

Supporting Information

Indolizine Synthesis via Copper-Catalyzed Cyclization of *gem*-Difluoroalkenes and 2-(Pyridin-2-yl)acetate Derivatives

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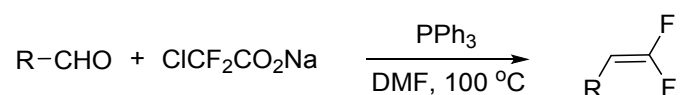
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1. Materials and methods

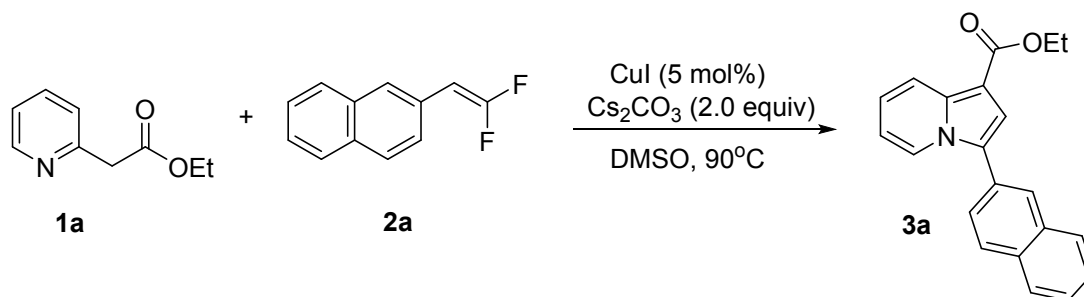
Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware heated under oven for two hours prior to use. ^1H and ^{13}C spectra were recorded on Bruker AVANCE III 500 MHz and Bruker AVANCE III 125 MHz using $\text{CDCl}_3/\text{DMSO}$ as solvent with TMS as internal standard. Anhydrous dioxane, THF and DMF were freshly distilled over Na and stored under nitrogen. Commercial reagents were used as received without further purification unless otherwise noticed. HRMS were recorded on Agilent 6210 TOF LC/MS mass spectrometer. Column chromatography was carried out using silica gel (200-300 mesh). Compound **1** was purchased from commercial sources.

2. General procedure for the synthesis of *gem*-difluoroalkenes



Sodium 2-chloro-2,2-difluoroacetate (1.2 equiv., 6 mmol) was added in the mixture of corresponding aldehyde (5 mmol) and triphenyl phosphine (1.5 equiv., 7.5 mmol) in dry DMF (14 mL), the reaction was heated at 100 °C for 2 hours. Then water was added to the mixture slowly and the mixture was extracted with Et_2O . The combined organic layers were dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (SiO_2).

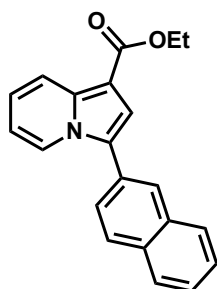
3. Typical procedure for the copper catalyzed cyclization of 2-(pyridin-2-yl)acetate with *gem*-difluoroalkenes



To a mixture of ethyl 2-(pyridin-2-yl)acetate **1a** (0.20 mmol, 1.0 equiv.), 2-

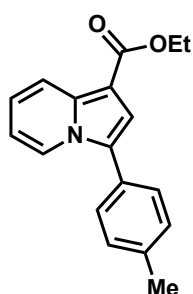
(2,2-difluorovinyl) naphthalene **2a** (0.3 mmol, 1.5 equiv), CuI (0.01 mmol, 5 mol%), Cs₂CO₃ (0.4 mmol, 2 equiv.) in a sealed tube was added 1.0 mL dry DMSO. The resulting mixture was then stirred at 90 °C under argon atmosphere for 12 h. The solvent was then removed under vacuum and the residue was purified with chromatography on silica (PE/EA = 30:1) to afford compound **3a**.

4. Characterization of the Title Compounds



3a

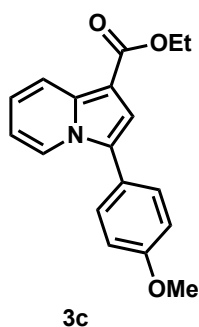
Ethyl 3-(naphthalen-2-yl)indolizine-1-carboxylate (3a), 47 mg, 75%, white solid, m. p. 65–67°C. ¹H NMR (500 MHz, CDCl₃) δ 8.40 (dt, *J* = 7.5, 1.5 Hz, 1H), 8.32 (dt, *J* = 9.0, 1.5 Hz, 1H), 8.04-8.02 (m, 1H), 7.97(d, *J* = 8.5 Hz, 1H), 7.92-7.87(m, 2H), 7.66(dd, *J* = 8.5, 2.0 Hz, 1H), 7.58-7.52(m, 2H), 7.44 (s, 1H), 7.137-7.096(m, 1H), 6.74(td, *J* = 6.5, 1.5 Hz, 1H), 4.44(q, *J* = 7.5 Hz, 2H), 1.46(t, *J* = 7.5 Hz, 3H). Characterization data is consistent with literature².



3b

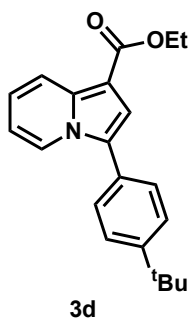
Ethyl 3-(p-tolyl)indolizine-1-carboxylate (3b), 45 mg, 81%, white solid, m. p. 93-95 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.29-8.25 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.34-7.28 (m, 3H), 7.09-7.05 (m, 1H), 6.71-6.68 (m, 1H), 4.41 (q, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.07, 137.94, 136.21, 129.75, 128.58, 128.32, 126.49, 123.39, 122.03, 120.14, 115.80, 112.43, 104.13, 59.50,

21.30, 14.67. Characterization data is consistent with literature².



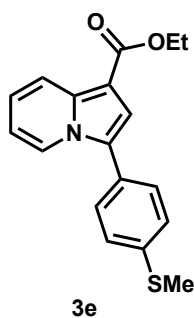
Ethyl 3-(4-methoxyphenyl)indolizine-1-carboxylate (3c), 49 mg, 83%, white solid, m. p. 124-126 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.26 (dt, *J* = 9.0, 1.5 Hz, 1H), 8.21 (dt, *J* = 7.0, 1.0 Hz, 1H), 7.48-7.44 (m, 2H), 7.27 (d, *J* = 10.5 Hz, 1H), 7.08-7.02 (m, 3H), 6.69 (td, *J* = 6.5, 1.5 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 1.43 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 165.09, 159.48, 136.04, 130.16, 126.24, 123.59, 123.32, 121.94, 120.11, 115.61, 114.53, 112.41, 103.99, 59.50, 55.39, 14.68.

Characterization data is consistent with literature².

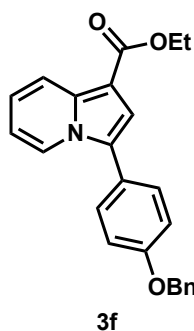


Ethyl 3-(4-(tert-butyl)phenyl)indolizine-1-carboxylate (3d), 50 mg, 79%, white solid, m. p. 133-135 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.32 (dt, *J* = 7.0, 1.0 Hz, 1H), 8.27 (dt, *J* = 9.0, 1.0 Hz, 1H), 7.56-7.47 (m, 4H), 7.30 (s, 1H), 7.09-7.05 (m, 1H), 6.70 (td, *J* = 7.0, 1.5 Hz, 1H), 4.41 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.40 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 165.09, 151.13, 136.24, 128.36, 128.33, 126.50, 125.99, 123.51, 122.06, 120.15, 115.87, 112.41, 104.17, 59.51, 34.75, 31.32, 14.68.

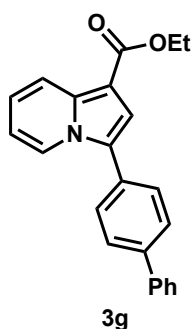
Characterization data is consistent with literature².



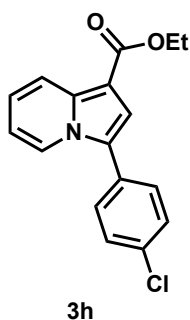
Ethyl 3-(4-(methylthio)phenyl)indolizine-1-carboxylate (3e), 48 mg, 78%, white solid, m. p. 107-109 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.28-8.21 (m, 2H), 7.46-7.42 (m, 2H), 7.37-7.34 (m, 2H), 7.29 (s, 1H), 7.08-7.03 (m, 1H), 6.69 (tt, *J* = 7.0, 1.5 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 2.53 (s, 3H), 1.43 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.87, 138.57, 136.24, 128.83, 127.72, 126.80, 125.82, 123.20, 122.10, 120.10, 115.90, 112.54, 104.22, 59.47, 15.58, 14.61. HRMS (ESI) *m/z* calculated for [C₁₈H₁₇NO₂S+H]⁺ 312.1053, found 312.1046.



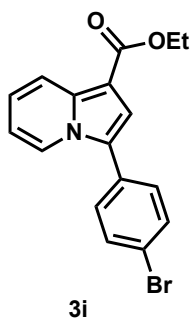
Ethyl 3-(4-(benzyloxy)phenyl)indolizine-1-carboxylate (3f), 64 mg, 87%, colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.29 (dt, *J* = 9.0, 1.5 Hz, 1H), 8.23 (dt, *J* = 7.0, 1.0 Hz, 1H), 7.49-7.46 (m, 2H), 7.44-7.40 (m, 3H), 7.39-7.33 (m, 2H), 7.17-7.15 (m, 2H), 7.10-7.02 (m, 2H), 6.67 (td, *J* = 7.0, 1.5 Hz, 1H), 5.15 (s, 2H), 4.43 (q, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.93, 159.09, 136.71, 136.36, 132.44, 130.12, 128.60, 127.97, 127.38, 126.14, 123.42, 122.18, 121.06, 120.08, 116.10, 114.83, 114.59, 112.54, 104.21, 70.01, 59.50, 14.62. HRMS (ESI) *m/z* calculated for [C₂₄H₂₁NO₃+H]⁺ 372.1594, found 372.1588.



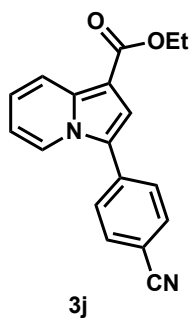
Ethyl 3-([1,1'-biphenyl]-4-yl)indolizine-1-carboxylate (3g), 52 mg, 77%, white solid, m. p. 150-152 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.37 (dt, *J* = 7.0, 1.0 Hz, 1H), 8.31 (dt, *J* = 9.0, 1.0 Hz, 1H), 7.77-7.72 (m, 2H), 7.70-7.66 (m, 2H), 7.66-7.62 (m, 2H), 7.52-7.48 (m, 2H), 7.43 – 7.37 (m, 2H), 7.12-7.08 (m, 1H), 6.74 (td, *J* = 7.0, 1.5 Hz, 1H), 4.44 (q, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 164.98, 140.68, 140.35, 136.45, 130.13, 128.87, 128.81, 127.69, 127.55, 126.98, 126.04, 123.39, 122.23, 120.19, 116.19, 112.63, 104.40, 59.55, 14.65. Characterization data is consistent with literature³.



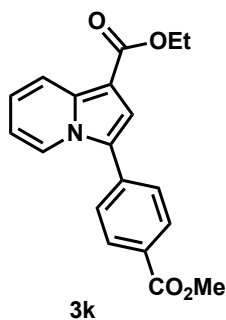
Ethyl 3-(4-chlorophenyl)indolizine-1-carboxylate (3h), 40 mg, 68%, yellow solid, m. p. 107-109 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.28 (dt, *J* = 9.0, 1.0 Hz, 1H), 8.24 (dt, *J* = 7.0, 1.0 Hz, 1H), 7.51-7.44 (m, 4H), 7.31 (s, 1H), 7.11-7.07 (m, 1H), 6.73 (td, *J* = 7.0, 1.5 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.89, 136.49, 133.85, 129.80, 129.74, 129.36, 125.09, 123.11, 122.38, 120.30, 116.38, 112.84, 104.51, 59.63, 14.66. Characterization data is consistent with literature².



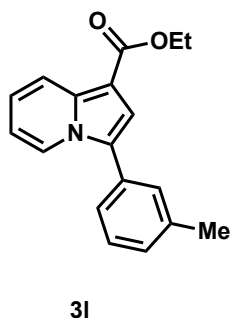
Ethyl 3-(4-bromophenyl)indolizine-1-carboxylate (3i), 48 mg, 71%, white solid, m. p. 93-95 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.28 (dt, *J* = 9.0, 1.0 Hz, 1H), 8.24 (dt, *J* = 7.0, 1.0 Hz, 1H), 7.66-7.60 (m, 2H), 7.44-7.40 (m, 2H), 7.31 (s, 1H), 7.11-7.07 (m, 1H), 6.73 (td, *J* = 7.0, 1.5 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.86, 136.50, 132.29, 130.18, 130.02, 125.07, 123.08, 122.39, 121.90, 120.29, 116.37, 112.86, 104.54, 59.62, 14.65. Characterization data is consistent with literature².



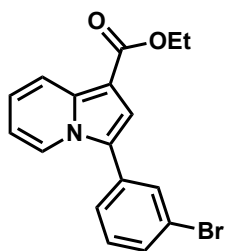
Ethyl 3-(4-cyanophenyl)indolizine-1-carboxylate (3j), 30 mg, 52%, white solid, m. p. 170-172 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.34 (dt, *J* = 7.0, 1.0 Hz, 1H), 8.30 (dt, *J* = 9.0, 1.5 Hz, 1H), 7.80-7.75 (m, 2H), 7.71-7.66 (m, 2H), 7.41 (s, 1H), 7.17-7.12 (m, 1H), 6.80 (td, *J* = 6.9, 1.4 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.59, 137.19, 135.85, 132.90, 128.24, 124.27, 123.09, 123.00, 120.50, 118.61, 117.69, 113.41, 110.95, 105.33, 59.77, 14.60. Characterization data is consistent with literature².



Ethyl 3-(4-(methoxycarbonyl)phenyl)indolizine-1-carboxylate (3k), 36 mg, 57%, pale yellow solid, m. p. 152-154 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.36 (dd, *J* = 7.0, 1.0 Hz, 1H), 8.29 (dt, *J* = 9.0, 1.5 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 2H), 7.67-7.62 (m, 2H), 7.40 (s, 1H), 7.14-7.09 (m, 1H), 6.76 (td, *J* = 7.0, 1.5 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 3.96 (s, 3H), 1.43 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 166.60, 164.77, 136.94, 135.76, 130.38, 129.14, 127.80, 125.26, 123.27, 122.72, 120.36, 117.14, 113.06, 104.94, 59.66, 52.21, 14.63. Characterization data is consistent with literature³.

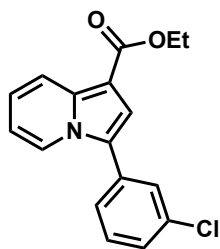


Ethyl 3-(m-tolyl)indolizine-1-carboxylate (3l), 45 mg, 81%, colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.31 (dt, *J* = 7.0, 1.0 Hz, 1H), 8.27 (dt, *J* = 9.0, 1.5 Hz, 1H), 7.42-7.34 (m, 3H), 7.31 (s, 1H), 7.25-7.21 (m, 1H), 7.10-7.06 (m, 1H), 6.71 (td, *J* = 7.0, 1.5 Hz, 1H), 4.41 (q, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 165.07, 138.84, 136.31, 131.19, 129.34, 128.93, 128.79, 126.59, 125.61, 123.47, 122.13, 120.15, 116.00, 112.49, 104.19, 59.53, 21.48, 14.67. Characterization data is consistent with literature².



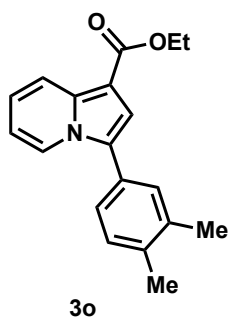
3m

Ethyl 3-(3-bromophenyl)indolizine-1-carboxylate (3m), 52 mg, 75%, white solid, m. p. 105-107 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.30-8.24 (m, 2H), 7.70 (t, *J* = 1.5 Hz, 1H), 7.54-7.50 (m, 1H), 7.48 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.38-7.31 (m, 2H), 7.12-7.07 (m, 1H), 6.74 (td, *J* = 7.0, 1.5 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.77, 136.56, 133.29, 131.26, 130.86, 130.53, 126.91, 124.64, 123.09, 122.49, 120.25, 116.67, 112.91, 104.58, 59.59, 14.63. Characterization data is consistent with literature².

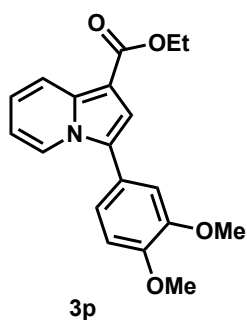


3n

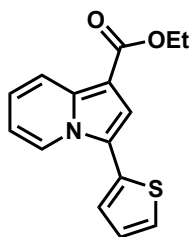
Ethyl 3-(3-chlorophenyl)indolizine-1-carboxylate (3n), 36 mg, 63%, white solid, m. p. 96-98 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.31-8.27 (m, 2H), 7.56-7.54 (m, 1H), 7.46-7.41 (m, 2H), 7.40-7.36 (m, 1H), 7.33 (s, 1H), 7.12-7.08 (m, 1H), 6.75 (td, *J* = 7.0, 1.5 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.84, 136.59, 135.01, 133.06, 130.34, 128.41, 127.99, 126.51, 124.82, 123.15, 122.51, 120.29, 116.66, 112.93, 104.60, 59.63, 14.65. Characterization data is consistent with literature².



