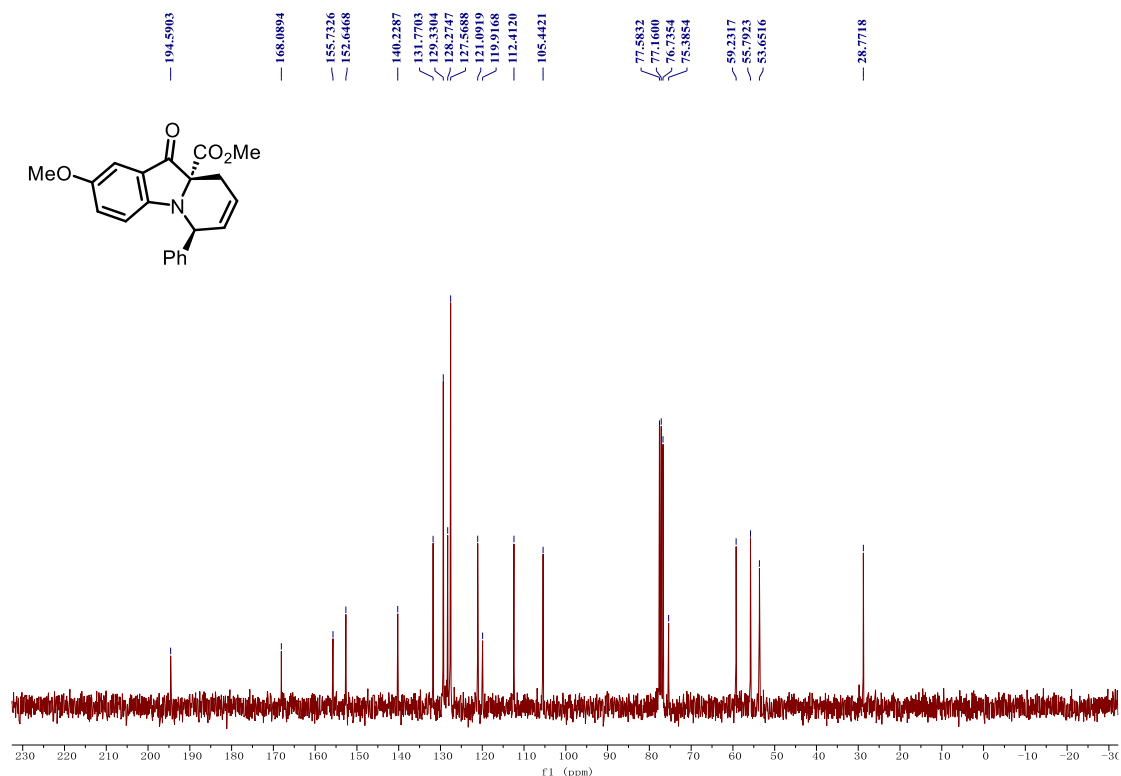
¹³C NMR Spectrum of 3fa (75 MHz, CDCl₃)



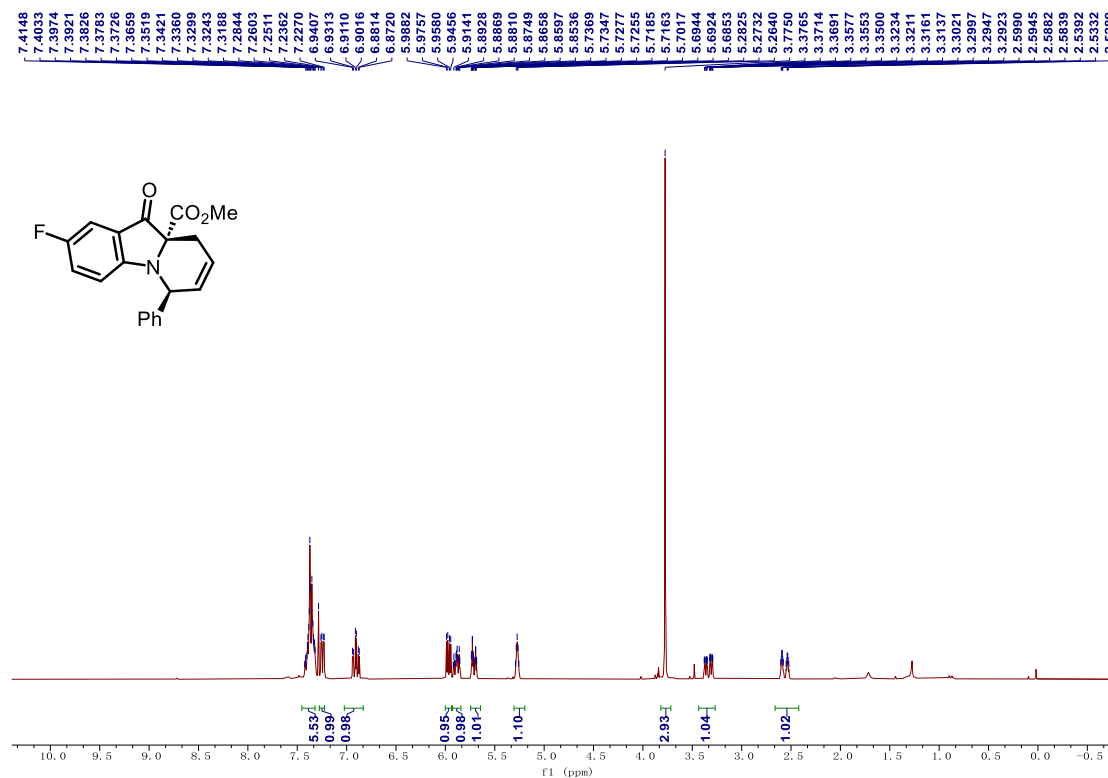
¹H NMR Spectrum of 3ga (300 MHz, CDCl₃)



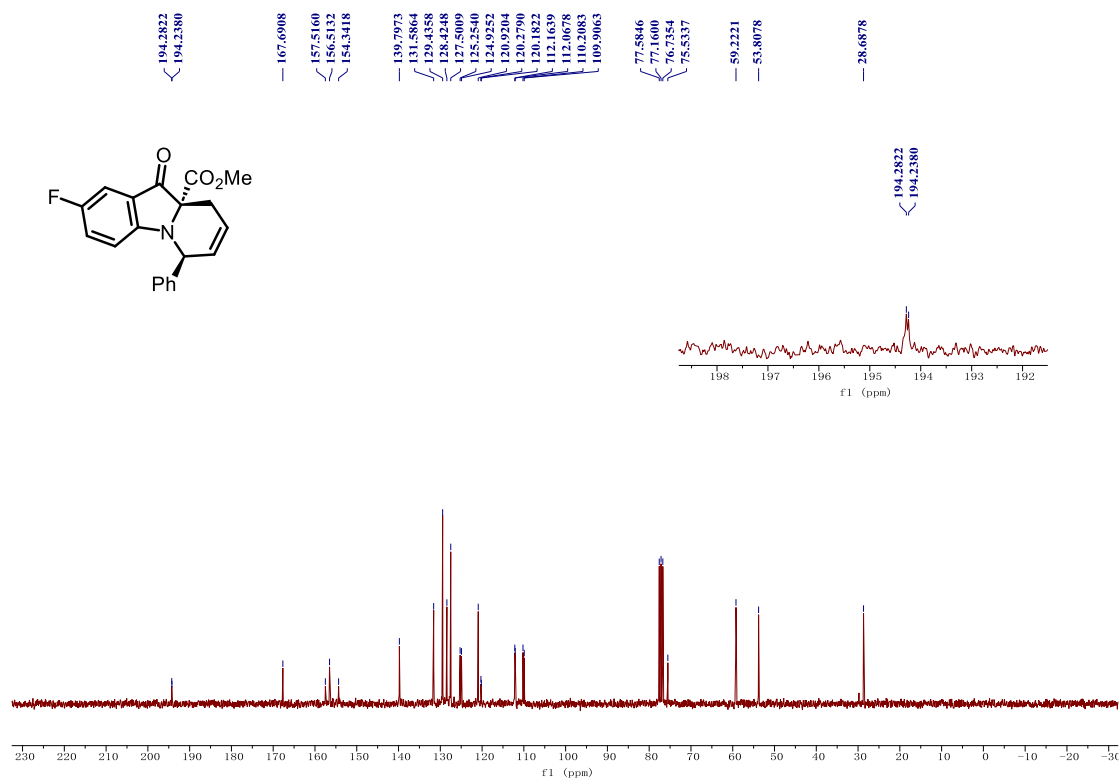
¹³C NMR Spectrum of 3ga (75 MHz, CDCl₃)



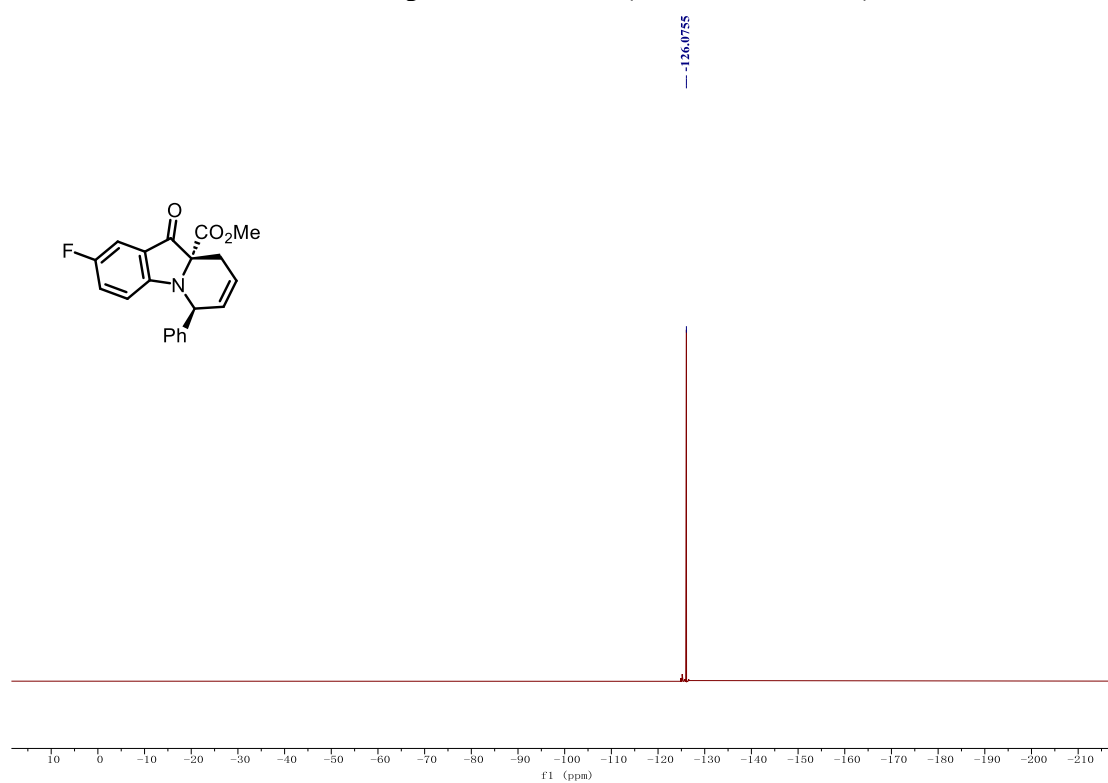
¹H NMR Spectrum of 3ha (300 MHz, CDCl₃)



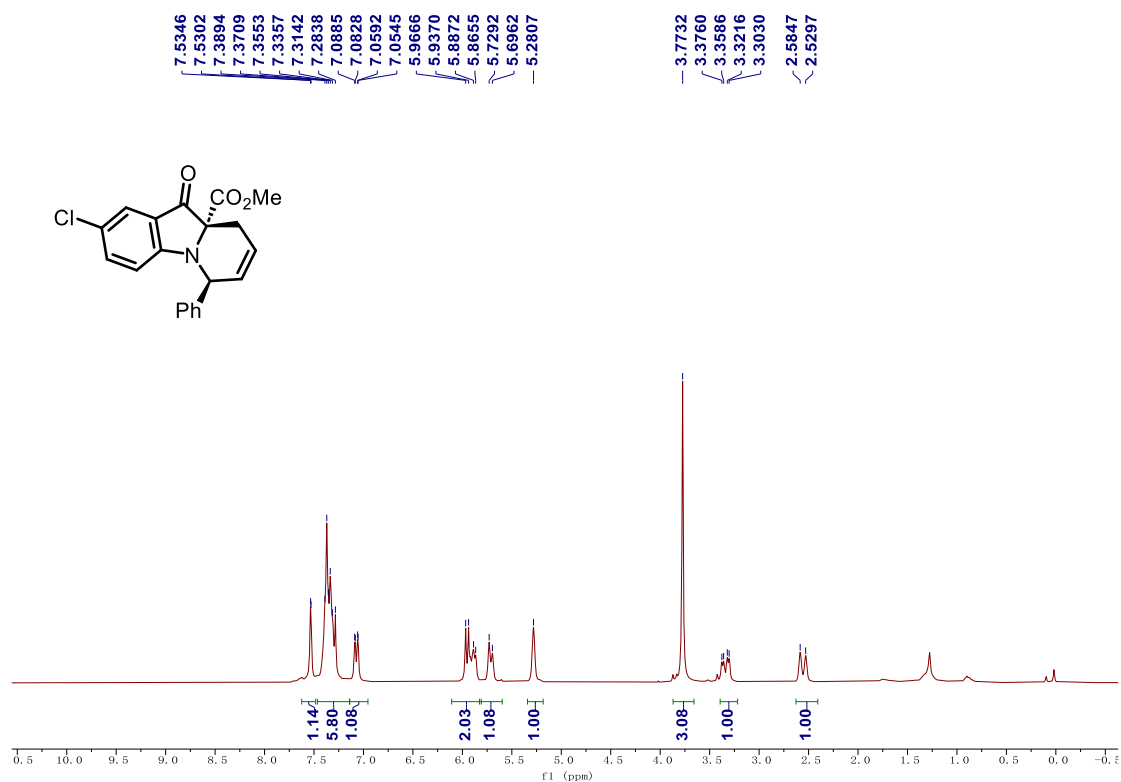
¹³C NMR Spectrum of 3ha (75 MHz, CDCl₃)



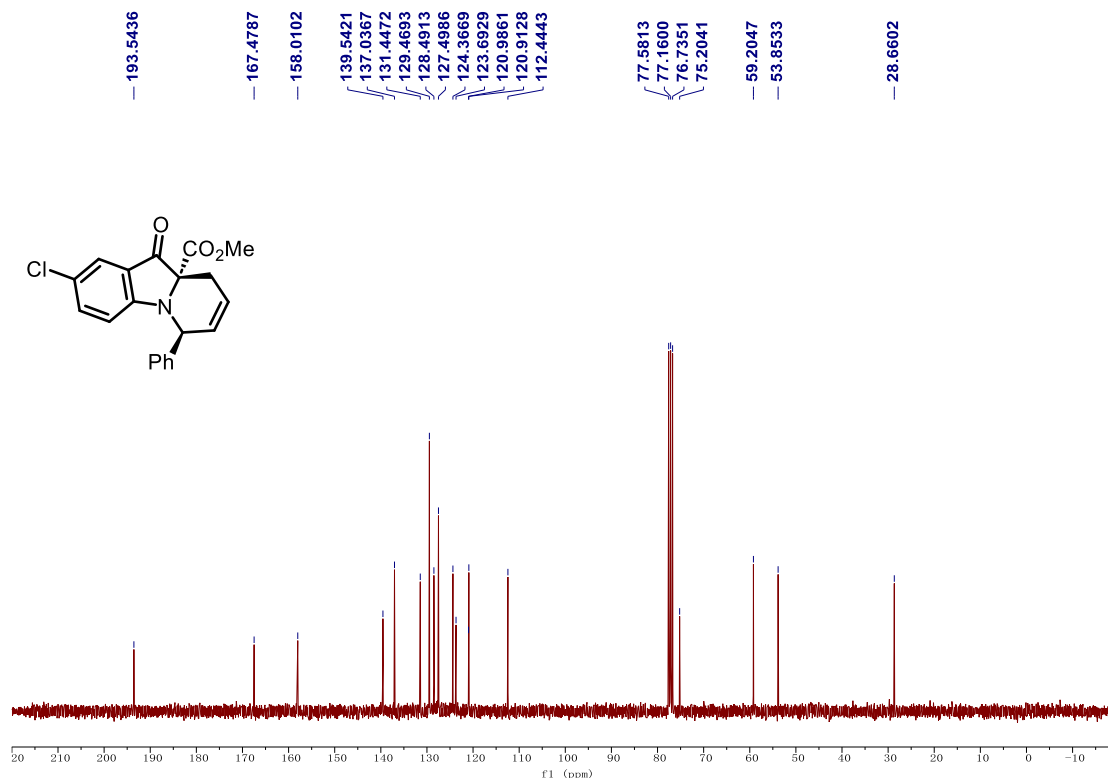
^{19}F NMR Spectrum of 3ha (282 MHz, CDCl_3)



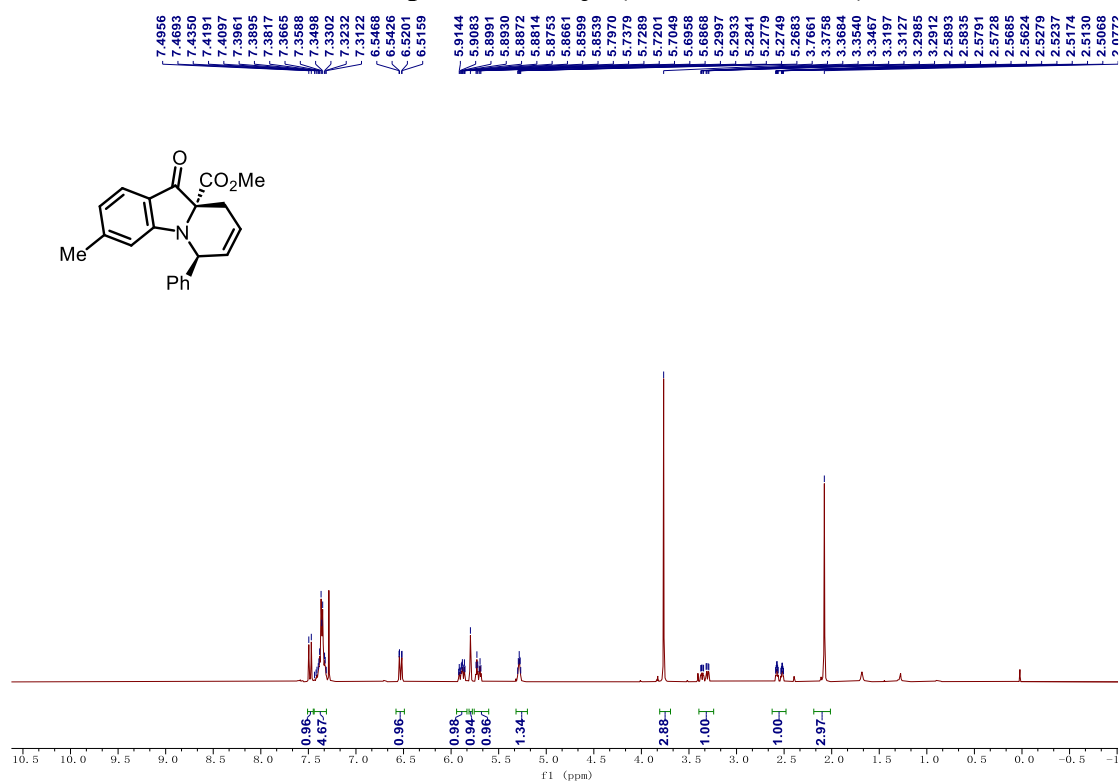
¹H NMR Spectrum of 3ia (300 MHz, CDCl₃)



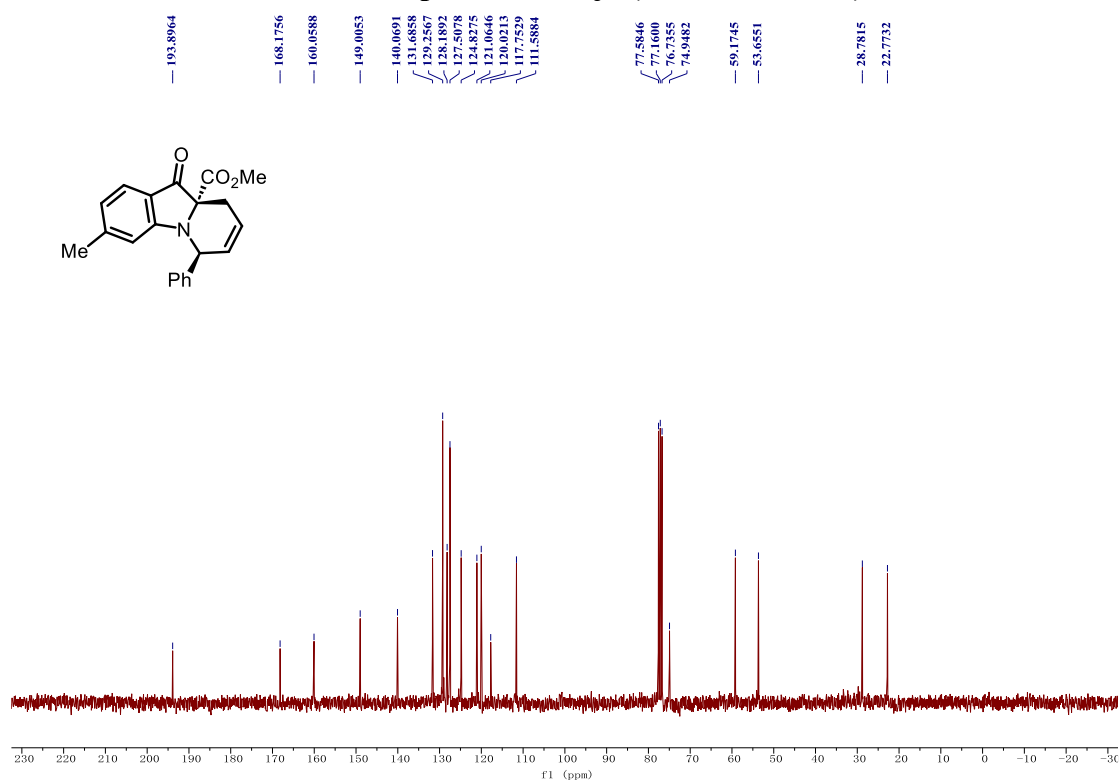
¹³C NMR Spectrum of 3ia (75 MHz, CDCl₃)



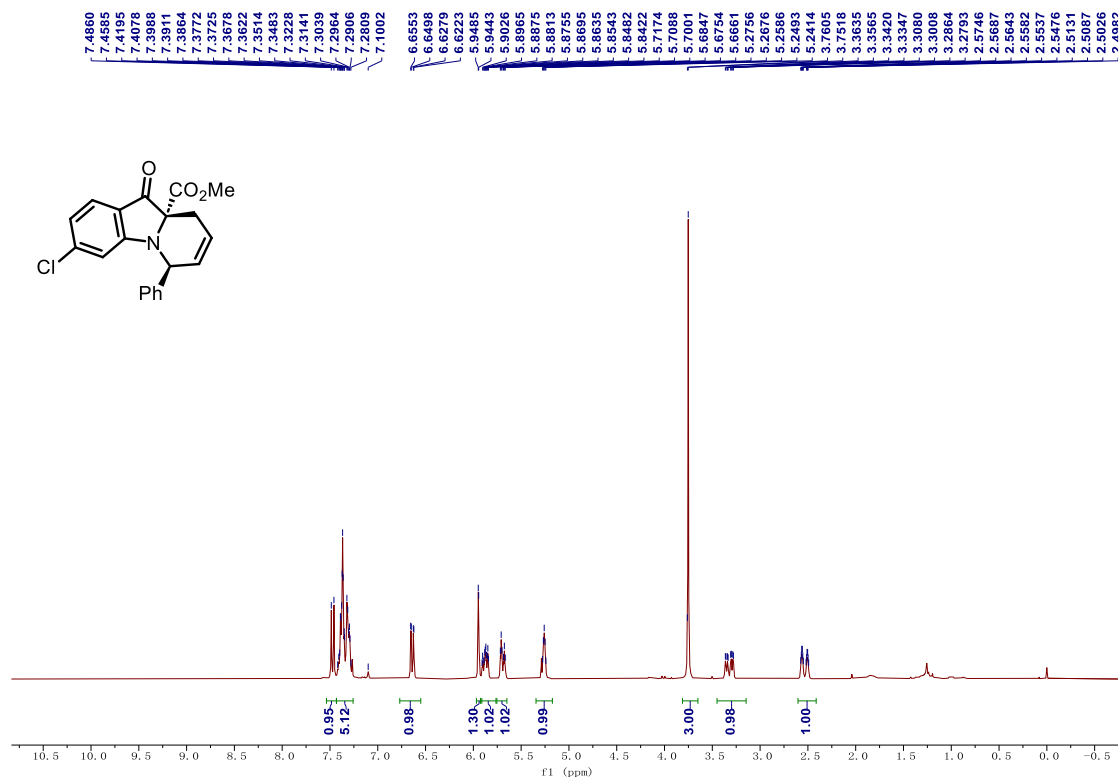
¹H NMR Spectrum of 3ja (300 MHz, CDCl₃)



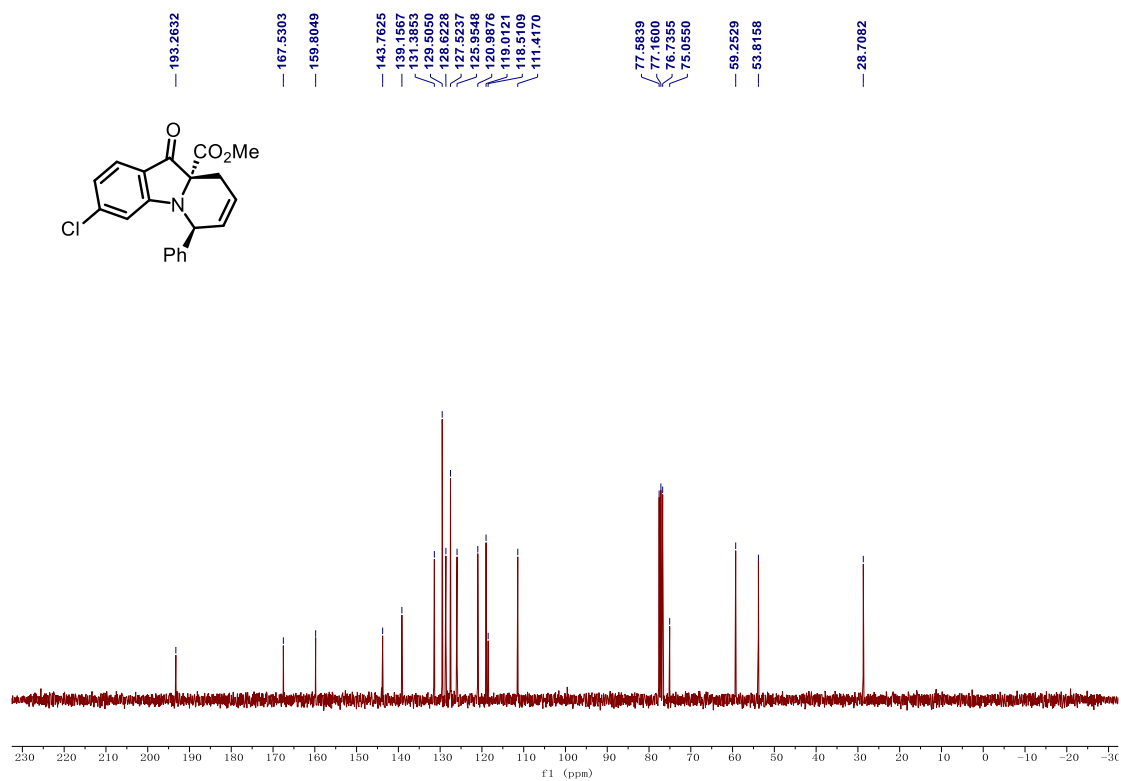
¹³C NMR Spectrum of 3ja (75 MHz, CDCl₃)



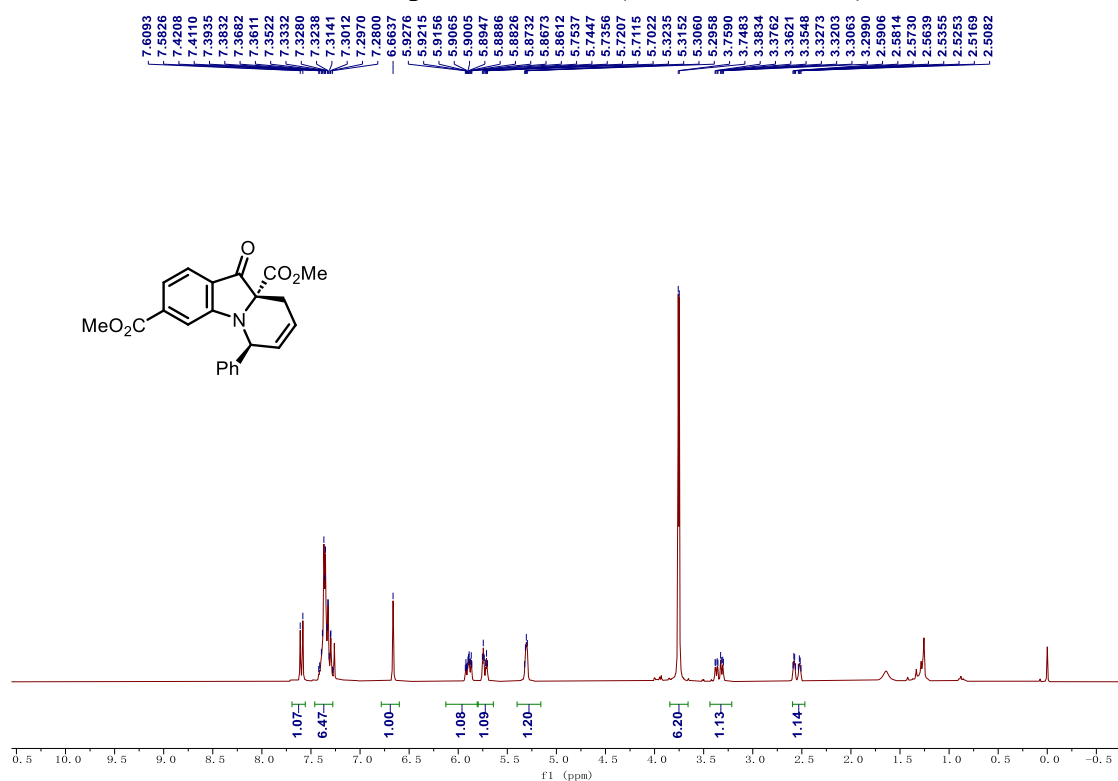
¹H NMR Spectrum of 3ka (300 MHz, CDCl₃)



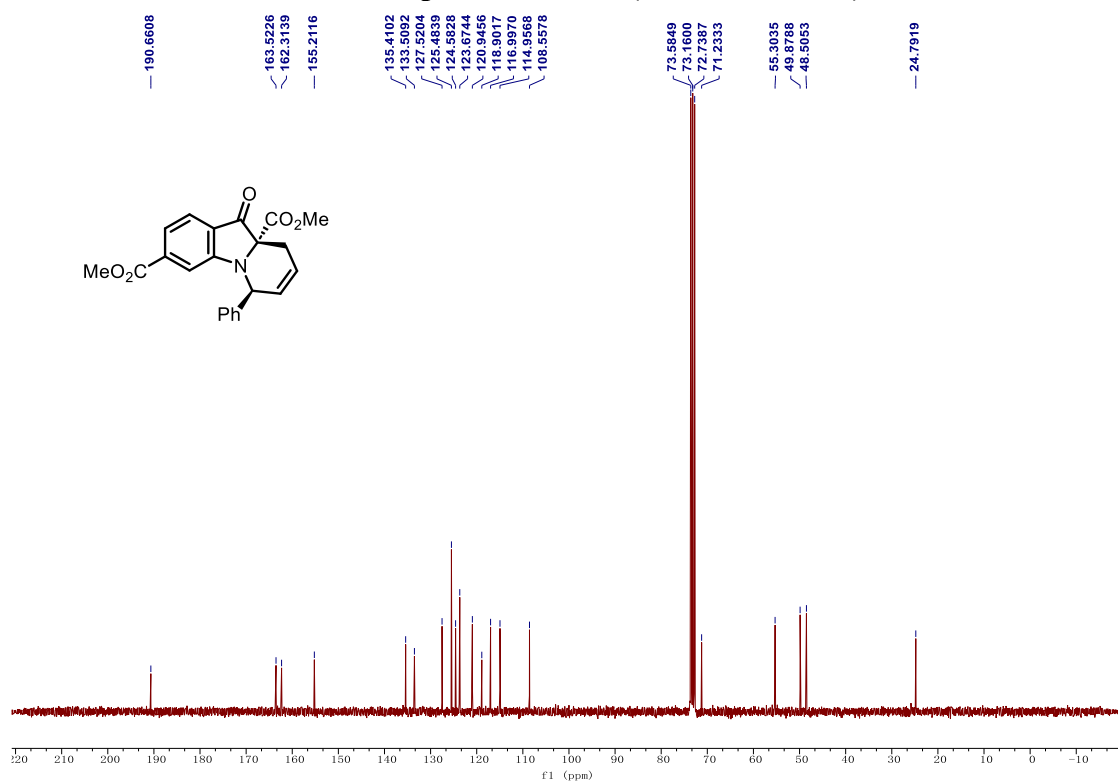
¹³C NMR Spectrum of 3ka (75 MHz, CDCl₃)



