Electronic Supplementary Information for Synthesis of Substituted Indolizines via Radical Oxidative Decarboxylative Annulation of 2-(Pyridin-2-yl)acetate Derivatives with α,β-Unsaturated Carboxylic Acids

Jian Gu,[a] Chun Cai[a]*

[a] Chemical Engineering College, Nanjing University of Science & Technology, Nanjing, Jiangsu 210094, P. R. China

* Corresponding Author Fax: (+86)-25-8431-5030; phone: (+86)-25-8431-5514; e-mail: c.cai@mail.njust.edu.cn

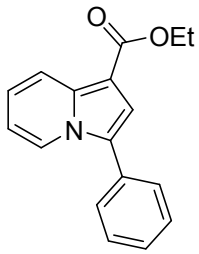
1. General Information

All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are characterized by ^{1}H NMR, ^{13}C NMR , and compared with previously reported data. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Thermo Scientific ISQ LT GC-MS instrument in the electron ionization (EI) mode. ^{1}H NMR and ^{13}C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in $CDCl_3$, respectively, and chemical shifts are reported in ppm. High-resolution mass spectra data were obtained on Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. General Procedure

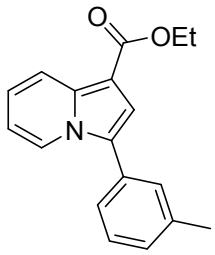
General Procedure for the Synthesis of Indolizines: A mixture of 2-(pyridin-2-yl)acetate derivatives (1.0 mmol), α,β-unsaturated carboxylic acids (0.5 mmol), $Cu(OAc)_2$ (0.5 mmol), TBP (1.5 mmol) in DCE (2.0 mL) was stirred at 110°C for 16 h. Upon completion, the reaction mixture was diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layer. The volatiles were removed under vacuum to afford the crude product. The crude product was purified by column chromatography on silica gel and eluted with EtOAc/hexanes (5/95) to afford the desired pure product.

3. Characterization Data



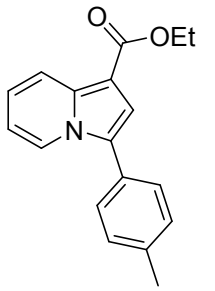
3aa : ethyl 3-phenylindolizine-1-carboxylate **3aa**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (t, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.31 (s, 1H), 7.10 – 7.03 (m, 1H), 6.69 (t, *J* = 6.8 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.20 (s), 136.48 (s), 131.39 (s), 129.23 (s), 128.74 (s), 128.14 (s), 126.56 (s), 123.49 (s), 122.38 (s), 120.31 (s), 116.24 (s), 112.73 (s), 104.39 (s), 59.70 (s), 14.82 (s). MS (EI) *m/z*: 265 [M^+].



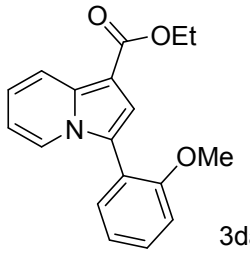
3ba : ethyl 3-m-tolylindolizine-1-carboxylate **3ba**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 16.4, 8.1 Hz, 2H), 7.35 (dd, *J* = 14.5, 8.4 Hz, 3H), 7.29 (s, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.09 – 7.03 (m, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.21 (s), 138.98 (s), 136.45 (s), 131.31 (s), 129.46 (s), 129.07(s), 128.93 (s), 126.73 (s), 125.73 (s), 123.60 (s), 122.28 (s), 120.28 (s), 116.14 (s), 112.64 (s), 104.32 (s), 59.66 (s), 21.61 (s), 14.81 (s). MS (EI) *m/z*: 279 [M^+].



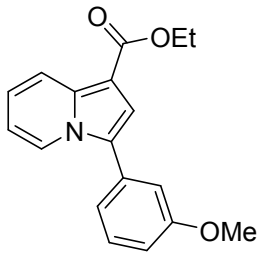
3ca : ethyl 3-p-tolylindolizine-1-carboxylate **3ca**[1].

^{1}H NMR (500 MHz, $CDCl_3$) 1H NMR (500 MHz, $CDCl_3$) δ 8.32 – 8.23 (m, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.10 – 7.01 (m, 1H), 6.69 (t, J = 6.8 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.24 (s), 138.08 (s), 136.35 (s), 129.90 (s), 128.70 (s), 126.64 (s), 123.54 (s), 122.22 (s), 120.26 (s), 115.94 (s), 112.60 (s), 104.23 (s), 59.66 (s), 21.45 (s), 14.82 (s). MS (EI) *m/z*: 279 [M^+].



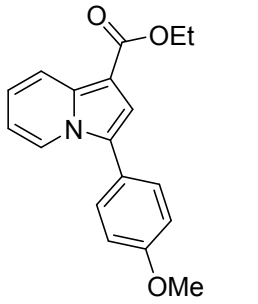
3da : ethyl 3-(2-methoxyphenyl)indolizine-1-carboxylate **3da**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.0 Hz, 1H), 7.69 (d, *J* = 7.0 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.40 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.29 (s, 1H), 7.08 (t, *J* = 7.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.67 (t, *J* = 6.8 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.30 (s), 157.59 (s), 136.32 (s), 132.54 (s), 130.29 (s), 125.34 (s), 123.88 (s), 122.16 (s), 121.19 (s), 120.10(s), 119.80 (s), 116.75 (s), 111.82 (s), 111.25 (s), 103.91 (s), 59.54 (s), 55.58 (s), 14.85 (s). MS (EI) *m/z*: 295 [M^+].



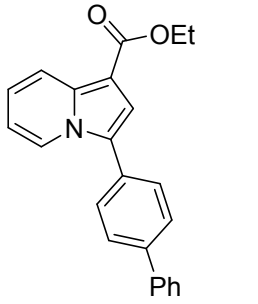
3ea : ethyl 3-(3-methoxyphenyl)indolizine-1-carboxylate **3ea**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.1 Hz, 1H), 8.26 (d, *J* = 9.1 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.31 (s, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 10.3 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.16 (s), 160.26 (s), 136.52 (s), 132.65 (s), 130.23 (s), 126.42 (s), 123.66 (s), 122.39 (s), 120.93 (s), 120.29 (s), 116.26 (s), 114.33 (s), 113.70 (s), 112.73 (s), 104.37 (s), 59.69 (s), 55.49 (s), 14.80 (s). MS (EI) *m/z*: 295 [M^+].



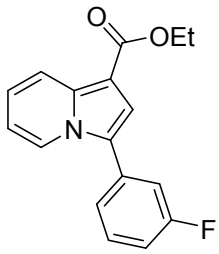
3fa : ethyl 3-(4-methoxyphenyl)indolizine-1-carboxylate **3fa**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 30.7, 8.1 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.24 (s, 1H), 7.02 (dd, *J* = 14.9, 8.2 Hz, 3H), 6.65 (t, *J* = 6.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.23 (s), 159.59 (s), 136.17 (s), 130.24 (s), 126.38 (s), 123.70 (s), 123.45 (s), 122.12 (s), 120.20 (s), 115.72 (s), 114.64 (s), 112.57 (s), 104.08 (s), 59.64 (s), 55.49 (s), 14.82 (s). MS (EI) *m/z*: 295 [M^+].



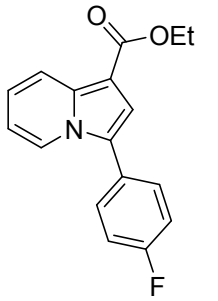
3ga : ethyl 3-(biphenyl-4-yl)indolizine-1-carboxylate **3ga**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.1 Hz, 1H), 8.29 (d, *J* = 9.1 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.65 (dd, *J* = 14.8, 7.8 Hz, 4H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.34 (m, 2H), 7.15 – 7.04 (m, 1H), 6.74 (t, *J* = 7.2 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.18 (s), 140.86 (s), 140.54 (s), 136.64 (s), 129.06 (s), 127.88 (s), 127.75(s), 127.17 (s), 123.58 (s), 122.44 (s), 120.38 (s), 116.38 (s), 112.83 (s), 104.58 (s), 59.73 (s), 14.83 (s). HRMS (ESI) Calcd. For 364.1313, $C_{23}H_{19}NO_2$ [M-Na]$^+$, found 364.1309.



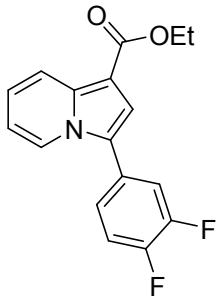
3ha ： ethyl 3-(3-fluorophenyl)indolizine-1-carboxylate **3ha**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 2H), 7.55 (s, 1H), 7.43 (dd, *J* = 4.2, 2.7 Hz, 2H), 7.40 – 7.36 (m, 1H), 7.33 (s, 1H), 7.10 (dd, *J* = 9.6, 6.3 Hz, 1H), 6.82 – 6.72 (m, 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 164.98 (s), 144.16 (s), 136.72 (s), 135.13 (s), 133.17 (s), 130.48 (s), 128.54 (s), 128.32 (d, *J* = 51.6 Hz), 126.63 (s), 123.29 (s), 122.66 (s), 120.41 (s), 116.80 (s), 113.07 (s), 104.71 (s), 59.77 (s), 14.78 (s). HRMS (ESI) Calcd. For 306.0906, $C_{17}H_{14}FNO_2$ [M-Na]$^+$, found 306.0907.



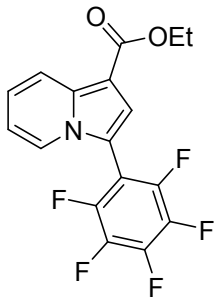
3ia : ethyl 3-(4-fluorophenyl)indolizine-1-carboxylate **3ia**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.1 Hz, 1H), 8.18 (d, *J* = 7.1 Hz, 1H), 7.50 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.27 (s, 1H), 7.19 (t, *J* = 8.6 Hz, 2H), 7.12 – 7.03 (m, 1H), 6.71 (t, *J* = 7.3 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 165.11 (s), 163.54 (s), 161.57 (s), 136.37 (s), 130.64 (s), 127.44 (s), 125.40 (s), 123.23 (s), 122.39 (s), 120.33 (s), 116.30 (d, *J* = 20.7 Hz), 115.85 – 115.44 (m), 112.85 (s), 104.36 (s), 59.73 (s), 14.79 (s). MS (EI) *m/z*: 283 [M$^+$].



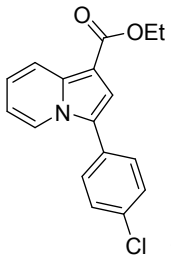
3ja : ethyl 3-(3,4-difluorophenyl)indolizine-1-carboxylate **3ja**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 33.3, 8.1 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.28 (dd, *J* = 15.1, 6.1 Hz, 3H), 7.15 – 7.00 (m, 1H), 6.75 (t, *J* = 7.4 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 164.93 (s), 143.39 (s), 136.58 (s), 128.37 (s), 124.58 (d, *J* = 94.0 Hz), 124.20 – 123.92 (m), 123.06 (s), 122.64 (s), 120.44 (s), 118.89 (s), 119.00 – 117.61 (m), 117.61 – 117.16 (m), 116.72 (s), 113.15 (s), 104.64 (s), 59.79 (s), 14.75 (s). HRMS (ESI) Calcd. For 324.0812, $C_{17}H_{13}F_2NO_2$ [M-Na]$^+$, found 324.0809.



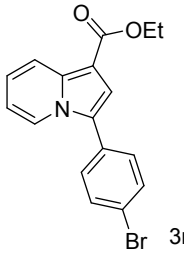
3ka：ethyl 3-(perfluorophenyl)indolizine-1-carboxylate **3ka**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9.1 Hz, 1H), 7.70 (d, *J* = 7.0 Hz, 1H), 7.46 (s, 1H), 7.23 – 7.13 (m, 1H), 6.83 (t, *J* = 7.3 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 164.59 (s), 137.36 (s), 124.01 (s), 123.38 (s), 120.30 (d, *J* = 12.5 Hz), 113.45 (s), 109.36 (s), 59.96 (s), 14.73 (s). HRMS (ESI) Calcd. For 378.0529, $C_{17}H_{10}F_5NO_2$ $[M\text{-}Na]^+$, found 378.0526.



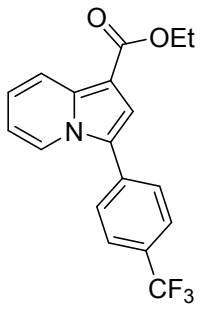
3la：ethyl 3-(4-chlorophenyl)indolizine-1-carboxylate **3la**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 26.3, 8.0 Hz, 2H), 7.45 (s, 4H), 7.28 (s, 1H), 7.11 – 7.03 (m, 1H), 6.70 (t, *J* = 6.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.03 (s), 136.60 (s), 133.93 (s), 129.89 (s), 129.48 (s), 125.20 (s), 123.24 (s), 122.54 (s), 120.39 (s), 116.50 (s), 112.98 (s), 104.60 (s), 59.76 (s), 14.79 (s). MS (EI) *m/z*: 299 $[M^+]$.



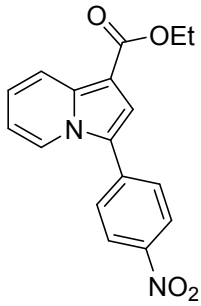
3ma：ethyl 3-(4-bromophenyl)indolizine-1-carboxylate **3ma**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 20.5, 8.1 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (s, 1H), 7.08 (dd, *J* = 9.2, 6.9 Hz, 1H), 6.72 (t, *J* = 7.4 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 165.01 (s), 144.42 (s), 136.65 (s), 132.43 (s), 130.15 (s), 125.21 (s), 123.23 (s), 122.55 (s), 122.03(s), 120.42 (s), 118.11 (s), 116.51 (s), 113.01 (s), 104.67 (s), 59.76 (s), 14.79 (s). MS (EI) *m/z*: 343 $[M^+]$.



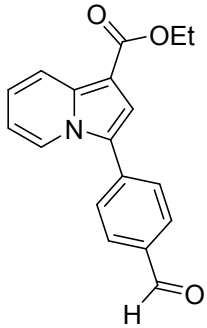
3na : ethyl 3-(4-(trifluoromethyl)phenyl)indolizine-1-carboxylate **3na**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 7.6, 4.6 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.37 (s, 1H), 7.11 (dd, *J* = 10.0, 6.6 Hz, 1H), 6.75 (t, *J* = 6.8 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 164.89 (s), 143.87 (s), 136.97 (s), 135.02 (s), 128.41 (d, *J* = 28.8 Hz), 126.39 (s), 126.11 (d, *J* = 28.1 Hz), 125.25 (s), 124.89 (s), 123.03 (d, *J* = 39.9 Hz), 122.41 (s), 120.51 (s), 120.00 (s), 117.20 (s), 113.24 (s), 105.02 (s), 59.82 (s), 14.74 (s). HRMS (ESI) Calcd. For 356.0874, $C_{18}H_{14}F_3NO_2$ [M-Na]$^+$, found 356.0871.



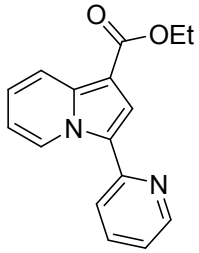
3oa : ethyl 3-(4-nitrophenyl)indolizine-1-carboxylate **3oa**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.23 (m, 4H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.46 (s, 1H), 7.20 – 7.13 (m, 1H), 6.82 (t, *J* = 6.9 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.67 (s), 146.75 (s), 137.94 (s), 137.60 (s), 128.21 (s), 124.72 (s), 124.11 (s), 123.45(s), 123.23(s), 120.74 (s), 118.33 (s), 113.76 (s), 105.77 (s), 59.97 (s), 14.75 (s). MS (EI) *m/z*: 310 [M$^+$].



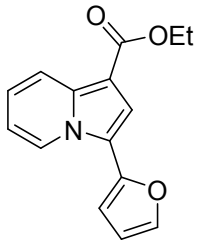
3pa : ethyl 3-(4-formylphenyl)indolizine-1-carboxylate **3pa**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.35 (dd, *J* = 44.8, 8.1 Hz, 2H), 8.00 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.43 (s, 1H), 7.18 – 7.09 (m, 1H), 6.79 (t, *J* = 6.8 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.52 (s), 164.84 (s), 137.35 (s), 135.35 (s), 130.67 (s), 128.75 (s), 128.29 (s), 125.14 (s), 123.42 (s), 123.16 (s), 120.60 (s), 117.80 (s), 113.44 (s), 105.39 (s), 59.89 (s), 14.76 (s). HRMS (ESI) Calcd. For 316.0950, $C_{18}H_{15}NO_3$ [M-Na]$^+$, found 316.0943.



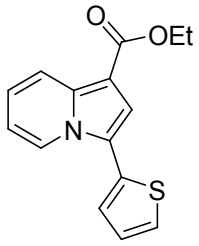
3qa : ethyl 3-(pyridin-2-yl)indolizine-1-carboxylate **3qa**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (d, *J* = 7.2 Hz, 1H), 8.63 (d, *J* = 4.8 Hz, 1H), 8.30 (d, *J* = 11.2 Hz, 1H), 7.77 (s, 1H), 7.72 (d, *J* = 3.2 Hz, 2H), 7.23 – 7.11 (m, 2H), 6.86 (t, *J* = 7.6 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.94 (s), 151.95 (s), 148.39 (s), 138.01 (s), 136.74 (s), 127.99 (s), 123.71 (s), 121.29 (s), 120.76 (s), 119.57 (s), 118.04 (s), 113.17 (s), 104.76 (s), 59.81 (s), 14.78 (s). HRMS (ESI) Calcd. For 289.0953, $C_{16}H_{14}N_2O_2$ [M-Na]$^+$, found 289.0951.



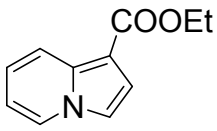
3ra : ethyl 3-(furan-2-yl)indolizine-1-carboxylate **3ra**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.0 Hz, 1H), 8.26 (d, *J* = 9.0 Hz, 1H), 7.54 (s, 1H), 7.47 (s, 1H), 7.14 – 7.06 (m, 1H), 6.80 (t, *J* = 6.8 Hz, 1H), 6.59 (d, *J* = 3.3 Hz, 1H), 6.55 (d, *J* = 1.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.91 (s), 141.83 (s), 125.14 (s), 122.68 (s), 120.10 (s), 116.05 (s), 113.25 (s), 111.52 (s), 107.07 (s), 59.80 (s), 14.76 (s). HRMS (ESI) Calcd. For 278.0793, $C_{15}H_{13}NO_3$ [M-Na]$^+$, found 278.0797.



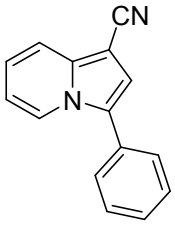
3sa : ethyl 3-(thiophen-2-yl)indolizine-1-carboxylate **3sa**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 50.2, 8.0 Hz, 2H), 7.38 (d, *J* = 5.0 Hz, 2H), 7.24 (d, *J* = 3.5 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.10 – 7.04 (m, 1H), 6.74 (dd, *J* = 9.9, 3.8 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 164.92 (s), 136.71 (s), 132.43 (s), 127.83 (s), 126.30 (s), 125.92 (s), 123.91 (s), 122.63 (s), 120.15 (s), 119.32 (s), 117.57 (s), 113.08 (s), 104.50 (s), 59.76 (s), 14.80 (s). HRMS (ESI) Calcd. For 294.0565, $C_{15}H_{13}NO_2S$ [M-Na]$^+$, found 294.0568.