Ethyl 3-(3,4-dimethylphenyl)indolizine-1-carboxylate (3o), 48 mg, 83%, white solid, m. p. 94-96 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.31- 8.25 (m, 2H), 7.34-7.24 (m, 4H), 7.08-7.04 (m, 1H), 6.69 (td, *J* = 7.0, 1.5 Hz, 1H), 4.42 (q, *J* = 7.0 Hz, 2H), 2.35 (s, 6H), 1.45 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 165.01, 137.29, 136.55, 136.11, 130.17, 129.80, 128.64, 126.58, 125.92, 123.41, 121.90, 120.02, 115.64, 112.31, 104.00, 59.40, 19.75, 19.51, 14.62. Characterization data is consistent with literature².

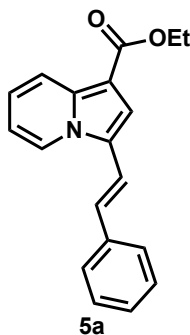


Ethyl 3-(3,4-dimethoxyphenyl)indolizine-1-carboxylate (3p), 52 mg, 82%, white solid, m. p. 78-80 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.27-8.21 (m, 2H), 7.26 (s, 1H), 7.08 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.07-7.02 (m, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.68 (td, *J* = 7.0, 1.0 Hz, 1H), 4.39 (q, *J* = 7.0 Hz, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 1.42 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.95, 149.37, 148.98, 135.98, 126.26, 123.76, 123.30, 121.92, 121.18, 120.03, 115.55, 112.40, 112.21, 111.54, 103.90, 59.44, 55.97, 55.93, 14.60. Characterization data is consistent with literature⁴.

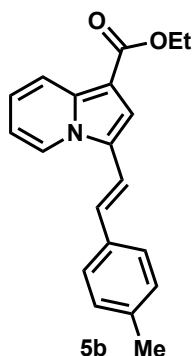


3q

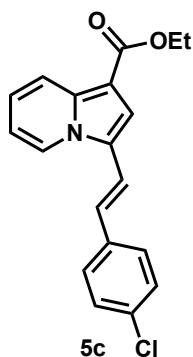
Ethyl 3-(thiophen-2-yl)indolizine-1-carboxylate (3q), 34 mg, 64%, white solid, m. p. 76-78 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.40 (dt, *J* = 7.0, 1.0 Hz, 1H), 8.28 (dt, *J* = 9.0, 1.5 Hz, 1H), 7.45-7.39 (m, 2H), 7.27 (d, *J* = 1.5 Hz, 1H), 7.19 (dd, *J* = 5.0, 3.5 Hz, 1H), 7.13-7.09 (m, 1H), 6.79 (td, *J* = 7.0, 1.5 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.81, 136.60, 132.34, 127.69, 126.24, 125.84, 123.80, 122.49, 120.06, 119.17, 117.47, 112.95, 104.39, 59.63, 14.66. Characterization data is consistent with literature³.



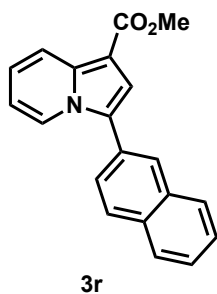
Ethyl (E)-3-styrylindolizine-1-carboxylate (5a), 23 mg, total isolated yield: 40%, *E/Z* = 3.3:1, yellow solid, m. p. 90-92 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.25 (dt, *J* = 9.0, 1.0 Hz, 1H), 8.19 (dt, *J* = 7.0, 1.0 Hz, 1H), 7.58-7.56 (m, 1H), 7.55-7.51 (m, 2H), 7.42-7.37 (m, 2H), 7.31-7.28 (m, 1H), 7.23 (d, *J* = 16.0 Hz, 1H), 7.13 (d, *J* = 16.0 Hz, 1H), 7.11-7.08 (m, 1H), 6.83 (td, *J* = 7.0, 1.5 Hz, 1H), 4.41 (q, *J* = 7.0 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.83, 137.28, 136.49, 128.80, 128.18, 127.62, 126.21, 124.55, 122.93, 122.20, 120.25, 114.49, 113.98, 113.02, 105.00, 59.66, 14.66. Characterization data is consistent with literature⁵.



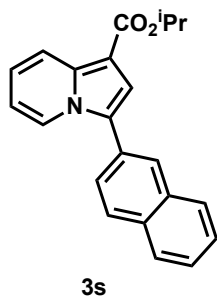
Ethyl (E)-3-(4-methylstyryl)indolizine-1-carboxylate (5b), 27 mg, total isolated yield: 45%, *E/Z*= 7.4:1, yellow solid, m. p. 79-81 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.24 (dt, *J* = 9.0, 1.0 Hz, 1H), 8.16 (dt, *J* = 7.0, 1.0 Hz, 1H), 7.54 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 16.0 Hz, 1H), 7.10 (d, *J* = 16.0 Hz, 1H), 7.10-7.06 (m, 1H), 6.81 (td, *J* = 7.0, 1.5 Hz, 1H), 4.41 (q, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.87, 137.60, 136.40, 134.50, 129.52, 128.31, 126.15, 124.74, 122.93, 122.07, 120.23, 113.72, 113.54, 112.94, 104.91, 59.64, 21.28, 14.67. HRMS (ESI) *m/z* calculated for [C₂₀H₁₉NO₂+H]⁺ 306.1488, found 306.1481.



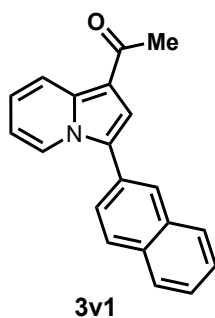
Ethyl (E)-3-(4-chlorostyryl)indolizine-1-carboxylate (5c), 32 mg, total isolated yield: 50%, *E/Z*= 3.8:1, yellow solid, m. p. 109-111 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.25 (dt, *J* = 9.0, 1.0 Hz, 1H), 8.18 (dt, *J* = 7.0, 1.1 Hz, 1H), 7.56 (s, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.21-7.19 (m, 1H), 7.13-7.08 (m, 1H), 7.06 (d, *J* = 16.0 Hz, 1H), 6.84 (td, *J* = 7.0, 1.5 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H). HRMS (ESI) *m/z* calculated for [C₁₉H₁₆NO₂+H]⁺ 326.0942, found 326.0938.



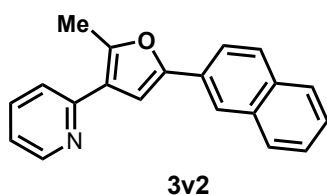
Methyl 3-(naphthalen-2-yl)indolizine-1-carboxylate (3r), 44 mg, 74%, white solid, m. p. 118-120 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.39 (dt, *J* = 7.0, 1.0 Hz, 1H), 8.32 (dt, *J* = 9.0, 1.0 Hz, 1H), 8.01 (d, *J* = 1.0 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.92-7.86 (m, 2H), 7.64 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.57-7.52 (m, 2H), 7.42 (s, 1H), 7.13-7.09 (m, 1H), 6.73 (td, *J* = 7.0, 1.5 Hz, 1H), 3.96 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 165.32, 136.53, 133.54, 132.77, 128.77, 128.51, 127.94, 127.76, 127.31, 126.64, 126.41, 126.26, 123.34, 122.41, 120.14, 116.43, 112.73, 104.10, 50.91. Characterization data is consistent with literature⁶.



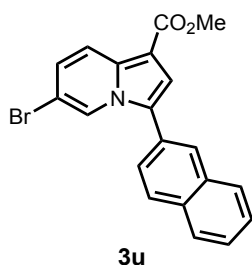
Isopropyl 3-(naphthalen-2-yl)indolizine-1-carboxylate (3s), 49 mg, 75%, colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.40 (d, *J* = 7.0 Hz, 1H), 8.32 (d, *J* = 9.0 Hz, 1H), 8.03 (d, *J* = 0.9 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.93-7.87 (m, 2H), 7.67 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.59-7.52 (m, 2H), 7.44 (s, 1H), 7.11 m, 1H), 6.74 (td, *J* = 7.0, 1.5 Hz, 1H), 5.37-5.31 (m, 1H), 1.44 (d, *J* = 6.5 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 164.60, 136.37, 133.57, 132.76, 128.77, 128.64, 127.96, 127.79, 127.32, 126.64, 126.40, 126.33, 126.28, 123.33, 122.24, 120.26, 116.57, 112.65, 104.91, 66.68, 22.31. HRMS (ESI) *m/z* calculated for [C₂₂H₁₉NO₂+H]⁺ 330.1488, found 330.1480.



1-(3-(Naphthalen-2-yl)indolizin-1-yl)ethan-1-one (3v1), 16 mg, 28%, white solid, m. p. 136-138 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.58 (dt, *J* = 9.0, 1.5 Hz, 1H), 8.40 (dt, *J* = 7.0, 1.0 Hz, 1H), 8.03 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.94-7.88 (m, 2H), 7.66 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.60-7.54 (m, 2H), 7.32 (s, 1H), 7.23-7.28 (m, 1H), 6.82 (td, *J* = 6.5, 1.5 Hz, 1H), 2.61 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 193.03, 136.07, 133.62, 132.89, 128.91, 128.45, 127.99, 127.85, 127.58, 126.78, 126.58, 126.34, 126.31, 123.97, 123.25, 121.19, 116.87, 113.76, 113.73, 28.03.



2-(2-Methyl-5-(naphthalen-2-yl)furan-3-yl)pyridine (3v2), 36 mg, 63%, white solid, m. p. 96-98 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.70-8.68 (m, 1H), 8.19 (s, 1H), 7.92-7.80 (m, 4H), 7.71 (td, *J* = 8.0, 2.0 Hz, 1H), 7.53-7.44 (m, 3H), 7.18-7.13 (m, 2H), 2.78 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 153.17, 151.76, 151.07, 149.50, 136.28, 133.57, 132.58, 128.33, 128.08, 128.00, 127.72, 126.41, 125.74, 122.85, 122.13, 121.65, 121.08, 120.85, 106.13, 14.10.



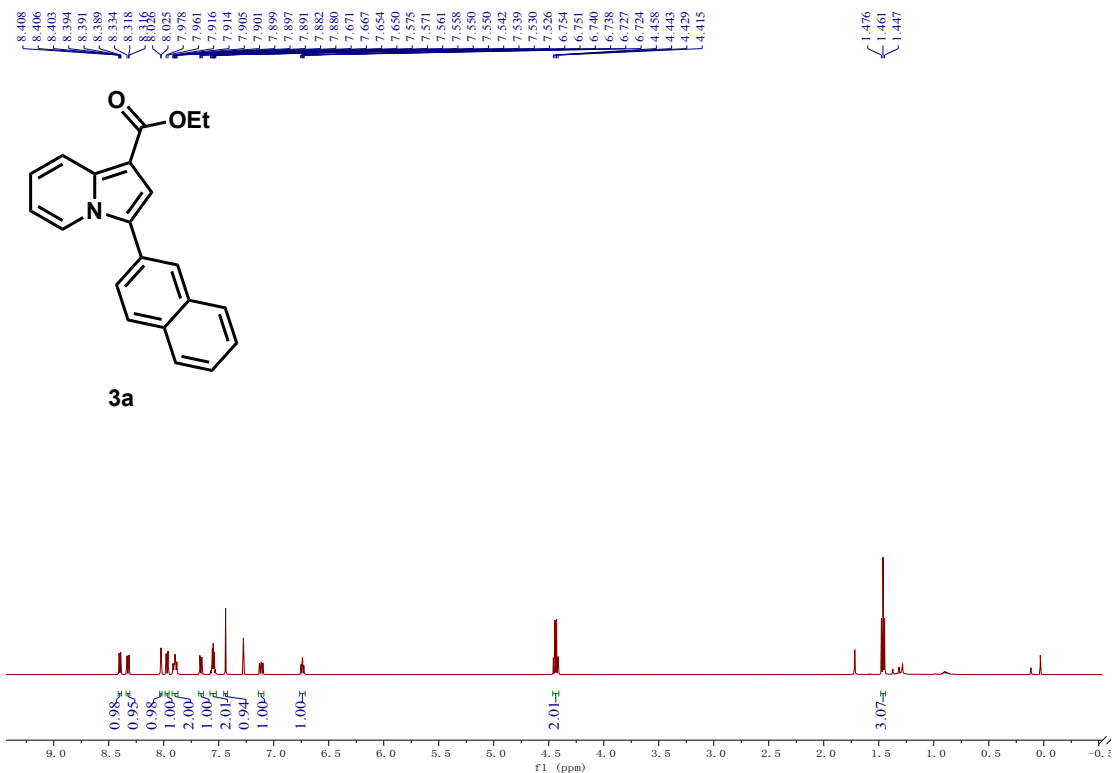
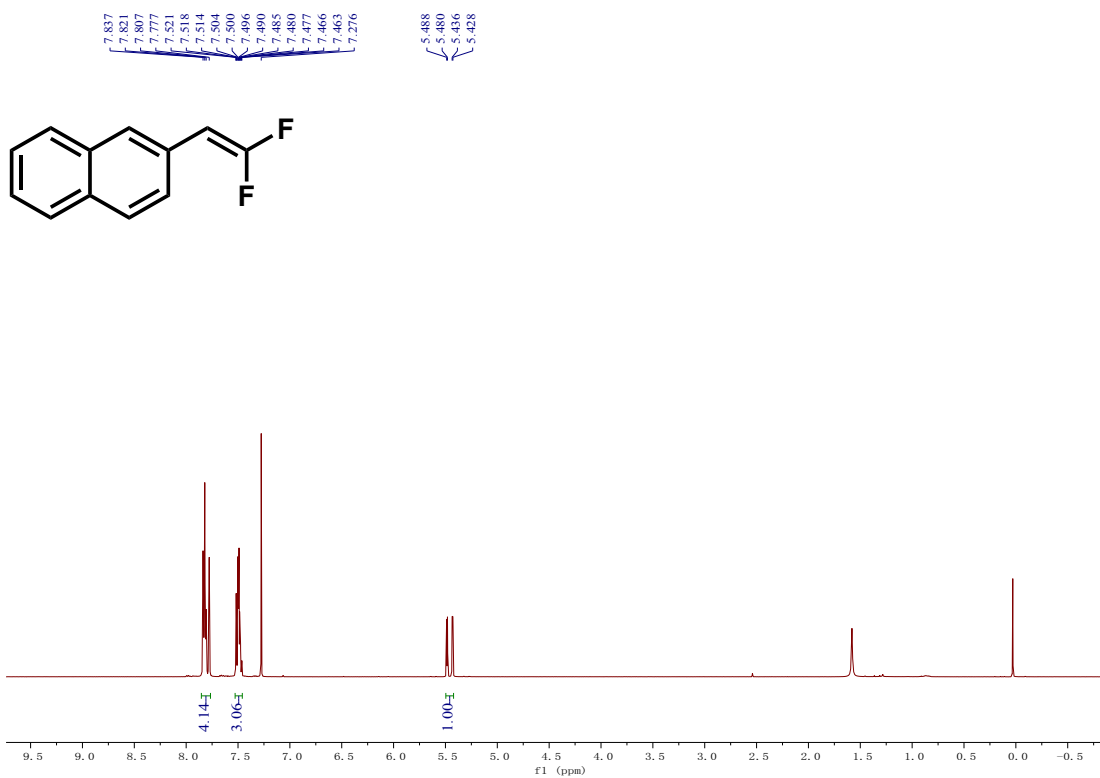
Methyl 6-bromo-3-(naphthalen-2-yl)indolizine-1-carboxylate (3u), 53 mg, 70%, white solid, m. p. 176-178 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.48 (dd, *J* = 1.5, 1.0 Hz, 1H), 8.21 (dd, *J* = 9.5, 0.5 Hz, 1H), 8.01-7.97 (m, 2H), 7.94-7.89 (m, 2H), 7.62 (dd, *J*

