

Supplementary Information

Iron-Catalyzed Radical Cascade 6-*endo* Cyclization of Diene toward Fused Nitrogen Heterocycles Initiated by Alkoxy carbonyl Radical

Shanshan Qiao,[†] Peng-Cheng Qian,^{*,‡} Fan Chen,[‡] and Jiang Cheng^{*,†,‡}

[†] School of Petrochemical Engineering, and Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, Changzhou University, Changzhou 213164, P. R. China, and [‡] Institute of New Materials & Industry Technology, College of Chemistry & Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. China.

Email: qpc@wzu.edu.cn, jiangcheng@cczu.edu.cn or jiangcheng@wzu.edu.cn

Table of Contents

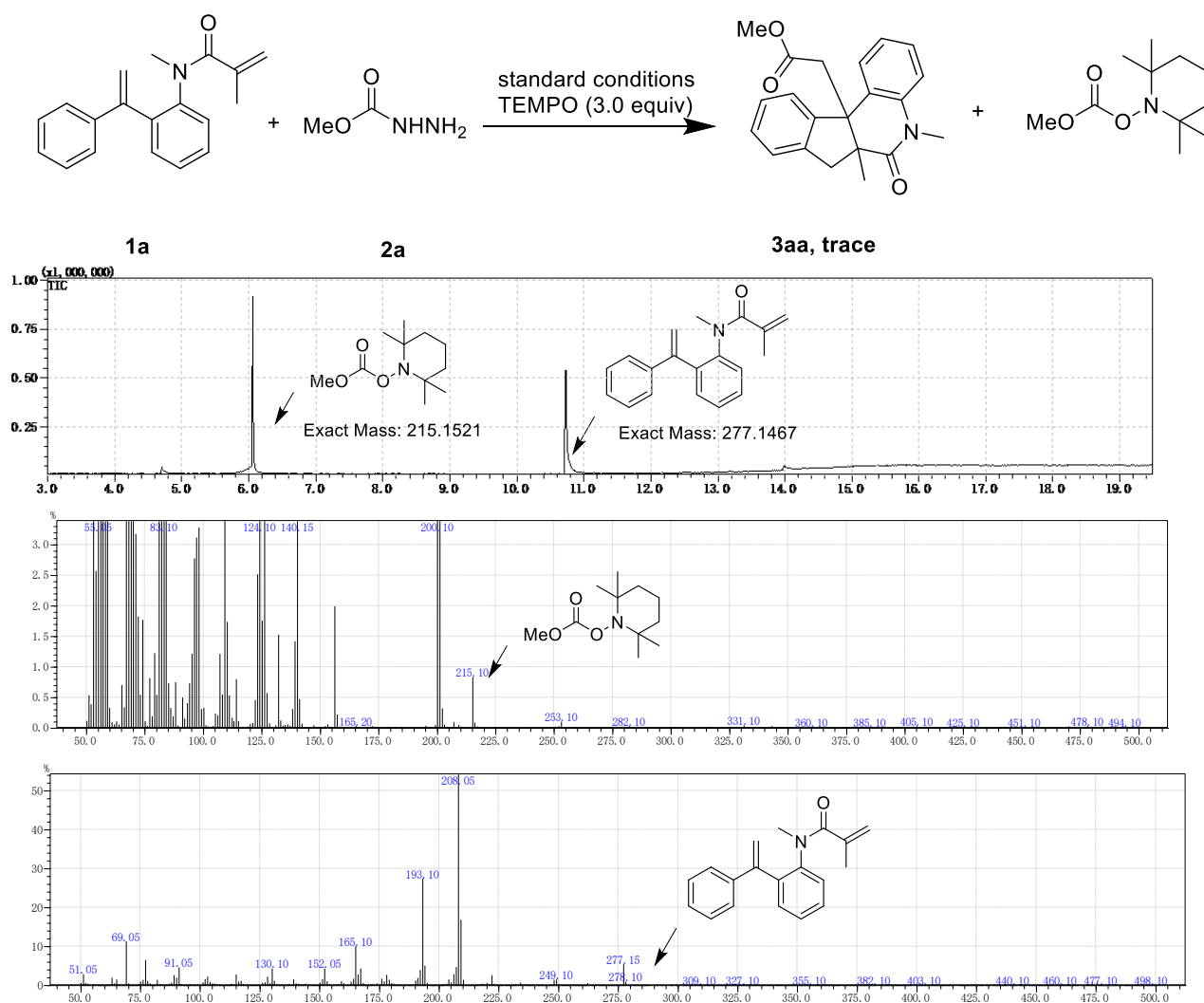
1. General Conditions	S2
2. Mechanism Study	S2-S4
3. Preparation of starting materials	S4
4. Experimental Procedures	S5
5. Characterization Data for the Products	S6-S14
6. References	S15
7. Copies of the ¹ H NMR and ¹³ C NMR Spectra	S16-S33

1. General Conditions

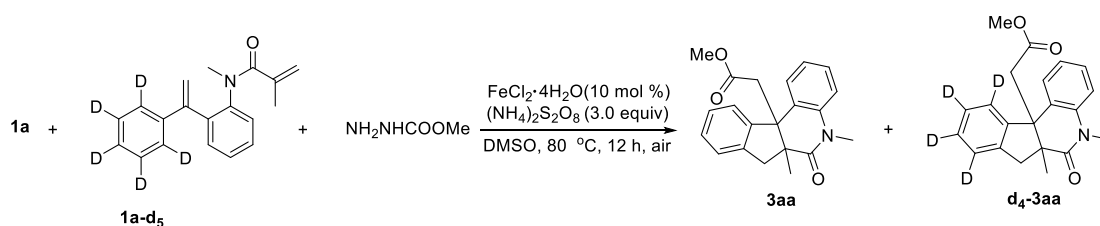
Unless otherwise noted, all chemicals were purchased from commercial suppliers (Adamas, Aladdin, etc) and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl_3 (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

2. Mechanism Study.

2.1 GC-MS spectra of reaction mixture after adding 3 equivalents of TEMPO

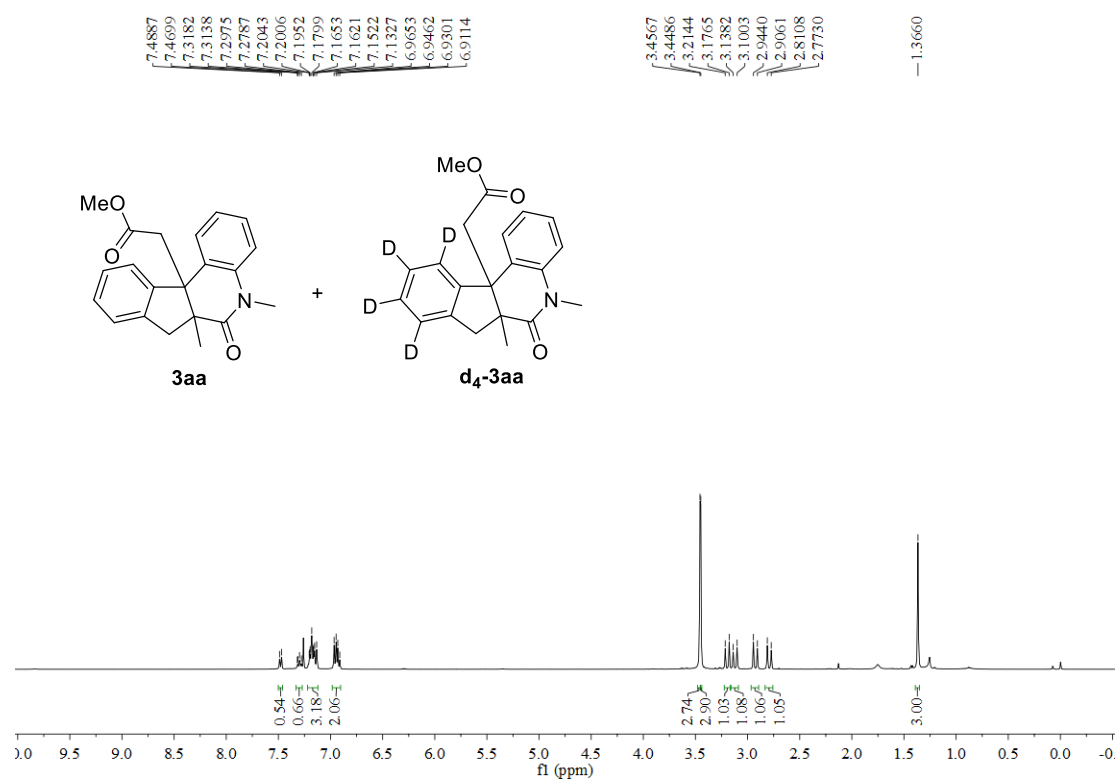


2.2 Intermolecular KIE study

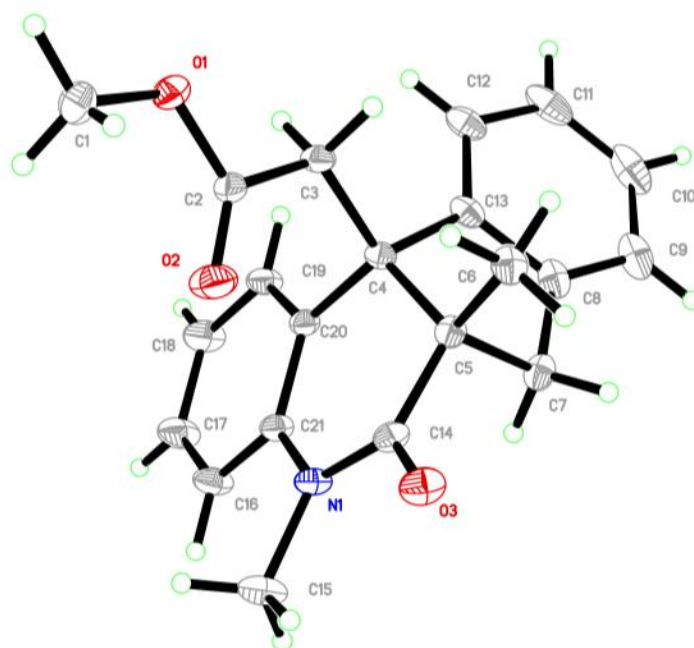


Under air, a 10 mL Schlenk tube equipped with a stir bar was charged with **1a** (0.1 mmol, 27.7 mg, 1.0 equiv), **1a-d₅** (0.1 mmol, 28.2 mg, 1.0 equiv), methyl *N*-aminocarbamate (72.6 mg, 0.8 mmol, 4.0 equiv), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (136.9 mg, 0.6 mmol, 3.0 equiv), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol, 10 mol %), DMSO (2.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 80 °C for 12 h in oil bath. After cooling to room temperature, the reaction mixture was diluted with saturated aqueous NaCl solution (15 mL $\times$ 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo. The residue was purified by silica gel (300–400 mesh) column chromatography using hexane/EtOAc (5:1, v/v) as eluent to afford the desired product **3aa** and **d₄-3aa**.

^1H NMR (CDCl_3 , 400 MHz): δ 7.48 (d, J = 7.52 Hz, 0.5H), 7.32-7.30 (m, 0.6H), 7.20-7.13 (m, 3H), 6.96-6.91 (m, 2H), 3.46 (s, 3H), 3.45 (s, 3H), 3.20 (d, J = 15.2 Hz, 1H), 3.12 (d, J = 15.2 Hz, 1H), 2.92 (d, J = 15.2 Hz, 1H), 2.79 (d, J = 15.1 Hz, 1H), 1.40 (s, 3H).



2.3 X-Ray Structure of Sulfonyl Hydrazone **3aa**

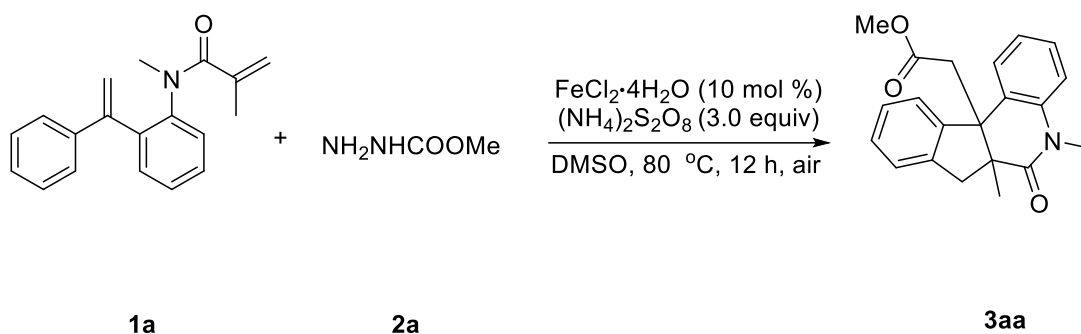


3. Preparation of starting materials **1**

Synthesis of substrates **1a-1o**, and **1s** were according to the published procedure.^[1]

1p-1r, was known compounds and prepared according to published procedures.^[2]

4. Experimental Procedures

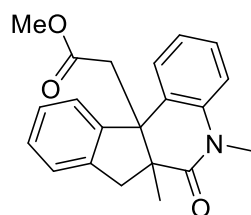


Under air, a 10 mL Schlenk tube equipped with a stir bar was charged with **1a** (0.2 mmol, 1.0 equiv), methyl *N*-aminocarbamate (72.6 mg, 0.8 mmol, 4.0 equiv) **2a**, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (136.9 mg, 0.6 mmol, 3.0 equiv), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol, 10 mol %), DMSO (2.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 80 °C for 12 h in oil bath. After cooling to room temperature, the reaction mixture was diluted with saturated aqueous NaCl solution (15 mL $\times$ 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo. The residue was purified by silica gel (300–400 mesh) column chromatography using hexane/EtOAc (5:1, v/v) as eluent to afford the desired product **3aa**.

5. Characterization Data for the Products

cis-Methyl

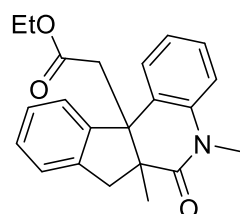
2-(5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11b*H*-indeno[2,1-*c*]quinolin-11b-yl)acetate (**3a**)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3a** (45.5 mg, 68% yield) as yellow solid. M.p. 122.8-124.9 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.49 (d, J = 7.6 Hz, 1H), 7.31-7.28 (m, 1H), 7.21-7.13 (m, 4H), 6.96-6.91 (m, 2H), 3.45 (s, 3H), 3.43 (s, 3H), 3.19 (d, J = 15.2 Hz, 1H), 3.12 (d, J = 15.2 Hz, 1H), 2.92 (d, J = 15.2 Hz, 1H), 2.79 (d, J = 15.2 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.9, 170.7, 146.9, 140.7, 139.2, 129.2, 127.8, 127.1, 126.6, 125.5, 124.9, 123.7, 122.8, 114.2, 53.9, 52.5, 51.3, 44.5, 41.2, 29.9, 18.6. HRMS (ESI-TOF): calculated for $[\text{M}+\text{H}]^+ \text{C}_{21}\text{H}_{22}\text{NO}_3^+$ 336.1594, found 336.1606. MS (m/z): 335.2 $[\text{M}]^+$.

cis-Methyl

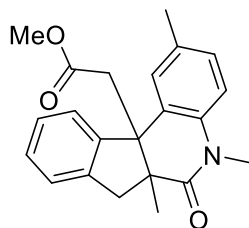
2-(5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11b*H*-indeno[2,1-*c*]quinolin-11b-yl)acetate (**3b**)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3b** (37.0 mg, 53% yield) as yellow solid. M.p. 101.4-103.2 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.48 (d, J = 7.5 Hz, 1H), 7.30-7.27 (m, 1H), 7.20-7.15 (m, 4H), 6.95-6.90 (m, 2H), 3.94-3.84 (m, 2H), 3.43 (s, 3H), 3.18 (d, J = 15.0 Hz, 1H), 3.12 (d, J = 15.2 Hz, 1H), 2.90 (d, J = 14.9 Hz, 1H), 2.79 (d, J = 15.2 Hz, 1H), 1.38 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.0, 170.4, 147.0, 140.7, 139.2, 129.3, 127.7, 127.1, 126.6, 125.5, 124.9, 123.7, 122.7, 114.1, 60.4, 54.0, 52.5, 44.5, 41.4, 29.9, 18.7, 13.8. HRMS (ESI-TOF): calculated for $[\text{M}+\text{H}]^+ \text{C}_{22}\text{H}_{24}\text{NO}_3^+$ 350.1751, found 350.1763. MS (m/z): 349.2 $[\text{M}]^+$.

