

## *Supporting Information*

### **Regioselective synthesis of indazolo[2,3-*a*]quinazolines enabled by I<sub>2</sub>/S-facilitated annulation relay dehydrogenative aromatization of cyclohexanones**

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## 1. General

All substrates aldehydes (**1**), 3-aminoindazoles (**2**), cycloketones (**3**) and reagents were commercially available and used without further purification. All aldehydes (**1**) and 3-aminoindazoles, cycloketones (**3**) are known compounds. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). <sup>1</sup>H spectra were recorded in CDCl<sub>3</sub> on 400 MHz NMR spectrometers and resonances ( $\delta$ ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. <sup>13</sup>C spectra were recorded in CDCl<sub>3</sub> on 100 MHz NMR spectrometers and resonances ( $\delta$ ) are given in ppm. HRMS analysis of compounds was performed with a time-of-flight mass spectrometer (micrOTOF-Q, Bruker Daltonik, Germany) equipped with an electrospray ionization source. The X-ray crystal-structure determinations of **4h** was obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected. All reactions were heated by a metal sand bath (WATTCAS, LAB-500, <https://www.wattcas.com>).

## 2. General procedure for the synthesis of compounds 4 (4a as an example)

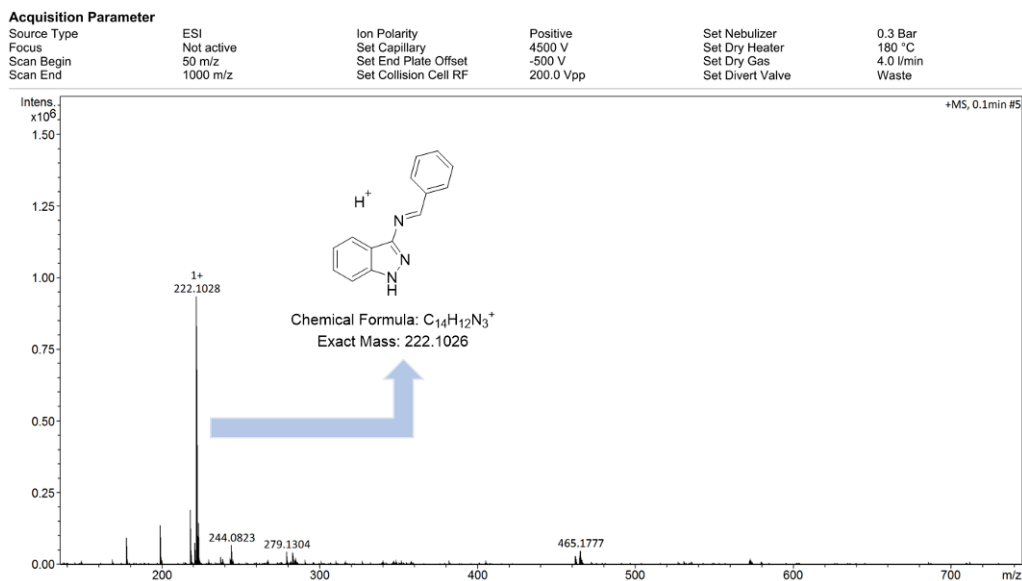
Benzaldehyde **1a** (63.7 mg, 0.6 mmol), 3-aminoindazoles **2a** (79.9 mg, 0.6 mmol), cyclohexanone **3a** (39.3 mg, 0.4 mmol), I<sub>2</sub> (50.8 mg, 0.2 mmol), S (25.7 mg, 0.8 mmol) and NMP (2.0 mL) were charged into a pressure tube (35 mL) and were stirred at 120 °C under air for 20 h. After disappearance of the reactant (monitored by TLC), added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (w/w), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to afford the product **4a** as a yellow solid (80 mg, 68% yield).

## 3. Experimental details

(1) the control experiment: (Scheme 4e)

Benzaldehyde **1a** (63.7 mg, 0.6 mmol) and 3-aminoindazoles **2a** (79.9 mg, 0.6 mmol), were charged into a pressure tube (50 mL) and were stirred at 120 °C for 4 h. The imine intermediate **7** was clearly detected by HRMS. HRMS (ESI): m/z [M + H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>: 222.1026; found: 222.1028. Then, I<sub>2</sub> (50.8 mg, 0.2 mmol), S (25.7 mg, 0.8 mmol) and **3a** were added into the pressure tube, afterward, the mixture was stirred at 120 °C for 20 h. After disappearance of the reactant (monitored by TLC), and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (w/w), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporation. The residue was

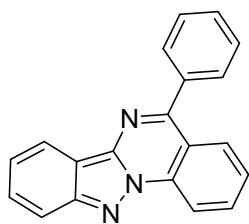
purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to afford the product **4a** as a yellow solid (80 mg, 68% yield).



(2) in 1.0 mmol scale

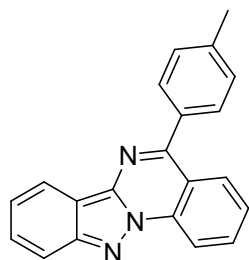
Benzaldehyde **1a** (159 mg, 1.5 mmol), 3-aminoindazoles **2a** (200 mg, 1.5 mmol), cyclohexanone **3a** (98 mg, 1 mmol), I<sub>2</sub> (127 mg, 0.5 mmol), S (64 mg, 2 mmol) and NMP (5 mL) were charged into a pressure tube (35 mL) and were stirred at 120 °C under air for 2 d. After disappearance of the reactant (monitored by TLC), added 125 mL water to the mixture, then extracted with EtOAc 3 times (3 × 125 mL). The extract was washed with 10% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (w/w), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to afford the product **4a** as a yellow solid (177 mg, 60% yield).

#### 4. Characterization data for compounds



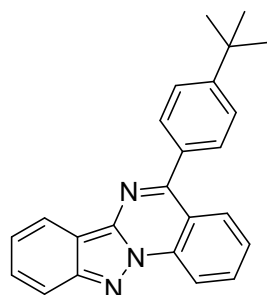
##### 5-phenylindazolo[2,3-*a*]quinazoline (**4a**):

Yield 68% (80 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 205–207 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.92 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.01 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.85 (m, 2H), 7.66–7.58 (m, 5H), 7.35–7.30 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 156.8, 150.0, 139.1, 137.6, 136.0, 133.6, 130.0, 129.6, 129.0, 128.9, 128.7, 126.3, 121.5, 120.7, 119.0, 116.7, 116.6, 115.5; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>14</sub>N<sub>3</sub>: 296.1182; found: 296.1186.



