Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Relay Photocatalytic Cascade Reaction: Synthesis of Indolo[2,1-*a*]isoquinoline Derivatives *via* Double C(sp^3)-H Bonds Functionalization

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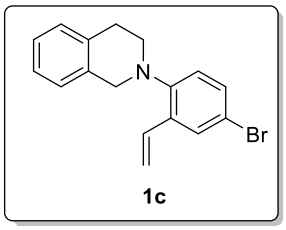
General information

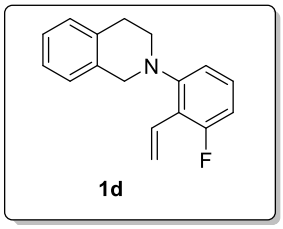
The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were tested by the Bruker AVANCE III-400 spectrometer. Tetramethylsilane (TMS) was selected as the internal reference and chemical shifts (δ) were reported in ppm. The abbreviations of the signal couplings were used in s (singlet); d (doublet); t (triplet) and m (multiplet). The high resolution mass spectra (HRMS) were tested by the ESI mode of the Micromass Q-Tof instrument. IR spectra were detected with the ATR mode of the Nicolet iS50 FT-IR of Thermo Scientific. Chemicals were purchased from chemical suppliers without purification. The 5-W blue LEDs was afforded by the supermarket. All of experiments were carried out under Argon atmosphere unless otherwise explanation. All starting compounds were synthesized according to the literature.[1]

Characterization of unknown starting materials



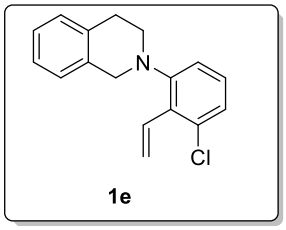
1c

2-(4-bromo-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1c): The compound **1c** was synthesized according the previous literature,[1] as light red oil. IR (neat, cm^{-1}): 2983, 2934, 1736, 1394, 1233, 1043, 937, 812. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 2.4 Hz, 1H), 7.36 – 7.26 (m, 1H), 7.21 – 7.12 (m, 3H), 7.08 – 7.02 (m, 1H), 7.01 – 6.89 (m, 2H), 5.69 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.26 (dd, *J* = 11.2, 1.2 Hz, 1H), 4.09 (s, 2H), 3.21 (t, *J* = 6.0 Hz, 2H), 2.96 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.6 , 134.8 , 134.5, 134.4, 133.3, 131.2, 129.6, 129.0, 126.4, 126.4, 125.9, 120.7, 116.1, 114.9, 54.3, 50.6, 29.4. HRMS (ESI) Calcd for $C_{17}H_{17}BrN$ $[M+H]^{+}$: 314.0539, 316.0518; found: 314.0533, 316.0517.



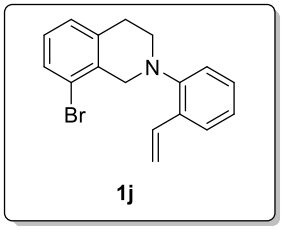
1d

2-(3-fluoro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1d): The compound **1d** was synthesized according the previous literature,[1] as light red oil. IR (neat, cm^{-1}): 2984, 2941, 1736, 1372, 1233, 1043, 937, 847. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 2.4 Hz, 1H), 7.33 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.25 – 7.11 (m, 3H), 7.10 – 7.03 (m, 1H), 7.03 – 6.90 (m, 2H), 5.70 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.27 (dd, *J* = 11.2, 1.2 Hz, 1H), 4.11 (s, 2H), 3.24 (t, *J* = 6.0 Hz, 2H), 2.98 (t, *J* = 6.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -119.67. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.52 , 134.73 , 134.46 , 134.36 , 133.22 , 131.11 , 129.58 , 128.96 , 126.40 , 126.37 , 125.87 , 120.66 , 116.04 , 114.88 , 54.26 , 50.57 , 29.31 . HRMS (ESI) Calcd for $C_{17}H_{17}FN$ $[M+H]^+$: 254.1340, found: 254.1349.



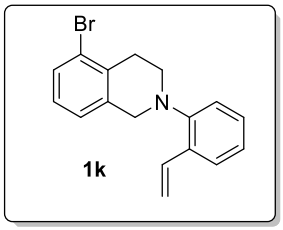
1e

2-(3-chloro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1e): The compound **1e** was synthesized according the previous literature,[1] as light red oil. IR (neat, cm^{-1}): 2983, 2941, 1736, 1393, 1233, 1043, 938, 847. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 – 7.12 (m, 3H), 7.12 – 7.08 (m, 2H), 7.08 – 7.03 (m, 1H), 7.01 – 6.93 (m, 1H), 6.80 (dd, *J* = 18.0, 12.0 Hz, 1H), 5.96 (dd, *J* = 18.0, 2.0 Hz, 1H), 5.57 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.14 (s, 2H), 3.28 (t, *J* = 6.0 Hz, 2H), 2.94 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.8 , 134.9, 134.5, 133.8, 131.6, 130.5, 129.0, 128.2, 126.4, 126.4, 125.8, 124.5, 120.5, 117.4, 53.8, 50.3, 29.4. HRMS (ESI) Calcd for $C_{17}H_{17}ClN$ $[M+H]^+$: 270.1044, 272.1015; found: 270.1040, 272.1015.



1j

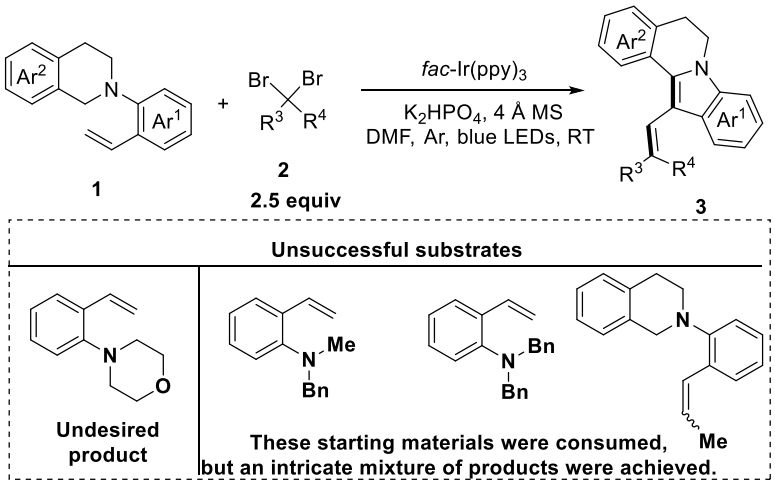
8-bromo-2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1j): The compound **1j** was synthesized according the previous literature,[1] as light yellow oil. IR (neat, cm^{-1}): 2984, 2941, 1736, 1393, 1233, 1043, 938, 847. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37 (dd, *J* = 7.6, 2 Hz, 1H), 7.32 – 7.19 (m, 1H), 7.13 – 6.94 (m, 5H), 5.70 (dd, *J* = 17.6, 1.6 Hz, 1H), 5.23 (dd, *J* = 11.2, 1.6 Hz, 1H), 4.11 (s, 2H), 3.20 (t, *J* = 5.6 Hz, 2H), 2.94 (t, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.2, 137.6, 134.7, 134.3, 132.6, 130.0, 128.7, 128.2, 127.5, 127.0, 123.4, 122.8, 119.3, 114.0, 55.2, 50.1, 29.9. HRMS (ESI) Calcd for $C_{17}H_{17}BrN$ $[M+H]^+$: 314.0539, 316.0518, found: 314.0538, 316.0520.



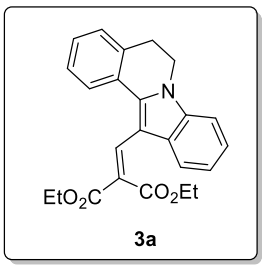
1k

5-bromo-2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1k): The compound **1k** was synthesized according the previous literature,[1] as light red oil. IR (neat, cm^{-1}): 2984, 2941, 1736, 1372, 1233, 1043, 937, 847. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.44 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.34 – 7.19 (m, 1H), 7.11 – 6.96 (m, 5H), 5.71 (dd, *J* = 18.0, 1.6 Hz, 1H), 5.24 (dd, *J* = 11.2, 1.6 Hz, 1H), 4.12 (s, 2H), 3.26 (t, *J* = 6.0 Hz, 2H), 2.95 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.0, 137.8, 134.5, 134.2, 132.5, 130.4, 128.6, 127.1, 126.9, 125.6, 125.5, 123.3, 118.8, 114.0, 54.5, 50.8, 30.7. HRMS (ESI) Calcd for $C_{17}H_{17}BrN$ $[M+H]^+$: 314.0539, 316.0518, found: 314.0536, 316.0517.

General procedure for the desired compounds

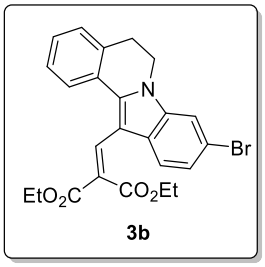


4 Å molecular sieve (100 mg), *fac*-Ir(ppy)$_3$ (1 mg, 0.0015 mmol, 0.5 mol %) and anhydrous K_2HPO_4 (157 mg, 0.9 mmol, 3 equiv) were charged into 10 ml Schlenk tube. The mixture solution of 2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline derivative **1** (0.3 mmol) and dibromide **2** (0.75 mmol, 2.5 equiv) dissolved in the anhydrous DMF (2 mL) was syringed into the Schlenk tube under argon atmosphere. The reaction solution was stirred and irradiated by the 5-W blue LEDs at 25^o C. When the starting material **1** was completely consumed by the TLC analysis, reaction solution was quenched by water (25 mL), extracted by ethyl acetate (3 × 20 mL), dried, filtered and collected organic solvent. The organic solvent was removed under reduced pressure. The desired product **3** was afforded by column chromatography on silica gel (PE: EtOAc = 1:35 ~ 1:4).

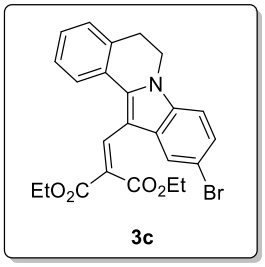


diethyl 2-((5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene)malonate (3a): According to the general procedure using 2-(2-vinylphenyl)-1,2,3,4-tetrahydro isoquinoline **1a** (71 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3a** (81 mg, 70%) was obtained as yellow

solid (mp: 174.0 -174.6 ºC). IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 937, 847. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.31 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.59 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.41 (ddd, *J* = 7.6, 5.2, 3.6 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.31 – 7.23 (m, 1H), 7.16 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.17 (t, *J* = 6.4 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.0, 165.6, 140.1, 136.9, 136.0, 134.2, 128.6, 128.5, 128.2 (2C), 127.7, 126.4, 123.2, 123.0, 121.1, 120.5, 109.3, 107.4, 61.2 (2C), 40.0, 29.5, 14.3, 13.8. HRMS (ESI) Calcd for $C_{24}H_{24}NO_4$ $[M+H]^+$: 390.1700, found: 390.1699.

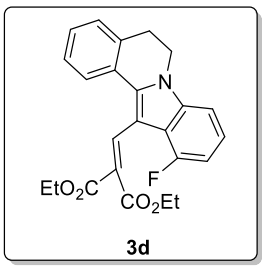


Diethyl 2-((9-bromo-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3b): According to the general procedure using 2-(5-bromo-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1b** (94 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3b** (112 mg, 80%) was obtained as light yellow solid (mp: 132.0 -132.5 ºC). IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.22 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.47 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.20 (t, *J* = 6.4 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.14 (t, *J* = 6.4 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.7, 165.3, 139.3, 137.1, 136.8, 134.0, 128.9, 128.4, 128.3, 127.8 (2C), 125.3, 124.3, 124.2, 121.6, 116.5, 112.5, 107.2, 61.4, 61.3, 40.2, 29.4, 14.3, 13.9. HRMS (ESI) Calcd for $C_{24}H_{23}BrNO_4$ $[M+H]^+$: 468.0805, 470.0785, found: 468.0802, 470.0788.



3c

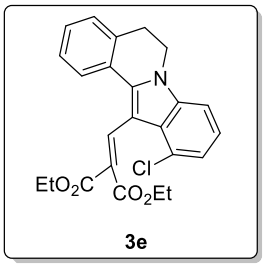
diethyl 2-((10-bromo-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (1c): According to the general procedure using 2-(4-bromo-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1c** (94 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3c** (84 mg, 60%) was obtained as light yellow solid (mp: 134.0 -134.6 ºC). IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 917, 847. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (s, 1H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.30 (m, 4H), 7.20 (d, *J* = 8.8 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.23 (p, *J* = 7.2 Hz, 4H), 3.16 (t, *J* = 6.4 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.8, 165.3, 139.0, 137.6, 134.7, 134.1, 128.9, 128.5, 128.3, 127.8, 127.7, 125.7, 124.3, 122.9, 114.4, 110.8, 106.5, 61.7, 61.3, 40.2, 29.4, 14.3, 13.9. HRMS (ESI) Calcd for $C_{24}H_{23}BrNO_4$ $[M+H]^+$: 468.0805, 470.0785, found: 468.0805, 470.0789.



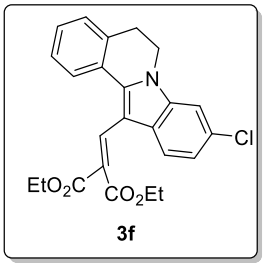
3d

diethyl 2-((11-fluoro-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3d): According to the general procedure using 2-(3-fluoro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1d** (76 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3d** (85 mg, 70%) was obtained as light yellow solid (mp: 175.0 -175.4 ºC). IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. ^{1}H NMR (400 MHz, $CDCl_3$) δ =

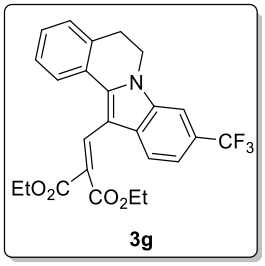
8.36 (s, 1H), 7.69 (d, *J* = 6.8 Hz, 1H), 7.34 (ddd, *J* = 12.8, 5.6, 3.2 Hz, 3H), 7.18 – 7.11 (m, 2H), 6.84 – 6.77 (m, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.22 (t, *J* = 6.4 Hz, 2H), 3.93 (q, *J* = 7.2 Hz, 2H), 3.16 (t, *J* = 6.4 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -118.15. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.8, 165.3 (d, *J* = 1.4 Hz), 156.9 (d, *J* = 248.8 Hz), 140.9 (d, *J* = 1.7 Hz), 138.3 (d, *J* = 10.6 Hz), 135.7, 134.0, 128.7, 128.1, 128.0, 127.8, 127.6, 125.0 (d, *J* = 1.1 Hz), 123.3 (d, *J* = 8.2 Hz), 115.8, 106.6 (d, *J* = 20.4 Hz), 105.4 (d, *J* = 3.5 Hz), 61.3, 60.6, 40.6, 29.6, 14.3, 13.7. HRMS (ESI) Calcd for $C_{24}H_{23}FNO_4$ $[M+H]^+$: 408.1606, found: 408.1603.



diethyl 2-((11-chloro-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3e): According to the general procedure using 2-(3-chloro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1e** (81 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3e** (82 mg, 65%) was obtained as light yellow solid (mp: 115.0 -115.5 ºC). IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.75 (s, 1H), 7.83 (dd, *J* = 6.8, 1.6 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.21 (dt, *J* = 7.6, 3.6 Hz, 1H), 7.15 – 7.10 (m, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.23 – 4.11 (m, 2H), 3.62 (q, *J* = 6.8 Hz, 2H), 3.13 (t, *J* = 6.4 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.2, 165.0, 141.2, 137.0, 134.5, 133.6, 128.5, 128.0, 127.5, 127.3, 127.0, 126.5, 125.1, 123.0, 121.9, 107.8, 106.0, 61.3, 60.4, 40.6, 29.6, 14.2, 13.5. HRMS (ESI) Calcd for $C_{24}H_{23}ClNO_4$ $[M+H]^+$: 424.1310, 426.1281; found: 424.1309, 426.1283.

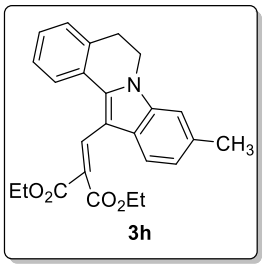


diethyl 2-((9-chloro-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3f): According to the general procedure using 2-(5-chloro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1f** (81 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3f** (99 mg, 80%) was obtained as light yellow solid (mp: 138.0 -138.4 ºC). IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.48 (d, J = 8.8 Hz, 1H), 7.43 – 7.30 (m, 4H), 7.10 (dd, *J* = 8.8, 1.6 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.20 (t, *J* = 6.4 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.15 (t, *J* = 6.4 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.8, 165.3, 139.3, 137.2, 136.5, 134.0, 128.8, 128.4, 128.3, 127.8, 127.7, 124.9, 124.2, 121.5, 121.3, 109.4, 107.2, 61.4, 61.3, 40.2, 29.4, 14.3, 13.8. HRMS (ESI) Calcd for $C_{24}H_{23}ClNO_4$ $[M+H]^+$: 424.1310, 426.1281; found: 424.1309, 426.1283.

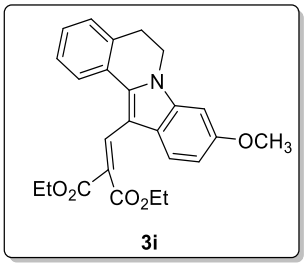


diethyl 2-((9-(trifluoromethyl)-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl) methylene)malonate (3g): According to the general procedure using 2-(5-(trifluoromethyl)-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1g** (91 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3g** (96 mg, 70%) was obtained as light yellow solid (mp: 120.0 -120.5 ºC). IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847. ^{1}H NMR (400 MHz,

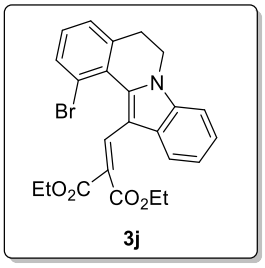
$CDCl_3$) δ = 8.24 (s, 1H), 7.66 (dd, *J* = 14.8, 6.8 Hz, 3H), 7.46 – 7.34 (m, 4H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.32 (t, *J* = 6.4 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.21 (t, *J* = 6.4 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -60.83. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.6, 165.2, 139.1, 138.6, 135.0, 134.2, 129.2, 128.7, 128.6, 128.4, 127.9, 127.6, 125.0, 124.9 (q, *J* = 272.6 Hz), 124.8 (q, *J* = 32.3 Hz), 120.6, 117.5 (q, *J* = 3.5 Hz), 107.1, 107.0 (q, *J* = 4.3 Hz), 61.5, 61.4, 40.3, 29.4, 14.3, 13.8. HRMS (ESI) Calcd for $C_{25}H_{23}F_3NO_4$ $[M+H]^+$: 458.1574, found: 458.1572.



diethyl 2-((9-methyl-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3h): According to the general procedure using 2-(5-methyl-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1h** (75 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3h** (72 mg, 60%) was obtained as light yellow solid (mp: 149.0 -149.3 ºC). IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.29 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.39 (dt, *J* = 7.6, 4.4 Hz, 1H), 7.32 (d, *J* = 4.0 Hz, 2H), 7.14 (s, 1H), 7.02 – 6.93 (m, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.22 (t, *J* = 6.4 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.14 (t, *J* = 6.4 Hz, 2H), 2.48 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.1, 165.7, 140.2, 136.7, 136.4, 134.1, 133.0, 128.4, 128.4, 128.3, 128.2, 127.6, 124.3, 122.9, 122.6, 120.2, 109.3, 107.4, 61.2, 39.9, 29.6, 21.8, 14.3, 13.8. HRMS (ESI) Calcd for $C_{25}H_{26}NO_4$ $[M+H]^+$: 404.1856, found: 404.1855.

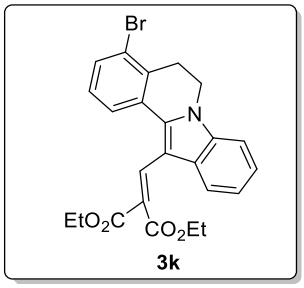


diethyl 2-((9-methoxy-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3i): According to the general procedure using 2-(5-methoxy-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1i** (70 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3i** (57 mg, 45%) was obtained as light yellow solid (mp: 131.0 -131.4 ºC). IR (neat, cm-1): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.39 (dt, *J* = 8.0, 4.4 Hz, 1H), 7.34 – 7.29 (m, 2H), 6.83 – 6.76 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.21 (t, *J* = 6.4 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 3.15 (t, *J* = 6.4 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.1, 165.6, 157.0, 140.0, 137.0, 136.4, 133.8, 128.3, 128.2, 128.2, 127.6, 122.9, 121.3, 120.6, 110.7, 110.4, 107.5, 92.9, 61.2, 55.7, 40.1, 29.6, 14.3, 13.8. HRMS (ESI) Calcd for $C_{25}H_{26}NO_5$ $[M+H]^+$: 420.1805, found: 420.1804.

