Electronic Supplementary Information

P^{III}-Mediated Intramolecular Cyclopropanation and Metal-Free Synthesis of Cyclopropane-Fused Heterocycles

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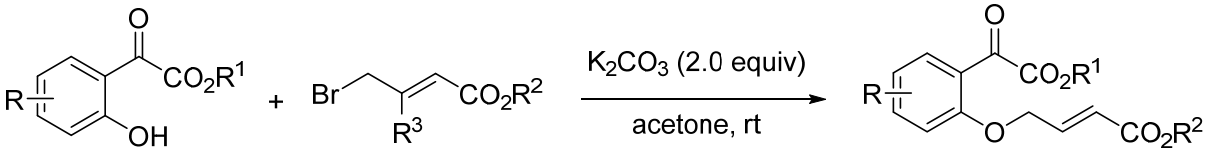
I. General Information

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. The solvents were purified by distillation or dried according to the conventional procedures. Other chemicals from commercial sources were used without further purification. Column chromatography was performed on silica gel (200-300 mesh) as stationary phase eluted with a mixture of petroleum ether (PE) (60-90 °C) and ethyl acetate (EA). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at ambient temperature in $CDCl_3$. Chemical shifts were reported in parts per million (ppm) with tetramethylsilane (TMS) used as the internal standard. HRMS spectra were acquired in the ESI mode with the mass analyzer of TOF. Chiral phosphines **P1**[1a] and **P2**[1b] were prepared according to the reported procedures.

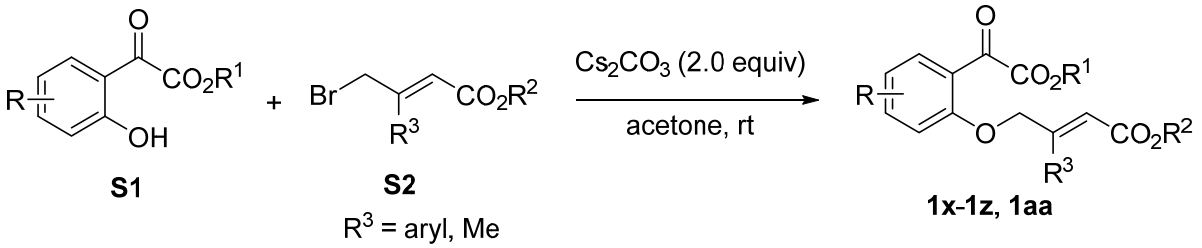
II. Preparation of Substrates 1, 3, and 5

1. Preparation of Substrates 1

General Procedure A:



General Procedure B:



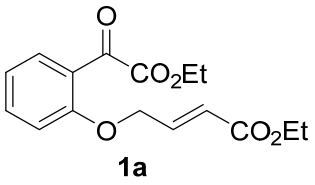
Starting materials **S1**[2] and **S2**[3] were prepared according to known literature procedures.

General procedure A for preparation of substrates 1a–1w, **1ab:** To a solution of **S1** (1.0 mmol) in acetone (10 mL) was added potassium carbonate (2.0 mmol, 2.0 equiv) and the bromide **S2** (1.1 mmol, 1.1 equiv). The resulting mixture was stirred at rt and monitored by TLC until **S1** was consumed. The reaction mixture was then filtered through a plug of celite and washed with acetone (10 mL × 3). The filtrate was concentrated under reduced pressure

and the crude product was purified by column chromatography with PE/EA (10:1, v/v) to afford pure substrate (**1a–1w**, **1ab**).

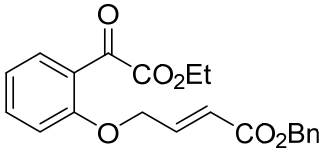
General procedure B for preparation of substrates 1x–1z, **1aa:** To a solution of **S1** (1.0 mmol) in acetone (15 mL) was added cesium carbonate (2.0 mmol, 2.0 equiv) and the bromide **S2** (1.1 mmol, 1.1 equiv). The resulting mixture was stirred at rt and monitored by TLC until **S1** was consumed. The reaction mixture was then filtered through a plug of celite and washed with acetone (10 mL × 3). The filtrate was concentrated under reduced pressure and the crude product was purified by column chromatography with PE/EA (10:1–5:1, v/v) to afford pure substrate (**1x–1z**, **1aa**).

Ethyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1a):[4] Following the general procedure A, the known compound **1a** was obtained as yellow oil (272.6 mg, 89% yield). R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (dd, J = 7.8, 1.8 Hz, 1H), 7.58 (ddd, J = 8.5, 7.4, 1.8 Hz, 1H), 7.15 – 7.09 (m, 1H), 7.03 (dt, J = 15.8, 4.3 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.15 (dt, J = 15.8, 2.0 Hz, 1H), 4.78 (dd, J = 4.4, 2.0 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 4.22 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.5, 165.7, 165.0, 158.6, 140.7, 136.1, 131.2, 123.4, 123.0, 122.0, 112.9, 67.6, 62.1, 60.8, 14.2, 14.0; HRMS **(**ESI**):** *m/z* calcd for $C_{16}H_{22}NO_6$ $[M+NH_4]^+$ 324.1447, found 324.1441.



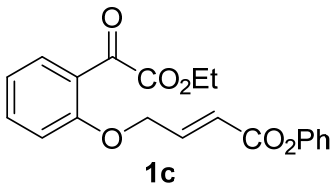
1a

Benzyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1b): Following the general procedure A, the substrate **1b** was obtained as yellow oil (291.5 mg, 79% yield). R_f = 0.20 (PE:EA 8:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.87 (dd, J = 7.8, 1.8 Hz, 1H), 7.56 (ddd, J = 8.9, 7.4, 1.8 Hz, 1H), 7.40 – 7.31 (m, 5H), 7.13 – 7.02 (m, 2H), 6.92 (d, J = 8.4 Hz, 1H), 6.19 (d, J = 15.8 Hz, 1H), 5.20 (s, 2H), 4.76 (dd, J = 4.3, 2.0 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.5, 165.5, 165.0, 158.6, 141.5, 136.2, 135.7, 131.2, 128.6, 128.4, 128.3, 123.4, 122.6, 122.1, 112.9, 67.6, 66.6, 62.1, 14.0; HRMS (ESI): *m/z* calcd for $C_{21}H_{21}O_6$ $[M+H]^+$ 369.1333, found 369.1335.



1b

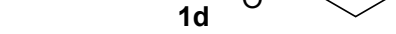
Phenyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1c): Following the general procedure A, the substrate **1c** was obtained as yellow oil (257.8 mg, 73% yield). R_f = 0.35



1c

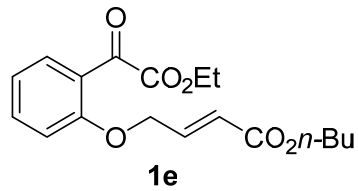
(PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (dd, J = 7.8, 1.8 Hz, 1H), 7.59 (ddd, J = 8.5, 7.4, 1.8 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.26 – 7.19 (m, 2H), 7.15 – 7.10 (m, 3H), 6.97 (d, J = 8.4 Hz, 1H), 6.36 (dt, J = 15.8, 2.0 Hz, 1H), 4.84 (dd, J = 4.2, 2.0 Hz, 2H), 4.39 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.5, 165.0, 164.1, 158.5, 150.5, 143.1, 136.2, 131.3, 129.5, 126.0, 123.4, 122.2, 122.0, 121.5, 113.0, 67.6, 62.2, 14.1; HRMS (ESI): *m/z* calcd for $C_{20}H_{19}O_6$ $[M+H]^+$ 355.1176, found 355.1181.

Cyclohexyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1d): Following the general procedure A, the substrate **1d** was obtained as yellow oil (305.2 mg, 85% yield). R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (dd, J = 7.8, 1.7 Hz, 1H), 7.62 – 7.53 (m, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.01 (dt, J = 15.8, 4.4 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.13 (dt, J = 15.8, 1.7 Hz, 1H), 4.88 – 4.81 (m, 1H), 4.77 (dd, J = 4.4, 1.9 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 1.92 – 1.85 (m, 2H), 1.74 (m, 2H), 1.59 – 1.52 (m, 1H), 1.49 – 1.40 (m, 3H), 1.39 – 1.35 (t, J = 7.2 Hz, 3H), 1.33 – 1.14 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.5, 165.1, 165.0, 158.7, 140.4, 136.2, 131.1, 123.5, 123.3, 122.0, 112.9, 73.1, 67.7, 62.1, 31.6, 25.3, 23.8, 14.0; HRMS (ESI): *m/z* calcd for $C_{20}H_{25}O_6$ $[M+H]^+$ 361.1646, found 361.1642.



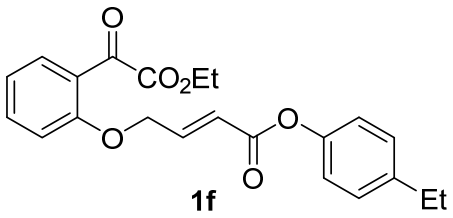
1d

Butyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1e): Following the general procedure A, the substrate **1e** was obtained as yellow oil (296.7 mg, 89% yield). R_f = 0.28 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (dd, J = 7.8, 1.7 Hz, 1H), 7.58 (ddd, J = 8.9, 7.5, 1.8 Hz, 1H), 7.13 (t, J = 8.2, 1H), 7.04 (dt, J = 15.8, 4.4 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.16 (dt, J = 15.8, 1.9 Hz, 1H), 4.79 (dd, J = 4.3, 1.9 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 4.18 (t, J = 6.7 Hz, 2H), 1.70 – 1.61 (m, 2H), 1.46-1.40 (m, 2H), 1.38 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.5, 165.8, 165.0, 158.6, 140.7, 136.1, 131.2, 123.4, 123.0, 122.0, 112.9, 67.6, 64.7, 62.1, 30.6, 19.1, 14.0, 13.7; HRMS (ESI): *m/z* calcd for $C_{18}H_{26}NO_6$ $[M+NH_4]^+$ 352.1760, found 352.1757.



1e

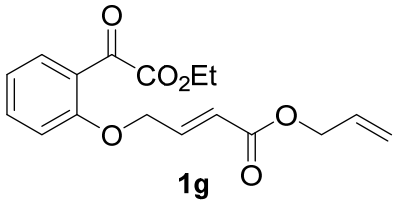
4-Ethylphenyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1f): Following the general procedure A, the substrate **1f** was obtained as yellow oil (320.9 mg, 84% yield). R_f =



1f

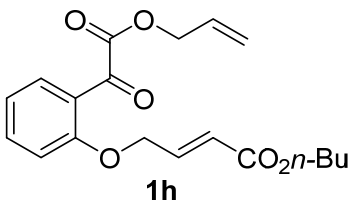
0.40 (PE:EA 8:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.90 (dd, J = 7.8, 1.8 Hz, 1H), 7.60 (ddd, J = 8.6, 7.4, 1.8 Hz, 1H), 7.24 – 7.12 (m, 4H), 7.05 – 7.00 (m, 2H), 6.97 (d, J = 8.5 Hz, 1H), 6.36 (dt, J = 15.8, 2.0 Hz, 1H), 4.84 (dd, J = 4.2, 2.0 Hz, 2H), 4.39 (q, J = 7.2 Hz, 2H), 2.65 (q, J = 7.6 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.4, 165.0, 164.3, 158.5, 148.4, 142.8, 142.0, 136.1, 131.3, 128.8, 123.5, 122.2, 122.1, 121.1, 112.9, 67.6, 62.2, 28.3, 15.6, 14.1; HRMS (ESI): *m/z* calcd for $C_{22}H_{23}O_6$ $[M+H]^+$ 383.1489, found 383.1494.

Allyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1g): Following the general procedure A, the substrate **1g** was obtained as colorless oil (228.5 mg, 72% yield). R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (dd, J = 7.7, 1.6 Hz, 1H), 7.61 – 7.51 (m, 1H), 7.14 – 6.99 (m, 2H), 6.92 (d, J = 8.4 Hz, 1H), 6.21 – 6.10 (m, 1H), 5.96 – 5.88 (m, 1H), 5.29 (ddd, J = 13.8, 11.1, 0.9 Hz, 2H), 4.77 (dd, J = 4.2, 1.9 Hz, 2H), 4.65 (d, J = 5.7 Hz, 2H), 4.34 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.5, 165.3, 165.0, 158.6, 141.3, 136.1, 131.9, 131.2, 123.4, 122.6, 122.1, 118.6, 112.9, 67.6, 65.4, 62.1, 14.0; HRMS (ESI): *m/z* calcd for $C_{17}H_{19}O_6$ $[M+H]^+$ 319.1176, found 319.1174.



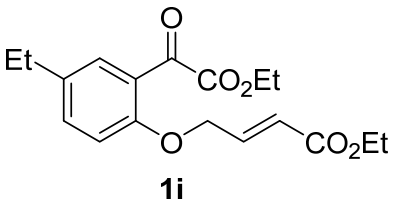
1g

Butyl (*E*)-4-(2-(2-(allyloxy)-2-oxoacetyl)phenoxy)but-2-enoate (1h): Following the general procedure A, the substrate **1h** was obtained as colorless oil (238.8 mg, 69% yield). R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (dd, J = 7.8, 1.8 Hz, 1H), 7.55 (m, 1H), 7.12 – 7.06 (m, 1H), 7.02 – 6.96 (m, 1H), 6.91 (d, J = 8.3 Hz, 1H), 6.11 (dt, J = 15.8, 2.0 Hz, 1H), 5.98 – 5.90 (m, 1H), 5.38 (dd, J = 17.2, 1.4 Hz, 1H), 5.27 (dd, J = 10.4, 1.2 Hz, 1H), 4.75 (m, 4H), 4.14 (t, J = 6.7 Hz, 2H), 1.65 – 1.60 (m, 2H), 1.36 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.1, 165.8, 164.6, 158.7, 140.7, 136.2, 131.2, 131.0, 123.1, 122.0, 119.6, 113.0, 67.7, 66.4, 64.7, 30.6, 19.1, 13.7; HRMS (ESI): *m/z* calcd for $C_{19}H_{23}O_6$ $[M+H]^+$ 347.1489, found 347.1492.



1h

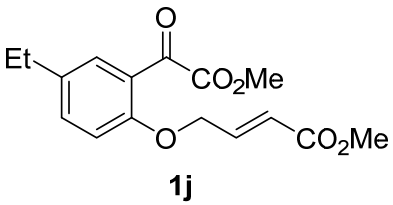
Ethyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)-4-ethylphenoxy)but-2-enoate (1i): Following the general procedure A, the substrate **1i** was obtained as yellow oil (284.5 mg, 81% yield). R_f =



1i

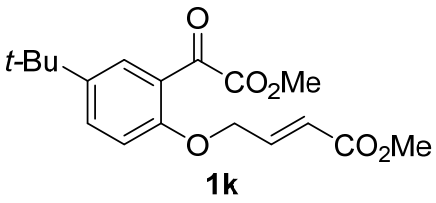
0.30 (PE:EA 8:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (d, J = 2.3 Hz, 1H), 7.40 (dd, J = 8.5, 2.3 Hz, 1H), 7.02 (dt, J = 15.8, 4.3 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 6.14 (dt, J = 15.8, 2.0 Hz, 1H), 4.75 (dd, J = 4.3, 2.0 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 2.64 (q, J = 7.6 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.7, 165.8, 165.2, 156.9, 141.1, 138.0, 135.8, 130.0, 123.1, 122.8, 113.0, 67.8, 62.0, 60.7, 27.8, 15.5, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{18}H_{26}NO_6$ $[M+NH_4]^+$ 352.1755, found 352.1757.

Methyl (*E*)-4-(4-ethyl-2-(2-methoxy-2-oxoacetyl)phenoxy)but-2-enoate (1j): Following the general procedure A, the substrate **1j** was obtained as yellow oil (238.0 mg, 78% yield). R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, J = 2.3 Hz, 1H), 7.40 (dd, J = 8.5, 2.3 Hz, 1H), 7.03 (dt, J = 15.8, 4.3 Hz, 1H), 6.89 (d, J = 8.6 Hz, 1H), 6.16 (dt, J = 15.8, 1.9 Hz, 1H), 4.75 (dd, J = 4.3, 2.0 Hz, 2H), 3.89 (s, 3H), 3.76 (s, 3H), 2.63 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.4, 166.2, 165.5, 156.8, 141.3, 137.9, 135.9, 129.8, 122.9, 122.3, 113.1, 67.7, 52.5, 51.8, 27.7, 15.4; HRMS (ESI): *m/z* calcd for $C_{16}H_{19}O_6$ $[M+H]^+$ 307.1176, found 307.1179.



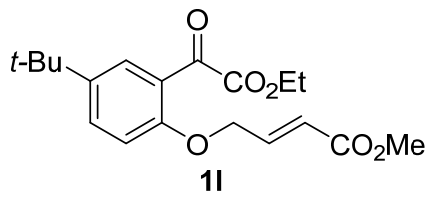
1j

Methyl (*E*)-4-(4-(*tert*-butyl)-2-(2-methoxy-2-oxoacetyl)phenoxy)but-2-enoate (1k): Following the general procedure A, the substrate **1k** was obtained as yellow oil (297.3 mg, 89% yield). R_f = 0.28 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (d, J = 2.4 Hz, 1H), 7.61 (dd, J = 8.8, 2.6 Hz, 1H), 7.04 (dt, J = 15.8, 4.3 Hz, 1H), 6.88 (d, J = 8.8 Hz, 1H), 6.16 (d, J = 15.8 Hz, 1H), 4.76 (dd, J = 4.0, 1.8 Hz, 2H), 3.89 (s, 3H), 3.77 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.5, 166.2, 165.6, 156.6, 145.1, 141.3, 133.6, 127.6, 122.6, 122.4, 112.7, 67.7, 52.6, 51.9, 34.4, 31.2; HRMS (ESI): *m/z* calcd for $C_{18}H_{23}O_6$ $[M+H]^+$ 335.1489, found 335.1489.



1k

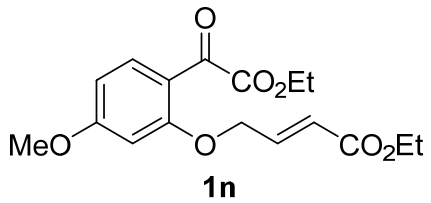
Methyl (*E*)-4-(4-(*tert*-butyl)-2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1l): Following the general procedure A, the substrate **1l** was obtained as yellow oil (275.1 mg, 79% yield). R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (d, J =



1l

2.6 Hz, 1H), 7.60 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.04 (d, *J* = 15.8 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.16 (dt, *J* = 15.8, 2.0 Hz, 1H), 4.77 (dd, *J* = 4.3, 2.0 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.7, 166.2, 165.3, 156.6, 145.0, 141.4, 133.5, 127.6, 122.6, 122.4, 112.7, 67.6, 62.0, 51.8, 34.3, 31.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{19}H_{25}O_6$ $[M+H]^+$ 349.1646, found 349.1646.

Ethyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)-4-methoxyphenoxy)but-2-enoate (1m):[4] Following the general procedure A, the known compound **1m** was obtained as yellow oil (241.3 mg, 72% yield). R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 (d, *J* = 3.2 Hz, 1H), 7.14 (dd, *J* = 9.1, 3.2 Hz, 1H), 7.02 (d, *J* = 15.8 Hz, 1H), 6.90 (d, *J* = 9.1 Hz, 1H), 6.13 (d, *J* = 15.8, 2.0 Hz, 1H), 4.72 (dd, *J* = 4.3, 2.0 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.2, 165.7, 165.1, 154.5, 153.3, 141.2, 123.7, 123.6, 122.8, 115.1, 113.1, 68.5, 62.1, 60.7, 55.9, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{17}H_{21}O_7$ $[M+H]^+$ 337.1282, found 337.1280.

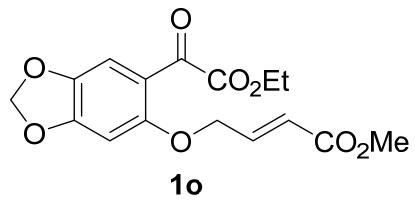


1m

Ethyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)-5-methoxyphenoxy)but-2-enoate (1n): Following the general procedure A, the substrate **1n** was obtained as yellow oil (228.0 mg, 68% yield). R_f = 0.30 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81 (d, *J* = 8.8 Hz, 1H), 6.94 (dt, *J* = 15.8, 4.4 Hz, 1H), 6.55 (dd, *J* = 8.8, 1.8 Hz, 1H), 6.33 (d, *J* = 1.9 Hz, 1H), 6.08 (d, *J* = 15.8 Hz, 1H), 4.68 (dd, *J* = 4.2, 1.4 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 184.9, 166.6, 165.7, 165.6, 160.6, 140.6, 133.1, 123.1, 116.1, 107.3, 99.1, 67.5, 61.8, 60.7, 55.8, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{17}H_{21}O_7$ $[M+H]^+$ 337.1282, found 337.1284.

1n

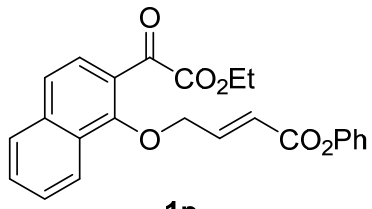
Methyl (*E*)-4-((6-(2-ethoxy-2-oxoacetyl)benzo[*d*][1,3]dioxol-5-yl)oxy)but-2-enoate (1o): Following the general procedure A, the substrate **1o** was obtained as yellow oil (252.1 mg, 75% yield). R_f = 0.30 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30 (s, 1H), 7.00 (dt, 15.8, 4.4 Hz, 1H), 6.48 (s, 1H), 6.14



1o

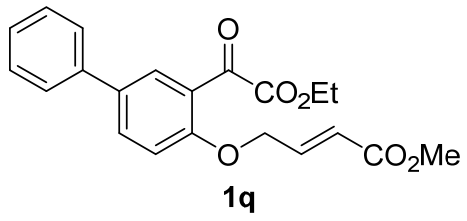
(d, *J* = 15.8 Hz, 1H), 6.04 (s, 2H), 4.71 (dd, *J* = 4.3, 1.8 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 184.6, 166.0, 165.6, 157.2, 154.9, 143.1, 141.0, 122.7, 116.1, 108.1, 102.7, 95.6, 68.7, 61.8, 51.8, 13.9; HRMS (ESI): m/z calcd for $C_{16}H_{17}O_8$ $[M+H]^+$ 337.0918, found 337.0917.

Phenyl (*E*)-4-((2-(2-ethoxy-2-oxoacetyl)naphthalen-1-yl)oxy)but-2-enoate (1p): Following the general procedure A, the substrate **1p** was obtained as yellow oil (330.5 mg, 82% yield). R_f = 0.28 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.06 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.75 – 7.55 (m, 3H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.33 (dt, *J* = 15.7, 3.7 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.64 (dt, *J* = 15.6, 1.9 Hz, 1H), 4.81 (dd, *J* = 3.5, 2.2 Hz, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.7, 165.6, 164.3, 158.3, 150.6, 144.0, 138.4, 129.9, 129.5, 128.8, 127.5, 126.9, 126.0, 125.7, 124.4, 123.0, 122.9, 121.6, 121.0, 75.1, 62.4, 14.1; HRMS (ESI): *m/z* calcd for $C_{24}H_{24}NO_6$ $[M+NH_4]^+$ 422.1598, found 422.1595.



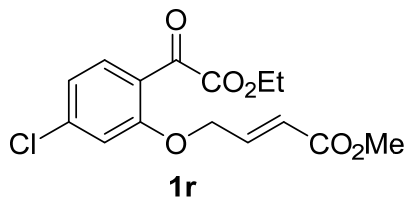
1p

Methyl (*E*)-4-((3-(2-ethoxy-2-oxoacetyl)-[1,1'-biphenyl]-4-yl)oxy)but-2-enoate (1q): Following the general procedure A, the substrate **1q** was obtained as colorless oil (264.3 mg, 72% yield). R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.10 (d, *J* = 2.4 Hz, 1H), 7.79 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.06 (dt, 15.8, 4.3 Hz, 1H), 7.01 (d, J = 8.7 Hz, 1H), 6.19 (d, *J* = 15.8 Hz, 1H), 4.82 (dd, *J* = 4.3, 2.0 Hz, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.5, 166.2, 165.0, 157.9, 141.0, 139.1, 135.3, 134.6, 129.5, 129.0, 127.6, 126.8, 123.6, 122.6, 113.4, 67.7, 62.2, 51.9, 14.0; HRMS (ESI): m/z calcd for $C_{21}H_{21}O_6$ $[M+H]^+$ 369.1333, found 369.1331.



1q

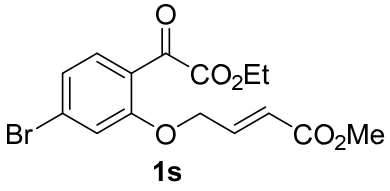
Methyl (*E*)-4-(5-chloro-2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1r): Following the general procedure A, the substrate **1r** was obtained as yellow oil (286.9 mg, 88% yield). R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.82 (d, *J* = 8.4 Hz, 1H), 7.11 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.02 (dt, *J* = 15.8, 4.4 Hz, 1H), 6.94 (d, *J* = 1.7 Hz, 1H), 6.16 (dt, *J* = 15.8, 1.9 Hz, 1H), 4.78 (dd, *J* = 4.3, 1.9 Hz,



1r

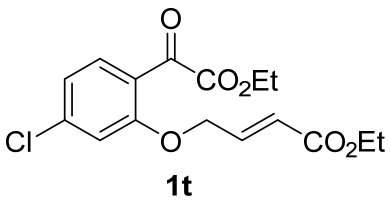
2H), 4.35 (q, J = 7.2 Hz, 2H), 3.78 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.3, 165.9, 164.6, 158.8, 142.2, 140.2, 132.2, 122.9, 122.6, 121.9, 113.6, 67.9, 62.2, 51.9, 13.9; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}ClO_6$ $[M+H]^+$ 327.0630, found 327.0632.

Methyl (*E*)-4-(5-bromo-2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1s): Following the general procedure A, the substrate **1s** was obtained as yellow oil (300.7 mg, 81% yield). R_f = 0.30 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (d, J = 8.3 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.12 (s, 1H), 7.01 (dt, J = 15.8, 4.3 Hz, 1H), 6.16 (d, J = 15.8 Hz, 1H), 4.78 (dd, J = 4.1, 1.6 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 3.77 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.5, 165.9, 164.6, 158.6, 140.3, 132.2, 130.7, 125.5, 122.8, 122.3, 116.5, 67.9, 62.2, 51.9, 13.9; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}BrO_6$ $[M+H]^+$ 371.0125, found 371.0123.



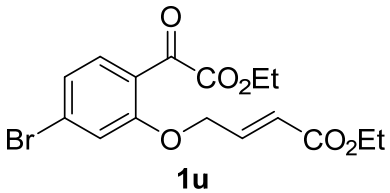
1s

Ethyl (*E*)-4-(5-chloro-2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1t):[4] Following the general procedure A, the known compound **1t** was obtained as yellow oil (285.7 mg, 84% yield). R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.82 (d, J = 8.4 Hz, 1H), 7.11 (dd, J = 8.4, 1.7 Hz, 1H), 7.01 (dt, J = 15.8, 4.4 Hz, 1H), 6.94 (d, J = 1.6 Hz, 1H), 6.14 (dt, J = 15.8, 1.8 Hz, 1H), 4.77 (dd, J = 4.4, 1.9 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.3, 165.5, 164.6, 158.9, 142.2, 139.9, 132.2, 123.4, 122.5, 121.9, 113.6, 67.9, 62.2, 60.8, 14.2, 14.0; HRMS (ESI): m/z calcd for $C_{16}H_{18}ClO_6$ $[M+H]^+$ 341.0786, found 341.0787.



1t

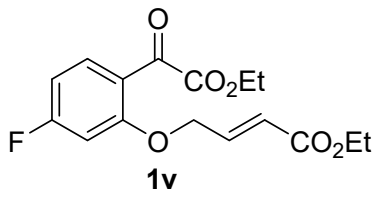
Ethyl (*E*)-4-(5-bromo-2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1u): Following the general procedure A, the substrate **1u** was obtained as colorless oil (298.7 mg, 78% yield). R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74 (dd, J = 8.3, 1.8 Hz, 1H), 7.32 – 7.23 (m, 1H), 7.12 (s, 1H), 7.06 – 6.95 (m, 1H), 6.14 (dd, J = 15.8, 1.9 Hz, 1H), 4.89 – 4.67 (m, 2H), 4.42 – 4.29 (q, J = 7.1 Hz, 2H), 4.28 – 4.17 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1, 1.8 Hz, 3H), 1.31 (t, J = 7.1, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.6, 165.5, 164.6, 158.7, 140.0, 132.2, 130.7, 125.5, 123.3,



1u

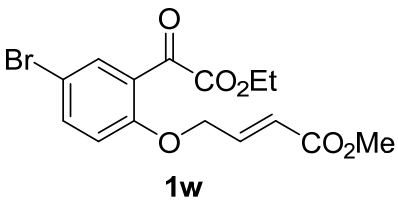
122.3, 116.5, 67.9, 62.3, 60.8, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{16}H_{18}BrO_6$ $[M+H]^+$ 385.0281, found 385.0280.

Ethyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)-5-fluorophenoxy)but-2-enoate (1v): Following the general procedure A, the substrate **1v** was obtained as yellow oil (256.0 mg, 79% yield). R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 (dd, J = 8.7, 6.7 Hz, 1H), 6.92 (dt, J = 15.8, 4.4 Hz, 1H), 6.76 – 6.71 (m, 1H), 6.58 (dd, J = 10.4, 2.1 Hz, 1H), 6.09 – 6.03 (m, 1H), 4.69 (dd, J = 4.4, 1.8 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.0, 168.9, 166.4, 165.2 (d, J = 61.6 Hz), 160.3 (d, J = 11.1 Hz), 139.9, 133.4 (d, J = 11.5 Hz), 123.4, 119.7 (d, J = 2.8 Hz), 109.5 (d, J = 23.2 Hz), 101.0 (d, J = 26.3 Hz), 67.9, 62.1, 60.8, 14.2, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) - 98.6; HRMS (ESI): *m/z* calcd for $C_{16}H_{18}FO_6$ $[M+H]^+$ 325.1082, found 325.1082.



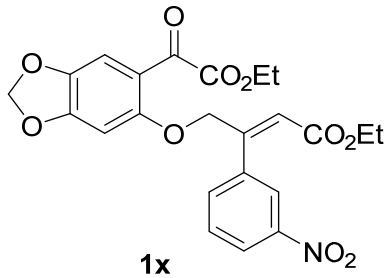
1v

Methyl (*E*)-4-(4-bromo-2-(2-ethoxy-2-oxoacetyl)phenoxy)but-2-enoate (1w): Following the general procedure A, the substrate **1w** was obtained as colorless oil (307.1 mg, 83% yield). R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (d, J = 2.5 Hz, 1H), 7.64 (dd, J = 8.9, 2.6 Hz, 1H), 7.00 (dt, J = 15.8, 4.3 Hz, 1H), 6.83 (d, J = 8.9 Hz, 1H), 6.12 (dt, J = 15.8, 1.8 Hz, 1H), 4.75 (dd, J = 4.3, 2.0 Hz, 2H), 4.34 (q, J = 7.2 Hz, 2H), 3.76 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.2, 166.0, 164.2, 157.4, 140.5, 138.4, 133.6, 125.0, 122.8, 114.8, 114.5, 67.9, 62.4, 51.9, 14.0; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}BrO_6$ $[M+H]^+$ 371.0125, found 371.0129.



1w

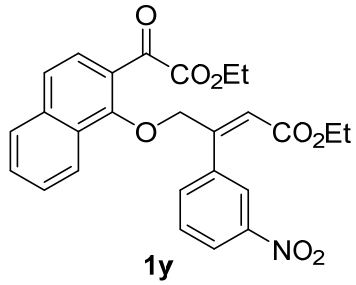
Ethyl (*E*)-4-((6-(2-ethoxy-2-oxoacetyl)benzo[*d*][1,3]dioxol-5-yl)oxy)-3-(3-nitrophenyl)-but-2-enoate (1x): Following the general procedure B, the substrate **1x** was obtained as yellow oil (366.6 mg, 78% yield). R_f = 0.30 (PE:EA 8:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 – 8.26 (m, 1H), 8.23 – 8.18 (m, 1H), 7.76 (dd, J = 7.8, 0.9 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.20 (s, 1H), 6.64 (s, 1H), 6.35 (s, 1H), 6.00 (s, 2H), 5.58 (s, 2H), 4.25 (q, J = 7.1 Hz, 2H), 4.06 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 184.5, 165.1, 165.0, 157.1, 154.8, 150.0, 148.3,



1x

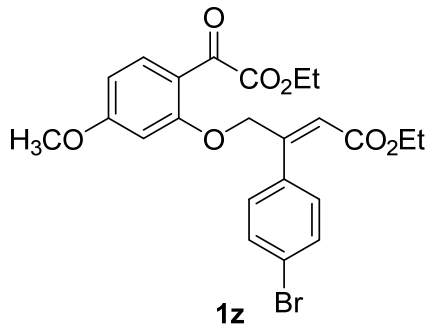
142.9, 139.2, 133.3, 129.9, 124.2, 123.4, 121.9, 115.8, 108.4, 102.6, 95.3, 65.7, 61.5, 61.2, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{23}H_{22}NO_{10}$ $[M+H]^+$ 472.1238, found 472.1240.

Ethyl (*E*)-4-((2-(2-ethoxy-2-oxoacetyl)naphthalen-1-yl)oxy)-3-(3-nitrophenyl)but-2-enoate (1y): Following the general procedure B, the substrate **1y** was obtained as yellow oil (338.3 mg, 71% yield). R_f = 0.20 (PE:EA 8:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.47 (s, 1H), 8.27 (d, J = 8.3 Hz, 1H), 8.04 – 7.96 (m, 2H), 7.87 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.6 Hz, 1H), 7.68 – 7.61 (m, 3H), 7.57 – 7.51 (m, 1H), 6.27 (s, 1H), 5.72 (s, 2H), 4.24 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 187, 164.9, 164.4, 158.7, 150.2, 148.3, 140.1, 137.9, 133.7, 129.6, 129.5, 128.4, 127.5, 127.0, 125.0, 124.9, 123.8, 123.5, 123.2, 123.1, 122.6, 72.9, 62.1, 60.9, 14.1, 14.0; HRMS (ESI): *m/z* calcd for $C_{26}H_{24}NO_8$ $[M+H]^+$ 478.1496, found 478.1493.



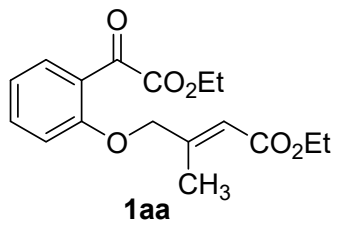
1y

Ethyl (*E*)-3-(4-bromophenyl)-4-(2-(2-ethoxy-2-oxoacetyl)-5-methoxyphenoxy)but-2-enoate (1z): Following the general procedure B, the substrate **1z** was obtained as yellow oil (373.2 mg, 76% yield). R_f = 0.20 (PE:EA 8:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81 (d, J = 8.7 Hz, 1H), 7.49 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 6.64 – 6.49 (m, 2H), 6.32 (s, 1H), 5.56 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 4.00 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.0, 166.6, 165.4, 165.3, 161.0, 150.6, 136.7, 132.9, 131.9, 128.6, 124.1, 121.6, 115.8, 107.3, 98.8, 64.8, 61.4, 60.8, 55.8, 14.2, 13.9; HRMS (ESI): *m/z* calcd for $C_{23}H_{24}BrO_7$ $[M+H]^+$ 491.0700, found 491.0703.



1z

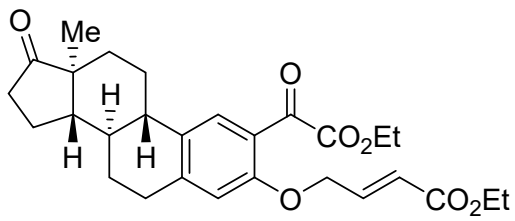
Ethyl (*E*)-4-(2-(2-ethoxy-2-oxoacetyl)phenoxy)-3-methylbut-2-enoate (1aa): Following the general procedure B, the substrate **1aa** was obtained as yellow oil (262.5 mg, 82% yield). R_f = 0.20 (PE:EA 8:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (dd, J = 7.8, 1.8 Hz, 1H), 7.56 (ddd, J = 8.6, 7.4, 1.8 Hz, 1H), 7.21 – 7.05 (m, 1H), 6.92 (d, J = 8.4 Hz, 1H), 5.98 (dd, J = 2.8, 1.4 Hz, 1H), 4.58 (s, 2H), 4.34 (q, J = 7.2 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 2.20 (d, J = 1.1 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.5, 166.1, 164.9, 158.7,



1aa

151.3, 136.2, 131.0, 123.3, 121.9, 116.5, 113.1, 72.7, 62.0, 60.0, 15.6, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{17}H_{21}O_6$ $[M+H]^+$ 321.1333, found 321.1335.

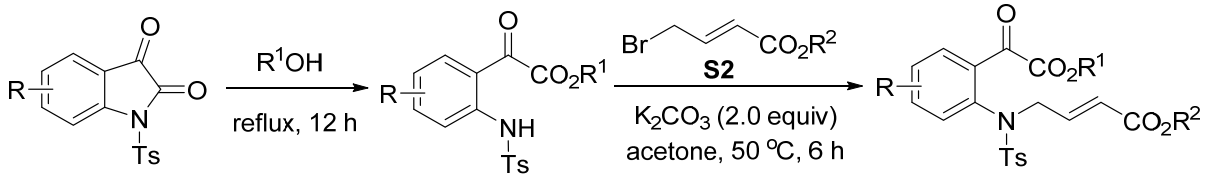
Ethyl (*E*)-4-(((8*R*, 9*S*, 13*S*, 14*S*)-2-(2-ethoxy-2-oxoacetyl)-13-methyl-17-oxo-7, 8, 9, 11, 12,13, 14, 15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)but-2-enoate (1ab):



1ab

Following the general procedure A, the substrate **1ab** was obtained as white solid (357.1 mg, 74% yield); m.p. 118–121°C; R_f = 0.20 (PE:EA 8:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80 (s, 1H), 7.02 (dt, J = 15.8, 4.3 Hz, 1H), 6.64 (s, 1H), 6.14 (dt, J = 15.8, 1.8 Hz, 1H), 4.74 (dd, J = 4.2, 1.9 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.01 – 2.86 (m, 2H), 2.56 – 2.42 (m, 2H), 2.28 – 2.41 (m, 1H), 2.18 – 2.10 (m, 1H), 2.08 – 1.94 (m, 3H), 1.63 – 1.43 (m, 6H), 1.36 (t, J = 7.1 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H), 0.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 220.4, 186.2, 165.8, 165.4, 156.6, 146.5, 141.1, 134.0, 128.1, 122.8, 120.9, 113.0, 67.6, 61.9, 60.7, 50.3, 47.9, 43.7, 37.9, 35.8, 31.4, 30.2, 26.1, 25.7, 21.6, 14.2, 14.0, 13.8; HRMS (ESI): *m/z* calcd for $C_{28}H_{35}O_7$ $[M+H]^+$ 483.2377, found 483.2377.

2. Preparation of Substrates 3



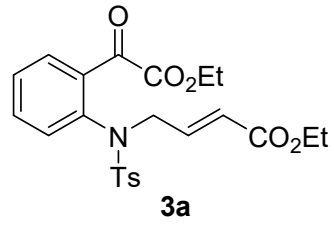
S3 **S4** **3**

General procedure:

Starting from the commercially obtained isatin, the corresponding tosylated derivative **S3** was smoothly prepared according to a literature procedure.[5] The alcoholysis of **S3** (1.0 mmol) was carried out in the specified alcohol R^1OH (10 mL) at 80 °C for 12 h to deliver the pure intermediates **S4** after column chromatographic isolation (PE/EA 10:1–5:1, v/v).

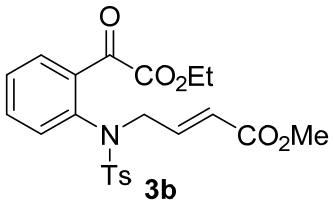
To a solution of **S4** (1.0 mmol) in acetone (10 mL) were added potassium carbonate (2.0 mmol, 2.0 equiv) and (*E*)-4-bromobut-2-enoate **S2** (1.1 mmol, 1.1 equiv). The resulting mixture was stirred at 50 °C for 6 h and monitored by TLC until **S4** was consumed. The reaction mixture was filtered through a plug of celite and washed with acetone (10 mL × 3). The filtrate was concentrated under reduced pressure and the crude product was isolated by

column chromatography (PE/EA 10:1–5:1, v/v) to afford **3**.

Ethyl (*E*)-4-((*N*-(2-(2-ethoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido)but-2-enoate (3a): 

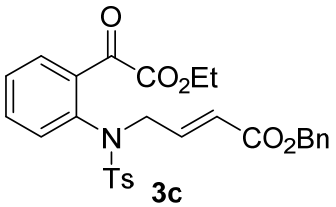
3a

Following the general procedure, the substrate **3a** was obtained as white solid (390.2 mg, 85% yield); m.p. 126–128°C; R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91 (dd, J = 7.4, 1.9 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 6.91 (dt, J = 15.7 Hz, 6.8 Hz, 1H), 6.60 (dd, J = 7.7, 1.2 Hz, 1H), 5.86 (d, J = 15.7 Hz, 1H), 4.49 (q, J = 7.2 Hz, 2H), 4.28 (s, 2H), 4.15 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.49 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.3, 165.4, 164.1, 144.6, 141.1, 139.0, 135.8, 133.3, 133.0, 131.3, 129.6, 128.7, 128.3, 127.2, 124.8, 62.7, 60.6, 52.5, 21.6, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{23}H_{26}NO_7S$ $[M+H]^+$ 460.1424, found 460.1424.

Methyl (*E*)-4-((*N*-(2-(2-ethoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido)but-2-enoate (3b): 

3b

Following the general procedure, the substrate **3b** was obtained as white solid (338.3 mg, 76% yield); m.p. 132–135°C; R_f = 0.25 (10:1 v/v, PE:EA); **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.95 – 7.85 (m, 1H), 7.50 – 7.39 (m, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 6.91 (dt, J = 15.7, 6.8 Hz, 1H), 6.58 (dd, J = 7.7, 1.3 Hz, 1H), 5.86 (dt, J = 15.7, 1.4 Hz, 1H), 4.48 (q, J = 7.2 Hz, 2H), 4.17 (s, 2H), 3.68 (s, 3H), 2.41 (s, 3H), 1.48 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.3, 165.8, 164.2, 144.6, 141.4, 138.9, 135.8, 133.3, 132.8, 131.3, 129.6, 128.7, 128.3, 127.0, 124.5, 62.7, 52.3, 51.8, 21.6, 14.0; HRMS (ESI): *m/z* calcd for $C_{22}H_{23}NNaO_7S$ $[M+Na]^+$ 468.1087, found 468.1085.

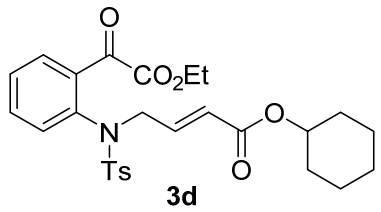
Benzyl (*E*)-4-((*N*-(2-(2-ethoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido)but-2-enoate (3c): 

3c

Following the general procedure, the substrate **3c** was obtained as yellow solid (354.4 mg, 68% yield); m.p. 108–110°C; R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, J = 7.4 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.29 – 7.25 (m, 4H), 7.23 (d, J = 8.3 Hz, 2H), 7.19 (s, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.01 – 7.25 (m, 1H), 6.52 (d, J = 7.7 Hz, 1H), 5.85 (d, J = 15.7 Hz, 1H), 5.07 (s, 2H), 4.38 (q, J = 7.2 Hz, 2H), 4.21 (s, 2H), 2.33 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.3, 165.2, 164.1, 144.6, 141.9, 139.0, 135.8, 135.7, 133.3, 133.1,

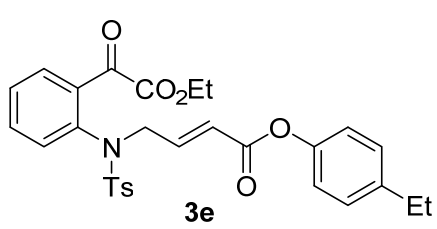
131.4, 129.6, 128.7, 128.6, 128.3, 128.2, 128.1, 127.2, 124.5, 66.4, 62.7, 52.6, 21.6, 14.0; HRMS (ESI): *m/z* calcd for $C_{28}H_{28}NO_7S$ $[M+H]^+$ 522.1581, found 522.1581.

Cyclohexyl (*E*)-4-((*N*-(2-(2-ethoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido) but-2-enoate (3d): Following the general procedure, the substrate **3d** was obtained as white solid (364.4 mg, 71% yield); m.p. 135–137°C; R_f = 0.30 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.53 – 7.40 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.90 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.71 – 6.51 (m, 1H), 5.86 (d, *J* = 15.7 Hz, 1H), 4.84 – 4.70 (m, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.26 (s, 2H), 2.42 (s, 3H), 1.85 – 1.79 (m, 2H), 1.75 – 1.67 (m, 2H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.45 – 1.33 (m, 4H), 1.32 – 1.23 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.3, 164.8, 164.1, 144.5, 140.8, 139.1, 135.8, 133.3, 131.3, 129.6, 128.7, 128.3, 127.4, 125.4, 72.9, 62.6, 52.7, 31.6, 25.4, 23.6, 21.6, 14.0; HRMS (ESI): *m/z* calcd for $C_{27}H_{32}NO_7S$ $[M+H]^+$ 514.1894, found 514.1896.



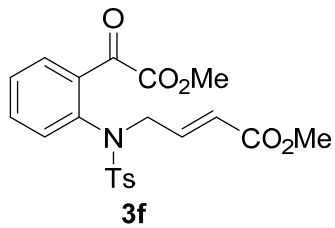
3d

4-Ethylphenyl (*E*)-4-((*N*-(2-(2-ethoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido) but-2-enoate (3e): Following the general procedure, the substrate **3e** was obtained as yellow solid (436.4 mg, 82% yield); m.p. 145–148°C; R_f = 0.35 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96 – 7.88 (m, 1H), 7.52 – 7.43 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.24 (s, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.15 – 7.07 (m, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.76 – 6.59 (m, 1H), 6.07 (d, *J* = 15.7 Hz, 1H), 4.58 – 4.43 (q, J = 7.2 Hz, 2H), 4.32 (s, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.49 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.2, 164.0, 163.9, 148.4, 144.6, 143.3, 141.9, 139.1, 135.8, 133.4, 133.1, 131.4, 129.6, 128.8, 128.7, 128.3, 127.3, 123.9, 121.1, 62.7, 52.7, 28.3, 21.6, 15.6, 14.0; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}NO_7S$ $[M+H]^+$ 536.1737, found 536.1740.



3e

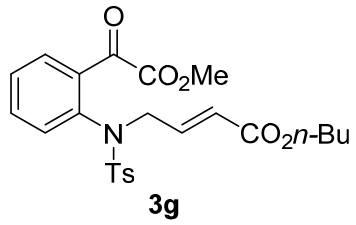
Methyl (*E*)-4-((*N*-(2-(2-methoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido)but-2-enoate (3f): Following the general procedure, the substrate **3f** was obtained as white solid (326.2 mg, 72% yield); m.p. 124–126°C; R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99 – 7.88 (m, 1H), 7.53 – 7.42 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.93 (dt, *J* = 15.7, 6.8 Hz, 1H),



3f

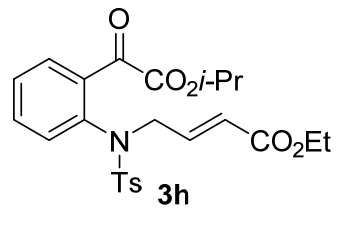
6.67 – 6.53 (m, 1H), 5.89 (dt, J = 15.7, 1.4 Hz, 1H), 4.6 (s, 2H), 4.05 (s, 3H), 3.71 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.0, 165.8, 164.5, 144.7, 141.3, 139.0, 135.7, 133.5, 132.7, 131.3, 129.7, 128.7, 128.3, 126.9, 124.5, 53.0, 52.4, 51.8, 21.6; HRMS (ESI): *m/z* calcd for $C_{21}H_{21}NNaO_7S$ $[M+Na]^+$ 454.0931, found 454.0936.

Butyl (*E*)-4-((*N*-(2-(2-methoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido)but-2-enoate (3g): Following the general procedure, the substrate **3g** was obtained as yellow solid (416.4 mg, 88% yield); m.p. 112–115°C; R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85 (dd, J = 7.3, 2.0 Hz, 1H), 7.40 (dt, J = 7.0, 4.1 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 6.84 (dt, J = 15.6, 6.8 Hz, 1H), 6.58 – 6.46 (m, 1H), 5.80 (d, J = 15.7 Hz, 1H), 4.19 (s, 2H), 4.02 (t, J = 6.7 Hz, 2H), 3.96 (s, 3H), 2.35 (s, 3H), 1.58 – 1.47 (m, 2H), 1.36 – 1.23 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.0, 165.5, 164.4, 144.6, 141.0, 139.1, 135.7, 133.4, 133.0, 131.3, 129.6, 128.7, 128.3, 127.2, 124.9, 64.5, 53.0, 52.5, 30.6, 21.6, 19.1, 13.7; HRMS (ESI): *m/z* calcd for $C_{24}H_{27}NNaO_7S$ $[M+Na]^+$ 496.1400, found 496.1404.



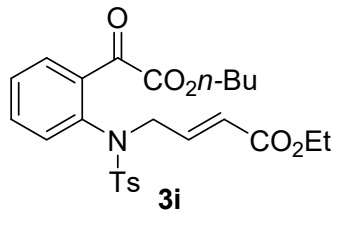
3g

Ethyl (*E*)-4-((*N*-(2-(2-isopropoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido)but-2-enoate (3h): Following the general procedure, the substrate **3h** was obtained as white solid (369.1 mg, 78% yield); m.p. 129–133°C; R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80 (dd, J = 7.4, 1.9 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.22 (t, J = 9.2 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 6.88 (dt, J = 15.6, 6.8 Hz, 1H), 6.53 (dd, J = 7.7, 1.2 Hz, 1H), 5.80 (d, J = 15.7 Hz, 1H), 5.27 – 5.20 (m, 1H), 4.22 (s, 2H), 4.08 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 1.42 (s, 6H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.4, 165.4, 163.5, 144.5, 141.3, 138.9, 135.9, 133.2, 131.4, 129.6, 128.6, 128.3, 127.4, 124.7, 71.0, 60.6, 52.6, 21.7, 21.6, 14.2; HRMS (ESI): *m/z* calcd for $C_{24}H_{28}NO_7S$ $[M+H]^+$ 474.1581, found 474.1578.



3h

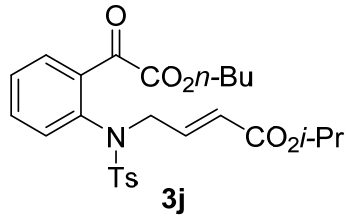
Ethyl (*E*)-4-((*N*-(2-(2-butoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido)but-2-enoate (3i): Following the general procedure, the substrate **3i** was obtained as white solid (345.9 mg, 71% yield); m.p. 132–135°C; R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96 – 7.85 (m, 1H), 7.51 – 7.40 (m, 2H), 7.32 (d, J = 8.3



3i

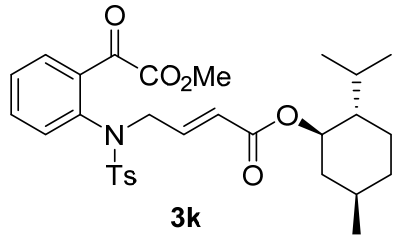
Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.93 (dt, *J* = 15.7, 6.8 Hz, 1H), 6.61 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.87 (d, *J* = 15.7 Hz, 1H), 4.43 (t, *J* = 6.8 Hz, 2H), 4.27 (s, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.88 – 1.80 (m, 2H), 1.57 – 1.45 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.2, 165.4, 164.2, 144.5, 141.2, 139.0, 135.7, 133.3, 133.0, 131.3, 129.6, 128.7, 128.3, 127.3, 124.8, 66.4, 60.6, 52.6, 30.4, 21.6, 19.1, 14.2, 13.8; HRMS (ESI): *m/z* calcd for $C_{25}H_{30}NO_7S$ $[M+H]^+$ 488.1737, found 488.1740.

Isopropyl (*E*)-4-((*N*-(2-(2-butoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido)but-2-enoate (3j): Following the general procedure, the substrate **3j** was obtained as white solid (370.8 mg, 74% yield); m.p. 141–144°C; R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 – 7.85 (m, 1H), 7.51 – 7.42 (m, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.91 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.67 – 6.55 (m, 1H), 5.92 – 5.77 (m, 1H), 5.04 – 4.98 (m, 1H), 4.43 (t, *J* = 6.8 Hz, 2H), 4.25 (s, 2H), 2.42 (s, 3H), 1.88 – 1.80 (m, 2H), 1.57 – 1.47 (m, 2H), 1.23 (d, *J* = 6.3 Hz, 6H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.2, 164.9, 164.1, 144.5, 140.9, 139.1, 135.7, 133.3, 133.2, 131.3, 129.6, 128.7, 128.3, 127.4, 125.2, 68.0, 66.4, 52.7, 30.4, 21.8, 21.6, 19.1, 13.8; HRMS (ESI): *m/z* calcd for $C_{26}H_{32}NO_7S$ $[M+H]^+$ 502.1894, found 502.1896.

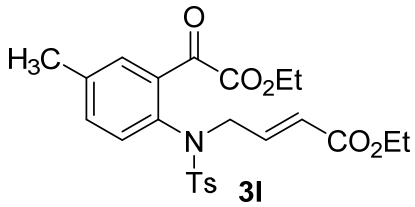


3j

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (*E*)-4-((*N*-(2-(2-methoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido)but-2-enoate (3k): Following the general procedure, the substrate **3k** was obtained as white solid (377.5 mg, 68% yield); m.p. 142–145°C; R_f = 0.30 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 – 7.80 (m, 1H), 7.44 – 7.34 (m, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.81 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.53 (d, *J* = 7.0 Hz, 1H), 5.79 (d, *J* = 15.7 Hz, 1H), 4.60 (m, 1H), 4.19 (s, 2H), 3.96 (s, 3H), 2.35 (s, 3H), 1.94 – 1.85 (m, 1H), 1.81 – 1.50 (m, 4H), 1.49 – 1.30 (m, 2H), 1.29 – 1.18 (m, 2H), 0.93 – 0.87 (m, 1H), 0.84 – 0.79 (m, 5H), 0.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.1, 165.0, 164.4, 144.6, 140.7, 135.7, 133.4, 131.2, 129.6, 128.7, 128.3, 127.3, 125.4, 74.5, 53.0, 52.6, 47.0, 40.8, 34.2, 31.4, 26.3, 23.6, 22.0, 21.6, 20.7, 16.5; HRMS (ESI): *m/z* calcd for $C_{30}H_{38}NO_7S$ $[M+H]^+$ 556.2363, found 556.2361.

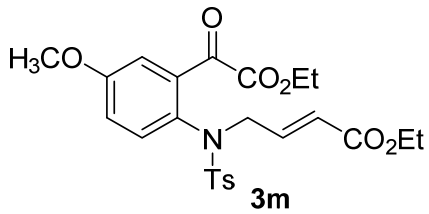


3k

Ethyl (*E*)-4-((*N*-(2-(2-ethoxy-2-oxoacetyl)-4-methylphenyl)-4-methylphenyl)sulfonamido) but-2-enoate (3l): 

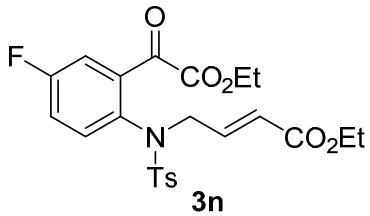
3l

Following the general procedure, the substrate **3l** was obtained as white solid (354.9 mg, 75% yield); m.p. 118–121°C; R_f = 0.30 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, J = 1.3 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.3 Hz, 3H), 6.91 (dt, J = 15.6, 6.8 Hz, 1H), 6.48 (d, J = 8.2 Hz, 1H), 5.85 (d, J = 15.7 Hz, 1H), 4.48 (s, 2H), 4.30 (s, 2H), 4.15 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 2.40 (s, 3H), 1.49 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.6, 165.3, 164.3, 144.7, 141.2, 138.9, 136.4, 135.3, 134.1, 132.6, 131.4, 129.6, 128.3, 126.6, 124.6, 62.5, 60.5, 52.3, 21.5, 20.9, 14.1, 14.0; HRMS (ESI): *m/z* calcd for $C_{24}H_{28}NO_7S$ $[M+H]^+$ 474.1581, found 474.1585.

Ethyl (*E*)-4-((*N*-(2-(2-ethoxy-2-oxoacetyl)-4-methoxyphenyl)-4-methylphenyl) sulfonamido)but-2-enoate (3m): 

3m

Following the general procedure, the substrate **3m** was obtained as yellow solid (410.9 mg, 84% yield); m.p. 128–131°C; R_f = 0.30 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, J = 3.0 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 6.99 – 6.83 (m, 2H), 6.48 (d, J = 8.8 Hz, 1H), 5.85 (d, J = 15.7 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 4.29 (s, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 2.43 (s, 3H), 1.50 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.3, 165.4, 164.2, 159.3, 144.5, 141.1, 136.8, 133.1, 131.5, 129.6, 128.4, 124.8, 120.0, 114.6, 62.7, 60.6, 55.8, 52.6, 21.6, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{24}H_{28}NO_8S$ $[M+H]^+$ 490.1530, found 490.1534.

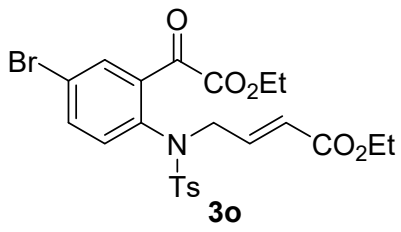
Ethyl (*E*)-4-((*N*-(2-(2-ethoxy-2-oxoacetyl)-4-fluorophenyl)-4-methylphenyl)sulfonamido) but-2-enoate (3n): 

3n

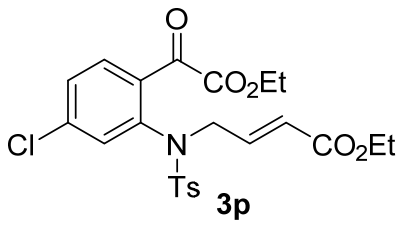
Following the general procedure, the substrate **3n** was obtained as white solid (329.2 mg, 69% yield); m.p. 125–128°C; R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63 (dd, J = 8.2, 2.8 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.20 – 7.10 (m, 1H), 6.99 – 6.85 (m, 1H), 6.59 (dd, J = 8.8, 4.5 Hz, 1H), 5.88 (d, J = 15.8 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 4.34 (s, 2H), 4.17 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 1.51 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 184.9, 165.3, 163.6, 161.8 (d, J = 252.5 Hz), 144.8, 140.7, 137.9 (d, J = 7.3 Hz), 134.8 (d, J = 3.4 Hz), 132.9, 129.7, 129.1

(d, J = 8.3 Hz), 128.3, 125.2, 120.2 (d, J = 23.2 Hz), 118.1 (d, J = 24.2 Hz), 62.9, 60.7, 52.6, 21.6, 14.2, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -110.8; HRMS (ESI): *m/z* calcd for $C_{23}H_{25}FNO_7S$ $[M+H]^+$ 478.1330, found 478.1327.

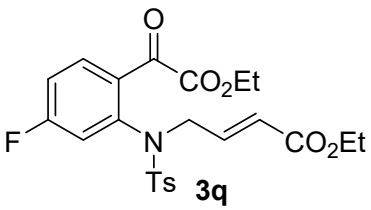
Ethyl (*E*)-4-((*N*-(4-bromo-2-(2-ethoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido) but-2-enoate (3o): Following the general procedure, the substrate **3o** was obtained as yellow solid (408.2 mg, 76% yield); m.p. 122–125°C; R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02 (d, J = 2.4 Hz, 1H), 7.54 (dd, J = 8.5, 2.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.9 Hz, 2H), 6.88 (dt, J = 15.7, 6.8 Hz, 1H), 6.44 (d, J = 8.5 Hz, 1H), 5.86 (d, J = 15.7 Hz, 1H), 4.50 (q, J = 7.2 Hz, 2H), 4.32 (s, 2H), 4.15 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.49 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 184.8, 165.3, 163.6, 144.9, 140.5, 137.9, 137.4, 136.1, 134.1, 132.5, 129.8, 128.3, 128.2, 125.2, 122.7, 62.9, 60.7, 52.3, 21.6, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{23}H_{25}BrNO_7S$ $[M+H]^+$ 538.0530, found 538.0533.



Ethyl (*E*)-4-((*N*-(5-chloro-2-(2-ethoxy-2-oxoacetyl)phenyl)-4-methylphenyl)sulfonamido) but-2-enoate (3p): Following the general procedure, the substrate **3p** was obtained as white solid (409.3 mg, 83% yield); m.p. 138–141°C; R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.87 (d, J = 8.4 Hz, 1H), 7.46 (dd, J = 8.4, 1.3 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 6.91 (dt, J = 15.4, 6.7 Hz, 1H), 6.55 (d, J = 1.2 Hz, 1H), 5.89 (d, J = 15.7 Hz, 1H), 4.49 (d, J = 7.1 Hz, 2H), 4.28 (s, 2H), 4.17 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 1.49 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.1, 165.3, 163.8, 145.08, 140.6, 140.3, 139.2, 134.2, 132.5, 132.3, 129.8, 129.0, 128.3, 127.3, 125.1, 62.8, 60.7, 52.5, 21.7, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{23}H_{25}ClNO_7S$ $[M+H]^+$ 494.1035, found 494.1037.

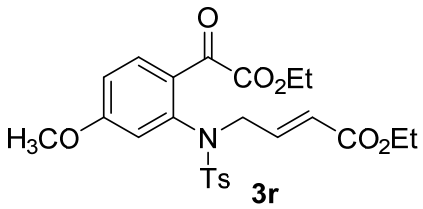


Ethyl (*E*)-4-((*N*-(2-(2-ethoxy-2-oxoacetyl)-5-fluorophenyl)-4-methylphenyl)sulfonamido) but-2-enoate (3q): Following the general procedure, the substrate **3q** was obtained as white solid (405.5 mg, 85% yield); m.p. 128–131°C; R_f = 0.20 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95 (dd, J = 8.7, 6.3 Hz, 1H), 7.35 (d, J



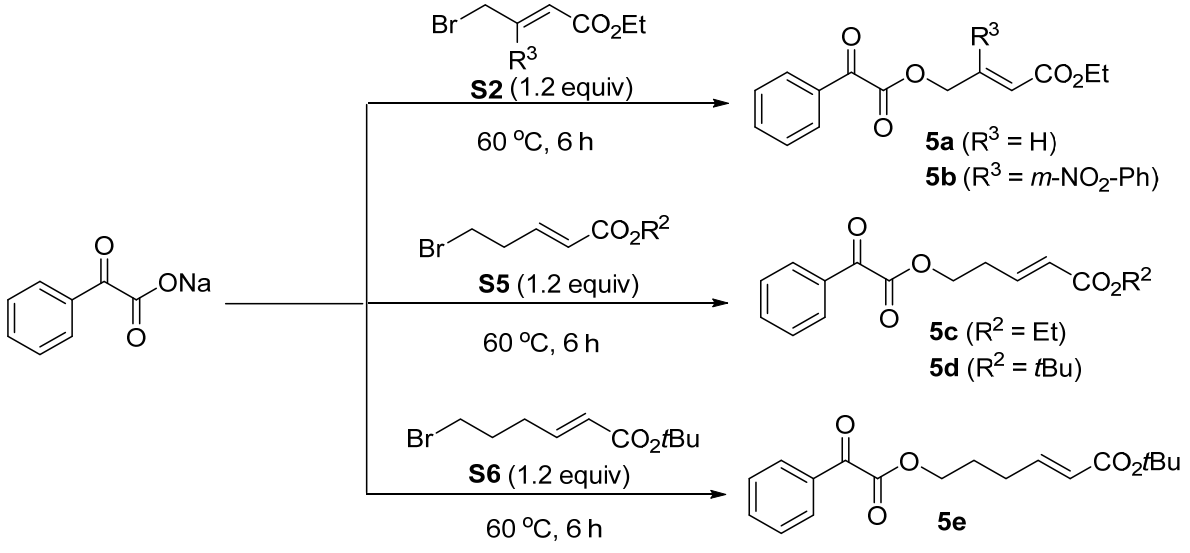
= 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.09 (m, 1H), 6.91 (dt, *J* = 15.7, 6.8 Hz, 1H), 6.31 (dd, *J* = 9.2, 2.4 Hz, 1H), 5.88 (d, *J* = 15.7 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.29 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.0, 166.2, 165.3, 163.8 (d, *J* = 40.4 Hz), 145.0, 141.2 (d, *J* = 9.4 Hz), 140.5, 133.4 (d, *J* = 10.1 Hz), 132.4, 132.2 (d, *J* = 3.5 Hz), 129.8, 128.3, 125.2, 116.1 (d, *J* = 22.2 Hz), 114.4 (d, *J* = 23.2 Hz), 62.8, 60.7, 52.4, 21.7, 14.2, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -102.5; HRMS (ESI): *m/z* calcd for $C_{23}H_{25}FNO_7S$ $[M+H]^+$ 478.1330, found 478.1327.

Ethyl (*E*)-4-((*N*-(2-(2-ethoxy-2-oxoacetyl)-5-methoxyphenyl)-4-methylphenyl) sulfonamido)but-2-enoate (3r): Following the general procedure, the substrate **3r** was obtained as white solid (425.5 mg, 87% yield); m.p. 135–138°C; R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.90 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.29 (s, 2H), 7.05 – 6.88 (m, 2H), 6.20 (d, *J* = 2.1 Hz, 1H), 5.88 (d, *J* = 15.7 Hz, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.27 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 2.45 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.2, 165.4, 164.6, 163.6, 144.5, 141.3, 141.1, 133.6, 129.6, 128.4, 127.5, 124.7, 114.4, 113.7, 62.5, 60.6, 55.7, 52.7, 21.6, 14.2, 14.1; HRMS (ESI): *m/z* calcd for $C_{24}H_{28}NO_8S$ $[M+H]^+$ 490.1530, found 490.1534.



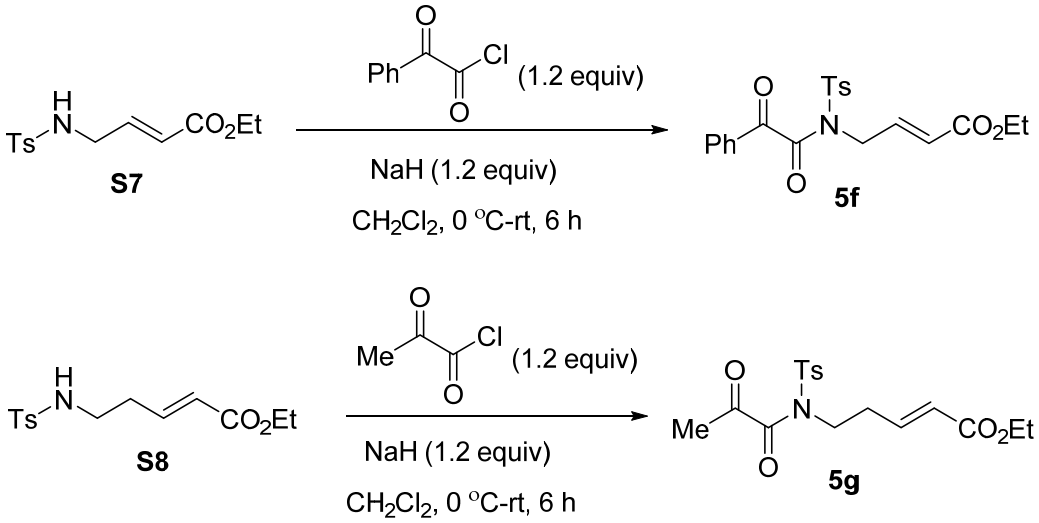
3. Preparation of Substrates 5

General procedure A:



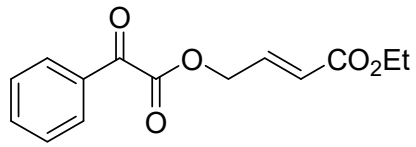
To a solution of 2-oxo-2-phenylacetic acid (1.0 mmol) in DMF (5 mL) was added $NaHCO_3$ (168.0 mg, 2.0 mmol, 2.0 equiv) and stirred for 2 h at rt. Then the bromide **S2** (1.2 mmol, 1.2 equiv) was added into it and the reaction mixture was heated at 60 °C with stirring for 6 h and monitored by TLC until the starting material was consumed. Water (20 mL) was added and the mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with saturated $NaHCO_3$ (20 mL) and dried over anhydrous $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure and the pure **5a** and **5b** were obtained after purification by silica gel column chromatography (PE:EA 10:1, v/v). Similarly, the substrates **5c-5e** were prepared by using the bromides **S5** and **S6** which were prepared by the known method.[6]

General procedure B:



To a solution of **S7** or **S8** (1.0 mmol, prepared by known procedures[7]) in dry CH_2Cl_2 (20 mL) was slowly added at 0 °C with stirring an excess of sodium hydride (48.0 mg, 1.2 mmol, 60% dispersion in mineral oil) and stirred for additional 30 min. Then 2-oxo-2-phenylacetyl chloride or 2-oxo-propionyl chloride (1.2 mmol) was dropwise added by a syringe. The reaction mixture was stirred at 0 °C for 1 h and then was warmed up to rt and stirred for 6 h. The mixture was cautiously poured into water (20 mL) and the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was then dried over anhydrous $MgSO_4$ and filtered. After concentration under reduced pressure, the crude product was isolated by silica gel column chromatography (PE:EA 10:1, v/v) to afford **5f** or **5g**.

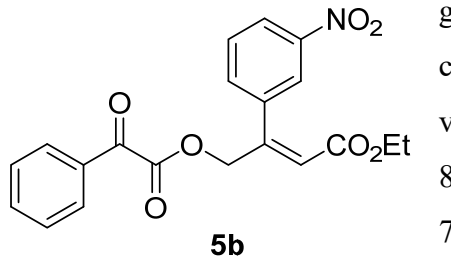
Ethyl (*E*)-4-(2-oxo-2-phenylacetoxy)but-2-enoate (5a): Following the general procedure A, the substrate **5a** was obtained as colorless oil (223.0 mg, 85% yield); R_f = 0.60 (PE:EA 10:1,



5a

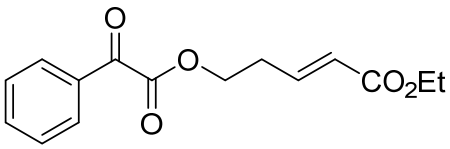
v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02 (dd, J = 8.3, 1.2 Hz, 2H), 7.73 – 7.63 (m, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.01 (dt, J = 15.7, 4.8 Hz, 1H), 6.14 (dt, J = 15.7, 1.8 Hz, 1H), 5.04 (dd, J = 4.8, 1.9 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.4, 165.5, 162.9, 139.3, 135.2, 132.2, 130.1, 129.0, 123.6, 63.9, 60.7, 14.2; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}O_5$ $[M+H]^+$ 263.0914, found 263.0911.

Ethyl (*E*)-3-(3-nitrophenyl)-4-(2-oxo-2-phenylacetoxy)but-2-enoate (5b): Following the general procedure A, the substrate **5b** was obtained as colorless oil (302.6 mg, 79% yield); R_f = 0.40 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.33 (s, 1H), 8.25 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 7.8 Hz, 3H), 7.63 – 7.57 (m, 2H), 7.42 (t, J = 7.7 Hz, 2H), 6.34 (s, 1H), 5.93 (s, 2H), 4.29 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.5, 164.9, 163.1, 148.9, 148.4, 139.4, 135.1, 133.1, 132.1, 129.9, 129.8, 128.9, 124.1, 123.9, 122.2, 61.8, 61.1, 14.2; HRMS (ESI): *m/z* calcd for $C_{20}H_{18}NO_7$ $[M+H]^+$ 384.1078, found 384.1075.



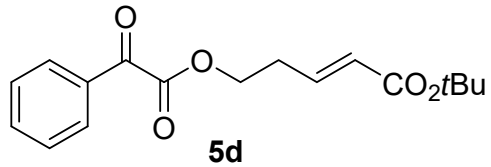
5b

Ethyl (*E*)-5-(2-oxo-2-phenylacetoxy)pent-2-enoate (5c): Following the general procedure A, the substrate **5c** was obtained as colorless oil (218.1 mg, 79% yield); R_f = 0.70 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99 (d, J = 7.7 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.07 – 6.80 (m, 1H), 5.95 (d, J = 15.7 Hz, 1H), 4.51 (t, J = 6.5 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 2.70 (q, J = 6.5 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 185.9, 166.0, 163.6, 142.9, 135.1, 132.3, 130.1, 128.9, 124.4, 63.9, 60.5, 31.2, 14.2; HRMS (ESI): *m/z* calcd for $C_{15}H_{17}O_5$ $[M+H]^+$ 277.1071, found 277.1074.



5c

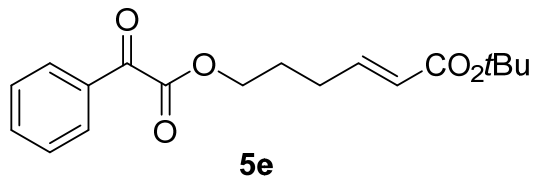
***tert*-Butyl (*E*)-5-(2-oxo-2-phenylacetoxy)pent-2-enoate (5d):** Following the general procedure A, the substrate **5d** was obtained as colorless oil (255.4 mg, 84% yield); R_f = 0.50 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.13 – 7.88 (m, 2H), 7.70 – 7.63 (m, 1H), 7.52 (t, J = 7.8 Hz, 2H), 6.84 (dt, J = 15.7, 6.9 Hz, 1H), 5.88 (dt, J = 15.7, 1.5 Hz, 1H), 4.50 (t, J =



5d

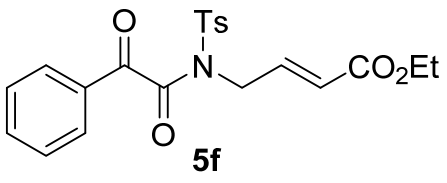
6.6 Hz, 2H), 2.67 (qd, *J* = 6.7, 1.5 Hz, 2H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 186.0, 165.3, 163.6, 141.6, 135.0, 132.3, 130.1, 129.0, 126.0, 80.5, 64.1, 31.1, 28.1; HRMS (ESI): *m/z* calcd for $C_{17}H_{21}O_5$ $[M+H]^+$ 305.1384, found 305.1387.

***tert*-Butyl (*E*)-6-(2-oxo-2-phenylacetoxy)hex-2-enoate (5e) :** Following the general procedure A, the substrate **5e** was obtained as colorless oil (232.3 mg, 73% yield); R_f = 0.50 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.68 – 7.64 (m, 1H), 7.54 – 7.50 (m, 2H), 6.86 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.80 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.41 (t, *J* = 6.5 Hz, 2H), 2.39 – 2.25 (m, 2H), 2.01 – 1.87 (m, 2H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 186.1, 165.6, 163.7, 145.6, 135.0, 132.3, 129.9, 128.9, 124.1, 80.1, 65.2, 28.1, 28.0, 26.9; HRMS (ESI): *m/z* calcd for $C_{18}H_{23}O_5$ $[M+H]^+$ 319.1540, found 319.1540.



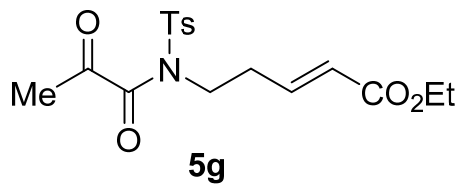
5e

Ethyl (*E*)-4-(2-oxo-2-phenyl-*N*-tosylacetamido)but-2-enoate (5f): Following the general procedure B, the substrate **5f** was obtained as colorless oil (265.7 mg, 64% yield); R_f = 0.25 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96 (d, *J* = 7.8 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 6.76 (dt, *J* = 15.8, 5.6 Hz, 1H), 5.91 (d, *J* = 15.7 Hz, 1H), 4.50 (d, *J* = 5.6 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 187.6, 166.8, 165.4, 146.2, 139.5, 134.7, 134.0, 132.6, 130.2, 129.8, 129.0, 128.6, 124.5, 60.6, 45.3, 21.8, 14.2; HRMS (ESI): *m/z* calcd for $C_{21}H_{22}NO_6S$ $[M+H]^+$ 416.1162, found 416.1166.



5f

Ethyl (*E*)-5-(2-oxo-*N*-tosylpropanamido)pent-2-enoate (5g): Following the general procedure B, the substrate **5g** was obtained as colorless oil (135.6 mg, 74% yield); R_f = 0.30 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 6.85 – 6.65 (m, 1H), 5.78 (dd, *J* = 15.7, 1.0 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.70 – 3.54 (m, 2H), 2.51 (s, 3H), 2.47 (d, *J* = 8.2 Hz, 2H), 2.46 (s, 3H), 1.26 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 194.9, 168.0, 165.9, 146.2, 143.2, 133.9, 130.2, 128.3, 123.9, 60.4, 43.4, 30.7, 26.8, 21.7, 14.2; HRMS (ESI): *m/z* calcd for $C_{17}H_{22}NO_6S$ $[M+H]^+$ 368.1162, found 368.1159.



5g

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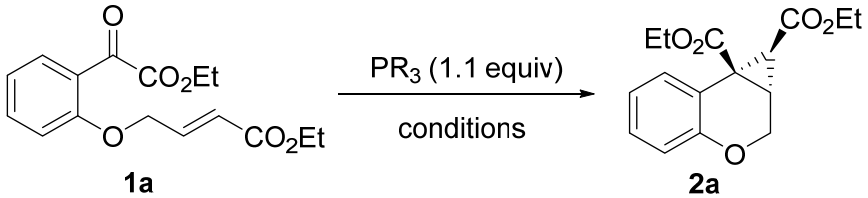
III. Optimization of the Reaction Conditions

Table S1. Survey on conditions of the model reaction of 1a[a]

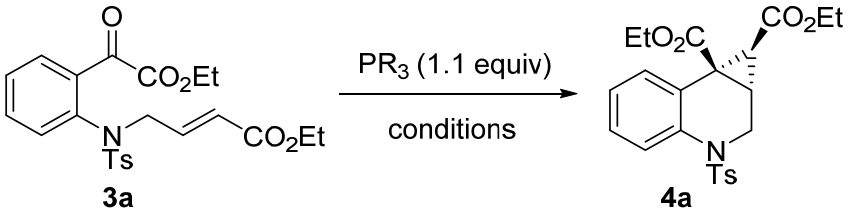


1a **2a**

Entry	PR_3	Solvent	*T* (ºC)	Time (h)	Yield (%)[b]	dr[c]
1	$P(OMe)_3$	CH_2Cl_2	−78	10	11	5:1
2	$P(OEt)_3$	CH_2Cl_2	−78	10	17	7:1
3	PPh_3	CH_2Cl_2	−78	10	0	/
4	PBu_3	CH_2Cl_2	−78	10	12	4:1
5	$P(NMe_2)_3$	CH_2Cl_2	−78	10	42	10:1
6	$P(NMe_2)_3$	toluene	−78	10	28	10:1
7	$P(NMe_2)_3$	THF	−78	10	37	10:1
8	$P(NMe_2)_3$	$CHCl_3$	−60	10	67	10:1
9	$P(NMe_2)_3$	$CHCl_3$	−60	15	72	10:1
10	$P(NMe_2)_3$	$CHCl_3$	−60	24	61	10:1
11	**$P(NMe_2)_3$**	**$CHCl_3$**	**−60**	**18**	**82**	**10:1**

[a] All reactions were carried out using **1a** (0.20 mmol) in 2.0 mL of solvent with PR_3 (1.1 equiv) under N_2 atmosphere. [b] Isolated yield of **2a** after column chromatography. [c] Diastereomeric ratio (dr) value was determined by ^1H NMR assay.

Table S2. Survey on conditions of the reaction of 3a[a]

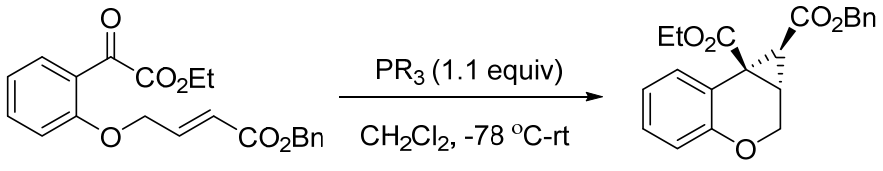


3a **4a**

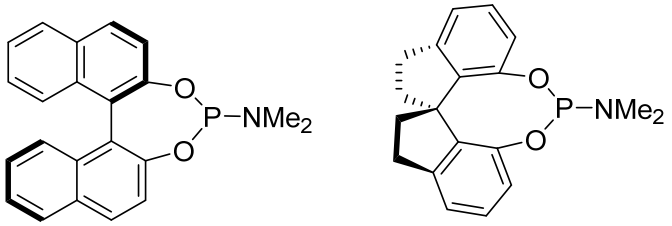
Entry	PR_3	Solvent	*T* (ºC)	Time (h)	Yield (%)[b]	dr[c]
1	$P(OMe)_3$	CH_2Cl_2	−78	8	14	20:1
2	$P(OEt)_3$	CH_2Cl_2	−78	8	trace	/
3	PPh_3	CH_2Cl_2	−78	8	0	/
4	PBu_3	CH_2Cl_2	−78	8	16	20:1
5	$P(NMe_2)_3$	CH_2Cl_2	−78	8	73	20:1
6	$P(NMe_2)_3$	THF	−78	8	54	20:1
7	$P(NMe_2)_3$	toluene	−78	8	48	20:1
8	$P(NMe_2)_3$	$CHCl_3$	−60	8	57	20:1
9	**$P(NMe_2)_3$**	**CH_2Cl_2**	**−78**	**12**	**86**	**20:1**
10	$P(NMe_2)_3$	CH_2Cl_2	−78	16	71	20:1

[a] All reactions were carried out using **3a** (0.20 mmol) in 2.0 mL of solvent with PR_3 (1.1 equiv) under N_2 atmosphere. [b] Isolated yield of **4a** after column chromatography. [c] Diastereomeric ratio (dr) value was determined by ^1H NMR assay.

Table S3. A brief survey on the asymmetric reaction of 1b[a]

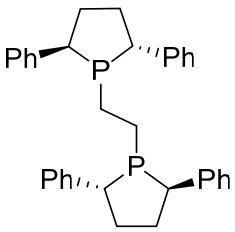


1b **Chiral-2b**



P1

P2



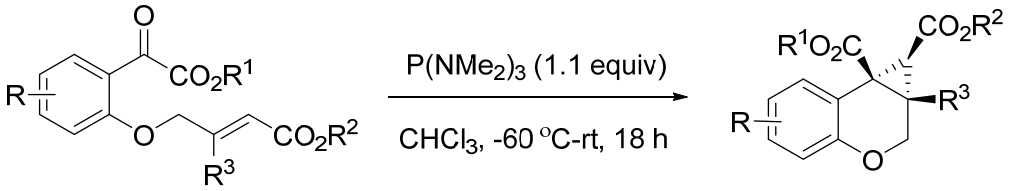
P3

Entry	PR_3	Time (h)	Yield (%)[b]	dr[c]	*ee*[d]
1	**P1**	12	0	/	/
2	**P2**	10	trace	/	/
3	**P3**	12	29	20:1	95

[a] All reactions were carried out using **1b** (0.10 mmol) in CH_2Cl_2 (1.0 mL) with chiral phosphine PR_3 (1.1 equiv) under N_2 atmosphere. [b] Isolated yield of product after column chromatography. [c] Diastereomeric ratio (dr) value was determined by ^1H NMR assay. [d] The enantiomeric excess of **Chiral-2b** was measured by HPLC analysis with a Chiralcel AS-H column (hexane/*i*-PrOH: 90/10, flow rate: 1.0 mL/min, λ = 254 nm, t_{major} = 19.1 min, t_{minor} = 20.5 min).

IV. General Procedures for $P(NMe_2)_3$-Mediated Reductive Intramolecular Cyclopropanations

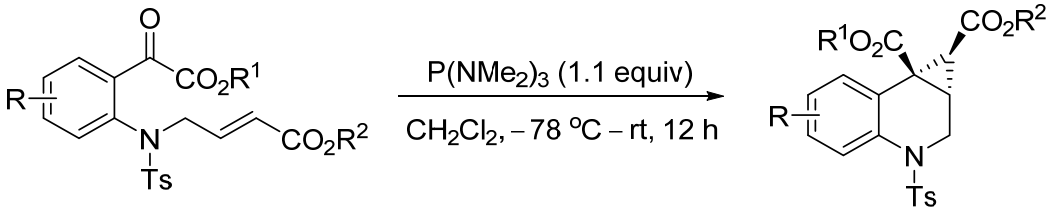
1. General procedure for synthesis of cyclopropane-fused chromanes 2 (Table 1)



1a-1z, 1aa, 1ab → **2a-2z, 2aa, 2ab**

To a solution of substrate **1** (0.2 mmol) in dry $CHCl_3$ (1.0 mL) was dropwise added a solution of $P(NMe_2)_3$ (35.9 mg, 0.22 mmol) in dry $CHCl_3$ (1.0 mL) via a syringe at –60 °C with stirring over 20 min. The resulting reaction mixture was stirred at –60 °C for 1 h and then slowly warmed up to rt and stirred for additional 17 h. After the solvent was removed on a rotary evaporator under reduced pressure, the residue was subjected to isolation by silica gel column chromatography (PE/EA 15:1–10:1, v/v) to give product **2**.

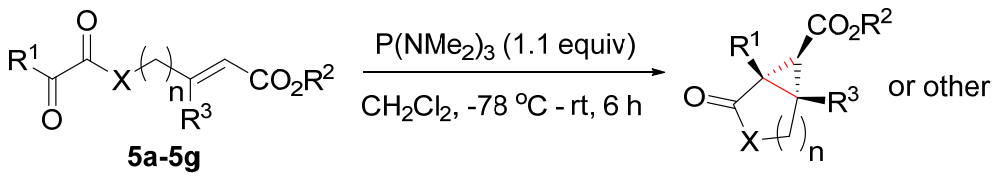
2. General procedure for synthesis of cyclopropane-fused tetrahydroquinolines 4 (Table 2)



3a-3r → **4a-4r**

To a solution of substrate **3** (0.2 mmol) in dry CH_2Cl_2 (1.0 mL) was dropwise added a solution of $P(NMe_2)_3$ (35.9 mg, 0.22 mmol) in dry CH_2Cl_2 (1.0 mL) via a syringe at –78 °C with stirring over 20 min. The resulting reaction mixture was stirred at –78 °C for 1 h and then slowly warmed up to rt and stirred for additional 11 h. After the solvent was removed on a rotary evaporator under reduced pressure, the residue was subjected to isolation by silica gel column chromatography (PE/EA 10:1–5:1, v/v) to give product **4**.

3. General procedure for synthesis of cyclopropane-fused lactones or lactams 6 (Table 3)



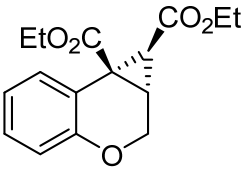
5a-5g
X = O, NTs; n = 1, 2, 3

→ **6a-6d, 6g**

To a solution of substrate **5** (0.2 mmol) in dry CH_2Cl_2 (1.0 mL) was dropwise added a solution of $P(NMe_2)_3$ (35.9 mg, 0.22 mmol) in dry CH_2Cl_2 (1.0 mL) via a syringe at –78 °C with stirring over 20 min. The resulting reaction mixture was stirred at –78 °C for 1 h and then slowly warmed up to rt and stirred for additional 5 h. After the solvent was removed on a rotary evaporator under reduced pressure, the residue was subjected to isolation by silica gel column chromatography (PE/EA 10:1, v/v) to give product **6**.

V. Characterization Data of Compounds 2, 4 and 6

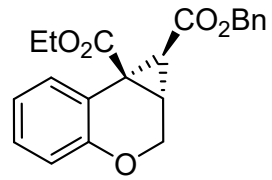
Diethyl 1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2a): colorless oil,



2a

47.6 mg, 82% yield; R_f = 0.80 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 (dd, J = 7.8, 1.5 Hz, 1H), 7.09 (td, J = 7.8, 1.6 Hz, 1H), 6.88 (td, J = 7.6, 1.2 Hz, 1H), 6.78 (dd, J = 8.1, 1.1 Hz, 1H), 4.28 (dd, J = 11.2, 1.5 Hz, 1H), 4.21 (tt, J = 7.2, 3.5 Hz, 2H), 4.10 (dt, J = 7.2, 2.9 Hz, 2H), 3.96 (dd, J = 11.1, 1.5 Hz, 1H), 2.71 (dt, J = 5.5, 1.6 Hz, 1H), 2.44 (d, J = 5.5 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 167.6, 152.3, 128.2, 127.0, 122.0, 121.2, 118.0, 61.7, 61.3, 60.6, 33.9, 30.3, 29.7, 14.2, 14.1; HRMS (ESI): *m/z* calcd for $C_{16}H_{19}O_5$ $[M+H]^+$ 291.1227, found 291.1230.

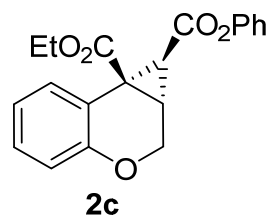
Benzyl 7b-ethyl 1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2b):



2b

colorless oil, 63.0 mg, 84% yield; R_f = 0.75 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.43 (dd, J = 7.8, 1.6 Hz, 1H), 7.40 – 7.33 (m, 5H), 7.19 – 7.11 (m, 1H), 6.95 (td, J = 7.6, 1.3 Hz, 1H), 6.84 (dd, J = 8.1, 1.2 Hz, 1H), 5.15 (s, 2H), 4.35 (dd, J = 11.2, 1.6 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 4.03 (dd, J = 11.2, 1.2 Hz, 1H), 2.81 (dt, J = 5.5, 1.6 Hz, 1H), 2.58 (d, J = 5.5 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.5, 167.5, 152.3, 135.5, 128.6, 128.4, 128.3, 127.1, 122.0, 121.1, 118.0, 67.1, 61.7, 60.5, 34.0, 30.2, 29.9, 14.1; HRMS (ESI): *m/z* calcd for $C_{21}H_{20}NaO_5$ $[M+Na]^+$ 375.1203, found 375.1208.

7b-Ethyl 1-phenyl 1a, 2-dihydrocyclopropa[*c*]chromene-1, 7b(1*H*)-dicarboxylate (2c):

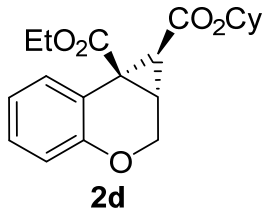


2c

colorless oil, 59.0 mg, 87% yield; R_f = 0.60 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.51 (dd, J = 7.8, 1.5 Hz, 1H), 7.40 (t, J = 7.9 Hz, 2H), 7.28 – 7.19 (m, 2H), 7.17 – 7.11 (m, 2H), 7.02 (td, J = 7.6, 1.0 Hz, 1H), 6.92 (dd, J = 8.1, 0.9 Hz, 1H), 4.46 (dd, J = 11.2,

1.5 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.12 (dd, J = 11.2, 1.3 Hz, 1H), 2.94 (dt, J = 5.5, 1.4 Hz, 1H), 2.78 (d, J = 5.5 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.3, 167.4, 152.4, 150.7, 129.4, 128.5, 127.2, 126.0, 122.1, 121.4, 120.9, 118.1, 61.9, 60.5, 34.6, 30.2, 30.1, 14.1; HRMS (ESI): *m/z* calcd for $C_{20}H_{19}O_5$ $[M+H]^+$ 339.1227, found 339.1224.

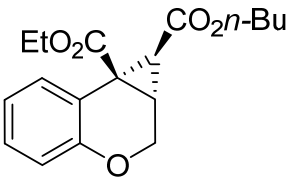
1-Cyclohexyl 7b-ethyl 1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2d):



2d

colorless oil, 63.5 mg, 92% yield; R_f = 0.70 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46 (dd, J = 7.8, 1.6 Hz, 1H), 7.21 – 7.14 (m, 1H), 6.97 (td, J = 7.6, 1.3 Hz, 1H), 6.87 (dd, J = 8.1, 1.2 Hz, 1H), 4.85 – 4.74 (m, 1H), 4.38 (dd, J = 11.2, 1.5 Hz, 1H), 4.35 – 4.20 (q, J = 7.2 Hz, 2H), 4.05 (dd, J = 11.1, 1.2 Hz, 1H), 2.79 (dt, J = 5.5, 1.6 Hz, 1H), 2.52 (d, J = 5.5 Hz, 1H), 1.89 – 1.86 (m, 2H), 1.78 – 1.72 (m, 2H), 1.58 – 1.52 (m, 1H), 1.46 – 1.38 (m, 3H), 1.35 (t, J = 7.2 Hz, 3H), 1.33 – 1.19 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.2, 167.6, 152.4, 128.2, 127.0, 122.0, 121.4, 118.0, 73.8, 61.6, 60.6, 33.8, 31.6, 31.5, 30.5, 29.6, 25.3, 23.8, 23.7, 14.2; HRMS (ESI): *m/z* calcd for $C_{20}H_{25}O_5$ $[M+H]^+$ 345.1697, found 345.1699.

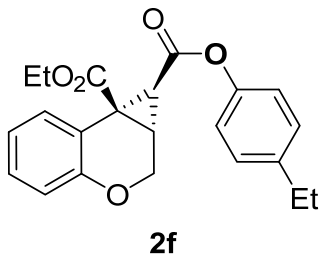
1-Butyl 7b-ethyl 1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2e):



2e

colorless oil, 56.2 mg, 88% yield; R_f = 0.80 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46 (dd, J = 7.8, 1.3 Hz, 1H), 7.22 – 7.14 (m, 1H), 6.99 – 6.96 (m, 1H), 6.88 (d, J = 8.1 Hz, 1H), 4.38 (dd, J = 11.1, 1.3 Hz, 1H), 4.31 (q, J = 7.1, 2H), 4.13 (t, J = 6.7, 2H), 4.05 (dd, J = 11.2, 0.9 Hz, 1H), 2.80 (dt, J = 5.5, 2.0 Hz, 1H), 2.53 (d, J = 5.5 Hz, 1H), 1.67 – 1.59 (m, 2H), 1.47 – 1.37 (m, 2H), 1.35 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.8, 167.6, 152.3, 128.2, 127.0, 122.0, 121.2, 118.0, 65.2, 61.7, 60.6, 33.8, 30.6, 30.3, 29.7, 19.1, 14.1, 13.7; HRMS (ESI): *m/z* calcd for $C_{18}H_{23}O_5$ $[M+H]^+$ 319.1540, found 319.1545.

7b-Ethyl 1-(4-ethylphenyl) 1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate

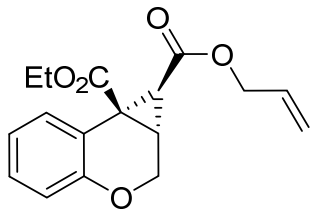


2f

(2f): colorless oil, 54.3 mg, 74% yield; R_f = 0.75 (10:1 v/v, PE:EA); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41 (dd, J = 7.8, 1.5 Hz, 1H), 7.14 – 7.10 (m, 3H), 6.97 – 6.89 (m, 3H), 6.82 (dd, J = 8.1, 1.1 Hz, 1H), 4.36 (dd, J = 11.2, 1.5 Hz, 1H), 4.26 – 4.16 (m, 2H), 4.02 (dd, J = 11.2, 1.2 Hz, 1H), 2.83 (dt, J = 5.5, 1.6 Hz, 1H),

2.67 (d, *J* = 5.6 Hz, 1H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.5, 167.4, 152.4, 148.6, 141.9, 128.8, 128.4, 127.2, 122.1, 121.1, 120.9, 118.1, 61.9, 60.5, 34.6, 30.2, 30.1, 28.3, 15.6, 14.2; HRMS (ESI): *m/z* calcd for $C_{22}H_{23}O_5$ $[M+H]^+$ 367.1540, found 367.1538.

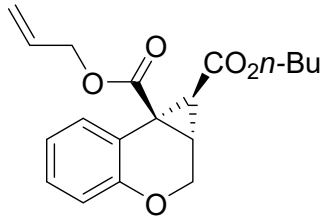
1-Allyl 7b-ethyl 1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2g):



2g

colorless oil, 49.1 mg, 81% yield; R_f = 0.70 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.16 (td, 7.8, 1.6 Hz, 1H), 6.95 (td, *J* = 7.6, 1.2 Hz, 1H), 6.86 (dd, *J* = 8.1, 1.2 Hz, 1H), 5.98 – 5.83 (m, 1H), 5.39 – 5.21 (m, 2H), 4.65 – 4.56 (m, 2H), 4.36 (dd, *J* = 11.2, 1.5 Hz, 1H), 4.28 (q, *J* = 7.1, 2H), 4.04 (dd, *J* = 11.2, 1.5 Hz, 1H), 2.80 (dt, *J* = 5.5, 1.6 Hz, 1H), 2.55 (d, *J* = 5.5 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.4, 167.5, 152.3, 131.8, 128.3, 127.0, 122.0, 121.1, 118.6, 118.0, 65.9, 61.7, 60.5, 34.0, 30.1, 29.8, 14.1; HRMS (ESI): *m/z* calcd for $C_{17}H_{19}O_5$ $[M+H]^+$ 303.1227, found 303.1229.

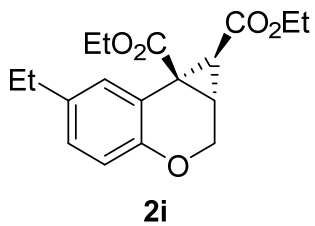
7b-Allyl 1-butyl 1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2h):



2h

colorless oil, 58.3 mg, 88% yield; R_f = 0.65 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.43 (d, *J* = 1.5 Hz, 1H), 7.14 (td, *J* = 7.8, 1.2 Hz, 1H), 6.93 (td, *J* = 7.6, 1.3 Hz, 1H), 6.83 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.00 – 5.90 (m, 1H), 5.35 (ddd, *J* = 17.2, 2.9, 1.5 Hz, 1H), 5.26 (ddd, *J* = 10.4, 2.4, 1.2 Hz, 1H), 4.70 (ddd, *J* = 5.9, 2.7, 1.4 Hz, 2H), 4.33 (dd, *J* = 11.2, 1.6 Hz, 1H), 4.13 – 4.04 (m, 2H), 4.02 (dd, *J* = 11.2, 1.2 Hz, 1H), 2.77 (dt, *J* = 5.5, 1.6 Hz, 1H), 2.50 (d, *J* = 5.6 Hz, 1H), 1.61 – 1.57 (m, 2H), 1.38 – 1.32 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 167.3, 152.3, 131.7, 128.5, 127.1, 122.0, 121.1, 119.0, 118.0, 66.4, 65.2, 60.6, 33.8, 30.6, 30.3, 29.8, 19.1, 13.7; HRMS (ESI): *m/z* calcd for $C_{19}H_{23}O_5$ $[M+H]^+$ 331.1540, found 331.1543.

Diethyl 6-ethyl-1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2i): yellow

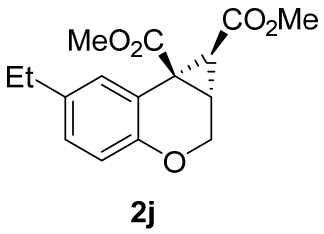


2i

oil, 50.4 mg, 79% yield; R_f = 0.80 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.25 (d, *J* = 2.0 Hz, 1H), 6.98 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 4.36 – 4.26 (m, 3H), 4.20 – 4.15 (m, 2H), 4.00 (dd, *J* = 11.0, 1.3 Hz, 1H), 2.76 (dt, *J* = 5.5, 1.5 Hz, 1H), 2.57 (q, *J* = 7.7 Hz, 2H), 2.50 (d, *J* = 5.5 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz,

$CDCl_3$): δ (ppm) 169.8, 167.7, 150.3, 137.8, 127.5, 126.2, 120.8, 117.7, 61.6, 61.2, 60.6, 34.0, 30.2, 29.7, 28.3, 15.7, 14.2, 14.1; HRMS (ESI): *m/z* calcd for $C_{18}H_{23}O_5$ $[M+H]^+$ 319.1540, found 319.1540.

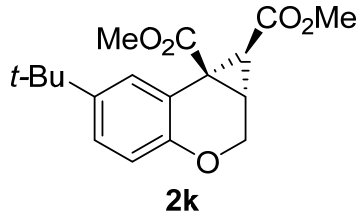
Dimethyl 6-ethyl-1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2j):



2j

colorless oil, 48.9 mg, 84% yield; R_f = 0.70 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.22 (d, *J* = 1.8 Hz, 1H), 6.99 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 4.32 (dd, *J* = 11.2, 1.3 Hz, 1H), 4.00 (dd, *J* = 11.1, 1.0 Hz, 1H), 3.83 (s, 3H), 3.72 (s, 3H), 2.77 (d, *J* = 5.5 Hz, 1H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.52 (d, *J* = 5.5 Hz, 1H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 170.3, 168.2, 150.2, 138.0, 127.7, 126.3, 120.5, 117.8, 60.6, 52.6, 52.3, 33.9, 30.1, 29.9, 28.3, 15.8; HRMS (ESI): *m/z* calcd for $C_{16}H_{19}O_5$ $[M+H]^+$ 291.1227, found 291.1225.

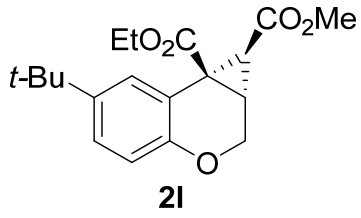
Dimethyl 6-(*tert*-butyl)-1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2k):



2k

white solid, 52.3 mg, 82% yield; m.p. 108–110 °C; R_f = 0.80 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (d, *J* = 2.4 Hz, 1H), 7.18 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 4.32 (dd, *J* = 11.2, 1.5 Hz, 1H), 4.01 (dd, *J* = 11.2, 1.4 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 2.77 (td, *J* = 5.5, 1.6 Hz, 1H), 2.52 (d, *J* = 5.6 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 170.3, 168.3, 149.9, 144.8, 125.4, 123.7, 120.0, 117.4, 60.6, 52.6, 52.3, 34.3, 33.9, 31.4, 30.1, 29.9; HRMS (ESI): *m/z* calcd for $C_{18}H_{23}O_5$ $[M+H]^+$ 319.1540, found 319.1541.

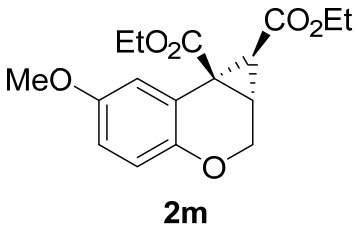
7b-Ethyl 1-methyl 6-(*tert*-butyl)-1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2l):



2l

colorless oil, 47.3 mg, 71% yield; R_f = 0.70 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.35 (dd, *J* = 7.7, 2.4 Hz, 1H), 7.11 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 4.29 – 4.20 (m, 2H), 3.94 (dd, *J* = 11.2, 1.6 Hz, 1H), 3.76 (s, 1H), 3.65 (s, 3H), 2.74 – 2.65 (m, 1H), 2.45 (d, *J* = 5.5 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 170.2, 167.8, 149.9, 144.7, 125.3, 123.8, 120.2, 117.4, 61.6, 60.6, 52.3, 34.4, 34.1, 31.4, 30.0, 29.8, 14.3; HRMS (ESI): *m/z* calcd for $C_{19}H_{25}O_5$ $[M+H]^+$ 333.1697, found 333.1696.

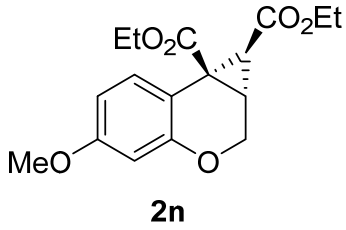
Diethyl 6-methoxy-1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2m):



2m

colorless oil, 48.2 mg, 75% yield; R_f = 0.85 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.02 (d, J = 2.9 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H), 6.71 (dd, J = 8.8, 2.9 Hz, 1H), 4.36 – 4.24 (m, 3H), 4.20 – 4.14 (m, 2H), 3.97 (dd, J = 11.1, 1.2 Hz, 1H), 3.75 (s, 3H), 2.76 (dt, J = 5.5, 1.6 Hz, 1H), 2.52 (d, J = 5.6 Hz, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 167.5, 154.4, 146.2, 121.8, 118.5, 113.6, 112.3, 61.7, 61.3, 60.7, 55.7, 34.0, 30.1, 29.6, 14.2; HRMS (ESI): *m/z* calcd for $C_{17}H_{21}O_6$ $[M+H]^+$ 321.1333, found 321.1329.

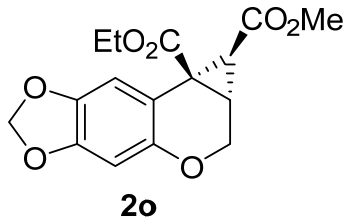
Diethyl 5-methoxy-1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2n):



2n

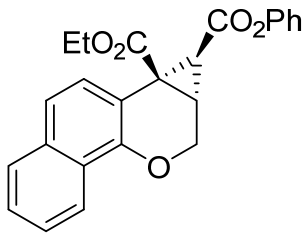
colorless oil, 55.9 mg, 87% yield; R_f = 0.65 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.27 (d, J = 8.6 Hz, 1H), 6.45 (dd, J = 8.6, 2.5 Hz, 1H), 6.35 (d, J = 2.5 Hz, 1H), 4.28 (d, J = 7.6 Hz, 1H), 4.24 – 4.18 (m, 2H), 4.12 – 4.06 (m, 2H), 3.99 (dd, J = 11.2, 1.3 Hz, 1H), 3.68 (s, 3H), 2.66 (d, J = 5.5 Hz, 1H), 2.34 (d, J = 5.5 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 167.8, 159.7, 153.4, 127.8, 113.3, 108.2, 103.4, 61.6, 61.2, 61.1, 55.4, 33.4, 30.6, 29.0, 14.2, 14.1; HRMS (ESI): *m/z* calcd for $C_{17}H_{21}O_6$ $[M+H]^+$ 321.1333, found 321.1333.

8b-Ethyl 1-methyl 1a, 2-dihydrocyclopropa[*c*][1,3]dioxolo[*4,5-g*]chromene-1,8b(1*H*)-dicarboxylate (2o): colorless oil, 52.0 mg, 81% yield; R_f = 0.65 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.94 (s, 1H), 6.40 (s, 1H), 5.90 (d, J = 1.9 Hz, 2H), 4.35 – 4.24 (m, 3H), 4.02 (dd, J = 11.2, 1.9 Hz, 1H), 3.71 (s, 3H), 2.72 (dt, J = 5.4, 1.8 Hz, 1H), 2.43 (d, J = 5.6 Hz, 1H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 170.1, 167.8, 147.6, 147.1, 142.4, 112.9, 106.6, 101.3, 100.0, 61.8, 61.2, 52.3, 33.8, 30.4, 29.0, 14.1; HRMS (ESI): *m/z* calcd for $C_{16}H_{17}O_7$ $[M+H]^+$ 321.0969, found 321.0971.



2o

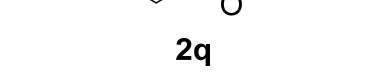
7a-Ethyl 7-phenyl 6a, 7-dihydrobenzo[*h*]cyclopropa[*c*]chromene-7, 7a(6*H*)-dicarboxylate (2p): colorless oil, 73.9 mg, 95% yield; R_f = 0.70 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.21 – 8.10 (m, 1H), 7.77 (dd, J = 6.7, 2.7 Hz, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.37 (t, J = 7.9 Hz, 2H), 7.23 – 7.19 (m, 1H), 7.14 (d, J =



2p

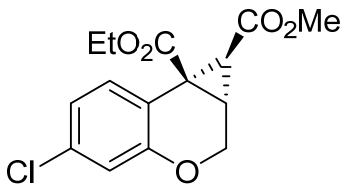
7.7 Hz, 2H), 4.63 (dd, *J* = 11.2, 1.5 Hz, 1H), 4.35 – 4.29 (m, 2H), 4.25 (dd, *J* = 11.2, 1.8 Hz, 1H), 3.02 (td, *J* = 5.5, 1.6 Hz, 1H), 2.80 (d, *J* = 5.6 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.2, 167.8, 150.7, 148.0, 133.5, 129.5, 127.6, 126.5, 126.0, 125.9, 125.4, 124.3, 121.7, 121.5, 121.3, 115.1, 62.0, 61.1, 34.5, 31.6, 30.6, 14.2; HRMS (ESI): *m/z* calcd for $C_{24}H_{21}O_5$ $[M+H]^+$ 389.1384, found 389.1383.

7b-Ethyl 1-methyl 6-phenyl-1a,2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2q): colorless oil, 62.9 mg, 89% yield; R_f = 0.80 (10:1 v/v, PE:EA); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (d, *J* = 2.2 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.45 – 7.39 (m, 3H), 7.37 – 7.31 (m, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 4.41 (dd, *J* = 11.2, 1.6 Hz, 1H), 4.38 – 4.26 (m, 2H), 4.11 (dd, *J* = 11.2, 1.3 Hz, 1H), 3.76 (s, 3H), 2.84 (dt, *J* = 5.6, 1.7 Hz, 1H), 2.59 (d, *J* = 5.7 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 170.1, 167.6, 151.8, 140.6, 135.3, 128.8, 127.0, 126.9, 126.8, 125.9, 121.2, 118.3, 61.8, 60.7, 52.3, 33.8, 30.3, 29.6, 14.2; HRMS (ESI): *m/z* calcd for $C_{21}H_{21}O_5$ $[M+H]^+$ 353.1384, found 353.1379.



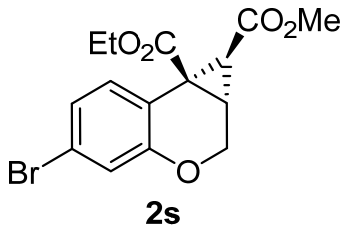
2q

7b-Ethyl 1-methyl 5-chloro-1a, 2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2r): colorless oil, 52.9 mg, 85% yield; R_f = 0.80 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, *J* = 8.4 Hz, 1H), 6.93 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.87 (d, *J* = 2.2 Hz, 1H), 4.36 (dd, *J* = 11.2, 1.5 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.05 (dd, *J* = 11.3, 1.4 Hz, 1H), 3.72 (s, 3H), 2.78 (d, *J* = 5.6 Hz, 1H), 2.47 (d, *J* = 5.6 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.8, 167.3, 152.9, 133.5 128.1, 122.2, 119.6, 118.3, 61.9, 60.8, 52.3, 33.2, 30.5, 29.3, 14.1; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}ClO_5$ $[M+H]^+$ 311.0681, found 311.0682.



