Supporting Information for

Synthesis and electrochemical and spectroscopic characterization of 4,7-diamino-1,10-phenanthrolines and their precursors

Jacek E. Nycz 1,*, Jakub Wantulok 1, Romana Sokolova 2, Lukasz Pajchel 3, Marek Stankevič 4, Marcin Szala 5, Jan Grzegorz Malecki 1 and Daniel Swoboda 1

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Table S1. Crystal data and structure refinement details of compounds 5d, 6a and 6b.

<table>
<thead>
<tr>
<th></th>
<th>5d</th>
<th>6a</th>
<th>6b</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C$<em>2$H$</em>{22}$FN$_4$, 2(CHCl$_3$)</td>
<td>C$<em>{17}$H$</em>{21}$N$_2$O$_2$. 2(C$<em>6$H$</em>{12}$O)$_2$</td>
<td>C$<em>2$H$</em>{22}$N$_2$OS$_2$. 2(C$<em>6$H$</em>{12}$O)</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>603.19</td>
<td>727.84</td>
<td>759.91</td>
</tr>
<tr>
<td><strong>Temperature [K]</strong></td>
<td>295(2)</td>
<td>295(2)</td>
<td>295(2)</td>
</tr>
<tr>
<td><strong>Wavelength (Å)</strong></td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>triclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P–1</td>
<td>P–1</td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a [Å]</td>
<td>9.1767(13)</td>
<td>12.1394(7)</td>
<td>9.0665(4)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>10.3249(14)</td>
<td>12.6397(5)</td>
<td>15.0843(5)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>14.9935(12)</td>
<td>12.9635(6)</td>
<td>90</td>
</tr>
<tr>
<td>α [°]</td>
<td>83.725(9)</td>
<td>89.230(4)</td>
<td>91.867(4)</td>
</tr>
<tr>
<td>β [°]</td>
<td>82.567(9)</td>
<td>75.454(4)</td>
<td>90</td>
</tr>
<tr>
<td>γ [°]</td>
<td>87.109(12)</td>
<td>79.332(4)</td>
<td>90</td>
</tr>
<tr>
<td><strong>Volume [Å$^3$]</strong></td>
<td>1399.3(3)</td>
<td>1890.91(16)</td>
<td>3692.3(2)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td><strong>Calculated density [Mg/m$^3$]</strong></td>
<td>1.432</td>
<td>1.278</td>
<td>1.367</td>
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<tr>
<td><strong>Absorption coefficient [mm$^{-1}$]</strong></td>
<td>0.642</td>
<td>0.083</td>
<td>0.195</td>
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<tr>
<td><strong>F(000)</strong></td>
<td>620</td>
<td>768</td>
<td>1592</td>
</tr>
<tr>
<td><strong>Crystal dimensions [mm]</strong></td>
<td>0.36 x 0.08 x 0.06</td>
<td>0.17 x 0.08 x 0.07</td>
<td>0.37 x 0.15 x 0.14</td>
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<tr>
<td><strong>θ range for data collection [°]</strong></td>
<td>3.33 − 25.05</td>
<td>3.57 − 27.95</td>
<td>3.46 − 29.56</td>
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<tr>
<td><strong>Index ranges</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>−12 ≤ h ≤ 12</td>
<td>−16 ≤ h ≤ 15</td>
<td>−10 ≤ h ≤ 11</td>
</tr>
<tr>
<td>k</td>
<td>−12 ≤ k ≤ 14</td>
<td>−15 ≤ k ≤ 14</td>
<td>−36 ≤ k ≤ 27</td>
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<tr>
<td>l</td>
<td>−18 ≤ l ≤ 21</td>
<td>−17 ≤ l ≤ 14</td>
<td>−20 ≤ l ≤ 15</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>11285</td>
<td>16918</td>
<td>22276</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>6529 [R(int) = 0.0784]</td>
<td>8928 [R(int) = 0.0412]</td>
<td>9010 [R(int) = 0.0310]</td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>6529/0/328</td>
<td>8928/2/516</td>
<td>9010/0/500</td>
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<tr>
<td><strong>Goodness-of-fit on F$^2$</strong></td>
<td>0.912</td>
<td>1.019</td>
<td>1.034</td>
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<tr>
<td><strong>Final R indices [I&gt;2σ(I)]$^*$</strong></td>
<td>$R_1$ = 0.0650, R$_{w1}$ = 0.1458</td>
<td>$R_1$ = 0.0667, R$_{w1}$ = 0.1589</td>
<td>$R_1$ = 0.0604, R$_{w1}$ = 0.1438</td>
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<tr>
<td><strong>R indices (all data)</strong></td>
<td>$R_1$ = 0.1830, R$_{w1}$ = 0.2091</td>
<td>$R_1$ = 0.1391, R$_{w1}$ = 0.1999</td>
<td>$R_1$ = 0.0991, R$_{w1}$ = 0.1665</td>
</tr>
<tr>
<td><strong>Largest diff. Peak and hole</strong></td>
<td>0.530 /-0.437</td>
<td>0.312/-0.266</td>
<td>0.401/-0.329</td>
</tr>
<tr>
<td><strong>CCDC number</strong></td>
<td>1479401</td>
<td>1917090</td>
<td>1919692</td>
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</table>

