Facile Synthesis of indolizines *via* 1,3-dipolar cycloadditions in [Omim]Br: The promotion of the reaction through non-covalent interactions

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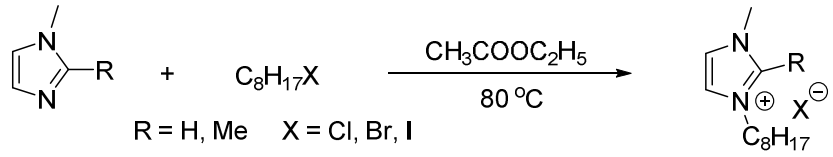
1 Experimental

1.1 Experimental Procedure



General procedures for the synthesis of ionic liquids[1]: *N*-Methylimidazole or 1,2-dimethyl-imidazole 40 mmol, 1-haloctane 48 mmol and ethyl acetate 10 mL were heated under reflux for 24 h. The biphasic system obtained was separated and the upper organic phase discharged. The bottom product phase was washed with ethyl acetate (3 × 10 mL), and dried under vacuum to give corresponding ionic liquid as a colourless liquid.

1.2 Recycling Studies

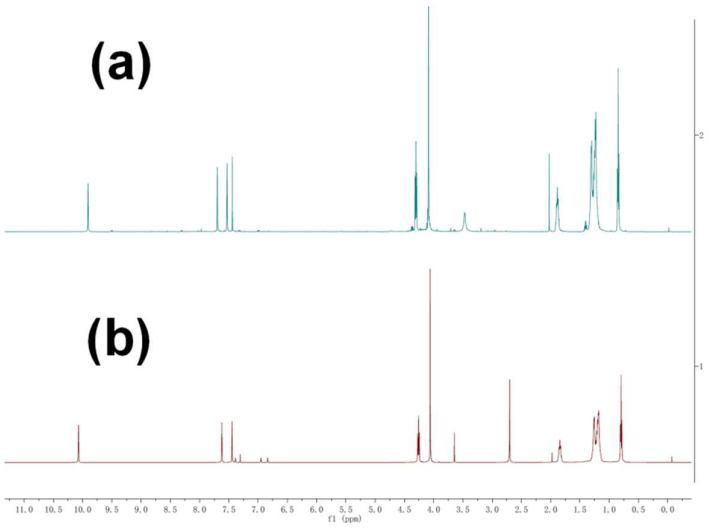
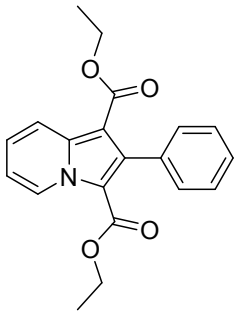


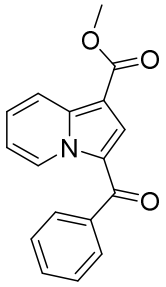
Figure S1. The ^{1}H NMR spectra of recovered [Omim]Br (a) and fresh [Omim]Br (b)

2 Characterization Data



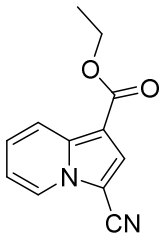
Chemical Formula: $C_{20}H_{19}NO_4$
Mass: 337
Elemental Analysis: C, 71.20; H, 5.68;
N, 4.15; O, 18.97

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **4a, 6q**, white solid, mp: 96-97 ^{o}C, yield 74%, 124.6 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 (d, J = 7.1 Hz, 1H), 8.42 (d, J = 9.0 Hz, 1H), 7.35 (d, J = 5.8 Hz, 4H), 7.26 (d, J = 4.5 Hz, 2H), 7.00 (t, J = 6.9 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 4.03 (q, J = 7.1 Hz, 2H), 1.00 (t, J = 7.1 Hz, 3H), 0.84 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 160.9, 139.0, 137.7, 135.3, 128.2, 127.0, 125, 125.8, 124.9, 118.7, 113.5, 112.6, 104.1, 58.9, 58.5, 12.8, 12.4. GC-MS (EI) *m/z*: 337. Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.20%; H, 5.68%; N, 4.15%. Found: C, 70.81%; H, 5.89%; N, 4.05%.



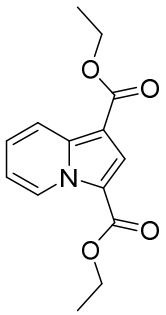
Chemical Formula: $C_{17}H_{13}NO_3$
Mass: 279

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **4b**[2], brown red solid, mp: 160-162 ^{o}C. (lit. 161-163 ^{o}C), yield 79%, 110.2 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (d, J = 7.0 Hz, 1H), 8.40 (d, J = 8.9 Hz, 1H), 7.81 (d, J = 6.9 Hz, 3H), 7.58 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.10 (t, J = 6.9 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.7, 163.5, 138.9, 139.0, 130.5, 128.3, 128.1 128.0, 127.4, 126.8, 121.6, 118.5, 114.4, 104.9, 50.3. GC-MS (EI) *m/z*: 279.



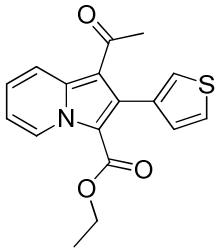
Chemical Formula: $C_{12}H_{10}N_2O_2$
Mass: 214

Ethyl 1-(4-nitrophenyl)indolizine-3-carboxylate **4c**[3], brown solid, mp: 106-108 °C, yield 55%, 58.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (t, *J* = 8.0 Hz, 2H), 7.79 (s, 1H), 7.38 – 7.30 (m, 1H), 7.04 (t, *J* = 6.9 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 136.8, 125.0, 124.8, 124.2, 119.5, 114.0, 111.7, 105.0, 95.7, 59.3, 13.5. GC-MS (EI) *m/z*: 214.



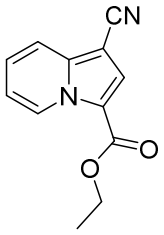
Chemical Formula: $C_{14}H_{15}NO_4$
Mass: 261

Ethyl 1-(4-nitrophenyl)indolizine-3-carboxylate **4d**[4], grey solid, mp: 128-129 °C. (lit. 130-131 °C), yield 88%, 114.8mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.52 (d, *J* = 7.1 Hz, 1H), 8.33 (d, *J* = 9.0 Hz, 1H), 7.99 (s, 1H), 7.33 – 7.28 (m, 1H), 6.97 (t, *J* = 6.8 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 4H), 1.42 (td, *J* = 7.1, 4.3 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 160.2, 138.1, 126.9, 124.6, 123.3, 118.6, 113.8, 113.4, 104.2, 59.3, 59.0, 13.6, 13.5. GC-MS (EI) *m/z*: 261.



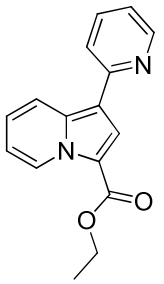
Chemical Formula: $C_{17}H_{15}NO_3S$
Mass: 313
Elemental Analysis: C, 65.16; H, 4.82; N, 4.47; O, 15.32; S, 10.23

Ethyl 2-acetyl-1-(thiophen-2-yl)indolizine-3-carboxylate **4e**, brown solid, mp: 105-107 °C, yield 23%, 36.0 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (d, *J* = 7.1 Hz, 1H), 8.67 (d, *J* = 9.0 Hz, 1H), 7.45 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.14 – 7.08 (m, 1H), 7.06 (t, *J* = 6.9 Hz, 1H), 7.02 (d, *J* = 3.4 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.2, 160.6, 137.4, 134.8, 129.6, 127.4, 126.6, 126.3, 125.7, 125.4, 119.7, 115.0, 114.6, 113.6, 59.1, 29.0, 12.6. GC-MS (EI) *m/z*: 313. Anal. Calcd for $C_{17}H_{15}NO_3S$: C, 65.16%; H, 4.82%; N, 4.47%. Found: C, 64.70%; H, 4.95%; N, 4.35%.



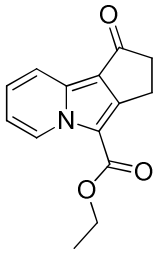
Chemical Formula: $C_{12}H_{10}N_2O_2$
Mass: 214

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **4f**[5], brown solid, mp: 73-74 °C. (lit. 75 °C), yield 82%, 87.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.52 (d, *J* = 7.1 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.39 – 7.32 (m, 1H), 7.04 (t, *J* = 6.9 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 139.6, 127.3, 124.9, 123.7, 116.6, 114.5 (2C), 114.0, 82.7, 59.8, 13.5. GC-MS (EI) *m/z*: 214.



Chemical Formula: $C_{16}H_{14}N_2O_2$
Mass: 266
Elemental Analysis: C, 72.17; H, 5.30; N, 10.52; O, 12.02

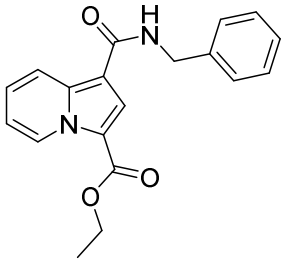
Ethyl 1-(4-nitrophenyl)indolizine-3-carboxylate **4g**, pale brown solid, mp: 97-100 °C, yield 67%, 89.2 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (d, *J* = 7.1 Hz, 1H), 8.73 (d, *J* = 9.0 Hz, 1H), 8.64 (d, *J* = 4.7 Hz, 1H), 7.94 (s, 1H), 7.73 – 7.63 (m, 2H), 7.23 – 7.16 (m, 1H), 7.14 – 7.06 (m, 1H), 6.93 – 6.85 (m, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 153.7, 148.2, 135.4 (2C), 126.5, 122.6, 119.4 (3C), 119.1, 113.3 (2C), 112.8, 59.0, 13.6. GC-MS (EI) *m/z*: 266. Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.17%; H, 5.30%; N, 10.52%. Found: C, 71.89%; H, 5.51%; N, 10.78%.



Chemical Formula: $C_{14}H_{13}NO_3$
Mass: 243
Elemental Analysis: C, 69.12; H, 5.39; N, 5.76; O, 19.73

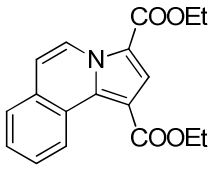
Ethyl 1-(4-nitrophenyl)indolizine-3-carboxylate **4h**, pale white solid, mp: 155-157 °C , yield 34%, 41.4 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57 (d, *J* = 7.0 Hz, 1H), 7.99 (d,

J = 8.7 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.33 – 3.22 (m, 2H), 2.99 – 2.89 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, CDCl3) δ 196.6, 160.3, 155.3, 131.3, 127.8, 125.7 (2C), 117.6 (2C), 114.5, 59.2, 40.7, 21.9, 13.6. GC-MS (EI) *m/z*: 243. Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12%; H, 5.39%; N, 5.76%. Found: C, 68.95%; H, 5.45%; N, 5.69%.



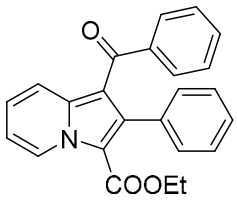
Chemical Formula: $C_{19}H_{18}N_2O_3$
Mass: 322

Ethyl 1-(4-nitrophenyl)indolizine-3-carboxylate **4i**[6], white solid, mp: 151-154 °C, yield 90%, 145.0 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.46 (d, *J* = 7.1 Hz, 1H), 8.55 (d, *J* = 9.0 Hz, 1H), 7.68 (s, 1H), 7.42 – 7.32 (m, 4H), 7.28 (dt, *J* = 15.7, 7.7 Hz, 2H), 6.95 (t, *J* = 6.9 Hz, 1H), 6.30 (s, 1H), 4.66 (d, *J* = 5.7 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 160.1, 137.8, 127.8, 127.4, 127.0, 126.9, 126.5, 124.0, 119.3, 118.6, 113.5, 112.9, 106.9, 59.3, 42.5, 13.6. GC-MS (EI) *m/z*: 322.



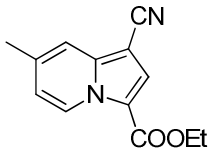
Chemical Formula: $C_{18}H_{17}NO_4$
Mass: 311
Elemental Analysis: C, 69.44; H, 5.50; N, 4.50; O, 20.56

Ethyl 1-(4-nitrophenyl)indolizine-3-carboxylate **4j**, pale black solid, mp: 113-114 °C , yield 79%, 122.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (d, *J* = 8.2 Hz, 1H), 9.36 (d, *J* = 7.5 Hz, 1H), 8.02 (s, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.61 (dt, *J* = 13.7, 7.1 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 4.41 (p, *J* = 7.2 Hz, 4H), 1.45 (dt, *J* = 10.4, 7.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 160.1, 134.9, 128.7, 127.8, 126.8, 126.7, 125.7, 124.2, 124.0, 123.4, 114.9, 113.9, 108.6, 59.5 (2C), 13.6 (2C). GC-MS (EI) *m/z*: 311. Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44%; H, 5.50%; N, 4.50%. Found: C, 69.31%; H, 5.60%; N, 4.87%.



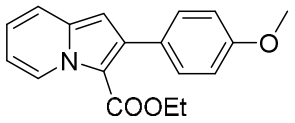
Chemical Formula: $C_{24}H_{19}NO_3$
Mass: 369

Ethyl 1-benzoyl-2-phenylindolizine-3-carboxylate **4k**[7], orange solid, mp: 113-114 °C. (lit. 115-116 °C), yield 85%, 156.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.66 (d, *J* = 7.1 Hz, 1H), 8.07 (d, *J* = 8.9 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.34 – 7.27 (m, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 3.6 Hz, 2H), 7.13 – 7.04 (m, 5H), 7.02 (t, *J* = 6.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.8, 161.0, 138.7, 137.9, 133.5, 130.3, 130.0, 128.3, 127.6, 127.0, 126.6, 126.0, 125.9, 125.0, 118.4, 113.8, 113.7, 111.8, 59.1, 12.6. GC-MS (EI) *m/z*: 369.



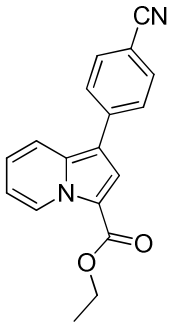
Chemical Formula: $C_{13}H_{12}N_2O_2$
Mass: 228
Elemental Analysis: C, 68.41; H, 5.30; N, 12.27; O, 14.02

Ethyl 1-cyano-7-methylindolizine-3-carboxylate **4l**, brown solid, mp: 73-75 °C , yield 61%, 69.5 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.38 (d, *J* = 7.2 Hz, 1H), 7.70 (s, 1H), 7.51 (s, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 140.2, 136.4, 126.7, 123.8, 116.5, 115.3, 114.8, 113.9, 81.3, 59.6, 20.3, 13.5. GC-MS (EI) *m/z*: 228. Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41%; H, 5.30%; N, 12.27%. Found: C, 68.23%; H, 5.65%; N, 12.11%.



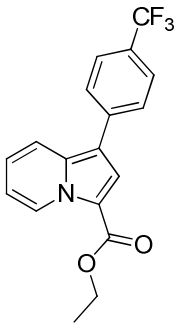
Chemical Formula: $C_{18}H_{17}NO_3$
Mass: 295

ethyl 2-(4-methoxyphenyl)indolizine-3-carboxylate **4m**[8], white solid, mp: 98-100 °C (lit. 99-101 °C), yield 45%, 66.4 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, *J* = 7.2 Hz, 1H), 7.44 (dd, *J* = 17.4, 8.7 Hz, 3H), 7.07 – 6.97 (m, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.47 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 157.9, 136.9, 135.9, 130.1, 128.1, 126.9, 121.1, 117.3, 111.9, 111.5, 109.9, 102.7, 58.6, 54.4, 13.1. GC-MS (EI) *m/z*: 295.



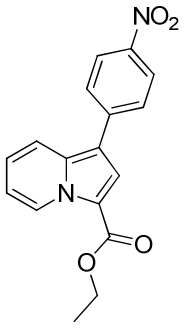
Chemical Formula: $C_{18}H_{14}N_2O_2$
Mass: 290
Elemental Analysis: C, 74.47; H, 4.86;
N, 9.65; O, 11.02

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **6a**, white solid, mp: 145-148 ^{o}C , yield 92%, 133.4 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53 (d, J = 7.1 Hz, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.78 – 7.64 (m, 5H), 7.22 – 7.11 (m, 1H), 6.91 (t, J = 6.9 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 134.2, 129.0, 126.9, 122.2, 122.0, 117.8, 115.1, 113.5, 111.6, 109.1, 108.2, 107.8, 103.4, 54.4, 8.8. GC-MS (EI) *m/z*: 290. Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47%; H, 4.86%; N, 9.65%. Found: C, 74.15%; H, 4.95%; N, 9.50%.



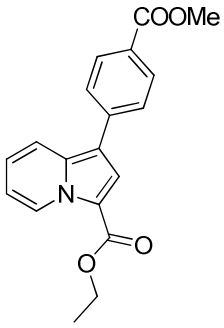
Chemical Formula: $C_{18}H_{14}F_3NO_2$
Mass: 333
Elemental Analysis: C, 64.86; H, 4.23;
F, 17.10; N, 4.20; O, 9.60

Ethyl 1-(4-nitrophenyl)indolizine-3-carboxylate **6b**, pale yellow solid, mp: 115-118 ^{o}C , yield 88%, 146.6 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, J = 7.1 Hz, 1H), 7.81 (d, J = 9.0 Hz, 1H), 7.70 (s, 1H), 7.69 (s, 4H), 7.16 – 7.08 (m, 1H), 6.88 (t, J = 6.9 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 137.9, 133.9, 126.8 (m, 4C), 124.8, 123.4 (q, J = 270.0 Hz, 1C) 122.1, 119.9, 116.4, 113.6, 113.5, 112.4, 59.1, 13.6. GC-MS (EI) *m/z*: 333. Anal. Calcd for $C_{18}H_{14}F_3NO_2$: C, 64.86%; H, 4.23%; N, 4.20%. Found: C, 64.49%; H, 4.52%; N, 4.57%.



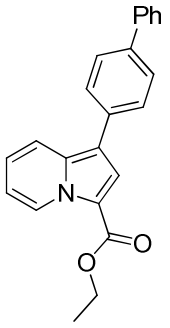
Chemical Formula: $C_{17}H_{14}N_2O_4$
Mass: 310
Elemental Analysis: C, 65.80; H, 4.55;
N, 9.03; O, 20.62

Ethyl 1-(4-nitrophenyl)indolizine-3-carboxylate **6c**, red solid, mp: 147-149 ^{o}C, yield 97%, 150.4 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (d, J = 7.1 Hz, 1H), 8.30 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 9.0 Hz, 1H), 7.79 – 7.68 (m, 3H), 7.24 – 7.15 (m, 1H), 6.93 (t, J = 6.9 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 144.7, 141.2, 134.1, 127.1, 126.6, 123.4, 123.0, 120.1, 116.4, 114.1, 112.8 (2C), 59.3, 13.6. GC-MS (EI) *m/z*: 310. Anal. Calcd for $C_{17}H_{14}N_2O_4$: C, 65.80%; H, 4.55%; N, 9.03%. Found: C, 65.97%; H, 4.88%; N, 8.64%.



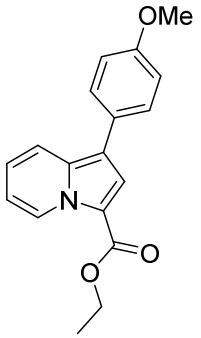
Chemical Formula: $C_{19}H_{17}NO_4$
Mass: 323
Elemental Analysis: C, 70.58; H,
5.30; N, 4.33; O, 19.79

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **6d**, pale yellow solid, mp: 142-144 ^{o}C, yield 95%, 153,4 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, J = 7.1 Hz, 1H), 8.11 (d, J = 8.3 Hz, 2H), 7.85 (d, J = 9.0 Hz, 1H), 7.73 (s, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.18 – 7.08 (m, 1H), 6.88 (t, J = 6.6 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 160.3, 139.0, 133.9, 129.2, 126.8, 126.6 126.3, 122.2, 119.95, 116.7, 114.0, 113.6, 112.4, 59.1, 51.1, 13.6. GC-MS (EI)*m/z*: 323. Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.58%; H, 5.30%; N, 4.33%. Found: C, 70.29%; H, 5.68%; N, 4.50%.



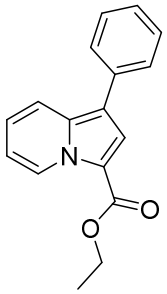
Chemical Formula: $C_{23}H_{19}NO_2$
Mass: 341
Elemental Analysis: C, 80.92; H, 5.61; N, 4.10; O, 9.37

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **6e**, pale yellow solid, mp: 179-181 ^{o}C , yield 28%, 47.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (d, *J* = 7.1 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.72 (s, 1H), 7.67 (dd, *J* = 12.3, 5.2 Hz, 6H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.14 – 7.06 (m, 1H), 6.86 (t, *J* = 6.8 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 139.9, 138.0, 133.9, 133.2, 127.9, 127.2, 126.7, 126.6, 126.3, 126.0, 121.48, 119.7, 116.9, 114.8, 113.1, 112.2, 59.0, 13.7. GC-MS (EI) *m/z*: 341. Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.92%; H, 5.61%; N, 4.10%. Found: C, 80.56%; H, 5.79%; N, 4.03%.



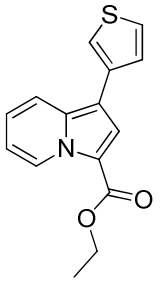
Chemical Formula: $C_{18}H_{17}NO_3$
Mass: 295

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **6f**[9], grey solid, mp: 136-138 ^{o}C , yield 31%, 45.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (d, *J* = 7.1 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.61 (s, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.07 – 7.02 (m, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.82 (t, *J* = 6.9 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 157.3, 133.7, 128.1, 126.7, 126.5, 121.0, 119.4, 116.8, 115.1, 113.3, 112.7, 111.9, 58.9, 54.4, 13.7. GC-MS (EI) *m/z*: 295.



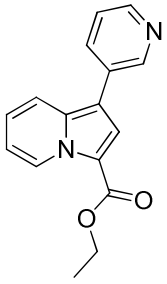
Chemical Formula: $C_{17}H_{15}NO_2$
Mass: 265

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **6g**[9], grey solid, mp: 94-96 ^{o}C , yield 93%, 123.2 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (d, *J* = 7.1 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.67 (s, 1H), 7.59 (d, *J* = 9.2 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.03 (m, 1H), 6.84 (t, *J* = 6.9 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 134.2, 133.8, 127.9, 126.9, 126.6, 125.3, 121.4, 119.7, 116.8, 115.3, 113.0, 112.1, 58.9, 13.7. GC-MS (EI) *m/z*: 265.



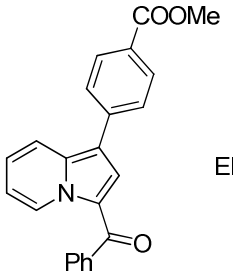
Chemical Formula: $C_{15}H_{13}NO_2S$
Mass: 271
Elemental Analysis: C, 66.40; H, 4.83; N, 5.16; O, 11.79; S, 11.82

Ethyl 1-(4-nitrophenyl)indolizine-3-carboxylate **6h**, brown solid, mp: 133-135 ^{o}C , yield 26%, 35.2 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (d, *J* = 7.1 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.65 (s, 1H), 7.43 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.37 (dd, *J* = 6.7, 3.8 Hz, 2H), 7.12 – 7.05 (m, 1H), 6.84 (t, *J* = 6.9 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 134.5, 133.8, 126.5 (2C), 124.8, 121.3, 119.5, 118.3, 116.9, 112.7, 112.1, 110.5, 58.9, 13.7. GC-MS (EI) *m/z*: 271. Anal. Calcd for $C_{15}H_{13}NO_2S$: C, 66.40%; H, 4.83%; N, 5.16%. Found: C, 66.12%; H, 4.99%; N, 5.03%.



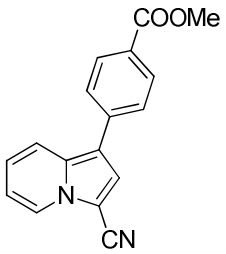
Chemical Formula: $C_{16}H_{14}N_2O_2$
Mass: 266
Elemental Analysis: C, 72.17; H, 5.30; N, 10.52; O, 12.02

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **6i**, grey solid, mp: 86-88 ^{o}C , yield 94%, 125.0 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, J = 7.1 Hz, 1H), 8.87 (s, 1H), 8.54 (d, J = 4.6 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 9.0 Hz, 1H), 7.69 (s, 1H), 7.42 – 7.31 (m, 1H), 7.18 – 7.06 (m, 1H), 6.88 (t, J = 6.9 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 147.8, 146.3, 133.9 (2C), 130.2, 126.8, 122.7, 122.1, 119.7, 116.3, 113.6, 112.4, 111.3, 59.1, 13.6. GC-MS (EI) *m/z*: 266. Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.17%; H, 5.30%; N, 10.52%. Found: C, 71.88%; H, 5.69%; N, 10.22%.



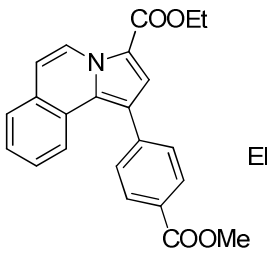
Chemical Formula: $C_{23}H_{17}NO_3$
Mass: 355
Elemental Analysis: C, 77.73; H, 4.82; N, 3.94; O, 13.51

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **6j**, yellow solid, mp: 117-119 ^{o}C , yield 93%, 165.0 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (d, J = 7.1 Hz, 1H), 8.10 (d, J = 8.3 Hz, 2H), 7.92 (d, J = 8.9 Hz, 1H), 7.84 (d, J = 7.1 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.35 – 7.29 (m, 1H), 7.03 (t, J = 6.8 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.9, 166.0, 139.6, 138.5, 135.5, 130.2, 129.3, 128.2, 128.0, 127.4, 126.5, 124.7, 124.6, 121.6, 116.5, 115.3, 113.6, 51.2. GC-MS (EI) *m/z*: 355. Anal. Calcd for $C_{23}H_{17}NO_3$: C, 77.73%; H, 4.82%; N, 3.94%. Found: C, 77.45%; H, 5.02%; N, 3.85%.



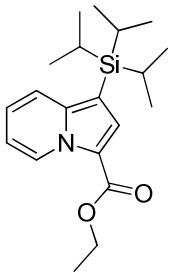
Chemical Formula: $C_{17}H_{12}N_2O_2$
Mass: 276
Elemental Analysis: C, 73.90; H, 4.38; N, 10.14; O, 11.58

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **6k**, brown solid, mp: 106-108 ^{o}C, yield 81%, 111.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 7.0 Hz, 1H), 8.12 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 9.1 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.51 (s, 1H), 7.17 – 7.12 (m, 1H), 6.93 (t, J = 7.2 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 137.8, 132.5, 129.4, 127.2, 126.4, 124.8, 122.5, 120.6, 117.5, 114.5, 113.0, 112.6, 95.2, 51.2. GC-MS (EI) *m/z*: 276. Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90%; H, 4.38%; N, 10.14%. Found: C, 73.57%; H, 4.74%; N, 9.89%.



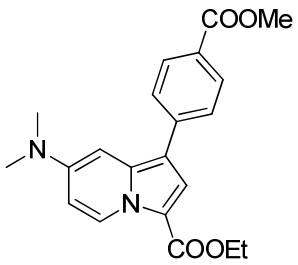
Chemical Formula: $C_{23}H_{19}NO_4$
Mass: 373
Elemental Analysis: C, 73.98; H, 5.13; N, 3.75; O, 17.14

Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **6l**, pale yellow solid, mp: 133-135 ^{o}C , yield 48%, 89.6 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.28 (d, *J* = 7.5 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 3H), 7.46 – 7.35 (m, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 160.33, 141.2, 129.3, 128.9, 127.9, 127.7, 126.4, 126.1, 124.3, 123.7, 122.6, 121.4, 117.9, 114.9, 112.2, 59.2, 51.2, 13.6. GC-MS (EI) *m/z*: 373. Anal. Calcd for $C_{23}H_{19}NO_4$: C, 73.98%; H, 5.13%; N, 3.75%. Found: C, 73.65%; H, 5.47%; N, 3.64%.



Chemical Formula: $C_{20}H_{31}NO_2Si$
Mass: 345
Elemental Analysis: C, 69.52; H, 9.04; N, 4.05;
O, 9.26; Si, 8.13

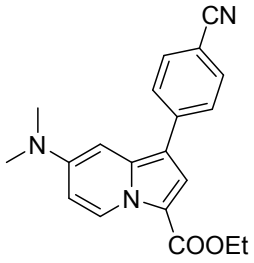
Ethyl 1-(triisopropylsilyl)indolizine-3-carboxylate **6m**, pale blue liquid, yield 54%, 93.2 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.40 (d, *J* = 7.1 Hz, 1H), 7.53 (s, 1H), 7.47 (d, *J* = 9.0 Hz, 1H), 6.97 – 6.90 (m, 1H), 6.73 (t, *J* = 6.8 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.42 (dt, *J* = 14.8, 7.4 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.03 (d, *J* = 7.5 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 142.2, 129.2, 126.9, 120.8, 119.6, 114.5, 111.6, 103.2, 58.8, 17.8, 13.7, 11.1. GC-MS (EI) *m/z*: 345. Anal. Calcd for $C_{20}H_{31}NO_2Si$: C, 69.52%; H, 9.04%; N, 4.05%. Found: C, 69.17%; H, 9.38%; N, 3.99%.



Chemical Formula: $C_{21}H_{22}N_2O_4$
Mass: 366
Elemental Analysis: C, 68.84; H, 6.05;
N, 7.65; O, 17.47

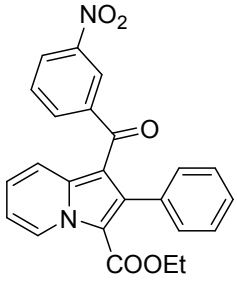
Ethyl 7-(dimethylamino)-1-(4-(methoxycarbonyl)phenyl)indolizine-3-carboxylate **6n**,

red solid, mp: 200-202 °C , yield 78%, 142.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.31 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.9 Hz, 3H), 6.81 (s, 1H), 6.56 (d, *J* = 9.9 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 3.05 (s, 6H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 160.3, 145.6, 140.1, 136.8, 129.2 (3C), 127.7, 125.7, 125.5 (3C), 121.2, 103.2, 93.0, 58.6, 51.0, 39.3, 13.7. GC-MS (EI) *m/z*: 366. Anal. Calcd for $C_{21}H_{22}N_2O_4$: C, 68.84%; H, 6.05%; N, 7.65%. Found: C, 68.69%; H, 6.23%; N, 7.51%.



Chemical Formula: $C_{20}H_{19}N_3O_2$
Mass: 333
Elemental Analysis: C, 72.05; H, 5.74;
N, 12.60; O, 9.60

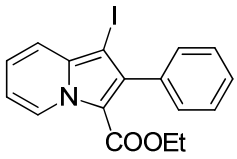
Ethyl 1-(4-cyanophenyl)-7-(dimethylamino)indolizine-3-carboxylate **6o**, brown solid, mp: 209-211 °C, yield 75%, 124.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.31 (d, *J* = 7.9 Hz, 1H), 7.66 (m, 4H), 7.60 (s, 1H), 6.75 (d, *J* = 2.5 Hz, 1H), 6.57 (d, *J* = 10.5 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.06 (s, 6H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 146.2, 140.2, 136.9, 131.6, 127.7, 125.9, 121.2, 118.6, 111.2, 108.9, 106.7, 103.3, 92.1, 58.6, 39.1, 13.7. GC-MS (EI) *m/z*: 333. Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05%; H, 5.74%; N, 12.60%. Found: C, 71.98%; H, 5.92%; N, 12.44%.



Chemical Formula: $C_{24}H_{18}N_2O_5$
Mass: 414
Elemental Analysis: C, 69.56; H, 4.38;
N, 6.76; O, 19.30

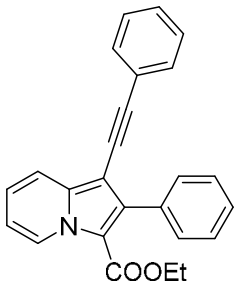
Ethyl 1-(3-nitrobenzoyl)-2-phenylindolizine-3-carboxylate **6p**, yellow solid, mp: 152-154 °C, yield 72%, 149.0 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (d, *J* = 7.1 Hz, 1H), 8.44 (d, *J* = 8.9 Hz, 1H), 8.03 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.15 – 7.08 (m, 3H), 7.02 – 6.93 (m, 3H), 4.10 (q, *J* = 7.1 Hz, 2H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.0, 160.7, 145.8, 140.1, 138.7, 137.8, 133.2 (2C), 130.0, 127.7, 127.3, 126.5, 126.4, 125.9, 124.0, 123.5, 118.6, 114.6, 112.4, 112.6, 59.3, 12.6. GC-MS (EI)

m/z: 414. Anal. Calcd for $C_{24}H_{18}N_2O_5$: C, 69.56%; H, 4.38%; N, 6.76%. Found: C, 69.24%; H, 4.66%; N, 6.45%.



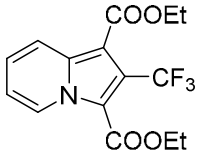
Chemical Formula: $C_{17}H_{14}INO_2$
Mass: 391
Elemental Analysis: C, 52.19; H, 3.61; I, 32.44; N, 3.58; O, 8.18

Ethyl 1-iodo-2-phenylindolizine-3-carboxylate **6r**, pale yellow solid, mp: 101-103 ^oC , yield 62%, 121.2 mg. ^1H NMR (500 MHz, $CDCl_3$) δ 9.59 (d, *J* = 7.9 Hz, 1H), 7.51 (ddd, *J* = 23.4, 15.7, 7.9 Hz, 6H), 7.09 – 6.94 (m, 1H), 6.82 (t, *J* = 6.9 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 1.55 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 134.5, 133.8, 129.9, 127.4, 126.8, 126.5, 121.7, 121.5, 116.2, 113.2, 112.2, 81.6, 59.5, 13.5. GC-MS (EI) *m/z*: 391. Anal. Calcd for $C_{17}H_{14}INO_2$: C, 52.19%; H, 3.61%; N, 3.58%. Found: C, 52.01%; H, 3.92%; N, 3.44%.