cis-Methyl

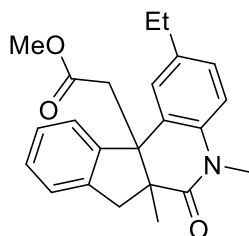
2-(2,5,6a-trimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3d** (37.7 mg, 54% yield) as yellow solid. M.p. 141.0-142.3 °C. ¹H NMR (CDCl₃, 300 MHz): δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.33-7.27 (m, 1H), 7.22-7.17 (m, 2H), 7.00-6.96 (m, 1H), 6.90 (s, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 3.46 (s, 3H), 3.42 (s, 3H), 3.18 (d, *J* = 15.2 Hz, 1H), 3.11 (d, *J* = 15.2 Hz, 1H), 2.91 (d, *J* = 15.1 Hz, 1H), 2.77 (d, *J* = 15.2 Hz, 1H), 2.18 (s, 3H), 1.35 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 170.7, 147.1, 140.7, 136.9, 132.0, 129.7, 128.5, 127.1, 126.6, 125.2, 124.9, 123.7, 114.2, 53.9, 52.5, 51.3, 44.5, 41.3, 29.9, 20.6, 18.7. HRMS (ESI-TOF): calculated for [M+H]⁺ C₂₂H₂₄NO₃⁺ 350.1751, found 350.1766. MS (m/z): 349.2 [M]⁺.

cis-Methyl

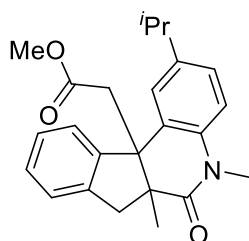
2-(2-ethyl-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3e** (40.0 mg, 55% yield) as yellow solid. M.p. 98.5-100.6 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.31-7.29 (s, 1H), 7.21-7.16 (m, 2H), 7.02-7.00 (m, 1H), 6.94 (s, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 3.46 (s, 3H), 3.43 (s, 3H), 3.19 (d, *J* = 15.2 Hz, 1H), 3.12 (d, *J* = 15.2 Hz, 1H), 2.91 (d, *J* = 15.2 Hz, 1H), 2.78 (d, *J* = 15.2 Hz, 1H), 2.52-2.46 (m, 2H), 1.35 (s, 3H), 1.13-1.09 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.9, 170.8, 147.2, 140.8, 138.4, 137.1, 128.7, 127.1, 126.6, 125.3, 124.9, 123.7, 114.2, 54.0, 52.6, 51.4, 44.5, 41.4, 30.0, 27.9, 18.7, 15.1. HRMS (ESI-TOF): calculated for [M+H]⁺ C₂₃H₂₆NO₃⁺ 364.1907, found 364.1924. MS (m/z): 363.2 [M]⁺.

cis-Methyl

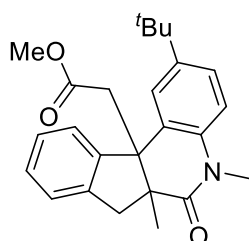
2-(2-isopropyl-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3f)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3f** (44.5 mg, 59% yield) as yellow solid. M.p. 127.4-129.3 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.49 (d, J = 7.6 Hz, 1H), 7.30-7.26 (m, 1H), 7.20-7.15 (m, 2H), 7.05-7.02 (m, 2H), 6.88 (d, J = 8.4 Hz, 1H), 3.45 (s, 3H), 3.43 (s, 3H), 3.19 (d, J = 15.4 Hz, 1H), 3.13 (d, J = 15.2 Hz, 1H), 2.92 (d, J = 15.2 Hz, 1H), 2.78 (d, J = 15.2 Hz, 1H), 1.35 (s, 3H), 1.12-1.10 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.9, 170.8, 147.1, 143.0, 140.8, 137.1, 127.5, 127.1, 126.6, 125.5, 125.2, 124.9, 123.7, 114.1, 54.0, 52.6, 51.4, 44.5, 41.4, 33.1, 29.9, 23.8, 23.7, 18.7. HRMS (ESI-TOF): calculated for $[\text{M}+\text{H}]^+$ $\text{C}_{24}\text{H}_{28}\text{NO}_3^+$ 378.2064, found 378.2078. MS (m/z): 377.2 $[\text{M}]^+$.

cis-Methyl

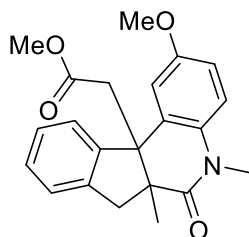
2-(2-(tert-butyl)-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3g)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3g** (49.3 mg, 63% yield) as yellow solid. M.p. 87.1-89.7 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.49 (d, J = 7.6 Hz, 1H), 7.31-7.27 (m, 1H), 7.48-7.44 (m, 2H), 7.19-7.15 (m, 4H), 6.88 (d, J = 9.3 Hz, 1H), 3.45 (s, 3H), 3.43 (s, 3H), 3.20 (d, J = 15.2 Hz, 1H), 3.14 (d, J = 15.1 Hz, 1H), 2.93 (d, J = 15.3 Hz, 1H), 2.78 (d, J = 15.2 Hz, 1H), 1.35 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 170.9, 147.2, 145.3, 140.8, 136.7, 127.1, 126.5, 126.3, 124.9, 124.6, 123.6, 113.8, 54.1, 52.6, 51.4, 44.5, 41.4, 34.1, 31.1, 29.9, 18.7. HRMS (ESI-TOF): calculated for $[\text{M}+\text{H}]^+$ $\text{C}_{25}\text{H}_{30}\text{NO}_3^+$ 392.2220, found 392.2229. MS (m/z): 391.2 $[\text{M}]^+$.

cis-Methyl

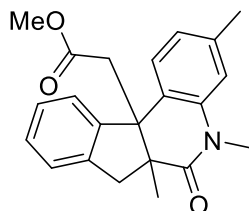
2-(2-methoxy-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3h** (52.6 mg, 72% yield) as yellow solid. M.p. 145.9-147.8 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.45 (d, *J* = 7.56 Hz, 1H), 7.29 (d, *J* = 6.7 Hz, 1H), 7.20-7.15 (m, 2H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.73-6.69 (m, 2H), 3.67 (s, 3H), 3.46 (s, 3H), 3.41 (s, 3H), 3.18 (d, *J* = 15.2 Hz, 1H), 3.10 (d, *J* = 15.2 Hz, 1H), 2.90 (d, *J* = 15.2 Hz, 1H), 2.80 (d, *J* = 15.2 Hz, 1H), 1.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.4, 170.7, 155.0, 146.9, 140.7, 133.1, 127.2, 127.1, 126.7, 125.0, 123.5, 115.6, 115.1, 112.2, 55.20, 54.1, 52.4, 51.4, 44.3, 41.2, 30.1, 18.7. HRMS (ESI-TOF): calculated for [M+H]⁺ C₂₂H₂₄NO₄⁺ 366.1700, found 366.1716 MS (m/z): 365.2 [M]⁺.

cis-Methyl

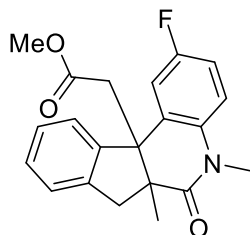
2-(3,5,6a-trimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3i)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3i** (39.0 mg, 42% yield) as solid. M.p. 102.6-104.7 °C. ¹H NMR (CDCl₃, 300 MHz): δ 7.45 (d, *J* = 7.6 Hz, 1H), 7.31-7.28 (m, 1H), 7.20-7.16 (m, 2H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.77-6.76 (m, 2H), 3.47 (s, 3H), 3.44 (s, 3H), 3.18 (d, *J* = 15.2 Hz, 1H), 3.11 (d, *J* = 15.3 Hz, 1H), 2.91 (d, *J* = 15.2 Hz, 1H), 2.78 (d, *J* = 15.2 Hz, 1H), 2.29 (s, 3H), 1.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 173.0, 170.7, 147.1, 140.5, 138.9, 137.4, 128.9, 126.9, 126.4, 124.7, 123.5, 123.5, 122.5, 114.8, 53.5, 52.3, 51.2, 44.4, 41.1, 29.8, 21.2, 18.5. HRMS (ESI-TOF): calculated for [M+H]⁺ C₂₂H₂₄NO₃⁺ 350.1751, found 350.1765. MS (m/z): 349.2 [M]⁺.

cis-Methyl

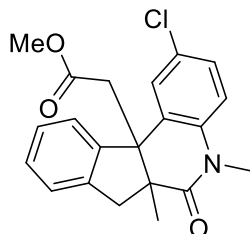
2-(2-fluoro-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3j)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3j** (24.7 mg, 35% yield) as yellow solid. M.p. 159.9-161.7 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.32-7.29 (m, 1H), 7.23-7.17 (m, 2H), 6.92-6.83 (m, 3H), 3.47 (s, 3H), 3.42 (s, 3H), 3.17 (d, *J* = 15.3 Hz, 1H), 3.10 (d, *J* = 15.2 Hz, 1H), 2.91 (d, *J* = 15.3 Hz, 1H), 2.79 (d, *J* = 15.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 172.5, 170.5, 158.3 (d, *J*_{C-F} = 241.0 Hz), 146.4, 140.7, 135.7 (d, *J*_{C-F} = 3.0 Hz), 127.8 (d, *J*_{C-F} = 6.0 Hz), 127.5, 126.9, 125.0, 123.5, 116.0 (d, *J*_{C-F} = 23.0 Hz), 115.5 (d, *J*_{C-F} = 8.0 Hz), 114.5 (d, *J*_{C-F} = 23.0 Hz), 54.0, 52.2, 51.5, 44.4, 41.1, 30.2, 18.7. HRMS (ESI-TOF): calculated for [M+H]⁺ C₂₁H₂₁FNO₃⁺ 354.1500, found 354.1512 MS (m/z): 353.1 [M]⁺.

cis-Methyl

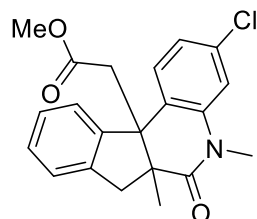
2-(2-chloro-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3k)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3k** (42.0 mg, 57% yield) as yellow solid. M.p. 159.4-161.2 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.45 (d, *J* = 7.6 Hz, 1H), 7.33-7.29 (m, 1H), 7.23-7.17 (m, 2H), 7.14-7.11 (m, 1H), 7.08 (d, *J* = 2.3 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 3.47 (s, 3H), 3.42 (s, 3H), 3.18 (d, *J* = 15.5 Hz, 1H), 3.10 (d, *J* = 15.2 Hz, 1H), 2.91 (d, *J* = 15.5 Hz, 1H), 2.79 (d, *J* = 15.2 Hz, 1H), 1.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.7, 170.5, 146.3, 140.6, 138.1, 129.2, 127.9, 127.8, 127.6, 127.5, 127.0, 125.0, 123.6, 115.6, 53.9, 52.4, 51.5, 44.5, 41.2, 30.1, 18.6. HRMS (ESI-TOF): calculated for [M+H]⁺ C₂₁H₂₁ClNO₃⁺ 370.1204, found 370.1217. MS (m/z): 369.1 [M]⁺.

***cis*-Methyl**

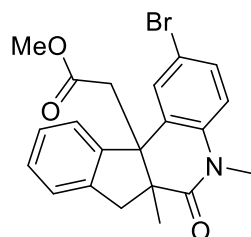
2-(3-chloro-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11b*H*-indeno[2,1-*c*]quinolin-11b-yl)acetate (3l**)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3l** (28.1 mg, 38% yield) as yellow solid. M.p. 86.6-88.7 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.70 (d, *J* = 7.4 Hz, 1H), 7.21-7.12 (m, 4H), 6.97-6.93 (m, 2H), 4.07 (d, *J* = 16.2 Hz, 1H), 3.51 (s, 3H), 3.45 (s, 3H), 3.27 (d, *J* = 15.0 Hz, 1H), 2.87 (d, *J* = 16.2 Hz, 1H), 2.68 (d, *J* = 15.0 Hz, 1H), 1.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.4, 170.9, 144.1, 142.6, 142.1, 134.8, 129.4, 128.5, 127.1, 126.6, 124.6, 124.5, 123.5, 114.1, 55.3, 54.7, 51.5, 44.9, 36.4, 31.5, 18.1. HRMS (ESI-TOF): calculated for [M+H]⁺ C₂₁H₂₁ClNO₃⁺ 370.1204, found 370.1219. MS (*m/z*): 369.1 [M]⁺.

***cis*-Methyl**

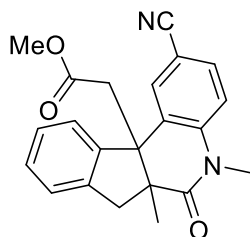
2-(2-bromo-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11b*H*-indeno[2,1-*c*]quinolin-11b-yl)acetate (3m**)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3m** (42.1 mg, 51% yield) as yellow solid. M.p. 161.7-163.5 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.44 (d, *J* = 7.5 Hz, 1H), 7.34-7.27 (m, 2H), 7.23-7.17 (m, 3H), 6.82 (d, *J* = 8.8 Hz, 1H), 3.48 (s, 3H), 3.41 (s, 3H), 3.18 (d, *J* = 15.6 Hz, 1H), 3.10 (d, *J* = 15.4 Hz, 1H), 2.91 (d, *J* = 15.6 Hz, 1H), 2.79 (d, *J* = 15.2 Hz, 1H), 1.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.7, 170.6, 146.3, 140.6, 138.7, 132.1, 130.8, 128.0, 127.5, 127.1, 125.1, 123.6, 116.0, 115.4, 53.8, 52.4, 51.5, 44.5, 41.3, 30.1, 18.7. HRMS (ESI-TOF): calculated for [M+H]⁺ C₂₁H₂₁BrNO₃⁺ 414.0699, found 414.0711. MS (*m/z*): 413.1 [M]⁺.

cis-Methyl

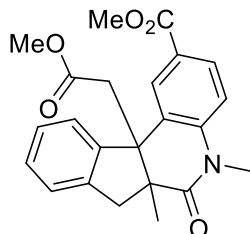
2-(2-cyano-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3n)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3n** (23.8mg, 33% yield) as yellow solid. M.p. 151.3-153.2 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 7.48-7.45 (m, 2H), 7.42 (s, 1H), 7.37-7.33 (m, 1H), 7.24-7.18 (m, 2H), 7.01 (d, J = 8.52 Hz, 1H), 3.49 (s, 3H), 3.46 (s, 3H), 3.19 (d, J = 16.0 Hz, 1H), 3.09 (d, J = 15.4 Hz, 1H), 2.94 (d, J = 16.0 Hz, 1H), 2.82 (d, J = 15.3 Hz, 1H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.0, 170.5, 145.8, 143.3, 140.4, 133.5, 132.0, 127.9, 127.4, 127.3, 125.2, 123.6, 118.8, 114.8, 105.8, 53.7, 52.3, 51.7, 44.8, 41.4, 30.2, 18.6. HRMS (ESI-TOF): calculated for $[\text{M}+\text{H}]^+$ $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_3^+$ 361.1547, found 361.1556. MS (m/z): 360.1 $[\text{M}]^+$.

cis-Methyl

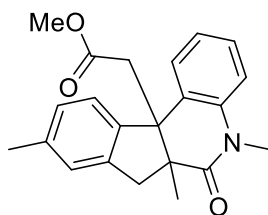
11b-(2-methoxy-2-oxoethyl)-5,6a-dimethyl-6-oxo-6,6a,7,11b-tetrahydro-5H-indeno[2,1-c]quinoline-2-carboxylate (3o)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3o** (48.0 mg, 61% yield) as yellow oil. ^1H NMR (CDCl_3 , 400 MHz): δ 7.83 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.56 Hz, 1H), 7.34-7.29 (m, 1H), 7.20-7.14 (m, 2H), 6.98 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H), 3.46 (s, 3H), 3.44 (s, 3H), 3.27 (d, J = 15.8 Hz, 1H), 3.10 (d, J = 15.2 Hz, 1H), 2.93 (d, J = 15.8 Hz, 1H), 2.80 (d, J = 15.2 Hz, 1H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.2, 170.6, 166.1, 146.5, 143.2, 140.4, 130.9, 129.4, 127.4, 127.1, 125.8, 124.8, 124.2, 123.7, 114.1, 53.7, 52.3, 51.8, 51.4, 44.8, 41.4, 30.1, 18.6. HRMS (ESI-TOF): calculated for $[\text{M}+\text{H}]^+$ $\text{C}_{23}\text{H}_{24}\text{NO}_5^+$ 394.1649, found 394.1663. MS (m/z): 393.2 $[\text{M}]^+$.