$^*$Structure was refined on $F_o^2$: $wR2 = \sqrt{\sum (w(F_o^2-F_c^2))^2/\sum w(F_o^2)^2})^{1/2}$, where $w^{-1} = \sum (F_o^2) + (aP)^2 + bP$ and $P = \max(F_o^2, 0) + 2F_c^2/3.$

Table S2. Hydrogen bonds for compounds 5d and 6a (Å and °).

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D–H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5d</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(19)–H(19B)...F(1)</td>
<td>0.97</td>
<td>2.16</td>
<td>2.715(5)</td>
<td>116.0</td>
</tr>
<tr>
<td>C(23)–H(23)...N(1)</td>
<td>0.98</td>
<td>2.43</td>
<td>3.281(6)</td>
<td>145.2</td>
</tr>
<tr>
<td>C(23)–H(23)...N(2)</td>
<td>0.98</td>
<td>2.34</td>
<td>3.205(5)</td>
<td>147.2</td>
</tr>
<tr>
<td>6a</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

S2
### Table S3. C–X...π stacking interactions in compounds 5d, 6b and π...π interaction in 6a, 6b.

<table>
<thead>
<tr>
<th>Y–X(I)•••Cg(J)</th>
<th>X(I)•••Cg(J) [Å]</th>
<th>X-Perp [Å]</th>
<th>γ [°]</th>
<th>Y–X(I)•••Cg(J) [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5d</td>
<td>Cg(I): N(2)–C(10)–C(9)–C(8)–C(7)–C(11); Cg(2): C(4)–C(5)–C(6)–C(7)–C(11)–C(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(24)–Cl(4)•••Cg(1)</td>
<td>3.882(2)</td>
<td>-3.619</td>
<td>21.20</td>
<td>108.06(17)</td>
</tr>
<tr>
<td>C(24)–Cl(5)•••Cg(2)</td>
<td>3.942(2)</td>
<td>-3.767</td>
<td>17.13</td>
<td>132.07(17)</td>
</tr>
</tbody>
</table>

| 6b | Cg(I): S(2)–C(31)–C(26)–N(5)–C(37)–C(32) |
| C(21)–H(21)•••Cg(1) | 2.690 | 2.674 | 5.67 | 135.0 |
| C(13)–N(3)•••Cg(1) | 3.180 | -3.137 | 9.45 | 81.05 |

#### 6a

<table>
<thead>
<tr>
<th>Cg(I)•••Cg(J)</th>
<th>Cg(I)•••Cg(J) [Å]</th>
<th>α [°]</th>
<th>β [°]</th>
<th>γ [°]</th>
<th>Cg(I)-Perp [Å]</th>
<th>Cg(J)-Perp [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cg(1): N(1)–C(12)–C(4)–C(3)–C(2)–C(1); Cg(2): N(2)–C(11)–C(7)–C(8)–C(9)–C(10)</td>
<td>Cg(1)•••Cg(2)</td>
<td>3.887</td>
<td>0.00</td>
<td>8.06</td>
<td>85.40</td>
<td>-4.773</td>
</tr>
</tbody>
</table>