2r

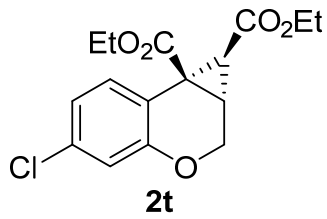
7b-Ethyl 1-methyl 5-bromo-1a,2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2s): colorless oil, 56.1 mg, 79% yield; R_f = 0.80 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26 (d, *J* = 8.3 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.96 (d, *J* = 1.5 Hz, 1H), 4.28 (d, *J* = 11.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.97 (d, *J* = 11.2 Hz,



2s

1H), 3.65 (s, 3H), 2.71 (d, *J* = 5.5 Hz, 1H), 2.39 (d, *J* = 5.6 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 167.3, 153.0, 128.4, 125.1, 121.2, 120.2, 61.9, 60.8, 52.3, 33.2, 30.4, 29.3, 14.1; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}BrO_5$ $[M+H]^+$ 355.0176, found 355.0160.

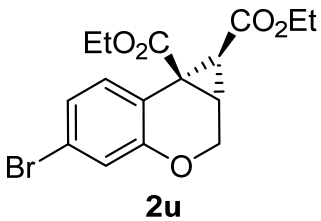
Diethyl 5-chloro-1a,2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2t):



2t

colorless oil, 61.1 mg, 94% yield; R_f = 0.70 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, *J* = 8.4 Hz, 1H), 6.93 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.87 (d, *J* = 2.1 Hz, 1H), 4.36 (dd, *J* = 11.2, 1.5 Hz, 1H), 4.31 – 4.25 (m, 2H), 4.20 – 4.14 (m, 2H), 4.04 (dd, *J* = 11.2, 1.4 Hz, 1H), 2.78 (dt, *J* = 5.6, 1.6 Hz, 1H), 2.45 (d, *J* = 5.6 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.26 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.3, 167.3, 152.9, 133.4, 128.1, 122.1, 119.7, 118.3, 61.8, 61.4, 60.8, 33.2, 30.6, 29.2, 14.2, 14.1; HRMS (ESI): *m/z* calcd for $C_{16}H_{18}ClO_5$ $[M+H]^+$ 325.0837, found 325.0833.

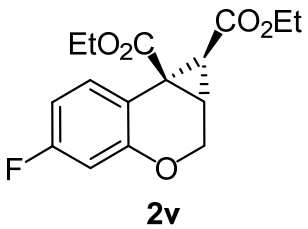
Diethyl 5-bromo-1a,2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2u):



2u

colorless oil, 62.0 mg, 84% yield; R_f = 0.80 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.34 (d, *J* = 8.4 Hz, 1H), 7.08 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.03 (d, *J* = 1.9 Hz, 1H), 4.37 – 4.34 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.20 – 4.14 (m, 2H), 4.04 (dd, *J* = 11.2, 1.6 Hz, 1H), 2.78 (dt, *J* = 5.6, 1.6 Hz, 1H), 2.46 (d, *J* = 5.6 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.3, 167.3, 153.0, 128.4, 125.1, 121.2, 121.1, 120.3, 61.8, 61.4, 60.8, 33.2, 30.5, 29.3, 14.2, 14.1; HRMS (ESI): *m/z* calcd for $C_{16}H_{18}BrO_5$ $[M+H]^+$ 369.0332, found 369.0330.

Diethyl 5-fluoro-1a,2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2v):

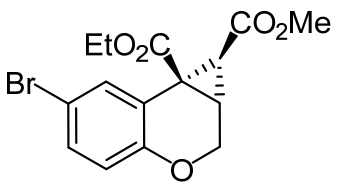


2v

colorless oil, 48.8 mg, 79% yield; R_f = 0.70 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.43 (dd, *J* = 8.7, 6.3 Hz, 1H), 6.67 (td, *J* = 8.5, 2.6 Hz, 1H), 6.59 (dd, *J* = 9.6, 2.6 Hz, 1H), 4.35 (dd, *J* = 11.3, 1.0 Hz, 1H), 4.31 – 4.25 (m, 2H), 4.20 – 4.14 (m, 2H), 4.06 (dd, *J* = 11.2, 1.4 Hz, 1H), 2.76 (d, *J* = 5.6 Hz, 1H), 2.42 (d, *J* = 5.6 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.4, 167.5, 162.2 (d, *J* = 246.4 Hz), 153.4 (d, *J* = 11.9 Hz), 128.2 (d, *J* = 9.7 Hz), 116.9 (d, *J* = 3.4 Hz), 109.0 (d, *J* = 22.2 Hz), 105.5 (d, *J* = 25.3 Hz), 61.7, 61.3, 61.0,

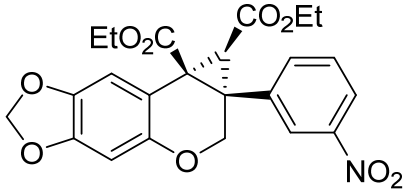
33.1, 30.6, 29.0, 14.2, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) 136.9; HRMS (ESI): *m/z* calcd for $C_{16}H_{18}FO_5$ $[M+H]^+$ 309.1133, found 309.1131.

7b-Ethyl 1-methyl 6-bromo-1a,2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2w): colorless oil, 51.1 mg, 72% yield; R_f = 0.80 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (d, *J* = 2.4 Hz, 1H), 7.25 (d, *J* = 2.4 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 4.35 (dd, *J* = 11.3, 1.6 Hz, 1H), 4.33 – 4.27 (m, 2H), 4.02 (dd, *J* = 11.2, 1.3 Hz, 1H), 3.72 (s, 3H), 2.79 (dt, *J* = 5.7, 1.6 Hz, 1H), 2.49 (d, *J* = 5.7 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 167.1, 151.4, 131.2, 130.0, 123.0, 119.7, 114.2, 62.0, 60.6, 52.4, 33.2, 30.4, 29.4, 14.1; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}BrO_5$ $[M+H]^+$ 355.0176, found 355.0180.



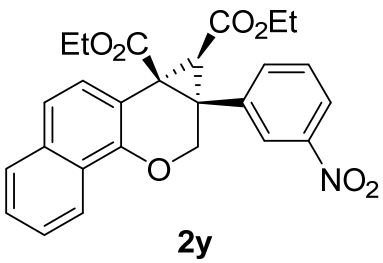
2w

Diethyl 1a-(3-nitrophenyl)-1a,2-dihydrocyclopropa[*c*][1,3]dioxolo[4,5-g]chromene-1,8b(1*H*)-dicarboxylate (2x): yellow solid, 62.0 mg, 68% yield; m.p. 145–148 °C; R_f = 0.60 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.37 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 6.81 (s, 1H), 6.47 (s, 1H), 5.95 (s, 2H), 4.27 – 4.02 (m, 5H), 3.80 (d, *J* = 11.3 Hz, 1H), 3.07 (s, 1H), 1.25 – 1.19 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.1, 166.2, 147.9, 147.8, 147.4, 142.9, 137.6, 134.5, 128.7, 126.2, 122.9, 114.5, 106.7, 101.5, 100.0, 68.9, 61.8, 61.3, 43.8, 38.9, 31.4, 14.1, 13.8; HRMS (ESI): *m/z* calcd for $C_{23}H_{22}NO_9$ $[M+H]^+$ 456.1289, found 456.1289.

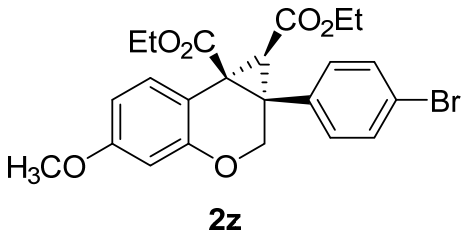


2x

Diethyl 6a-(3-nitrophenyl)-6a,7-dihydrobenzo[*h*]cyclopropa[*c*]chromene-7,7a(6H)-dicarboxylate (2y): colorless oil, 54.5 mg, 59% yield; R_f = 0.50 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.44 (t, *J* = 1.8 Hz, 1H), 8.22 – 8.10 (m, 2H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.83 – 7.80 (m, 1H), 7.58 – 7.48 (m, 4H), 7.43 (d, *J* = 8.7 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 4.30 – 4.20 (m, 2H), 4.18 – 4.11 (m, 2H), 4.00 (d, *J* = 11.2 Hz, 1H), 3.22 (s, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 167.9, 166.4, 148.2, 147.9, 137..7, 134.6, 133.4, 128.8, 127.5, 126.7, 126.2, 126.1, 125.1, 124.2, 123.0, 121.8, 121.5, 117.0, 68.7, 61.8, 61.3, 45.1, 38.8, 32.3, 14.1, 13.9; HRMS (ESI): *m/z* calcd for $C_{26}H_{24}NO_7$ $[M+H]^+$ 462.1547, found 462.1545.

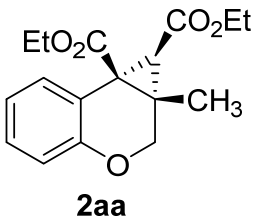


2y

Diethyl 1a-(4-bromophenyl)-5-methoxy-1a,2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2z): 

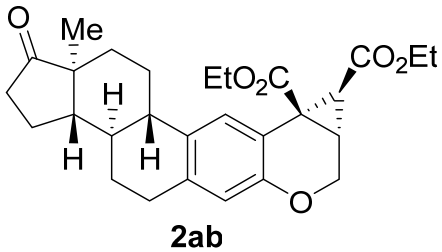
2z

colorless oil, 77.0 mg, 81% yield; R_f = 0.70 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.47 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 7.26 (s, 1H), 6.60 (dd, J = 8.6, 2.6 Hz, 1H), 6.44 (d, J = 2.6 Hz, 1H), 4.52 (d, J = 11.7 Hz, 1H), 4.16 (d, J = 11.7 Hz, 1H), 4.09 – 4.02 (m, 2H), 3.93 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.49 (s, 1H), 1.10 (t, J = 7.1 Hz, 3H), 0.96 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 167.1, 165.5, 158.8, 152.6, 131.7, 130.5, 130.1, 126.8, 121.0, 114.1, 107.6, 102.3, 67.8, 60.3, 59.9, 54.4, 43.1, 37.4, 30.5, 13.1, 12.9; HRMS (ESI): *m/z* calcd for $C_{23}H_{24}BrO_6$ $[M+H]^+$ 475.0751, found 475.0741.

Diethyl 1a-methyl-1a,2-dihydrocyclopropa[*c*]chromene-1,7b(1*H*)-dicarboxylate (2aa): 

2aa

colorless oil, 30.3 mg, 31% yield; R_f = 0.65 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.15 (dd, J = 7.8, 1.5 Hz, 1H), 7.08 (td, J = 8.0, 1.6 Hz, 1H), 6.87 (td, J = 7.6, 1.2 Hz, 1H), 6.78 (dd, J = 8.1, 1.1 Hz, 1H), 4.33 – 4.21 (m, 2H), 4.12 – 4.05 (m, 3H), 3.65 (d, J = 11.0 Hz, 1H), 2.55 (s, 1H), 1.47 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.9, 166.8, 152.4, 127.9, 126.9, 123.0, 122.1, 117.8, 66.8, 61.4, 60.7, 38.0, 35.0, 30.9, 14.2, 14.1, 11.2; HRMS (ESI): *m/z* calcd for $C_{17}H_{20}NaO_5$ $[M+Na]^+$ 327.1203, found 327.1207.

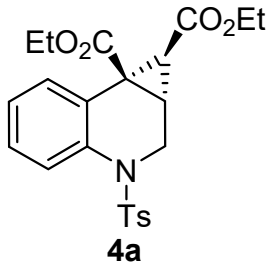
Diethyl (3a*S*,3b*R*,10b*S*,12a*S*)-12a-methyl-1-oxo-2, 3, 3a, 3b, 4, 5, 8a, 9, 10b, 11, 12, 12a-dodecahydro -1*H*- cyclopenta [5,6] naphtha [1,2-*g*]cyclopropa [*c*] chromene-9,9a (8*H*)-dicarboxylate (2ab): 

2ab

white solid, 21.4 mg, 46% yield; m.p. 118–120 °C; R_f = 0.30 (PE:EA 8:1, v/v); a diastereomeric mixture with dr 1:1; ^{1}H NMR (400 MHz, $CDCl_3$): (ppm) δ 7.38 (d, J = 6.1 Hz, 1H), 6.60 (s, 1H), 4.41 – 4.22 (m, 3H), 4.22 – 4.08 (m, 2H), 4.01 (dd, J = 10.5, 4.0 Hz, 1H), 2.84 (dd, J = 9.1, 5.7 Hz, 2H), 2.78 – 2.66 (m, 1H), 2.60 – 2.41 (m, 2H), 2.40 – 2.29 (m, 1H), 2.06 (dddd, J = 30.1, 16.8, 12.5, 6.9 Hz, 5H), 1.69 – 1.45 (m, 6H), 1.33 (td, J = 7.1, 1.8 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H), 0.90 (d, J = 8.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): (ppm) δ 220.9, 220.8, 169.7, 169.6, 167.7, 167.6, 150.2, 150.1, 136.9, 133.5, 124.0, 123.8, 118.4, 118.3, 117.8, 117.7, 61.6, 61.5, 61.2,

50.4, 48.0, 44.1, 38.2, 38.1, 35.9, 33.8, 33.7, 31.5, 30.5, 30.4, 29.1, 29.0, 26.5, 26.4, 25.9, 25.8, 21.6, 14.2, 14.1, 13.8; HRMS (ESI): *m/z* calcd for $C_{28}H_{35}O_6$ $[M+H]^+$ 467.2428, found 467.2429.

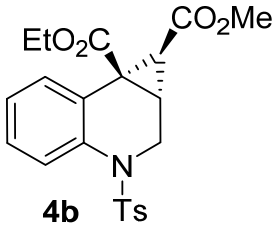
Diethyl 3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4a):



4a

yellow solid, 76.4 mg, 86% yield; m.p. 134–136°C; R_f = 0.40 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.62 (dd, J = 8.2, 3.2 Hz, 3H), 7.52 (dd, J = 7.8, 1.1 Hz, 1H), 7.28 (d, J = 8.8 Hz, 3H), 7.20 – 7.17 (m, 1H), 4.18 – 4.05 (m, 5H), 3.95 (dd, J = 8.7, 4.1 Hz, 1H), 2.69 (dd, J = 9.3, 4.0 Hz, 1H), 2.43 (s, 3H), 1.84 (d, J = 5.5 Hz, 1H), 1.28 – 1.23 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.9, 167.6, 143.9, 136.9, 134.8, 130.0, 128.8, 127.8, 127.1, 127.0, 125.8, 125.2, 61.6, 61.3, 43.7, 33.8, 33.5, 29.0, 21.6, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{23}H_{26}NO_6S$ $[M+H]^+$ 444.1475, found 444.1470.

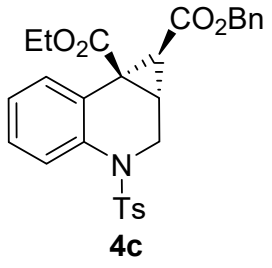
7b-Ethyl 1-methyl 3-tosyl-1, 1a, 2, 3-tetrahydro-7b*H*-cyclopropa[c]quinoline-1,7b-dicarboxylate (4b):



4b

yellow solid, 82.3 mg, 91% yield; m.p. 123–125°C; R_f = 0.35 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (d, J = 8.2 Hz, 3H), 7.50 (dd, J = 7.8, 1.5 Hz, 1H), 7.29 – 7.26 (m, 3H), 7.17 (td, J = 7.7, 1.1 Hz, 1H), 4.08 (q, J = 7.0 Hz, 2H), 4.05 – 3.86 (m, 2H), 3.66 (s, 3H), 2.66 (dd, J = 9.6, 4.2 Hz, 1H), 2.40 (s, 3H), 1.83 (d, J = 5.6 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.3, 167.7, 143.9, 136.8, 134.9, 130.0, 128.9, 127.8, 127.0, 126.0, 125.9, 125.4, 61.6, 52.3, 43.9, 33.7, 33.6, 28.7, 21.6, 13.9; HRMS (ESI): *m/z* calcd for $C_{22}H_{23}NNaO_6S$ $[M+Na]^+$ 452.1138, found 452.1142.

1-Benzyl 7b-ethyl 3-tosyl-1, 1a, 2, 3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1, 7b-dicarboxylate (4c):

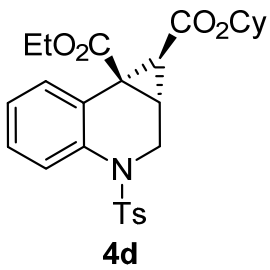


4c

yellow oil, 93.1 mg, 92% yield; R_f = 0.40 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57 (d, J = 8.1 Hz, 1H), 7.49 (d, J = 8.2 Hz, 2H), 7.41 (dd, J = 7.8, 1.2 Hz, 1H), 7.35 – 7.21 (m, 5H), 7.19 – 7.14 (m, 1H), 7.11 – 7.06 (m, 3H), 5.00 (s, 2H), 4.03 (dd, J = 14.5, 3.8 Hz, 1H), 3.98 – 3.92 (m, 2H), 3.86 (dd, J = 14.5, 4.1 Hz, 1H), 2.62 (dd, J = 9.4, 4.0 Hz, 1H), 2.21 (s, 3H), 1.74 (d, J = 5.5 Hz, 1H), 1.10 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.8, 167.6, 143.9, 136.7, 135.5, 134.8, 130.0, 128.8, 128.6, 128.4, 127.9, 127.0, 126.9, 125.8, 125.3, 67.1,

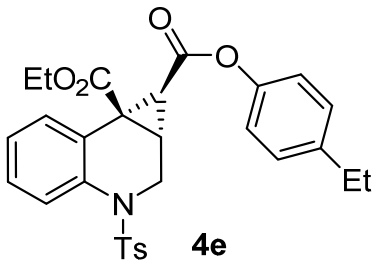
61.6, 43.6, 34.0, 33.4, 29.2, 21.4, 13.9; HRMS (ESI): *m/z* calcd for $C_{28}H_{28}NO_6S$ $[M+H]^+$ 506.1632, found 506.1623.

1-Cyclohexyl 7b-ethyl 3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4d): colorless oil, 89.7 mg, 90% yield; R_f = 0.40 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63 – 7.59 (m, 3H), 7.49 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.27 – 7.22 (m, 3H), 7.17 – 7.13 (m, 1H), 4.72 – 4.67 (m, 1H), 4.17 – 4.04 (m, 3H), 3.90 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.67 (dd, *J* = 9.2, 3.9 Hz, 1H), 2.40 (s, 3H), 1.83 (d, *J* = 5.5 Hz, 1H), 1.81 – 1.76 (m, 2H), 1.75 – 1.68 (m, 2H), 1.57 – 1.50 (m, 1H), 1.41 – 1.31 (m, 4H), 1.30 – 1.25 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.4, 167.6, 143.8, 136.9, 134.8, 130.0, 128.7, 127.7, 127.1, 127.0, 125.7, 125.1, 73.8, 61.6, 43.6, 33.9, 33.6, 31.6, 31.5, 29.0, 25.3, 23.8, 23.7, 21.6, 14.0; HRMS (ESI): *m/z* calcd for $C_{27}H_{32}NO_6S$ $[M+H]^+$ 498.1945, found 498.1944.



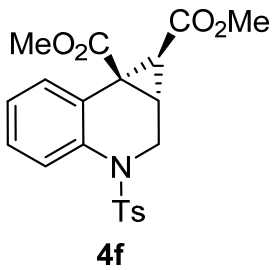
4d

7b-Ethyl 1-(4-ethylphenyl) 3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4e): colorless oil, 87.4 mg, 84% yield; R_f = 0.50 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 – 7.65 (m, 3H), 7.52 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.18 (d, *J* = 8.3 Hz, 3H), 6.95 (d, *J* = 8.5 Hz, 2H), 4.20 (dd, *J* = 14.5, 3.7 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.95 (dd, *J* = 14.5, 3.9 Hz, 1H), 2.77 (d, *J* = 5.5 Hz, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 1.98 (d, *J* = 5.6 Hz, 1H), 1.27 – 1.22 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 167.7, 167.5, 148.5, 144.1, 141.9, 136.8, 134.8, 130.1, 128.8, 128.7, 128.0, 127.0, 126.7, 125.9, 125.3, 121.0, 61.9, 43.4, 34.6, 33.2, 29.6, 28.3, 21.6, 15.5, 14.0; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}NO_6S$ $[M+H]^+$ 520.1788, found 520.1783.



4e

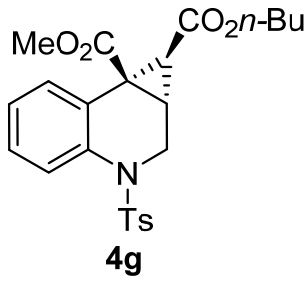
Dimethyl 3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4f): white solid, 82.4 mg, 94% yield; m.p. 147–149 °C; R_f = 0.50 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66 – 7.54 (m, 3H), 7.51 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.27 – 7.22 (m, 3H), 7.21 – 7.15 (m, 1H), 4.09 (dd, *J* = 14.7, 4.9 Hz, 1H), 3.92 (dd, *J* = 14.7, 4.3 Hz, 1H), 3.66 (s, 3H), 3.59 (s, 3H), 2.63 (dd, *J* = 10.0, 4.8 Hz, 1H), 2.41 (s, 3H), 1.83 (d, *J* = 5.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.4, 168.2, 143.9, 136.7, 135.1, 130.0, 129.1, 128.0, 127.1, 127.0, 126.1, 125.7, 52.6,



4f

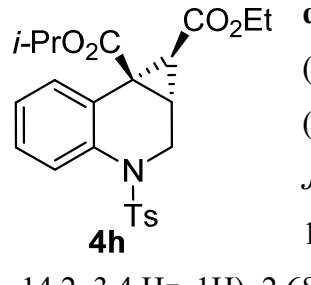
52.4, 44.5, 34.3, 33.3, 28.2, 21.6; HRMS (ESI): *m/z* calcd for $C_{21}H_{21}NNaO_6S$ $[M+Na]^+$ 438.0982, found 438.0986.

1-Butyl 7b-methyl 3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4g): colorless oil, 79.8 mg, 84% yield; R_f = 0.40 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65 (dd, J = 8.1, 0.8 Hz, 1H), 7.60 (d, J = 8.3 Hz, 2H), 7.54 (dd, J = 7.8, 1.4 Hz, 1H), 7.29 – 7.25 (m, 3H), 7.20 (td, J = 7.6, 1.1 Hz, 1H), 4.17 – 4.07 (m, 2H), 4.04 – 3.97 (m, 2H), 3.62 (s, 3H), 2.66 (dd, J = 9.8, 4.7 Hz, 1H), 2.43 (s, 3H), 1.87 (d, J = 5.5 Hz, 1H), 1.64 – 1.57 (m, 2H), 1.41 – 1.36 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.0, 168.2, 143.8, 136.8, 135.1, 129.9, 129.1, 127.9, 127.1, 127.0, 126.0, 125.6, 65.3, 52.5, 44.4, 34.3, 33.4, 30.6, 28.3, 21.6, 19.0, 13.7; HRMS (ESI): *m/z* calcd for $C_{24}H_{31}N_2O_6S$ $[M+NH_4]^+$ 475.1897, found 475.1894.



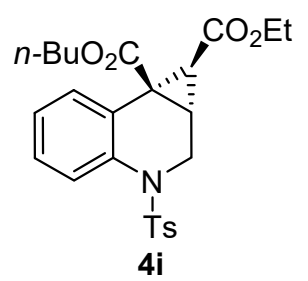
4g

1-Ethyl 7b-isopropyl 3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4h): yellow oil, 84.3 mg, 92% yield; R_f = 0.40 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63 – 7.58 (m, 3H), 7.47 (dd, J = 7.8, 1.4 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.22 (dd, J = 8.1, 1.4 Hz, 1H), 7.14 (td, J = 7.7, 1.1 Hz, 1H), 5.04 – 4.94 (m, 1H), 4.23 (dd, J = 14.3, 3.3 Hz, 1H), 4.10 (q, J = 7.1, 2H), 3.77 (dd, J = 14.2, 3.4 Hz, 1H), 2.68 (dt, J = 6.5, 3.3 Hz, 1H), 2.41 (s, 3H), 1.81 (d, J = 5.5 Hz, 1H), 1.27 (d, J = 6.4 Hz, 3H), 1.24 (d, J = 6.4 Hz, 3H), 1.20 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.0, 167.0, 143.9, 137.1, 134.6, 130.0, 128.2, 127.6, 127.0, 126.9, 125.6, 124.8, 69.4, 61.2, 42.8, 34.4, 32.5, 29.7, 21.8, 21.6, 21.5, 14.2; HRMS (ESI): *m/z* calcd for $C_{24}H_{28}NO_6S$ $[M+H]^+$ 458.1632, found 458.1631.



4h

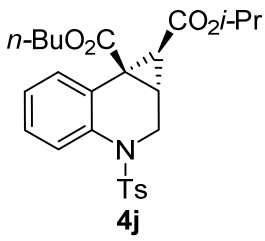
7b-Butyl 1-ethyl 3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4i): colorless oil, 85.0 mg, 90% yield; R_f = 0.40 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (d, J = 8.2 Hz, 3H), 7.48 (dd, J = 7.8, 1.2 Hz, 1H), 7.27 – 7.23 (m, 3H), 7.20 – 7.16 (m, 1H), 4.14 – 4.06 (m, 3H), 4.03 (t, J = 6.8 Hz, 2H), 3.92 (dd, J = 14.4, 4.1 Hz, 1H), 2.66 (dd, J = 9.4, 4.0 Hz, 1H), 2.43 (s, 3H), 1.85 (d, J = 5.6 Hz, 1H), 1.62 – 1.53 (m, 2H), 1.39 – 1.31 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ



4i

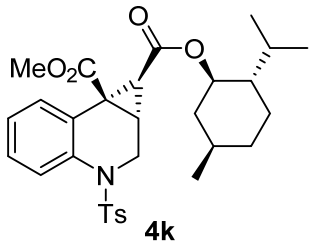
(ppm) 168.9, 167.7, 143.9, 136.9, 134.8, 130.0, 128.8, 127.8, 127.1, 127.0, 125.8, 125.2, 65.6, 61.3, 43.7, 33.9, 33.5, 30.4, 29.0, 21.6, 19.1, 14.2, 13.7; HRMS (ESI): *m/z* calcd for $C_{25}H_{30}NO_6S$ $[M+H]^+$ 472.1788, found 472.1783.

7b-Butyl 1-isopropyl -3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4j): yellow oil, 83.6 mg, 86% yield; R_f = 0.50 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (dd, J = 8.7, 2.0 Hz, 3H), 7.47 (dd, J = 7.8, 1.5 Hz, 1H), 7.27 – 7.21 (m, 3H), 7.15 (td, J = 7.6, 1.3 Hz, 1H), 5.01 – 4.85 (m, 1H), 4.13 (dd, J = 14.4, 3.7 Hz, 1H), 4.03 (t, J = 6.8 Hz, 2H), 3.89 (dd, J = 14.4, 4.0 Hz, 1H), 2.66 (dt, J = 5.5, 3.8 Hz, 1H), 2.41 (s, 3H), 1.80 (d, J = 5.6 Hz, 1H), 1.62 – 1.55 (m, 2H), 1.40 – 1.31 (m, 2H), 1.22 (d, J = 6.3 Hz, 3H), 1.20 (d, J = 6.3 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.4, 167.7, 143.8, 136.9, 134.8, 130.0, 128.7, 127.7, 127.1, 127.0, 125.7, 125.1, 68.8, 65.6, 43.5, 34.0, 33.5, 30.4, 29.1, 21.8, 21.7, 21.6, 19.1, 13.7; HRMS (ESI): *m/z* calcd for $C_{26}H_{32}NO_6S$ $[M+H]^+$ 486.1945, found 486.1950.



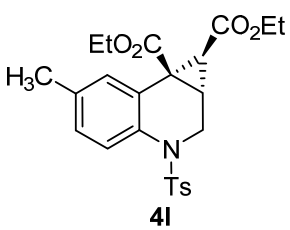
4j

1-((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl) 7b-methyl 3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4k): colorless oil, 92.9 mg, 86% yield; R_f = 0.50 (PE:EA 10:1, v/v); a diastereomeric mixture with dr 1:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 – 7.57 (m, 3H), 7.55 – 7.51 (m, 1H), 7.29 – 7.23 (m, 3H), 7.23 – 7.16 (m, 1H), 4.70 – 4.60 (m, 1H), 4.26 – 3.90 (m, 2H), 3.61 (s, 3H), 2.72 – 2.57 (m, 1H), 2.43 (s, 3H), 2.03 – 1.77 (m, 3H), 1.72 – 1.66 (m, 2H), 1.52 – 1.43 (m, 1H), 1.39 – 1.31 (m, 1H), 1.11 – 1.02 (m, 1H), 0.96 – 0.87 (m, 8H), 0.76 (d, J = 6.9, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.6, 168.0, 143.8, 143.7, 136.8, 136.7, 130.0, 129.9, 129.3, 129.0, 127.9, 127.8, 127.2, 127.1, 126.0, 125.9, 125.5, 125.4, 75.4, 75.3, 52.5, 52.4, 47.0, 46.9, 44.7, 44.2, 40.9, 40.8, 34.7, 34.2, 33.7, 33.3, 31.4, 31.3, 28.4, 27.8, 26.1, 23.4, 23.3, 22.0, 21.7, 21.6, 20.9, 20.7, 16.4, 16.3; HRMS (ESI): *m/z* calcd for $C_{30}H_{38}NO_6S$ $[M+H]^+$ 540.2414, found 540.2406.



4k

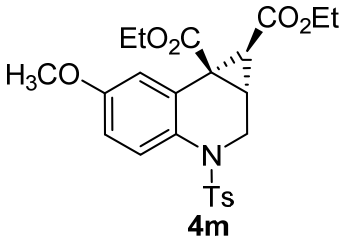
Diethyl 6-methyl-3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4l): yellow oil, 78.8 mg, 86% yield; R_f = 0.40 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.3 Hz, 1H), 7.21 (d, J = 1.7 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.01 – 6.94 (m, 1H), 4.05 – 3.95 (m, 5H), 3.86



4l

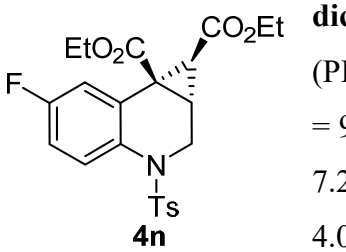
(dd, J = 14.5, 4.3 Hz, 1H), 2.55 (dt, J = 5.5, 4.1 Hz, 1H), 2.32 (s, 3H), 2.23 (s, 3H), 1.66 (d, J = 5.6 Hz, 1H), 1.18 – 1.13 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.9, 167.7, 143.7, 136.9, 135.7, 132.2, 130.0, 129.2, 128.6, 127.0, 126.8, 125.2, 61.5, 61.2, 60.4, 43.8, 33.7, 28.7, 21.6, 21.1, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{24}H_{28}NO_6S$ $[M+H]^+$ 458.1632, found 458.1638.

Diethyl 6-methoxy-3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4m): colorless oil, 89.1 mg, 94% yield; R_f = 0.50 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.54 (d, J = 8.7 Hz, 3H), 7.24 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 2.9 Hz, 1H), 6.81 (dd, J = 9.0, 3.0 Hz, 1H), 4.14 – 4.01 (m, 5H), 3.93 (dd, J = 14.8, 4.1 Hz, 1H), 3.79 (s, 3H), 2.58 (dd, J = 10.0, 4.6 Hz, 1H), 2.40 (s, 3H), 1.69 (d, J = 5.7 Hz, 1H), 1.25 – 1.20 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.8, 167.5, 157.3, 143.7, 136.7, 129.9, 128.4, 127.7, 127.1, 114.1, 113.5, 61.5, 61.3, 55.5, 44.5, 34.6, 33.5, 27.9, 21.6, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{24}H_{28}NO_7S$ $[M+H]^+$ 474.1581, found 474.1578.



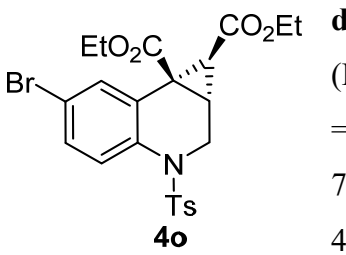
4m

Diethyl 6-fluoro-3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4n): yellow oil, 69.3 mg, 75% yield; R_f = 0.40 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (dd, J = 9.1, 5.3 Hz, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 3.0 Hz, 1H), 7.25 (d, J = 4.2 Hz, 2H), 7.02 – 6.94 (m, 1H), 4.13 – 4.04 (m, 4H), 4.00 (dd, J = 6.5, 4.4 Hz, 2H), 2.63 (dd, J = 10.0, 4.4 Hz, 1H), 2.41 (s, 3H), 1.73 (d, J = 5.7 Hz, 1H), 1.25 – 1.21 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.4, 167.1, 160.1 (d, J = 246.4 Hz), 144.0, 136.5, 130.8 (d, J = 2.0 Hz), 130.0, 129.2 (d, J = 8.1 Hz), 127.5 (d, J = 8.1 Hz), 127.1, 115.9 (d, J = 24.2 Hz), 114.9 (d, J = 23.2 Hz), 61.7, 61.3, 43.9, 33.8, 33.2, 28.4, 21.6, 14.2, 13.9; ^{19}F NMR (376 MHz, $CHCl_3$): δ (ppm) -115.3; HRMS (ESI): *m/z* calcd for $C_{23}H_{25}FNO_6S$ $[M+H]^+$ 462.1381, found 462.1376.



4n

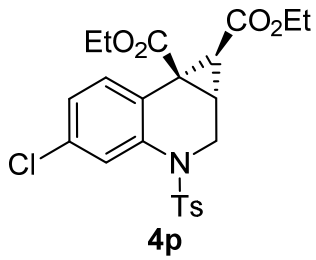
Diethyl 6-bromo-3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4o): colorless oil, 76.2 mg, 73% yield; R_f = 0.45 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 (d, J = 2.3 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.39 (dd, J = 8.8, 2.3 Hz, 1H), 7.30 (s, 1H), 7.27 (s, 1H), 4.15 – 4.11 (m, 4H), 4.07 – 4.02 (m, 1H), 3.97 (dd, J = 14.6, 4.4 Hz, 1H),



4o

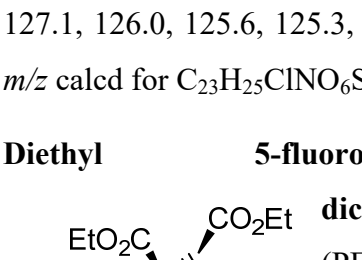
2.69 – 2.61 (m, 1H), 2.43 (s, 3H), 1.74 (d, J = 5.7 Hz, 1H), 1.28 – 1.22(m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.5, 167.1, 144.2, 136.4, 133.9, 131.8, 130.9, 130.1, 129.0, 127.0, 126.9, 119.2, 61.8, 61.4, 43.7, 34.0, 33.2, 28.5, 21.6, 14.2, 13.9; HRMS (ESI): *m/z* calcd for $C_{23}H_{25}BrNO_6S$ $[M+H]^+$ 522.0580, found 522.0572.

Diethyl 5-chloro-3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[c]quinoline-1,7b-dicarboxylate (4p): yellow oil, 83.2 mg, 87% yield; R_f = 0.40 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, J = 1.9 Hz, 1H), 7.63 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.5 Hz, 1H), 7.30 (d, J = 7.1 Hz, 2H), 7.16 (dd, J = 8.4, 2.0 Hz, 1H), 4.19 – 4.08 (m, 4H), 4.04 (d, J = 3.9 Hz, 1H), 3.96 (dd, J = 14.6, 4.3 Hz, 1H), 2.67 (dd, J = 9.5, 4.1 Hz, 1H), 2.44 (s, 3H), 1.76 (d, J = 5.6 Hz, 1H), 1.28 – 1.22 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.6, 167.3, 144.2, 136.4, 135.9, 133.4, 130.1, 129.9, 127.1, 126.0, 125.6, 125.3, 61.7, 61.4, 43.8, 33.8, 33.2, 28.6, 21.6, 14.2, 13.9; HRMS (ESI): *m/z* calcd for $C_{23}H_{25}ClNO_6S$ $[M+H]^+$ 478.1086, found 478.1079.



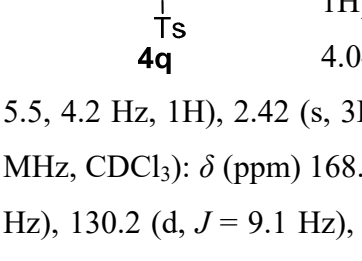
4p

Diethyl 5-fluoro-3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4q): yellow oil, 84.1 mg, 91% yield; R_f = 0.50 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65 – 7.56 (m, 2H), 7.49 (dd, J = 8.8, 6.1 Hz, 1H), 7.42 (dd, J = 10.4, 2.7 Hz, 1H), 7.30 – 7.27 (m, 2H), 6.92 – 6.87 (m, 1H), 4.14 – 4.06 (m, 4H), 4.04 (d, J = 4.0 Hz, 1H), 3.98 (dd, J = 14.6, 4.4 Hz, 1H), 2.65 (dt, J = 5.5, 4.2 Hz, 1H), 2.42 (s, 3H), 1.73 (d, J = 5.6 Hz, 1H), 1.27 – 1.21 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.7, 167.5, 161.4 (d, J = 247.5 Hz), 144.2, 136.4, 136.2 (d, J = 11.1 Hz), 130.2 (d, J = 9.1 Hz), 130.1, 127.0 (d, J = 2.0 Hz), 122.8 (d, J = 3.0 Hz), 113.0 (d, J = 22.2 Hz), 112.6 (d, J = 25.3 Hz), 61.7, 61.3, 43.9, 33.8, 33.2, 28.4, 21.6, 14.2, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -111.9; HRMS (ESI): *m/z* calcd for $C_{23}H_{25}FNO_6S$ $[M+H]^+$ 462.1381, found 462.1378.



4q

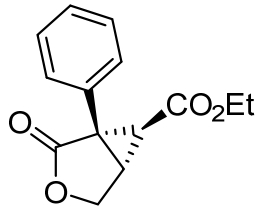
Diethyl 5-methoxy-3-tosyl-1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (4r): yellow oil, 81.6 mg, 86% yield; R_f = 0.50 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.7 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 2.6 Hz, 1H), 6.74 (dd, J = 8.7, 2.7 Hz, 1H), 4.16 – 4.01 (m, 5H), 3.98 (d, J = 4.3 Hz, 1H), 3.79 (s, 3H), 2.58



4r

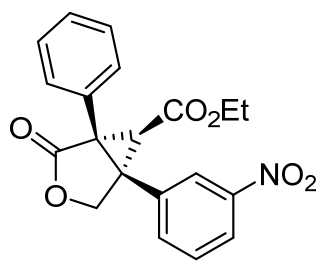
(dd, J = 10.0, 4.5 Hz, 1H), 2.40 (s, 3H), 1.70 (d, J = 5.6 Hz, 1H), 1.25 – 1.19 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.9, 167.8, 158.8, 143.9, 136.7, 136.0, 130.0, 129.7, 127.1, 119.2, 112.4, 110.5, 61.5, 61.2, 55.5, 44.5, 34.4, 33.1, 27.7, 21.6, 14.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{24}H_{28}NO_7S$ $[M+H]^+$ 474.1581, found 474.1580.

Ethyl 2-oxo-1-phenyl-3-oxabicyclo[3.1.0]hexane-6-carboxylate (6a): yellow oil, 35.6 mg, 72% yield; R_f = 0.80 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.45 – 7.40 (m, 2H), 7.36 (d, J = 6.8 Hz, 3H), 4.56 (dd, J = 9.7, 4.2 Hz, 1H), 4.40 (d, J = 9.7 Hz, 1H), 3.93 (q, J = 7.1 Hz, 2H), 3.28 (t, J = 3.9 Hz, 1H), 2.37 (d, J = 3.7 Hz, 1H), 1.00 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 173.7, 166.7, 130.1, 129.2, 128.6, 128.4, 67.7, 61.3, 39.1, 31.6, 27.5, 13.9; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}O_4$ $[M+H]^+$ 247.0965, found 247.0966.



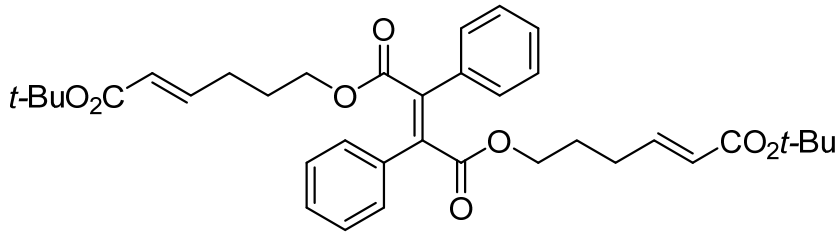
6a

Ethyl 5-(3-nitrophenyl)-2-oxo-1-phenyl-3-oxabicyclo[3.1.0]hexane-6-carboxylate (6b): yellow oil, 40.8 mg, 53% yield; R_f = 0.70 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15 – 8.05 (m, 2H), 7.54 (d, J = 7.9 Hz, 1H), 7.46 (t, J = 8.1 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.24 – 7.20 (m, 2H), 4.87 (d, J = 10.3 Hz, 1H), 4.67 (d, J = 10.2 Hz, 1H), 4.39 – 4.29 (m, 2H), 3.36 (s, 1H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 172.5, 166.4, 148.4, 136.1, 135.1, 130.1, 129.8, 129.4, 129.0, 128.9, 124.1, 123.6, 70.4, 62.4, 46.1, 45.3, 33.1, 14.1; HRMS (ESI): *m/z* calcd for $C_{20}H_{21}N_2O_6$ $[M+NH_4]^+$ 385.1394, found 385.1396.



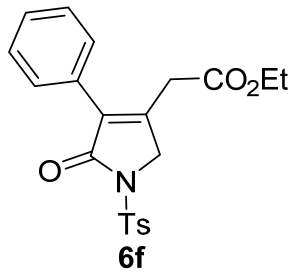
6b

Bis((*E*)-6-(tert-butoxy)-6-oxohex-4-en-1-yl) 2,3-diphenylfumarate (6e): colorless oil, 46.0 mg, 76% yield; R_f = 0.65 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36 – 7.29 (m, 4H), 7.19 – 7.09 (m, 6H), 6.83 – 6.76 (m, 2H), 5.71 (dt, J = 15.6, 1.4 Hz, 2H), 4.29 – 4.14 (m, 4H), 2.20 (td, J = 8.1, 1.2 Hz, 4H), 1.85 – 1.77 (m, 4H), 1.48 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 167.0, 165.8, 145.9, 130.8, 128.6, 127.8, 127.5, 124.0, 80.2, 69.0, 65.3, 28.2, 28.1, 26.9; HRMS (ESI): *m/z* calcd for $C_{36}H_{44}NaO_8$ $[M+Na]^+$ 627.2928, found 627.2925.



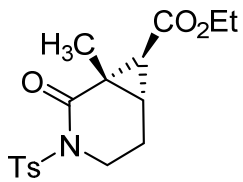
6e

Ethyl 2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)acetate (6f): colorless oil, 71.2 mg, 89% yield; R_f = 0.60 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99 (d, J = 8.4 Hz, 2H), 7.38 – 7.30 (m, 7H), 4.61 (s, 2H), 4.19 (q, J = 7.1 Hz, 2H), 3.54 (s, 2H), 2.40 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.6, 167.5, 147.3, 145.2, 135.3, 134.6, 129.8, 129.1, 129.0, 128.6, 128.2, 61.8, 52.2, 34.5, 21.7, 14.1; HRMS (ESI): *m/z* calcd for $C_{21}H_{22}NO_5S$ $[M+H]^+$ 400.1213, found 400.1215.



6f

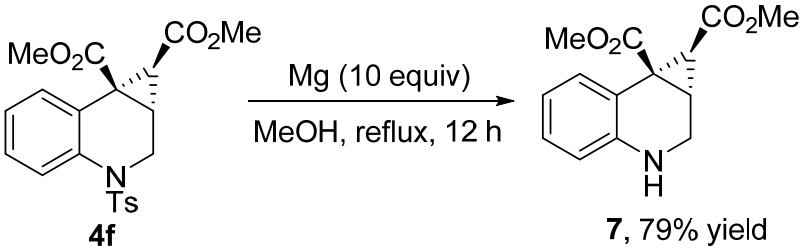
Ethyl 1-methyl-2-oxo-3-tosyl-3-azabicyclo[4.1.0]heptane-7-carboxylate (6g): white solid, 66.2 mg, 94% yield; m.p. 176–178 °C; R_f = 0.50 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.87 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.30 (dd, J = 14.3, 4.8 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.41 (td, J = 12.6, 4.7 Hz, 1H), 2.44 (s, 3H), 2.36 (d, J = 5.3 Hz, 1H), 2.25 – 2.04 (m, 3H), 1.33 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 170.3, 169.0, 144.8, 136.2, 129.5, 128.5, 61.4, 42.6, 30.5, 28.3, 26.3, 21.7, 20.4, 14.2, 13.1; HRMS (ESI): *m/z* calcd for $C_{17}H_{22}NO_5S$ $[M+H]^+$ 352.1213, found 352.1210.



6g

VI. Synthesis of Compounds 7–10

1. Removal of tosyl group of 4f

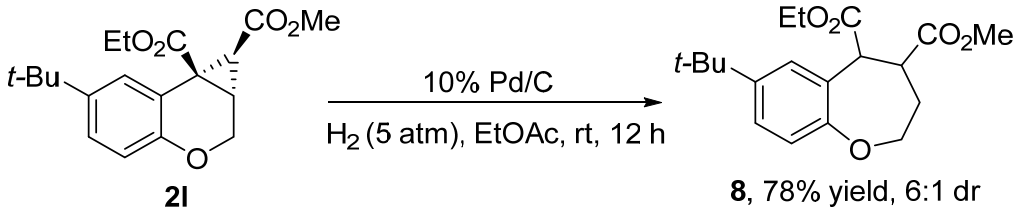


4f **7**, 79% yield

To a solution of **4f** (0.1 mmol) in anhydrous methanol (5 mL) was added Mg fine powder (24.0 mg, 1.0 mmol). The reaction mixture was heated to reflux for 12 h. After cooling down to rt, the reaction mixture was diluted with CH_2Cl_2 (10 mL) followed by addition of 1M HCl (10 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 3) and the combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The residue was isolated by silica gel column chromatography (PE/EA 10:1, v/v) to afford **7**.

Dimethyl 1,1a,2,3-tetrahydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (7): white solid, 20.6 mg, 79% yield; m.p. 90–93 °C; R_f = 0.40 (PE:EA 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33 (dd, J = 7.8, 1.1 Hz, 1H), 7.10 – 6.98 (m, 1H), 6.73 (t, J = 7.6 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 3.42 (d, J = 2.1 Hz, 3H), 2.80 (d, J = 5.6 Hz, 1H), 2.77 – 2.71 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 171.1, 169.0, 142.1, 127.8, 127.3, 119.0, 118.7, 115.3, 52.5, 52.2, 37.0, 35.3, 30.6, 27.9; HRMS (ESI): *m/z* calcd for $C_{14}H_{16}NO_4$ $[M+H]^+$ 262.1074, found 262.1080.

2. Catalytic hydrogenative ring expansion of 2l, 4j and 6g



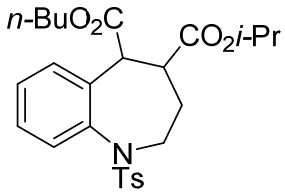
2l **8**, 78% yield, 6:1 dr

To a solution of **2l** (0.1 mmol) in anhydrous EtOAc (2 mL) was added 10% Pd/C (20.0 mg) in an autoclave, which was then charged with 5 atm H_2. After stirred at rt for 12 h, the reaction mixture was filtered through a plug of celite and washed with EtOAc (10 mL × 3). The filtrate was concentrated under reduced pressure and the residue was subjected to silica gel column chromatography isolation (PE/EA 10:1, v/v) to afford **8**.

Following the above procedure, compounds **9** and **10** were smoothly prepared from **4j** (0.1 mmol) and **6g** (0.1 mmol), respectively.

5-Ethyl 4-methyl 7-(*tert*-butyl)-2,3,4,5-tetrahydrobenzo[*b*]oxepine-4,5-dicarboxylate (8): colorless oil as a diastereomeric mixture with *cis*:*trans* 6:1, 26.1 mg, 78% yield; R_f = 0.75 (PE:EA 10:1, v/v); for *cis*-isomer, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.28 (d, J = 2.2 Hz, 1H), 7.19 (dd, J = 8.6, 2.3 Hz, 1H), 6.78 (d, J = 8.6 Hz, 1H), 4.35 (dd, J = 11.2, 2.4 Hz, 1H), 4.26 – 4.10 (m, 2H), 4.04 (ddd, J = 11.2, 3.9, 1.2 Hz, 1H), 3.69 (s, 3H), 3.57 (d, J = 2.3 Hz, 1H), 2.86 (qd, J = 7.0, 3.6 Hz, 1H), 2.49 (dd, J = 16.6, 7.2 Hz, 1H), 2.38 (dd, J = 16.6, 7.3 Hz, 1H), 1.31 – 1.24 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 172.8, 172.4, 151.6, 143.4, 127.4, 125.9, 116.6, 116.1, 66.6, 61.2, 51.8, 44.9, 35.0, 34.1, 31.5, 30.8, 14.2; HRMS (ESI): *m/z* calcd for $C_{19}H_{27}O_5$ $[M+H]^+$ 335.1853, found 335.1861.

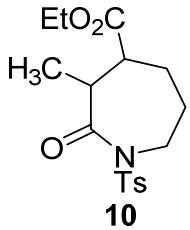
5-Butyl 4-isopropyl 1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine-4,5-dicarboxylate (9): colorless oil as a diastereomeric mixture with *cis*:*trans* 4:1, 45.8 mg, 94% yield; R_f = 0.50 (PE:EA 10:1, v/v); for *cis*-isomer, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.90 (dd, J = 8.4, 0.9



9

Hz, 1H), 7.58 (d, J = 8.3 Hz, 2H), 7.26 – 7.17 (m, 3H), 7.11 (dd, J = 7.7, 1.5 Hz, 1H), 7.06 – 7.02 (m, 1H), 5.09 – 5.03 (m, 1H), 4.28 (dd, J = 13.8, 3.0 Hz, 1H), 3.99 (t, J = 6.7 Hz, 2H), 3.78 (dd, J = 13.3, 11.3 Hz, 1H), 3.71 (d, J = 5.0 Hz, 1H), 2.36 (s, 3H), 2.32 (d, J = 7.5 Hz, 1H), 2.30 – 2.17 (m, 2H), 1.56 – 1.49 (m, 2H), 1.32 – 1.23 (m, 8H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 171.7, 170.6, 143.8, 136.4, 136.2, 129.6, 129.5, 128.0, 127.3, 125.2, 124.4, 123.3, 68.4, 64.9, 46.8, 46.0, 35.3, 30.5, 30.1, 21.9, 21.8, 21.5, 19.0, 13.6; HRMS (ESI): *m/z* calcd for $C_{26}H_{34}NO_6S$ $[M+H]^+$ 488.2101, found 488.2104.

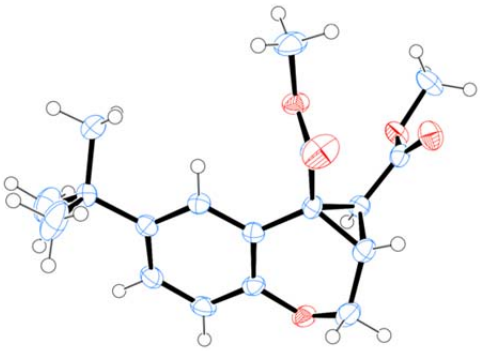
Ethyl 3-methyl-2-oxo-1-tosylazepane-4-carboxylate (10): colorless oil as a diastereomeric mixture with *trans*:*cis* 3:1, 18.7 mg, 53% yield; R_f = 0.70 (PE:EA 10:1, v/v); for *trans*-isomer, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.16 (q, J = 7.2 Hz, 2H), 4.15 – 4.06 (m, 1H), 3.87 – 3.77 (m, 1H), 2.52 (dd, J = 20.0, 4.3 Hz, 1H), 2.45 (s, 3H), 2.26 – 2.11 (m, 3H), 2.06 – 1.98 (m, 1H), 1.74 – 1.66 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H), 1.21 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 172.6, 171.7, 144.8, 136.0, 129.4, 128.6, 60.8, 45.0, 43.6, 38.5, 35.8, 28.5, 21.7, 14.7, 14.2. HRMS (ESI): *m/z* calcd for $C_{17}H_{24}NO_5S$ $[M+H]^+$ 354.1370, found 354.1374.

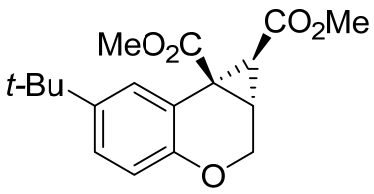


10

VII. X-Ray Crystallographic Data of 2k, 2x, 4a and 6g

1. X-Ray crystal data of 2k





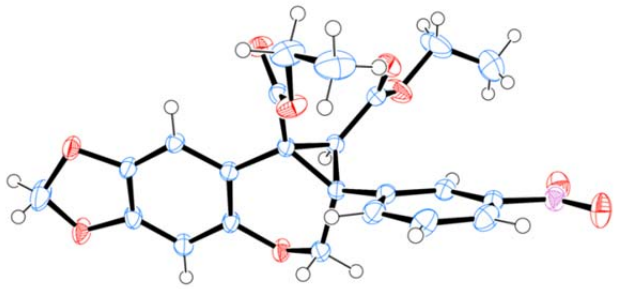
2k (CCDC 1947437)

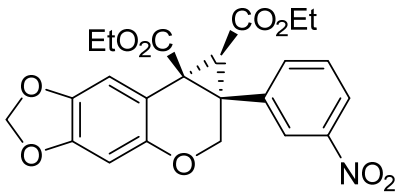
Table S4. Crystal data and structure refinement for compound **2k**

Identification code	**2k**
Empirical formula	C_{18} H_{22} O_5

Formula weight	318.35
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 31.452(6) Å α = 90°.
	b = 5.5892(11) Å β = 90.16(3)°.
	c = 19.232(4) Å γ = 90°.
Volume	3380.8(12) $Å^3$
Z, Calculated density	8, 1.251 Mg/m^3
Absorption coefficient	0.091 mm^{-1}
F(000)	1360
Crystal size	0.200 x 0.180 x 0.120 mm^3
Theta range for data collection	2.590 to 27.837°
Limiting indices	-40<=h<=40, -7<=k<=7, -25<=l<=25
Reflections collected / unique	19193 / 4017 [R(int) = 0.0802]
Completeness to theta = 25.242	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.7288
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4017 / 0 / 213
Goodness-of-fit on F^2	1.097
Final R indices [I>2sigma(I)]	R1 = 0.0649, wR2 = 0.1375
R indices (all data)	R1 = 0.0968, wR2 = 0.1525
Extinction coefficient	n/a
Largest diff. peak and hole	0.253 and 0.244 e. $Å^3$

2. X-Ray crystal data of 2x





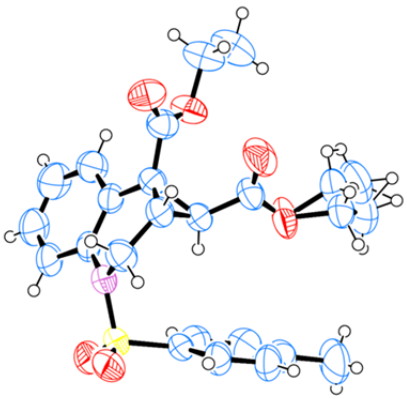
2x (CCDC 1947438)

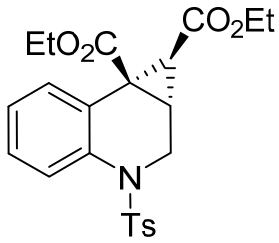
Table S5. Crystal data and structure refinement for compound **2x**

Identification code	**2x**
Empirical formula	$C_{23}H_{21}NO_9$
Formula weight	455.41
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.4995(19) Å α = 97.84(3)°
	b = 9.5604(19) Å β = 105.01(3)°
	c = 12.684(3) A γ = 103.90(3)°
Volume	1055.6(4) $Å^3$
Z, Calculated density	2, 1.433 Mg/m^3
Absorption coefficient	0.112 mm^{-1}
F(000)	476
Crystal size	0.200 x 0.180 x 0.120 mm^3
Theta range for data collection	1.701 to 27.882°
Limiting indices	-12<=h<=12, -12<=k<=12, -16<=l<=16
Reflections collected / unique	12755 / 5013 [R(int) = 0.0422]
Completeness to theta = 25.242	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.7642
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5013 / 0 / 300
Goodness-of-fit on F^2	0.990

Final R indices [I>2sigma(I)]	R1 = 0.0498, wR2 = 0.1302
R indices (all data)	R1 = 0.0705, wR2 = 0.1436
Extinction coefficient	n/a
Largest diff. peak and hole	0.383 and 0.390 e. Å^3

3. X-Ray crystal data of 4a





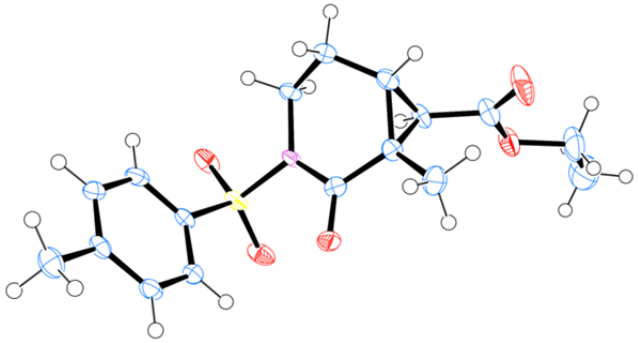
4a (CCDC 1947441)

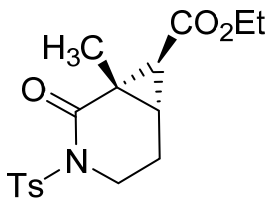
Table S6. Crystal data and structure refinement for **4a**

Identification code	**4a**
Empirical formula	$C_{23}H_{25}NO_6S$
Formula weight	443.50
Temperature/K	294.15
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 8.7393(2) Å α = 80.848(2)°
	b = 9.8405(3) Å β = 87.645(2)°
	c = 28.4880(6) γ = 69.047(2)°
Volume/Å^3	2258.48(10)
Z	4
ρcalcg/cm^3	1.304
μ/mm^{-1}	1.603
F(000)	936.0
Crystal size/mm^3	0.36 × 0.26 × 0.22
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.286 to 148.662

Index ranges	$-10 \le h \le 10, -11 \le k \le 11, -9 \le l \le 35$
Reflections collected	8595
Independent reflections	8595 [Rint = ?, Rsigma = 0.0276]
Data/restraints/parameters	8595/64/606
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R1 = 0.0766, wR2 = 0.2291
Final R indexes [all data]	R1 = 0.0803, wR2 = 0.2315
Largest diff. peak/hole / e $Å^3$	0.32/0.33

4. X-Ray crystal data of 6g





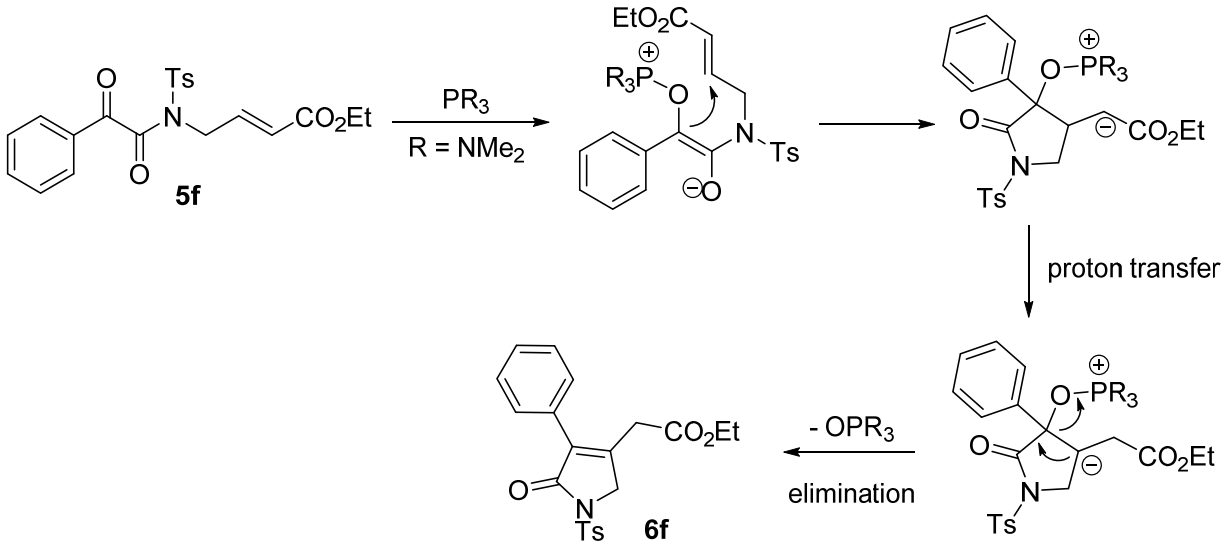
6g (CCDC 1947443)

Table S7. Crystal data and structure refinement for compound **6g**

Identification code	**6g**
Empirical formula	$C_{17}H_{21}NO_5S$
Formula weight	351.4
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.0259(12) Å α = 115.34(3)°.
	b = 12.569(3) Å β = 93.96(3)°.
	c = 12.930(3) Å γ = 100.21(3)°
Volume	859.4(4) $Å^3$
Z, Calculated density	2, 1.435 Mg/m^3
Absorption coefficient	0.211 mm^{-1}
F(000)	372
Crystal size	0.200 x 0.180 x 0.120 mm^3
Theta range for data collection	1.842 to 27.900°

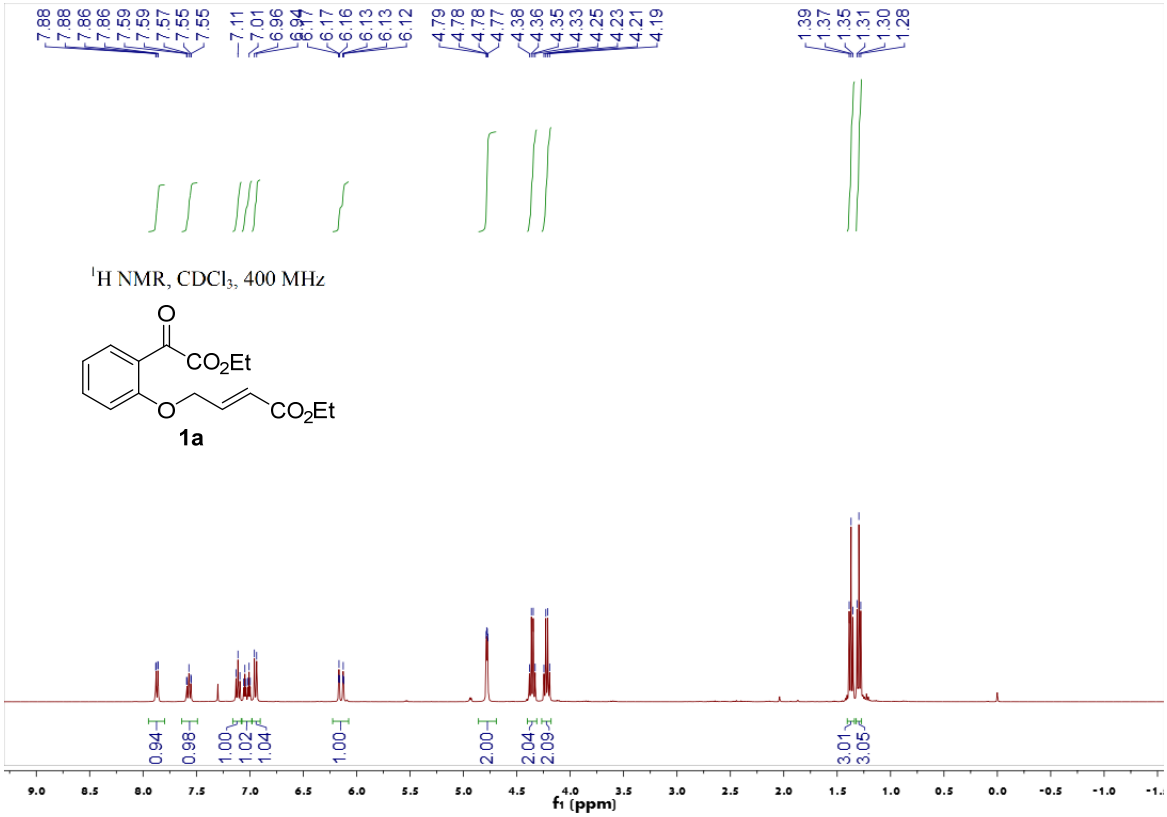
Limiting indices	-7<=h<=7, -16<=k<=16, -16<=l<=16
Reflections collected / unique	10454 / 4067 [R(int) = 0.0744]
Completeness to theta = 25.242	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.4708
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4067 / 0 / 220
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1210
R indices (all data)	R1 = 0.0834, wR2 = 0.1615
Extinction coefficient	n/a
Largest diff. peak and hole	0.395 and 0.646 e.A^3

VIII. A Plausible Mechanism for Formation of 6f



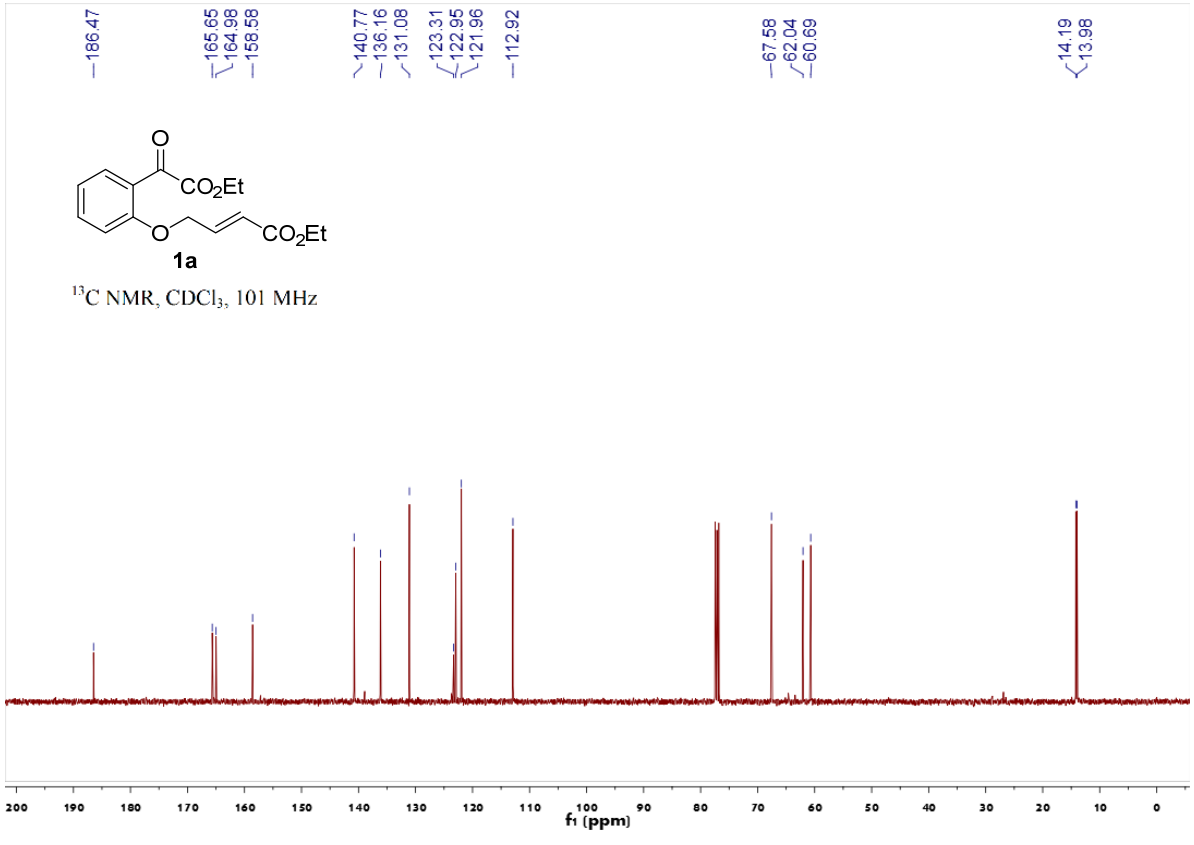
Scheme S1. Plausible mechanism for formation of **6f**

IX. NMR Spectra of New Compounds 1–10



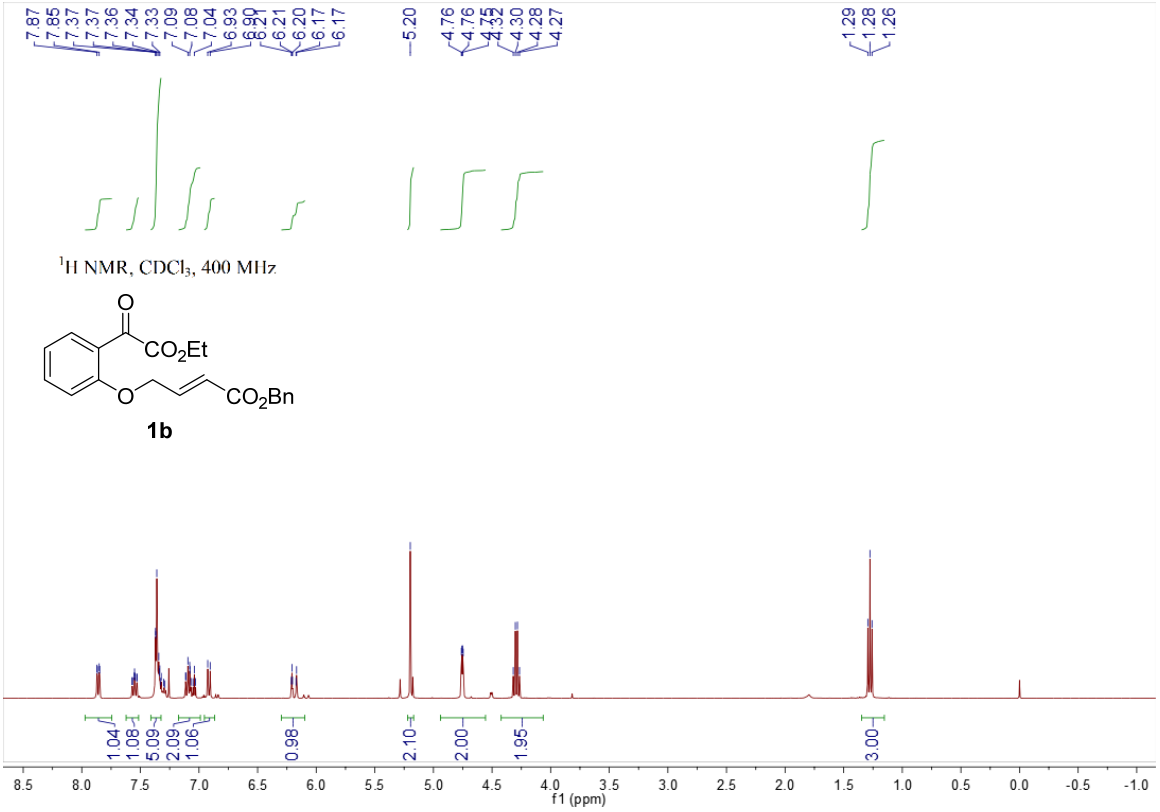
^{1}H NMR, $CDCl_3$, 400 MHz

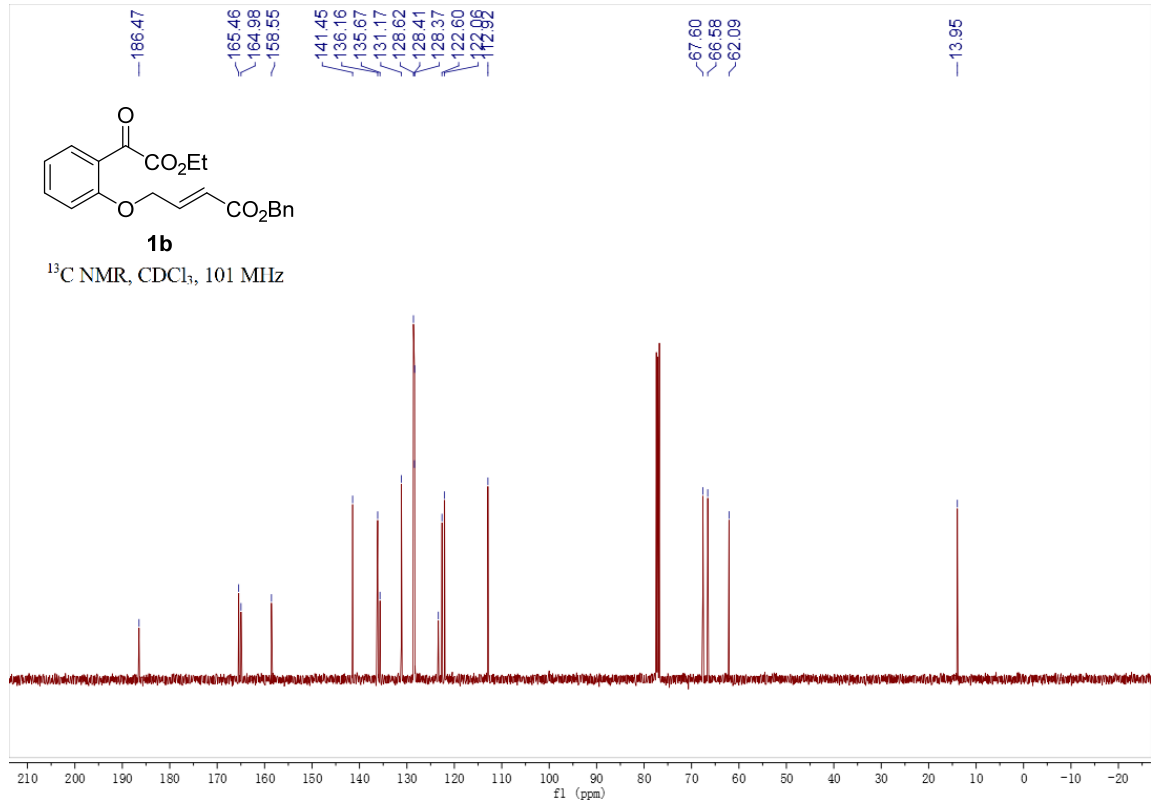
1a

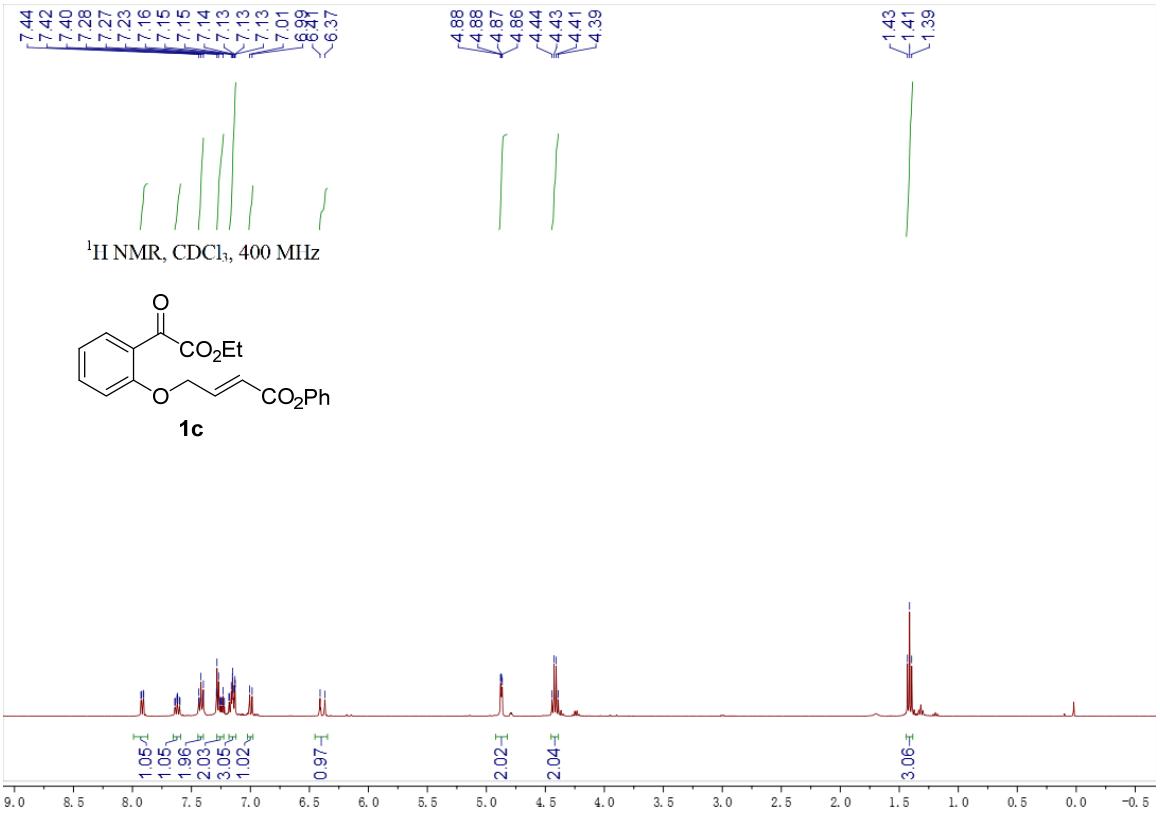


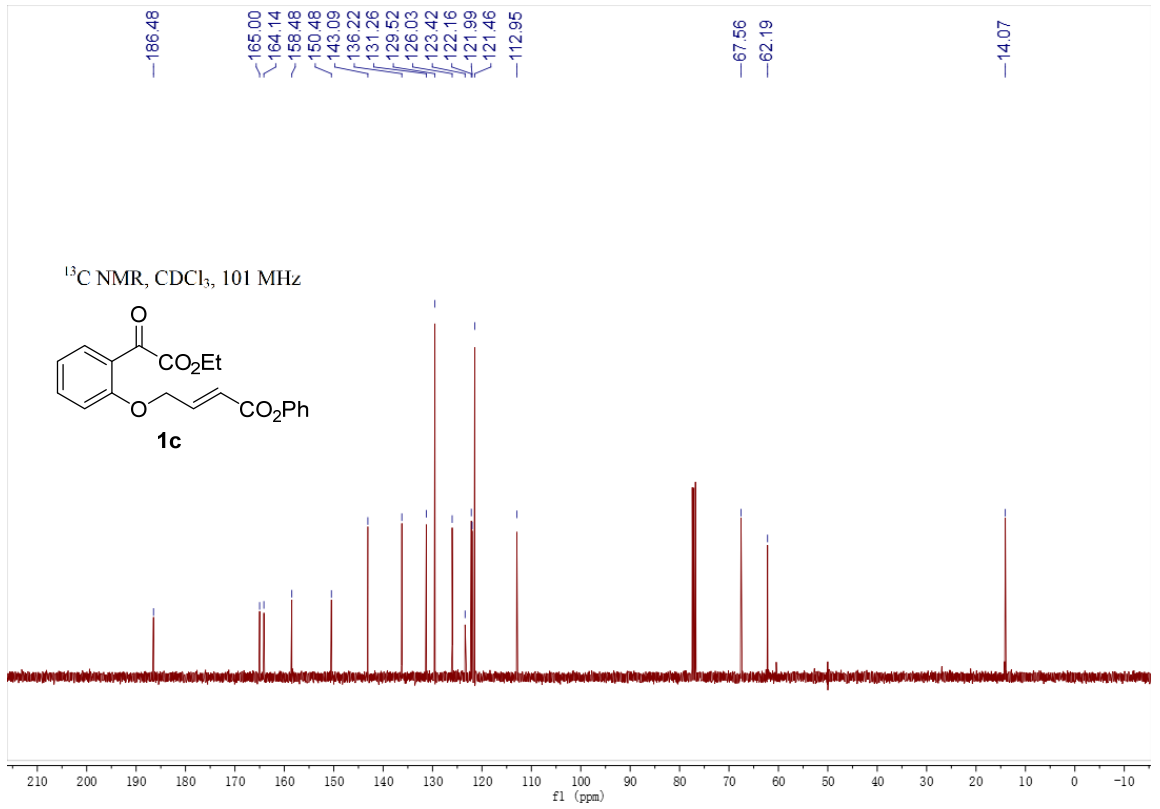
1a

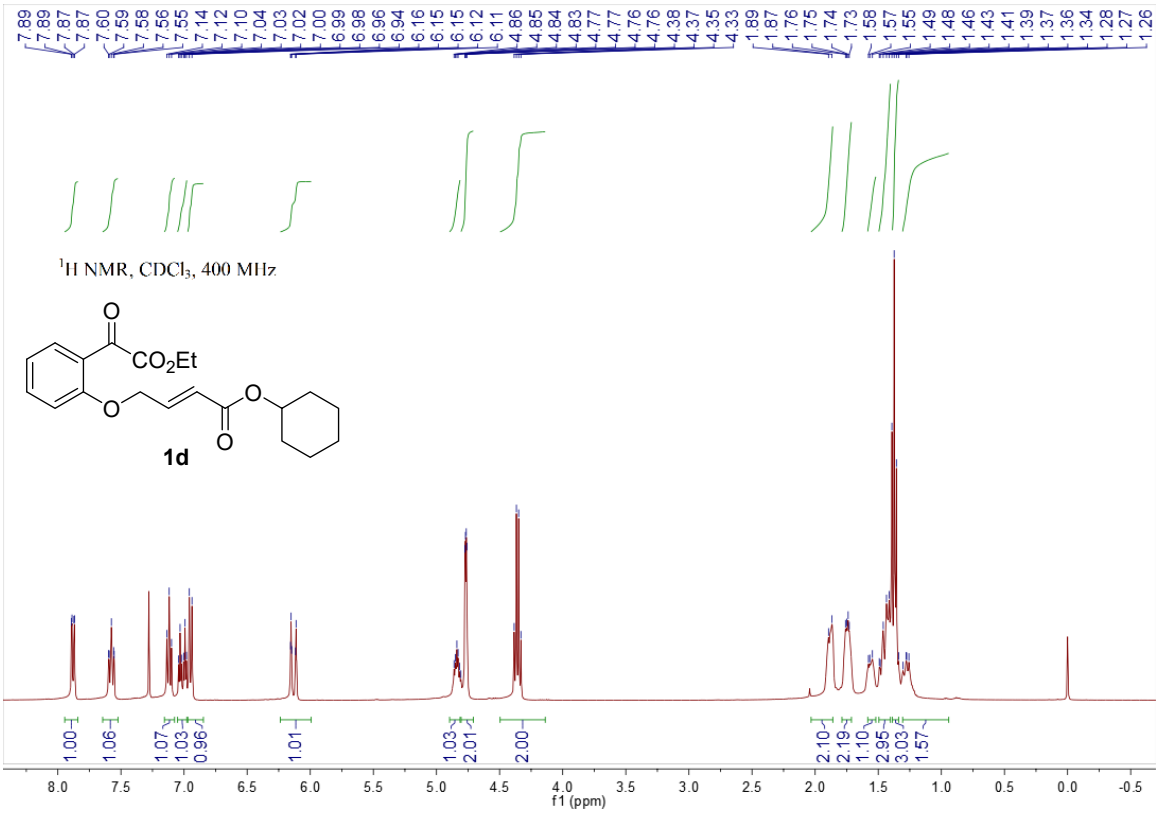
^{13}C NMR, $CDCl_3$, 101 MHz

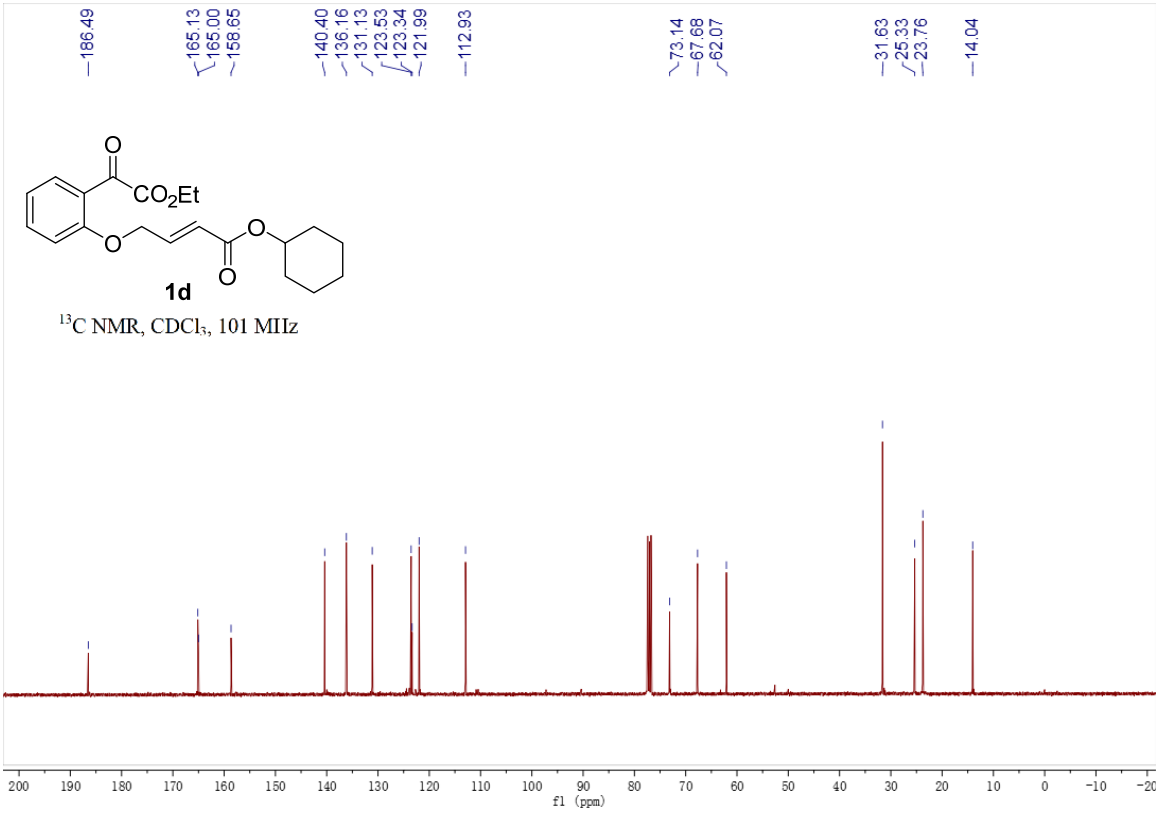

7.87
7.85
7.37
7.37
7.36
7.34
7.33
7.09
7.08
7.04
6.93
6.90
6.21
6.20
6.17
6.17
5.20
4.76
4.76
4.75
4.32
4.30
4.28
4.27
1.29
1.28
1.26
1H NMR, CDCl3, 400 MHz
CO2Et
CO2Bn
1b
1.04
1.08
5.09
2.09
1.06
0.98
2.10
2.00
1.95
3.00
f1 (ppm)

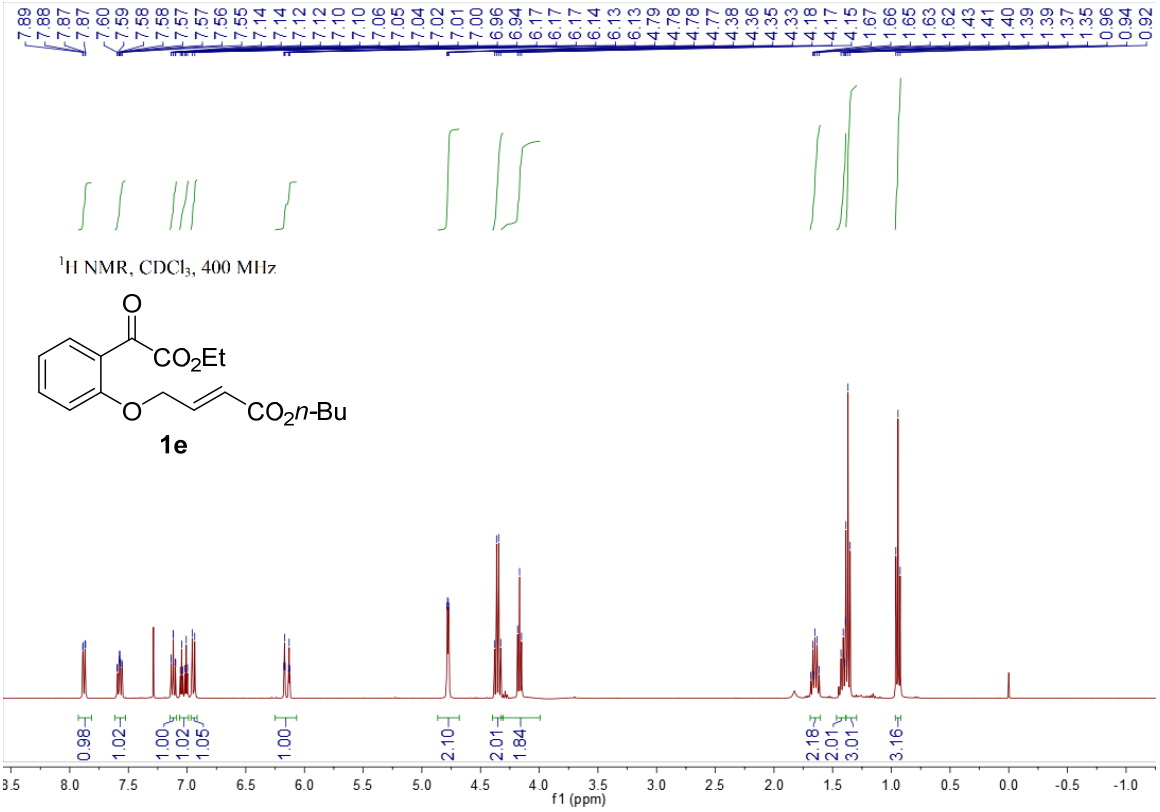

186.47
165.46
164.98
158.55
141.45
136.16
135.67
131.17
128.62
128.41
128.37
122.60
67.60
66.58
62.09
13.95
CO2Et
CO2Bn
1b
13C NMR, CDCl3, 101 MHz
f1 (ppm)


7.44
7.42
7.40
7.28
7.27
7.23
7.16
7.15
7.15
7.14
7.13
7.13
7.13
7.01
6.99
6.41
6.37
4.88
4.88
4.87
4.86
4.44
4.43
4.41
4.39
1.43
1.41
1.39
1H NMR, CDCl3, 400 MHz
O
CO2Et
O
CO2Ph
1c
1.05
1.05
1.96
2.03
3.05
1.02
0.97
2.02
2.04
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


186.48
165.00
164.14
158.48
150.48
143.09
136.22
131.26
129.52
126.03
123.42
122.16
121.99
121.46
112.95
67.56
62.19
14.07
13C NMR, CDCl3, 101 MHz
O
CO2Et
O
CO2Ph
1c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

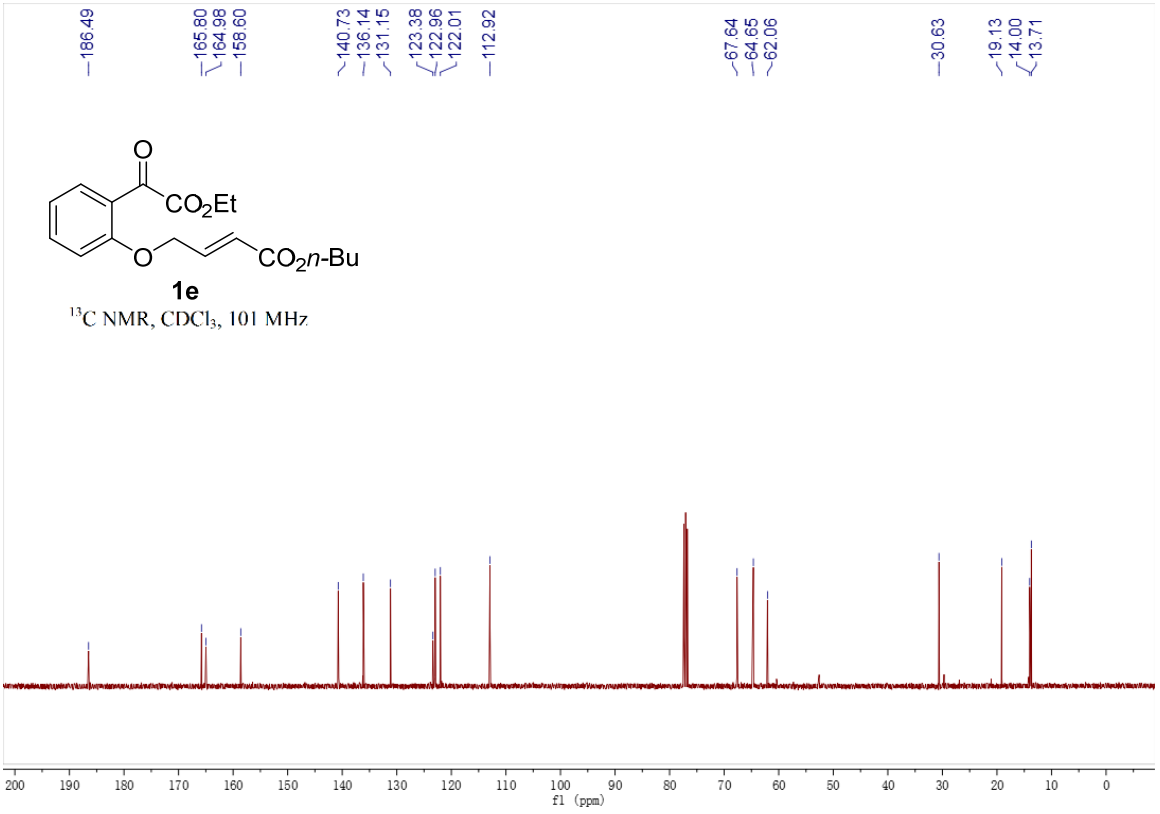

7.89 7.89 7.87 7.87 7.60 7.59 7.58 7.56 7.55 7.14 7.12 7.10 7.04 7.03 7.02 7.00 6.99 6.98 6.96 6.94 6.16 6.15 6.15 6.12 6.11 4.86 4.85 4.84 4.83 4.77 4.77 4.76 4.76 4.38 4.37 4.35 4.33 1.89 1.87 1.76 1.75 1.74 1.73 1.58 1.57 1.55 1.49 1.48 1.46 1.43 1.41 1.39 1.37 1.36 1.34 1.28 1.27 1.26
1H NMR, CDCl3, 400 MHz
CO2Et
1d
1.00 1.06 1.07 1.03 0.96 1.01 1.03 2.01 2.00 2.10 2.19 1.10 2.95 3.03 1.57
f1 (ppm)


186.49
165.13 165.00 158.65
140.40 136.16 131.13 123.53 123.34 121.99
112.93
73.14 67.68 62.07
31.63 25.33 23.76
14.04
CO2Et
1d
13C NMR, CDCl3, 101 MHz
f1 (ppm)



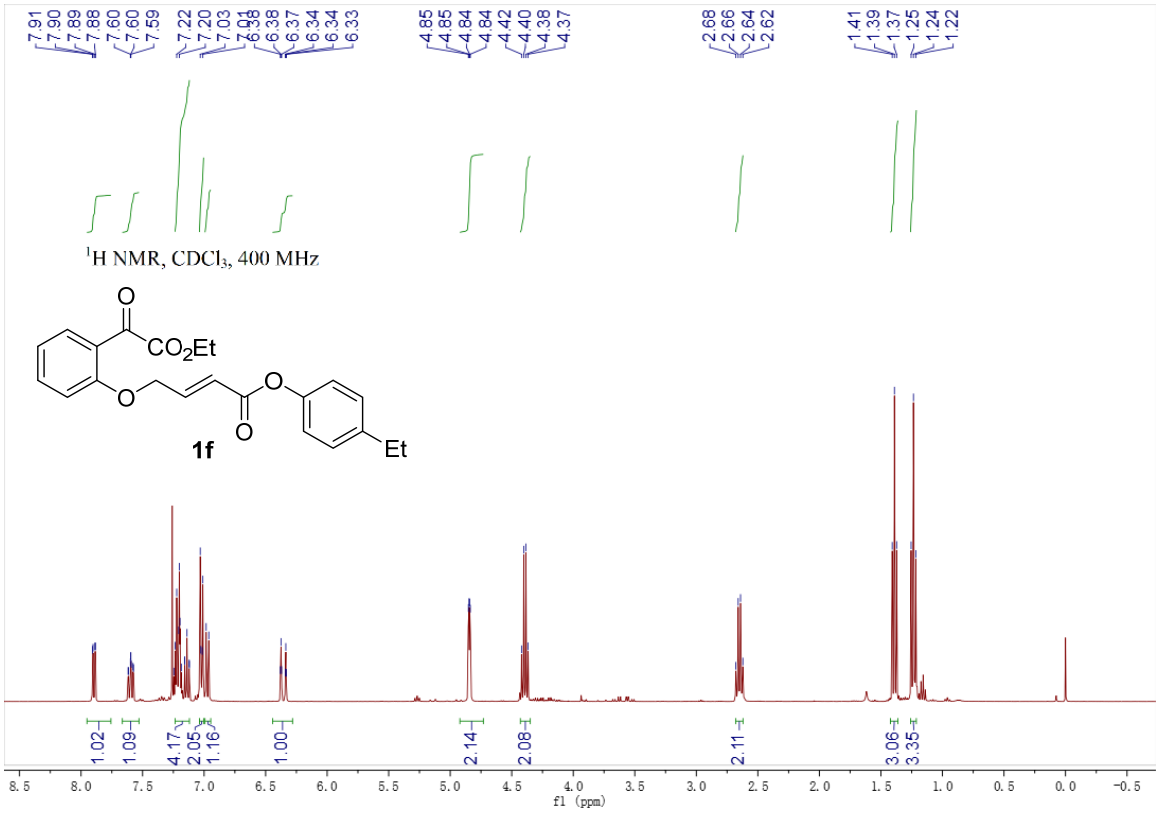
^{1}H NMR, $CDCl_3$, 400 MHz

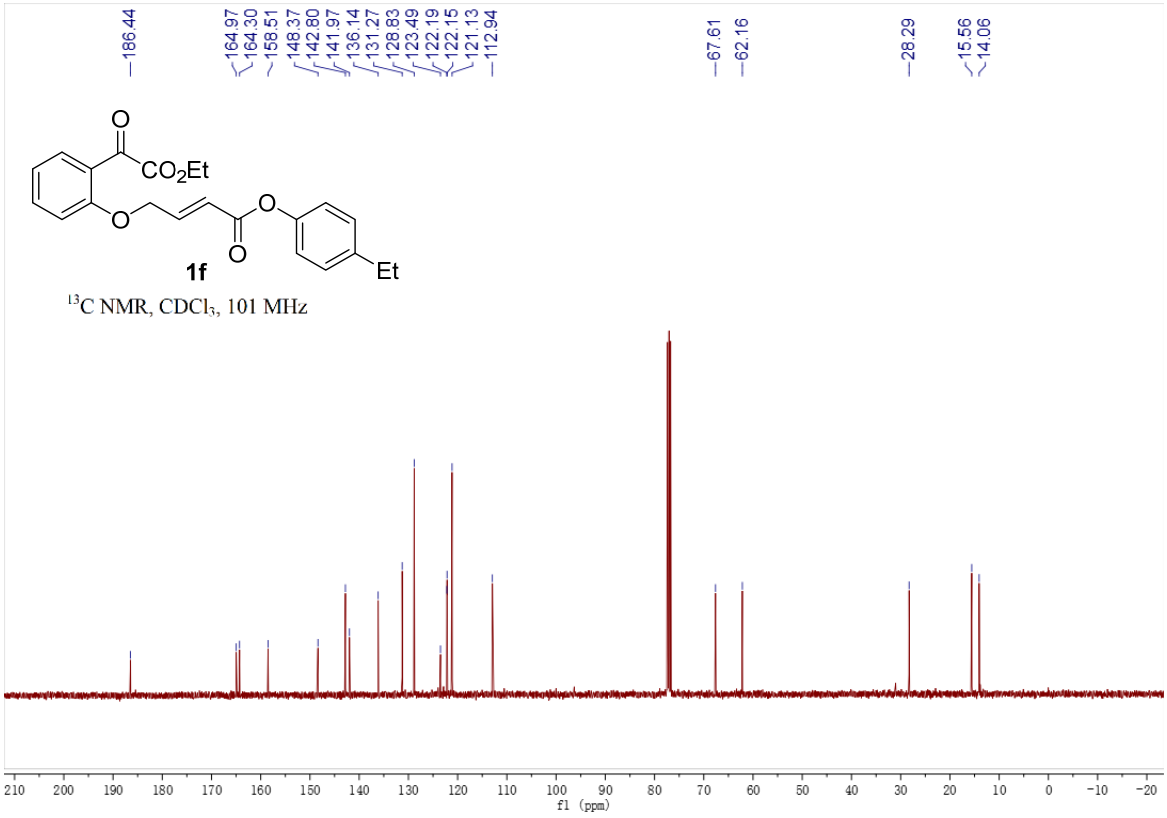
1e

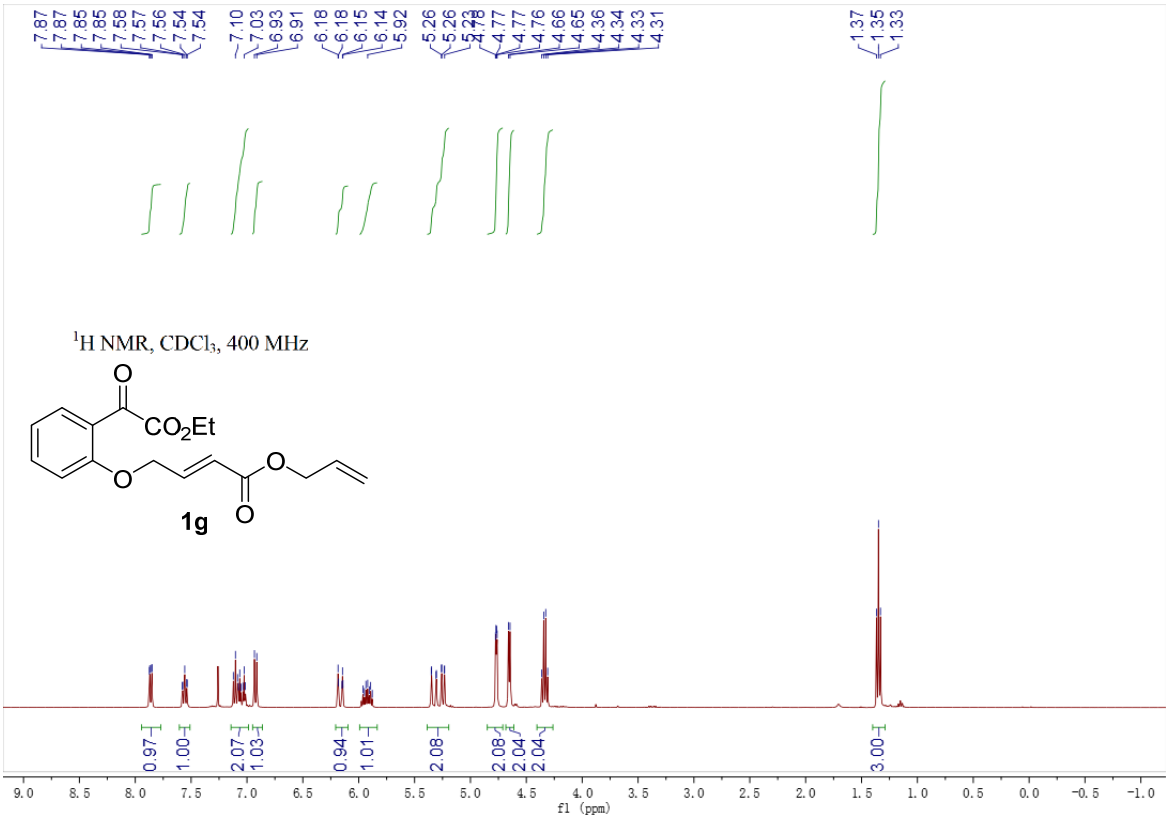


1e

^{13}C NMR, $CDCl_3$, 101 MHz

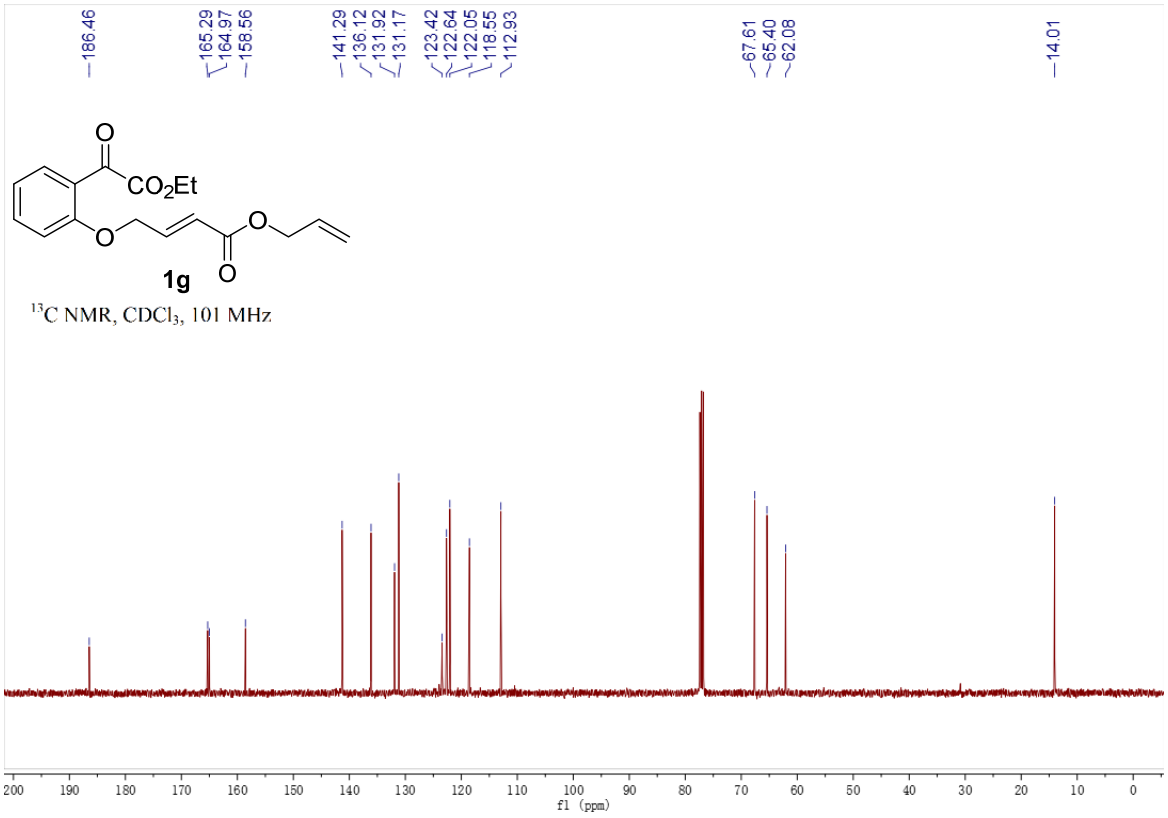

7.91
7.90
7.89
7.88
7.60
7.60
7.59
7.22
7.20
7.03
7.01
6.38
6.37
6.34
6.34
6.33
4.85
4.85
4.84
4.84
4.42
4.40
4.38
4.37
2.68
2.66
2.64
2.62
1.41
1.39
1.37
1.25
1.24
1.22
^{1}H NMR, $CDCl_3$, 400 MHz
O
CO_2Et
O
O
O
Et
1f
1.02
1.09
4.17
2.05
1.16
1.00
2.14
2.08
2.11
3.06
3.35
f1 (ppm)


186.44
164.97
164.30
158.51
148.37
142.80
141.97
136.14
131.27
128.83
123.49
122.19
122.15
121.13
112.94
67.61
62.16
28.29
15.56
14.06
O
CO_2Et
O
O
O
Et
1f
^{13}C NMR, $CDCl_3$, 101 MHz
f1 (ppm)



