Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Cooperative photoactivation/Lewis base catalyzed [4+2] annulations of α-diazoketones and *ortho*-amino MBH carbonates to access dihydroquinolinone frameworks

Jin Zhou,‡ Chen Chen,‡ Qiwen Pang, Wei-Fang Zuo, Xiang Li, Gu Zhan, Qian-Qian Yang * and Bo Han *

State Key Laboratory of Southwestern Chinese Medicine Resources, Hospital of Chengdu University of Traditional Chinese Medicine, School of Pharmacy, Chengdu University of Traditional Chinese Medicine, Chengdu, 611137, China.

Supporting Information

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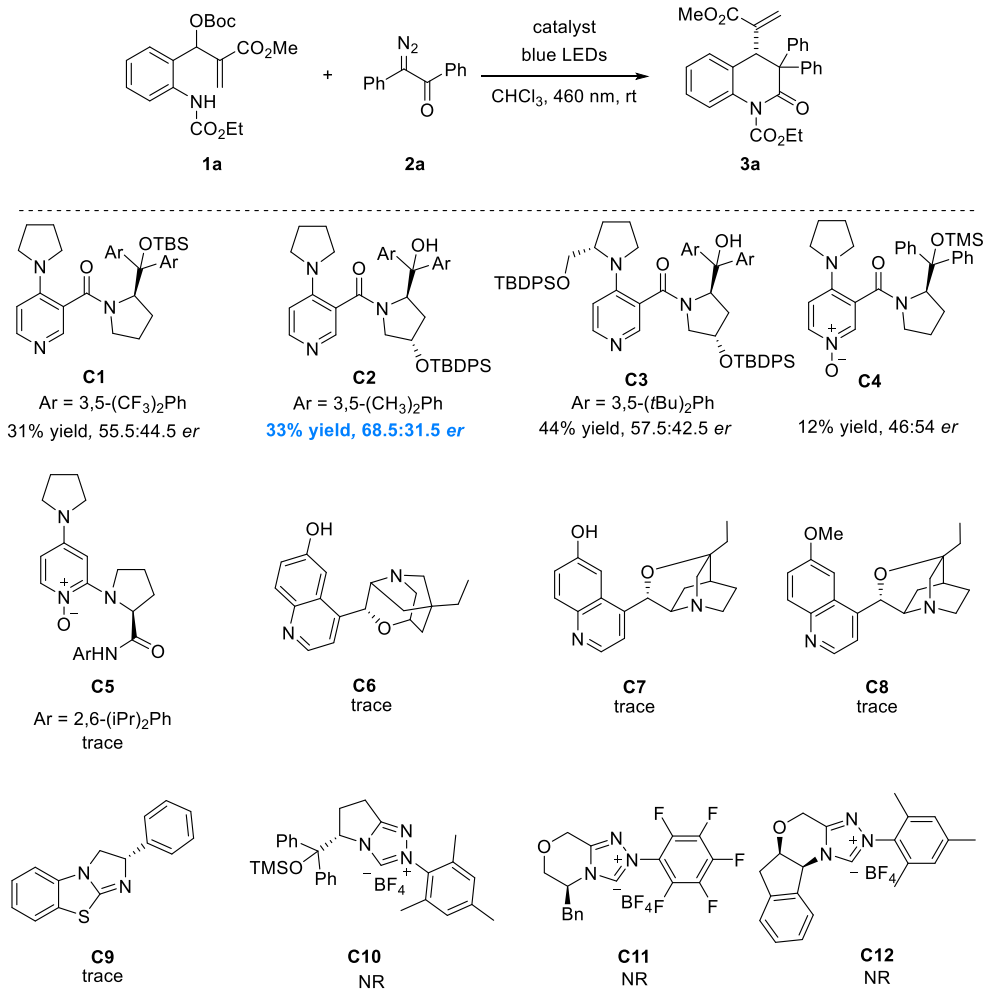
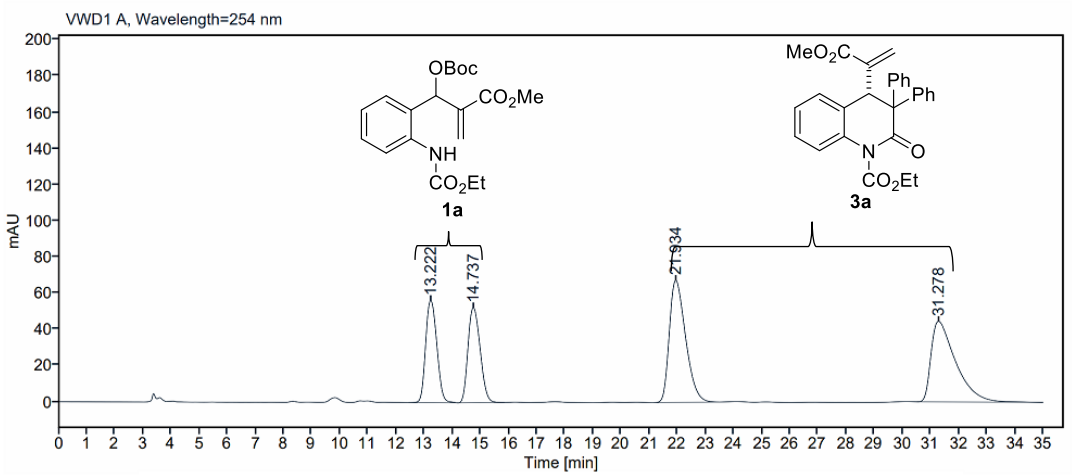
1.General information

Nuclear magnetic resonance (NMR) spectra were recorded in DMSO-d_6 and $CDCl_3$ on JEOL 600 NMR instrument. Proton chemical shifts are reported in parts per million (δ scale). The ^1H NMR chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as standard. The ^{13}C NMR chemical shifts were given using Chloroform-*d* or DMSO-d_6 as the internal standard (Chloroform-*d*: δ = 77.00 ppm, DMSO-d_6: δ = 39.50 ppm). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant(*J*) (Hz), integration]. High-resolution mass spectra (HRMS) were obtained using Agilent P/N G1969-90010 or Waters/Acquity UPLC-Synapt G2HDMS. High-resolution mass spectra were reported for the molecular ion $[M+Na]^+$. X-ray diffraction experiment was carried out on an Agilent Gemini and the data obtained were deposited at the Cambridge Crystallographic Data Centre. UV detection was performed at 254 nm. Column chromatography was performed on silica gel (200-300 mesh) using an eluent of ethyl acetate (EtOAc) and petroleum ether (PE). TLC was performed on glass-backed silica plates; products were visualized using UV light. All reagents and solvents were obtained commercially and used without further purification. *o*-amino MBH carbonates **1**[1], α-diazoketones **2**[2] were prepared according to the literature procedures. Six positions parallel photocatalytic reactors were used as the reaction instrument. Melting points were recorded on the BUCHI Melting Point M-565 instrument. Unless otherwise noted, all reagents were obtained commercially and used without further purification.

2. Attempt of asymmetric version



To a mixture of *ortho*-amino MBH carbonates **1** (0.10 mmol), α-diazoketones **2** (0.20 mmol) in $CHCl_3$ (1.0 mL) was added chiral catalysts (0.02 mmol) at room temperature, the reaction mixture was then irradiated under blue LEDs for 2 hours. Unfortunately, after investigating different types of chiral catalysts, 4-pyrrolidinopyridine catalysts **C1**-**C4** performed a certain of enantiocontrol, constructing chiral product **3a** in 33% yield with 37% ee in the best result. Cinchona alkaloid-type Lewis base **C6**-**C8** performed inferior activities. We also attempted the NHC catalysts and BTM (**C9**-**C12**) used in literature work to interact with ketene via a double activation strategy, however, there were no good results at last.



Signal: VWD1 A, Wavelength=254 nm

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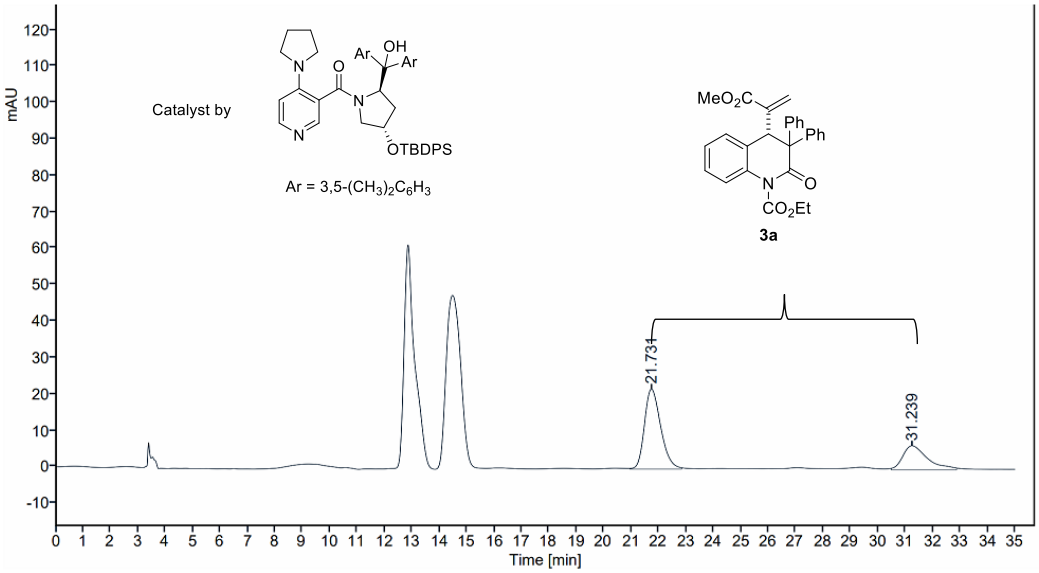
14.737	BB	0.4823	1577.2189	52.5311	18.4342	
21.934	BB	0.6227	2713.1472	67.5381	31.7107	
31.278	BBA	0.9022	2704.4839	44.5508	31.6095	
		Sum	8555.9231			



Signal: VWD1 A, Wavelength=254 nm

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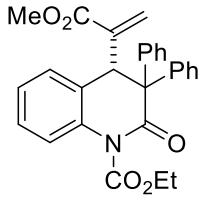
21.731	MM	0.6851	904.4374	22.0014	68.4851	
31.239	MM	1.0514	416.1972	6.5977	31.5149	
		Sum	1320.6346			

3.General procedure for the synthesis of products 3

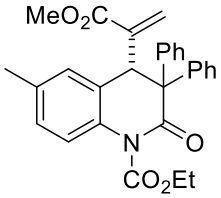
To a mixture of *o*-amino MBH carbonates **1** (0.10 mmol), α-diazoketones **2** (0.20 mmol) in $CHCl_3$ (1.0 mL) was added DMAP (2.44 mg, 0.02 mmol) at room temperature, the reaction mixture was then irradiated under blue LEDs for 2 hours. After completed (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel (PE/EA = 25/1) to give the pure products **3**.

Ethyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3a)



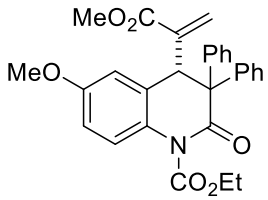
The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3a** as a white solid in 77% yield (35.2 mg), m. p. 241.6-243.6 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.8 Hz, 2H), 7.20 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.16 – 7.09 (m, 3H), 7.09 – 7.04 (m, 4H), 7.03 – 6.97 (m, 3H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.27 (s, 1H), 5.57 (s, 1H), 5.08 (s, 1H), 4.46 – 4.35 (m, 2H), 3.28 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 168.9, 166.4, 153.8, 140.0, 139.6, 138.9, 135.7, 130.6, 128.6, 128.55, 128.49, 128.3, 127.9, 127.5, 127.1, 126.6, 124.9, 116.8, 64.9, 59.7, 51.9, 46.5, 13.9. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{28}H_{25}NO_5Na$ 478.1630; found 478.1623.

Ethyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)-6-methyl-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3b)



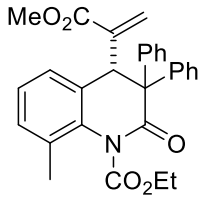
The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3b** as a white solid in 89% yield (41.8 mg), m. p. 157.5 – 158.4 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.2 Hz, 2H), 7.16 – 7.10 (m, 3H), 7.10 – 7.04 (m, 3H), 7.00 – 6.99 (m, 3H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 6.27 (s, 1H), 5.56 (s, 1H), 5.02 (s, 1H), 4.45 – 4.34 (m, 2H), 3.27 (s, 3H), 2.21 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 168.8, 166.4, 154.0, 140.2, 139.8, 139.0, 134.6, 133.3, 130.7, 128.8, 128.55, 128.51, 128.3, 127.8, 127.4, 127.1, 126.5, 116.8, 64.8, 59.9, 51.8, 46.5, 20.7, 13.9. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{29}H_{27}NO_5Na$ 492.1787; found 492.1779.

Ethyl 6-methoxy-4-(3-methoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3c)



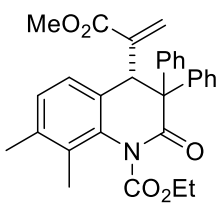
The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3c** as a white solid in 78% yield (38.0 mg), m. p. 229.2-230.2 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.2 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 6.6 Hz, 1H), 7.08 – 7.05 (m, 3H), 7.01 – 6.98 (m, 2H), 6.72 (d, *J* = 3.0 Hz, 1H), 6.62 – 6.55 (m, 2H), 6.28 (s, 1H), 5.59 (s, 1H), 5.01 (s, 1H), 4.47 – 4.33 (m, 2H), 3.69 (s, 3H), 3.28 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 168.6, 166.4, 156.6, 154.0, 140.1, 139.5, 139.0, 130.7, 129.5, 129.3, 128.6, 128.4, 128.3, 127.4, 127.1, 126.6, 118.5, 113.5, 113.1, 64.7, 59.9, 55.5, 51.9, 46.7, 13.9. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ Calcd for $C_{29}H_{27}NO_6Na$ 508.1736; found 508.1732.

Ethyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)-8-methyl-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3d)



The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3d** as a white solid in 60% yield (28.3 mg), m. p. 156.8 – 157.4 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 7.2 Hz, 2H), 7.11 – 7.06 (m, 5H), 7.05 (t, *J* = 6.6 Hz, 2H), 7.02 – 7.00 (m, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.32 (s, 1H), 5.72 (s, 1H), 5.04 (s, 1H), 4.44 – 4.32 (m, 2H), 3.29 (s, 3H), 1.91 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.4, 166.7, 153.9, 140.1, 139.5, 138.9, 135.6, 131.8, 130.52, 130.49, 129.5, 128.7, 128.11, 128.09, 127.2, 127.1, 126.6, 126.1, 125.9, 64.4, 61.1, 51.9, 47.0, 18.2, 14.1. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ Calcd for $C_{29}H_{27}NO_5Na$ 492.1787; found 492.1785.

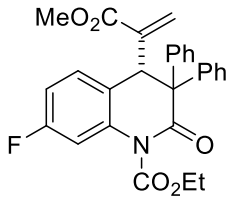
Ethyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)-7,8-dimethyl-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3e)



The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3e** as a white solid in 45% yield (21.8 mg), m. p. 153.2 – 154.6 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 7.2 Hz, 2H), 7.10 – 7.02 (m, 6H), 7.01 – 6.99 (m, 2H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.28 (s,

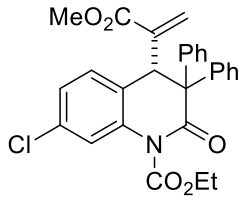
1H), 5.67 (s, 1H), 5.00 (s, 1H), 4.44 – 4.30 (m, 2H), 3.28 (s, 3H), 2.08 (s, 3H), 1.78 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.8, 166.7, 154.0, 140.4, 139.8, 139.1, 136.9, 135.7, 130.5, 129.8, 128.6, 128.5, 128.11, 128.09, 127.7, 127.11, 127.10, 126.6, 125.3, 64.2, 61.4, 51.9, 46.9, 20.4, 14.7, 14.1. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{30}H_{29}NO_5Na$ 506.1943; found 506.1943.

Ethyl 7-fluoro-4-(3-methoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3g)



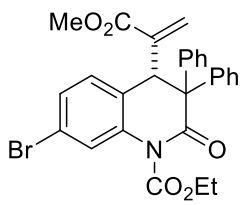
The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3g** as a white solid in 72% yield (34.3 mg), m. p. 316.7 -317.4 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 6.6 Hz, 2H), 7.18 – 7.12 (m, 4H), 7.10 – 7.05 (m, 3H), 7.02 – 6.98 (m, 2H), 6.70 (td, *J* = 7.8, 2.4 Hz, 1H), 6.40 (dd, *J* = 10.2, 2.4 Hz, 1H), 6.26 (s, 1H), 5.53 (s, 1H), 5.07 (s, 1H), 4.50 – 4.32 (m, 2H), 3.30 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 168.8, 166.3, 161.7 (d, J_{CF} = 244.5 Hz), 153.5, 139.7, 139.6, 138.7, 136.7 (d, J_{CF} = 10.5 Hz), 130.5, 129.9 (d, J_{CF} = 9.0 Hz), 128.41, 128.40, 128.3, 127.7, 127.2, 126.7, 123.5 (d, J_{CF} = 3.0 Hz), 111.7 (d, J_{CF} = 21.0 Hz), 104.5 (d, J_{CF} = 27.0 Hz), 65.2, 59.6, 51.9, 46.1, 13.9. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{28}H_{24}FNO_5Na$ 496.1536; found 496.1541.

Ethyl 7-chloro-4-(3-methoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3h)



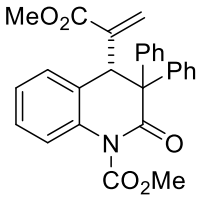
The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3h** as a white solid in 76% yield (37.4 mg), m. p. 153.3 – 154.2 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 7.2 Hz, 2H), 7.18 – 7.12 (m, 4H), 7.10 – 7.06 (m, 3H), 6.99 – 6.96 (m, 3H), 6.66 (d, *J* = 1.8 Hz, 1H), 6.26 (s, 1H), 5.53 (s, 1H), 5.06 (s, 1H), 4.50 – 4.35 (m, 2H), 3.30 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 168.7, 166.2, 153.4, 139.6, 139.4, 138.6, 136.6, 133.4, 130.5, 129.6, 128.51, 128.45, 128.3, 127.7, 127.2, 126.7, 126.2, 124.9, 117.0, 65.2, 59.5, 51.9, 46.2, 13.9. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{28}H_{24}ClNO_5Na$ 512.1241; found 512.1238.

Ethyl 7-bromo-4-(3-methoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3i)



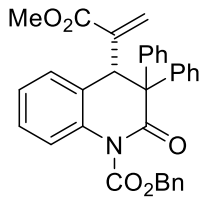
The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3i** as a white solid in 75% yield (40.2 mg), m. p. 167.6 – 168.4 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 6.6 Hz, 2H), 7.16 (q, *J* = 8.4 Hz, 3H), 7.12 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.10 – 7.05 (m, 4H), 7.01 – 6.97 (m, 2H), 6.81 (d, *J* = 1.8 Hz, 1H), 6.26 (s, 1H), 5.53 (s, 1H), 5.05 (s, 1H), 4.50 – 4.32 (m, 2H), 3.29 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 168.7, 166.2, 153.4, 139.6, 139.3, 138.5, 136.8, 130.5, 129.9, 128.5, 128.5, 128.3, 127.8, 127.7, 127.2, 126.73, 126.71, 121.1, 119.8, 65.2, 59.5, 51.9, 46.3, 13.9. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{28}H_{24}BrNO_5Na$ 556.0736; found 556.0744.

Methyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3j)



The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3j** as a white solid in 59% yield (26.2 mg), m. p. 225.1 – 226.1 ℃.^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 6.6 Hz, 2H), 7.11 – 7.04 (m, 5H), 7.01 – 6.98 (m, 3H), 6.61 (d, *J* = 8.4 Hz, 1H), 6.26 (s, 1H), 5.54 (s, 1H), 5.08 (s, 1H), 3.94 (s, 3H), 3.28 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 168.9, 166.3, 154.5, 140.0, 139.6, 138.8, 135.6, 130.6, 128.50, 128.48, 128.4, 128.3, 127.91, 127.89, 127.5, 127.1, 126.6, 125.0, 117.0, 59.8, 55.2, 51.8, 46.6. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{27}H_{23}NO_5Na$ 464.1474; found 464.1466.

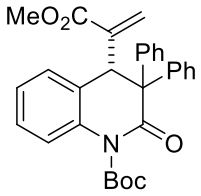
Benzyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3k)



The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3k** as a white solid in 75% yield (38.9 mg), m. p. 187.6 – 188.2 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 6.6 Hz, 2H), 7.32 – 7.26 (m, 5H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.13 – 7.05 (m, 6H), 7.02 – 6.99 (m, 2H), 6.98 – 6.96 (m, 2H), 6.52 – 6.47 (m, 1H), 6.25 (s, 1H), 5.55 (s, 1H), 5.39 (d, *J* = 12.6 Hz, 1H), 5.33 (d, *J* = 12.0 Hz,

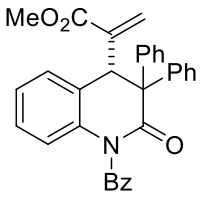
1H), 5.07 (s, 1H), 3.27 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 168.9, 166.3, 153.8, 140.0, 139.6, 138.7, 135.6, 134.3, 130.6, 128.7, 128.61, 128.57, 128.45, 128.41, 128.3, 127.9, 127.8, 127.5, 127.2, 126.6, 124.9, 117.0, 70.3, 59.9, 51.8, 46.6. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{33}H_{27}NO_5Na$ 540.1787; found 540.1795.

Tert-butyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3l)



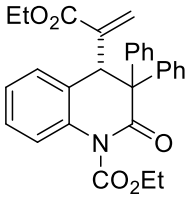
The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3l** as a white solid in 87% yield (42.1 mg), m. p. 147.6 – 148.2 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 6.6 Hz, 2H), 7.18 (d, *J* = 6.0 Hz, 1H), 7.15 – 7.10 (m, 3H), 7.08 – 7.04 (m, 4H), 7.02 – 7.01 (m, 2H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.28 (s, 1H), 5.57 (s, 1H), 5.09 (s, 1H), 3.27 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 168.7, 166.4, 151.9, 139.9, 139.7, 138.9, 135.8, 130.7, 128.6, 128.49, 128.47, 128.2, 127.9, 127.5, 127.4, 127.1, 126.5, 124.5, 115.8, 85.3, 59.5, 51.8, 46.4, 27.5. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{30}H_{29}NO_5Na$ 506.1943; found 506.1947.

Methyl 2-(1-benzoyl-2-oxo-3,3-diphenyl-1,2,3,4-tetrahydroquinolin-4-yl)acrylate (3m)



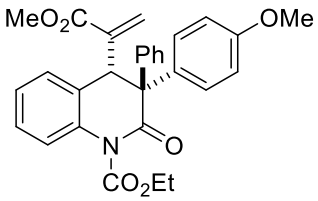
The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3m** as a white solid in 56% yield (27.5 mg), m. p. 307.1 -308.0 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.8 Hz, 3H), 7.35 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 6.6 Hz, 3H), 7.07 – 7.03 (m, 5H), 7.02 – 7.00 (m, 2H), 6.53 – 6.46 (m, 1H), 6.27 (s, 1H), 5.68 (s, 1H), 5.09 (s, 1H), 3.29 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.0, 169.9, 166.3, 140.4, 140.0, 139.4, 137.2, 134.2, 134.1, 130.9, 129.6, 129.2, 128.9, 128.8, 128.5, 128.3, 128.1, 128.0, 127.9, 127.1, 126.5, 124.9, 117.0, 59.6, 51.8, 47.3. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{32}H_{25}NO_4Na$ 510.1681; found 510,1683.

Ethyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3n)



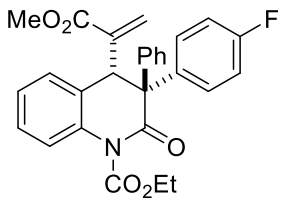
The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3n** as a white solid in 86% yield (40.5 mg), m. p. 146.8 – 147.4 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.2 Hz, 2H), 7.20 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.13 (t, *J* = 6.6 Hz, 2H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.09 – 7.03 (m, 4H), 7.03 – 6.97 (m, 3H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.28 (s, 1H), 5.58 (s, 1H), 5.11 (s, 1H), 4.47 – 4.34 (m, 2H), 3.73 – 36.5 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 168.9, 165.9, 153.9, 140.0, 139.9, 138.9, 135.6, 130.7, 128.48, 128.45, 128.3, 128.2, 128.1, 127.8, 127.5, 127.1, 126.6, 124.8, 116.7, 64.9, 60.9, 59.8, 46.3, 13.94, 13.88. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ Calcd for $C_{29}H_{27}NO_5Na$ 492.1787; found 492.1796.

Ethyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-(4-methoxyphenyl)-2-oxo-3-phenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3o)



The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3o** as a white solid in 91% yield (44.3 mg), m. p. 153.4 – 153.9 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 – 7.17 (m, 3H), 7.09 – 7.04 (m, 4H), 7.00 (d, *J* = 7.8 Hz, 3H), 6.67 – 6.61 (m, 3H), 6.25 (s, 1H), 5.54 (s, 1H), 5.02 (s, 1H), 4.43 – 4.37 (m, 2H), 3.64 (s, 3H), 3.26 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 166.3, 158.6, 153.9, 140.3, 139.8, 135.7, 130.6, 129.7, 128.5, 128.4, 128.3, 127.8, 127.1, 126.5, 124.8, 116.7, 113.6, 112.5, 64.9, 59.1, 55.0, 51.8, 46.7, 13.9. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ Calcd for $C_{29}H_{27}NO_6Na$ 508.1736; found 508.1732.

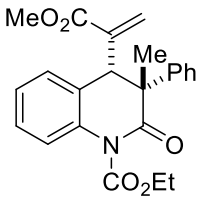
Ethyl 3-(4-fluorophenyl)-4-(3-methoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-phenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3p)



The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3p** as a white solid in 53% yield (25.3 mg), m. p. 167.8 – 168.4 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.11 – 7.06 (m, 4H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.99 – 6.97 (m, 2H), 6.83 (t, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.27 (s, 1H), 5.55 (s, 1H), 5.02 (s, 1H), 4.45 – 4.38 (m, 2H), 3.28 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 168.7, 166.3, 161.9 (d, J_{CF} = 246.0 Hz), 153.7, 139.8, 139.5, 135.6, 134.7 (d, J_{CF} = 4.5 Hz), 132.4

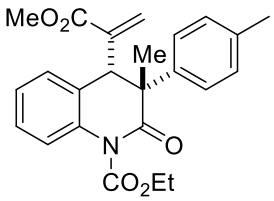
(d, J_{CF} = 9.0 Hz), 130.6, 130.3 (d, J_{CF} = 9.0 Hz), 128.6, 128.5, 128.4, 128.0, 127.2, 126.7, 125.0, 116.8, 115.3 (d, J_{CF} = 21.0 Hz), 113.90 (d, J_{CF} = 21.0 Hz), 65.0, 59.2, 51.9, 46.8, 13.9. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{28}H_{24}FNO_5Na$ 496.1536; found 496.1545.

Ethyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-methyl-2-oxo-3-phenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (3q)



The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3q** as oil in 86% yield (33.8 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 6.6 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.18 (d, *J* = 6.0 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.03 (td, *J* = 7.8, 1.2 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.17 (s, 1H), 5.28 (s, 1H), 4.50 – 4.39 (m, 2H), 4.29 (s, 1H), 3.31 (s, 3H), 1.62 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.4, 166.6, 153.7, 139.4, 138.7, 135.9, 128.9, 128.8, 128.1, 128.0, 127.6, 127.0, 126.6, 124.8, 116.4, 64.9, 51.8, 50.7, 50.2, 24.6, 13.9. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{23}H_{23}NO_5Na$ 416.1474; found 416.1468.

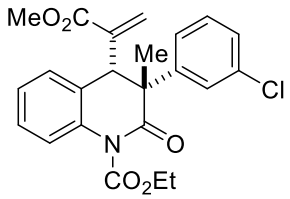
Ethyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-methyl-2-oxo-3-(p-tolyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (3r)



The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3r** as oil in 45% yield (18.5 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 (t, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.02 (td, *J* = 7.2, 1.2 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.16 (s, 1H), 5.26 (s, 1H), 4.48 – 4.39 (m, 2H), 4.29 (s, 1H), 3.33 (s, 3H), 2.22 (s, 3H), 1.59 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.5, 166.6, 153.7, 139.4, 136.5, 136.0, 135.6, 128.9, 128.6, 128.3, 128.0, 127.9, 126.7, 124.8, 116.4, 64.9, 51.8, 50.4, 50.1, 24.6, 20.8, 13.9. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{24}H_{25}NO_5Na$ 430.1630; found 430.1634.

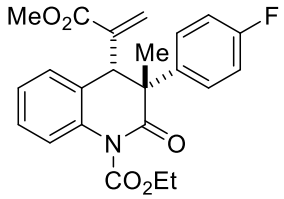
Ethyl 3-(3-chlorophenyl)-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-methyl-2-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate (3s)

The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3s** as oil in 76%



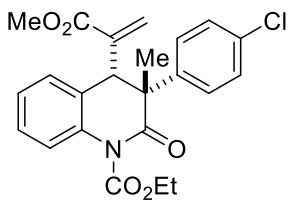
yield (32.6 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (s, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 1.8 Hz, 1H), 7.14 (d, *J* = 4.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.18 (s, 1H), 5.33 (s, 1H), 4.49 – 4.41 (m, 2H), 4.24 (s, 1H), 3.36 (s, 3H), 1.61 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.7, 166.4, 153.5, 140.9, 139.4, 135.8, 133.5, 129.4, 129.0, 128.8, 128.3, 128.1, 127.1, 126.9, 126.2, 125.0, 116.5, 65.1, 51.9, 50.6, 50.3, 24.5, 13.9. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{23}H_{22}ClNO_5Na$ 450.1084; found 450.1083.

Ethyl 3-(4-fluorophenyl)-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-methyl-2-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate (3t)



The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3t** as a white solid in 73% yield (30.2 mg), m. p. 155.9 – 156.6 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (dd, *J* = 9.0, 5.4 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.92 – 6.87 (m, 3H), 6.17 (s, 1H), 5.31 (s, 1H), 4.50 – 4.39 (m, 2H), 4.26 (s, 1H), 3.36 (s, 3H), 1.61 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.1, 166.5, 161.7 (d, J_{CF} = 244.5 Hz), 153.6, 139.5, 135.8, 134.6 (d, J_{CF} = 3.0 Hz), 130.6 (d, J_{CF} = 7.5 Hz), 129.0, 128.2, 128.0, 126.4, 124.9, 116.4, 114.3 (d, J_{CF} = 21.0 Hz), 65.1, 51.9, 50.3, 50.2, 24.8, 13.9. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{23}H_{22}FNO_5Na$ 434.1380; found 434.1379.

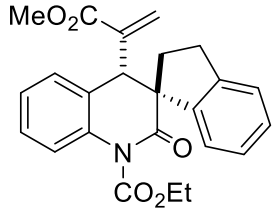
Ethyl 3-(4-chlorophenyl)-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-methyl-2-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate (3u)



The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3r** as oil in 66% yield (28.3 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 – 7.21 (m, 3H), 7.16 (d, *J* = 9.0 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.16 (s, 1H), 5.31 (s, 1H), 4.49 – 4.40 (m, 2H), 4.26 (s, 1H), 3.35 (s, 3H), 1.60 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.9, 166.4, 153.5, 139.4, 137.4, 135.8, 132.9, 130.3, 129.0, 128.2, 128.0, 127.6, 126.3, 125.0, 116.4, 65.1, 52.0, 50.4, 50.2, 24.6, 13.9. HRMS (ESI-TOF) m/z [M + Na]$^+$

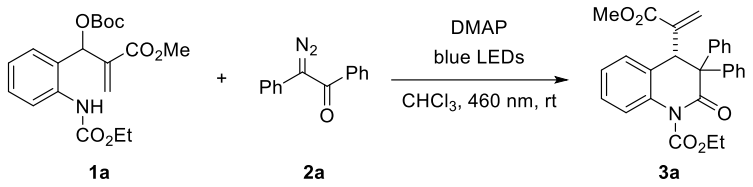
Calcd for $C_{23}H_{22}ClNO_5Na$ 450.1084; found 450.1079.

Ethyl 4'-(3-methoxy-3-oxoprop-1-en-2-yl)-2'-oxo-2,3-dihydro-2'H-spiro[indene-1,3'-quinoline]-1'(4'*H*)-carboxylate (3v)

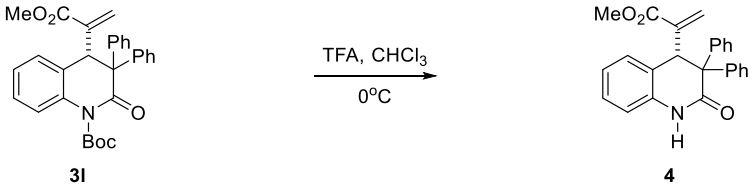


The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **3v** as oil in 64% yield (26.0 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.13 (q, *J* = 3.6 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.04 (td, *J* = 7.8, 1.2 Hz, 1H), 7.02 (d, *J* = 3.6 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.27 (s, 1H), 5.40 (s, 1H), 4.48 – 4.37 (m, 2H), 4.33 (s, 1H), 3.33 (s, 3H), 3.10 – 3.02 (m, 1H), 2.83 (dd, *J* = 16.2, 9.0 Hz, 1H), 2.30 – 2.24 (m, 1H), 2.09 – 2.06 (m, 1H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.7, 166.6, 154.0, 143.8, 140.3, 139.5, 136.4, 129.3, 128.1, 128.0, 127.6, 127.2, 125.7, 124.8, 124.5, 117.4, 64.9, 59.5, 52.0, 45.1, 35.8, 29.5, 13.9. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{24}H_{23}NO_5Na$ 428.1474; found 428.1473.

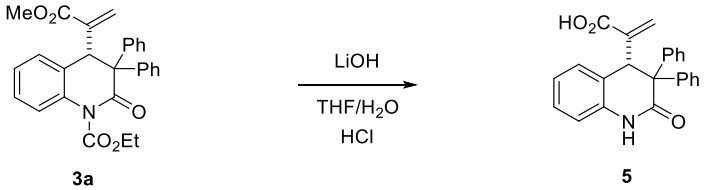
4.Scale-up reaction and transformations of product 3



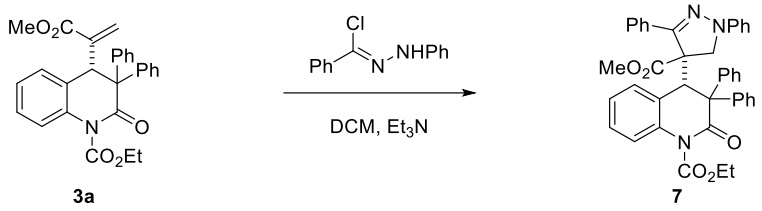
To a mixture of *ortho*-amino MBH carbonates **1a** (379.4 mg, 1.0 mmol), α-diazoketones **2a** (444.5 mg, 2.0 mmol) in $CHCl_3$ (10.0 mL) was added DMAP (24.4 mg, 0.2 mmol) at room temperature, the reaction mixture was then irradiated under blue LEDs for 2 hours. After completed (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel (PE/EA = 25/1) to give the pure product **3a** (300.0 mg, 66% yield) as a white solid.



Compound **4** was prepared by a modified reported procedure[3]. The corresponding compound **3l** (48.36 mg, 0.10 mmol) was dissolved in 1.0 mL $CHCl_3$ and slowly added TFA (5.70 mg, 0.05 mmol) to the mixture at 0 °C. After completed (monitored by TLC), the reaction mixture was extracted with ethyl acetate/NaCl (aq.) for three times. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford the pure product **4** (31.1 mg, 81% yield) as a white solid.

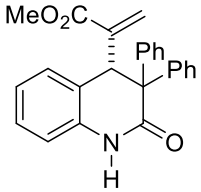


Compound **5** was prepared by a modified reported procedure[4]. To a solution of substrate **3a** (45.55 mg, 0.10 mmol) in THF/H_2O (1:1, 1.0 mL) was added LiOH (11.97 mg, 0.50 mmol) at 80 ℃. After completed (monitored by TLC), cooled down the reaction to room temperature and extracted with diethyl ether, the aqueous phase was acidified with 2M HCl and extracted with ethyl acetate, and then the combined organic layers were dried over $MgSO_4$. The volatile compounds were removed in vacuo to afford the crude product **5** (32.2 mg, 87% yield) as a white solid.



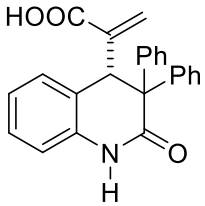
To a mixture of compound **3a** (45.55 mg, 0.10 mmol), *N*-phenyl phenylhydrazine acyl chloride (27.68 mg, 0.12 mmol) in DCM (1.0 mL) was added Et_3N (15.18 mg, 0.15 mmol) at room temperature. The mixture was stirred for 12h. After completed (monitored by TLC), the mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford the pure product **7** (60.0 mg, 92% yield) as a white solid.

Methyl 2-(2-oxo-3,3-diphenyl-1,2,3,4-tetrahydroquinolin-4-yl)acrylate (4)



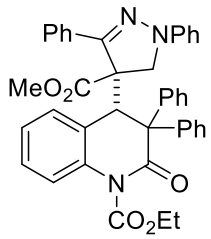
The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **4** as a white solid in 81% yield (31.1 mg), m. p. 283.2 – 283.9 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.11 – 7.70 (m, 1H), 7.43 – 7.35 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.14 – 7.11 (m, 3H), 7.08 (t, *J* = 7.8 Hz, 3H), 7.05 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.4 Hz, 2H), 6.95 (td, *J* = 7.2, 1.2 Hz, 1H), 6.59 – 6.55 (m, 1H), 6.12 (s, 1H), 5.33 (s, 1H), 5.08 (s, 1H), 3.24 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.7, 166.4, 140.85, 140.83, 140.4, 140.2, 136.05, 136.03, 131.1, 128.7, 128.4, 128.1, 128.0, 127.9, 127.5, 127.1, 126.4, 123.9, 115.1, 59.4, 51.7, 47.0. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{25}H_{21}NO_3Na$ 406.1419; found 406.1419.

2-(2-oxo-3,3-diphenyl-1,2,3,4-tetrahydroquinolin-4-yl)acrylic acid (5)



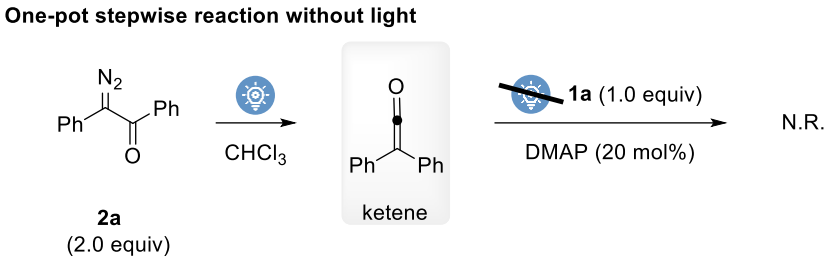
The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **5** as a white solid in 87% yield (32.2 mg), m. p. 233.2 – 234.5 ℃. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.27 (s, 1H), 10.46 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 3H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.16 – 7.12 (m, 2H), 7.10 (d, *J* = 6.6 Hz, 2H), 6.97 (td, *J* = 7.2, 1.2 Hz, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.09 (s, 1H), 5.49 (s, 1H), 5.16 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 169.9, 166.9, 141.43, 141.40, 141.3, 136.8, 130.6, 128.1, 128.0, 127.9, 127.6, 127.1, 126.7, 126.2, 126.0, 125.9, 122.6, 115.0, 57.7, 46.2. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{24}H_{19}NO_3Na$ 392.1263; found 392.1259.

Ethyl 4-(4-(methoxycarbonyl)-1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-4-yl)-2-oxo-3,3-diphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (7)

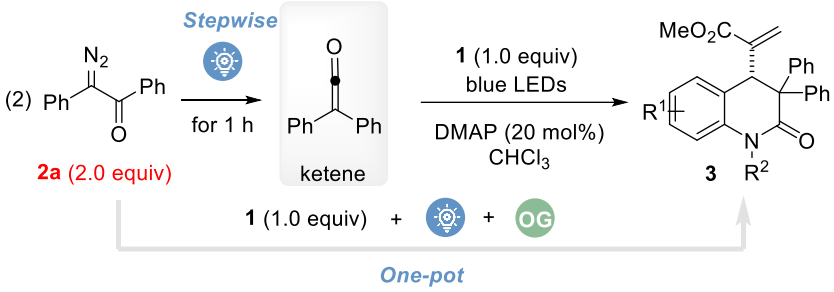


The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **7** as a white solid in 92% yield (60.0 mg), m. p. 189.9 – 190.5 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 6.6 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.25 (q, *J* = 6.6 Hz, 3H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 9.6 Hz, 3H), 7.13 (d, *J* = 6.6 Hz, 2H), 7.10 (d, *J* = 6.6 Hz, 3H), 6.94 – 6.90 (m, 2H), 6.83 (t, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 5.14 (s, 1H), 4.34 – 4.17 (m, 3H), 3.93 (d, *J* = 16.8 Hz, 1H), 2.65 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 169.4, 166.0, 152.8, 148.6, 144.4, 140.3, 139.0, 135.0, 132.3, 131.8, 131.0, 128.9, 128.6, 128.44, 128.35, 128.3, 128.2, 127.7, 127.5, 127.0, 126.1, 123.9, 122.7, 122.3, 119.8, 115.3, 77.4, 65.0, 58.0, 52.0, 49.5, 39.8, 13.7. HRMS (ESI-TOF) m/z [M + Na]+ Calcd for $C_{41}H_{35}N_3O_5Na$ 672.2474; found 672.2472.

5. Control experiments

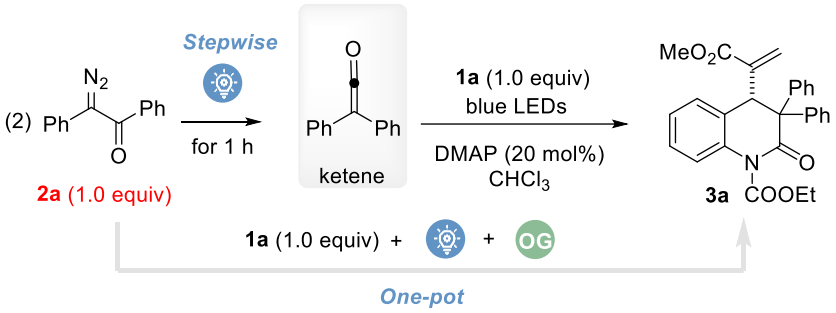


The mixture of **2a** (0.20 mmol) in $CHCl_3$ (1.0 mL) was irradiated under blue LEDs at room temperature for 1 hours. After **2a** completely transformed into the ketene (monitored by color), **1a** (0.10 mmol) and DMAP (0.02 mmol) was added to the solution and conducted in the dark environment for another 1 hour, no product was detected in the progress at last.



Entry	R^1, R^2	Yield of **3** (*one-pot*)	Yield of **3** (*stepwise*)
1	R^1 = H, R^2 = CO_2Me	**3j**, 59%	**3j**, 48%
2	R^1 = 4-CH_3, R^2 = CO_2Et	**3b**, 89%	**3b**, 45%
3	R^1 = 5-F, R^2 = CO_2Et	**3g**, 72%	**3g**, 39%

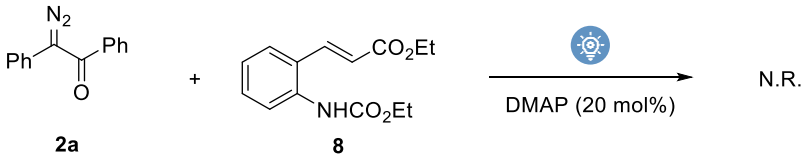
The mixture of **2a** (0.20 mmol) in $CHCl_3$ (1.0 mL) was irradiated under blue LEDs at room temperature for 1 hour. After **2a** completely transformed into the ketene (monitored by color), **1** (0.10 mmol) and DMAP (0.02 mmol) was added to the solution, and then irradiated under blue LEDs for another 1 hour. After completed (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel (PE/EA = 25/1) to give the pure products **3j** (48% yield), **3b** (45% yield) and **3g** (39% yield) respectively which lower than *one-pot* process.



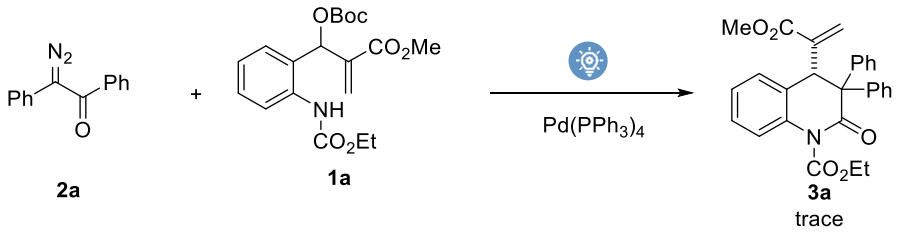
Entry	Yield of **3a** (*one-pot*)	Yield of **3a** (*stepwise*)
1	58% yield	15% yield

One-pot procedure: to a mixture of *o*-amino-acylation aryl MBH carbonates **1** (0.10 mmol), α-diazoketones **2** (0.10 mmol) in $CHCl_3$ (1.0 mL) was added DMAP (2.44 mg, 0.02 mmol) at room temperature, the reaction mixture was then irradiated under blue LEDs for 2 hours. After completed (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel (PE/EA = 25/1) to give the pure product **3a** in 58% yield.

Stepwise procedure: the mixture of **2a** (0.10 mmol) in $CHCl_3$ (1.0 mL) was irradiated under blue LEDs at room temperature for 1 hour. After **2a** completely transformed into the ketene (monitored by color), **1** (0.10 mmol) and DMAP (0.02 mmol) was added to the solution, and then irradiated under blue LEDs for another 1 hour. After completed (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel (PE/EA = 25/1) to give the pure product **3a** in 15% yield.

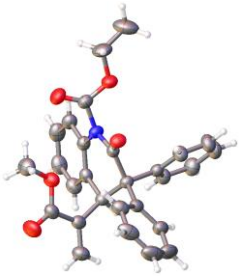


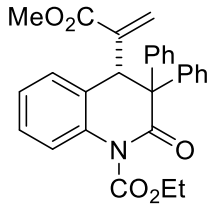
To a mixture of compound **8** (0.10 mmol) and α-diazoketone **2a** (0.20 mmol) in $CHCl_3$ (1.0 mL) was added DMAP (0.02 mmol) at room temperature, the reaction mixture was then irradiated under blue LEDs for 2 hours. Finally, no product was detected in the progress.