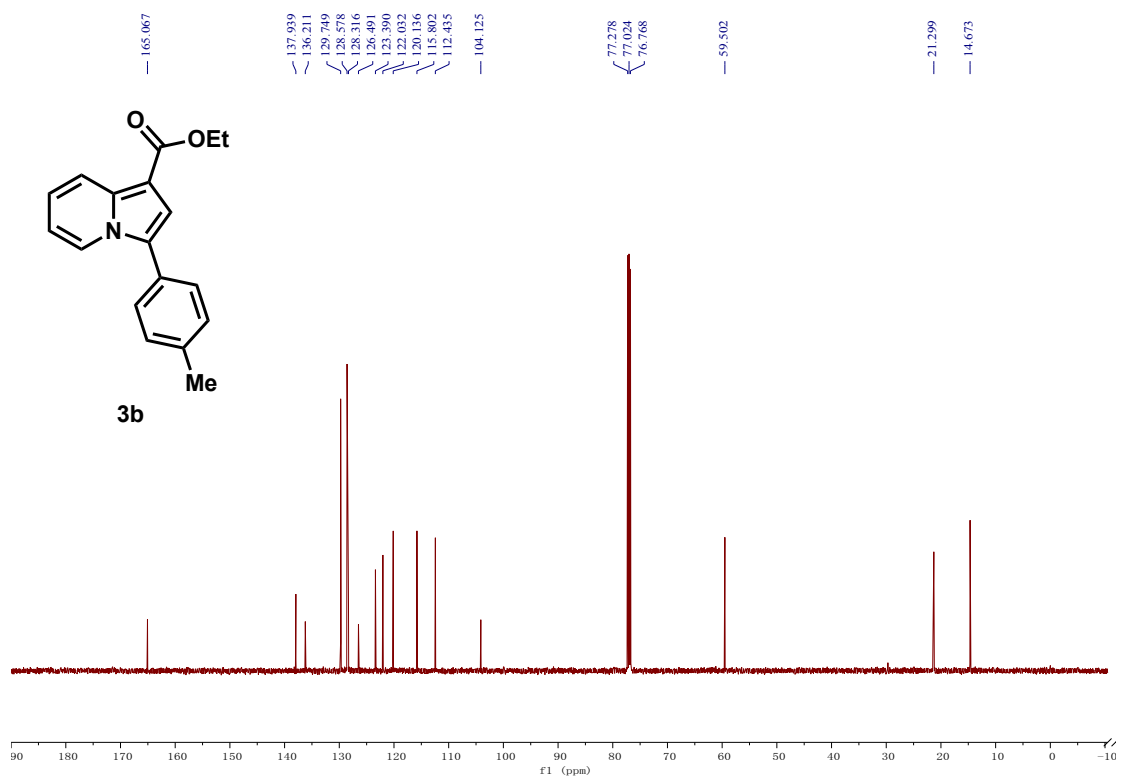
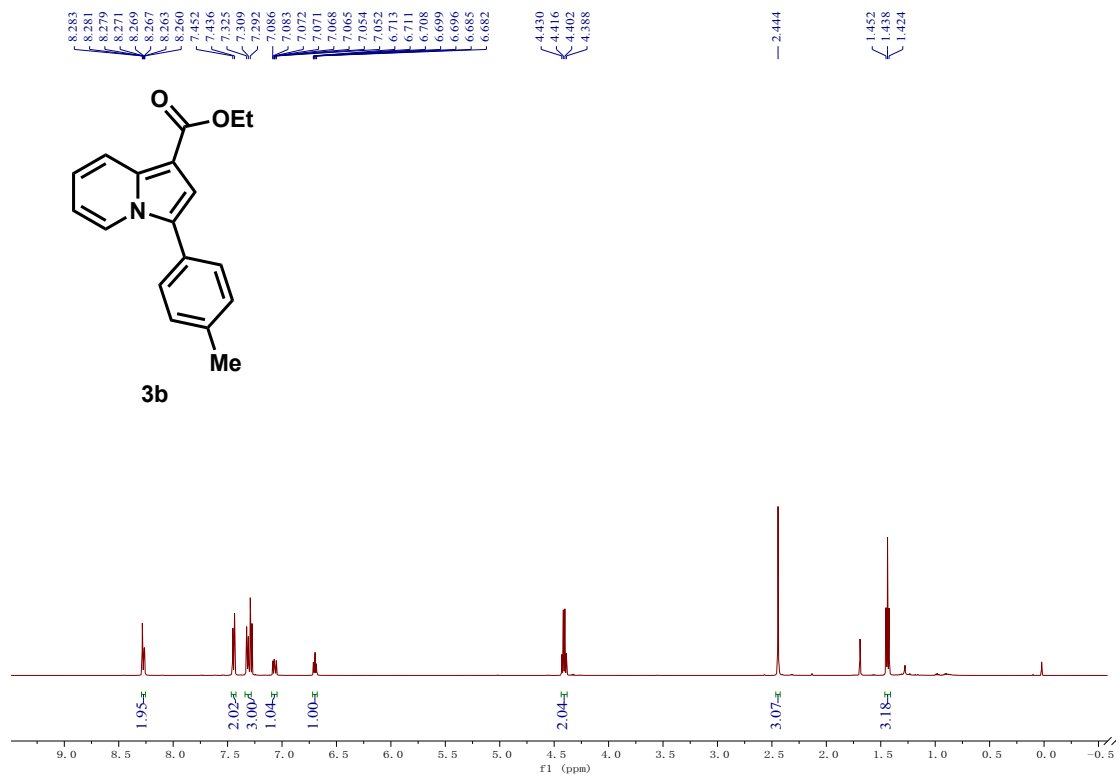
= 8.5, 2.0 Hz, 1H), 7.59-7.54 (m, 2H), 7.38 (s, 1H), 7.15 (dd, $J = 9.5, 2.0$ Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (125MHz, CDCl_3) δ 164.97, 134.48, 133.53, 132.98, 129.07, 128.07, 127.87, 127.84, 127.66, 126.82, 126.72, 126.10, 125.42, 123.29, 120.82, 116.81, 107.95, 105.36, 51.12.

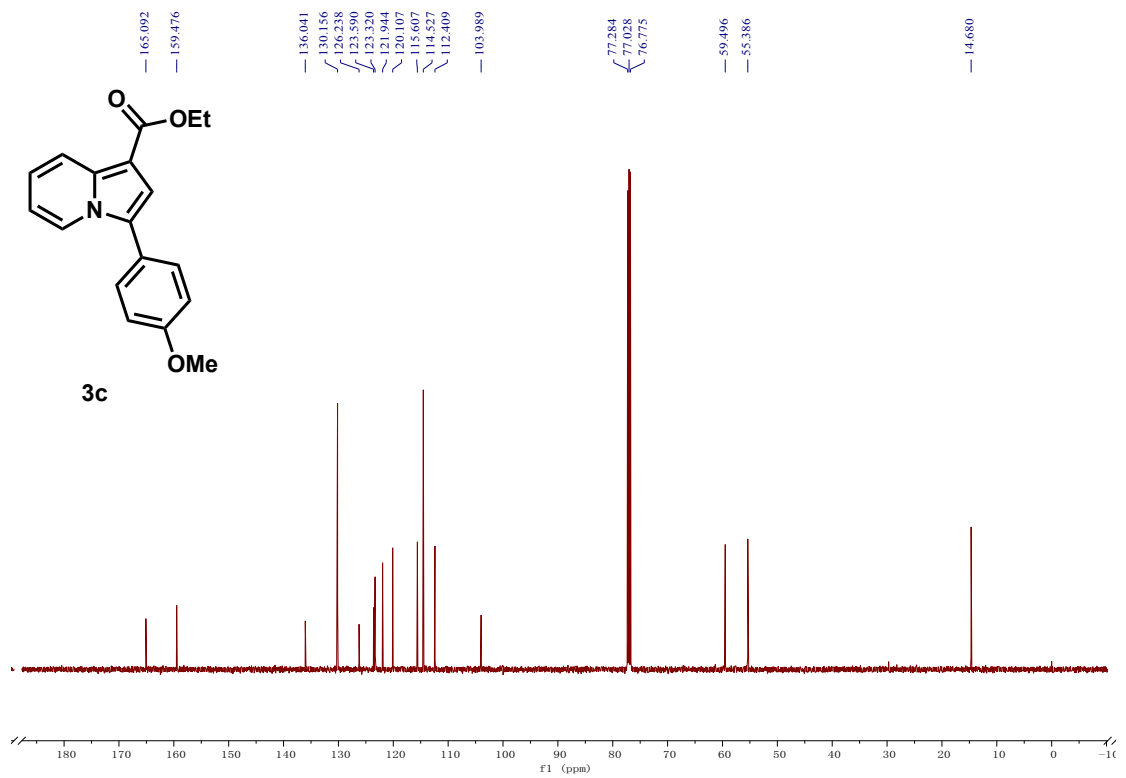
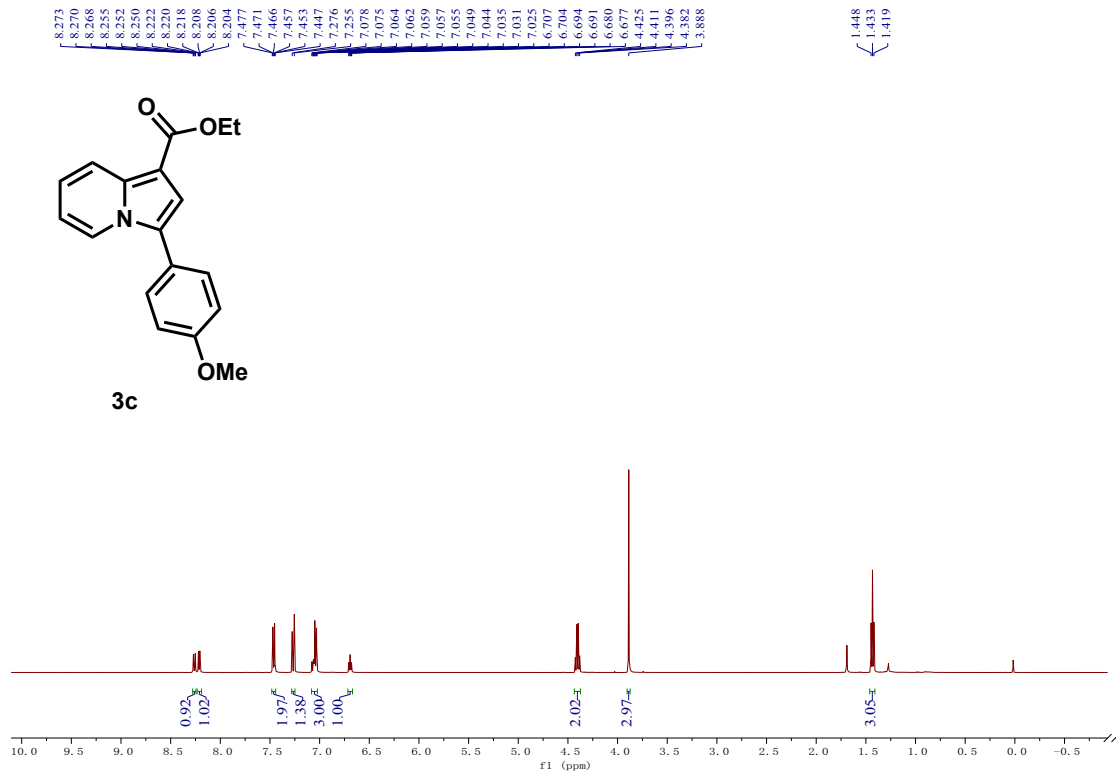
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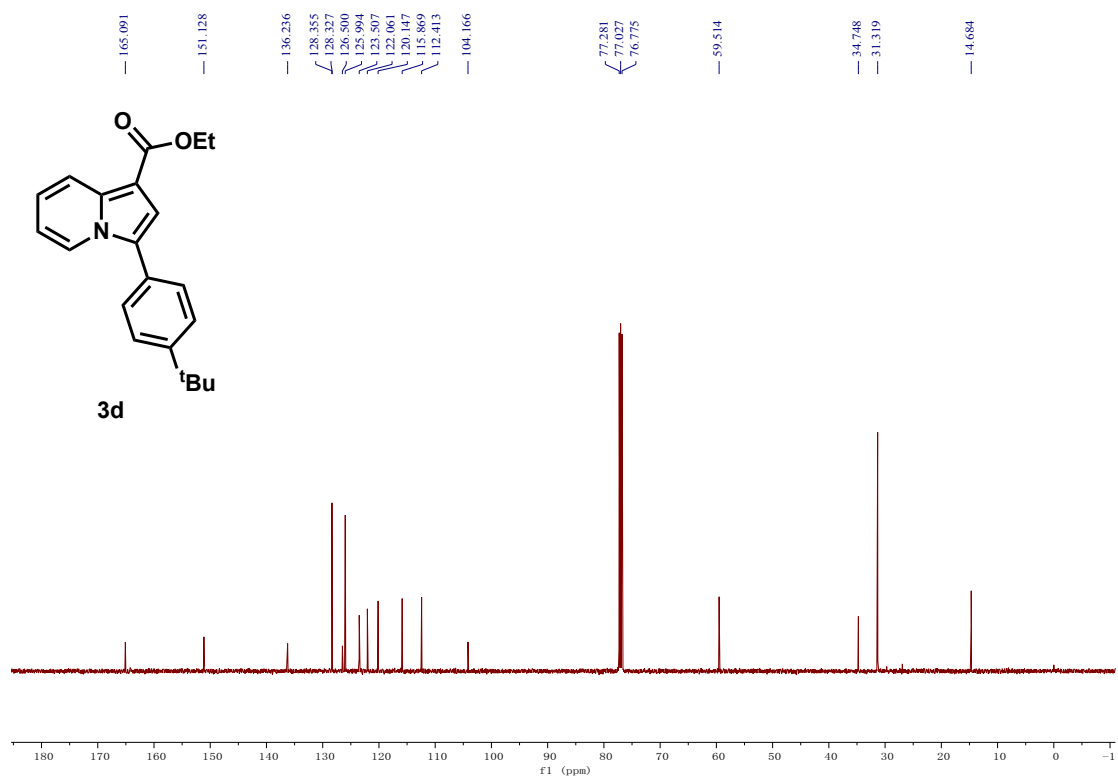
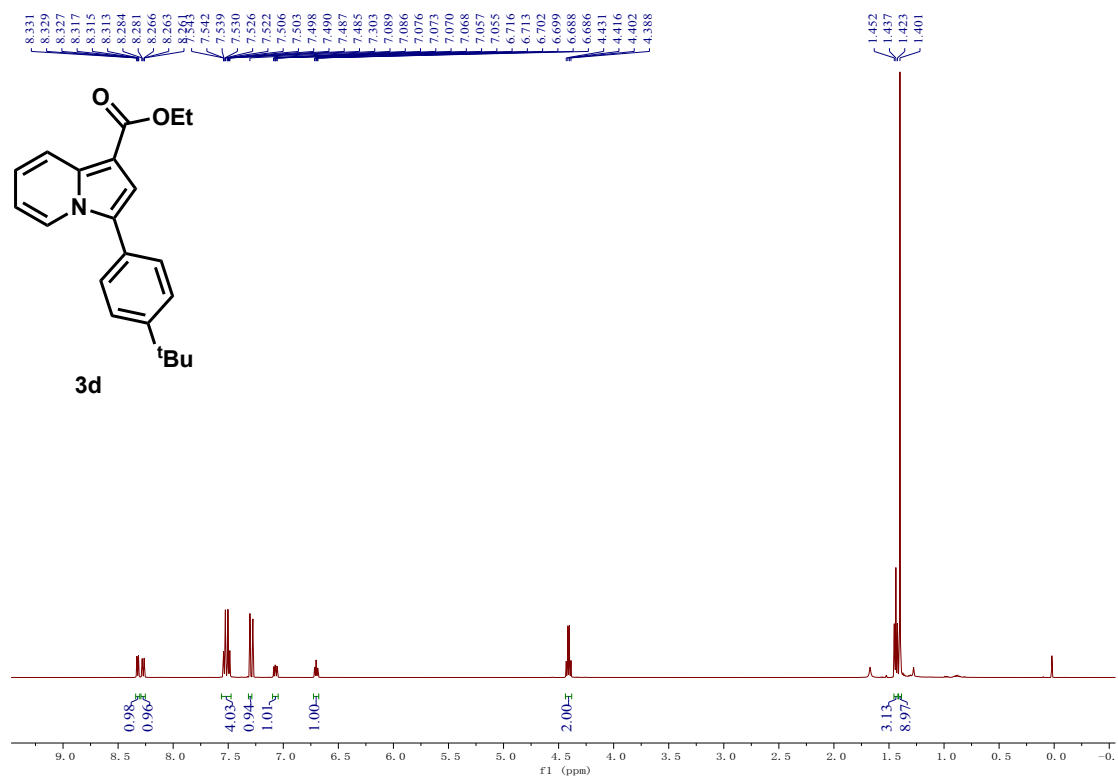
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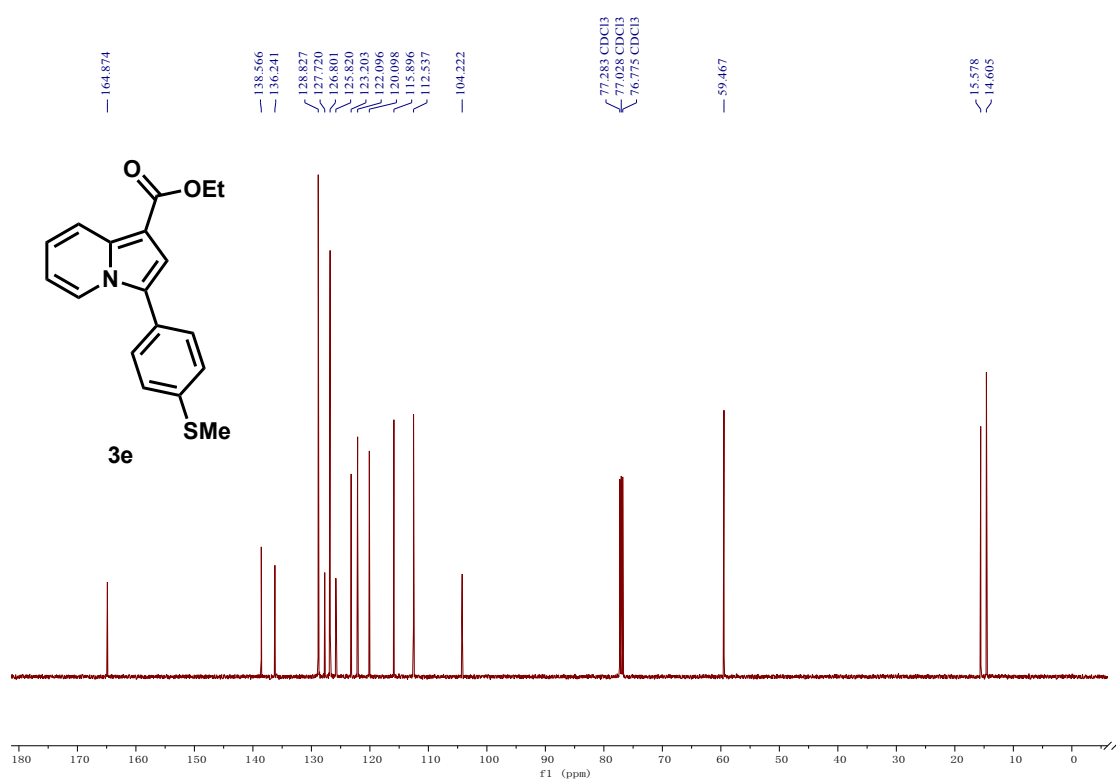
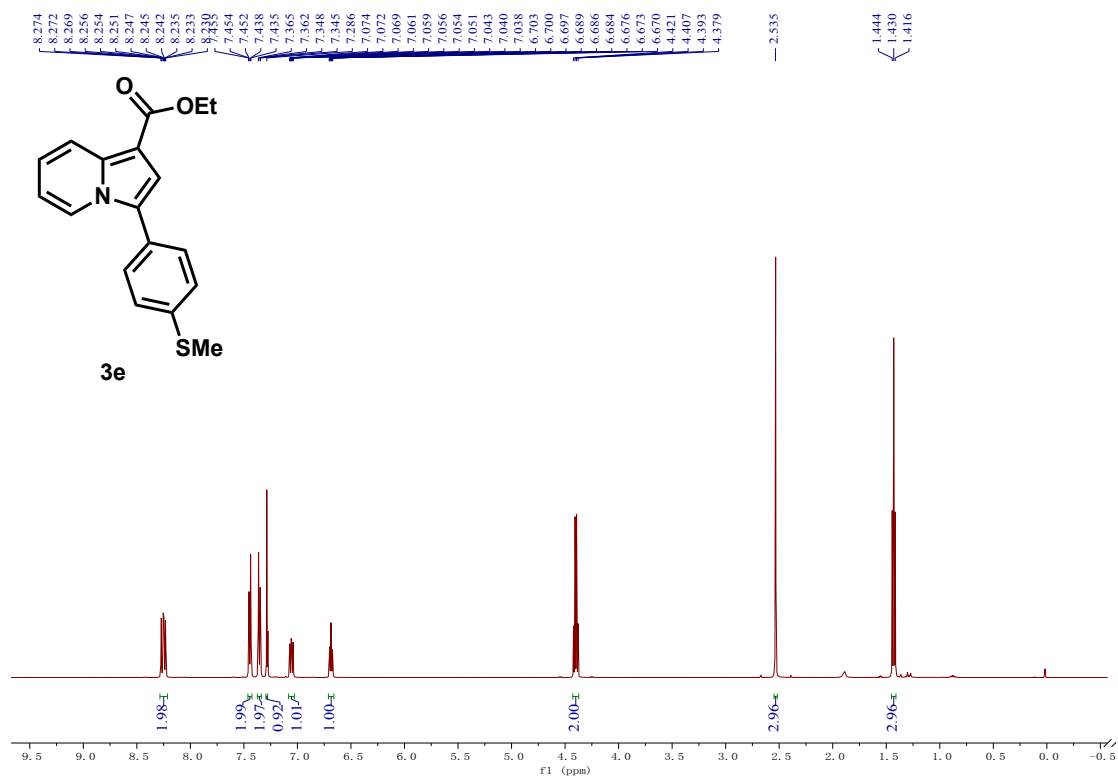
¹H, ¹³C NMR Spectra of the Title Compounds