#### 6b

<table>
<thead>
<tr>
<th>Cg(I)•••Cg(J)</th>
<th>Cg(I)•••Cg(J) [Å]</th>
<th>α [°]</th>
<th>β [°]</th>
<th>γ [°]</th>
<th>Cg(I)-Perp [Å]</th>
<th>Cg(J)-Perp [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cg(2): C(20)–C(21)–C(22)–C(23)–C(24)–C(25)</td>
<td>Cg(2)•••Cg(2)</td>
<td>3.7791(14)</td>
<td>0.00</td>
<td>13.89</td>
<td>89.72</td>
<td>-5.068</td>
</tr>
</tbody>
</table>

α = dihedral angle between Cg(I) and Cg(J); Cg(I)-Perp = Perpendicular distance of Cg(I) on ring J; Cg(J)-Perp = perpendicular distance of Cg(J) on ring I; β = angle Cg(I)–Cg(J) vector and normal to ring I; γ = angle Cg(I) → Cg(J) vector and normal to plane J

Symmetry code: #1 = x,1+y,z; #2 = 1-x,1-y,1-z; #3 = x,-1+y,z; #4 = -x,1-y,1-z

### Table S4. The experimental ¹H chemical shifts of compounds 4, 5 and 6 in CDCl₃ (* in D₂O/KOD).

<table>
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<th>Aromatic</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>7.71, 8.24, 9.06</td>
</tr>
<tr>
<td>4b</td>
<td>7.75, 7.77, 7.94, 9.02, 9.08</td>
</tr>
<tr>
<td>4c</td>
<td>7.85, 8.41, 9.12, 9.18</td>
</tr>
<tr>
<td>4d</td>
<td>7.69, 7.72, 8.04, 8.99, 9.00</td>
</tr>
<tr>
<td>4e</td>
<td>7.84, 8.88, 9.13, 9.19</td>
</tr>
<tr>
<td>4f*</td>
<td>6.47, 6.61, 7.69, 8.05, 8.28</td>
</tr>
<tr>
<td>4g</td>
<td>7.63, 8.24</td>
</tr>
<tr>
<td>4h</td>
<td>7.67, 7.68, 7.86</td>
</tr>
</tbody>
</table>
For clarity the coupling constants are omitted. SI purchased from Sigma–Aldrich

Table S5. The experimental $^{13}$C{[^1H]} chemical shifts of compounds 4, 5 and 6 in CDCl$_3$ (° in D$_2$O/KOD).

