Supporting Information for

Facile Synthesis of 1,3,4-Benzotriazepines and 1-Aryl amide-1H-indazoles via Palladium Catalyzed Cyclization of Aryl Isocyanates and Aryl Hydrazones under Microwave Irradiation

Chune Dong*, Lingli Xie, Xiaohong Mou, Yashan Zhong, Wei Su

College of Pharmacy, State Key Laboratory of Virology,
Wuhan University, Wuhan, 430072, China

cdong@whu.edu.cn, Tel: 86-27-68759586; Fax: 86-27-68759850
List of Contents

1) General information

2) Optimized conditions for the reaction of 1a with 3d catalyzed by palladium complexes (Table S1).

3) General procedure for the reaction of hydrazones with isocyanates

4) Characterization data for compounds 4 and 5

5) Copies of $^1$HNMR, $^{13}$C NMR spectra of 4a, 4b, 4d, 4i, 4g, 4h, 5d, 5g and 5i

6) Crystallographic data for 5d
1) General information

Unless otherwise noted, reagents and materials were obtained from commercial suppliers and were used without further purification. All solvents were purified according to reported procedures. Reactions were monitored by thin layer chromatography (TLC) and column chromatography purifications were performed using 230-400 mesh silica gel.

Melting points were uncorrected and measured on an SGW X-4 apparatus. IR spectra were recorded from KBr pellets at a range of 400-4000 cm\(^{-1}\) on a Thermo Nicolet Nexus 470 FTIR spectrometer. \(^1\)H and \(^{13}\)C NMR spectra were obtained on a Bruker DPX400 apparatus in CDCl\(_3\) with TMS as internal standard. Single-crystal X-ray-diffraction measurements were carried out on a Bruker Smart-APEX-CCD diffractometer. All microwave irradiation experiments were carried out using the microwave oven XH-100B from Xianghu Company, China. The reactions were performed in microwave vials sealed with a septum. The irradiation power was set at 500W. The temperature in the MW experiments was measured by an internal IR sensor.

2) Optimized conditions for the reaction of 1a with 3d catalyzed by palladium complexes (Table S1).

Under a stream of argon, to a solution of catalyst (2-5 mol\%) and ligand (10-40 mol\%) in dried solvent (3 mL) was added hydrazone 1a (0.36 mmol) followed by the isocyanate 3d (0.432 mmol) and base (0.54 mmol). The resulting mixture was stirred at room temperature for 0.5 h and then the mixture was transferred into the microwave vial. The
vial was sealed; the irradiation power was set at 500W and irradiated in the microwave reactor at 80°C for 20min. When the vial was removed from the apparatus, the solvent was evaporated under vacuum. The residue was added 5 mL of water and extracted with ethyl acetate (3 × 20 mL). Then the organic layer was washed with brine and dried with anhydrous sodium sulfate. Evaporation of ethyl acetate gave a pale yellow residue, which was purified by column chromatography to afford the pure product.

