Supplementary Information

Metal-Free Photoinduced Alkylative [3+2] Annulation of Terminal Alkynes with N-Alkyl Isoquinolin-2-iums by Catalytic Isoquinoline-Based Electron Donor-Acceptor Complex

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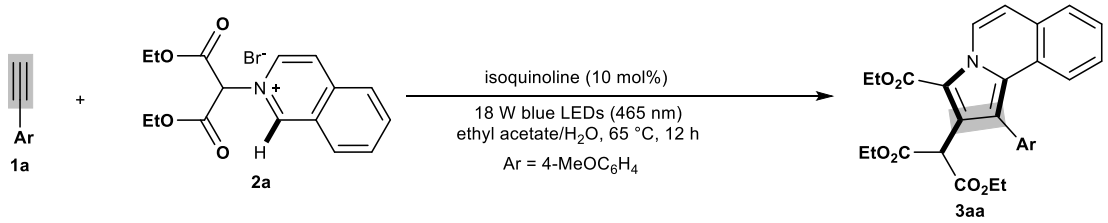
(A) General Information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 500 (500 MHz, 125 MHz, and 471 MHz) and advance spectrometer at room temperature in $CDCl_3$ (solvent signals, δ 7.26 and 77.0 ppm) using TMS as internal standard. High-resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. All the substrates **1** were prepared according to the known procedures. Unless otherwise noted, all reactions were carried out using standard Schlenk techniques, and the starting materials and solvents were commercially available and were used without further purification. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA).

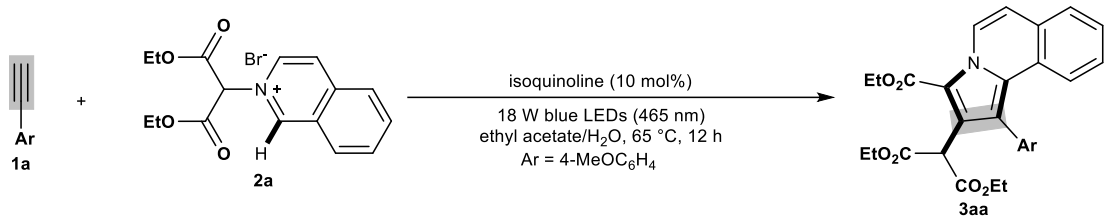
(a) General Procedure for the Photocatalyzed Alkylative [3+2] Annulation between Alkynes (1) and N-Alkyl Isoquinolin-2-iums (2):

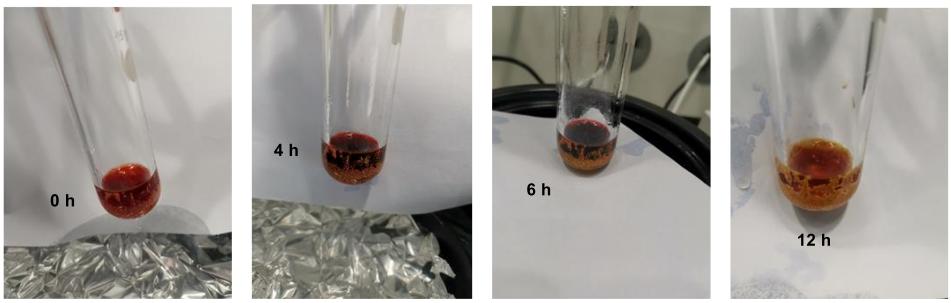


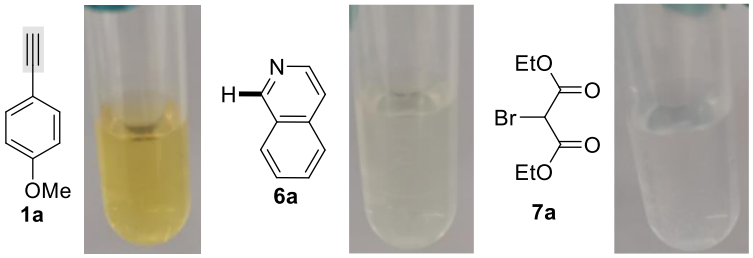
To a Schlenk tube were added 1-ethynyl-4-methoxybenzene **1a** (0.2 mmol), 2-(1,3-diethoxy-1,3-dioxopropan-2-yl)isoquinolin-2-ium **2a** (0.4 mmol; 2 equiv), isoquinoline (10 mol%) and ethyl acetate/H_2O (1:1; 2 mL). Then the mixture was charged with argon three times, and was stirred at 65 °C under 18 W blue LEDs light for 12 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was concentrated in vacuum, diluted in diethyl ether, and washed with saturated brine. The combined organic extracts were

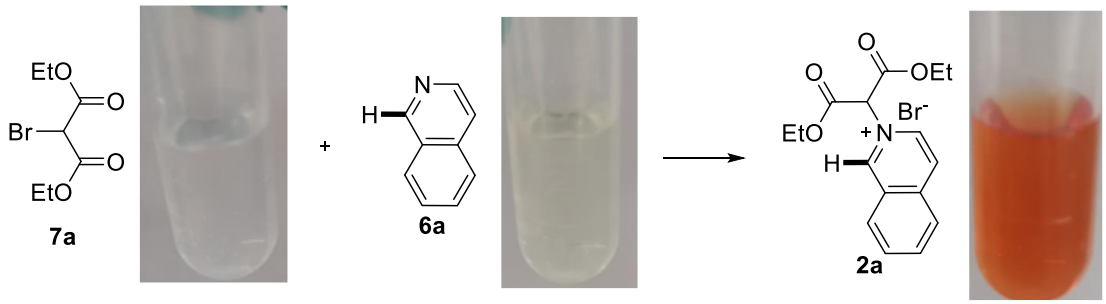
dried over Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10 : 1; R_f = 0.1) to provide **3aa** in 80% isolated yield (80.5 mg).

(b) The Color Changes in the Photocatalyzed Alkylative [3+2] Annulation between Alkynes (1) and N-Alkyl Isoquinolin-2-iums:









1a, **2a**, **6a**, **7a**, 0.2mmol in MeCN

(c) Stern-Volmer Fluorescence Quenching Experiments:

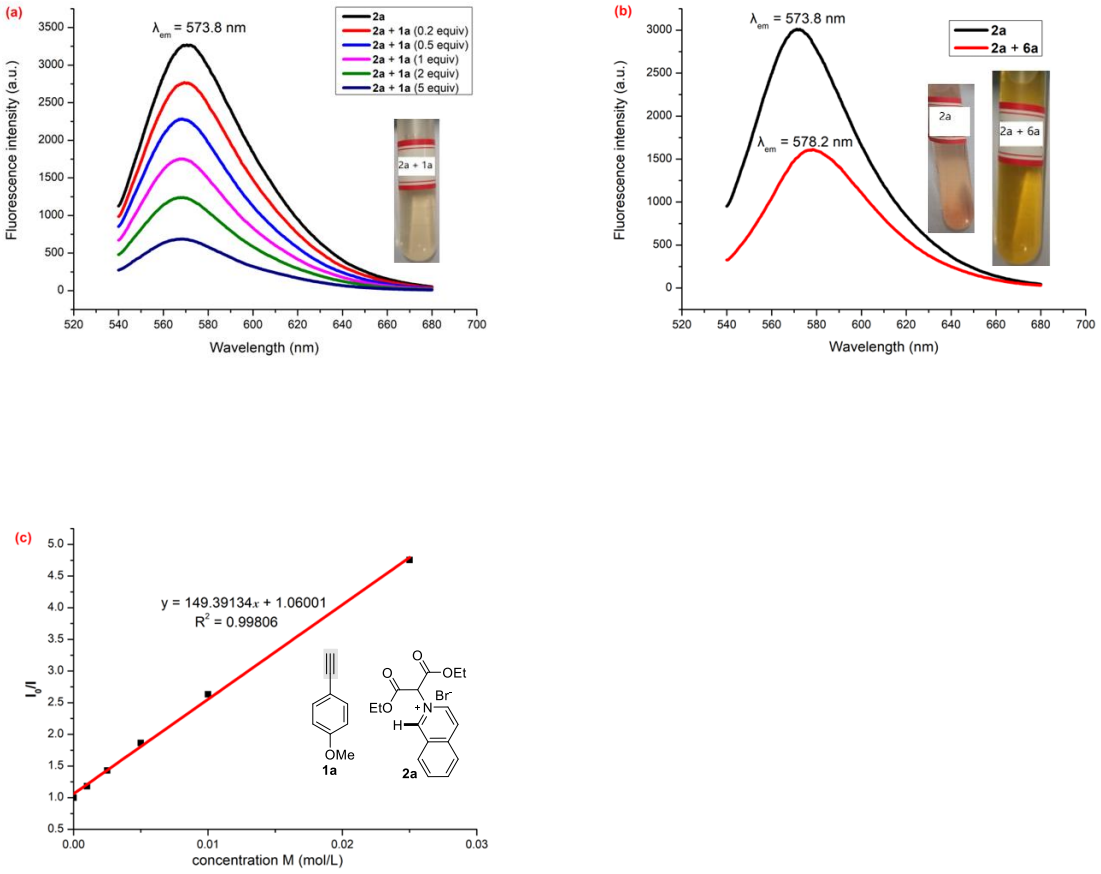


Figure S1. Stern-Volmer Fluorescence Quenching Experiments. (a) The fluorescence quenching experiments of 4-ethynylanisole **1a** with 2-(1,3-diethoxy-1,3-dioxopropan-2-yl)isoquinolin-2-ium bromide **2a**. Quenching of the isoquinolinium bromide **2a** (5×10-3 M in MeCN) in the presence of increasing amount of **1a** (Excitation wavelength: 520 nm, Ex bandwidth: 5.0 nm, Em bandwidth: 5.0 nm). (b) The fluorescence quenching experiments of 2-(1,3-diethoxy-1,3-dioxopropan-2-yl)isoquinolin-2-ium bromide **2a** with isoquinoline **6a**. Isoquinolinium bromide **2a** (5 × 10-3 M in MeCN) was quenched with the addition of **6a** (Excitation wavelength: 520 nm, Ex bandwidth: 5.0 nm, Em bandwidth: 5.0 nm). (c) Stern-Volmer plot for a mixture of isoquinolinium bromide **2a** with alkyne **1a**.

(d) UV-vis Absorption Experiments:

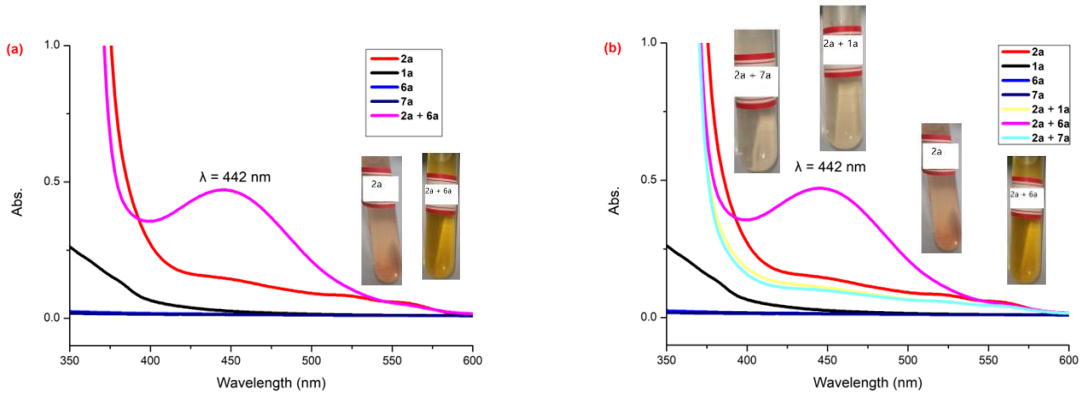


Figure S2. UV-vis Absorption Experiments. (a) Absorption spectra for **1a, 2a, 6a, 7a** and **2a + 6a**. (b) Absorption spectra for **1a, 2a, 6a, 7a, 2a + 1a**, **2a + 6a**, and **2a + 7a** (based on 0.1 M of **2a** in MeCN).

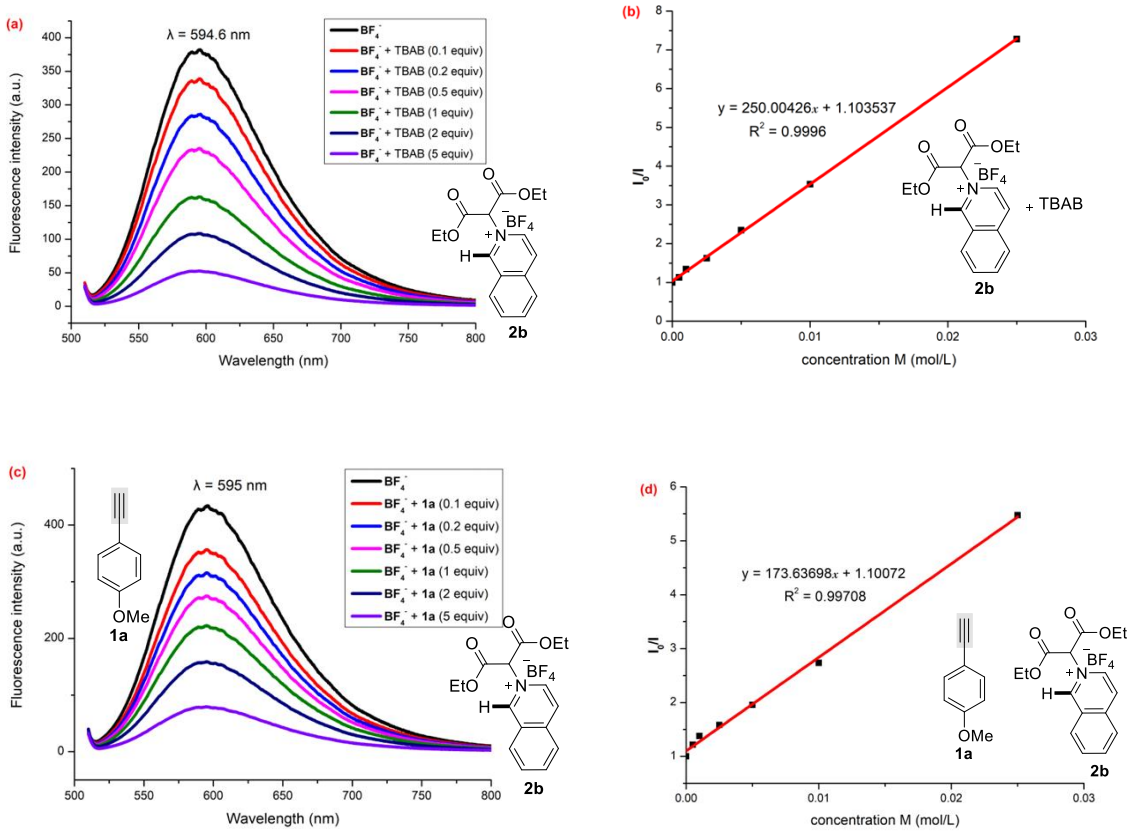


Figure S3. Stern-Volmer Fluorescence Quenching Experiments. (a) The fluorescence quenching experiments of isoquinolin-2-ium tetrafluoroborate **2b** (5×10^{-3} M in MeCN) with TBAB were quenched with stirring for different times (Excitation wavelength: 520 nm, Ex bandwidth: 5.0 nm, Em bandwidth: 5.0 nm). (b) Stern-Volmer plot for a mixture of isoquinolinium tetrafluoroborate **2b** with TBAB. (c) The fluorescence quenching experiments of isoquinolin-2-ium tetrafluoroborate **2b** with alkyne **1a**. Quenching of the **2b** (5×10^{-3} M in MeCN) in the presence of increasing amount of **1a** (Excitation wavelength: 520 nm, Ex bandwidth: 5.0 nm, Em bandwidth: 5.0 nm). (d) Stern-Volmer plot for a mixture of isoquinolinium tetrafluoroborate **2b** with alkyne **1a**.

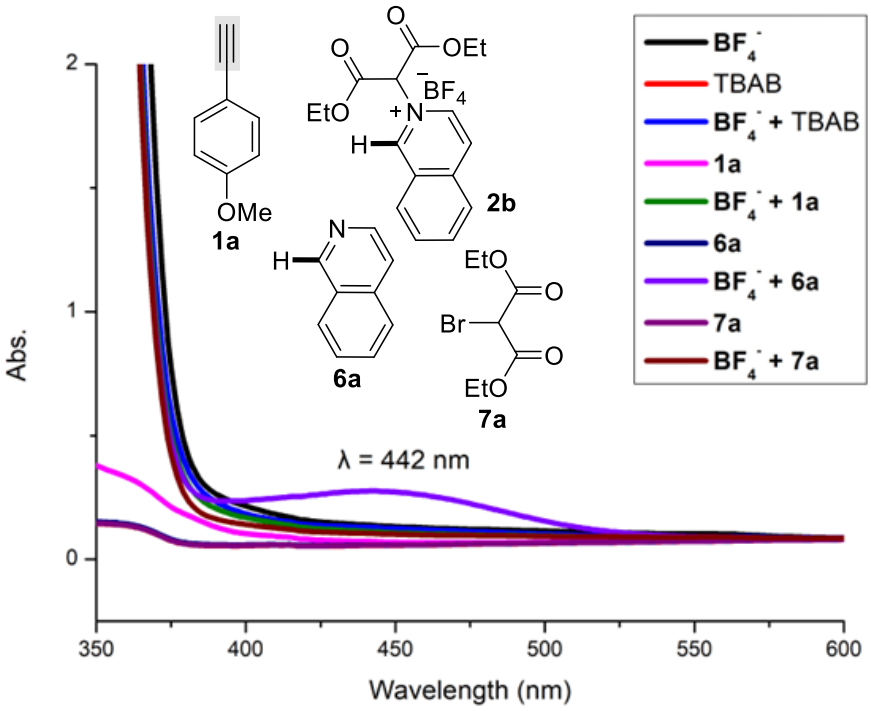


Figure S4. UV-vis Absorption Experiments. Absorption spectra for isoquinolin-2-ium tetrafluoroborate **2b** with different reaction components TBAB, **1a, 6a and 7a** (based on 0.1 M of **2b** in MeCN).

(e) Intermittent Illumination Experiment:

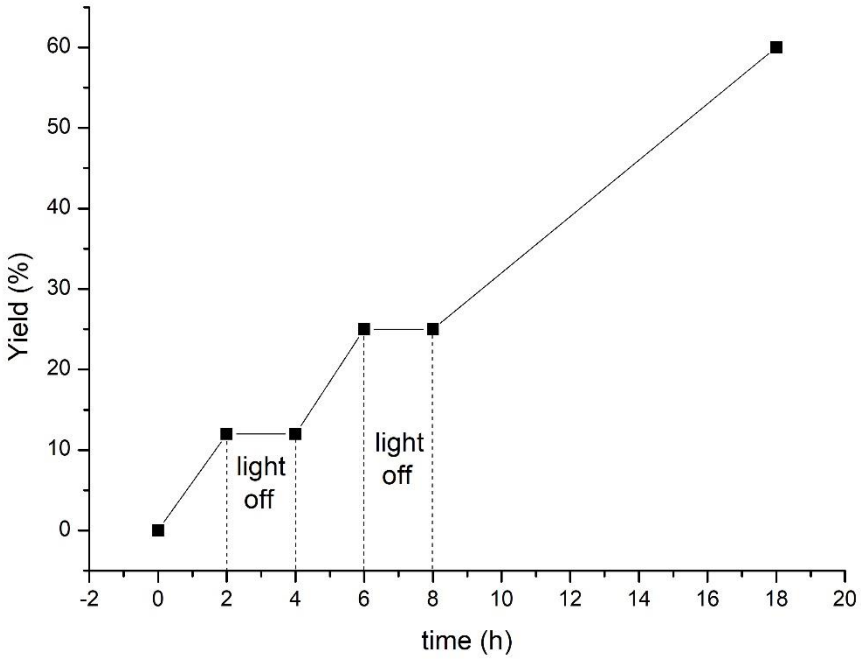
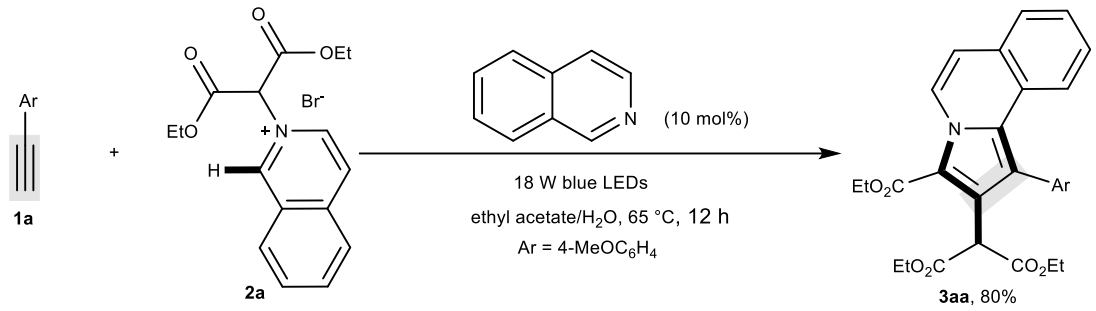
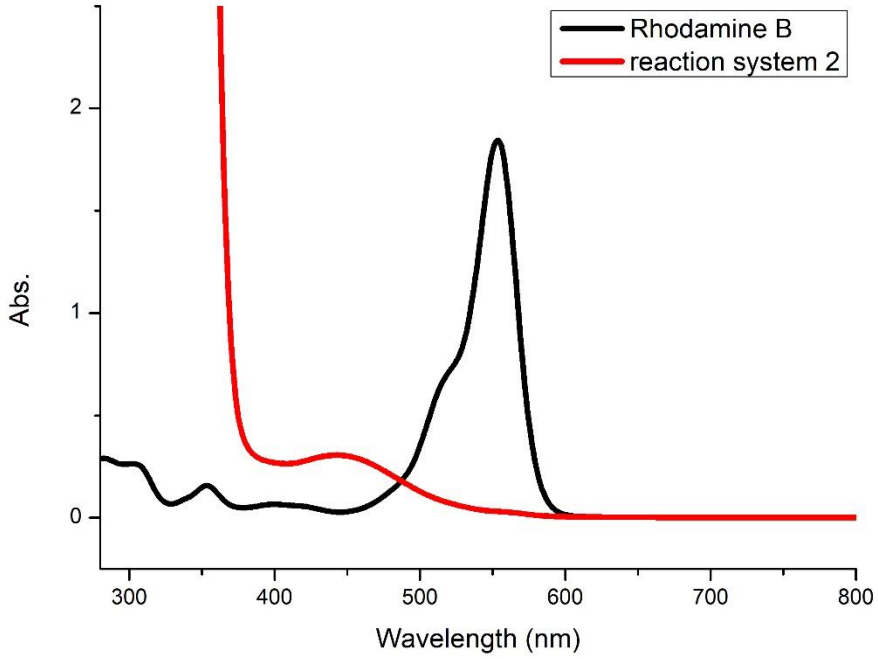


Figure S5. Intermittent Illumination Experiment. Profile of **3aa** with the light on or off over time NMR yield using diphenylacetonitrile as an internal standard.

(f) Quantum Yield Measurements:[1]

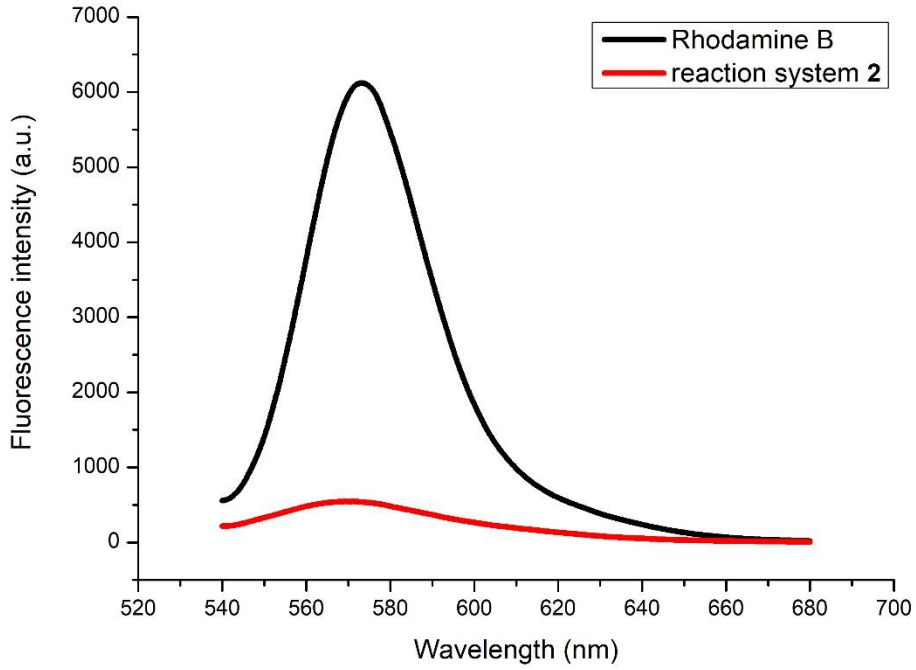
The [3+2] Annulation Reaction





A_s UV-Vis absorbtion of Rhodamine B at 350nm: 0.1494 (black line)

A_x UV-Vis absorbtion of reaction system 1 at 450nm: 0.302 (red line)



F_s Integrated area of fluorescence of Rhodamine B: 244045 (black line)

F_x Integrated area of fluorescence of reaction system: 17398 (red line)

n_s Rhodamine B is Dissolved in water, refractivity of water is 1.3

n_x Solvent of reaction system is MeCN, refractivity of MeCN is 1.344

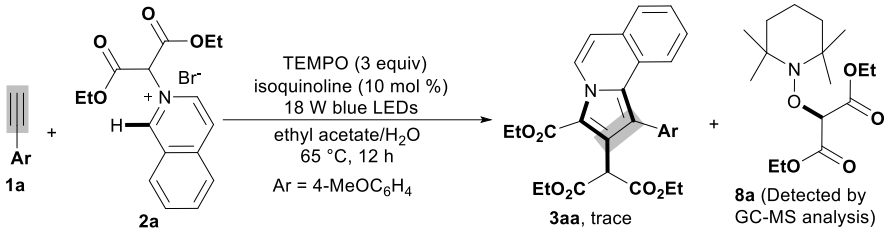
Φ_s quantum yield of Rhodamine B: 0.9

$$\Phi_x = \Phi_s(n_x/n_s)^2(A_s/A_x)(F_x/F_s)$$

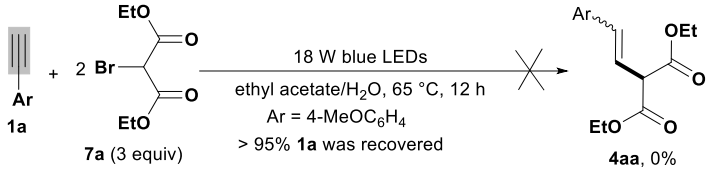
$$= 0.9\times(1.3/1.344)^2\times(0.1494/0.302)\times(17398/244045)$$

$$= 0.071$$

(g) Control Experiments:

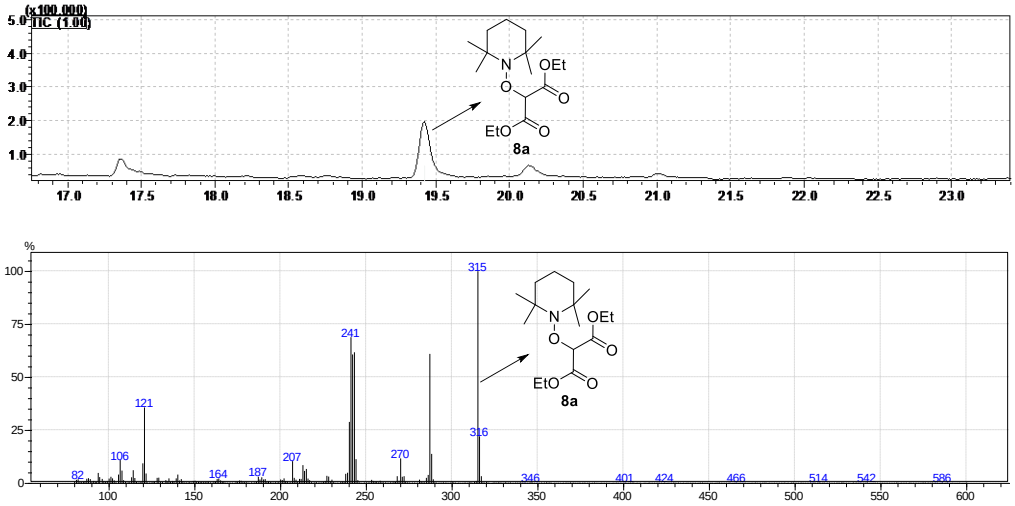


(1)



(2)

GC-MS dates of 8a:



[MS Spectrum]

# of Peaks 520

Raw Spectrum 19.425 (scan : 3086)

Background No Background Spectrum

Base Peak m/z 315.10 (Inten : 25,614)

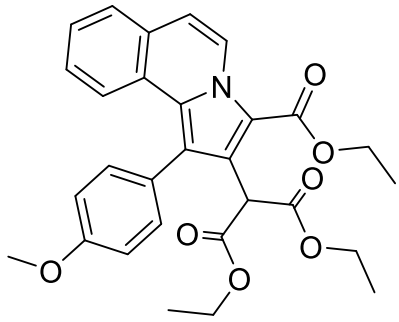
Event# 1

m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
100.05	508	1.98	107.40	1414	5.52	120.60	8782	34.29
101.00	714	2.79	108.35	393	1.53	121.55	1134	4.43
102.05	570	2.23	113.05	674	2.63	238.00	1156	4.51
103.00	284	1.11	114.05	1462	5.71	239.00	1121	4.38
105.55	910	3.55	115.10	575	2.24	240.00	7116	27.78
106.50	2841	11.09	119.65	2228	8.70	241.05	16923	66.07

242.05	14907	58.20	271.05	679	2.65	313.00	175	0.68
243.05	15375	60.03	272.00	780	3.05	314.10	215	0.84
244.05	2875	11.22	281.00	367	1.43	**315.10**	**25614**	**100.00**
245.10	350	1.37	285.00	618	2.41	316.05	5797	22.63
253.10	332	1.30	286.05	843	3.29	317.05	818	3.19
268.05	853	3.33	287.05	15861	61.92	318.00	98	0.38
269.00	273	1.07	288.05	3422	13.36			
270.05	3020	11.79	289.05	479	1.87			

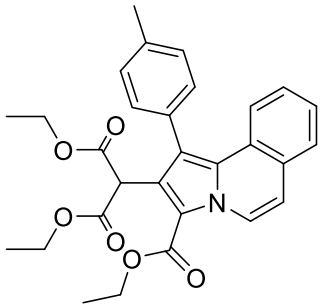
(B) Analytical data

diethyl 2-(3-(ethoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3aa):



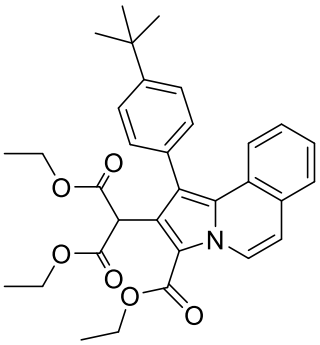
80.5 mg, 80% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.34 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.41 - 7.33 (m, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 3H), 5.19 (s, 1H), 4.41 – 4.35 (m, 2H), 4.08 – 4.02 (m, 4H), 3.91 (s, 3H), 1.38 (t, *J* = 6.8 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.0, 161.5, 159.5, 132.9, 130.5, 128.6, 127.1, 126.9, 126.8, 126.6, 126.2, 125.5, 124.7, 123.8, 120.4, 114.3, 113.9, 113.1, 77.4, 77.0, 76.7, 61.4, 60.3, 55.3, 50.6, 14.4, 14.0; HRMS *m/z* (ESI) calcd for $C_{29}H_{30}NO_7$ ($[M+H]^+$) 504.2017, found 504.2021.

diethyl 2-(3-(ethoxycarbonyl)-1-(p-tolyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ba):