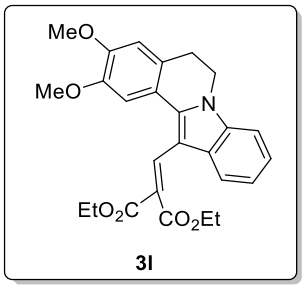


diethyl 2-((1-bromo-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3j): According to the general procedure using 8-bromo-2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1j** (94 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3j** (116 mg, 83%) was obtained as light yellow solid (mp: 145.0 -145.3 ºC). IR (neat, cm-1): 2984, 1736, 1373, 1233, 1043, 938, 847. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09

(s, 1H), 7.70 – 7.59 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 8.8 Hz, 2H), 7.17 (q, *J* = 8.0 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 4.17 - 4.11 (m, 2H), 3.96 (q, *J* = 7.2 Hz, 2H), 2.97 (t, *J* = 6.4 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.9, 165.6, 141.9, 139.2, 136.4, 135.8, 133.8, 129.9, 129.7, 126.7, 123.3, 122.0, 121.1, 120.5, 109.5, 108.9, 61.2, 60.9, 40.4, 31.8, 14.3, 13.8. HRMS (ESI) Calcd for $C_{24}H_{23}BrNO_4$ $[M+H]^+$: 468.0805, 470.0785, found: 468.0802, 470.0782.

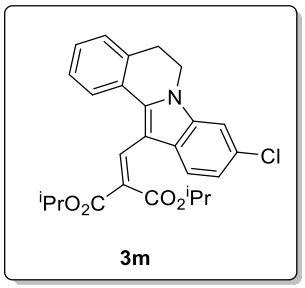


diethyl 2-((4-bromo-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3k): According to the general procedure using 5-bromo-2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1k** (94 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3k** (91 mg, 65%) was obtained as light yellow solid (mp: 177.0 -177.6 ºC). IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (s, 1H), 7.64 – 7.56 (m, 3H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.20 – 7.12 (m, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.31 (t, *J* = 6.4 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.7, 165.4, 139.6, 135.8, 135.3, 133.6, 132.4, 130.2, 128.7, 127.4, 126.5, 124.3, 124.2, 123.4, 121.3, 120.5, 109.4, 107.9, 61.4, 61.3, 39.6, 29.3, 14.3, 13.8. HRMS (ESI) Calcd for $C_{24}H_{23}BrNO_4$ $[M+H]^+$: 468.0805, 470.0785, found: 468.0804, 470.0783.



3l

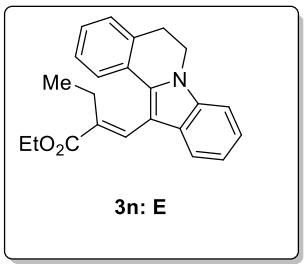
diethyl 2-((2,3-dimethoxy-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3l): According to the general procedure using 6,7-dimethoxy-2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1l** (88 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2a** (237 mg, 0.75 mmol, 2.5 equiv), the desired product **3l** (87 mg, 65%) was obtained as light yellow solid (mp: 140.0 -140.5 ºC). IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.15 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 6.85 (s, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.24 (t, *J* = 6.4 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 6H), 3.10 (t, *J* = 6.4 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.1, 165.6, 149.4, 148.2, 140.0, 137.7, 136.1, 127.3, 126.5, 122.7, 121.8, 121.1, 120.6, 120.3, 111.5, 111.3, 109.2, 106.2, 61.2, 56.0, 40.1, 29.1, 14.4, 13.8. HRMS (ESI) Calcd for $C_{26}H_{28}NO_6$ $[M+H]^+$: 450.1911, found: 450.1911.



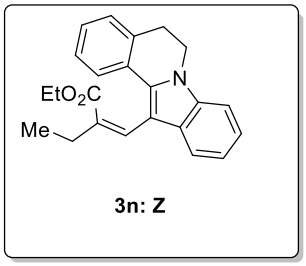
3m

diisopropyl 2-((9-chloro-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3m): According to the general procedure using 2-(5-chloro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1f** (81 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate **2b** (258 mg, 0.75 mmol, 2.5 equiv), the desired product **3m** (108 mg, 80%) was obtained as light yellow solid (mp: 166.0 -166.5 ºC). IR (neat, cm^{-1}): 2984, 1736, 1372, 1232, 1043, 938, 847. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16

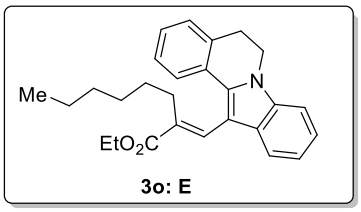
(s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.42 – 7.29 (m, 4H), 7.09 (dd, *J* = 8.8, 1.6 Hz, 1H), 5.23 (q, *J* = 6.4 Hz, 1H), 5.05 (p, *J* = 6.4 Hz, 1H), 4.20 (t, *J* = 6.4 Hz, 2H), 3.13 (d, *J* = 6.4 Hz, 2H), 1.36 (d, *J* = 6.4 Hz, 6H), 1.17 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.4, 164.9, 138.5, 136.9, 136.4, 134.0, 128.8, 128.7, 128.3, 127.9, 127.7, 125.5, 124.9, 121.5, 121.3, 109.4, 107.2, 68.9, 68.9, 40.2, 29.4, 22.0, 21.6. HRMS (ESI) Calcd for $C_{26}H_{27}ClNO_4$ $[M+H]^+$: 452.1623, 454.1594; found: 452.1620, 454.1593.



ethyl (*E*)-2-((5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene)butanoate (3n: *E*): According to the general procedure using 2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1a** (71 mg, 0.3 mmol) and ethyl 2,2-dibromobutanoate **2e** (204 mg, 0.75 mmol, 2.5 equiv), the desired product **3n: *E*** (28 mg, 27.5%) was obtained as light yellow oil. IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 7.17 – 7.13 (m, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 3.19 (t, *J* = 6.4 Hz, 2H), 2.49 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.4, 135.8, 135.8, 133.3, 132.8, 132.7, 129.2, 128.2, 127.6, 127.4, 126.9, 126.8, 122.3, 120.4, 120.1, 109.1, 107.8, 60.5, 40.1, 29.6, 22.3, 14.4, 13.7. HRMS (ESI) Calcd for $C_{23}H_{24}NO_2$ $[M+H]^+$: 346.1802, found: 346.1798.

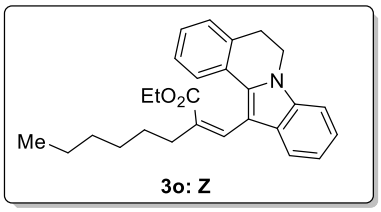


ethyl (Z)-2-((5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene)butanoate (3n: Z): the desired product **3n: *Z*** (28 mg, 27.5%) was obtained as light yellow oil. IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.23 (m, 4H), 7.20 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.10 – 7.02 (m, 2H), 4.26 (t, *J* = 6.4 Hz, 2H), 3.89 (q, *J* = 7.2 Hz, 2H), 3.15 (t, *J* = 6.4 Hz, 2H), 2.64 (qd, *J* = 7.2, 1.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.75 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.3, 135.6, 135.5, 133.5, 132.0, 129.5, 129.0, 128.2, 127.5, 127.3, 127.2, 126.9, 122.1, 120.1, 119.9, 109.6, 108.8, 60.2, 40.0, 29.8, 28.2, 14.0, 13.5. HRMS (ESI) Calcd for $C_{23}H_{24}NO_2$ $[M+H]^+$: 346.1802, found: 346.1801.



ethyl (*E*)-2-((5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene)octanoate (3o: *E*): According to the general procedure using 2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1a** (71 mg, 0.3 mmol) and ethyl 2,2-dibromooctanoate **2f** (246 mg, 0.75 mmol, 2.5 equiv), the desired product **3o: *E*** (25 mg, 21%) was obtained as light yellow oil. IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.93 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 7.18 – 7.12 (m, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 3.19 (t, *J* = 6.4 Hz, 2H), 2.53 – 2.42 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 5H), 1.28 (dd, *J* = 13.2, 5.6 Hz, 3H), 1.09 – 1.04 (m, 4H), 0.70 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.5,

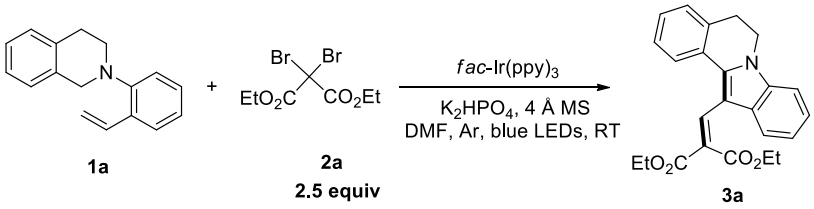
135.8, 134.4, 133.3, 133.2, 129.2, 128.2, 127.6, 127.4, 126.9, 122.3, 120.5, 120.1, 119.9, 119.3, 109.0, 108.0, 60.5, 40.1, 31.5, 29.7, 28.9, 28.8, 28.8, 22.5, 14.4, 14.0. HRMS (ESI) Calcd for $C_{27}H_{32}NO_2$ $[M+H]^+$: 402.2428, found: 402.2433.

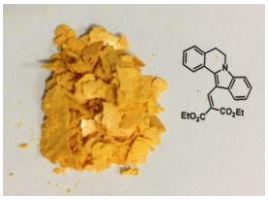


ethyl (*Z*)-2-((5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene)octanoate (3o: *Z*): the desired product **3o: *Z*** (35 mg, 29%) was obtained as light yellow oil. IR (neat, cm^{-1}): 2984, 1736, 1372, 1233, 1043, 938, 847. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 7.6 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.35 – 7.25 (m, 4H), 7.22 – 7.17 (m, 1H), 7.08 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.01 (s, 1H), 4.25 (t, *J* = 6.4 Hz, 2H), 3.88 (q, *J* = 7.2 Hz, 2H), 3.15 (t, *J* = 6.4 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 1.66 (p, *J* = 7.2 Hz, 2H), 1.46 (dd, *J* = 8.4, 5.6 Hz, 2H), 1.40 – 1.34 (m, 4H), 0.95 – 0.89 (m, 3H), 0.75 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.3, 135.6, 134.2, 133.5, 132.0, 129.8, 129.5, 128.2, 127.5, 127.3, 127.1, 127.0, 122.1, 120.1, 119.9, 109.7, 108.8, 60.2, 40.0, 35.2, 31.8, 29.8, 29.3, 29.0, 22.7, 14.2, 13.5. HRMS (ESI) Calcd for $C_{27}H_{32}NO_2$ $[M+H]^+$: 402.2428, found: 402.2428.

The 2.6 mmol scale reaction and Stern-Volmer quenching studies

(a) The 2.6 mmol reaction



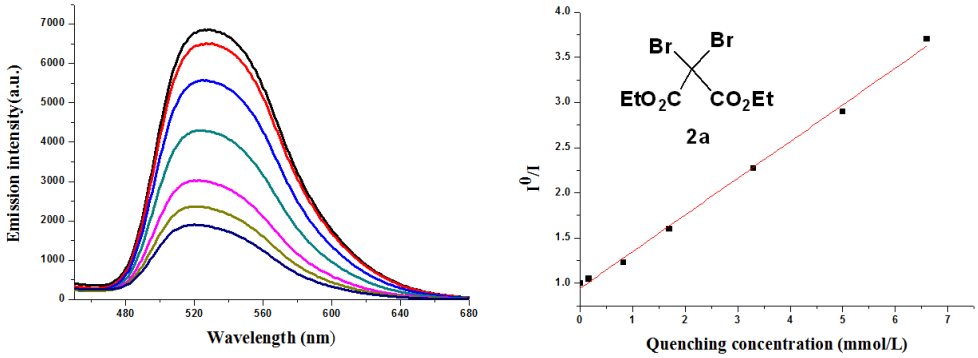


4 Å molecular sieve (400 mg), *fac*-Ir(ppy)$_3$ (10 mg, 0.5 mol %) and anhydrous K_2HPO_4 (1300 mg, 7.7 mmol, 3 equiv) were charged into 35 ml Schlenk tube. The mixture solution of ortho-tetrahydroisoquinoline-substituted styrene **1a** (600 mg, 2.6 mmol) and diethyl 2,2-dibromomalonate **2a** (2000 mg, 6.4 mmol, 2.5 equiv) dissolved

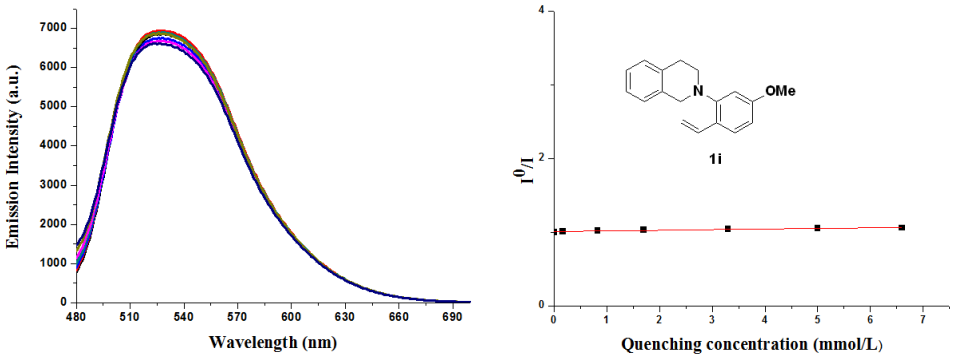
in the anhydrous DMF (10 mL) was syringed into the Schlenk tube under argon atmosphere. The reaction solution was stirred and irradiated by the 40-W blue LEDs at 25° C. When the starting material **1a** was completely consumed by the TLC analysis, reaction solution was quenched by water (35 mL), extracted by ethyl acetate (3 × 30 mL), dried, filtered and collected organic solvent. The organic solvent was removed under reduced pressure. The desired product **3** (620 mg, 63%) was afforded by column chromatography on silica gel.

(b) Stern-Volmer quenching studies

The Stern-Volmer quenching dates were measured by Cary Eclipse fluorescent spectrophotometer (F-7000, HITACHI). Experiments were conducted in 0.05mmol/L of *fac*-Ir(ppy)$_3$/DMF at 25 ^{0}C and the excitation wavelength was 375 nm. The quenching's concentration in DMF were 0, 0.17 mmol/L, 0.85 mmol/L, 1.7 mmol/L, 3.3 mmol/L, 5.0 mmol/L, 6.6 mmol/L.



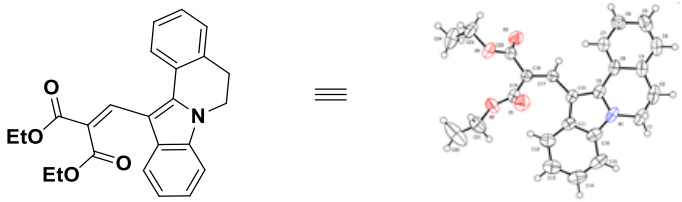
Stern-Volmer quenching of *fac*-Ir(ppy)$_3$ by diethyl 2,2-dibromomalonate **2a**



Stern-Volmer quenching of *fac*-Ir(ppy)$_3$ by

2-(5-methoxy-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline **1i**

X-ray crystal diffraction data



3a ≡ CCDC 1534996

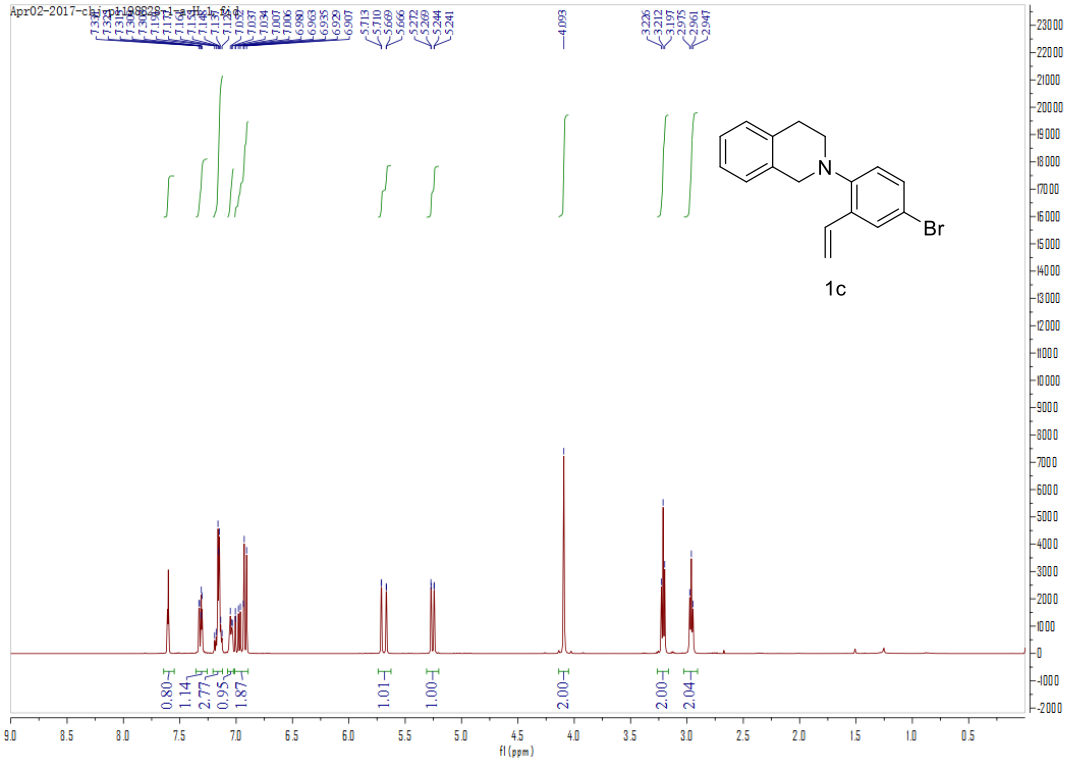
Identification code	**CCDC 1534996**
Empirical formula	C24H23NO4
Formula weight	389.43
Temperature	293(2)K
Wavelength	0.71073Å
Crystal system, space group	monoclinic, P, 2yb
Unit cell dimensions	a = 9.593(10) Å alpha = 90 deg.
	b = 8.000(8) Å beta = 103.143(19) deg
	c = 13.517(14) Å gamma = 90 deg.
Volume	1010.3(18) $Å^3$
Z, Calculated density	2, 1.280Mg/m^3
Absorption coefficient	0.087mm^{-1}
F(000)	412.0
Crystal size	0.30 x 0.25 x 0.09 mm
Theta range for data collection	2.55 to 24.32 deg
Limiting indices	-9<=h=<11, -9<=k=<9, -16<=l=<12
Reflections collected / unique	3437 / 3003 [R(int) = 0.0259]
Completeness to theta = 27.73	99.5%
Absorption correction	multi-scan
Max. and min. transmission	0.992, 0.974
Data / restraints / parameters	2900 / 0 / 228
Goodness-of-fit on F^2	1.093
Final R indices [I>2sigma(I)]	R_1 = 0.0393, wR_2 = 0.1159
R indices (all data)	R_1 = 0.0476, wR_2 = 0.1323
Largest diff. peak and hole	0.193 and -0.181 e. $Å^{-3}$

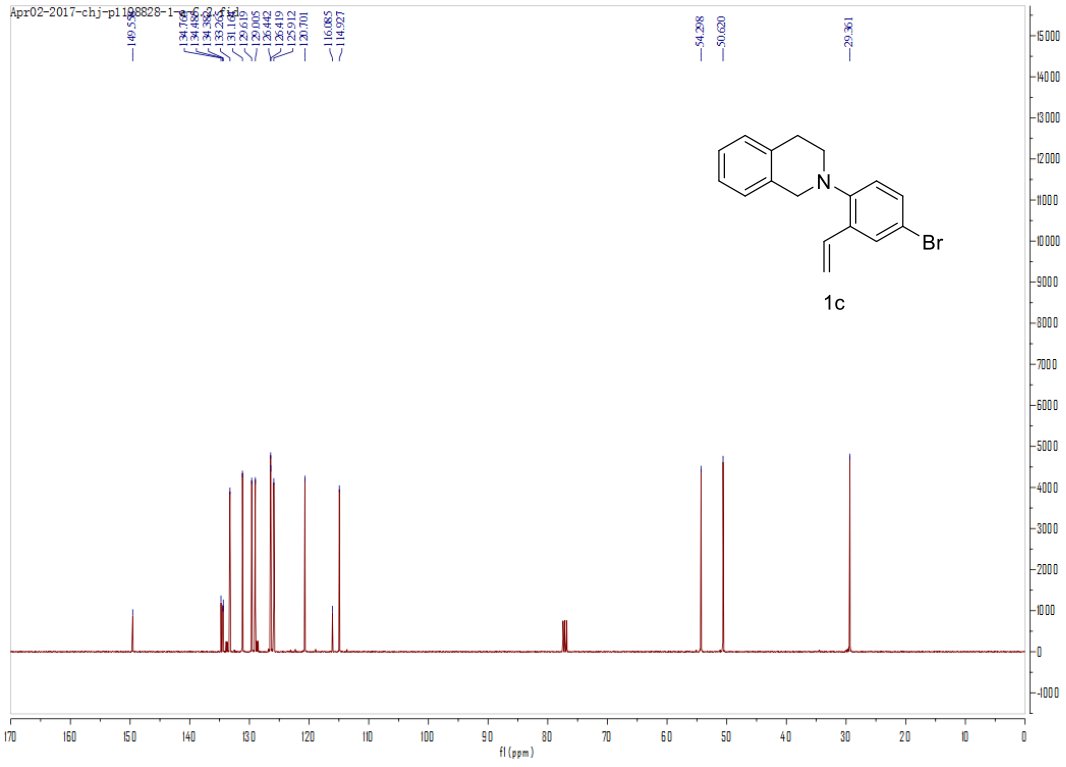
Reference

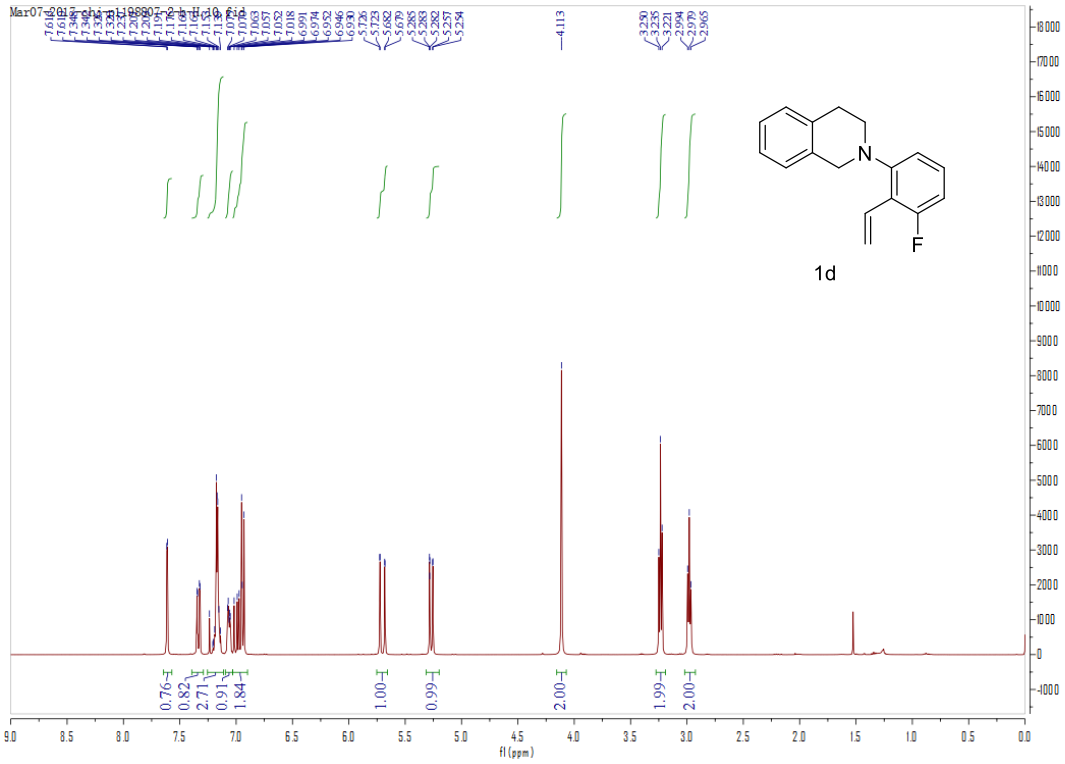
[1] Chen, Y. Y.; Zhang, X. J.; Yuan, H. M.; Wei, W. T.; Yan, M. *Chem. Commun.2013, 49, 10974.*