cis-Methyl

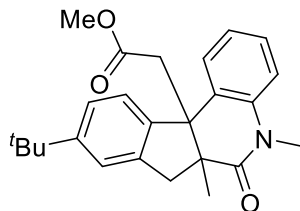
2-(5,6a,9-trimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3p)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3p** (32.1 mg, 46% yield) as yellow oil. ^1H NMR (CDCl_3 , 400 MHz): δ 7.36 (d, J = 7.8 Hz, 1H), 7.19-7.09 (m, 4H), 7.00 (s, 1H), 6.96-6.91 (m, 2H), 3.45 (s, 3H), 3.44 (s, 3H), 3.17 (d, J = 15.2 Hz, 1H), 3.08 (d, J = 15.1 Hz, 1H), 2.90 (d, J = 15.3 Hz, 1H), 2.74 (d, J = 15.2 Hz, 1H), 2.31 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.1, 170.8, 144.2, 140.8, 139.2, 136.9, 129.2, 127.7, 127.3, 125.9, 125.7, 123.4, 122.8, 114.2, 53.6, 52.5, 51.4, 44.5, 41.4, 29.9, 21.2, 18.7. HRMS (ESI-TOF): calculated for $[\text{M}+\text{H}]^+ \text{C}_{22}\text{H}_{24}\text{NO}_3^+$ 350.1751, found 350.1765. MS (m/z): 349.2 $[\text{M}]^+$.

cis-Methyl

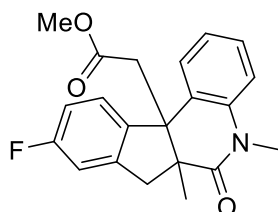
2-(9-(tert-butyl)-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3q):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3q** (32.9 mg, 42% yield) as yellow oil. ^1H NMR (CDCl_3 , 400 MHz): δ 7.38 (d, J = 7.8 Hz, 1H), 7.31-7.28 (m, 1H), 7.18-7.15 (m, 3H), 6.95-6.91 (m, 2H), 3.45 (s, 3H), 3.44 (s, 3H), 3.19 (d, J = 15.4 Hz, 1H), 3.10 (d, J = 15.0 Hz, 1H), 2.91 (d, J = 15.3 Hz, 1H), 2.77 (d, J = 15.0 Hz, 1H), 1.38 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.2, 170.8, 150.3, 143.9, 140.4, 139.2, 129.4, 127.7, 125.9, 123.5, 123.1, 122.7, 121.9, 114.2, 53.6, 52.5, 51.3, 44.8, 41.4, 34.5, 31.4, 29.9, 18.8. HRMS (ESI-TOF): calculated for $[\text{M}+\text{H}]^+ \text{C}_{25}\text{H}_{30}\text{NO}_3^+$ 392.2220, found 392.2235. MS (m/z): 391.2 $[\text{M}]^+$.

cis-Methyl

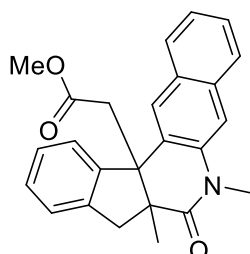
2-(9-fluoro-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3r)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3r** (26.1 mg, 37% yield) as yellow solid. M.p. 125.5-127.6 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.44-7.40 (m, 1H), 7.20-7.16 (m, 1H), 7.11-7.08 (m, 1H), 6.99-6.91 (m, 3H), 6.86 (d, *J* = 8.5 Hz, 1H), 3.43 (s, 3H), 3.42 (s, 3H), 3.14 (d, *J* = 15.2 Hz, 1H), 3.09 (d, *J* = 15.2 Hz, 1H), 2.89 (d, *J* = 15.0 Hz, 1H), 2.75 (d, *J* = 15.4 Hz, 1H), 1.35 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 172.4, 170.6, 162.1 (d, *J*_{C-F} = 244.0 Hz), 143.0 (d, *J*_{C-F} = 9.0 Hz), 142.6 (d, *J*_{C-F} = 3.0 Hz), 139.1, 129.1, 128.0, 125.3, 124.7 (d, *J*_{C-F} = 9.0 Hz), 122.8, 114.3, 113.3, 112.4, 53.3, 52.8, 51.4, 44.1, 41.2, 30.0, 18.6. HRMS (ESI-TOF): calculated for [M+H]⁺ C₂₁H₂₁FNO₃⁺ 354.1500, found 354.1516. MS (m/z): 353.1 [M]⁺.

cis-Methyl

2-(6,7a-dimethyl-7-oxo-6,7,7a,8-tetrahydro-12bH-benzo[glindeno[2,1-c]quinolin-12b-yl)acetate(3s)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3s** (16.2 mg, 21% yield) as yellow solid. M.p. 191.2-193.3 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.54 (d, *J* = 8.8 Hz, 1H), 7.78-7.66 (m, 3H), 7.38-7.28 (m, 2H), 7.24-7.20 (m, 2H), 7.08-7.04 (m, 2H), 3.98 (d, *J* = 15.4 Hz, 1H), 3.53 (s, 3H), 3.41 (s, 3H), 3.33 (d, *J* = 14.9 Hz, 1H), 3.12 (d, *J* = 15.4 Hz, 1H), 2.63 (d, *J* = 14.9 Hz, 1H), 1.26 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.7, 170.7, 147.0, 142.5, 138.3, 131.6, 130.9, 129.9, 129.0, 126.9, 125.7, 125.3, 125.0, 124.4, 123.7, 118.0, 116.0, 55.9, 55.3, 51.4, 44.3, 38.2, 31.6, 18.1. HRMS (ESI-TOF): calculated for [M+H]⁺ C₂₅H₂₄NO₃⁺ 386.1751, found 386.1759. MS (m/z): 385.2 [M]⁺.

6. References

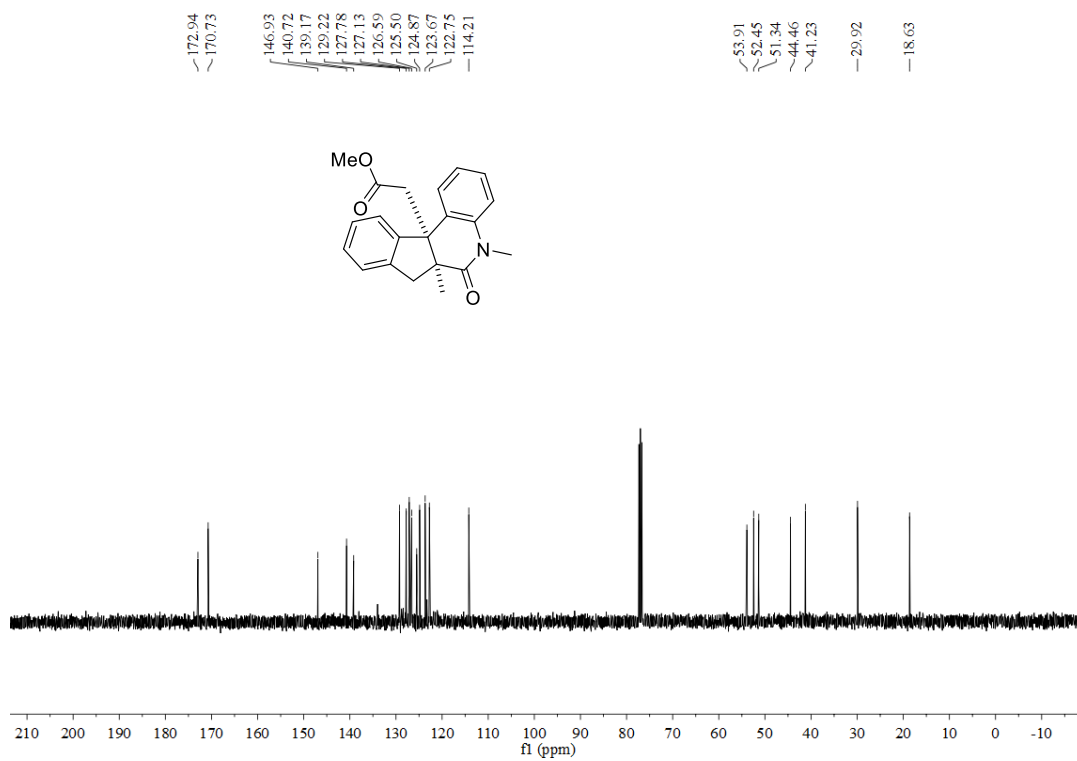
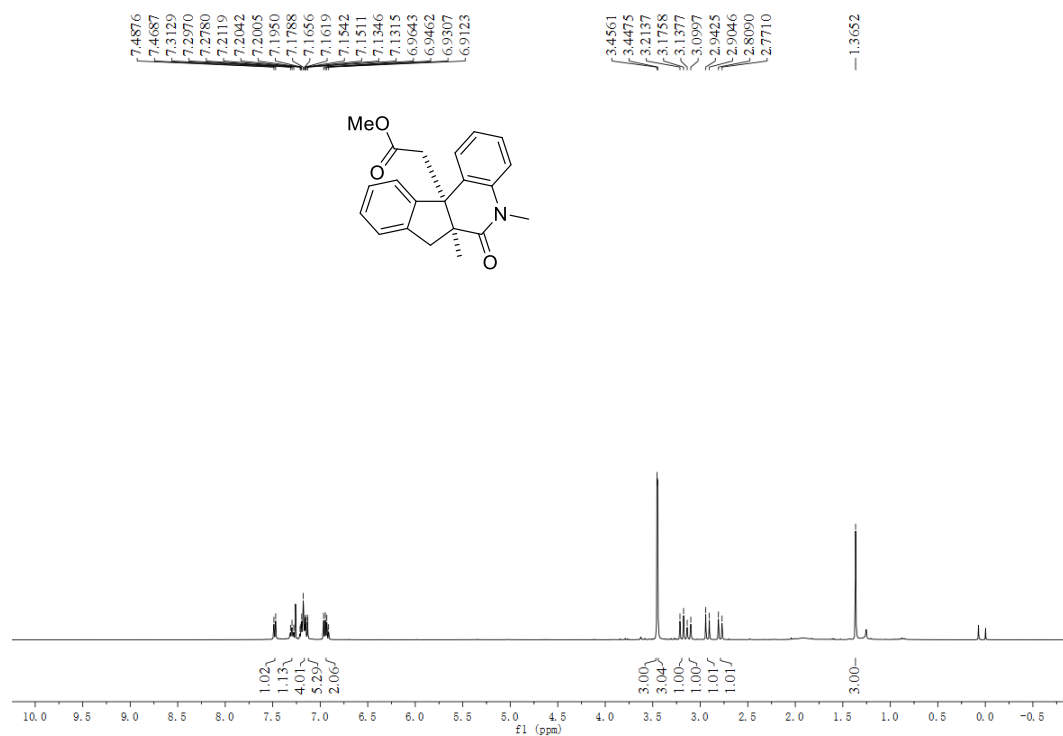
[1] H. Wang, B. Wang, S. Sun, J. Cheng, *Org. Chem. Front.*, 2018, **5**, 2547.

[2] S. Song, C. Zhou, J.-T. Yu, J. Cheng, *Org. Let.*, 2019, **21**, 6579.

7. Copies of the ^1H NMR and ^{13}C NMR Spectra

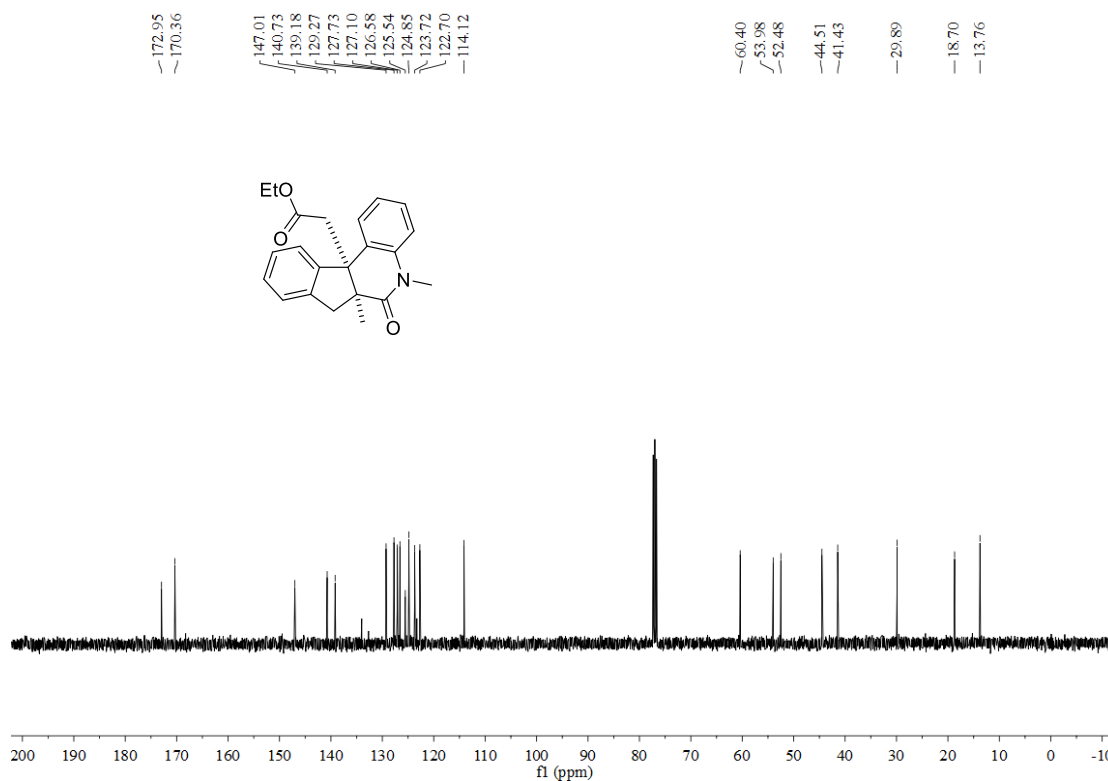
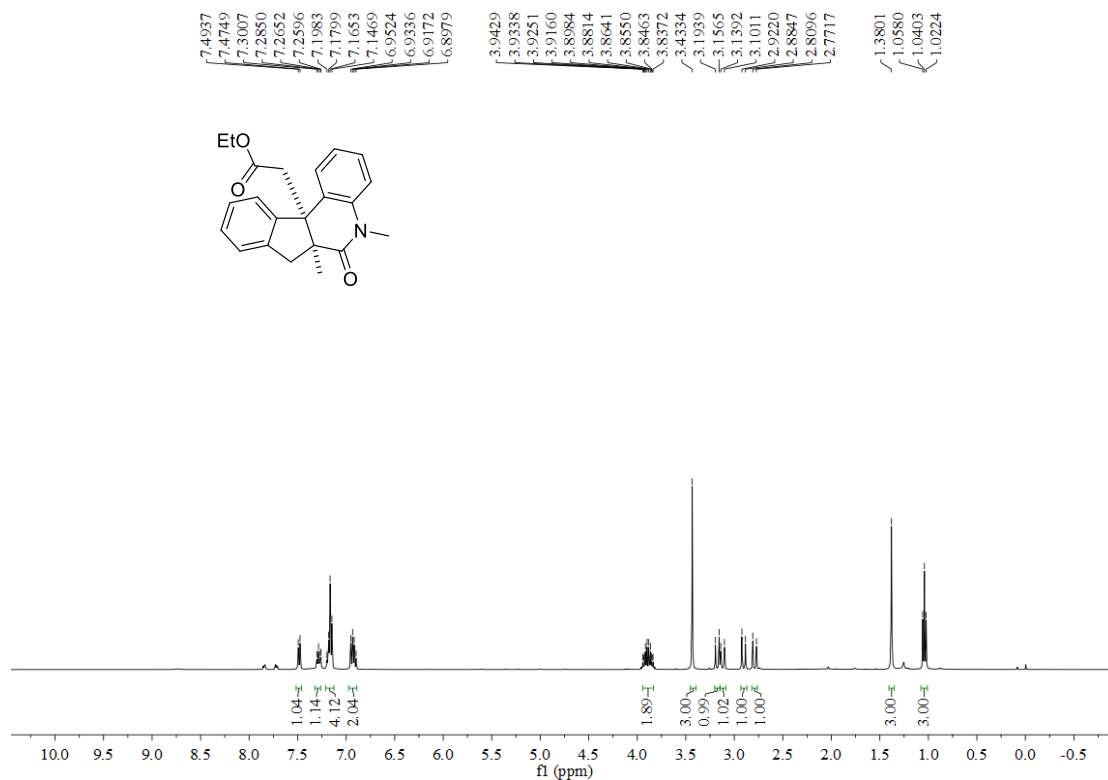
cis-Methyl

2-(5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11*bH*-indeno[2,1-*c*]quinolin-11*b*-yl)acetate (3a)