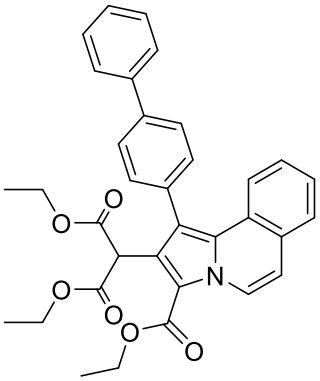
75.0 mg, 77% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.34 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.30 (s, 4H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 5.14 (s, 1H), 4.40 - 4.35 (m, 2H), 4.07 - 4.02 (m, 4H), 2.47 (s, 3H), 1.38 (t, *J* = 6.8 Hz, 3H), 1.19 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 161.5, 137.8, 131.6, 131.5, 130.3, 129.6, 128.6, 127.1, 126.9, 126.7, 126.0, 125.5, 124.8, 123.8, 120.8, 113.9, 113.0, 77.4, 77.1, 76.7, 61.4, 60.3, 50.6, 21.4, 14.4, 14.0; HRMS *m/z* (ESI) calcd for $C_{29}H_{30}NO_6$ ($[M+H]^+$) 488.2068, found 488.2071.

diethyl 2-(1-(4-(tert-butyl)phenyl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ca):



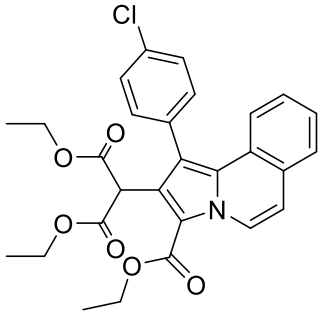
79.4 mg, 75% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.34 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 4H), 7.26 (s, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 5.16 (s, 1H), 4.40 - 4.35 (m, 2H), 4.07 - 4.35 (m, 4H), 1.41 (s, 9H), 1.38 (t, *J* = 6.8 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.0, 161.5, 151.0, 131.5, 131.3, 130.4, 128.6, 127.1, 126.9, 126.7, 126.0, 125.7, 125.5, 124.7, 123.9, 120.8, 113.9, 113.1, 77.4, 77.0, 76.7, 61.3, 60.3, 50.6, 34.7, 31.4, 14.4, 14.0; HRMS *m/z* (ESI) calcd for $C_{32}H_{36}NO_6$ ($[M+H]^+$) 530.2537, found 530.2544.

diethyl 2-(1-([1,1'-biphenyl]-4-yl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3da):



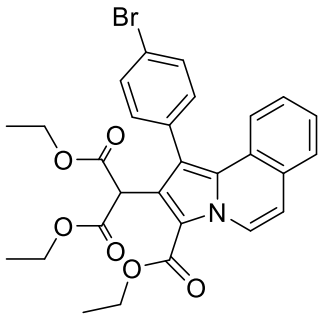
85.7 mg, 78% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 9.36 (d, *J* = 7.5 Hz, 1H), 7.74 (t, *J* = 8.5 Hz, 4H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.54 – 7.48 (m, 4H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 5.23 (s, 1H), 4.42 – 4.37 (m, 2H), 4.07 – 4.02 (m, 4H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 168.0, 161.5, 140.7, 140.6, 133.7, 132.2, 130.3, 128.9, 128.7, 127.6, 127.4, 127.2, 127.1, 126.8, 125.9, 125.4, 124.8, 123.9, 120.3, 114.1, 113.2, 77.3, 77.0, 76.8, 61.5, 60.4, 50.6, 14.4, 14.0; HRMS *m/z* (ESI) calcd for $C_{34}H_{32}NO_6$ ($[M+H]^+$) 550.2224, found 550.2235.

diethyl 2-(1-(4-chlorophenyl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ea):



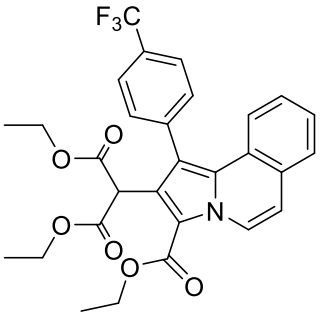
72.0 mg, 71% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.33 (d, *J* = 6.4 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.41 (d, *J* = 6.8 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.21 - 7.17 (m, 2H), 7.03 (d, *J* = 7.2 Hz, 1H), 5.24 (s, 1H), 4.42 - 4.37 (m, *J* = 6.2, 2H), 4.06 - 4.01 (m, 4H), 1.39 (t, *J* = 6.8 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 161.4, 134.3, 133.3, 133.3, 130.3, 129.0, 128.7, 127.3, 127.2, 126.9, 125.7, 125.2, 124.7, 123.6, 119.2, 114.3, 113.3, 77.4, 77.1, 76.7, 61.5, 60.5, 50.6, 14.3, 14.0; HRMS *m/z* (ESI) calcd for $C_{28}H_{27}ClNO_6$ ($[M+H]^+$) 508.1521, found 508.1522.

diethyl 2-(1-(4-bromophenyl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3fa):



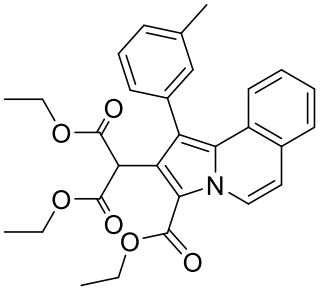
80.5 mg, 73% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.33 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 3H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 3H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 5.23 (s, 1H), 4.42 - 4.36 (m, 2H), 4.06 - 4.01 (m, 4H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 161.4, 133.8, 133.6, 132.0, 130.2, 128.7, 127.3, 127.2, 126.9, 125.7, 125.2, 124.7, 123.6, 122.5, 119.2, 114.3, 113.3, 77.4, 77.1, 76.7, 61.5, 60.5, 50.6, 14.3, 14.0; HRMS *m/z* (ESI) calcd for $C_{28}H_{27}BrNO_6$ ($[M+H]^+$) 552.1016, found 552.1018.

diethyl 2-(3-(ethoxycarbonyl)-1-(4-(trifluoromethyl)phenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ga):



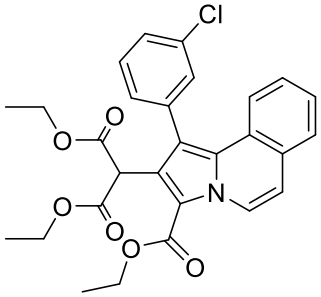
68.2 mg, 63% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.35 (d, *J* = 6.8 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 3H), 7.44 - 7.35 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 6.8 Hz, 1H), 5.25 (s, 1H), 4.43 - 4.38 (m, 2H), 4.04 – 3.98 (m, 4H), 1.40 (t, *J* = 6.0 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -62.5; ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.8, 161.4, 139.0, 132.5, 130.2, 130.1, 128.8, 127.3, 127.3, 127.0, 125.7, 125.6, 125.6, 125.6, 125.0, 124.7, 123.5, 122.9, 119.0, 114.5, 113.4, 77.4, 77.0, 76.7, 61.6, 60.6, 50.6, 14.3, 14.0, 13.9; HRMS *m/z* (ESI) calcd for $C_{29}H_{27}F_3NO_6$ ($[M+H]^+$) 542.1785, found 542.1793.

diethyl 2-(3-(ethoxycarbonyl)-1-(m-tolyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ha):



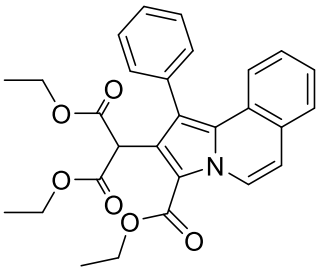
61.4 mg, 63% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.34 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.37 (q, *J* = 7.6, 6.9 Hz, 3H), 7.26 (t, *J* = 10.4 Hz, 3H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 5.12 (s, 1H), 4.40 - 4.36 (m, 2H), 4.09 - 4.02 (m, 4H), 2.40 (s, 3H), 1.38 (t, *J* = 6.4 Hz, 3H), 1.20 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 161.5, 138.4, 134.6, 132.2, 130.1, 128.9, 128.8, 128.7, 128.6, 127.1, 126.9, 126.8, 125.9, 125.4, 124.8, 123.9, 121.0, 114.0, 113.1, 77.4, 77.1, 76.8, 61.4, 60.3, 50.6, 21.5, 14.4, 14.1; HRMS *m/z* (ESI) calcd for $C_{29}H_{30}NO_6$ ($[M+H]^+$) 488.2068, found 488.2062.

diethyl 2-(1-(3-chlorophenyl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ia):



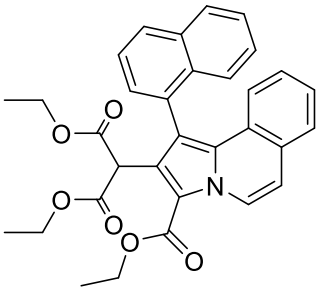
57.8 mg, 57% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.34 (d, *J* = 6.4 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 10.4 Hz, 3H), 7.42 – 7.37 (m, 3H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 5.23 (s, 1H), 4.42 - 4.38 (m, 2H), 4.08 – 4.03 (m, 4H), 1.39 (t, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.8, 161.43, 136.7, 134.5, 131.8, 130.2, 130.2, 130.1, 128.7, 128.4, 127.3, 127.2, 127.1, 126.9, 125.7, 125.1, 124.7, 123.7, 119.1, 114.3, 113.3, 77.4, 77.0, 76.7, 61.6, 60.5, 50.6, 14.3, 14.0; LRMS (EI, 70 eV) *m/z* (%): 355 (M^+, 12), 263 (28), 226 (89), 189 (100); HRMS *m/z* (ESI) calcd for $C_{28}H_{27}ClNO_6$ ($[M+H]^+$) 508.1521, found 508.1527.

diethyl 2-(3-(ethoxycarbonyl)-1-phenylpyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ja):



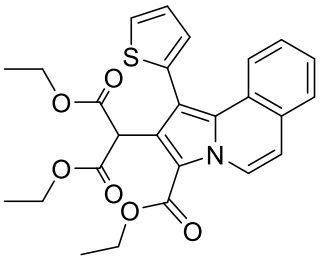
61.5 mg, 65% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (ppm) (d, *J* = 6.8 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 12.4 Hz, 4H), 7.38 - 7.32 (m, 2H), 7.14 (t, *J* = 7.6Hz, 1H), 7.02 (d, *J* = 6.8 Hz, 1H), 5.17 (s, 1H), 4.41 - 4.37 (m, 2H), 4.06 - 4.01 (m, 4H), 1.38 (t, *J* = 6.4 Hz, 3H), 1.19 (d, *J* = 12. Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 161.5, 134.7, 131.8, 130.2, 128.8, 128.7, 128.2, 127.1, 127.0, 126.8, 125.8, 125.4, 124.7, 123.8, 120.8, 114.0, 113.1, 77.4, 77.0, 76.7, 61.4, 60.4, 506, 14.4, 14.0; HRMS *m/z* (ESI) calcd for $C_{28}H_{28}NO_6$ ($[M+H]^+$) 474.1911, found 474.1911.

diethyl 2-(3-(ethoxycarbonyl)-1-(naphthalen-1-yl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ka):



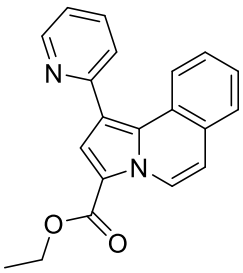
62.8 mg, 60% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 9.37 (d, *J* = 7.5 Hz, 1H), 7.96 (q, *J* = 9.5 Hz, 3H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.58 - 7.52 (m, 3H), 7.42 – 7.30 (m, 2H), 7.04 (t, *J* = 10.0 Hz, 2H), 5.21 (s, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 4.03 (q, *J* = 7.0 Hz, 2H), 4.05 -4.01 (m, 1H), 3.84 - 3.77 (m, 1H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 168.0, 167.9, 161.6, 133.6, 133.0, 132.2, 130.8, 130.4, 129.6, 128.7, 128.4, 128.2, 127.9, 127.2, 127.1, 126.8, 126.4, 126.4, 126.1, 125.4, 124.8, 124.0, 120.6, 114.2, 113.2, 77.3, 77.1, 76.8, 61.4, 60.4, 50.7, 14.4, 14.0, 13.8; HRMS *m/z* (ESI) calcd for $C_{32}H_{30}NO_6$ ($[M+H]^+$) 524.2068, found 524.2077.

diethyl 2-(3-(ethoxycarbonyl)-1-(thiophen-2-yl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3la):



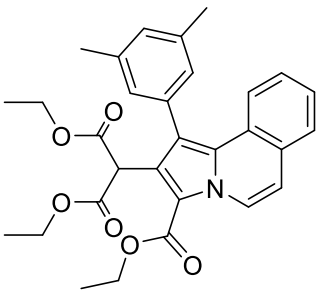
62.3 mg, 65% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.33 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 6.8 Hz, 1H), 7.54 (s, 1H), 7.46 - 7.40 (m, 2H), 7.27 – 7.20 (m, 2H), 7.12 (s, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 5.21 (s, 1H), 4.42 - 4.36 (m, 2H), 4.13 – 4.11 (m, 4H), 1.38 (t, *J* = 6.8 Hz, 3H), 1.23 (t, *J* = 8.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.7, 161.4, 135.0, 131.6, 130.2, 128.8, 128.1, 127.7, 127.6, 127.4, 127.4, 127.2, 126.8, 125.0, 124.6, 123.9, 114.4, 113.4, 111.9, 77.4, 77.0, 76.7, 61.5, 60.5, 50.4, 14.3, 14.0; HRMS *m/z* (ESI) calcd for $C_{26}H_{26}NO_6S$ ($[M+H]^+$) 480.1475, found 480.1474.

ethyl 1-(pyridin-2-yl)pyrrolo[2,1-a]isoquinoline-3-carboxylate (3ma):



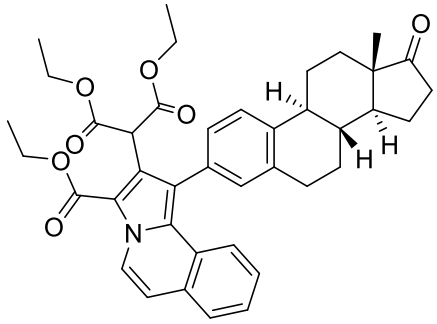
40.5 mg, 64% yield; Yellow oil; R_f = 0.2 (PE/EA = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.33 (d, *J* = 7.2 Hz, 1H), 8.77 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 7.2 Hz, 1H), 7.67 – 7.57 (m, 3H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 6.8 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.4, 155.9, 149.4, 136.9, 131.2, 128.9, 127.6, 127.1, 127.0, 125.3, 124.7, 124.7, 124.3, 123.0, 122.0, 119.2, 115.9, 113.5, 77.4, 77.1, 76.8, 60.2, 14.5; HRMS *m/z* (ESI) calcd for $C_{20}H_{17}N_2O_2$ ($[M+H]^+$) 317.1285, found 317.1288.

diethyl 2-(1-(3,5-dimethylphenyl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3na):



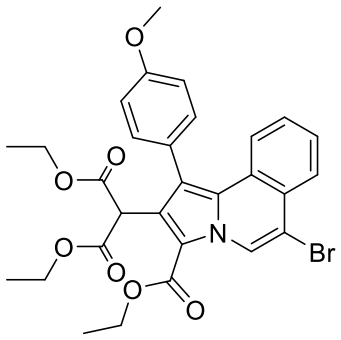
73.2 mg, 73% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.34 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 7.01 (d, *J* = 11.6 Hz, 3H), 5.06 (s, 1H), 4.40 - 4.35 (m, 2H), 4.11 - 4.03 (m, 4H), 2.36 (s, 6H), 1.37 (t, *J* = 6.8 Hz, 3H), 1.20 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 161.6, 138.3, 134.5, 130.0, 129.7, 129.2, 128.6, 127.1, 126.9, 126.7, 125.9, 125.5, 124.8, 124.0, 121.2, 113.9, 113.0, 77.4, 77.1, 76.8, 61.3, 60.3, 50.5, 21.4, 14.4, 14.1; HRMS *m/z* (ESI) calcd for $C_{30}H_{32}NO_6$ ($[M+H]^+$) 502.2224, found 502.2230.

diethyl 2-(3-(ethoxycarbonyl)-1-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3oa):



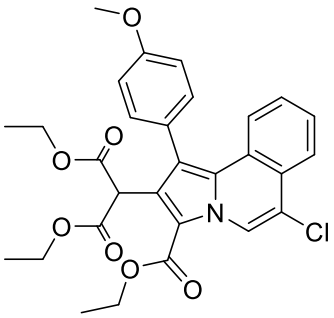
79.2 mg, 61% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.34 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.55 - 7.49 (m, 1H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.22 – 7.11 (m, 3H), 7.01 (d, *J* = 7.2 Hz, 1H), 5.04 (d, *J* = 11.6 Hz, 1H), 4.37 (q, *J* = 6.0 Hz, 2H), 4.08 (q, *J* = 4.4 Hz, 4H), 2.98 - 2.91 (m, 2H), 2.60 – 2.42 (m, 3H), 2.18 – 1.99 (m, 4H), 1.73 - 1.65 (m, 3H), 1.61 - 1.51 (m, 3H), 1.37 (t, *J* = 6.4 Hz, 3H), 1.21 (t, *J* = 6.0 Hz, 6H), 1.00 (d, *J* = 17.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 161.5, 139.6, 139.5, 136.9, 136.8, 132.0, 131.9, 131.9, 131.8, 130.0, 128.9, 128.8, 128.6, 128.6, 128.5, 127.1, 126.9, 126.8, 126.1, 126.0, 125.8, 125.5, 124.8, 123.9, 123.9, 120.9, 113.9, 113.0, 77.4, 77.1, 76.7, 61.3, 60.3, 50.7, 50.5, 48.1, 48.0, 44.6, 44.4, 38.2, 38.1, 35.9, 31.7, 29.4, 29.3, 26.6, 25.7, 21.7, 14.4, 14.1, 14.1, 14.1, 13.9; HRMS *m/z* (ESI) calcd for $C_{40}H_{44}NO_7$ ($[M+H]^+$) 650.3112, found 650.3114.

diethyl 2-(6-bromo-3-(ethoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ag):



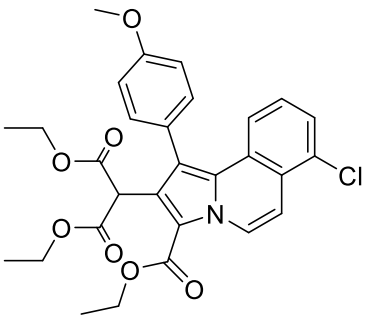
81.4 mg, 70% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.83 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.77 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 9.6 Hz, 1H), 4.10 - 4.03 (m, 4H), 3.90 – 3.78 (m, 2H), 3.76 (s, 3H), 1.39 - 1.26 (m, 3H), 1.14 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.6, 159.7, 158.2, 144.2, 142.4, 135.2, 131.8, 131.6, 130.3, 128.7, 128.4, 127.9, 127.5, 126.4, 121.4, 119.4, 114.1, 114.0, 77.4, 77.0, 76.7, 62.0, 61.7, 55.3, 52.6, 13.9; HRMS *m/z* (ESI) calcd for $C_{29}H_{29}BrNO_7$ ($[M+H]^+$) 582.1122, found 582.1118.

diethyl 2-(6-chloro-3-(ethoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ah):



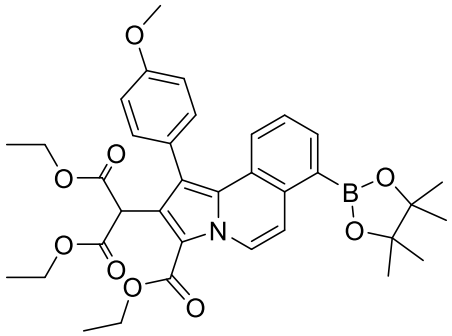
69.8 mg, 65% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.69 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.79 (d, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 9.6 Hz, 1H), 4.12 - 4.03 (m, 4H), 3.91 – 3.78 (m, 2H), 3.76 (s, 3H), 1.37 - 1.25 (m, 3H), 1.14 (t, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.6, 159.7, 157.5, 142.5, 141.4, 134.0, 131.9, 131.4, 130.3, 128.4, 128.3, 128.1, 127.9, 127.4, 123.7, 121.4, 114.1, 114.0, 77.4, 77.1, 76.7, 62.0, 61.7, 55.3, 52.6, 14.1, 13.9; HRMS *m/z* (ESI) calcd for $C_{29}H_{29}ClNO_7$ ($[M+H]^+$) 538.1627, found 538.1642.

diethyl 2-(7-chloro-3-(ethoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ai):



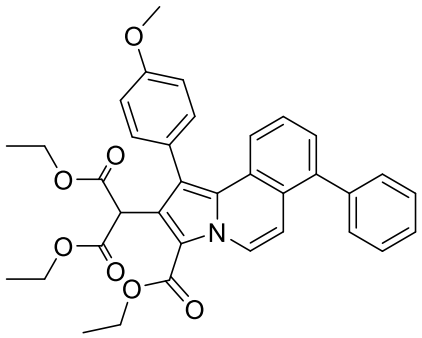
55.9 mg, 52% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.40 (d, *J* = 8.0 Hz, 1H), 7.47 - 7.41(m, 2H), 7.33 (t, *J* = 8.0 Hz, 3H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 5.16 (s, 1H), 4.42 - 4.36 (m, 2H), 4.09 - 4.02 (m, 4H), 3.91 (s, 3H), 1.38 (t, *J* = 6.8 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.8, 161.4, 159.6, 132.7, 131.1, 129.6, 127.3, 127.2, 127.0, 126.6, 126.3, 125.8, 122.6, 121.0, 114.4, 114.2, 108.8, 77.3, 77.0, 76.7, 61.5, 60.5, 55.3, 50.5, 14.3, 14.0; HRMS *m/z* (ESI) calcd for $C_{29}H_{29}ClNO_7$ ($[M+H]^+$) 538.1627, found 538.1635.

diethyl 2-(3-(ethoxycarbonyl)-1-(4-methoxyphenyl)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3aj):



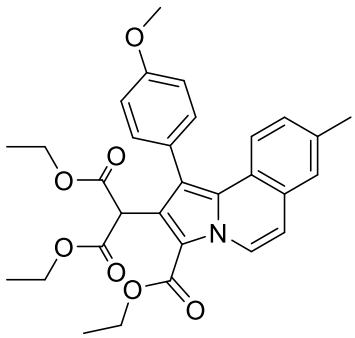
104.4 mg, 83% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.79 (s, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 2H), 5.14 (s, 1H), 4.44 - 4.36 (m, 2H), 4.08 - 4.02 (m, 4H), 3.90 (s, 3H), 1.41 (s, 12H), 1.25 (d, *J* = 9.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.8, 161.4, 159.5, 134.0, 132.8, 131.0, 130.7, 127.7, 127.5, 127.1, 126.7, 126.6, 125.3, 123.8, 120.4, 114.3, 114.0, 83.9, 77.4, 77.0, 76.7, 61.4, 60.4, 55.3, 50.5, 24.9, 24.9, 14.3, 14.0; HRMS *m/z* (ESI) calcd for $C_{35}H_{41}BNO_9$ ($[M+H]^+$) 630.2869, found 630.2882.

diethyl 2-(3-(ethoxycarbonyl)-1-(4-methoxyphenyl)-7-phenylpyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ak):



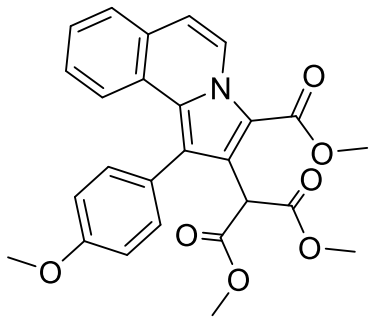
90.4 mg, 78% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.34 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.41 (m, 6H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 5.18 (s, 1H), 4.38 - 4.31 (m, 2H), 4.10 - 4.00 (m, 4H), 3.92 (s, 3H), 1.36 (t, *J* = 6.8 Hz, 3H), 1.21 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.0, 161.5, 159.5, 137.2, 132.8, 130.3, 130.1, 128.5, 127.8, 127.1, 126.8, 126.7, 126.3, 126.1, 125.6, 125.5, 124.0, 120.3, 114.4, 113.9, 77.4, 77.0, 76.7, 61.4, 60.3, 55.3, 50.6, 14.3, 14.0; HRMS *m/z* (ESI) calcd for $C_{35}H_{34}NO_7$ ($[M+H]^+$) 580.2330, found 580.2338.

diethyl 2-(3-(ethoxycarbonyl)-1-(4-methoxyphenyl)-8-methylpyrrolo[2,1-a]isoquinolin-2-yl)malonate (3al):



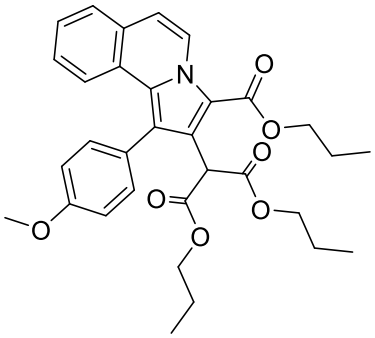
73.4 mg, 71% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.31 (d, *J* = 7.6 Hz, 1H), 7.40 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 9.2 Hz, 1H), 7.01 (d, *J* = 5.6 Hz, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 5.21 (s, 1H), 4.41 - 4.34 (m, 2H), 4.07 - 4.01 (m, 4H), 3.90 (s, 3H), 2.39 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.1, 161.6, 159.4, 136.9, 132.9, 130.8, 128.8, 128.7, 126.7, 126.5, 126.1, 124.8, 123.7, 123.2, 119.8, 114.2, 113.6, 112.9, 77.4, 77.0, 76.7, 61.4, 60.3, 55.3, 50.7, 21.4, 14.4, 14.0; HRMS *m/z* (ESI) calcd for $C_{30}H_{32}NO_7$ ($[M+H]^+$) 518.2173, found 518.2173.

dimethyl 2-(3-(methoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3am):



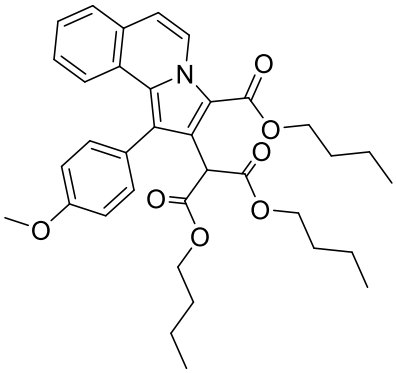
71.9 mg, 78% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.28 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 3H), 5.10 (s, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.4, 161.7, 159.6, 132.6, 130.5, 128.6, 127.2, 127.1, 126.8, 126.4, 126.1, 125.4, 124.6, 123.8, 120.5, 114.5, 113.6, 113.3, 77.4, 77.1, 76.7, 55.3, 52.6, 51.0, 50.1; HRMS *m/z* (ESI) calcd for $C_{26}H_{24}NO_7$ ($[M+H]^+$) 462.1547, found 462.1545.

dipropyl 2-(1-(4-methoxyphenyl)-3-(propoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3an):



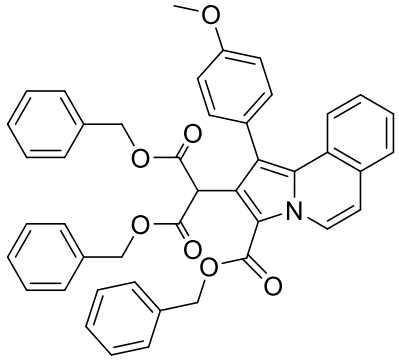
66.5 mg, 61% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.33 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.33 (m, 4H), 7.16 (t, *J* = 8 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 3H), 5.24 (s, 1H), 4.28 (t, *J* = 6.8 Hz, 2H), 3.94 (t, *J* = 6.4 Hz, 4H), 3.90 (s, 3H), 1.82 – 1.76 (m, 2H), 1.60 – 1.55 (m, 4H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.1, 161.6, 159.5, 132.9, 130.5, 128.6, 127.1, 126.9, 126.8, 126.7, 126.3, 125.5, 124.8, 123.8, 120.4, 114.3, 113.9, 113.0, 77.4, 77.0, 76.7, 67.1, 66.1, 55.3, 50.5, 22.1, 21.8, 10.5, 10.3; HRMS *m/z* (ESI) calcd for $C_{32}H_{36}NO_7$ ($[M+H]^+$) 546.2486, found 546.2498.

dibutyl 2-(3-(butoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ao):



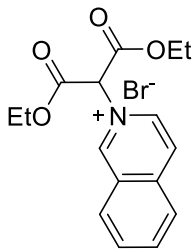
58.7 mg, 50% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.33 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.33 (m, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 3H), 5.24 (s, 1H), 4.32 (t, *J* = 6.8 Hz, 2H), 4.02 – 3.94 (m, 4H), 3.90 (s, 3H), 1.79 - 1.71 (m, 2H), 1.57 - 1.52 (m, 4H), 1.46 - 1.41 (m, 2H), 1.33 – 1.26 (m, 4H), 0.98 (t, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.1, 161.6, 159.5, 132.9, 130.6, 128.6, 127.1, 126.9, 126.7, 126.6, 126.3, 125.5, 124.8, 123.8, 120.4, 114.2, 113.9, 113.0, 77.4, 77.0, 76.7, 65.4, 64.3, 55.3, 50.5, 30.8, 30.4, 19.2, 19.1, 13.8, 13.7; HRMS *m/z* (ESI) calcd for $C_{35}H_{42}NO_7$ ($[M+H]^+$) 588.2956, found 588.2960.

dibenzyl 2-(3-((benzyloxy)carbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ap):



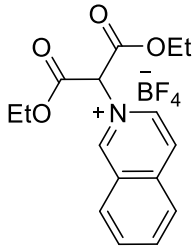
77.2 mg, 56% yield; Yellow oil; R_f = 0.1 (PE/EA = 10 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.33 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 4H), 7.29 – 7.26 (m, 11H), 7.17 – 7.15 (m, 5H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 2H), 5.24 (s, 1H), 5.19 (d, *J* = 11.6 Hz, 2H), 4.91 – 4.84 (m, 4H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.6, 161.1, 159.5, 136.2, 135.5, 132.8, 130.8, 128.7, 128.5, 128.4, 128.2, 128.1, 127.2, 127.1, 126.8, 126.4, 126.3, 125.4, 124.8, 123.8, 120.7, 114.4, 113.5, 113.3, 77.4, 77.0, 76.7, 67.1, 65.6, 55.3, 50.6; HRMS *m/z* (ESI) calcd for $C_{44}H_{36}NO_7$ ($[M+H]^+$) 690.2486, found 690.2488.

2-(1,3-diethoxy-1,3-dioxopropan-2-yl)isoquinolin-2-ium bromide (2a):[2,3]



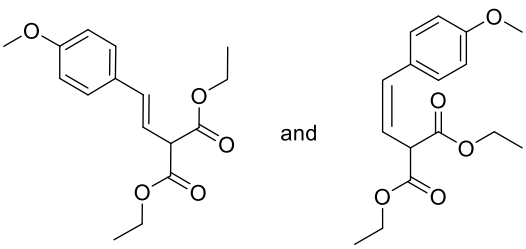
Red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.25 (s, 1H), 9.00 (d, *J* = 7.5 Hz, 1H), 8.67 - 8.60 (m, 2H), 8.36 (d, *J* = 8.5 Hz, 1H), 8.25 (t, *J* = 8.0 Hz, 1H), 8.06 – 7.96 (m, 2H), 4.52 – 4.32 (m, 4H), 1.37 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 162.8, 152.3, 138.6, 135.1, 131.5, 131.5, 127.4, 127.1, 125.5, 77.6, 77.3, 77.1, 71.2, 64.5, 13.9.

