Supporting Information

Highly Efficient Vinylaromatics Generation via Iron-Catalyzed $sp^3$ C-H Bond Functionalization CDC Reaction: A Novel Approach to Preparing Substituted Benzo[$\alpha$]phenazines

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Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>General</td>
<td>S2</td>
</tr>
<tr>
<td>General synthesis of 2-(2-bromoaromatic)-3-methylquinoxalines (1p-1v)</td>
<td>S2–S5</td>
</tr>
<tr>
<td>Screening the different metal catalysts and oxidants</td>
<td>S5–S6</td>
</tr>
<tr>
<td>Typical experimental procedure for the synthesis of 2, 4 and 5</td>
<td>S6</td>
</tr>
<tr>
<td>Characterization of all products</td>
<td>S7–S17</td>
</tr>
<tr>
<td>Preliminary mechanistic studies</td>
<td>S17–S23</td>
</tr>
<tr>
<td>References</td>
<td>S23</td>
</tr>
<tr>
<td>$^1$H and $^{13}$C NMR spectra of all products</td>
<td>S24–S113</td>
</tr>
</tbody>
</table>
General

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without purifications. FeCl₃ (>99.99%, trace metal basis) were purchased from Sigma-Aldrich. NEt₃ and DMA applied in the Heck closure were dried, distilled and degassed prior to use according to standard methods. Starting materials 2-aryl-3-methylquinoxalines and 2-phenyl-3-ethylquinoxaline (1a–o)[1,2], 2-methyl-3-phenoxyquinoxaline (3b)[3], 2-methoxy-3-methylquinoxaline (3c)[4], methyl 3-methylquinoxaline-2-carboxylate (3d)[5], 2-methyl-3-phenylpyrazine (3e)[6], 2-aryl-3-methylquinolines (3g, 3h)[7], diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (3j)[8], were synthesized according to the literature procedures. Melting points are uncorrected. ¹H NMR and ¹³C NMR spectra were obtained on a Bruker AVANCE III 500 instrument in CDCl₃ using TMS as internal standard, operating at 500 MHz and 125 MHz, respectively. Chemical shifts (δ) are expressed in ppm and coupling constants (J) are given in Hz. GC-MS experiments were performed with an Agilent 6890N GC system equipped with a 5973N mass-selective detector. High resolution mass spectra (HRMS) of starting materials and products were obtained on a Water GCT Premier TOF MS with EI source. Electrospray ionization (ESI) mass experiments were performed on a Thermo LCQ fleet. High resolution mass spectra (HRMS) of CDC intermediate 9 was obtained on a Agilent 6210 TOF LC/MS with ESI source.

General synthesis of 2-(2-bromoaromatic)-3-methylquinoxalines (1p-1v)

O-methyl oximes I were synthesized according to the literature procedures[9]. Then, I (5.0 mmol) were combined with NBS (5.5 mmol, 1.1 equiv.), Pd(OAc)₂ (0.25 mmol, 5 mol%) and AcOH (30 mL), the mixture was heated at 100 °C for 12 h (monitored by TLC) to give II according to previous report by Sanford[10]. II underwent deprotection and α-bromination using general procedures. Finally, III were treated with o-PDA (o-phenylenediamine) as the preparation of substrates (1a–1o) to gain the desired 1p-1v.

![Figure 1. synthesis of substrates](image-url)
Characterization of some new reaction substrates

2-(2-bromophenyl)-3-methylquinoxaline (1j)

White solid; $R_f = 0.37$ (petroleum ether-EtOAc = 6:1); mp 87-88°C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.14-8.10$ (m, 2H), 7.82-7.73 (m, 3H), 7.61-7.59 (m, 1H), 7.43-7.36 (m, 2H), 2.62 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 154.7, 153.0, 141.7, 140.6, 140.0, 132.9, 130.4, 130.2, 130.1, 129.3, 128.5, 127.9, 122.4, 23.0$ ppm; MS (EI, 70eV): $m/z$ (%) = 298 (60) [M+], 219 (100); HRMS (EI) for C$_{13}$H$_{11}$N$_2$Br: calcd. 298.0016, found 298.0099.

2-(2-bromo-4-methylphenyl)-3-methylquinoxaline (1p)

White solid; $R_f = 0.38$ (petroleum ether-EtOAc = 6:1); mp 83-84°C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.13-8.10$ (m, 2H), 7.81-7.73 (m, 2H), 7.56 (s, 1H), 7.30 (s, 2H), 2.63 (s, 3H), 2.45 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 154.8, 153.2, 141.6, 140.8, 140.7, 137.1, 133.3, 130.0, 129.9, 129.3, 129.2, 128.6, 128.4, 122.1, 23.1, 21.0$ ppm; MS (EI, 70eV): $m/z$ (%) = 312 (52) [M+], 233 (100); HRMS (EI) for C$_{16}$H$_{13}$N$_2$Br: calcd. 312.0262, found 312.0282.

2-(2-bromo-4-methoxyphenyl)-3-methylquinoxaline (1q)

Pale yellow solid; $R_f = 0.21$ (petroleum ether-EtOAc = 6:1); mp 88-89°C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.13-8.10$ (m, 2H), 7.80-7.73 (m, 2H), 7.33 (d, $J = 8.5$ Hz, 1H), 7.27 (d, $J = 2.5$ Hz, 1H), 7.03 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.5$ Hz, 1H), 3.89 (s, 3H), 2.63 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 160.6, 154.6, 153.5, 141.6, 140.7, 132.3, 130.8, 130.0, 129.3, 129.2, 128.4, 122.8, 118.1, 114.0, 55.7, 23.2$ ppm; MS (EI, 70eV): $m/z$ (%) = 328 (100) [M+], 249 (83); HRMS (EI) for C$_{16}$H$_{13}$N$_2$OBr: calcd. 328.0211, found 328.0211.

2-(2-bromo-4-fluorophenyl)-3-methylquinoxaline (1r)

White solid; $R_f = 0.34$ (petroleum ether-EtOAc = 6:1); mp 103-104°C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.13-8.10$ (m, 2H), 7.83-7.75 (m, 2H), 7.49 (dd, $J_1 = 8.3$ Hz, $J_2 = 2.3$ Hz, 1H), 7.42 (dd, $J_1 = 8.5$ Hz, $J_2 = 5.5$ Hz, 1H), 7.23 (td, $J_1 = 8.3$ Hz, $J_2 =
2.5 Hz, 1H), 2.62 (s, 3H) ppm; 13C NMR (125 MHz, CDCl3): δ = 162.6 (d, J = 251.5 Hz), 153.8, 152.9, 141.7, 140.6, 136.2, 131.3 (d, J = 8.5 Hz), 130.3, 129.4, 129.2, 128.4, 122.8 (d, J = 9.9 Hz), 120.3 (d, J = 24.4 Hz), 115.3 (d, J = 21.1 Hz), 23.1 ppm; MS (EI, 70eV): m/z (%) = 316 (77) [M+], 237 (100); HRMS (EI) for C15H10N3BrF: calcd. 316.0011, found 315.9993.

2-(3-bromobiphenyl-4-yl)-3-methylquinoxaline (1s)

White solid; Rf =0.32 (petroleum ether-EtOAc= 6:1); mp 134-135°C; 1H NMR (500 MHz, CDCl3): δ = 8.16-8.12 (m, 2H), 7.97 (d, J = 1.0 Hz, 1H), 7.83-7.71 (m, 3H), 7.65 (d, J = 7.5 Hz, 2H), 7.53-7.49 (m, 3H), 7.36 (t, J = 7.5 Hz, 1H), 2.69 (s, 3H) ppm; 13C NMR (125 MHz, CDCl3): δ = 154.6, 153.1, 143.8, 141.8, 140.7, 139.1, 138.7, 131.5, 130.5, 130.2, 129.3, 129.0, 128.5, 128.2, 127.2, 126.6, 122.8, 22.3 ppm; MS (EI, 70eV): m/z (%) = 348 (52) [M+], 295 (100); HRMS (EI) for C21H12N2Br: calcd. 374.0419, found 374.0438.

