Supporting Information

For

Synthesis of indolizines from pyridinium 1,4-zwitterionic thiolates and α-functionalized bromoalkanes via a stepwise [(5 + 1) - 1] pathway

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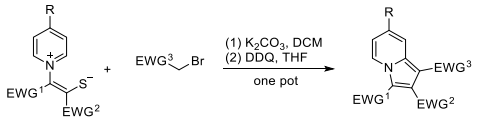
1. General information

All isolated compounds were characterized on Bruker 400, JEOL 400 MHz spectrometers in $CDCl_3$ or $(CD_3)_2SO$. Chemical shifts were reported as δ values relative to internal $CHCl_3$ (δ 7.26 for ^1H NMR and 77.16 for ^{13}C NMR) and $(CH_3)_2SO$ (δ 2.50 for ^1H NMR and δ 39.52 for ^{13}C NMR). ^{19}F NMR chemical shifts were determined as δ values relative to external standard $PhCF_3$ at −63.00. High-resolution mass spectra (HRMS) were obtained on a 4G mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QTof). All melting points were measured with the samples after column chromatography and uncorrected. Column chromatography was performed on silica gel.

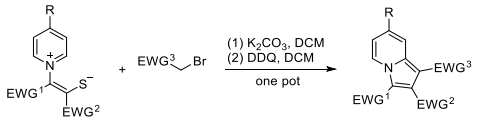
2. General experimental procedure

2.1 General procedure for the synthesis of indolizines (5-17) in one pot



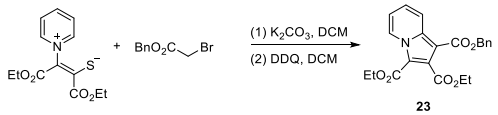
To a solution of α-functionalized bromoalkane (0.3 mmol, 1.0 equiv) in DCM (3 mL) were added pyridinium 1,4-zwitterionic thiolate (0.45 mmol, 1.5 equiv) and K_2CO_3 (0.6 mmol, 2.0 equiv) at room temperature, then the mixture was stirred at the same temperature for 12 h. After completion of the annulation reaction as monitored by TLC, the solvent was evaporated. Then the residue was redissolved in THF (3 mL) and DDQ (0.6 mmol, 2.0 equiv) were added. After completion of the ring-contraction reaction as monitored by TLC, the solvent was evaporated and the residue was purified by silica gel column chromatography to give the corresponding two indolizines.

2.2 General procedure for the synthesis of indolizines (18-33) in one pot



To a solution of α-functionalized bromoalkane (0.3 mmol, 1.0 equiv) in DCM (3 mL) were added pyridinium 1,4-zwitterionic thiolate (0.45 mmol, 1.5 equiv) and K_2CO_3 (0.6 mmol, 2.0 equiv) at room temperature, then the mixture was stirred at the same temperature for 12 h. After completion of the annulation reaction as monitored by TLC, DDQ (0.6 mmol, 2.0 equiv) were directly added. After completion of the ring-contraction reaction as monitored by TLC, the solvent was evaporated and the residue was purified by silica gel column chromatography to give the corresponding indolizine. It is noteworthy that the amount of DDQ should be reduced to 1.0 equiv for the formation of **30**.

Scale-up experiment for 23:



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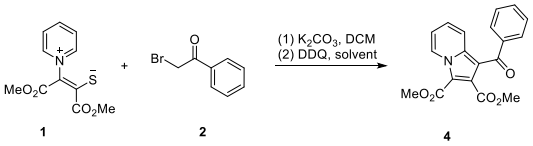
To a solution of benzyl 2-bromoacetate (0.16 mL, 1.0 mmol) in DCM (10 mL) were added thiolate (422 mg, 1.5 mmol, 1.5 equiv) and K_2CO_3 (276 mg, 2.0 mmol, 2.0 equiv) at room temperature, then the mixture was stirred at the same temperature for 12 h. After completion of the annulation reaction as monitored by TLC, DDQ (454 mg, 2.0 mmol, 2.0 equiv) were directly added. After completion of the ring-contraction reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified by silica gel column chromatography to give the corresponding indolizine **23** (0.32 g, 81%)

2.3. General information for the preparation of pyridinium 1,4-zwitterionic thiolates

Pyridinium 1,4-zwitterionic thiolates were prepared according to the literature (Moafi, L.; Ahadi, S.; Khavasi, H. R.; Bazgir, A. *Synthesis* **2011**, 1399).

3. Table S1. Optimization of the reaction conditions for the formation of **4**[a]

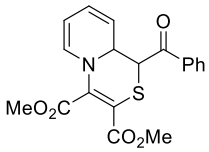


1 2 4

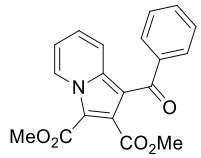
Entry	Solvent	Yield (%) **4**, **4'**	Entry	Solvent	Yield (%) **4**, **4'**
1	DCM	19, 75	7	EtOAc	55, 32
2	THF	72, 24	8	dioxane	48, 26
3	$(CH_3)_2CO$	54, 32	9	PhMe	21, 43
4	$CHCl_3$	15, 84	10	MeOH	12, 72
5	MeCN	36, 60	11	Et_2O	17, 75
6	DCE	17, 80			

[a] Reaction conditions: thiolate (0.3 mmol, 1.5 equiv), 2-bromo-1-phenylethan-1-one (0.2 mmol), K_2CO_3 (0.4 mmol, 2.0 equiv), DCM (2 mL), 25 ℃; then DDQ (2.0 equiv), solvent (2 mL), 25 ℃. The yields were determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as the internal standard.

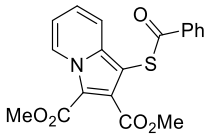
4. Characterization Data of Products



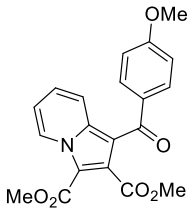
Dimethyl 1-benzoyl-1,9a-dihydropyrido[2,1-c][1,4]thiazine-3,4-dicarboxylate. Compound **3** was obtained as a mixture of diastereoisomers (a yellow oil, 72 mg, Y = 65%, dr = 1:1.2, R_f = 0.47 (PE:EA = 2:1)) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 2.4H), 7.90 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1.2H), 7.56 (t, J = 7.2 Hz, 1H), 7.53–7.40 (m, 4.4H), 6.17 (d, J = 8.0 Hz, 1H), 6.10 (d, J = 7.6 Hz, 1.2H), 5.86 (dd, J = 9.6, 5.6 Hz, 1.2H), 5.81–5.73 (m, 1H), 5.52 (dd, J = 10.0, 4.0 Hz, 1.2H), 5.41 (dd, J = 10.0, 3.6 Hz, 1H), 5.05 (t, J = 6.8 Hz, 1.2H), 4.93–4.83 (m, 3.2H), 4.82–4.77 (m, 1H), 4.65–4.56 (m, 1.2H), 3.89 (s, 6.6H), 3.74 (s, 3.6H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 193.1, 164.5, 164.4, 164.0, 139.2, 138.7, 136.7, 136.0, 134.2, 133.2, 129.1, 128.9 (2C), 128.8, 128.6, 128.5, 123.2, 118.6, 118.5, 107.1, 101.5, 100.9, 100.6, 58.6, 58.4, 53.25 (2C), 52.6, 52.4, 47.6, 42.7, (2C missing); ESI-HRMS m/z calcd for $C_{19}H_{17}NO_5SNa$ $[M + Na]^+$ 394.0720, found 394.0718.



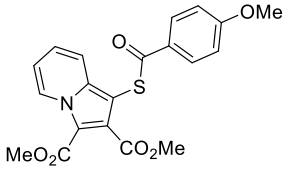
Dimethyl 1-benzoylindolizine-2,3-dicarboxylate. Compound **4** (74 mg, Y = 73%, R_f = 0.47 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, J = 7.2 Hz, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.95–7.83 (m, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.36–7.25 (m, 1H), 7.05 (td, J = 6.8, 0.8 Hz, 1H), 3.90 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 165.7, 160.8, 140.0, 138.1, 132.0, 130.4, 128.8, 128.3, 128.0, 126.9, 120.0, 115.8, 112.8, 112.6, 52.5, 52.1; ESI-HRMS m/z calcd for $C_{19}H_{16}NO_5$ $[M + H]^+$ 338.1023, found 338.1022.



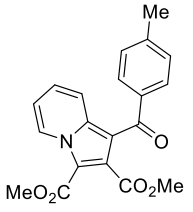
Dimethyl 1-(benzoylthio)indolizine-2,3-dicarboxylate. Compound **4'** (29 mg, Y = 26%, R_f = 0.50 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, J = 7.6 Hz, 1H), 8.09–8.01 (m, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.53 (d, J = 9.2 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.23–7.16 (m, 1H), 6.97 (td, J = 7.0, 1.2 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 165.5, 160.5, 139.2, 136.2, 133.9, 132.8, 128.8, 128.0, 127.8, 124.7, 117.9, 115.1, 112.6, 95.1, 52.8, 51.8; ESI-HRMS m/z calcd for $C_{19}H_{15}NO_5SNa$ $[M + Na]^+$ 392.0563, found 392.0560.



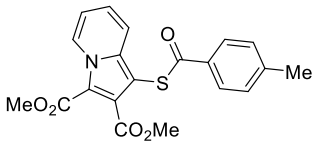
Dimethyl 1-(4-methoxybenzoyl)indolizine-2,3-dicarboxylate. Compound **5** (69 mg, Y = 63%, R_f = 0.40 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (d, J = 6.8 Hz, 1H), 7.82 (d, J = 9.2 Hz, 1H), 7.73 (d, J = 8.8 Hz, 2H), 7.27 (t, J = 7.6 Hz, 1H), 7.03 (td, J = 7.0, 0.8 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 165.9, 163.0, 160.9, 137.7, 132.4, 131.4, 130.2, 127.9, 126.4, 119.9, 115.6, 113.6, 113.4, 112.5, 55.6, 52.7, 52.1; ESI-HRMS m/z calcd for $C_{20}H_{18}NO_6$ $[M + H]^+$ 368.1129, found 368.1126.



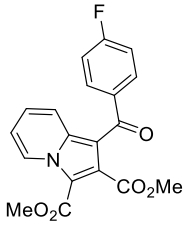
Dimethyl 1-((4-methoxybenzoyl)thio)indolizine-2,3-dicarboxylate. Compound **5'** (16 mg, Y = 13%, R_f = 0.44 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, J = 7.2 Hz, 1H), 8.02 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.23–7.16 (m, 1H), 7.00–6.92 (m, 3H), 3.90 (s, 3H), 3.90 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 165.6, 164.2, 160.5, 139.3, 132.9, 130.1, 128.9, 128.0, 124.7, 118.0, 115.0, 114.0, 112.4, 95.3, 55.6, 52.8, 51.8; ESI-HRMS m/z calcd for $C_{20}H_{18}NO_6S$ $[M + H]^+$ 400.0849, found 400.0845.



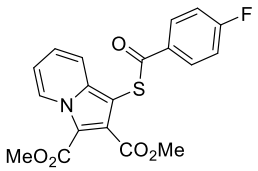
Dimethyl 1-(4-methylbenzoyl)indolizine-2,3-dicarboxylate. Compound **6** (64 mg, Y = 61%, R_f = 0.58 (PE:EA = 2:1)) was isolated as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, J = 6.8 Hz, 1H), 7.84 (d, J = 9.2 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.32–7.20 (m, 3H), 7.04 (t, J = 6.8 Hz, 1H), 3.90 (s, 3H), 3.61 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 165.9, 160.9, 142.8, 137.9, 137.2, 130.3, 129.1, 129.0, 128.0, 126.6, 120.0, 115.7, 113.2, 112.6, 52.6, 52.1, 21.8; ESI-HRMS m/z calcd for $C_{20}H_{18}NO_5$ $[M + H]^+$ 352.1179, found 352.1176.



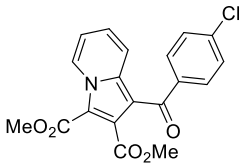
Dimethyl 1-((4-methylbenzoyl)thio)indolizine-2,3-dicarboxylate. Compound **6'** (24 mg, Y = 21%, R_f = 0.65 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, J = 7.2 Hz, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 6.99 (td, J = 7.6, 0.8 Hz, 1H), 3.90 (s, 6H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 165.6, 160.6, 145.0, 139.3, 133.7, 132.9, 129.5, 128.0 (2C), 124.7, 118.0, 115.1, 112.5, 95.4, 52.8, 51.9, 21.9; ESI-HRMS m/z calcd for $C_{20}H_{18}NO_5S$ $[M + H]^+$ 384.0900, found 384.0897.



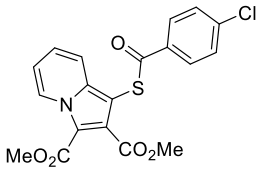
Dimethyl 1-(4-fluorobenzoyl)indolizine-2,3-dicarboxylate. Compound **7** (80 mg, Y = 75%, R_f = 0.58 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, J = 7.2 Hz, 1H), 7.91 (d, J = 9.2 Hz, 1H), 7.79–7.69 (m, 2H), 7.38–7.29 (m, 1H), 7.13 (t, J = 8.8 Hz, 2H), 7.07 (td, J = 7.2, 1.2 Hz, 1H), 3.90 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 165.7, 165.2 (d, J = 251.6 Hz), 160.8, 138.1, 136.2 (d, J = 3.1 Hz), 131.4 (d, J = 9.0 Hz), 130.2, 128.1, 127.1, 119.9, 116.0, 115.5 (d, J = 21.7 Hz), 112.7, 112.6, 52.6, 52.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –106.9; ESI-HRMS m/z calcd for $C_{19}H_{14}FNO_5Na$ $[M + Na]^+$ 378.0748, found 378.0741.



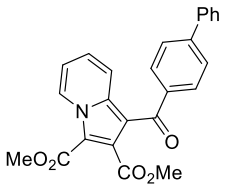
Dimethyl 1-((4-fluorobenzoyl)thio)indolizine-2,3-dicarboxylate. Compound **7'** (27 mg, Y = 23%, R_f = 0.64 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, J = 7.2 Hz, 1H), 8.10–8.02 (m, 2H), 7.51 (d, J = 9.2 Hz, 1H), 7.20–7.11 (m, 3H), 6.96 (td, J = 7.2, 0.8 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 166.2 (d, J = 254.4 Hz), 165.4, 160.4, 139.1, 132.7, 132.4 (d, J = 2.7 Hz), 130.4 (d, J = 9.4 Hz), 127.9, 124.8, 117.8, 116.0 (d, J = 22.1 Hz), 115.1, 112.5, 94.6, 52.7, 51.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –103.9; ESI-HRMS m/z calcd for $C_{19}H_{14}FNO_5SNa$ $[M + Na]^+$ 410.0469, found 410.0466.



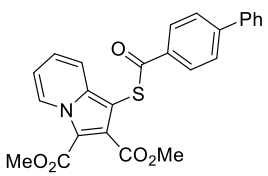
Dimethyl 1-(4-chlorobenzoyl)indolizine-2,3-dicarboxylate. Compound **8** (68 mg, Y = 61%, R_f = 0.58 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (d, J = 7.2 Hz, 1H), 7.92 (d, J = 9.2 Hz, 1H), 7.66 (d, J = 6.8 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.38–7.30 (m, 1H), 7.08 (td, J = 7.0, 1.2 Hz, 1H), 3.90 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 165.7, 160.7, 138.3 (2C), 138.1, 130.3, 128.6, 128.1, 127.3, 119.9, 116.0, 112.8, 112.4, 52.7, 52.2, (1C missing); ESI-HRMS m/z calcd for $C_{19}H_{15}ClNO_5$ $[M + H]^+$ 372.0633, found 372.0628.



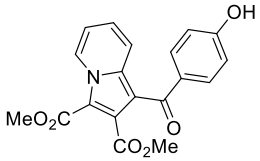
Dimethyl 1-((4-chlorobenzoyl)thio)indolizine-2,3-dicarboxylate. Compound **8'** (33 mg, Y = 27%, R_f = 0.63 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, J = 6.8 Hz, 1H), 7.98 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 6.98 (t, J = 6.0 Hz, 1H), 3.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 165.4, 160.4, 140.4, 139.2, 134.5, 132.7, 129.2, 128.0, 124.8, 117.8, 115.1, 112.7, 94.6, 52.8, 51.9, (1C missing); ESI-HRMS m/z calcd for $C_{19}H_{14}ClNO_5SNa$ $[M + Na]^+$ 426.0173, found 426.0170.



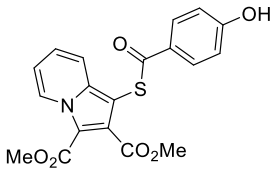
Dimethyl 1-([1,1'-biphenyl]-4-carbonyl)indolizine-2,3-dicarboxylate. Compound **9** (87 mg, Y = 70%, R_f = 0.48 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (d, J = 7.2 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.71–7.64 (m, 4H), 7.48 (t, J = 7.6 Hz, 2H), 7.43–7.38 (m, 1H), 7.36–7.30 (m, 1H), 7.08 (td, J = 6.8, 1.2 Hz, 1H), 3.91 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 165.8, 160.9, 144.8, 140.2, 138.7, 138.1, 130.4, 129.6, 129.1, 128.3, 128.1, 127.4, 127.0, 126.9, 120.1, 115.9, 113.0, 112.8, 52.7, 52.2; ESI-HRMS m/z calcd for $C_{25}H_{20}NO_5$ $[M + H]^+$ 414.1336, found 414.1329.



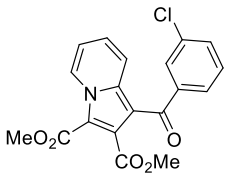
Dimethyl 1-(([1,1'-biphenyl]-4-carbonyl)thio)indolizine-2,3-dicarboxylate. Compound **9'** (35 mg, Y = 26%, R_f = 0.56 (PE:EA = 2:1)) was isolated as a yellow solid; mp 138−139 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, J = 7.2 Hz, 1H), 8.14 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.8 Hz, 1H), 7.47 (t, J = 7.4 Hz, 2H), 7.43–7.38 (m, 1H), 7.23–7.16 (m, 1H), 6.96 (td, J = 7.0, 0.8 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 165.5, 160.4, 146.6, 139.6, 139.2, 134.7, 132.8, 129.0, 128.4, 128.3, 127.9, 127.4, 127.2, 124.7, 117.8, 115.0, 112.5, 95.0, 52.8, 51.8; ESI-HRMS m/z calcd for $C_{25}H_{20}NO_5S$ $[M + H]^+$ 446.1057, found 446.1053.



Dimethyl 1-(4-hydroxybenzoyl)indolizine-2,3-dicarboxylate. Compound **10** (55 mg, Y = 52%, R_f = 0.36 (PE:EA = 1:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, J = 7.2 Hz, 1H), 7.90 (br s, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 7.0 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H), 3.90 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 166.6, 160.8 (2C), 137.8, 131.7, 131.5, 130.2, 128.0, 126.7, 119.9, 115.8, 115.4, 113.3, 112.7, 53.0, 52.2; ESI-HRMS m/z calcd for $C_{19}H_{15}NO_6Na$ $[M + Na]^+$ 376.0792, found 376.0789.

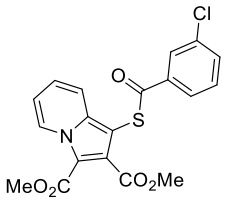


Dimethyl 1-((4-hydroxybenzoyl)thio)indolizine-2,3-dicarboxylate. Compound **10'** (23 mg, Y = 20%, R_f = 0.44 (PE:EA = 1:1)) was isolated as a white solid; mp 184−185 ℃. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 9.82 (s, 1H), 8.54 (d, J = 7.2 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H), 6.77–6.67 (m, 1H), 6.56–6.47 (m, 1H), 6.37 (td, J = 6.8, 1.2 Hz, 1H), 6.06 (d, J = 8.8 Hz, 2H), 2.99 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 186.3, 164.6, 163.2, 159.7, 138.7, 132.3, 130.1, 127.5, 126.4, 125.5, 117.8, 115.9, 115.8, 111.6, 94.5, 52.7, 52.0; ESI-HRMS m/z calcd for $C_{19}H_{16}NO_6S$ $[M + H]^+$ 386.0693, found 386.0691.

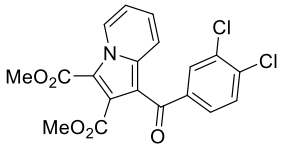


Dimethyl 1-(3-chlorobenzoyl)indolizine-2,3-dicarboxylate. Compound **11** (52 mg, Y = 47%, R_f = 0.52 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (d, J = 7.2 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.67 (t, J = 2.0 Hz, 1H), 7.59 (dt, J = 7.6, 1.2 Hz, 1H), 7.55–7.49 (m, 1H),

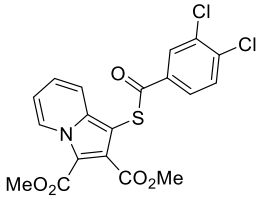
7.43–7.35 (m, 2H), 7.10 (td, *J* = 7.0, 1.2 Hz, 1H), 3.90 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 165.6, 160.8, 141.6, 138.4, 134.4, 131.9, 130.3, 129.8, 128.9, 128.2, 127.6, 126.9, 120.1, 116.2, 112.9, 112.1, 52.6, 52.2; ESI-HRMS m/z calcd for $C_{19}H_{15}ClNO_5$ $[M + H]^+$ 372.0633, found 372.0631.



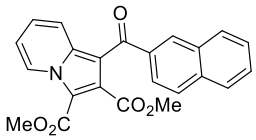
Dimethyl 1-((3-chlorobenzoyl)thio)indolizine-2,3-dicarboxylate. Compound **11'** (35 mg, Y = 29%, R_f = 0.59 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, *J* = 7.2 Hz, 1H), 8.00 (t, *J* = 1.8 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.61–7.54 (m, 1H), 7.51 (d, *J* = 9.2 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.24–7.18 (m, 1H), 6.99 (td, *J* = 7.0, 1.2 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 165.4, 160.4, 139.1, 137.6, 135.1, 133.8, 132.7, 130.2, 128.0, 127.7, 125.9, 124.9, 117.8, 115.2, 112.7, 94.3, 52.9, 51.9; ESI-HRMS m/z calcd for $C_{19}H_{14}ClNO_5SNa$ $[M + Na]^+$ 426.0173, found 426.0170.



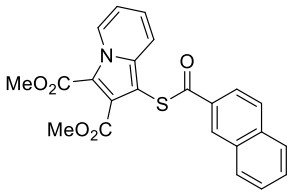
Dimethyl 1-(3,4-dichlorobenzoyl)indolizine-2,3-dicarboxylate. Compound **12** (46 mg, Y = 38%, R_f = 0.60 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.78 (s, 1H), 7.54 (s, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 6.8 Hz, 1H), 3.90 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 165.5, 160.6, 139.6, 138.3, 136.3, 132.7, 130.8, 130.5, 130.2, 128.2, 127.9, 127.7, 120.0, 116.3, 113.0, 111.7, 52.7, 52.2; ESI-HRMS m/z calcd for $C_{19}H_{14}C_{l2}NO_5$ $[M + H]^+$ 406.0244, found 406.0241.



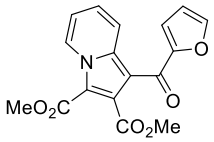
Dimethyl 1-((3,4-dichlorobenzoyl)thio)indolizine-2,3-dicarboxylate. Compound **12'** (56 mg, Y = 43%, R_f = 0.67 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, *J* = 7.2 Hz, 1H), 8.13 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.0 Hz, 1H), 3.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 165.4, 160.4, 139.1, 138.5, 135.6, 133.6, 132.6, 131.0, 129.6, 128.1, 126.8, 125.0, 117.8, 115.2, 112.8, 93.9, 52.9, 52.0; ESI-HRMS m/z calcd for $C_{19}H_{14}Cl_2NO_5S$ $[M + H]^+$ 437.9964, found 437.9959.



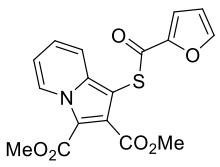
Dimethyl 1-(2-naphthoyl)indolizine-2,3-dicarboxylate. Compound **13** (48 mg, Y = 41%, R_f = 0.42 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 7.2 Hz, 1H), 8.19 (s, 1H), 8.01–7.83 (m, 5H), 7.62–7.51 (m, 2H), 7.35–7.28 (m, 1H), 7.08 (t, J = 6.8 Hz, 1H), 3.90 (s, 3H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 165.9, 160.8, 138.2, 137.1, 135.1, 132.2, 130.5, 130.3, 129.3, 128.5, 128.1, 128.0 (2C), 127.0, 126.9, 125.0, 120.1, 116.0, 113.0, 112.6, 52.6, 52.2; ESI-HRMS m/z calcd for $C_{23}H_{18}NO_5$ $[M + H]^+$ 388.1179, found 388.1172.



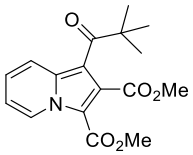
Dimethyl 1-((2-naphthoyl)thio)indolizine-2,3-dicarboxylate. Compound **13'** (54 mg, Y = 43%, R_f = 0.50 (PE:EA = 2:1)) was isolated as a yellow solid; mp 110−111 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, J = 7.2 Hz, 1H), 8.66 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.88 (t, J = 9.0 Hz, 2H), 7.64–7.54 (m, 3H), 7.20 (t, J = 8.0 Hz, 1H), 6.97 (t, J = 6.8 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 165.6, 160.4, 139.2, 136.0, 133.4, 132.8, 132.5, 129.6, 129.5, 128.8, 128.7, 128.0, 127.9, 127.1, 124.8, 123.4, 117.9, 115.1, 112.5, 95.1, 52.8, 51.8; ESI-HRMS m/z calcd for $C_{23}H_{18}NO_5S$ $[M + H]^+$ 420.0900, found 420.896.



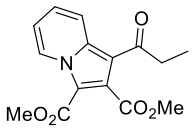
Dimethyl 1-(furan-2-carbonyl)indolizine-2,3-dicarboxylate. Compound **14** (45 mg, Y = 46%, R_f = 0.33 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, J = 7.2 Hz, 1H), 8.06 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 1.2 Hz, 1H), 7.37–7.29 (m, 1H), 7.20 (d, J = 3.6 Hz, 1H), 7.04 (td, J = 7.0, 1.2 Hz, 1H), 6.56 (dd, J = 3.6, 2.0 Hz, 1H), 3.91 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 165.8, 160.9, 153.1, 146.2, 137.8, 129.2, 127.9, 126.8, 120.0, 118.2, 115.9, 112.9, 112.4, 112.3, 52.8, 52.1; ESI-HRMS m/z calcd for $C_{17}H_{14}NO_6$ $[M + H]^+$ 328.0816, found 328.0808.



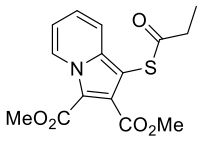
Dimethyl 1-((furan-2-carbonyl)thio)indolizine-2,3-dicarboxylate. Compound **14'** (9 mg, Y = 8%, R_f = 0.42 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, J = 7.2 Hz, 1H), 7.65 (d, J = 0.8 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.00 (td, J = 7.0, 0.8 Hz, 1H), 6.59 (dd, J = 3.4, 1.8 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 165.5, 160.5, 150.2, 146.9, 139.4, 132.9, 128.0, 124.9, 118.0, 116.8, 115.2, 112.6, 93.8, 52.8, 51.9, (1C missing); ESI-HRMS m/z calcd for $C_{23}H_{13}NO_6SNa$ $[M + Na]^+$ 382.0356, found 382.0354.



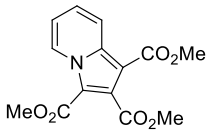
Dimethyl 1-pivaloylindolizine-2,3-dicarboxylate. Compound **15** (52 mg, Y = 55%, R_f = 0.56 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 9.2 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 6.91 (t, J = 7.0 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 166.2, 160.8, 134.5, 127.5, 127.2, 124.7, 119.5, 115.1, 114.7, 112.0, 52.6, 51.9, 44.7, 27.2; ESI-HRMS m/z calcd for $C_{17}H_{20}NO_5$ $[M + H]^+$ 318.1336, found 318.1332.



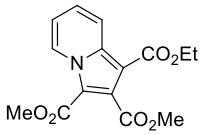
Dimethyl 1-propionylindolizine-2,3-dicarboxylate. Compound **16** (55 mg, Y = 63%, R_f = 0.48 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (d, J = 7.2 Hz, 1H), 8.50 (d, J = 8.8 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.06 (td, J = 7.0, 1.2 Hz, 1H), 4.01 (s, 3H), 3.91 (s, 3H), 2.83 (q, J = 7.2 Hz, 2H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 167.4, 160.6, 137.8, 129.6, 128.0, 127.7, 120.7, 115.9, 112.2, 53.2, 52.1, 34.1, 8.0, (1C missing); ESI-HRMS m/z calcd for $C_{15}H_{15}NO_5Na$ $[M + Na]^+$ 312.0842, found 312.0835.



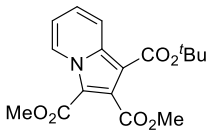
Dimethyl 1-(propionylthio)indolizine-2,3-dicarboxylate. Compound **16'** (24 mg, Y = 25%, R_f = 0.57 (PE:EA = 2:1)) was isolated as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (d, J = 7.2 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 6.96 (td, J = 7.0, 0.8 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H). 2.66 (q, J = 7.2 Hz, 2H), 1.19 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 165.6, 160.4, 138.8, 132.3, 127.9, 124.7, 117.8, 115.1, 112.3, 96.2, 52.8, 51.9, 36.5, 9.6; ESI-HRMS m/z calcd for $C_{15}H_{16}NO_5S$ $[M + H]^+$ 322.0744, found 322.0739.



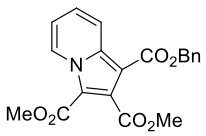
Trimethyl indolizine-1,2,3-tricarboxylate. Compound **17** (55 mg, Y = 63%, R_f = 0.47 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, J = 7.2 Hz, 1H), 8.30 (d, J = 8.8 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.02 (td, J = 6.8, 0.4 Hz, 1H), 3.98 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 163.4, 160.5, 137.9, 130.7, 128.0, 126.8, 120.0, 115.5, 111.9, 103.1, 53.0, 52.1, 51.7; ESI-HRMS m/z calcd for $C_{14}H_{14}NO_6$ $[M + H]^+$ 292.0816, found 292.0811.



1-Ethyl 2,3-dimethyl indolizine-1,2,3-tricarboxylate. Compound **18** (61 mg, Y = 67%, R_f = 0.43 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, J = 7.2 Hz, 1H), 8.34 (d, J = 8.8 Hz, 1H), 7.40–7.33 (m, 1H), 7.03 (td, J = 7.0, 1.2 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 3.98 (s, 3H), 3.90 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 163.0, 160.6, 138.0, 130.6, 128.0, 126.8, 120.1, 115.5, 111.9, 103.4, 60.5, 52.8, 52.0, 14.4; ESI-HRMS m/z calcd for $C_{15}H_{16}NO_6$ $[M + H]^+$ 306.0972, found 306.0971.

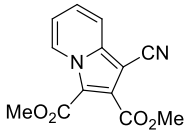


1-tert-Butyl 2,3-dimethyl indolizine-1,2,3-tricarboxylate. Compound **19** (60 mg, Y = 60%, R_f = 0.46 (PE:EA = 3:1)) was isolated as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, J = 7.2 Hz, 1H), 8.33 (d, J = 8.8 Hz, 1H), 7.36–7.29 (m, 1H), 7.00 (td, J = 7.0, 1.2 Hz, 1H), 3.97 (s, 3H), 3.89 (s, 3H), 1.58 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 162.3, 160.6, 138.0, 130.4, 127.9, 126.4, 120.1, 115.4, 111.5, 104.8, 81.3, 52.7, 52.0, 28.5; ESI-HRMS m/z calcd for $C_{17}H_{19}NO_6Na$ $[M + Na]^+$ 356.1105, found 356.1103.

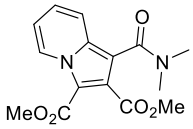


1-Benzyl 2,3-dimethyl indolizine-1,2,3-tricarboxylate. Compound **20** (83 mg, Y = 75%, R_f = 0.52 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, J = 6.8 Hz, 1H), 8.35 (d, J = 8.8 Hz, 1H), 7.45–7.30 (m, 6H), 7.02 (t, J = 6.8 Hz, 1H), 5.33 (s, 2H), 3.88 (s, 3H), 3.71 (s,

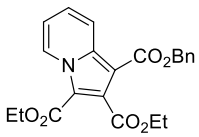
3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 162.7, 160.5, 138.2, 136.0, 130.6, 128.6, 128.5, 128.3, 128.0, 127.0, 120.0, 115.6, 111.9, 102.8, 66.5, 52.6, 52.0; ESI-HRMS m/z calcd for $C_{20}H_{18}NO_6$ $[M + H]^+$ 368.1129, found 368.1127.



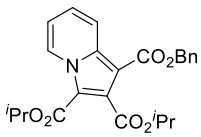
Dimethyl 1-cyanoindolizine-2,3-dicarboxylate. Compound **21** (49 mg, Y = 64%, R_f = 0.55 (PE:EA = 2:1)) was isolated as a red solid; mp 166−167 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.46–7.34 (m, 1H), 7.09 (td, J = 6.8, 1.2 Hz, 1H), 4.01 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 160.2, 139.3, 129.6, 128.3, 126.9, 118.1, 116.2, 113.6, 113.5, 84.7, 53.2, 52.4; ESI-HRMS m/z calcd for $C_{13}H_{11}N_2O_4$ $[M + H]^+$ 259.0713, found 259.0712.



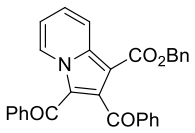
Dimethyl 1-(dimethylcarbamoyl)indolizine-2,3-dicarboxylate. Compound **22** (25 mg, Y = 27%, R_f = 0.35 (PE:EA = 1:2)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (dt, J = 7.2, 1.0 Hz, 1H), 7.54 (dt, J = 8.8, 1.2 Hz, 1H), 7.22–7.14 (m, 1H), 6.94 (td, J = 6.8, 1.2 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 160.9, 134.2, 127.6, 126.8, 124.4, 118.7, 114.8, 111.7, 110.2, 52.8, 52.0, 29.8, 29.4; ESI-HRMS m/z calcd for $C_{15}H_{16}N_2O_5Na$ $[M + Na]^+$ 327.0951, found 327.0946.



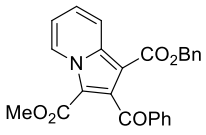
1-Benzyl 2,3-diethyl indolizine-1,2,3-tricarboxylate. Compound **23** (103 mg, Y = 87%, R_f = 0.63 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, J = 7.2 Hz, 1H), 8.34 (d, J = 8.8 Hz, 1H), 7.49–7.28 (m, 6H), 6.99 (t, J = 7.0 Hz, 1H), 5.33 (s, 2H), 4.34 (q, J = 7.2 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 162.7, 160.1, 138.2, 136.0, 130.6, 128.6, 128.4, 128.2, 127.9, 126.8, 119.8, 115.4, 112.0, 102.6, 66.3, 61.7, 60.8, 14.2, 13.9; ESI-HRMS m/z calcd for $C_{22}H_{22}NO_6$ $[M + H]^+$ 396.1442, found 396.1434.



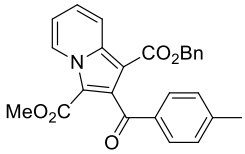
1-Benzyl 2,3-diisopropyl indolizine-1,2,3-tricarboxylate. Compound **24** (111 mg, Y = 87%, R_f = 0.59 (PE:EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, J = 7.2 Hz, 1H), 8.33 (d, J = 9.2 Hz, 1H), 7.45–7.27 (m, 6H), 6.98 (td, J = 7.0, 1.2 Hz, 1H), 5.37 (s, 2H). 5.33–5.24 (m, 1H), 5.19–5.10 (m, 1H), 1.36 (d, J = 6.4 Hz, 6H), 1.31 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 162.8, 159.9, 138.2, 136.3, 130.7, 128.6, 128.1, 128.0 (2C), 126.7, 119.9, 115.3, 112.2, 102.5, 69.8, 68.8, 66.0, 22.0, 21.8; ESI-HRMS m/z calcd for $C_{24}H_{26}NO_6$ $[M + H]^+$ 424.1755, found 424.1749.