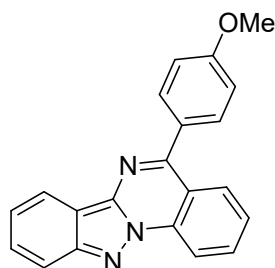
**5-(p-tolyl)indazolo[2,3-a]quinazoline (4b):**

Yield 68% (84 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 207–209 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.91 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.21 (dd, *J* = 8.0, 4 Hz, 1H), 8.00 (m, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.61 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 7.7, 6.8 Hz, 1H), 2.50 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 156.9, 150.0, 139.7, 139.2, 136.0, 134.8, 133.4, 129.9, 129.4, 129.0, 128.9, 126.3, 121.4, 120.7, 119.0, 116.7, 116.6, 115.6, 21.4; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>N<sub>3</sub>: 310.1339; found: 310.1341.



**5-(4-(tert-butyl)phenyl)indazolo[2,3-a]quinazoline (4c):**

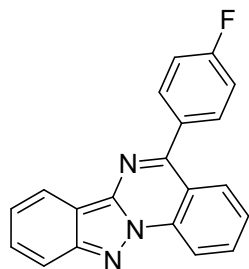
Yield 66% (93 mg; petroleum ether/EtOAc = 100:1); yellow solid; mp 115–118 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.91 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.26 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.00 (m, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.82–7.78 (m, 2H), 7.66–7.62 (m, 3H), 7.61–7.58 (m, 1H), 7.33–7.29 (m, 1H), 1.43 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 156.9, 152.8, 150.0, 139.2, 136.0, 134.8, 133.5, 129.7, 129.1, 128.9, 126.3, 125.7, 121.4, 120.7, 119.0, 116.7, 116.6, 115.5, 34.9, 31.3; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>22</sub>N: 312.1747; found: 312.1748.



**5-(4-methoxyphenyl)indazolo[2,3-a]quinazoline (4d):**

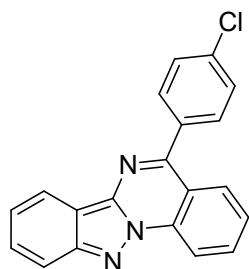
Yield 67% (87 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 205–208 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.92 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.04–7.99 (m, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.85–7.81 (m, 2H), 7.67–7.58 (m, 2H), 7.34–7.29 (m, 1H), 7.16–7.12 (m, 2H), 3.94 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 160.8, 156.6, 150.1, 139.2, 136.1, 133.5, 131.5, 130.1, 129.6, 129.1, 128.9, 126.3, 121.3,

120.7, 119.0, 116.7, 115.4, 114.2, 55.5; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{21}H_{16}N_3O$ : 326.1288; found: 326.1299.



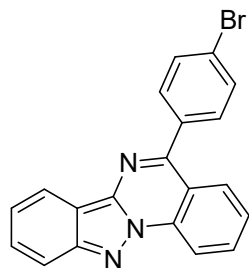
**5-(4-fluorophenyl)indazolo[2,3-*a*]quinazoline (4e):**

Yield 68% (85 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 208–210 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm); 8.92 (d,  $J = 8.4$  Hz, 1H), 8.33 (d,  $J = 8.4$  Hz, 1H), 8.15 (d,  $J = 8.0$  Hz, 1H), 8.02 (t,  $J = 8.0$  Hz, 1H), 7.95 (d,  $J = 8.8$  Hz, 1H), 7.88–7.83 (m, 2H), 7.67–7.59 (m, 2H), 7.35–7.29 (m, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm); 164.9, 162.4, 155.6, 150.0, 139.0, 136.0, 133.73, 133.69, 133.65, 132.0, 131.9, 129.0, 128.6, 126.4, 121.6, 120.6, 118.8, 116.8, 116.7, 115.9, 115.7, 115.5. HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{20}H_{13}FN_3$ : 314.1088; found: 314.1082.



**5-(4-chlorophenyl)indazolo[2,3-*a*]quinazoline (4f):**

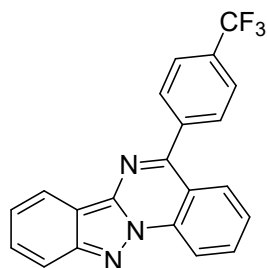
Yield 62% (82 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 214–216 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.93 (d,  $J = 8.4$  Hz, 1H), 8.33 (d,  $J = 8.4$  Hz, 1H), 8.15 (d,  $J = 8.4$  Hz, 1H), 8.05–8.00 (m, 1H), 7.96 (d,  $J = 8.8$  Hz, 1H), 7.83–7.79 (m, 2H), 7.68–7.67 (m, 1H), 7.63–7.57 (m, 3H), 7.36–7.31 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 155.3, 150.1, 139.0, 136.04, 135.98, 135.9, 133.7, 131.3, 129.0(0), 128.5, 126.5, 121.7, 120.5, 118.7, 116.79, 116.77, 115.5; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{20}H_{13}ClN_3$ : 330.0793; found: 330.0795.



**5-(4-bromophenyl)indazolo[2,3-*a*]quinazoline (4g):**

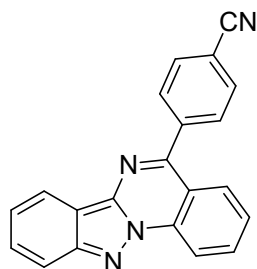
Yield 65% (97 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 215–218 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.91 (d,  $J = 8.4$  Hz, 1H), 8.32 (d,  $J = 8.4$  Hz, 1H), 8.12 (d,  $J = 8.0$  Hz, 1H), 8.03–7.98 (m, 1H), 7.94 (d,  $J = 8.8$  Hz, 1H), 7.77–7.71 (m, 4H), 7.66–7.59 (m, 2H), 7.35–7.30 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 155.3, 150.0, 139.0, 136.5, 135.9,

133.7, 131.9, 131.6, 129.0, 128.4, 126.5, 124.2, 121.7, 120.5, 118.6, 116.8, 116.7, 115.5; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{20}H_{13}BrN_3$ : 374.0287; found: 374.0285.



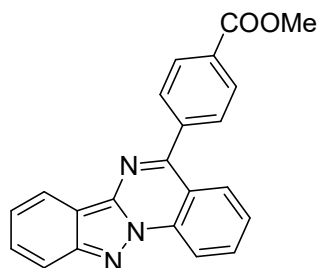
**5-(4-(trifluoromethyl)phenyl)indazolo[2,3-*a*]quinazoline (4h):**

Yield 60% (87 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 195–197 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.94 (d,  $J = 8.4$  Hz, 1H), 8.33 (d,  $J = 8.4$  Hz, 1H), 8.11 (d,  $J = 8.4$  Hz, 1H), 8.06–8.01 (m, 1H), 7.97 (t,  $J = 7.6$  Hz, 3H), 7.89 (d,  $J = 8.0$  Hz, 2H), 7.68–7.60 (m, 2H), 7.37–7.32 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 154.8, 150.1, 141.11, 141.09, 138.9, 135.9, 133.8, 131.7, 131.3, 130.4, 129.1, 128.3, 126.6, 125.7(7), 125.7(7), 125.6, 125.3, 122.6, 121.9, 120.5, 118.6, 116.9, 116.8, 115.6; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{21}H_{13}F_3N_3$ : 364.1056; found: 364.1060.