<table>
<thead>
<tr>
<th></th>
<th>Aromatic</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>123.1, 123.9, 126.6, 142.8, 146.9, 150.2</td>
<td>–</td>
</tr>
<tr>
<td>4b</td>
<td>106.7, 119.9, 124.4, 126.3, 126.8, 140.3, 142.0, 144.7, 148.9, 149.7, 151.0, 156.3</td>
<td>–</td>
</tr>
<tr>
<td>4c</td>
<td>124.8, 124.9, 125.6, 126.4, 128.1, 130.7, 143.2, 143.3, 144.4, 147.3, 149.9, 150.4</td>
<td>–</td>
</tr>
<tr>
<td>4d</td>
<td>124.1, 124.9, 126.3, 126.5, 127.2, 134.9, 141.8, 143.1, 146.6, 148.7, 149.5, 149.6</td>
<td>26.5</td>
</tr>
<tr>
<td>4e</td>
<td>108.1, 118.1, 124.2, 125.2, 125.3, 126.5, 135.4, 142.3, 143.6, 147.5, 148.1, 151.5, 153.4</td>
<td>–</td>
</tr>
<tr>
<td>4f*</td>
<td>111.5, 111.6, 114.8, 120.7, 125.1, 132.5, 138.1, 139.2, 140.7, 149.3, 173.8, 178.0, 179.7</td>
<td>–</td>
</tr>
<tr>
<td>4g</td>
<td>122.3, 124.4, 125.1, 143.0, 146.2, 160.1</td>
<td>26.0</td>
</tr>
<tr>
<td>4h</td>
<td>105.6, 118.0, 125.1, 126.1, 140.3, 142.8, 147.0, 154.9, 157.5, 159.1, 161.3</td>
<td>25.3, 25.5</td>
</tr>
<tr>
<td>4i</td>
<td>122.7, 124.5, 124.6, 125.0, 128.0, 129.0, 142.1, 142.3, 144.8, 147.6, 160.2, 160.3</td>
<td>25.3, 25.7</td>
</tr>
<tr>
<td>4j</td>
<td>116.2, 123.2, 125.0, 125.1, 127.8, 129.2, 142.1, 143.0, 145.0, 147.2, 160.0, 160.5</td>
<td>25.2, 25.8</td>
</tr>
<tr>
<td>4k</td>
<td>123.9, 124.5, 124.6, 125.4, 126.9, 133.8, 142.3, 143.1, 144.9, 147.2, 159.0, 159.1</td>
<td>25.2, 25.6, 26.3</td>
</tr>
<tr>
<td>4l</td>
<td>106.9, 118.4, 122.6, 123.7, 125.6, 127.0, 134.3, 142.2, 143.7, 146.1, 146.8, 161.6, 163.8</td>
<td>25.6, 26.2</td>
</tr>
<tr>
<td>4m</td>
<td>122.1, 123.5, 123.8, 124.9, 126.0, 129.3, 141.7, 143.6, 146.3, 146.6, 160.5, 161.5, 169.0</td>
<td>14.1, 25.5, 25.9, 62.6</td>
</tr>
<tr>
<td>5a</td>
<td>105.6, 119.5, 119.6, 148.5, 149.4, 152.9</td>
<td>26.1, 52.4</td>
</tr>
<tr>
<td>5b</td>
<td>105.9, 107.9, 117.7, 118.5, 122.4, 124.1, 145.2, 147.7, 148.2, 148.9, 152.7, 153.9</td>
<td>25.1, 26.1, 52.1, 52.4</td>
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</table>
For clarity the coupling constants are omitted. **SI** purchased from Sigma–Aldrich

### Table S6. The experimental CP/MAS $^{13}$C chemical shifts of selected compounds **4** and **5**.

<table>
<thead>
<tr>
<th></th>
<th>Aromatic</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>4g</strong></td>
<td>121.7, 141.3, 143.8, 159.3</td>
<td>25.1</td>
</tr>
<tr>
<td><strong>4k</strong></td>
<td>122.5, 123.5, 131.0, 139.0, 143.3, 145.3, 158.3</td>
<td>25.0, 27.5</td>
</tr>
<tr>
<td><strong>5c</strong></td>
<td>104.7, 117.5, 147.3, 149.6, 154.6</td>
<td>26.0, 51.8</td>
</tr>
<tr>
<td><strong>5f</strong></td>
<td>109.4, 120.2, 122.0, 123.6, 124.8, 127.4, 139.4, 141.2, 147.5, 149.2, 150.3</td>
<td>–</td>
</tr>
<tr>
<td><strong>5h</strong></td>
<td>111.3, 116.6, 120.7, 123.3, 126.7, 128.2, 133.7, 136.6, 142.0, 147.4, 148.5, 150.3</td>
<td>23.4</td>
</tr>
<tr>
<td><strong>5k</strong></td>
<td>116.8, 123.4, 124.6, 127.2, 135.3, 141.5, 144.8, 147.1, 149.0, 152.6, 153.5, 155.6</td>
<td>25.9</td>
</tr>
<tr>
<td><strong>5l</strong></td>
<td>101.4, 122.9, 130.5, 132.4, 140.8, 142.9, 145.4, 146.5, 152.7</td>
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### Table S7. The experimental CP/MAS $^{15}$N chemical shifts of selected compounds **4** and **5**.

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<th>Others</th>
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<tbody>
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<td><strong>4g</strong></td>
<td>−76.15</td>
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<tr>
<td><strong>4k</strong></td>
<td>−75.52</td>
<td>–</td>
</tr>
<tr>
<td><strong>5c</strong></td>
<td>−62.66</td>
<td>−291.94</td>
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<tr>
<td><strong>5f</strong></td>
<td>−73.05</td>
<td>−250.68</td>
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<tr>
<td><strong>5h</strong></td>
<td>−78.17, −54.38</td>
<td>−254.60, −249.48</td>
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<tr>
<td><strong>5k</strong></td>
<td>−62.21, −51.07</td>
<td>−273.57</td>
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Table S8. Calculated HOMO and LUMO distribution of selected compounds 4.