2-(1,3-diethoxy-1,3-dioxopropan-2-yl)isoquinolin-2-ium tetrafluoroborate (2b):[2,3]



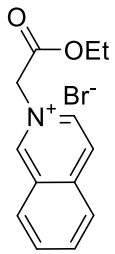
Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.96 (s, 1H), 8.60 (d, *J* = 8.8 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 7.2 Hz, 1H), 8.07 (d, *J* = 4.4 Hz, 2H), 7.87 - 7.83 (m, 1H), 6.72 (s, 1H), 4.43 – 4.28 (m, 4H), 1.29 (t, *J* = 7.2 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -150.56; ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.6, 151.9, 138.7, 138.2, 135.1, 131.7, 131.5, 127.3, 127.1, 125.6, 77.5, 77.1, 76.8, 72.2, 64.7, 13.8.

diethyl 2-(4-methoxystyryl)malonate (4aa):



Z/*E* = 1 : 1.5; Yellow oil; R_f = 0.1 (PE/EA = 20 : 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.52 (d, *J* = 9.0 Hz, 1.5H), 7.33 (d, *J* = 9.0 Hz, 2H), 6.88 (t, *J* = 8.5 Hz, 3.5H), 6.44 - 6.41 (m, 1.5H), 4.66 (d, *J* = 9.0 Hz, 0.75H), 4.27 - 4.19 (m, 7H), 4.07 (d, *J* = 10.5 Hz, 1H), 3.83 (s, 5H), 1.32 - 1.26 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 167.2, 167.0, 160.4, 160.2, 131.5, 130.4, 130.0, 129.8, 129.2, 126.7, 124.2, 121.1, 113.8, 113.6, 77.3, 77.0, 76.8, 62.0, 62.0, 56.0, 55.4, 55.4, 53.6, 14.1, 14.0.

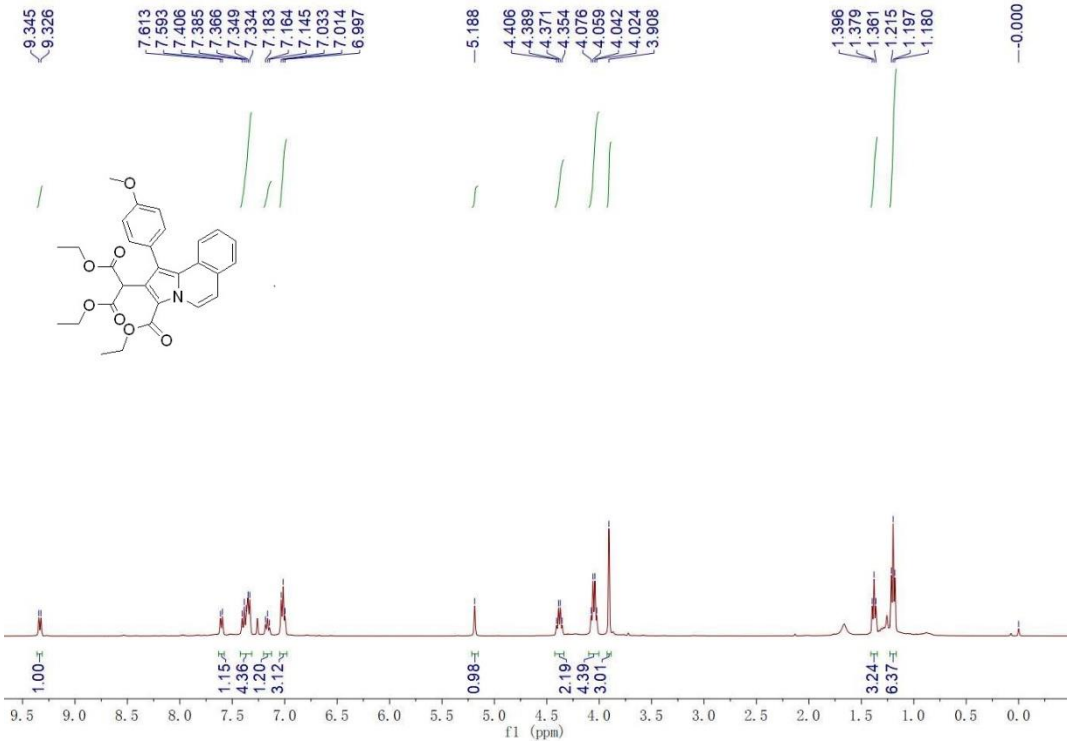
2-(2-ethoxy-2-oxoethyl)isoquinolin-2-ium bromide (5aa):



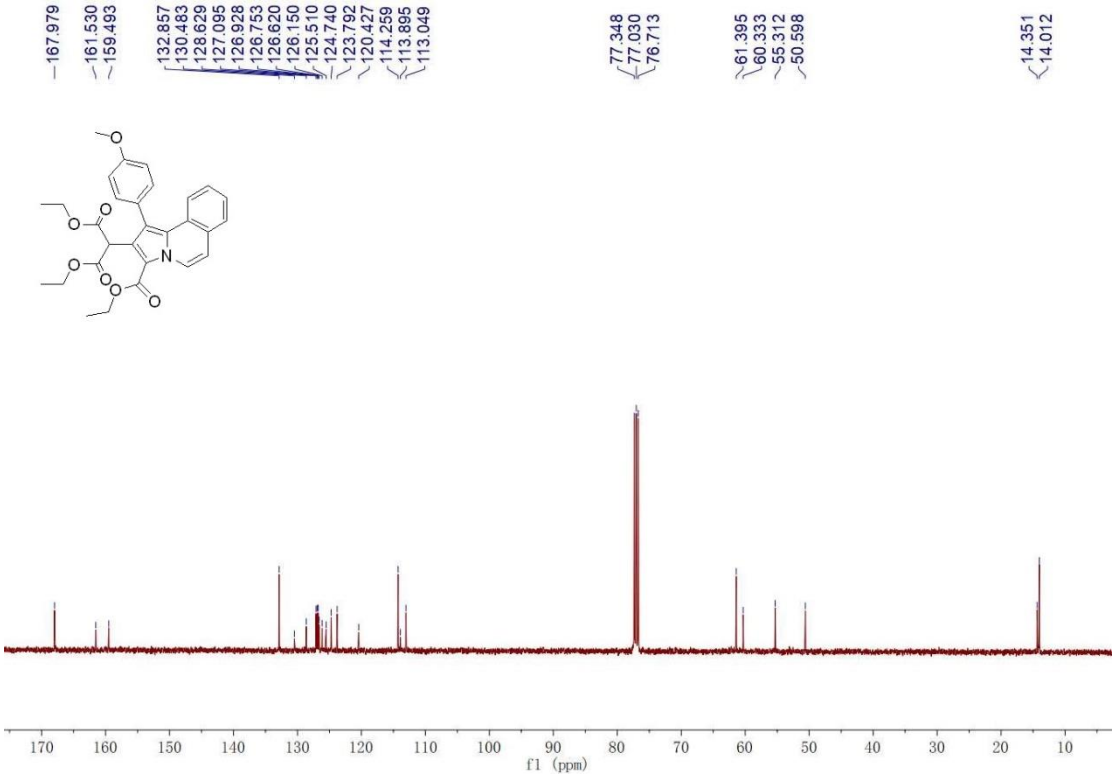
White solid; ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm) 10.21 (s, 1H), 8.85 (d, *J* = 6.8 Hz, 1H), 8.72 (d, *J* = 6.8 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.34 (t, *J* = 5.6 Hz, 1H), 8.13 (t, *J* = 7.2 Hz, 1H), 5.90 (s, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d6) δ (ppm) 167.0, 152.3, 138.2, 137.8, 136.7, 132.0, 131.1, 127.9, 127.2, 125.9, 62.8, 60.7, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 14.5.

(C) Spectra

diethyl 2-(3-(ethoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3aa)

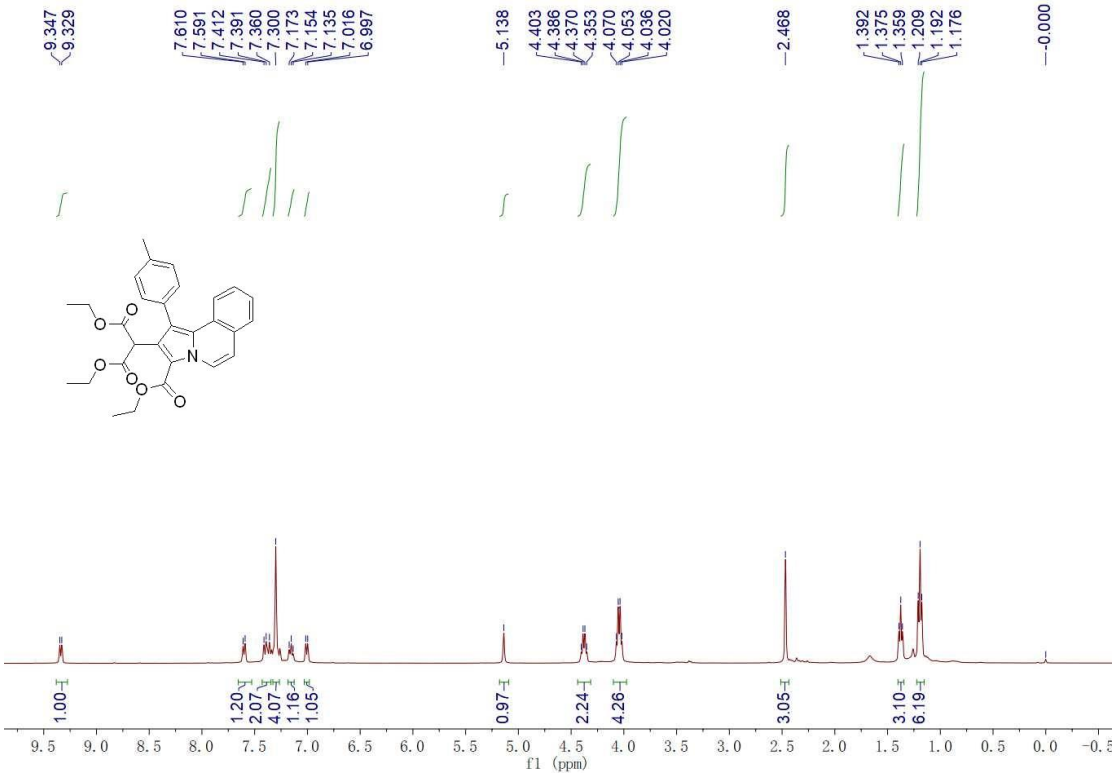


^{1}H-NMR (400 MHz, $CDCl_3$)

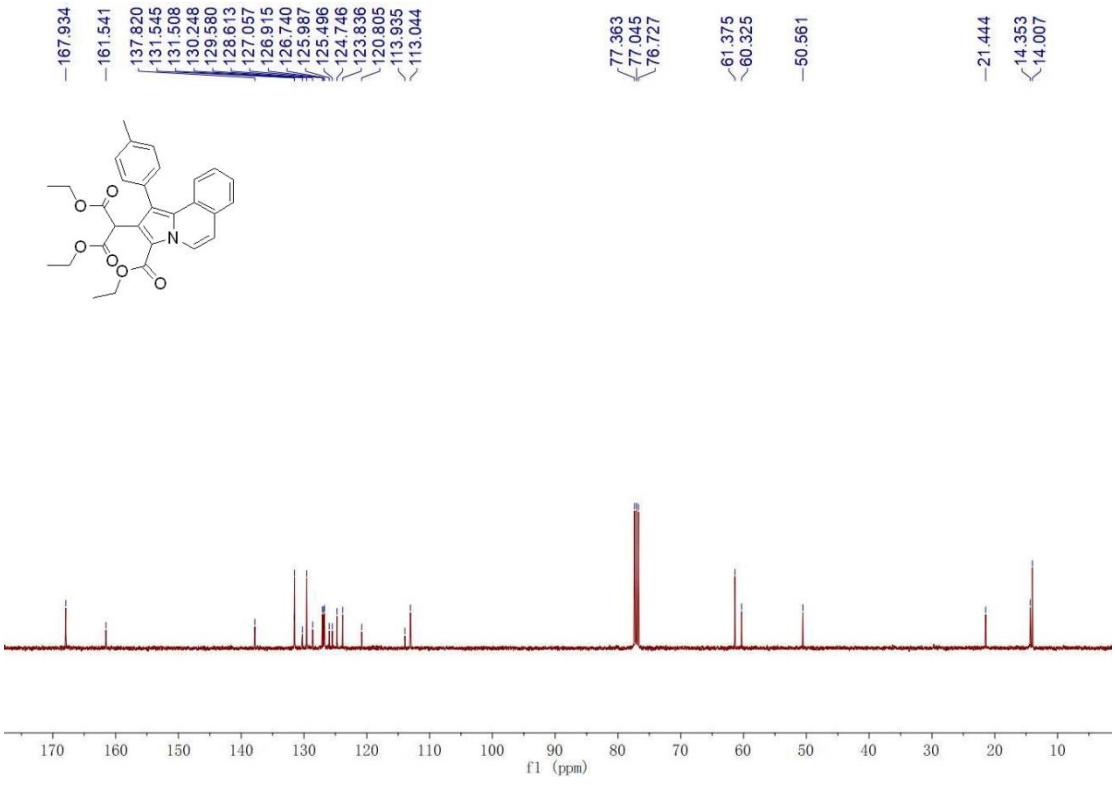


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(3-(ethoxycarbonyl)-1-(p-tolyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ba)

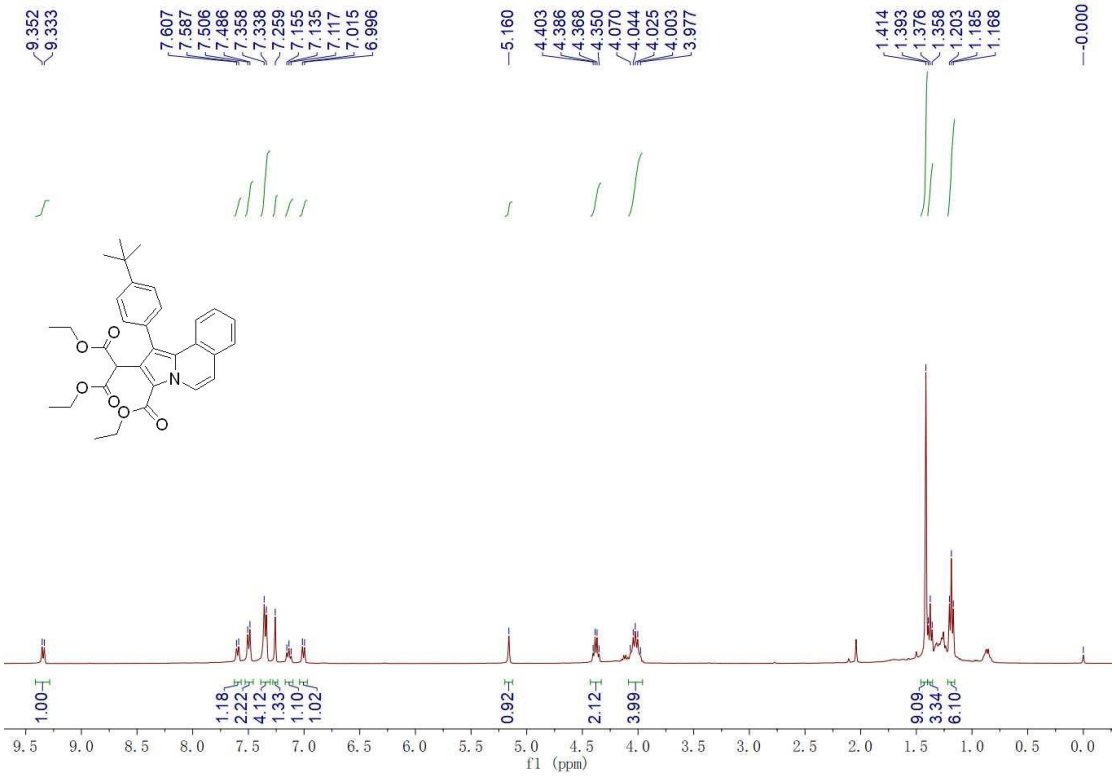


^{1}H-NMR (400 MHz, $CDCl_3$)

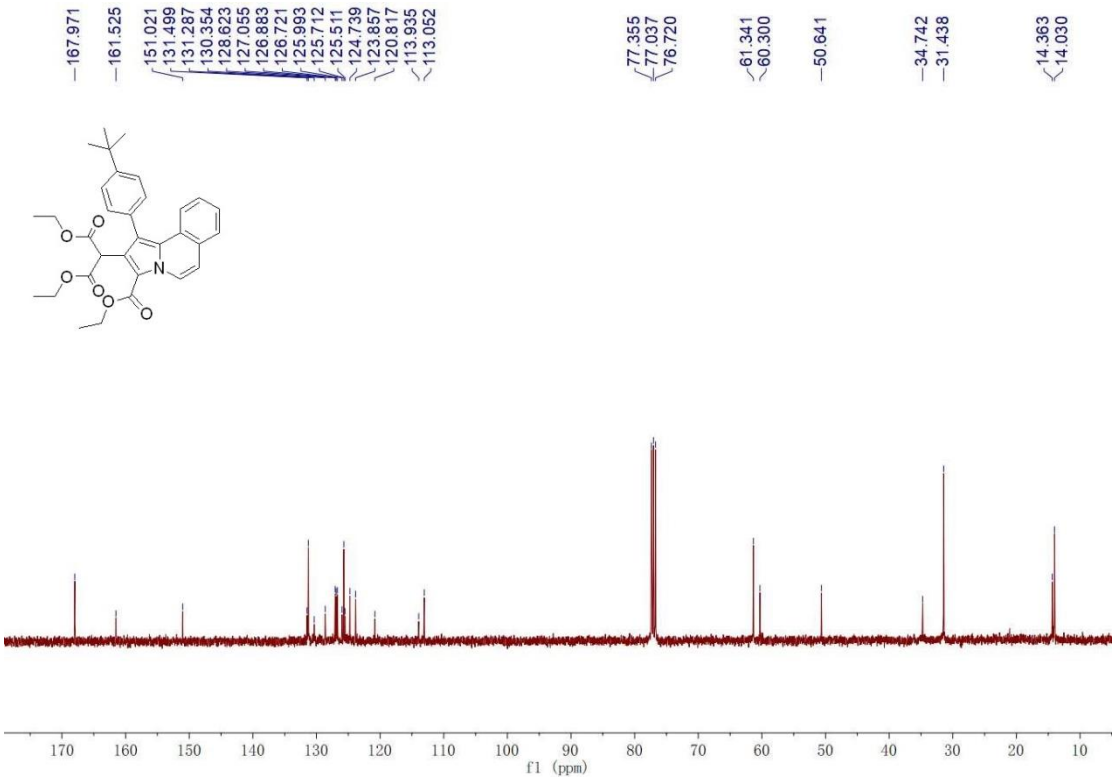


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(1-(4-(tert-butyl)phenyl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ca)

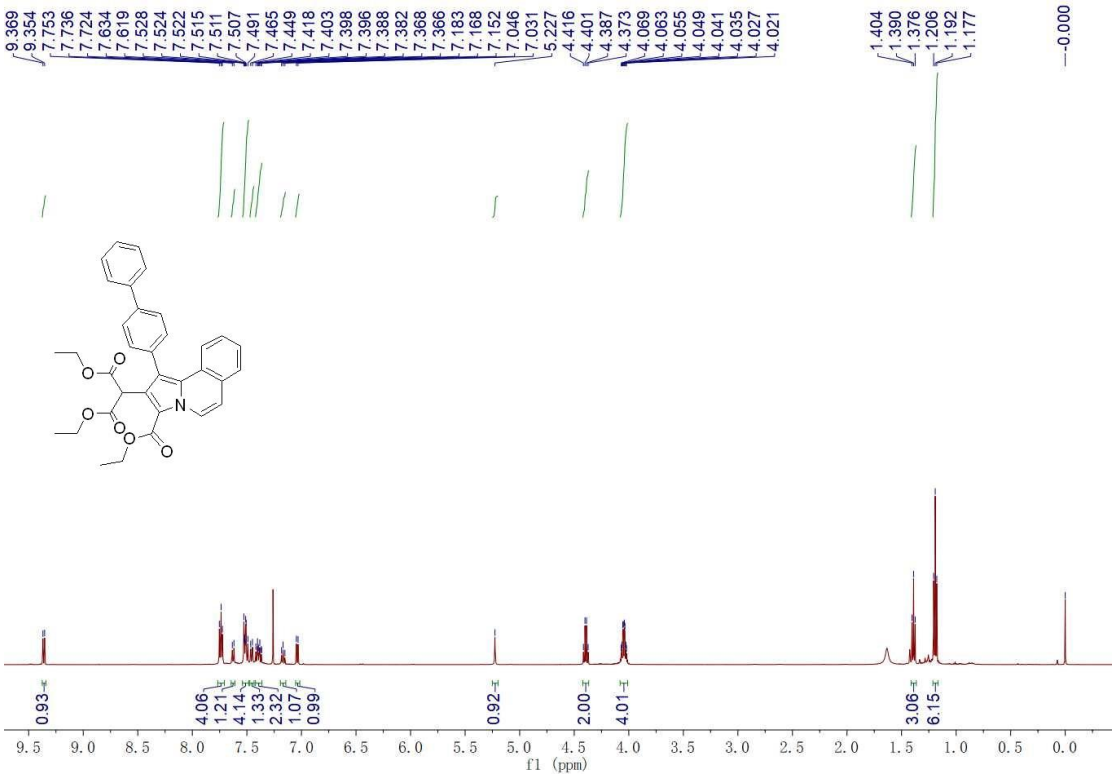


^{1}H-NMR (400 MHz, $CDCl_3$)

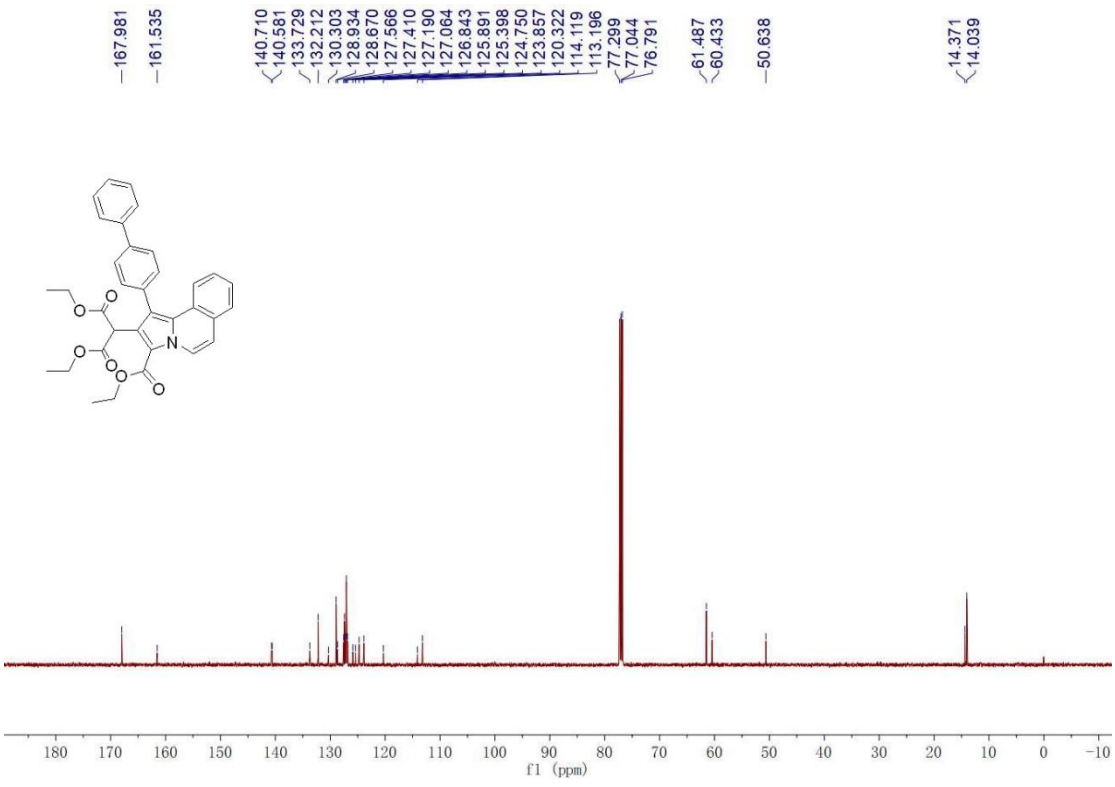


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(1-([1,1'-biphenyl]-4-yl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3da)

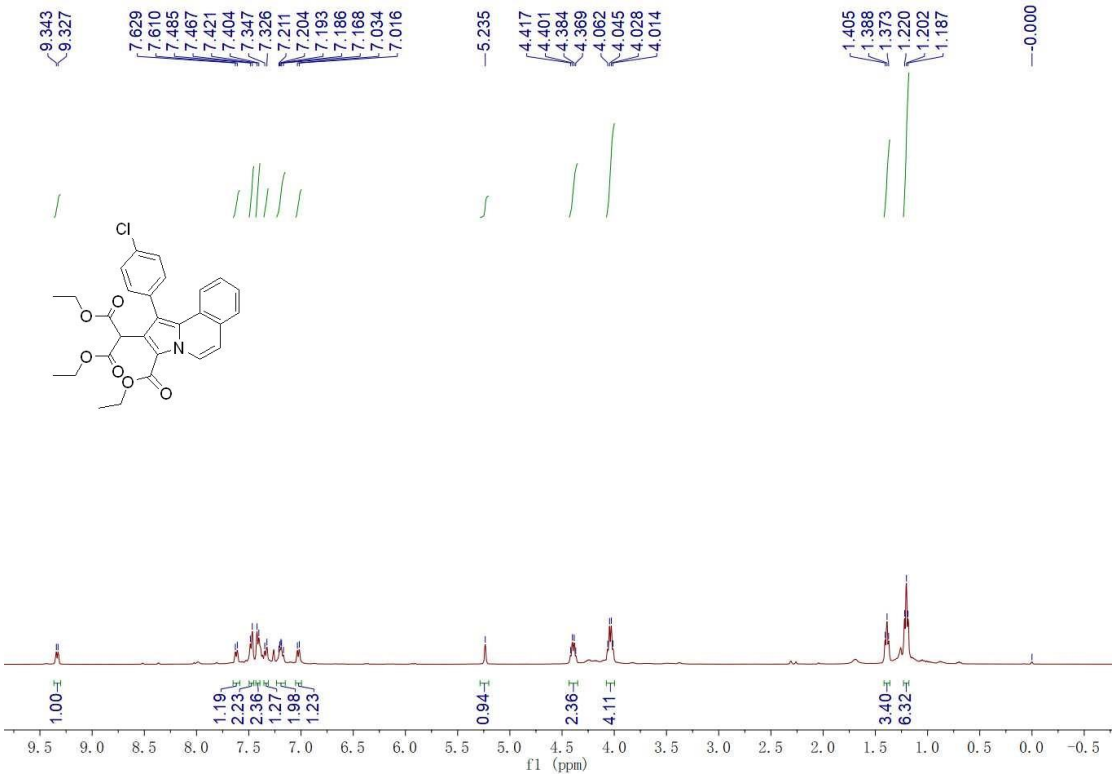


^{1}H-NMR (500 MHz, $CDCl_3$)

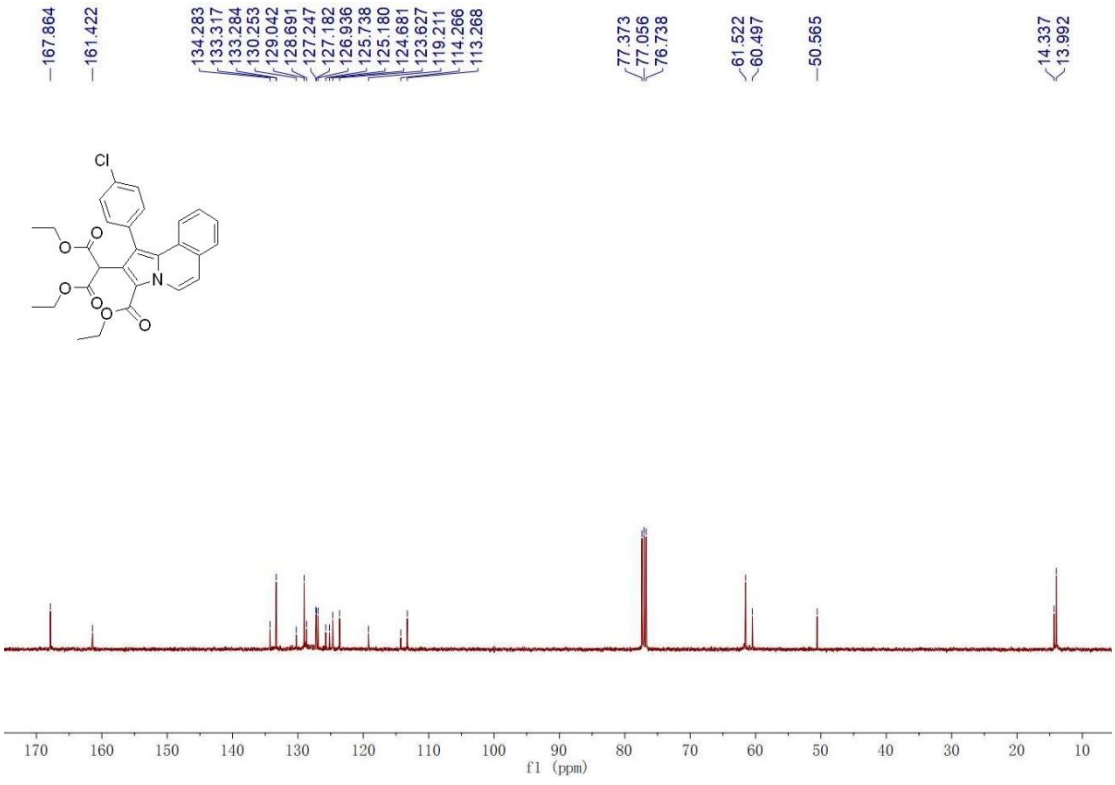


^{13}C-NMR (125 MHz, $CDCl_3$)

diethyl 2-(1-(4-chlorophenyl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ea)

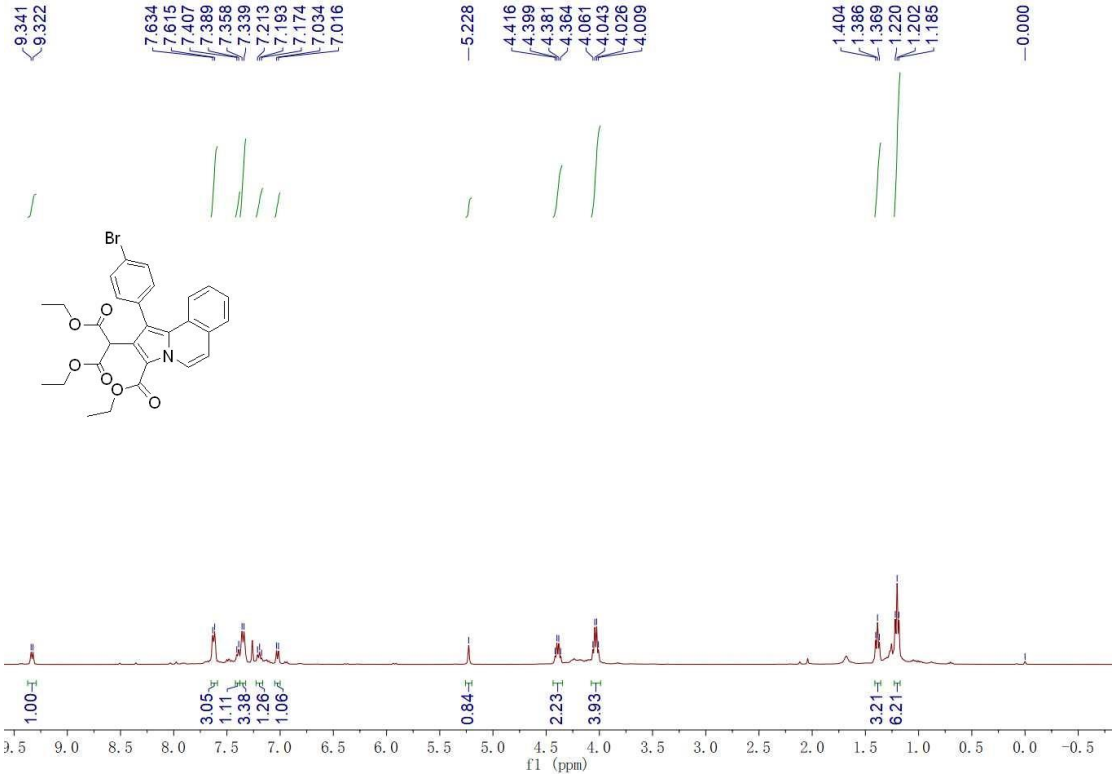


^{1}H-NMR (400 MHz, $CDCl_3$)