**4-(indazolo[2,3-*a*]quinazolin-5-yl)benzonitrile (4i):**

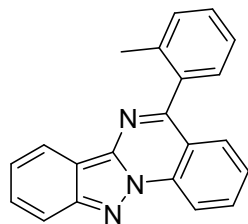
Yield 58% (74 mg; petroleum ether/EtOAc = 10:1); yellow solid; mp 181–184 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.96 (d,  $J = 8.0$  Hz, 1H), 8.33 (d,  $J = 8.4$  Hz, 1H), 8.09 (d,  $J = 8.8$  Hz, 1H), 8.08–8.03 (m, 1H), 7.99 (dd,  $J = 11.2, 4.8$  Hz, 3H), 7.94–7.91 (m, 2H), 7.71–7.62 (m, 2H), 7.39–7.35 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 154.0, 150.1, 142.0, 138.9, 136.0, 134.0, 132.4, 130.8, 129.2, 128.0, 126.7, 122.1, 120.4, 118.4, 118.3, 117.0, 115.7, 113.3; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{21}H_{13}N_4$ : 321.1135; found: 321.1130.



**methyl 4-(indazolo[2,3-*a*]quinazolin-5-yl)benzoate (4j):**

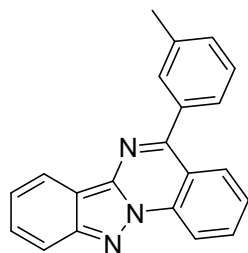
Yield 58% (82 mg; petroleum ether/EtOAc = 20:1); yellow solid; mp 212–214 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.96 (d,  $J = 8.4$  Hz, 1H), 8.36 (d,  $J = 8.4$  Hz, 1H), 8.32–8.28 (m, 2H), 8.15 (dd,  $J = 8.4, 0.8$  Hz, 1H), 8.07–8.02 (m, 1H), 7.98 (d,  $J = 8.4$  Hz, 1H), 7.96–7.93 (m, 2H), 7.70–7.62 (m, 2H), 7.38–7.33 (m, 1H), 4.01 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 166.7, 155.4, 150.1, 141.9, 139.0, 136.0, 133.8, 131.0, 130.1, 129.9, 129.1, 128.5,

126.6, 121.8, 120.6, 118.7, 116.9, 116.8, 115.7, 52.4; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{22}H_{16}N_3O_2$ : 354.1237; found: 354.1241.



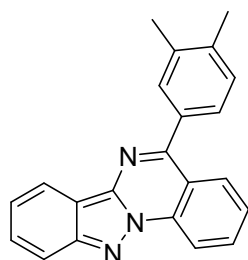
**5-(o-tolyl)indazolo[2,3-a]quinazoline (4k):**

Yield 40% (49 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 183–186 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.92 (d,  $J = 8.0$  Hz, 1H), 8.35 (d,  $J = 8.0$  Hz, 1H), 8.05–7.99 (m, 1H), 7.98–7.94 (m, 1H), 7.76–7.71 (m, 1H), 7.64–7.57 (m, 2H), 7.50–7.44 (m, 2H), 7.43–7.38 (m, 2H), 7.35–7.30 (m, 1H), 2.22 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 157.7, 150.0, 139.1, 136.9, 136.7, 135.7, 133.7, 130.7, 129.6, 129.3, 128.9, 128.8, 126.5, 125.9, 121.6, 120.6, 119.8, 116.7, 116.5, 115.4, 20.0; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{21}H_{16}N_3$ : 310.1339; found: 310.1341.



**5-(m-tolyl)indazolo[2,3-a]quinazoline (4l):**

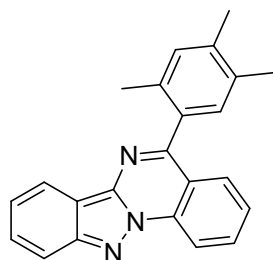
Yield 64% (78 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 180–182 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.90 (d,  $J = 8.4$  Hz, 1H), 8.35 (d,  $J = 8.4$  Hz, 1H), 8.18 (dd,  $J = 8.4, 0.8$  Hz, 1H), 8.02–7.96 (m, 1H), 7.94 (d,  $J = 8.8$  Hz, 1H), 7.66 (s, 1H), 7.64–7.58 (m, 3H), 7.49 (t,  $J = 7.6$  Hz, 1H), 7.39 (d,  $J = 7.6$  Hz, 1H), 7.34–7.28 (m, 1H), 2.51 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 157.1, 150.0, 139.1, 138.6, 137.5, 135.9, 133.5, 130.5, 130.3, 129.1, 128.9, 128.4, 127.1, 126.3, 121.4, 120.7, 119.0, 116.7, 116.5, 115.5, 21.5; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{21}H_{16}N_3$ : 310.1339; found: 310.1343.



**5-(3,4-dimethylphenyl)indazolo[2,3-a]quinazoline (4m):**

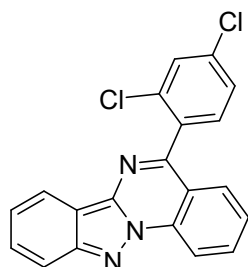
Yield 63% (81 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 202–205 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.91 (d,  $J = 8.4$  Hz, 1H), 8.36 (d,  $J = 8.4$  Hz, 1H), 8.24 (d,  $J = 8.4$  Hz, 1H), 8.03–7.98 (m, 1H), 7.95 (d,  $J = 8.8$  Hz, 1H), 7.67–7.59 (m, 3H), 7.59–7.54 (m, 1H), 7.37 (d,  $J = 7.6$  Hz, 1H), 7.33–7.29 (m, 1H), 2.42 (s, 3H), 2.41 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 157.2, 150.0, 139.2, 138.4, 137.2, 136.0, 135.2, 133.4, 131.0, 129.8, 129.2,

128.9, 127.5, 126.2, 121.3, 120.8, 119.1, 116.7, 116.6, 115.5, 19.9, 19.8; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{22}H_{18}N_3$ : 324.1495; found: 324.1502.



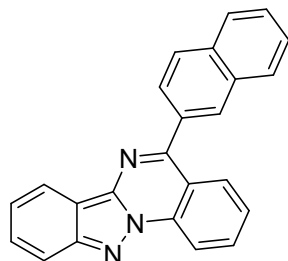
**5-(2,4,5-trimethylphenyl)indazolo[2,3-*a*]quinazoline (4n):**

Yield 58% (78 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 183–185°C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.90 (d,  $J = 8.0$  Hz, 1H), 8.35 (d,  $J = 8.4$  Hz, 1H), 8.02–7.94 (m, 2H), 7.78 (dd,  $J = 8.4, 0.8$  Hz, 1H), 7.63–7.56 (m, 2H), 7.34–7.29 (m, 1H), 7.23 (s, 1H), 7.18 (s, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 2.14 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 158.2, 150.0, 139.2, 137.8, 135.6, 134.3, 134.1, 133.8, 133.6, 131.9, 130.6, 129.1, 128.9, 126.4, 121.4, 120.7, 119.9, 116.6, 116.4, 115.4, 19.6, 19.4, 19.3; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{23}H_{20}N_3$ : 338.1652; found: 338.1656.