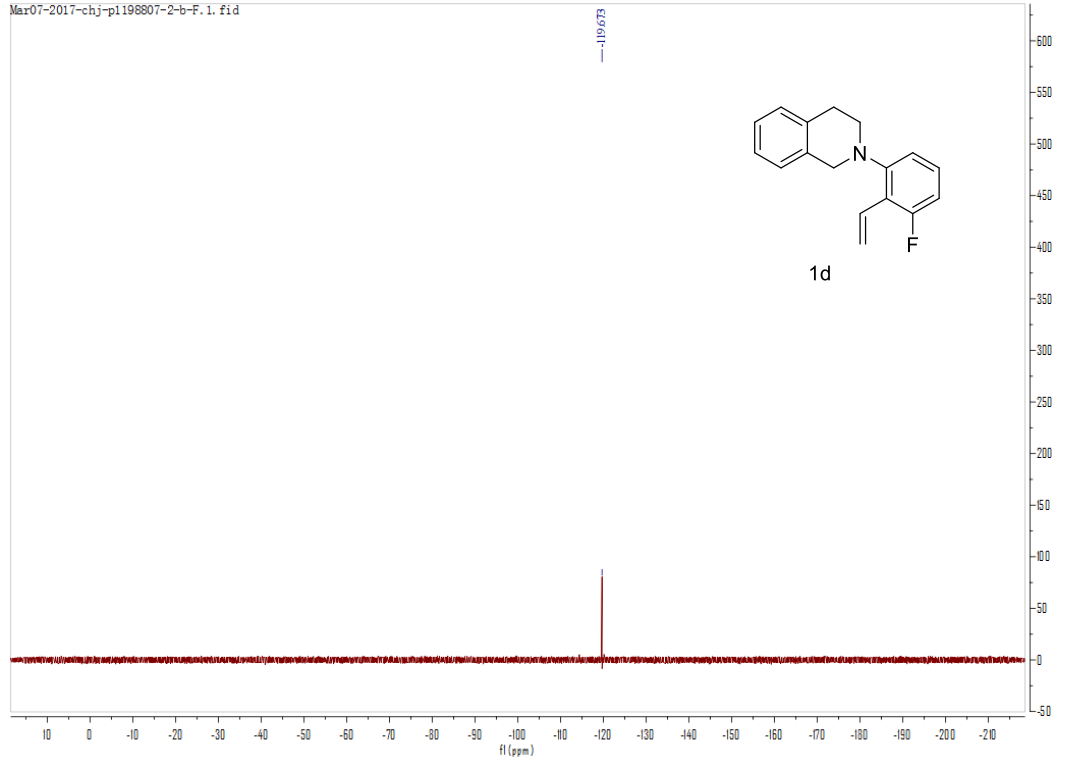
NMR spectra of the unknown compounds

(a) The NMR spectra of the unknown starting materials






1d
0.76
0.82
2.71
0.91
1.84
1.00
0.99
2.00
1.99
2.00
f1 (ppm)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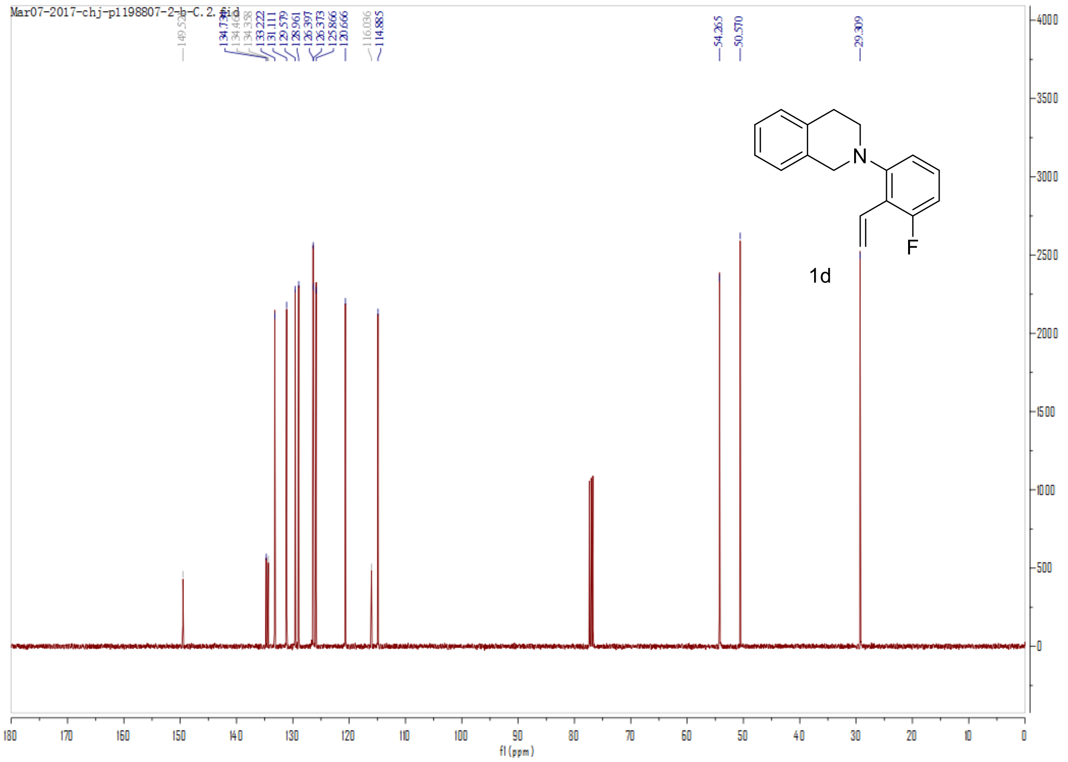
-119.673
1d
f1 (ppm)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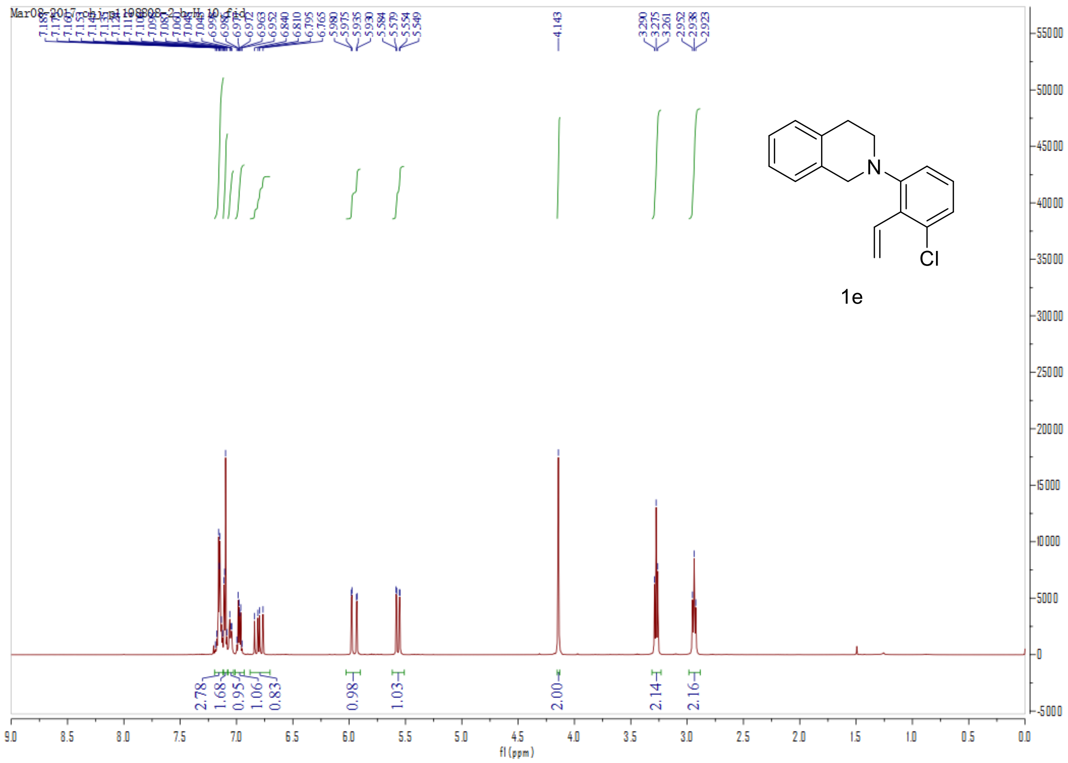
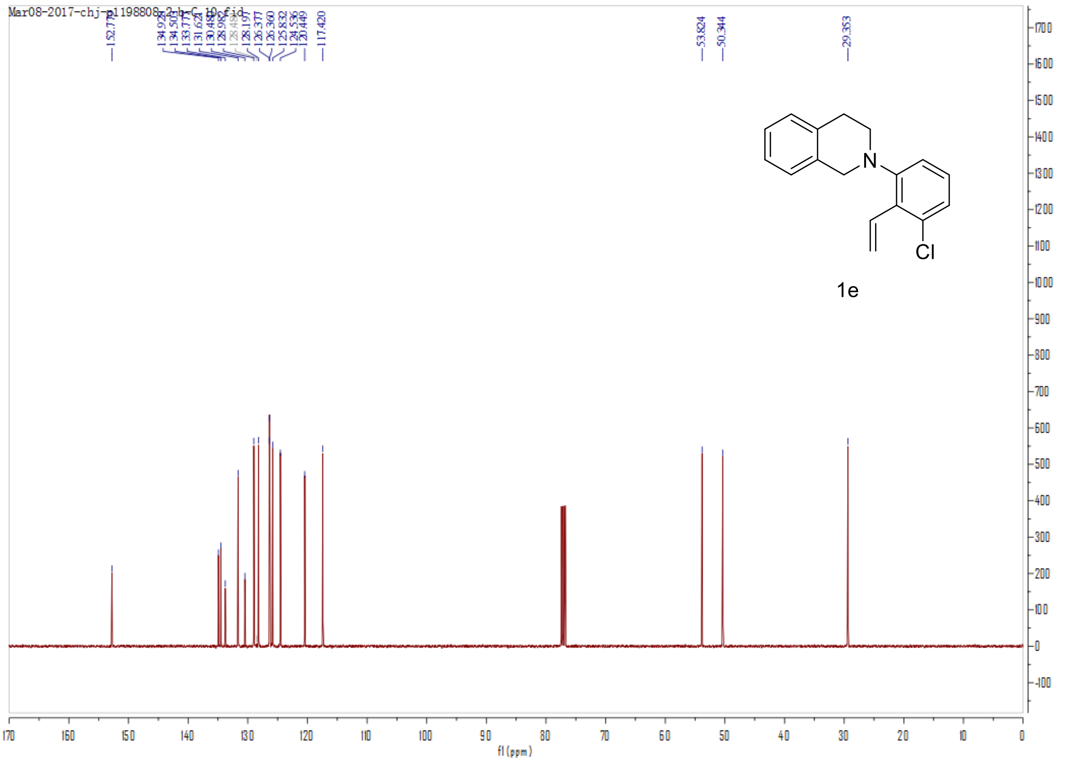
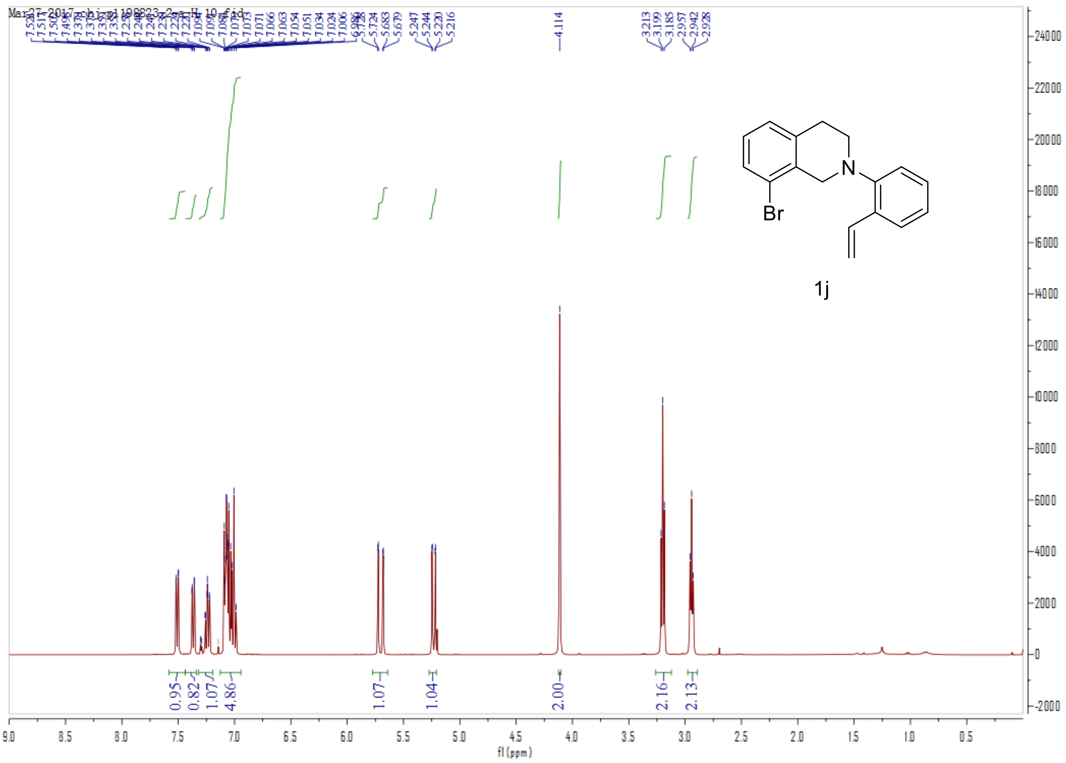
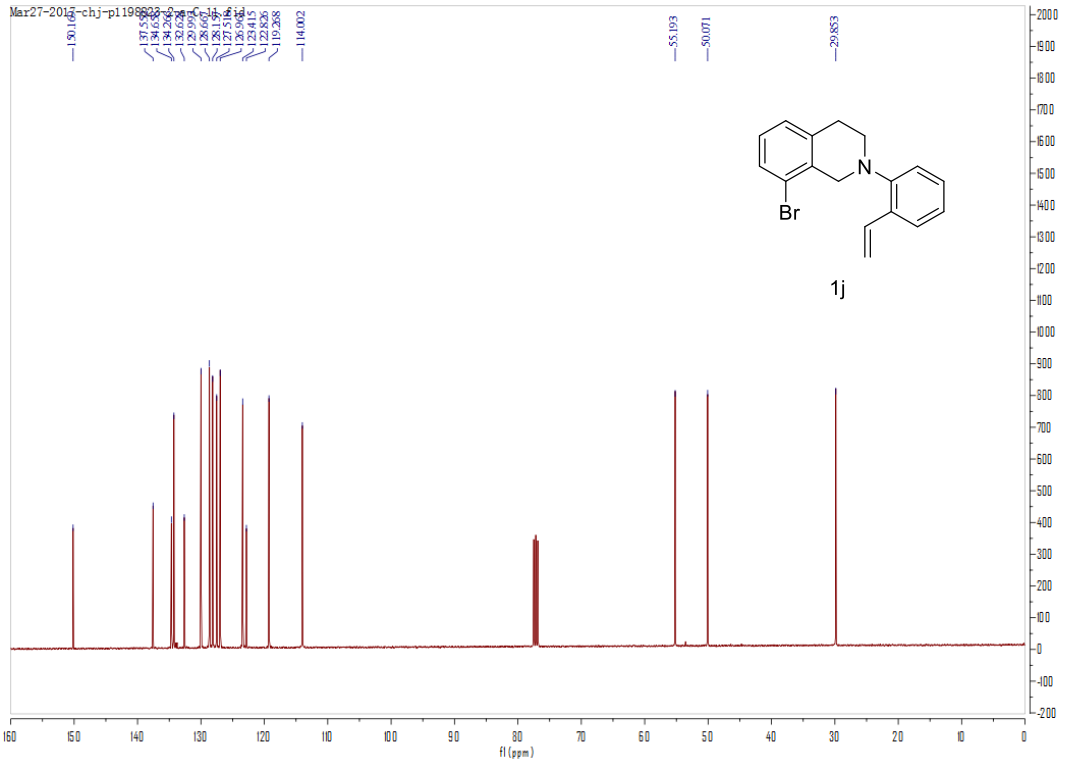
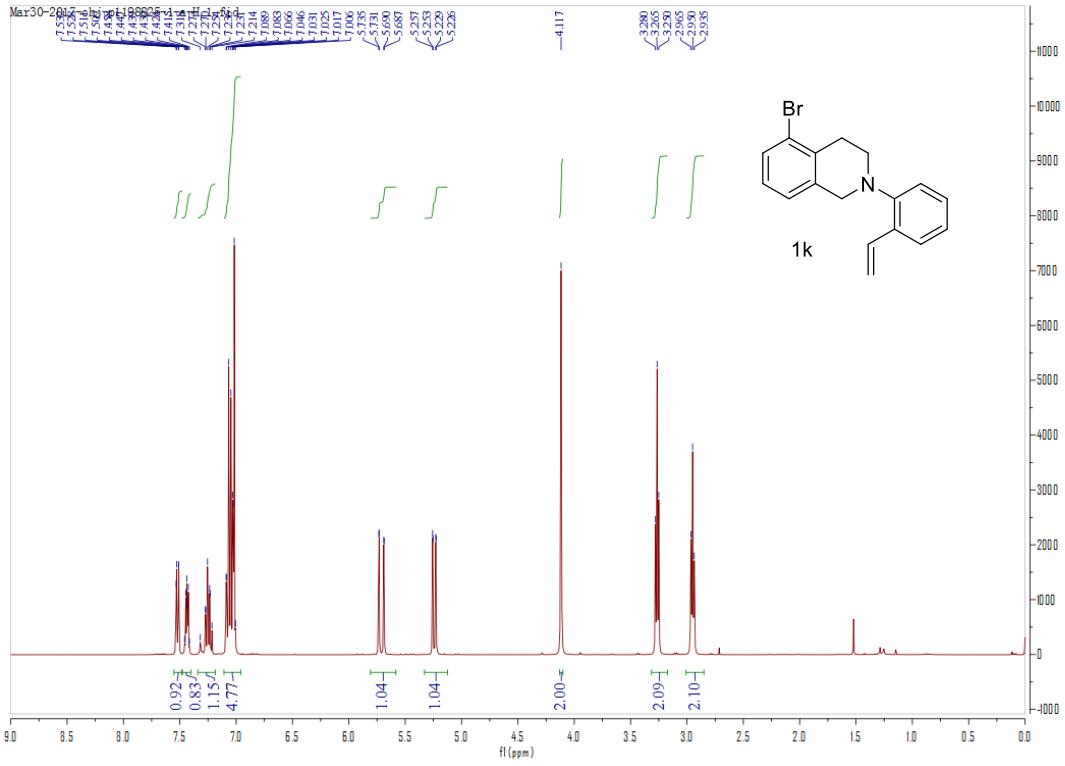
1d
N
F
fl (ppm)


1e
N
Cl
fl (ppm)