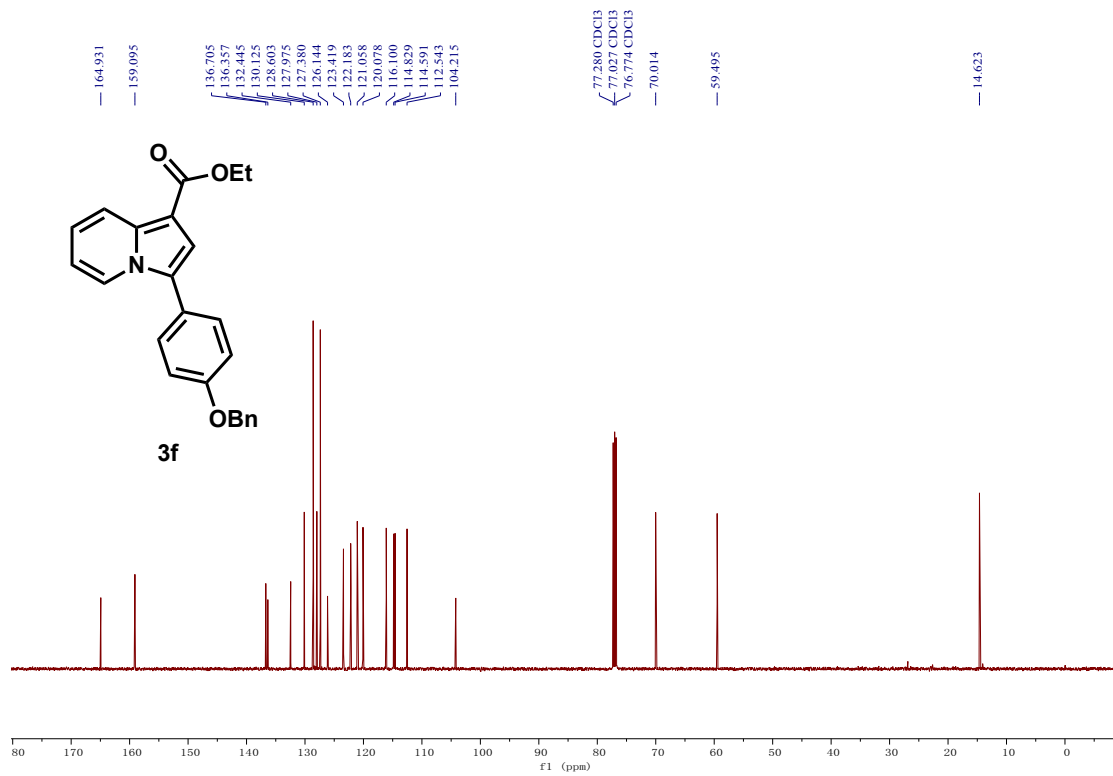
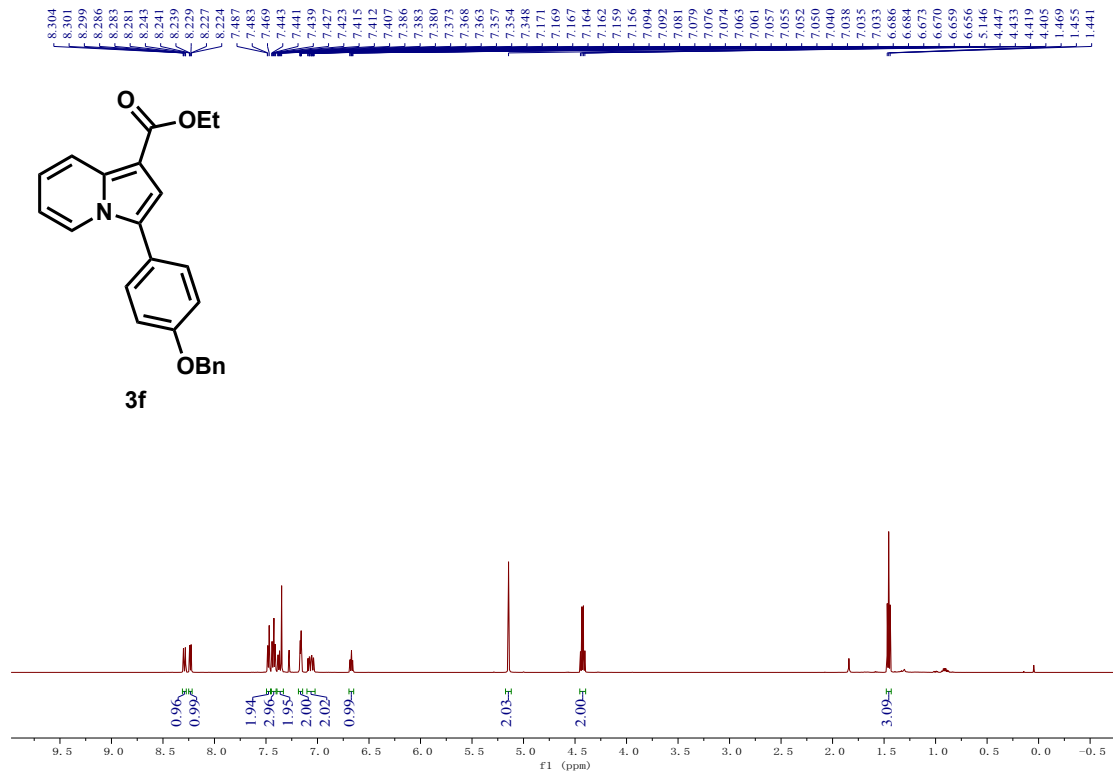


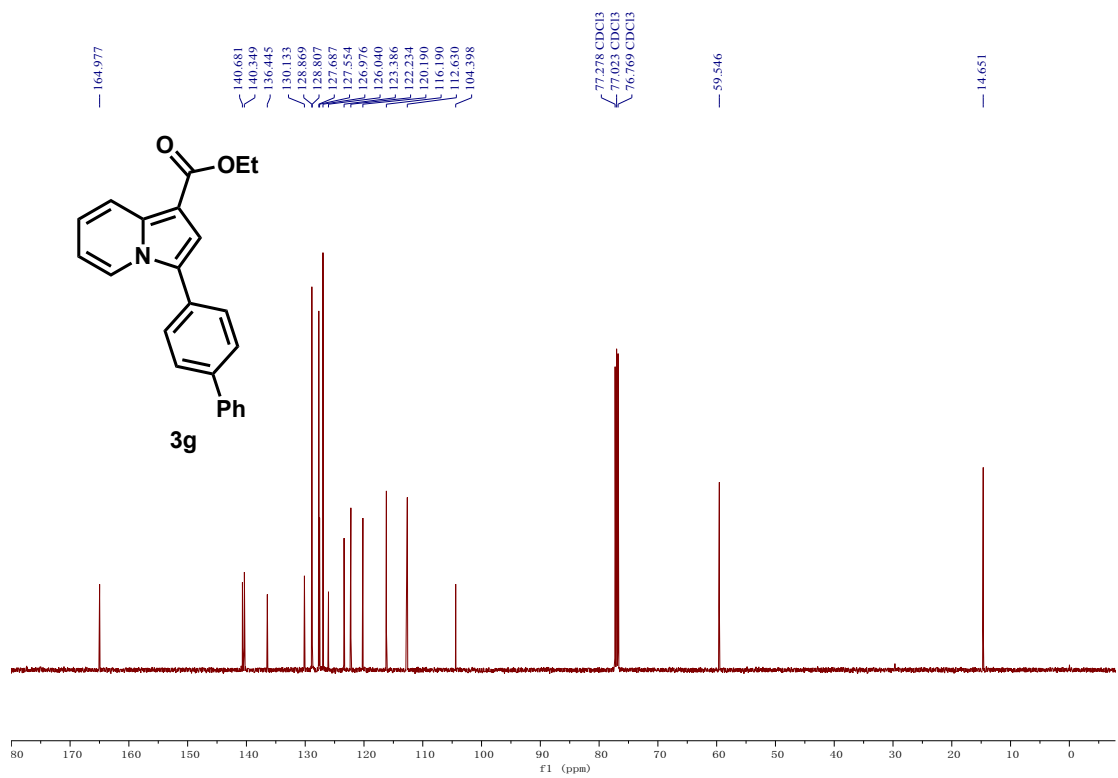
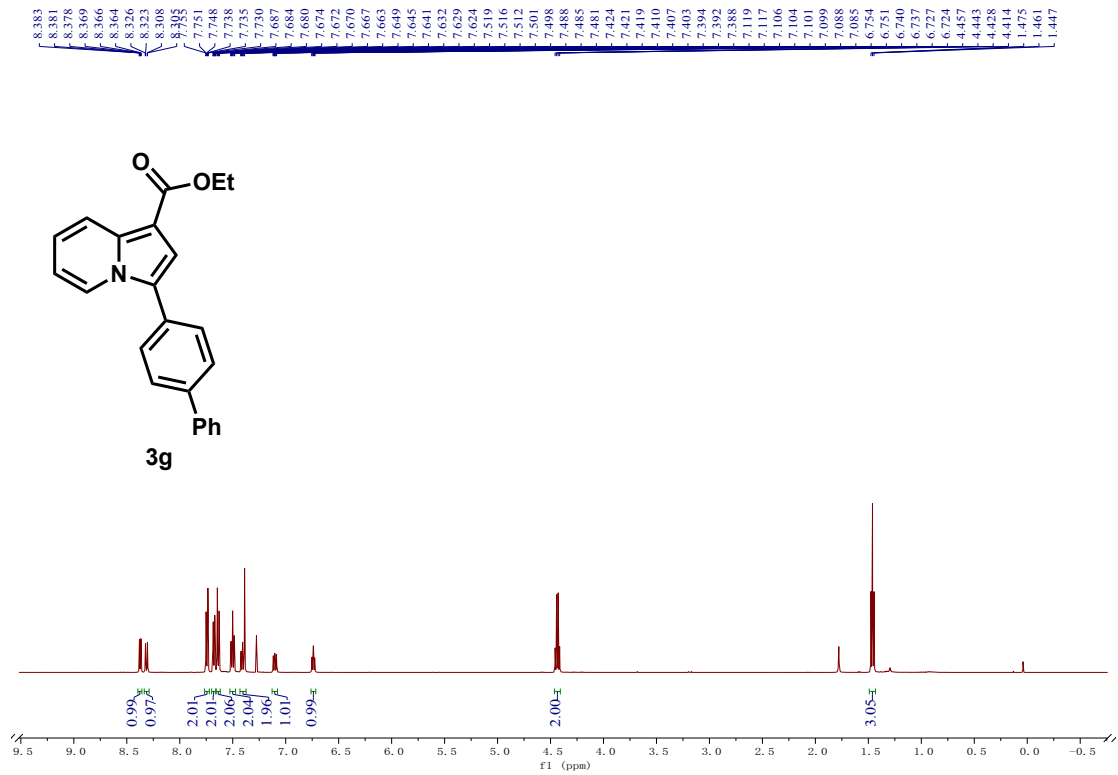


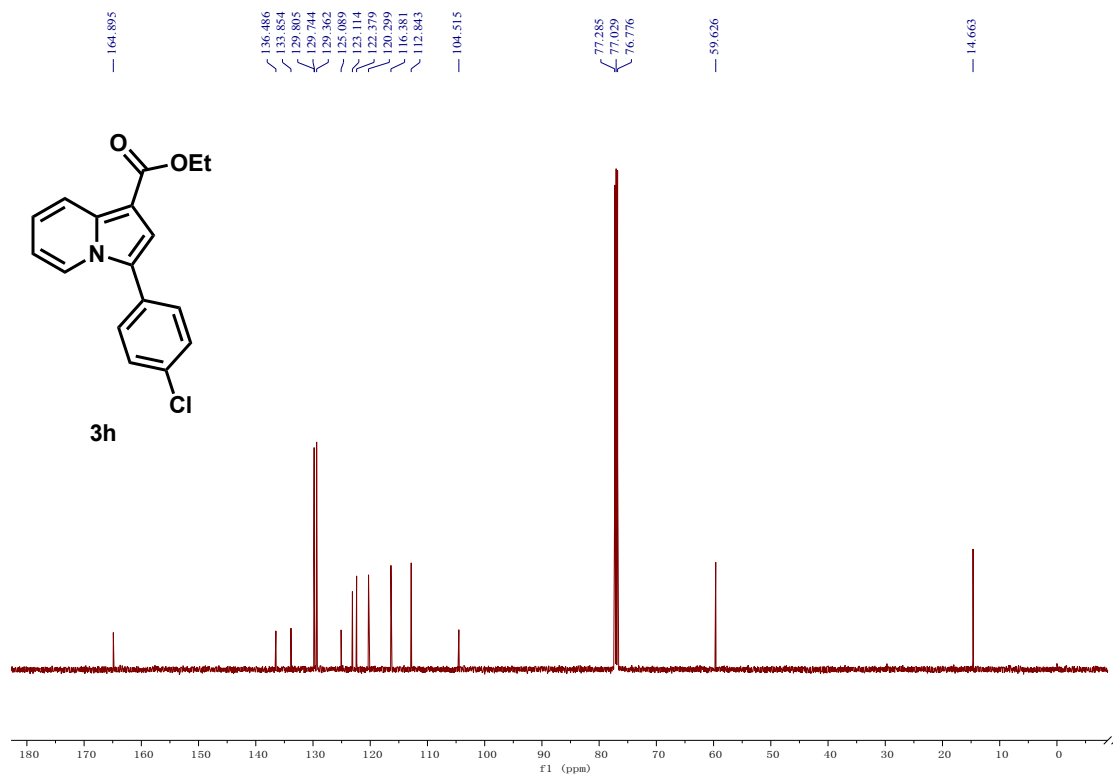
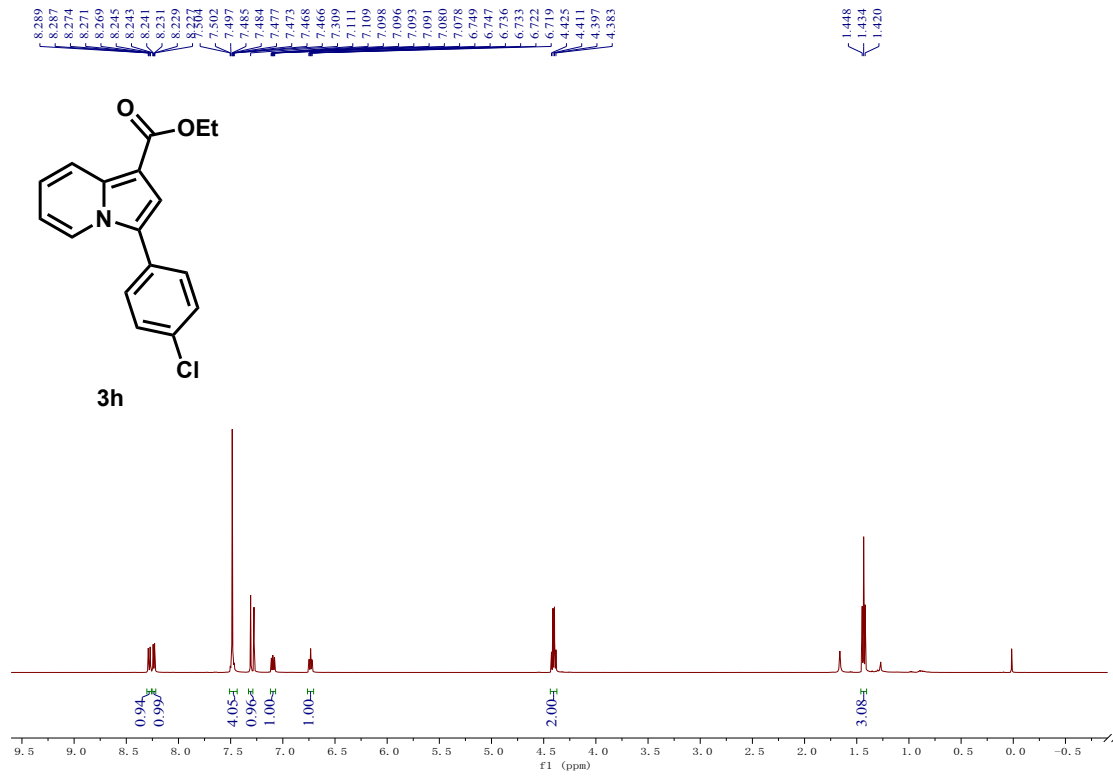