To a solution of $Pd(PPh_3)_4$ (5.78 mg, 0.005 mmol) and *o*-amino MBH carbonate **1a** (0.10 mmol) in $CHCl_3$ (1.0 mL) was added α-diazoketones **2** (0.20 mmol) at room temperature, the reaction mixture was irradiated under blue LEDs for 2 hours. Finally, trace amounts of product were detected.

6.Single crystal X-ray diffraction analysis and crystal data





CCDC = 2222974

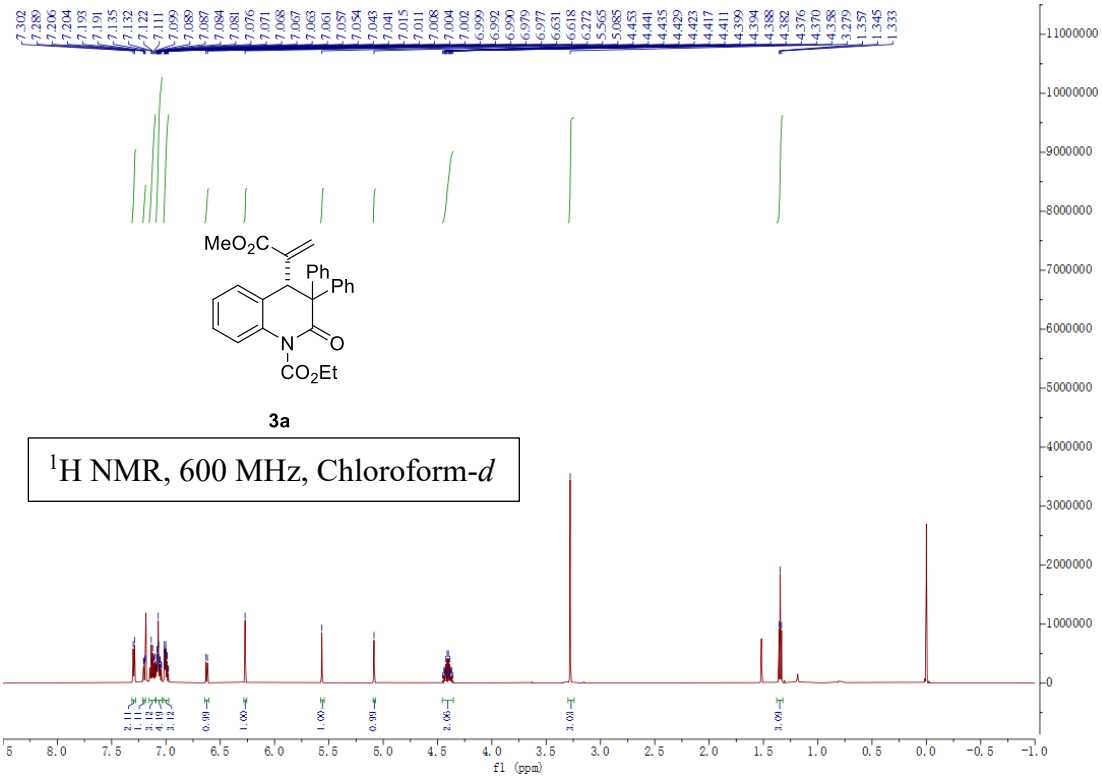
To a 5 mL tube containing **3a** (30 mg) was added a 1:3 mixture of dichloromethane and petroleum ether (4 mL). A clear solution was obtained through ultrasound treatment and was kept at room temperature for 3 day to get crystals of **3a**, which were characterized by single crystal X-ray diffraction. The data were collected by an Agilent Gemini. **3a** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

(Ellipsoid contour probability 50%)

Empirical formula	$C_{28}H_{25}NO_5$
Formula weight	455.49
Temperature/K	250.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.5036(3)
b/Å	15.2463(4)
c/Å	16.0722(6)
α/°	90
β/°	96.9700(10)
γ/°	90
Volume/Å3	2311.57(13)
Z	4
ρcalcg/cm3	1.309
μ/mm-1	0.090
F(000)	960.0
Crystal size/mm3	0.46 × 0.45 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.078 to 50
Index ranges	-11 ≤ h ≤ 11, -17 ≤ k ≤ 18, -19 ≤ l ≤ 19
Reflections collected	27969
Independent reflections	4049 [Rint = 0.1000, Rsigma = 0.0597]
Data/restraints/parameters	4049/0/310

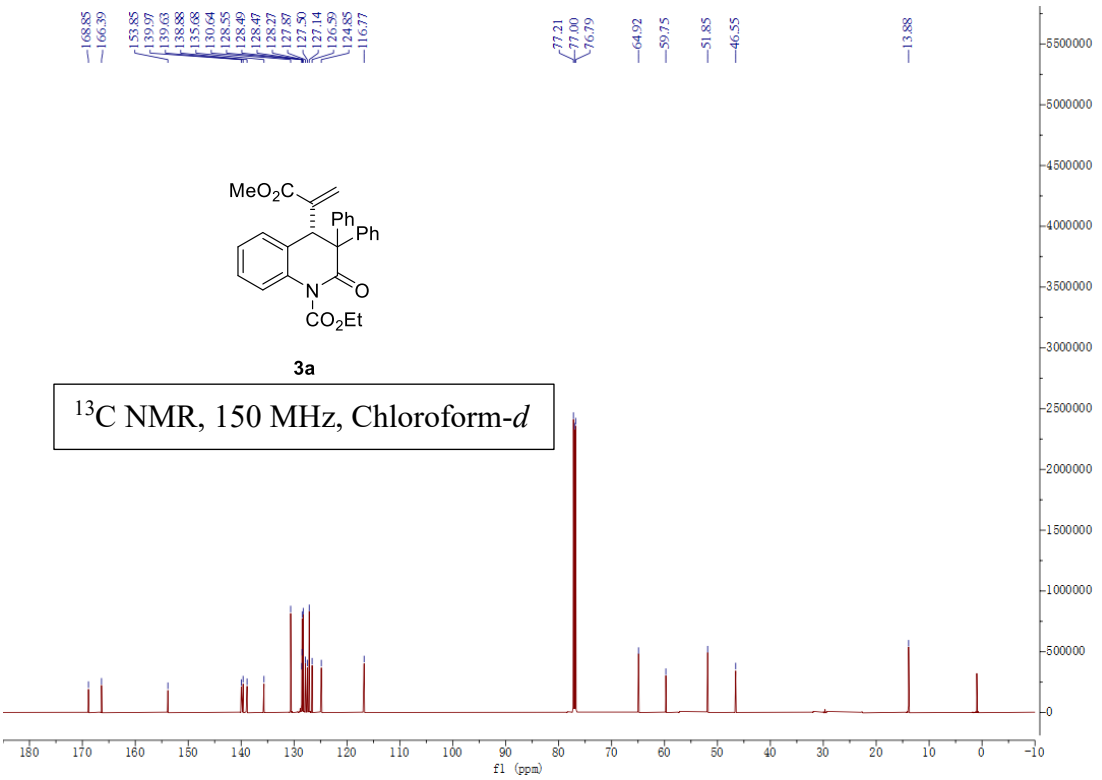
Goodness-of-fit on F2	1.027
Final R indexes [I>=2σ (I)]	R1 = 0.0639, wR2 = 0.1733
Final R indexes [all data]	R1 = 0.0793, wR2 = 0.1922
Largest diff. peak/hole / e Å-3	0.38/-0.38

7.^{1}H NMR and ^{13}C NMR spectra



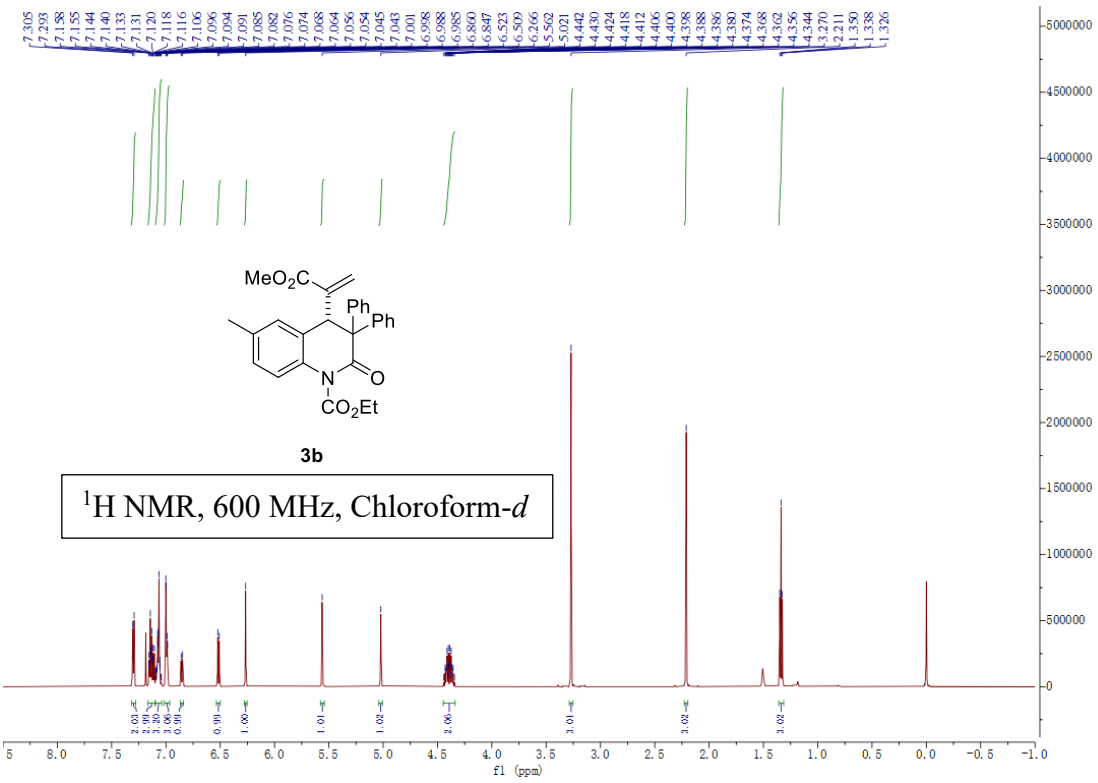
3a

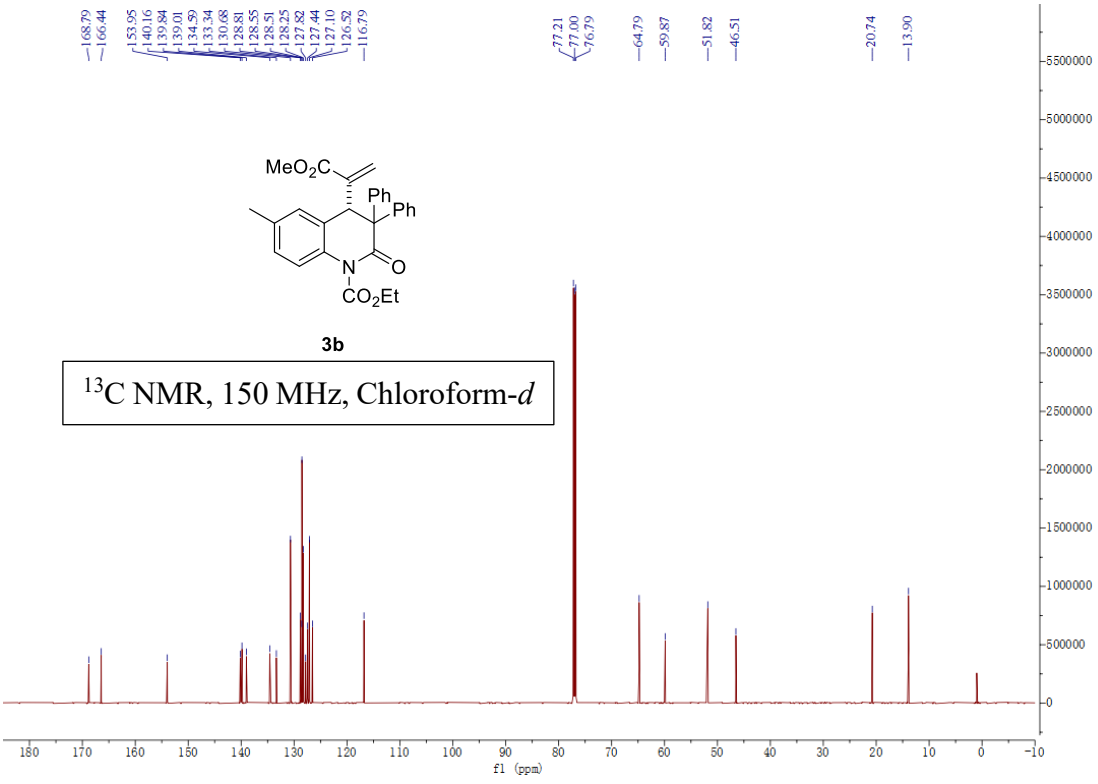
^{1}H NMR, 600 MHz, Chloroform-*d*

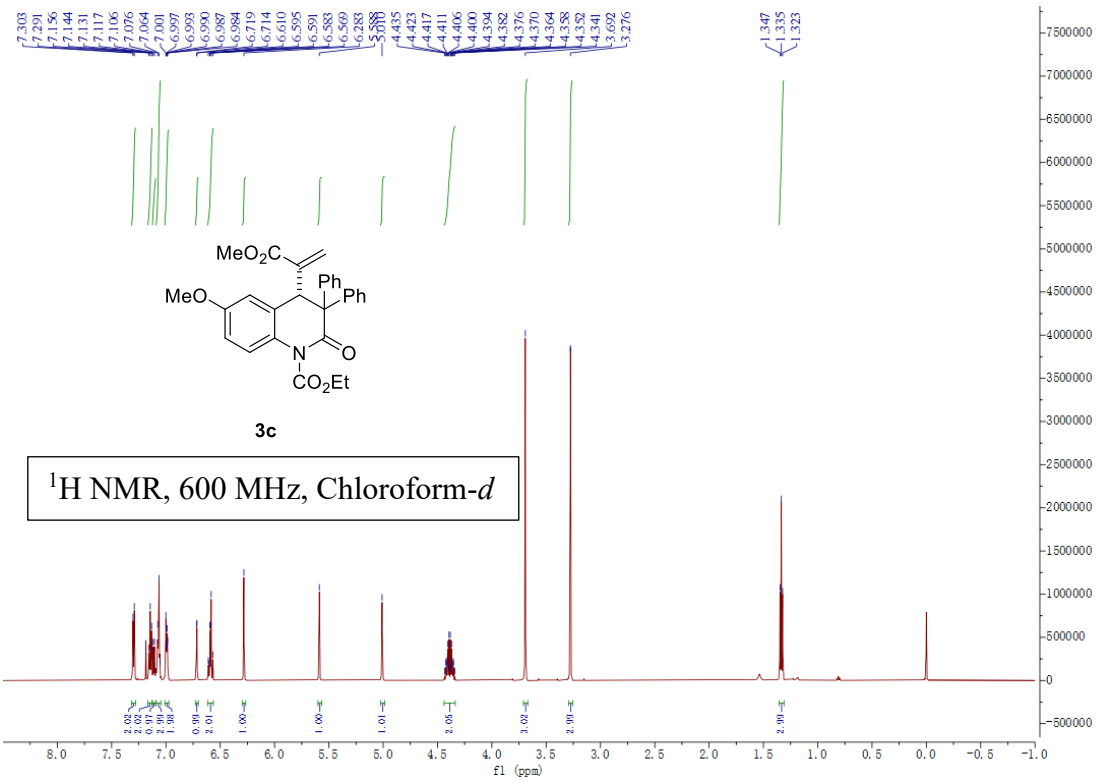


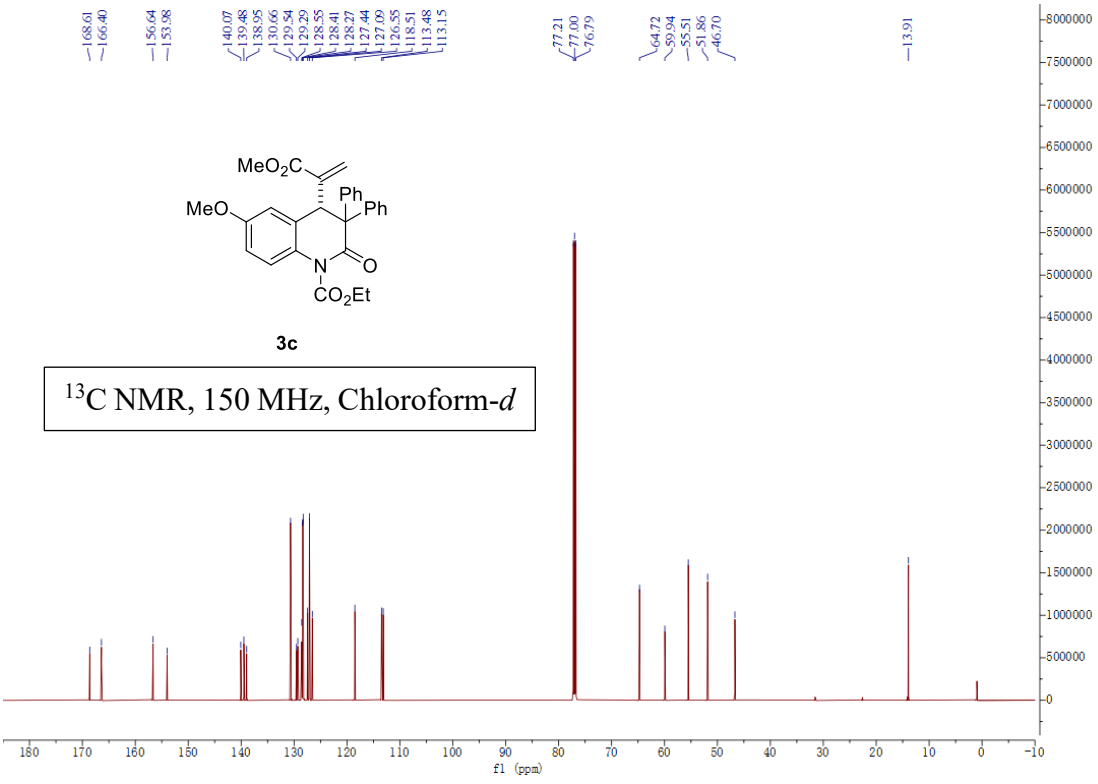
3a

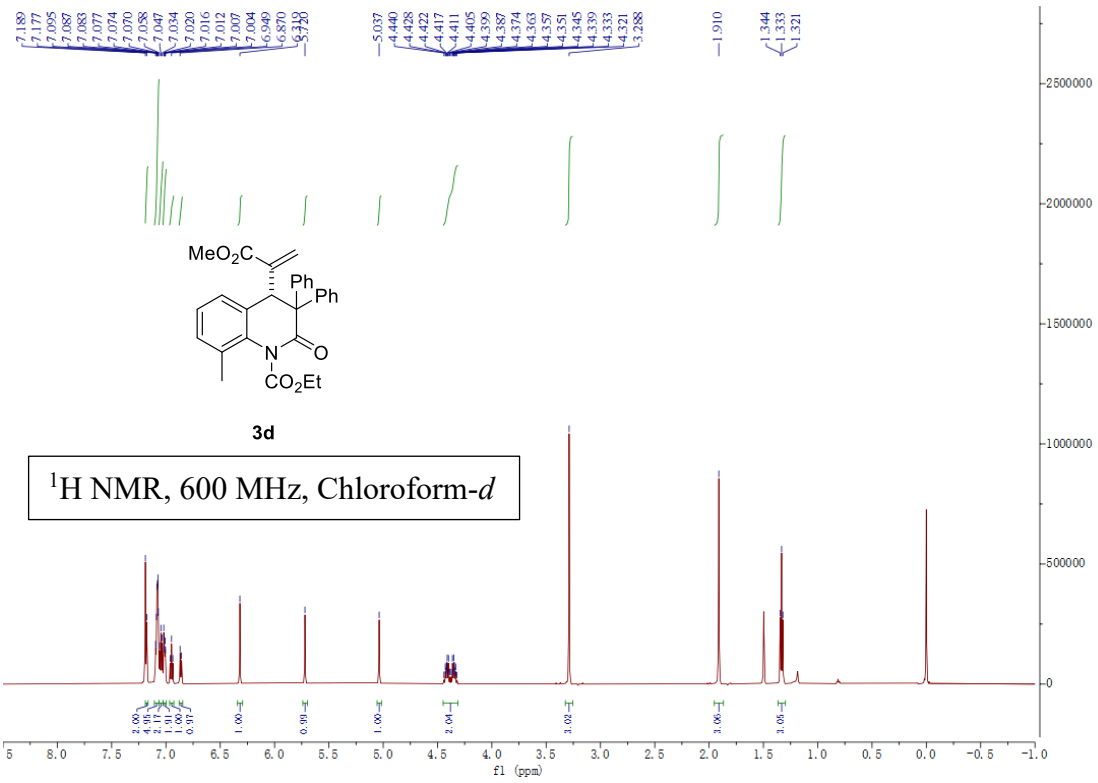
^{13}C NMR, 150 MHz, Chloroform-*d*

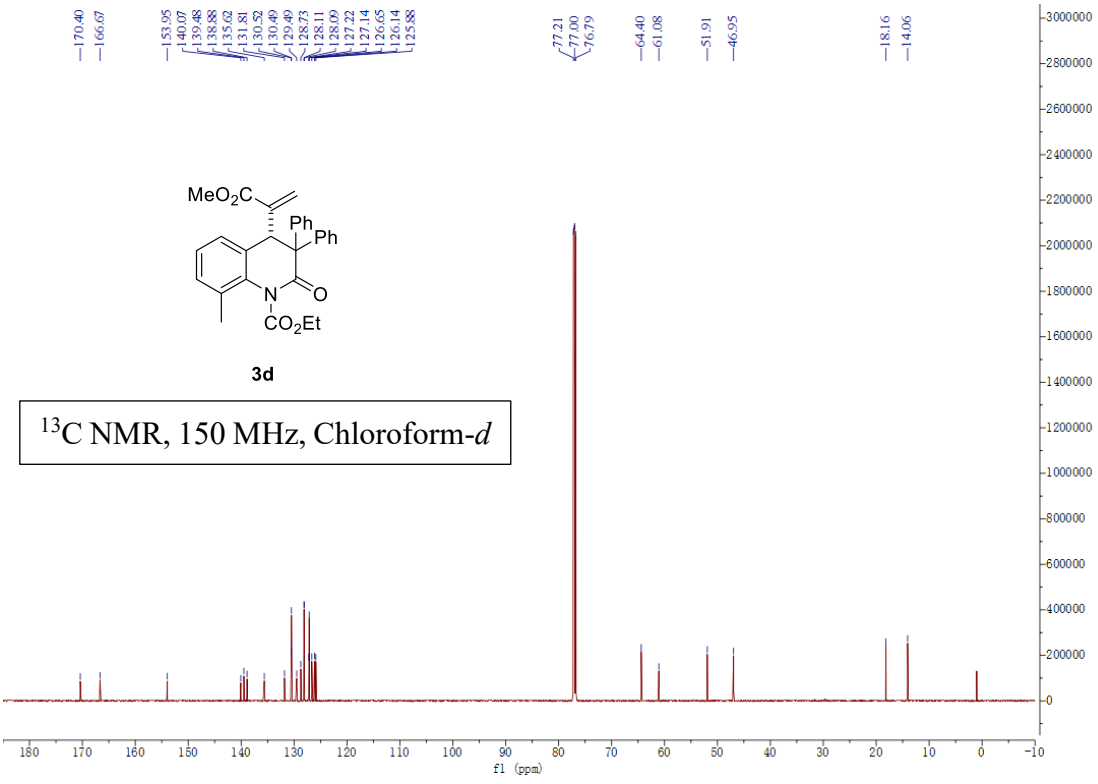

MeO2C
Ph
Ph
N
O
CO2Et
3b
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)