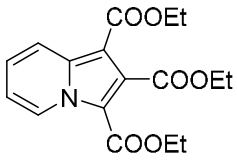
Chemical Formula: $C_{25}H_{19}NO_2$
Mass: 365
Elemental Analysis: C, 82.17; H, 5.24; N, 3.83; O, 8.76

Ethyl 2-phenyl-1-(phenylethynyl)indolizine-3-carboxylate **6s**, pale yellow solid, mp: 87-90 ^oC, yield 65%, 118.6 mg. ^1H NMR (500 MHz, $CDCl_3$) δ 9.58 – 9.51 (m, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 6.8 Hz, 2H), 7.29 – 7.24 (m, 3H), 7.20 – 7.15 (m, 1H), 6.89 (t, *J* = 6.9 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 138.2, 137.6, 133.5, 130.1, 129.6, 127.3, 127.2, 126.5, 126.2, 123.1, 122.7, 117.2, 113.0, 110.5, 97.0, 92.1, 81.7, 58.9, 12.9. GC-MS (EI)*m/z*: 365. Anal. Calcd for $C_{25}H_{19}NO_2$: C, 82.17%; H, 5.24%; N, 3.83%. Found: C, 81.95%; H, 5.56%; N, 3.57%.



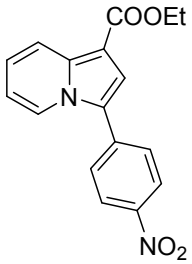
Chemical Formula: $C_{15}H_{14}F_3NO_4$
Mass: 329
Elemental Analysis: C, 54.72; H, 4.29; F, 17.31; N, 4.25; O, 19.44

Diethyl 1-(trifluoromethyl)indolizine-2,3-dicarboxylate **6t**, pale yellow liquid, yield 43%, 70.7 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, *J* = 7.2 Hz, 1H), 8.17 (d, *J* = 9.1 Hz, 1H), 7.30 – 7.26 (m, 1H), 6.99 (t, *J* = 6.9 Hz, 1H), 4.43 (dq, *J* = 18.5, 7.1 Hz, 4H), 1.42 (td, *J* = 7.1, 4.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 159.8, 135.7, 125.7, 124.4 (m, 2C), 123.3 (q, *J* = 275.0 Hz, 1C) 118.9, 114.4 (2C), 113.9, 60.8, 60.0, 13.1, 12.9. GC-MS (EI) *m/z*: 329. Anal. Calcd for $C_{15}H_{14}F_3NO_4$: C, 54.72%; H, 4.29%; N, 4.25%. Found: C, 54.48%; H, 4.67%; N, 4.33%.



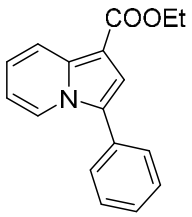
Chemical Formula: $C_{17}H_{19}NO_6$
Mass: 333

Triethyl indolizine-1,2,3-tricarboxylate **6u**[10], pale yellow solid, mp: 115-117 °C, yield 74%, 123.2 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (d, *J* = 7.1 Hz, 1H), 8.36 (d, *J* = 9.0 Hz, 1H), 7.43 – 7.31 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 4.38 (qd, *J* = 7.1, 4.1 Hz, 4H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.38 (td, *J* = 7.1, 4.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 162.0, 159.2, 137.0, 129.7, 126.9, 125.6, 119.0, 114.3, 110.9, 102.2, 60.8, 59.9, 59.3, 13.4, 13.2, 13.1. GC-MS (EI) *m/z*: 333.



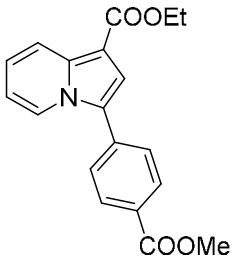
Chemical Formula: $C_{17}H_{14}N_2O_4$
Mass: 310

Ethyl 3-(4-nitrophenyl)indolizine-1-carboxylate **7a**[11], orange solid, mp: 148-150 °C , yield 95%, 147.2 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.1 Hz, 1H), 8.30 (t, *J* = 9.1 Hz, 3H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.44 (s, 1H), 7.19 – 7.09 (m, 1H), 6.82 (t, *J* = 6.8 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 145.5, 136.8, 136.5, 127.0, 123.6, 123.0, 122.40 122.2, 119.5, 117.2, 112.7, 104.6, 58.9, 13.7. GC-MS (EI) *m/z*: 310.



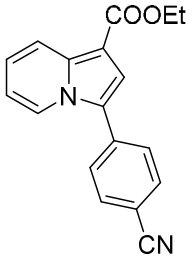
Chemical Formula: $C_{17}H_{15}NO_2$
Mass: 265

Ethyl 3-phenylindolizine-1-carboxylate **7b**[11], deep blue solid, mp: 135-138 °C , yield 35%, 46.4 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 15.3, 8.1 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.31 (s, 1H), 7.11 – 7.02 (m, 1H), 6.70 (t, *J* = 6.8 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 135.4, 130.3, 128.1, 127.7, 127.1, 125.46, 122.4, 121.3, 119.2, 116.4, 115.2, 111.6, 58.6, 13.7. GC-MS (EI) *m/z*: 265.



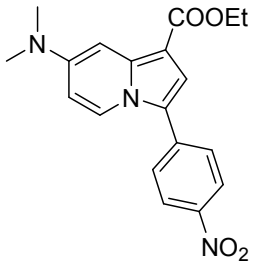
Chemical Formula: $C_{19}H_{17}NO_4$
Mass: 323

Ethyl 3-(4-(methoxycarbonyl)phenyl)indolizine-1-carboxylate **7c**[12], light grey solid, mp: 151-152 °C , yield 61%, 98.5 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.1 Hz, 1H), 8.28 (d, *J* = 9.0 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.38 (s, 1H), 7.14 – 7.06 (m, 1H), 6.74 (t, *J* = 7.3 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, CDCl3) δ 165.6, 163.8, 136.0, 134.8, 129.4, 128.1, 126.8, 124.3, 122.3, 121.7, 119.3, 116.2, 112.1, 103.9, 58.7, 51.2, 13.7. GC-MS (EI) *m/z*: 323.



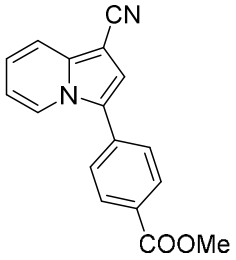
Chemical Formula: $C_{18}H_{14}N_2O_2$
Mass: 290

Ethyl 3-(4-cyanophenyl)indolizine-1-carboxylate **7d**[13], green solid, mp: 164-166 °C, yield 58%, 84.1 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 19.3, 8.1 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.39 (s, 1H), 7.18 – 7.08 (m, 1H), 6.79 (t, *J* = 6.4 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 136.2, 134.8, 131.9, 127.2, 123.3, 122.1 (2C), 119.5, 117.7, 116.7, 112.5, 109.9, 104.3, 58.8, 13.6. GC-MS (EI) *m/z*: 290.



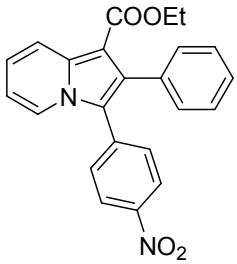
Chemical Formula: $C_{19}H_{19}N_3O_4$
Mass: 353
Elemental Analysis: C, 64.58; H, 5.42;
N, 11.89; O, 18.11

Ethyl 7-(dimethylamino)-3-(4-nitrophenyl)indolizine-1-carboxylate **7e**, red solid, mp: 160-162 ^{o}C , yield 50%, ^{1}H NMR (500 MHz, CDCl3) δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.26 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.53 (d, *J* = 7.8 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.10 (s, 6H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, CDCl3) δ 164.1, 146.1, 144.6, 140.6, 137.4, 125.7, 123.7, 123.3, 120.6, 117.6, 103.5, 99.9, 95.3, 58.3, 39.1, 13.8. GC-MS (EI) *m/z*: 353. Anal. Calcd for $C_{19}H_{19}N_3O_4$: C, 64.58%; H, 5.42%; N, 11.89%. Found: C, 64.32%; H, 5.79%; N, 11.57%.



Chemical Formula: $C_{17}H_{12}N_2O_2$
Mass: 276

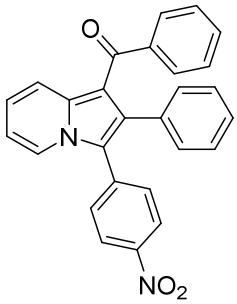
Methyl 4-(1-cyanoindolizin-3-yl)benzoate **7g**[14], grey solid, mp: 186-188 ^{o}C, yield 43%, 59.3 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.1 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.16 – 7.11 (m, 2H), 6.81 (t, *J* = 6.9 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 138.0, 133.7, 129.6, 128.9, 127.12, 124.9, 122.7, 121.9, 117.5, 116.3, 115.5, 112.6, 82.1, 51.4. GC-MS (EI) *m/z*: 276.



Chemical Formula: $C_{23}H_{18}N_2O_4$
Mass: 386
Elemental Analysis: C, 71.49; H, 4.70;
N, 7.25; O, 16.56

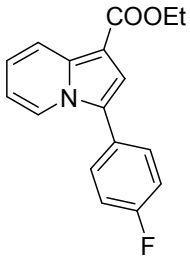
Ethyl 3-(4-nitrophenyl)-2-phenylindolizine-1-carboxylate **7h**, red solid, mp: 202-204 ^{o}C , yield 48%, 92.6 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 9.1 Hz, 1H), 8.17 (t, *J* = 7.6 Hz, 3H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.29 – 7.25 (m, 3H), 7.22 – 7.15 (m, 3H),

6.79 (t, *J* = 6.8 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 145.7, 136.2, 135.9, 133.3, 131.2, 130.0, 129.8, 126.6, 126.2, 123.1, 122.5, 121.7, 121.2, 119.7, 112.6, 102.9, 58.5, 13.1. GC-MS (EI) *m/z*: 386. Anal. Calcd for $C_{23}H_{18}N_2O_4$: C, 71.49%; H, 4.70%; N, 7.25%. Found: C, 71.30%; H, 4.90%; N, 7.11%.



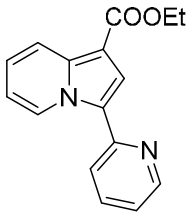
Chemical Formula: $C_{27}H_{18}N_2O_3$
Mass: 418

(3-(4-Nitrophenyl)-2-phenylindolizin-1-yl)(phenyl)methanone **7i**[15], red solid, mp: 239-241 °C, yield 67%, 140.0 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.7 Hz, 2H), 8.18 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.20 – 7.14 (m, 1H), 7.09 (t, *J* = 7.7 Hz, 2H), 6.97 (q, *J* = 8.4 Hz, 3H), 6.92 (d, *J* = 7.4 Hz, 2H), 6.83 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.3, 146.0, 139.0, 136.3 (2C), 132.4, 130.5 (2C), 130.1 (2C), 128.4, 126.8, 126.5, 125.9, 123.2, 122.9, 121.5, 120.5, 119.5, 113.0, 112.0. GC-MS (EI) *m/z*: 418.



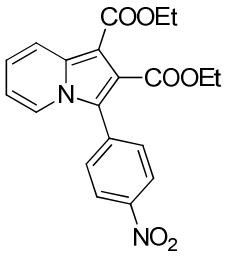
Chemical Formula: $C_{17}H_{14}FNO_2$
Mass: 283

Ethyl 3-(4-fluorophenyl)indolizine-1-carboxylate **7j**[16], pale yellow solid, mp: 113-115 °C, yield 64%, 90.6 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.0 Hz, 1H), 8.08 (d, *J* = 7.0 Hz, 1H), 7.41 – 7.39 (m, 2H), 7.18 (s, 1H), 7.09 (t, *J* = 7.5 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.61 (t, *J* = 7.0 Hz, 1H), 4.30 (q, *J* = 7.0 Hz, 2H), 1.33 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 164.7, 162.7, 137.5, 131.8, 128.6, 126.5, 124.4, 123.5, 121.5, 117.4, 114.0, 105.5, 60.9, 16.0. GC-MS (EI) *m/z*: 283.



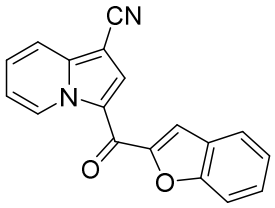
Chemical Formula: $C_{16}H_{14}N_2O_2$
Mass: 266

Ethyl 3-(pyridin-2-yl)indolizine-1-carboxylate **7k**[11], yellow solid, mp: 144-146 ^oC, yield 67%, 89.1 mg. ^1H NMR (500 MHz, $CDCl_3$) δ 9.99 (d, J = 7.0 Hz, 1H), 8.55 (d, J = 5.0 Hz, 1H), 8.21 (d, J = 10.0 Hz, 1H), 7.69 (s, 1H), 7.65-7.63 (m, 2H), 7.12 – 7.05 (m, 2H), 6.78 (t, J = 7.5 Hz, 1H), 4.33 (q, J = 7.0 Hz, 2H), 1.36 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 151.0, 147.5, 137.1, 135.8, 127.1, 122.9 (2C), 120.4, 119.9, 118.7, 117.1, 112.3, 103.9, 58.9, 13.9. GC-MS (EI) *m/z*: 266.



Chemical Formula: $C_{20}H_{18}N_2O_6$
Mass: 382

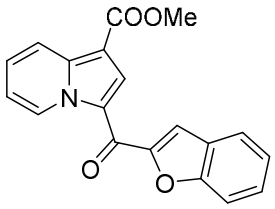
Diethyl 3-(4-nitrophenyl)indolizine-1,2-dicarboxylate **7l**[17], yellow solid, mp: 167-169 ^oC, yield 72%, 137.5 mg. ^1H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 8.8 Hz, 2H), 8.29 (d, J = 9.1 Hz, 1H), 8.09 (d, J = 7.1 Hz, 1H), 7.74 (d, J = 8.8 Hz, 2H), 7.24 – 7.14 (m, 1H), 6.82 (t, J = 7.4 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 162.5, 146.6, 135.0, 134.8, 129.5, 123.4, 123.2, 122.8, 122.0, 121.0, 119.8, 113.4, 102.2, 60.8, 59.2, 13.5, 13.1. GC-MS (EI) *m/z*: 382.



Chemical Formula: $C_{18}H_{10}N_2O_2$
Mass: 286

3-(Benzofuran-2-carbonyl)indolizine-1-carbonitrile **8a**[18], pale green solid, mp: 173-175 ^oC. (lit. 175-177 ^oC), yield 39%, 55.8 mg. ^1H NMR (500 MHz, $CDCl_3$) δ 10.09 (d, J = 7.1 Hz, 1H), 8.58 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 7.8 Hz,

1H), 7.71 (s, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.52 (t, J = 7.2 Hz, 2H), 7.36 (t, J = 7.9 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 154.8, 152.4, 140.3, 128.8, 128.0, 127.3, 127.0, 126.0, 123.1, 122.1, 121.2, 116.7, 115.2, 114.2, 113.0, 111.4, 84.9. GC-MS (EI) *m/z*: 286.



Chemical Formula: $C_{19}H_{13}NO_4$
Mass: 319

Methyl 3-(benzofuran-2-carbonyl)indolizine-1-carboxylate **8b**[18], light green solid, mp: 166-168 °C. (lit. 168-170 °C), yield 92%, 146.7 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.07 (d, J = 7.0 Hz, 1H), 8.65 (s, 1H), 8.42 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.66 (s, 1H), 7.53 – 7.43 (m, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 6.9 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 163.5, 154.7, 152.7, 139.1, 128.5, 127.2 (2C), 126.6, 126.2, 122.9, 121.9, 120.9, 118.6, 114.6, 112.4, 111.4, 105.8, 50.4. GC-MS (EI) *m/z*: 319.

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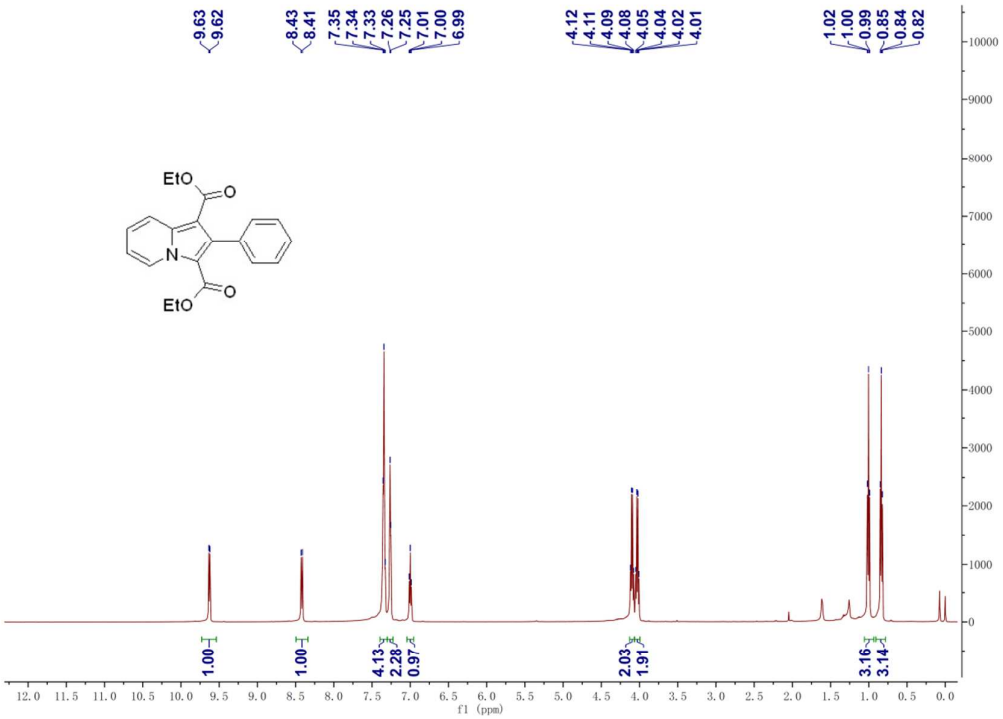
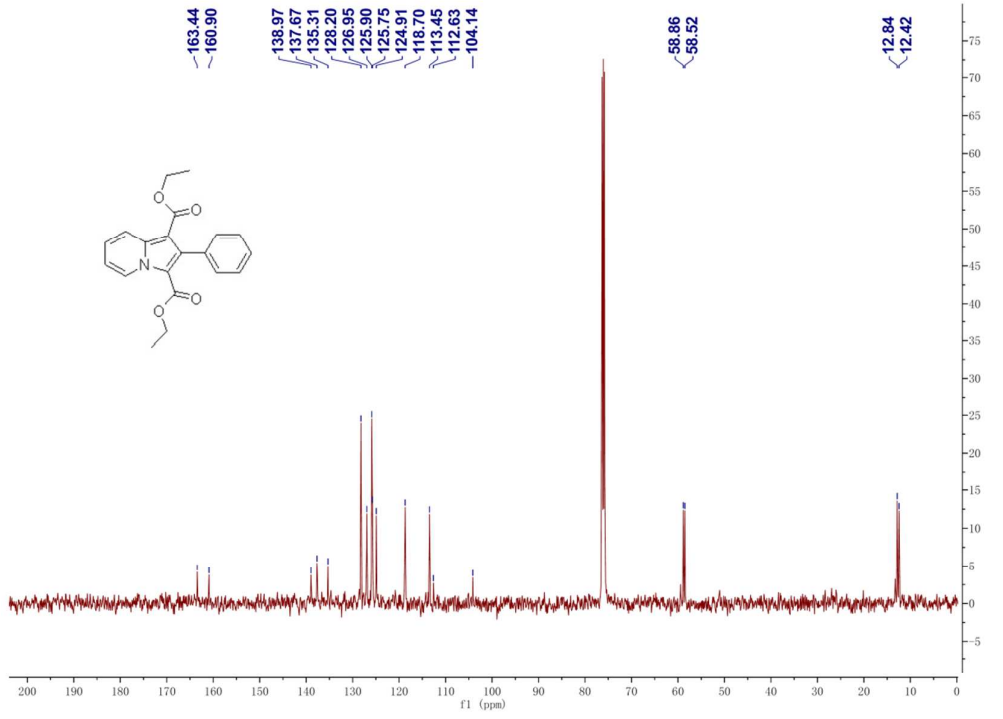
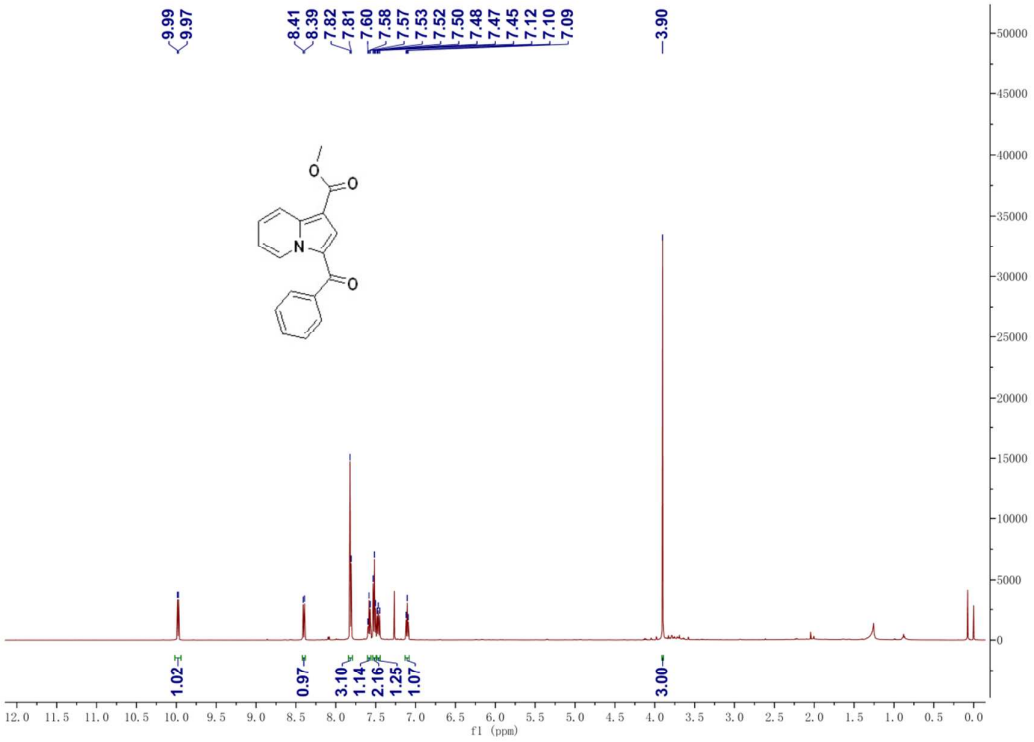
3 NMR Spectra of All Products



^{1}H NMR of **4a and 6q**



^{13}C NMR of **4a and 6q**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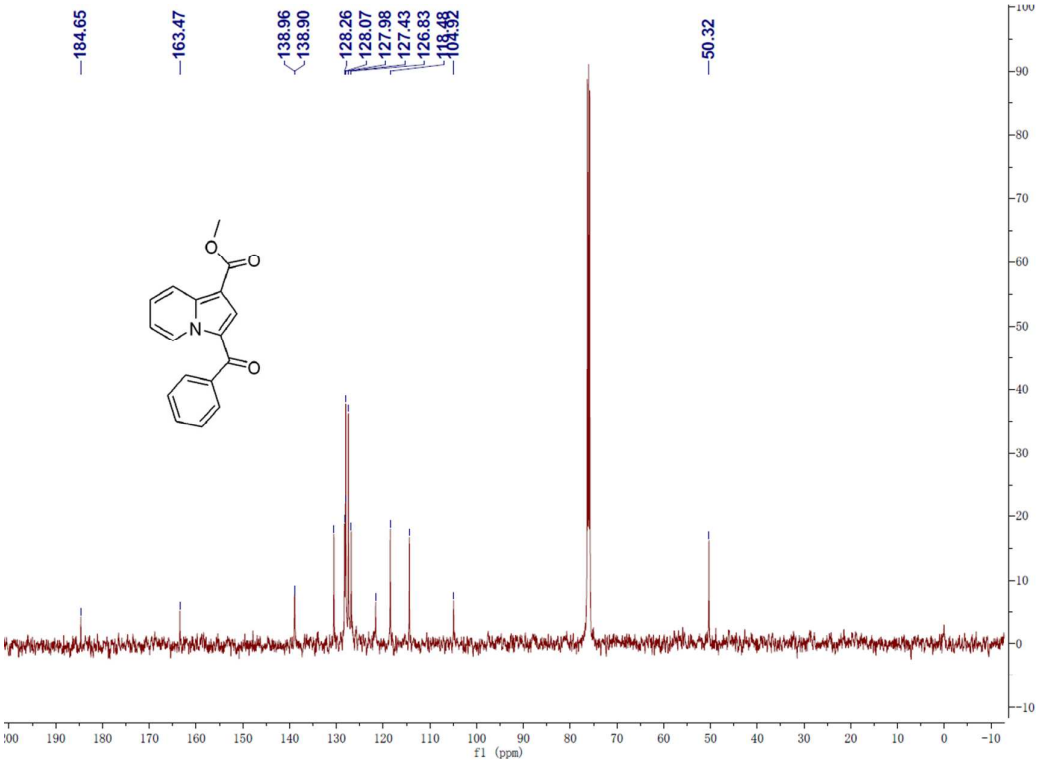
9.97
8.41
8.39
7.82
7.81
7.60
7.58
7.57
7.53
7.52
7.50
7.48
7.47
7.45
7.12
7.10
7.09
3.90
1.02
0.97
3.10
1.14
2.16
1.25
1.07
3.00
f1 (ppm)

^{1}H NMR of **4b**


184.65
163.47
138.96
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128.26
128.07
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50.32
f1 (ppm)

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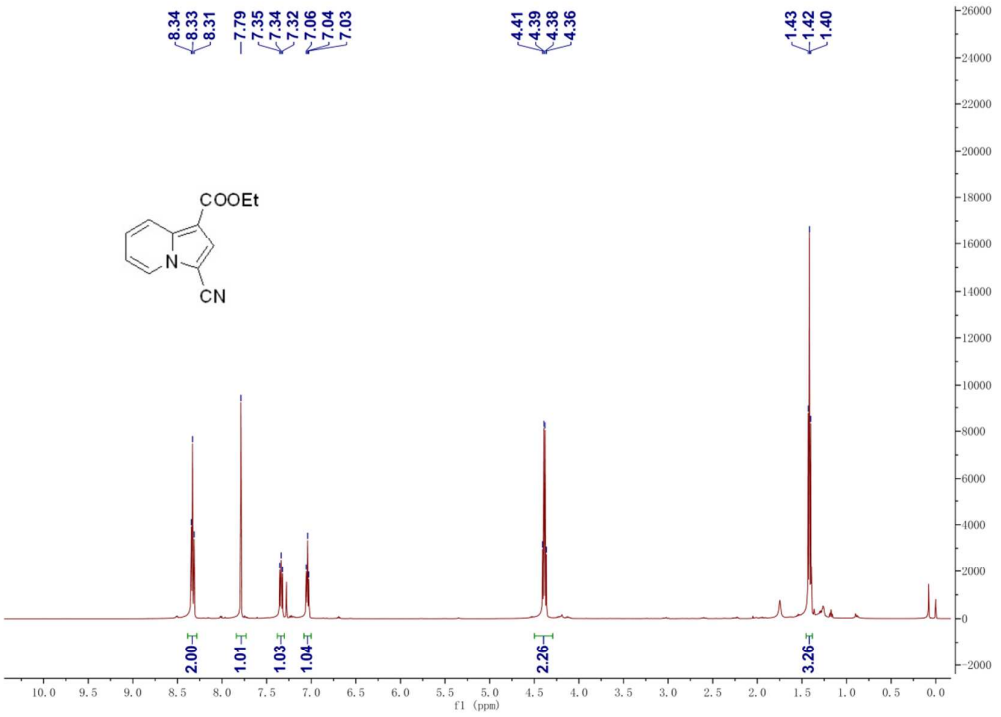

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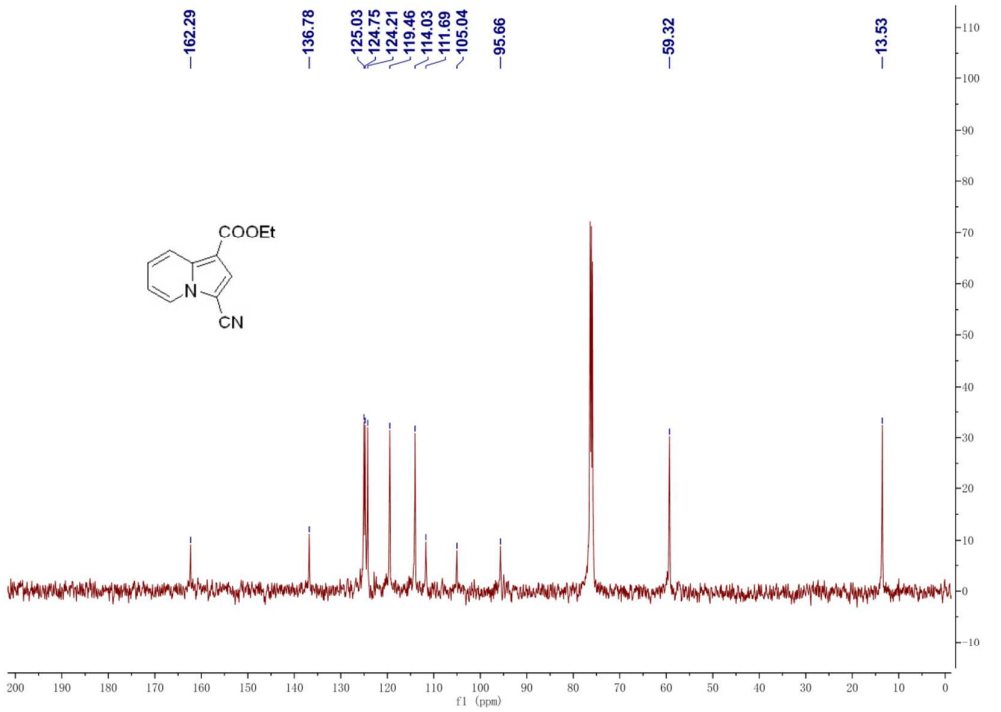

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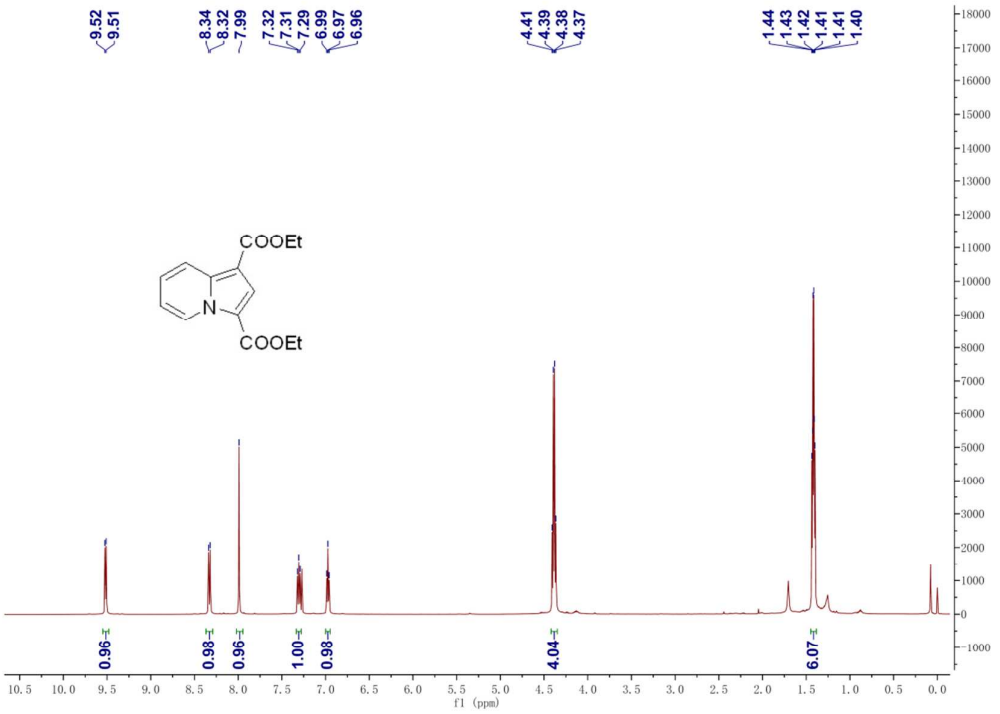

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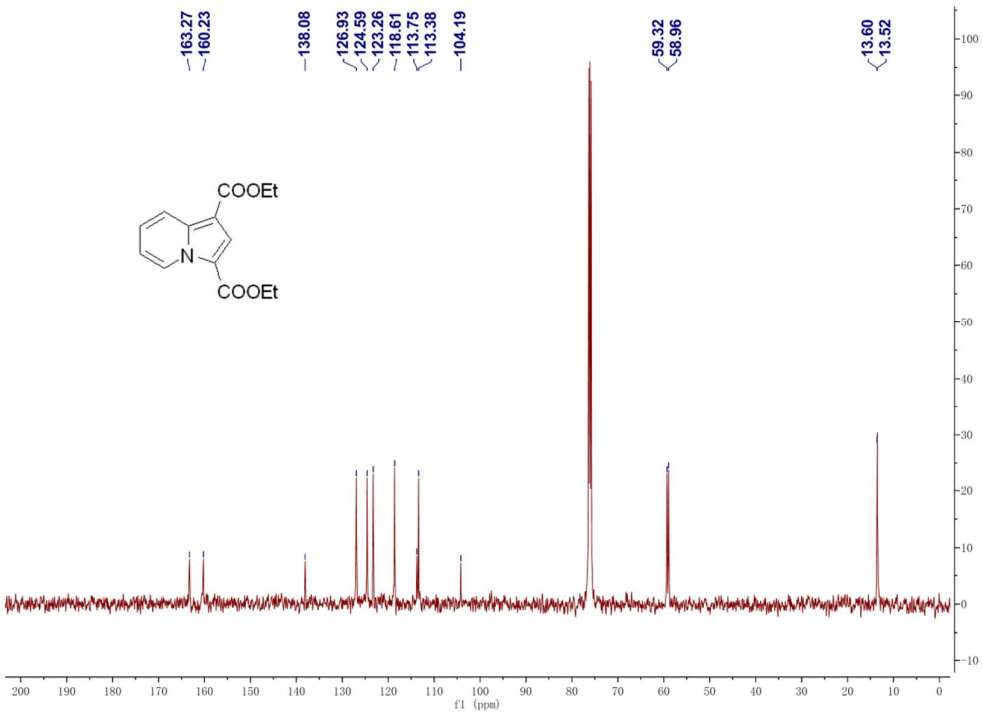