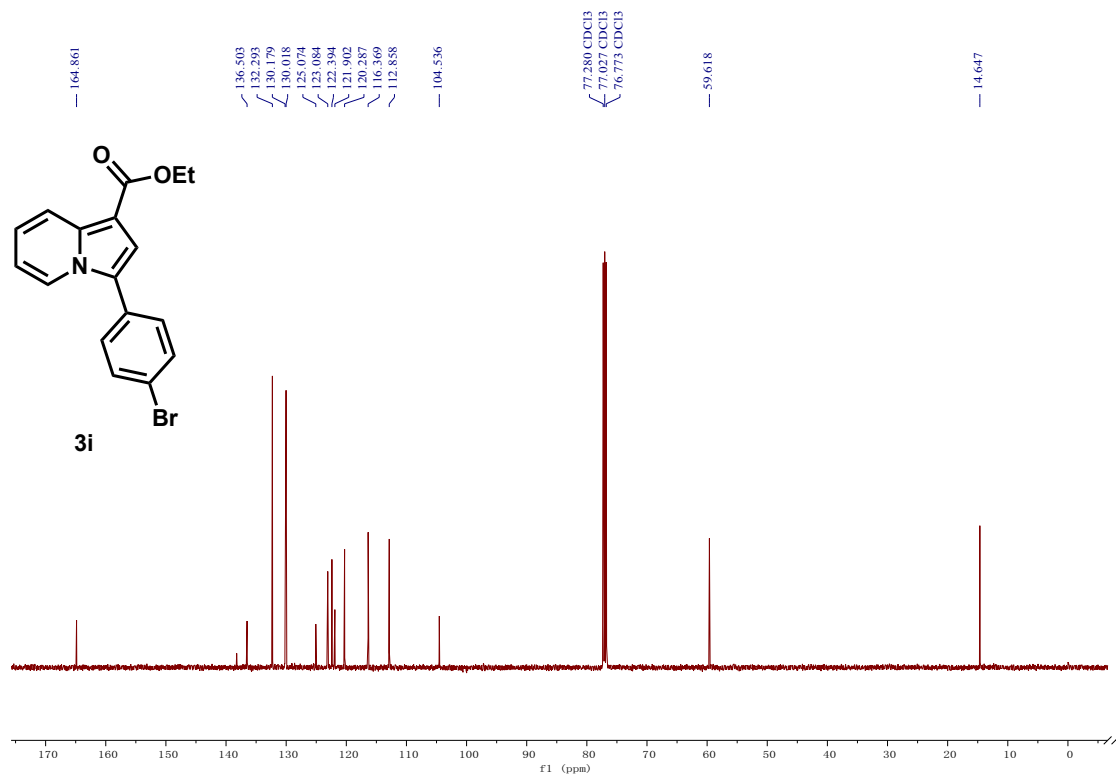
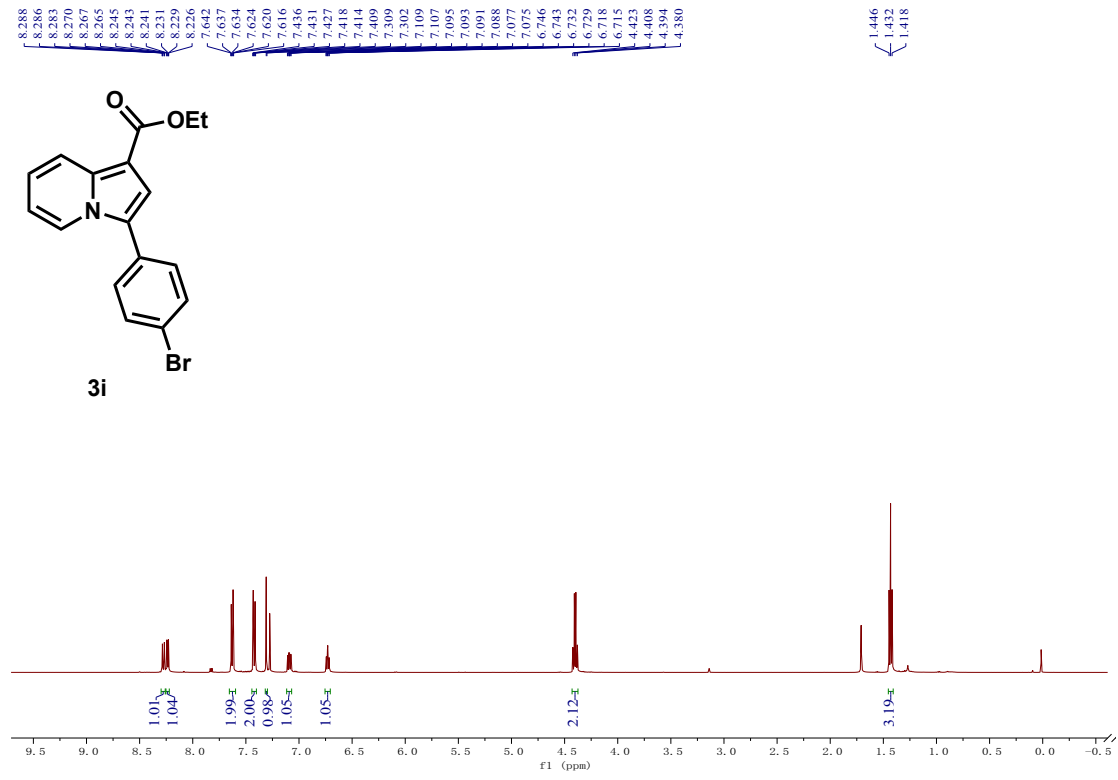


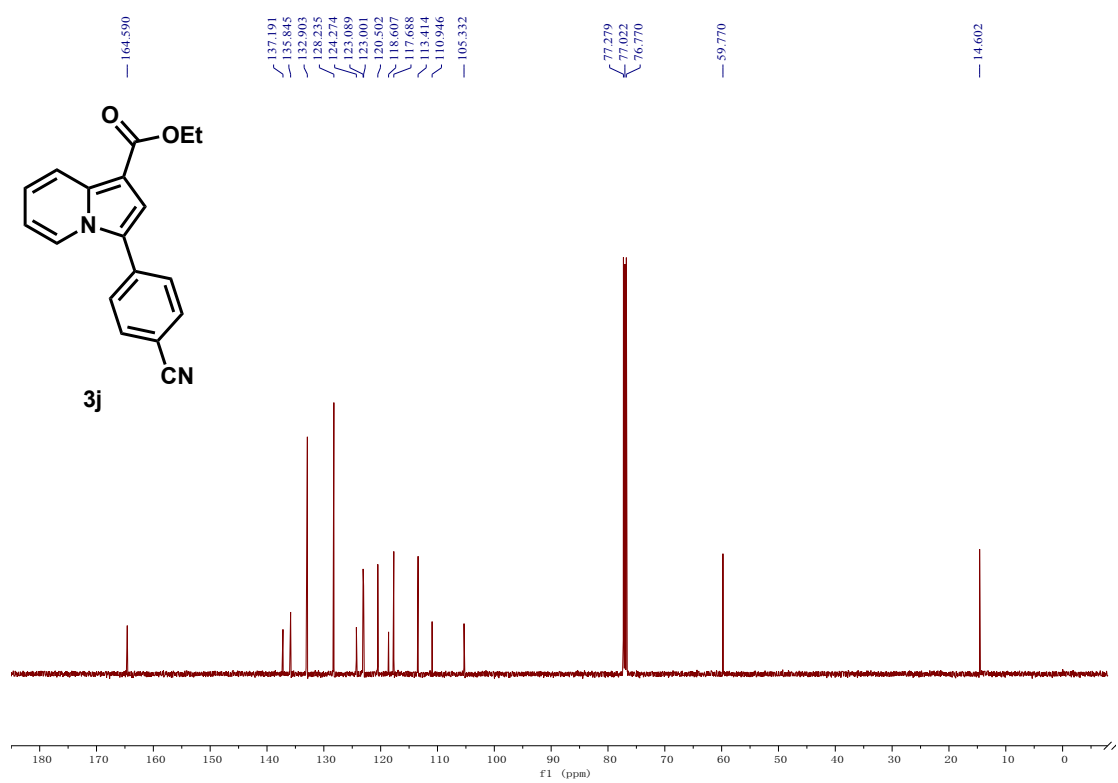
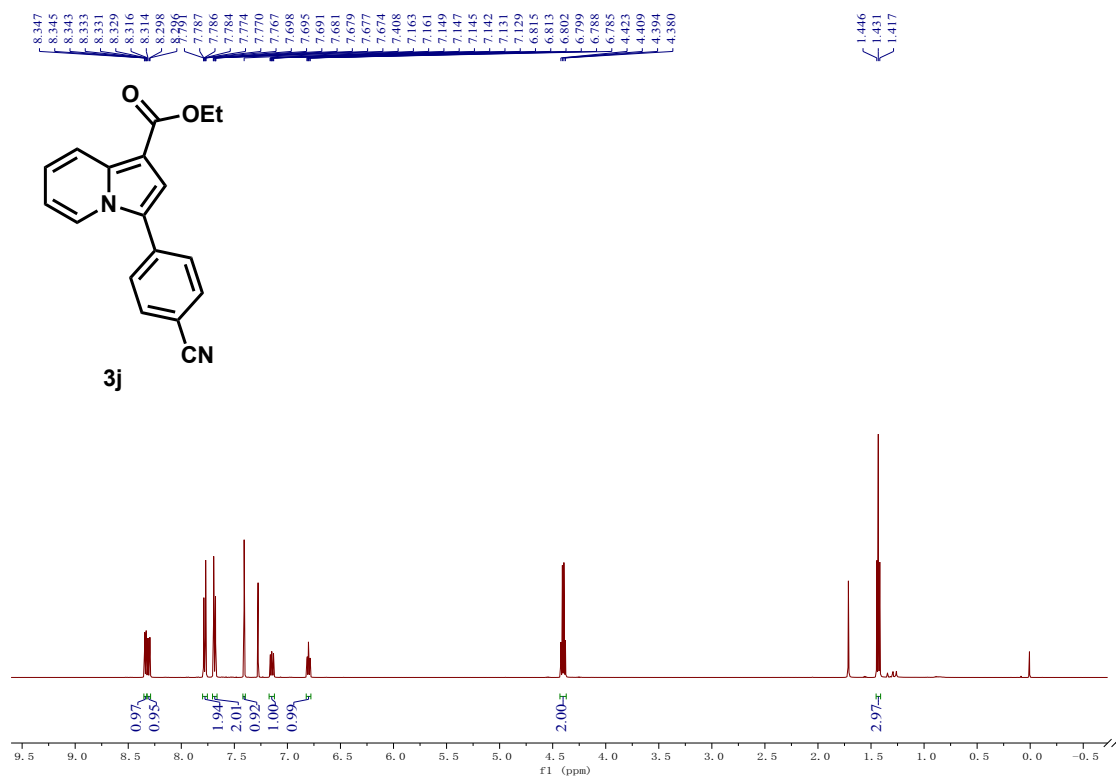


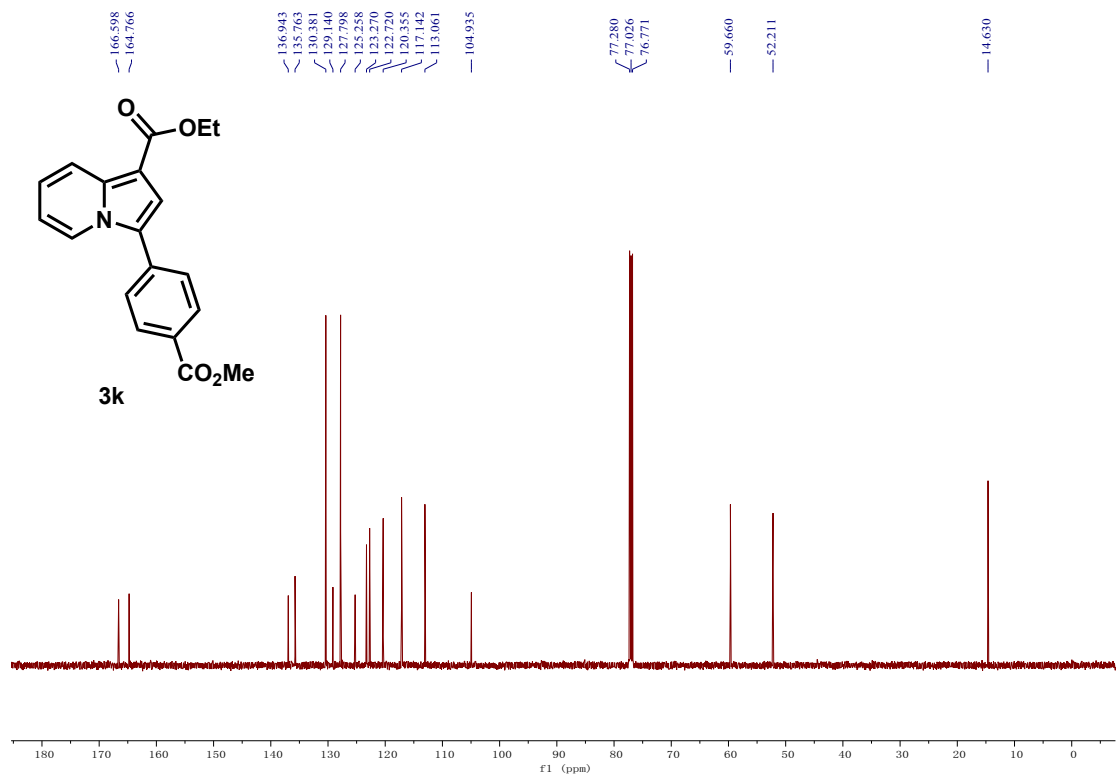
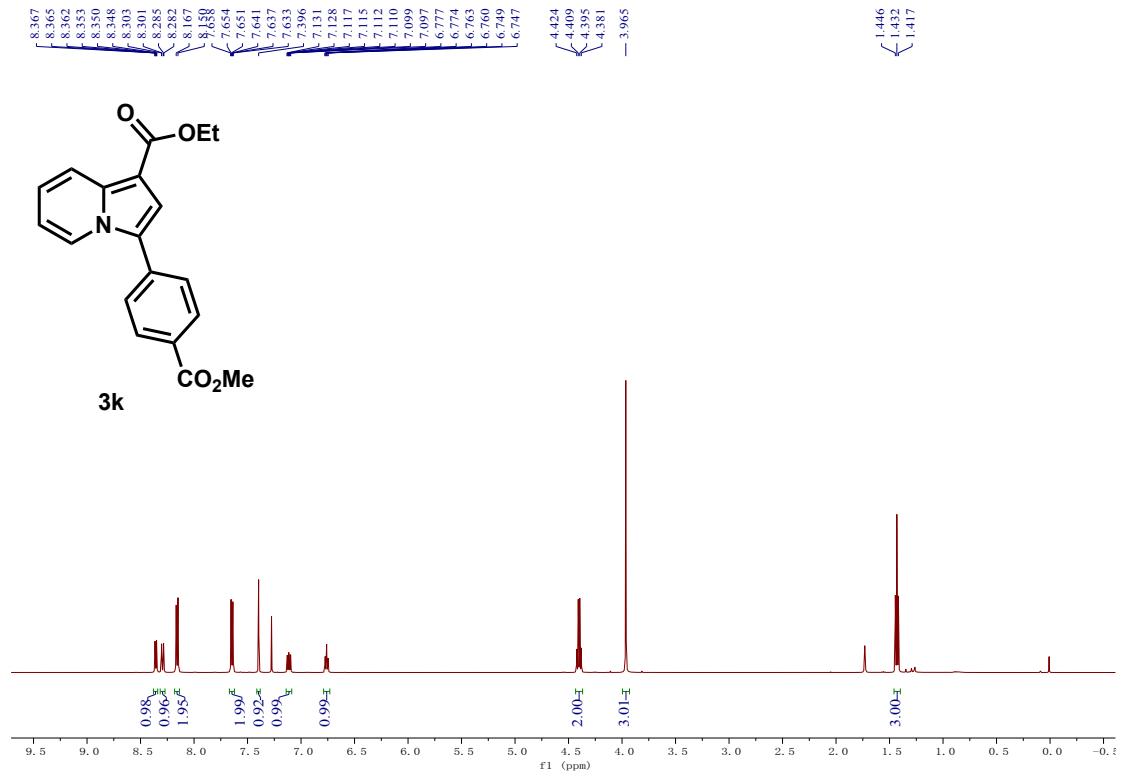