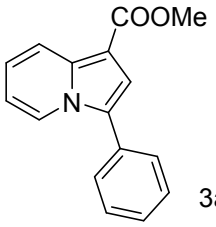
3ta : ethyl indolizine-1-carboxylate **3ta**[2].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.1 Hz, 1H), 7.99 (d, *J* = 6.9 Hz, 1H), 7.25 (d, *J* = 3.0 Hz, 1H), 7.22 (d, *J* = 2.9 Hz, 1H), 7.03 (dd, *J* = 9.6, 6.2 Hz, 1H), 6.69 (t, *J* = 6.8 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.12 (s), 135.85 (s), 126.12 (s), 122.23 (s), 120.10 (s), 116.34 (s), 113.69 (s), 112.46 (s), 104.20 (s), 59.57 (s), 14.76 (s). MS (EI) *m/z*: 189 [M^+].



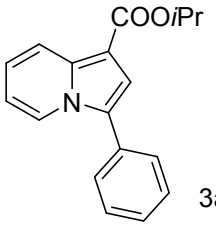
3ab : 3-phenylindolizine-1-carbonitrile **3ab**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.1 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.52 (d, *J* = 4.4 Hz, 4H), 7.48 – 7.42 (m, 1H), 7.12 – 7.07 (m, 1H), 7.06 (s, 1H), 6.75 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.56 (s), 130.35 (s), 129.40 (s), 128.84 (s), 128.76(s), 127.12 (s), 123.88 (s), 122.48 (s), 118.38 (s), 117.05(s), 116.41 (s), 113.24 (s), 82.38 (s). MS (EI) *m/z*: 218 [M^+].



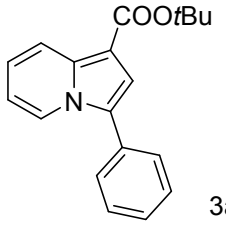
3ac : methyl 3-phenylindolizine-1-carboxylate **3ac**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 14.9, 8.1 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.30 (s, 1H), 7.13 – 7.03 (m, 1H), 6.71 (t, *J* = 6.8 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.55(s), 136.57 (s), 131.36 (s), 129.23 (s), 128.77(s), 128.17(s), 126.64 (s), 123.50 (s), 122.48 (s), 120.27 (s), 116.16 (s), 112.78 (s), 51.07 (s). MS (EI) *m/z*: 251 [M^+].



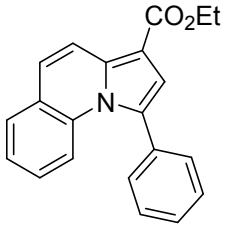
3ad : isopropyl 3-phenylindolizine-1-carboxylate **3ad**[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 – 8.21 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.31 (s, 1H), 7.12 – 7.02 (m, 1H), 6.69 (t, *J* = 6.8 Hz, 1H), 5.30 (dt, *J* = 12.5, 6.2 Hz, 1H), 1.41 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.77 (s), 136.38 (s), 131.44 (s), 129.22 (s), 128.73 (s), 128.11 (s), 126.48 (s), 123.45 (s), 122.27 (s), 120.34 (s), 116.32 (s), 112.66 (s), 104.86 (s), 66.79 (s), 22.46 (s). MS (EI) *m/z*: 279 [M^+].



3ae： tert-butyl 3-phenylindolizine-1-carboxylate **3ae**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 15.3, 8.1 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.28 (s, 1H), 7.09 – 7.00 (m, 1H), 6.66 (t, *J* = 6.8 Hz, 1H), 1.66 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.76 (s), 136.06 (s), 131.52 (s), 129.21 (s), 128.74 (s), 128.07 (s), 126.27 (s), 123.40 (s), 122.02 (s), 120.33 (s), 116.48 (s), 112.52 (s), 106.06 (s), 79.75 (s), 28.80 (s). HRMS (ESI) Calcd. For 316.1313, $C_{19}H_{19}NO_2$ $[M\text{-}Na]^+$, found 316.1308.

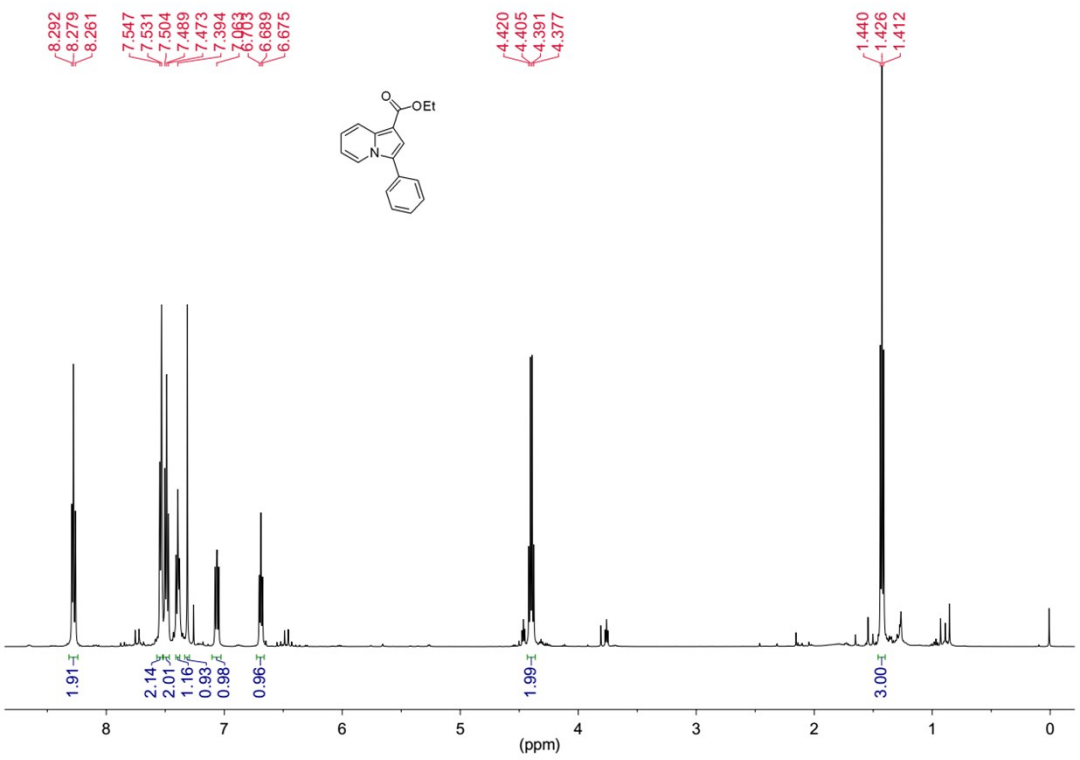


3af： ethyl 1-phenylpyrrolo[1,2-a]quinoline-3-carboxylate **3af**[1].

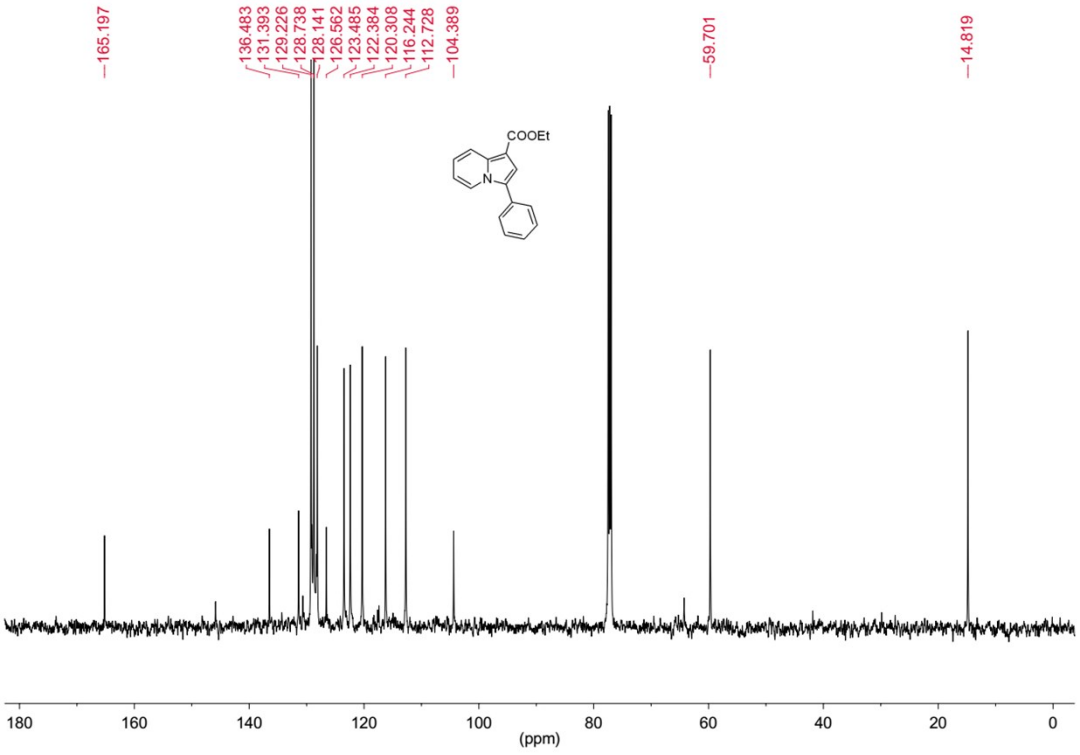
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.4 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.48 (dt, *J* = 5.7, 4.2 Hz, 6H), 7.37 (d, *J* = 9.4 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.18 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.13 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.08 (s), 134.59 (s), 133.92 (s), 132.97 (s), 129.41 (s), 128.62 (s), 127.74 (s), 127.30 (s), 127.11(s), 126.32 (s), 124.40 (s), 123.26 (s), 122.94 (s), 117.76 (s), 117.00 (s), 116.70 (s), 106.02 (s), 58.80 (s), 13.64 (s). MS (EI) m/z: 315 $[M^+]$.

[1] R. Liu, J. Hong, C. Lu, M. Xu, J. Gao, Y. Jia, *Org. Lett.*, 2015, **17**, 3050
[2] L. Huang, T. Niu, J. Wu, Y. Zhang, *J. Org. Chem.,* 2011, **6**, 1759