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<th>LUMO</th>
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<td><img src="image" alt="LUMO 4b" /></td>
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<tr>
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<tr>
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<tr>
<td>4i</td>
<td><img src="image" alt="HOMO 4i" /></td>
<td><img src="image" alt="LUMO 4i" /></td>
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</table>
Table S9. Calculated HOMO and LUMO distribution of selected compounds 5.

<table>
<thead>
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<th>LUMO</th>
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</thead>
<tbody>
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<td><img src="image1" alt="HOMO" /></td>
<td><img src="image2" alt="LUMO" /></td>
</tr>
<tr>
<td>5c</td>
<td><img src="image3" alt="HOMO" /></td>
<td><img src="image4" alt="LUMO" /></td>
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<td><img src="image6" alt="LUMO" /></td>
</tr>
<tr>
<td>5h</td>
<td><img src="image7" alt="HOMO" /></td>
<td><img src="image8" alt="LUMO" /></td>
</tr>
</tbody>
</table>
Fig. S1. Natural atomic charges of compounds 5m (left) and 5n (right).
Fig. S2. The plot of the electrostatic potential for compounds 5m (left) and 5n (right). The calculations were done with the use of the density functional theory (DFT) and were carried out using the Gaussian09 program [1] on B3LYP/6-31g++ level [2, 3]. Molecular geometry of the singlet ground state of the compounds was optimized in the gas phase.


Fig. S1a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 4a.
Fig. S1b. $^{13}$C-$^1$H NMR (CDCl$_3$; 100.5 MHz) spectrum of 4a.
Fig. S2a. $^1$H NMR (CDCl$_3$; 600.2 MHz) spectrum of 4b.

Fig. S2b. $^{13}$C{$^1$H} NMR (CDCl$_3$; 150.0 MHz) spectrum of 4b.

Fig. S2c. $^{19}$F NMR (CDCl$_3$; 470.5 MHz) spectrum of 4b.
**Fig. S2d.** $^{19}$F$^{1}$H NMR (CDCl$_3$; 470.5 MHz) spectrum of 4b.

**Fig. S2e.** MS spectrum of 4b.
**Fig. S3a.** $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 4c.
Fig. S3b. $^{13}\text{C}^{1}\text{H}$ NMR (CDCl$_3$; 100.5 MHz) spectrum of 4c.
Fig. S3c. MS spectrum of 4c.
Fig. S4a. $^1$H NMR (CDCl$_3$; 600.1 MHz) spectrum of 4d.

Fig. S4b. $^{13}$C($^1$H) NMR (CDCl$_3$; 150.0 MHz) spectrum of 4d.
Fig. S4c. MS spectrum of 4d.
**Fig. S5a.** $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 4e

**Fig. S5b.** $^{13}$C{$^1$H} NMR (CDCl$_3$; 100.5 MHz) spectrum of 4e.
Fig. S5c. MS spectrum of 4e
Fig. S6a. $^1$H NMR (D$_2$O/KOD; 500.1 MHz) spectrum of 4f.

Fig. S6b. $^1$H NMR (D$_2$O/D$_2$SO$_4$; 400.1 MHz) spectrum of 4f.
**Fig. S6c.** $^{13}$C$^{1}$H NMR (D$_2$O/KOD; 125.5 MHz) spectrum of 4f.

**Fig. S6d.** $^1$H, $^{13}$C NMR HMQC in D$_2$O spectrum of 4f.
Fig. S6e. $^1$H, $^{13}$C NMR HSQC in D$_2$O spectrum of 4f.

Fig. S6e. MS spectrum of 4f.
Fig. S7a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 4g.

Fig. S7b. $^{13}$C{$^1$H} NMR (CDCl$_3$; 100.5 MHz) spectrum of 4g.
Fig. S7c. $^{13}$C CP/MAS NMR spectrum of 4g.

Fig. S7d. $^{15}$N CP/MAS NMR spectrum of 4g.
Fig. S8a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 4h.

Fig. S8b. $^{13}$C{$^1$H} NMR (CDCl$_3$; 100.5 MHz) spectrum of 4h.