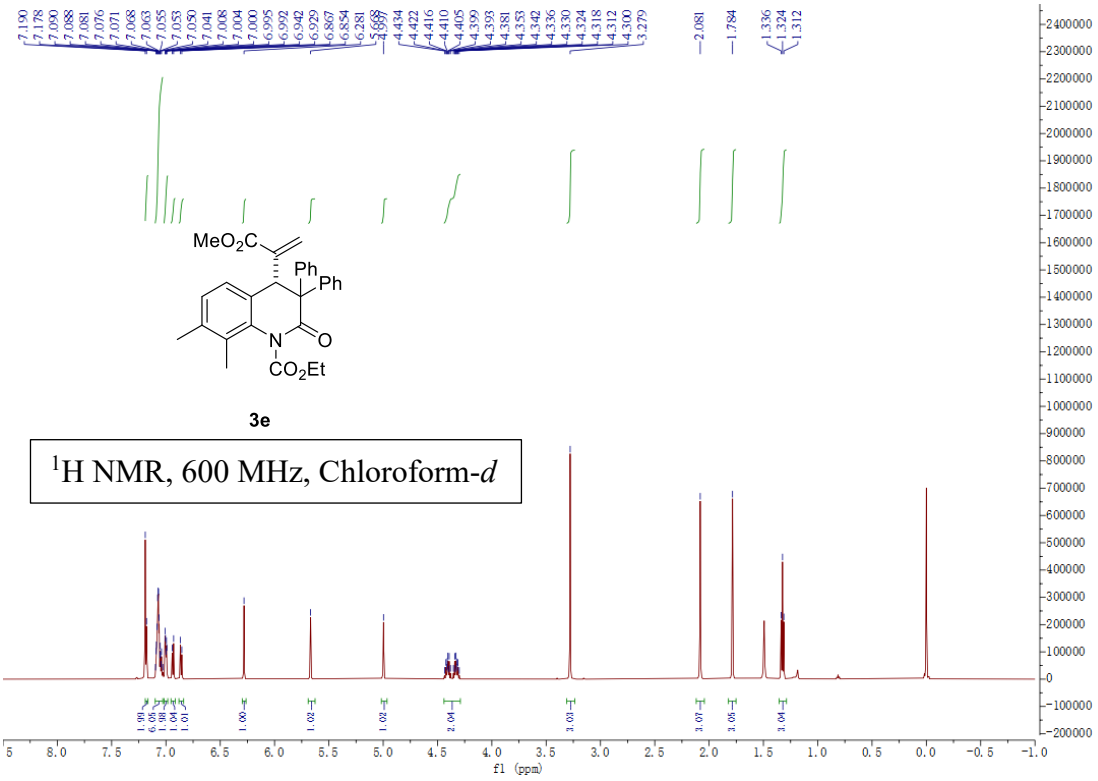

MeO2C
Ph
Ph
N
O
CO2Et
3b
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)


MeO2C
Ph
Ph
MeO
N
O
CO2Et
3c
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)


MeO2C
Ph
Ph
MeO
N
O
CO2Et
3c
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)

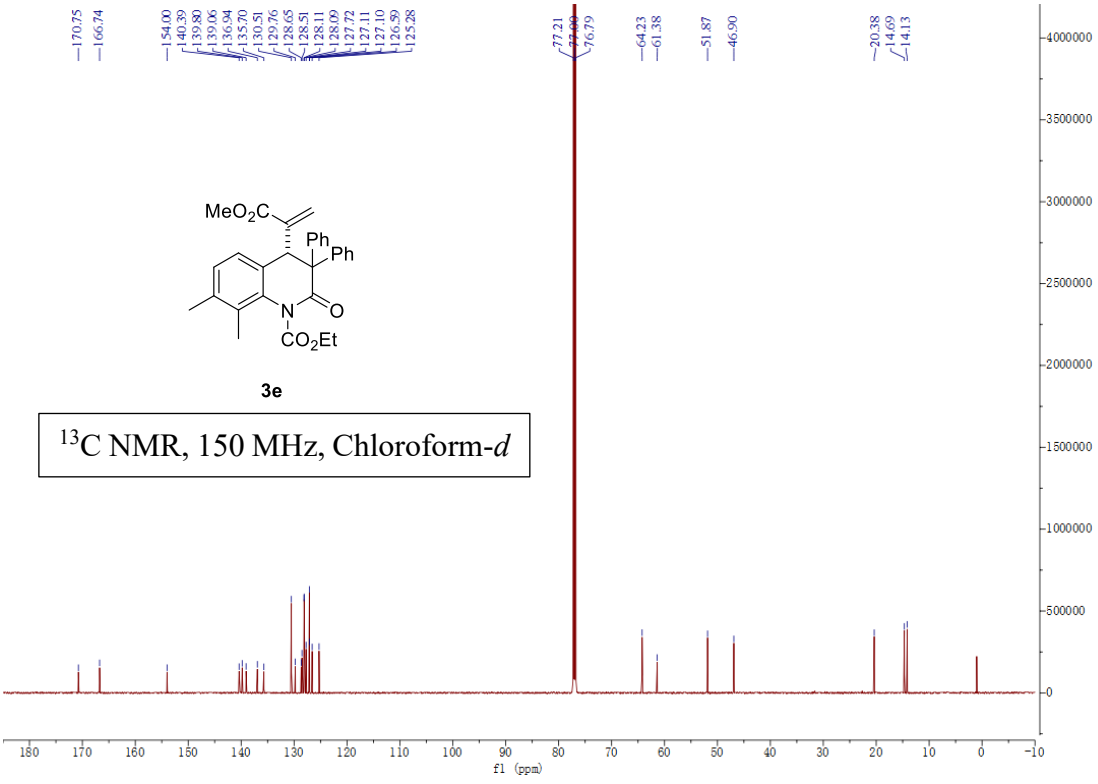

MeO2C
Ph
Ph
N
O
CO2Et
3d
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)


MeO2C
Ph
Ph
N
O
CO2Et
3d
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)



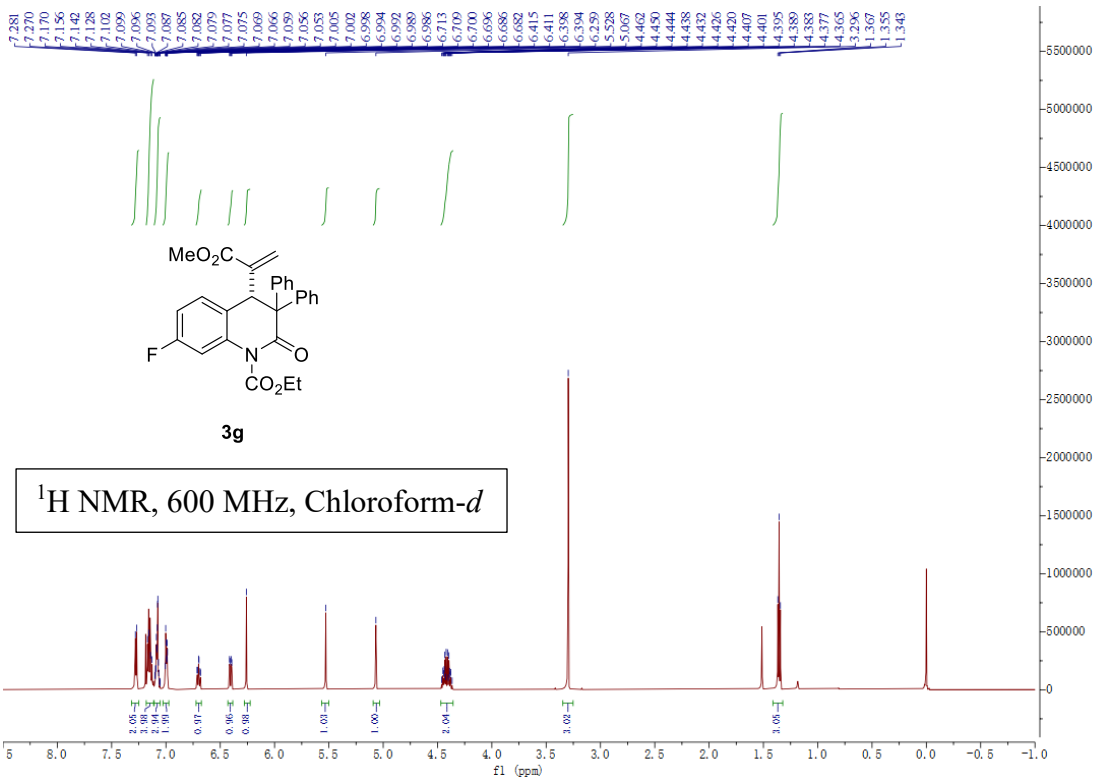
3e

^{1}H NMR, 600 MHz, Chloroform-*d*



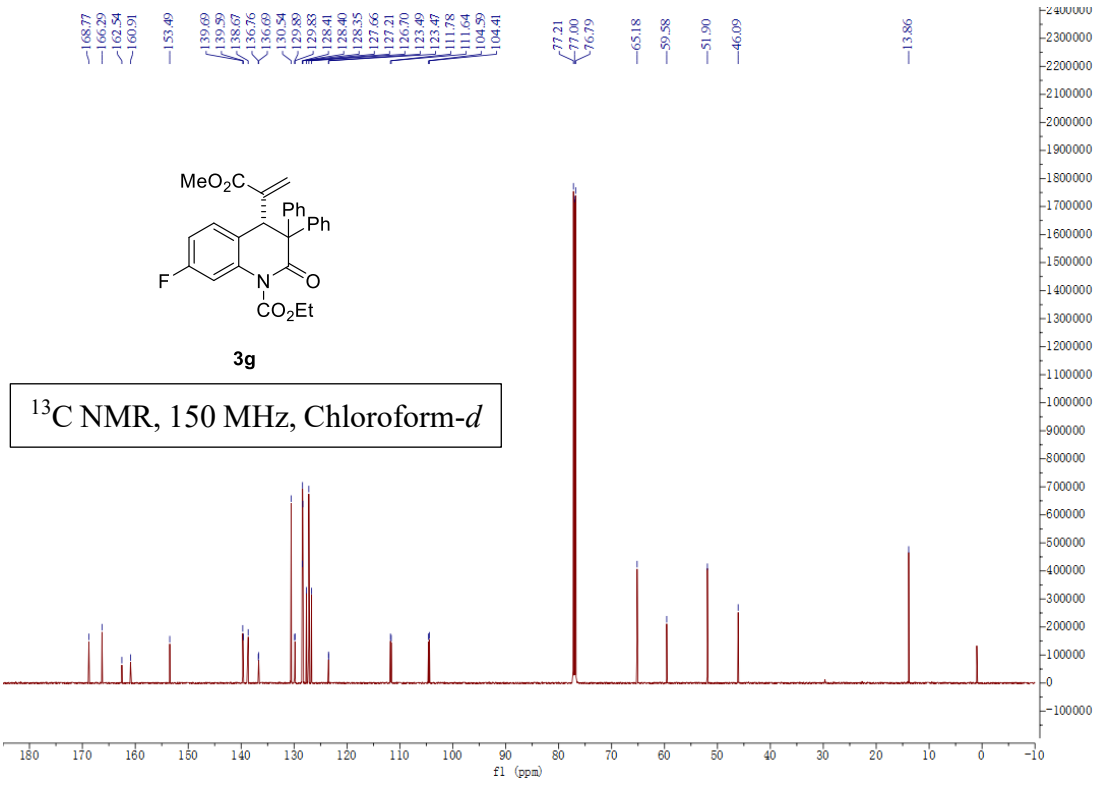
3e

^{13}C NMR, 150 MHz, Chloroform-*d*



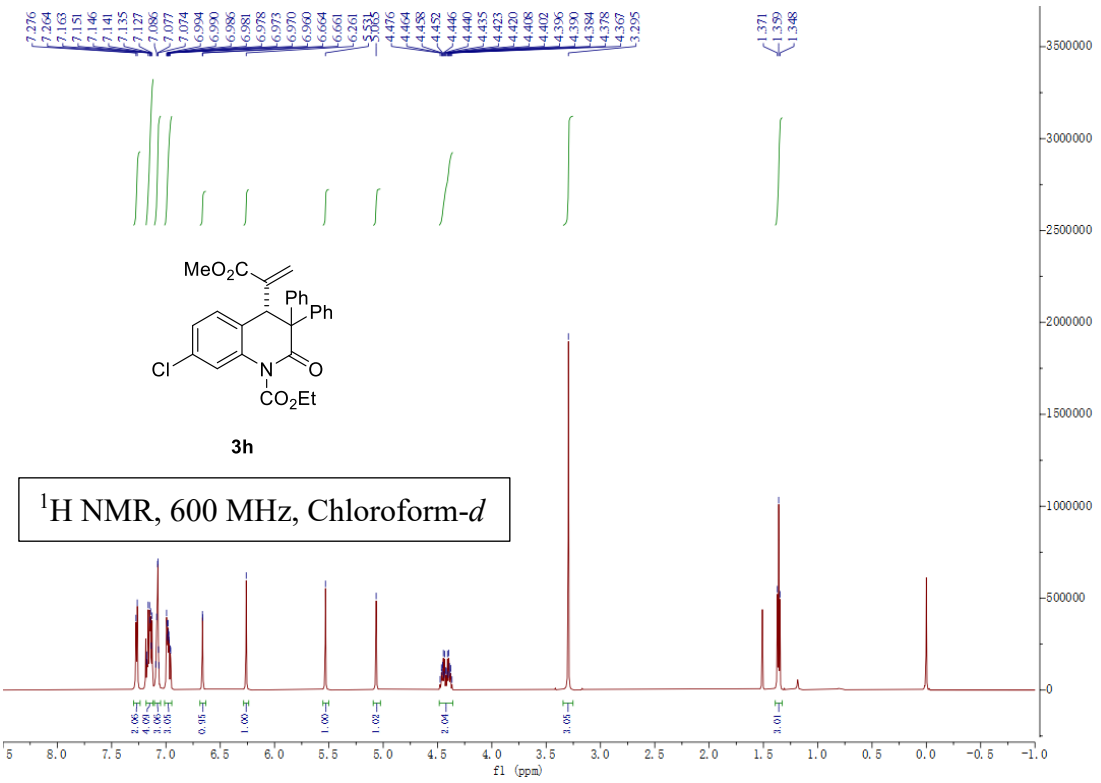
3g

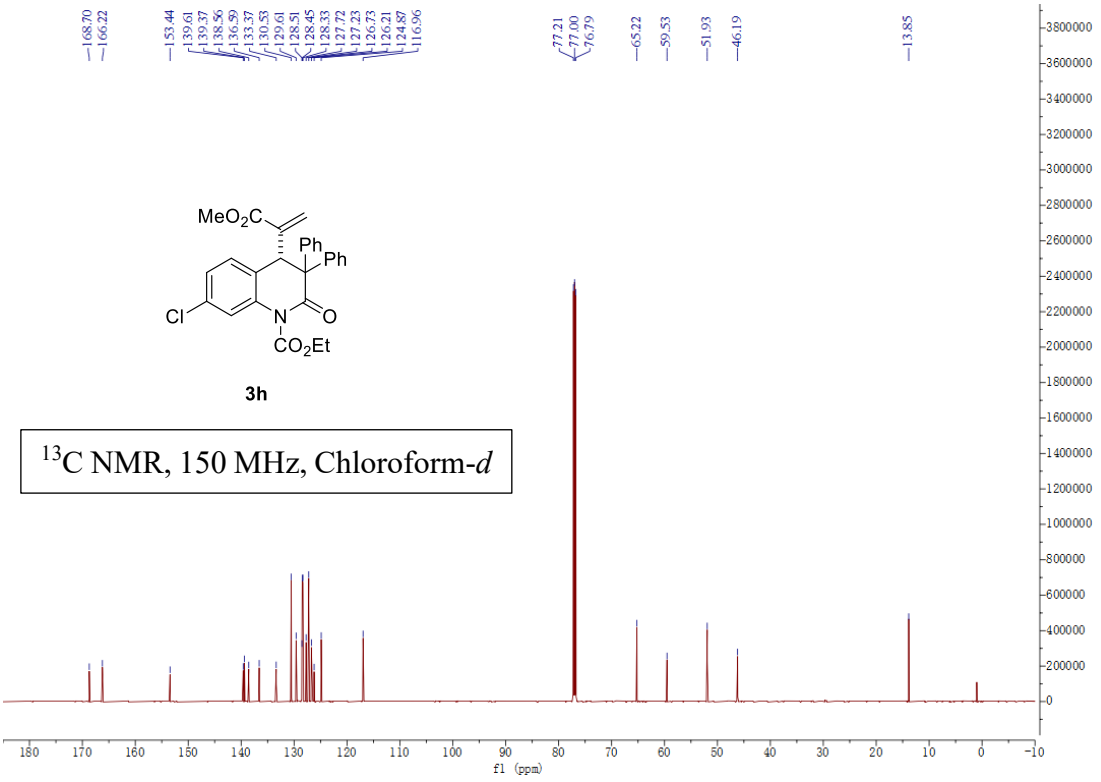
^{1}H NMR, 600 MHz, Chloroform-*d*

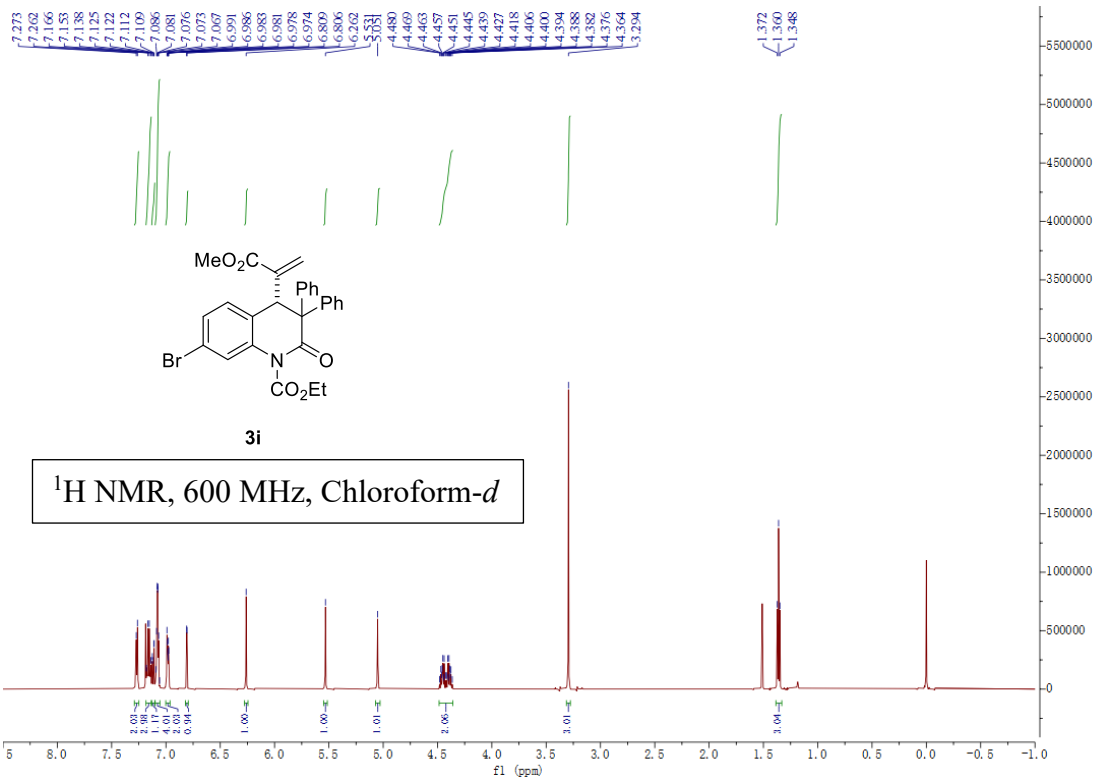


3g

^{13}C NMR, 150 MHz, Chloroform-*d*

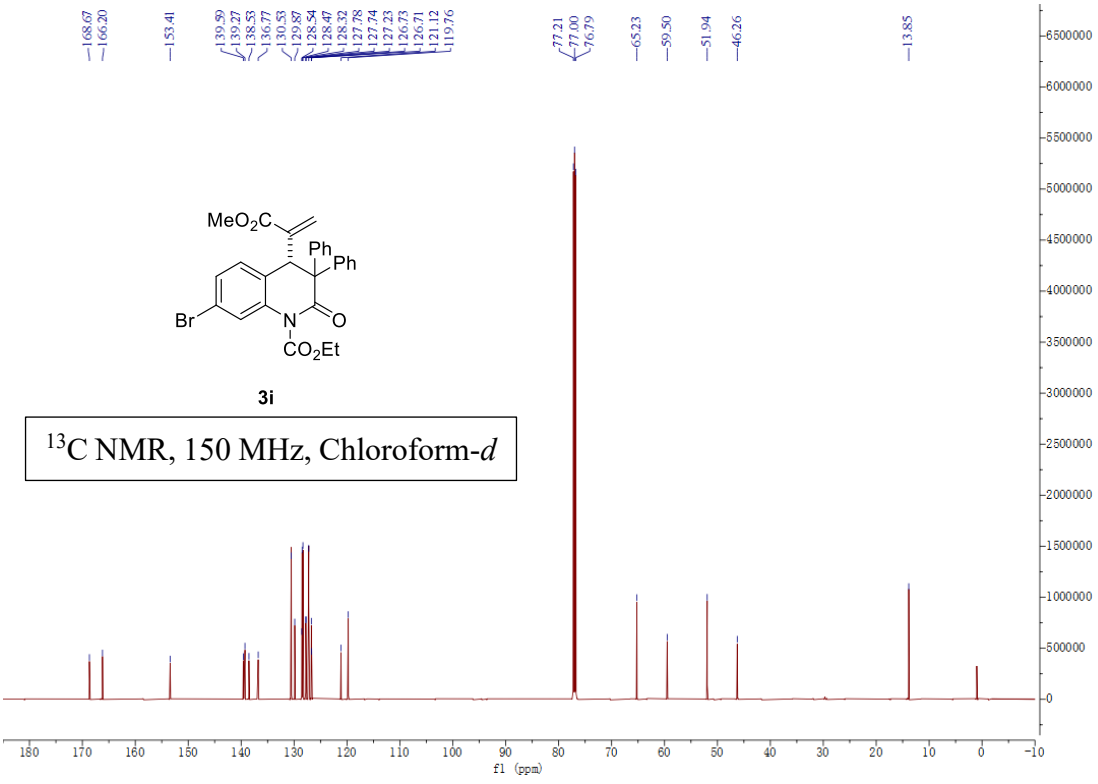

MeO2C
Ph
Ph
Cl
N
O
CO2Et
3h
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)


MeO2C
Ph
Ph
Cl
N
O
CO2Et
3h
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)