**Table S1** Optimized Conditions for the Reaction of 1a with 3d Catalyzed by Palladium Complex

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst&lt;sup&gt;a&lt;/sup&gt; (mol%)</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Overall yield</th>
<th>4d/6d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A (5/20)</td>
<td>Toluene</td>
<td>110</td>
<td>75%</td>
<td>1/2.0</td>
</tr>
<tr>
<td>2</td>
<td>A (5/20)</td>
<td>THF</td>
<td>80</td>
<td>65%</td>
<td>1/2.2</td>
</tr>
<tr>
<td>3</td>
<td>A (5/20)</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>80</td>
<td>51%</td>
<td>1/1.3</td>
</tr>
<tr>
<td>4</td>
<td>A (5/20)</td>
<td>DMF</td>
<td>120</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>A (5/40)</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>80</td>
<td>60%</td>
<td>1/1.6</td>
</tr>
<tr>
<td>6</td>
<td>B (5/10)</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>80</td>
<td>98%</td>
<td>1/2.7</td>
</tr>
<tr>
<td>7</td>
<td>B (5/20)</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>80</td>
<td>40%</td>
<td>1/1.4</td>
</tr>
<tr>
<td>8</td>
<td>B (5/10)</td>
<td>Toluene</td>
<td>110</td>
<td>47%</td>
<td>1/2.1</td>
</tr>
<tr>
<td>9&lt;sup&gt;c&lt;/sup&gt;</td>
<td>C (5/20)</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>80</td>
<td>41%</td>
<td>1/8.0</td>
</tr>
<tr>
<td>10&lt;sup&gt;c, d&lt;/sup&gt;</td>
<td>C (5/20)</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>80</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td>11&lt;sup&gt;c&lt;/sup&gt;</td>
<td>C (5/20)</td>
<td>Toluene</td>
<td>110</td>
<td>43%</td>
<td>1/1.9</td>
</tr>
<tr>
<td>12&lt;sup&gt;c&lt;/sup&gt;</td>
<td>C (5/20)</td>
<td>DMF</td>
<td>120</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>13</td>
<td>D (2.5/5)</td>
<td>Toluene</td>
<td>110</td>
<td>63%</td>
<td>1/2</td>
</tr>
<tr>
<td>14&lt;sup&gt;d&lt;/sup&gt;</td>
<td>E (5/10)</td>
<td>Toluene</td>
<td>110</td>
<td>0</td>
<td>---</td>
</tr>
</tbody>
</table>
15e A (5/20) Toluene 110 90% 1/1.9
16e A (5/20) THF 80 88% 1/2.0
17e A (5/20) CH$_3$CN 80 93% 1/1.1

a Unless otherwise specified, the reaction was carried out with 0.36 mmol of 1a and 0.432 mmol of 3d, 0.54 mmol of K$_2$CO$_3$ in 3 mL solvent at indicated temperature for 18 h. b Catalyst: A (Pd(OAc)$_2$/PPh$_3$); B (Pd$_2$(dba)$_3$/PPh$_3$); C (Pd(OAc)$_2$/norbornene); D ([Rh(COD)-Cl]$_2$/norbornene); E (CuI/dppf). c BTEAC was added as PTC. d Cs$_2$CO$_3$ was used as base. e Microwave irradiation power: 500 W, the reaction mixture was held at 80°C for 20 min. The temperature in the MW experiments was measured by an eternal IR sensor.

3) General procedure for the cyclization of aryl hydrazones with aryl isocyanates under microwave irradiation

Under a stream of argon, to a solution of Pd(OAc)$_2$ (11.1 mg, 0.05 mmol, 5 mol%) and PPh$_3$ (52.5 mg, 0.2 mmol, 20 mol%) in dried acetonitrile (5 mL) was added hydrazone 1 (1 mmol) followed by the isocyanate 3 (1.2 mmol) and K$_2$CO$_3$ (1.5 mmol). The resulting mixture was stirred at room temperature for 0.5 h and then the mixture was transferred into the microwave vial. The vial was sealed; the irradiation power was set at 500W and irradiated in the microwave reactor at 80°C for 20 min. When the vial was removed from the apparatus, the solvent was evaporated under vacuum. The residue was added 5 mL of water and extracted with ethyl acetate (3 × 20 mL). Then the organic layer was washed with brine and dried with anhydrous sodium sulfate. Evaporation of ethyl acetate gave a pale yellow residue, which was purified by column chromatography to afford the pure product, and the side product, if any of which was observed.

4) Characterization data for 4 and 5

4a: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH$_2$Cl$_2$ = 1:1:1), white solid, m. p. 194-196°C; IR (KBr, cm$^{-1}$): $\nu$ 3243, 2962, 1675,
1528, 1498; \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 2.23\) (s, 3H), 6.99 (t, \(J = 7.5\) Hz, 1H), 7.04 (d, \(J = 1.4\) Hz, 1H), 7.27-7.16 (m, 3H), 7.36 (dt, \(J = 7.5\) Hz, 1H), 7.44 (d, \(J = 8.0\) Hz, 2H), 7.60 (d, \(J = 8.0\) Hz, 1H), 8.12 (s, 1H); \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 22.84, 118.51, 119.31, 122.33, 127.35, 127.60, 127.95, 128.14, 129.91, 130.18, 132.72, 134.50, 136.93, 146.14, 151.47\); MS (m/z): 252. [M + H]\textsuperscript{+}.