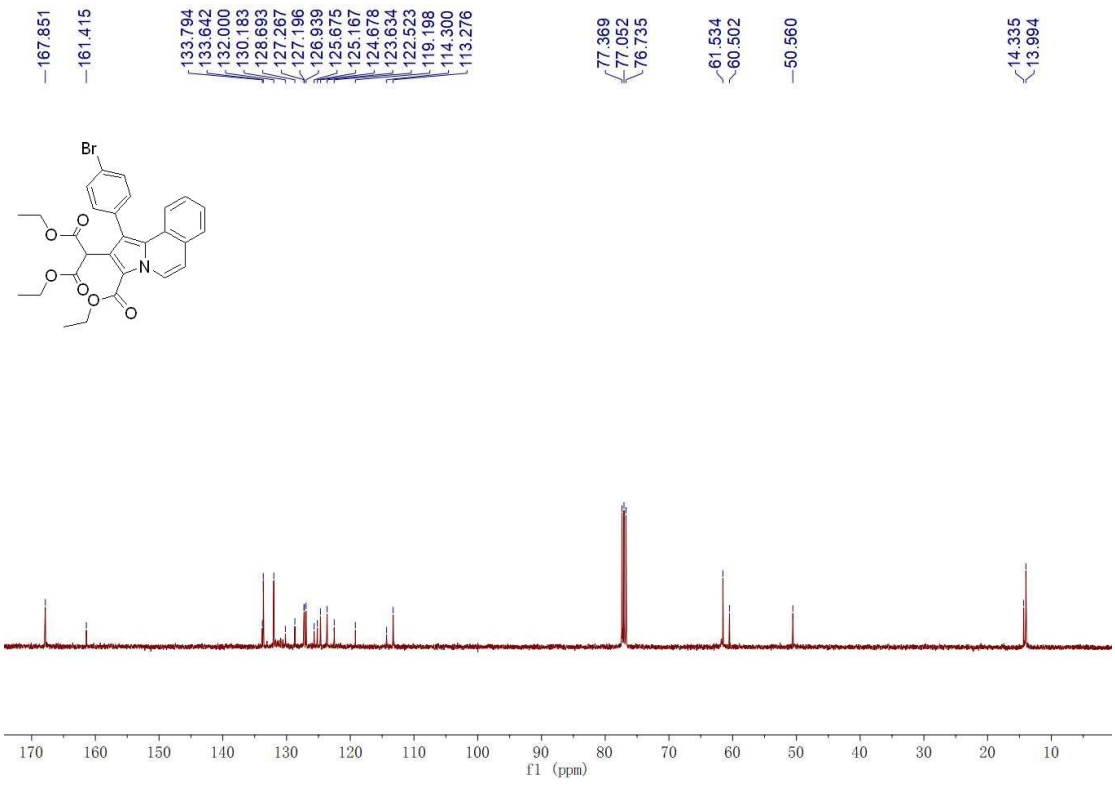


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(1-(4-bromophenyl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3fa)

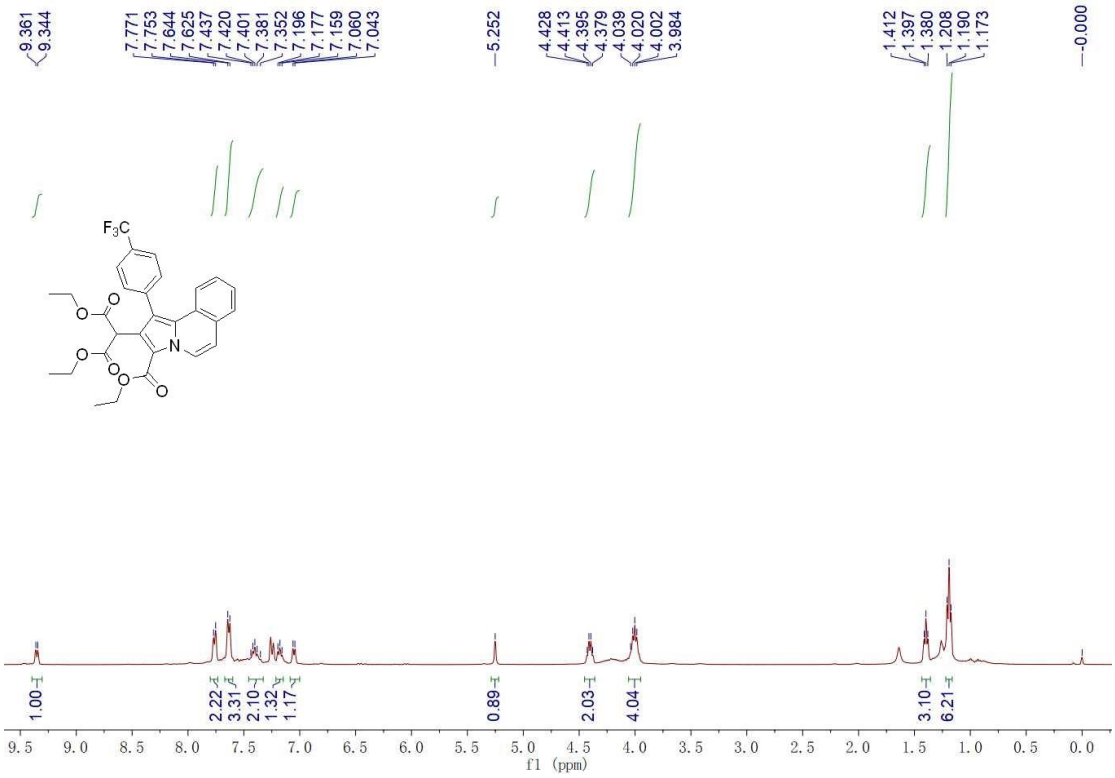


^{1}H-NMR (400 MHz, $CDCl_3$)

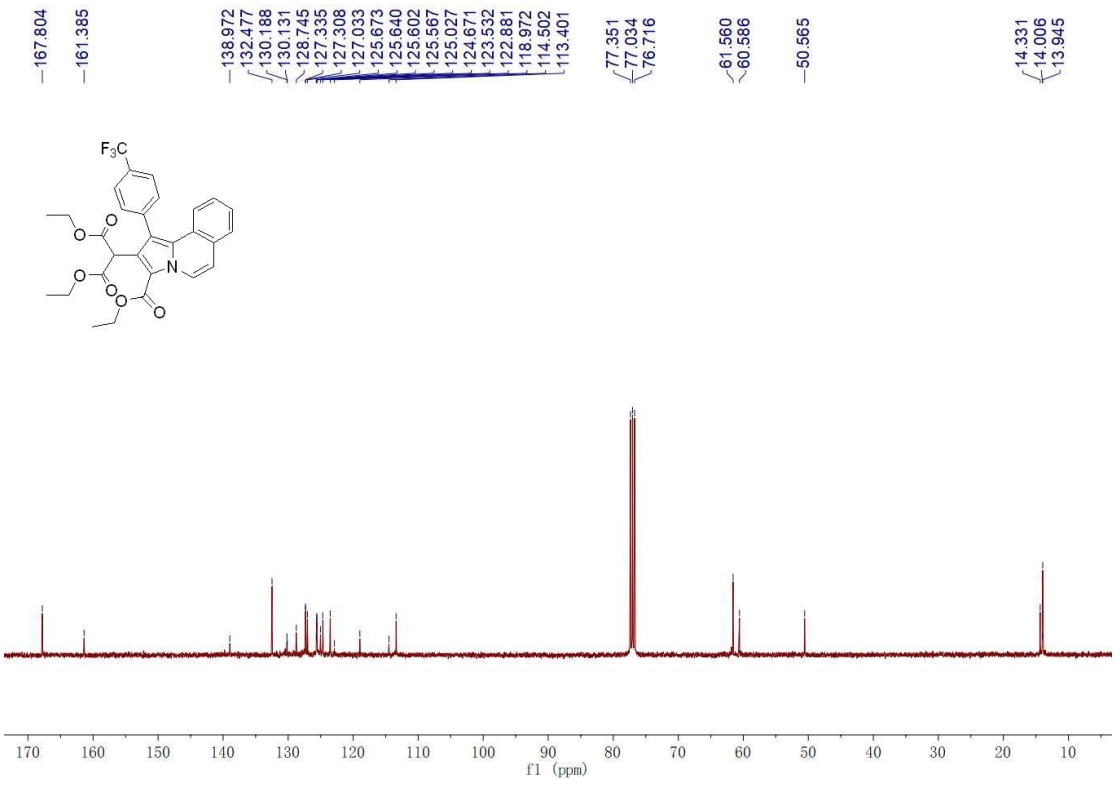


^{13}C-NMR (100 MHz, $CDCl_3$)

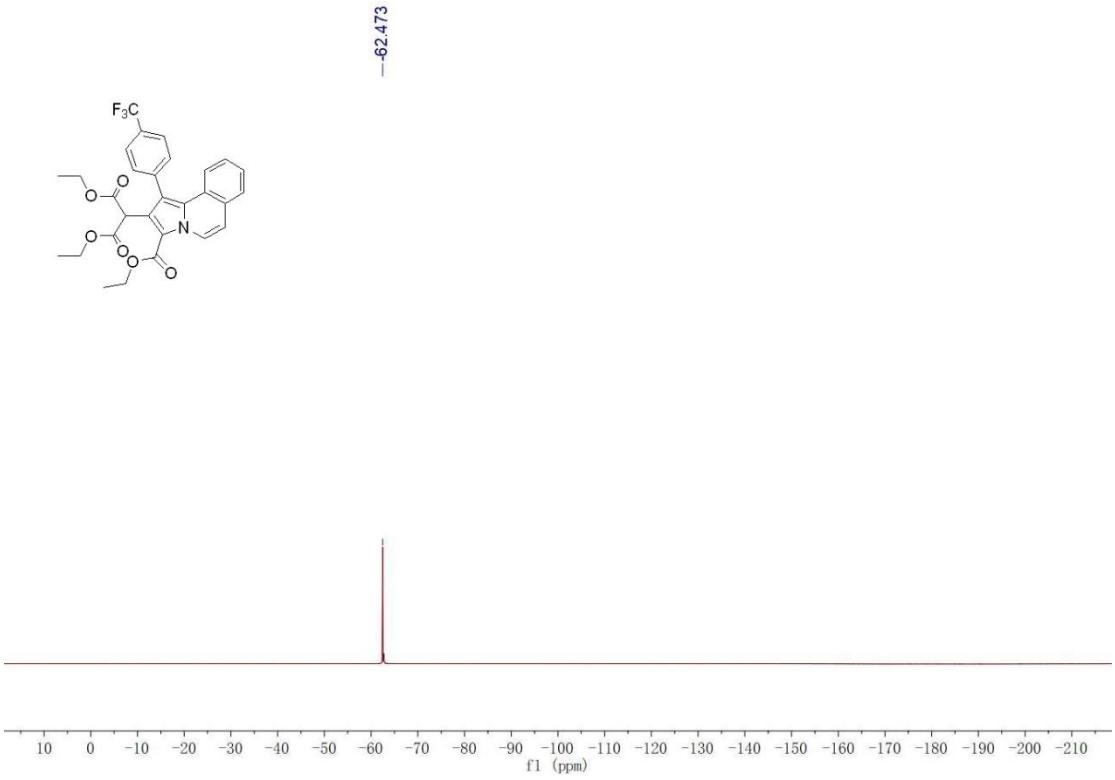
diethyl 2-(3-(ethoxycarbonyl)-1-(4-(trifluoromethyl)phenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ga)



^{1}H-NMR (400 MHz, $CDCl_3$)

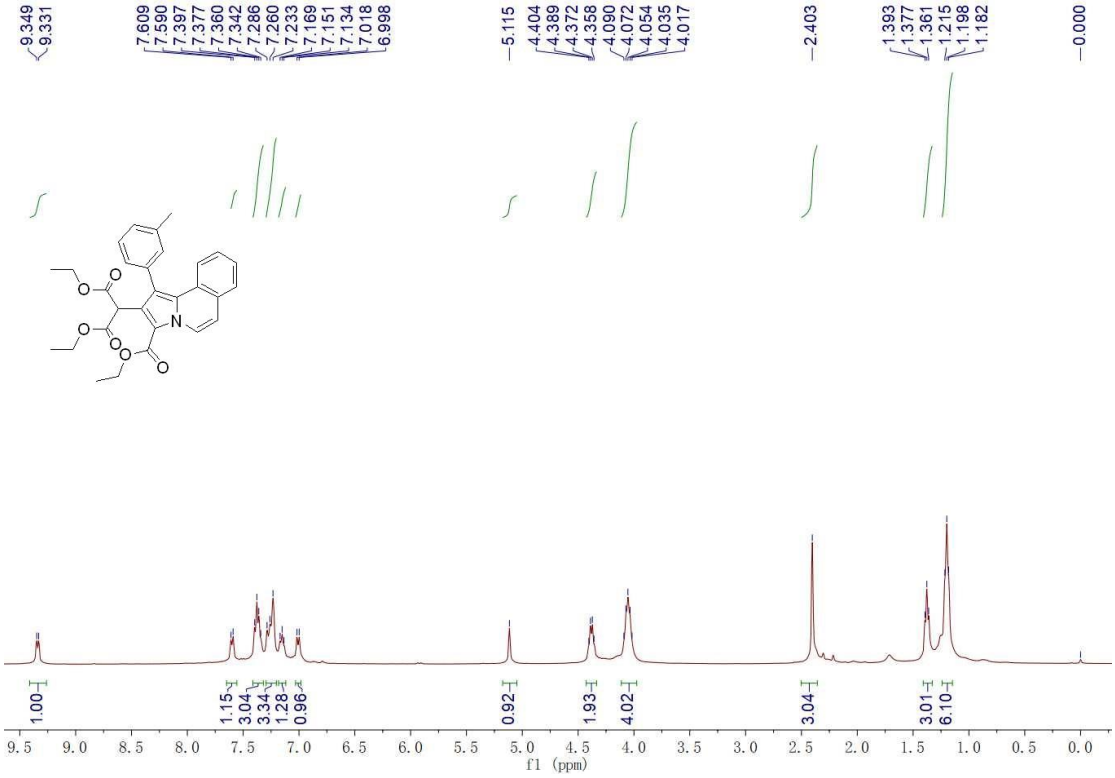


^{13}C-NMR (100 MHz, $CDCl_3$)

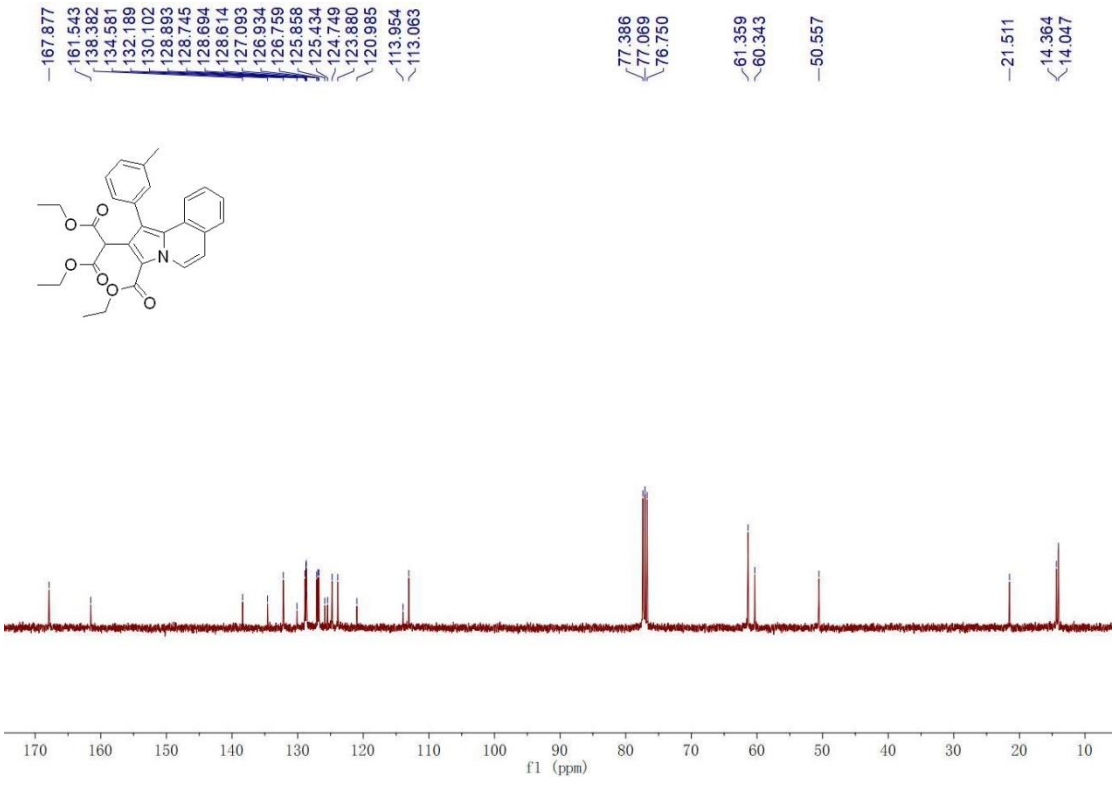


^{19}F NMR (376 MHz, $CDCl_3$)

diethyl 2-(3-(ethoxycarbonyl)-1-(m-tolyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ha):

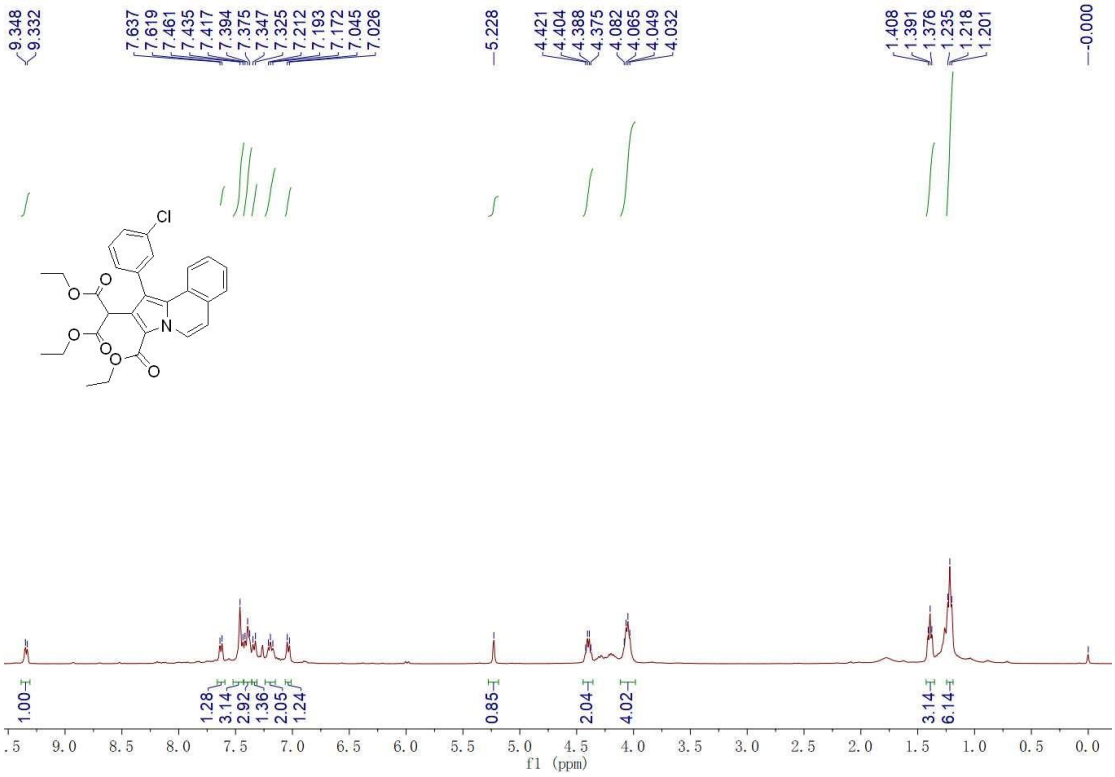


^{1}H-NMR (400 MHz, CDCl3)

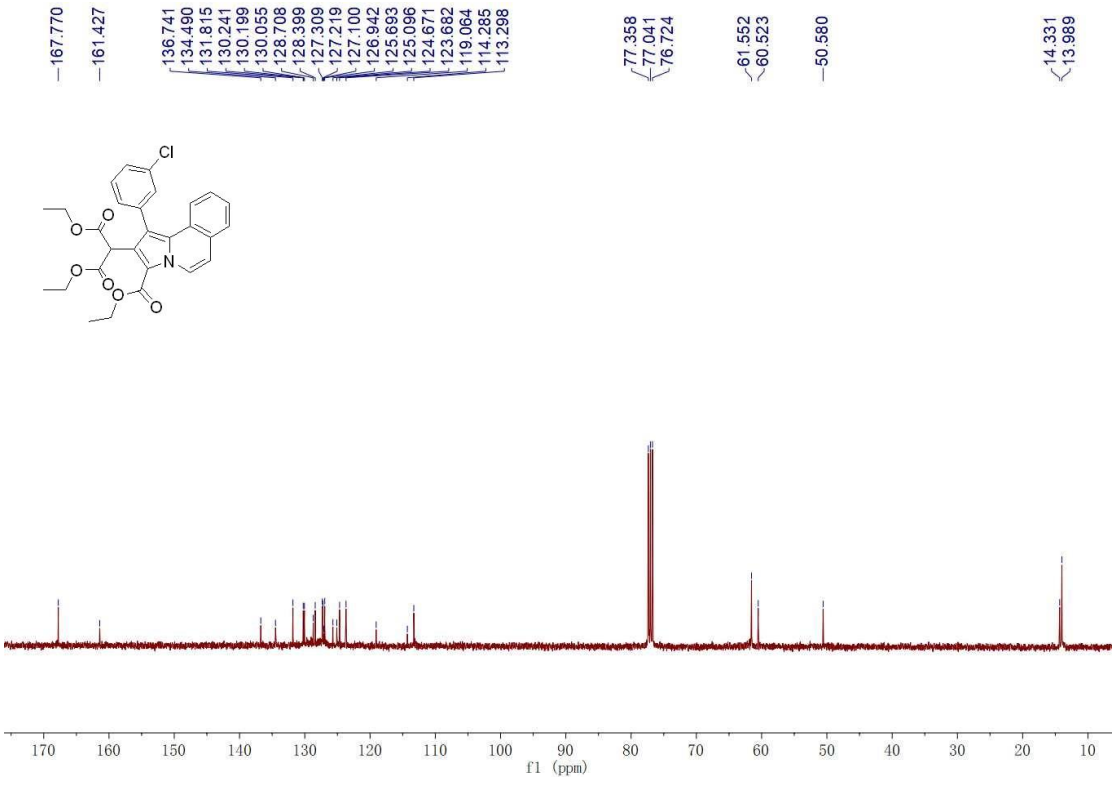


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(1-(3-chlorophenyl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ia)

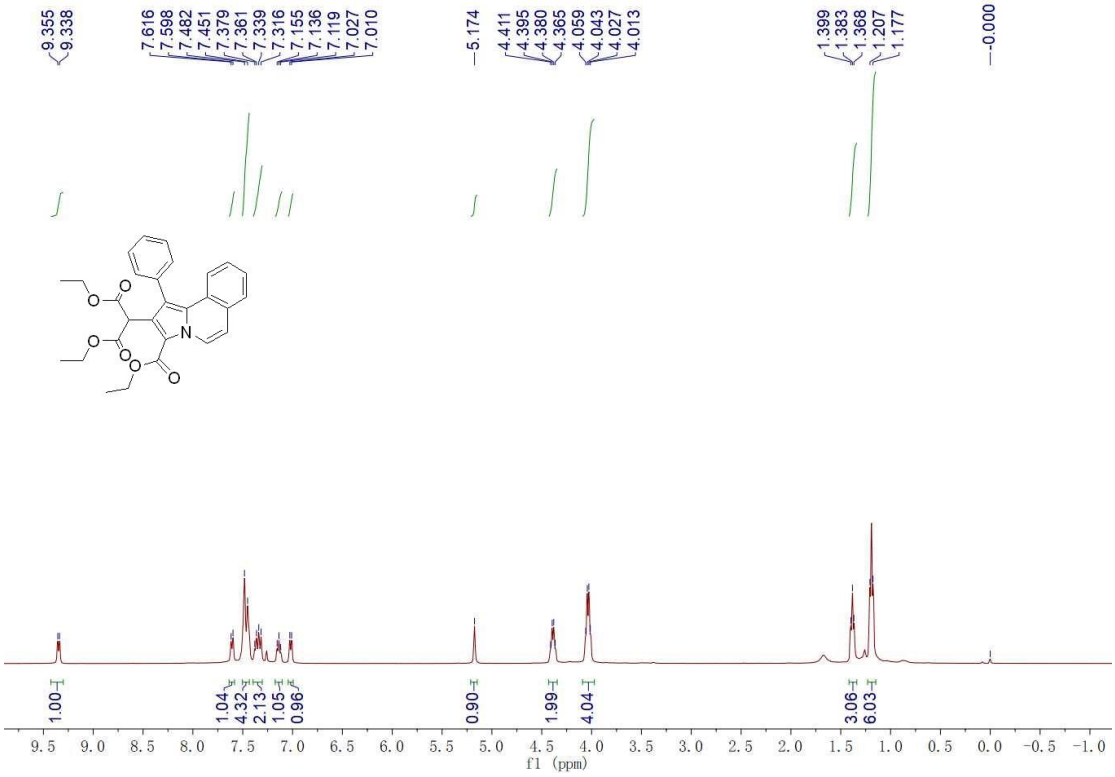


^{1}H-NMR (400 MHz, $CDCl_3$)

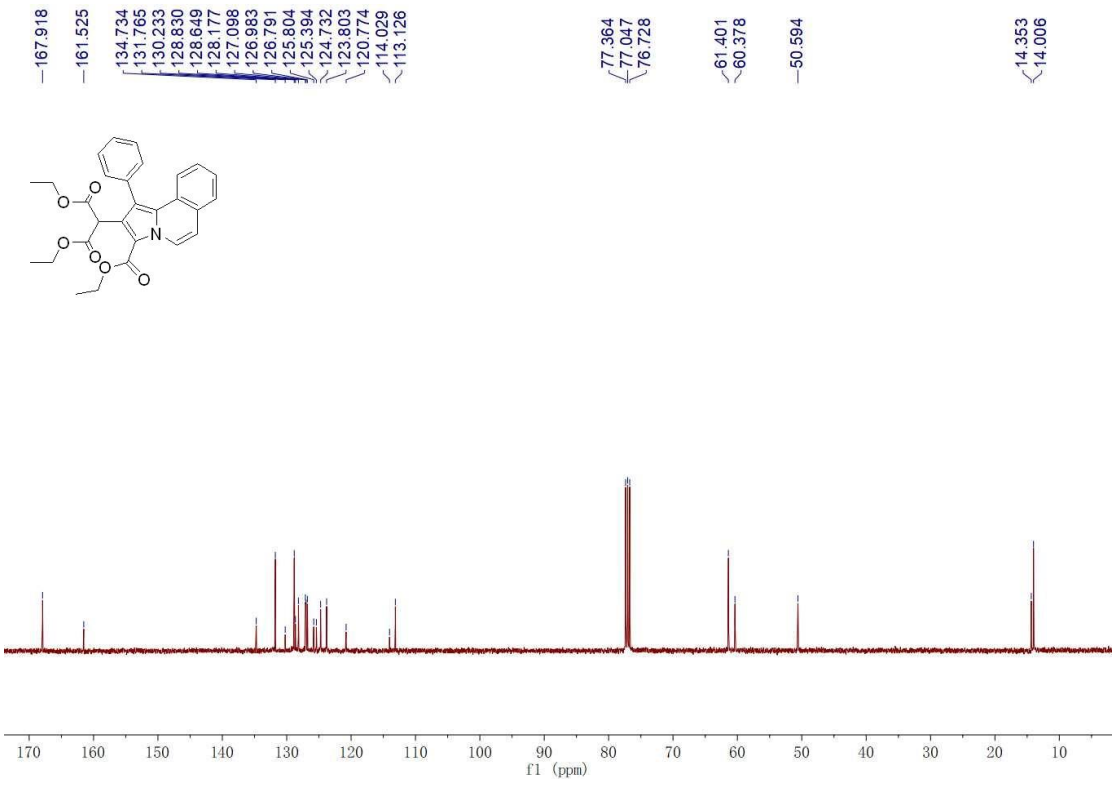


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(3-(ethoxycarbonyl)-1-phenylpyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ja)

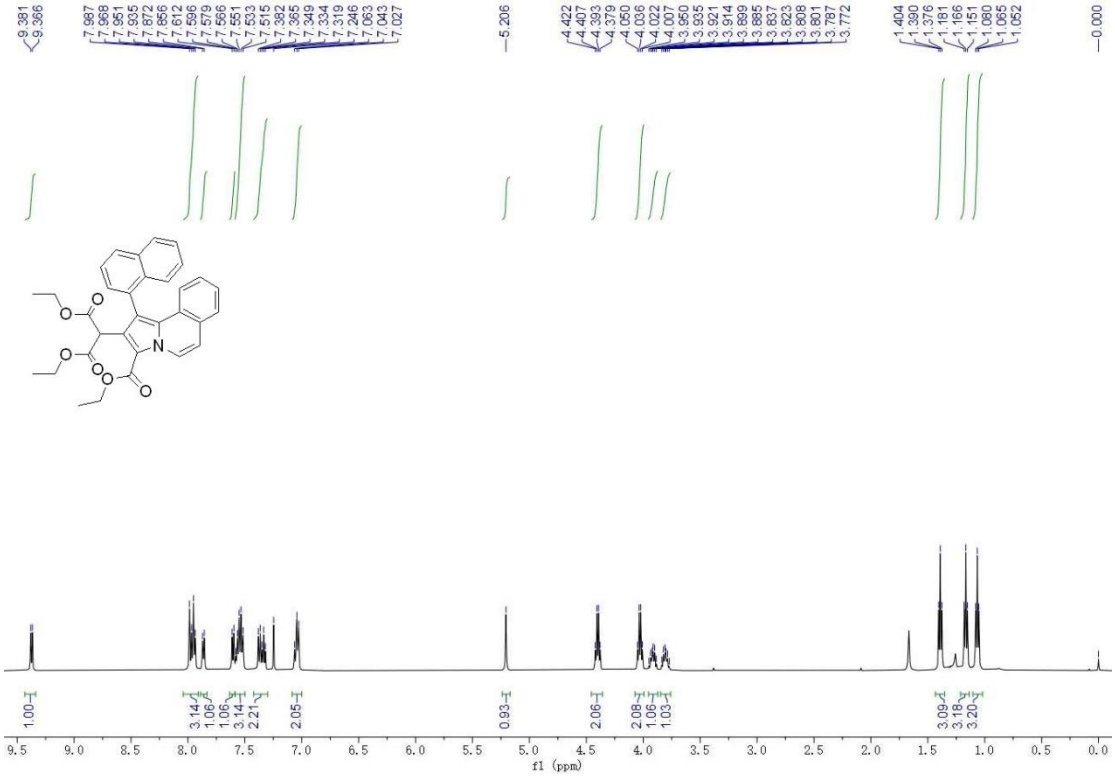


^{1}H-NMR (400 MHz, $CDCl_3$)