Benzyl 2,3-dibenzoylindolizine-1-carboxylate. Compound **25** (61 mg, Y = 44%, R_f = 0.56 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, J = 7.2 Hz, 1H), 8.48 (d, J = 9.2 Hz, 1H), 7.53–7.47 (m, 1H), 7.43–7.38 (m, 1H), 7.38–7.34 (m, 2H), 7.30–7.27 (m, 3H), 7.20–7.12 (m, 6H), 7.06–7.00 (m, 4H), 5.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 187.5, 163.0, 139.3, 139.2, 138.3, 137.8, 135.6, 133.0, 131.6, 129.0 (2C), 128.5, 128.4, 128.1 (2C), 128.0, 127.8, 121.7, 120.0, 116.1, 105.1, 66.4, (1C missing); ESI-HRMS m/z calcd for $C_{30}H_{22}NO_4$ $[M + H]^+$ 460.1543, found 460.1537.

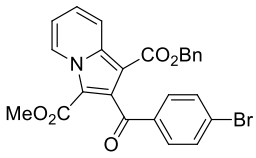


1-Benzyl 3-methyl 2-benzoylindolizine-1,3-dicarboxylate. Compound **26** (45 mg, Y = 36%, R_f = 0.58 (PE:EA = 2:1)) was isolated as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 7.2 Hz, 1H), 8.42 (d, J = 9.2 Hz, 1H). 7.79–7.71 (m, 2H), 7.55–7.49 (m, 1H), 7.44–7.38 (m, 1H), 7.38–7.33 (m, 2H), 7.24–7.17 (m, 3H), 7.11–7.02 (m, 3H), 5.23–4.96 (m, 2H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 162.9, 160.8, 138.9, 137.6, 137.0, 135.8, 133.0, 129.2, 128.4, 128.2, 128.1, 128.0, 127.1, 120.0, 115.6, 112.5, 104.0, 66.3, 51.5, (1C missing); ESI-HRMS m/z calcd for $C_{25}H_{19}NO_5Na$ $[M + Na]^+$ 436.1155, found 436.1148.

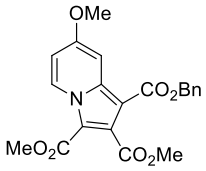


1-Benzyl 3-methyl 2-(4-methylbenzoyl)indolizine-1,3-dicarboxylate. Compound **27** (80 mg, Y = 62%, R_f = 0.57 (PE:EA = 2:1)) was isolated as a yellow solid; mp 130−131 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 7.2 Hz, 1H), 8.41 (d, J = 9.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.42–7.34 (m, 1H), 7.24–7.17 (m, 3H), 7.15 (d, J = 8.0 Hz, 2H), 7.09–7.01 (m, 3H), 5.20 (d, J = 12.0 Hz, 1H), 5.05 (d,

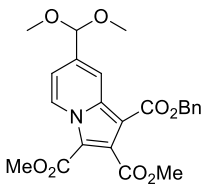
J = 12.0 Hz, 1H), 3.60 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 162.9, 160.8, 143.8, 138.7, 137.2, 135.8, 135.1, 129.2, 129.1, 128.3, 128.1, 128.0, 127.8, 127.0, 119.9, 115.5, 112.3, 103.9, 66.1, 51.5, 21.8; ESI-HRMS m/z calcd for $C_{26}H_{22}NO_5$ $[M + H]^+$ 428.1492, found 428.1484.



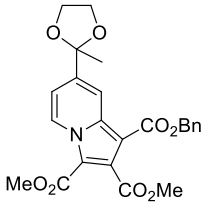
1-Benzyl 3-methyl 2-(4-bromobenzoyl)indolizine-1,3-dicarboxylate. Compound **28** (66 mg, Y = 45%, R_f = 0.50 (PE:EA = 2:1)) was isolated as a yellow solid; mp 168−169 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (d, *J* = 7.2 Hz, 1H), 8.42 (d, *J* = 9.2 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.48–7.38 (m, 3H), 7.28–7.20 (m, 3H), 7.11–7.02 (m, 3H), 5.22 (d, *J* = 10.8 Hz, 1H), 5.00 (d, *J* = 10.4 Hz, 1H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 162.8, 160.6, 138.8, 136.3, 136.2, 135.5, 131.8, 130.5, 128.4 (2C), 128.3, 128.1 (2C), 127.2, 119.9, 115.7, 112.3, 103.9, 66.4, 51.7; ESI-HRMS m/z calcd for $C_{25}H_{19}BrNO_5$ $[M + H]^+$ 492.0441, found 492.0438.



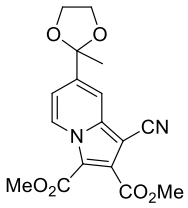
1-Benzyl 2,3-dimethyl 7-methoxyindolizine-1,2,3-tricarboxylate. Compound **29** (74 mg, Y = 62%, R_f = 0.46 (PE:EA = 2:1)) was isolated as a white solid; mp 149−150 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.45–7.29 (m, 5H), 6.67 (dd, *J* = 7.6, 2.4 Hz, 1H), 5.29 (s, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.0, 160.4, 159.1, 140.8, 136.1, 130.8, 129.1, 128.6, 128.4, 128.3, 110.8, 109.9, 100.8, 97.5, 66.3, 55.7, 52.6, 51.8; ESI-HRMS m/z calcd for $C_{21}H_{20}NO_7$ $[M + H]^+$ 398.1234, found 398.1230.



1-Benzyl 2,3-dimethyl 7-(dimethoxymethyl)indolizine-1,2,3-tricarboxylate. Compound **30** (102 mg, Y = 77%, R_f = 0.41 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 7.2 Hz, 1H), 8.47 (s, 1H), 7.49–7.31 (m, 5H), 7.14 (dd, *J* = 7.4, 1.4 Hz, 1H), 5.42 (s, 1H), 5.34 (s, 2H), 3.89 (s, 3H), 3.71 (s, 3H), 3.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 162.7, 160.5, 137.9, 137.8, 136.0, 130.8, 128.7, 128.5, 128.4, 127.9, 118.0, 114.3, 112.1, 103.4, 101.5, 66.6, 52.9, 52.7, 52.1; ESI-HRMS m/z calcd for $C_{23}H_{23}NO_8Na$ $[M + Na]^+$ 464.1316, found 464.1310.

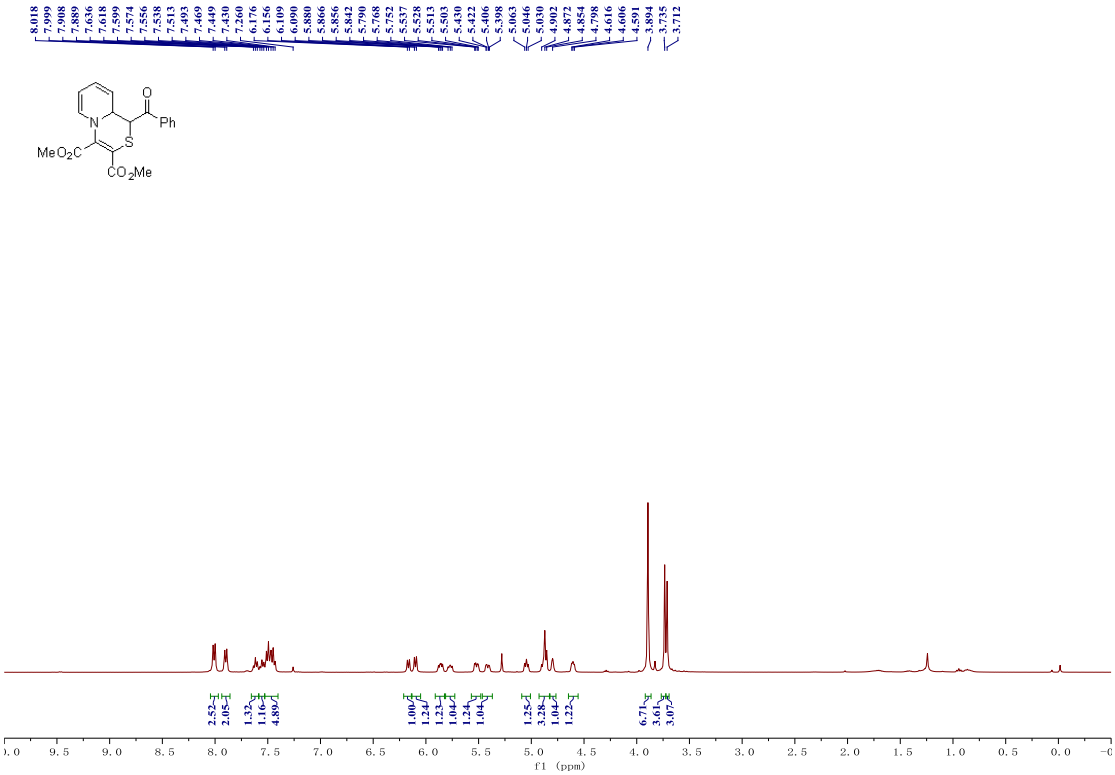


1-Benzyl 2,3-dimethyl 7-(2-methyl-1,3-dioxolan-2-yl)indolizine-1,2,3-tricarboxylate. Compound **31** (99 mg, Y = 73%, R_f = 0.50 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (dd, J = 7.2, 0.8 Hz, 1H), 8.46 (br s, 1H), 7.51–7.28 (m, 5H), 7.13 (dd, J = 7.4, 2.0 Hz, 1H), 5.33 (s, 2H), 4.08–4.01 (m, 2H), 3.87 (s, 3H), 3.80–3.73 (m, 2H), 3.71 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 162.6, 160.4, 143.0, 138.0, 136.0, 130.9, 128.6, 128.4, 128.3, 128.0, 115.8, 113.8, 111.9, 107.9, 103.2, 66.5, 64.8, 52.6, 52.0, 26.7; ESI-HRMS m/z calcd for $C_{24}H_{23}NO_8Na$ $[M + Na]^+$ 476.1316, found 476.1314.

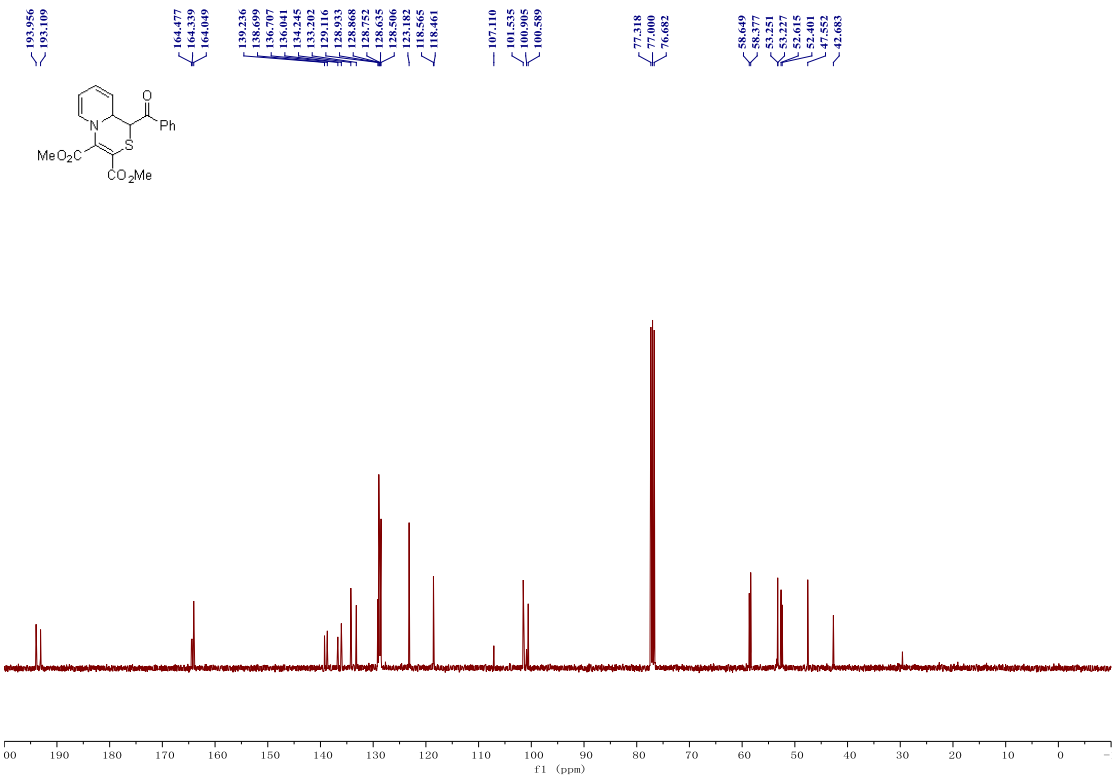


Dimethyl 1-cyano-7-(2-methyl-1,3-dioxolan-2-yl)indolizine-2,3-dicarboxylate. Compound **32** (51 mg, Y = 49%, R_f = 0.43 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, J = 7.2 Hz, 1H), 7.88 (s, 1H), 7.18 (dd, J = 7.2, 1.6 Hz, 1H), 4.14–4.06 (m, 2H), 4.00 (s, 3H), 3.92 (s, 3H), 3.84–3.79 (m, 2H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 160.2, 143.4, 139.1, 129.9, 128.3, 114.6, 113.9, 113.8, 113.5, 107.7, 85.1, 65.1, 53.2, 52.4, 26.9; ESI-HRMS m/z calcd for $C_{17}H_{16}N_2O_6Na$ $[M + Na]^+$ 367.0901, found 367.0898.

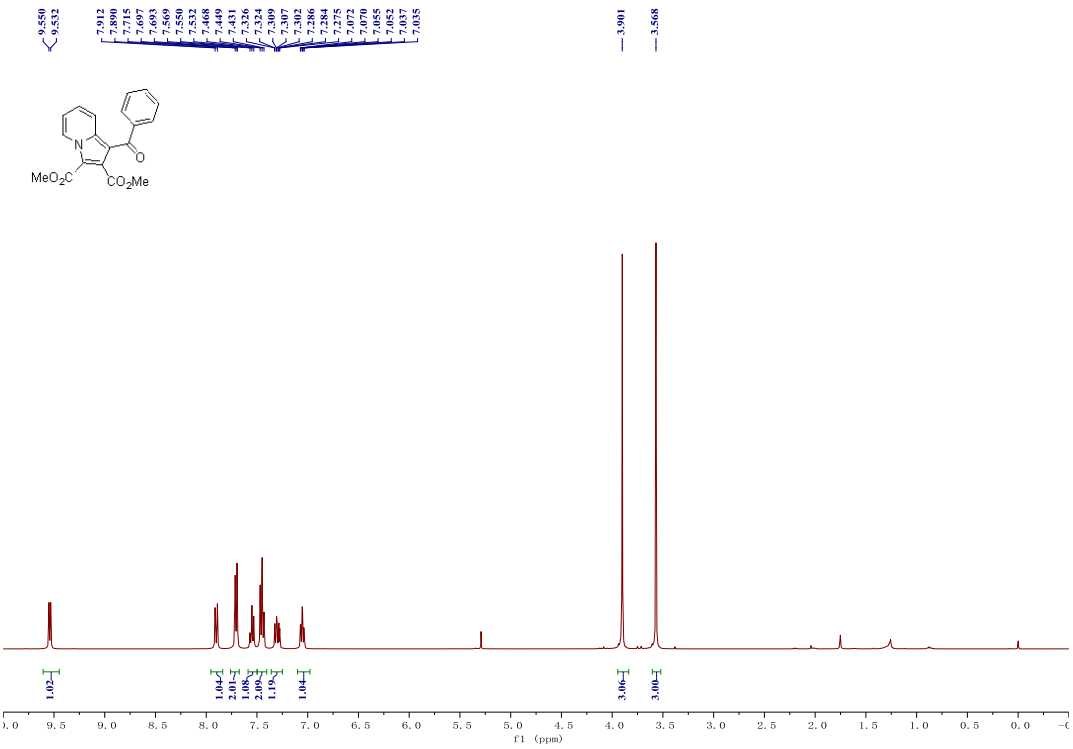
5. NMR spectra



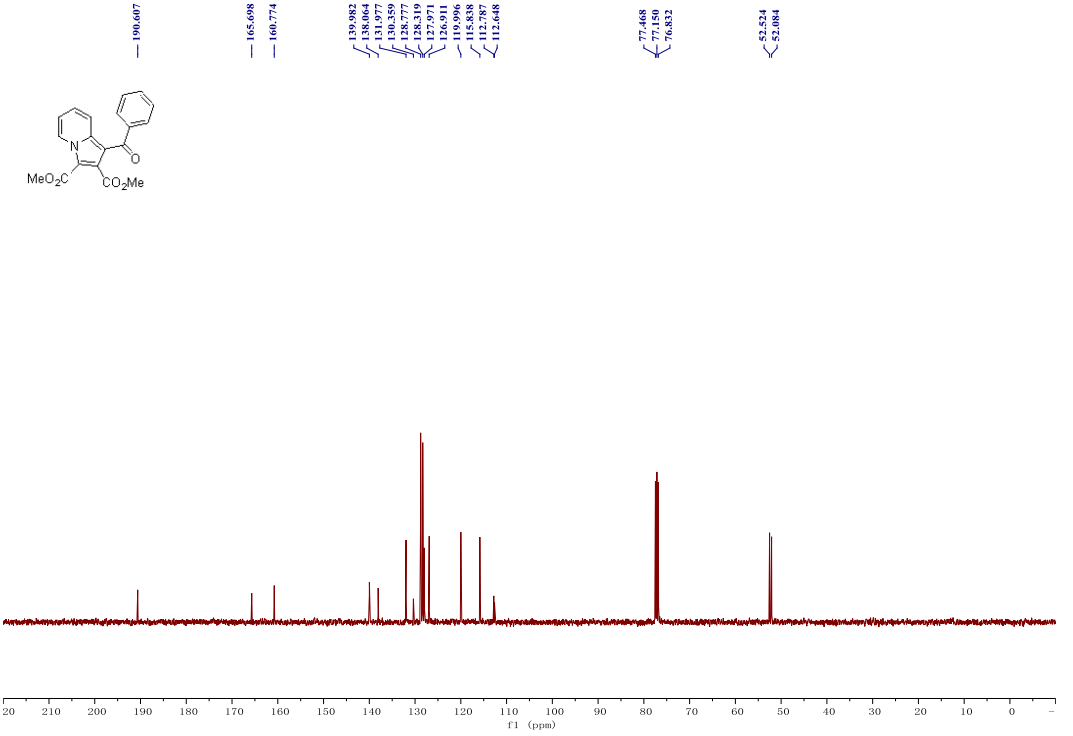
^{1}H NMR of compound **3** (400 MHz, $CDCl_3$)



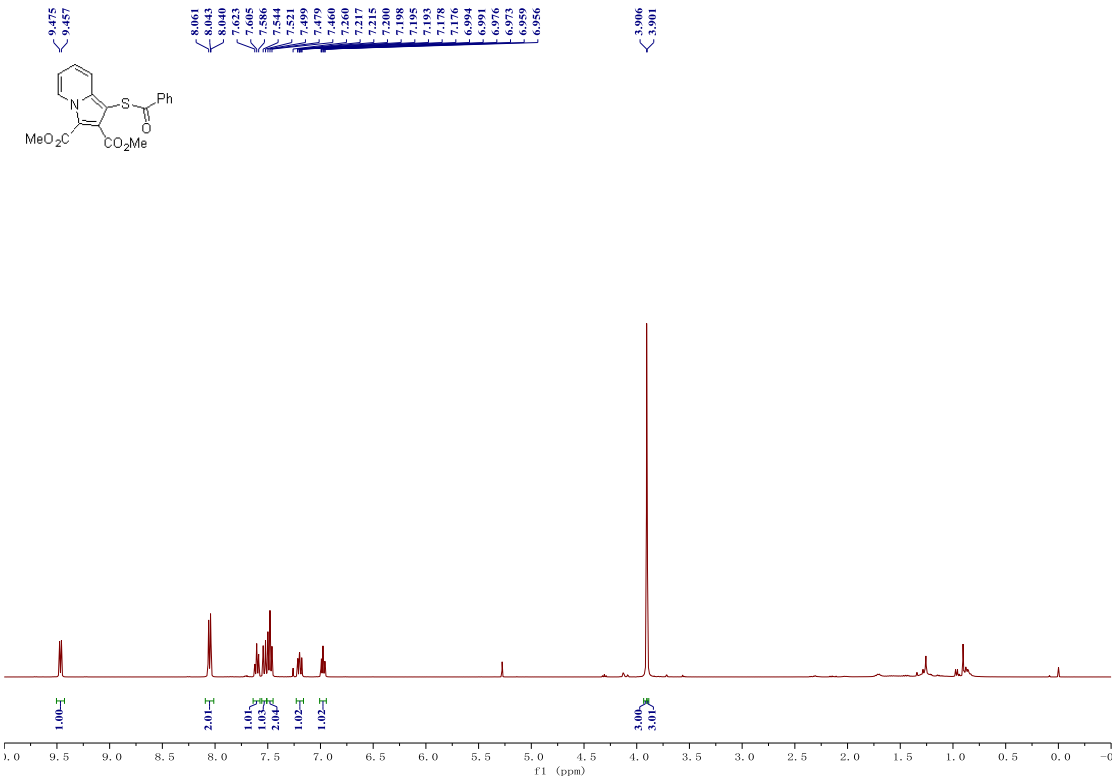
^{13}C NMR of compound **3** (100 MHz, $CDCl_3$)



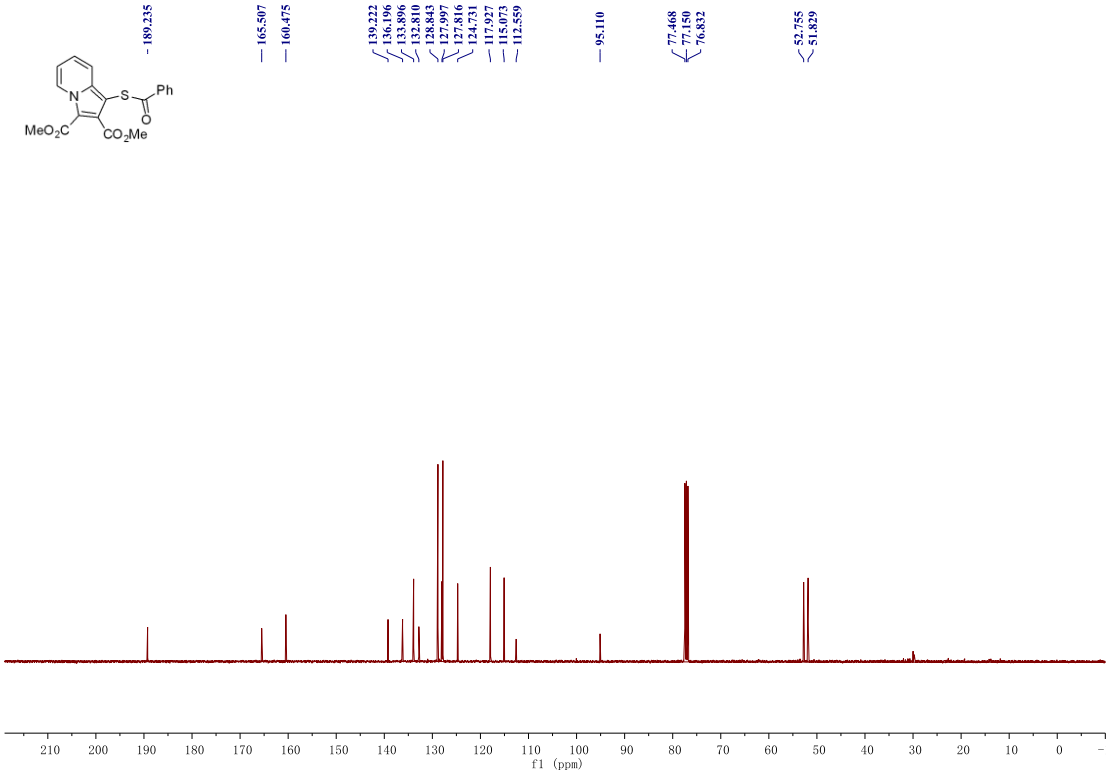
^{1}H NMR of compound **4** (400 MHz, $CDCl_3$)



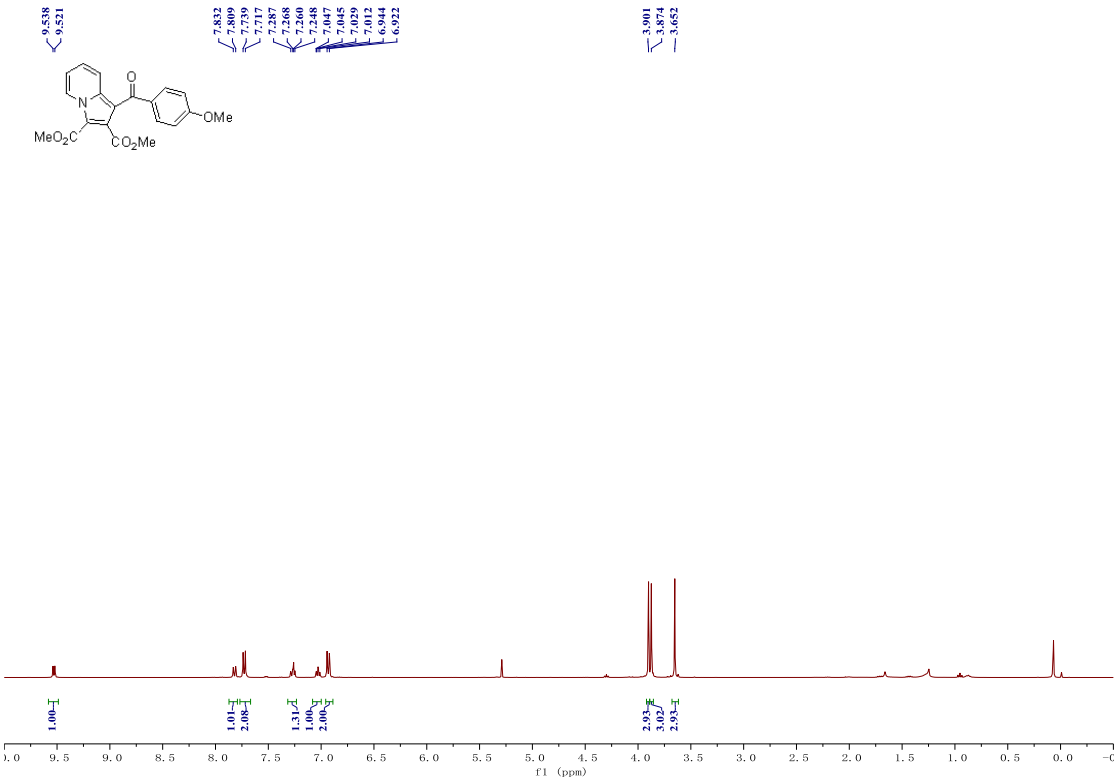
^{13}C NMR of compound **4** (100 MHz, $CDCl_3$)



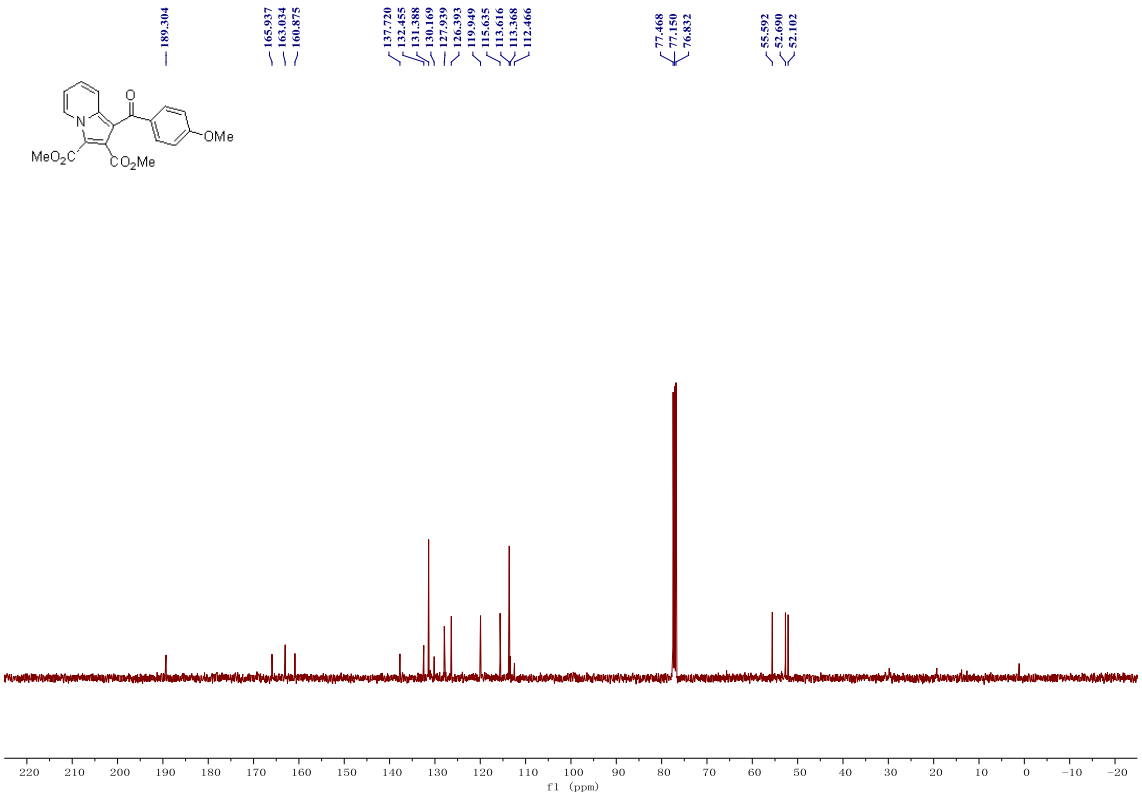
^{1}H NMR of compound **4'** (400 MHz, $CDCl_3$)



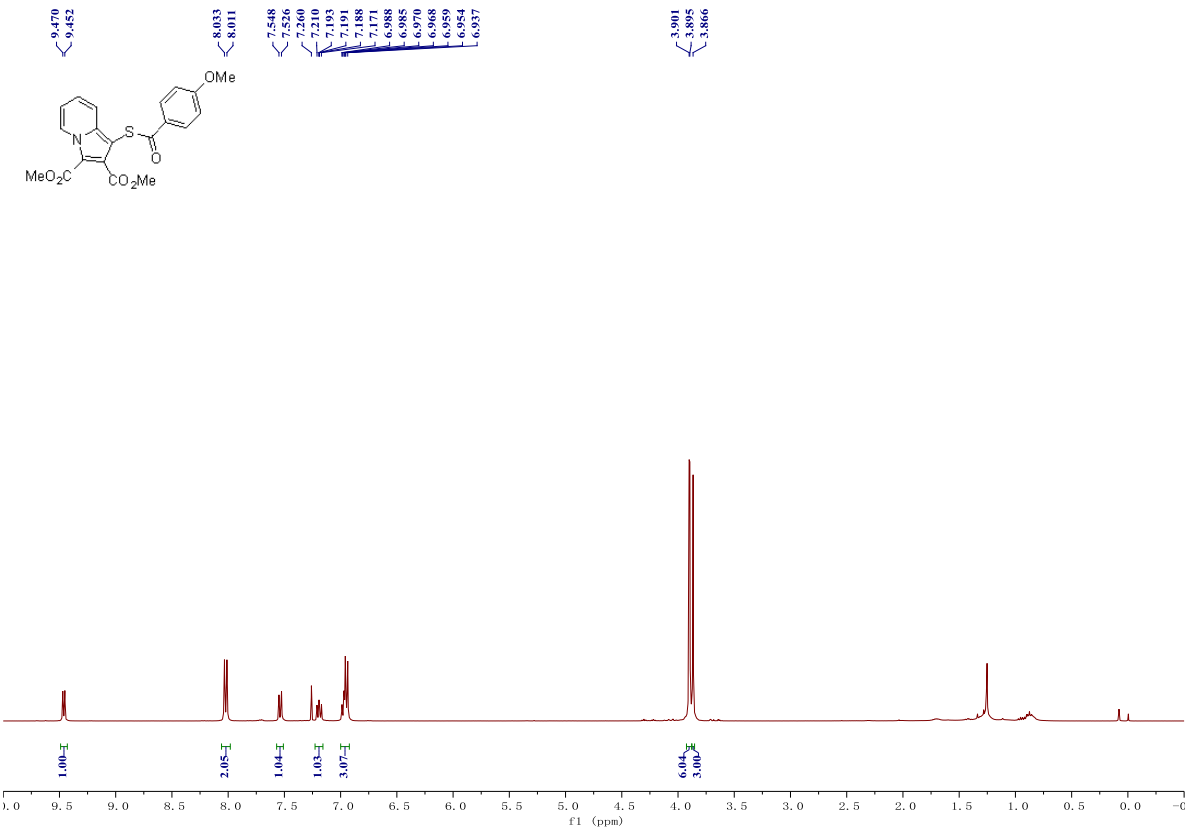
^{13}C NMR of compound **4'** (100 MHz, $CDCl_3$)



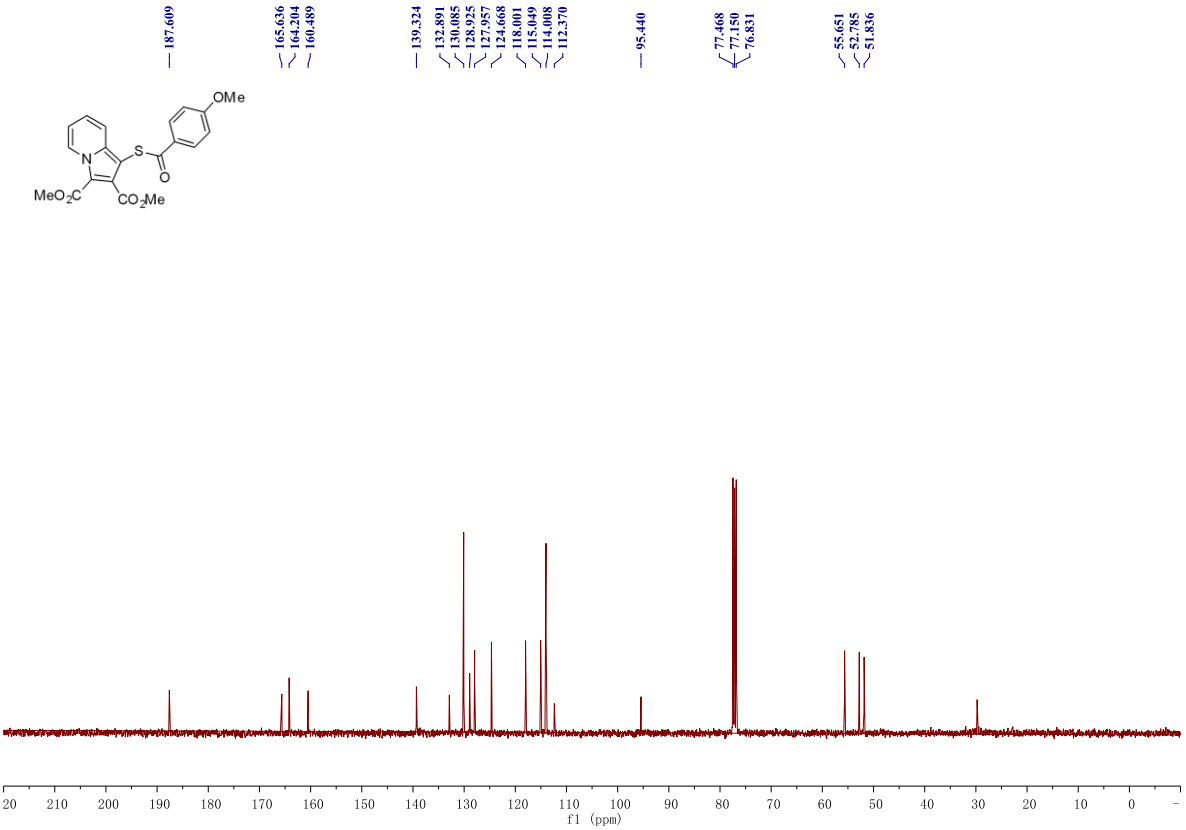
^{1}H NMR of compound **5** (400 MHz, $CDCl_3$)