2-(3-bromonaphthalen-2-yl)-3-methylquinoxaline (1t)

White solid; Rf =0.36 (petroleum ether-EtOAc= 6:1); mp 144-145°C; 1H NMR (500 MHz, CDCl3): δ = 8.26 (s, 1H), 8.15 (td, J1 = 8.2 Hz, J2 = 1.0 Hz, 2H), 7.93 (s, 1H), 7.89-7.86 (m, 2H), 7.84-7.76 (m, 2H), 7.62-7.57 (m, 2H), 2.65 (s, 3H) ppm; 13C NMR (125 MHz, CDCl3): δ = 154.7, 153.3, 141.8, 140.6, 137.4, 134.4, 132.2, 131.6, 130.1, 129.6, 129.3, 139.3, 128.5, 128.1, 127.6, 127.0, 136.9, 119.4, 23.3 ppm; MS (EI, 70eV): m/z (%) = 348 (27) [M+], 269 (100); HRMS (EI) for C19H12N2Br: calcd. 348.0262, found 348.0259.

2-(2-bromo-5-chlorophenyl)-3-methylquinoxaline (1u)

White solid; Rf =0.47 (petroleum ether-EtOAc= 6:1); mp 122-123°C; 1H NMR (500 MHz, CDCl3): δ = 8.13-8.10 (m, 2H), 7.83-7.75 (m, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.43 (d, J = 2.5 Hz, 1H), 7.36 (dd, J1 = 8.5 Hz, J2 = 2.5 Hz, 1H), 2.64 (s, 3H) ppm; 13C NMR (125 MHz, CDCl3): δ = 153.3, 152.6, 141.9, 141.5, 140.5, 134.1, 134.0, 130.5, 130.4, 130.3, 129.5, 129.3, 128.5, 120.4, 23.0 ppm; MS (EI, 70eV): m/z (%) = 332 (48) [M+], 253 (100); HRMS (EI) for C17H10N2ClBr: calcd. 331.9716, found 331.9712.

2-(2-bromophenyl)-3,6,7-trimethylquinoxaline (1v)
Yellow solid; $R_f$ = 0.35 (petroleum ether-EtOAc = 6:1); mp 119-120°C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.86 (d, $J$ = 7.5 Hz, 2H), 7.26-7.10 (m, 1H), 7.48 (td, $J_1$ = 7.6 Hz, $J_2$ = 0.9 Hz, 1H), 7.41 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.7 Hz, 1H), 7.36 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.7 Hz, 1H), 2.58 (s, 3H), 2.53 (s, 3H), 2.50 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 153.7, 151.8, 140.7, 140.6, 140.3, 139.7, 139.5, 132.8, 130.2, 128.3, 127.8, 127.5, 23.0, 20.4, 20.3 ppm; MS (EI, 70eV): $m/z$ (%) = 326 (100) [M+], 247 (64); HRMS (EI) for C$_{17}$H$_{15}$N$_2$Br: calcd. 326.0419, found 326.0421.

**Screening the different iron catalysts and oxidants**

**Table 1.** Screening of iron catalysts $^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Fe]</th>
<th>T (°C)</th>
<th>Time (hr)</th>
<th>Yield (%) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCl$_3$</td>
<td>r.t.</td>
<td>24</td>
<td>0$^c$</td>
</tr>
<tr>
<td>2</td>
<td>FeCl$_3$</td>
<td>60</td>
<td>24</td>
<td>27$^c$</td>
</tr>
<tr>
<td>3</td>
<td>FeCl$_3$</td>
<td>110</td>
<td>3</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>FeCl$_3$·6H$_2$O</td>
<td>110</td>
<td>3</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>FeCl$_3$·4H$_2$O</td>
<td>110</td>
<td>3</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>FeSO$_4$·7H$_2$O</td>
<td>110</td>
<td>3</td>
<td>91</td>
</tr>
<tr>
<td>7</td>
<td>Fe Powder</td>
<td>110</td>
<td>3</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>Fe$_3$O$_4$</td>
<td>110</td>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>9</td>
<td>Fe(acac)$_3$</td>
<td>110</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td>&gt;99.99%, FeCl$_3$</td>
<td>110</td>
<td>3</td>
<td>94</td>
</tr>
<tr>
<td>11</td>
<td>—</td>
<td>110</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

$^a$Reaction condition: 1a (0.2 mmol), [Fe] (0.004 mmol), K$_2$S$_2$O$_8$ (0.4 mmol), DMA (1.5 mL), 110 °C. $^b$GC-MS yield. $^c$10 mol % FeCl$_3$ was used, DMF served as solvent.

**Table 2.** Screening of other metal catalysts $^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[M]</th>
<th>T (°C)</th>
<th>Time (hr)</th>
<th>Yield (%) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuCl$_2$·2H$_2$O</td>
<td>110</td>
<td>3</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>PdCl$_2$</td>
<td>110</td>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>AuCl$_3$</td>
<td>110</td>
<td>3</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>AlCl$_3$</td>
<td>110</td>
<td>3</td>
<td>28</td>
</tr>
</tbody>
</table>

$^a$Reaction condition: 1a (0.2 mmol), [M] (0.004 mmol), K$_2$S$_2$O$_8$ (0.4 mmol), DMA (1.5 mL), 110 °C. $^b$GC-MS yield.
Table 3. Screening of oxidants

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidants</th>
<th>Time (hr)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K2S2O8 (1.0 equiv)</td>
<td>8</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>K2S2O8 (2.0 equiv)</td>
<td>3</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>Na2S2O8 (2.0 equiv)</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>(NH4)2S2O8 (2.0 equiv)</td>
<td>3</td>
<td>52</td>
</tr>
<tr>
<td>5</td>
<td>OXONE (2.0 equiv)</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>BQ (2.0 equiv)</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>CAN (2.0 equiv)</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>O3 (balloon)</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Phl(OAc)2 (2.0 equiv)</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>i-BuOOH (2.0 equiv)</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>DDQ (2.0 equiv)</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>H2O2 (2.0 equiv)</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>Ag2O (2.0 equiv)</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>NaIO4 (2.0 equiv)</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

a Reaction condition: 1a (0.2 mmol), FeCl3·6H2O (0.004 mmol), oxidant (0.4 mmol), DMA = N,N-dimethylacetamide (1.5 ml), 110 ºC, BQ = 1,4-Benzquinone, CAN = Ammonium ceric nitrate, DDQ = 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone. b GC-MS yield.

Typical experimental procedure for the synthesis of 2, 4 and 5

1 or 3 (0.2 mmol), FeCl3·6H2O (1.1 mg, 0.004 mmol), K2S2O8 (108 mg, 0.4 mmol) and DMA (1.5 mL) were sequentially added to a 10-mL tube under air. Then the tube was sealed and stirred at 110 ºC for 3 h. Upon completion (monitored by TLC), the resulting mixture was diluted with Et2O (15 mL) and washed by brine (10 mL × 3). The organic layer was then dried over Na2SO4, filtered and evaporated in vacuo, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent to give desired products 2 or 4.

To an oven-dried 10-mL tube were added 2j, 2p-2v (0.15 mmol), Pd(PPh3)4 (7.3 mg, 0.0075 mmol) and Ag2SO4 (94 mg, 0.30 mmol) sequentially, then the tube was evacuated and backfilled with Argon. NEt3 (61 mg, 0.6 mmol) and degassed DMA (2.0 mL) were added by syringe under Argon. The tube was heated at 140 ºC with stirring for 3 hours, then the resulting mixture was diluted with Et2O (10 mL) and washed by brine (10 mL × 3). The organic layer was then dried over Na2SO4, filtered and evaporated in vacuo, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent to give desired products 5.
Characterization of all Products

2-phenyl-3-vinylquinoxaline (2a)

Orange oil; \( R_f = 0.69 \) (petroleum ether-EtOAc= 6:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.13 \) (dt, \( J = 7.5 \) Hz, \( J = 2.0 \) Hz, 2H), 7.78-7.70 (m, 4H), 7.57-7.51 (m, 3H), 7.08 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.5 \) Hz, 1H), 6.67 (dd, \( J_1 = 16.8 \) Hz, \( J_2 = 1.75 \) Hz, 1H), 5.64 (dd, \( J_1 = 10.5 \) Hz, \( J_2 = 2.0 \) Hz, 1H) ppm; \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 153.9, 148.9, 141.6, 141.4, 139.2, 135.4, 133.9, 129.7, 129.6, 129.2, 128.1, 122.3 \) ppm; MS (EI, 70eV); \( m/\epsilon \) (%) = 231 (48) [M-H]\(^+\); HRMS (EI) for C\(_{16}\)H\(_{13}\)N\(_2\): calcd. 232.1000, found 232.1005.