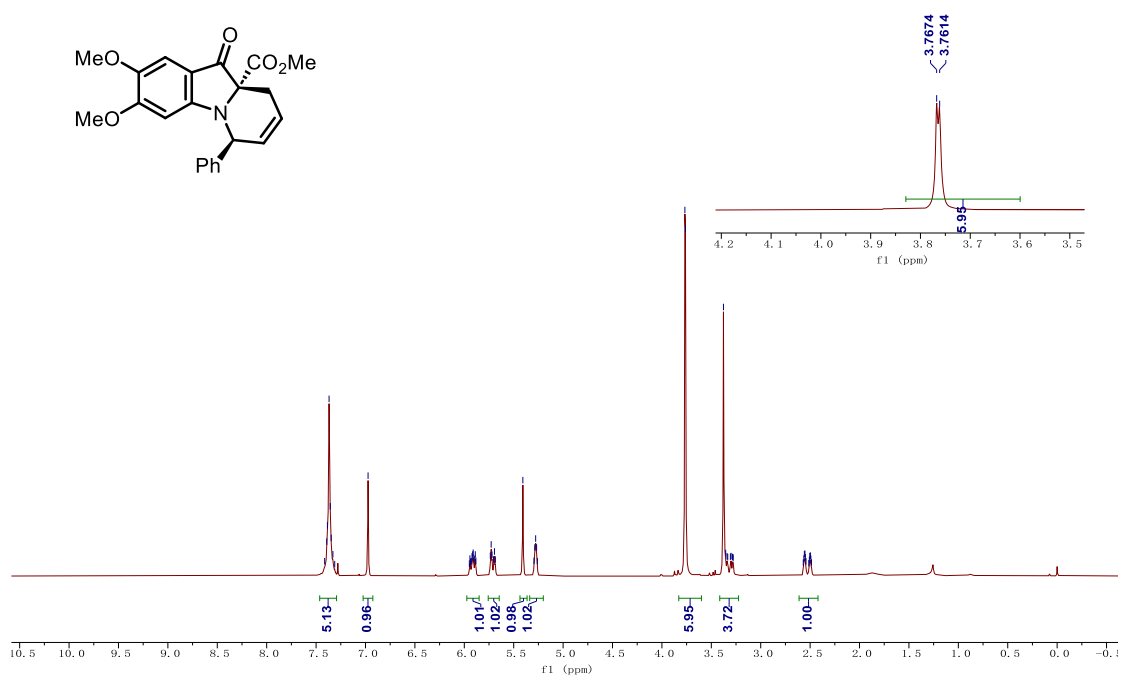
¹H NMR Spectrum of 3la (300 MHz, CDCl₃)



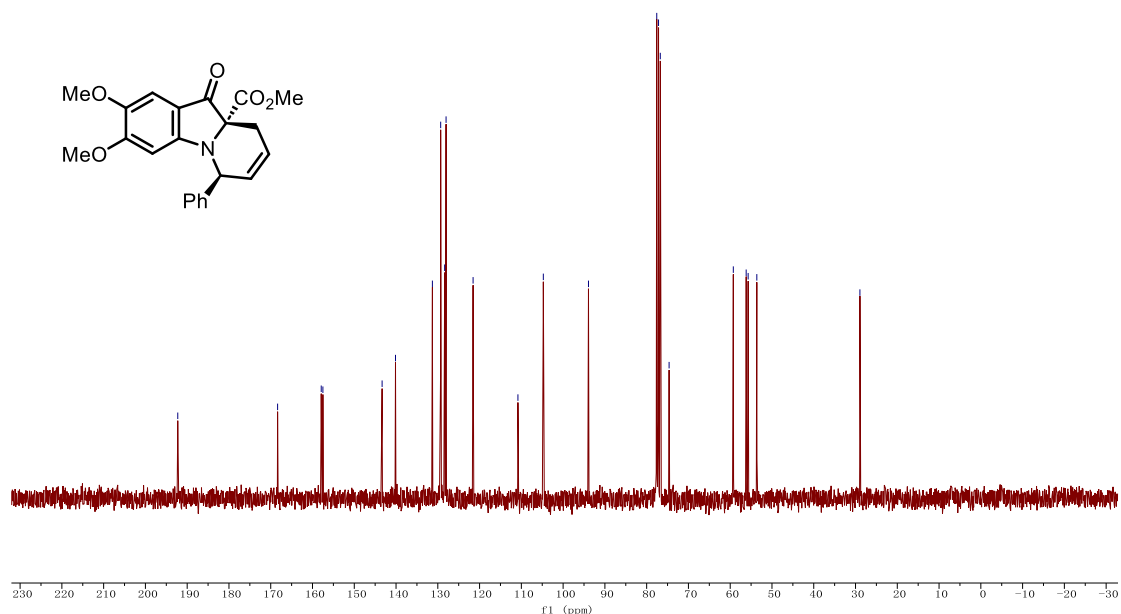
¹³C NMR Spectrum of 3la (75 MHz, CDCl₃)



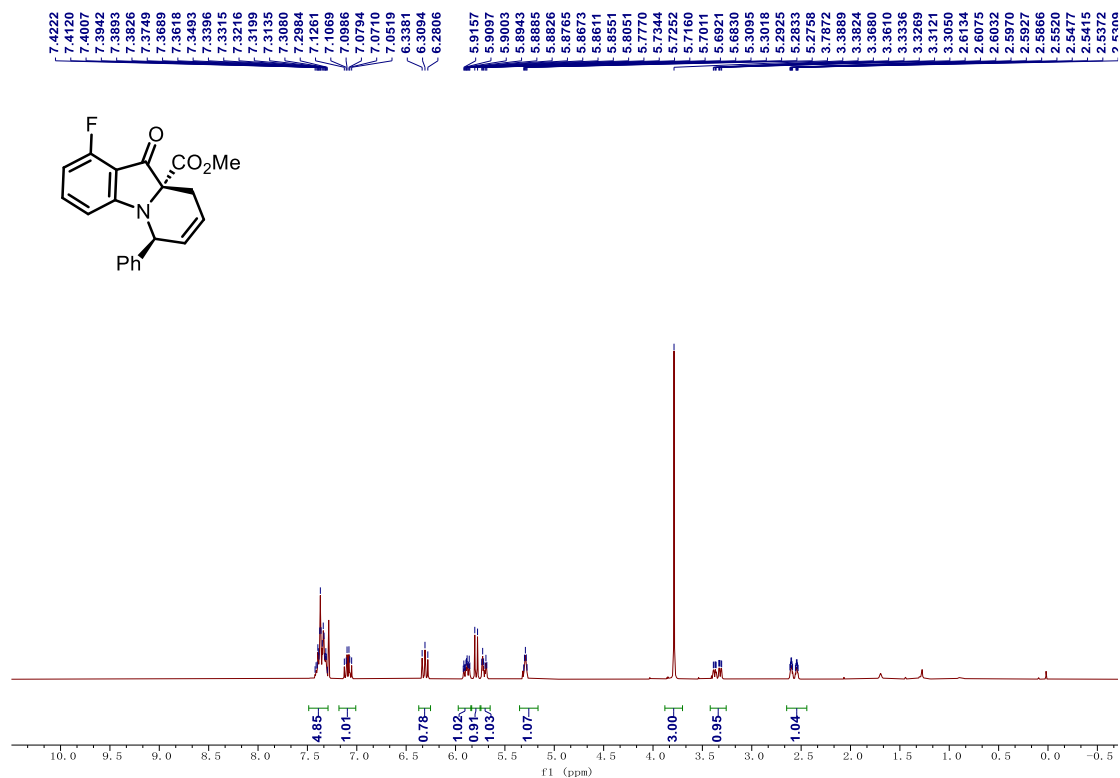
7.4134
7.3921
7.3852
7.3685
7.3563
7.3469
7.3298
7.3115
6.9739
5.9430
5.9368
5.9279
5.9217
5.9159
5.9099
5.9038
5.8949
5.8886
5.8825
5.7368
5.7280
5.7192
5.7038
5.6947
5.6856
5.6774
5.6714
3.7770
3.3547
3.3413
3.3337
3.3070
3.2996
3.2853
3.2778
2.5691
2.5632
2.5523
2.5479
2.5417
2.5134
2.5077
2.5031
2.4969
2.4923
2.4860



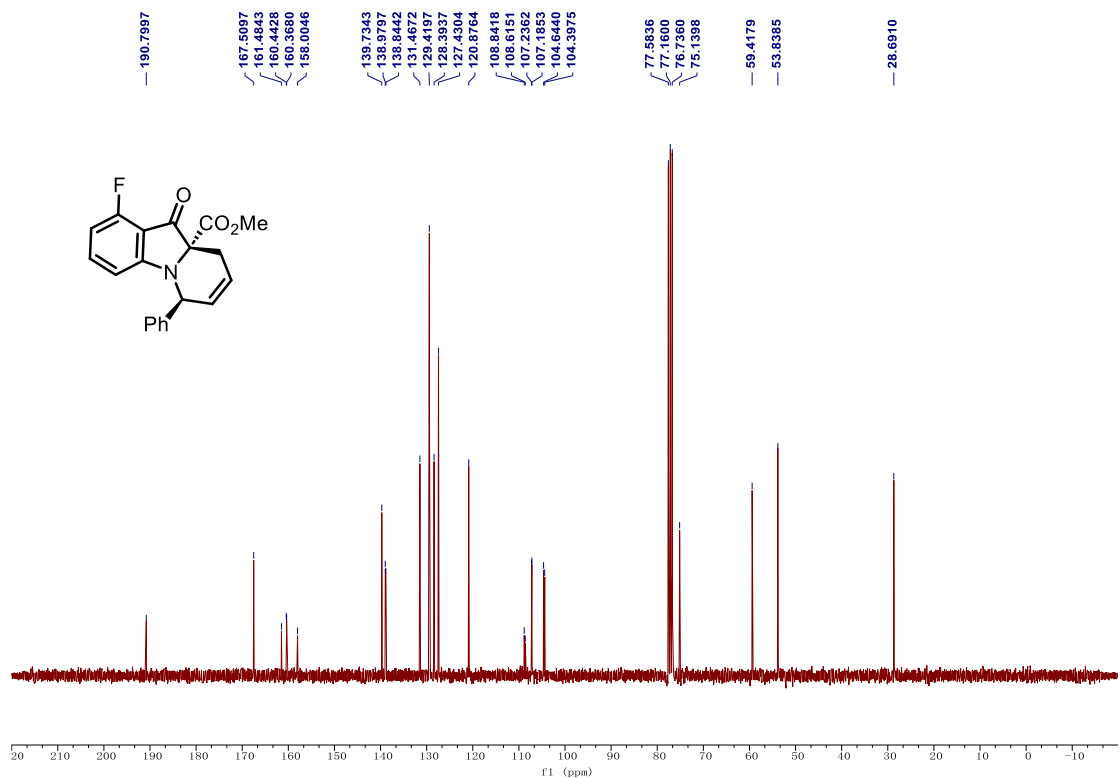
-192.2546	-168.3525	157.9090	157.5115	143.3362	140.1303	131.2966	129.3132	128.3671	128.0222	121.5537	110.8182	104.7408	93.9284	77.5831	77.1600	76.7354	74.6287	59.2546	56.1766	55.7051	53.6267	28.9461
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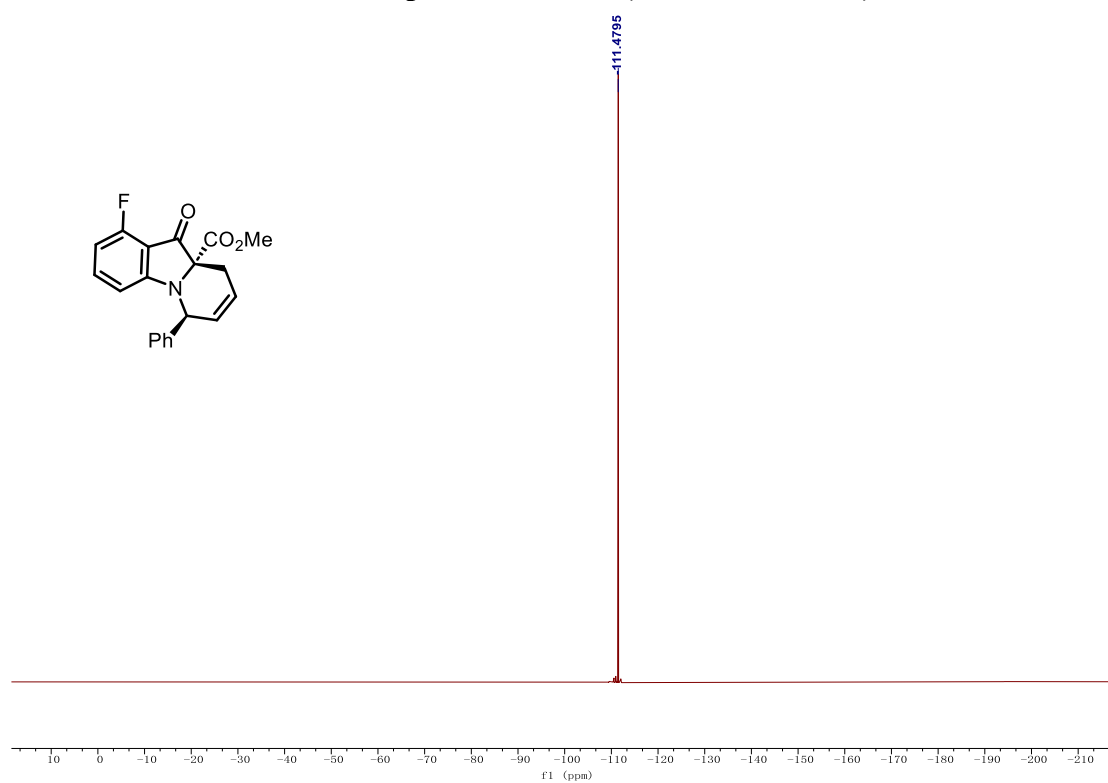
¹H NMR Spectrum of 3na (300 MHz, CDCl₃)



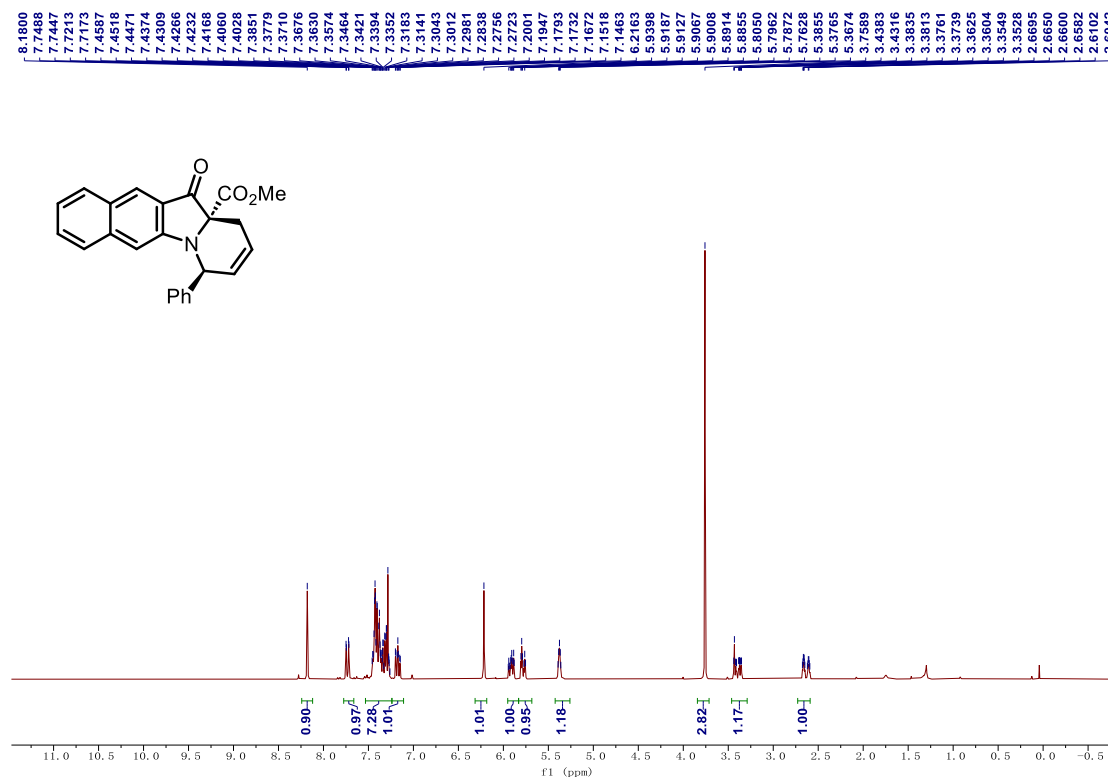
¹³C NMR Spectrum of 3na (75 MHz, CDCl₃)



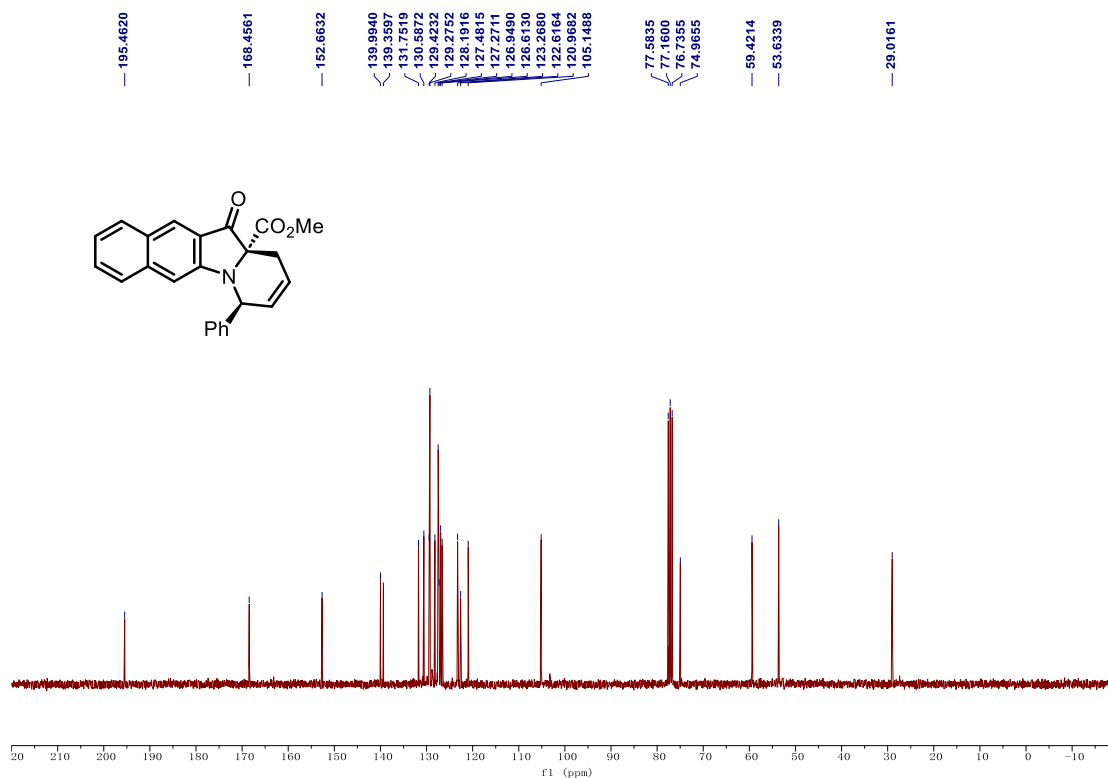
^{19}F NMR Spectrum of 3na (282 MHz, CDCl_3)



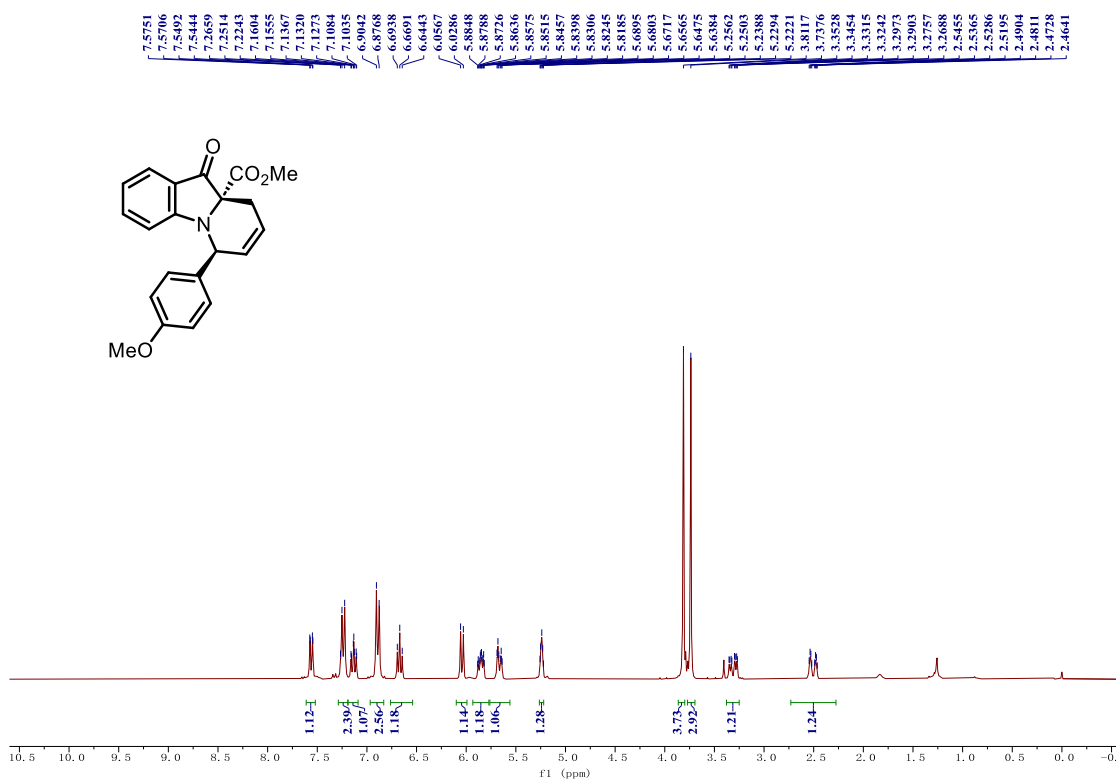
¹H NMR Spectrum of 3oa (282 MHz, CDCl₃)



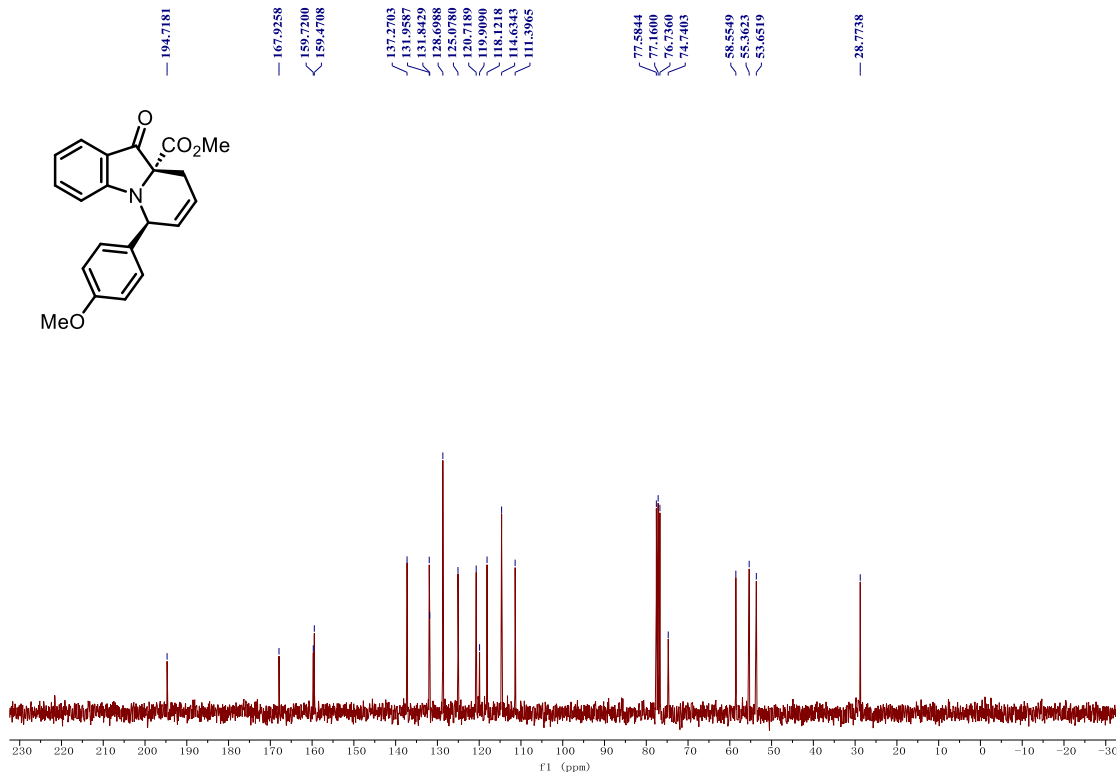
¹³C NMR Spectrum of 3oa (75 MHz, CDCl₃)



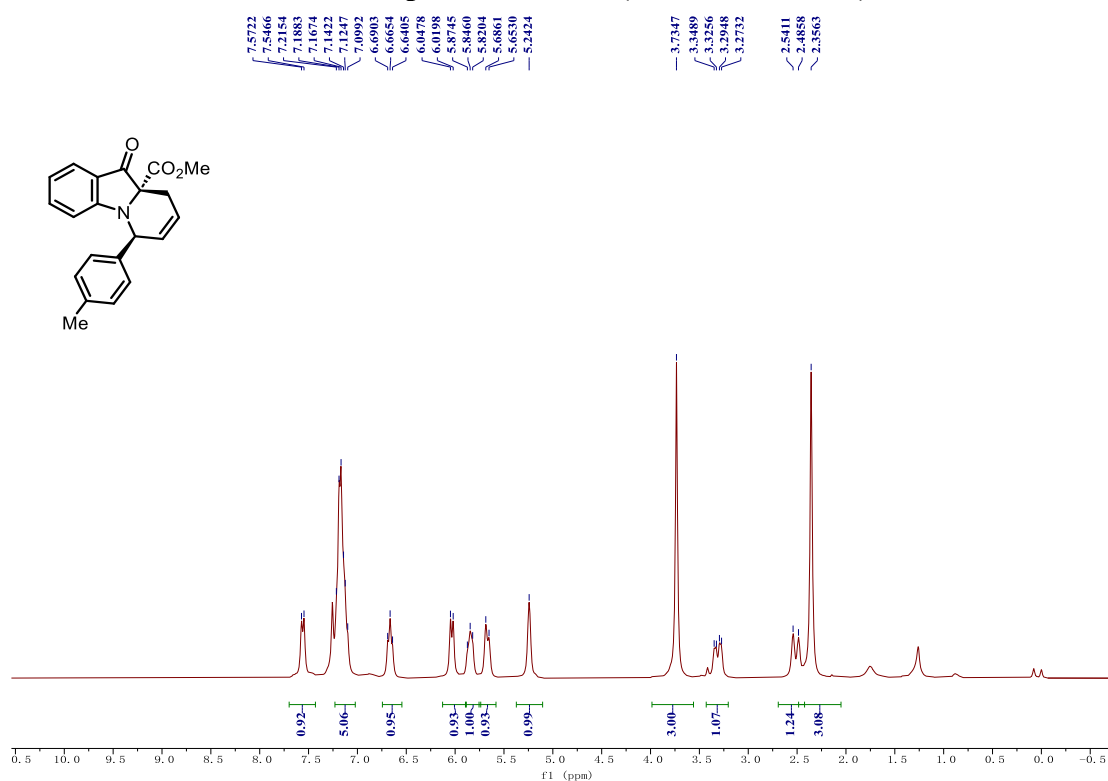
¹H NMR Spectrum of 3ab (300 MHz, CDCl₃)



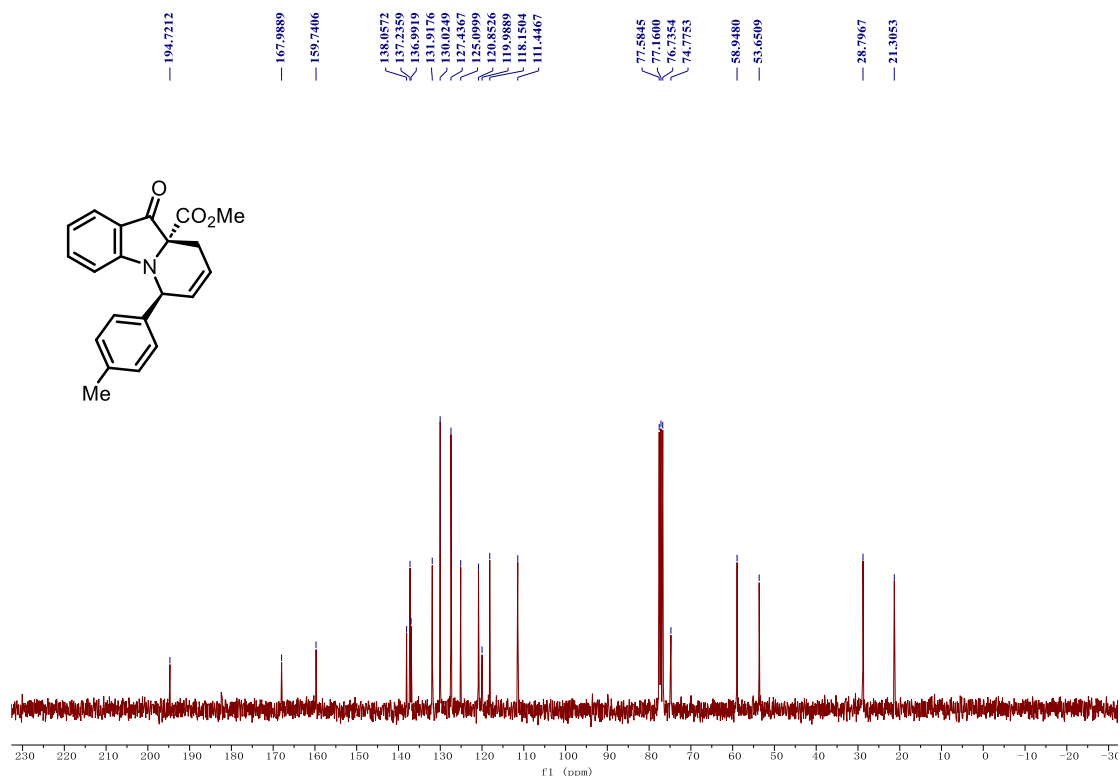
¹³C NMR Spectrum of 3ab (75MHz, CDCl₃)