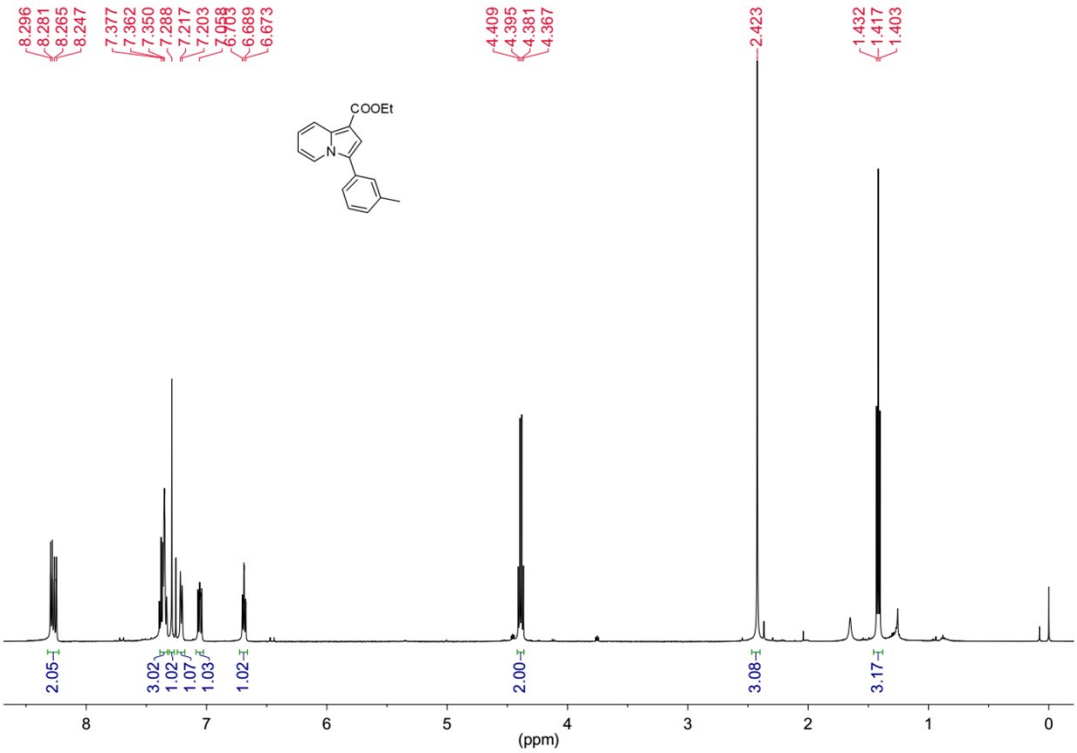
4. NMR Spectra of All Products



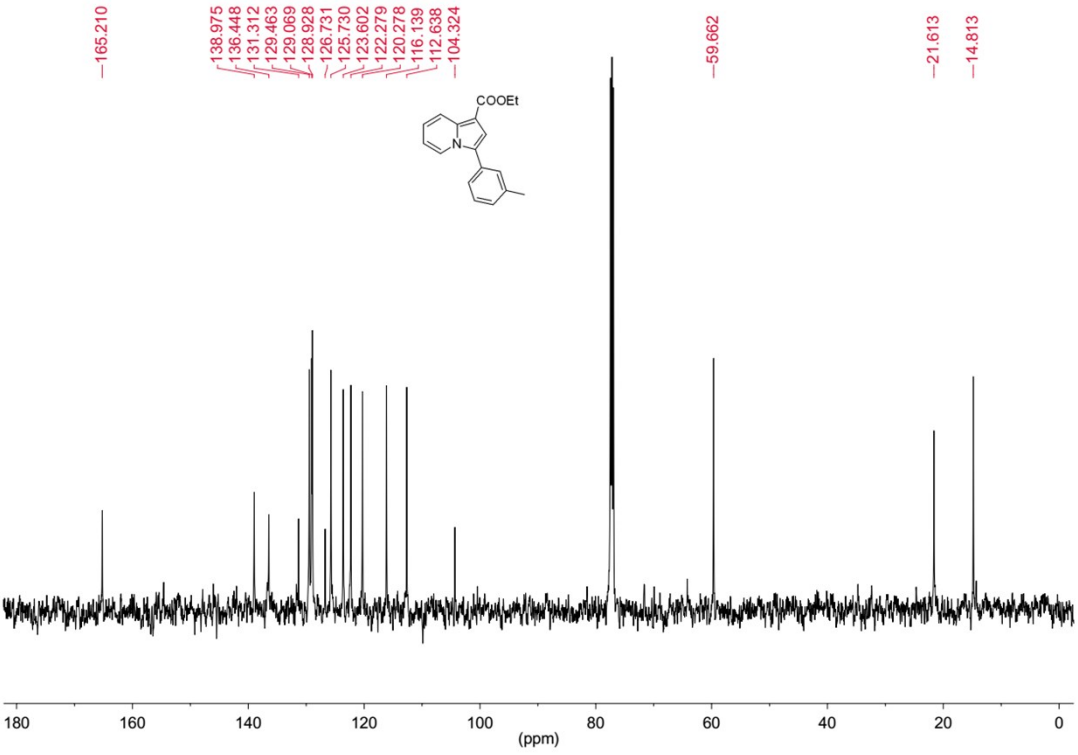
^{1}H NMR **3aa**



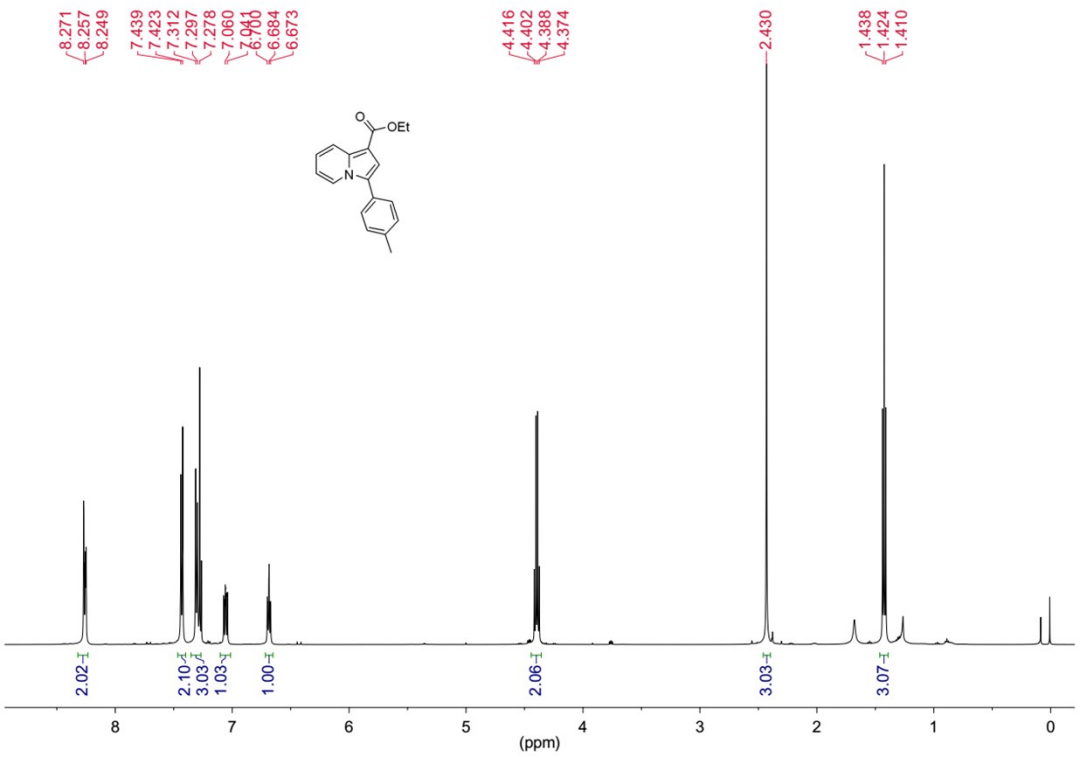
^{13}C NMR **3aa**



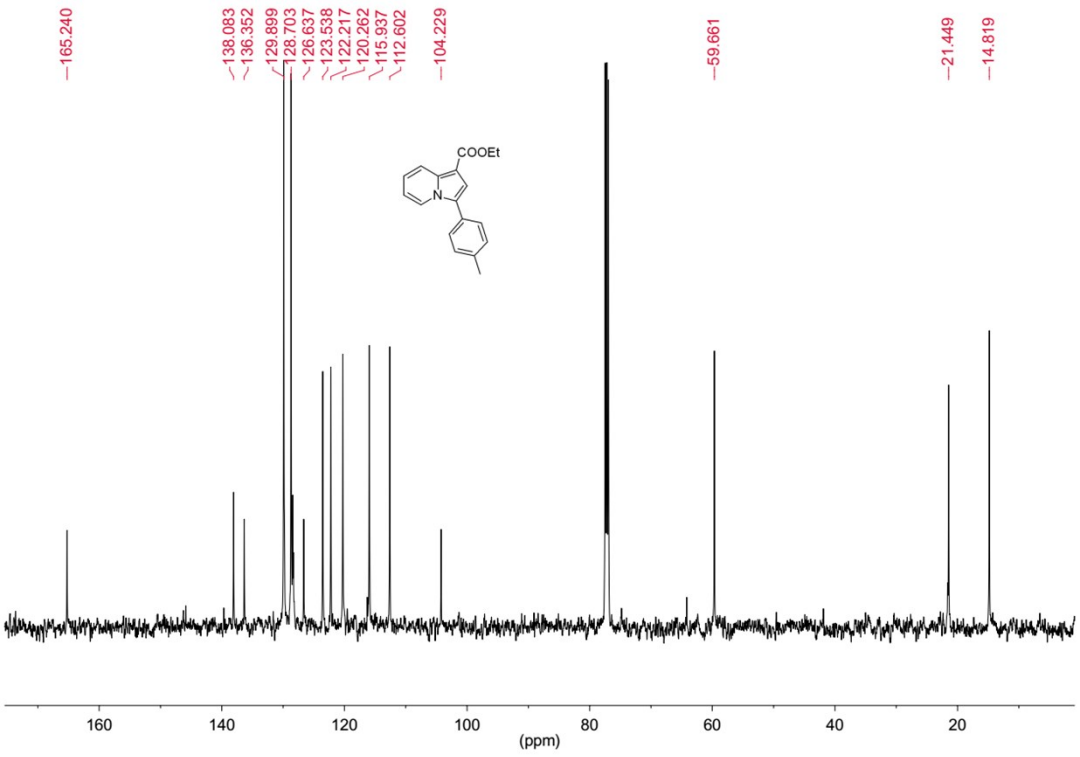
^{1}H NMR **3ba**



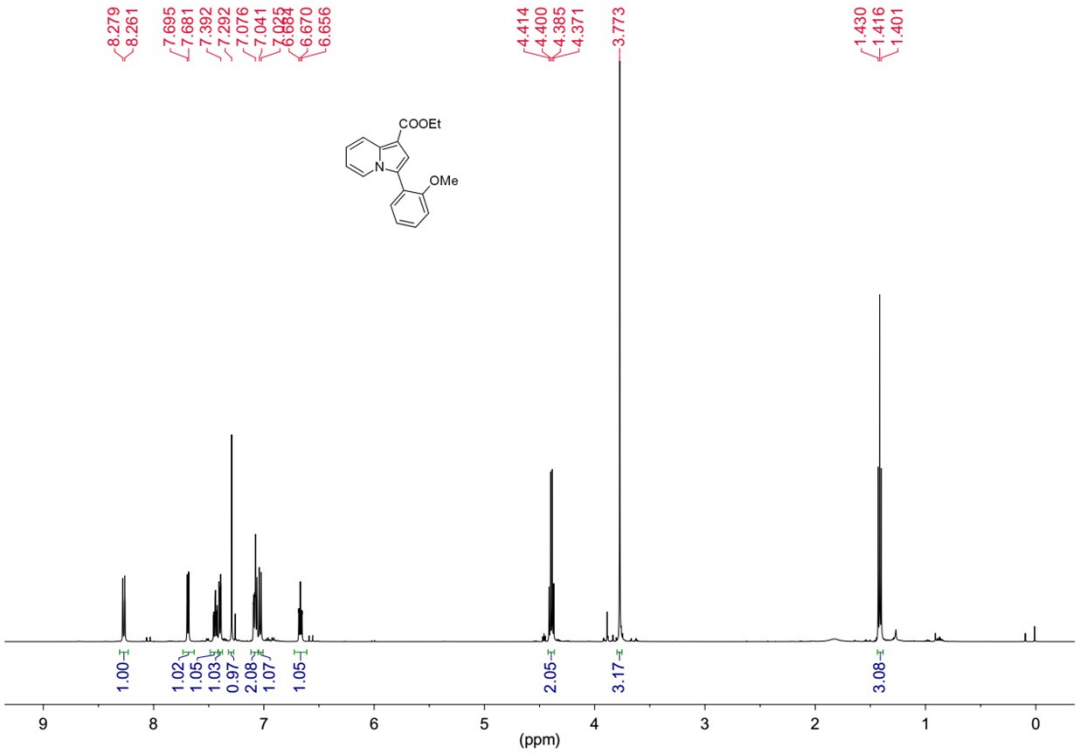
^{13}C NMR **3ba**



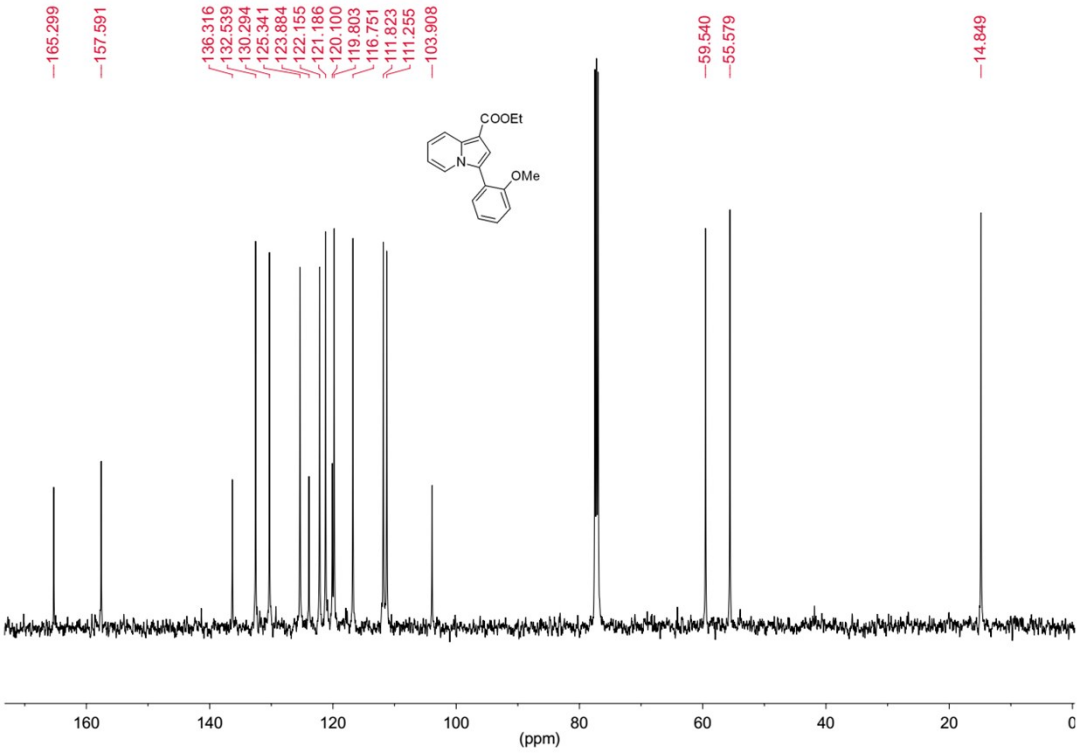
^{1}H NMR **3ca**



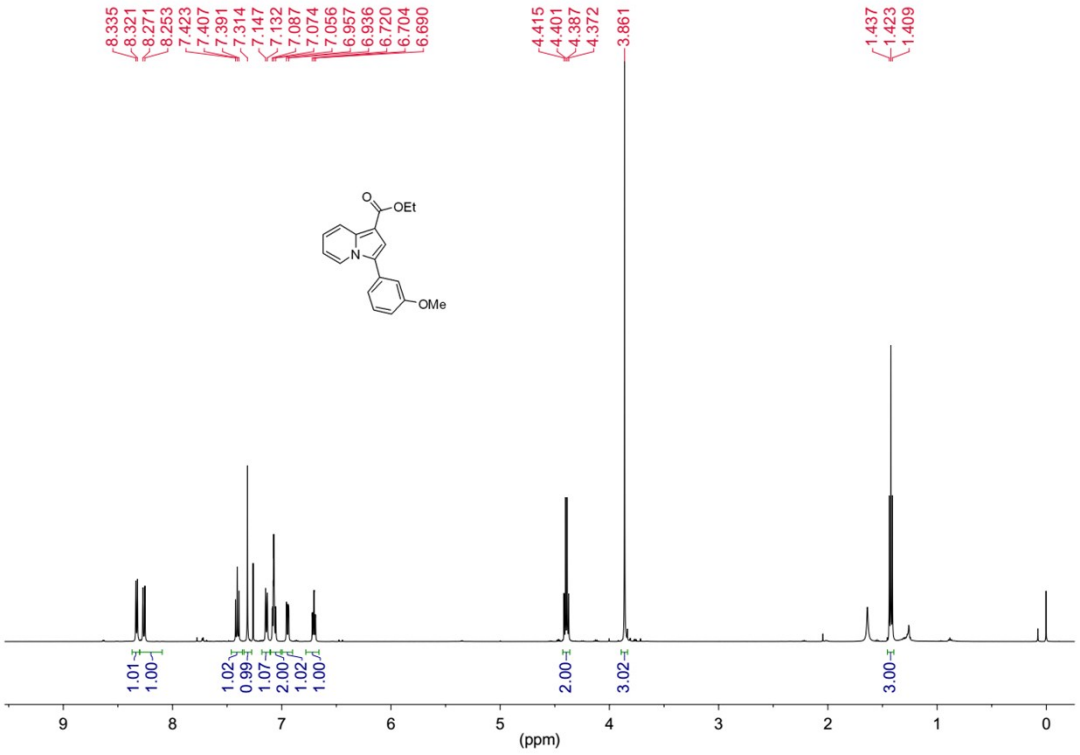
^{13}C NMR **3ca**



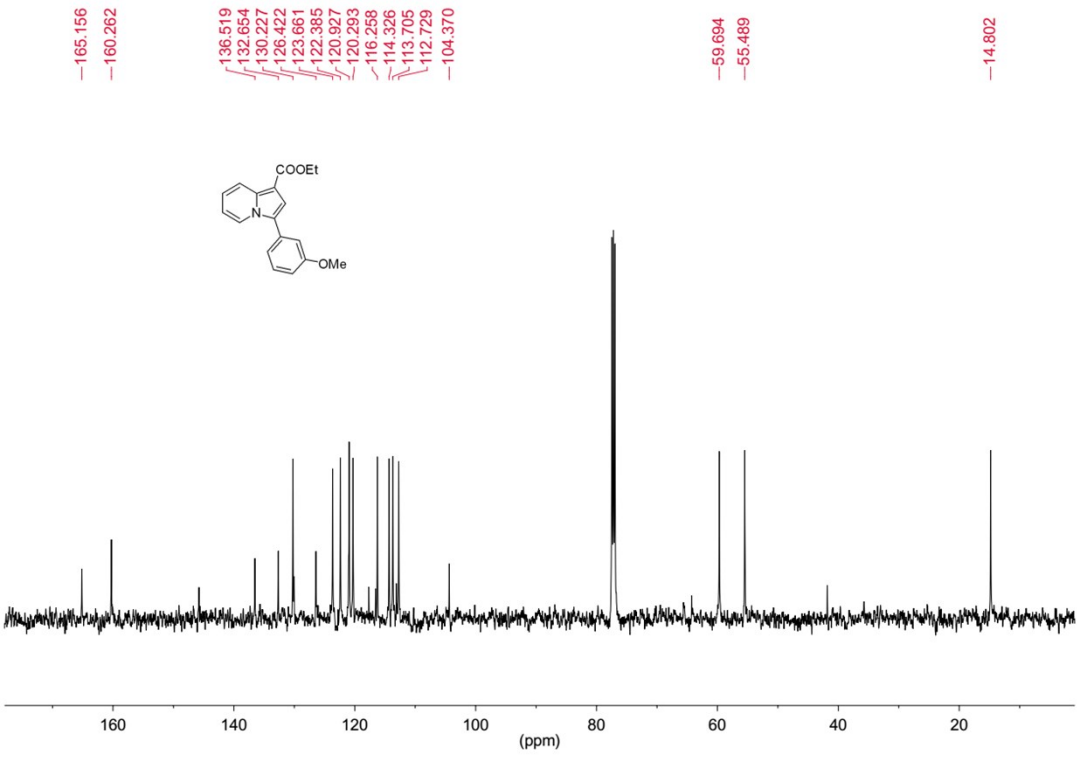
^{1}H NMR **3da**