2-(4-methoxyphenyl)-3-vinylquinoxaline (2b)

Yellow solid; \( R_f = 0.38 \) (petroleum ether-EtOAc= 6:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.13-8.10 \) (m, 2H), 7.76-7.72 (m, 2H), 7.69 (dd, \( J = 6.5 \) Hz, \( J = 2.0 \) Hz, 2H), 7.11 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.5 \) Hz, 1H), 7.07 (dd, \( J_1 = 6.5 \) Hz, \( J_2 = 2.0 \) Hz, 2H), 6.65 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 5.65 (dd, \( J_1 = 10.5 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 3.91 (s, 3H) ppm; \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 160.5, 153.4, 148.9, 141.6, 141.3, 134.1, 131.2, 130.6, 129.6, 129.6, 129.1, 129.0, 122.2, 114.0, 55.4 \) ppm; MS (EI, 70eV); \( m/\epsilon \) (%) = 261 (100) [M-H]\(^+\), 231 (45); HRMS (EI) for C\(_{17}\)H\(_{13}\)N\(_2\)O: calcd. 261.1028, found 261.1029.

2-p-tolyl-3-vinylquinoxaline (2c)

Orange solid; \( R_f = 0.59 \) (petroleum ether-EtOAc= 6:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.14-8.11 \) (m, 2H), 7.76-7.72 (m, 2H), 7.62 (d, \( J = 8.0 \) Hz, 2H), 7.35 (d, \( J = 8.0 \) Hz, 2H), 7.10 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.5 \) Hz, 1H), 6.66 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 1.5 \) Hz, 1H), 5.64 (dd, \( J_1 = 10.5 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 2.47 (s, 3H) ppm; \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 153.8, 148.8, 141.5, 141.5, 138.2, 133.7, 129.9, 129.7, 129.6, 129.1, 129.1, 128.5, 122.4, 21.4 \) ppm; MS (EI, 70eV); \( m/\epsilon \) (%) = 245 (100) [M-H]\(^+\), 231 (59); HRMS (EI) for C\(_{17}\)H\(_{13}\)N\(_2\): calcd. 246.1157, found 246.1174.

2-(2,4-dimethylphenyl)-3-vinylquinoxaline (2d)
Yellow solid; \( R_f = 0.58 \) (petroleum ether-EtOAc = 6:1); mp = 65-66°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.16-8.10 \) (m, 2H), 7.79-7.73 (m, 2H), 7.22 (d, \( J = 8.5 \) Hz, 1H), 7.17-7.15 (m, 2H), 6.77 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.5 \) Hz, 1H), 6.63 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 5.56 (dd, \( J_1 = 10.5 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 2.42 (s, 3H), 2.13 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 154.9, 149.4, 141.6, 141.5, 138.8, 136.1, 135.0, 133.0, 131.2, 129.9, 129.6, 129.2, 126.8, 122.5, 21.3, 19.6 \) ppm; MS (EI, 70eV): \( m/z \) (%) = 259 (28) [M-H]^+, 245 (100); HRMS (EI) for \( C_{18}H_{16}N_2 \): calcd. 260.1313, found 260.1304.

**2-(biphenyl-4-yl)-3-vinylquinoxaline (2e)**

![Structure of 2-(biphenyl-4-yl)-3-vinylquinoxaline (2e)](image)

Yellow solid; \( R_f = 0.63 \) (petroleum ether-EtOAc = 6:1); mp = 89-90°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.17-8.14 \) (m, 2H), 7.75-7.83 (m, 6H), 7.70 (d, \( J = 7.0 \) Hz, 2H), 7.51 (t, \( J = 7.5 \) Hz, 2H), 7.42 (t, \( J = 7.5 \) Hz, 1H), 7.17 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 11.0 \) Hz, 1H), 6.71 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 1.5 \) Hz, 1H), 5.69 (dd, \( J_1 = 10.5 \) Hz, \( J_2 = 2.0 \) Hz, 1H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 153.4, 148.8, 142.0, 141.7, 141.5, 140.5, 137.1, 133.8, 130.2, 129.9, 129.8, 129.2, 127.7, 127.3, 127.2, 122.5 \) ppm; MS (EI, 70eV): \( m/z \) (%) = 307 (100) [M-H]^+, 231 (100); HRMS (EI) for \( C_{23}H_{19}N_2 \): calcd. 308.1313, found 308.1315.

**2-(4-fluorophenyl)-3-vinylquinoxaline (2f)**

![Structure of 2-(4-fluorophenyl)-3-vinylquinoxaline (2f)](image)

Orange solid; \( R_f = 0.66 \) (petroleum ether-EtOAc = 6:1); mp = 68-69°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.15-8.10 \) (m, 2H), 7.78-7.71 (m, 4H), 7.28-7.22 (m, 2H), 7.05 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 11.0 \) Hz, 1.2H), 6.67 (dd, \( J_1 = 16.8 \) Hz, \( J_2 = 1.75 \) Hz, 1H), 5.67 (dd, \( J_1 = 11.0 \) Hz, \( J_2 = 2.0 \) Hz, 0.8H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 163.4 \) (d, \( J = 250.0 \) Hz), 152.6, 148.7, 141.5, 134.3, 133.6, 131.7 (d, \( J = 8.8 \) Hz), 130.0, 129.9, 129.2, 129.1, 128.8, 122.7, 115.6 (d, \( J = 21.3 \) Hz) ppm; MS (EI, 70eV): \( m/z \) (%) = 249 (100) [M-H]^+, 231 (100); HRMS (EI) for \( C_{16}H_{11}F_{2} \): calcd. 250.0906, found 250.0889.

**2-(4-chlorophenyl)-3-vinylquinoxaline (2g)**

![Structure of 2-(4-chlorophenyl)-3-vinylquinoxaline (2g)](image)

Yellow solid; \( R_f = 0.69 \) (petroleum ether-EtOAc = 6:1); mp = 94-95°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.15-8.10 \) (m, 2H), 7.80-7.74 (m, 2H), 7.67 (dd, \( J_1 = 6.5 \) Hz, \( J_2 = 2.0 \) Hz, 2H), 7.53 (dd, \( J_1 = 6.5 \) Hz, \( J_2 = 2.0 \) Hz, 2H), 7.04 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.5 \) Hz, 1H), 6.67 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 1.5 \) Hz, 1H), 5.67 (dd, \( J_1 = 10.5 \) Hz, \( J_2 = 2.0 \) Hz, 1H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 152.5, 148.6, 141.6, 141.5, 136.7, 135.4, 133.4, 131.1, 130.1, 129.9, 129.7, 129.2, 129.1, 128.8, 128.5, 122.8 \) ppm; MS (EI, 70eV): \( m/z \) (%) = 265 (49) [M-H]^+, 231 (100); HRMS (EI) for \( C_{16}H_{13}Cl_2 \): calcd. 266.0611, found 266.0624.

**2-(4-bromophenyl)-3-vinylquinoxaline (2h)**
Yellow solid; \( R_f = 0.67 \) (petroleum ether-\( \text{EtOAc} \approx 6:1 \)); mp = 105-106°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.15-8.10 \) (m, 2H), 7.80-7.74 (m, 2H), 7.69 (dd, \( J_1 = 6.5 \) Hz, \( J_2 = 2.0 \) Hz, 2H), 7.61 (dd, \( J_1 = 6.5 \) Hz, \( J_2 = 2.0 \) Hz, 2H), 7.03 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 11.0 \) Hz, 1H), 6.67 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 5.67 (dd, \( J_1 = 10.75 \) Hz, \( J_2 = 1.75 \) Hz, 1H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 152.5, 148.6, 141.6, 141.5, 137.2, 133.4, 131.7, 131.3, 130.2, 130.1, 129.9, 129.2, 129.1, 127.9, 123.7, 122.9 \) ppm; MS (EI, 70eV): \( m/\ell \) (\%) = 311 (13) [M+], 231 (100); HRMS (EI) for \( \text{C}_{16}\text{H}_{12}\text{Br} \): calcd. 310.0106, found 310.0095.

