Supporting Information

Base-Promoted Selective C2−N1 Ring-Expansion Reaction of Indolones toward Substituted Quinolines

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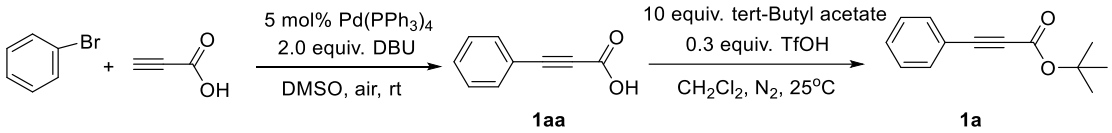
1. General information

Unless noted, all commercial reagents were used without further purification. Reactions were monitored by thin layer chromatography. Purification of reaction products was carried out by flash chromatography on silica gel (200~300 mesh). ^{1}H NMR spectra were recorded at 500 MHz or 600 MHz; ^{13}C NMR spectra were recorded at 125 MHz or 150 MHz in $CDCl_3$ (containing 0.03% TMS) or d^6-DMSO solutions. ^{1}H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) or d^6-DMSO (δ = 2.50 ppm) as the internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) or d^6-DMSO (δ = 39.52 ppm) as the internal reference. High-resolution mass spectra were recorded on a mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer. Single crystal X-raydiffraction data was collected in Bruker SMARTAPEX diffractiometers with molybdenum cathodes.

2. Synthesis of 1

General procedure: Synthesis of 1[1,2](Take 1a as an example).

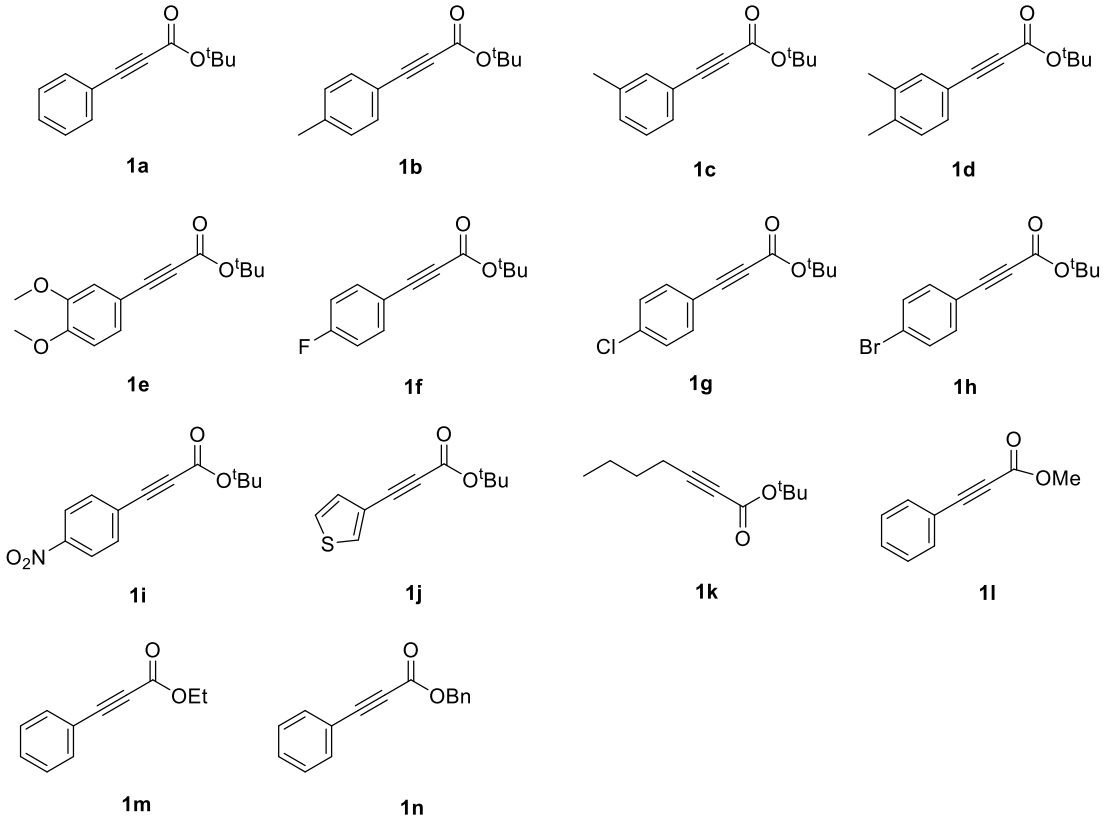


Propiolic acid (2.4 mmol, 1.2 equiv., 148 uL) was diluted with DMSO (2.5 mL). The solution was added to a mixture of $Pd(PPh_3)_4$ (0.1 mmol, 115.6 mg), aryl bromide (2.0 mmol), DBU (4.0 mmol, 0.6 mL), and DMSO (2.5 mL) in a small round-bottom flask at room temperature and stirred overnight. After the reaction finished, the reaction mixture was diluted with 25 mL of ethyl acetate, and extracted with saturated aqueous $NaHCO_3$ solution. The aqueous layer was separated, acidified to pH = 1 with 2M HCl, and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated in vacuo of **1aa** as a white solid (263.1 mg, 90%).

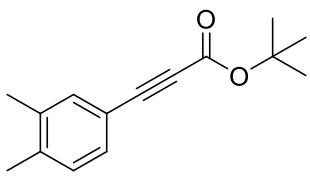
To a solution of phenylpropiolic acid (1 mmol, 0.1461 g) in 10 mL of DCM at 25°C

was added ^{t}BuOAc (10 mmol, 10 equiv., 1.34 ml) and TfOH (0.3 mmol, 0.3 equiv., 32 uL) dropwise. The resulting solution was stirred at room temperature for 2 hours and carefully washed with saturated $NaHCO_3$. The aqueous layer was extracted 3 times with DCM and the combined extracts were wash with saturated NaCl then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting oil was purified by column chromatography to give **1a** (77%) as a colourless oil.

Other tert-butyl 3-propiolates (**1b – 1j**) were prepared by using the same procedure as that of tert-butyl 3-phenylpropiolate (**1a**).

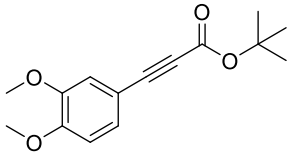


alkynoates **1k**,[3] **1l-1n**[2] were synthesized according to the reported methods. The analytical data of **1d-1f** and **1i** are as follows.

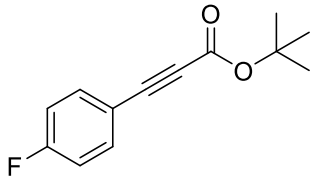


tert-butyl 3-(3,4-dimethylphenyl)propiolate (**1d**). Yellow solid, obtained in 2 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield:

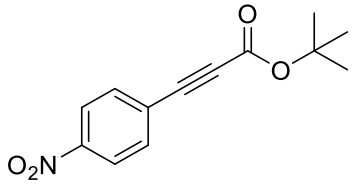
(0.8 mmol scale, 141.4 mg, 77%); m.p. 45-47 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.36 (s, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 2.27 (s, 3H), 2.24 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 139.7, 136.9, 133.9, 130.4, 129.8, 117.1, 84.5, 83.2, 81.5, 28.1, 19.9, 19.5. HRMS (ESI) calcd for $C_{15}H_{18}NaO_2$, $[M+Na]^+$: 253.1199, found: 253.1202.



tert-butyl 3-(3,4-dimethoxyphenyl)propiolate (**1e**). Light yellow solid, obtained in 2 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (0.5 mmol scale, 70.5 mg, 54%); m.p. 67-69 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.22 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz 1H), 3.91 (s, 3H), 3.88 (s, 3H), 1.54 (d, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 151.2, 148.6, 127.0, 115.2, 111.8, 110.9, 84.6, 83.3, 81.1, 55.93, 55.90, 28.1. HRMS (ESI) calcd for $C_{15}H_{18}NaO_4$, $[M+Na]^+$: 285.1097, found: 285.1100.



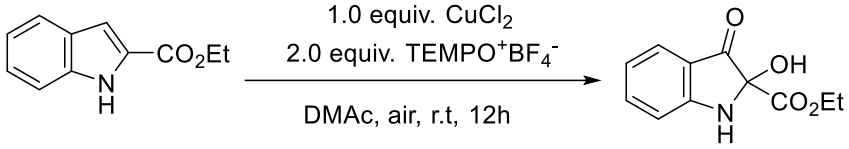
tert-butyl 3-(4-fluorophenyl)propiolate (**1f**). Yellow oil, obtained in 2 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (1.0 mmol scale, 145.3 mg, 66%); ^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.59-7.55 (m, 2H), 7.08-7.04 (m, 2H), 1.55 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7 (d, $J_{C\text{-}F}$ = 251.1 Hz), 153.0, 135.0 (d, $J_{C\text{-}F}$ = 8.75 Hz), 116.0 (d, $J_{C\text{-}F}$ = 22.2 Hz), 83.6, 82.7, 81.9, 28.0. HRMS (ESI) calcd for $C_{13}H_{13}NaFO_2$, $[M+Na]^+$: 243.0792, found: 243.0798.



tert-butyl 3-(4-nitrophenyl)propiolate (**1i**). Light yellow solid, obtained in 2 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (0.6 mmol scale, 137.8 mg, 93%); m.p. 115-117 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.24 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 2H), 1.56 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 148.3, 133.5, 126.7, 123.6, 85.6, 84.4, 80.6, 28.0. HRMS (ESI) calcd for $C_{13}H_{13}NaNO_4$, $[M+Na]^+$: 270.0737, found: 270.0744.

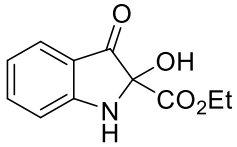
3. Synthesis of 2

General procedure: Synthesis of 2 (Take 2a as an example).

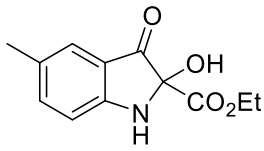


2aa **2a**

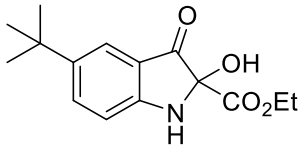
To a solution of ethyl 1H-indole-2-carboxylate (2.0 mmol, 0.378 g), $CuCl_2$ (2.0 mmol, 0.2689 g), $TEMPO^+BF_4^-$ (4.0 mmol, 0.9722g) and three drops of water in DMAc (4 mL) at room temperature and stirred overnight. The reaction mixture was treated with H_2O, then extracted with EA and dried over Na_2SO_4. After removal of the EA, the residue was purified by chromatography on silica gel (PE: EA = 2:1) to afford **2a**.



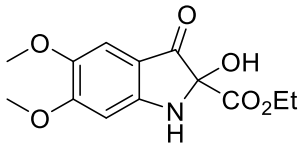
ethyl 2-hydroxy-3-oxoindoline-2-carboxylate (**2a**). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); (5 mmol scale, 0.8988g, 81%); m.p. 96-98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.61 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 6.95-6.91 (m, 2H), 5.15 (s, 1H), 4.46 (s, 1H), 4.33-4.22 (m, 2H), 1.27-1.24 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 195.9, 169.1, 160.8, 138.4, 125.6, 120.8, 118.4, 113.0, 86.1, 63.6, 13.9. HRMS (ESI) calcd for $C_{11}H_{11}NaNO_4$, $[M+Na]^+$: 244.0580, found: 244.0583.



ethyl 2-hydroxy-5-methyl-3-oxoindoline-2-carboxylate (**2p**). The structure of **2p** was confirmed by X-ray crystallography (CCDC 2264615). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); (1.0 mmol scale, 167.4mg, 71%); m.p. 105-107 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.39 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.18 (s, 1H), 4.60 (s, 1H), 4.29-4.21 (m, 2H), 2.30 (s, 3H), 1.26-1.23 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 196.0, 169.2, 159.2, 139.6, 130.5, 125.0, 118.6, 113.0, 86.6, 63.5, 20.5, 13.9. HRMS (ESI) calcd for $C_{12}H_{13}NaNO_4$, $[M+Na]^+$: 258.0737, found: 258.0739.

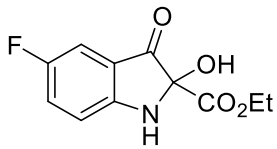


ethyl 5-(tert-butyl)-2-hydroxy-3-oxoindoline-2-carboxylate (**2q**). Yellow oil, obtained in 12 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); (1.3 mmol scale, 251.4mg, 70%); ^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.61-7.58 (m, 2H), 6.89-6.86 (m, 1H), 5.09 (s, 1H), 4.47 (s, 1H), 4.33-4.22 (m, 2H), 1.30 (s, 9H), 1.28-1.25 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 196.2, 169.2, 159.1, 144.3, 136.5, 121.5, 118.2, 112.8, 86.6, 63.5, 34.4, 31.2, 14.0. HRMS (ESI) calcd for $C_{15}H_{19}NaNO_4$, $[M+Na]^+$: 300.1206, found: 300.1212.

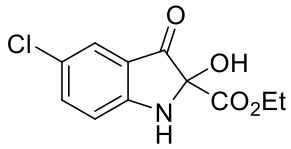


ethyl 2-hydroxy-5,6-dimethoxy-3-oxoindoline-2-carboxylate (**2r**). Yellow oil, obtained in 12 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); (1.0 mmol scale, 193.5mg, 69%); ^{1}H NMR (500 MHz, d^6-DMSO) δ. 7.53 (s, 1H), 6.90 (d, *J* = 1.0 Hz, 1H), 6.85 (s, 1H), 6.38 (d, *J* = 1.0 Hz, 1H), 4.12-4.05

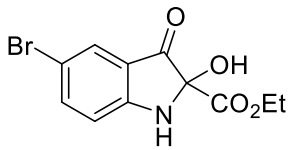
(m, 2H), 3.84 (s, 3H), 3.70 (s, 3H), 1.12 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, d^6-DMSO) δ. 194.9, 168.7, 159.3, 158.6, 143.5, 108.4, 104.9, 94.9, 86.9, 61.2, 56.0, 55.8, 14.0. HRMS (EI) calcd for $C_{13}H_{15}NaNO_6$, $[M+Na]^+$: 304.0792, found: 304.0789.



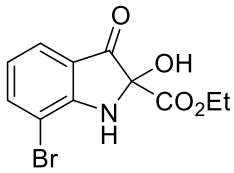
ethyl 5-fluoro-2-hydroxy-3-oxoindoline-2-carboxylate (2s). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); (1.3 mmol scale, 233.9 mg, 75%); m.p. 102-105 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.30-7-25 (m, 2H), 6.91-6.89 (m, 1H), 5.24 (s, 1H), 4.67 (s, 1H), 4.33-4.22 (m, 2H), 1.25 (t, J = 7.0 Hz, 3H). 1^{13}C NMR (125 MHz, $CDCl_3$) δ. 195.7 (d, $J_{C\text{-}F}$ = 3.8 Hz), 168.8, 157.4 (d, $J_{C\text{-}F}$ = 240.4 Hz), 157.3, 126.1 (d, $J_{C\text{-}F}$ = 24.9 Hz), 119.0 (d, $J_{C\text{-}F}$ = 7.6 Hz), 114.2 (d, $J_{C\text{-}F}$ = 7.5 Hz), 110.7 (d, $J_{C\text{-}F}$ = 23.0 Hz), 87.0, 63.7, 13,9. HRMS (ESI) calcd for $C_{11}H_{10}FNaNO_4$, $[M+Na]^+$: 262.0486, found: 262.0491.



ethyl 5-chloro-2-hydroxy-3-oxoindoline-2-carboxylate (2t). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); (1.0 mmol scale, 210 mg, 82%); m.p. 78-80 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.55 (s, 1H), 7.45 (d, J = 8.5 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 5.29 (s, 1H), 4.64 (s, 1H), 4.31-4.23 (m, 2H), 1.25 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 194.9, 168.7, 159.0, 138.1, 126.1, 124.9, 119.4, 114.1, 86.5, 63.8, 13.9. HRMS (ESI) calcd for $C_{11}H_{10}ClNaNO_4$, $[M+Na]^+$: 278.0191, found: 278.0193.

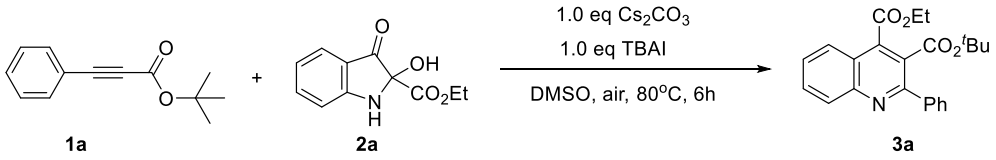


ethyl 5-bromo-2-hydroxy-3-oxoindoline-2-carboxylate (2u). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); (1.2 mmol scale, 254.4 mg, 71%); m.p. 95-97 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ. 7.70 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.36 (s, 1H), 4.69 (s, 1H), 4.31-4.21 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ. 194.7, 168.7, 159.4, 140.8, 128.0, 119.9, 114.5, 112.9, 86.4, 63.7, 13.9. HRMS (ESI) calcd for $C_{11}H_{10}BrNaNO_4$, $[M+Na]^+$: 321.9685, found: 321.9684.



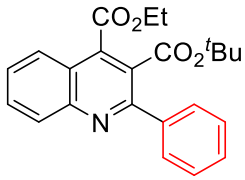
ethyl 7-bromo-2-hydroxy-3-oxoindoline-2-carboxylate (2v). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); (0.9 mmol scale, 219 mg, 81%); m.p. 105-107 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ. 7.68 (d, *J* = 8.0 Hz 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 5.39 (s, 1H), 4.66 (s, 1H), 4.35-4.23 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ. 195.4, 168.7, 158.3, 140.2, 124.5, 121.6, 119.8, 106.3, 85.9, 63.8, 13.9. HRMS (ESI) calcd for $C_{11}H_{10}BrNaNO_4$, $[M+Na]^+$: 321.9685, found: 321.9690.

4. Synthesis of 3

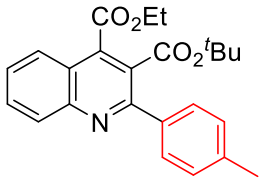


In a Schlenk tube, indolone **2a** (0.15 mmol, 1.4 equiv., 30.9 mg), Cs_2CO_3(0.1 mmol, 32.6 mg), TBAI (0.1 mmol, 36.9 mg), DMSO (1.0 mL), and alkynoate **1a** (0.1 mmol, 20.2 mg) were stirred at 80 °C in the oil bath for 6h under air. Then, the reaction mixture was cooled to room temperature and was treated with saturated NH_4Cl, then extracted

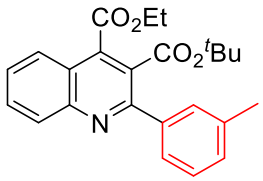
with EA and dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on basic silica gel (PE: EA = 10: 1) to afford **3a** (light yellow solid, 28.9 mg, 77%).



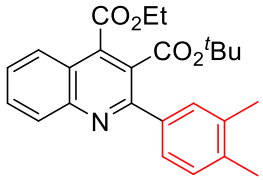
3-(tert-butyl) 4-ethyl 2-phenylquinoline-3,4-dicarboxylate (**3a**). Light yellow solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (28.9 mg, 77%); m.p. 112-114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.19 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.66-7.62 (m, 3H), 7.48-7.46 (m, 3H), 4.55 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.29 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 166.1, 157.2, 147.8, 140.4, 139.6, 131.2, 129.9, 128.7, 128.7, 128.3, 128.0, 125.3, 125.2, 122.2, 83.1, 62.5, 27.4, 14.1. HRMS (ESI) calcd for $C_{23}H_{24}NO_4$, $[M+H]^+$: 378.1700, found: 378.1704.



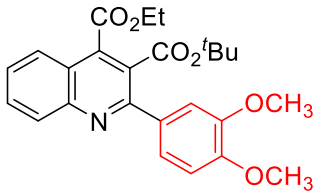
3-(tert-butyl) 4-ethyl 2-(p-tolyl)quinoline-3,4-dicarboxylate (**3b**). Light yellow solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (28.0 mg, 72%); m.p. 106-108 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.17 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.61 (m, *J* = 7.8 Hz 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 4.57-4.53 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.47-1.44 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 166.2, 157.2, 147.9, 139.5, 138.7, 137.5, 131.0, 129.9, 128.9, 128.6, 127.8, 125.2, 125.1, 122.1, 83.1, 62.5, 27.5, 21.3, 14.1. HRMS (ESI) calcd for $C_{24}H_{26}NO_4$, $[M+H]^+$: 392.1856, found: 392.1862.



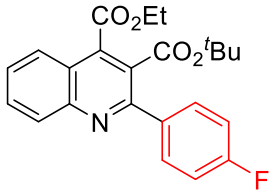
3-(tert-butyl) 4-ethyl 2-(m-tolyl)quinoline-3,4-dicarboxylate (**3c**). Light yellow solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (30.5 mg, 78%); m.p. 86-88 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.19 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.45-7.44 (m, 2H), 7.38-7.35 (m, 1H), 7.28-7.26 (m, 1H), 4.56 (q, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H), 1.30 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 166.5, 166.2, 157.4, 147.8, 140.3, 139.6, 137.9, 131.1, 129.9, 129.5, 129.2, 128.3, 127.9, 125.8, 125.3, 125.2, 122.2, 83.1, 62.5, 27.4, 21.4, 14.1. HRMS (ESI) calcd for $C_{24}H_{26}NO_4$, $[M+H]^+$: 392.1856, found: 392.1859.



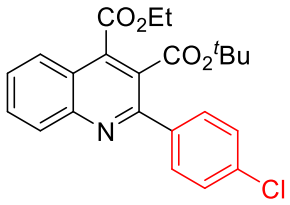
3-(tert-butyl) 4-ethyl 2-(3,4-dimethylphenyl)quinoline-3,4-dicarboxylate (**3d**). Grey white solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (28.0 mg, 69%); m.p. 104-106 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.18 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.42 (s, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 4.55 (q, *J* = 7.2 Hz, 2H), 2.32 (s, 6H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 166.6, 166.3, 157.4, 147.8, 139.4, 137.8, 137.4, 136.4, 131.0, 129.9, 129.8, 129.6, 127.8, 126.1, 125.2, 125.1, 122.1, 83.0, 62.5, 27.5, 19.8, 19.6, 14.1. HRMS (ESI) calcd for $C_{25}H_{28}NO_4$, $[M+H]^+$: 406.2013, found: 406.2022.



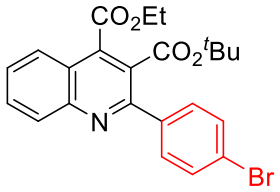
3-(tert-butyl) 4-ethyl 2-(3,4-dimethoxyphenyl)quinoline-3,4-dicarboxylate (**3e**). Yellow solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (18.8 mg, 43%); m.p. 115-117 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.18 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.27-7.26 (m, 1H), 7.22-7.19 (m, 1H), 6.98-6.96 (m, 1H), 4.56 (q, *J* = 7.0 Hz, 2H), 3.95 (s, 6H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 166.5, 166.4, 156.7, 149.8, 148.9, 147.8, 139.4, 133.1, 131.1, 129.8, 127.8, 125.3, 125.1, 122.1, 121.5, 111.8, 110.9, 83.1, 62.5, 56.1, 55.9, 27.6, 14.1. HRMS (ESI) calcd for $C_{25}H_{27}NaNO_6$, $[M+Na]^+$: 460.1731, found: 460.1735.



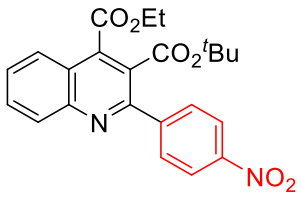
3-(tert-butyl) 4-ethyl 2-(4-fluorophenyl)quinoline-3,4-dicarboxylate (**3f**). Light yellow solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (24.9 mg, 63%); m.p. 83-85 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.17 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.82 (t, *J* = 7.2 Hz, 1H), 7.66-7.63 (m, 3H), 7.18 (t, *J* = 8.5 Hz, 2H), 4.56 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 166.4, 166.1, 164.3 (d, $J_{C\text{-}F}$ = 246.9 Hz) 156.0, 147.8, 139.7, 136.5 (d, $J_{C\text{-}F}$ = 3.1 Hz), 131.3, 130.6 (d, $J_{C\text{-}F}$ = 8.2 Hz), 129.8, 128.1, 125.2, 125.1, 122.2, 115.3 (d, $J_{C\text{-}F}$ = 21.6 Hz), 83.3, 62.6, 27.5, 14.1. HRMS (ESI) calcd for $C_{23}H_{23}FNO_4$, $[M+H]^+$: 396.1606, found: 396.1614.



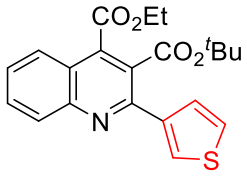
3-(tert-butyl) 4-ethyl 2-(4-chlorophenyl)quinoline-3,4-dicarboxylate (**3g**). Grey white solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (26.4 mg, 64%); m.p. 97-99 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.17 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 6.5 Hz, 2H), 7.47 (d, *J* = 6.5 Hz, 2H), 4.56 (q, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.0 Hz, 3H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 166.4, 166.0, 155.9, 147.9, 139.9, 138.8, 135.1, 131.4, 130.1, 129.9, 128.5, 128.3, 125.2, 125.0, 122.3, 83.5, 62.6, 27.6, 14.1. HRMS (ESI) calcd for $C_{23}H_{22}NaClNO_4$, $[M+Na]^+$: 434.1130, found: 434.1133.



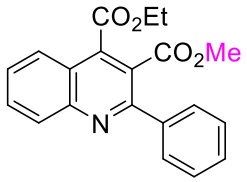
3-(tert-butyl) 4-ethyl 2-(4-bromophenyl)quinoline-3,4-dicarboxylate (**3h**). Grey white solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (28.8 mg, 63%); m.p. 126-128 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.17 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.66-7.62 (m, 3H), 7.54 (d, *J* = 8.5 Hz, 2H), 4.56 (q, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 165.9, 155.9, 147.8, 139.9, 139.3, 131.4, 131.4, 130.4, 129.9, 128.2, 125.2, 124.9, 123.3, 122.3, 83.5, 62.6, 27.5, 14.1. HRMS (ESI) calcd for $C_{23}H_{22}NaBrNO_4$, $[M+Na]^+$: 478.0624, found: 478.0633.



3-(tert-butyl) 4-ethyl 2-(4-nitrophenyl)quinoline-3,4-dicarboxylate (**3i**). Yellow solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (21.9 mg, 52%); m.p. 159-161 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.36 (d, *J* = 7.0 Hz, 2H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.88-7.84 (m, 3H), 7.70 (t, *J* = 7.5 Hz, 1H), 4.58 (q, *J* = 7.2 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 166.1, 165.4, 154.8, 148.0, 147.8, 146.6, 140.4, 131.8, 130.0, 129.8, 128.8, 125.3, 124.6, 123.5, 122.6, 83.8, 62.7, 27.6, 14.1. HRMS (ESI) calcd for $C_{23}H_{23}N_2O_6$, $[M+H]^+$: 423.1551, found: 423.1550.

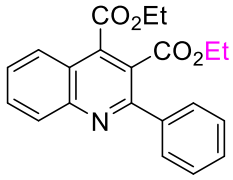


3-(tert-butyl) 4-ethyl 2-(thiophen-3-yl)quinoline-3,4-dicarboxylate (**3j**). Light yellow solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (25.8 mg, 67%); m.p. 130-132 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.16 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.67 (s, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.47-7.46 (m, 1H), 7.42-7.40 (m, 1H), 4.55 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.40 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 166.4, 166.3, 152.0, 147.9, 141.1, 139.0, 131.1, 129.8, 128.4, 127.9, 125.63, 125.60, 125.4, 125.2, 122.2, 83.4, 62.5, 27.6, 14.1. HRMS (ESI) calcd for $C_{21}H_{22}NO_4S$, $[M+H]^+$: 384.1264, found: 384.1266.

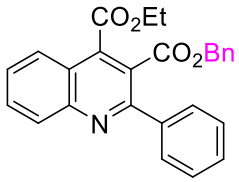


4-ethyl 3-methyl 2-phenylquinoline-3,4-dicarboxylate (**3l**). Yellow oil, obtained in 2 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (12.6 mg, 38%); ^{1}H NMR (600 MHz, $CDCl_3$) δ. 8.21 (d, *J* = 9.0 Hz, 1H), 8.10

(d, *J* = 8.4 Hz, 1H), 7.83 (t, *J* = 7.8 Hz, 1H), 7.68-7.64 (m, 3H), 7.50-7.44 (m, 3H), 4.53 (q, *J* = 7.0 Hz, 2H), 3.68 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.0, 166.0, 156.6, 148.2, 139.8, 139.3, 131.4, 130.0, 129.0, 128.5, 128.3, 128.2, 125.3, 124.4, 122.1, 62.6, 52.6, 14.0. HRMS (ESI) calcd for $C_{20}H_{17}NaNO_4$, $[M+Na]^+$: 358.1050, found: 358.1054.

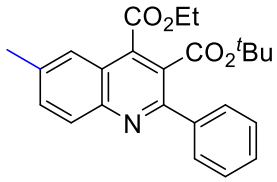


diethyl 2-phenylquinoline-3,4-dicarboxylate (**3m**). Light yellow solid, obtained in 2 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (16.2 mg, 46%); m.p. 49-51 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.21 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.67-7.64 (m, 3H), 7.50-7.44 (m, 3H), 4.54 (q, *J* = 7.2 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 166.1, 156.8, 148.2, 140.0, 139.3, 131.3, 130.0, 128.9, 128.4, 128.4, 128.2, 125.3, 124.6, 122.1, 62.5, 61.9, 14.0, 13.5. HRMS (ESI) calcd for $C_{21}H_{20}NO_4$, $[M+H]^+$: 350.1387, found: 350.1387.

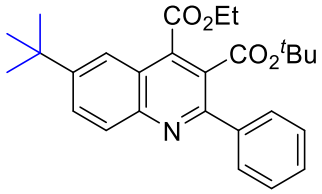


3-benzyl 4-ethyl 2-phenylquinoline-3,4-dicarboxylate (**3n**). Yellow oil, obtained in 2 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (19.4 mg, 47%); ^{1}H NMR (600 MHz, $CDCl_3$) δ. 8.20 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.83-7.81 (m, 1H), 7.65-7.61 (m, 3H), 7.43-7.40 (m, 3H), 7.30-7.24 (m, 3H), 7.05-7.04 (m, 2H), 5.10 (s, 2H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4, 166.0, 156.6, 148.2, 139.8, 139.4, 134.5,

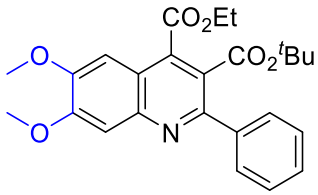
131.4, 130.0, 129.0, 128.5, 128.5, 128.5, 128.4, 128.2, 125.3, 124.3, 122.1, 67.8, 62.5, 14.0. HRMS (ESI) calcd for $C_{26}H_{22}NO_4$, $[M+H]^+$: 412.1543, found: 412.1544.



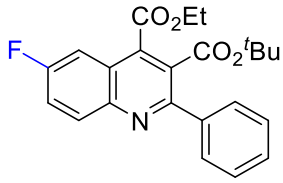
3-(tert-butyl) 4-ethyl 6-methyl-2-phenylquinoline-3,4-dicarboxylate (**3p**). Grey white solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (28.7 mg, 73%); m.p. 132-134 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ. 8.08 (d, *J* = 8.4 Hz, 1H), 7.73 (s, 1H), 7.64-7.62 (m, 3H), 7.48-7.43 (m, 3H), 4.55 (q, *J* = 7.0 Hz, 2H), 2.56 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H), 1.28 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ. 166.7, 166.3, 156.3, 146.6, 140.6, 139.0, 138.2, 133.5, 129.6, 128.7, 128.6, 128.3, 125.1, 123.8, 122.2, 83.0, 62.4, 27.4, 21.9, 14.1. HRMS (ESI) calcd for $C_{24}H_{26}NO_4$, $[M+H]^+$: 392.1856, found: 392.1860.