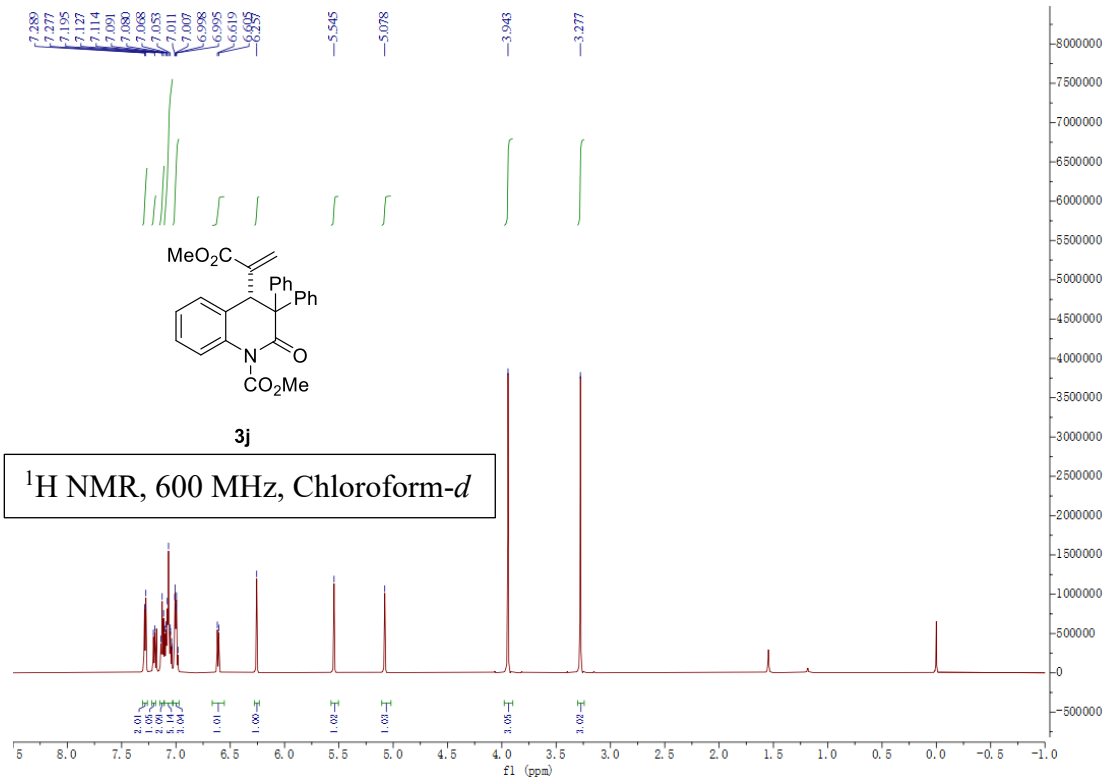
3i

^{1}H NMR, 600 MHz, Chloroform-*d*



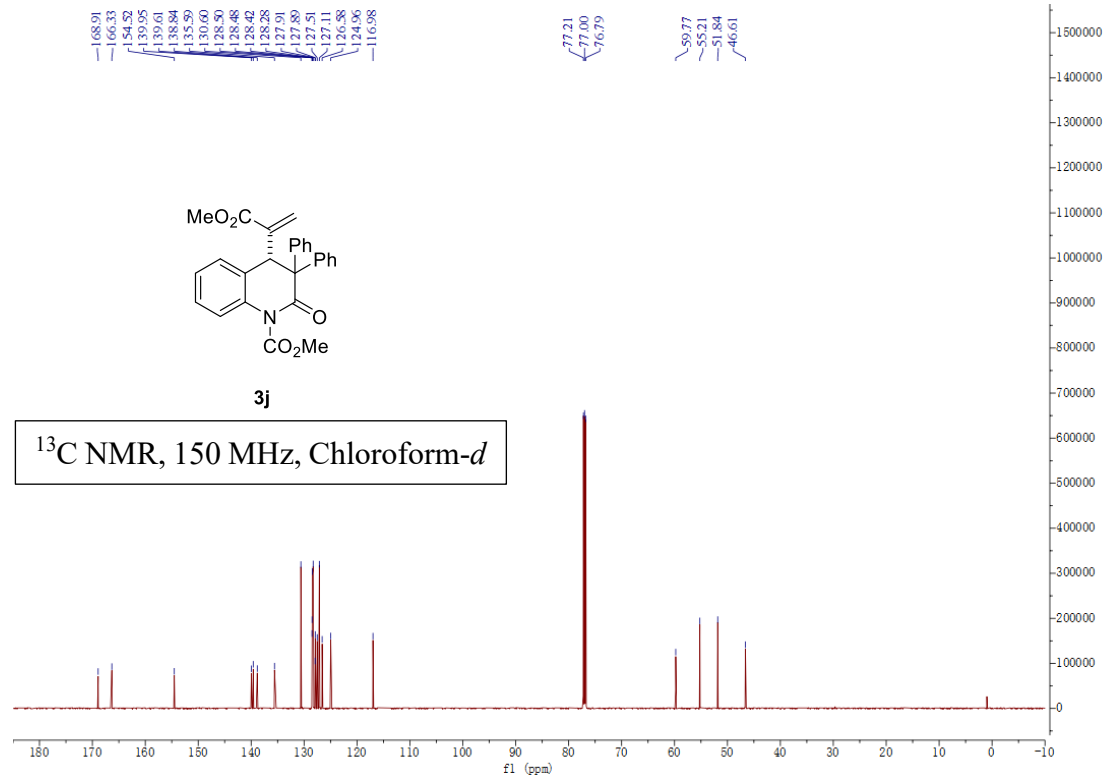
3i

^{13}C NMR, 150 MHz, Chloroform-*d*



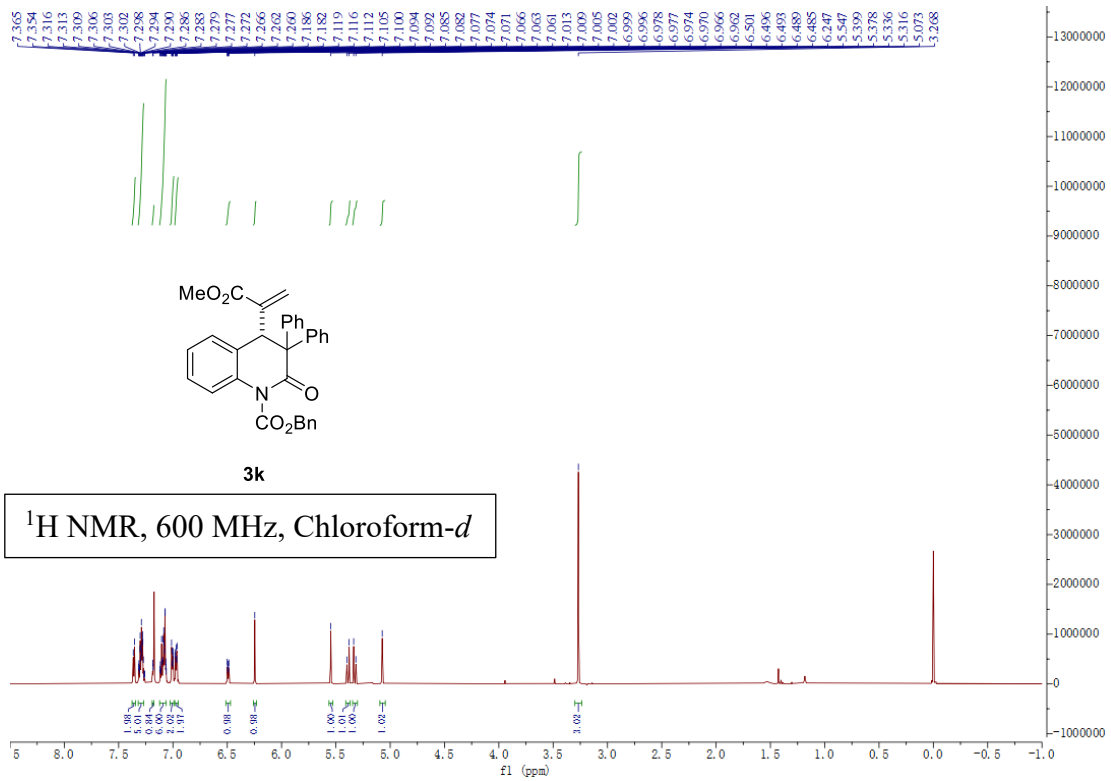
3j

^{1}H NMR, 600 MHz, Chloroform-*d*



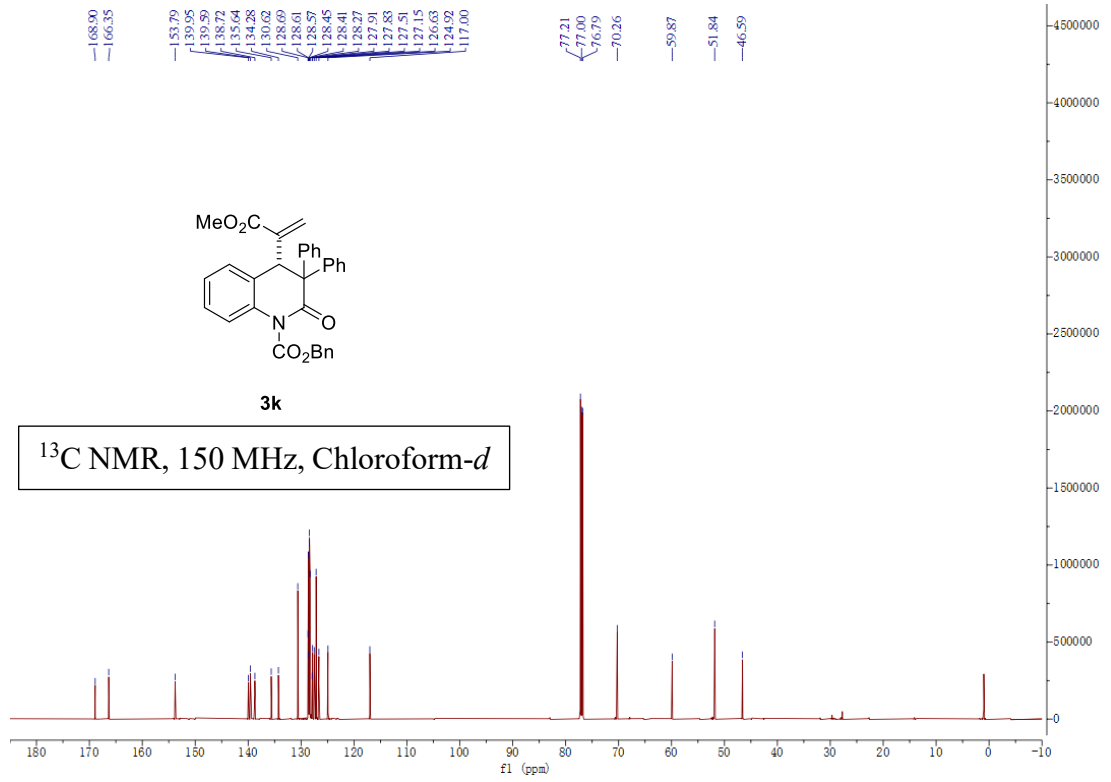
3j

^{13}C NMR, 150 MHz, Chloroform-*d*



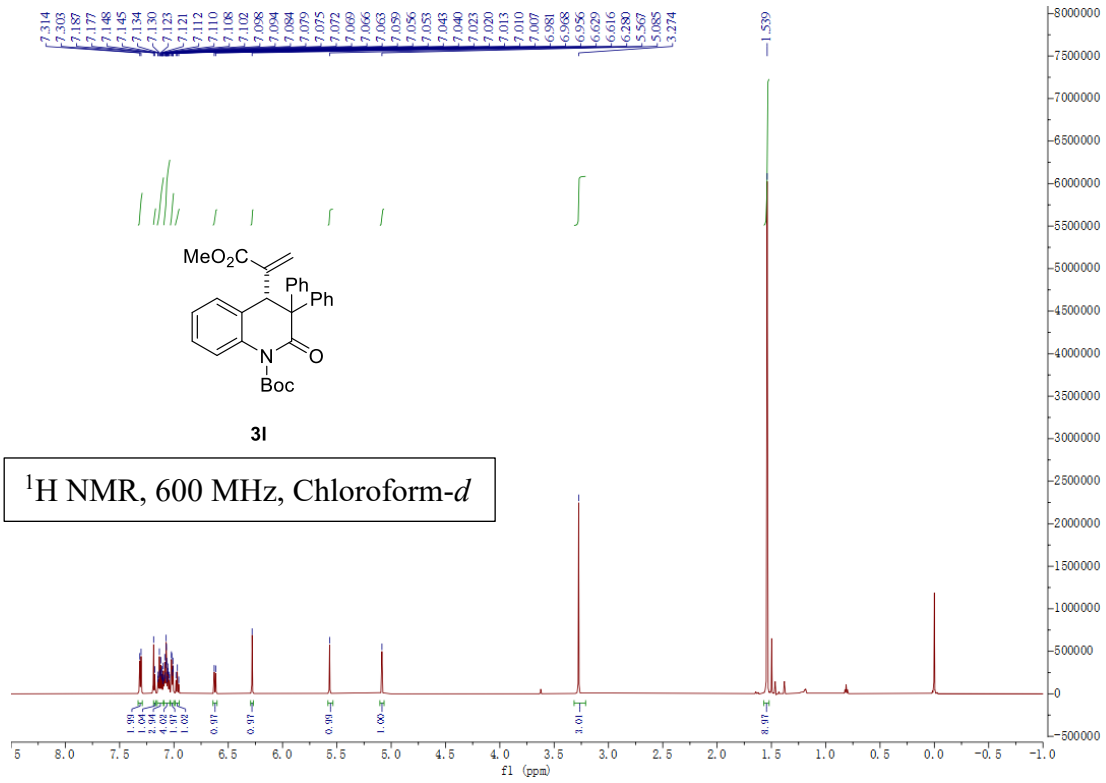
3k

^{1}H NMR, 600 MHz, Chloroform-*d*



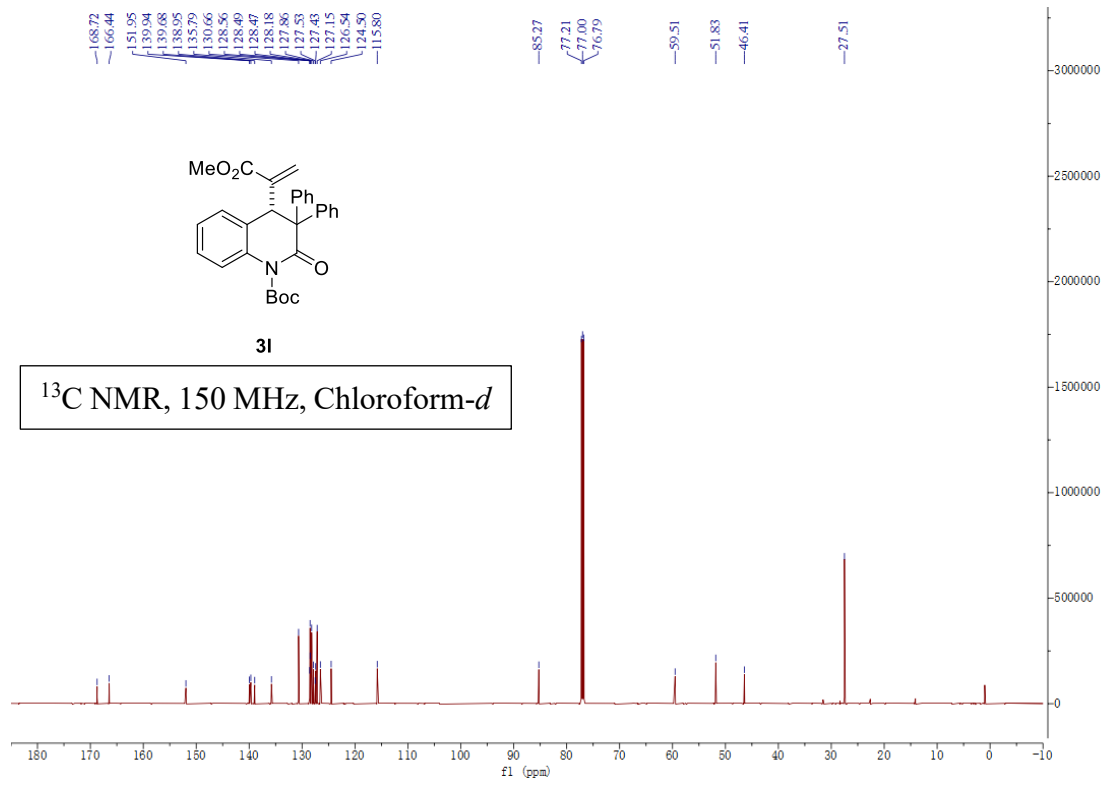
3k

^{13}C NMR, 150 MHz, Chloroform-*d*



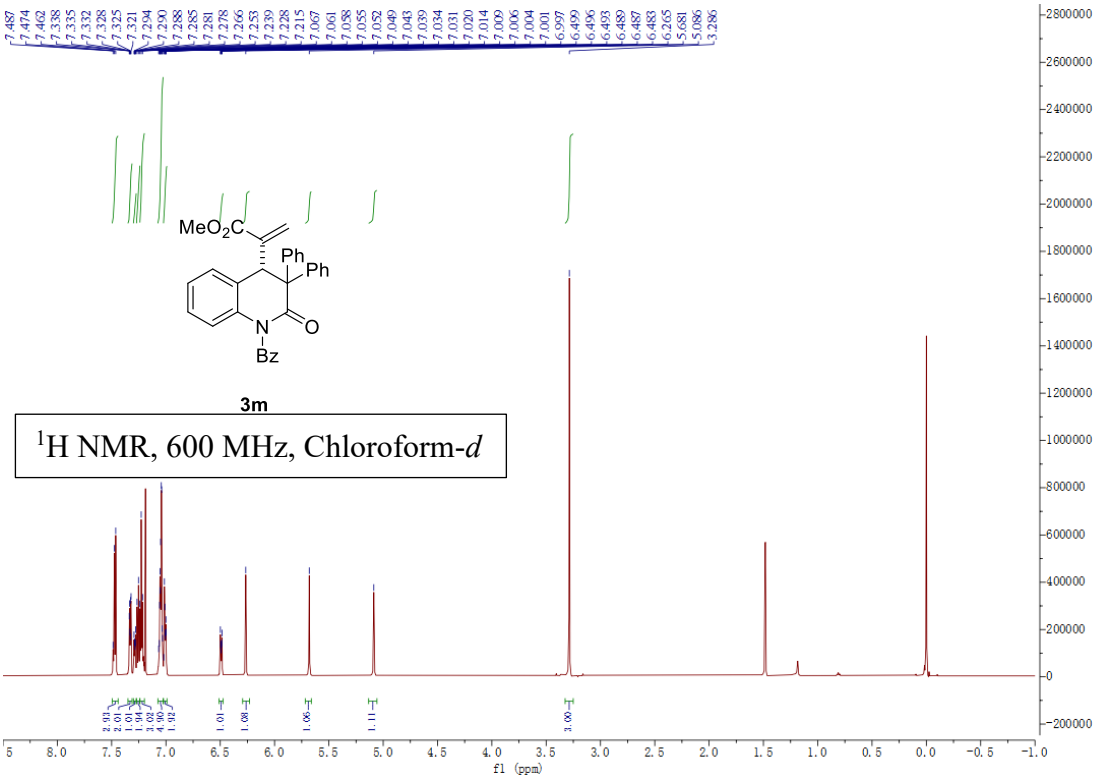
3l

^{1}H NMR, 600 MHz, Chloroform-*d*



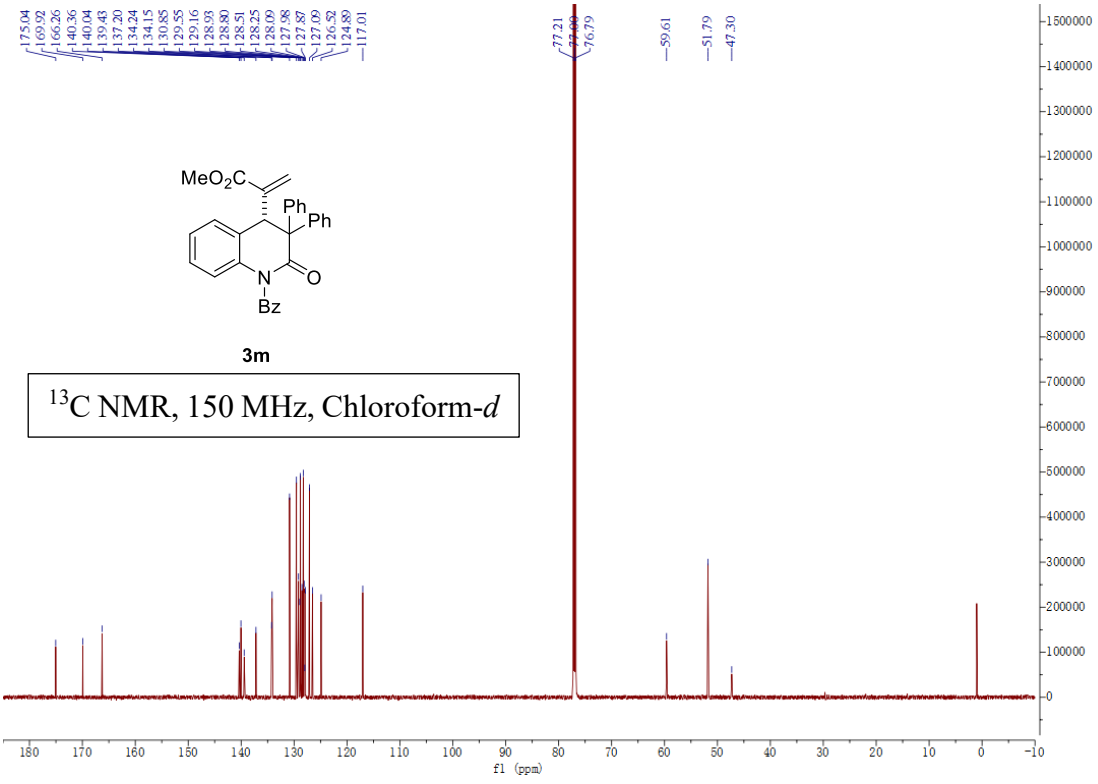
3l

^{13}C NMR, 150 MHz, Chloroform-*d*



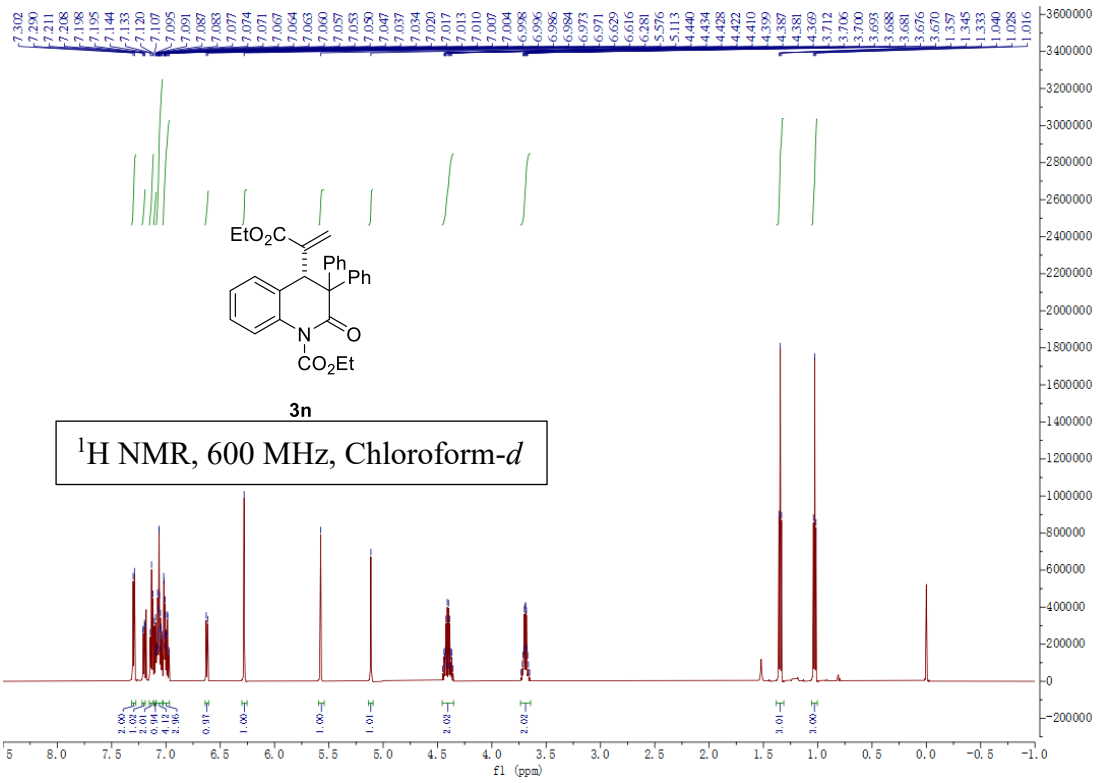
3m

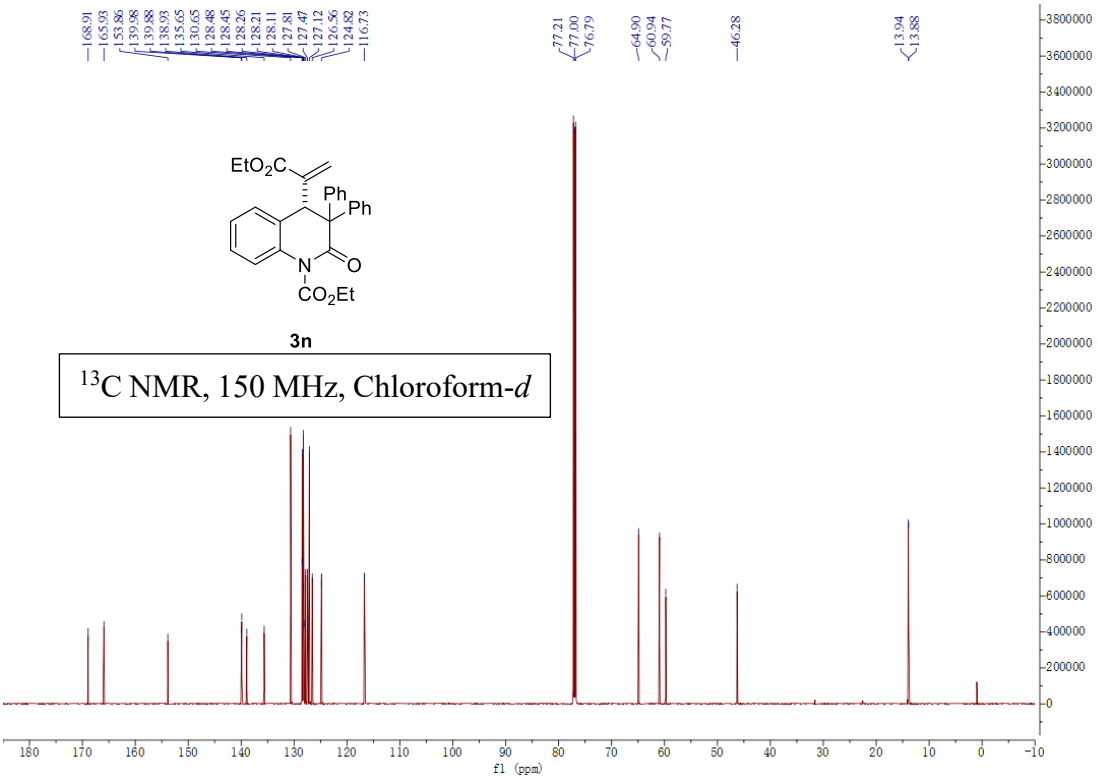
^{1}H NMR, 600 MHz, Chloroform-*d*