2-(4-iodophenyl)-3-vinylquinoxaline (2i)

Yellow solid; \( R_f = 0.58 \) (petroleum ether-\( \text{EtOAc} \approx 6:1 \)); mp = 96-97°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.14-8.10 \) (m, 2H), 7.89 (d, \( J = 8.5 \) Hz, 2H), 7.80-7.75 (m, 2H), 7.47 (d, \( J = 8.0 \) Hz, 2H), 7.03 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.5 \) Hz, 1H), 6.67 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 2.0 \)Hz, 1H), 5.66 (dd, \( J_1 = 10.75 \) Hz, \( J_2 = 1.75 \) Hz, 1H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 152.6, 148.5, 141.6, 137.7, 137.7, 133.4, 131.5, 130.1, 129.9, 129.2, 129.1, 122.9, 95.5 \) ppm; MS (EI, 70eV): \( m/\ell \) (\%) = 357 (10) [M-H]+, 231 (100); HRMS (EI) for \( \text{C}_{16}\text{H}_{12}\text{I} \): calcd. 357.9967, found 357.9956.

2-(2-bromophenyl)-3-vinylquinoxaline (2j)

Pale yellow solid; \( R_f = 0.58 \) (petroleum ether-\( \text{EtOAc} \approx 6:1 \)); mp = 95-96°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.18-8.12 \) (m, 2H), 7.83-7.73 (m, 3H), 7.52-7.49 (m, 1H), 7.67 (dd, \( J_1 = 7.8 \) Hz, \( J_2 = 1.9 \) Hz, 1H), 7.39 (td, \( J = 7.8, 1.9 \) Hz, 1H), 6.73 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.5 \) Hz, 1H), 6.66 (dd, \( J_1 = 16.8 \) Hz, \( J_2 = 1.8 \) Hz, 1H), 5.60 (dd, \( J_1 = 10.3 \) Hz, \( J_2 = 2.3 \) Hz, 1H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 153.5, 148.9, 142.0, 141.2, 139.3, 132.9, 132.6, 130.9, 130.3, 130.3, 129.8, 129.3, 129.2, 127.8, 122.9, 122.8 \) ppm; MS (EI, 70eV): \( m/\ell \) (\%) = 310 (3) [M+], 231 (100); HRMS (EI) for \( \text{C}_{16}\text{H}_{12}\text{Br} \): calcd. 310.0106, found 310.0108.

2-(3-nitrophenyl)-3-vinylquinoxaline (2k)

Yellow solid; \( R_f = 0.38 \) (petroleum ether-\( \text{EtOAc} \approx 6:1 \)); mp = 88-89°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.65 \) (t, \( J = 2.0 \) Hz, 1H), 8.39 (dd, \( J_1 = 8.5 \) Hz, \( J_2 = 1.5 \) Hz, 1H), 8.17 (dd, \( J_1 = 8.0 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 8.13 (dd, \( J_1 = 8.0 \) Hz, \( J_2 = 1.5 \) Hz, 1H), 8.08 (dd, \( J_1 = 6.5 \) Hz, \( J_2 = 1.0 \) Hz, 1H), 7.85-7.78 (m, 2H), 7.74 (t, \( J = 8.0 \) Hz, 1H), 7.00 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.5 \) Hz, 1H), 6.73 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 1.5 \) Hz, 1H), 5.73 (dd, \( J_1 = 10.75 \) Hz, \( J_2 = 1.75 \) Hz, 1H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = \)
150.9, 148.4, 148.4, 141.9, 141.5, 140.0, 135.7, 132.8, 130.7, 130.3, 129.6, 129.3, 129.2, 124.9, 123.9, 123.8 ppm; MS (EI, 70eV): m/z (%) = 277 (50) [M+], 230 (100); HRMS (EI) for C_{16}H_{11}N_{2}O_{2}: calc. 277.0851, found 277.0859.

2-(3-(trifluoromethyl)phenyl)-3-vinylquinoxaline (2l)

Orange oil; R_f = 0.62 (petroleum ether-EtOAc = 6:1); ¹H NMR (500 MHz, CDCl₃): δ = 8.17-8.13 (m, 2H), 8.03 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.83-7.77 (m, 3H), 7.69 (t, J = 8.0 Hz, 1H), 7.01 (dd, J₁ = 17.0 Hz, J₂ = 11.0 Hz, 1H), 6.71 (dd, J₁ = 16.8 Hz, J₂ = 1.8 Hz, 1H), 5.70 (dd, J₁ = 10.5 Hz, J₂ = 2.0 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 152.1, 148.5, 141.7, 141.5, 139.1, 133.1, 133.0, 131.1 (q, J = 32.5 Hz), 130.4, 130.1, 129.3, 129.2, 129.0, 126.6 (q, J = 3.8 Hz), 125.9 (q, J = 3.8 Hz), 123.9 (q, J = 271.1 Hz), 123.2 ppm; MS (EI, 70eV): m/z (%) = 299 (100) [M-H]^+; 231 (41); HRMS (EI) for C_{17}H_{11}N_{2}F₃: calc. 300.0874, found 300.0865.

6,7-dimethyl-2-phenyl-3-vinylquinoxaline (2m)

Yellow solid; R_f = 0.53 (petroleum ether-EtOAc = 6:1); mp = 82-83°C; ¹H NMR (500 MHz, CDCl₃): δ = 7.88 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 7.0 Hz, 2H), 7.54-7.49 (m, 3H), 7.05 (dd, J₁ = 17.0 Hz, J₂ = 11.0 Hz, 1H), 6.61 (dd, J₁ = 17.0 Hz, J₂ = 1.5 Hz, 1H), 5.59 (dd, J₁ = 10.5 Hz, J₂ = 1.5 Hz, 1H), 2.52 (s, 3H), 2.51 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 152.9, 147.8, 140.6, 140.4, 140.3, 138.6, 133.9, 129.7, 128.8, 128.4, 128.2, 121.4, 20.4, 20.3 ppm; MS (EI, 70eV): m/z (%) = 259 (100) [M-H]^+; HRMS (EI) for C_{18}H_{16}N_{2}: calc. 260.1313, found 260.1322.

2-(thiophen-2-yl)-3-vinylquinoxaline (2n)

Brown oil; R_f = 0.55 (petroleum ether-EtOAc = 6:1); ¹H NMR (500 MHz, CDCl₃): δ = 8.10-8.07 (m, 2H), 7.74-7.72 (m, 2H), 7.63 (d, J = 4.0 Hz, 1H), 7.57 (d, J = 4.5 Hz, 1H), 7.41 (dd, J₁ = 16.8 Hz, J₂ = 10.75 Hz, 1H), 7.21 (dd, J₁ = 5.0 Hz, J₂ = 3.5 Hz, 1H), 6.64 (dd, J₁ = 17.0 Hz, J₂ = 2.0 Hz, 1H), 5.77 (dd, J₁ = 10.75 Hz, J₂ = 1.75 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 148.3, 147.0, 141.8, 141.4, 140.9, 134.0, 129.9, 129.8, 129.3, 129.1, 128.8, 127.8, 123.0 ppm; MS (EI, 70eV): m/z (%) = 237 (50) [M-H]^+; HRMS (EI) for C_{14}H_{10}NS: calc. 238.0565, found 238.0560.