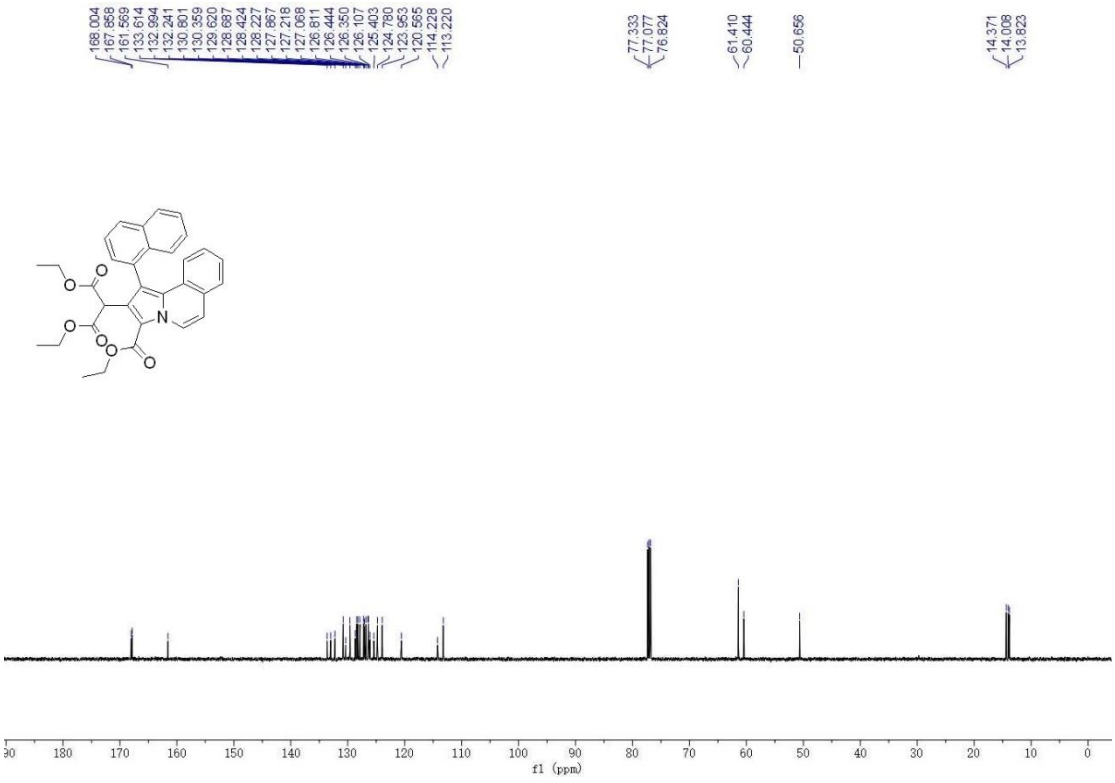


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(3-(ethoxycarbonyl)-1-(naphthalen-1-yl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ka)

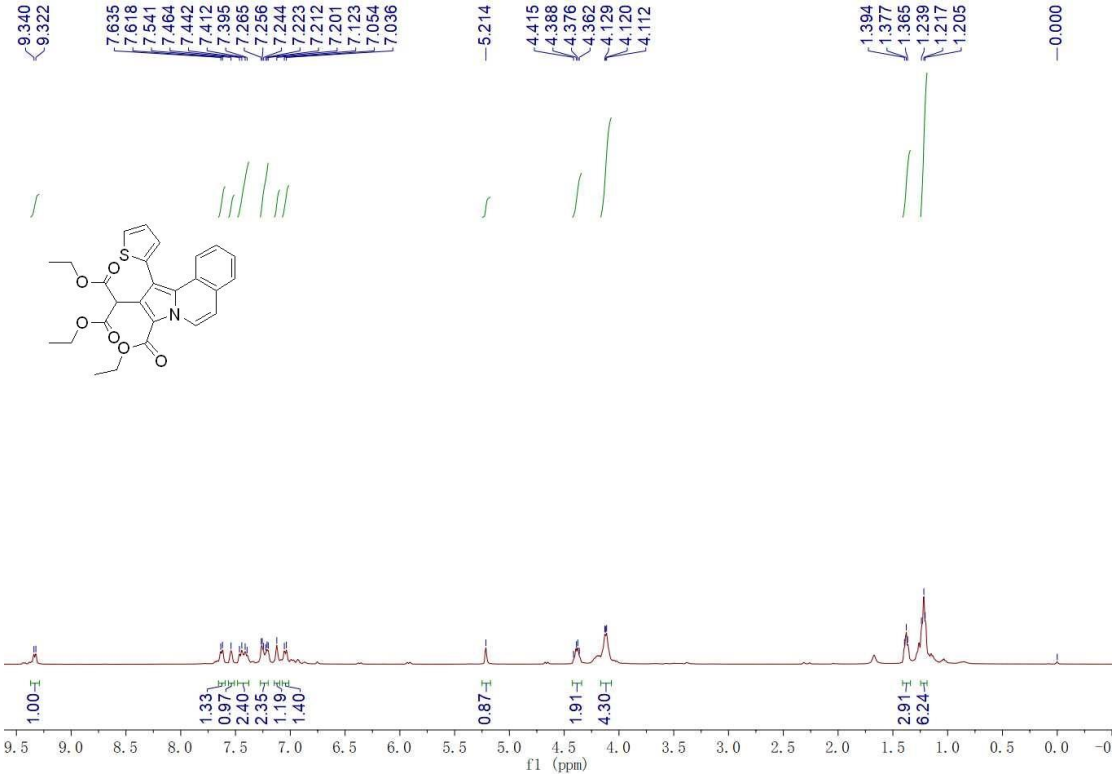


^{1}H-NMR (500 MHz, $CDCl_3$)

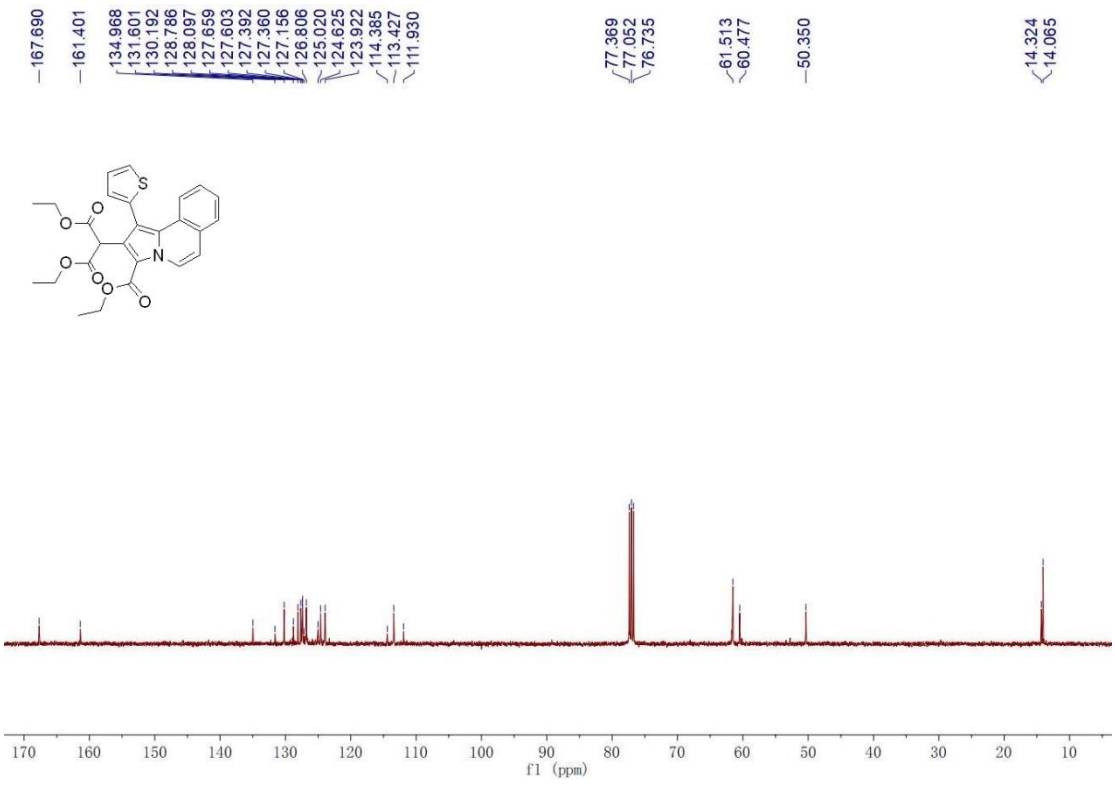


^{13}C-NMR (125 MHz, $CDCl_3$)

diethyl 2-(3-(ethoxycarbonyl)-1-(thiophen-2-yl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3la)

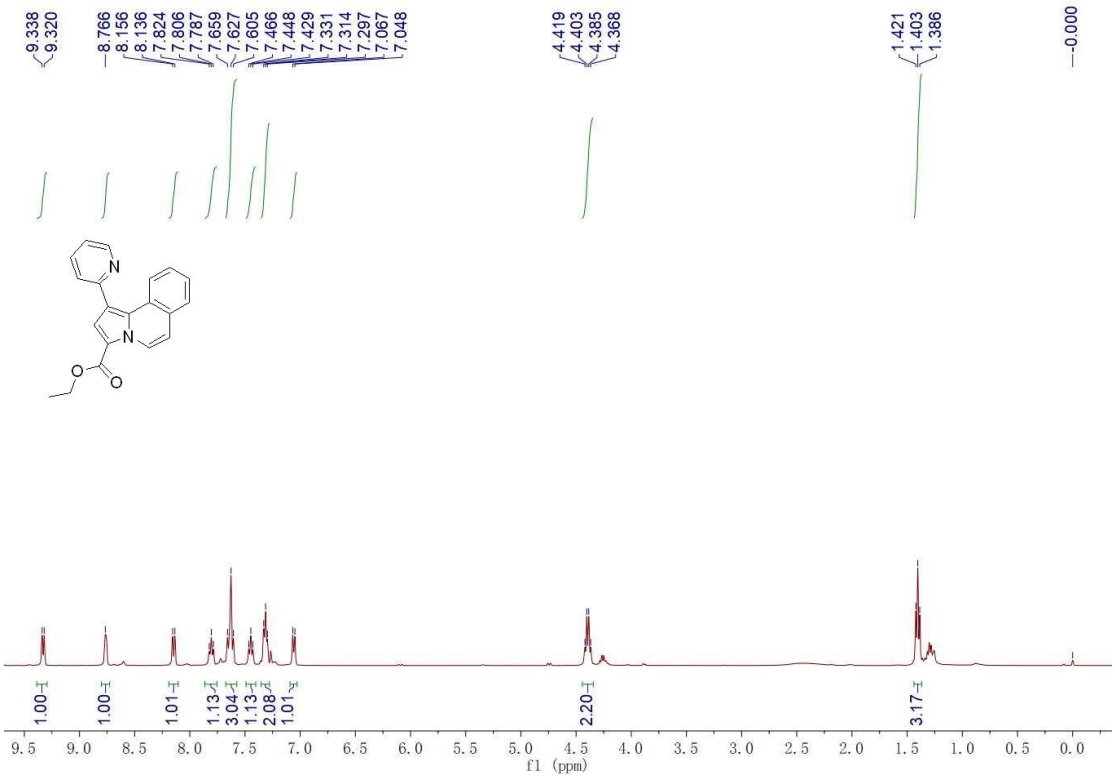


^{1}H-NMR (400 MHz, $CDCl_3$)

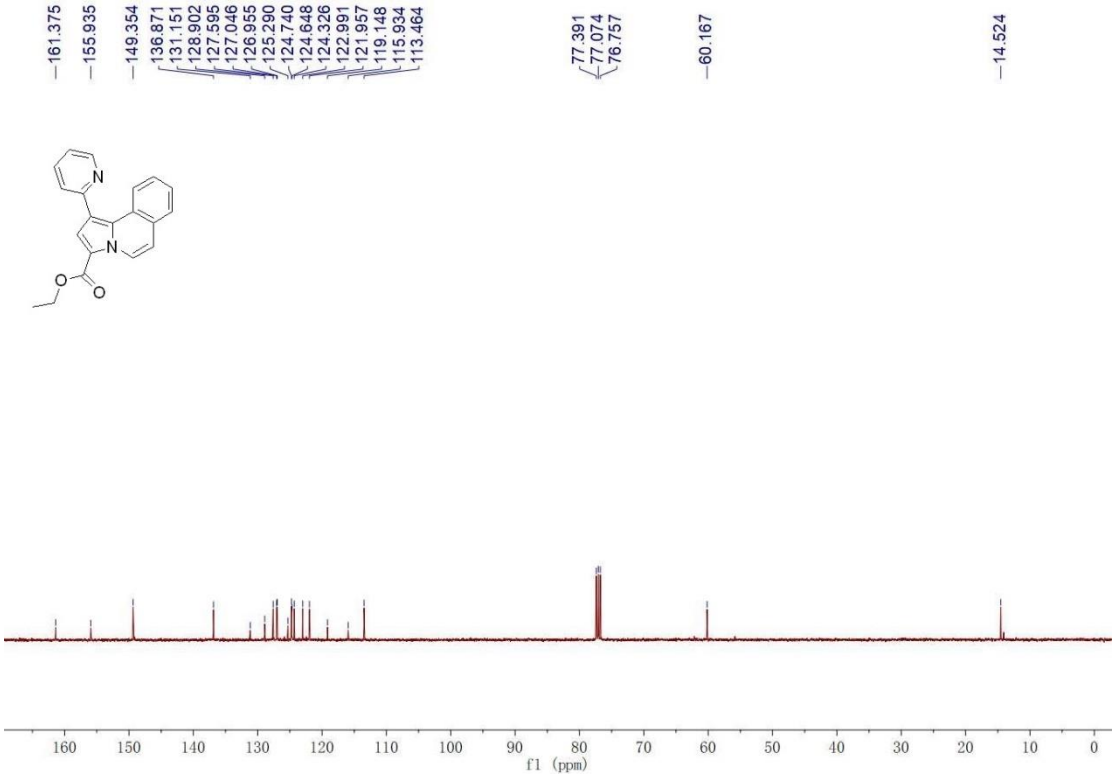


^{13}C-NMR (100 MHz, $CDCl_3$)

ethyl 1-(pyridin-2-yl)pyrrolo[2,1-a]isoquinoline-3-carboxylate (3ma)

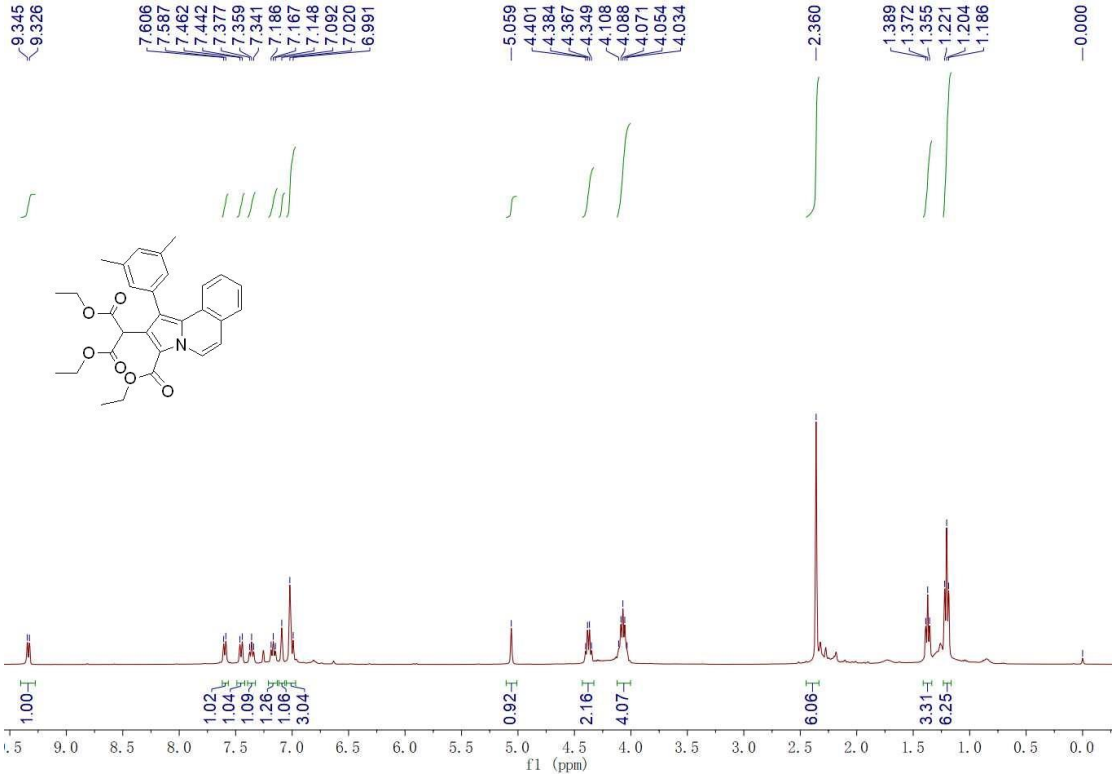


^{1}H-NMR (400 MHz, $CDCl_3$)

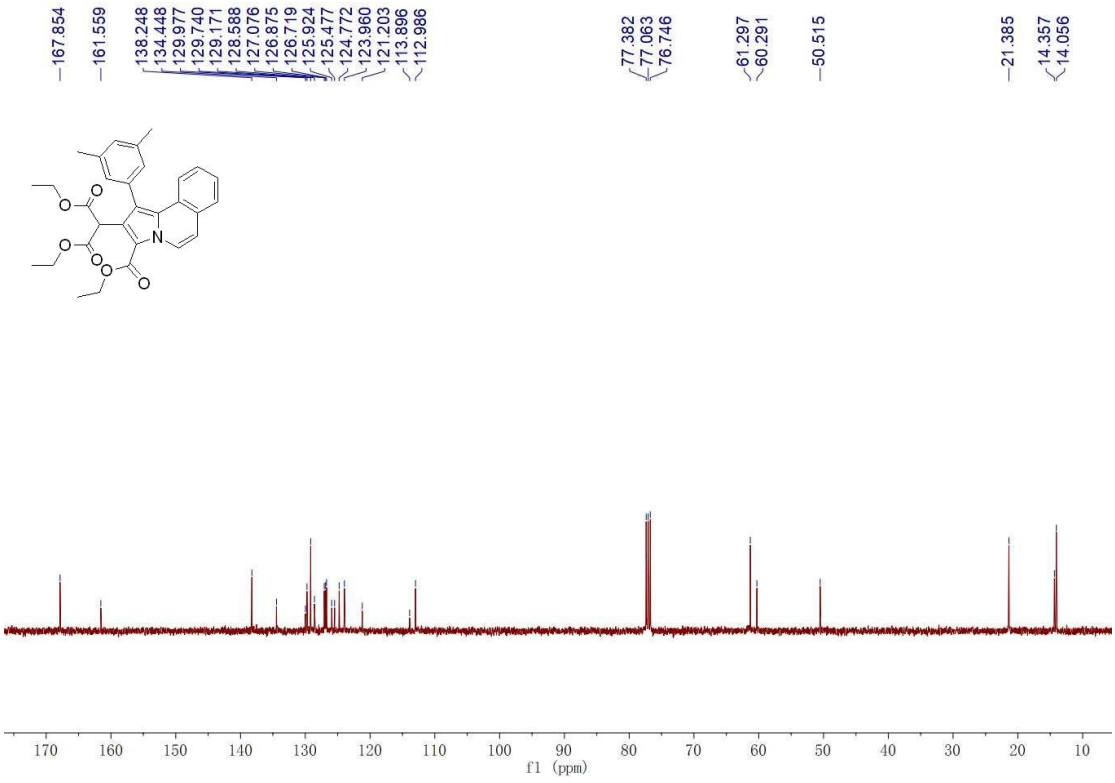


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(1-(3,5-dimethylphenyl)-3-(ethoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3na)

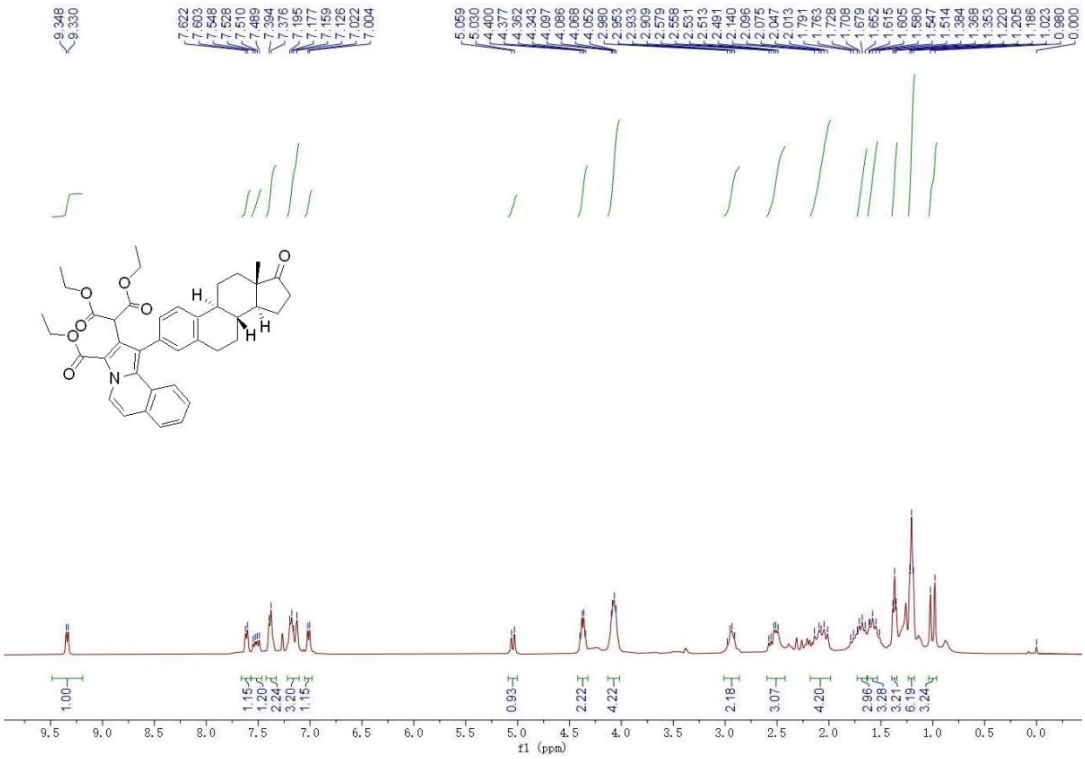


^{1}H-NMR (400 MHz, $CDCl_3$)

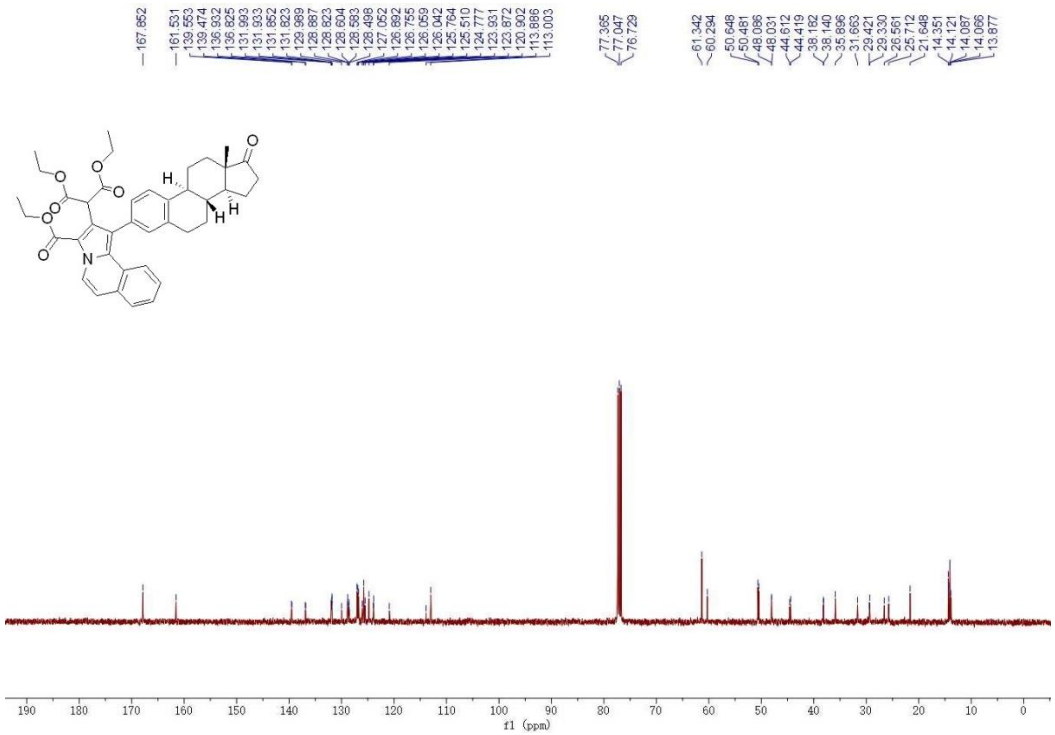


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(3-(ethoxycarbonyl)-1-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3oa)

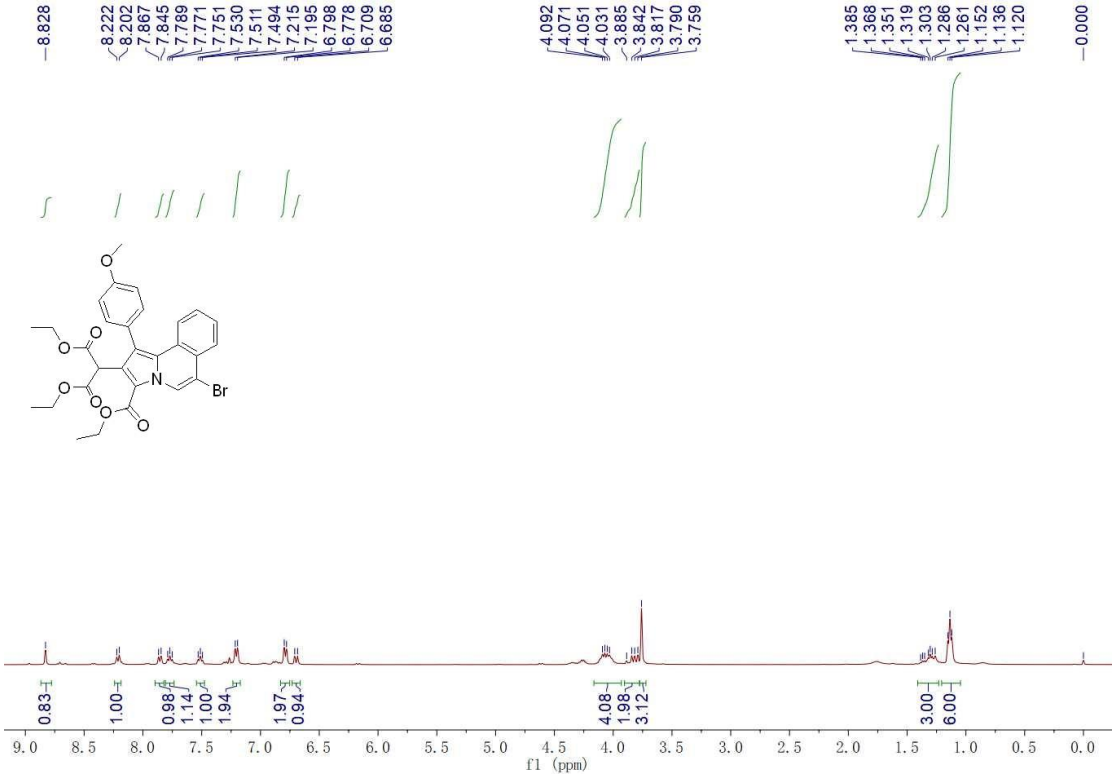


^{1}H-NMR (400 MHz, $CDCl_3$)

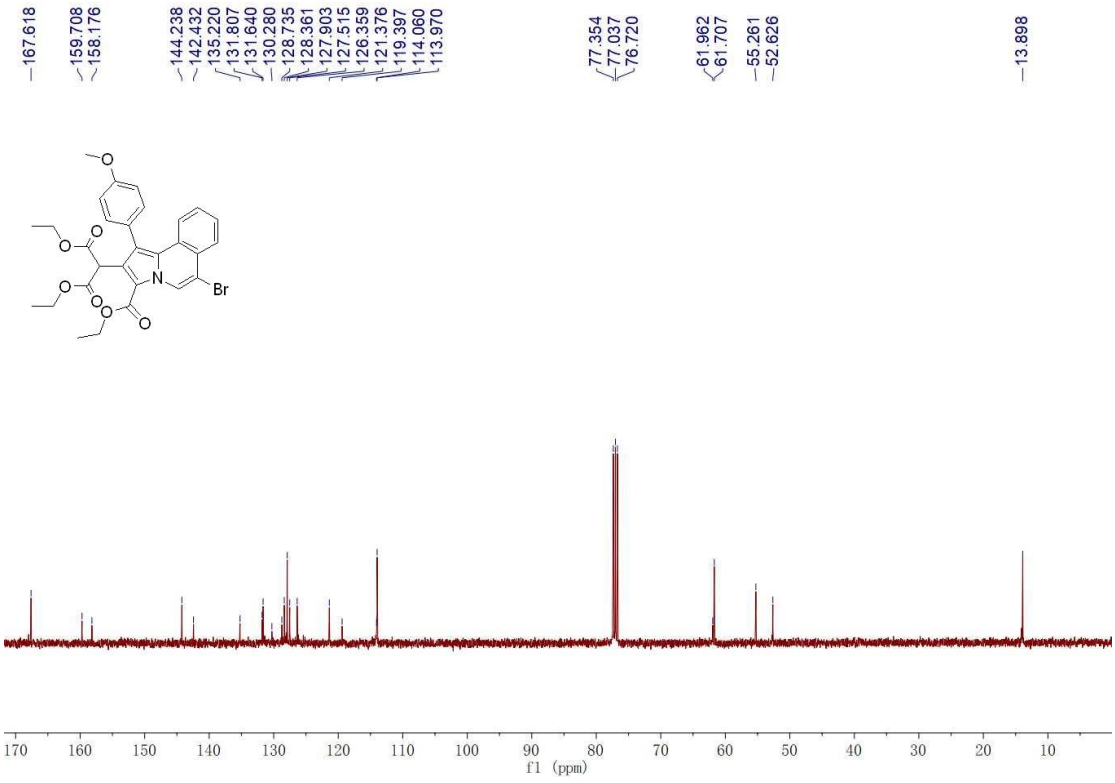


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(6-bromo-3-(ethoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ag)

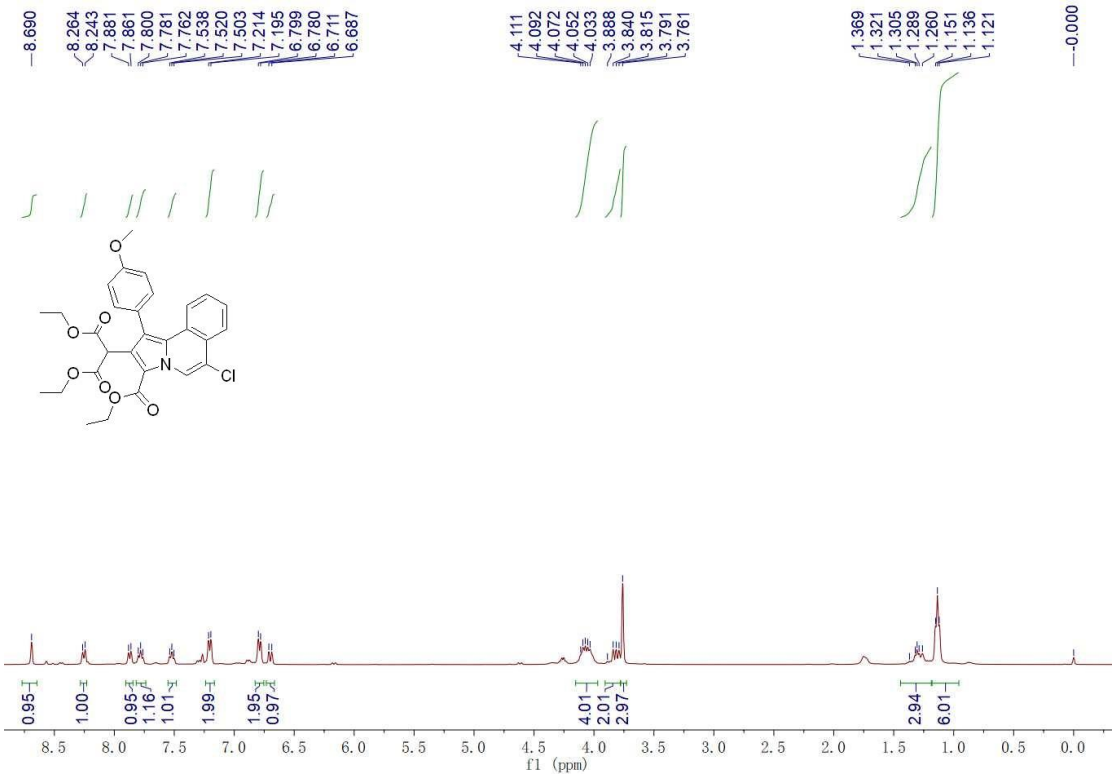


^{1}H-NMR (500 MHz, $CDCl_3$)