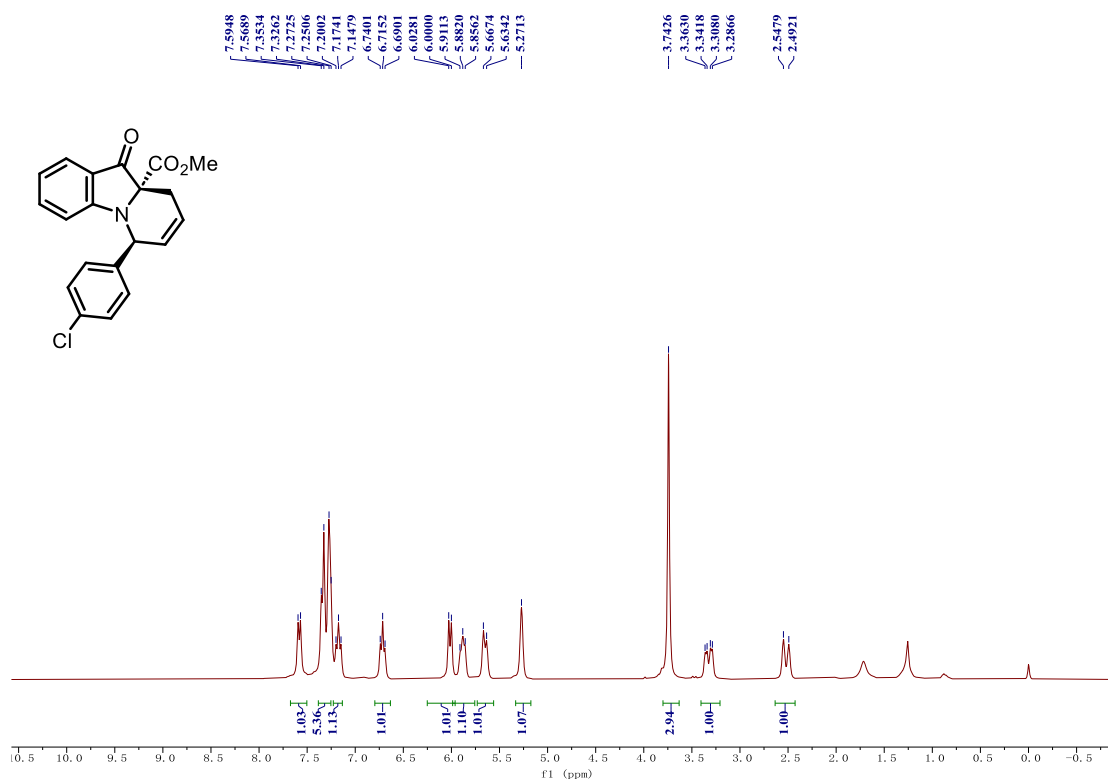
¹H NMR Spectrum of 3ac (300 MHz, CDCl₃)



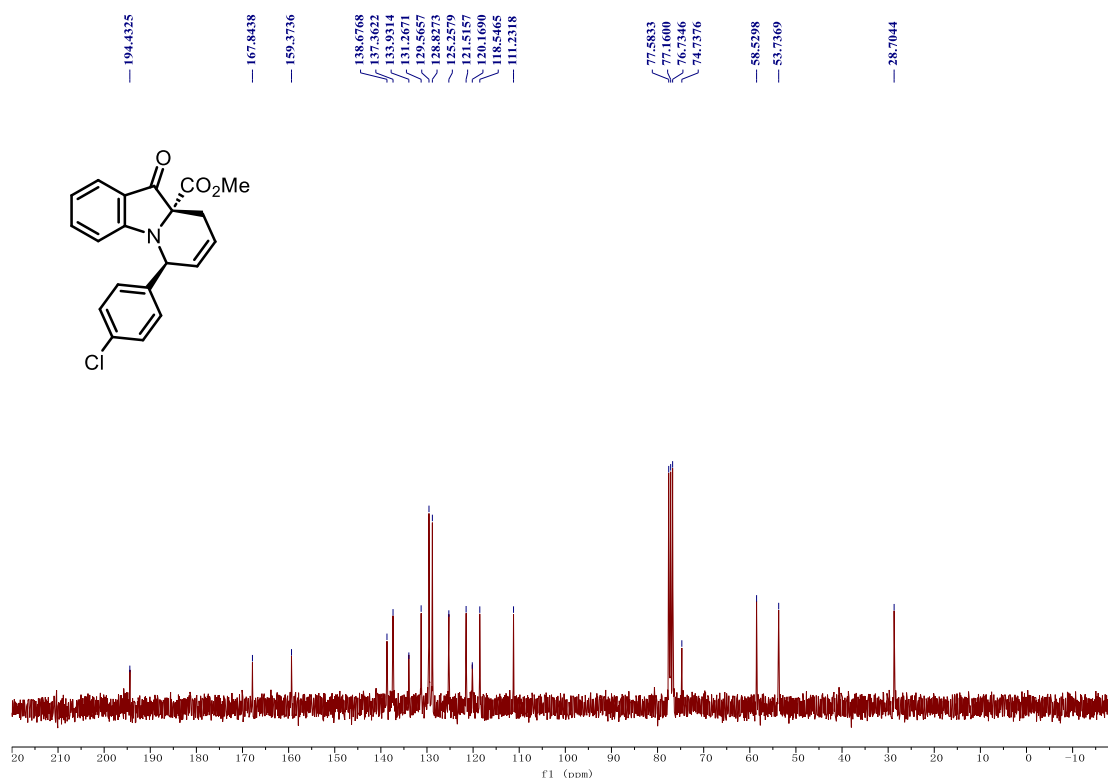
¹³C NMR Spectrum of 3ac (75 MHz, CDCl₃)



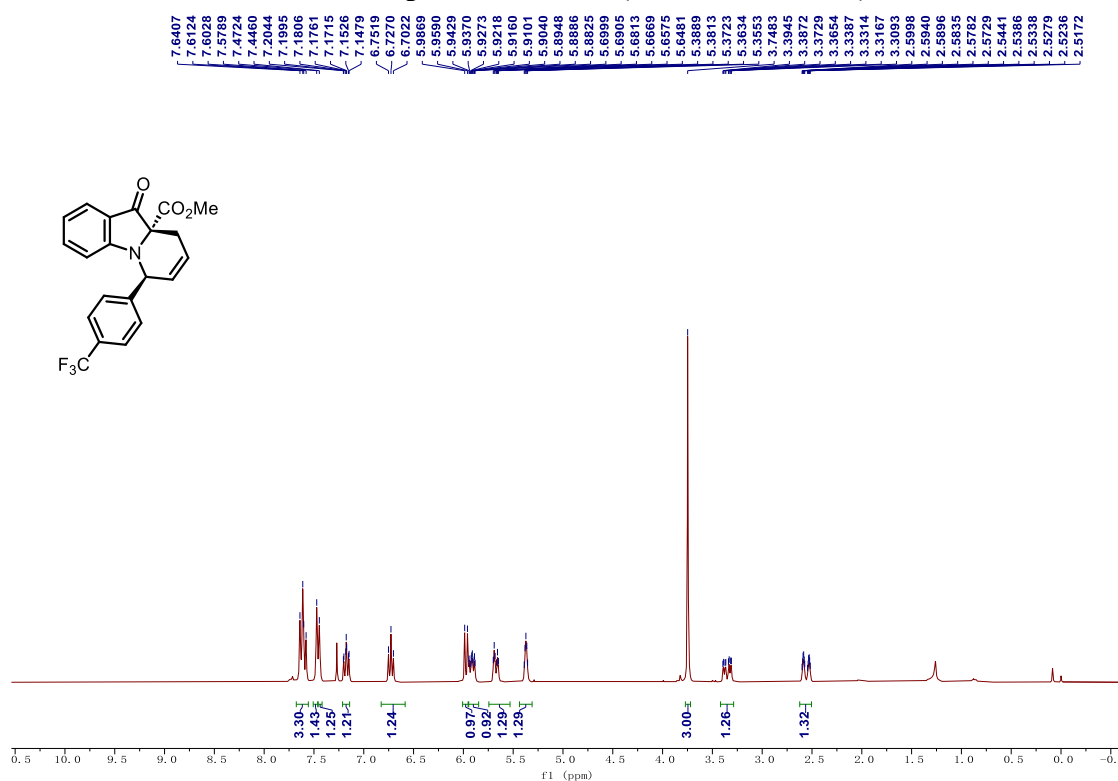
¹H NMR Spectrum of 3ad (300 MHz, CDCl₃)



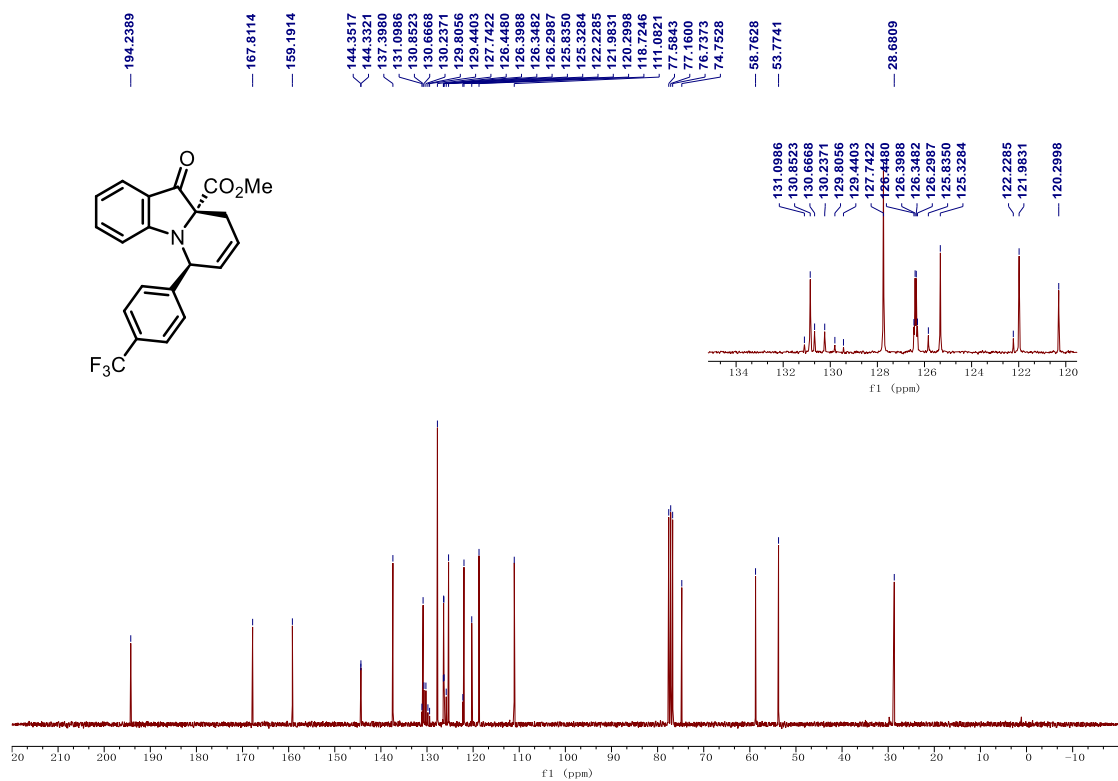
¹³C NMR Spectrum of 3ad (75 MHz, CDCl₃)



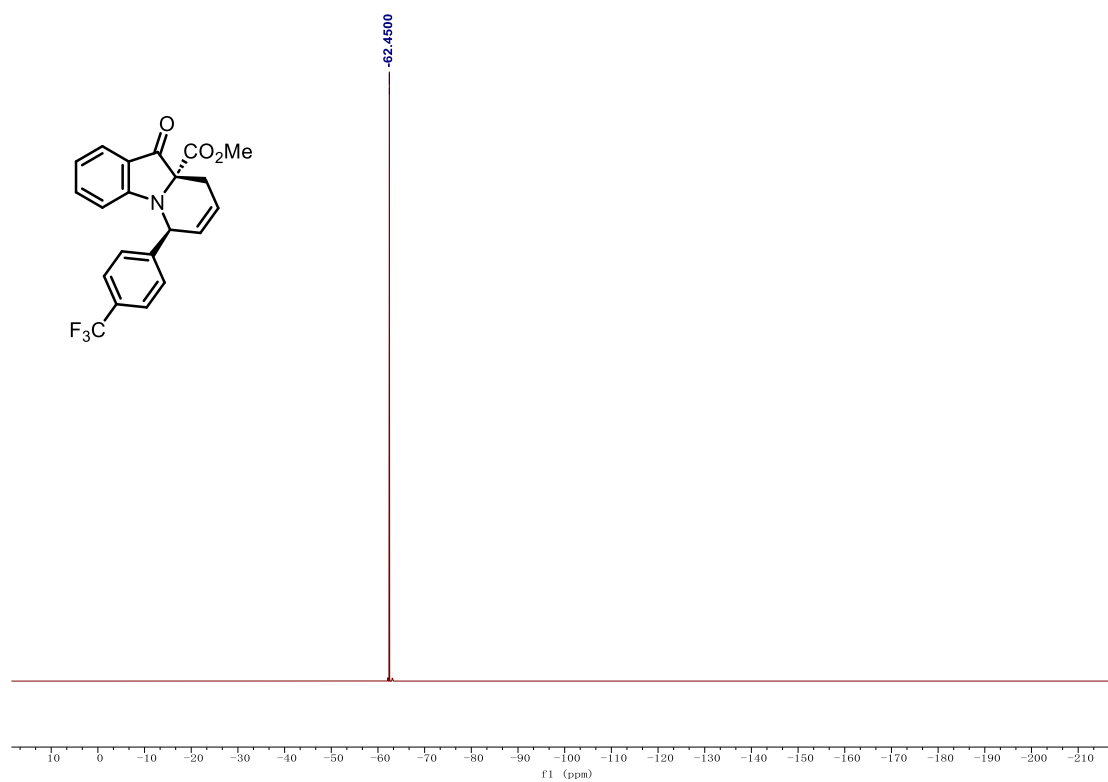
¹H NMR Spectrum of 3ae (300 MHz, CDCl₃)



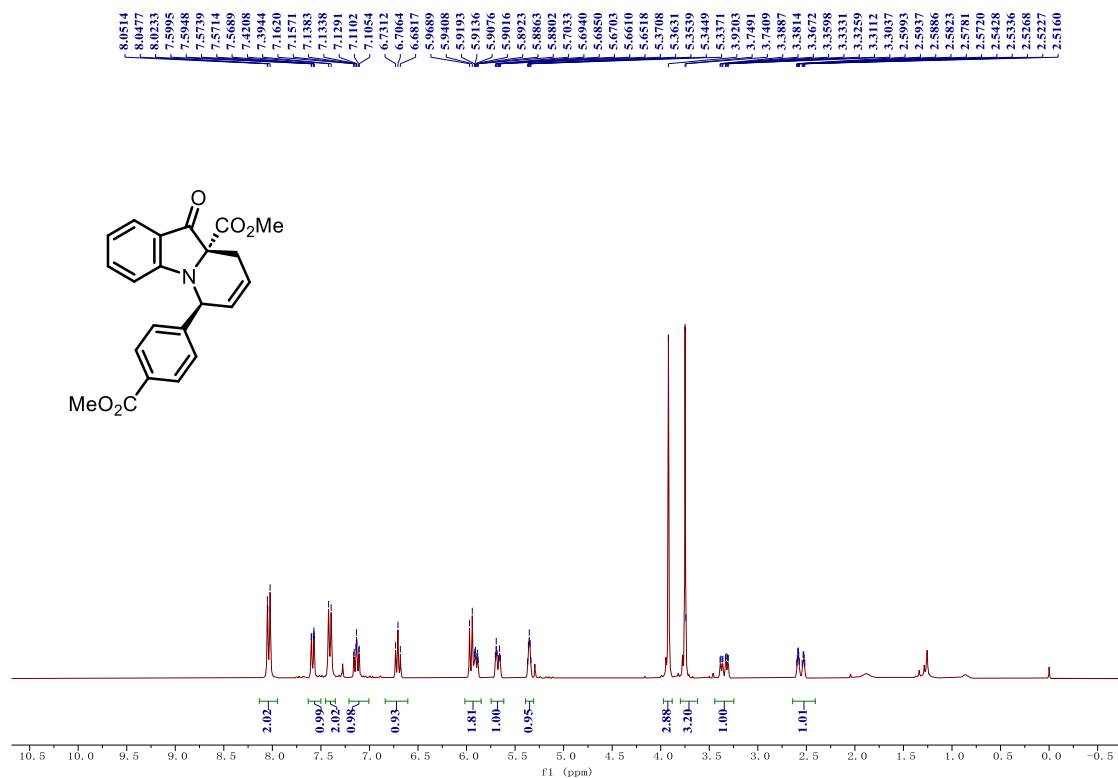
¹³C NMR Spectrum of 3ae (300 MHz, CDCl₃)



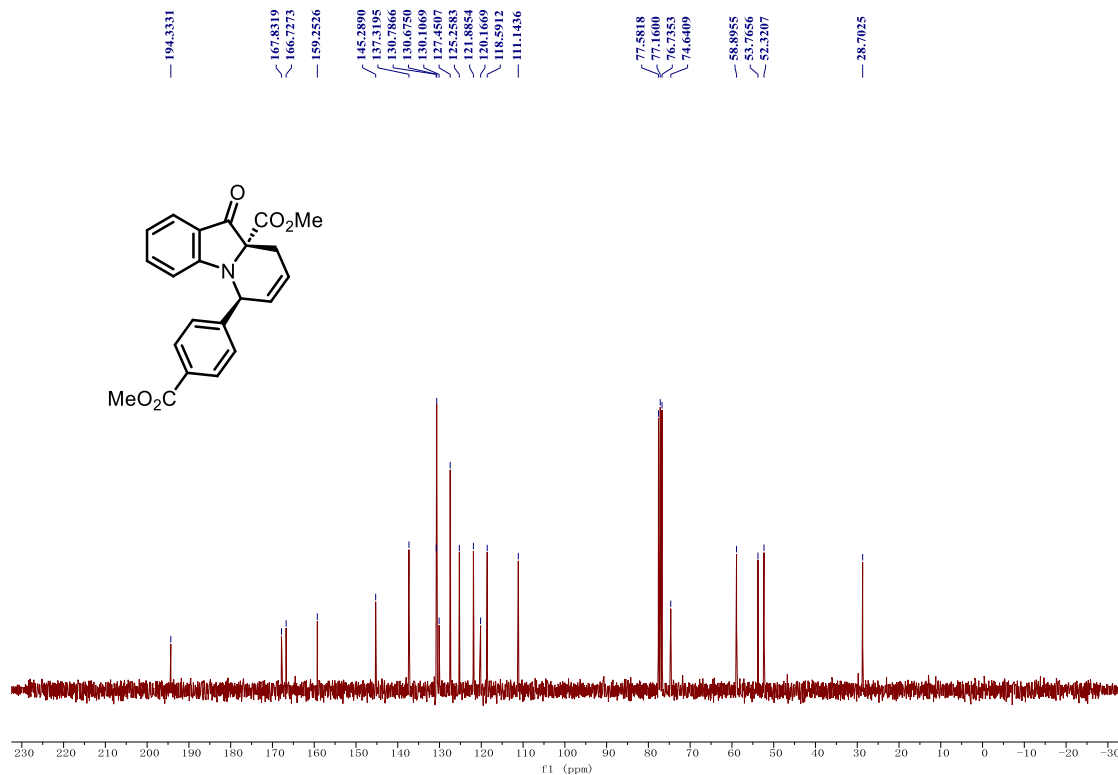
^{19}F NMR Spectrum of 3ae (282 MHz, CDCl_3)



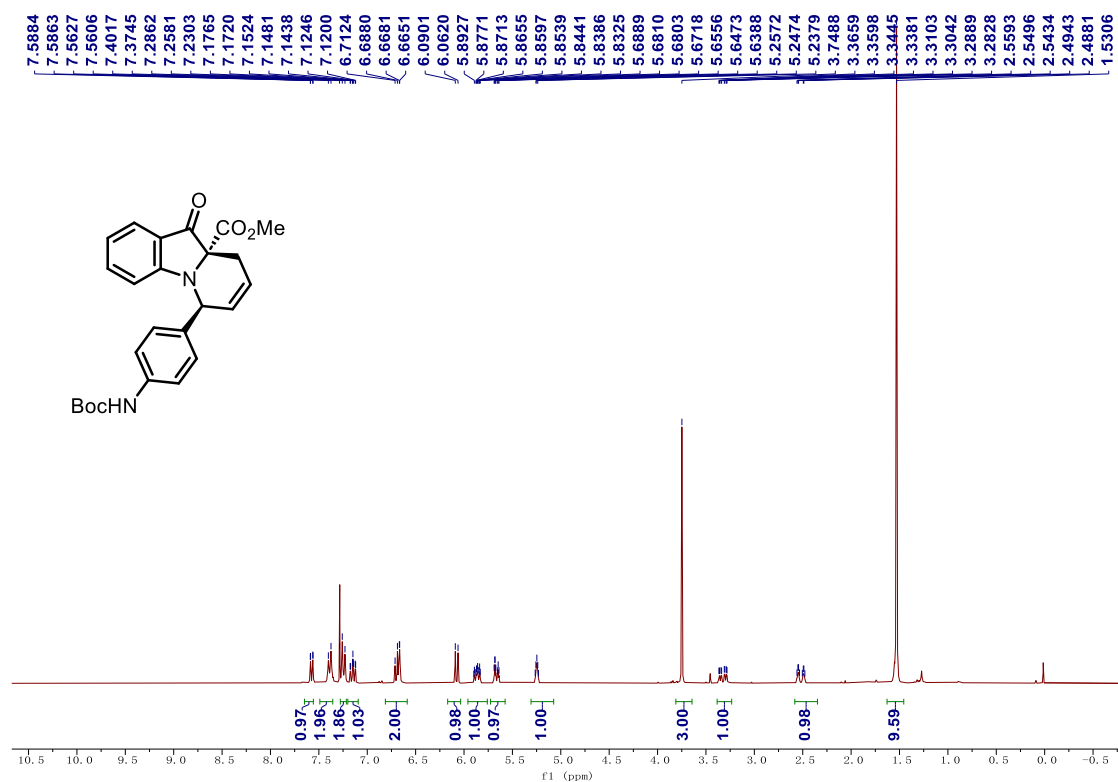
¹H NMR Spectrum of 3af (300 MHz, CDCl₃)



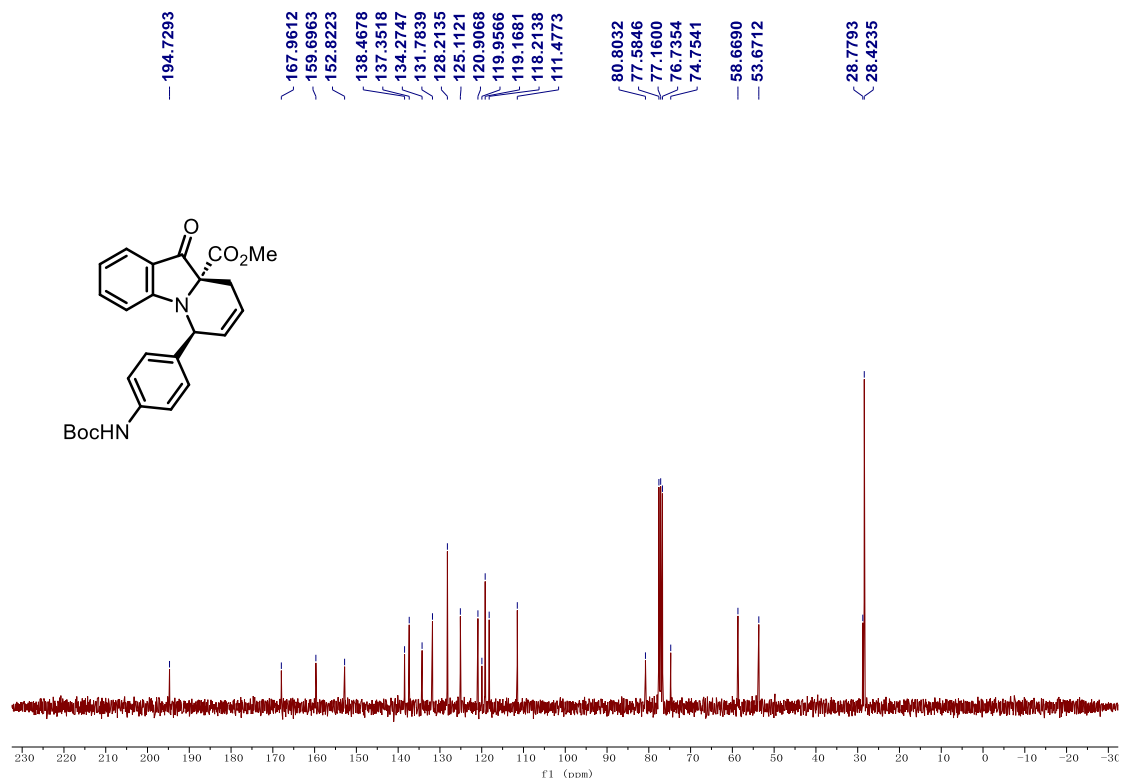
¹³C NMR Spectrum of 3af (75 MHz, CDCl₃)



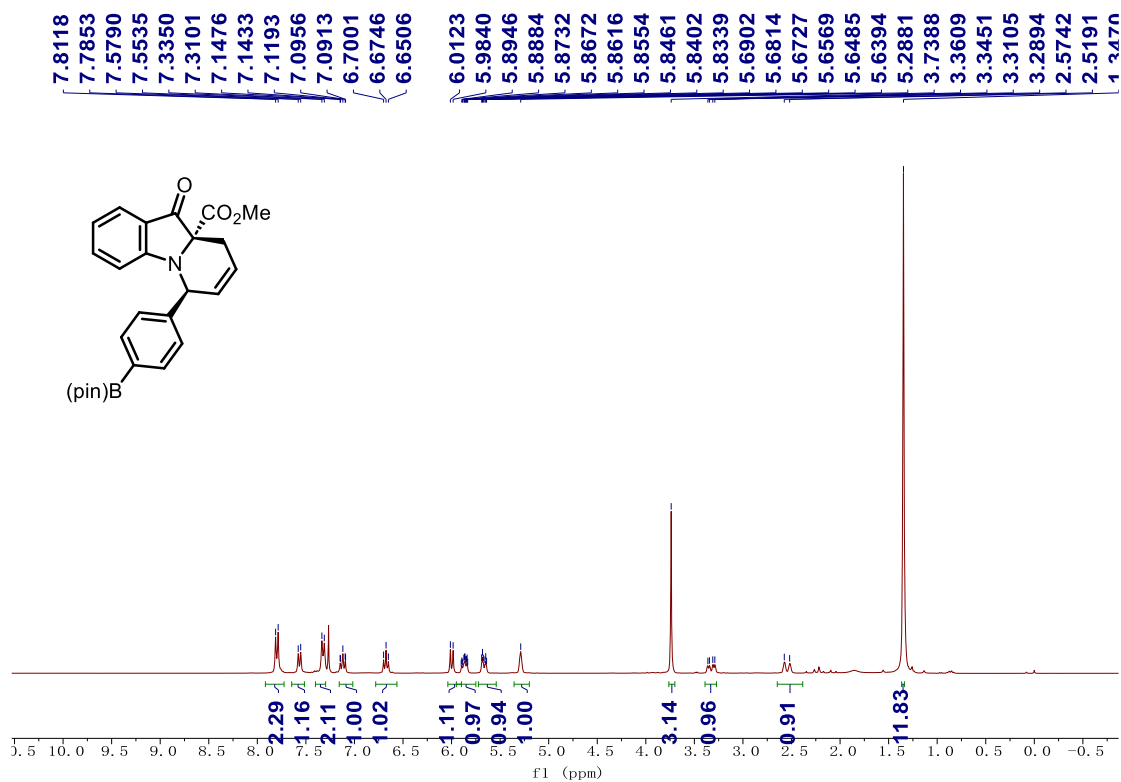
¹H NMR Spectrum of 3ag (300 MHz, CDCl₃)



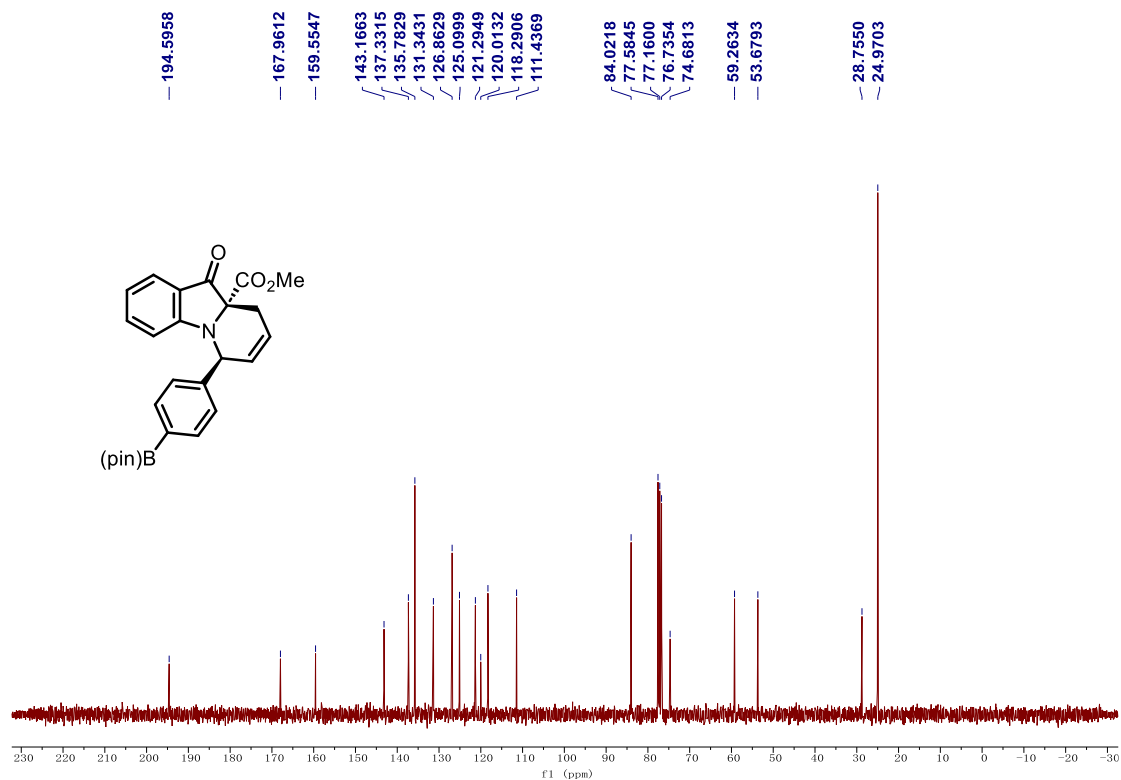
¹³C NMR Spectrum of 3ag (75 MHz, CDCl₃)



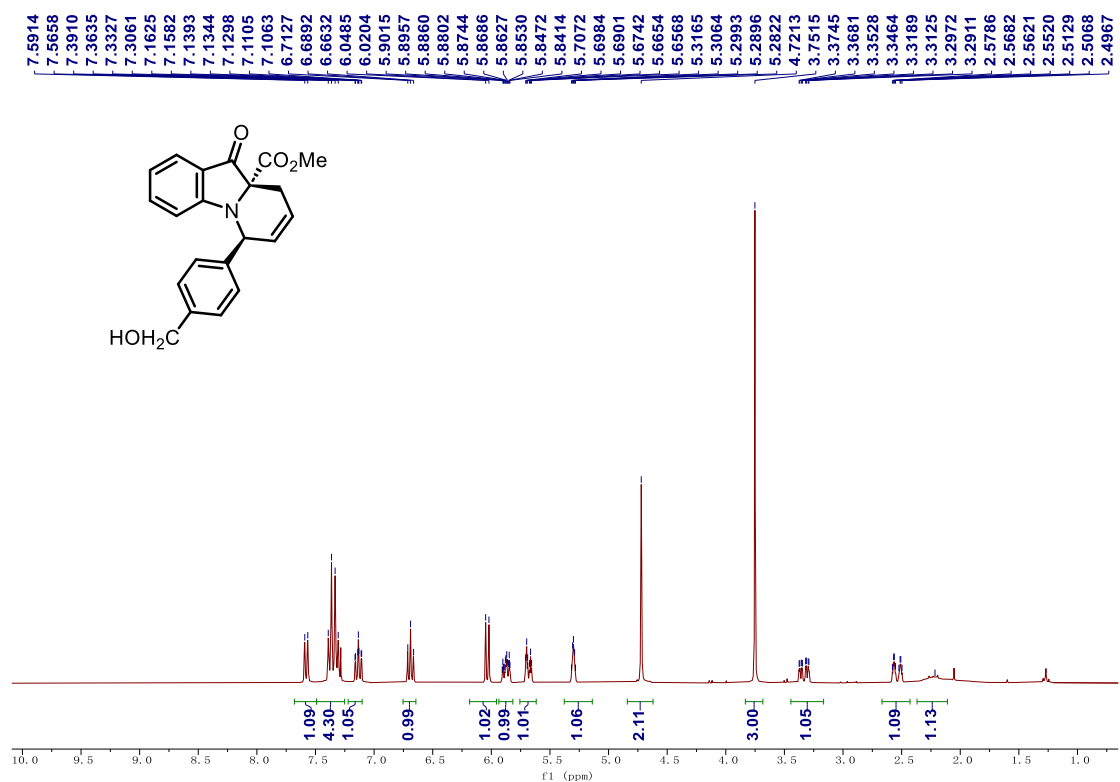
¹H NMR Spectrum of 3ah (300 MHz, CDCl₃)