1e


1j


Br
N
1j
f1 (ppm)


Br
N
1k
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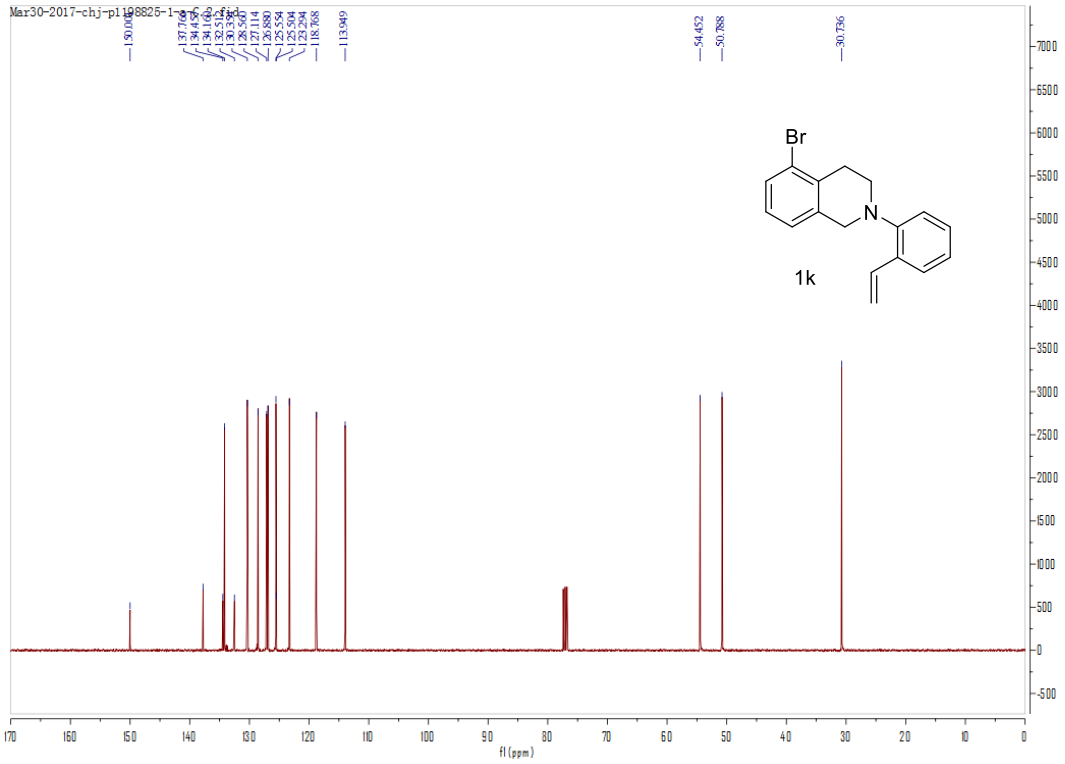
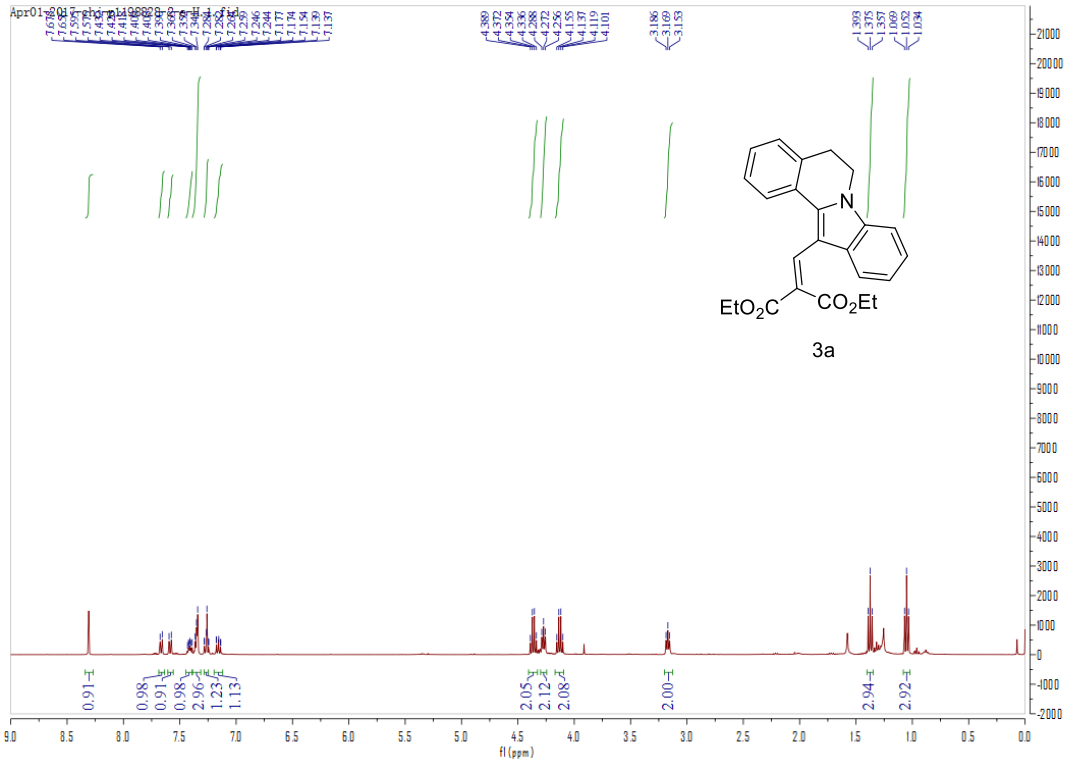
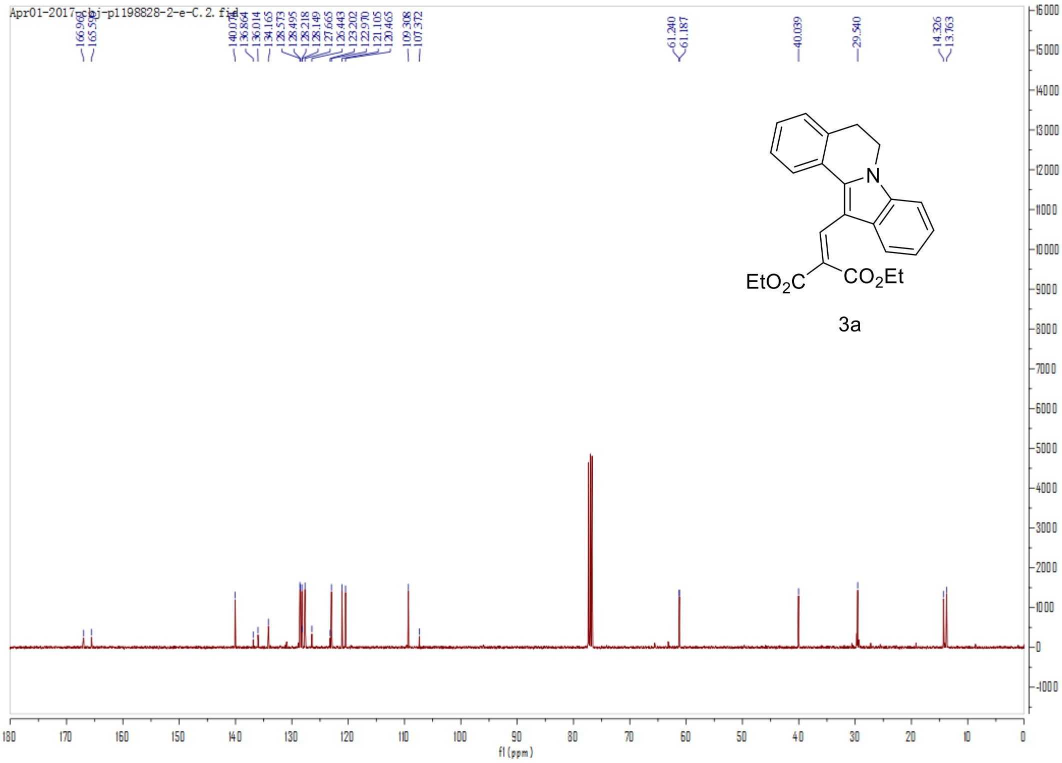
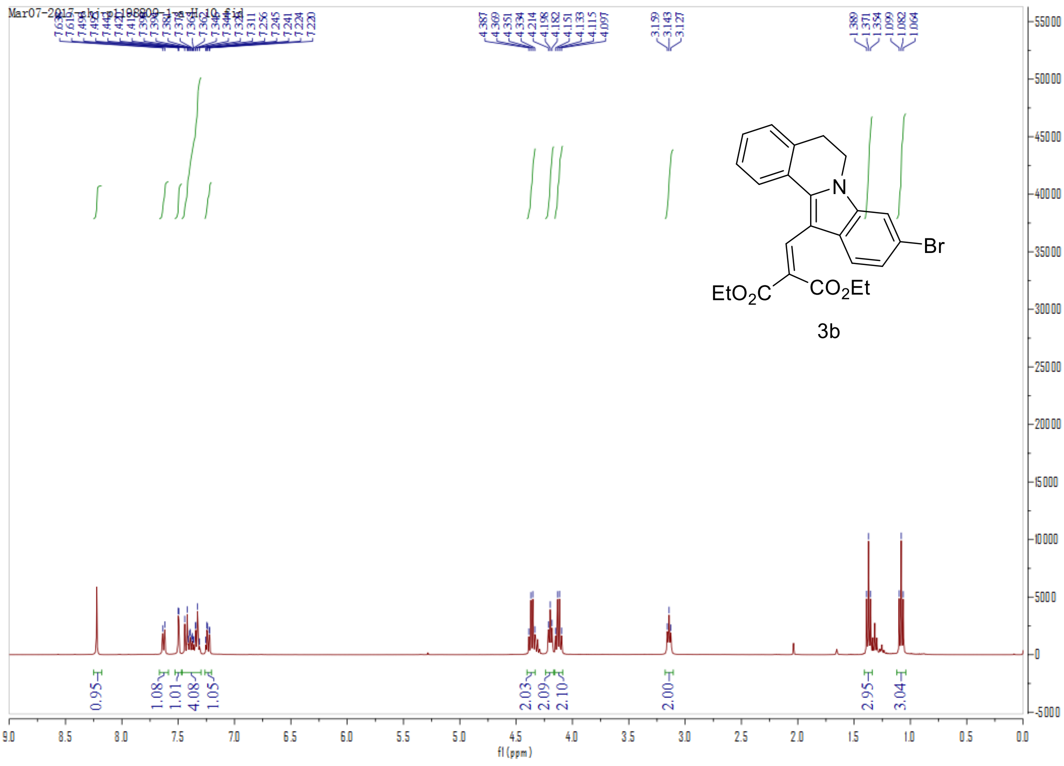
0.83
1.15
4.77
1.04
1.04
2.00
2.09
2.10
f1 (ppm)

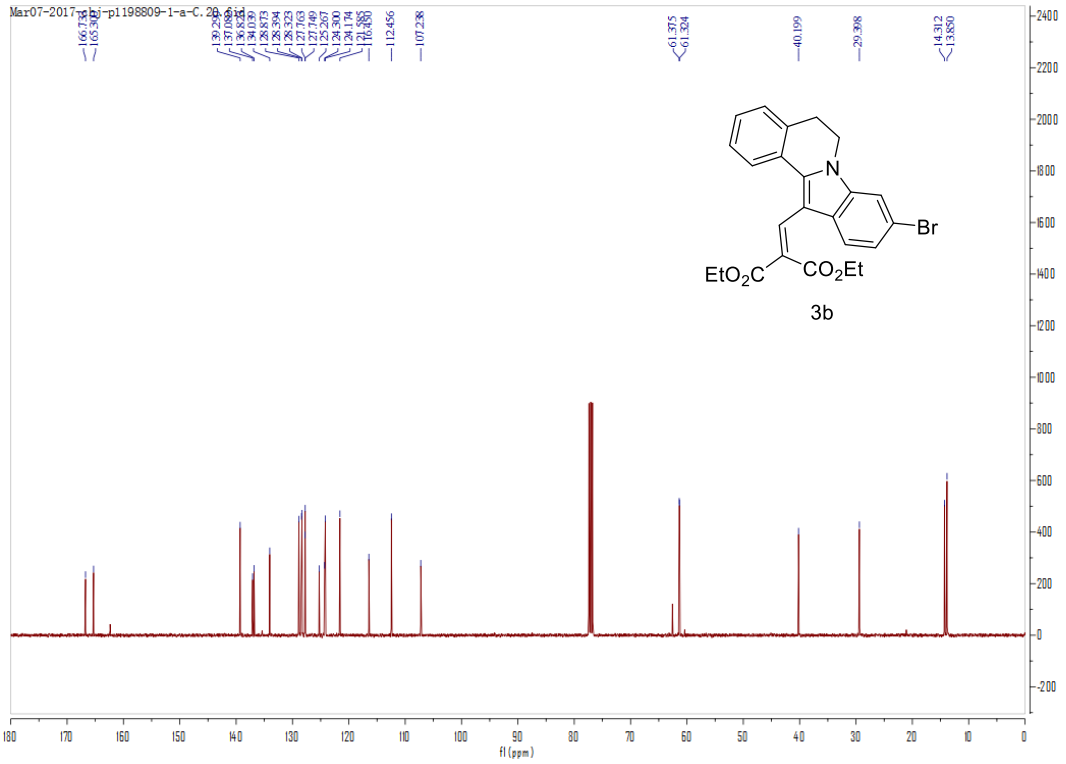


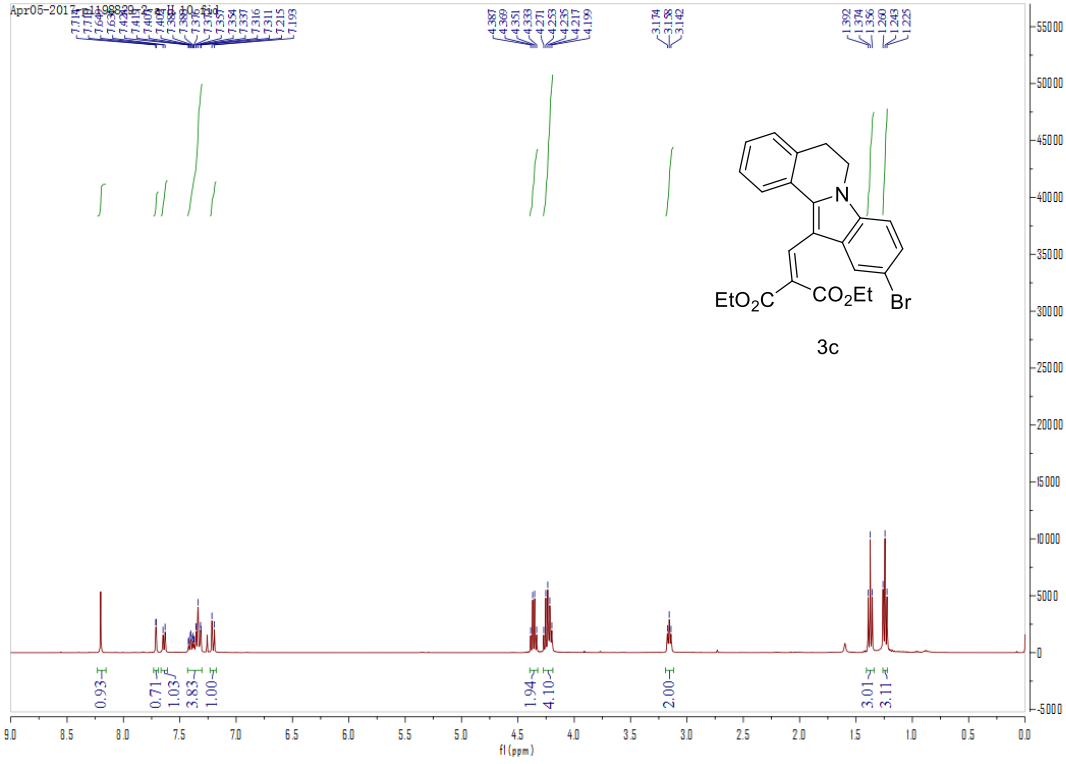
(b) The NMR spectra of the desired compounds

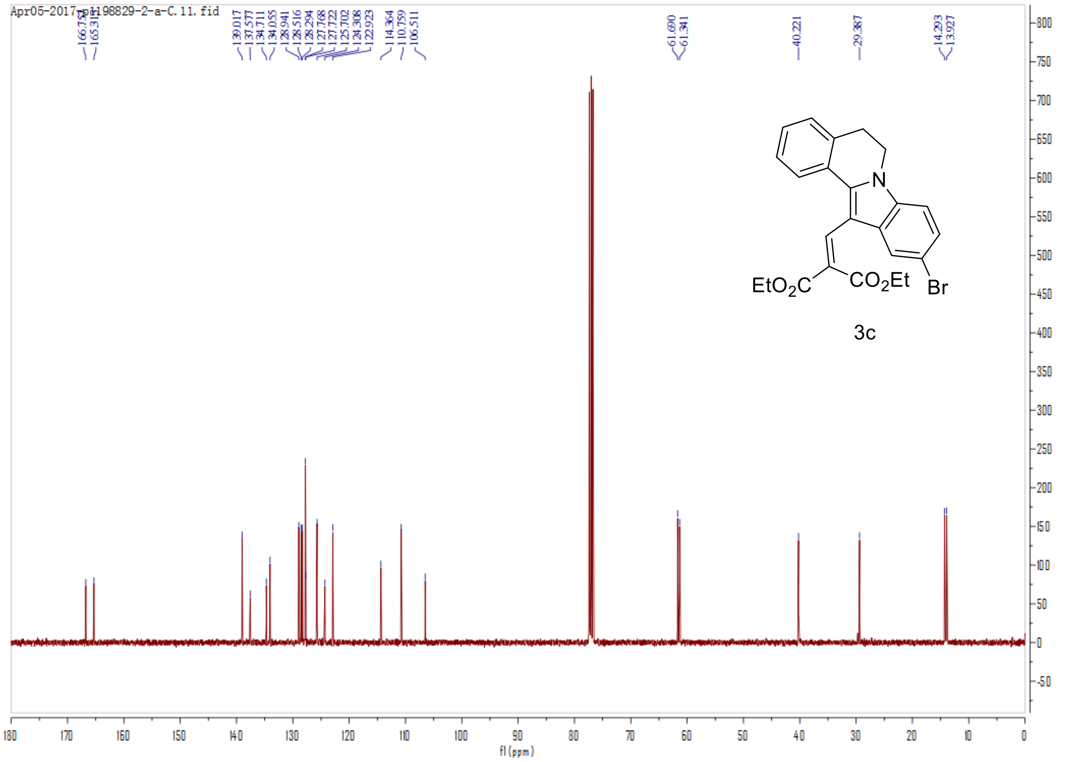



EtO2C
CO2Et
N
3a
f1 (ppm)


EtO2C
CO2Et
N
Br
3b
f1 (ppm)


Mar07-2017-xj-p1198809-1-a-C.20.fid
61.375
61.324
40.199
29.398
14.312
13.890
112.456
107.238
N
Br
EtO2C
CO2Et
3b
f1 (ppm)