**5-(2,4-dichlorophenyl)indazolo[2,3-*a*]quinazoline (4o):**

Yield 45% (66 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 222–224 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.92 (d,  $J = 8.4$  Hz, 1H), 8.33 (d,  $J = 8.4$  Hz, 1H), 8.05–8.00 (m, 1H), 7.98 (d,  $J = 8.8$  Hz, 1H), 7.72–7.68 (m, 1H), 7.66–7.60 (m, 3H), 7.56 (d,  $J = 8.4$  Hz, 1H), 7.53–7.48 (m, 1H), 7.38–7.33 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm): 153.7, 150.0, 138.9, 136.1, 135.6, 135.0, 134.4, 133.9, 132.2, 129.9, 129.1, 128.3, 127.6, 126.6, 122.0, 120.5, 119.2, 116.9, 116.6, 115.6; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{20}H_{12}Cl_2N_3$ : 364.0403; found: 364.0399.

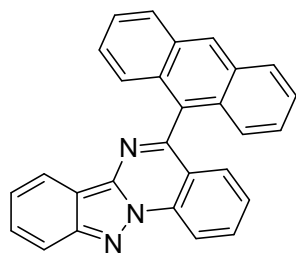


**5-(naphthalen-2-yl)indazolo[2,3-*a*]quinazoline (4p):**

Yield 63% (87 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 197–199 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.95 (d,  $J = 8.0$  Hz, 1H), 8.38 (d,  $J = 8.4$  Hz, 1H), 8.33 (s, 1H), 8.26 (d,  $J = 8.0$  Hz, 1H), 8.08 (d,  $J = 8.4$  Hz, 1H), 8.05–7.96 (m, 5H), 7.68–7.59 (m, 4H), 7.36–7.31 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 156.7, 150.1, 139.2, 136.0, 135.0,

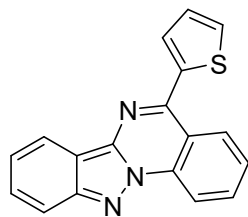


133.7, 133.6, 133.0, 129.9, 129.1, 129.0, 128.6, 128.5, 127.8, 127.2, 127.1, 126.7, 126.4, 121.5, 120.7, 119.1, 116.7(9), 115.6; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{24}H_{16}N_3$ : 346.1339; found: 346.1340.



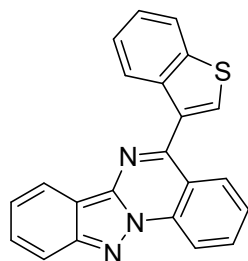
**5-(anthracen-9-yl)indazolo[2,3-*a*]quinazoline (4q):**

Yield 63% (100 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 191–193 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 9.02 (d,  $J = 8.4$  Hz, 1H), 8.71 (s, 1H), 8.35 (d,  $J = 8.4$  Hz, 1H), 8.15 (d,  $J = 8.4$  Hz, 2H), 8.05 (d,  $J = 8.4$  Hz, 1H), 8.03–7.98 (m, 1H), 7.69–7.64 (m, 1H), 7.53–7.45 (m, 4H), 7.42–7.37 (m, 1H), 7.36–7.28 (m, 4H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 156.4, 150.1, 139.6, 135.6, 134.1, 131.3, 130.7, 130.5, 129.1, 129.0, 128.8, 128.7, 126.8, 126.6, 125.7, 125.5, 121.9, 121.3, 120.7, 116.8, 116.5, 115.5; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{28}H_{18}N_3$ : 396.1495; found: 396.1493.



**5-(thiophen-2-yl)indazolo[2,3-*a*]quinazoline (4r):**

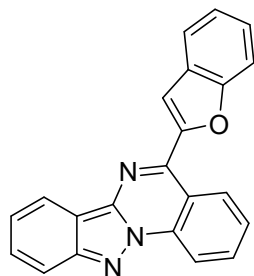
Yield 59% (71 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 151–153 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.91 (dd,  $J = 8.8, 0.4$  Hz, 1H), 8.61 (dd,  $J = 8.4, 0.8$  Hz, 1H), 8.34 (d,  $J = 8.0$  Hz, 1H), 8.05–8.00 (m, 1H), 7.93 (d,  $J = 8.8$  Hz, 1H), 7.77 (dd,  $J = 3.6, 0.8$  Hz, 1H), 7.73–7.69 (m, 1H), 7.65 (dd,  $J = 5.2, 1.2$  Hz, 1H), 7.63–7.59 (m, 1H), 7.35–7.31 (m, 1H), 7.28 (dd,  $J = 5.2, 3.6$  Hz, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 150.1, 149.4, 140.9, 138.9, 136.0, 133.6, 130.0, 129.3, 129.0, 128.2, 127.9, 126.7, 121.6, 120.8, 118.3, 116.8, 116.7, 115.5; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{18}H_{12}N_3S$ : 302.0746; found: 302.0752.



**5-(benzo[*b*]thiophen-3-yl)indazolo[2,3-*a*]quinazoline (4s):**

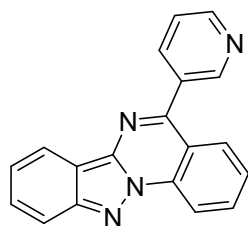
Yield 58% (82 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 206–208 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.95 (d,  $J = 8.4$  Hz, 1H), 8.35 (d,  $J = 8.0$  Hz, 1H), 8.18 (d,  $J = 8.4$  Hz, 1H), 8.05–7.96 (m, 4H), 7.92 (s, 1H), 7.65–7.59 (m, 2H), 7.49–7.40 (m, 2H), 7.36–7.32

(m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 151.6, 150.1, 140.3, 139.1, 138.4, 136.0, 133.8, 133.1, 129.3, 129.0, 128.6, 126.5, 125.1, 124.9, 123.7, 122.7, 121.7, 120.6, 119.7, 116.8, 116.6, 115.5; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{14}\text{N}_3\text{S}$ : 352.0903; found: 352.0900.