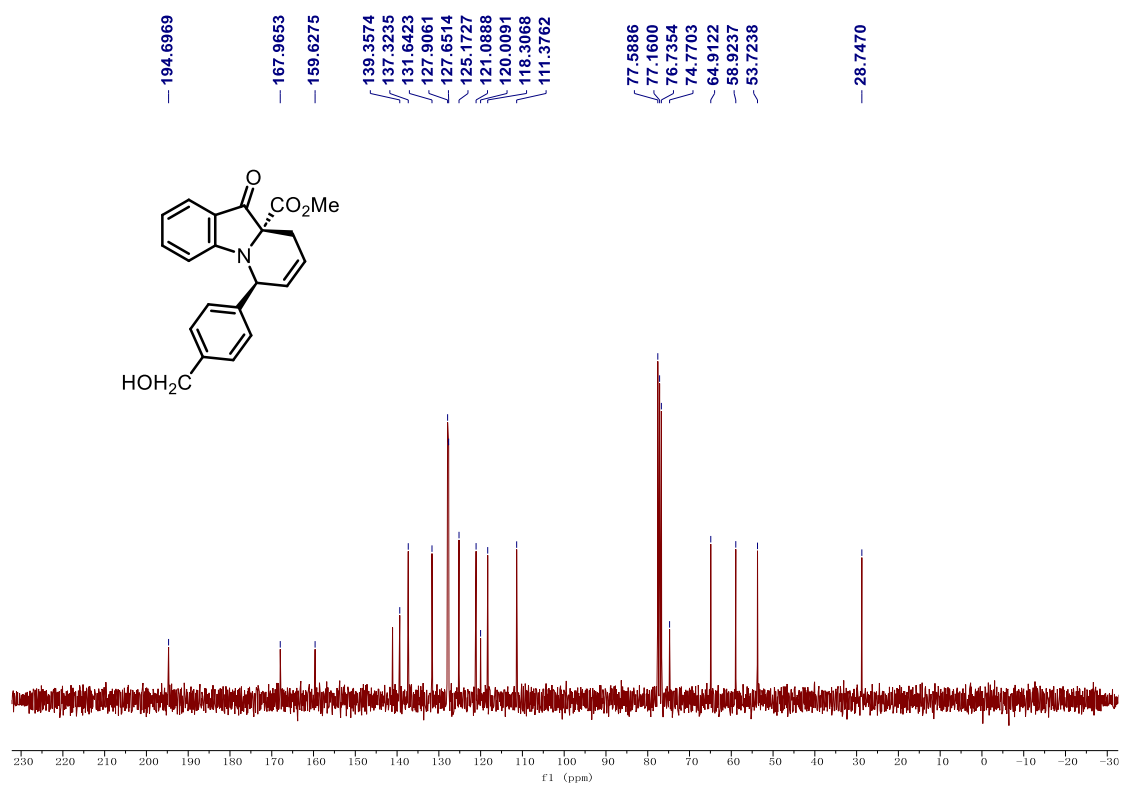
¹³C NMR Spectrum of 3ah (75 MHz, CDCl₃)



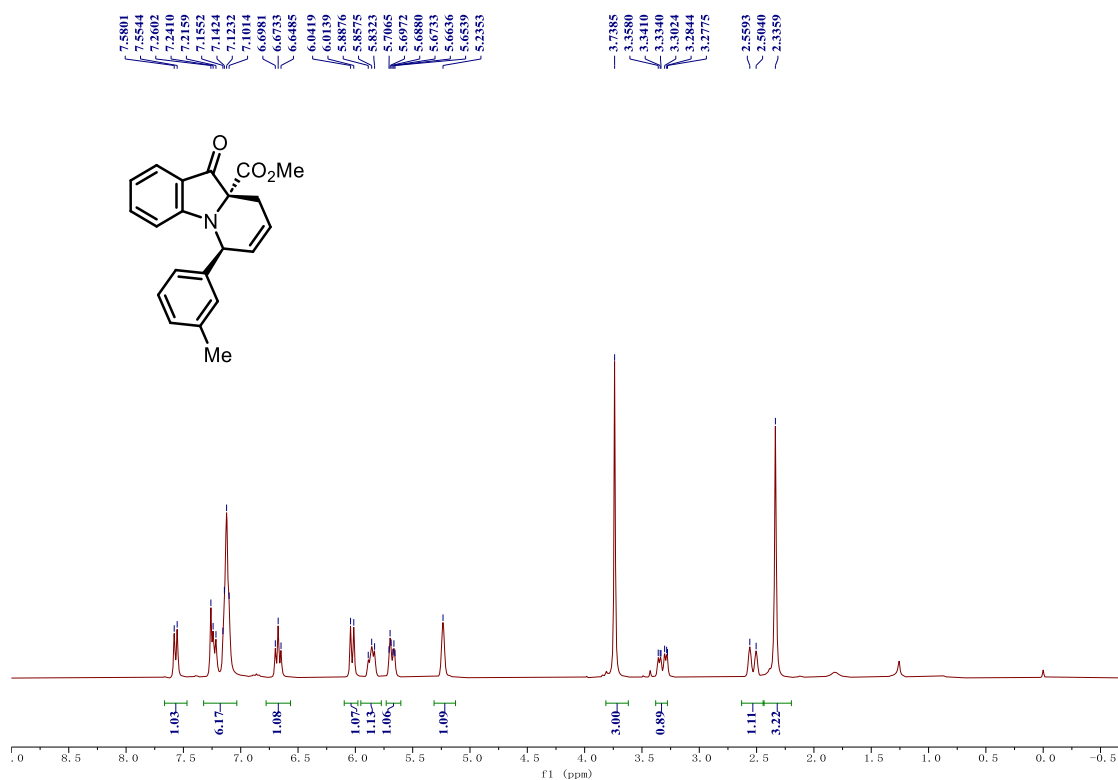
¹H NMR Spectrum of 3ai (300 MHz, CDCl₃)



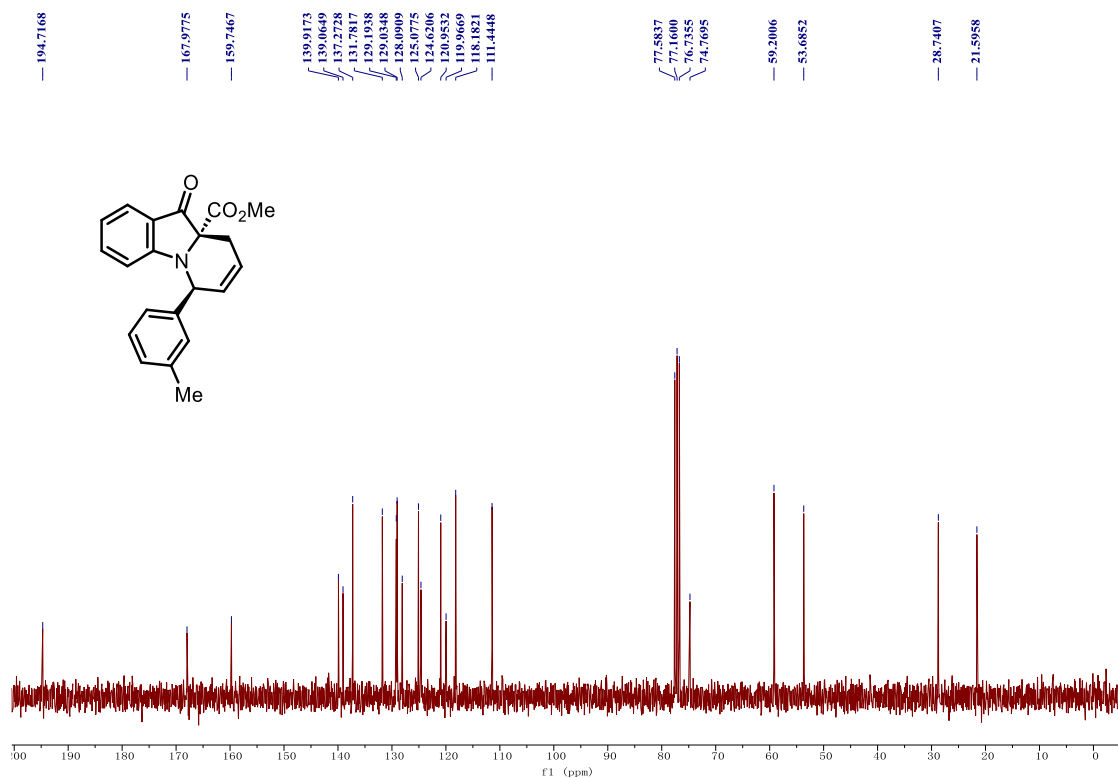
¹³C NMR Spectrum of 3ai (75 MHz, CDCl₃)



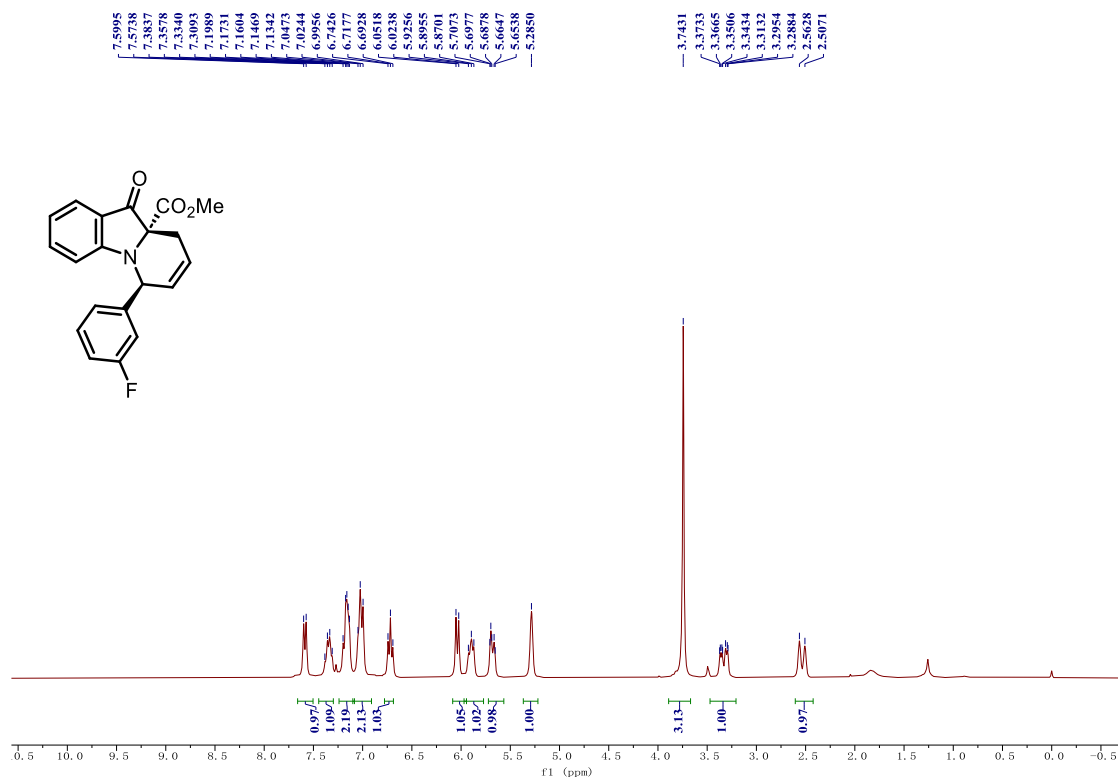
¹H NMR Spectrum of 3aj (300 MHz, CDCl₃)



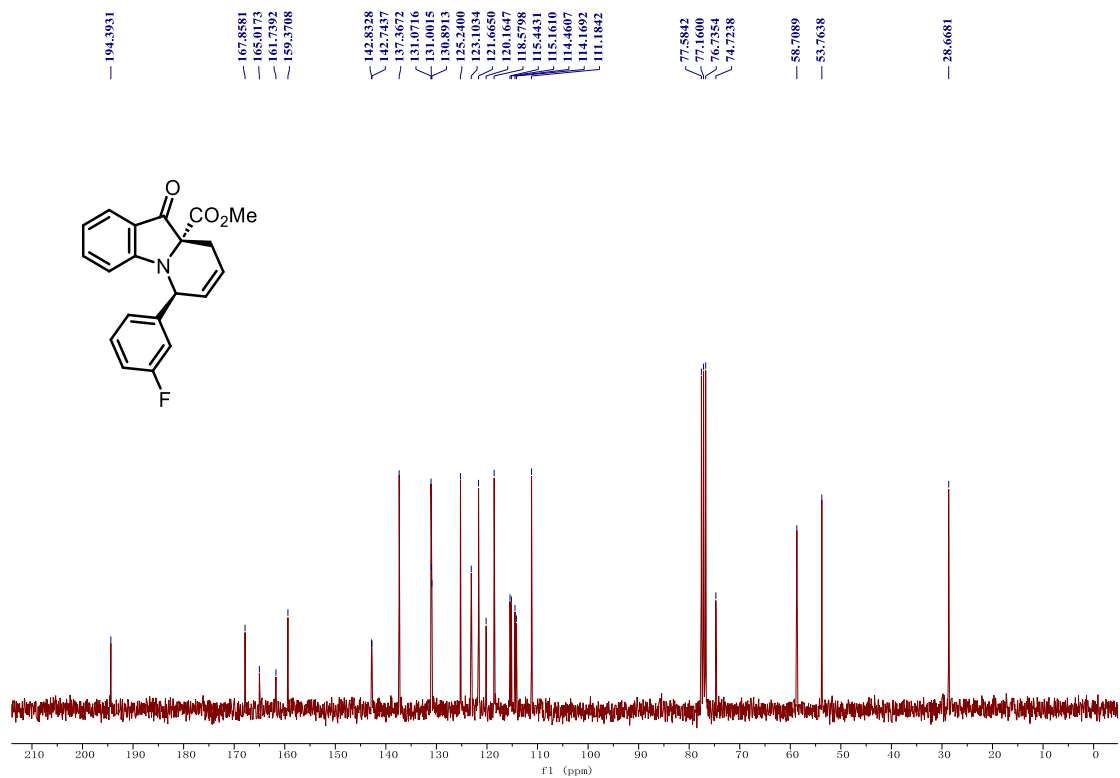
¹³C NMR Spectrum of 3aj (75 MHz, CDCl₃)



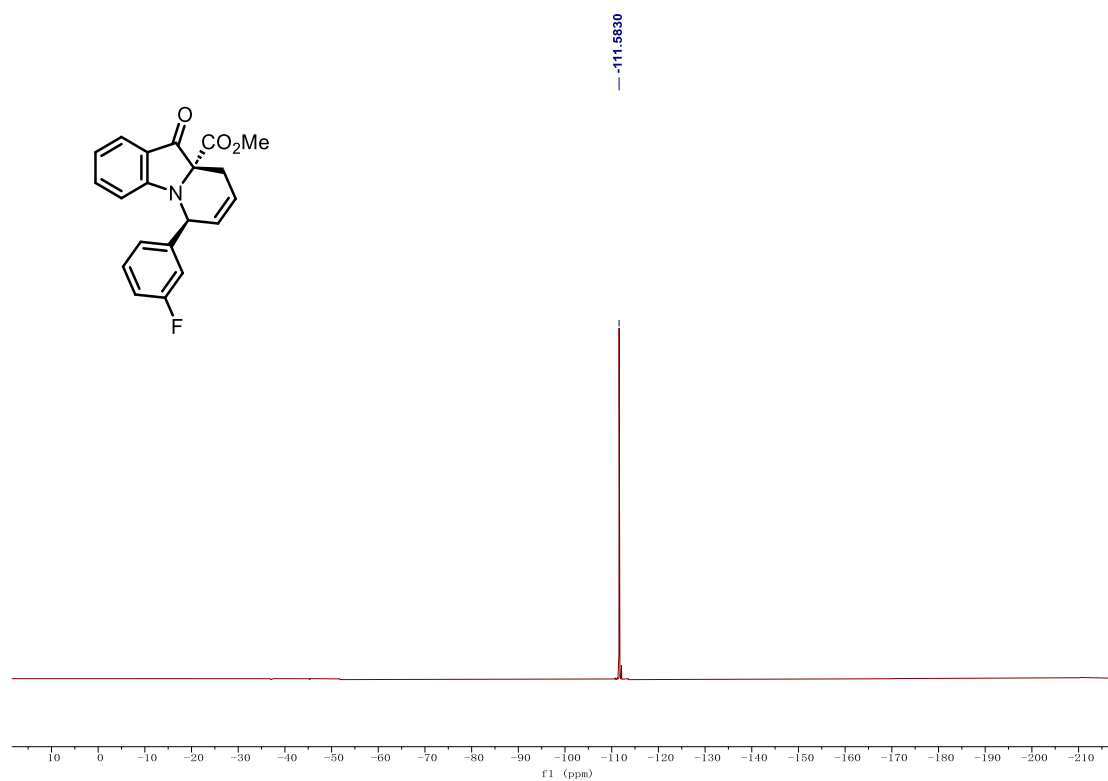
¹H NMR Spectrum of 3ak (300 MHz, CDCl₃)



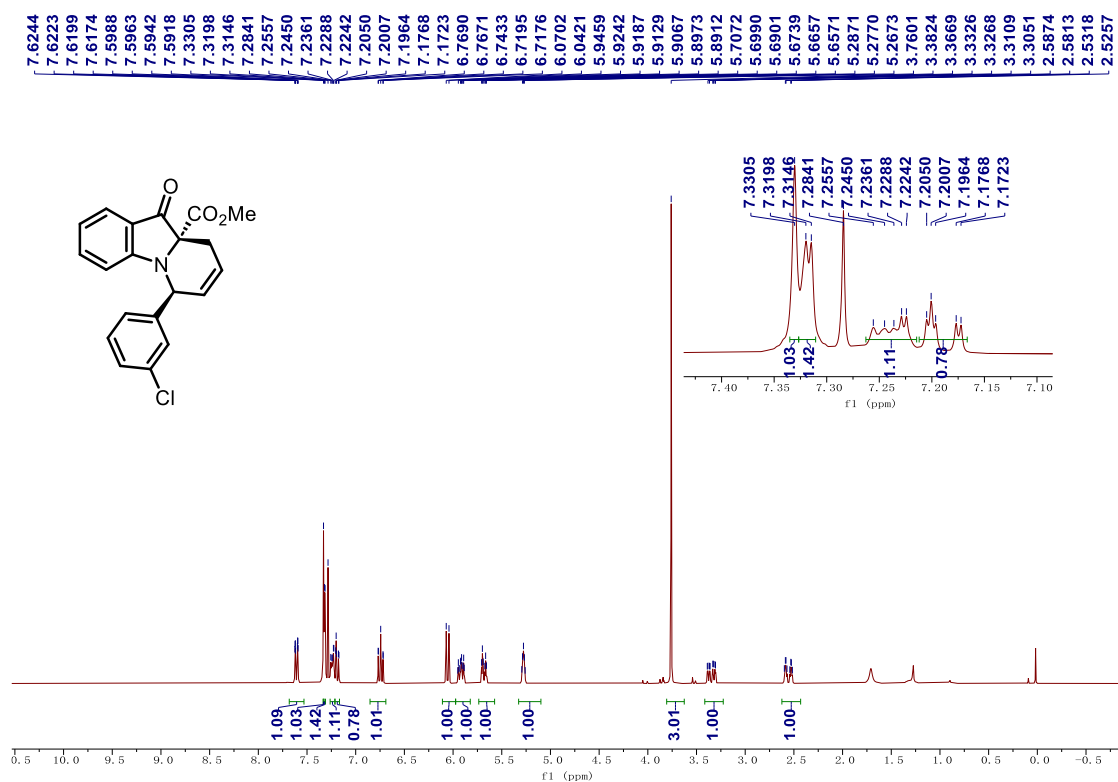
¹³C NMR Spectrum of 3ak (75 MHz, CDCl₃)



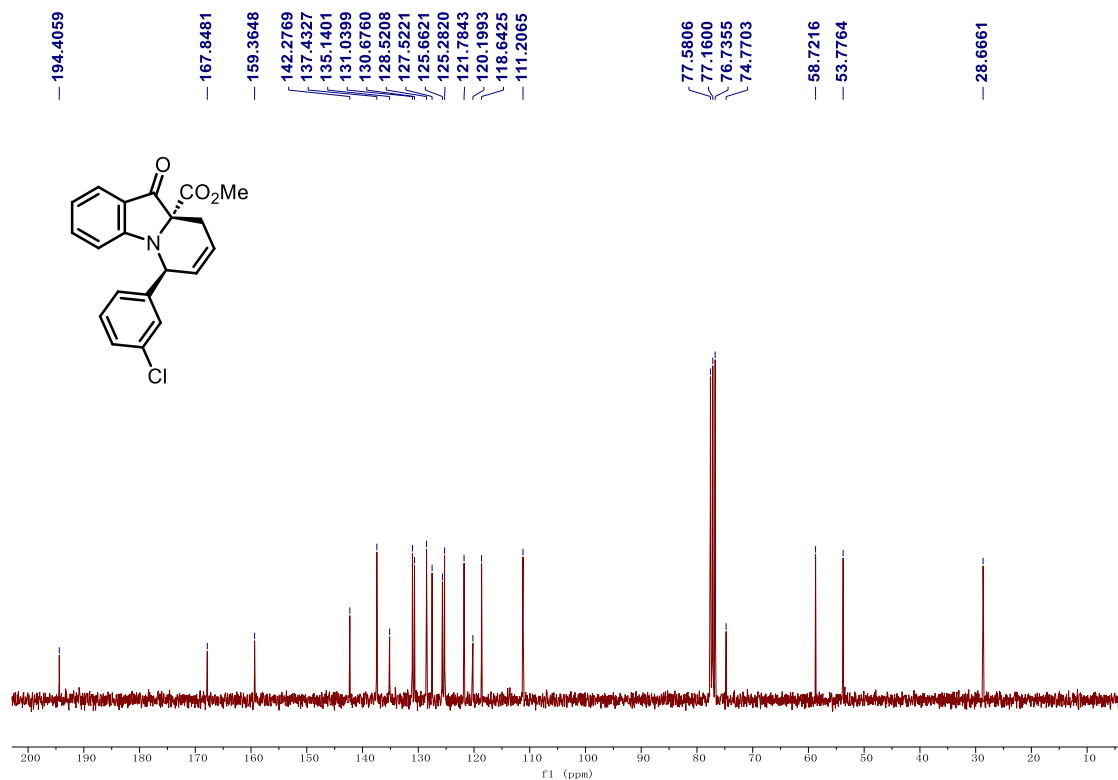
^{19}F NMR Spectrum of 3ak (282 MHz, CDCl_3)



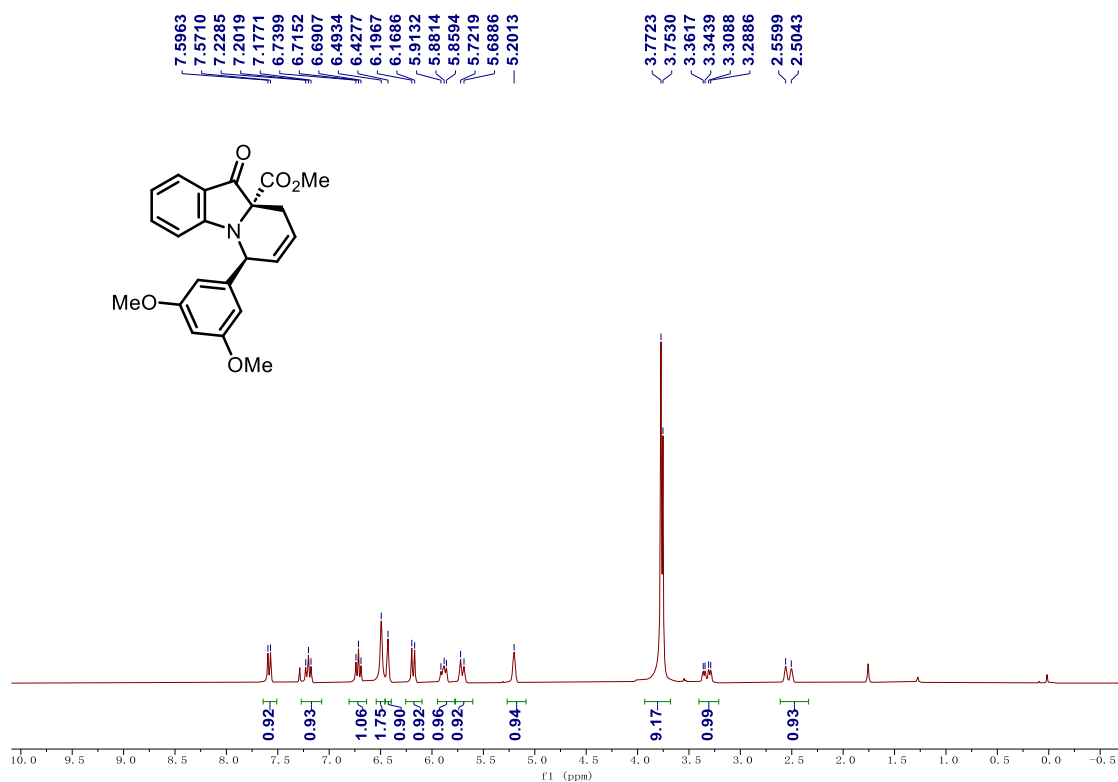
¹H NMR Spectrum of 3al (300 MHz, CDCl₃)



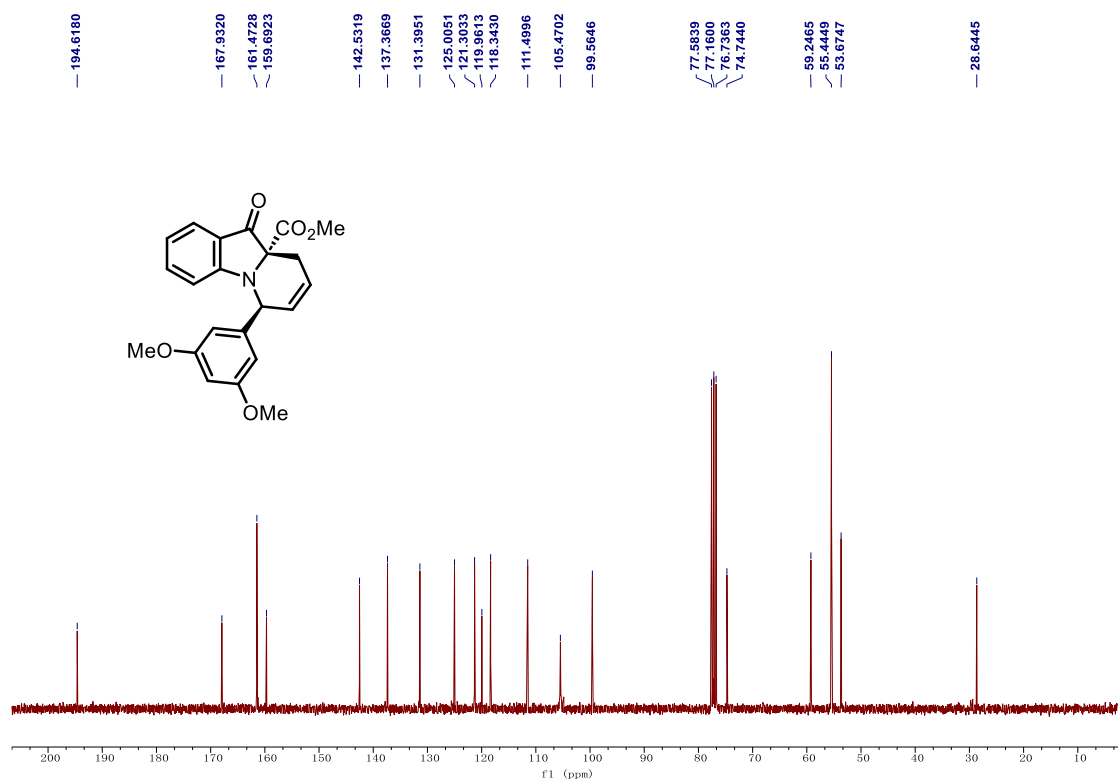
¹³C NMR Spectrum of 3al (75 MHz, CDCl₃)



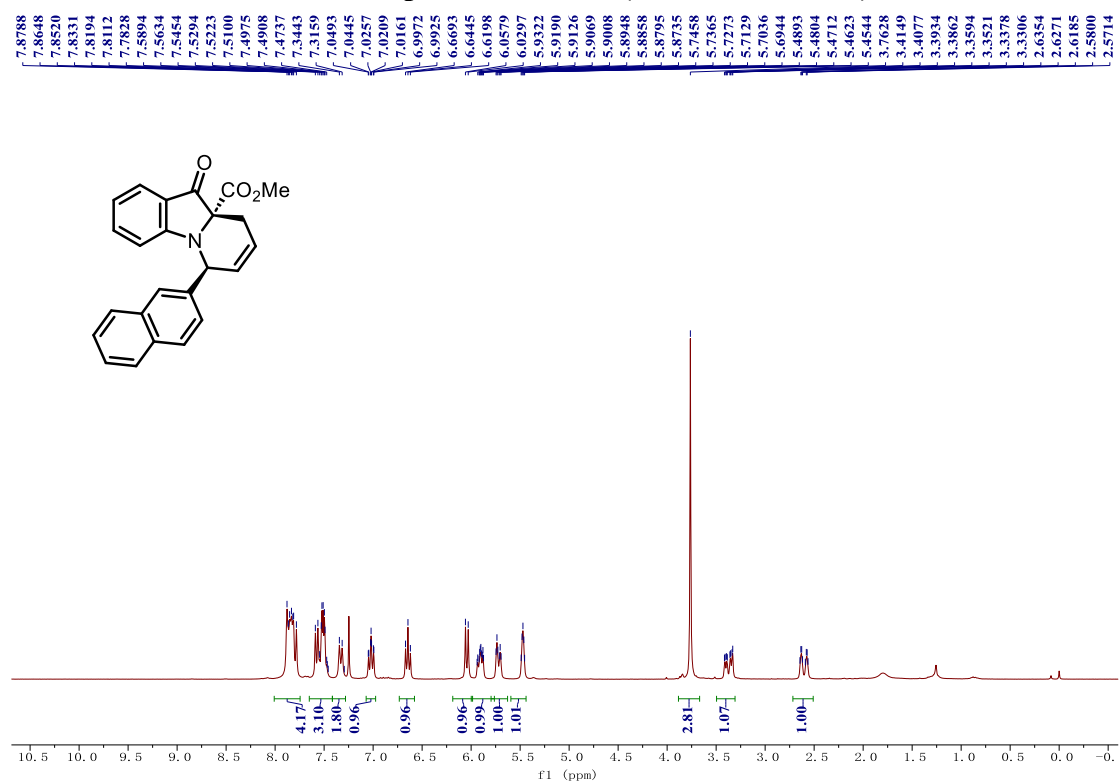
¹H NMR Spectrum of 3am (300 MHz, CDCl₃)