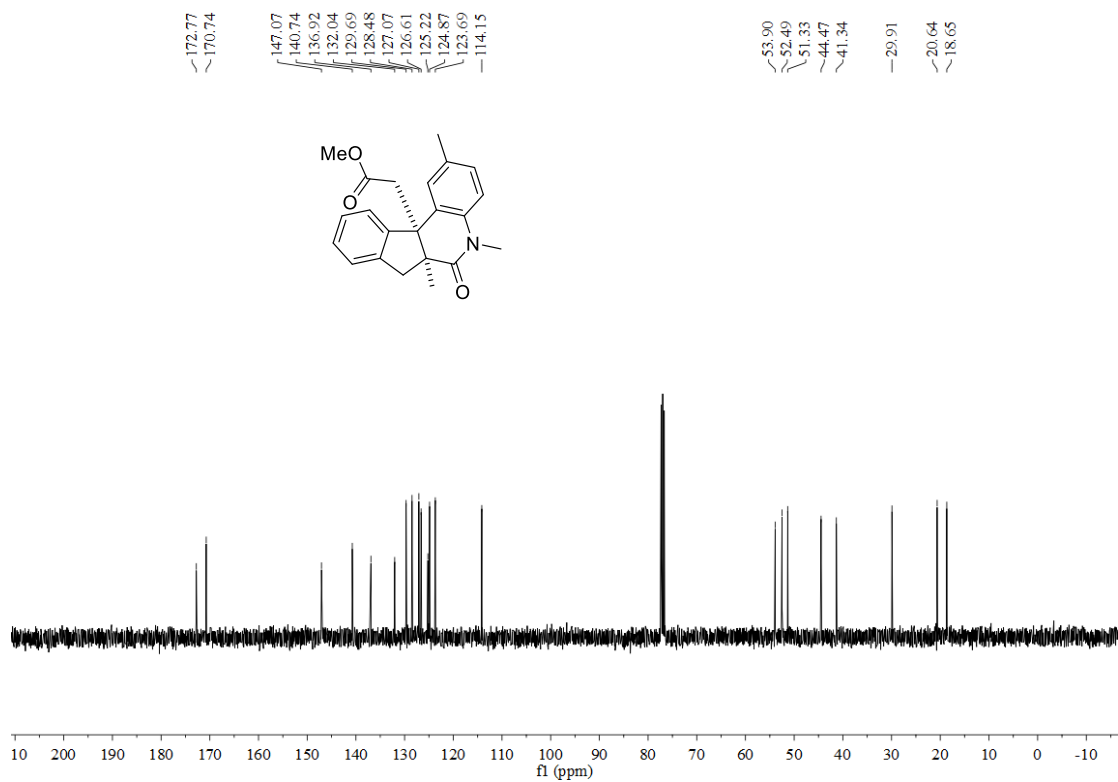
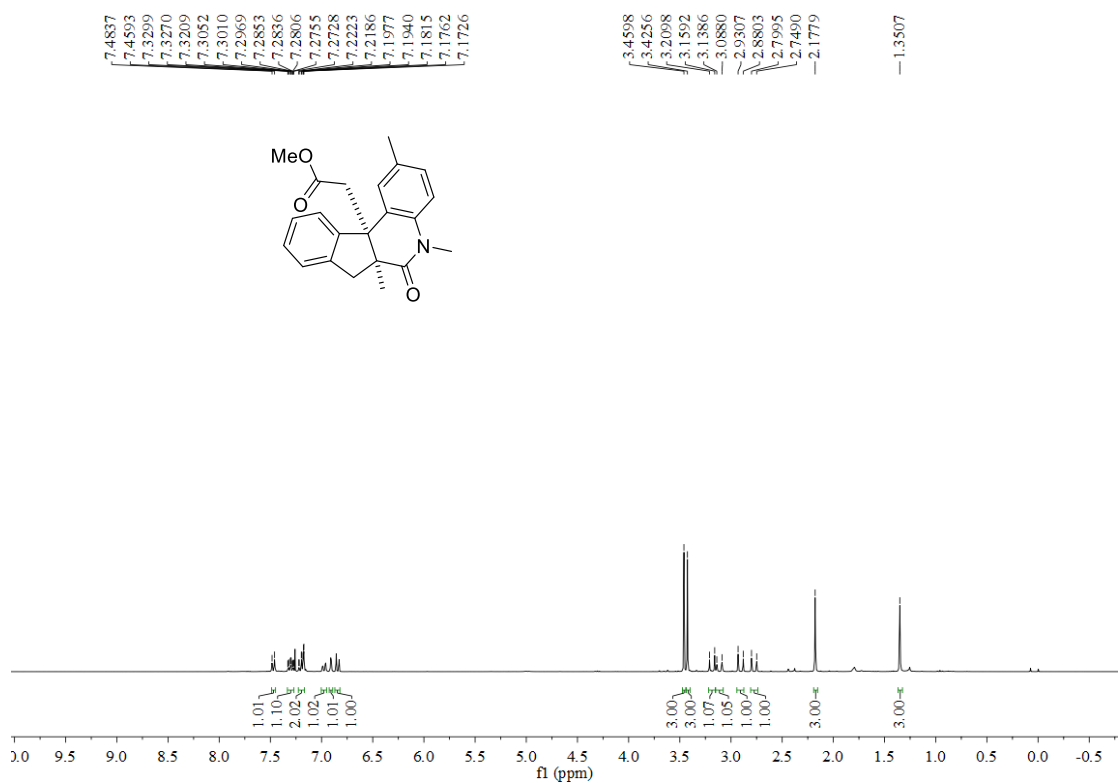


cis-Methyl

2-(5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3b)

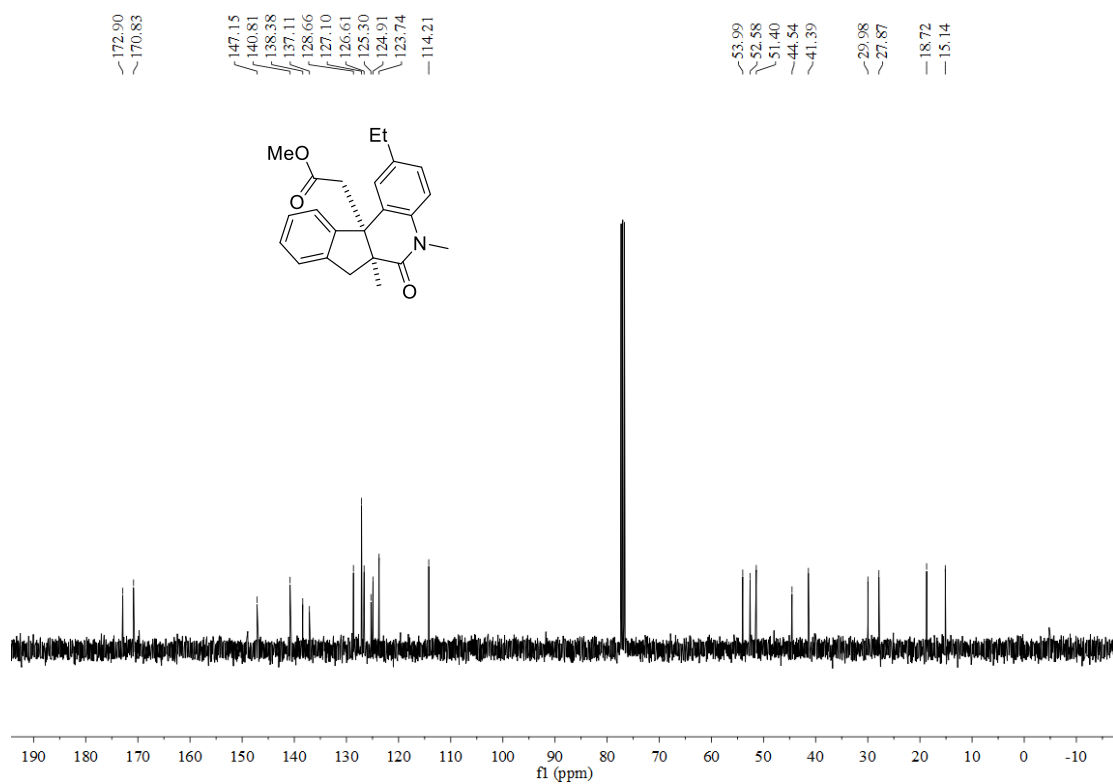
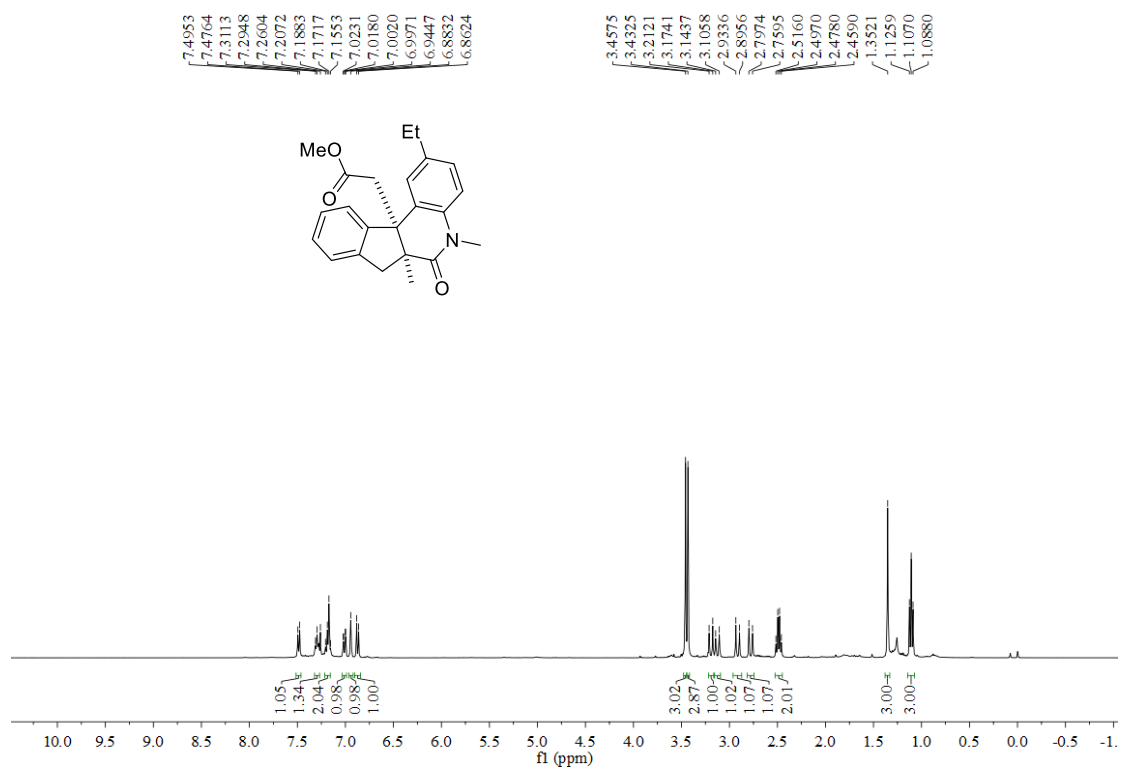


cis-Methyl
2-(2,5,6a-trimethyl-6-oxo-5,6,6a,7-tetrahydro-11b*H*-indeno[2,1-*c*]quinolin-11b-yl)
acetate (3d)



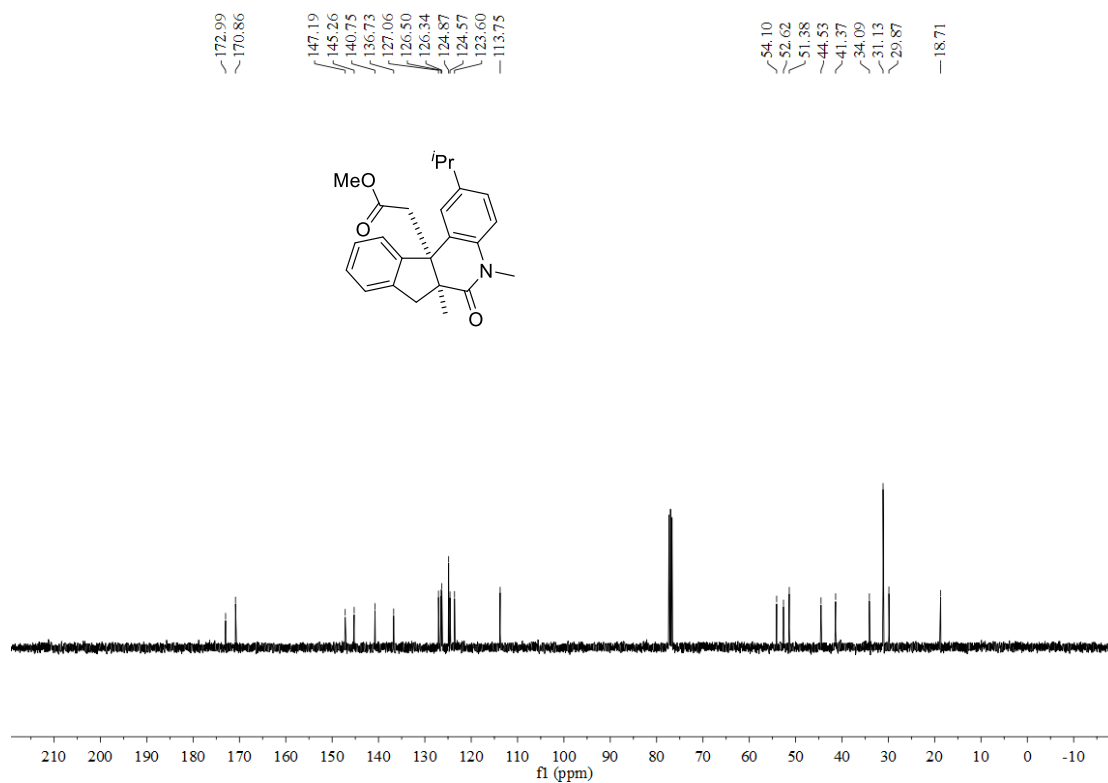
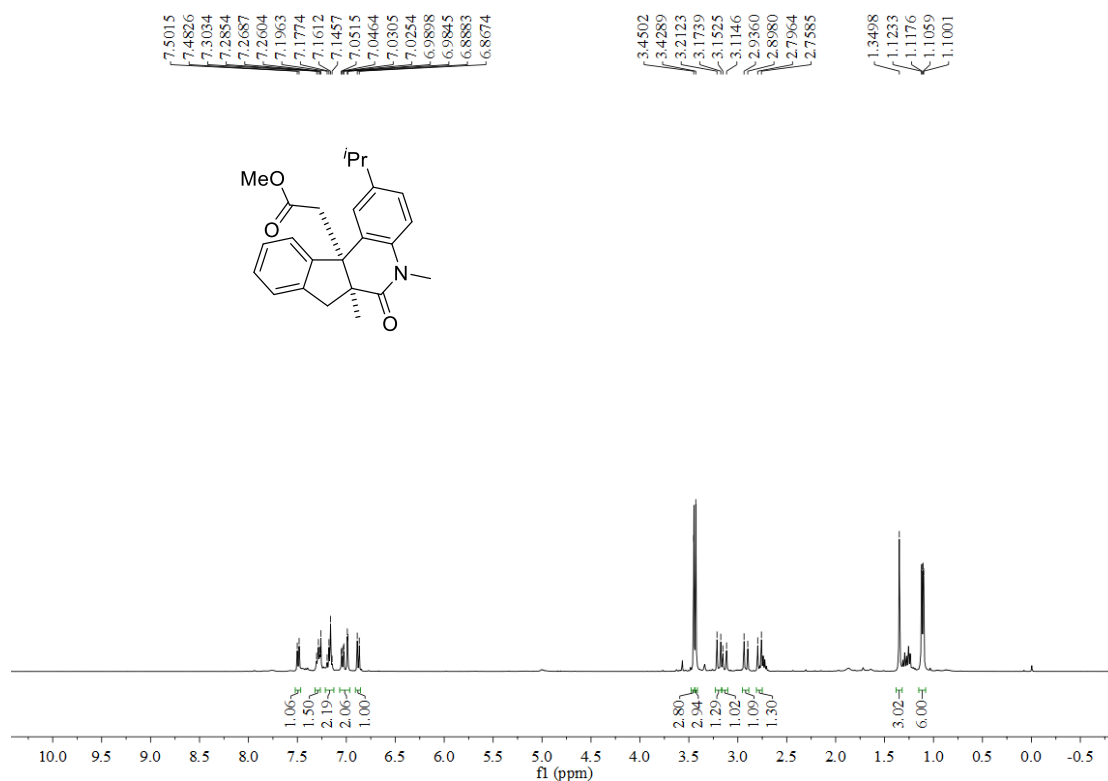
cis-Methyl

2-(2-ethyl-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11b*H*-indeno[2,1-*c*]quinolin-11b-yl)acetate (3e)