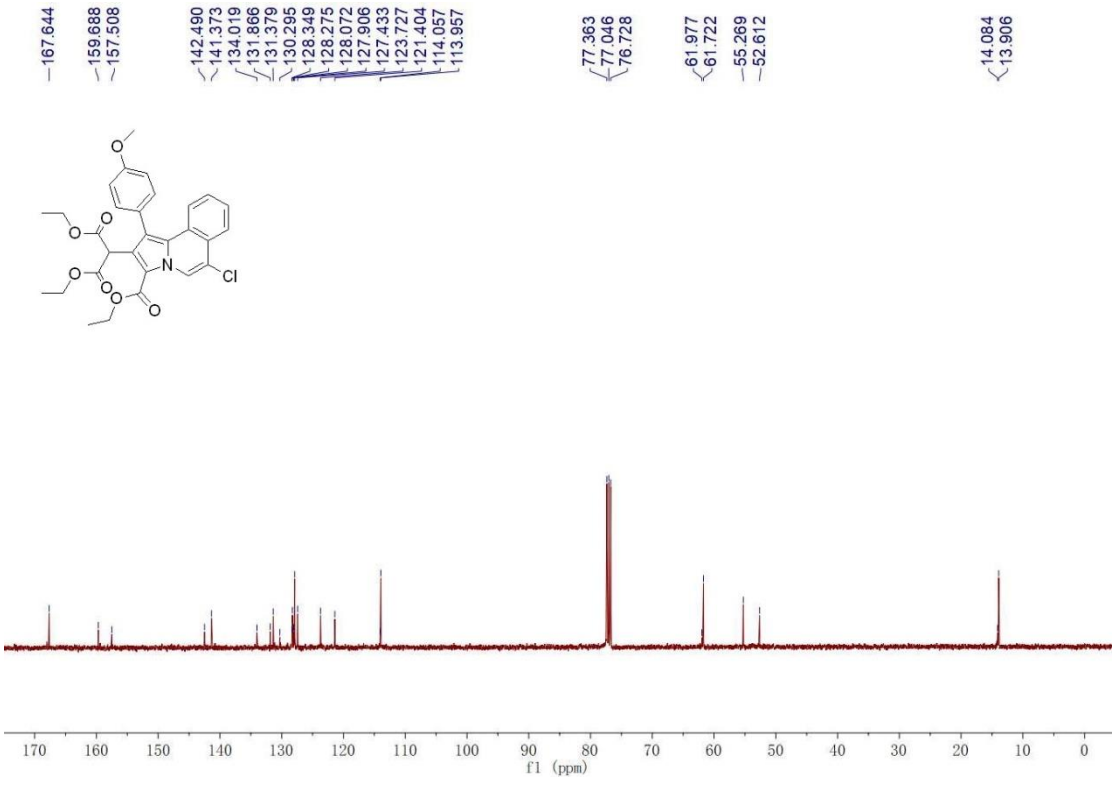


^{13}C-NMR (125 MHz, $CDCl_3$)

diethyl 2-(6-chloro-3-(ethoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ah)

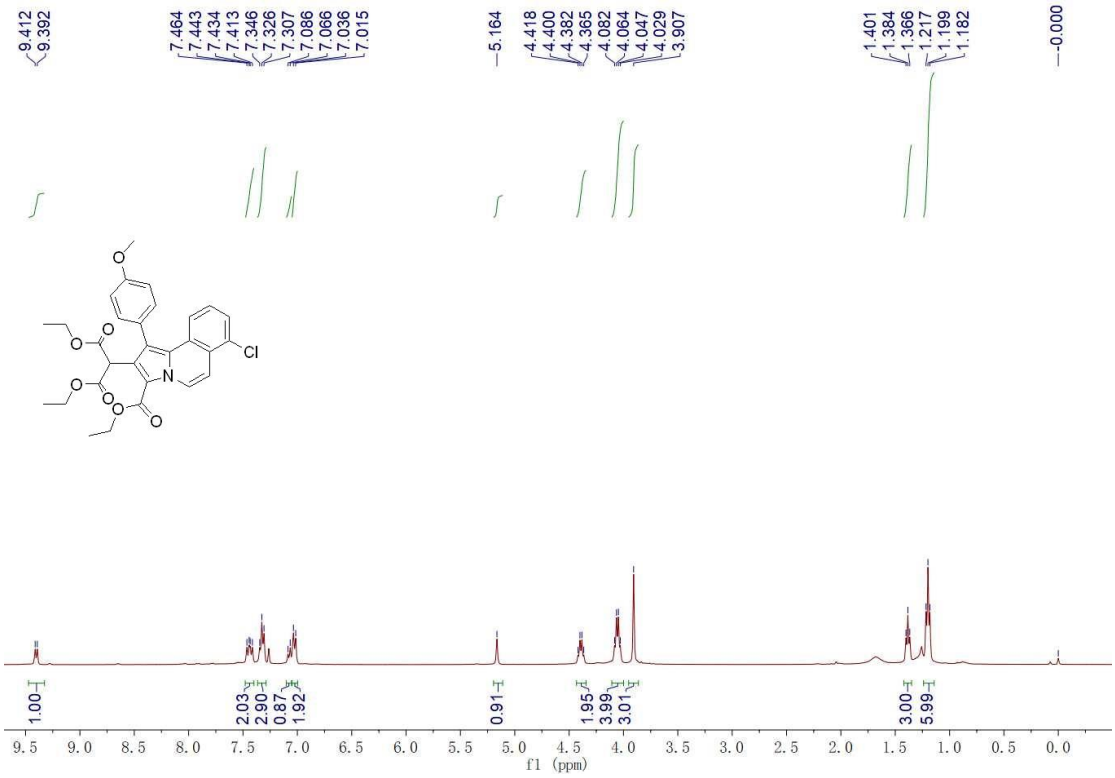


^{1}H-NMR (400 MHz, $CDCl_3$)

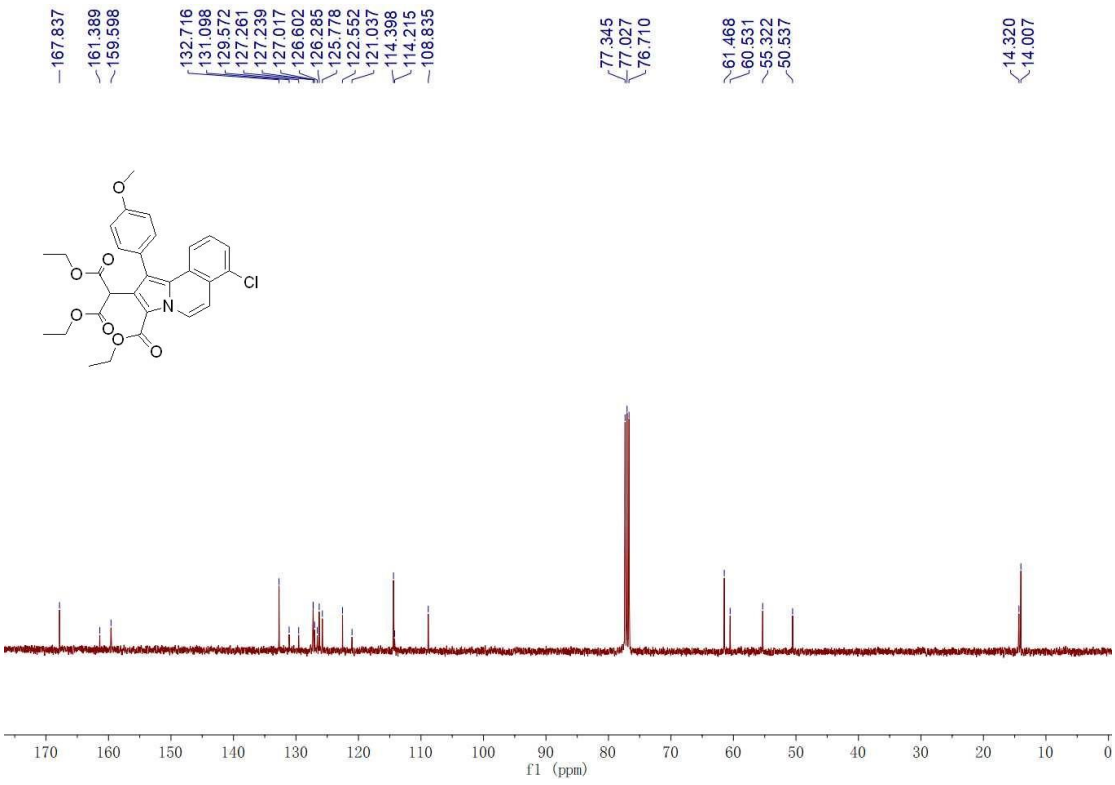


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(7-chloro-3-(ethoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ai)

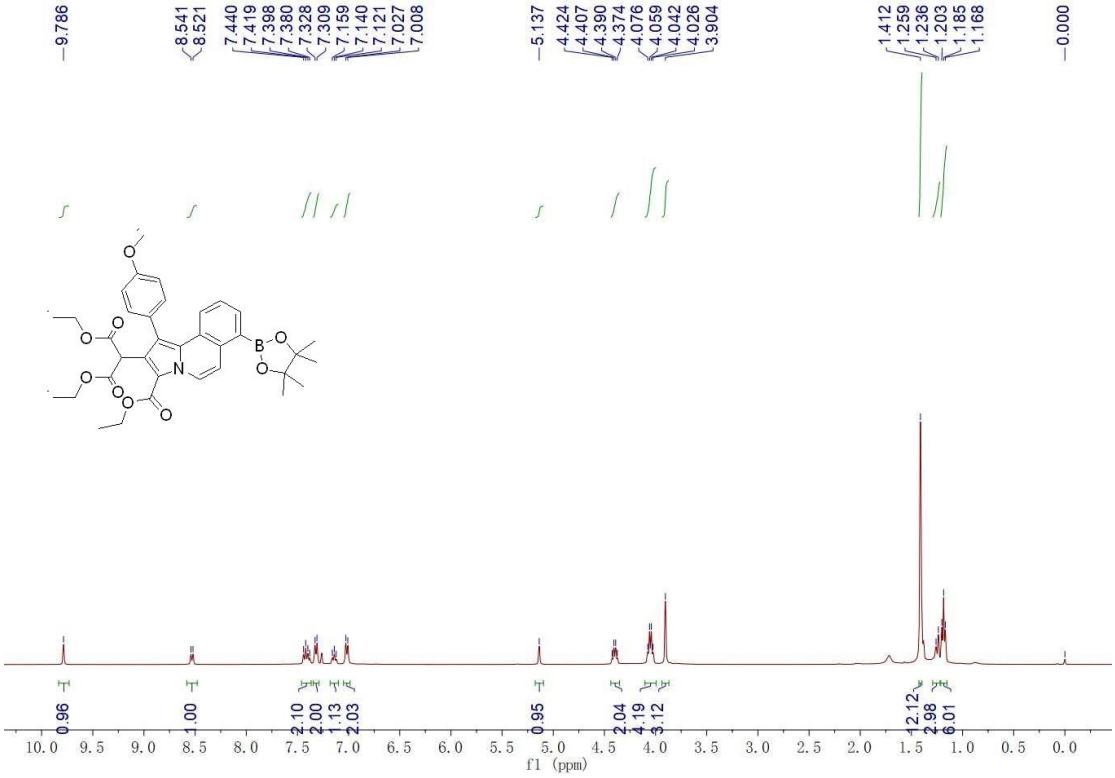


^{1}H-NMR (400 MHz, $CDCl_3$)

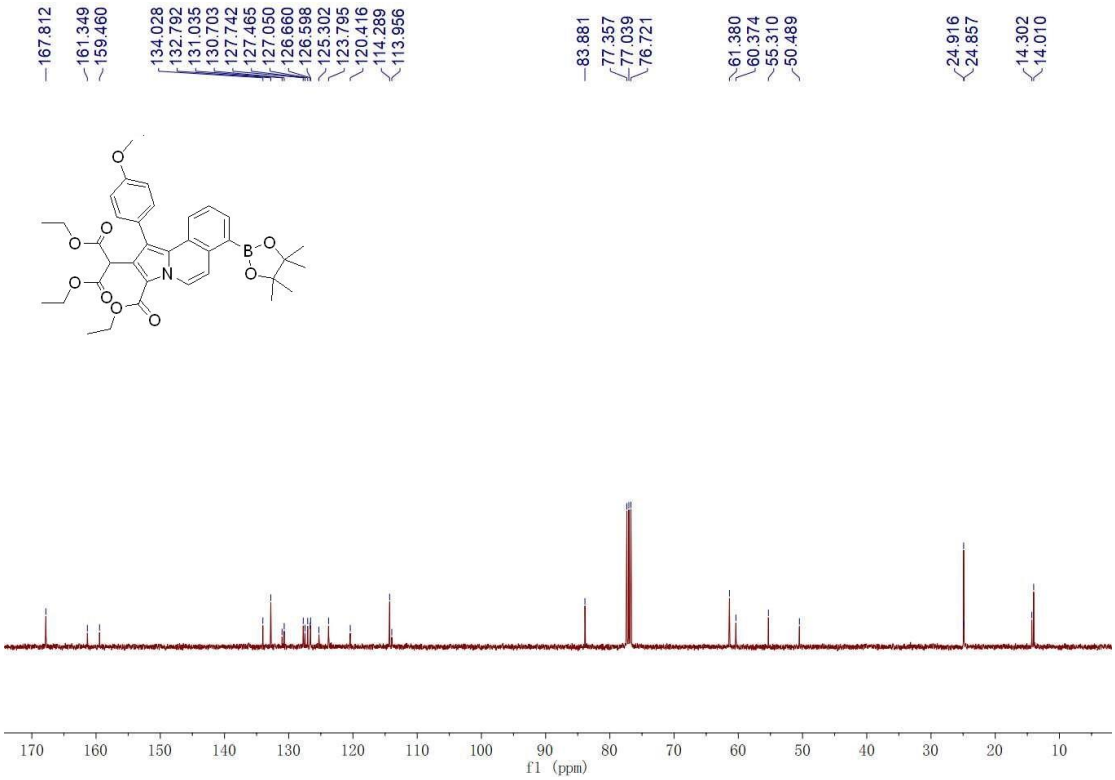


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(3-(ethoxycarbonyl)-1-(4-methoxyphenyl)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3aj)

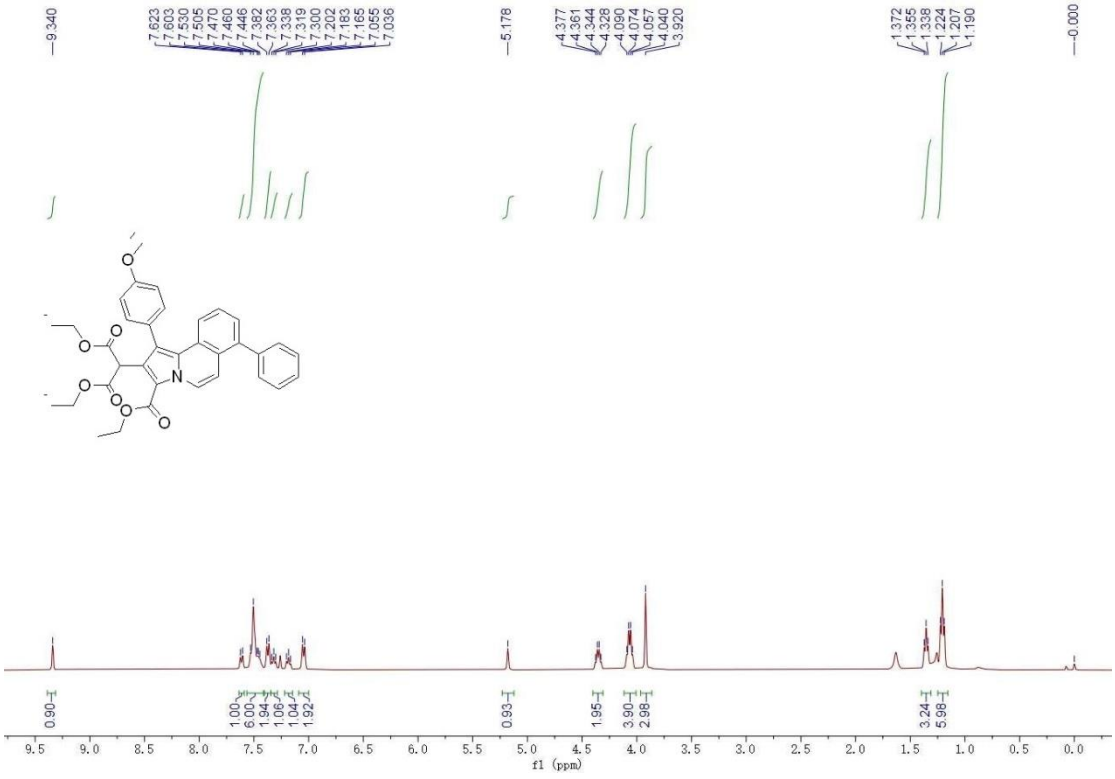


^{1}H-NMR (400 MHz, $CDCl_3$)

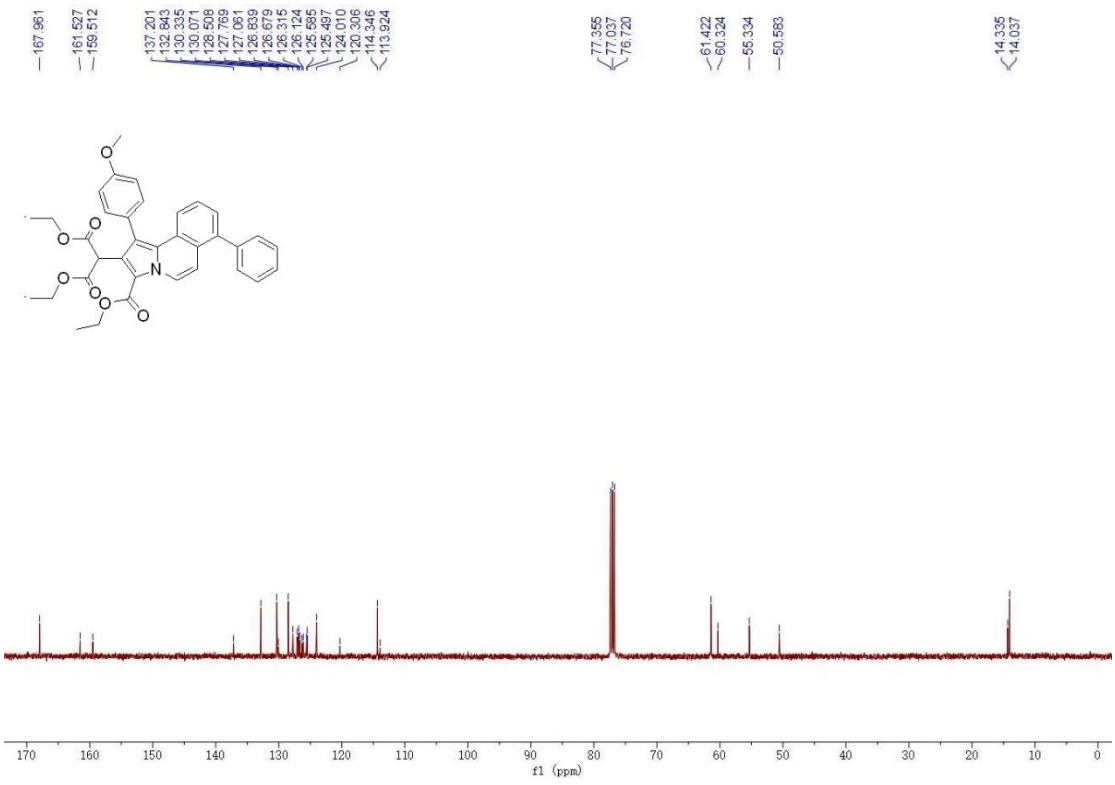


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(3-(ethoxycarbonyl)-1-(4-methoxyphenyl)-7-phenylpyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ak)

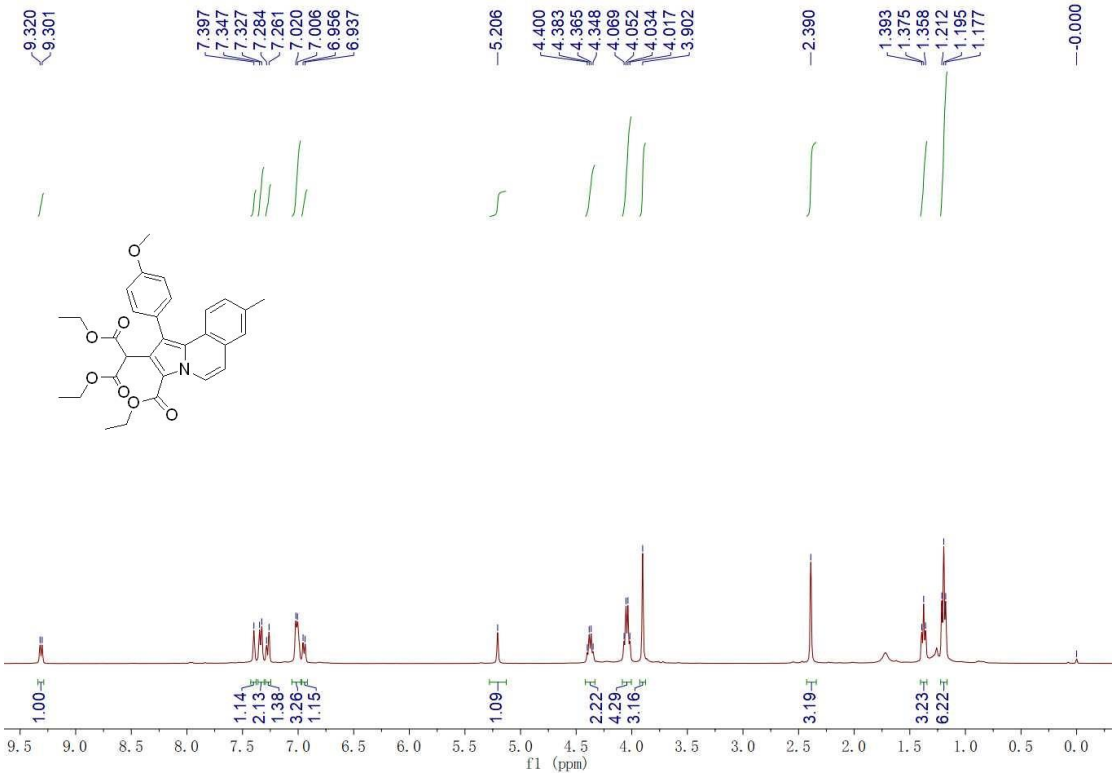


^{1}H-NMR (400 MHz, $CDCl_3$)

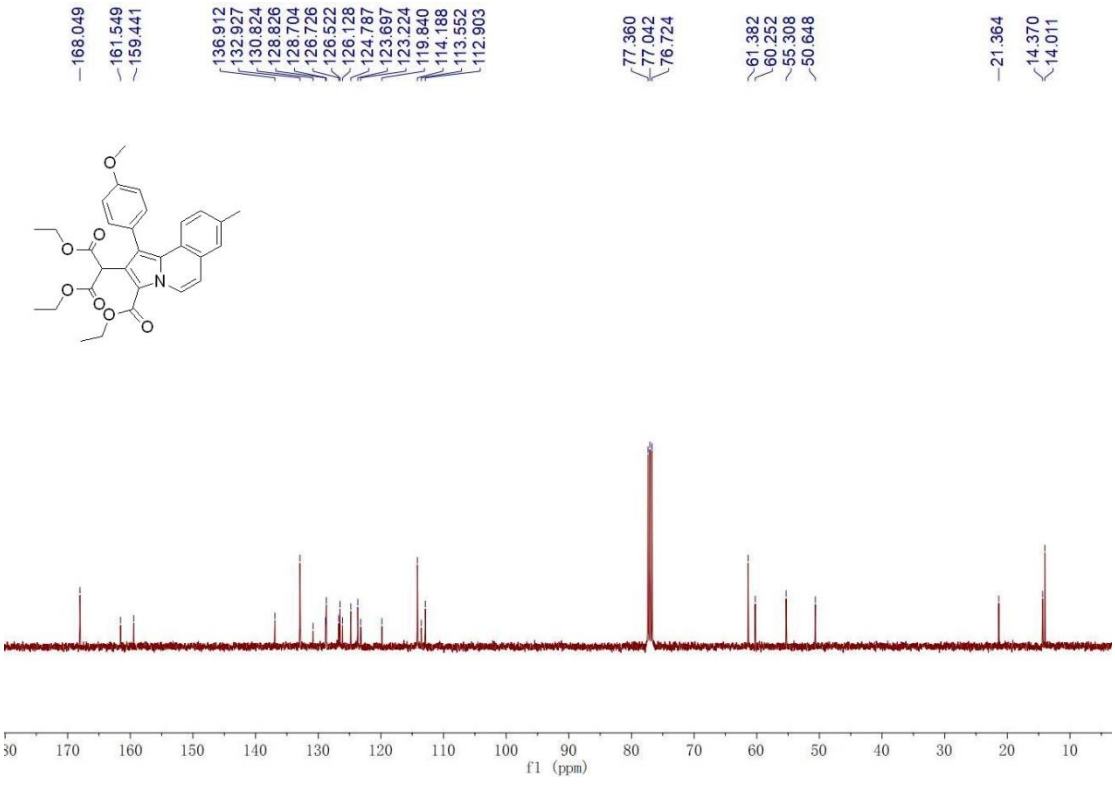


^{13}C-NMR (100 MHz, $CDCl_3$)

diethyl 2-(3-(ethoxycarbonyl)-1-(4-methoxyphenyl)-8-methylpyrrolo[2,1-a]isoquinolin-2-yl)malonate (3al)

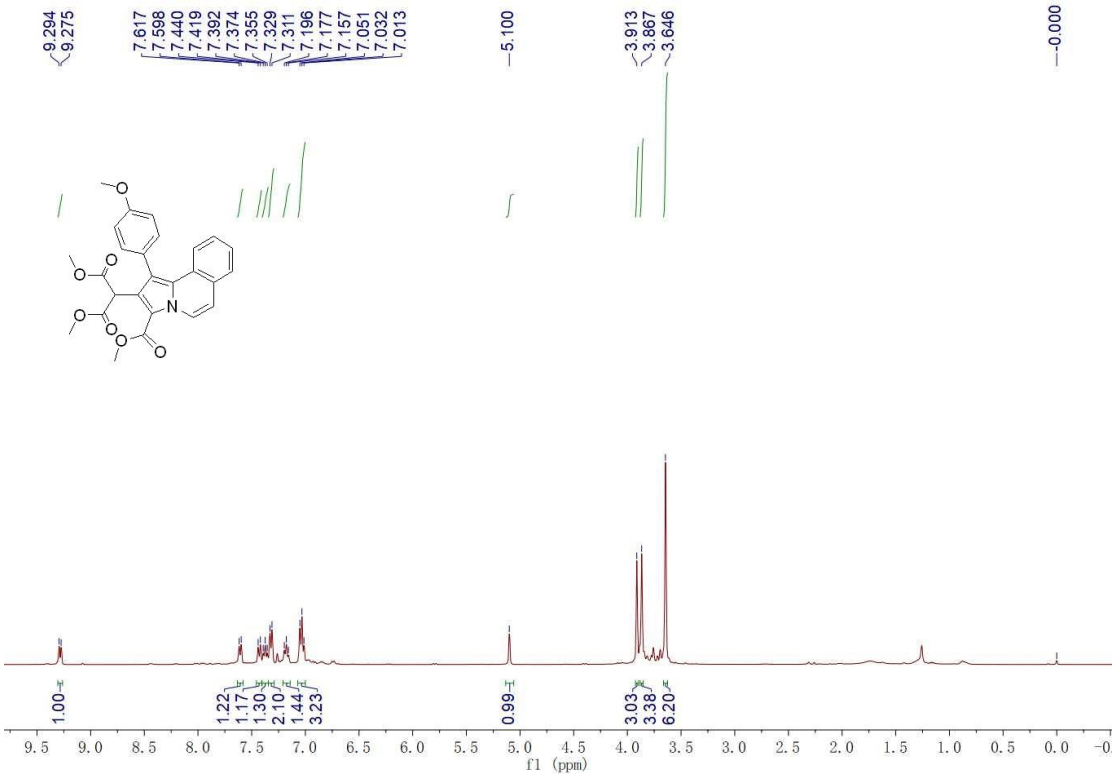


^{1}H-NMR (400 MHz, $CDCl_3$)

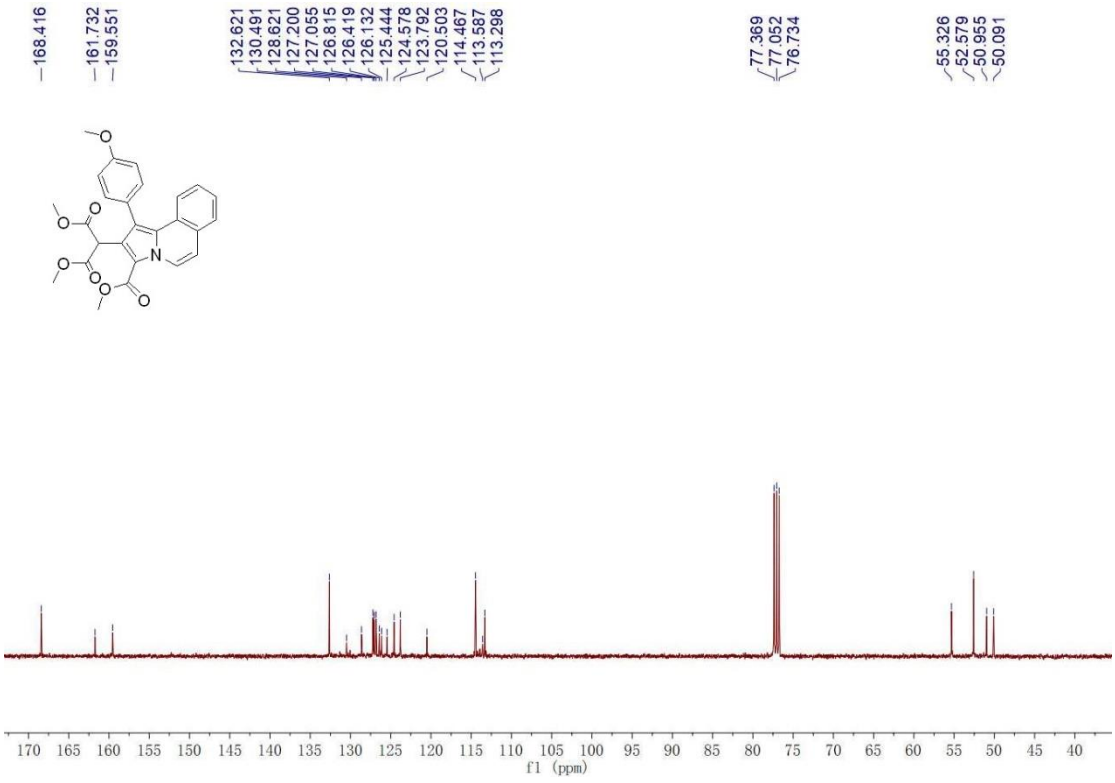


^{13}C-NMR (100 MHz, $CDCl_3$)

dimethyl 2-(3-(methoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3am)

