

**Cascade reaction of *o*-enoyl arylisocyanide and *o*-hydroxy aromatic
aldimine: a diastereoselective access to polycyclic spirobenzoxazine
chromeno[4,3-*b*]pyrrole derivative**

Yao Xiao,^a Xin Peng,^a Jie Shen,^a Lei Cui,^{*a} Shanya Lu,^a Xueshun Jia,^a Chunju Li^b
and Jian Li^{*a,c}

^a Department of Chemistry, College of Sciences & Institute for Sustainable Energy,
Shanghai University, 99 Shangda Road, Shanghai 200444, P. R. China.

^b Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry,
Ministry of Education, Tianjin Key Laboratory of Structure and Performance for
Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin
300387, P. R. China.

^c School of Chemistry and Chemical Engineering, Henan Normal University,
Xinxiang, Henan 453007, P. R. China, P. R. China.

E-mail: cuilei@shu.edu.cn; lijian@shu.edu.cn

Supporting Information

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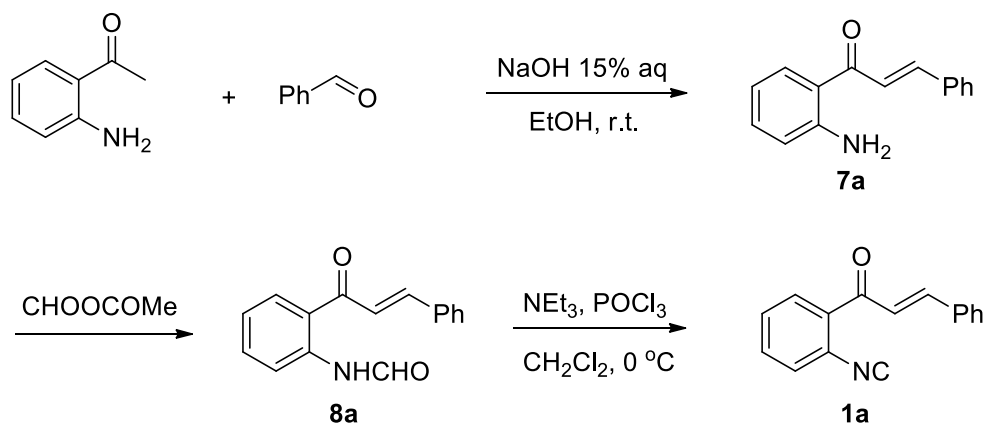
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1. General Information

The NMR spectra were recorded on Bruker AC-400 spectrometer (400 MHz for ^1H NMR and 101 MHz for ^{13}C NMR) with CDCl_3 as the solvent and TMS as internal reference. ^1H NMR spectral data were reported as follows: chemical shift (δ , ppm), multiplicity, integration, and coupling constant (Hz). ^{13}C NMR spectral data were reported in terms of the chemical shift. The following abbreviations were used to indicate multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. Melting points were obtained on an X-4 digital melting point apparatus without correction. Purification of products was accomplished by column chromatography packed with silica gel. Unless otherwise stated, all reagents were commercially purchased and used without further purification.

2. General Procedure

2.1 General procedure for the synthesis of *o*-enoyl arylisocyanide 1



To a solution of 1-(2-aminophenyl)ethanone (1.22 mL, 10 mmol) and benzaldehyde (1.02 mL, 10 mmol) in EtOH (10 mL) was added NaOH (15% aq) (EtOH: NaOH aq = 1:1), the reaction mixture was stirred at room temperature for about 4 h. Upon the consumption of the substrate (monitored by TLC), the reaction was poured slowly into water (50 mL) under stirring, the precipitation was collected by filtration to give **7a** (74% yield) as a yellow solid, it was used in the formylation step directly.

To a solution of **7a** (10 mmol) in DCM (50 mL) was added acetic formic anhydride (25 mmol), the reaction mixture was stirred at room temperature for about 20 minutes. Upon the consumption of the substrate (monitored by TLC), the mixture was washed by saturated aqueous sodium bicarbonate solution and then extracted with CH₂Cl₂ (3 × 20 mL), the combined organic phase was dried over Na₂SO₄, and concentrated in vacuo to give **8a** (96% yield), which was used in the next step without purification.

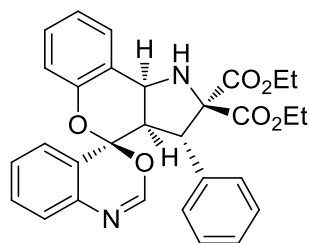
A solution of **8a** and NEt₃ (3.5 equiv) in CH₂Cl₂ was cooled at 0 °C, then POCl₃ (1.5 equiv) was added dropwise. After the reaction was completed (monitored by TLC), a saturated Na₂HCO₃ solution was added at 0 °C to quench the reaction. Then the mixture was extracted with CH₂Cl₂ (3 × 20 mL), the combined organic phase was dried over Na₂SO₄, and concentrated in vacuo. The residue was subjected to column chromatography on silica-gel [eluant: petroleum ether/ethyl ether = 20:1] to give *o*-enoyl arylisocyanide (**1a**, 72% yield) as a pale yellow solid.

2.2 General procedure for the synthesis of product 3

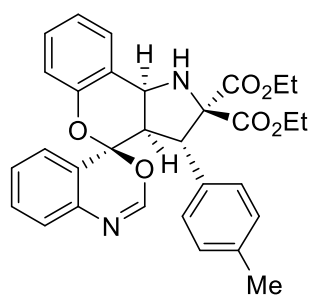
Under air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with *o*-enoyl arylisocyanide **1** (0.5 mmol), *o*-hydroxy aromatic aldimine **2** (0.6 mmol) and NaOH (1 mmol) in 5 mL of DCM at room temperature. After completion of the reaction, the reaction mixture was concentrated under vacuum. The residue was purified by thin layer chromatography [eluant: petroleum ether/ethyl acetate = 2:1] to afford the desired product **3**.

3. Characterization Data

Spectroscopic Data of All Compounds

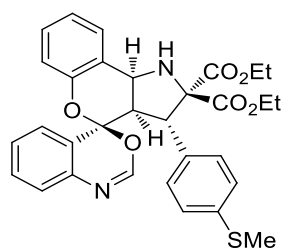


(3a) 250 mg, 98% yield, yellow solid: m. p. 156-158 °C. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.56 (dd, $J = 7.7$, 1.7 Hz, 1H), 7.41-7.32 (m, 2H), 7.25-7.17 (m, 4H), 7.15-7.09 (m, 4H), 7.02 (ddd, $J = 8.5$, 5.7, 3.2 Hz, 1H), 6.90 (t, $J = 8.0$ Hz, 2H), 5.28 (d, $J = 7.7$ Hz, 1H), 4.42 (d, $J = 3.8$ Hz, 1H), 4.25 (dq, $J = 10.6$, 7.1 Hz, 1H), 4.08 (dq, $J = 10.8$, 7.2 Hz, 1H), 3.75 (dq, $J = 10.8$, 7.1 Hz, 1H), 3.58 (dd, $J = 7.8$, 3.9 Hz, 1H), 3.46 (s, 1H), 3.35 (dq, $J = 10.8$, 7.2 Hz, 1H), 1.20 (t, $J = 7.1$ Hz, 3H), 0.73 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 171.02, 169.06, 150.11, 147.86, 140.06, 138.07, 130.77, 129.58, 129.45, 128.54, 128.47, 127.61, 127.34, 125.95, 124.62, 123.13, 123.02, 122.62, 118.10, 98.40, 78.15, 62.23, 61.75, 56.32, 53.36, 50.52, 13.98, 13.43. HRMS (ESI): Calcd. for $\text{C}_{30}\text{H}_{29}\text{N}_2\text{O}_6$ $[\text{M} + \text{H}]^+$ 513.2020, Found: 513.2024.

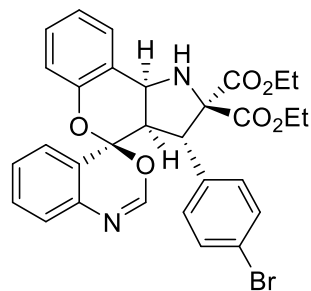


(3b) 236 mg, 90% yield, yellow solid: m. p. 160-162 °C. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.56 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.40-7.33 (m, 2H), 7.23 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.12 (d, $J = 7.9$ Hz, 2H), 7.05 (ddd, $J = 8.4$, 6.1, 2.4 Hz, 1H), 7.01-6.99 (m, 4H), 6.91 (dd, $J = 16.7$, 7.9 Hz, 2H), 5.27 (d, $J = 7.7$ Hz, 1H), 4.39 (d, $J = 3.7$ Hz, 1H), 4.25 (dq, $J = 10.9$, 7.2 Hz, 1H), 4.08 (dq, $J = 10.7$, 7.1 Hz, 1H), 3.74 (dq, $J = 10.6$, 7.1 Hz, 1H), 3.56 (dd, $J = 7.8$, 3.8 Hz, 1H), 3.43 (d, $J = 4.4$ Hz, 1H), 3.38 (dq, $J = 10.6$, 7.1 Hz, 1H), 2.28 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 3H), 0.75 (t, $J =$

7.1 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 171.06, 169.15, 150.12, 147.87, 138.08, 136.94, 136.89, 130.75, 129.56, 129.50, 129.08, 128.38, 127.65, 125.93, 124.64, 123.10, 123.06, 122.63, 118.08, 98.45, 78.20, 62.20, 61.73, 56.34, 53.07, 50.38, 21.12, 13.99, 13.41. HRMS (ESI): Calcd. for $\text{C}_{31}\text{H}_{31}\text{N}_2\text{O}_6$ $[\text{M} + \text{H}]^+$ 527.2177, Found: 527.2178.

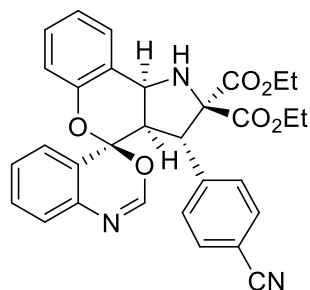


(3c) 256 mg, 92% yield, yellow oil. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.55 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.39-7.34 (m, 2H), 7.26-7.17 (m, 2H), 7.12 (dd, $J = 7.5, 1.2$ Hz, 1H), 7.10-7.05 (m, 5H), 6.91 (ddd, $J = 17.9, 7.9, 1.3$ Hz, 2H), 5.25 (d, $J = 7.8$ Hz, 1H), 4.37 (d, $J = 4.0$ Hz, 1H), 4.24 (dq, $J = 10.7, 7.2$ Hz, 1H), 4.08 (dq, $J = 10.7, 7.2$ Hz, 1H), 3.77 (dq, $J = 10.7, 7.2$ Hz, 1H), 3.54 (dd, $J = 7.8, 3.9$ Hz, 1H), 3.44-3.39 (m, 2H), 2.43 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 3H), 0.78 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 170.92, 169.05, 150.10, 147.79, 138.04, 137.51, 136.73, 130.79, 129.59, 129.45, 129.26, 129.01, 127.71, 126.53, 126.43, 125.97, 124.59, 123.13, 123.01, 122.55, 118.09, 98.38, 78.13, 62.25, 61.82, 56.34, 52.99, 50.42, 15.84, 13.98, 13.49. HRMS (ESI): Calcd. for $\text{C}_{31}\text{H}_{31}\text{N}_2\text{O}_6\text{S}$ $[\text{M} + \text{H}]^+$ 559.1897, Found: 559.1902.

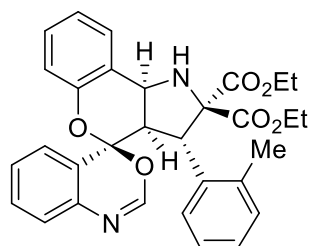


(3d) 259 mg, 88% yield, yellow oil. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.53 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.37-7.30 (m, 4H), 7.22 (td, $J = 7.8, 1.7$ Hz, 1H), 7.12-7.08 (m, 2H), 7.07-6.99 (m, 3H), 6.89 (ddd, $J = 14.5, 8.0, 1.3$ Hz, 2H), 5.23 (d, $J = 7.8$ Hz, 1H), 4.37 (d, $J = 4.1$ Hz, 1H), 4.24 (dq, $J = 10.8, 7.1$ Hz, 1H),

4.07 (dq, $J = 10.9, 7.1$ Hz, 1H), 3.79 (dq, $J = 10.8, 7.1$ Hz, 1H), 3.51 (dd, $J = 7.9, 4.0$ Hz, 1H), 3.43 (dq, $J = 10.8, 7.1$ Hz, 1H), 1.18 (t, $J = 7.1$ Hz, 3H), 0.78 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM- D) δ 170.74, 168.89, 150.04, 147.75, 139.04, 137.98, 131.53, 130.87, 130.31, 129.63, 129.38, 127.74, 126.01, 124.52, 123.19, 122.90, 122.47, 121.30, 118.11, 98.26, 77.98, 62.34, 61.89, 56.29, 52.87, 50.55, 13.98, 13.48. HRMS (ESI): Calcd. for $\text{C}_{30}\text{H}_{28}\text{BrN}_2\text{O}_6$ $[\text{M} + \text{H}]^+$ 591.1125, Found: 591.1128.

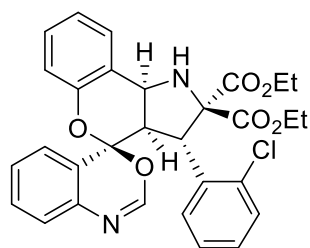


(3e) 249 mg, 93% yield, yellow oil. ^1H NMR (400 MHz, CHLOROFORM- D) δ 7.55-7.48 (m, 3H), 7.39-7.33 (m, 2H), 7.25 (t, $J = 8.1$ Hz, 3H), 7.14-7.09 (m, 2H), 7.03 (ddd, $J = 7.8, 6.8, 1.9$ Hz, 1H), 6.88 (ddd, $J = 7.5, 5.5, 1.1$ Hz, 2H), 5.26 (d, $J = 7.9$ Hz, 1H), 4.44 (d, $J = 4.3$ Hz, 1H), 4.26 (dq, $J = 10.8, 7.1$ Hz, 1H), 4.09 (dq, $J = 10.8, 7.2$ Hz, 1H), 3.81 (dq, $J = 10.7, 7.1$ Hz, 1H), 3.54 (dd, $J = 7.9, 4.3$ Hz, 1H), 3.41 (dq, $J = 10.7, 7.1$ Hz, 1H), 1.20 (t, $J = 7.1$ Hz, 3H), 0.78 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM- D) δ 170.43, 168.63, 149.97, 147.66, 145.44, 137.93, 132.20, 131.01, 129.84, 129.75, 129.50, 129.27, 127.74, 126.15, 124.37, 123.32, 122.75, 122.31, 118.56, 118.19, 111.29, 98.07, 77.97, 62.54, 61.95, 56.32, 53.38, 50.82, 13.98, 13.54. HRMS (ESI): Calcd. for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{O}_6$ $[\text{M} + \text{H}]^+$ 538.1973, Found: 538.1969.

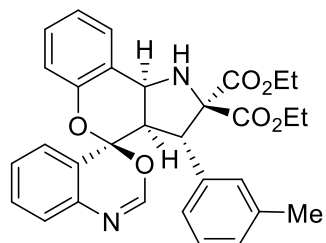


(3f) 226 mg, 86% yield, yellow solid: m. p. 169-171 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CHLOROFORM- D) δ 7.56 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.44-7.37 (m, 2H), 7.25-7.22 (m, 1H),

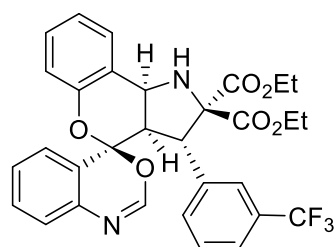
7.18-7.10 (m, 4H), 7.08-7.03 (m, 2H), 6.95 (d, $J = 7.5$ Hz, 1H), 6.92-6.88 (m, 2H), 5.26 (d, $J = 7.6$ Hz, 1H), 4.76 (d, $J = 3.0$ Hz, 1H), 4.29-4.19 (m, 1H), 4.08-4.00 (m, 1H), 3.78-3.67 (m, 1H), 3.55 (s, 1H), 3.43 (dd, $J = 7.7, 3.1$ Hz, 1H), 3.32-3.22 (m, 1H), 1.85 (s, 3H), 1.17 (td, $J = 7.2, 0.8$ Hz, 3H), 0.69 (td, $J = 7.2, 0.8$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 171.27, 169.18, 150.18, 148.13, 139.84, 138.20, 137.74, 130.82, 130.13, 129.64, 129.59, 127.68, 127.07, 126.84, 126.32, 125.98, 124.69, 123.12, 123.10, 122.57, 118.13, 98.35, 78.47, 62.21, 61.74, 56.77, 53.21, 47.92, 19.46, 13.93, 13.32. HRMS (ESI): Calcd. for $\text{C}_{31}\text{H}_{31}\text{N}_2\text{O}_6$ $[\text{M} + \text{H}]^+$ 527.2177, Found: 527.2175.



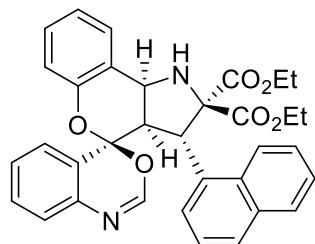
(3g) 245 mg, 90% yield, yellow solid: m. p. 202-204 °C. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.56 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.42-7.34 (m, 2H), 7.30 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.25-7.17 (m, 3H), 7.14-7.03 (m, 4H), 6.89 (ddd, $J = 7.7, 5.0, 1.2$ Hz, 2H), 5.21 (d, $J = 8.0$ Hz, 1H), 5.16 (d, $J = 3.5$ Hz, 1H), 4.21 (dq, $J = 10.8, 7.2$ Hz, 1H), 4.07 (dq, $J = 10.6, 7.1$ Hz, 1H), 3.81 (dq, $J = 10.6, 7.1$ Hz, 1H), 3.54 (s, 1H), 3.45-3.33 (m, 2H), 1.17 (t, $J = 7.1$ Hz, 3H), 0.76 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 170.83, 168.58, 150.17, 147.74, 138.92, 138.13, 135.32, 130.81, 129.63, 129.58, 129.52, 128.56, 128.40, 127.63, 127.02, 126.12, 124.42, 123.11, 122.93, 122.45, 118.17, 98.06, 78.16, 62.29, 61.82, 56.60, 53.51, 48.50, 13.96, 13.42. HRMS (ESI): Calcd. for $\text{C}_{30}\text{H}_{28}\text{ClN}_2\text{O}_6$ $[\text{M} + \text{H}]^+$ 547.1630, Found: 547.1629.



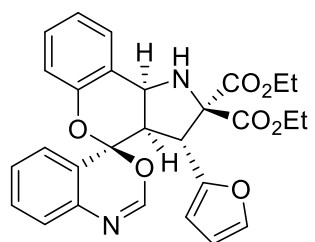
(3h) 241 mg, 92% yield, yellow solid: m. p. 210-212 °C. ¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.57 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.43-7.31 (m, 2H), 7.27-7.19 (m, 1H), 7.17-7.00 (m, 4H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.97-6.85 (m, 4H), 5.27 (d, *J* = 7.7 Hz, 1H), 4.39 (d, *J* = 3.8 Hz, 1H), 4.32-4.20 (m, 1H), 4.16-4.04 (m, 1H), 3.79-3.71 (m, 1H), 3.57 (dd, *J* = 7.8, 3.9 Hz, 1H), 3.49-3.32 (m, 2H), 2.25 (s, 3H), 1.20 (td, *J* = 7.0, 0.8 Hz, 3H), 0.74 (td, *J* = 7.1, 0.7 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 171.03, 169.11, 150.15, 147.85, 140.00, 138.10, 137.94, 130.73, 129.56, 129.48, 129.23, 128.33, 128.00, 127.60, 125.93, 125.54, 124.67, 123.09, 122.64, 118.09, 98.45, 78.16, 62.19, 61.70, 56.36, 53.30, 50.52, 21.41, 13.98, 13.40. HRMS (ESI): Calcd. for C₃₁H₃₁N₂O₆ [M + H]⁺ 527.2177, Found: 527.2174.



(3i) 278 mg, 96% yield, yellow solid: m. p. 189-191 °C. ¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.55 (dt, *J* = 6.0, 3.2 Hz, 1H), 7.45 (dt, *J* = 6.7, 1.9 Hz, 1H), 7.40-7.30 (m, 5H), 7.27-7.21 (m, 1H), 7.16-7.08 (m, 2H), 7.05-6.98 (m, 1H), 6.93-6.86 (m, 2H), 5.33-5.26 (m, 1H), 4.47-4.45 (m, 1H), 4.32-4.20 (m, 1H), 4.16-4.06 (m, 1H), 3.82-3.73 (m, 1H), 3.59-3.55 (m, 1H), 3.49-3.44 (m, 1H), 3.44-3.37 (m, 1H), 1.20 (td, *J* = 7.1, 3.8 Hz, 3H), 0.74 (td, *J* = 7.1, 3.8 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 170.62, 168.80, 150.03, 147.68, 140.97, 137.96, 132.16, 130.91, 130.75(q, *J* = 32.3 Hz), 129.65, 129.29, 129.01, 127.67, 126.09, 125.25 (q, *J* = 5.1 Hz), 124.47, 124.21 (q, *J* = 4.0 Hz), 123.94(q, *J* = 273.7 Hz), 123.26, 122.82, 118.17, 98.17, 77.93, 62.42, 61.87, 56.19, 53.17, 50.87, 13.96, 13.32. HRMS (ESI): Calcd. for C₃₁H₂₈F₃N₂O₆ [M + H]⁺ 581.1894, Found: 581.1899.

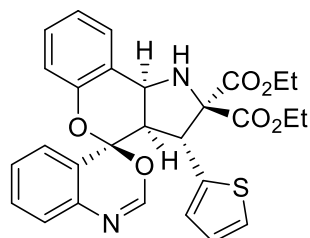


(3j) 266 mg, 95% yield, yellow solid: m. p. 201-203 °C. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 8.06 (d, $J = 8.6$ Hz, 1H), 7.72 (ddd, $J = 10.2, 8.1, 1.4$ Hz, 2H), 7.60 (dd, $J = 7.4, 1.6$ Hz, 1H), 7.45-7.35 (m, 3H), 7.34-7.25 (m, 4H), 7.19 (td, $J = 7.6, 1.8$ Hz, 1H), 7.15 (d, $J = 5.0$ Hz, 2H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.83-6.73 (m, 2H), 5.45 (d, $J = 3.2$ Hz, 1H), 5.38 (d, $J = 7.6$ Hz, 1H), 4.24 (dq, $J = 10.9, 7.2$ Hz, 1H), 4.06 (dq, $J = 10.9, 7.1$ Hz, 1H), 3.65 (dd, $J = 7.7, 3.2$ Hz, 1H), 3.51 (dq, $J = 10.8, 7.1$ Hz, 1H), 2.93 (dq, $J = 10.5, 7.1$ Hz, 1H), 1.16 (t, $J = 7.2$ Hz, 3H), 0.22 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 171.08, 169.31, 150.33, 148.00, 138.10, 137.98, 133.44, 132.43, 130.64, 129.67, 128.19, 128.00, 127.63, 126.33, 125.90, 125.77, 125.08, 124.63, 124.37, 123.89, 123.10, 123.00, 122.50, 118.13, 98.57, 78.69, 62.30, 61.46, 56.92, 53.58, 46.67, 13.93, 12.79. HRMS (ESI): Calcd. for $\text{C}_{34}\text{H}_{31}\text{N}_2\text{O}_6$ $[\text{M} + \text{H}]^+$ 563.2177, Found: 563.2180.

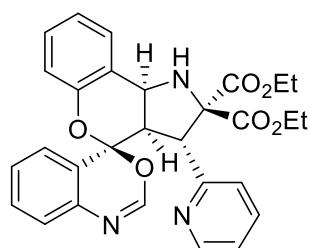


(3k) 218 mg, 87% yield, yellow solid: m. p. 160-162 °C. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.51 (dt, $J = 7.7, 2.8$ Hz, 1H), 7.43-7.32 (m, 2H), 7.30-7.27 (m, 1H), 7.25-7.18 (m, 1H), 7.18-7.07 (m, 3H), 7.05-7.02 (m, 1H), 6.90-6.84 (m, 1H), 6.21-6.18 (m, 1H), 5.96-5.94 (m, 1H), 5.21-5.18 (m, 1H), 4.47-4.45 (m, 1H), 4.31-4.19 (m, 1H), 4.14-3.96 (m, 2H), 3.81-3.70 (m, 2H), 3.47 (s, 1H), 1.23-1.17 (m, 3H), 1.03-0.97 (m, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 170.65, 168.59, 151.68, 149.93, 147.75, 141.88, 137.99, 130.83, 129.43, 129.10, 127.56, 125.98, 124.54, 123.22, 123.04, 122.94, 118.11, 110.76, 108.48, 97.85, 75.84, 62.34, 62.31,

55.07, 47.27, 46.90, 13.98, 13.77. HRMS (ESI): Calcd. for $C_{28}H_{27}N_2O_7$ $[M + H]^+$
503.1813, Found: 503.1825.

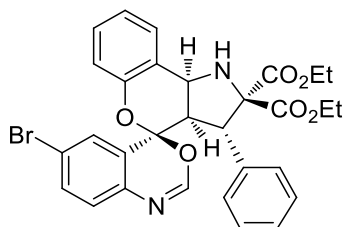


(3l) 217 mg, 84% yield, yellow solid: m. p. 157-159 °C. 1H
NMR (400 MHz, CHLOROFORM-*D*) δ 7.58-7.51 (m, 1H),
7.43-7.33 (m, 2H), 7.26-7.21 (m, 1H), 7.14-7.07 (m, 5H),
6.89 (dd, $J = 8.2, 1.4$ Hz, 1H), 6.86-6.81 (m, 2H), 5.28 (d, $J = 7.7$ Hz, 1H), 4.64 (d, J
 $= 4.3$ Hz, 1H), 4.26 (dq, $J = 10.8, 7.1, 1.2$ Hz, 1H), 4.12 (dq, $J = 10.8, 7.2, 1.2$ Hz,
1H), 3.88 (dq, $J = 10.7, 7.1, 1.2$ Hz, 1H), 3.68-3.59 (m, 2H), 3.45 (s, 1H), 1.22 (td, J
 $= 7.1, 1.3$ Hz, 3H), 0.90 (td, $J = 7.2, 1.3$ Hz, 3H). ^{13}C NMR (101 MHz,
CHLOROFORM-*D*) δ 170.64, 169.00, 150.01, 147.58, 142.28, 137.95, 130.87,
129.57, 129.37, 127.71, 126.90, 126.29, 126.03, 124.68, 124.45, 123.19, 122.94,
122.63, 118.10, 98.16, 77.98, 62.34, 62.02, 55.58, 51.79, 48.68, 14.00, 13.62. HRMS
(ESI): Calcd. for $C_{28}H_{27}N_2O_6S$ $[M + H]^+$ 519.1584, Found: 519.1599.