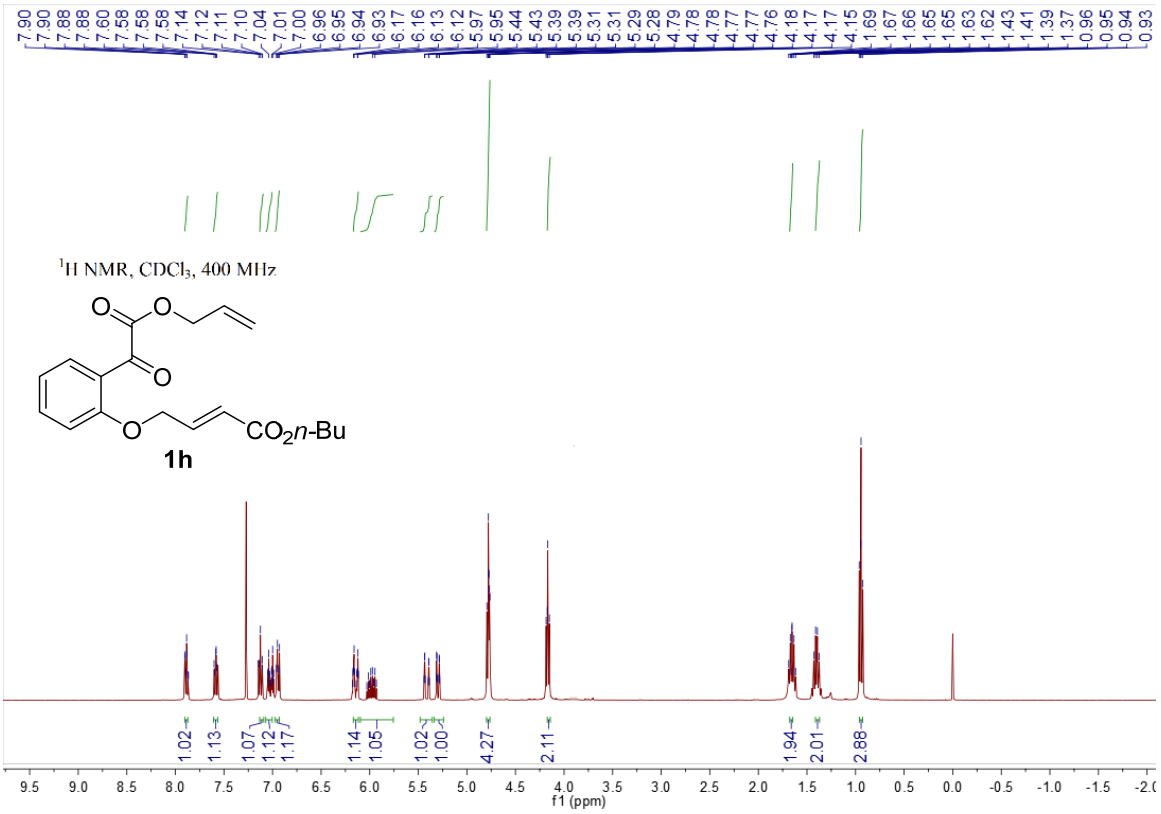
^{1}H NMR, $CDCl_3$, 400 MHz

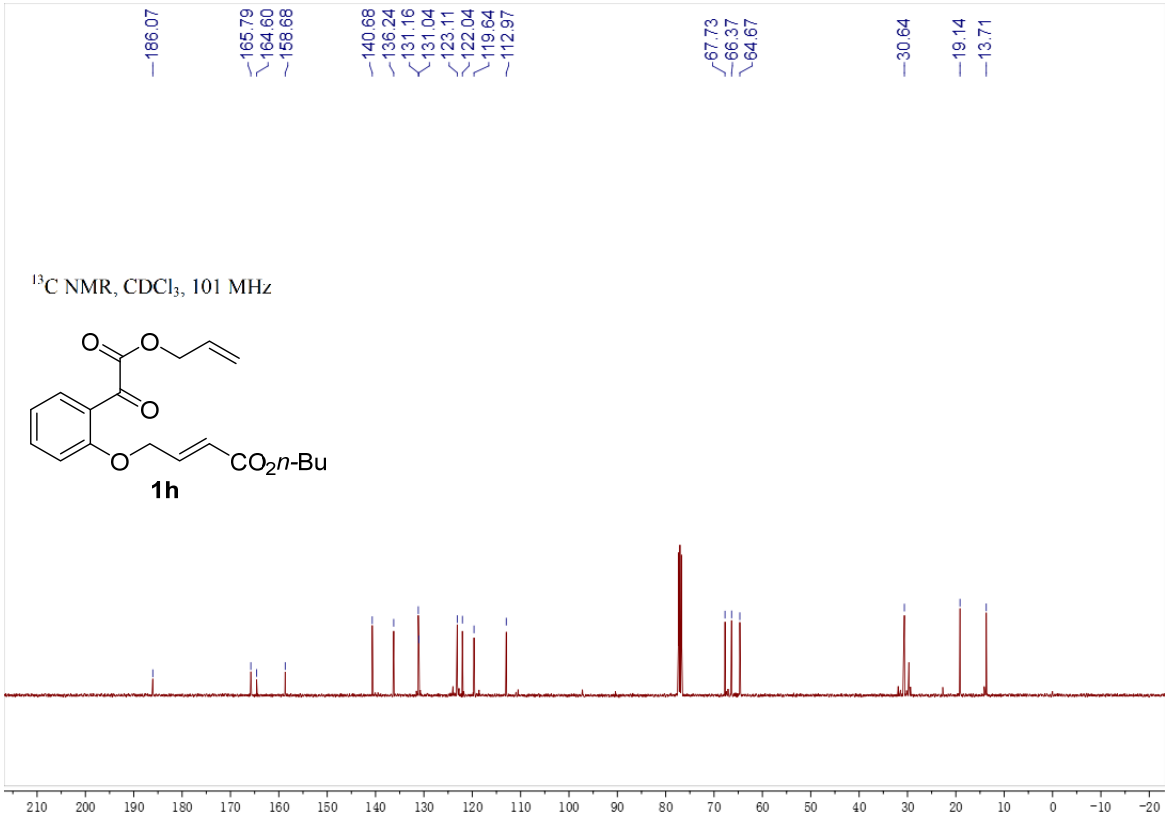
1g

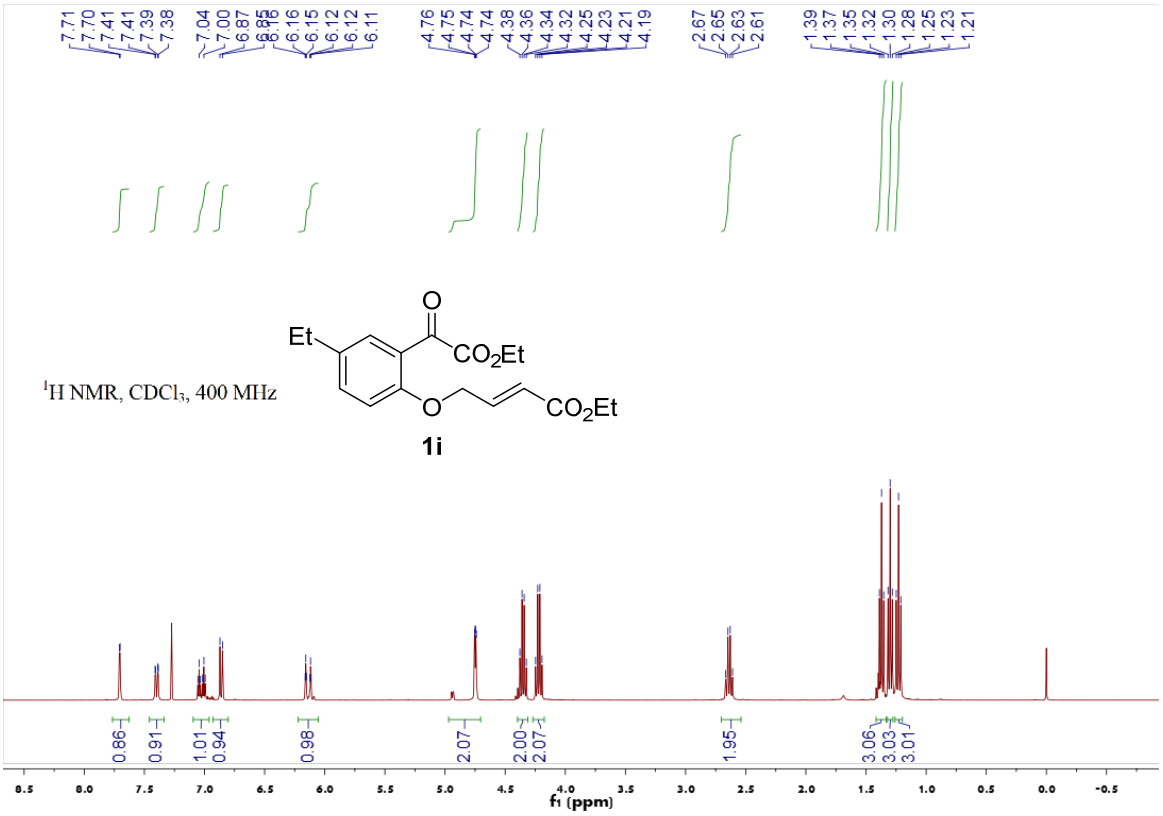


1g

^{13}C NMR, $CDCl_3$, 101 MHz

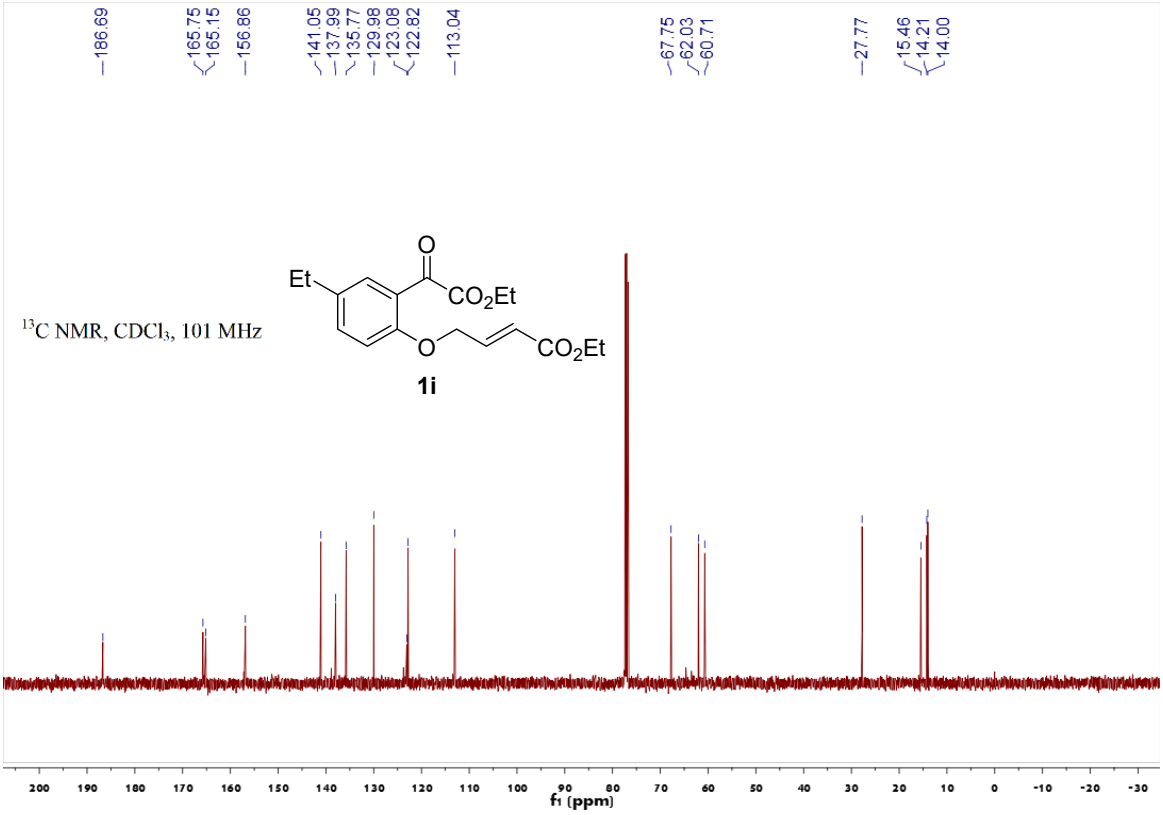

7.90 7.90 7.88 7.88 7.60 7.58 7.58 7.58 7.14 7.12 7.11 7.10 7.04 7.01 7.00 6.96 6.95 6.94 6.93 6.17 6.16 6.13 6.12 5.97 5.95 5.44 5.43 5.39 5.39 5.31 5.31 5.29 5.28 4.79 4.78 4.78 4.77 4.77 4.76 4.18 4.17 4.17 4.15 1.69 1.67 1.66 1.65 1.65 1.63 1.62 1.43 1.41 1.39 1.37 0.96 0.95 0.94 0.93
^{1}H NMR, CDCl$_3$, 400 MHz
CO$_2$n-Bu
1h
1.02 1.13 1.07 1.12 1.17 1.14 1.05 1.02 1.00 4.27 2.11 1.94 2.01 2.88
f1 (ppm)


186.07
165.79 164.60 158.68
140.68 136.24 131.16 131.04 123.11 122.04 119.64 112.97
67.73 66.37 64.67
30.64
19.14 13.71
^{13}C NMR, CDCl$_3$, 101 MHz
CO$_2$n-Bu
1h



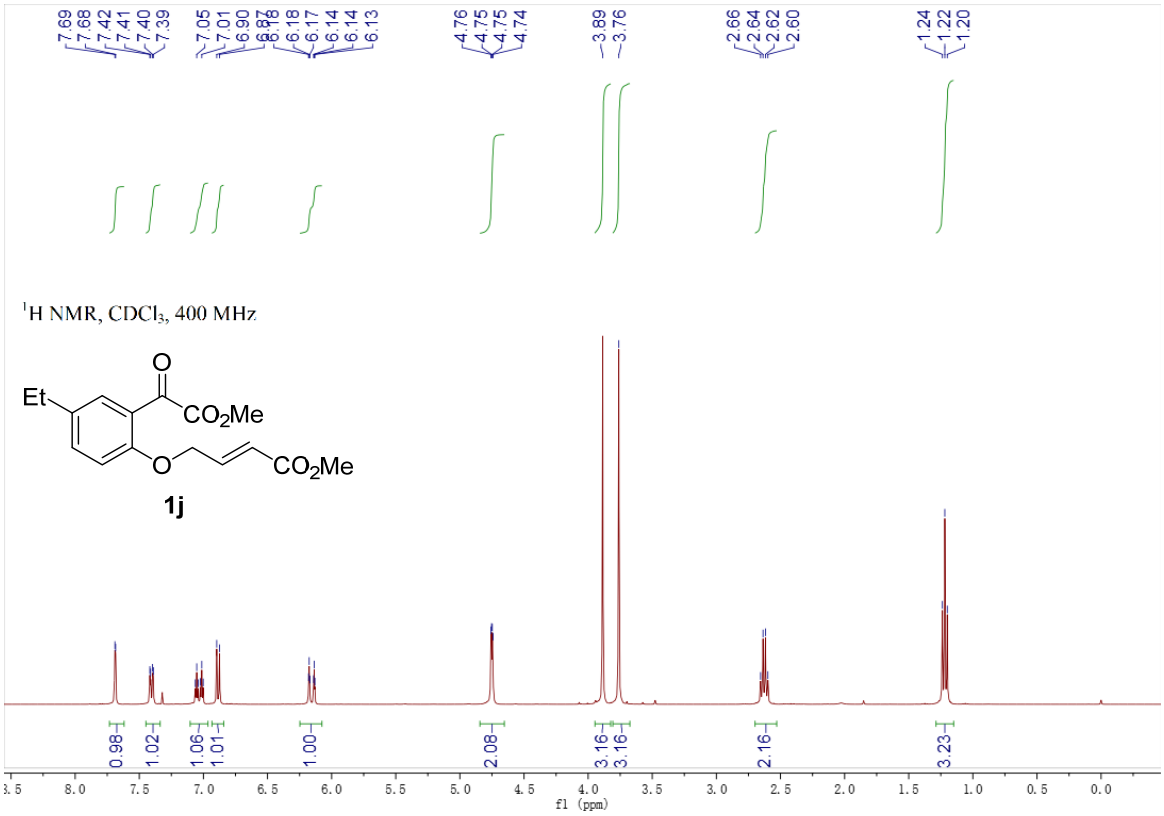
^{1}H NMR, $CDCl_3$, 400 MHz

1i



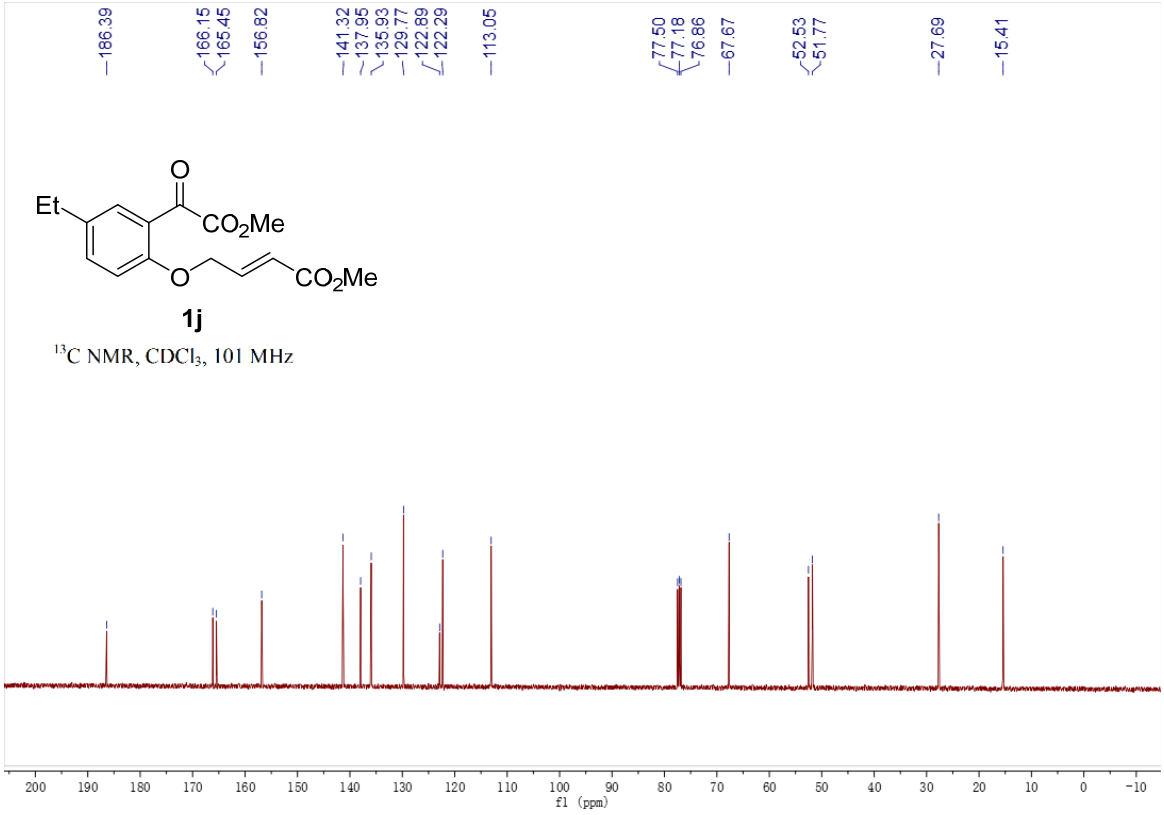
^{13}C NMR, $CDCl_3$, 101 MHz

1i



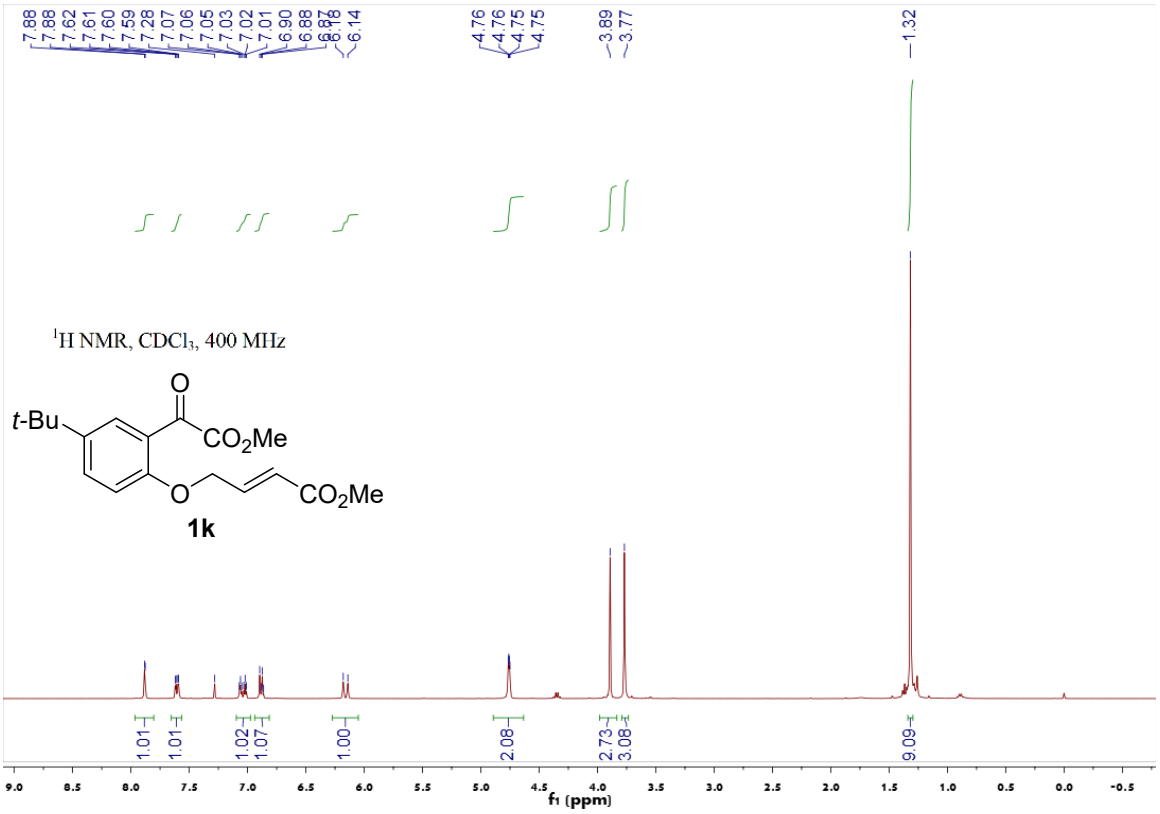
^{1}H NMR, $CDCl_3$, 400 MHz

1j



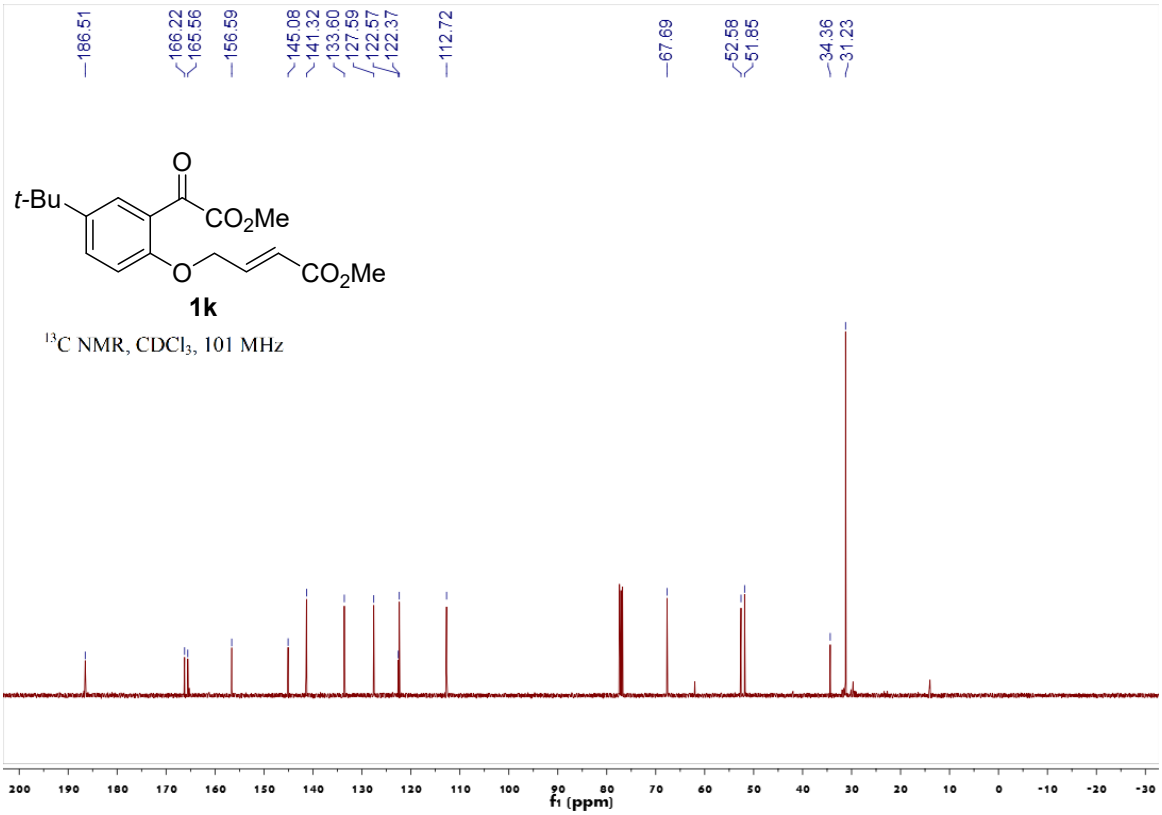
1j

^{13}C NMR, $CDCl_3$, 101 MHz



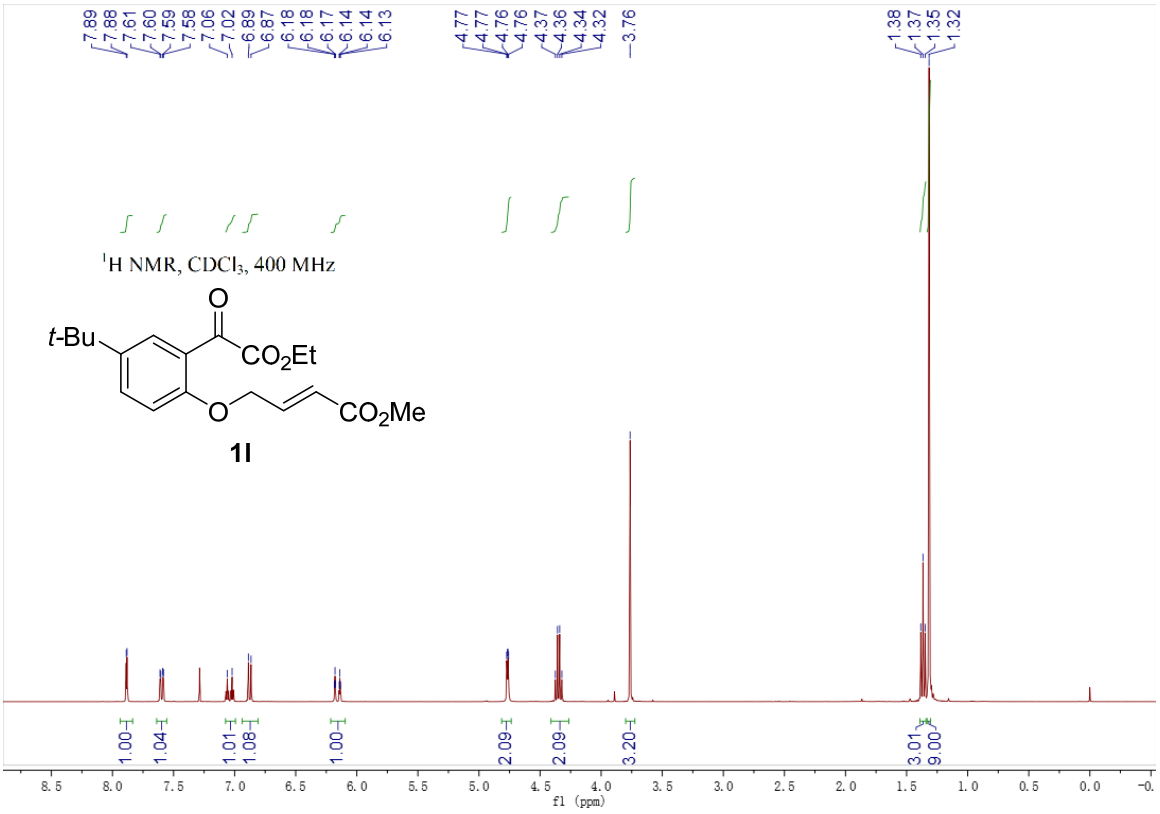
^{1}H NMR, $CDCl_3$, 400 MHz

1k



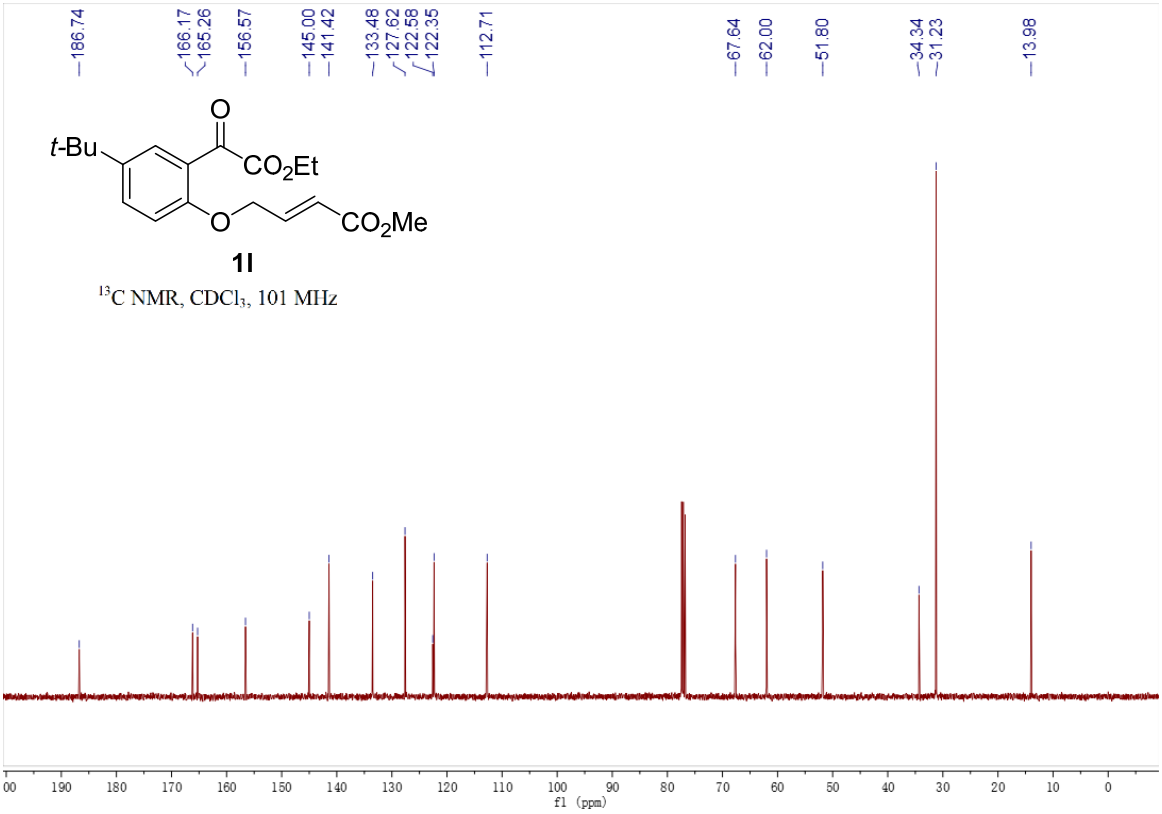
1k

^{13}C NMR, $CDCl_3$, 101 MHz



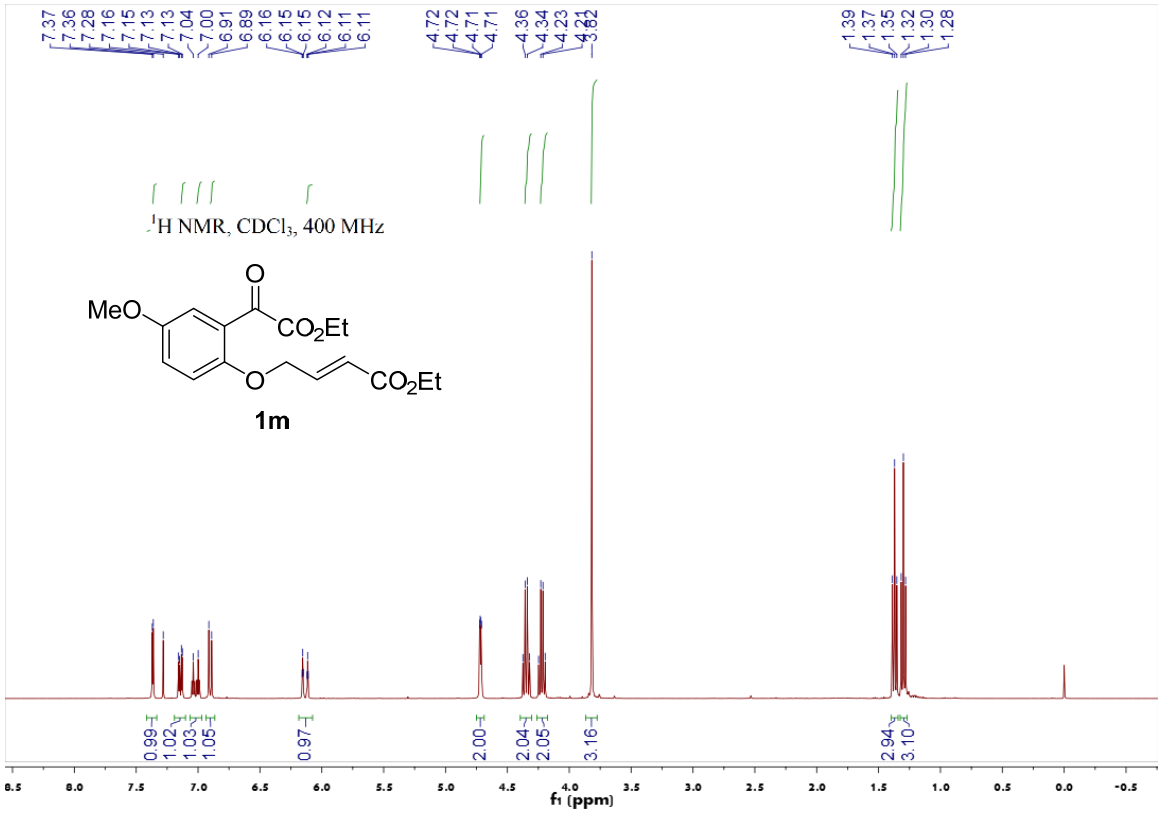
^{1}H NMR, $CDCl_3$, 400 MHz

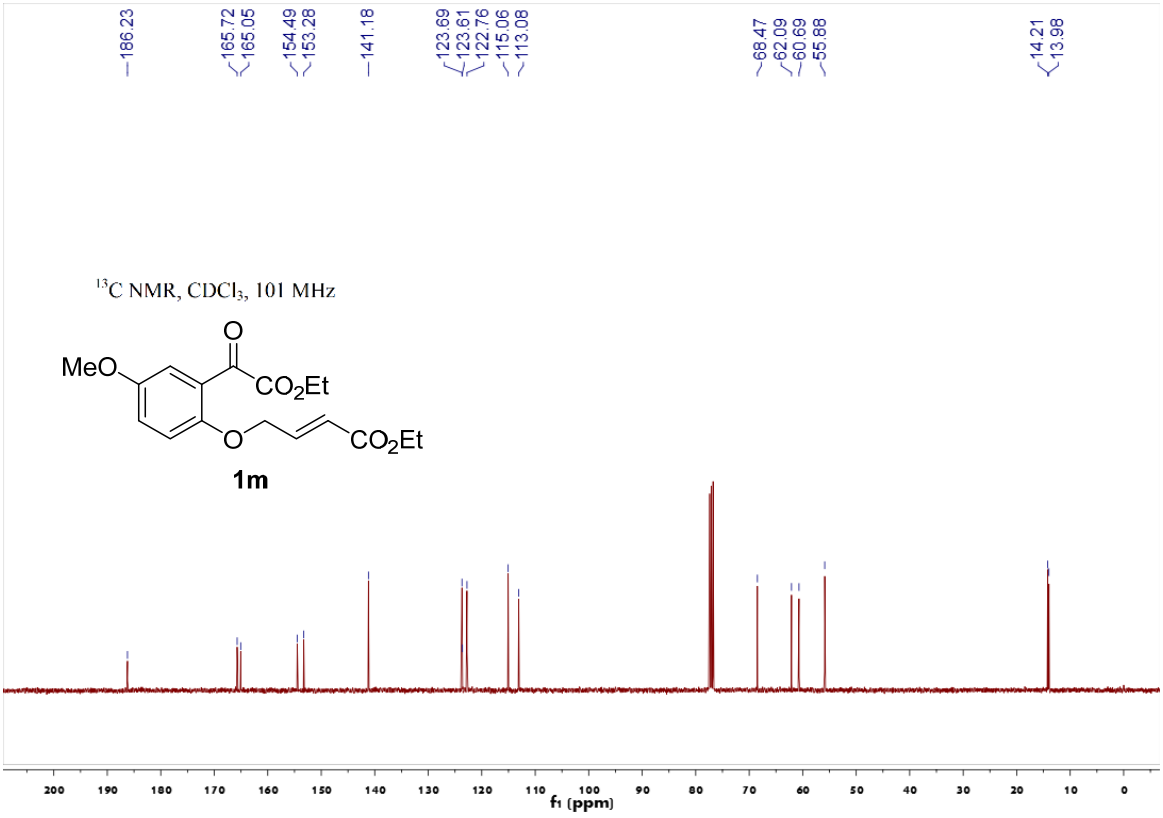
1l

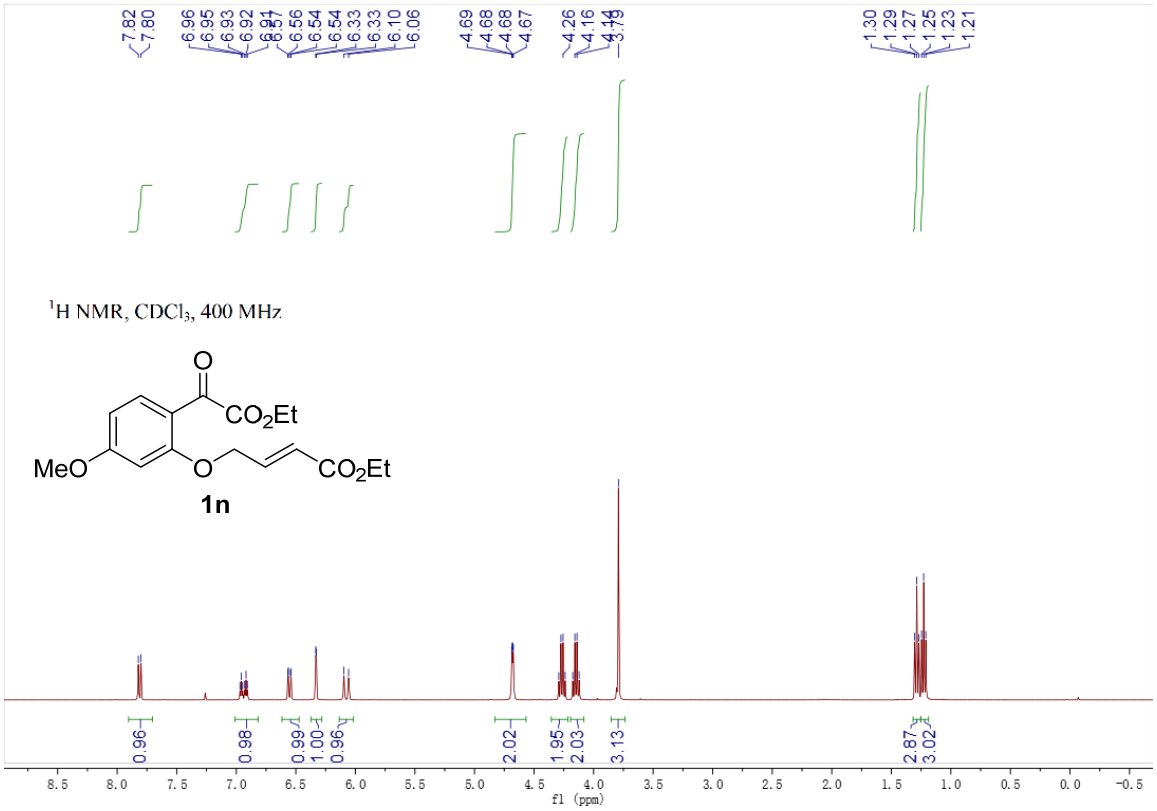


1l

^{13}C NMR, $CDCl_3$, 101 MHz

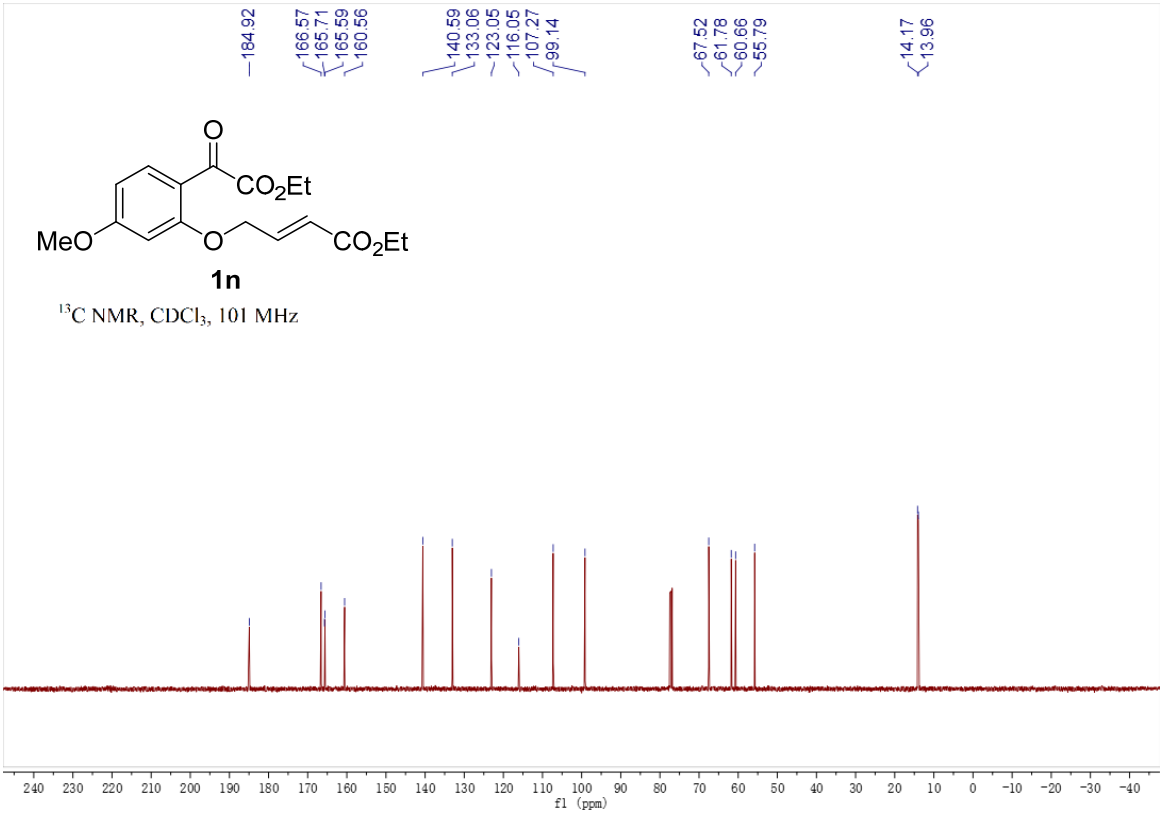

7.37
7.36
7.28
7.16
7.15
7.13
7.13
7.04
7.00
6.91
6.89
6.16
6.15
6.15
6.12
6.11
6.11
4.72
4.72
4.71
4.71
4.36
4.34
4.23
4.21
3.82
1.39
1.37
1.35
1.32
1.30
1.28
^{1}H NMR, CDCl$_3$, 400 MHz
MeO
O
CO$_2$Et
O
CO$_2$Et
1m
0.99
1.02
1.03
1.05
0.97
2.00
2.04
2.05
3.16
2.94
3.10
f$_1$ (ppm)


186.23
165.72
165.05
154.49
153.28
141.18
123.69
123.61
122.76
115.06
113.08
68.47
62.09
60.69
55.88
14.21
13.98
^{13}C NMR, CDCl$_3$, 101 MHz
MeO
O
CO$_2$Et
O
CO$_2$Et
1m
f$_1$ (ppm)



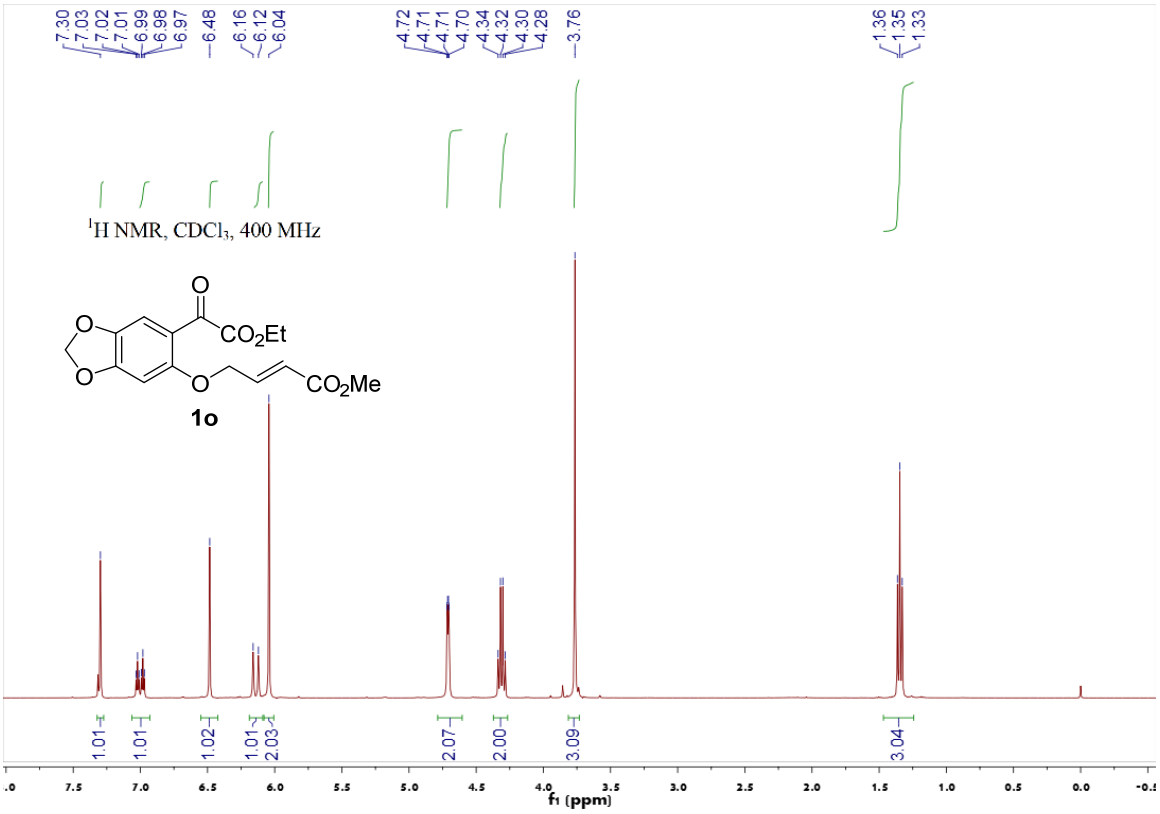
^{1}H NMR, $CDCl_3$, 400 MHz

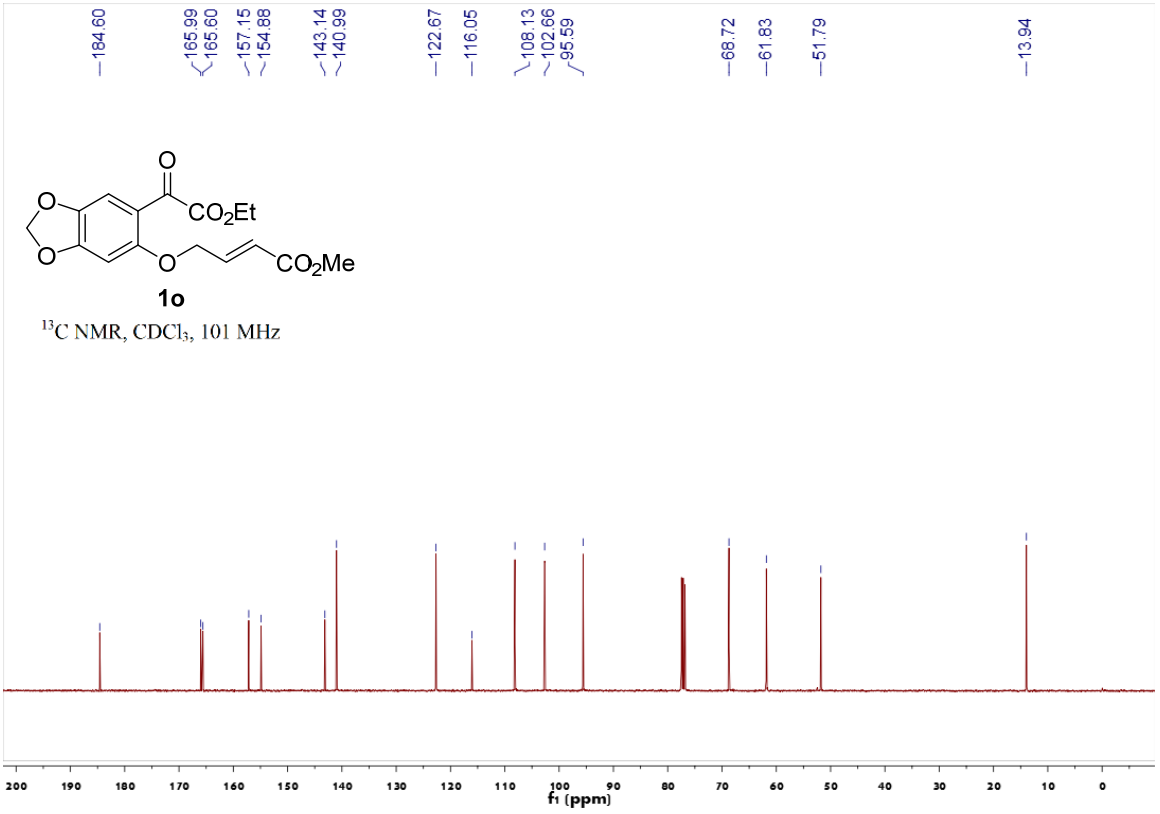
1n

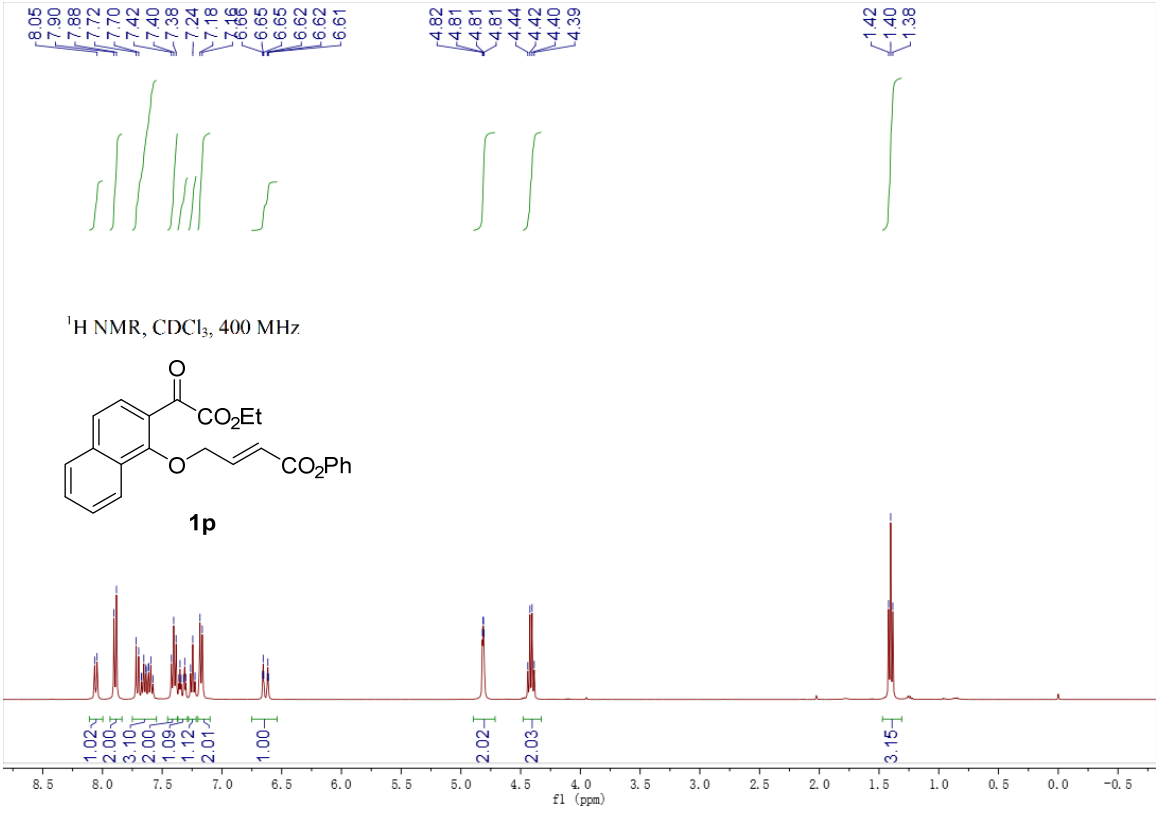


1n

^{13}C NMR, $CDCl_3$, 101 MHz

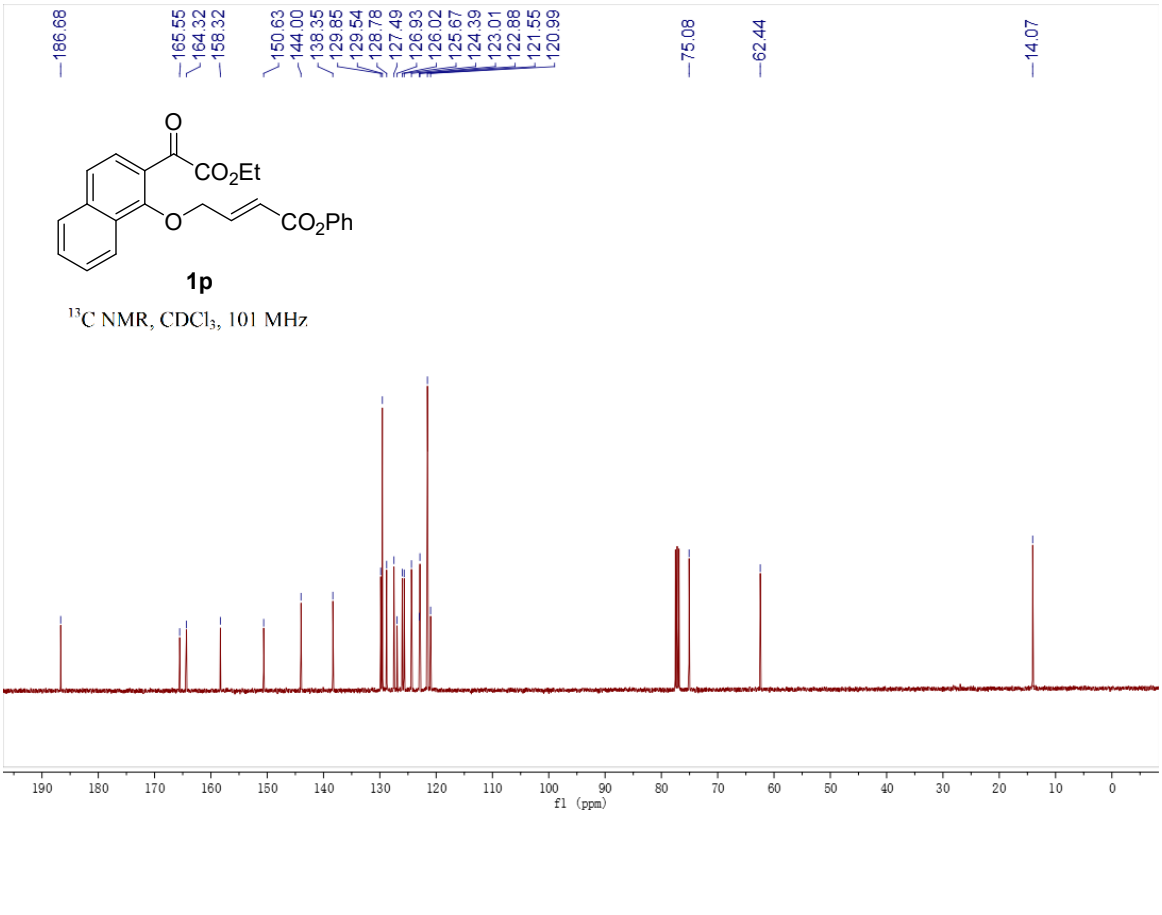

7.30
7.03
7.02
7.01
6.99
6.98
6.97
6.48
6.16
6.12
6.04
4.72
4.71
4.71
4.70
4.34
4.32
4.30
4.28
3.76
1.36
1.35
1.33
^{1}H NMR, CDCl$_3$, 400 MHz
O
CO$_2$Et
O
O
O
CO$_2$Me
1o
1.01
1.01
1.02
1.01
2.03
2.07
2.00
3.09
3.04
f$_1$ (ppm)


184.60
165.99
165.60
157.15
154.88
143.14
140.99
122.67
116.05
108.13
102.66
95.59
68.72
61.83
51.79
13.94
O
CO$_2$Et
O
O
O
CO$_2$Me
1o
^{13}C NMR, CDCl$_3$, 101 MHz
f$_1$ (ppm)



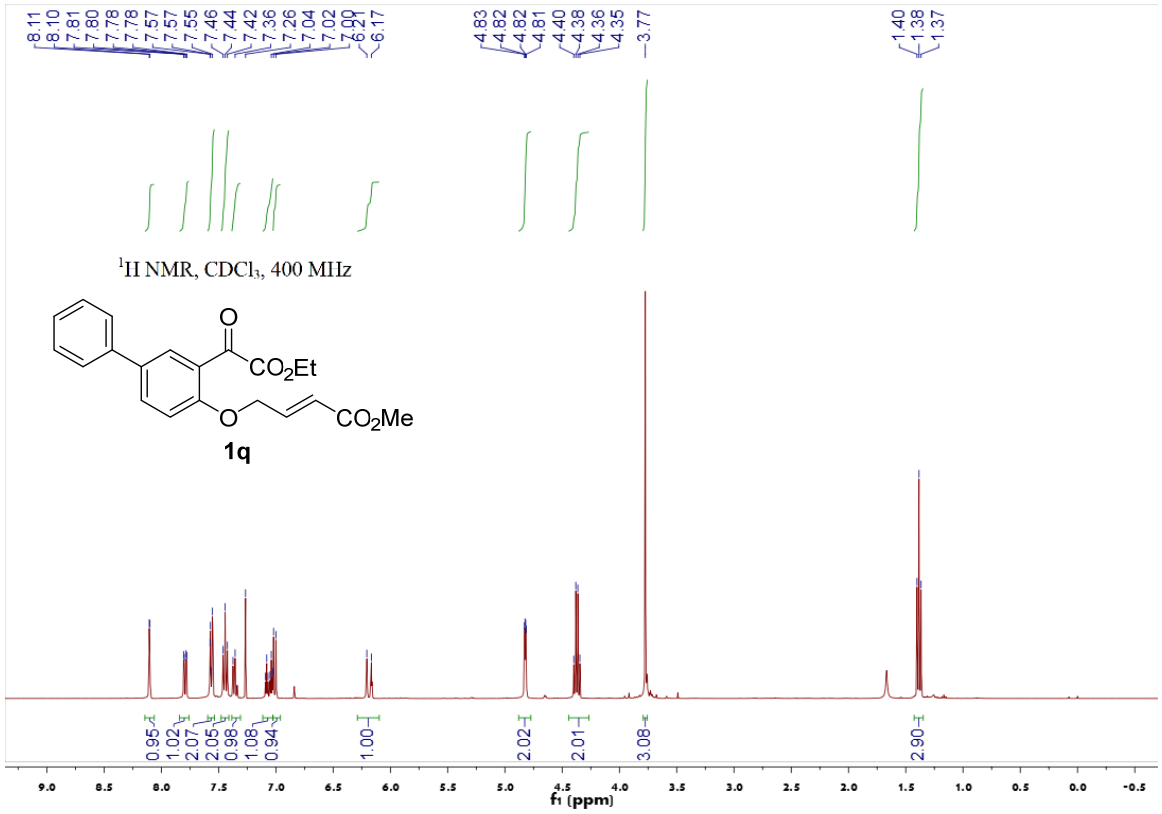
^{1}H NMR, $CDCl_3$, 400 MHz

1p



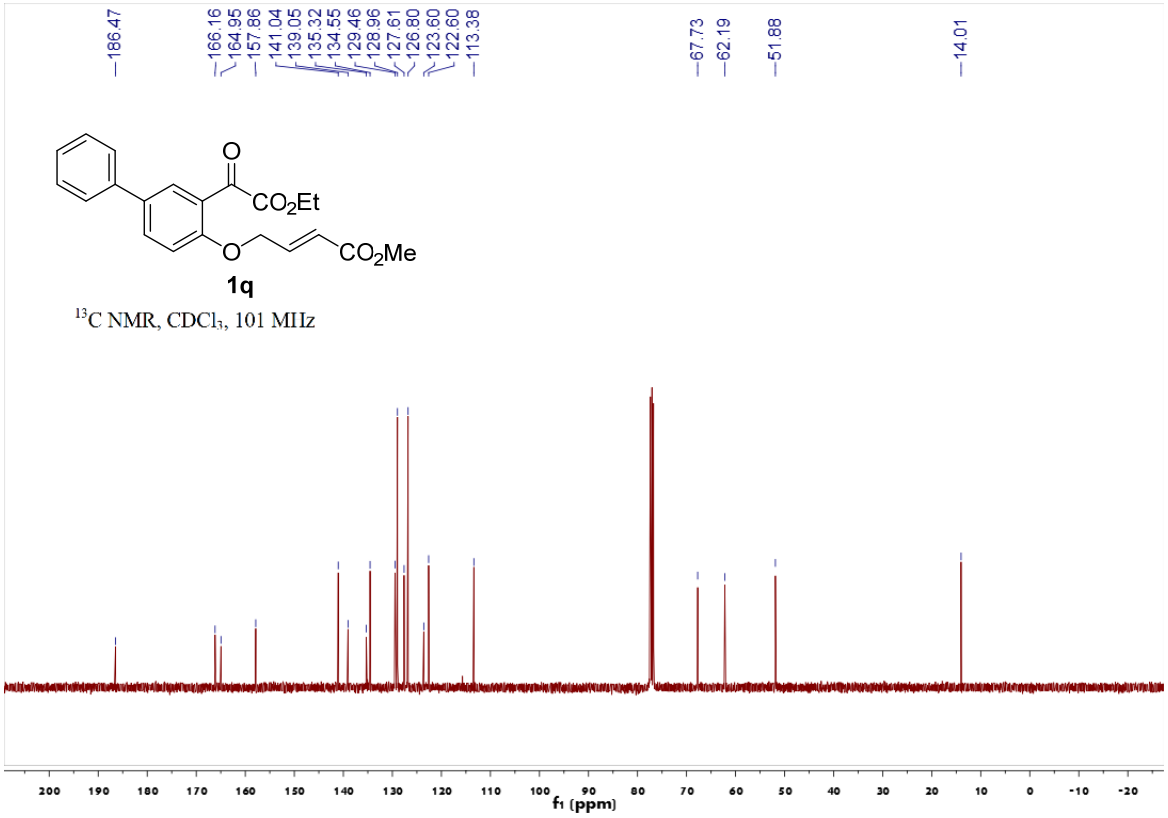
1p

^{13}C NMR, $CDCl_3$, 101 MHz



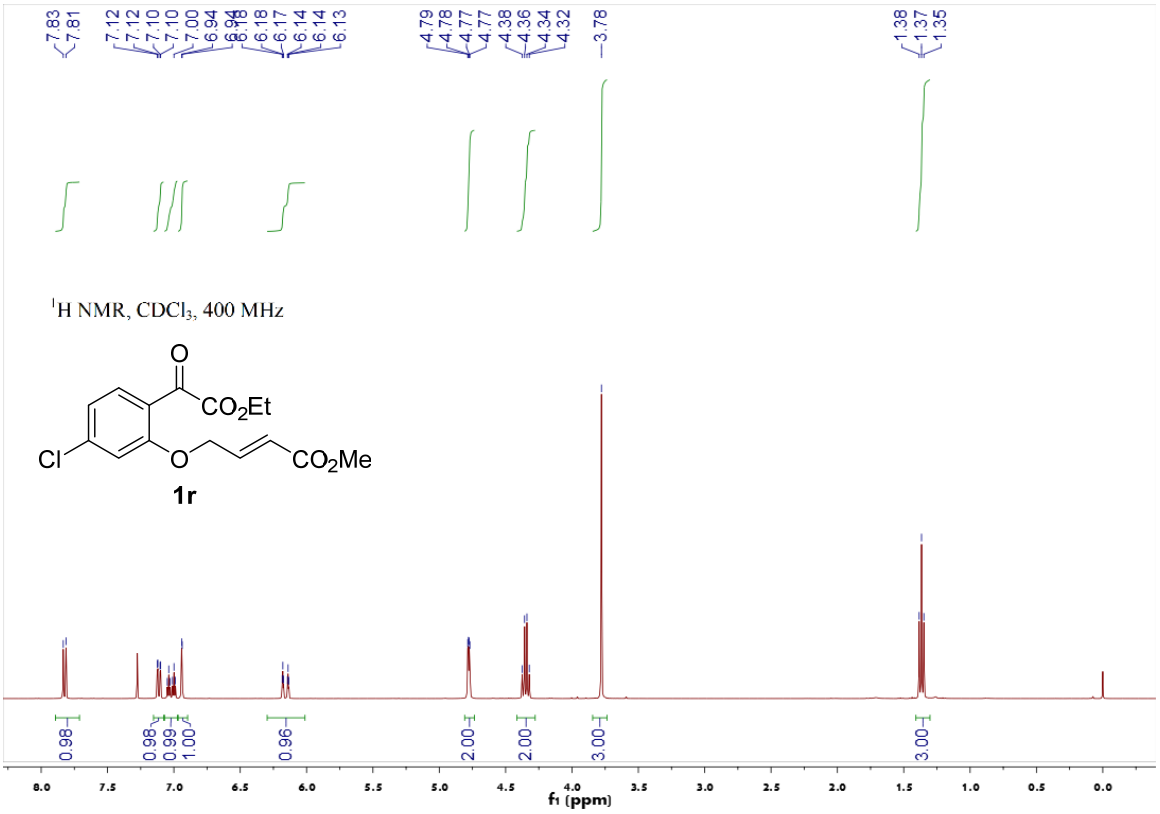
^{1}H NMR, $CDCl_3$, 400 MHz

1q



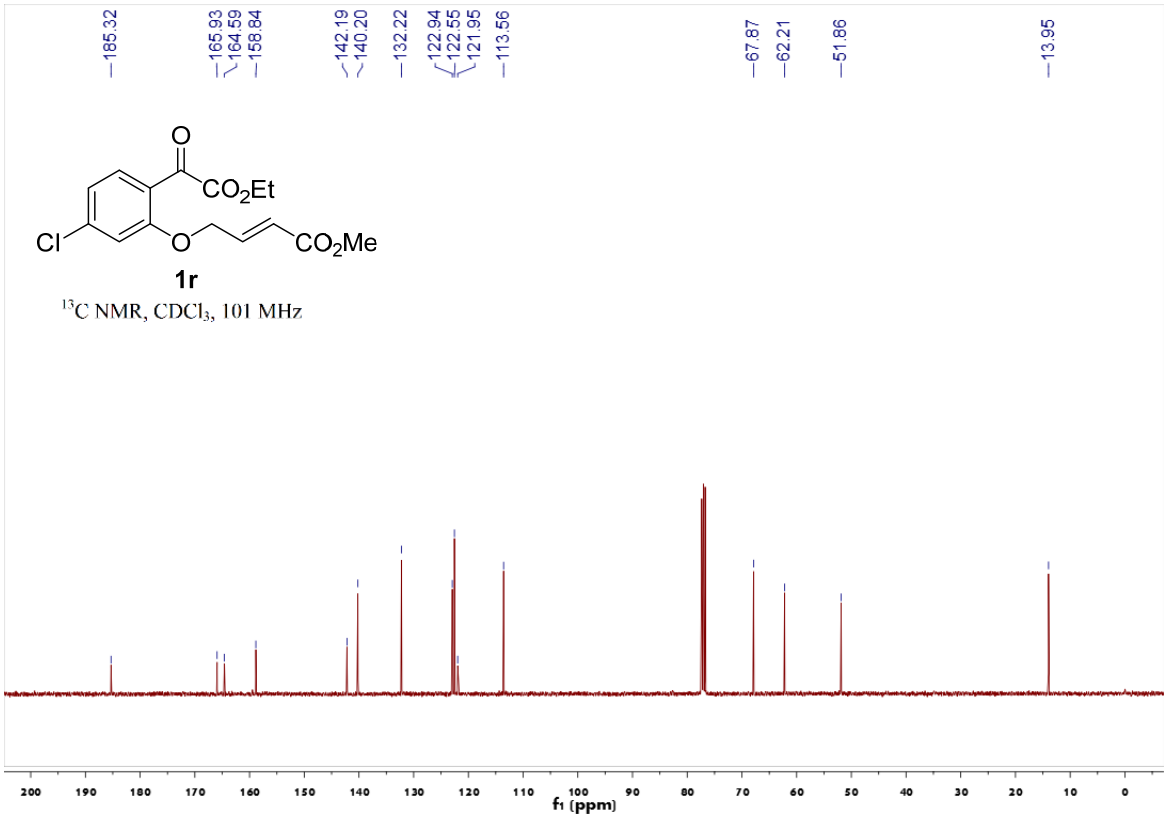
1q

^{13}C NMR, $CDCl_3$, 101 MHz



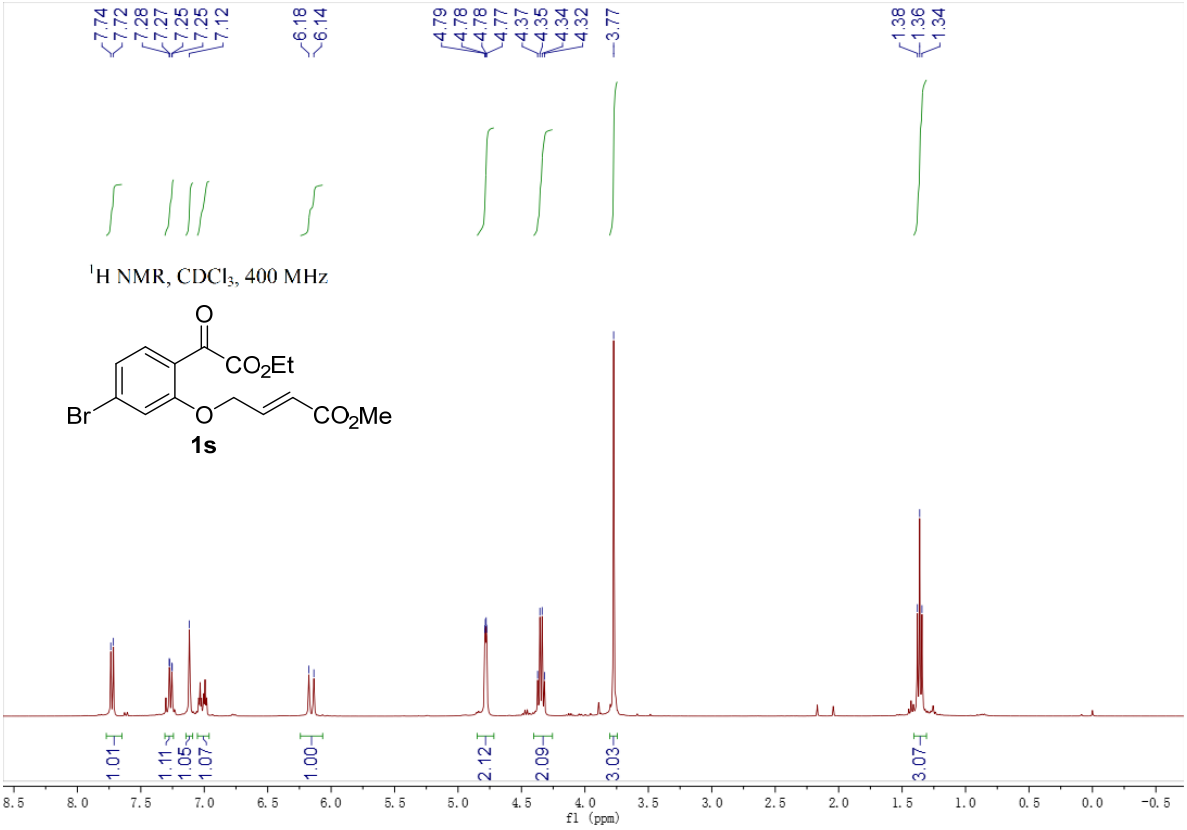
^{1}H NMR, $CDCl_3$, 400 MHz

1r



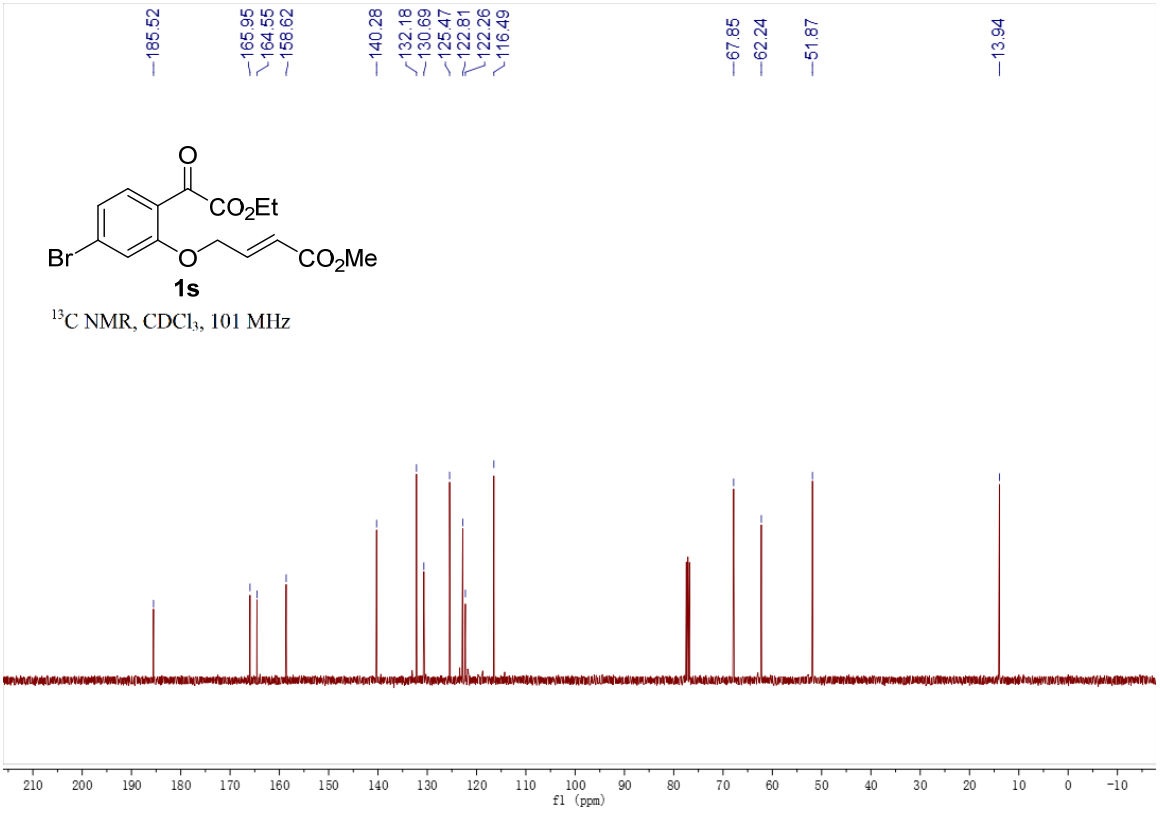
1r

^{13}C NMR, $CDCl_3$, 101 MHz



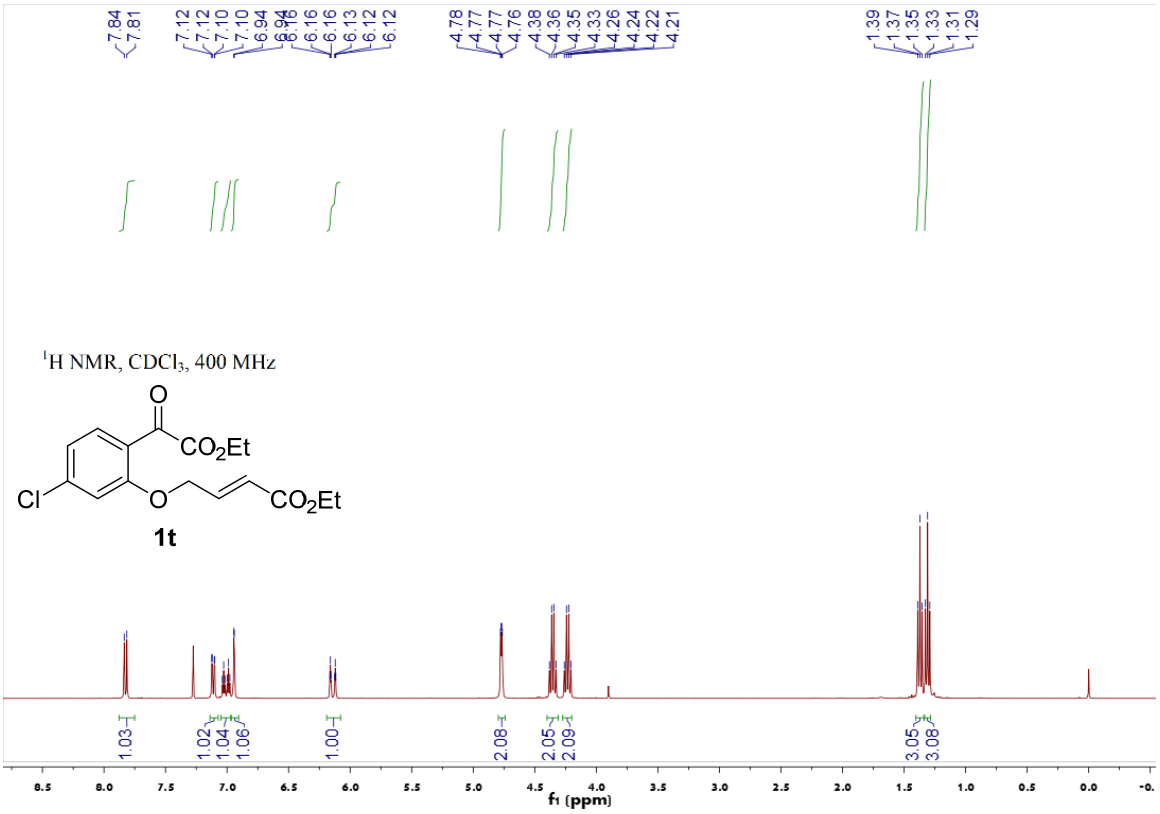
^{1}H NMR, $CDCl_3$, 400 MHz

1s



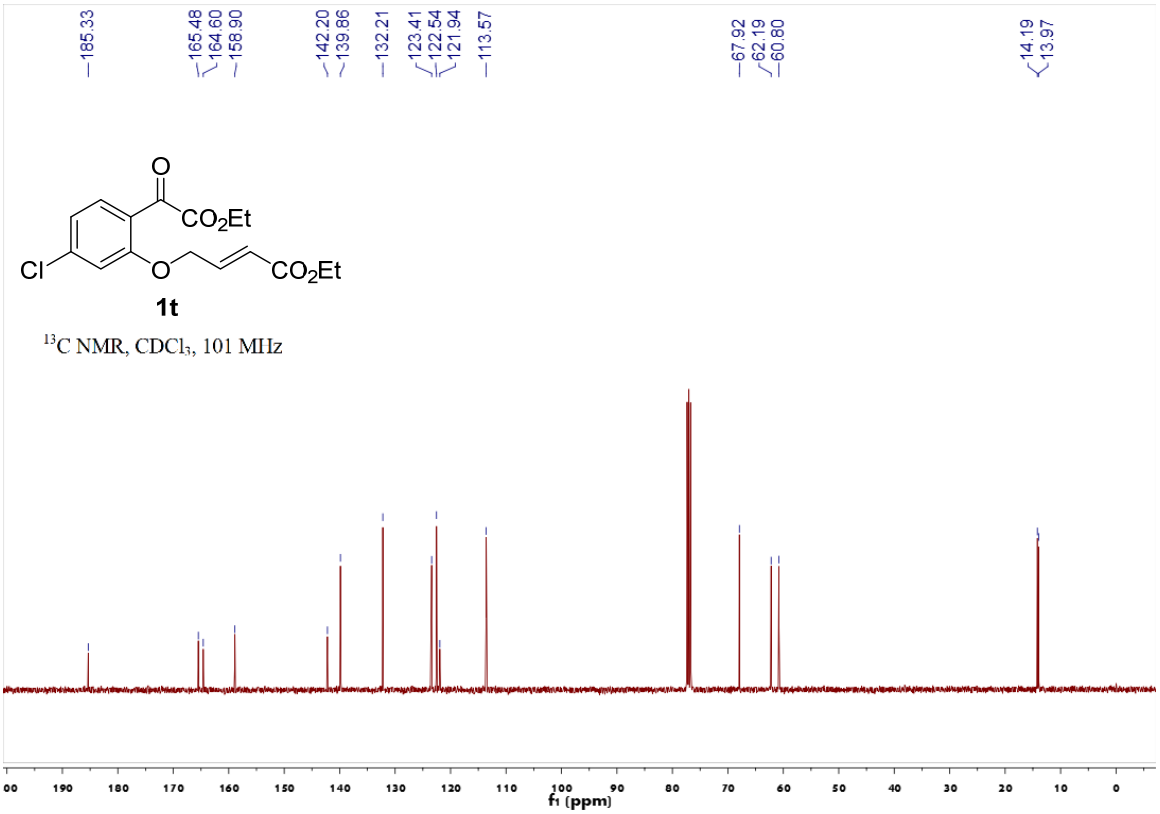
1s

^{13}C NMR, $CDCl_3$, 101 MHz



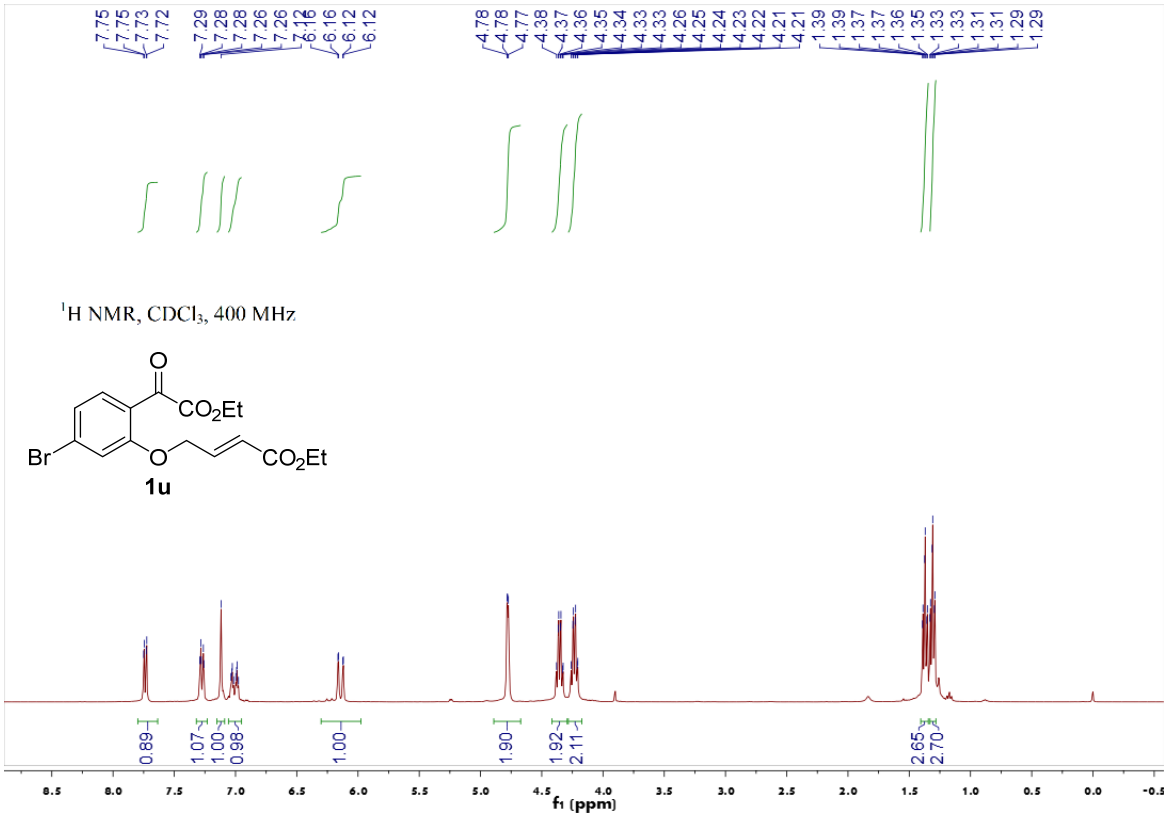
^{1}H NMR, $CDCl_3$, 400 MHz

1t



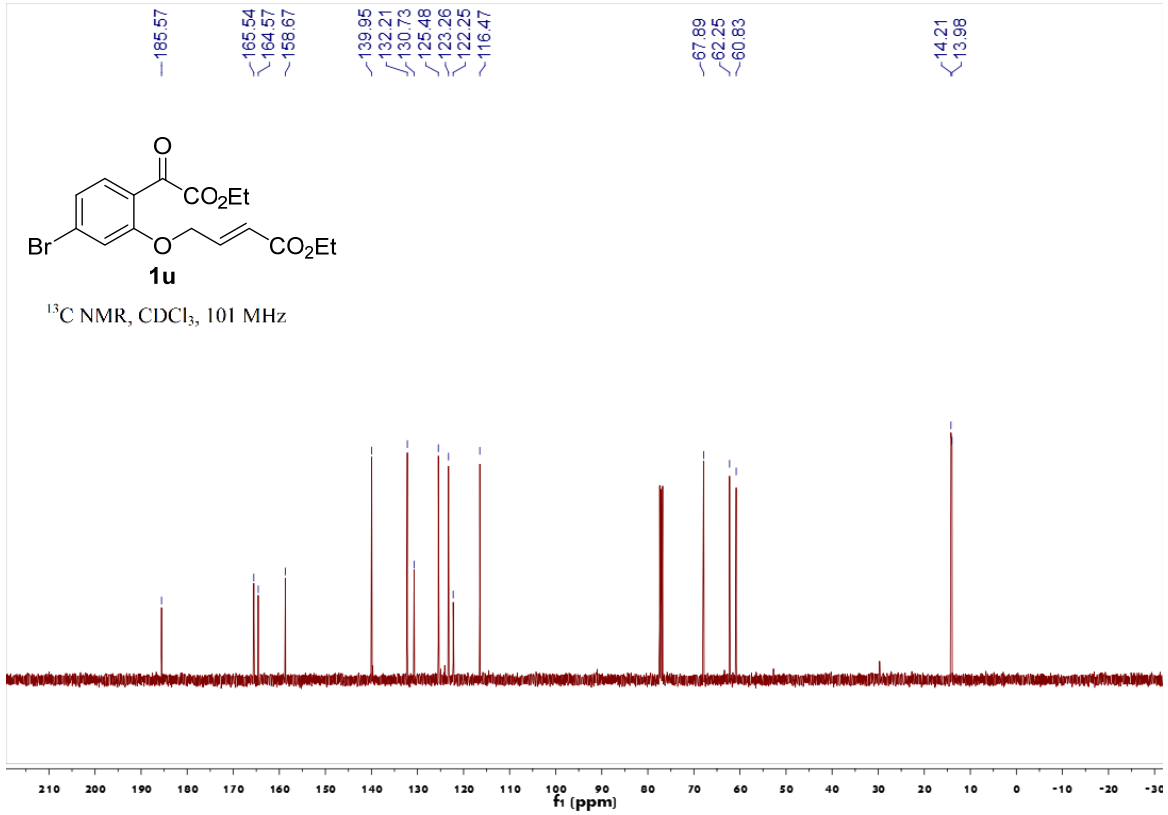
1t

^{13}C NMR, $CDCl_3$, 101 MHz



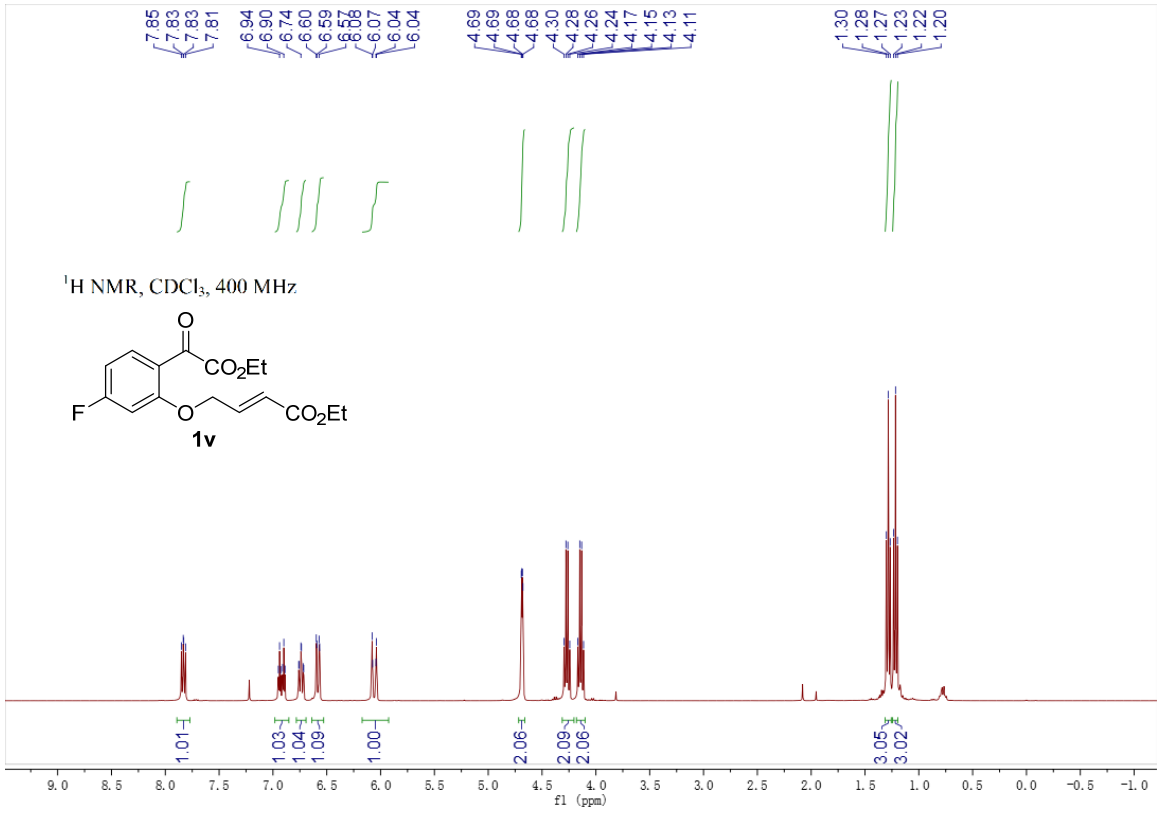
^{1}H NMR, $CDCl_3$, 400 MHz

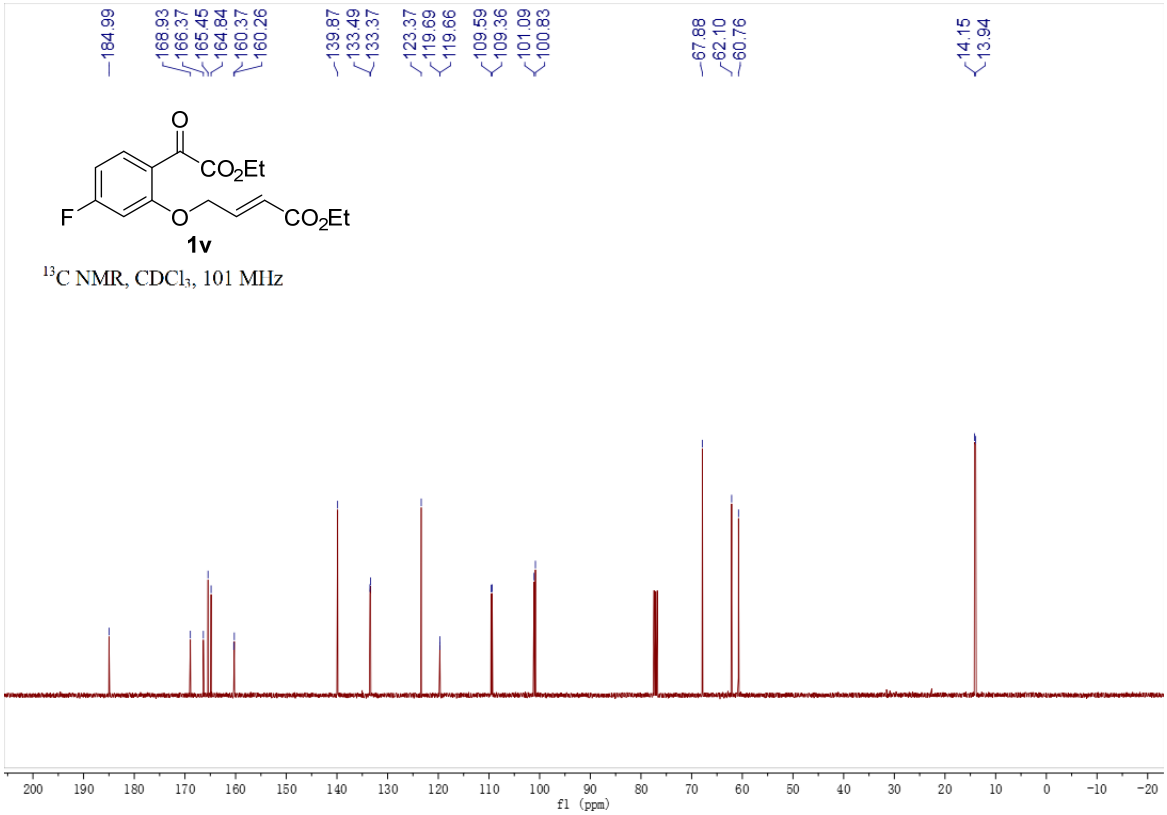
1u

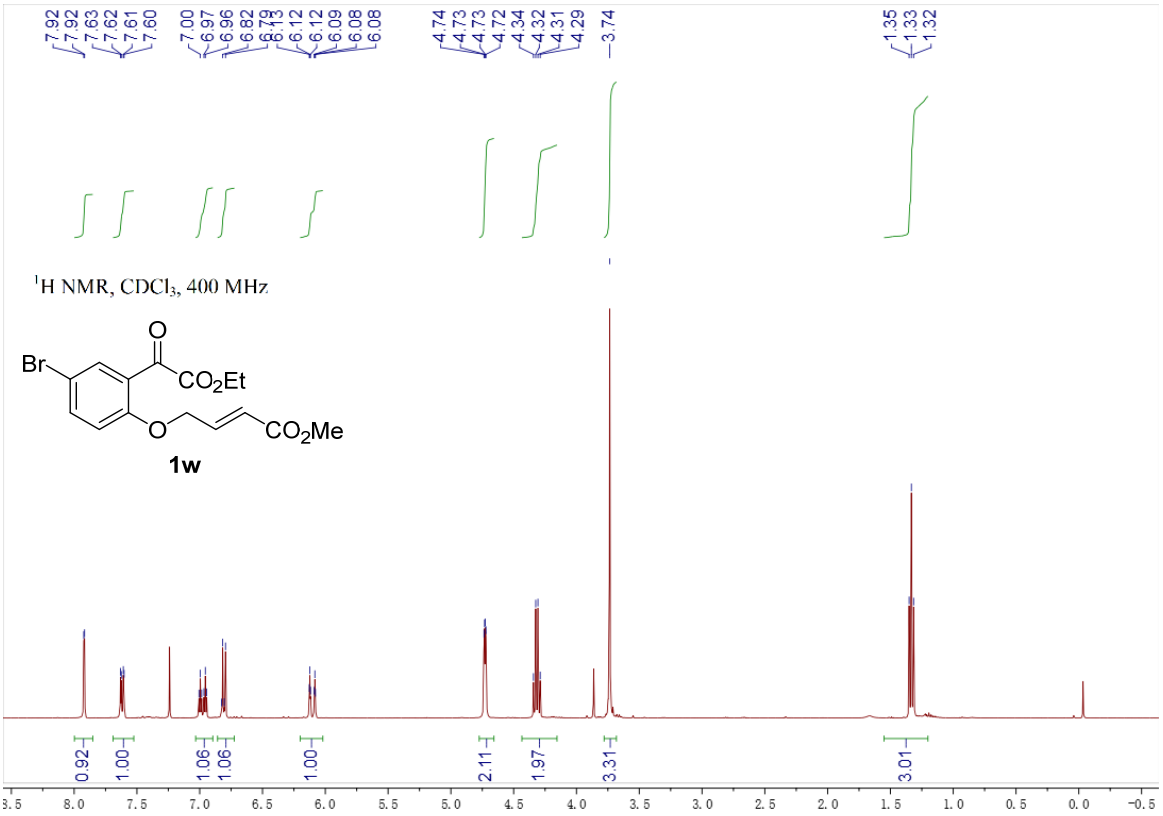


1u

^{13}C NMR, $CDCl_3$, 101 MHz

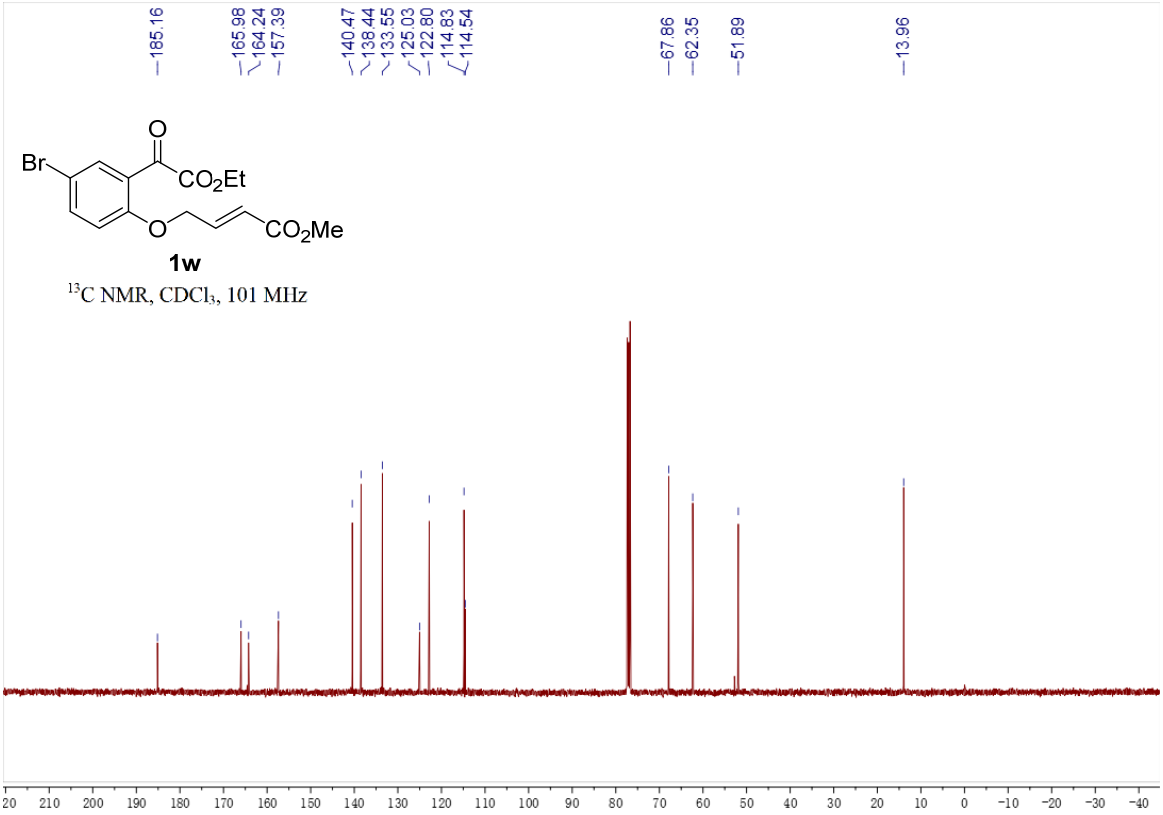

7.85
7.83
7.83
7.81
6.94
6.90
6.74
6.60
6.59
6.57
6.08
6.07
6.04
6.04
4.69
4.69
4.68
4.68
4.30
4.28
4.26
4.24
4.17
4.15
4.13
4.11
1.30
1.28
1.27
1.23
1.22
1.20
1H NMR, CDCl3, 400 MHz
O
CO2Et
F
O
CO2Et
1v
1.01
1.03
1.04
1.09
1.00
2.06
2.09
2.06
3.05
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


184.99
168.93
166.37
165.45
164.84
160.37
160.26
139.87
133.49
133.37
123.37
119.69
119.66
109.59
109.36
101.09
100.83
67.88
62.10
60.76
14.15
13.94
O
CO2Et
F
O
CO2Et
1v
13C NMR, CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



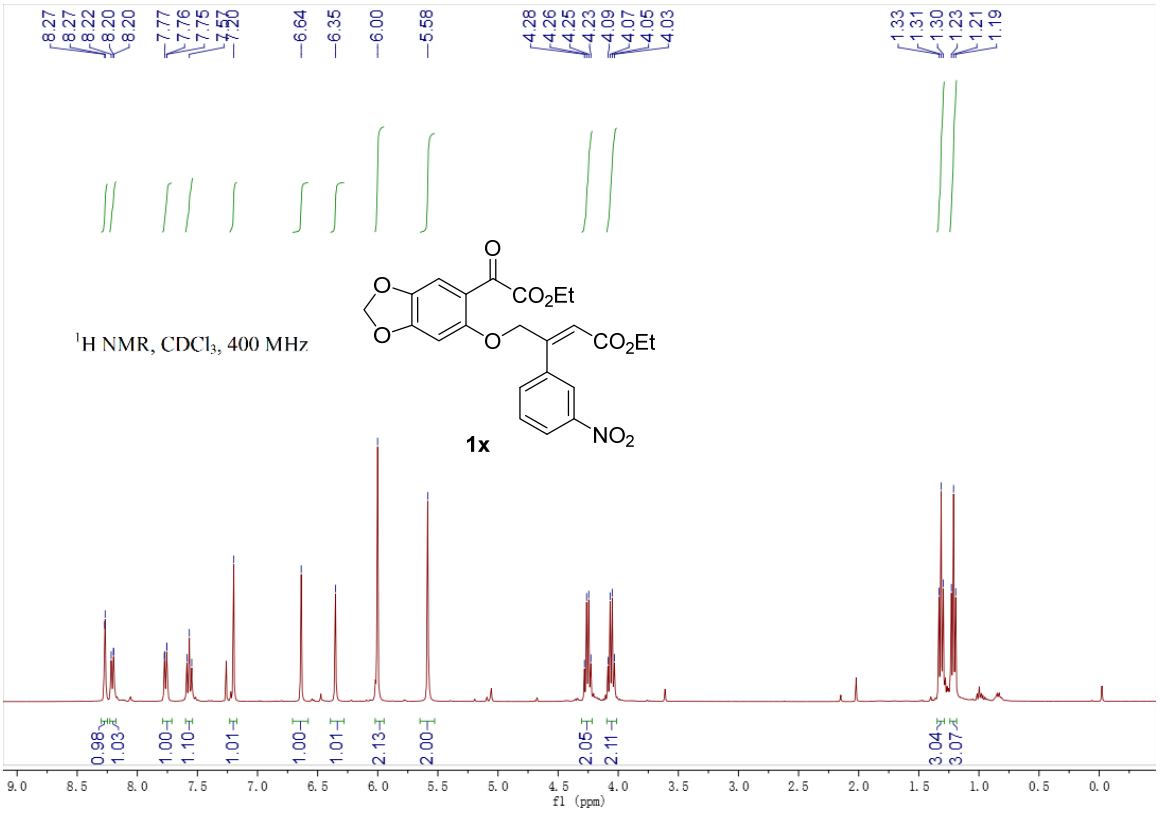
^{1}H NMR, $CDCl_3$, 400 MHz

1w

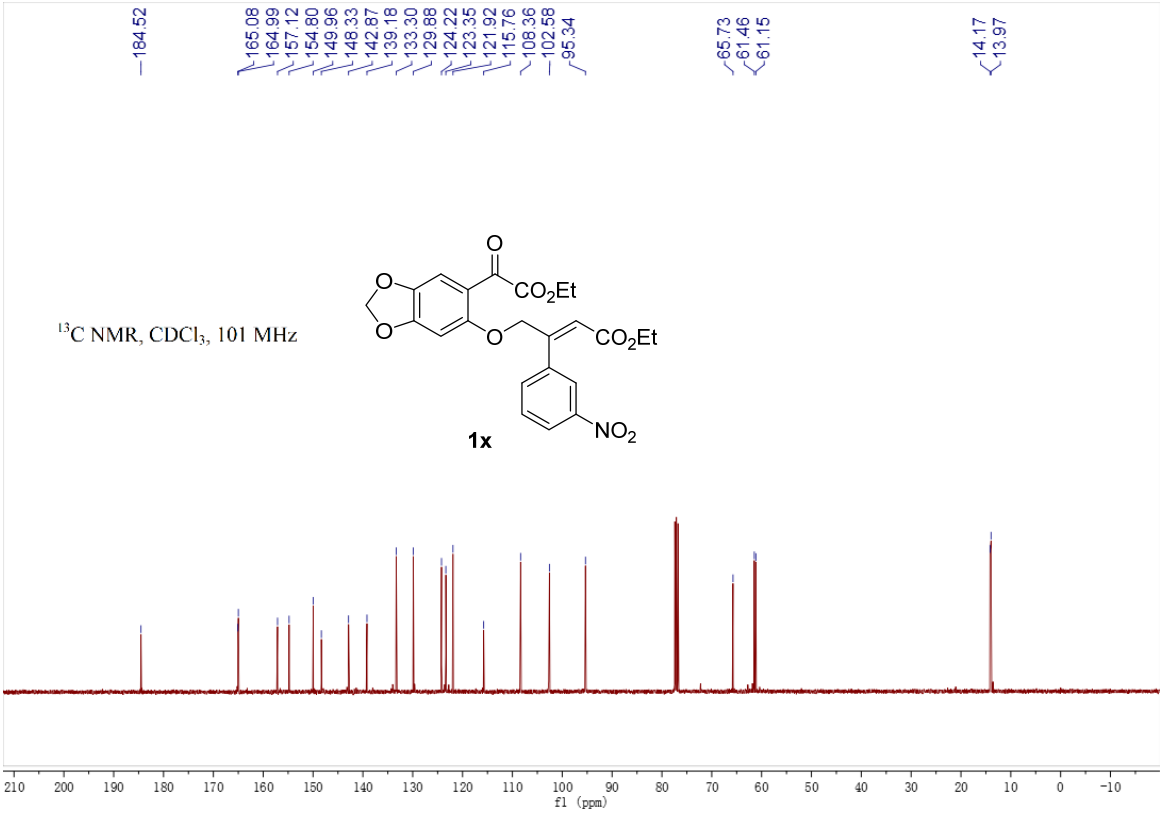


1w

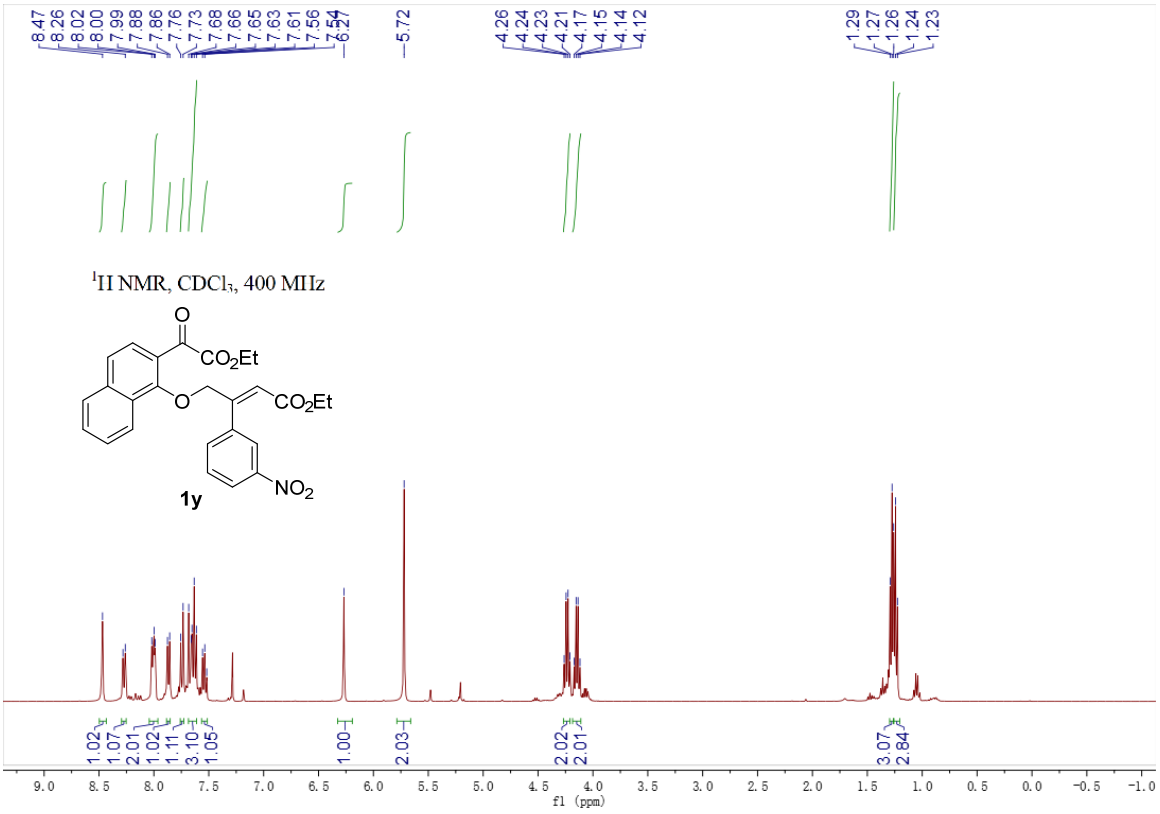
^{13}C NMR, $CDCl_3$, 101 MHz

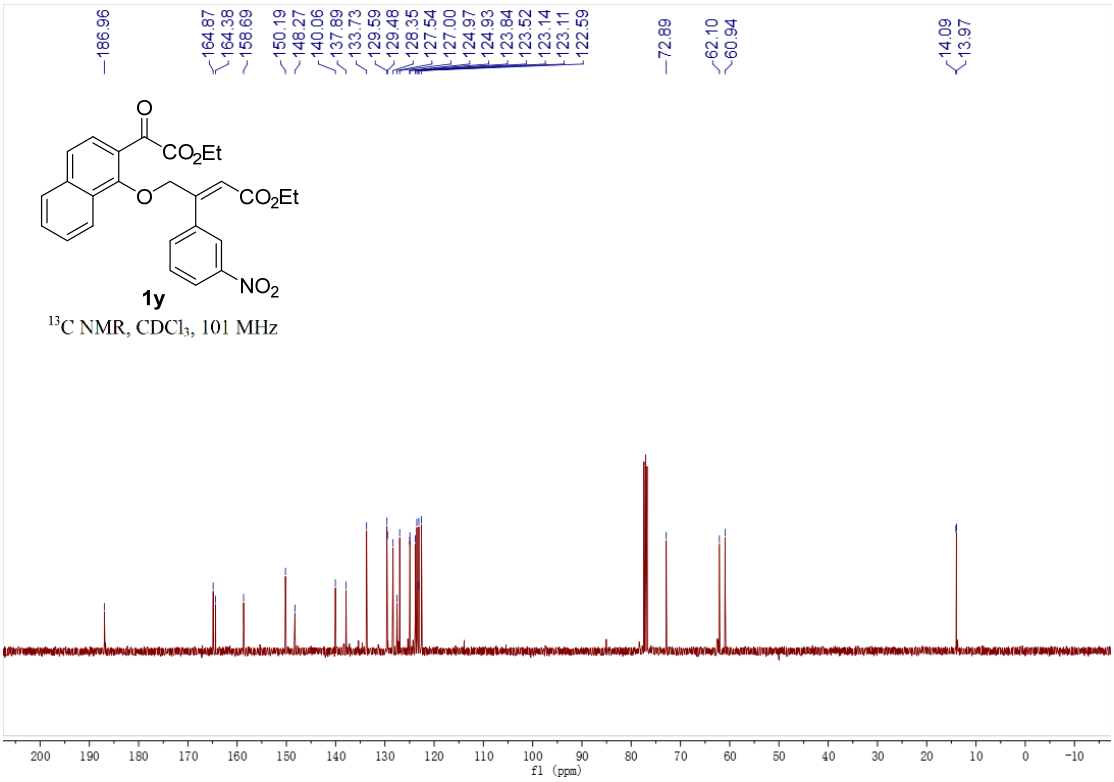


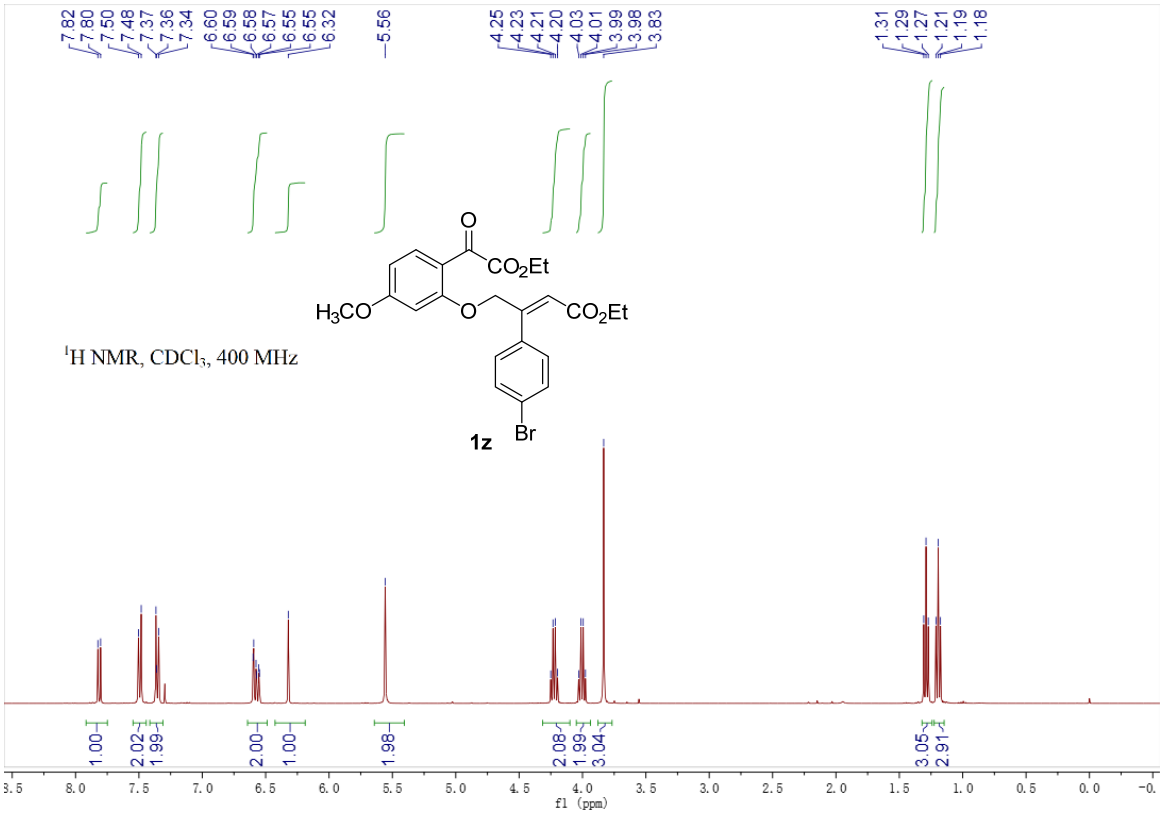
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz