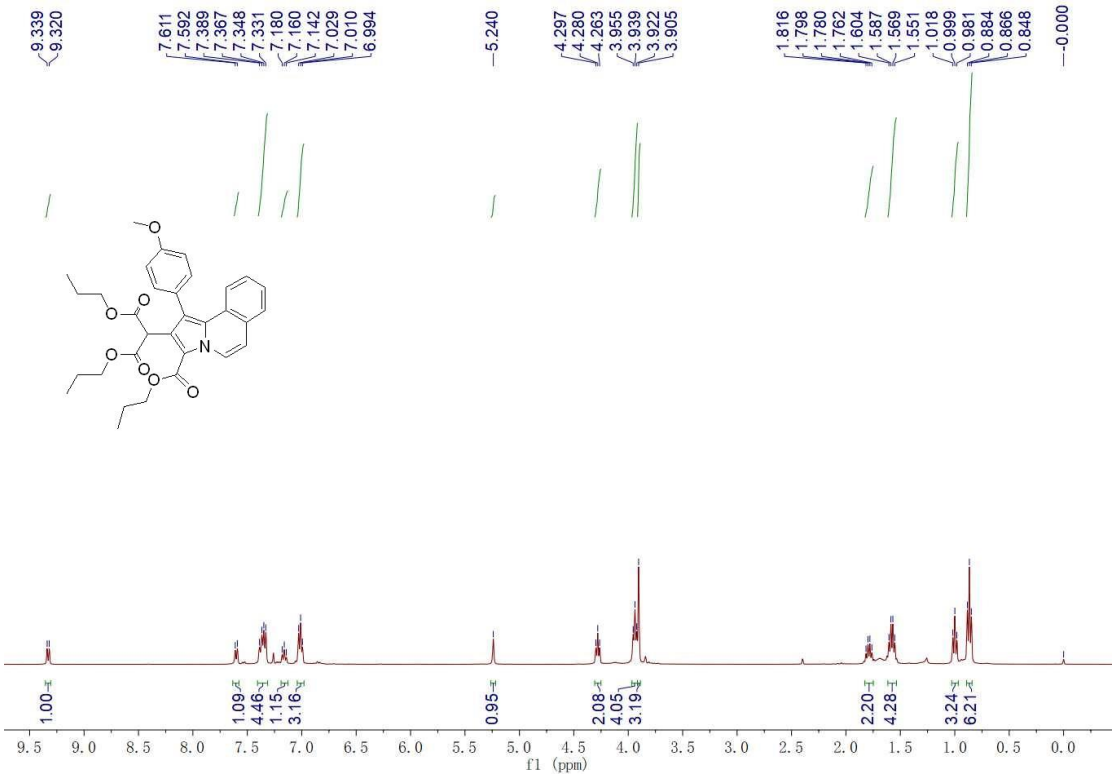


^{1}H-NMR (400 MHz, $CDCl_3$)

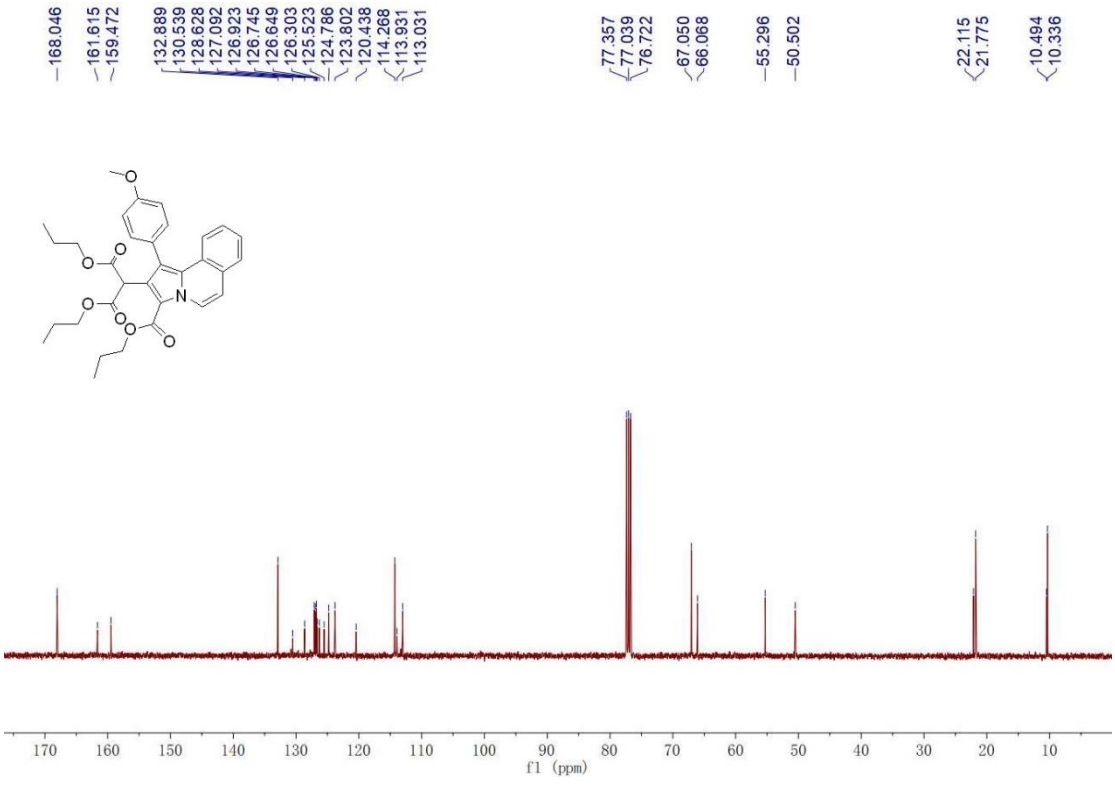


^{13}C-NMR (100 MHz, $CDCl_3$)

dipropyl 2-(1-(4-methoxyphenyl)-3-(propoxycarbonyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3an)

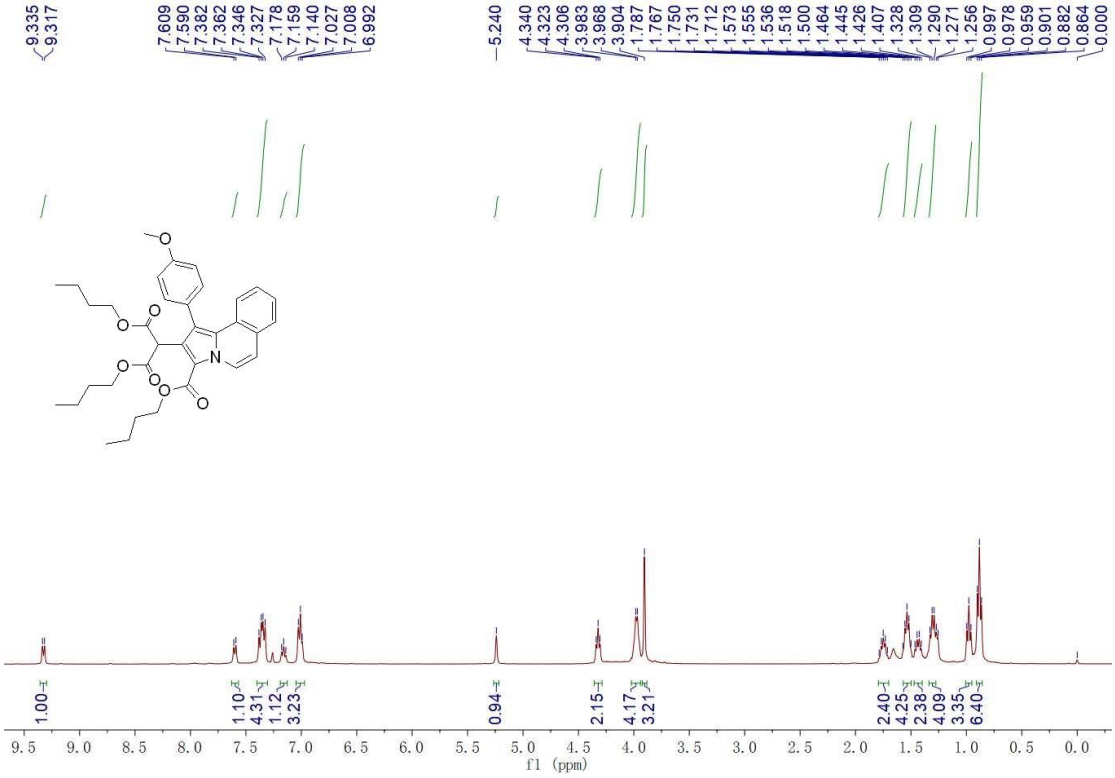


^{1}H-NMR (400 MHz, $CDCl_3$)

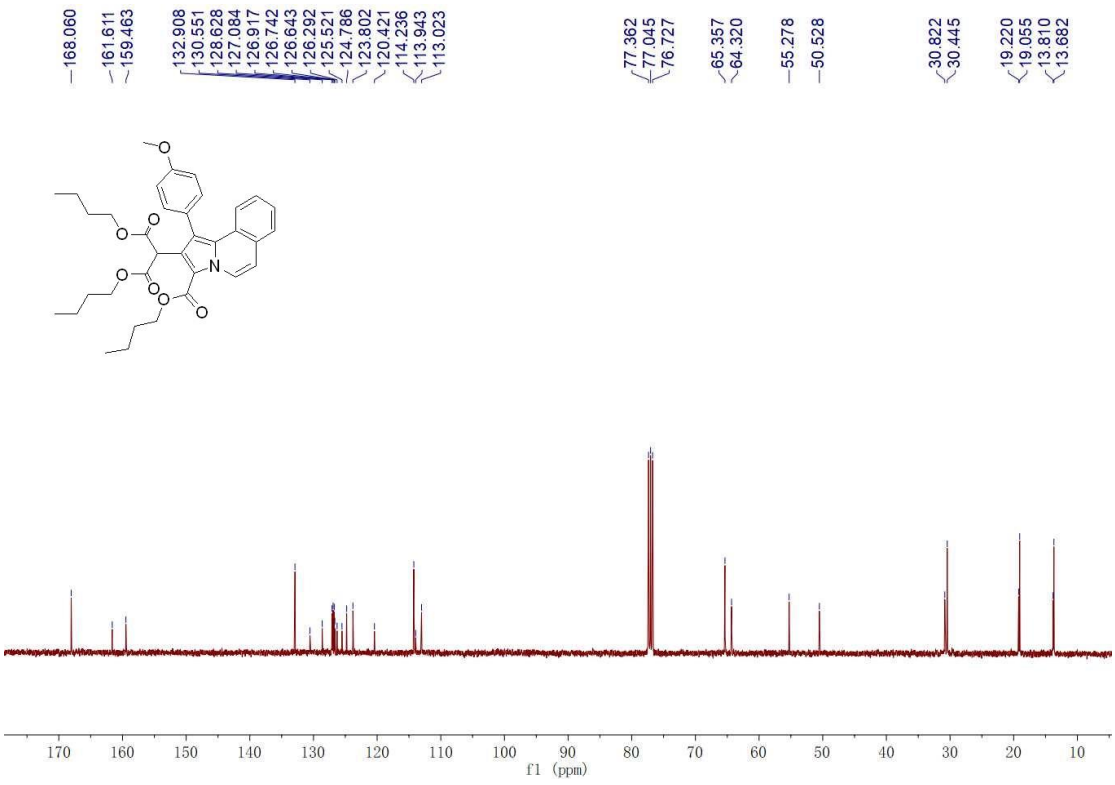


^{13}C-NMR (100 MHz, $CDCl_3$)

dibutyl 2-(3-(butoxycarbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ao)

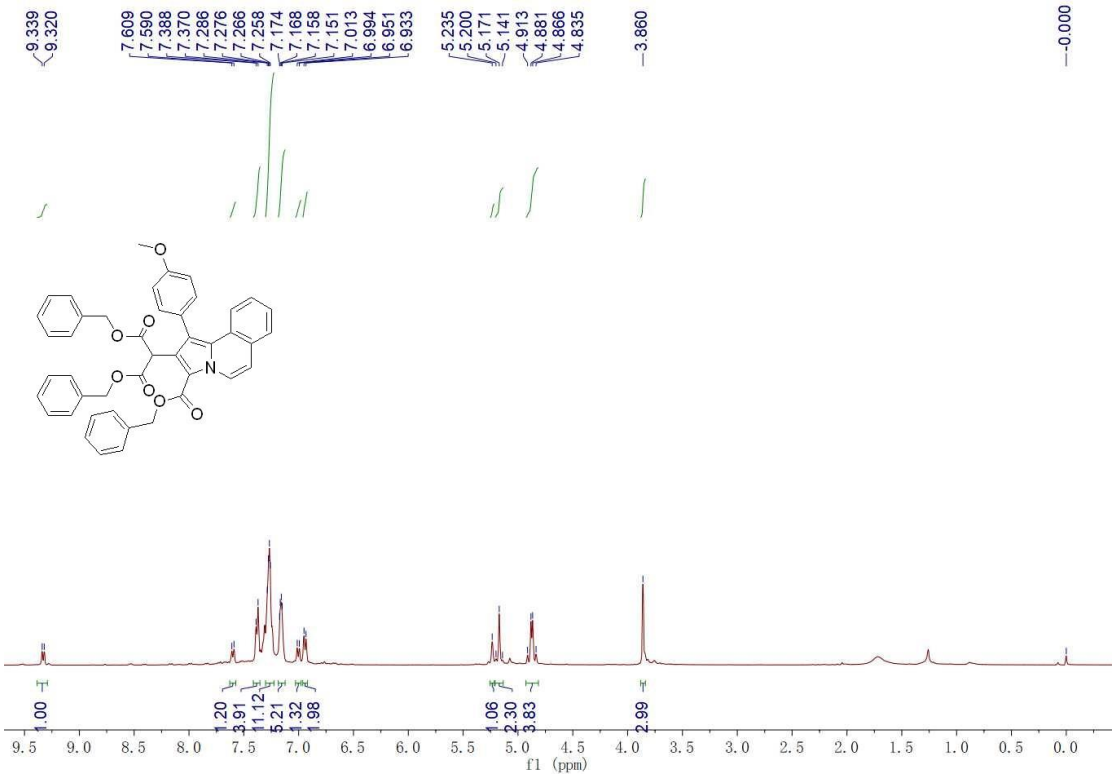


^{1}H-NMR (400 MHz, $CDCl_3$)

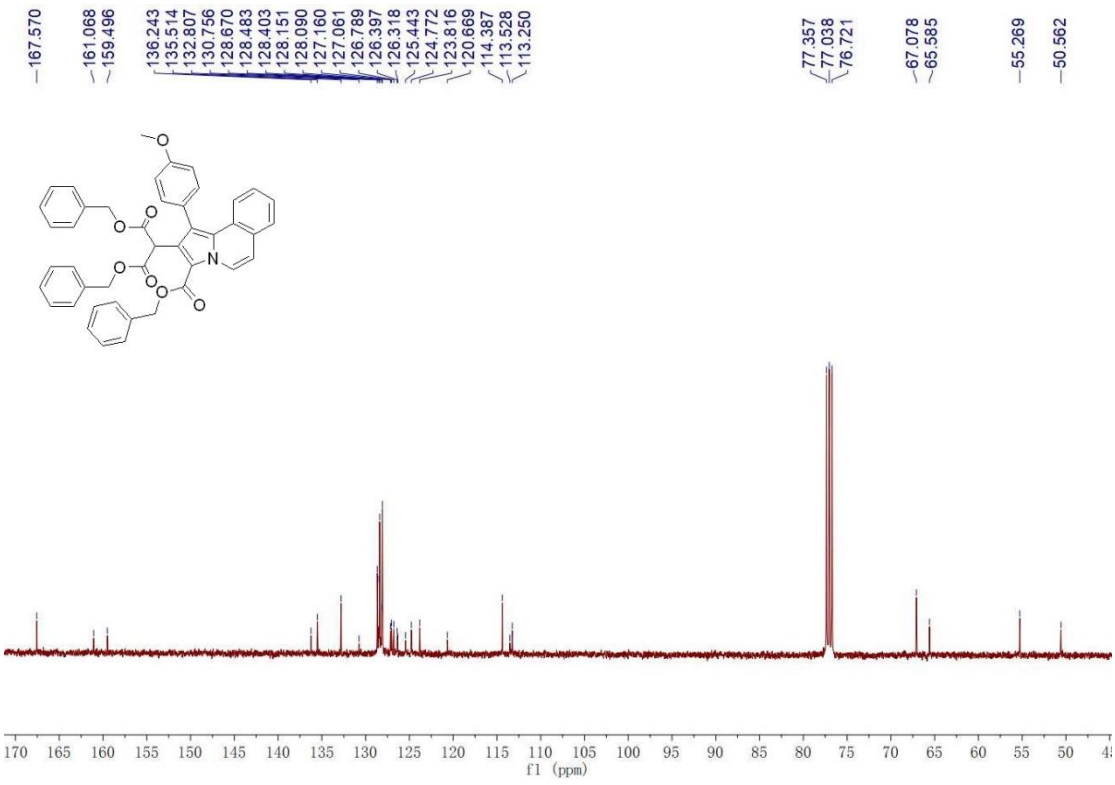


^{13}C-NMR (100 MHz, $CDCl_3$)

dibenzyl 2-(3-((benzyloxy)carbonyl)-1-(4-methoxyphenyl)pyrrolo[2,1-a]isoquinolin-2-yl)malonate (3ap)

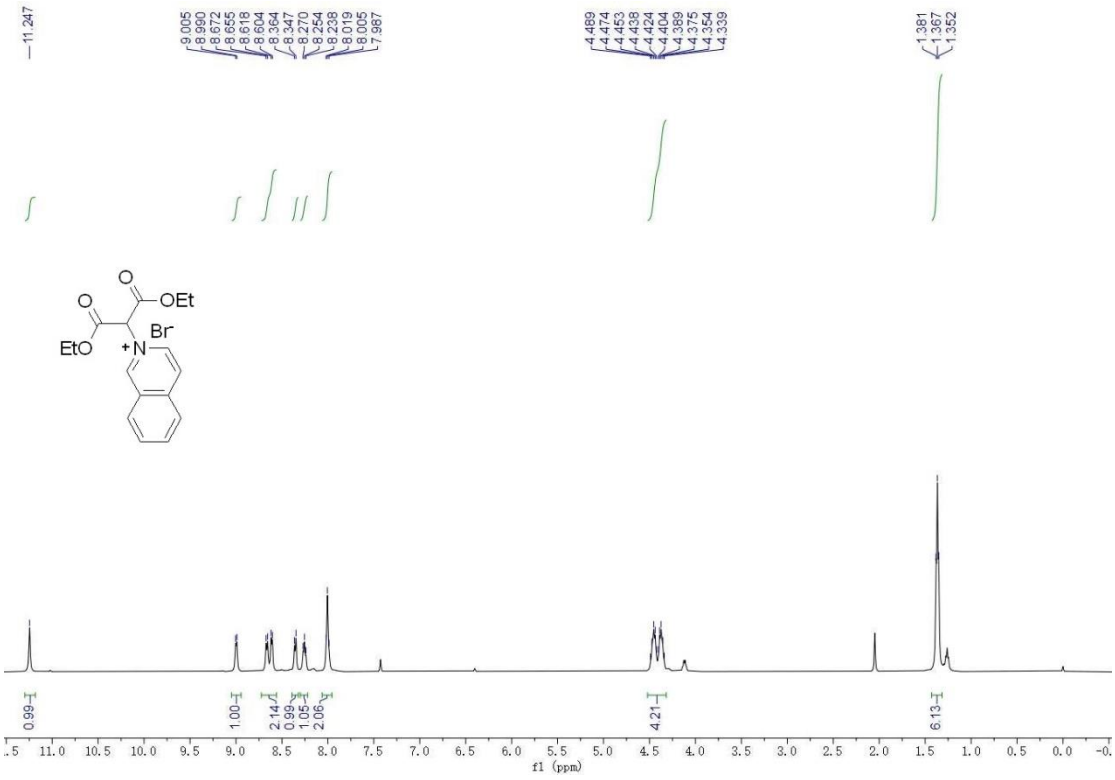


^{1}H-NMR (400 MHz, $CDCl_3$)

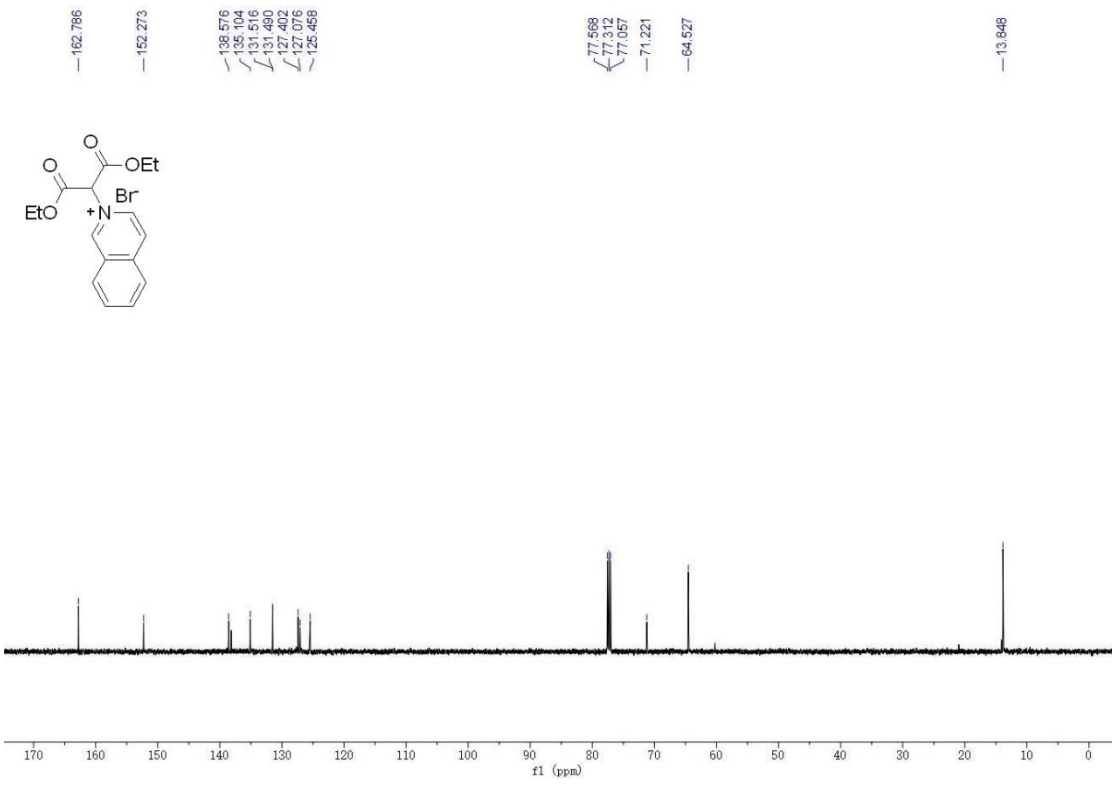


^{13}C-NMR (100 MHz, $CDCl_3$)

2-(1,3-diethoxy-1,3-dioxopropan-2-yl)isoquinolin-2-ium bromide (2a)

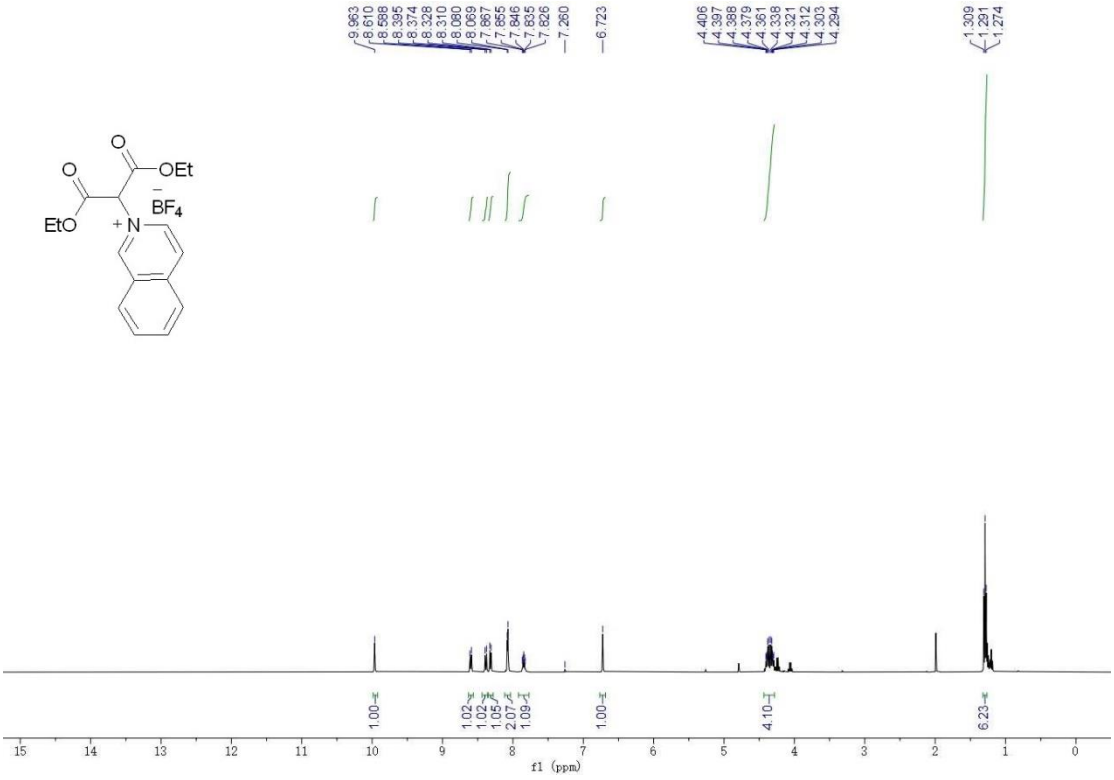


^{1}H-NMR (500 MHz, $CDCl_3$)

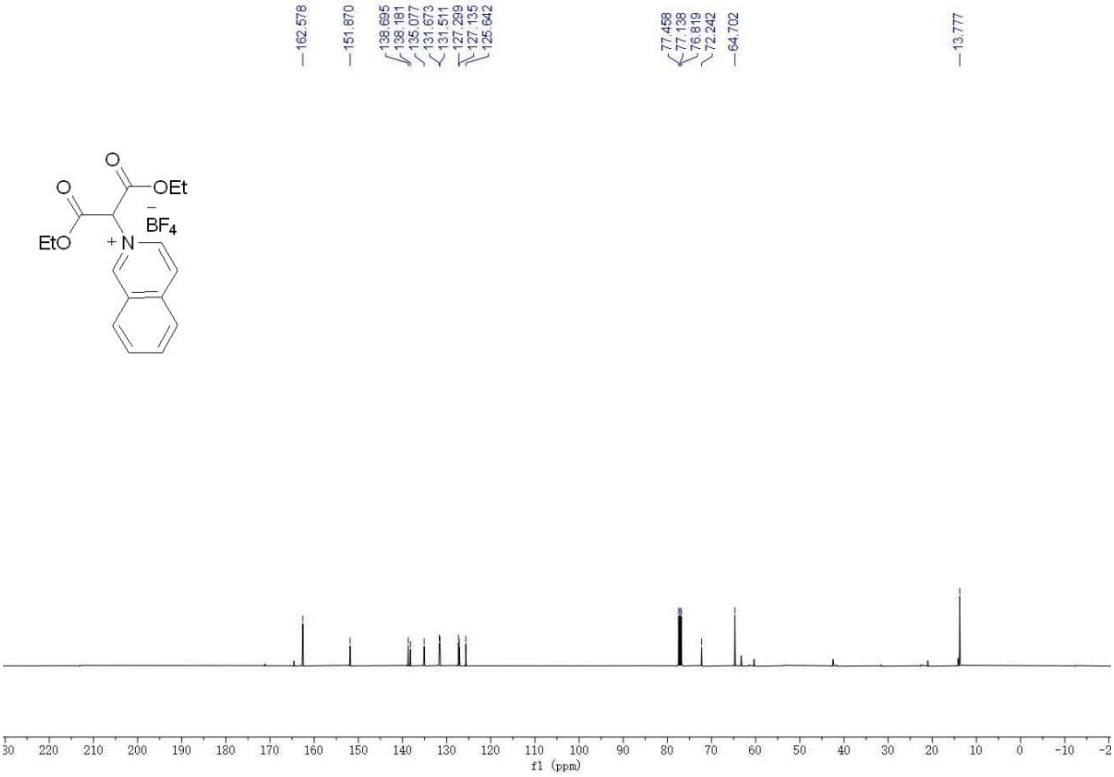


^{13}C-NMR (125 MHz, $CDCl_3$)

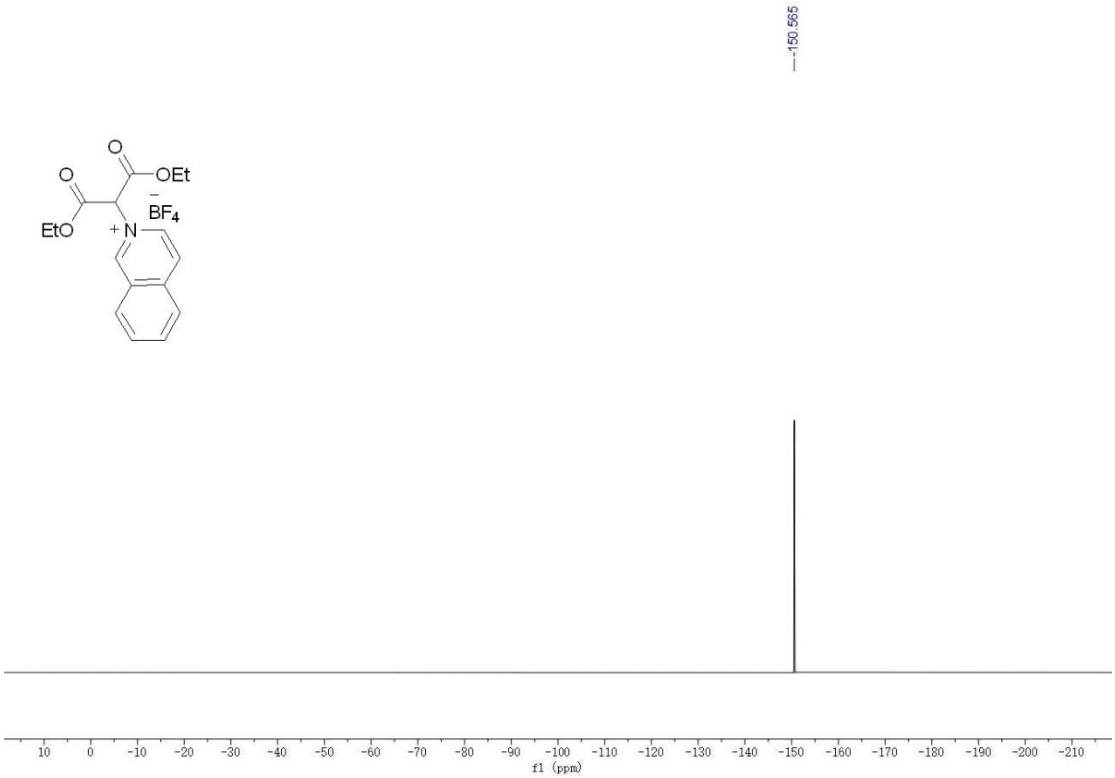
2-(1,3-diethoxy-1,3-dioxopropan-2-yl)isoquinolin-2-ium tetrafluoroborate (2b)



^{1}H-NMR (400 MHz, $CDCl_3$)