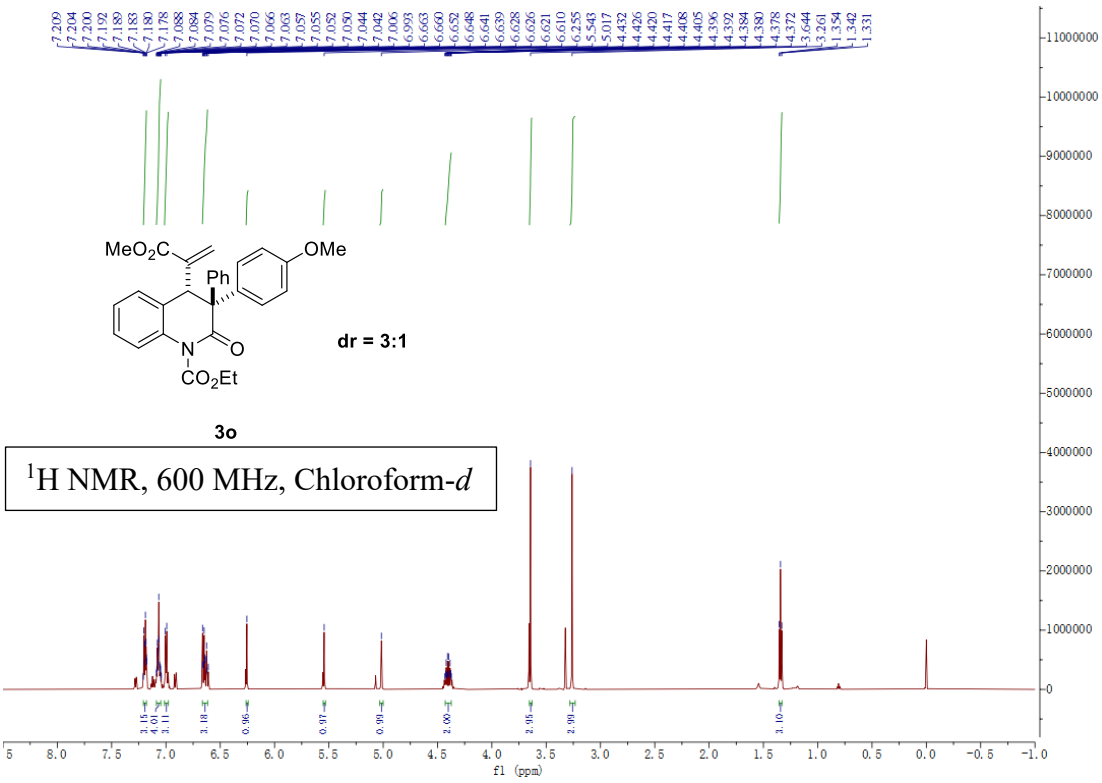


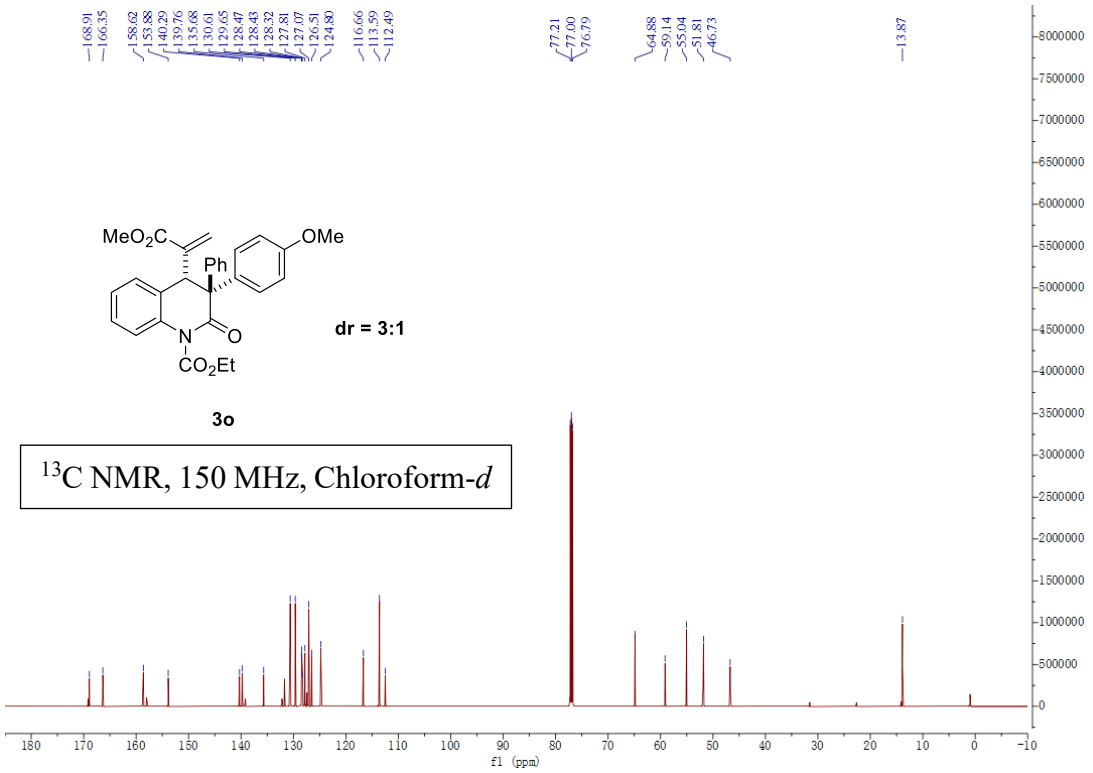
3m

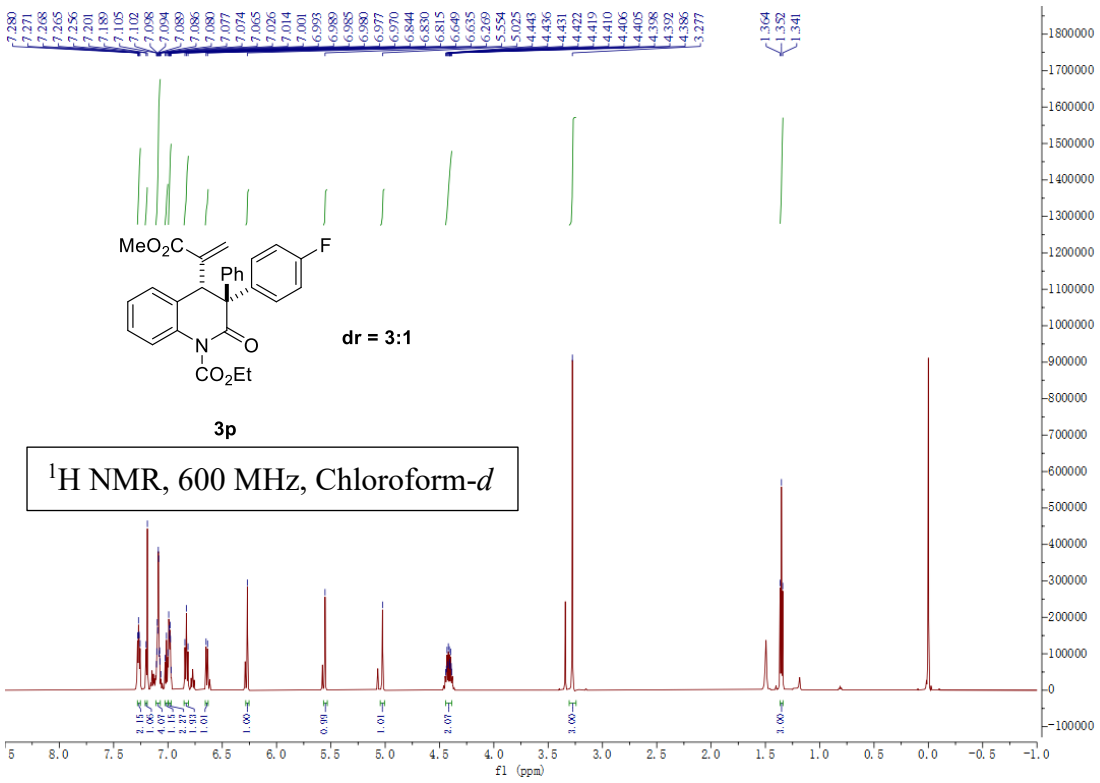
^{13}C NMR, 150 MHz, Chloroform-*d*

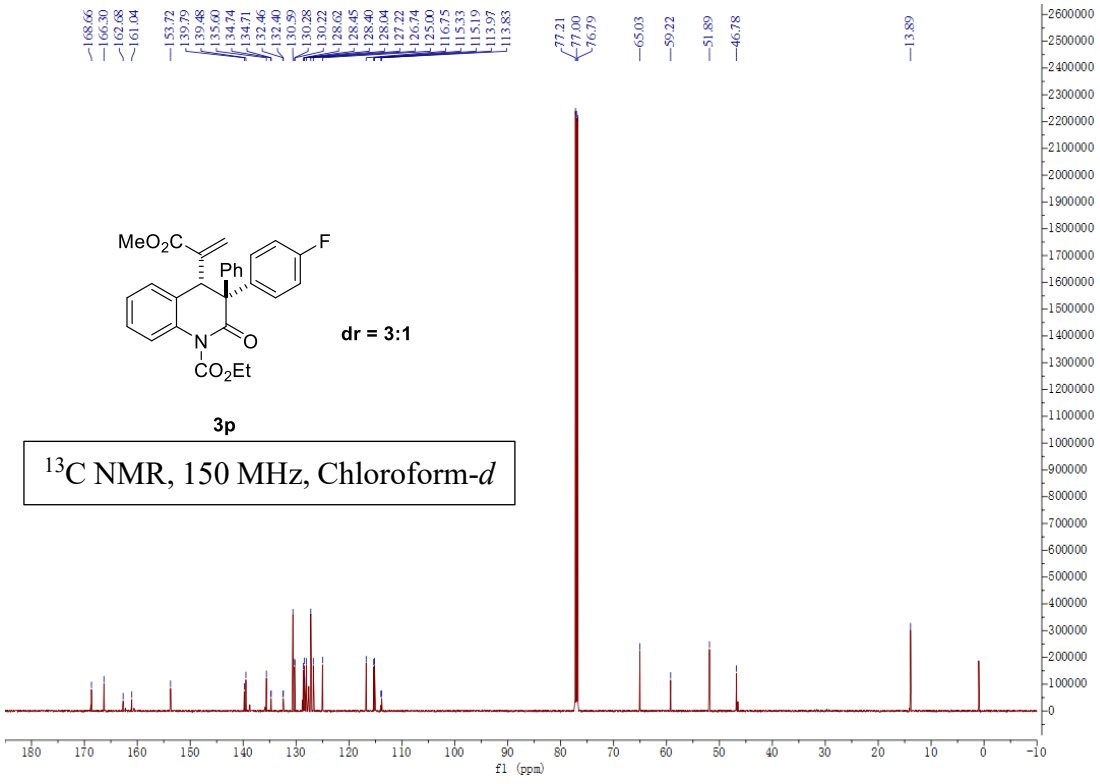

EtO2C
Ph
Ph
N
O
CO2Et
3n
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)

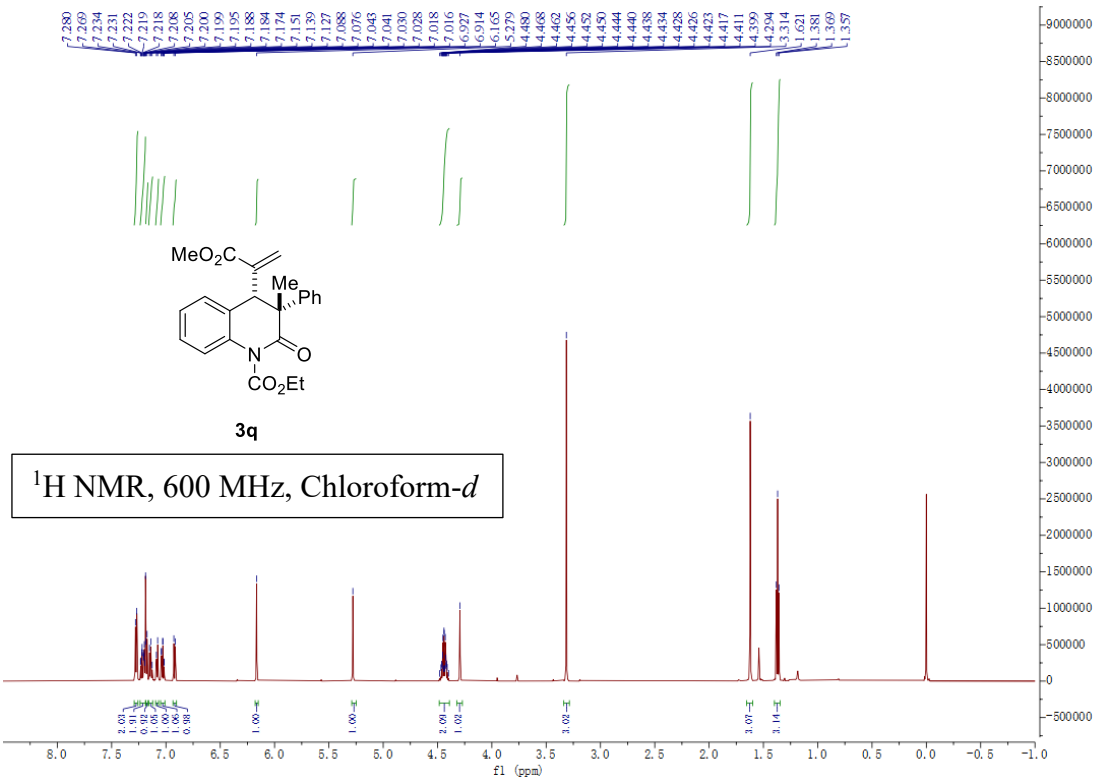

EtO2C
Ph
Ph
N
O
CO2Et
3n
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)


MeO2C
OMe
Ph
N
O
CO2Et
dr = 3:1
3o
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)


MeO2C
OMe
Ph
N
O
CO2Et
dr = 3:1
3o
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)

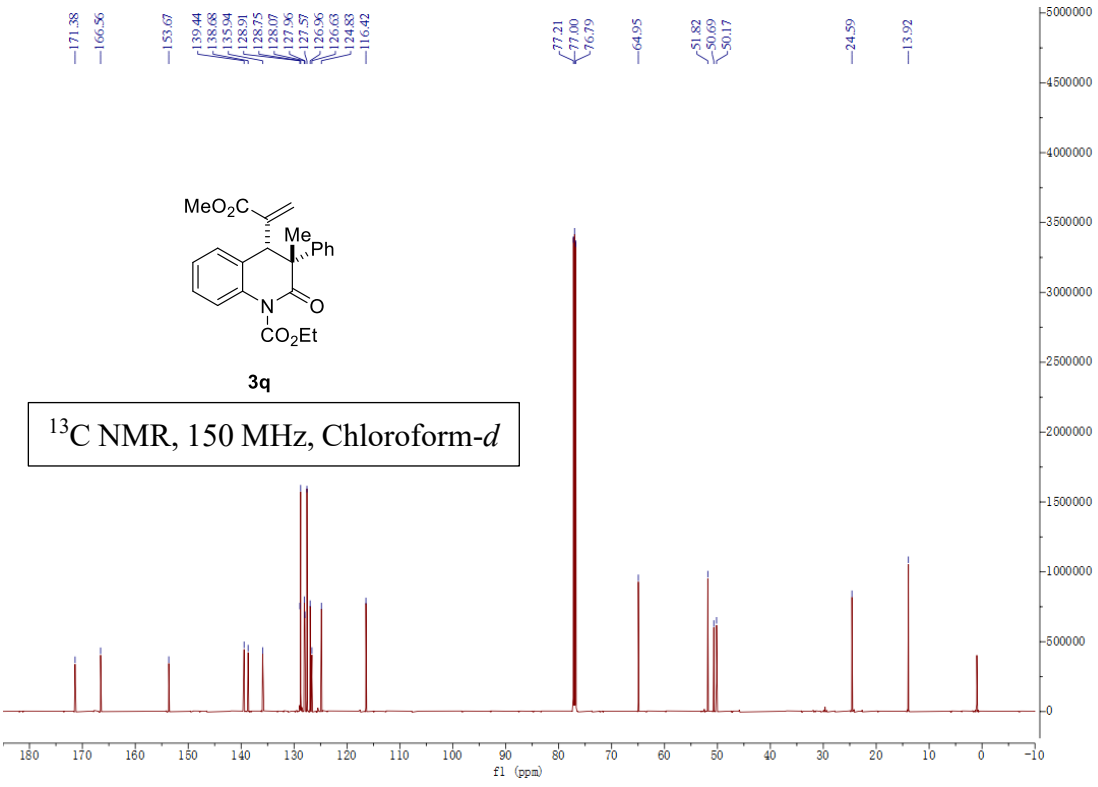

MeO2C
Ph
F
N
O
CO2Et
dr = 3:1
3p
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)


MeO2C
Ph
F
N
O
CO2Et
dr = 3:1
3p
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)