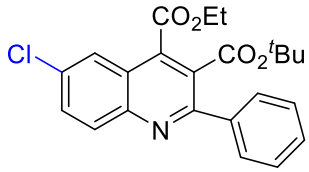
3-(tert-butyl) 4-ethyl 6-(tert-butyl)-2-phenylquinoline-3,4-dicarboxylate (**3q**). Grey white solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (24.8 mg, 57%); m.p. 103-105 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ. 8.12 (d, *J* = 9.0 Hz, 1H), 7.91-7.89 (m, 1H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.48-7.44 (m, 3H), 4.57 (q, *J* = 7.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H), 1.42 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ. 166.8, 166.3, 156.6, 151.0, 146.5, 140.5, 139.5, 130.3, 129.4, 128.7, 128.6, 128.3, 125.2, 121.9, 119.9, 83.0, 62.3, 35.2, 31.0, 27.4, 14.2. HRMS (ESI) calcd for $C_{27}H_{32}NO_4$ $[M+H]^+$: 434.2326, found: 434.2334.



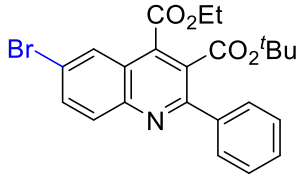
3-(tert-butyl) 4-ethyl 6,7-dimethoxy-2-phenylquinoline-3,4-dicarboxylate (**3r**). Yellow solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (20.6 mg, 47%); m.p. 195-197 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ. 7.60-7.58 (m, 2H), 7.50 (s, 1H), 7.47-7.42 (m, 3H), 7.27-7.25 (m, 1H), 4.54 (q, *J* = 7.2 Hz, 2H), 4.04 (s, 3H), 4.02 (s, 3H), 1.45 (t, *J* = 6.9 Hz, 3H), 1.27 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ. 166.9, 166 .5, 155.3, 153.8, 151.0, 145.6, 140.7, 137.5, 128.6, 128.4, 128.2, 123.7, 118.1, 108.3, 102.4, 82.8, 62.3, 56.3, 56.1, 27.4, 14.1. HRMS (ESI) calcd for $C_{25}H_{28}NO_6$, $[M+H]^+$: 438.1911, found: 438.1917.



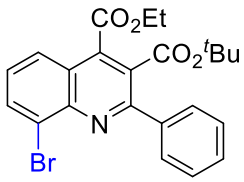
3-(tert-butyl) 4-ethyl 6-fluoro-2-phenylquinoline-3,4-dicarboxylate (**3s**). Light yellow solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (20.9 mg, 53%); m.p. 123-125 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ. 8.20-8.18 (m, 1H), 7.68-7.66 (m, 1H), 7.64-7.62 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.47 (m, 3H), 4.55 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.29 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ. 166.0, 165.9, 161.3, (d, $J_{C\text{-}F}$ = 248.8 Hz), 156.6 (d, $J_{C\text{-}F}$ = 2.7 Hz), 145.0, 140.0, 138.6 (d, $J_{C\text{-}F}$ = 5.8 Hz), 132.5 (d, $J_{C\text{-}F}$ = 9.3 Hz), 128.8, 128.6, 128.3, 126.4, 123.1 (d, $J_{C\text{-}F}$ =10.5 Hz), 121.5 (d, $J_{C\text{-}F}$ = 25.6 Hz), 108.9 (d, $J_{C\text{-}F}$ = 24.0 Hz), 83.4, 62.7, 27.4, 14.1. HRMS (ESI) calcd for $C_{23}H_{23}FNO_4$, $[M+H]^+$: 396.1606, found: 396.1611.



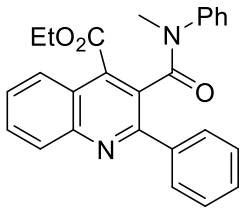
3-(tert-butyl) 4-ethyl 6-chloro-2-phenylquinoline-3,4-dicarboxylate (**3t**). Grey white solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (25.5 mg, 62%); m.p. 116-118 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.13-8.11 (m, 1H), 8.01-8.00 (m, 1H), 7.75-7.72 (m, 1H), 7.64-7.61 (m, 2H), 7.50-7.46 (m, 3H), 4.56 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.29 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 165.9, 165.8, 157.4, 146.2, 140.0, 138.5, 134.0, 132.1, 131.4, 128.9, 128.6, 128.4, 126.3, 124.1, 122.9, 83.5, 62.8, 27.4, 14.1. HRMS (ESI) calcd for $C_{23}H_{22}NaClNO_4$, $[M+Na]^+$: 434.1130, found: 434.1134.



3-(tert-butyl) 4-ethyl 6-bromo-2-phenylquinoline-3,4-dicarboxylate (**3u**). Light yellow solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (33.8 mg, 74%); m.p. 132-134 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.18-8.17 (m, 1H), 8.06-8.04 (m, 1H), 7.88-7.86 (m, 1H), 7.64-7.62 (m, 2H), 7.50-7.46 (m, 3H), 4.56 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.29 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 165.9, 165.8, 157.6, 146.4, 140.0, 138.4, 134.7, 131.5, 129.0, 128.6, 128.4, 127.4, 126.3, 123.4, 122.3, 83.5, 62.8, 27.4, 14.1. HRMS (ESI) calcd for $C_{23}H_{22}NaBrNO_4$, $[M+Na]^+$: 478.0624, found: 478.0630.

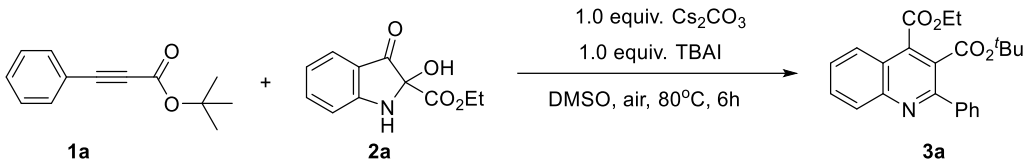


3-(tert-butyl) 4-ethyl 8-bromo-2-phenylquinoline-3,4-dicarboxylate (**3v**). Grey white solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: (14.1 mg, 31%); m.p. 93-95 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.14-8.12 (m, 1H), 7.94-7.92 (m, 1H), 7.78-7.76 (m, 2H), 7.50-7.44 (m, 4H), 4.55 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 3H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 166.1, 166.0, 157.6, 144.7, 140.3, 139.8, 134.7, 129.1, 128.3, 128.1, 125.8, 125.7, 124.9, 123.5, 83.5, 62.7, 27.5, 14.1. HRMS (ESI) calcd for $C_{23}H_{23}BrNO_4$, $[M+H]^+$: 456.0805, found: 456.0809.



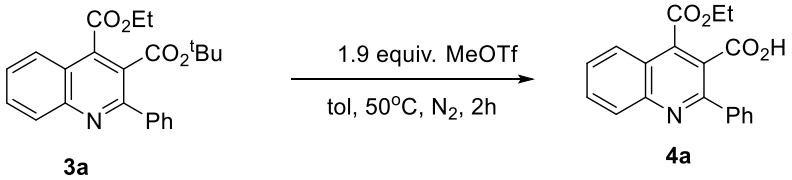
ethyl 3-(methyl(phenyl)carbamoyl)-2-phenylquinoline-4-carboxylate (3w). Yellow solid, obtained in 6 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yield: (19.3 mg, 47%); m.p. 165-167 ^{o}C. 1H NMR (600 MHz, $CDCl_3$) δ. 8.09 (d, *J* = 9.0 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H),7.74-7.72 (m, 1H), 7.61-7.59 (m, 1H), 7.47-7.44 (m, 3H), 7.41-7.37 (m, 2H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.8 Hz, 2H), 6.42 (d, *J* = 7.8 Hz, 2H), 4.70-4.59 (m, 2H), 3.29 (s, 3H), 1.51 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ. 168.2, 166.9, 154.5, 147.9, 141.9, 139.4, 139.2, 130.5, 129.9, 129.2, 129.1, 128.6, 128.3, 128.1, 127.7, 126.3, 125.6, 125.1, 122.4, 62.5, 37.0, 14.1. **3w** exists as a mixture of rotamers and the spectroscopic data of the major rotamer are reported. HRMS (ESI) calcd for $C_{26}H_{22}NaN_2O_3$, $[M+Na]^+$: 433.1523, found: 433.1526.

5. 1.0 mmol Scale reaction

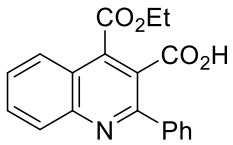


In a Schlenk tube, indolone **2a** (1.5 mmol, 1.4 equiv., 0.309 g), Cs_2CO_3(1.0 mmol, 0.326 g), TBAI (1.0 mmol, 0.369 g), DMSO (10 mL), and alkynoate **1a** (1.0 mmol, 0.202g mg) were stirred at 80 °C in the oil bath for 6h under air. Then, the reaction mixture was cooled to room temperature and was treated with saturated NH_4Cl, then extracted with EA and dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on basic silica gel (PE: EA = 10: 1) to afford **3a** (Light yellow solid, 0.1923 g, 51%).

6. Synthesis of 4a and 5a

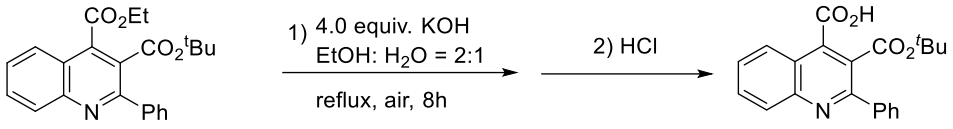


A solution of Quinoline **3a** (75.4 mg, 0.2 mmol) in 2 mL anhydrous toluene was added MeOTf (62 mg, 0.38 mmol, 1.9 equiv.) under N_2. The resulting mixture was stirred in a preheated oil bath at 50 °C for 2 h. Then, Solvent was removed under in vacuo, the resultant residue was taken up in H_2O, acidified to pH = 1 with 2M HCl, and extracted with EA (3 × 10 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated in vacuo of **4a** as a white solid (59.7 mg, 93%).



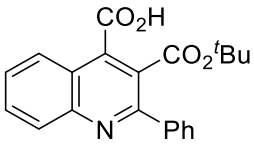
4-(ethoxycarbonyl)-2-phenylquinoline-3-carboxylic acid (**4a**). m.p. 78-80 °C. ^1H NMR (500 MHz, d^6-DMSO) δ. 8.17 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.94

(t, *J* = 7.5 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.72-7.70 (m, 2H), 7.54-7.49 (m, 3H), 4.48 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, d_6-DMSO) δ. 168.2, 165.7, 155.8, 147.1, 139.4, 138.5, 131.8, 129.5, 129.1, 128.7, 128.5, 128.3, 125.2, 125.0, 121.3, 62.4, 13.7. HRMS (ESI) calcd for $C_{19}H_{16}NO_4$, $[M+H]^+$: 322.1074, found: 322.1070.



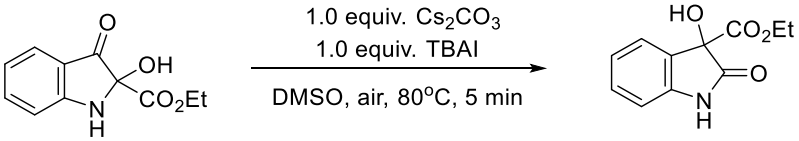
3a **5a**

Quinoline **3a** (75.4 mg, 0.2 mmol) was dissolved in EtOH (1.0 mL), H_2O (0.5 mL), and KOH (44.9 mg, 0.8 mmol) and heated to reflux for 8 h. Solvent was removed under in vacuo, the resultant residue was taken up in H_2O, acidified to pH = 1 with 2M HCl, and extracted with EA (3 × 10 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated in vacuo of **5a** as a white solid (63.5 mg, 91%).



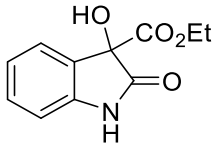
3-(tert-butoxycarbonyl)-2-phenylquinoline-4-carboxylic acid (**5a**). m.p. 187-189 °C. ^{1}H NMR (500 MHz, d^6-DMSO) δ. 8.14 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.93 (t, *J* = 7.5 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.63-7.62 (m, 2H), 7.53-7.51 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, d_6-DMSO) δ. 167.2, 165.6, 156.2, 147.2, 140.5, 139.6, 131.6, 129.4, 128.9, 128.5, 128.4, 128.2, 125.4, 124.4, 121.3, 82.7, 27.1. HRMS (ESI) calcd for $C_{21}H_{20}NO_4$, $[M+H]^+$: 350.1387, found: 350.1394.

7. Mechanistic Experiments

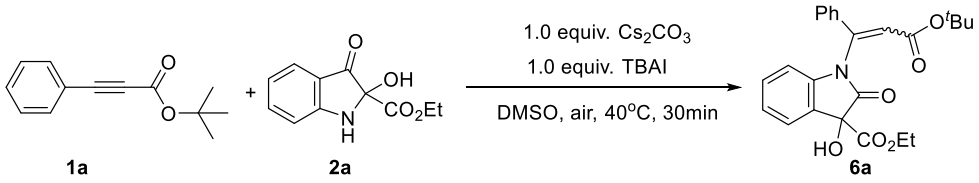


2a **2a'**

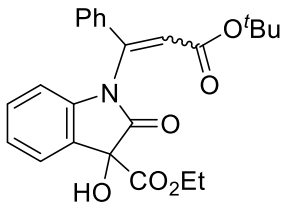
In a Schlenk tube, indolone **2a** (0.2 mmol, 44.2 mg), Cs_2CO_3(0.2 mmol, 65.2 mg), TBAI (0.2 mmol, 73.9 mg), DMSO (2.0 mL) were stirred at 80 ^oC in the oil bath for 5 min. Then, the reaction mixture was cooled to room temperature and was treated with saturated NH_4Cl, then extracted with EA and dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on basic silica gel (PE: EA = 1: 1) to afford **2a'** (white solid, 34.9 mg, 79%).



ethyl 3-hydroxy-2-oxoindoline-3-carboxylate (**2a'**). m.p. 151-153 ^oC. ^1H NMR (500 MHz, d^6-DMSO) δ. 10.57 (s, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.00 (s, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 4.14-4.01 (m, 2H), 1.05 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, d_6-DMSO) δ. 174.7, 169.3, 142.8, 130.2, 129.2, 123.8, 122.1, 110.1, 77.6, 61.3, 13.9. HRMS (ESI) calcd for $C_{11}H_{11}NaNO_4$, $[M+Na]^+$: 244.0580, found: 244.0583.



In a Schlenk tube, indolone **2a** (0.28 mmol, 1.4 equiv., 61.9 mg), Cs_2CO_3 (0.2 mmol, 65.2 mg), TBAI (0.2 mmol, 73.8 mg), DMSO (2.0 mL), and alkynoate **1a** (0.2 mmol, 40.4 mg) were stirred at 40 ^oC in the oil bath for 40 min under air. Then, the reaction mixture was cooled to room temperature and was treated with saturated NH_4Cl, then extracted with EA and dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on basic silica gel (PE: EA = 2: 1) to afford **6a** (white solid, 16.9 mg, 20%).



ethyl 1-(3-(tert-butoxy)-3-oxo-1-phenylprop-1-en-1-yl)-3-hydroxy-2-oxoindoline-3-carboxylate (**6a**). m.p. 133-135 °C. ^{1}H NMR (500 MHz, d^{6}-DMSO) δ. 7.68 (d, *J* = 7.5 Hz, 2H), 7.52 (s, 1H), 7.48-7.42 (m, 3H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.71 (s, 1H), 6.44 (d, *J* = 7.5 Hz, 1H), 4.26-4.11 (m, 2H), 1.23 (s, 9H), 1.15 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (125 MHz, d_6-DMSO) δ. 171.8, 169.4, 162.9, 143.3, 140.1, 133.4, 130.7, 130.2, 129.0, 127.7, 126.5, 123.9, 123.2, 120.2, 110.4, 80.8, 77.7, 62.0, 27.3, 13.9. HRMS (ESI) calcd for $C_{24}H_{25}NaNO_6$, $[M+Na]^+$: 446.1574, found: 446.1579.

8. References

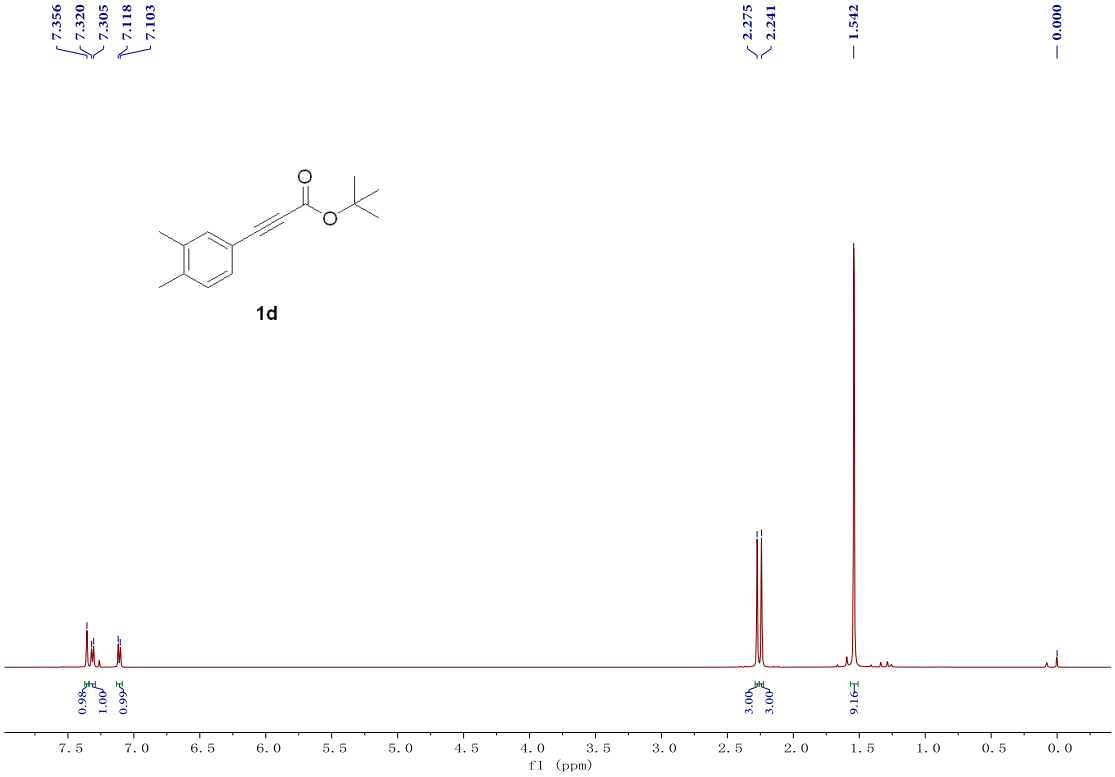
[1] Park, K.; You, J.; Jeon, S.; Lee, S. *Eur. J. Org. Chem.* **2013**, *10*, 1973-1978.

[2] Vercruysse, S.; Cornelissen, L.; Nahra, F.; Collard, L.; Riant, O. *Chemistry*. **2014**, *20*, 1834-1838.

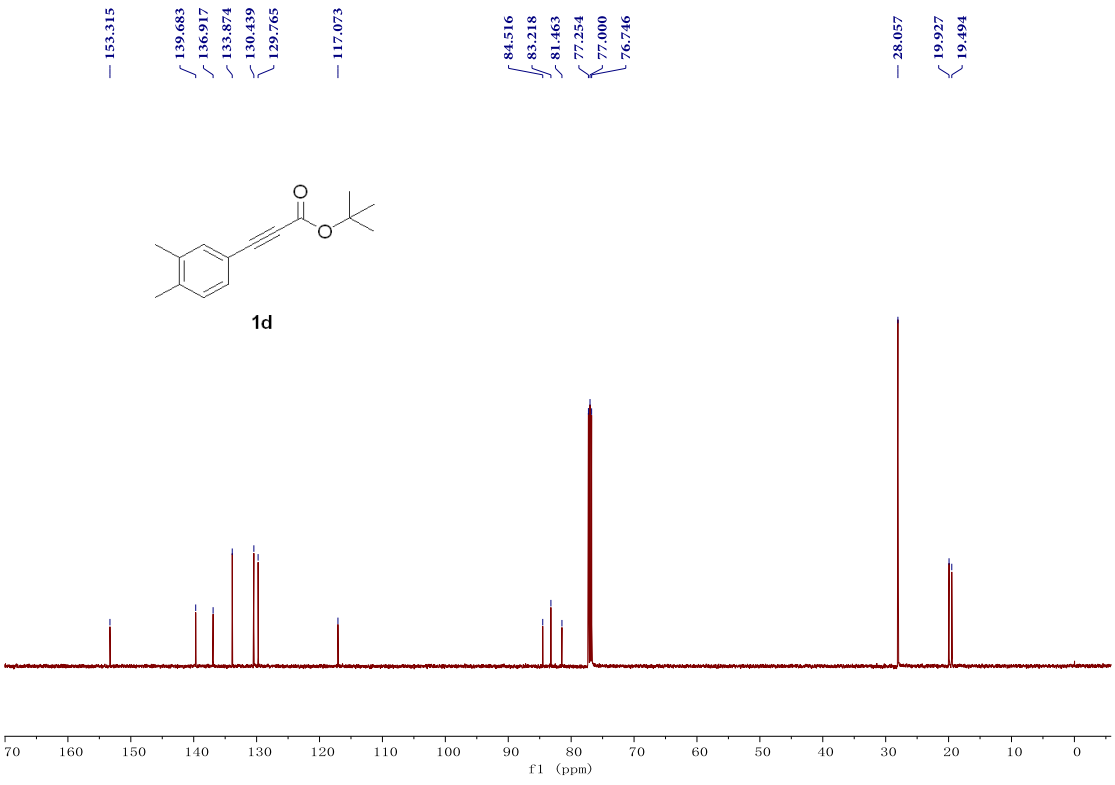
[3] Rooke, D. A.; Ferreira, E. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 3225-3230.

9. Copies of spectra of new products

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



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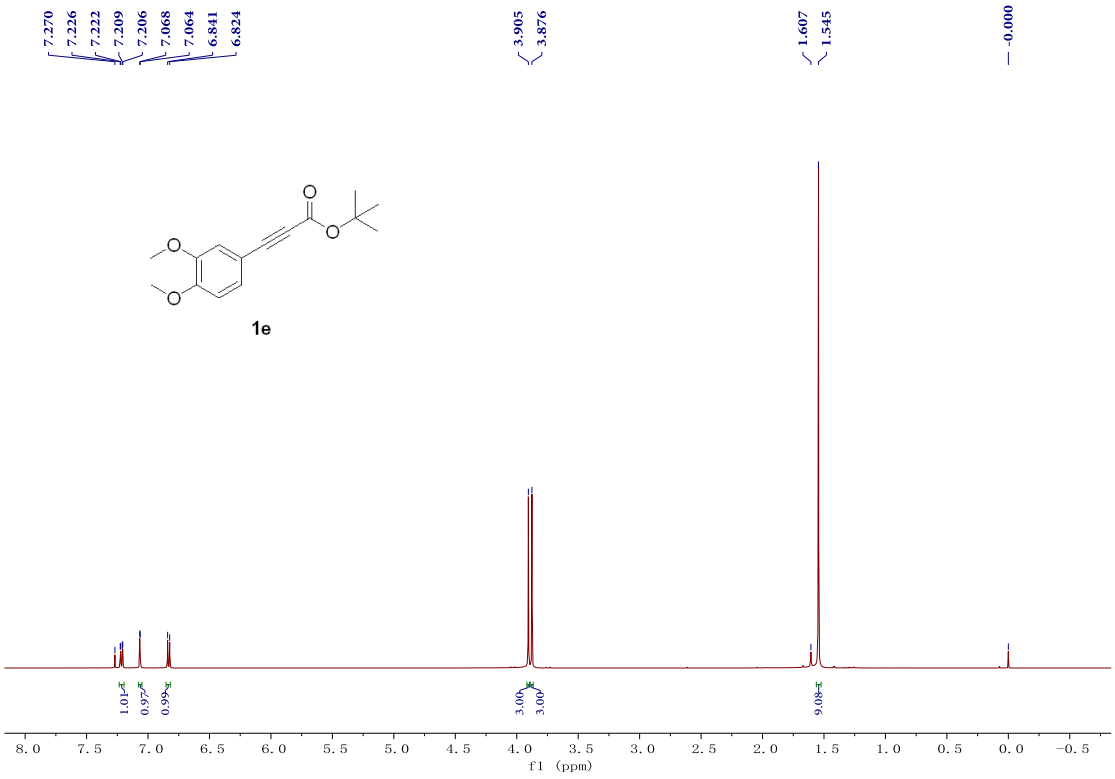
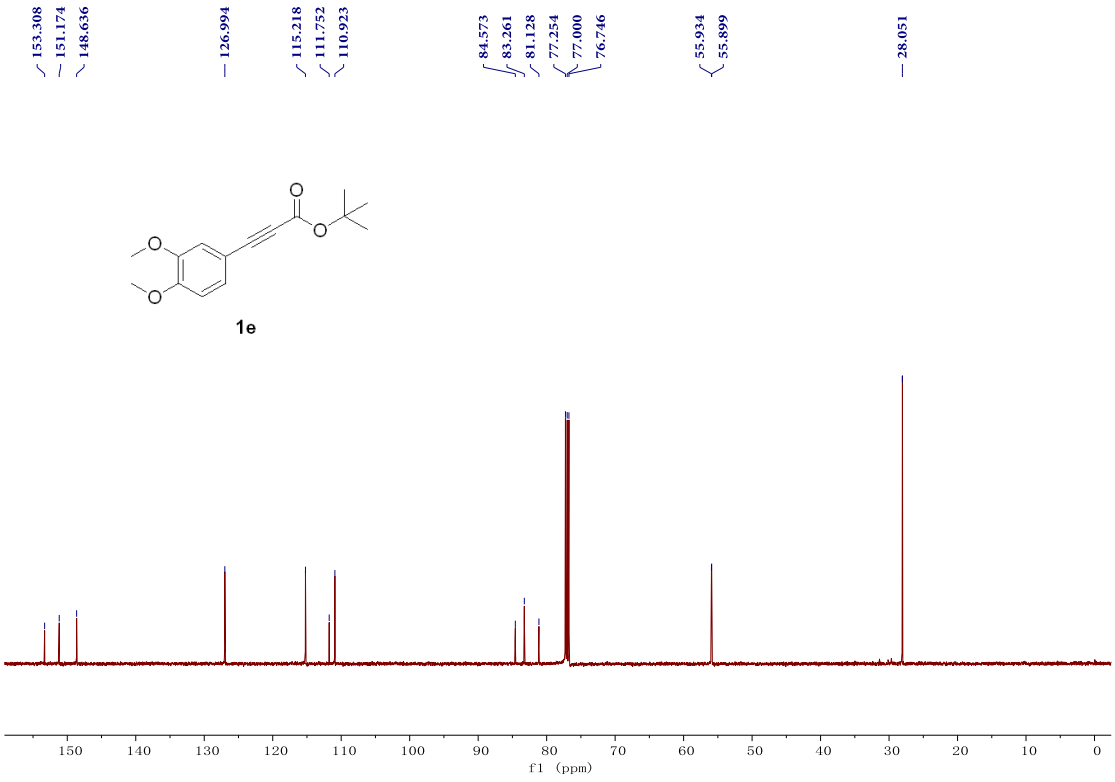


^{13}C NMR (125 MHz, $CDCl_3$)



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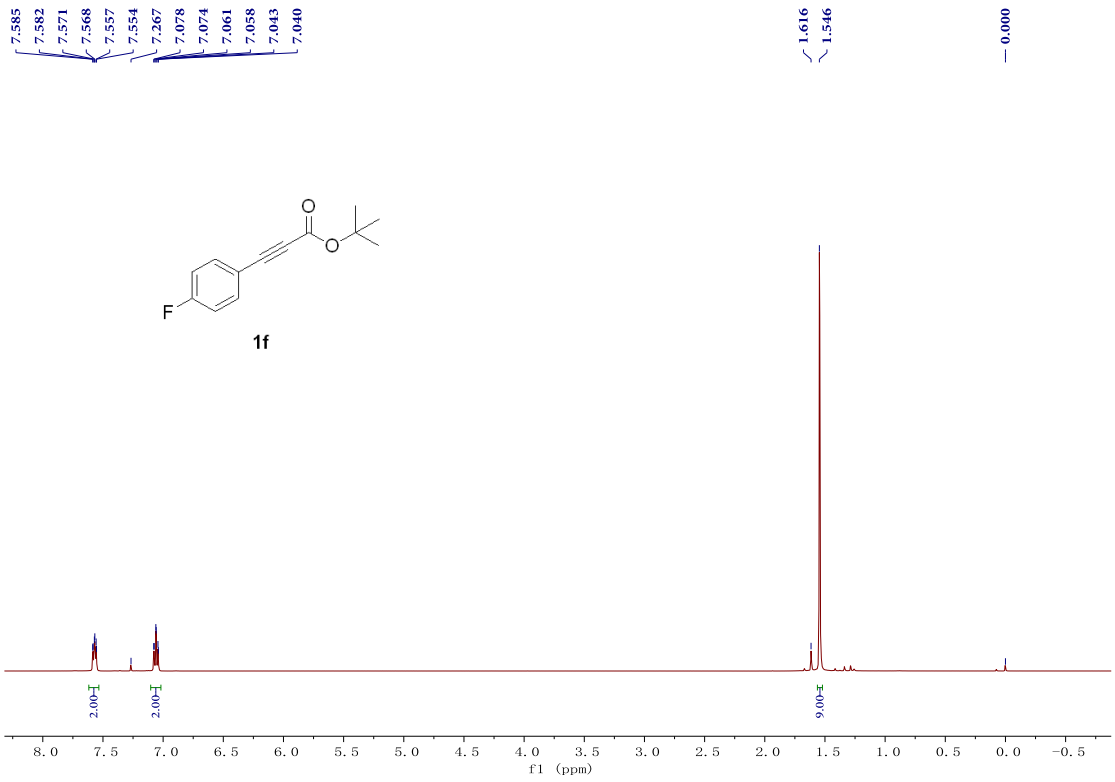

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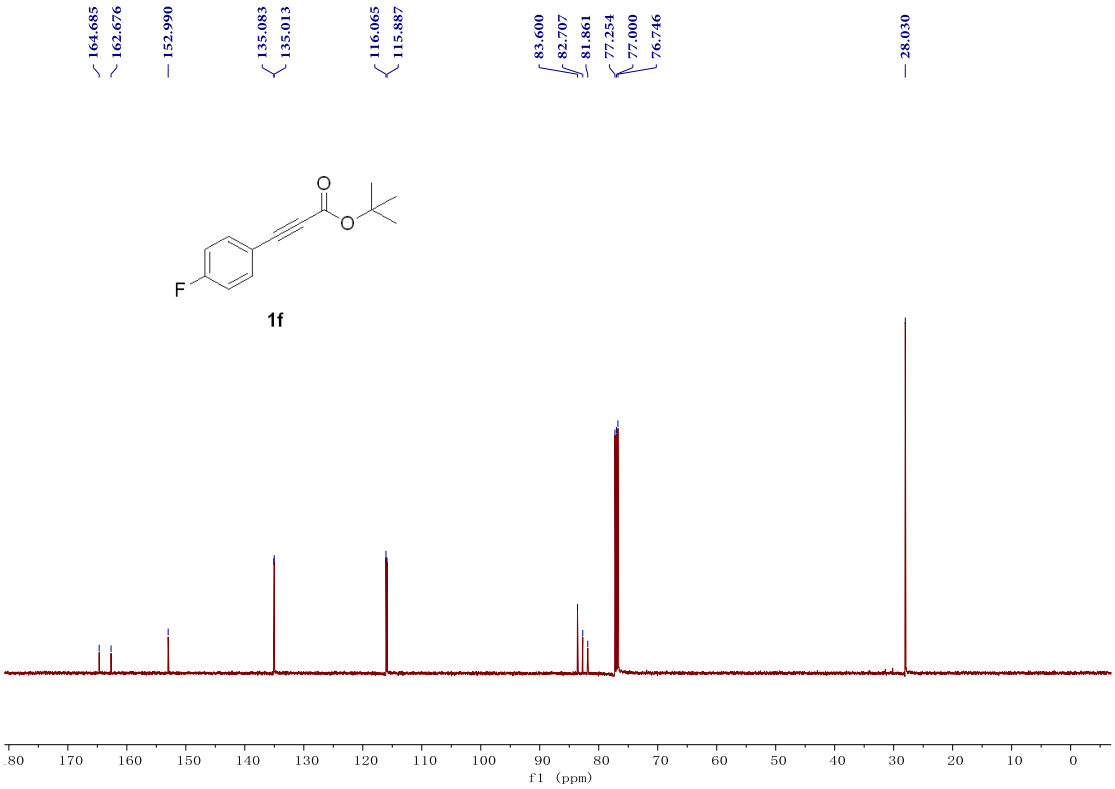