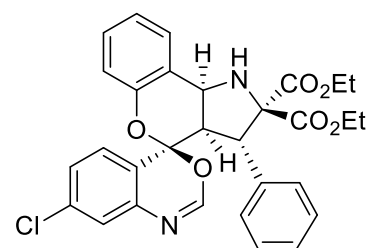
(3m) 230 mg, 90% yield, yellow solid: m. p. 178-180 °C. 1H
NMR (400 MHz, CHLOROFORM-*D*) δ 8.54-8.50 (m, 1H),
7.54-7.47 (m, 1H), 7.44-7.37 (m, 1H), 7.33-7.27 (m, 2H),
7.25-7.13 (m, 2H), 7.12-7.04 (m, 2H), 7.02-6.91 (m, 2H), 6.90-6.83 (m, 2H),
5.30-5.24 (m, 1H), 4.52-4.45 (m, 1H), 4.29-4.19 (m, 1H), 4.13-4.01 (m, 2H),
3.91-3.80 (m, 1H), 3.57-3.56 (m, 1H), 3.51-3.40 (m, 1H), 1.18 (dt, $J = 9.4, 7.1$ Hz,
3H), 0.75 (dt, $J = 9.5, 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ
170.55, 168.90, 158.90, 150.02, 149.28, 148.19, 138.11, 136.31, 130.64, 129.24,
129.05, 127.32, 125.82, 125.06, 124.80, 123.49, 123.17, 123.14, 122.13, 118.09,

98.20, 76.93, 62.25, 61.78, 55.26, 54.41, 48.55, 13.96, 13.51. HRMS (ESI): Calcd. for $C_{29}H_{28}N_3O_6$ $[M + H]^+$ 514.1973, Found: 514.1985.



(3n) 268 mg, 91% yield, yellow solid: m. p. 185-187 °C.

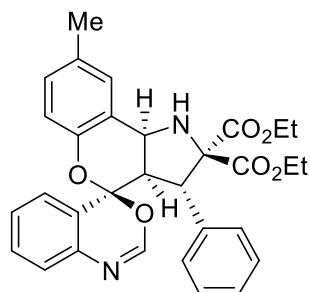
1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.56-7.51 (m, 1H), 7.45 (dt, $J = 8.4, 1.5$ Hz, 1H), 7.26-7.19 (m, 5H), 7.15-7.11 (m, 4H), 7.00 (d, $J = 2.1$ Hz, 1H), 6.88 (dd, $J = 8.1, 1.2$ Hz, 1H), 5.29 (d, $J = 8.0$ Hz, 1H), 4.37 (d, $J = 4.3$ Hz, 1H), 4.25 (dq, $J = 10.7, 7.1$ Hz, 1H), 4.07 (dq, $J = 10.8, 7.1$ Hz, 1H), 3.79 (dq, $J = 10.7, 7.1$ Hz, 1H), 3.51 (dd, $J = 8.1, 4.4$ Hz, 1H), 3.47 (s, 1H), 3.40 (dq, $J = 10.7, 7.1$ Hz, 1H), 1.19 (t, $J = 7.1$ Hz, 3H), 0.72 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 171.11, 168.89, 149.79, 148.30, 139.60, 137.20, 133.81, 129.60, 129.23, 128.63, 128.41, 128.09, 127.58, 127.49, 124.60, 123.41, 122.89, 120.39, 118.10, 97.71, 77.70, 62.23, 61.81, 55.69, 52.94, 50.69, 13.96, 13.42. HRMS (ESI): Calcd. for $C_{30}H_{28}BrN_2O_6$ $[M + H]^+$ 591.1125, Found: 591.1136.



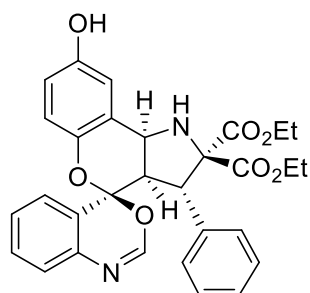
(3o) 256 mg, 94% yield, yellow solid: m. p. 177-179 °C.

1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.54 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.33-7.27 (m, 2H), 7.26-7.19 (m, 4H), 7.15-7.10 (m, 4H), 6.90-6.84 (m, 2H), 5.28 (d, $J = 8.0$ Hz, 1H), 4.38 (d, $J = 4.4$ Hz, 1H), 4.25 (dq, $J = 10.8, 7.1$ Hz, 1H), 4.07 (dq, $J = 10.8, 7.2$ Hz, 1H), 3.78 (dq, $J = 10.7, 7.1$ Hz, 1H), 3.53-3.43 (m, 2H), 3.38 (dq, $J = 10.7, 7.1$ Hz, 1H), 1.19 (t, $J = 7.1$ Hz, 3H), 0.72 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 171.09, 168.92, 149.82, 148.15, 139.61, 136.77, 132.70, 130.86, 129.59, 129.26, 128.60,

128.41, 127.55, 127.24, 125.09, 124.36, 123.39, 122.84, 118.08, 97.87, 77.76, 62.22, 61.79, 55.77, 52.96, 50.76, 13.96, 13.41. HRMS (ESI): Calcd. for C₃₀H₂₈ClN₂O₆ [M + H]⁺ 547.1630, Found: 547.1641.

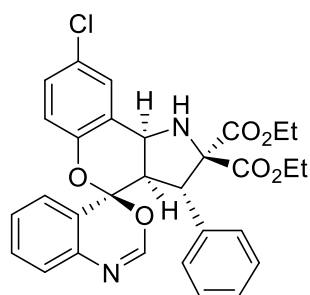


(4a) 239 mg, 91% yield, yellow solid: m. p. 193-195 °C. ¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.39-7.32 (m, 3H), 7.22-7.15 (m, 3H), 7.15-7.09 (m, 3H), 7.05-6.97 (m, 2H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.24 (d, *J* = 7.8 Hz, 1H), 4.41 (d, *J* = 3.8 Hz, 1H), 4.24 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.08 (dq, *J* = 10.5, 7.1 Hz, 1H), 3.74 (dq, *J* = 10.5, 7.1 Hz, 1H), 3.56 (dd, *J* = 7.9, 3.9 Hz, 1H), 3.42 (d, *J* = 7.3 Hz, 1H), 3.34 (dq, *J* = 10.6, 7.1 Hz, 1H), 2.33 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.73 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 170.95, 169.06, 147.87, 140.08, 138.09, 132.54, 130.69, 130.18, 129.69, 128.54, 128.43, 127.54, 127.30, 125.90, 124.64, 123.13, 122.30, 117.82, 98.48, 78.23, 62.17, 61.69, 56.41, 53.50, 50.65, 20.71, 13.98, 13.44. HRMS (ESI): Calcd. for C₃₁H₃₁N₂O₆ [M + H]⁺ 527.2177, Found: 527.2188.

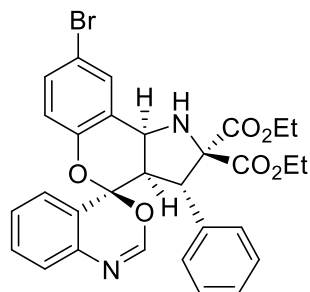


(4b) 221 mg, 84% yield, yellow solid: m. p. 130-132 °C. ¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.36 (dd, *J* = 4.0, 1.0 Hz, 2H), 7.22-7.18 (m, 3H), 7.15-7.10 (m, 3H), 7.05-6.99 (m, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 1.7 Hz, 2H), 5.23 (d, *J* = 7.8 Hz, 1H), 4.41 (d, *J* = 3.7 Hz, 1H), 4.31-4.22 (m, 1H), 4.16-4.06 (m, 1H), 3.81-3.71 (m, 1H), 3.55 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.39-3.29 (m, 1H), 1.19 (td, *J* = 7.1, 1.3 Hz, 3H), 0.72 (td, *J* = 7.1, 1.2 Hz, 3H). ¹³C NMR (101 MHz,

CHLOROFORM-*D*) δ 171.06, 169.01, 152.01, 148.28, 143.40, 139.97, 137.87, 134.42, 130.78, 128.82, 128.65, 128.51, 128.01, 127.65, 127.41, 125.80, 124.64, 123.06, 118.93, 117.25, 115.62, 98.48, 78.18, 62.41, 61.95, 56.57, 53.42, 50.46, 13.98, 13.39. HRMS (ESI): Calcd. for $C_{30}H_{29}N_2O_7$ $[M + H]^+$ 529.1969, Found: 529.1987.

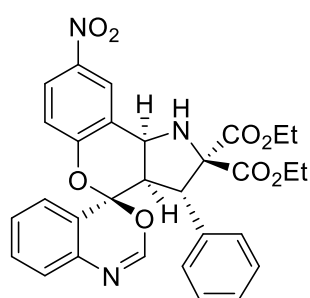


(4c) 253 mg, 93% yield, yellow solid: m. p. 200-202 °C. 1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.55 (d, $J = 2.6$ Hz, 1H), 7.42-7.34 (m, 2H), 7.23-7.17 (m, 4H), 7.11 (dd, $J = 7.4$, 2.2 Hz, 2H), 7.08 (s, 1H), 7.03 (ddd, $J = 8.6$, 6.5, 2.1 Hz, 1H), 6.92-6.89 (m, 1H), 6.83 (d, $J = 8.7$ Hz, 1H), 5.23 (d, $J = 7.9$ Hz, 1H), 4.41 (d, $J = 4.3$ Hz, 1H), 4.26 (dq, $J = 10.9$, 7.1 Hz, 1H), 4.09 (dq, $J = 10.9$, 7.3 Hz, 1H), 3.76 (dq, $J = 10.6$, 7.1 Hz, 1H), 3.58 (dd, $J = 7.9$, 4.3 Hz, 1H), 3.46 (s, 1H), 3.36 (dq, $J = 10.9$, 7.3 Hz, 1H), 1.21 (t, $J = 7.2$ Hz, 3H), 0.73 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 170.93, 168.97, 148.76, 147.58, 139.75, 137.96, 130.91, 129.56, 129.09, 128.51, 128.08, 127.67, 127.43, 126.01, 124.58, 124.54, 122.73, 119.52, 98.45, 77.92, 62.31, 61.86, 55.92, 53.04, 50.45, 13.97, 13.42. HRMS (ESI): Calcd. for $C_{30}H_{28}ClN_2O_6$ $[M + H]^+$ 547.1630, Found: 547.1636.



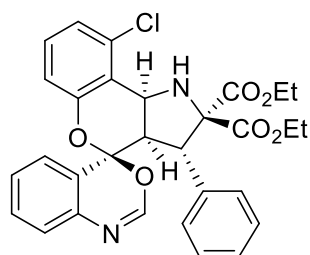
(4d) 265 mg, 90% yield, yellow solid: m. p. 196-198 °C. 1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.74-7.65 (m, 1H), 7.37-7.31 (m, 3H), 7.20-7.17 (m, 3H), 7.14-7.09 (m, 2H), 7.08-6.98 (m, 2H), 6.93-6.88 (m, 1H), 6.77 (dd, $J = 8.6$, 2.1 Hz, 1H), 5.22 (d, $J = 8.0$ Hz, 1H), 4.40 (d, $J = 4.2$ Hz, 1H), 4.25 (dq, $J = 10.7$, 7.1, 1.3 Hz, 1H), 4.09 (dq, $J = 10.8$, 7.1, 1.5 Hz, 1H), 3.75 (dq, $J = 10.7$, 7.2, 1.4 Hz,

1H), 3.57 (dd, $J = 8.1, 4.3$ Hz, 1H), 3.46 (s, 1H), 3.35 (dq, $J = 10.7, 7.2, 1.2$ Hz, 1H), 1.20 (td, $J = 7.1, 1.5$ Hz, 3H), 0.72 (td, $J = 7.2, 1.4$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 170.87, 168.97, 149.32, 147.52, 139.73, 137.97, 132.43, 132.04, 130.90, 128.50, 127.66, 127.42, 126.01, 125.13, 124.54, 122.74, 119.92, 115.43, 98.42, 77.93, 62.29, 61.83, 55.86, 53.07, 50.50, 13.98, 13.42. HRMS (ESI): Calcd. for $\text{C}_{30}\text{H}_{28}\text{BrN}_2\text{O}_6$ $[\text{M} + \text{H}]^+$ 591.1125, Found: 591.1138.



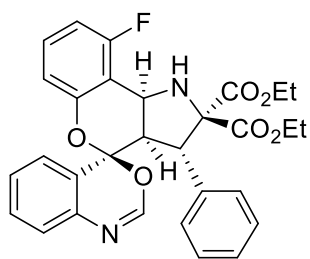
(4e) 236 mg, 85% yield, yellow solid: m. p. 222-224 °C. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 8.50 (d, $J = 2.7$ Hz, 1H), 8.14 (dd, $J = 9.0, 2.7$ Hz, 1H), 7.42-7.36 (m, 2H), 7.23-7.19 (m, 3H), 7.13-7.10 (m, 2H), 7.09-7.04 (m, 2H),

7.00 (d, $J = 8.9$ Hz, 1H), 6.92 (dd, $J = 7.9, 1.3$ Hz, 1H), 5.31 (d, $J = 7.5$ Hz, 1H), 4.43 (d, $J = 4.4$ Hz, 1H), 4.25 (dq, $J = 10.8, 7.1$ Hz, 1H), 4.08 (dq, $J = 10.8, 7.2$ Hz, 1H), 3.79 (dq, $J = 10.6, 7.1$ Hz, 1H), 3.65-3.61 (m, 2H), 3.37 (dq, $J = 10.7, 7.2$ Hz, 1H), 1.20 (t, $J = 7.1$ Hz, 3H), 0.73 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 170.93, 168.86, 155.44, 147.09, 143.22, 139.43, 137.87, 131.24, 128.60, 128.44, 127.87, 127.58, 126.22, 125.60, 125.26, 124.51, 124.22, 122.02, 118.98, 98.82, 77.63, 62.39, 62.01, 55.54, 52.68, 50.28, 13.94, 13.40. HRMS (ESI): Calcd. for $\text{C}_{30}\text{H}_{28}\text{N}_3\text{O}_8$ $[\text{M} + \text{H}]^+$ 558.1871, Found: 558.1885.

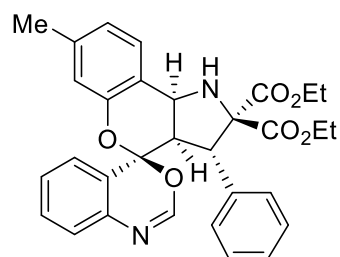


(4f) 253 mg, 93% yield, yellow solid: m. p. 159-161 °C. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.41-7.36 (m, 2H), 7.23-7.15 (m, 6H), 7.13-7.08 (m, 2H), 7.05-6.99 (m, 1H),

6.90-6.86 (m, 1H), 6.81 (dd, $J = 7.0, 2.4$ Hz, 1H), 5.41 (d, $J = 7.9$ Hz, 1H), 4.45 (d, $J = 3.2$ Hz, 1H), 4.30 (dq, $J = 10.7, 7.1$ Hz, 1H), 4.25 (s, 1H), 4.04 (dq, $J = 10.8, 7.2$ Hz, 1H), 3.76 (dq, $J = 10.6, 7.2$ Hz, 1H), 3.52 (dd, $J = 7.8, 3.2$ Hz, 1H), 3.33 (dq, $J = 10.6, 7.2$ Hz, 1H), 1.18 (t, $J = 7.1$ Hz, 3H), 0.71 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 171.73, 168.91, 151.52, 148.10, 140.47, 138.34, 135.07, 130.93, 130.03, 128.58, 127.58, 127.38, 126.05, 124.68, 123.77, 122.30, 121.60, 116.88, 97.79, 77.35, 62.23, 61.84, 54.83, 51.46, 49.71, 13.91, 13.41. HRMS (ESI): Calcd. for $\text{C}_{30}\text{H}_{28}\text{ClN}_2\text{O}_6$ $[\text{M} + \text{H}]^+$ 547.1630, Found: 547.1632.

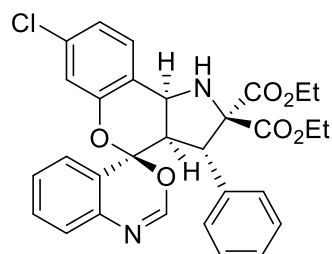


(4g) 238 mg, 90% yield, yellow oil. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.37-7.34 (m, 2H), 7.22-7.15 (m, 5H), 7.09 (dd, $J = 7.3, 2.3$ Hz, 2H), 6.98 (ddd, $J = 7.8, 4.9, 3.7$ Hz, 1H), 6.87-6.81 (m, 2H), 6.69 (d, $J = 8.3$ Hz, 1H), 5.45 (d, $J = 8.2$ Hz, 1H), 4.42 (d, $J = 3.8$ Hz, 1H), 4.27 (dq, $J = 10.8, 7.1$ Hz, 1H), 4.04 (dq, $J = 10.7, 7.2$ Hz, 1H), 3.84 (s, 1H), 3.77 (dq, $J = 10.7, 7.1$ Hz, 1H), 3.55 (dd, $J = 8.1, 3.7$ Hz, 1H), 3.33 (dq, $J = 10.6, 7.2$ Hz, 1H), 1.18 (t, $J = 7.1$ Hz, 3H), 0.70 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 171.60, 168.89, 161.80 (d, $J = 246.3$ Hz, ArF), 148.00, 140.19, 138.20, 130.90, 129.89 (d, $J = 10.2$ Hz, ArF), 128.84, 128.54, 127.44 (d, $J = 14.1$ Hz, ArF), 126.00, 124.74, 122.30, 113.74 (d, $J = 3.1$ Hz, ArF), 112.05 (d, $J = 21.5$ Hz, ArF), 109.46 (d, $J = 20.9$ Hz, ArF), 98.04, 77.42, 62.17, 61.78, 51.81, 51.48, 49.47, 13.91, 13.41. HRMS (ESI): Calcd. for $\text{C}_{30}\text{H}_{28}\text{FN}_2\text{O}_6$ $[\text{M} + \text{H}]^+$ 531.1926, Found: 531.1911.



(4h) 236 mg, 90% yield, yellow solid: m. p. 175-177 °C.

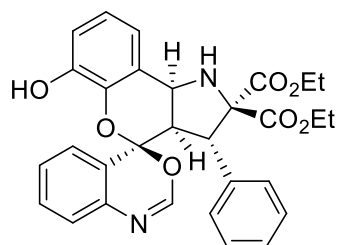
¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.44 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.36-7.34 (m, 2H), 7.21-7.09 (m, 6H), 7.04-6.99 (m, 1H), 6.92 (ddd, *J* = 12.3, 8.1, 1.5 Hz, 2H), 6.71 (d, *J* = 2.1 Hz, 1H), 5.23 (d, *J* = 7.6 Hz, 1H), 4.41 (d, *J* = 3.7 Hz, 1H), 4.24 (dq, *J* = 10.8, 7.1, 1.3 Hz, 1H), 4.09 (dq, *J* = 10.8, 7.1, 1.3 Hz, 1H), 3.73 (dq, *J* = 10.7, 7.1, 1.4 Hz, 1H), 3.55 (dd, *J* = 7.8, 3.8 Hz, 1H), 3.40-3.31 (m, 2H), 2.29 (d, *J* = 1.9 Hz, 3H), 1.19 (td, *J* = 7.1, 1.4 Hz, 3H), 0.72 (td, *J* = 7.1, 1.4 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 170.94, 169.11, 149.94, 147.86, 140.13, 139.83, 138.09, 130.69, 129.22, 128.63, 128.55, 128.43, 127.57, 127.29, 125.91, 124.61, 124.03, 123.16, 119.50, 118.38, 98.52, 78.29, 62.18, 61.69, 56.29, 53.50, 50.65, 21.30, 13.98, 13.43. HRMS (ESI): Calcd. for C₃₁H₃₁N₂O₆ [M + H]⁺ 527.2177, Found: 527.2170.



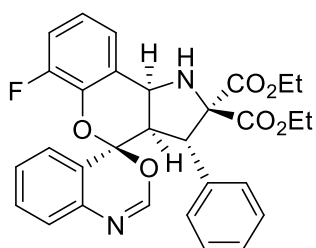
(4i) 232 mg, 85% yield, yellow solid: m. p. 169-171 °C.

¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.48 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.40-7.34 (m, 2H), 7.21-7.17 (m, 3H), 7.13-7.08 (m, 4H), 7.05-7.00 (m, 1H), 6.90 (dd, *J* = 8.3, 1.6 Hz, 2H), 5.23 (d, *J* = 7.8 Hz, 1H), 4.40 (d, *J* = 4.0 Hz, 1H), 4.25 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.09 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.74 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.57 (dd, *J* = 7.8, 4.0 Hz, 1H), 3.43 (s, 1H), 3.34 (dq, *J* = 10.7, 7.2 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.72 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 170.94, 168.96, 150.82, 147.50, 139.83, 138.00, 134.69, 130.93, 130.36, 128.72, 128.50, 127.69, 127.42, 126.05, 124.57,

123.42, 122.57, 121.42, 118.40, 98.48, 78.03, 62.28, 61.82, 55.86, 53.19, 50.42, 13.97, 13.41. HRMS (ESI): Calcd. for C₃₀H₂₈ClN₂O₆ [M + H]⁺ 547.1630, Found: 547.1637.

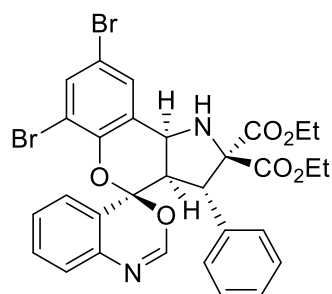


(4j) 227mg, 86% yield, yellow oil. ¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.21-7.14 (m, 5H), 7.11-7.05 (m, 4H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.94 (ddd, *J* = 8.5, 5.6, 3.0 Hz, 1H), 6.91-6.84 (m, 2H), 5.29 (d, *J* = 7.9 Hz, 1H), 4.36 (d, *J* = 4.0 Hz, 1H), 4.23 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.04 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.73 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.60 (dd, *J* = 7.8, 4.0 Hz, 1H), 3.32 (dq, *J* = 10.7, 7.2 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.70 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 171.07, 168.89, 147.99, 146.06, 139.95, 137.64, 137.47, 130.90, 128.46, 127.49, 127.34, 125.67, 124.72, 123.42, 123.20, 122.25, 119.99, 115.69, 98.51, 77.91, 62.21, 61.74, 56.19, 53.07, 50.64, 13.94, 13.40. HRMS (ESI): Calcd. for C₃₀H₂₉N₂O₇ [M + H]⁺ 529.1969, Found: 529.1968.



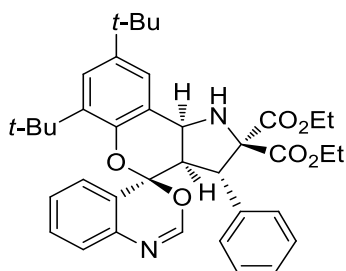
(4k) 233 mg, 88% yield, yellow oil. ¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.41-7.32 (m, 3H), 7.20-7.16 (m, 3H), 7.12-7.07 (m, 3H), 7.06-6.98 (m, 3H), 6.93-6.91 (m, 1H), 5.29 (d, *J* = 7.9 Hz, 1H), 4.40 (d, *J* = 4.0 Hz, 1H), 4.25 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.17 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.75 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.59 (dd, *J* = 7.9, 4.1 Hz, 1H), 3.48 (s, 1H), 3.34 (dq, *J* = 10.7, 7.2 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.71 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 171.07, 168.92, 152.24 (d, *J* = 248.0 Hz, ArF), 147.38, 139.81, 138.03, 130.92, 128.74 (d, *J* = 6.2 Hz, ArF), 128.49, 128.46, 127.68, 127.41, 126.04, 125.46, 124.83, 124.23 (d, *J* = 3.7 Hz, ArF),

122.79, 122.72, 122.30, 116.05 (d, $J = 18.1$ Hz, ArF), 98.26, 77.84, 62.27, 61.83, 55.90 (d, $J = 2.8$ Hz), 53.07, 50.73, 13.96, 13.40. HRMS (ESI): Calcd. for $C_{30}H_{28}FN_2O_6$ $[M + H]^+$ 531.1926, Found: 531.1792.



(4l) 297 mg, 89% yield, yellow solid: m. p. 220-222 °C.

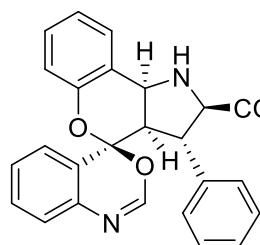
1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.67-7.58 (m, 2H), 7.39-7.32 (m, 2H), 7.18 (dd, $J = 5.2, 1.9$ Hz, 3H), 7.10-7.07 (m, 2H), 7.06-6.99 (m, 2H), 6.95-6.88 (m, 1H), 5.23 (d, $J = 8.1$ Hz, 1H), 4.38 (d, $J = 4.8$ Hz, 1H), 4.24 (dq, $J = 10.8, 7.1$ Hz, 1H), 4.09 (dq, $J = 10.8, 7.1$ Hz, 1H), 3.76 (dq, $J = 10.7, 7.1$ Hz, 1H), 3.65 (dd, $J = 8.1, 4.8$ Hz, 1H), 3.48 (s, 1H), 3.35 (dq, $J = 10.6, 7.1$ Hz, 1H), 1.19 (t, $J = 7.1$ Hz, 3H), 0.71 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 170.90, 168.89, 147.01, 146.48, 139.31, 137.94, 135.14, 131.01, 130.95, 128.52, 128.47, 127.71, 127.50, 127.04, 126.06, 124.65, 122.34, 115.43, 113.40, 98.70, 77.74, 62.31, 61.93, 55.97, 52.70, 50.65, 13.99, 13.41. HRMS (ESI): Calcd. for $C_{30}H_{27}Br_2N_2O_6$ $[M + H]^+$ 669.0230, Found: 669.0235.



(4m) 255 mg, 82% yield, yellow solid: m. p. 147-149 °C.