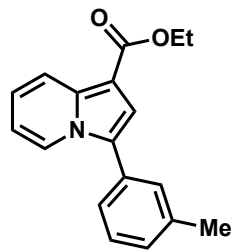




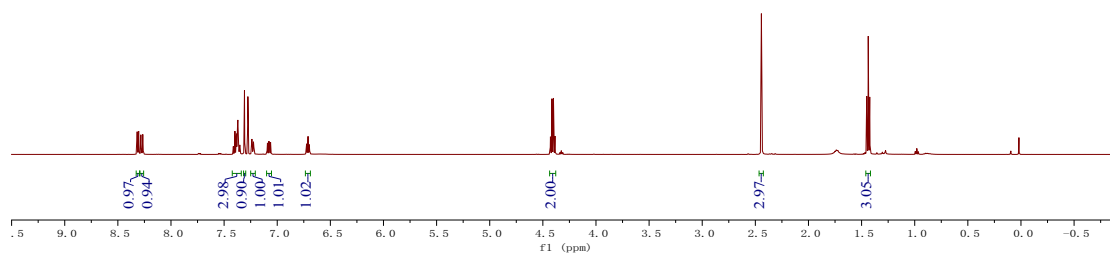




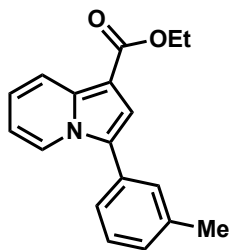
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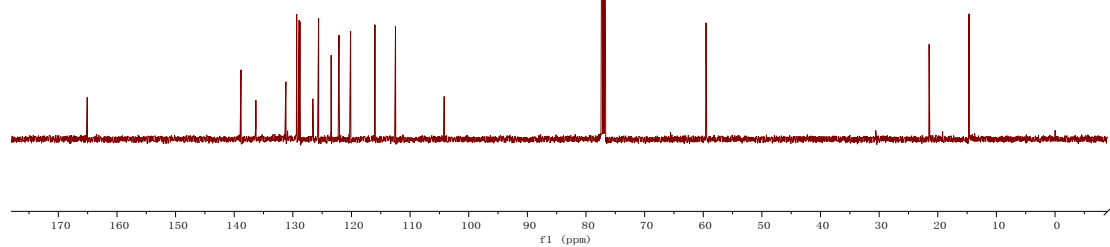
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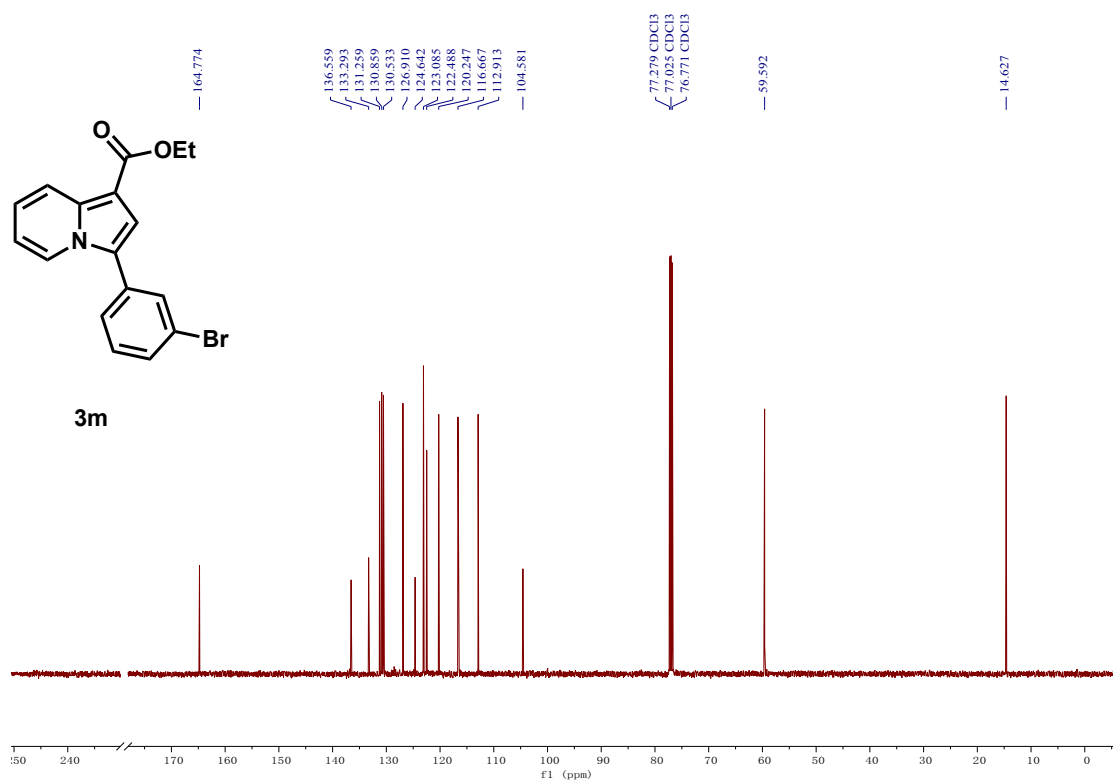
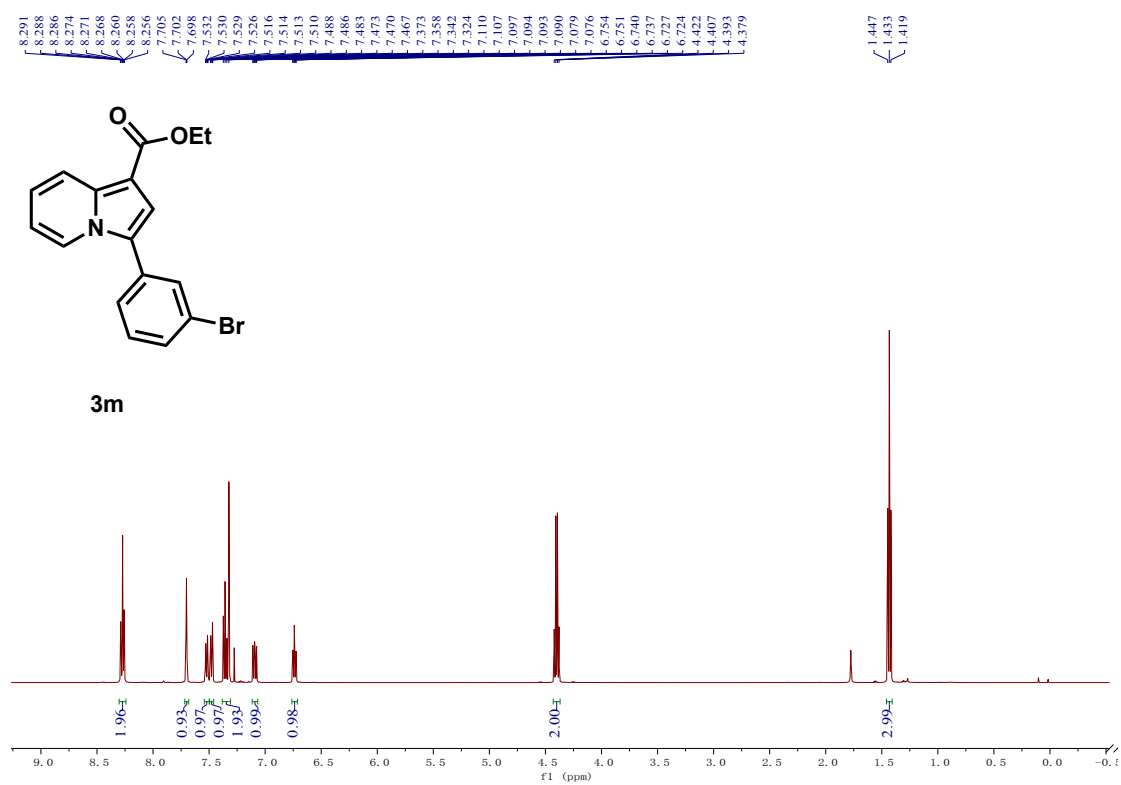


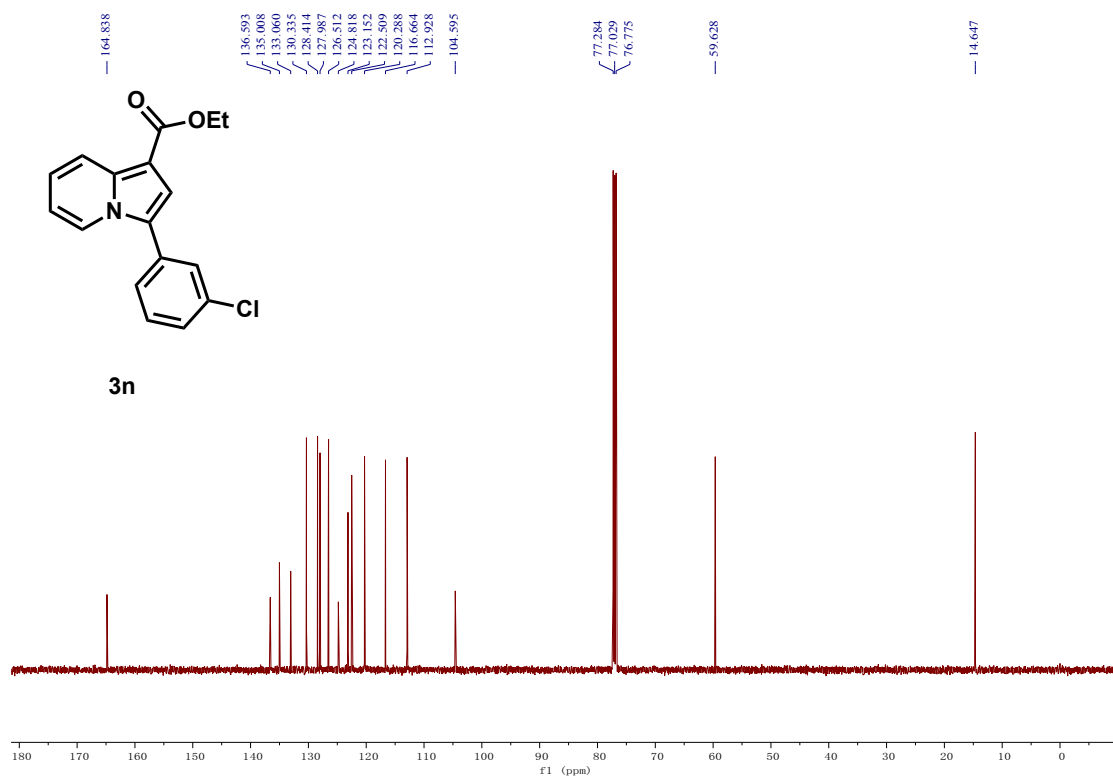
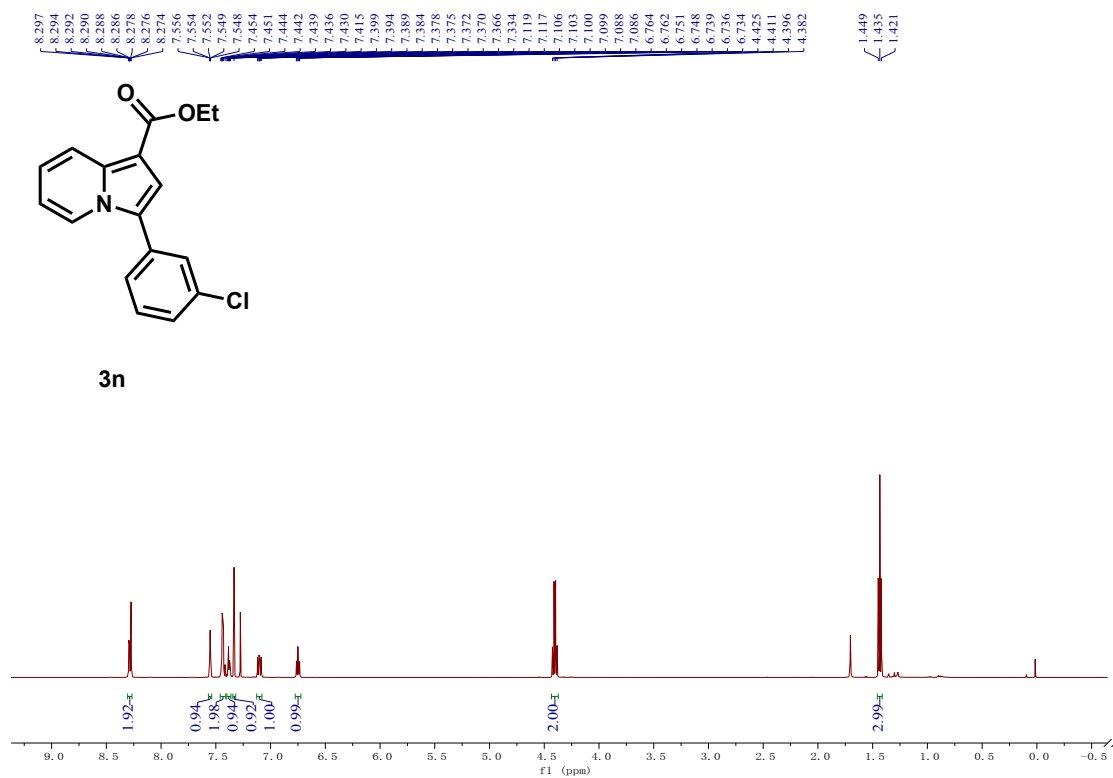
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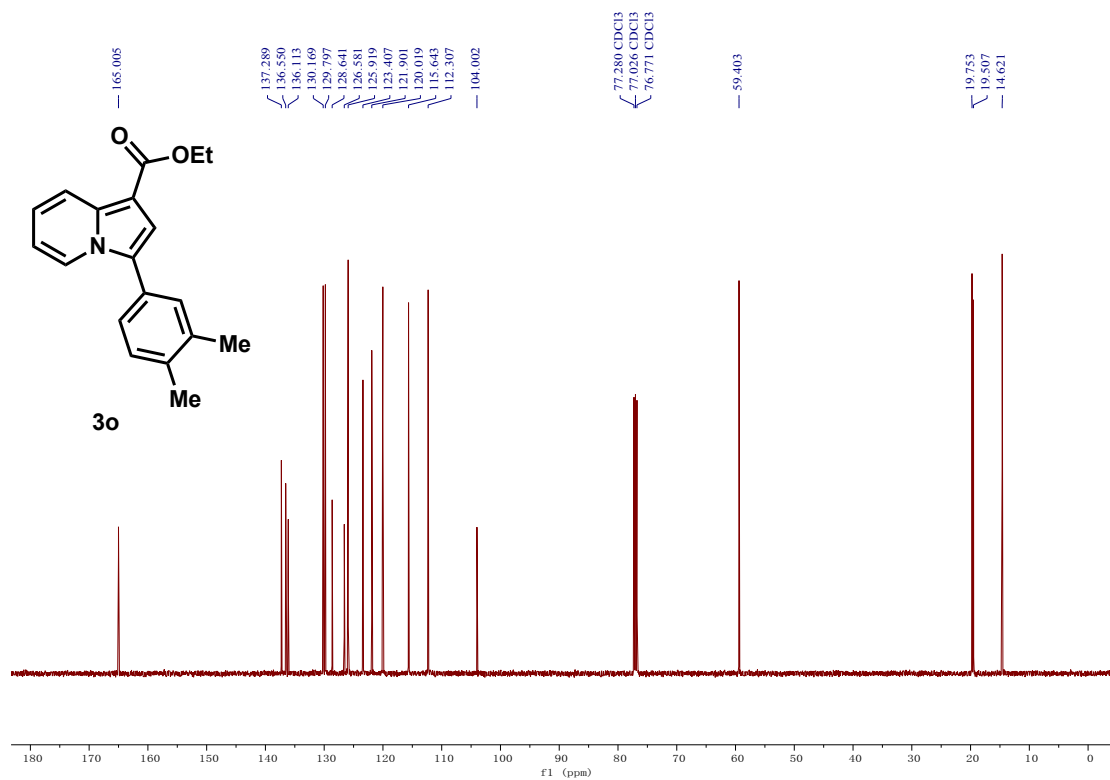
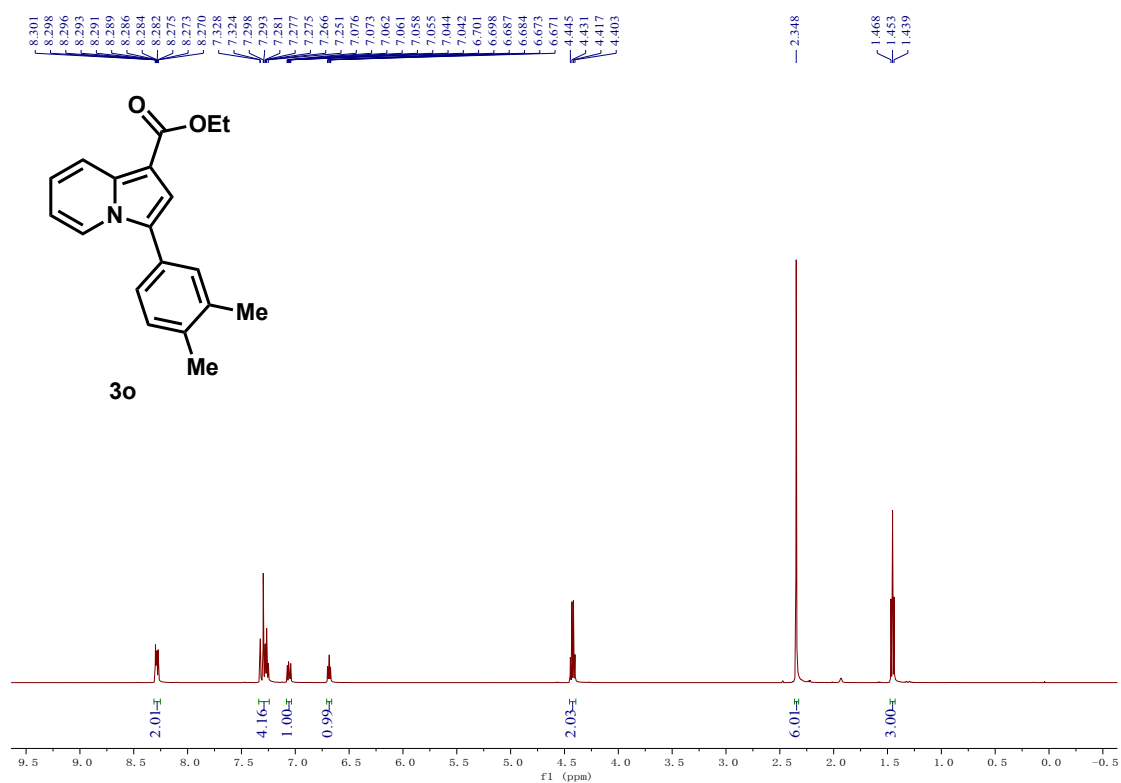