4b: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH\textsubscript{2}Cl\textsubscript{2} = 1:1:1), light yellow solid, m. p. 183-185°C; IR (KBr, cm\textsuperscript{-1}): \(\nu = 3264, 1655, 1557, 1508, 1316\); \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 2.29\) (s, 3H), 2.30 (s, 3H), 7.11-7.4 (m, 7H), 7.66 (d, \(J = 8.0\) Hz, 1H), 8.12 (s, 1H); \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 20.80, 23.85, 119.75, 120.36, 128.40, 128.61, 129.47, 129.60, 131.17, 132.93, 133.73, 135.33, 135.59, 146.9574, 152.62\); MS (m/z): 265 [M]\textsuperscript{+}.

4c: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH\textsubscript{2}Cl\textsubscript{2} = 2:1:1), white solid, m. p. 179-182°C; IR (KBr, cm\textsuperscript{-1}): \(\nu = 3264, 1669, 1557, 1488, 827\); \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 2.33\) (s, 3H), 7.04 (d, \(J = 1.2\) Hz, 1H), 7.18-7.39 (m, 7H), 8.13 (s, 1H); \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 23.88, 115.77, 120.27, 120.97, 128.31, 128.65, 131.27, 131.87, 133.77, 135.39, 137.15, 147.62, 152.25\); MS (m/z): 330 [M]\textsuperscript{+}.

4d: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH\textsubscript{2}Cl\textsubscript{2} = 1:1:1), light yellow solid, m. p. 187-189°C; IR (KBr, cm\textsuperscript{-1}): \(\nu = 3267, 1670, 1554, 1492, 827\); \textsuperscript{1}H-NMR(400 MHz, CDCl\textsubscript{3}): \(\delta = 2.30\) (s, 3H), 7.12 (d, \(J = 1.6\) Hz, 1H), 7.26-7.35 (m, 3H), 7.42-7.67 (m, 3H), 7.69 (d, 1H), 8.20 (s, 1H); \textsuperscript{13}C-NMR (100 MHz,
CDCl₃):  δ = 22.84, 119.22, 119.61, 127.14, 127.28, 127.59, 127.87, 130.21, 132.70, 134.36, 135.62, 146.55, 151.28; MS: (m/z) 285.5 [M]+.

4f: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH₂Cl₂ = 2:1:1), white solid, m. p. 140-143°C; IR (KBr, cm⁻¹): ν 3194, 2954, 1686, 1525, 1403; ¹H-NMR (400 MHz, CDCl₃): δ = 0.83 (t, J = 6.9 Hz, 3H), 1.28-1.33 (m, 4H), 1.51-1.57 (m, 2H), 2.50 (t, J = 5.2 Hz, 2H), 6.97-7.03 (m, 2H), 7.17-7.27 (m, 3H), 7.35 (d, J = 6.7 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 8.13 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃): δ = 14.04, 22.51, 25.64, 31.44, 37.23, 119.51, 119.81, 120.77, 123.34, 128.38, 128.91, 128.98, 131.10, 133.75, 134.95, 137.99, 150.57, 152.61; MS (m/z): 308.1 [M+H]+.

4g: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH₂Cl₂ = 2:1:1), light yellow solid, m. p. 146-149°C; IR (KBr, cm⁻¹): ν 3269, 2917, 1660, 1555; ¹H-NMR (400 MHz, CDCl₃): δ = 0.84 (t, J = 6.9 Hz, 3H), 1.28-1.33 (m, 4H), 1.50-1.55 (m, 2H), 2.24 (s, 3H), 2.52 (dt, J = 5.3 Hz, 2H), 7.01-7.04 (m, 3H), 7.06-7.59 (m, 4H), 7.60 (d, J = 7.4 Hz, 1H), 8.04 (s, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ = 13.01, 19.78, 21.48, 24.63, 28.68, 30.43, 36.19, 118.70, 119.78, 127.34, 127.92, 128.45, 130.04, 131.88, 132.72, 133.99, 134.33, 149.32, 151.70; MS (m/z): 321 [M]+.