1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.39-7.33 (m, 3H), 7.28 (d, $J = 2.4$ Hz, 1H), 7.21-7.16 (m, 4H), 7.11 (dd, $J = 7.4, 2.2$ Hz, 2H), 7.02-6.98 (m, 1H), 6.92 (d, $J = 7.9$ Hz, 1H), 5.31 (d, $J = 8.0$ Hz, 1H), 4.41 (d, $J = 3.7$ Hz, 1H), 4.27 (dq, $J = 10.8, 7.1$ Hz, 1H), 4.08 (dq, $J = 10.8, 7.1$ Hz, 1H), 3.75 (dq, $J = 10.7, 7.1$ Hz, 1H), 3.55 (dd, $J = 8.0, 3.7$ Hz, 1H), 3.47 (s, 1H), 3.34 (dq, $J = 10.7, 7.2$ Hz, 1H), 1.34 (s, 9H), 1.19 (m, 12H),

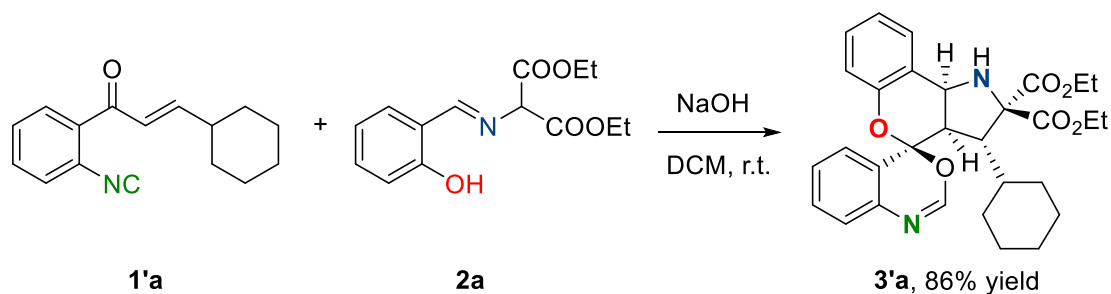
Hz, 1H), 3.34 (s, 1H), 2.95 (dd, $J = 7.1, 2.6$ Hz, 1H), 2.83 (dd, $J = 4.8, 2.6$ Hz, 1H), 1.74-1.65 (m, 1H), 1.60 (d, $J = 11.5$ Hz, 2H), 1.51 (t, $J = 15.6$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.14-1.00 (m, 3H), 0.97-0.88 (m, 1H), 0.68-0.54 (m, 1H), 0.51-0.42 (m, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 171.75, 170.44, 150.12, 147.77, 137.99, 130.80, 130.01, 129.41, 127.56, 126.58, 125.76, 123.23, 122.78, 121.73, 117.81, 99.44, 75.83, 62.26, 62.14, 56.27, 54.25, 47.96, 38.34, 33.51, 30.12, 26.90, 26.68, 26.20, 14.15, 14.04. HRMS (ESI): Calcd. for $\text{C}_{30}\text{H}_{35}\text{N}_2\text{O}_6$ [$\text{M} + \text{H}$] $^+$ 519.2490, Found: 519.2494.



(6a) 204 mg, 93% yield, red solid: m. p. 164-166 °C. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.65 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.45-7.36 (m, 2H), 7.29-7.21 (m, 4H), 7.19 (s, 1H), 7.16-7.09 (m, 2H), 6.99-6.95 (m, 3H), 6.91 (dd, $J = 8.2, 1.2$ Hz, 1H), 4.68 (d, $J = 7.3$ Hz, 1H), 4.17-4.06 (m, 2H), 3.99 (d, $J = 7.4$ Hz, 1H), 3.30 (ddd, $J = 15.5, 7.4, 3.4$ Hz, 2H), 3.14 (s, 1H), 1.14 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 172.24, 150.33, 147.79, 142.98, 137.97, 130.90, 130.13, 129.62, 128.97, 127.83, 127.24, 127.13, 125.92, 125.14, 122.99, 122.89, 121.88, 118.03, 98.83, 69.35, 61.35, 57.91, 55.17, 53.64, 14.25. HRMS (ESI): Calcd. for $\text{C}_{27}\text{H}_{25}\text{N}_2\text{O}_4$ [$\text{M} + \text{H}$] $^+$ 441.1809, Found: 441.1818.

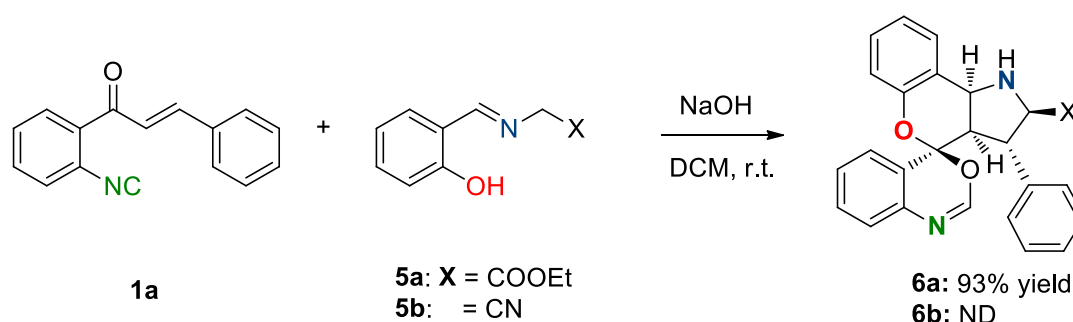
4. Synthetic applications

a) Reaction with substituted isocyanide 1'a



Under air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with isocyanide **1'a** (0.5 mmol, 119.5 mg), *o*-hydroxy aromatic aldimine **2a** (0.6 mmol, 167.4 mg) and NaOH (1 mmol, 40 mg) in 5 mL of DCM at room temperature. After completion of the reaction, the reaction mixture was concentrated under vacuum. The residue was purified by thin layer chromatography [eluant: petroleum ether/ethyl acetate = 2 : 1] to afford the desired product **3'a**. 207 mg, 86% yield, yellow solid.

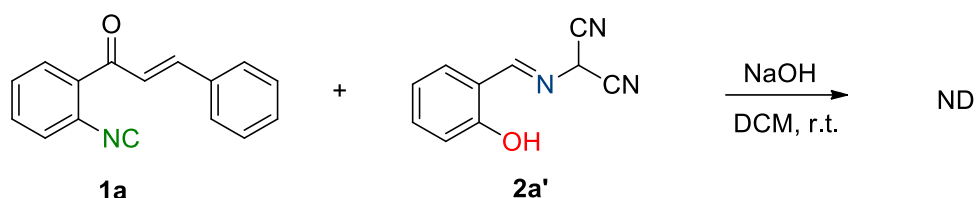
b) Reaction with other aldimine esters



Under air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with *o*-enoyl arylisocyanide **1a** (0.5 mmol, 116.5 mg), aldimine ester **5a** (0.6 mmol, 124.2 mg) and NaOH (1 mmol, 40 mg) in 5 mL of DCM at room temperature. After completion of the reaction, the reaction mixture was concentrated

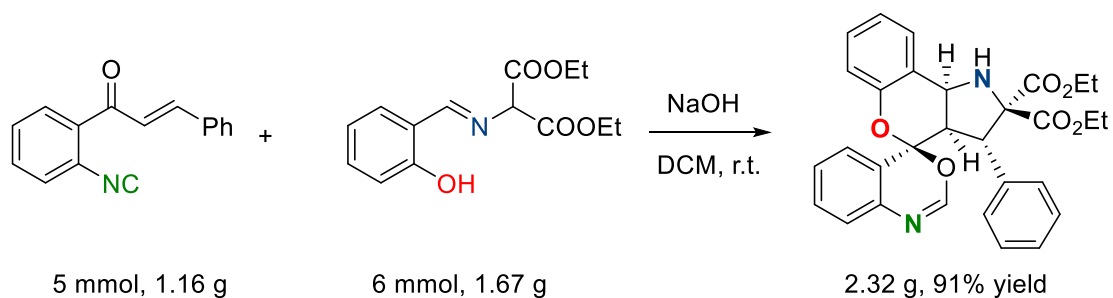
under vacuum. The residue was purified by thin layer chromatography [eluant: petroleum ether/ethyl acetate = 2 : 1] to afford the desired product **6a**. 204.6 mg, 93% yield, yellow solid.

c) Reaction with derivative of aldimine ester



Under air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with *o*-enoyl arylisocyanide **1a** (0.5 mmol, 116.5 mg), derivative of aldimine ester **2a'** (0.6 mmol, 92.5 mg) and NaOH (1 mmol, 40 mg) in 5 mL of DCM at room temperature. After completion of the reaction, the reaction mixture was concentrated under vacuum.

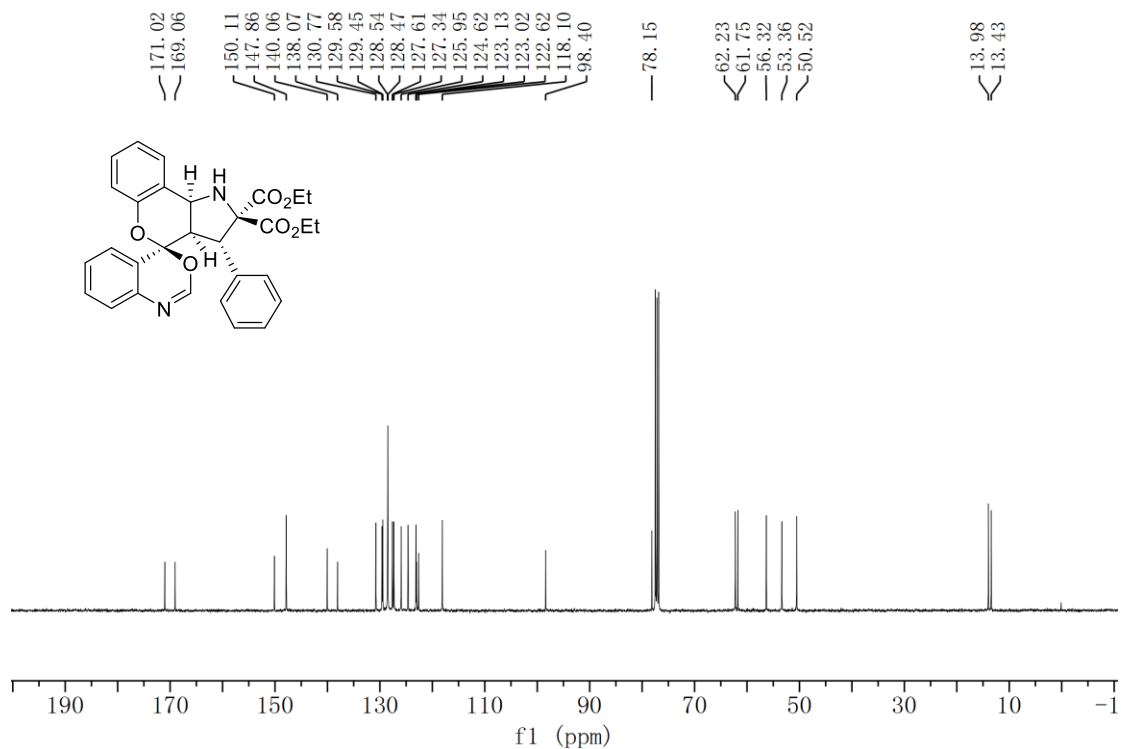
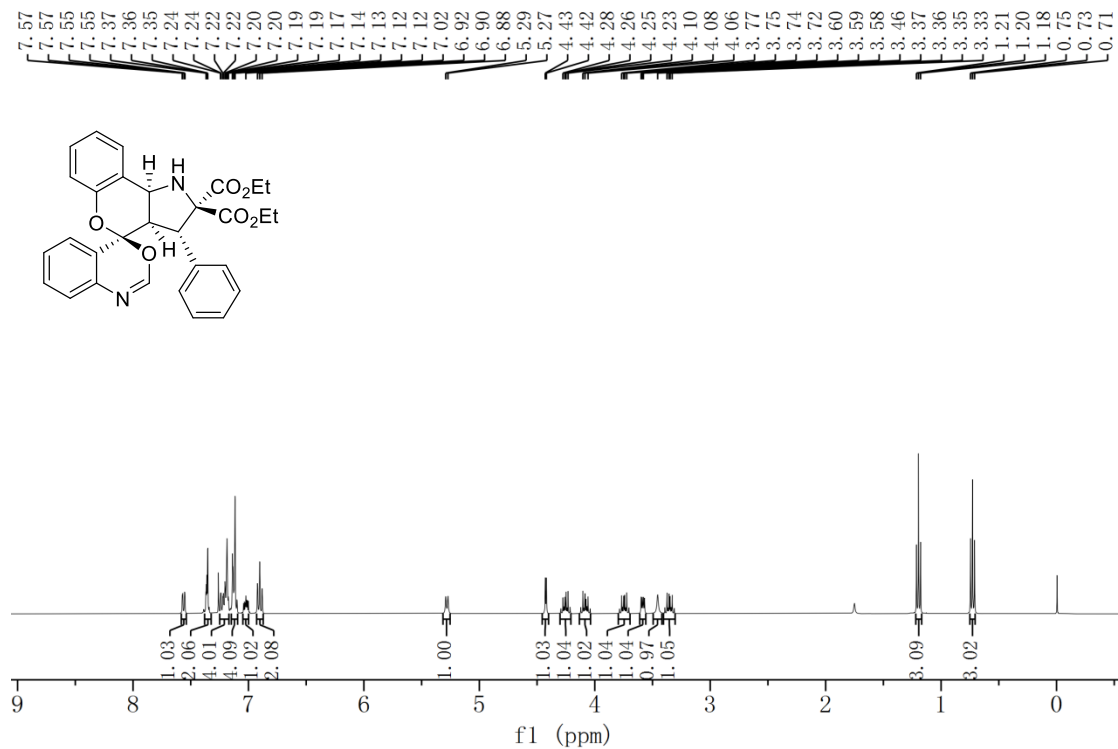
d) Gram-scale reaction



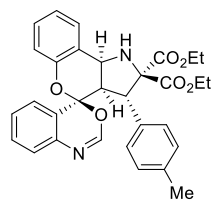
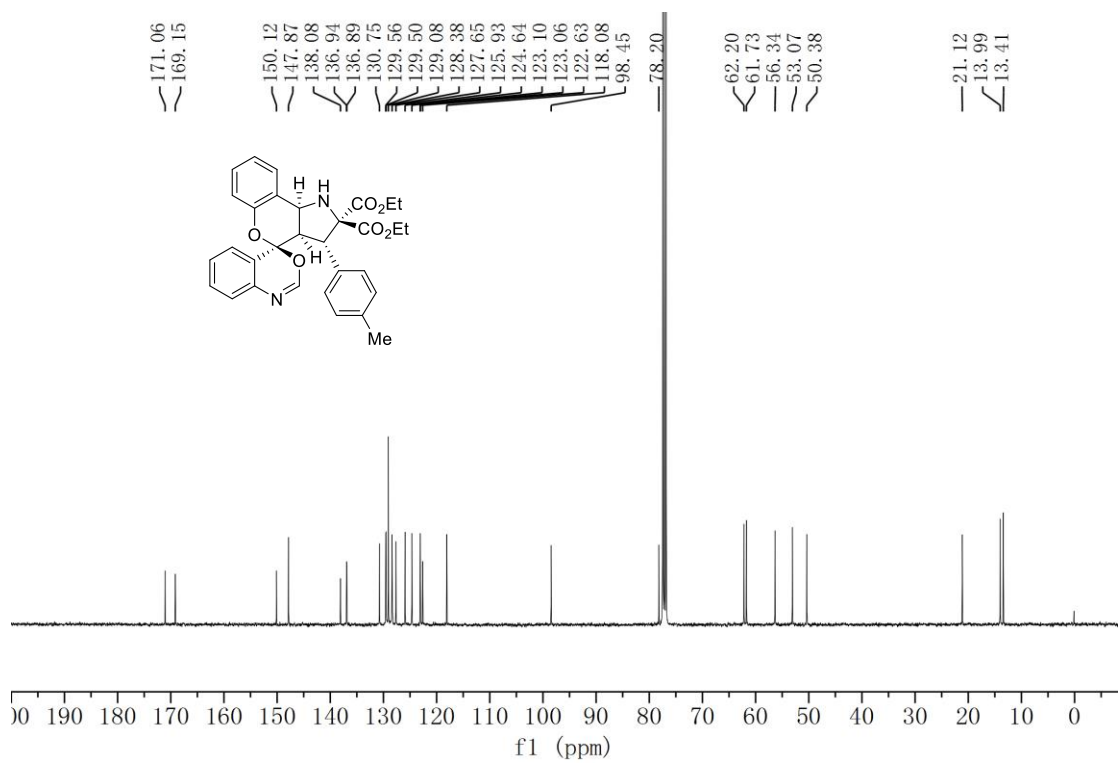
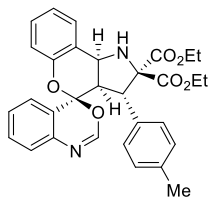
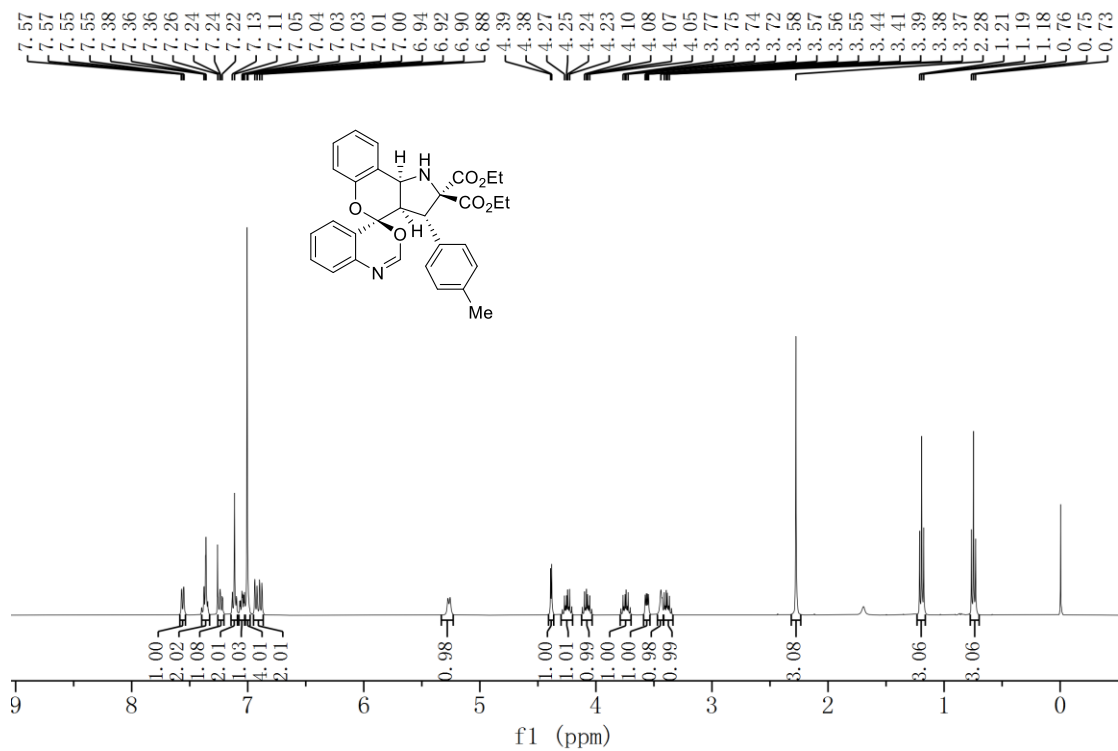
Under air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with *o*-enoyl arylisocyanide **1a** (5 mmol, 1.16 g), *o*-hydroxy aromatic aldimine **2a** (6 mmol, 1.67 g) and NaOH (10 mmol, 0.4 g) in 50 mL of DCM at room temperature. After completion of the reaction, the reaction mixture was concentrated under vacuum. The residue was purified by recrystallization to afford the desired product **3a**. 2.32 g, 91% yield, yellow solid.

5. ¹H NMR and ¹³C NMR Spectra of All Compounds

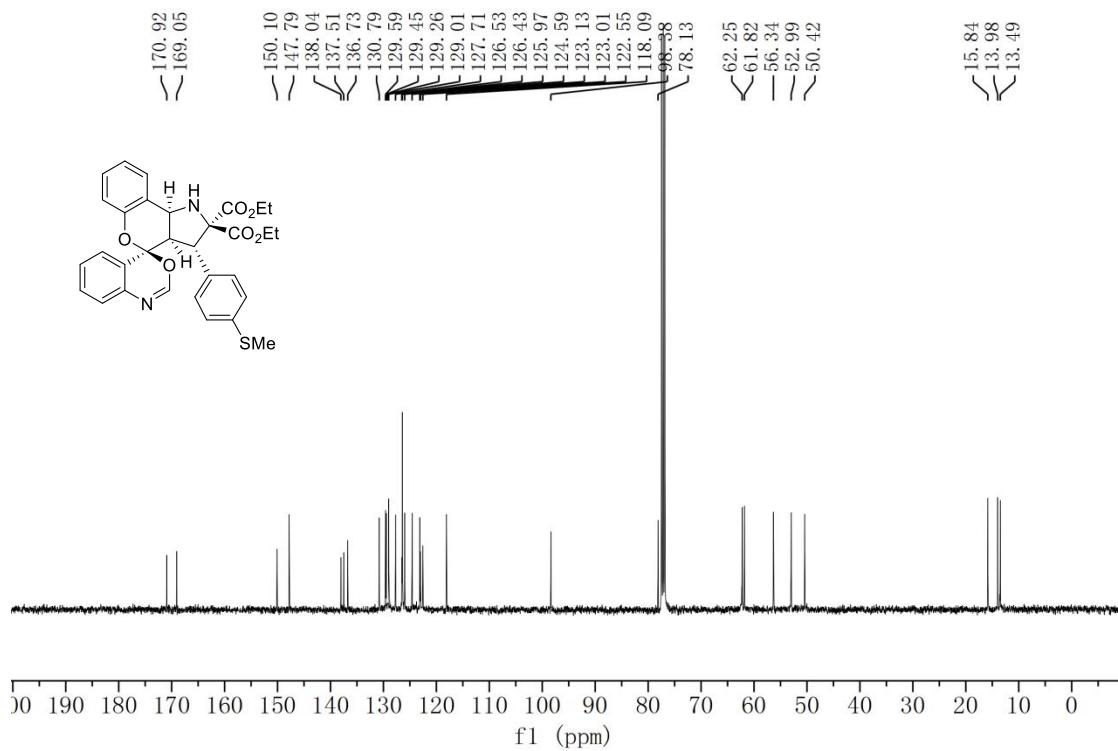
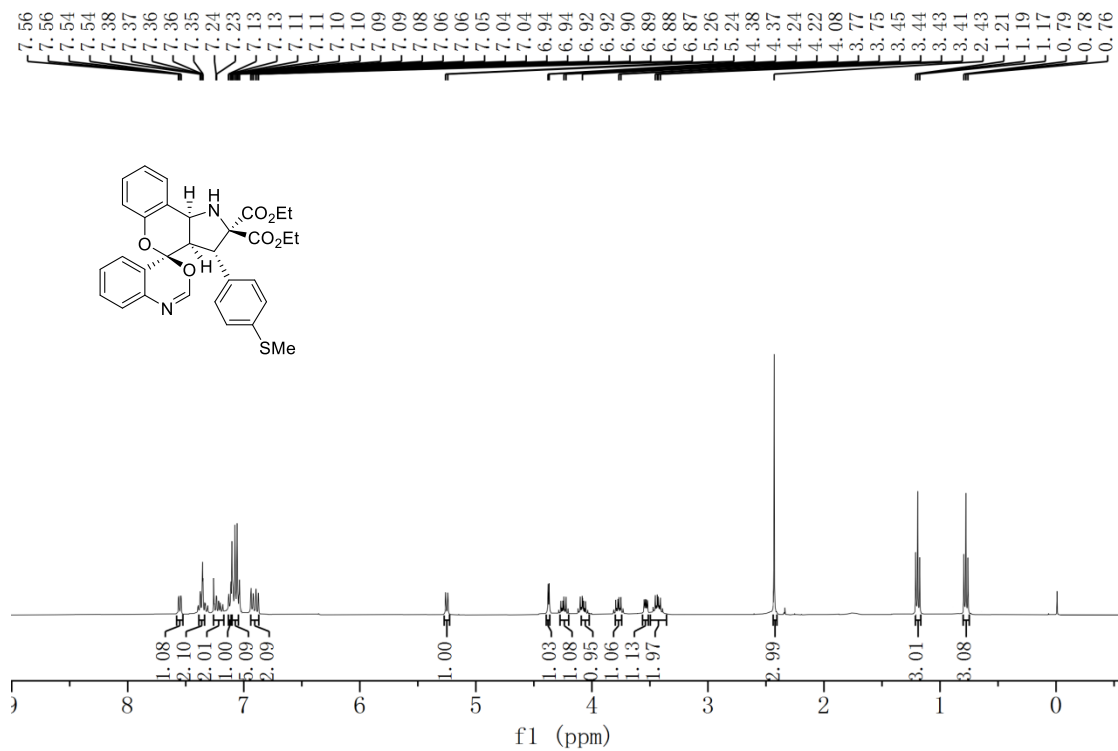
Compound 3a



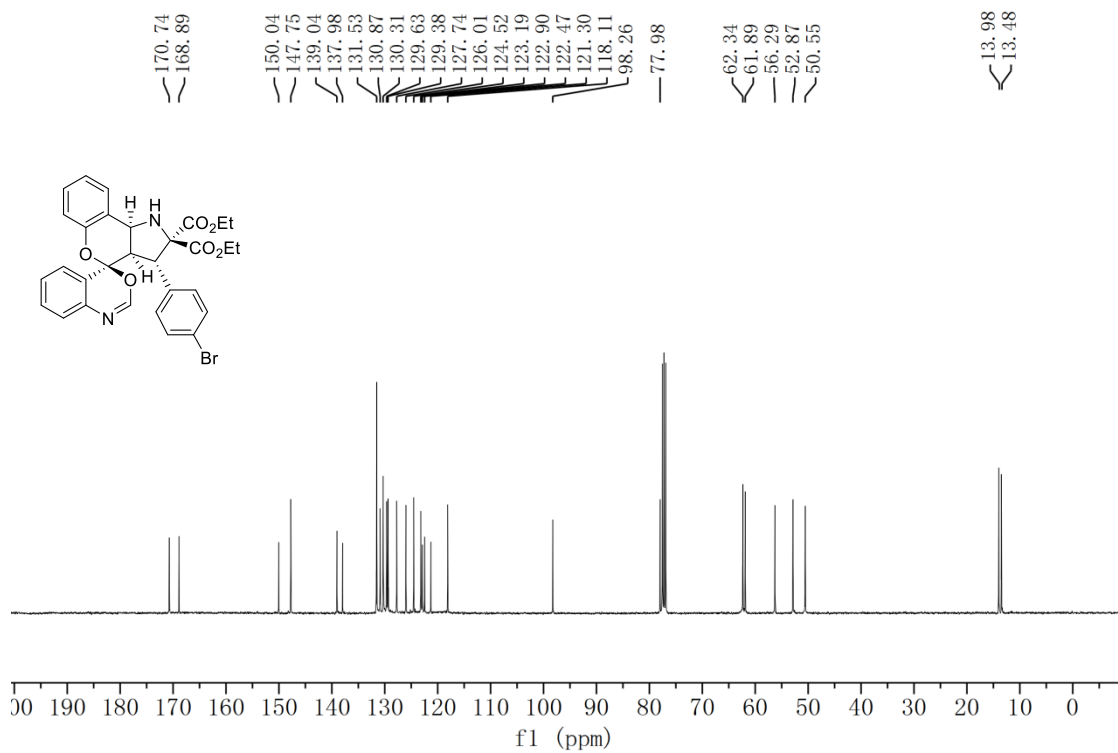
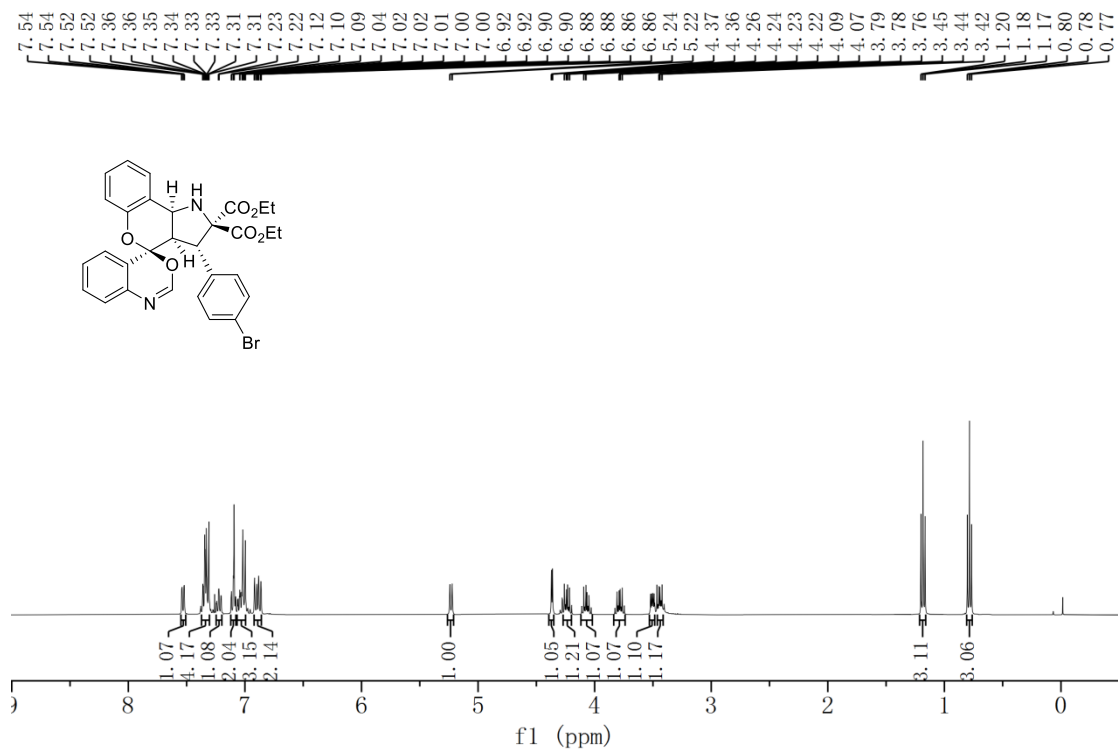
Compound 3b