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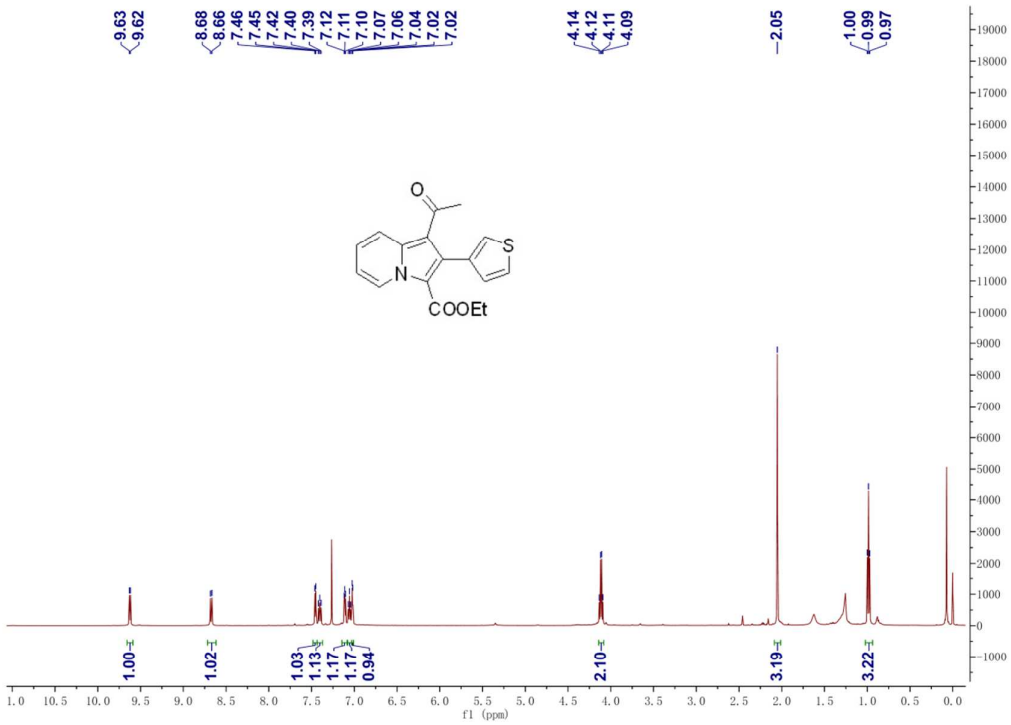

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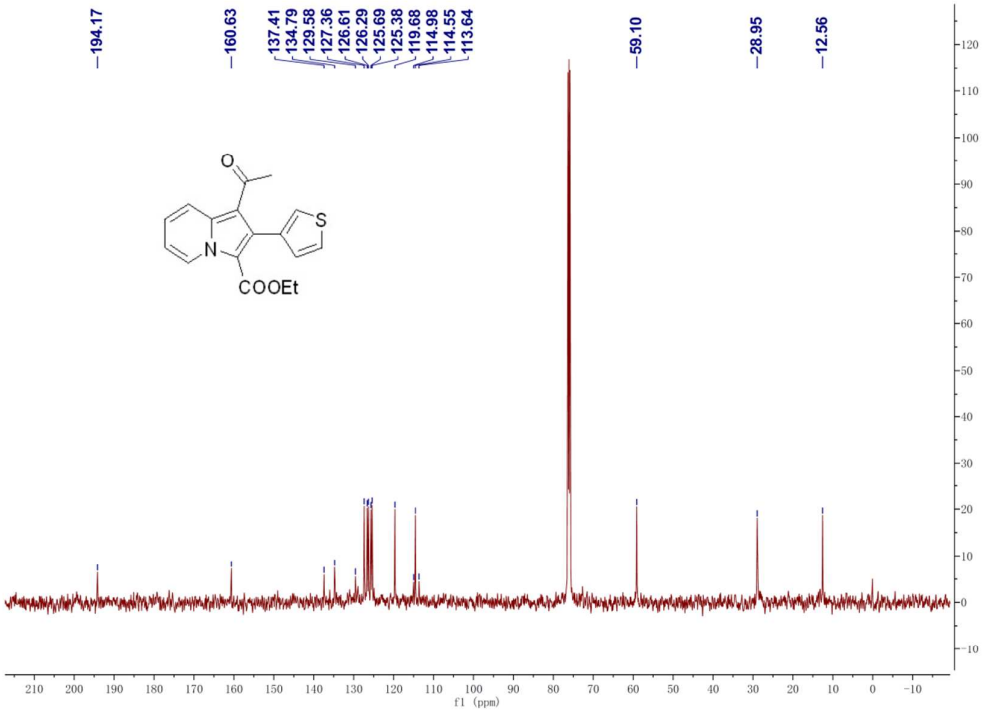

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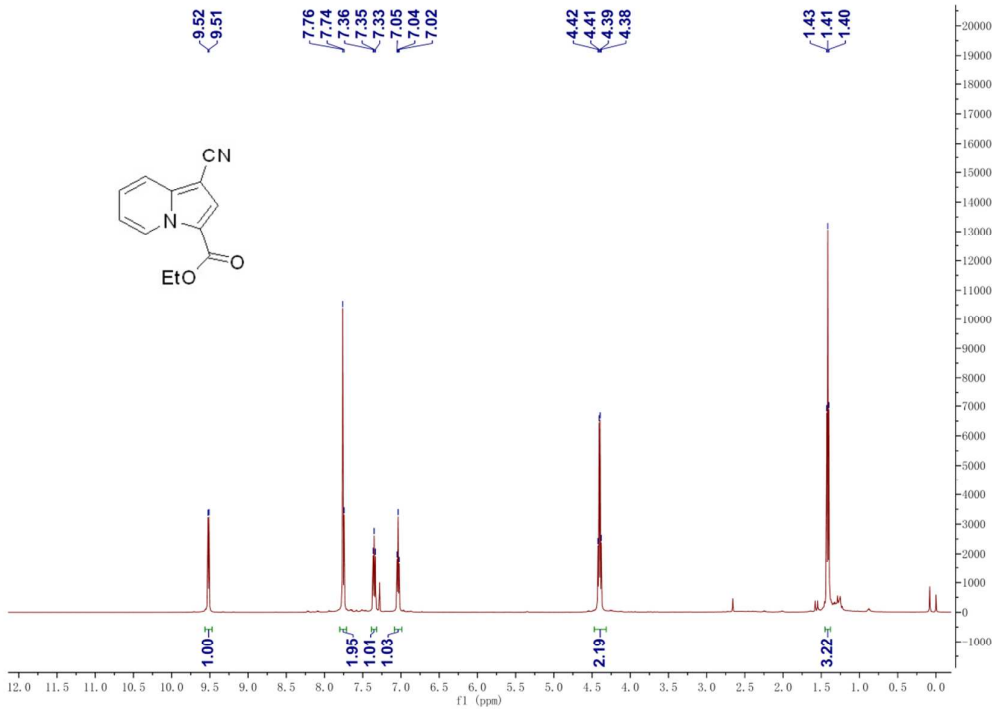

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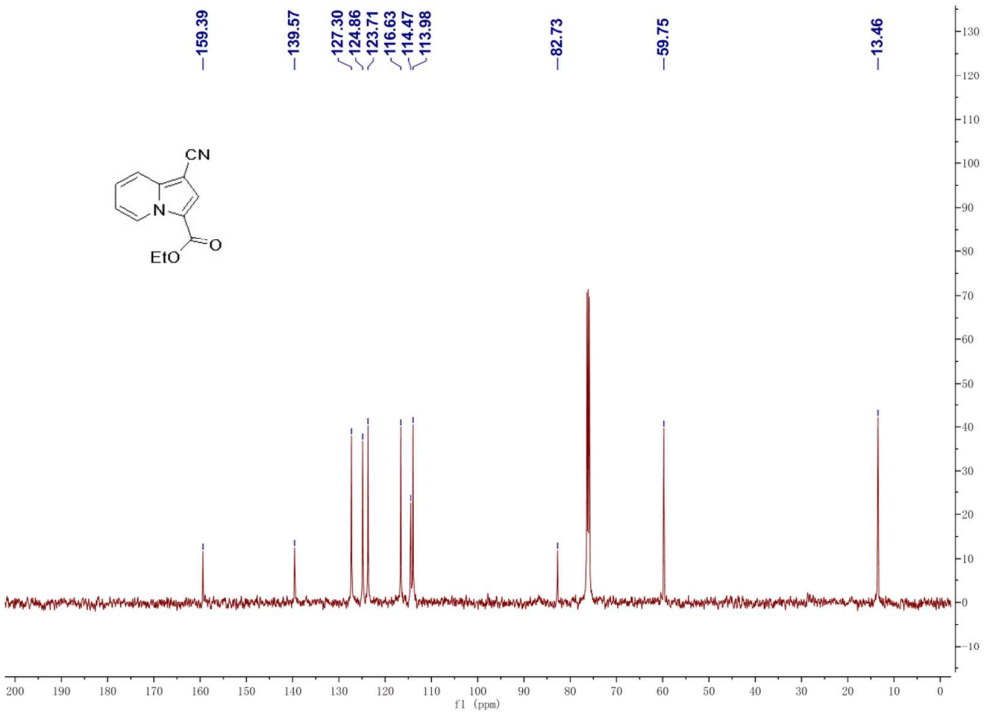

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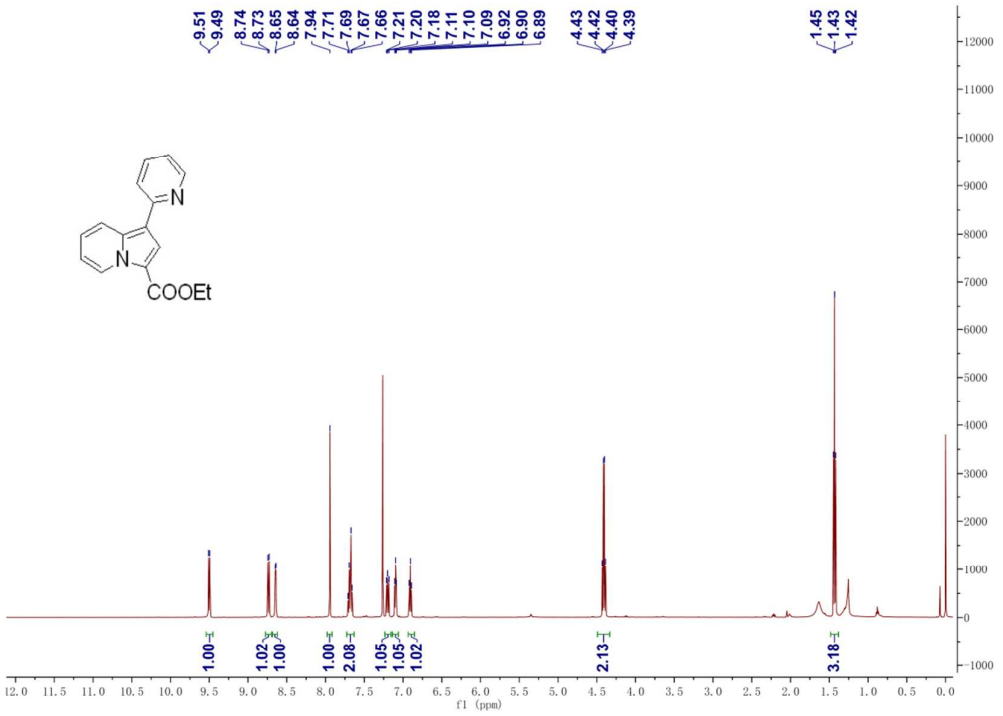

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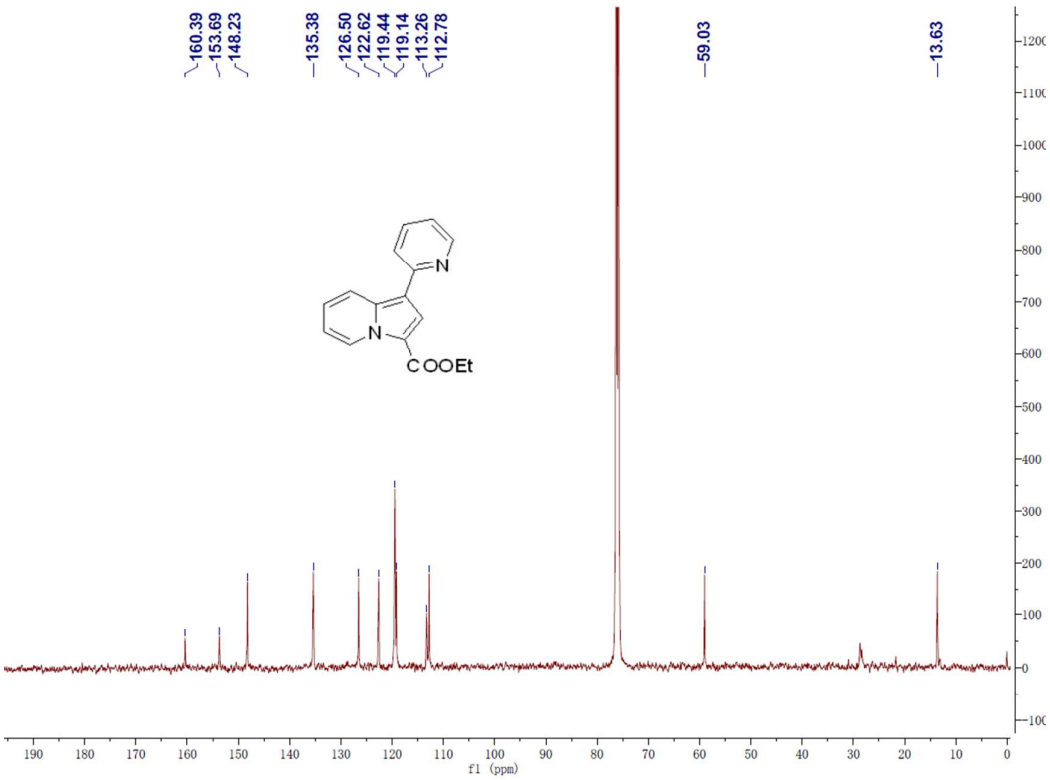

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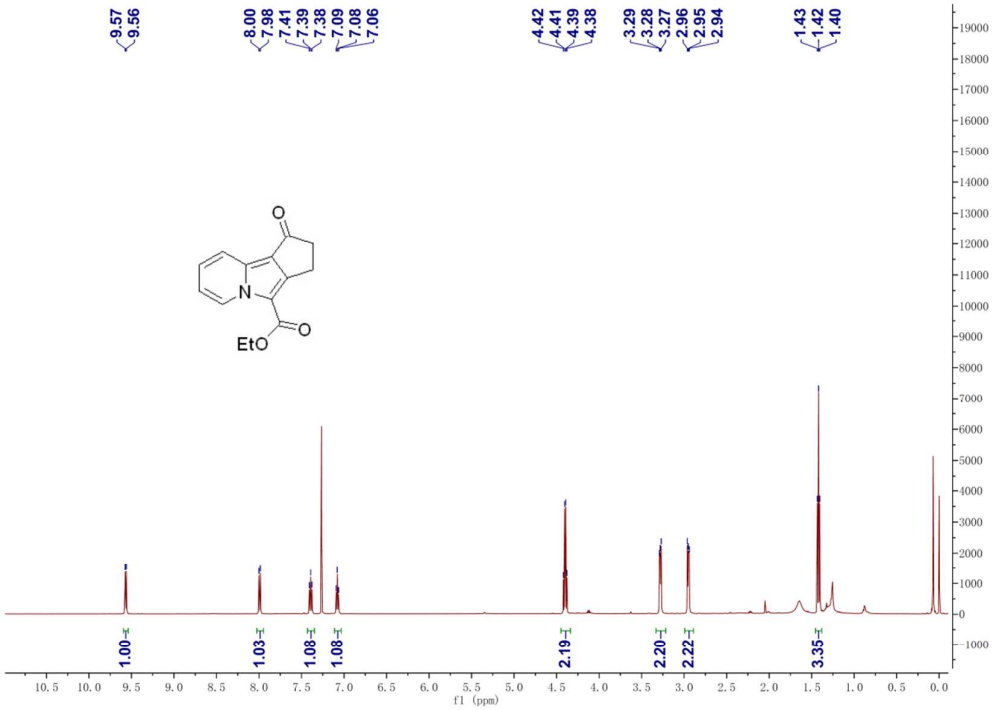

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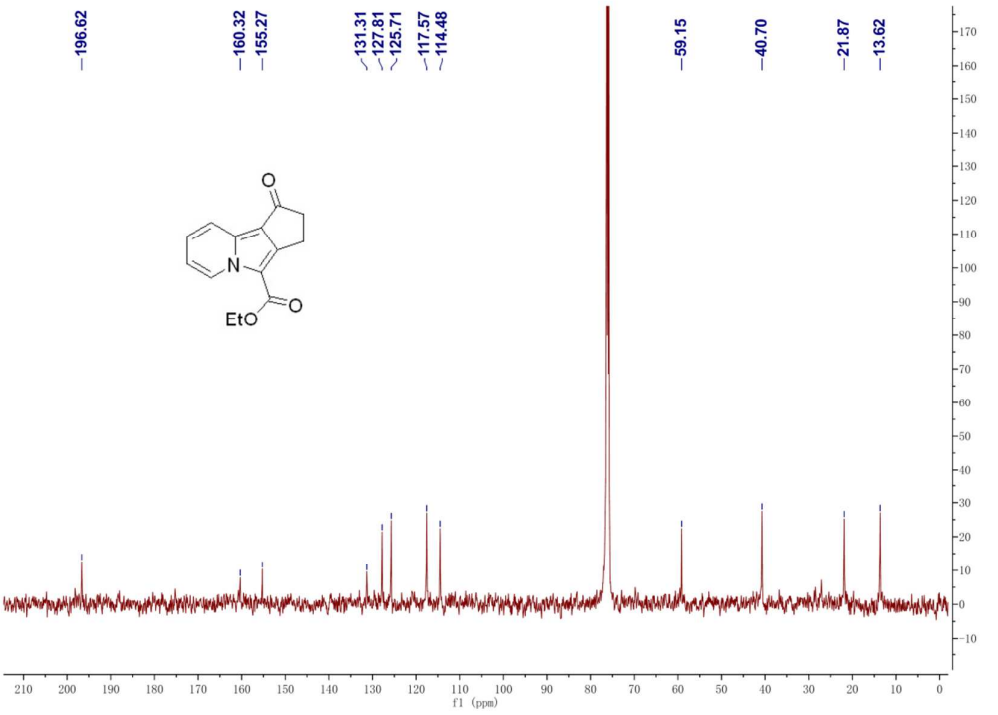

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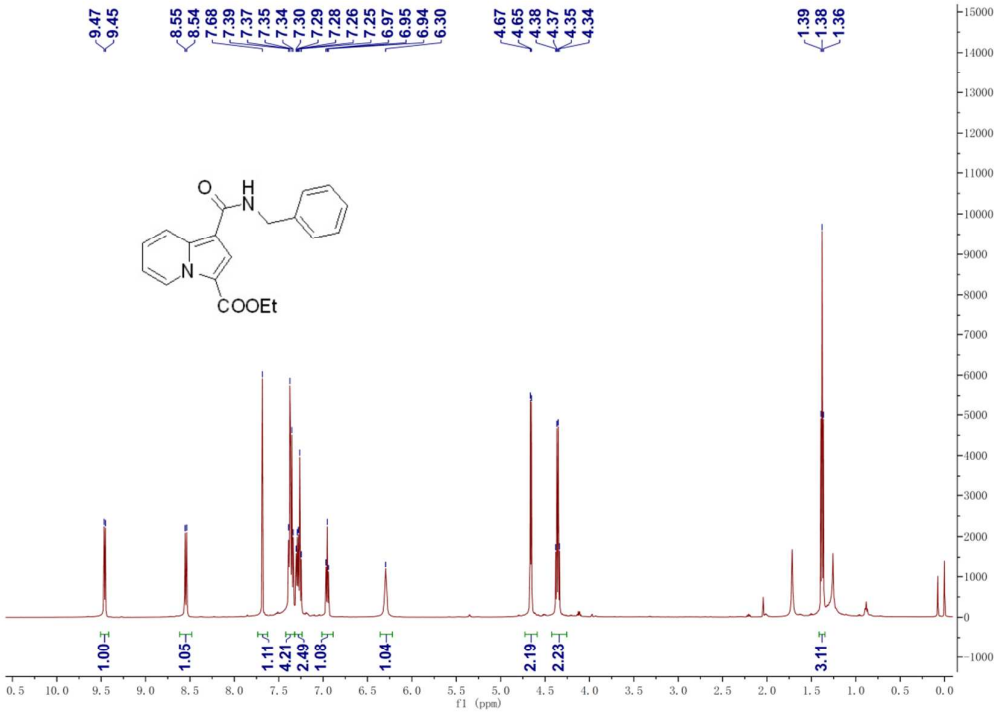

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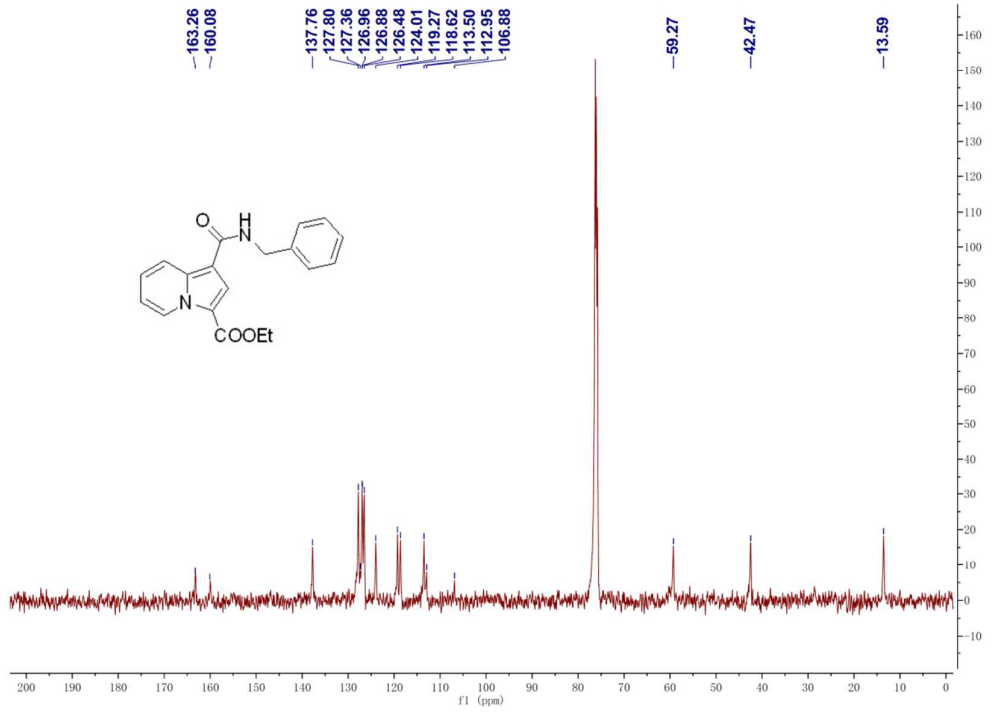

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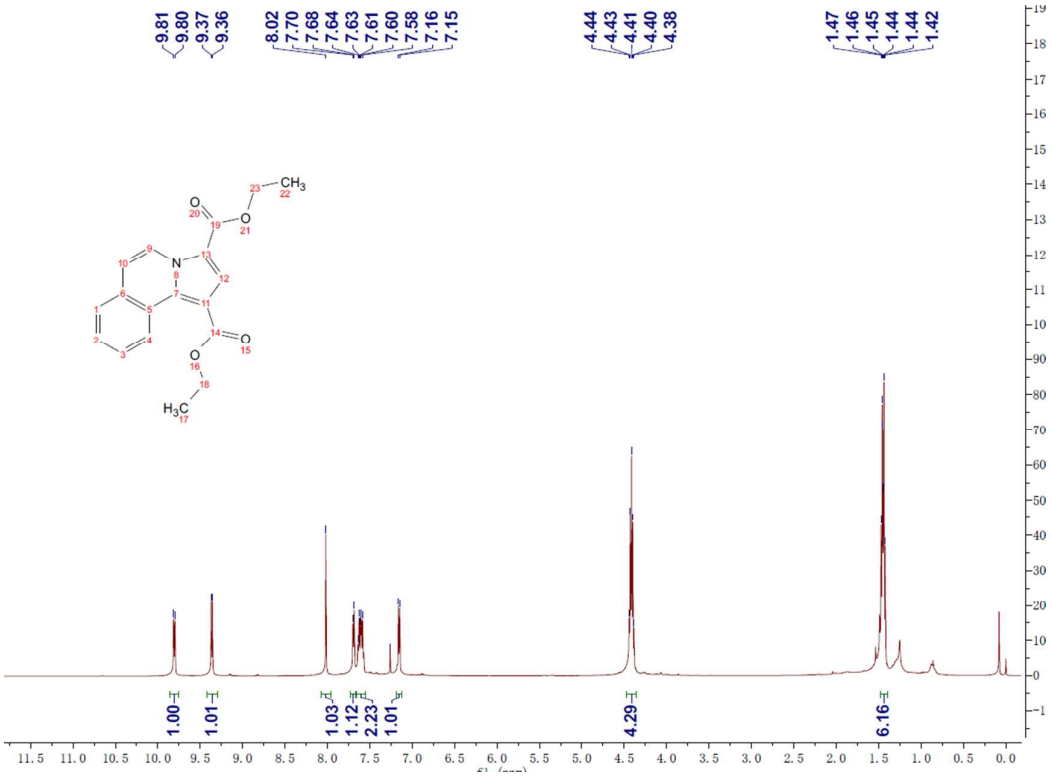
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8.02
7.70
7.68
7.64
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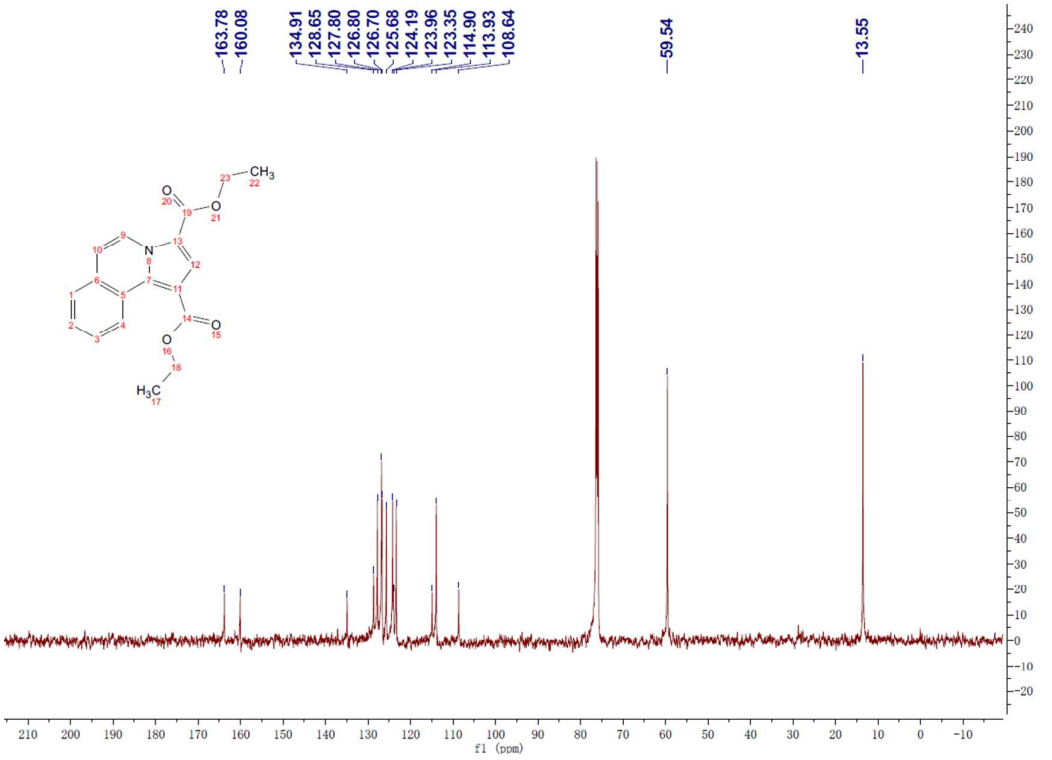
7.61
7.60
7.58
7.16
7.15
4.44
4.43
4.41
4.40
4.38
1.47
1.46
1.45
1.44
1.44
1.42
1.00
1.01
1.03
1.12
2.23
1.01
4.29
6.16

^{1}H NMR of **4j**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123.35
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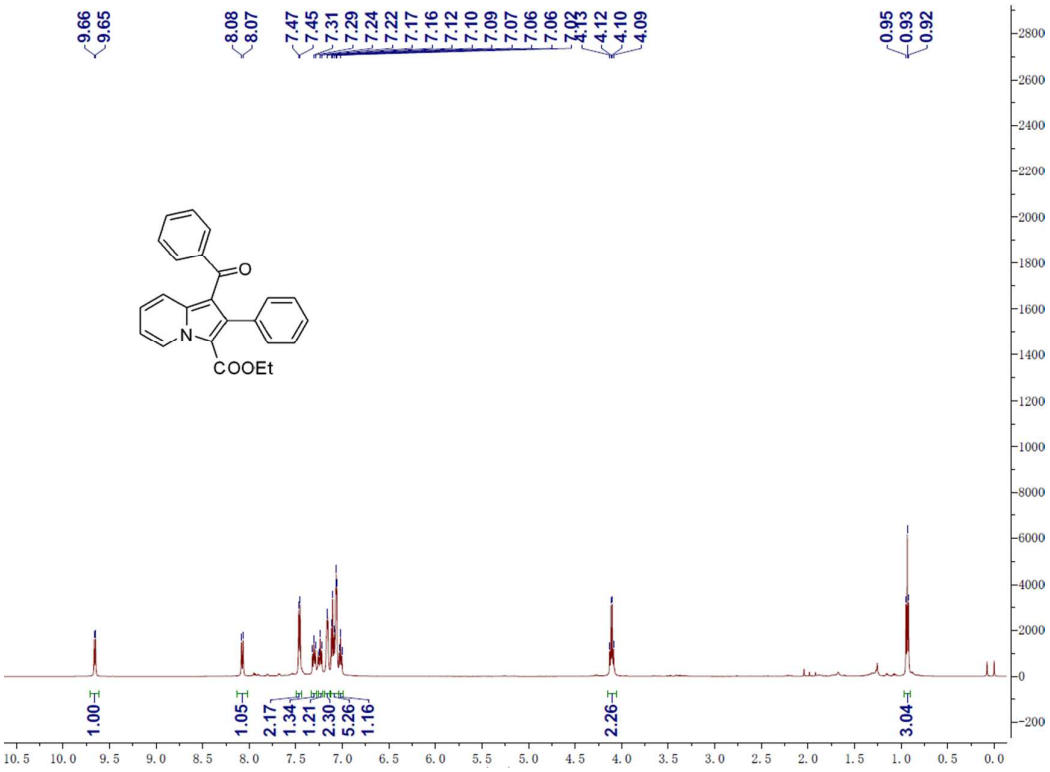
59.54
13.55
f1 (ppm)

^{13}C NMR of **4j**



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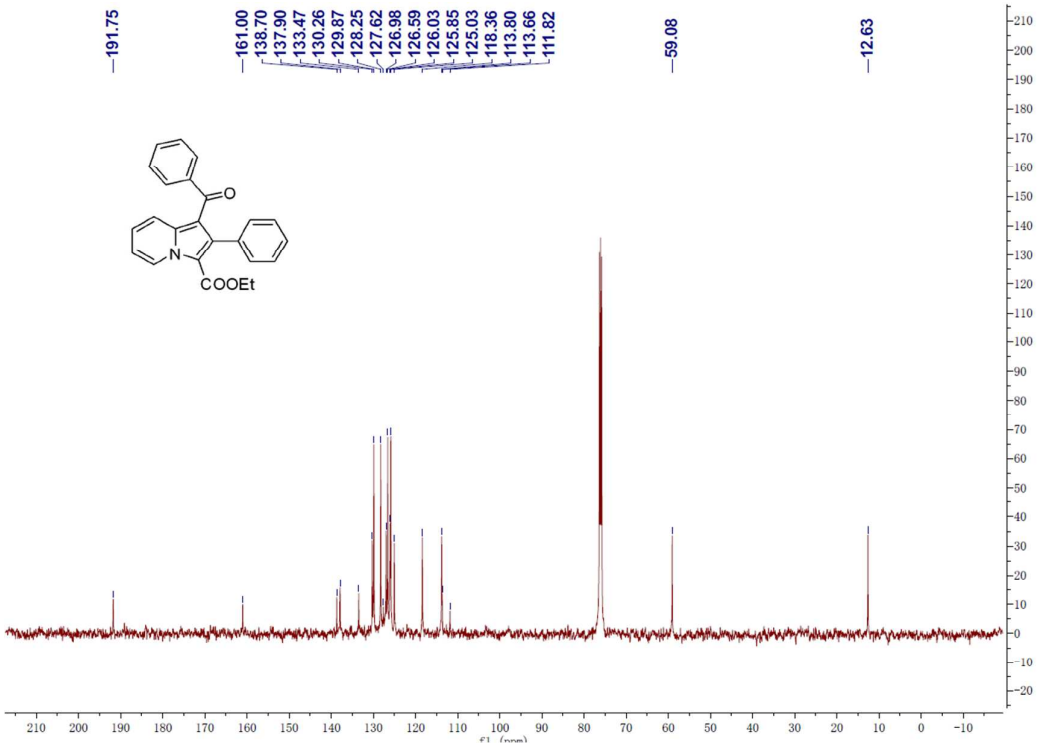

