Supporting Information

Free-radical initiated cascade methylation or trideuteromethylation of isocyanides with dimethyl Sulfoxides

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General Information

1H and 13C NMR spectra were recorded on a Bruker advance III 600 spectrometer in CDCl3 with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. Element analysis (EA) data were measured on a Vario EL. All products were identified by 1H and 13C NMR, MS, HRMS. The starting materials were purchased from Energy, J&K Chemicals or Aldrich and used without further purification.

Typical procedure

(1) A mixture of isocyanides (1 equiv., 0.25 mmol), Iron(II) chloride (0.2 equiv., 0.05 mmol), Hydrogen peroxide (3 eq, 0.75 mmol) and DMSO (3 mL) was stirred at 25 °C under nitrogen condition for 6 h in a sealed tube (15 mL). After the reaction finished, the mixture was extracted
with ethyl acetate and water, evaporated under vacuum and purified by column chromatography to afford the desired product.

(2) A mixture of isocyanides (1 equiv., 0.25 mmol), Iron(II) chloride (0.2 equiv., 0.05 mmol), Hydrogen peroxide (3 eq, 0.75 mmol) and DMSO-\textsuperscript{d6} (1 mL) was stirred at 20 °C under nitrogen condition for 12 h in a sealed tube (15 mL). After the reaction finished, the mixture was extracted with ethyl acetate and water, evaporated under vacuum and purified by column chromatography to afford the desired product.

The modification of the methylation reaction condition

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (equiv)</th>
<th>Hydrogen peroxide (30 %), (equiv)</th>
<th>t/h</th>
<th>Yield (%)\textsuperscript{a}</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCl\textsubscript{2} (0.5)</td>
<td>3</td>
<td>3</td>
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</tr>
<tr>
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<tr>
<td>3</td>
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<tr>
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<td>7</td>
<td>-</td>
<td>3</td>
<td>6</td>
<td>n. r.</td>
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<td>FeCl\textsubscript{2} (0.2)</td>
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<td>FeCl\textsubscript{2} (0.2)</td>
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<td>n. r.</td>
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<tr>
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<td>6</td>
<td>n. r.</td>
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<tr>
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<td>6</td>
<td>n. r.</td>
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<tr>
<td>19\textsuperscript{e}</td>
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<td>6</td>
<td>n. r.</td>
</tr>
<tr>
<td>20°</td>
<td>FeCl₂ (0.2)</td>
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<td>n. r.</td>
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<tr>
<td>-----</td>
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</tbody>
</table>

* Reaction conditions: 2-isocyano-5-methyl-1,1’-biphenyl (1 equiv., 0.25 mmol), DMSO (3 mL), 25 °C, N₂.

* Isolated yields.  

* DMSO (1 mL).  

* DMSO (2 mL).  

* DMSO (4 mL).  

* DMF (3 mL).  

* CH₃CN (3 mL).

Physical data and references for the following products

All known compounds are determined by ¹H NMR and ¹³C NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS.

References:

Physical data for the following products:
1. 6-methylphenanthidine
   A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 69-71°C.

   ![6-methylphenanthidine](image)

   ¹H NMR (600 MHz, CDCl₃): δ 8.63 (d, J = 8.4 Hz, 1H), 8.54 (dd, J = 8.4, 1.2 Hz, 1H), 8.22 (dd, J = 7.8, 0.6 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.84 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.63 – 7.61 (m, 1H), 7.25 (s, 2H).

   ¹³C NMR (150 MHz, CDCl₃): δ 158.8, 143.7, 132.6, 130.4, 129.4, 128.6, 127.3, 126.5, 126.3, 125.9, 123.8, 122.3, 121.9, 23.3.

   MS(EI): m/z(%): 193(100.0), 178(14.3), 165(14.0).

2. 8-chloro-6-methylphenanthidine
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 105-107°C.