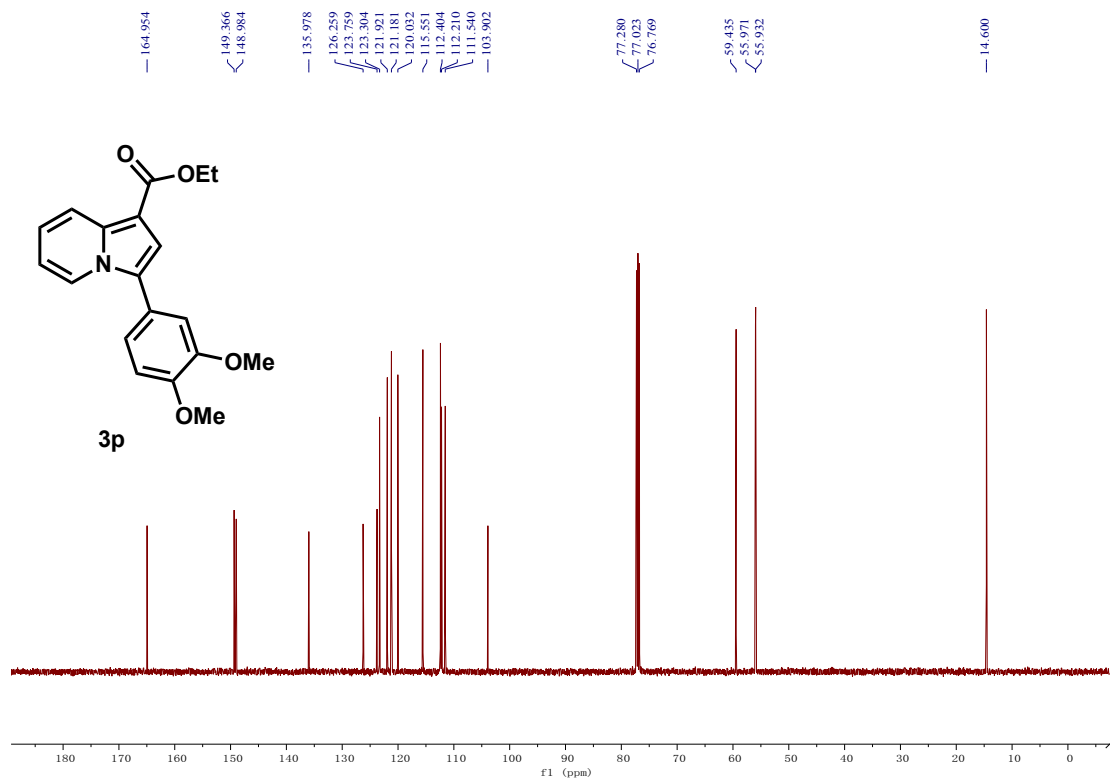
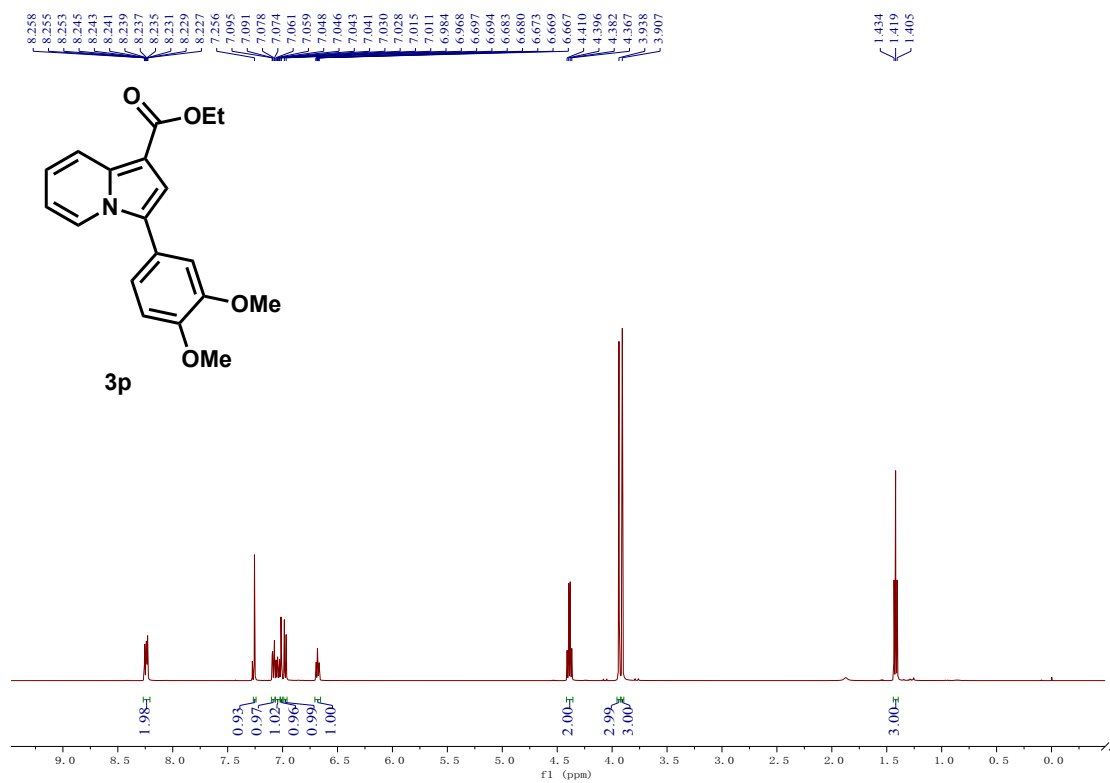
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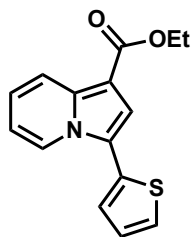




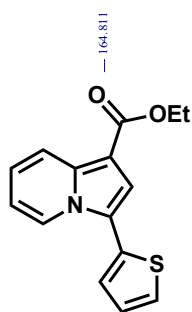
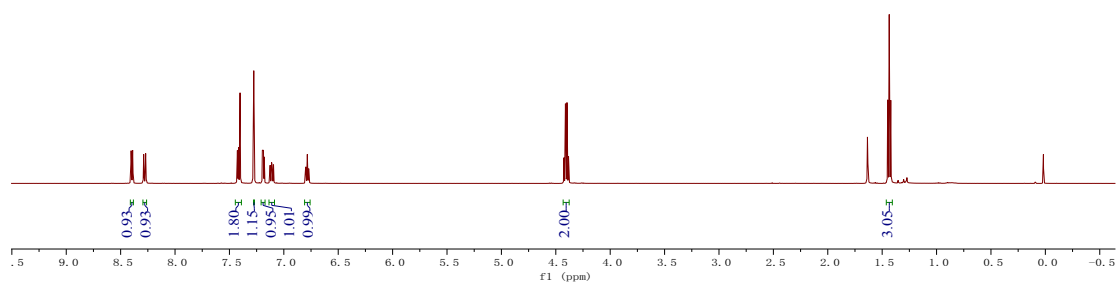


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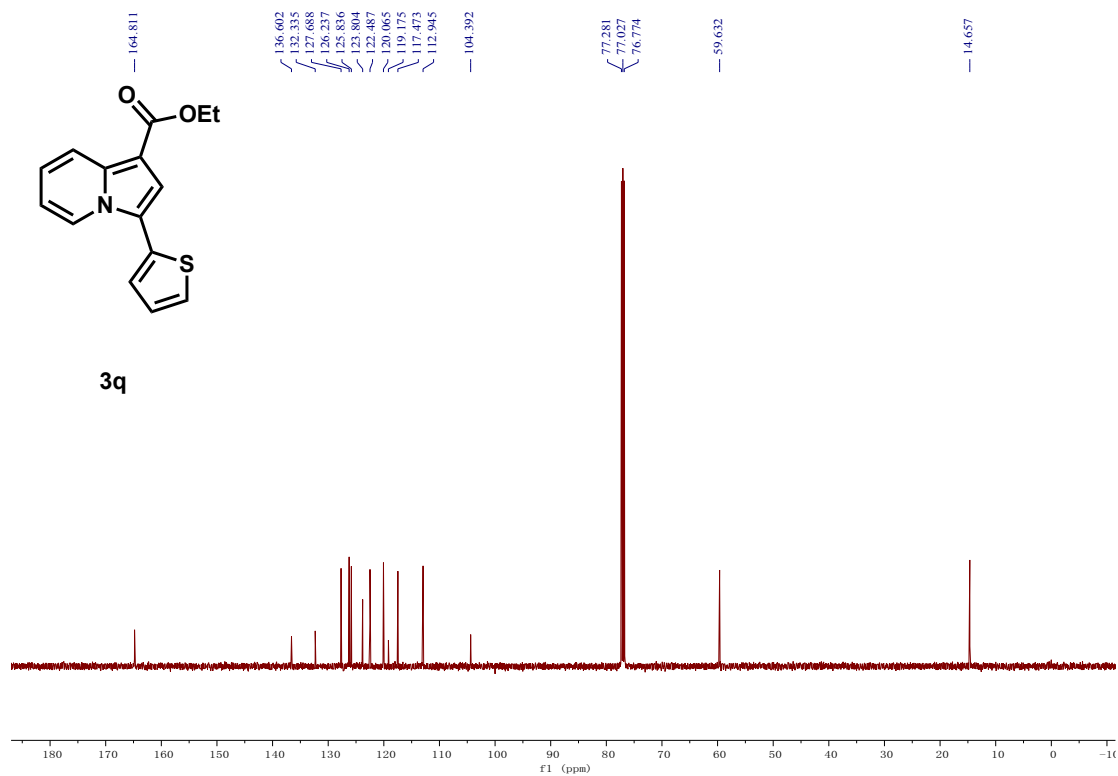
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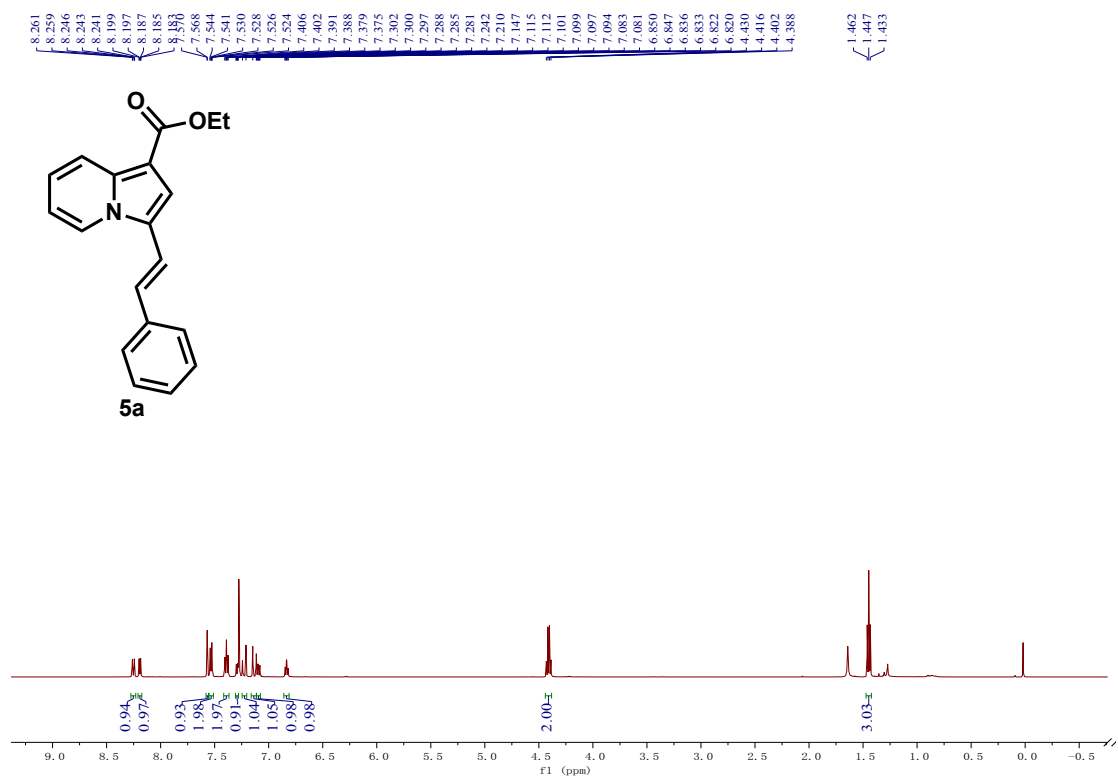
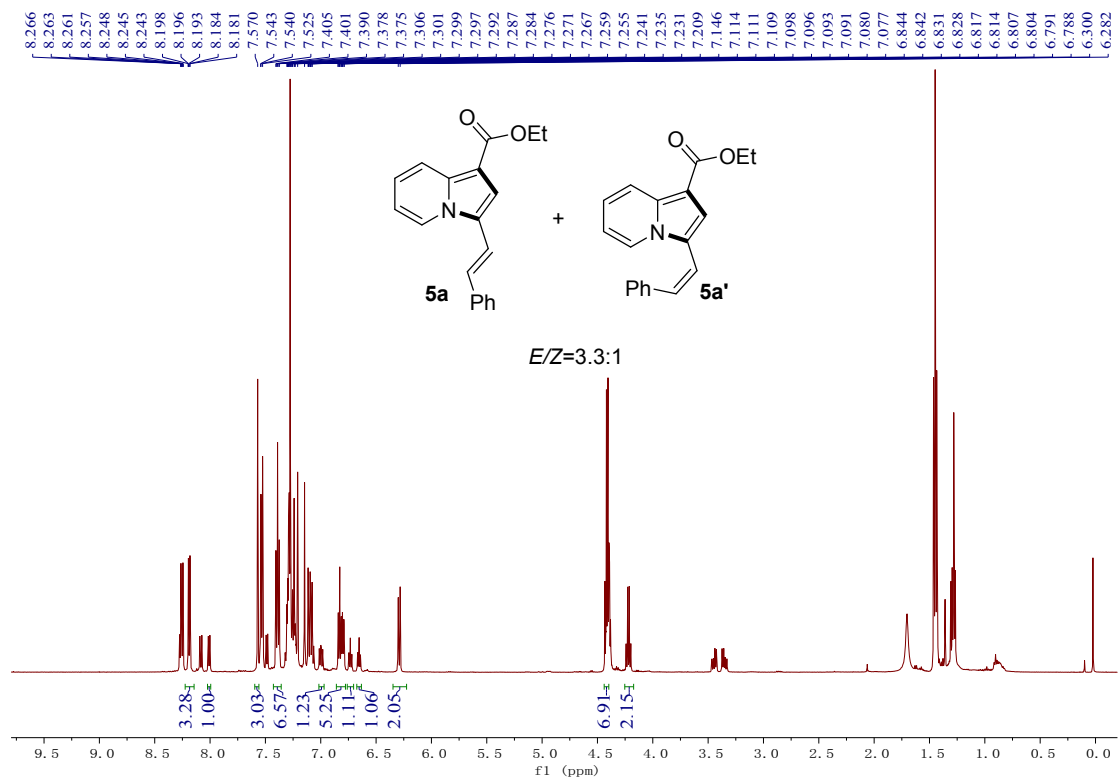