4h: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH₂Cl₂ = 3:1:1), white solid, m. p. 144-146°C; IR (KBr, cm⁻¹): ν 3368, 2924, 1690, 1524, 1129, 825; ¹H-NMR (400 MHz, CDCl₃): δ = 0.83 (t, J = 7.0 Hz, 3H), 1.24-1.36 (m,
4H), 1.40-1.46 (m, 2H), 2.79 (t, J = 7.4 Hz, 2H), 7.26-7.46 (m, 7H), 7.65 (d, J = 7.9 Hz, 1H), 8.38 (s, 1H); MS (m/z): 386 [M]+.

4i: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH₂Cl₂ = 2:1:1), light yellow solid, m. p. 154-157°C; IR (KBr, cm⁻¹): ν 3270, 2955, 1661, 1557, 1402; ¹H-NMR (400 MHz, CDCl₃): δ = 0.84 (t, J = 7.0 Hz, 3H), 1.30-1.33 (m, 4H), 1.49-1.56 (m, 2H), 2.52 (t, J = 1.3 Hz, 2H), 7.00 (d, J = 1.3 Hz, 1H), 7.17-7.27 (m, 4H), 7.35-7.41 (m, 2H), 7.60 (d, J = 7.9 Hz, 1H), 8.13 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃): δ = 14.04, 22.49, 25.65, 31.44, 37.26, 120.63, 120.71, 128.19, 128.40, 128.88, 128.93, 131.17, 133.76, 134.82, 136.66, 151.03, 152.45; MS (m/z): 341.5 [M]+.

4j: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH₂Cl₂ = 2:1:1), white solid, m. p. 186-189°C; IR (KBr, cm⁻¹): ν 3261, 2956, 1681, 1594, 1427, 775; ¹H-NMR (400 MHz, CDCl₃): δ = 0.90 (t, J = 6.9 Hz, 3H), 1.23-1.35 (m, 4H), 1.58-1.66 (m, 2H), 2.61 (t, J = 6.8 Hz, 2H), 7.04 (d, J = 1.0 Hz, 1H), 7.06 (d, J = 1.0 Hz, 1H), 7.10-7.47 (m, 5H), 7.69 (d, J = 8.0 Hz, 1H), 8.25 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃): δ = 13.86, 22.38, 29.72, 31.71, 37.32 119.51, 119.81, 120.77, 123.34, 128.38, 128.91, 128.98, 131.10, 133.75, 134.95, 137.99, 150.57, 152.61; MS (m/z): 342 [M+H]+.

4k: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH₂Cl₂ = 4:1:1), white solid, m. p. 200-202°C; IR (KBr, cm⁻¹): ν 3262, 3083, 1659, 1618, 1560, 1498; ¹H-NMR (400 MHz, CDCl₃): δ = 7.03-7.05 (m, 1H), 7.15-7.18 (m, 2H), 7.26-7.50 (m, 10H), 7.70 (d, J = 8.0 Hz, 1H), 8.24 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃): δ
4l: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH$_2$Cl$_2$ = 6:1:1), white solid, m. p. 151-154°C; IR (KBr, cm$^{-1}$): $\nu$ 3263, 2922, 1658, 1557, 1464, 1126; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 2.25 (s, 3H), 7.06 (d, $J$ = 8.2 Hz, 2H), 7.13-7.18 (m, 1H), 7.29-7.45 (m, 9H), 7.68 (d, $J$ = 8.0 Hz, 1H), 8.16 (s, 1H); $^{13}$C-NMR(100 MHz, CDCl$_3$): $\delta$ = 20.86, 119.98, 122.36, 126.74, 128.64, 128.68, 129.57, 129.77, 130.31, 131.64, 133.14, 133.28, 133.97, 135.07, 135.48, 146.97, 152.66; MS (m/z): 327 [M$^+$].

4m: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH$_2$Cl$_2$ = 4:1:1), light yellow, m. p. 122-124°C; IR (KBr, cm$^{-1}$): 3340, 1700, 1521, 1488, 824; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.12 (dd, $J$ = 5.8 Hz, 1.6 Hz, 1H), 7.29-7.45 (m, 11H), 7.69 (d, $J$ = 7.2 Hz, 1H), 8.27 (s, 1H); MS (m/z): 392 [M$^+$].