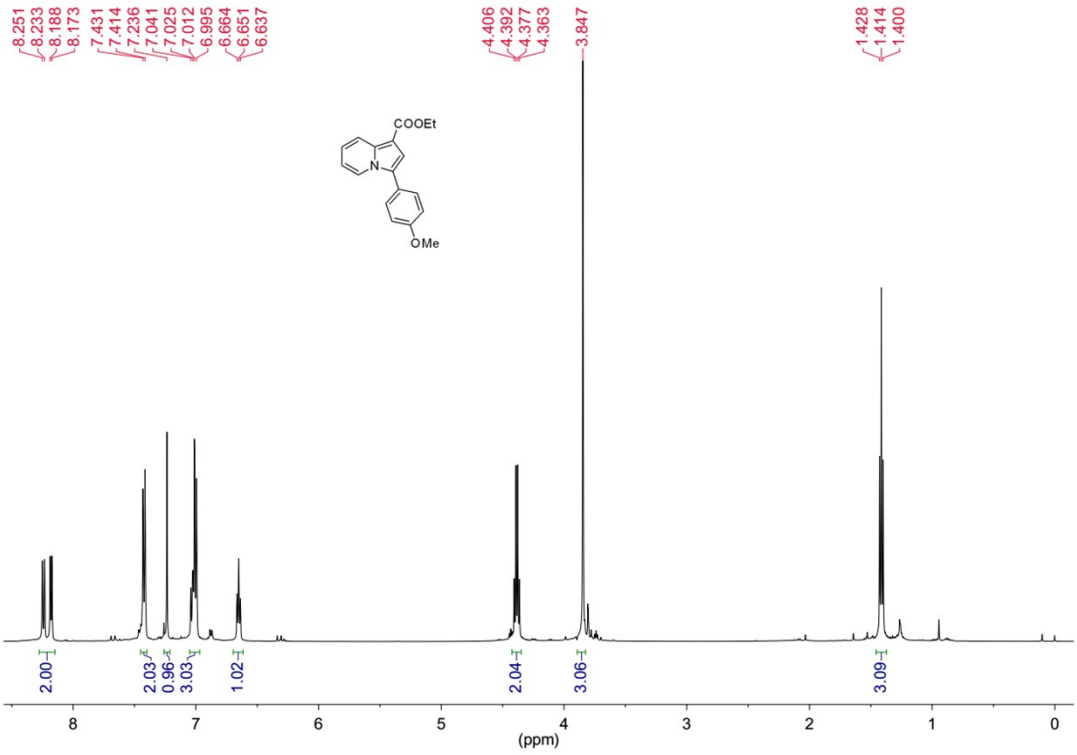
^{13}C NMR **3da**



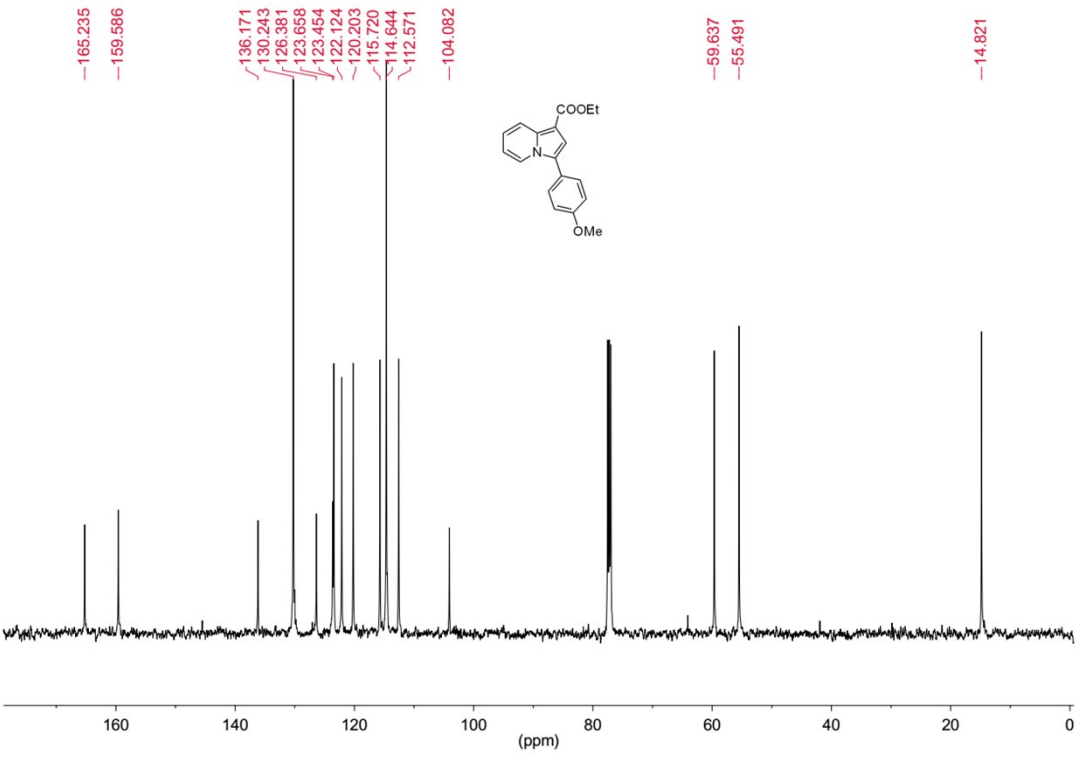
^{1}H NMR **3ea**



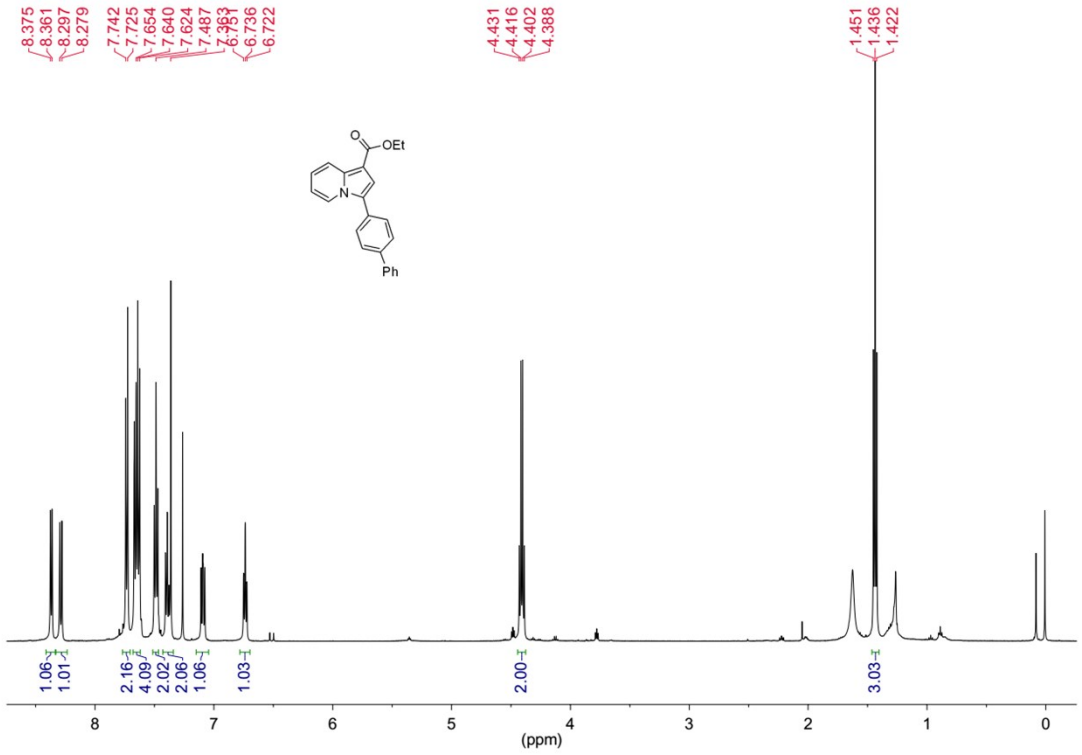
^{13}C NMR **3ea**



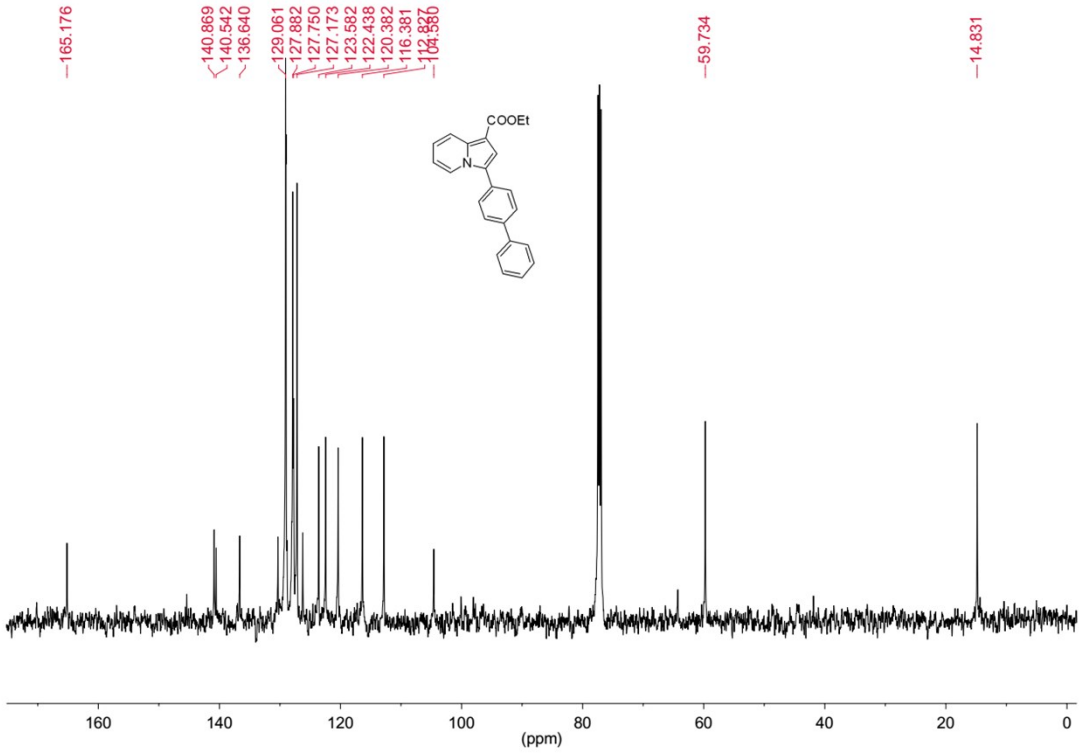
^{1}H NMR **3fa**



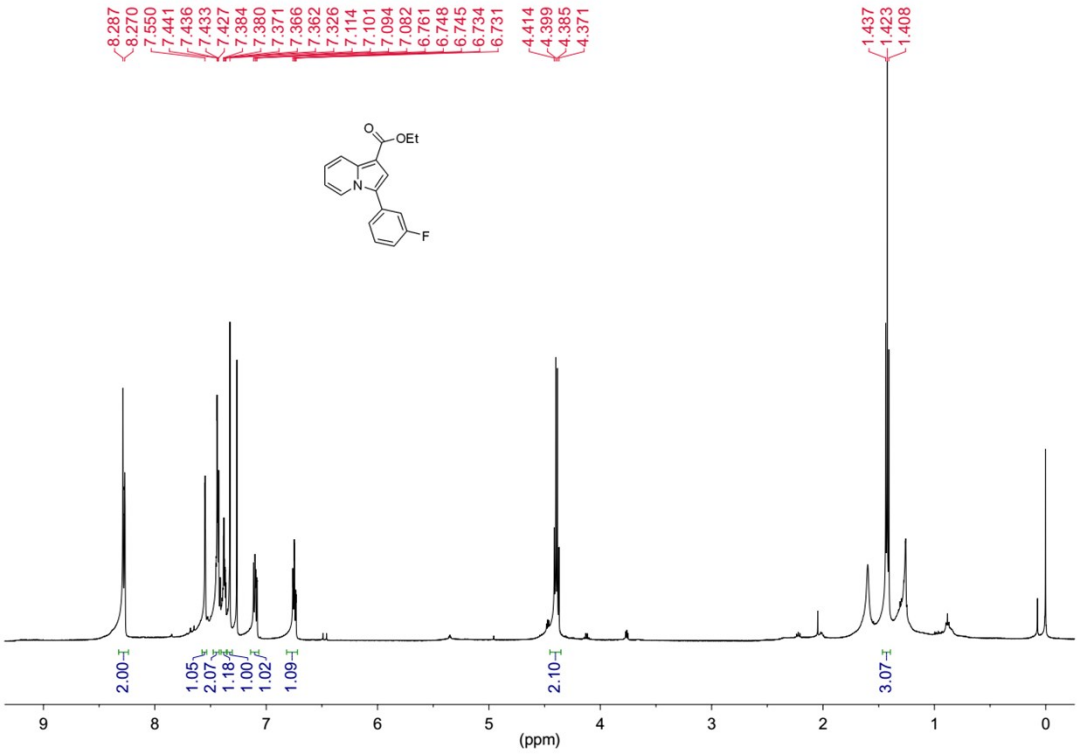
^{13}C NMR **3fa**



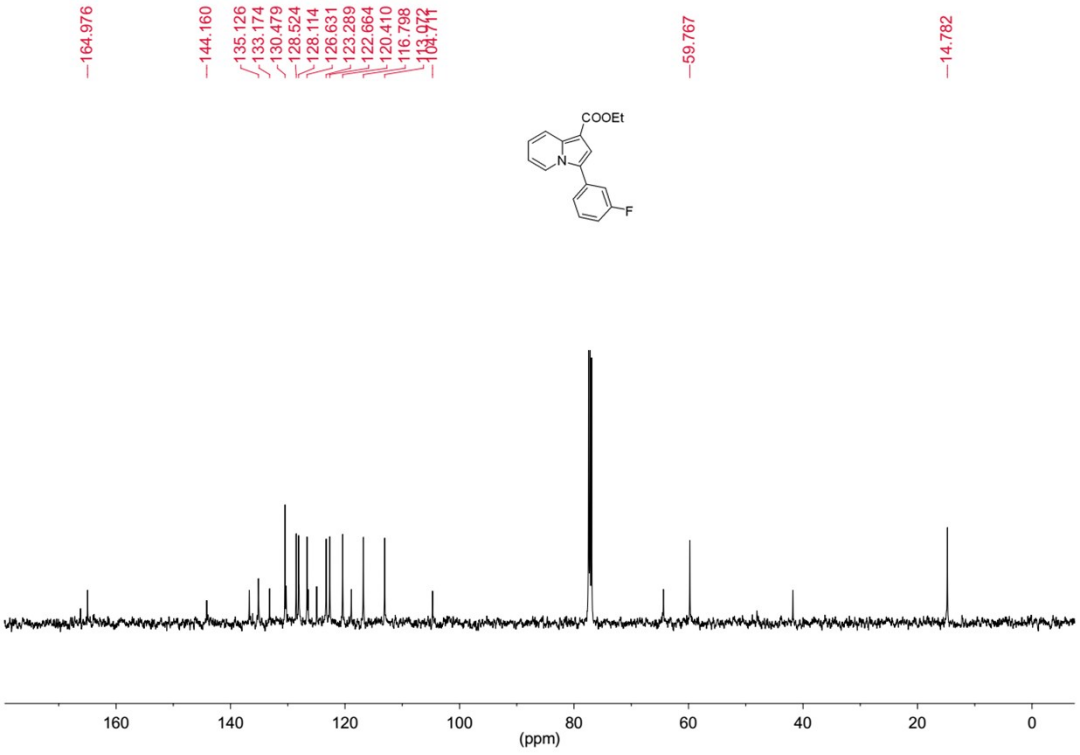
^{1}H NMR **3ga**



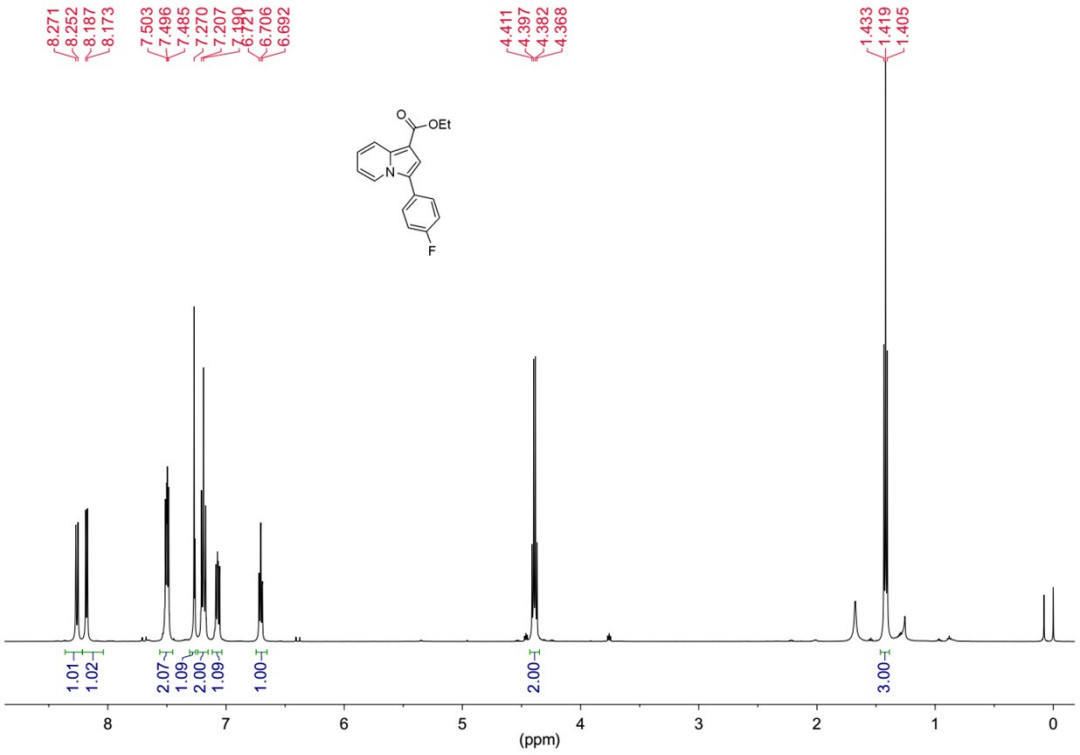
^{13}C NMR **3ga**



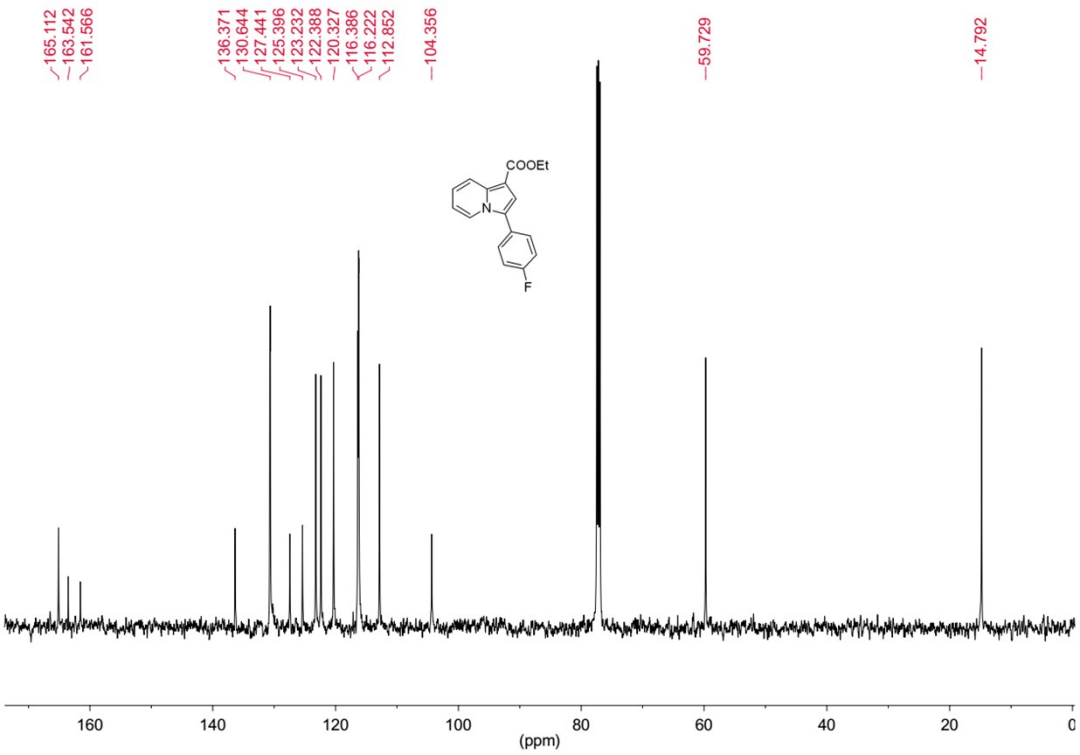
^{1}H NMR **3ha**