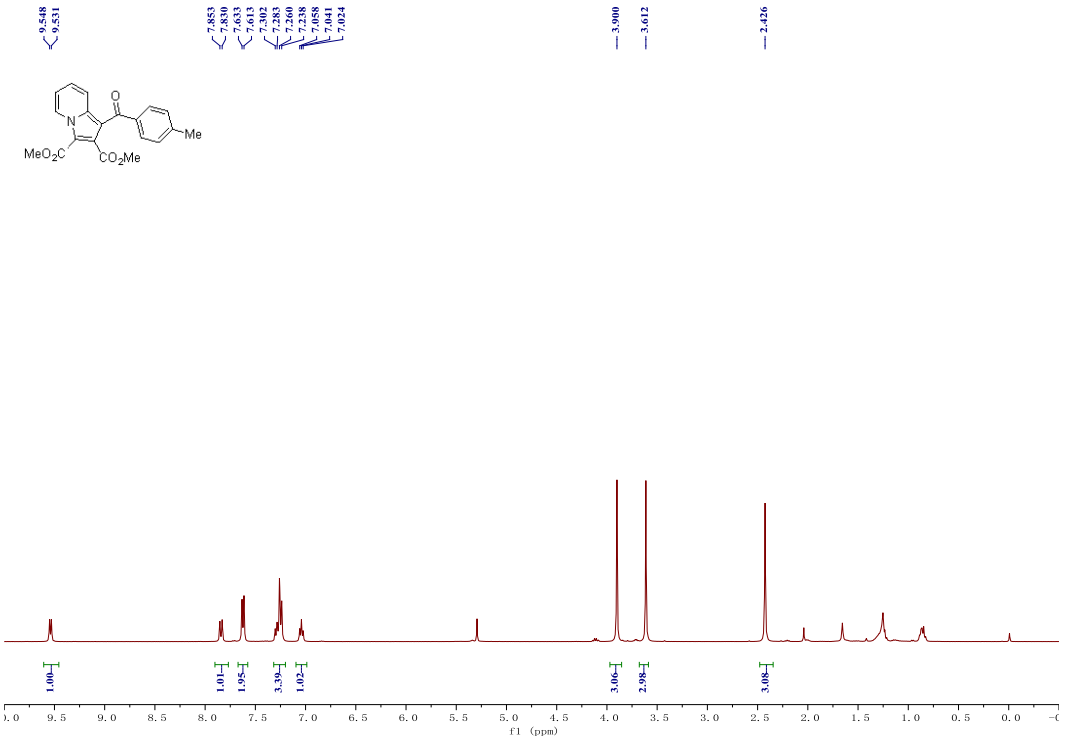
^{13}C NMR of compound **5** (100 MHz, $CDCl_3$)



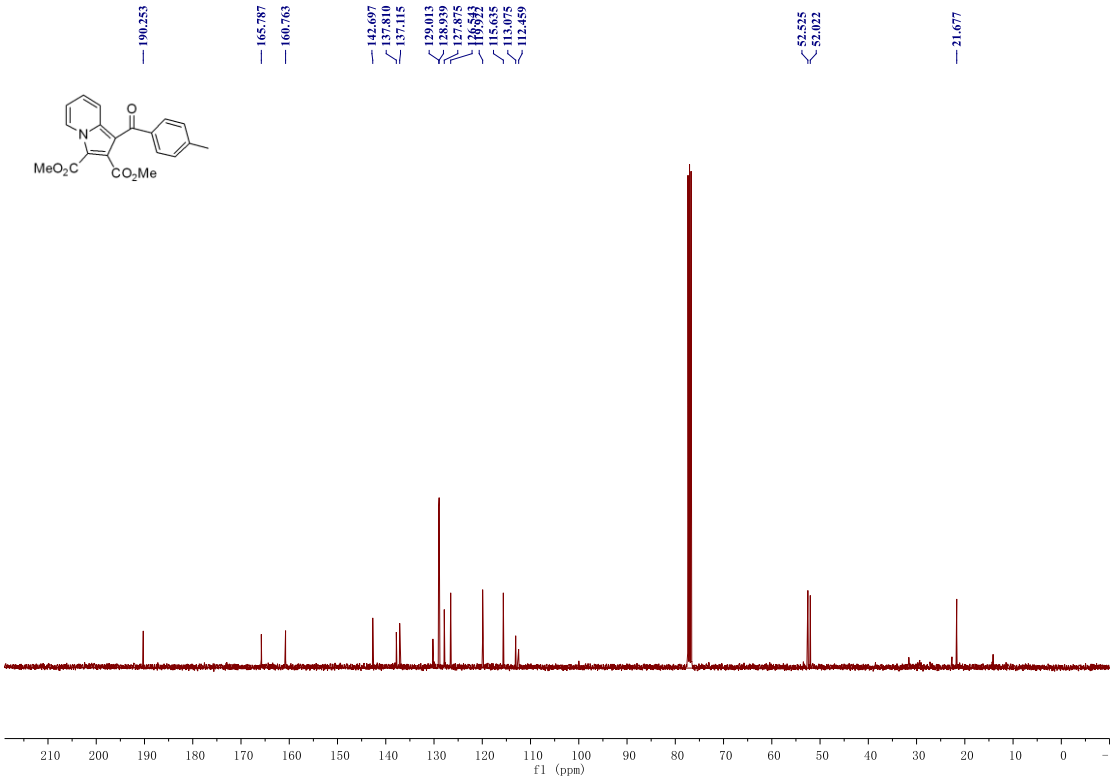
^{1}H NMR of compound **5'** (400 MHz, $CDCl_3$)



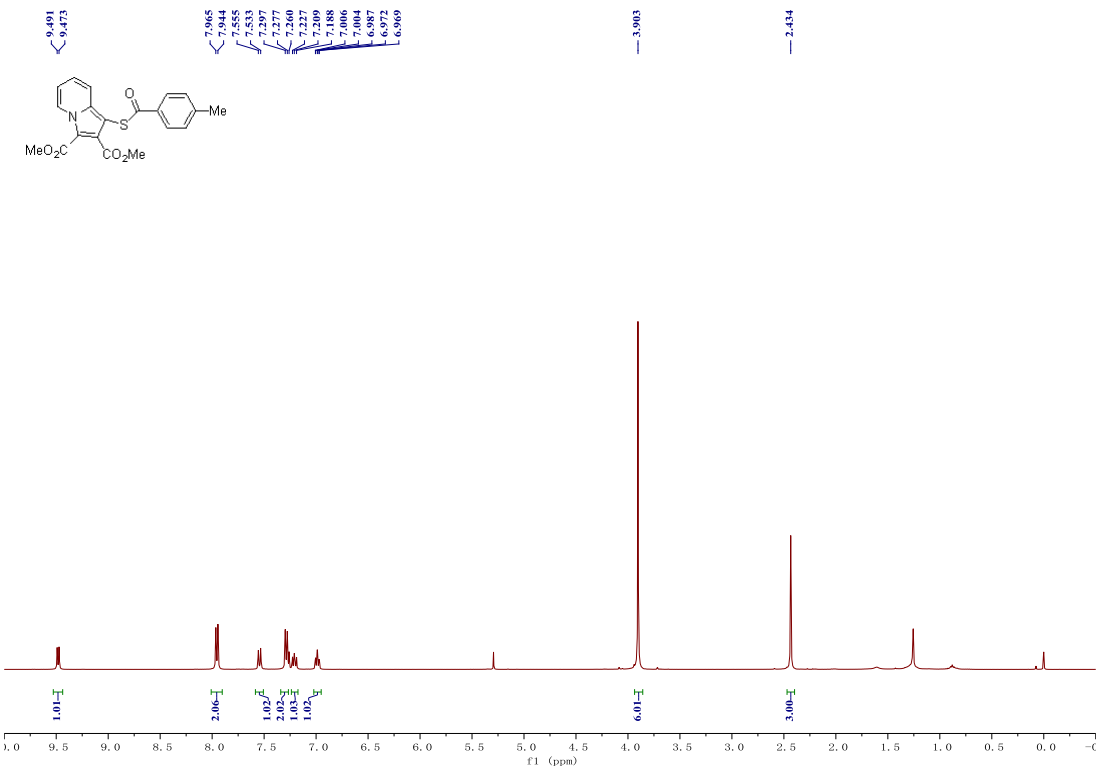
^{13}C NMR of compound **5'** (100 MHz, $CDCl_3$)



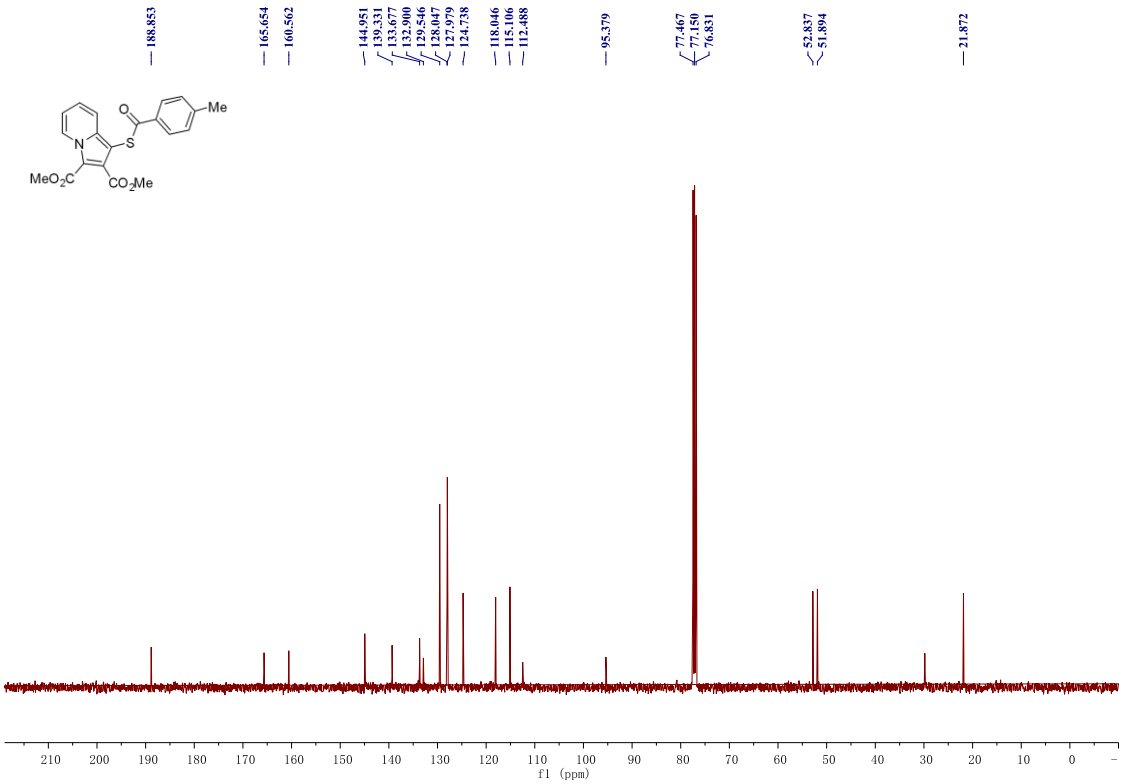
^{1}H NMR of compound **6** (400 MHz, $CDCl_3$)



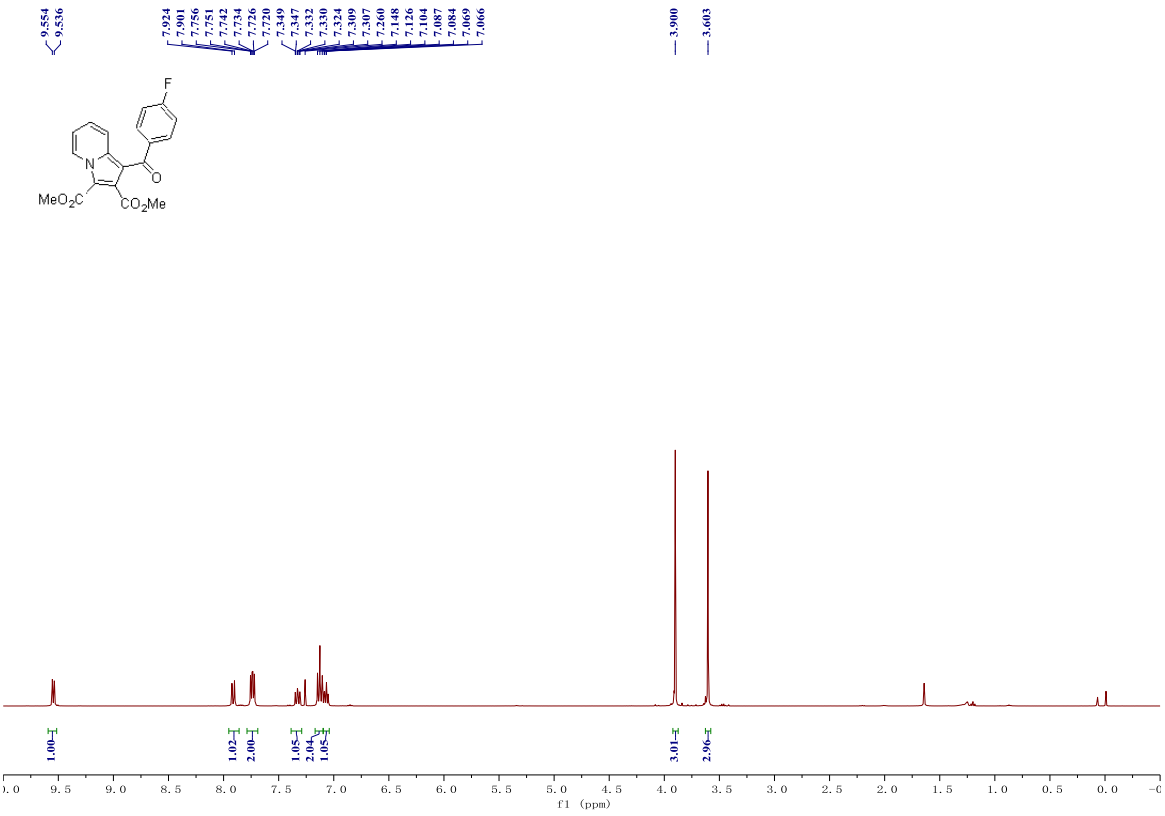
^{13}C NMR of compound **6** (100 MHz, $CDCl_3$)



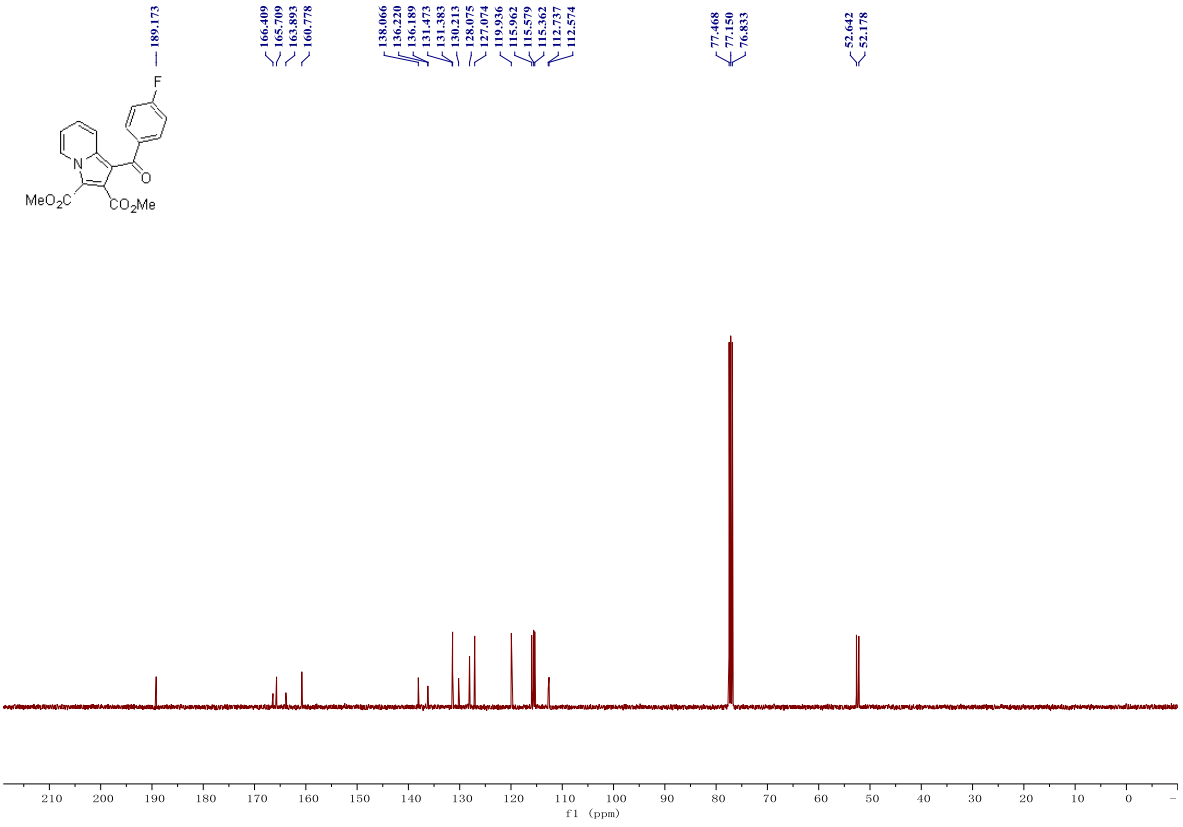
^{1}H NMR of compound **6'** (400 MHz, $CDCl_3$)



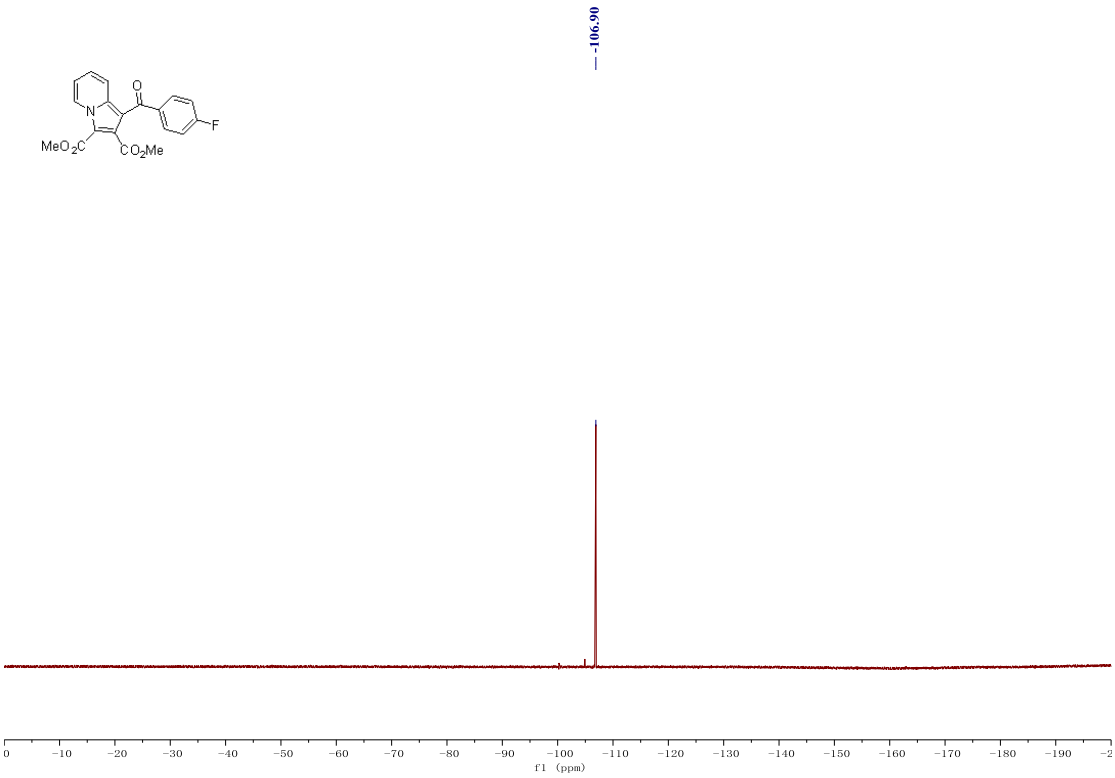
^{13}C NMR of compound **6'** (100 MHz, $CDCl_3$)



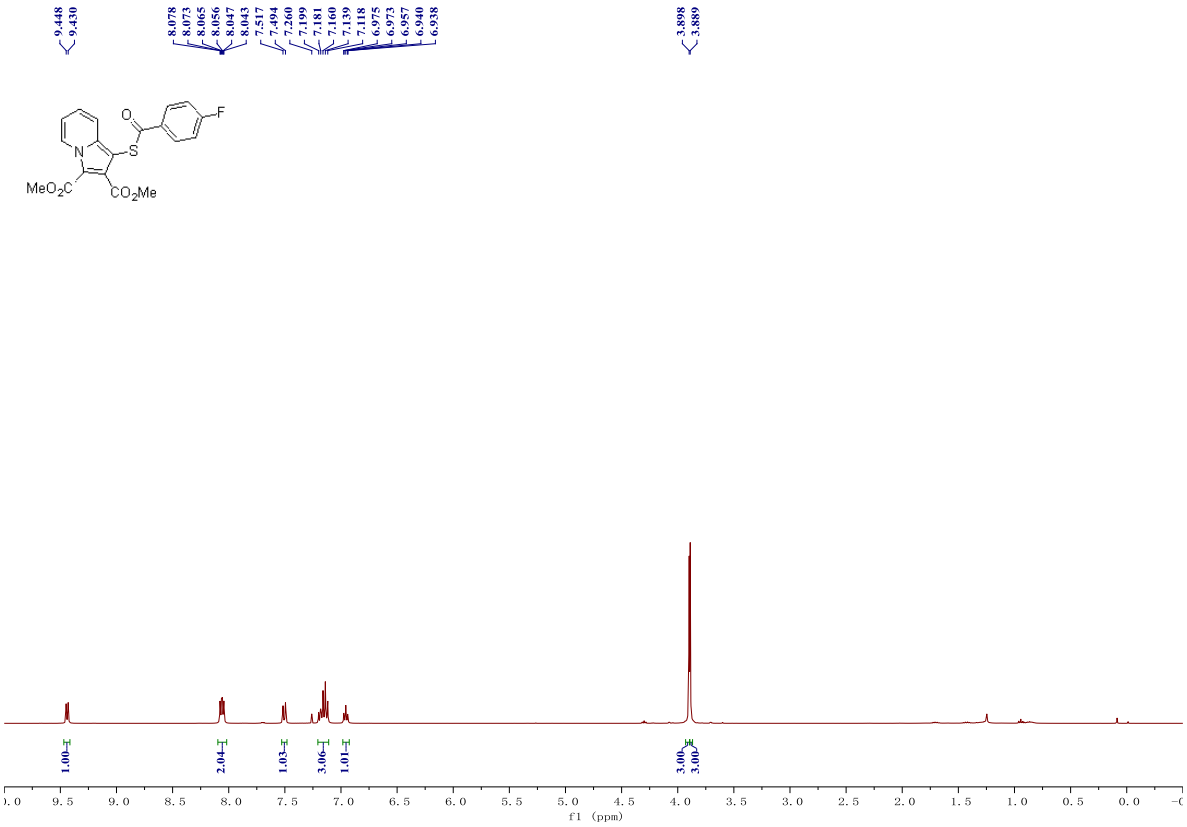
^{1}H NMR of compound **7** (400 MHz, $CDCl_3$)



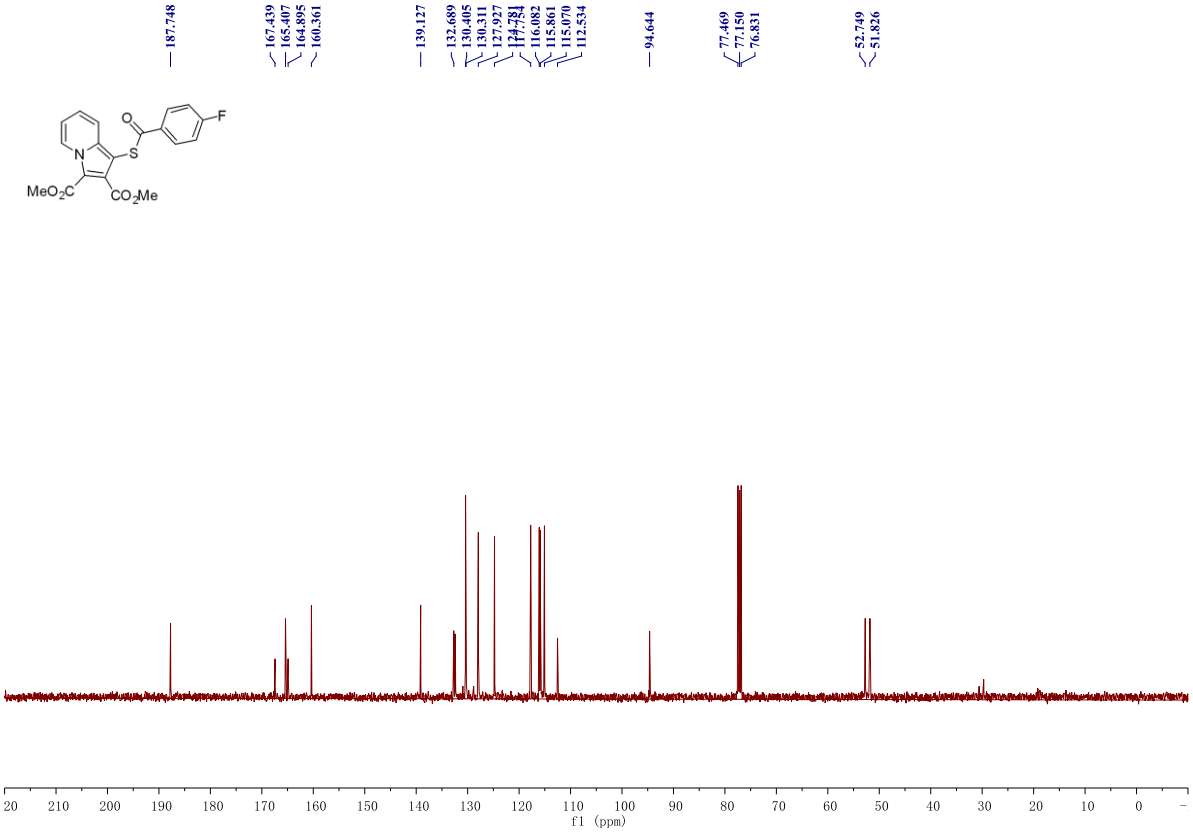
^{13}C NMR of compound **7** (100 MHz, $CDCl_3$)



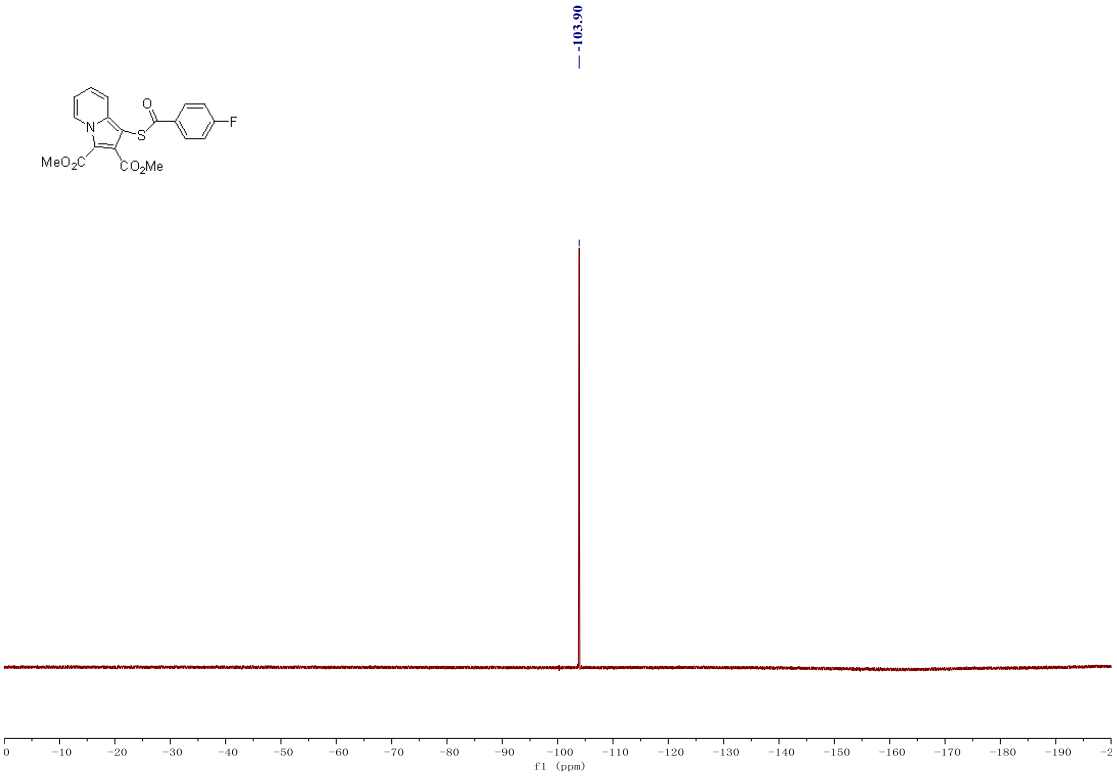
^{19}F NMR of compound **7** (376 MHz, $CDCl_3$)



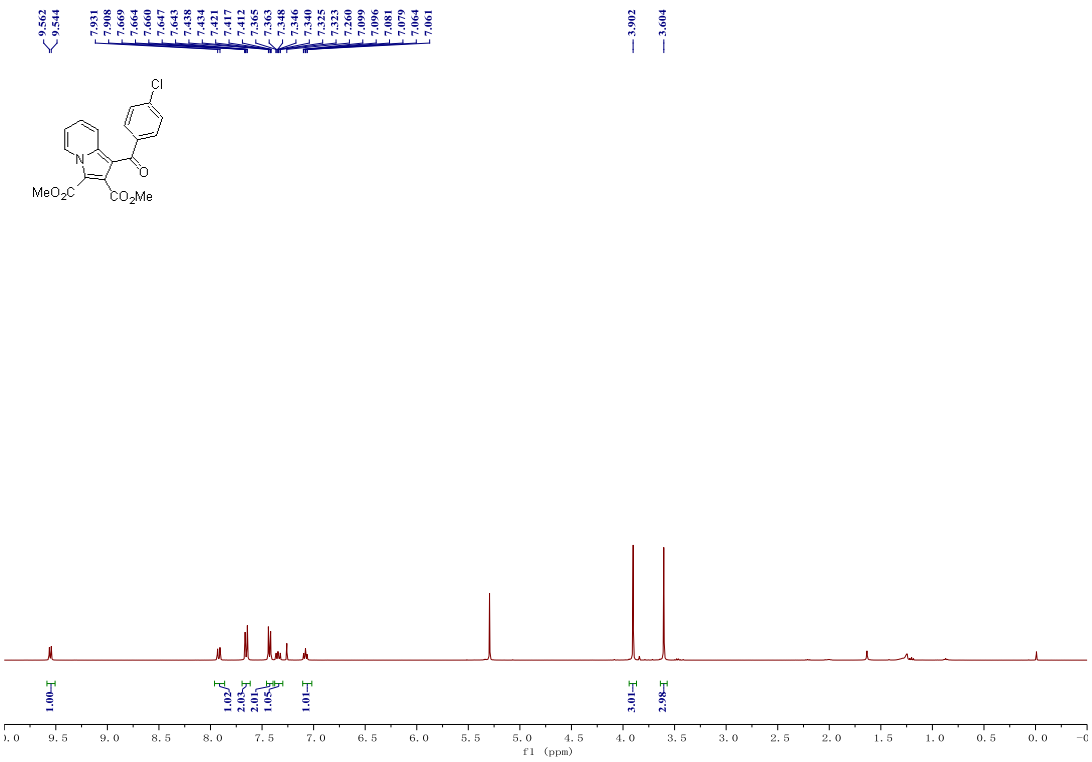
^{1}H NMR of compound **7'** (400 MHz, $CDCl_3$)



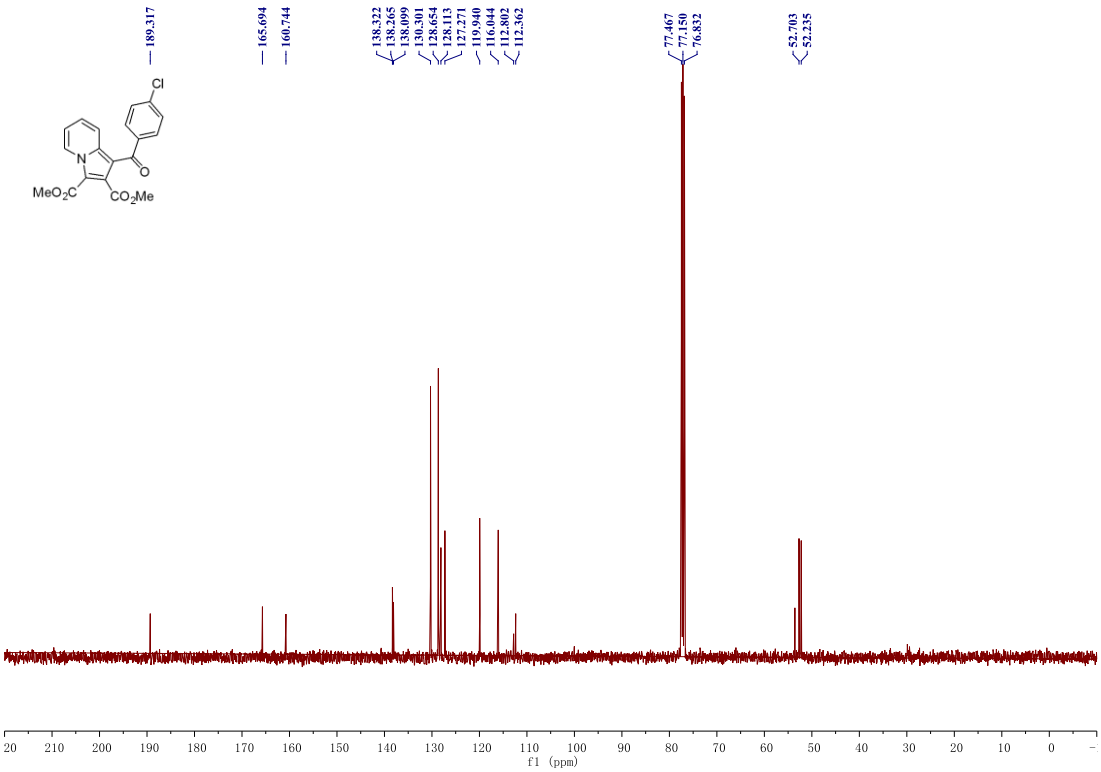
^{13}C NMR of compound **7'** (100 MHz, $CDCl_3$)



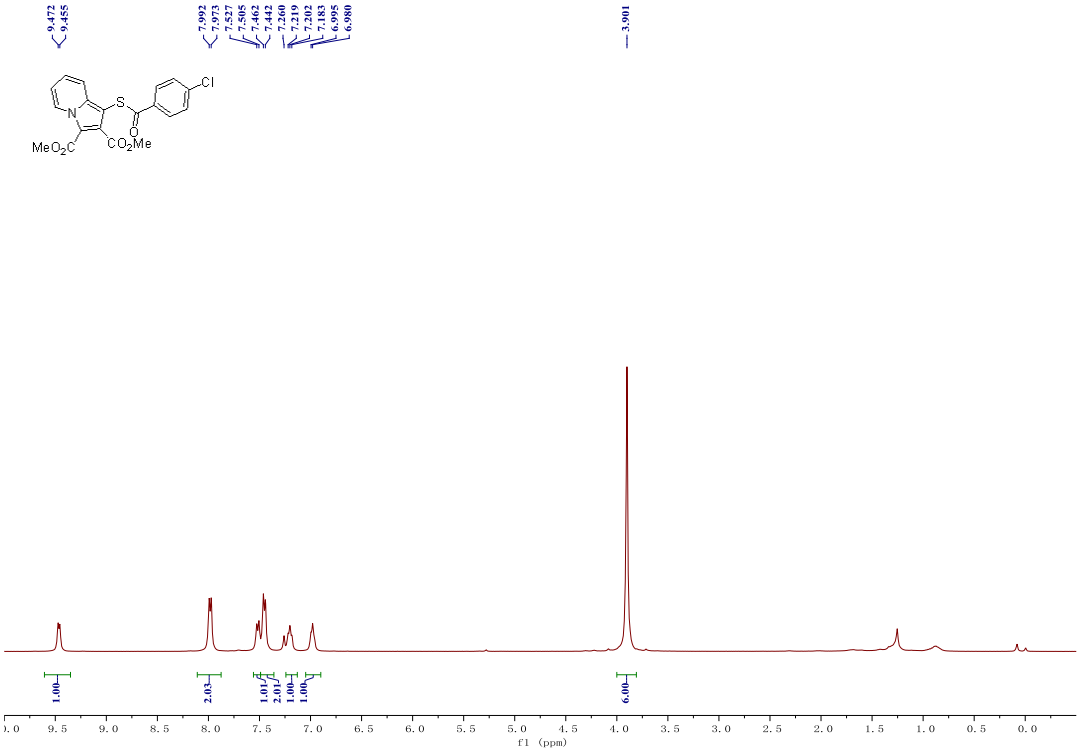
^{19}F NMR of compound **7'** (376 MHz, $CDCl_3$)



