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, Chun Cai*

* 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
2. General Procedure
3. Characterization Data
4. NMR spectra
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), $\alpha,\beta$-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](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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), 116.37 (s), 116.24 (s), 112.73 (s), 104.39 (s), 59.70 (s), 14.82 (s). MS (EI) $m/z$: 265 [M$^+$].
N$\text{O}$

**3ba**: ethyl 3-m-tolylindolizine-1-carboxylate $3\text{ba}^{[1]}$. 

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$^+$].

$\text{N}$$\text{O}$

**3ca**: ethyl 3-p-tolylindolizine-1-carboxylate $3\text{ca}^{[1]}$. 

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 165.24 (s), 138.98 (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$^+$].

$\text{N}$$\text{O}$

**3da**: ethyl 3-(2-methoxyphenyl)indolizine-1-carboxylate $3\text{da}^{[1]}$. 

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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

\[\text{N} \quad \text{O} \quad \text{OEt} \quad \text{OMe} \quad \text{3ea}\]

\[\text{1H NMR (500 MHz, CDCl}_3\text{) } \delta 8.33 (d, J = 7.1 \text{ Hz}, 1H), 8.26 (d, J = 9.1 \text{ Hz}, 1H), 7.41 (t, J = 7.9 \text{ Hz}, 1H), 7.31 (s, 1H), 7.14 (d, J = 7.6 \text{ Hz}, 1H), 7.07 (t, J = 7.8 \text{ Hz}, 2H), 6.95 (d, J = 10.3 \text{ Hz}, 1H), 6.70 (t, J = 7.4 \text{ Hz}, 1H), 4.39 (q, J = 7.1 \text{ Hz}, 2H), 3.86 (s, 3H), 1.42 (t, J = 7.1 \text{ Hz}, 3H). \]

\[\text{13C NMR (125 MHz, CDCl}_3\text{) } \delta 165.16 (s), 160.26 (s), 136.52 (s), 130.23 (s), 126.42 (s), 123.66 (s), 122.39 (s), 120.93 (s), 120.29 (s), 116.26 (s), 114.33 (s), 113.70 (s), 112.73 (s), 104.37 (s), 59.69 (s), 55.49 (s), 14.80 (s). \]

\[\text{MS (EI) } m/z: 295 \text{ [M}^+\text{].} \]

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

\[\text{N} \quad \text{O} \quad \text{OEt} \quad \text{OMe} \quad \text{3fa}\]

\[\text{1H NMR (500 MHz, CDCl}_3\text{) } \delta 8.21 (dd, J = 30.7, 8.1 \text{ Hz}, 2H), 7.42 (d, J = 8.6 \text{ Hz}, 2H), 7.24 (s, 1H), 7.02 (dd, J = 14.9, 8.2 \text{ Hz}, 3H), 6.65 (t, J = 6.8 \text{ Hz}, 1H), 4.38 (q, J = 7.1 \text{ Hz}, 2H), 3.85 (s, 3H), 1.41 (t, J = 7.1 \text{ Hz}, 3H). \]

\[\text{13C NMR (125 MHz, CDCl}_3\text{) } \delta 165.23 (s), 159.59 (s), 136.17 (s), 130.24 (s), 126.38 (s), 123.70 (s), 123.45 (s), 122.12 (s), 120.20 (s), 115.72 (s), 114.64 (s), 112.57 (s), 104.08 (s), 59.64 (s), 55.49 (s), 14.82 (s). \]

\[\text{MS (EI) } m/z: 295 \text{ [M}^+\text{].} \]