1H NMR (600 MHz, CDCl₃): δ 8.50 (d, J = 9.0 Hz, 1H), 8.44 (d, J = 7.8 Hz, 1H), 8.14 (d, J = 1.8 Hz, 1H), 8.08 (dd, J = 7.8, 0.6 Hz, 1H), 7.75 (dd, J = 9.0, 2.4 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.62 – 7.60 (m, 1H), 2.99 (s, 3H).

13C NMR (150 MHz, CDCl₃): δ 157.7, 143.6, 133.1, 130.9, 130.9, 129.5, 128.9, 126.8, 126.7, 125.8, 124.1, 123.1, 121.8, 23.2.

MS(El): m/z(%): 230(4.9), 229(30.6), 228(16.7), 227(100.0), 192(9.4), 191(7.0), 190(6.2), 165(5.9).

3. 2,6-dimethylphenanthridine
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 69-71°C.

1H NMR (600 MHz, CDCl₃): δ 8.61 (d, J = 8.4 Hz, 1H), 8.31 (s, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.81 (t, J = 8.4 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.53 (dd, J = 7.8, 1.8 Hz, 1H), 3.02 (s, 3H), 2.61 (s, 3H).

13C NMR (150 MHz, CDCl₃): δ 157.8, 142.0, 136.0, 132.3, 130.3, 130.2, 129.1, 127.1, 126.5, 126.0, 123.6, 122.3, 121.6, 23.3, 21.9.

MS(El): m/z(%): 208(17.6), 207(100.0), 206(35.9), 192(6.9), 190(5.2), 165(8.1).

4. 2,6,8-trimethylphenanthridine
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 106-108°C.
5. 8-chloro-2,6-dimethylphenanthridine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), M. P.: 132-134°C.

\[\text{\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): } \delta 8.50 (d, J = 8.4 \text{ Hz}, 1H), 8.28 (s, 1H), 7.97 - 7.96 (m, 2H), 7.65 (dd, J = 8.4, 1.8 Hz, 1H), 7.50 (dd, J = 8.4, 1.2 Hz, 1H), 3.00 (s, 3H), 2.60 (s, 6H).\]

\[\text{\textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}): } \delta 157.5, 141.7, 137.0, 136.0, 131.9, 130.2, 129.8, 129.0, 126.1, 126.0, 123.7, 122.2, 121.4, 23.3, 21.9, 21.8\]

MS(EI): m/z(%): 222(16.8), 221(100.0), 220(37.1), 206(38.0).

6. 8-(tert-butyl)-2,6-dimethylphenanthridine

A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 109-110°C.

\[\text{\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): } \delta 8.54 (d, J = 8.4, 2.4 Hz, 1H), 8.29 (s, 1H), 8.13 (s, 1H), 7.97 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 9.0, 1H), 7.53 (d, J = 7.8 Hz, 1H), 2.98 (s, 3H), 2.60 (s, 3H).\]

\[\text{\textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}): } \delta 156.6, 142.0, 136.6, 133.0, 130.7, 130.7, 130.6, 129.2, 126.9, 125.8, 124.0, 122.9, 121.4, 23.2, 21.9.\]

HRMS (ESI, m/z): Calculated for C\textsubscript{19}H\textsubscript{22}N (M+H)\textsuperscript{+} 264.1747, found 264.1751.
7. 2,6-dimethyl-8-phenylphenanthridine
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 118-120°C.

\[
\text{H NMR (600 MHz, CDCl}_3\text{): } \delta 8.66 (d, J = 9.0 \text{ Hz, 1H}), 8.37 (d, J = 1.8 \text{ Hz, 1H}), 8.33 (s, 1H),
8.06 (dd, J = 8.4, 1.2 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.54 (t, J = 7.2 Hz, 3H), 7.44 (t, J = 7.2 Hz, 1H), 3.08 (s, 3H), 2.63 (s, 3H).
\]

\[
\text{C NMR (150 MHz, CDCl}_3\text{): } \delta 157.9, 142.0, 140.5, 140.0, 136.2, 131.4, 130.3, 129.5, 129.1, 129.0, 127.8, 127.4, 126.3, 124.6, 123.4, 122.9, 121.6, 23.3, 21.9.
\]

HRMS (ESI, m/z): Calculated for C\text{21}H\text{18}N (M+H)\text{+} 284.1434, found 284.1438.