8.47
8.26
8.02
8.00
7.99
7.88
7.86
7.76
7.73
7.68
7.66
7.65
7.63
7.61
7.56
7.54
6.27
5.72
4.26
4.24
4.23
4.21
4.17
4.15
4.14
4.12
1.29
1.27
1.26
1.24
1.23
1H NMR, CDCl3, 400 MHz
CO2Et
CO2Et
NO2
1y
1.02
1.07
2.01
1.02
1.11
3.10
1.05
1.00
2.03
2.02
2.01
3.07
2.84
f1 (ppm)


186.96
164.87
164.38
158.69
150.19
148.27
140.06
137.89
133.73
129.59
129.48
128.35
127.54
127.00
124.97
124.93
123.84
123.52
123.14
123.11
122.59
72.89
62.10
60.94
14.09
13.97
CO2Et
CO2Et
NO2
1y
13C NMR, CDCl3, 101 MHz
f1 (ppm)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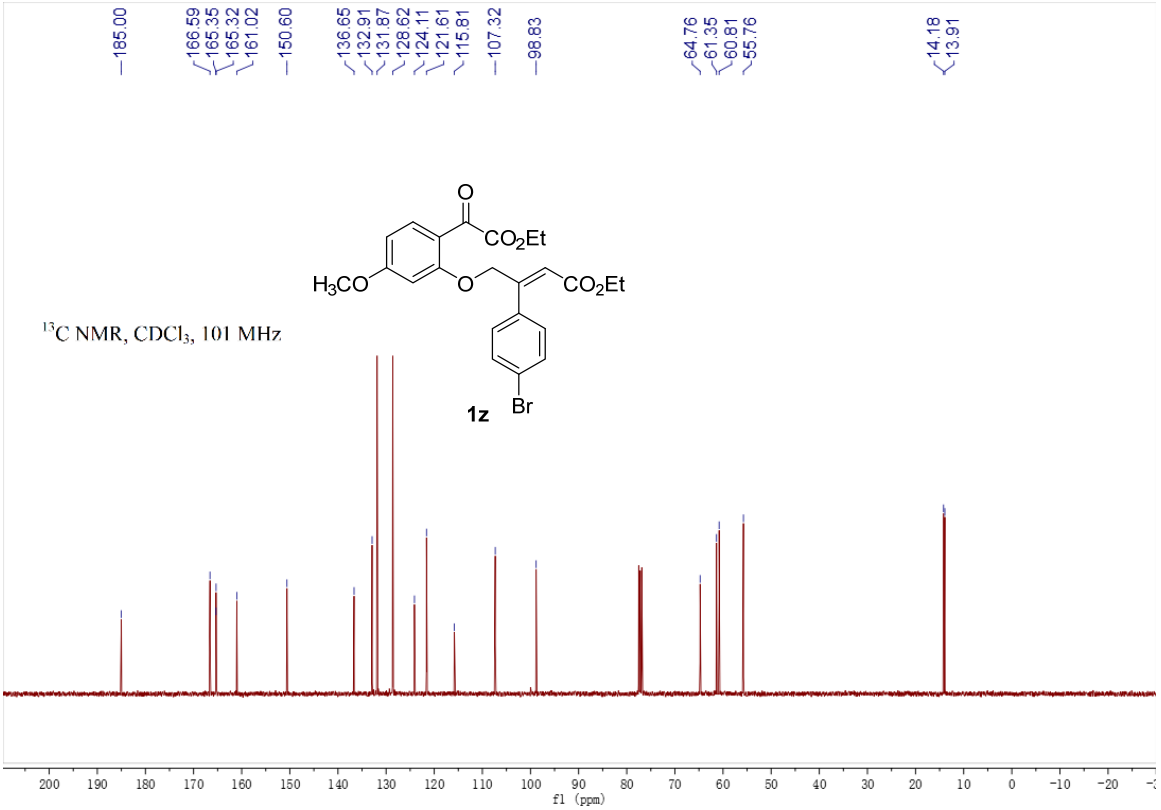
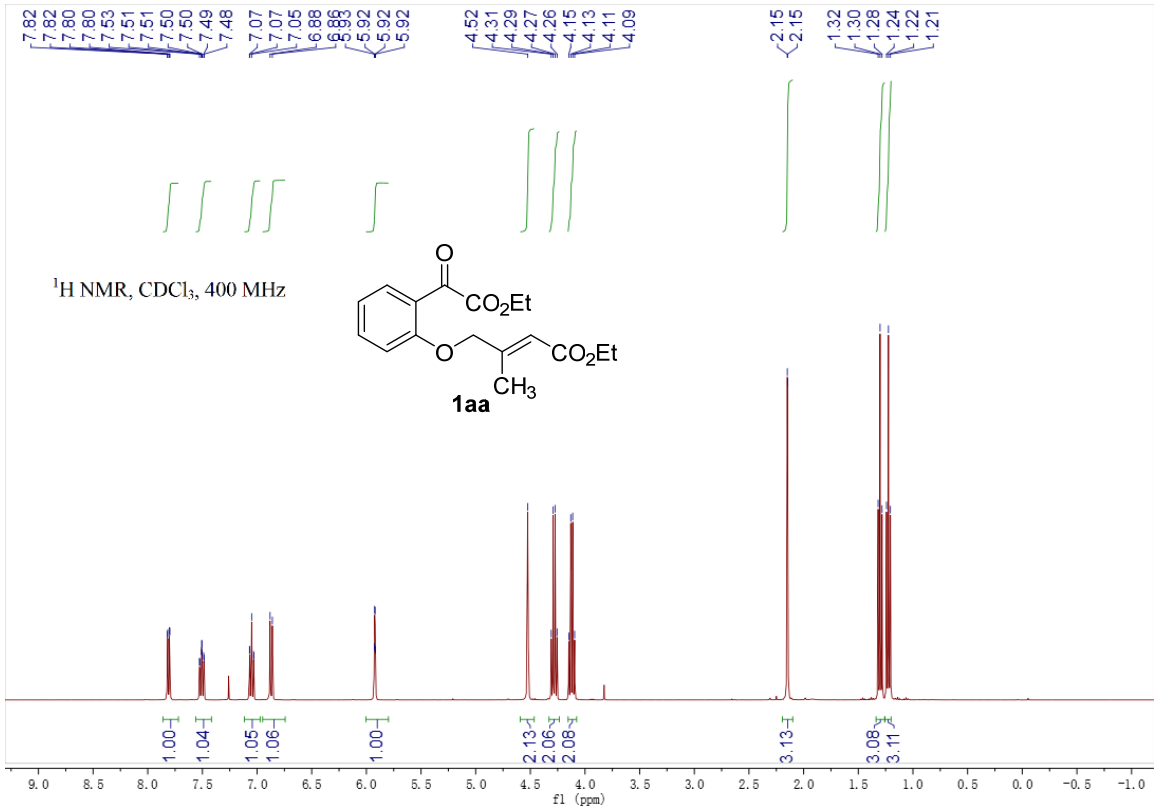
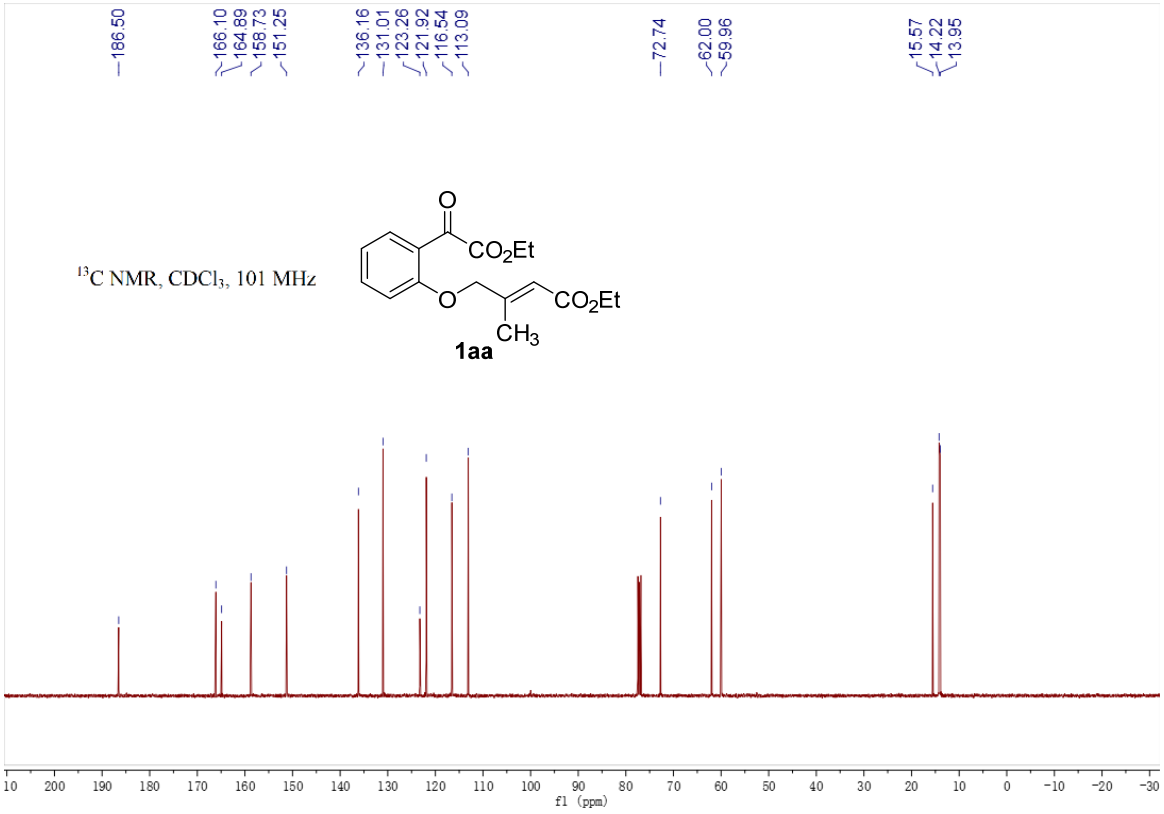
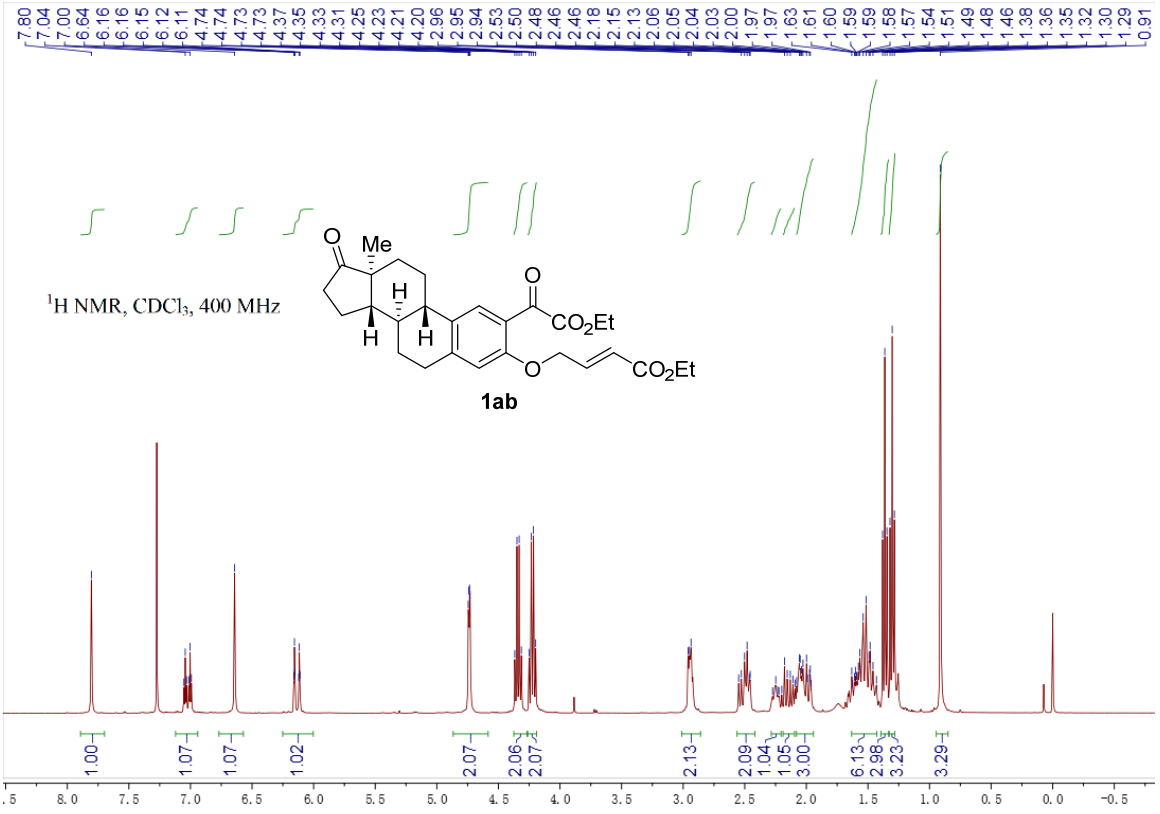
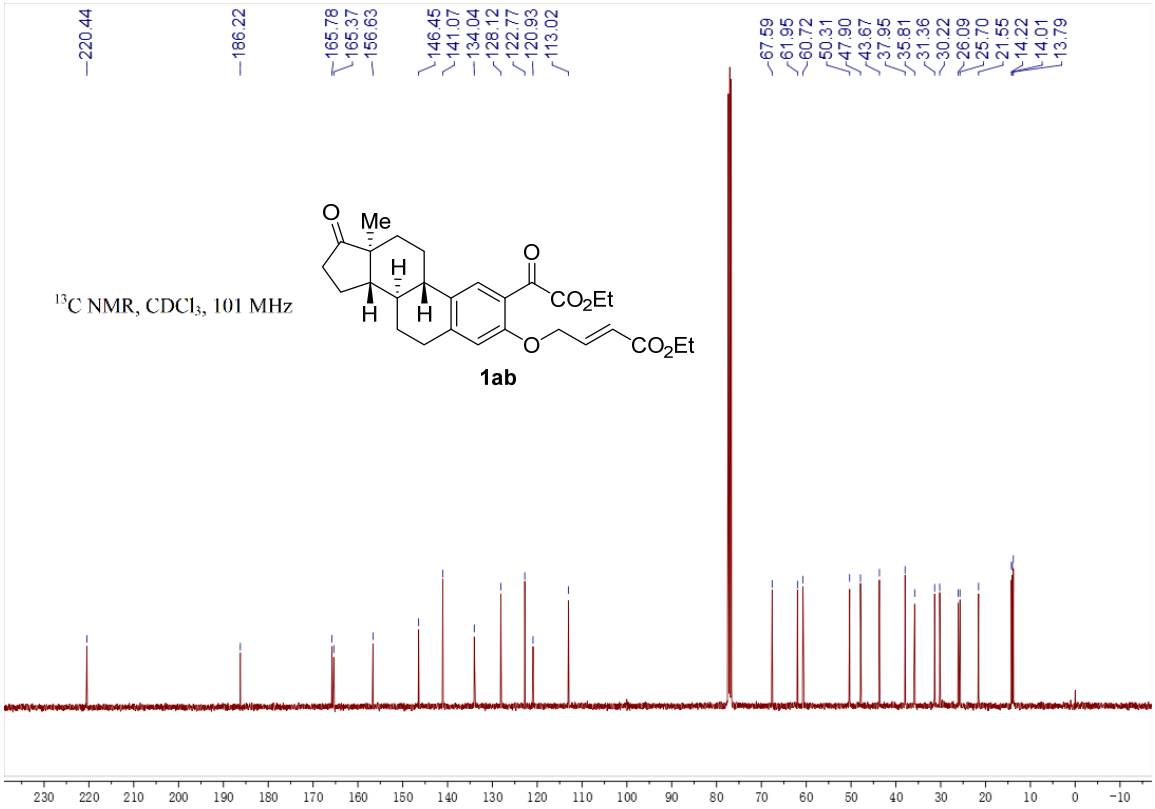
7.80
7.50
7.48
7.37
7.36
7.34
6.60
6.59
6.58
6.57
6.55
6.55
6.32
5.56
4.25
4.23
4.21
4.20
4.03
4.01
3.99
3.98
3.83
1.31
1.29
1.27
1.21
1.19
1.18
O
CO2Et
H3CO
O
CO2Et
Br
1z
1H NMR, CDCl3, 400 MHz
1.00
2.02
1.99
2.00
1.00
1.98
2.08
1.99
3.04
3.05
2.91
f1 (ppm)

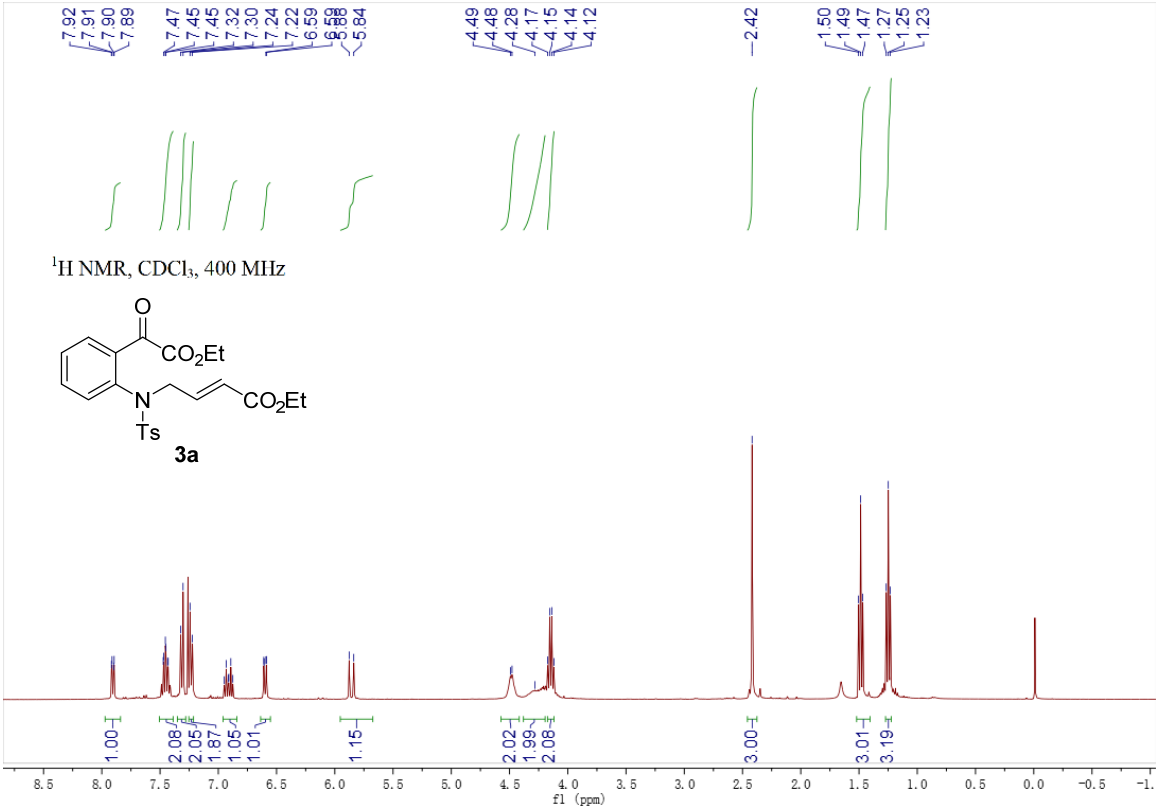

185.00
166.59
165.35
165.32
161.02
150.60
136.65
132.91
131.87
128.62
124.11
121.61
115.81
107.32
98.83
64.76
61.35
60.81
55.76
14.18
13.91
O
CO2Et
H3CO
O
CO2Et
Br
1z
13C NMR, CDCl3, 101 MHz
f1 (ppm)

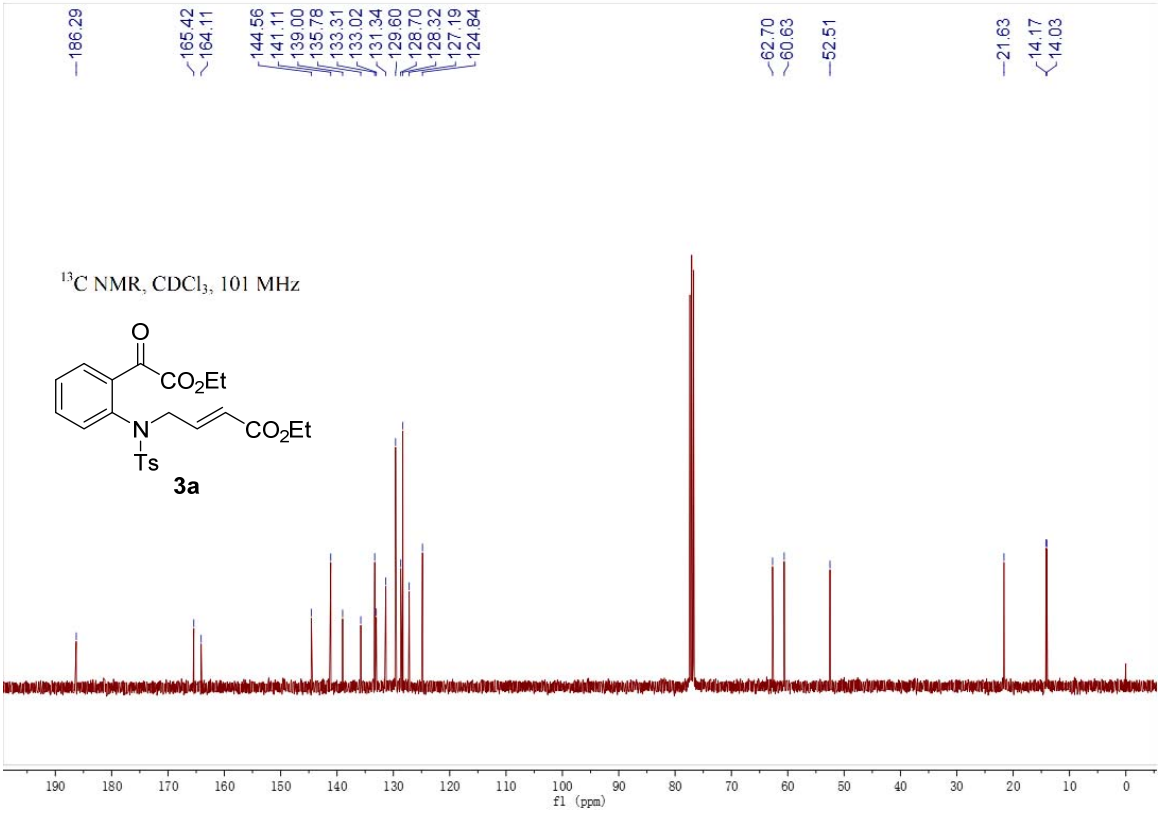

7.82
7.82
7.80
7.80
7.53
7.51
7.51
7.50
7.50
7.49
7.48
7.07
7.07
7.05
6.88
5.92
5.92
5.92
4.52
4.31
4.29
4.27
4.26
4.15
4.13
4.11
4.09
2.15
2.15
1.32
1.30
1.28
1.24
1.22
1.21
1H NMR, CDCl3, 400 MHz
O
CO2Et
O
CO2Et
CH3
1aa
1.00
1.04
1.05
1.06
1.00
2.13
2.06
2.08
3.13
3.08
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

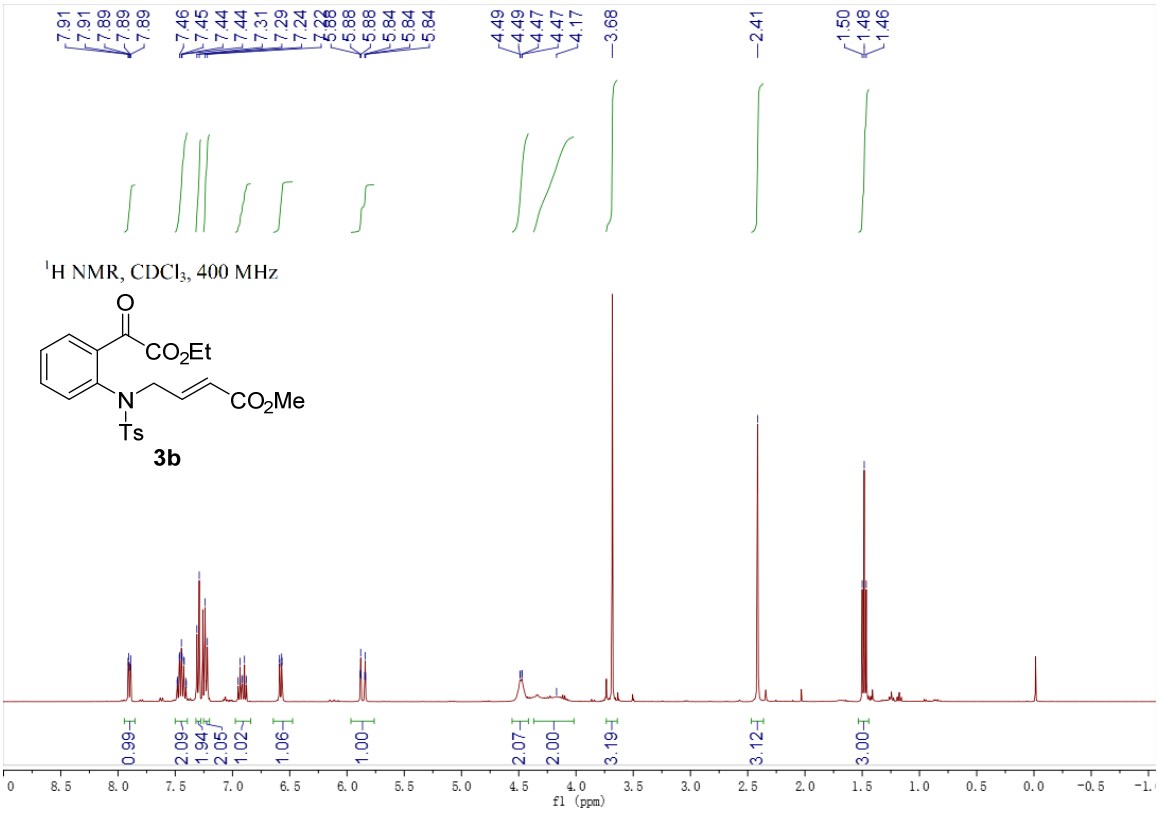

186.50
166.10
164.89
158.73
151.25
136.16
131.01
123.26
121.92
116.54
113.09
72.74
62.00
59.96
15.57
14.22
13.95
13C NMR, CDCl3, 101 MHz
O
CO2Et
O
CO2Et
CH3
1aa
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


7.80 7.04 7.00 6.64 6.16 6.16 6.15 6.12 6.11 4.74 4.74 4.73 4.73 4.37 4.35 4.33 4.31 4.25 4.23 4.21 4.20 2.96 2.95 2.94 2.53 2.50 2.48 2.46 2.46 2.18 2.15 2.13 2.06 2.05 2.04 2.03 2.00 1.97 1.97 1.63 1.61 1.60 1.59 1.59 1.58 1.57 1.54 1.51 1.49 1.48 1.46 1.38 1.36 1.35 1.32 1.30 1.29 0.91
^{1}H NMR, CDCl$_3$, 400 MHz
Me
H
H
H
O
CO$_2$Et
O
CO$_2$Et
1ab
1.00 1.07 1.07 1.02 2.07 2.06 2.07 2.13 2.09 1.04 1.05 3.00 6.13 2.98 3.23 3.29


220.44 186.22 165.78 165.37 156.63 146.45 141.07 134.04 128.12 122.77 120.93 113.02 67.59 61.95 60.72 50.31 47.90 43.67 37.95 35.81 31.36 30.22 26.09 25.70 21.55 14.22 14.01 13.79
^{13}C NMR, CDCl$_3$, 101 MHz
Me
H
H
H
O
CO$_2$Et
O
CO$_2$Et
1ab


7.92
7.91
7.90
7.89
7.47
7.45
7.45
7.32
7.30
7.24
7.22
6.59
5.88
5.84
4.49
4.48
4.28
4.17
4.15
4.14
4.12
2.42
1.50
1.49
1.47
1.27
1.25
1.23
1H NMR, CDCl3, 400 MHz
O
CO2Et
N
Ts
CO2Et
3a
1.00
2.08
2.05
1.87
1.05
1.01
1.15
2.02
1.99
2.08
3.00
3.01
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


186.29
165.42
164.11
144.56
141.11
139.00
135.78
133.31
133.02
131.34
129.60
128.70
128.32
127.19
124.84
62.70
60.63
52.51
21.63
14.17
14.03
13C NMR, CDCl3, 101 MHz
O
CO2Et
N
Ts
CO2Et
3a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.91
7.91
7.89
7.89
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7.44
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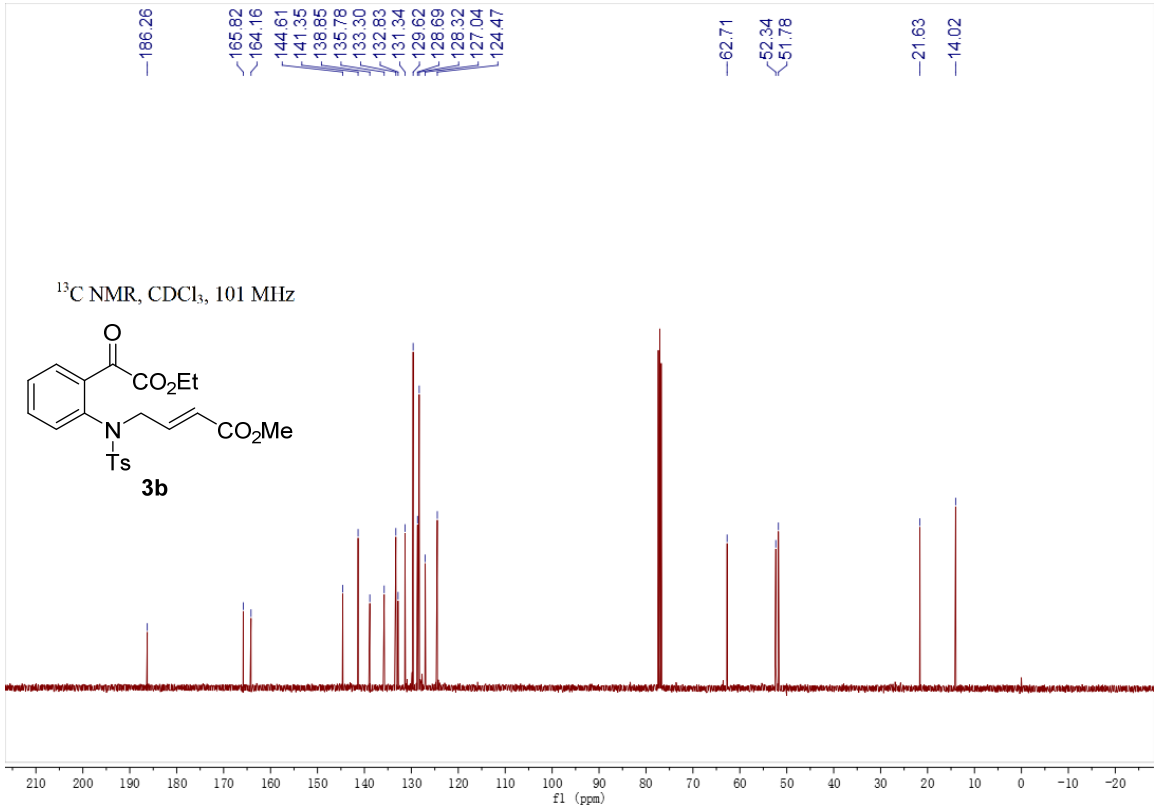
5.88
5.88
5.84
5.84
5.84
4.49
4.49
4.47
4.47
4.17
3.68
2.41
1.50
1.48
1.46
^{1}H NMR, CDCl$_3$, 400 MHz
O
CO$_2$Et
N
Ts
CO$_2$Me
3b
0.99
2.09
1.94
2.05
1.02
1.06
1.00
2.07
2.00
3.19
3.12
3.00
f1 (ppm)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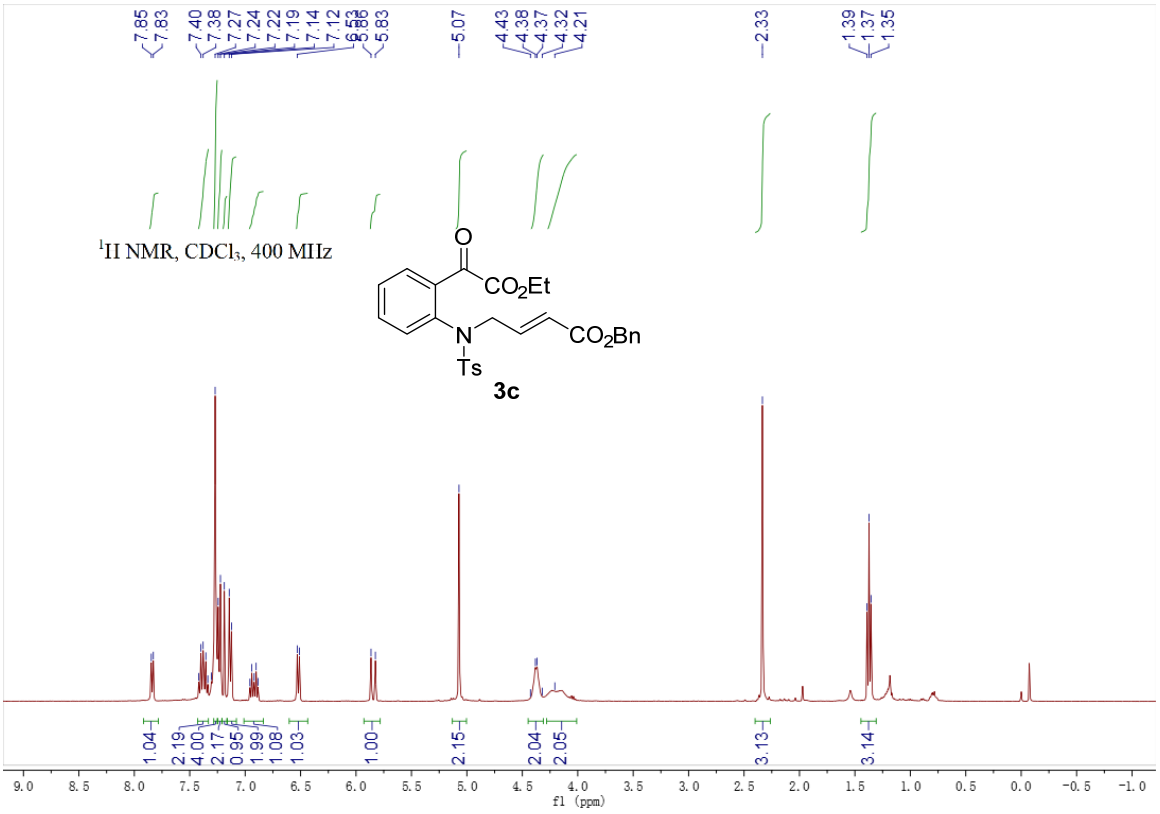
131.34
129.62
128.69
128.32
127.04
124.47
62.71
52.34
51.78
21.63
14.02
^{13}C NMR, CDCl$_3$, 101 MHz
O
CO$_2$Et
N
Ts
CO$_2$Me
3b
f1 (ppm)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5.07
4.43
4.38
4.37
4.32
4.21
2.33
1.39
1.37
1.35
1H NMR, CDCl3, 400 MHz
O
CO2Et
N
Ts
CO2Bn
3c
1.04
2.19
4.00
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1.08
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1.00
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2.05
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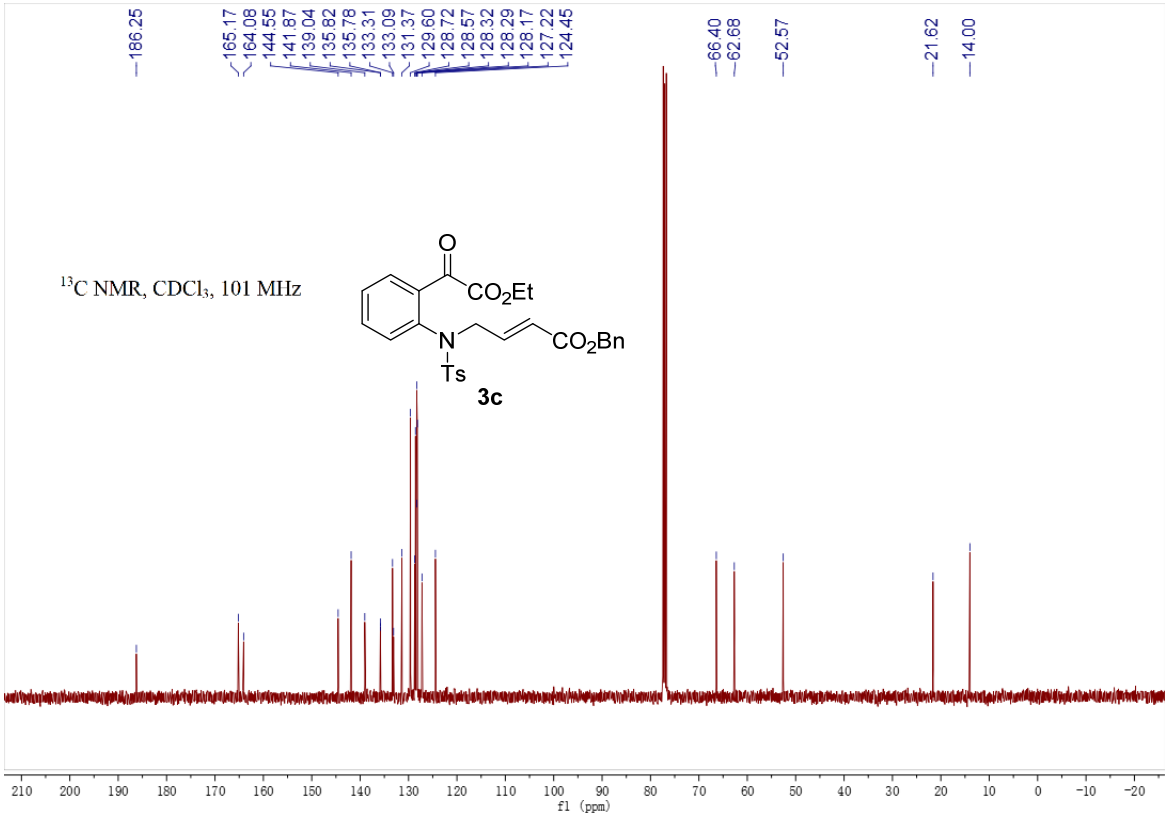
f1 (ppm)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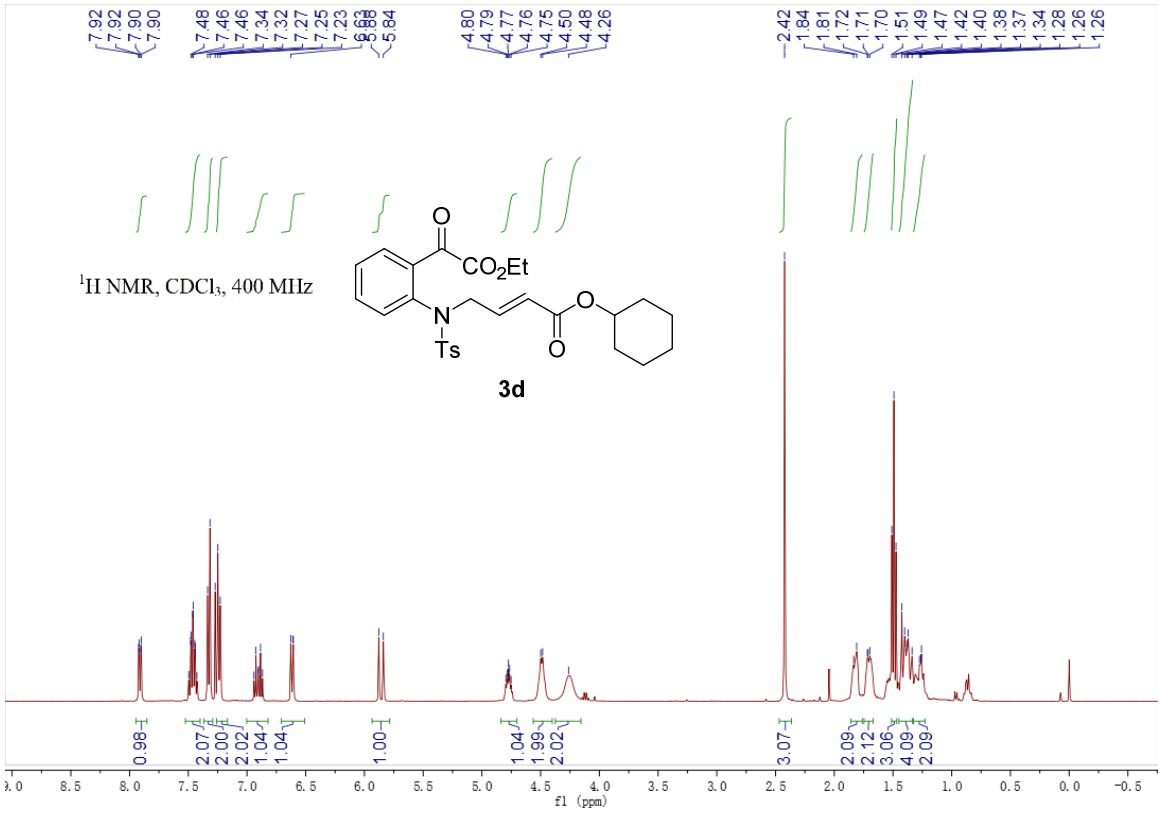
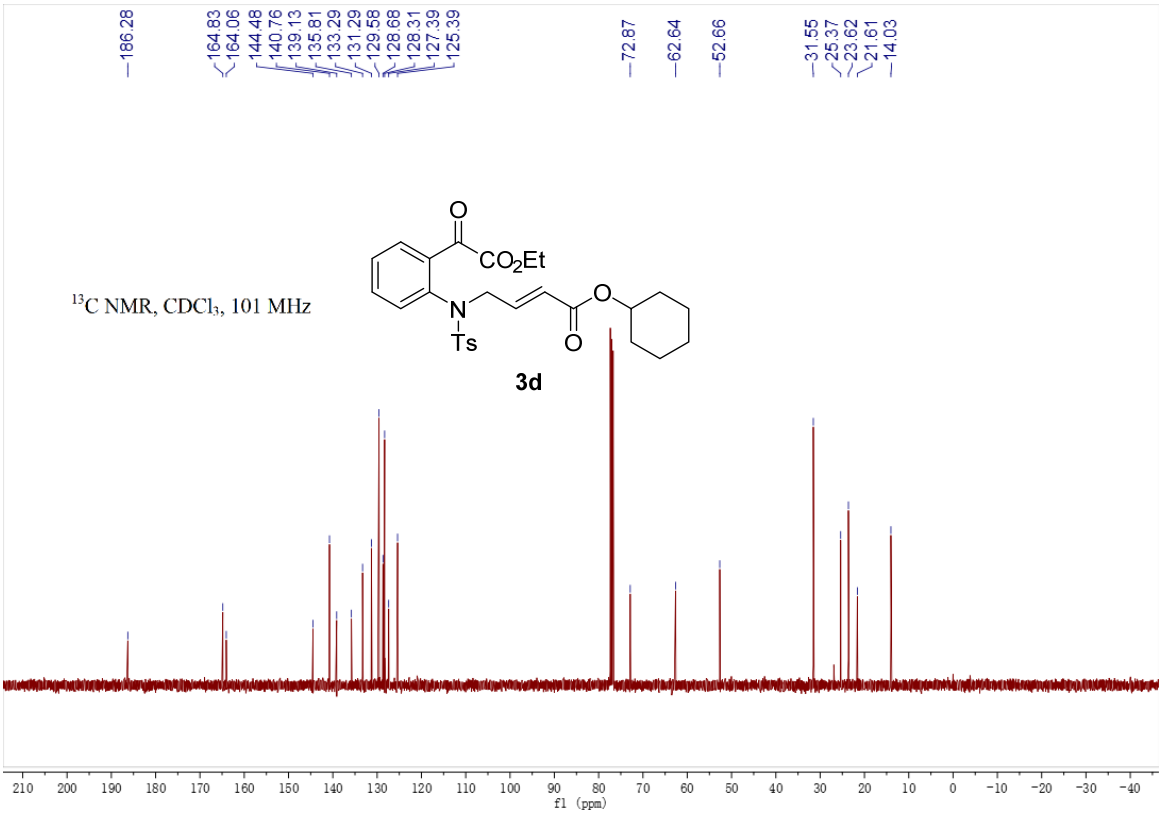
128.57
128.32
128.29
128.17
127.22
124.45
66.40
62.68
52.57
21.62
14.00
13C NMR, CDCl3, 101 MHz
O
CO2Et
N
Ts
CO2Bn
3c
f1 (ppm)



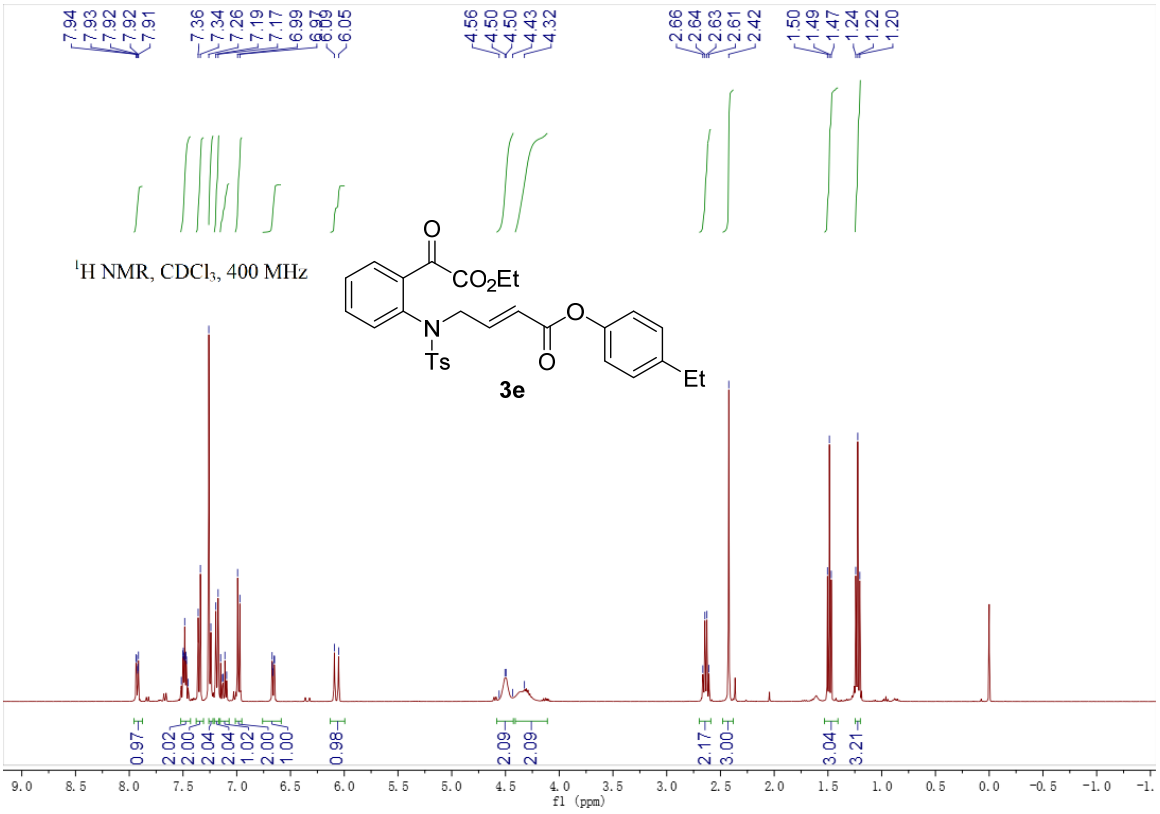
^{1}H NMR, $CDCl_3$, 400 MHz

3d



^{13}C NMR, $CDCl_3$, 101 MHz

3d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6.05
4.56
4.50
4.50
4.43
4.32
2.66
2.64
2.63
2.61
2.42
1.50
1.49
1.47
1.24
1.22
1.20
^{1}H NMR, CDCl$_3$, 400 MHz
O
CO$_2$Et
N
Ts
O
O
O
Et
3e
0.97
2.02
2.00
2.04
2.04
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3.04
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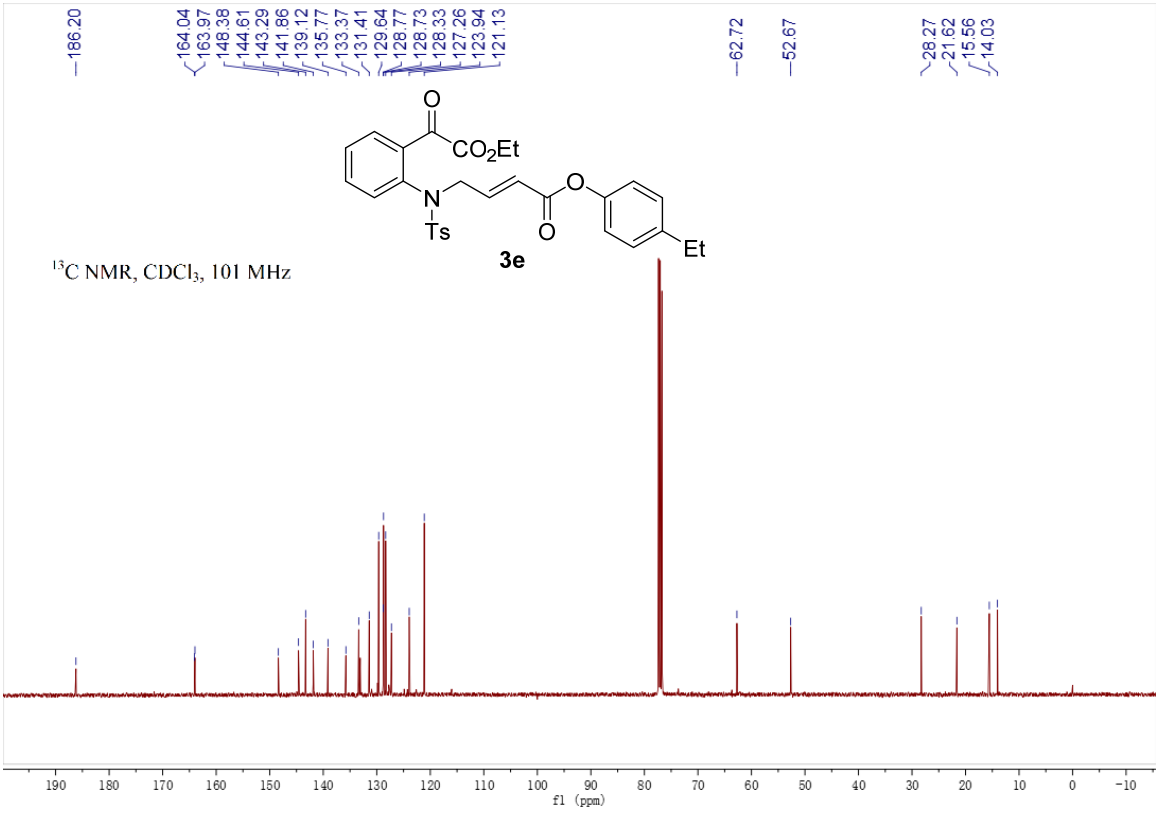
f1 (ppm)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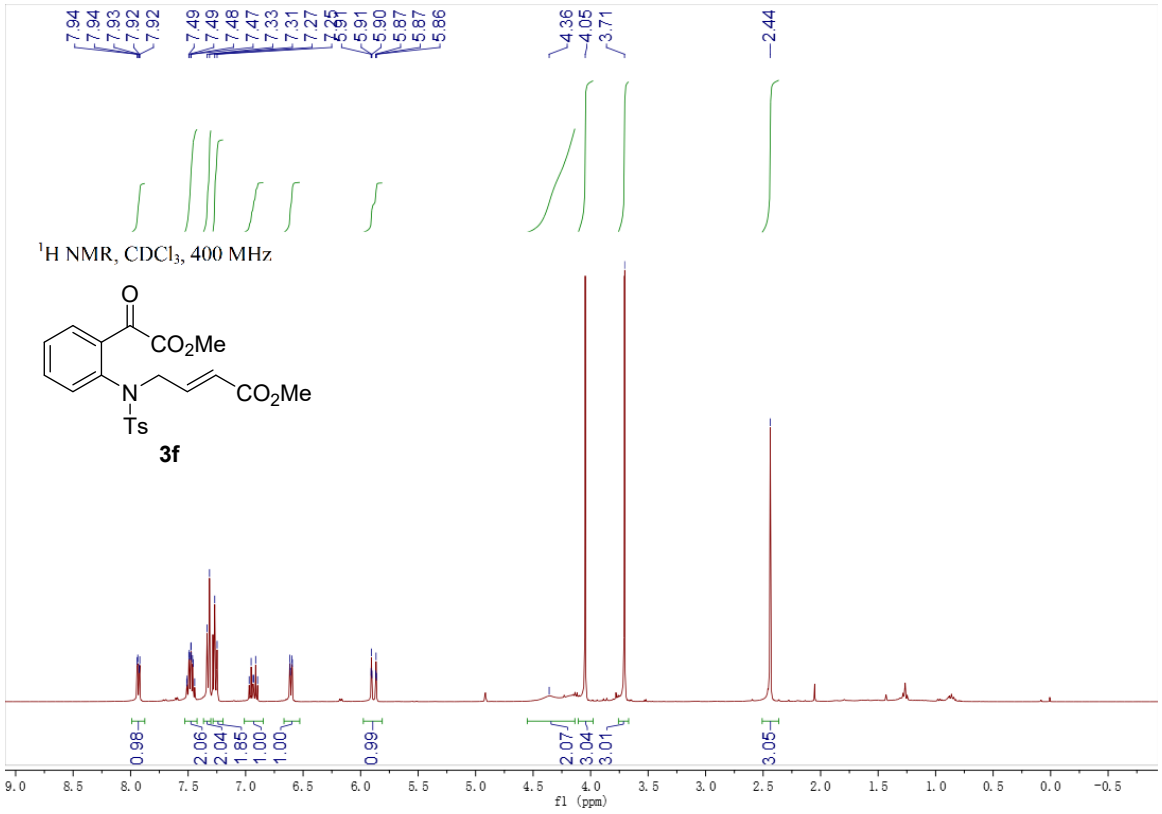
128.73
128.33
127.26
123.94
121.13
62.72
52.67
28.27
21.62
15.56
14.03
^{13}C NMR, CDCl$_3$, 101 MHz
O
CO$_2$Et
N
Ts
O
O
O
Et
3e
f1 (ppm)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7.31
7.27
5.91
5.90
5.87
5.87
5.86
4.36
4.05
3.71
2.44
^{1}H NMR, $CDCl_3$, 400 MHz
O
CO_2Me
N
Ts
CO_2Me
3f
0.98
2.06
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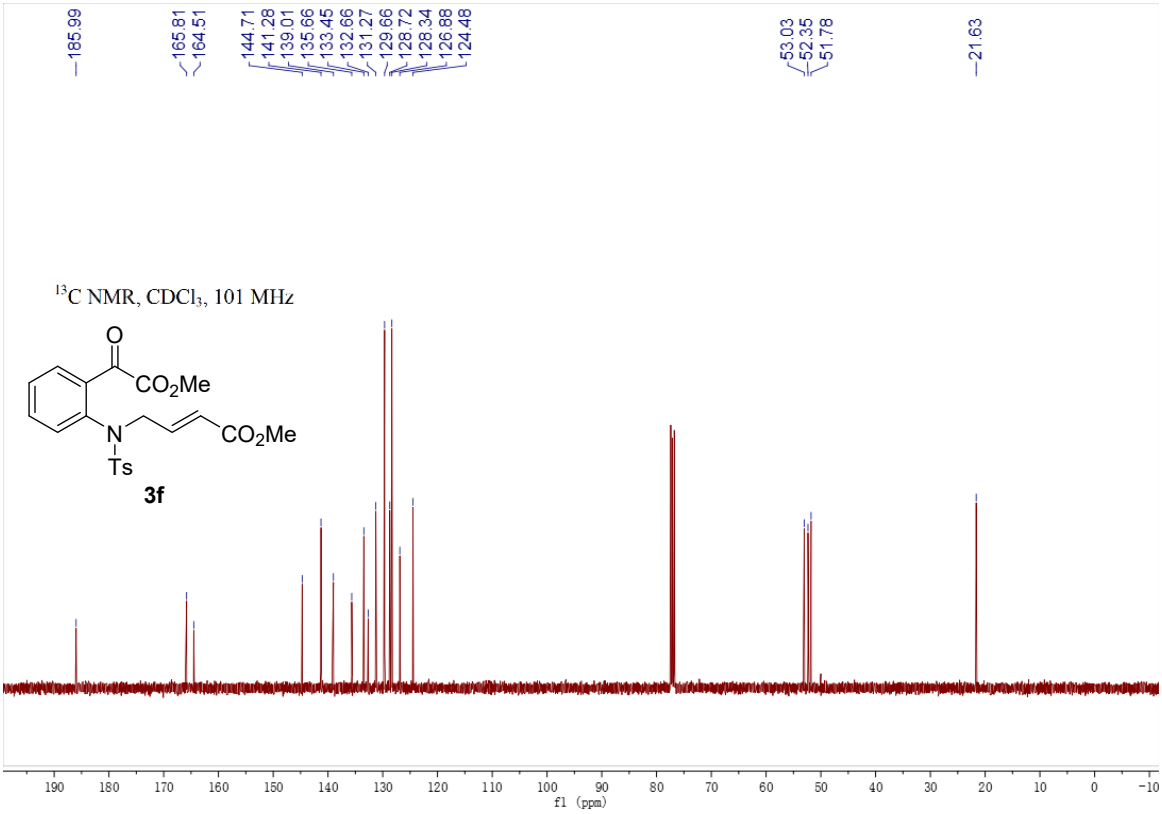
1.85
1.00
1.00
0.99
2.07
3.04
3.01
3.05
f1 (ppm)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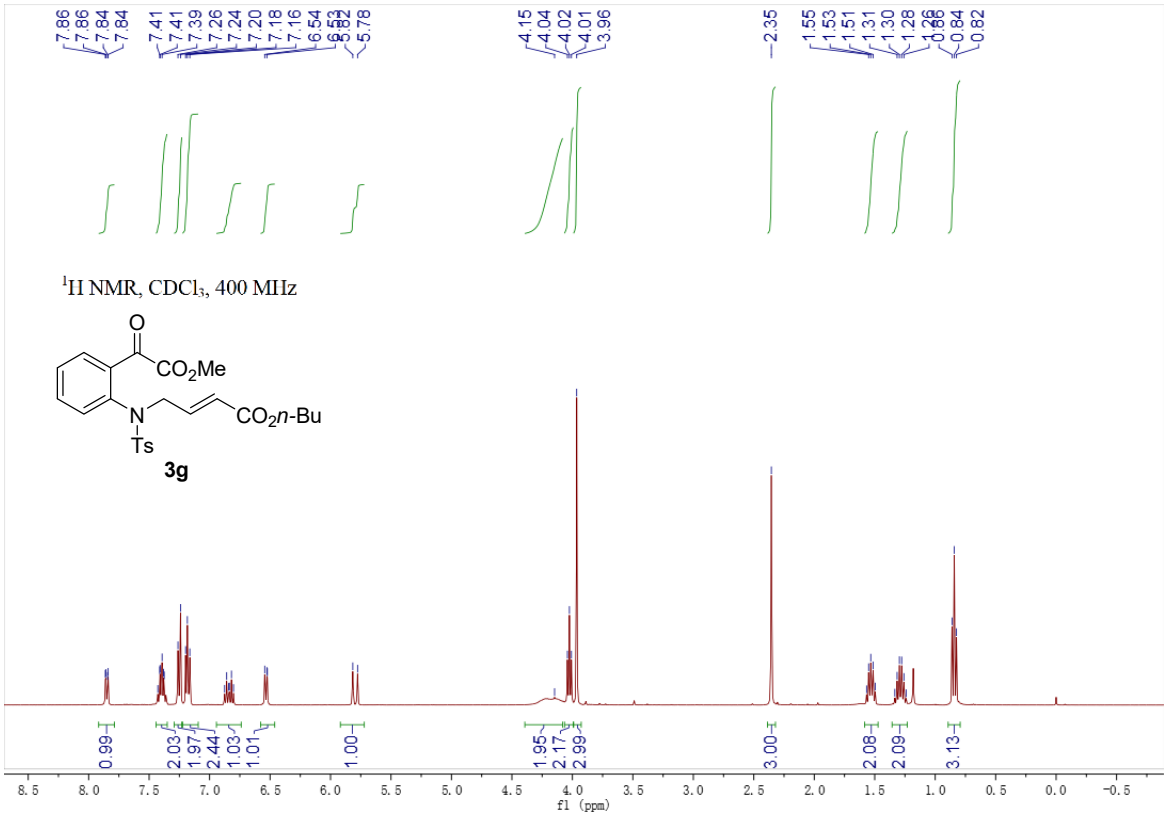
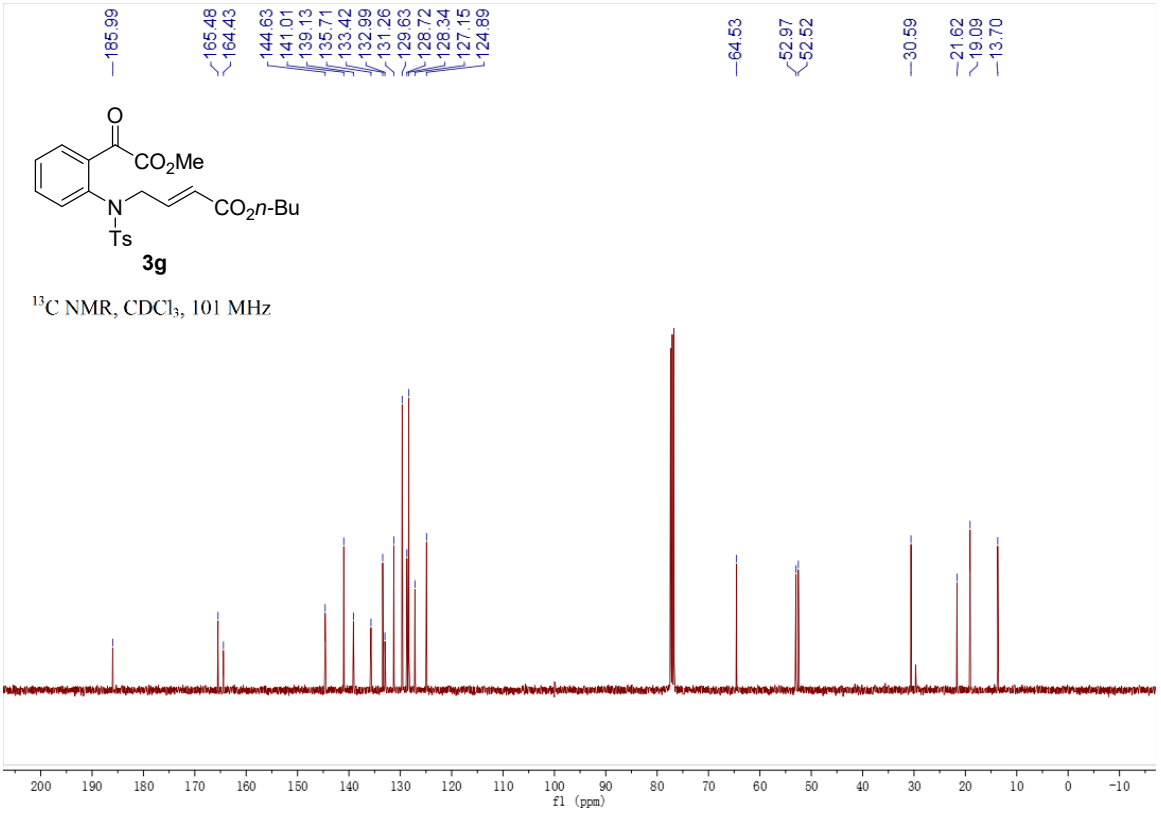
133.45
132.66
131.27
129.66
128.72
128.34
126.88
124.48
53.03
52.35
51.78
21.63
^{13}C NMR, $CDCl_3$, 101 MHz
O
CO_2Me
N
Ts
CO_2Me
3f
f1 (ppm)



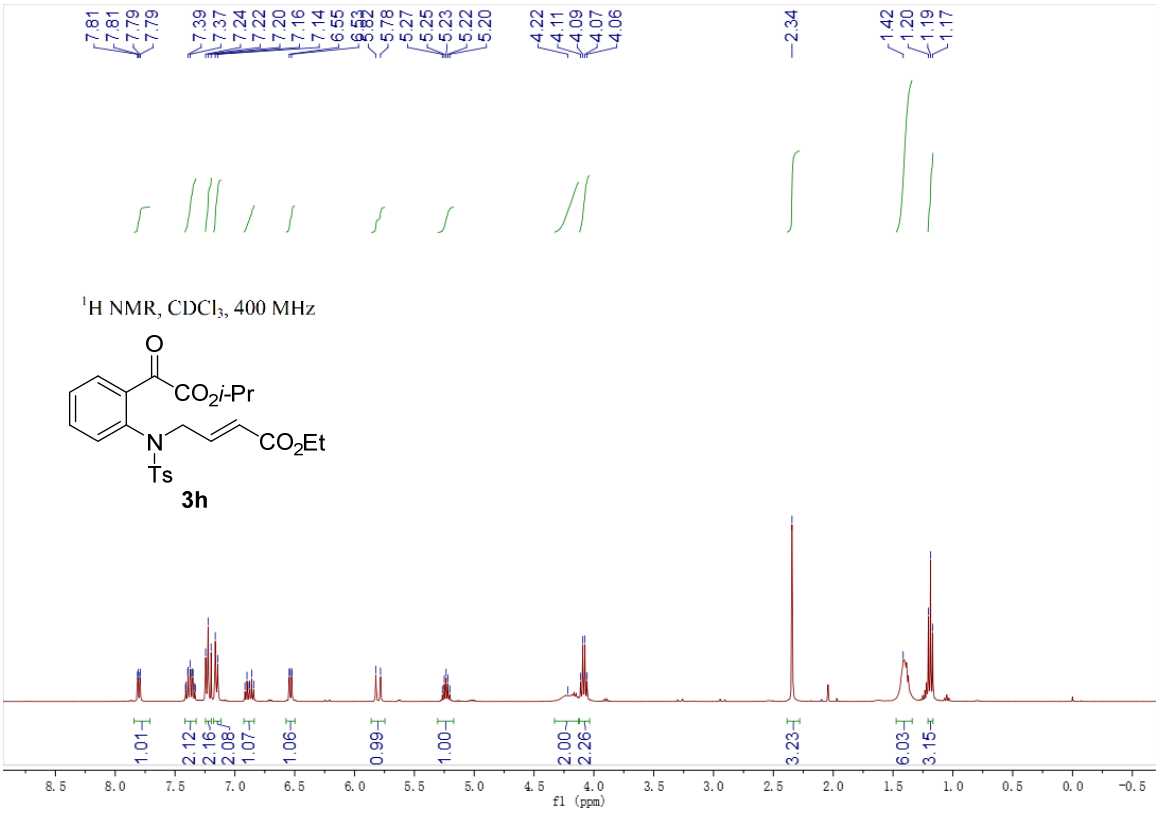
^{1}H NMR, $CDCl_3$, 400 MHz

3g



3g

^{13}C NMR, $CDCl_3$, 101 MHz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7.81
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7.22
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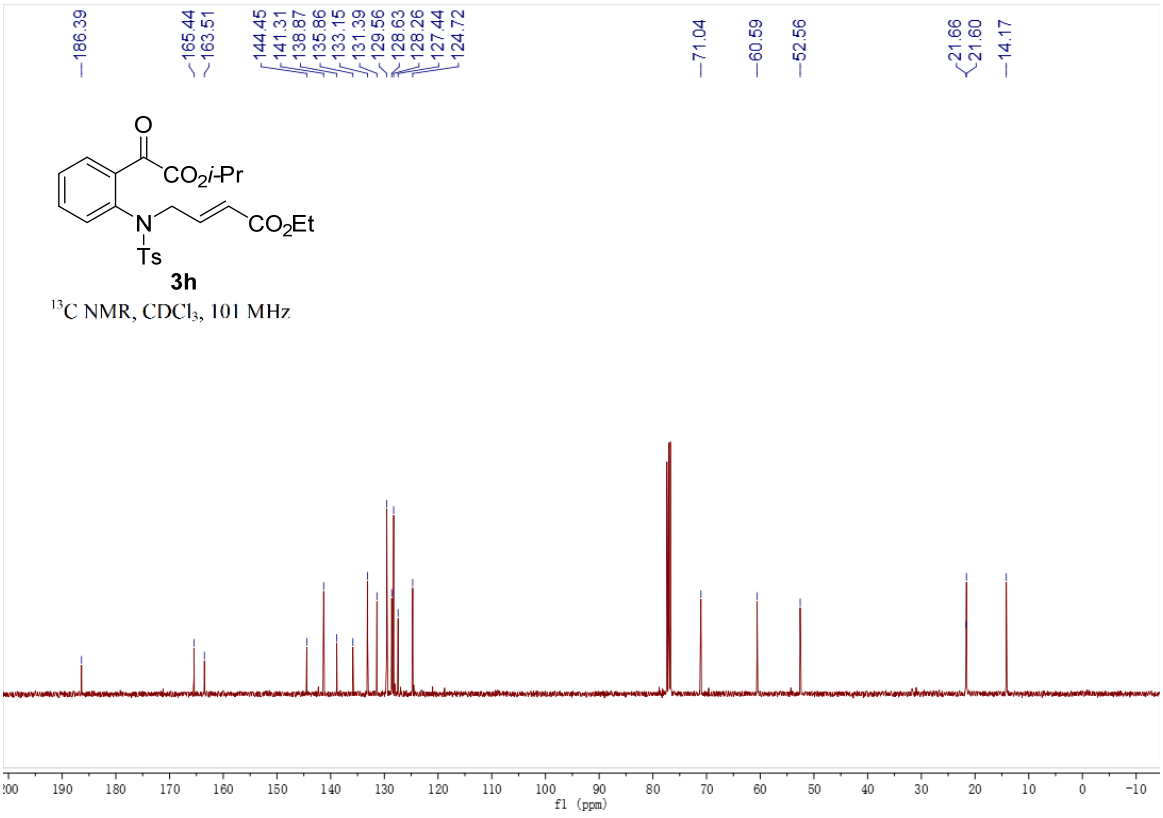
7.16
7.14
6.55
5.78
5.27
5.25
5.23
5.22
5.20
4.22
4.11
4.09
4.07
4.06
2.34
1.42
1.20
1.19
1.17
1H NMR, CDCl3, 400 MHz
O
CO2i-Pr
N
Ts
CO2Et
3h
1.01
2.12
2.16
2.08
1.07
1.06
0.99
1.00
2.00
2.26
3.23
6.03
3.15
f1 (ppm)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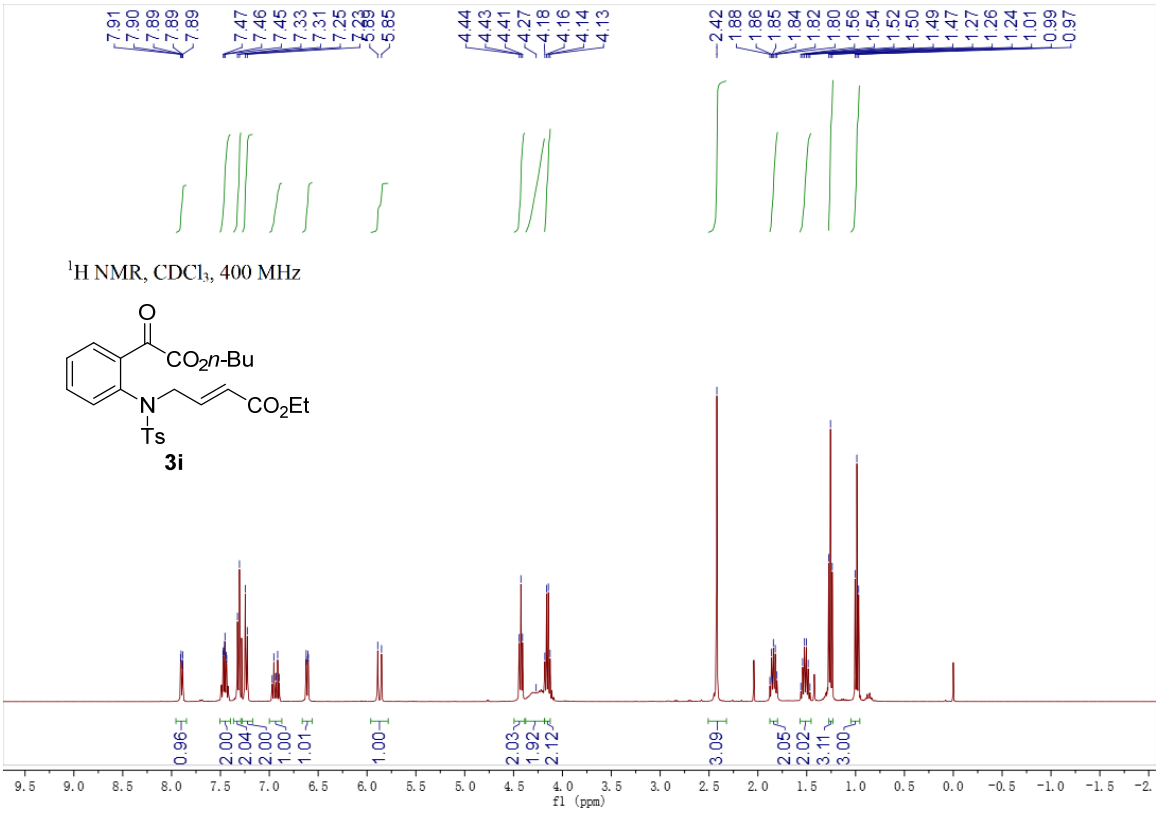
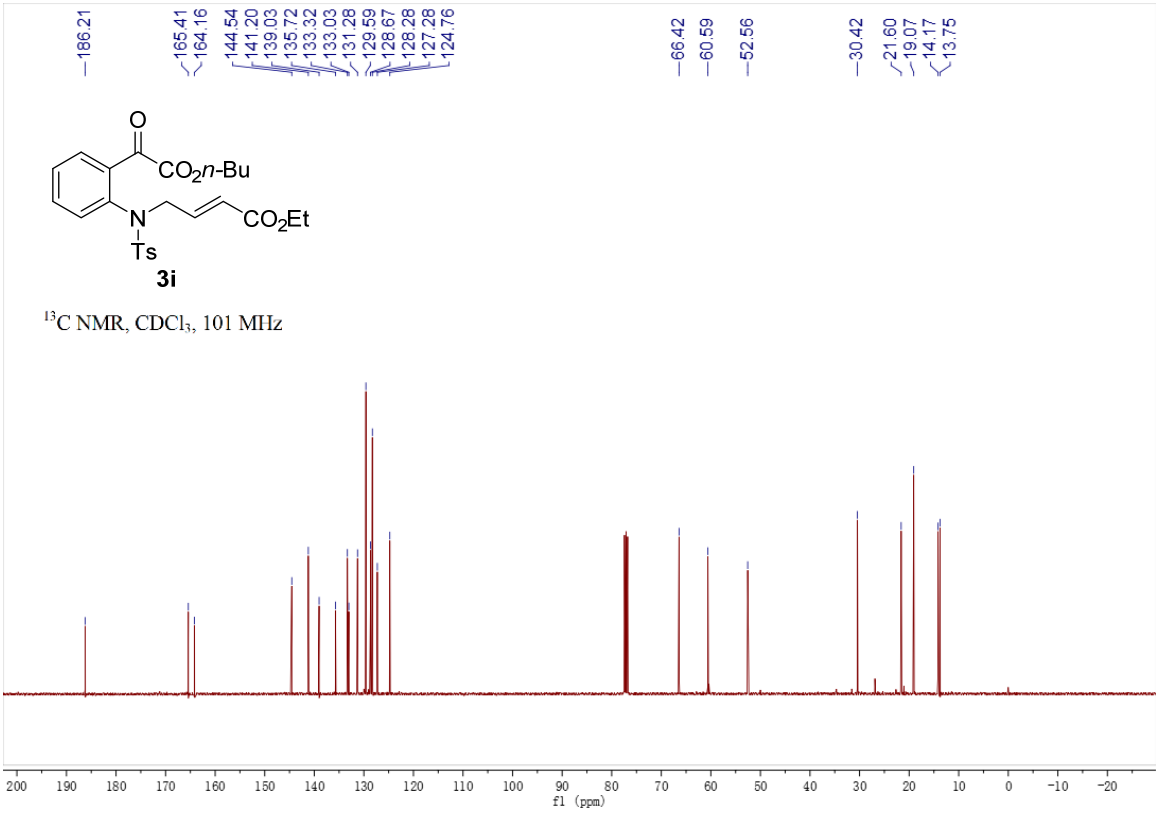
144.45
141.31
138.87
135.86
133.15
131.39
129.56
128.63
128.26
127.44
124.72
71.04
60.59
52.56
21.66
21.60
14.17
O
CO2i-Pr
N
Ts
CO2Et
3h
13C NMR, CDCl3, 101 MHz
f1 (ppm)



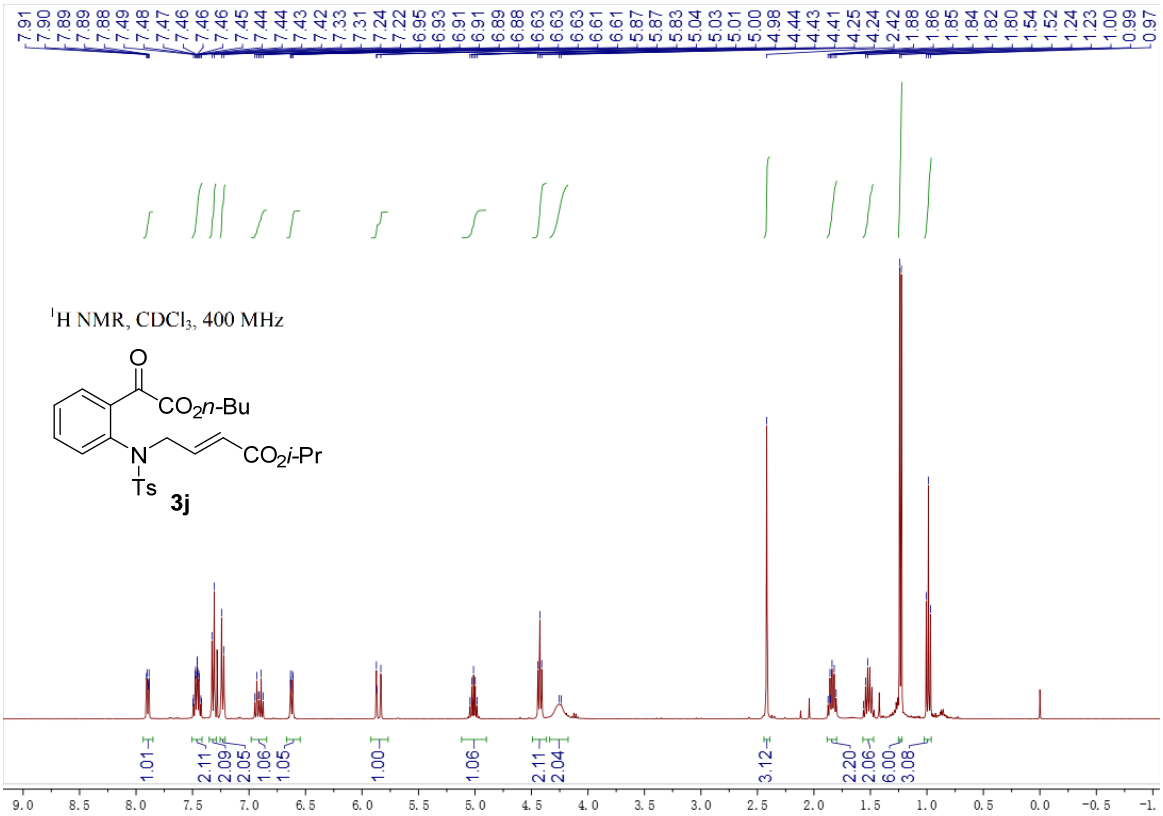
^{1}H NMR, $CDCl_3$, 400 MHz

3i



3i

^{13}C NMR, $CDCl_3$, 101 MHz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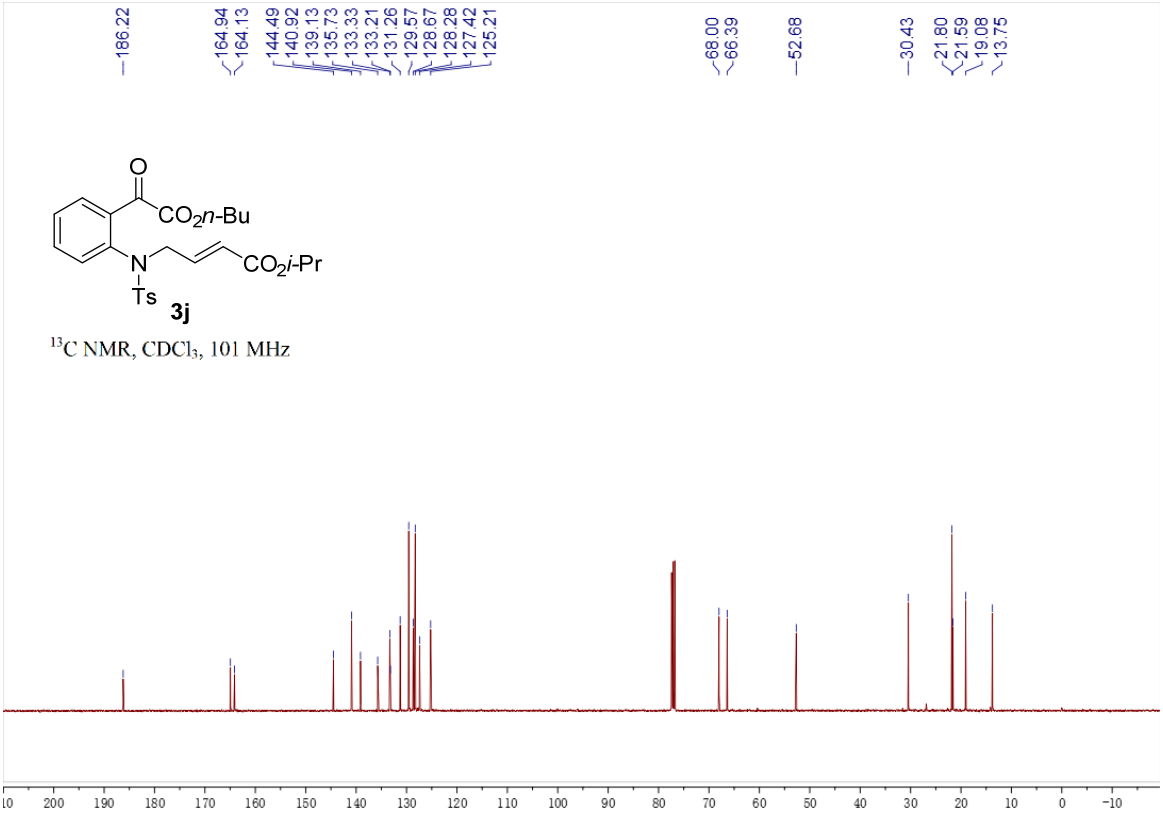
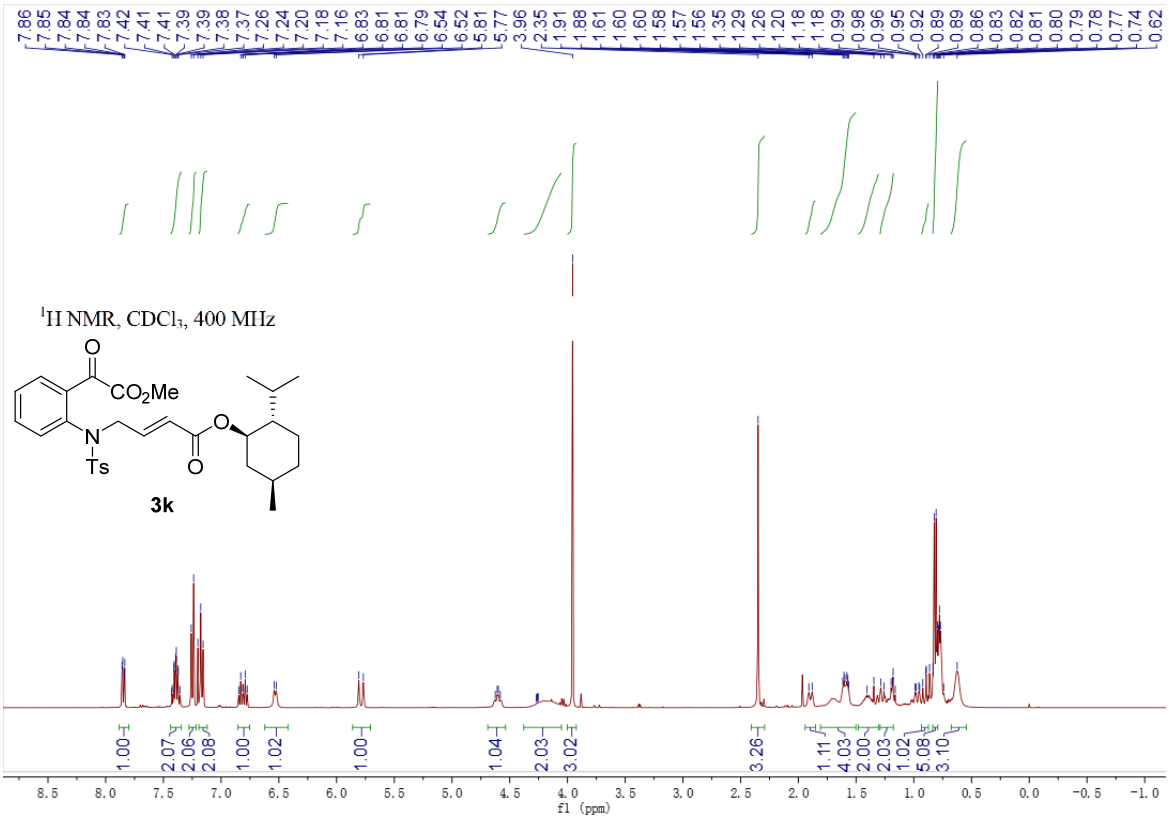
1H NMR, CDCl3, 400 MHz
CO2n-Bu
CO2i-Pr
N
Ts
3j
1.01 2.11 2.09 2.05 1.06 1.05 1.00 1.06 2.11 2.04 3.12 2.20 2.06 6.00 3.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.


186.22
164.94 164.13 144.49 140.92 139.13 135.73 133.33 133.21 131.26 129.57 128.67 128.28 127.42 125.21
68.00 66.39 52.68 30.43 21.80 21.59 19.08 13.75
CO2n-Bu
CO2i-Pr
N
Ts
3j
13C NMR, CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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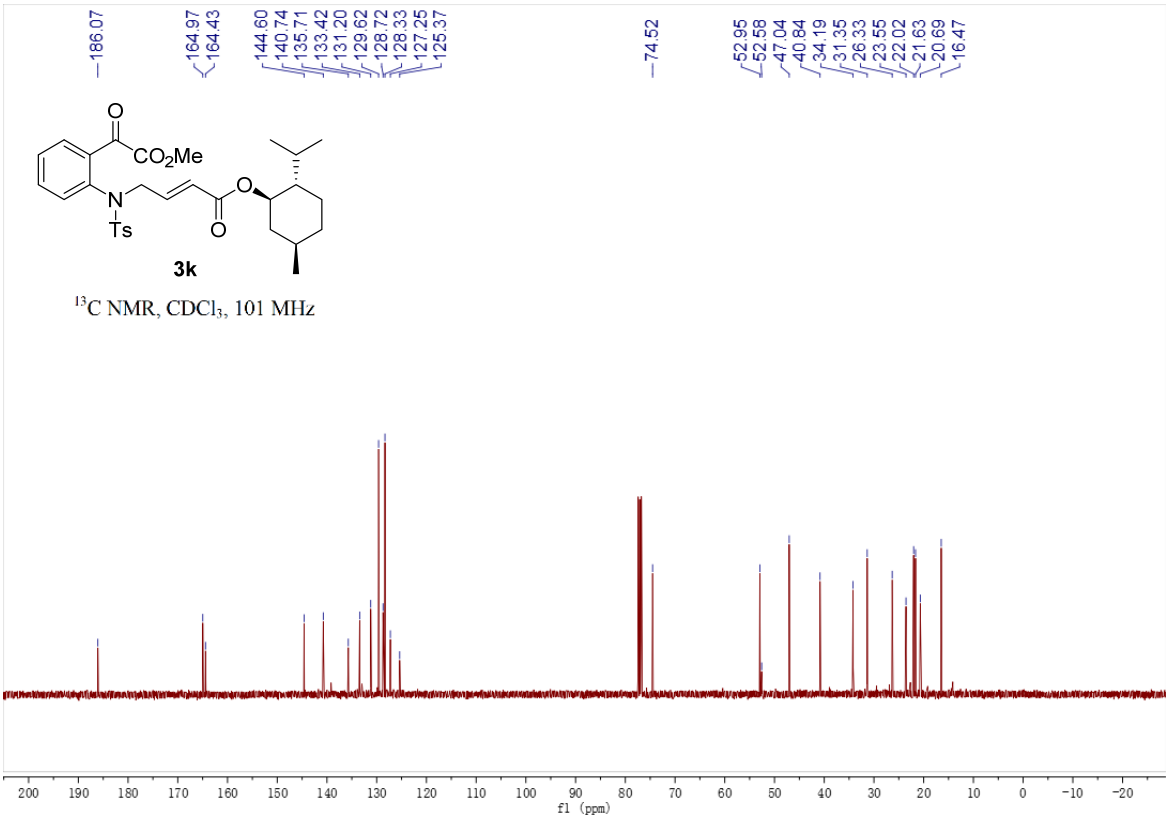
1H NMR, CDCl3, 400 MHz
CO2Me
N
Ts
O
O
O
3k
1.00 2.07 2.06 2.08 1.00 1.02 1.00 1.04 2.03 3.02 3.26 1.11 4.03 2.00 2.03 1.02 5.08 3.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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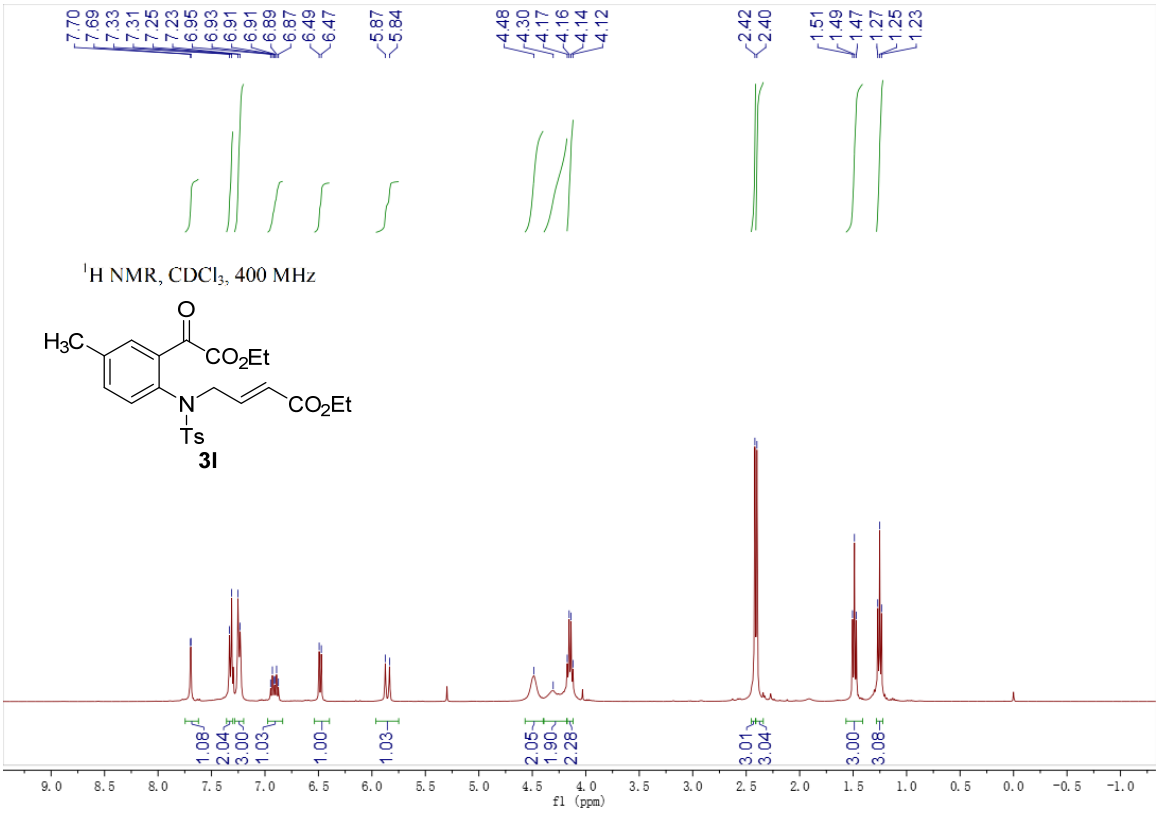
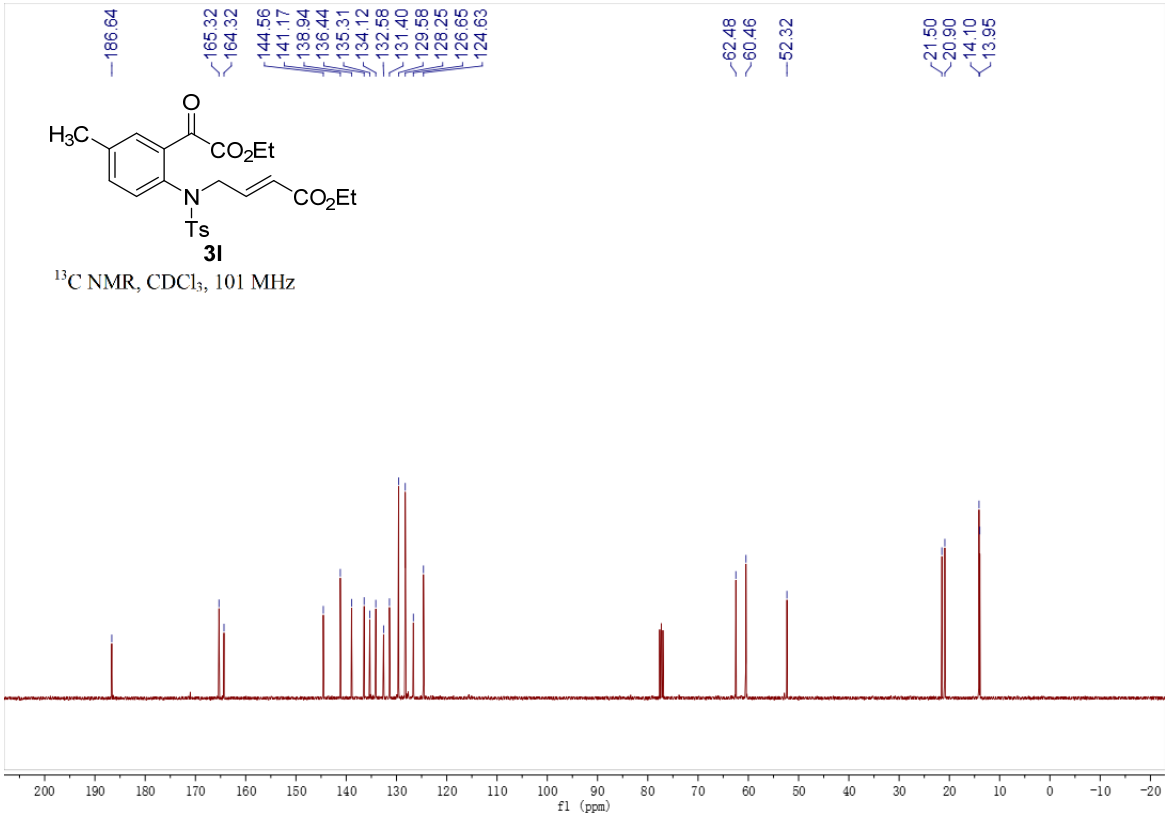
CO2Me
N
Ts
O
O
O
3k
13C NMR, CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



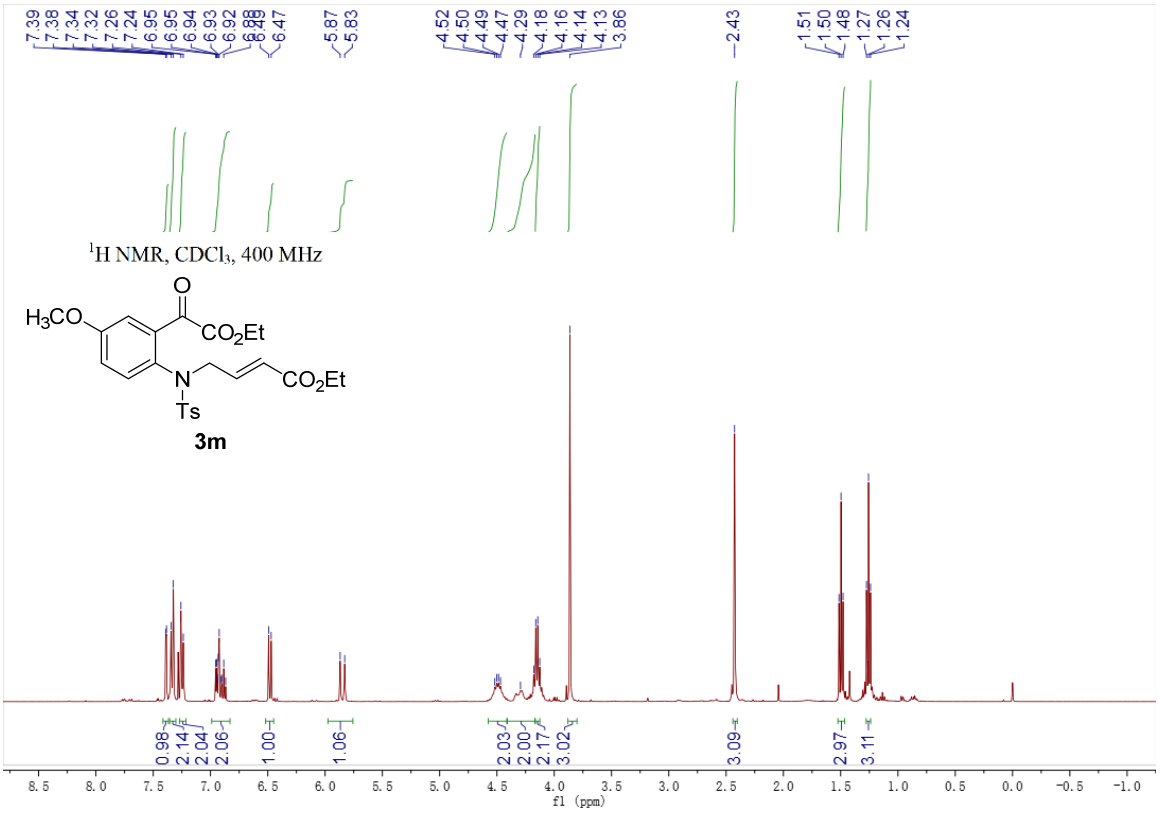
^{1}H NMR, $CDCl_3$, 400 MHz

3l



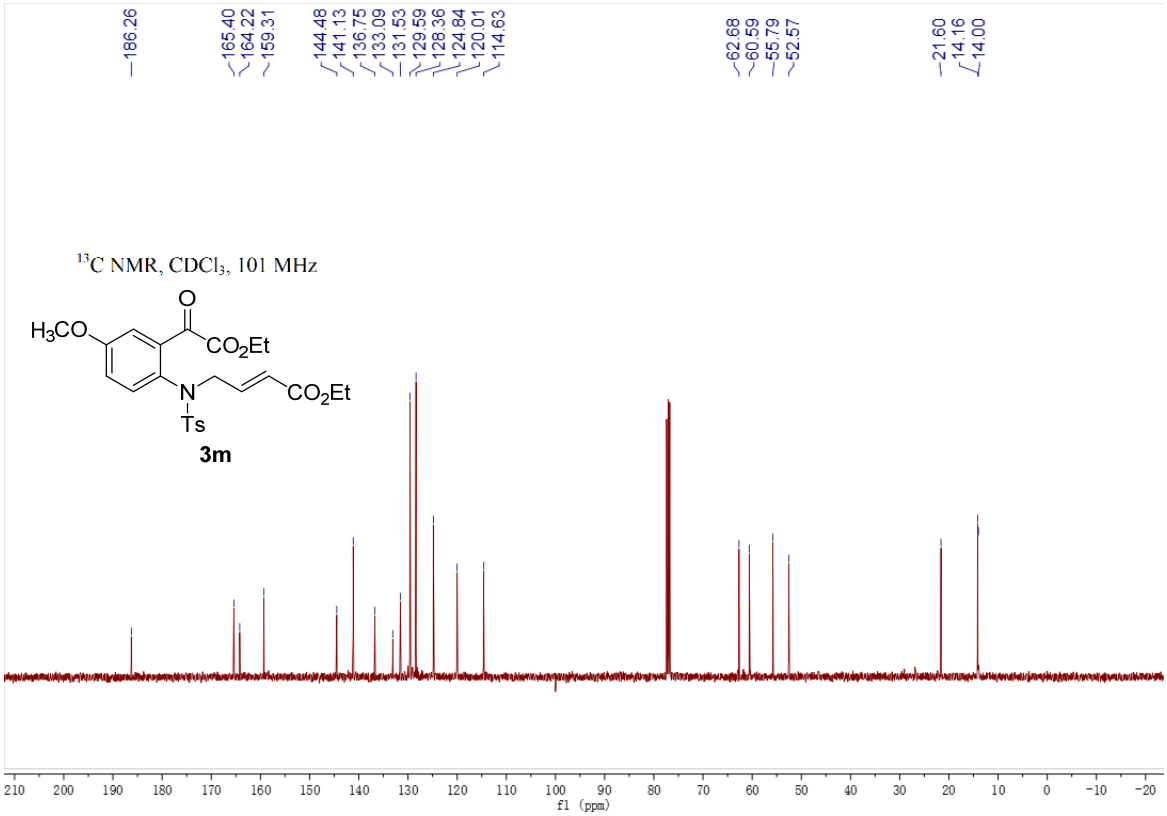
3l

^{13}C NMR, $CDCl_3$, 101 MHz



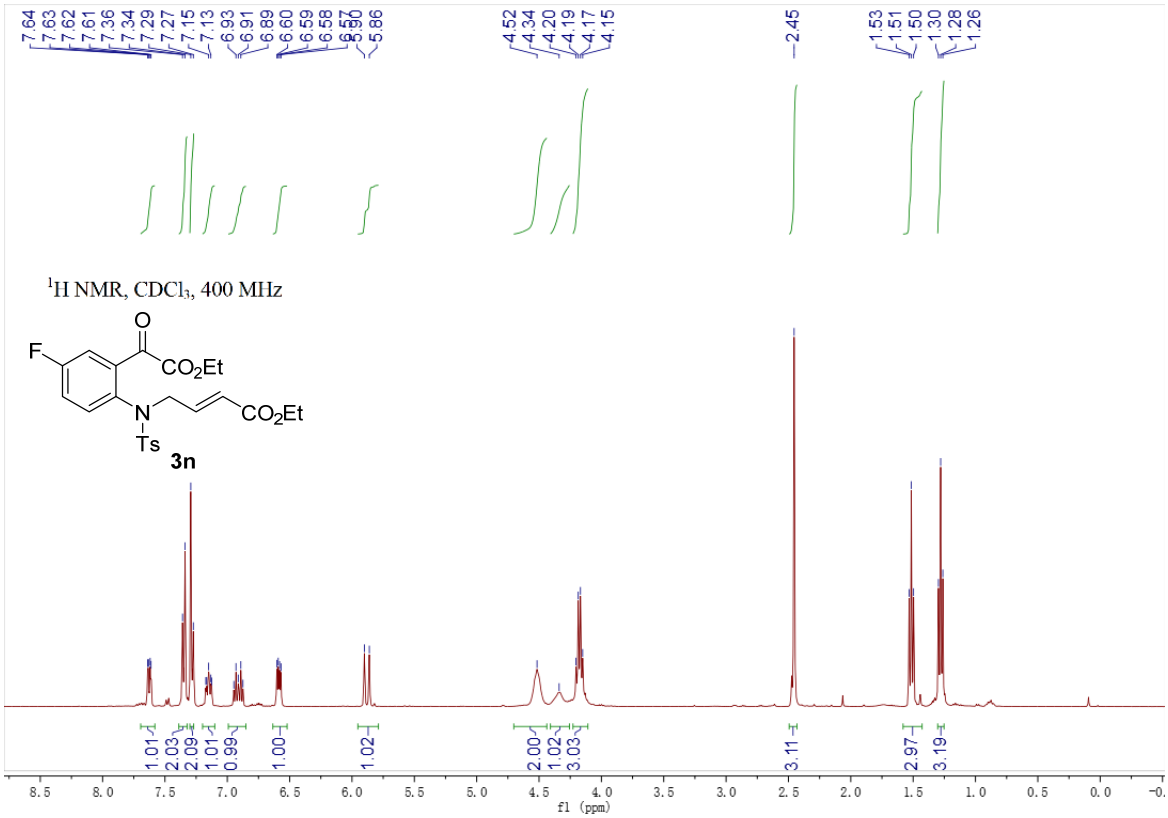
^{1}H NMR, $CDCl_3$, 400 MHz

3m



^{13}C NMR, $CDCl_3$, 101 MHz

3m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6.89
6.60
6.59
6.58
5.90
5.86
4.52
4.34
4.20
4.19
4.17
4.15
2.45
1.53
1.51
1.50
1.30
1.28
1.26
1H NMR, CDCl3, 400 MHz
O
F
CO2Et
N
CO2Et
Ts
3n
1.01
2.03
2.09
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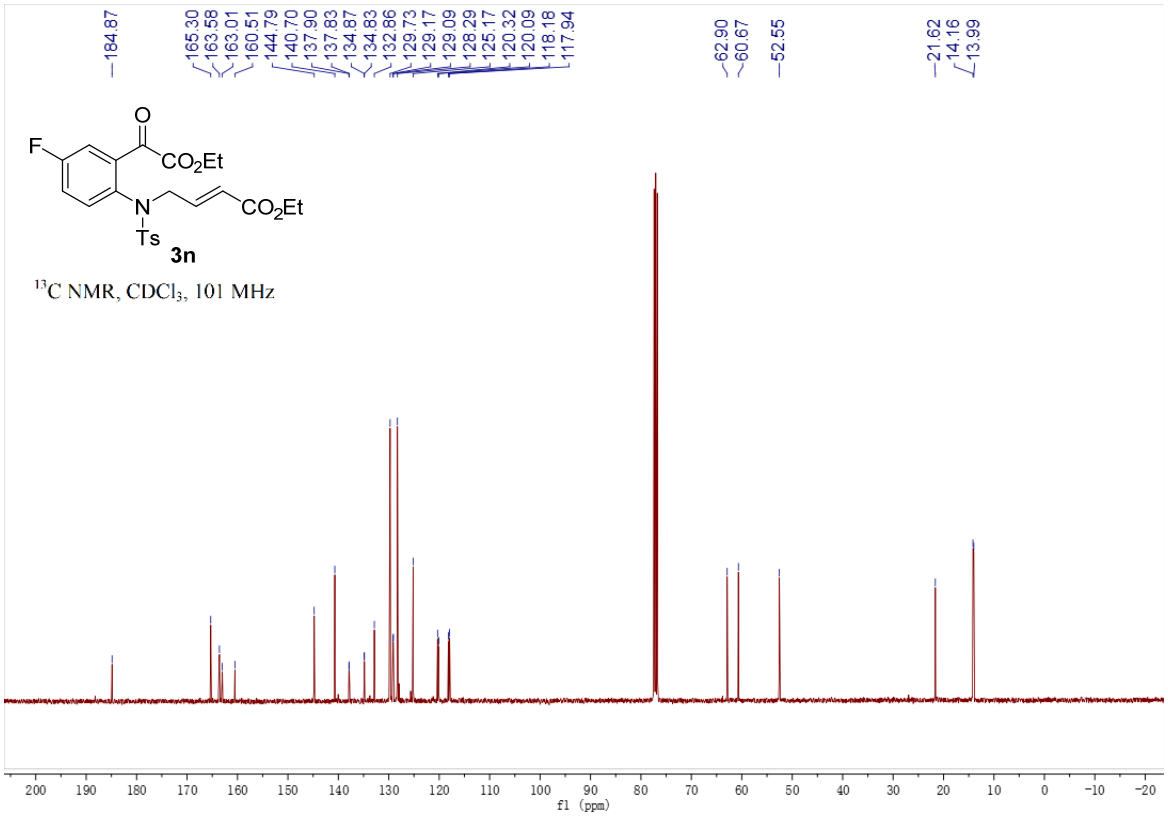
2.00
1.02
3.03
3.11
2.97
3.19
f1 (ppm)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165.30
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163.01
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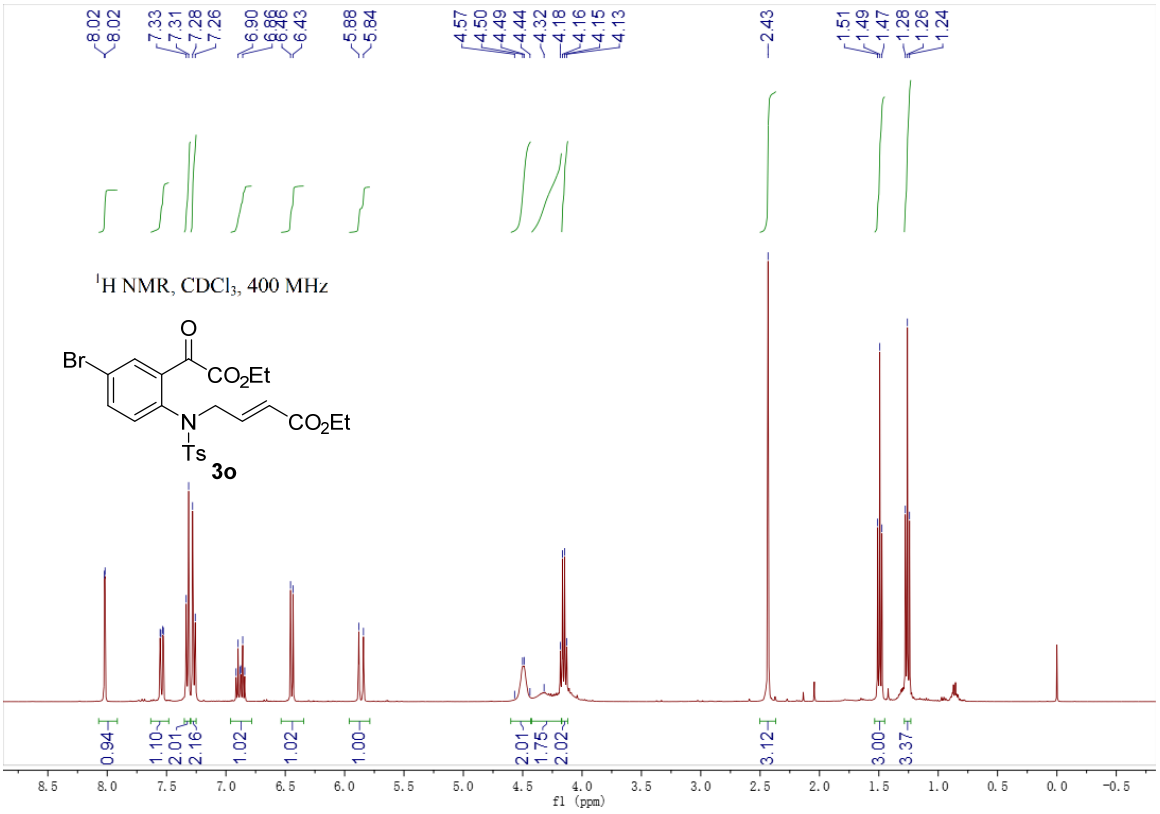
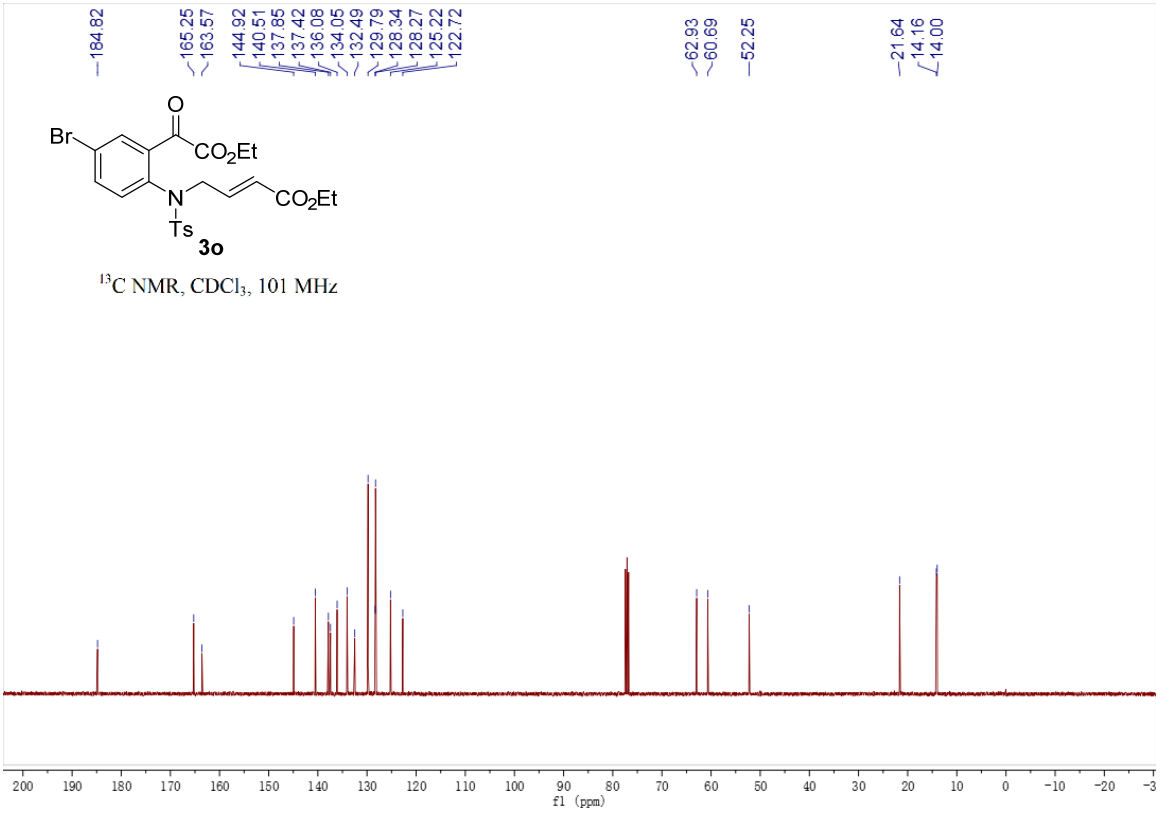
140.70
137.90
137.83
134.87
134.83
132.86
129.73
129.17
129.09
128.29
125.17
120.32
120.09
118.18
117.94
62.90
60.67
52.55
21.62
14.16
13.99
O
F
CO2Et
N
CO2Et
Ts
3n
13C NMR, CDCl3, 101 MHz
f1 (ppm)