4n: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH$_2$Cl$_2$ = 6:1:1), white solid, m. p. 161-163°C; IR (KBr, cm$^{-1}$): $\nu$ 3266, 1693, 1524, 1491, 829; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.13-7.24 (m, 3H), 7.43-7.45 (m, 5H), 7.31-7.36 (m, 4H), 7.69 (d, $J$ = 8.0 Hz, 1H), 8.24 (s, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 120.85, 122.27, 126.79, 128.53, 128.68, 128.73, 129.93, 130.25, 131.74, 132.98, 134.02, 135.30, 136.43, 147.44, 152.20; MS (m/z): 348.5 [M+H$^+$].

5a: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3:1), white solid, m. p. 69-71°C; IR (KBr, cm$^{-1}$): $\nu$ 3446, 1683, 1593, 1526, 1456; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 2.53 (s, 3H), 7.06 (t, $J$ = 8.0 Hz, 1H), 7.22 (t, $J$ = 8.0 Hz,
2H), 7.24 (t, J = 8.0 Hz, 1H), 7.31 (t, J = 8.0 Hz, 2H), 7.45 (t, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 8.32 (d, J = 8.0 Hz, 1H), 8.96 (s, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 12.1, 110.0, 114.8, 119.6, 123.1, 124.7, 129.1, 129.2, 137.3, 139.7, 146.9, 148.9; MS (m/z): 252 [M + H]$^+$. 

$5b$: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 4:1), white solid, m. p. 114-116°C; IR (KBr, cm$^{-1}$): $\nu$ 3446, 1716, 1558, 1076; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 2.28 (s, 3H), 2.53 (s,3H), 7.11 (d, J = 8.0 Hz, 1H), 8.90 (s, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 11.1, 19.8, 113.8, 118.6, 122.0, 124.8, 128.1, 132.6, 133.7, 138.3, 145.7, 147.9; MS (m/z): 265.5 [M]$^+$, 267.5 [M+2H]$^+$. 

$5c$: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3:1), light yellow, m. p. 129-130°C; IR (KBr, cm$^{-1}$): $\nu$ 3445, 1691, 1593, 1532, 1403; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 2.53 (s, 3H), 7.19-7.61 (m, 7H), 8.32(d, J = 8.0 Hz, 1H), 8.98 (s, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 12.1, 114.8, 116.6, 120.3, 121.0, 126.0, 129.3, 132.1, 136.5, 139.5, 147.2, 148.7; MS (m/z): 330 [M]$^+$. 

$5d$: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3:1), light yellow, m. p. 123-126°C; IR (KBr, cm$^{-1}$): $\nu$ 3443, 1640, 1535, 1407; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 2.61 (s, 3H), 7.26 (m, 3H), 7.34 (t, 1H), 7.56 (dd, J = 8.0, 12 Hz, 3H), 8.37 (d, J = 12.0 Hz, 1H), 9.06 (s, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 12.1, 114.3, 120.3, 120.6, 123.2, 125.9, 129.0, 129.1, 136.0, 139.6, 147.1, 148.7; MS: (m/z) 285.5 [M]$^+$. 

Supplementary Material (ESI) for Organic & Biomolecular Chemistry 
This journal is (c) The Royal Society of Chemistry 2010
5e: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 5:1), white powder, m. p. 102-105 °C; IR (KBr, cm⁻¹): ν 3445, 1720, 1596, 1540, 1426; ¹H-NMR (400 MHz, CDCl₃): δ = 2.60 (s, 3H), 7.11 (d, J = 4.0 Hz, 1H), 7.28 (m, 2H), 7.50-7.81 (m, 4H), 8.38 (d, J = 8.0 Hz, 1H), 9.08(s, 1H); ¹³C-NMR (100 MHz, CDCl₃): δ = 12.1, 114.8, 117.4, 119.5, 123.3, 124.0, 129.4, 130.1, 134.8, 138.5, 139.3, 147.3, 148.3; MS (m/z): 285.5 [M]+.