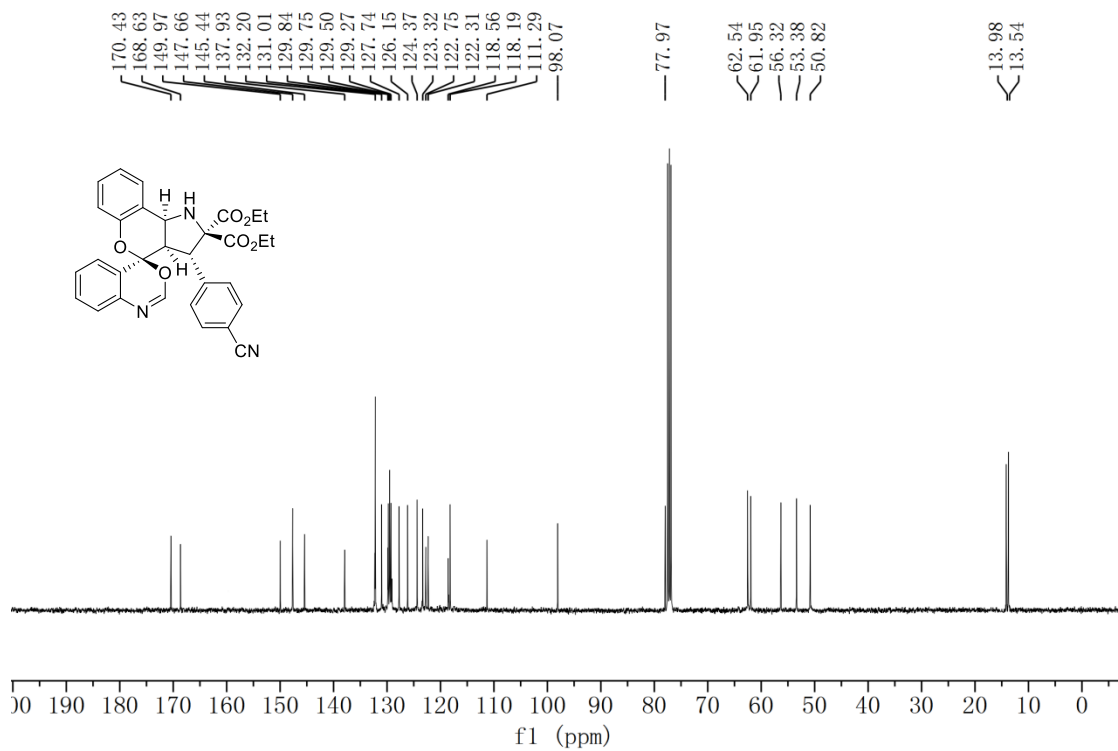
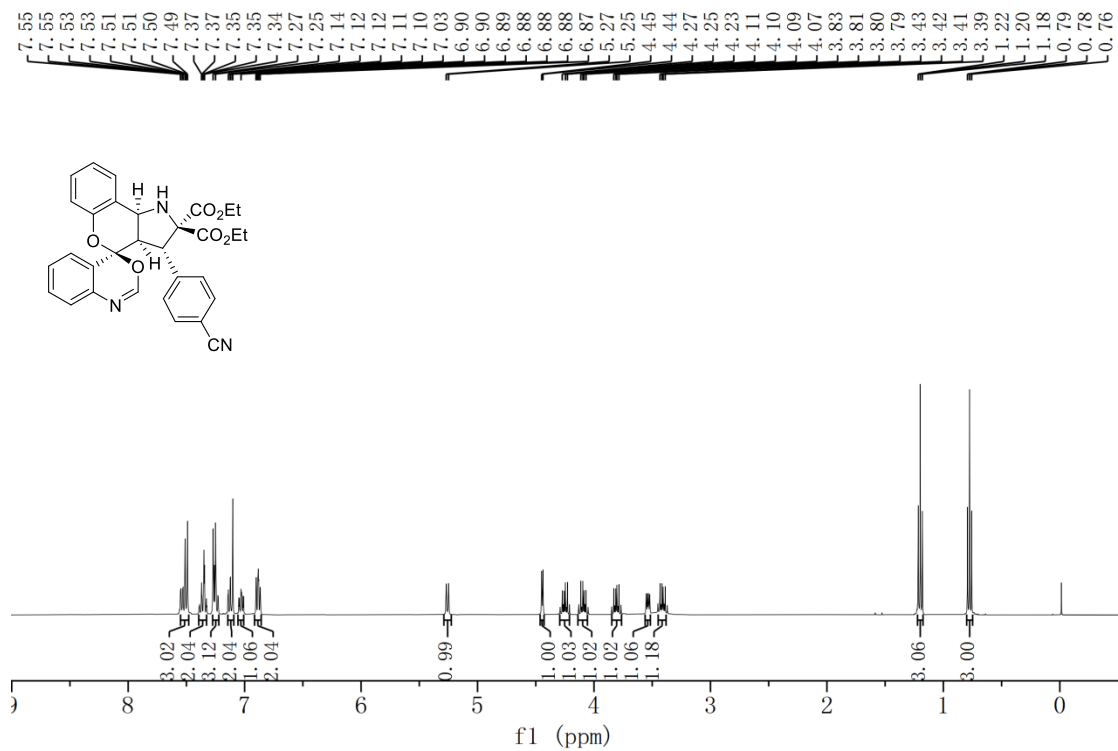
Compound 3c



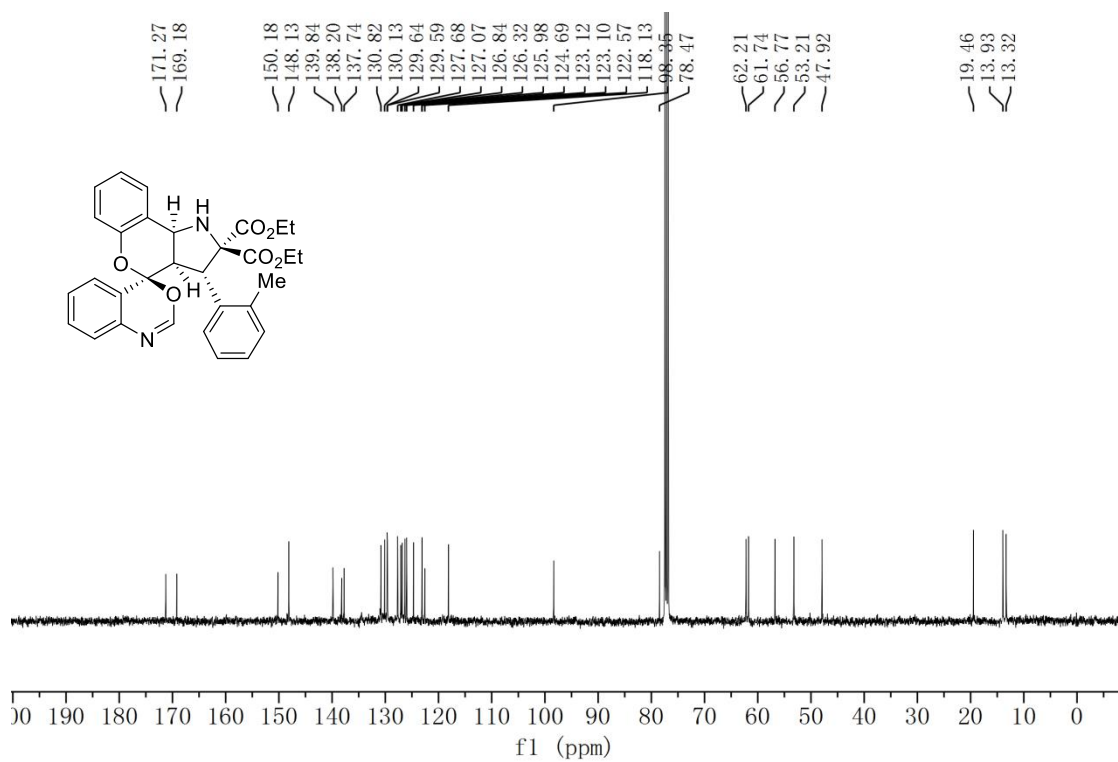
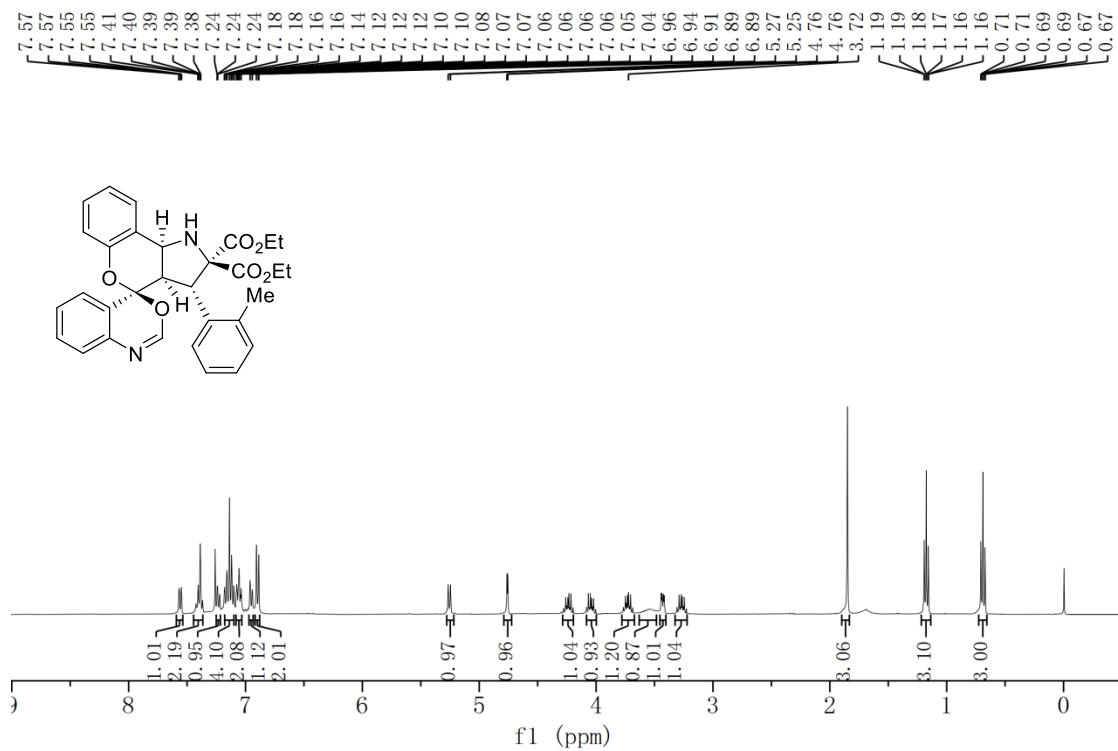
Compound 3d



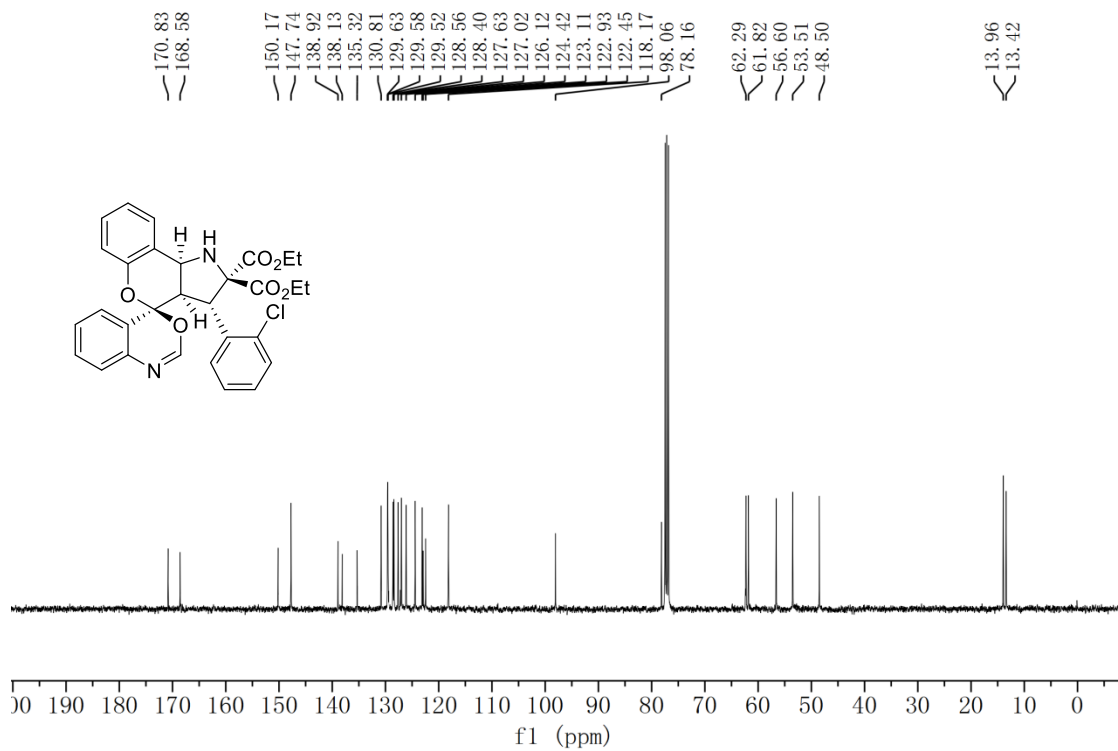
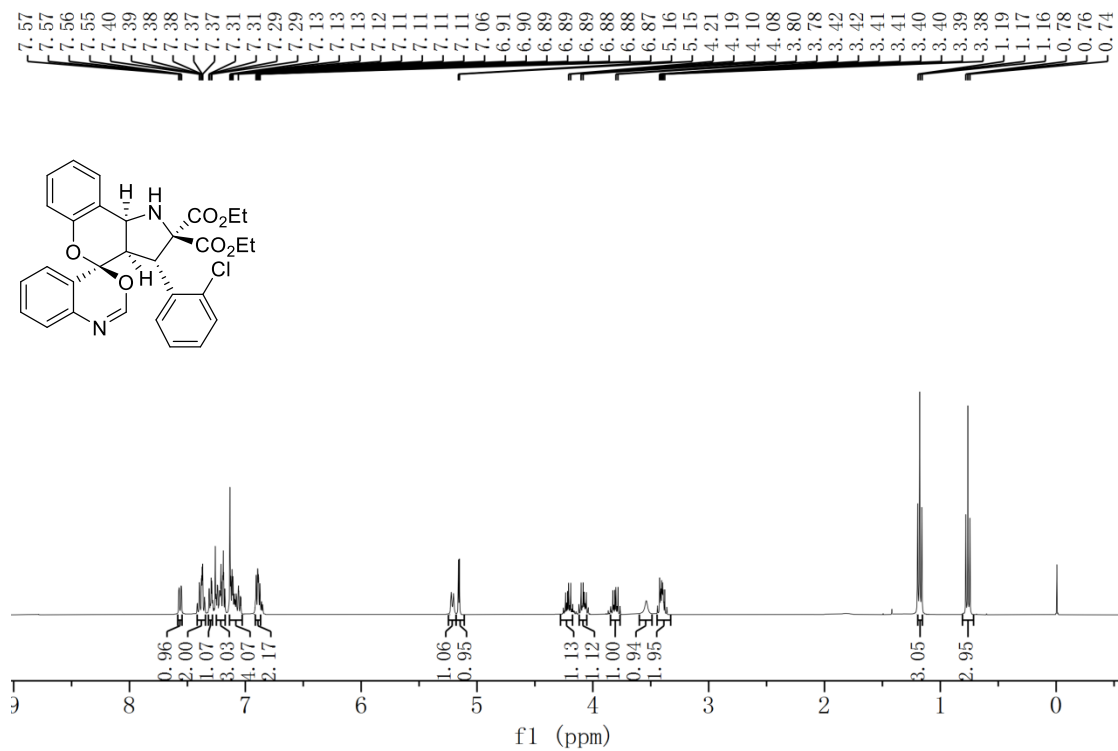
Compound 3e



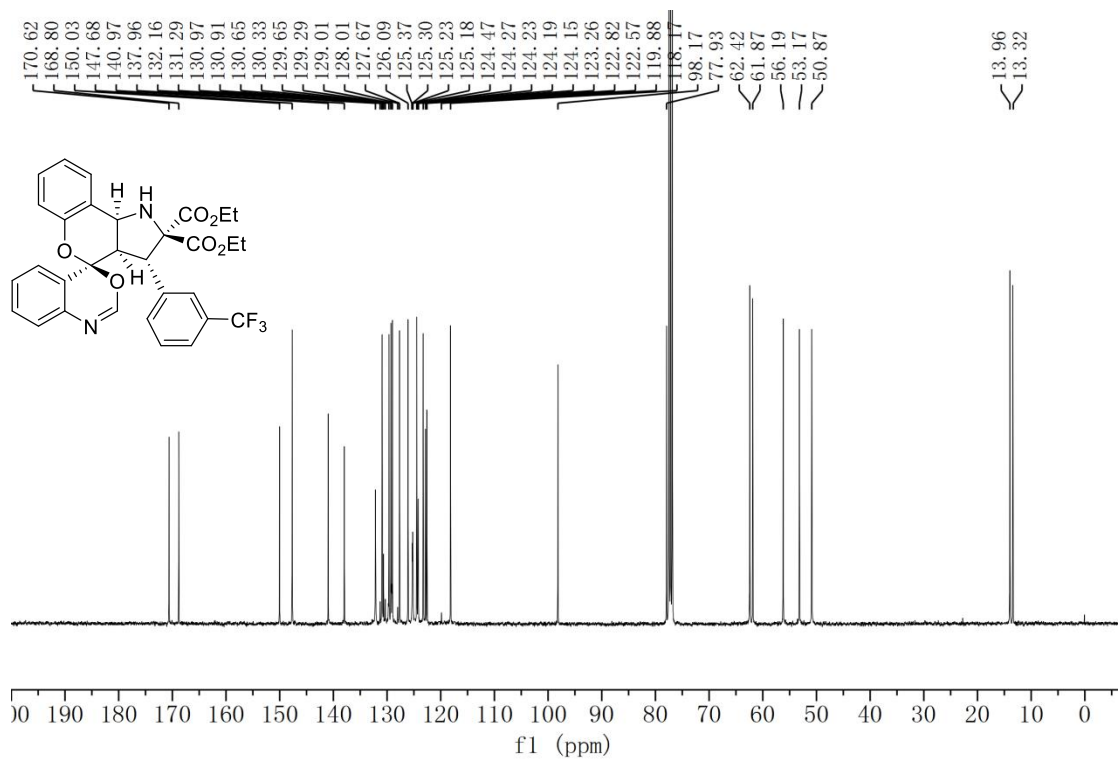
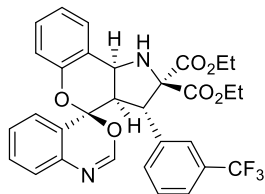
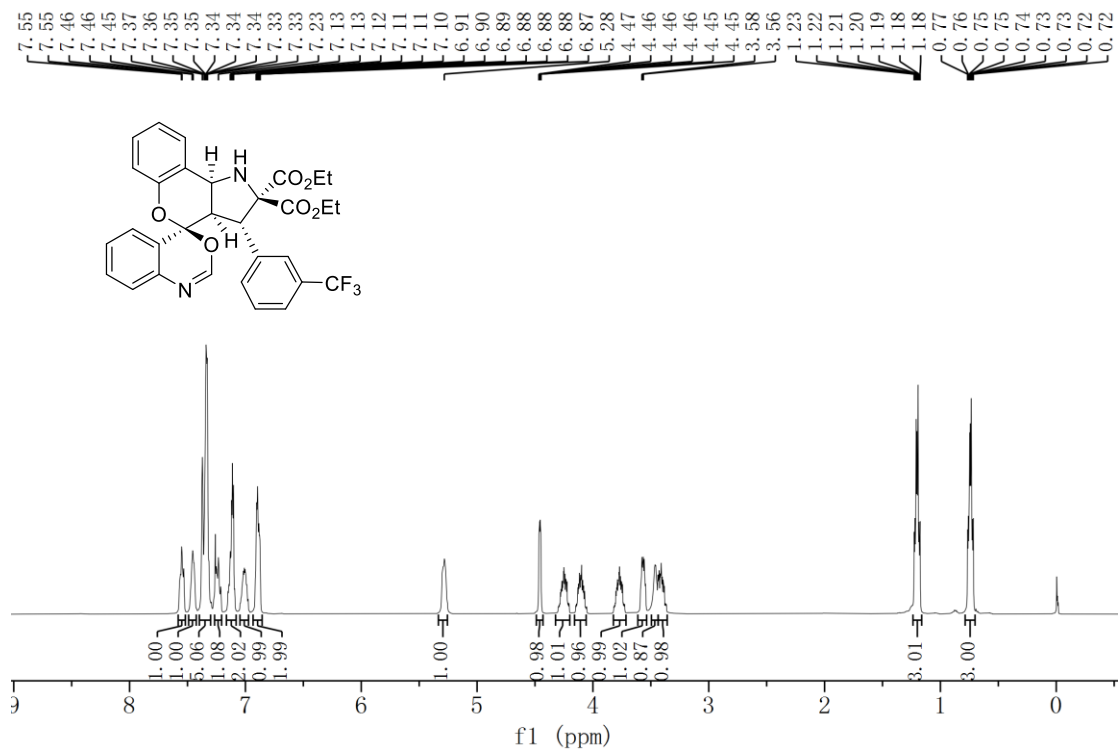
Compound 3f



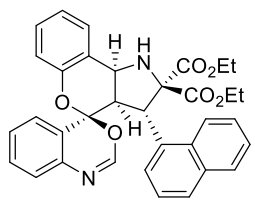
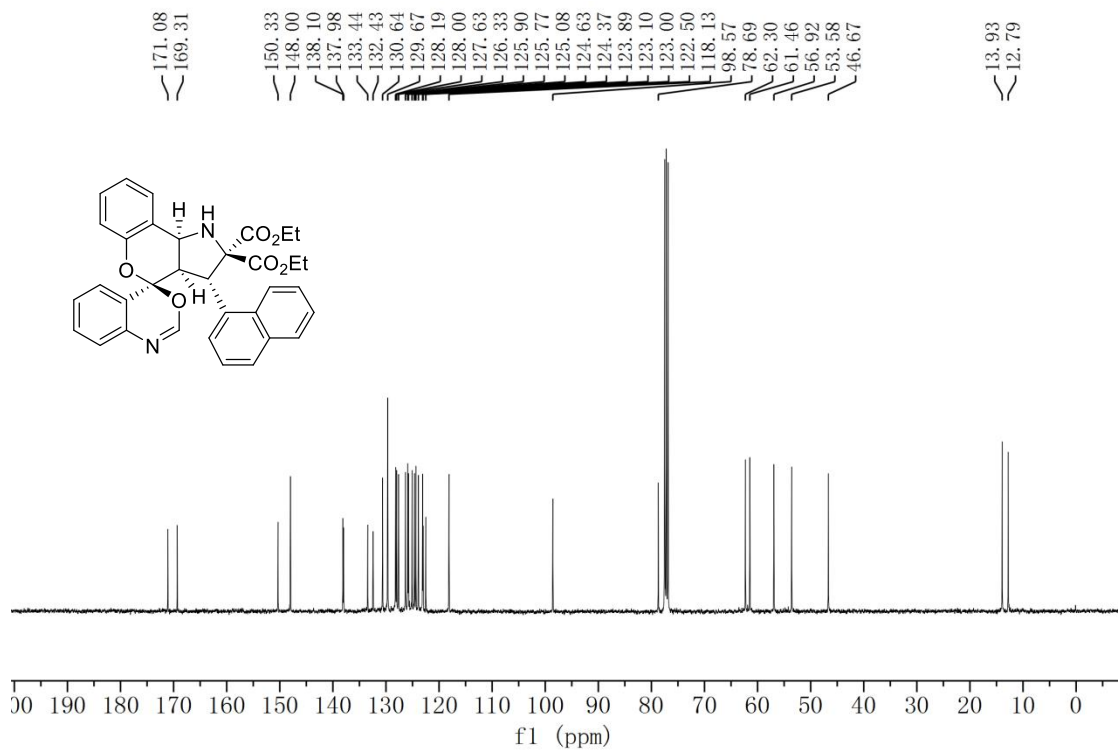
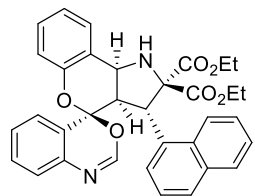
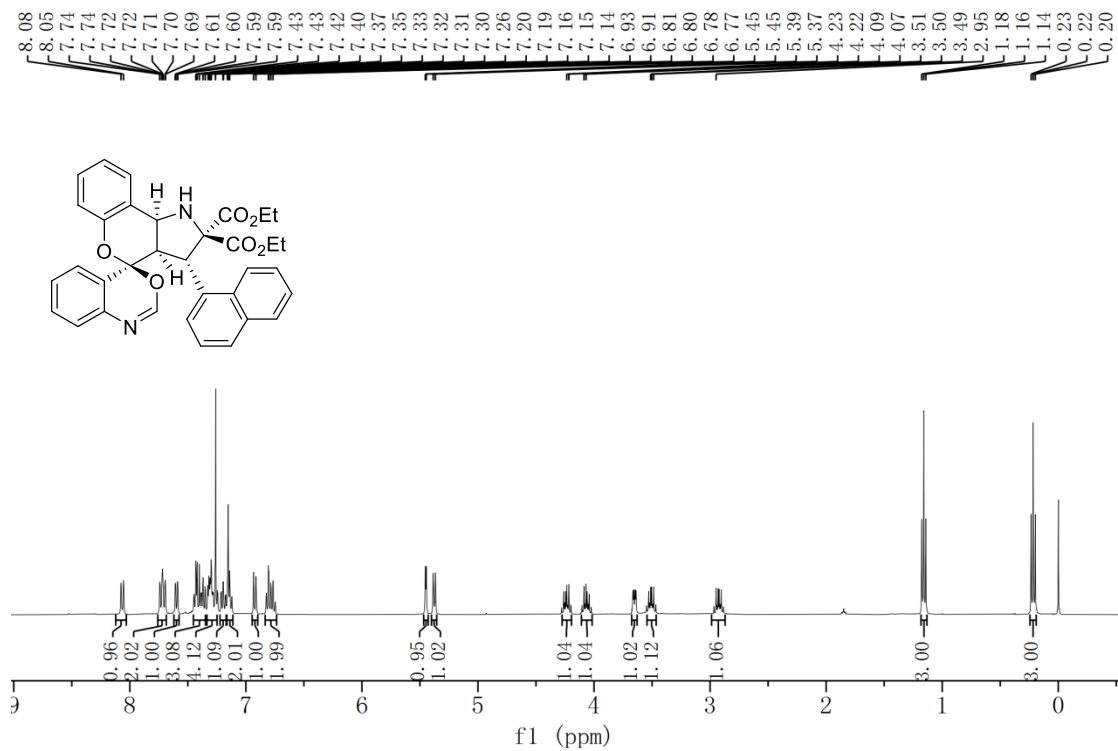
Compound 3g