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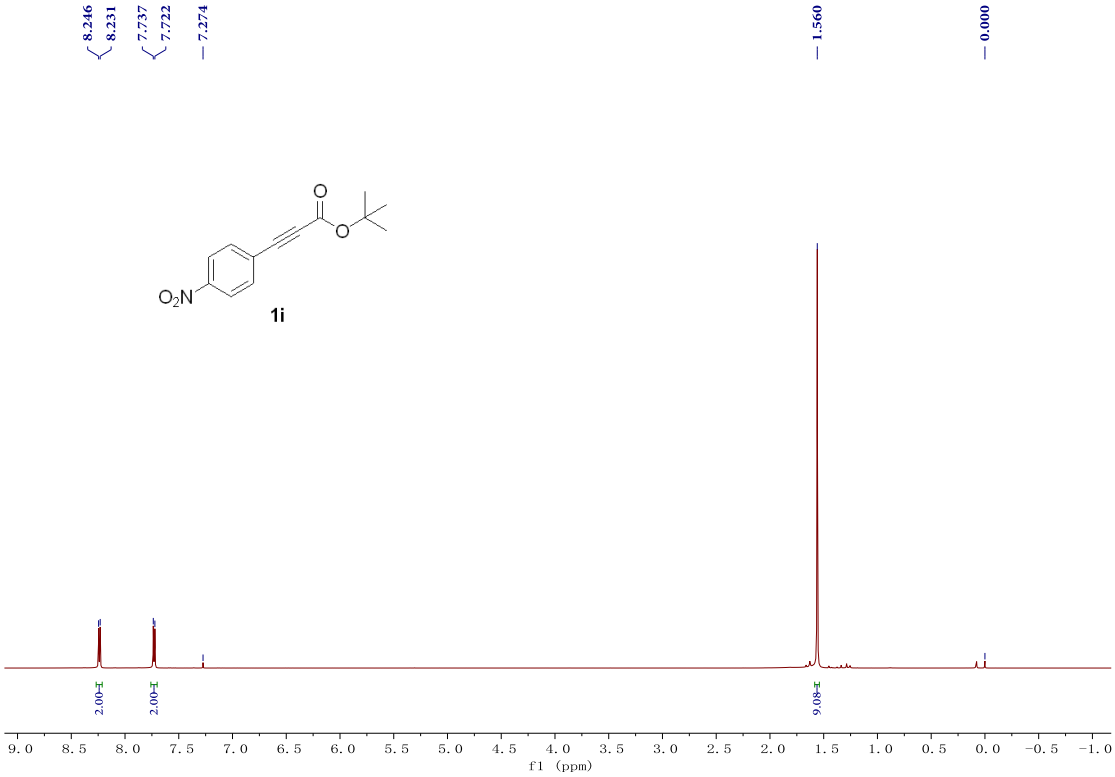
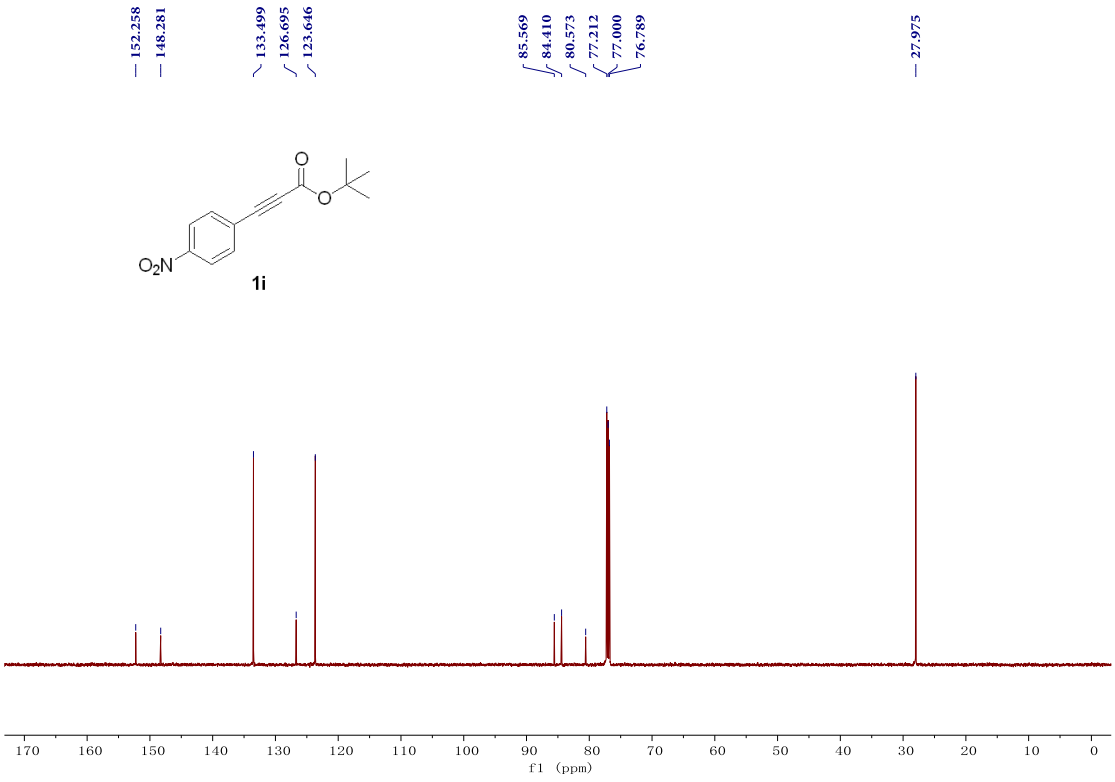


^{13}C NMR (125 MHz, $CDCl_3$)



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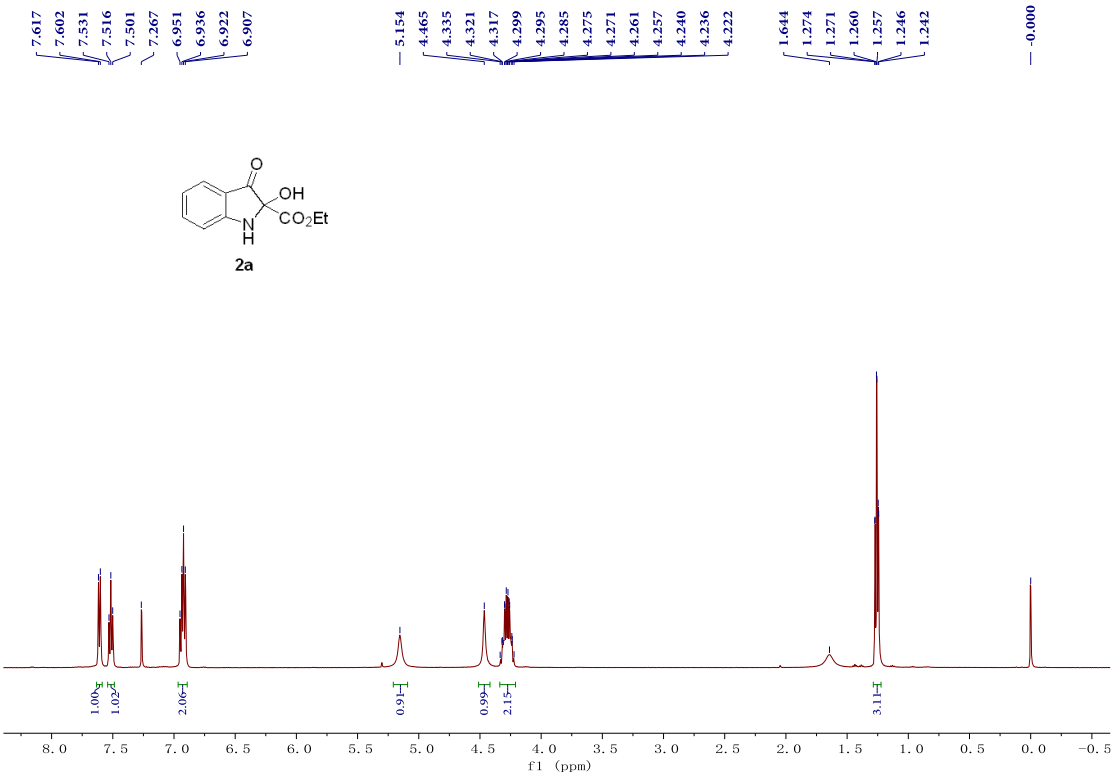

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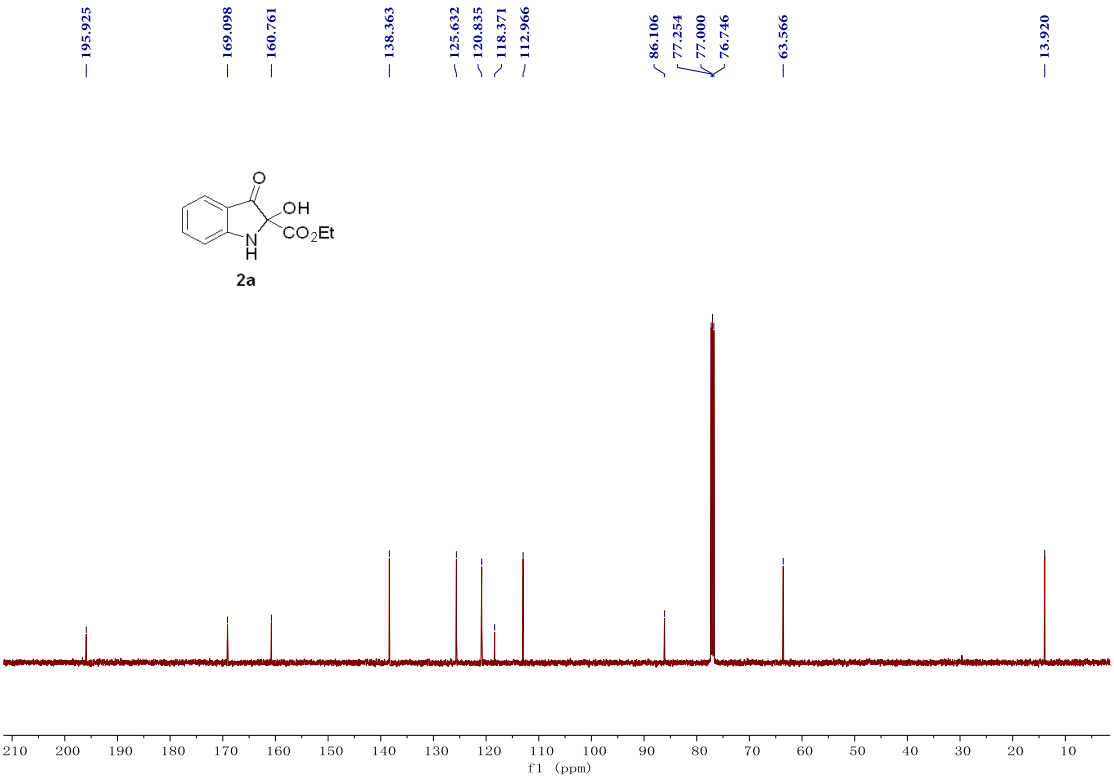

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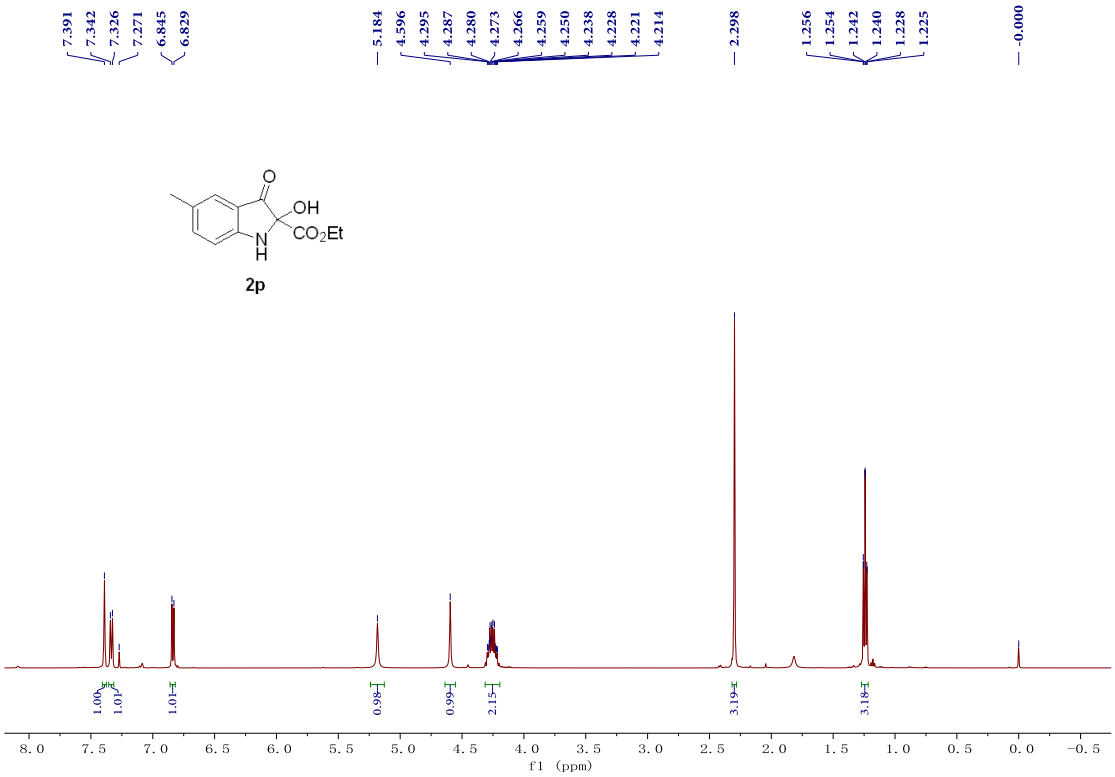
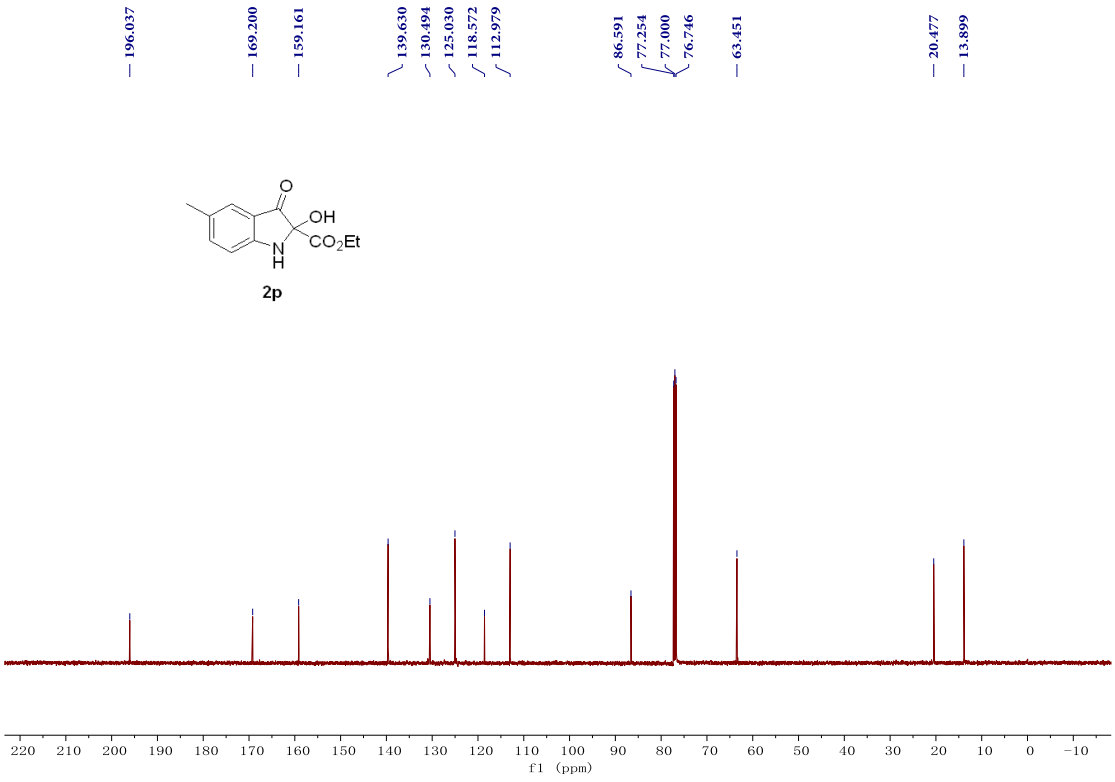


^{13}C NMR (125 MHz, $CDCl_3$)



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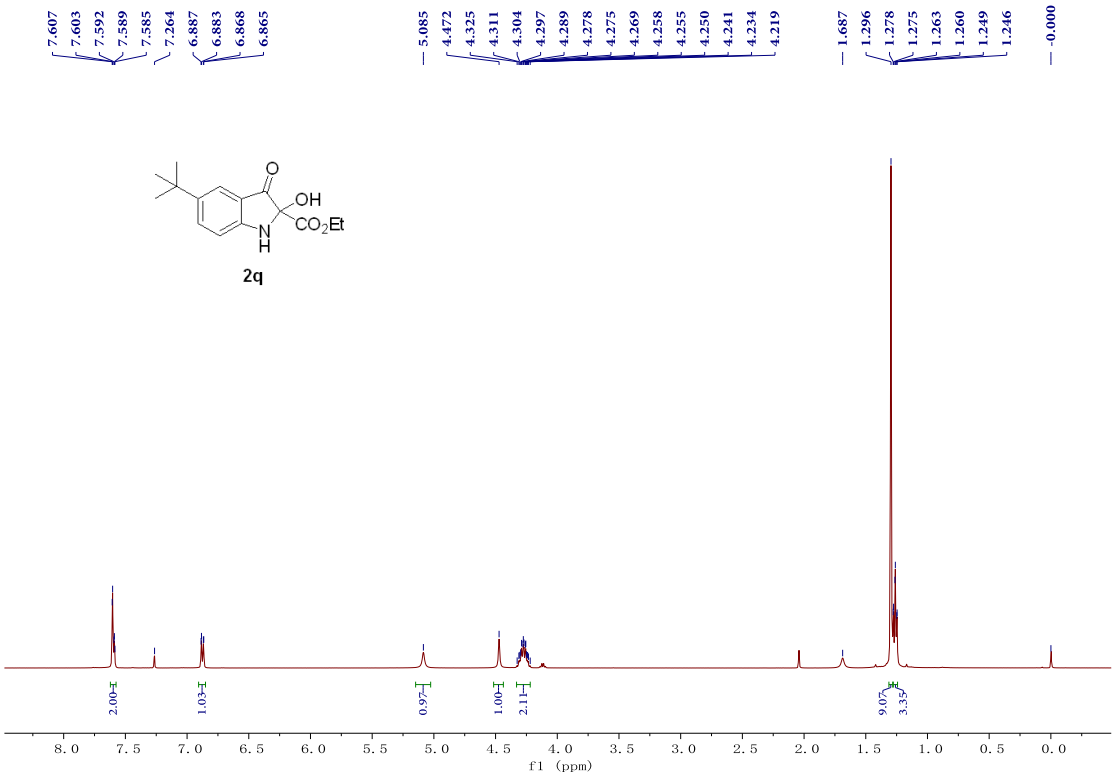
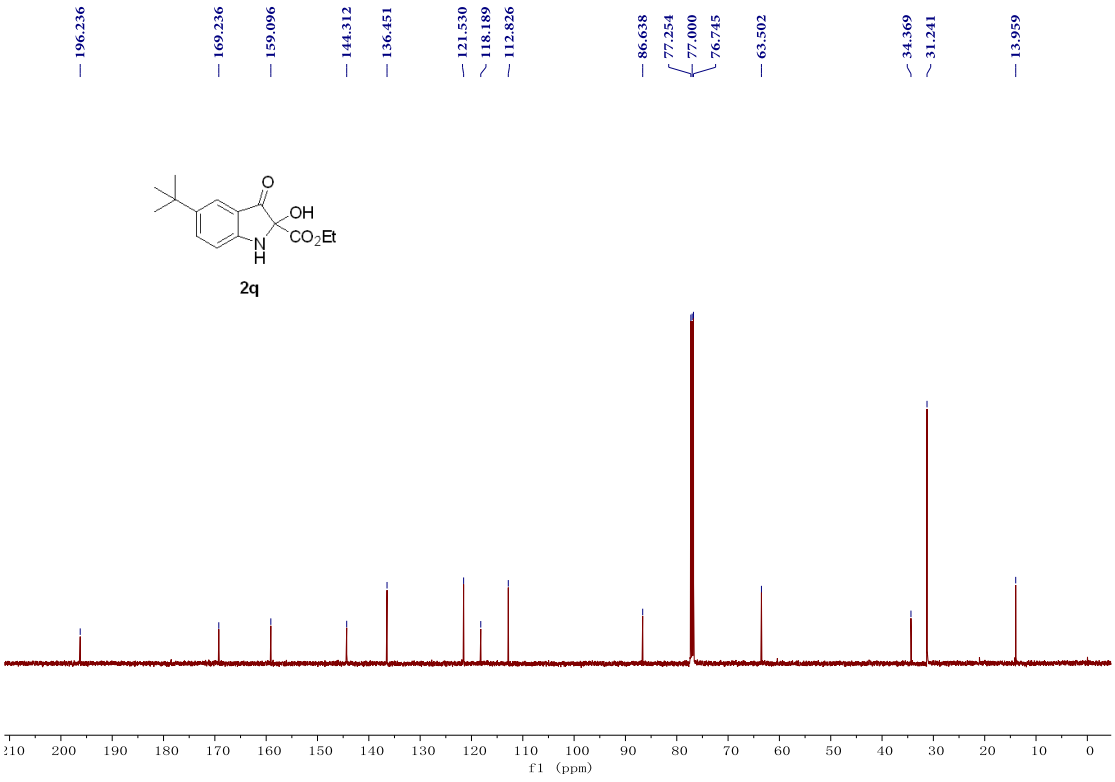
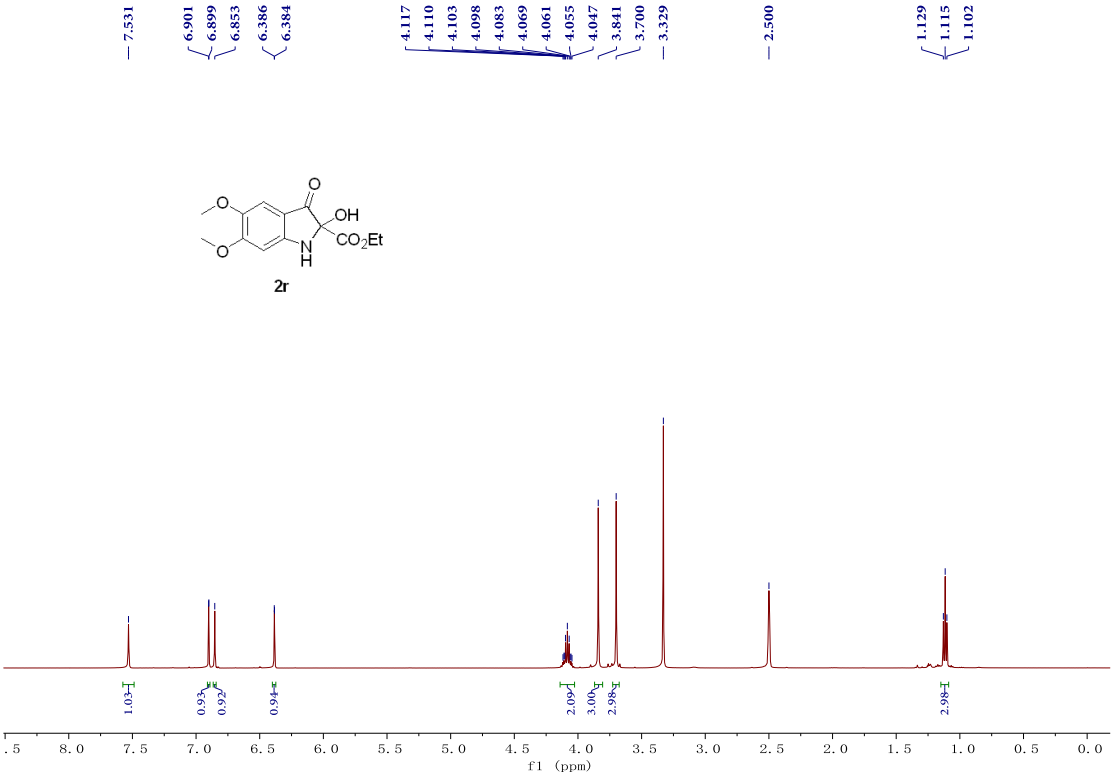


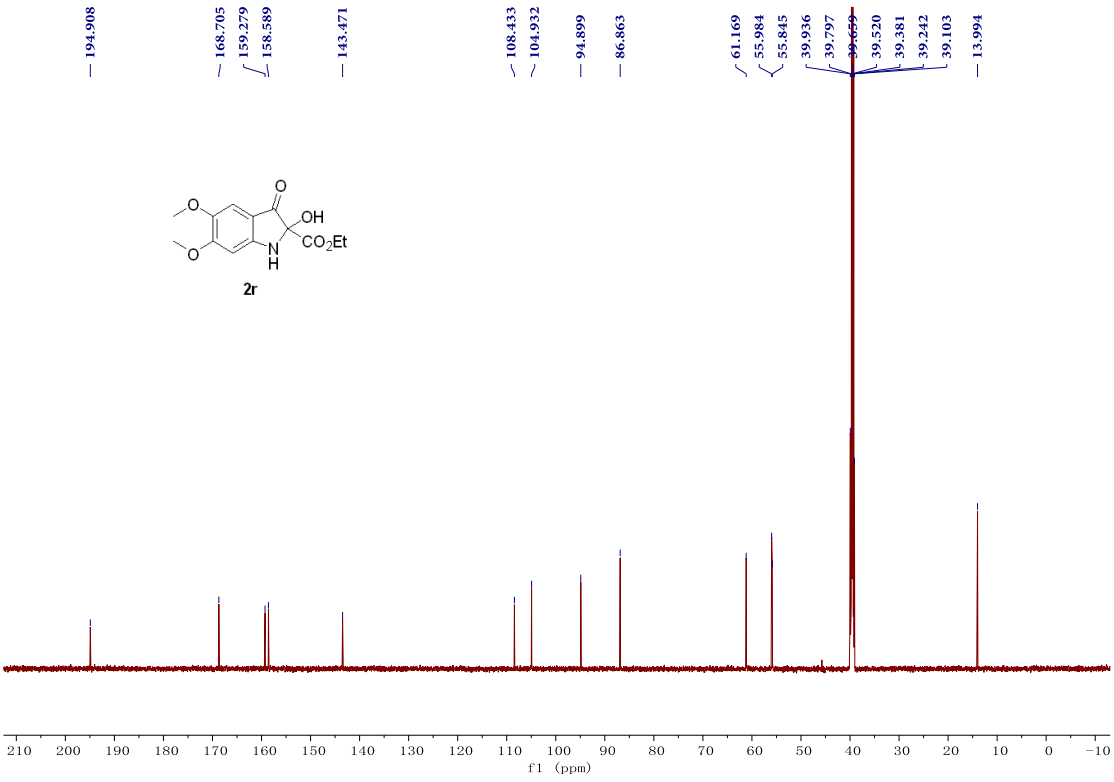
^{13}C NMR (125 MHz, $CDCl_3$)



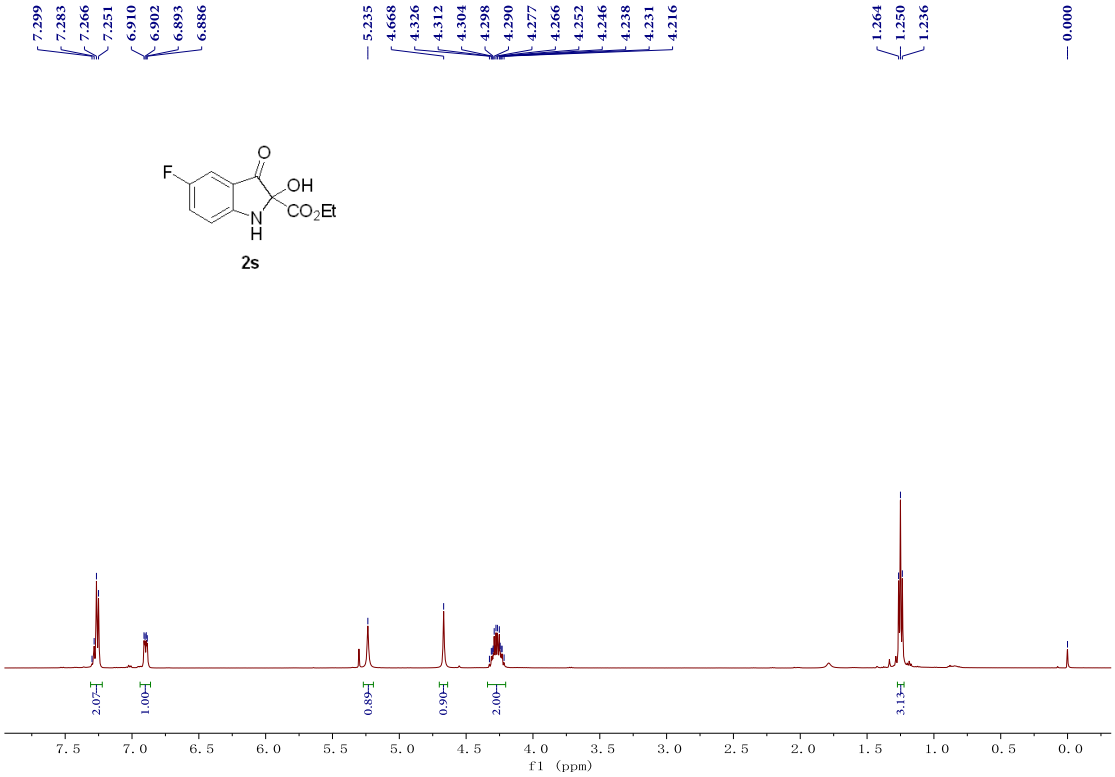
^{1}H NMR (500 MHz, d^{6}-DMSO)



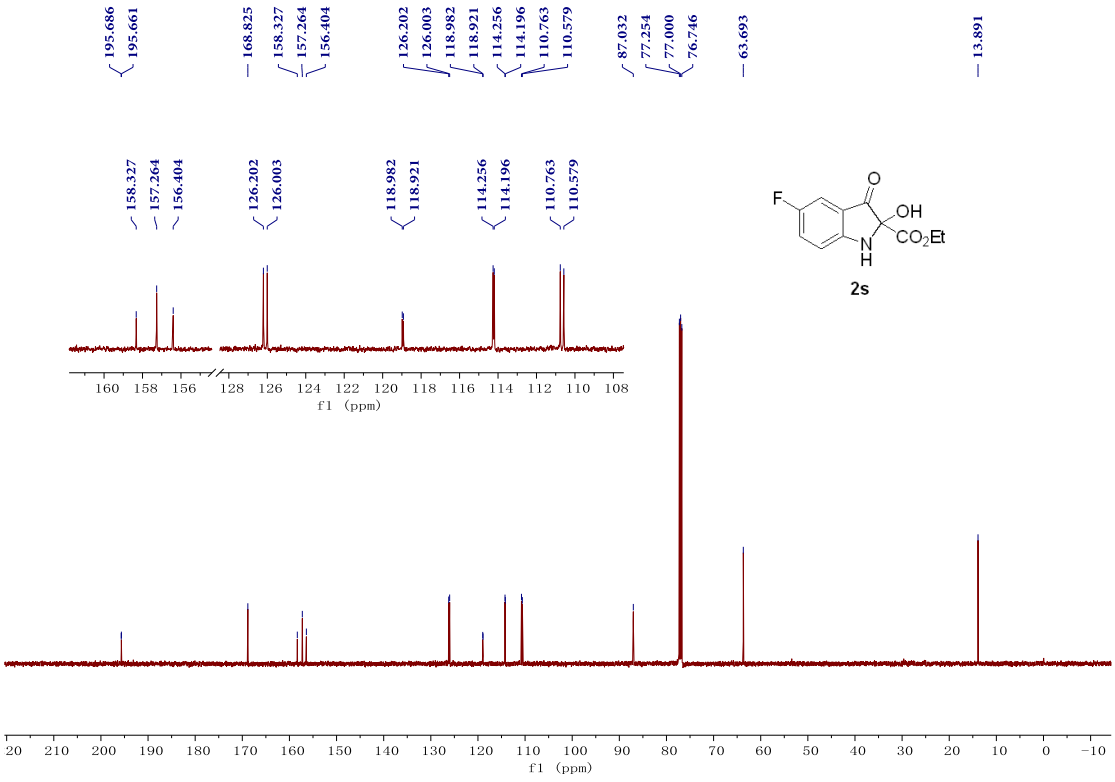
^{13}C NMR (125 MHz, d^{6}-DMSO)