2-phenyl-3-(prop-1-en-2-yl)quinoxaline (2o)
White solid; \( R_f = 0.56 \) (petroleum ether-EtOAc= 6:1); mp = 118-119\(^\circ\)C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.16-8.13 \) (m, 2H), 7.80-7.75 (m, 4H), 7.51-7.47 (m, 3H), 5.42 (t, \( J = 1.3 \) Hz, 1H), 5.33 (s, 1H), 2.05 (s, 3H) ppm; \(^13\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 155.4, 152.9, 144.1, 141.2, 140.7, 139.4, 129.8, 129.9, 129.1, 129.1, 129.0, 128.5, 120.6, 21.9 \) ppm; MS (EI, 70eV): \( m/z \) (%) = 245 (30) [M-H]\(^+\), 231 (100); HRMS (EI) for \( \text{C}_8\text{H}_{16}\text{N}_2\text{Br} \): calcd. 246.1157, found 246.1151.

**2-(2-bromo-4-methylphenyl)-3-vinylquinoxaline (2p)**

![](image)

Isolated as yellow solid in 86% yield; \( R_f = 0.57 \) (petroleum ether-EtOAc= 6:1); mp 115-116\(^\circ\)C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.17-8.11 \) (m, 2H), 7.82-7.74 (m, 2H), 7.56 (s, 1H), 7.34 (d, \( J = 8.0 \) Hz, 1H), 7.30 (d, \( J = 8.0 \) Hz, 1H), 6.75 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.5 \) Hz, 1H), 6.65 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 5.59 (dd, \( J_1 = 10.5 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 2.45 (s, 3H) ppm; \(^13\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 153.6, 149.1, 141.9, 141.3, 140.9, 136.4, 133.3, 132.3, 130.6, 130.2, 129.7, 129.3, 129.2, 128.6, 122.6, 122.5, 21.01 \) ppm; MS (EI, 70eV): \( m/z \) (%) = 324 (7) [M+], 245 (100); HRMS (EI) for \( \text{C}_{17}\text{H}_{15}\text{N}_2\text{Br} \): calcd. 324.0262, found 324.0277.

**2-(2-bromo-4-methoxyphenyl)-3-vinylquinoxaline (2q)**

![](image)

Isolated as pale yellow solid in 88% yield; \( R_f = 0.31 \) (petroleum ether-EtOAc= 6:1); mp 117-118\(^\circ\)C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.16-8.11 \) (m, 2H), 7.81-7.74 (m, 2H), 7.38 (d, \( J = 8.5 \) Hz, 1H), 7.27 (d, \( J = 8.0 \) Hz, 1H), 7.04 (dd, \( J_1 = 8.5 \) Hz, \( J_2 = 2.5 \) Hz, 1H), 6.77 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.5 \) Hz, 1H), 6.65 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 5.60 (dd, \( J_1 = 10.5 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 3.90 (s, 3H) ppm; \(^13\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 160.7, 153.4, 149.3, 141.9, 141.3, 132.9, 131.7, 131.5, 130.1, 129.6, 129.3, 129.2, 123.3, 122.6, 118.2, 113.9, 55.7 \) ppm; MS (EI, 70eV): \( m/z \) (%) = 340 (11) [M+], 261 (100); HRMS (EI) for \( \text{C}_{17}\text{H}_{15}\text{N}_2\text{Br} \): calcd. 338.0419, found 338.0447.

**2-(2-bromo-4-fluorophenyl)-3-vinylquinoxaline (2r)**

![](image)

Isolated as pale yellow solid in 83% yield; \( R_f = 0.58 \) (petroleum ether-EtOAc= 6:1); mp = 129-130\(^\circ\)C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.17-8.10 \) (m, 2H), 7.84-7.76 (m, 2H), 7.50-7.44 (m, 2H), 7.24 (td, \( J_1 = 8.3 \) Hz, \( J_2 = 2.5 \) Hz, 1H), 6.71 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 9.5 \) Hz, 1H), 6.66 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 2.5 \) Hz, 1H), 5.62 (dd, \( J_1 = 9.8 \) Hz, \( J_2 = 2.8 \) Hz, 1H) ppm; \(^13\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 162.7 \) (d, \( J = 252.5 \) Hz), 152.6, 149.0, 142.1, 141.2, 135.6 (d, \( J = 3.5 \) Hz), 132.4, 132.1 (d, \( J = 8.7 \) Hz), 130.5, 130.0, 129.4, 129.2, 123.3 (d, \( J = 9.4 \) Hz), 123.1, 120.3 (d, \( J = 24.5 \) Hz), 115.2 (d, \( J = 21.6 \) Hz) ppm; MS (EI, 70eV): \( m/z \) (%) = 328 (7) [M+], 249 (100); HRMS (EI) for \( \text{C}_{16}\text{H}_{16}\text{N}_2\text{F} \): calcd. 328.0011, found 328.0025.
2-(3-bromobiphenyl-4-yl)-3-vinylquinoxaline (2s)

Isolated as yellow solid in 82% yield; \( R_f \)=0.48 (petroleum ether-EtOAc= 6:1); mp = 122-123°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) = 8.19-8.13 (m, 2H), 7.97 (d, \( J = 2.0 \) Hz, 1H), 7.84-7.76 (m, 2H), 7.72 (dd, \( J_1 = 8.0 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 7.67-7.65 (m, 2H), 7.54-7.50 (m, 3H), 7.45-7.43 (m, 1H), 6.83 (dd, \( J_1 = 16.8 \) Hz, \( J_2 = 10.8 \) Hz, 1H), 6.70 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 5.64 (dd, \( J_1 = 10.8 \) Hz, \( J_2 = 1.8 \) Hz, 1H) ppm; \(^13\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) = 153.4, 149.0, 143.8, 142.0, 141.2, 139.1, 137.9, 132.7, 131.4, 131.2, 130.4, 129.8, 129.3, 129.2, 129.0, 128.2, 127.2, 126.5, 123.2, 122.9 ppm; MS (EI, 70eV): \( m/z \) (%): 386 (7) [M+], 307 (100); HRMS (EI) for \( \text{C}_{22}\text{H}_{15}\text{N}_3\text{Br} \): calcd. 386.0419, found 386.0418.

2-(3-bromonaphthalen-2-yl)-3-vinylquinoxaline (2t)

Isolated as yellow solid in 85% yield; \( R_f \)=0.56 (petroleum ether-EtOAc= 6:1); mp = 130-131°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) = 8.26 (s,1H), 8.20 (d, \( J = 8.5 \) Hz, 1H), 8.15 (d, \( J = 8.0 \) Hz, 1H), 7.97 (s,1H), 7.90-7.77 (m, 4H), 7.63-7.57 (m, 2H), 6.76 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.0 \) Hz, 1H), 6.67 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 2.0 \) Hz, 1H), 5.58 (dd, \( J_1 = 10.8 \) Hz, \( J_2 = 1.8 \) Hz, 1H) ppm; \(^13\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) = 153.5, 149.3, 142.0, 141.2, 136.7, 134.5, 132.7, 132.2, 131.6, 130.4, 129.9, 129.3, 129.3, 128.2, 127.7, 127.1, 126.9, 122.9, 119.8 ppm; MS (EI, 70eV): \( m/z \) (%): 360 (4) [M+], 281 (100); HRMS (EI) for \( \text{C}_{20}\text{H}_{16}\text{N}_3\text{Br} \): calcd. 360.0262, found 360.0257.

2-(2-bromo-5-chlorophenyl)-3-vinylquinoxaline (2u)

Isolated as yellow solid in 86% yield; \( R_f \)=0.65 (petroleum ether-EtOAc= 6:1); mp = 124-125°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) = 8.18-8.10 (m, 2H), 7.85-7.77 (m, 2H), 7.66 (d, \( J = 8.5 \) Hz, 1H), 7.47 (d, \( J = 2.5 \) Hz, 1H), 7.37 (dd, \( J_1 = 9.0 \) Hz, \( J_2 = 2.5 \) Hz, 1H), 6.72 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 9.0 \) Hz, 1H), 6.68 (dd, \( J_1 = 16.8 \) Hz, \( J_2 = 3.3 \) Hz, 1H), 5.64 (dd, \( J_1 = 9.0 \) Hz, \( J_2 = 3.5 \) Hz, 1H) ppm; \(^13\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) = 152.2, 148.6, 142.1, 141.1, 140.7, 134.0, 132.2, 130.9, 130.6, 130.0, 129.4, 129.2, 123.3, 120.8 ppm; MS (EI, 70eV): \( m/z \) (%): 344(1) [M+], 265 (100); HRMS (EI) for \( \text{C}_{16}\text{H}_{10}\text{N}_2\text{ClBr} \): calcd. 343.9716, found 343.9748.