8. 2,4,6-trimethylphenanthridine
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 99-100°C.

\[
\text{H NMR (600 MHz, CDCl}_3\text{): } \delta 8.61 (d, J = 8.4 \text{ Hz, 1H}), 8.19 (d, J = 8.4 \text{ Hz, 2H}), 7.80 - 7.78 (m, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.41 (s, 1H), 3.04 (s, 3H), 2.84 (s, 3H), 2.57 (s, 3H).
\]

\[
\text{C NMR (150 MHz, CDCl}_3\text{): } \delta 156.2, 140.8, 136.8, 135.3, 132.6, 131.0, 129.8, 126.8, 126.3, 125.7, 123.4, 122.5, 119.4, 23.6, 21.8, 18.2.
\]

HRMS (ESI, m/z): Calculated for C\text{16}H\text{16}N (M+H)\text{+} 222.1277, found 222.1280.

9. 2-fluoro-6-methylphenanthridine
A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 110-112°C.
1H NMR (600 MHz, CDCl₃): δ 8.50 (d, J = 7.8 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.14 (dd, J = 10.2, 3.0 Hz, 1H), 8.08 (dd, J = 9.0, 6.0 Hz, 1H), 7.86 (t, J = 7.8 Hz, 1H), 7.74 (t, J = 7.8 Hz, 1H), 7.46 – 7.43 (m, 1H), 3.02 (s, 3H).

13C NMR (150 MHz, CDCl₃): δ 161.7, 160.1, 158.0, 140.6, 131.5 (d, J = 9.0 Hz), 130.5, 127.9, 126.6, 125.9, 125.0 (d, J = 9.0 Hz), 122.5, 117.4 (d, J = 24.0 Hz), 106.9 (d, J = 22.9 Hz), 23.3.

MS(EI): m/z(%): 211(100.0), 196(12.0), 183(17.0).

10. 2-chloro-6-methylphenanthridine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 103-105°C.

1H NMR (600 MHz, CDCl₃): δ 8.49 (d, J = 8.4 Hz, 1H), 8.44 (d, J = 1.2 Hz, 1H), 8.19 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 9.0 Hz, 1H), 7.83 (t, J = 8.4 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.62 (dd, J = 8.4, 2.4 Hz, 1H), 3.00 (s, 3H).

13C NMR (150 MHz, CDCl₃): δ 159.1, 142.1, 132.1, 131.5, 130.8, 130.7, 129.0, 127.9, 126.5, 126.0, 124.8, 122.3, 121.6, 23.3.

MS(EI): m/z(%): 230(4.9), 229(30.7), 228(17.6), 227(100.0), 192(7.5), 191(6.5), 190(6.1), 165(6.2).

13. ethyl 1-methyl-4-phenylisoquinoline-3-carboxylate

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 104-106°C.

1H NMR (600 MHz, CDCl₃): δ 8.20 (d, J = 8.4 Hz, 1H), 7.67 (ddd, J = 8.4, 5.4, 3.0 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.49 – 7.43 (m, 3H), 7.34 (dd, J = 7.8, 1.8 Hz, 2H), 4.11 (q, J = 7.2 Hz, 2H), 3.06 (s, 3H), 0.97 (t, J = 7.2 Hz, 3H).
13C NMR (150 MHz, CDCl₃): δ 167.6, 158.4, 141.4, 136.4, 135.4, 131.9, 130.4, 129.9, 128.1, 128.0, 127.8, 127.7, 126.9, 125.6, 61.2, 22.6, 13.6.