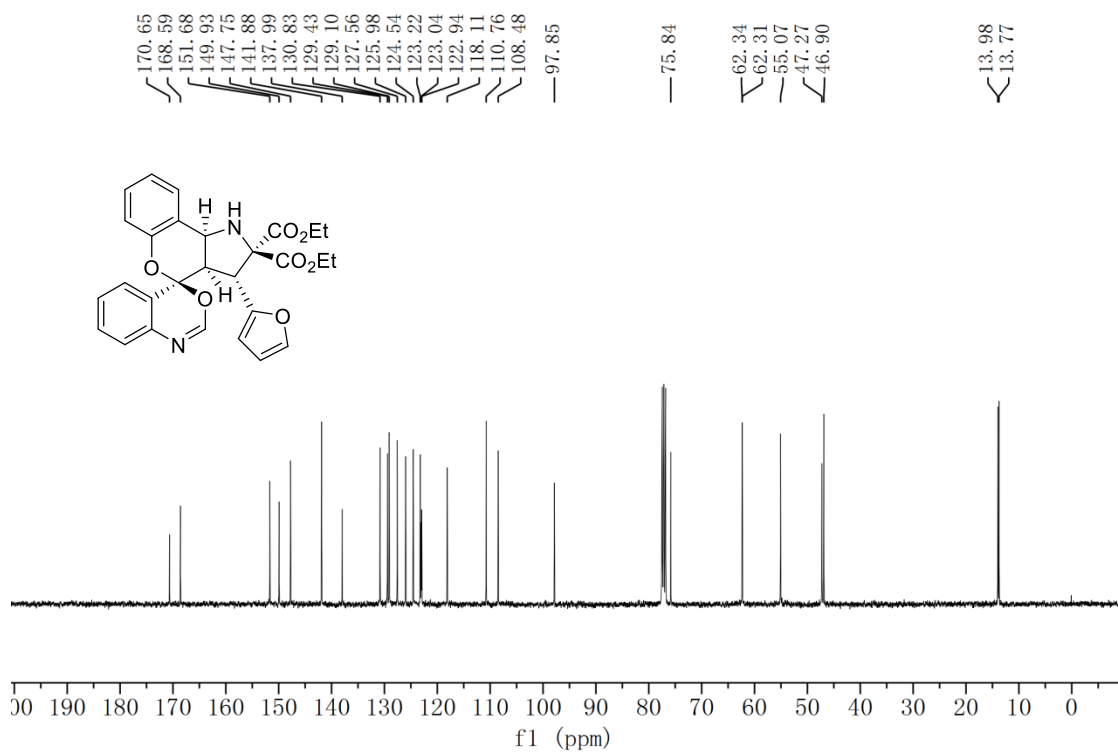
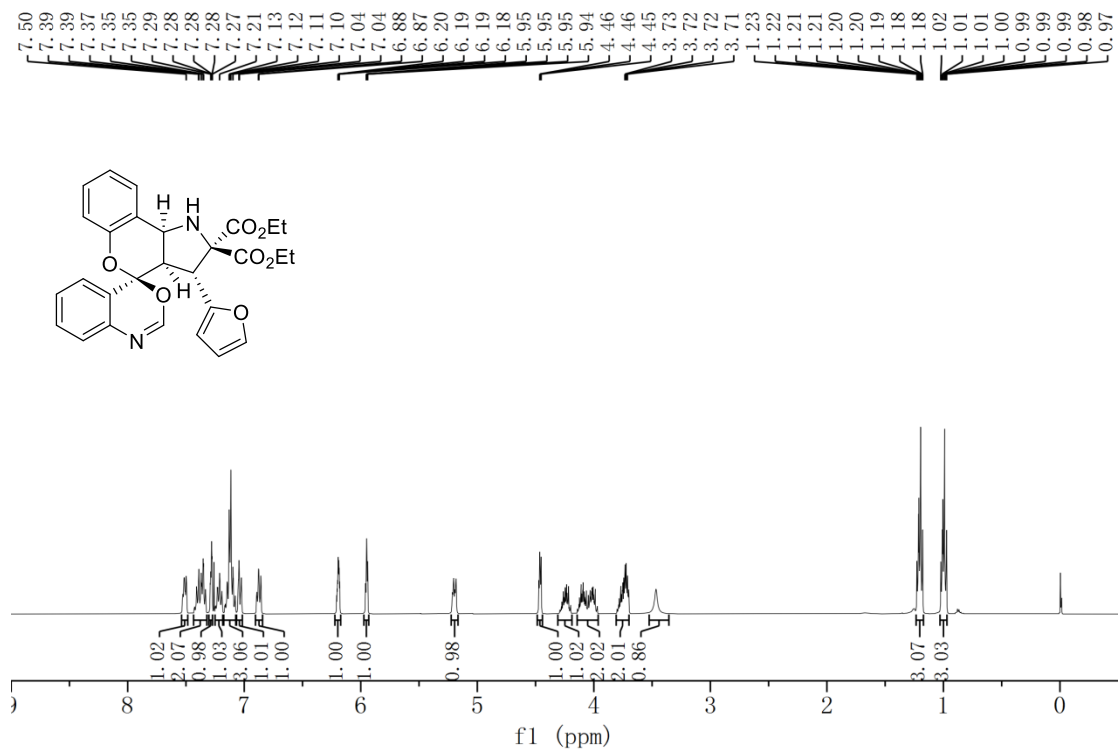
Compound 3i



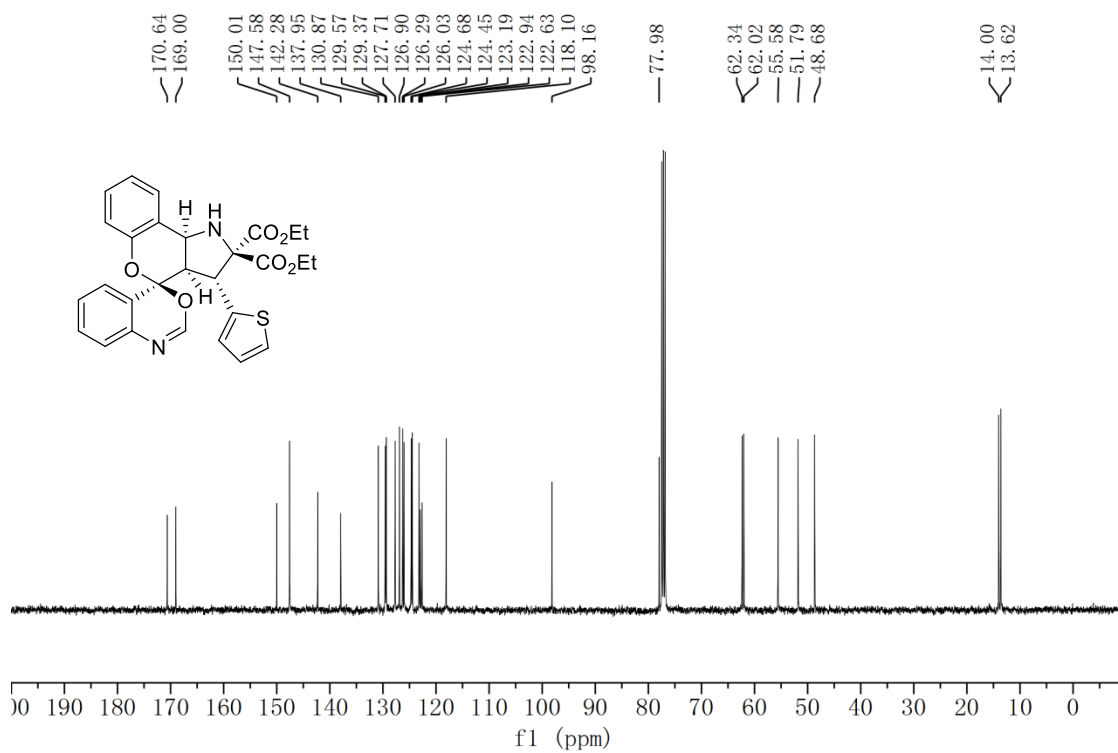
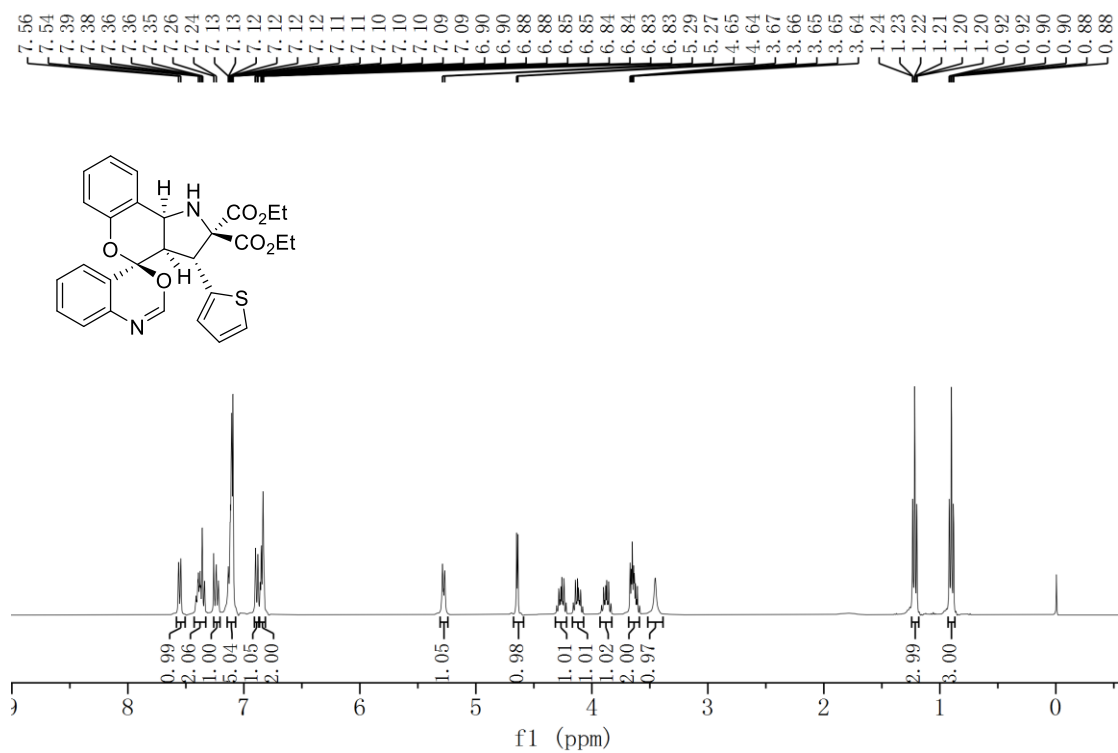
Compound 3j



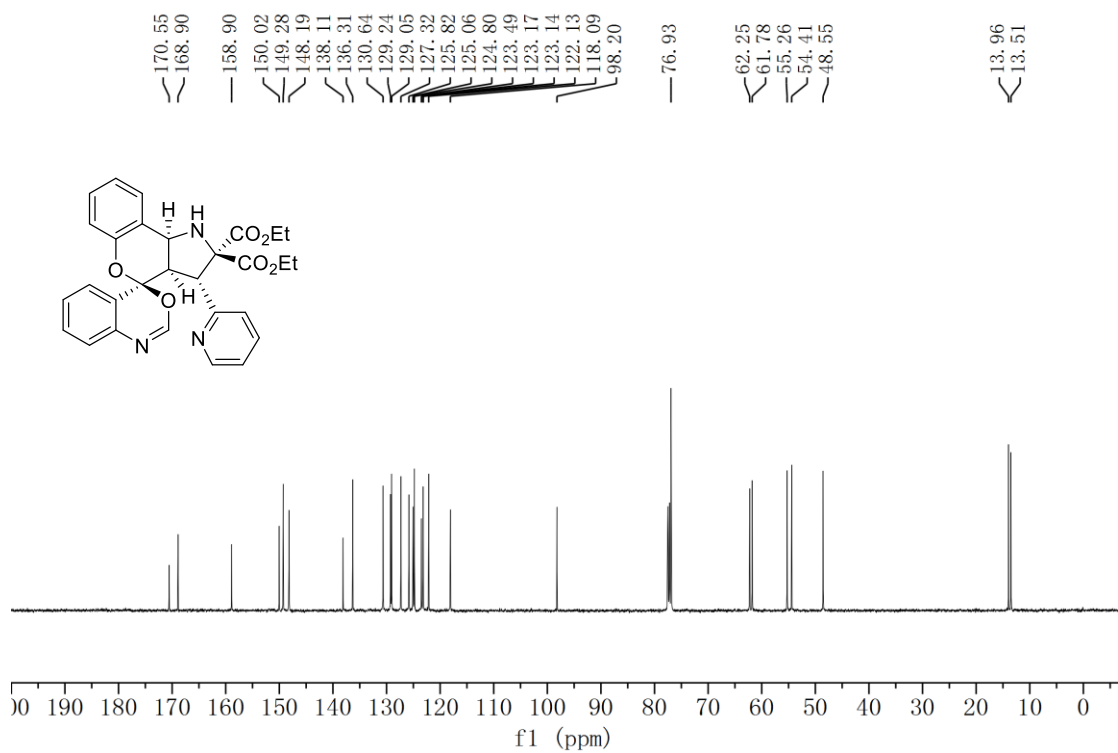
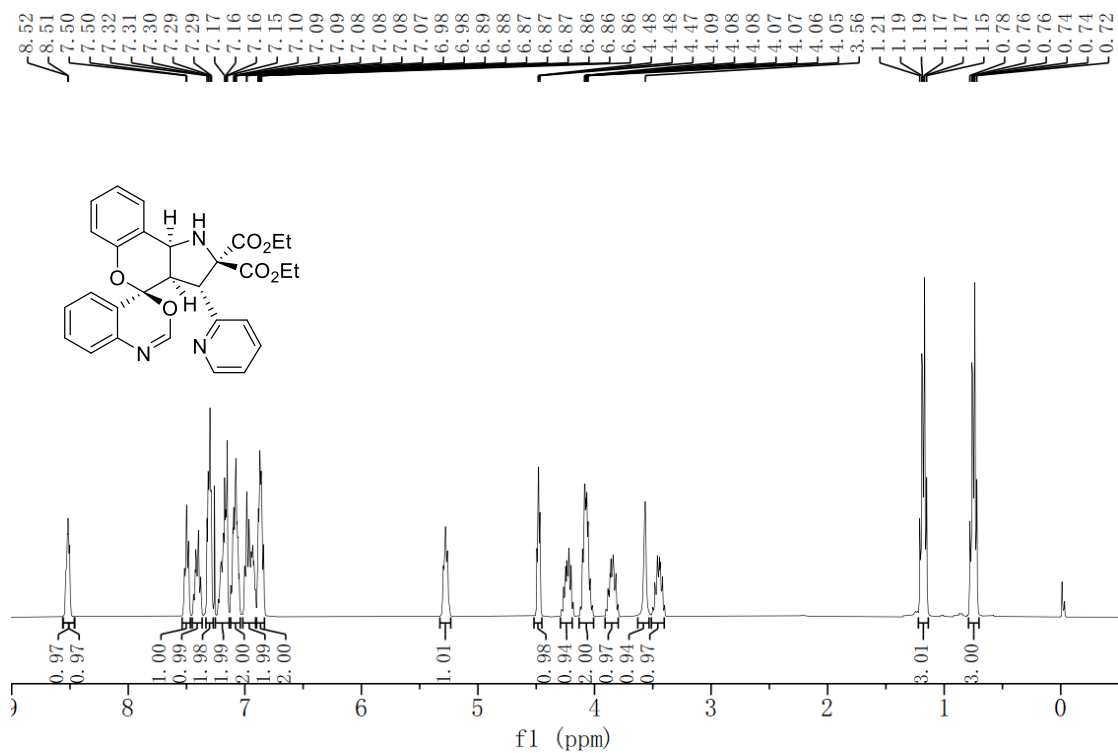
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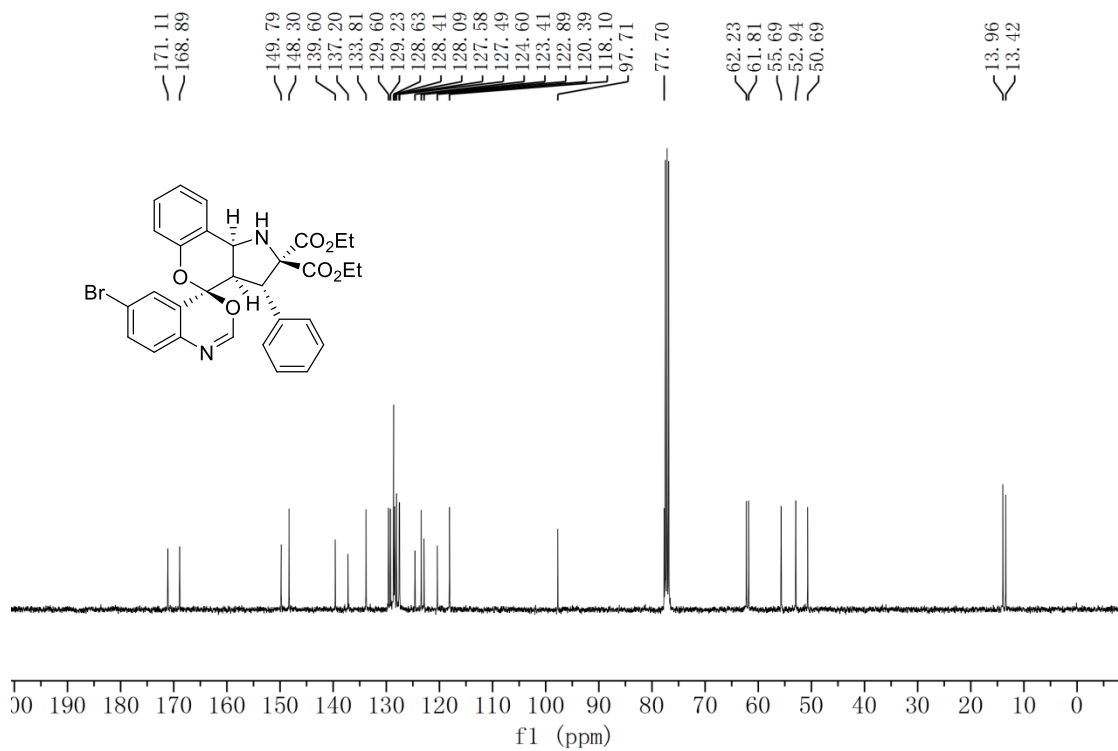
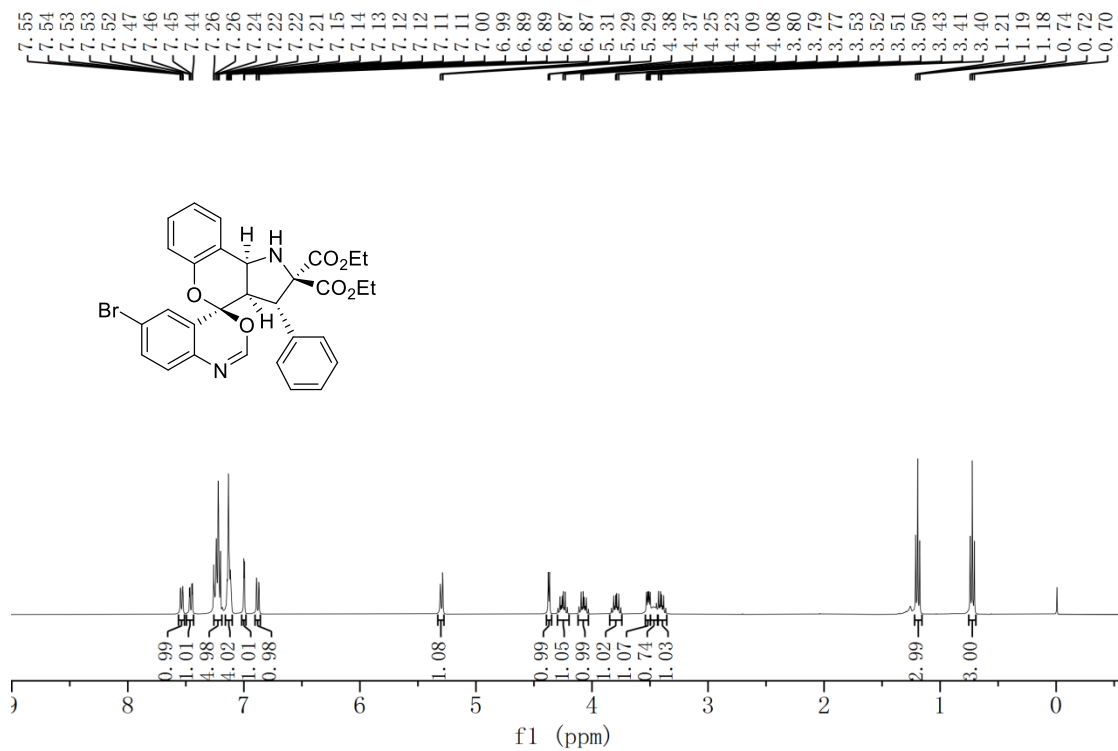
Compound 31



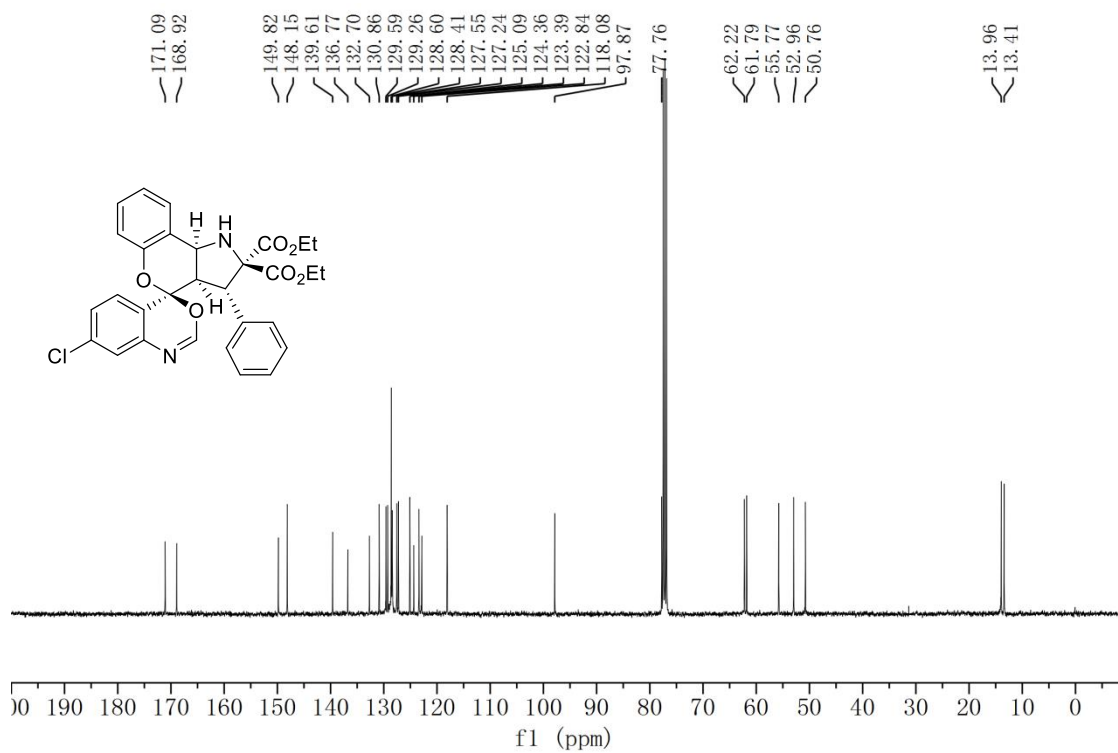
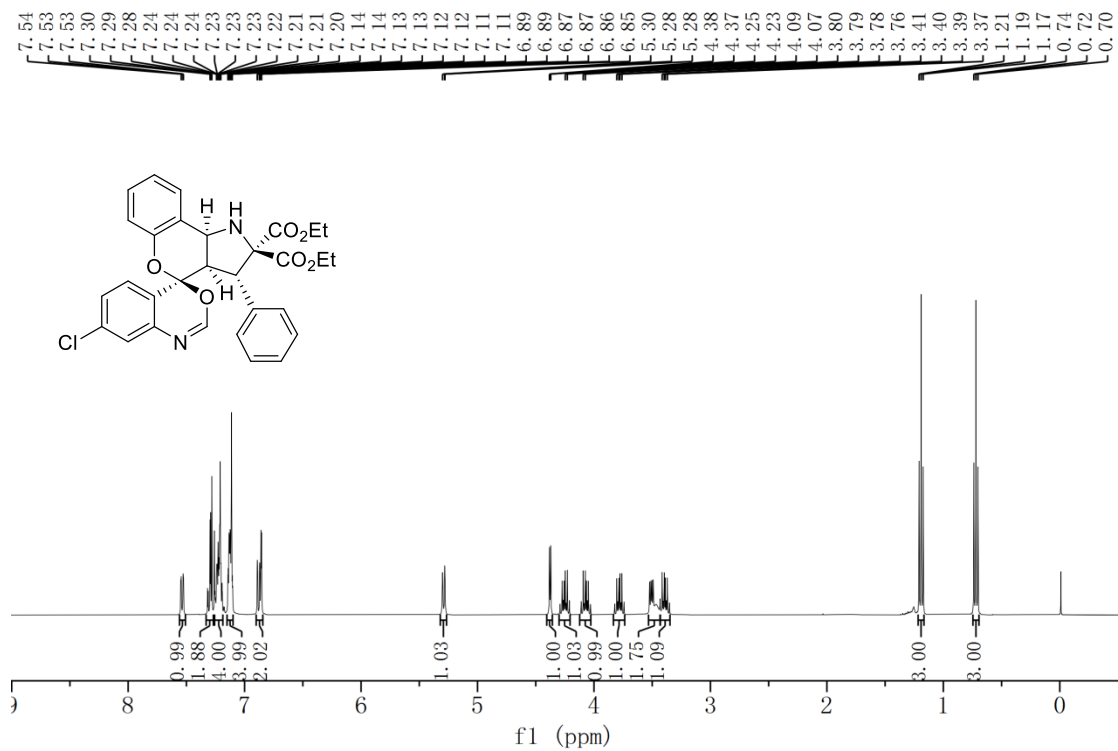
Compound 3m