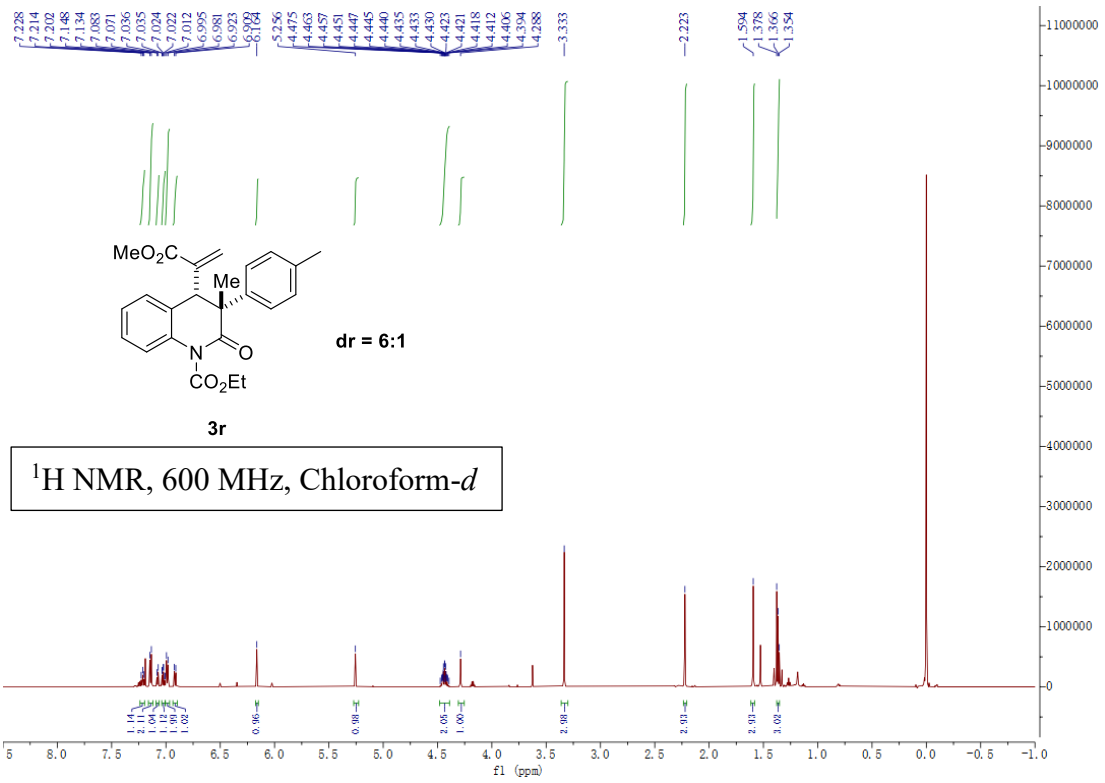
3q

^{1}H NMR, 600 MHz, Chloroform-*d*



3q

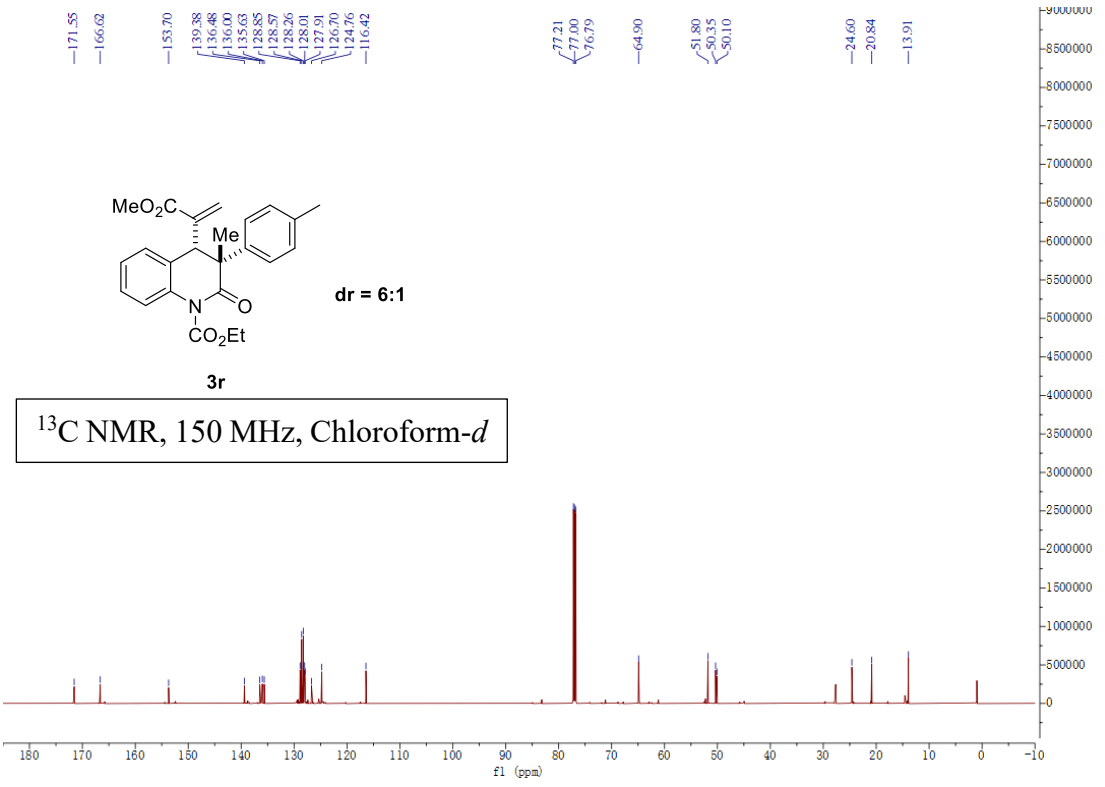
^{13}C NMR, 150 MHz, Chloroform-*d*



dr = 6:1

3r

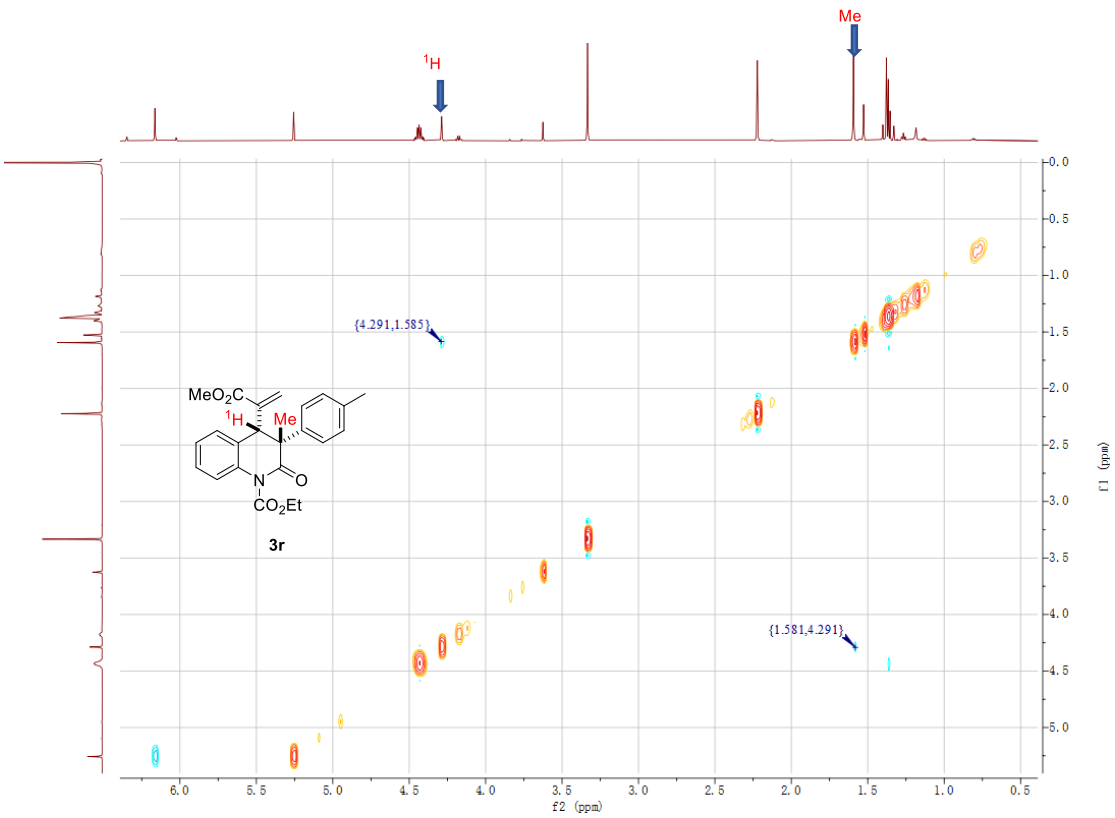
^{1}H NMR, 600 MHz, Chloroform-*d*

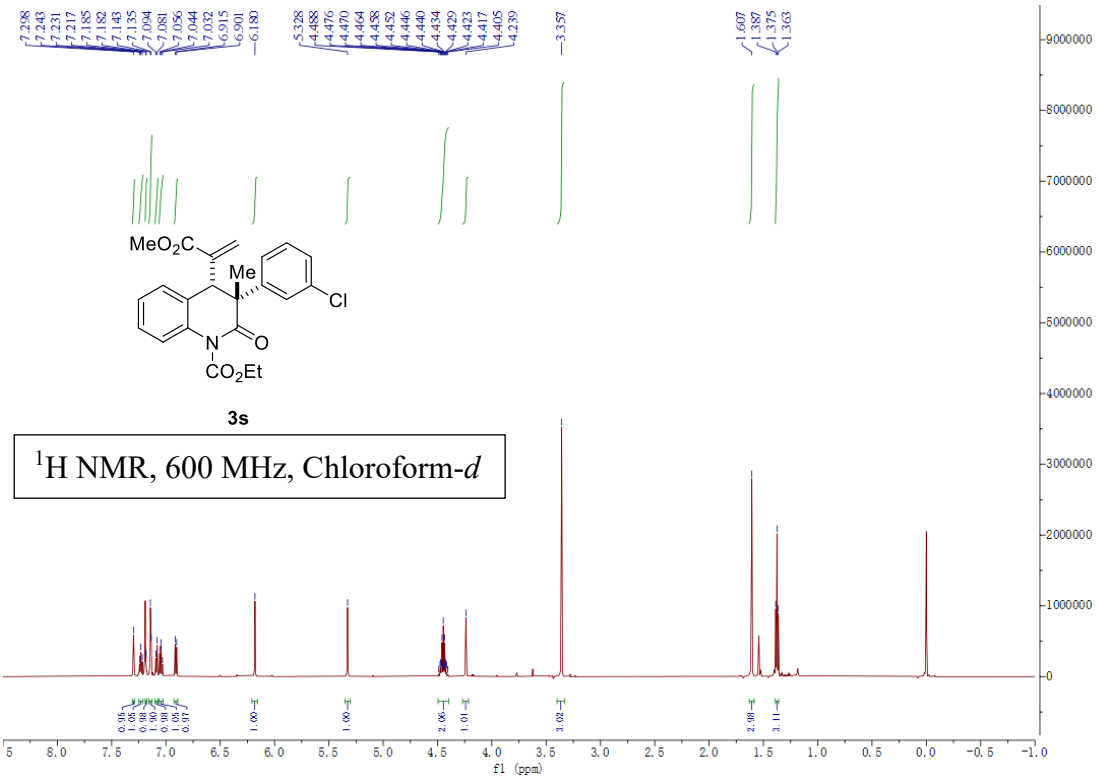


dr = 6:1

3r

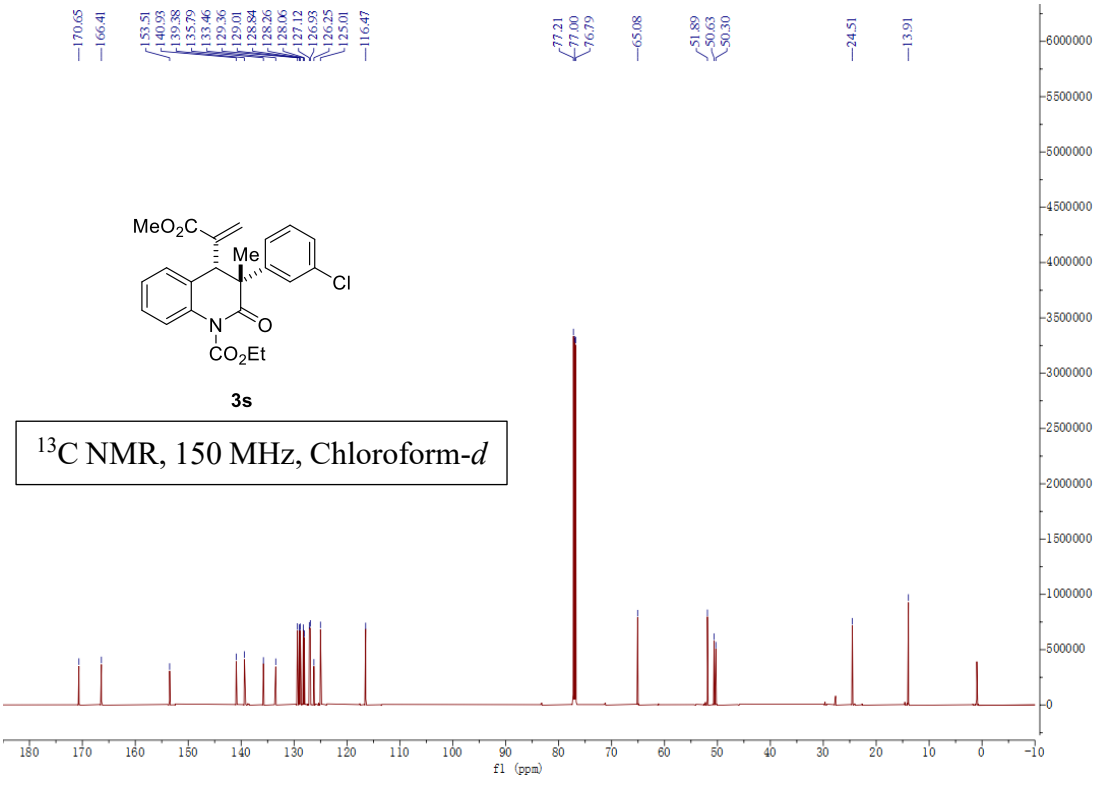
^{13}C NMR, 150 MHz, Chloroform-*d*


Me
1H
{4.291,1.585}
{1.581,4.291}
MeO2C
1H
Me
N
O
CO2Et
3r
f2 (ppm)
f1 (ppm)