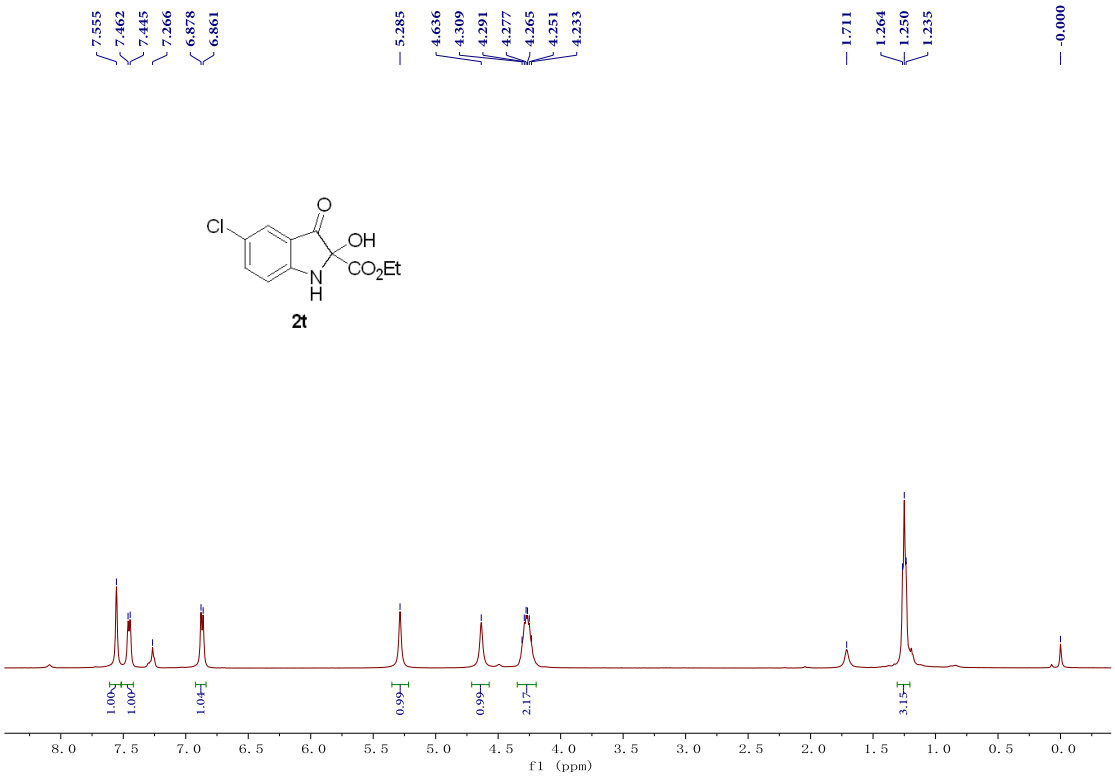
^{1}H NMR (500 MHz, $CDCl_3$)



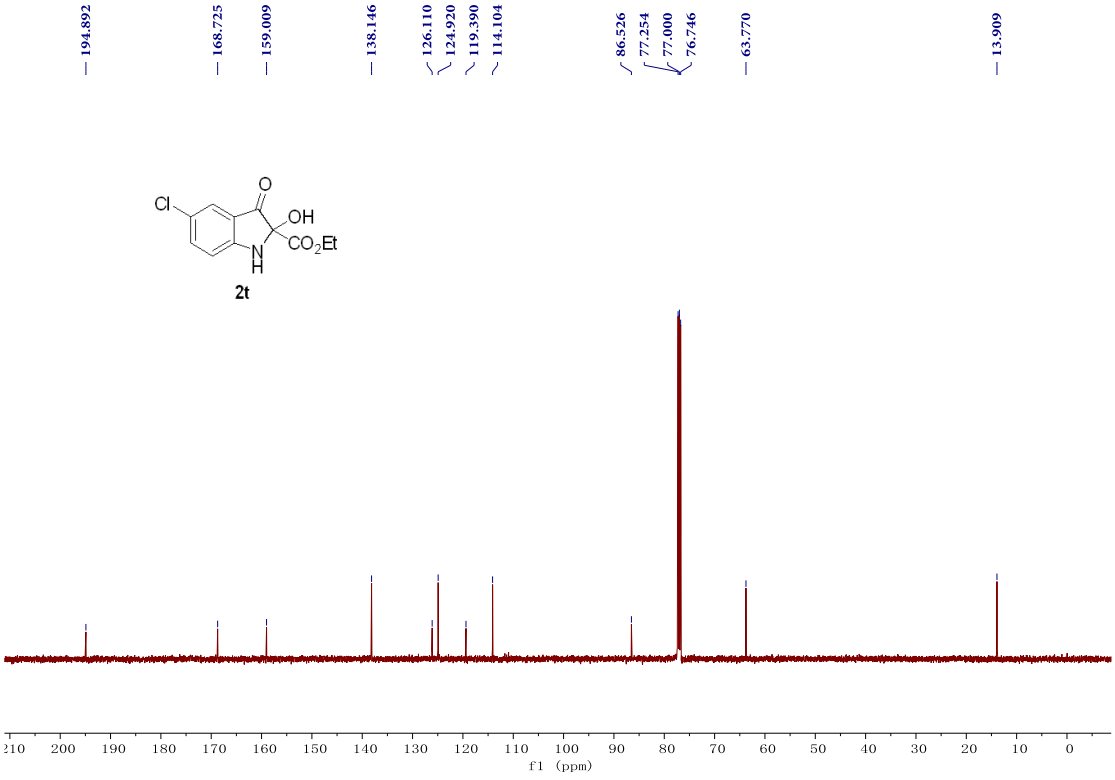
^{13}C NMR (125 MHz, $CDCl_3$)



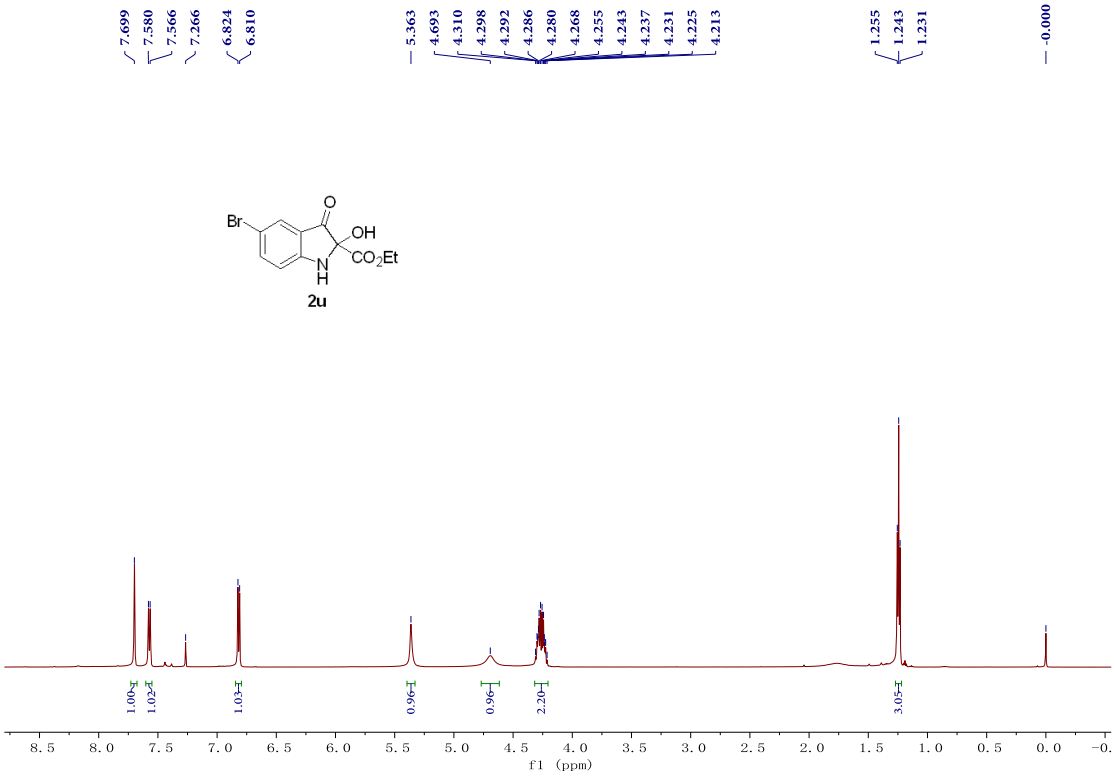
^{1}H NMR (500 MHz, $CDCl_3$)



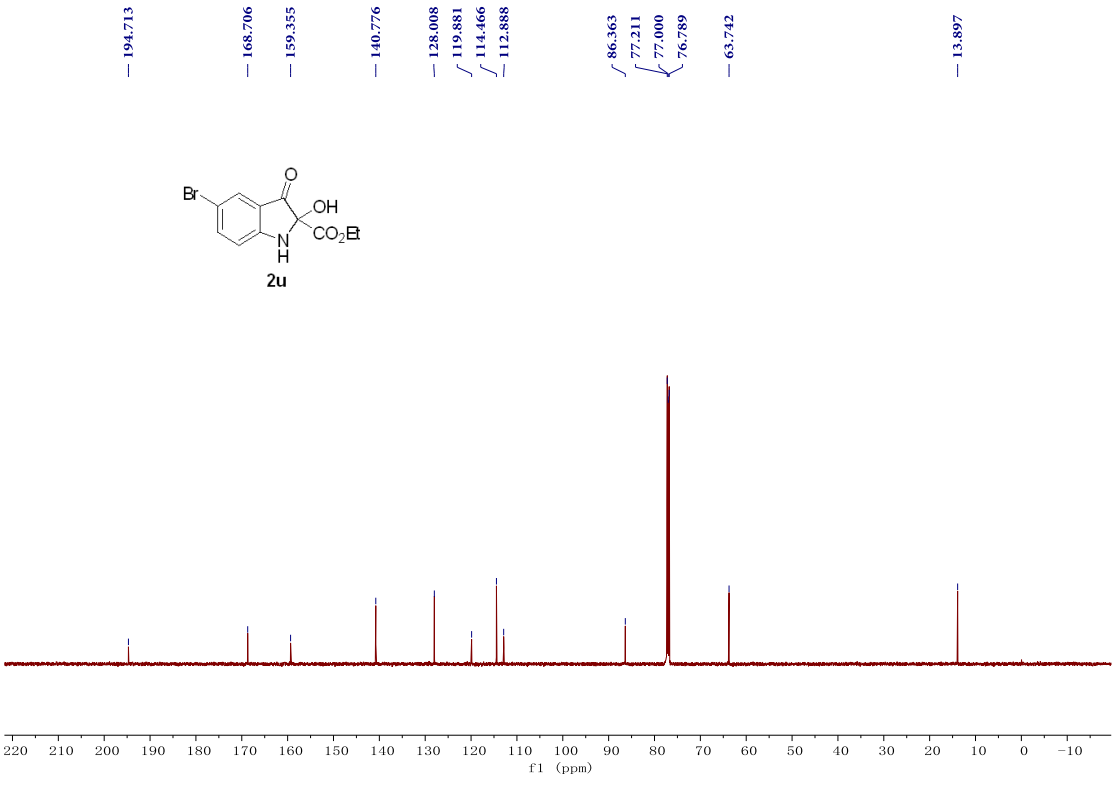
^{13}C NMR (125 MHz, $CDCl_3$)



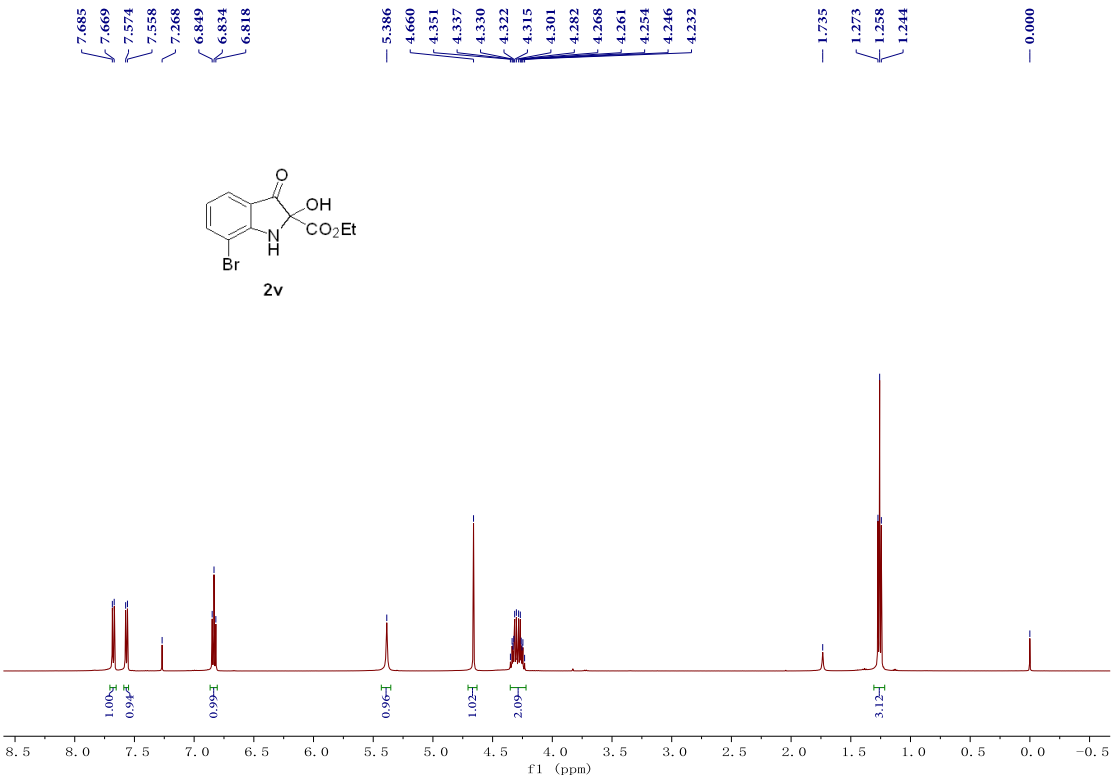
H NMR (600 MHz, $CDCl_3$)



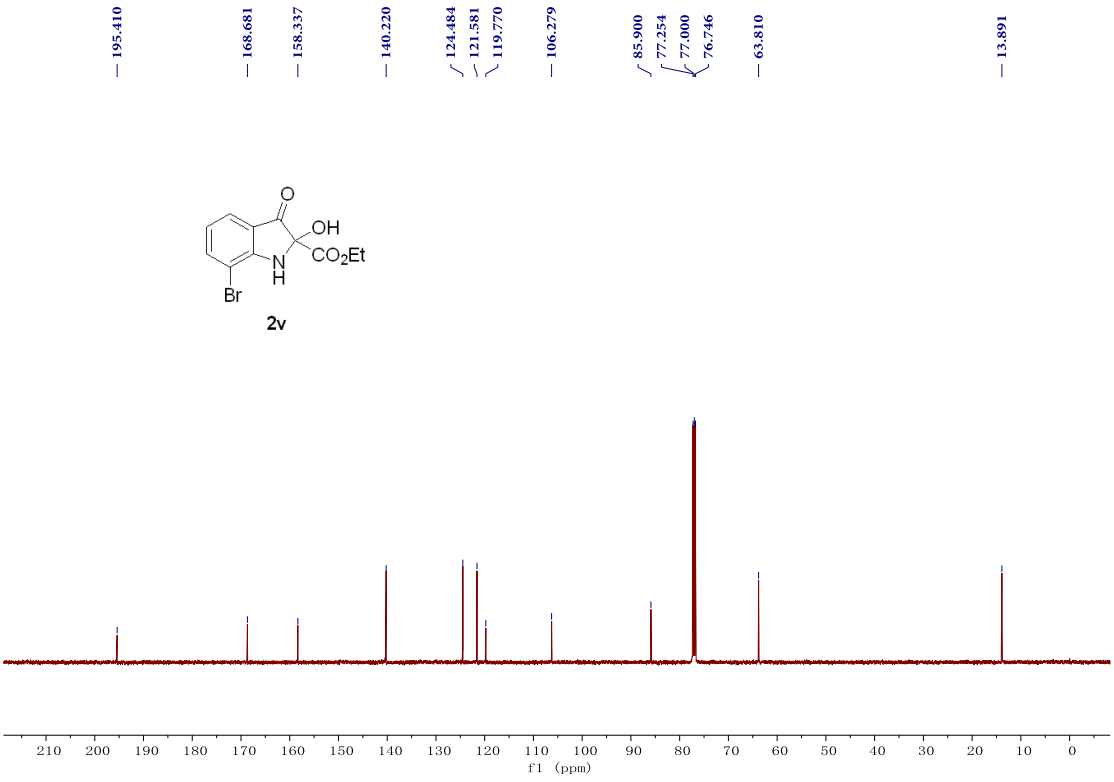
^{13}C NMR (150 MHz, $CDCl_3$)



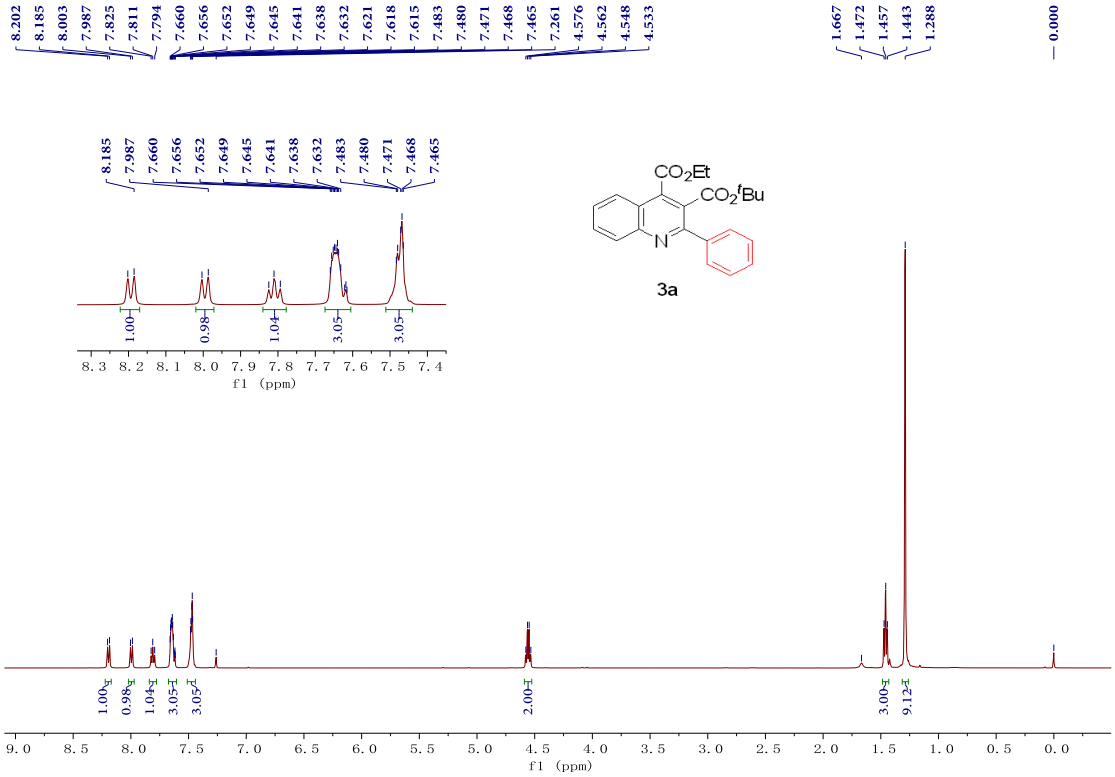
^{1}H NMR (600 MHz, $CDCl_3$)



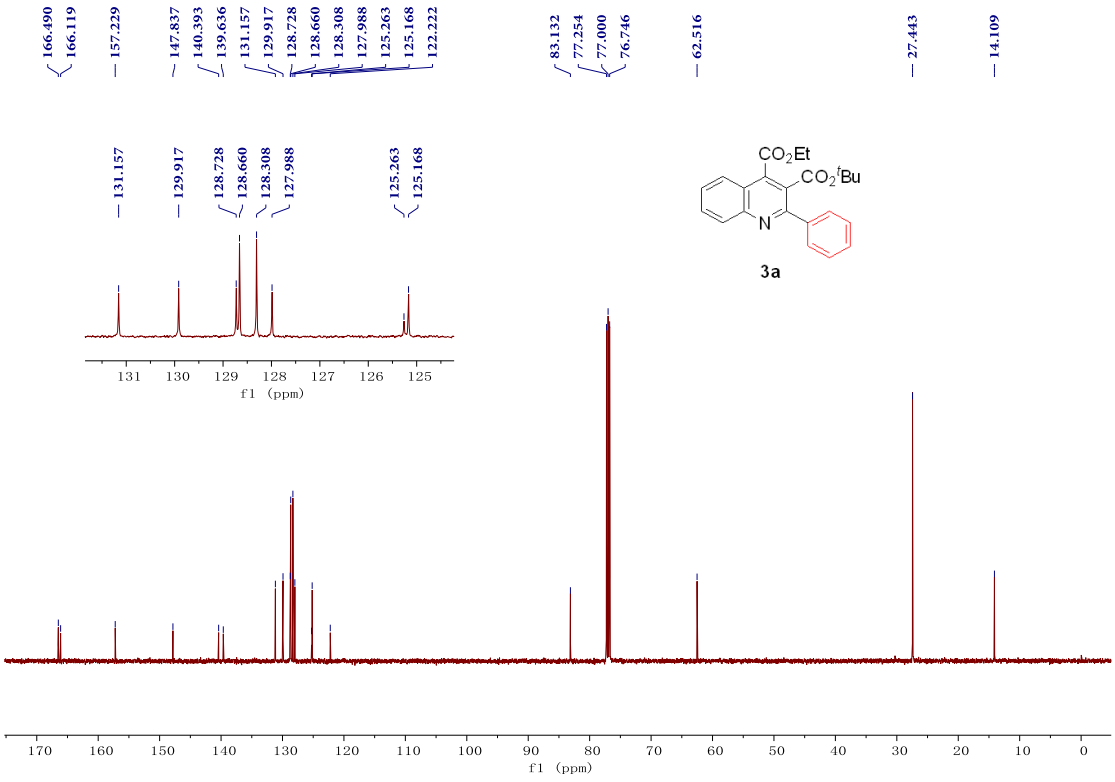
^{13}C NMR (150 MHz, $CDCl_3$)



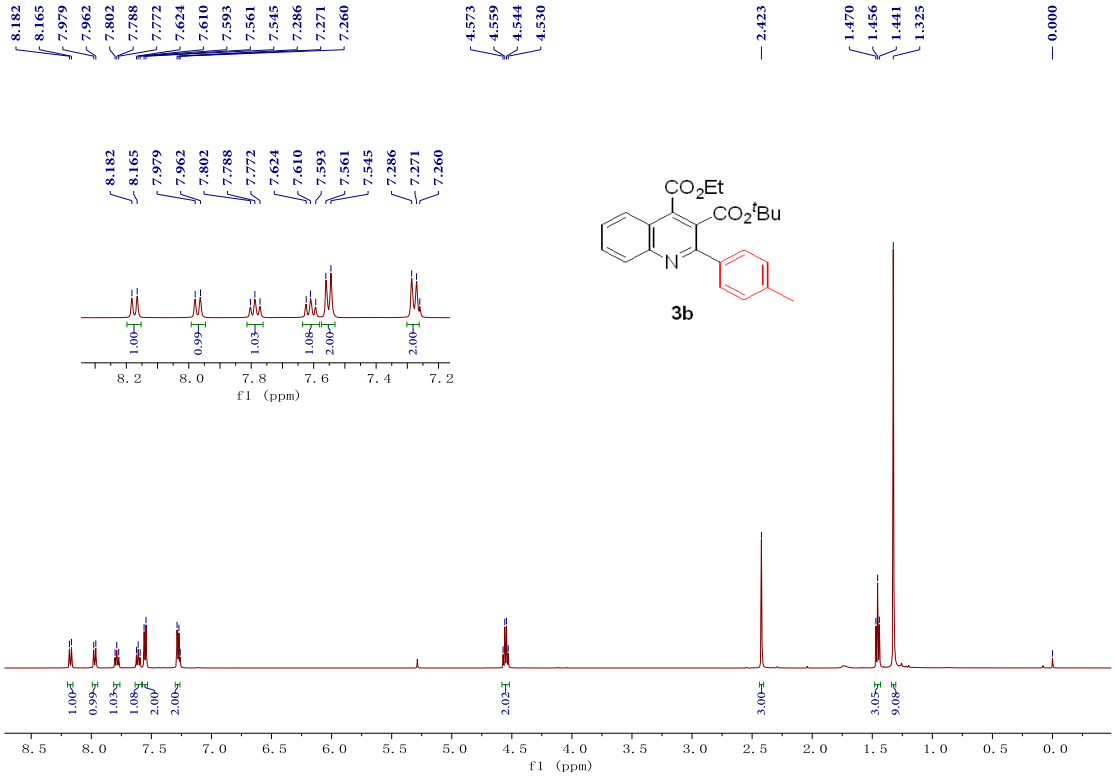
^{1}H NMR (500 MHz, $CDCl_3$)



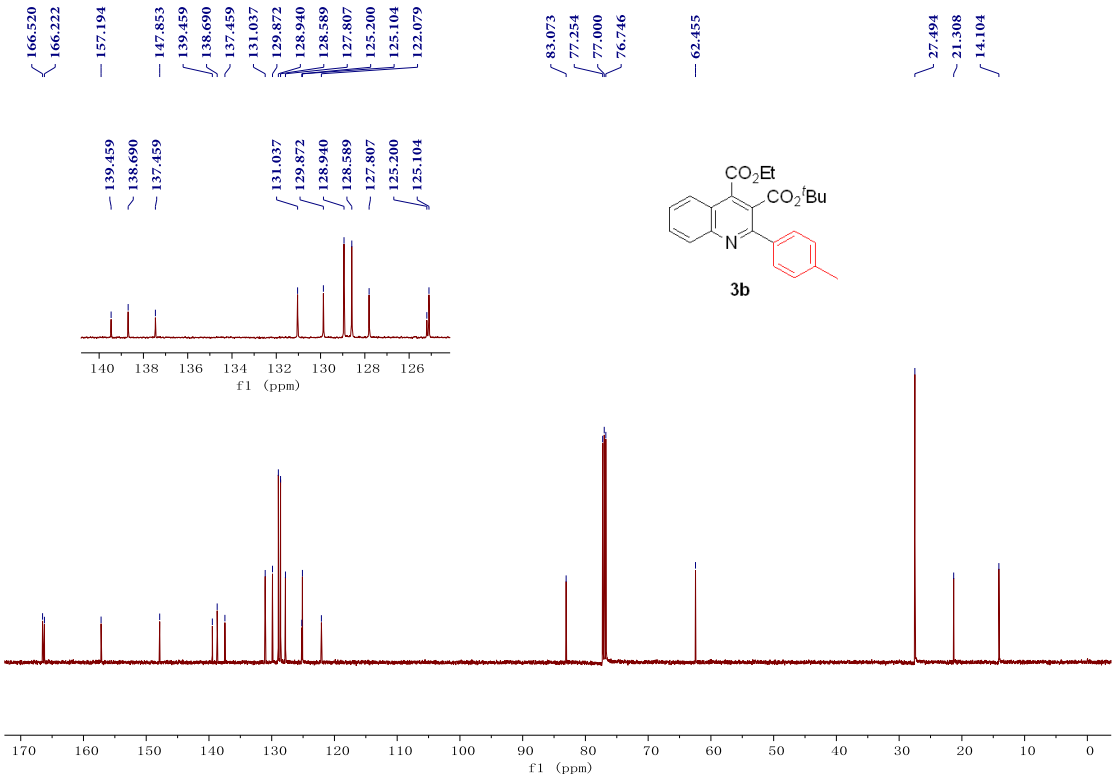
^{13}C NMR (125 MHz, $CDCl_3$)



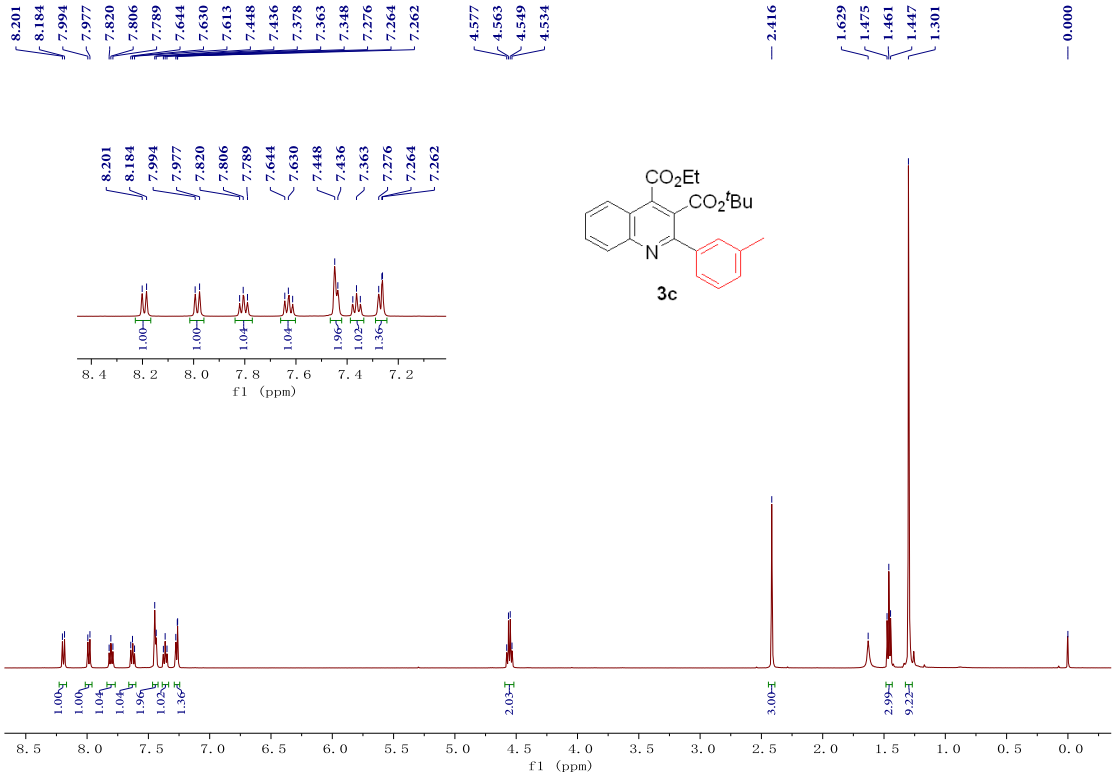
^{1}H NMR (500 MHz, $CDCl_3$)