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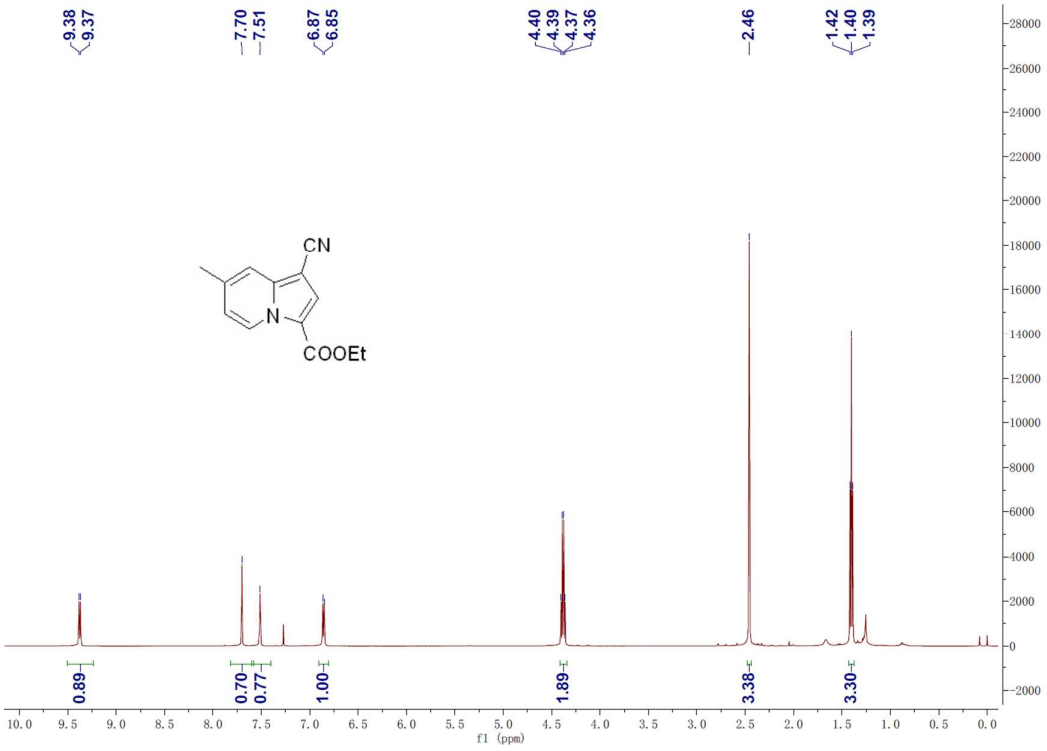

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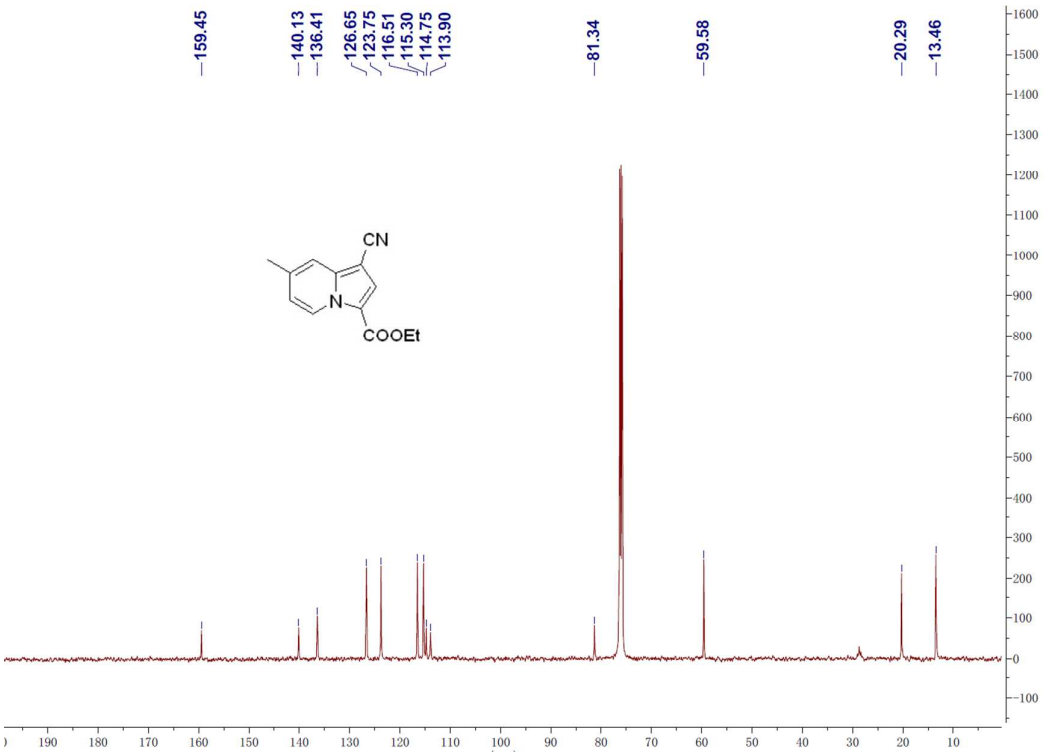
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126.65
123.75
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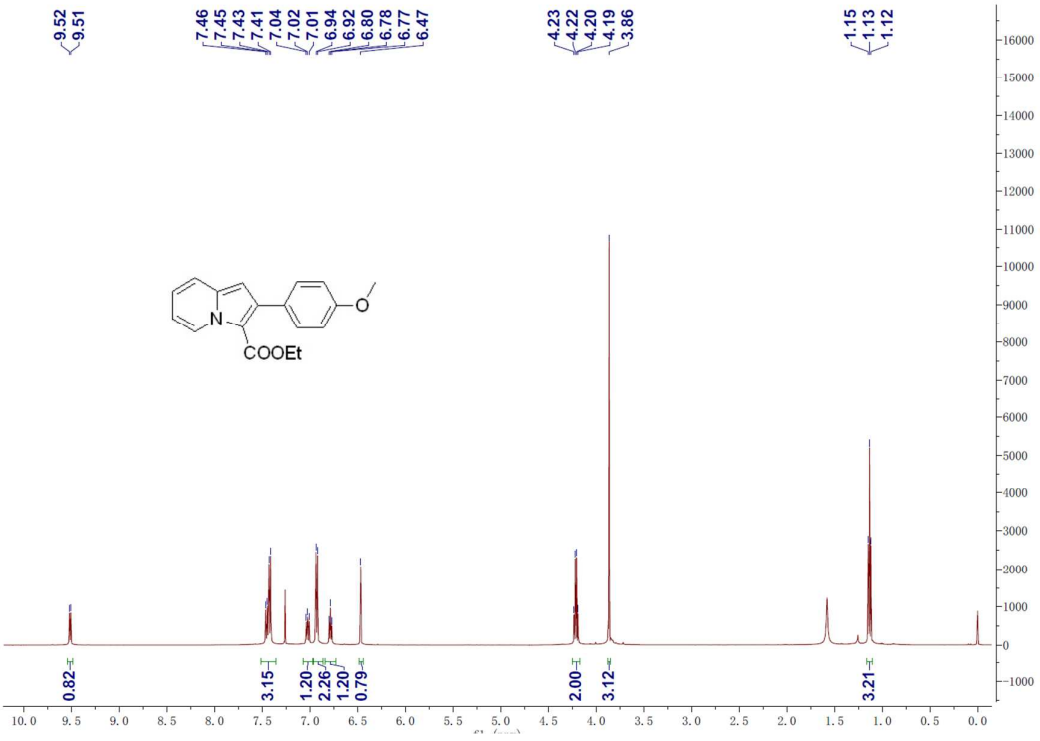
113.90
81.34
59.58
20.29
13.46
CN
N
COOEt

^{13}C NMR of **4l**



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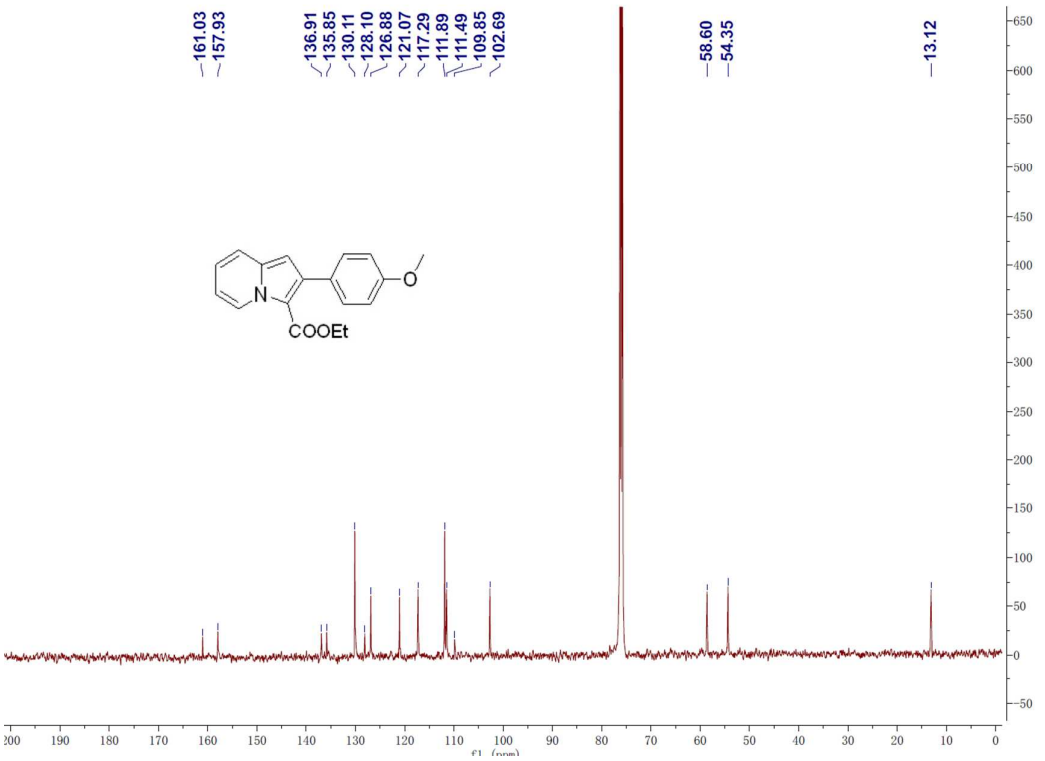

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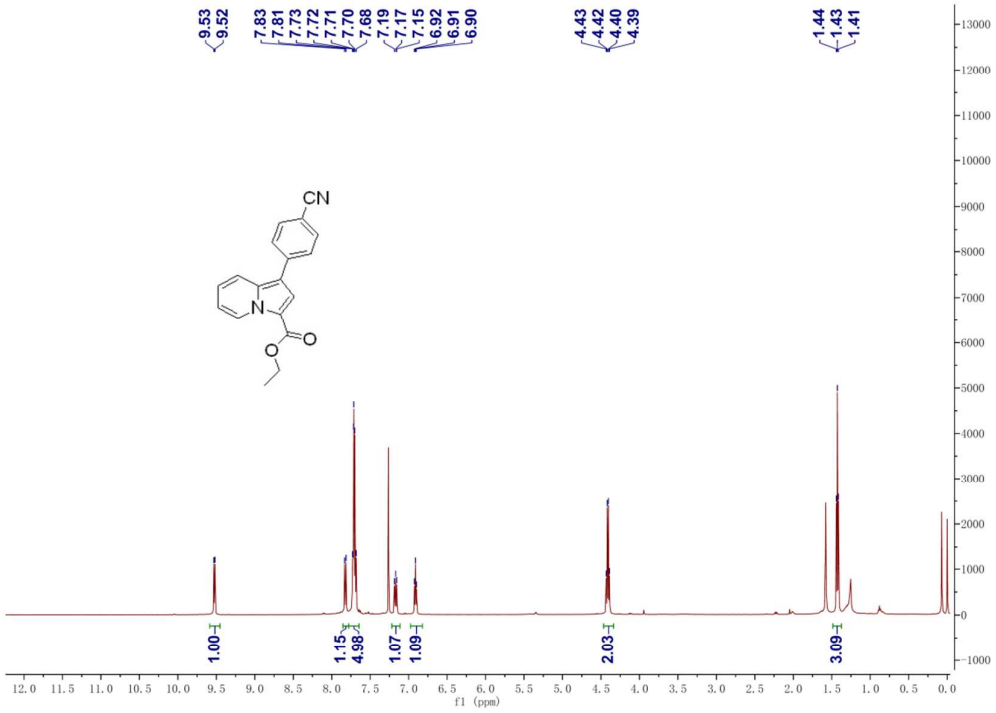

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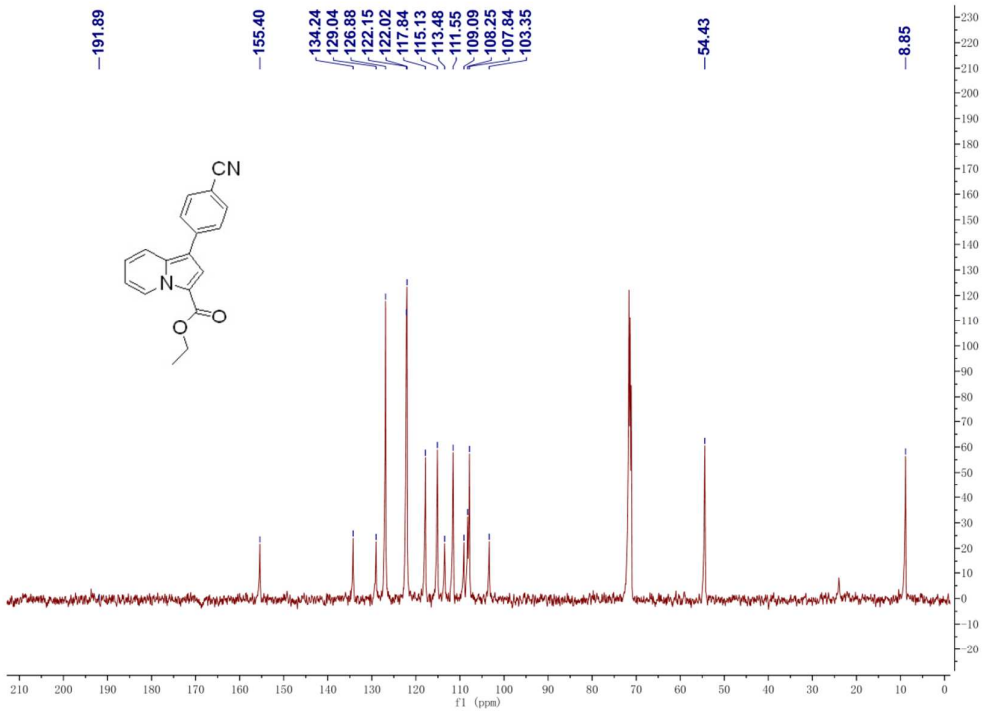

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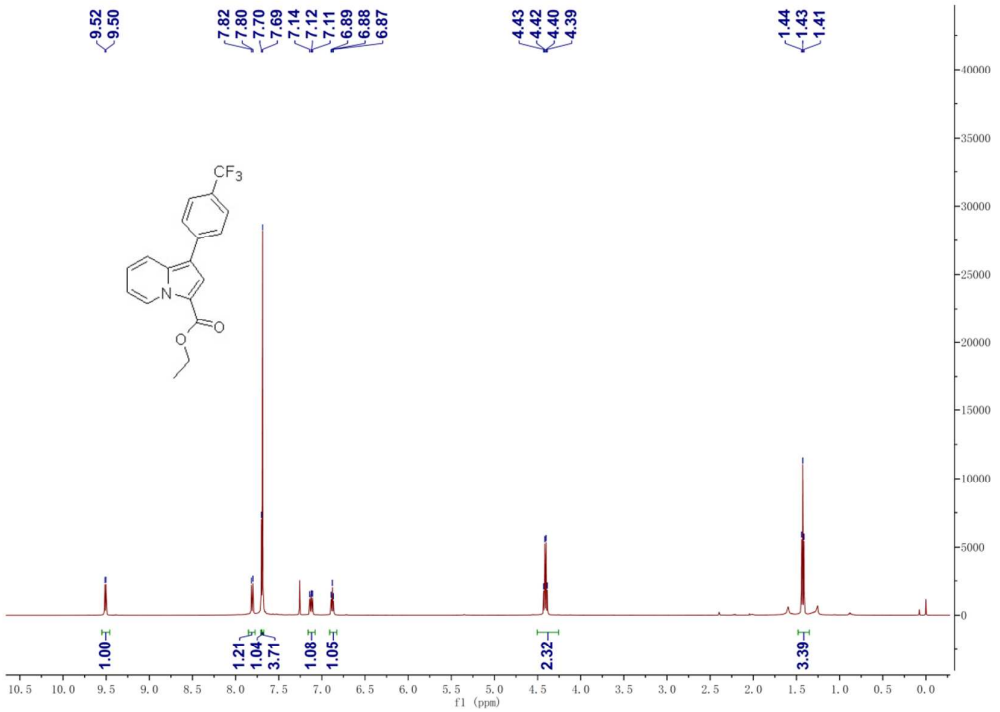

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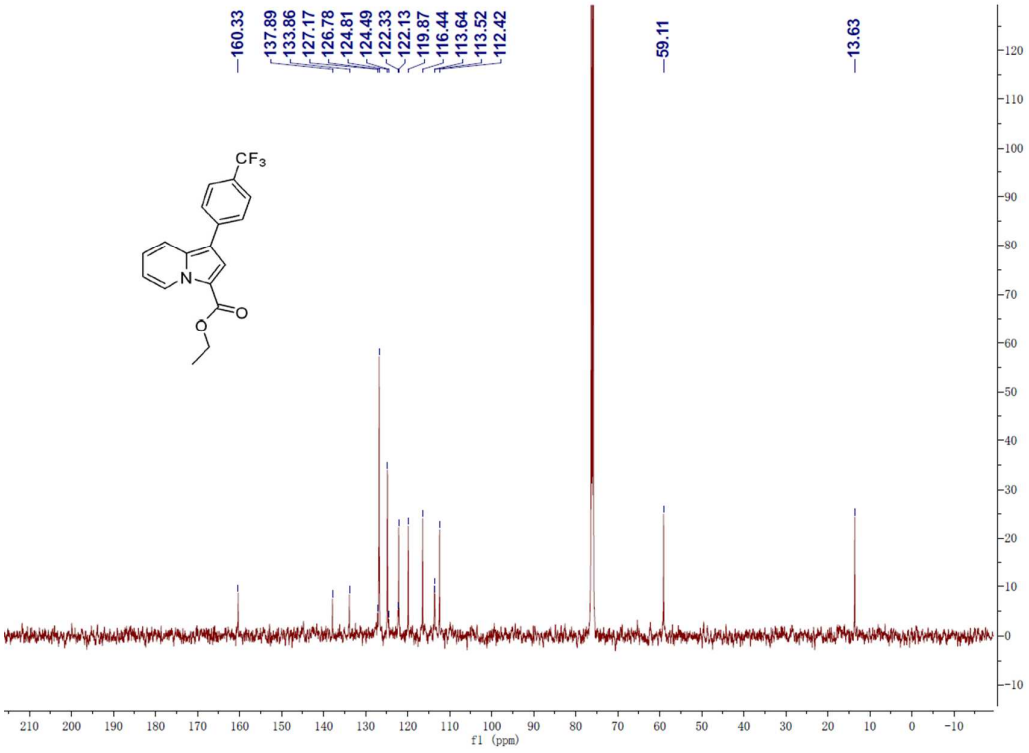

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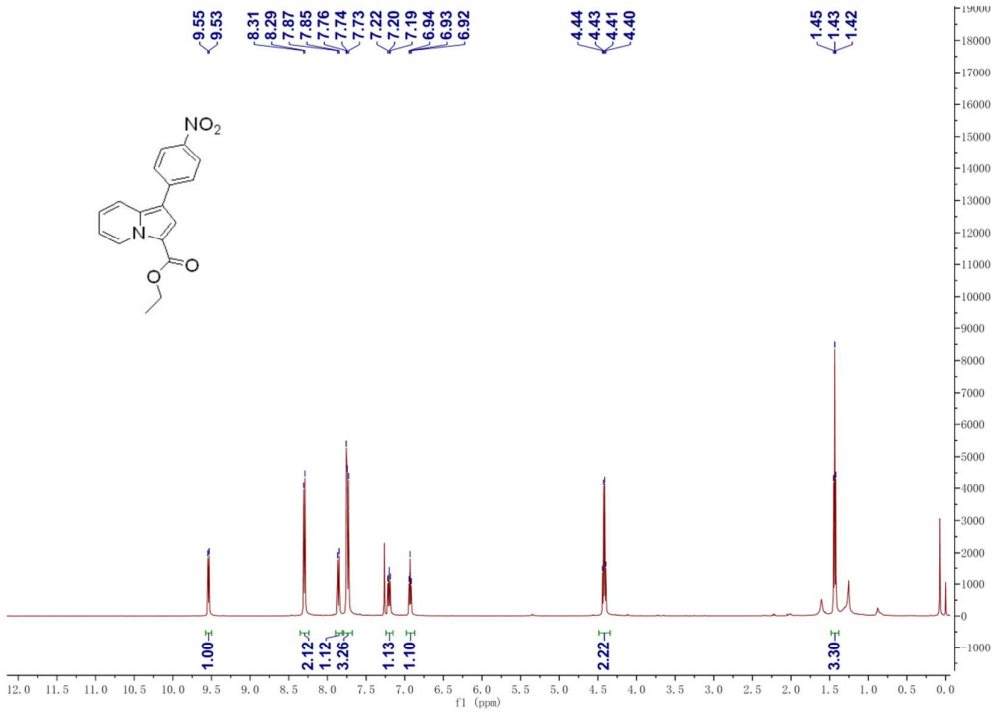

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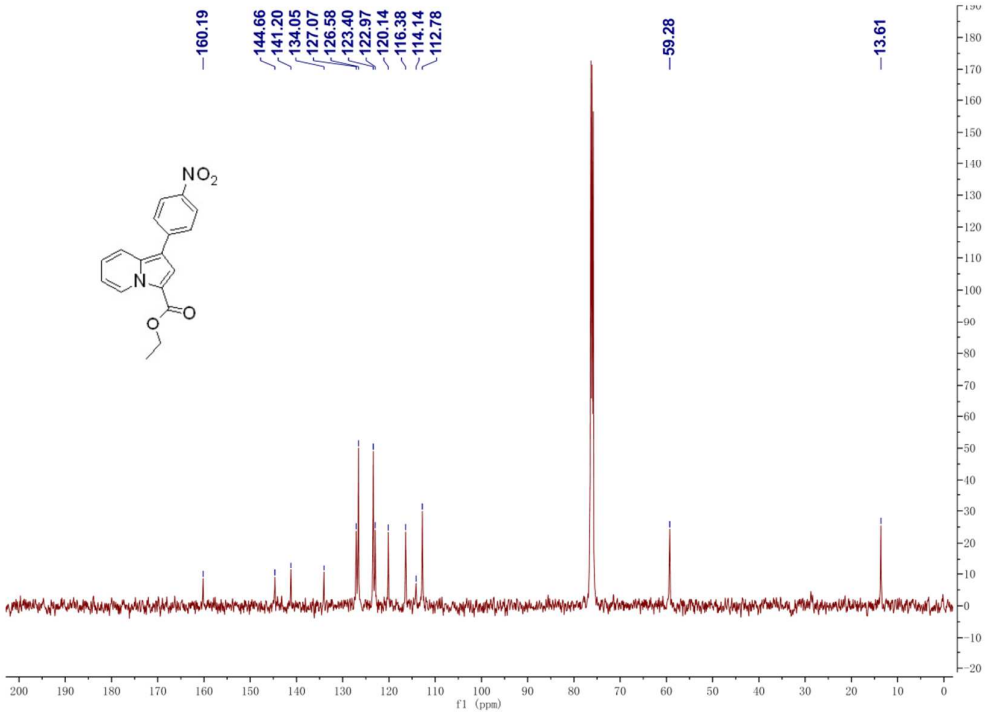

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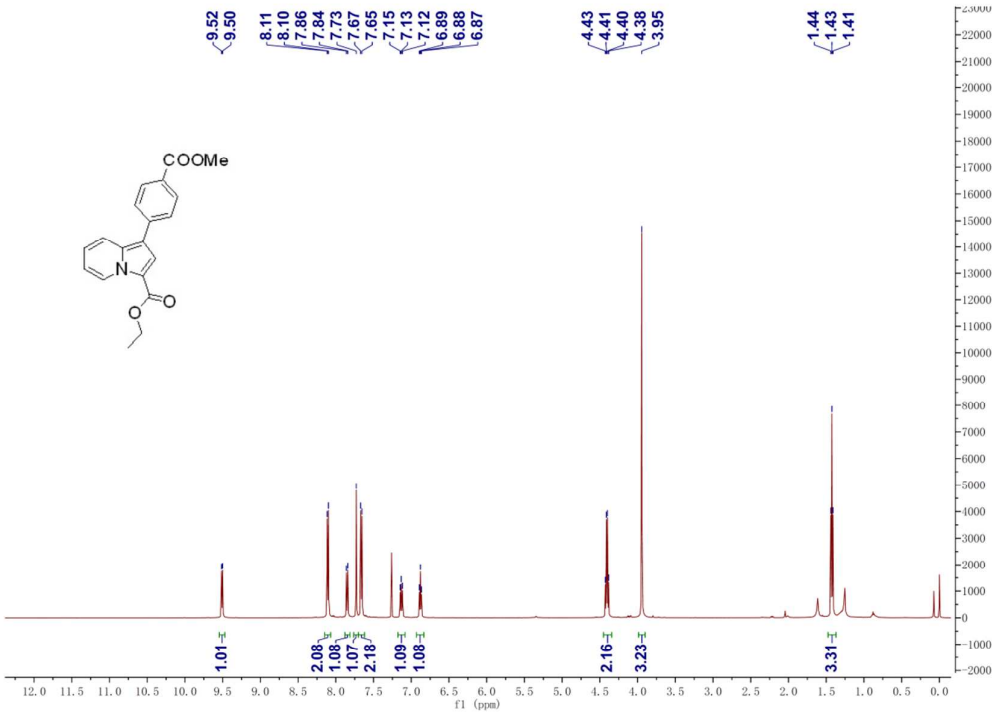

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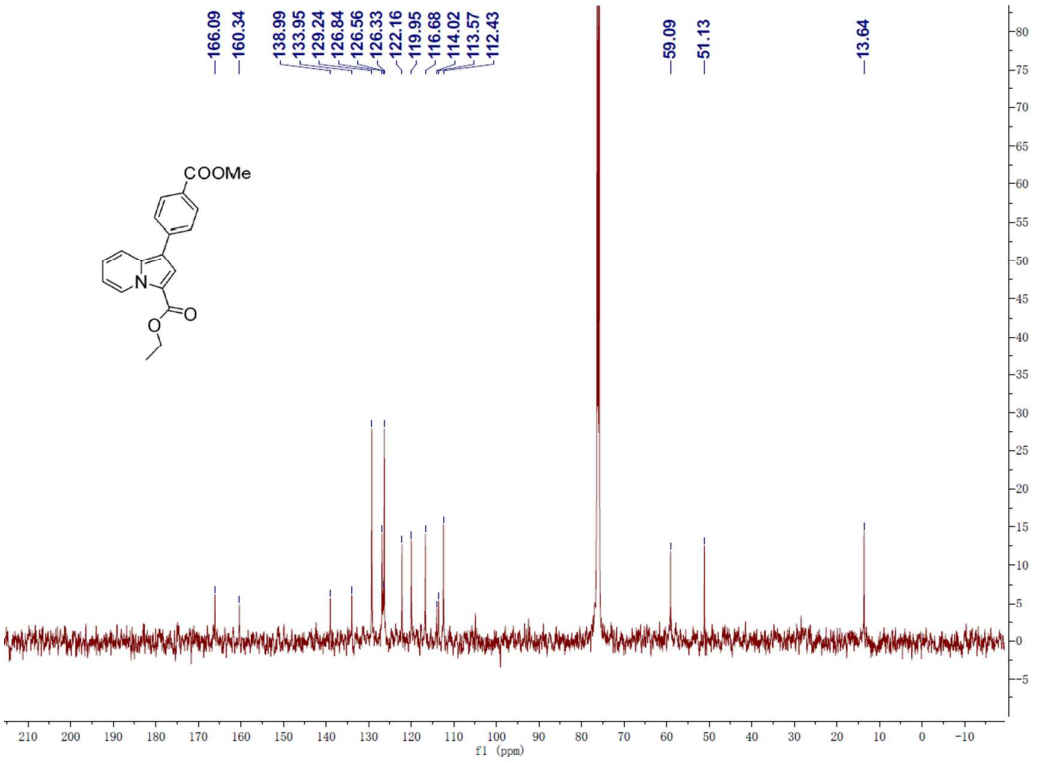

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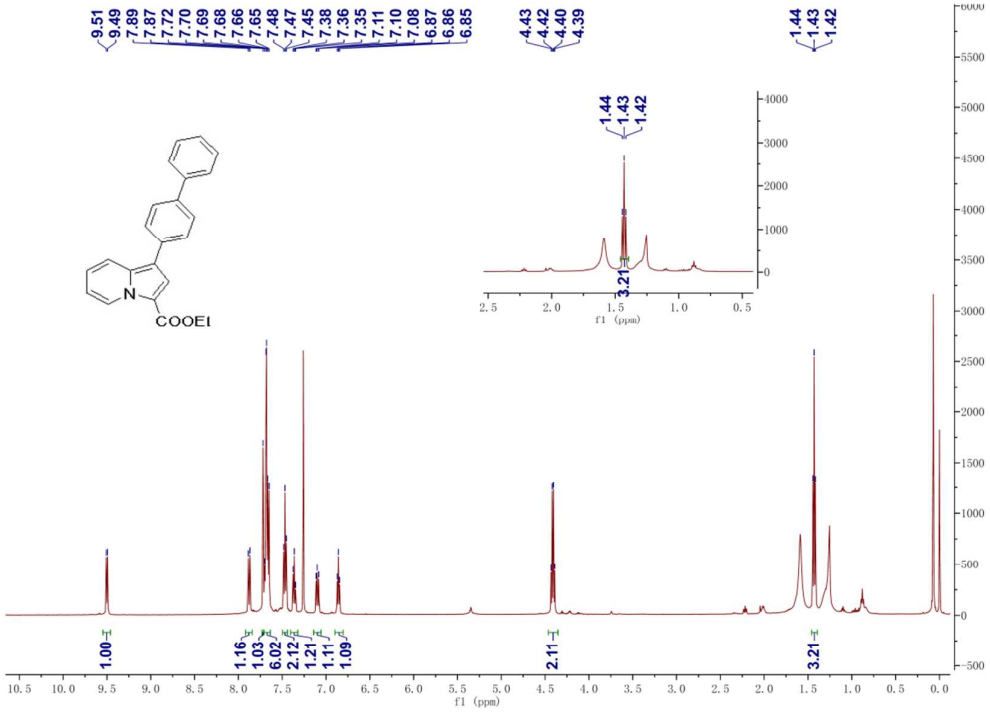

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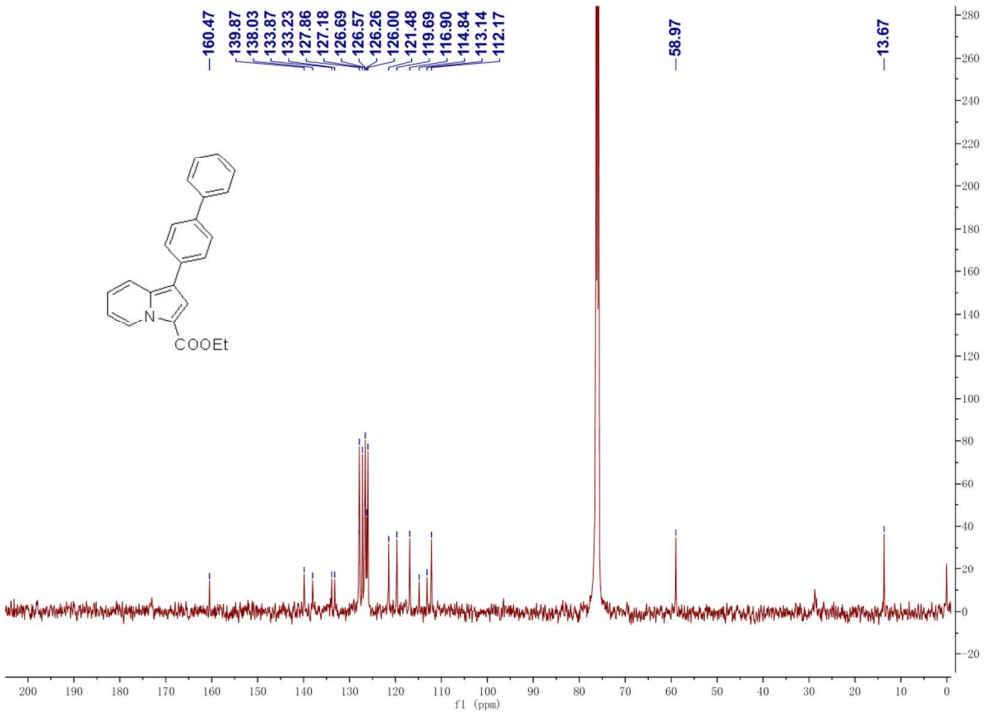