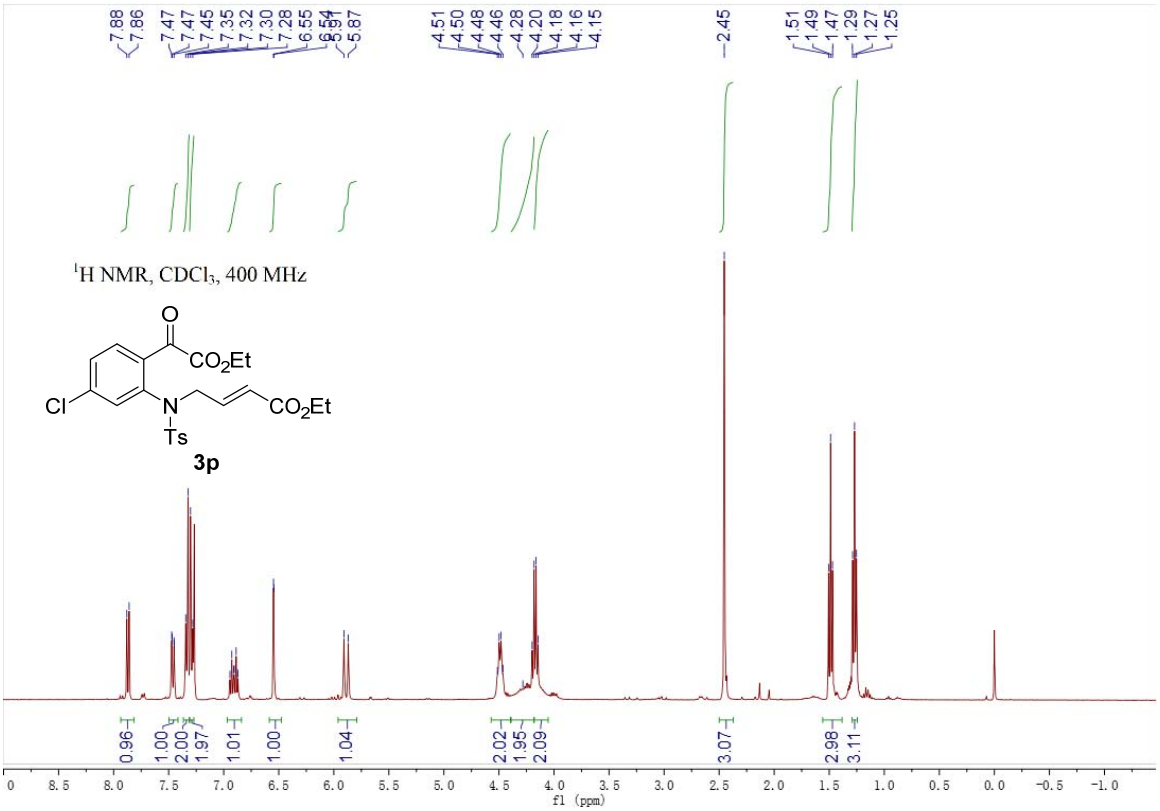
^{1}H NMR, $CDCl_3$, 400 MHz

3o



3o

^{13}C NMR, $CDCl_3$, 101 MHz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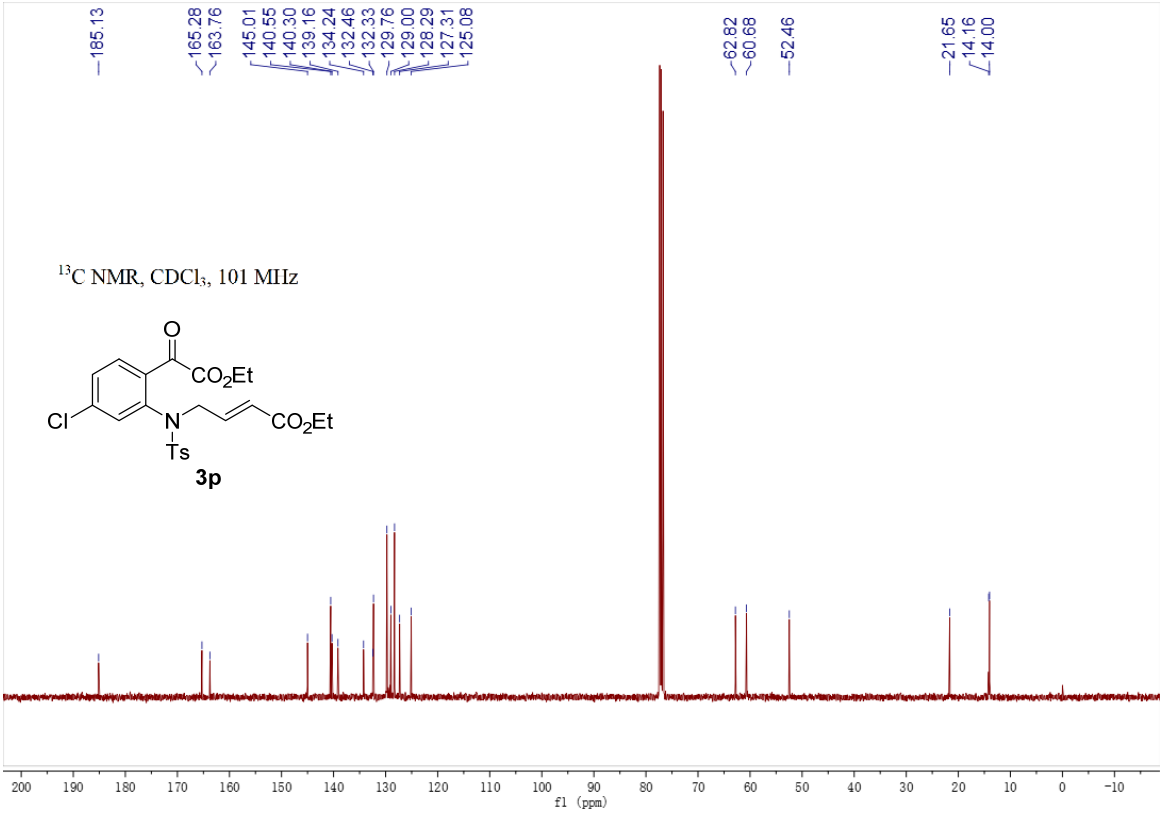
5.87
4.51
4.50
4.48
4.46
4.28
4.20
4.18
4.16
4.15
2.45
1.51
1.49
1.47
1.29
1.27
1.25
1H NMR, CDCl3, 400 MHz
O
CO2Et
Cl
N
CO2Et
Ts
3p
0.96
1.00
2.00
1.97
1.01
1.00
1.04
2.02
1.95
2.09
3.07
2.98
3.11
f1 (ppm)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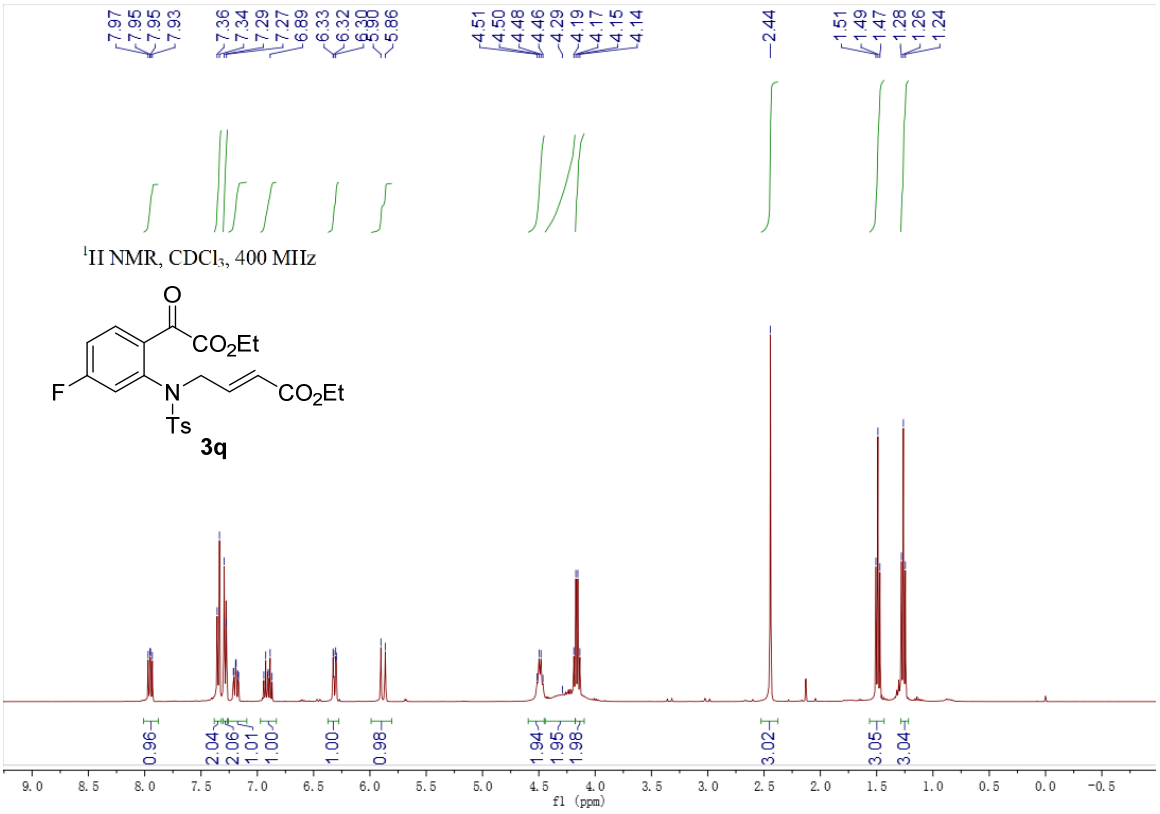
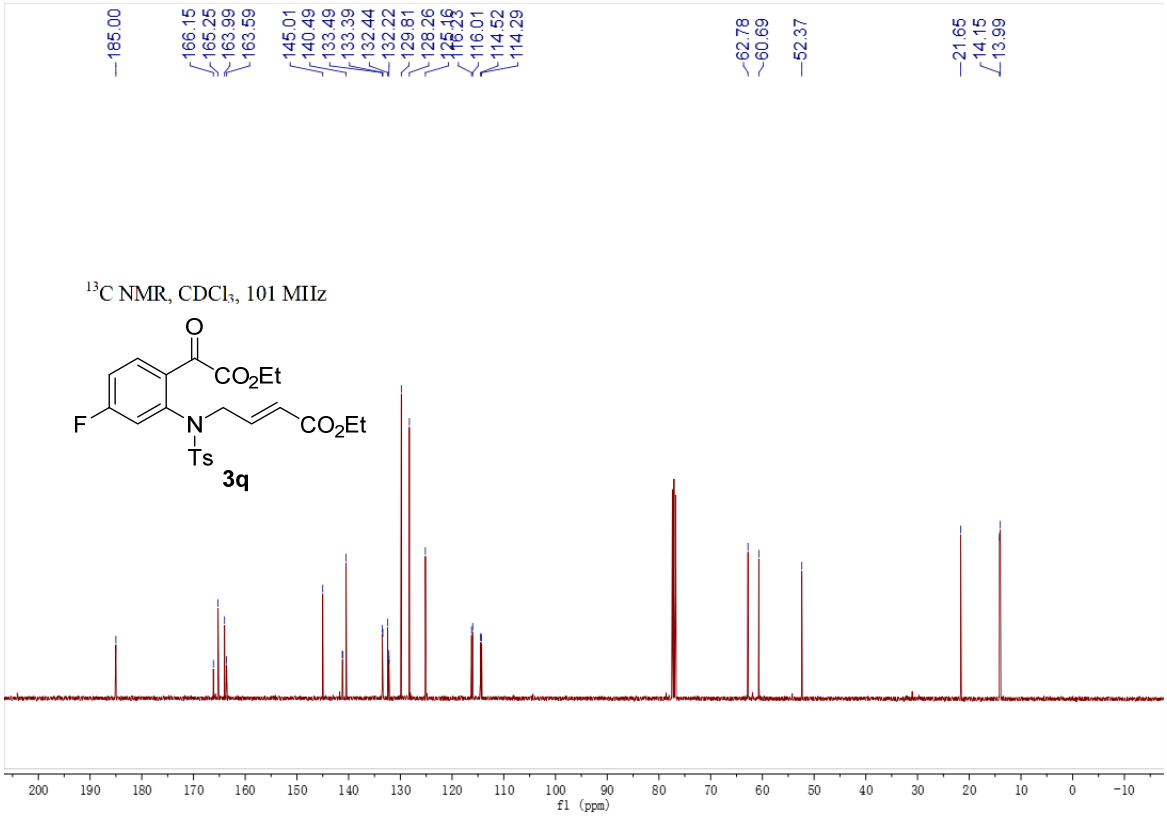
140.30
139.16
134.24
132.46
132.33
129.76
129.00
128.29
127.31
125.08
62.82
60.68
52.46
21.65
14.16
14.00
13C NMR, CDCl3, 101 MIHz
O
CO2Et
Cl
N
CO2Et
Ts
3p
f1 (ppm)



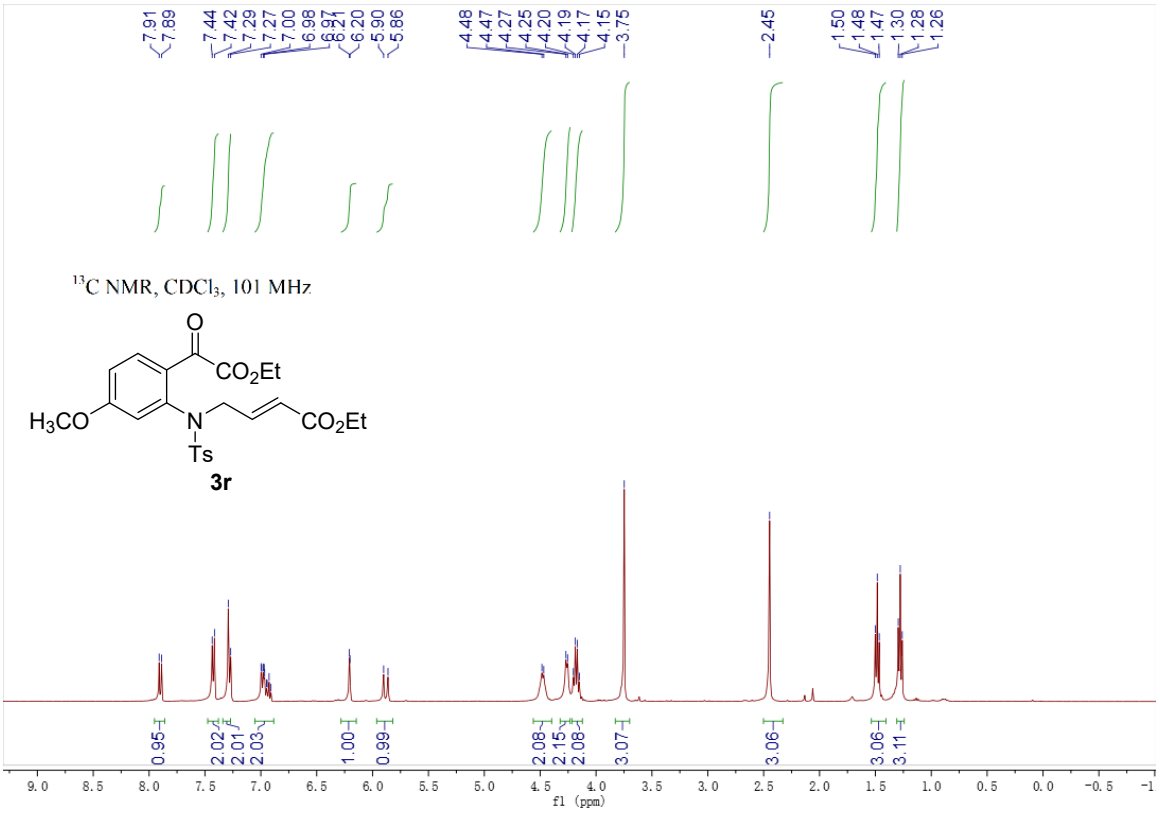
^{1}II NMR, $CDCl_3$, 400 MIIz

3q



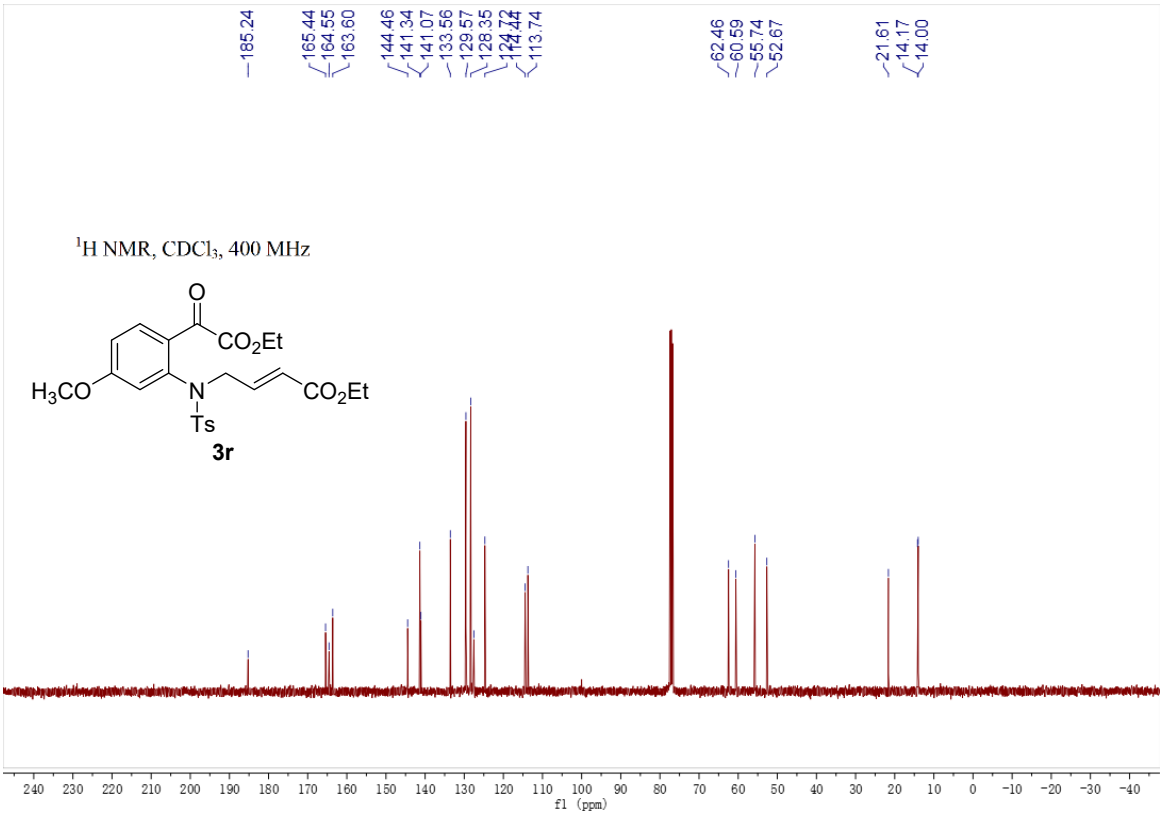
^{13}C NMR, $CDCl_3$, 101 MIIz

3q



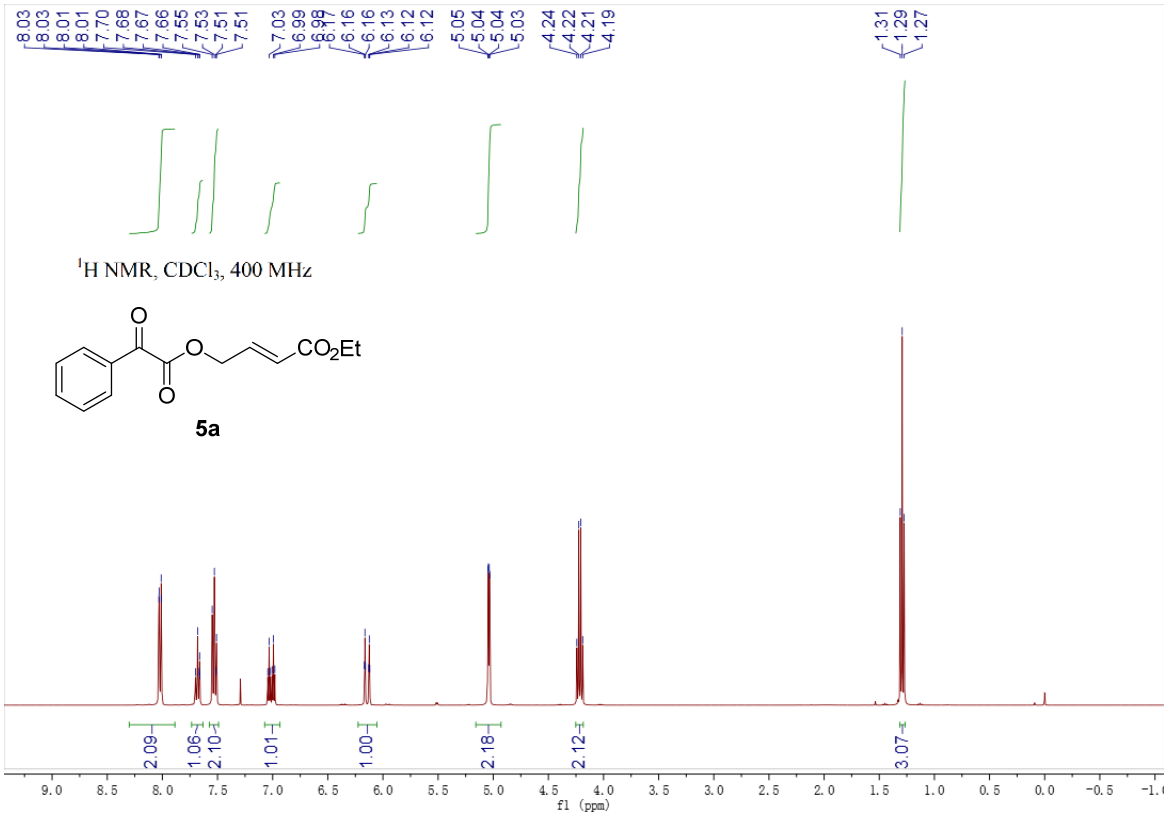
^{13}C NMR, $CDCl_3$, 101 MHz

3r



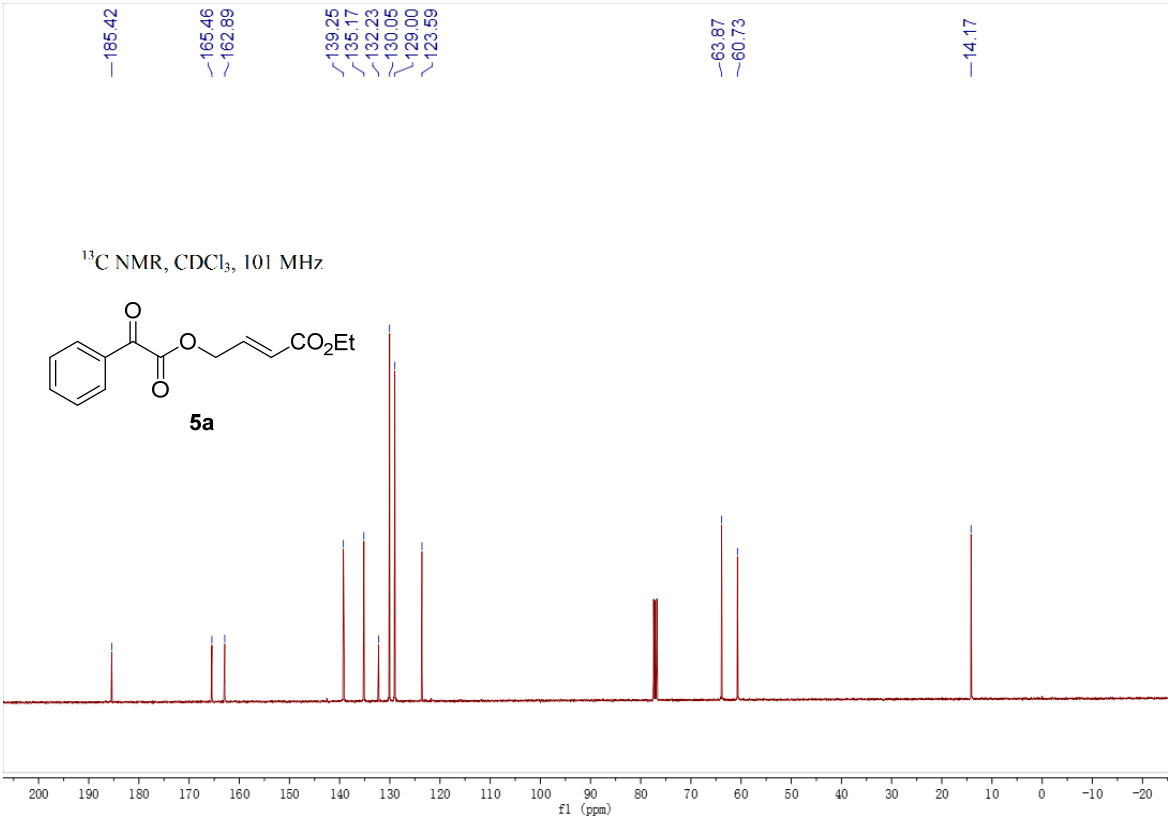
^{1}H NMR, $CDCl_3$, 400 MHz

3r



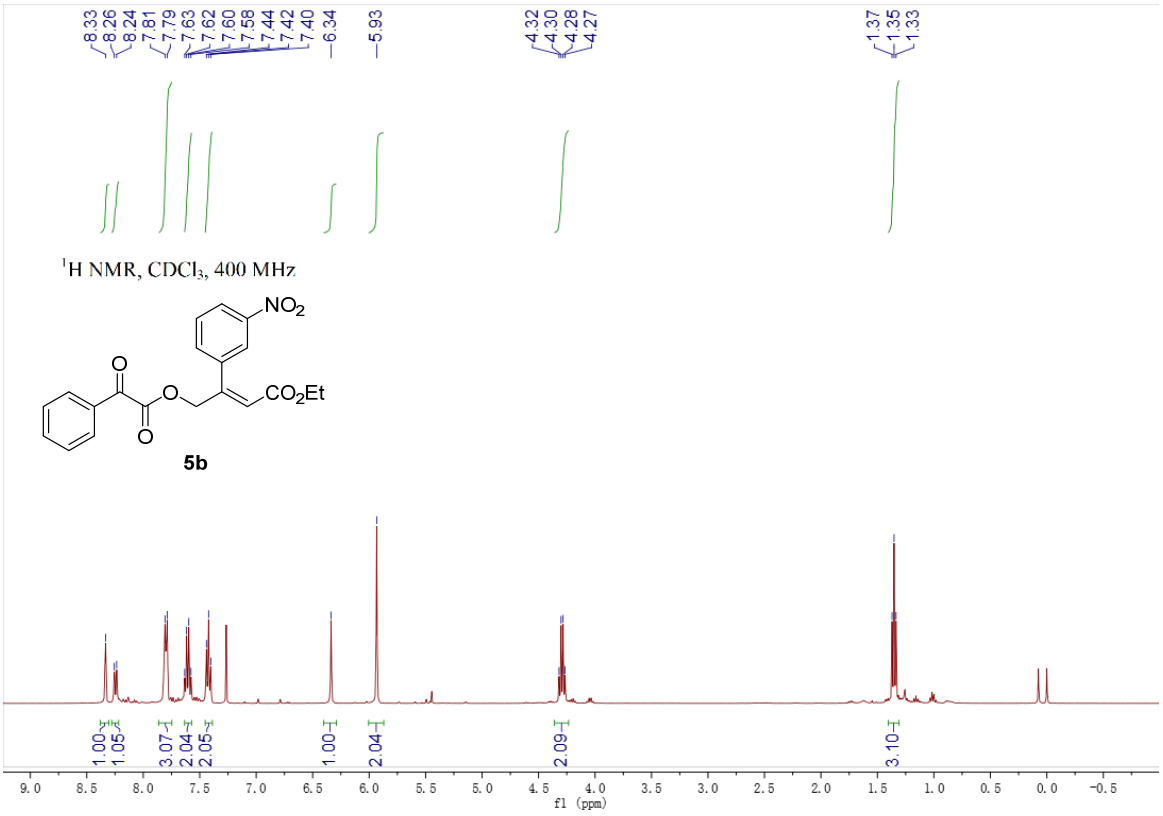
^{1}H NMR, $CDCl_3$, 400 MHz

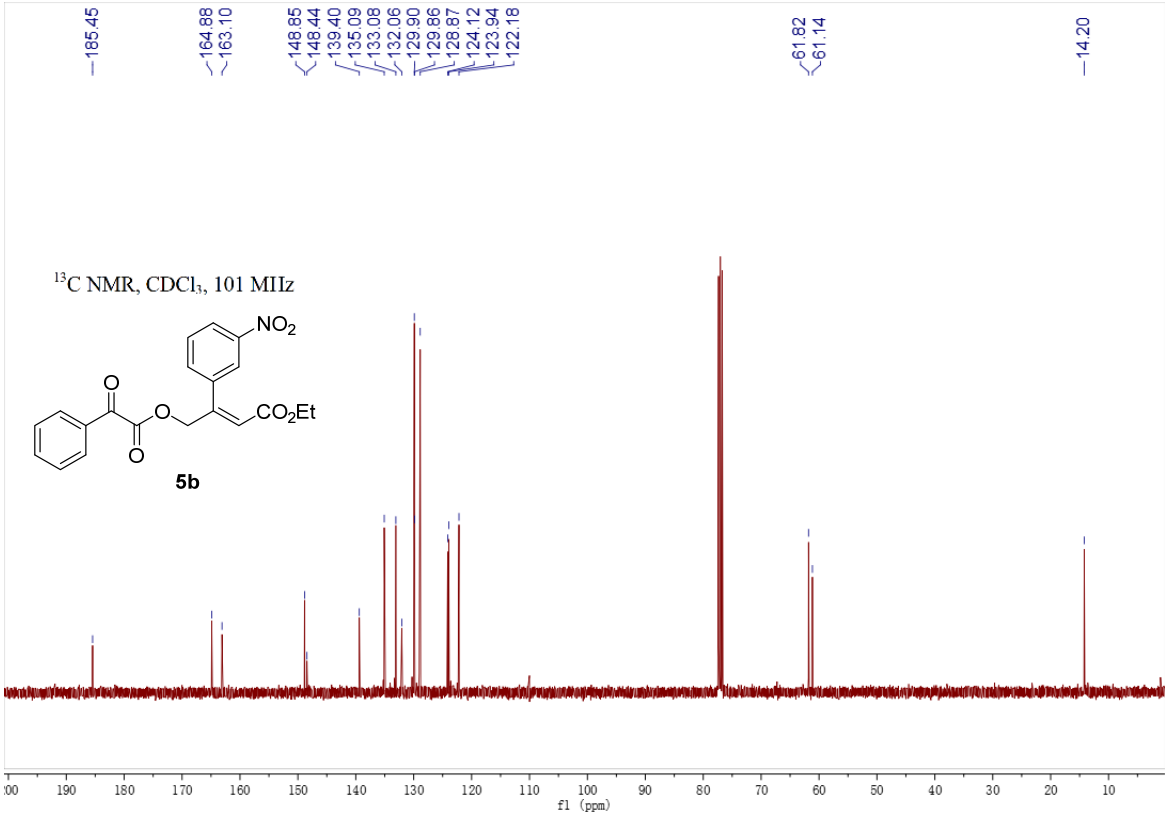
5a

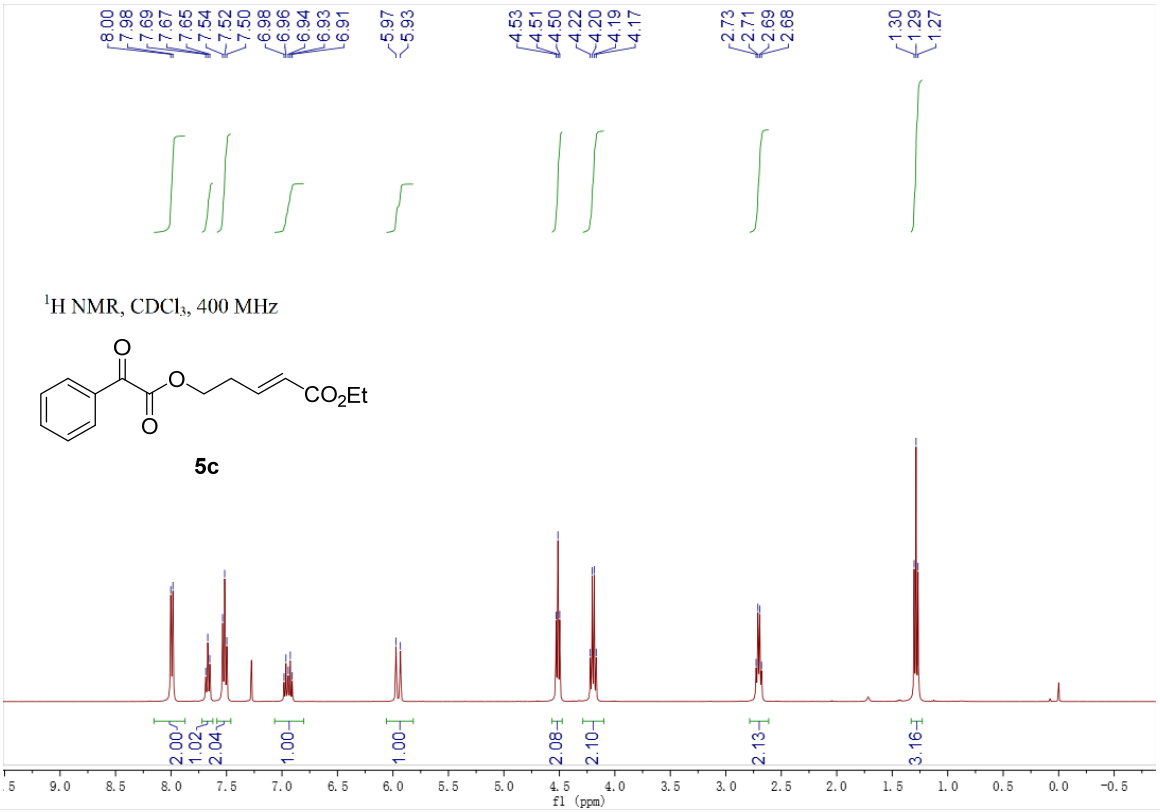


^{13}C NMR, $CDCl_3$, 101 MHz

5a

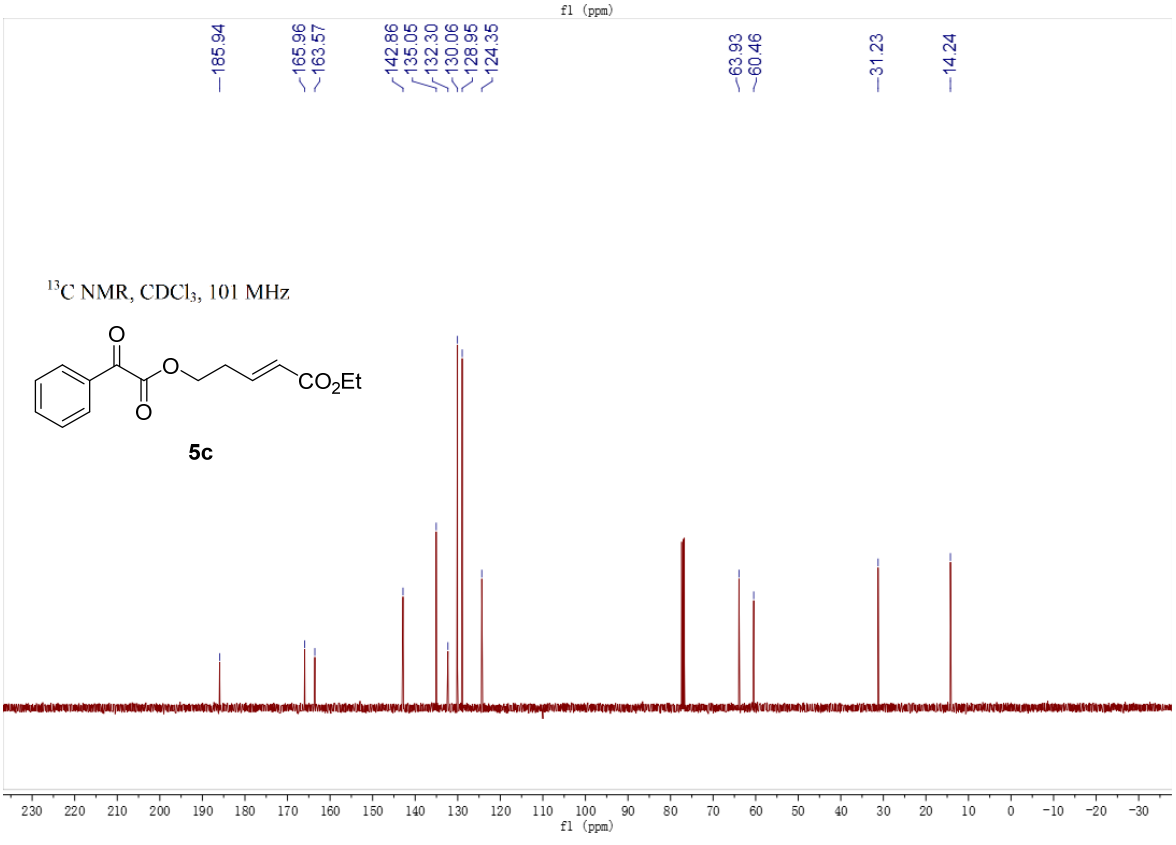

8.33
8.26
8.24
7.81
7.79
7.63
7.62
7.60
7.58
7.44
7.42
7.40
6.34
5.93
4.32
4.30
4.28
4.27
1.37
1.35
1.33
1H NMR, CDCl3, 400 MHz
NO2
O
O
O
CO2Et
O
5b
1.00
1.05
3.07
2.04
2.05
1.00
2.04
2.09
3.10
f1 (ppm)


185.45
164.88
163.10
148.85
148.44
139.40
135.09
133.08
132.06
129.90
129.86
128.87
124.12
123.94
122.18
61.82
61.14
14.20
13C NMR, CDCl3, 101 MIz
NO2
O
O
O
CO2Et
5b
f1 (ppm)



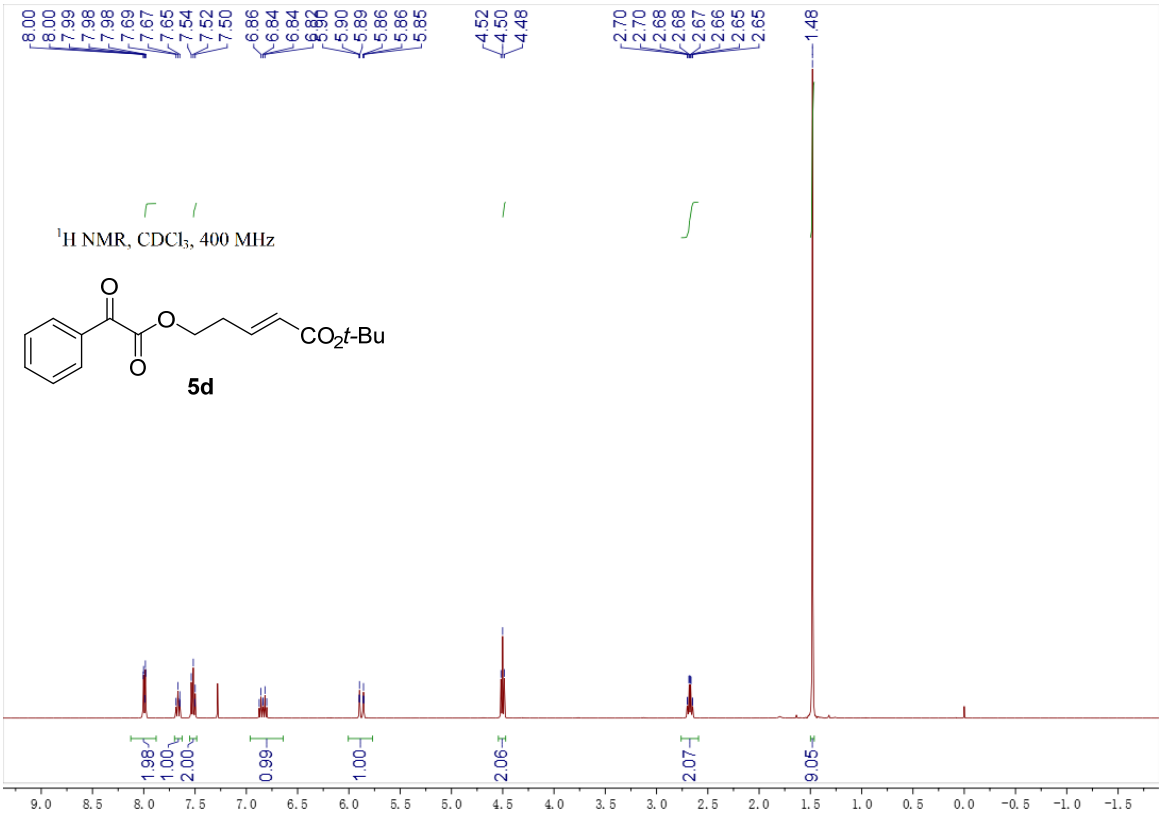
^{1}H NMR, $CDCl_3$, 400 MHz

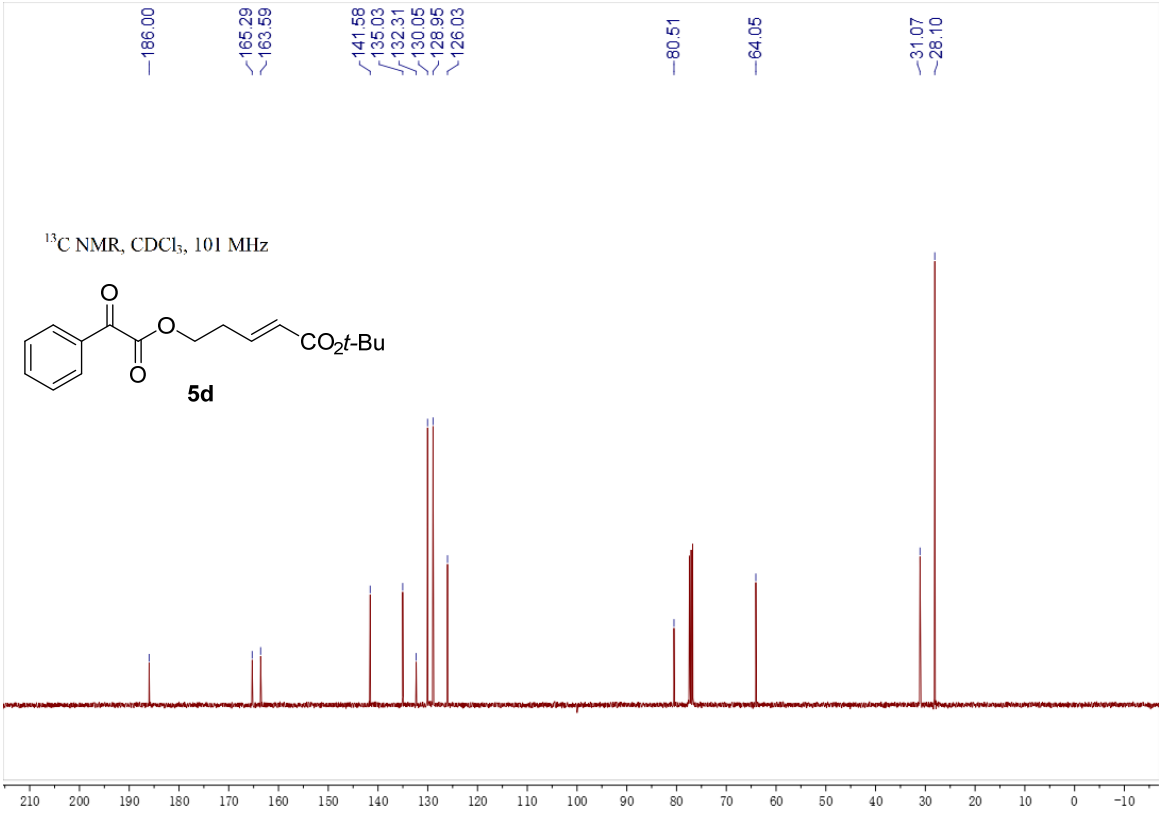
5c

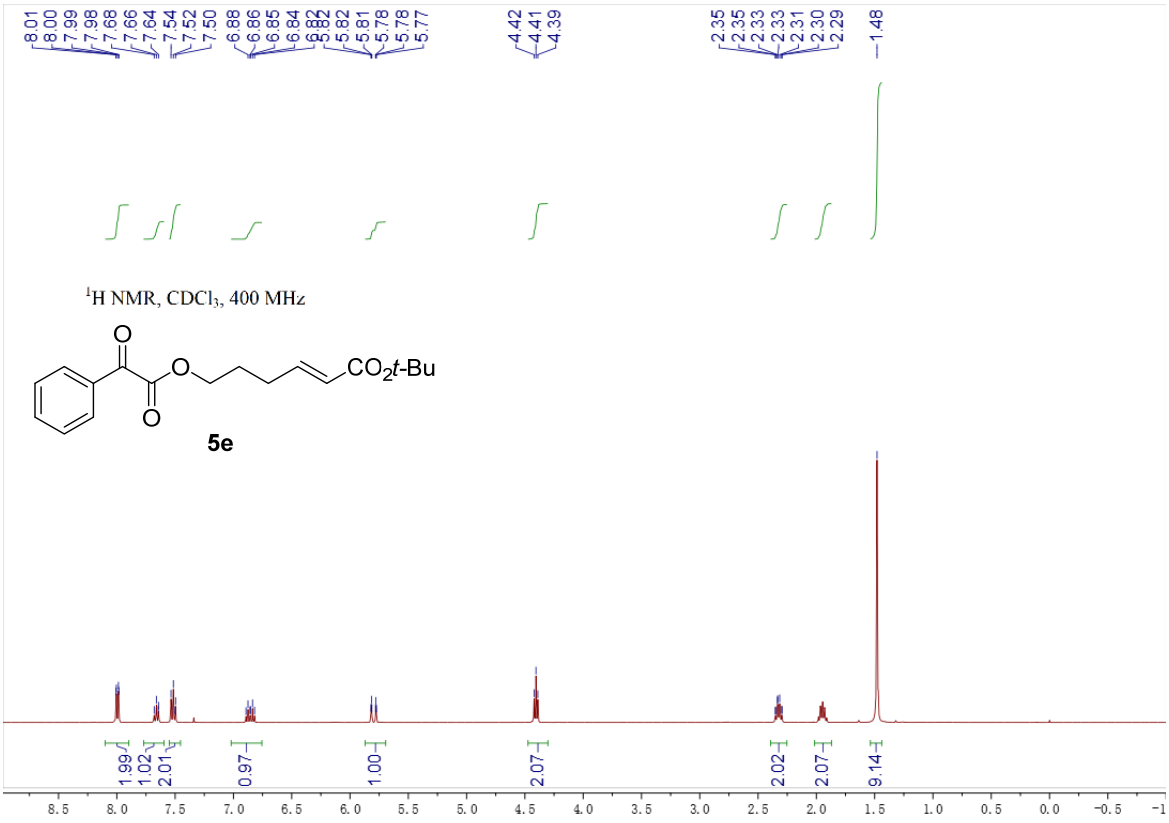


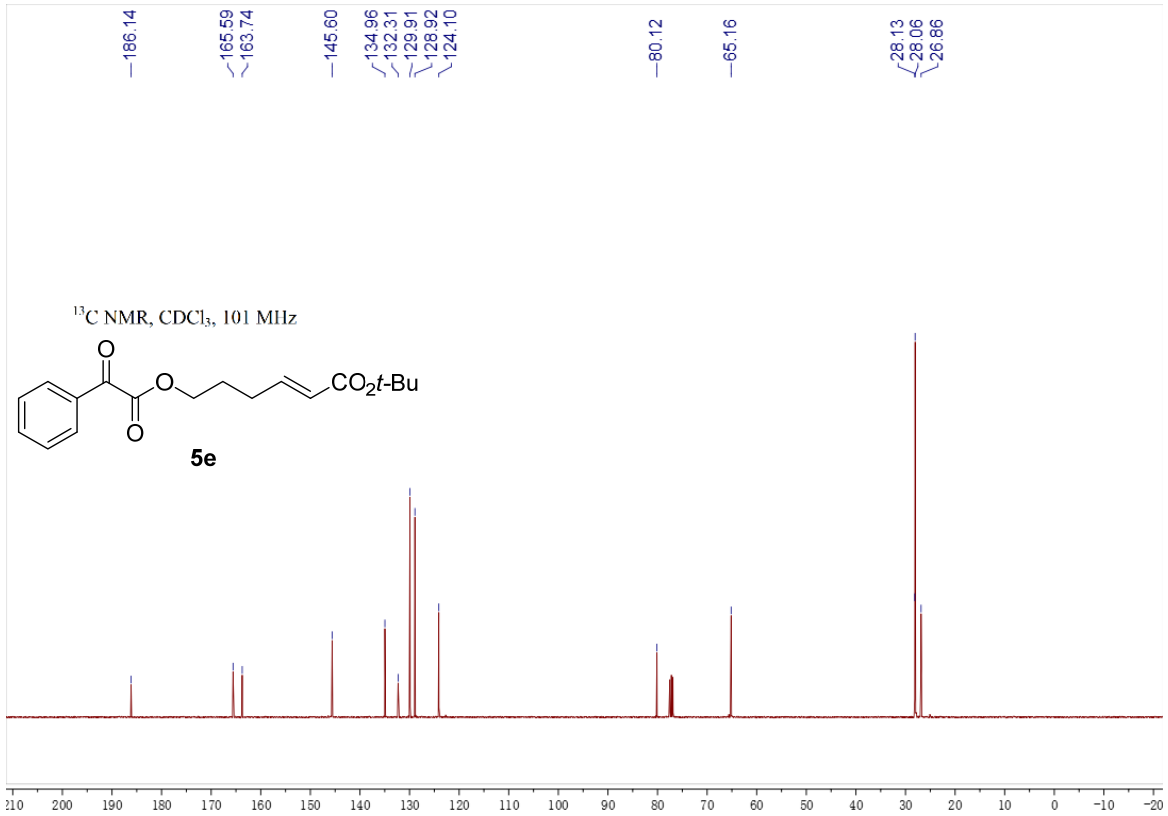
^{13}C NMR, $CDCl_3$, 101 MHz

5c


8.00
8.00
7.99
7.98
7.98
7.69
7.67
7.65
7.54
7.52
7.50
6.86
6.84
6.84
5.90
5.89
5.86
5.86
5.85
4.52
4.50
4.48
2.70
2.70
2.68
2.68
2.67
2.66
2.65
2.65
1.48
1H NMR, CDCl3, 400 MHz
O
O
O
CO2t-Bu
5d
1.98
1.00
2.00
0.99
1.00
2.06
2.07
9.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5


186.00
165.29
163.59
141.58
135.03
132.31
130.05
128.95
126.03
80.51
64.05
31.07
28.10
13C NMR, CDCl3, 101 MHz
O
O
O
CO2t-Bu
5d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


8.01
8.00
7.99
7.98
7.68
7.66
7.64
7.54
7.52
7.50
6.88
6.86
6.85
6.84
5.82
5.81
5.78
5.78
5.77
4.42
4.41
4.39
2.35
2.35
2.33
2.33
2.31
2.30
2.29
1.48
1H NMR, CDCl3, 400 MHz
O
O
O
CO2t-Bu
5e
1.99
1.02
2.01
0.97
1.00
2.07
2.02
2.07
9.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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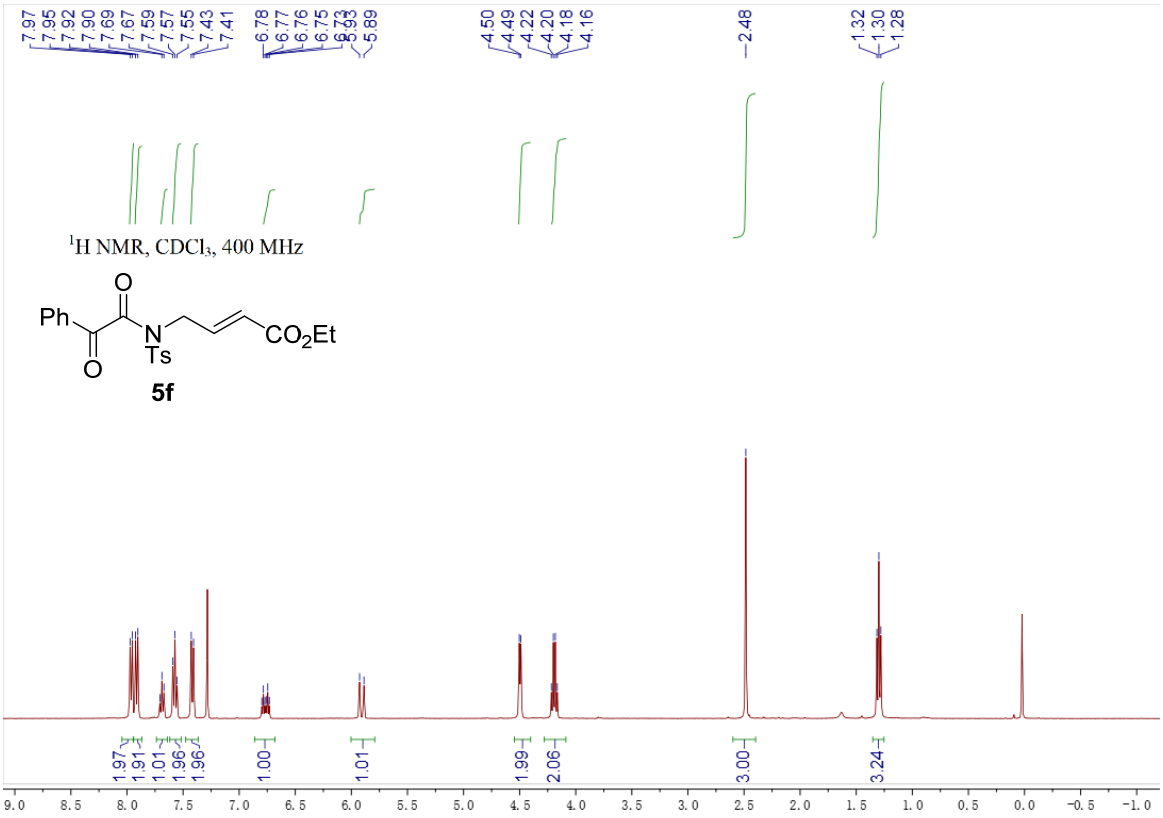
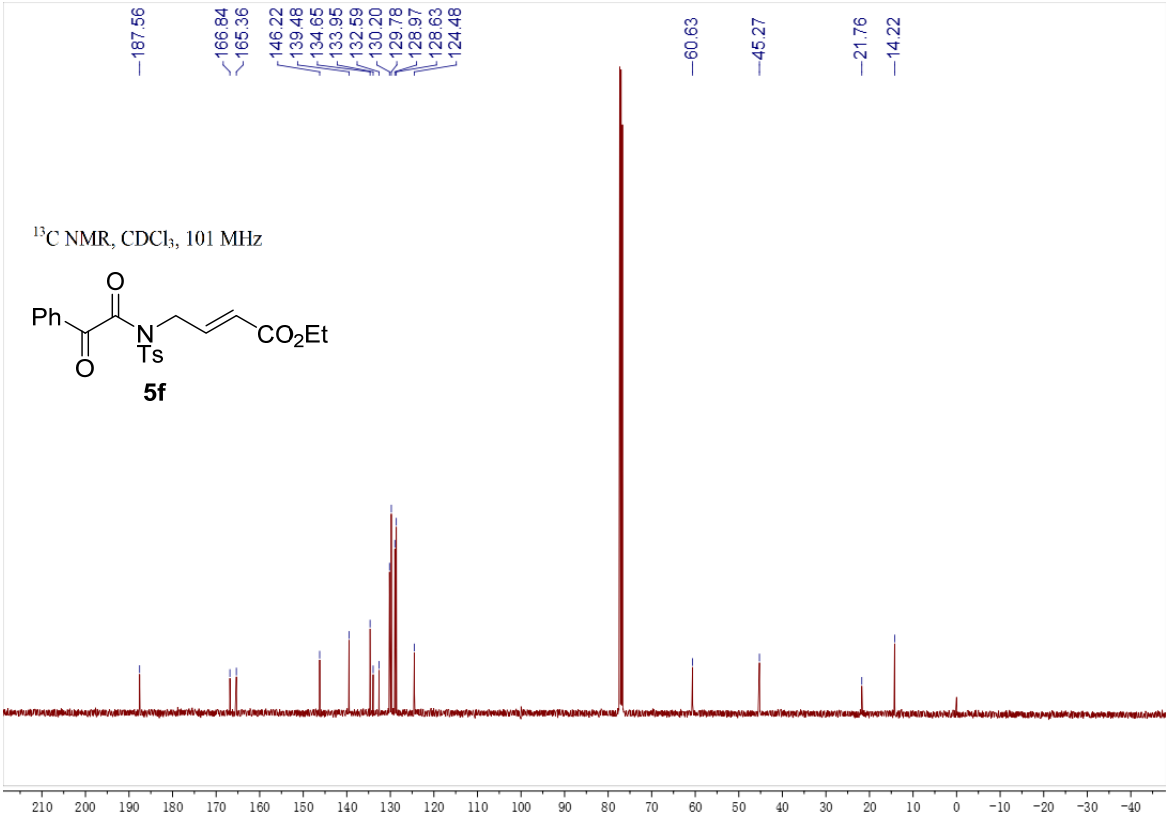
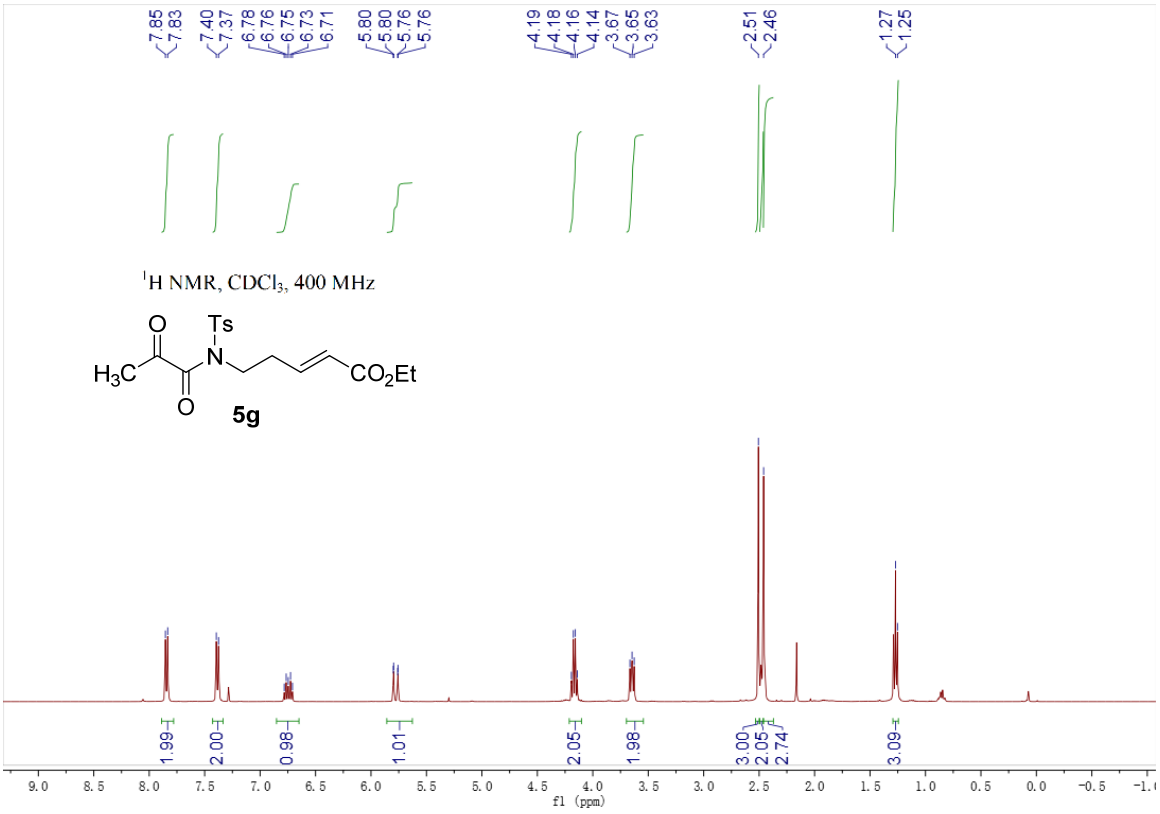
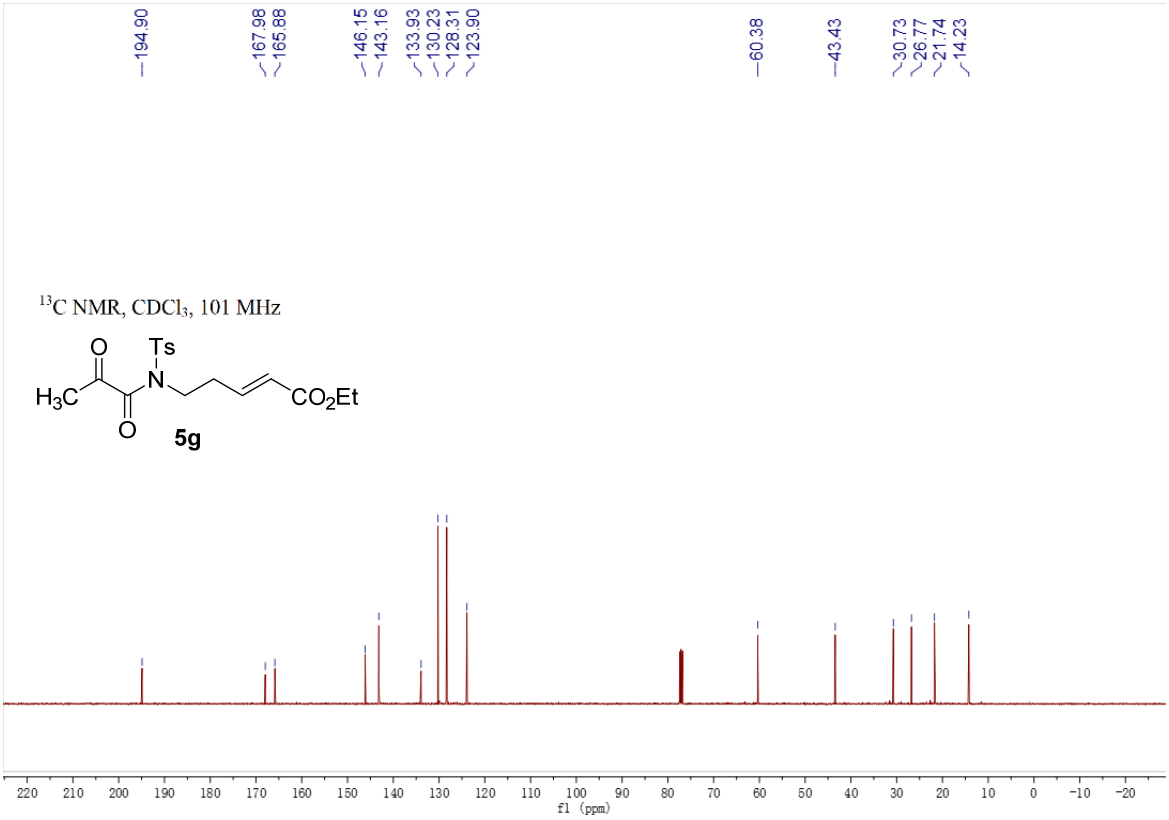
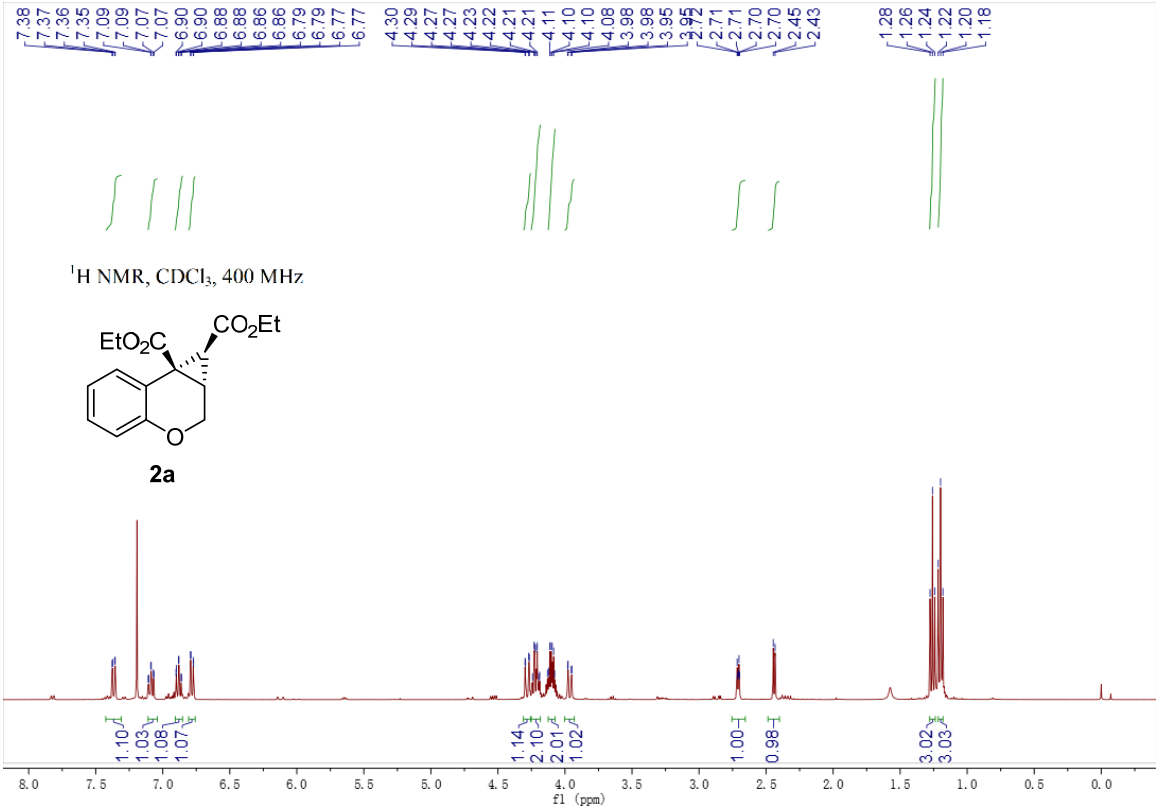
165.59
163.74
145.60
134.96
132.31
129.91
128.92
124.10
80.12
65.16
28.13
28.06
26.86
13C NMR, CDCl3, 101 MHz
O
O
O
CO2t-Bu
5e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

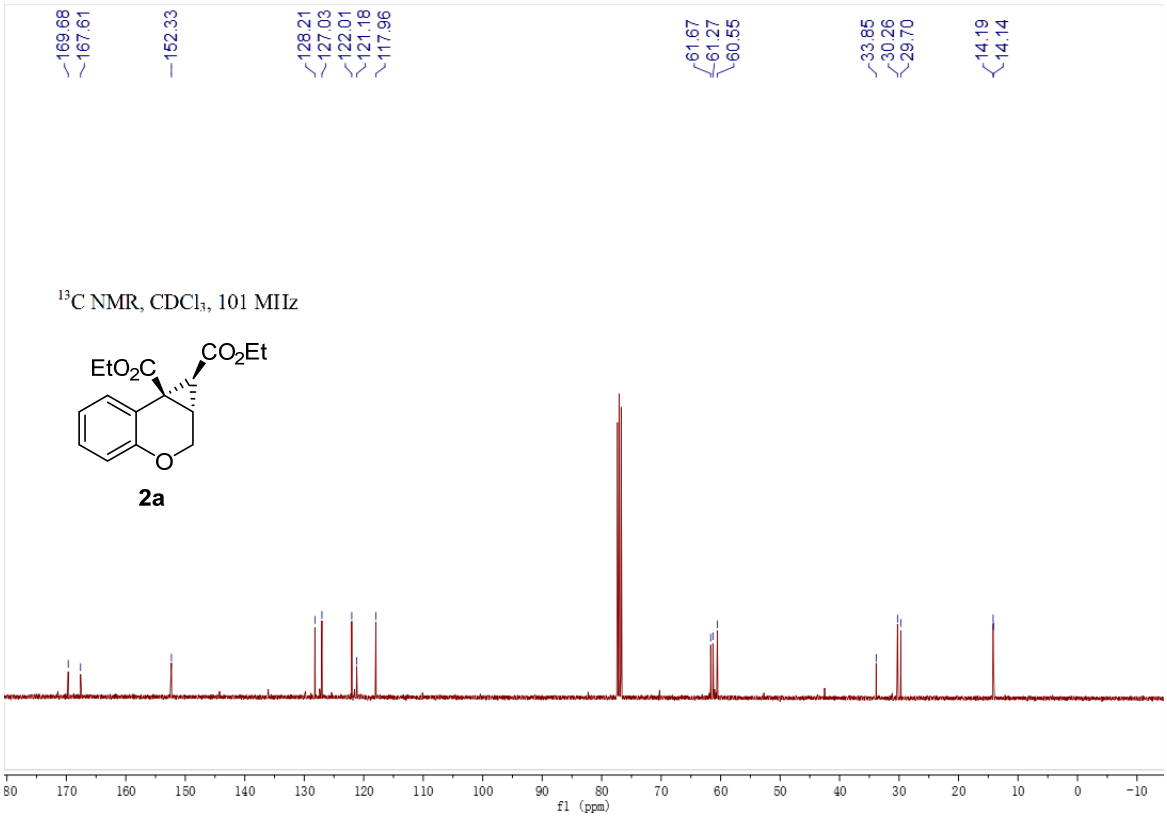

7.97
7.95
7.92
7.90
7.69
7.67
7.59
7.57
7.55
7.43
7.41
6.78
6.77
6.76
6.75
5.93
5.89
4.50
4.49
4.22
4.20
4.18
4.16
2.48
1.32
1.30
1.28
1H NMR, CDCl3, 400 MHz
Ph
O
N
Ts
CO2Et
5f
1.97
1.91
1.01
1.96
1.96
1.00
1.01
1.99
2.06
3.00
3.24


187.56
166.84
165.36
146.22
139.48
134.65
133.95
132.59
130.20
129.78
128.97
128.63
124.48
60.63
45.27
21.76
14.22
13C NMR, CDCl3, 101 MHz
Ph
O
N
Ts
CO2Et
5f


7.85
7.83
7.40
7.37
6.78
6.76
6.75
6.73
6.71
5.80
5.80
5.76
5.76
4.19
4.18
4.16
4.14
3.67
3.65
3.63
2.51
2.46
1.27
1.25
1H NMR, CDCl3, 400 MHz
O
Ts
N
H3C
CO2Et
O
5g
1.99
2.00
0.98
1.01
2.05
1.98
3.00
2.05
2.74
3.09
f1 (ppm)


194.90
167.98
165.88
146.15
143.16
133.93
130.23
128.31
123.90
60.38
43.43
30.73
26.77
21.74
14.23
13C NMR, CDCl3, 101 MHz
O
Ts
N
H3C
CO2Et
O
5g
f1 (ppm)


7.38
7.37
7.36
7.35
7.09
7.09
7.07
7.07
6.90
6.90
6.88
6.88
6.86
6.86
6.79
6.79
6.77
6.77
4.30
4.29
4.27
4.27
4.23
4.22
4.21
4.21
4.11
4.10
4.10
4.08
3.98
3.98
3.95
2.72
2.71
2.71
2.70
2.70
2.45
2.43
1.28
1.26
1.24
1.22
1.20
1.18
1H NMR, CDCl3, 400 MHz
EtO2C
CO2Et
O
2a
1.10
1.03
1.08
1.07
1.14
2.10
2.01
1.02
1.00
0.98
3.02
3.03
f1 (ppm)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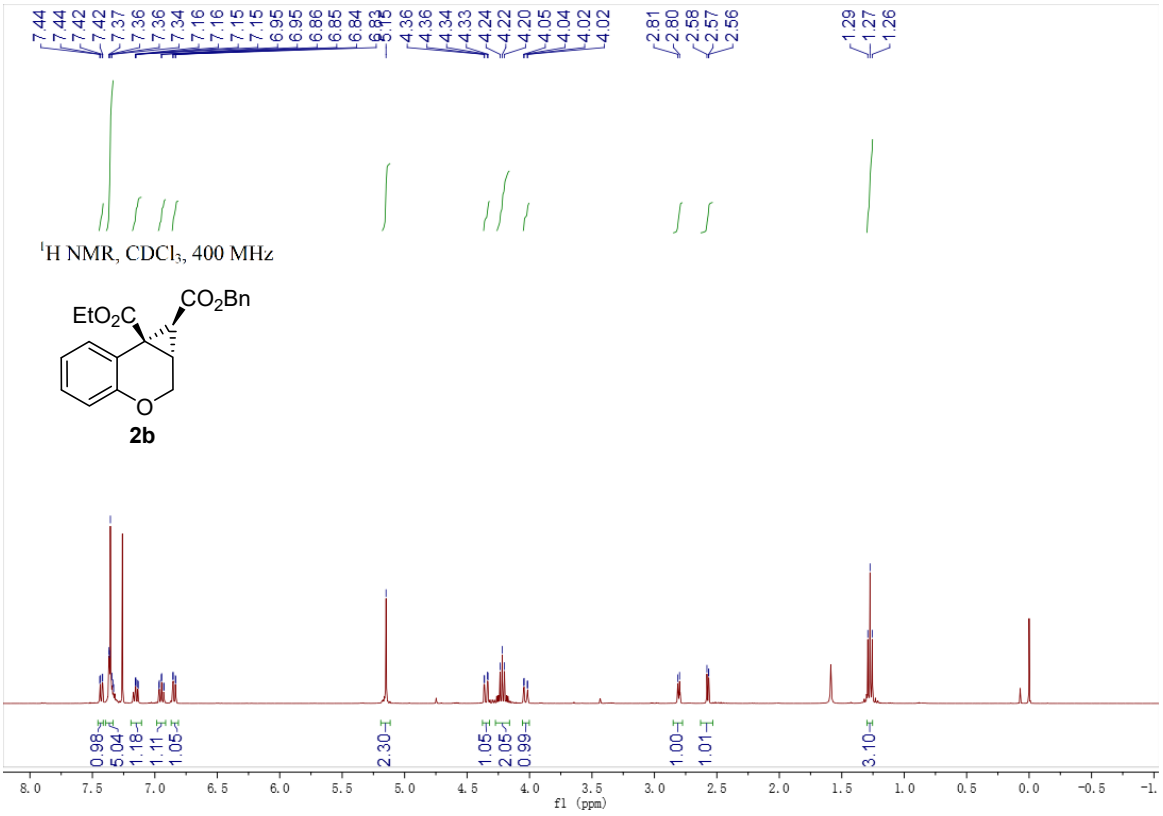
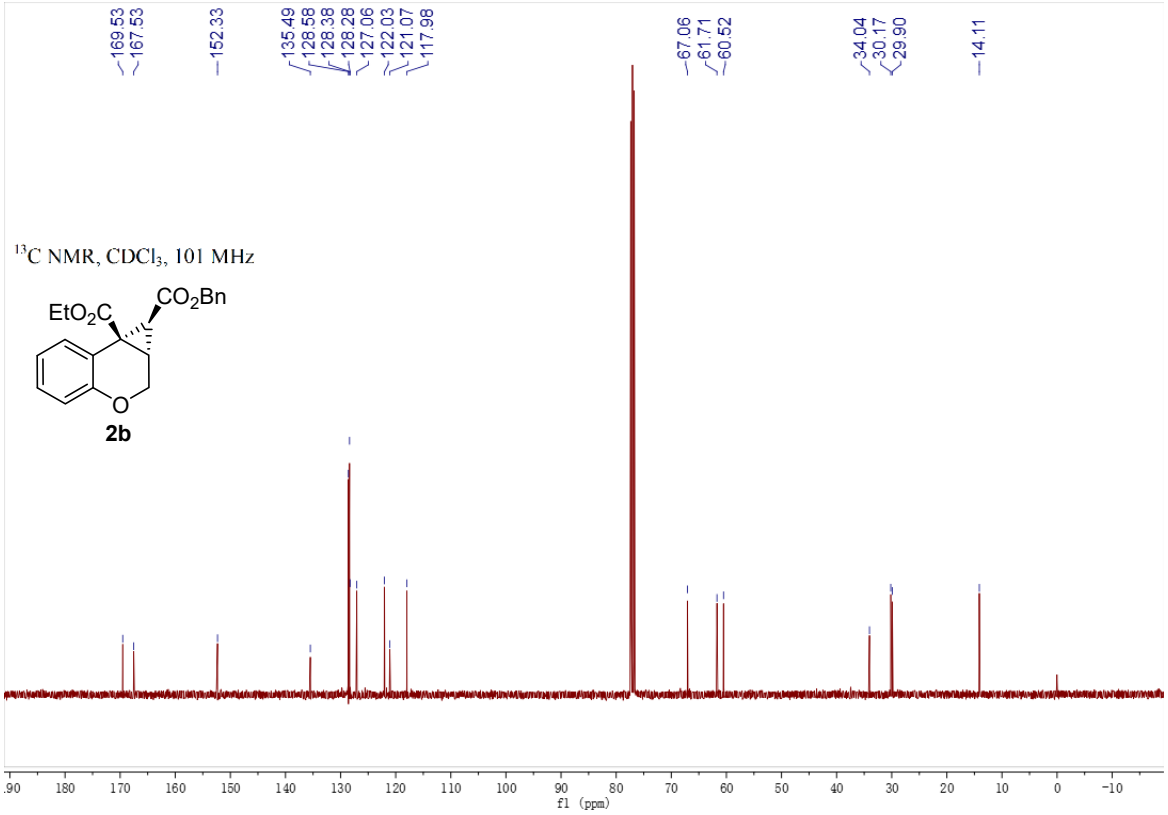
167.61
152.33
128.21
127.03
122.01
121.18
117.96
61.67
61.27
60.55
33.85
30.26
29.70
14.19
14.14
13C NMR, CDCl3, 101 MIIz
EtO2C
CO2Et
O
2a
f1 (ppm)


7.44
7.44
7.42
7.42
7.37
7.36
7.36
7.34
7.16
7.16
7.15
7.15
6.95
6.86
6.85
6.84
6.83
4.36
4.36
4.34
4.33
4.24
4.22
4.20
4.05
4.04
4.02
4.02
2.81
2.80
2.58
2.57
2.56
1.29
1.27
1.26
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Bn
O
2b
0.98
5.04
1.18
1.11
1.05
2.30
1.05
2.05
0.99
1.00
1.01
3.10
f1 (ppm)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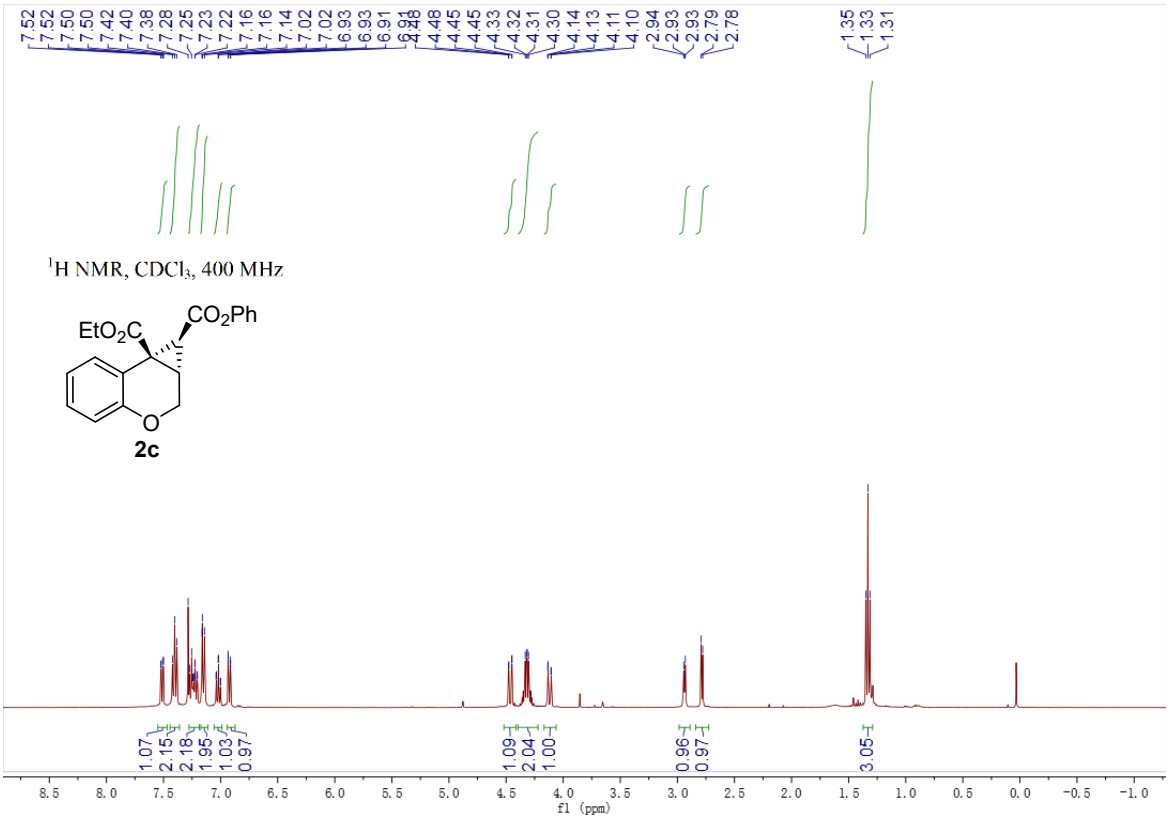
167.53
152.33
135.49
128.58
128.38
128.28
127.06
122.03
121.07
117.98
67.06
61.71
60.52
34.04
30.17
29.90
14.11
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Bn
O
2b
f1 (ppm)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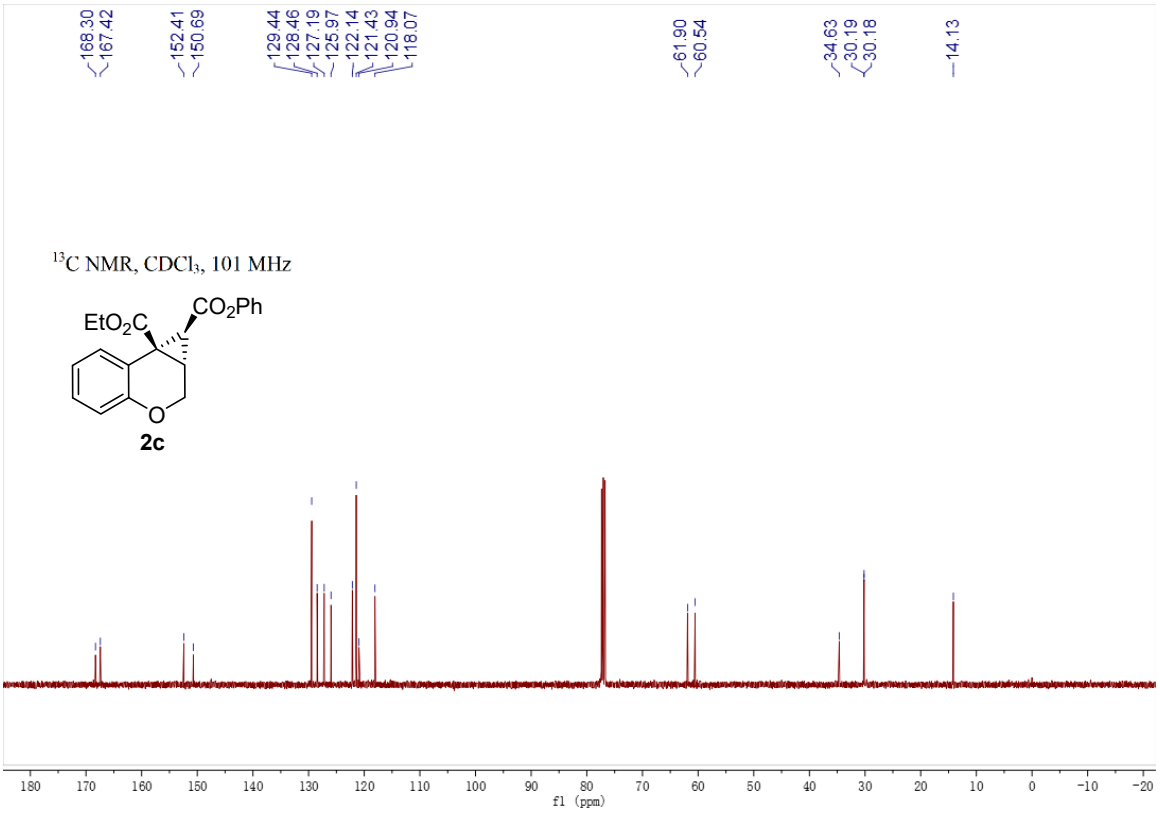
7.52
7.50
7.50
7.42
7.40
7.38
7.28
7.25
7.23
7.22
7.16
7.16
7.14
7.02
7.02
6.93
6.93
6.91
6.91
4.48
4.48
4.45
4.45
4.33
4.32
4.31
4.30
4.14
4.13
4.11
4.10
2.94
2.93
2.93
2.79
2.78
1.35
1.33
1.31
1H NMR, CDCl3, 400 MHz
EtO2C
CO2Ph
O
2c
1.07
2.15
2.18
1.95
1.03
0.97
1.09
2.04
1.00
0.96
0.97
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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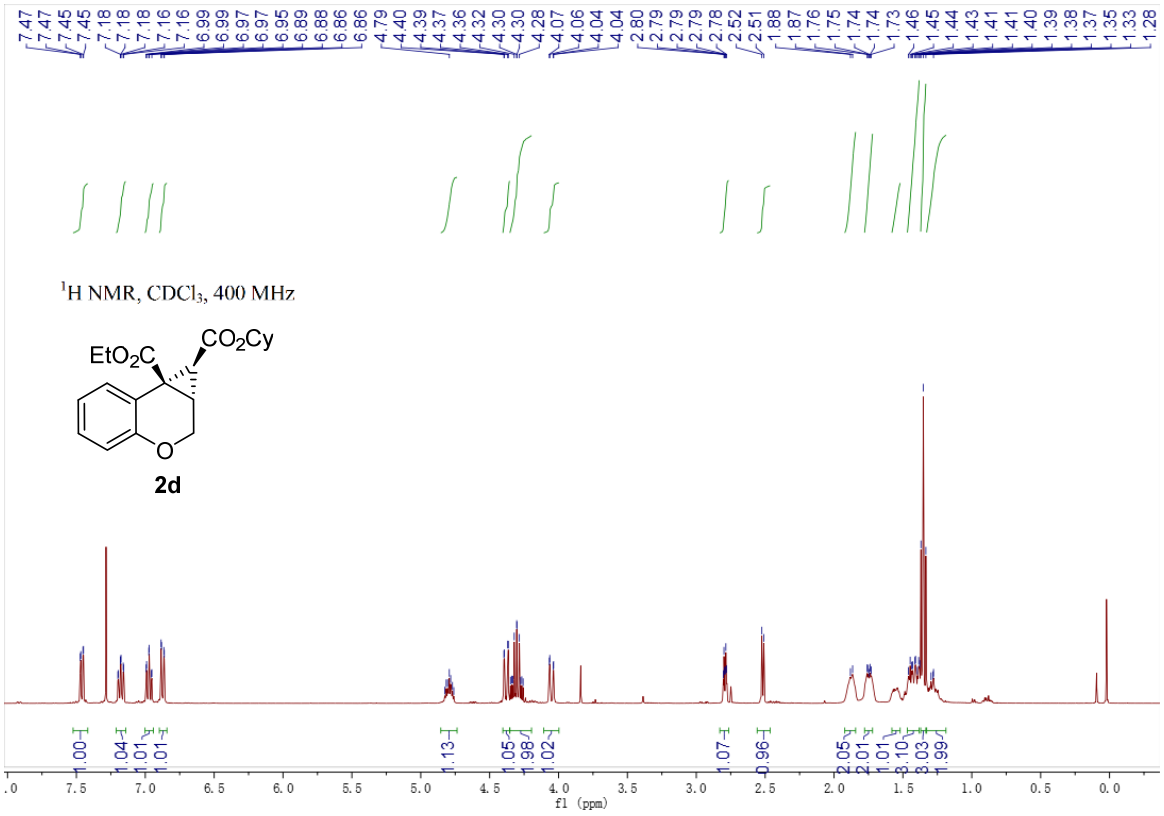
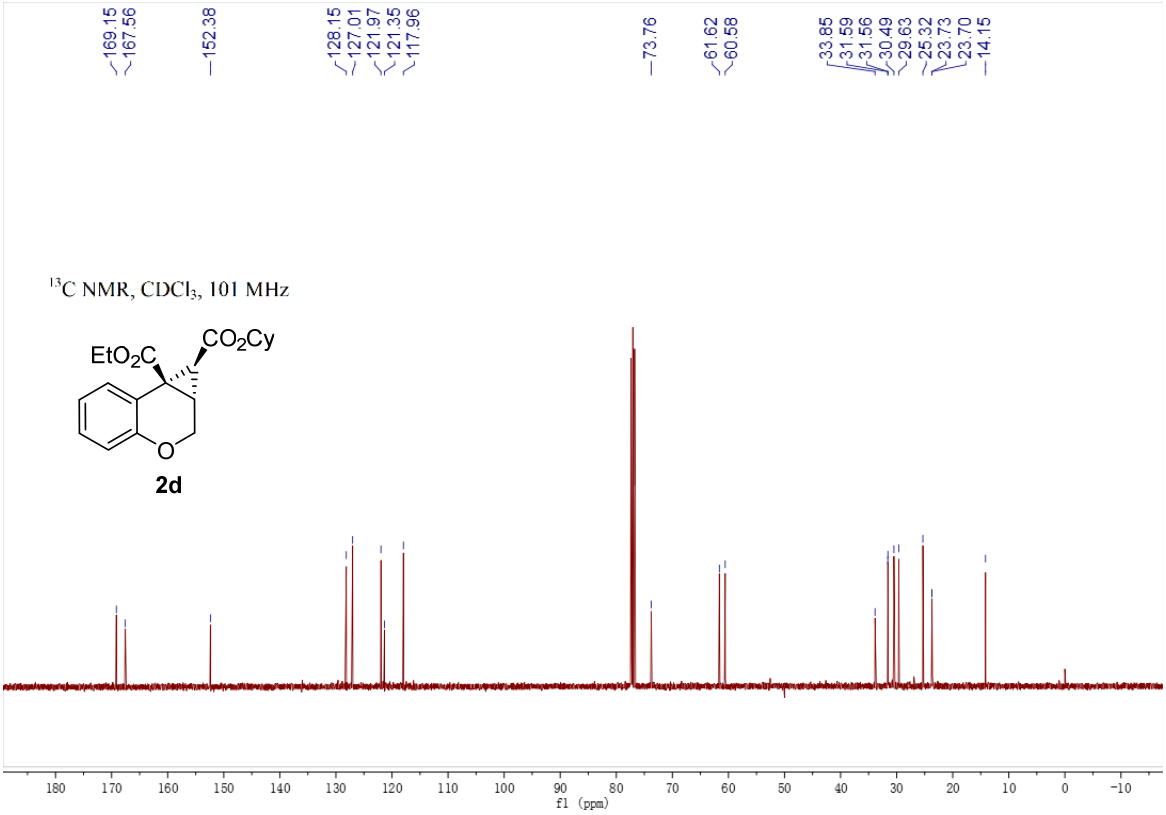
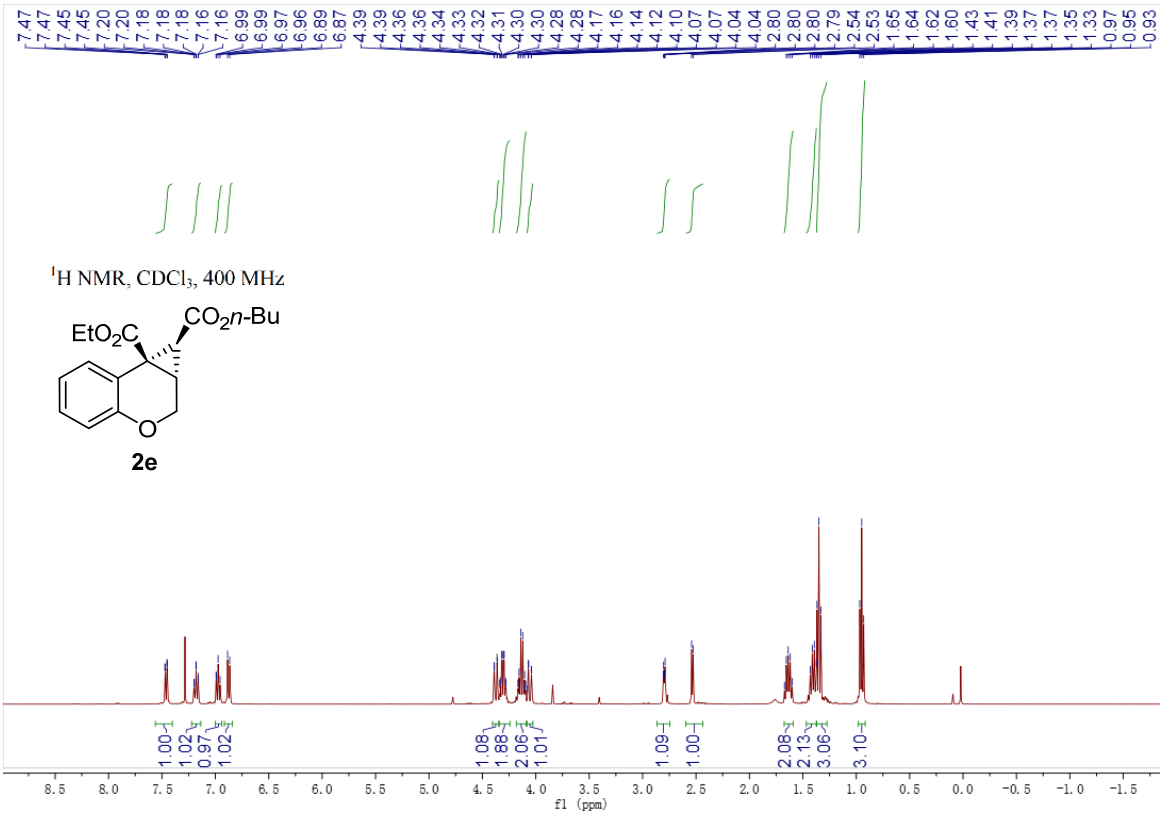
167.42
152.41
150.69
129.44
128.46
127.19
125.97
122.14
121.43
120.94
118.07
61.90
60.54
34.63
30.19
30.18
14.13
13C NMR, CDCl3, 101 MHz
EtO2C
CO2Ph
O
2c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

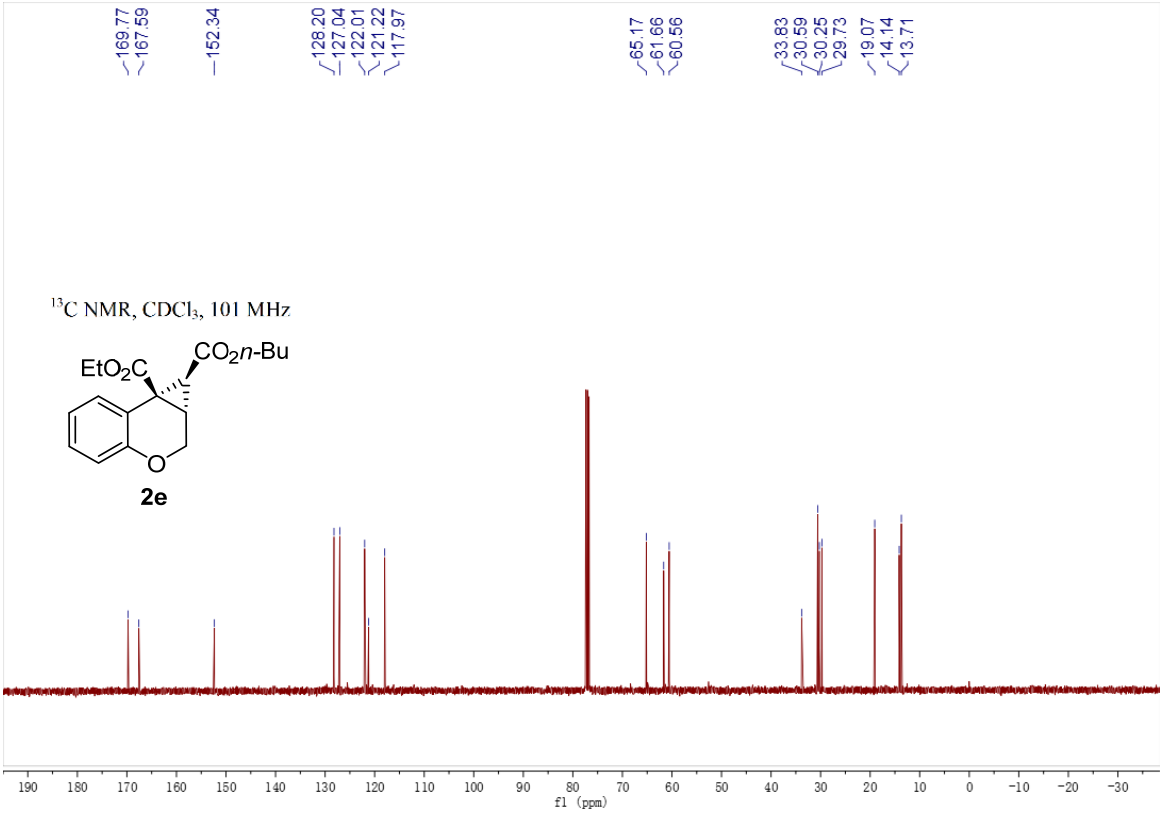

7.47 7.47 7.45 7.45 7.18 7.18 7.18 7.16 7.16 6.99 6.99 6.97 6.97 6.95 6.89 6.88 6.86 6.86 4.79 4.40 4.39 4.37 4.36 4.32 4.30 4.30 4.28 4.07 4.06 4.04 4.04 2.80 2.79 2.79 2.78 2.52 2.51 1.88 1.87 1.76 1.75 1.74 1.74 1.73 1.46 1.45 1.44 1.43 1.41 1.41 1.40 1.39 1.38 1.37 1.35 1.33 1.28
1H NMR, CDCl3, 400 MHz
EtO2C
CO2Cy
O
2d
1.00 1.04 1.01 1.01 1.13 1.05 1.98 1.02 1.07 0.96 2.05 2.01 1.01 3.10 3.03 1.99
f1 (ppm)


169.15 167.56 152.38 128.15 127.01 121.97 121.35 117.96 73.76 61.62 60.58 33.85 31.59 31.56 30.49 29.63 25.32 23.73 23.70 14.15
13C NMR, CDCl3, 101 MHz
EtO2C
CO2Cy
O
2d
f1 (ppm)