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

\[\text{N} \quad \text{O} \quad \text{OEt} \quad \text{Ph} \quad \text{3ga}\]

\[\text{1H NMR (500 MHz, CDCl}_3\text{) } \delta 8.37 (d, J = 7.1 \text{ Hz}, 1H), 8.29 (d, J = 9.1 \text{ Hz}, 1H), 7.73 (d, J = 8.2 \text{ Hz}, 2H), 7.65 (dd, J = 14.8, 7.8 \text{ Hz}, 4H), 7.49 (t, J = 7.6 \text{ Hz}, 2H), 7.43 – 7.34 (m, 2H), 7.15 – 7.04 (m, 1H), 6.74 (t, J = 7.2 \text{ Hz}, 1H), 4.41 (q, J = 7.1 \text{ Hz}, 2H), 1.44 (t, J = 7.1 \text{ Hz}, 3H). \]

\[\text{13C NMR (125 MHz, CDCl}_3\text{) } \delta 165.18 (s), 140.86 (s), 140.54 (s), 136.64 (s), 129.06 (s), 127.88 (s), 127.75 (s), 127.17 (s), 123.58 (s), 122.44 (s), 120.38 (s), 116.38 (s), 112.83 (s), 104.58 (s), 59.73 (s), 14.83 (s). \]

\[\text{HRMS (ESI) Calcd. For } \text{C}_{23}\text{H}_{19}\text{NO}_2 \text{ [M-Na]}^+, \text{found } 364.1309. \]
ethyl 3-(3-fluorophenyl)indolizine-1-carboxylate 3ha.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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.

ethyl 3-(4-fluorophenyl)indolizine-1-carboxylate 3ia.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$^+$].

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

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.24 (dd, $J = 33.3$, 8.1 Hz, 2H), 7.39 – 7.33 (m, 1H), 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$_3$) $\delta$ 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$_2$NO$_2$ [M-Na]$^+$, found 324.0809.
ethyl 3-(perfluorophenyl)indolizine-1-carboxylate 3ka.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_5$NO$_2$ [M-Na]$^+$, found 378.0526.

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

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$^+$].

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

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$^+$].
ethyl 3-(4-(trifluoromethyl)phenyl)indolizine-1-carboxylate 3na.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_{3}$NO$_{2}$ [M-Na]$^+$, found 356.0871.

ethyl 3-(4-nitrophenyl)indolizine-1-carboxylate 3oa$^1$.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 164.67 (s), 146.75 (s), 137.94 (s), 137.60 (s), 128.21 (s), 124.72 (s), 124.11 (s), 123.94(s), 123.23(s), 120.74(s), 118.33(s), 113.67(s), 105.77(s), 59.97(s), 14.75(s). MS (EI) m/z: 310 [M$^+$].

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

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_{13}$NO$_{3}$ [M-Na]$^+$, found 316.0943.
\textbf{3qa}: ethyl 3-(pyridin-2-yl)indolizine-1-carboxylate 3qa.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 164.94 (s), 151.95 (s), 148.39 (s), 138.01 (s), 136.74 (s), 127.99 (s), 123.71 (s), 121.29 (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$_2$O$_2$ [M-Na]$^+$, found 289.0951.

\textbf{3ra}: ethyl 3-(furan-2-yl)indolizine-1-carboxylate 3ra.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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.

\textbf{3sa}: ethyl 3-(thiophen-2-yl)indolizine-1-carboxylate 3sa.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_{13}$NOS [M-Na]$^+$, found 294.0568.

\textbf{3ta}: ethyl indolizine-1-carboxylate 3ta[2].
\[ \text{H NMR (500 MHz, CDCl}_3 \text{) } \delta \ \text{H NMR (500 MHz, CDCl}_3 \text{) } \delta 8.17 (d, J = 9.1 Hz, 1H), 7.99 (d, J = 6.9 Hz, 1H), 7.25 (d, J = 3.0 Hz, 1H), 7.22 (d, J = 2.9 Hz, 1H), 7.03 (dd, J = 9.6, 6.2 Hz, 1H), 6.69 (t, J = 6.8 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). \]

\[ \text{C NMR (125 MHz, CDCl}_3 \text{) } \delta 165.12 (s), 135.85 (s), 126.12 (s), 122.23 (s), 120.10 (s), 116.34 (s), 113.69 (s), 112.46 (s), 104.20 (s), 59.57 (s), 14.76 (s). \]

\[ \text{MS (EI) } m/z: 189 [M^+]. \]