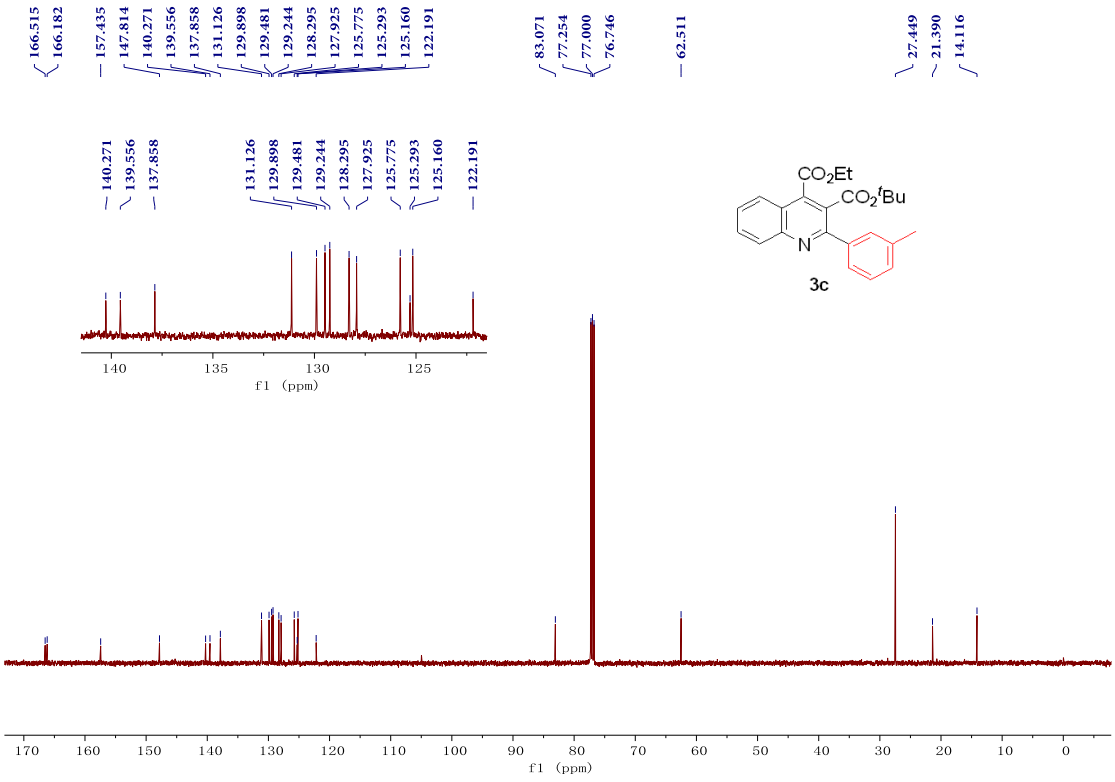
^{13}C NMR (125 MHz, $CDCl_3$)



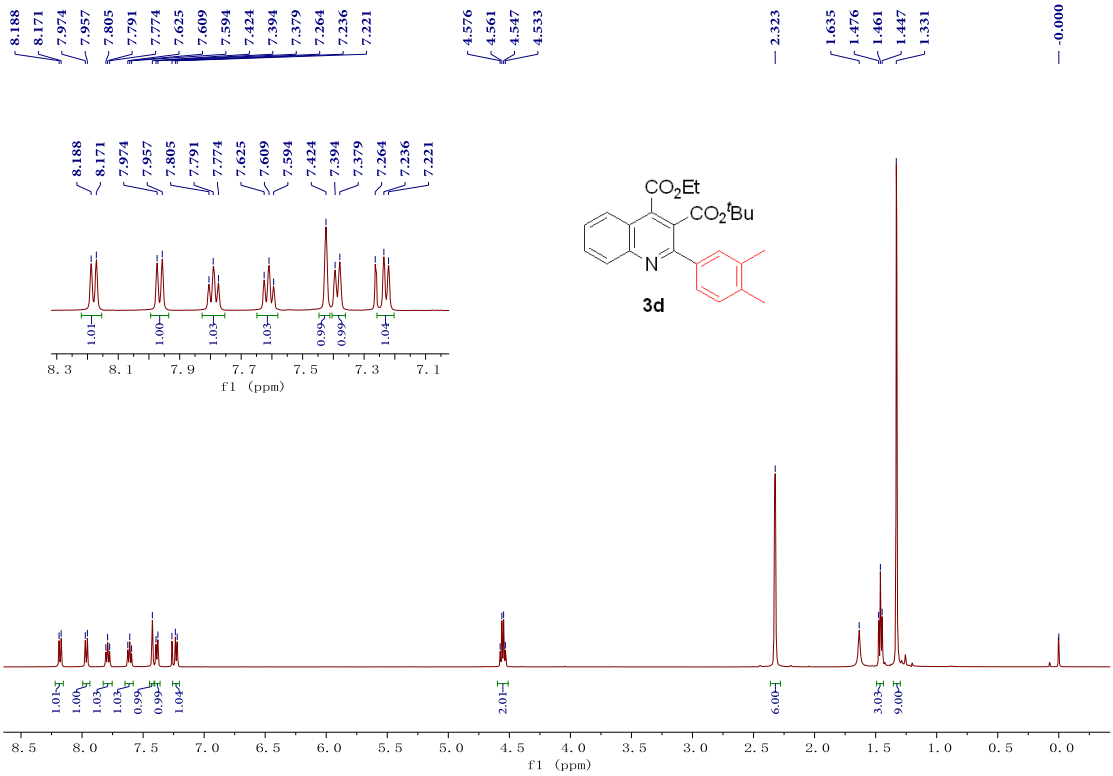
^{1}H NMR (500 MHz, $CDCl_3$)



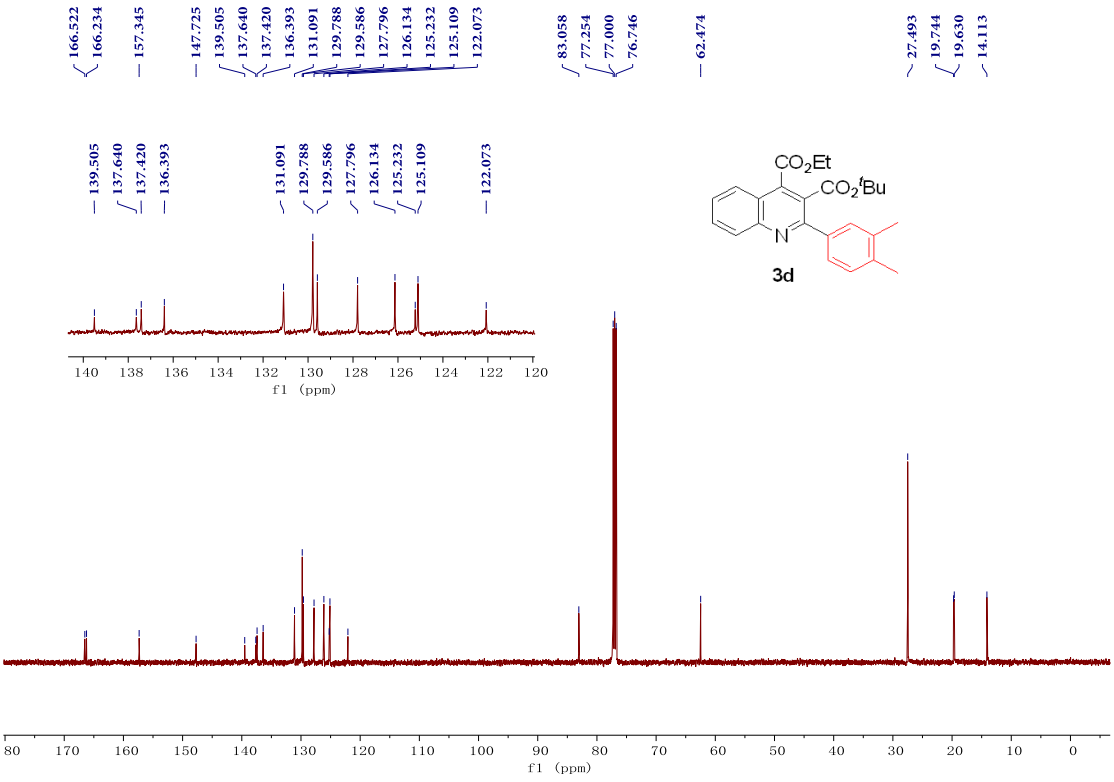
^{13}C NMR (125 MHz, $CDCl_3$)



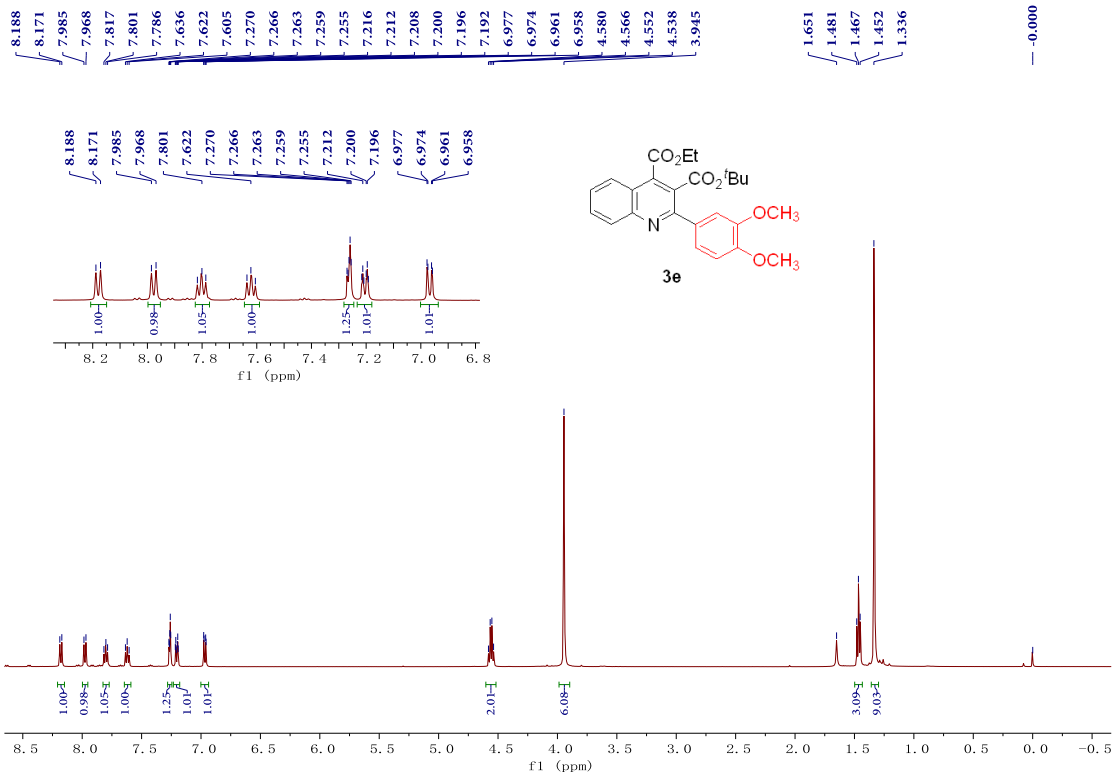
^{1}H NMR (500 MHz, $CDCl_3$)



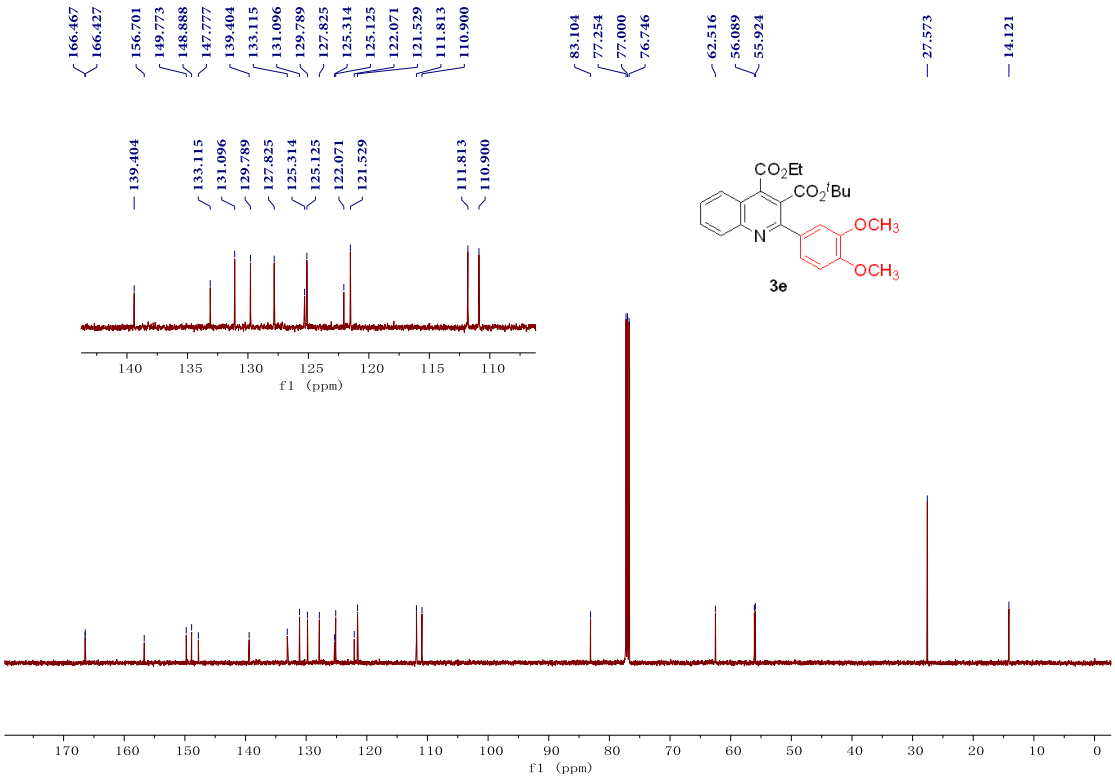
^{13}C NMR (125 MHz, $CDCl_3$)



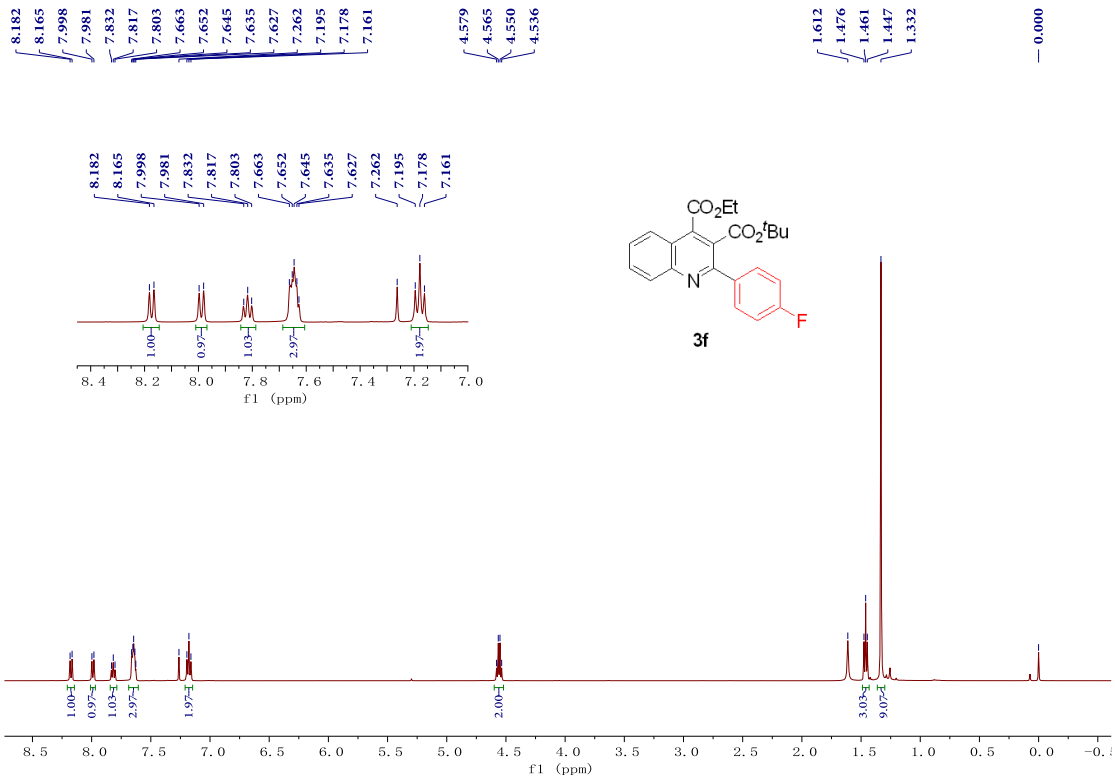
^{1}H NMR (500 MHz, $CDCl_3$)



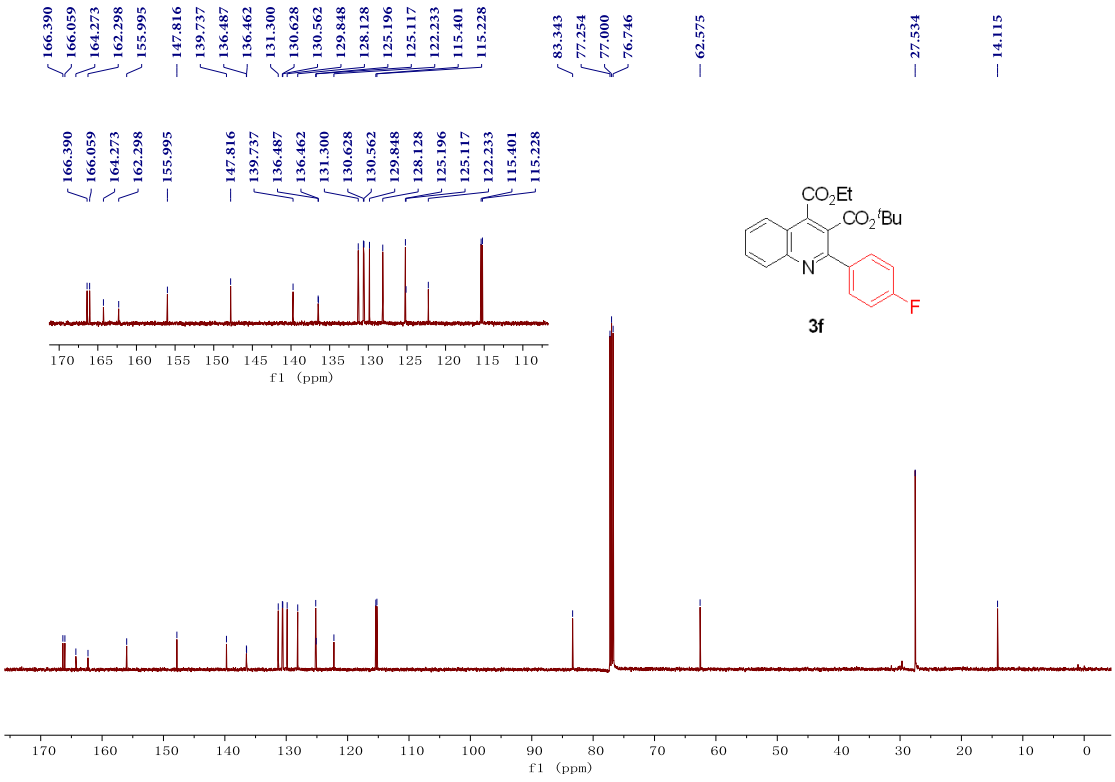
^{13}C NMR (125 MHz, $CDCl_3$)



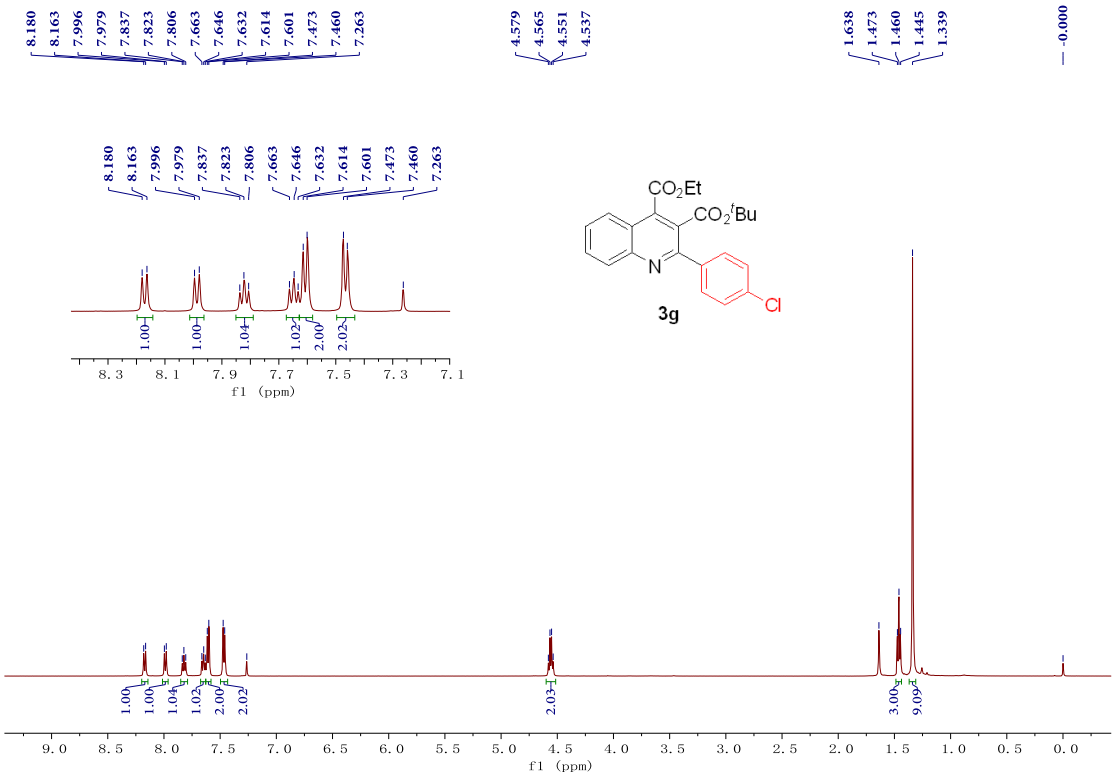
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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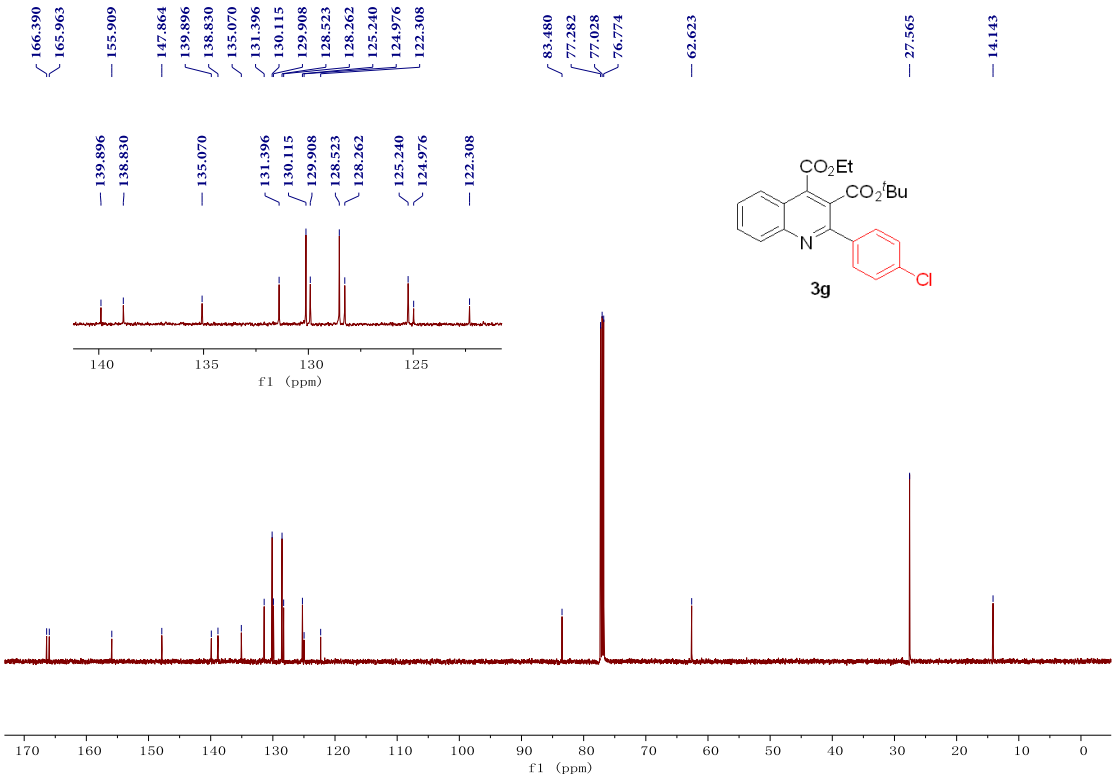

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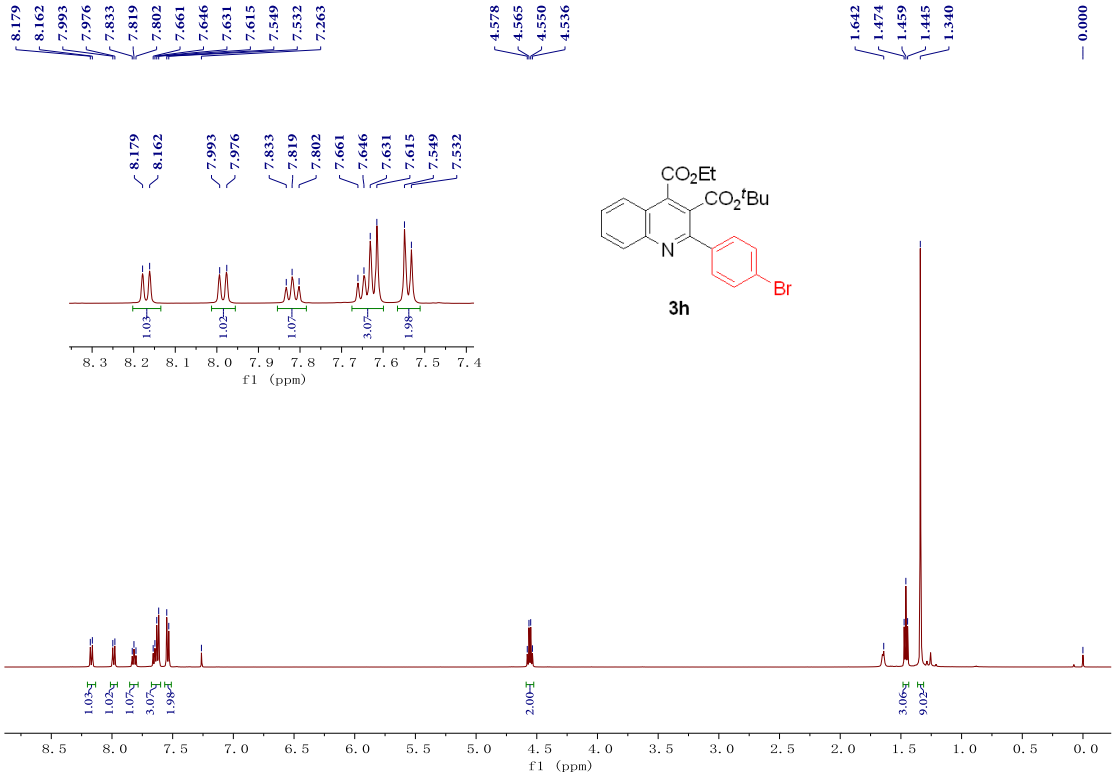
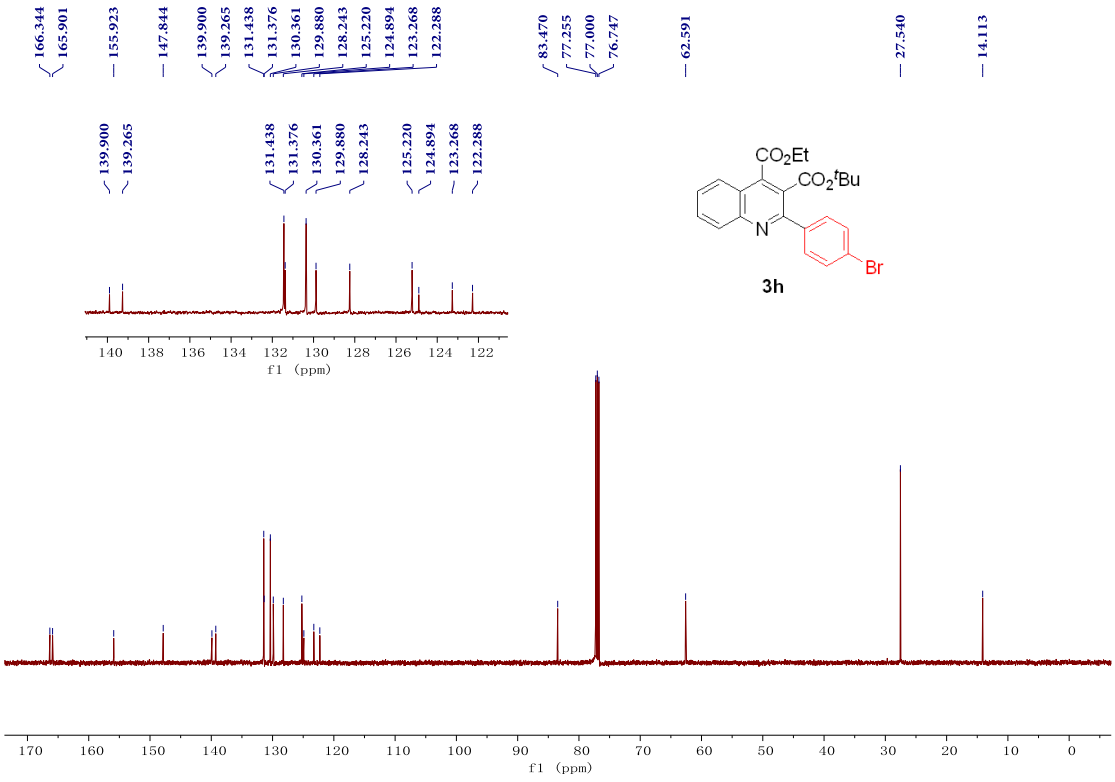
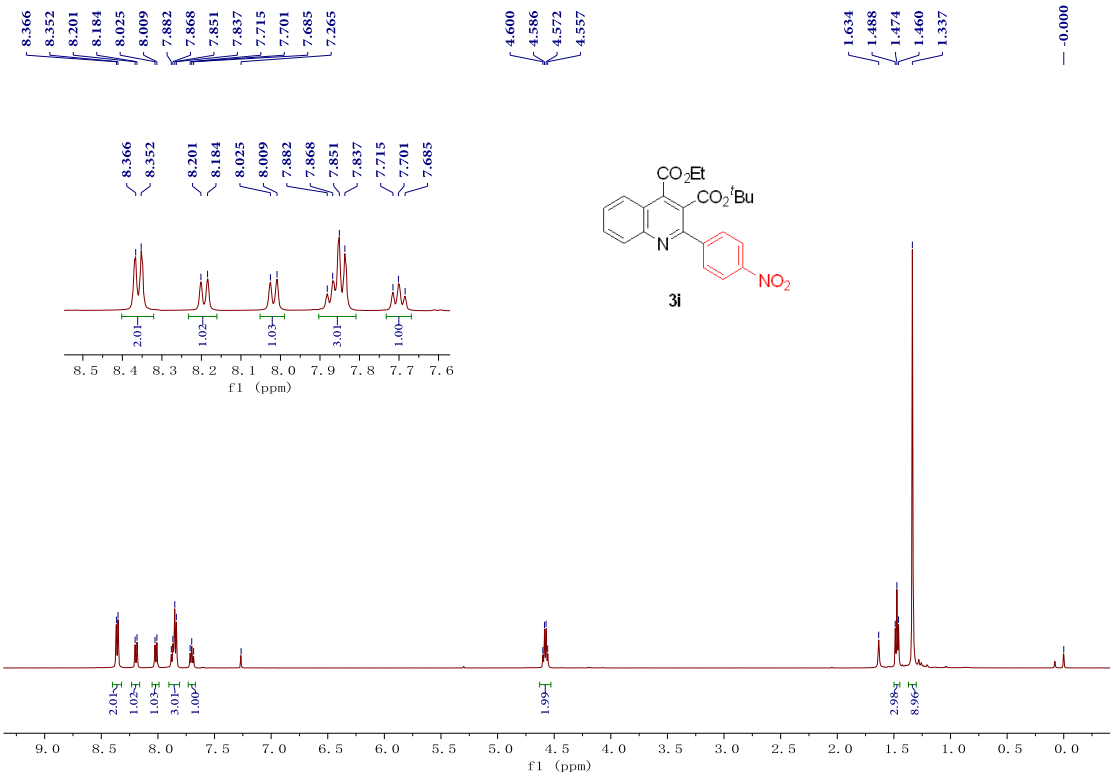