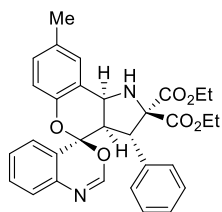
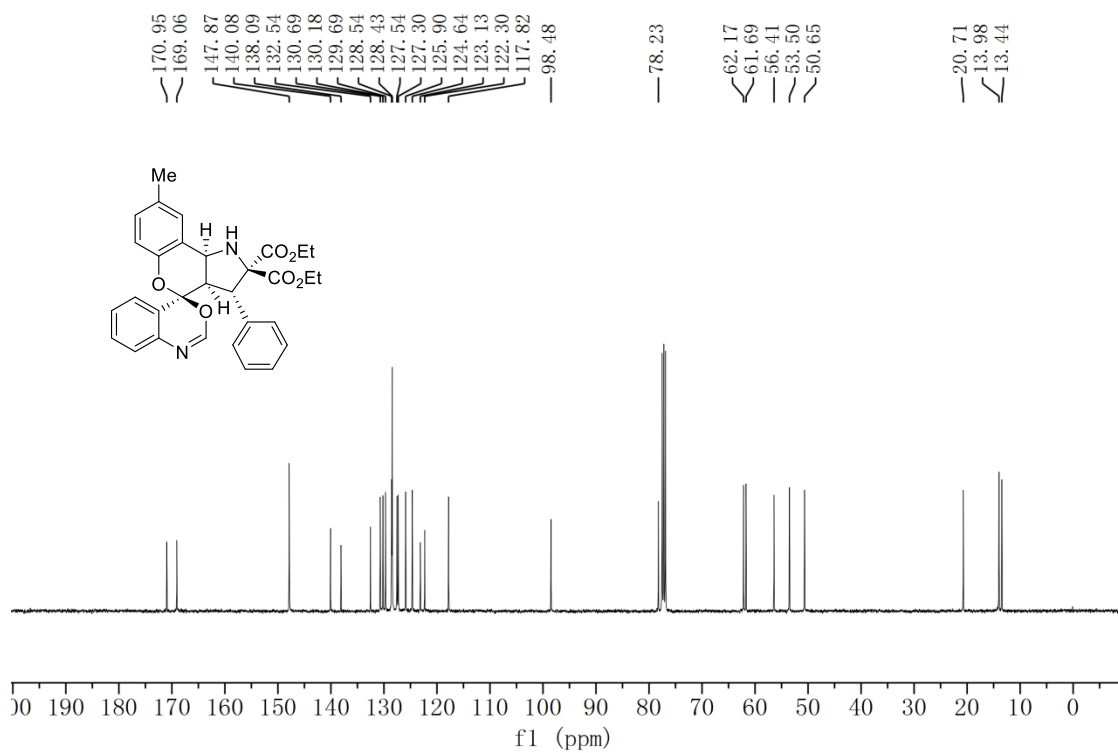
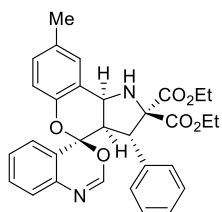
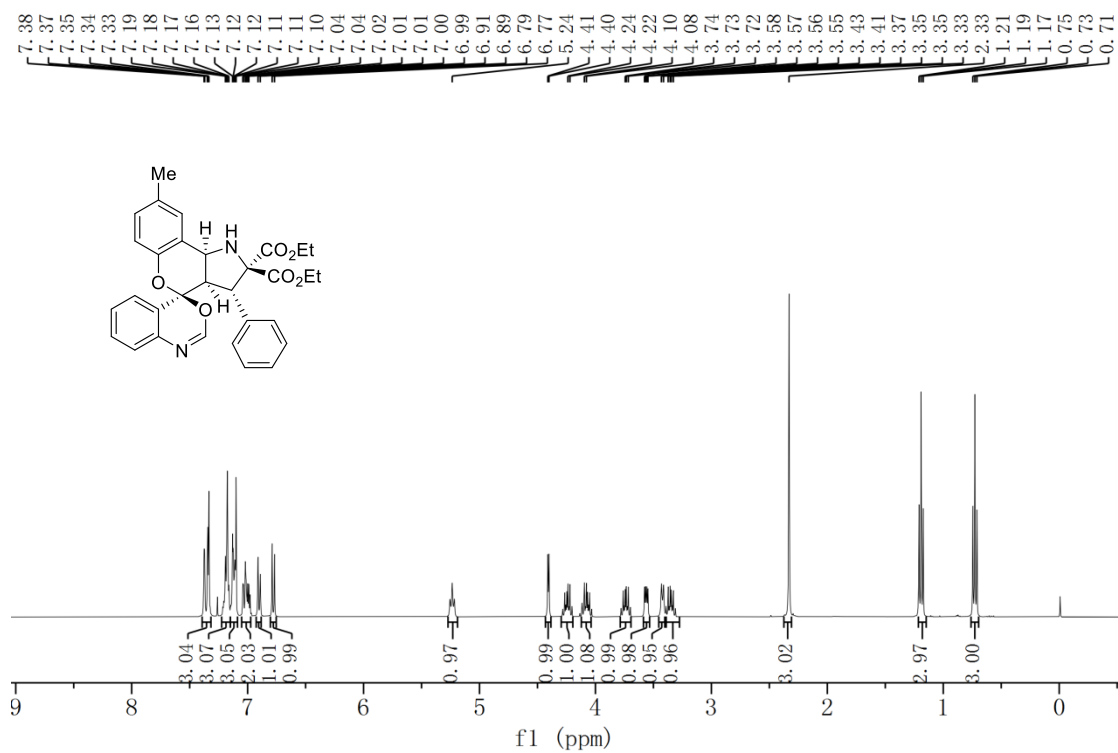
Compound 3n



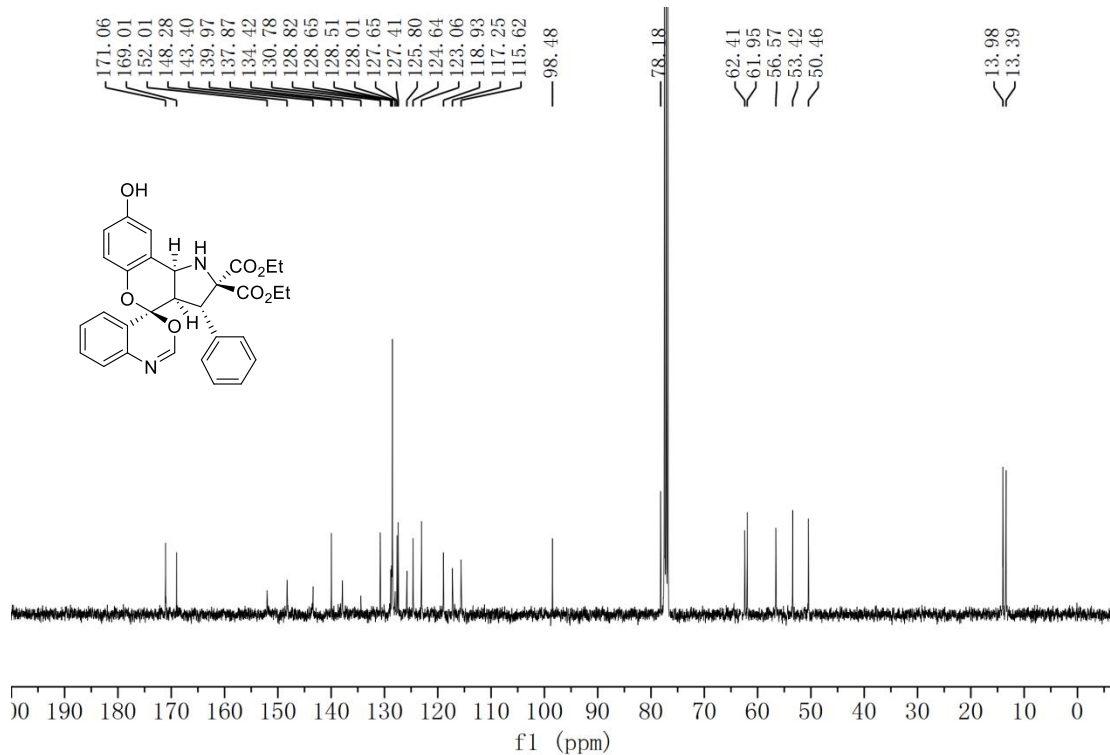
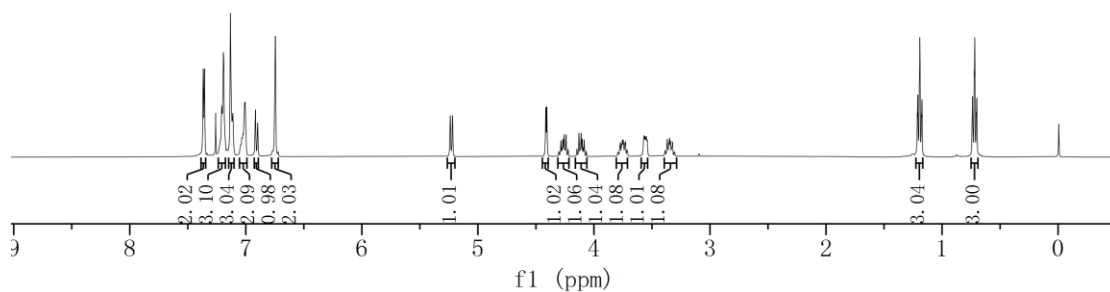
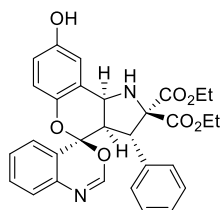
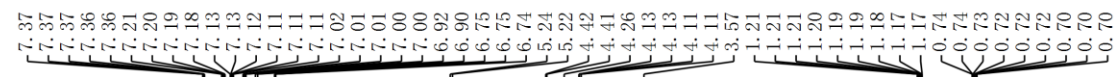
Compound 3o



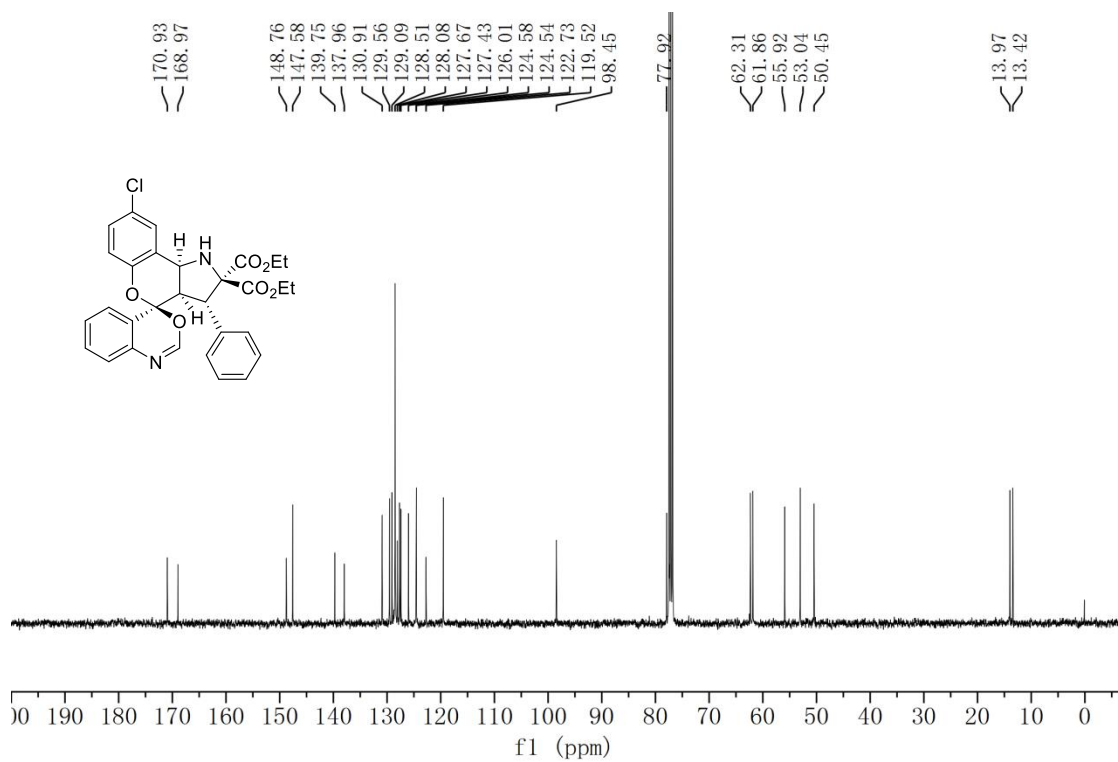
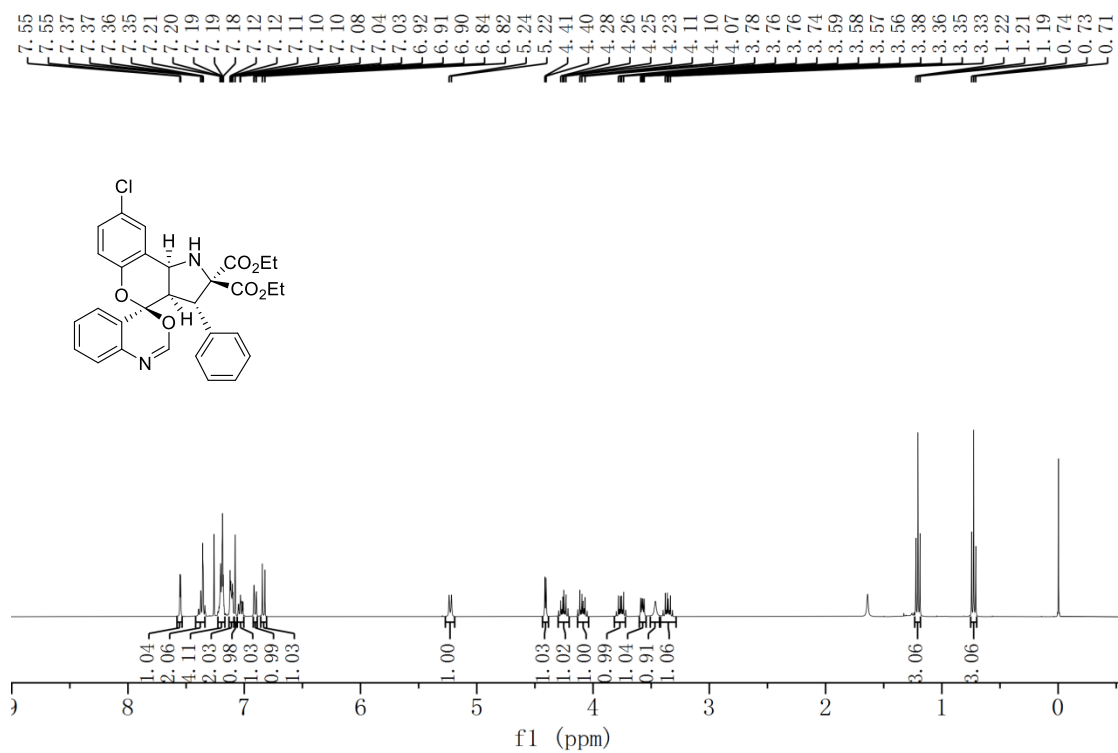
Compound 4a



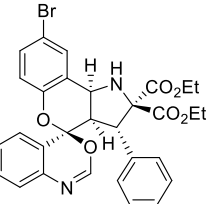
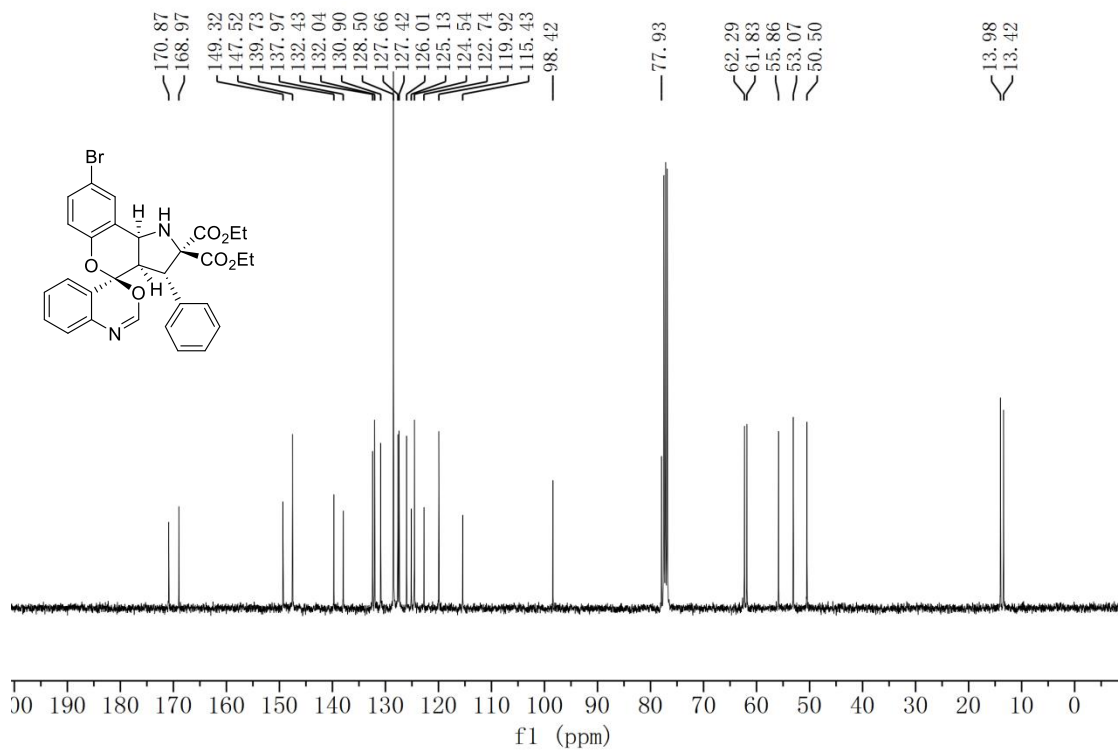
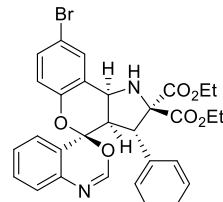
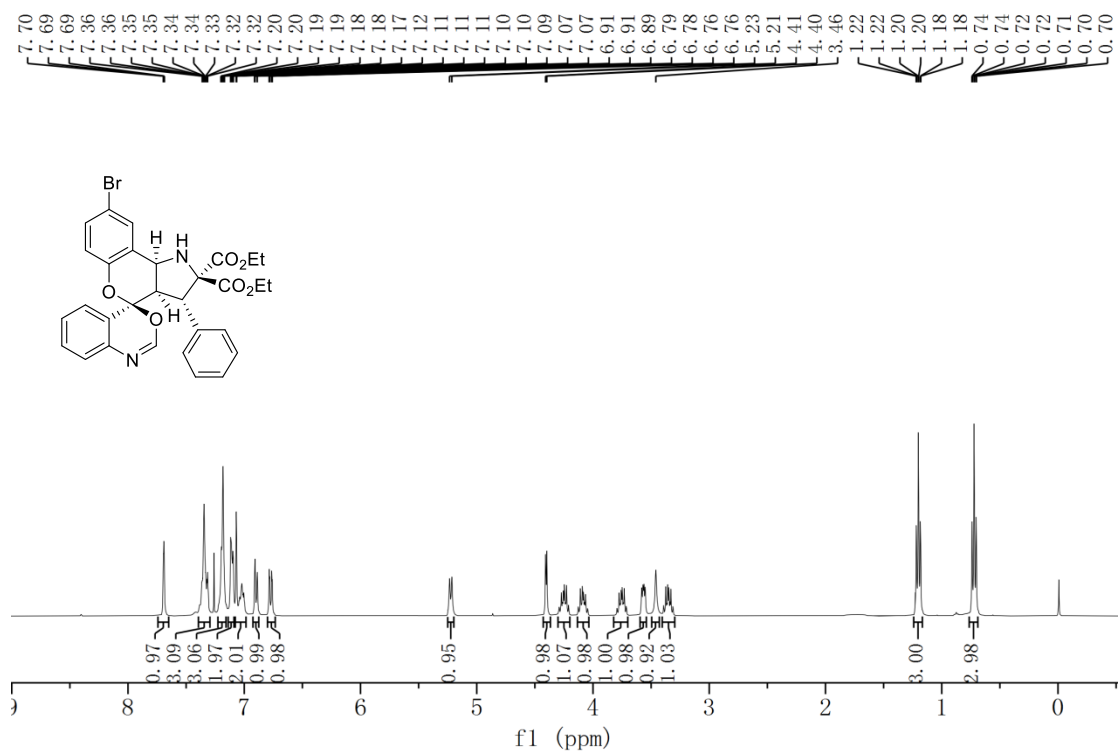
Compound 4b



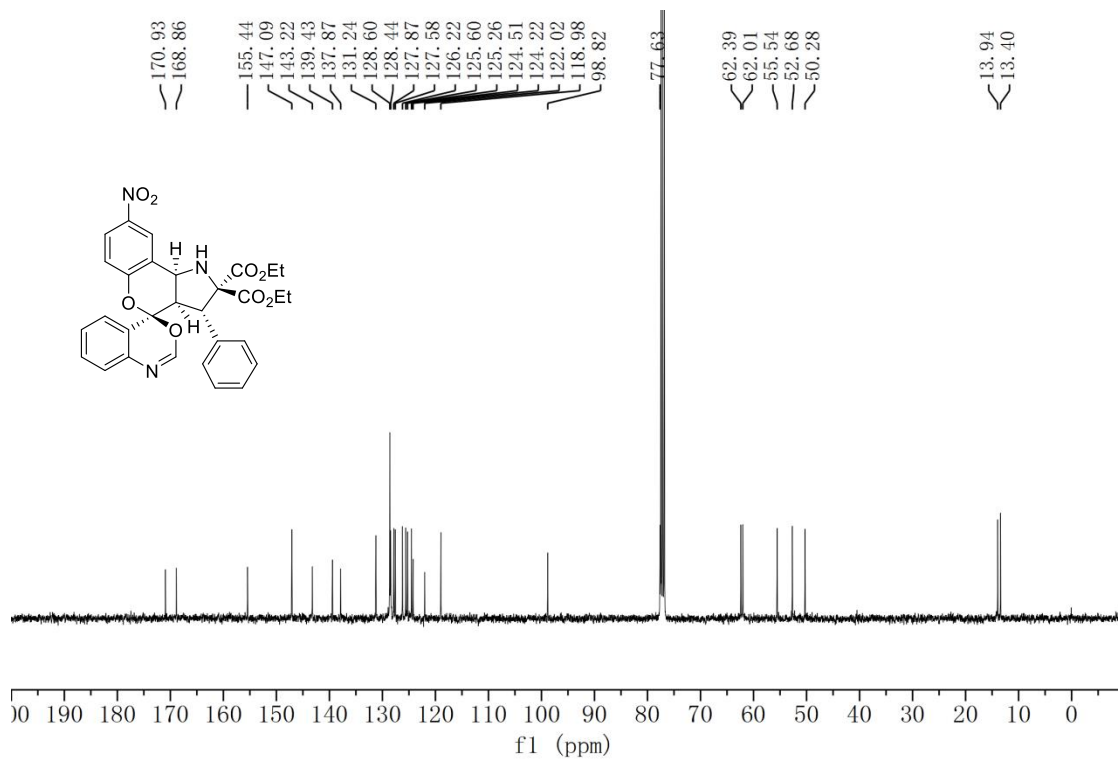
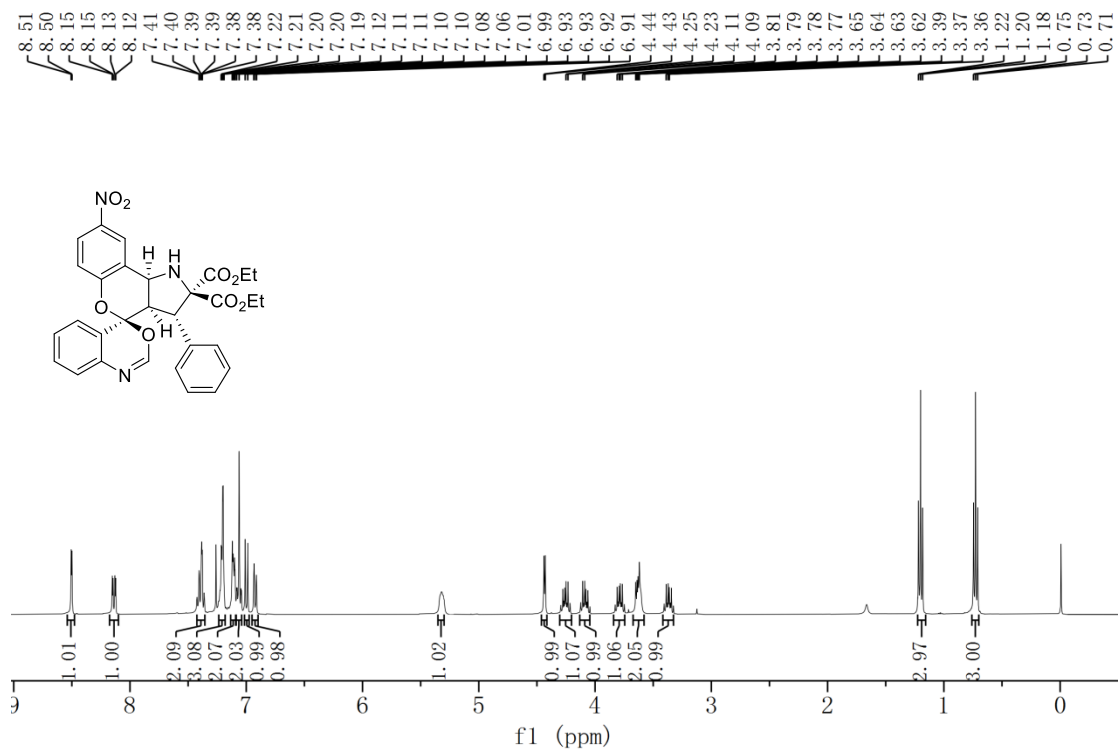
Compound 4c