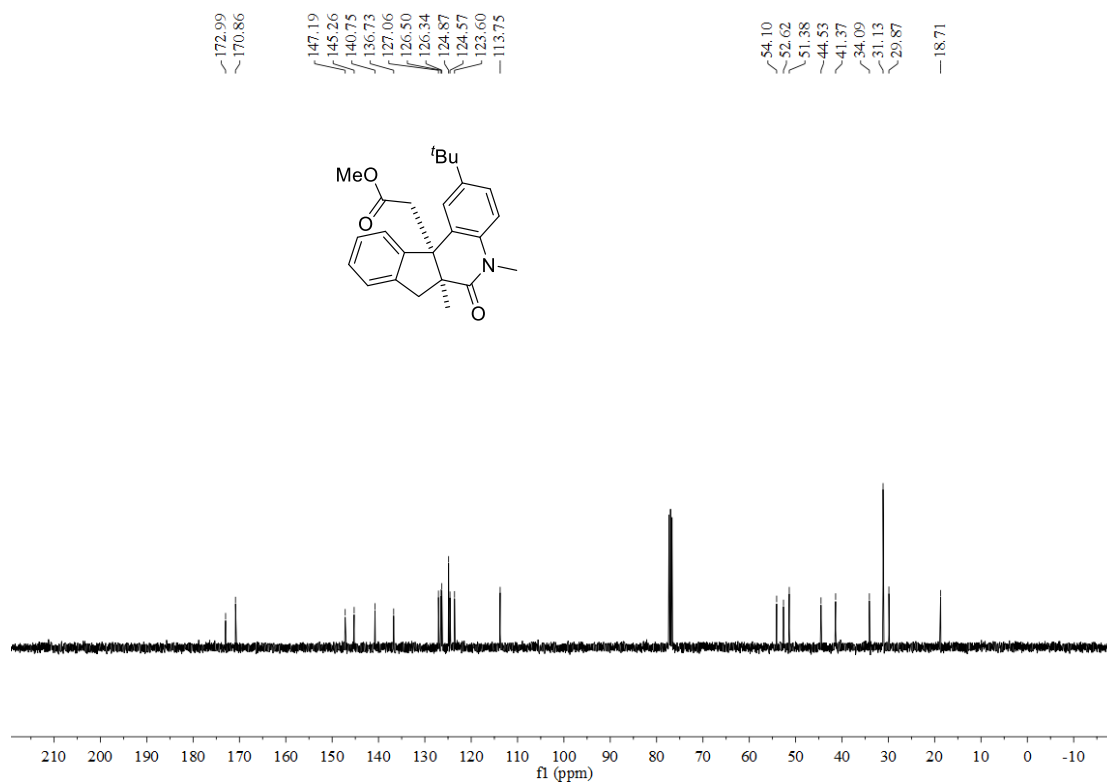
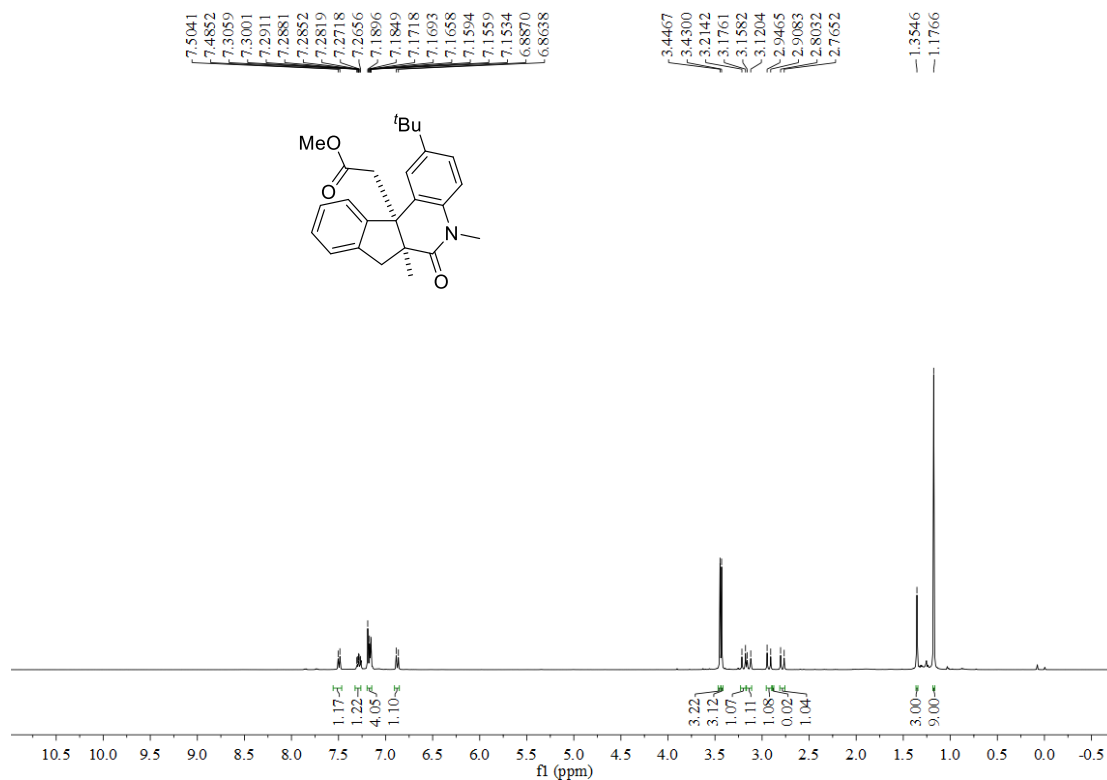
cis-Methyl

2-(2-isopropyl-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3f)



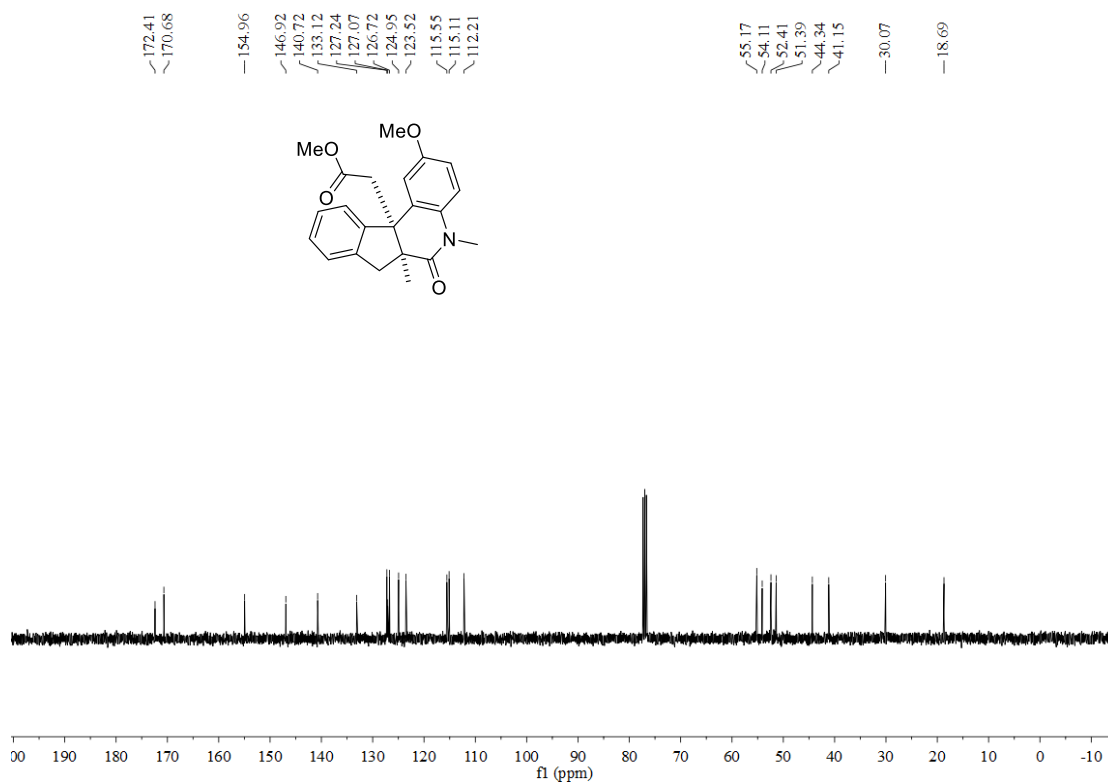
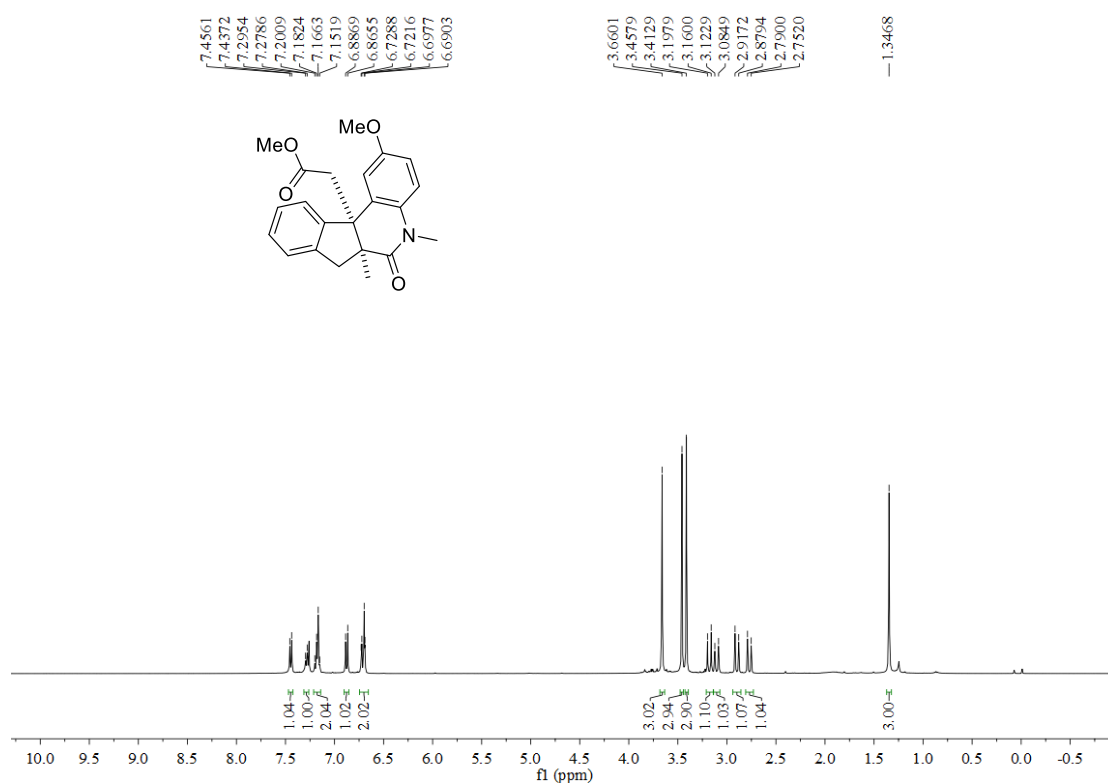
cis-Methyl

2-(2-(tert-butyl)-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11b*H*-indeno[2,1-*c*]quinolin-11b-yl)acetate (3g)



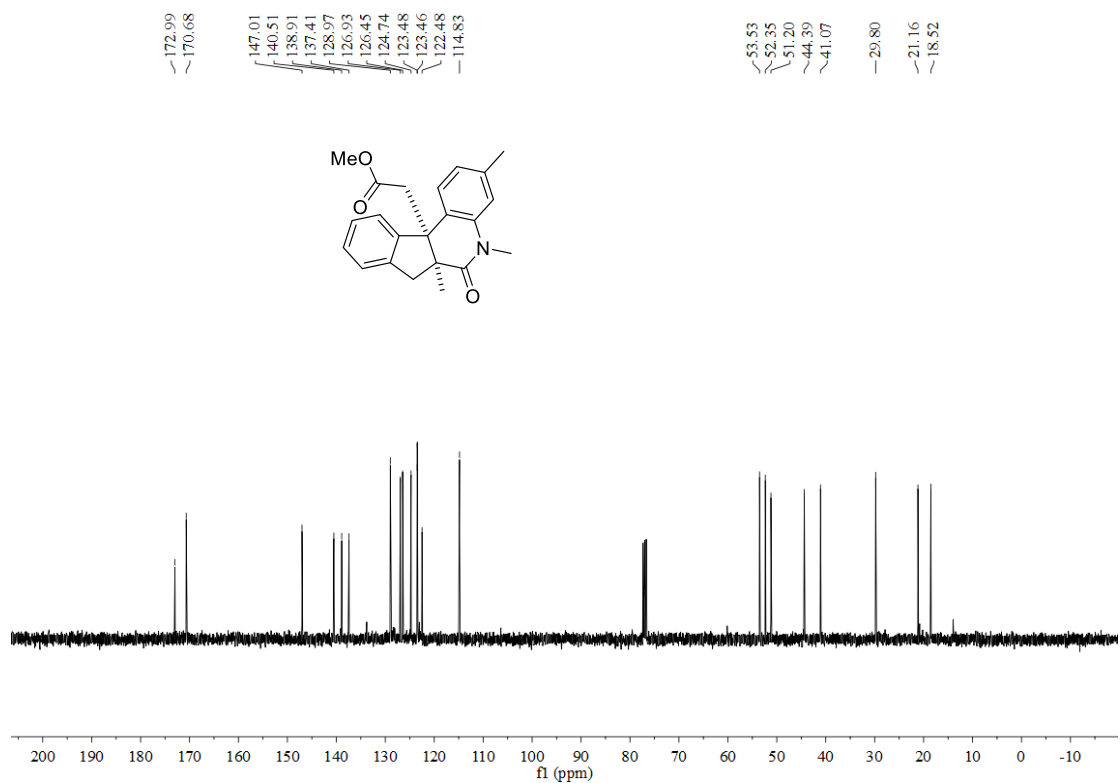
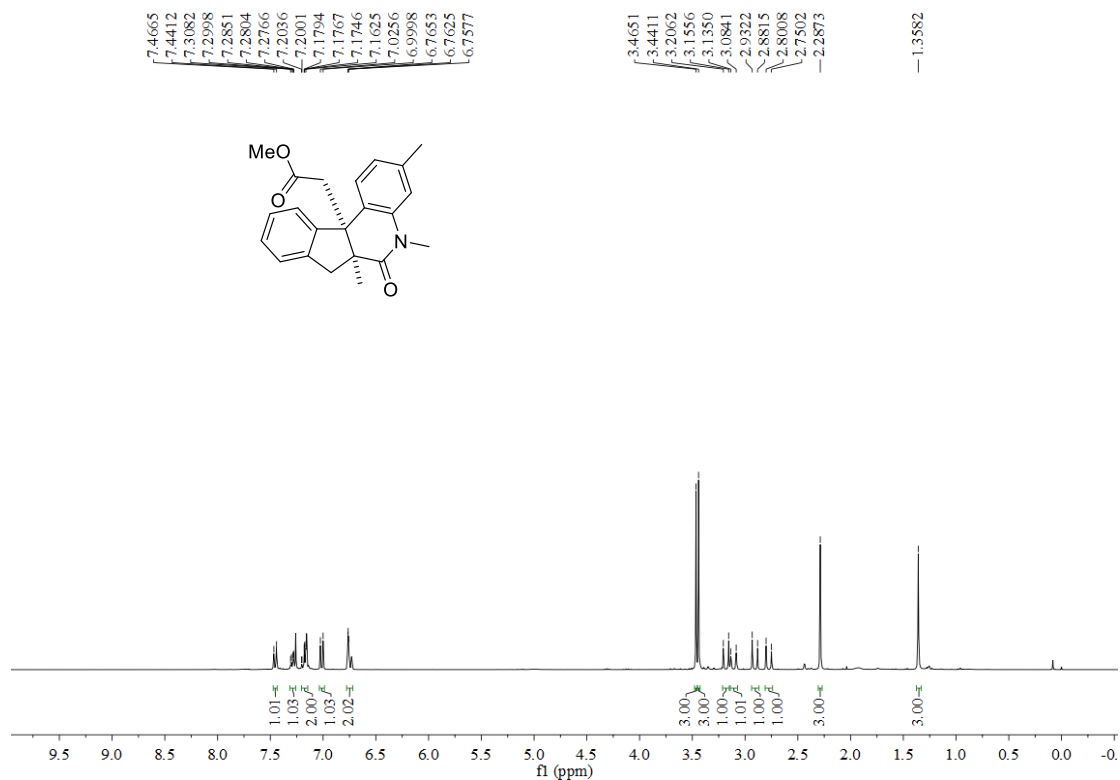
cis-Methyl

2-(2-methoxy-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11b*H*-indeno[2,1-*c*]quinolin-11b-yl)acetate (3h)