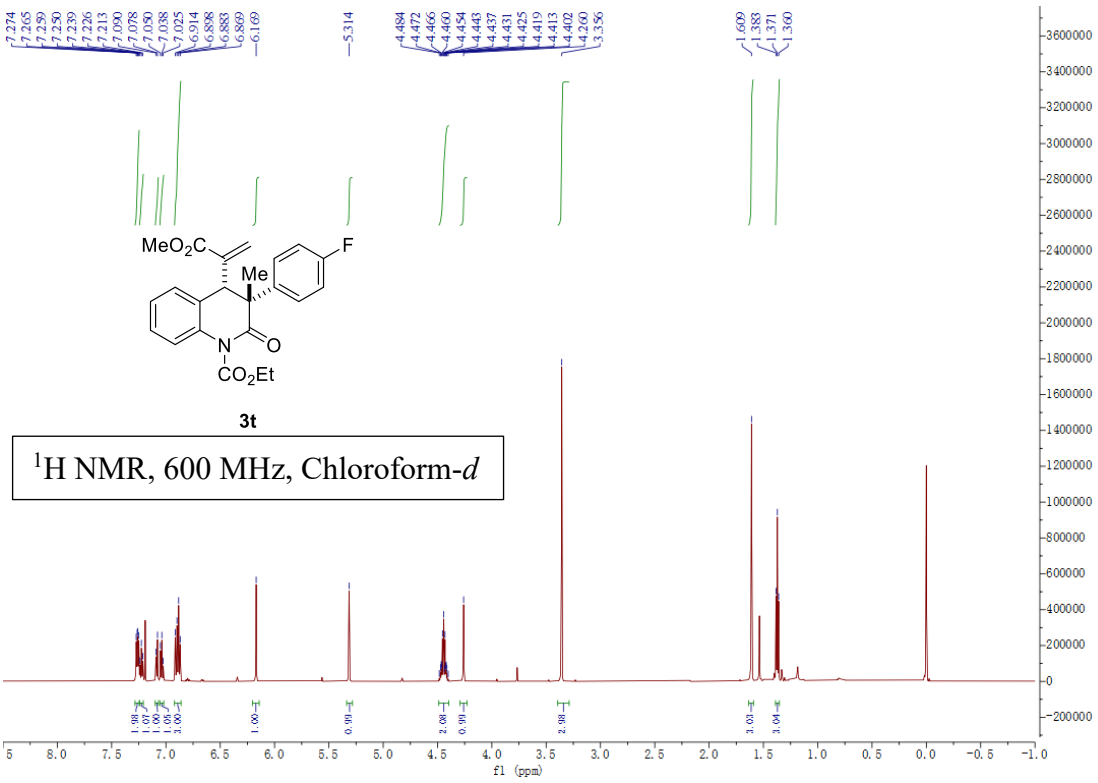
3s

^{1}H NMR, 600 MHz, Chloroform-*d*



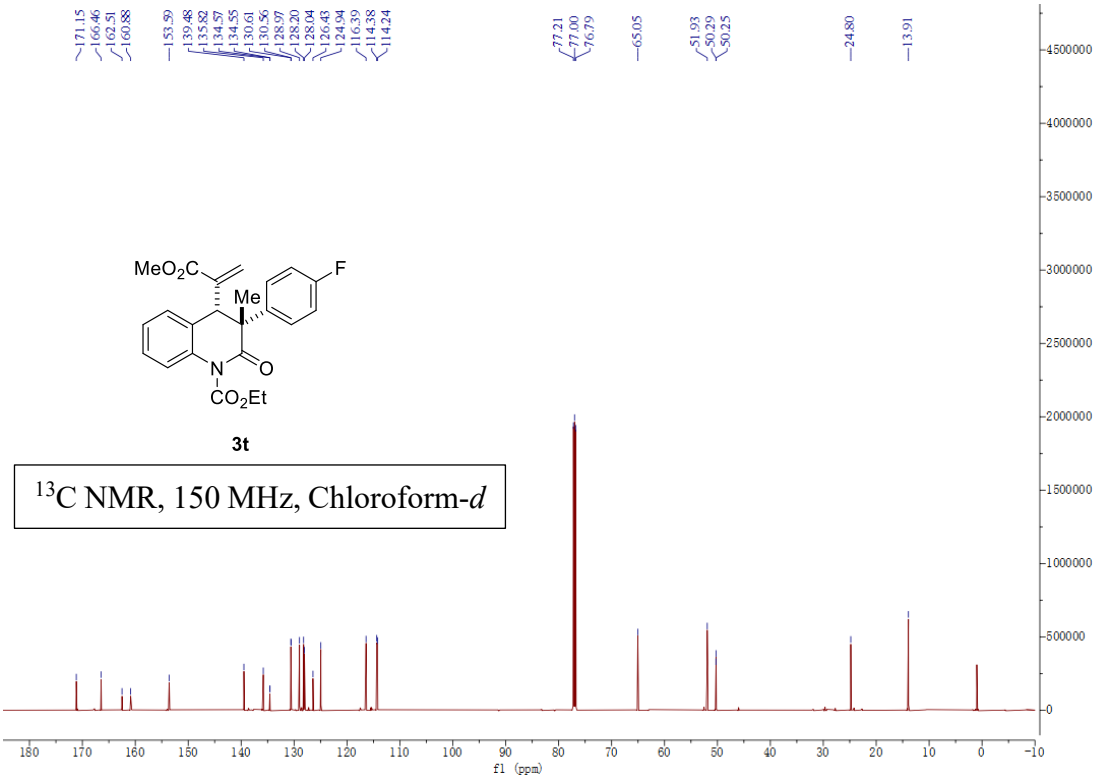
3s

^{13}C NMR, 150 MHz, Chloroform-*d*



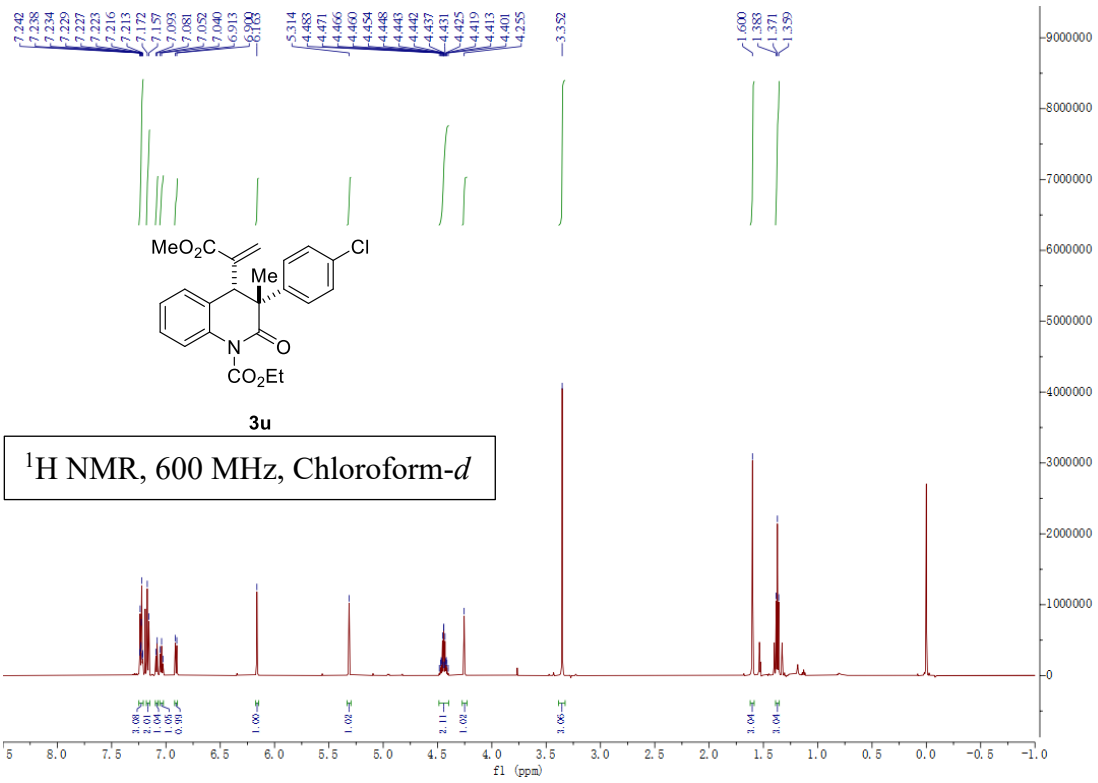
3t

^{1}H NMR, 600 MHz, Chloroform-*d*



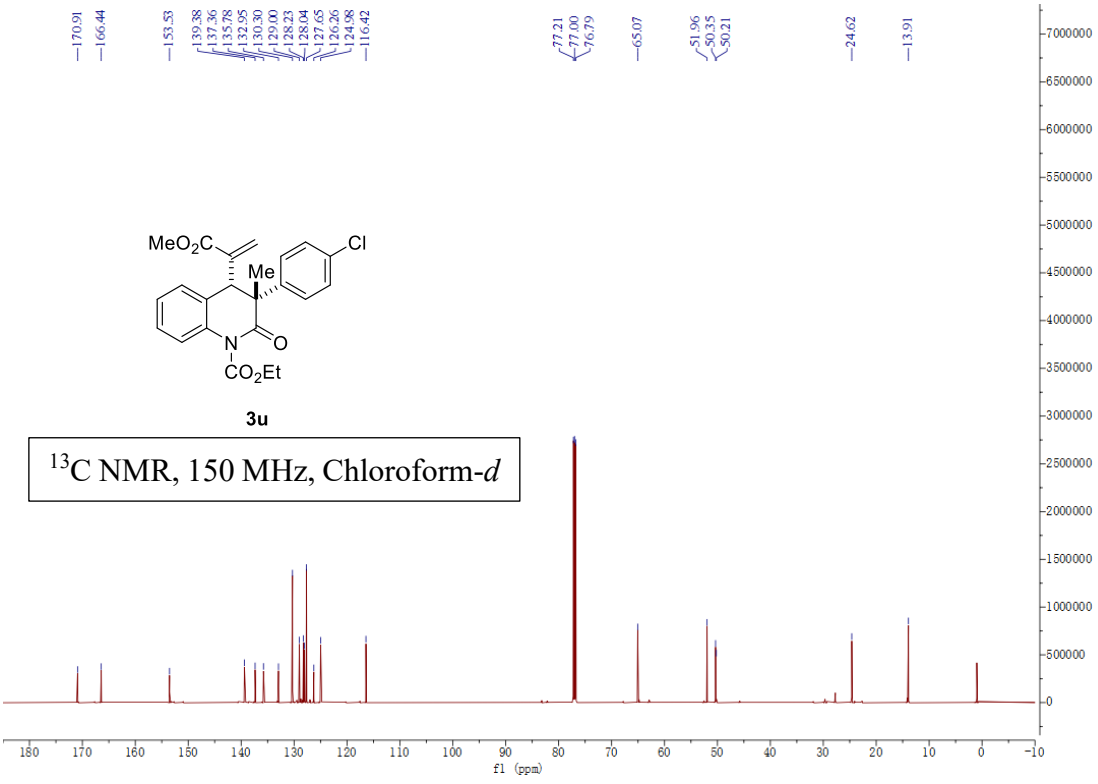
3t

^{13}C NMR, 150 MHz, Chloroform-*d*



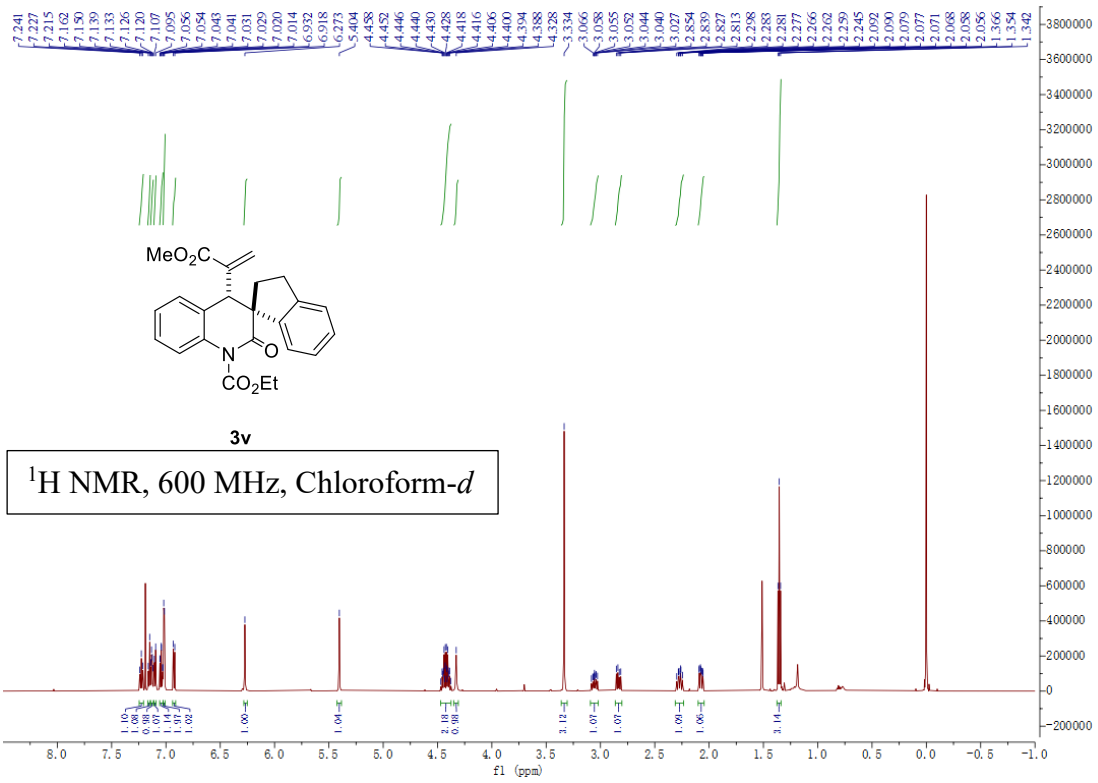
3u

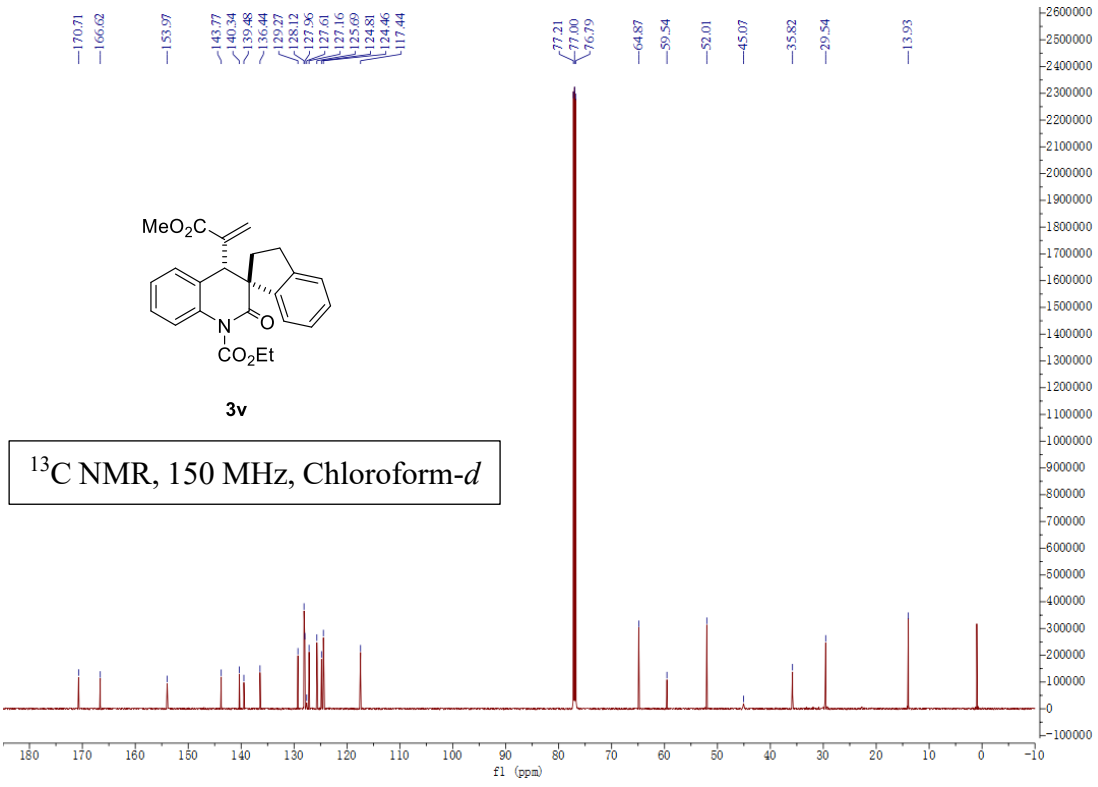
^{1}H NMR, 600 MHz, Chloroform-*d*

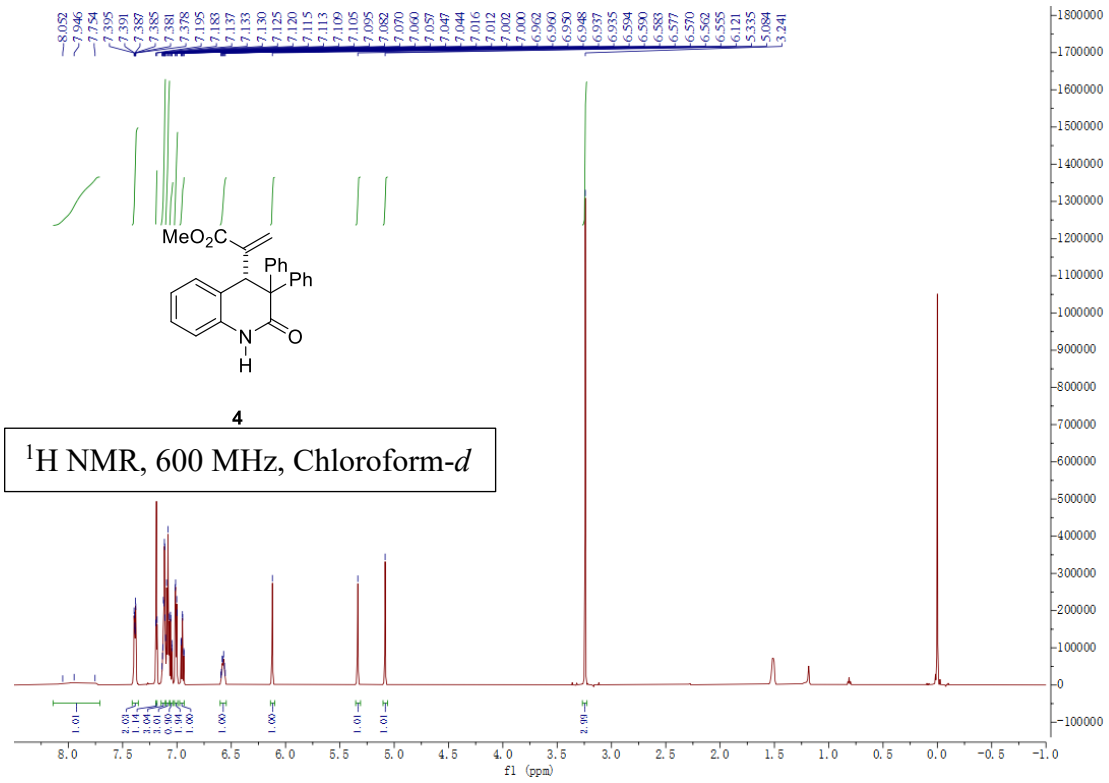


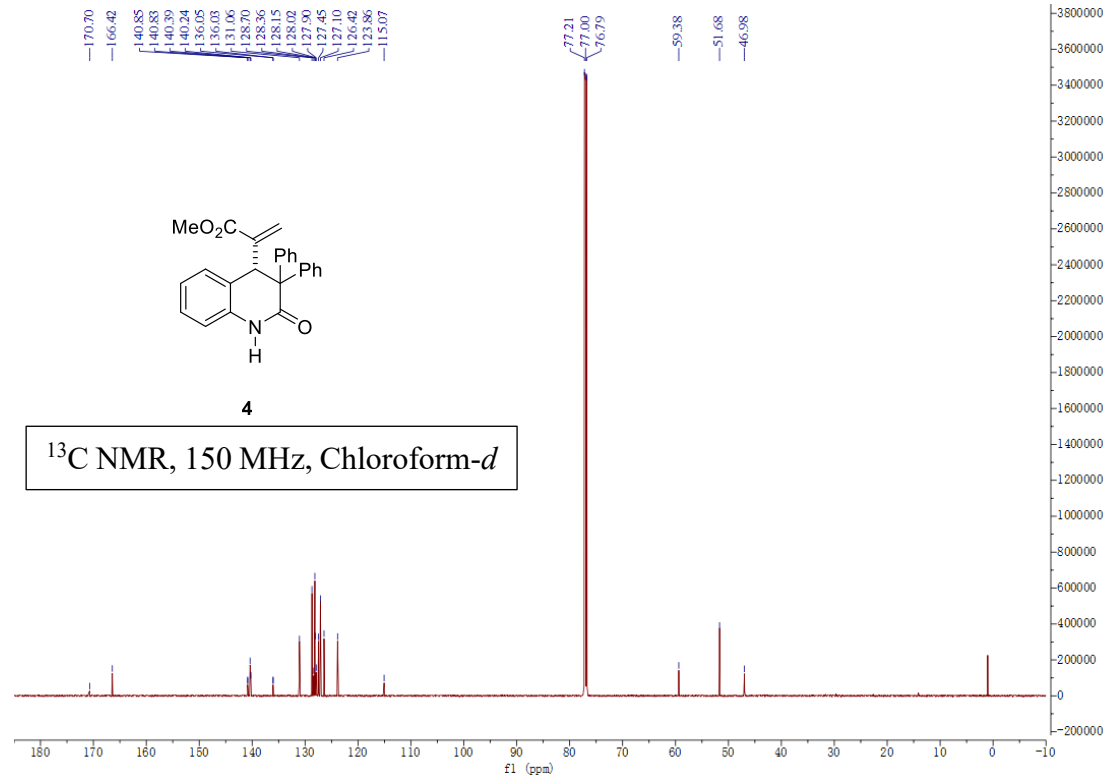
3u

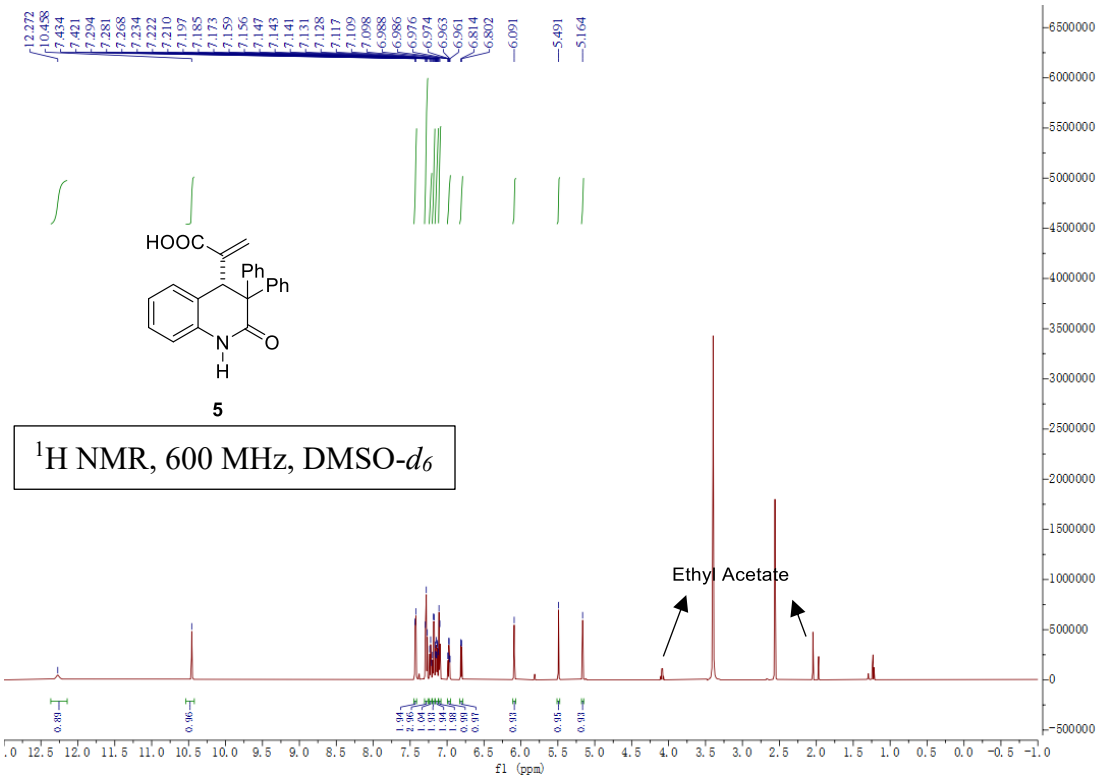
^{13}C NMR, 150 MHz, Chloroform-*d*


MeO2C
N
O
CO2Et
3v
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)


MeO2C
N
O
CO2Et
3v
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)

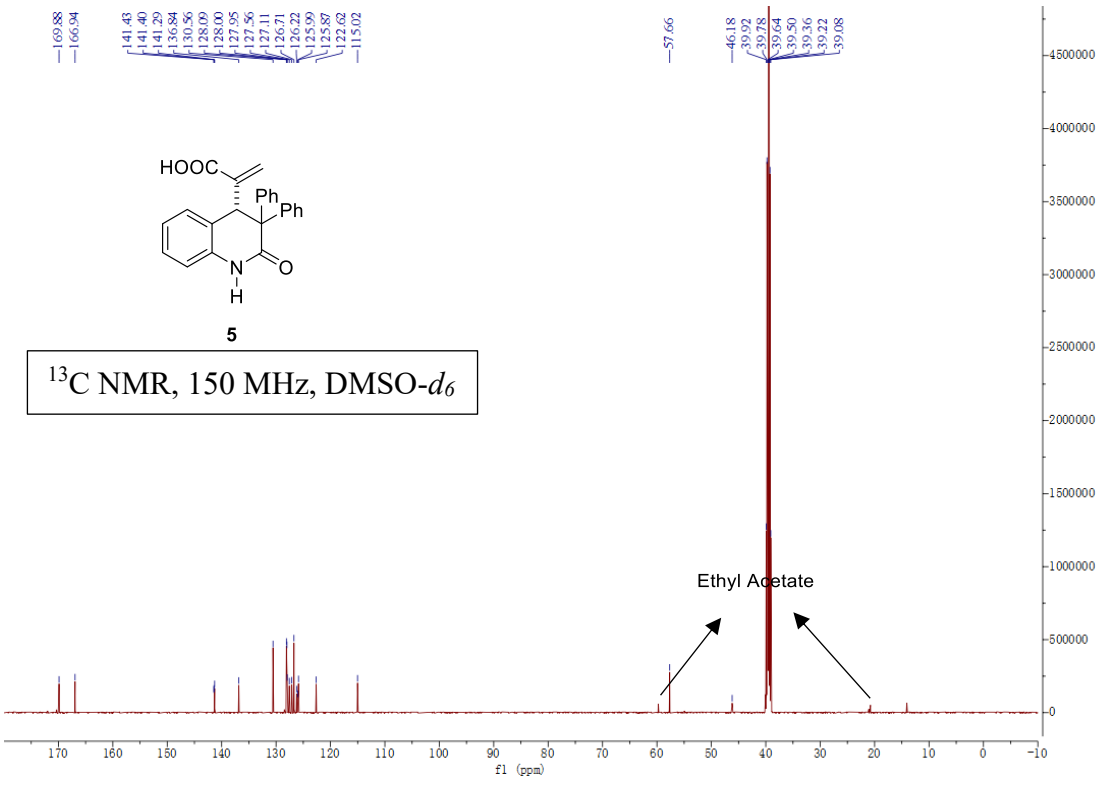

MeO2C
Ph
Ph
N
H
O
4
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)


MeO2C
Ph
Ph
N
H
O
4
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)



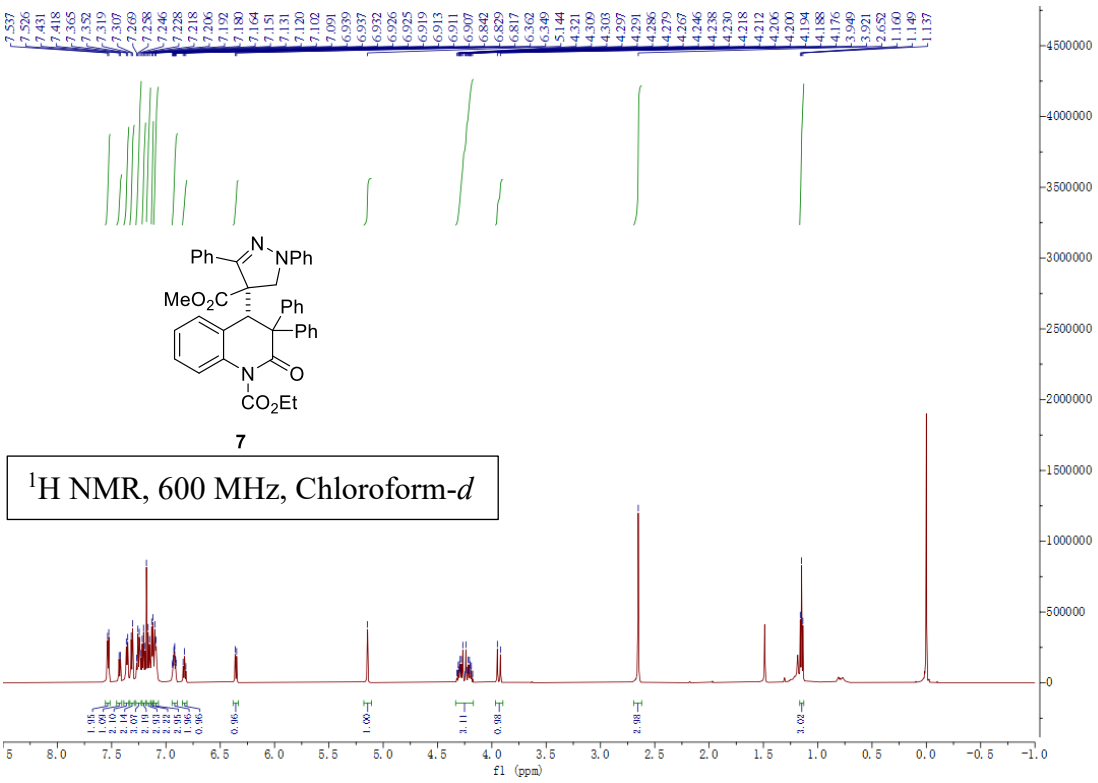
5

^{1}H NMR, 600 MHz, DMSO-*d*$_6$



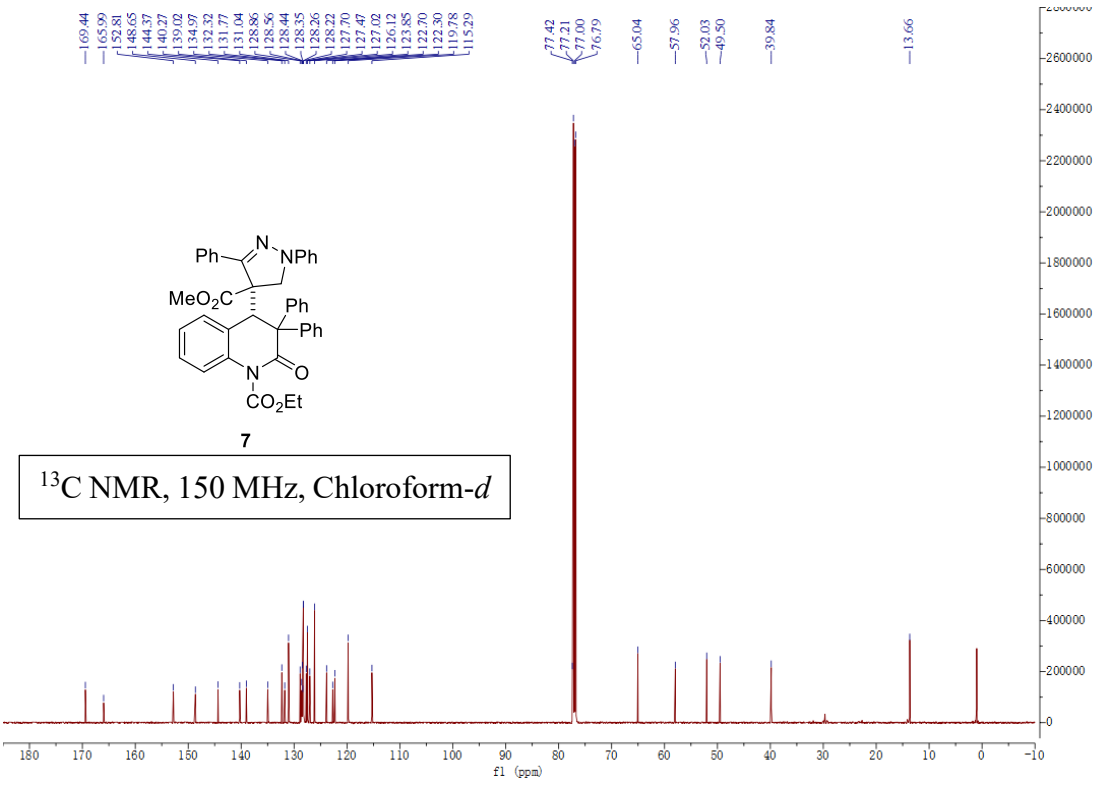
5

^{13}C NMR, 150 MHz, DMSO-*d*$_6$



7

^{1}H NMR, 600 MHz, Chloroform-*d*



7

^{13}C NMR, 150 MHz, Chloroform-*d*

8.References

[1] W. Cai, Y. Zhou, Y. He, K. Chen, C. Yu and Y. Huang, Designing and Accurately Developing a [6 + 2] Dipolar Cycloaddition for the Synthesis of Benzodiazocines, *Org. Lett.*, 2021, **23**, 5430-5434.

[2] J. R. Denton and H. M. L. Davies, Enantioselective Reactions of Donor/Acceptor Carbenoids Derived from α-Aryl-α-Diazoketones, *Org. Lett.*, 2009, **11**, 787-790.

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[4] H. Liu, S. Song, C.-Q. Wang, C. Feng and T.-P. Loh, Redox-Neutral Rhodium-Catalyzed [4+1] Annulation through Formal Dehydrogenative Vinylidene Insertion, *ChemSusChem*, 2017, **10**, 58-61.