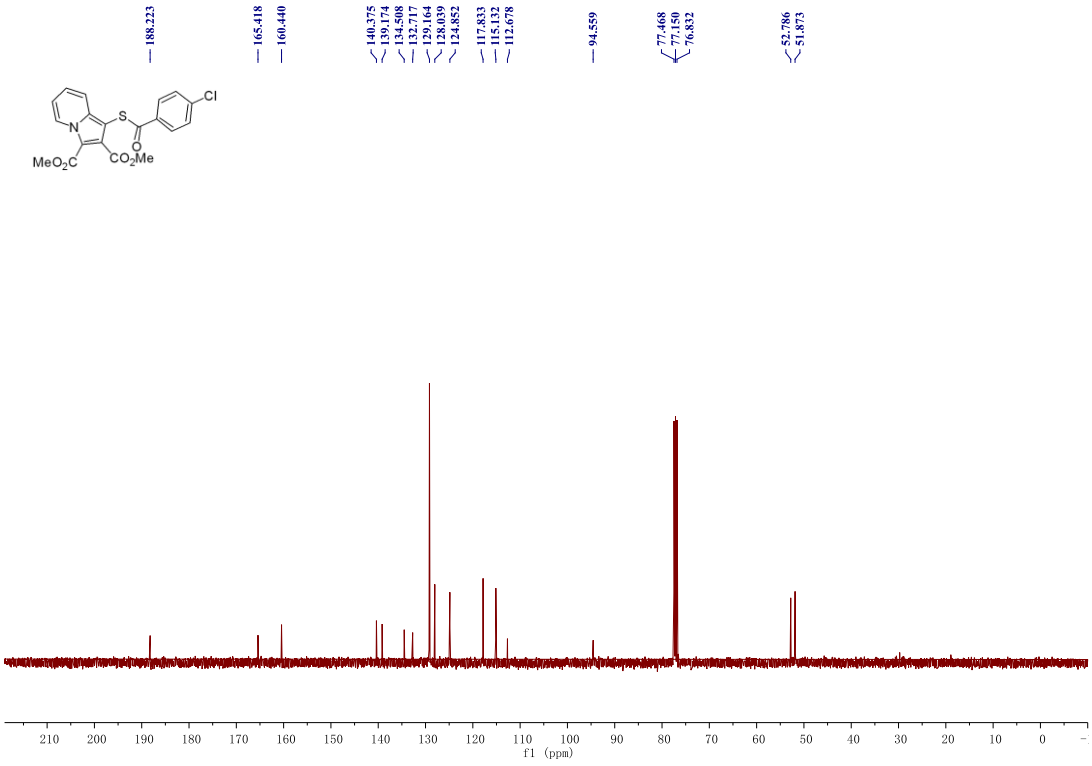
^{1}H NMR of compound **8** (400 MHz, $CDCl_3$)



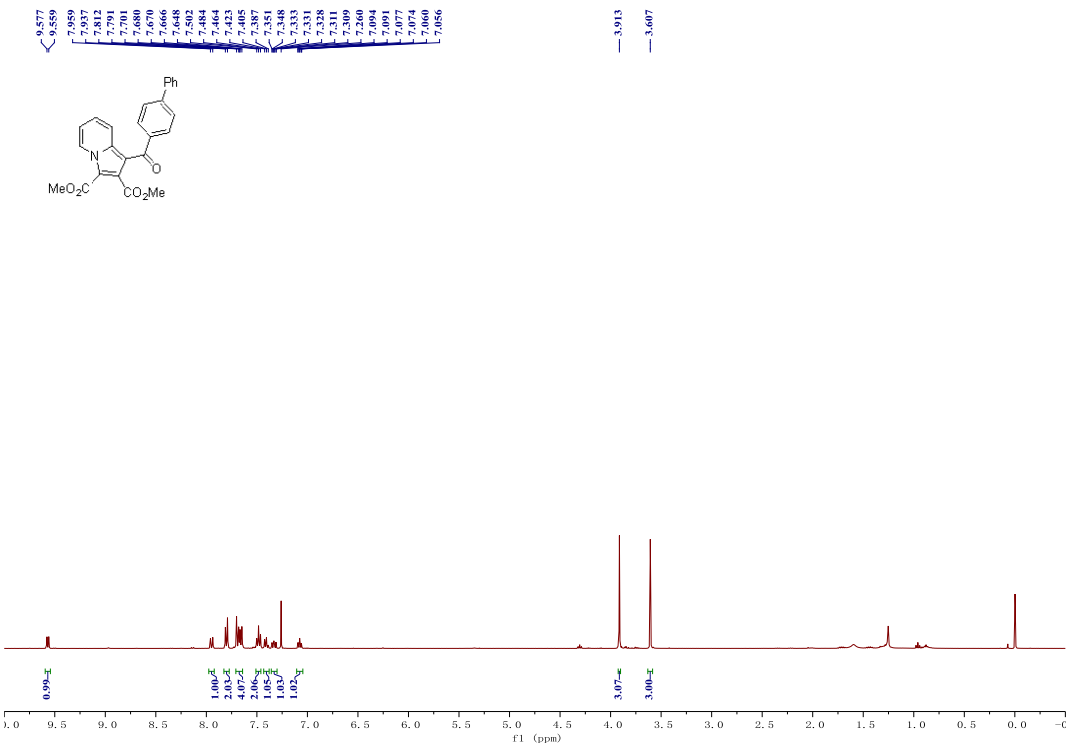
^{13}C NMR of compound **8** (100 MHz, $CDCl_3$)



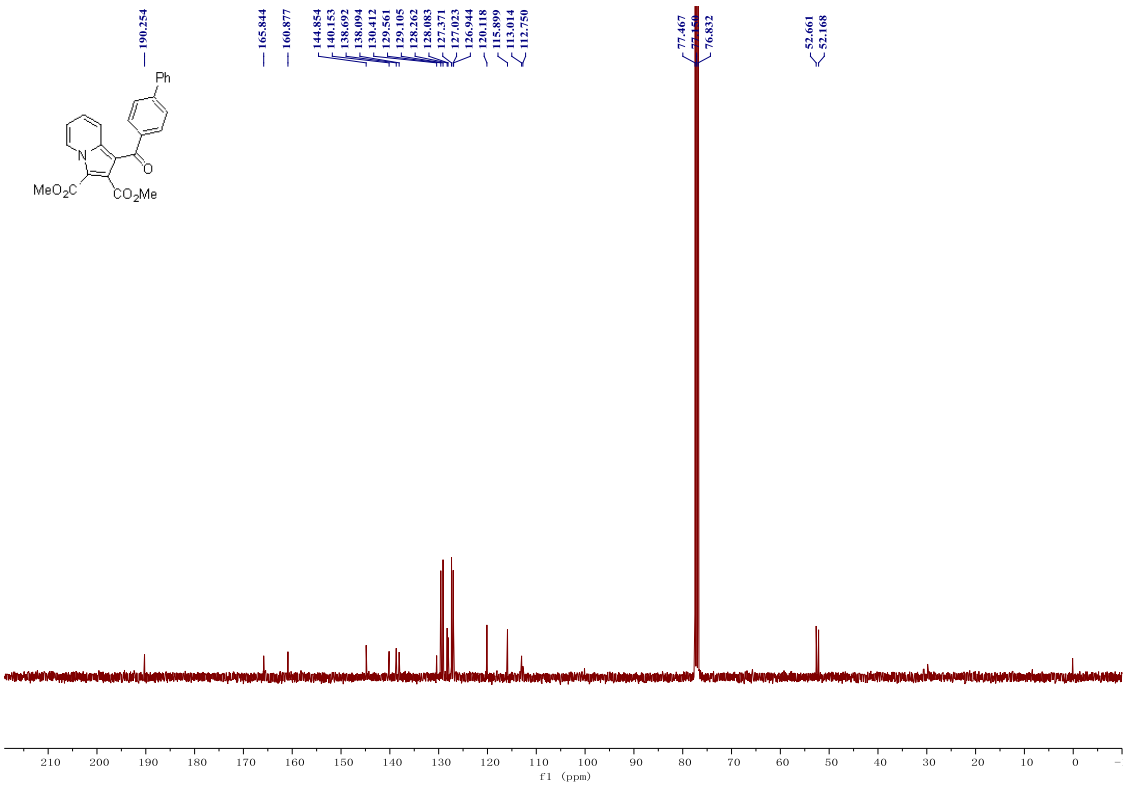
^{1}H NMR of compound **8'** (400 MHz, $CDCl_3$)



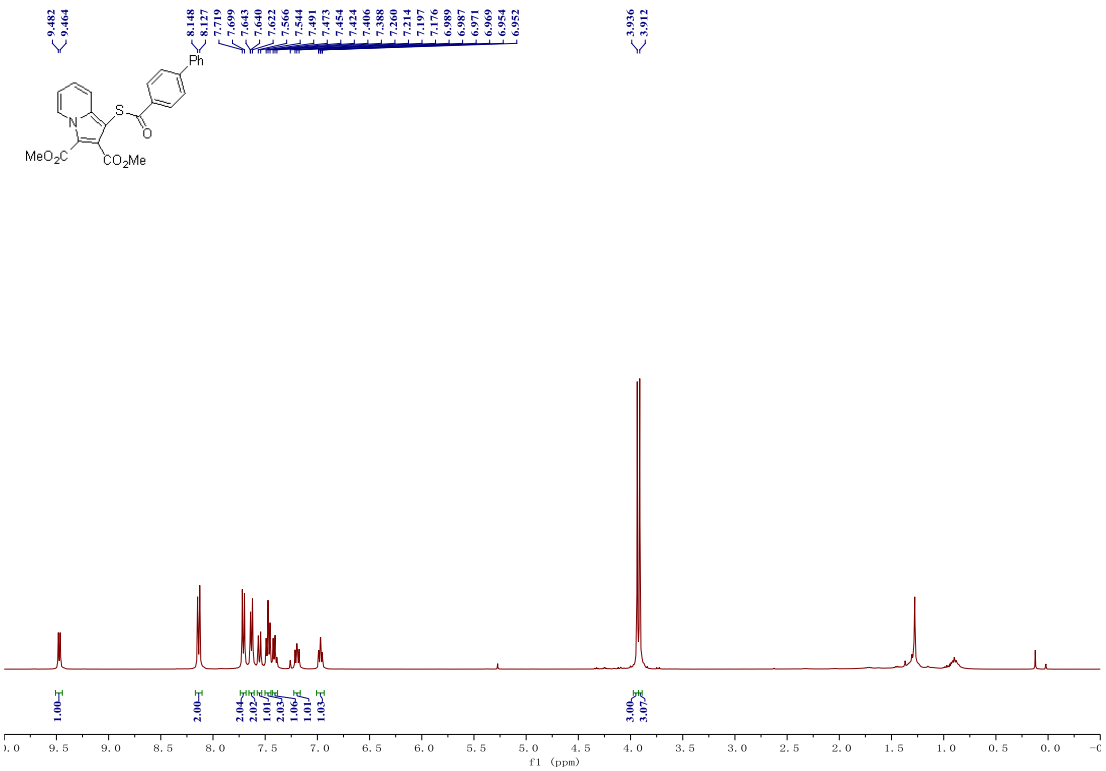
^{13}C NMR of compound **8'** (100 MHz, $CDCl_3$)



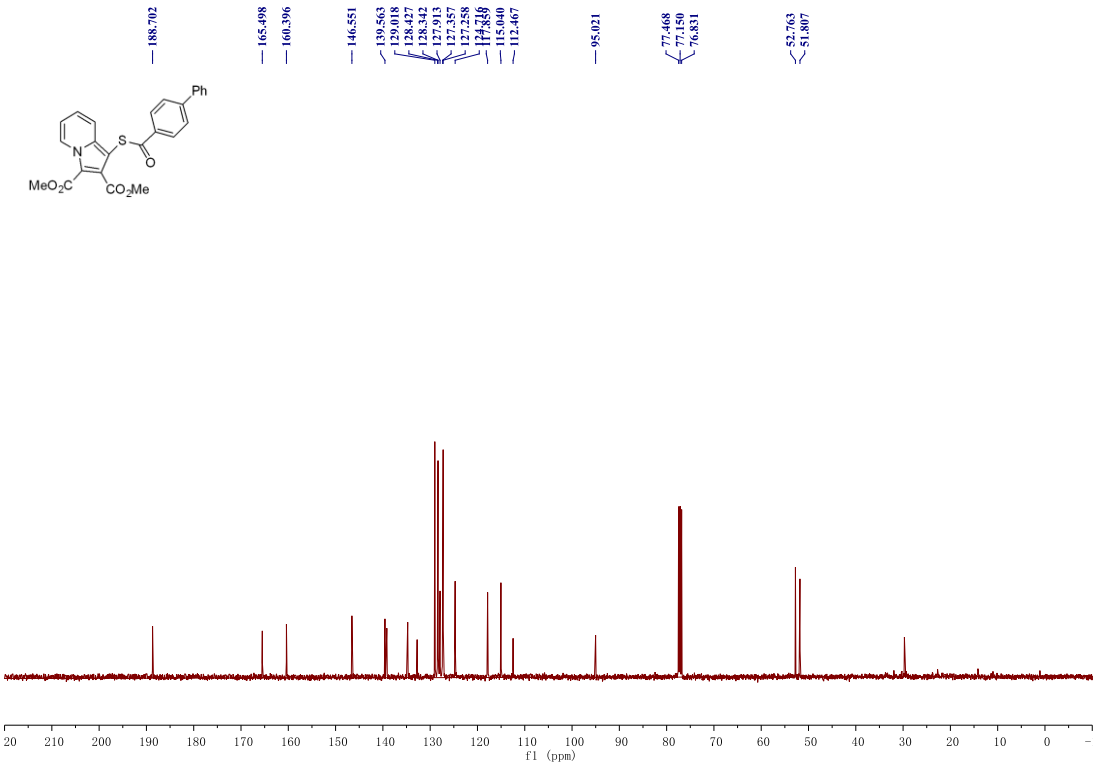
^{1}H NMR of compound **9** (400 MHz, $CDCl_3$)



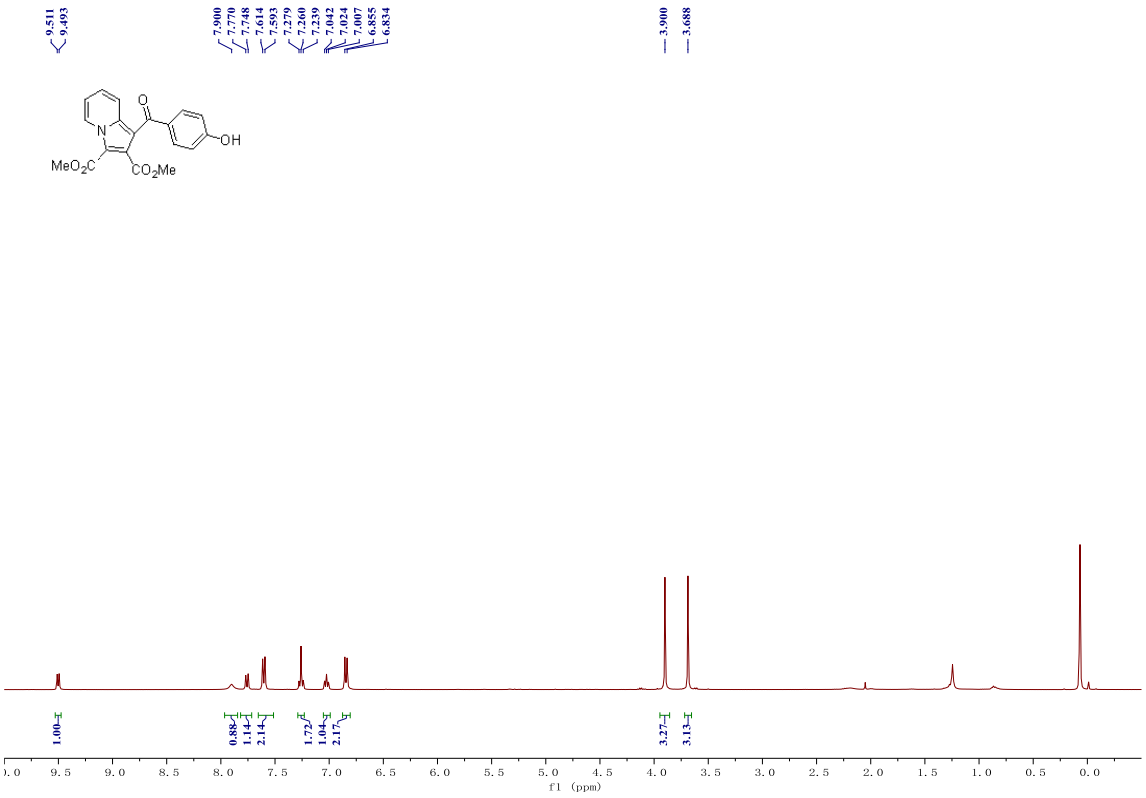
^{13}C NMR of compound **9** (100 MHz, $CDCl_3$)



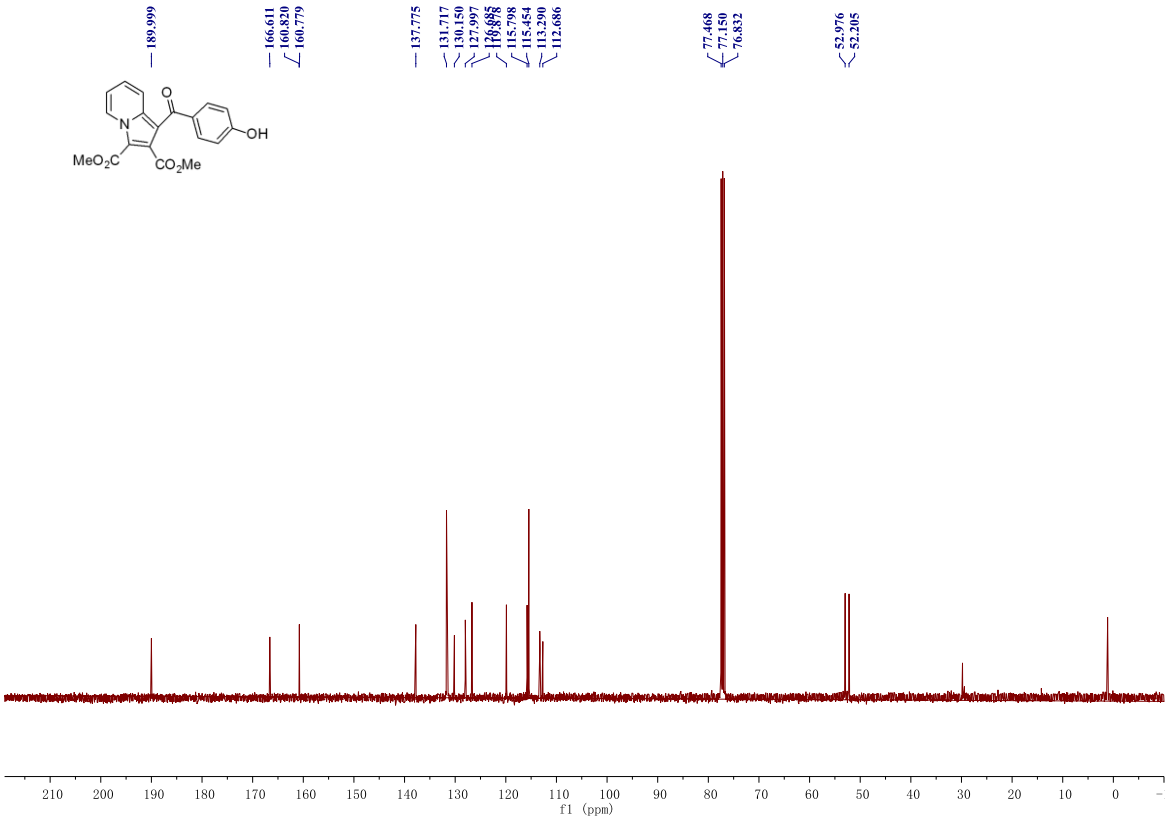
^{1}H NMR of compound **9'** (400 MHz, $CDCl_3$)



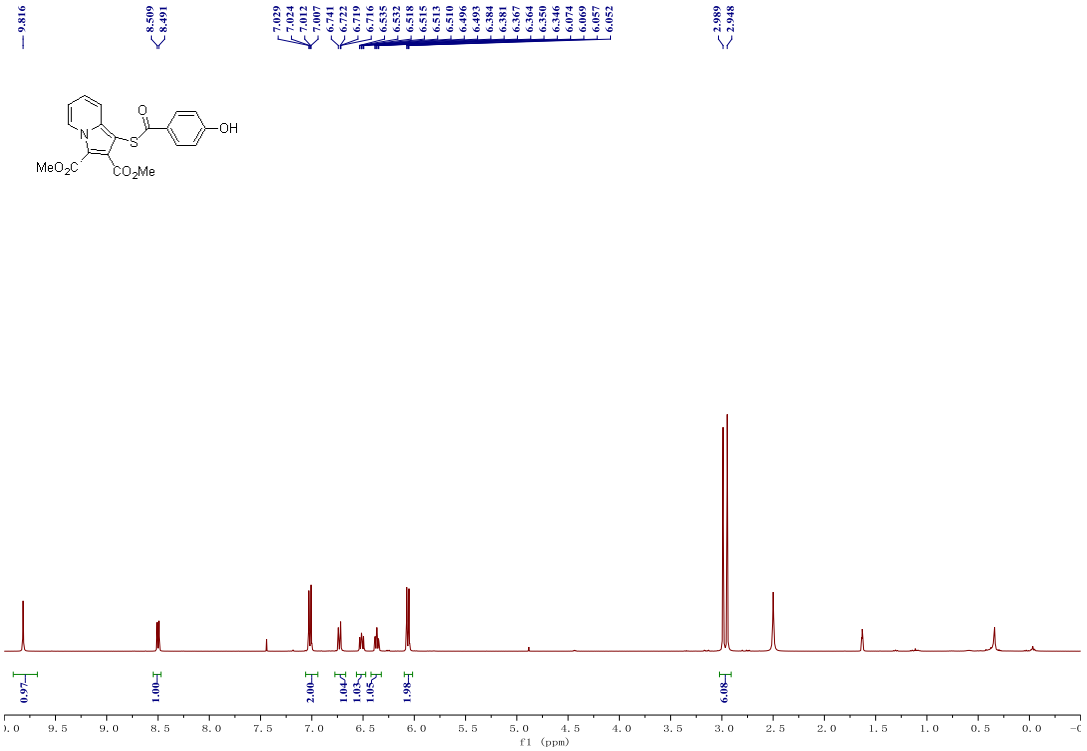
^{13}C NMR of compound **9'** (100 MHz, $CDCl_3$)



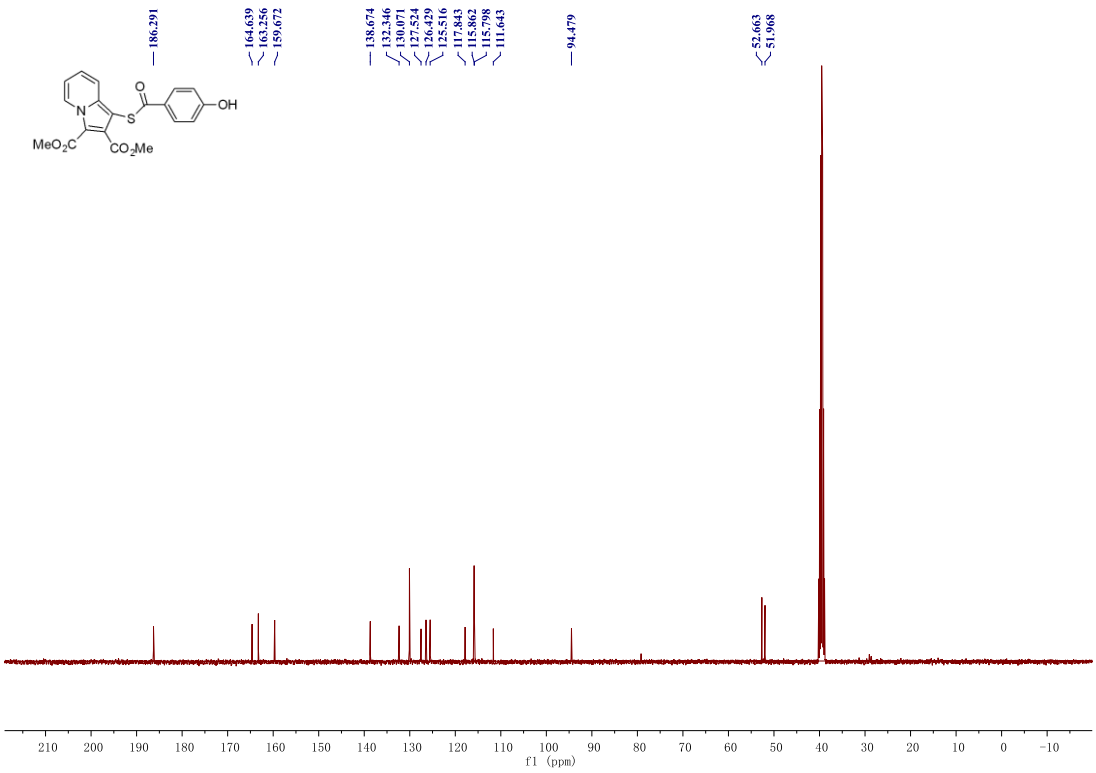
^{1}H NMR of compound **10** (400 MHz, $CDCl_3$)



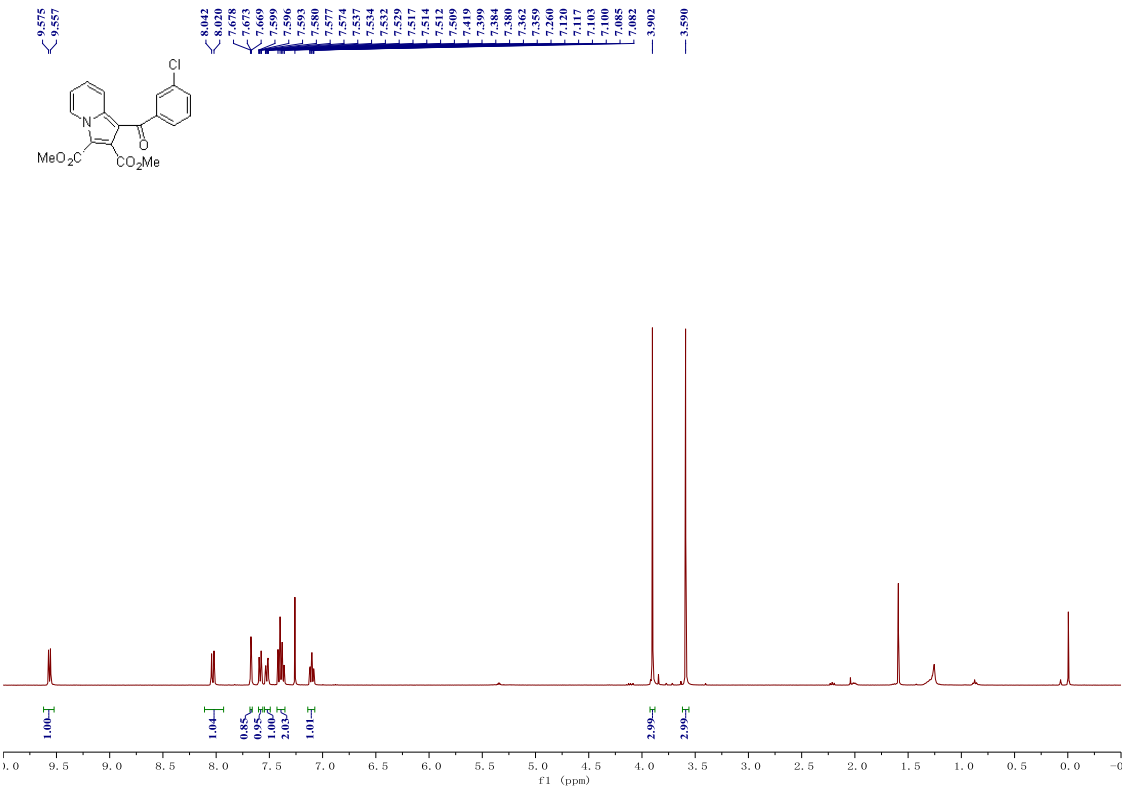
^{13}C NMR of compound **10** (100 MHz, $CDCl_3$)



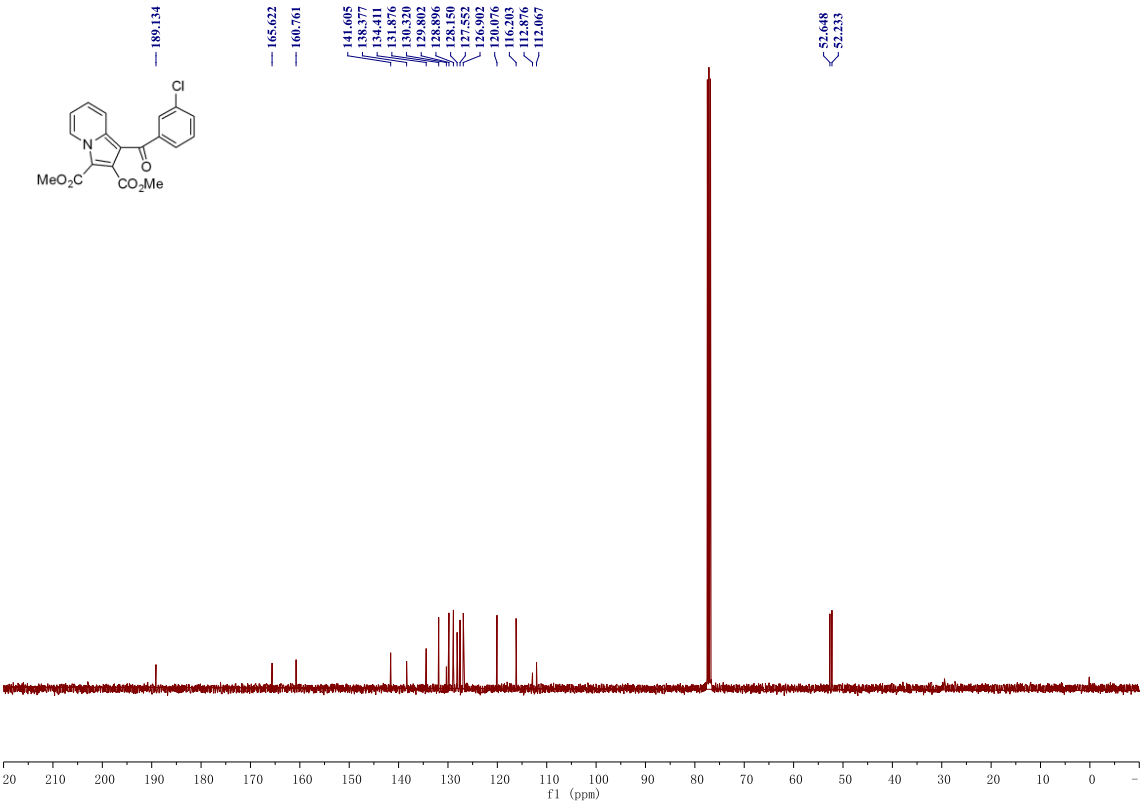
^{1}H NMR of compound **10'** (400 MHz, $(CD_3)_2SO$)



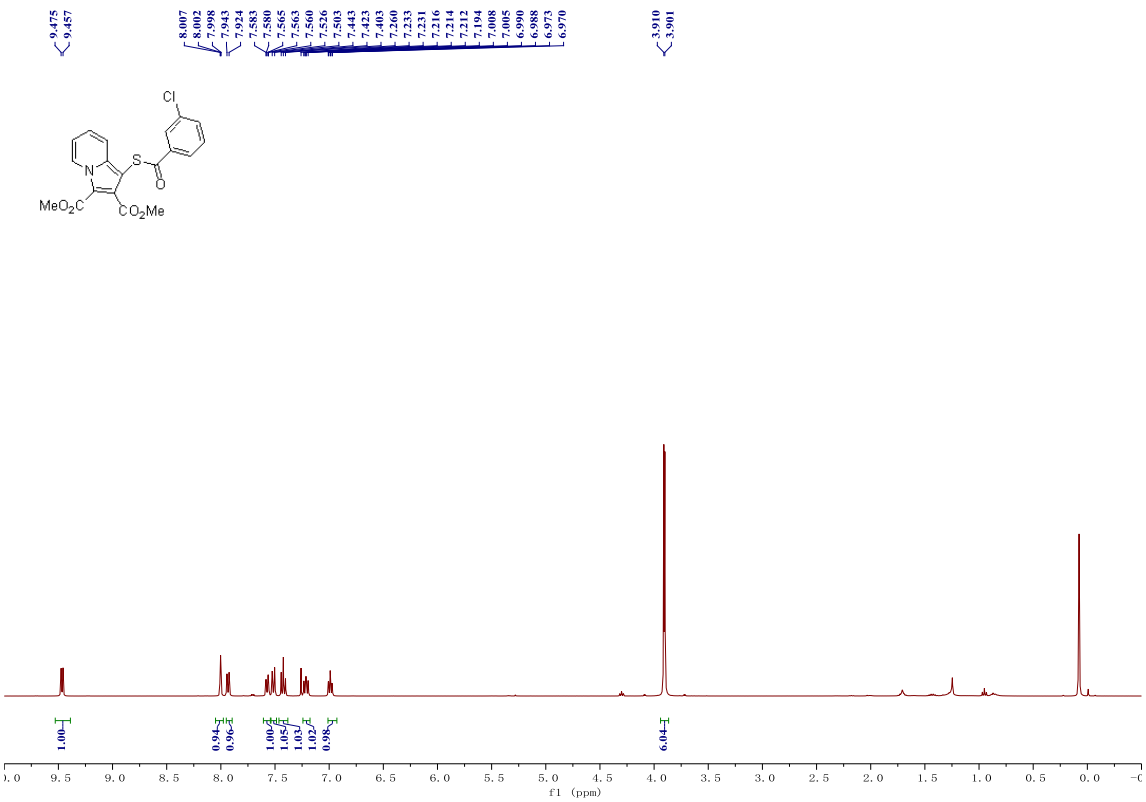
^{13}C NMR of compound **10'** (100 MHz, $(CD_3)_2SO$)



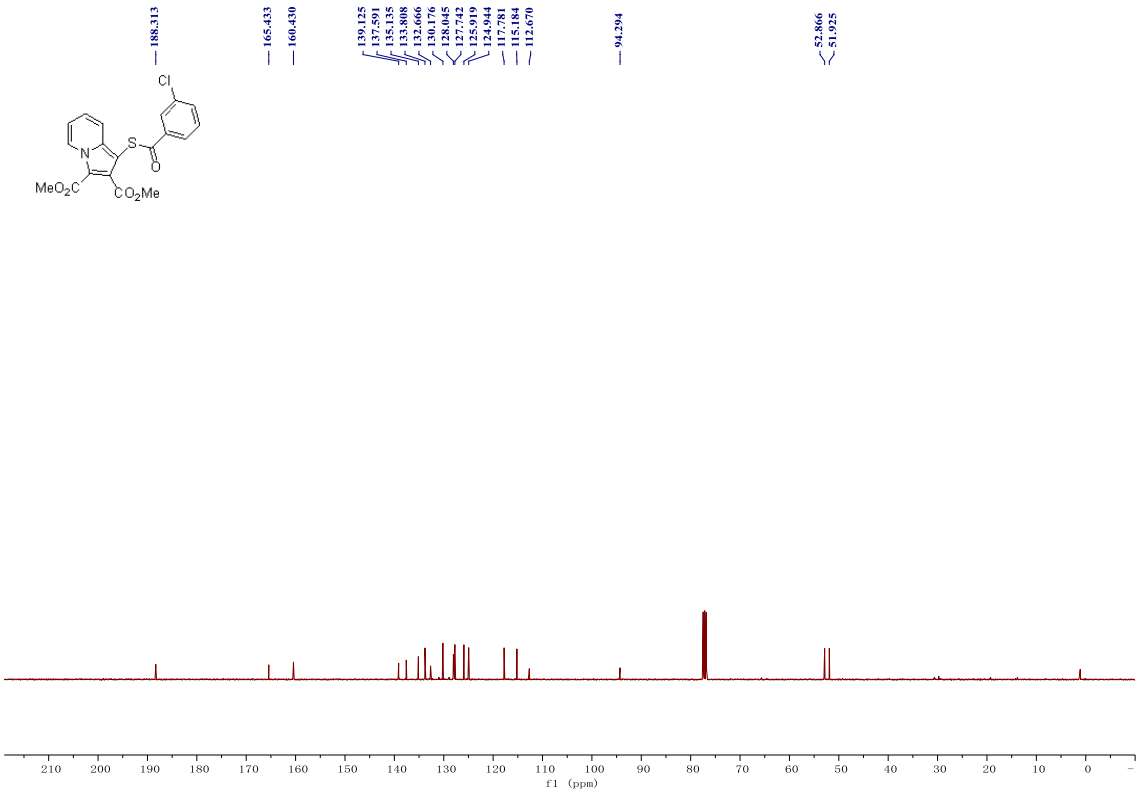
^{1}H NMR of compound **11** (400 MHz, $CDCl_3$)