Apr05-2017-xj198829-2-a-H-10.fid
4.387
4.369
4.351
4.333
4.271
4.253
4.235
4.217
4.199
3.174
3.158
3.142
1.392
1.374
1.356
1.260
1.243
1.225
0.93
0.71
1.03
3.83
1.00
1.94
4.10
2.00
3.01
3.11
N
EtO2C
CO2Et
Br
3c
f1 (ppm)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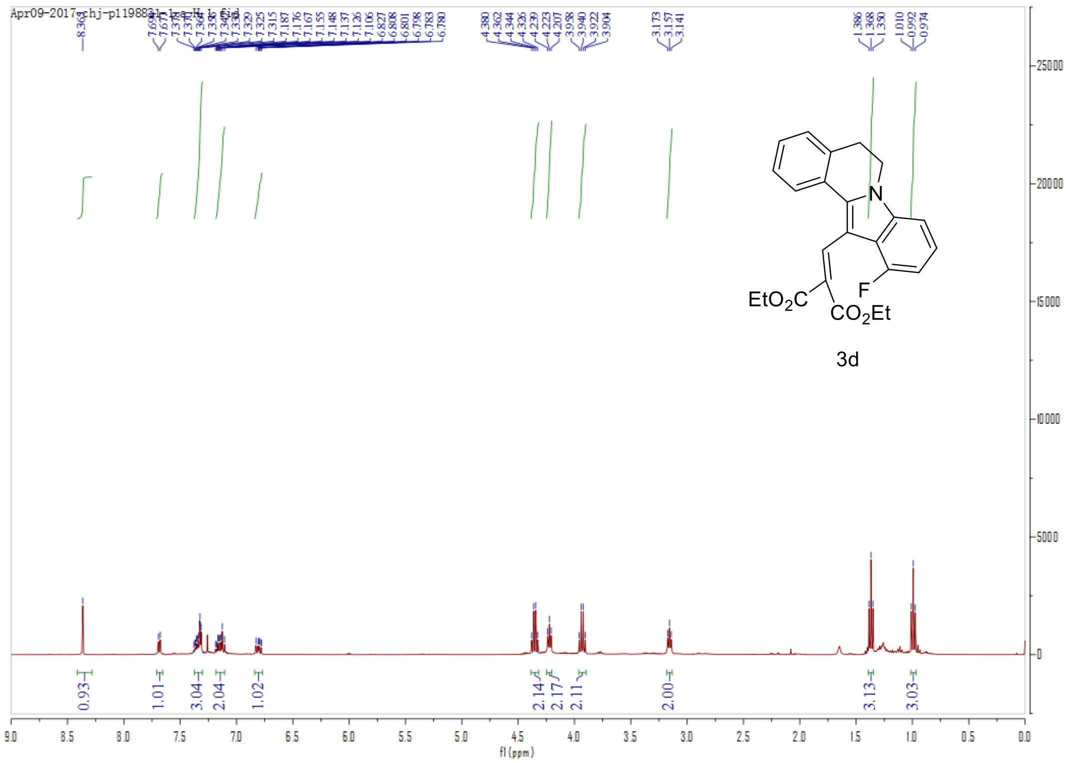
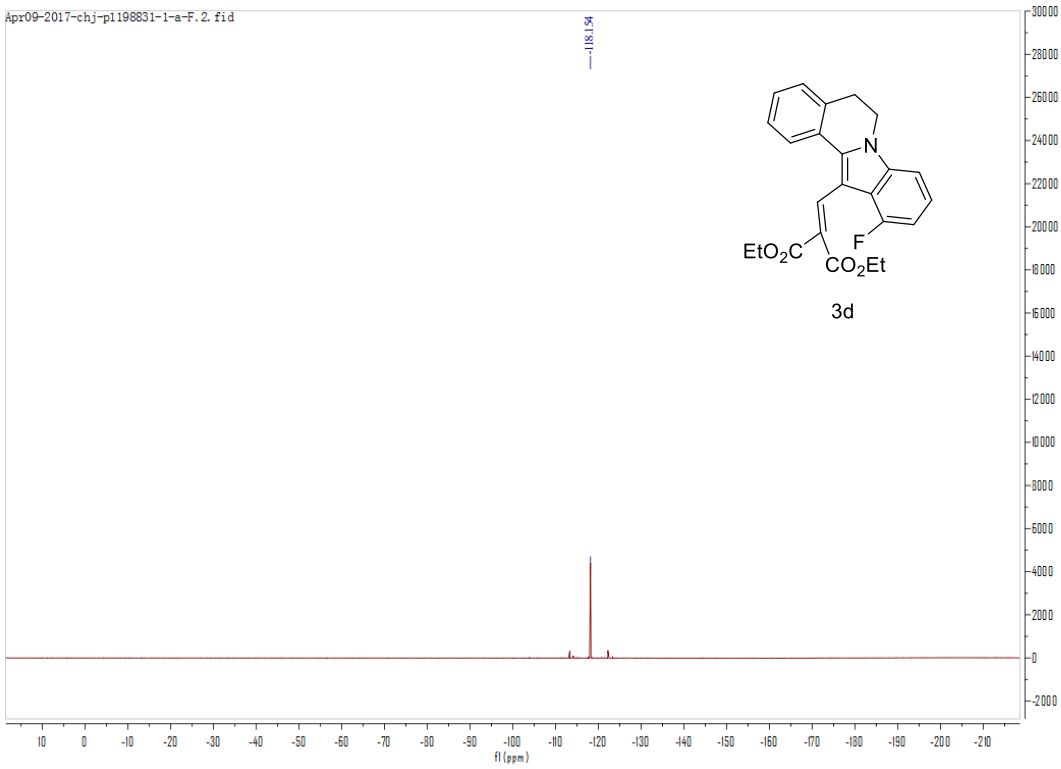
N
EtO2C
CO2Et
Br
3c
f1 (ppm)


N
F
EtO2C
CO2Et
3d
f1 (ppm)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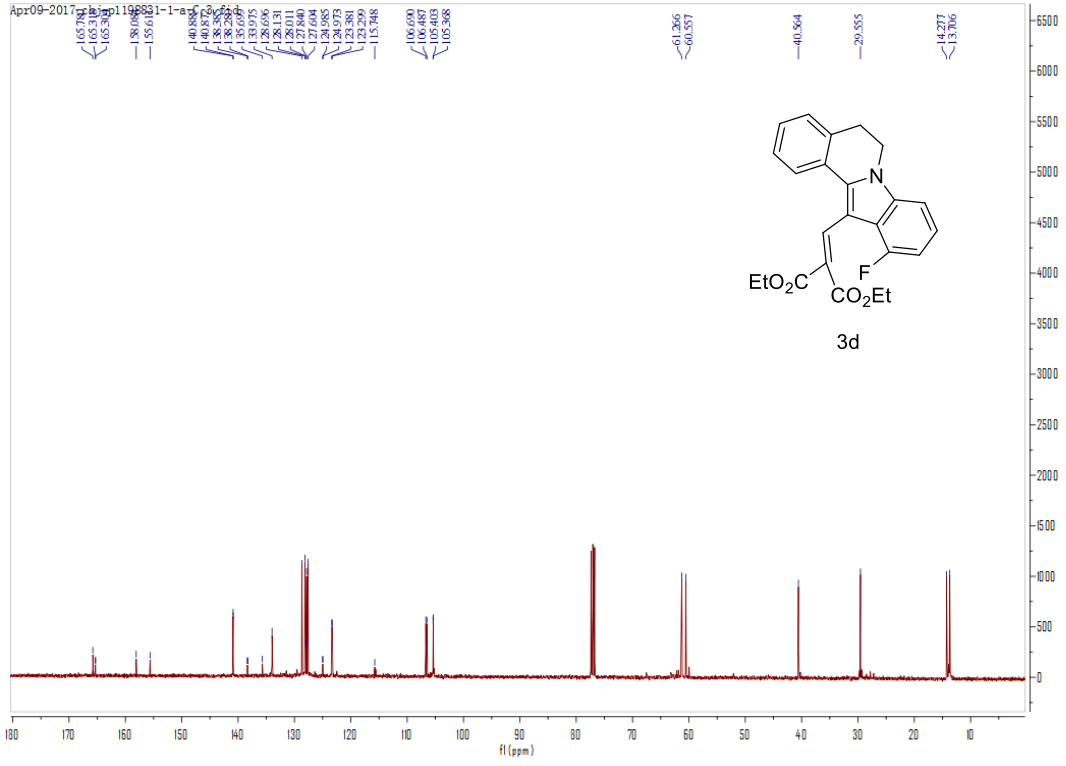
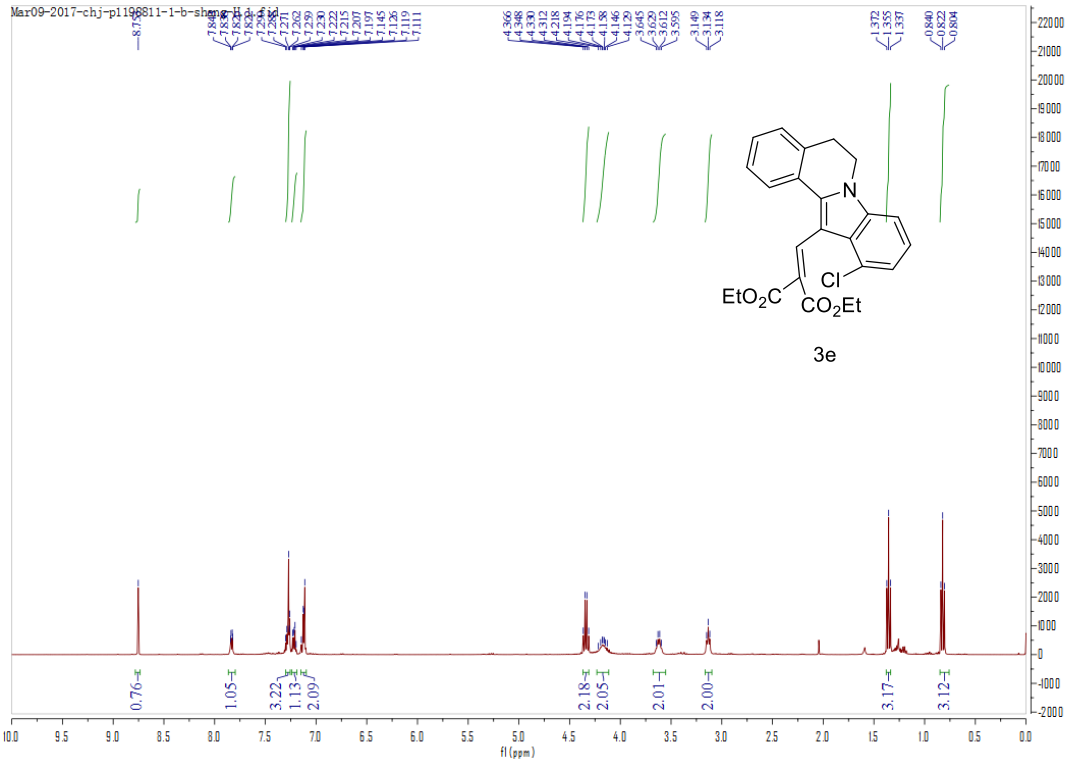
N
F
EtO2C
CO2Et
3d
f1 (ppm)