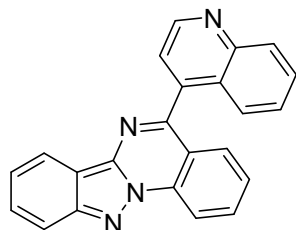
**5-(3a,7a-dihydrobenzofuran-2-yl)indazolo[2,3-a]quinazoline (4t):**

Yield 58% (77 mg; petroleum ether/EtOAc = 50:1); brown solid; mp 205–207 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.13 (d,  $J = 8.0$  Hz, 1H), 8.91 (d,  $J = 8.0$  Hz, 1H), 8.38 (d,  $J = 8.0$  Hz, 1H), 8.06–8.00 (m, 1H), 7.95 (d,  $J = 8.8$  Hz, 1H), 7.83 (s, 1H), 7.80–7.74 (m, 2H), 7.71 (d,  $J = 8.4$  Hz, 1H), 7.65–7.60 (m, 1H), 7.48–7.42 (m, 1H), 7.39–7.33 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 155.8, 154.4, 150.2, 144.2, 138.9, 135.9, 133.6, 129.1, 128.3, 128.0, 126.9, 126.1, 123.7, 122.1, 121.8, 120.7, 117.9, 116.8, 116.6, 115.7, 111.8, 110.5; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{14}\text{N}_3\text{O}$ : 336.1131; found: 336.1133.



**5-(pyridin-3-yl)indazolo[2,3-a]quinazoline (4u):**

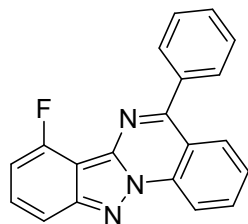
Yield 53% (63 mg; petroleum ether/EtOAc = 3:1); yellow solid; mp 191–193 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.12 (d,  $J = 2.0$  Hz, 1H), 8.96 (d,  $J = 8.4$  Hz, 1H), 8.84 (dd,  $J = 4.8, 1.6$  Hz, 1H), 8.35 (d,  $J = 8.0$  Hz, 1H), 8.22 (dt,  $J = 8.0, 2.0$  Hz, 1H), 8.15 (dd,  $J = 8.4, 0.8$  Hz, 1H), 8.09–8.04 (m, 1H), 7.98 (d,  $J = 8.8$  Hz, 1H), 7.72–7.67 (m, 1H), 7.67–7.62 (m, 1H), 7.59 (dd,  $J = 8.0, 4.8$  Hz, 1H), 7.39–7.34 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 153.3, 150.6, 150.5, 150.1, 139.1, 137.4, 136.0, 133.9, 133.6, 129.1, 128.1, 126.7, 123.6, 122.0, 120.5, 118.7, 116.89, 116.89, 115.6; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{13}\text{N}_4$ : 297.1135; found: 297.1139.



**5-(quinolin-4-yl)indazolo[2,3-a]quinazoline (4v):**

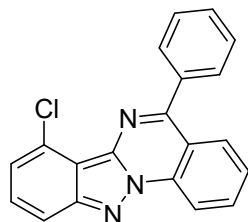
Yield 50% (70 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 230–233 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.08 (d,  $J = 4.0$  Hz, 1H), 8.90 (d,  $J = 8.4$  Hz, 1H), 8.23 (dd,  $J = 13.2, 8.4$  Hz, 2H), 7.99–7.91 (m, 2H), 7.72 (t,  $J = 7.2$  Hz, 1H), 7.60–7.54 (m, 4H), 7.47 (t,  $J =$

7.2 Hz, 1H), 7.40 (t,  $J = 7.2$  Hz, 1H), 7.30–7.26 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 153.5, 150.1, 149.9, 148.7, 143.2, 138.9, 135.6, 134.2, 130.1, 130.0, 129.2, 128.3, 127.5, 126.8, 126.7, 125.6, 122.2, 122.1, 120.4, 119.6, 116.9, 116.7, 115.6; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{15}\text{N}_4$ : 347.1291; found: 347.1289.



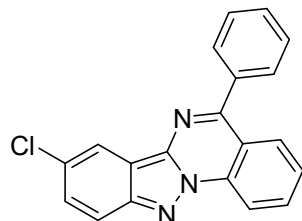
**7-fluoro-5-phenylindazolo[2,3-*a*]quinazoline (4w):**

Yield 65% (81 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 211–213 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.91 (d,  $J = 8.4$  Hz, 1H), 8.24 (dd,  $J = 8.0, 0.8$  Hz, 1H), 8.06–8.0 (m, 1H), 7.89–7.84 (m, 2H), 7.71 (d,  $J = 8.8$  Hz, 1H), 7.69–7.64 (m, 1H), 7.63–7.57 (m, 3H), 7.54–7.48 (m, 1H), 6.93 (dd,  $J = 10.4, 7.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 158.2, 157.9, 155.7, 151.8(8), 137.8(7), 137.4, 135.8, 133.8, 130.2, 129.7, 129.1(5), 128.6, 126.7, 118.8, 116.8, 112.74, 112.70, 106.2, 106.0, 105.3, 105.1; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{13}\text{FN}_3$ : 314.1088; found: 314.1095.



**7-chloro-5-phenylindazolo[2,3-*a*]quinazoline (4x):**

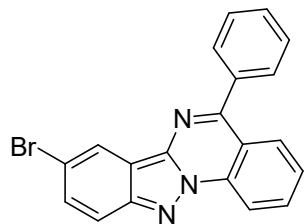
Yield 60% (79 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 210–212 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.92 (d,  $J = 8.4$  Hz, 1H), 8.30 (dd,  $J = 8.4, 0.8$  Hz, 1H), 8.06–8.01 (m, 1H), 7.95–7.91 (m, 2H), 7.85 (d,  $J = 8.8$  Hz, 1H), 7.71–7.67 (m, 1H), 7.65–7.58 (m, 3H), 7.52–7.48 (m, 1H), 7.30 (d,  $J = 7.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 157.2, 150.8, 138.8, 137.6, 135.9, 133.6, 130.3, 129.8, 129.0, 128.9, 128.6, 127.4, 126.8, 121.8, 118.8, 116.8, 115.4, 113.3; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{13}\text{ClN}_3$ : 330.0793; found: 330.0788.



**8-chloro-5-phenylindazolo[2,3-*a*]quinazoline (4y):**

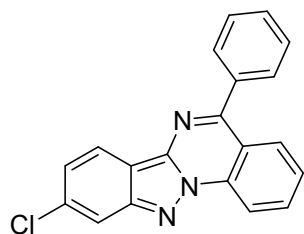
Yield 58% (77 mg; petroleum ether/EtOAc = 20:1); yellow solid; mp 216–219 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.86 (d,  $J = 8.4$  Hz, 1H), 8.30 (d,  $J = 1.6$  Hz, 1H), 8.19 (dd,  $J = 8.4, 0.8$  Hz, 1H), 8.03–7.98 (m, 1H), 7.87 (s, 1H), 7.84–7.81 (m, 2H), 7.67–7.60 (m, 4H), 7.50 (dd,  $J = 9.2, 2.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 157.3, 148.2, 138.6, 137.4,

135.9, 133.7, 130.1, 129.9, 129.7, 129.0, 128.7, 126.9, 126.7, 119.6, 119.0, 118.2, 116.6, 115.9; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{20}H_{13}ClN_3$ : 330.0793; found: 330.0800.