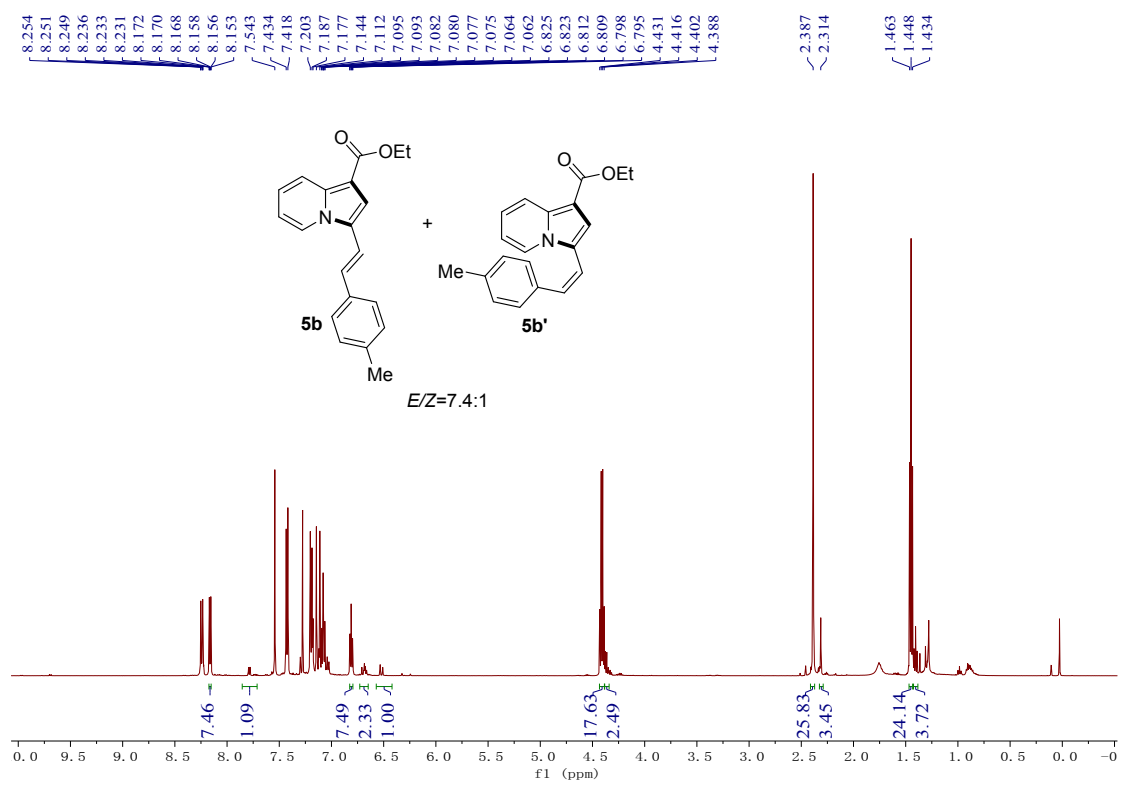
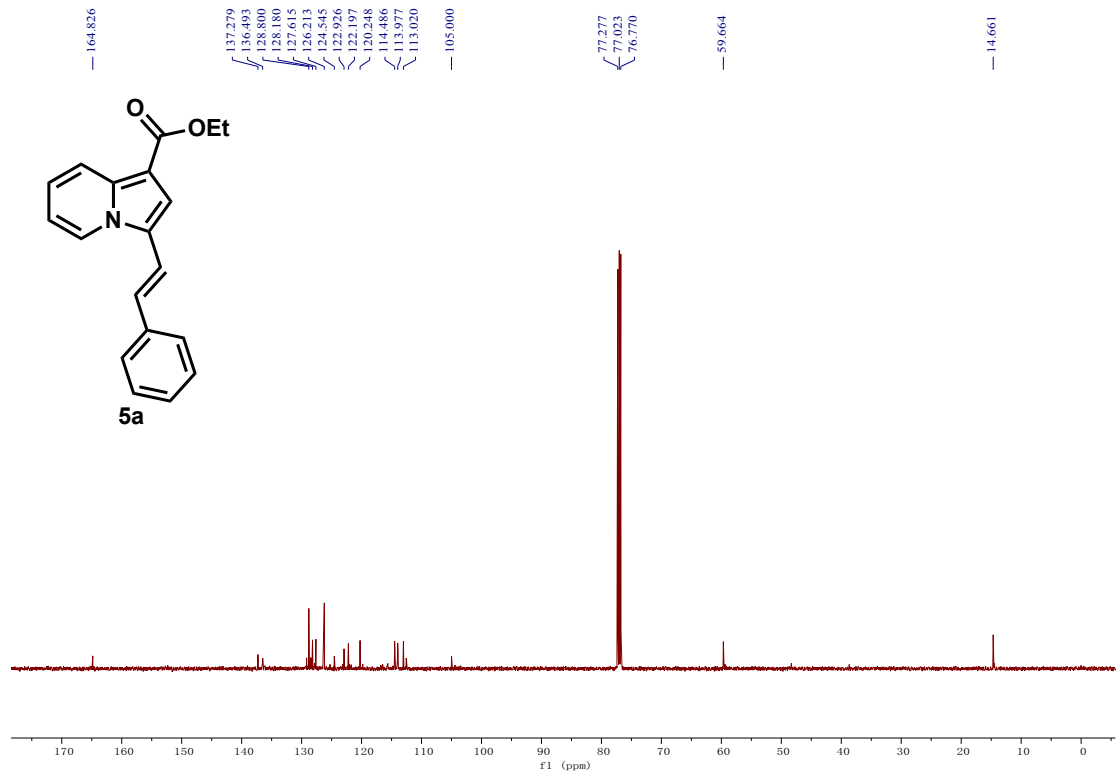
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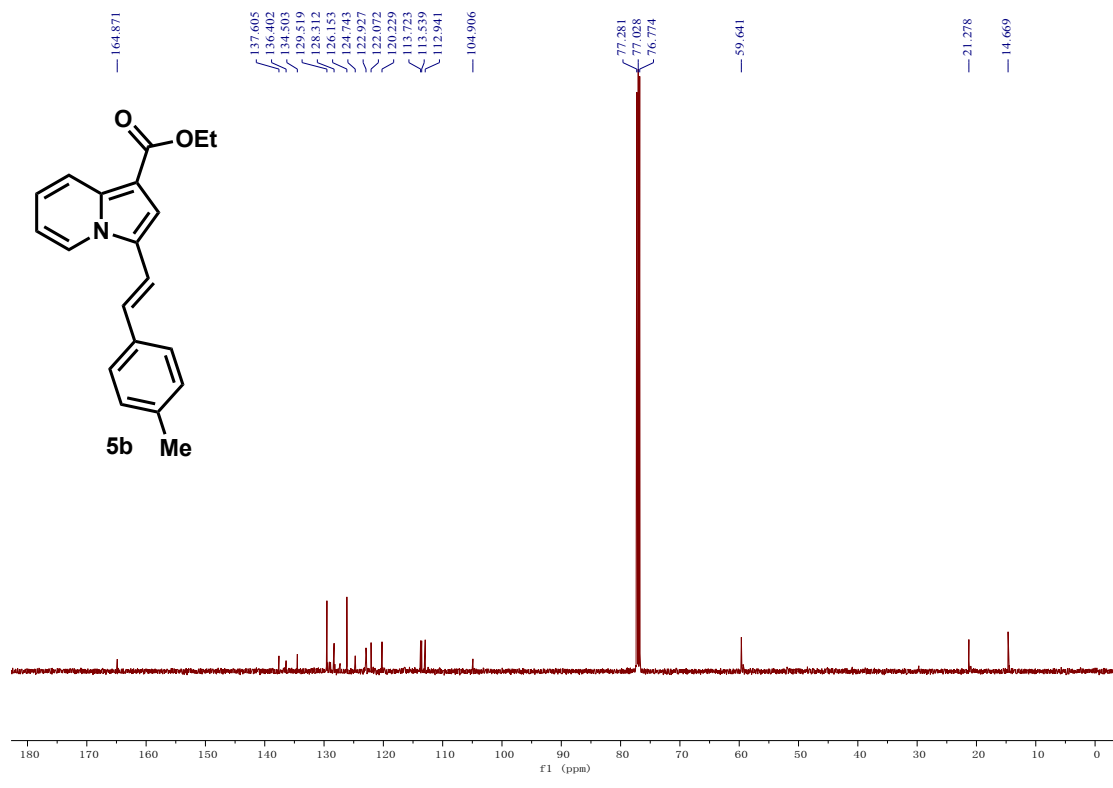
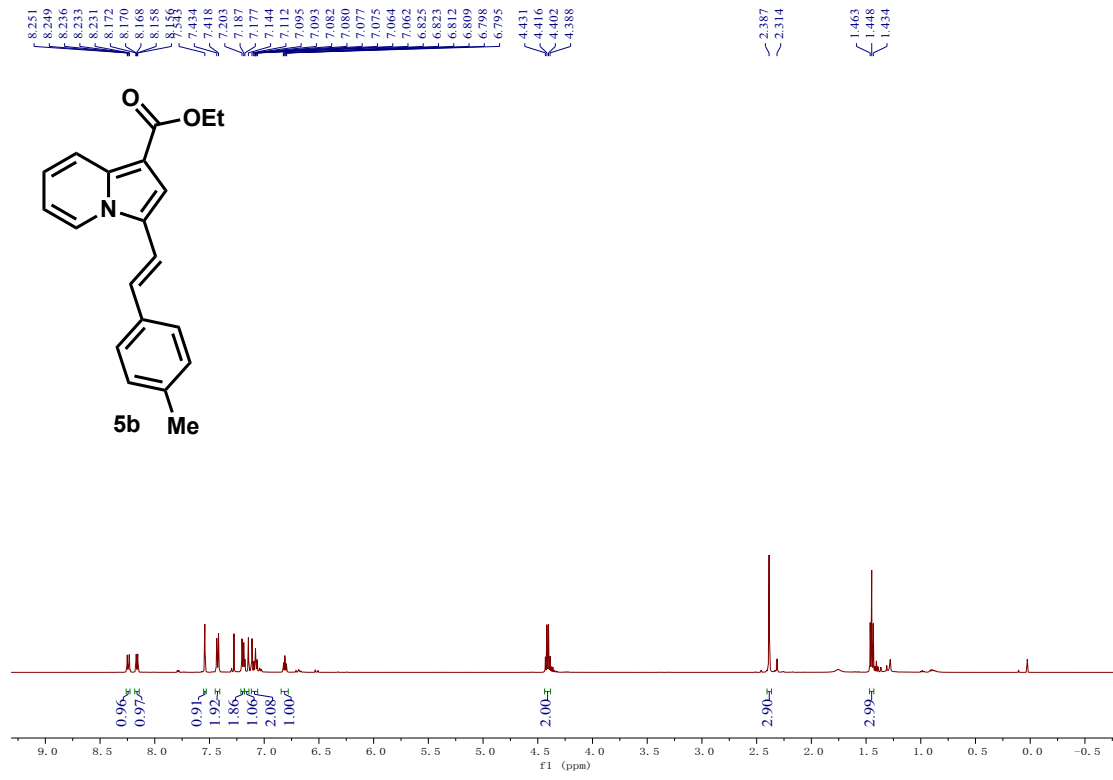


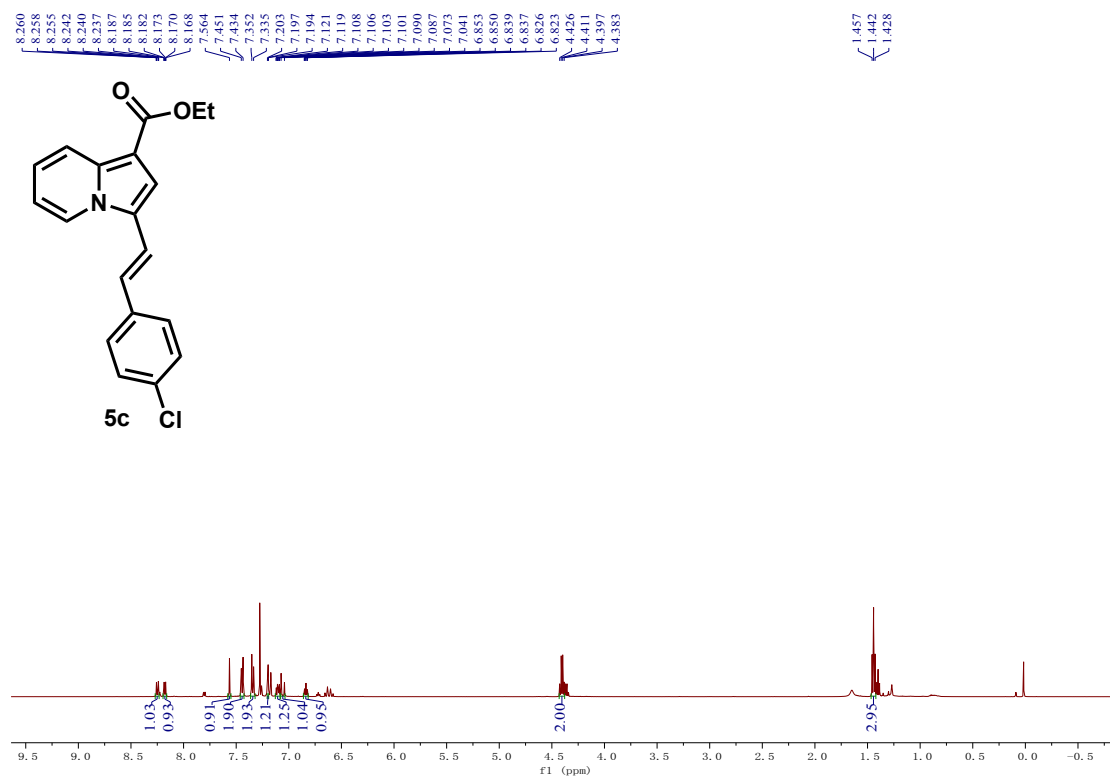
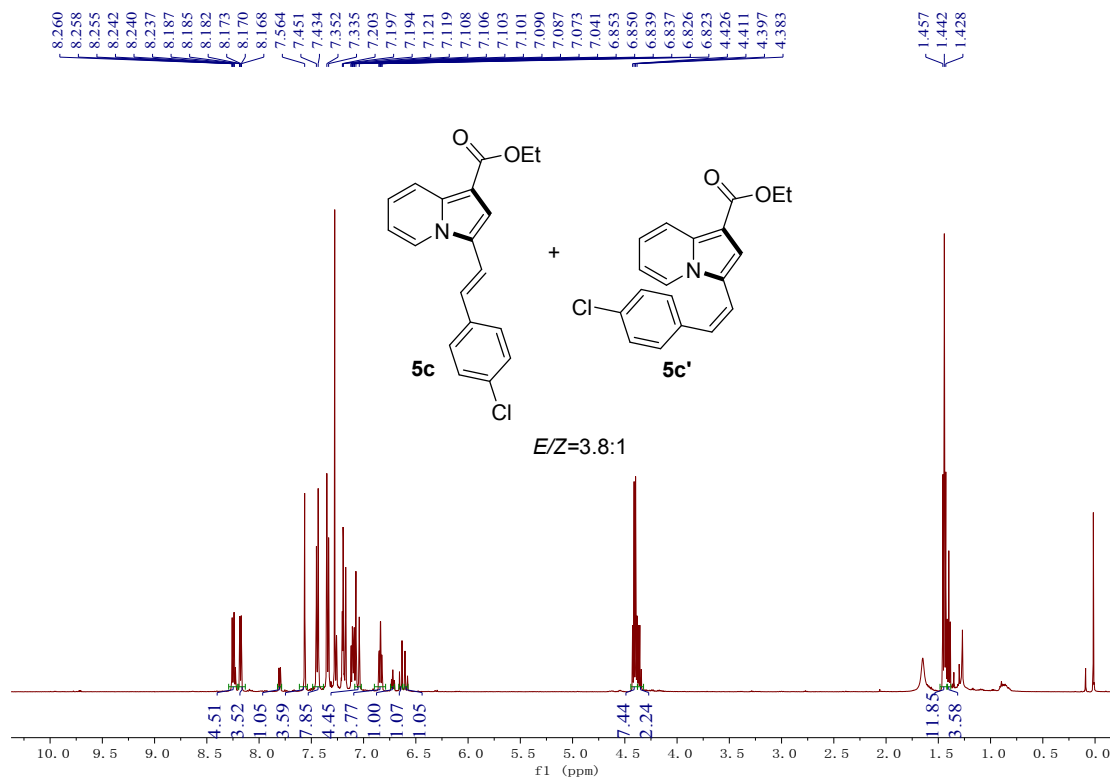
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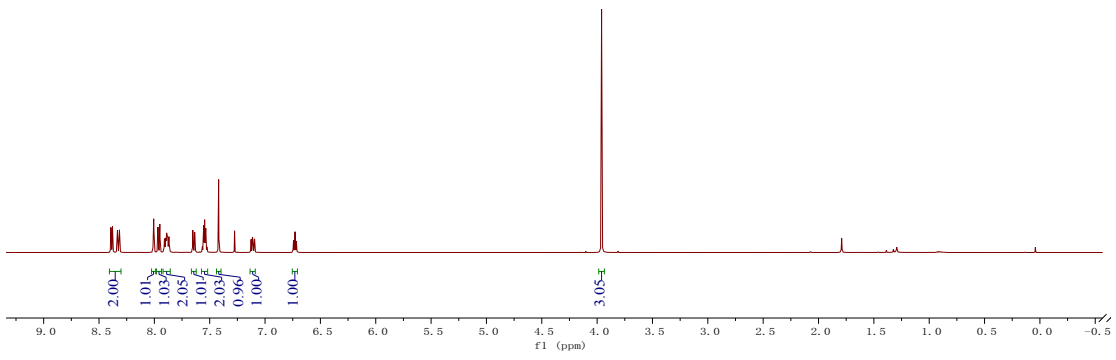
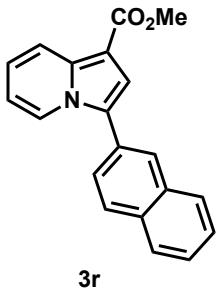








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7.128
7.126
7.115
7.113
7.110
7.108
7.097
7.094
6.745
6.742
6.731
6.729
6.718
6.715
3.960



165.321
136.535
133.539
132.766
128.769
128.506
127.941
127.762
127.309
126.636
126.411
123.338
122.413
120.142
116.429
112.730
104.098
77.283 CDCl₃
77.028 CDCl₃
76.774 CDCl₃
50.909