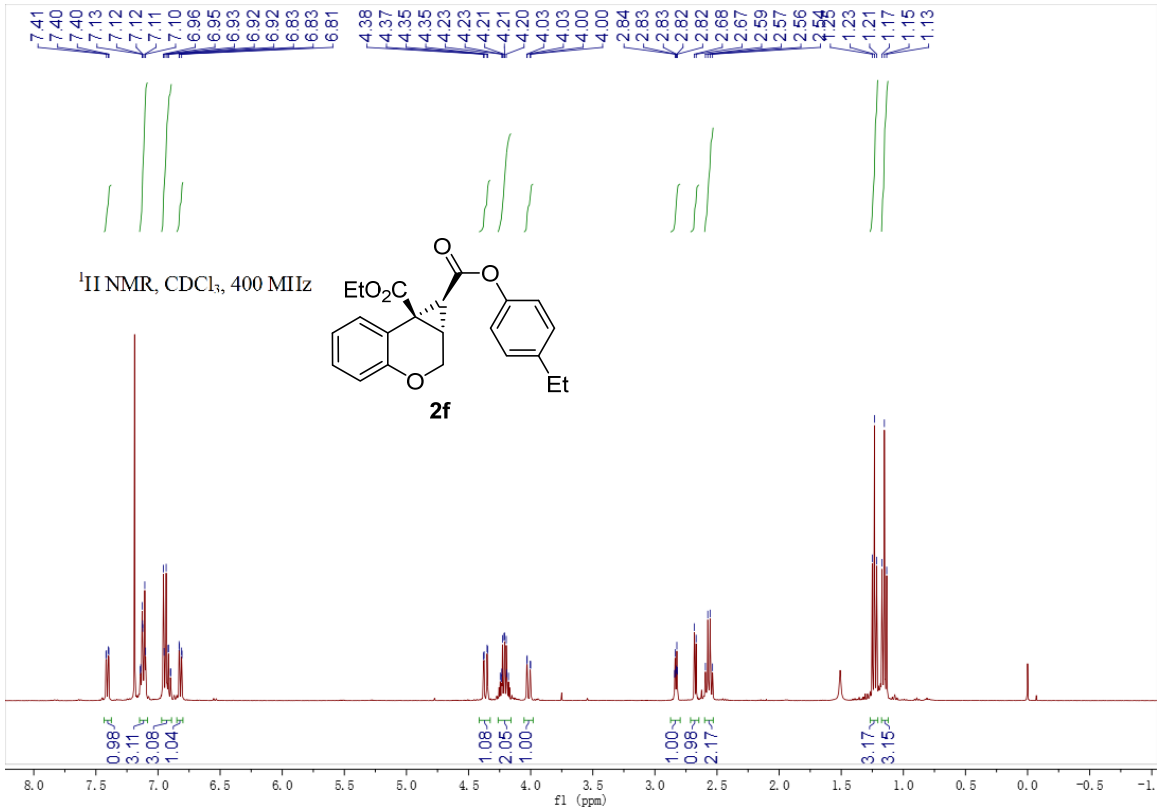
^{1}H NMR, $CDCl_3$, 400 MHz

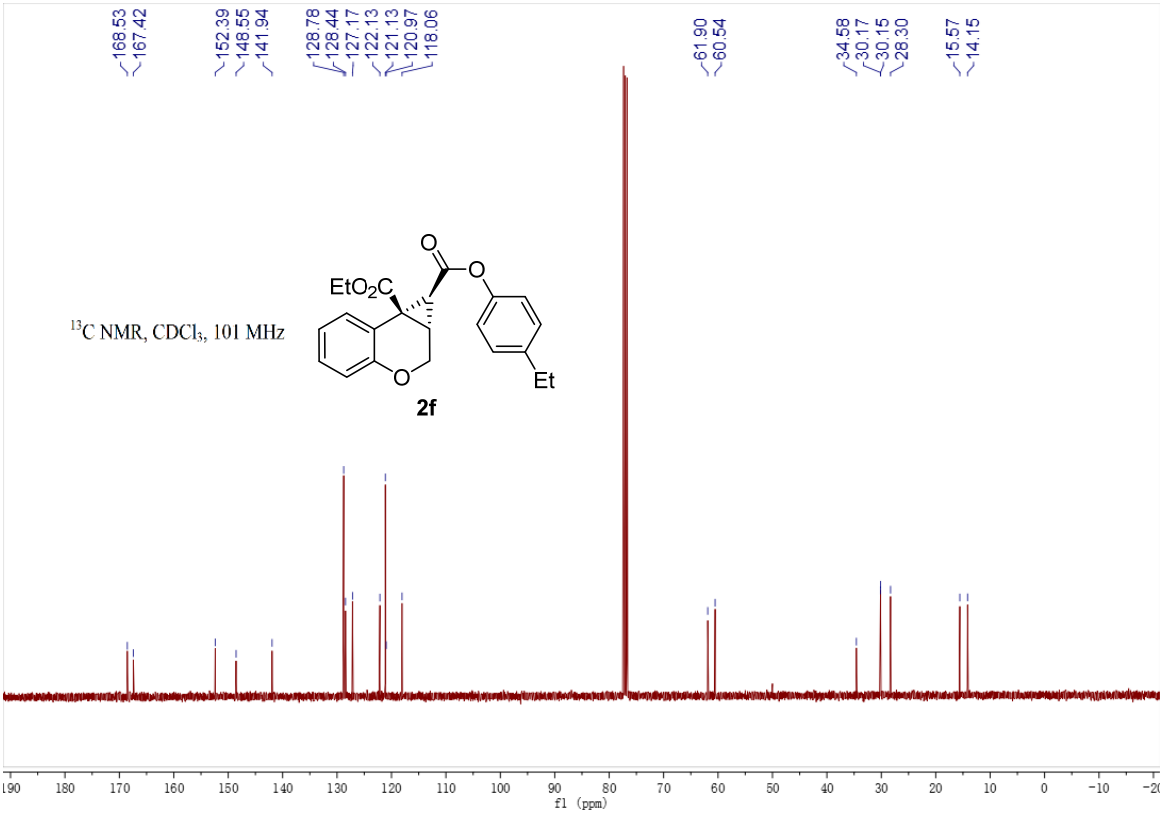
2e

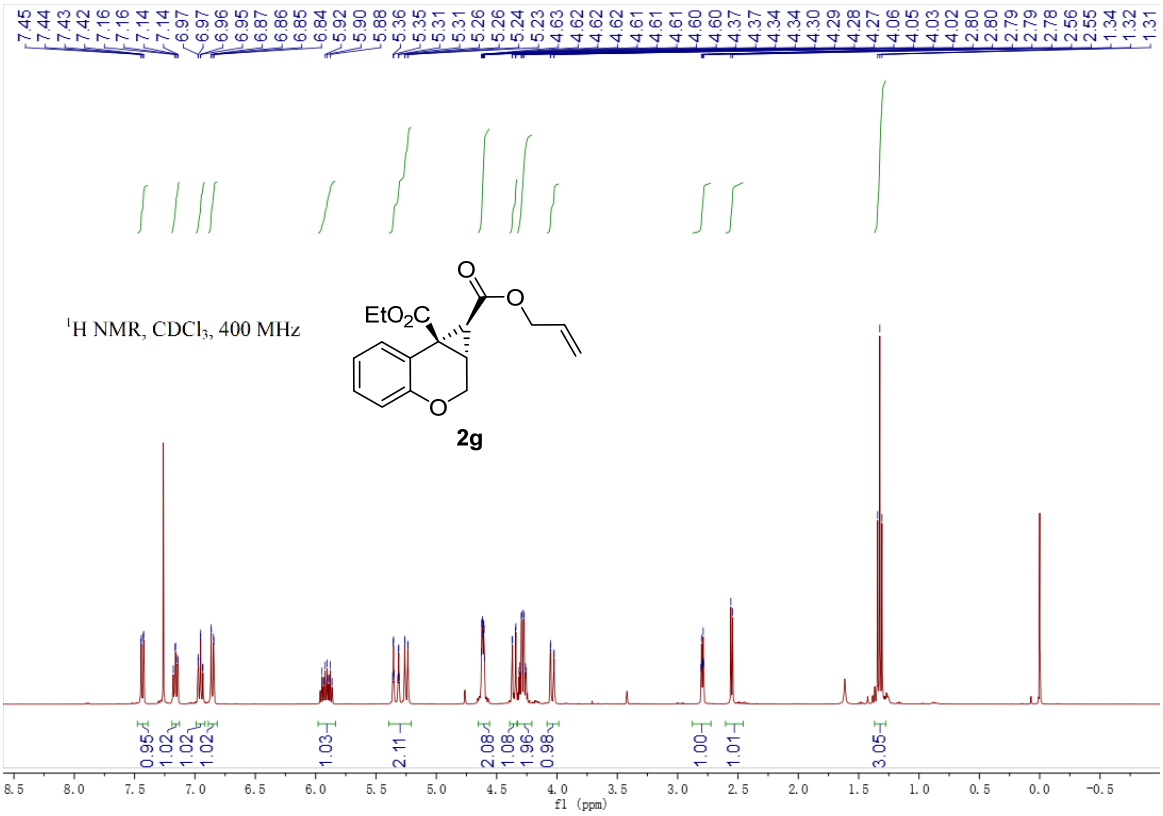


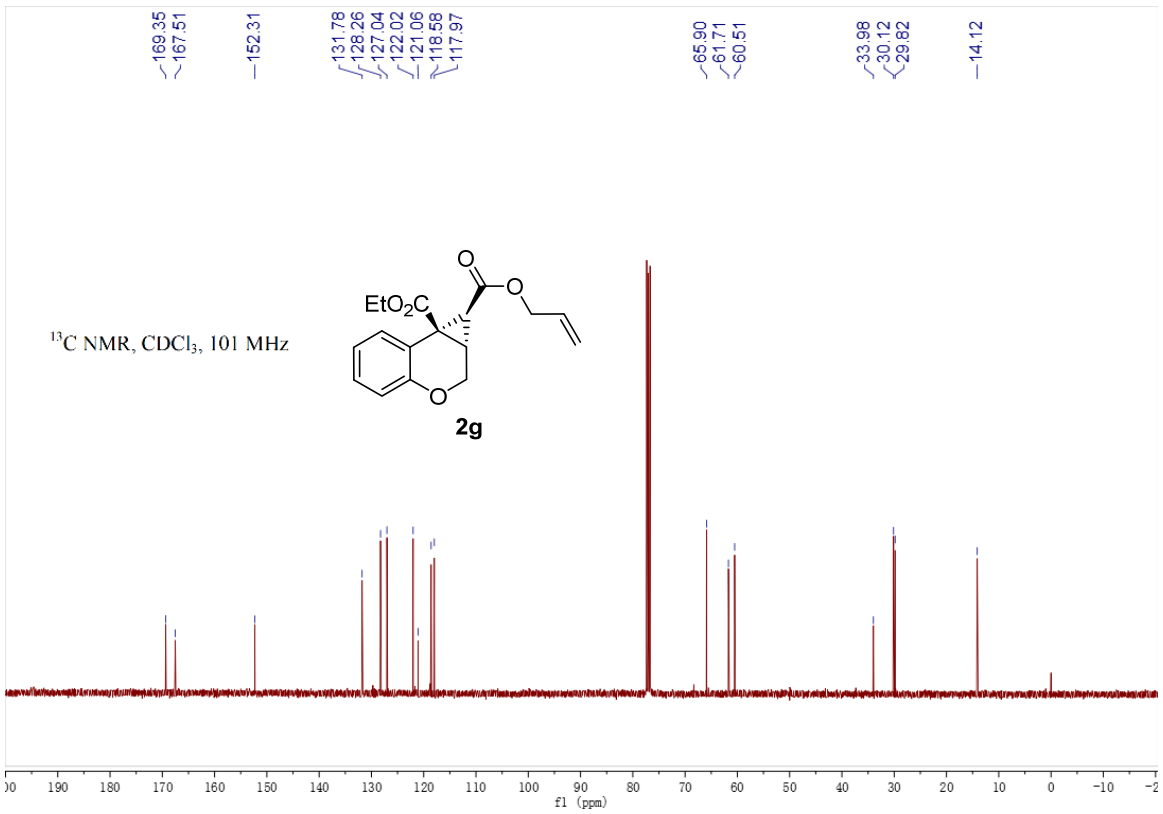
^{13}C NMR, $CDCl_3$, 101 MHz

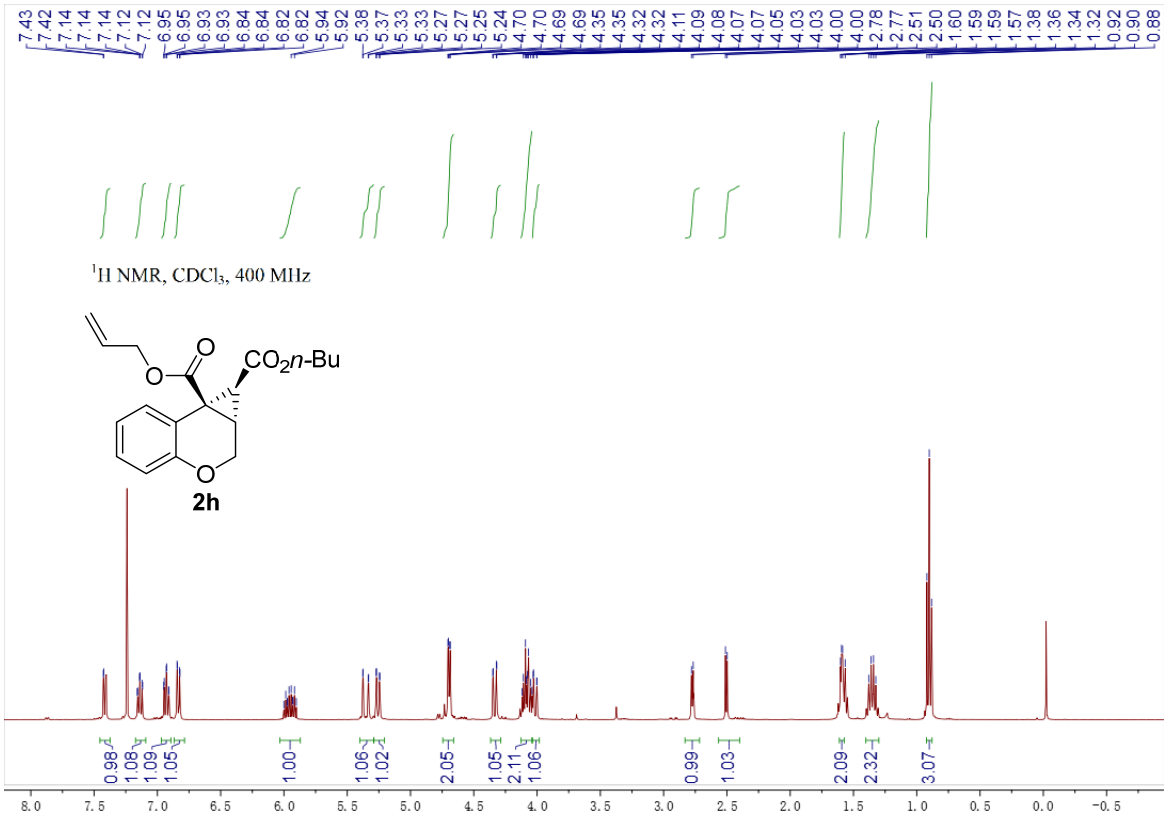
2e


7.41 7.40 7.40 7.13 7.12 7.12 7.11 7.10 6.96 6.95 6.93 6.92 6.92 6.83 6.83 6.81
4.38 4.37 4.35 4.35 4.23 4.21 4.21 4.20 4.03 4.03 4.00 4.00
2.84 2.83 2.82 2.82 2.68 2.67 2.59 2.57 2.56 2.54 1.23 1.21 1.17 1.15 1.13
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
O
O
Et
2f
0.98 3.11 3.08 1.04 1.08 2.05 1.00 1.00 0.98 2.17 3.17 3.15
f1 (ppm)


168.53 167.42 152.39 148.55 141.94 128.78 128.44 127.17 122.13 121.13 120.97 118.06
61.90 60.54 34.58 30.17 30.15 28.30 15.57 14.15
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
O
O
Et
2f
f1 (ppm)


7.45 7.44 7.43 7.42 7.16 7.16 7.14 7.14 6.97 6.97 6.96 6.95 6.87 6.86 6.85 6.84 5.92 5.90 5.88 5.36 5.35 5.31 5.31 5.26 5.26 5.24 5.23 4.63 4.62 4.62 4.62 4.61 4.61 4.61 4.60 4.60 4.37 4.37 4.34 4.34 4.30 4.29 4.28 4.27 4.06 4.05 4.03 4.02 2.80 2.80 2.79 2.79 2.78 2.56 2.55 1.34 1.32 1.31
^{1}H NMR, CDCl$_3$, 400 MHz
EtO2C
O
O
O
2g
0.95 1.02 1.02 1.02 1.03 2.11 2.08 1.08 1.96 0.98 1.00 1.01 3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


169.35 167.51 152.31 131.78 128.26 127.04 122.02 121.06 118.58 117.97 65.90 61.71 60.51 33.98 30.12 29.82 14.12
^{13}C NMR, CDCl$_3$, 101 MHz
EtO2C
O
O
O
2g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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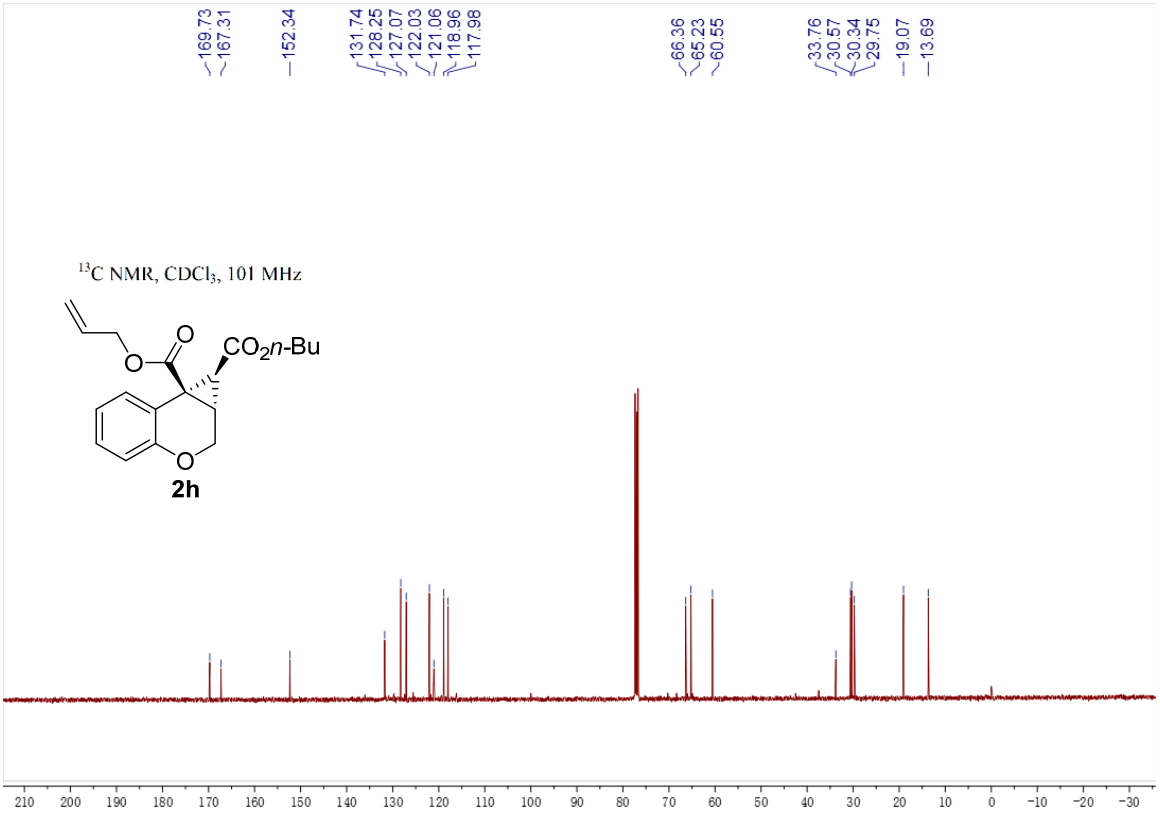
^{1}H NMR, CDCl$_3$, 400 MHz
CO$_2$n-Bu
2h
0.98 1.08 1.09 1.05 1.00 1.06 1.02 2.05 1.05 2.11 1.06 0.99 1.03 2.09 2.32 3.07
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


169.73 167.31 152.34 131.74 128.25 127.07 122.03 121.06 118.96 117.98 66.36 65.23 60.55 33.76 30.57 30.34 29.75 19.07 13.69
^{13}C NMR, CDCl$_3$, 101 MHz
CO$_2$n-Bu
2h
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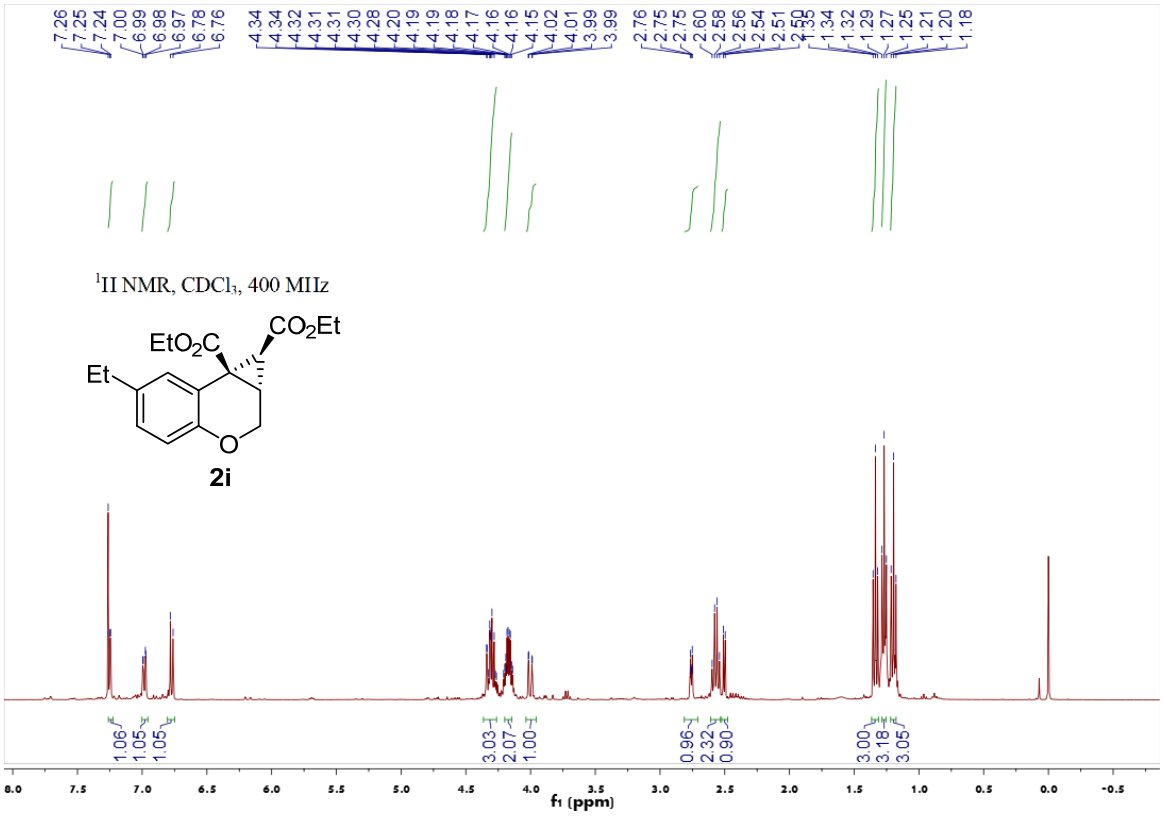
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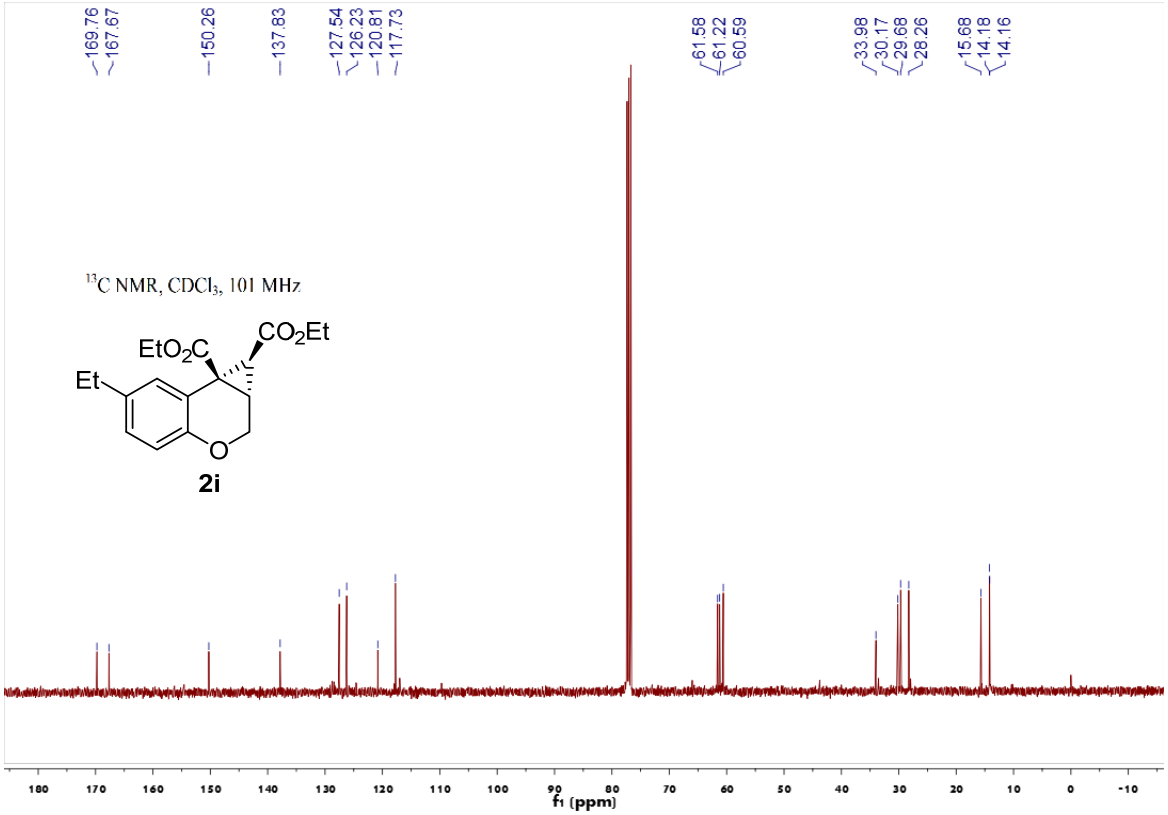
7.25
7.24
7.00
6.99
6.98
6.97
6.78
6.76
4.34
4.34
4.32
4.31
4.31
4.30
4.28
4.20
4.19
4.19
4.18
4.17
4.16
4.16
4.15
4.02
4.01
3.99
3.99
2.76
2.75
2.75
2.60
2.58
2.56
2.54
2.51
1.34
1.32
1.29
1.27
1.25
1.21
1.20
1.18
1H NMR, CDCl3, 400 MHz
EtO2C
CO2Et
Et
O
2i
1.06
1.05
1.05
3.03
2.07
1.00
0.96
2.32
0.90
3.00
3.18
3.05
f1 (ppm)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167.67
150.26
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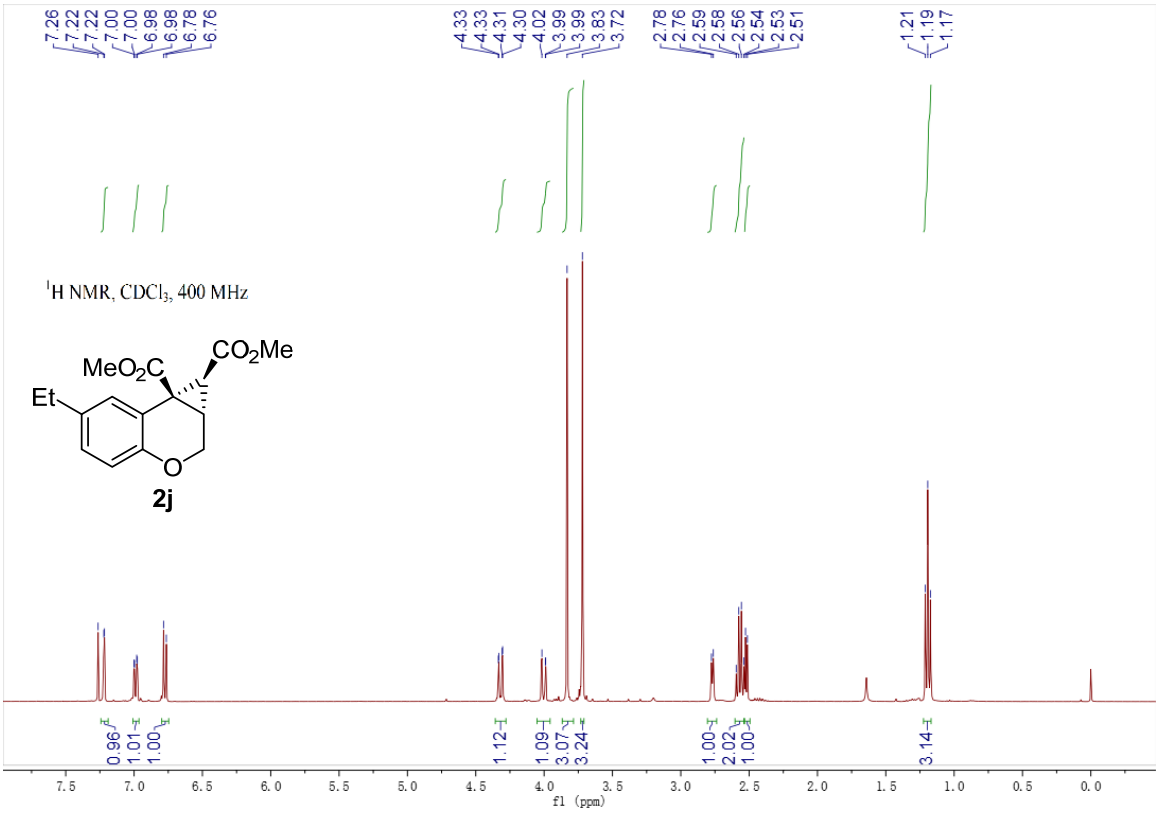
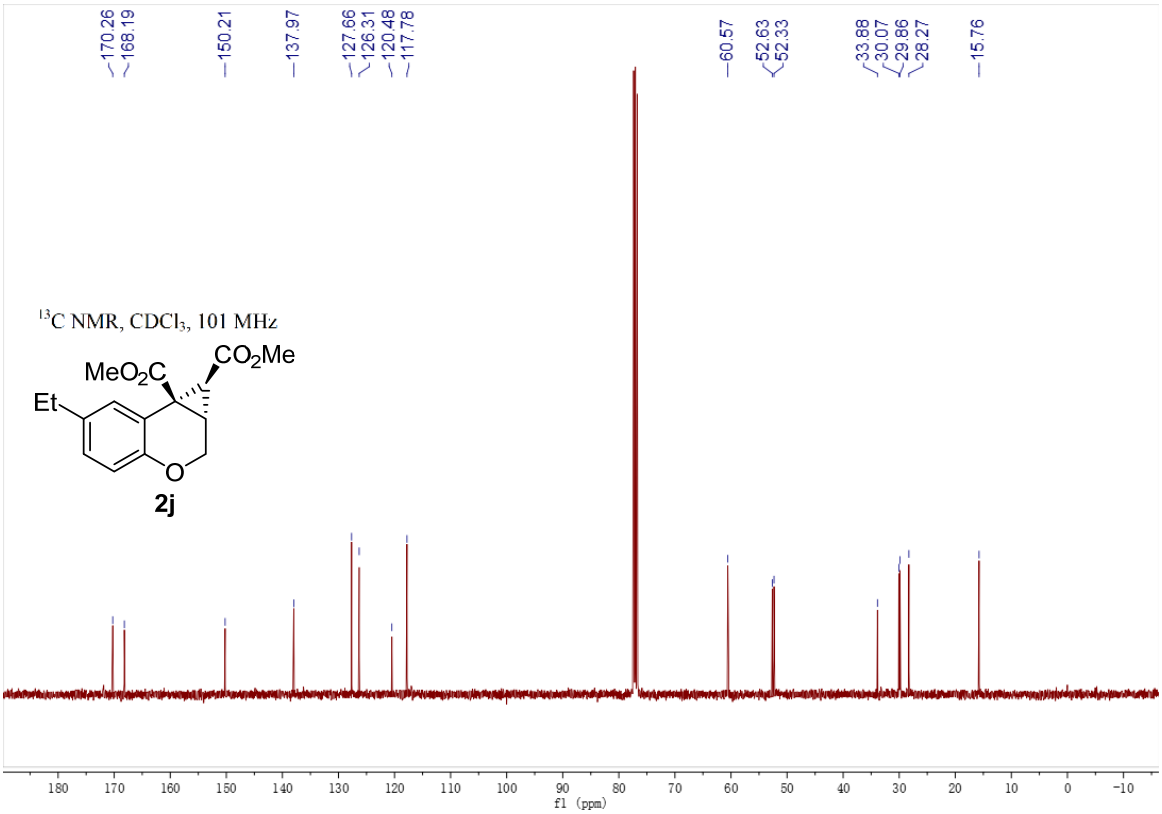
127.54
126.23
120.81
117.73
61.58
61.22
60.59
33.98
30.17
29.68
28.26
15.68
14.18
14.16
13C NMR, CDCl3, 101 MHz
EtO2C
CO2Et
Et
O
2i
f1 (ppm)


7.26
7.22
7.22
7.00
7.00
6.98
6.98
6.78
6.76
4.33
4.33
4.31
4.30
4.02
3.99
3.99
3.83
3.72
2.78
2.76
2.59
2.58
2.56
2.54
2.53
2.51
1.21
1.19
1.17
^{1}H NMR, $CDCl_3$, 400 MHz
MeO_2C
CO_2Me
Et
O
2j
0.96
1.01
1.00
1.12
1.09
3.07
3.24
1.00
2.02
1.00
3.14
f1 (ppm)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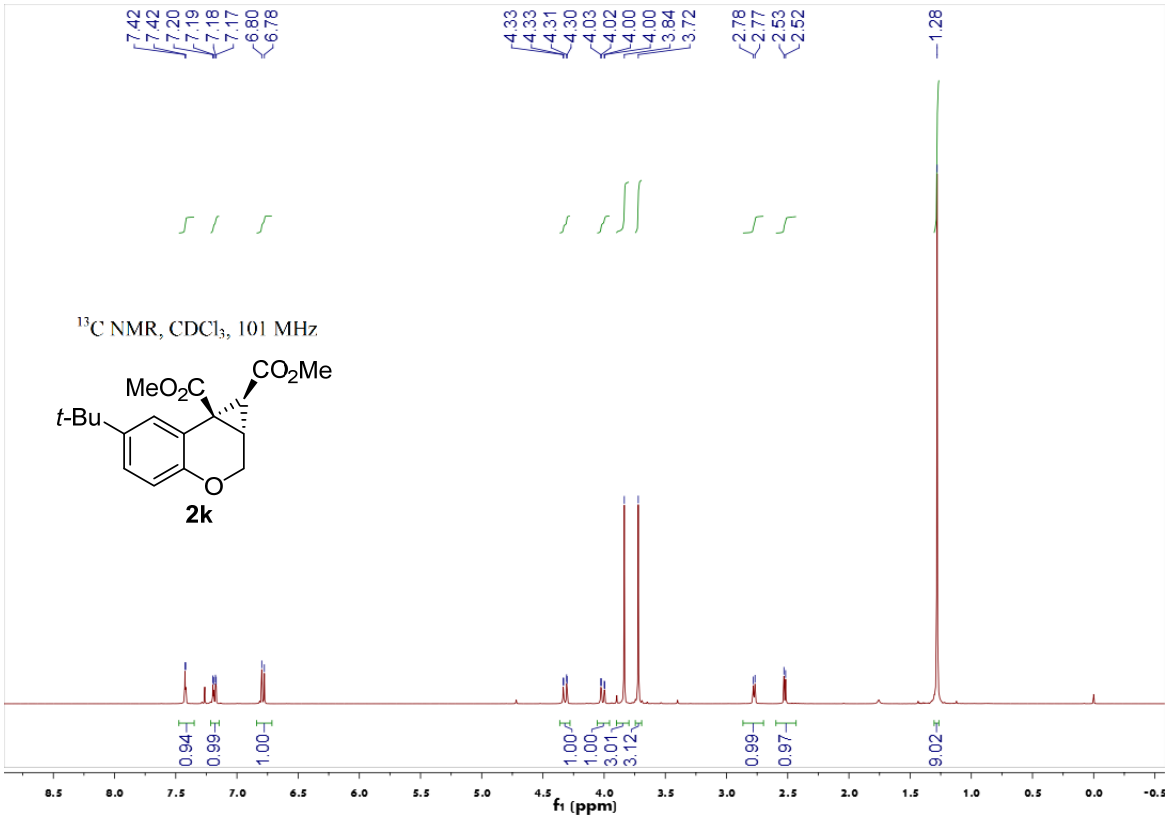
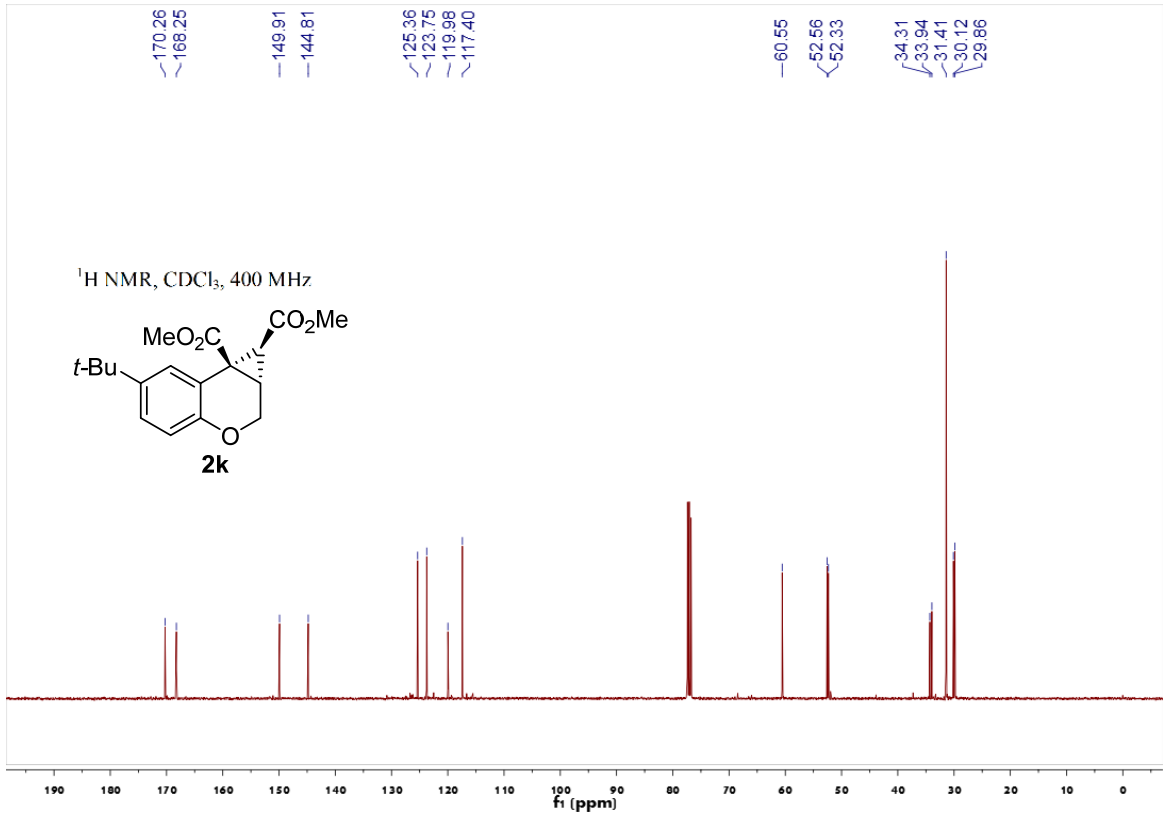
168.19
150.21
137.97
127.66
126.31
120.48
117.78
60.57
52.63
52.33
33.88
30.07
29.86
28.27
15.76
^{13}C NMR, $CDCl_3$, 101 MHz
MeO_2C
CO_2Me
Et
O
2j
f1 (ppm)


7.42
7.42
7.20
7.19
7.18
7.17
6.80
6.78
4.33
4.31
4.30
4.03
4.02
4.00
4.00
3.84
3.72
2.78
2.77
2.53
2.52
1.28
^{13}C NMR, CDCl$_3$, 101 MHz
MeO$_2$C
CO$_2$Me
t-Bu
O
2k
0.94
0.99
1.00
1.00
1.00
3.01
3.12
0.99
0.97
9.02
f$_1$ (ppm)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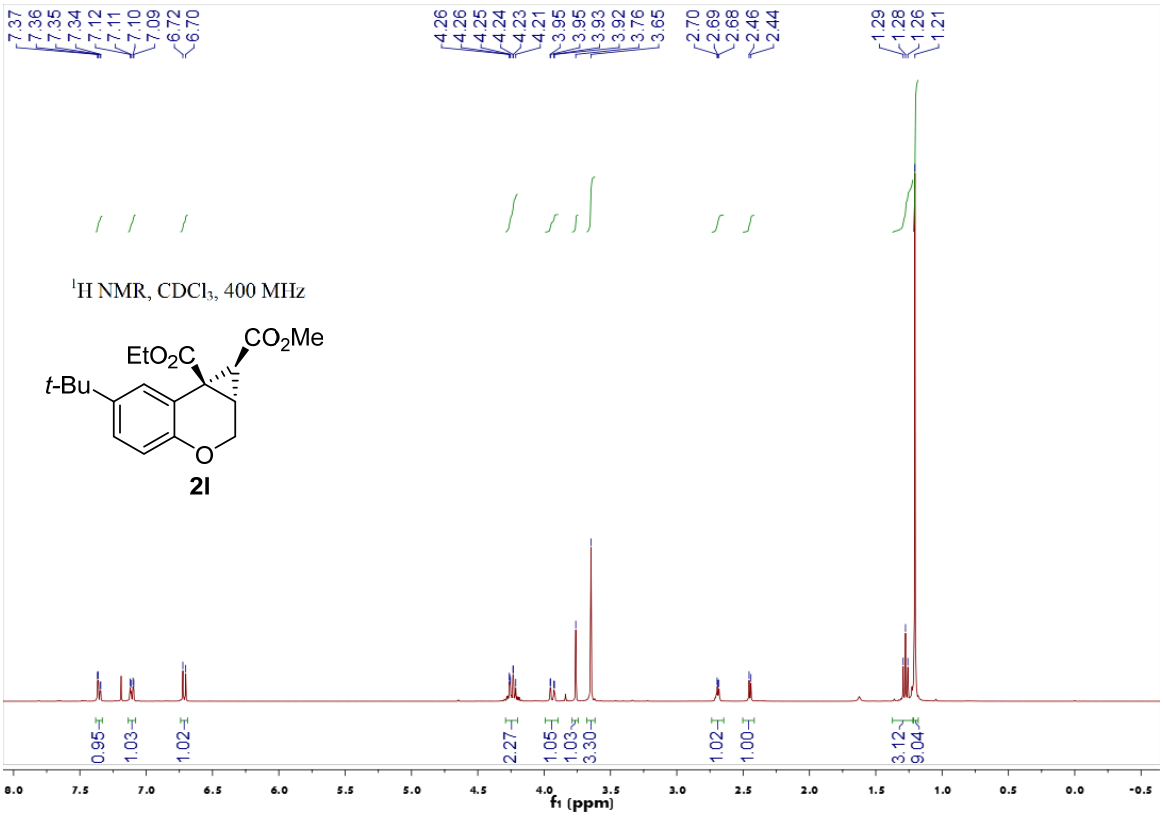
168.25
149.91
144.81
125.36
123.75
119.98
117.40
60.55
52.56
52.33
34.31
33.94
31.41
30.12
29.86
^{1}H NMR, CDCl$_3$, 400 MHz
MeO$_2$C
CO$_2$Me
t-Bu
O
2k
f$_1$ (ppm)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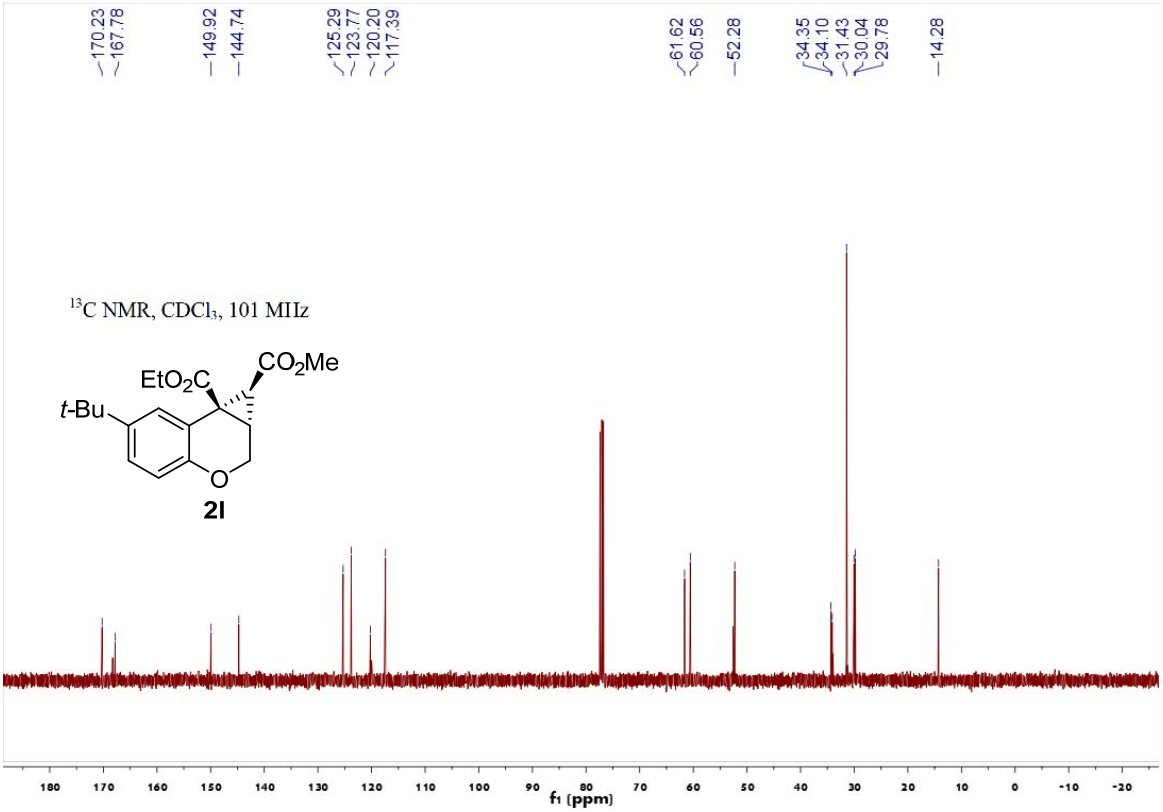
7.36
7.35
7.34
7.12
7.11
7.10
7.09
6.72
6.70
4.26
4.26
4.25
4.24
4.23
4.21
3.95
3.95
3.93
3.92
3.76
3.65
2.70
2.69
2.68
2.46
2.44
1.29
1.28
1.26
1.21
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Me
t-Bu
O
2l
0.95
1.03
1.02
2.27
1.05
1.03
3.30
1.02
1.00
3.12
9.04
f$_1$ (ppm)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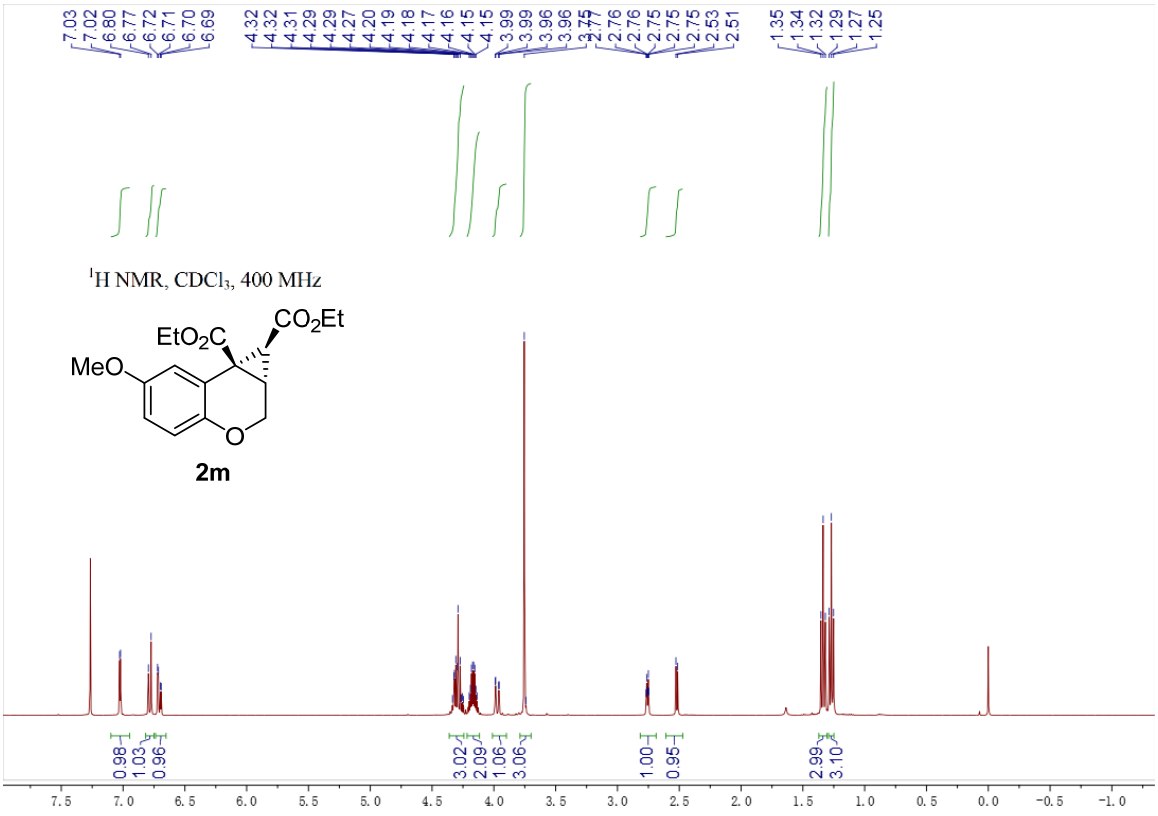
167.78
149.92
144.74
125.29
123.77
120.20
117.39
61.62
60.56
52.28
34.35
34.10
31.43
30.04
29.78
14.28
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Me
t-Bu
O
2l
f$_1$ (ppm)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7.02
6.80
6.77
6.72
6.71
6.70
6.69
4.32
4.32
4.31
4.29
4.29
4.27
4.20
4.19
4.18
4.17
4.16
4.15
4.15
3.99
3.99
3.96
3.96
2.76
2.76
2.75
2.75
2.75
2.53
2.51
1.35
1.34
1.32
1.29
1.27
1.25
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Et
MeO
O
2m
0.98
1.03
0.96
3.02
2.09
1.06
3.06
1.00
0.95
2.99
3.10
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
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0.5
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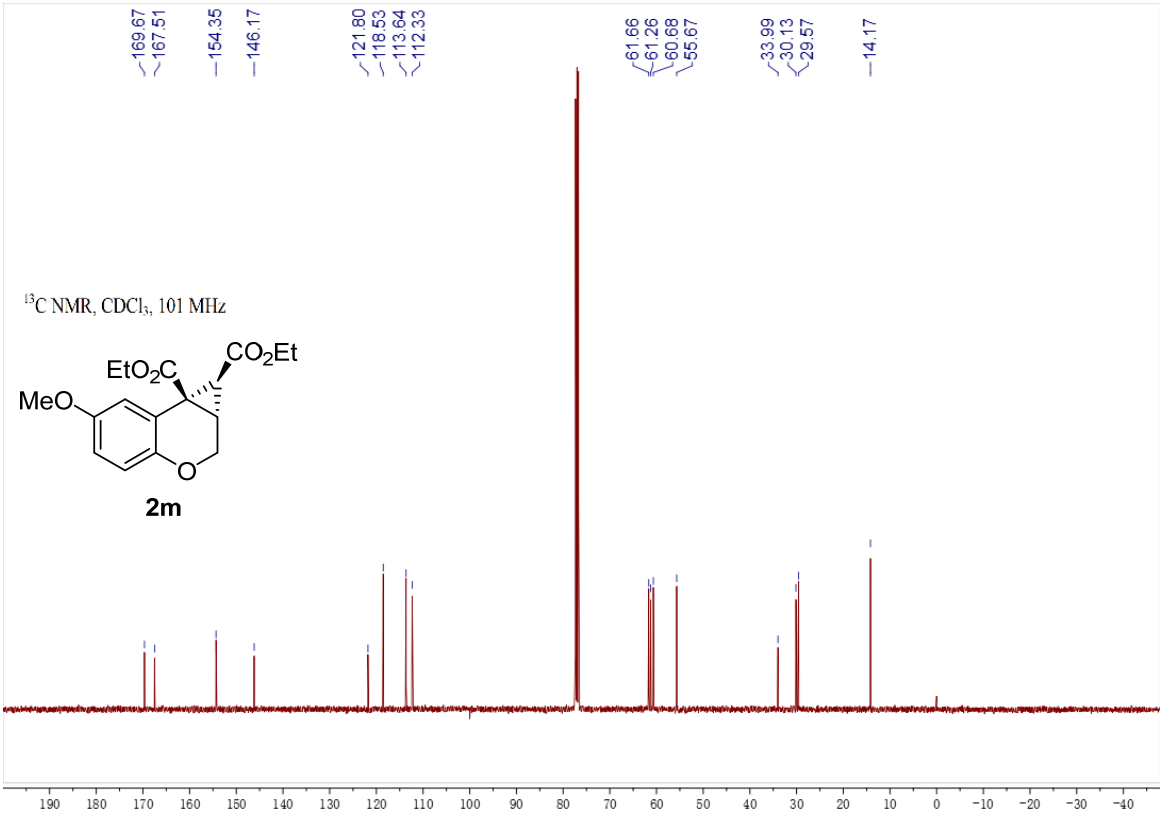
-0.5
-1.0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167.51
154.35
146.17
121.80
118.53
113.64
112.33
61.66
61.26
60.68
55.67
33.99
30.13
29.57
14.17
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Et
MeO
O
2m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
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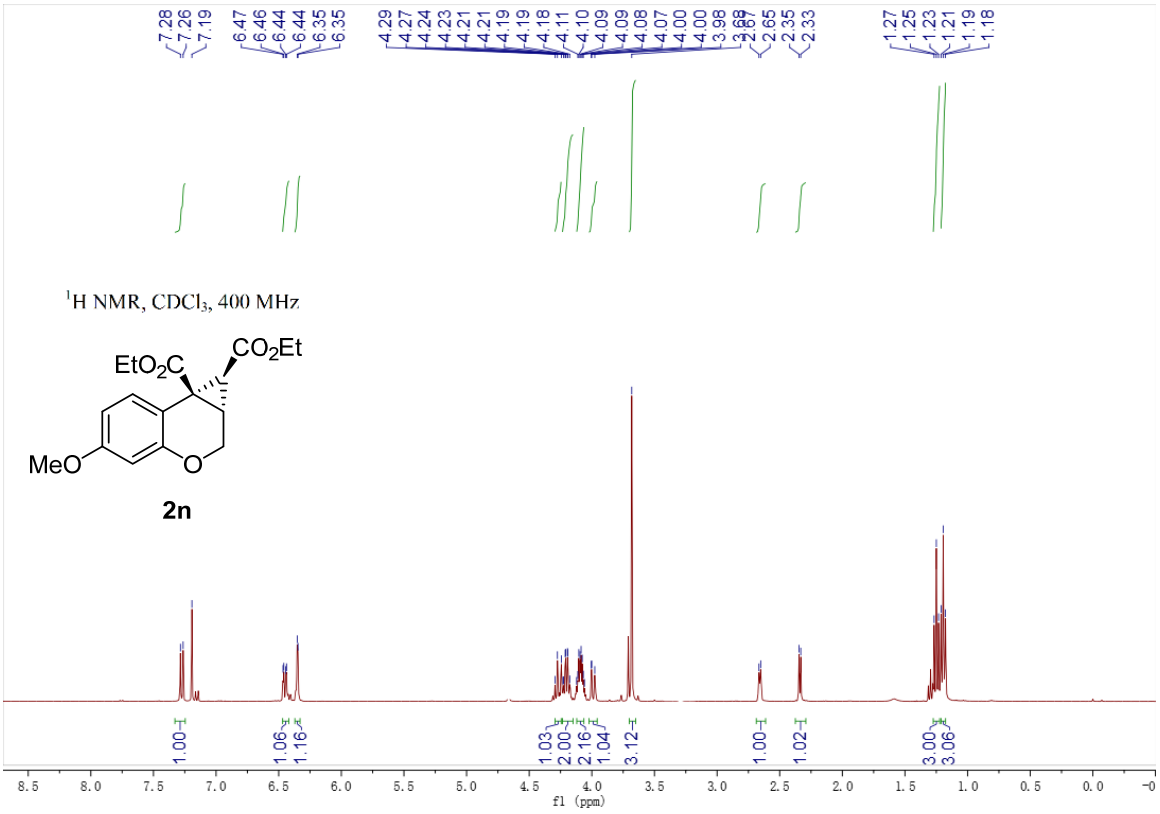
20
10
0
-10
-20
-30
-40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6.44
6.35
6.35
4.29
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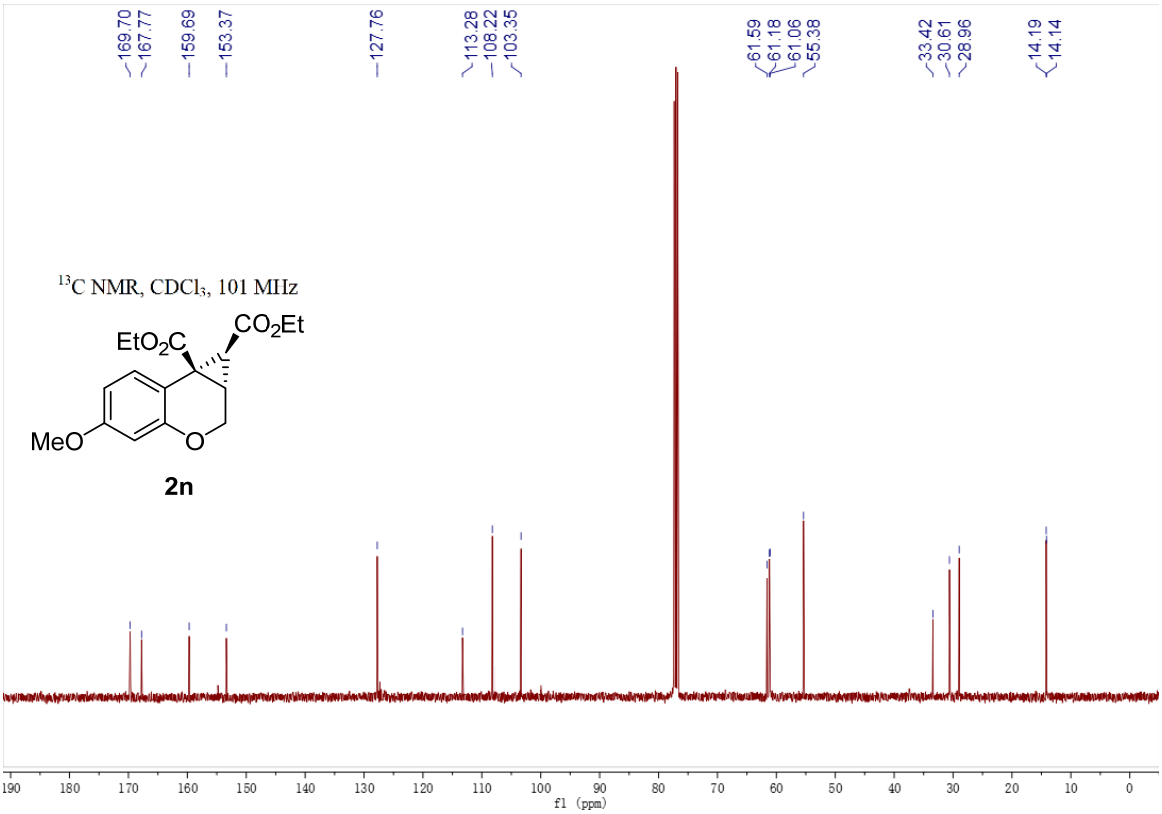
4.24
4.23
4.21
4.21
4.19
4.19
4.18
4.11
4.10
4.09
4.09
4.08
4.07
4.00
4.00
3.98
2.65
2.35
2.33
1.27
1.25
1.23
1.21
1.19
1.18
1H NMR, CDCl3, 400 MHz
EtO2C
CO2Et
MeO
O
2n
1.00
1.06
1.16
1.03
2.00
2.16
1.04
3.12
1.00
1.02
3.00
3.06
f1 (ppm)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159.69
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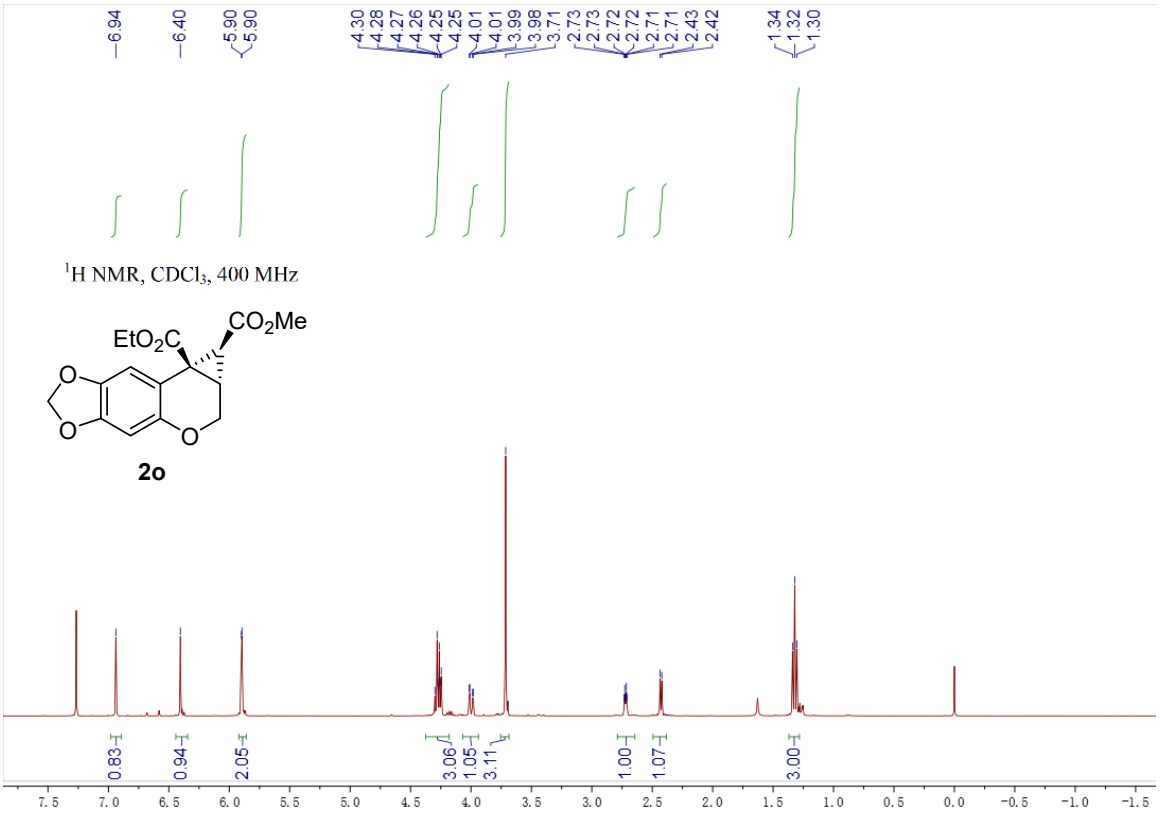
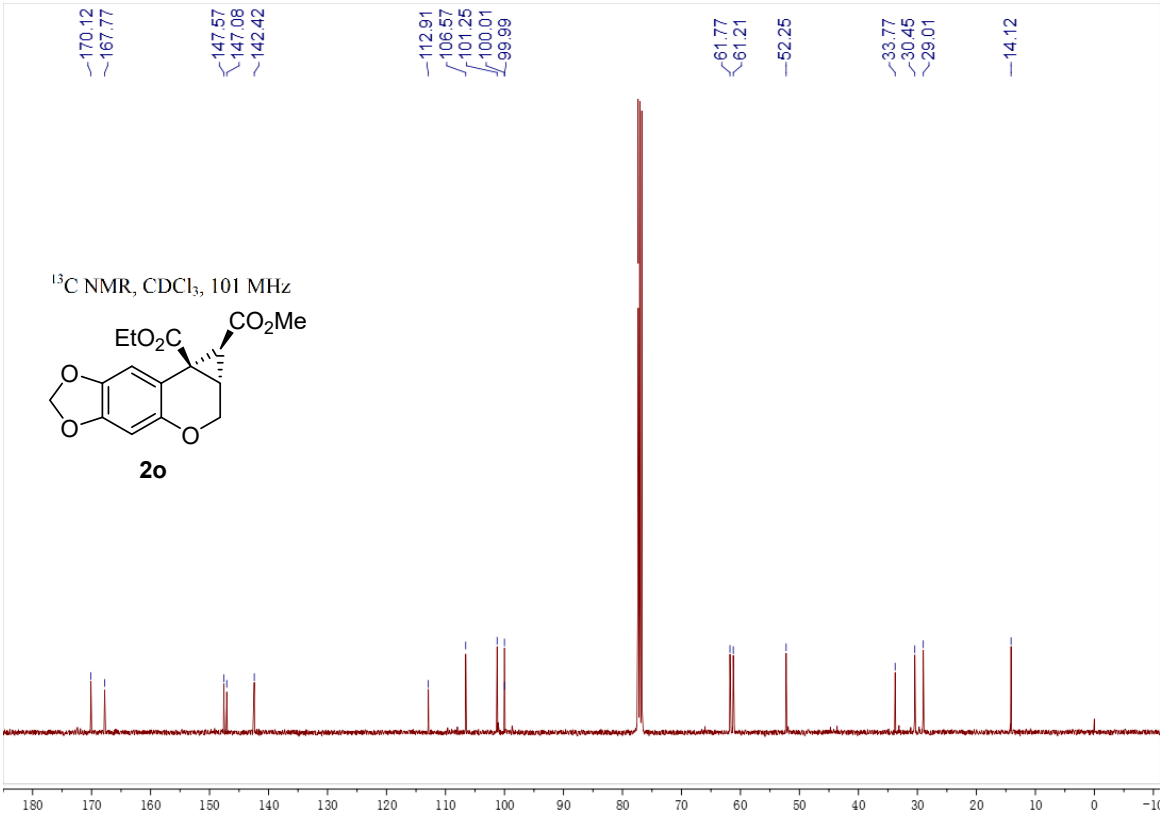
127.76
113.28
108.22
103.35
61.59
61.18
61.06
55.38
33.42
30.61
28.96
14.19
14.14
13C NMR, CDCl3, 101 MHz
EtO2C
CO2Et
MeO
O
2n
f1 (ppm)



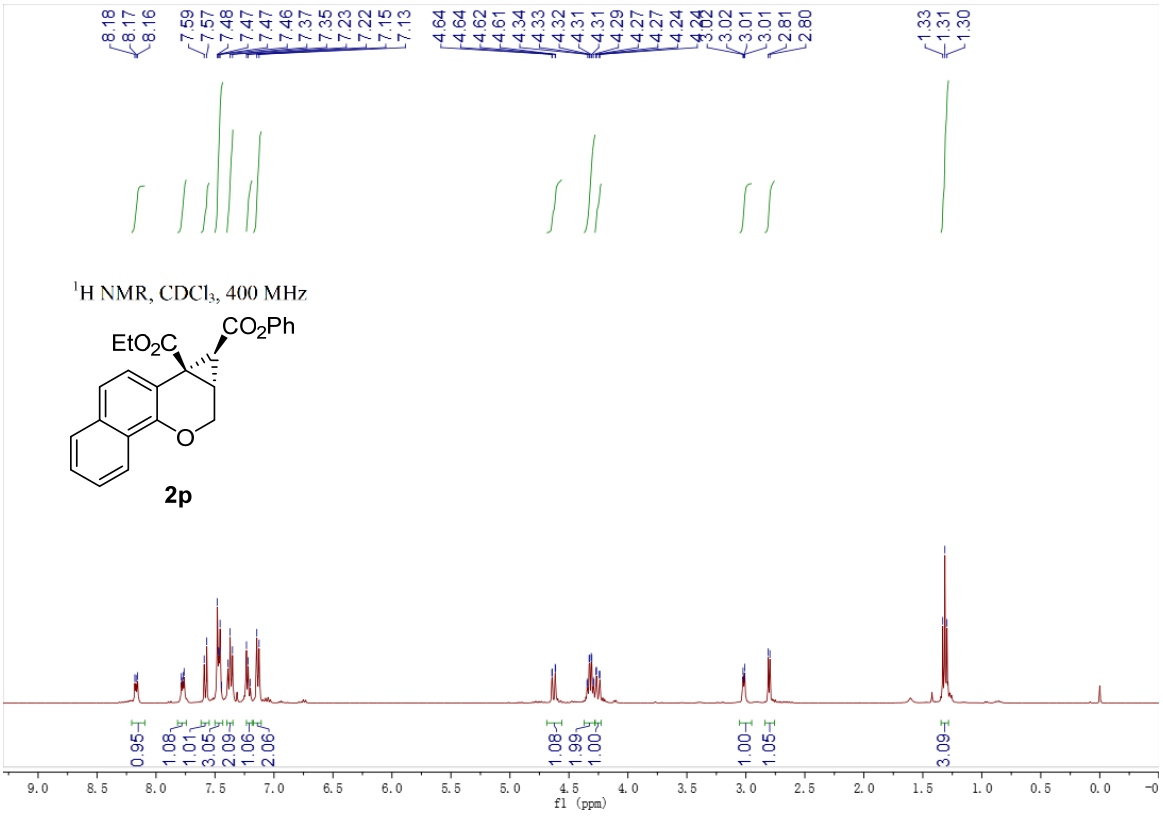
^{1}H NMR, $CDCl_3$, 400 MHz

2o



^{13}C NMR, $CDCl_3$, 101 MHz

2o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7.47
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7.35
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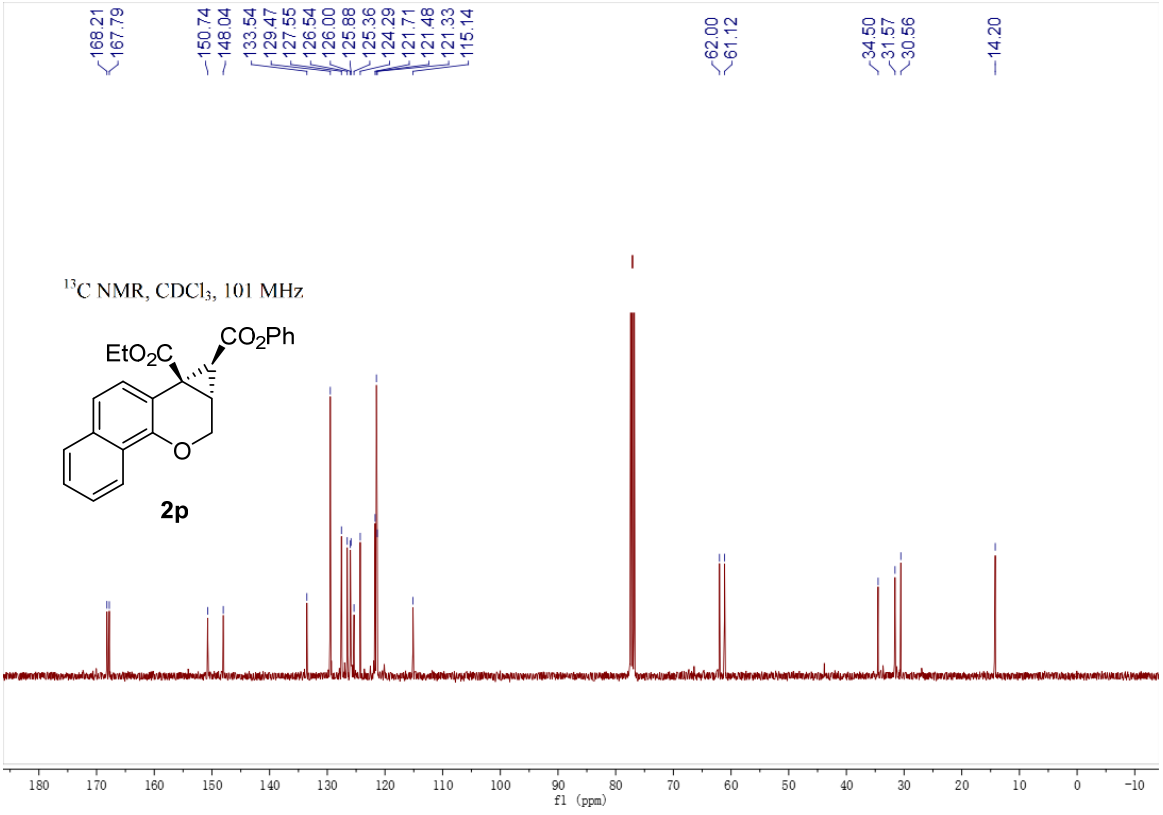
7.22
7.15
7.13
4.64
4.64
4.62
4.61
4.34
4.33
4.32
4.31
4.31
4.29
4.27
4.27
4.24
4.24
3.02
3.01
3.01
2.81
2.80
1.33
1.31
1.30
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Ph
O
2p
0.95
1.08
1.01
3.05
2.09
1.06
2.06
1.08
1.99
1.00
1.00
1.05
3.09
f1 (ppm)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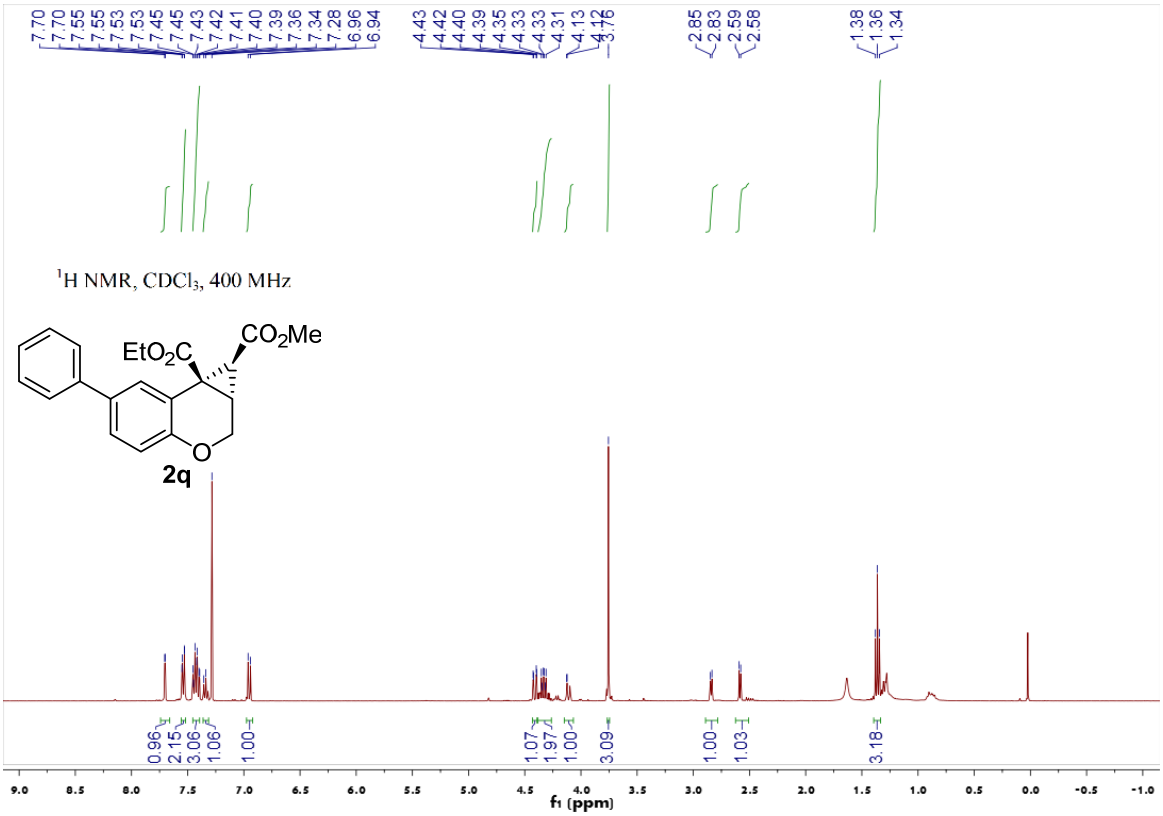
129.47
127.55
126.54
126.00
125.88
125.36
124.29
121.71
121.48
121.33
115.14
62.00
61.12
34.50
31.57
30.56
14.20
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Ph
O
2p
f1 (ppm)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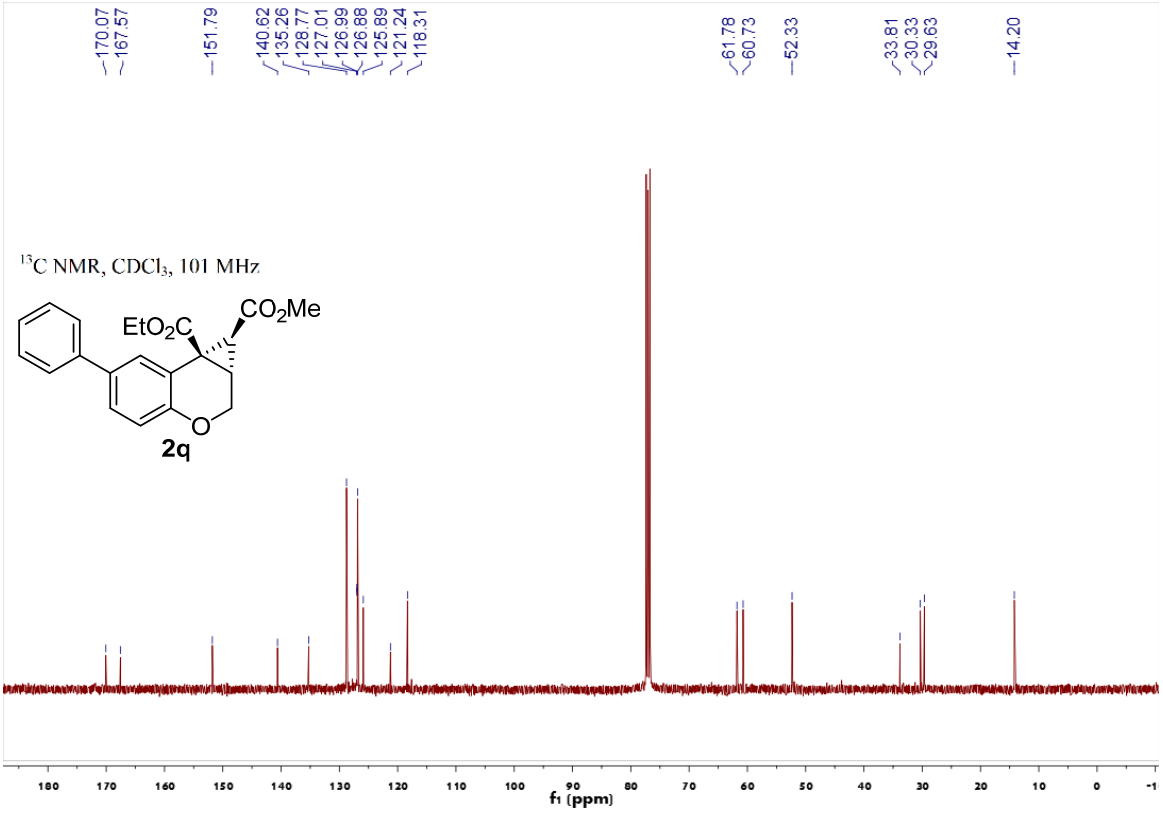
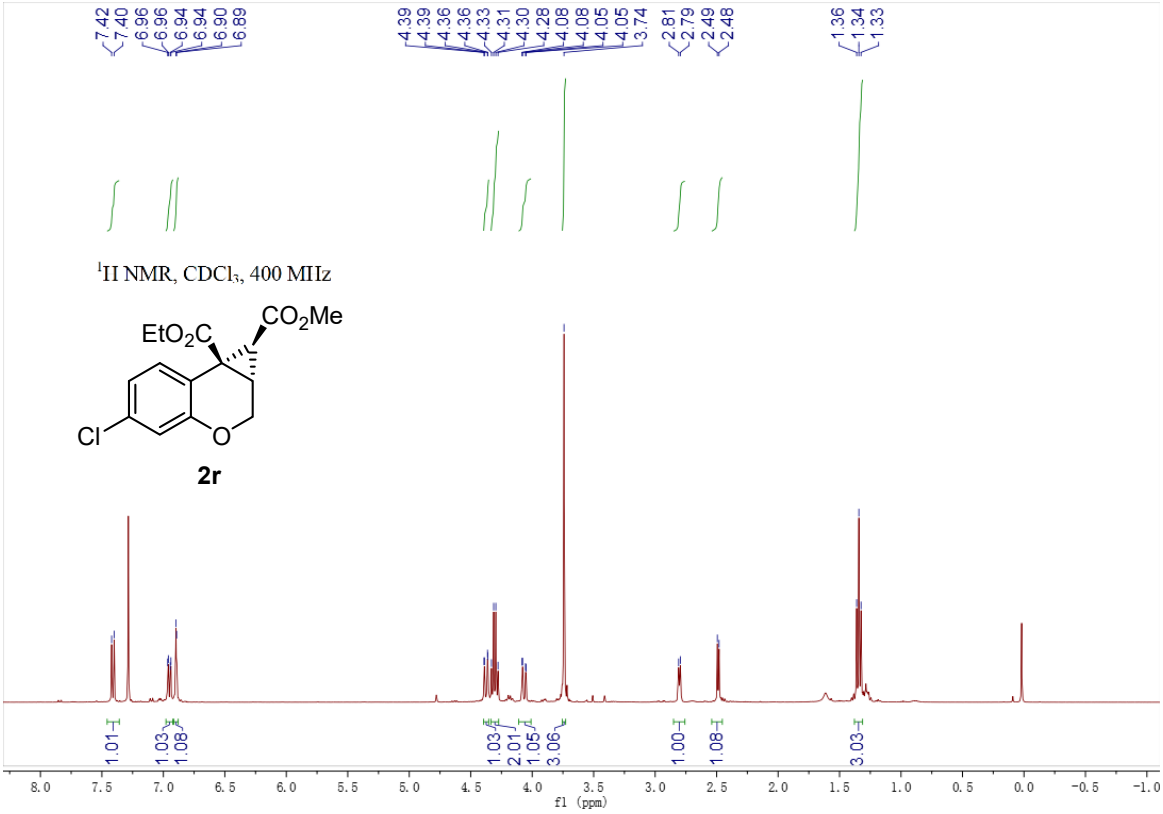
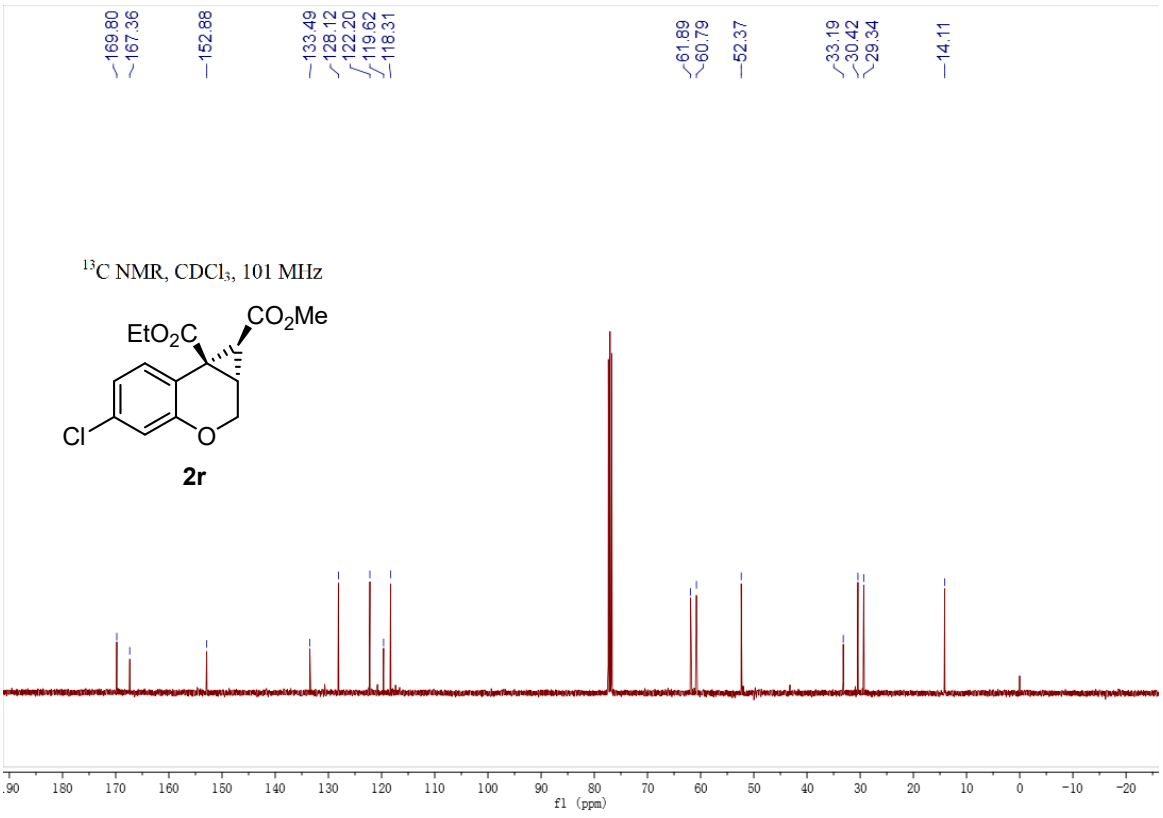
7.70
7.55
7.55
7.53
7.53
7.45
7.45
7.43
7.42
7.41
7.40
7.39
7.36
7.34
7.28
6.96
6.94
4.43
4.42
4.40
4.39
4.35
4.33
4.33
4.31
4.13
4.12
3.76
2.85
2.83
2.59
2.58
1.38
1.36
1.34
^{1}H NMR, $CDCl_3$, 400 MHz
EtO_2C
CO_2Me
O
2q
0.96
2.15
3.06
1.06
1.00
1.07
1.97
1.00
3.09
1.00
1.03
3.18
f1 (ppm)


170.07
167.57
151.79
140.62
135.26
128.77
127.01
126.99
126.88
125.89
121.24
118.31
61.78
60.73
52.33
33.81
30.33
29.63
14.20
^{13}C NMR, $CDCl_3$, 101 MHz
EtO_2C
CO_2Me
O
2q
f1 (ppm)



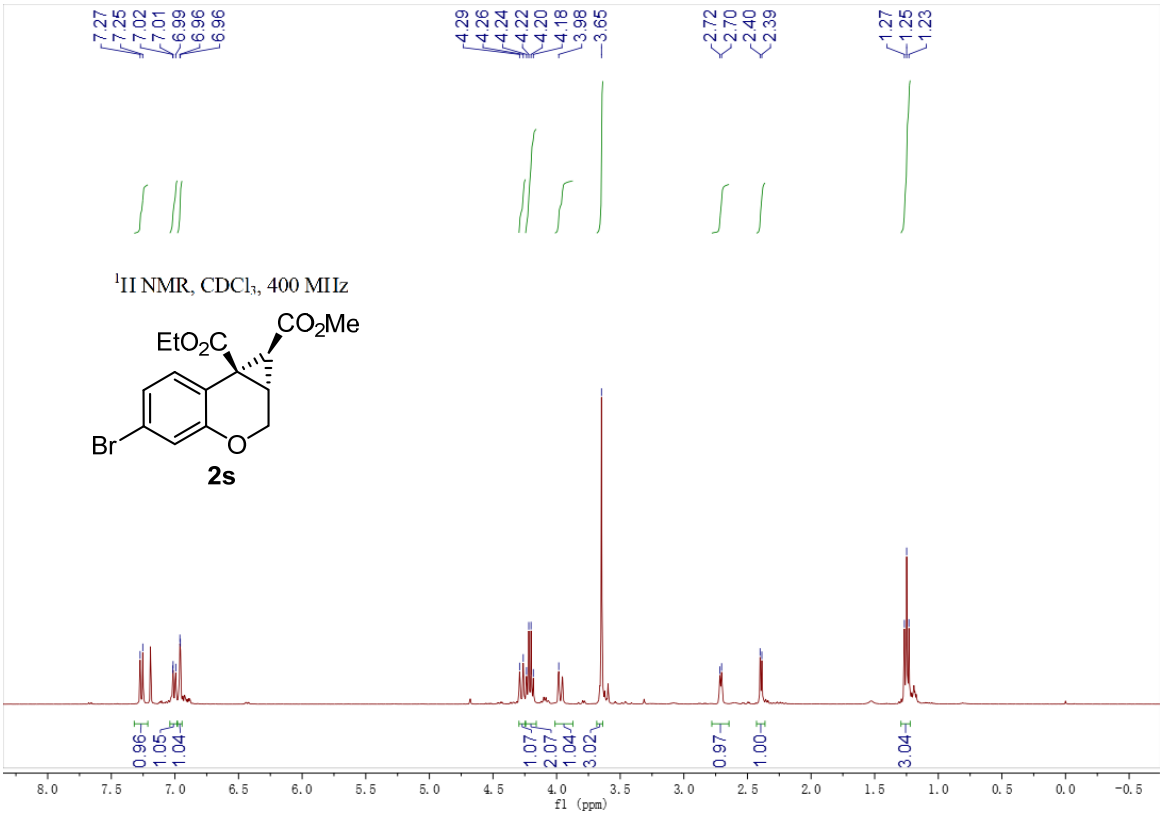
^{1}II NMR, $CDCl_3$, 400 MIz

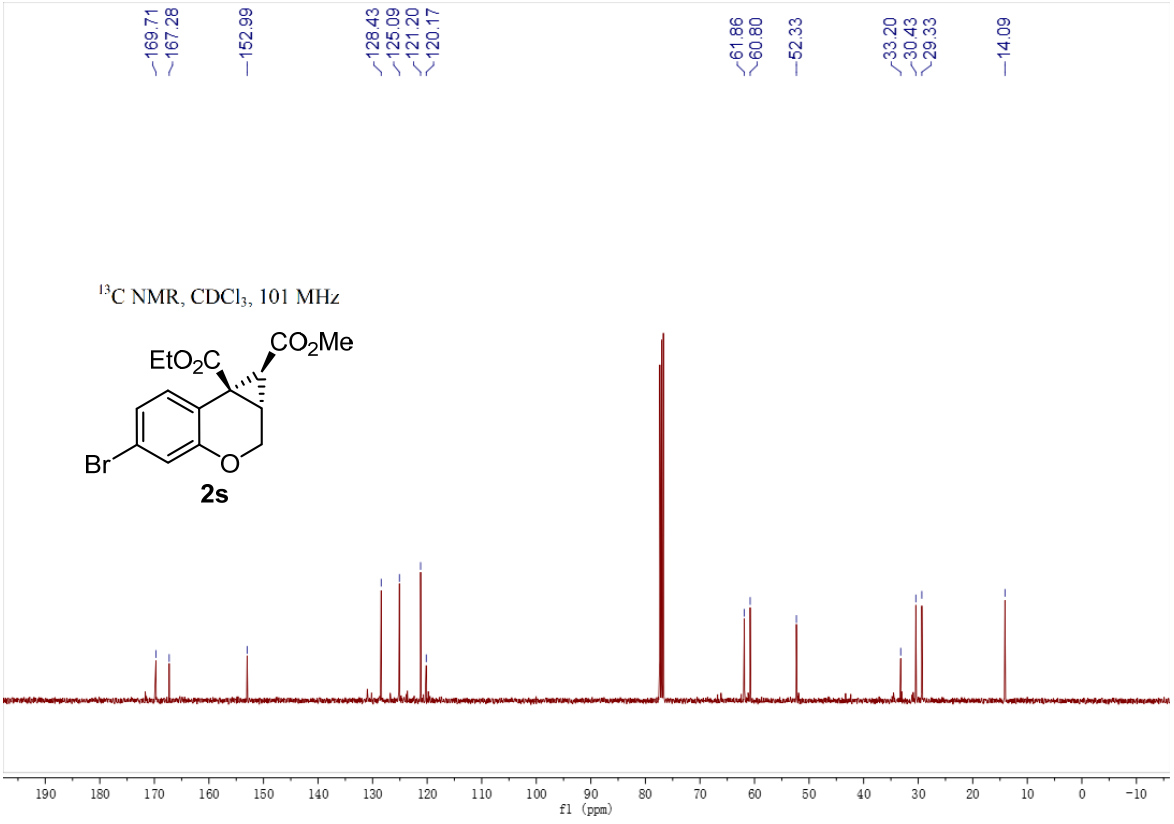
2r



^{13}C NMR, $CDCl_3$, 101 MHz

2r


7.27
7.25
7.02
7.01
6.99
6.96
6.96
4.29
4.26
4.24
4.22
4.20
4.18
3.98
3.65
2.72
2.70
2.40
2.39
1.27
1.25
1.23
^{1}H NMR, $CDCl_3$, 400 MHz
EtO_2C
CO_2Me
Br
O
2s
0.96
1.05
1.04
1.07
2.07
1.04
3.02
0.97
1.00
3.04
f1 (ppm)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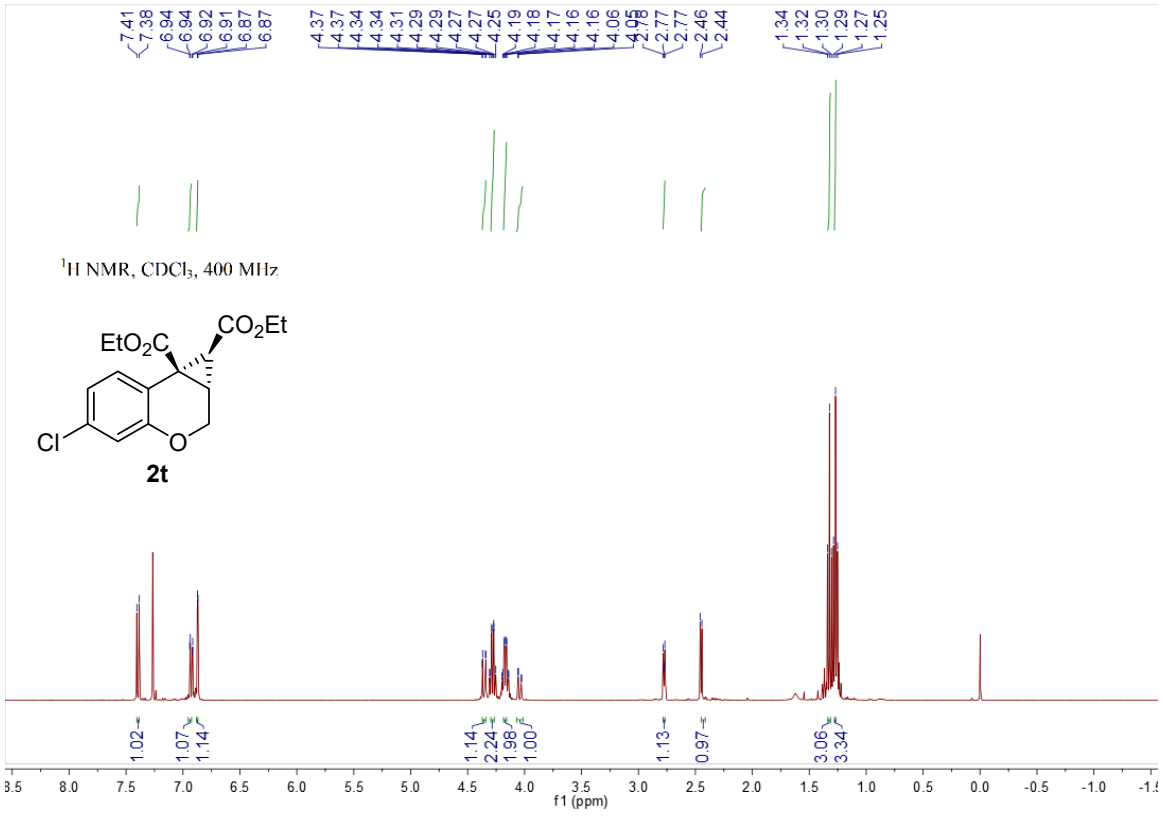
167.28
152.99
128.43
125.09
121.20
120.17
61.86
60.80
52.33
33.20
30.43
29.33
14.09
^{13}C NMR, $CDCl_3$, 101 MHz
EtO_2C
CO_2Me
Br
O
2s
f1 (ppm)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6.87
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4.37
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4.34
4.31
4.29
4.29
4.27
4.27
4.25
4.19
4.18
4.17
4.16
4.16
4.06
4.05
2.78
2.77
2.77
2.46
2.44
1.34
1.32
1.30
1.29
1.27
1.25
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Et
Cl
O
2t
1.02
1.07
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1.14
2.24
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0.97
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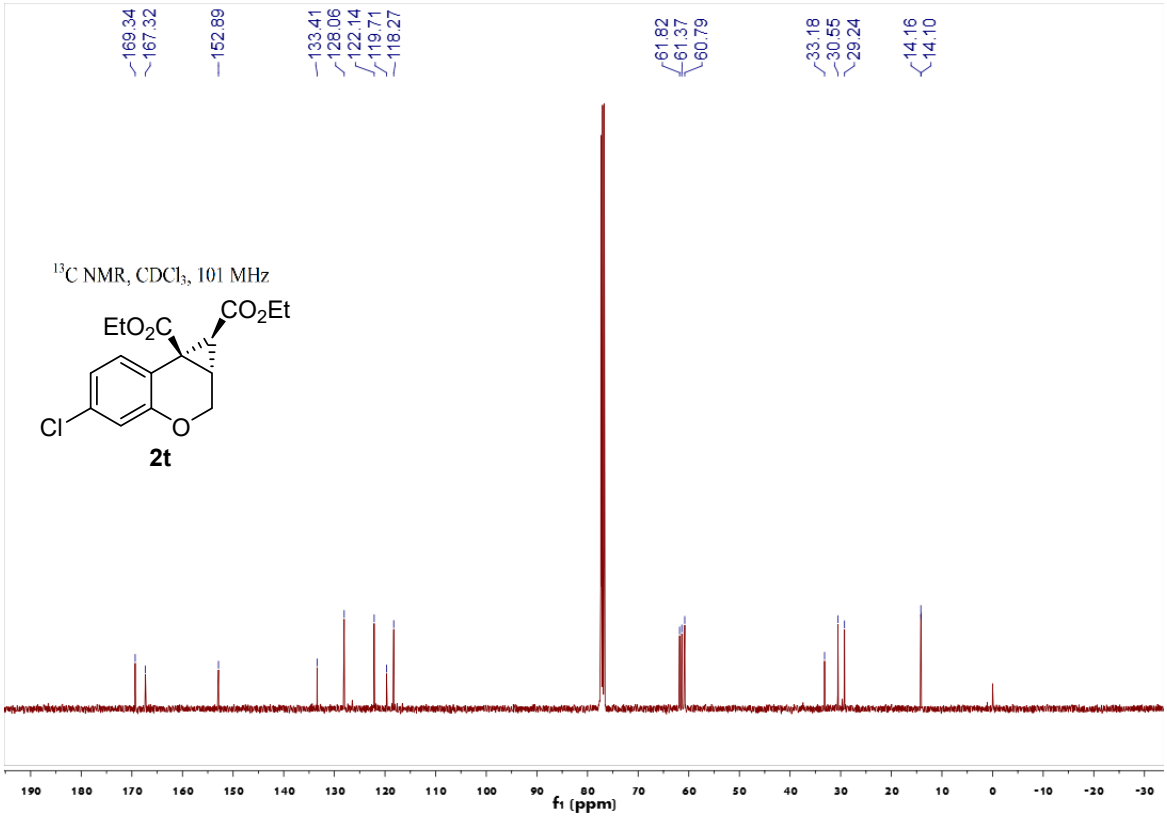
3.34
f1 (ppm)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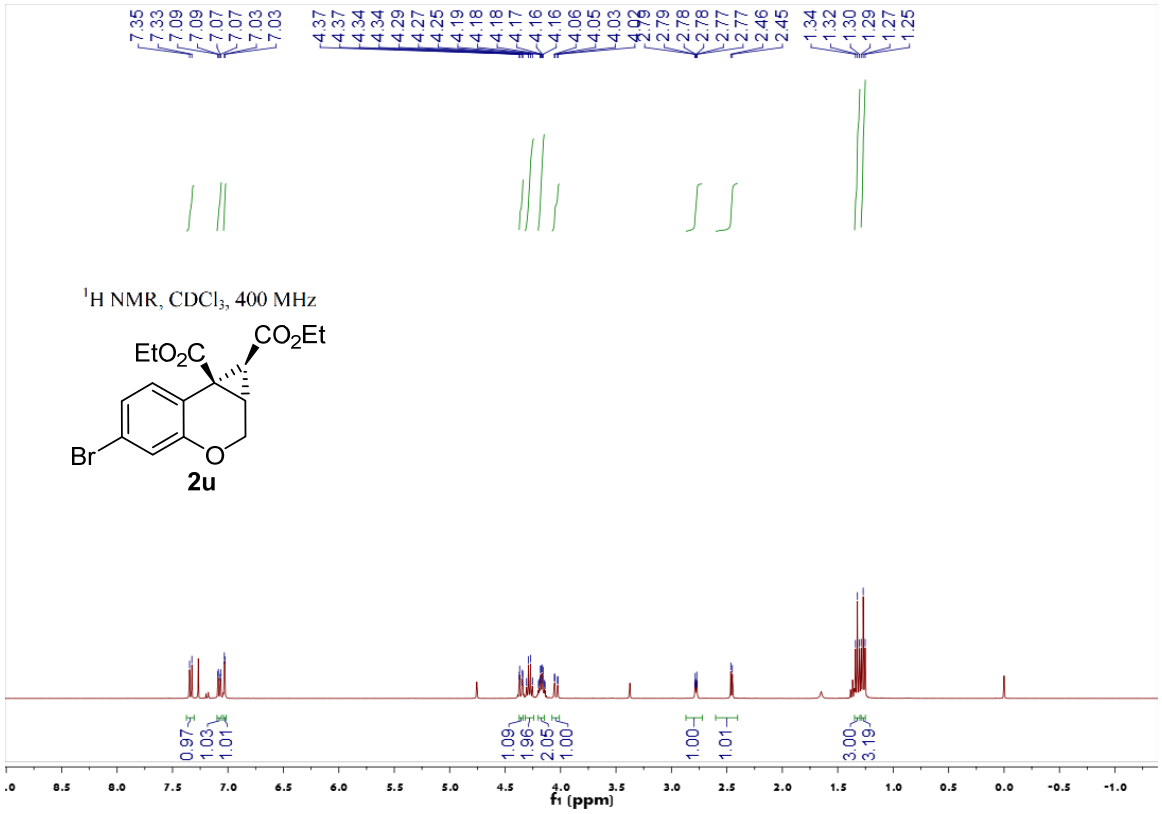
122.14
119.71
118.27
61.82
61.37
60.79
33.18
30.55
29.24
14.16
14.10
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Et
Cl
O
2t
f1 (ppm)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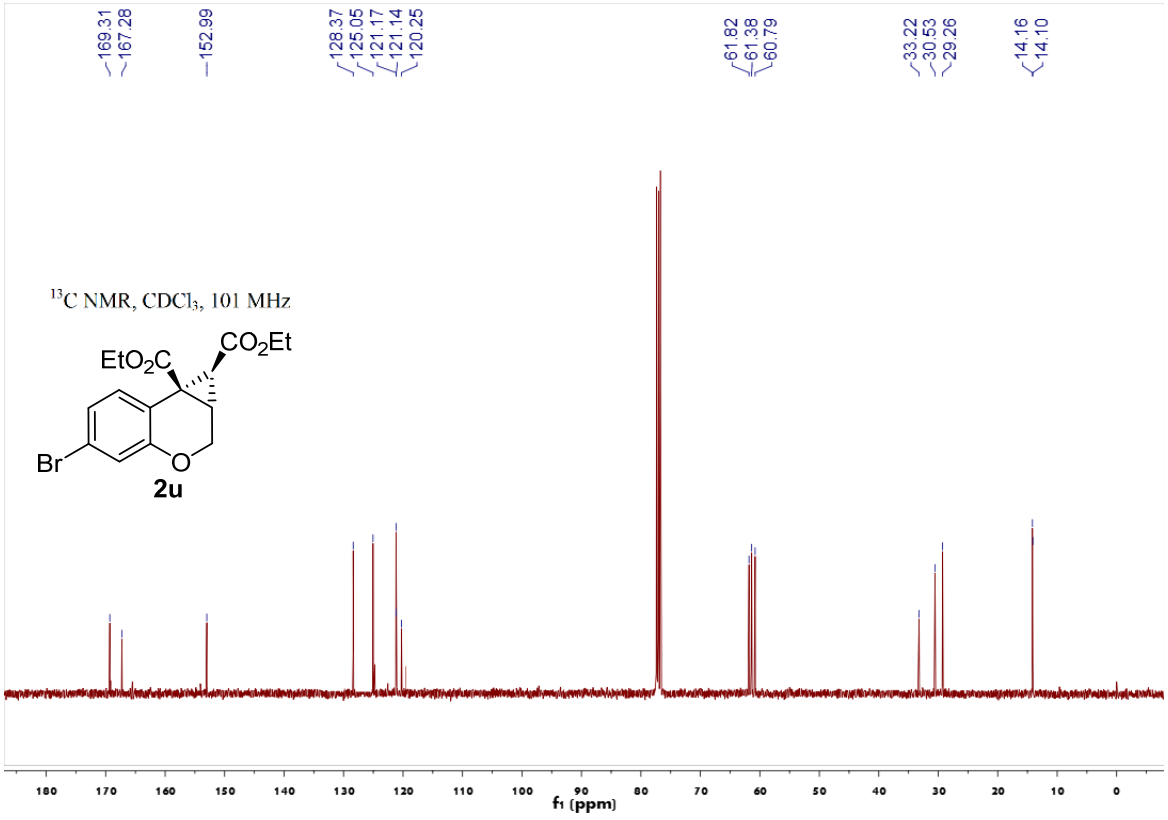
4.19
4.18
4.18
4.17
4.16
4.16
4.06
4.05
4.03
2.79
2.78
2.78
2.77
2.77
2.46
2.45
1.34
1.32
1.30
1.29
1.27
1.25
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Et
Br
O
2u
0.97
1.03
1.01
1.09
1.96
2.05
1.00
1.00
1.01
3.00
3.19
f$_1$ (ppm)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121.17
121.14
120.25
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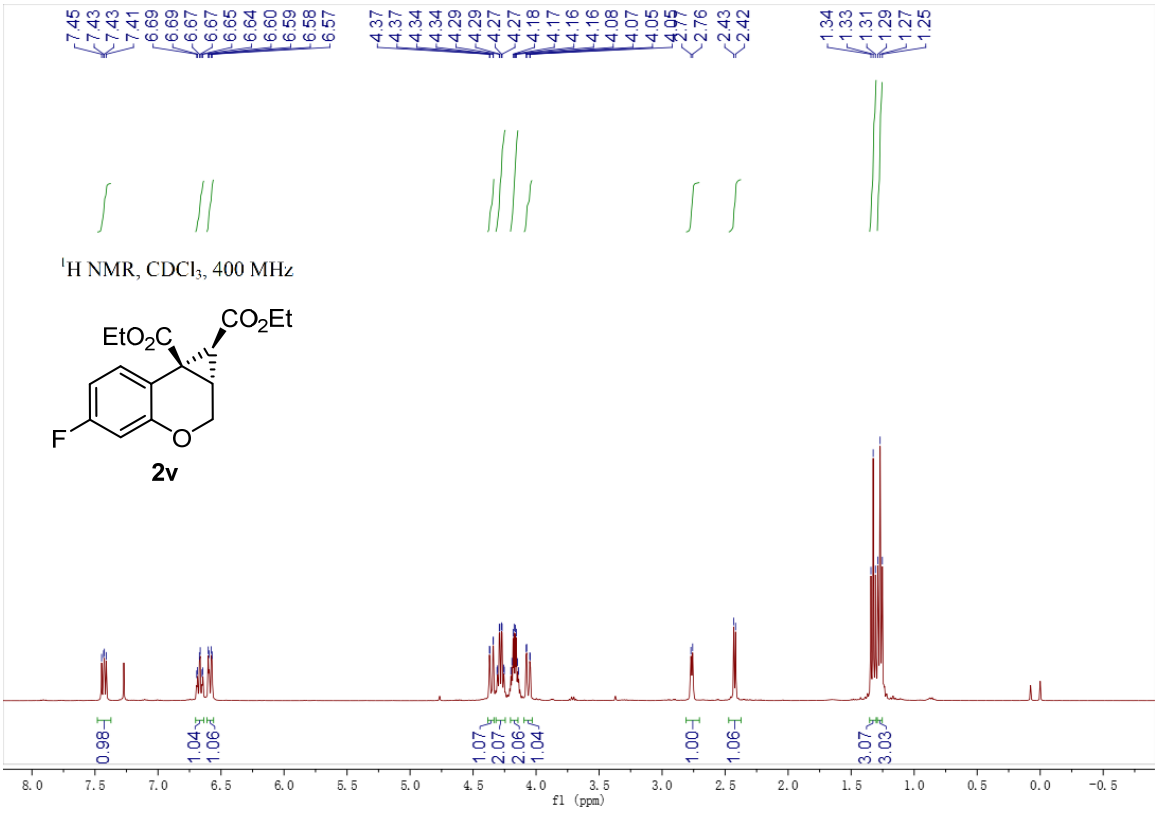
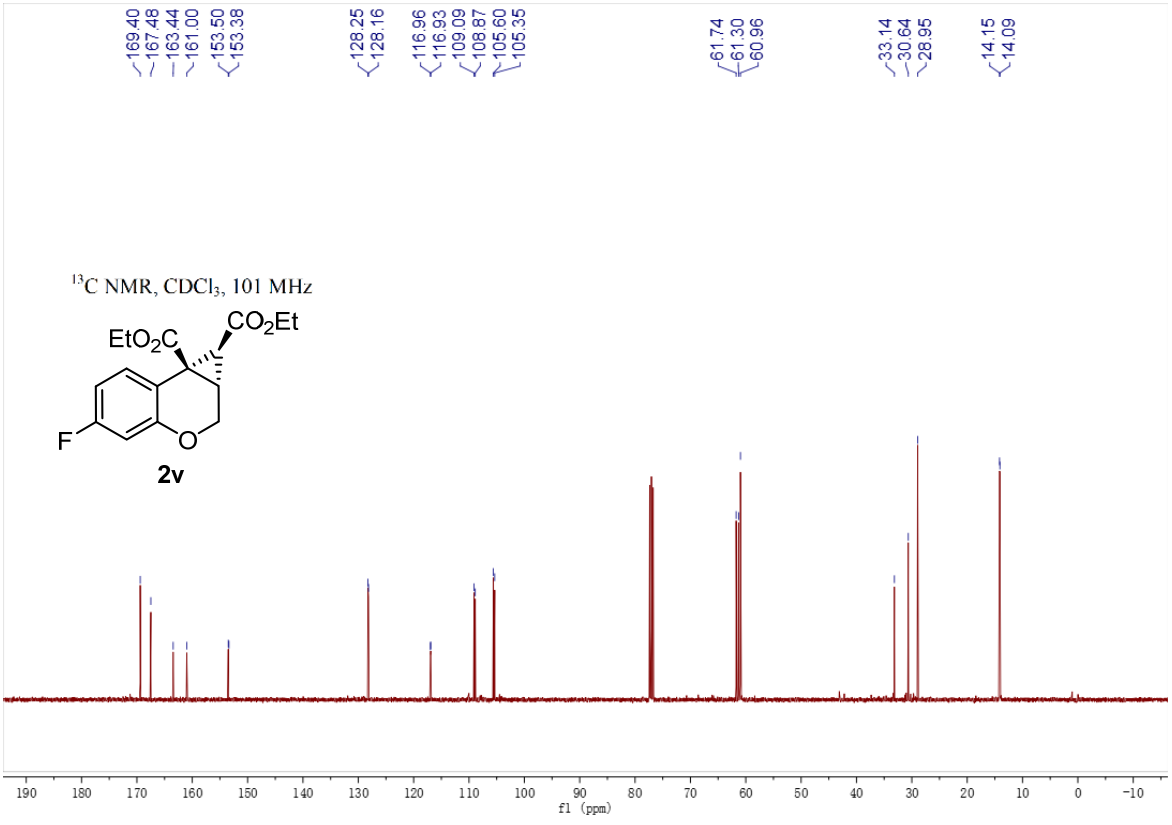
61.38
60.79
33.22
30.53
29.26
14.16
14.10
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Et
Br
O
2u
f$_1$ (ppm)