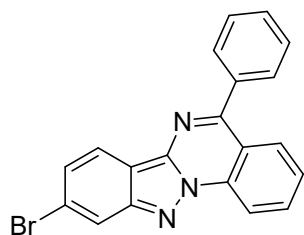
**8-bromo-5-phenylindazolo[2,3-*a*]quinazoline (4z):**

Yield 63% (94 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 225–227 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.77 (d,  $J = 8.4$  Hz, 1H), 8.39 (d,  $J = 1.6$  Hz, 1H), 8.10 (d,  $J = 8.0$  Hz, 1H), 7.94–7.89 (m, 1H), 7.77–7.73 (m, 2H), 7.71 (d,  $J = 9.2$  Hz, 1H), 7.58–7.51 (m, 5H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 157.4, 148.3, 138.3, 137.3, 135.8, 133.8, 132.3, 129.9, 129.7, 129.0, 128.7, 126.7, 123.0, 119.0, 118.4, 116.63, 116.60, 114.5; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{20}H_{13}BrN_3$ : 374.0287; found: 374.0289.



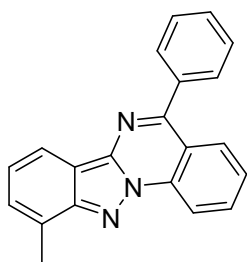
**9-chloro-5-phenylindazolo[2,3-*a*]quinazoline (4aa):**

Yield 64% (84 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 199–202 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.88 (d,  $J = 8.4$  Hz, 1H), 8.25 (d,  $J = 8.8$  Hz, 1H), 8.22–8.17 (m, 1H), 8.05–8.00 (m, 1H), 7.91 (d,  $J = 1.6$  Hz, 1H), 7.86–7.81 (m, 2H), 7.68–7.59 (m, 4H), 7.26–7.23 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 157.8, 150.2, 139.2, 137.4, 135.9, 134.8, 133.9, 129.9, 129.8, 129.1, 128.7, 126.6, 122.8, 121.9, 118.9, 116.7, 115.8, 113.9; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{20}H_{13}ClN_3$ : 330.0793; found: 330.0798.



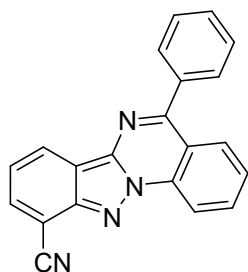
**9-bromo-5-phenylindazolo[2,3-*a*]quinazoline (4ab):**

Yield 60% (90 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 195–197 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.84 (dd,  $J = 8.4, 0.4$  Hz, 1H), 8.19–8.15 (m, 2H), 8.10–8.05 (m, 1H), 8.02–7.97 (m, 1H), 7.85–7.81 (m, 2H), 7.66–7.59 (m, 4H), 7.35 (dd,  $J = 8.8, 1.6$  Hz, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 157.7, 150.5, 139.2, 137.3, 135.8, 133.8, 129.9, 129.8, 129.0, 128.7, 126.6, 125.0, 123.1, 122.0, 119.2, 118.9, 116.6, 114.1; HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{20}H_{13}BrN_3$ : 374.0287; found: 374.0288.



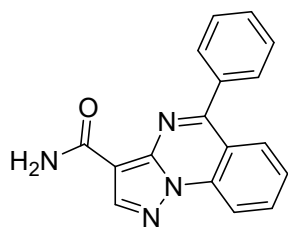
**10-methyl-5-phenylindazolo[2,3-*a*]quinazoline (4ac):**

Yield 59% (91 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 204–206 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.95 (d, *J* = 8.4 Hz, 1H), 8.19–8.13 (m, 2H), 8.00–7.94 (m, 1H), 7.87–7.82 (m, 2H), 7.63–7.56 (m, 4H), 7.37–7.34 (m, 1H), 7.24–7.19 (m, 1H), 2.83 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 156.4, 150.1, 139.3, 137.7, 136.1, 133.3, 130.0, 129.5, 128.8, 128.6, 127.9, 126.8, 126.1, 121.7, 118.8, 118.0, 116.8, 115.2, 16.9; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>N<sub>3</sub>: 310.1339; found: 310.1340.



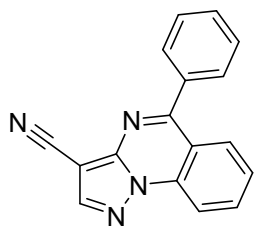
**5-phenylindazolo[2,3-*a*]quinazoline-10-carbonitrile (4ad):**

Yield 57% (73 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 234–237 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 9.05 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.08 (t, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.90–7.82 (m, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 5.6 Hz, 3H), 7.34 (t, *J* = 7.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 158.8, 148.4, 139.7, 137.1, 135.8, 135.4, 134.3, 130.0(7), 129.0, 128.8, 127.3, 126.5, 120.3, 119.3, 117.3, 117.1, 116.0, 100.0; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>13</sub>N<sub>4</sub>: 321.1135; found: 321.1137.



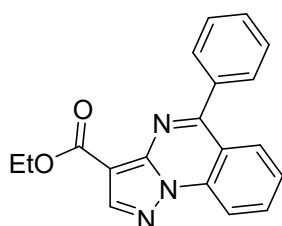
**5-phenylpyrazolo[1,5-*a*]quinazoline-3-carboxamide (4ae):**

Yield 55% (63 mg; petroleum ether/EtOAc = 3:1); brown solid; mp 162–164 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.66 (s, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.04 (s, 1H), 8.03–7.98 (m, 1H), 7.80–7.76 (m, 2H), 7.64–7.57 (m, 4H), 5.76 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 164.2, 162.2, 144.7, 142.6, 136.9, 136.7, 135.0, 130.3, 129.7, 129.6, 128.7, 126.0, 117.4, 115.6, 107.7; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>13</sub>N<sub>4</sub>O: 289.1084; found: 289.1083.



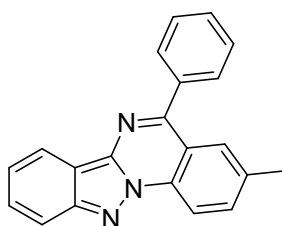
**5-phenylpyrazolo[1,5-*a*]quinazoline-3-carbonitrile (4af):**

Yield 53% (57 mg; petroleum ether/EtOAc = 10:1); white solid; mp 225–227 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.60 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.36 (s, 1H), 8.17 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.04–7.99 (m, 1H), 7.82–7.77 (m, 2H), 7.66–7.58 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 163.7, 146.8, 145.3, 136.4(2), 135.0, 130.5, 130.0, 129.6, 128.7, 126.5, 117.9, 115.6, 113.1, 85.6; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>11</sub>N<sub>4</sub>: 271.0978; found: 271.0982.