5f: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 4:1), yellow oil, IR (KBr, cm⁻¹): ν 3445, 1720, 1596, 1540, 1426; ¹H-NMR (400 MHz, CDCl₃): δ = 0.8 (t, J = 4.0 Hz, 3H), 1.30 (br, 4H), 1.93 (br, 2H), 2.87 (t, J = 8.0 Hz, 2H), 7.03 (t, J = 4.0 Hz, 1H), 7.06-7.19 (m, 3H), 7.27 (t, J = 8.0 Hz, 1H), 7.31 (m, 3H), 8.32 (d, J = 8.0 Hz, 1H), 8.97 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃): δ = 12.9, 21.4, 23.0, 25.9, 30.5, 113.8, 118.5, 119.3, 121.9, 123.0, 126.9, 127.4, 128.0, 136.3, 138.8, 147.9, 149.9; MS (m/z): 308 [M+H]+.

5g: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 4:1), white solid, m. p. 51-53 °C, IR (KBr, cm⁻¹): ν 3447, 2923, 1722, 1649, 1532, 1401; ¹H-NMR (400 MHz, CDCl₃): δ = 0.84 (t, J = 8.0 Hz, 3H), 1.36 (br, 4H), 1.84 (t, J = 8.0 Hz, 2H), 2.85 (t, J = 8.0 Hz, 2H), 7.09 (dt, J = 8.0 Hz, 2H), 7.18 (m, 1H), 7.42 (m, 3H), 7.56 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.80 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃): δ = 14.0, 20.8, 22.4, 27.5, 31.7, 114.9, 119.3, 120.3, 122.9, 125.4, 127.5, 128.0, 129.1, 133.3, 134.7, 139.9, 149.1, 150.9; MS (m/z): 321 [M]+.
5h: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 6:1), white solid, m. p. 74-75°C; IR (KBr, cm\(^{-1}\)): \(\nu\) 3445, 2956, 1708, 1648, 1523, 1425; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) = 0.81 (br, 3H), 1.30 (br, 4H), 1.75 (br, 2H), 2.90 (t, \(J = 4\) Hz, 2H), 7.22 (m, 1H), 7.36-7.48 (m, 5H), 7.49 (d, \(J = 4\) Hz, 1H), 8.31 (d, \(J = 8.0\) Hz, 1H), 8.99 (s, 1H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 12.9, 21.4, 25.7, 26.0, 30.6, 113.8, 115.5, 119.4, 120.0, 124.5, 128.2, 131.0, 135.5, 138.8, 147.8, 150.2; MS (m/z): 386 [M]+.

5i: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 7:1), yellow solid, m. p. 86-88°C; IR (KBr, cm\(^{-1}\)): \(\nu\) 3375, 2920, 1683, 1592, 1533, 1404; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) = 0.93 (t, \(J = 8\) Hz, 3H), 1.38 (br, 4H), 1.86 (t, \(J = 8\) Hz, 2H), 2.97 (t, \(J = 8\) Hz, 2H), 7.26-7.32 (m, 3H), 7.34 (t, \(J = 8\) Hz, 1H), 7.54 (d, \(J = 12\) Hz, 2H), 7.57 (d, 1H), 8.41 (d, \(J = 8.0\) Hz, 1H), 9.03 (s, 1H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 14.0, 22.4, 27.0, 31.7, 114.8, 120.4, 120.8, 123.1, 125.5, 129.0, 129.1, 136.0, 139.8, 148.9, 151.3; MS (m/z): 341.5 [M]+.