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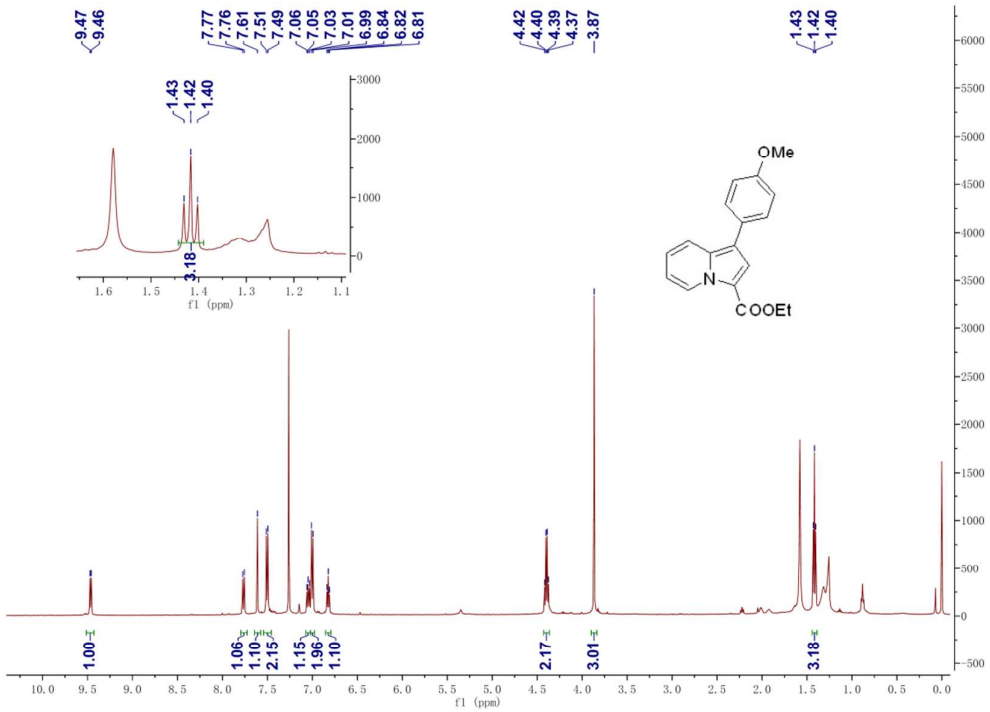

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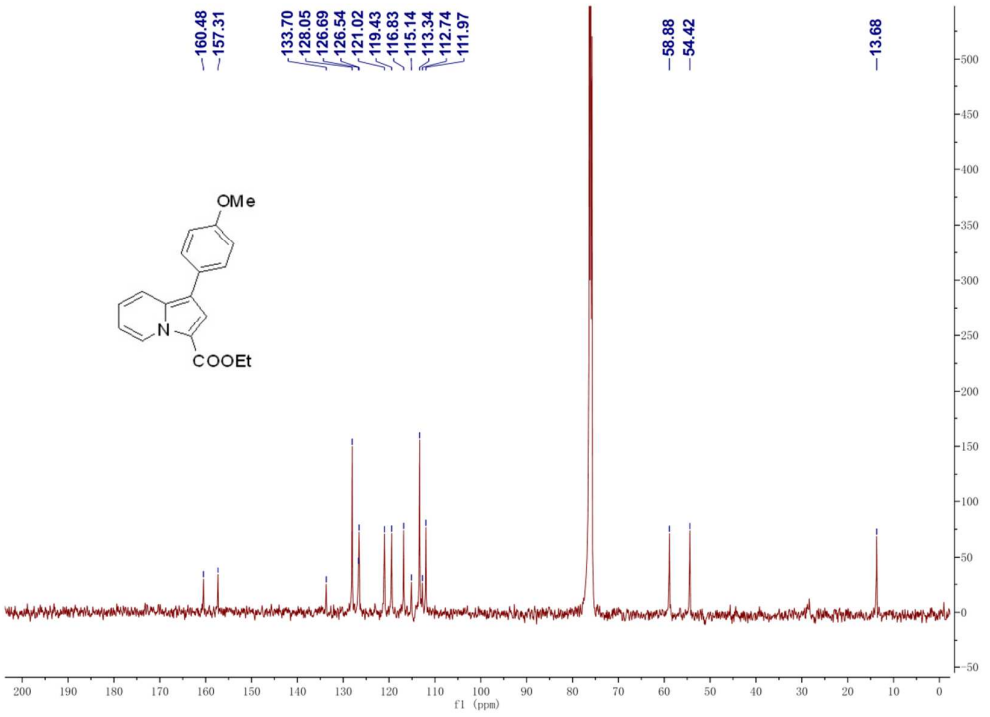

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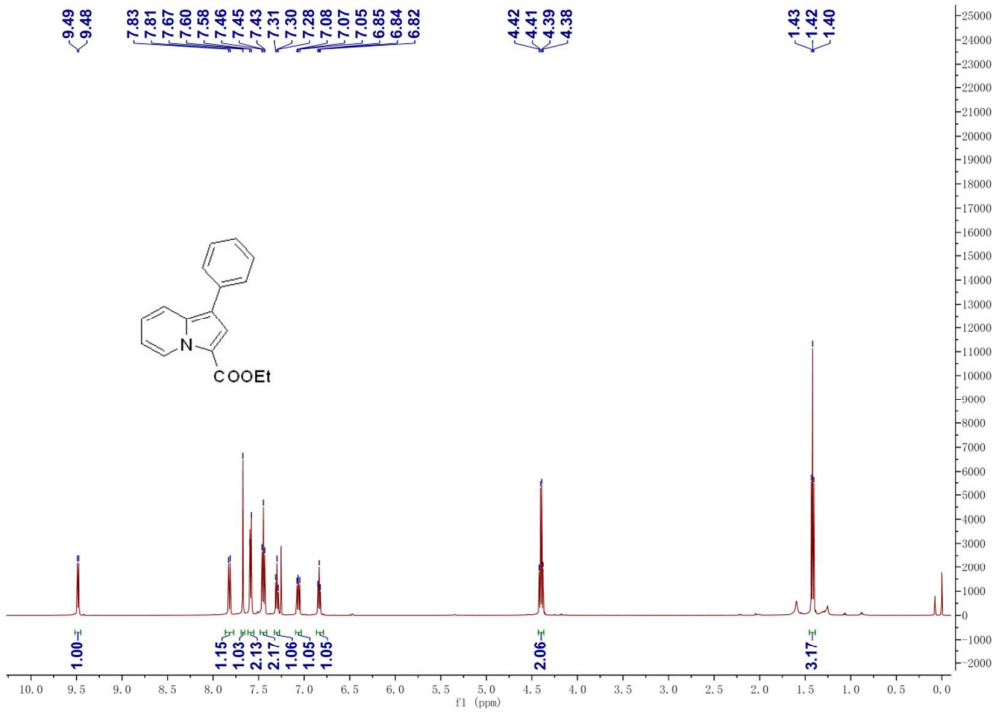

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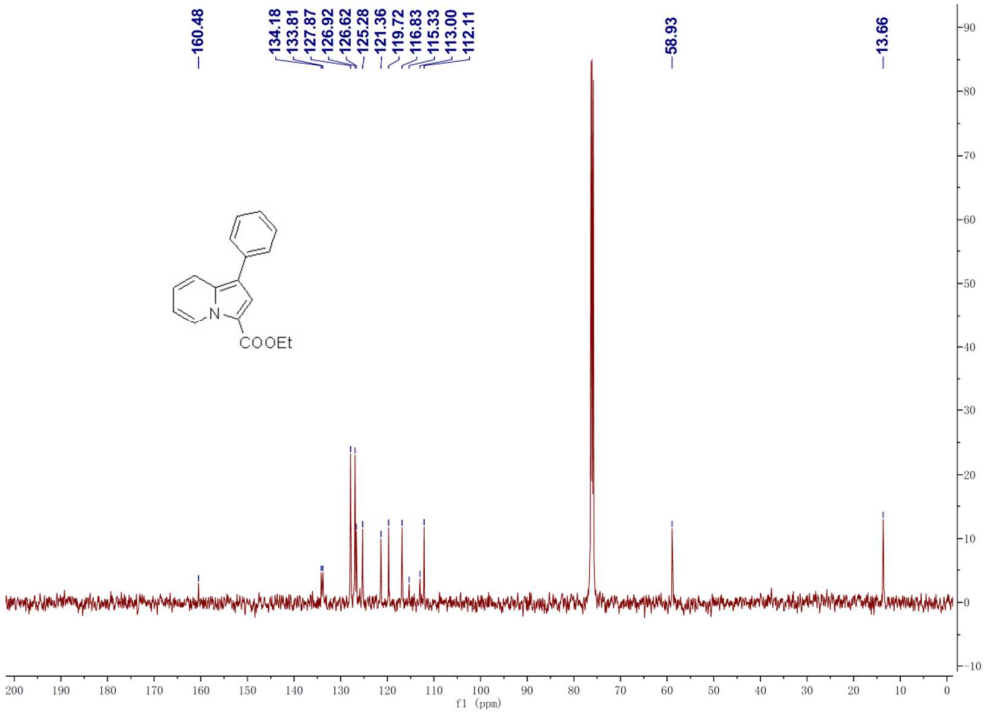

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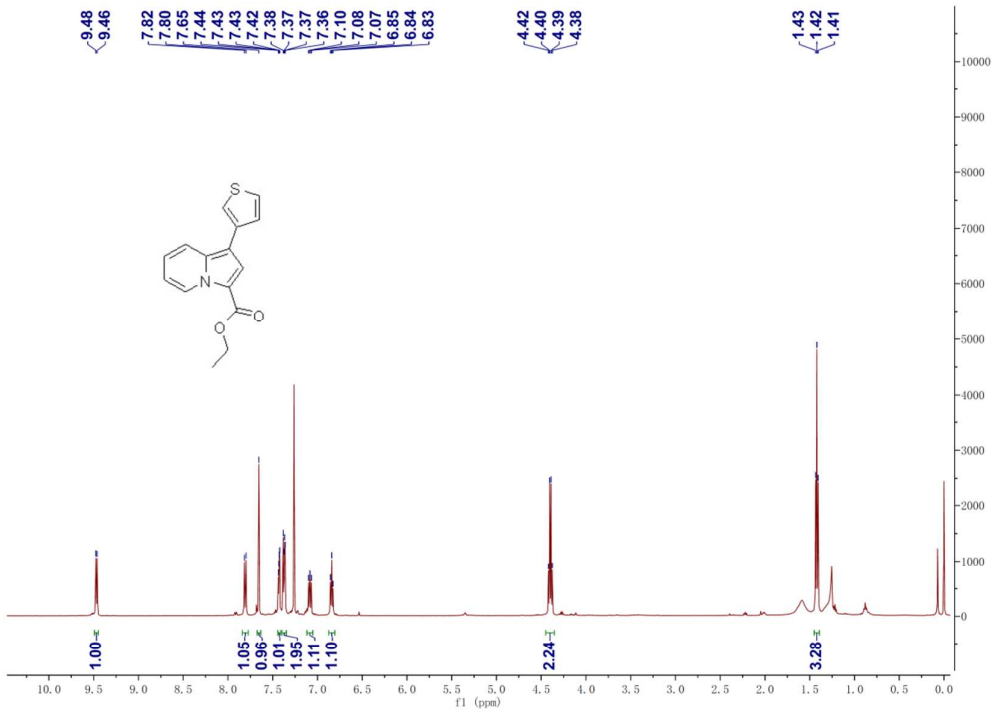

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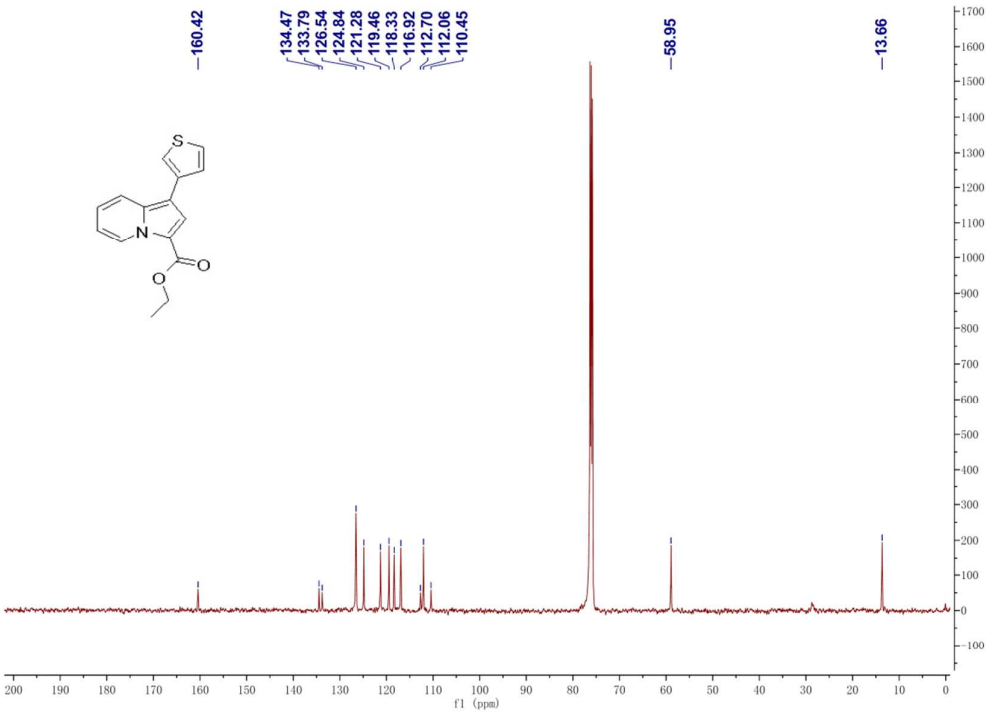

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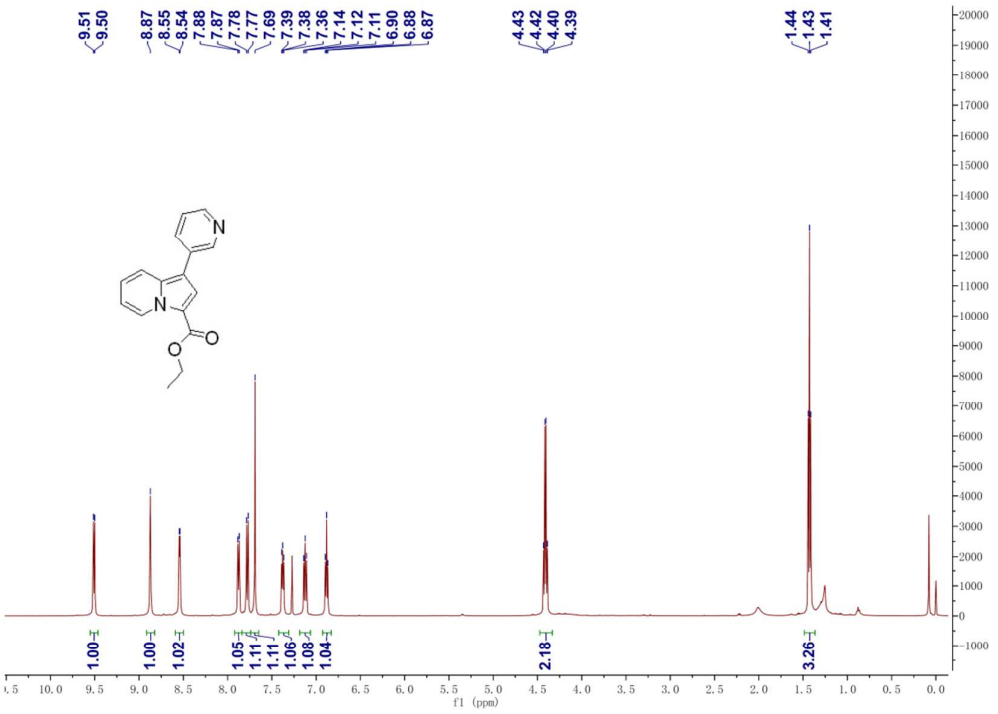

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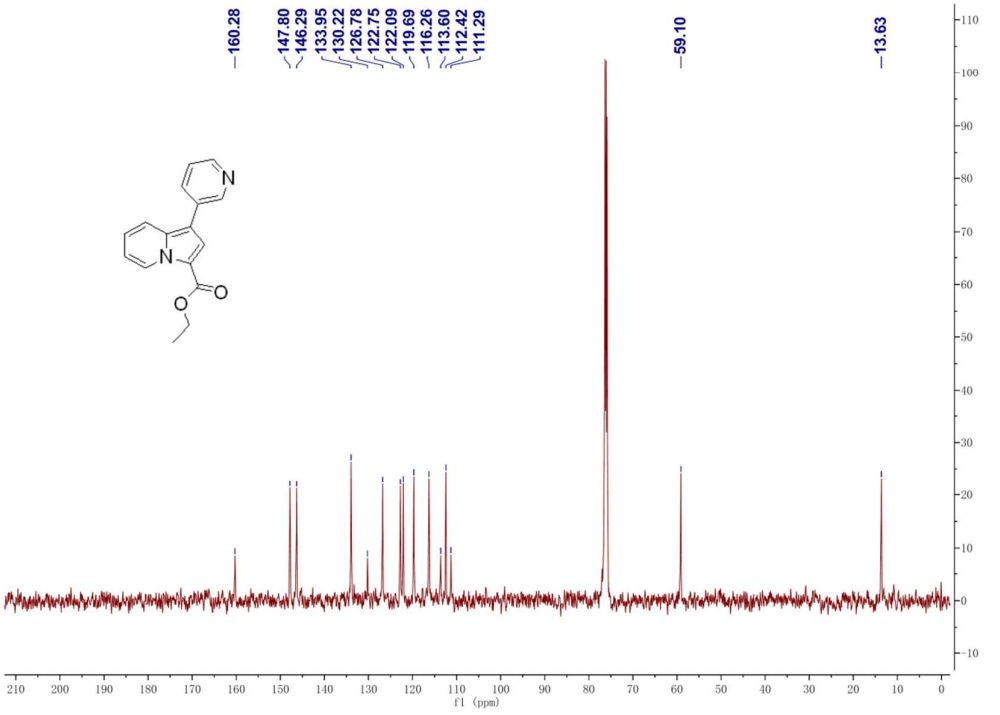

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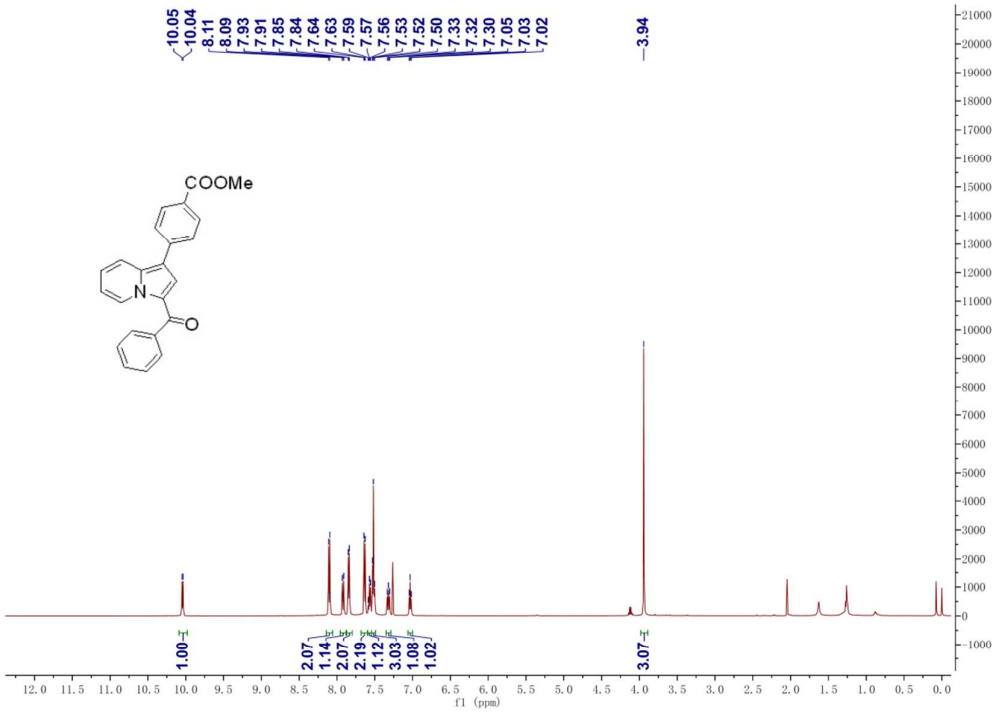

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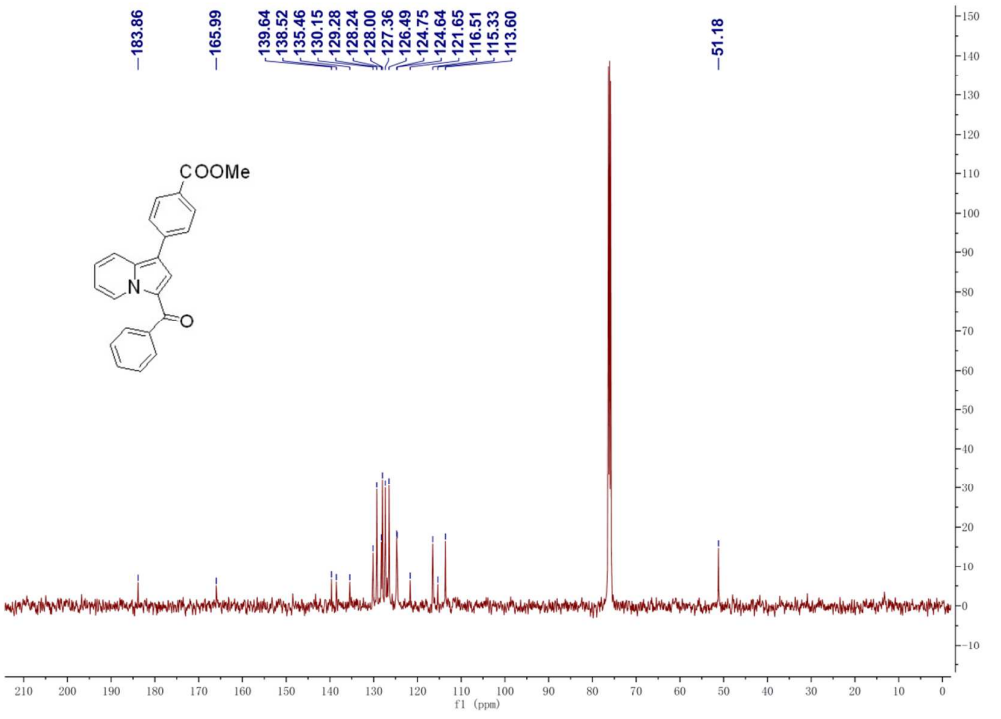

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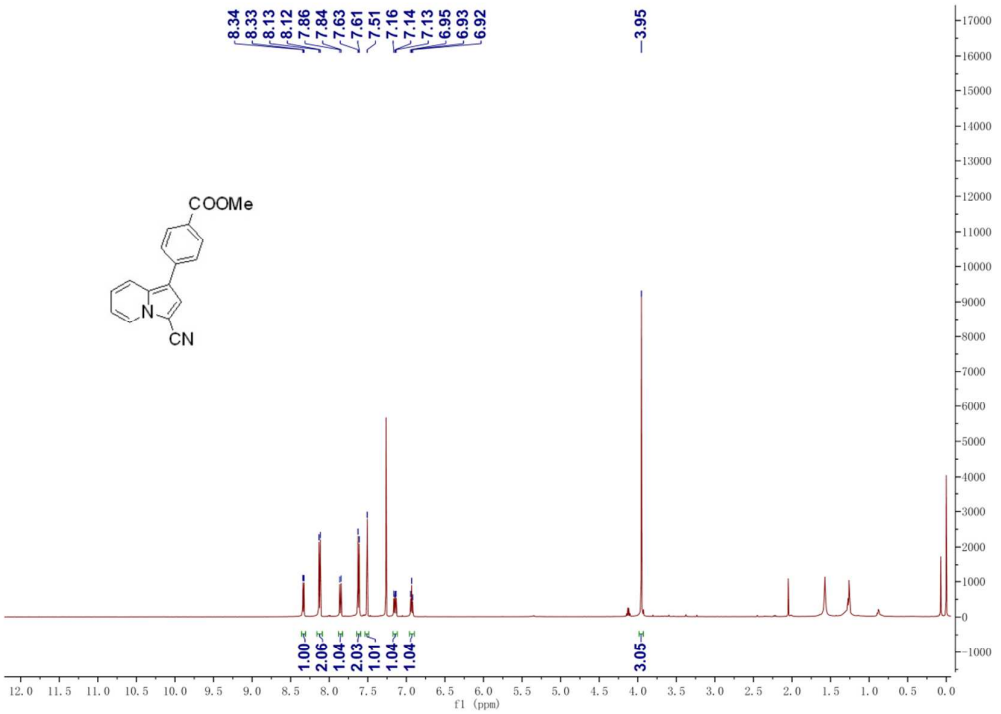
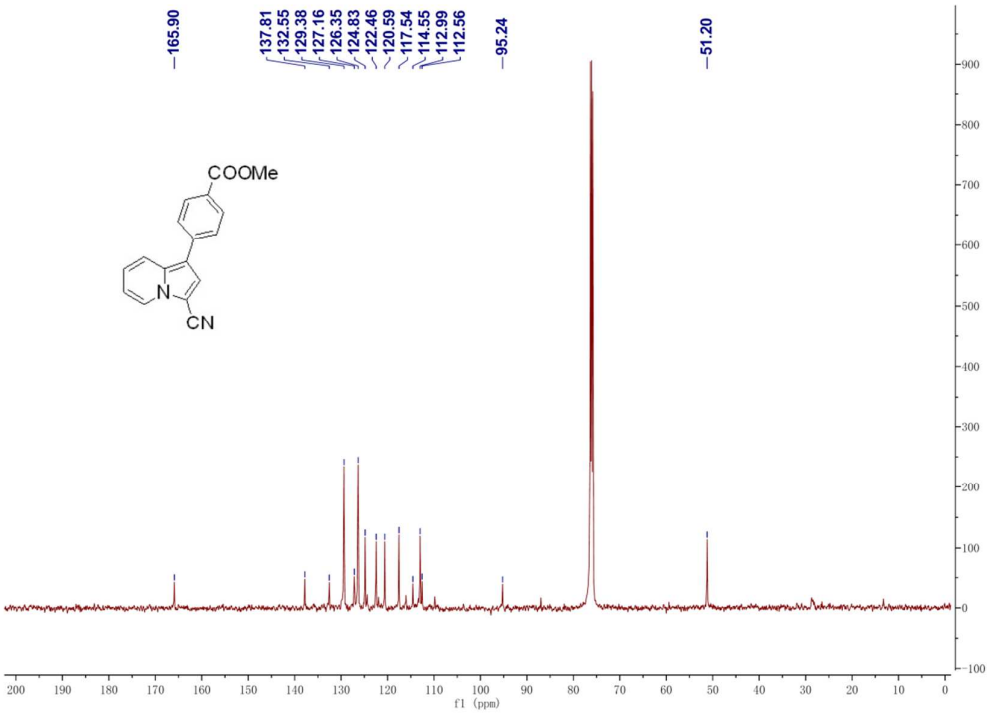
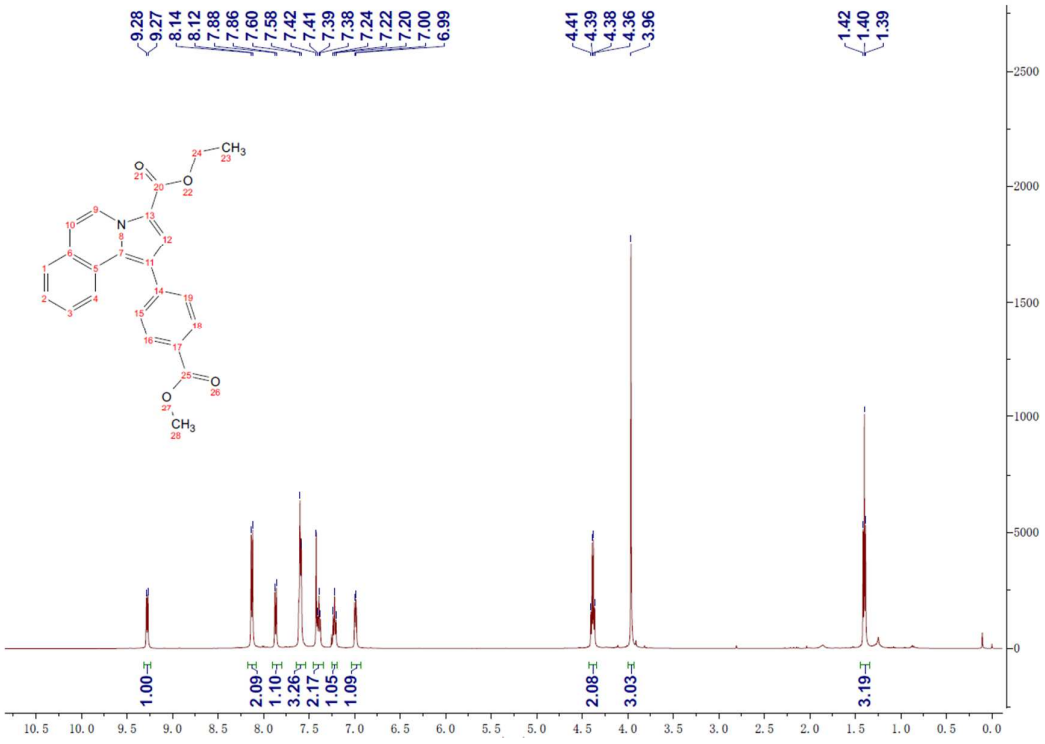