2-(2-bromophenyl)-6,7-dimethyl-3-vinylquinoxaline (2v)
Isolated as yellow solid in 88% yield; \( R_f = 0.56 \) (petroleum ether-EtOAc = 6:1); mp = 114-115°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.92 \) (s, 1 H), 7.87 (s, 1 H), 7.72 (dd, \( J = 8.0 \) Hz, \( J_2 = 1.0 \) Hz, 1 H), 7.49 (dd, \( J_1 = 7.5 \) Hz, \( J_2 = 1.0 \) Hz, 1 H), 7.44 (dd, \( J_1 = 7.5 \) Hz, \( J_2 = 2.0 \) Hz, 1 H), 7.37 (dd, \( J_1 = 7.5 \) Hz, \( J_2 = 2.0 \) Hz, 1 H), 6.70 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 10.5 \) Hz, 1 H), 6.59 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 2.0 \) Hz, 1 H), 5.54 (dd, \( J_1 = 10.5 \) Hz, \( J_2 = 2.0 \) Hz, 1 H), 2.53 (s, 3 H), 2.51 (s, 3 H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 152.6, 147.9, 141.0, 140.9, 140.5, 139.5, 132.8, 132.7, 130.9, 130.3, 128.2, 127.7, 123.0, 121.9, 20.4, 20.4 \) ppm; MS (EI, 70eV): \( m/\ell \) (%) = 338 (12) [M+], 259 (100); HRMS (EI) for C\(_{16}\)H\(_{13}\)N\(_2\)Br: calcd. 338.0419, found 338.0414.

### 2-phenoxy-3-vinylquinoxaline (4b)

Yellow solid; \( R_f = 0.75 \) (petroleum ether-EtOAc = 6:1); mp = 75-76°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.06-8.04 \) (m, 1 H), 7.72-7.69 (m, 1 H), 7.62-7.58 (m, 2 H), 7.48 (t, \( J = 7.8 \) Hz, 2 H), 7.42 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 11.0 \) Hz, 1 H), 7.32-7.29 (m, 3 H), 6.80 (dd, \( J_1 = 17.3 \) Hz, \( J_2 = 1.8 \) Hz, 1 H), 5.83 (dd, \( J_1 = 11.0 \) Hz, \( J_2 = 1.5 \) Hz, 1 H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 155.1, 153.0, 143.8, 139.7 \) (2C), 130.5, 129.6, 129.5, 128.8, 127.5, 127.3, 125.2, 123.6, 121.7 ppm; MS (EI, 70eV): \( m/\ell \) (%) = 248 (100) [M+], 219 (100); HRMS (EI) for C\(_{16}\)H\(_{13}\)N\(_2\): calcd. 248.0950, found 248.0962.

### 2-methoxy-3-vinylquinoxaline (4c)

Yellow oil; \( R_f = 0.75 \) (petroleum ether-EtOAc = 6:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.00 \) (dd, \( J_1 = 8.3 \) Hz, \( J_2 = 1.3 \) Hz, 1 H), 7.83 (dd, \( J_1 = 8.3 \) Hz, \( J_2 = 1.3 \) Hz, 1 H), 7.63 (dd, \( J_1 = 7.8 \) Hz, \( J_2 = 1.5 \) Hz, 1 H), 7.57-7.54 (m, 1 H), 7.23 (dd, \( J_1 = 17.5 \) Hz, \( J_2 = 11.0 \) Hz, 1 H), 6.67 (dd, \( J_1 = 17.5 \) Hz, \( J_2 = 2.0 \) Hz, 1 H), 5.74 (dd, \( J_1 = 11.0 \) Hz, \( J_2 = 2.0 \) Hz, 1 H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 155.8, 143.8, 140.2, 138.8, 130.8, 129.4, 128.8, 126.7, 126.6, 123.1, 53.7 \) ppm; MS (EI, 70eV): \( m/\ell \) (%) = 186 (100) [M+], 157 (43); HRMS (EI) for C\(_{11}\)H\(_{10}\)N\(_2\): calcd. 186.0793, found 186.0799.

### methyl 3-vinylquinoxaline-2-carboxylate (4d)

Orange solid; \( R_f = 0.32 \) (petroleum ether-EtOAc = 6:1); mp = 66-67°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.18 \) (dd, \( J_1 = 8.5 \) Hz, \( J_2 = 1.0 \) Hz, 1 H), 8.12 (dd, \( J_1 = 8.5 \) Hz, \( J_2 = 1.0 \) Hz, 1 H), 7.86 (dd, \( J_1 = 8.3 \) Hz, \( J_2 = 6.9 \) Hz, \( J_3 = 1.5 \) Hz, 1 H), 7.79 (ddd, \( J_1 = 8.3 \) Hz, \( J_2 = 6.9 \) Hz, \( J_3 = 1.4 \) Hz, 1 H), 7.54 (dd, \( J_1 = 17.0 \) Hz, \( J_2 = 11.0 \) Hz, 1 H), 6.70 (dd, \( J_1 = 16.8 \) Hz, \( J_2 = 1.8 \) Hz, 1 H), 5.77 (dd, \( J_1 = 10.8 \) Hz, \( J_2 = 1.8 \) Hz, 1 H), 4.10 (s, 3 H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 165.9, 148.9, 142.9 \) (2C), 140.4,
132.0 (2C), 130.4, 129.7, 129.3, 123.7, 53.3 ppm; MS (EI, 70eV): m/z (%) = 214 (86) [M+], 199 (59), 156 (100); HRMS (EI) for C₁₂H₁₀N₂O₂: calcd. 214.0742, found 214.0750.

2-phenyl-3-vinylpyrazine (4e)

![Structure](image1.png)

Yellow oil; Rf = 0.50 (petroleum ether-EtOAc= 6:1); ¹H NMR (500 MHz, CDCl₃): δ = 8.56 (s, 2 H), 7.63-7.62 (m, 2 H), 7.53-7.48 (m, 3 H), 6.95 (dd, J₁ = 17.0 Hz, J₂ = 10.5 Hz, 1 H), 6.56 (dd, J₁ = 17.0 Hz, J₂ = 2.0 Hz, 1 H), 5.58 (dd, J₁ = 11.0 Hz, J₂ = 1.5 Hz, 1 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 152.6, 148.1, 142.5, 142.4, 137.5, 132.8, 129.6, 129.0, 128.4, 121.5 ppm; MS (EI, 70eV): m/z (%) = 181 (100) [M-H]⁺; HRMS (EI) for C₁₃H₁₀N₂: calcd. 182.0844, found 182.0840.

3-phenyl-2-vinylquinoline (4g)

![Structure](image2.png)

Yellow oil; Rf =0.63 (petroleum ether-EtOAc= 6:1); ¹H NMR (500 MHz, CDCl₃): δ = 8.17 (d, J = 8.5 Hz, 1H), 8.05 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.75-7.71 (m, 1H), 7.55-7.45 (m, 6H), 6.99 (dd, J₁ = 17.0 Hz, J₂ = 10.5 Hz, 1H), 6.61 (dd, J₁ = 17.0 Hz, J₂ = 2.0 Hz, 1H), 5.53 (dd, J₁ = 10.5 Hz, J₂ = 2.0 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 153.5, 147.3, 139.1, 136.7, 134.8, 134.7, 129.8, 129.5, 129.4, 128.4, 127.7, 127.5, 127.4, 126.5, 120.9 ppm; MS (EI, 70eV): m/z (%) = 230 (100) [M-H]⁺; HRMS (EI) for C₁₃H₁₃N: calcd. 231.1048, found 231.1040.