N
F
EtO2C
CO2Et
3d
f1 (ppm)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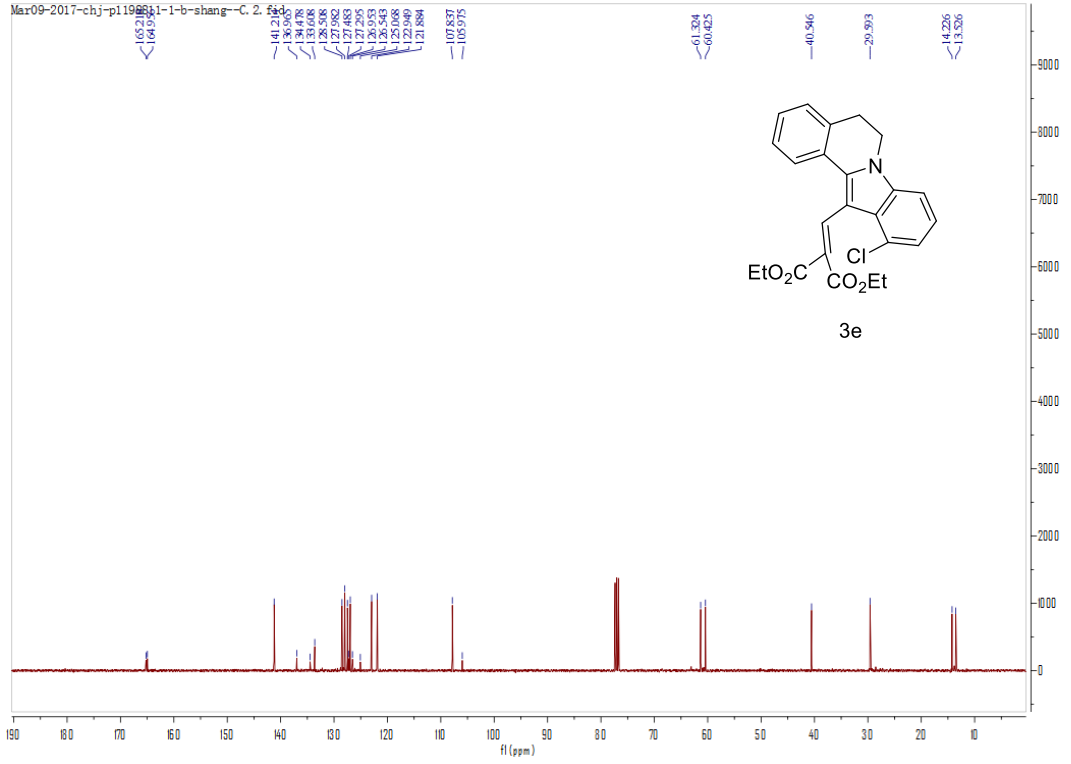
N
Cl
EtO2C
CO2Et
3e
f1 (ppm)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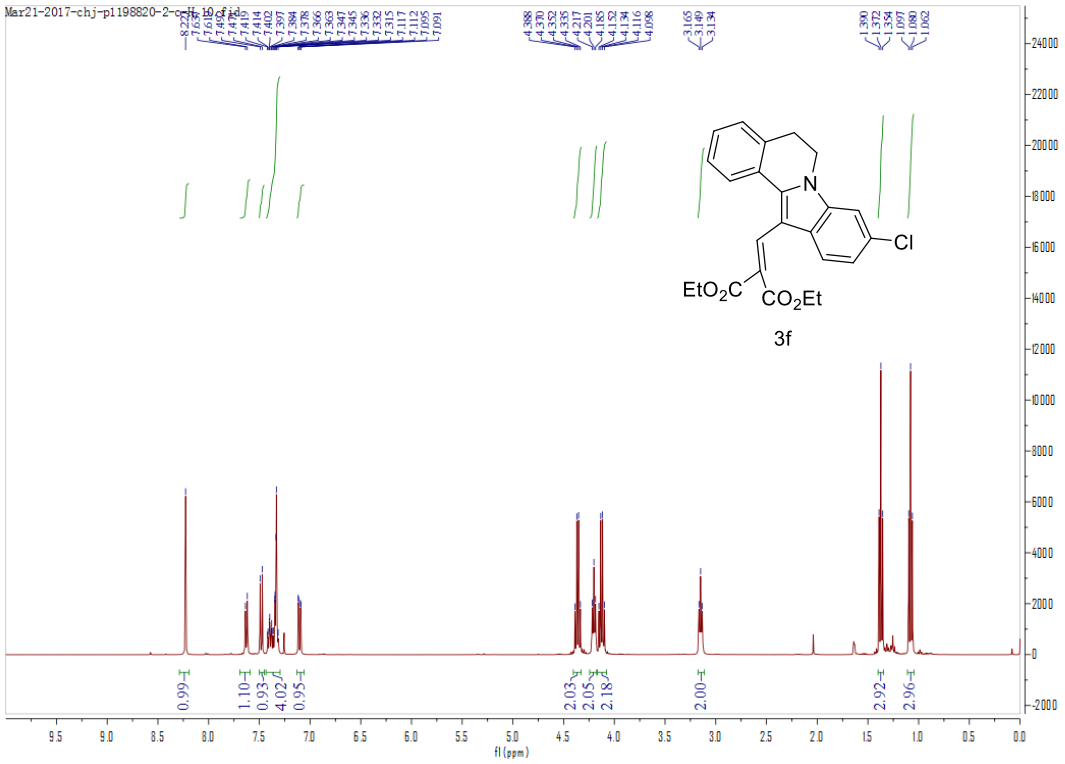
N
Cl
EtO2C
CO2Et
3e
f1 (ppm)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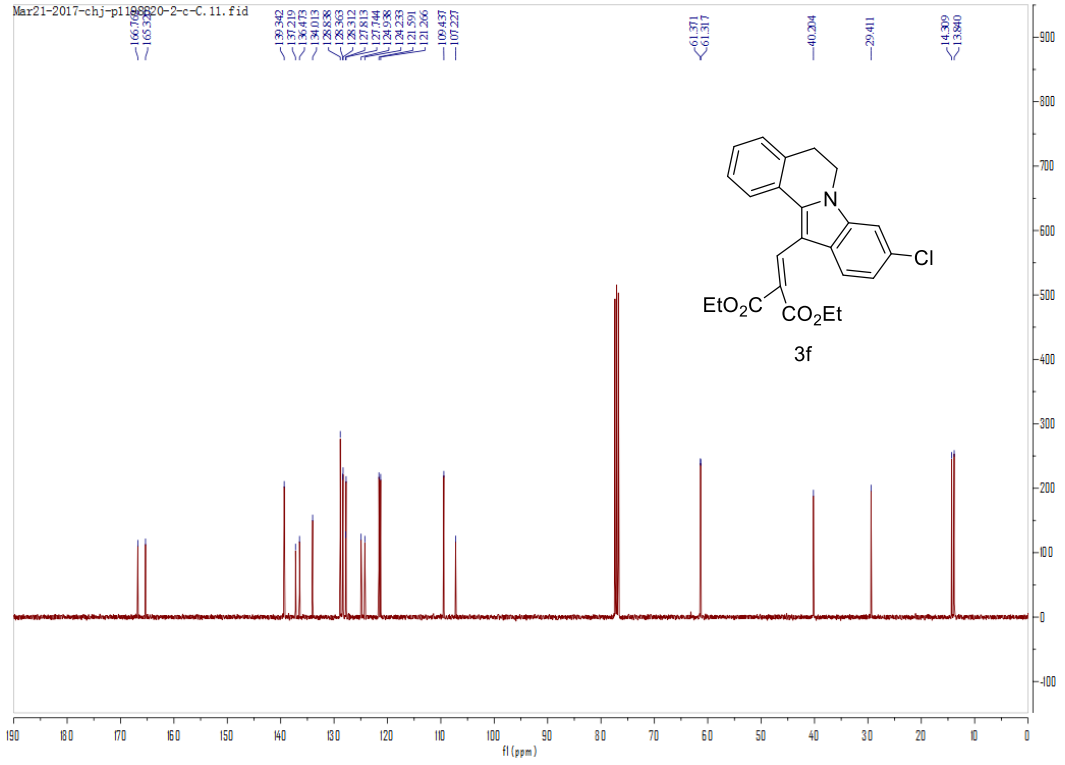
Cl
EtO2C
CO2Et
3f
f1 (ppm)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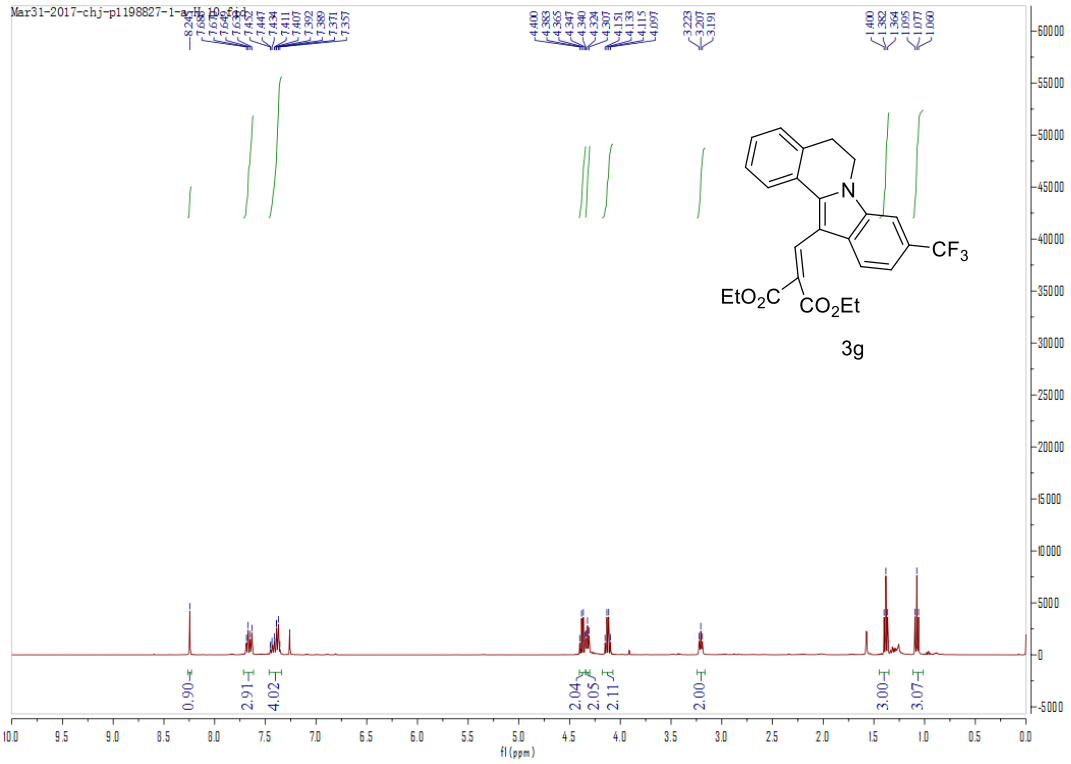
Cl
EtO2C
CO2Et
3f
f1 (ppm)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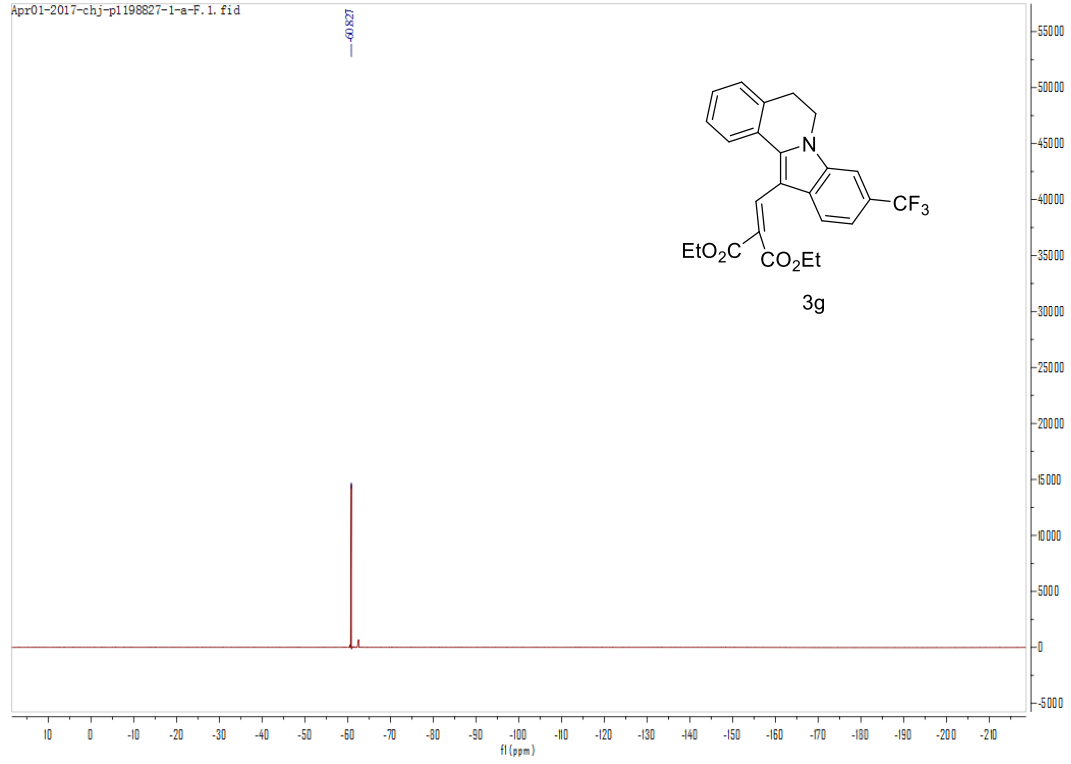
EtO2C
CO2Et
3g
f1 (ppm)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CF3
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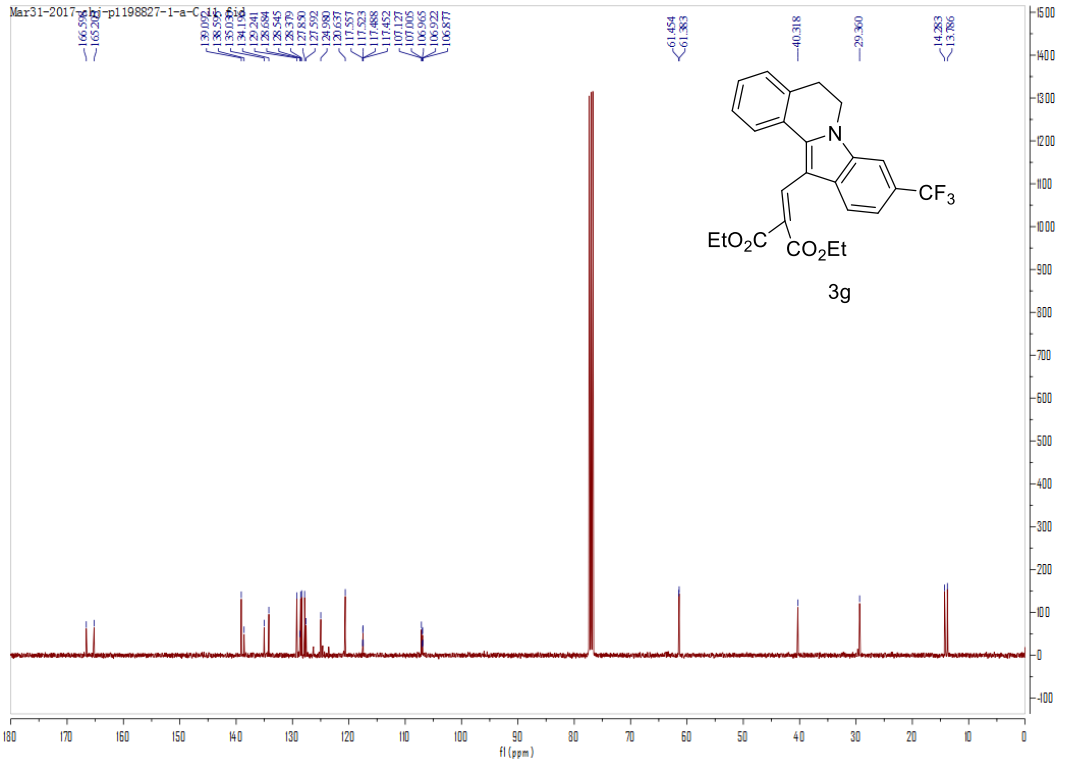
3g
f1 (ppm)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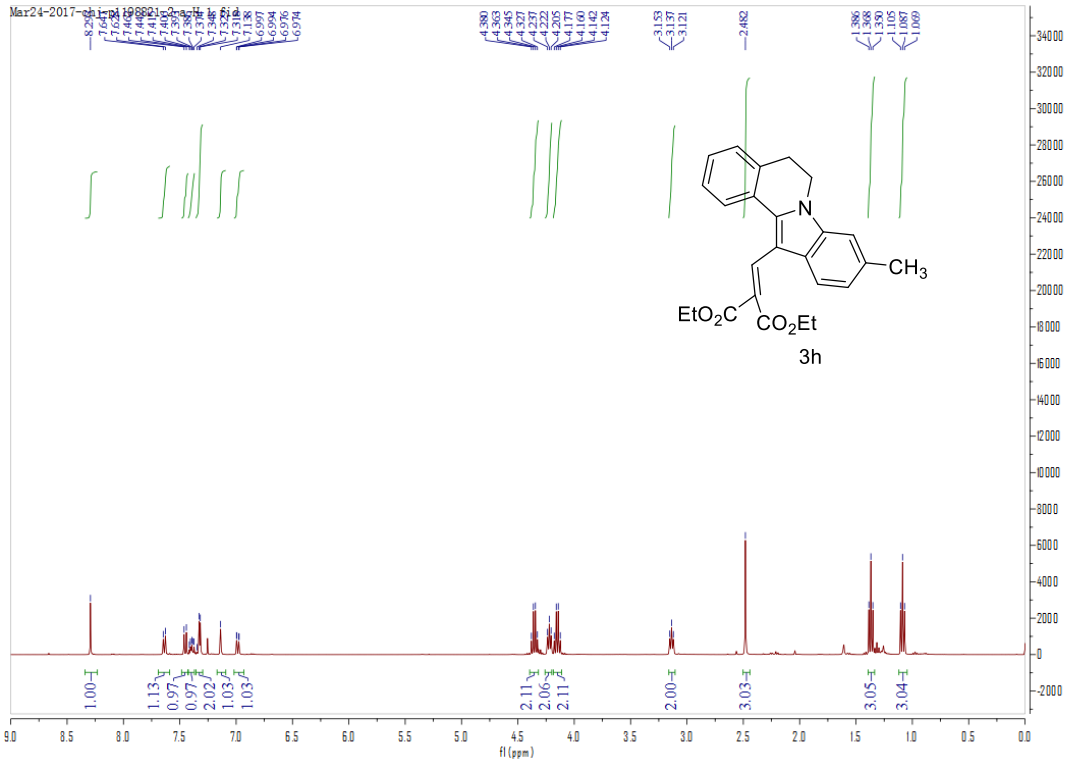
CF3
EtO2C
CO2Et
3g
f1 (ppm)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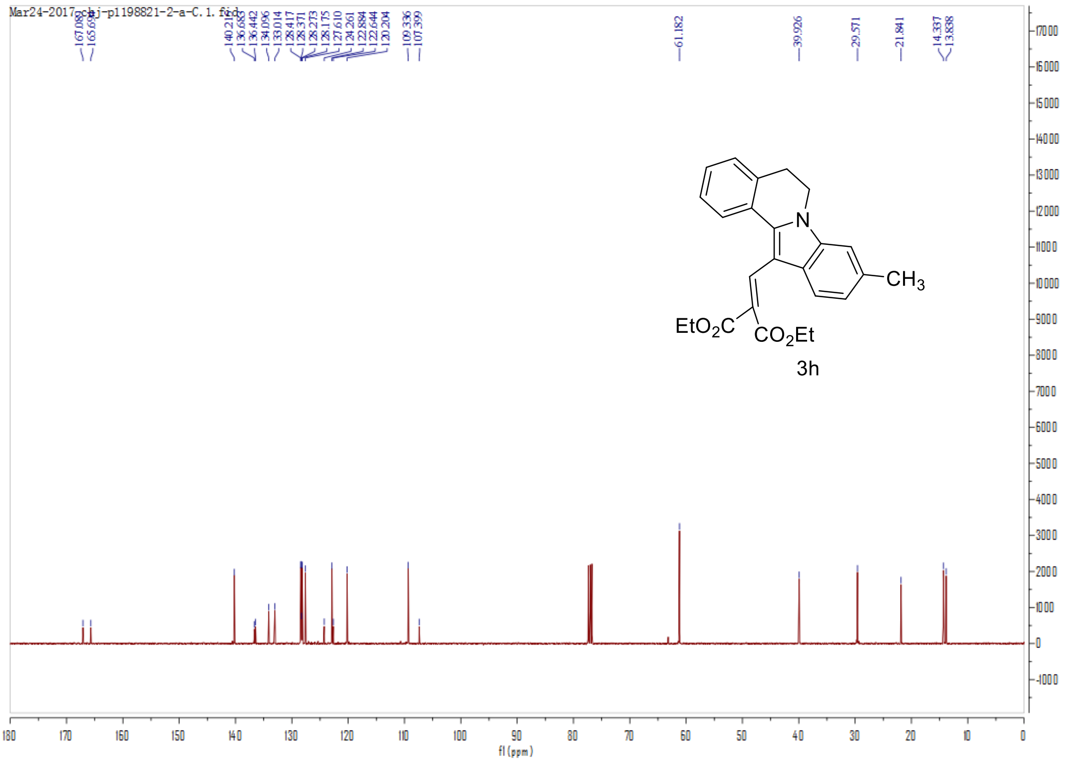
CH3
EtO2C
CO2Et
3h
f1 (ppm)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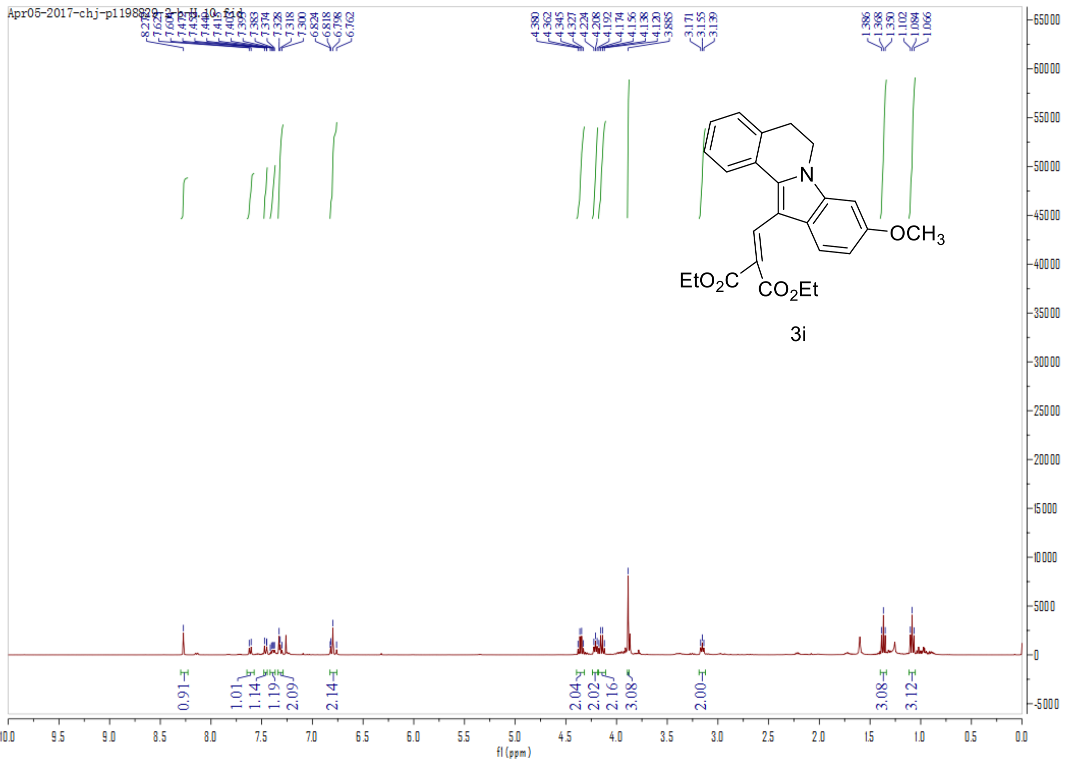
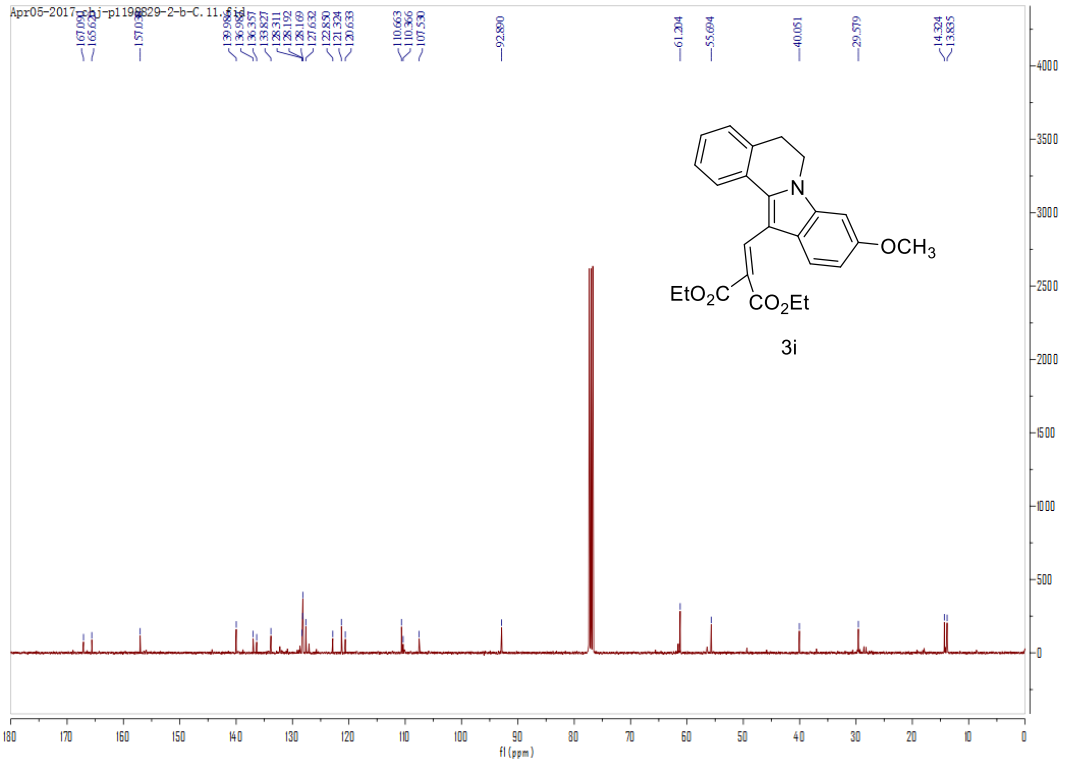
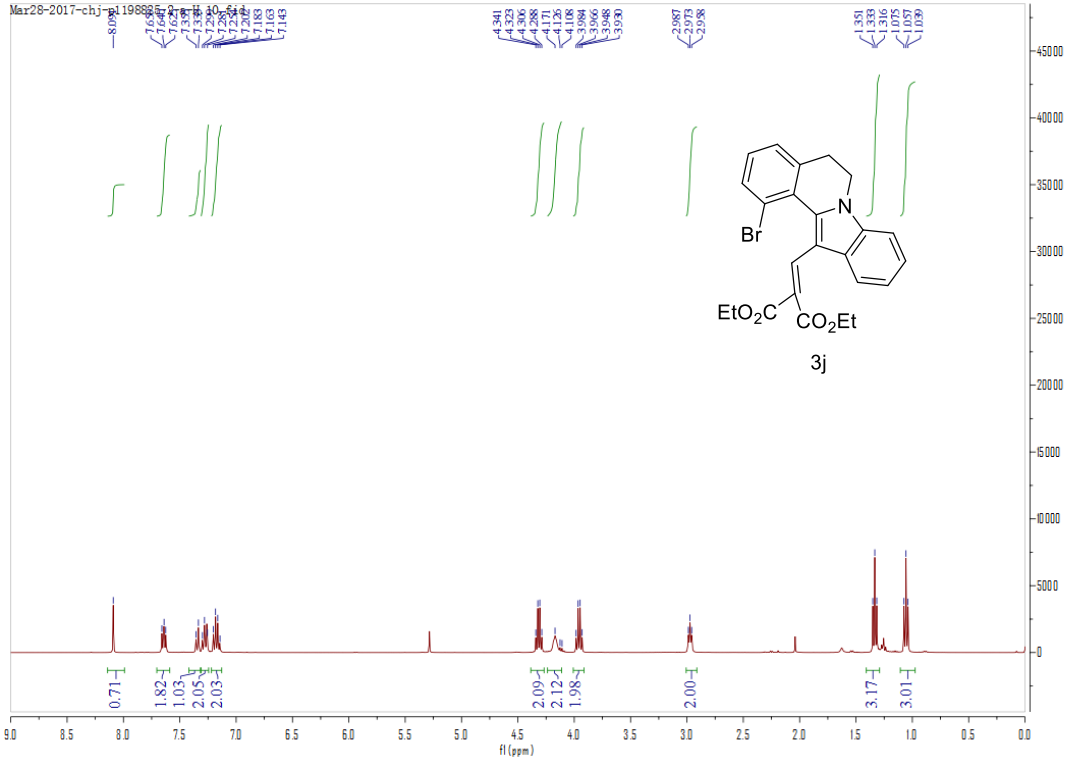
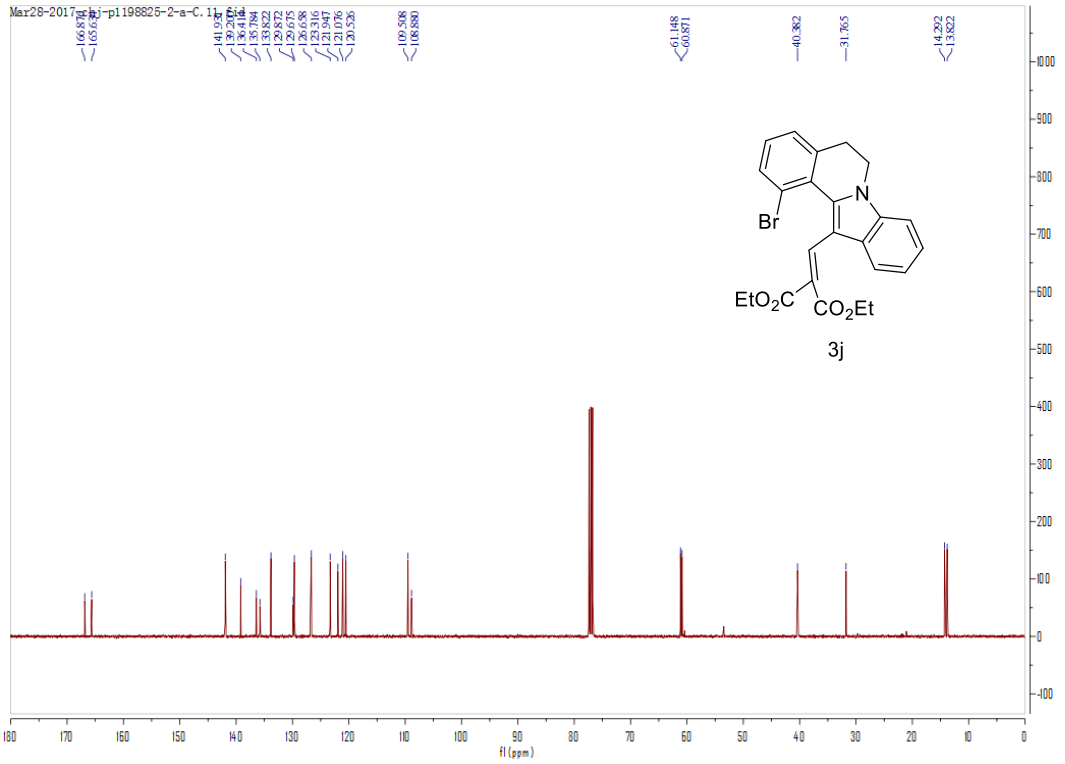
CO2Et
CH3
N
3h
f1 (ppm)


EtO2C
CO2Et
OCH3
N
3i
f1 (ppm)


OCH3
EtO2C
CO2Et
3i
f1 (ppm)