HRMS (ESI, m/z): Calculated for C₁₀H₁₈NO₂ (M+H)⁺ 292.1332, found 292.1331.

14. ethyl 1,7-dimethyl-4-(p-tolyl)isoquinoline-3-carboxylate

A light yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).

1H NMR (600 MHz, CDCl₃): δ 7.95 (s, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.45 (dd, J = 9.0, 1.2 Hz, 1H), 7.27 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 4.14 (q, J = 7.2 Hz, 2H), 3.02 (s, 3H), 2.57 (s, 3H), 2.45 (s, 3H), 1.02 (t, J = 7.2 Hz, 3H).

13C NMR (150 MHz, CDCl₃): δ 167.7, 157.4, 140.6, 138.2, 137.3, 133.7, 133.5, 132.4, 132.0, 129.8, 128.8, 128.0, 126.8, 124.6, 61.1, 22.6, 21.9, 21.3, 13.7.

HRMS (ESI, m/z): Calculated for C₂₁H₂₂N₂O₂ (M+H)⁺ 320.1645, found 320.1644.

15. ethyl 7-fluoro-4-(4-fluorophenyl)-1-methylisoquinoline-3-carboxylate

A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 130-132°C.

1H NMR (600 MHz, CDCl₃): δ 7.79 (dd, J = 9.6, 2.4 Hz, 1H), 7.61 (dd, J = 9.0, 5.4 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.31 – 7.28 (m, 2H), 7.18 (t, J = 8.4 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.01 (s, 3H), 1.04 (t, J = 7.2 Hz, 3H).

13C NMR (150 MHz, CDCl₃): δ 167.2, 162.1 (dd, J = 246.2, 162.6 Hz), 157.9, 141.1, 132.6, 131.9 (d, J = 3.6 Hz), 131.5 (d, J = 8.1 Hz), 130.8, 129.7 (d, J = 8.7 Hz), 129.0
(d, J = 8.3 Hz), 120.8 (d, J = 24.6 Hz), 115.3 (d, J = 21.5 Hz), 109.5 (d, J = 21.1 Hz), 61.4, 22.6, 13.8.

HRMS (ESI, m/z): Calculated for C\textsubscript{19}H\textsubscript{16}F\textsubscript{2}NO\textsubscript{2} (M+H)\textsuperscript{+} 328.1144, found 328.1146.

16. ethyl 7-chloro-4-(4-chlorophenyl)-1-methylisoquinoline-3-carboxylate

A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 106-108°C.

\[\text{\begin{center}
\text{Cl} \\
\text{Cl} \\
\text{\text{CO}_2\text{Et}} \\
\text{1H NMR (600 MHz, CDCl}_3\text{): } \delta 8.18 (d, J = 1.8 Hz, 1H), 7.59 (dd, J = 9.0, 2.4 Hz, 1H), 7.53 (d, J = 9.0 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 4.16 (q, J = 7.2 Hz, 2H), 3.03 (s, 3H), 1.06 (t, J = 7.2 Hz, 3H).
\end{center}}\]

\[\text{13C NMR (150 MHz, CDCl}_3\text{): } \delta 167.0, 158.0, 141.5, 134.5, 134.3, 134.2, 133.7, 131.5, 131.2, 130.6, 128.6, 124.8, 61.5, 22.6, 13.7.\]

HRMS (ESI, m/z): Calculated for C\textsubscript{19}H\textsubscript{16}Cl\textsubscript{2}N\textsubscript{O}\textsubscript{2} (M+H)\textsuperscript{+} 360.0553, found 360.0554.

17. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 75-76°C.

\[\text{\begin{center}
\text{1H NMR (600 MHz, CDCl}_3\text{): } \delta 8.63 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 7.8 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.71 (td, J = 8.4, 1.2 Hz, 2H), 7.64 – 7.61 (m, 1H).
\end{center}}\]

\[\text{13C NMR (150 MHz, CDCl}_3\text{): } \delta 158.8, 143.8, 132.6, 130.4, 129.4, 128.6, 127.3, 126.5, 126.3, 125.9, 123.8, 122.3, 121.9, 23.0 – 22.6 (m).
\]

HRMS (ESI, m/z): Calculated for C\textsubscript{14}H\textsubscript{9}D\textsubscript{3}N (M+H)\textsuperscript{+} 197.1199, found 197.1192.

18. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 78-79°C.
$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.61 (d, $J = 8.4$ Hz, 1H), 8.32 (s, 1H), 8.20 (d, $J = 8.4$ Hz, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.83 – 7.80 (m, 1H), 7.68 (t, $J = 7.8$ Hz, 1H), 7.53 (dd, $J = 8.4$, 1.8 Hz, 1H), 2.61 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 157.8, 142.0, 136.1, 132.4, 130.3, 130.2, 129.1, 127.1, 126.5, 126.0, 123.6, 122.3, 121.6, 23.0 – 22.5 (m), 21.9.

HRMS (ESI, m/z): Calculated for C$_{15}$H$_{11}$D$_3$N (M+H)$^+$ 211.1356, found 211.1358.

19. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 135-137°C.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.49 (d, $J = 8.4$ Hz, 1H), 8.21 (s, 1H), 8.11 (d, $J = 1.2$ Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 1H), 7.72 (d, $J = 9.0$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 2.59 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 156.6, 141.9, 136.6, 132.9, 130.7, 130.6, 129.2, 126.8, 125.8, 124.0, 122.9, 121.4, 23.0 – 22.5 (m), 21.9.

HRMS (ESI, m/z): Calculated for C$_{15}$H$_{10}$D$_2$ClN (M+H)$^+$ 245.0919, found 245.0920.

20. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 110-112°C.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.54 (d, $J = 9.0$ Hz, 1H), 8.29 (s, 1H), 8.14 (s, 1H), 7.97 (d, $J = 7.8$ Hz, 1H), 7.90 (dd, $J = 8.4$, 1.8 Hz, 1H), 7.50 (d, $J = 7.8$ Hz, 1H), 2.61 (s, 3H), 1.48 (s, 9H).
\[ \text{\(^{13}\)C NMR (150 MHz, CDCl\textsubscript{3}): \(\delta\) 157.8, 150.1, 141.8, 135.9, 130.1, 129.9, 128.9, 128.6, 125.9, 123.6, 122.1, 121.9, 121.4, 35.1, 31.3, 23.0 – 22.6 (m), 21.9.} \]

HRMS (ESI, m/z): Calculated for C\(_{19}\)H\(_{19}\)D\(_3\)N \((\text{M+H})^+\) 267.1935, found 267.1932.

21. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).

\[ \text{\(^1\)H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta\) 8.66 (d, \(J = 8.4\) Hz, 1H), 8.36 (s, 1H), 8.33 (s, 1H), 8.06 (dd, \(J = 8.4, 1.8\) Hz, 1H), 8.00 (d, \(J = 8.4\) Hz, 1H), 7.75 (d, \(J = 7.8\) Hz, 2H), 7.54 (t, \(J = 7.8\) Hz, 3H), 7.44 (t, \(J = 7.2\) Hz, 1H), 2.63 (s, 3H).} \]

\[ \text{\(^{13}\)C NMR (150 MHz, CDCl\textsubscript{3}): \(\delta\) 157.8, 142.0, 140.5, 140.0, 136.2, 131.4, 130.3, 129.5, 129.1, 129.0, 127.8, 127.4, 126.4, 124.6, 123.4, 122.9, 121.6, 21.9.} \]

HRMS (ESI, m/z): Calculated for C\(_{21}\)H\(_{15}\)D\(_3\)N \((\text{M+H})^+\) 287.1669, found 287.1667.