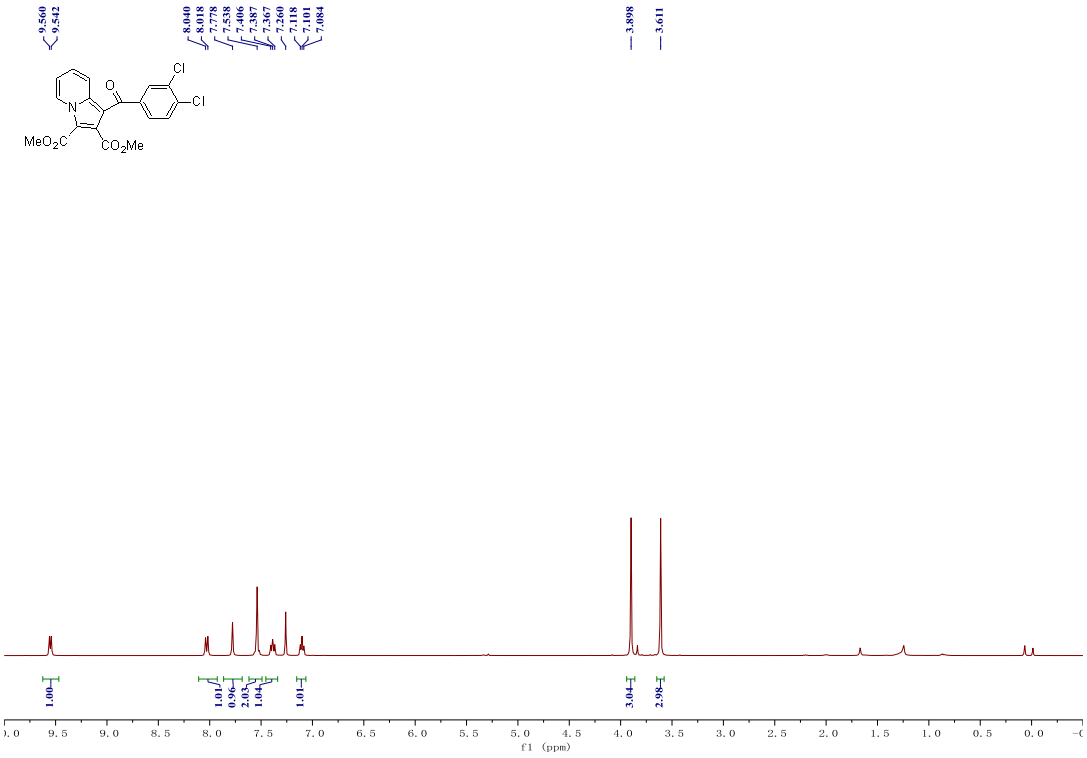
^{13}C NMR of compound **11** (100 MHz, $CDCl_3$)



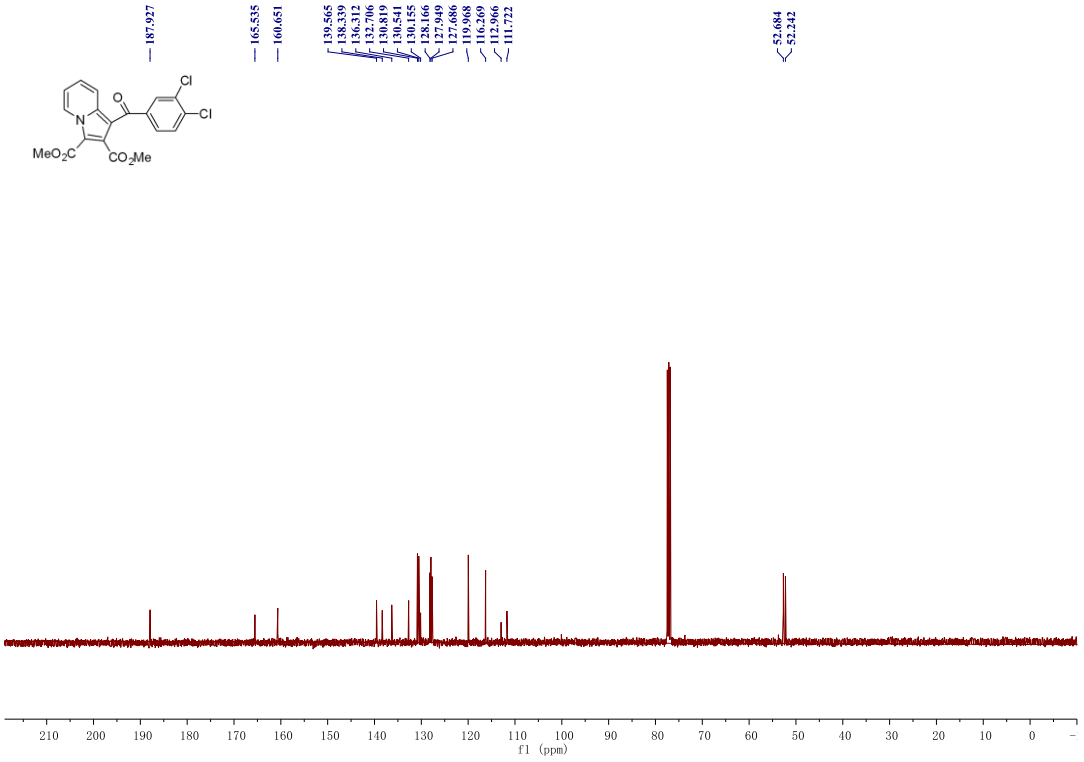
^{1}H NMR of compound **11'** (400 MHz, $CDCl_3$)



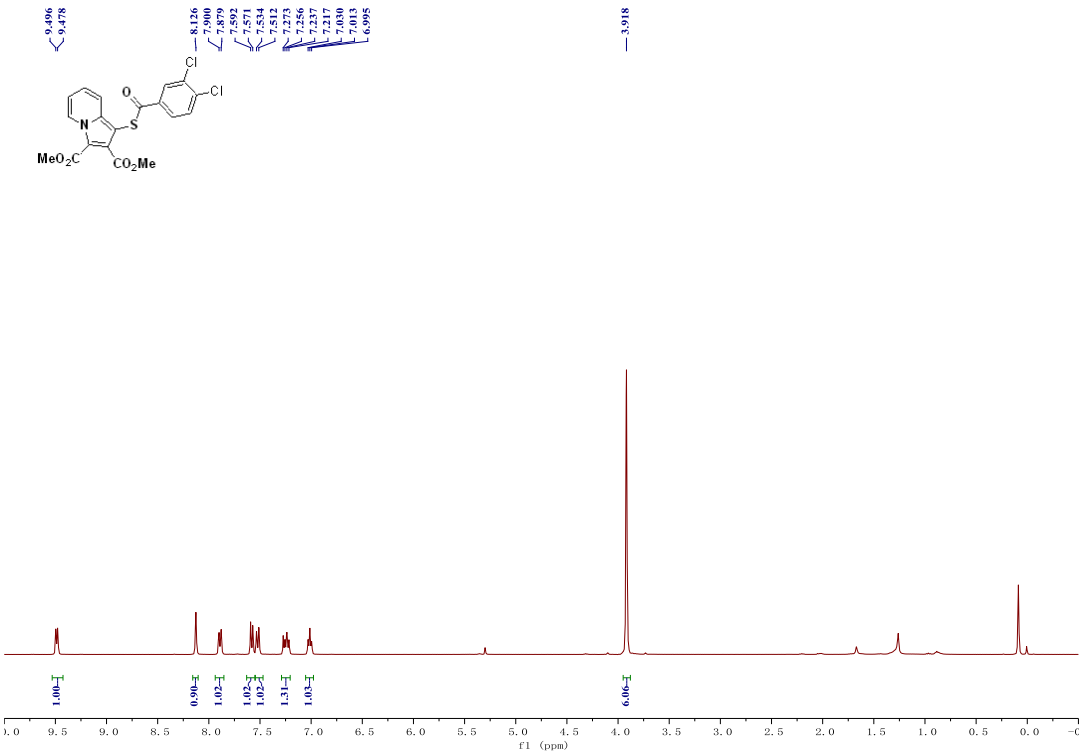
^{13}C NMR of compound **11'** (100 MHz, $CDCl_3$)



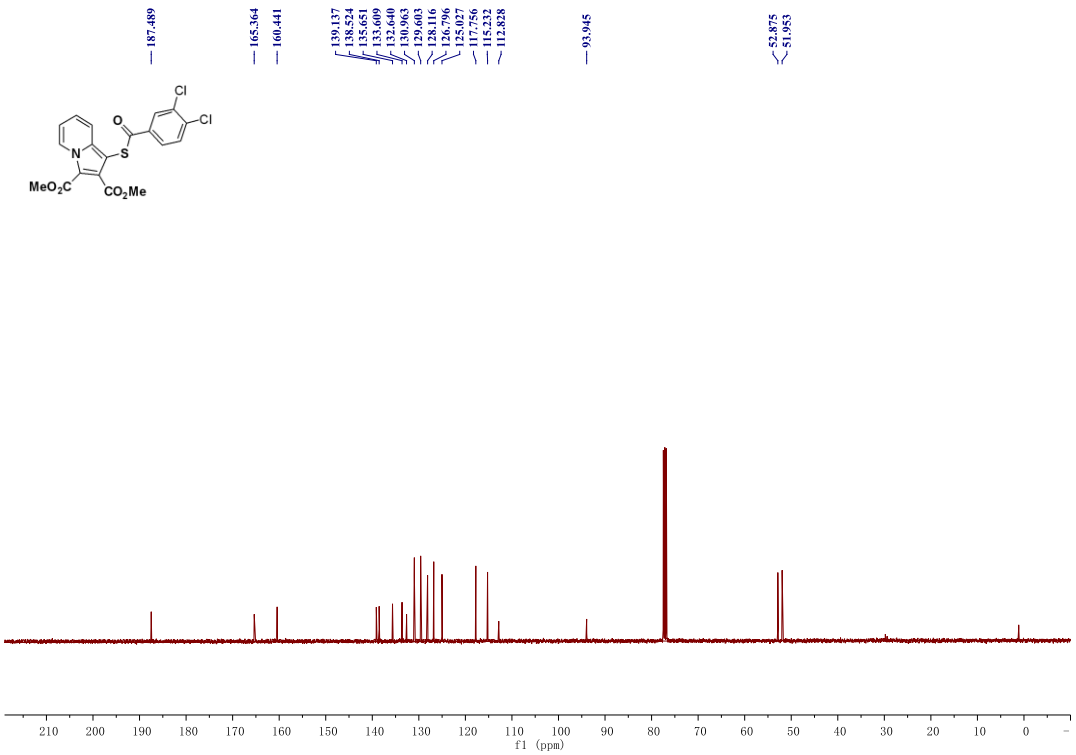
^{1}H NMR of compound **12** (400 MHz, $CDCl_3$)



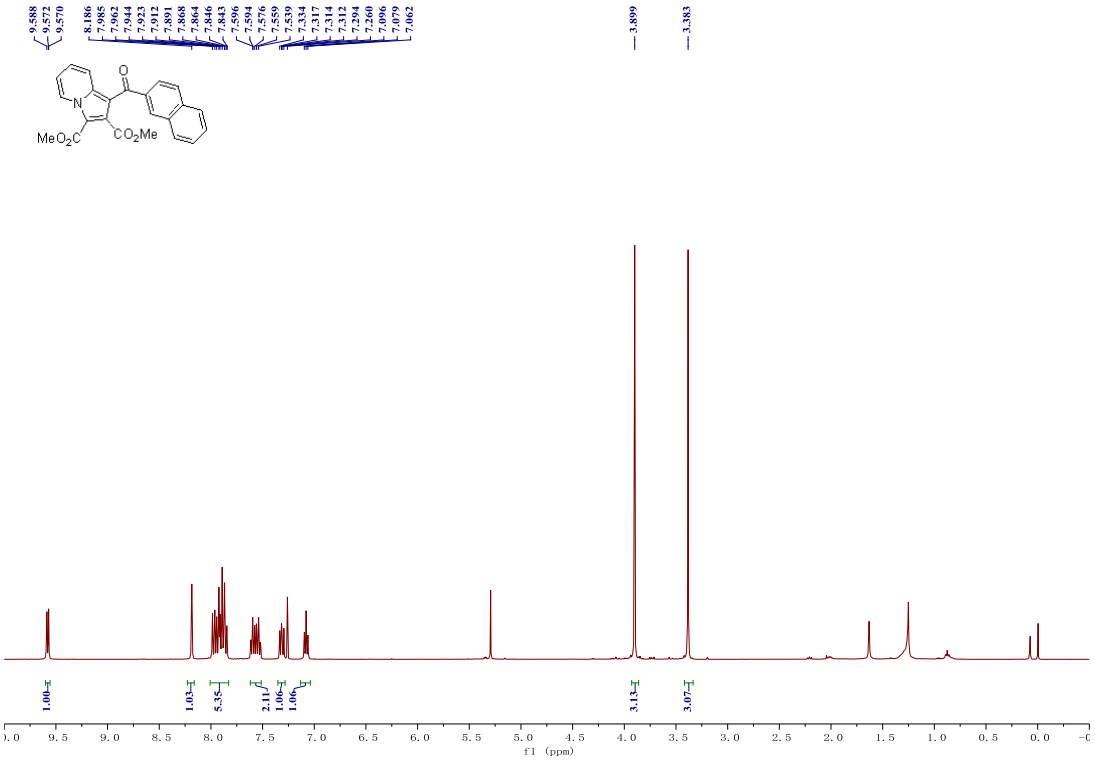
^{13}C NMR of compound **12** (100 MHz, $CDCl_3$)



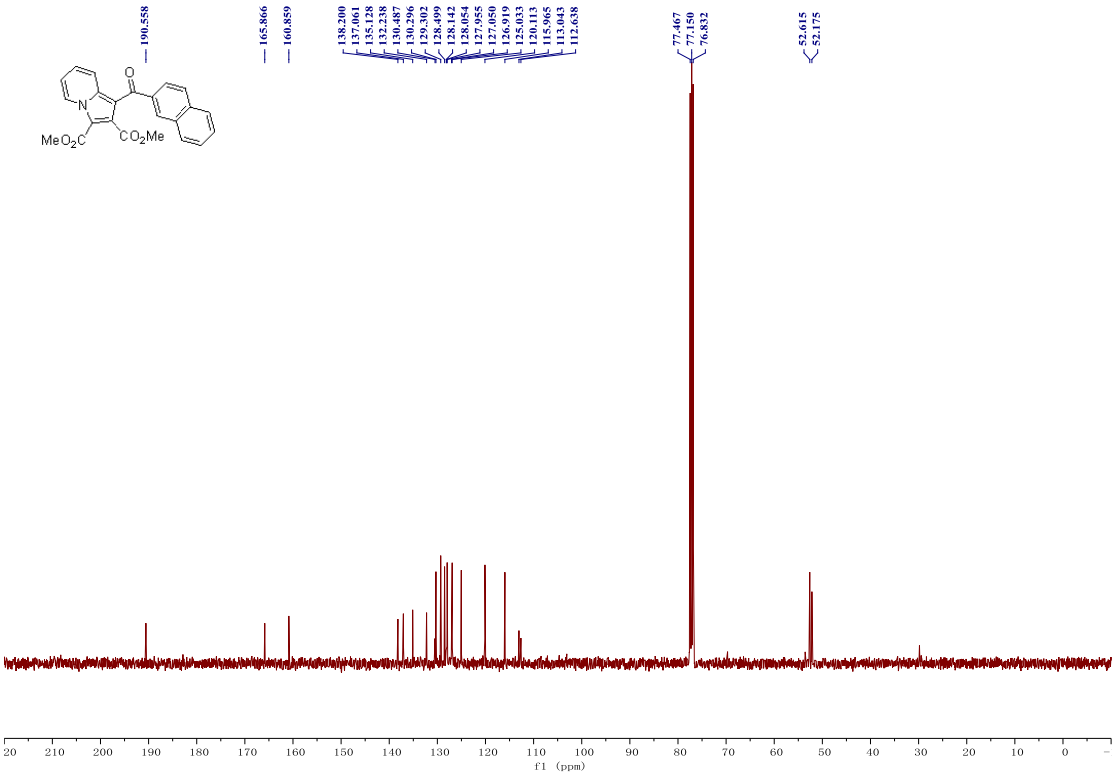
^{1}H NMR of compound **12'** (400 MHz, $CDCl_3$)



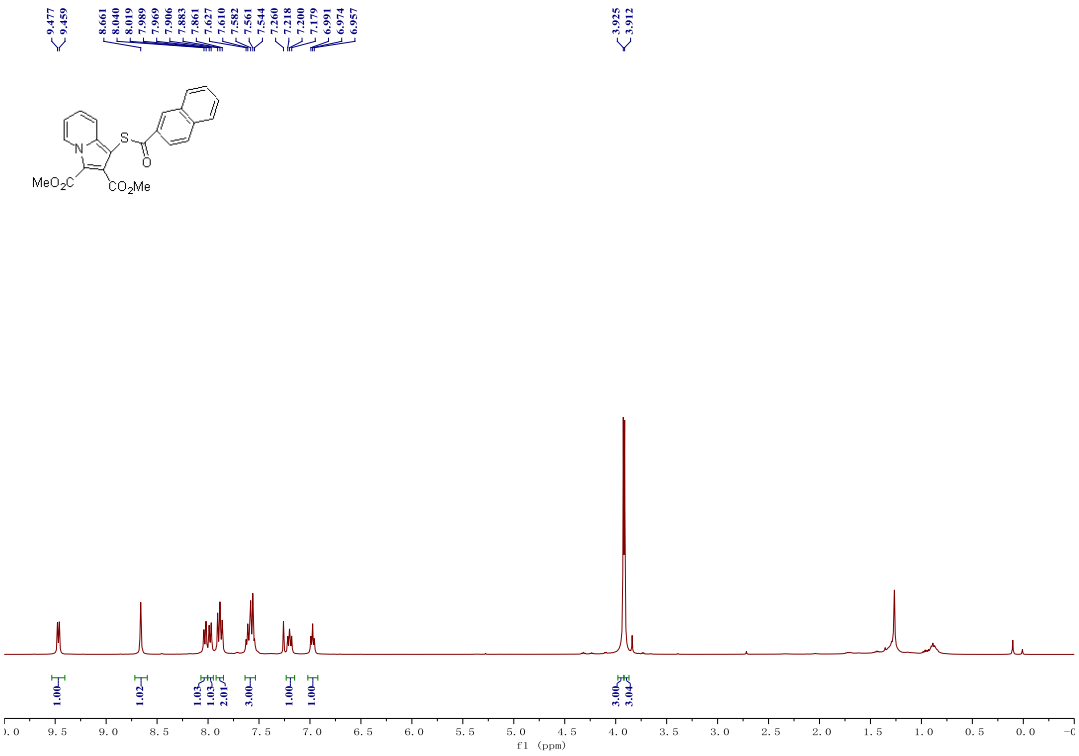
^{13}C NMR of compound **12'** (100 MHz, $CDCl_3$)



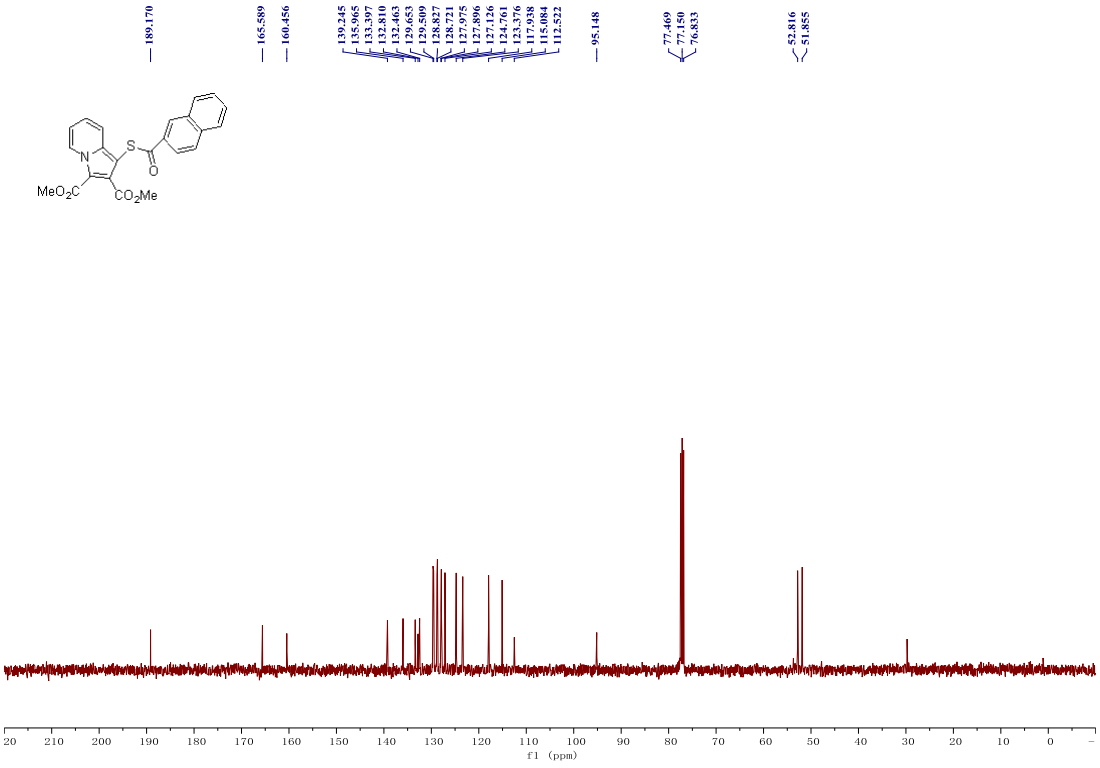
^{1}H NMR of compound **13** (400 MHz, $CDCl_3$)



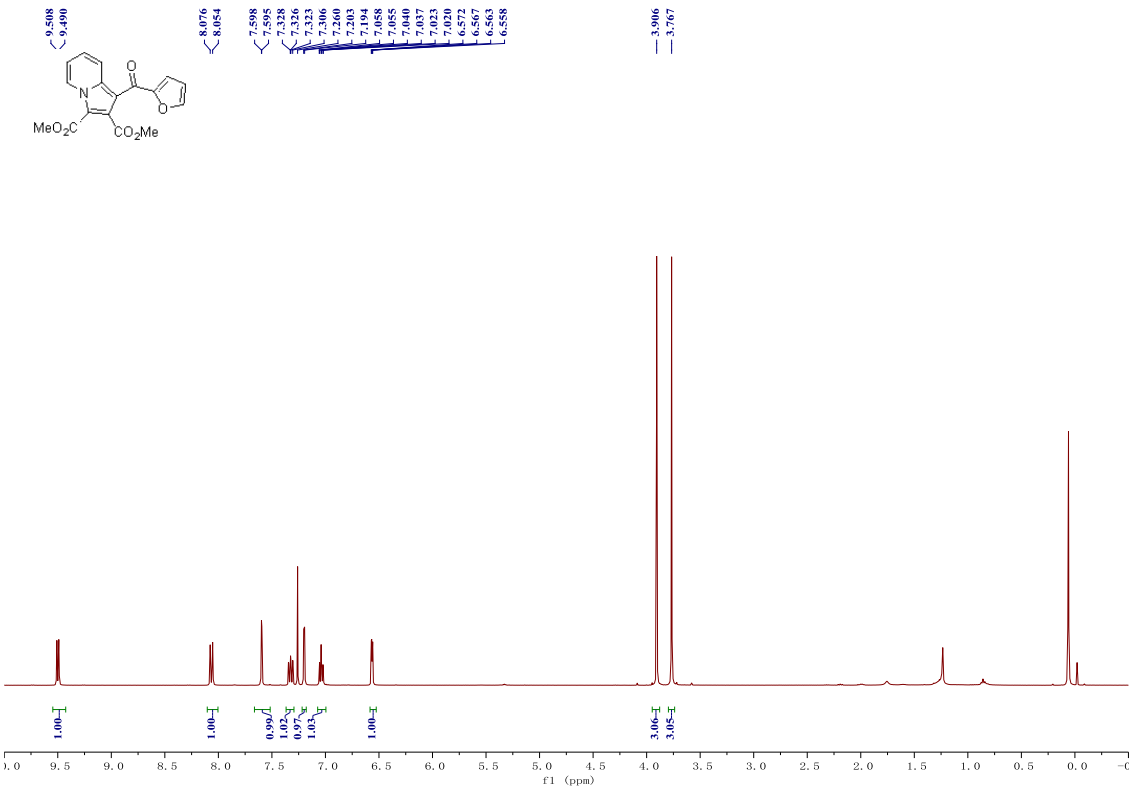
^{13}C NMR of compound **13** (100 MHz, $CDCl_3$)



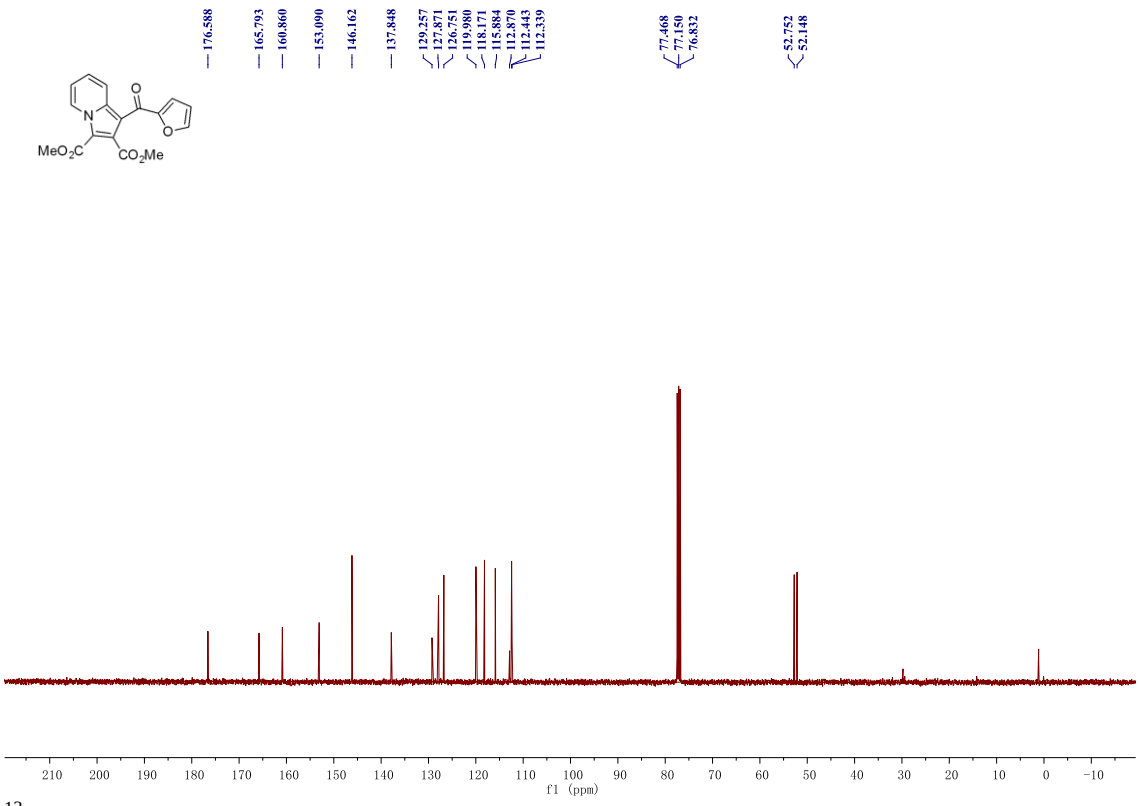
^{1}H NMR of compound **13'** (400 MHz, $CDCl_3$)



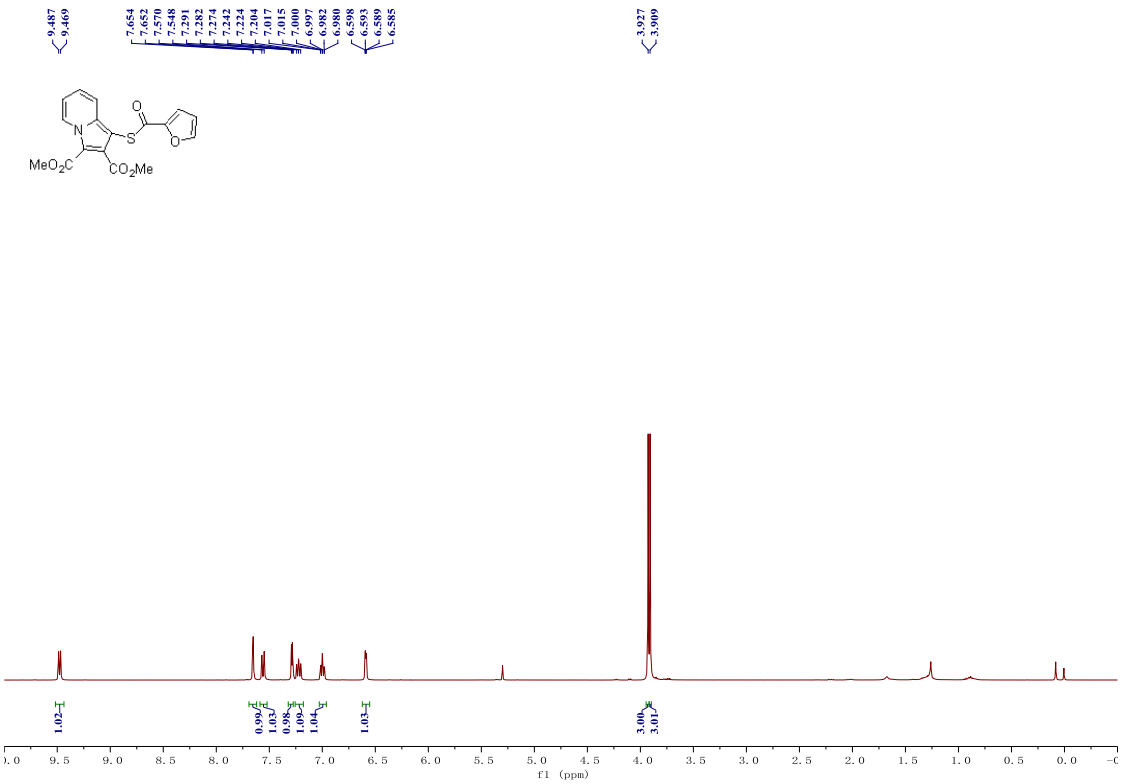
^{13}C NMR of compound **13'** (100 MHz, $CDCl_3$)



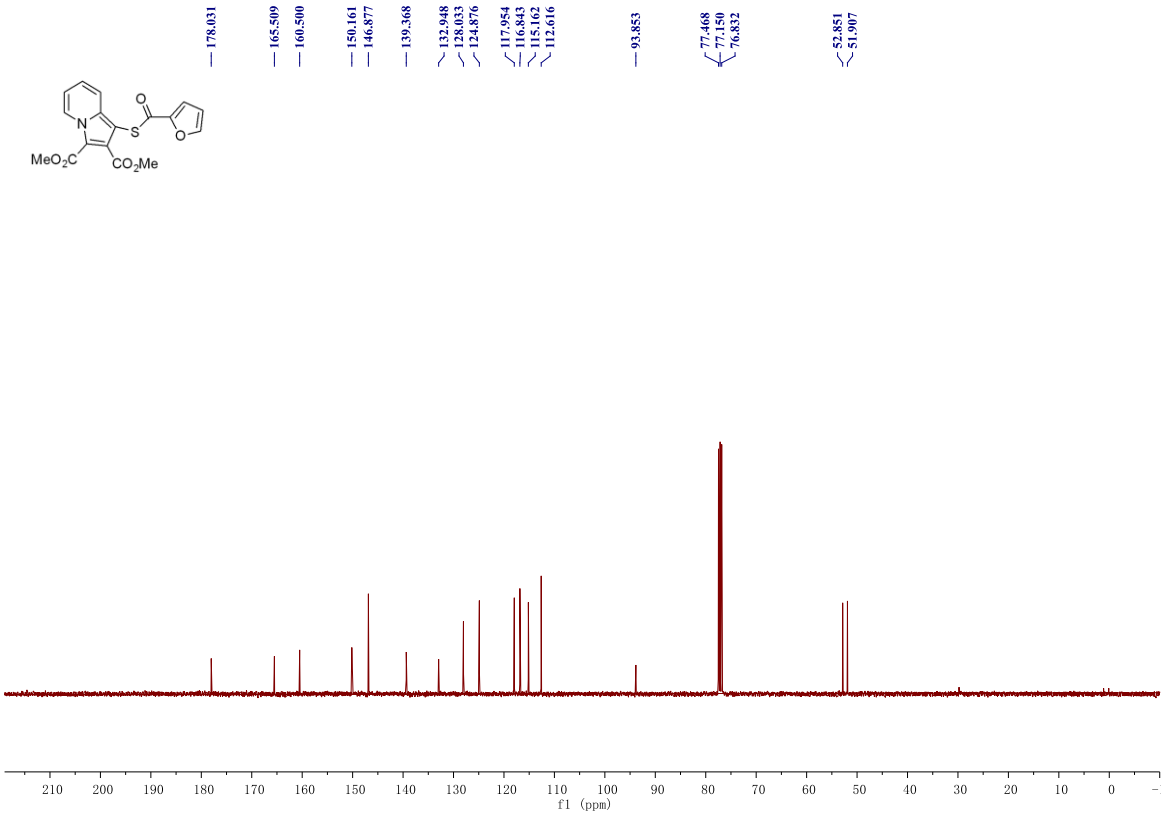
^{1}H NMR of compound **14** (400 MHz, $CDCl_3$)



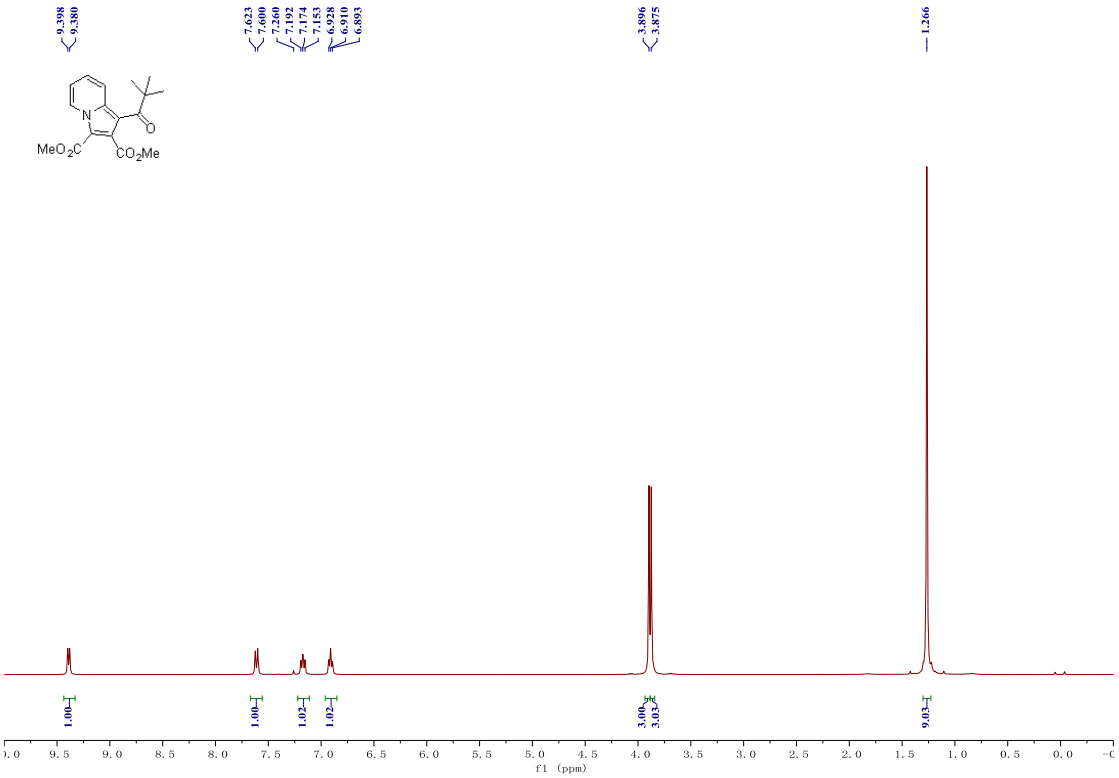
^{13}C NMR of compound **14** (100 MHz, $CDCl_3$)