: 3-phenylindolizine-1-carbonitrile 3ab\(^{[1]}\).

\[ \text{H NMR (500 MHz, CDCl}_3 \text{) } \delta 8.28 (d, J = 7.1 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.52 (d, J = 4.4 Hz, 4H), 7.48 – 7.42 (m, 1H), 7.12 – 7.07 (m, 1H), 7.06 (s, 1H), 6.75 (t, J = 6.9 Hz, 1H). \]

\[ \text{C NMR (125 MHz, CDCl}_3 \text{) } \delta 138.56 (s), 130.35 (s), 129.40 (s), 128.84 (s), 128.76 (s), 127.12 (s), 123.88 (s), 122.48 (s), 118.38 (s), 117.05 (s), 116.41 (s), 113.24 (s), 82.38 (s). \]

\[ \text{MS (EI) } m/z: 218 [M^+]. \]

\[ \text{methyl 3-phenylindolizine-1-carboxylate 3ac}\(^{[1]}\). \]

\[ \text{H NMR (500 MHz, CDCl}_3 \text{) } \delta 8.28 (dd, J = 14.9, 8.1 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.30 (s, 1H), 7.13 – 7.03 (m, 1H), 6.71 (t, J = 6.8 Hz, 1H), 3.92 (s, 3H). \]

\[ \text{C NMR (125 MHz, CDCl}_3 \text{) } \delta 165.55 (s), 136.57 (s), 131.36 (s), 129.23 (s), 128.84 (s), 128.76 (s), 127.12 (s), 123.88 (s), 122.48 (s), 118.38 (s), 117.05 (s), 116.41 (s), 113.24 (s), 82.38 (s). \]

\[ \text{MS (EI) } m/z: 251 [M^+]. \]

\[ \text{isopropyl 3-phenylindolizine-1-carboxylate 3ad}\(^{[1]}\). \]

\[ \text{H NMR (500 MHz, CDCl}_3 \text{) } \delta 8.36 – 8.21 (m, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 7.31 (s, 1H), 7.12 – 7.02 (m, 1H), 6.69 (t, J = 6.8 Hz, 1H), 5.30 (dt, J = 12.5, 6.2 Hz, 1H), 1.41 (d, J = 6.3 Hz, 6H). \]

\[ \text{C NMR (125 MHz, CDCl}_3 \text{) } \delta 164.77 (s), 136.57 (s), 131.36 (s), 129.23 (s), 128.77 (s), 128.17 (s), 126.64 (s), 123.50 (s), 122.48 (s), 120.27 (s), 116.16 (s), 112.78 (s), 51.07 (s). \]

\[ \text{MS (EI) } m/z: 279 [M^+]. \]
**3ae**: tert-butyl 3-phenylindolizine-1-carboxylate 3ae.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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 C$_{19}$H$_{19}$NO$_2$ [M-Na]$^+$, found 316.1308.

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

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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


**4. NMR Spectra of All Products**
$^1$H NMR 3ca

$^{13}$C NMR 3ca
**1H NMR 3da**

**13C NMR 3da**
$^1$H NMR 3fa

$^{13}$C NMR 3fa
$^1$H NMR 3ia

$^{13}$C NMR 3ia
$^1$H NMR 3ka

$^{13}$C NMR 3ka
$^{1}$H NMR 3na

$^{13}$C NMR 3na
$^1$H NMR 3qα

$^{13}$C NMR 3qα
$^{1}H$ NMR $3ra$

$^{13}C$ NMR $3ra$
$^1$H NMR 3ac

$^{13}$C NMR 3ac
$^1$H NMR 3ad

$^{13}$C NMR 3ad
$^1$H NMR 3af

$^{13}$C NMR 3af