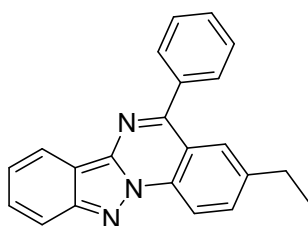
**ethyl 5-phenylpyrazolo[1,5-*a*]quinazoline-3-carboxylate (4ag):**

Yield 59% (75 mg; petroleum ether/EtOAc = 30:1); white solid; mp 177–179 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.60 (d, *J* = 8.4 Hz, 1H), 8.54 (s, 1H), 8.14 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.98–7.92 (m, 1H), 7.86–7.81 (m, 2H), 7.59–7.53 (m, 4H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 163.0, 162.7, 145.3, 144.3, 137.2, 136.5, 134.4, 130.2, 130.0, 129.3, 128.5, 125.8, 117.5, 115.6, 105.5, 60.3, 14.4; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub>: 318.1237; found: 318.1235.



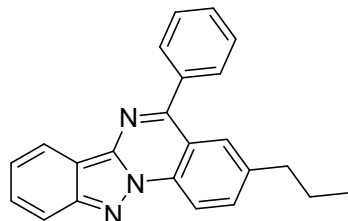
**3-methyl-5-phenylindazolo[2,3-*a*]quinazoline (4ah):**

Yield 68% (84 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 218–220 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.80 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.86–7.80 (m, 3H), 7.65–7.57 (m, 4H), 7.34–7.28 (m, 1H), 2.54 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 156.5, 149.9, 138.8, 137.8, 136.5, 135.2, 134.2, 129.9, 129.5, 128.7(7), 128.1, 121.3, 120.6, 119.0, 116.6, 116.5, 115.5, 21.6; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>N<sub>3</sub>: 310.1339; found: 310.1340.

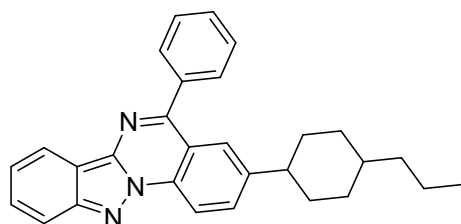


**3-ethyl-5-phenylindazolo[2,3-*a*]quinazoline (4ai):**

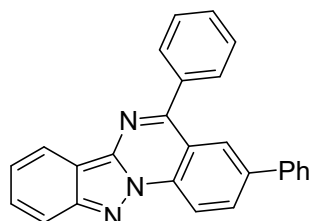
Yield 65% (84 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 190–193 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.84 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.98–7.92 (m, 2H), 7.90–7.83 (m, 3H), 7.66–7.57 (m, 4H), 7.34–7.29 (m, 1H), 2.84 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 156.6, 149.9, 142.8, 138.9, 137.8, 134.4, 134.1, 129.9, 129.5, 128.7(7), 127.1, 121.3, 120.6, 119.0, 116.6, 115.5, 28.9, 15.6; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>18</sub>N<sub>3</sub>: 324.1495; found: 324.1493.

**5-phenyl-3-propylindazolo[2,3-*a*]quinazoline (4aj):**

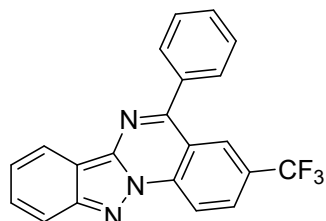
Yield 62% (84 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 193–195 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.84 (d, *J* = 8.4 Hz, 1H), 8.37–8.32 (m, 1H), 7.97–7.91 (m, 2H), 7.88–7.82 (m, 3H), 7.66–7.58 (m, 4H), 7.34–7.29 (m, 1H), 2.80–2.74 (m, 2H), 1.77–1.67 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 156.6, 149.9, 141.3, 138.9, 137.8, 134.6, 134.4, 129.9, 129.5, 128.74, 128.69, 127.7, 121.3, 120.6, 119.0, 116.6, 116.5, 115.5, 38.0, 24.6, 13.7; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>20</sub>N<sub>3</sub>: 338.1652; found: 338.1659.

**5-phenyl-3-(4-propylcyclohexyl)indazolo[2,3-*a*]quinazoline (4ak):**

Yield 60% (101 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 206–208 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.84 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 1.2 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.91 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.88–7.83 (m, 2H), 7.67–7.58 (m, 4H), 7.33–7.28 (m, 1H), 2.70–2.61 (m, 1H), 1.98–1.86 (m, 4H), 1.56–1.45 (m, 2H), 1.38–1.30 (m, 3H), 1.24–1.18 (m, 2H), 1.12–1.02 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 156.7, 149.9, 146.5, 138.9, 137.9, 134.5, 133.1, 130.0, 129.5, 128.7(7), 126.2, 121.3, 120.6, 119.0, 116.6, 116.5, 115.5, 44.6, 39.6, 36.8, 34.3, 33.3, 20.0, 14.4; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>29</sub>H<sub>30</sub>N<sub>3</sub>: 420.2434; found: 420.2429.

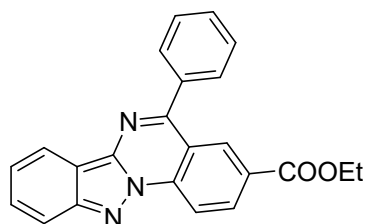
**3,5-diphenylindazolo[2,3-*a*]quinazoline (4al):**

Yield 57% (85 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 216–218 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.99 (d, *J* = 8.8 Hz, 1H), 8.39–8.34 (m, 2H), 8.26 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.91–7.87 (m, 2H), 7.67–7.59 (m, 6H), 7.52–7.47 (m, 2H), 7.44–7.40 (m, 1H), 7.36–7.31 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 156.9, 150.2, 139.5, 139.1, 137.6, 135.2, 132.8, 130.0, 129.7, 129.1, 129.0, 128.8, 128.1, 127.4, 126.8, 121.6, 120.7, 119.3, 117.2, 116.7, 115.6; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>18</sub>N<sub>3</sub>: 372.1495; found: 372.1488.



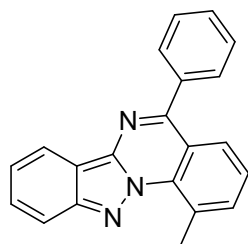
**5-phenyl-3-(trifluoromethyl)indazolo[2,3-*a*]quinazoline (4am):**

Yield 53% (77 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 237–239 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 9.05 (d, *J* = 8.8 Hz, 1H), 8.49 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.22 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.87–7.83 (m, 2H), 7.69–7.63 (m, 4H), 7.39–7.34 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 156.3, 150.6, 139.6, 137.5, 136.8, 130.1, 129.9, 129.6(2), 129.6(0), 129.6(6), 129.0, 128.5, 128.2, 126.7, 126.62, 126.57, 126.5, 122.3, 120.8, 118.3, 117.9, 117.0, 115.6; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>13</sub>F<sub>3</sub>N<sub>3</sub>: 364.1056; found: 364.1060.