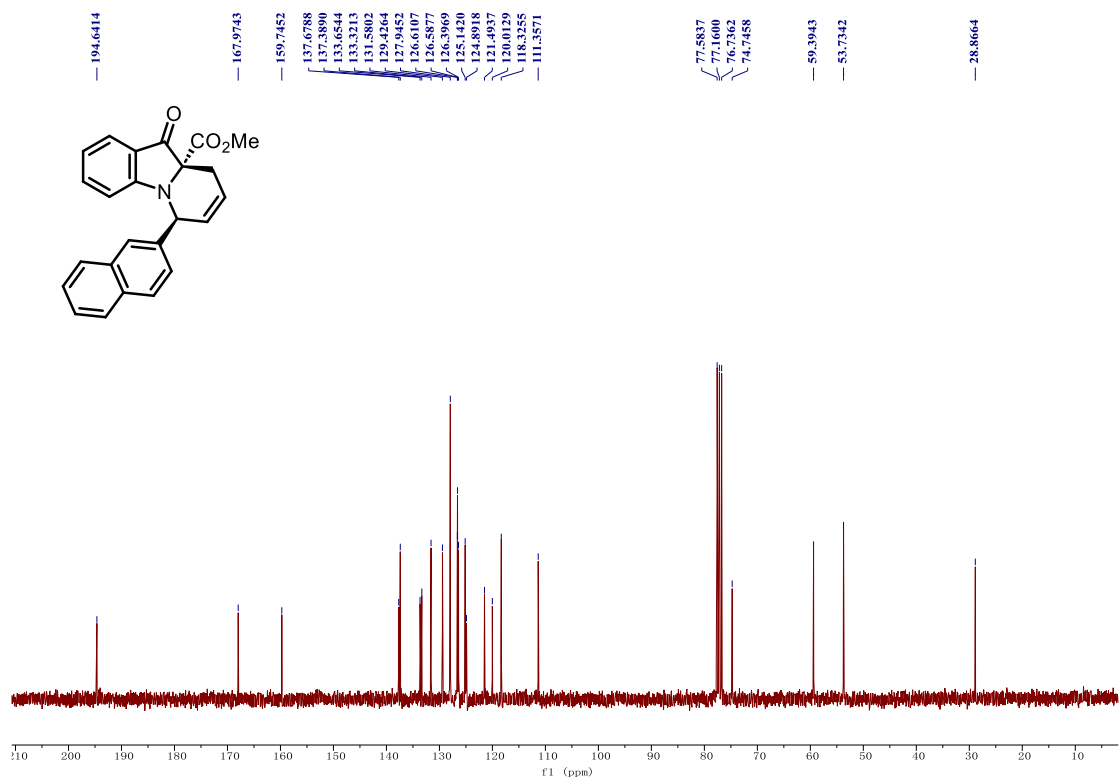
¹³C NMR Spectrum of 3am (75 MHz, CDCl₃)



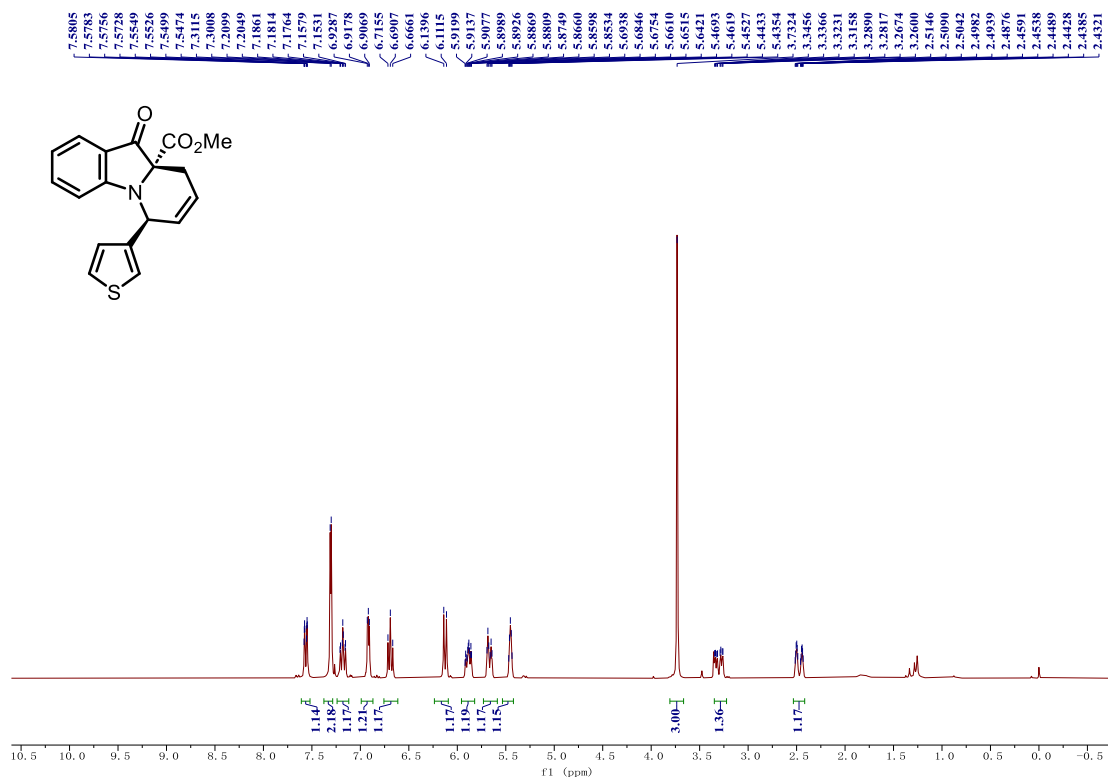
¹H NMR Spectrum of 3an (300 MHz, CDCl₃)



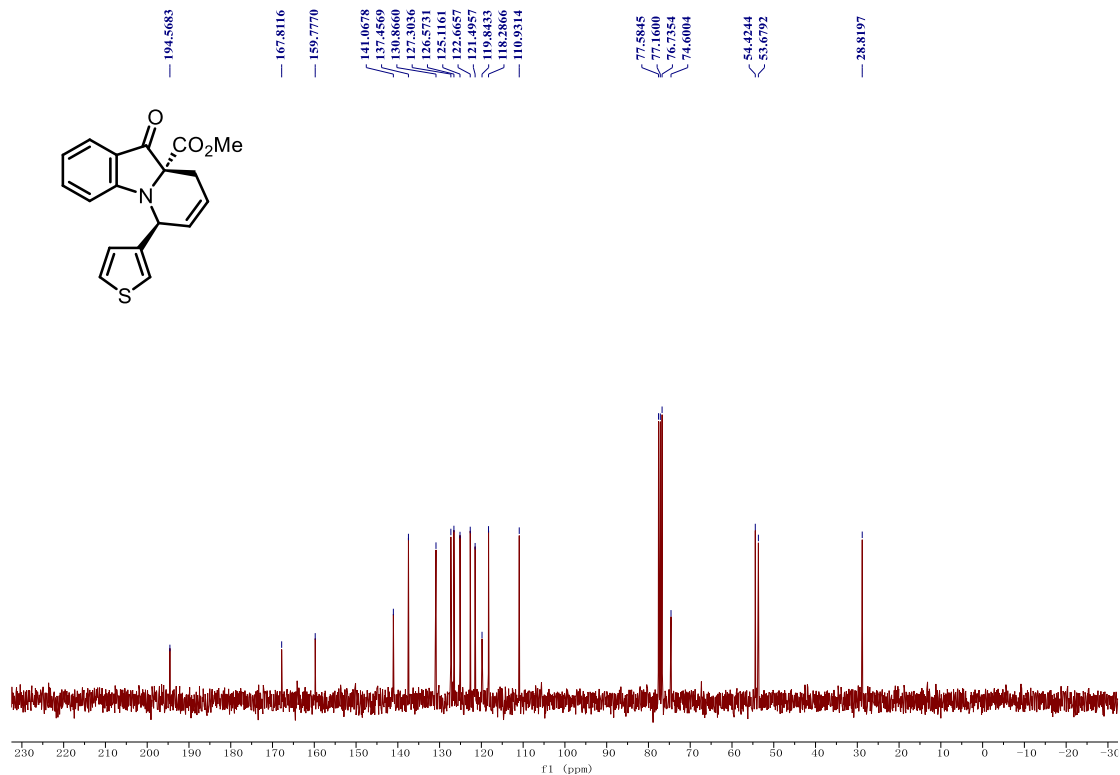
¹³C NMR Spectrum of 3an (75 MHz, CDCl₃)



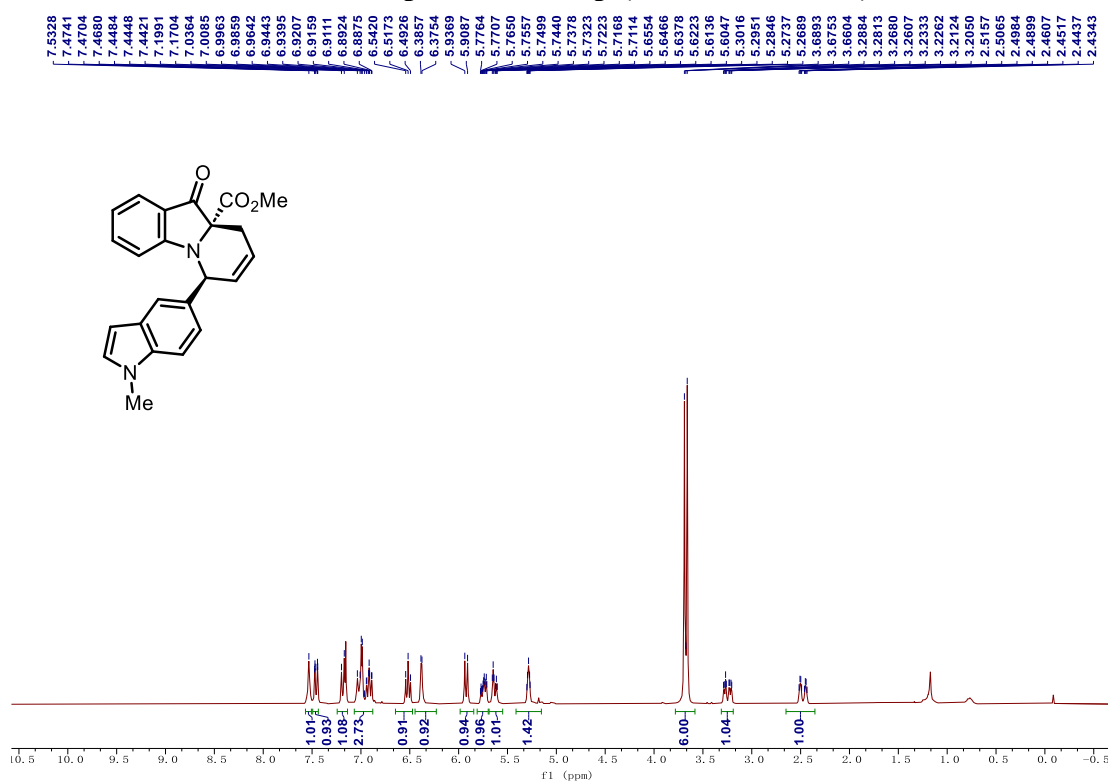
¹H NMR Spectrum of 3ao (300 MHz, CDCl₃)



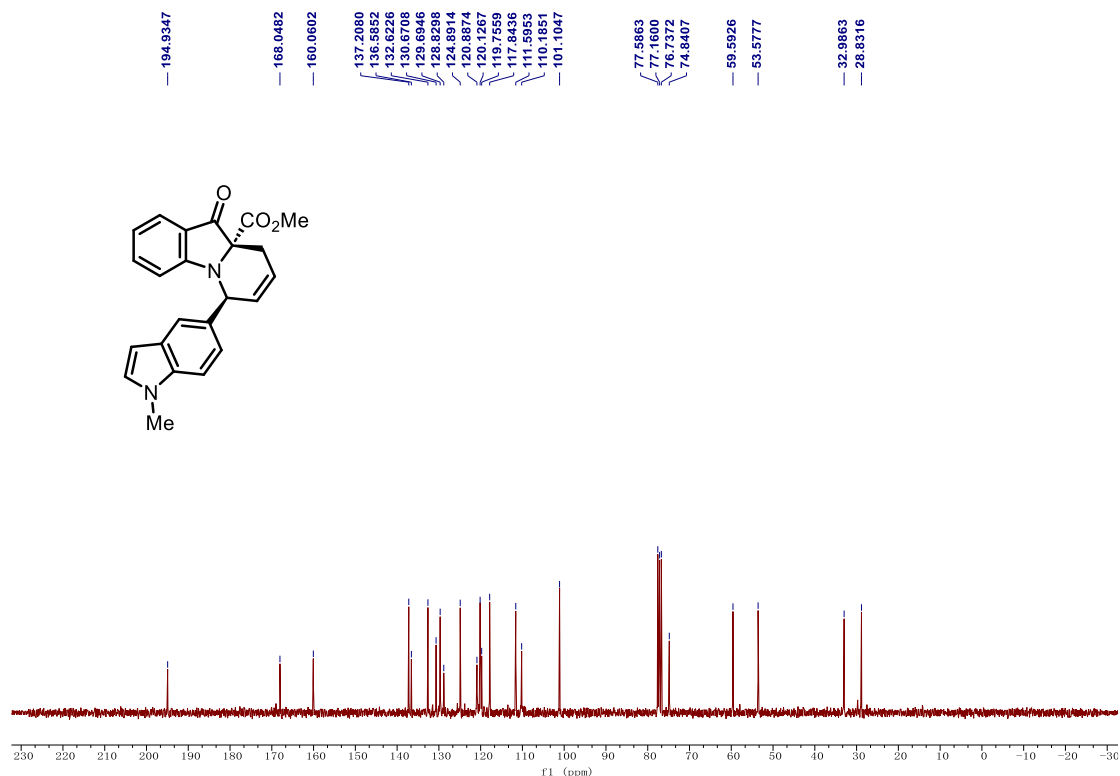
¹³C NMR Spectrum of 3ao (75 MHz, CDCl₃)



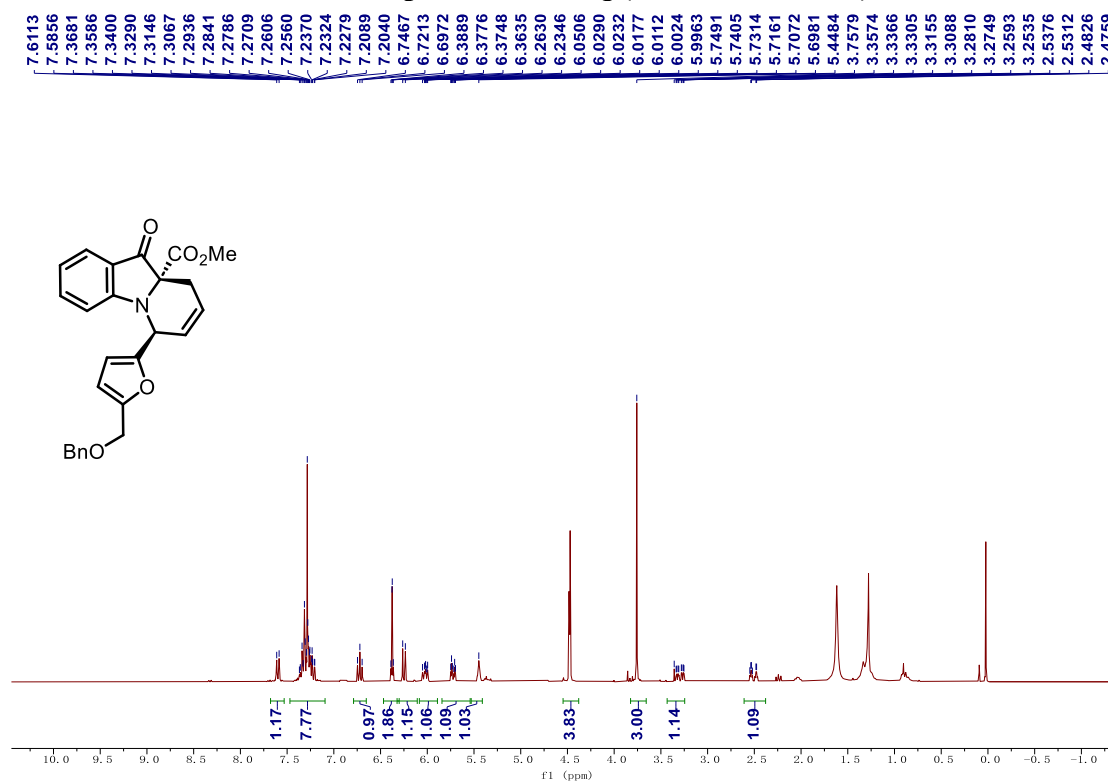
¹H NMR Spectrum of 3ap (300 MHz, CDCl₃)



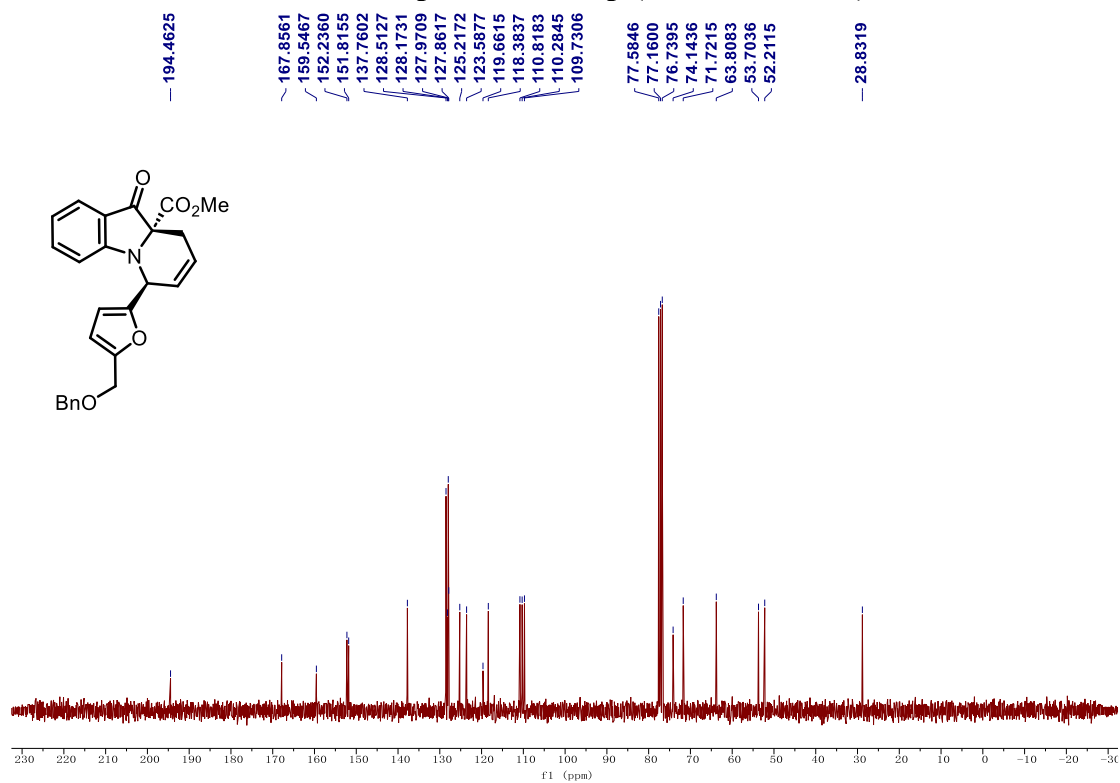
¹³C NMR Spectrum of 3ap (75 MHz, CDCl₃)



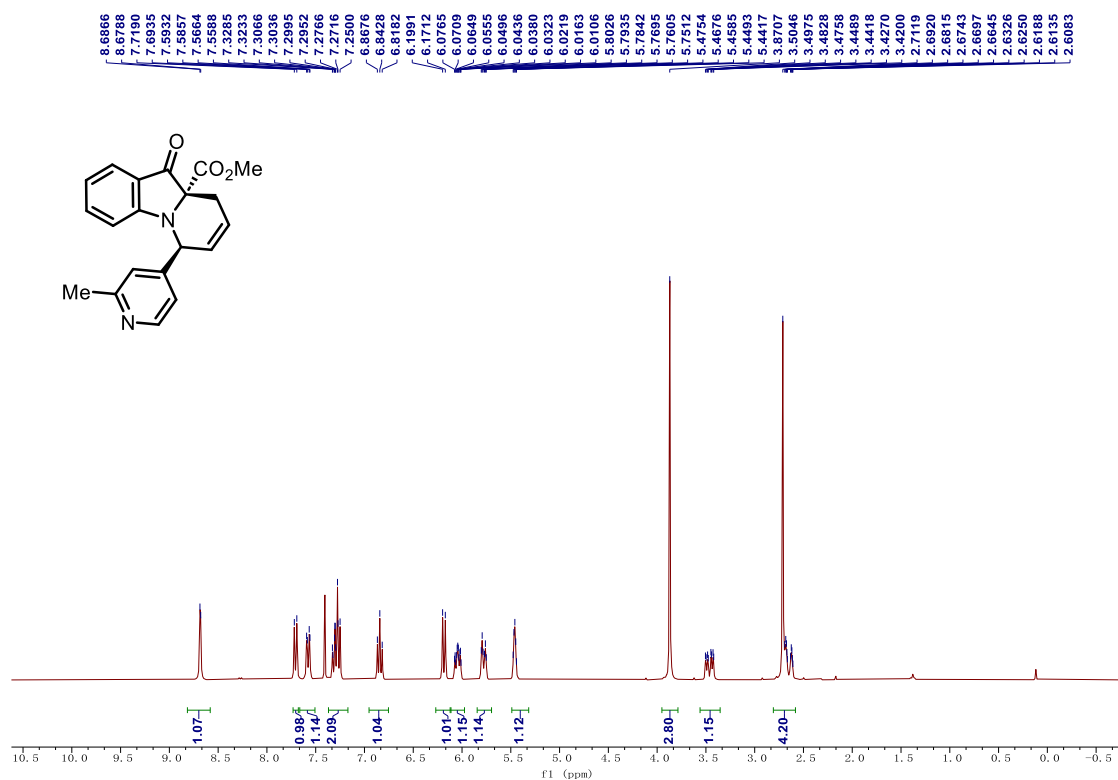
¹H NMR Spectrum of 3aq (300 MHz, CDCl₃)



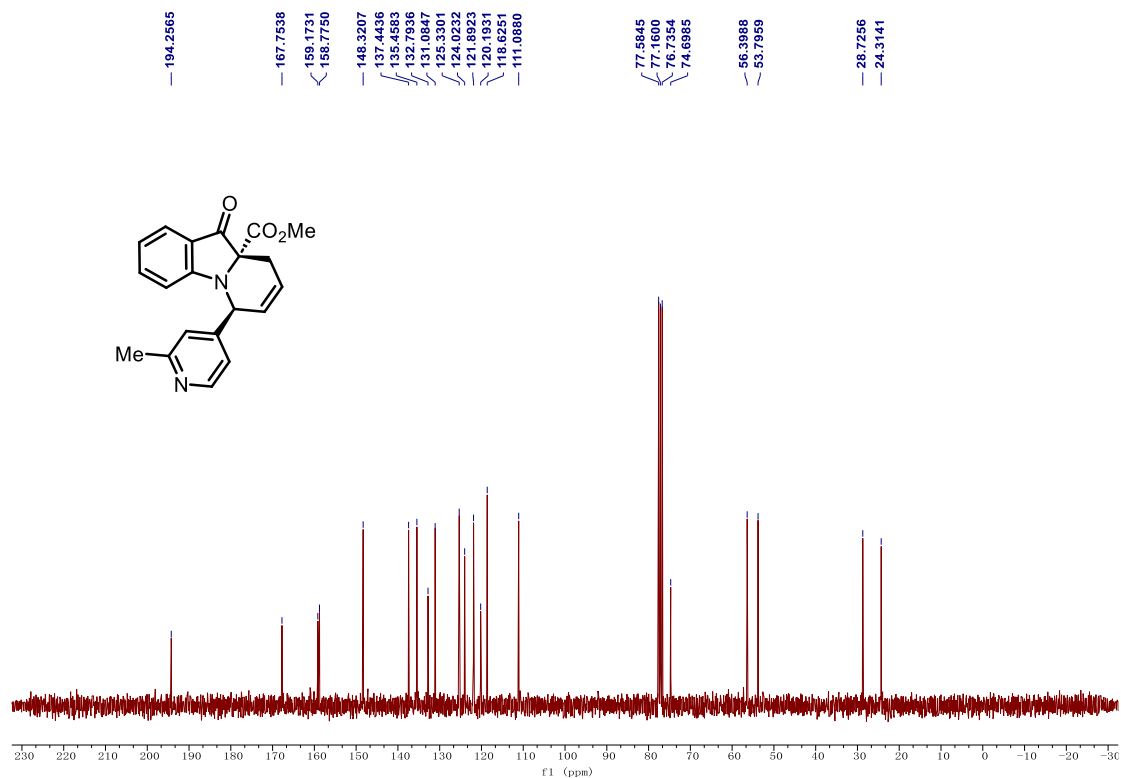
¹³C NMR Spectrum of 3ap (75 MHz, CDCl₃)



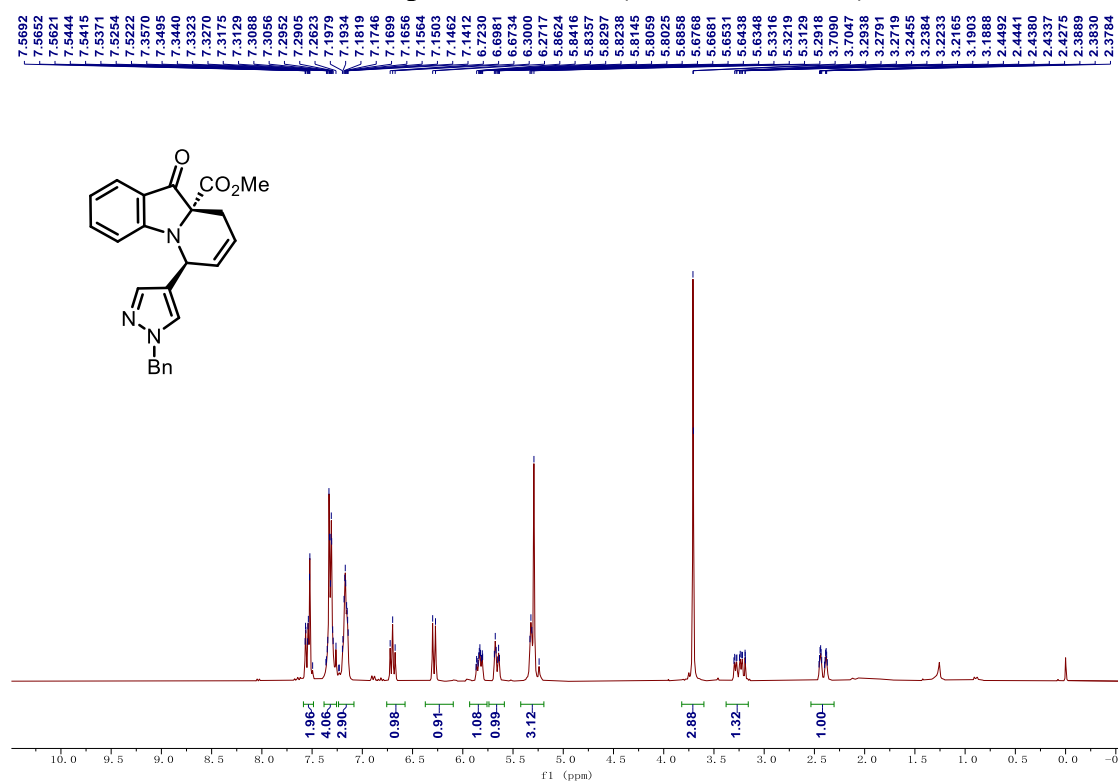
¹H NMR Spectrum of 3ar (300 MHz, CDCl₃)



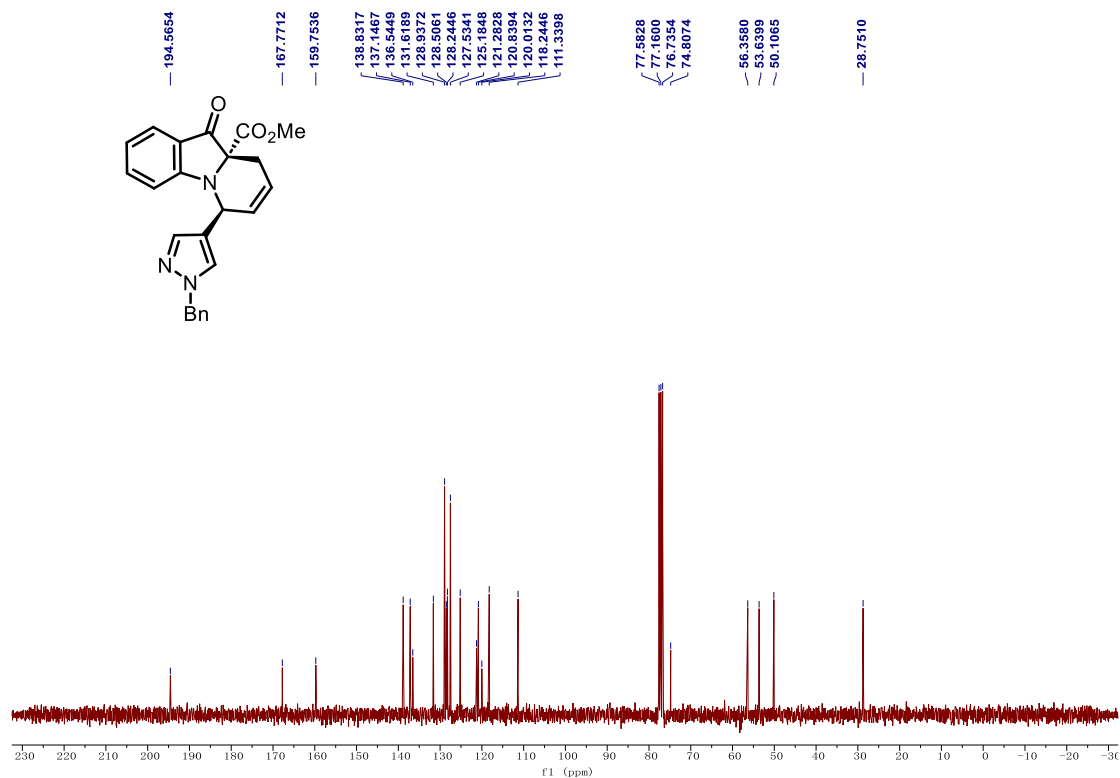
¹³C NMR Spectrum of 3ar (75 MHz, CDCl₃)



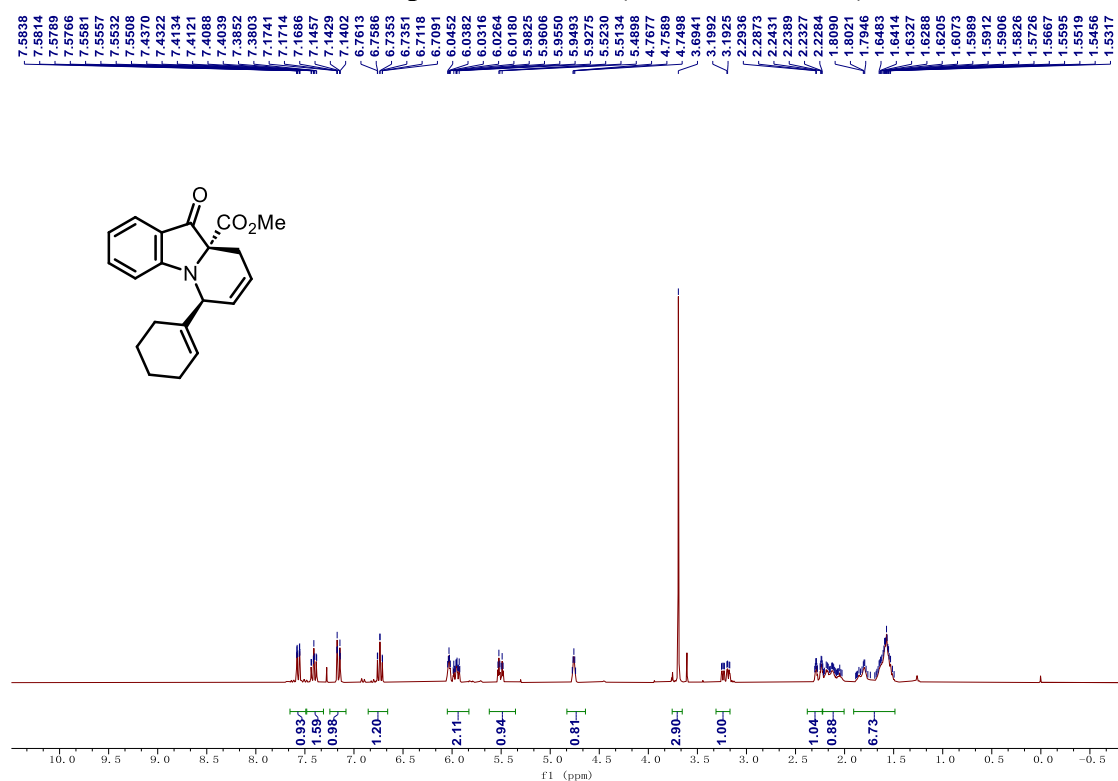
¹H NMR Spectrum of 3as (300 MHz, CDCl₃)