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**Fig. S8c.** $^{19}$F NMR (CDCl$\text{$_3$}$; 470.5 MHz) spectrum of 4h.

**Fig. S8d.** $^{19}$F{$^1$H} NMR (CDCl$\text{$_3$}$; 470.5 MHz) spectrum of 4h.
Fig. S8e. MS spectrum of 4h.
Fig. S9a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 4i.

Fig. S9b. $^{13}$C{$_^1$H} NMR (CDCl$_3$; 100.5 MHz) spectrum of 4i.
Fig. S9c. MS spectrum of 4i.
**Fig. S10a.** $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 4j.

**Fig. S10b.** $^{13}$C{$_^1$H} NMR (CDCl$_3$; 100.5 MHz) spectrum of 4j.
Fig. S10c. MS spectrum of 4j.
Fig. S11a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 4k.

Fig. S11b. $^{13}$C{$^1$H} NMR (CDCl$_3$; 100.5 MHz) spectrum of 4k.
Fig. S11c. $^{13}$C CP/MAS NMR spectrum of 4k.

Fig. S11d. $^{15}$N CP/MAS NMR spectrum of 4k.
Fig. S11e. MS spectrum of 4k.
Fig. S12a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 4l.

Fig. S12b. $^{13}$C{$^1$H} NMR (CDCl$_3$; 125.8 MHz) spectrum of 4l.
Fig. S12c. MS spectrum of 4l.
Fig. S13a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 4m.

Fig. S13b. $^{13}$C {$^1$H} NMR (CDCl$_3$; 100.5 MHz) spectrum of 4m.
Fig. S13c. MS spectrum of 4m.
**Fig. S14a.** $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 5a.

**Fig. S14b.** $^{13}$C{$^1$H} NMR (CDCl$_3$; 100.5 MHz) spectrum of 5a.
Fig. S14c. MS spectrum of 5a.
Fig. S15a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 5b.

Fig. S15b. $^{13}$C{$^1$H} NMR (CDCl$_3$; 100.5 MHz) spectrum of 5b.
Fig. S15c. $^1$H, $^{13}$C NMR HMQC in CDCl$_3$ spectrum of 5b.

Fig. S15d. MS spectrum of 5b.
Fig. S16a. $^1$H NMR (CDCl$_3$; 500.2 MHz) spectrum of 5c.

Fig. S16b. $^{13}$C($^1$H) NMR (CDCl$_3$; 100.5 MHz) spectrum of 5c.
Fig. S16c. $^{13}$C CP/MAS NMR spectrum of 5c.

Fig. S16d. $^{15}$N CP/MAS NMR spectrum of 5c.
Fig. S16e. MS spectrum of 5e.
Fig. S17a. $^1$H NMR (CDCl$_3$; 500.2 MHz) spectrum of 5d.

Fig. S17b. $^{13}$C{$^1$H} NMR (CDCl$_3$; 100.5 MHz) spectrum of 5d.
Fig. S17c. $^{19}$F NMR (CDCl$_3$; 470.5 MHz) spectrum of 5d.

Fig. S17d. $^{19}$F{${}^1$H} NMR (CDCl$_3$; 470.5 MHz) spectrum of 5d.

Fig. S17e. MS spectrum of 5d.
Fig. S18a. $^1\text{H}$ NMR (CDCl$_3$; 400.2 MHz) spectrum of 5e.

Fig. S18b. $^{13}\text{C} \{^1\text{H}\}$ NMR (CDCl$_3$; 100.5 MHz) spectrum of 5e.
Fig. S18c. $^1$H, $^{13}$C NMR HMOC in CDCl$_3$ spectrum of 5e.

Fig. S18d. MS spectrum of 5e
**Fig. S19a.** $^1$H NMR (CDCl$_3$; 500.2 MHz) spectrum of 5f.

**Fig. S19b.** $^{13}$C($^1$H) NMR (CDCl$_3$; 125.8 MHz) spectrum of 5f.
Fig. S19c. $^{13}$C CP/MAS NMR spectrum of 5f.

Fig. S19d. $^{15}$N CP/MAS NMR spectrum of 5f.
Fig. S20a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 5g.