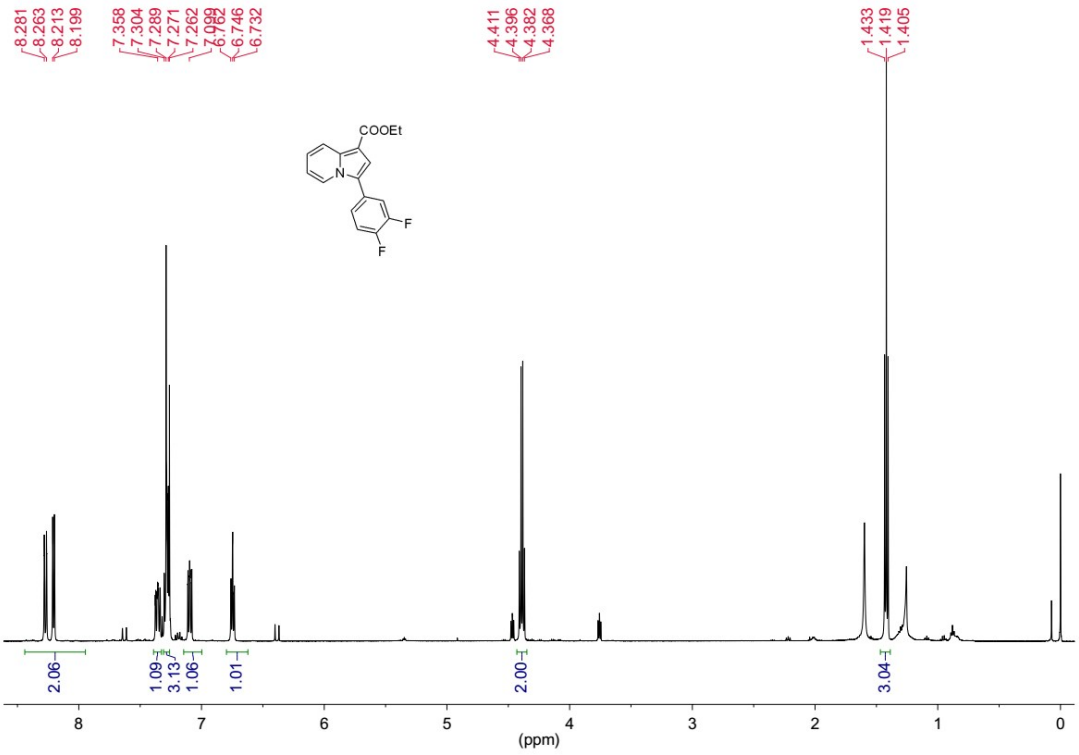
^{13}C NMR **3ha**



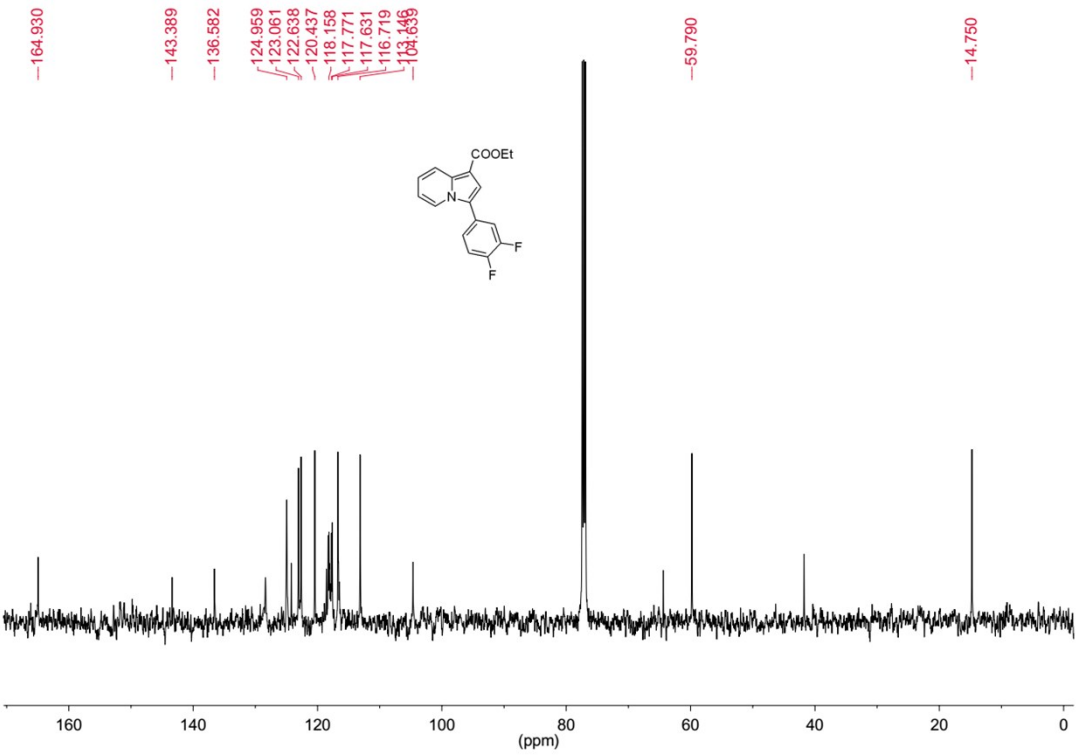
^{1}H NMR **3ia**



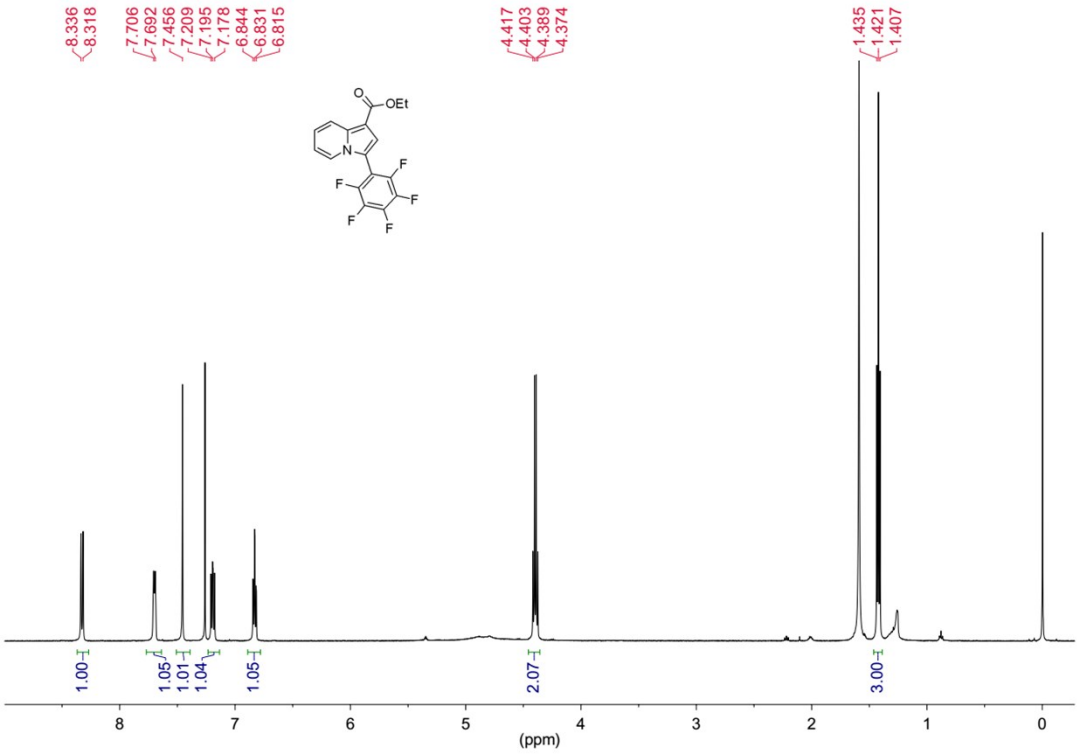
^{13}C NMR **3ia**



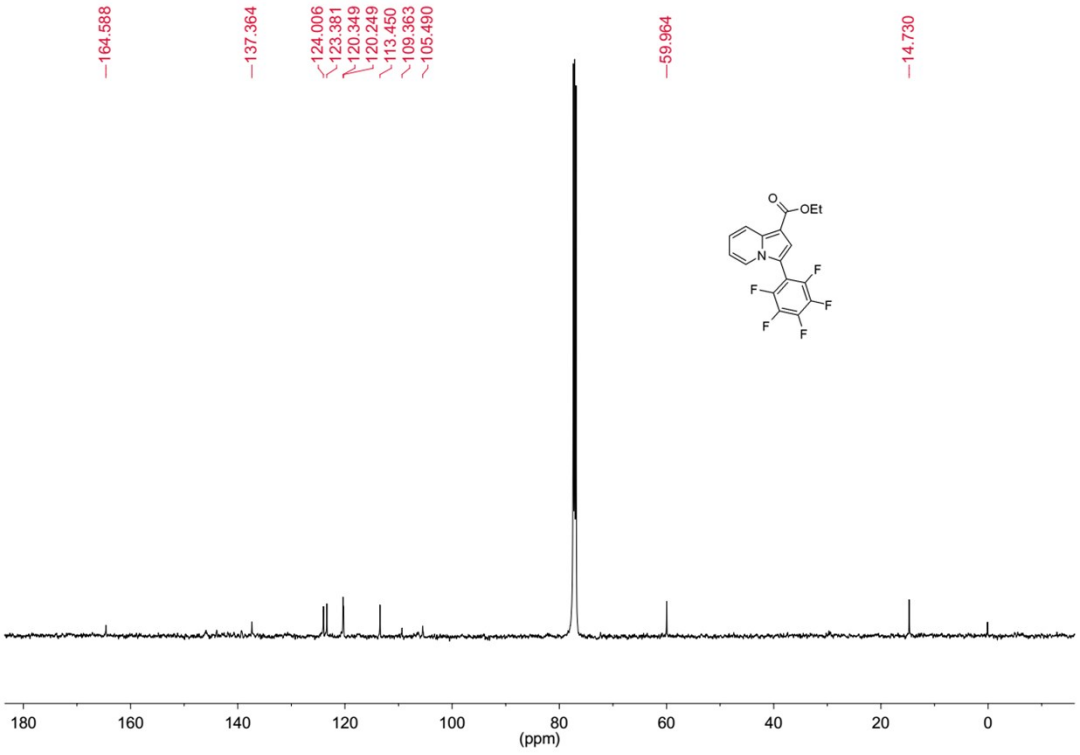
^{1}H NMR **3ja**



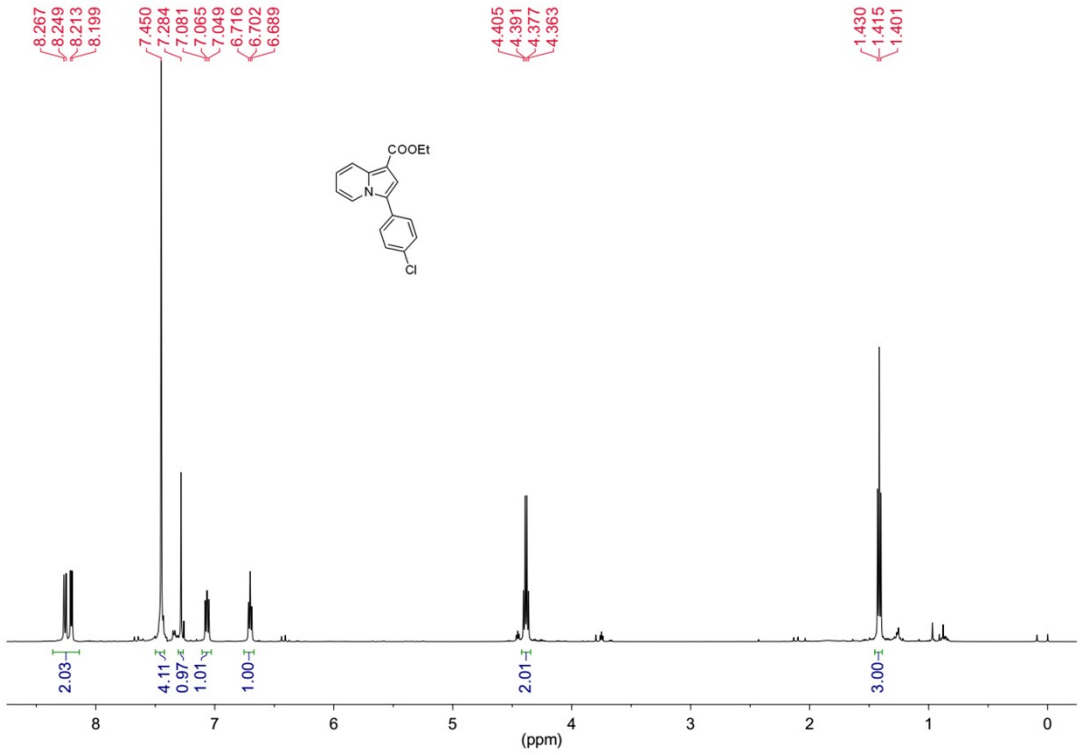
^{13}C NMR **3ja**



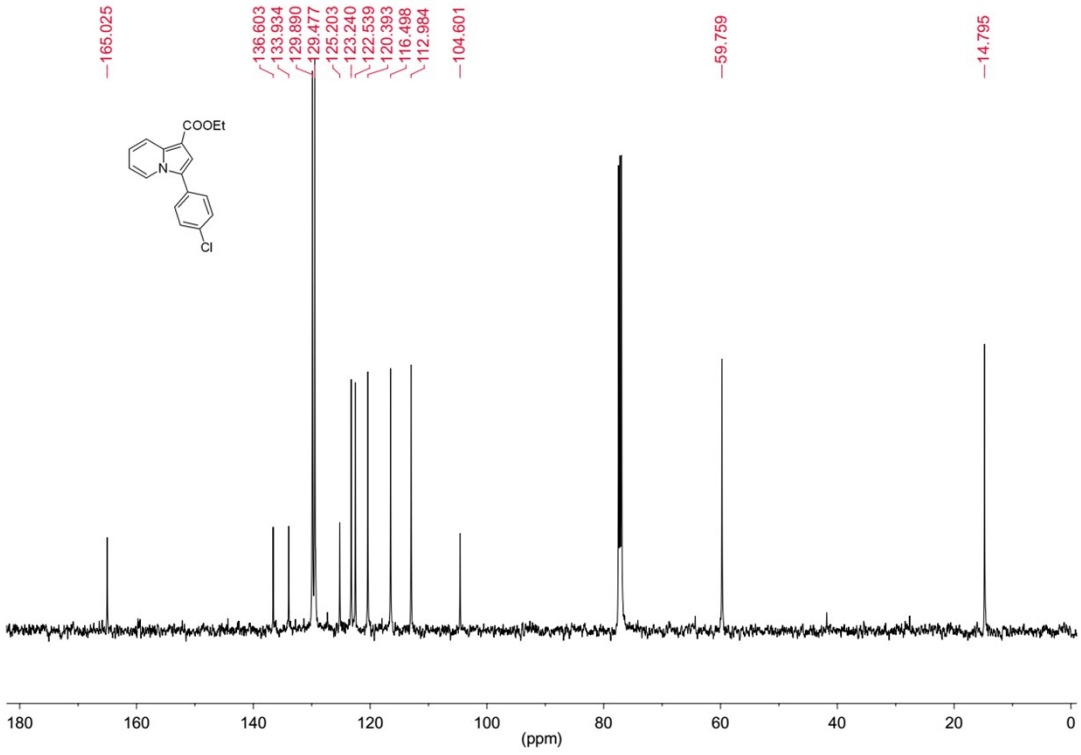
^{1}H NMR **3ka**



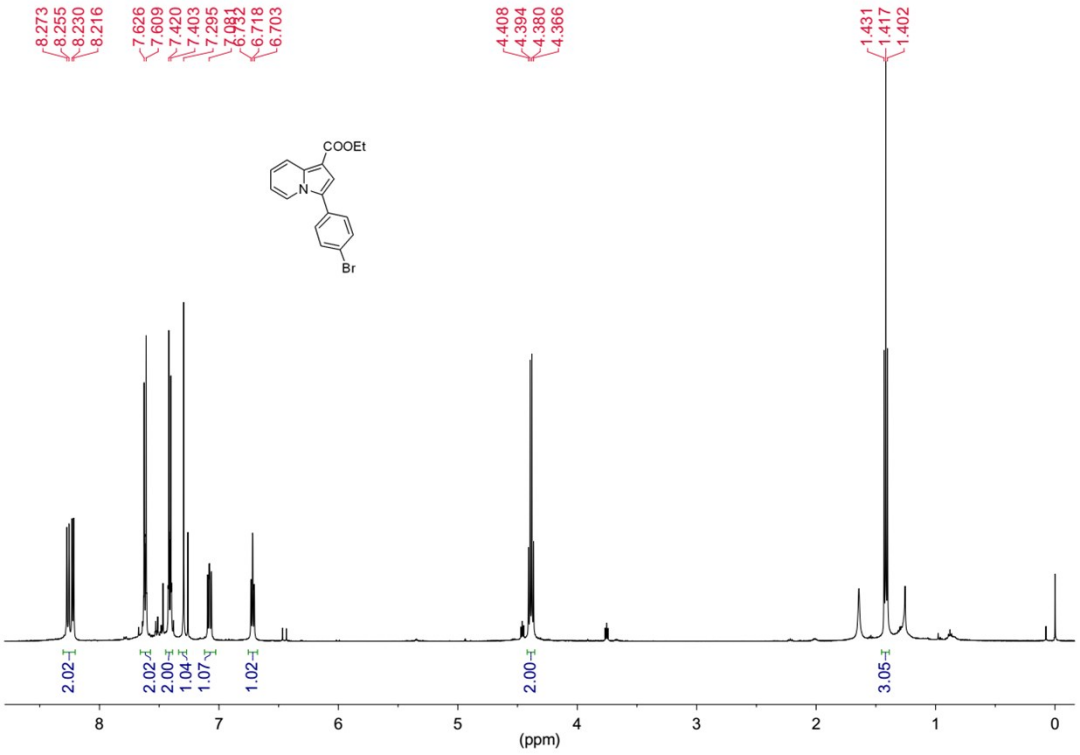
^{13}C NMR **3ka**



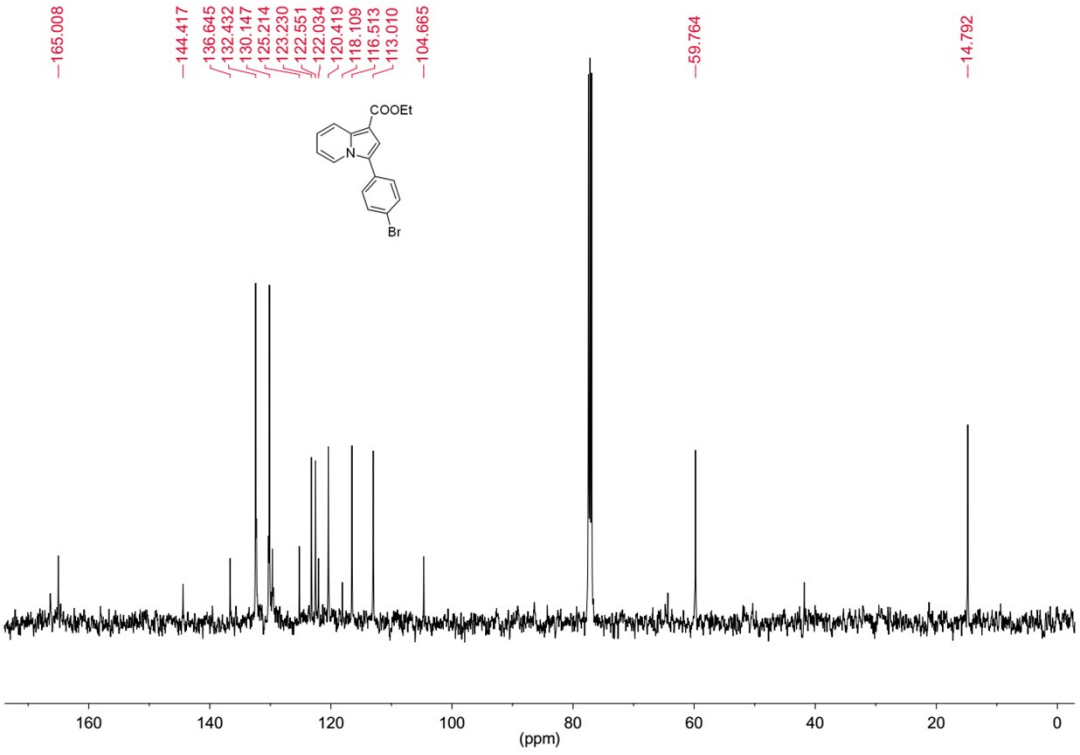
^{1}H NMR **3la**



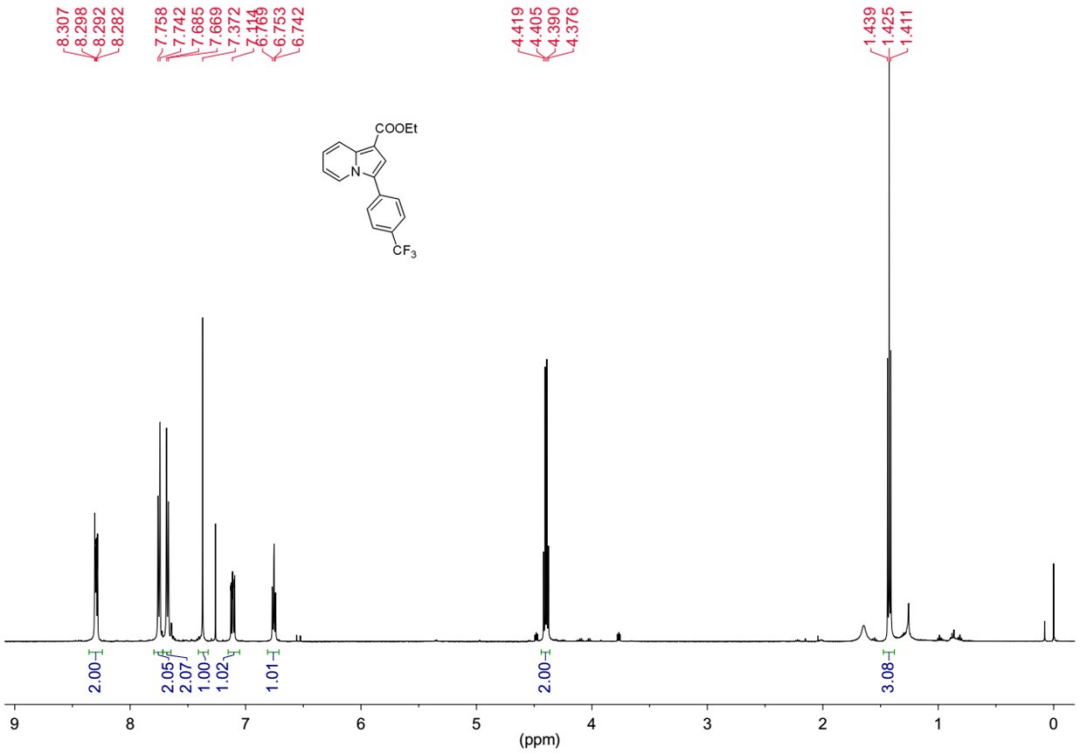