22. A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 124-126°C.

\[ \text{\(^1\)H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta\) 8.49 (d, \(J = 8.4\) Hz, 1H), 8.22 (d, \(J = 7.8\) Hz, 1H), 8.13 (dd, \(J = 9.6, 2.4\) Hz, 1H), 8.08 (dd, \(J = 9.0, 5.4\) Hz, 1H), 7.86 – 7.84 (m, 1H), 7.75 – 7.72 (m, 1H), 7.44 (td, \(J = 8.4, 2.4\) Hz, 1H).} \]

\[ \text{\(^{13}\)C NMR (150 MHz, CDCl\textsubscript{3}): \(\delta\) 160.9 (d, \(J = 244.3\) Hz), 158.0, 140.6, 132.0, 131.5 (d, \(J = 9.0\) Hz), 130.5, 127.9, 126.6, 126.0, 125.0 (d, \(J = 9.2\) Hz), 122.5, 117.4 (d, \(J = 24.0\) Hz), 106.9 (d, \(J = 23.1\) Hz).} \]

HRMS (ESI, m/z): Calculated for C\(_{14}\)H\(_8\)D\(_3\)F\(_{\text{N}}\) \((\text{M+H})^+\) 215.1105, found 215.1099.

23. A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 109-111°C.
\[ \text{\textit{H} NMR (600 MHz, CDCl}_3\text{): } \delta 8.52 (d, J = 8.4 \text{ Hz, 1H}), 8.47 (d, J = 2.4 \text{ Hz, 1H}), 8.21 (d, J = 8.4 \text{ Hz, 1H}), 8.01 (d, J = 9.0 \text{ Hz, 1H}), 7.86 – 7.84 \text{ (m, 1H)}, 7.74 – 7.71 \text{ (m, 1H)}, 7.64 (dd, J = 8.4, 2.4 \text{ Hz, 1H}).} \]

\[ \text{\textit{C} NMR (150 MHz, CDCl}_3\text{): } \delta 159.1, 142.1, 132.1, 131.5, 130.8, 130.7, 129.0, 127.9, 126.6, 126.0, 124.8, 122.3, 121.6, 23.2 – 22.6 \text{ (m)}.} \]

HRMS (ESI, m/z): Calculated for C\textsubscript{14}H\textsubscript{8}D\textsubscript{3}ClN (M+H\textsuperscript{+}) 231.0809, found 231.0807.

24. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 108-110°C.

\[ \text{\textit{H} NMR (600 MHz, CDCl}_3\text{): } \delta 8.20 (d, J = 8.4 \text{ Hz, 1H}), 7.69 – 7.66 \text{ (m, 1H)}, 7.65 – 7.63 \text{ (m, 2H)}, 7.49 – 7.44 \text{ (m, 3H)}, 7.34 (dd, J = 7.8, 1.8 \text{ Hz, 2H}), 4.11 (q, J = 7.2 \text{ Hz, 2H}), 0.97 (t, J = 7.2 \text{ Hz, 3H}).} \]

\[ \text{\textit{C} NMR (150 MHz, CDCl}_3\text{): } \delta 167.6, 158.4, 141.5, 136.4, 135.4, 131.9, 130.4, 130.0, 128.1, 128.1, 127.9, 127.8, 126.9, 125.6, 61.2, 22.1 – 21.7 \text{ (m), 13.6}.} \]

HRMS (ESI, m/z): Calculated for C\textsubscript{19}H\textsubscript{15}D\textsubscript{3}NO\textsubscript{2} (M+H\textsuperscript{+}) 295.1567, found 295.1565.

25. A light yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).
$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.94 (s, 1H), 7.56 (d, $J = 8.4$ Hz, 1H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.27 (d, $J = 7.8$ Hz, 2H), 7.21 (d, $J = 7.8$ Hz, 2H), 4.14 (q, $J = 7.2$ Hz, 2H), 2.57 (s, 3H), 2.45 (s, 3H), 1.02 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 167.7, 157.3, 140.6, 138.2, 137.3, 133.7, 132.4, 132.0, 129.8, 128.7, 128.0, 126.8, 124.6, 61.1, 21.9, 21.3, 13.7.