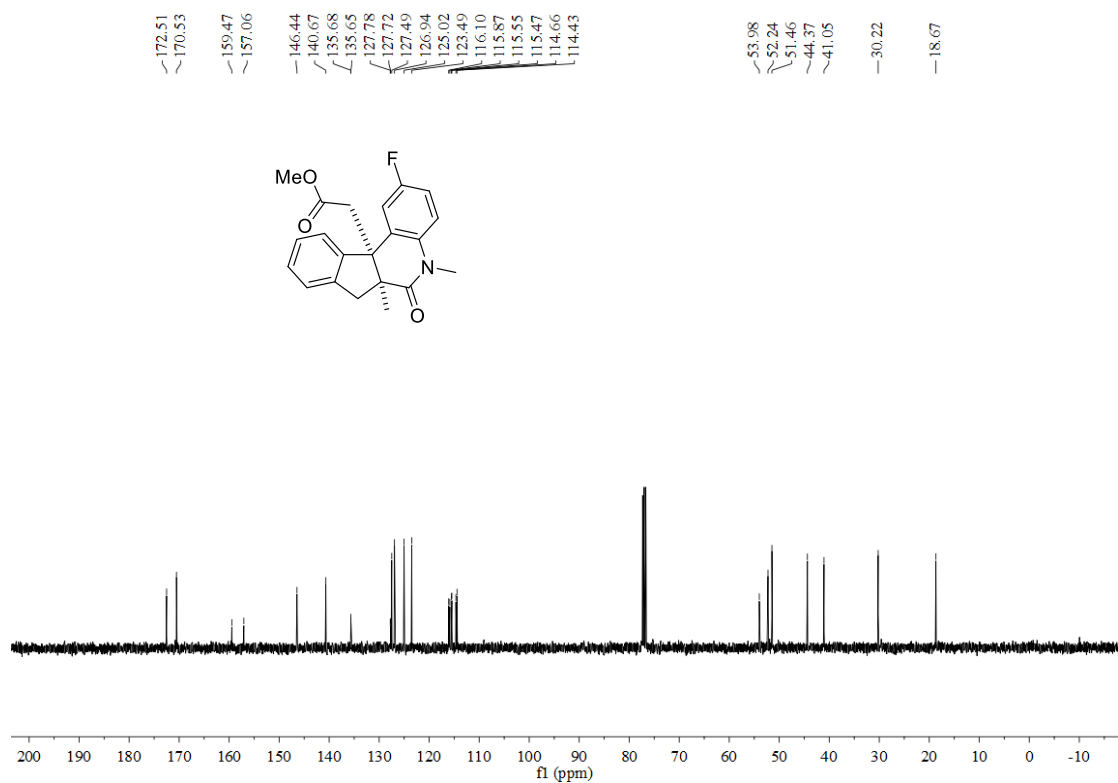
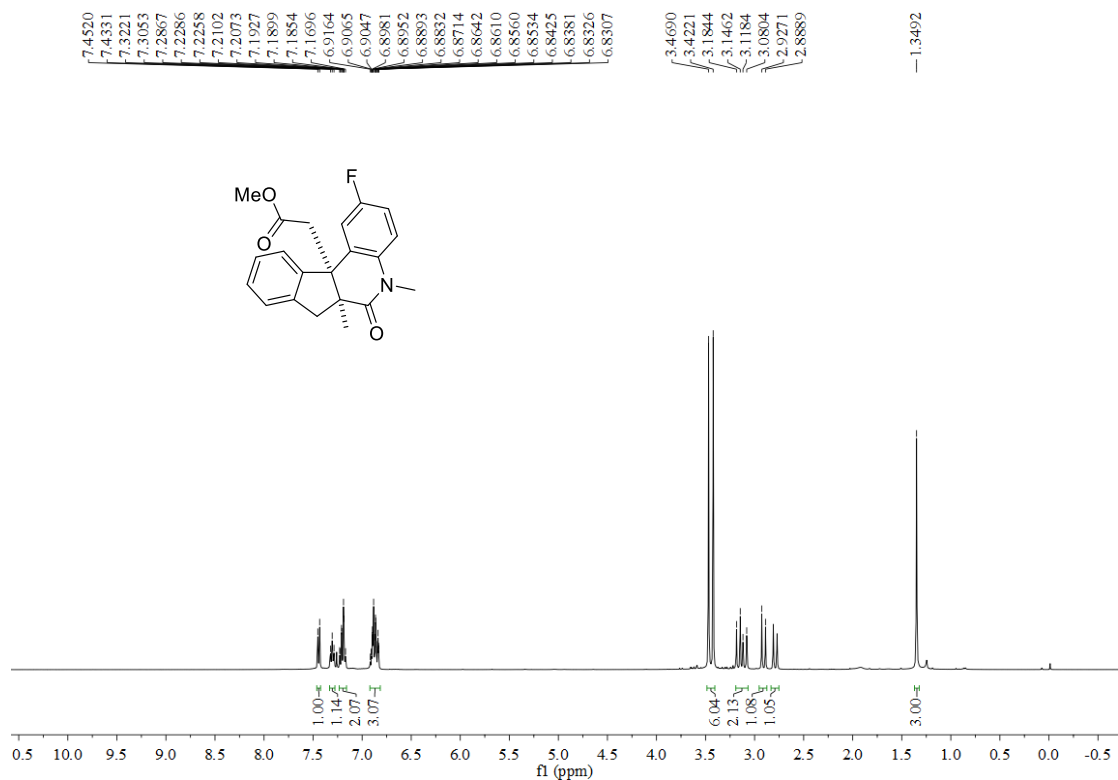
cis-Methyl

**2-(3,5,6a-trimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)
acetate (3i)**



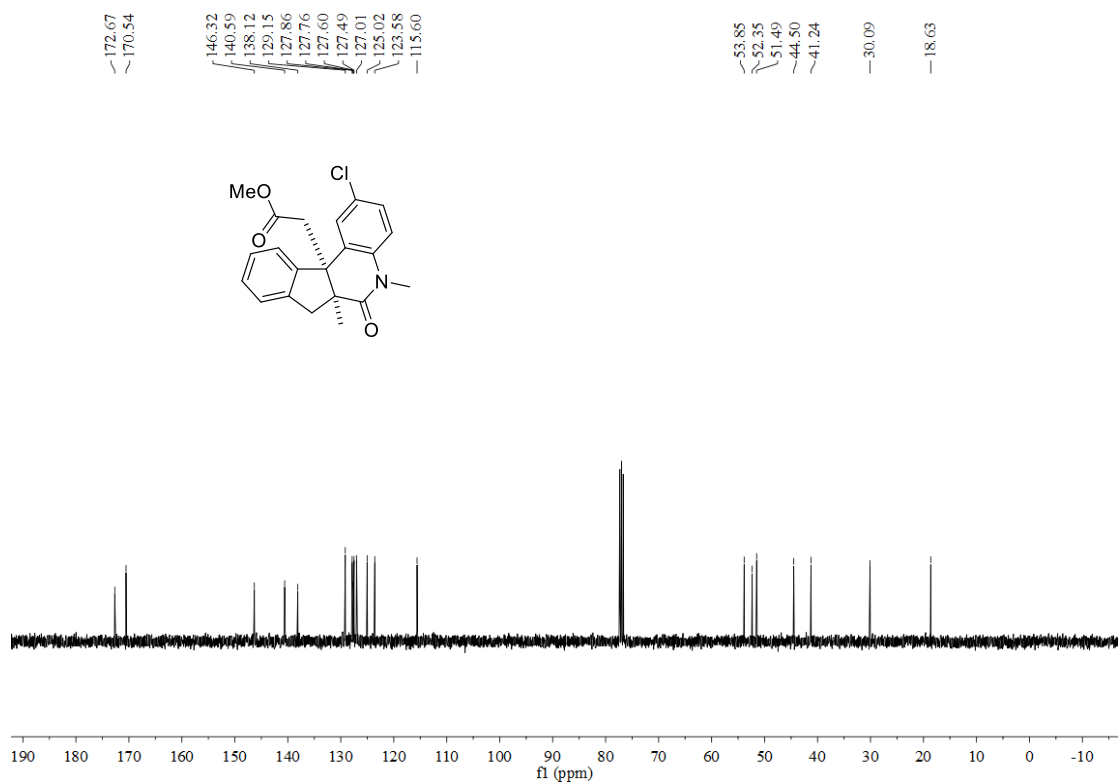
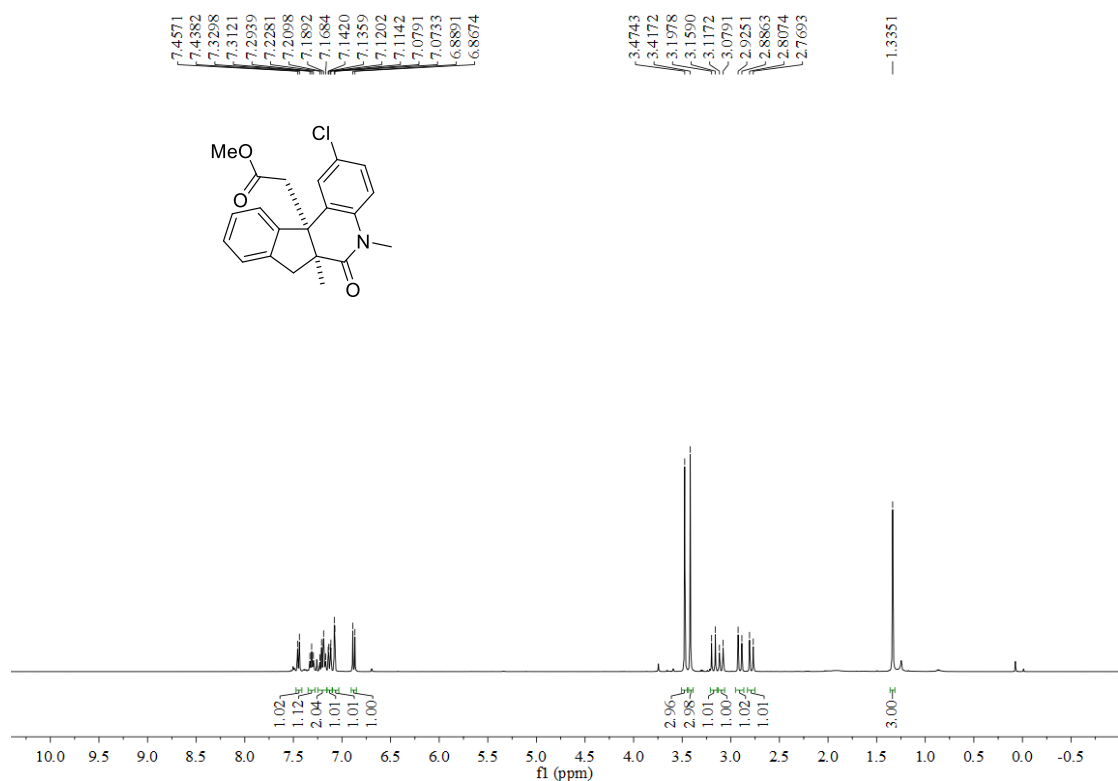
cis-Methyl

2-(2-fluoro-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3j)



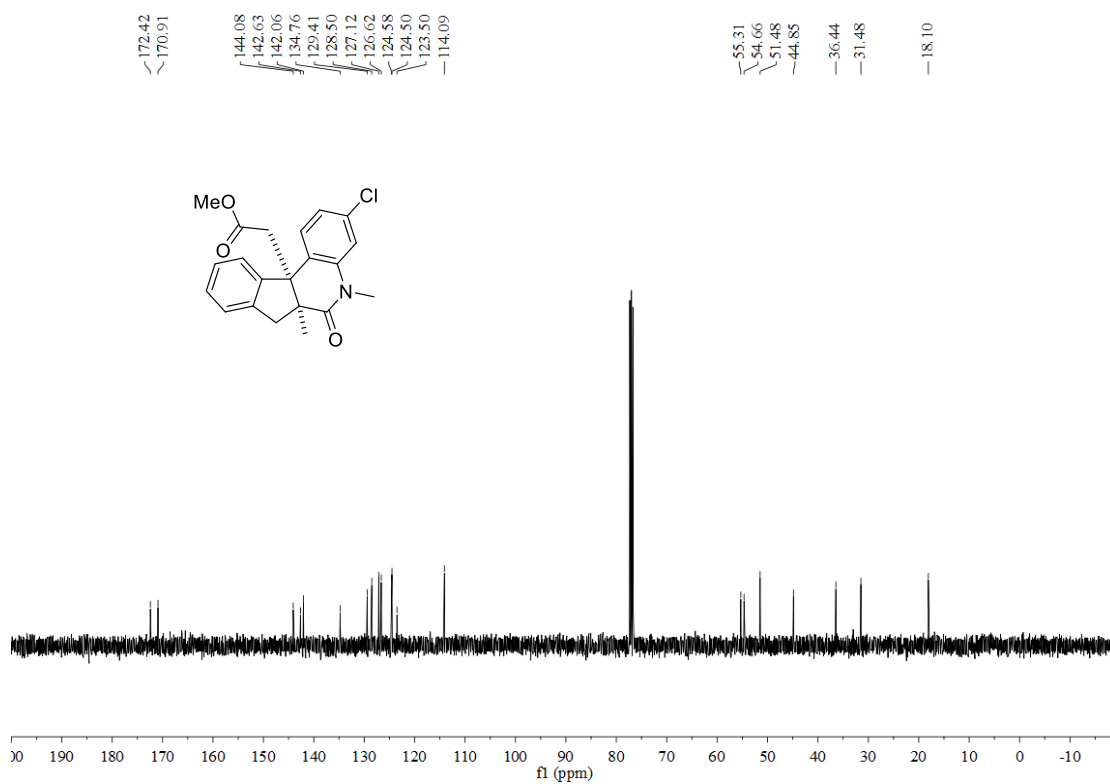
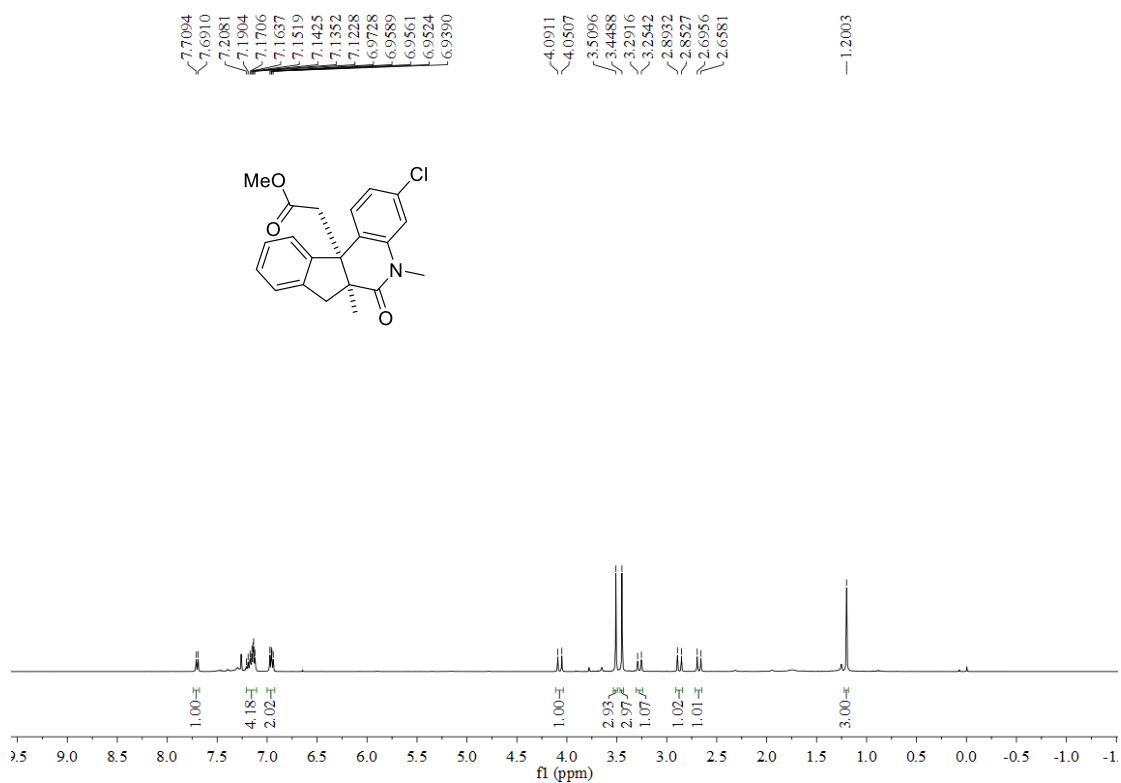
cis-Methyl

2-(2-chloro-5,6a-dimethyl-6-oxo-5,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3k)