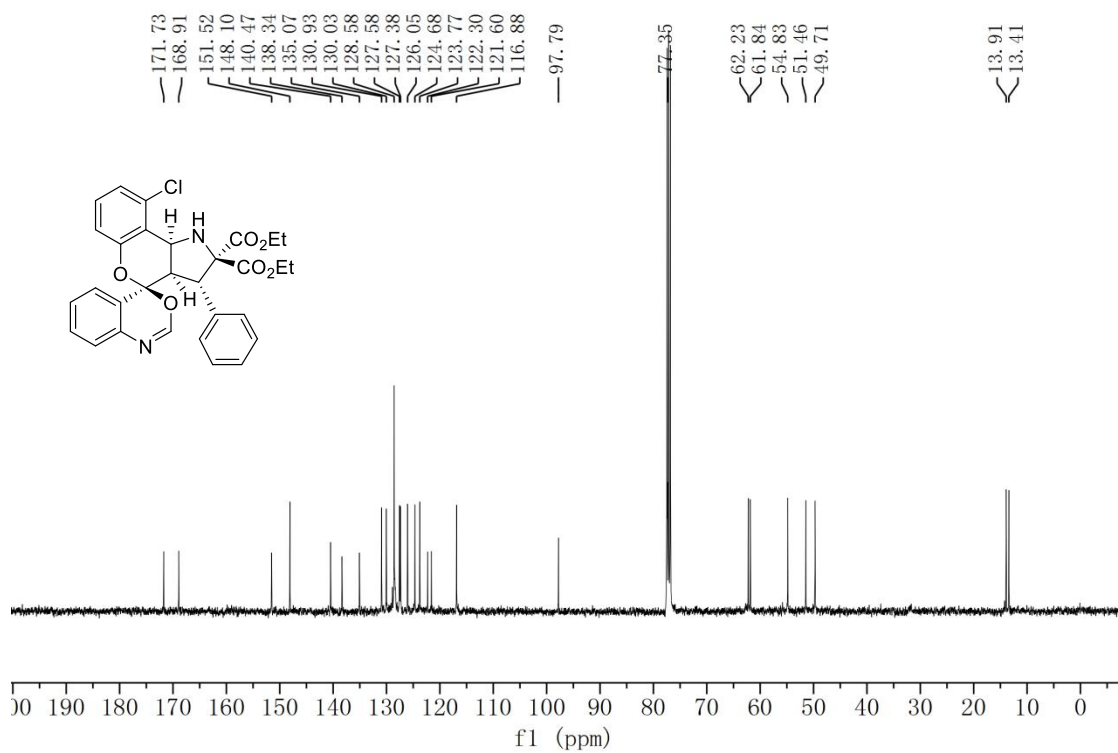
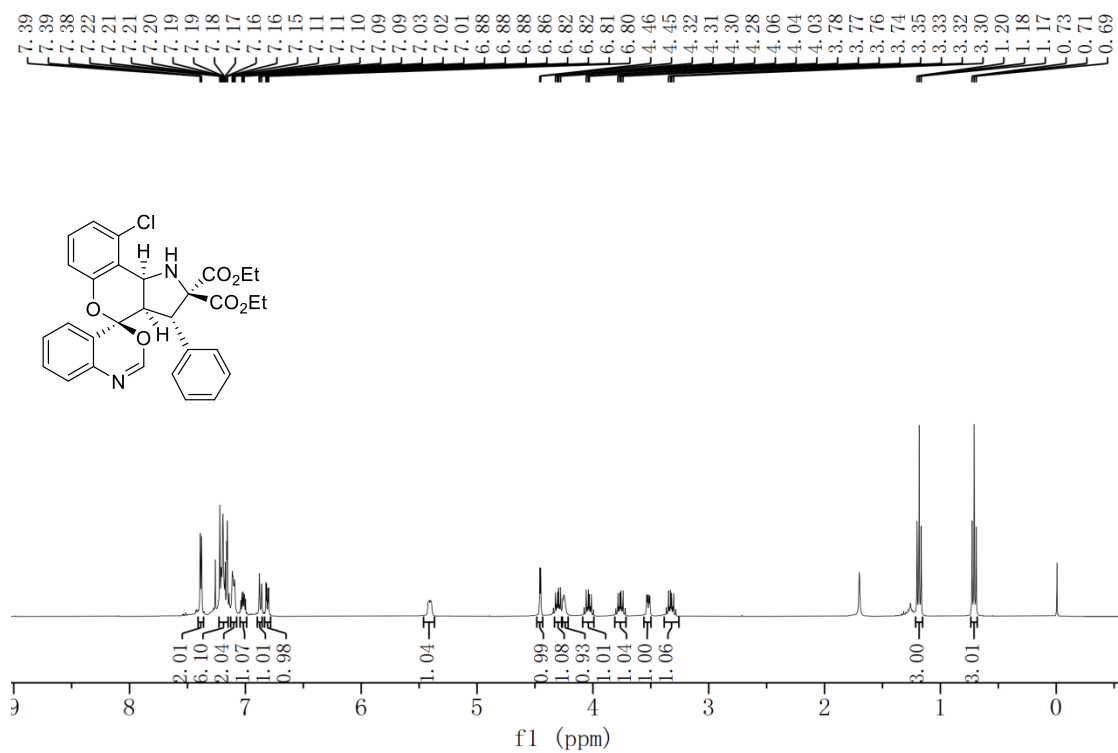
Compound 4d



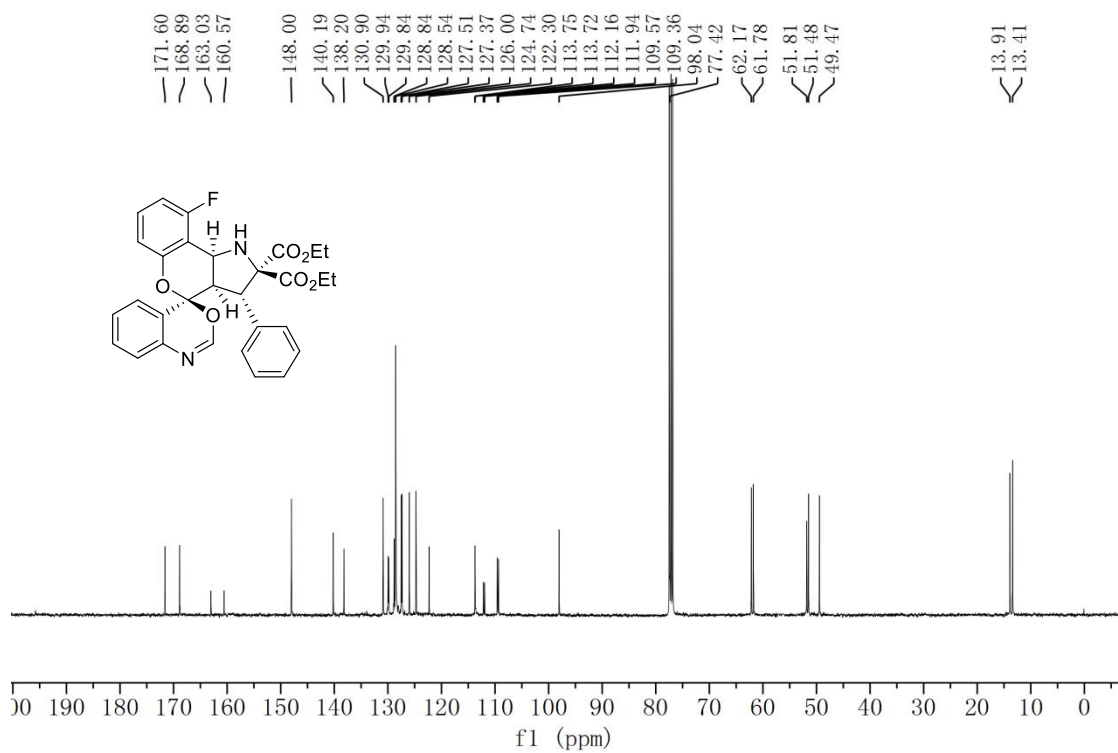
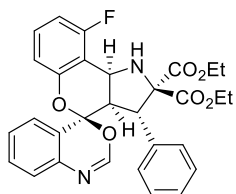
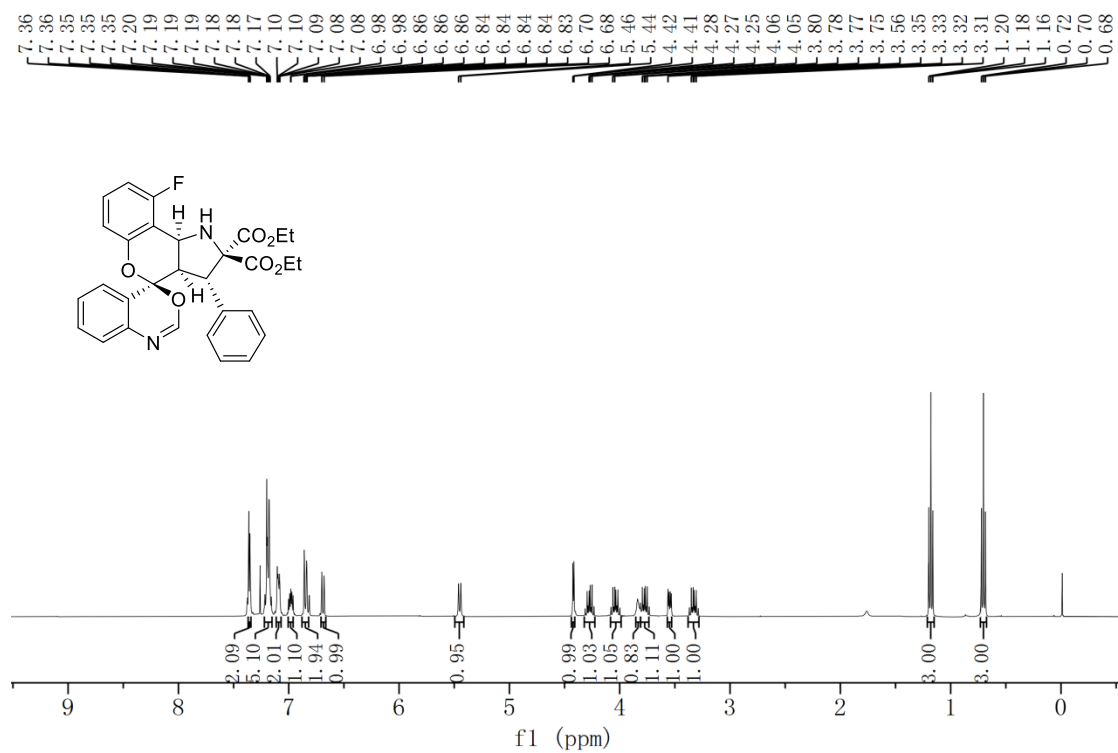
Compound 4e



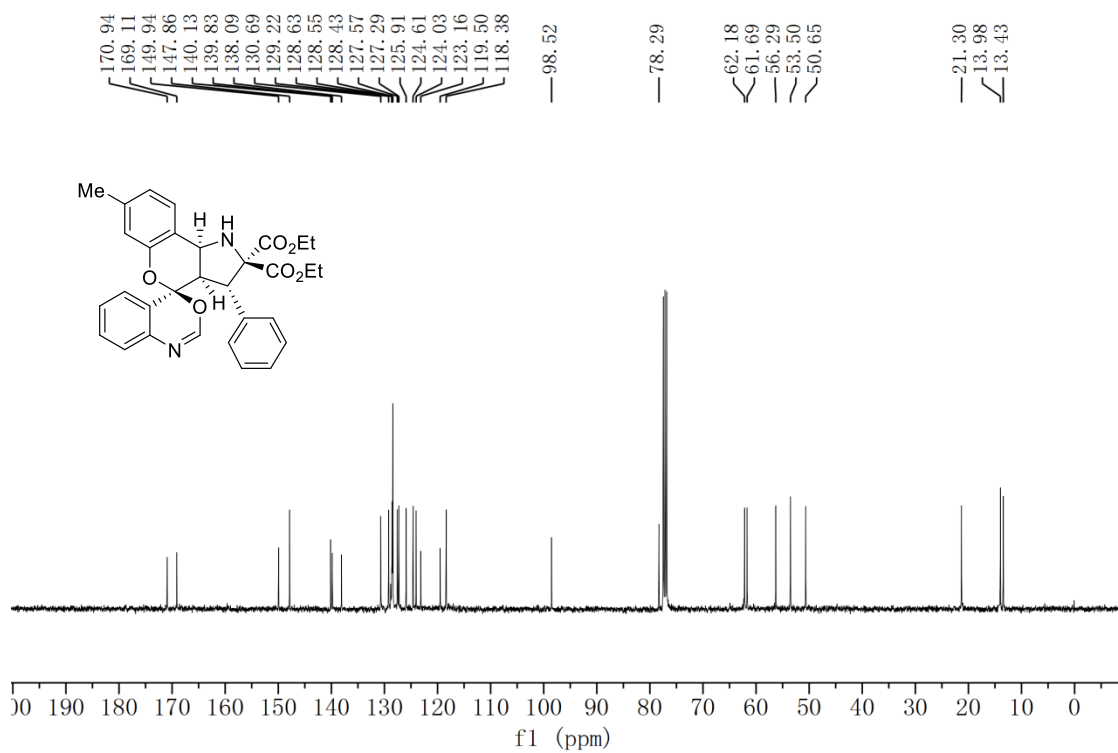
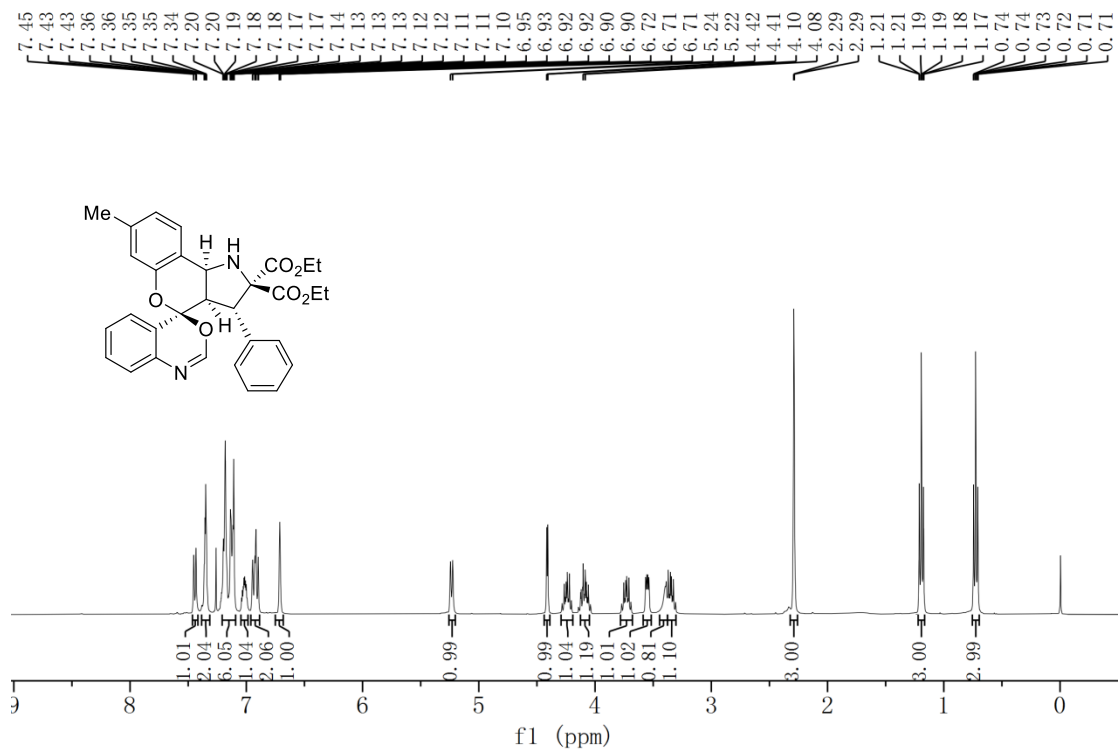
Compound 4f



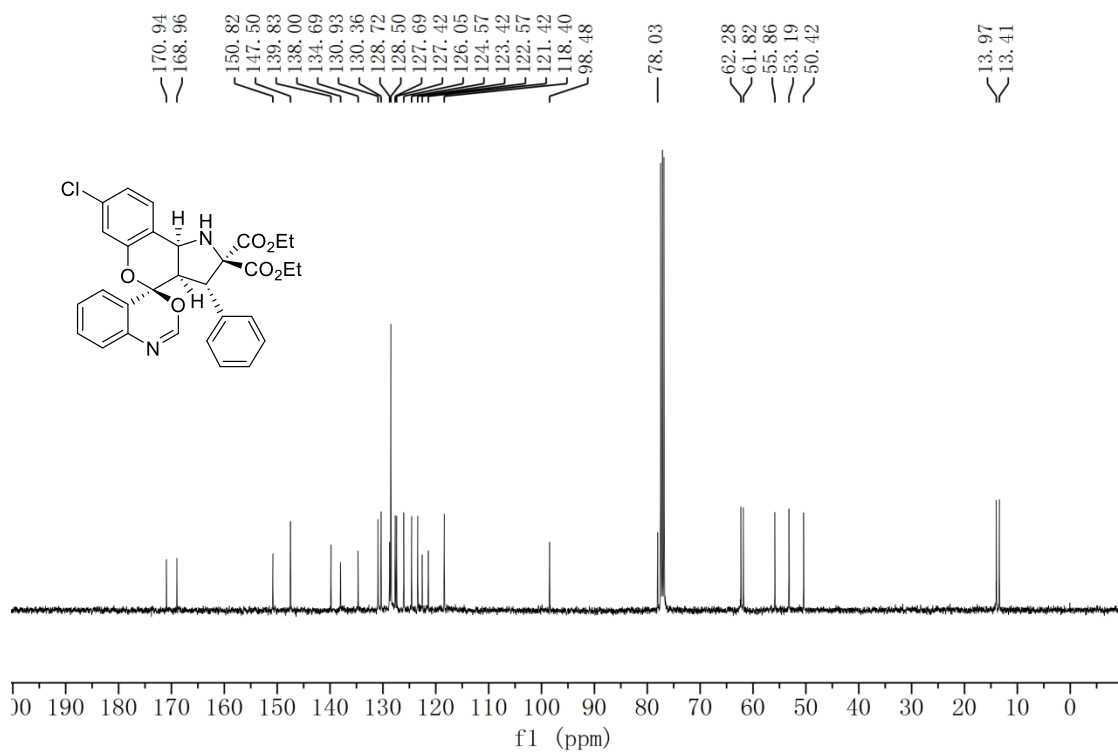
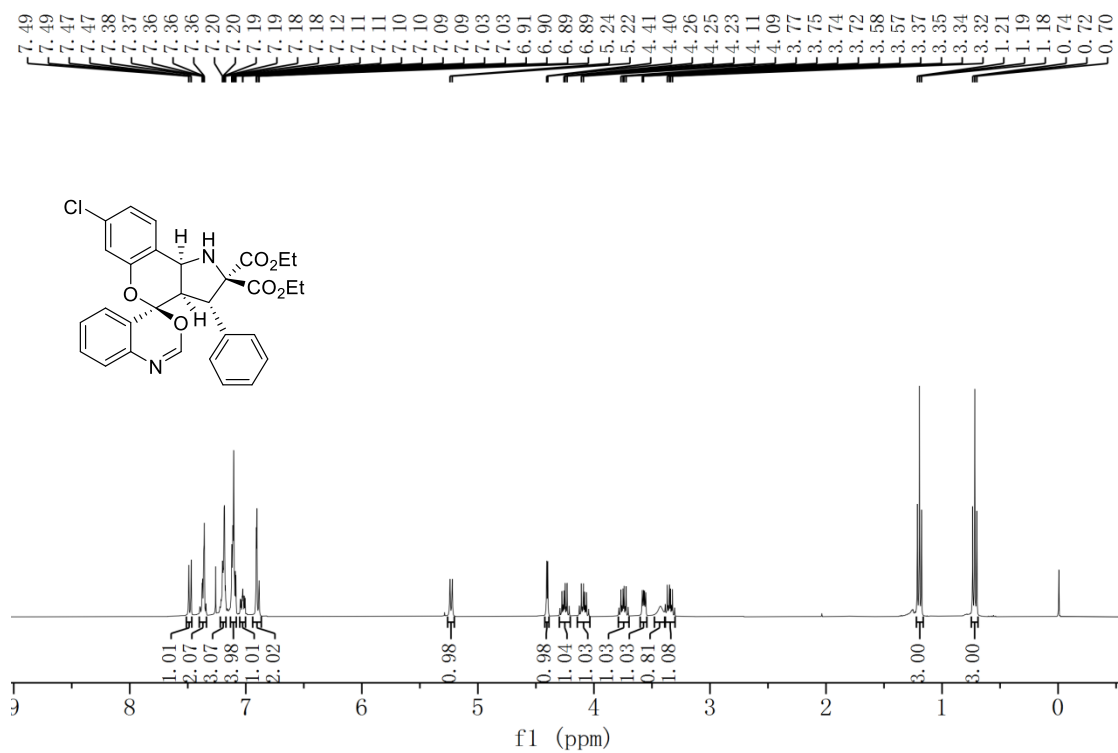
Compound 4g



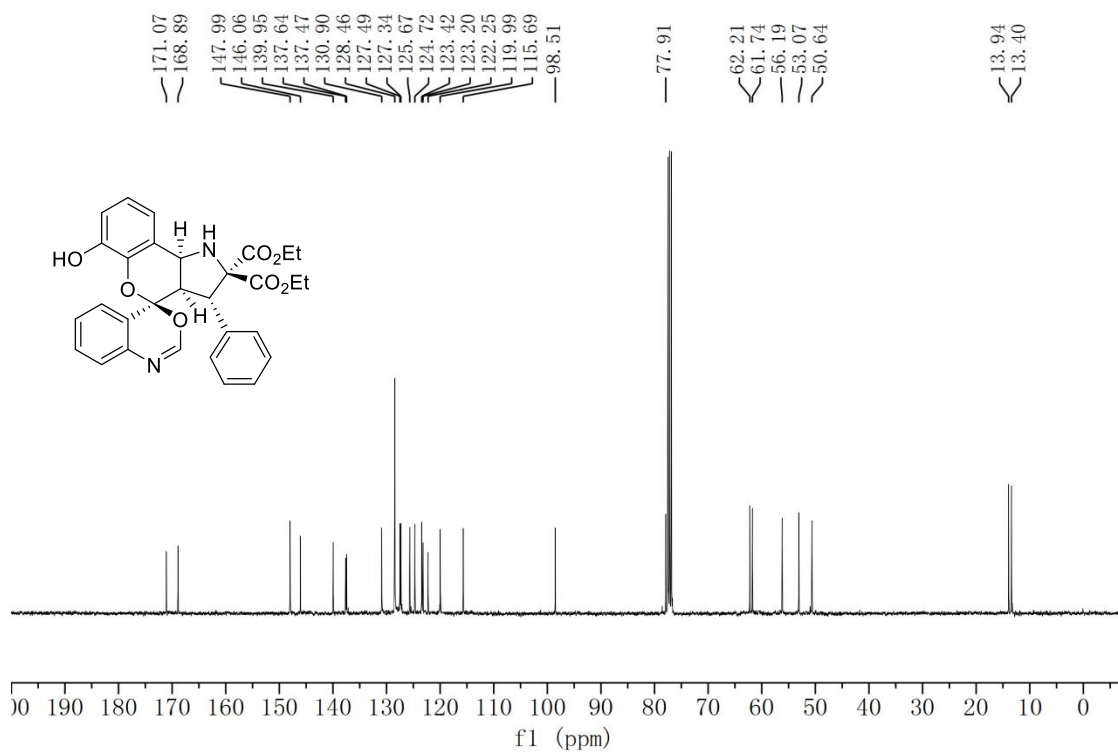
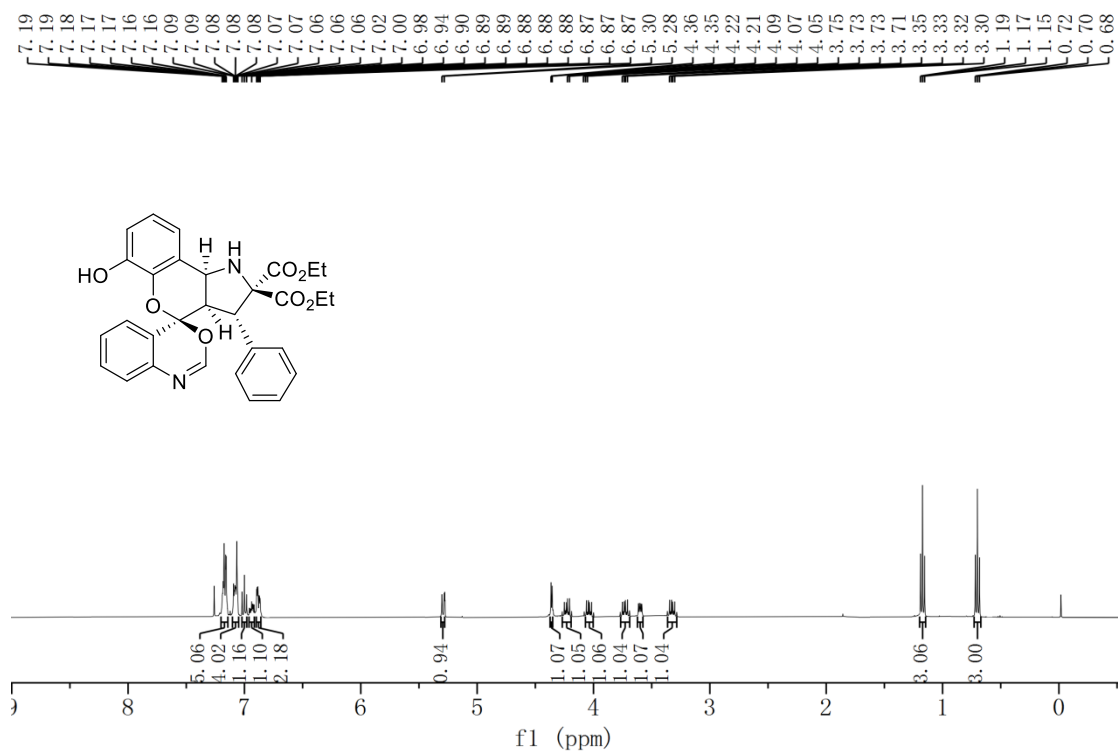
Compound 4h