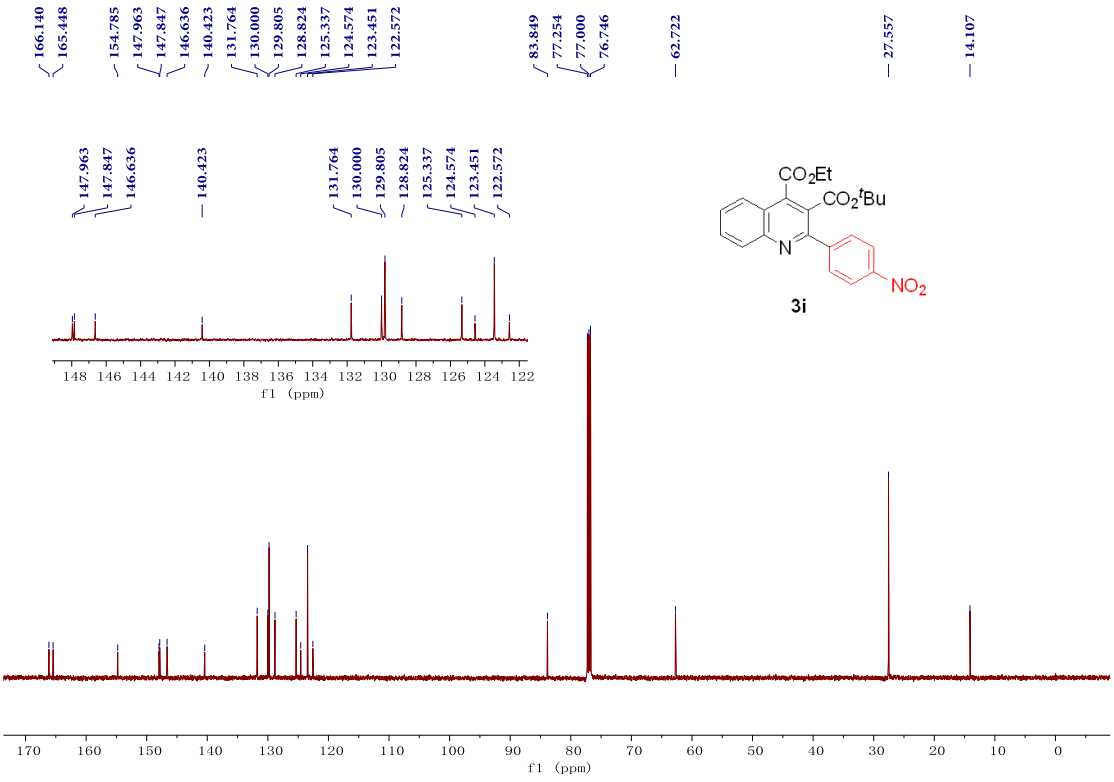
^{13}C NMR (125 MHz, $CDCl_3$)



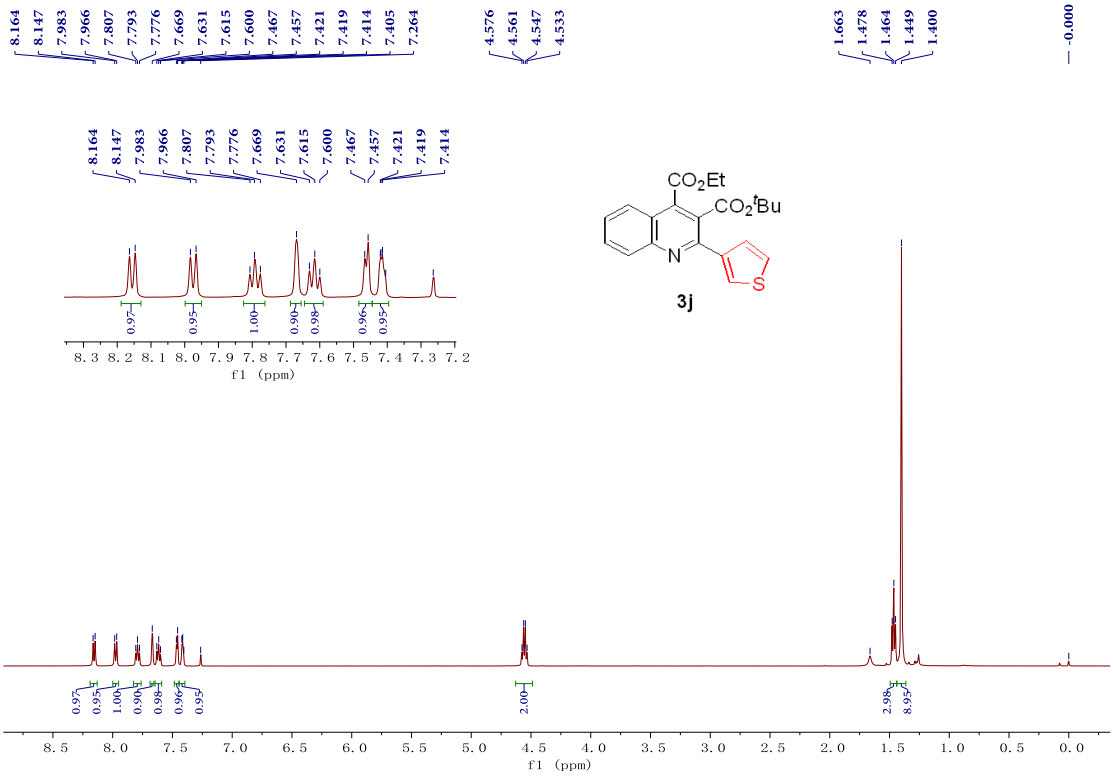
^{1}H NMR (500 MHz, $CDCl_3$)



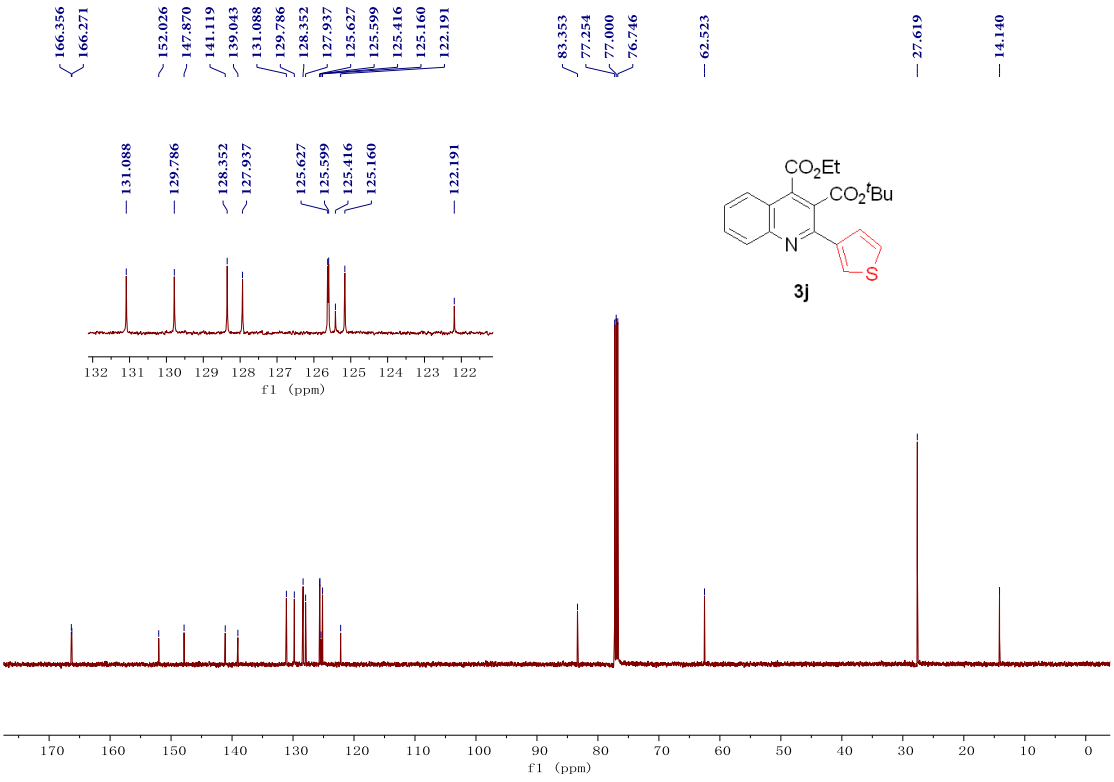
^{13}C NMR (125 MHz, $CDCl_3$)



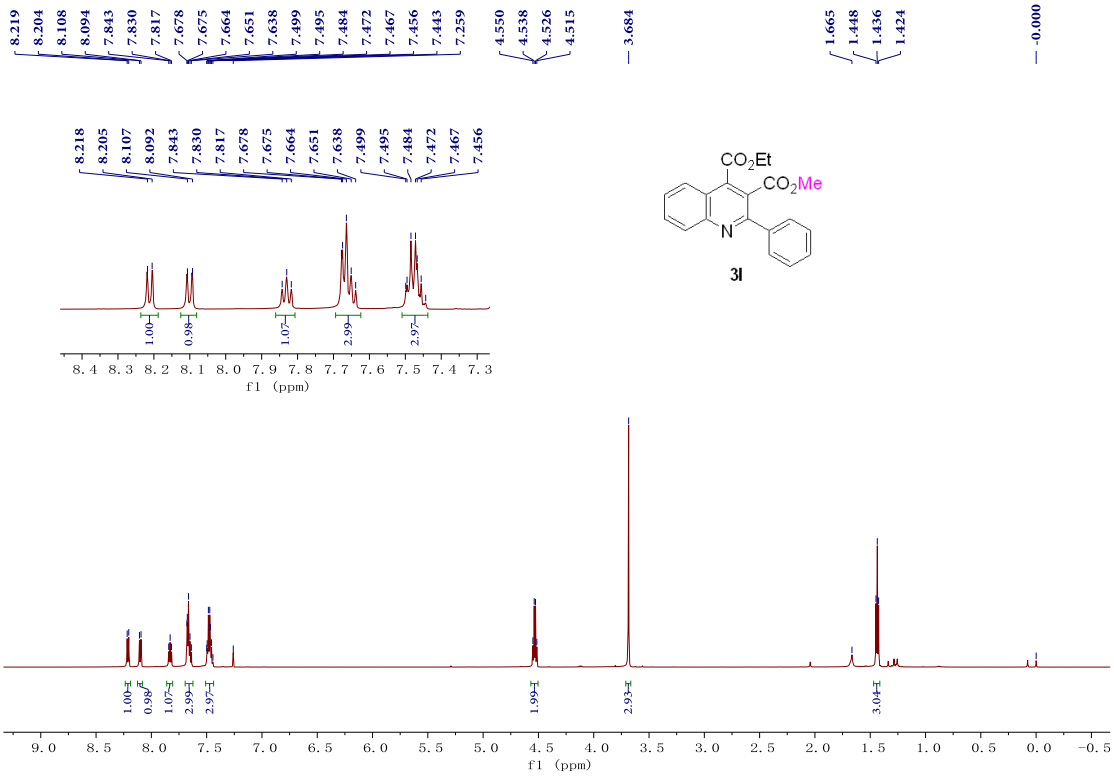
^{1}H NMR (500 MHz, $CDCl_3$)



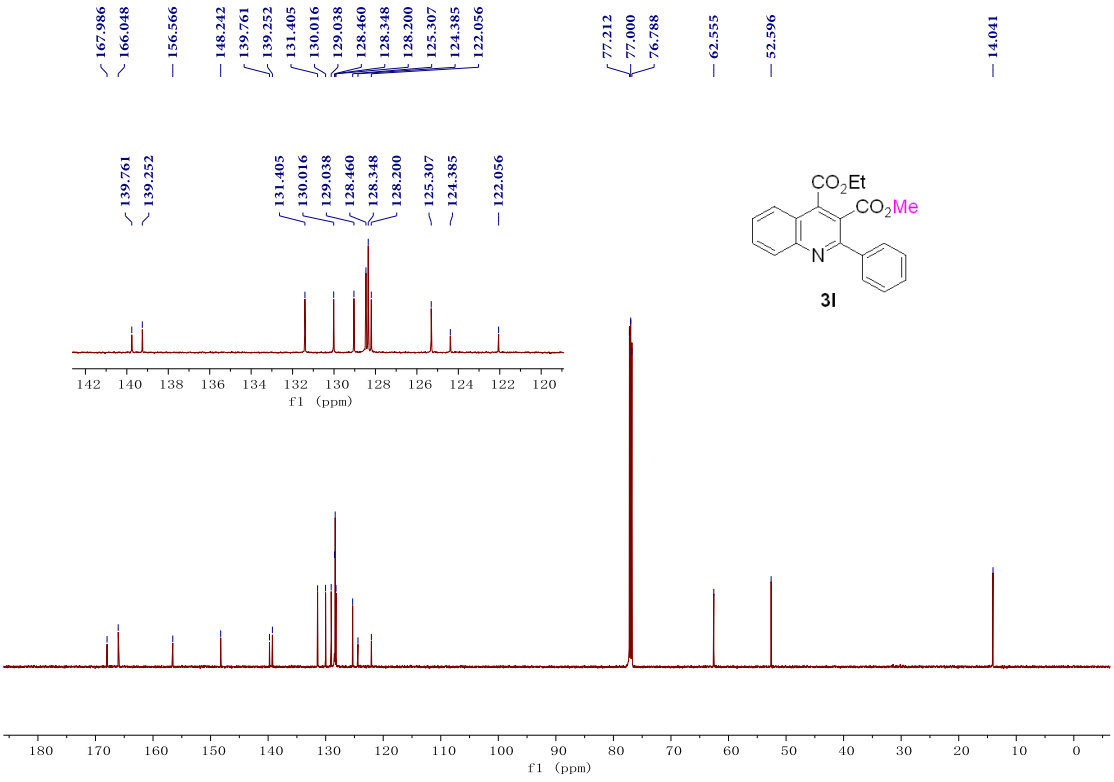
^{13}C NMR (125 MHz, $CDCl_3$)



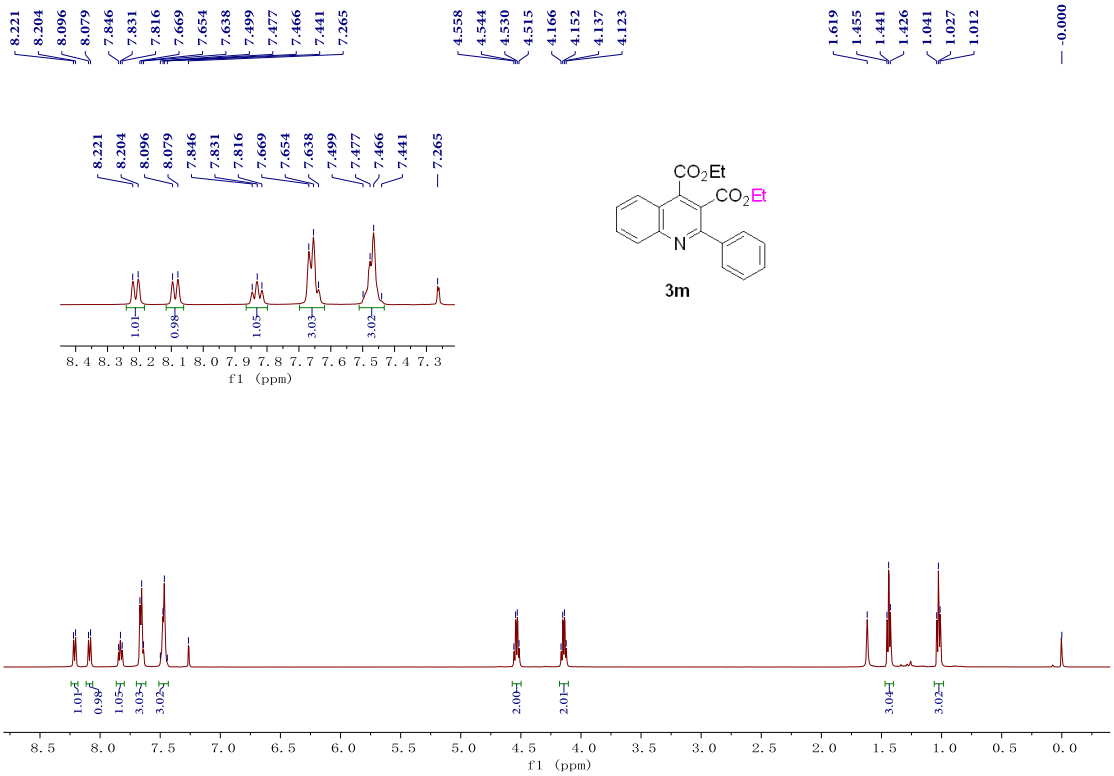
^{1}H NMR (600 MHz, $CDCl_3$)



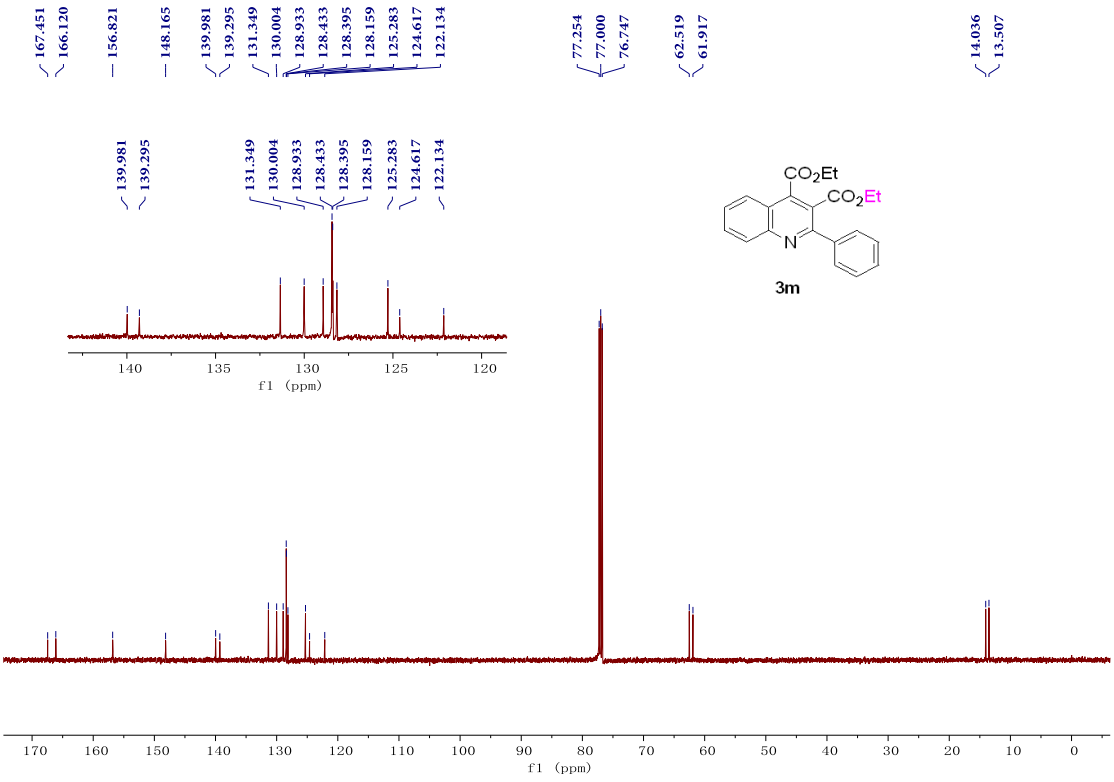
^{13}C NMR (150 MHz, $CDCl_3$)



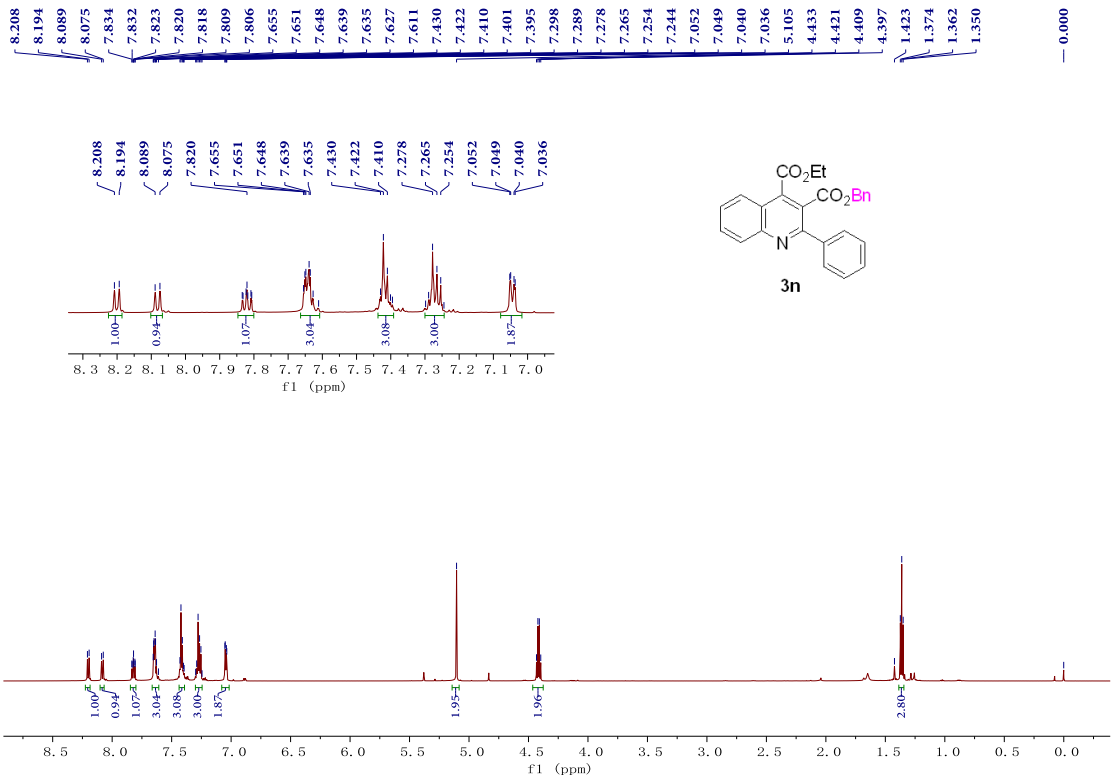
^{1}H NMR (500 MHz, $CDCl_3$)



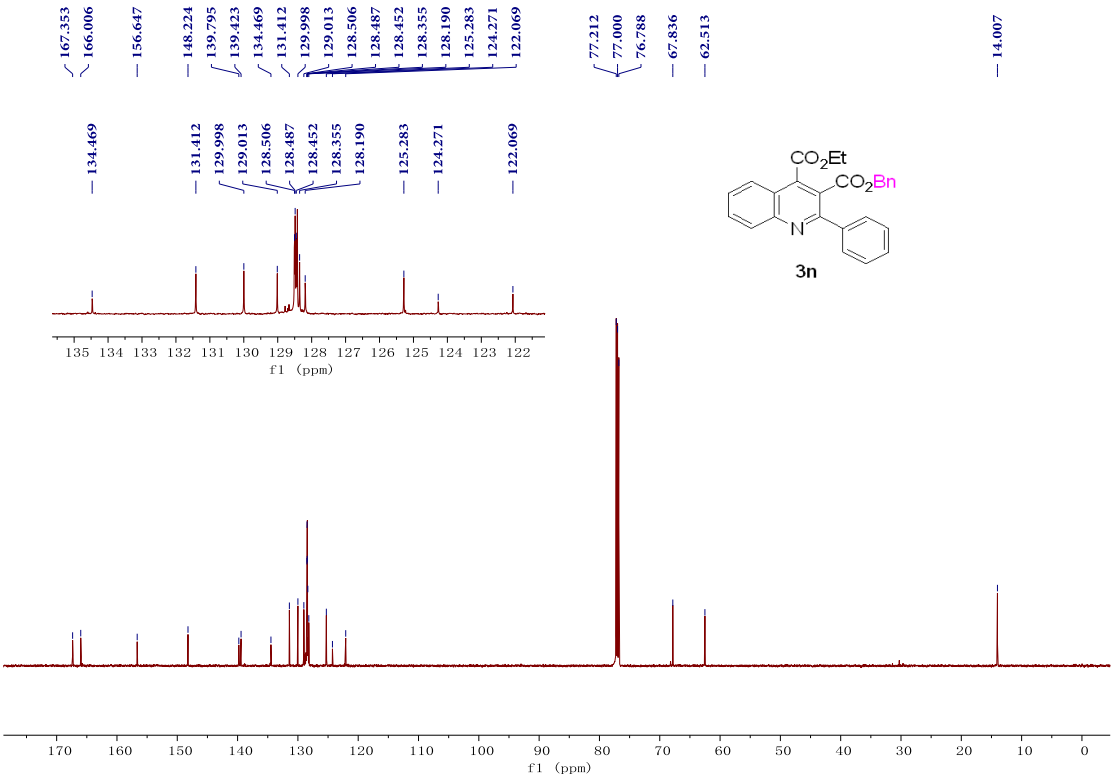
^{13}C NMR (125 MHz, $CDCl_3$)



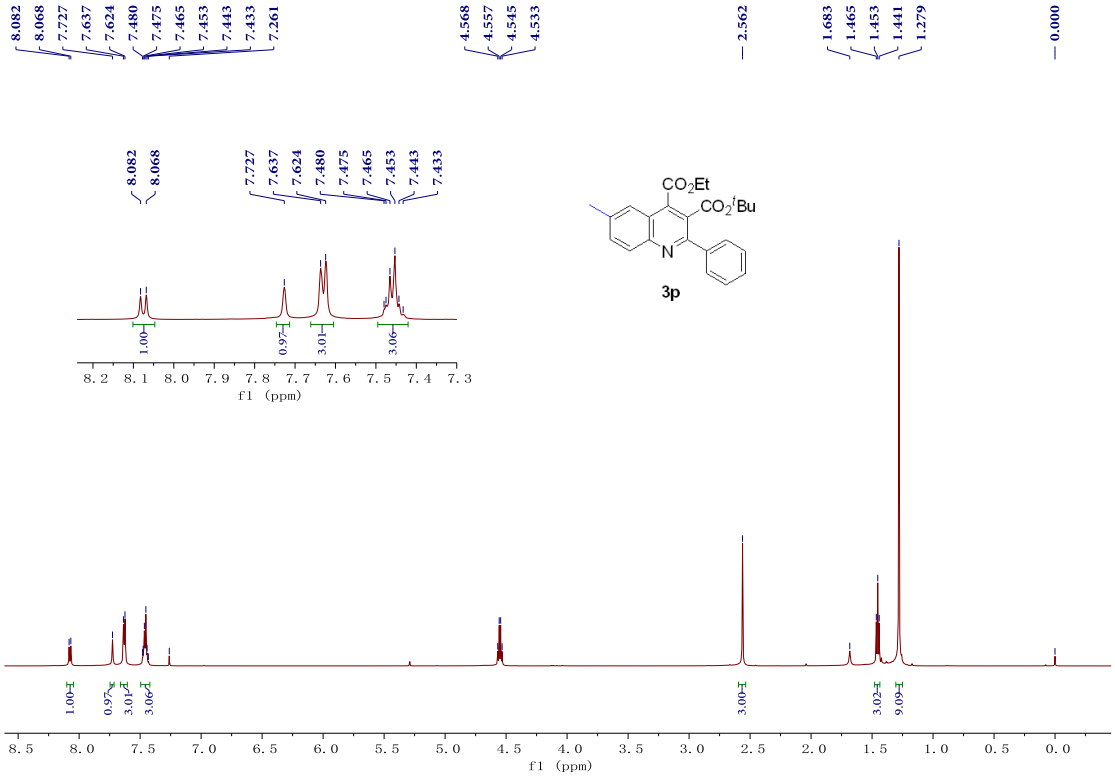
^{1}H NMR (600 MHz, $CDCl_3$)



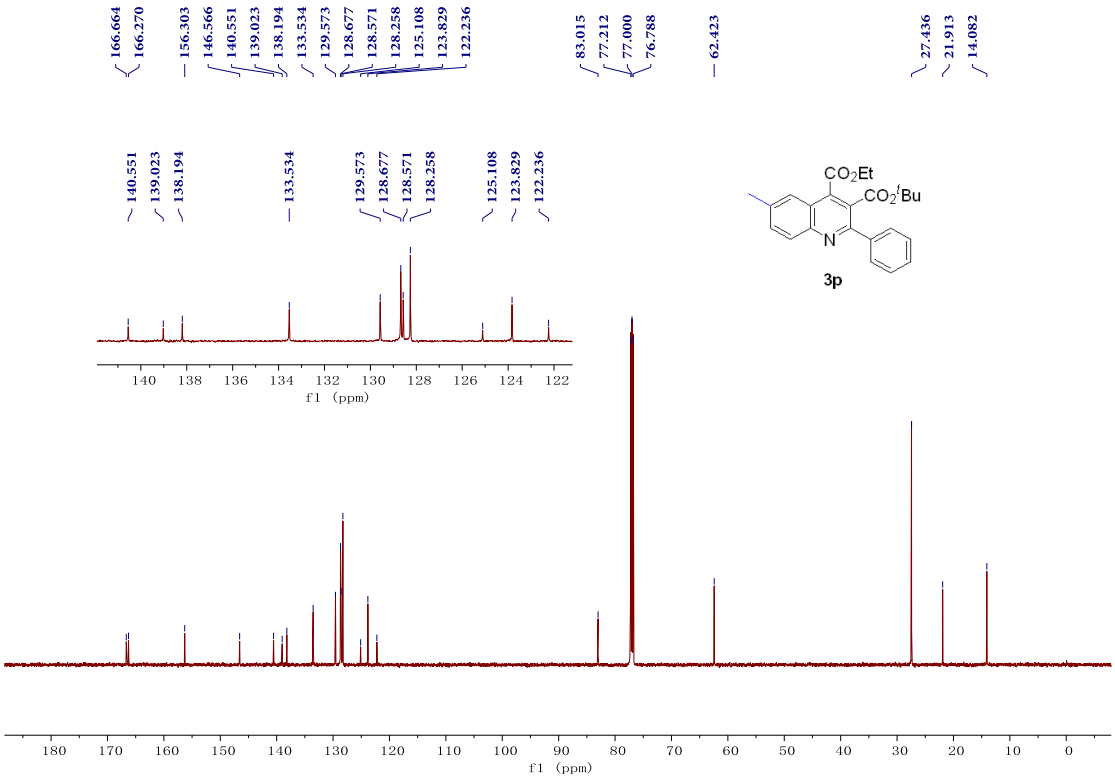
^{13}C NMR (150 MHz, $CDCl_3$)



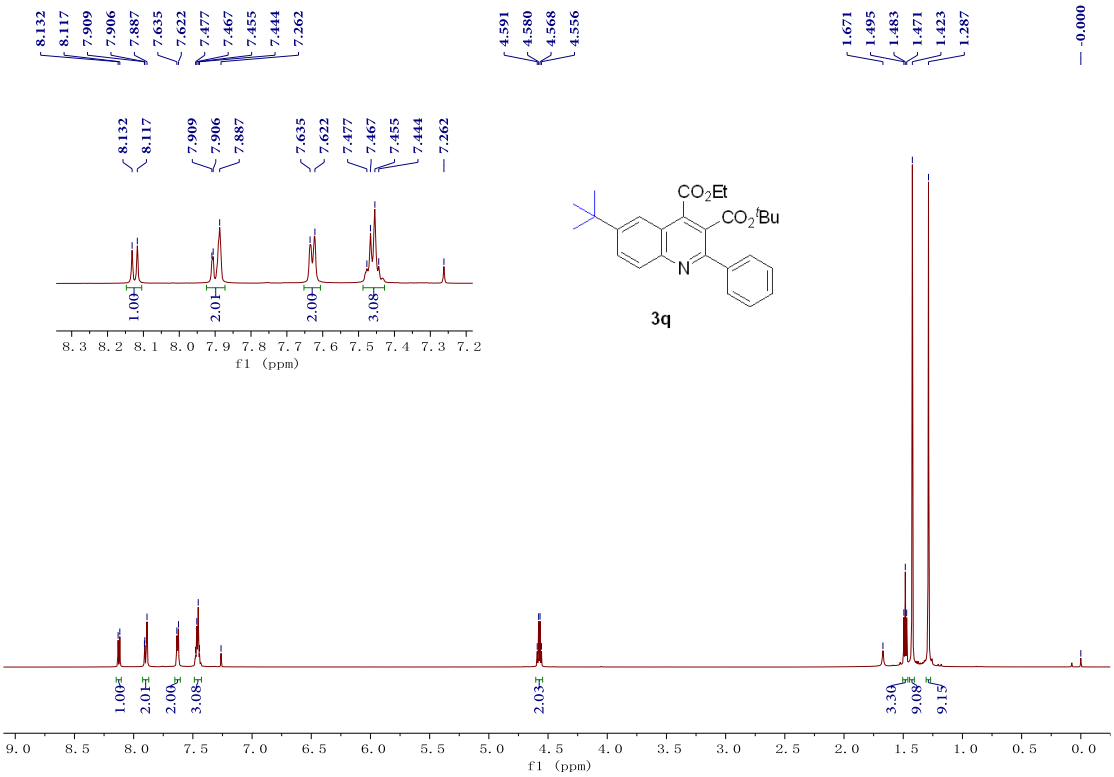
^{1}H NMR (600 MHz, $CDCl_3$)