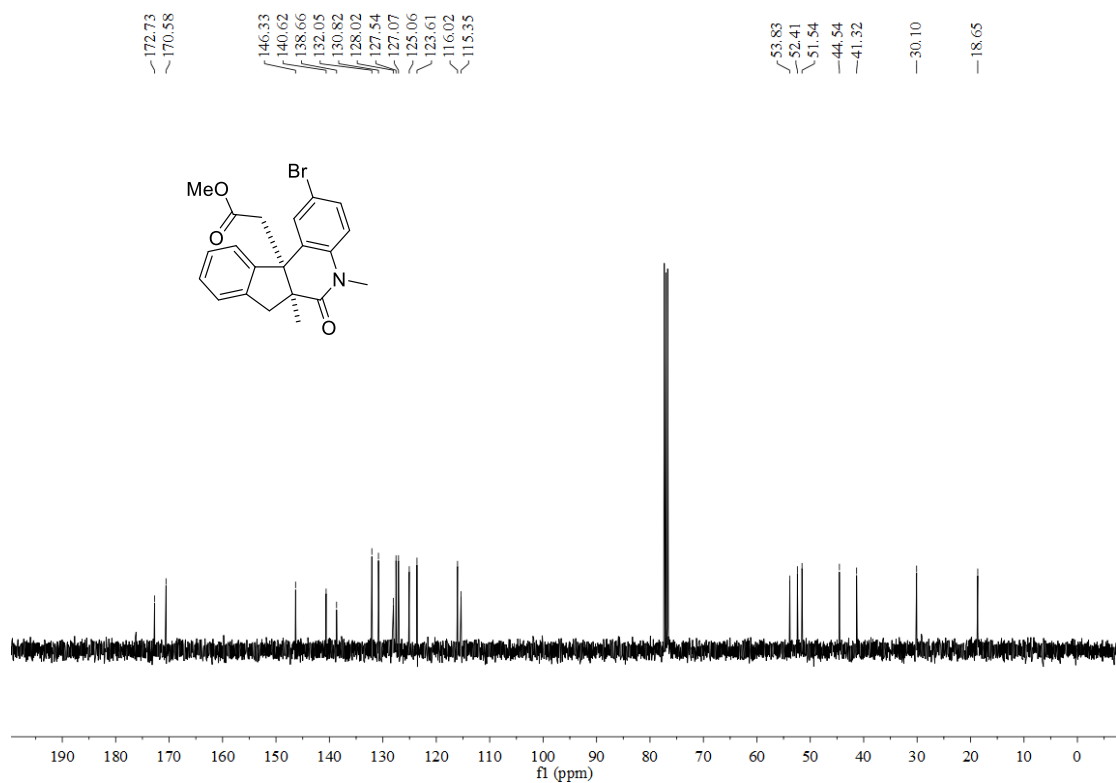
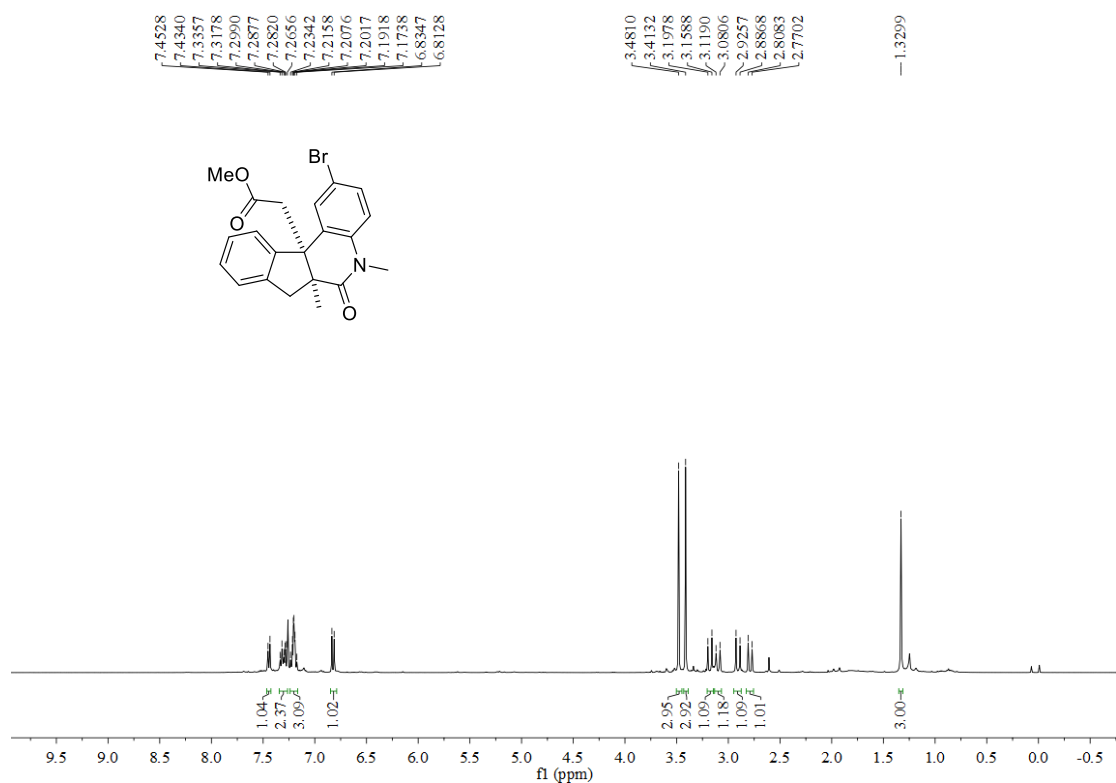
cis-Methyl

2-(3-chloro-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3l)



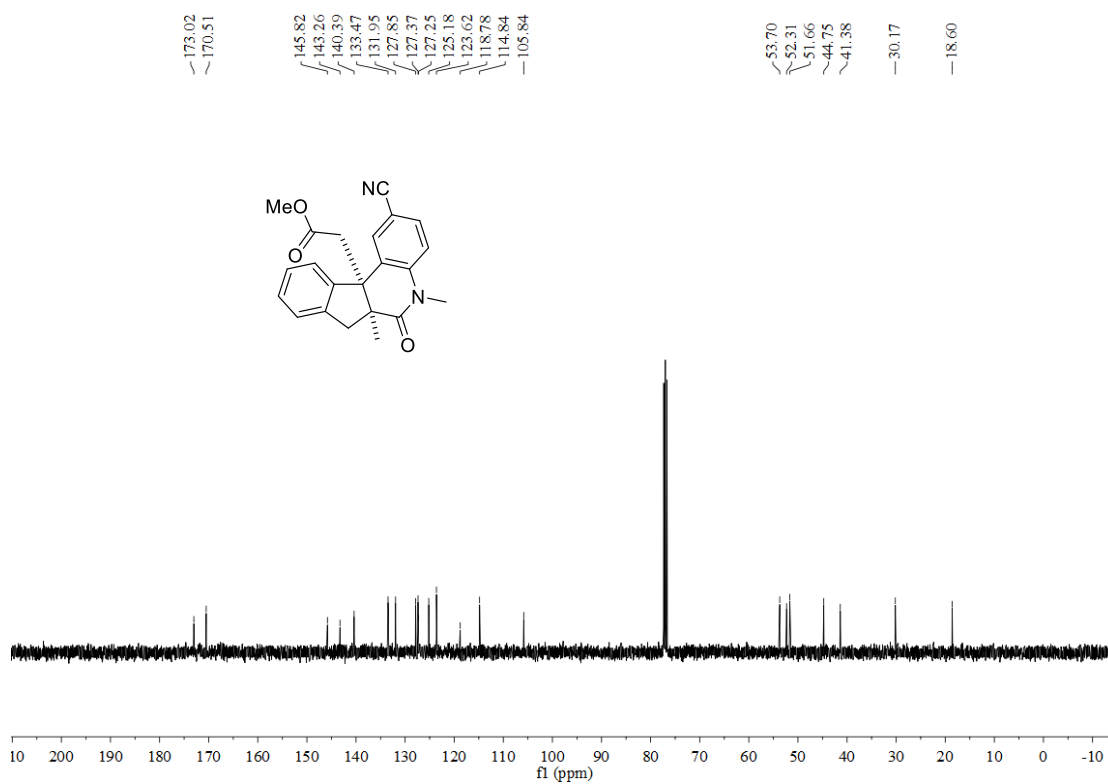
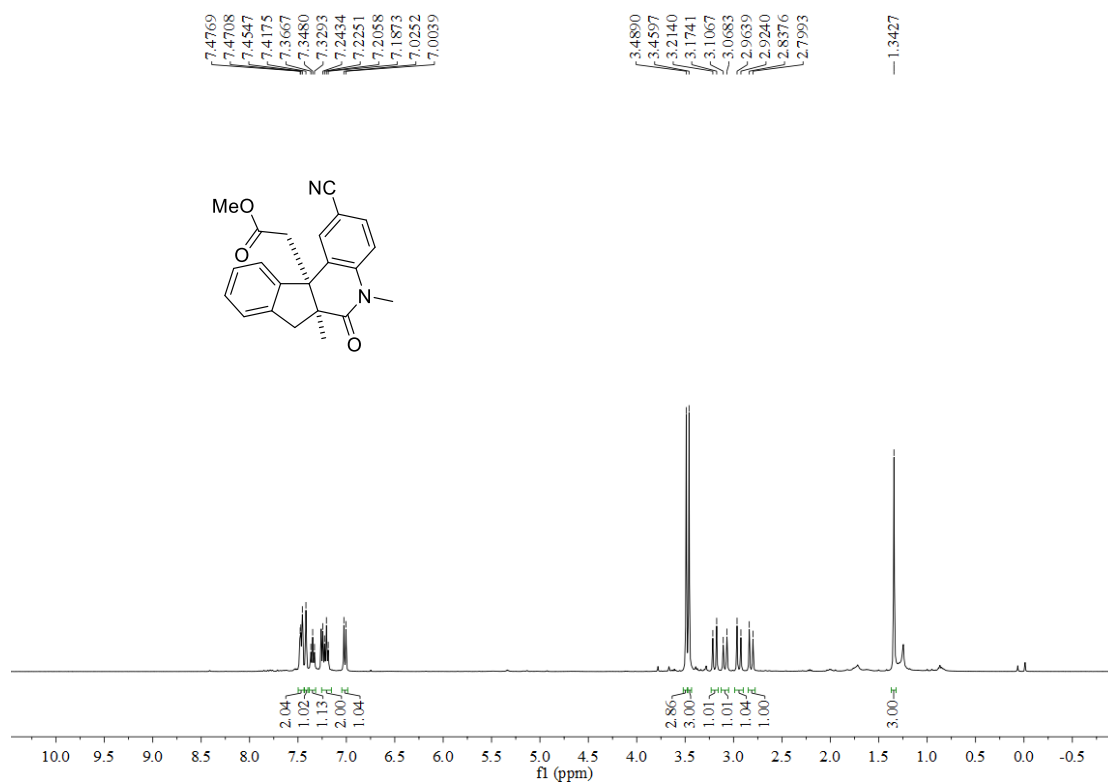
cis-Methyl

2-(2-bromo-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3m)



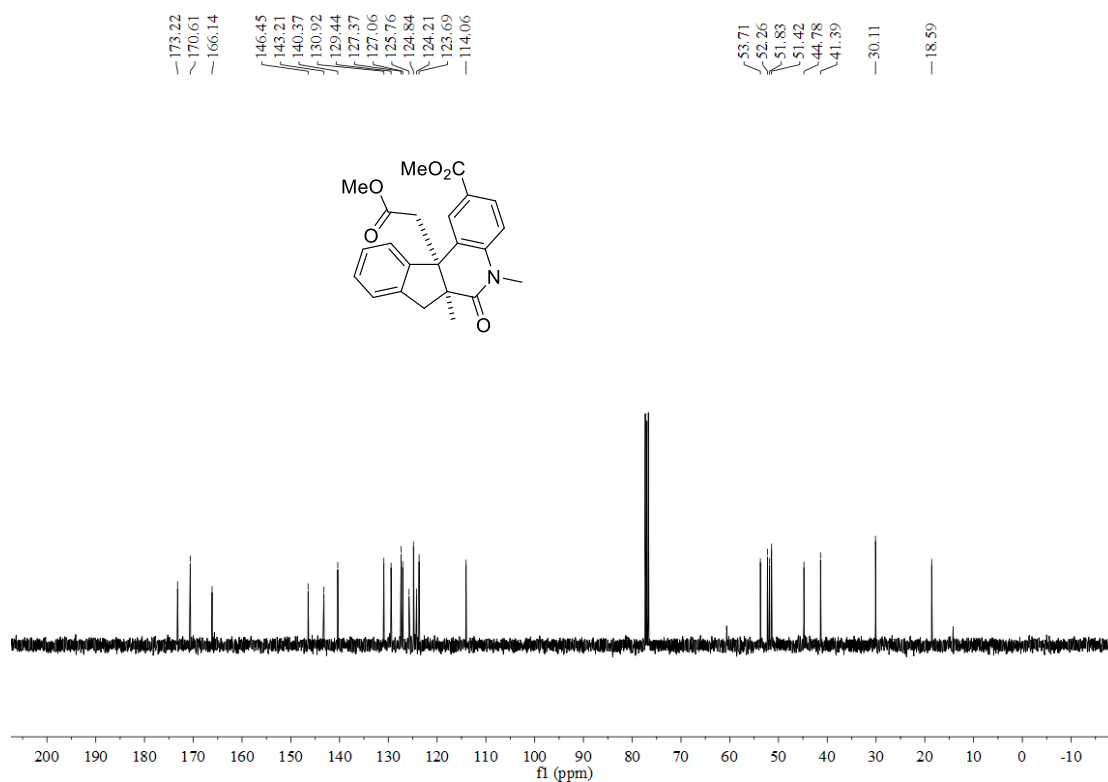
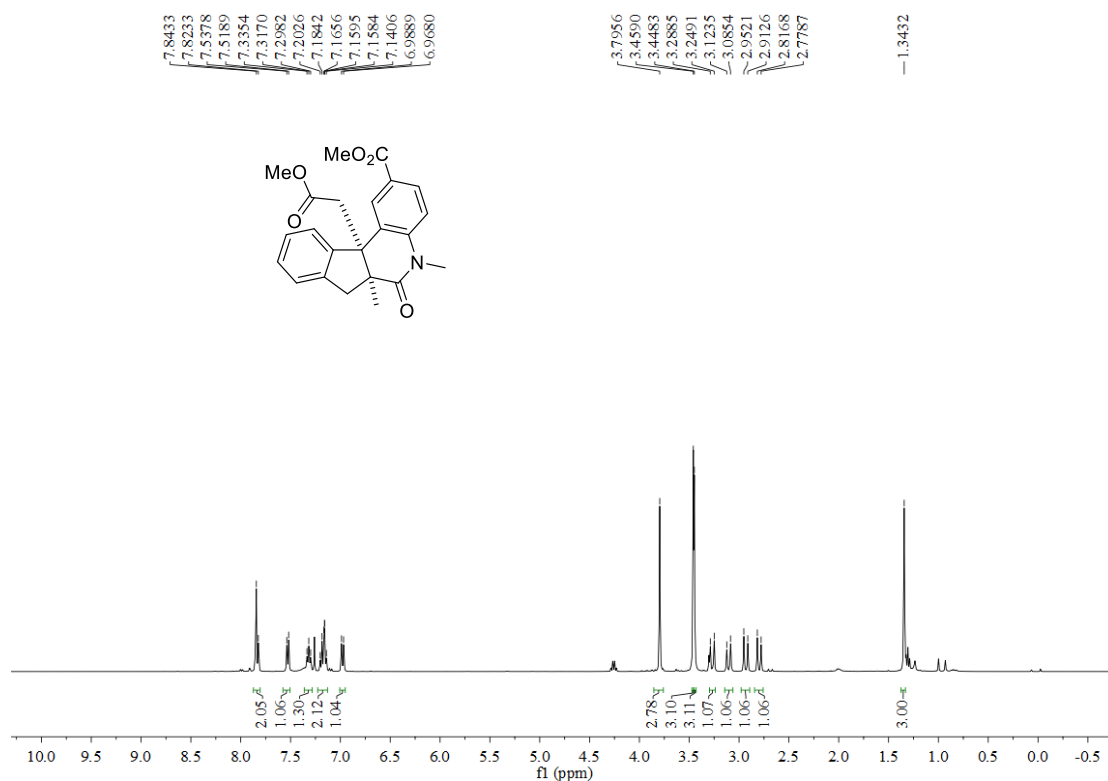
cis-Methyl

2-(2-cyano-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3n)