**ethyl 5-phenylindazolo[2,3-*a*]quinazoline-3-carboxylate (4an):**

Yield 55% (81 mg; petroleum ether/EtOAc = 20:1); yellow solid; mp 236–238 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.95 (d, *J* = 8.8 Hz, 1H), 8.93 (d, *J* = 1.6 Hz, 1H), 8.62 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.90–7.86 (m, 2H), 7.68–7.60 (m, 4H), 7.36–7.32 (m, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 165.3, 157.0, 150.6, 139.7, 138.1, 137.1, 133.6, 131.4, 130.0, 129.9, 129.5, 128.9, 128.3, 122.0, 120.8, 118.3, 116.9(8), 115.6, 61.7, 14.3; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>18</sub>N<sub>3</sub>O<sub>2</sub>: 368.1394; found: 368.1392.

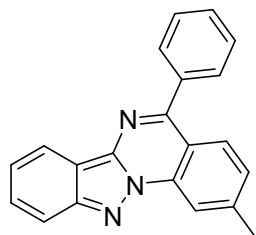


**1-methyl-5-phenylindazolo[2,3-*a*]quinazoline (4ao):**

Yield 49% (61 mg; petroleum ether/EtOAc = 100:1); yellow solid; mp 202–204 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.34 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.8

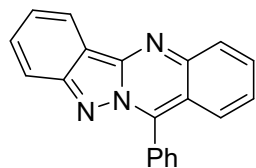


Hz, 1H), 7.81–7.75 (m, 3H), 7.62–7.54 (m, 4H), 7.48 (t,  $J = 8.0$  Hz, 1H), 7.30 (dd,  $J = 8.0, 7.2$  Hz, 1H), 3.42 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 157.3, 149.3, 140.1, 138.3, 136.4, 135.5, 130.1, 129.8, 129.3, 128.6, 128.3, 126.9, 125.6, 121.3, 120.5(5), 116.9, 114.4, 24.6; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{16}\text{N}_3$ : 310.1339; found: 310.1343.



**2-methyl-5-phenylindazolo[2,3-*a*]quinazoline (4ap):**

Yield 54% (67 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 203–206 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.74 (s, 1H), 8.35 (d,  $J = 8.0$  Hz, 1H), 8.07 (d,  $J = 8.4$  Hz, 1H), 7.94 (d,  $J = 8.8$  Hz, 1H), 7.86–7.82 (m, 2H), 7.64–7.58 (m, 4H), 7.45 (dd,  $J = 8.4, 0.8$  Hz, 1H), 7.33–7.29 (m, 1H), 2.70 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 156.8, 150.0, 145.3, 139.3, 137.8, 136.0, 129.9, 129.5, 128.9, 128.8, 128.7, 128.1, 121.3, 120.7, 117.0, 116.6, 116.2, 115.4, 22.3; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{16}\text{N}_3$ : 310.1339; found: 310.1344.

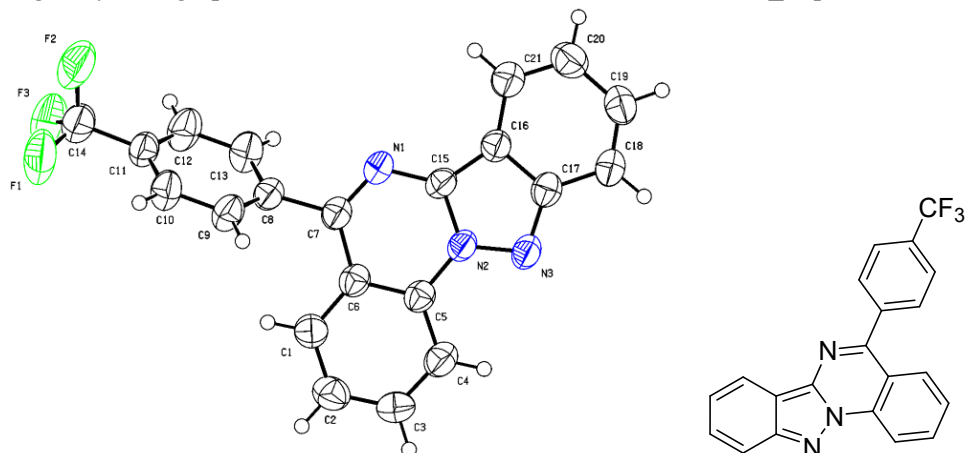


**7-phenylindazolo[3,2-*b*]quinazoline (9):**

Yield 25% (30 mg; petroleum ether/EtOAc = 30:1); red solid; mp 257–259 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.57 (d,  $J = 8.0$  Hz, 1H), 8.27 (d,  $J = 8.8$  Hz, 1H), 7.87–7.78 (m, 5H), 7.76–7.69 (m, 4H), 7.76–7.69 (m, 4H), 7.53–7.47 (m, 1H), 7.37–7.33 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 153.6, 145.2, 143.9, 141.8, 131.1, 130.7, 130.6(X2), 129.6, 129.0, 128.6, 126.5, 125.6, 121.8, 119.7, 117.9, 115.6, 112.4; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{14}\text{N}_3$ : 296.1182; found: 296.1187.

## 5. Crystallographic data and molecular structure of 4h

The crystal of **4h** for X-ray diffraction study has been obtained through the dissolving of compound in  $\text{CHCl}_3$ , followed by slow evaporation of the solvent at room temperature. The crystal was kept at 296(2) during data collection. CCDC 2296454 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Figure S1.** X-ray crystal structure of **4h**; the ellipsoids depicted at the 50% probability level.

Empirical formula	$\text{C}_{21}\text{H}_{12}\text{F}_3\text{N}_3$		Absorption coefficient	$0.112 \text{ mm}^{-1}$
Formula weight	363.34		F(000)	372.0
Temperature	296(2) K		Crystal size	$0.180 \times 0.160 \times 0.150 \text{ mm}^3$
Crystal system	triclinic		Theta range for data collection	4.248 to 54.976°
Space group	P-1		Reflections collected	5161
Unit cell dimensions	a = 9.105(4) Å	$\alpha =$ 97.386(6)°	Independent reflections	3685 [R(int) = 0.0247]
	b = 9.483(4) Å	$\beta =$ 107.310(6)°	Data / restraints / parameters	3685/0/244
	c = 10.167(4) Å	$\gamma =$ 93.704(6)°	Goodness-of-fit on $F^2$	1.080
Volume	$826.2(6) \text{ \AA}^3$		Final R indices [I > 2sigma(I)]	$R_1 = 0.0612$ , $wR_2 = 0.1736$
Z	2		R indices (all data)	$R_1 = 0.1035$ , $wR_2 = 0.2055$
Density (calculated)	$1.461 \text{ Mg/m}^3$		Largest diff. peak and hole	0.23/-0.21 $\text{e. \AA}^{-3}$

## 6. NMR spectra