3-(naphthalen-2-yl)-2-vinylquinoline (4h)

![Structure](image3.png)

Pale yellow solid; Rf =0.58 (petroleum ether-EtOAc= 6:1); mp = 85-86°C; ¹H NMR (500 MHz, CDCl₃): δ = 8.21 (d, J = 9.0 Hz, 1H), 7.92 (dd, J₁ = 9.0 Hz, J₂ = 5.5 Hz, 3H), 7.78-7.74 (m, 3H), 7.58-7.57 (m, 2H), 7.54-7.51 (m, 1H), 7.48-7.45 (m, 1H), 7.32 (ddd, J₁ = 8.2 Hz, J₂ = 6.8 Hz, J₃ = 1.2 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 6.86 (d, J = 2.0 Hz, 1H), 5.74 (d, J = 2.0 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 157.9, 148.1, 147.9, 138.6, 136.3, 133.7, 132.0, 129.8, 129.6, 128.3, 128.3, 127.5, 127.4, 126.3, 126.1, 125.9, 125.6, 121.6, 120.4 ppm; MS (EI, 70eV): m/z (%) = 280 (100) [M-H]⁺; HRMS (EI) for C₂₁H₁₅N: calcd. 281.1204, found 281.1205.

diethyl 2-methyl-6-vinylpyridine-3,5-dicarboxylate (4j)
White solid; \( R_f = 0.63 \) (petroleum ether-EtOAc= 6:1); mp = 47-48°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.67 \) (s, 1 H), 7.67 (dd, \( J = 16.9 \) Hz, \( J = 10.6 \) Hz, 1 H), 6.66 (dd, \( J = 16.9 \) Hz, \( J = 2.3 \) Hz, 1 H), 5.68 (dd, \( J = 10.6 \) Hz, \( J = 2.3 \) Hz, 1 H), 4.44-4.39 (m, 4H), 2.89 (s, 3 H), 1.43 (t, \( J = 7.1 \) Hz, 6H ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 165.9 \) (2C), 162.3, 156.3, 141.3, 133.3, 123.9, 123.7, 121.8, 61.6, 61.4, 25.3, 14.3 (2C) ppm; MS (EI, 70eV): \( m/z \) (%) = 263 (48) [M+], 234 (93), 206 (100) HRMS (EI) for C\(_{14}\)H\(_{17}\)NO\(_2\); calcd. 263.1158, found 263.1161.

**benzo[a]phenazine (5j)**

Yellow solid; \( R_f = 0.42 \) (petroleum ether-EtOAc= 6:1); mp = 142-143°C (lit.\(^{[11]}\) 142°C); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 9.41 \) (d, \( J = 8.5 \) Hz, 1H), 8.38-8.36 (m, 1H), 8.30-8.28 (m, 1H), 8.01 (d, \( J = 9.5 \) Hz, 1H), 7.97 (d, \( J = 9.5 \) Hz, 1H), 7.91-7.86 (m, 3H), 7.82-7.76 (m, 2H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 143.4, 142.7, 142.6, 142.0, 133.3, 133.2, 131.1, 130.0, 129.8 \) (2C), 129.7, 129.2, 128.2, 127.9, 127.1, 125.4 ppm; MS (EI, 70eV): \( m/z \) (%) = 230 (100) [M+].

**3-methylbenzo[a]phenazine (5p)**

Yellow solid; \( R_f = 0.48 \) (petroleum ether-EtOAc= 6:1); mp = 186-187°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 9.29 \) (d, \( J = 8.0 \) Hz, 1H), 8.38-8.29 (m, 2H), 7.97 (s, 2H), 7.89-7.85 (m, 2H), 7.71 (s, 1H), 7.64 (dd, \( J = 8.5 \) Hz, \( J = 1.0 \) Hz, 1H), 2.63 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 143.4, 142.9, 142.3, 142.1, 140.2, 133.4, 129.9, 129.8, 129, 1, 129.6, 129.1, 128.9, 128.2, 127.0, 125.4, 21.8 ppm; MS (EI, 70eV): \( m/z \) (%) = 244 (100) [M+]; HRMS (EI) for C\(_{14}\)H\(_{17}\)N\(_2\); calcd. 244.1000, found 244.0977.

**3-methoxybenzo[a]phenazine (5q)**

Yellow solid; \( R_f = 0.28 \) (petroleum ether-EtOAc= 6:1); mp = 166-167°C (lit.\(^{[12]}\) 160-161°C); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 9.30 \) (d, \( J = 8.5 \) Hz, 1H), 8.33 (dd, \( J = 7.3 \) Hz, \( J = 2.3 \) Hz, 1H), 8.27 (dd, \( J = 7.3 \) Hz, \( J = 2.3 \) Hz, 1H), 7.96 (d, \( J = 9.0 \) Hz, 1H), 7.93 (d, \( J = 9.0 \) Hz, 1H), 7.87-7.82 (m, 2 H), 7.38 (dd, \( J = 9.0 \) Hz, \( J = 2.5 \) Hz, 1H), 7.28 (d, \( J = 2.5 \) Hz, 1H), 4.00 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 161.1, 142.8, 142.7, 142.1, 142.0, 134.9, 133.2, 129.8, 129.6, 129.5, 129.1, 127.6, 127.2, 124.8, 117.1, 109.7, 55.6 ppm; MS (EI, 70eV): \( m/z \) (%) = 260 (100) [M+], 245 (7).
3-fluorobenzo[a]phenazine (5r)

Yellow solid; Rf = 0.54 (petroleum ether-EtOAc= 6:1); mp = 195-196°C; 1H NMR (500 MHz, CDCl3): δ = 9.42 (dd, J = 9.0 Hz, J2 = 6.0 Hz, 1H), 8.37-8.28 (m, 2H), 8.02 (d, J = 9.5 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.91-7.87 (m, 2H), 7.58-7.51 (m, 2H) ppm; 13C NMR (125 MHz, CDCl3): δ = 163.6, 144.6, 144.0, 142.4, 142.0, 135.0 (d, J = 9.1 Hz), 132.2, 130.1, 130.0, 129.9, 129.8, 129.5 (d, J = 9.1 Hz), 127.7, 116.4 (d, J = 23.1 Hz), 113.1 (d, J = 21.5 Hz) ppm; MS (EI, 70eV): m/z (%) = 248 (100) [M+]; HRMS (EI) for C16H14F: calcd. 248.0750, found 248.0748.

3-phenylbenzo[a]phenazine (5s)

Yellow solid; Rf = 0.50 (petroleum ether-EtOAc= 6:1); mp = 179-180°C; 1H NMR (500 MHz, CDCl3): δ = 9.44 (d, J = 8.5 Hz, 1H), 8.39-8.29 (m, 2H), 8.10 (d, J = 1.5 Hz, 1H), 8.11-8.04 (m, 2H), 8.00 (d, J = 9.5 Hz, 1H), 7.90-7.86 (m, 2H), 7.80 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.8 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H) ppm; 13C NMR (125 MHz, CDCl3): δ = 143.6, 142.6, 142.6, 142.1, 140.4, 133.6, 133.5, 130.1, 130.0, 129.9, 129.7, 129.1, 129.0, 128.0, 127.5, 127.0, 126.4, 126.0 ppm; MS (EI, 70eV): m/z (%) = 306 (100) [M+]; HRMS (EI) for C22H14N2: calcd. 306.1157, found 306.1151.

naphtho[2,3-a]phenazine (5t)

Yellow solid; Rf = 0.43 (petroleum ether-EtOAc= 6:1); mp = 225-226°C; 1H NMR (500 MHz, CDCl3): δ = 9.80 (s, 1H), 8.37-8.35 (m, 1H), 8.28-8.23 (m, 3H), 8.05 (dd, J1 = 8.5 Hz, J2 = 3.5 Hz, 1H), 7.98 (d, J = 9.5 Hz, 1H), 7.88-7.83 (m, 2H), 7.78 (d, J = 9.5 Hz, 1H), 7.65-7.62 (m, 2H) ppm; 13C NMR (125 MHz, CDCl3): δ = 144.6, 144.0, 142.4, 141.6, 134.2, 133.7, 132.4, 130.8, 129.8, 129.7, 129.5, 129.3, 129.0, 128.9, 128.1, 127.3, 127.2, 127.1, 126.7, 125.7 ppm; MS (EI, 70eV): m/z (%) = 280 (100) [M+].