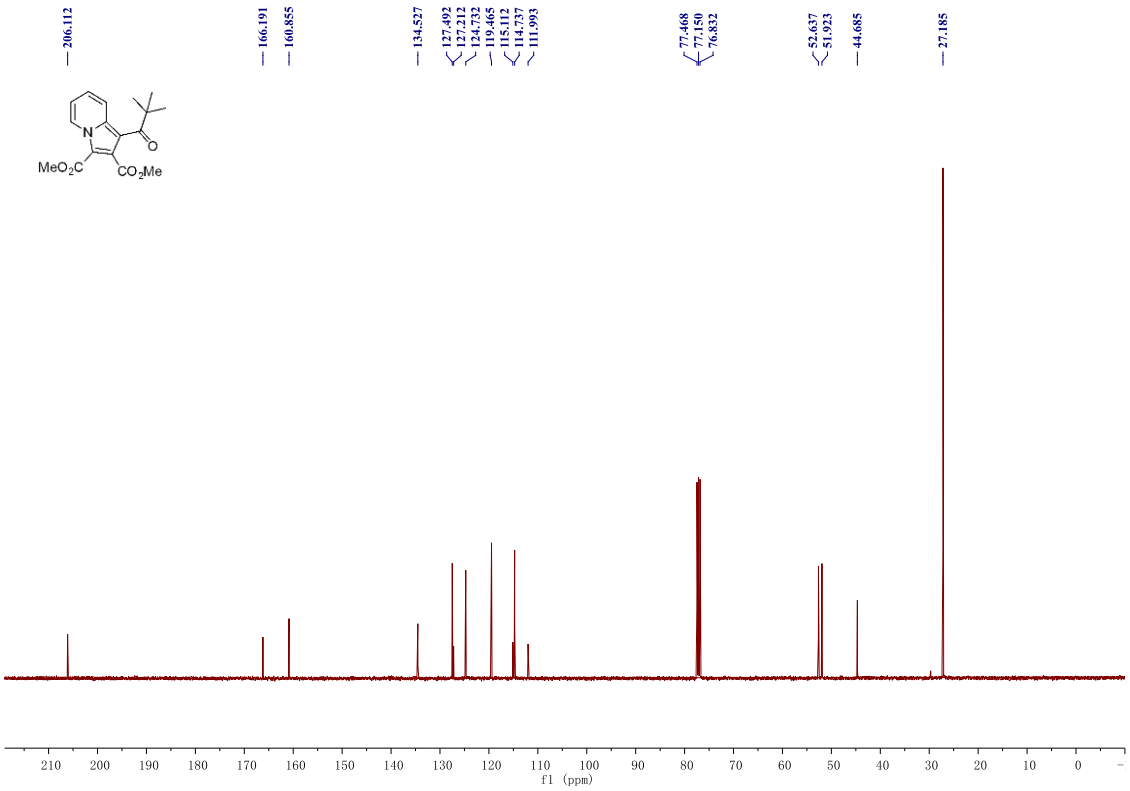
^{1}H NMR of compound **14'** (400 MHz, $CDCl_3$)



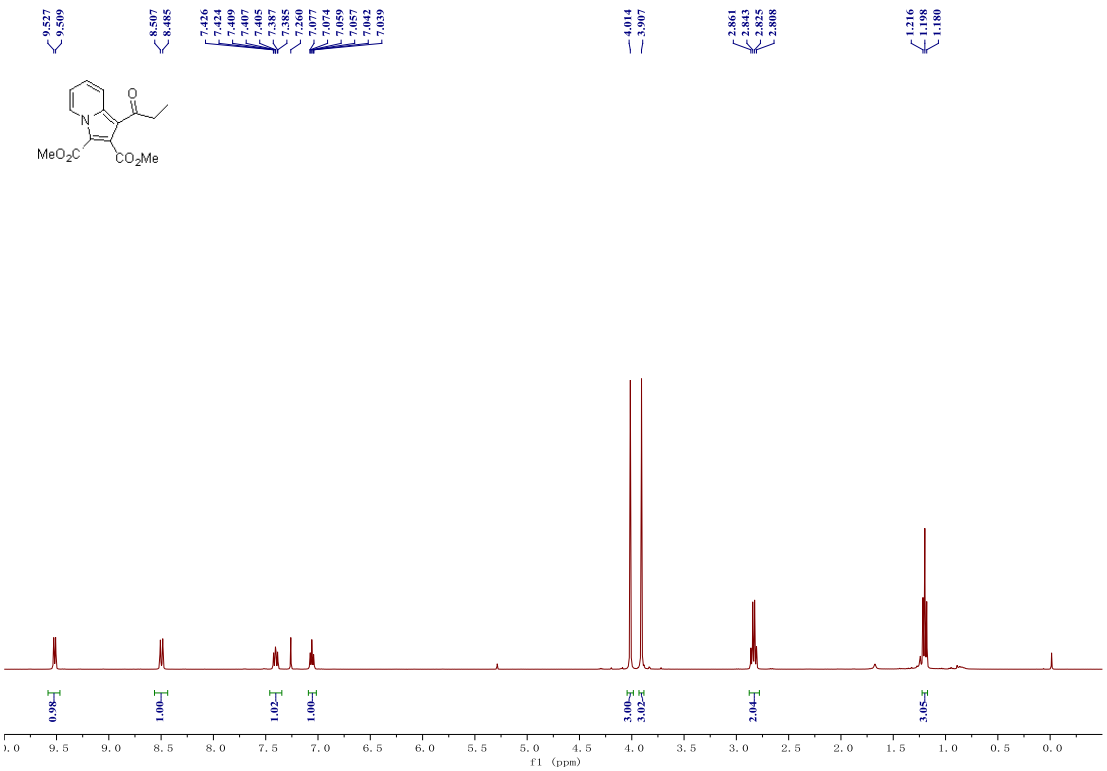
^{13}C NMR of compound **14'** (100 MHz, $CDCl_3$)



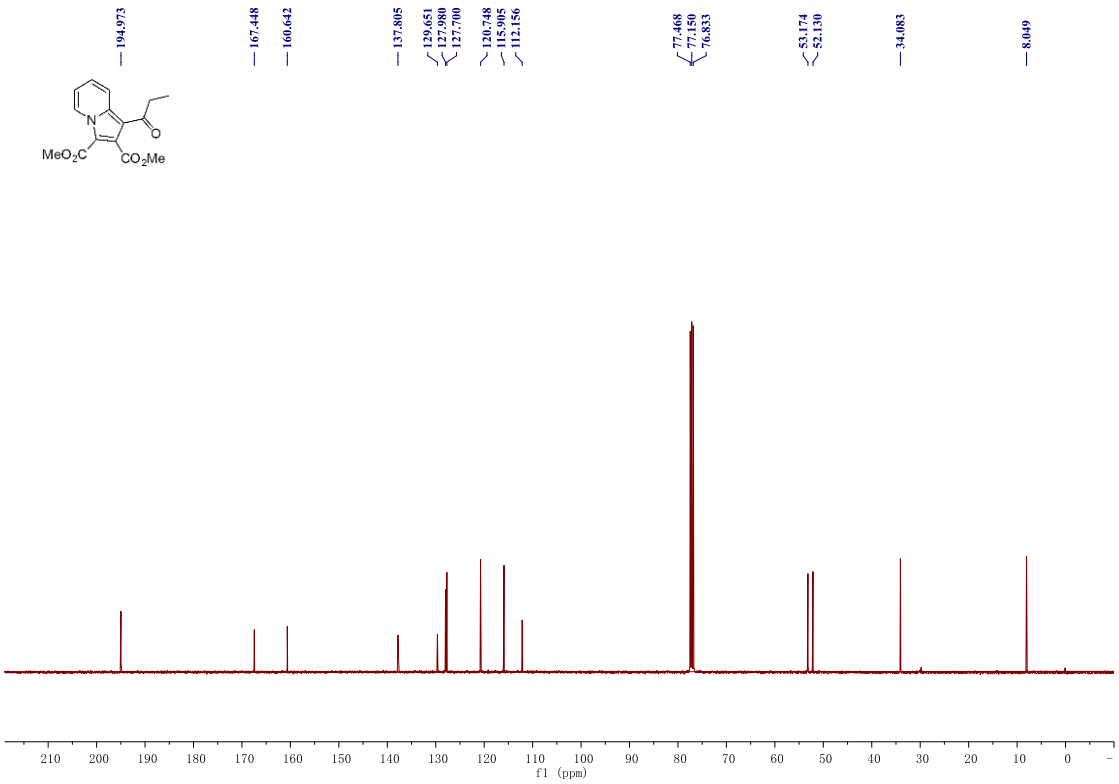
^{1}H NMR of compound **15** (400 MHz, $CDCl_3$)



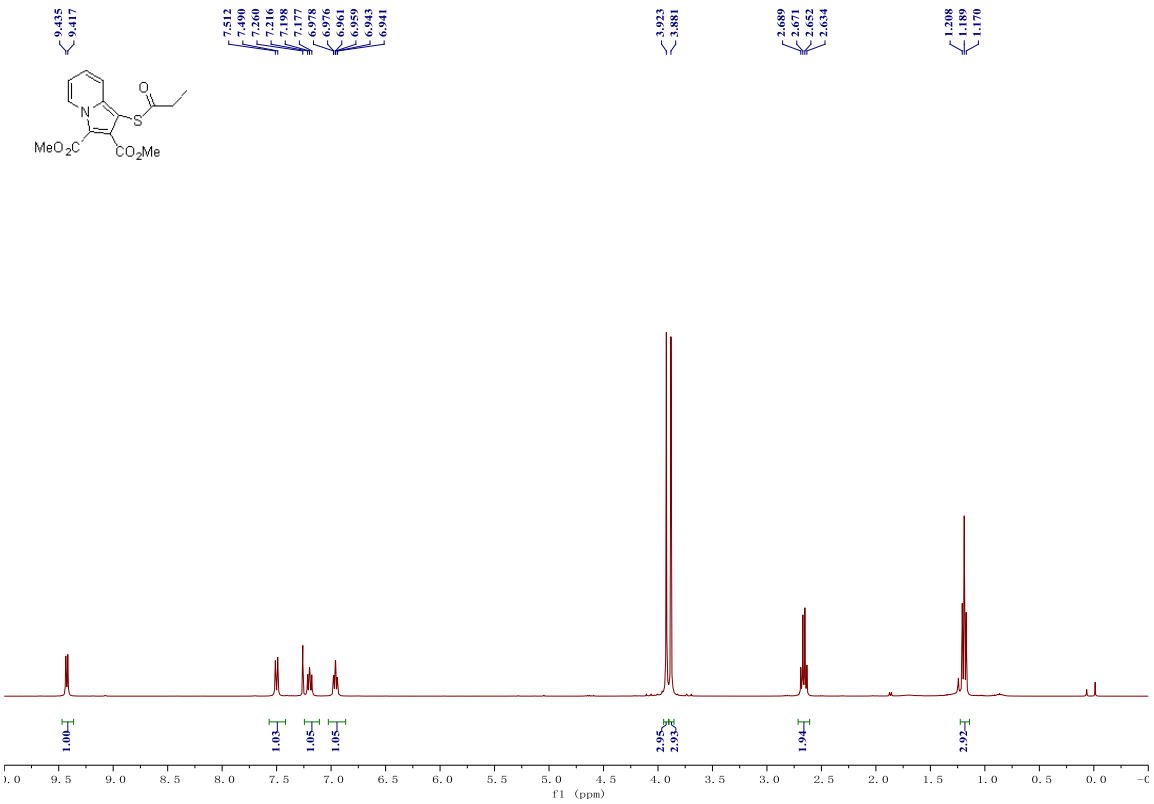
^{13}C NMR of compound **15** (100 MHz, $CDCl_3$)



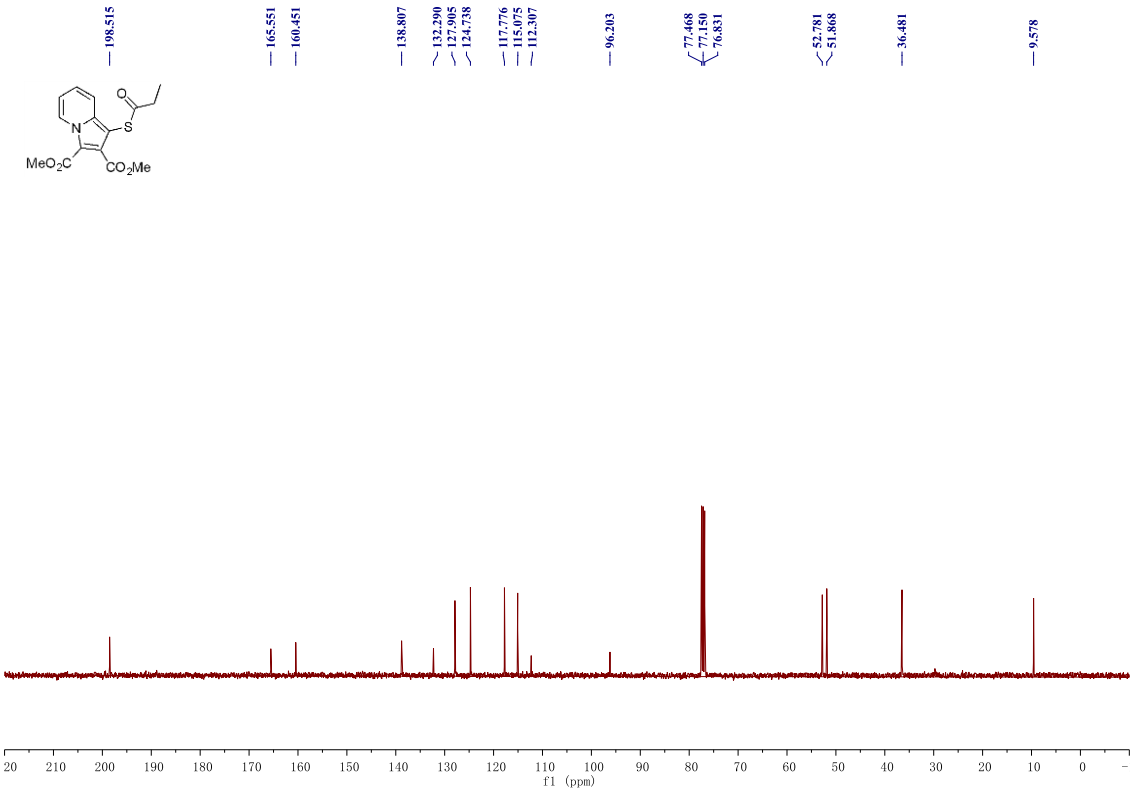
^{1}H NMR of compound **16** (400 MHz, $CDCl_3$)



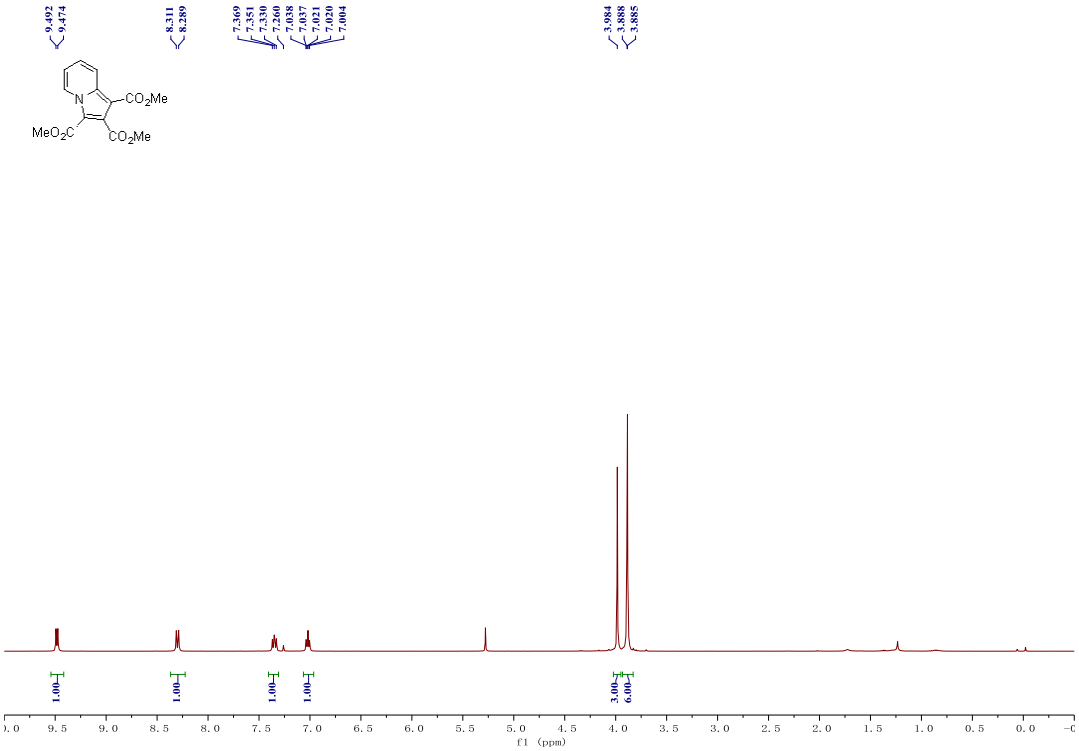
^{13}C NMR of compound **16** (100 MHz, $CDCl_3$)



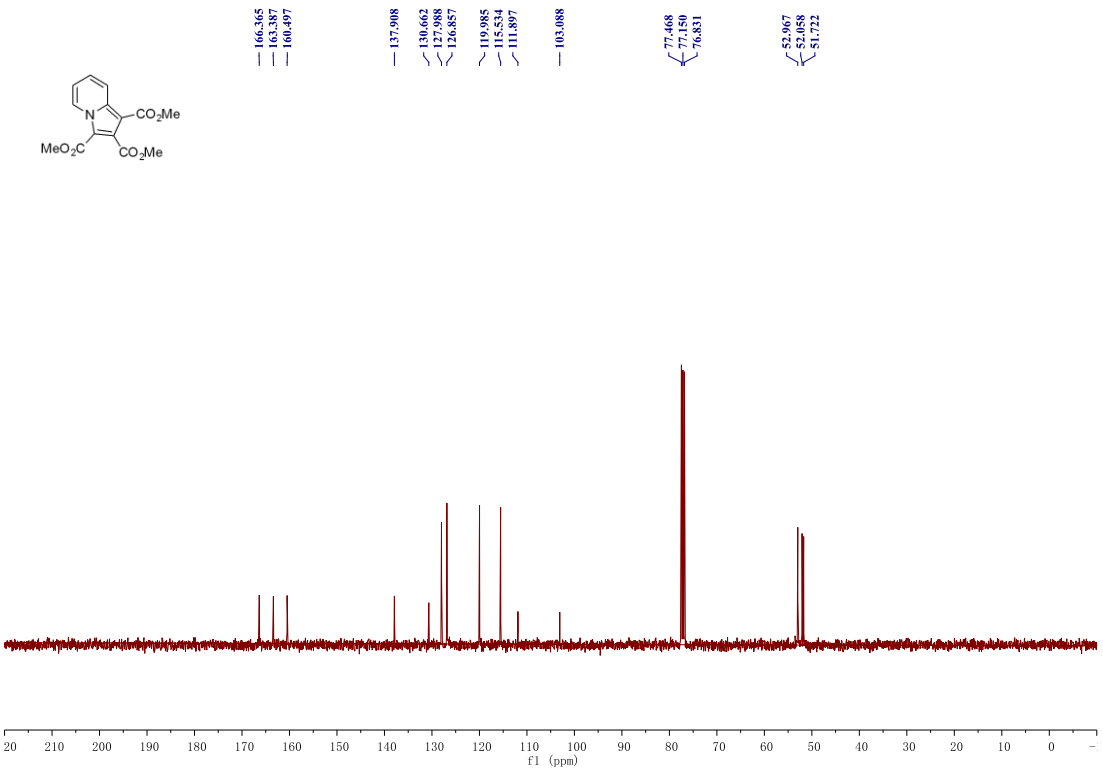
^{1}H NMR of compound **16'** (400 MHz, $CDCl_3$)



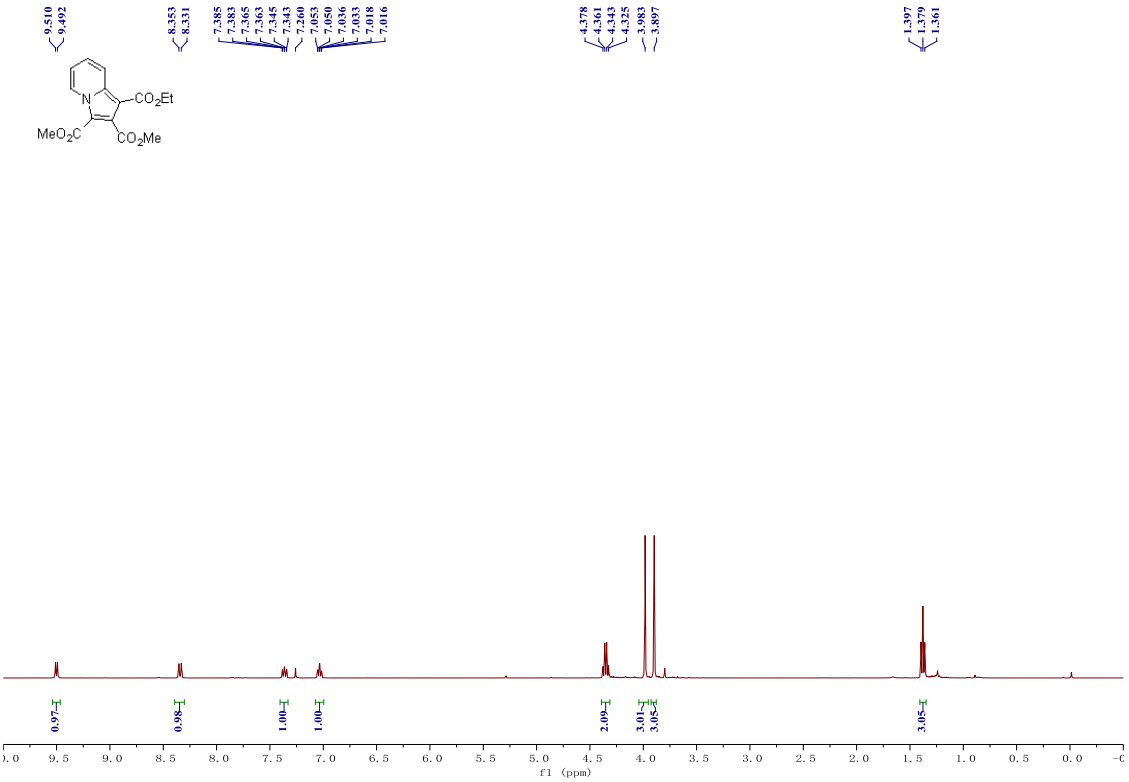
^{13}C NMR of compound **16'** (100 MHz, $CDCl_3$)



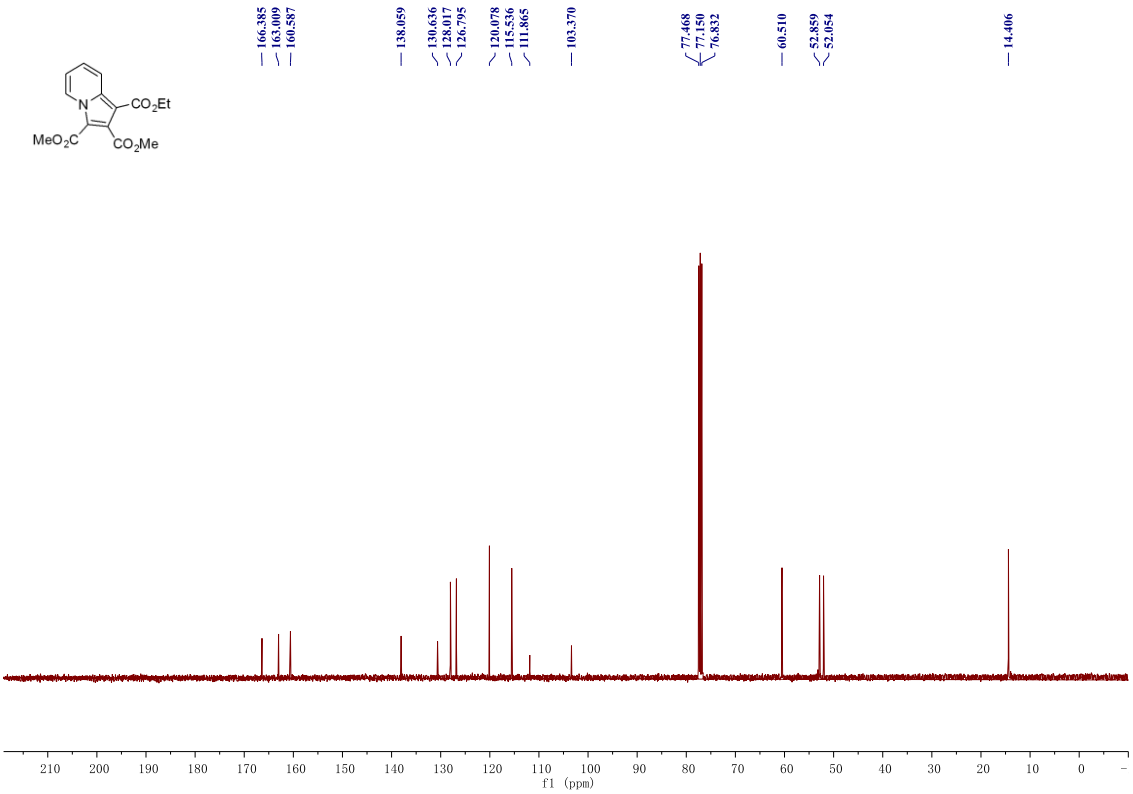
^{1}H NMR of compound **17** (400 MHz, $CDCl_3$)



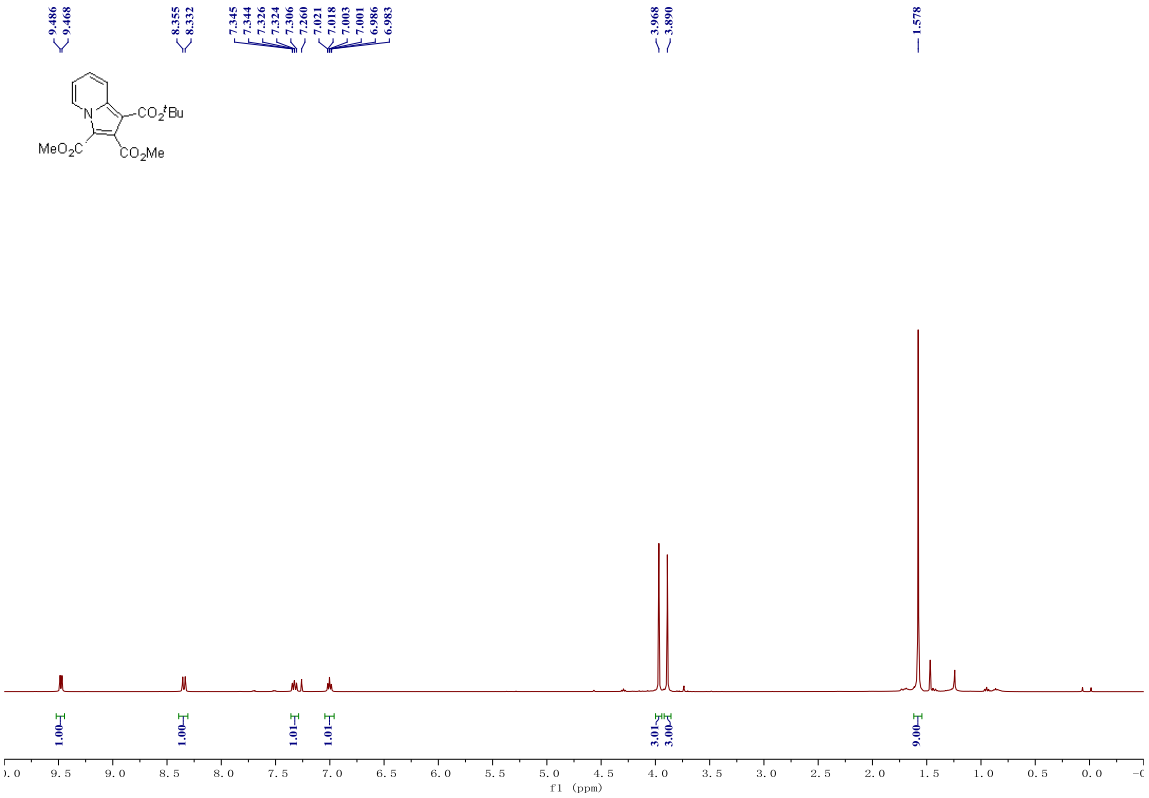
^{13}C NMR of compound **17** (100 MHz, $CDCl_3$)



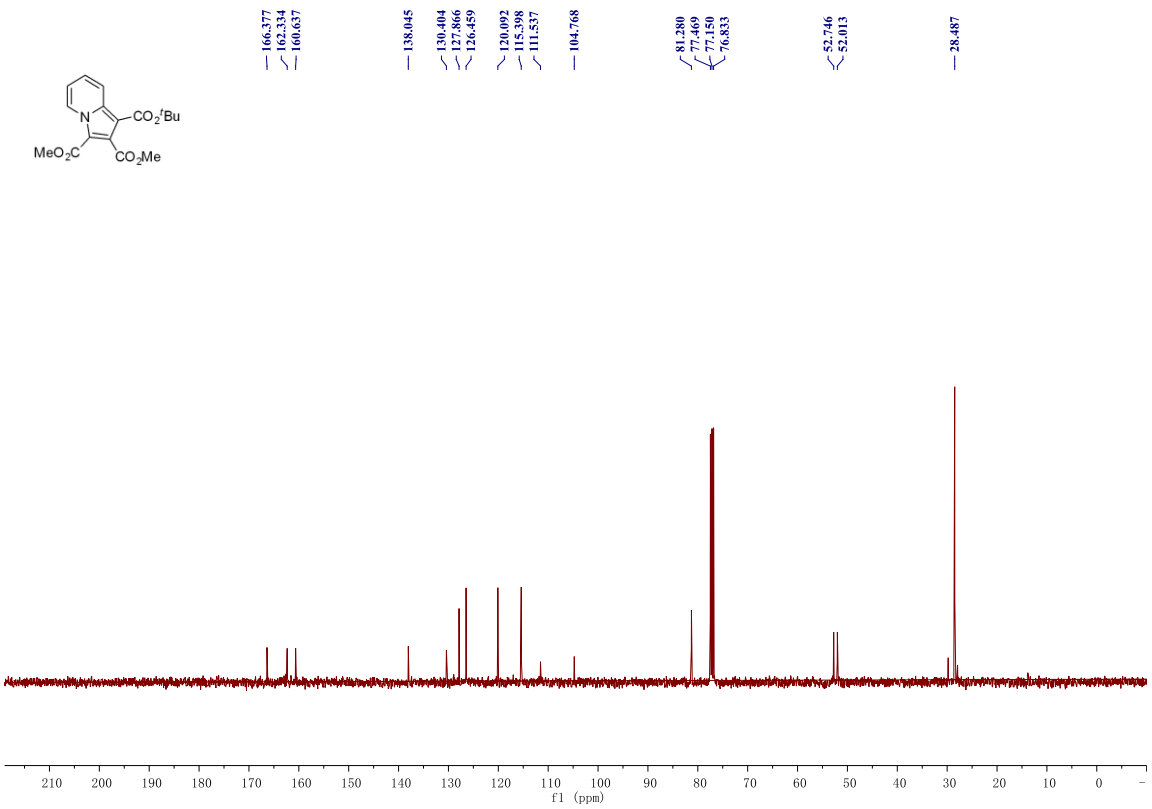
^{1}H NMR of compound **18** (400 MHz, $CDCl_3$)



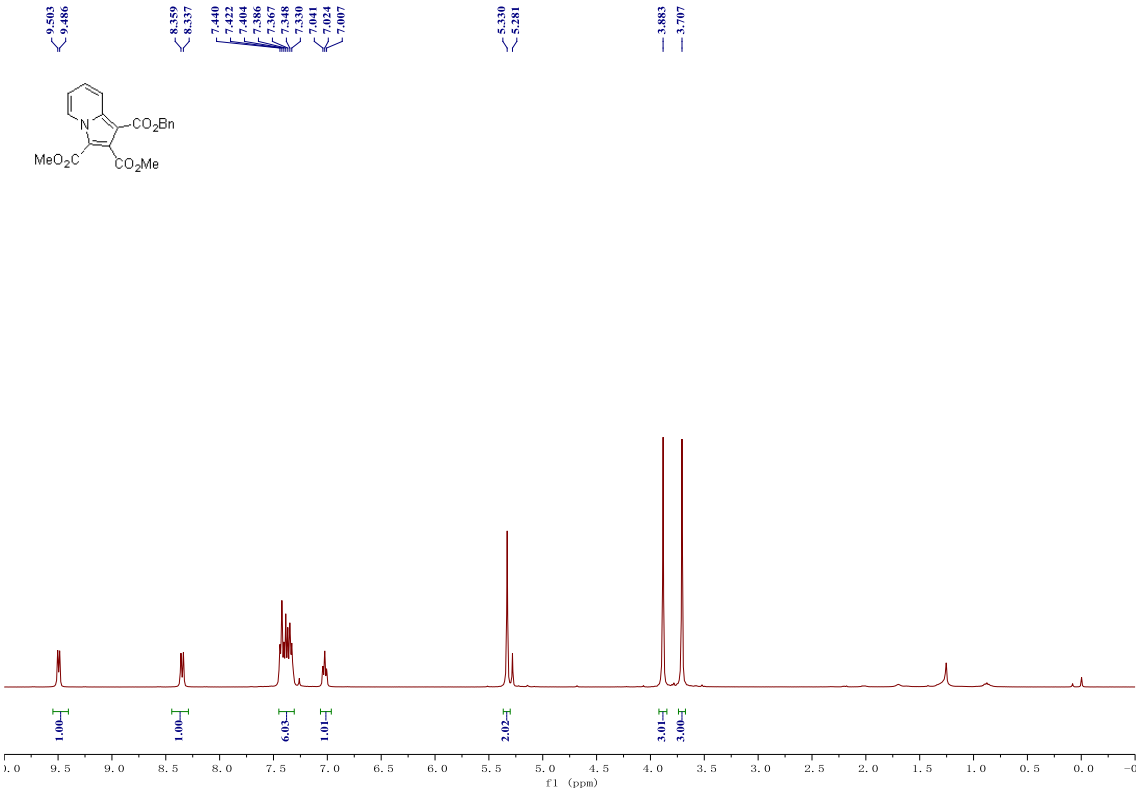
^{13}C NMR of compound **18** (100 MHz, $CDCl_3$)