5j: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 8:1), white, m. p. 57-60°C; IR (KBr, cm\(^{-1}\)): \(\nu\) 3371, 1720, 1599, 1530, 1445; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) = 0.85 (t, \(J = 8\) Hz, 3H), 1.34 (br, 4H), 1.78 (br, 2H), 2.88 (t, \(J = 8\) Hz, 2H), 7.02 (d, \(J = 8\) Hz, 1H), 7.18 (m, 2H), 7.21 (m, 2H), 7.45 (d, \(J = 12\) Hz, 1H), 7.70 (s, 1H), 8.30 (d, \(J = 12\) Hz, 1H), 9.00 (s, 1H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 12.9, 21.4, 24.9, 25.9, 30.6, 113.8, 116.4, 117.9, 119.4, 122.1, 123.9, 125.0, 128.2, 133.3, 137.5, 138.7, 147.3, 150.3; MS (m/z): 341.5 [M]+.
5k: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1), white, m. p. 104-107°C; IR (KBr, cm\(^{-1}\)): \( \nu \) 3445, 2921, 1652, 1557, 1401; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.00-7.26 \) (m, 6H), 7.40-7.46 (m, 5H), 7.52 (m, 1H), 7.62 (m, 1H), 8.56 (d, \( J = 8.0 \) Hz, 1H), 9.22 (s, 1H); MS (m/z): 313 [M]+.

5l: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1), light yellow, m. p. 113-114°C, IR (KBr, cm\(^{-1}\)): \( \nu \) 3445, 2959, 1633, 1536, 1411; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta = 2.39 \) (s, 3H), 7.23 (d, \( J = 8.0 \) Hz, 2H), 7.42 (t, \( J = 8.0 \) Hz, 1H), 7.44-7.65 (m, 6H), 8.02 (d, \( J = 8.0 \) Hz, 3H), 8.56 (d, \( J = 8.0 \) Hz, 1H), 9.17 (s, 1H) ; MS (m/z): 327 [M]+.

5m: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1), light yellow, m. p. 122-124°C; IR (KBr, cm\(^{-1}\)): \( \nu \) 3379, 2923, 1683, 1527, 1489; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.34 \) (t, \( J = 8.0 \) Hz, 1H), 7.44-7.55 (m, 8H), 7.92 (t, \( J = 8.0 \) Hz, 3H), 8.44 (d, \( J = 8.0 \) Hz, 1H), 9.15 (s, 1H); MS (m/z): 392 [M]+.

5n: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1), white, m. p. 161-164°C; IR (KBr, cm\(^{-1}\)): \( \nu \) 3446, 2924, 1694, 1589, 1527, 1404; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.32 \) (t, \( J = 8.0 \) Hz, 3H), 7.45-7.58 (m, 6H), 7.92 (dd, \( J = 8.0 \) Hz, 3H), 8.44 (d, \( J = 8.0 \) Hz, 1H), 9.15 (s, 1H); MS (m/z): 348.5 [M+H]+.
5) Copies of $^1$H NMR, $^{13}$C NMR spectra
6) Crystallographic data for 5d

![Crystal structure diagram]

**Bond precision:** C-C = 0.0021 Å  \( \text{Wavelength=0.71073} \)

**Cell:**
- \( a=23.441(6) \)
- \( b=6.2204(15) \)
- \( c=18.816(5) \)
- \( \alpha=90 \)
- \( \beta=98.452(4) \)
- \( \gamma=90 \)

**Temperature:** 293 K

**Calculated** | **Reported**
--- | ---
**Volume** | 2713.8(12) | 2713.7(11)
**Space group** | C2/c | C2/c
**Hall group** | -C 2yc | ?
**Moiety formula** | C15 H12 Cl N3 O | ?
**Sum formula** | C15 H12 Cl N3 O | C15 H12 Cl N3 O
**Mr** | 285.73 | 285.73
**Dx, g cm\(^{-3}\)** | 1.399 | 1.399
**Z** | 8 | 8
**\( \mu \) (mm\(^{-1}\))** | 0.280 | 0.280
**F000** | 1184.0 | 1184.0
**F000'** | 1185.58 | 
**h,k,lmax** | 28,7,23 | 28,7,23
**Nref** | 2667 | 2666
**Tmin, Tmax** | 0.914, 0.925 | 0.916, 0.926
**Tmin'** | 0.914 | 

**Correction method:** MULTI-SCAN

**Data completeness:** 1.000  \( \text{Theta(max)} = 26.000 \)

**R(reflections) = 0.0329 (2268)**  \( \text{wR2(reflections) = 0.0923 (2666)} \)

**S = 1.020**  \( \text{Npar} = 163 \)