Br
EtO2C
CO2Et
3j
f1 (ppm)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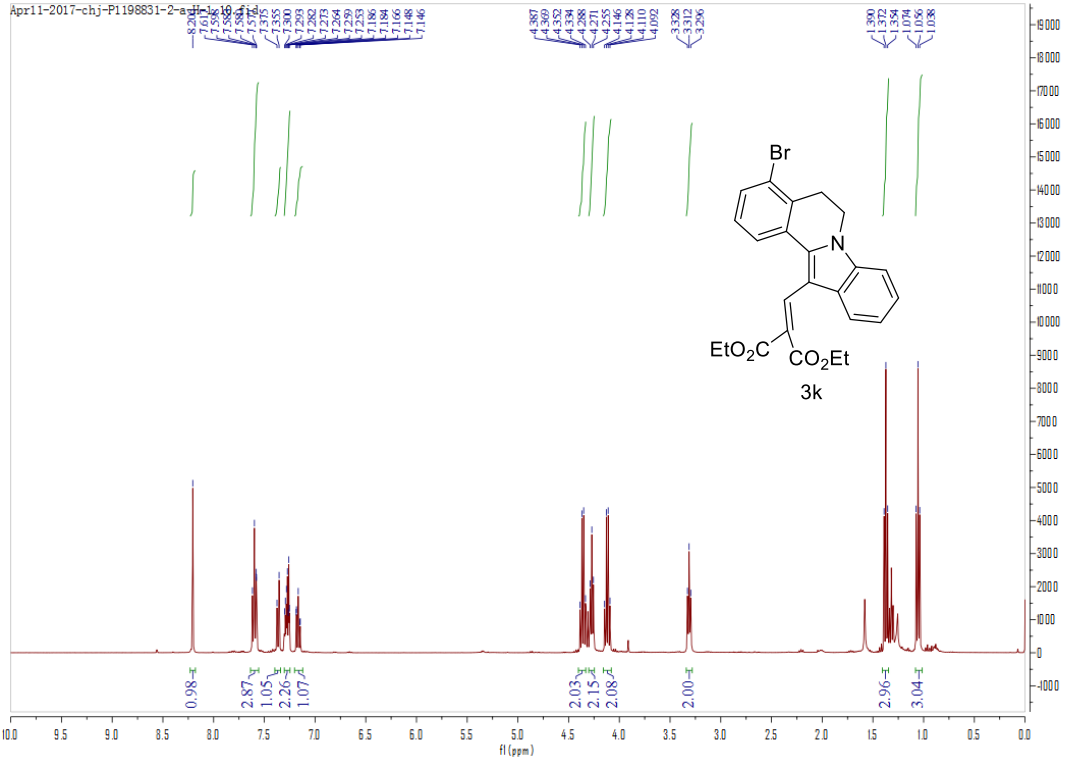
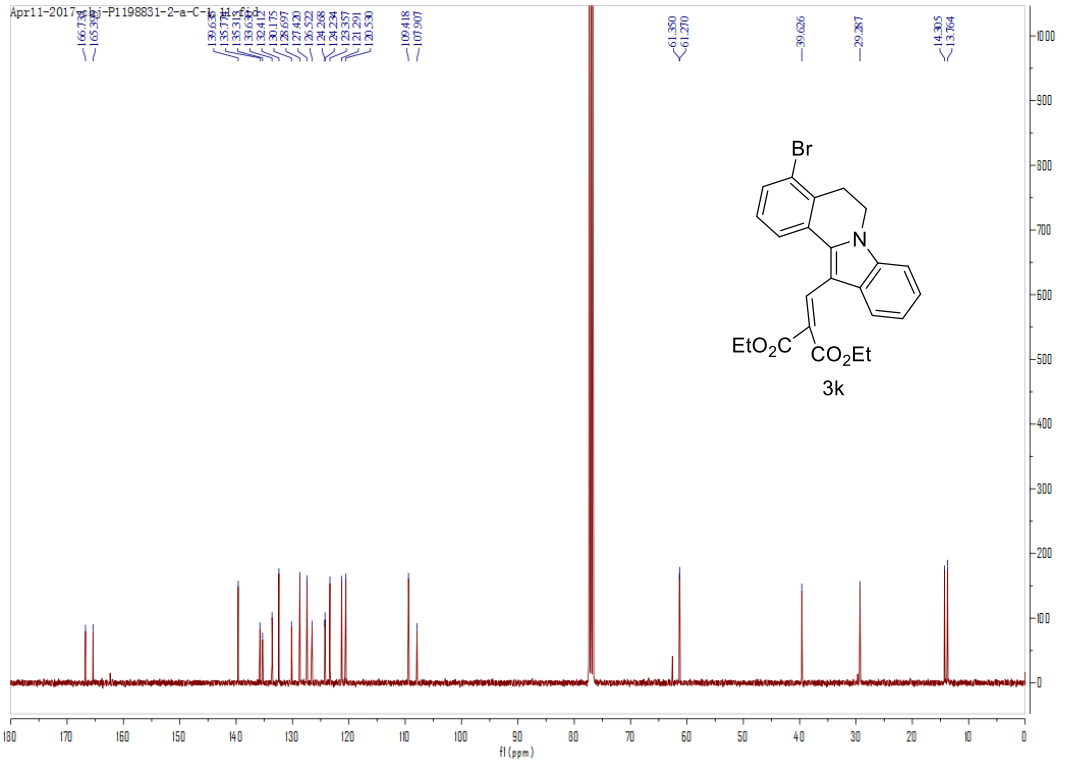
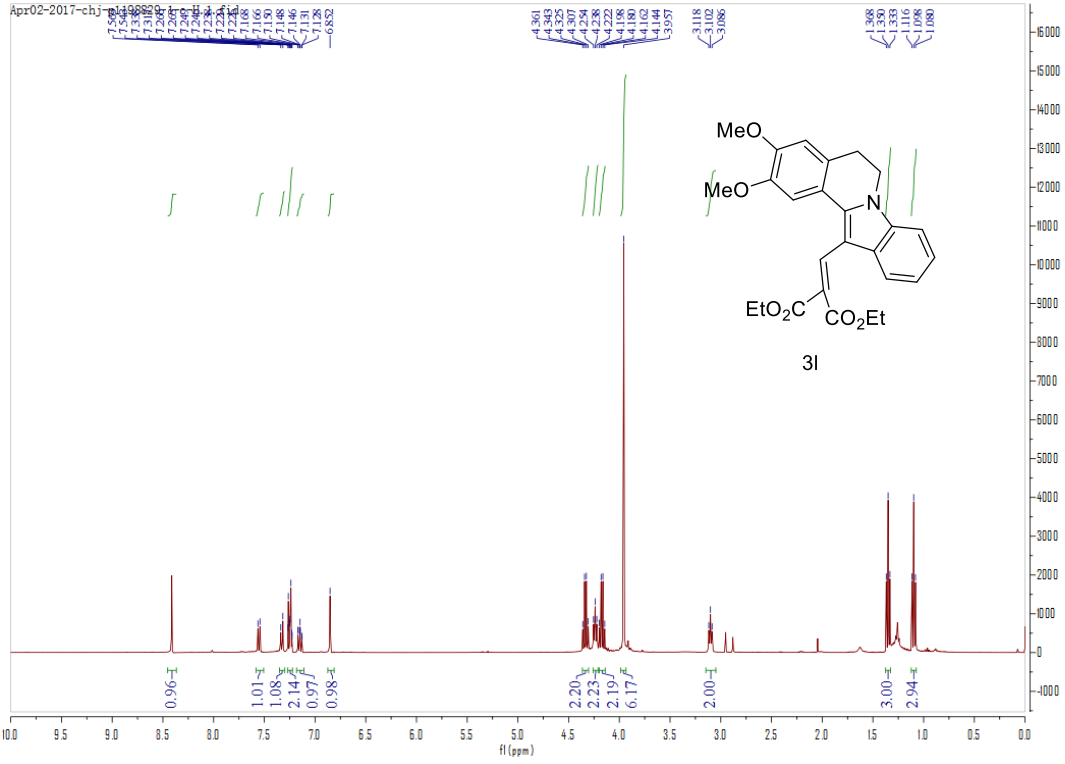
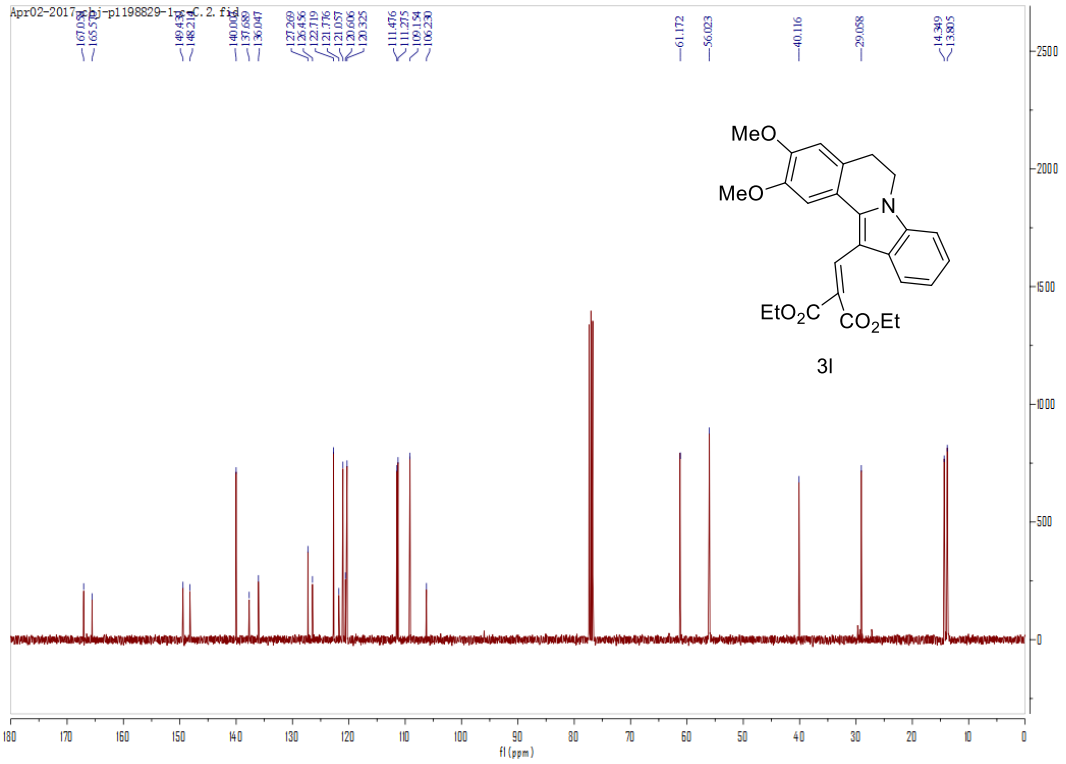
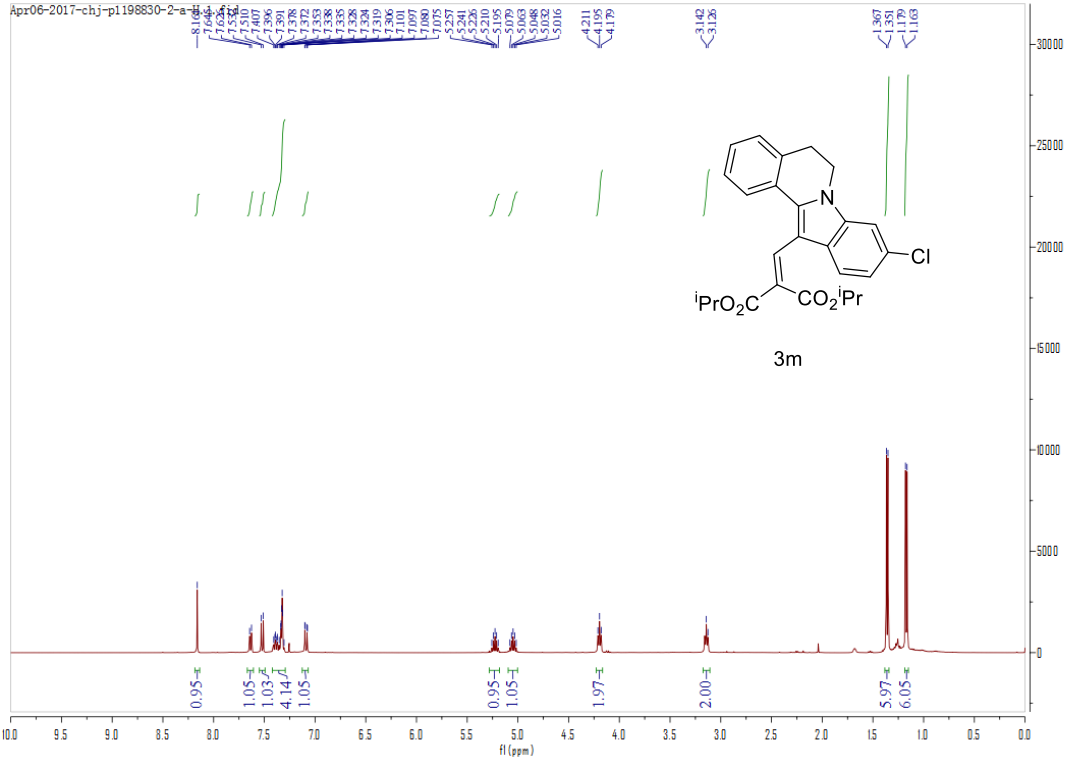
CO2Et
3j
f1 (ppm)

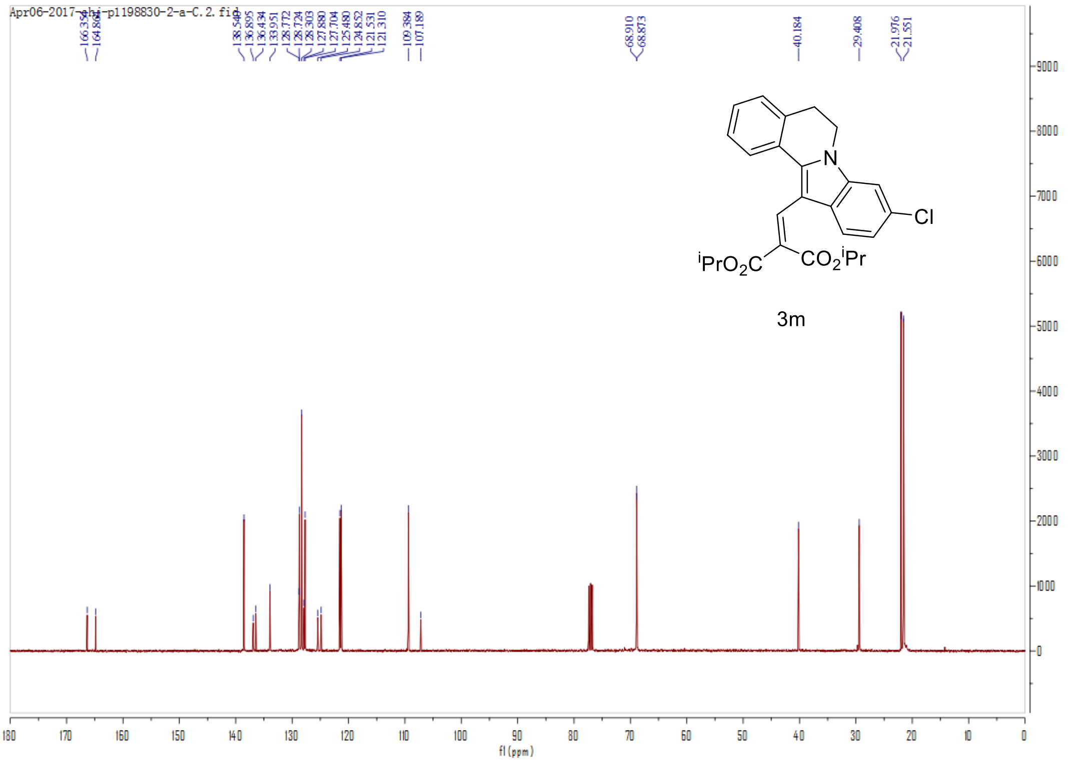

Br
N
EtO2C
CO2Et
3k
f1 (ppm)


Br
N
EtO2C
CO2Et
3k
f1 (ppm)


MeO
MeO
N
EtO2C
CO2Et
3l
f1 (ppm)


MeO
MeO
N
EtO2C
CO2Et
3l
f1 (ppm)


N
Cl
iPrO2C
CO2iPr
3m
f1 (ppm)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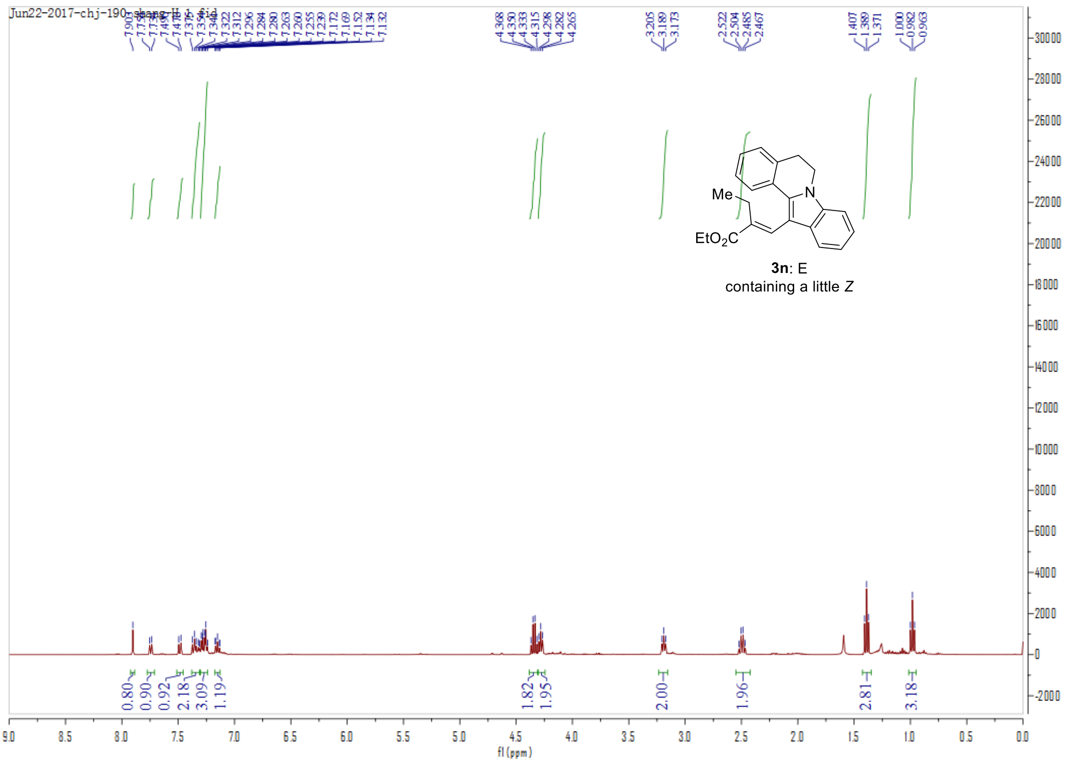
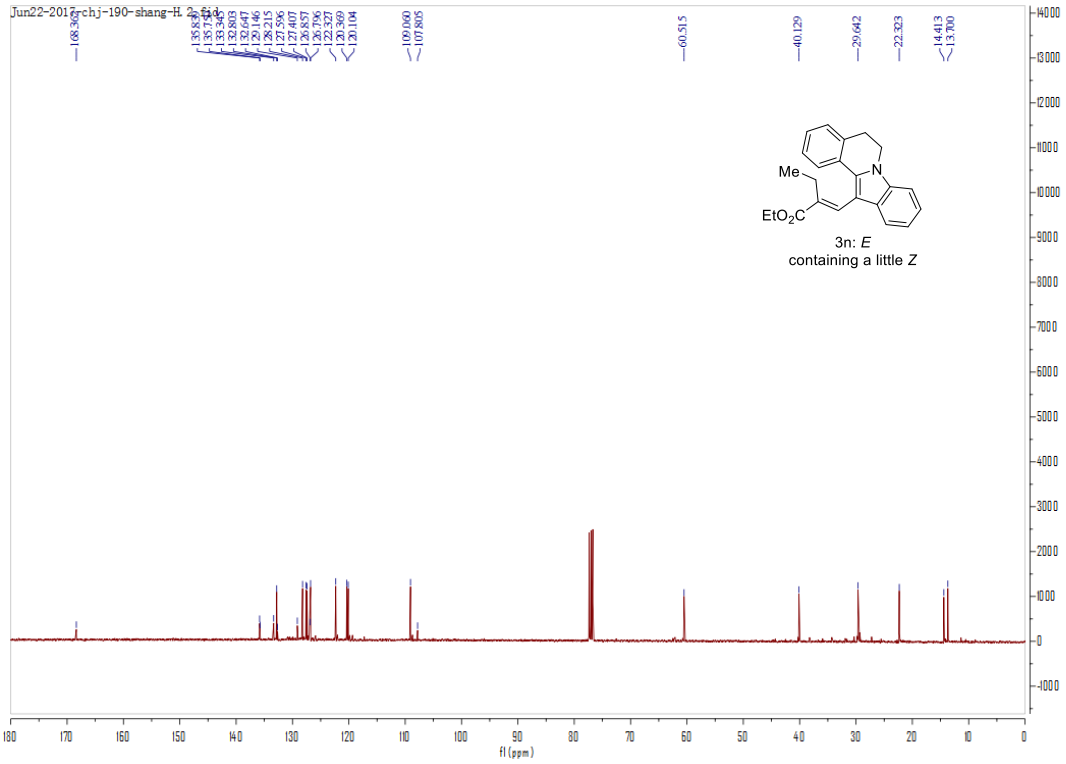
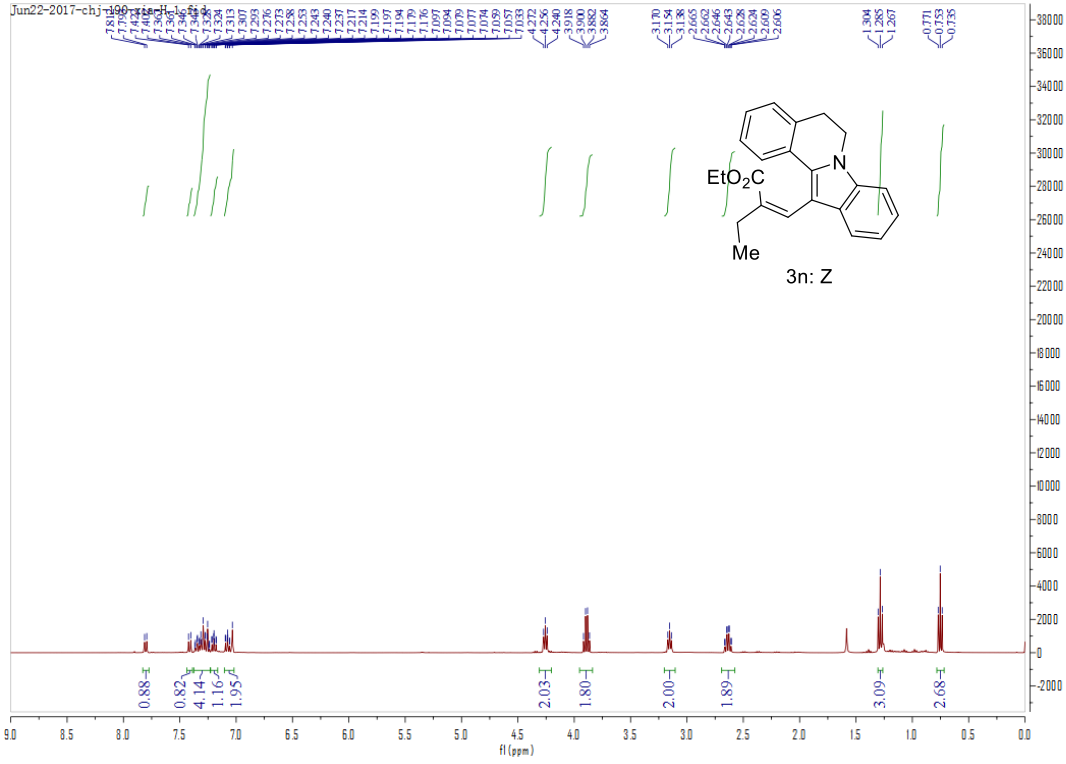
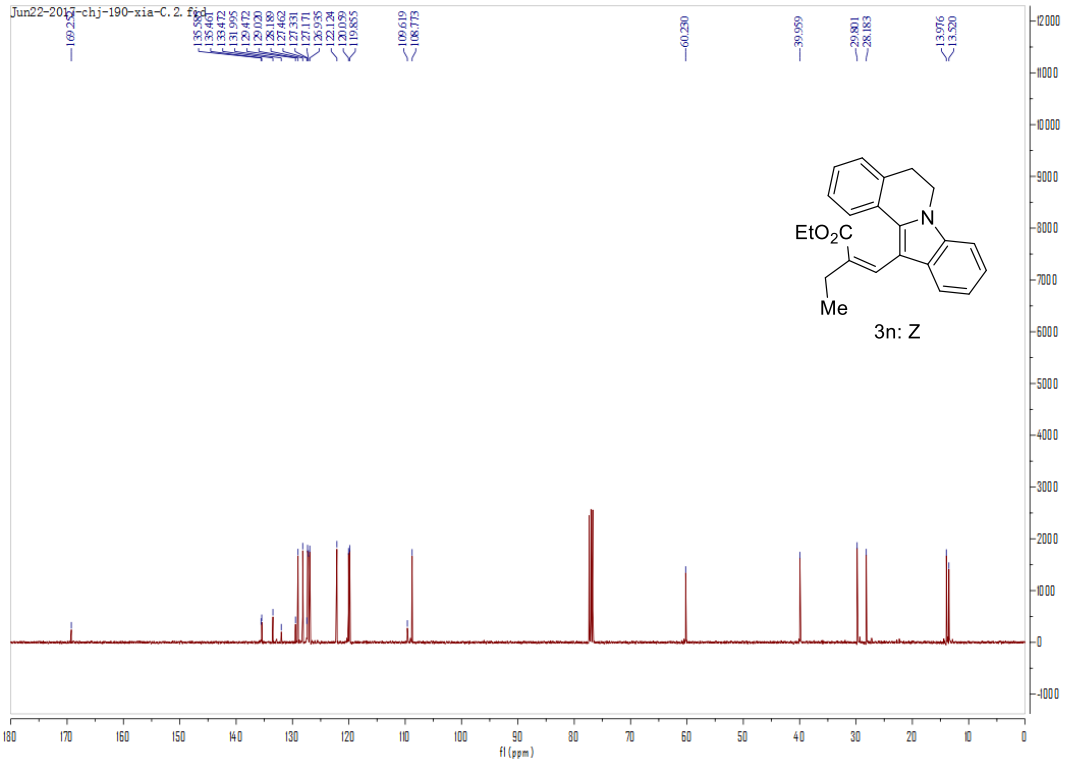
Cl
$^iPrO_2C$
$CO_2{}^iPr$
3m
f1 (ppm)