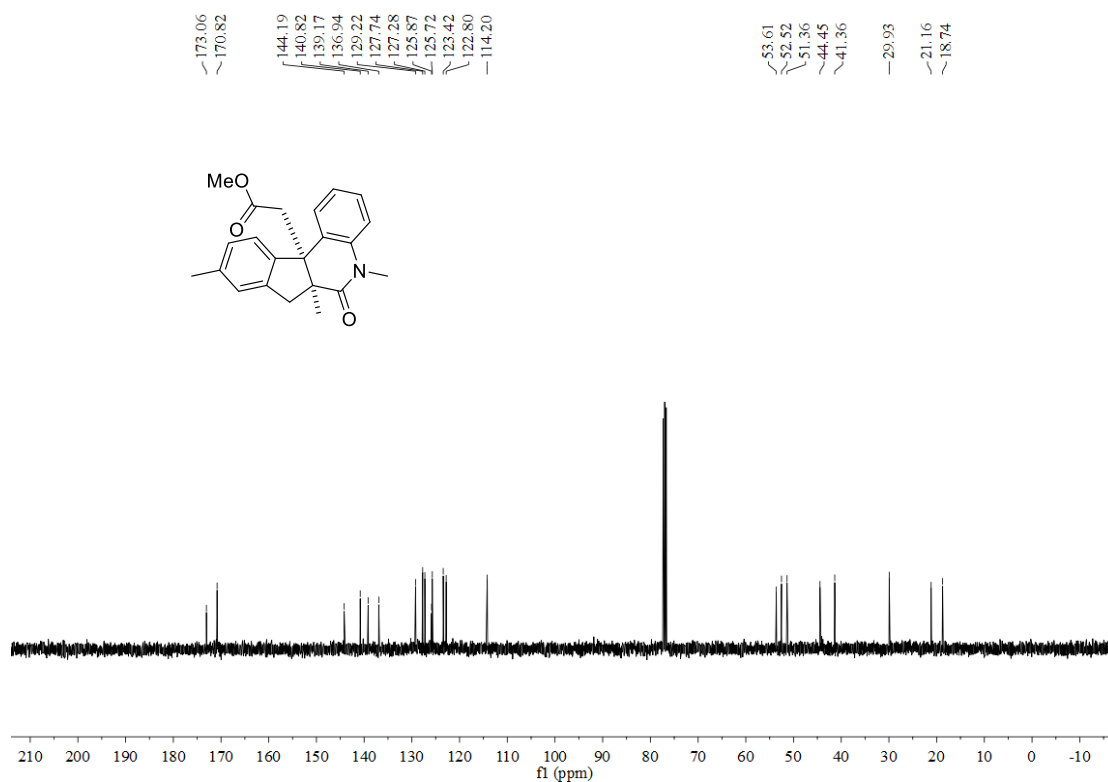
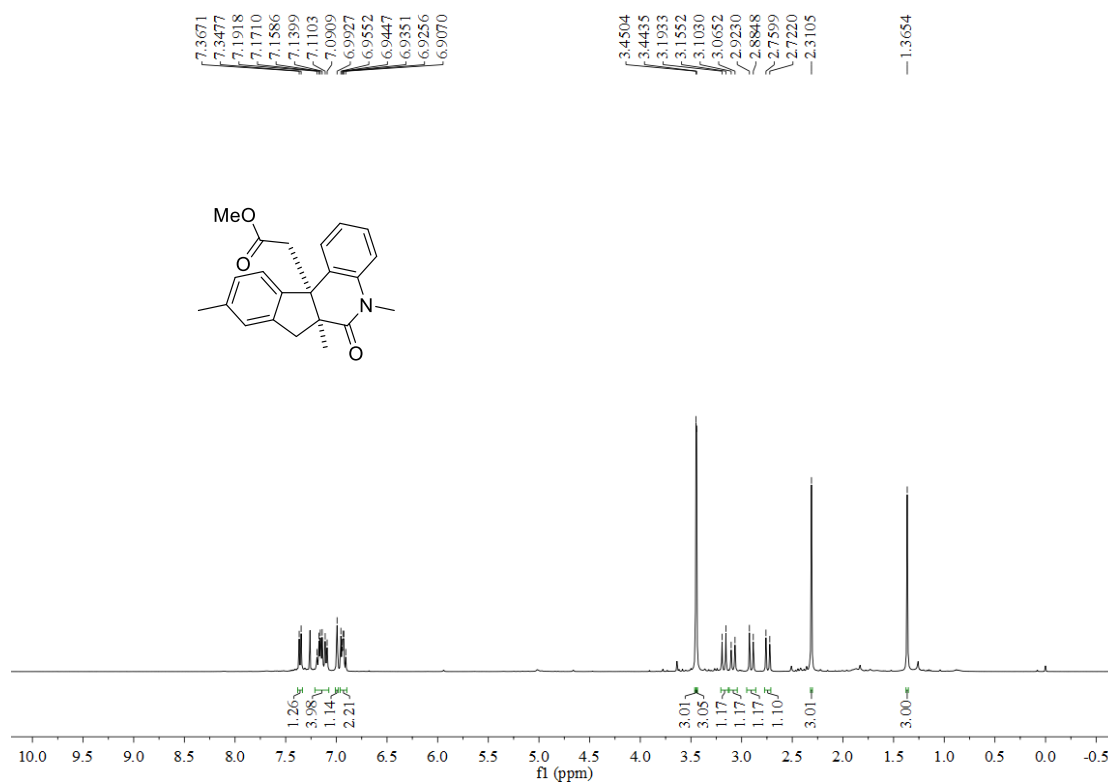


cis-Methyl

11b-(2-methoxy-2-oxoethyl)-5,6a-dimethyl-6-oxo-6,6a,7,11b-tetrahydro-5H-inden
o[2,1-c]quinoline-2-carboxylate (3o)

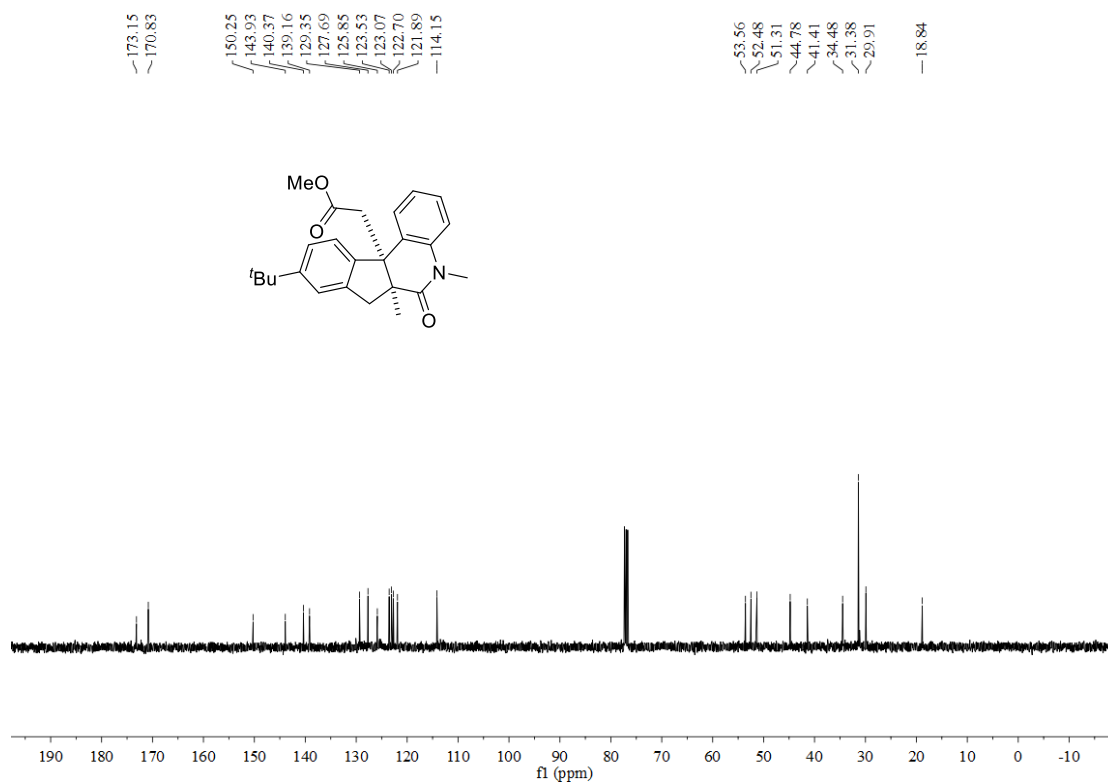
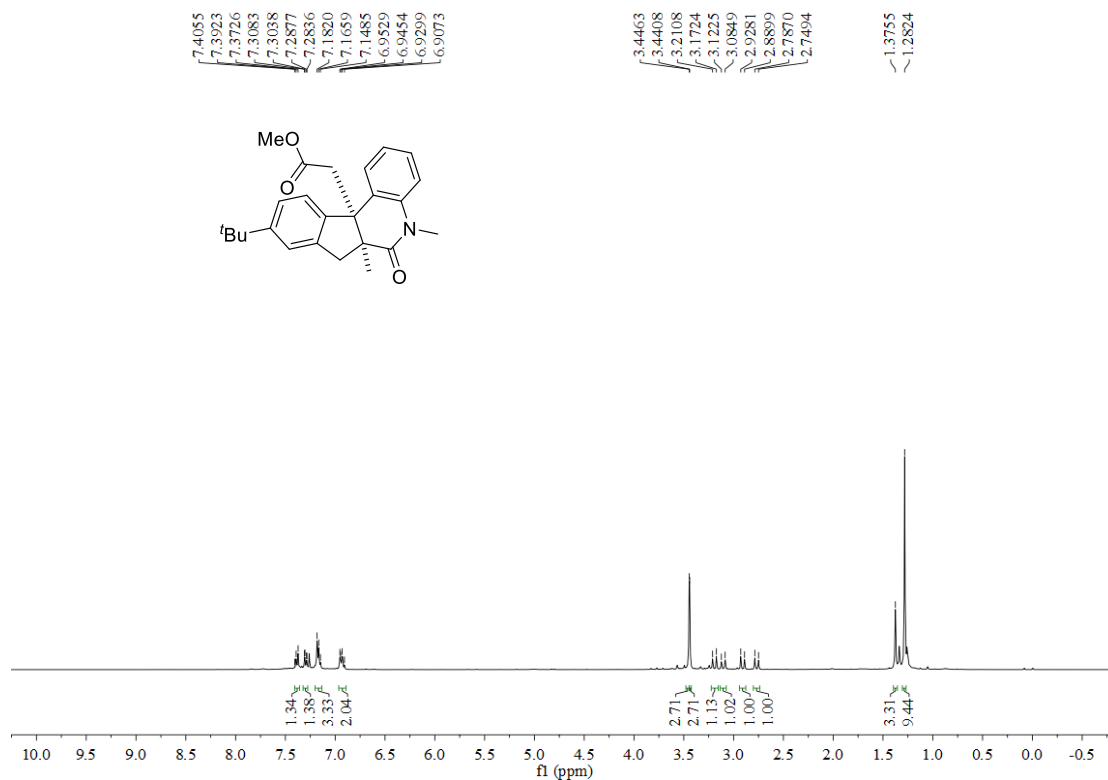


cis-Methyl
2-(5,6a,9-trimethyl-6-oxo-5,6,6a,7-tetrahydro-11b*H*-indeno[2,1-*c*]quinolin-11b-yl)
acetate (3p)



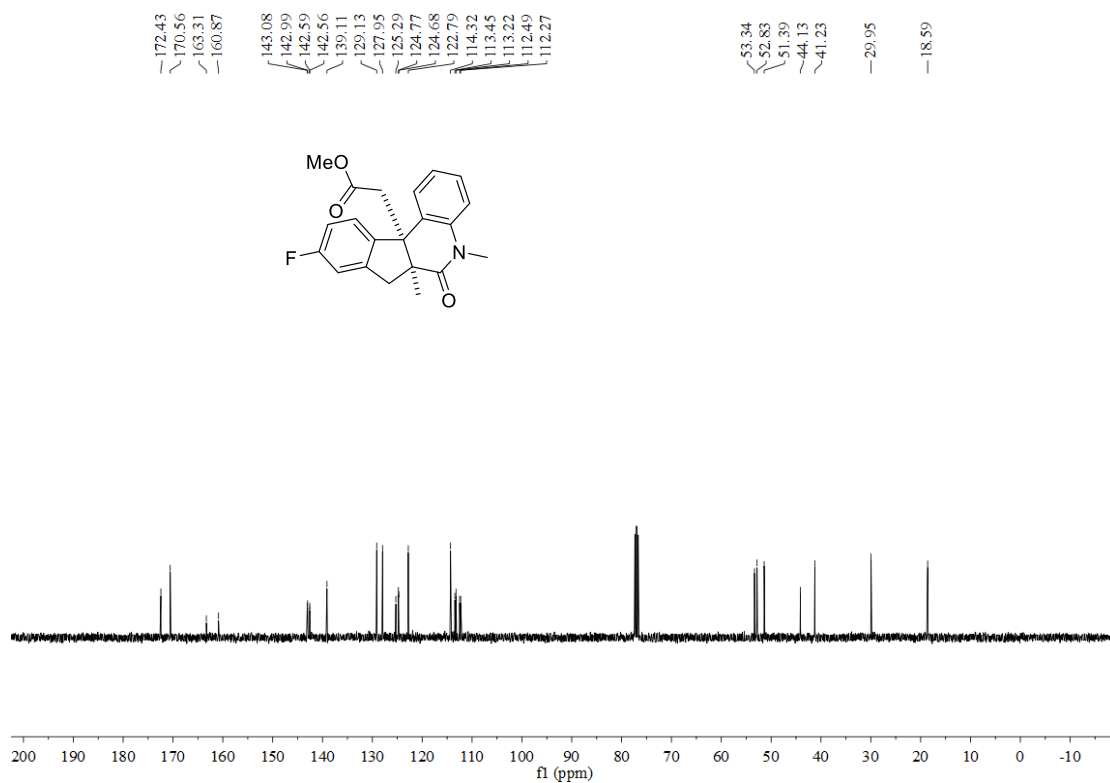
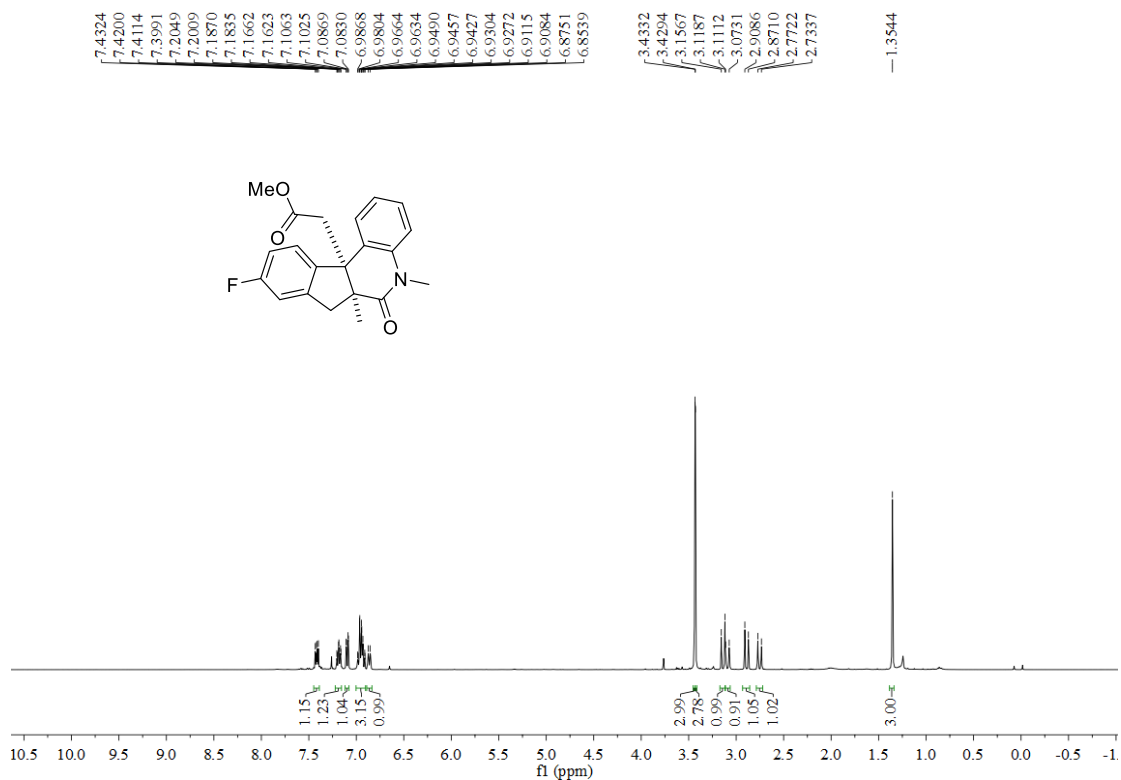
cis-Methyl

2-(9-(tert-butyl)-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3q)



cis-Methyl

2-(9-fluoro-5,6a-dimethyl-6-oxo-5,6,6a,7-tetrahydro-11bH-indeno[2,1-c]quinolin-11b-yl)acetate (3r)



cis-Methyl

2-(6,7a-dimethyl-7-oxo-6,7,7a,8-tetrahydro-12bH-benzo[gl]indeno[2,1-c]quinolin-12b-yl)acetate (3s)