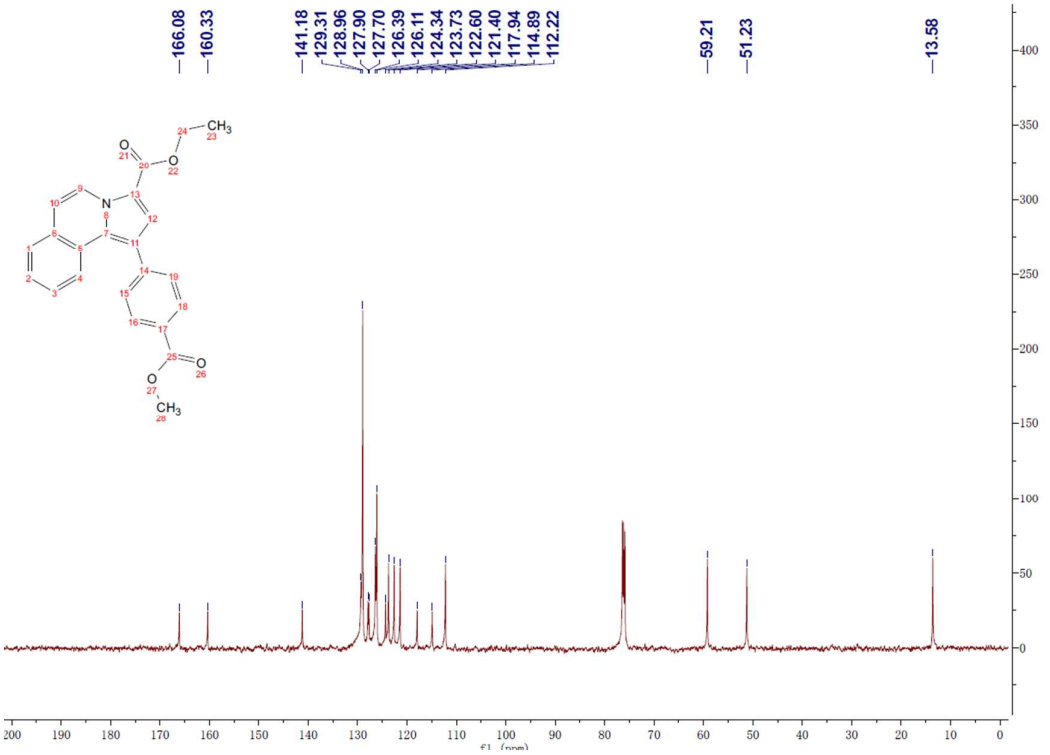
^{1}H NMR of **6k**



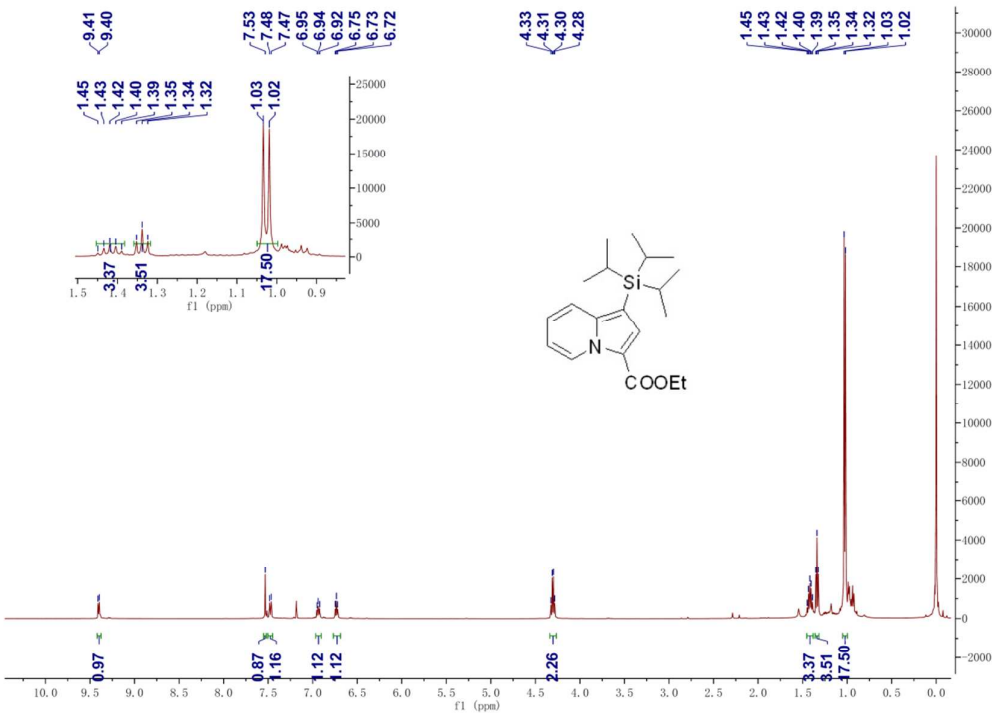
^{13}C NMR of **6k**



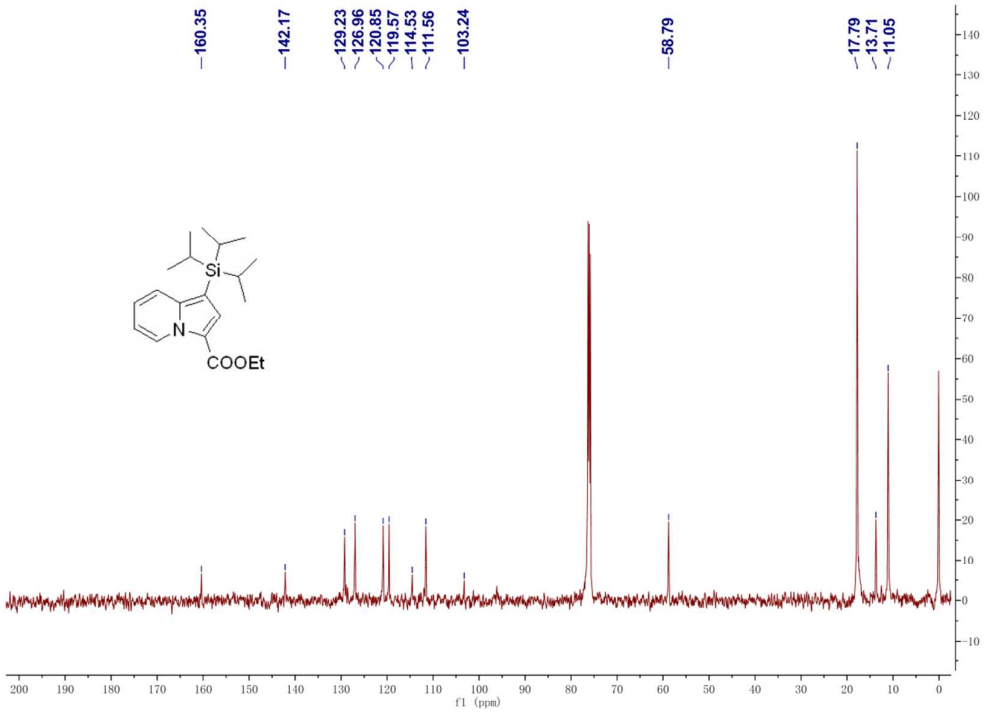
^{1}H NMR of **6l**



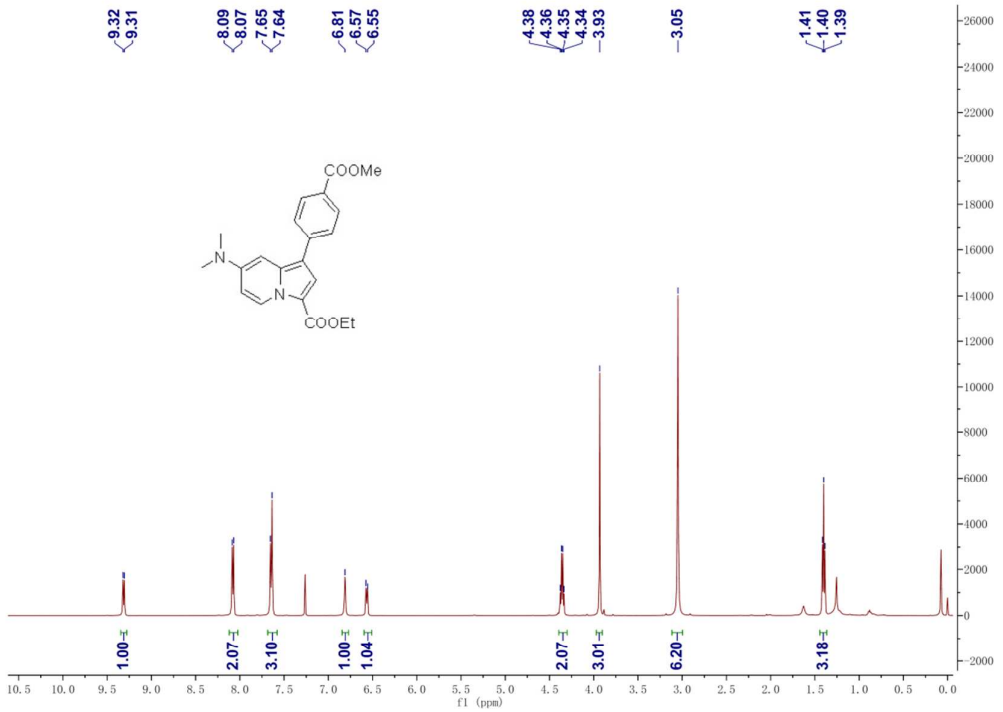
^{13}C NMR of **6l**



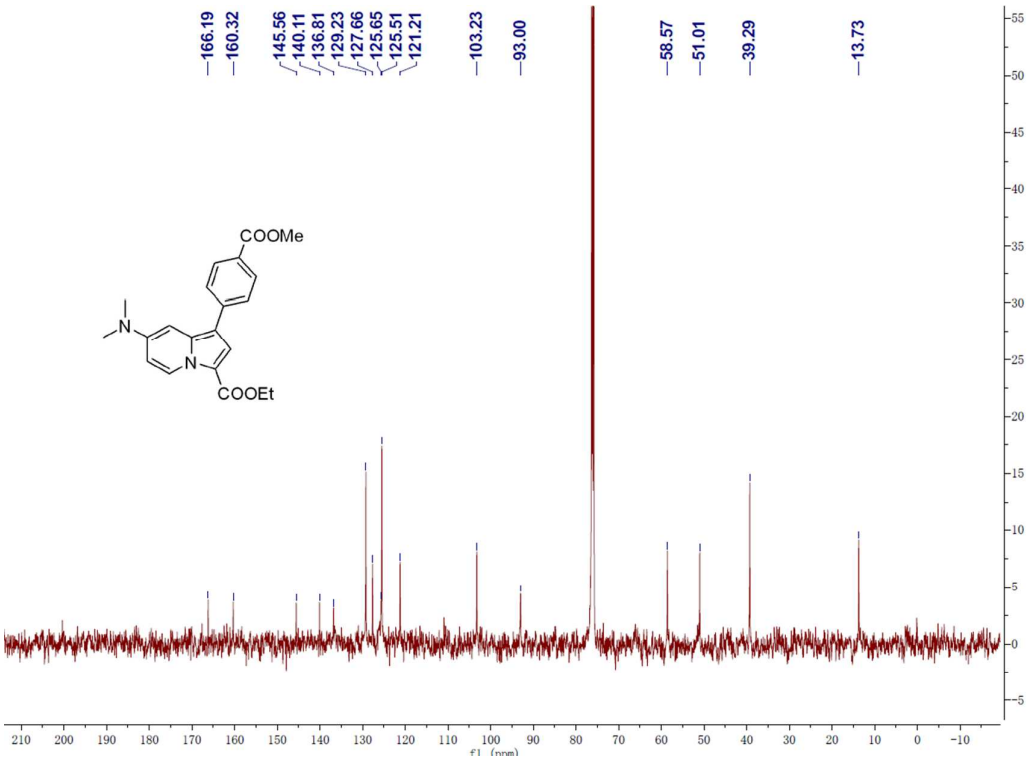
^{1}H NMR of **6m**



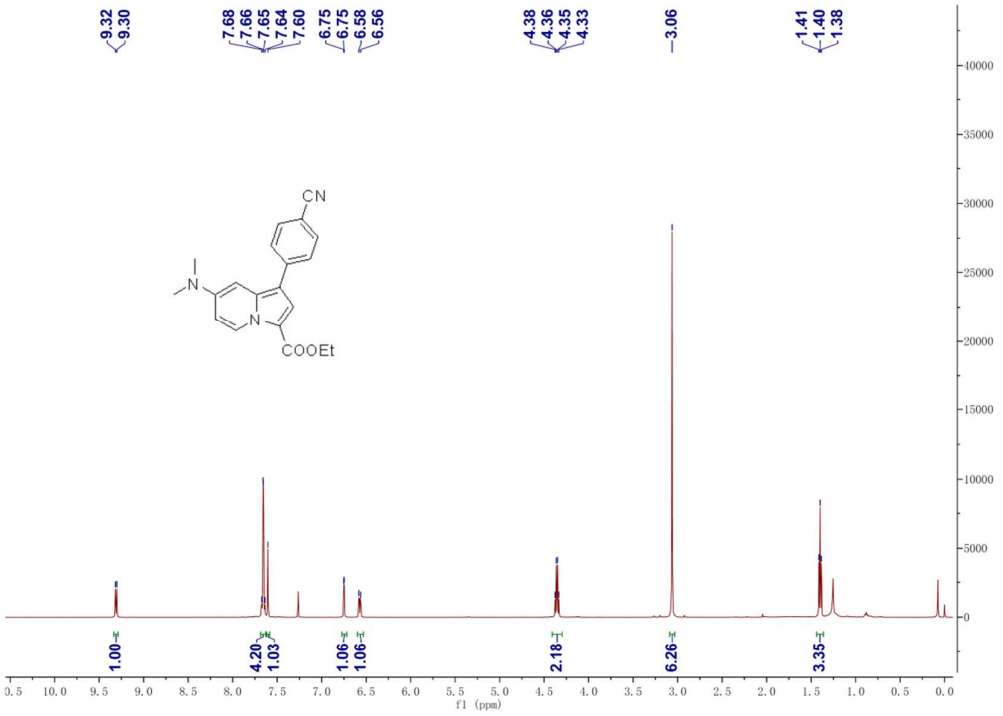
^{13}C NMR of **6m**



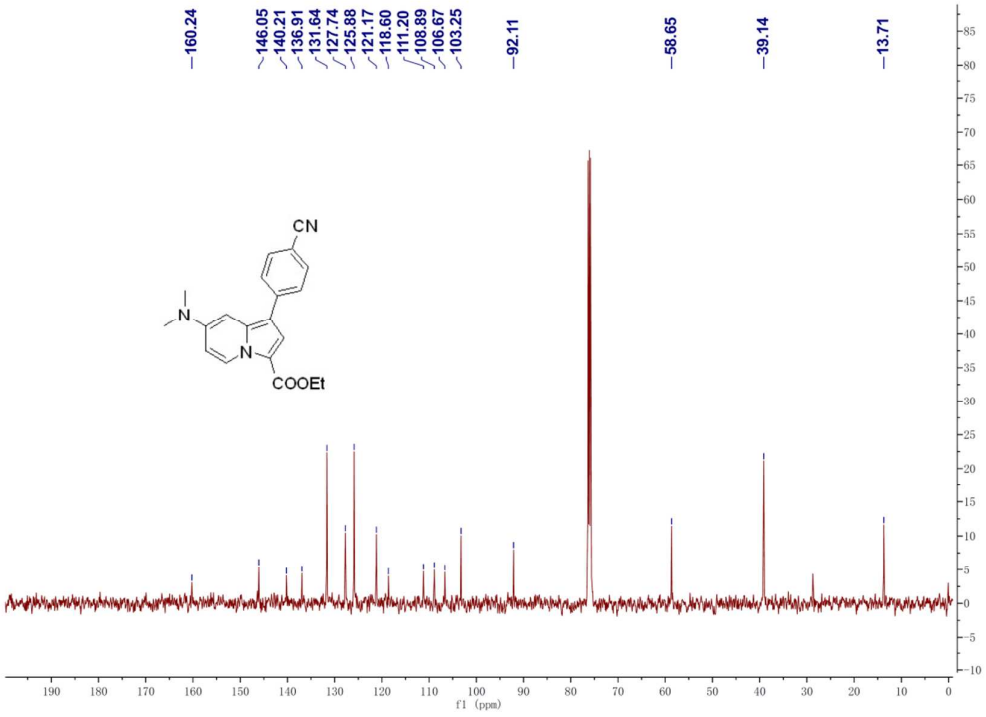
^{1}H NMR of **6n**



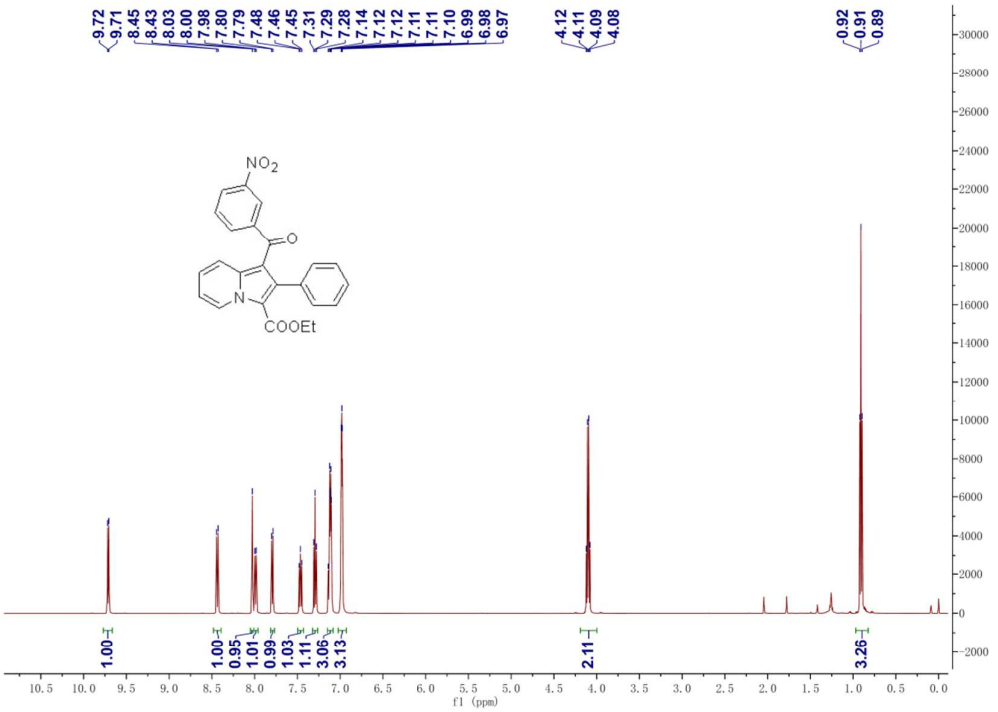
^{13}C NMR of **6n**



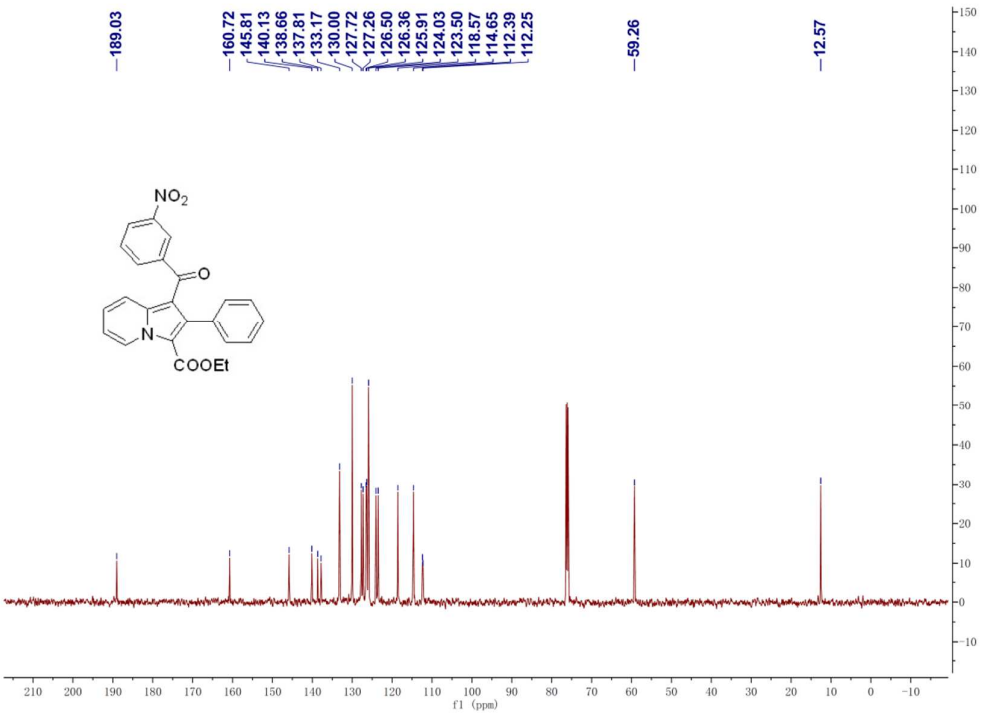
^{1}H NMR of **6o**



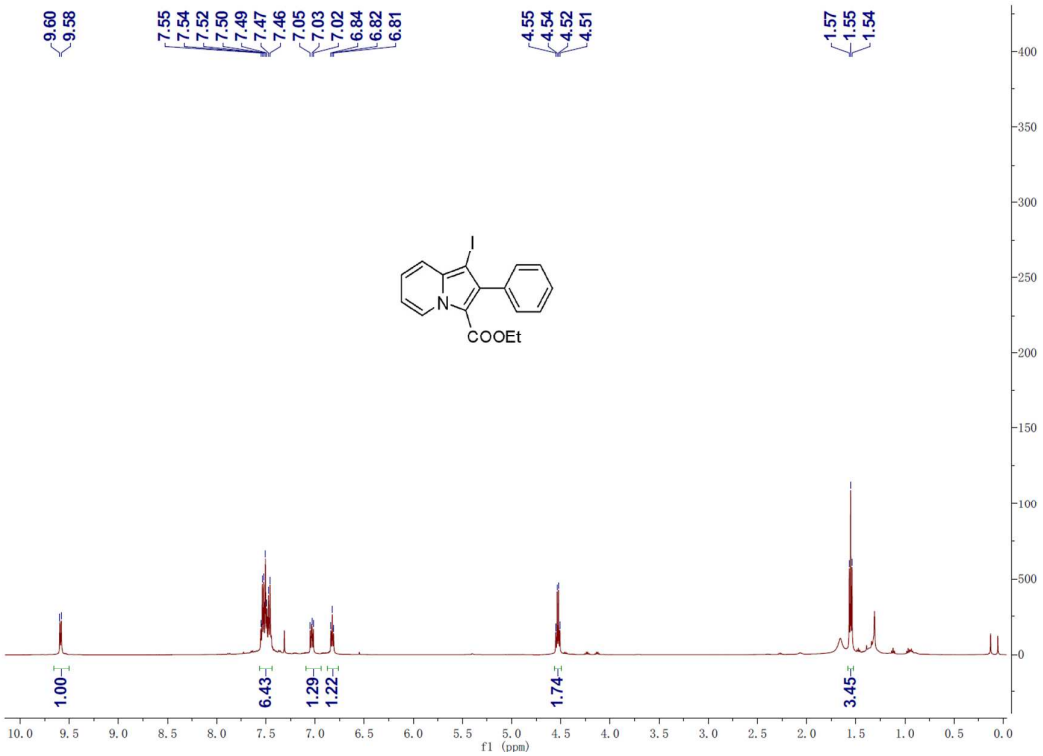
^{13}C NMR of **6o**



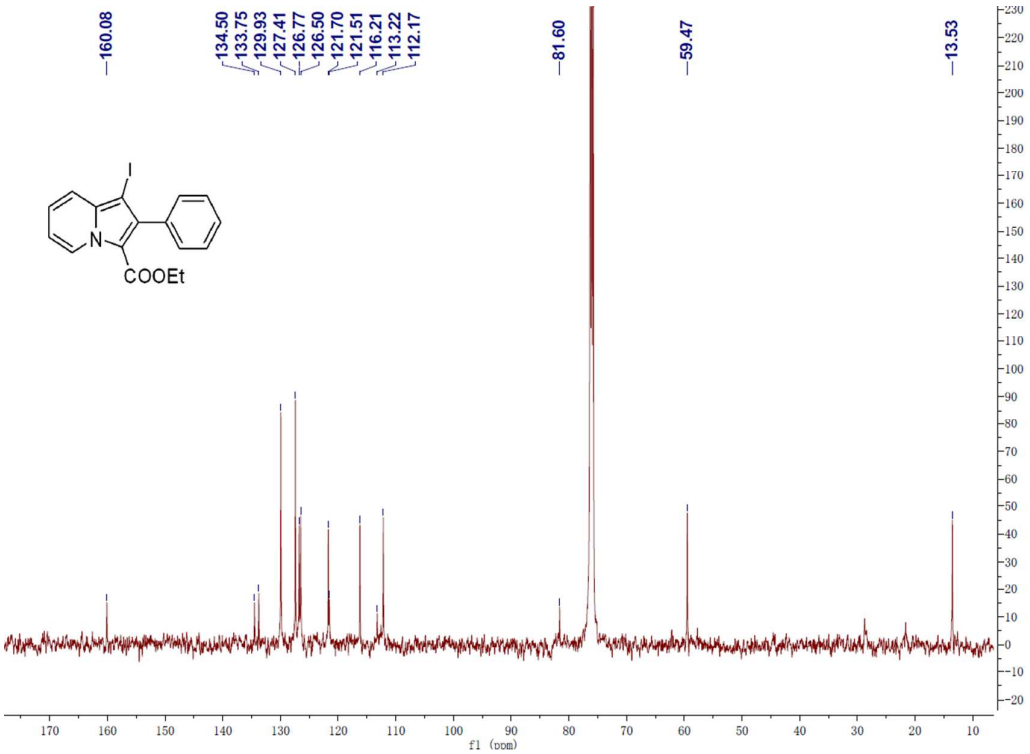
^{1}H NMR of **6p**



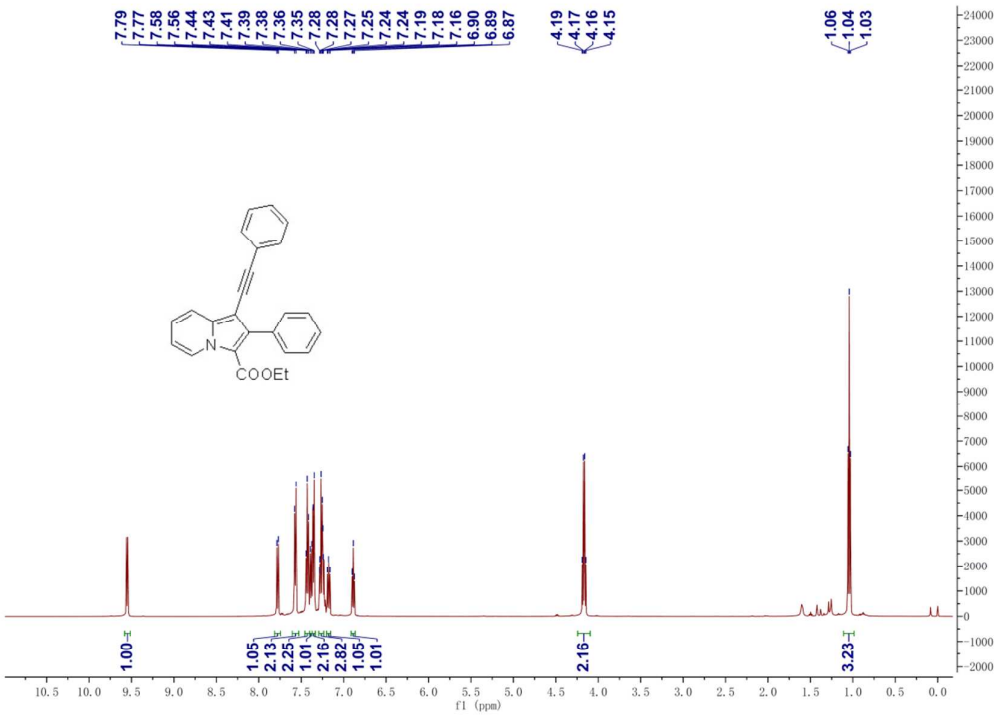
^{13}C NMR of **6p**


9.60
9.58
7.55
7.54
7.52
7.50
7.49
7.47
7.46
7.05
7.03
7.02
6.84
6.82
6.81
4.55
4.54
4.52
4.51
1.57
1.55
1.54
I
N
COOEt
1.00
6.43
1.29
1.22
1.74
3.45
f1 (ppm)

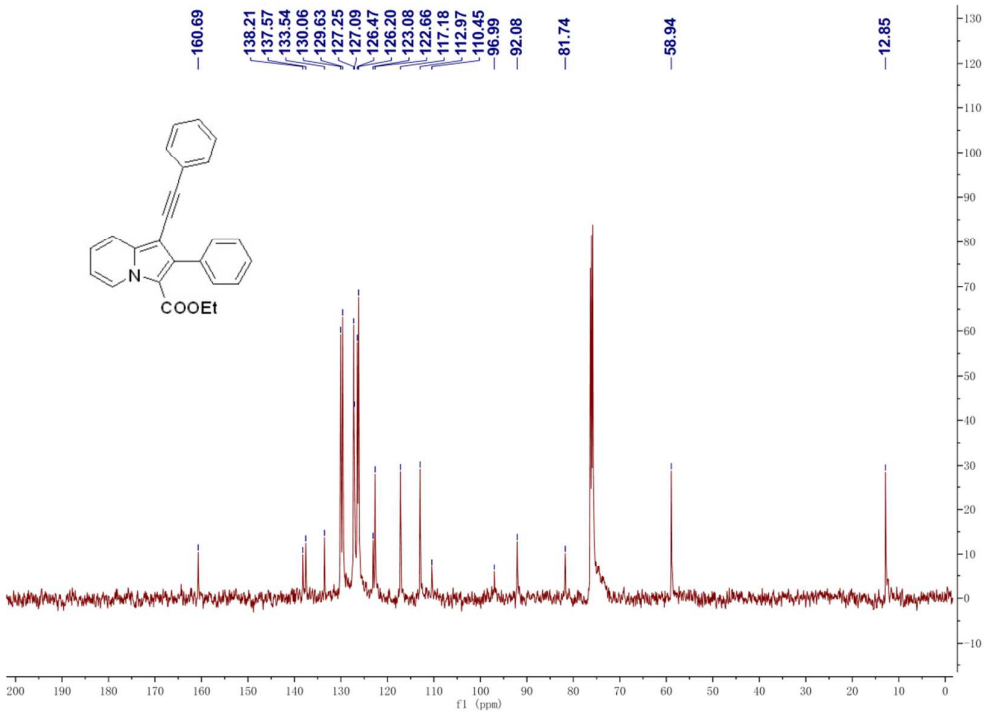
^{1}H NMR of **6r**


160.08
134.50
133.75
129.93
127.41
126.77
126.50
121.70
121.51
116.21
113.22
112.17
81.60
59.47
13.53
I
N
COOEt
f1 (ppm)

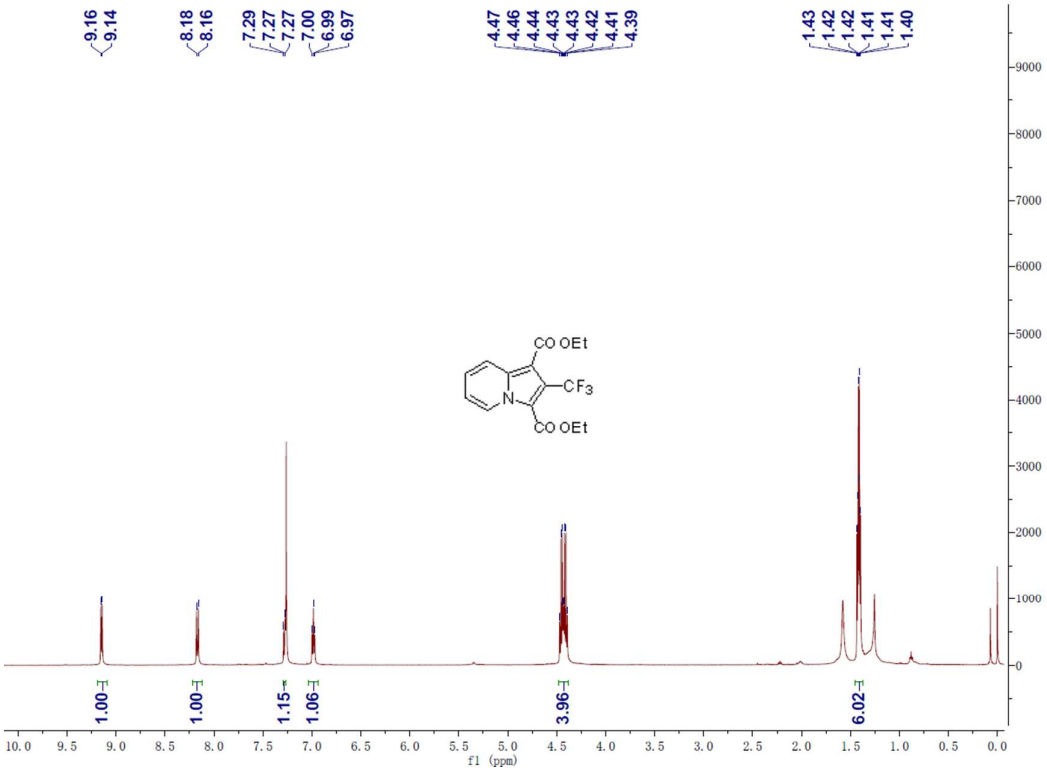
^{13}C NMR of **6r**



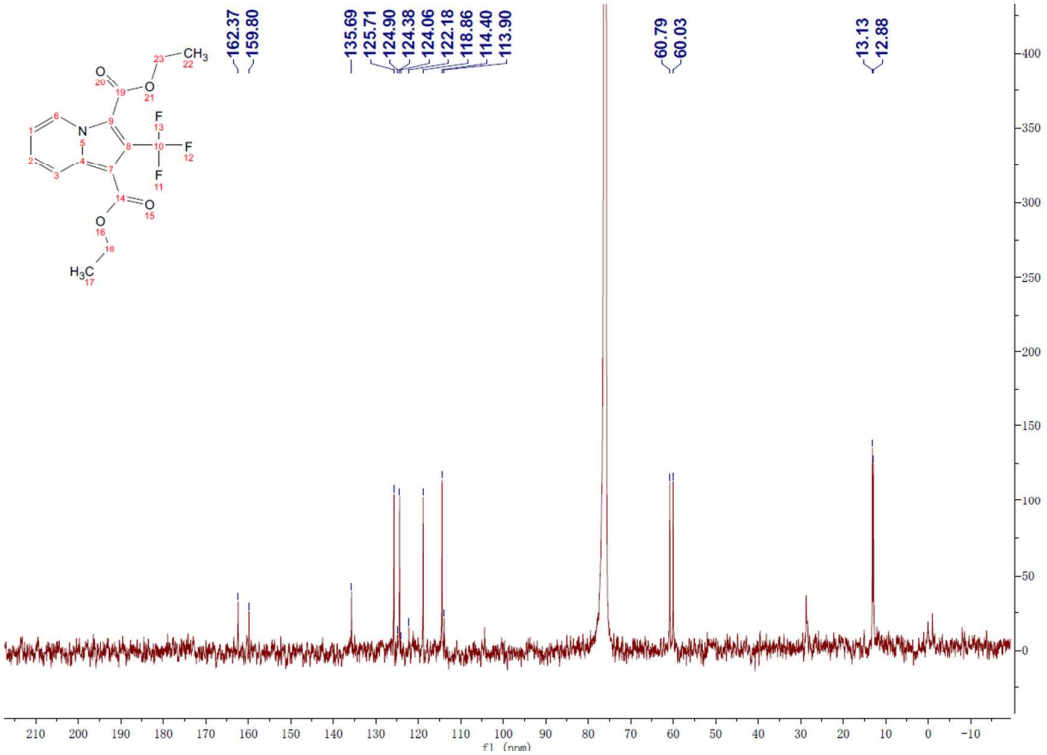
^{1}H NMR of **6s**



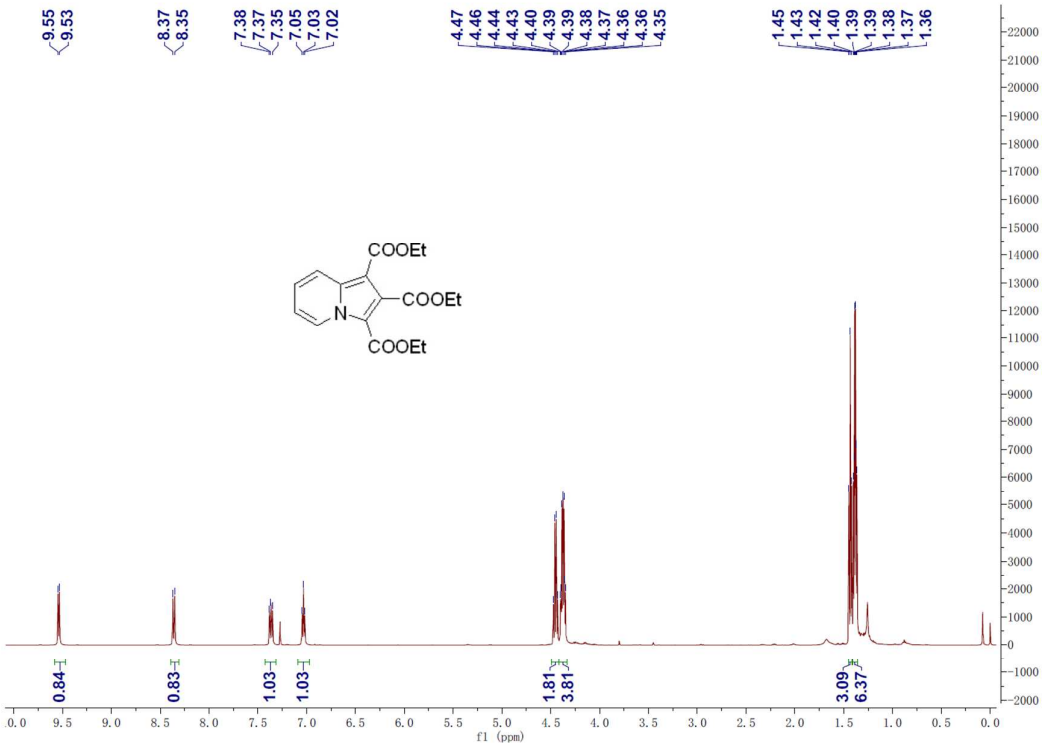
^{13}C NMR of **6s**


9.16
9.14
8.18
8.16
7.29
7.27
7.27
7.00
6.99
6.97
4.47
4.46
4.44
4.43
4.43
4.42
4.41
4.39
1.43
1.42
1.42
1.41
1.41
1.40
CO OEt
CF3
CO OEt
1.00
1.00
1.15
1.06
3.96
6.02
f1 (ppm)