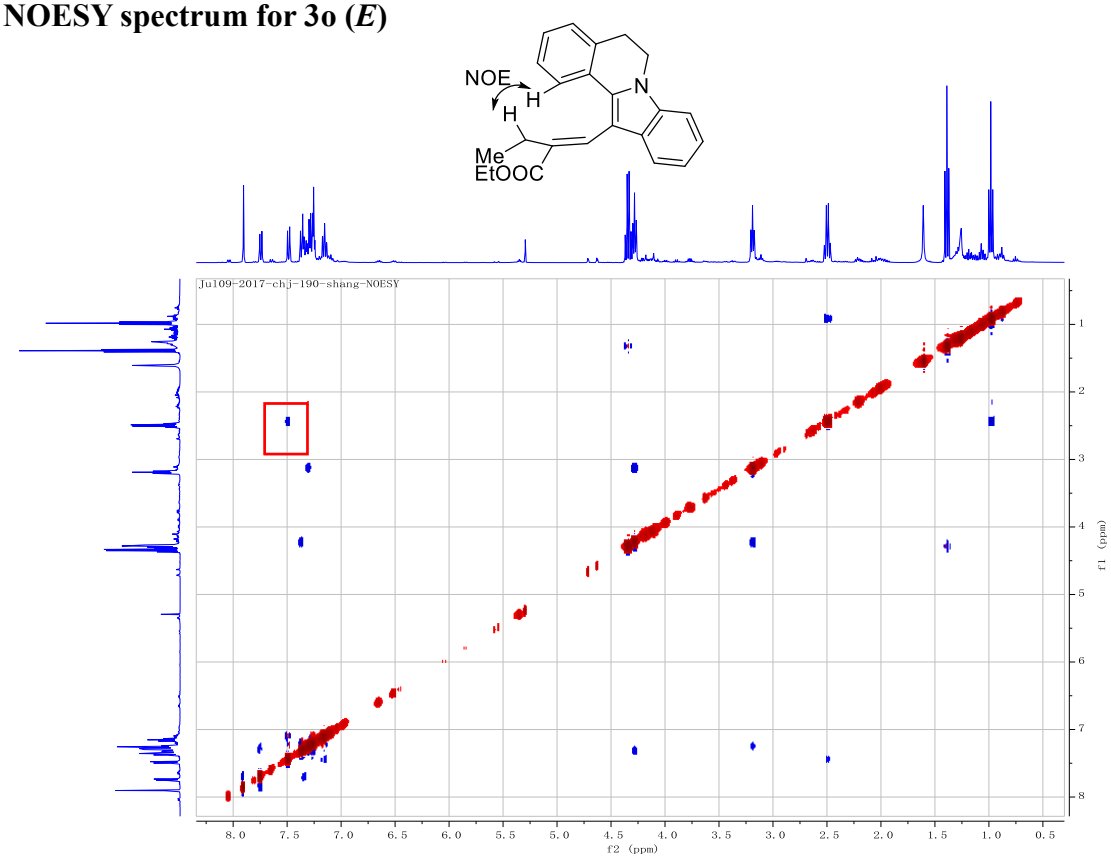

Me
N
EtO_2C
3n: E
containing a little Z
f1 (ppm)


Me
N
EtO2C
3n: E
containing a little Z
f1 (ppm)

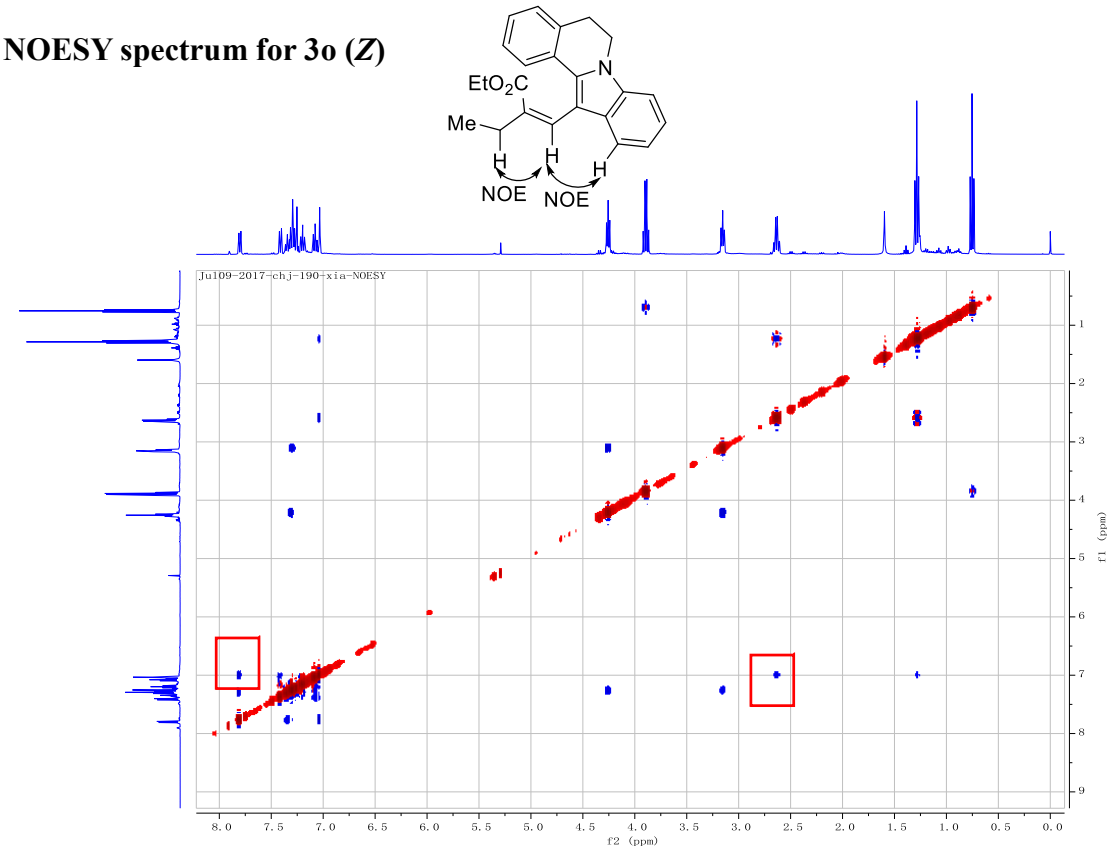

EtO2C
N
Me
3n: Z
f1 (ppm)

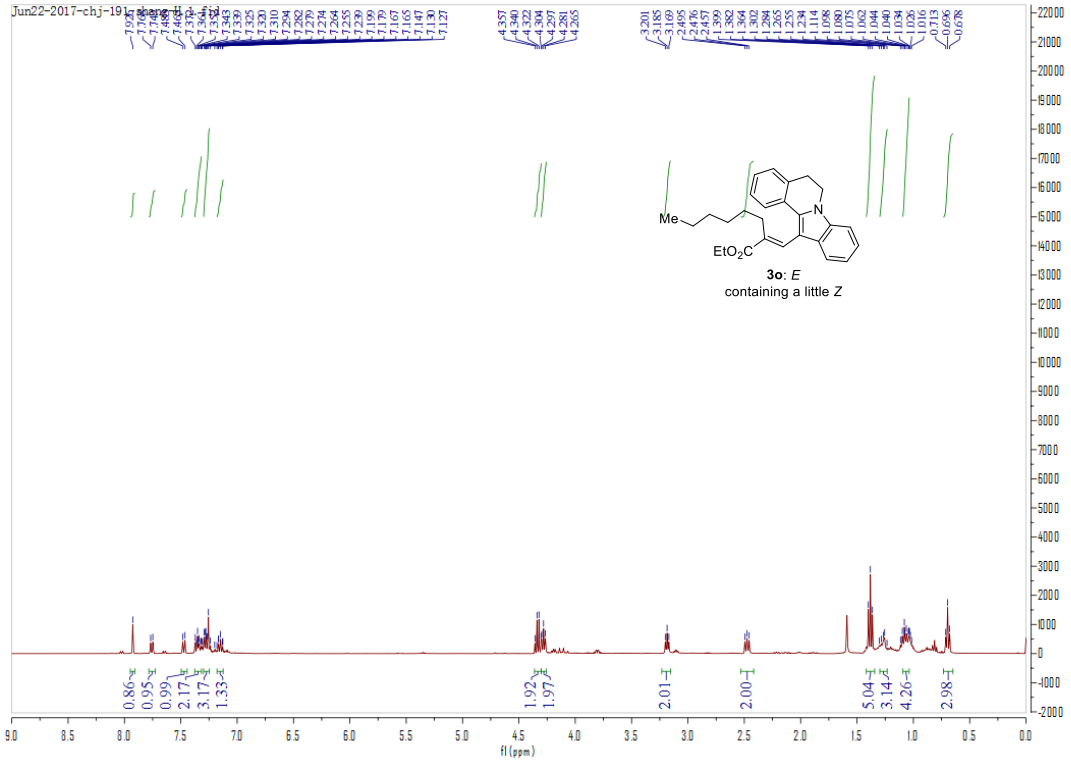


NOESY spectrum for 3o (*E*)

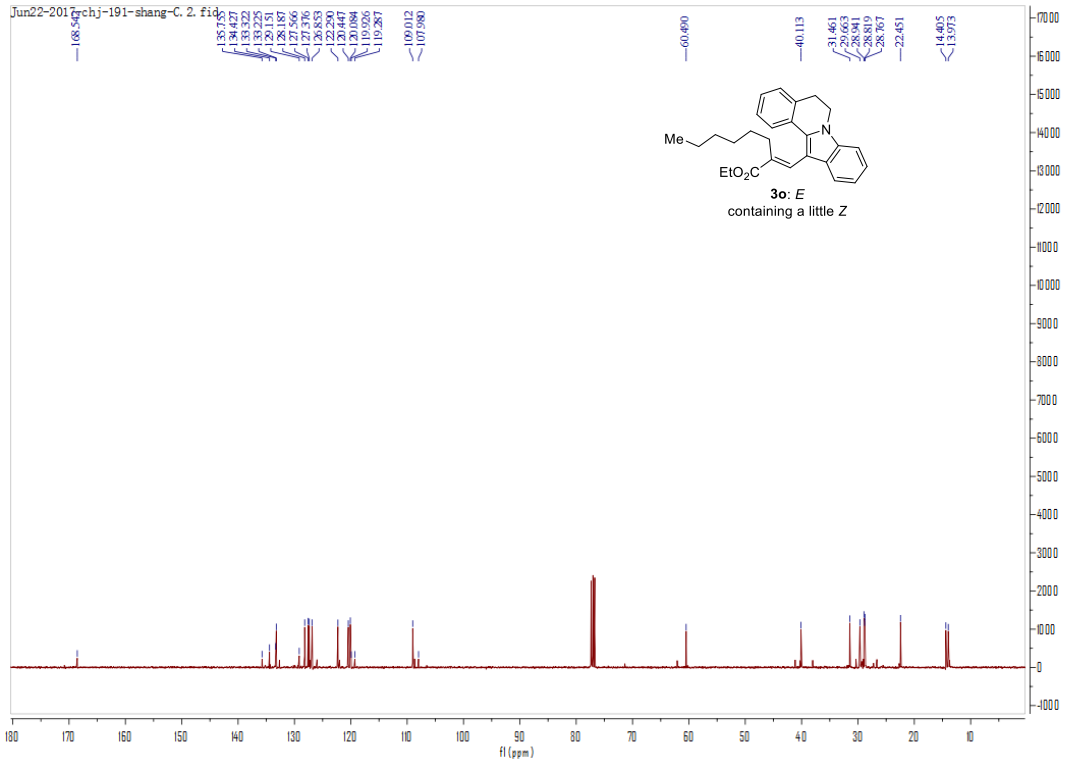


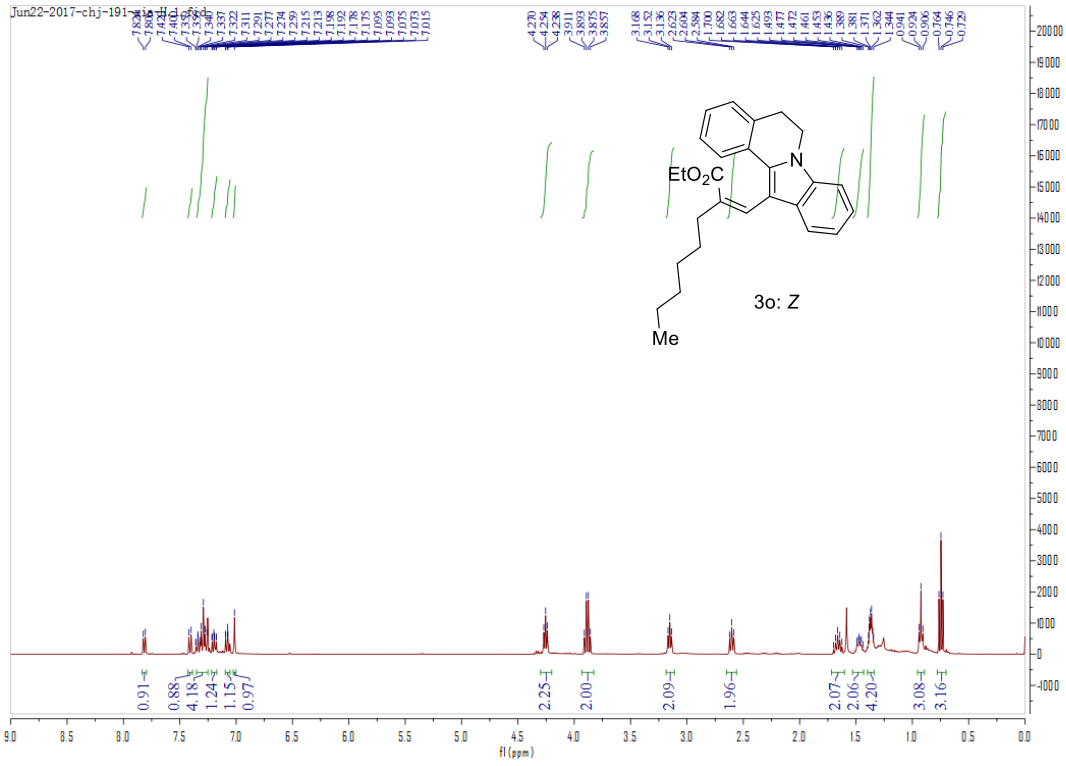
NOESY spectrum for 3o (*Z*)





3o: *E*
containing a little *Z*


Jun22-2017-chj-191-shang-C.2.fid
Me
EtO2C
N
3o: E
containing a little Z
f1 (ppm)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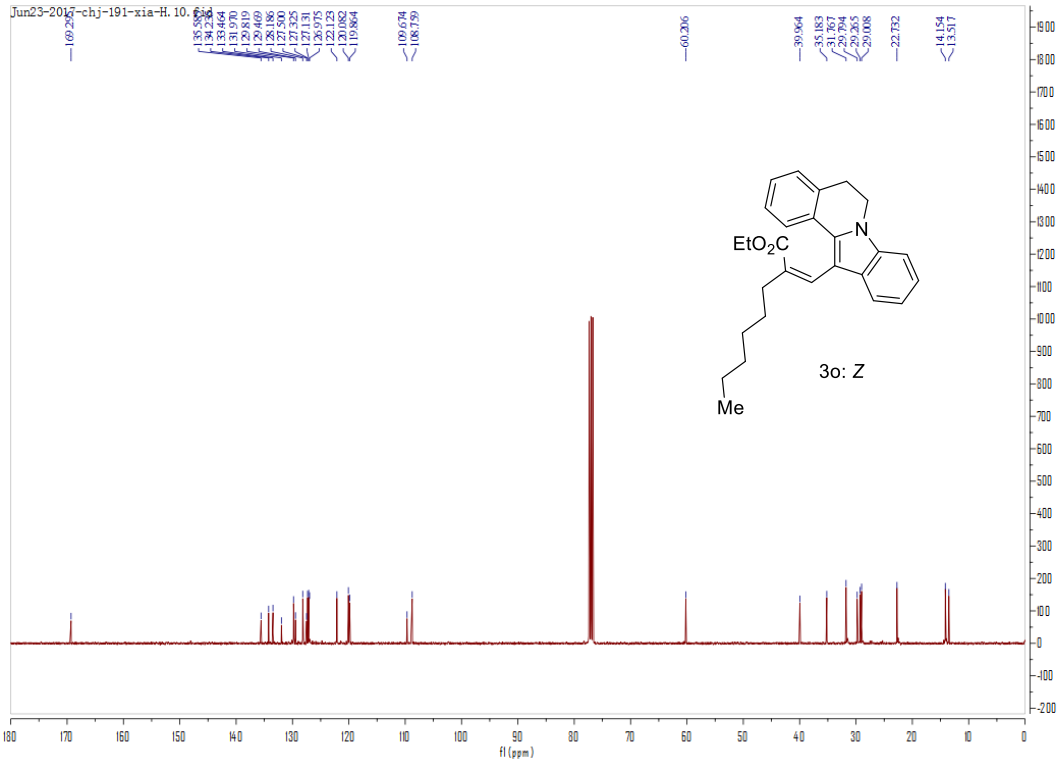
EtO2C
N
3o: Z
Me
f1 (ppm)


Jun23-2017-chj-191-xia-H.10.fid
169.297
135.552
134.228
133.464
131.970
129.819
129.469
128.186
127.500
127.135
127.131
126.975
122.123
120.082
119.864
109.674
108.759
60.206
39.964
35.183
31.767
29.794
29.265
29.008
22.732
14.154
13.517
EtO2C
N
Me
3o: Z
f1 (ppm)