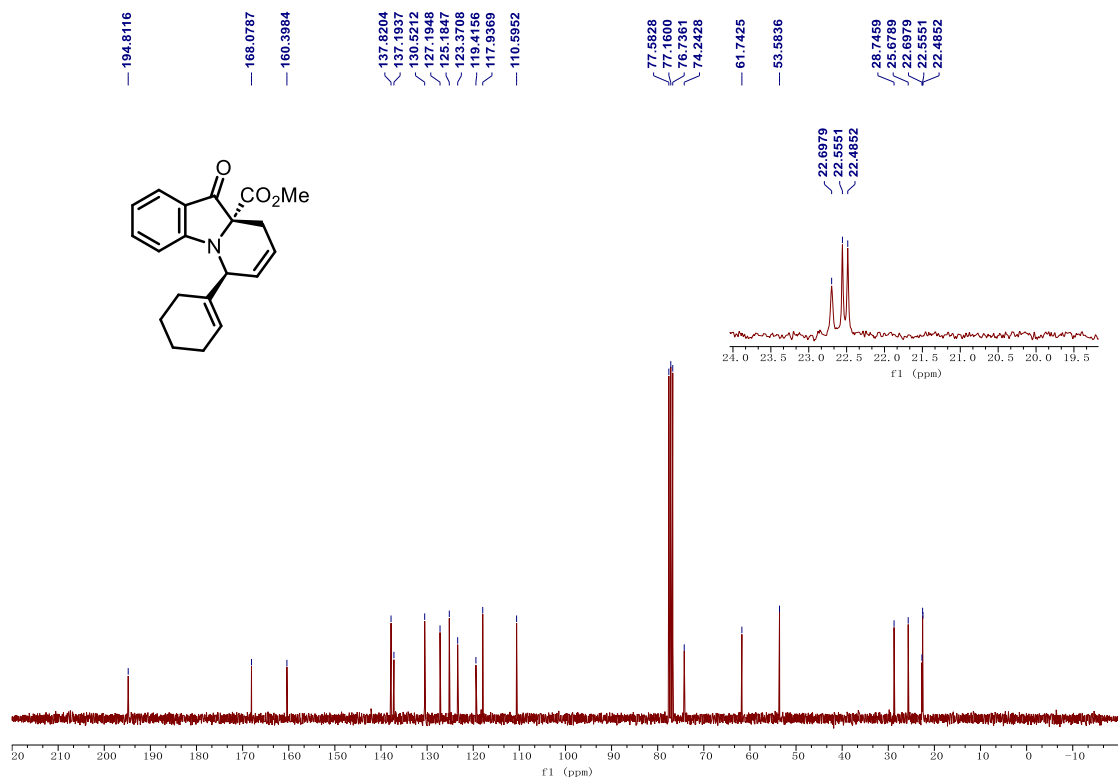
¹³C NMR Spectrum of 3as (75 MHz, CDCl₃)



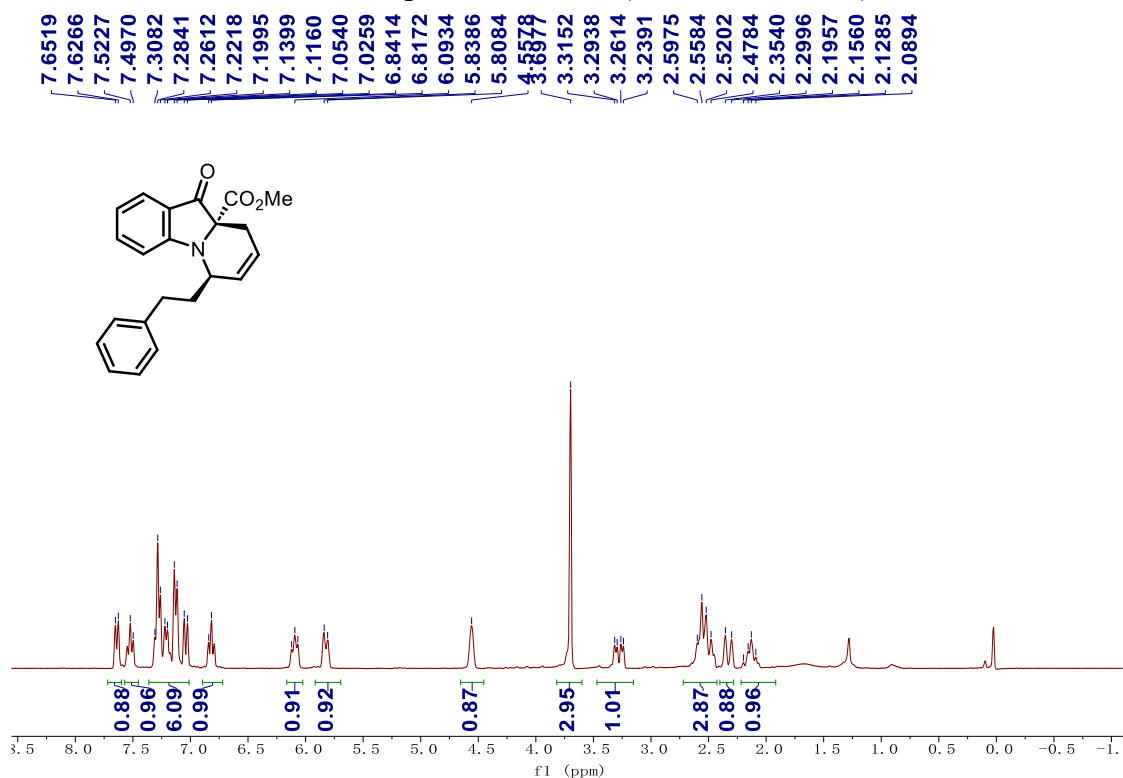
¹H NMR Spectrum of 3at (300 MHz, CDCl₃)



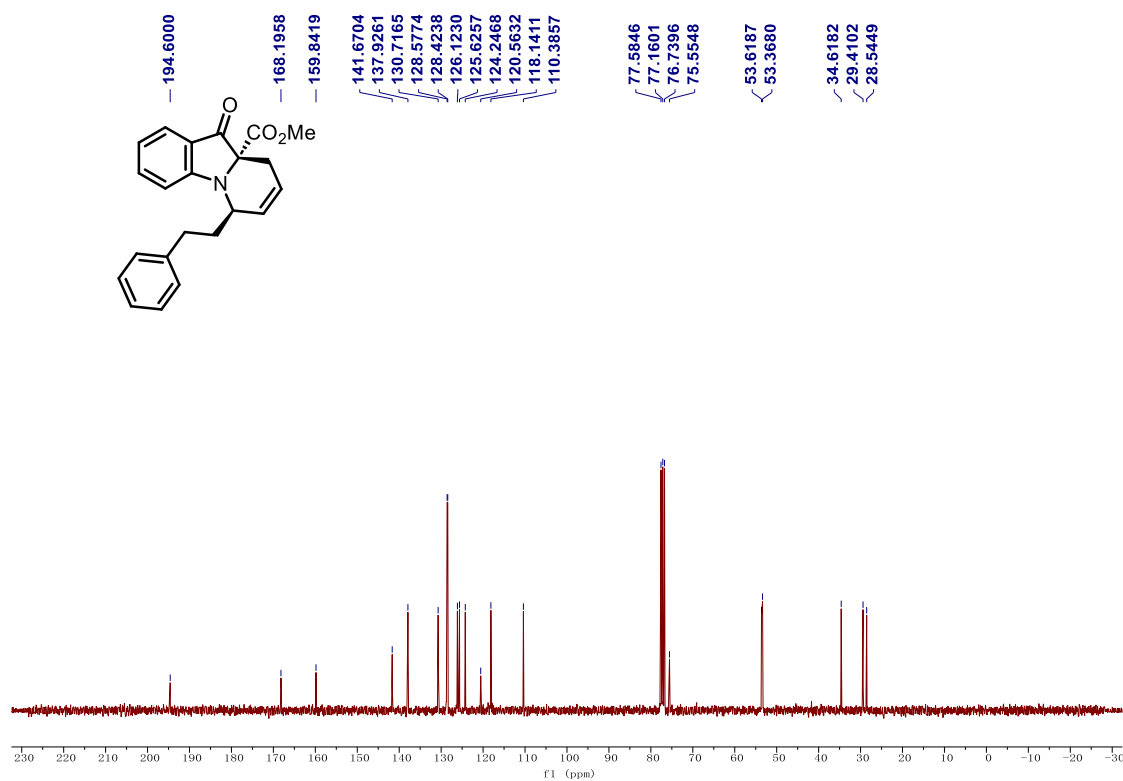
¹³C NMR Spectrum of 3at (75 MHz, CDCl₃)



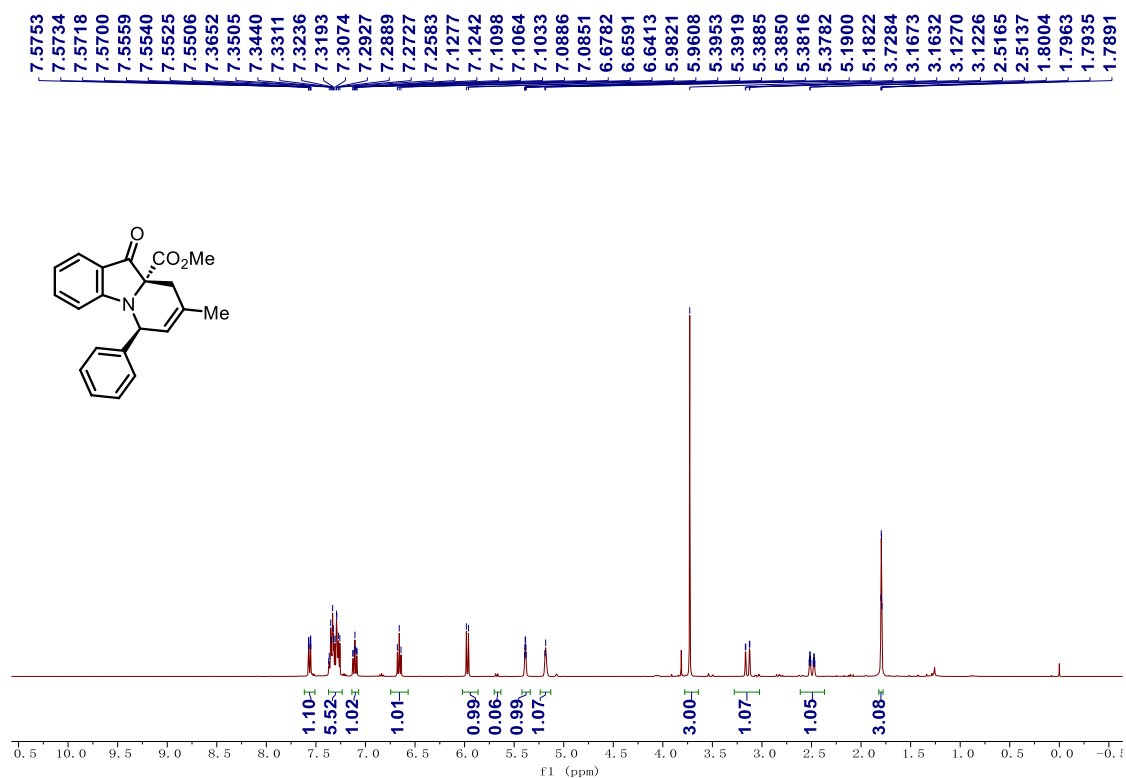
¹H NMR Spectrum of 3au (300 MHz, CDCl₃)



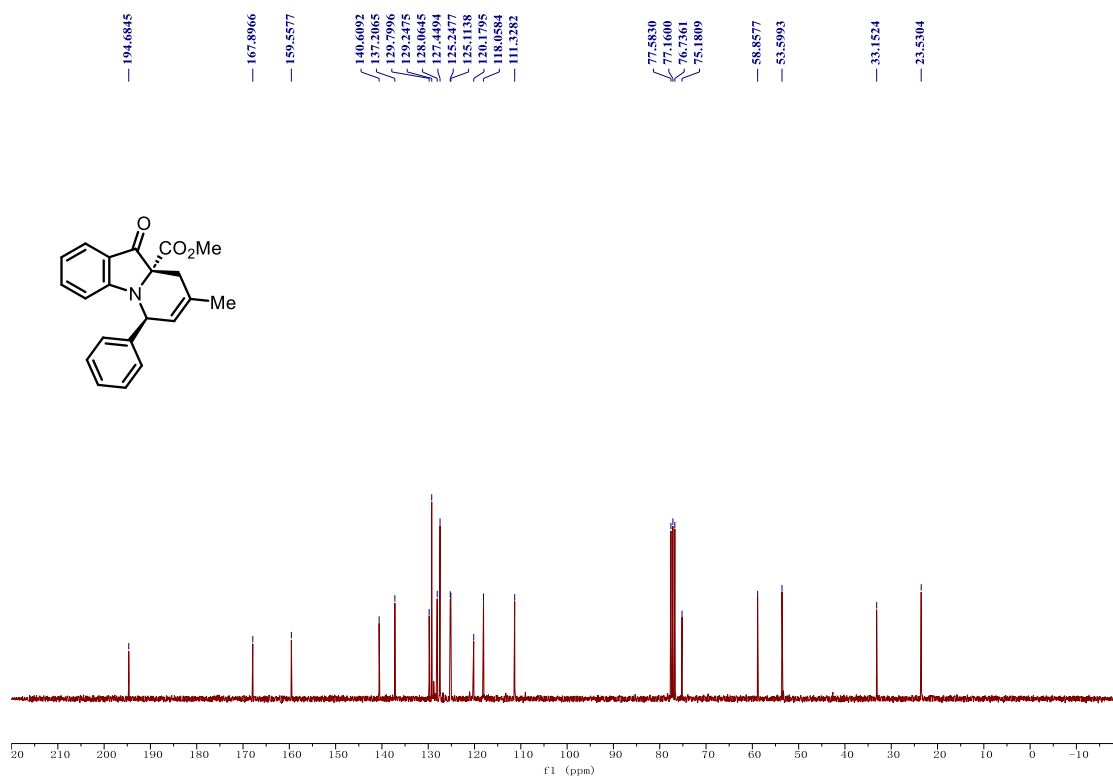
¹³C NMR Spectrum of 3au (75 MHz, CDCl₃)

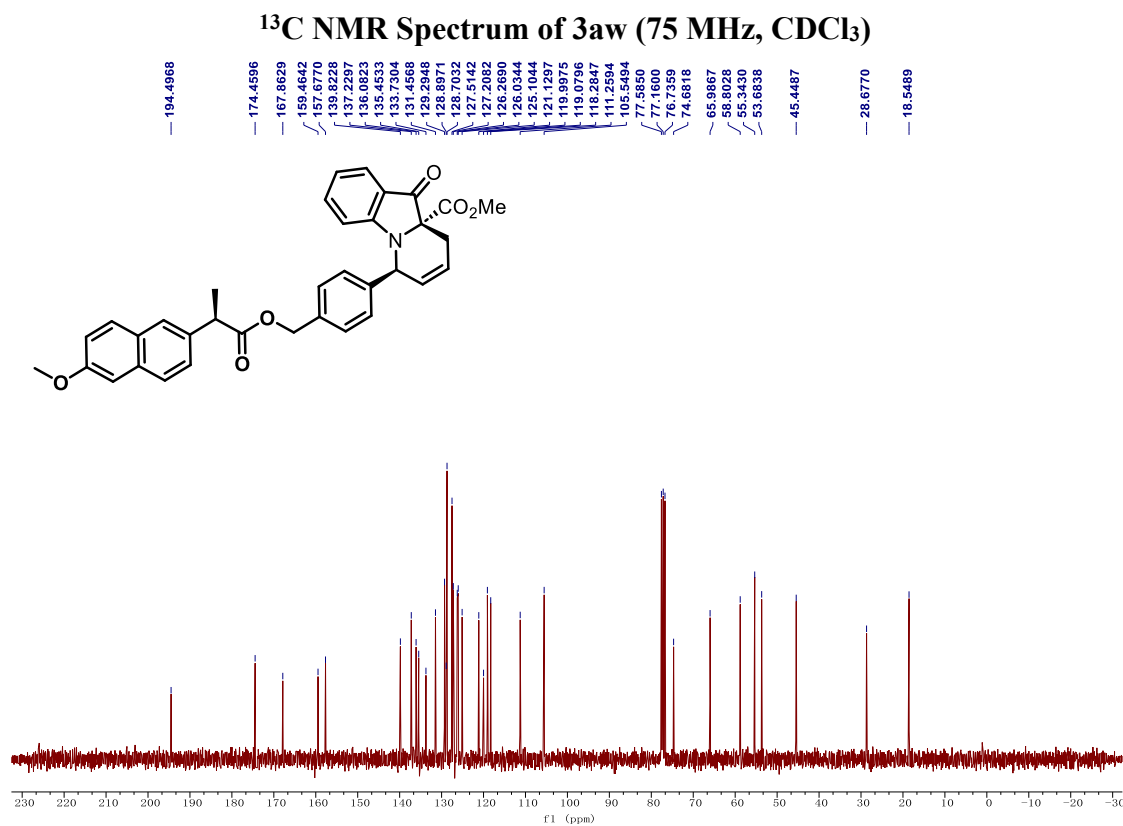
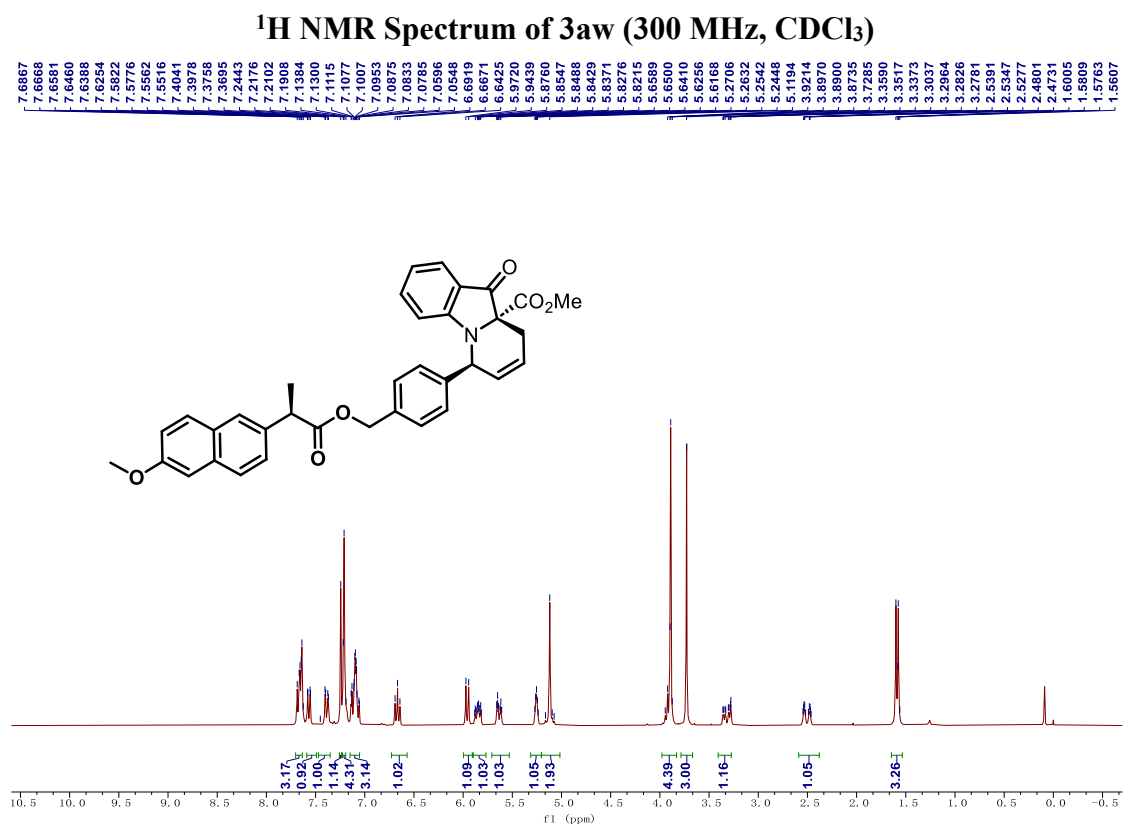


¹H NMR Spectrum of 3av (300 MHz, CDCl₃)



¹³C NMR Spectrum of 3av (75 MHz, CDCl₃)





Chemical structure of compound 10: COC(=O)[C@H]1Cc2ccccc2N1Cc3ccc(COC[C@@H]4O[C@H](C5C(C)(C)OC5)[C@H](OC6C(C)(C)OC6)[C@H]4O)cc3

¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift (δ) in ppm, ranging from 0 to 10. The spectrum shows several peaks, with integrations provided below the baseline and a list of chemical shifts (δ) on the right.

Chemical shifts (δ) (ppm): 7.6276, 7.6253, 7.6239, 7.6219, 7.5972, 7.4090, 7.3825, 7.3667, 7.3244, 7.2104, 7.2056, 7.1865, 7.1819, 7.1773, 7.1584, 7.1536, 6.7503, 6.7255, 6.7005, 6.0831, 6.0550, 5.9164, 5.9104, 5.9045, 5.8831, 5.7450, 5.7361, 5.7270, 5.7029, 5.6846, 5.5981, 5.5349, 5.3257, 5.3168, 4.7058, 4.6789, 4.6707, 4.6653, 4.6525, 4.6445, 4.6343, 4.5936, 4.3872, 4.3791, 4.3702, 4.3623, 4.3462, 4.3398, 4.3197, 4.3133, 4.1076, 4.1015, 4.0851, 4.0790, 4.0662, 4.0589, 3.7983, 3.7705, 3.7554, 3.7554, 3.7364, 3.7298, 3.7074, 3.6962, 3.3545, 3.3476, 2.6054, 2.5971, 2.5501, 2.5417, 1.5944, 1.4914, 1.3912, 1.3852.

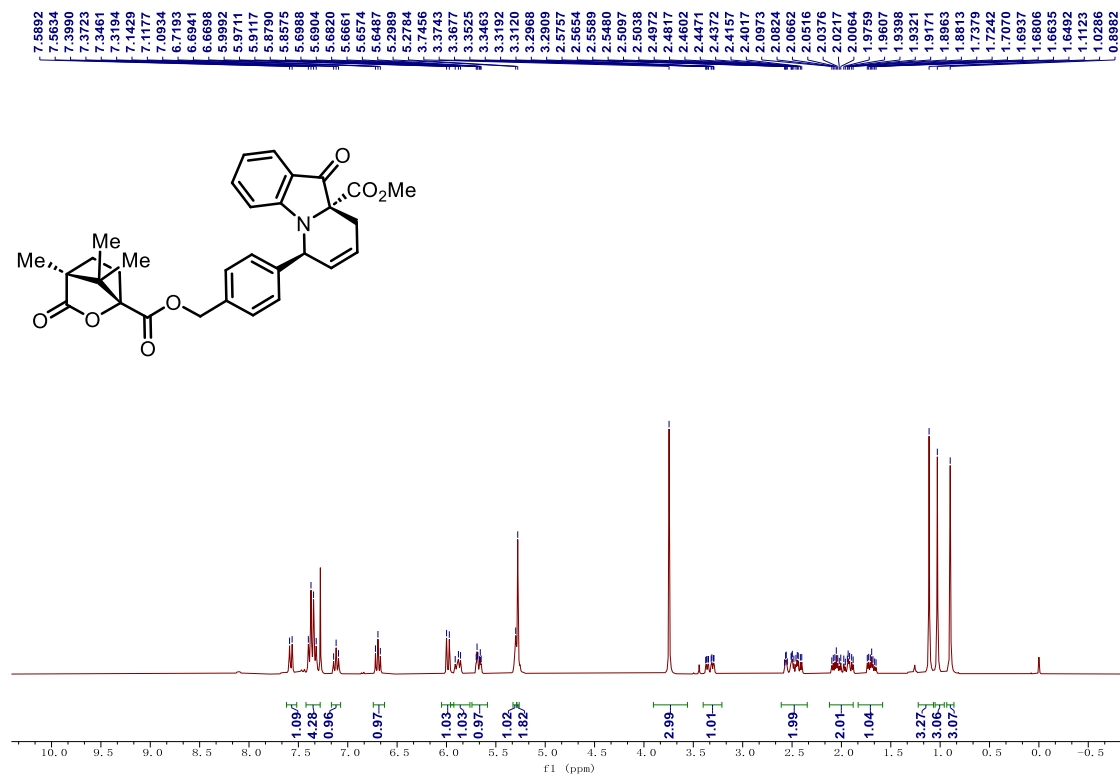
Integrations (from left to right): 0.98, 5.03, 0.98, 0.95, 1.06, 1.04, 1.15, 1.02, 3.12, 2.25, 1.12, 4.96, 1.00, 1.01, 3.21, 3.21, 6.81.

Chemical structure of the compound is shown above the spectrum. The structure is a complex molecule featuring a central benzene ring substituted with a *1,3-dimethyl-5-((methyl 1-oxo-2,3-dihydro-1H-indolizin-5-yl)methoxy)methyl* group and a *1,3-dimethyl-5-((methyl 1-oxo-2,3-dihydro-1H-indolizin-5-yl)methoxy)methyl* group.

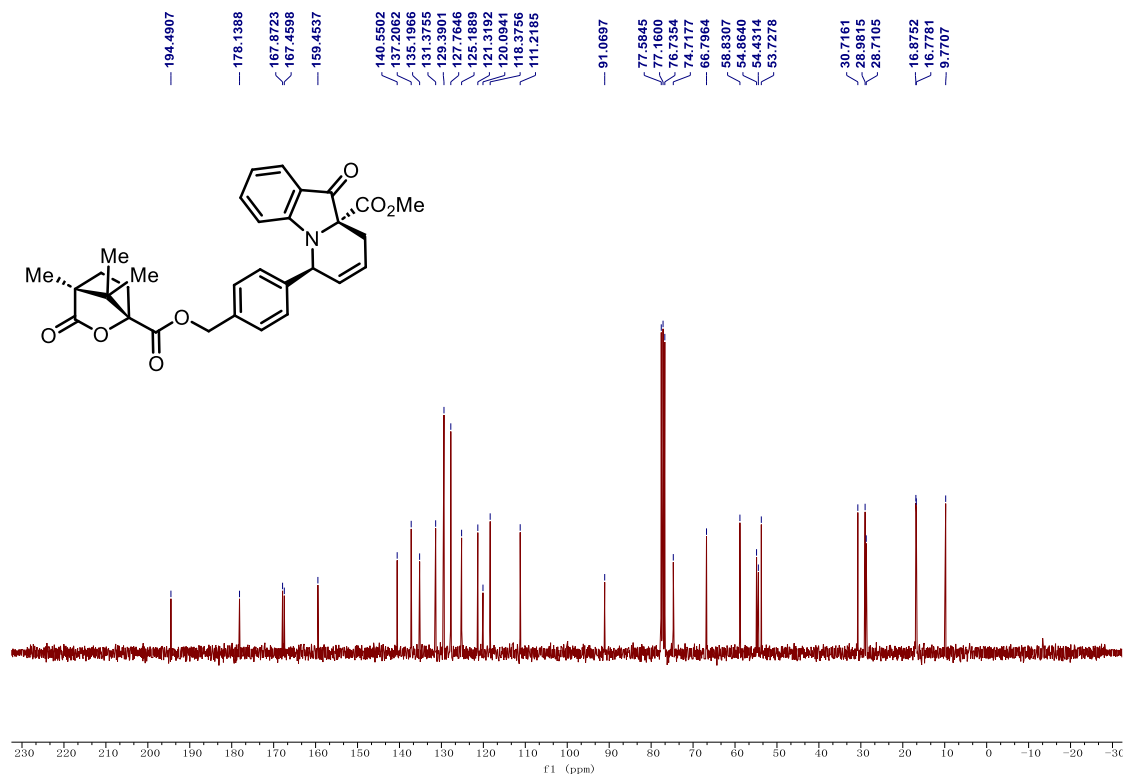
The ¹³C NMR spectrum (CDCl₃) shows the following chemical shifts (ppm):

Chemical Shift (ppm)
194.6121
167.9276
159.5931
139.2321
138.5042
137.3012
131.6707
128.3127
127.4382
125.0797
120.9877
119.9536
118.2139
111.4126
109.3193
108.6401
96.4314
77.5846
77.1600
76.7354
74.7171
72.9345
71.2658
70.6985
70.5824
69.1770
66.9623
58.9236
53.6712
28.7268
26.1685
26.0524
25.0049
24.5255

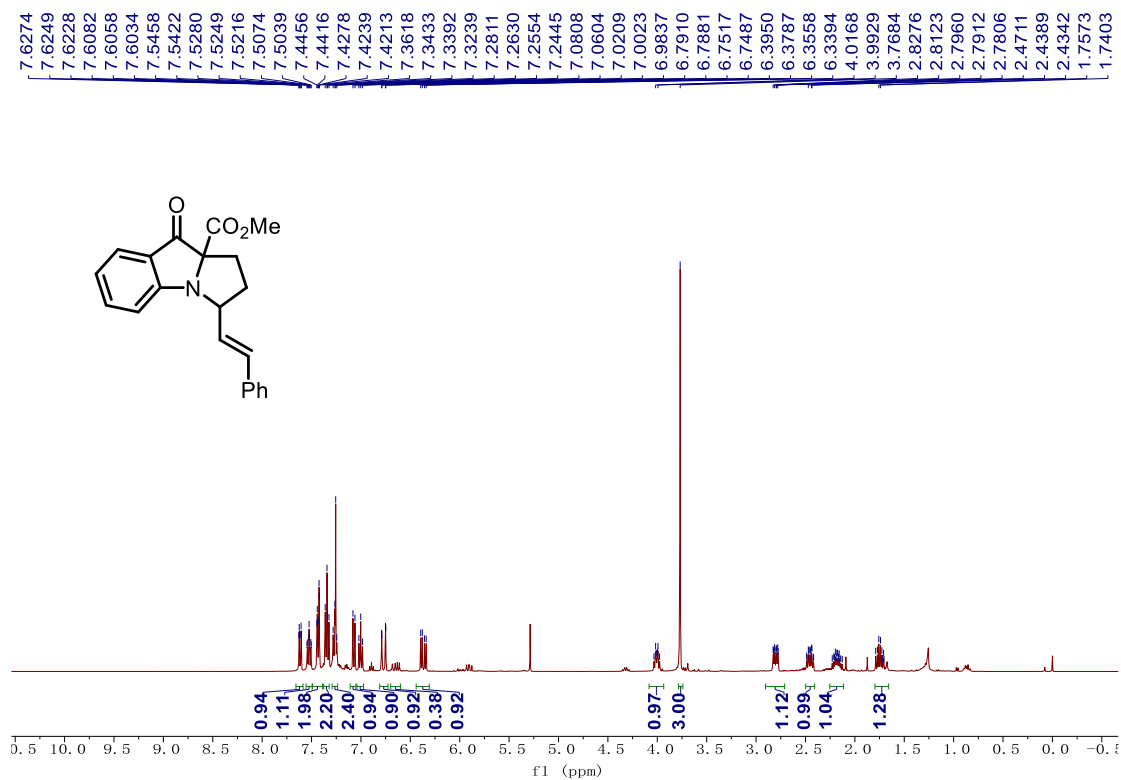
¹H NMR Spectrum of 3ay (300 MHz, CDCl₃)