HRMS (ESI, m/z): Calculated for C$_{21}$H$_{19}$D$_3$NO$_2$ (M+H)$^+$ 323.1880, found 323.1875.

26. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 138-140°C.

![Chemical Structure 1](image1)

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.79 (dd, $J = 9.6$, 2.4 Hz, 1H), 7.62 (dd, $J = 9.6$, 5.4 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.31 – 7.28 (m, 2H), 7.18 (t, $J = 8.4$ Hz, 2H), 4.15 (q, $J = 7.2$ Hz, 2H), 1.05 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 167.2, 162.1 (dd, $J = 246.2$, 162.6 Hz), 157.9, 141.2, 132.6, 131.9 (d, $J = 3.6$ Hz), 131.6 (d, $J = 8.1$ Hz), 130.8, 129.7 (d, $J = 8.7$ Hz), 129.0 (d, $J = 8.3$ Hz), 120.8 (d, $J = 24.6$ Hz), 115.3 (d, $J = 21.5$ Hz), 109.5 (d, $J = 21.1$ Hz), 61.4, 22.1-21.9 (m), 13.8.

HRMS (ESI, m/z): Calculated for C$_{19}$H$_{13}$D$_3$F$_2$NO$_2$ (M+H)$^+$ 331.1378, found 331.1375.

27. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 107-109°C.

![Chemical Structure 2](image2)
$^1$H NMR (600 MHz, CDCl$_3$): δ 8.18 (d, $J = 1.8$ Hz, 1H), 7.59 (dd, $J = 9.0$, 1.8 Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.47 (d, $J = 7.8$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 4.16 (q, $J$ = 7.2 Hz, 2H), 1.06 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$): δ 166.9, 157.9, 141.6, 134.5, 134.4, 134.3, 133.7, 131.5, 131.2, 130.6, 128.6, 128.4, 124.8, 61.5, 13.8.

HRMS (ESI, m/z): Calculated for C$_{19}$H$_{13}$D$_{2}$Cl$_{2}$NO$_2$ (M+H)$^+$ 363.0787, found 363.0785.
Copies of the $^1$H NMR, $^{13}$C NMR

$^1$H NMR

$^{13}$C NMR
2-$^1$H NMR

2-$^{13}$C NMR
$^{3-}^{1}H$ NMR

$^{3-}^{13}C$ NMR
$^{1}H$ NMR

$^{13}$C NMR
5-\textsuperscript{1}H NMR

5-\textsuperscript{13}C NMR
6-$^1$H NMR

6-$^{13}$C NMR
$^7$H NMR

$^13$C NMR
$^1$H NMR

$^{13}$C NMR
10-¹H NMR

10-¹³C NMR
13-$^1$H NMR

13-$^{13}$C NMR
14-\textsuperscript{1}H NMR

14-\textsuperscript{13}C NMR
15-$^1$H NMR

15-$^{13}$C NMR
$^{16}$H NMR

$^{16}$C NMR
17-¹H NMR

17-¹³C NMR
18\textsuperscript{-}1\text{H} NMR

18\textsuperscript{-}13\text{C} NMR
19-$^1$H NMR

19-$^{13}$C NMR
20-$^1$H NMR

20-$^{13}$C NMR
21-$^1$H NMR

21-$^{13}$C NMR
22-$^1$H NMR

22-$^{13}$C NMR
23-$^1$H NMR

23-$^{13}$C NMR
24-$^1$H NMR

24-$^{13}$C NMR
25-$^1$H NMR

25-$^{13}$C NMR
26-$^1$H NMR

26-$^{13}$C NMR
27-$^1$H NMR

27-$^{13}$C NMR