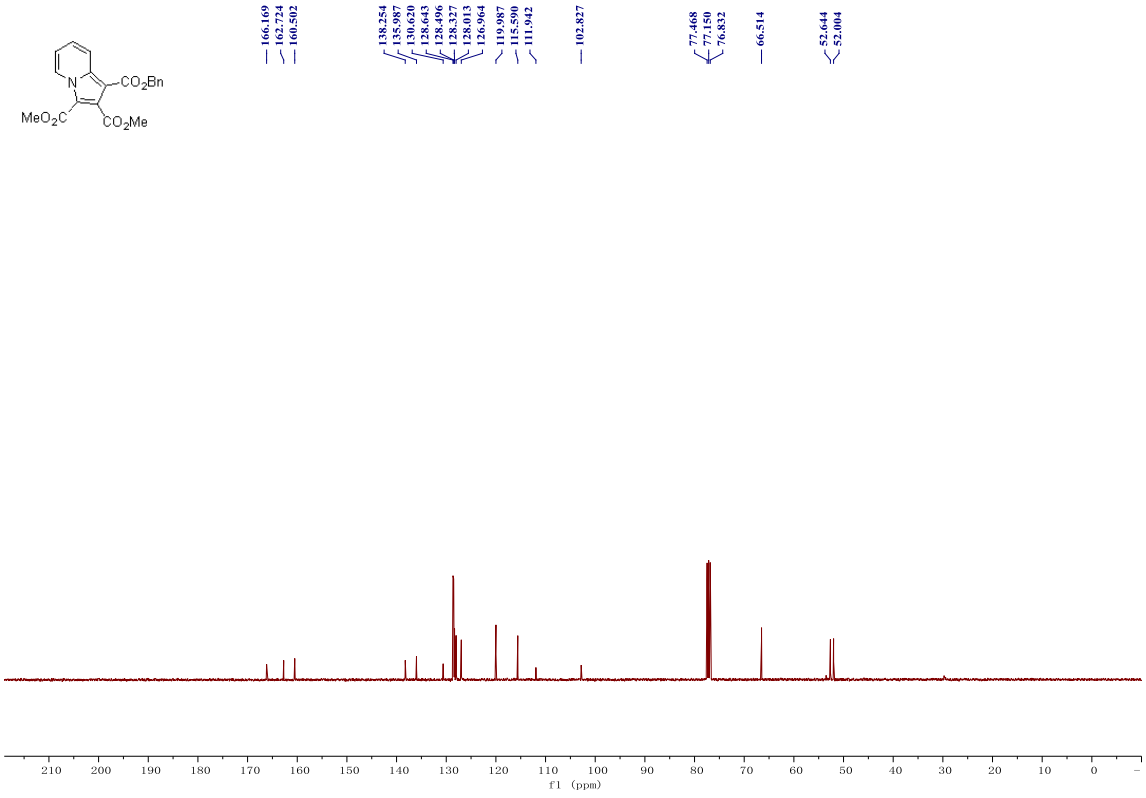
^{1}H NMR of compound **19** (400 MHz, $CDCl_3$)



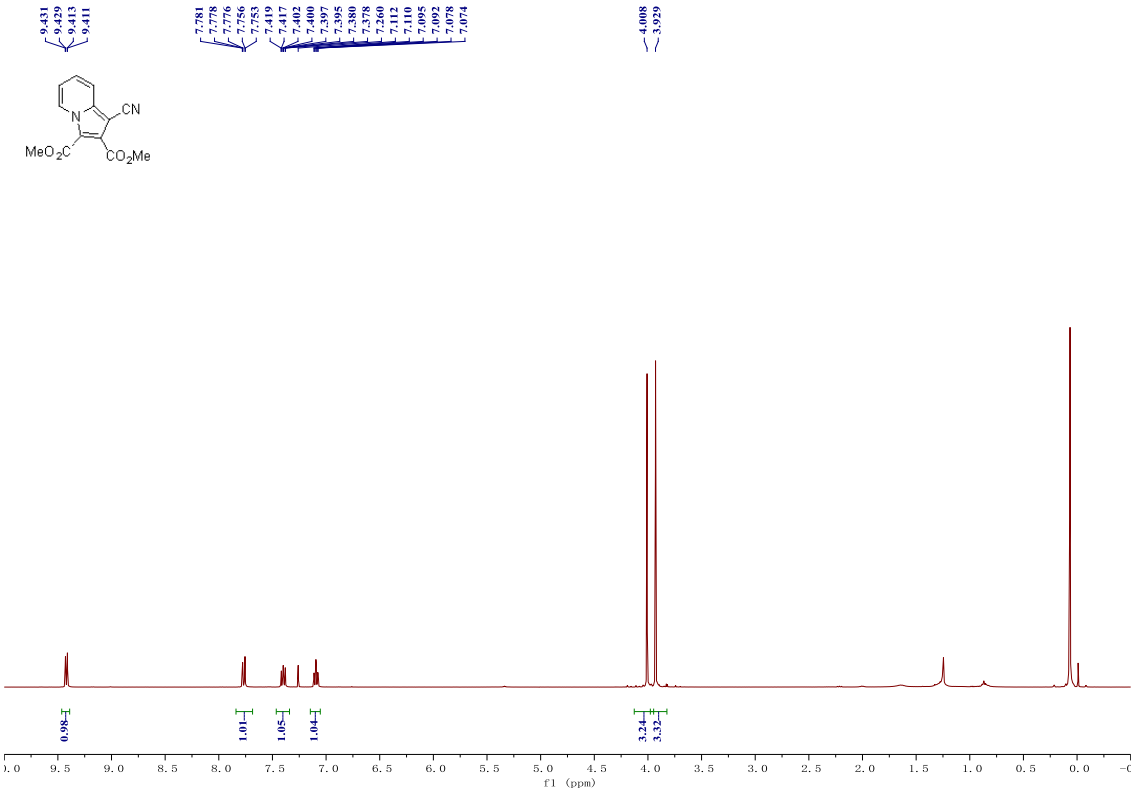
^{13}C NMR of compound **19** (100 MHz, $CDCl_3$)



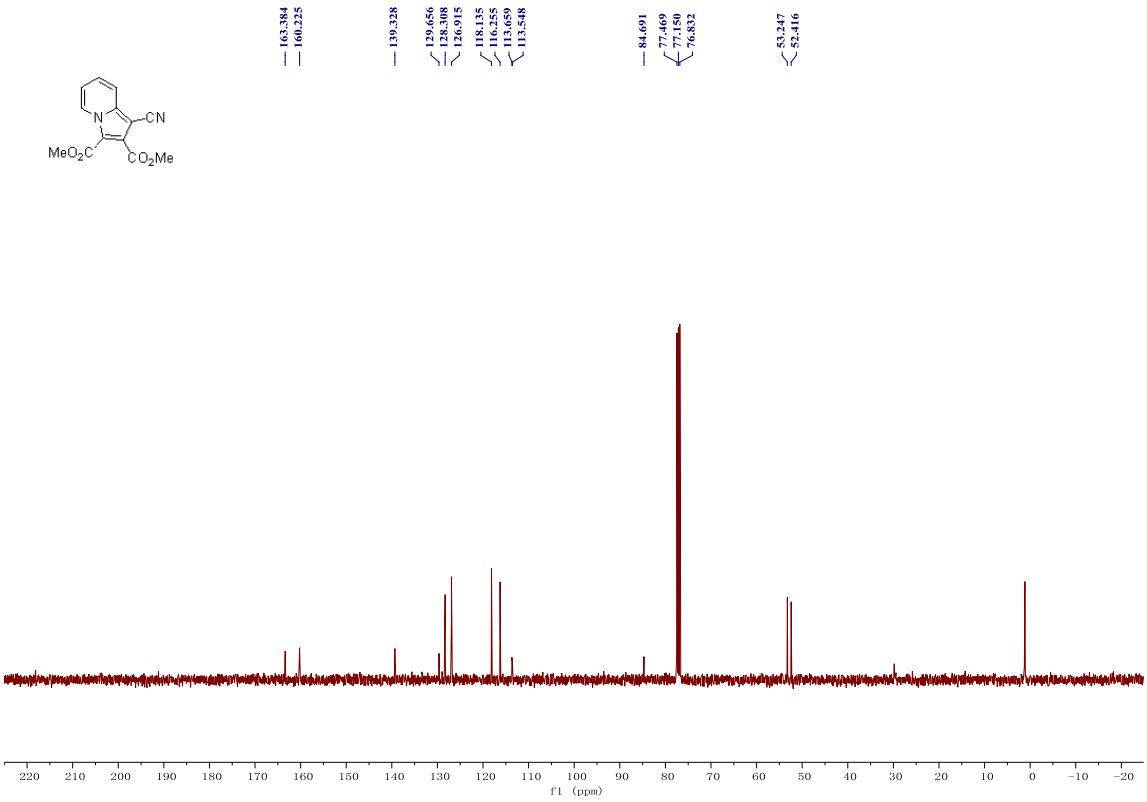
^{1}H NMR of compound **20** (400 MHz, $CDCl_3$)



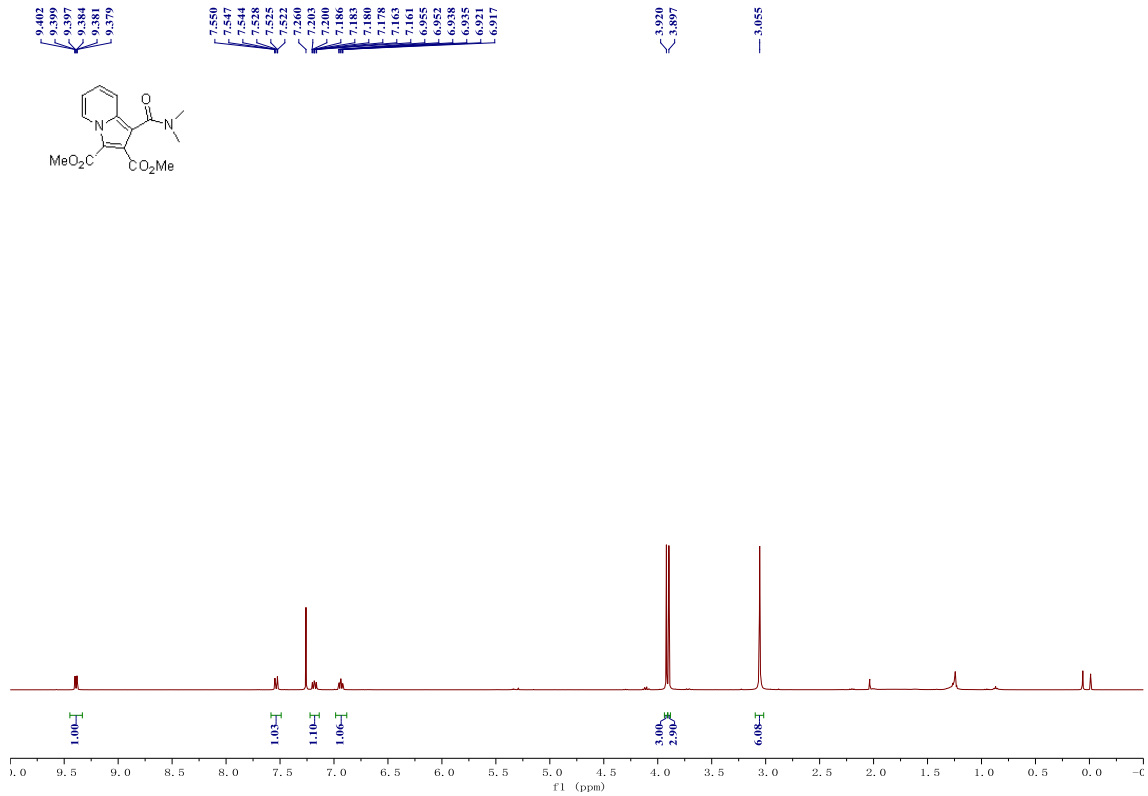
^{13}C NMR of compound **20** (100 MHz, $CDCl_3$)



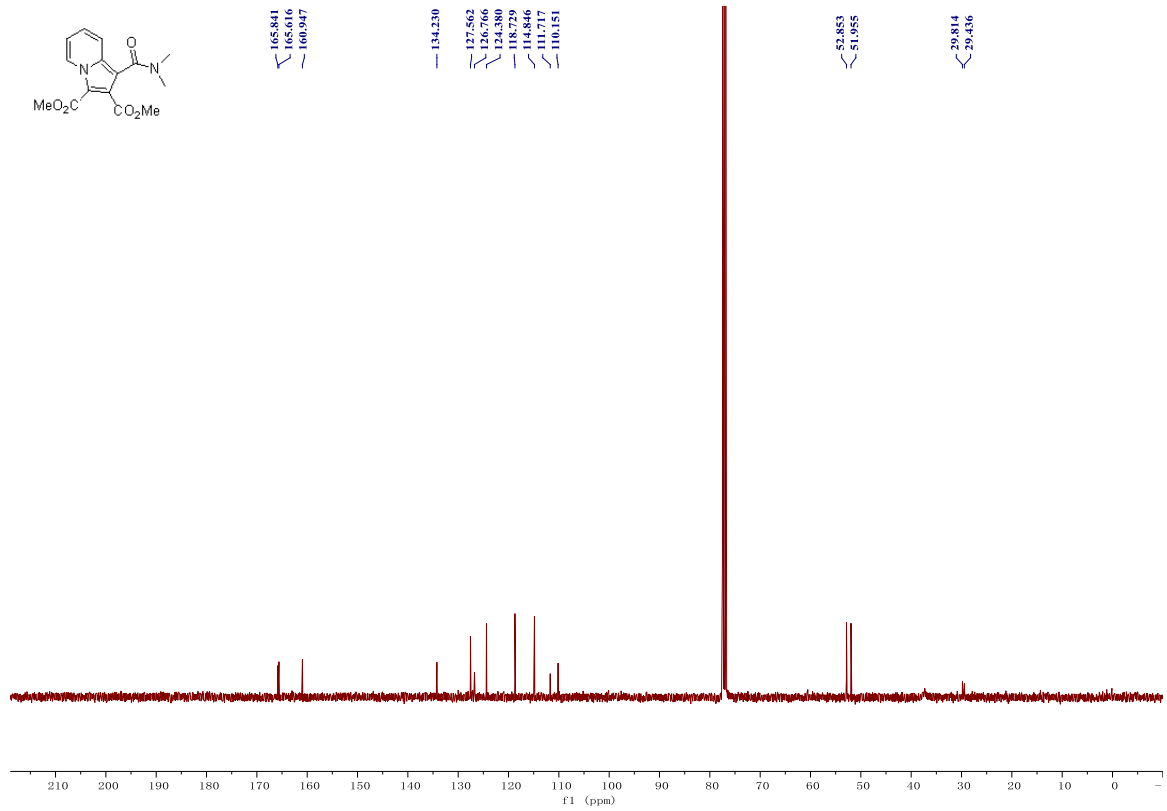
^{1}H NMR of compound **21** (400 MHz, $CDCl_3$)



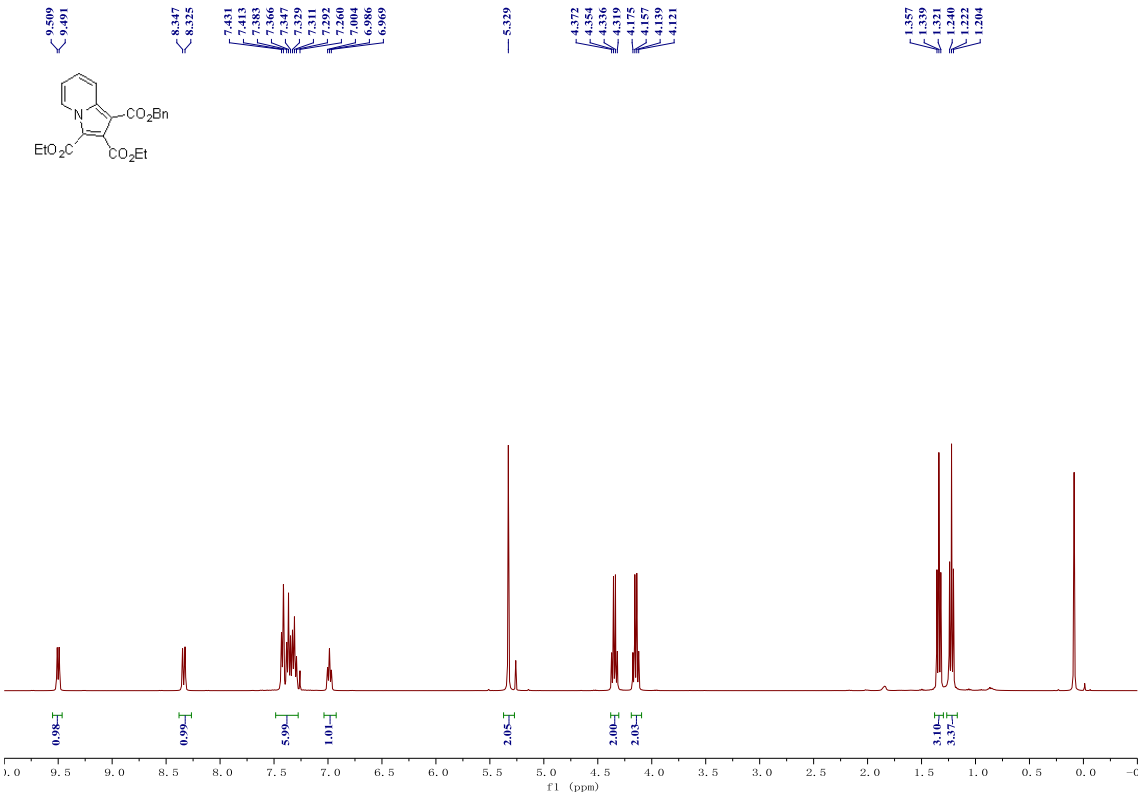
^{13}C NMR of compound **21** (100 MHz, $CDCl_3$)



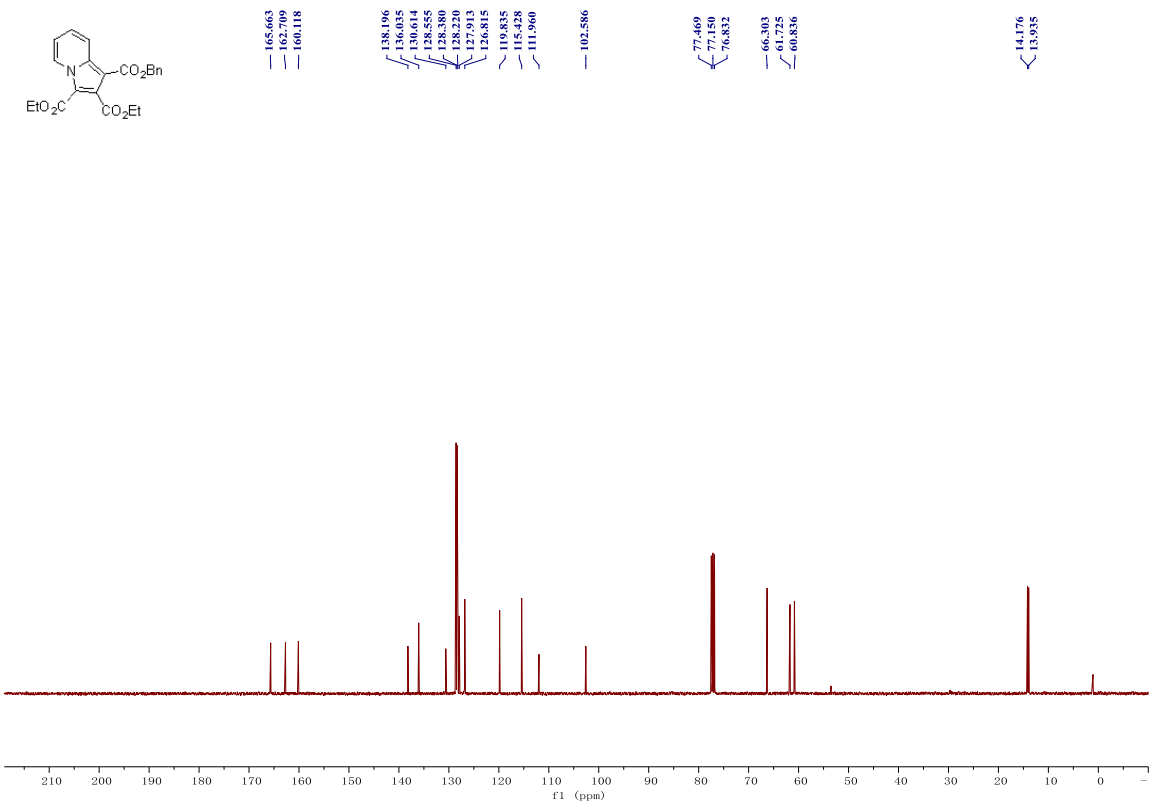
^{1}H NMR of compound **22** (400 MHz, $CDCl_3$)



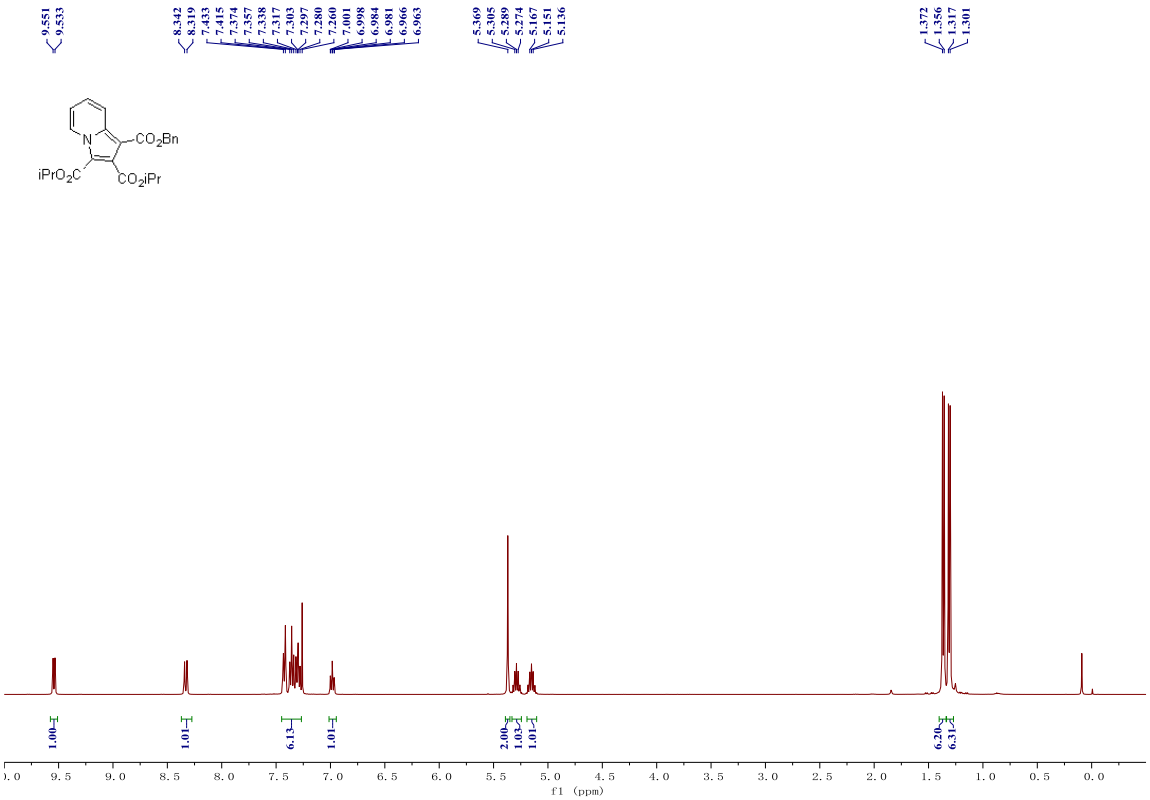
^{13}C NMR of compound **22** (100 MHz, $CDCl_3$)



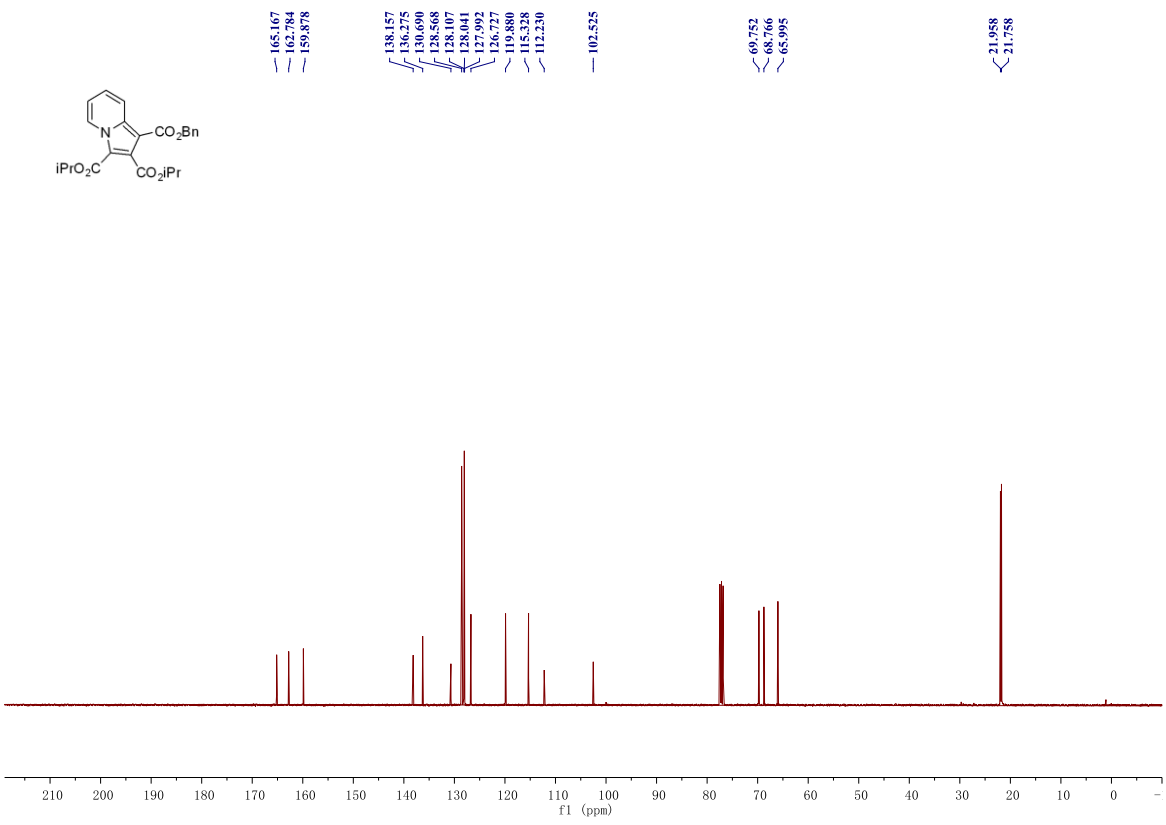
^{1}H NMR of compound **23** (400 MHz, $CDCl_3$)



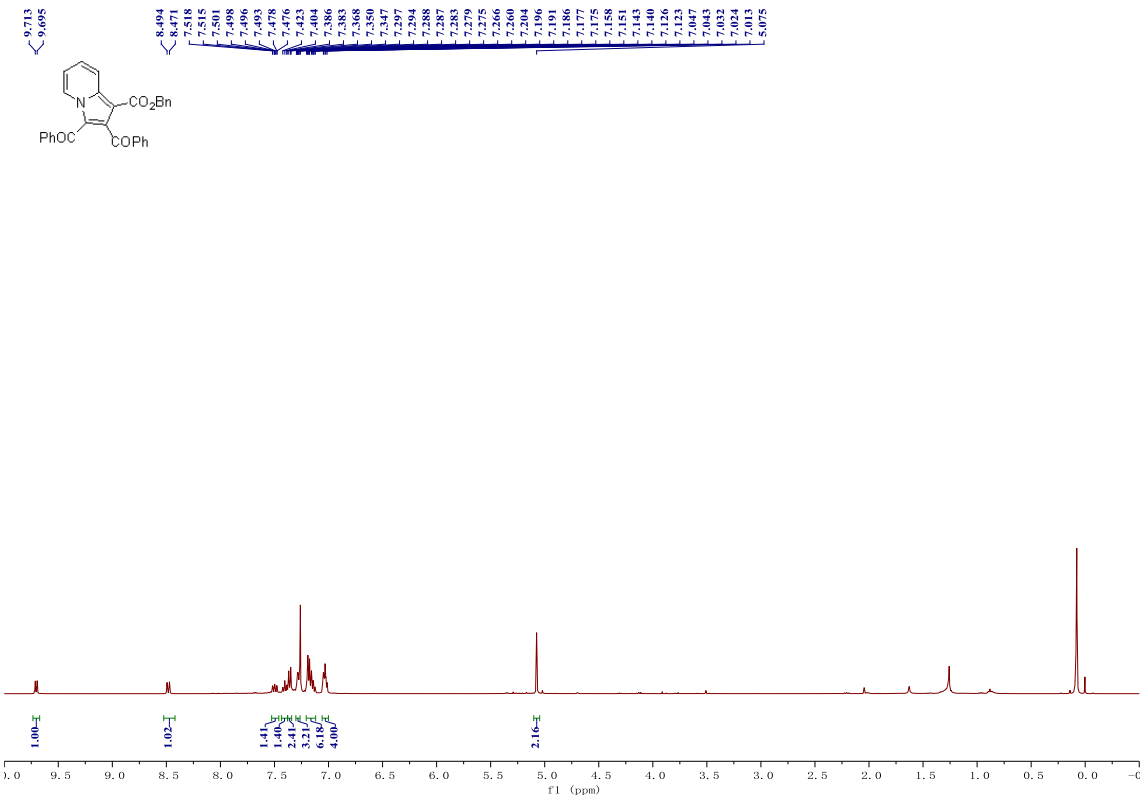
^{13}C NMR of compound **23** (100 MHz, $CDCl_3$)



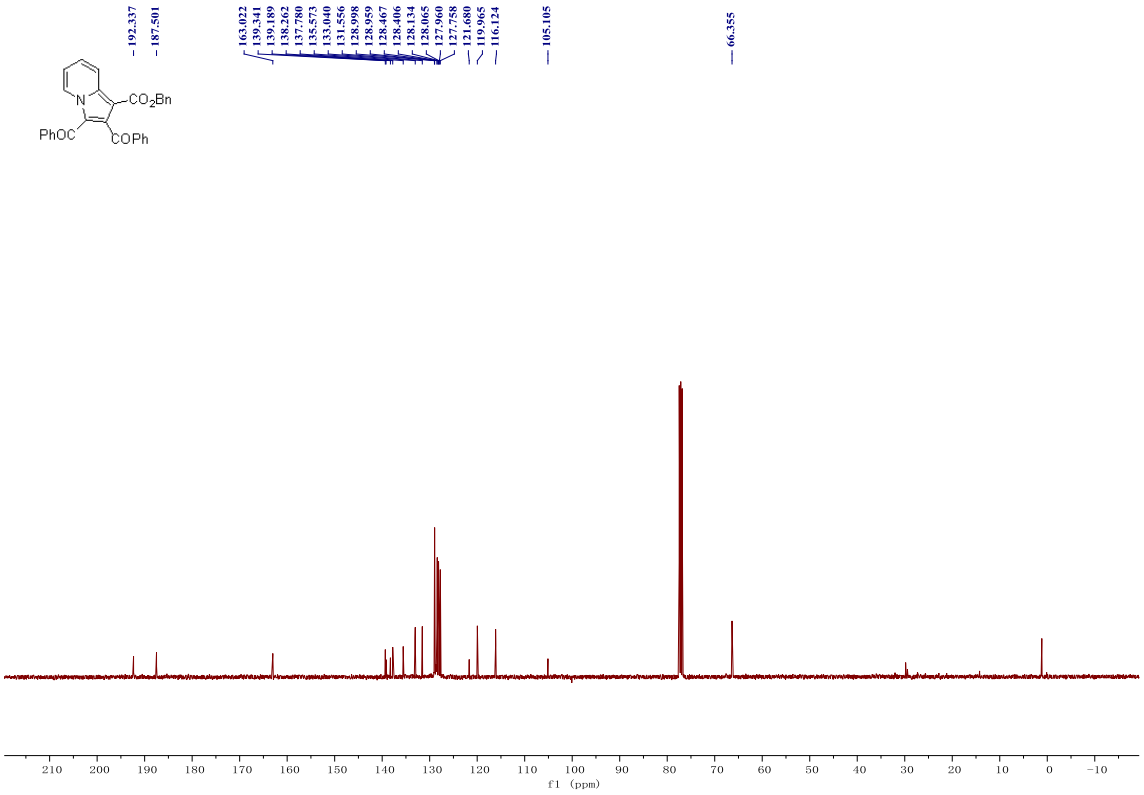
^{1}H NMR of compound **24** (400 MHz, $CDCl_3$)



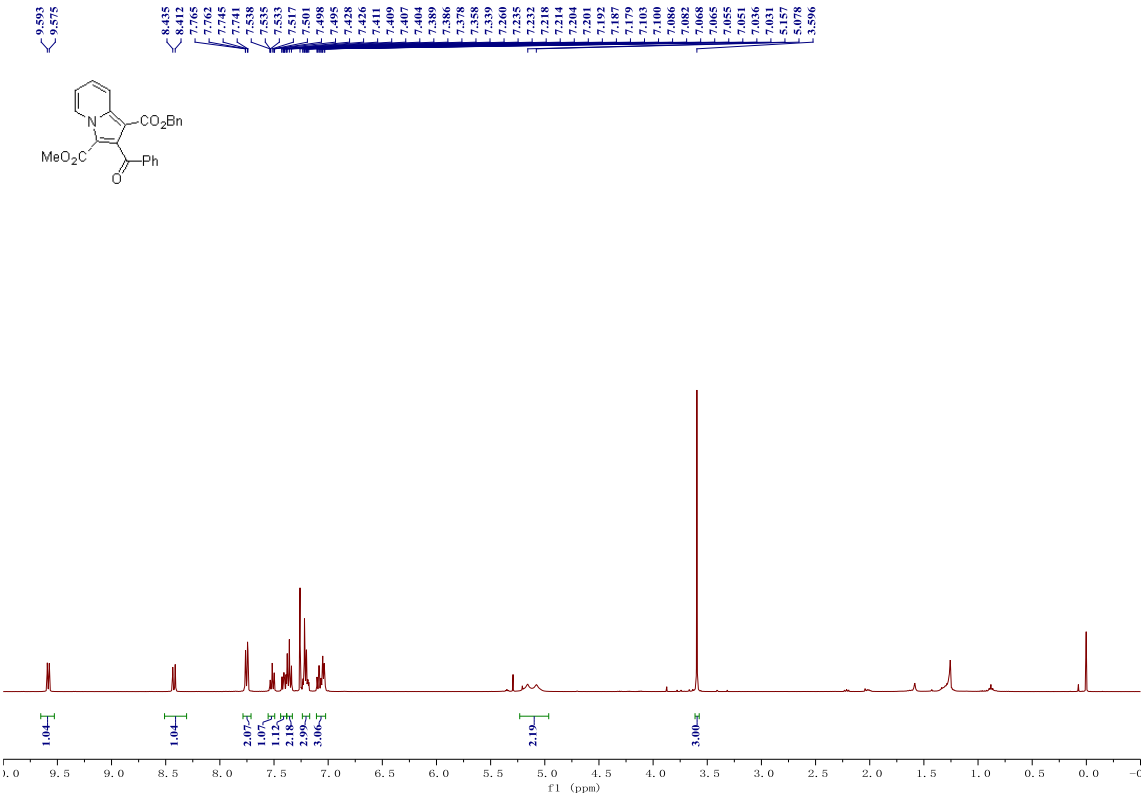
^{13}C NMR of compound **24** (100 MHz, $CDCl_3$)



^{1}H NMR of compound **25** (400 MHz, $CDCl_3$)



^{13}C NMR of compound **25** (100 MHz, $CDCl_3$)



^{1}H NMR of compound **26** (400 MHz, $CDCl_3$)