^{13}C NMR **3la**



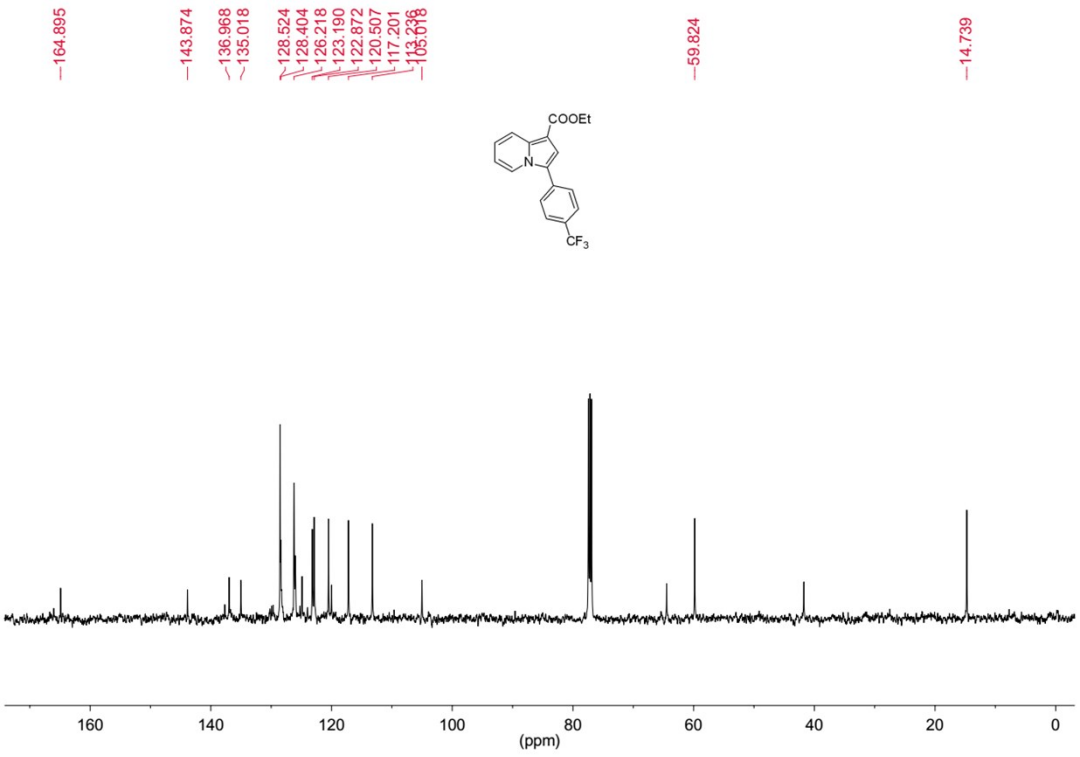
^{1}H NMR **3ma**



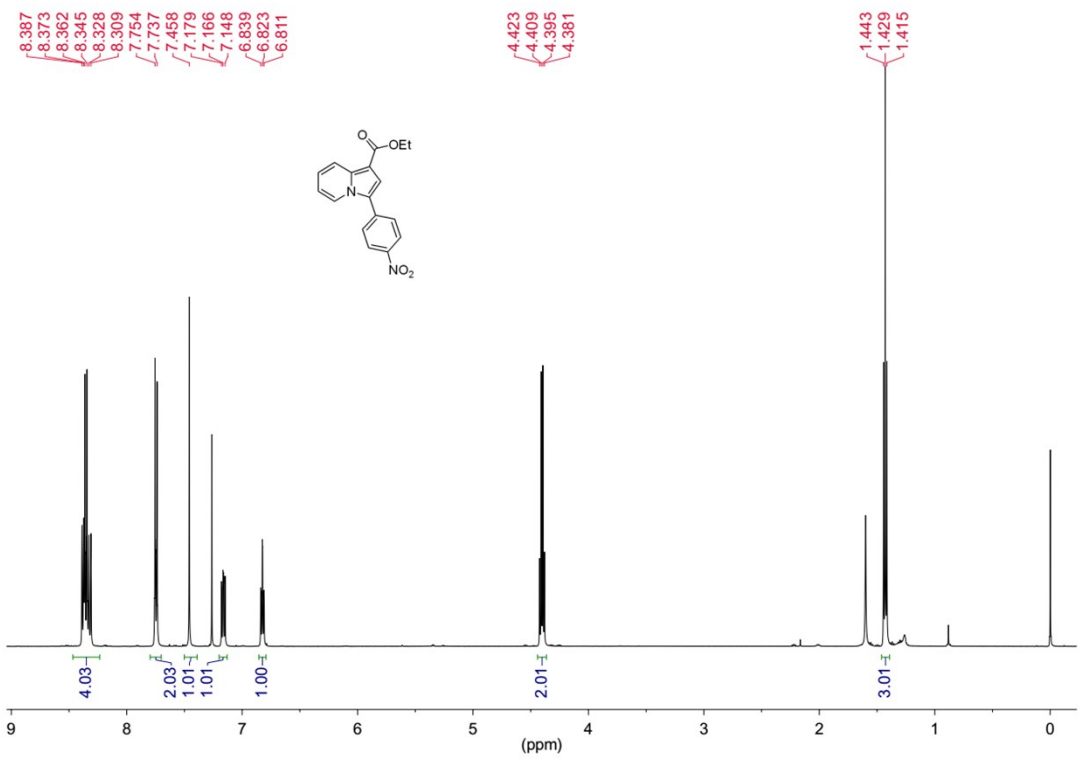
^{13}C NMR **3ma**



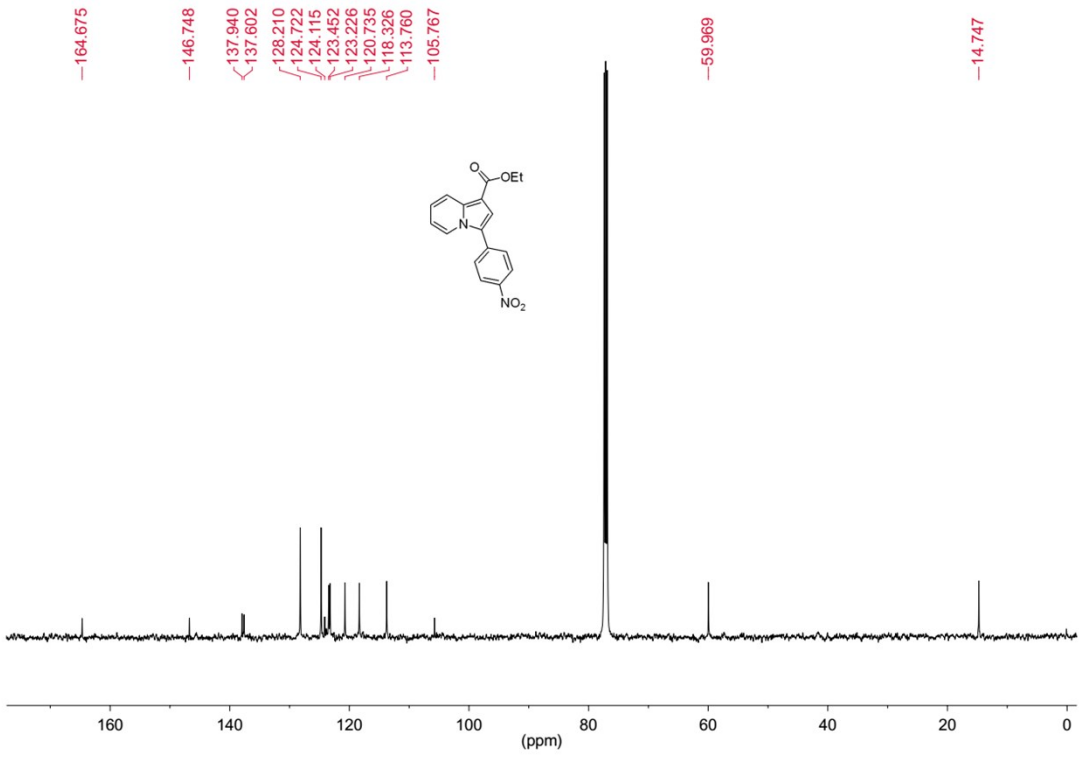
^{1}H NMR **3na**



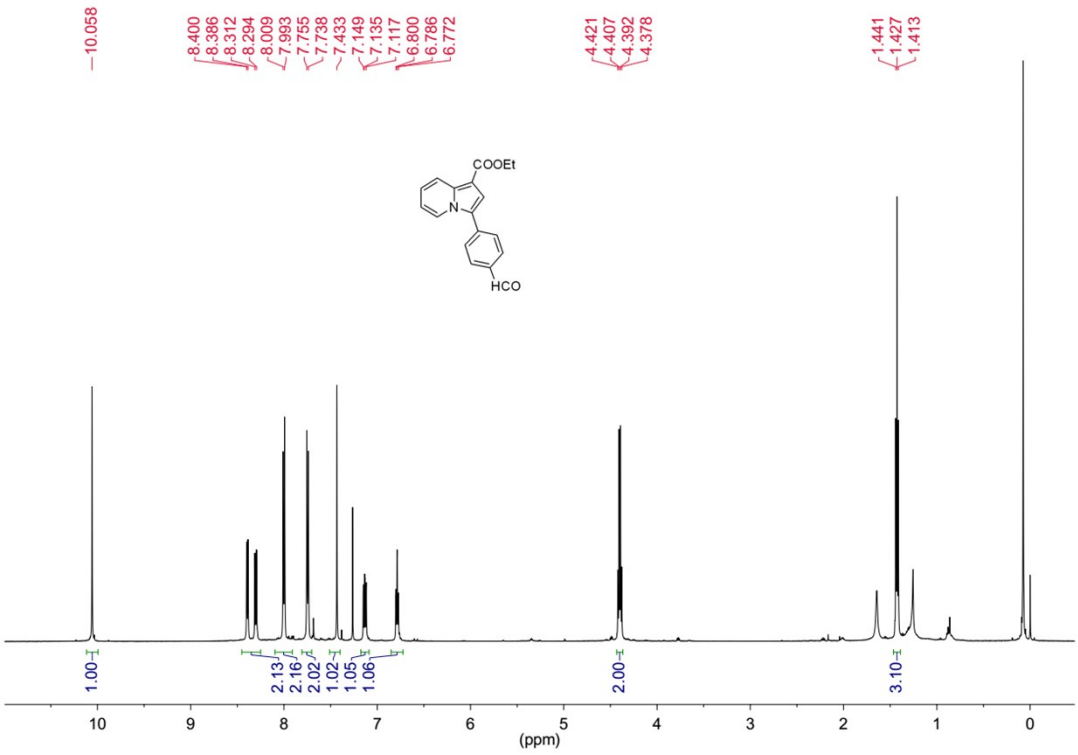
^{13}C NMR **3na**



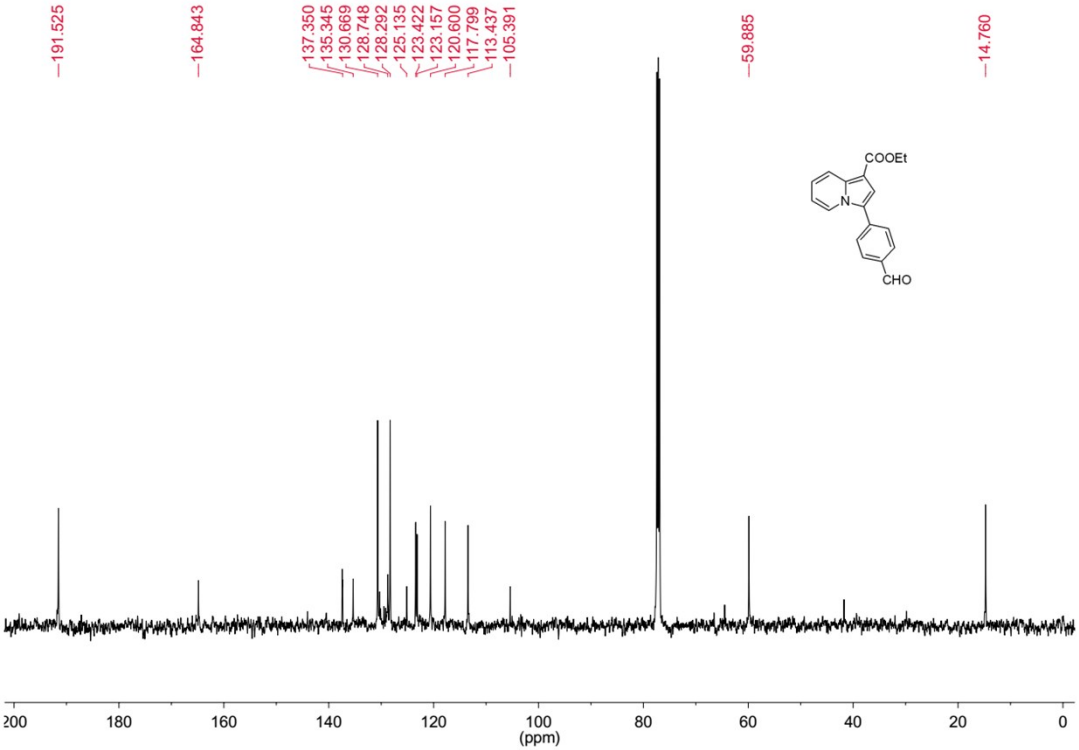
^{1}H NMR **3oa**



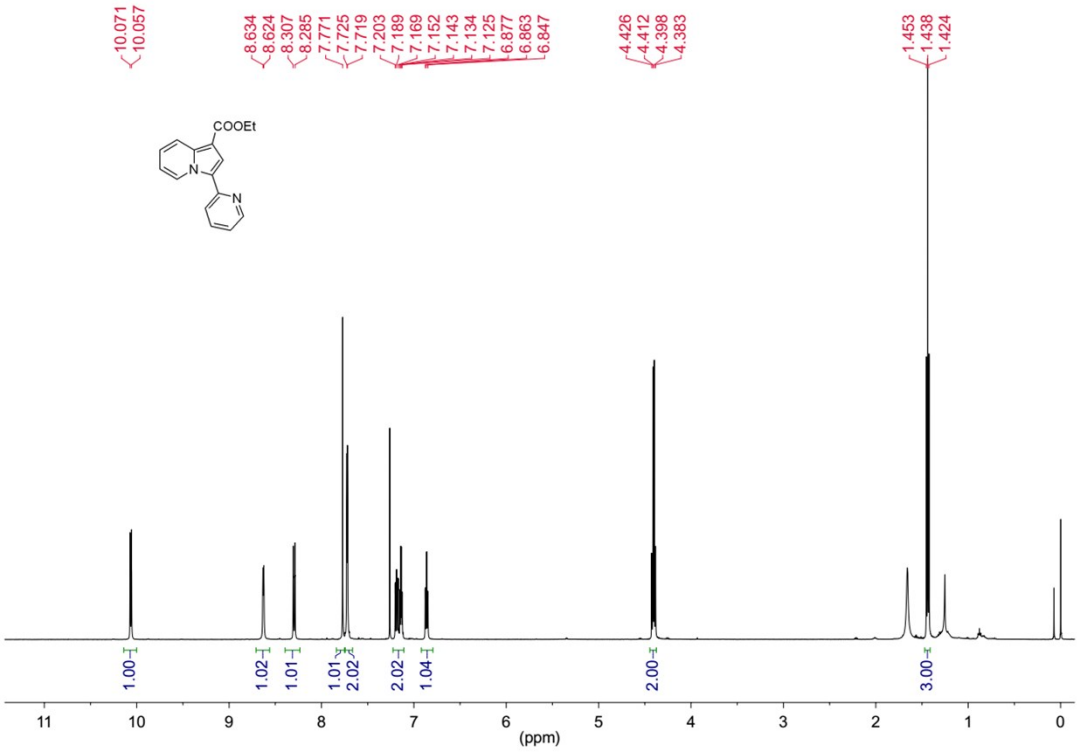
^{13}C NMR **3oa**



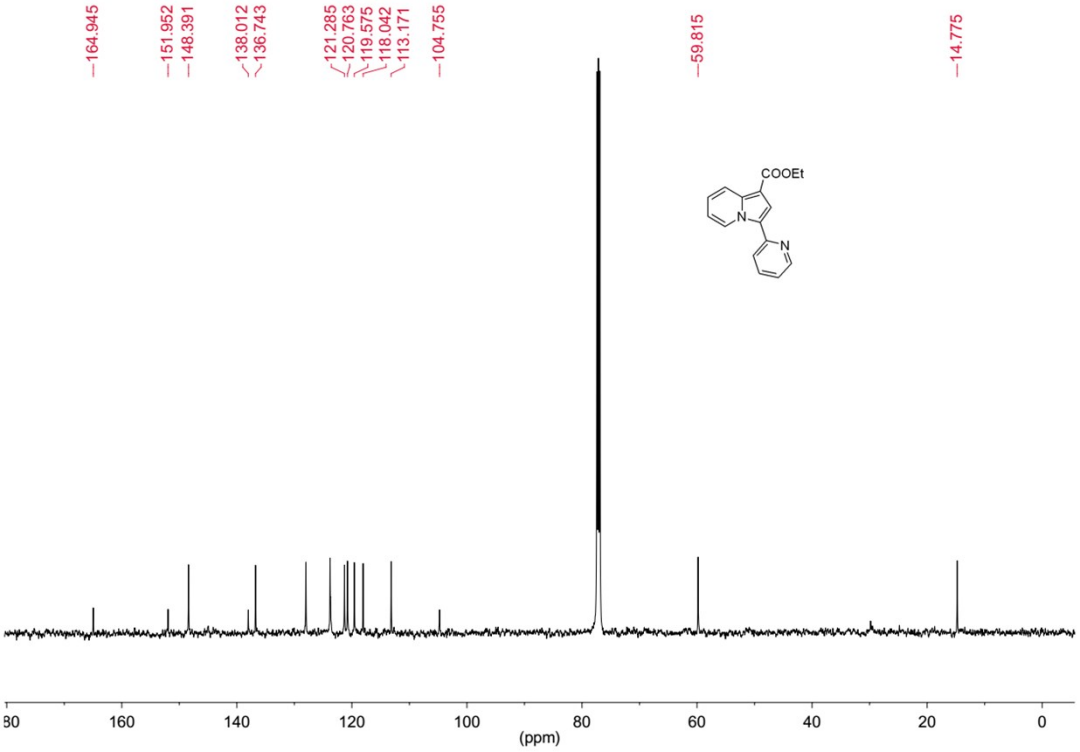
^{1}H NMR **3pa**



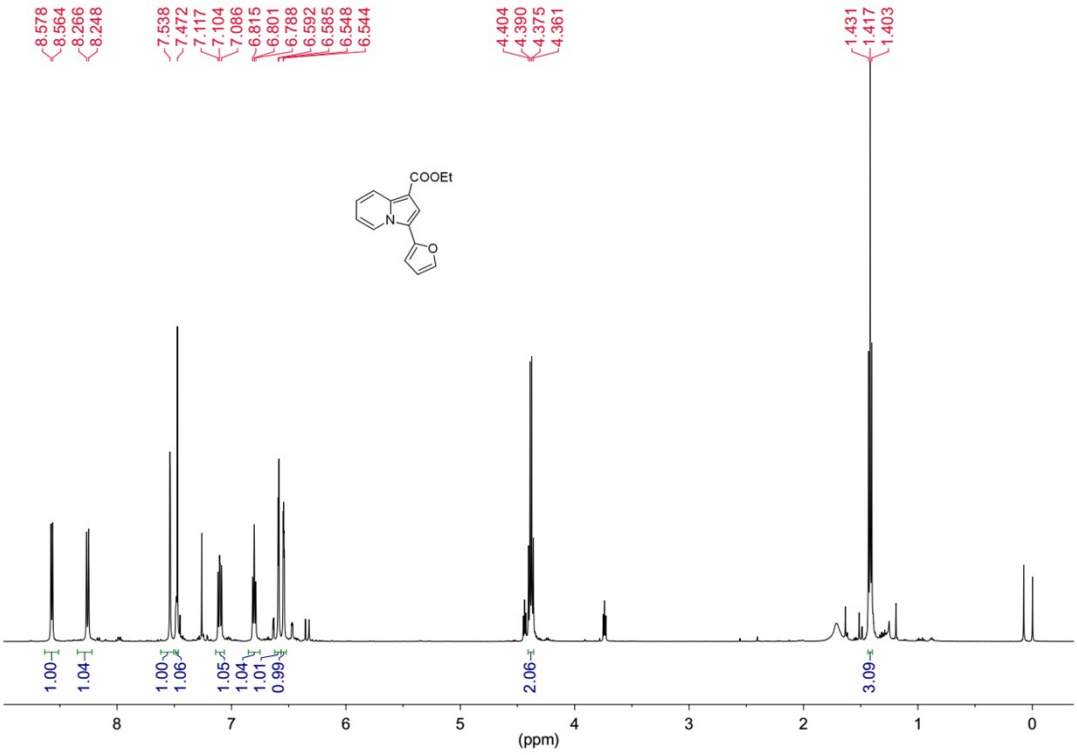