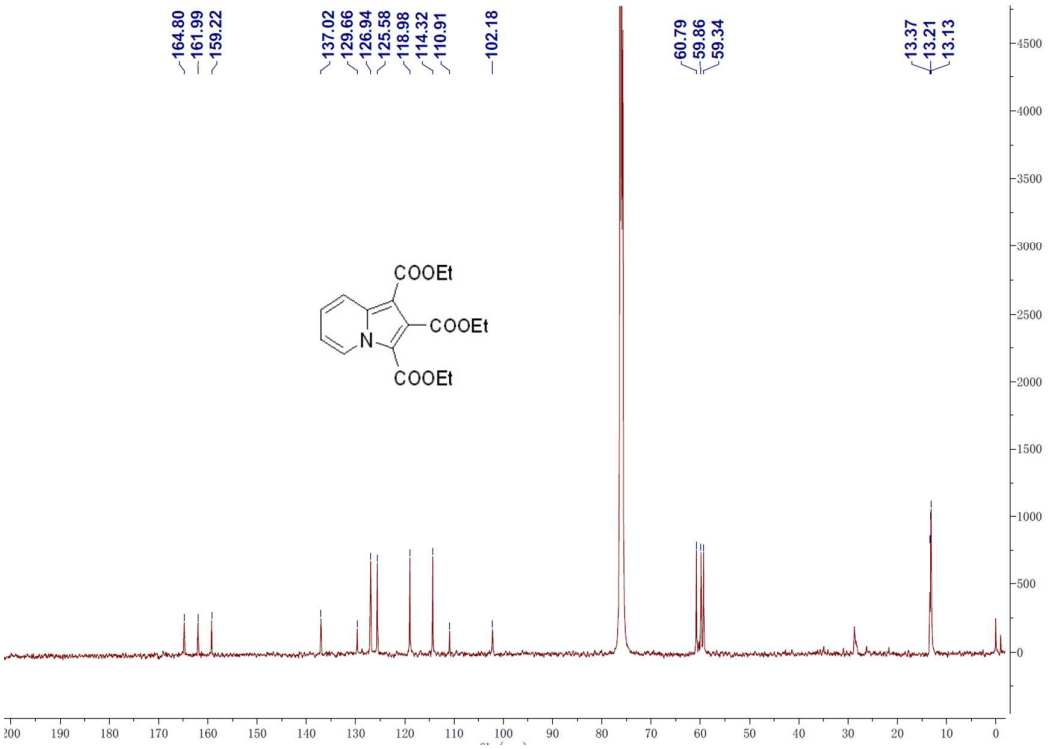
^{1}H NMR of **6t**


162.37
159.80
135.69
125.71
124.90
124.38
124.06
122.18
118.86
114.40
113.90
60.79
60.03
13.13
12.88
f1 (ppm)