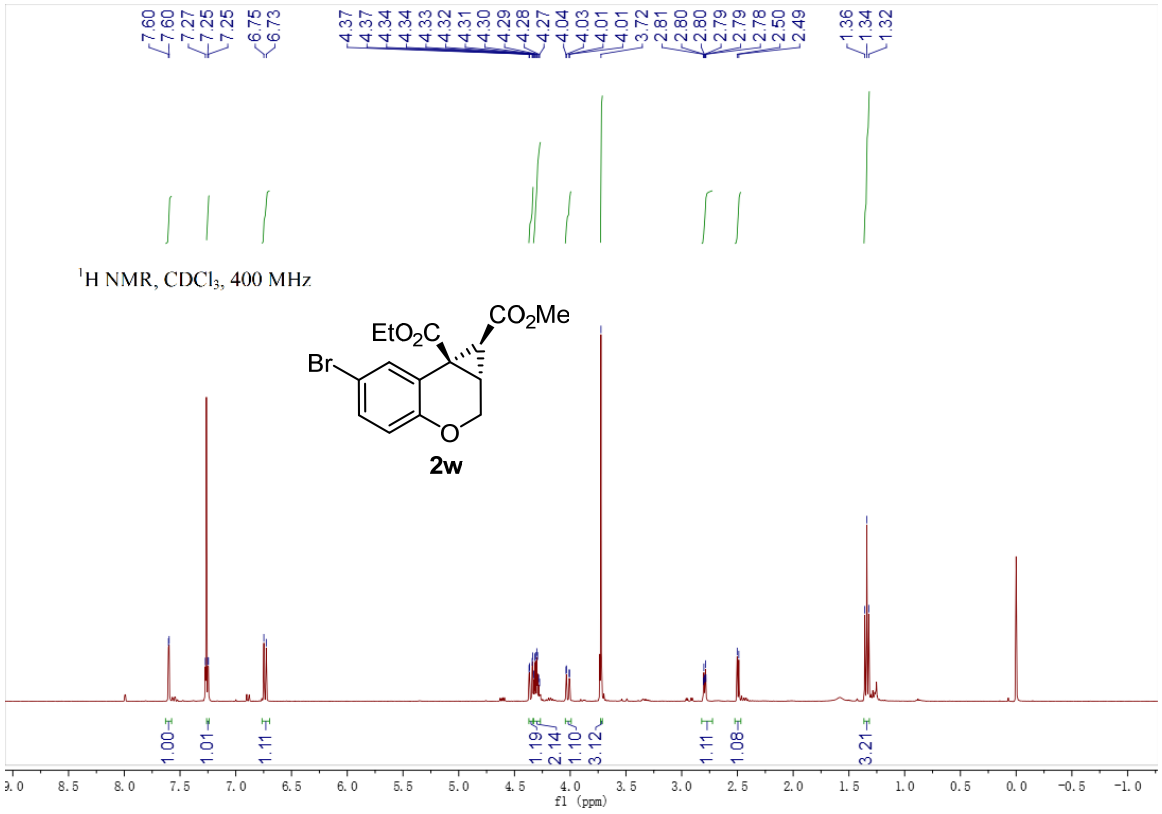
^{1}H NMR, $CDCl_3$, 400 MHz

2v



^{13}C NMR, $CDCl_3$, 101 MHz

2v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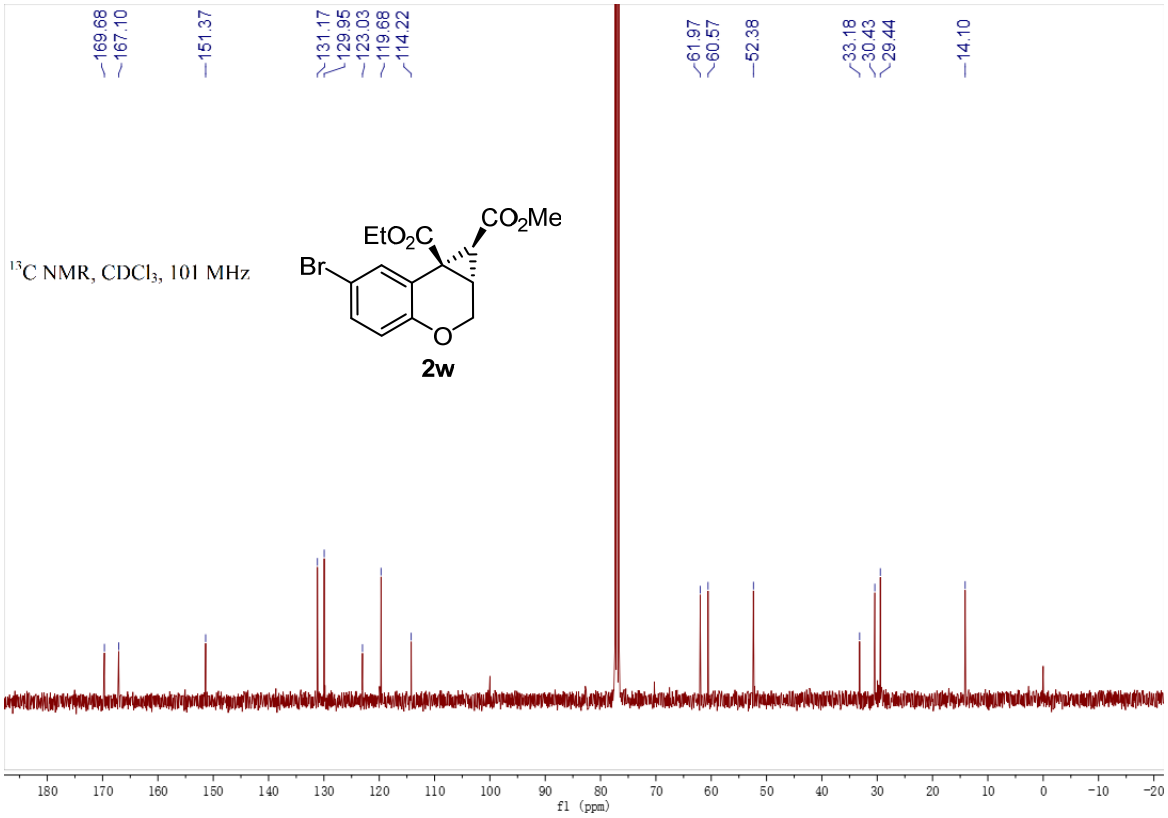
4.32
4.31
4.30
4.29
4.28
4.27
4.04
4.03
4.01
4.01
3.72
2.81
2.80
2.80
2.79
2.79
2.78
2.50
2.49
1.36
1.34
1.32
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Me
Br
O
2w
1.00
1.01
1.11
1.19
2.14
1.10
3.12
1.11
1.08
3.21
f1 (ppm)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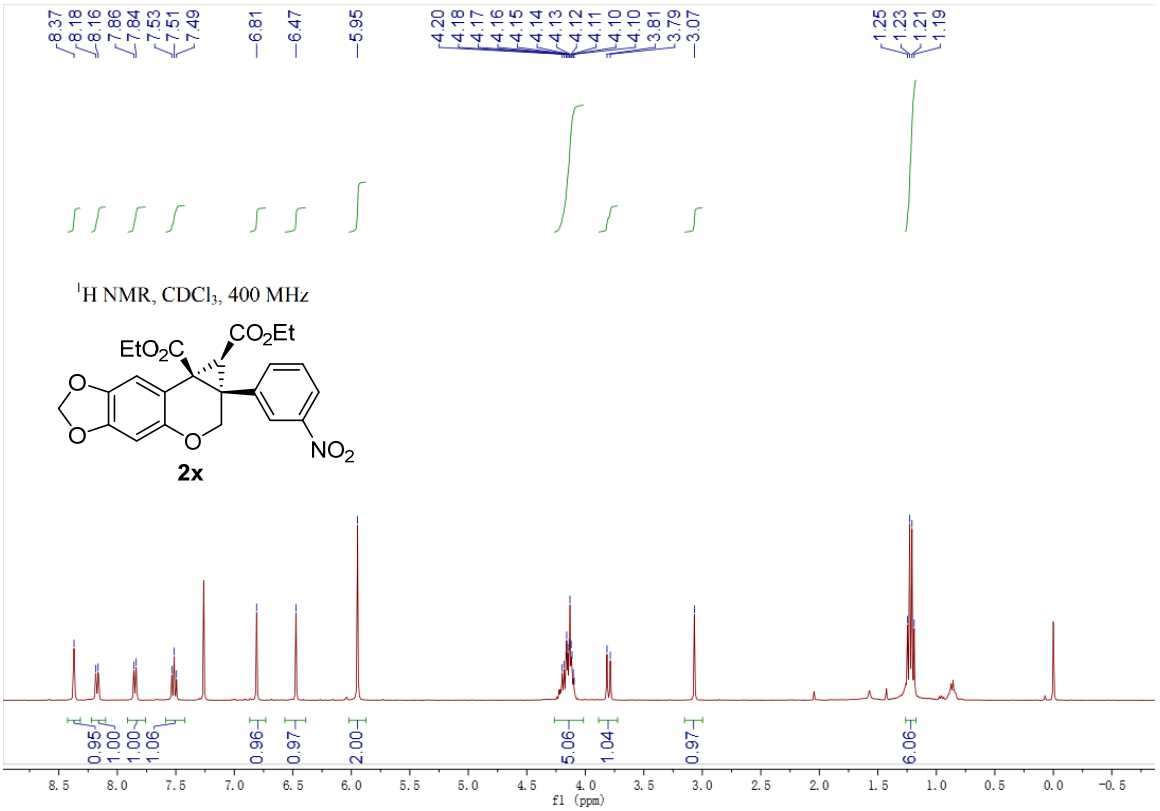
123.03
119.68
114.22
61.97
60.57
52.38
33.18
30.43
29.44
14.10
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Me
Br
O
2w
f1 (ppm)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7.51
7.49
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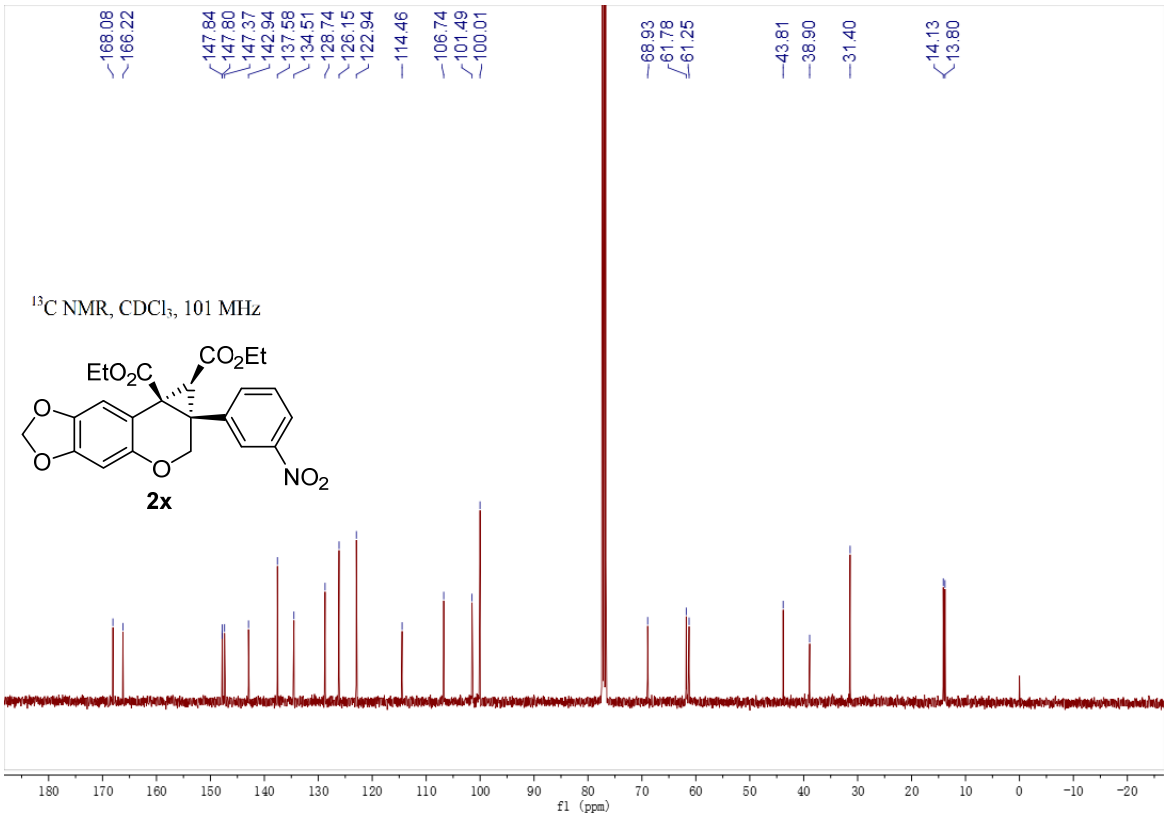
6.47
5.95
4.20
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.11
4.10
4.10
3.81
3.79
3.07
1.25
1.23
1.21
1.19
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Et
NO$_2$
2x
0.95
1.00
1.00
1.06
0.96
0.97
2.00
5.06
1.04
0.97
6.06
f1 (ppm)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147.37
142.94
137.58
134.51
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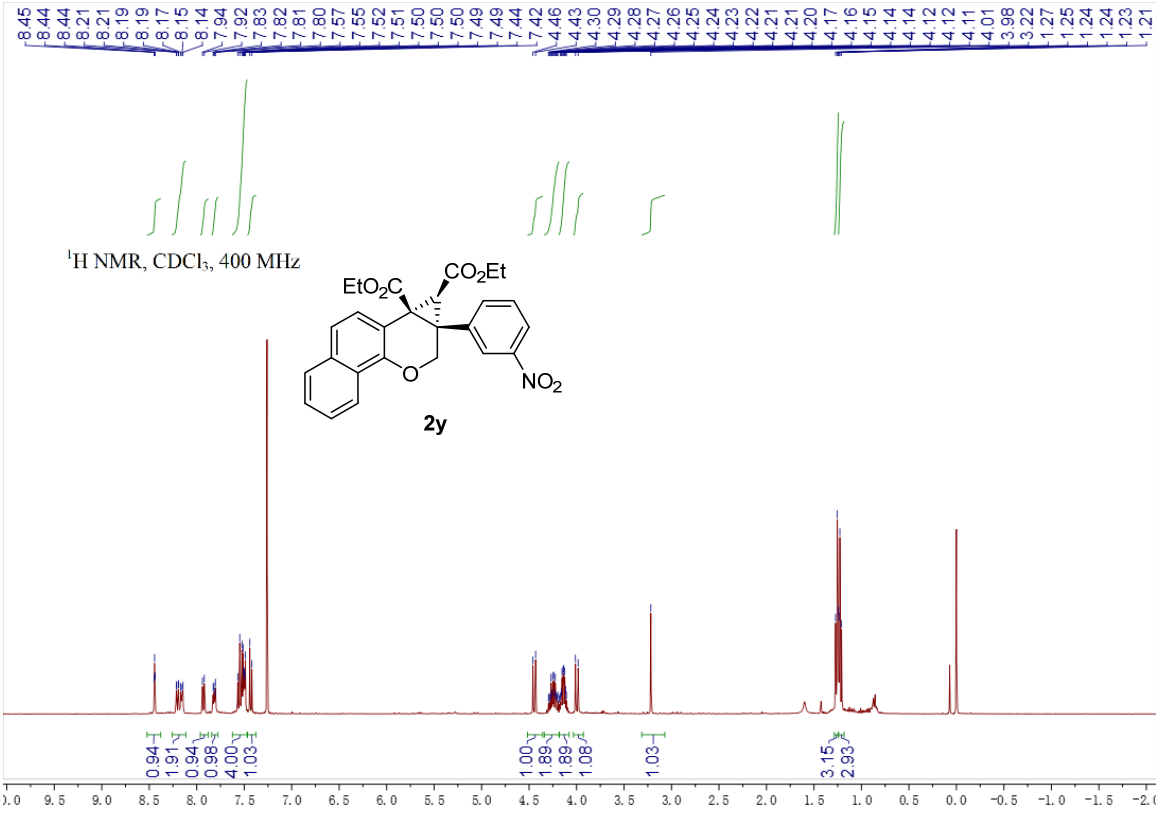
126.15
122.94
114.46
106.74
101.49
100.01
68.93
61.78
61.25
43.81
38.90
31.40
14.13
13.80
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Et
NO$_2$
2x
f1 (ppm)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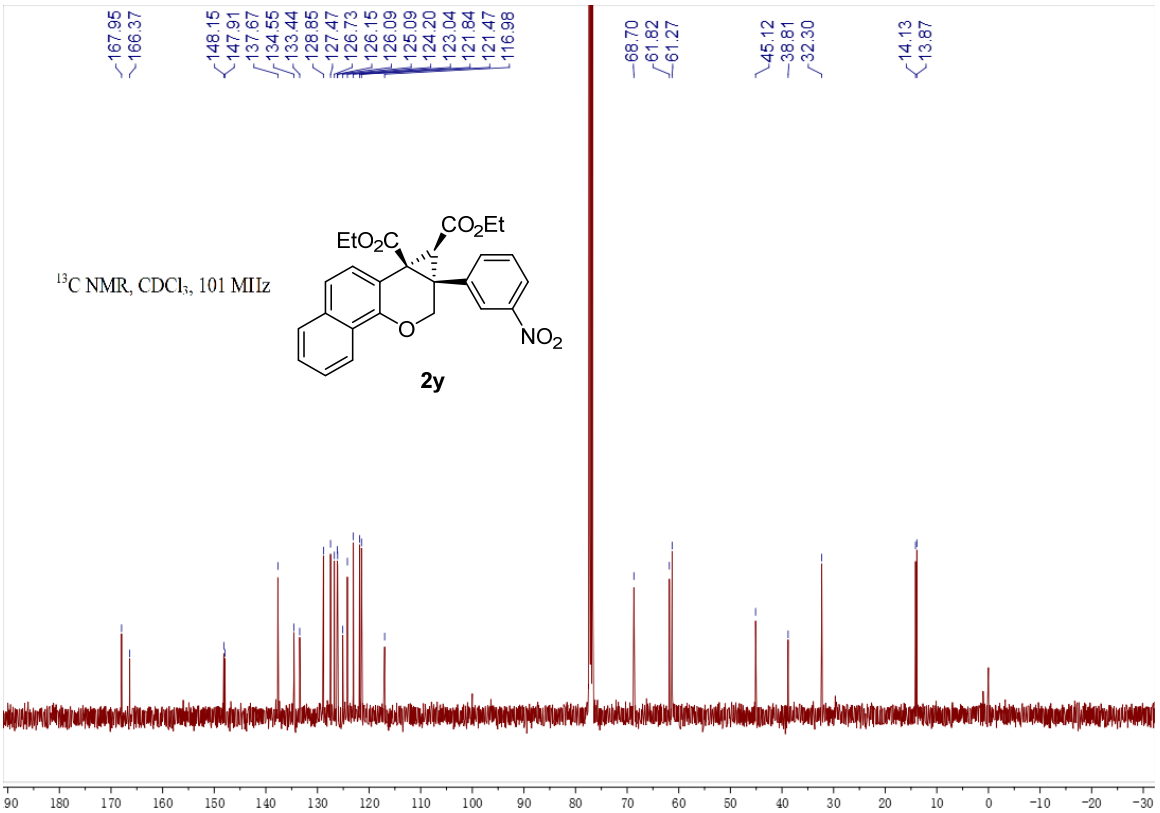
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Et
NO$_2$
O
2y
0.94 1.91 0.94 0.98 4.00 1.03 1.00 1.89 1.89 1.08 1.03 3.15 2.93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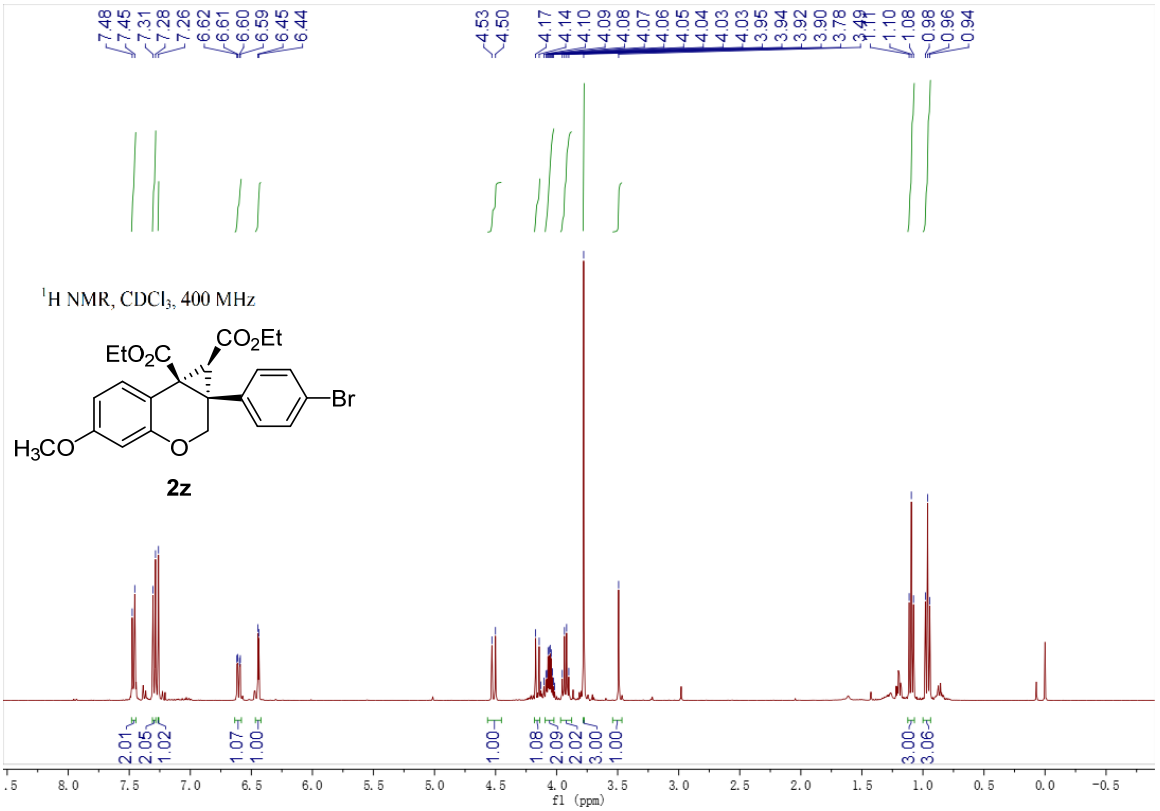
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Et
NO$_2$
O
2y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4.50
4.17
4.14
4.10
4.09
4.08
4.07
4.06
4.05
4.04
4.03
4.03
3.95
3.94
3.92
3.90
3.78
1.11
1.10
1.08
0.98
0.96
0.94
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Et
Br
H$_3$CO
O
2z
2.01
2.05
1.02
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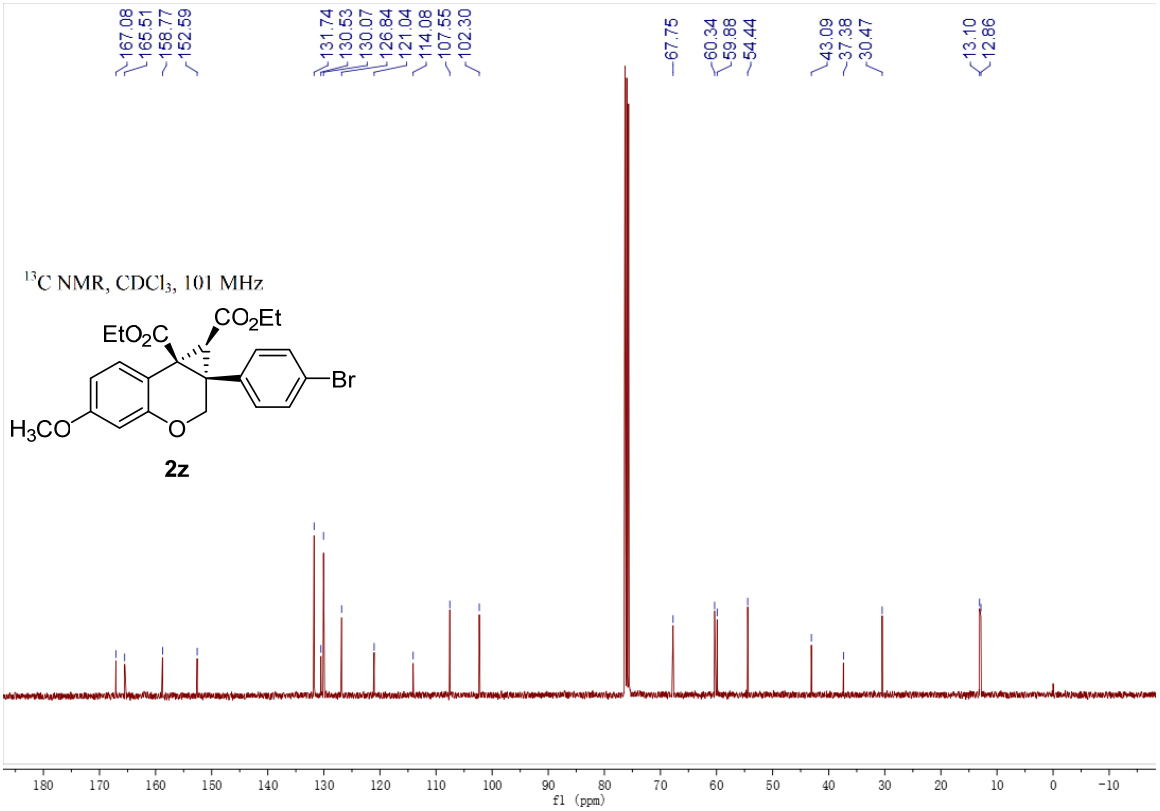
3.00
1.00
3.00
3.06
f1 (ppm)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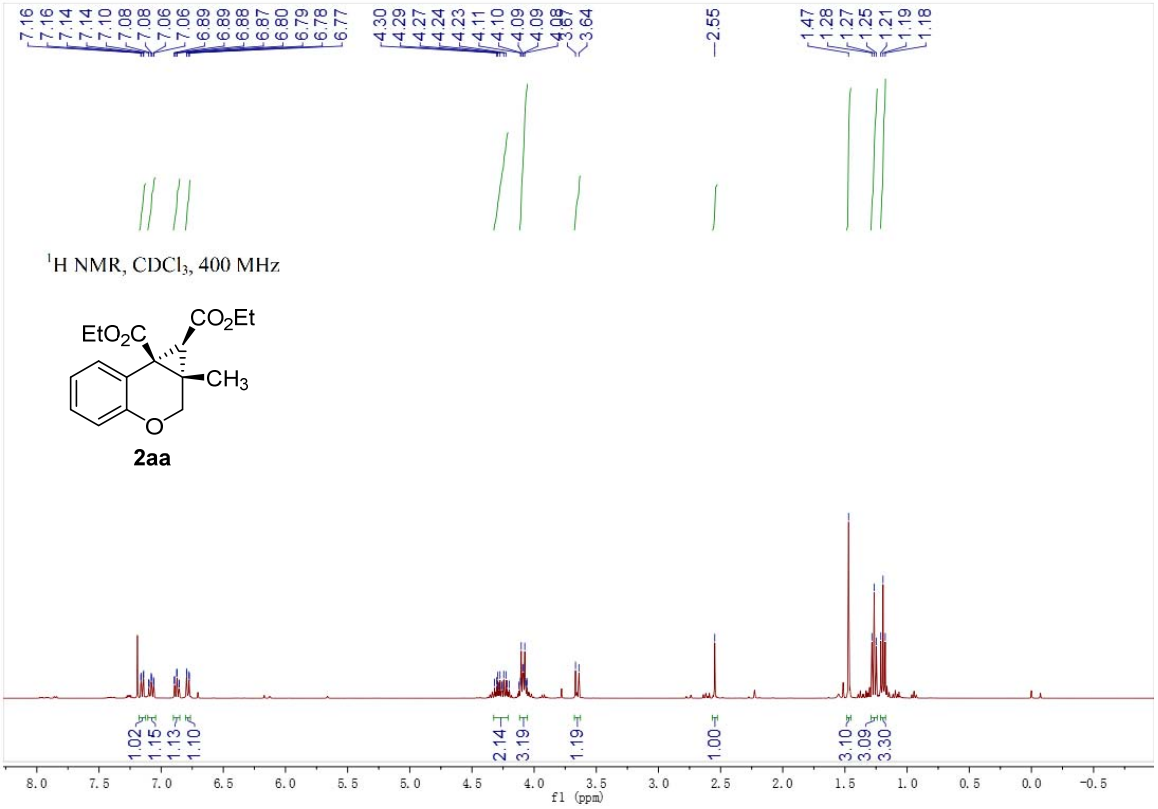
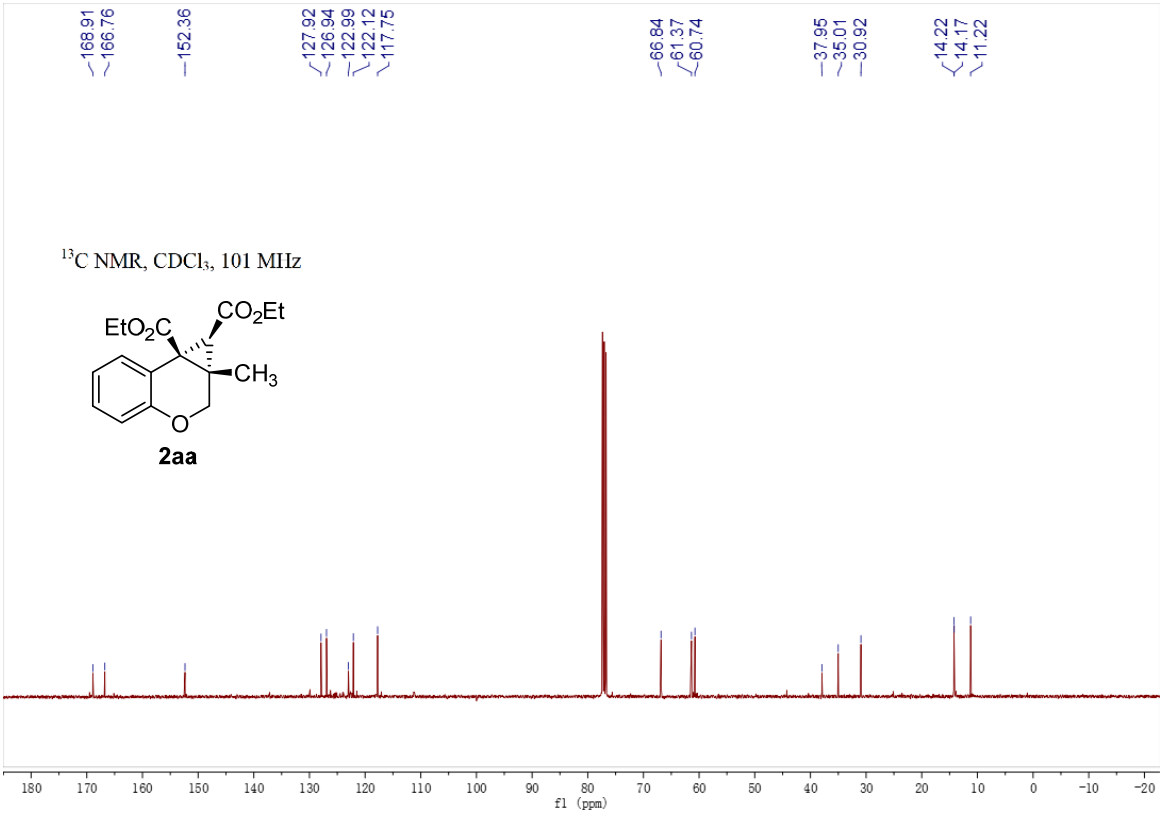
126.84
121.04
114.08
107.55
102.30
67.75
60.34
59.88
54.44
43.09
37.38
30.47
13.10
12.86
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Et
Br
H$_3$CO
O
2z
f1 (ppm)



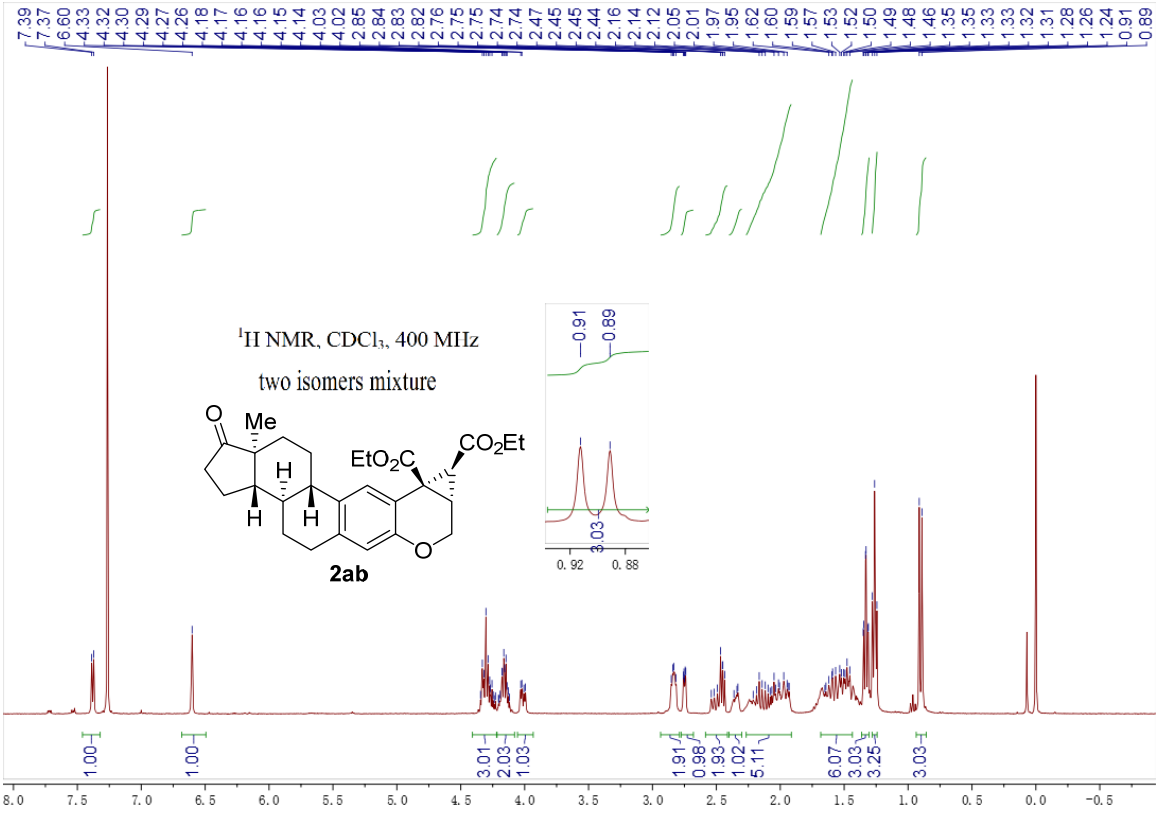
^{1}H NMR, $CDCl_3$, 400 MHz

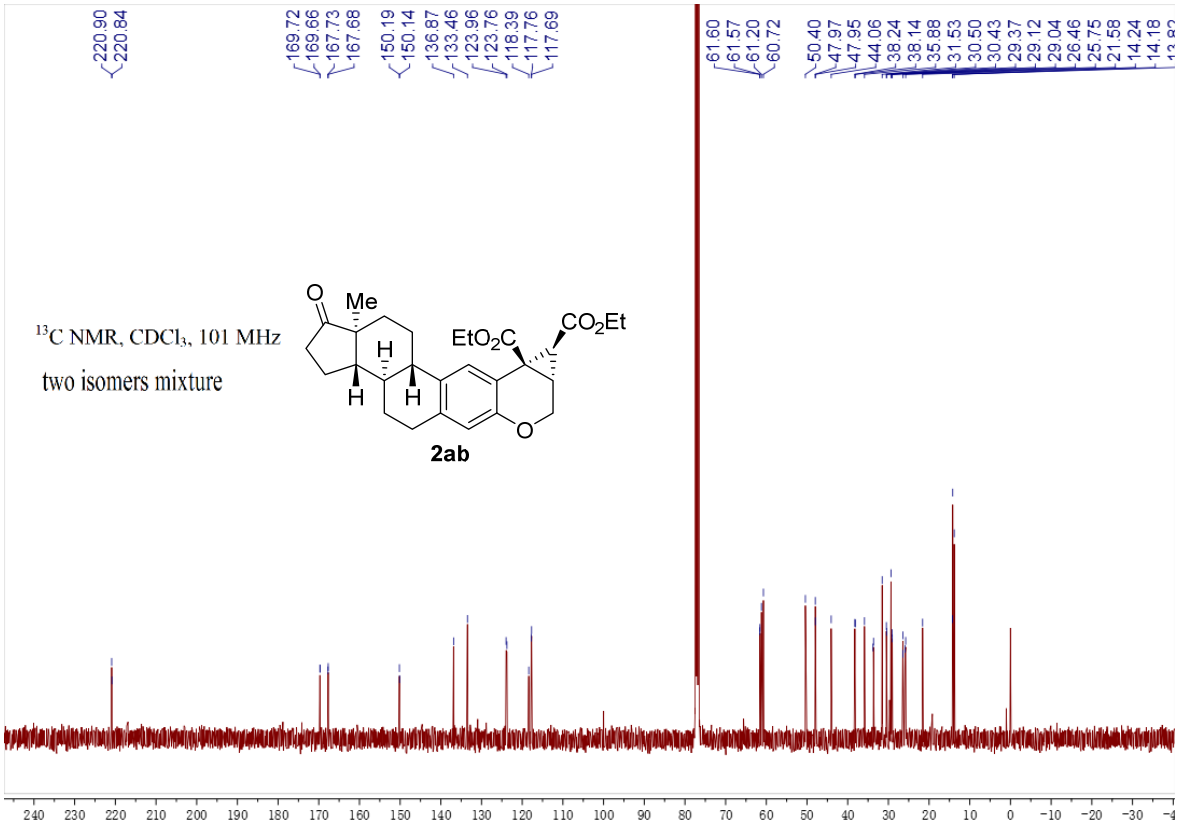
2aa

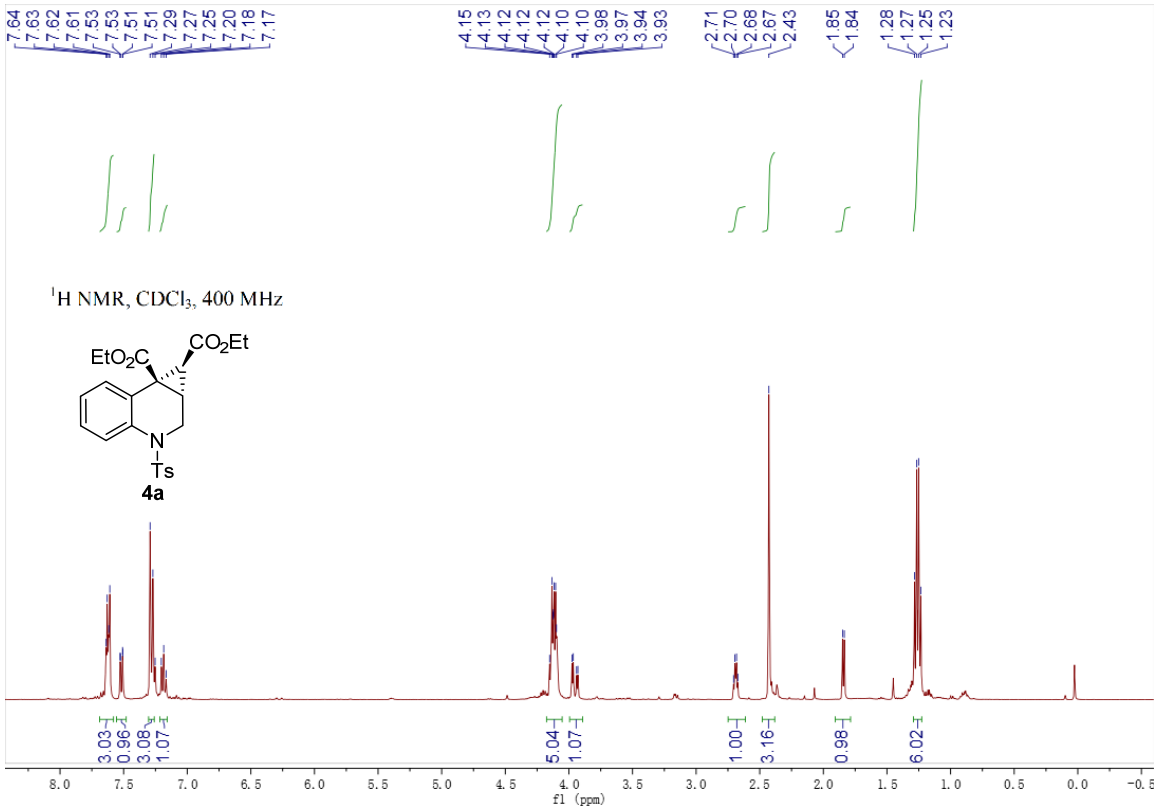


^{13}C NMR, $CDCl_3$, 101 MIz

2aa


^{1}H NMR, $CDCl_3$, 400 MHz
two isomers mixture
2ab


^{13}C NMR, $CDCl_3$, 101 MHz
two isomers mixture
2ab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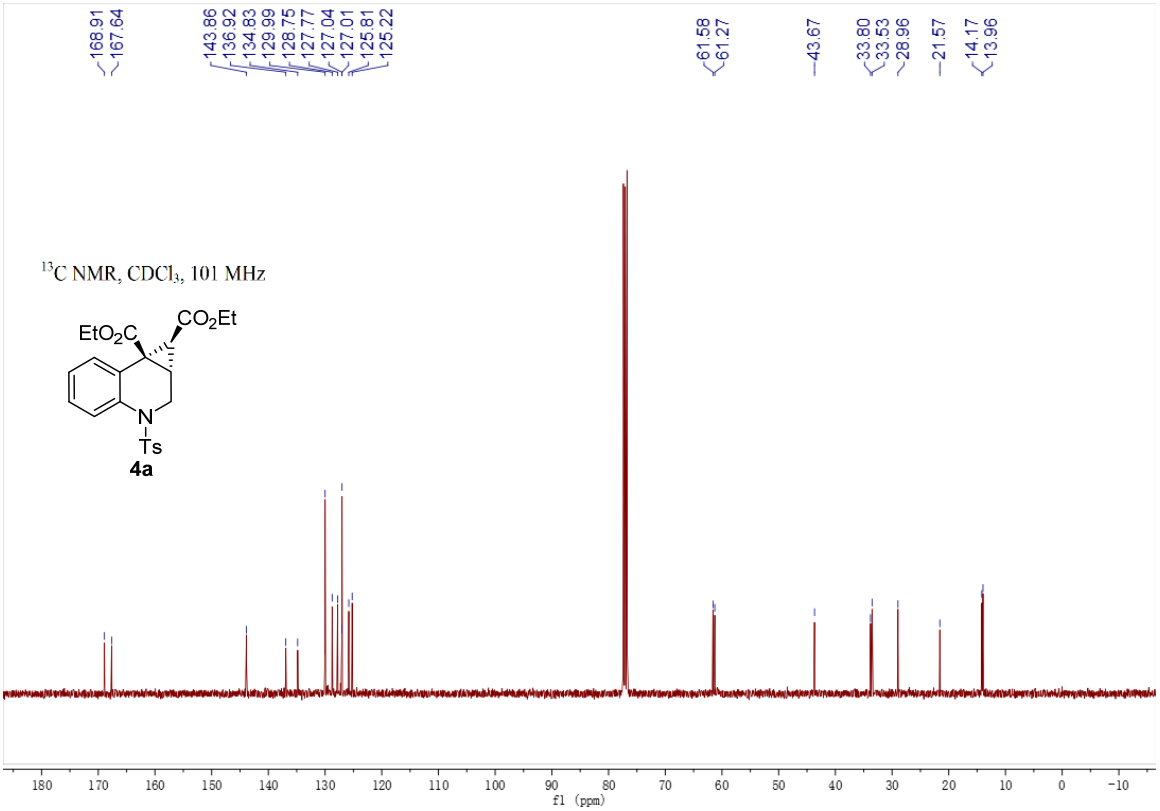
7.17
4.15
4.13
4.12
4.12
4.12
4.10
4.10
3.98
3.97
3.94
3.93
2.71
2.70
2.68
2.67
2.43
1.85
1.84
1.28
1.27
1.25
1.23
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Et
N
Ts
4a
3.03
0.96
3.08
1.07
5.04
1.07
1.00
3.16
0.98
6.02
f1 (ppm)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127.01
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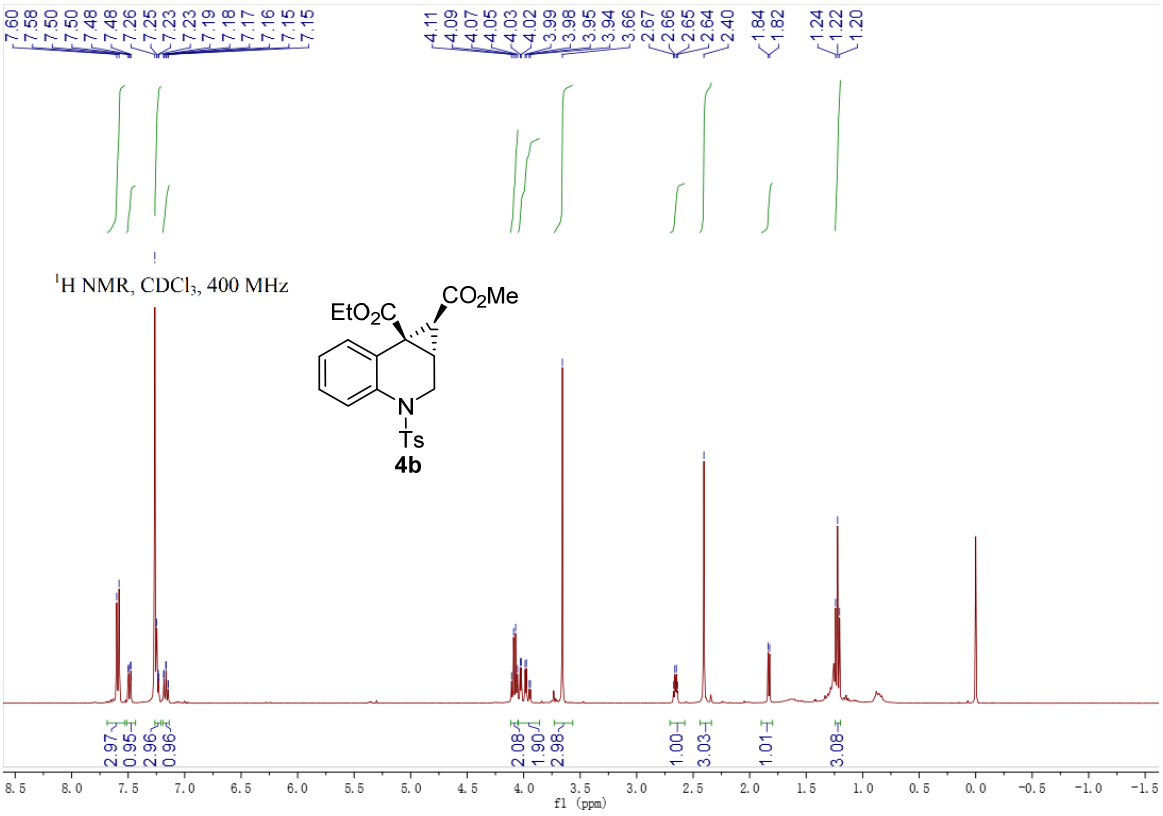
125.22
61.58
61.27
43.67
33.80
33.53
28.96
21.57
14.17
13.96
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Et
N
Ts
4a
f1 (ppm)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7.15
4.11
4.09
4.07
4.05
4.03
4.02
3.99
3.98
3.95
3.94
3.66
2.67
2.66
2.65
2.64
2.40
1.84
1.82
1.24
1.22
1.20
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Me
N
Ts
4b
2.97
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0.96
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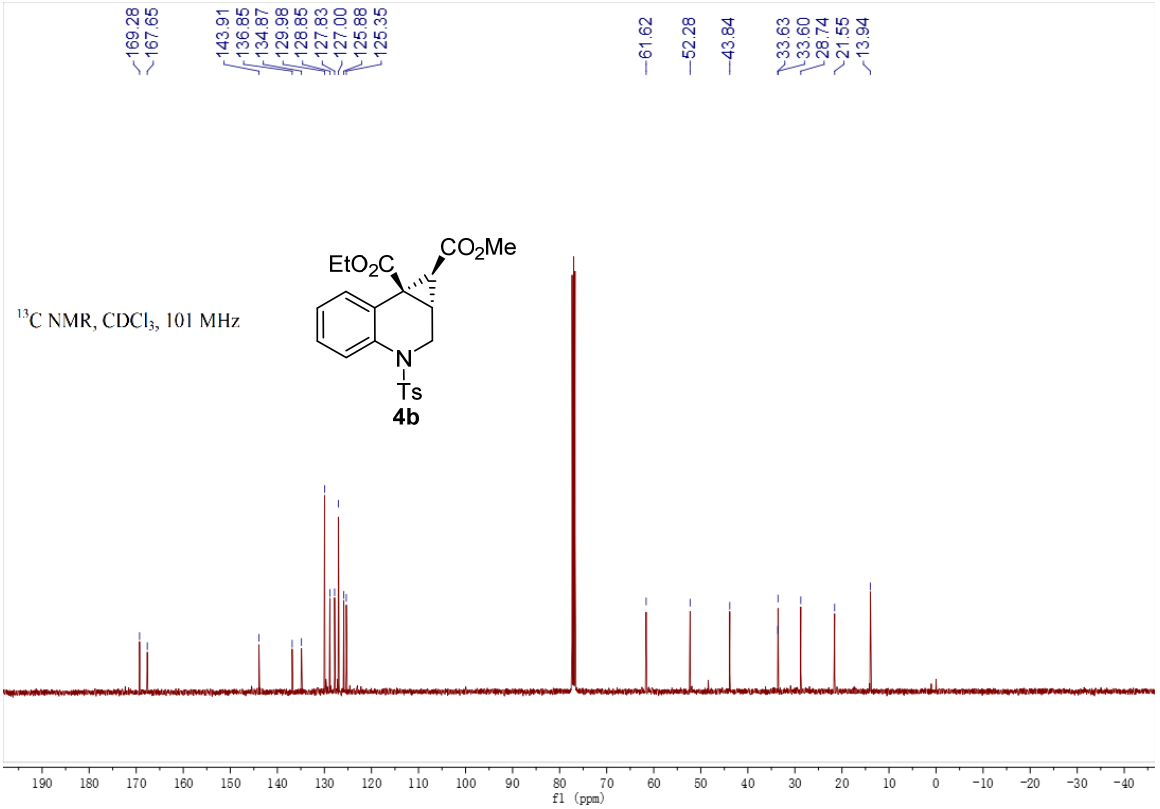
1.90
2.98
1.00
3.03
1.01
3.08
f1 (ppm)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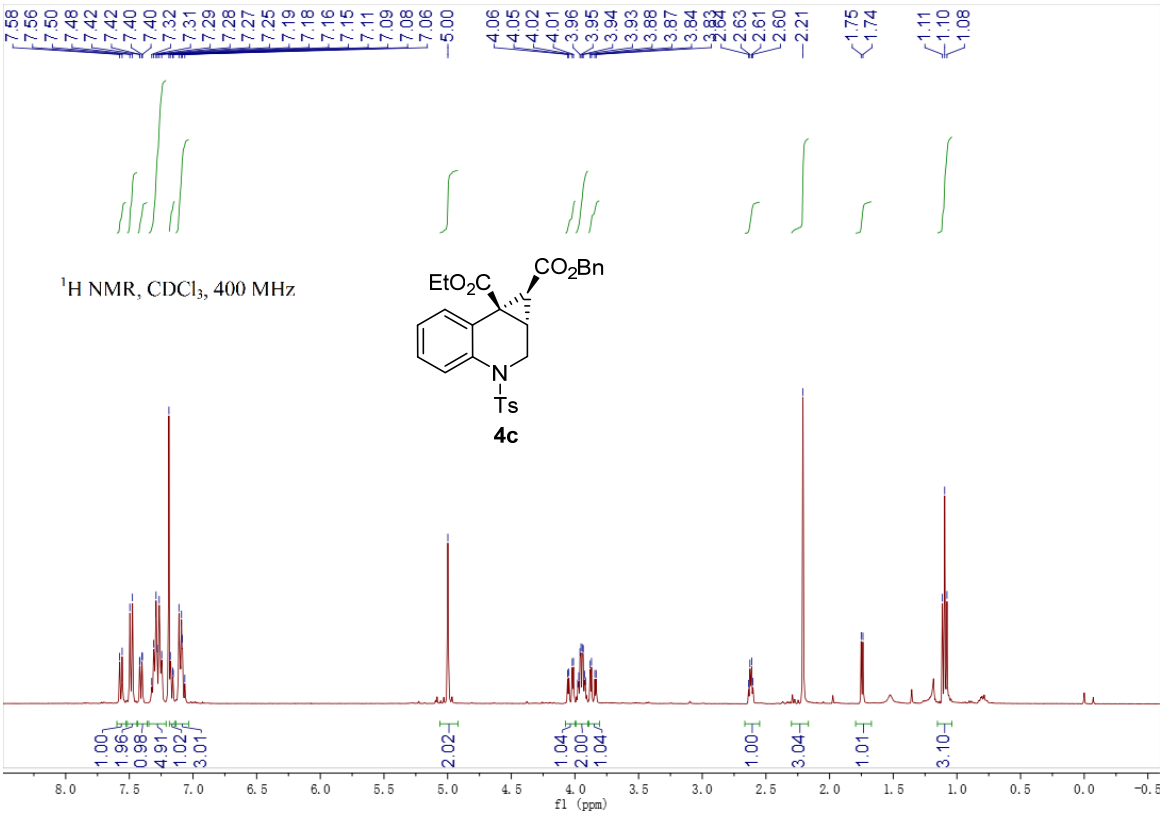
127.83
127.00
125.88
125.35
61.62
52.28
43.84
33.63
33.60
28.74
21.55
13.94
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Me
N
Ts
4b
f1 (ppm)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^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Bn
N
Ts
4c
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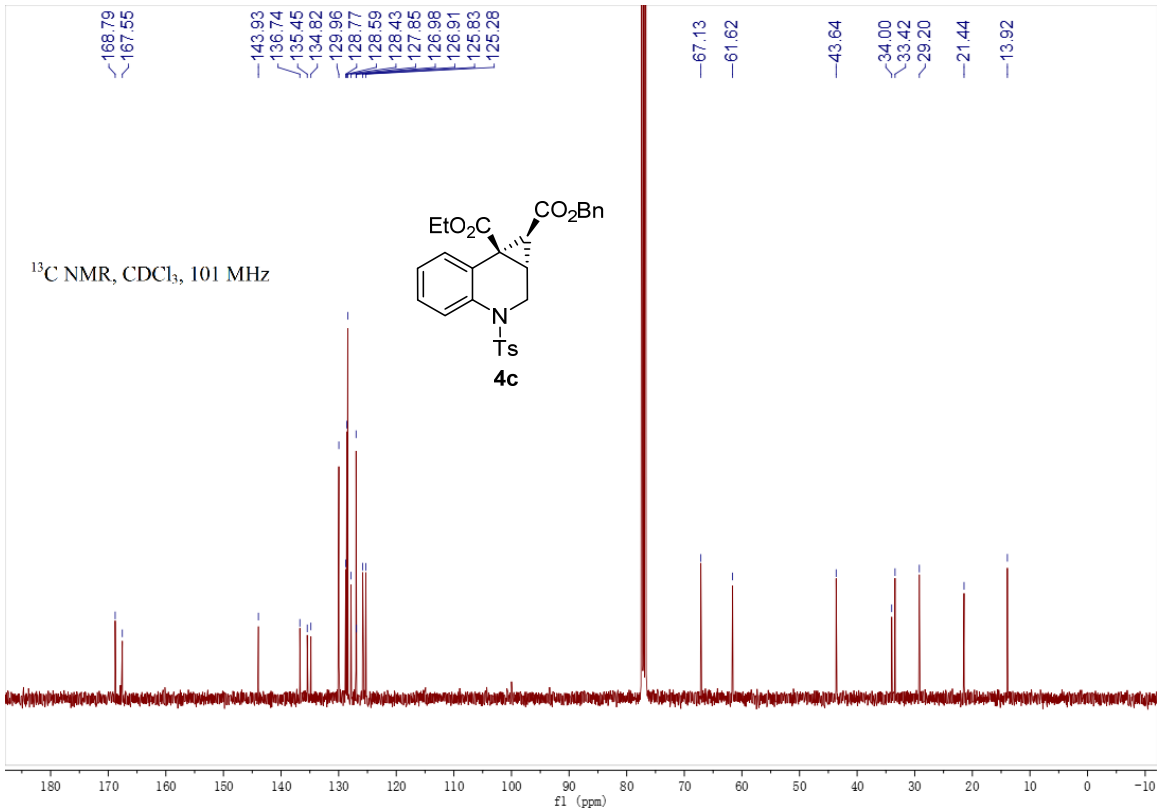
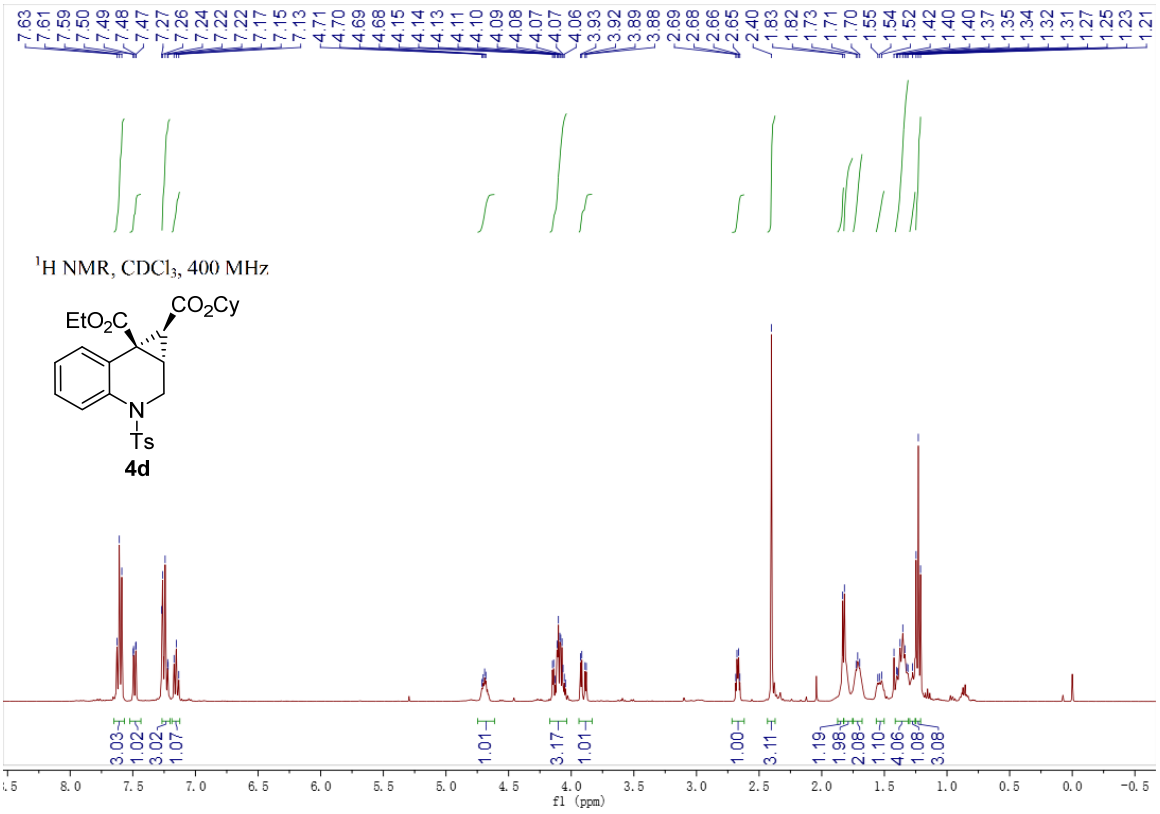
f1 (ppm)


168.79 167.55 143.93 136.74 135.45 134.82 129.96 128.77 128.59 128.43 127.85 126.98 126.91 125.83 125.28 67.13 61.62 43.64 34.00 33.42 29.20 21.44 13.92
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Bn
N
Ts
4c
f1 (ppm)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^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Cy
N
Ts
4d
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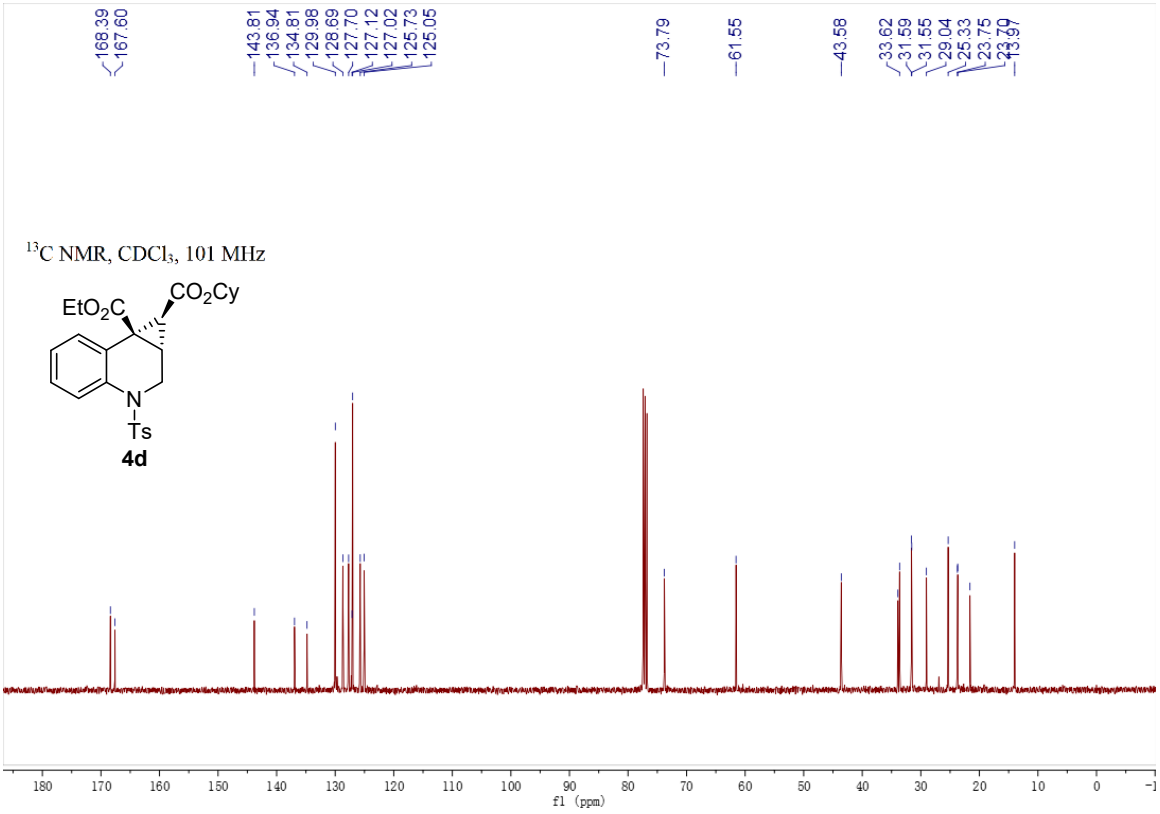
f1 (ppm)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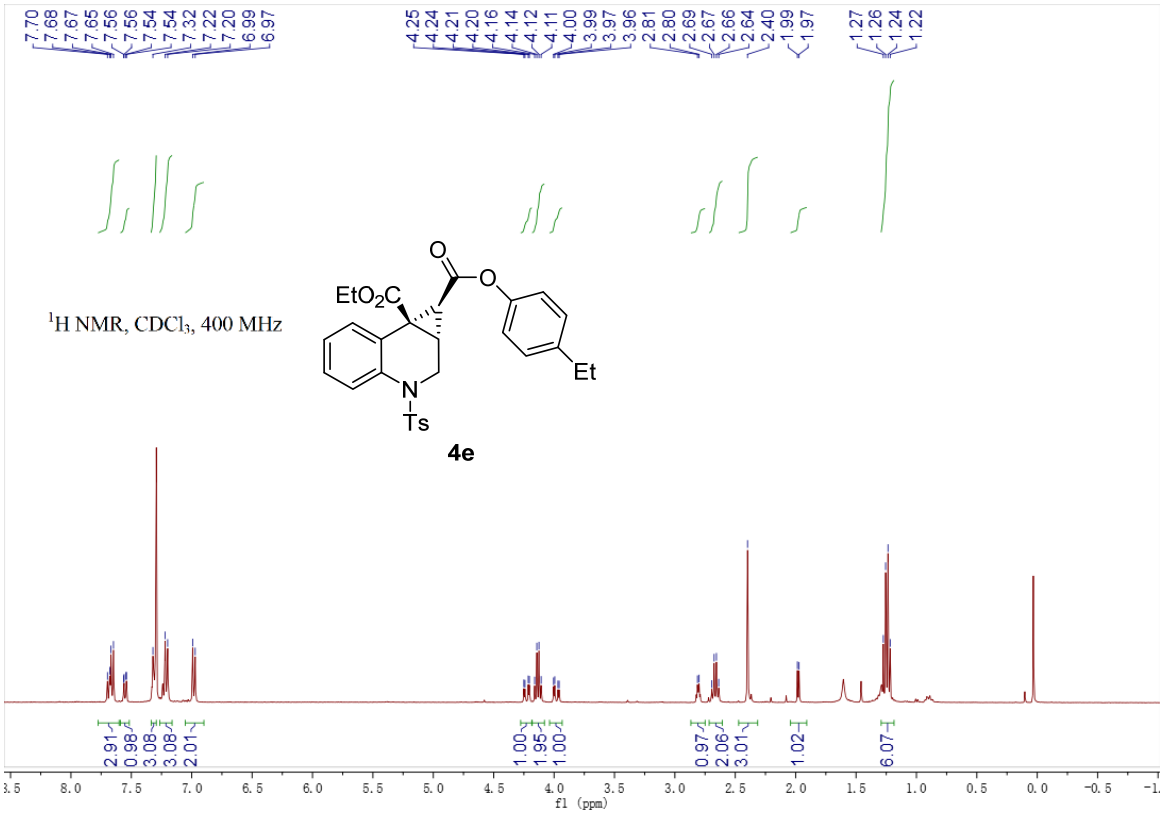
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Cy
N
Ts
4d
f1 (ppm)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6.97
4.25
4.24
4.21
4.20
4.16
4.14
4.12
4.11
4.00
3.99
3.97
3.96
2.81
2.80
2.69
2.67
2.66
2.64
2.40
1.99
1.97
1.27
1.26
1.24
1.22
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
O
O
Et
N
Ts
4e
2.91
0.98
3.08
3.08
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1.00
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3.01
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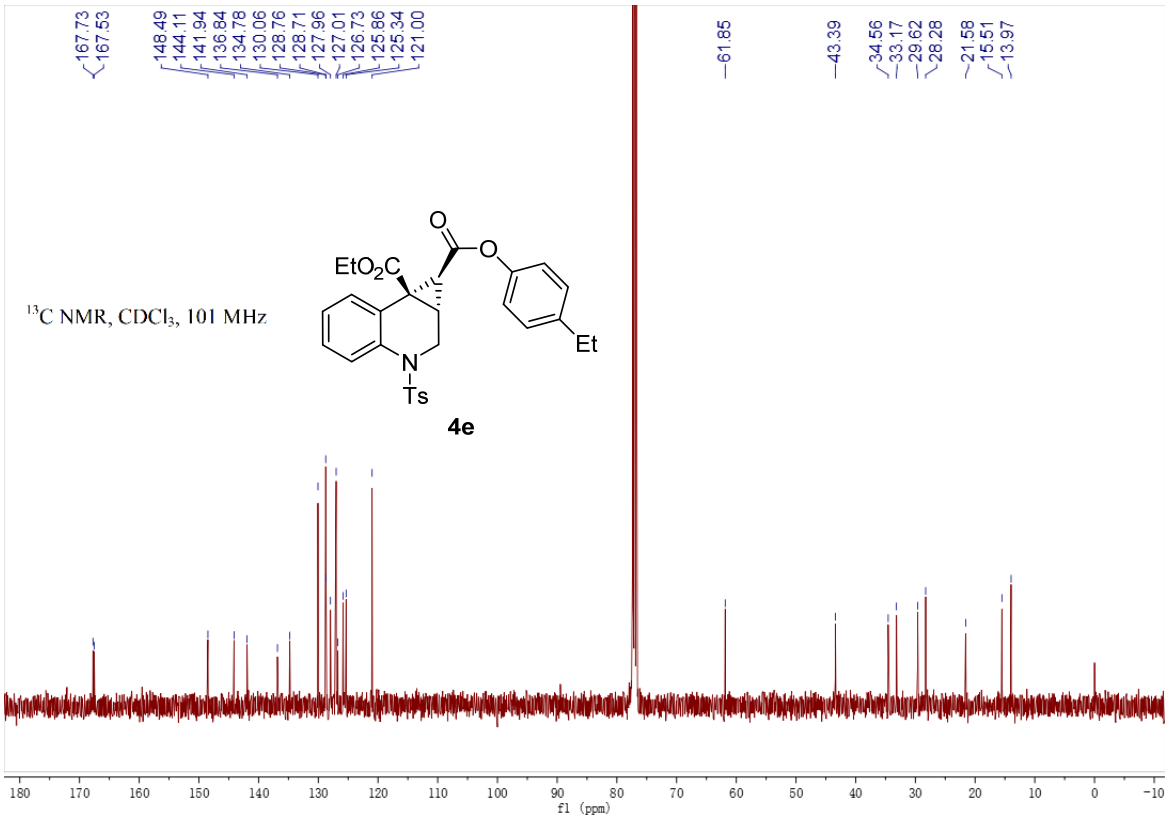
6.07
f1 (ppm)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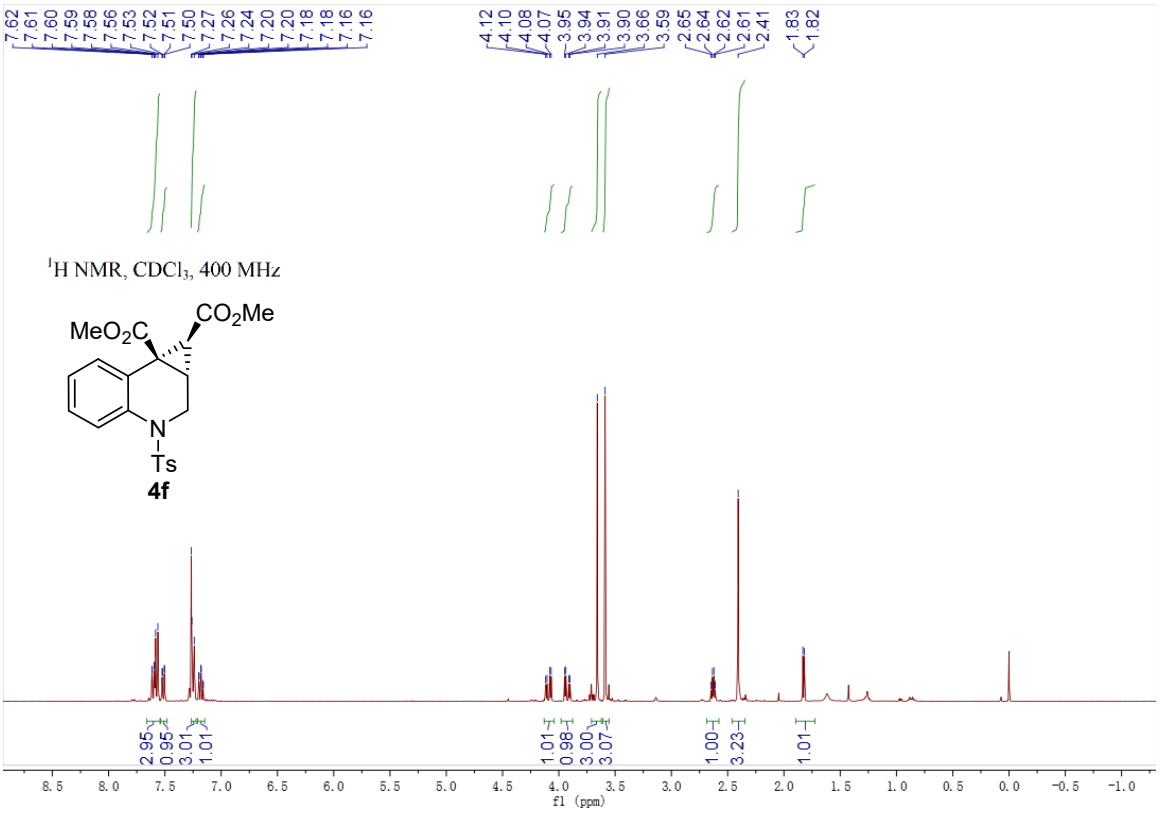
128.71
127.96
127.01
126.73
125.86
125.34
121.00
61.85
43.39
34.56
33.17
29.62
28.28
21.58
15.51
13.97
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
O
O
Et
N
Ts
4e
f1 (ppm)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7.24
7.20
7.18
7.16
7.16
4.12
4.10
4.08
4.07
3.95
3.94
3.91
3.90
3.66
3.59
2.65
2.64
2.62
2.61
2.41
1.83
1.82
^{1}H NMR, CDCl$_3$, 400 MHz
MeO$_2$C
CO$_2$Me
N
Ts
4f
2.95
0.95
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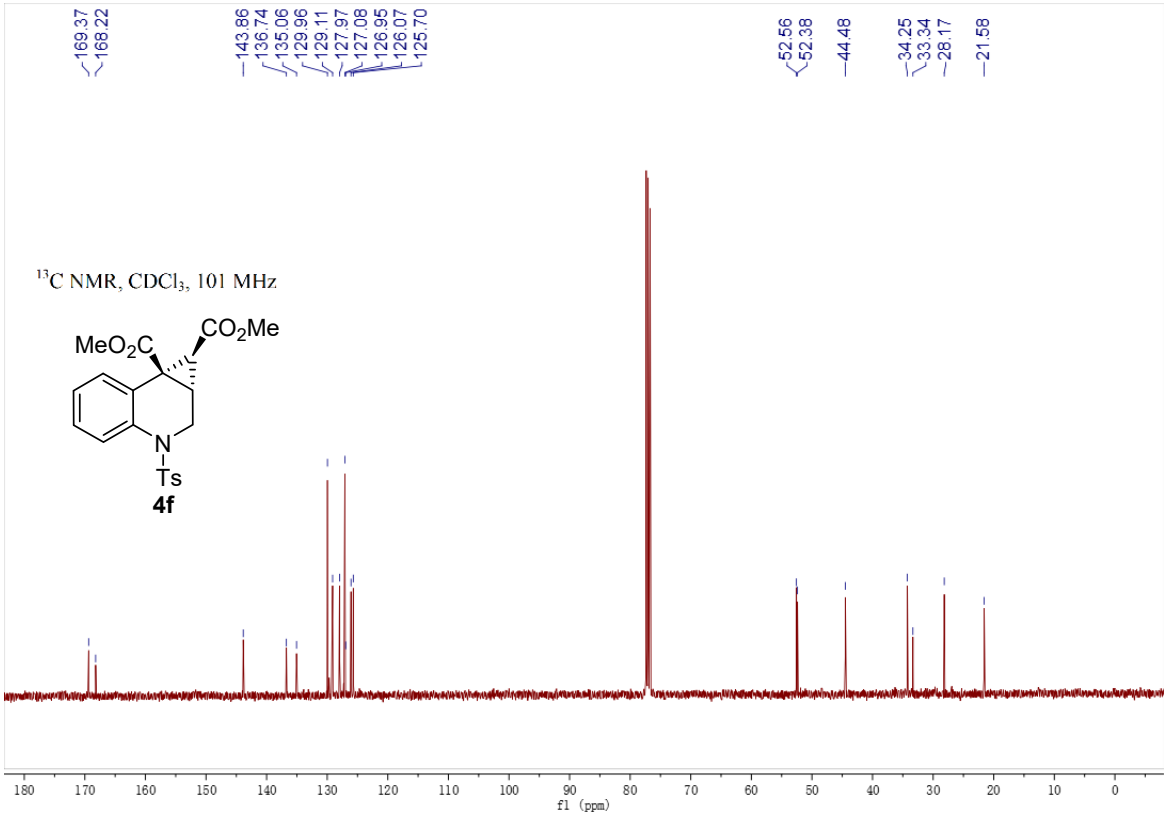
1.01
1.01
0.98
3.00
3.07
1.00
3.23
1.01
f1 (ppm)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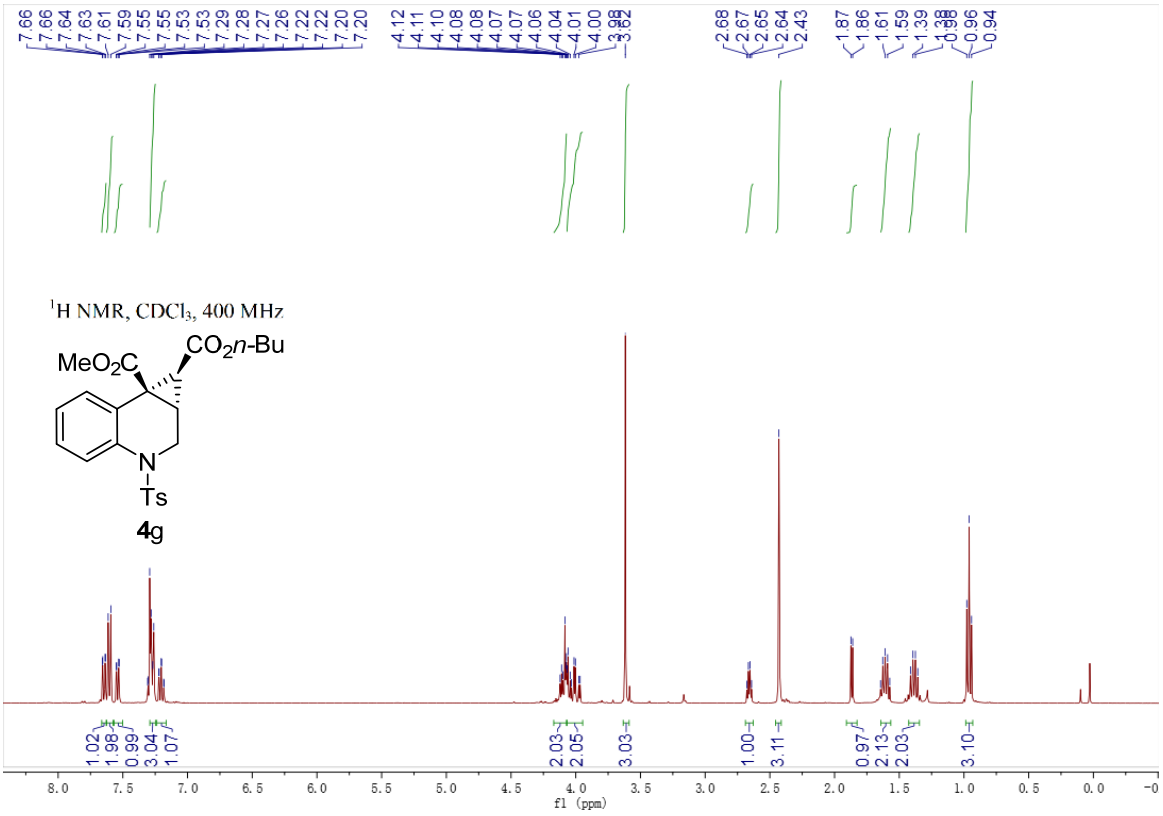
126.95
126.07
125.70
52.56
52.38
44.48
34.25
33.34
28.17
21.58
^{13}C NMR, CDCl$_3$, 101 MHz
MeO$_2$C
CO$_2$Me
N
Ts
4f
f1 (ppm)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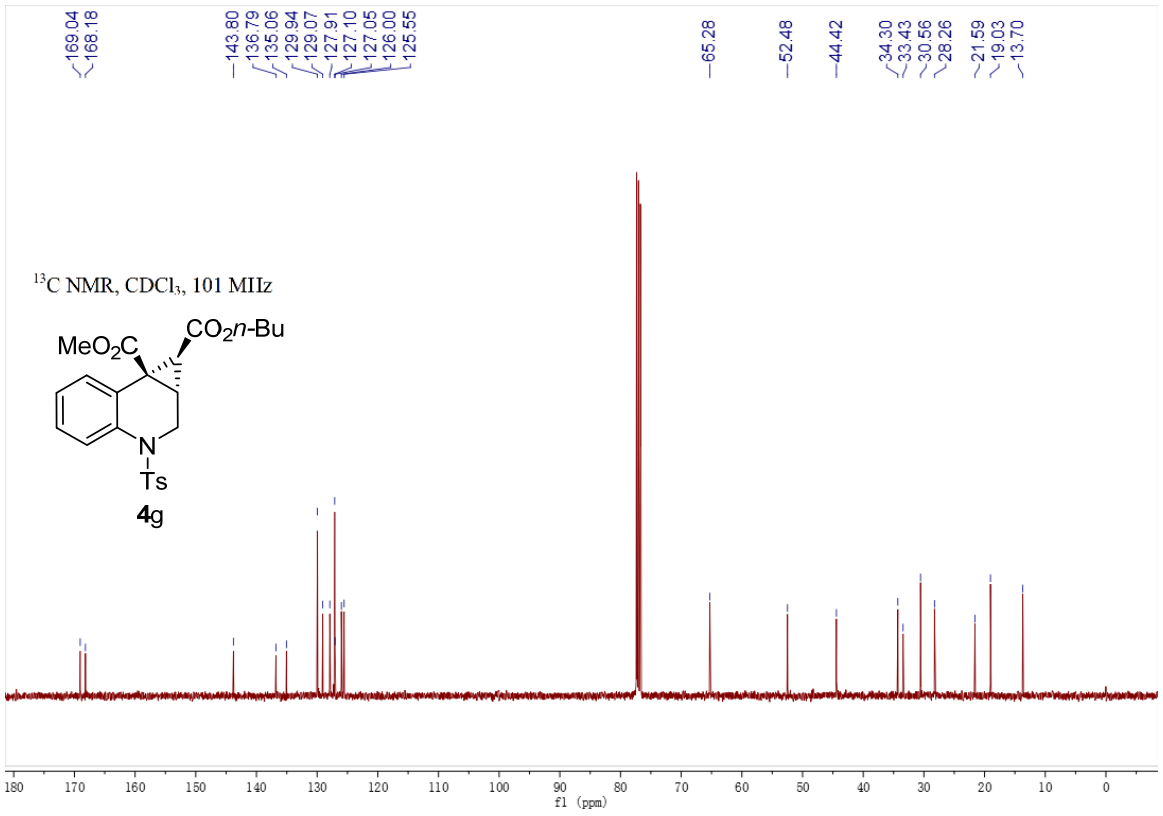
4.12 4.11 4.10 4.08 4.08 4.07 4.07 4.06 4.04 4.01 4.00 3.98 3.02
2.68 2.67 2.65 2.64 2.43
1.87 1.86 1.61 1.59 1.39 0.98 0.96 0.94
^{1}H NMR, CDCl$_3$, 400 MHz
MeO$_2$C
CO$_2$n-Bu
N
Ts
4g
1.02 1.98 0.99 3.04 1.07
2.03 2.05 3.03 1.00 3.11 0.97 2.13 2.03 3.10
f1 (ppm)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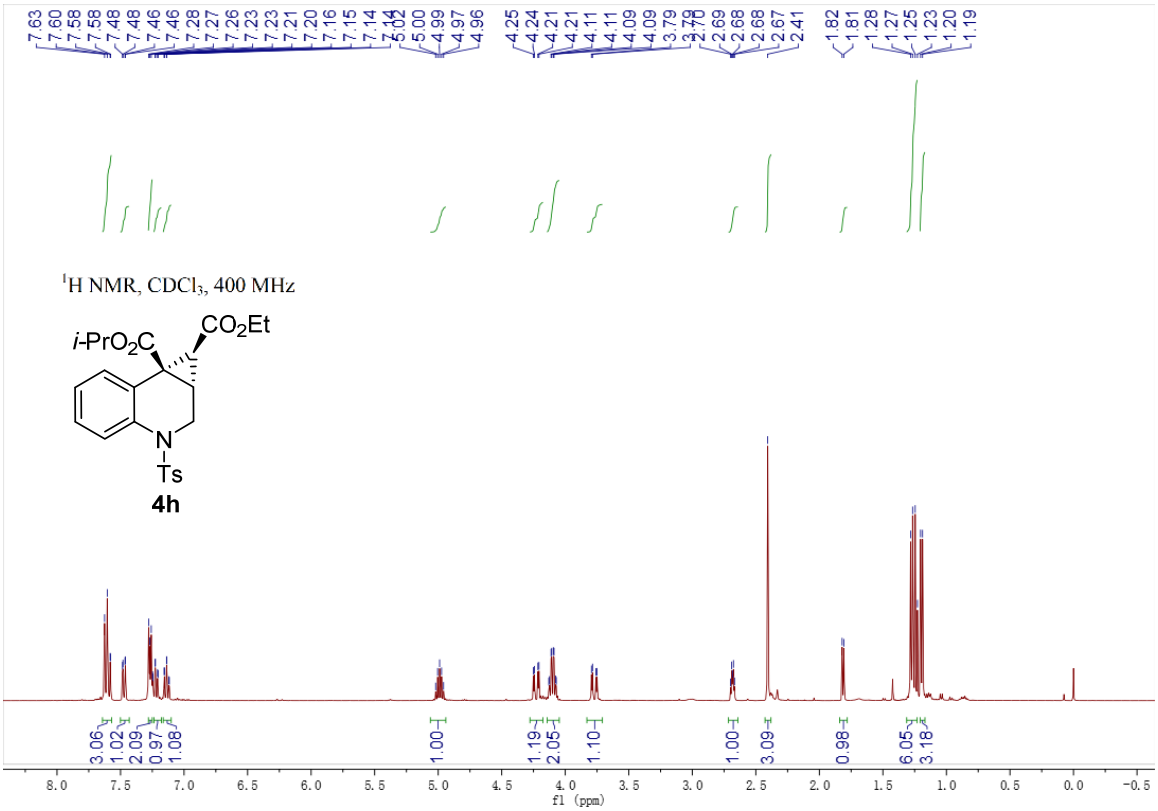
143.80 136.79 135.06 129.94 129.07 127.91 127.10 127.05 126.00 125.55
65.28 52.48 44.42
34.30 33.43 30.56 28.26 21.59 19.03 13.70
^{13}C NMR, CDCl$_3$, 101 MIIz
MeO$_2$C
CO$_2$n-Bu
N
Ts
4g
f1 (ppm)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4.25 4.24 4.21 4.21 4.11 4.11 4.09 4.09 3.79 3.79 2.70 2.69 2.68 2.68 2.67 2.41
1.82 1.81 1.28 1.27 1.25 1.23 1.20 1.19
^{1}H NMR, $CDCl_3$, 400 MHz
i-PrO_2C
CO_2Et
N
Ts
4h
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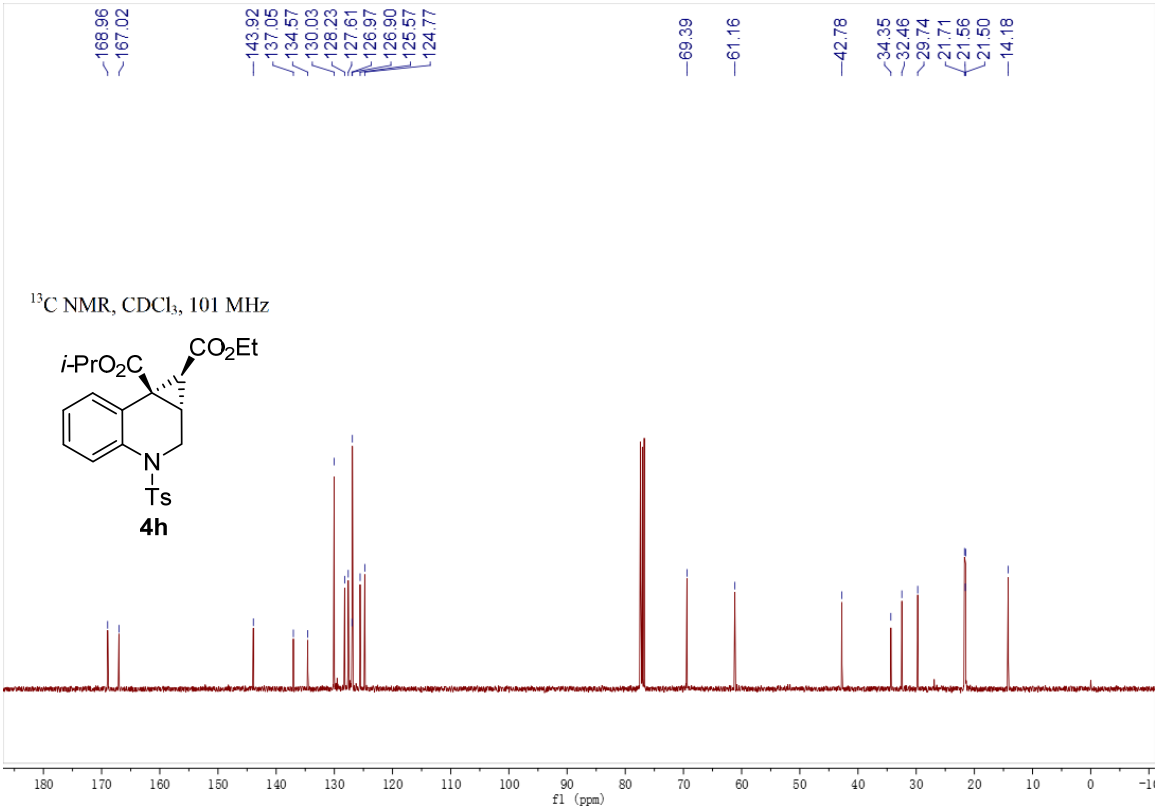
f1 (ppm)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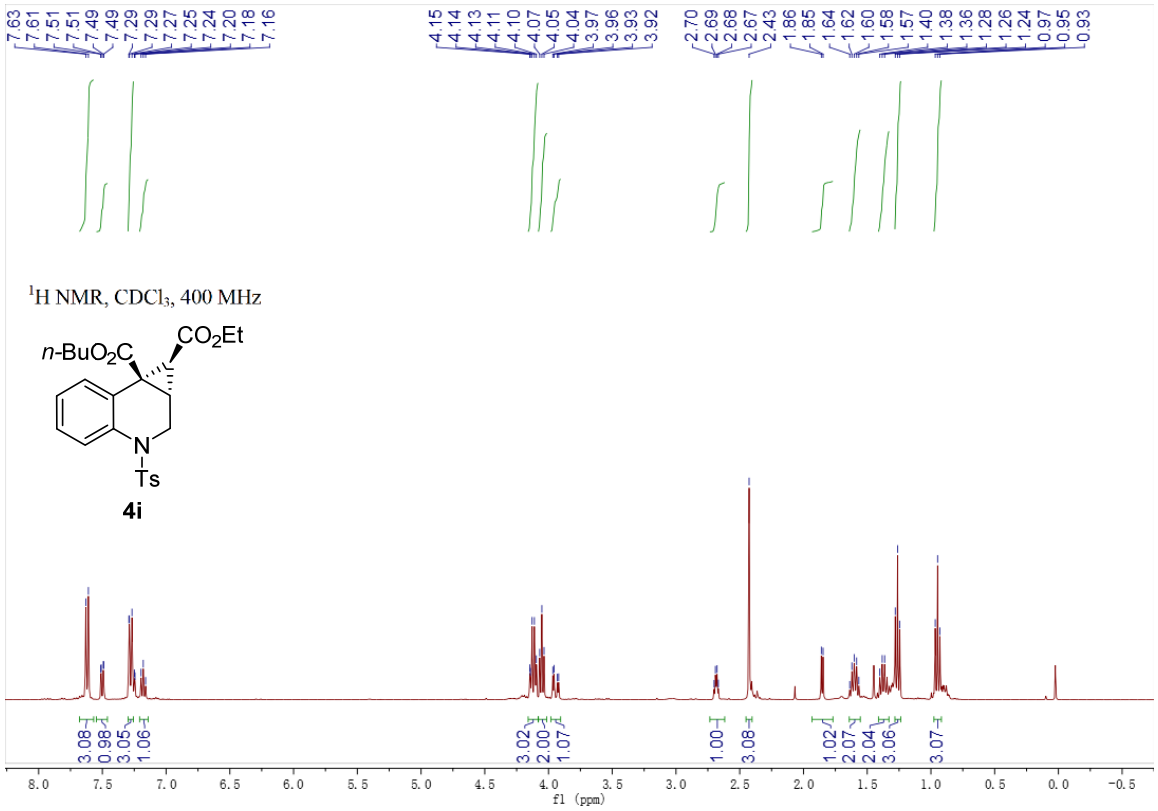
143.92 137.05 134.57 130.03 128.23 127.61 126.97 126.90 125.57 124.77
69.39 61.16
42.78
34.35 32.46 29.74 21.71 21.56 21.50 14.18
^{13}C NMR, $CDCl_3$, 101 MHz
i-PrO_2C
CO_2Et
N
Ts
4h
f1 (ppm)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4.15 4.14 4.13 4.11 4.10 4.07 4.05 4.04 3.97 3.96 3.93 3.92
2.70 2.69 2.68 2.67 2.43 1.86 1.85 1.64 1.62 1.60 1.58 1.57 1.40 1.38 1.36 1.28 1.26 1.24 0.97 0.95 0.93
^{1}H NMR, CDCl$_3$, 400 MHz
n-BuO2C
CO2Et
N
Ts
4i
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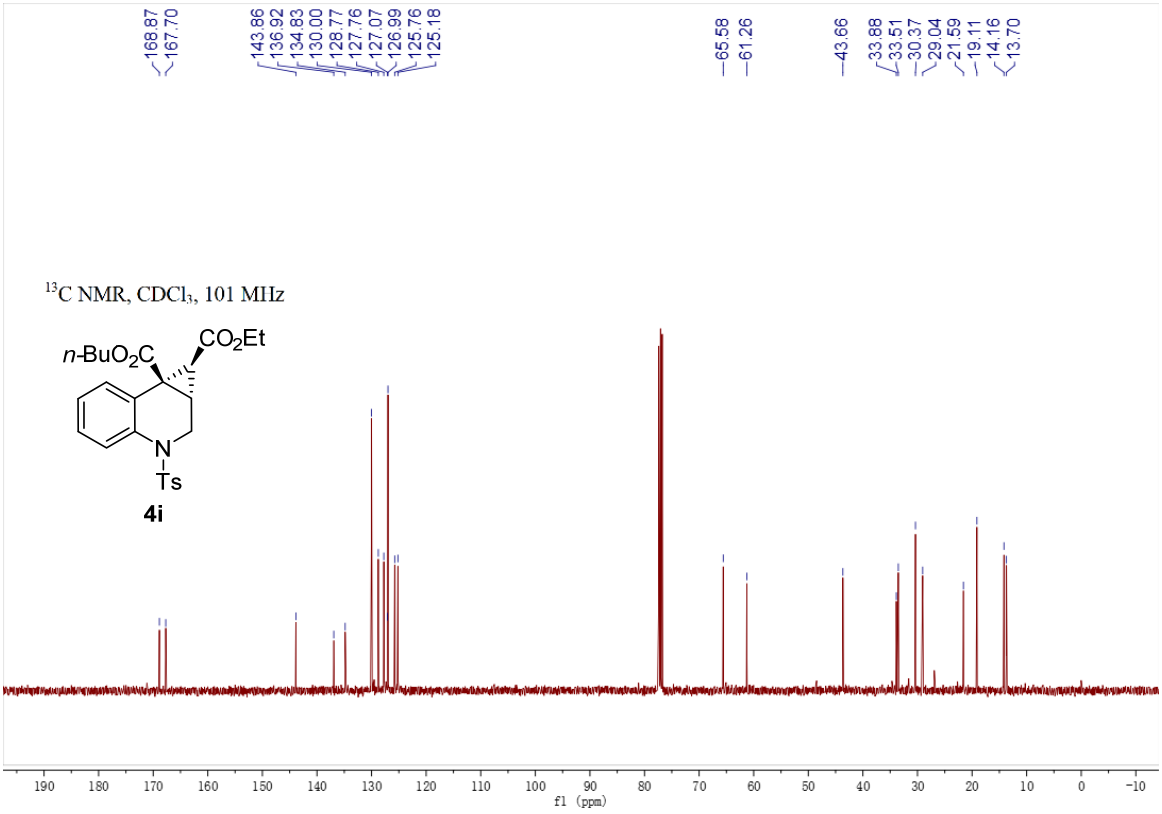
f1 (ppm)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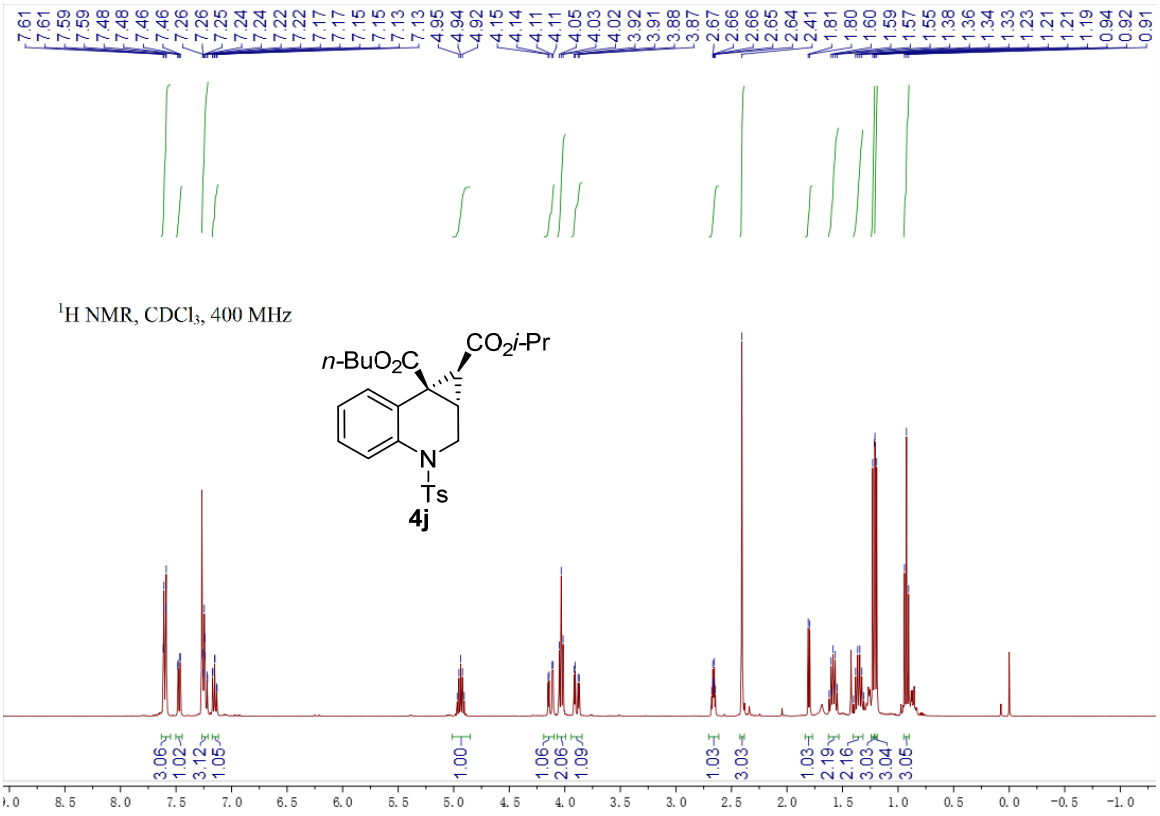
65.58 61.26 43.66 33.88 33.51 30.37 29.04 21.59 19.11 14.16 13.70
^{13}C NMR, CDCl$_3$, 101 MHz
n-BuO2C
CO2Et
N
Ts
4i
f1 (ppm)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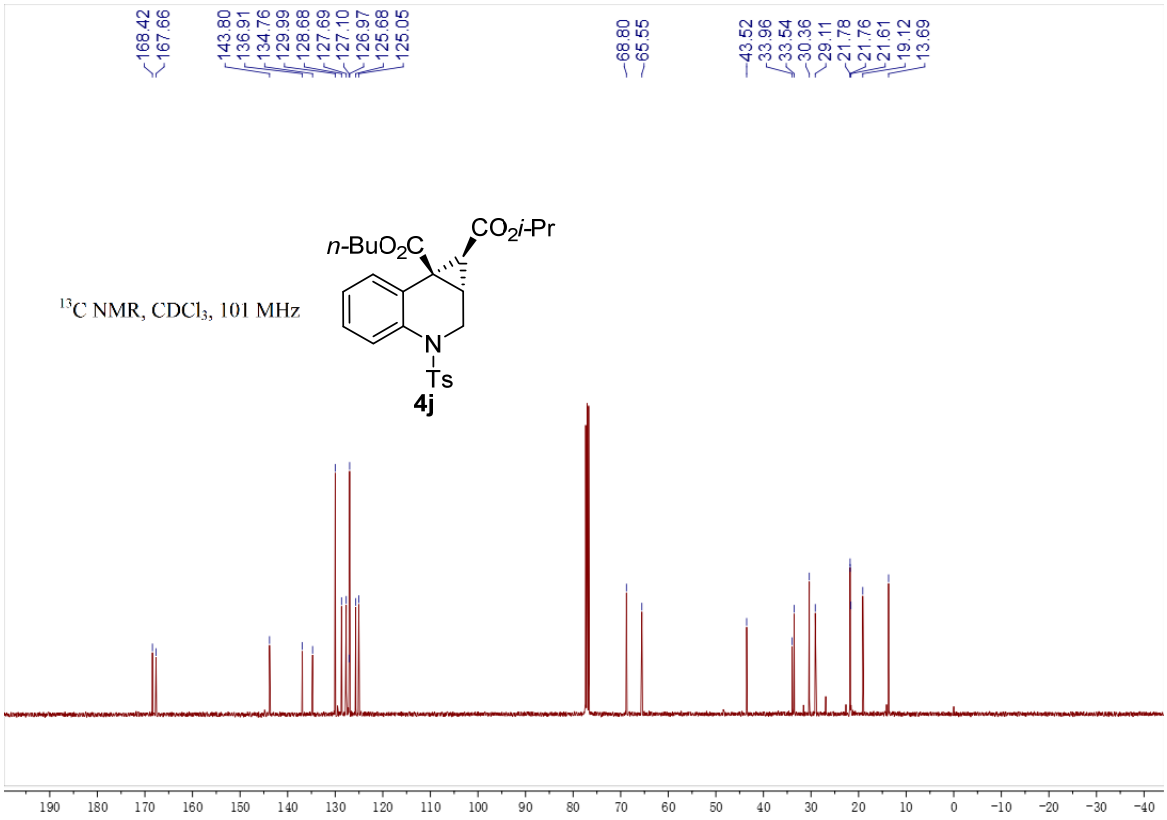
^{1}H NMR, CDCl$_3$, 400 MHz
n-BuO2C
CO2i-Pr
N
Ts
4j
3.06 1.02 3.12 1.05 1.00 1.06 2.06 1.09 1.03 3.03 1.03 2.19 2.16 3.03 3.04 3.05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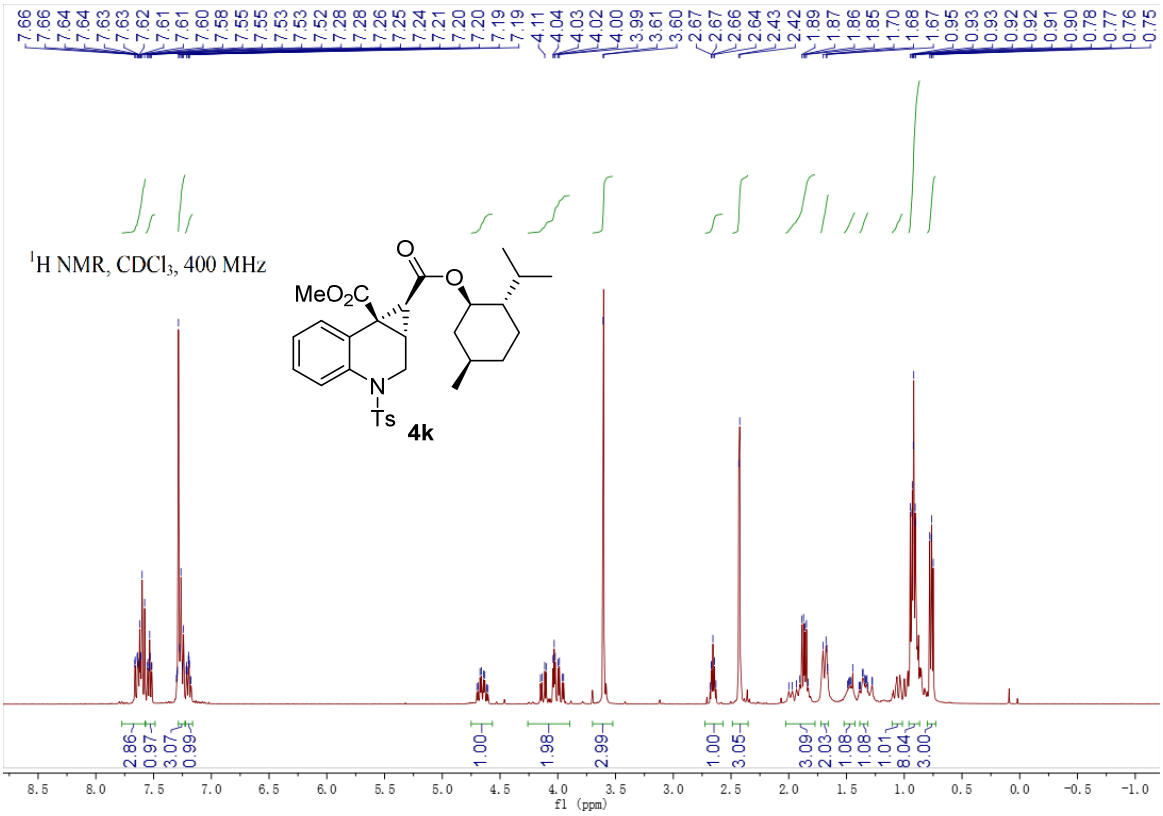
^{13}C NMR, CDCl$_3$, 101 MHz
n-BuO2C
CO2i-Pr
N
Ts
4j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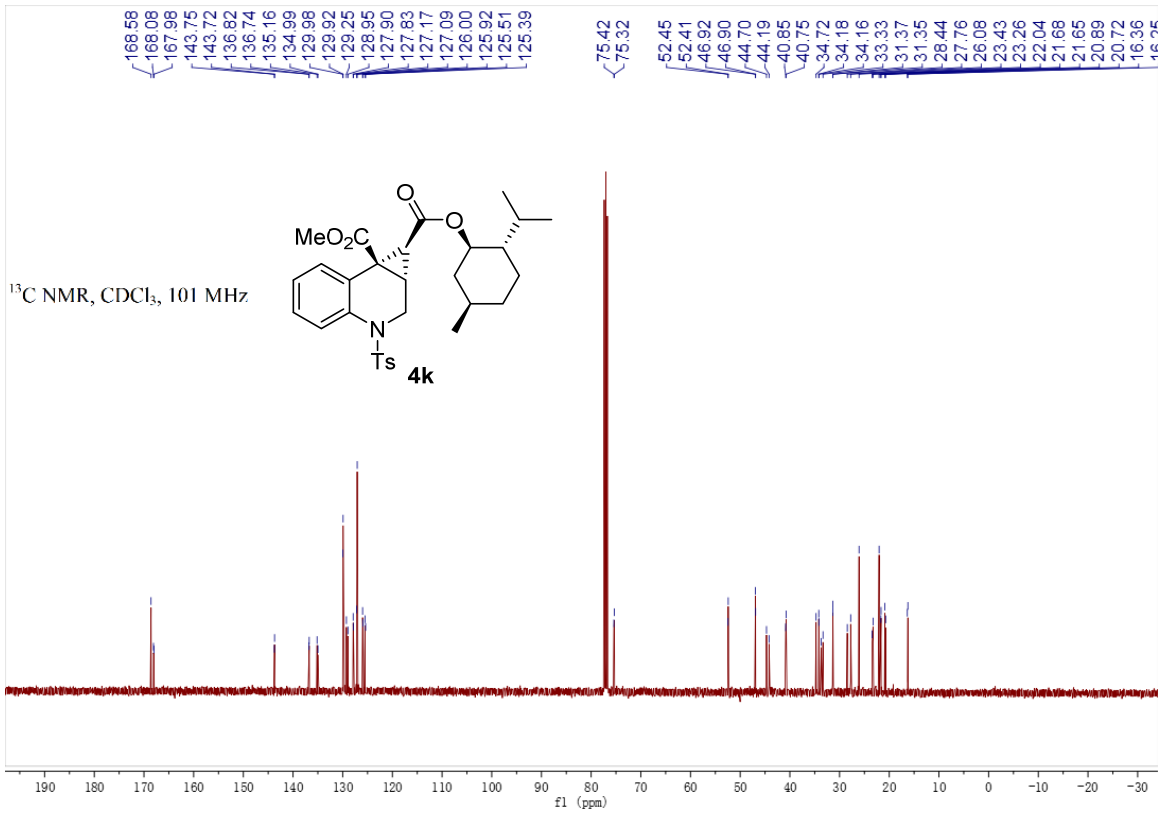
MeO_2C
N
Ts
4k
f1 (ppm)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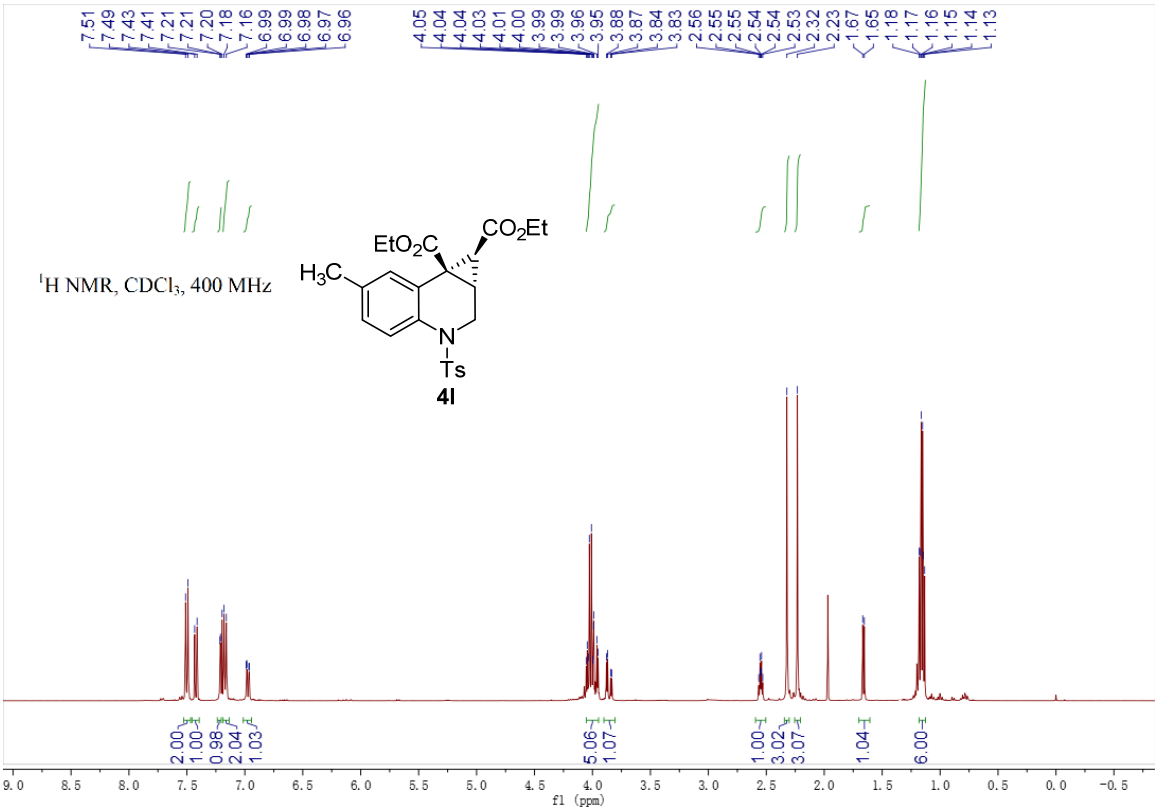
MeO_2C
N
Ts
4k
f1 (ppm)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6.98
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2.32
2.23
1.67
1.65
1.18
1.17
1.16
1.15
1.14
1.13
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Et
H$_3$C
N
Ts
4l
2.00
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1.03
5.06
1.07
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3.07
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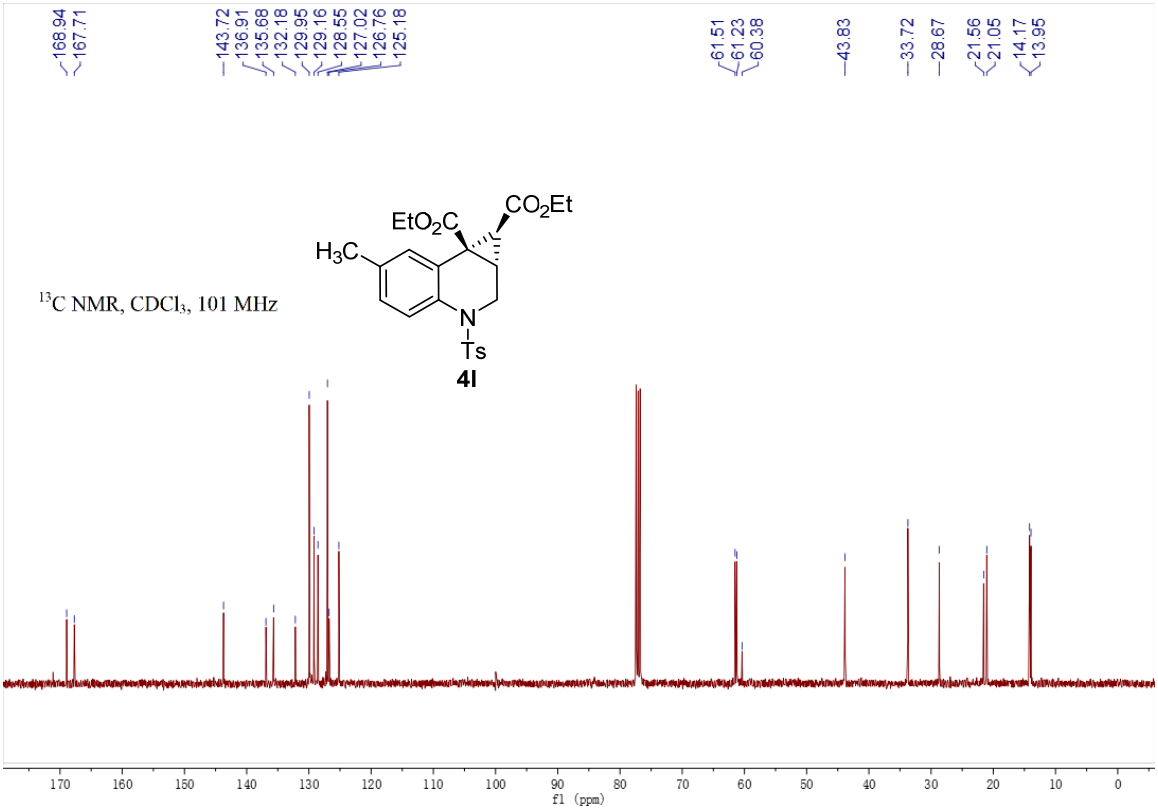
6.00
f1 (ppm)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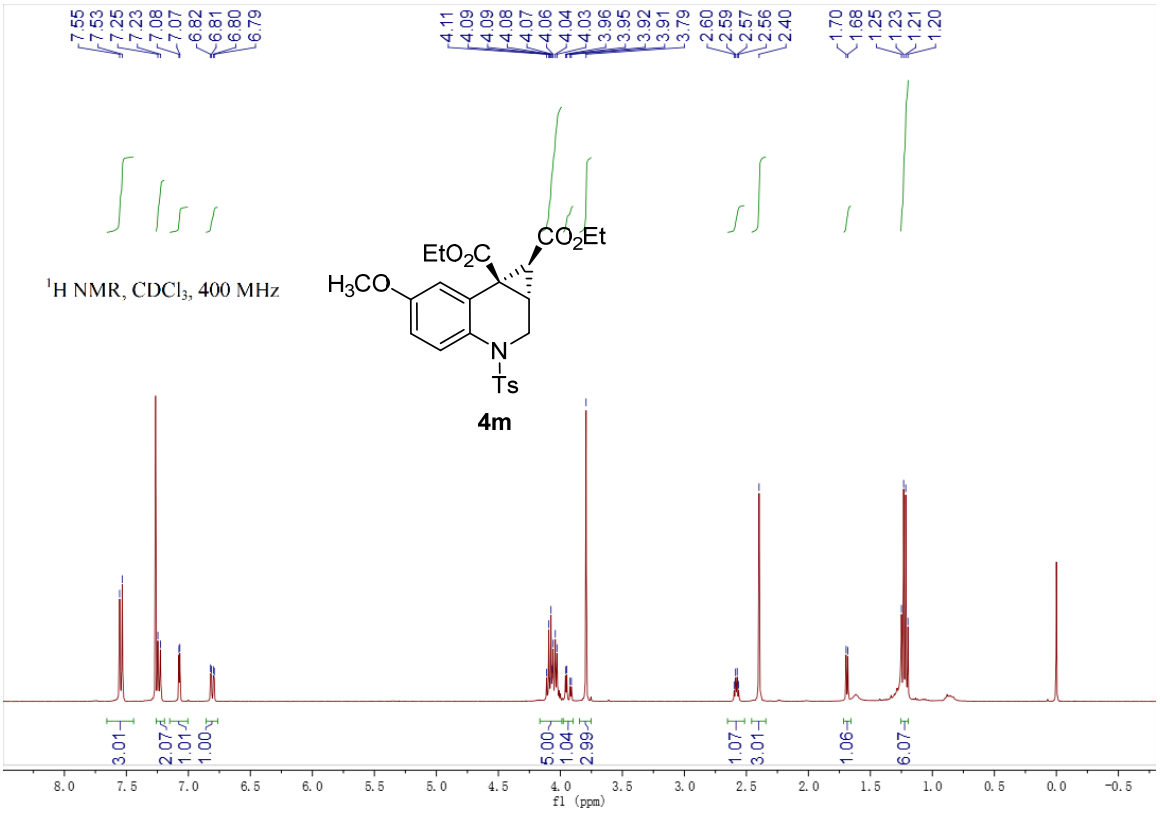
125.18
61.51
61.23
60.38
43.83
33.72
28.67
21.56
21.05
14.17
13.95
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Et
H$_3$C
N
Ts
4l
f1 (ppm)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4.08
4.07
4.06
4.04
4.03
3.96
3.95
3.92
3.91
3.79
2.60
2.59
2.57
2.56
2.40
1.70
1.68
1.25
1.23
1.21
1.20
^{1}H NMR, $CDCl_3$, 400 MHz
EtO_2C
CO_2Et
H_3CO
N
Ts
4m
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2.07
1.01
1.00
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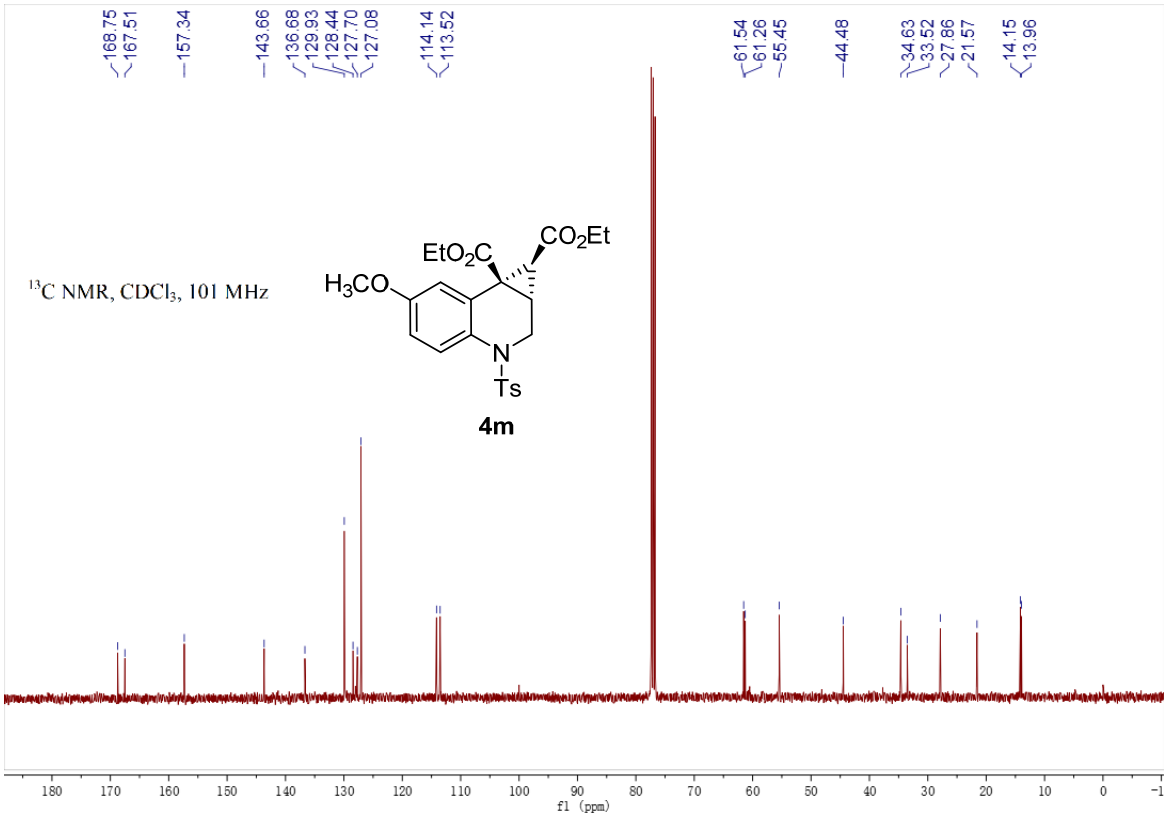
1.07
3.01
1.06
6.07
f1 (ppm)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44.48
34.63
33.52
27.86
21.57
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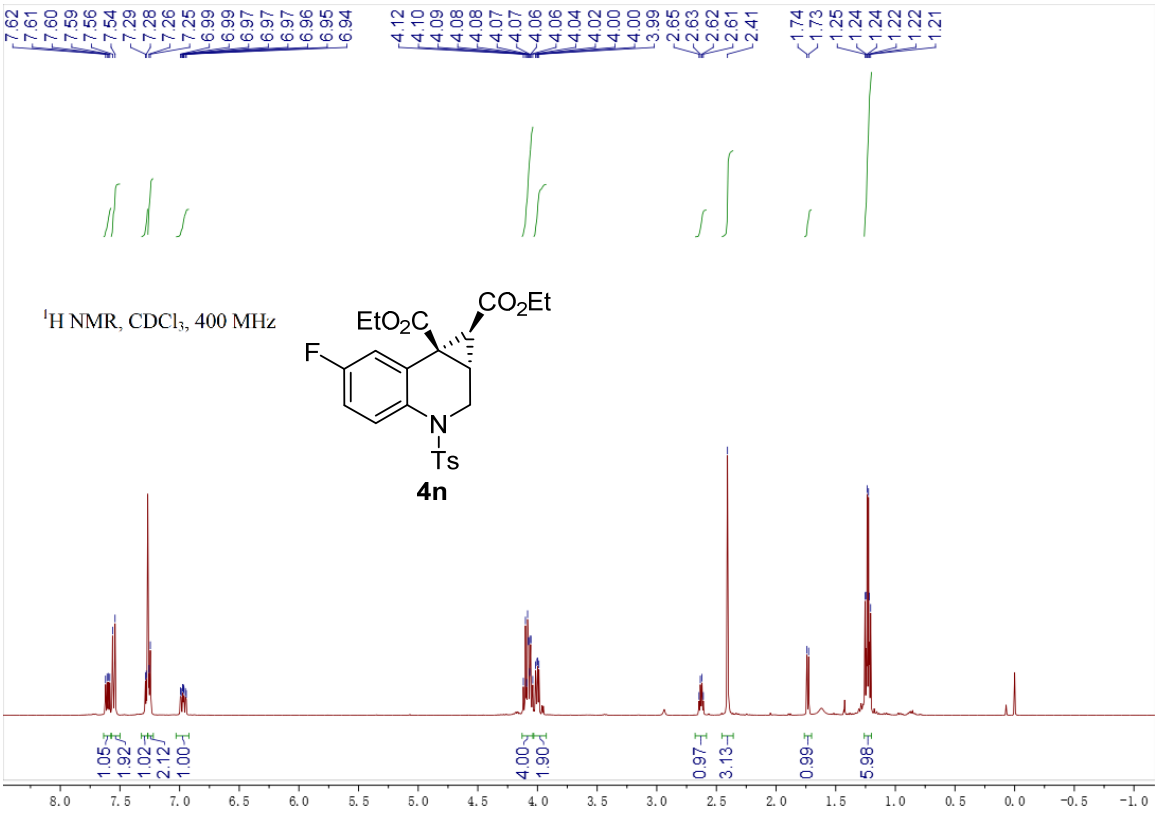
CO_2Et
H_3CO
N
Ts
4m
f1 (ppm)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1.74 1.73 1.25 1.24 1.24 1.22 1.22 1.21
^{1}H NMR, $CDCl_3$, 400 MHz
EtO2C
CO2Et
F
N
Ts
4n
1.05 1.92 1.02 2.12 1.00 4.00 1.90 0.97 3.13 0.99 5.98
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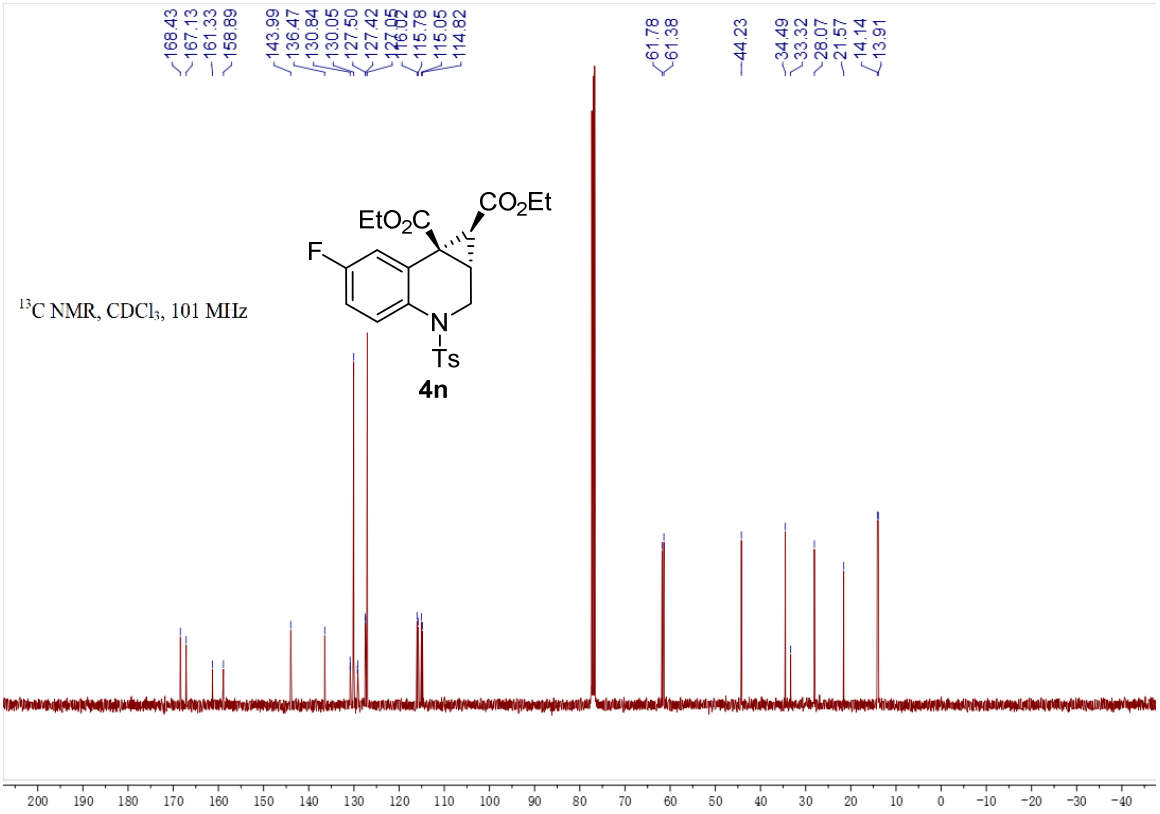
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61.78 61.38 44.23 34.49 33.32 28.07 21.57 14.14 13.91
^{13}C NMR, $CDCl_3$, 101 MHz
EtO2C
CO2Et
F
N
Ts
4n
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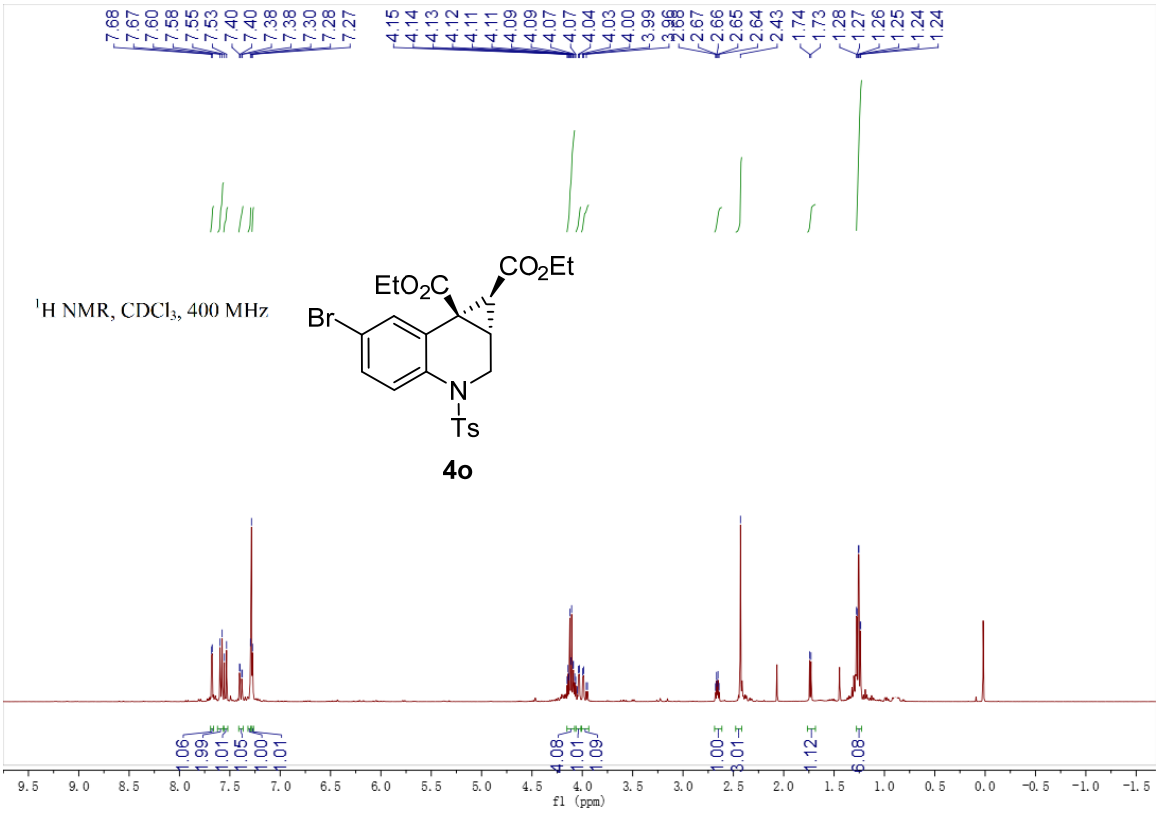
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2.64
2.43
1.74
1.73
1.28
1.27
1.26
1.25
1.24
1.24
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Et
Br
N
Ts
4o
1.06
1.99
1.01
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1.01
4.08
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3.01
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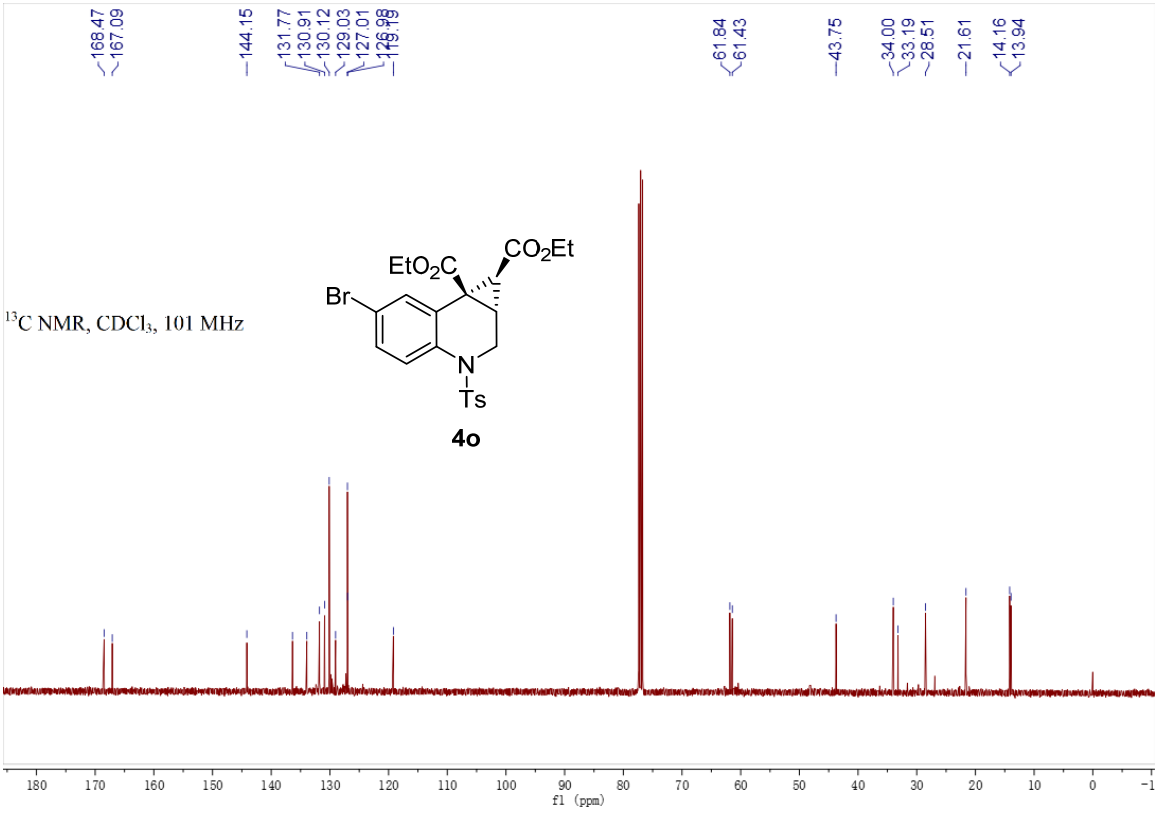
6.08
f1 (ppm)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127.01
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43.75
34.00
33.19
28.51
21.61
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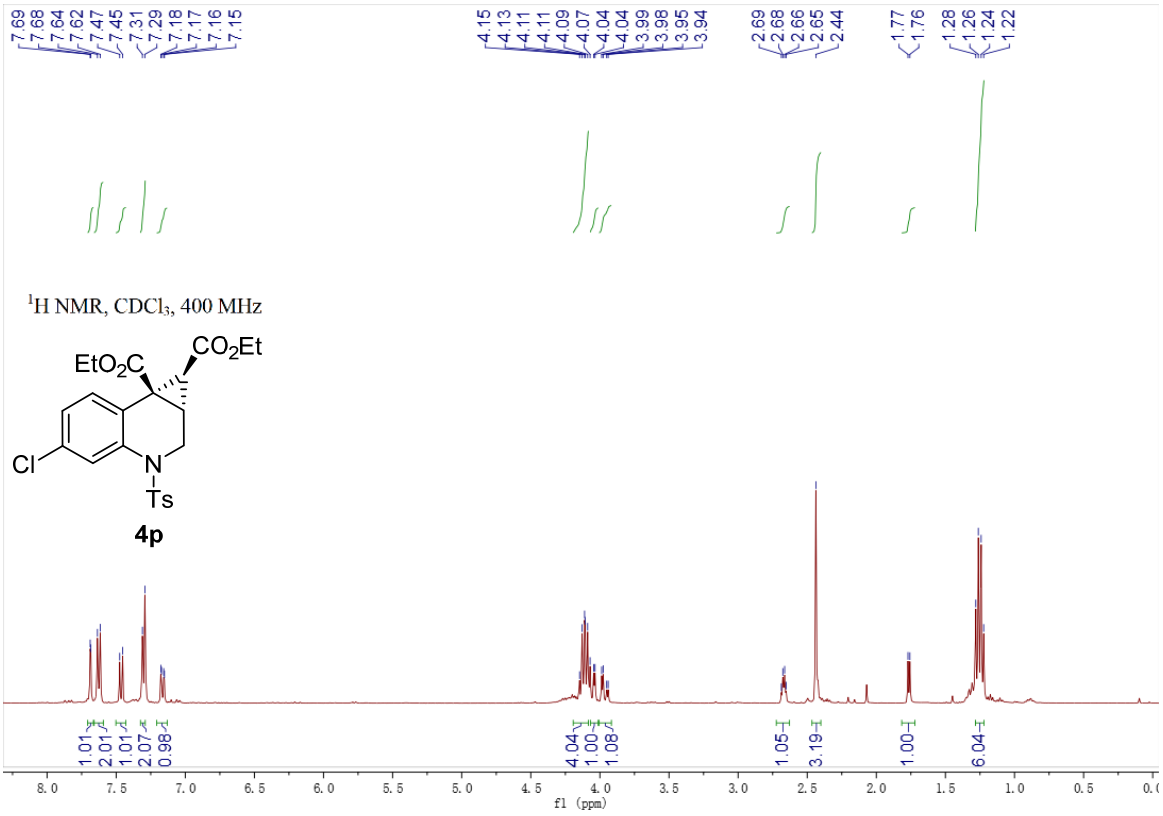
13.94
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Et
Br
N
Ts
4o
f1 (ppm)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4.11
4.09
4.07
4.04
3.99
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2.68
2.66
2.65
2.44
1.77
1.76
1.28
1.26
1.24
1.22
^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Et
Cl
N
Ts
4p
1.01
2.01
1.01
2.07
0.98
4.04
1.00
1.08
1.05
3.19
1.00
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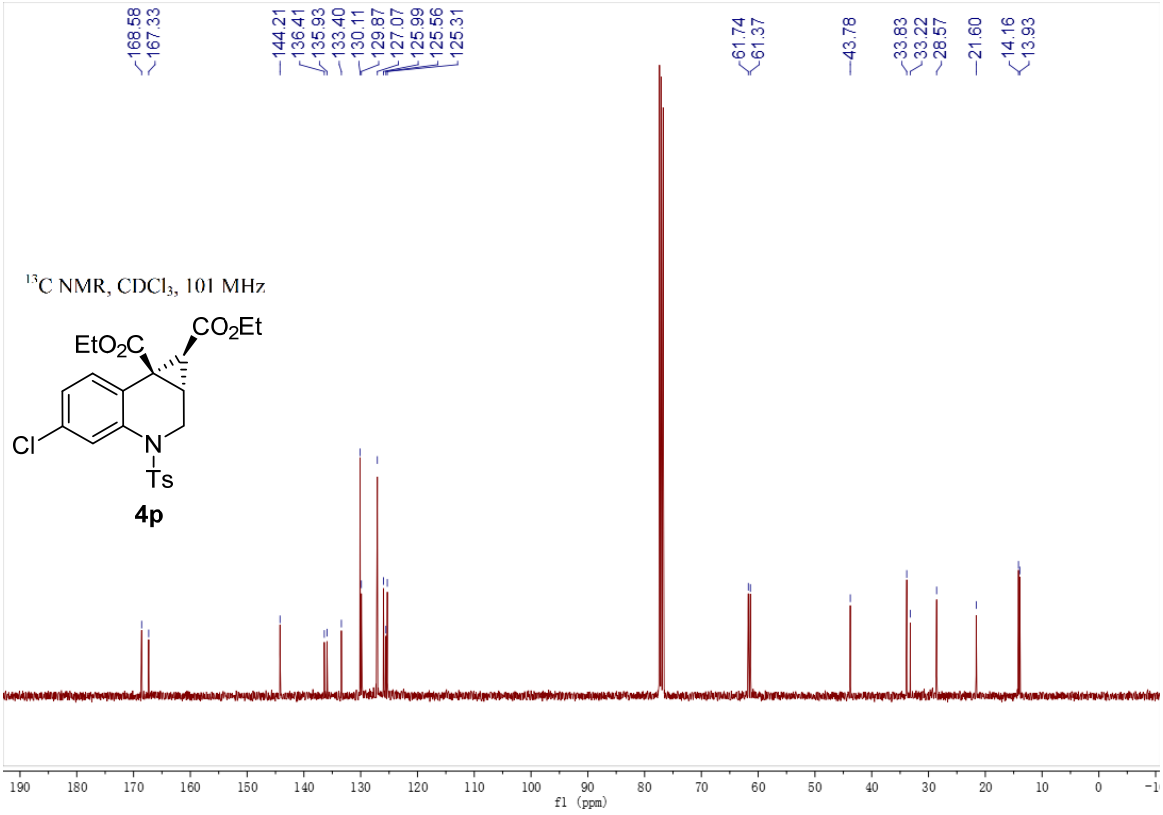
f1 (ppm)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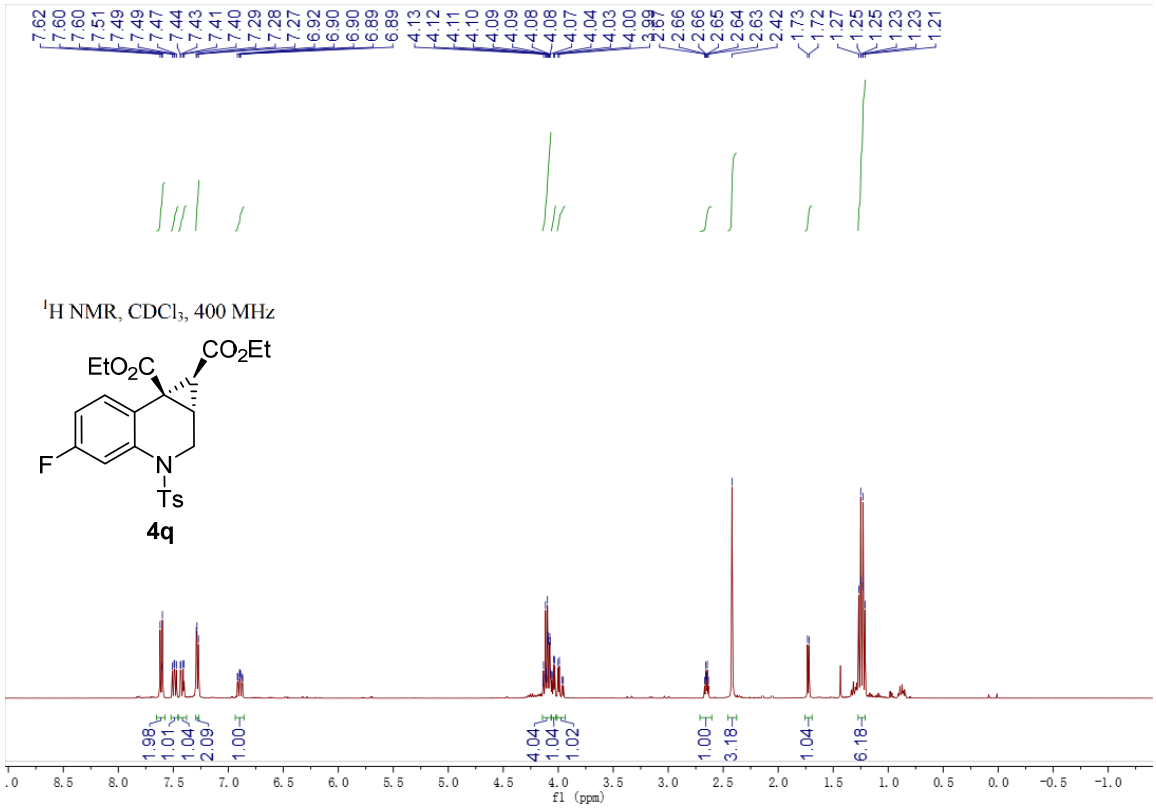
125.99
125.56
125.31
61.74
61.37
43.78
33.83
33.22
28.57
21.60
14.16
13.93
^{13}C NMR, CDCl$_3$, 101 MHz
EtO$_2$C
CO$_2$Et
Cl
N
Ts
4p
f1 (ppm)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7.27
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6.90
6.89
6.89
4.13
4.12
4.11
4.10
4.09
4.09
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2.63
2.42
1.73
1.72
1.27
1.25
1.25
1.23
1.23
1.21
1H NMR, CDCl3, 400 MHz
EtO2C
CO2Et
F
N
Ts
4q
1.98
1.01
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1.00
4.04
1.04
1.02
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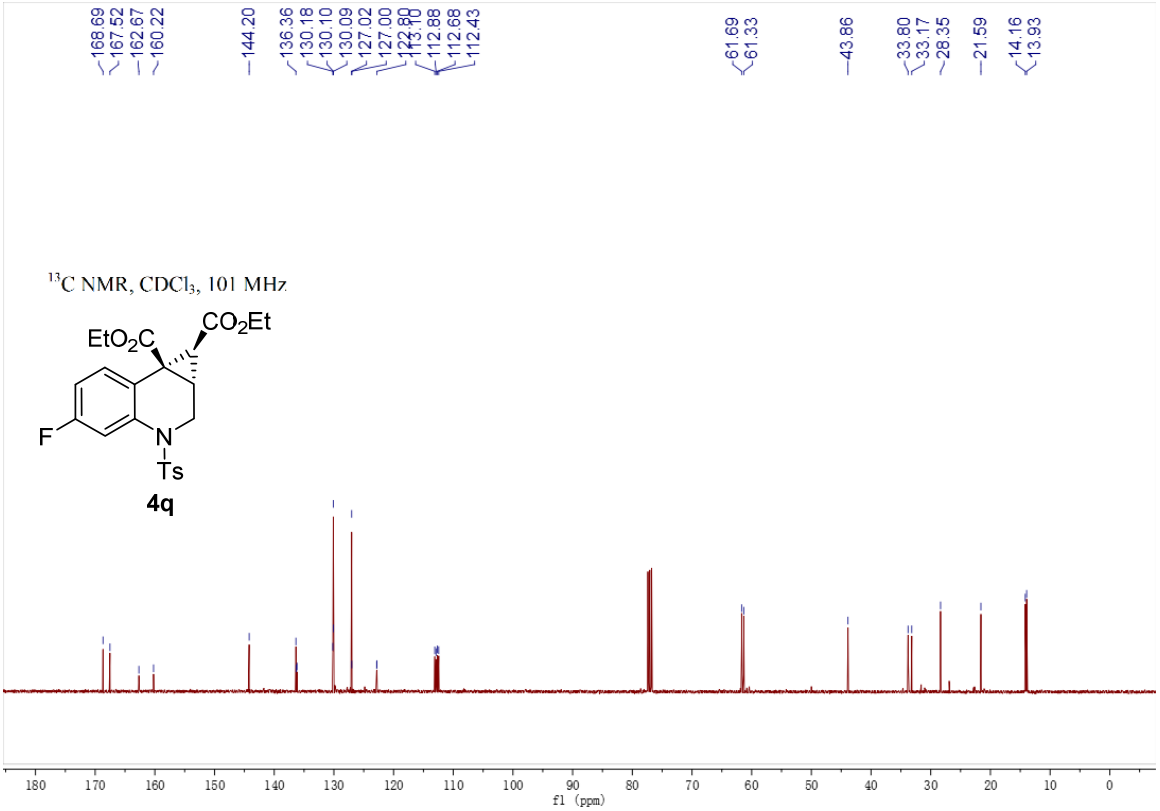
6.18
f1 (ppm)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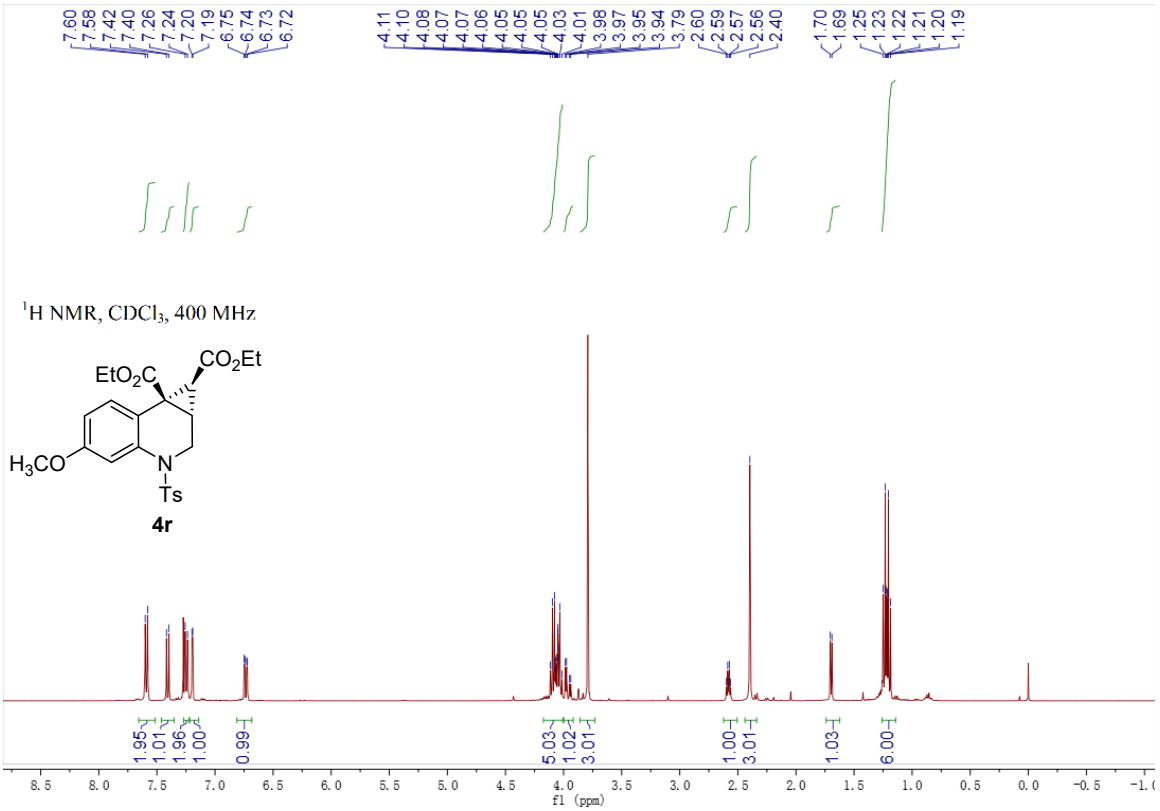
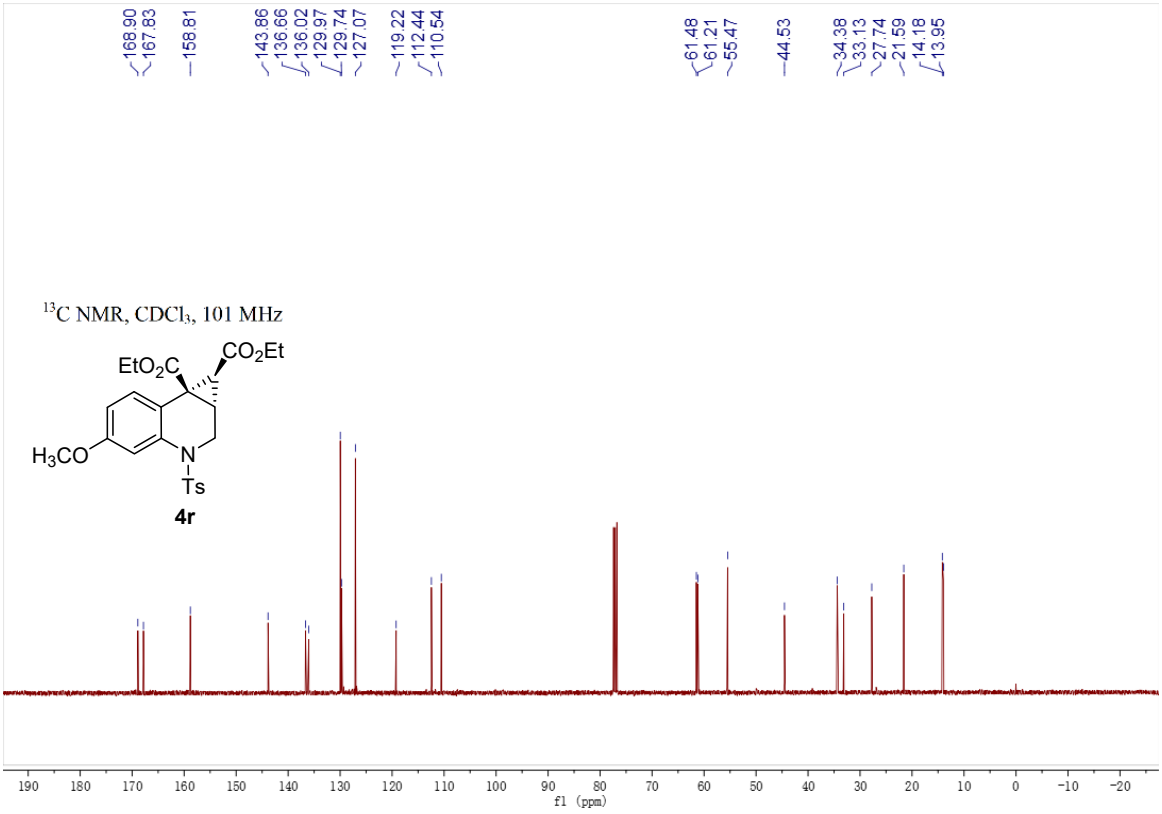
112.68
112.43
61.69
61.33
43.86
33.80
33.17
28.35
21.59
14.16
13.93
13C NMR, CDCl3, 101 MHz
EtO2C
CO2Et
F
N
Ts
4q
f1 (ppm)