^{13}C NMR **3pa**



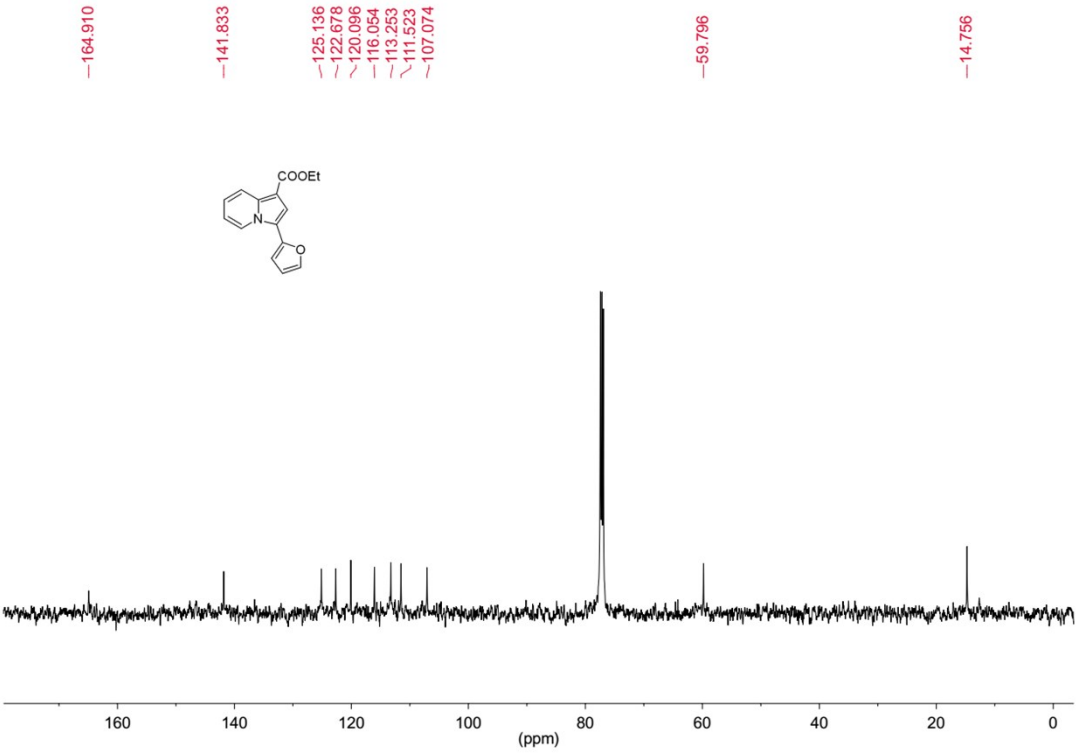
^{1}H NMR **3qa**



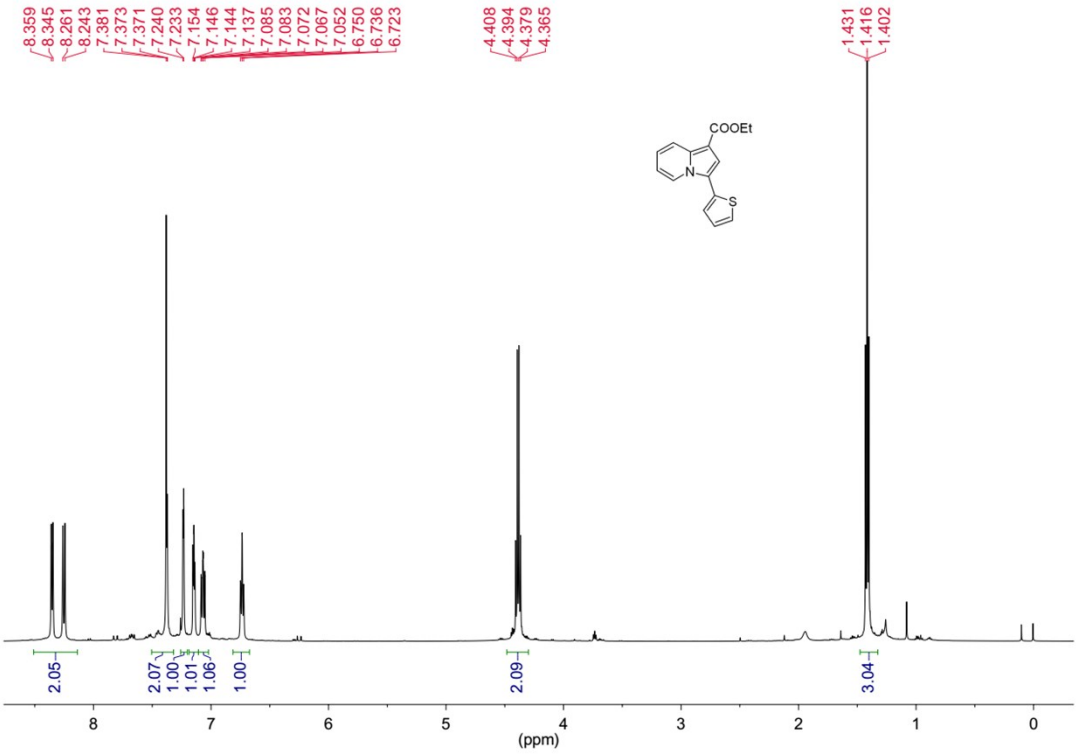
^{13}C NMR **3qa**



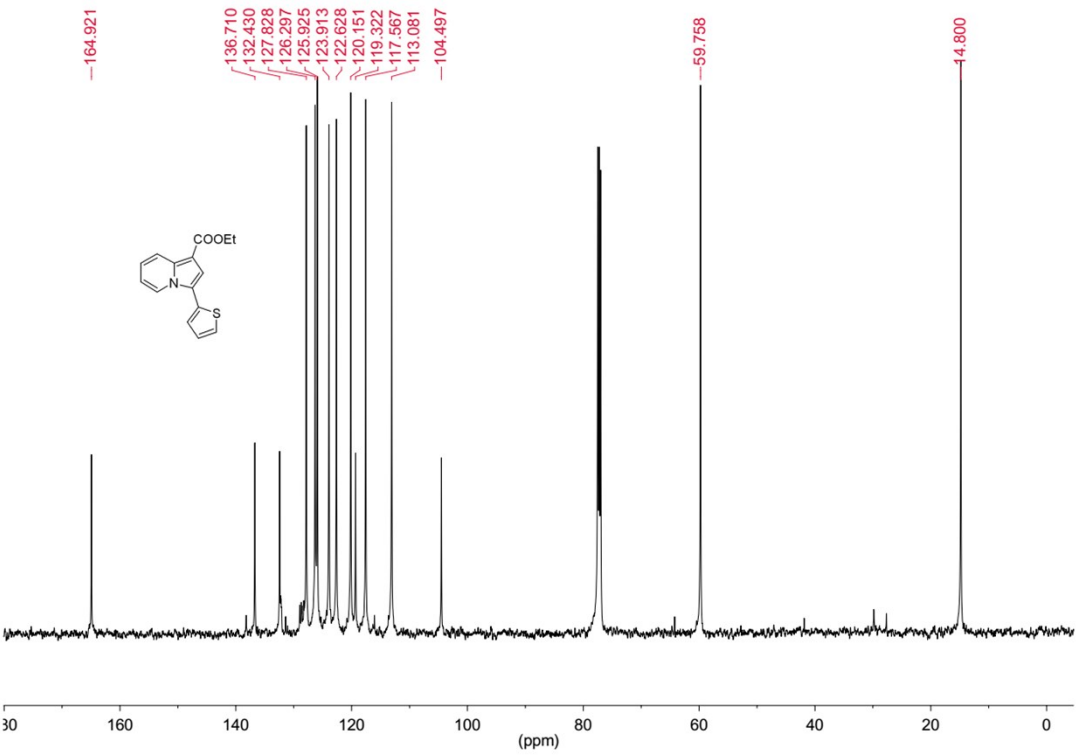
^{1}H NMR **3ra**



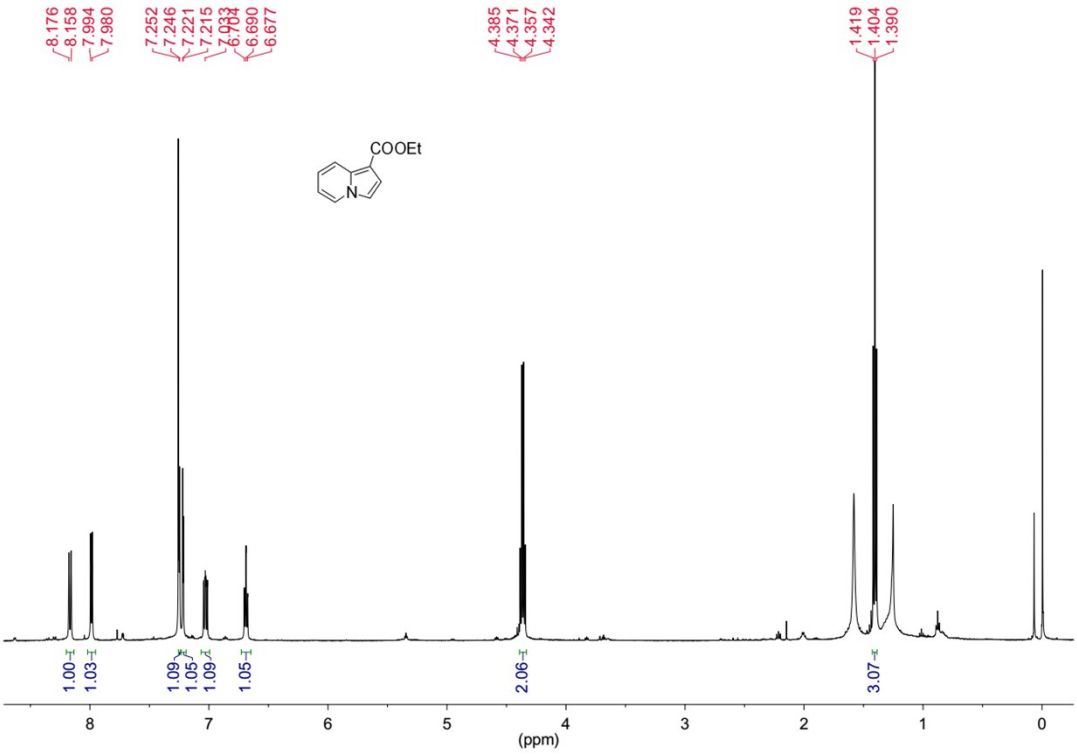
^{13}C NMR **3ra**



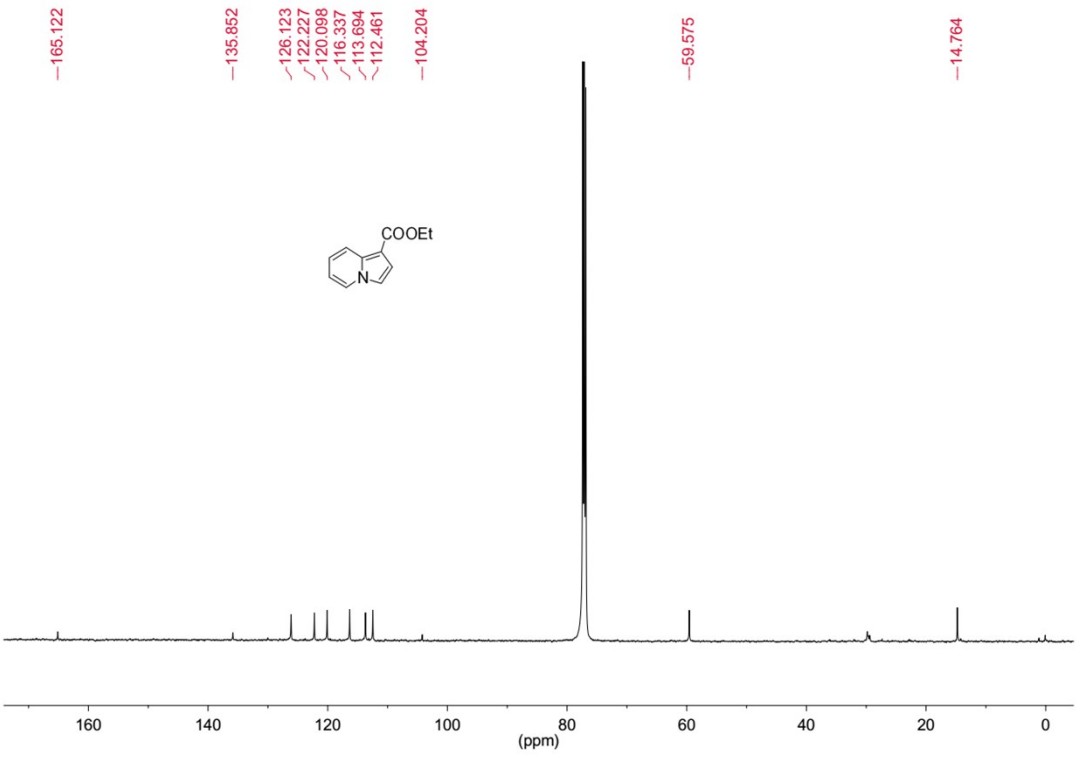
^{1}H NMR **3sa**



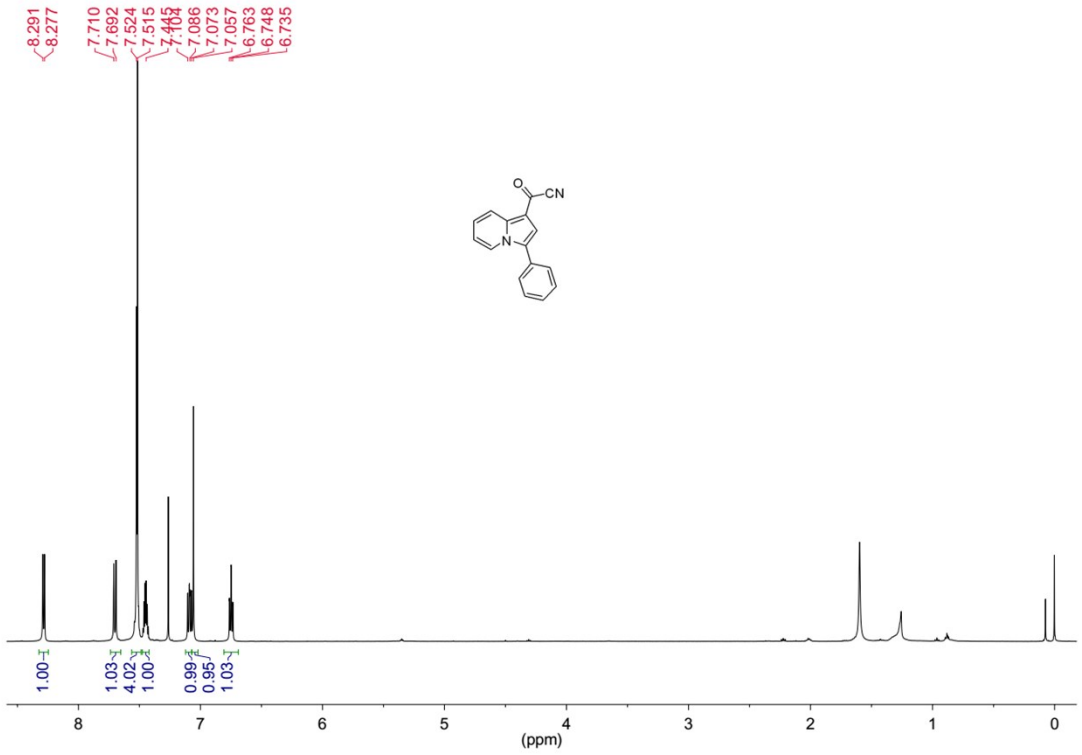
^{13}C NMR **3sa**



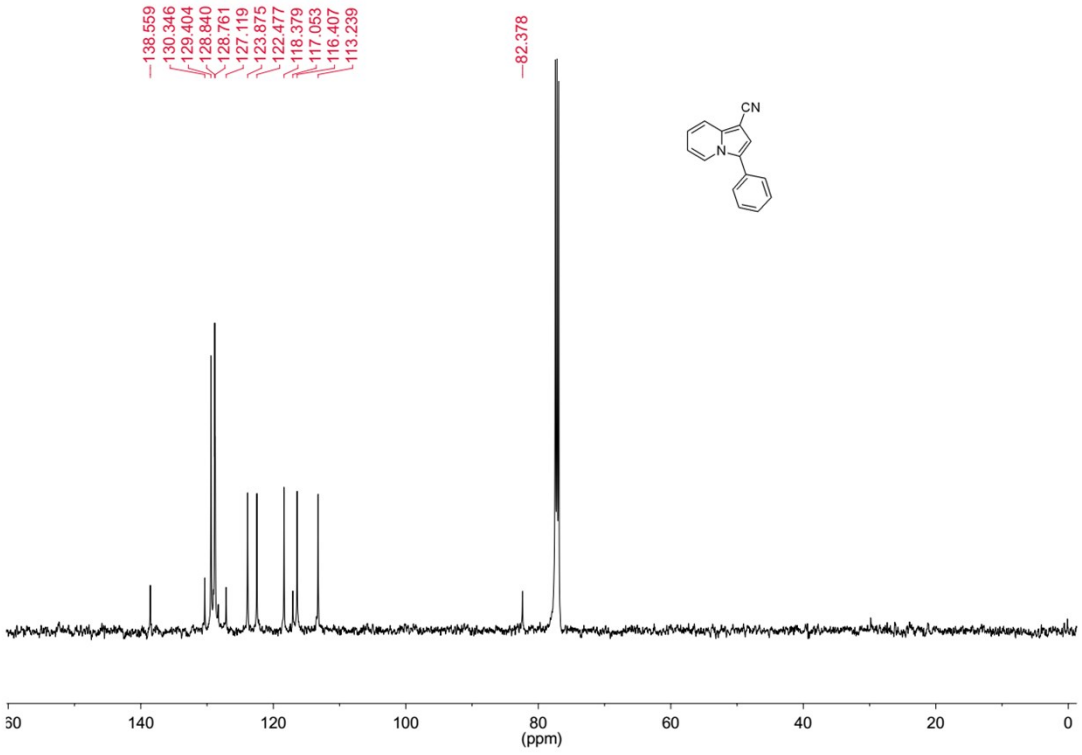
^{1}H NMR **3ta**



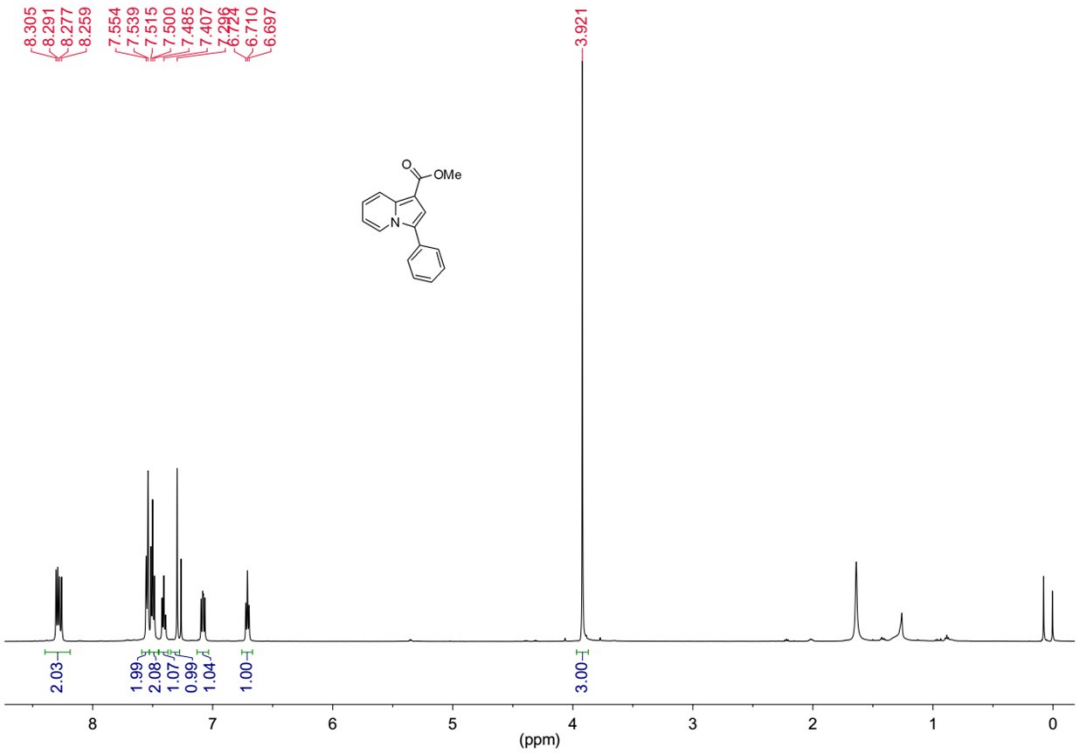