2-chlorobenzo[a]phenazine (5u)
Yellow solid; R_f = 0.49 (petroleum ether-EtOAc = 6:1); mp = 208-209°C; ^1^H NMR (500 MHz, CDCl_3): δ = 9.34 (d, J = 2.0 Hz, 1H), 7.96 (s, 2H), 7.90-7.88 (m, 2H), 7.83 (d, J = 8.5 Hz, 1H), 7.71 (d, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H) ppm; ^1^C NMR (125 MHz, CDCl_3): δ = 143.4, 143.0, 142.0, 141.5, 134.3, 132.4, 132.2, 131.4, 130.5, 130.1, 130.9, 129.8, 129.5, 129.2, 127.4, 125.0 ppm; MS (EI, 70eV): m/z (%) = 264 (100) [M^+], 229 (24); HRMS (EI) for C_{16}H_{17}N_2Cl: calcd. 264.0454, found 264.0462.

9,10-dimethylbenzo[a]phenazine (5v)

Pale yellow solid; R_f = 0.47 (petroleum ether-EtOAc = 6:1); mp = 211-212°C; ^1^H NMR (500 MHz, CDCl_3): δ = 9.39 (d, J = 8.0 Hz, 1H), 8.10 (s, 1H), 8.01 (s, 1H), 8.00-7.94 (m, 2H), 7.91 (d, J = 7.5 Hz, 1H), 7.81-7.74 (m, 2H), 7.91 (d, J = 7.5 Hz, 1H), 7.81-7.74 (m, 2H), 2.58 (s, 3H), 2.57 (s, 3H) ppm; ^1^C NMR (125 MHz, CDCl_3): δ = 143.0, 142.0, 142.0, 141.3, 141.1, 140.9, 133.1, 132.3, 131.4, 129.3, 128.4, 128.1, 127.9, 127.7, 127.3, 125.1, 20.6, 20.5 ppm; MS (EI, 70eV): m/z (%) = 258 (100), 243 (30) [M^+]; HRMS (EI) for C_{18}H_{14}N_2: calcd. 258.1157, found 258.1145.

**Preliminary mechanistic studies**

**Effect of radical scavenger TEMPO on the reaction**

Table 4. Effect of radical scavenger TEMPO

<table>
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<th>Entry</th>
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<th>Yields of 2a (%)^6</th>
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<tr>
<td>1</td>
<td>0</td>
<td>100</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>50 mol %</td>
<td>90</td>
<td>64^f</td>
</tr>
<tr>
<td>3</td>
<td>200 mol %</td>
<td>97</td>
<td>5</td>
</tr>
</tbody>
</table>

^a Reaction condition : 1a (0.2 mmol), FeCl_3·6H_2O (0.004 mmol), K_2S_2O_8 (0.4 mmol), DMA (1.5 mL), 110 °C, under air, 3h. ^b GC-MS yields. ^c An oxidation product 3-phenylquinoxaline-2-carbaldehyde was formed as a side product.

**Deuterated experiments**

All the deuterated experiments were carried out twice.

(a) 1a treated with [D_7]DMF under the present condition

1a (0.2 mmol), FeCl_3·6H_2O (1.1 mg, 0.004 mmol), K_2S_2O_8 (108 mg, 0.4 mmol) and [D_7] DMF (1.2 mL) were sequentially added to a 10-mL tube under air. Then the tube was sealed and stirred at 110 °C for 3 h. Upon completion (monitored by TLC), the resulting mixture was diluted with Et_2O (15 mL) and washed
by brine (10 mL × 3). The organic layer was then dried over Na₂SO₄, filtered and evaporated in vacuo, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent to give [D₂]2a and [D₃]2a in the ratio 2 : 1.

Scheme 1. Synthesis of [D₂]2a and [D₃]2a
Figure 2. $^1$H NMR spectra of deuterated products

(b) 2a treated with [D$_7$]DMF under the present condition

2a (0.2 mmol), FeCl$_3$ · 6H$_2$O (1.1 mg, 0.004 mmol), K$_2$S$_2$O$_8$ (108 mg, 0.4 mmol) and [D$_7$] DMF (1.2 mL) were sequentially added to a 10-mL tube under air. Then the tube was sealed and stirred at 110 °C for 3 h. The resulting mixture was diluted with Et$_2$O (15 mL) and washed by brine (10 mL × 3). The organic layer was then dried over Na$_2$SO$_4$, filtered and evaporated in vacuo, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent. 2a was recovered in 94% yield, and no obvious deuterated of 2a were detected according to the $^1$H NMR result.

Deuterated experiments (a) and (b) indicated that the C-H bond activation occurs on both coupling partners and the terminal vinyl carbon should be given by the N,N-dimethyl moiety of amides. In addition, the 2 : 1 ratio of [D$_2$]2a and [D$_3$]2a might be obtained through the following process. Firstly, the in-situ generated deuterium ion exchanged immediately with the benzylic hydrogen of [Fe]-promoted 1a to form
Then 6a or [D]6a fastly attacked the iminium 8, intermediate [D]9a and [D]9a was thus generated respectively in the ratio of 1:2. Then the [D]9a occurred elimination to form [D]2a entirely, meanwhile the [D]9a occurred elimination to give the product [D]3a and [D]2a in the ratio of 1:1. To sum up, the ratio of [D]2a and [D]3a was eventually come to 2:1.

**Figure 3.** Deuterated experiments

(c) Competing reaction between [D]DMF and DMF

1a (0.2 mmol), FeCl₃ · 6H₂O (1.1 mg, 0.004 mmol), K₂S₂O₈ (108 mg, 0.4 mmol) and [D] DMF / DMF (0.6 mL / 0.6 mL) were sequentially added to a 10-mL tube under air. Then the tube was sealed and stirred at 110 ºC for 3 h. Upon completion (monitored by TLC), the resulting mixture was diluted with Et₂O (15 mL) and washed by brine (10 mL × 3). The organic layer was then dried over Na₂SO₄, filtered and evaporated in vacuo, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent. A mixture of [D]2a, [D]3a and 2a was determined on the basis of ¹H NMR analysis. Based on the integrations related to different hydrogen resonances, the kinetic isotope effect is calculated to be $k_H / k_D \approx 2.0$, suggesting that the C-H bond cleavage of N, N-dimethyl amides is involved in the rate-determining step. Notably, KIE value was also obtained when the reaction was stop at a lower conversion of 26%, the result was the same as it obtained after full conversion.
Figure 4. $^1$H NMR spectra of KIE experiment (c1: 100% conversion of 1a)

Figure 5. $^1$H NMR spectra of KIE experiment (c2: 26% conversion of 1a)
ESI-MS studies to capture the coupling intermediate

1a (0.2 mmol), FeCl₃·6H₂O (1.1 mg, 0.004 mmol), K₂S₂O₈ (108 mg, 0.4 mmol) and DMA (1.5 mL) were sequentially added to a 10-mL tube under air. Then the tube was sealed and stirred at 110 ºC. The mixture was stopped heating and cooled to room temperature when almost half of the starting material 1a was converted to vinylation product 2a (monitored by TLC). Then the mixture was diluted by methanol and subjected directly to ESI-MS analysis. From the mass spectrum we could find the starting material 1a (m/z: 221) and the product 2a (m/z: 233). Notably, the coupling intermediate between 1a and N,N-dimethylacetamide (DMA) was detected (m/z: 306) and its structure was further confirmed by accurate mass data. The mass experiment result indicated that a key intermediate coupled between the substrate 1a and DMA was generated during the process, which then underwent a tandem elimination to give the final vinylation product 2a.

Figure 6. ESI-MS spectrum.
<table>
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<th>Ion Formula</th>
<th>m/z (measured)</th>
<th>m/z (calculated)</th>
<th>Diff (ppm)</th>
<th>DBE</th>
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<td>306.1606</td>
<td>2.61</td>
<td>11.5</td>
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</table>

References

$^1$H and $^{13}$C NMR spectra of all products
Electronic Supplementary Material (ESI) for Chemical Communications
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