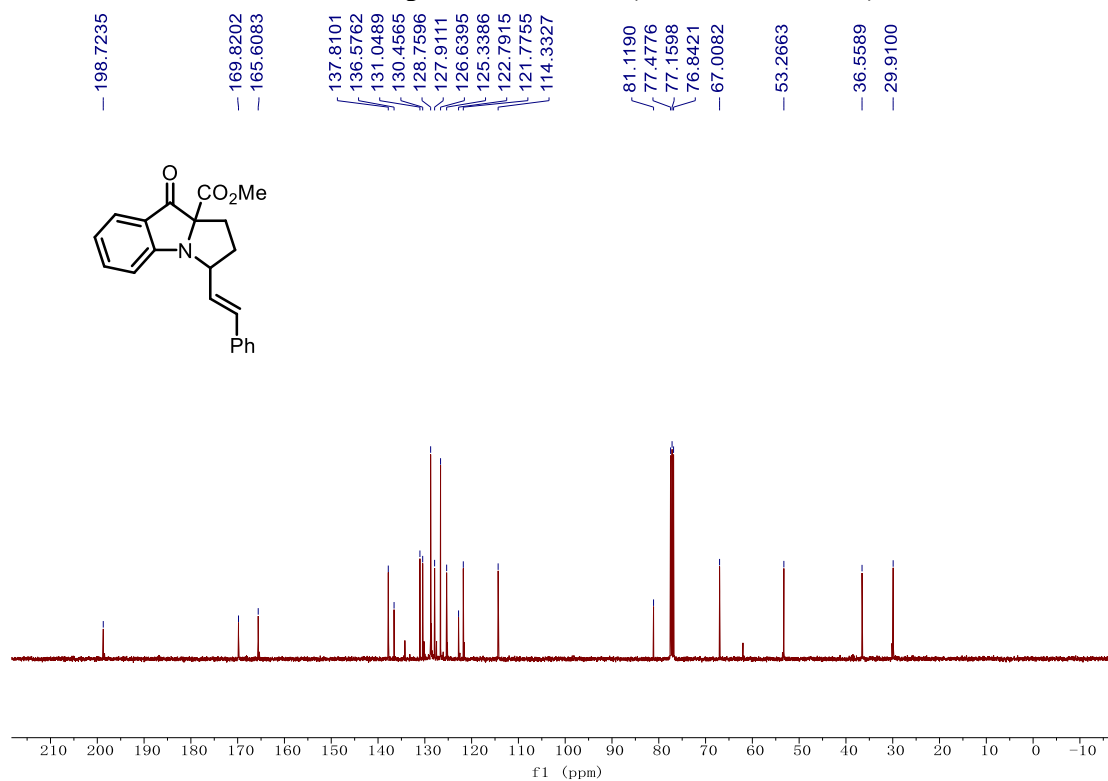
¹³C NMR Spectrum of 3ay (75 MHz, CDCl₃)



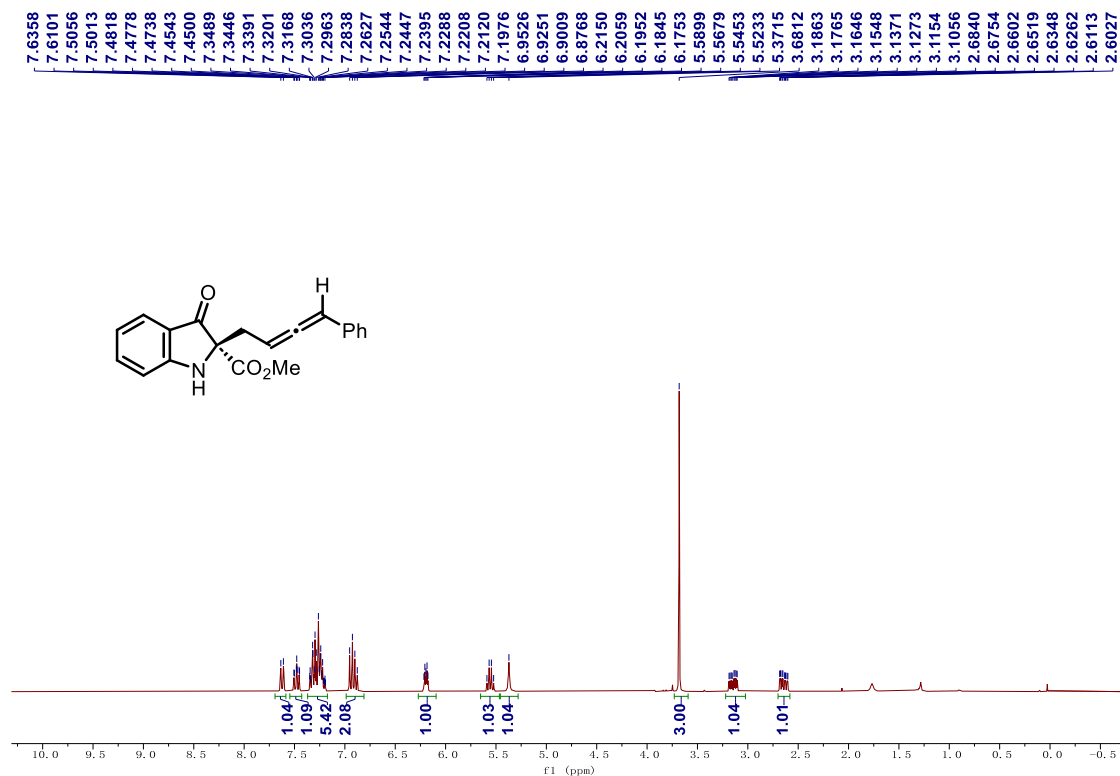
¹H NMR Spectrum of 3az' (400 MHz, CDCl₃)



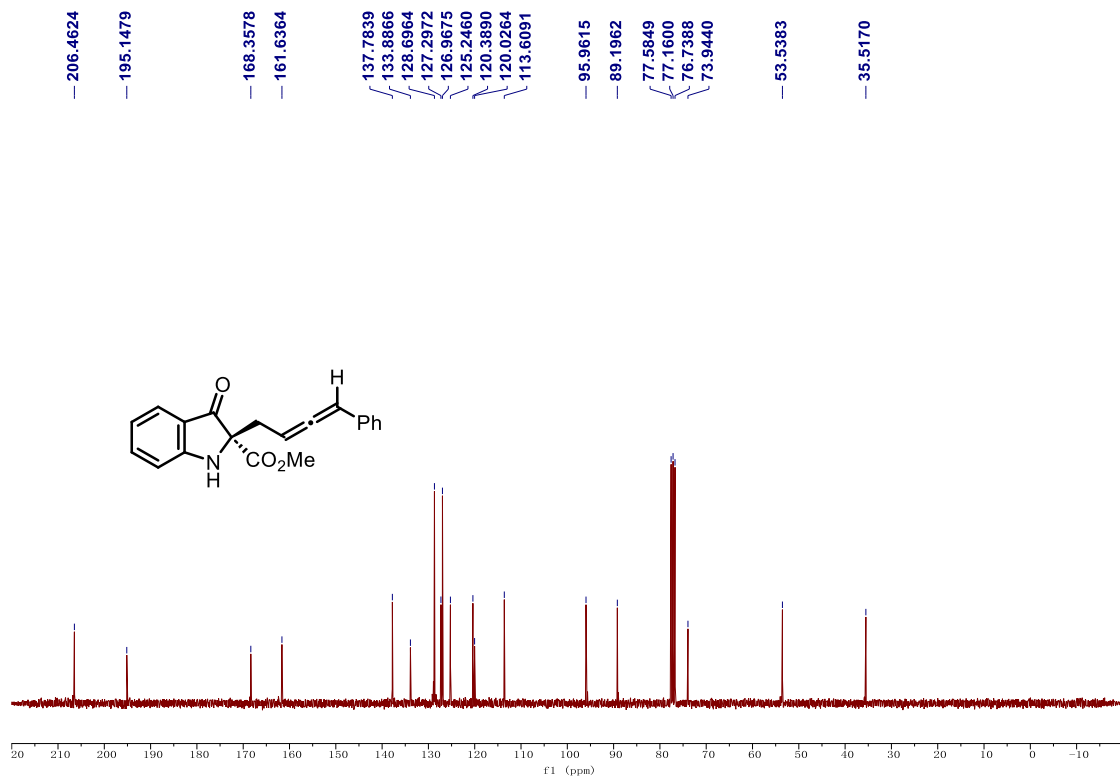
¹³C NMR Spectrum of 3az' (101 MHz, CDCl₃)



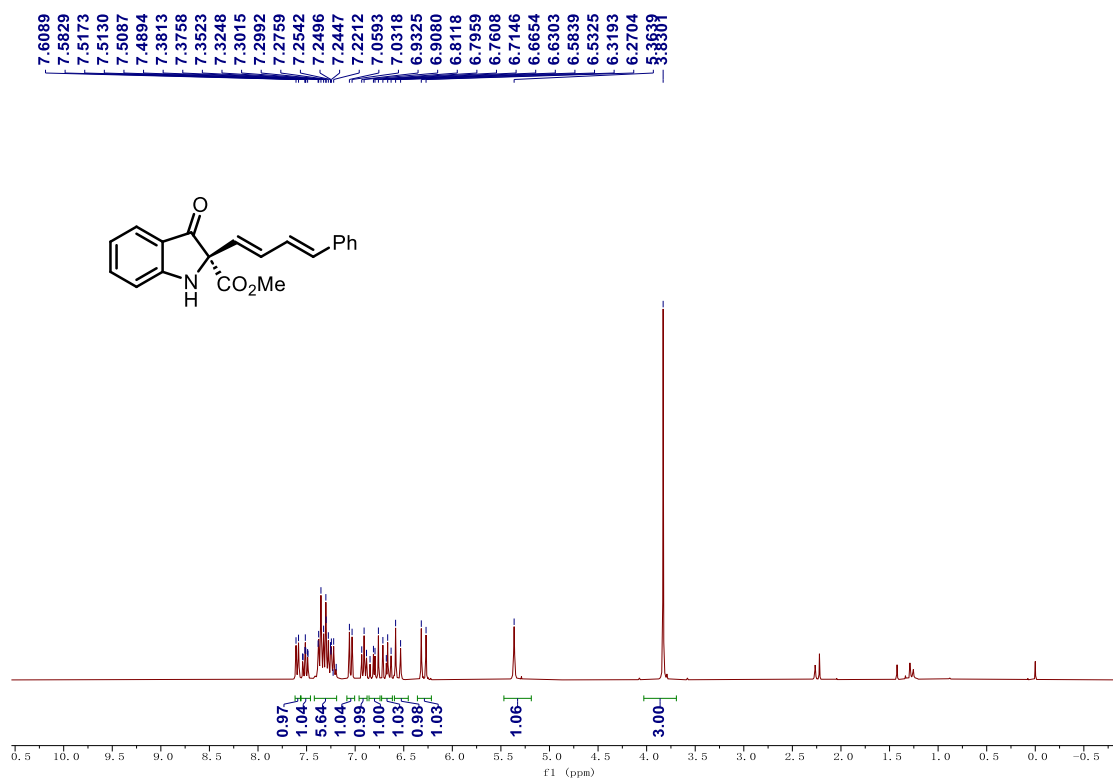
¹H NMR Spectrum of 4 (300 MHz, CDCl₃)



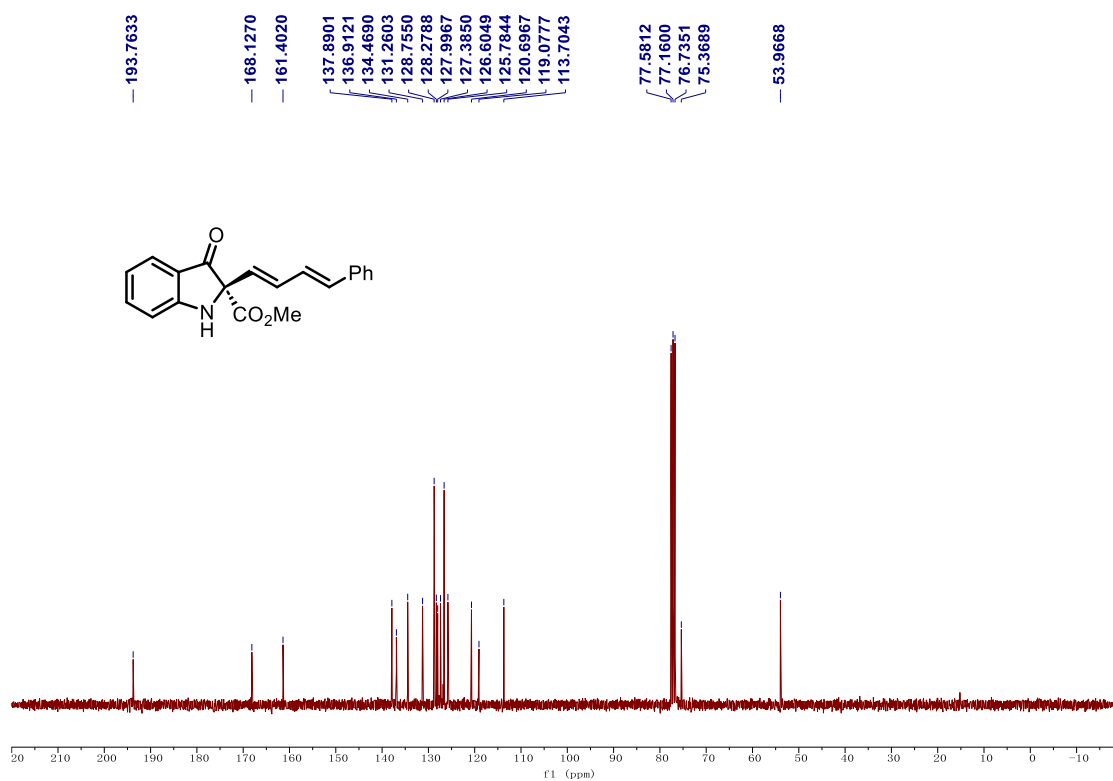
¹³C NMR Spectrum of 4 (75 MHz, CDCl₃)



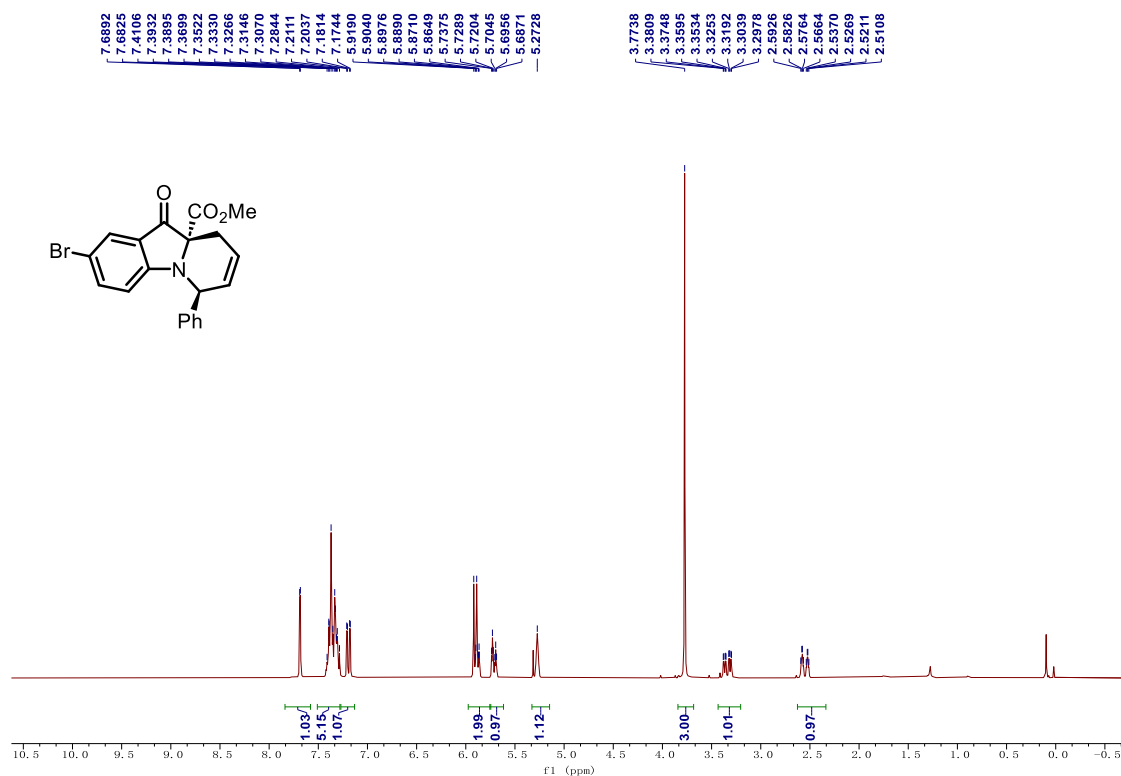
¹H NMR Spectrum of 5 (300 MHz, CDCl₃)



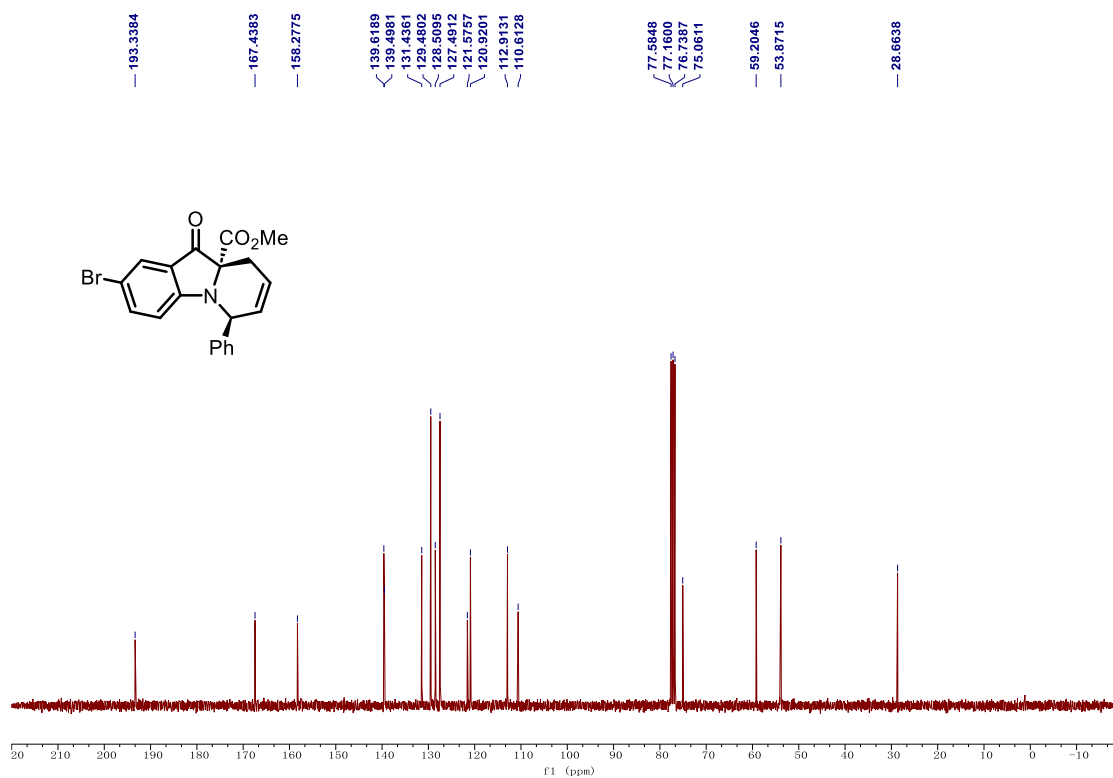
¹³C NMR Spectrum of 5 (75 MHz, CDCl₃)



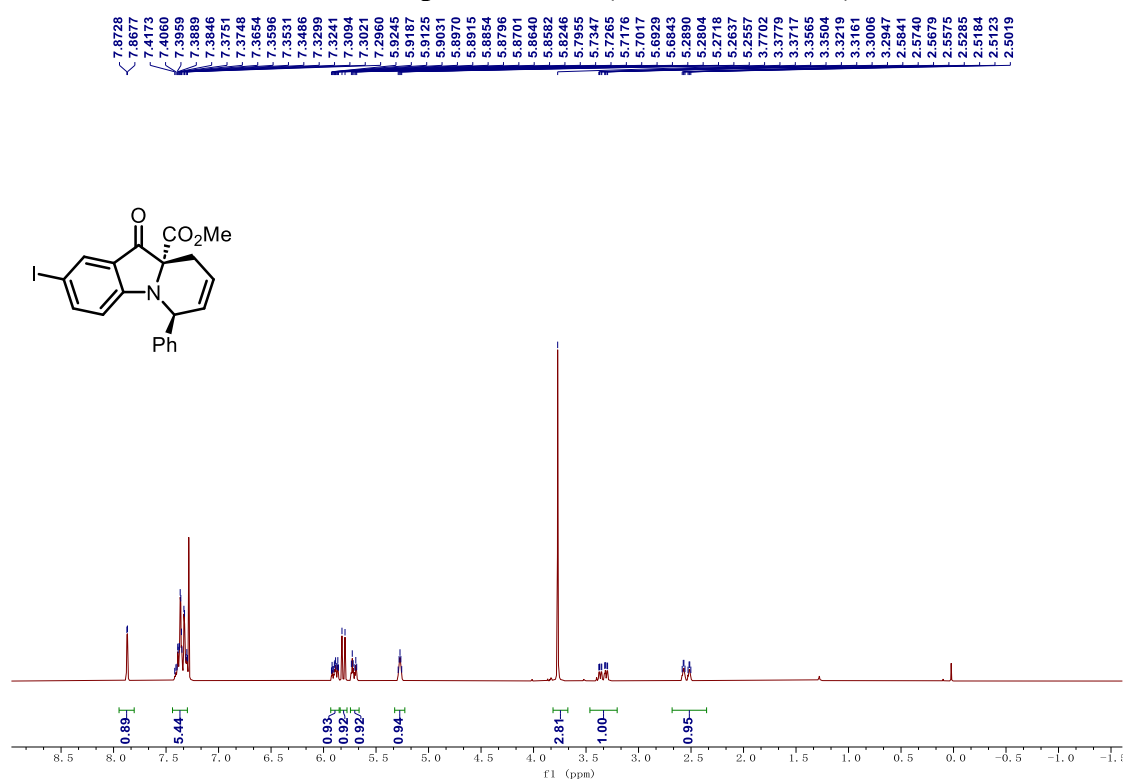
¹H NMR Spectrum of 6 (300 MHz, CDCl₃)



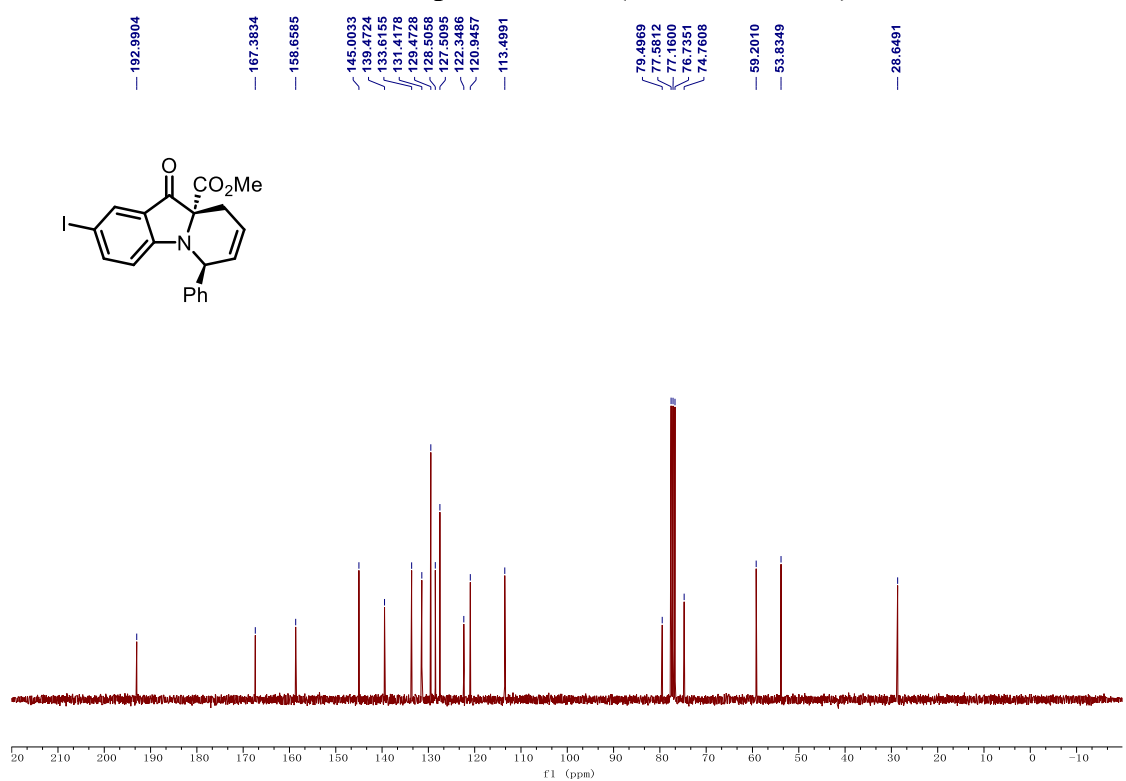
¹³C NMR Spectrum of 6 (75 MHz, CDCl₃)



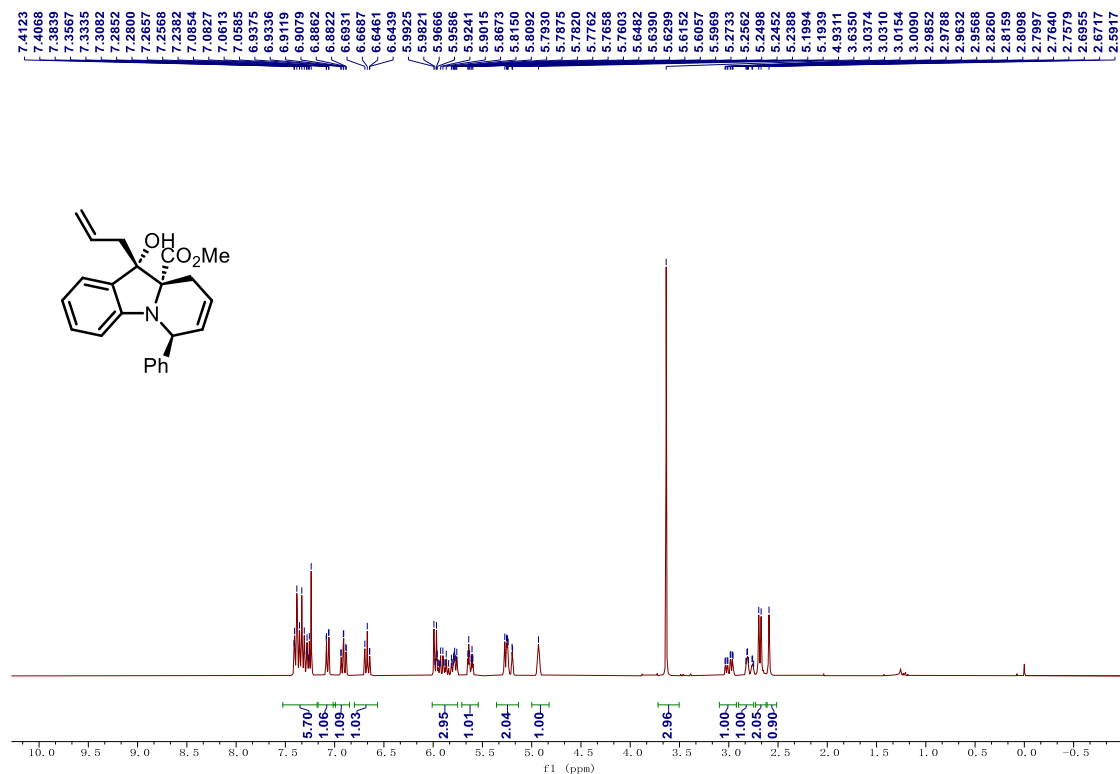
¹H NMR Spectrum of 7 (300 MHz, CDCl₃)



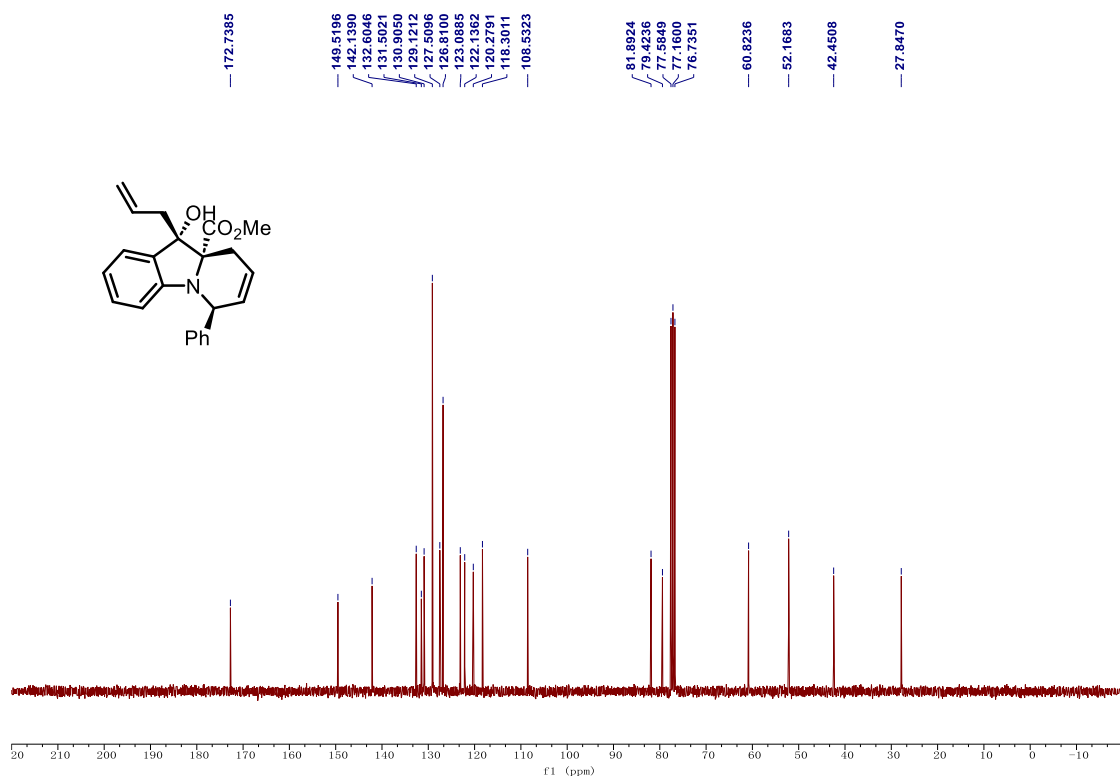
¹³C NMR Spectrum of 7 (75 MHz, CDCl₃)



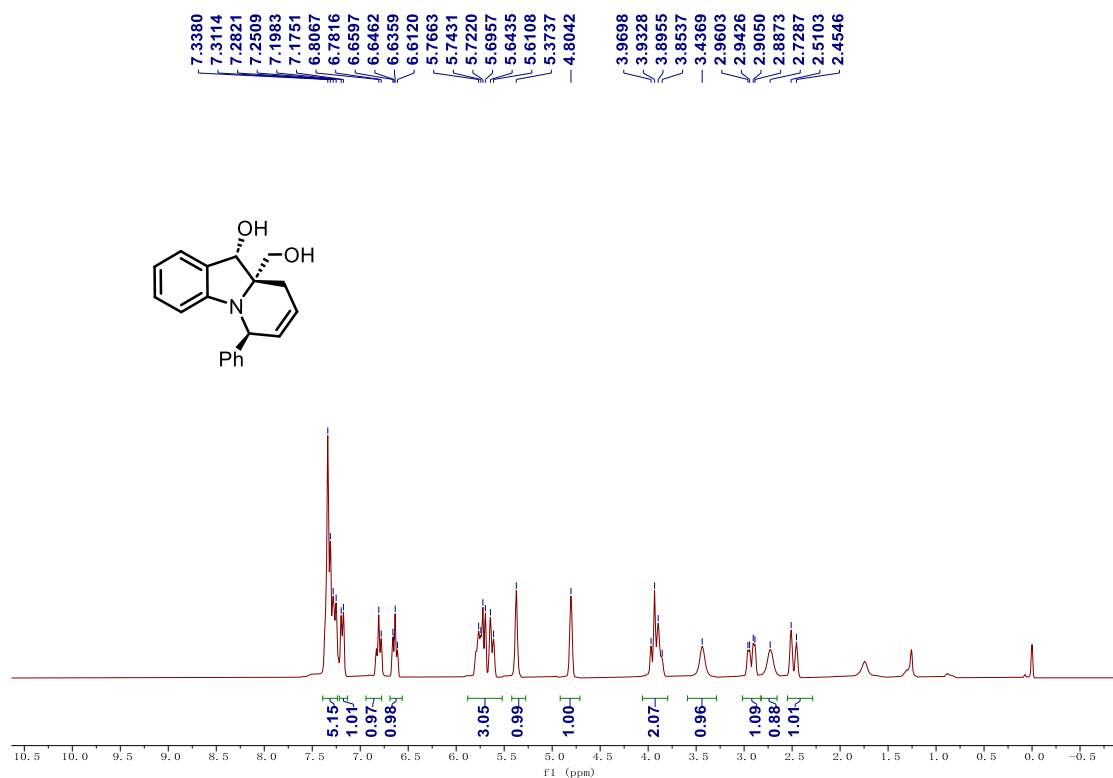
¹H NMR Spectrum of 8 (300 MHz, CDCl₃)