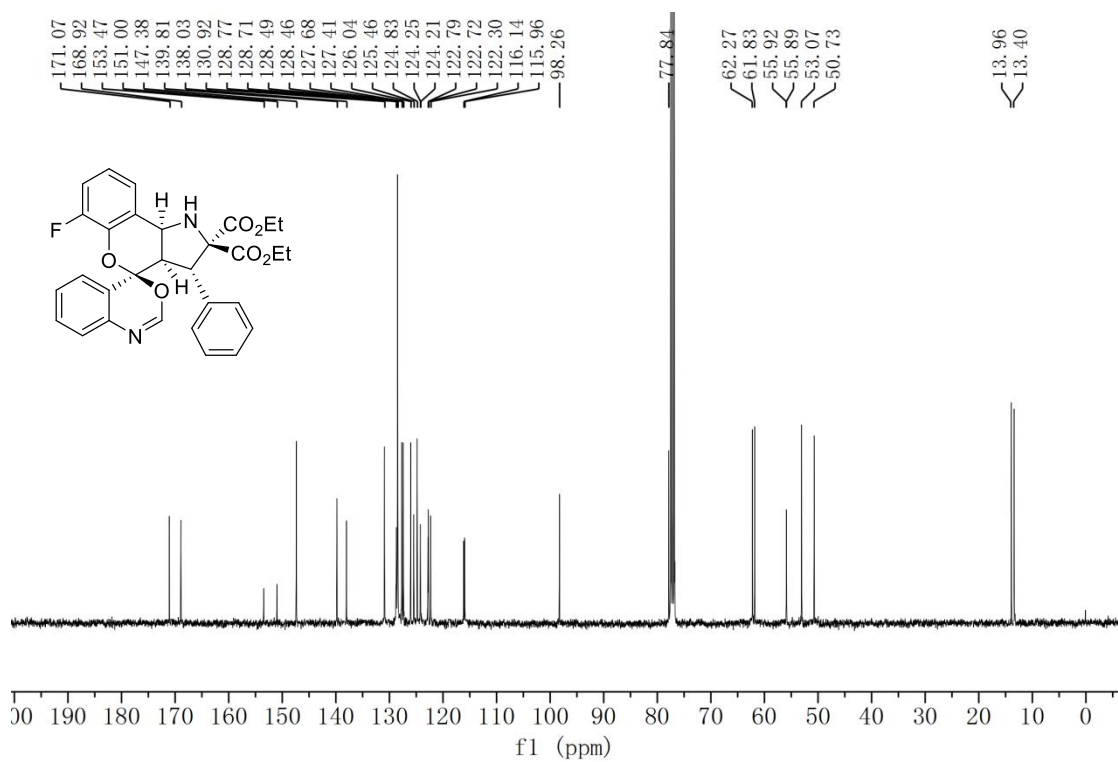
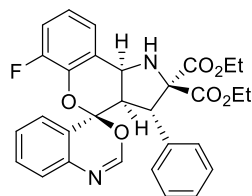
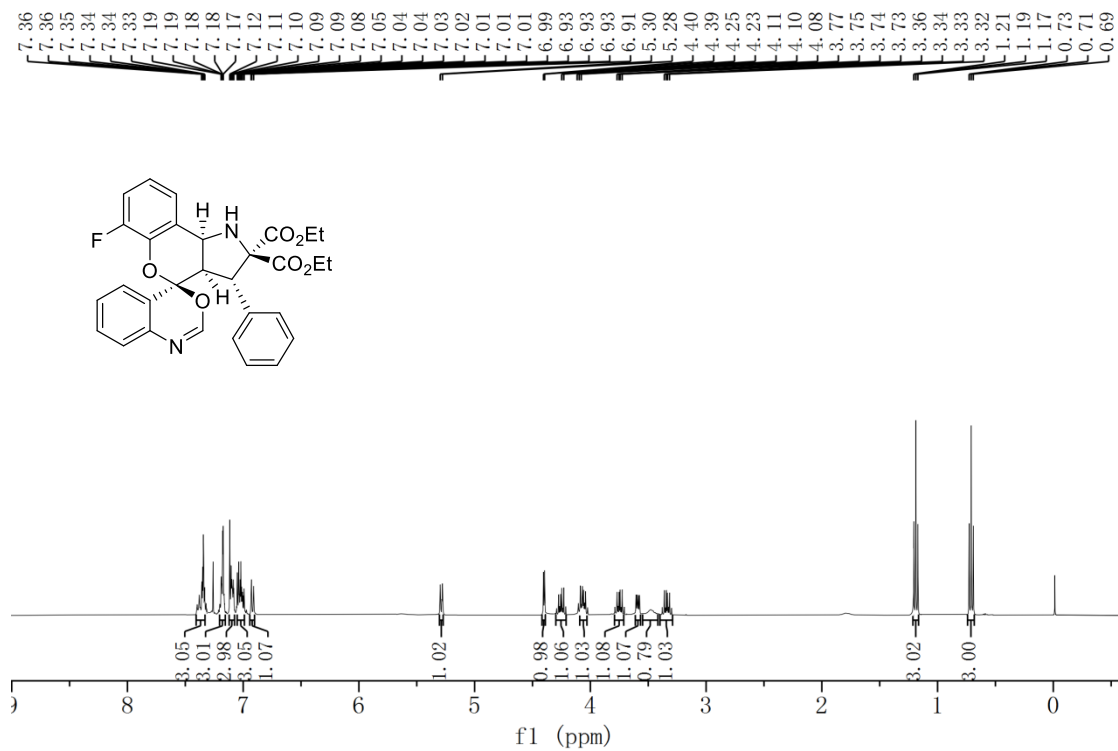
Compound 4i



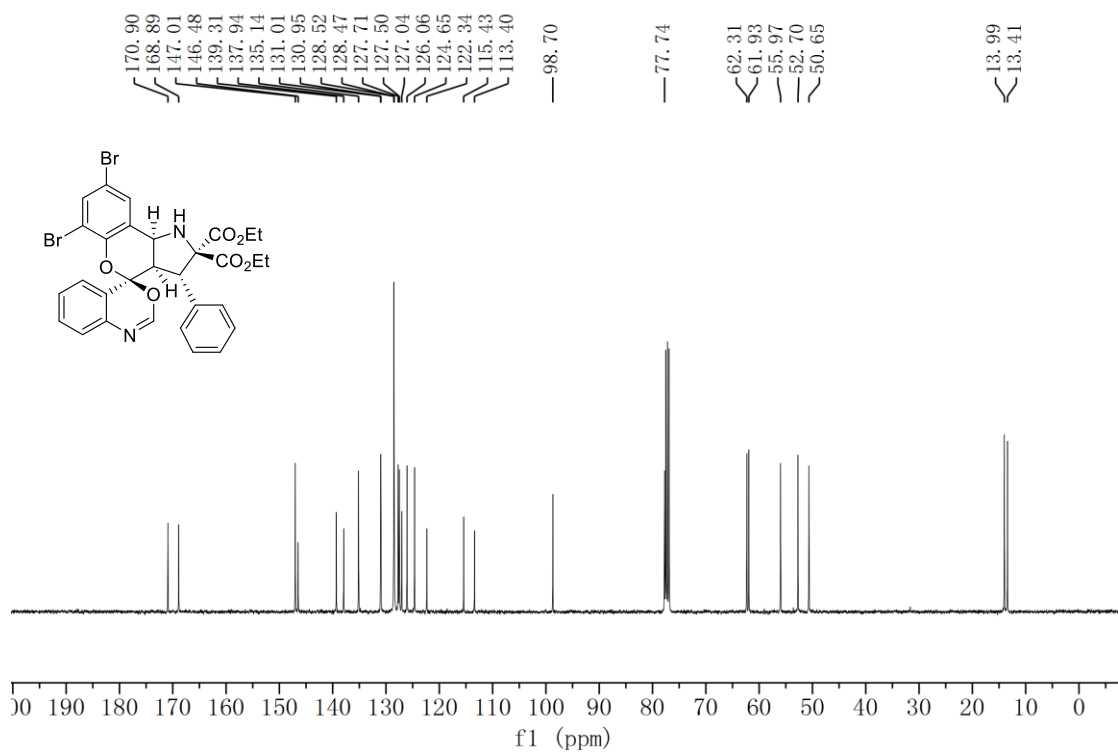
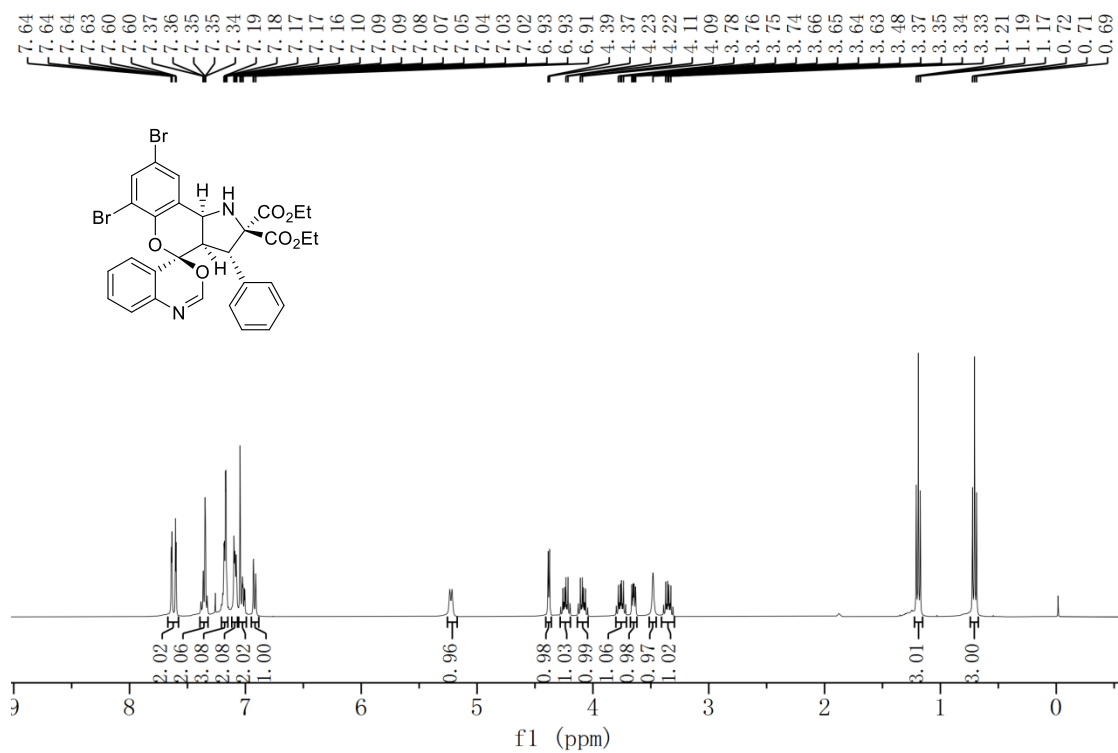
Compound 4j



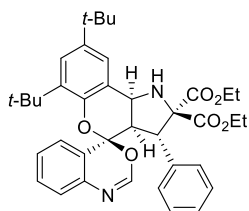
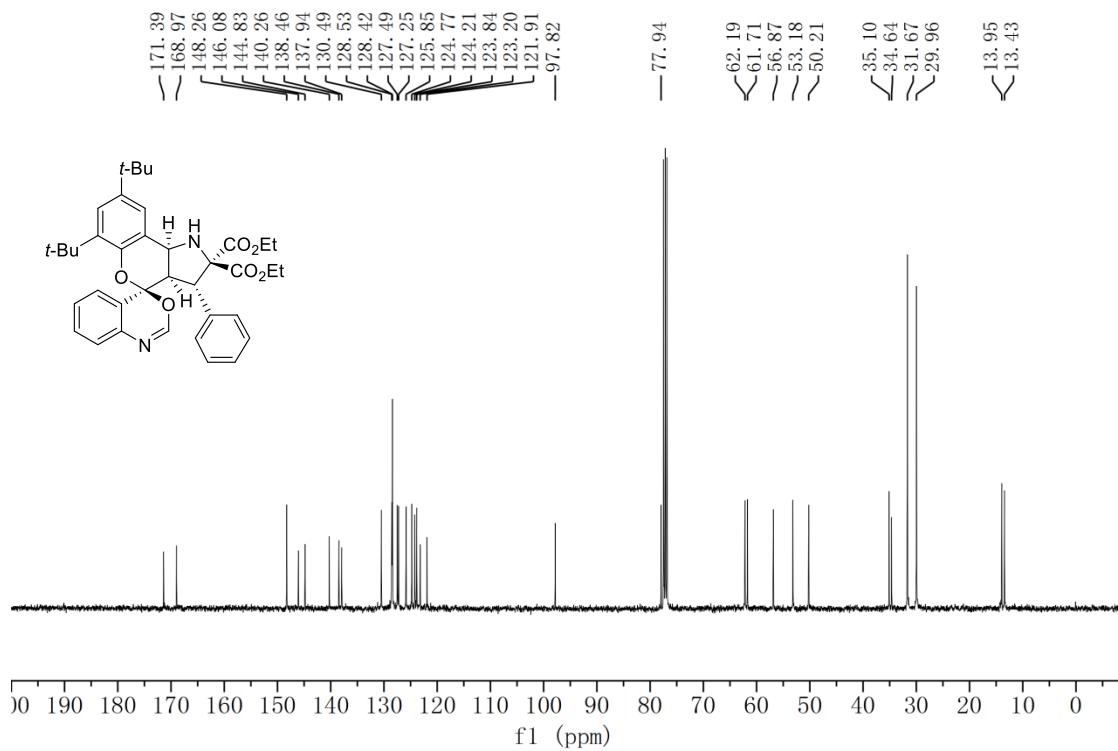
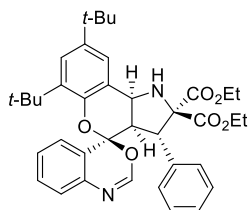
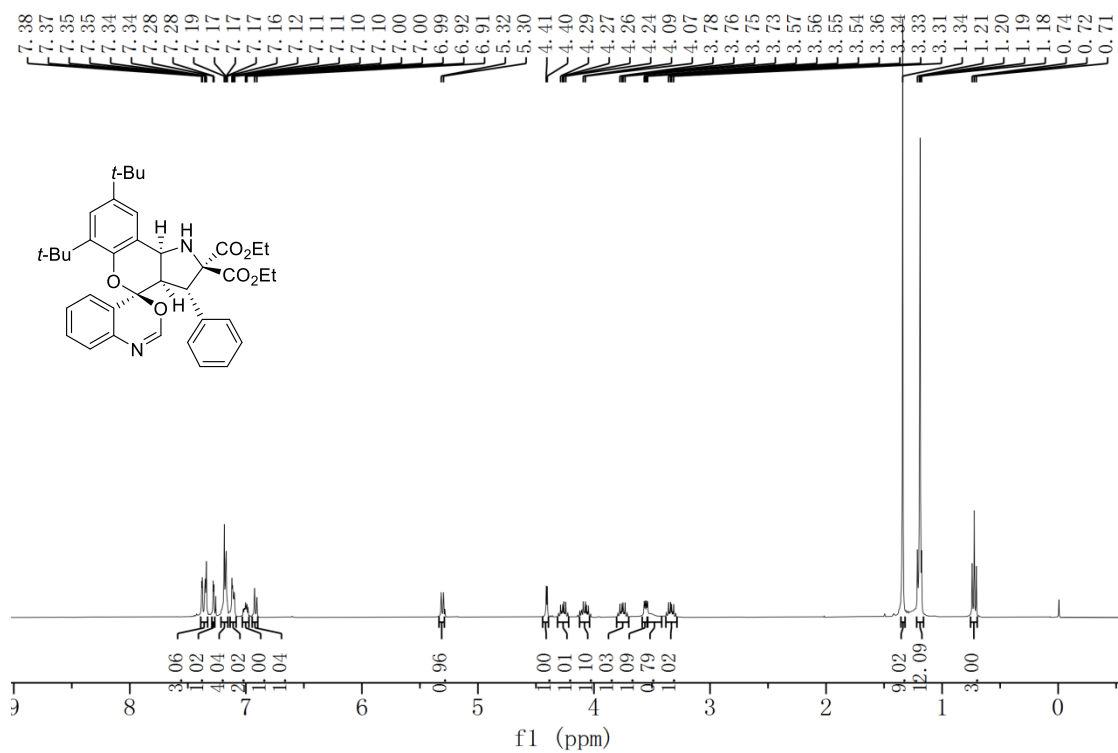
Compound 4k



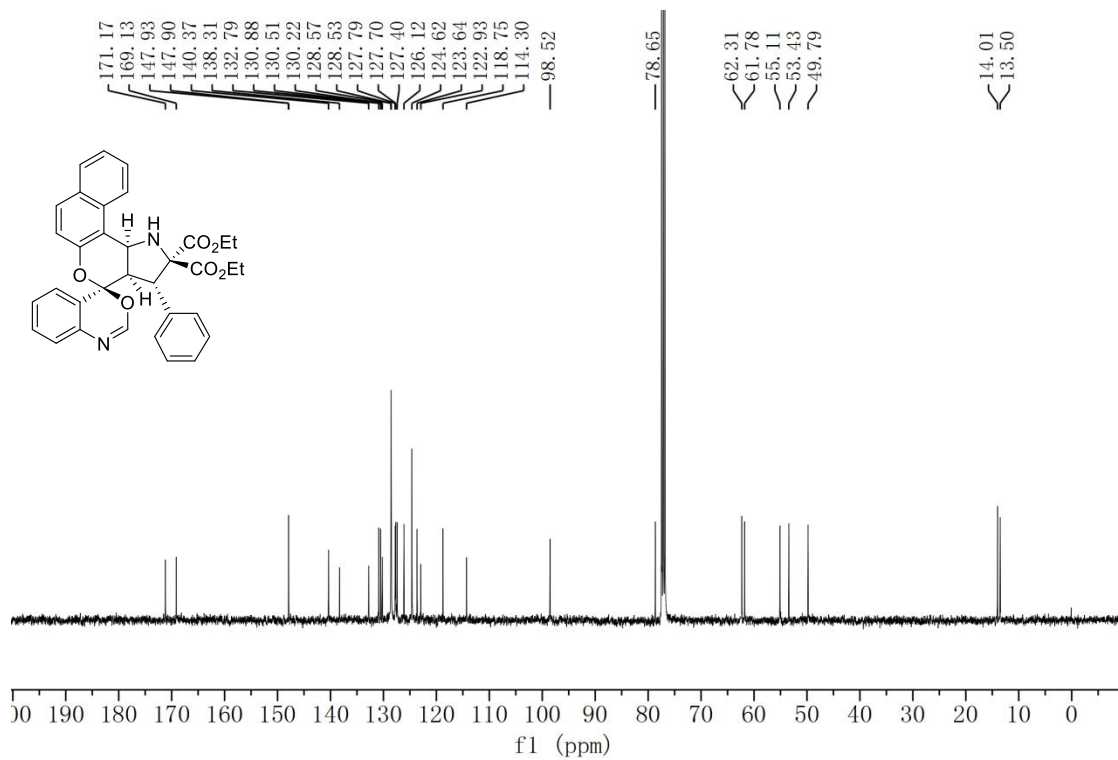
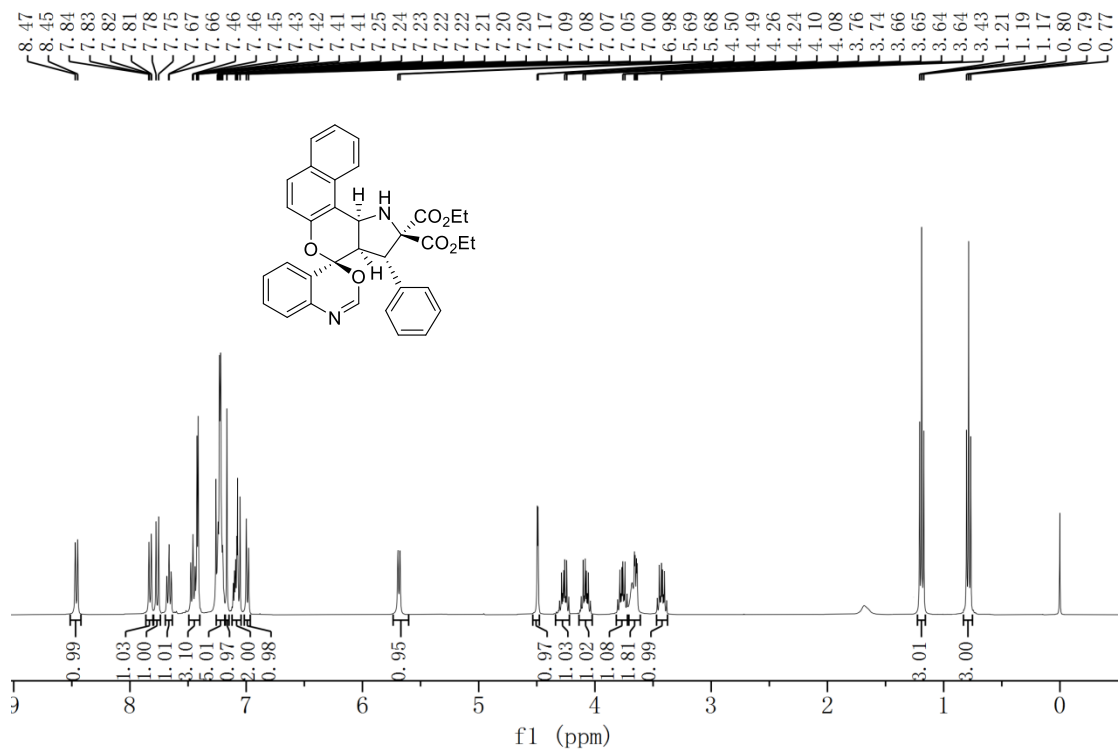
Compound 4I



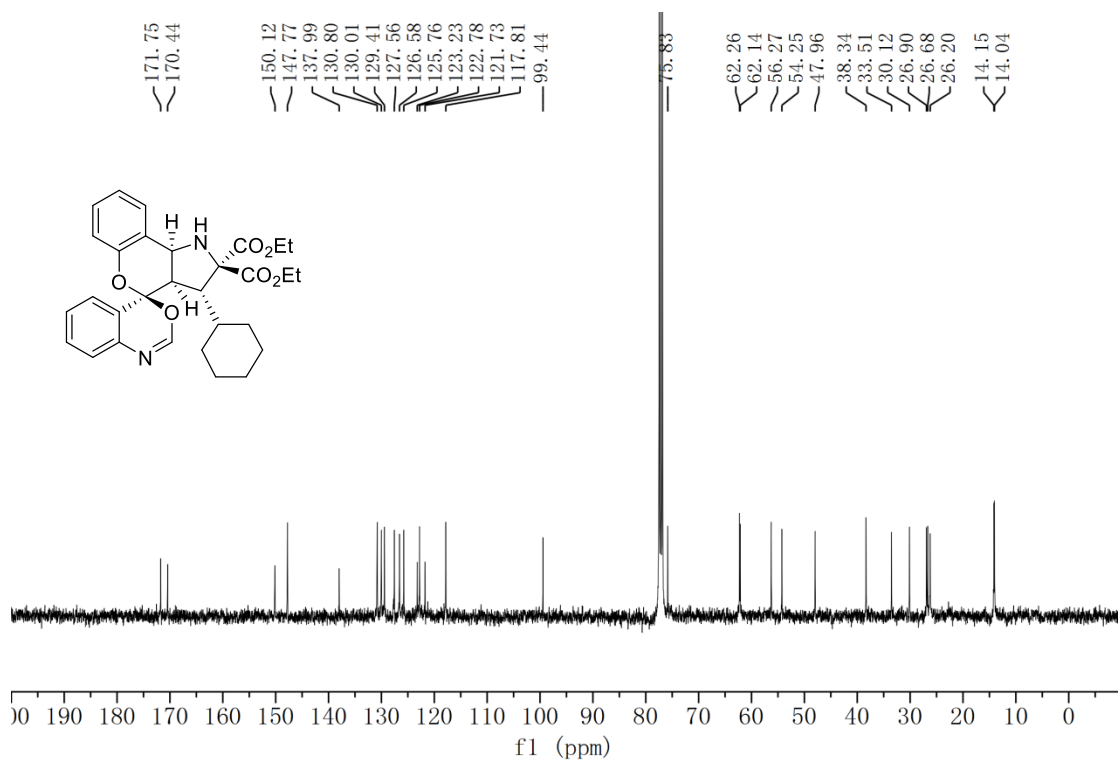
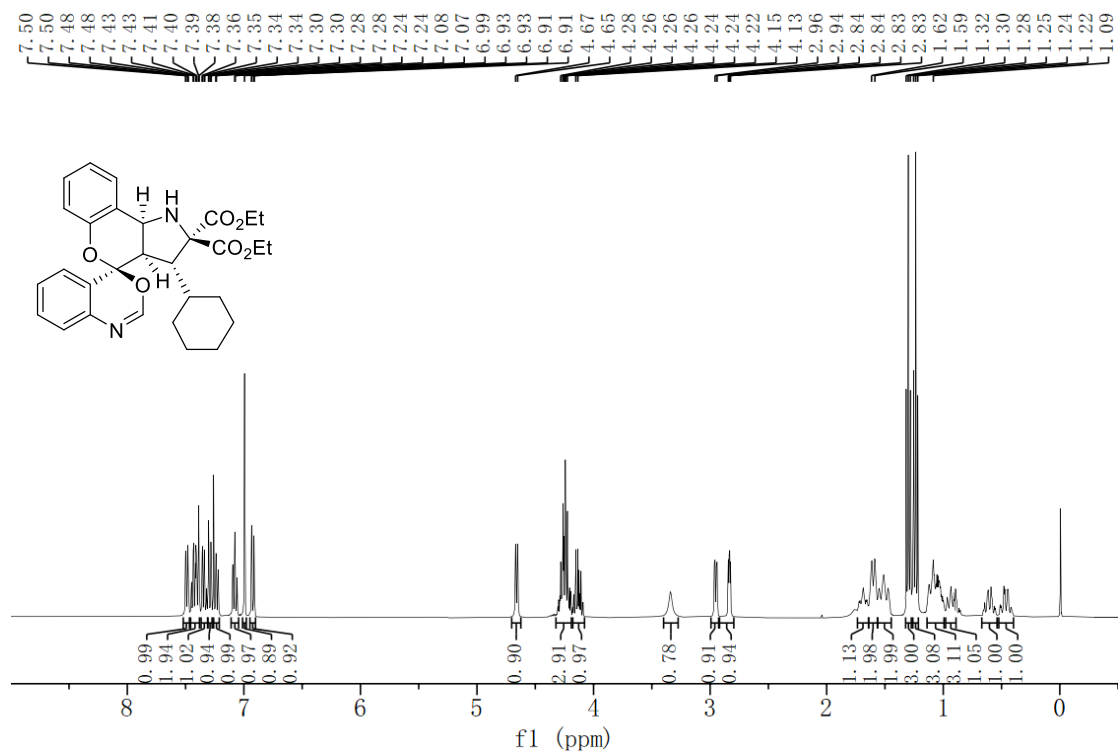
Compound 4m



Compound 4n



Compound 3'a



Compound 6a