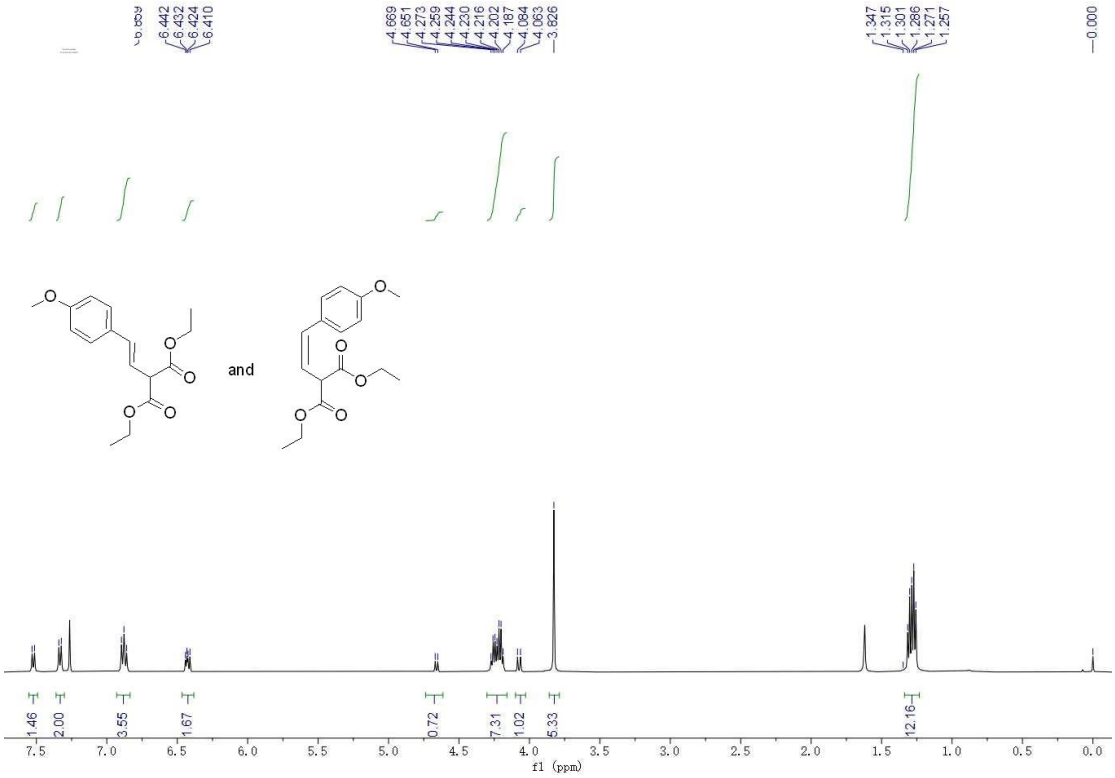


^{13}C-NMR (100 MHz, $CDCl_3$)

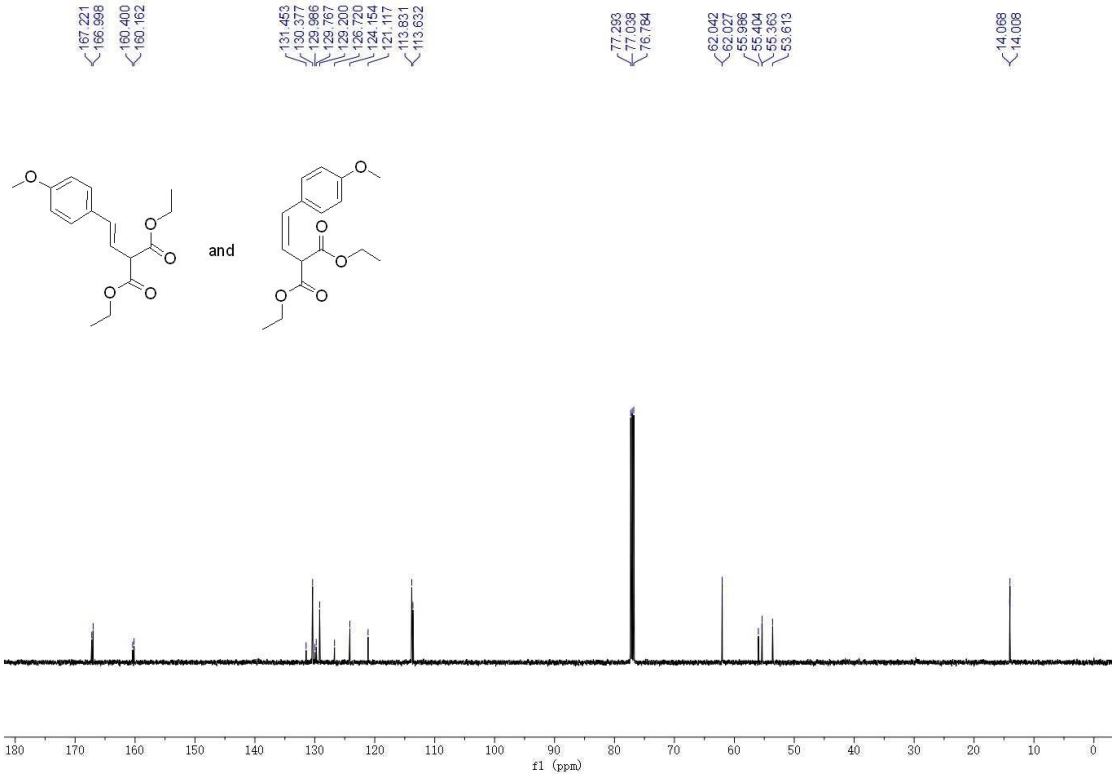


^{9}F NMR (376 MHz, $CDCl_3$)

diethyl 2-(4-methoxystyryl)malonate (4aa)

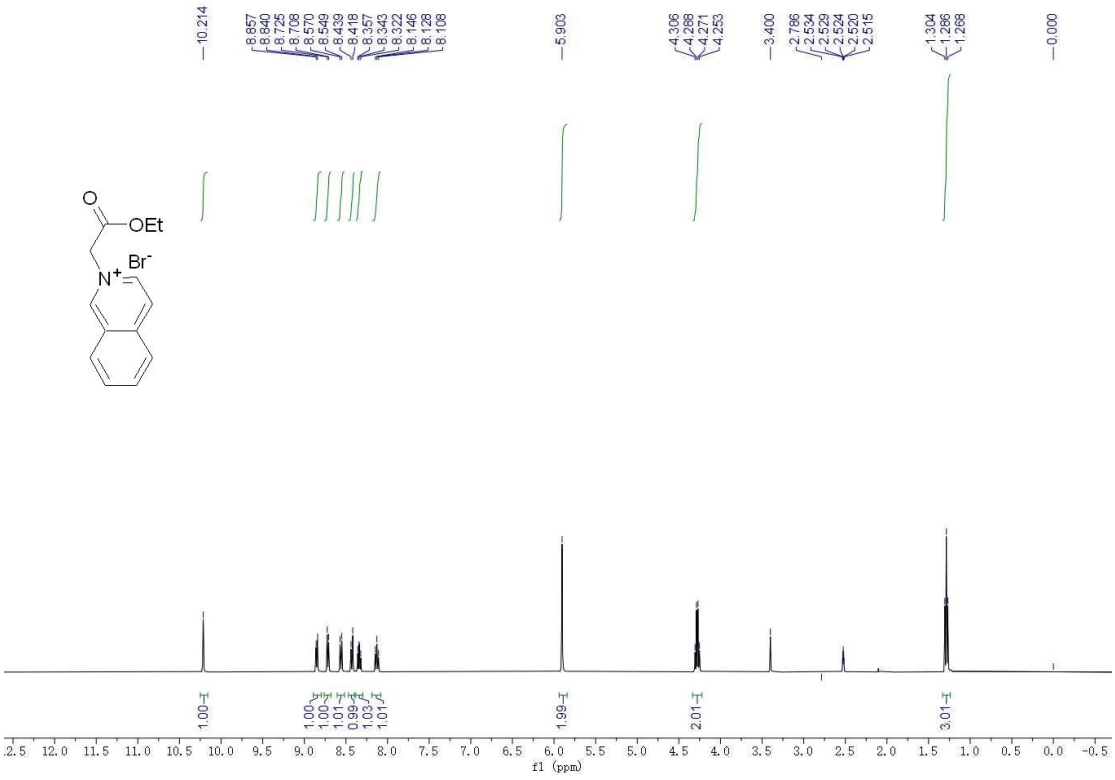


^{1}H-NMR (500 MHz, $CDCl_3$)

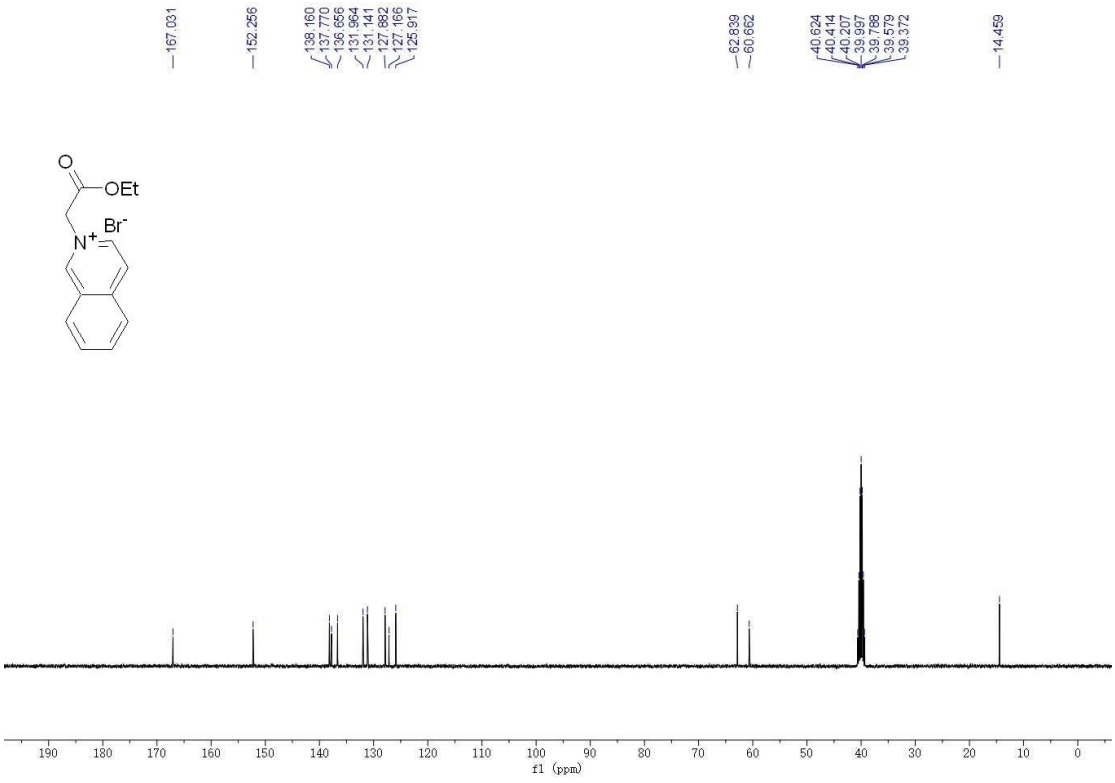


^{13}C-NMR (125 MHz, $CDCl_3$)

2-(2-ethoxy-2-oxoethyl)isoquinolin-2-ium bromide (5aa)



^{1}H-NMR (400 MHz, DMSO-d6)



^{13}C-NMR (100 MHz, DMSO-d6)

(D) The X-ray Single-Crystal Diffraction Analysis of 3ja (CCDC 2179830)

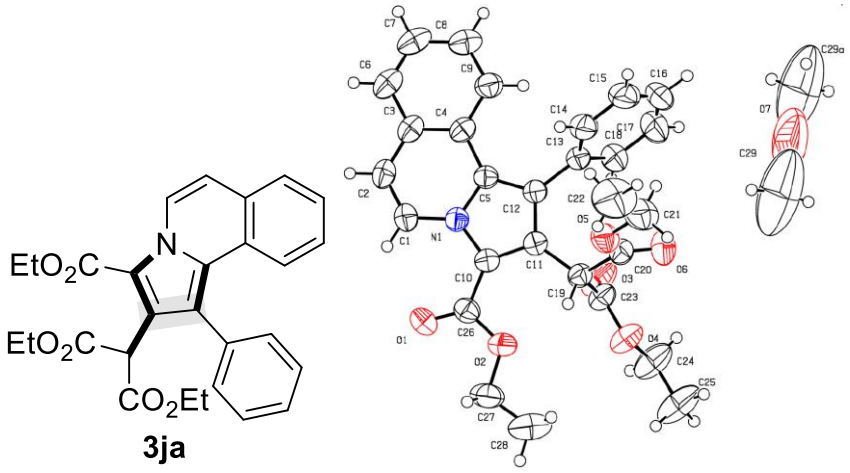


Table S1. Crystal data and structure refinement for A.

Identification code	a
Empirical formula	C29 H30 N O6.50
Formula weight	496.54
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.9999(14) A alpha = 93.793(2) deg.
	b = 11.2884(18) A beta = 102.953(2) deg.
	c = 14.212(2) A gamma = 96.345(2) deg.
Volume	1392.3(4) A^3
Z, Calculated density	2, 1.184 Mg/m^3
Absorption coefficient	0.084 mm^-1
F(000)	526
Crystal size	0.16 x 0.14 x 0.12 mm
Theta range for data collection	2.24 to 25.50 deg.
Limiting indices	-10<=h<=10, -13<=k<=13, -17<=l<=17
Reflections collected / unique	10857 / 5152 [R(int) = 0.0198]
Completeness to theta = 25.50	99.2 %

Absorption correction	None
Max. and min. transmission	0.9900 and 0.9867
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5152 / 1 / 335
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0675, wR2 = 0.2243
R indices (all data)	R1 = 0.0871, wR2 = 0.2494
Largest diff. peak and hole	0.695 and -0.286 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for A.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	2834(3)	4151(2)	10477(2)	51(1)
C(2)	2195(3)	4540(3)	11184(2)	55(1)
C(3)	1526(3)	5620(2)	11170(2)	50(1)
C(4)	1572(3)	6332(2)	10392(2)	46(1)
C(5)	2293(3)	5913(2)	9640(2)	42(1)
C(6)	798(3)	6002(3)	11896(2)	64(1)
C(7)	150(4)	7030(3)	11861(2)	69(1)
C(8)	195(3)	7729(3)	11092(2)	66(1)
C(9)	888(3)	7388(3)	10374(2)	56(1)
C(10)	3433(3)	4567(2)	8882(2)	44(1)
C(11)	3247(3)	5530(2)	8320(2)	43(1)
C(12)	2540(3)	6372(2)	8787(2)	44(1)
C(13)	2156(3)	7535(2)	8451(2)	50(1)
C(14)	2978(4)	8598(3)	8934(2)	65(1)
C(15)	2613(5)	9691(3)	8618(3)	87(1)
C(16)	1448(6)	9715(4)	7816(3)	96(1)
C(17)	623(5)	8668(4)	7330(3)	91(1)
C(18)	974(4)	7585(3)	7643(2)	67(1)
C(19)	3728(3)	5630(2)	7375(2)	46(1)
C(20)	4207(3)	6895(3)	7152(2)	54(1)
C(21)	5975(5)	8652(3)	7705(3)	88(1)

C(22)	7216(6)	9098(4)	8586(4)	123(2)
C(23)	2513(3)	5012(3)	6508(2)	55(1)
C(24)	2116(4)	4177(4)	4884(2)	92(1)
C(25)	3019(5)	3947(5)	4184(3)	114(2)
C(26)	4006(3)	3431(2)	8714(2)	49(1)
C(27)	4970(4)	2244(3)	7605(3)	78(1)
C(28)	5183(9)	2241(6)	6639(4)	159(3)
N(1)	2861(2)	4819(2)	9697(1)	43(1)
O(1)	4147(3)	2656(2)	9262(2)	74(1)
O(2)	4346(3)	3317(2)	7846(2)	67(1)
O(3)	1163(2)	4845(2)	6473(2)	82(1)
O(4)	3147(2)	4695(2)	5792(1)	68(1)
O(5)	5407(2)	7428(2)	7834(2)	63(1)
O(6)	3636(3)	7335(2)	6439(2)	81(1)
O(7)	0	10000	5000	280(7)
C(29)	1338(15)	9254(14)	4832(7)	341(10)

Table S3. Bond lengths [A] and angles [deg] for A.

C(1)-C(2)	1.338(4)
C(1)-N(1)	1.385(3)
C(1)-H(1)	0.9300
C(2)-C(3)	1.417(4)
C(2)-H(2)	0.9300
C(3)-C(6)	1.409(4)
C(3)-C(4)	1.416(4)
C(4)-C(9)	1.399(4)
C(4)-C(5)	1.448(3)
C(5)-N(1)	1.389(3)
C(5)-C(12)	1.403(3)
C(6)-C(7)	1.354(5)
C(6)-H(6)	0.9300
C(7)-C(8)	1.395(5)
C(7)-H(7)	0.9300
C(8)-C(9)	1.366(4)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(10)-C(11)	1.393(3)
C(10)-N(1)	1.393(3)
C(10)-C(26)	1.460(4)
C(11)-C(12)	1.410(3)
C(11)-C(19)	1.508(3)
C(12)-C(13)	1.476(3)
C(13)-C(14)	1.388(4)
C(13)-C(18)	1.388(4)
C(14)-C(15)	1.389(5)

C(14)-H(14)	0.9300
C(15)-C(16)	1.369(6)
C(15)-H(15)	0.9300
C(16)-C(17)	1.376(6)
C(16)-H(16)	0.9300
C(17)-C(18)	1.373(5)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-C(20)	1.520(4)
C(19)-C(23)	1.522(4)
C(19)-H(19)	0.9800
C(20)-O(6)	1.195(3)
C(20)-O(5)	1.333(3)
C(21)-O(5)	1.457(4)
C(21)-C(22)	1.494(6)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-O(3)	1.198(3)
C(23)-O(4)	1.322(3)
C(24)-C(25)	1.446(5)
C(24)-O(4)	1.453(4)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600

C(26)-O(1)	1.208(3)
C(26)-O(2)	1.337(3)
C(27)-C(28)	1.428(6)
C(27)-O(2)	1.443(3)
C(27)-H(27A)	0.9700
C(27)-H(27B)	0.9700
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
O(7)-C(29)	1.595(13)
O(7)-C(29)#1	1.595(13)
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600

C(2)-C(1)-N(1)	119.6(3)
C(2)-C(1)-H(1)	120.2
N(1)-C(1)-H(1)	120.2
C(1)-C(2)-C(3)	122.6(2)
C(1)-C(2)-H(2)	118.7
C(3)-C(2)-H(2)	118.7
C(6)-C(3)-C(4)	118.8(3)
C(6)-C(3)-C(2)	122.5(3)
C(4)-C(3)-C(2)	118.8(2)
C(9)-C(4)-C(3)	118.5(2)
C(9)-C(4)-C(5)	123.3(2)
C(3)-C(4)-C(5)	118.1(2)
N(1)-C(5)-C(12)	107.6(2)
N(1)-C(5)-C(4)	118.9(2)

C(12)-C(5)-C(4)	133.5(2)
C(7)-C(6)-C(3)	121.4(3)
C(7)-C(6)-H(6)	119.3
C(3)-C(6)-H(6)	119.3
C(6)-C(7)-C(8)	119.7(3)
C(6)-C(7)-H(7)	120.2
C(8)-C(7)-H(7)	120.2
C(9)-C(8)-C(7)	120.7(3)
C(9)-C(8)-H(8)	119.7
C(7)-C(8)-H(8)	119.7
C(8)-C(9)-C(4)	121.0(3)
C(8)-C(9)-H(9)	119.5
C(4)-C(9)-H(9)	119.5
C(11)-C(10)-N(1)	107.4(2)
C(11)-C(10)-C(26)	131.3(2)
N(1)-C(10)-C(26)	121.2(2)
C(10)-C(11)-C(12)	108.3(2)
C(10)-C(11)-C(19)	124.9(2)
C(12)-C(11)-C(19)	126.8(2)
C(5)-C(12)-C(11)	107.4(2)
C(5)-C(12)-C(13)	126.2(2)
C(11)-C(12)-C(13)	126.4(2)
C(14)-C(13)-C(18)	118.8(3)
C(14)-C(13)-C(12)	120.5(3)
C(18)-C(13)-C(12)	120.7(2)
C(13)-C(14)-C(15)	120.4(3)
C(13)-C(14)-H(14)	119.8
C(15)-C(14)-H(14)	119.8
C(16)-C(15)-C(14)	119.6(4)

C(16)-C(15)-H(15)	120.2
C(14)-C(15)-H(15)	120.2
C(15)-C(16)-C(17)	120.5(3)
C(15)-C(16)-H(16)	119.7
C(17)-C(16)-H(16)	119.7
C(18)-C(17)-C(16)	120.1(4)
C(18)-C(17)-H(17)	120.0
C(16)-C(17)-H(17)	120.0
C(17)-C(18)-C(13)	120.5(3)
C(17)-C(18)-H(18)	119.7
C(13)-C(18)-H(18)	119.7
C(11)-C(19)-C(20)	115.6(2)
C(11)-C(19)-C(23)	112.8(2)
C(20)-C(19)-C(23)	108.3(2)
C(11)-C(19)-H(19)	106.5
C(20)-C(19)-H(19)	106.5
C(23)-C(19)-H(19)	106.5
O(6)-C(20)-O(5)	124.3(3)
O(6)-C(20)-C(19)	124.8(3)
O(5)-C(20)-C(19)	110.9(2)
O(5)-C(21)-C(22)	106.9(3)
O(5)-C(21)-H(21A)	110.3
C(22)-C(21)-H(21A)	110.3
O(5)-C(21)-H(21B)	110.3
C(22)-C(21)-H(21B)	110.3
H(21A)-C(21)-H(21B)	108.6
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5

C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(3)-C(23)-O(4)	124.5(2)
O(3)-C(23)-C(19)	124.8(2)
O(4)-C(23)-C(19)	110.8(2)
C(25)-C(24)-O(4)	108.7(3)
C(25)-C(24)-H(24A)	109.9
O(4)-C(24)-H(24A)	109.9
C(25)-C(24)-H(24B)	109.9
O(4)-C(24)-H(24B)	109.9
H(24A)-C(24)-H(24B)	108.3
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
O(1)-C(26)-O(2)	122.2(2)
O(1)-C(26)-C(10)	126.1(2)
O(2)-C(26)-C(10)	111.7(2)
C(28)-C(27)-O(2)	109.5(3)
C(28)-C(27)-H(27A)	109.8
O(2)-C(27)-H(27A)	109.8
C(28)-C(27)-H(27B)	109.8
O(2)-C(27)-H(27B)	109.8
H(27A)-C(27)-H(27B)	108.2
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5

H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(1)-N(1)-C(5)	121.9(2)
C(1)-N(1)-C(10)	128.9(2)
C(5)-N(1)-C(10)	109.24(19)
C(26)-O(2)-C(27)	117.0(2)
C(23)-O(4)-C(24)	117.2(2)
C(20)-O(5)-C(21)	116.3(3)
C(29)-O(7)-C(29)#1	180.0(5)
O(7)-C(29)-H(29A)	109.5
O(7)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
O(7)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+1

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for A.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	53(1)	48(1)	50(1)	12(1)	9(1)	3(1)
C(2)	62(2)	58(2)	46(1)	12(1)	16(1)	0(1)
C(3)	47(1)	57(2)	42(1)	-1(1)	11(1)	-6(1)
C(4)	43(1)	51(1)	42(1)	-3(1)	10(1)	-1(1)
C(5)	42(1)	42(1)	42(1)	1(1)	9(1)	4(1)
C(6)	63(2)	77(2)	51(2)	-2(1)	22(1)	-6(2)
C(7)	65(2)	84(2)	62(2)	-12(2)	31(1)	0(2)
C(8)	63(2)	68(2)	72(2)	-8(2)	27(1)	9(1)
C(9)	59(2)	56(2)	57(2)	1(1)	20(1)	11(1)
C(10)	42(1)	44(1)	44(1)	2(1)	10(1)	4(1)
C(11)	42(1)	44(1)	44(1)	3(1)	10(1)	5(1)
C(12)	46(1)	43(1)	44(1)	3(1)	12(1)	7(1)
C(13)	61(2)	47(1)	51(1)	8(1)	25(1)	16(1)
C(14)	85(2)	50(2)	67(2)	6(1)	32(2)	12(1)
C(15)	134(3)	48(2)	98(3)	8(2)	65(3)	18(2)
C(16)	145(4)	71(3)	106(3)	42(2)	71(3)	60(3)
C(17)	109(3)	92(3)	90(2)	38(2)	35(2)	53(2)
C(18)	76(2)	68(2)	63(2)	16(1)	19(2)	26(2)
C(19)	46(1)	50(1)	44(1)	5(1)	14(1)	8(1)
C(20)	59(2)	59(2)	53(2)	14(1)	24(1)	15(1)
C(21)	106(3)	52(2)	118(3)	11(2)	54(2)	-4(2)
C(22)	124(4)	78(3)	153(4)	-16(3)	37(3)	-37(3)
C(23)	52(2)	69(2)	46(1)	3(1)	18(1)	9(1)

C(24)	69(2)	145(4)	53(2)	-18(2)	12(2)	-1(2)
C(25)	89(3)	186(5)	60(2)	-29(2)	22(2)	1(3)
C(26)	50(1)	43(1)	54(1)	2(1)	9(1)	5(1)
C(27)	93(2)	57(2)	90(2)	-5(2)	34(2)	23(2)
C(28)	244(7)	143(5)	126(4)	-2(4)	87(5)	103(5)
N(1)	45(1)	41(1)	41(1)	3(1)	8(1)	2(1)
O(1)	107(2)	51(1)	73(1)	16(1)	28(1)	29(1)
O(2)	90(1)	52(1)	68(1)	4(1)	34(1)	22(1)
O(3)	52(1)	134(2)	57(1)	-8(1)	18(1)	-2(1)
O(4)	55(1)	100(2)	48(1)	-11(1)	16(1)	5(1)
O(5)	68(1)	49(1)	72(1)	10(1)	22(1)	0(1)
O(6)	99(2)	82(2)	68(1)	32(1)	21(1)	20(1)
O(7)	280(13)	463(18)	172(7)	191(10)	87(8)	210(13)
C(29)	290(17)	550(30)	151(8)	131(13)	-6(10)	-22(17)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for A.

	x	y	z	U(eq)
H(1)	3258	3435	10509	61
H(2)	2189	4084	11705	66
H(6)	762	5539	12410	76
H(7)	-323	7269	12348	83
H(8)	-251	8434	11068	80
H(9)	906	7864	9866	68
H(14)	3778	8579	9474	78
H(15)	3157	10402	8948	104
H(16)	1212	10446	7597	115
H(17)	-173	8693	6790	109
H(18)	415	6880	7311	80
H(19)	4631	5206	7420	55
H(21A)	5151	9149	7639	106
H(21B)	6378	8671	7128	106
H(22A)	6786	9133	9145	184
H(22B)	7675	9884	8507	184
H(22C)	7986	8565	8670	184
H(24A)	1541	3436	4984	110
H(24B)	1391	4725	4646	110
H(25A)	3504	4692	4040	171
H(25B)	2361	3536	3600	171
H(25C)	3792	3459	4447	171
H(27A)	5947	2214	8055	93
H(27B)	4273	1545	7656	93

H(28A)	4199	2172	6189	239
H(28B)	5704	1575	6503	239
H(28C)	5787	2974	6574	239
H(29A)	899	8470	4527	511
H(29B)	2020	9183	5444	511
H(29C)	1902	9659	4422	511

Table S6. Torsion angles [deg] for A.

N(1)-C(1)-C(2)-C(3)	0.3(4)
C(1)-C(2)-C(3)-C(6)	177.3(2)
C(1)-C(2)-C(3)-C(4)	-1.7(4)
C(6)-C(3)-C(4)-C(9)	-0.1(3)
C(2)-C(3)-C(4)-C(9)	179.0(2)
C(6)-C(3)-C(4)-C(5)	-178.6(2)
C(2)-C(3)-C(4)-C(5)	0.5(3)
C(9)-C(4)-C(5)-N(1)	-176.3(2)
C(3)-C(4)-C(5)-N(1)	2.0(3)
C(9)-C(4)-C(5)-C(12)	1.6(4)
C(3)-C(4)-C(5)-C(12)	-180.0(2)
C(4)-C(3)-C(6)-C(7)	-0.1(4)
C(2)-C(3)-C(6)-C(7)	-179.1(3)
C(3)-C(6)-C(7)-C(8)	0.2(4)
C(6)-C(7)-C(8)-C(9)	-0.1(5)
C(7)-C(8)-C(9)-C(4)	-0.1(4)
C(3)-C(4)-C(9)-C(8)	0.2(4)
C(5)-C(4)-C(9)-C(8)	178.6(2)
N(1)-C(10)-C(11)-C(12)	-0.7(3)
C(26)-C(10)-C(11)-C(12)	175.8(2)
N(1)-C(10)-C(11)-C(19)	179.4(2)
C(26)-C(10)-C(11)-C(19)	-4.1(4)
N(1)-C(5)-C(12)-C(11)	0.8(3)
C(4)-C(5)-C(12)-C(11)	-177.3(2)
N(1)-C(5)-C(12)-C(13)	-178.1(2)
C(4)-C(5)-C(12)-C(13)	3.8(4)
C(10)-C(11)-C(12)-C(5)	-0.1(3)

C(19)-C(11)-C(12)-C(5)	179.8(2)
C(10)-C(11)-C(12)-C(13)	178.9(2)
C(19)-C(11)-C(12)-C(13)	-1.3(4)
C(5)-C(12)-C(13)-C(14)	70.0(3)
C(11)-C(12)-C(13)-C(14)	-108.7(3)
C(5)-C(12)-C(13)-C(18)	-110.3(3)
C(11)-C(12)-C(13)-C(18)	71.0(3)
C(18)-C(13)-C(14)-C(15)	0.5(4)
C(12)-C(13)-C(14)-C(15)	-179.9(3)
C(13)-C(14)-C(15)-C(16)	-0.8(5)
C(14)-C(15)-C(16)-C(17)	0.9(6)
C(15)-C(16)-C(17)-C(18)	-0.6(6)
C(16)-C(17)-C(18)-C(13)	0.2(5)
C(14)-C(13)-C(18)-C(17)	-0.2(4)
C(12)-C(13)-C(18)-C(17)	-179.8(3)
C(10)-C(11)-C(19)-C(20)	-149.4(2)
C(12)-C(11)-C(19)-C(20)	30.8(3)
C(10)-C(11)-C(19)-C(23)	85.2(3)
C(12)-C(11)-C(19)-C(23)	-94.6(3)
C(11)-C(19)-C(20)-O(6)	-123.1(3)
C(23)-C(19)-C(20)-O(6)	4.5(4)
C(11)-C(19)-C(20)-O(5)	60.3(3)
C(23)-C(19)-C(20)-O(5)	-172.1(2)
C(11)-C(19)-C(23)-O(3)	25.8(4)
C(20)-C(19)-C(23)-O(3)	-103.4(3)
C(11)-C(19)-C(23)-O(4)	-155.0(2)
C(20)-C(19)-C(23)-O(4)	75.8(3)
C(11)-C(10)-C(26)-O(1)	178.6(3)
N(1)-C(10)-C(26)-O(1)	-5.3(4)

C(11)-C(10)-C(26)-O(2)	-2.8(4)
N(1)-C(10)-C(26)-O(2)	173.3(2)
C(2)-C(1)-N(1)-C(5)	2.5(3)
C(2)-C(1)-N(1)-C(10)	-178.4(2)
C(12)-C(5)-N(1)-C(1)	177.9(2)
C(4)-C(5)-N(1)-C(1)	-3.6(3)
C(12)-C(5)-N(1)-C(10)	-1.3(2)
C(4)-C(5)-N(1)-C(10)	177.14(19)
C(11)-C(10)-N(1)-C(1)	-177.9(2)
C(26)-C(10)-N(1)-C(1)	5.2(4)
C(11)-C(10)-N(1)-C(5)	1.3(2)
C(26)-C(10)-N(1)-C(5)	-175.7(2)
O(1)-C(26)-O(2)-C(27)	-3.1(4)
C(10)-C(26)-O(2)-C(27)	178.2(2)
C(28)-C(27)-O(2)-C(26)	176.8(4)
O(3)-C(23)-O(4)-C(24)	3.9(5)
C(19)-C(23)-O(4)-C(24)	-175.3(3)
C(25)-C(24)-O(4)-C(23)	177.3(4)
O(6)-C(20)-O(5)-C(21)	3.7(4)
C(19)-C(20)-O(5)-C(21)	-179.7(2)
C(22)-C(21)-O(5)-C(20)	175.3(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+1

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