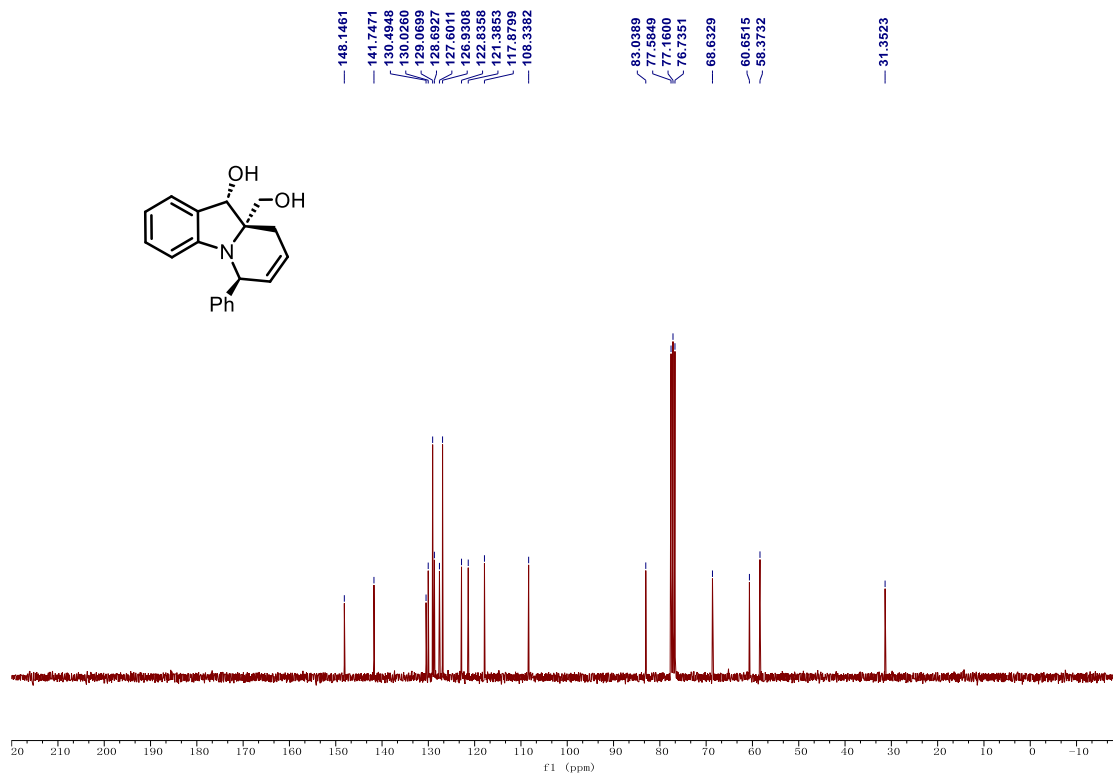
¹³C NMR Spectrum of 8 (75 MHz, CDCl₃)



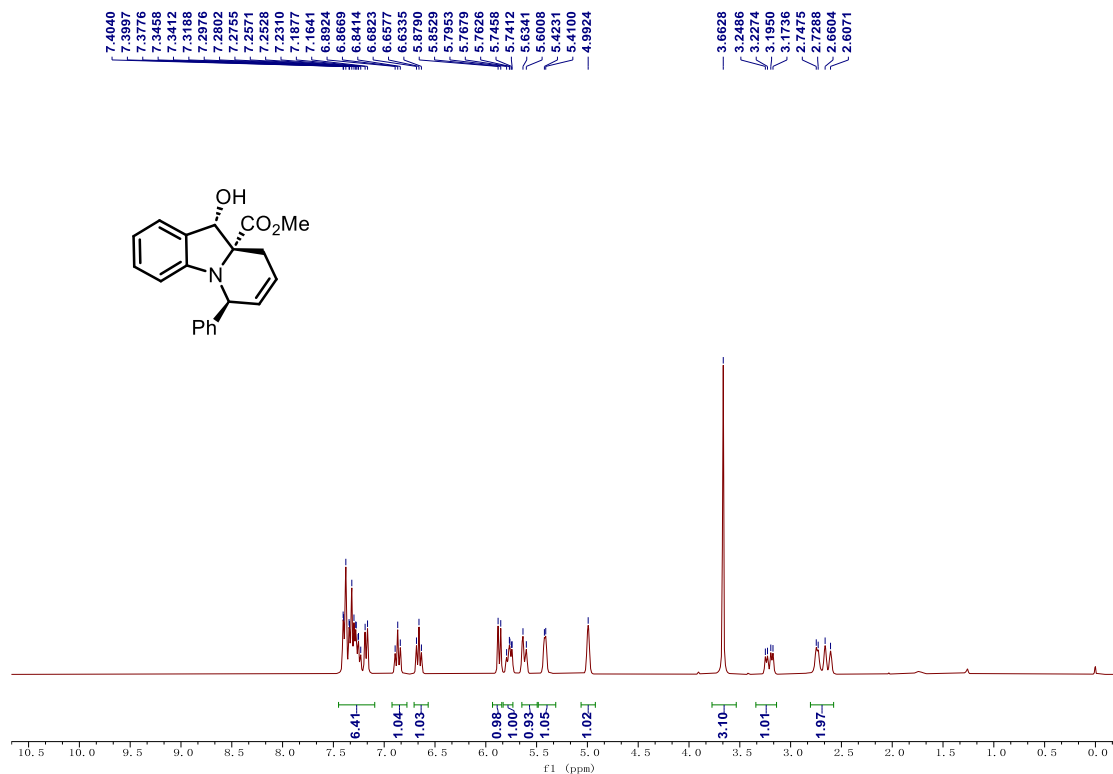
¹H NMR Spectrum of 9 (300 MHz, CDCl₃)



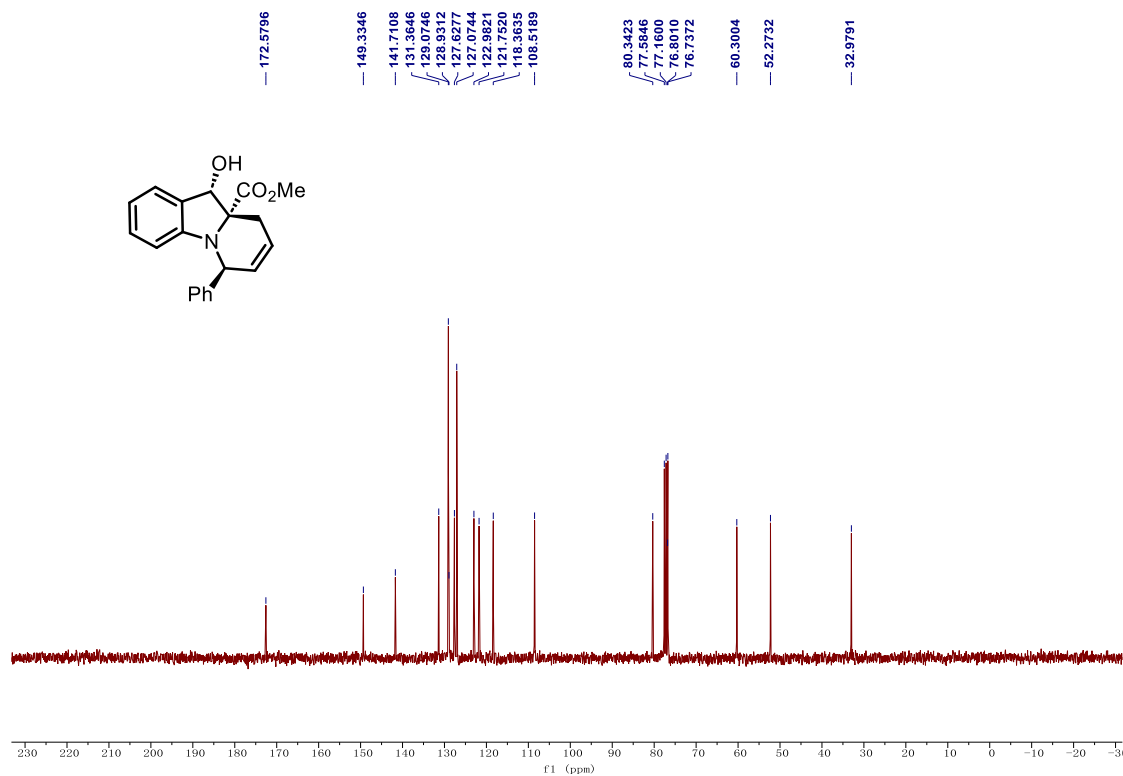
¹³C NMR Spectrum of 9 (75 MHz, CDCl₃)



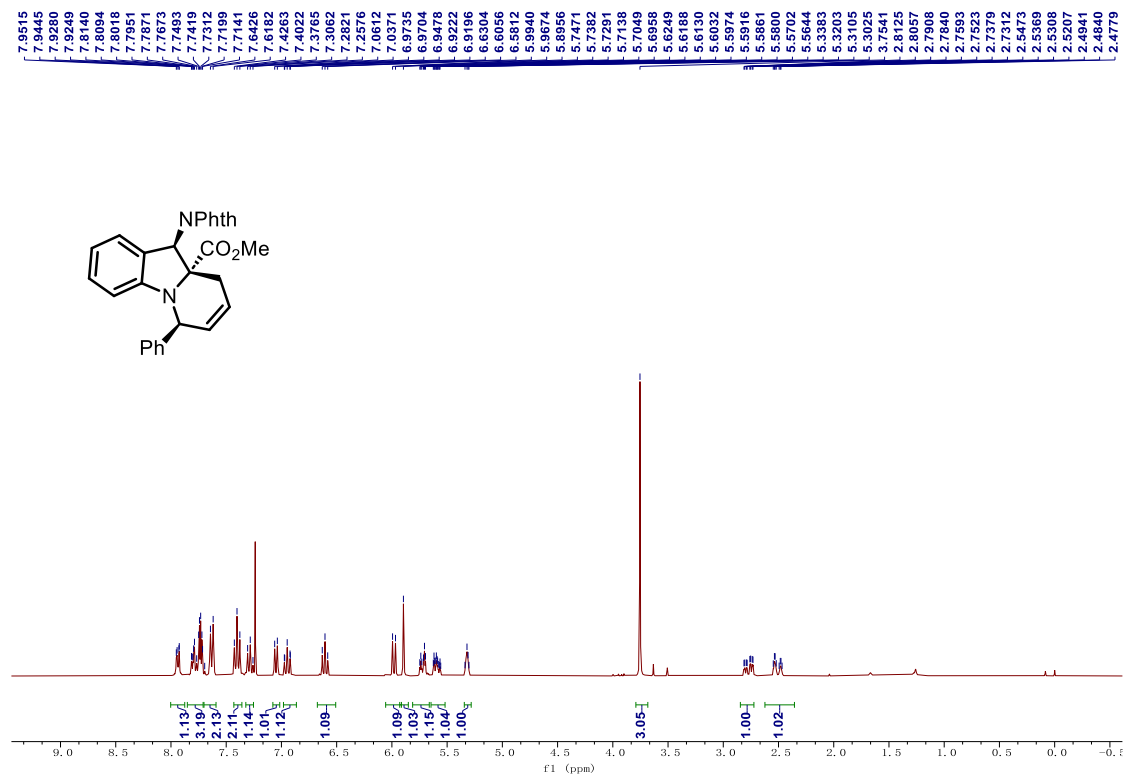
¹H NMR Spectrum of 10 (300 MHz, CDCl₃)



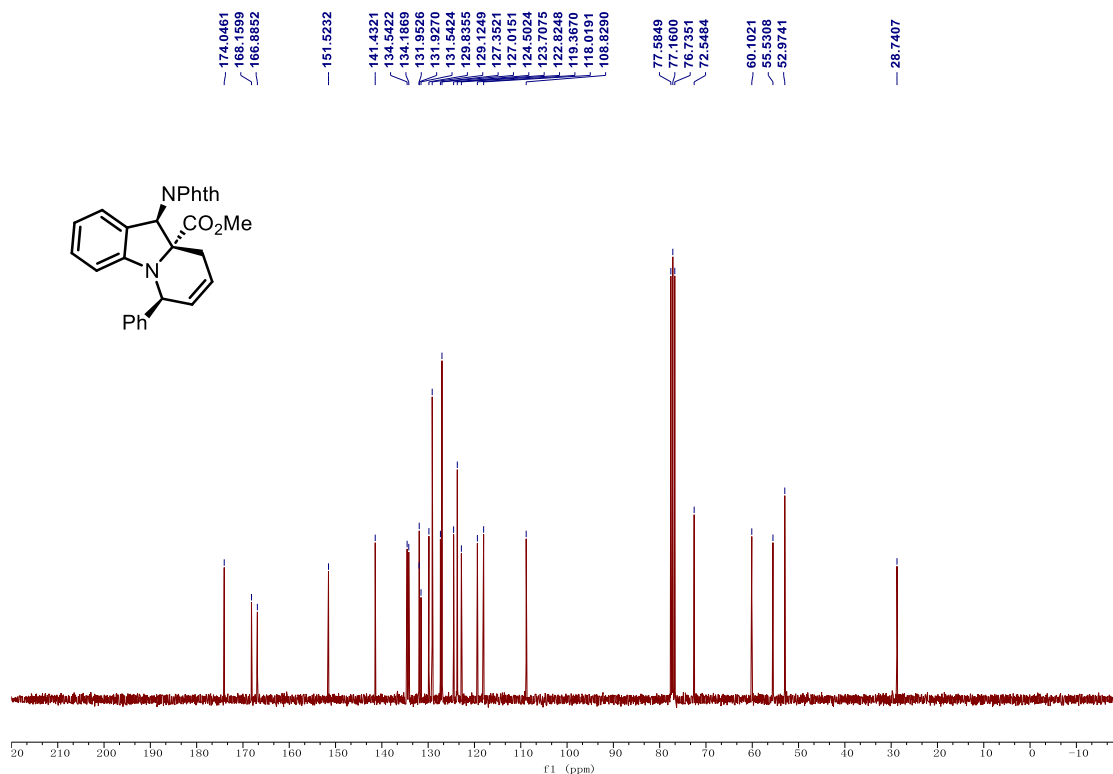
¹³C NMR Spectrum of 10 (75 MHz, CDCl₃)



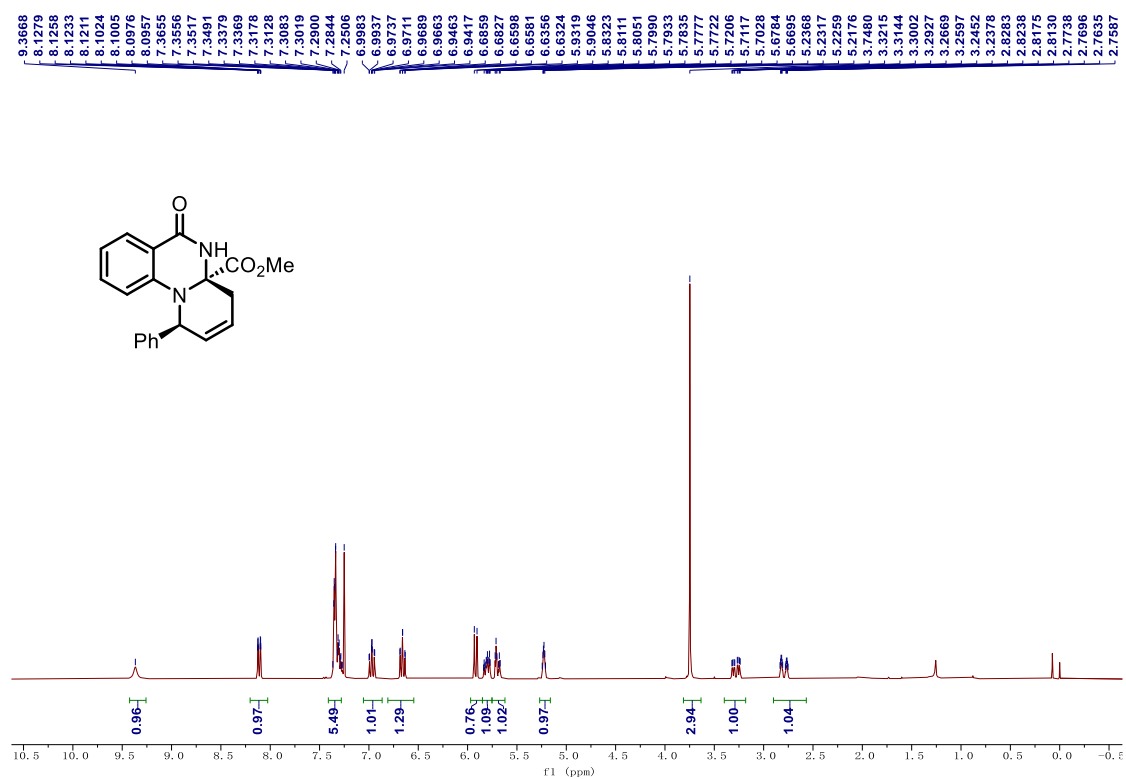
¹H NMR Spectrum of 11 (300 MHz, CDCl₃)



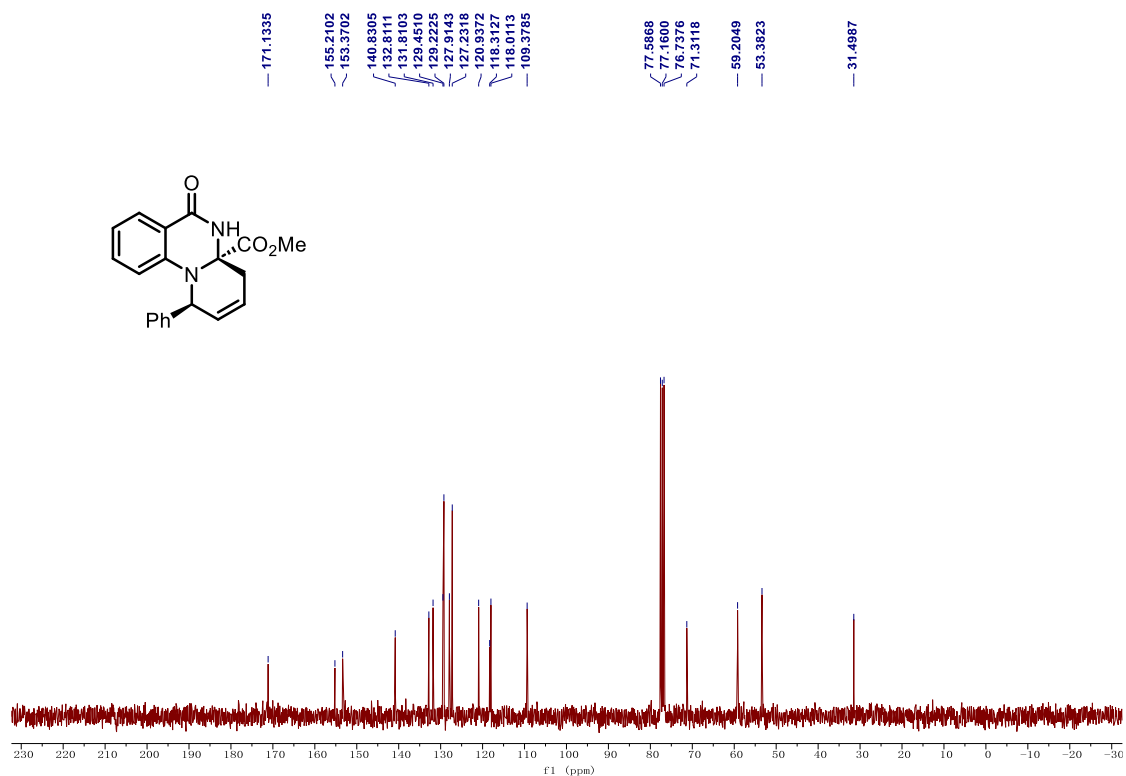
¹³C NMR Spectrum of 11 (75 MHz, CDCl₃)



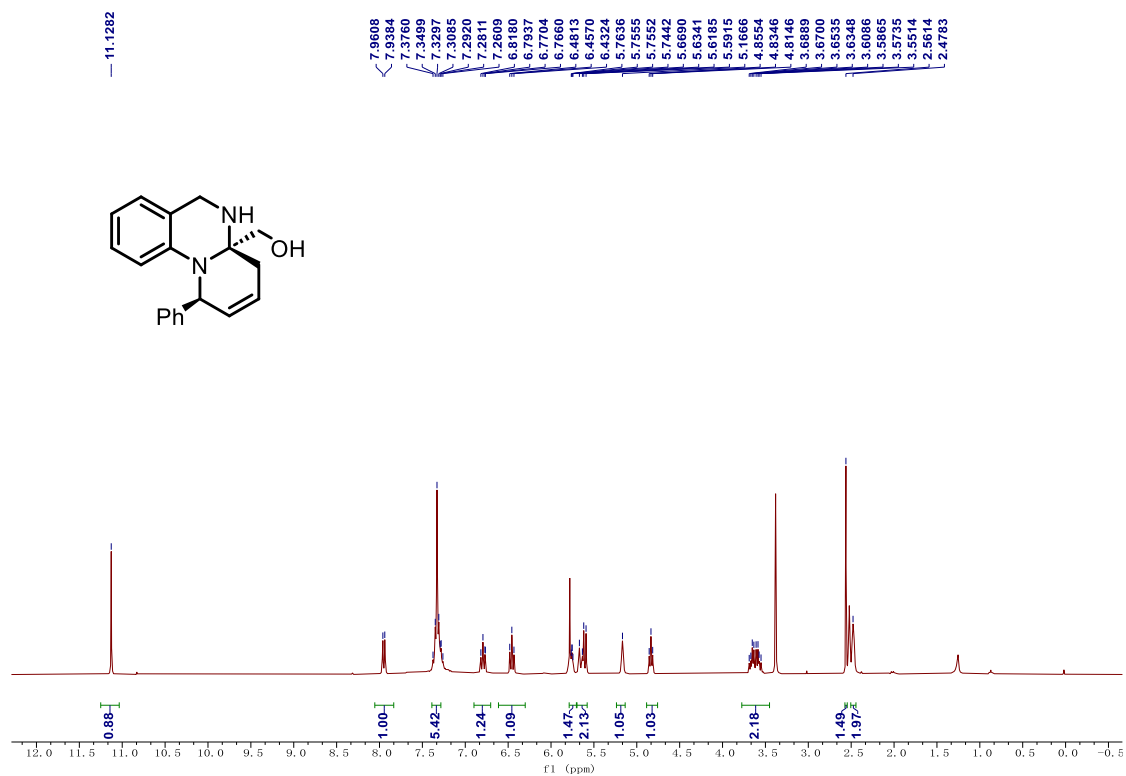
¹H NMR Spectrum of 12 (300 MHz, CDCl₃)



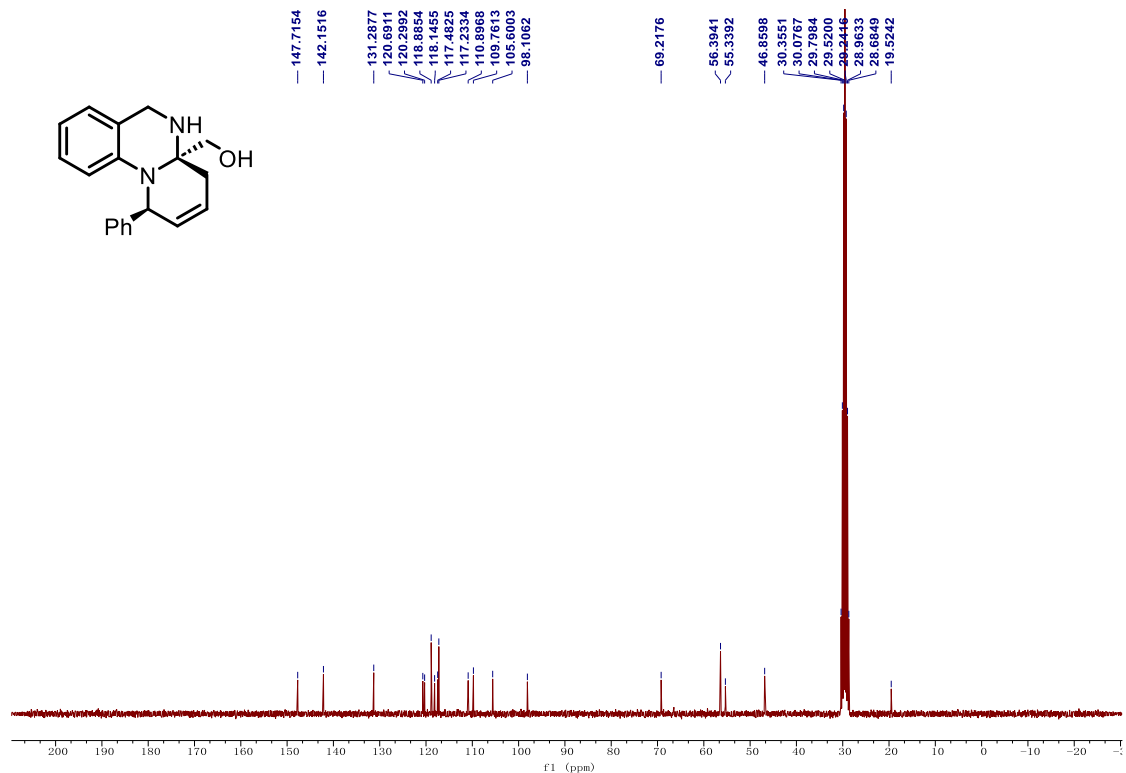
¹³C NMR Spectrum of 12 (75 MHz, CDCl₃)



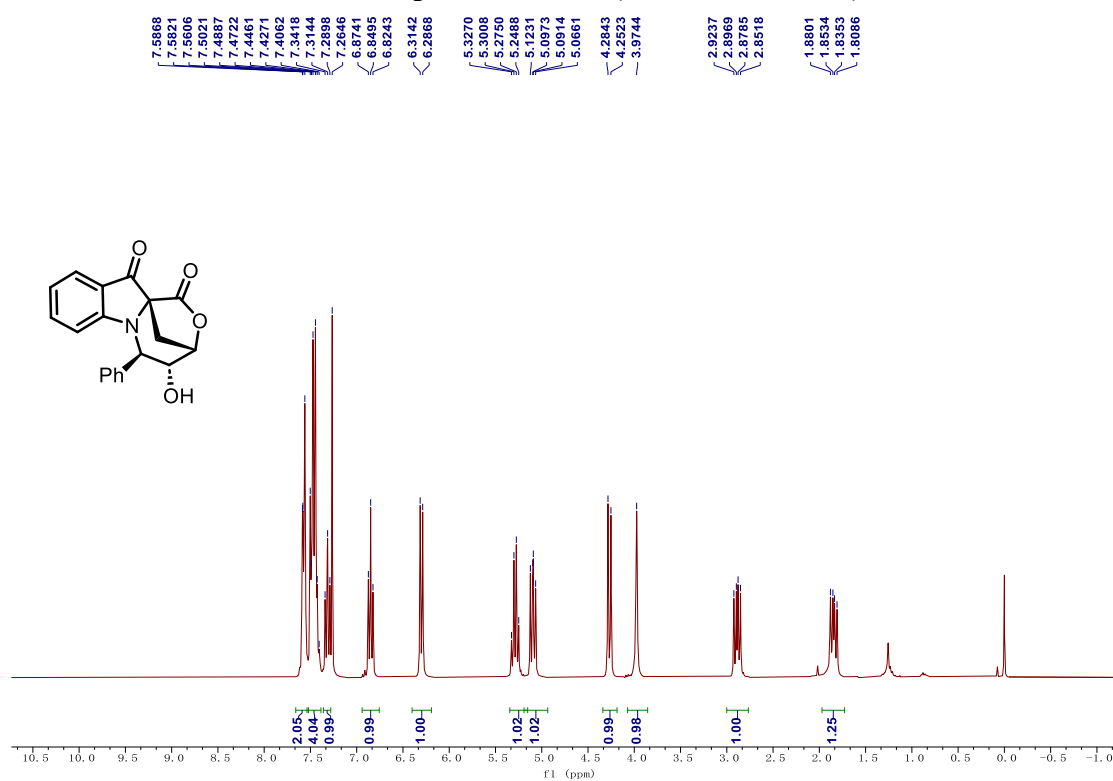
¹H NMR Spectrum of 13 (300 MHz, DMSO-*d*₆)



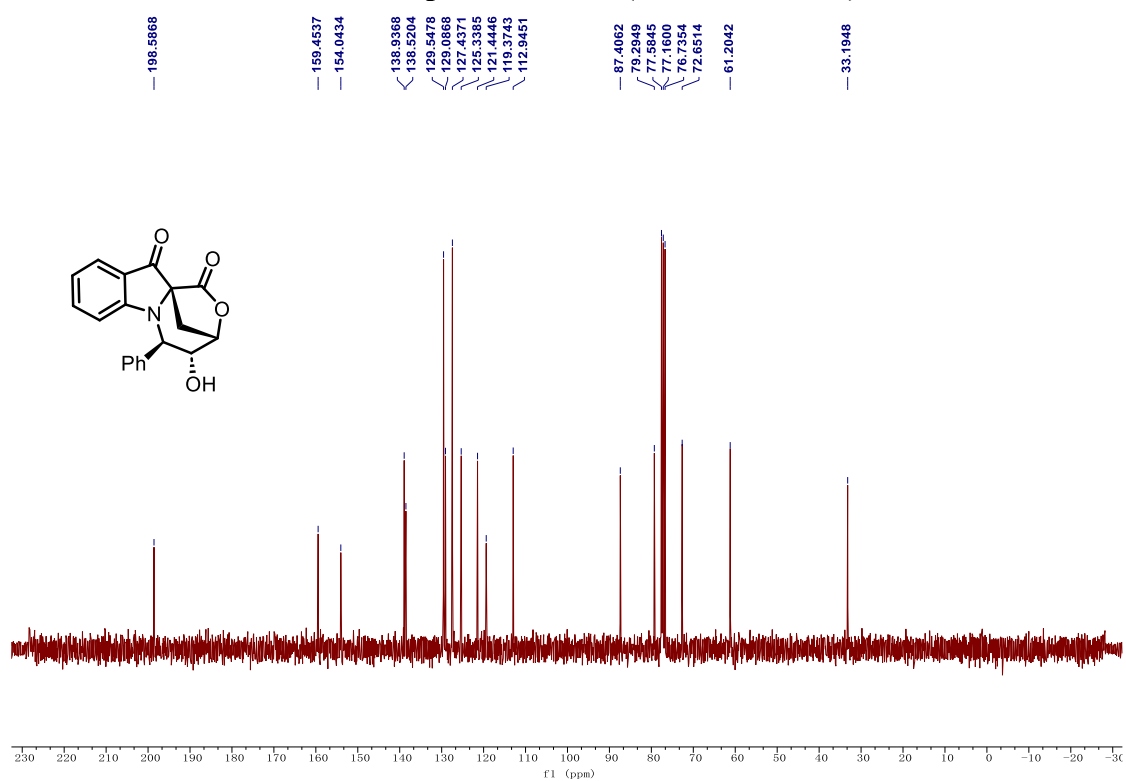
¹³C NMR Spectrum of 13 (75 MHz, DMSO-*d*₆)



¹H NMR Spectrum of 14 (300 MHz, CDCl₃)



¹³C NMR Spectrum of 14 (75 MHz, CDCl₃)



10. References

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