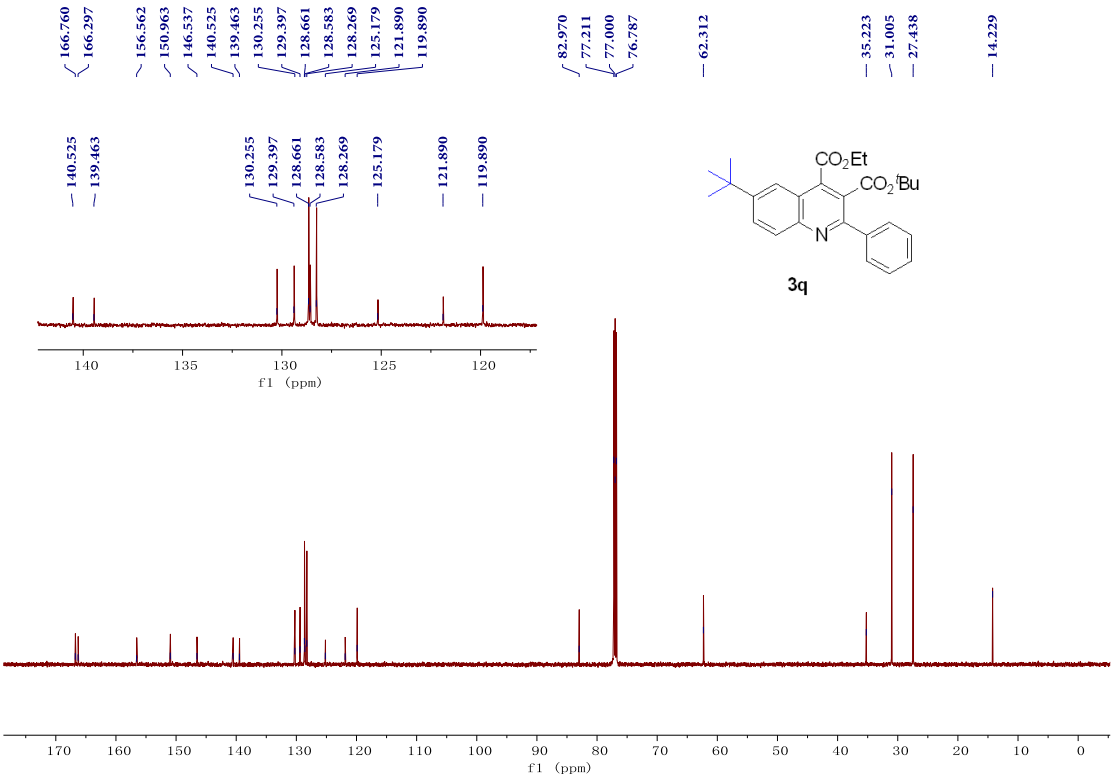
^{13}C NMR (150 MHz, $CDCl_3$)



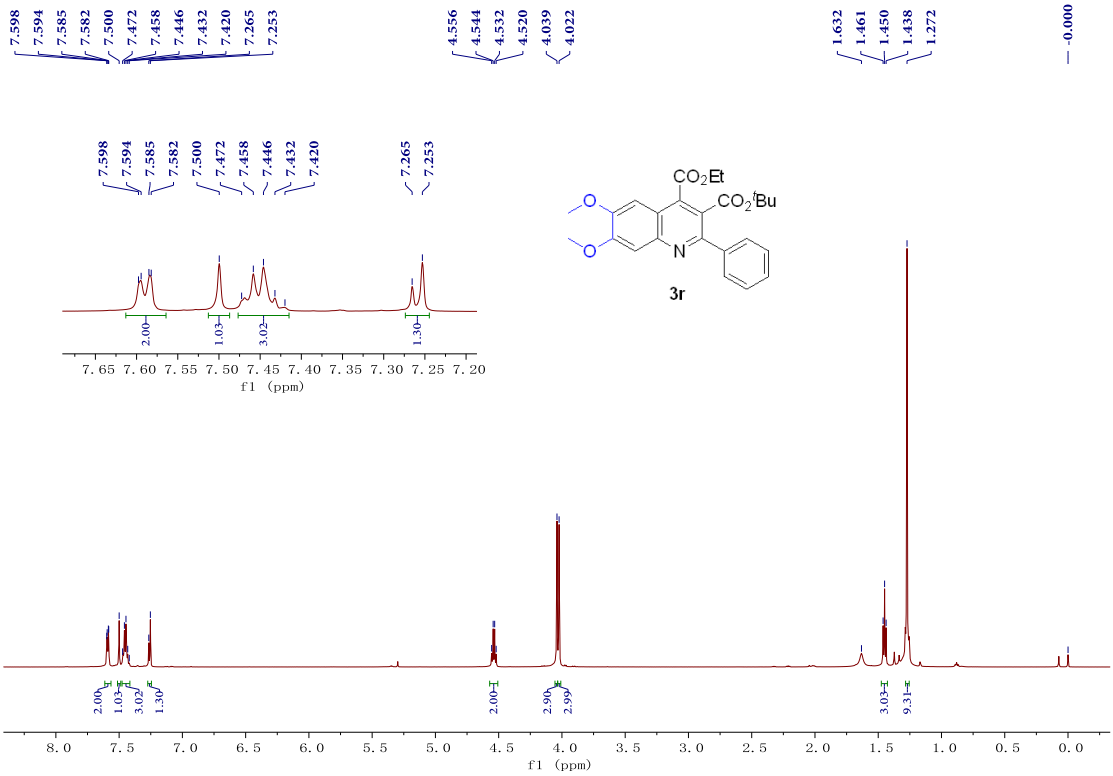
^{1}H NMR (600 MHz, $CDCl_3$)



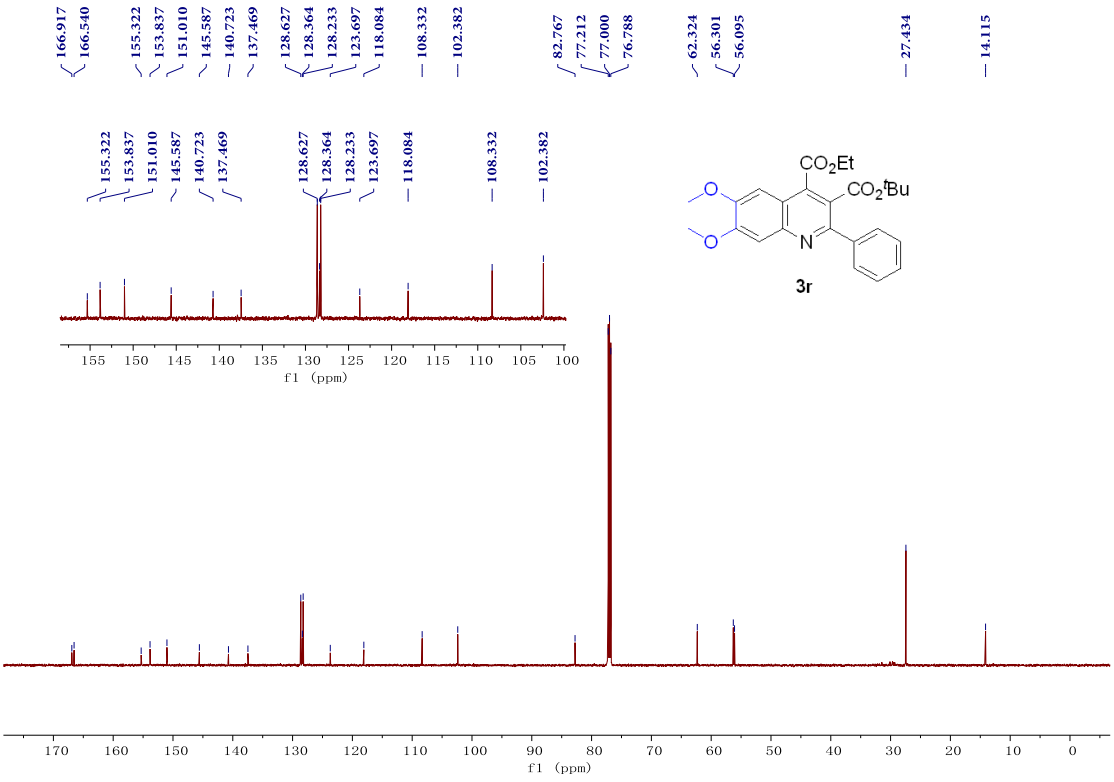
^{13}C NMR (150 MHz, $CDCl_3$)



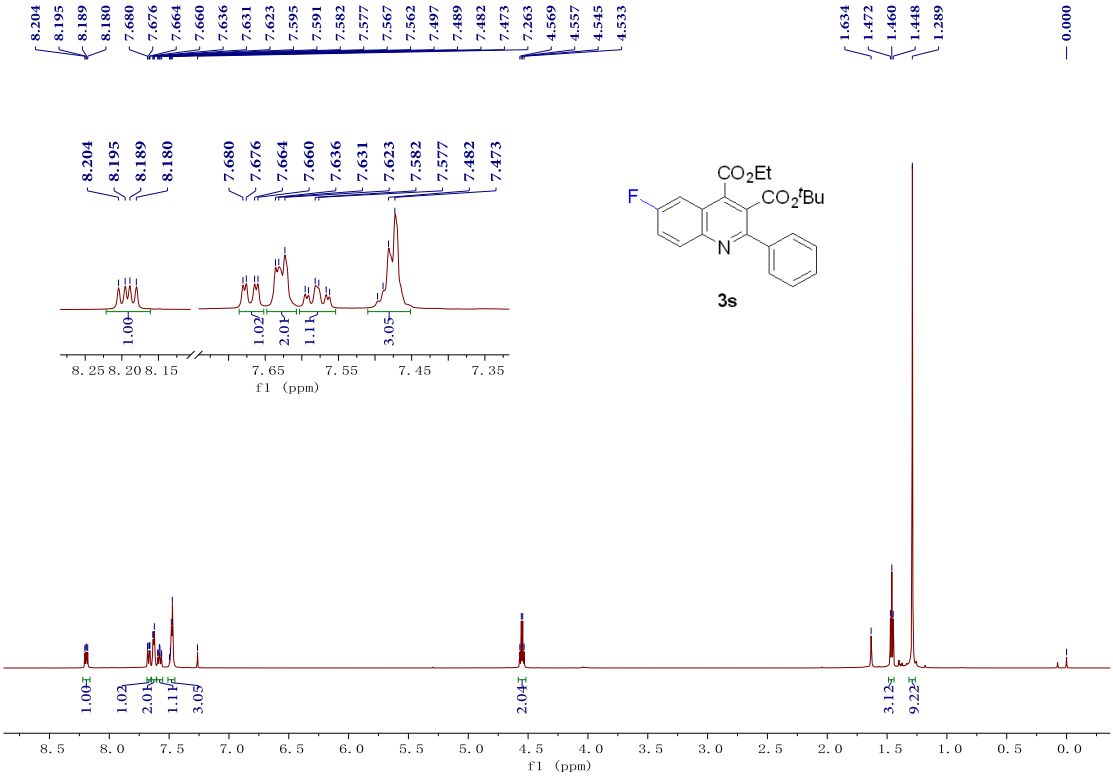
^{1}H NMR (600 MHz, $CDCl_3$)



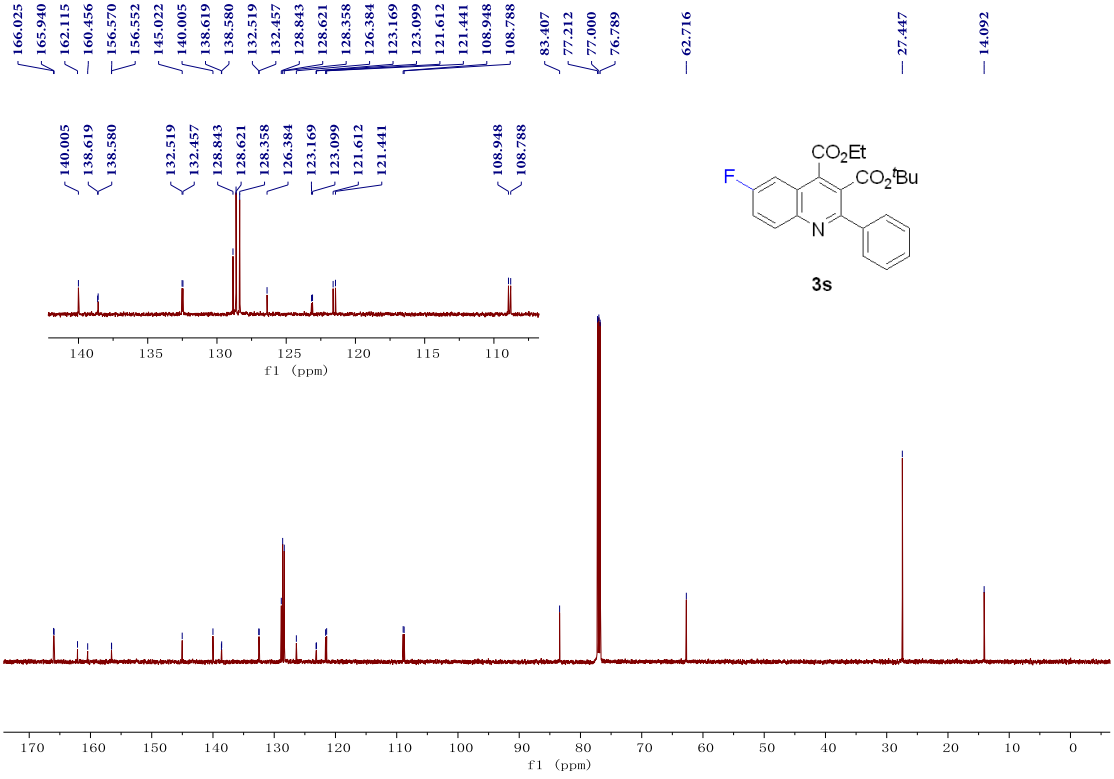
^{13}C NMR (150 MHz, $CDCl_3$)



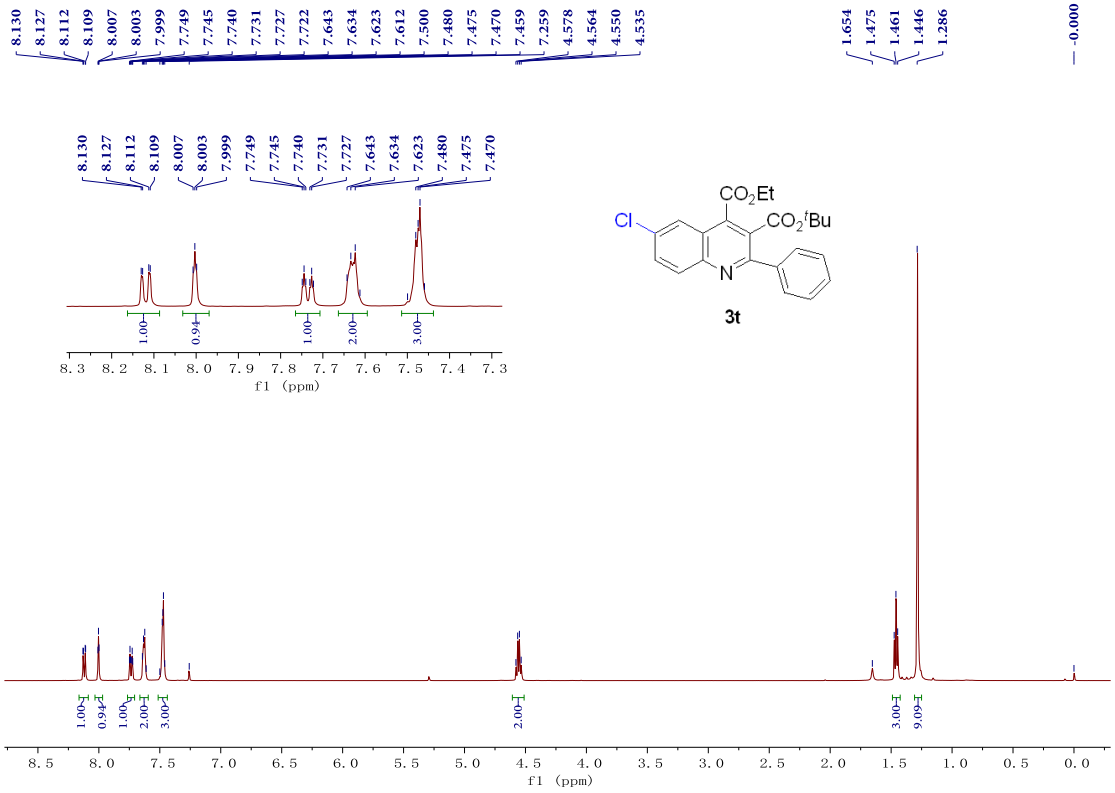
^{1}H NMR (600 MHz, $CDCl_3$)



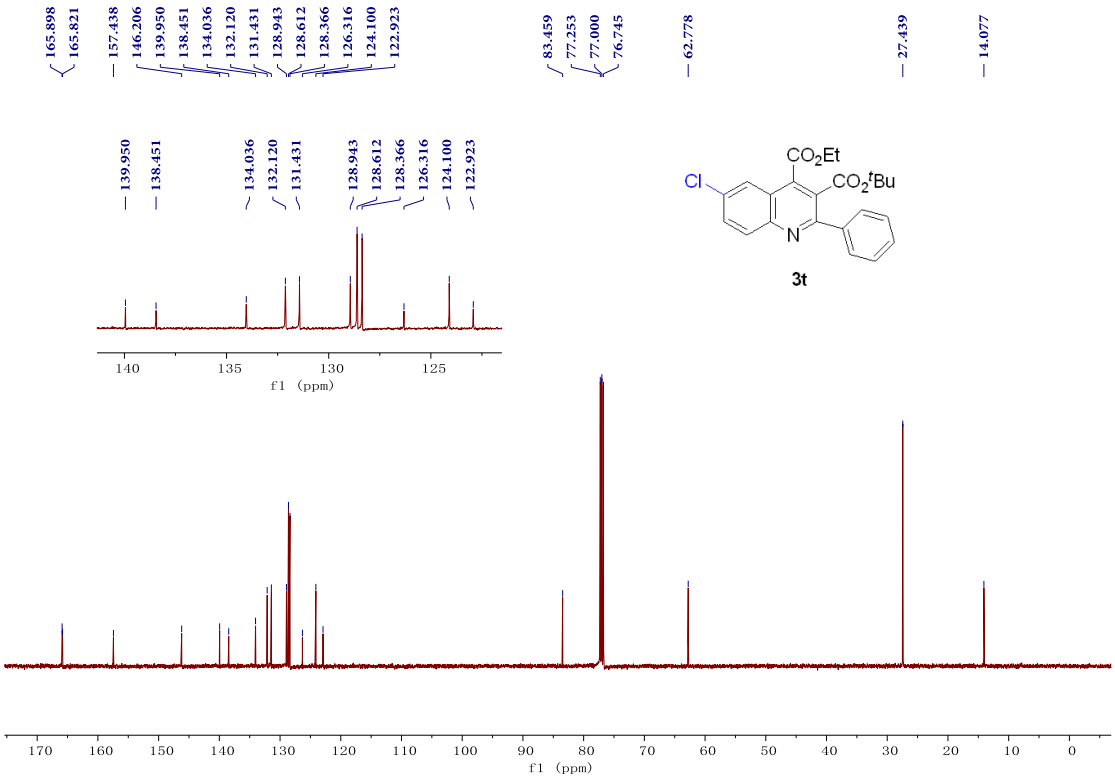
^{13}C NMR (150 MHz, $CDCl_3$)



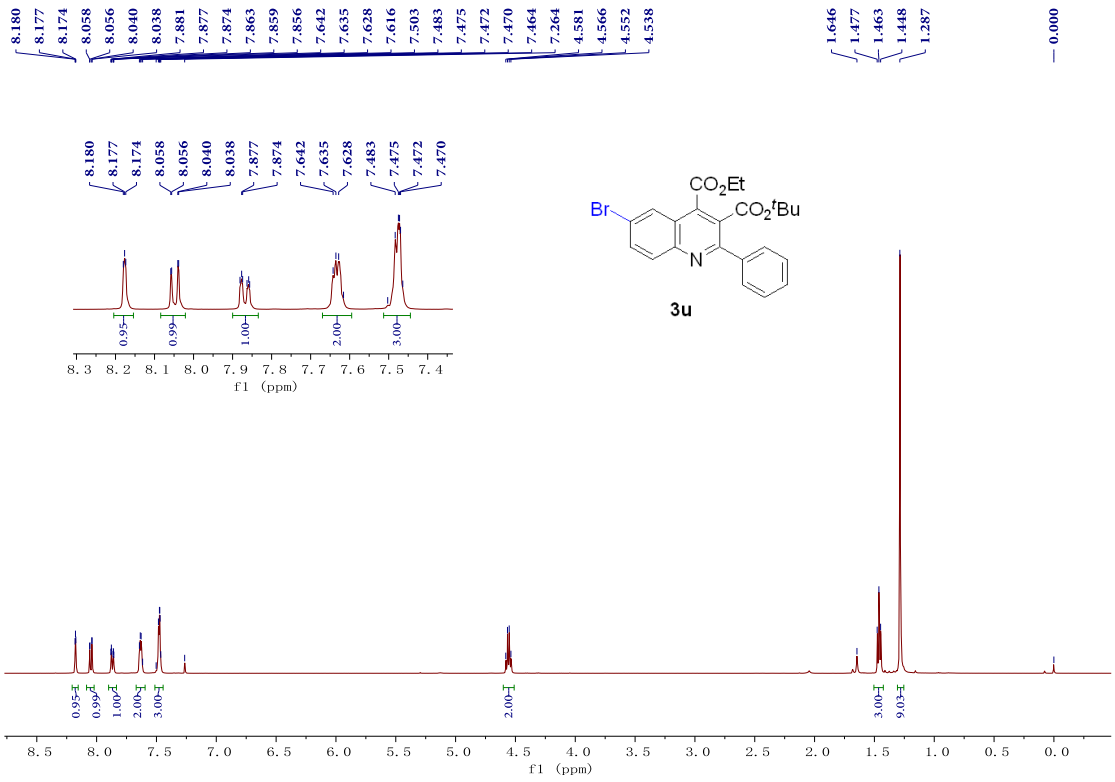
^{1}H NMR (500 MHz, $CDCl_3$)



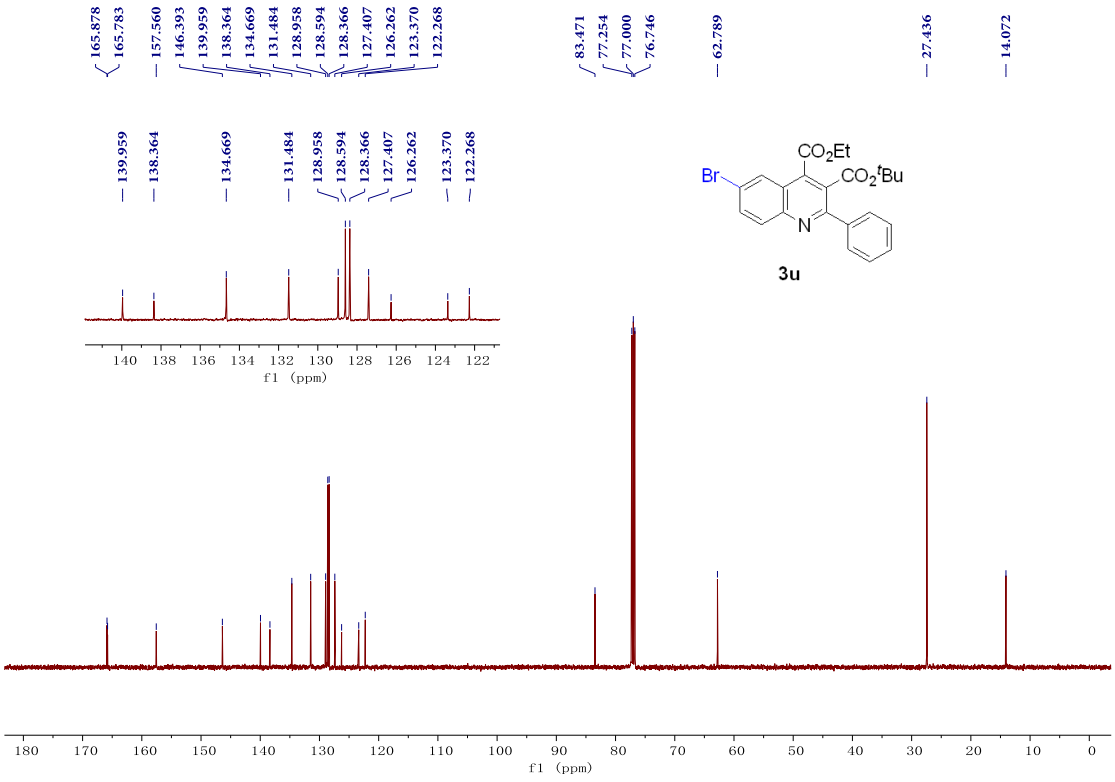
^{13}C NMR (125 MHz, $CDCl_3$)



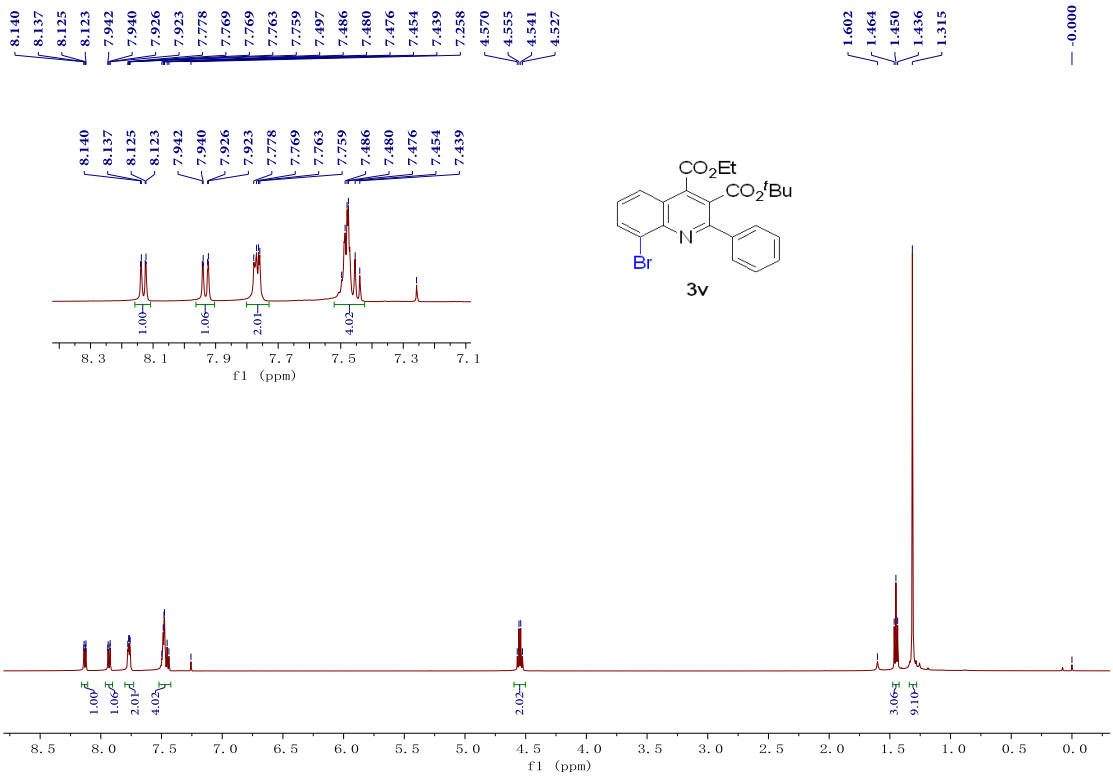
^{1}H NMR (500 MHz, $CDCl_3$)



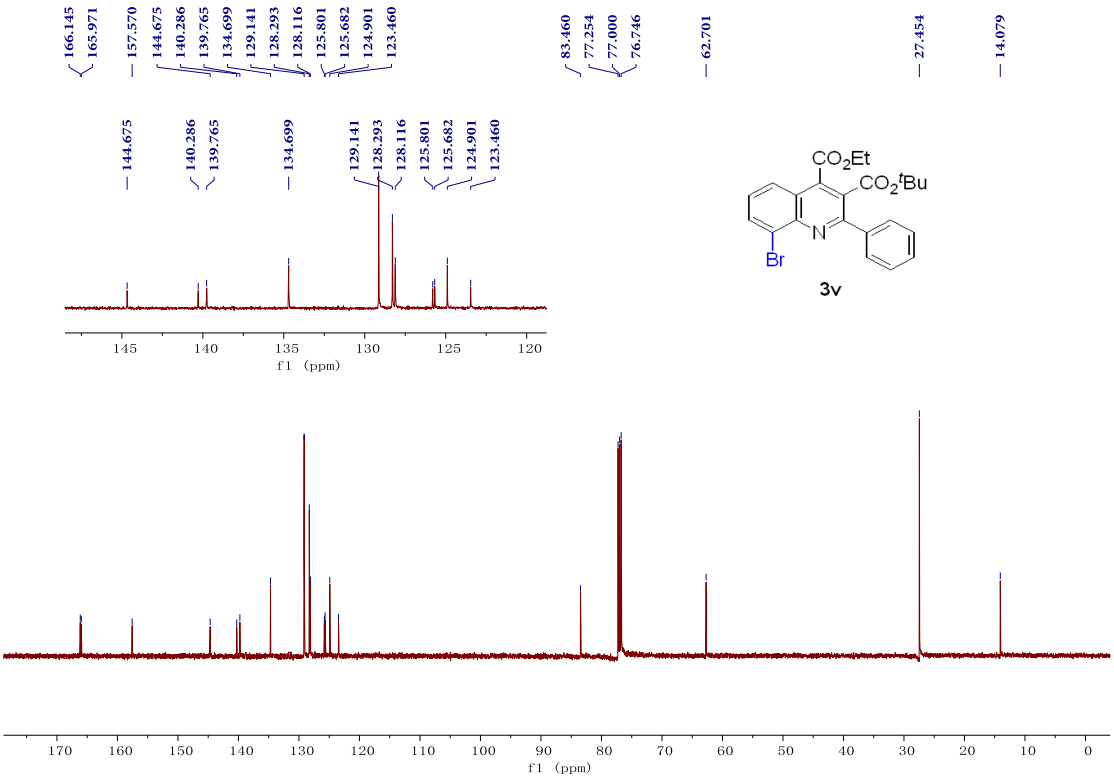
^{13}C NMR (125 MHz, $CDCl_3$)