^{13}C NMR **3ta**



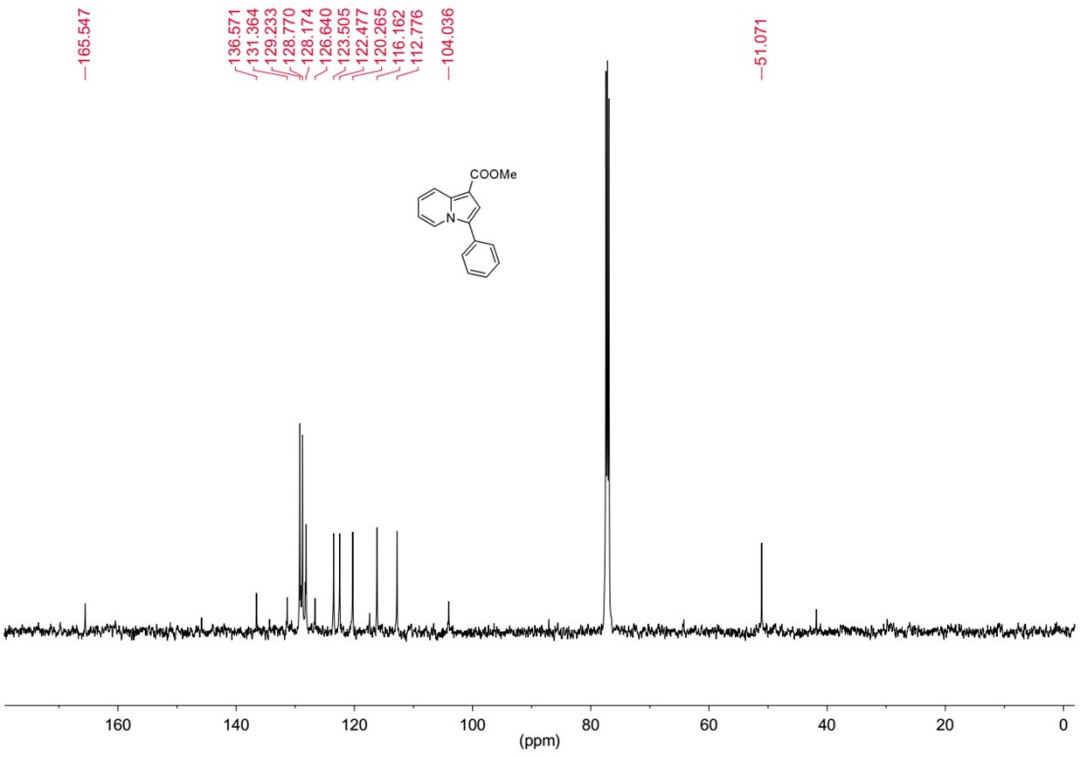
^{1}H NMR **3ab**



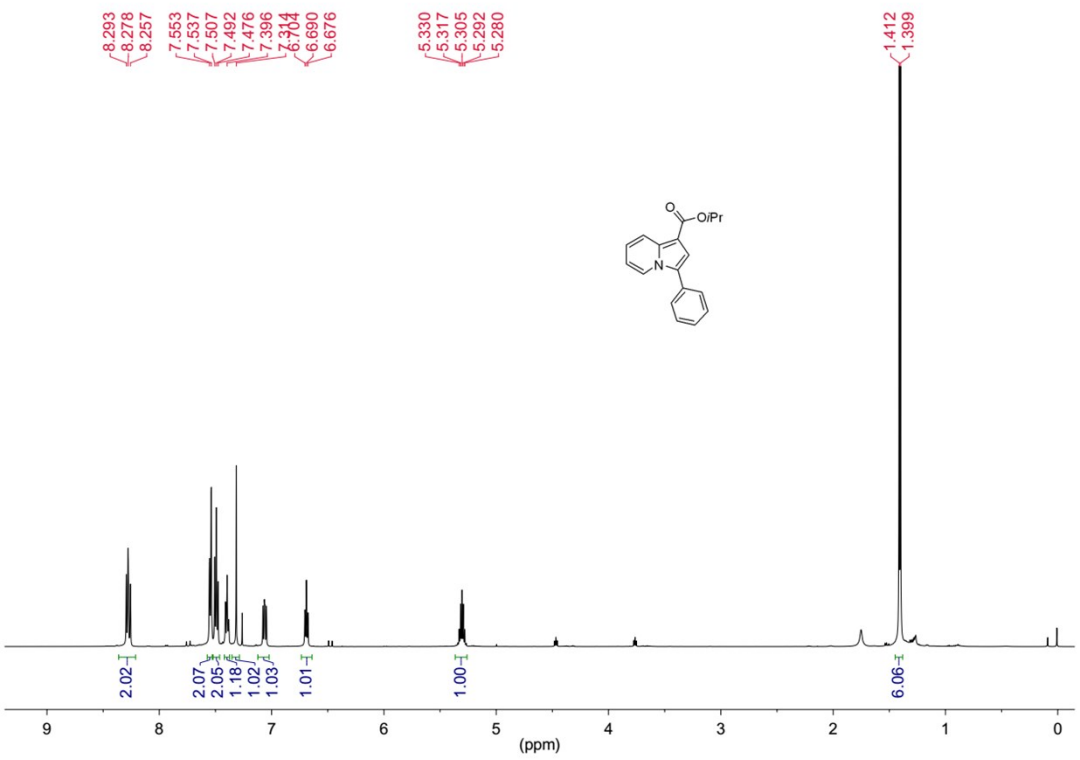
^{13}C NMR **3ab**



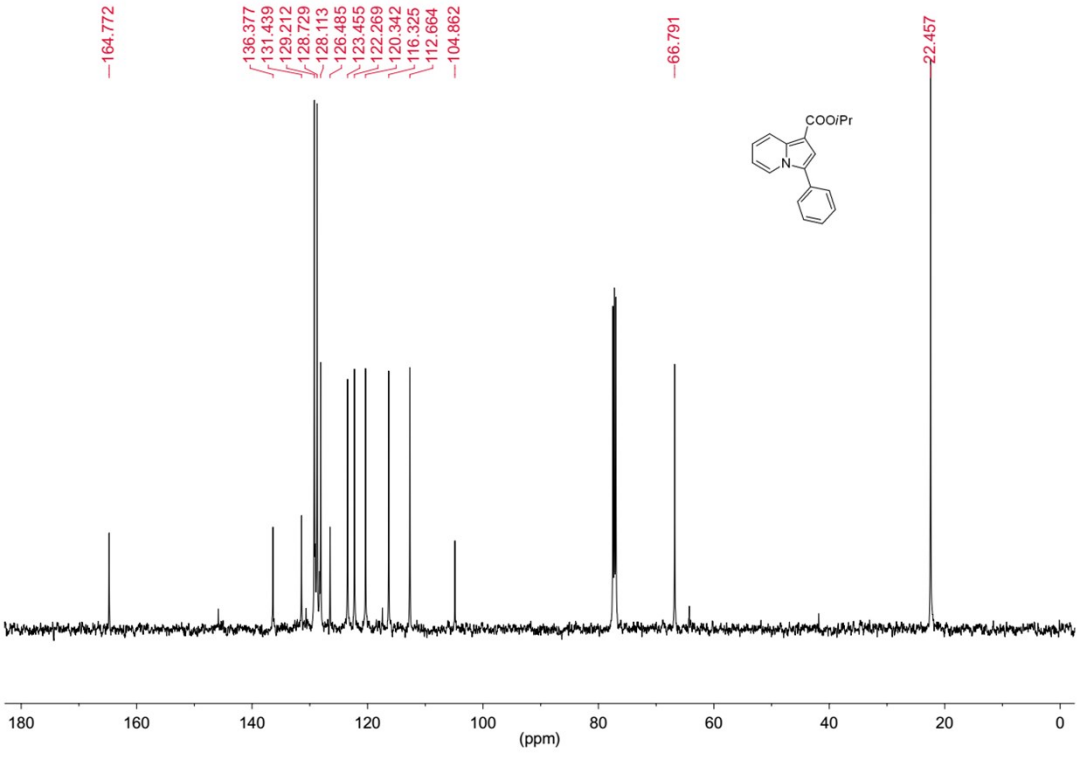
^{1}H NMR **3ac**



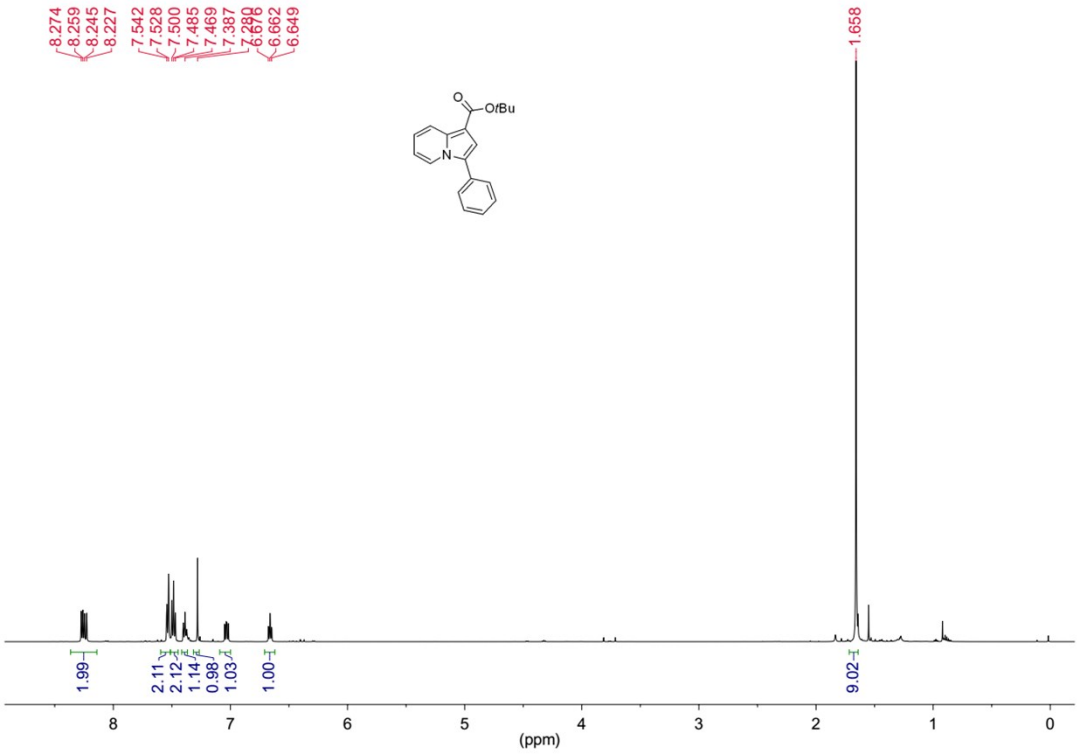
^{13}C NMR **3ac**



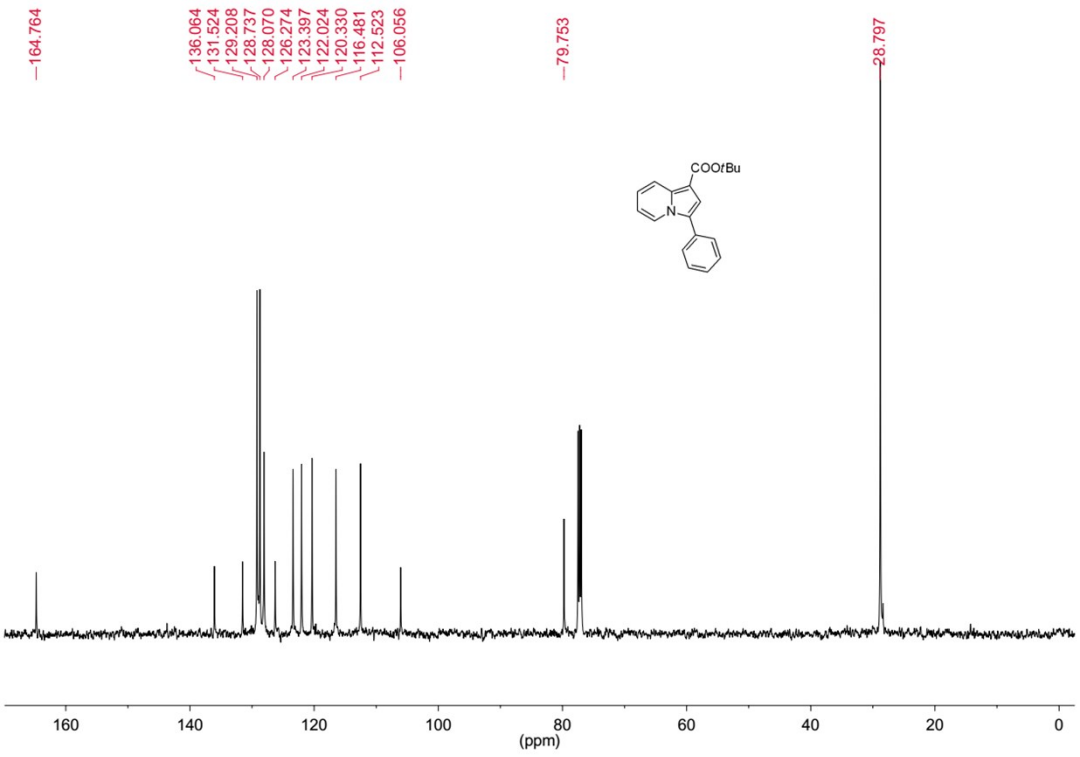
^{1}H NMR **3ad**



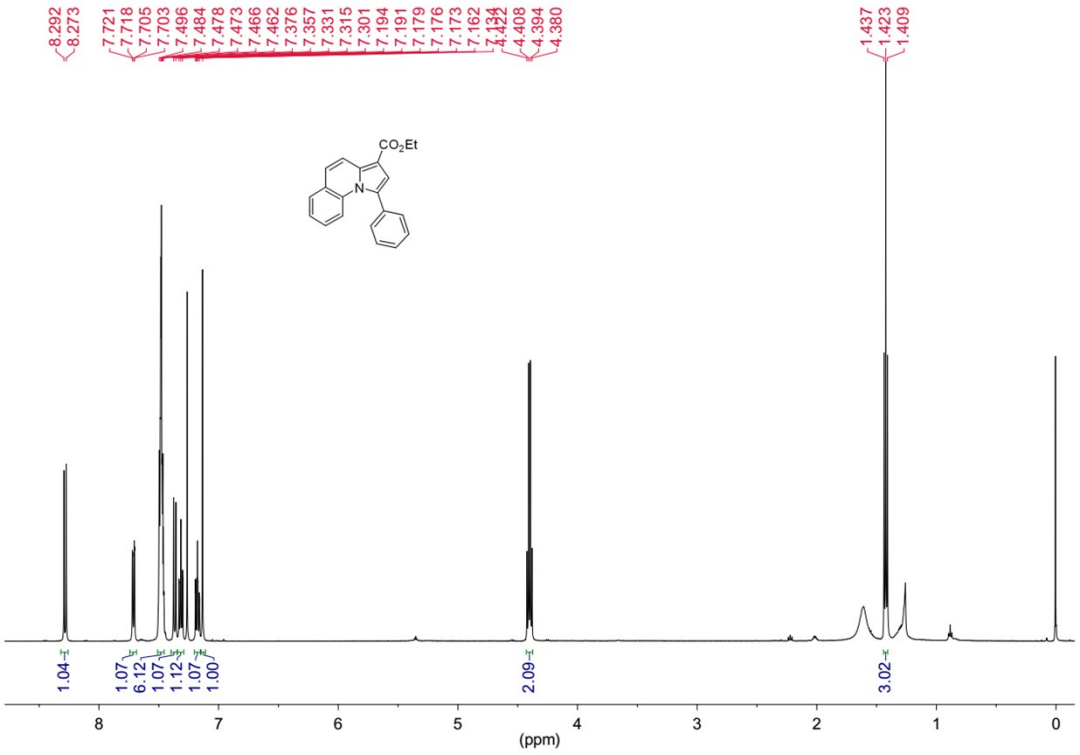
^{13}C NMR **3ad**



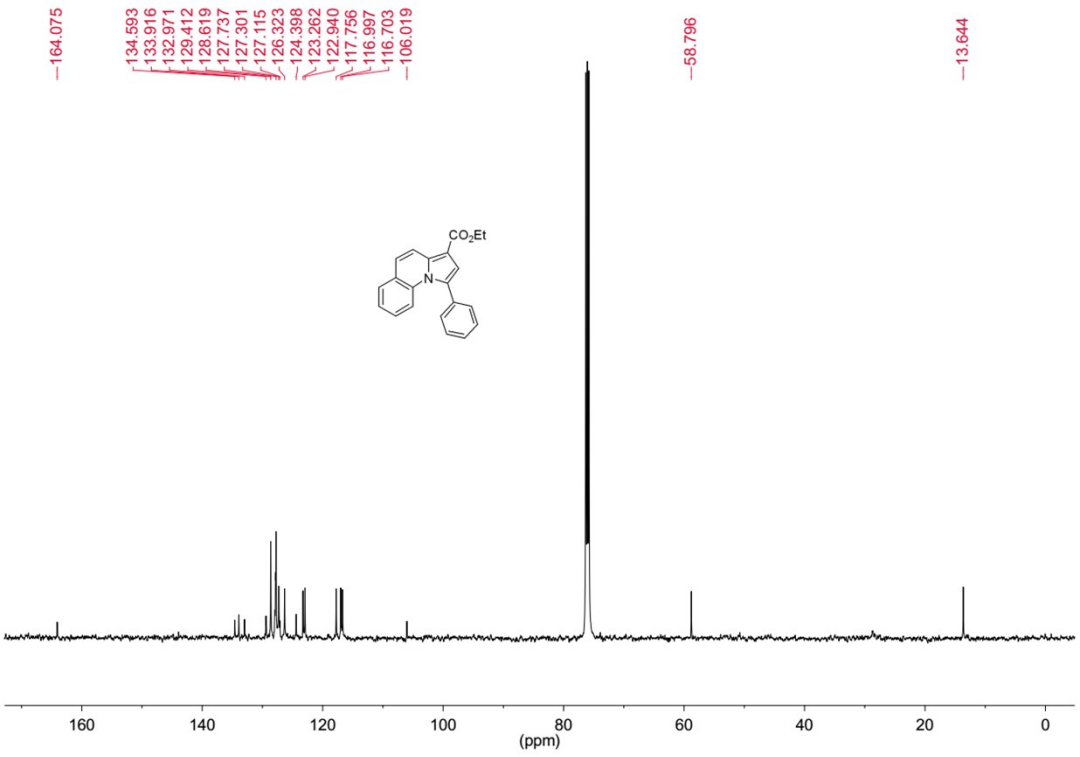
^{1}H NMR **3ae**



^{13}C NMR **3ae**



^{1}H NMR **3af**



^{13}C NMR **3af**