7.60
7.58
7.42
7.40
7.26
7.24
7.20
7.19
6.75
6.74
6.73
6.72
4.11
4.10
4.08
4.07
4.07
4.06
4.05
4.05
4.03
4.01
3.98
3.97
3.95
3.94
3.79
2.60
2.59
2.57
2.56
2.40
1.70
1.69
1.25
1.23
1.22
1.21
1.20
1.19
1H NMR, CDCl3, 400 MHz
EtO2C
CO2Et
H3CO
N
Ts
4r
1.95
1.01
1.96
1.00
0.99
5.03
1.02
3.01
1.00
3.01
1.03
6.00
f1 (ppm)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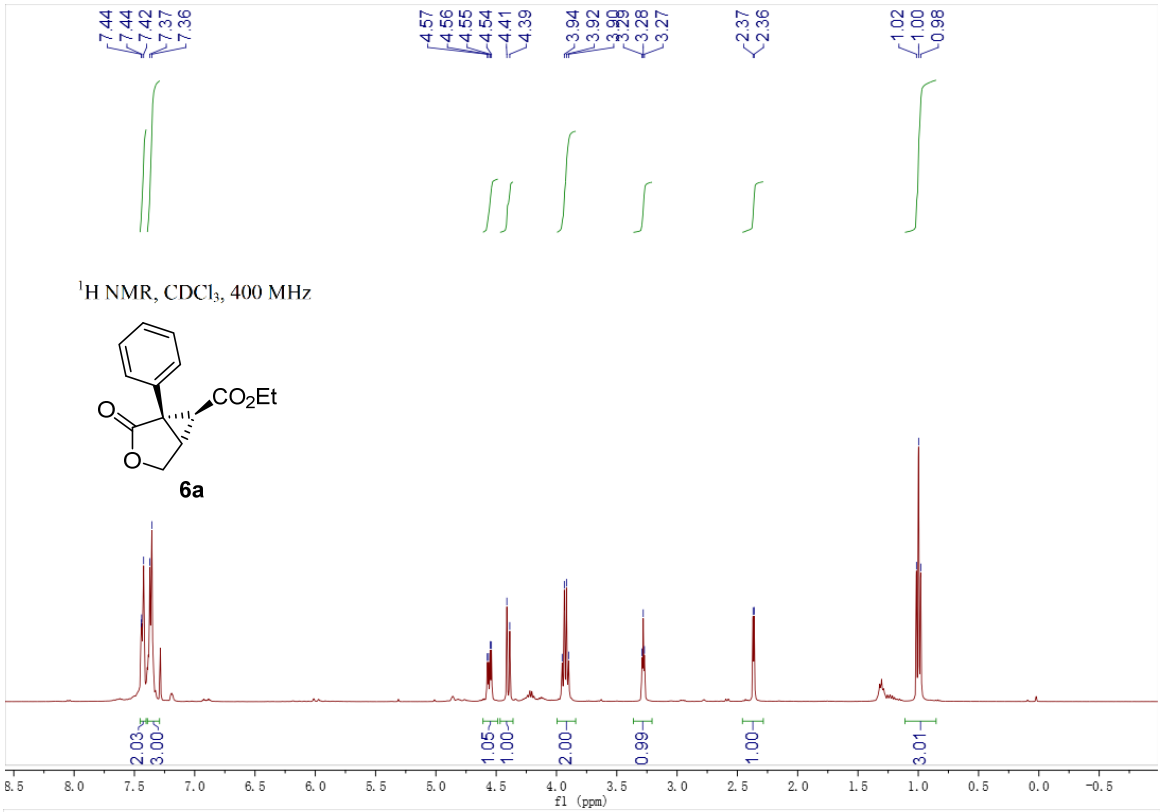
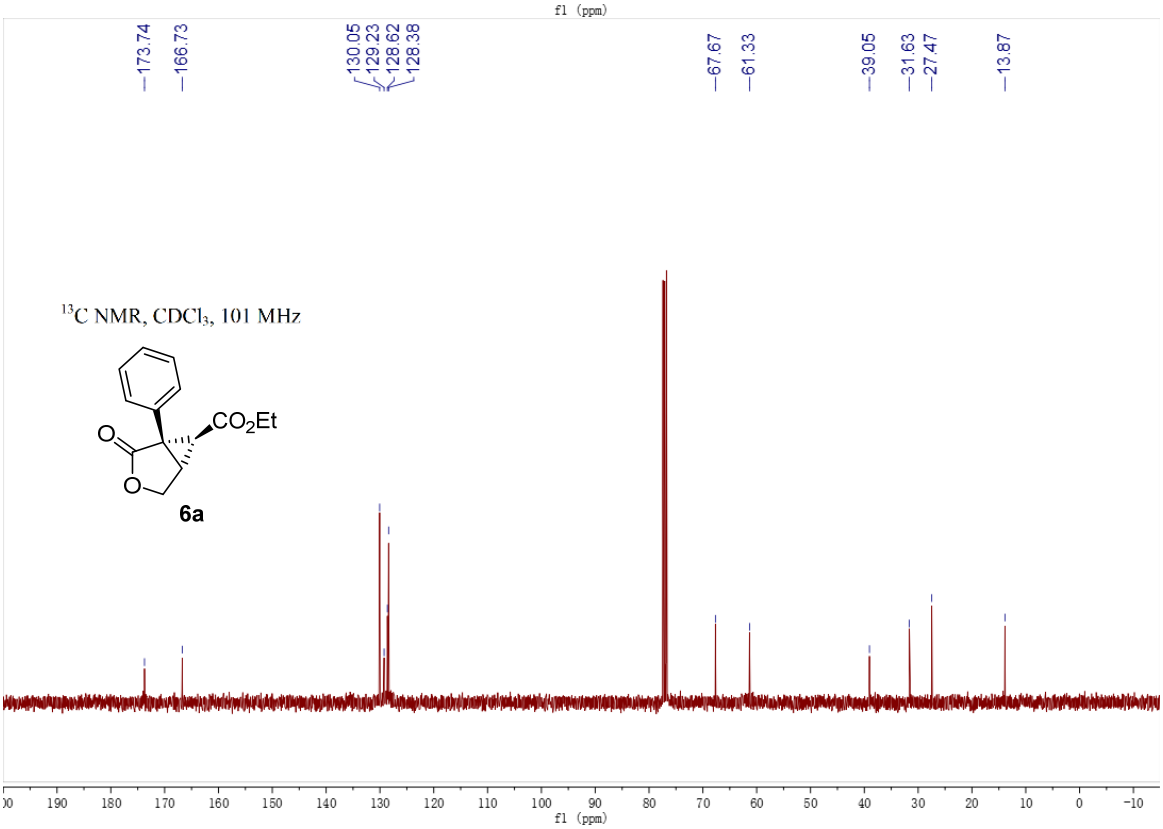
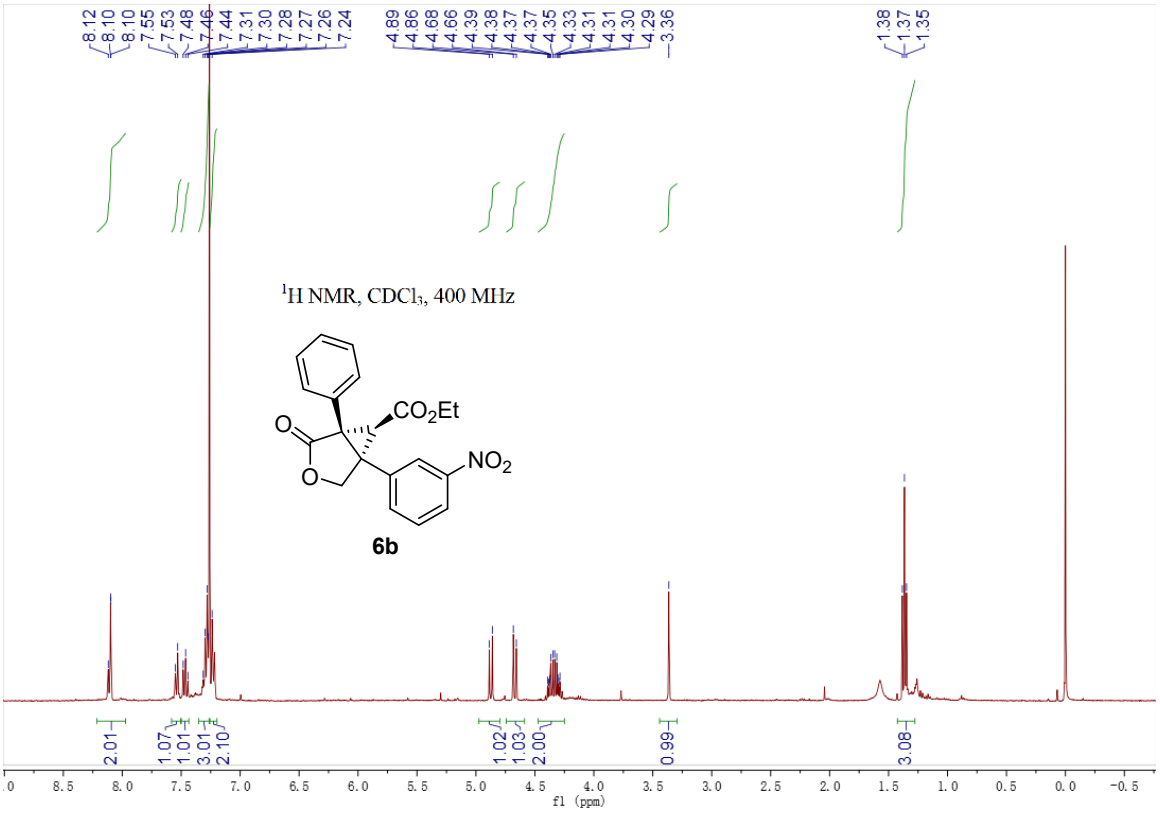
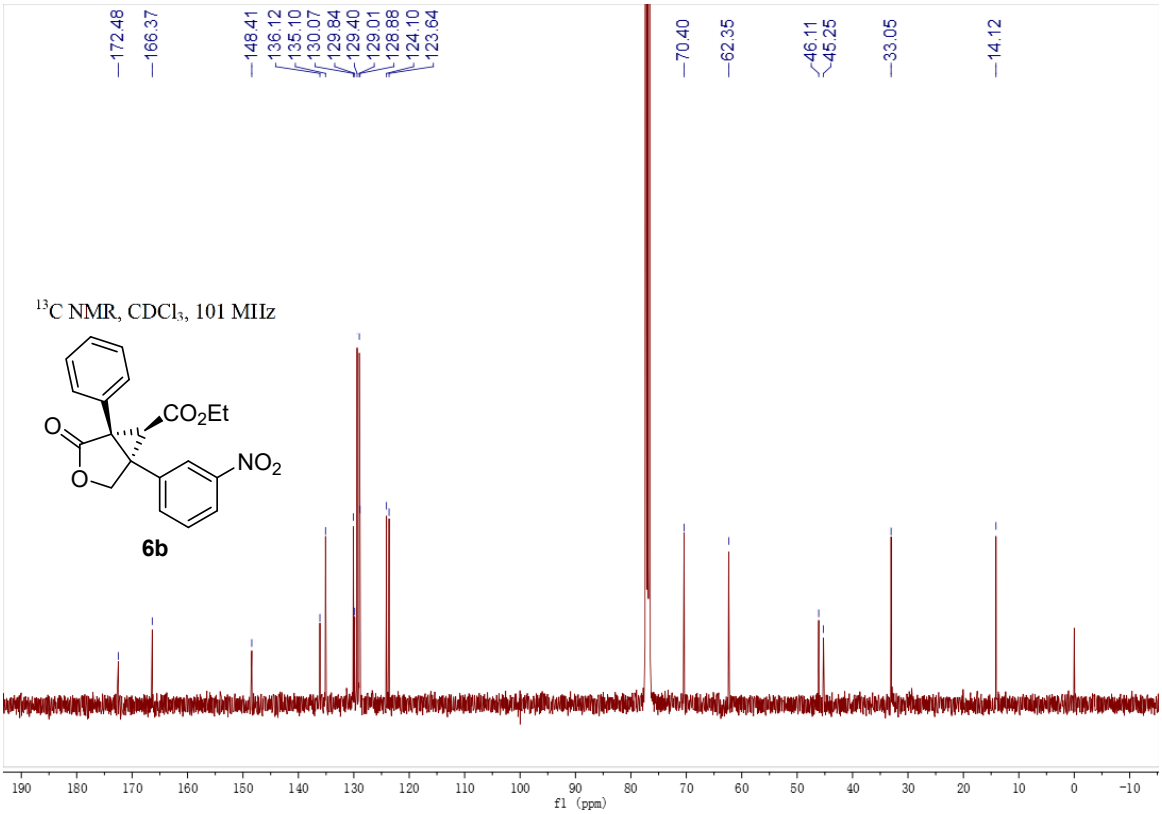
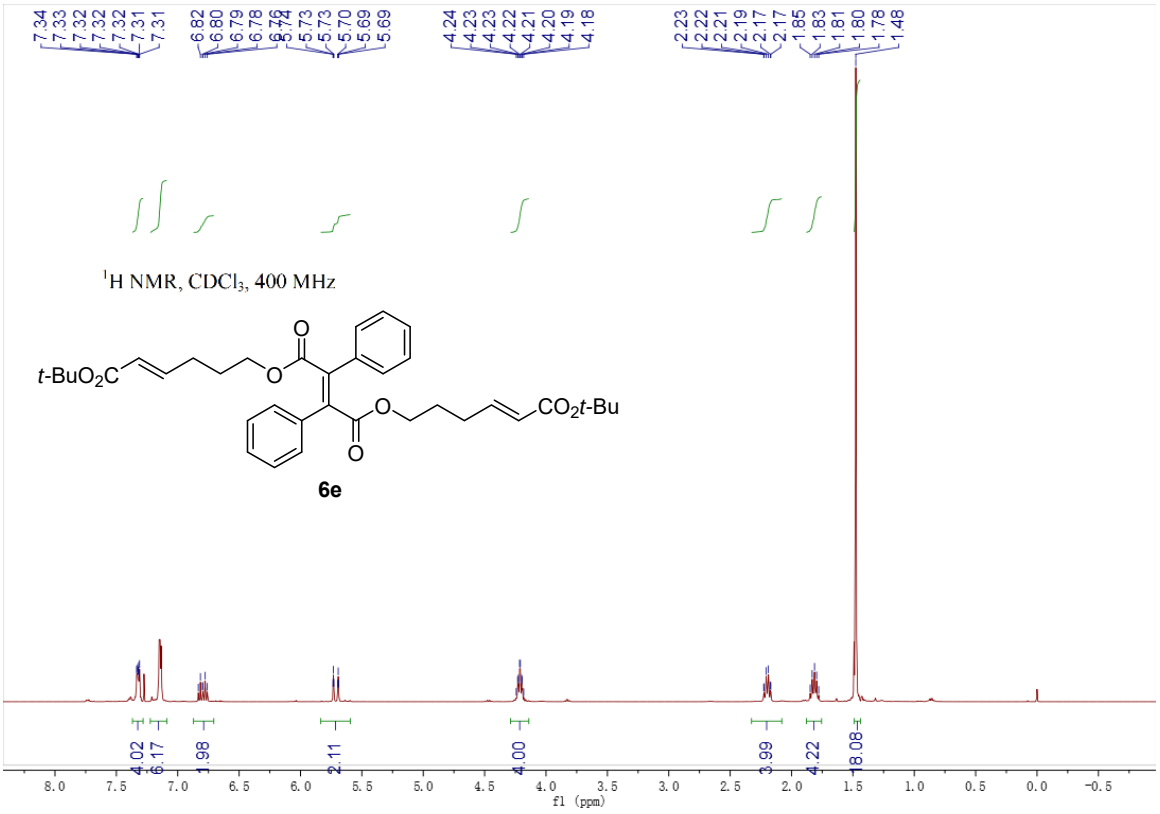
167.83
158.81
143.86
136.66
136.02
129.97
129.74
127.07
119.22
112.44
110.54
61.48
61.21
55.47
44.53
34.38
33.13
27.74
21.59
14.18
13.95
13C NMR, CDCl3, 101 MHz
EtO2C
CO2Et
H3CO
N
Ts
4r
f1 (ppm)


7.44
7.44
7.42
7.37
7.36
4.57
4.56
4.55
4.54
4.41
4.39
3.94
3.92
3.28
3.27
2.37
2.36
1.02
1.00
0.98
^{1}H NMR, CDCl$_3$, 400 MHz
CO$_2$Et
6a
2.03
3.00
1.05
1.00
2.00
0.99
1.00
3.01
f1 (ppm)


173.74
166.73
130.05
129.23
128.62
128.38
67.67
61.33
39.05
31.63
27.47
13.87
^{13}C NMR, CDCl$_3$, 101 MHz
CO$_2$Et
6a
f1 (ppm)

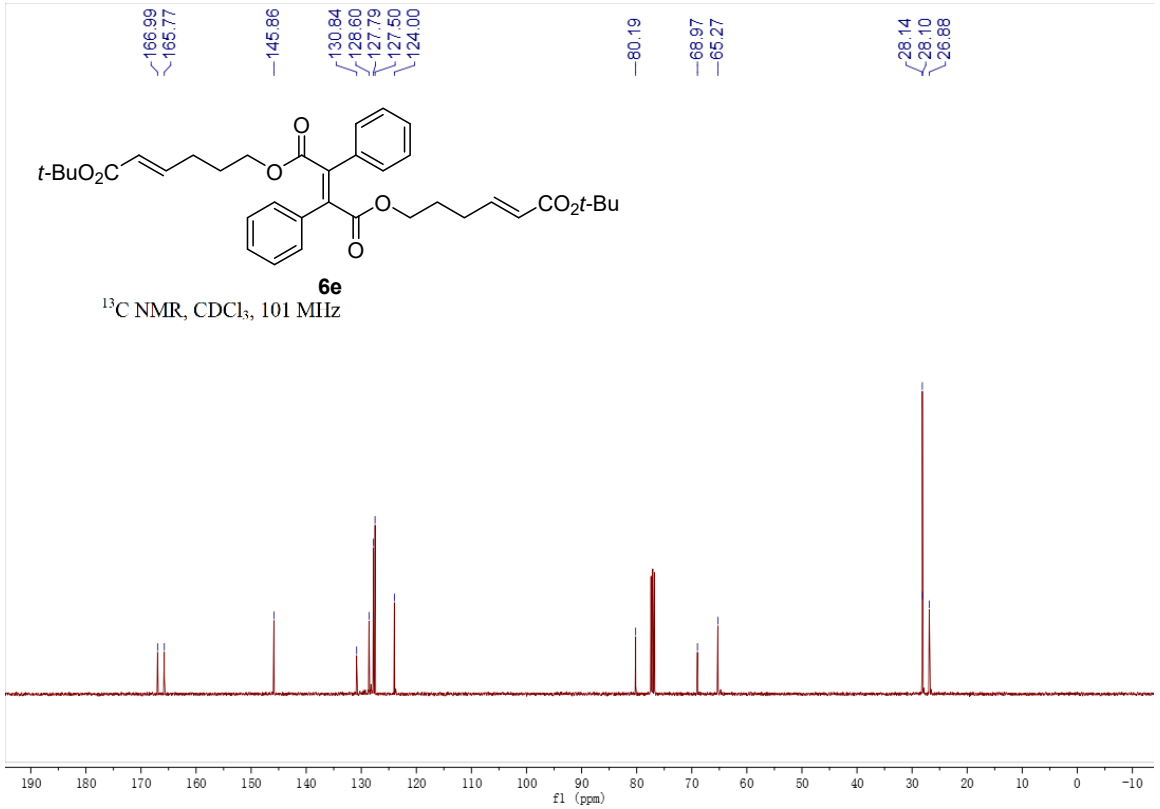

8.12
8.10
8.10
7.55
7.53
7.48
7.46
7.44
7.31
7.30
7.28
7.27
7.26
7.24
4.89
4.86
4.68
4.66
4.39
4.38
4.37
4.37
4.35
4.33
4.31
4.31
4.30
4.29
3.36
1.38
1.37
1.35
^{1}H NMR, $CDCl_3$, 400 MHz
CO_2Et
NO_2
O
O
6b
2.01
1.07
1.01
3.01
2.10
1.02
1.03
2.00
0.99
3.08
f1 (ppm)


172.48
166.37
148.41
136.12
135.10
130.07
129.84
129.40
129.01
128.88
124.10
123.64
70.40
62.35
46.11
45.25
33.05
14.12
^{13}C NMR, $CDCl_3$, 101 MIIz
CO_2Et
NO_2
O
O
6b
f1 (ppm)



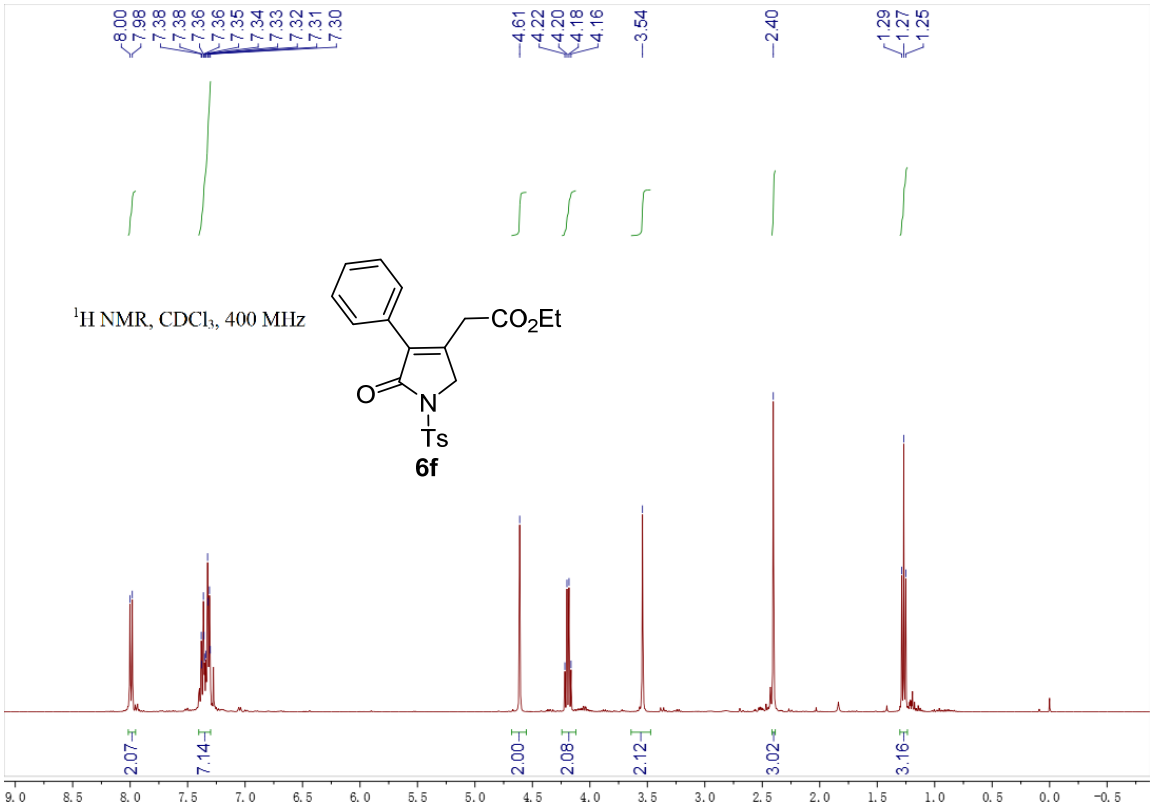
^{1}H NMR, $CDCl_3$, 400 MHz

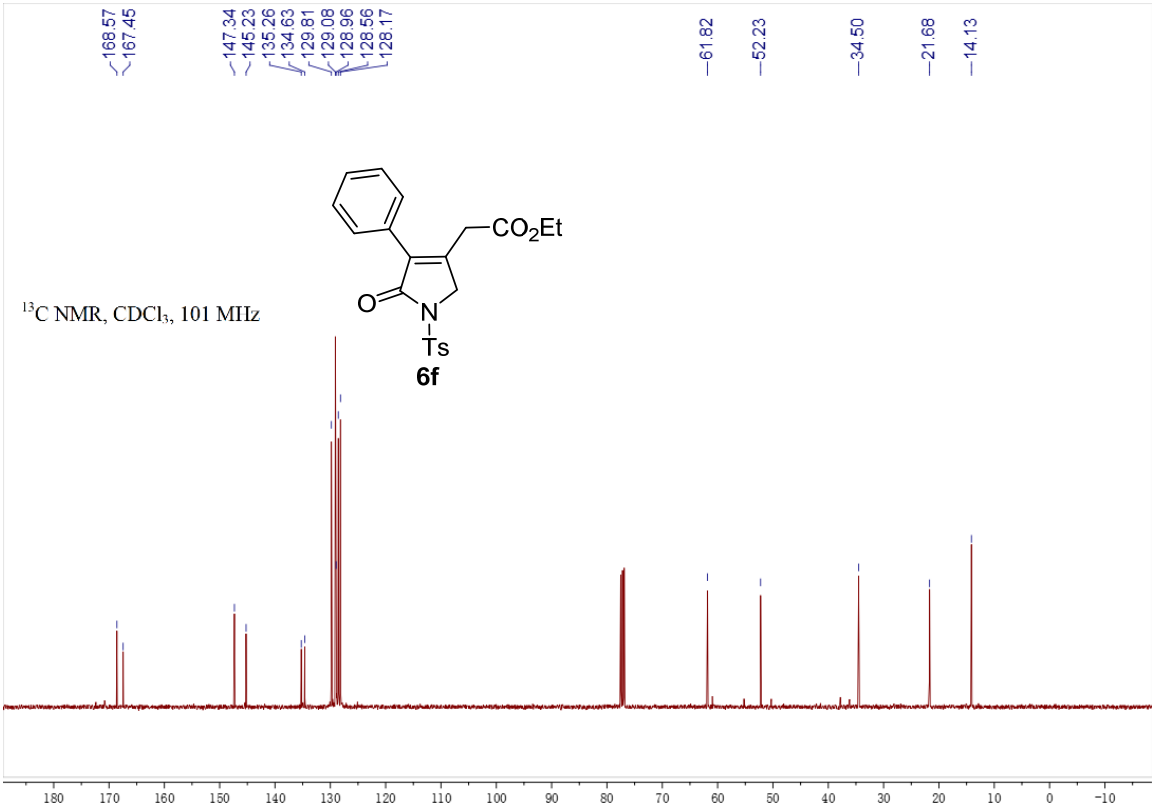
6e

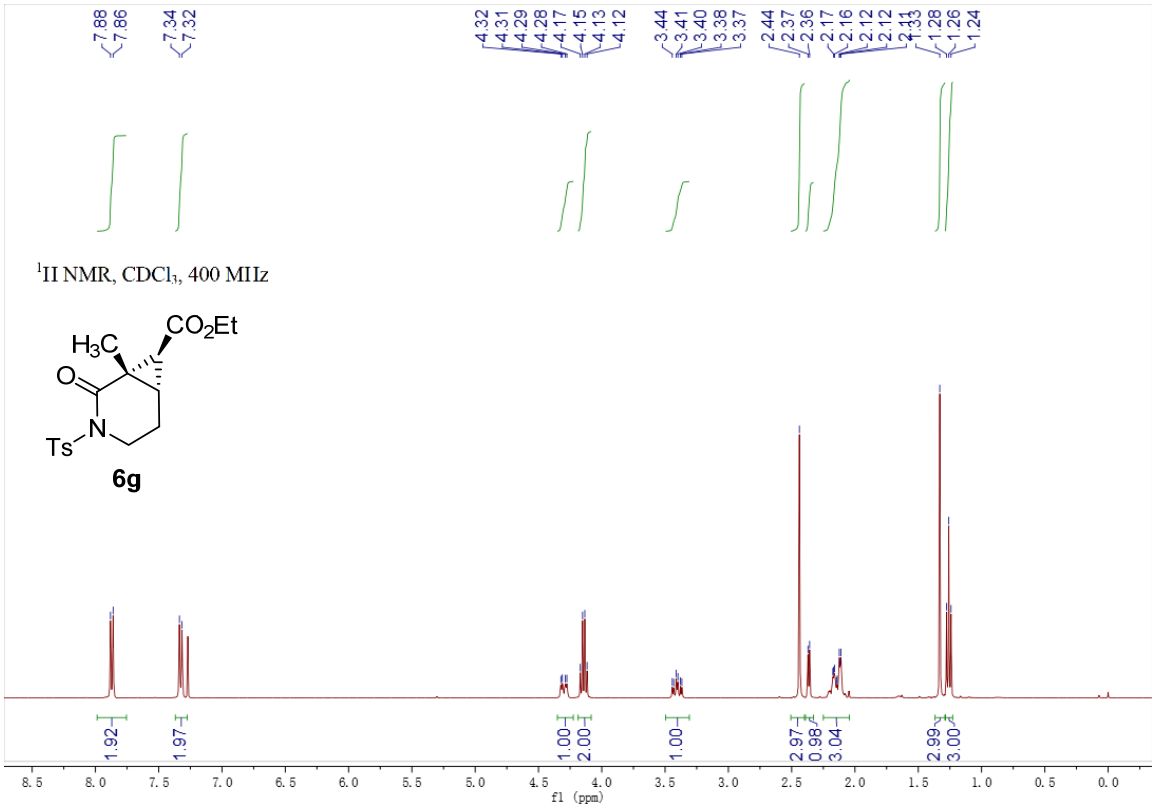


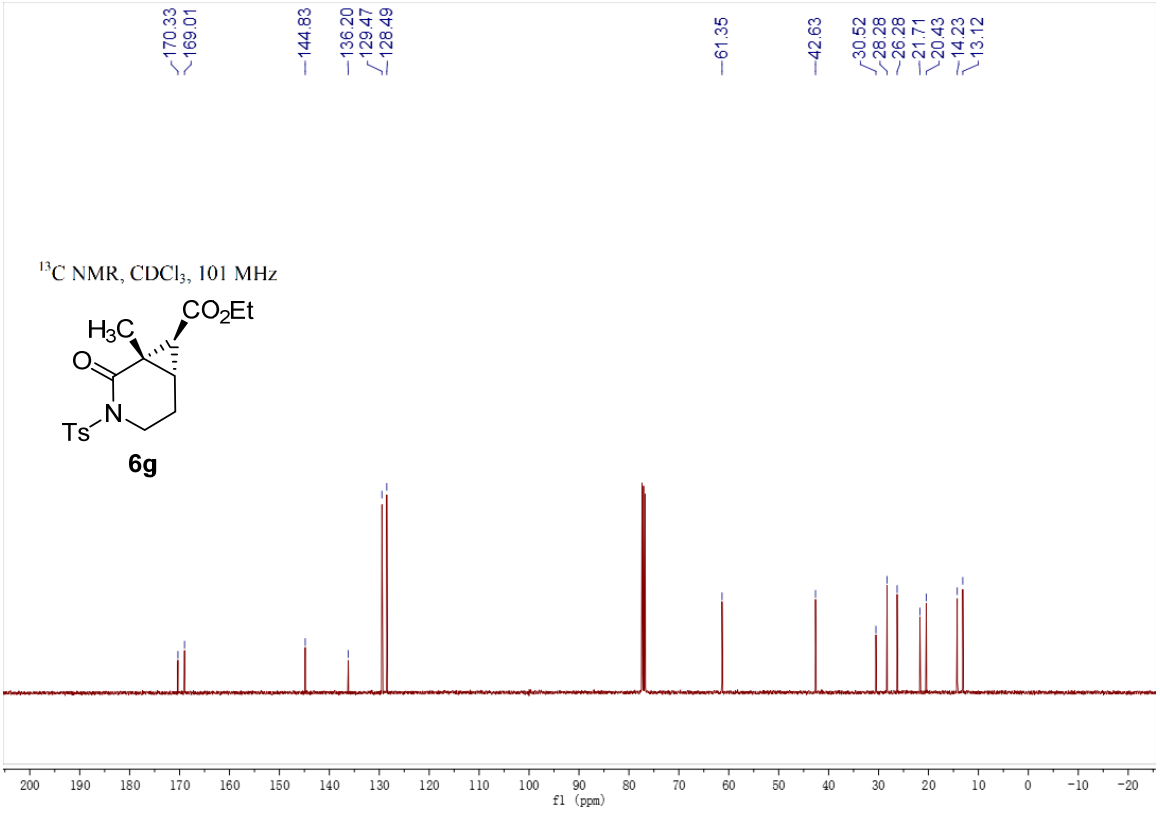
6e

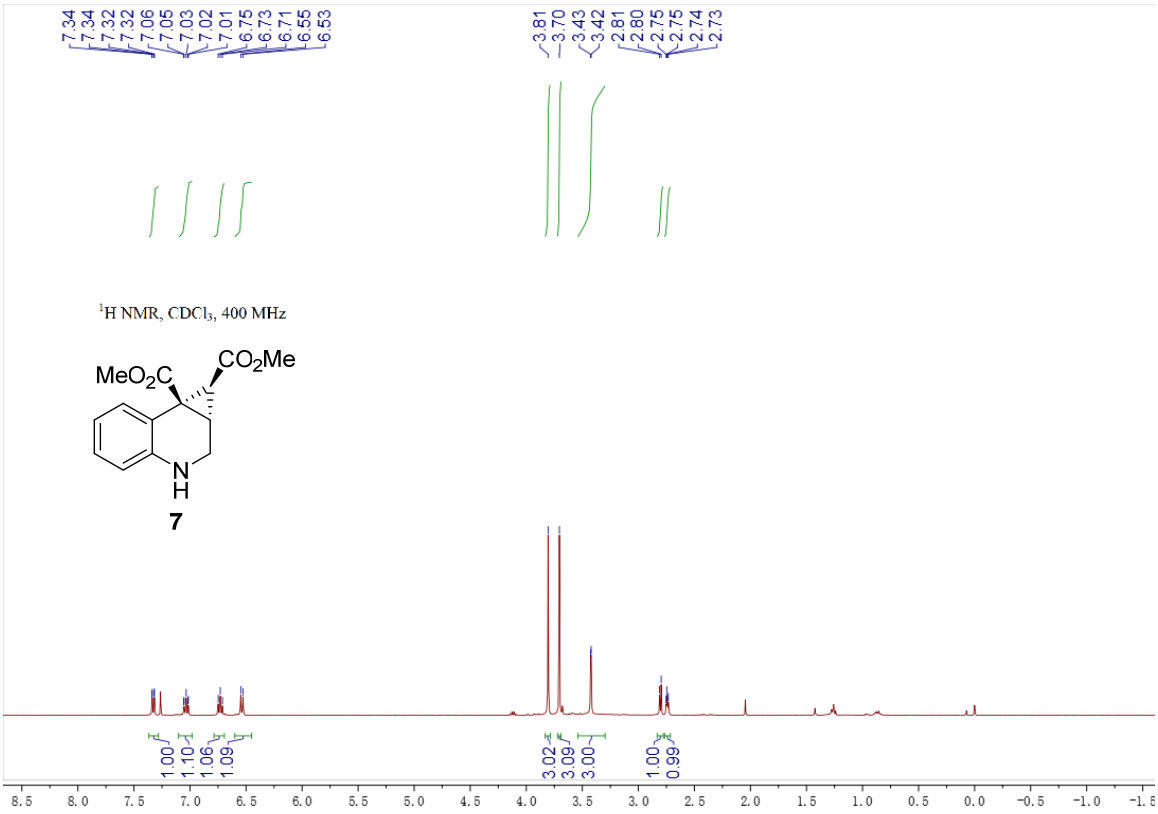
^{13}C NMR, $CDCl_3$, 101 MHz

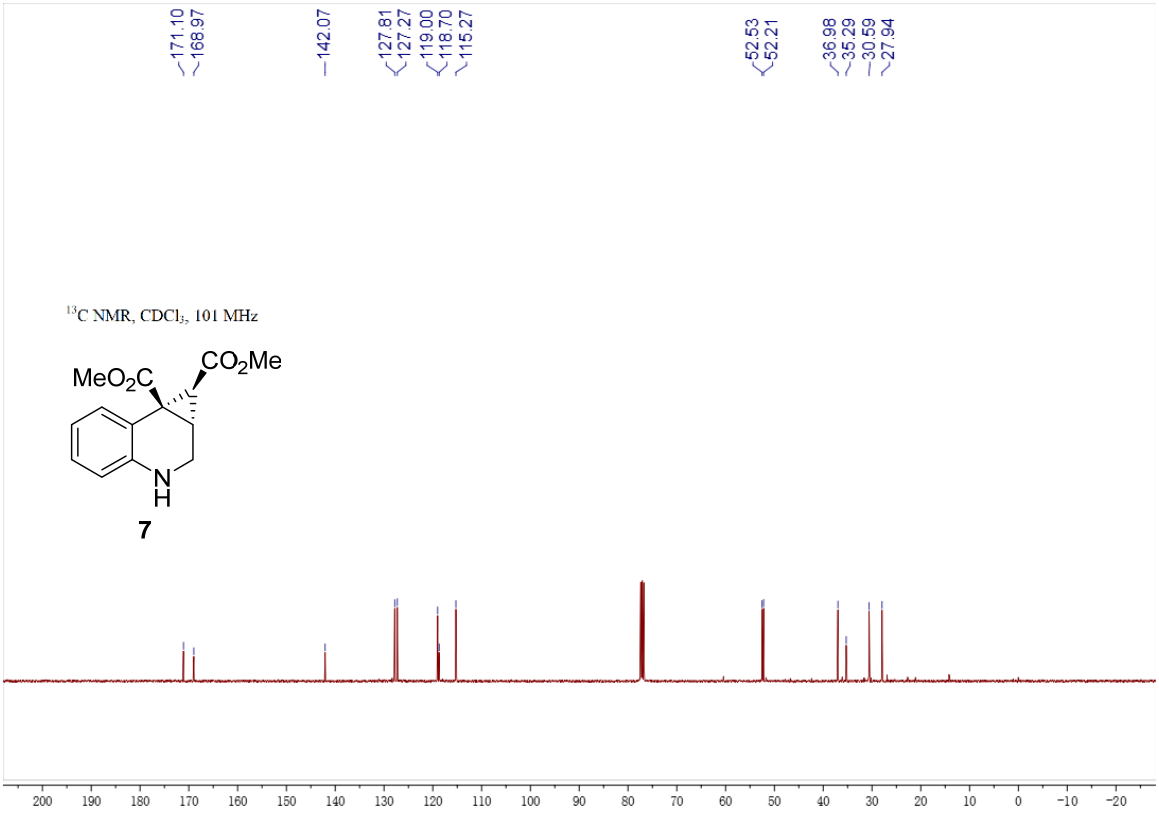

8.00
7.98
7.38
7.38
7.36
7.36
7.35
7.34
7.33
7.32
7.31
7.30
4.61
4.22
4.20
4.18
4.16
3.54
2.40
1.29
1.27
1.25
^{1}H NMR, CDCl$_3$, 400 MHz
CO$_2$Et
O
N
Ts
6f
2.07
7.14
2.00
2.08
2.12
3.02
3.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

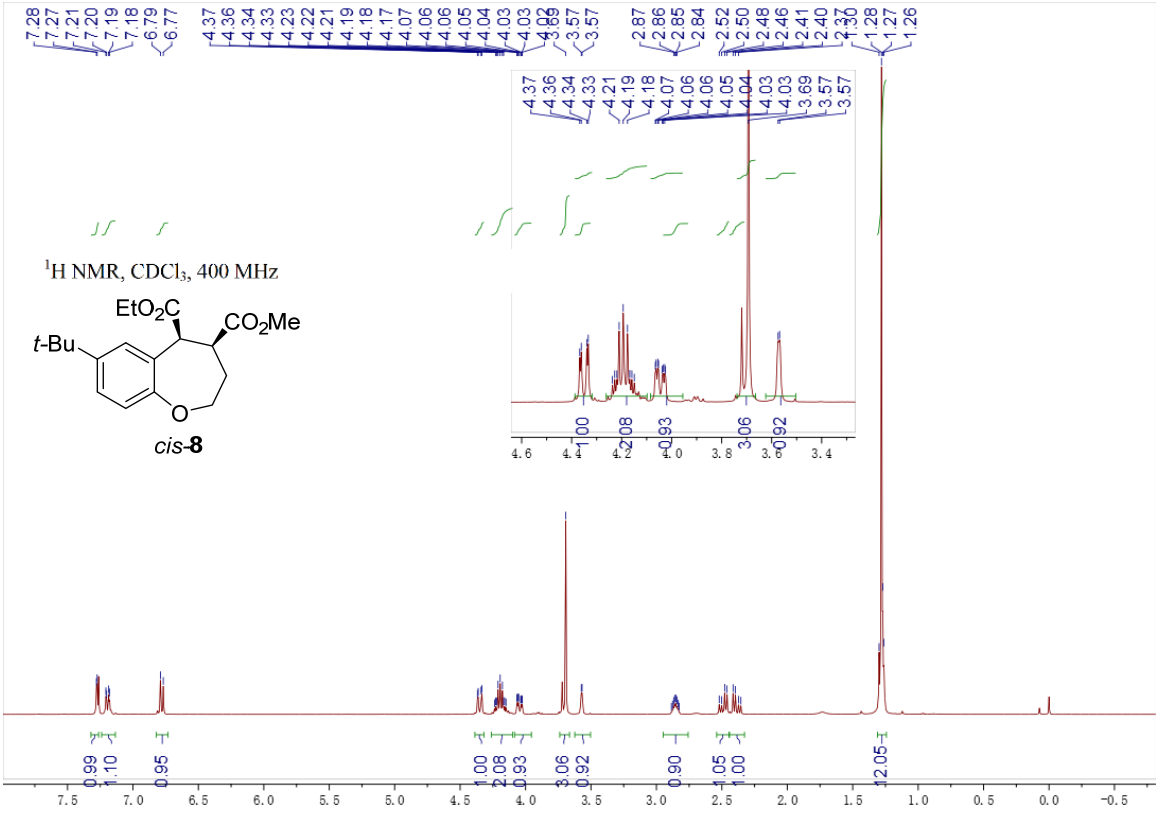

168.57
167.45
147.34
145.23
135.26
134.63
129.81
129.08
128.96
128.56
128.17
61.82
52.23
34.50
21.68
14.13
^{13}C NMR, CDCl$_3$, 101 MHz
CO$_2$Et
O
N
Ts
6f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

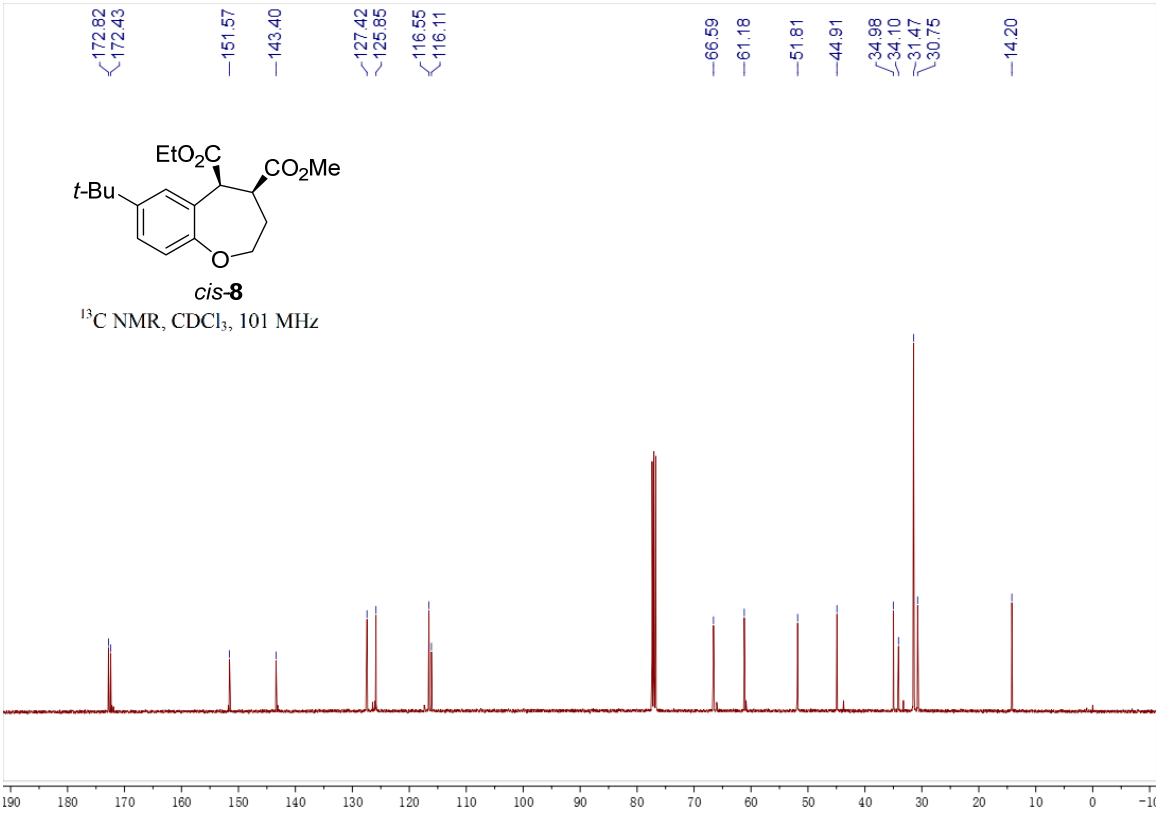

7.88
7.86
7.34
7.32
4.32
4.31
4.29
4.28
4.17
4.15
4.13
4.12
3.44
3.41
3.40
3.38
3.37
2.44
2.37
2.36
2.17
2.16
2.12
2.12
2.11
1.33
1.28
1.26
1.24
1H NMR, CDCl3, 400 MHz
CO2Et
H3C
O
N
Ts
6g
1.92
1.97
1.00
2.00
1.00
2.97
0.98
3.04
2.99
3.00
f1 (ppm)

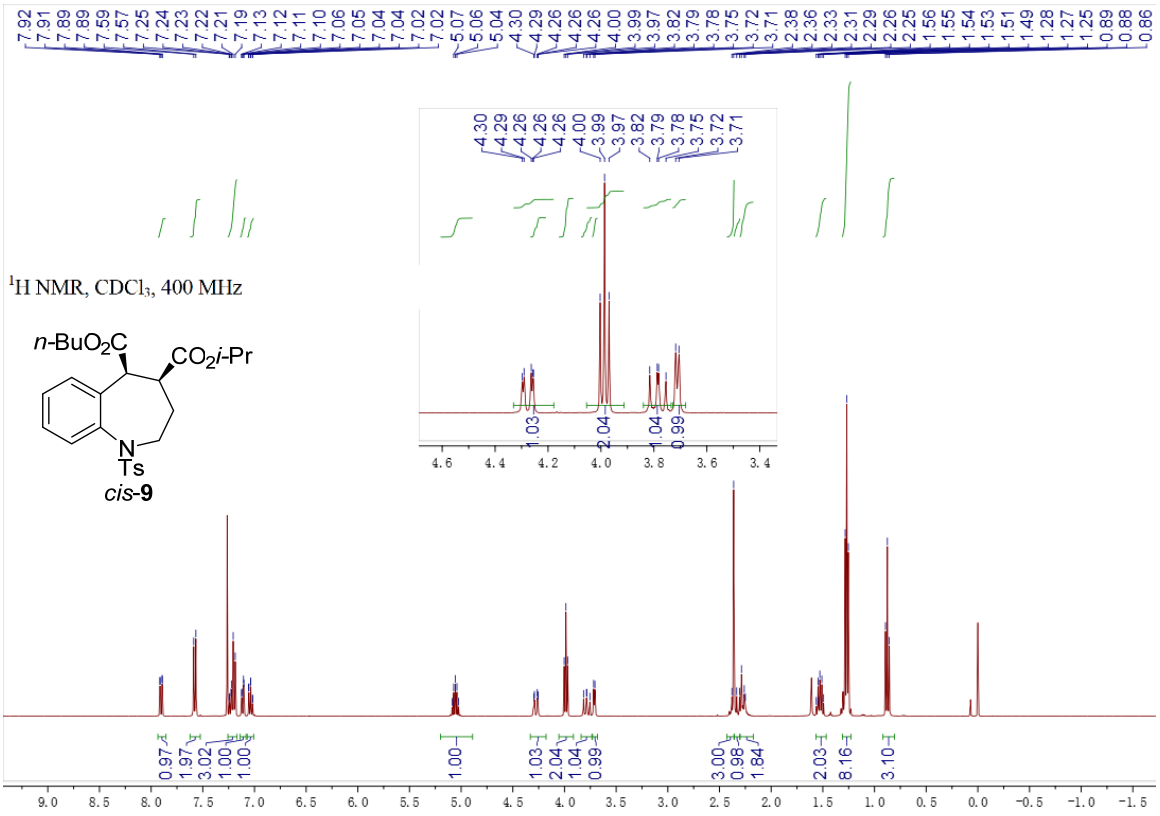

170.33
169.01
144.83
136.20
129.47
128.49
61.35
42.63
30.52
28.28
26.28
21.71
20.43
14.23
13.12
13C NMR, CDCl3, 101 MHz
CO2Et
H3C
O
N
Ts
6g
f1 (ppm)

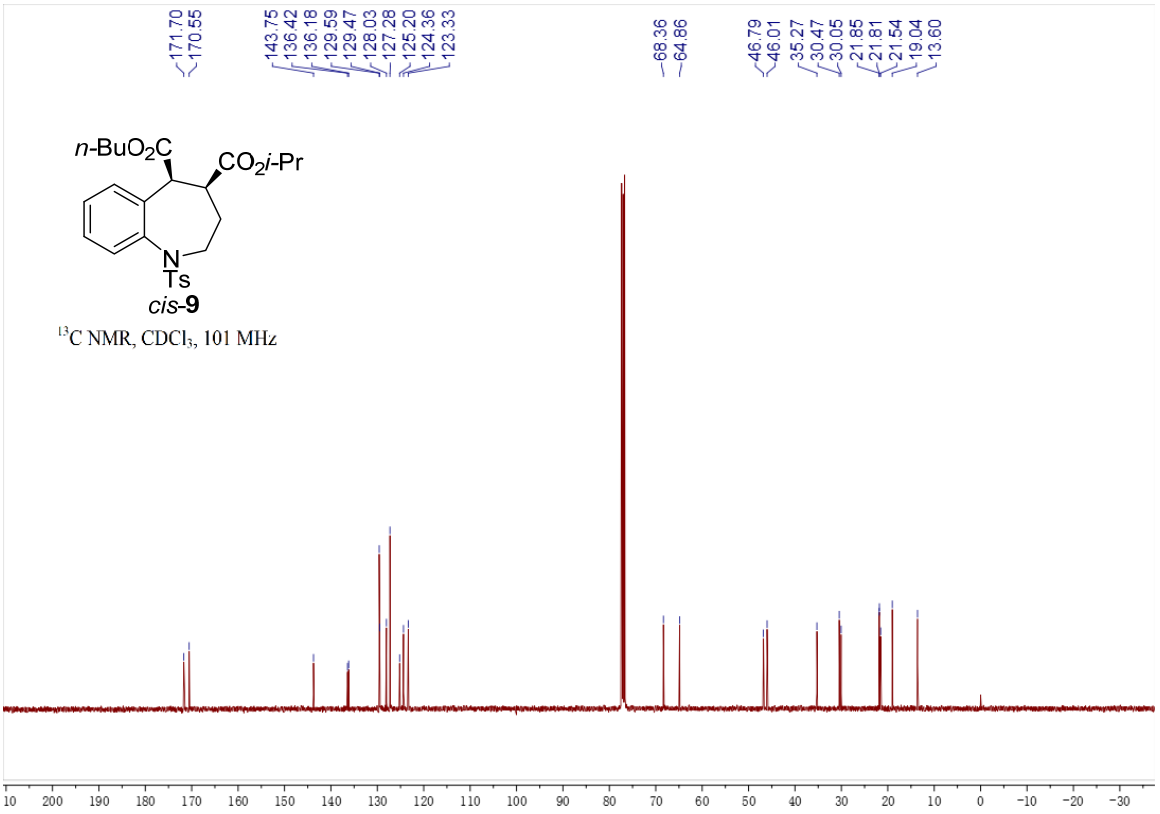

7.34
7.34
7.32
7.32
7.06
7.05
7.03
7.02
7.01
6.75
6.73
6.71
6.55
6.53
3.81
3.70
3.43
3.42
2.81
2.80
2.75
2.75
2.74
2.73
1H NMR, CDCl3, 400 MHz
MeO2C
CO2Me
N
H
7
1.00
1.10
1.06
1.09
3.02
3.09
3.00
1.00
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

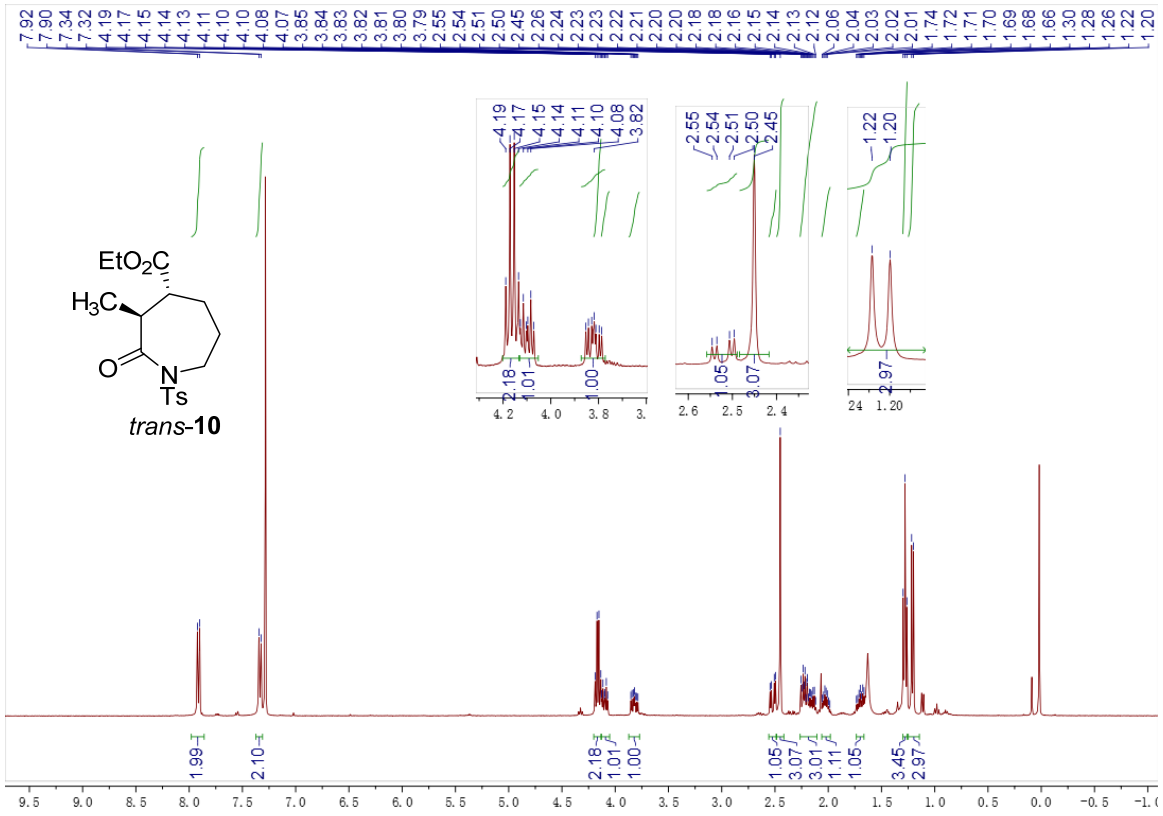

171.10
168.97
142.07
127.81
127.27
119.00
118.70
115.27
52.53
52.21
36.98
35.29
30.59
27.94
13C NMR, CDCl3, 101 MHz
MeO2C
CO2Me
N
H
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

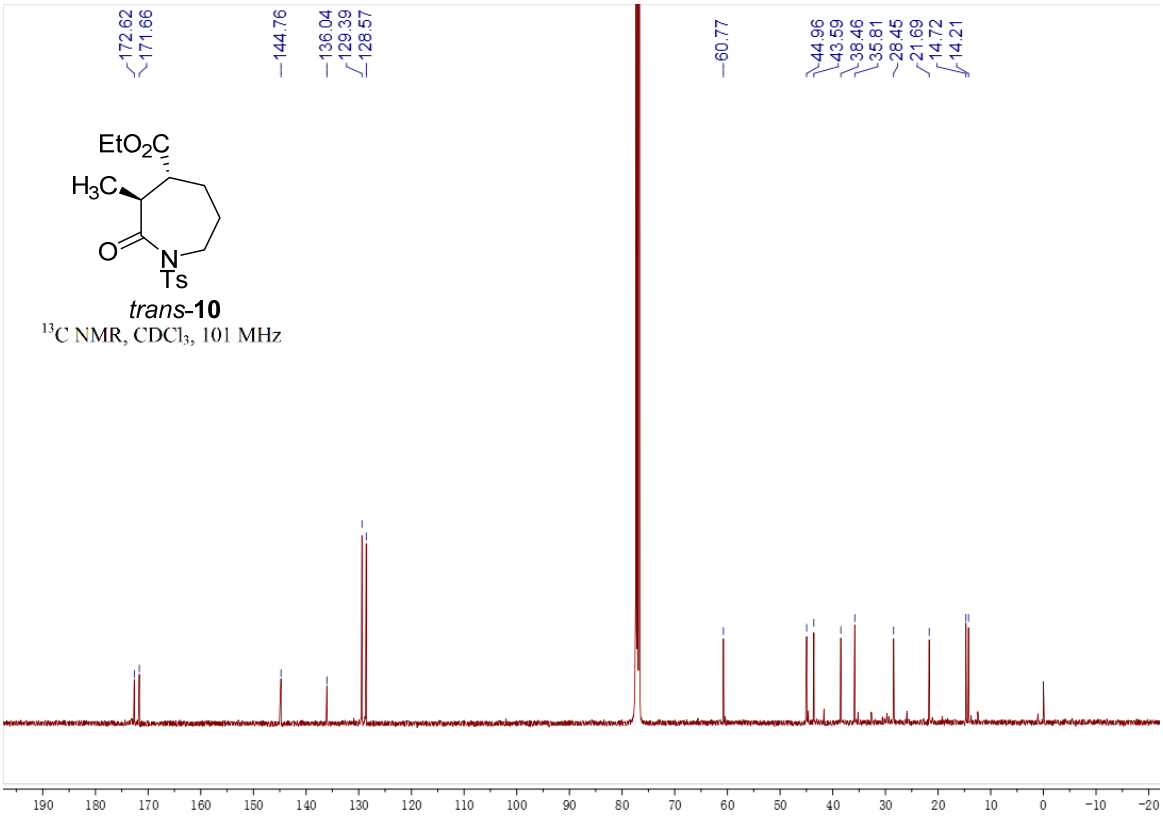

^{1}H NMR, CDCl$_3$, 400 MHz
EtO$_2$C
CO$_2$Me
t-Bu
O
cis-8


EtO$_2$C
CO$_2$Me
t-Bu
O
cis-8
^{13}C NMR, CDCl$_3$, 101 MHz


^{1}H NMR, CDCl$_3$, 400 MHz
n-BuO2C
CO2i-Pr
N
Ts
cis-9

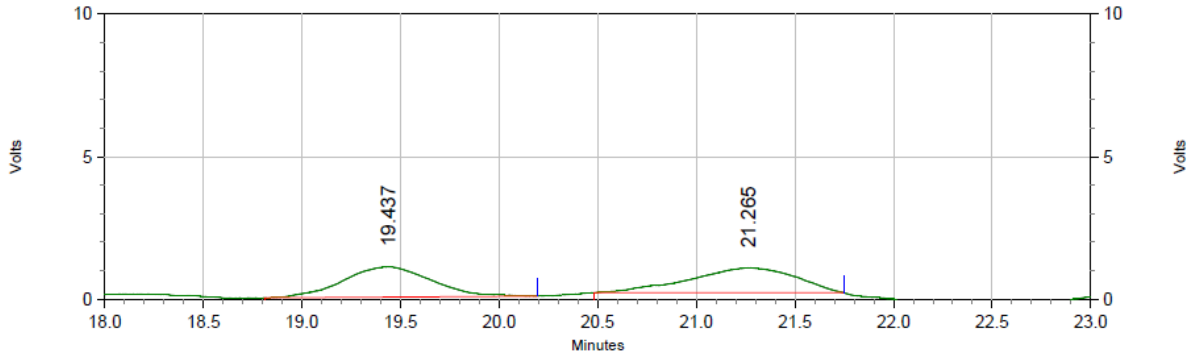

n-BuO2C
CO2i-Pr
N
Ts
cis-9
^{13}C NMR, CDCl$_3$, 101 MHz


EtO2C
H3C
O
N
Ts
trans-10


EtO2C
H3C
O
N
Ts
trans-10
13C NMR, CDCl3, 101 MHz

X. Chiral HPLC Analysis of Chiral-2b and 4k

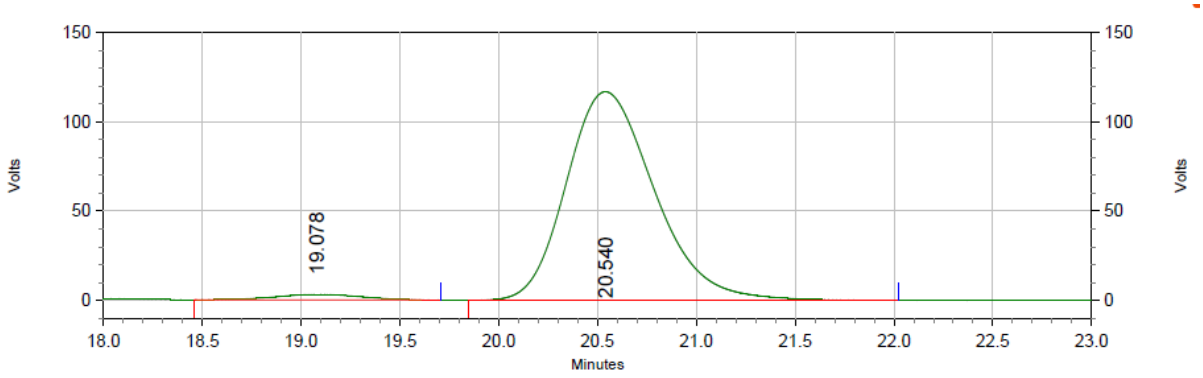
Racemate of **2b**:



UV1000-254nm
Results

Retention	Area	Area%	Height	Height%
19.437	32976	50.203	1055	54.635
21.265	32709	49.797	876	45.365
Totals	65685	100.000	1931	100.000

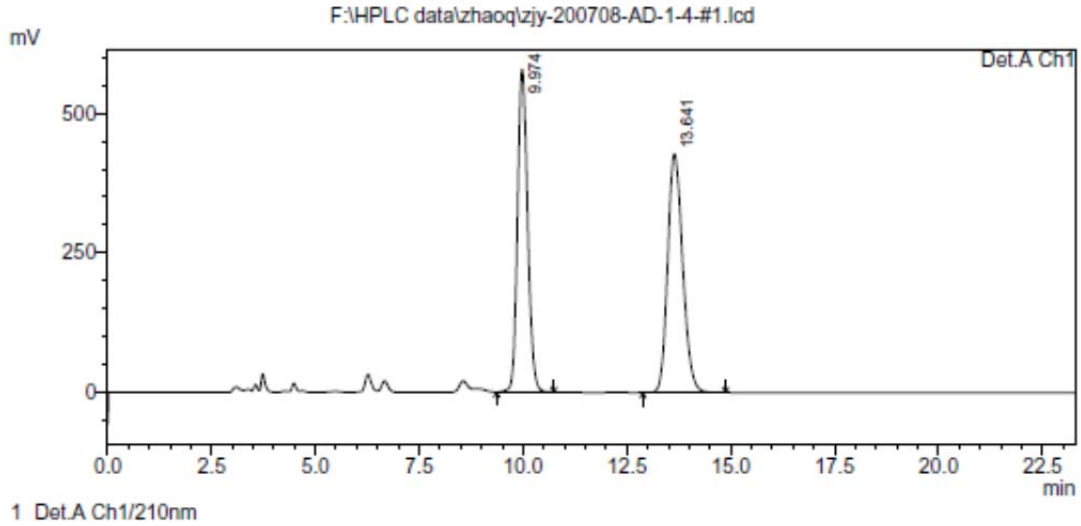
Chiral-2b:



UV1000-254nm
Results

Retention	Area	Area%	Hight	Hight%
19.078	92751	2.498	3080	2.570
20.540	3620541	97.502	116753	97.430
Totals	3713292	100.000	119833	100.000

HPLC Chromatogram of **4k** using a chiral AD column

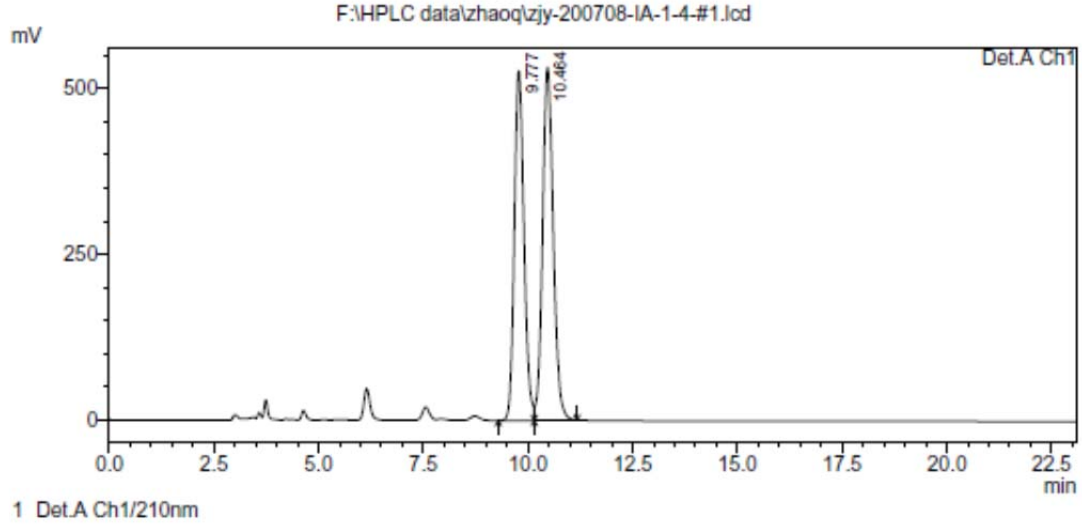


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.974	9829461	578812	47.729	57.501
2	13.641	10764998	427803	52.271	42.499
Total		20594459	1006614	100.000	100.000

HPLC Chromatogram of **4k** using a chiral IA column

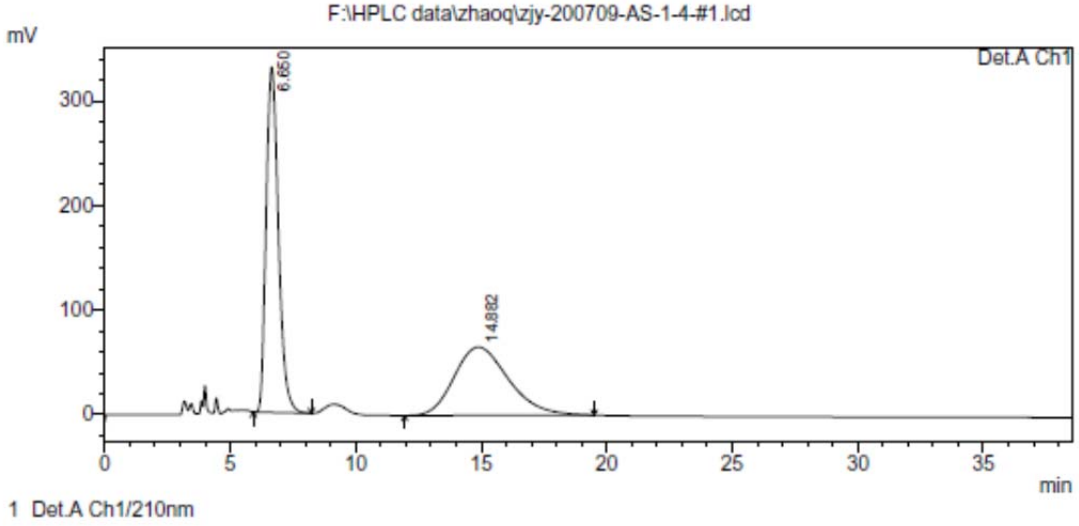


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.777	8455205	526902	47.183	49.763
2	10.464	9464802	531927	52.817	50.237
Total		17920007	1058829	100.000	100.000

HPLC Chromatogram of **4k** using a chiral AS column

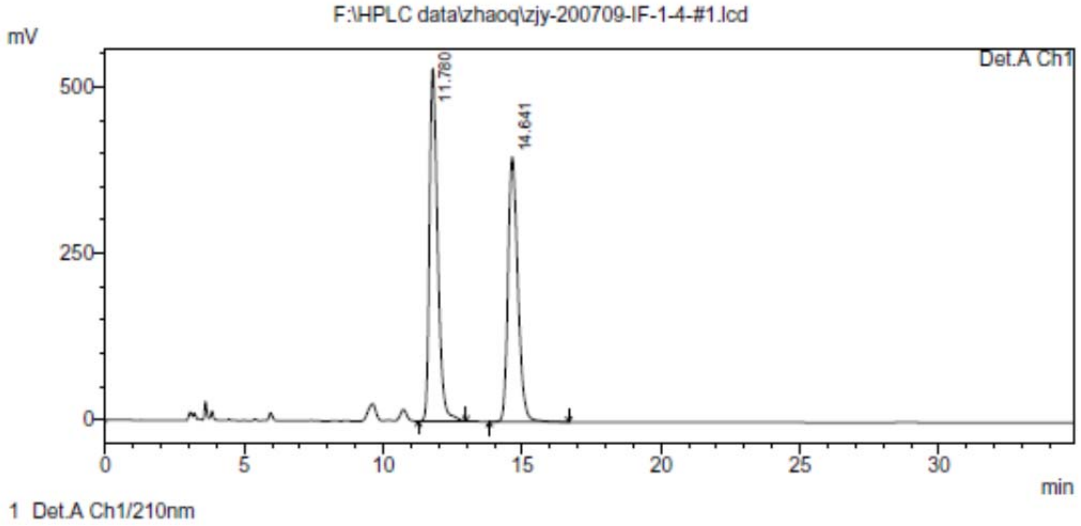


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.650	11255096	330030	53.337	83.474
2	14.882	9846585	65337	46.663	16.526
Total		21101681	395368	100.000	100.000

HPLC Chromatogram of **4k** using a chiral IF column



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.780	10855083	529141	52.538	57.125
2	14.641	9806406	397137	47.462	42.875
Total		20661490	926278	100.000	100.000