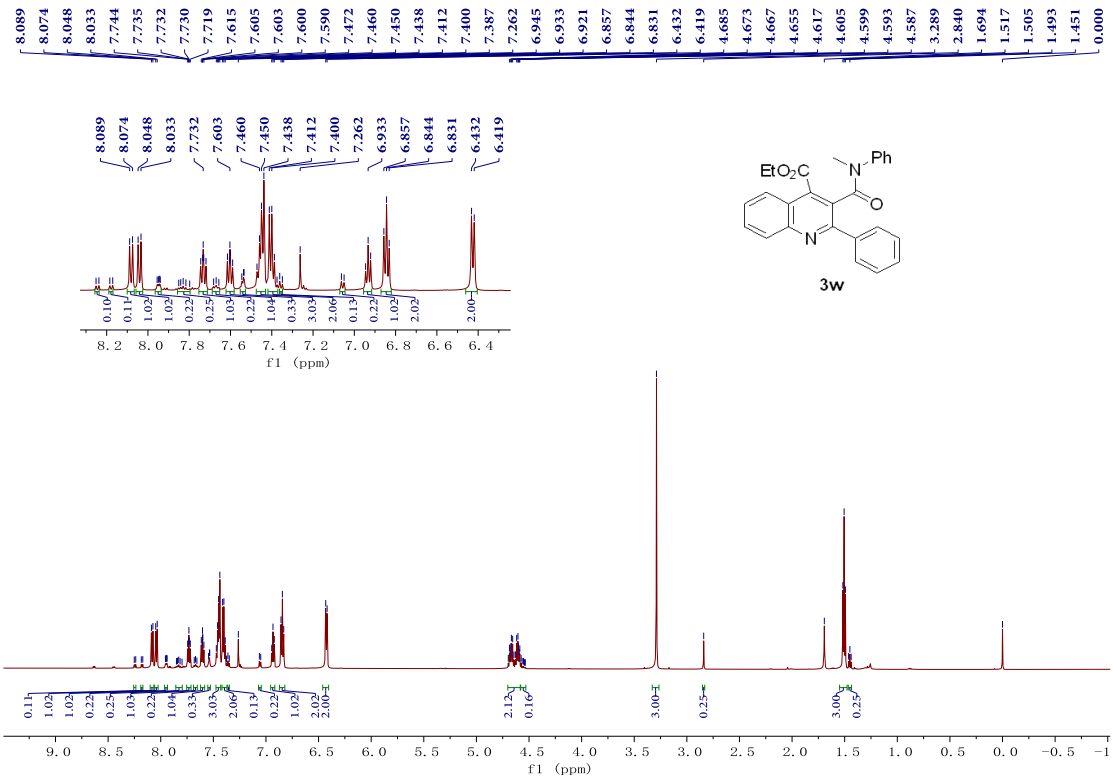
^{1}H NMR (500 MHz, $CDCl_3$)



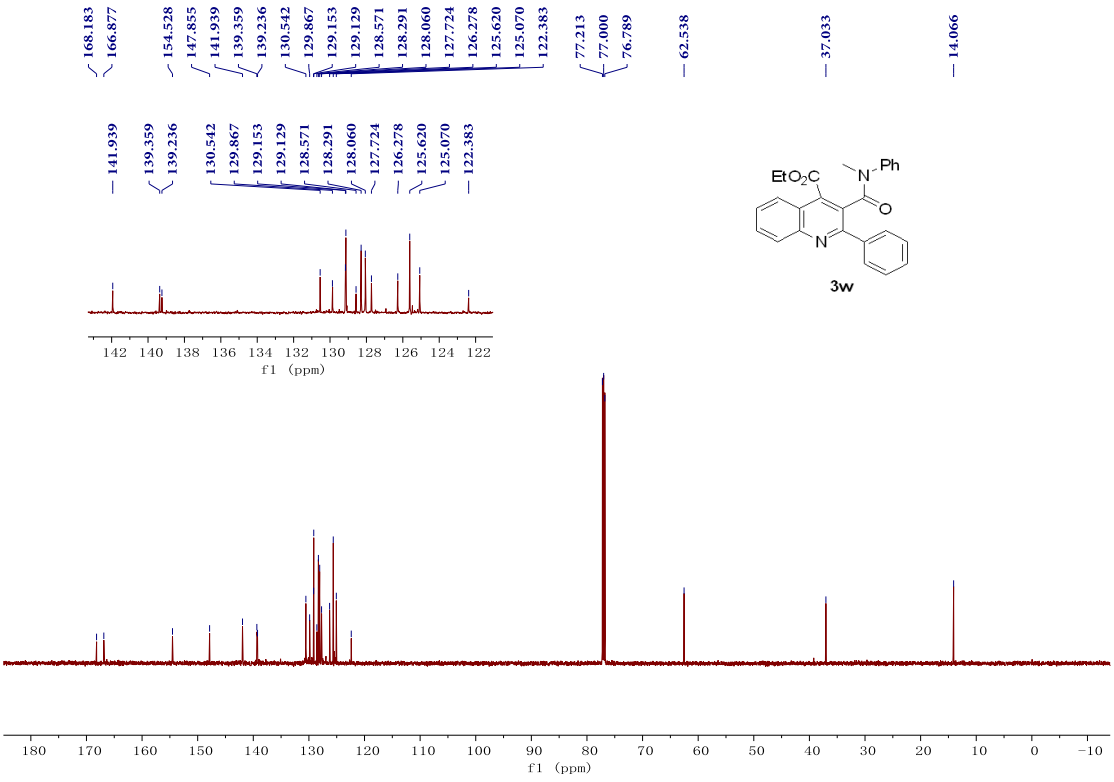
^{13}C NMR (125 MHz, $CDCl_3$)



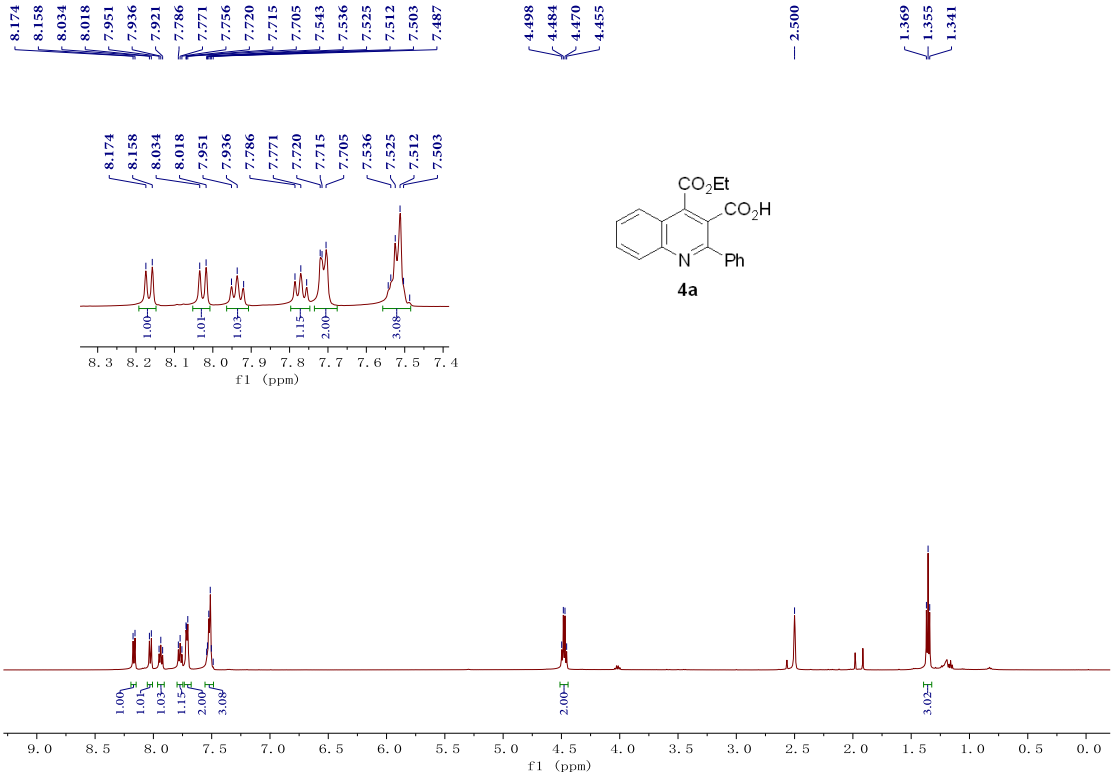
^{1}H NMR (600 MHz, $CDCl_3$)



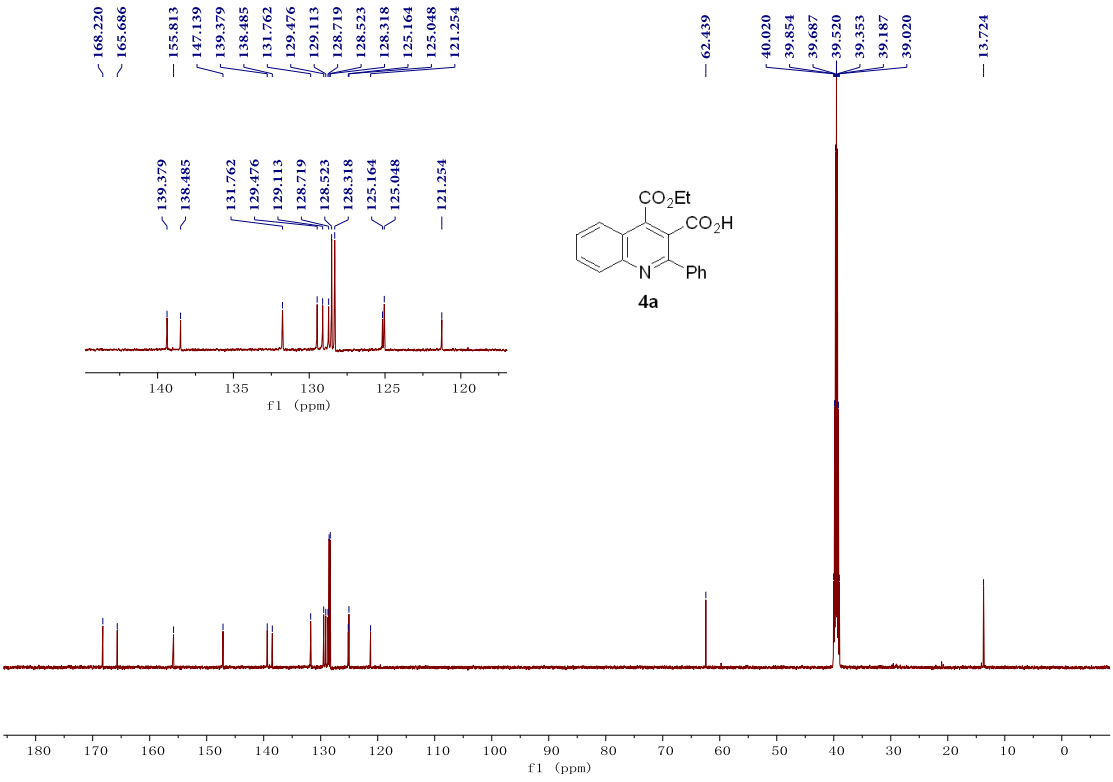
^{13}C NMR (150 MHz, $CDCl_3$)



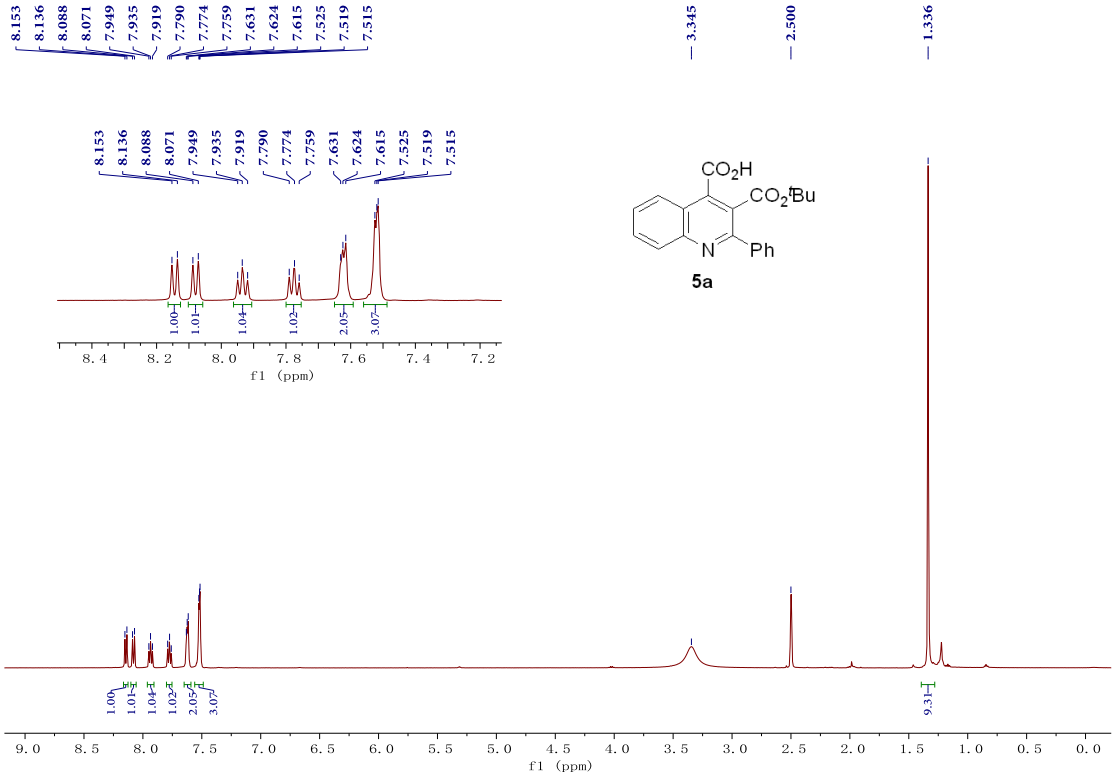
^{1}H NMR (500 MHz, d^{6}-DMSO)



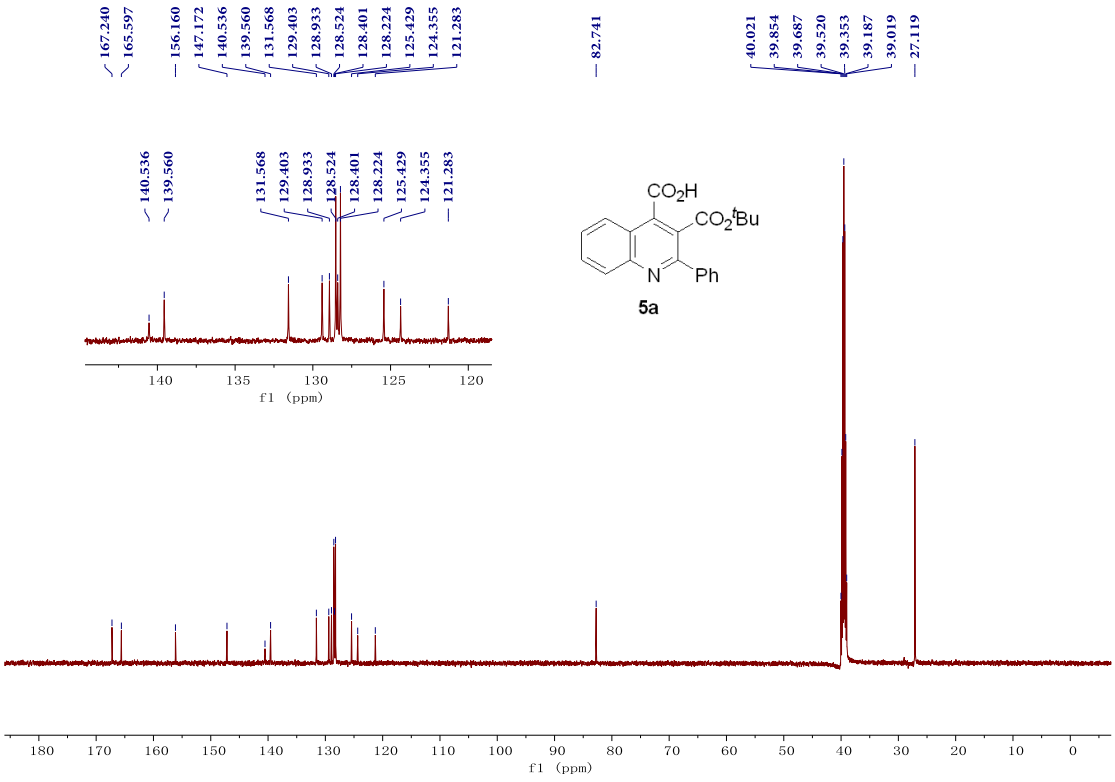
^{13}C NMR (125 MHz, d^{6}-DMSO)



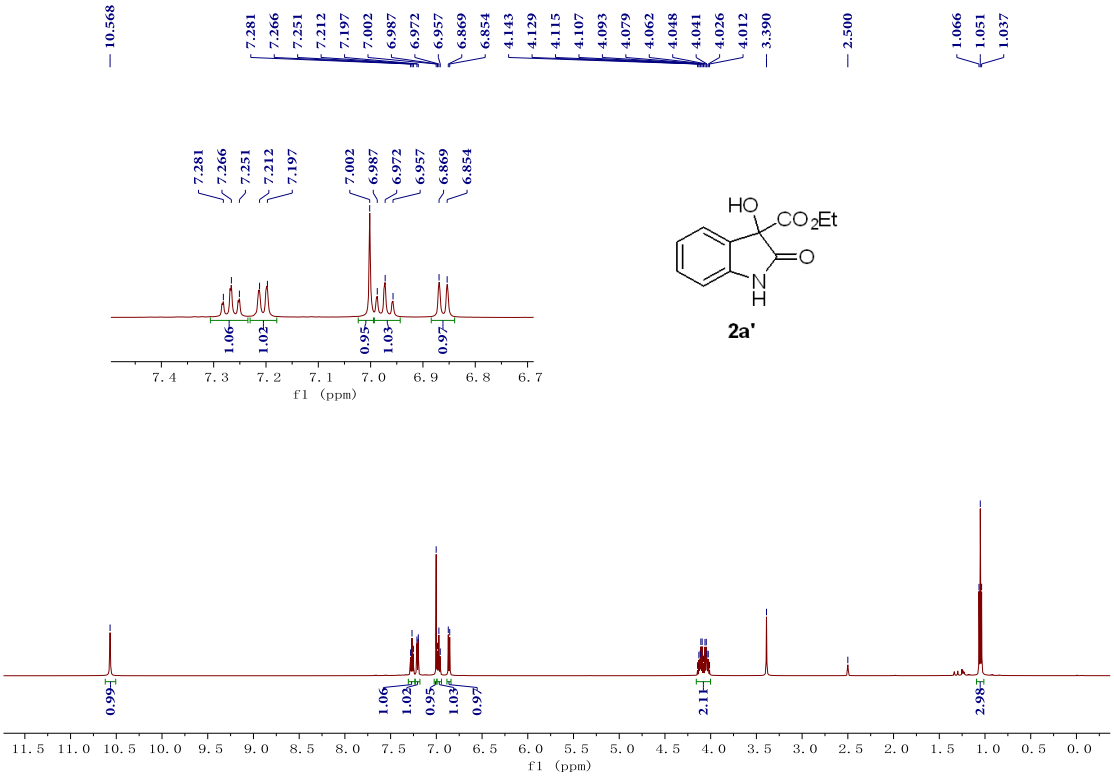
^{1}H NMR (500 MHz, d^{6}-DMSO)



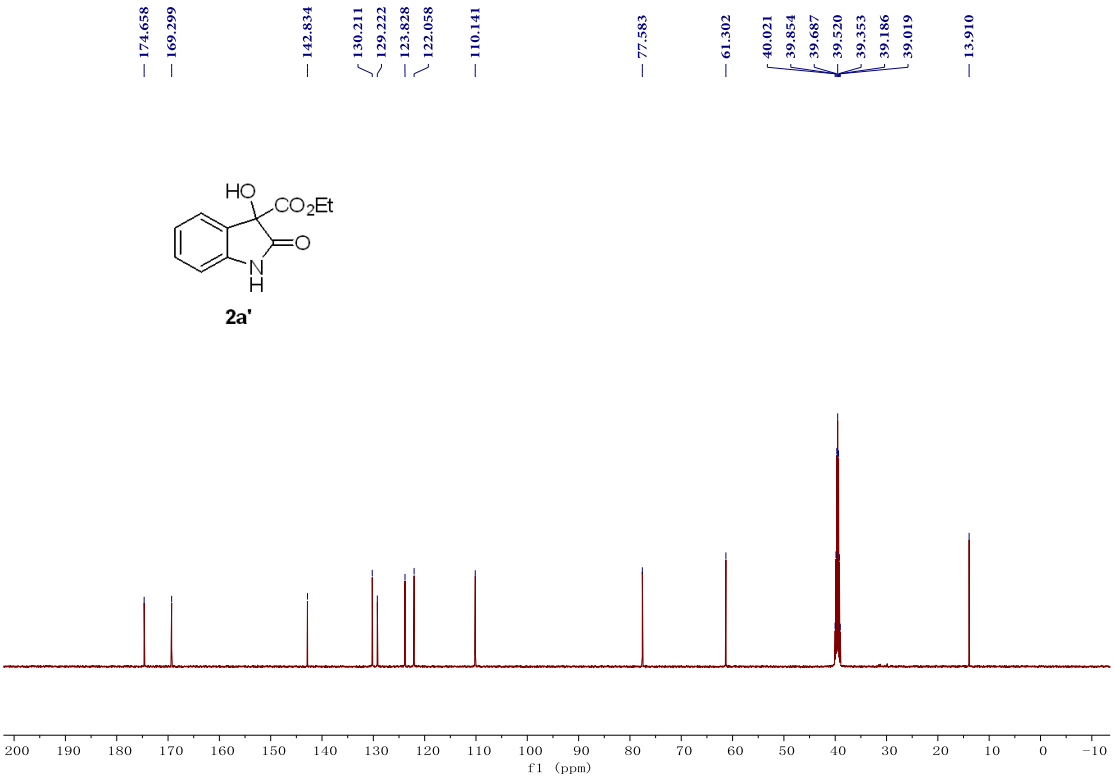
^{13}C NMR (125 MHz, d^{6}-DMSO)



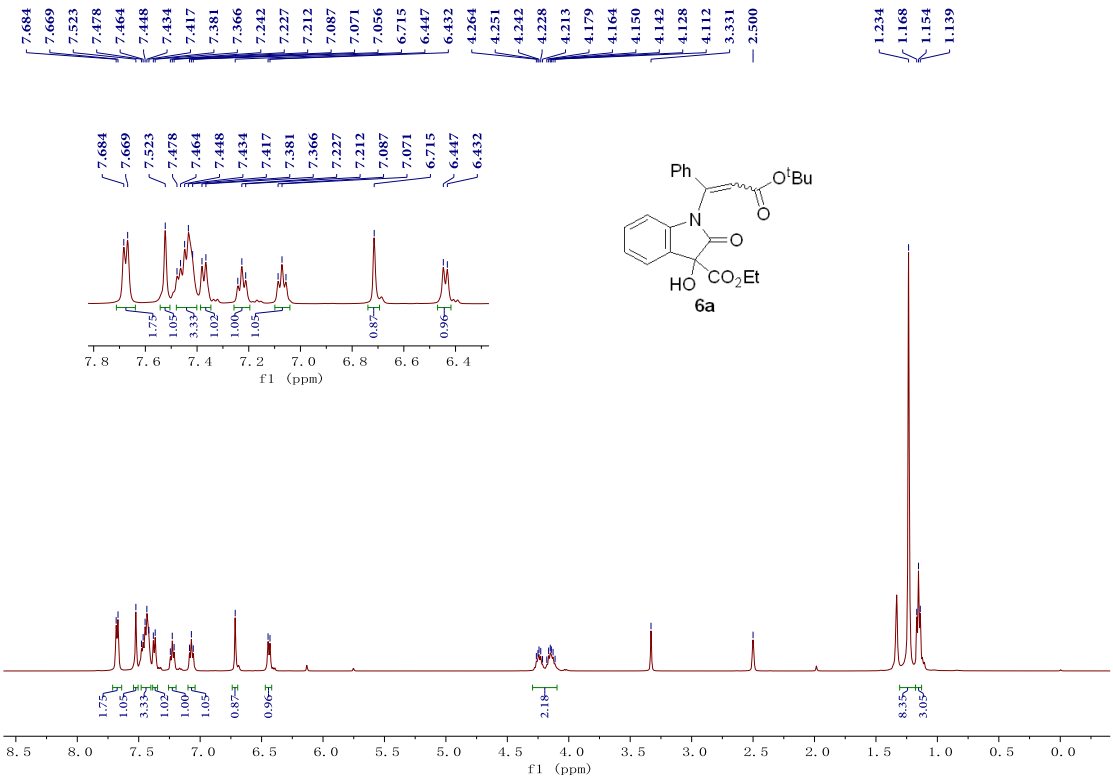
^{1}H NMR (500 MHz, d^{6}-DMSO)



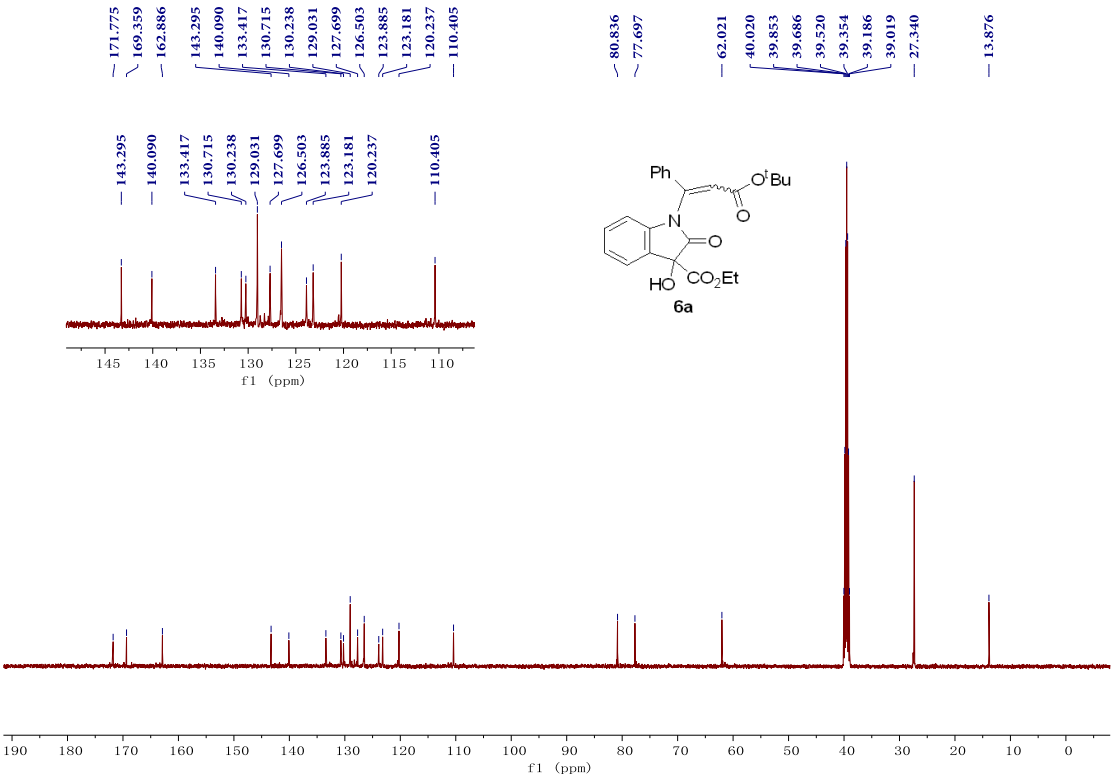
^{13}C NMR (125 MHz, d^{6}-DMSO)



^{1}H NMR (500 MHz, d^{6}-DMSO)



^{13}C NMR (125 MHz, d^{6}-DMSO)

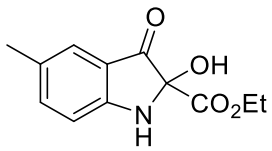


10. X-ray crystallography of compounds 2p and 3a.

ethyl 2-hydroxy-5-methyl-3-oxoindoline-2-carboxylate (**2p**, mo_d8v23248_0m.)

(Ortep ellipsoids are depicted at the 50% level)

Sample preparation for crystal growth: Compound **2p** (50 mg) was dissolved in the mixed solvent of dichloromethane/petroleum ether = 3 ml/6 ml in a 50 mL roundbottom flask. The yellow single crystal of **2p** was obtained by slowly evaporating mixed solvent at room temperature under air.

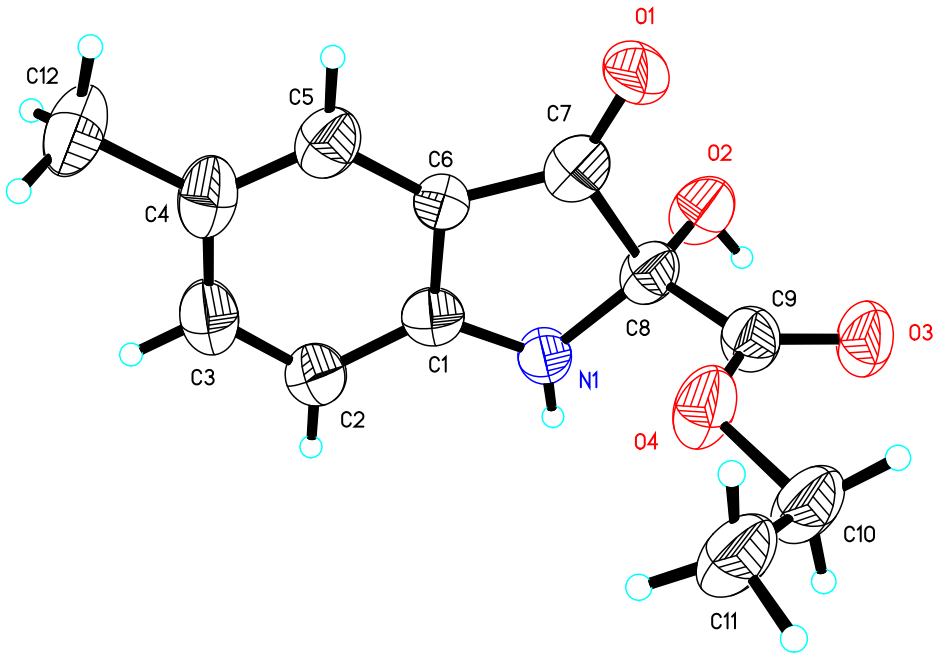


2p

Table S1. Crystal data and structure refinement for 2p.

Identification code	**2p**
Empirical formula	$C_{12}H_{13}NO_4$
Formula weight	235.23
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P b c a
Unit cell dimensions	a = 6.8757(8) Å α= 90°. b = 15.6611(17) Å β= 90°. c = 22.392(3) Å γ = 90°.
Volume	2411.2(5) $Å^3$
Z	8
Density (calculated)	1.296 Mg/m^3

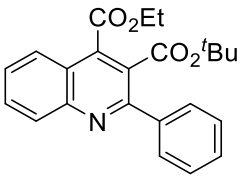
Absorption coefficient	0.098 mm^{-1}
F(000)	992
Crystal size	0.160 x 0.140 x 0.100 mm^3
Theta range for data collection	2.756 to 24.998°.
Index ranges	-8<=h<=8, -18<=k<=18, -26<=l<=26
Reflections collected	14179
Independent reflections	2120 [R(int) = 0.0752]
Completeness to theta = 25.242°	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6037
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2120 / 40 / 176
Goodness-of-fit on F^2	1.128
Final R indices [I>2sigma(I)]	R1 = 0.1405, wR2 = 0.3813
R indices (all data)	R1 = 0.2042, wR2 = 0.4327
Extinction coefficient	n/a
Largest diff. peak and hole	0.578 and -0.275 $e.Å^{-3}$



3-(tert-butyl) 4-ethyl 2-phenylquinoline-3,4-dicarboxylate (**3a**, dmj8v23138_0m.)

(Ortep ellipsoids are depicted at the 50% level)

Sample preparation for crystal growth: Compound **3a** (50 mg) was dissolved in the mixed solvent of dichloromethane/petroleum ether = 3 ml/6 ml in a 50 mL roundbottom flask. The white single crystal of **3a** was obtained by slowly evaporating mixed solvent at room temperature under air.



3a

Table S2. Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{23}H_{23}NO_4$
Formula weight	377.42

Temperature	213(2) K
Wavelength	1.34139 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 8.5232(3) Å α= 74.518(2)°. b = 10.7268(4) Å β= 79.312(2)°. c = 12.1464(4) Å γ = 70.566(2)°.
Volume	1003.51(6) $Å^3$
Z	2
Density (calculated)	1.249 Mg/m^3
Absorption coefficient	0.441 mm^{-1}
F(000)	400
Crystal size	0.140 x 0.120 x 0.090 mm^3
Theta range for data collection	3.303 to 55.062°.
Index ranges	-10<=h<=10, -13<=k<=12, -14<=l<=14
Reflections collected	10176
Independent reflections	3732 [R(int) = 0.0433]
Completeness to theta = 25.242°	97.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.5684
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3732 / 0 / 258
Goodness-of-fit on F^2	1.142
Final R indices [I>2sigma(I)]	R1 = 0.0752, wR2 = 0.1820

R indices (all data)	R1 = 0.0804, wR2 = 0.1919
Extinction coefficient	0.282(19)
Largest diff. peak and hole	0.475 and -0.450 e.Å^{-3}