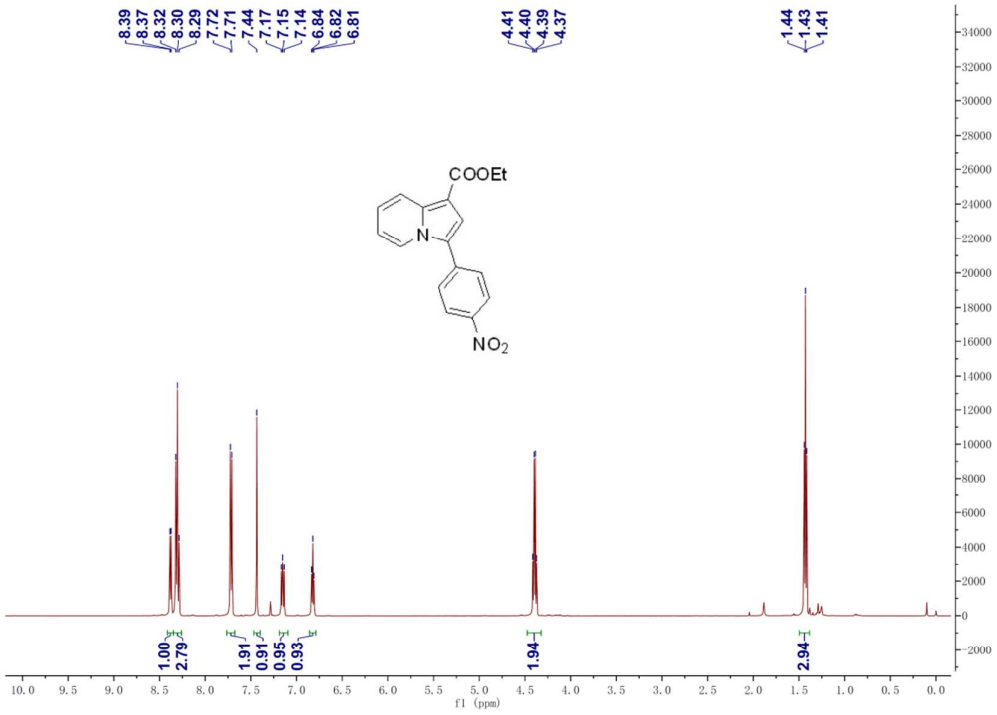
^{13}C NMR of **6t**



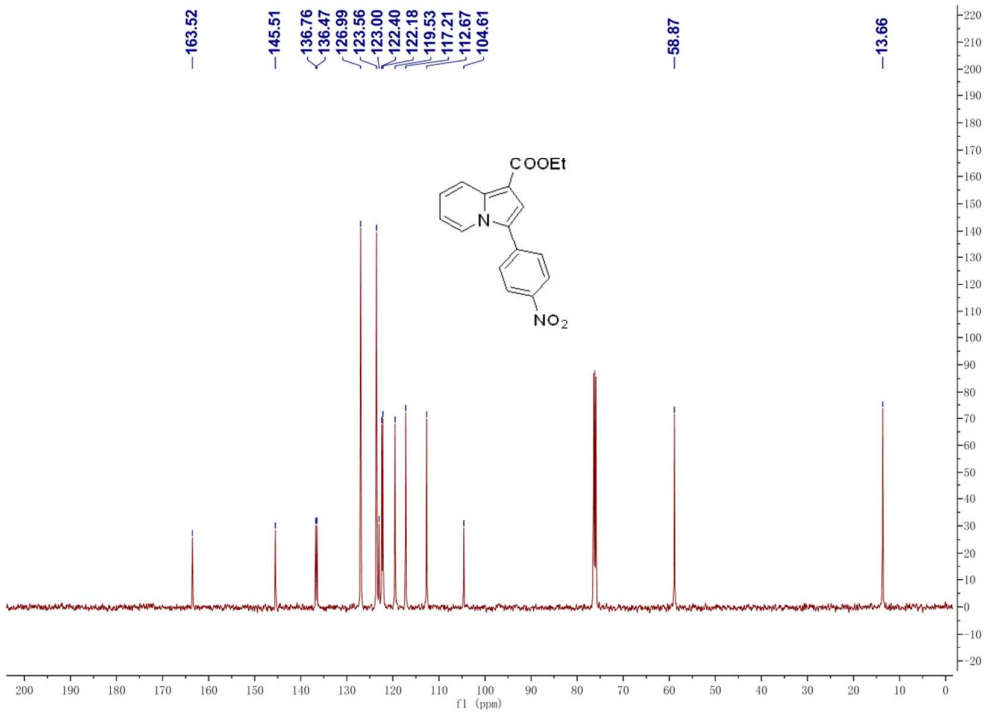
^{1}H NMR of **6u**



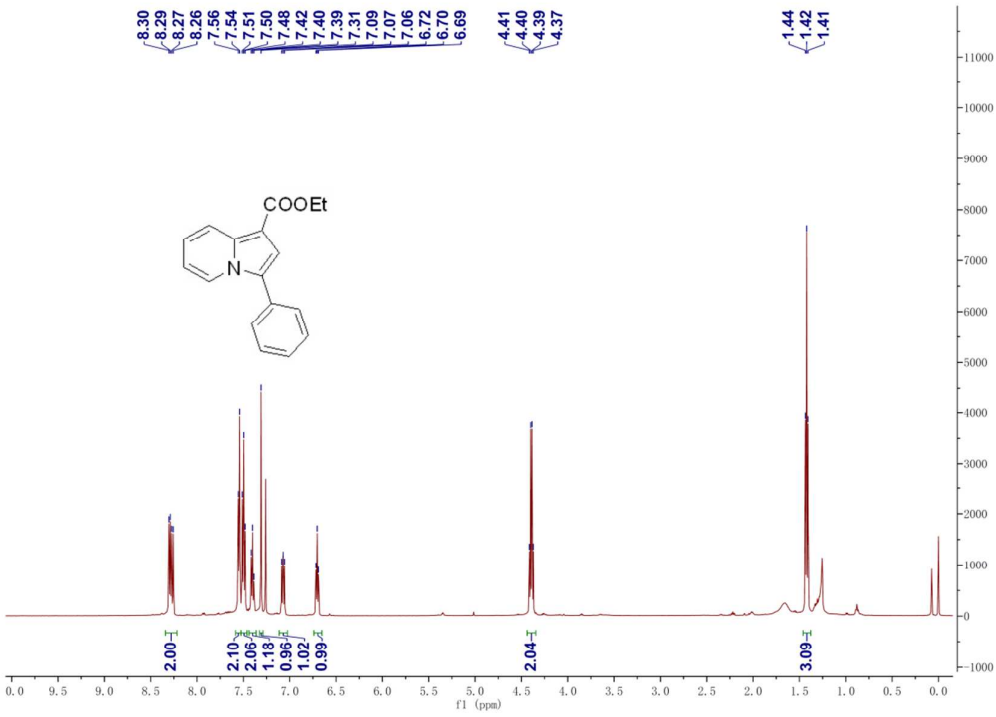
^{13}C NMR of **6u**



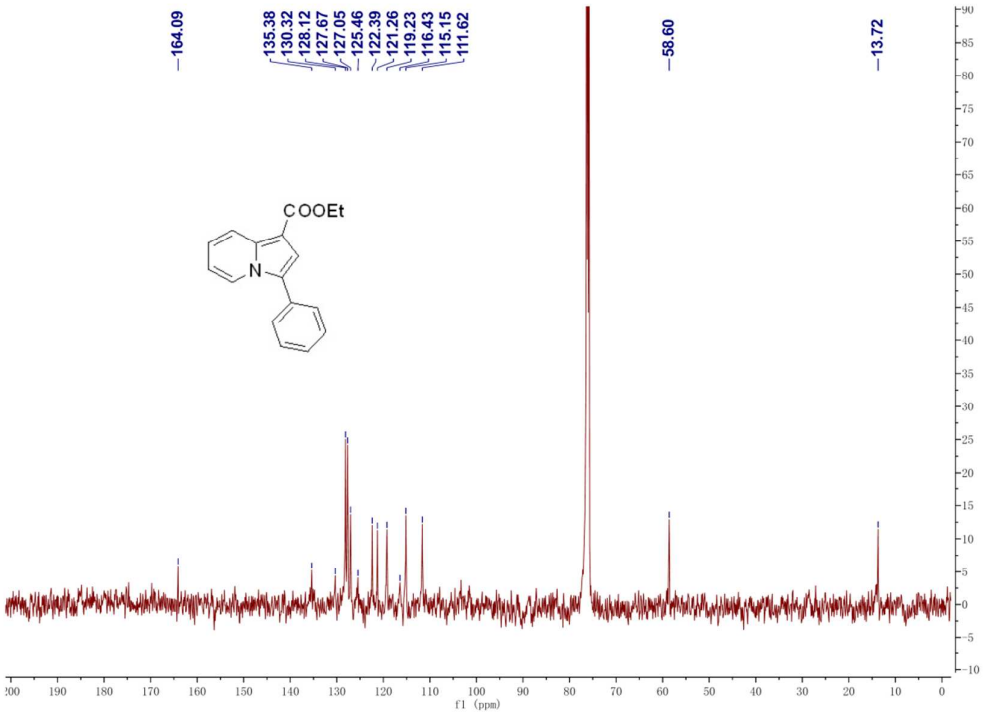
^{1}H NMR of **7a**



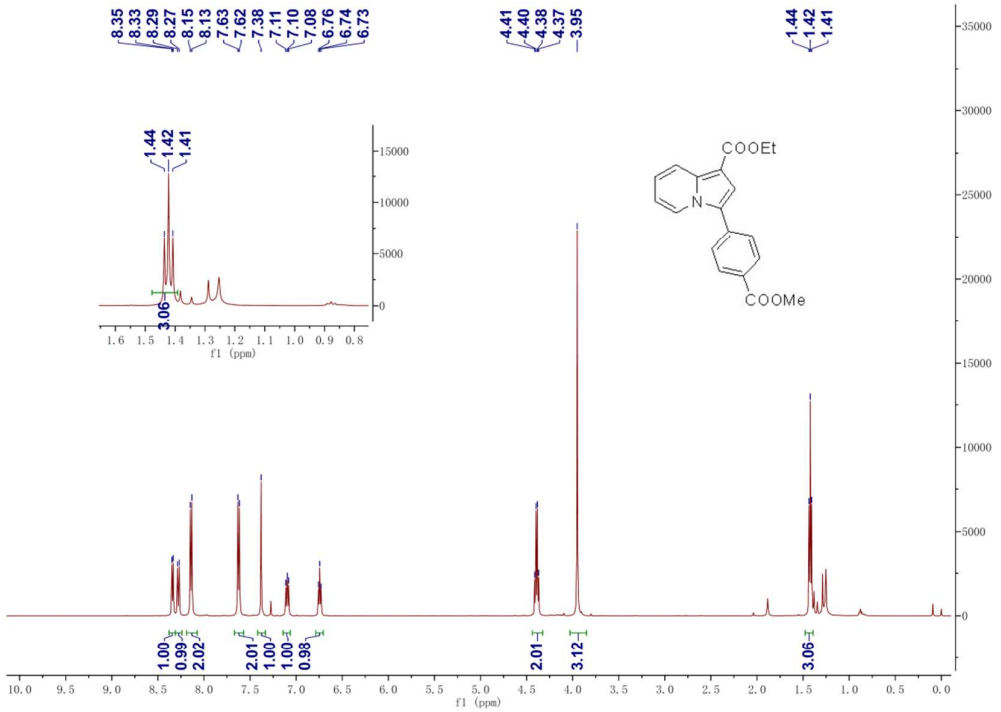
^{13}C NMR of **7a**



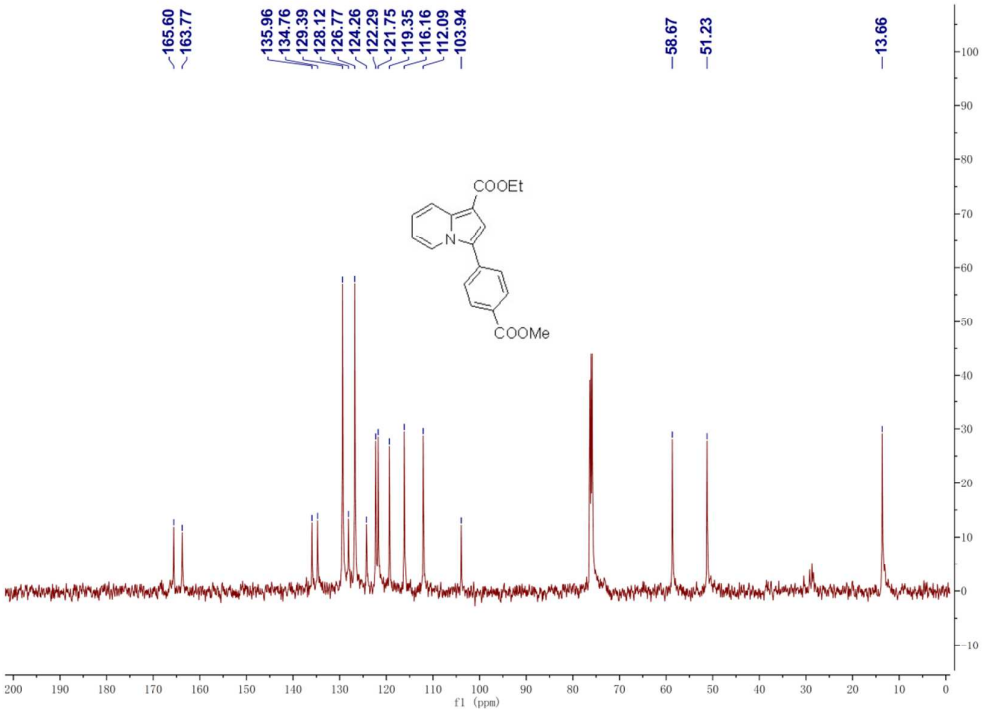
^{1}H NMR of **7b**



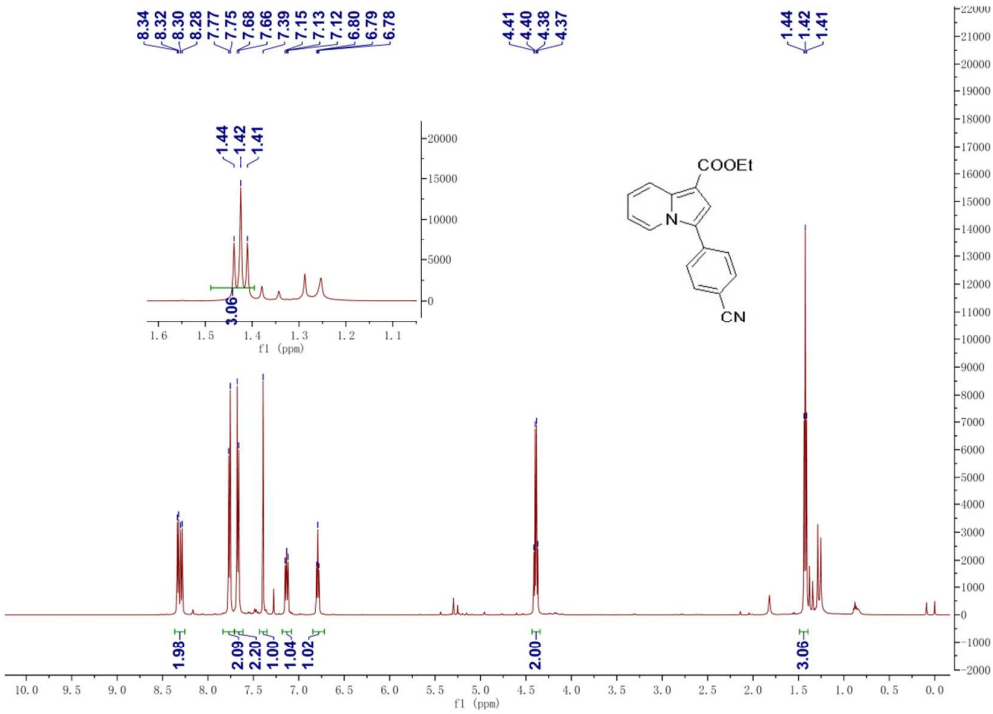
^{13}C NMR of **7b**



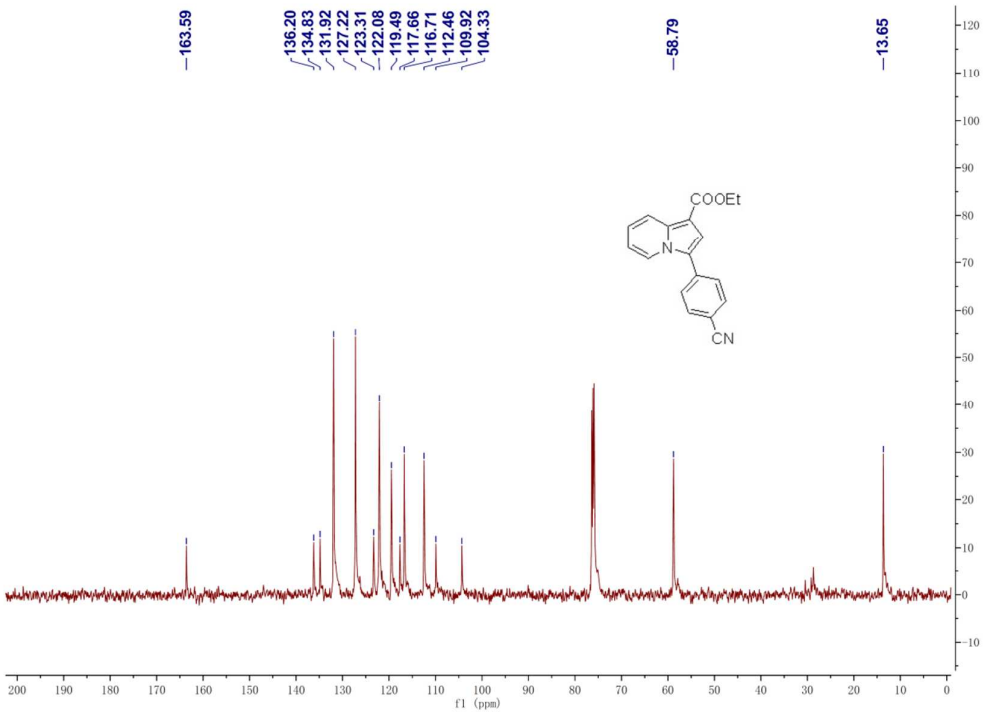
^{1}H NMR of **7c**



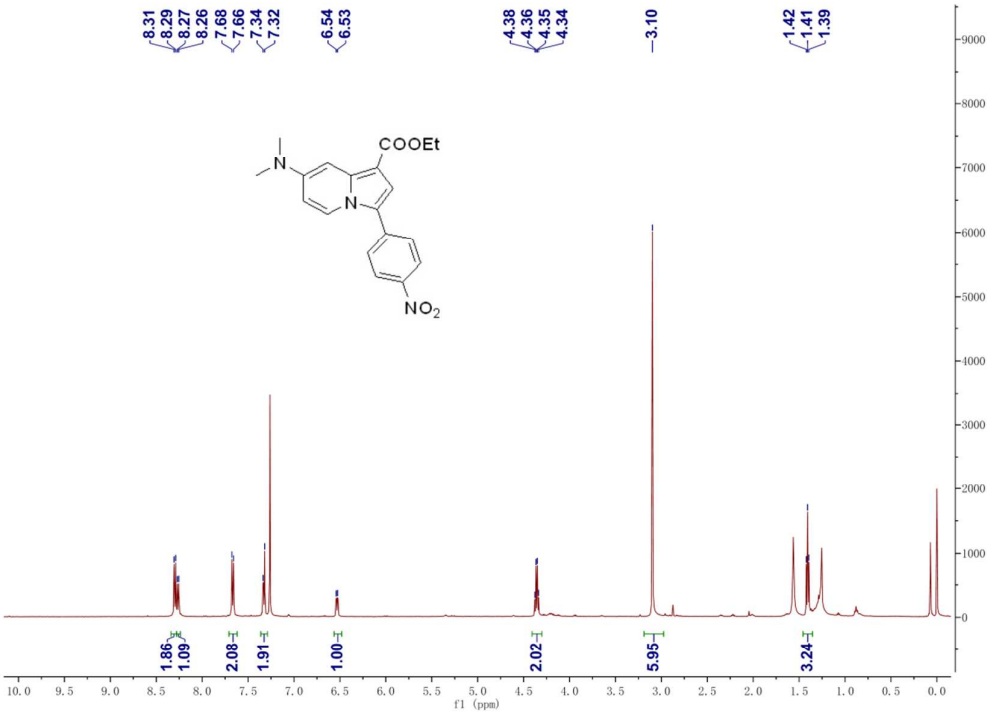
^{13}C NMR of **7c**



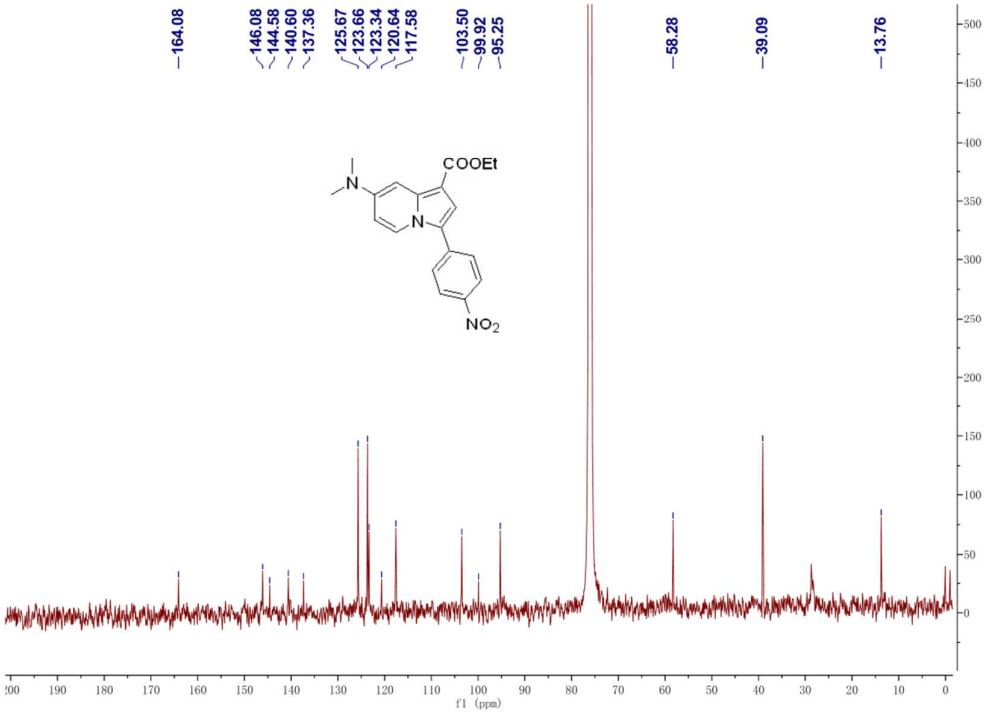
^{1}H NMR of **7d**



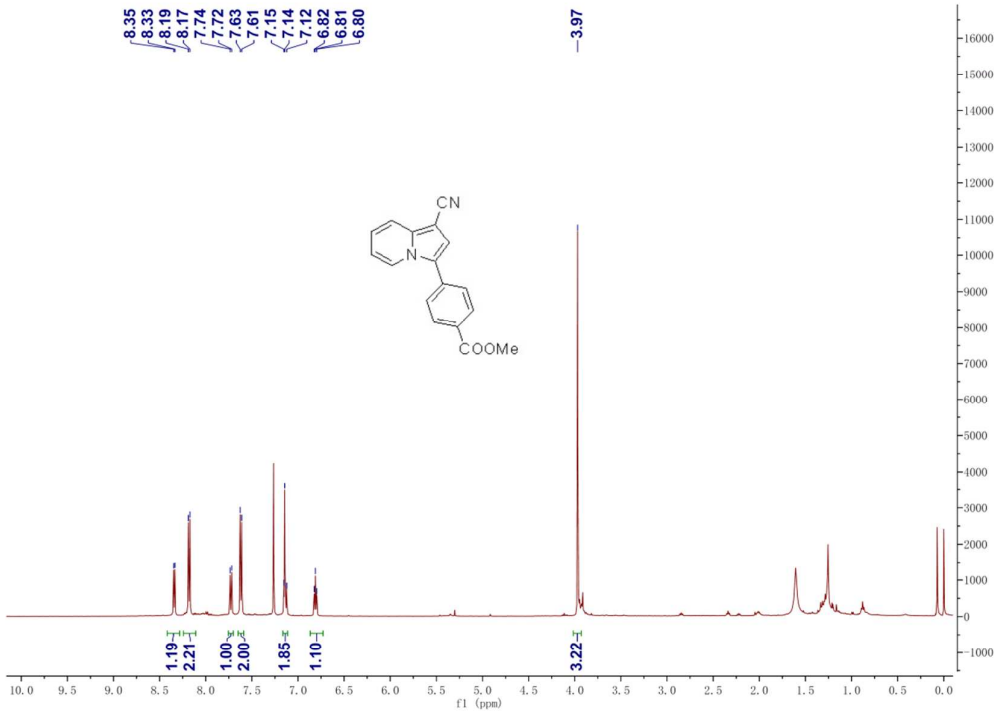
^{13}C NMR of **7d**



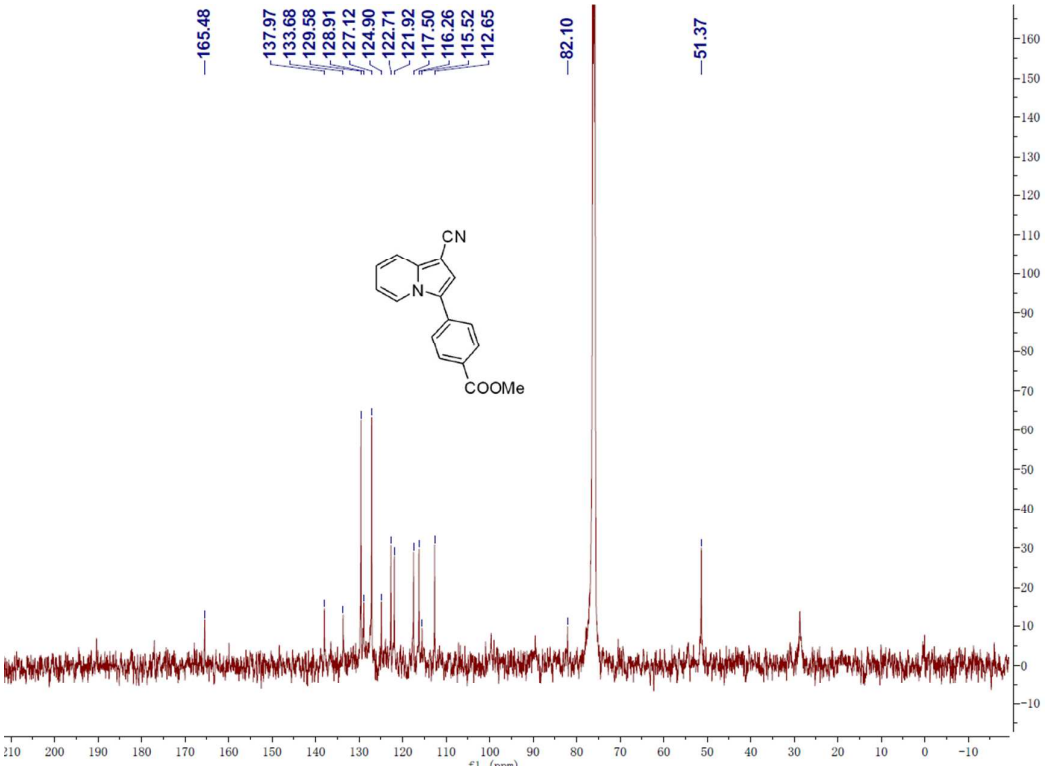
^{1}H NMR of **7e**



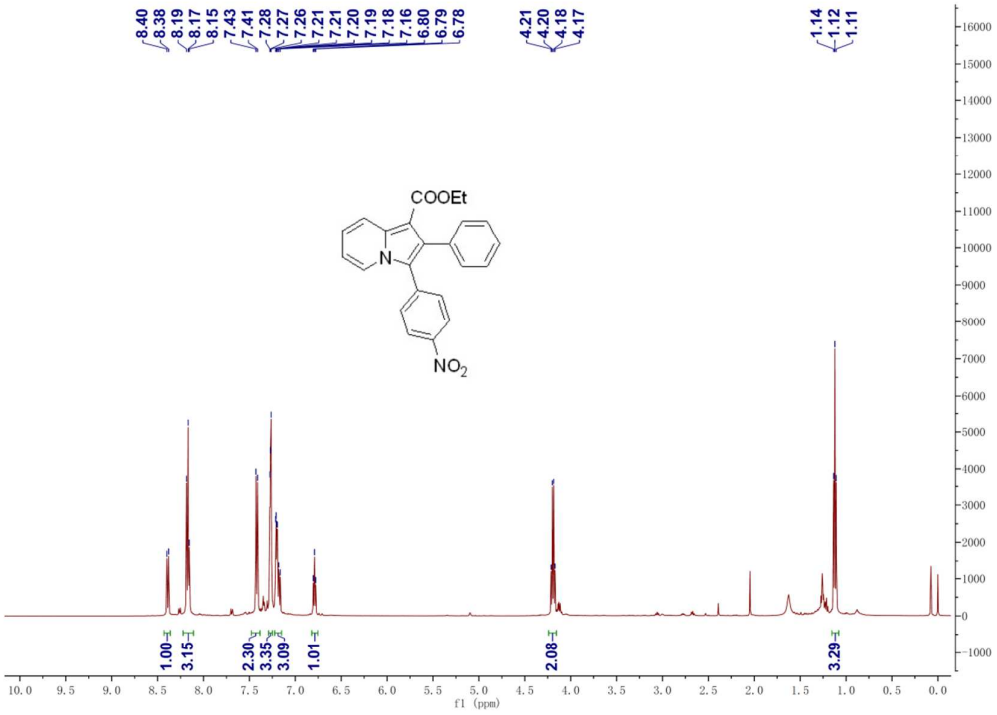
^{13}C NMR of **7e**



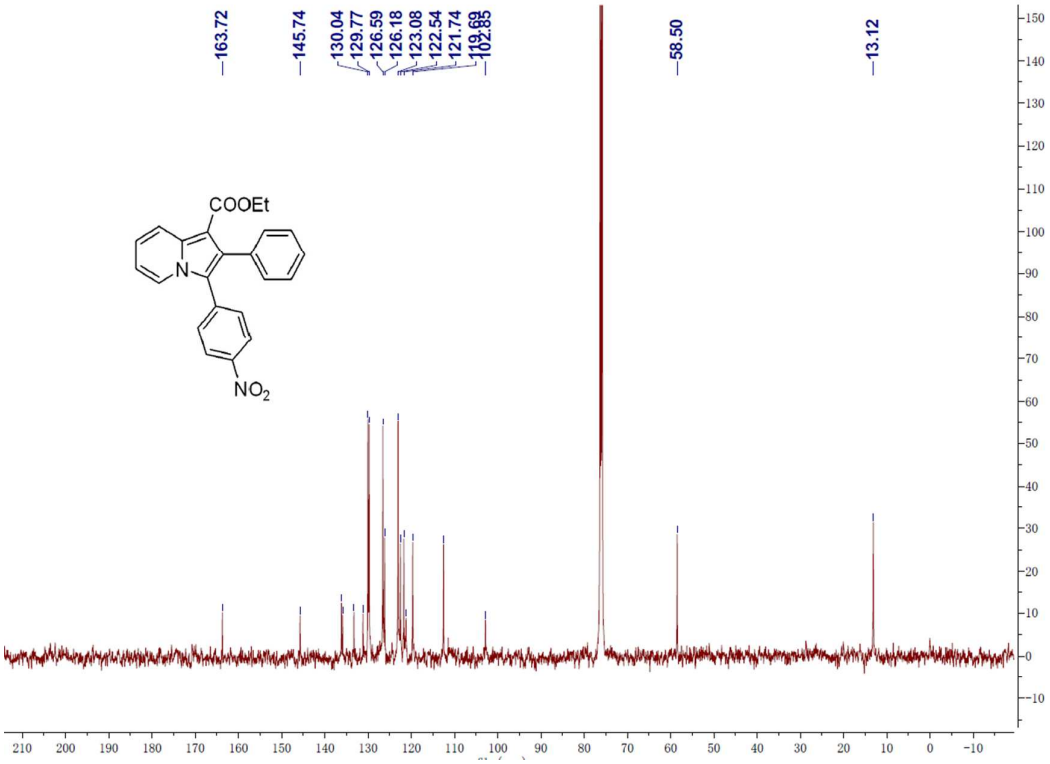
^{1}H NMR of **7g**



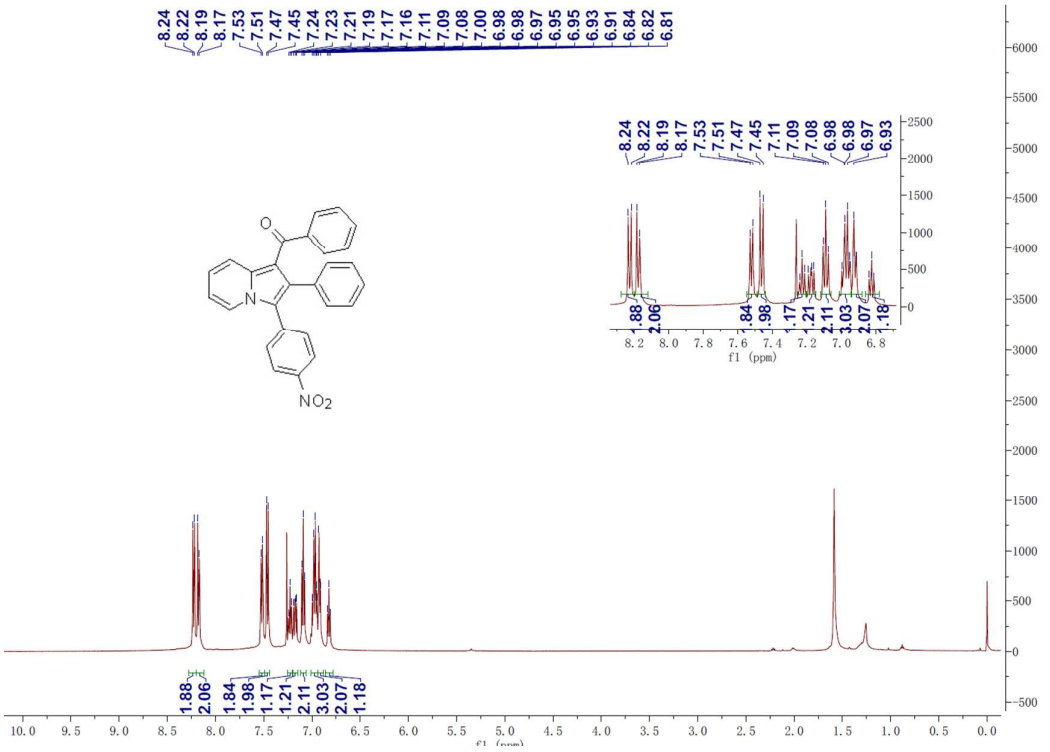
^{13}C NMR of **7g**



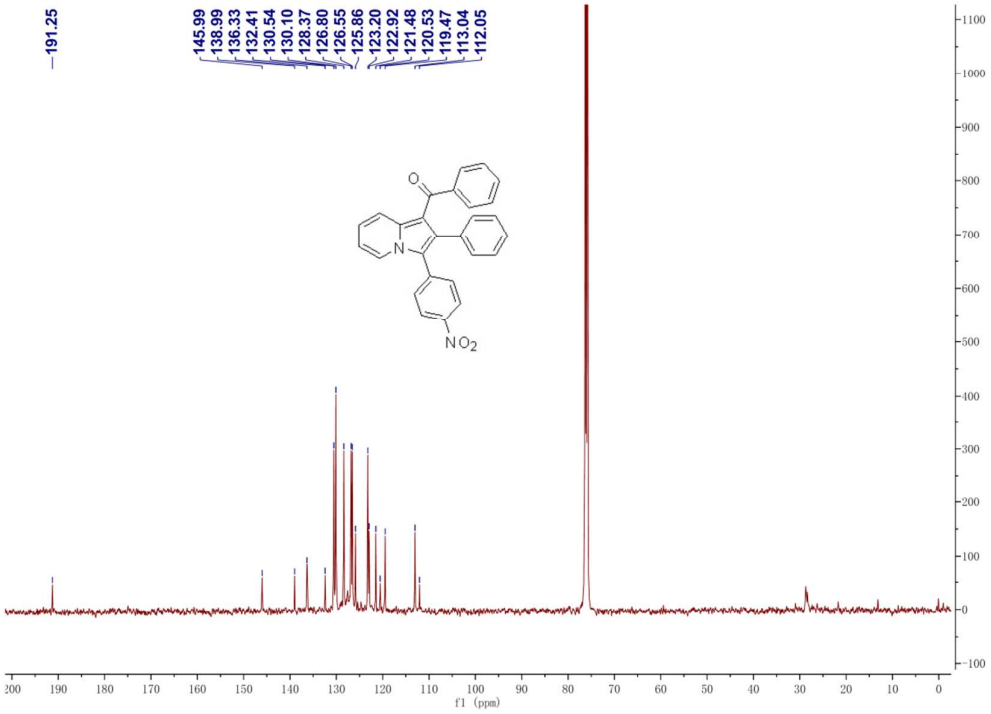
^{1}H NMR of **7h**


163.72
145.74
130.04
129.77
126.59
126.18
123.08
122.54
121.74
119.69
102.85
58.50
13.12
COOEt
N
NO2

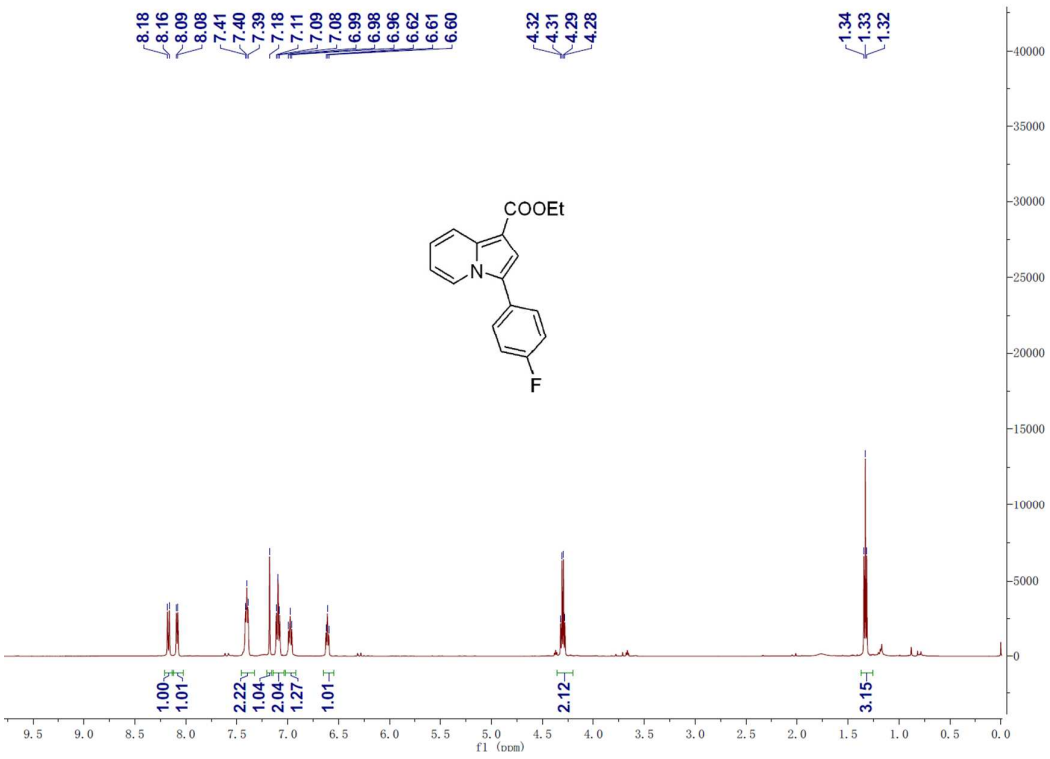
^{13}C NMR of **7h**


8.24
8.22
8.19
8.17
7.53
7.51
7.47
7.45
7.24
7.23
7.21
7.19
7.17
7.16
7.11
7.09
7.08
7.00
6.98
6.98
6.97
6.95
6.95
6.93
6.91
6.84
6.82
6.81
O
N
NO2
1.88
2.06
1.84
1.98
1.17
1.21
2.11
3.03
2.07
1.18
f1 (ppm)

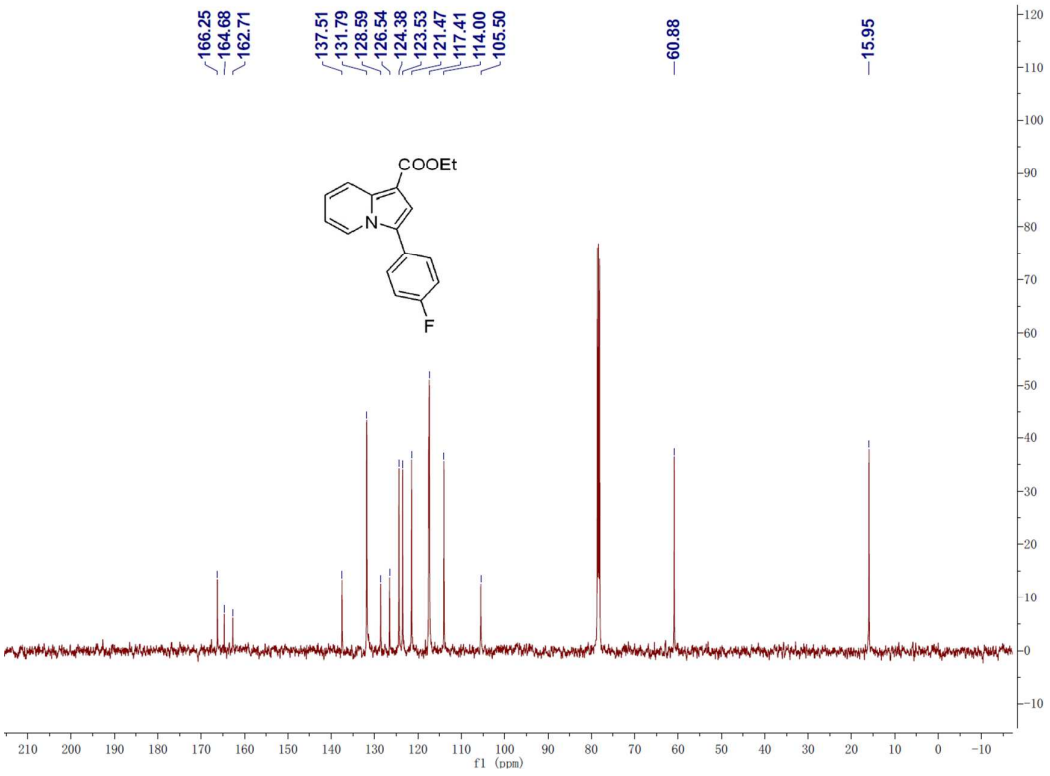
^{1}H NMR of **7i**



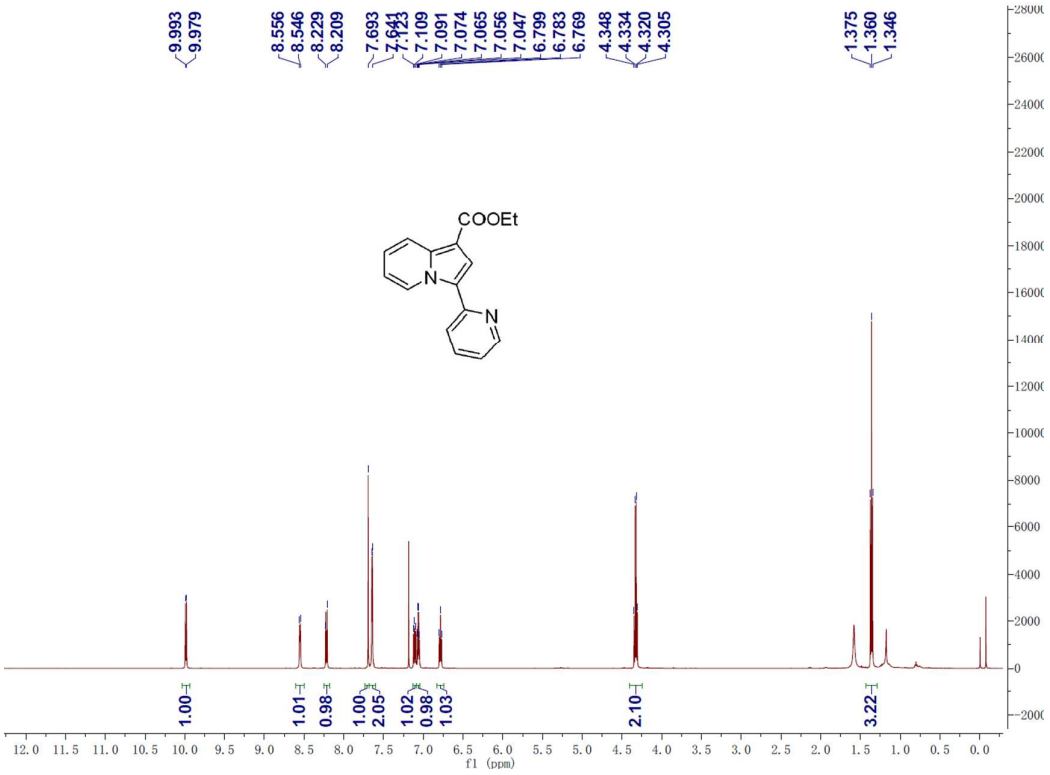
^{13}C NMR of **7i**


8.18
8.16
8.09
8.08
7.41
7.40
7.39
7.18
7.11
7.09
7.08
6.99
6.98
6.96
6.62
6.61
6.60
4.32
4.31
4.29
4.28
1.34
1.33
1.32
COOEt
N
F
1.00
1.01
2.22
1.04
2.04
1.27
1.01
2.12
3.15
f1 (ppm)

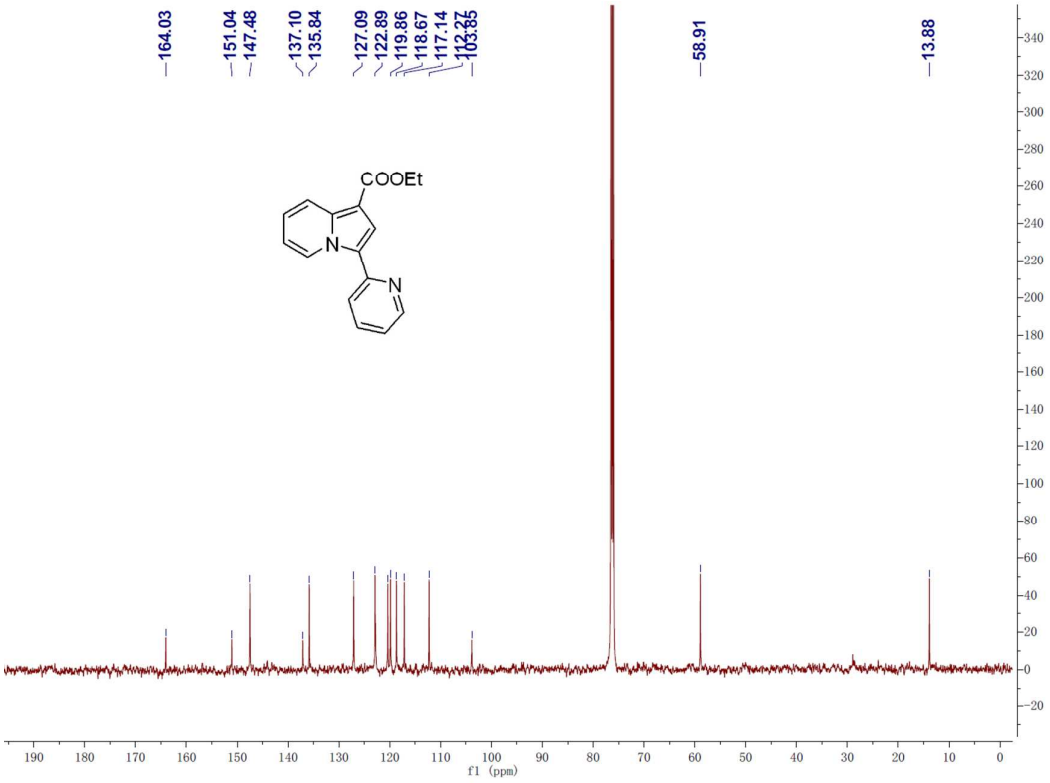
^{1}H NMR of **7j**


166.25
164.68
162.71
137.51
131.79
128.59
126.54
124.38
123.53
121.47
117.41
114.00
105.50
60.88
15.95
COOEt
N
F
f1 (ppm)

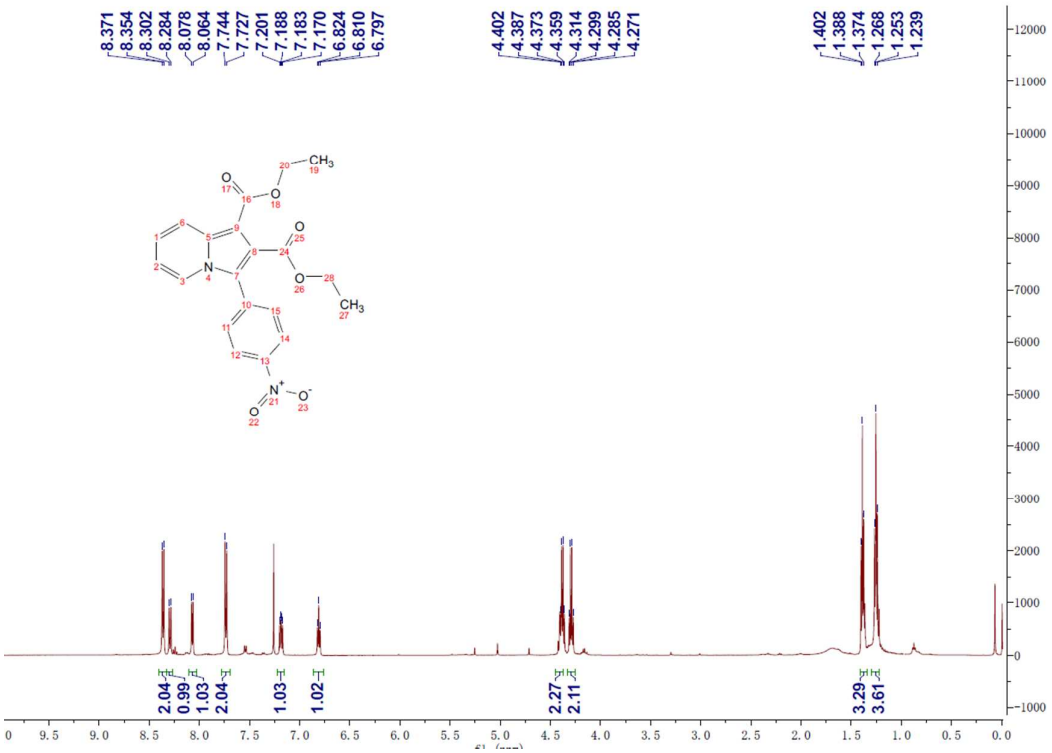
^{13}C NMR of **7j**


9.993
9.979
8.556
8.546
8.229
8.209
7.693
7.641
7.123
7.109
7.091
7.074
7.065
7.056
7.047
6.799
6.783
6.769
4.348
4.334
4.320
4.305
1.375
1.360
1.346
COOEt
N
N
1.00
1.01
0.98
1.00
2.05
1.02
0.98
1.03
2.10
3.22
f1 (ppm)

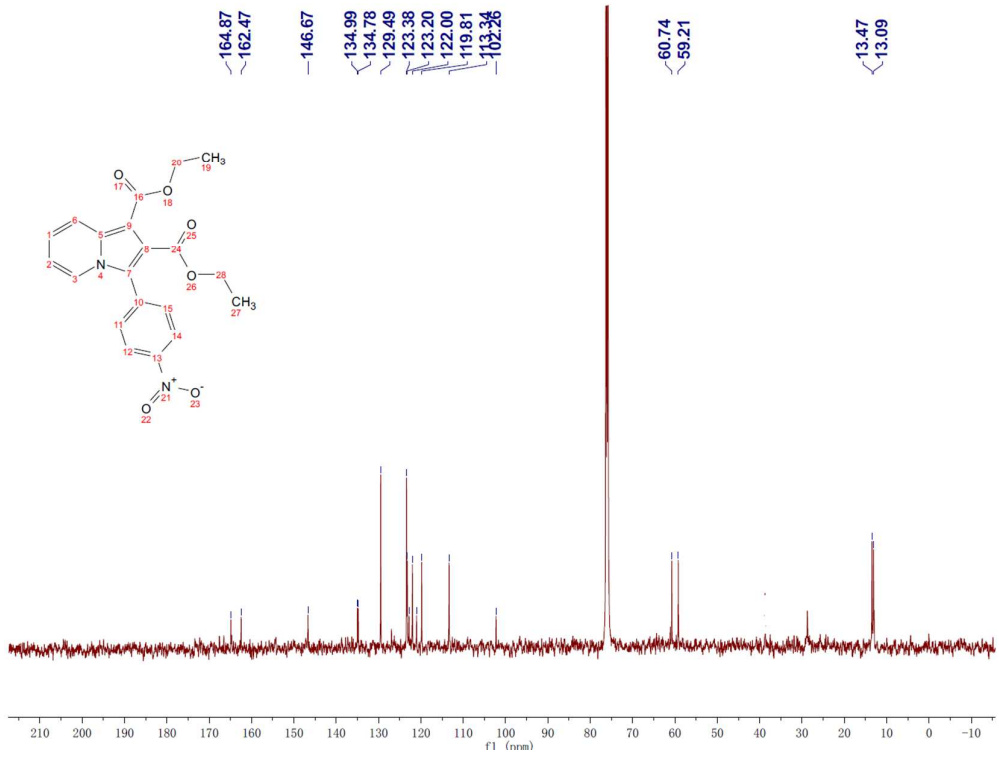
^{1}H NMR of **7k**



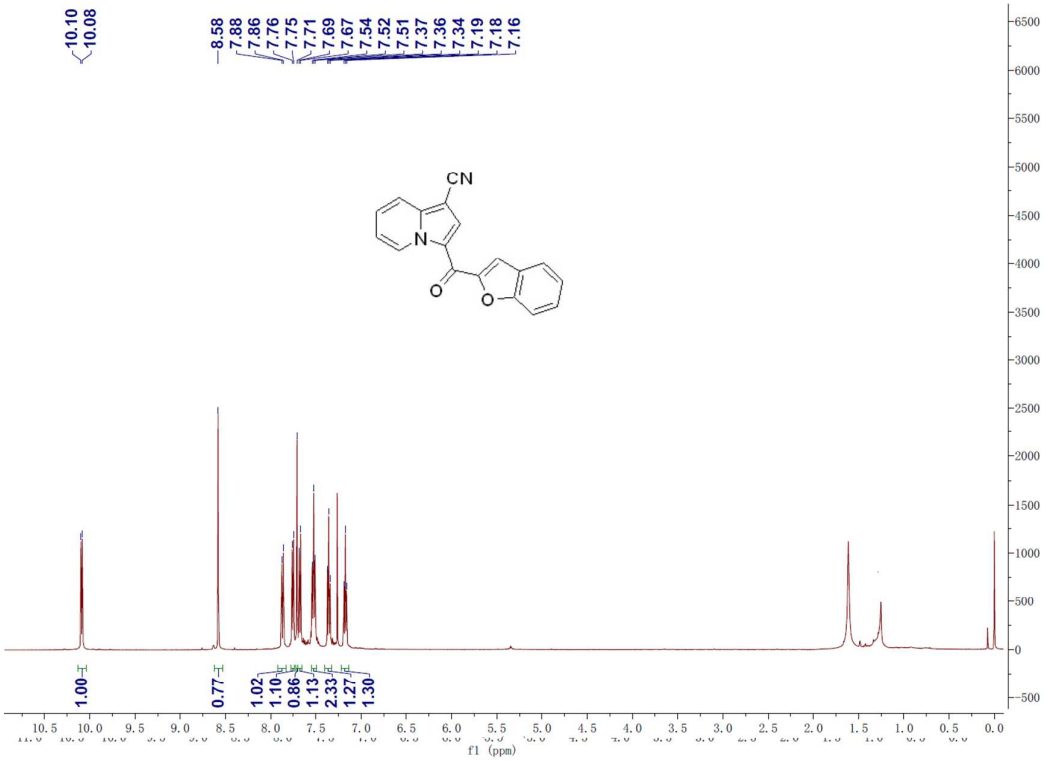
^{13}C NMR of **7k**


8.371
8.354
8.302
8.284
8.078
8.064
7.744
7.727
7.201
7.188
7.183
7.170
6.824
6.810
6.797
4.402
4.387
4.373
4.359
4.314
4.299
4.285
4.271
1.402
1.388
1.374
1.268
1.253
1.239
2.04
0.99
1.03
2.04
1.03
1.02
2.27
2.11
3.29
3.61

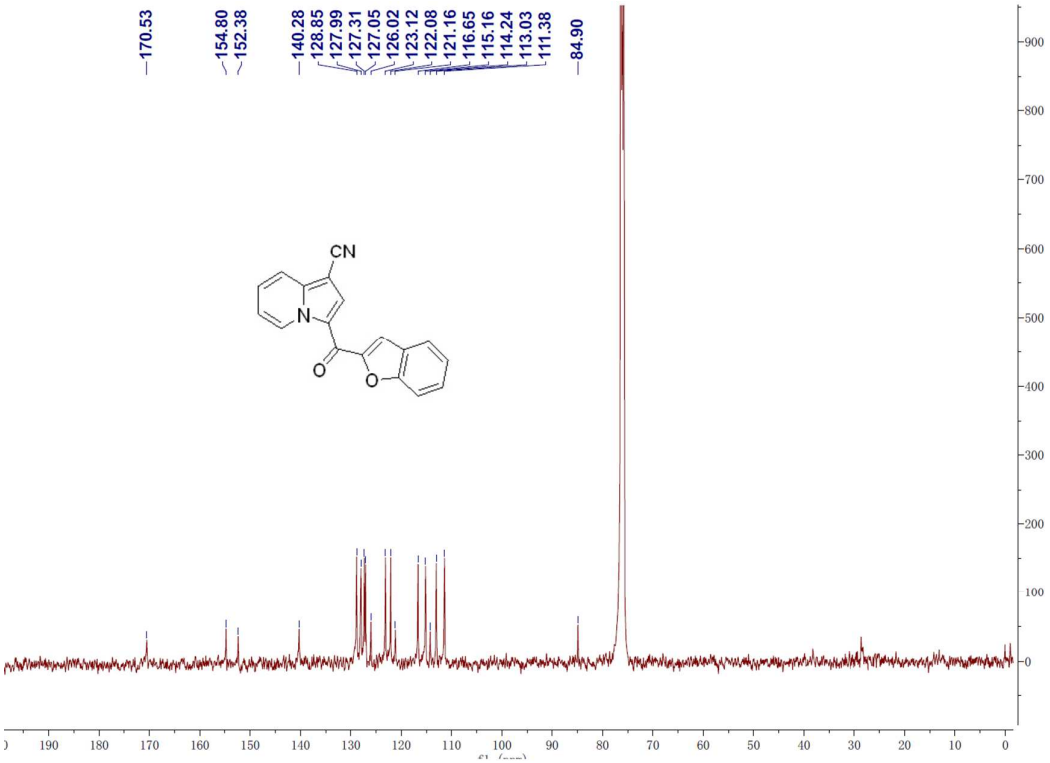
^{1}H NMR of **7l**


164.87
162.47
146.67
134.99
134.78
129.49
123.38
123.20
122.00
119.81
113.34
102.26
60.74
59.21
13.47
13.09

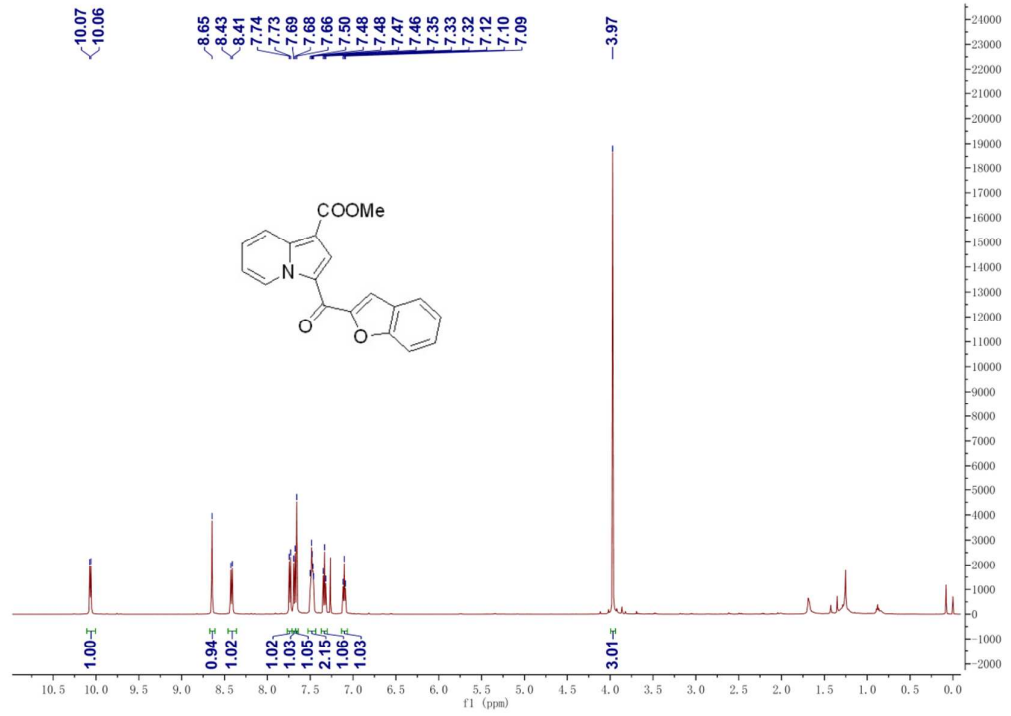
^{13}C NMR of **7l**



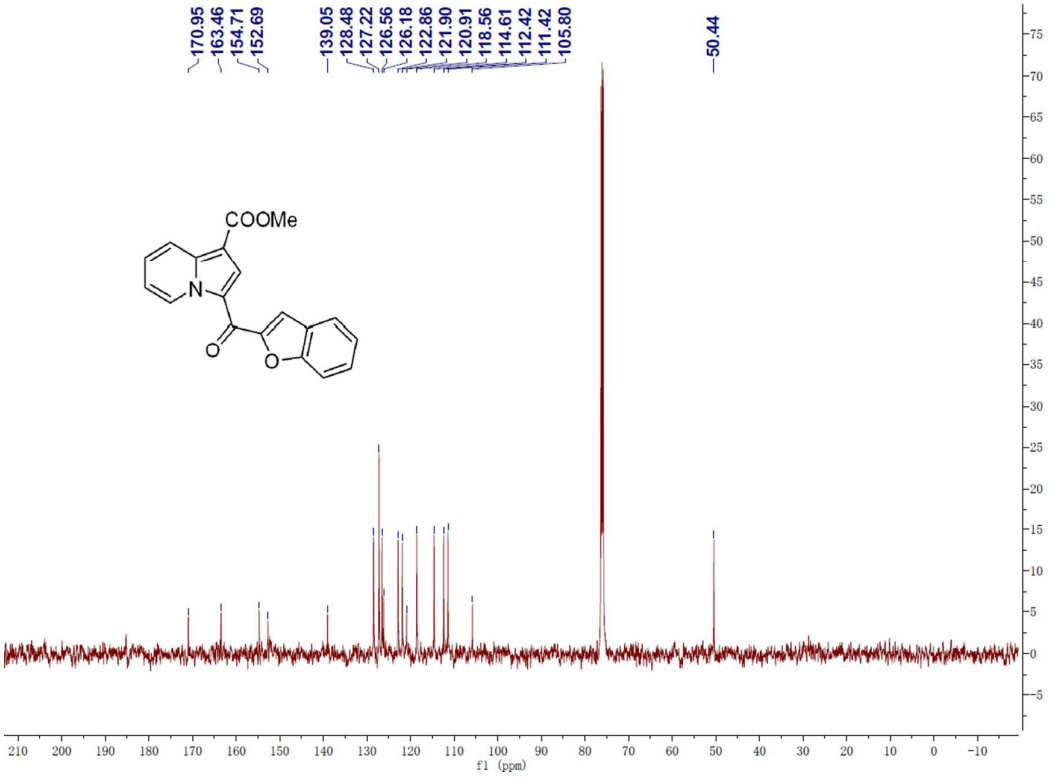
^{1}H NMR of **8a**



^{13}C NMR of **8a**



^{1}H NMR of **8b**


170.95
163.46
154.71
152.69
139.05
128.48
127.22
126.56
126.18
122.86
121.90
120.91
118.56
114.61
112.42
111.42
105.80
50.44
COOMe
N
O
O
f1 (ppm)

^{13}C NMR of **8b**