Fig. S20b. $^{13}$C$\{^1$H$\}$ NMR (CDCl$_3$; 100.5 MHz) spectrum of 5g.
Fig. S20c. $^{19}$F NMR (CDCl$_3$; 470.5 MHz) spectrum of 5g.

Fig. S20d. $^{19}$F{${}^1$H} NMR (CDCl$_3$; 470.5 MHz) spectrum of 5g.
Fig. S20e. $^1\text{H}, ^{13}\text{C}$ NMR HMQC in CDCl$_3$ spectrum of 5g.

Fig. S20f. MS spectrum of 5g.
Fig. S21a. $^1$H NMR (CDCl$_3$; 500.2 MHz) spectrum of 5h.

Fig. S21b. $^{13}$C{$^1$H} NMR (CDCl$_3$; 100.5 MHz) spectrum of 5h.
Fig. S21c. 2D-COSY NMR in CDCl₃ spectrum of 5h.

Fig. S21d. ¹H, ¹³C NMR HMQC in CDCl₃ spectrum of 5h.
**Fig. S21e.** $^{13}$C CP/MAS NMR spectrum of 5h.

**Fig. S21f.** $^{15}$N CP/MAS NMR spectrum of 5h.
Fig. S21g. MS spectrum of 5h.
**Fig. S22a.** $^1$H NMR (CDCl$_3$; 500.2 MHz) and spectrum of 5i.

**Fig. S22b.** $^{13}$C-$^1$H NMR (CDCl$_3$; 100.5 MHz) spectrum of 5i.
Fig. S22c. MS spectrum of 5i.
Fig. S23a. $^1$H NMR (CDCl$_3$; 500.2 MHz) spectrum of 5j.

Fig. S23b. $^{13}$C($^1$H) NMR (CDCl$_3$; 125.8 MHz) spectrum of 5j.

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Fig. S23c. $^{19}$F NMR (CDCl$_3$; 470.5 MHz) spectrum of 5j.

Fig. S23d. $^{19}$F{${}^1$H} NMR (CDCl$_3$; 470.5 MHz) spectrum of 5j.

Fig. S23e. MS spectrum of 5j.
Fig. S24a. $^1$H NMR (CDCl$_3$; 500.2 MHz) spectrum of $5k$.

Fig. S24b. $^{13}$C{[$^1$H]} NMR (CDCl$_3$; 100.5 MHz) spectrum of $5k$. 

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Fig. S24c. $^{13}$C CP/MAS NMR spectrum of 5k.

Fig. S24d. $^{15}$N CP/MAS NMR spectrum of 5k.
Fig. S24e. MS spectrum of 5k.
Fig. S25a. $^1$H NMR (CDCl$_3$; 500.2 MHz) spectrum of 5n.

Fig. S25b. $^{13}$C{$^1$H} NMR (CDCl$_3$; 125.8 MHz) spectrum of 5n.
Fig. S25c. MS spectrum of 5n.
Fig. S26a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 5m.

Fig. S26b. $^{13}$C{$^1$H} NMR (CDCl$_3$; 100.6 MHz) spectrum of 5m.
Fig. S26c. 2D-COSY NMR in CDCl$_3$ spectrum of 5m

Fig. S26c. $^1$H, $^{13}$C NMR HMQC in CDCl$_3$ spectrum of 5m.
Fig. S26d. MS spectrum of 5m.
Fig. S27a. $^{13}$C CP/MAS NMR spectrum of 5l.

Fig. S27b. $^{15}$N CP/MAS NMR spectrum of 5l.
Fig. S28a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 6a.

Fig. S28b. $^{13}$C{$^1$}H NMR (CDCl$_3$; 100.6 MHz) spectrum of 6a.
Fig. S28c. MS spectrum of 6a.
Fig. S29a. $^1$H NMR (CDCl$_3$; 400.2 MHz) spectrum of 6b.

Fig. S29b. $^{13}$C{$^1$H} NMR (CDCl$_3$; 100.6 MHz) spectrum of 6b.
Fig. S29c. $^1$H, $^{13}$C NMR HMQC in CDCl$_3$ spectrum of 6b.

Fig. S29d. MS spectrum of 6b.