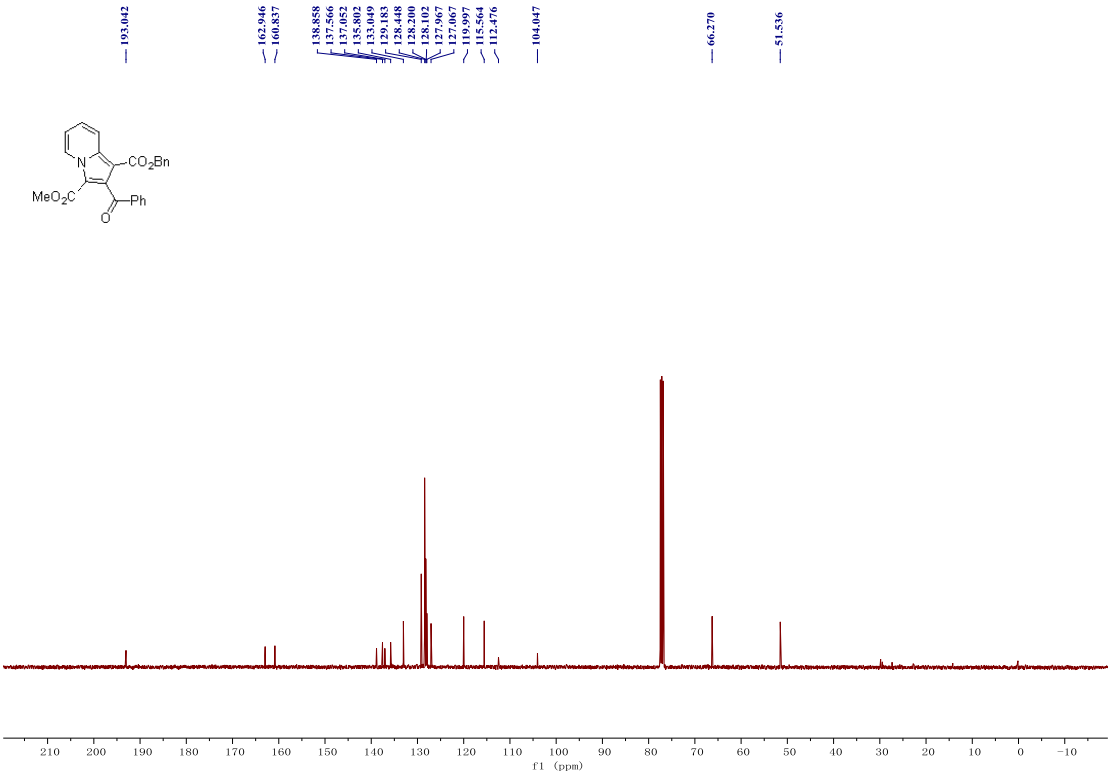
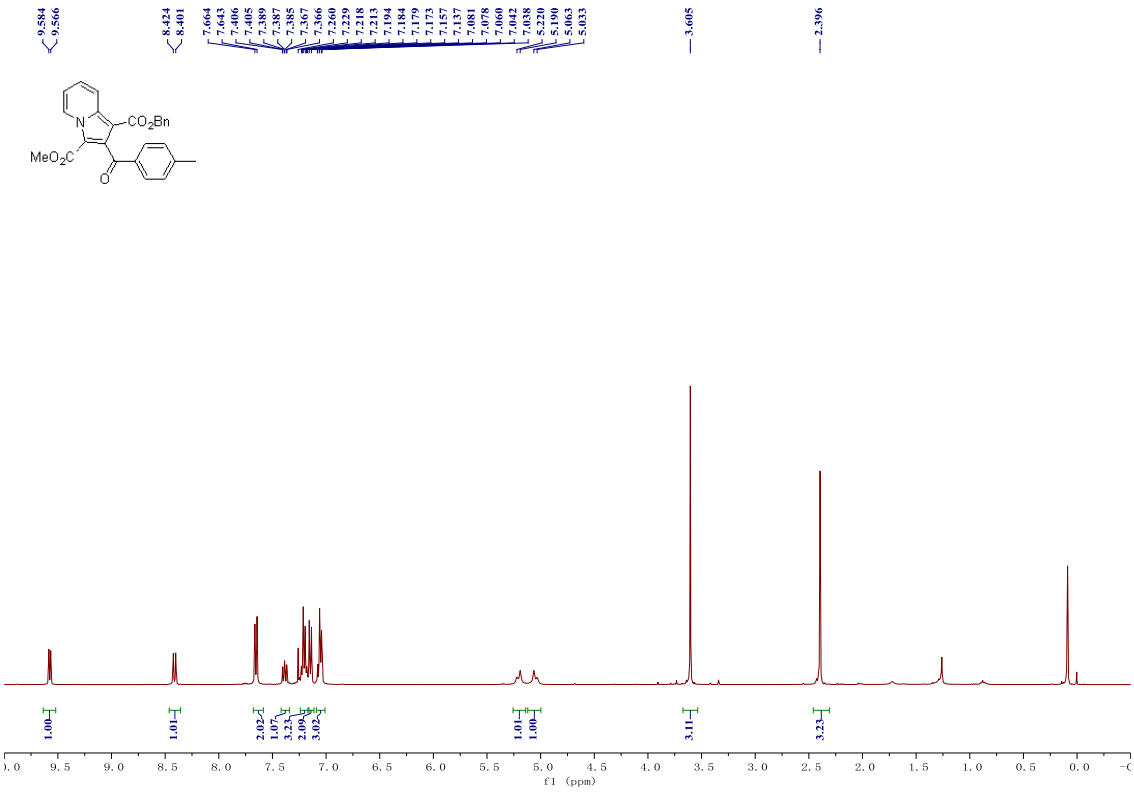
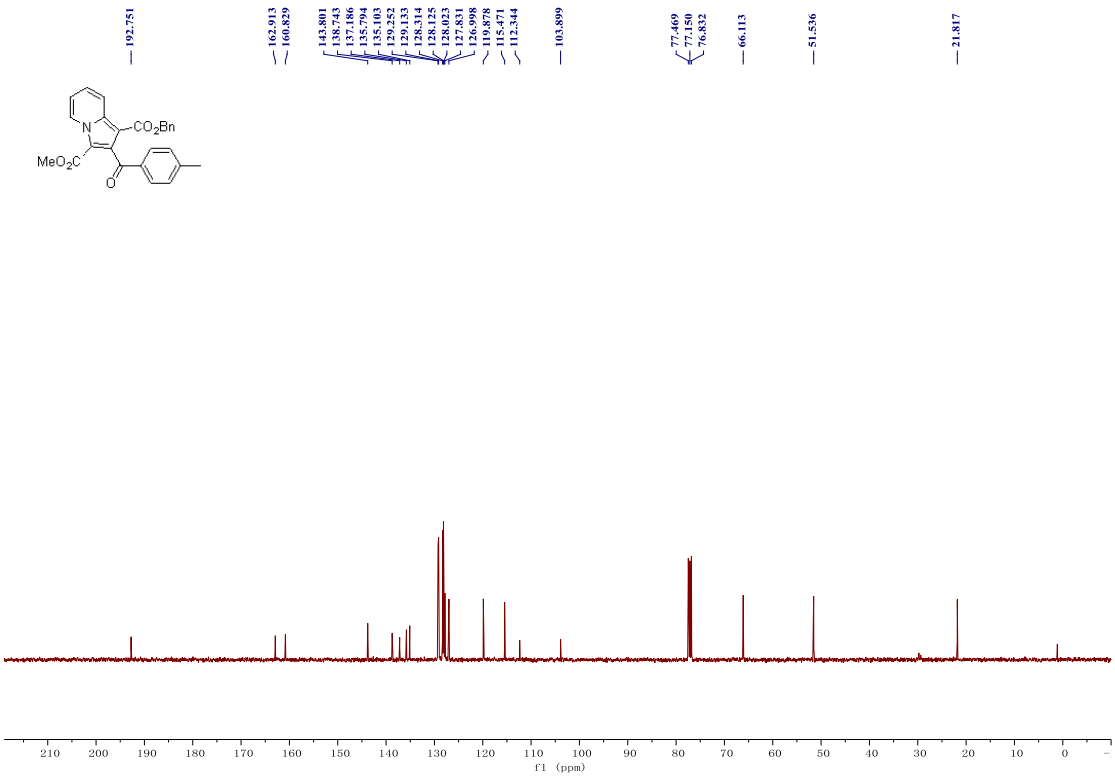


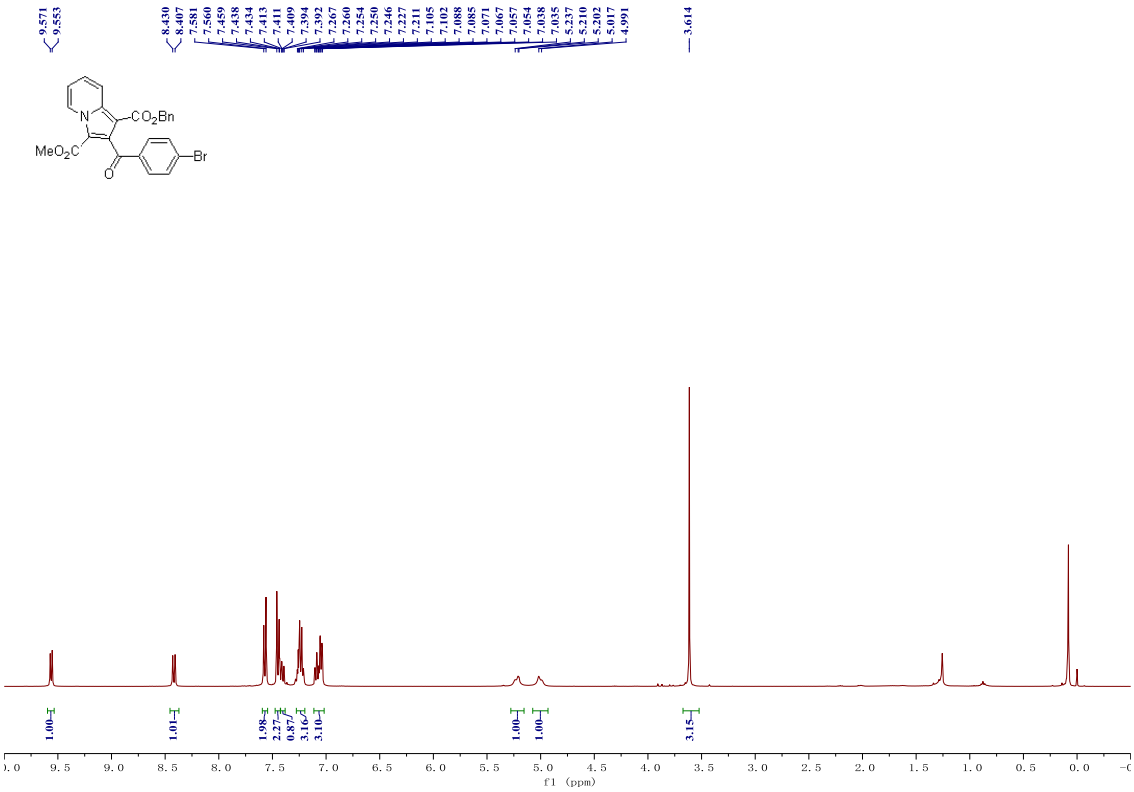
Fig. S70 ^{13}C NMR of compound **26** (100 MHz, $CDCl_3$)



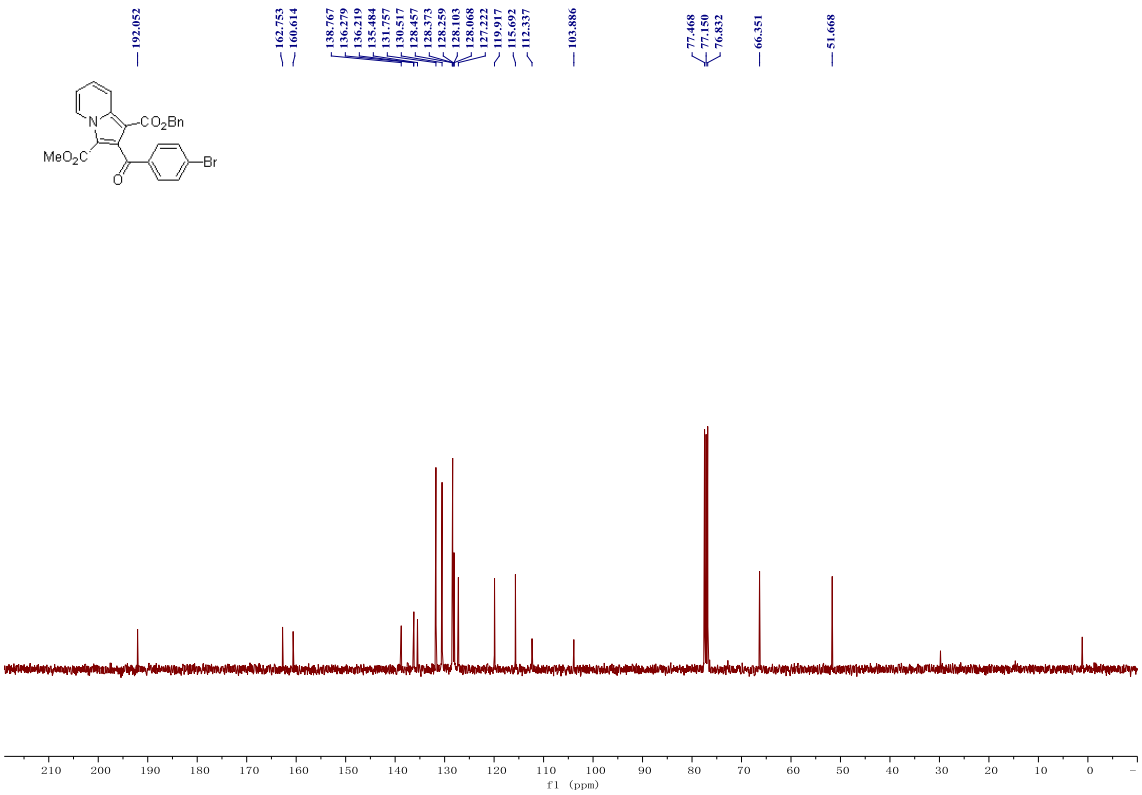
^{1}H NMR of compound **27** (400 MHz, $CDCl_3$)



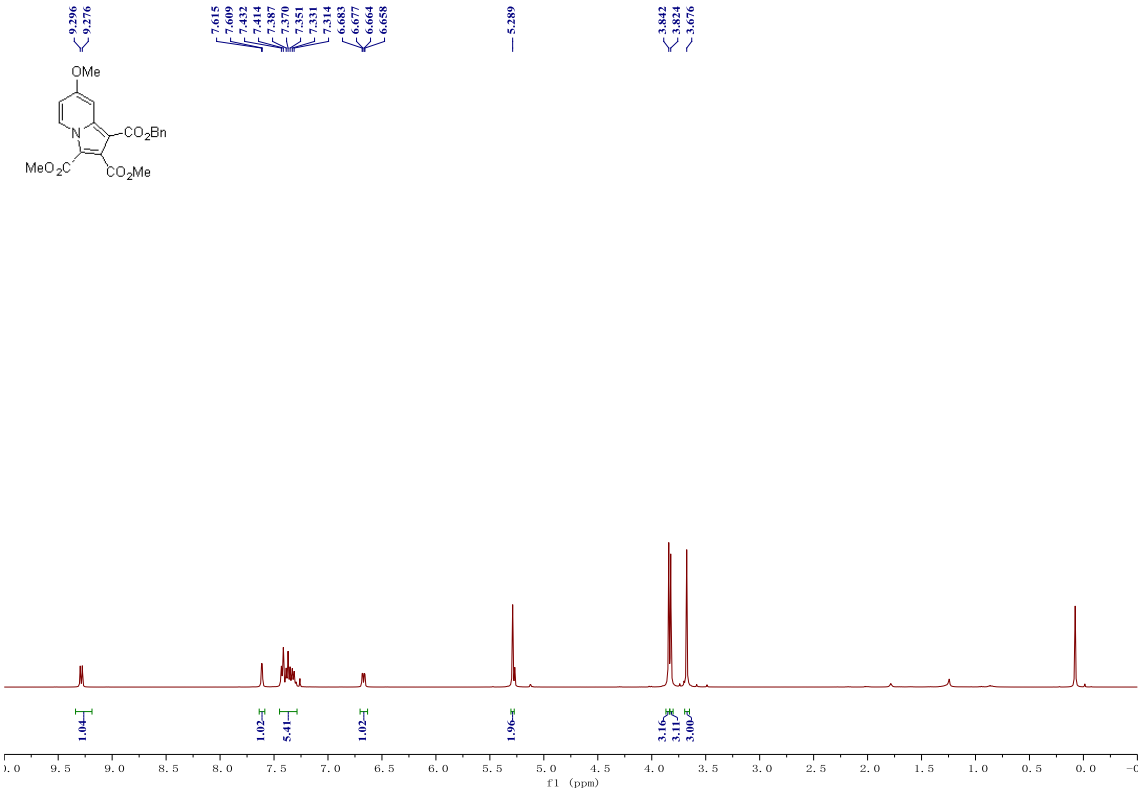
^{13}C NMR of compound **27** (100 MHz, $CDCl_3$)



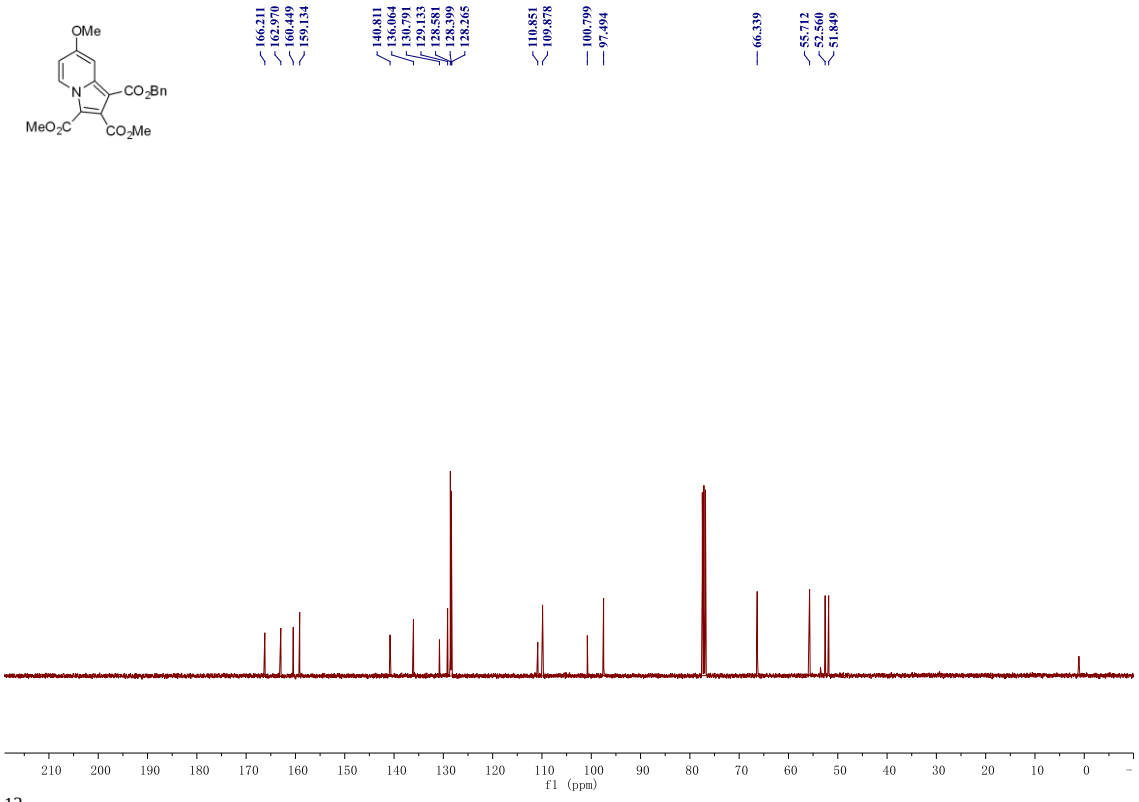
^{1}H NMR of compound **28** (400 MHz, $CDCl_3$)



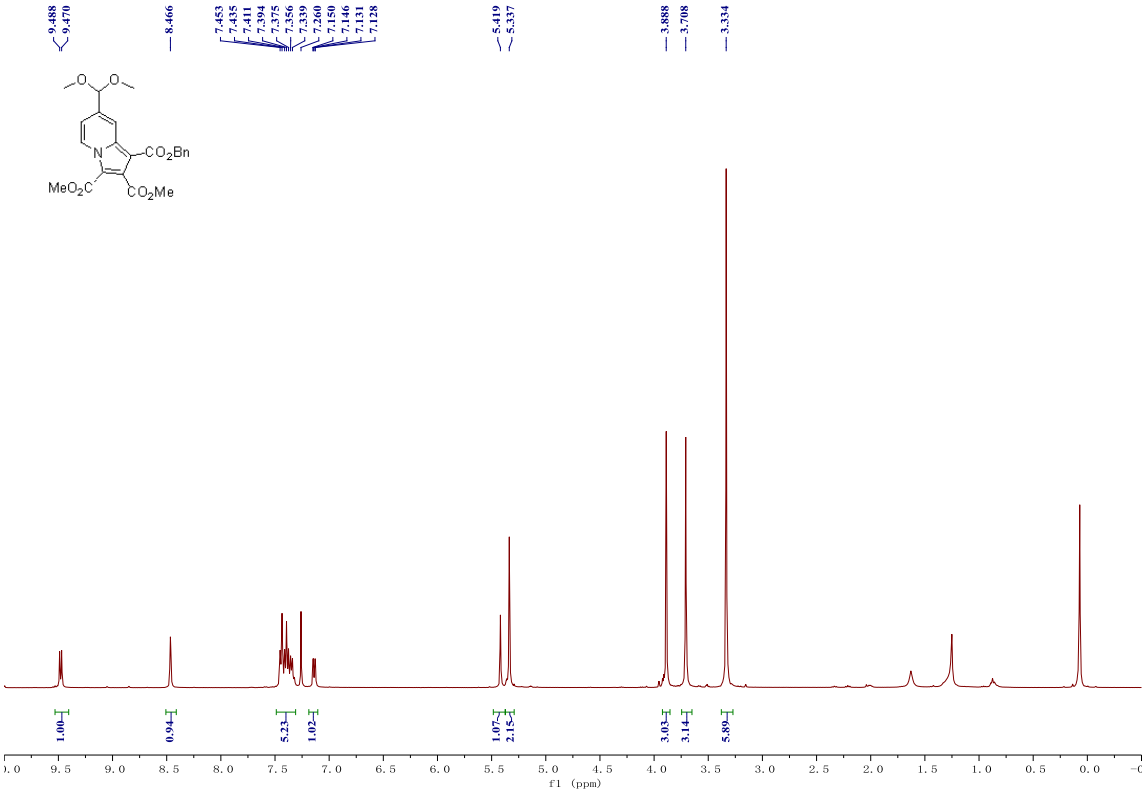
^{13}C NMR of compound **28** (100 MHz, $CDCl_3$)



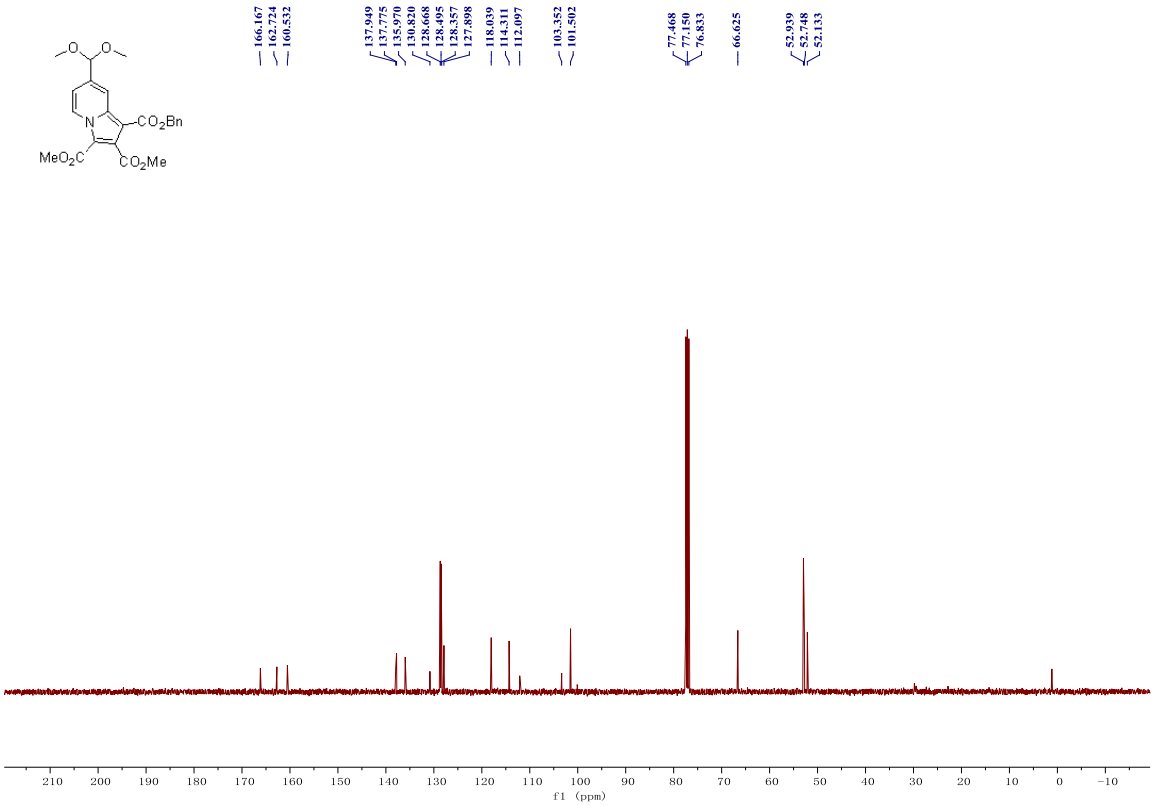
^{1}H NMR of compound **29** (400 MHz, $CDCl_3$)



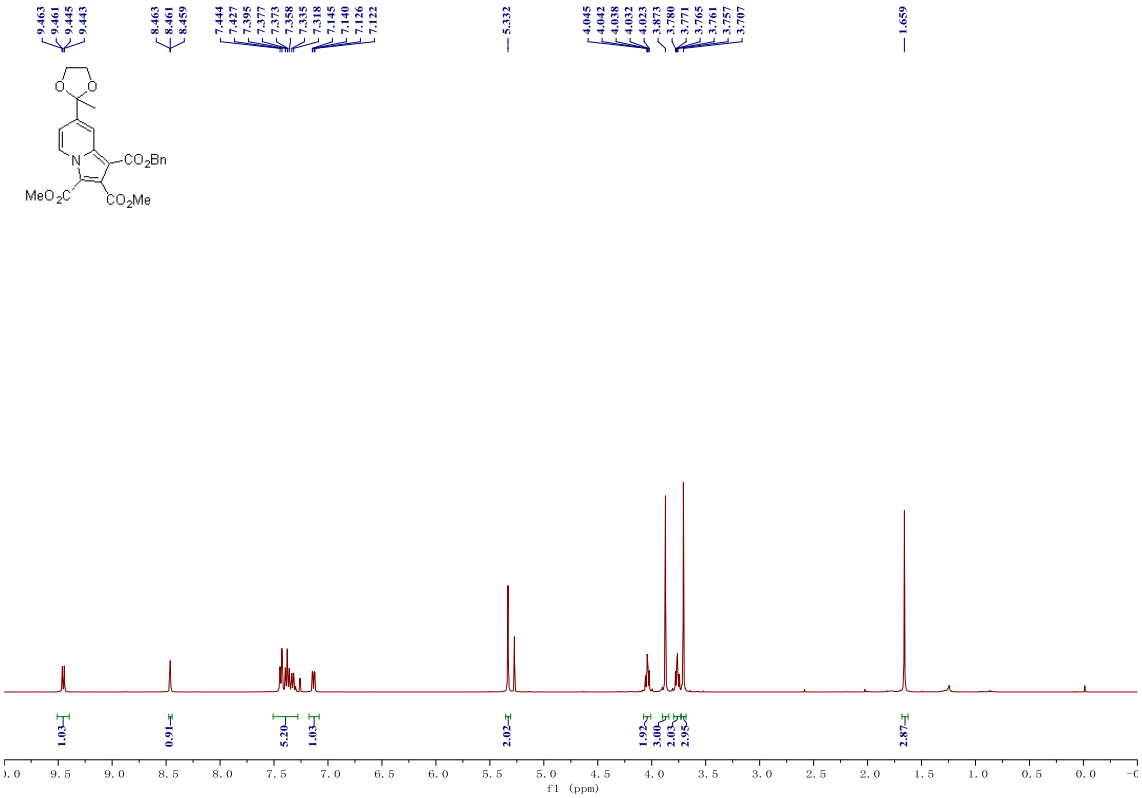
^{13}C NMR of compound **29** (100 MHz, $CDCl_3$)



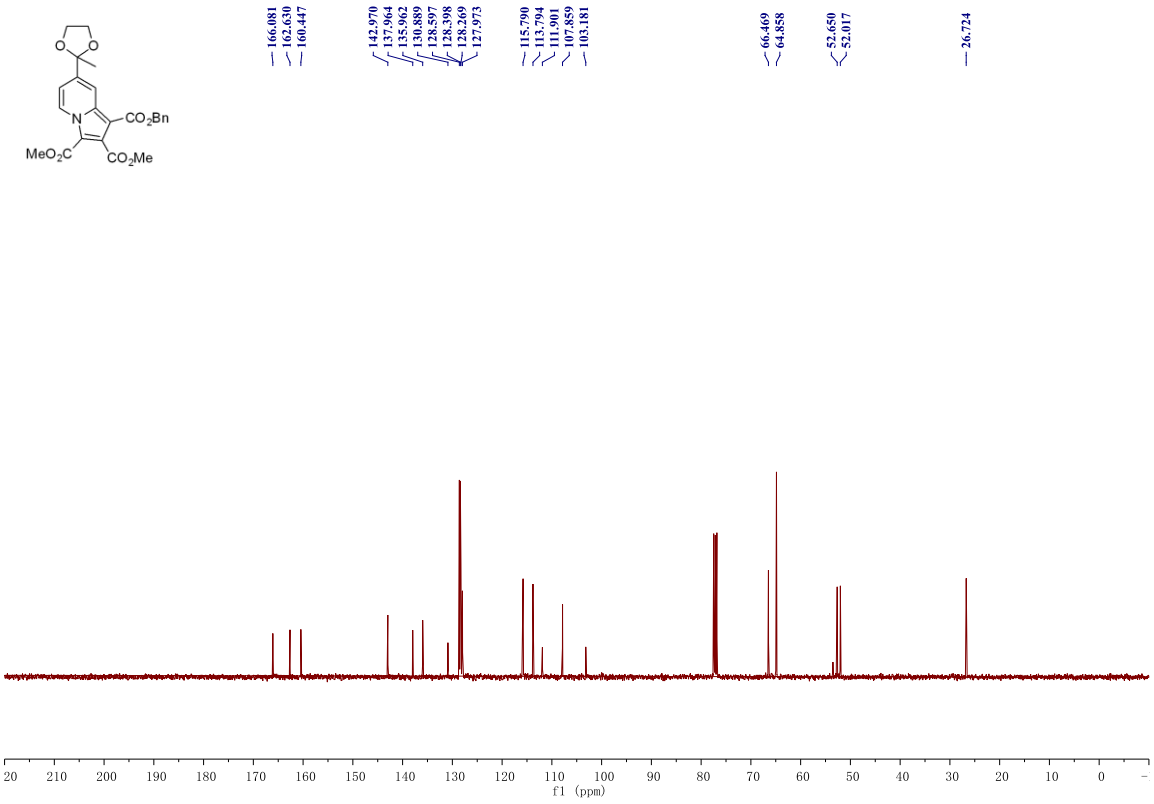
^{1}H NMR of compound **30** (400 MHz, $CDCl_3$)



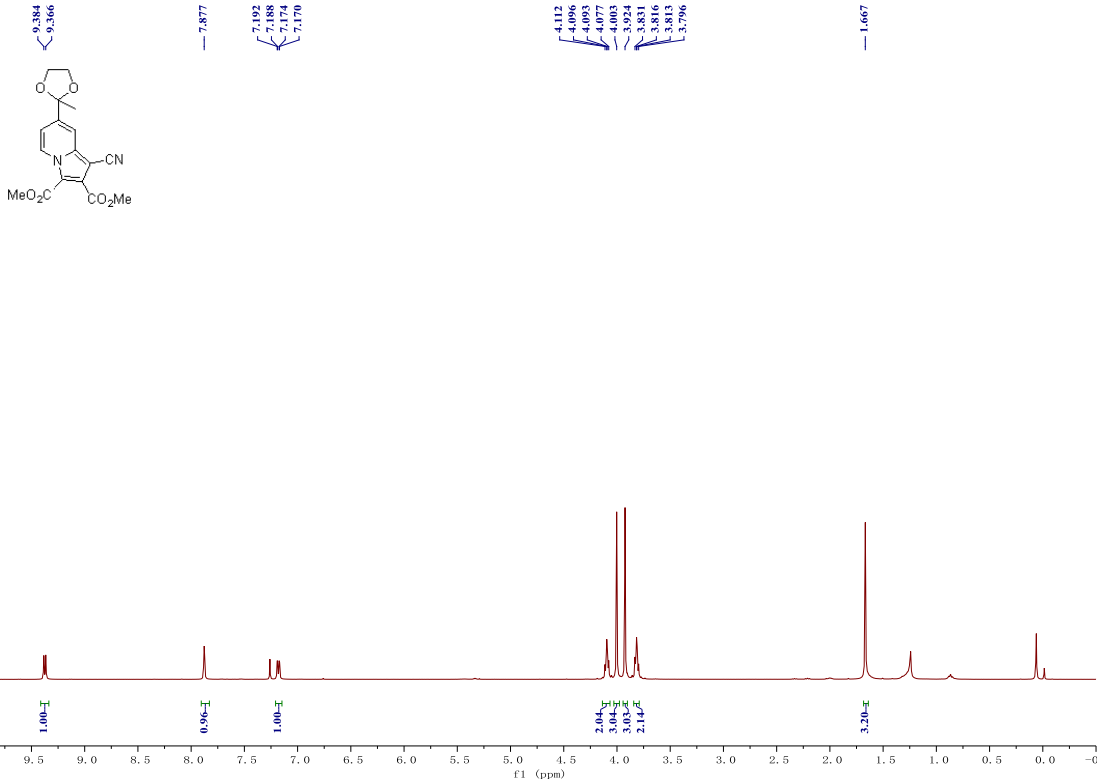
^{13}C NMR of compound **30** (100 MHz, $CDCl_3$)



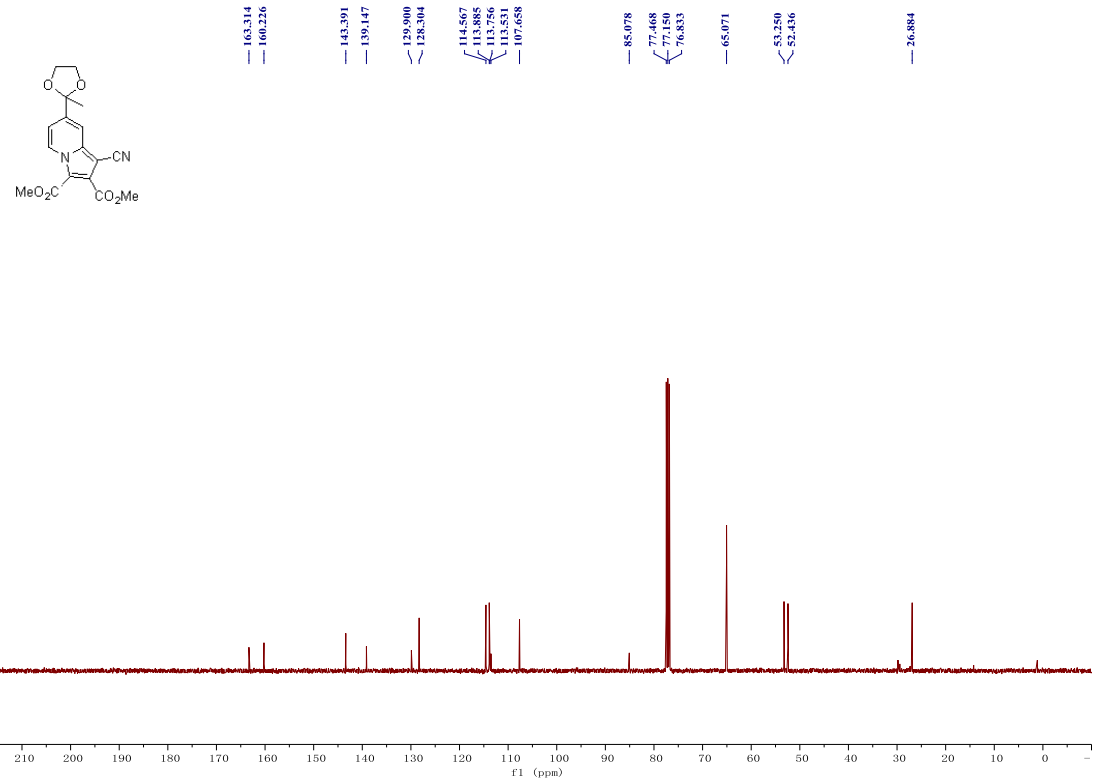
^{1}H NMR of compound **31** (400 MHz, $CDCl_3$)



^{13}C NMR of compound **31** (100 MHz, $CDCl_3$)



^{1}H NMR of compound **32** (400 MHz, $CDCl_3$)



^{13}C NMR of compound **32** (100 MHz, $CDCl_3$)