

## Supporting Information

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## 1. General methods

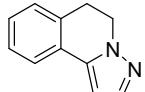
Unless otherwise mentioned, all reagents were purchased from commercial suppliers without further purification. Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Reactions were monitored using Merck Kieselgel 60F<sub>254</sub> aluminium plates. TLC was visualized by UV fluorescence (254 nm) then one of the following: KMnO<sub>4</sub>, phosphomolybdic acid, ninhydrin, *p*-anisaldehyde, vanillin. The Displacement ellipsoids are scaled to the 30% probability level. If not specially mentioned, flash column chromatography was performed using Yantai xinnuo Chemicals (China) (particle size 0.040–0.063 mm). NMR spectra were recorded on JEOL 400 instruments and calibrated by using residual undeuterated chloroform-d ( $\delta$  <sup>1</sup>H = 7.26 ppm,  $\delta$  <sup>13</sup>C = 77.0 ppm) as internal references. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, b = broad, td = triple doublet, dt = double triplet, dq = double quartet, m = multiplet. Infrared (IR) spectra were recorded on an iCAN 9-T FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Q Exactive Orbitrap mass spectrometer using ESI (electrospray ionization) as ionization method. *C,N*-Cyclic azomethine imines **1**<sup>[1]</sup> and enamides **2**<sup>[2]</sup> were synthesized according to the literature methods.

## 2. Experimental procedures and characterization data

### Synthesis of 5,6-dihydropyrazolo[5,1-*a*]isoquinolines

Typical Procedure: To a stirred solution of *C,N*-cyclic azomethine imines (0.22 mmol, 1.1 equiv) in THF (2.0 mL) was added enamides (0.2 mmol, 1.0 equiv) at room temperature. The reaction was stirred at room temperature for 24 h. The reaction mixture was directly charged to column chromatography on silica gel to give the cycloadduct.

#### 5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3aa)<sup>[3]</sup>



Yellow oil, isolated yield 92% (31 mg);

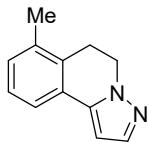
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.56-7.52 (m, 2H), 7.32-7.25 (m, 3H), 6.55 (d,  $J$  = 1.8 Hz, 1H), 4.37 (t,  $J$  = 6.9 Hz, 2H), 3.21 (t,  $J$  = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  139.2, 138.7, 131.7, 128.2, 128.0, 127.3, 127.0, 124.0, 100.5, 46.2, 29.2;

IR (neat):  $\nu$  3856, 3847, 3638, 3456, 2967, 2332, 1656, 1529, 1469, 1378, 1048, 669 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>11</sub>H<sub>11</sub>N<sub>2</sub>: 171.0917; found: 171.0914;

#### 7-methyl-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3ba)



Yellow oil, isolated yield 70% (26 mg);

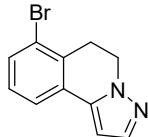
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.52 (d,  $J$  = 1.8 Hz, 1H), 7.42 (d,  $J$  = 7.5 Hz, 1H), 7.20 (t,  $J$  = 7.6 Hz, 1H), 7.13 (d,  $J$  = 7.5 Hz, 1H), 6.53 (d,  $J$  = 1.9 Hz, 1H), 4.36 (t,  $J$  = 7.0 Hz, 2H), 3.15 (t,  $J$  = 7.0 Hz, 2H), 2.35 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  139.2, 138.9, 135.8, 130.0, 129.8, 126.9, 126.8, 121.9, 100.6, 45.7, 25.5, 19.6;

IR (neat):  $\nu$  3905, 3841, 3653, 3427, 2923, 2851, 2370, 1651, 1260, 1096, 1017, 797 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>: 185.1073; found: 185.1070;

#### 7-bromo-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3ca)



Yellow solid, isolated yield 60% (30 mg);

mp: 42.4-43.2 °C;

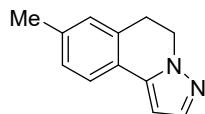
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.54 (d,  $J$  = 1.6 Hz, 1H), 7.51 (s, 1H), 7.49 (d,  $J$  = 1.1 Hz, 1H), 7.17 (t,  $J$  = 7.8 Hz, 1H), 6.56 (d,  $J$  = 1.6 Hz, 1H), 4.37 (t,  $J$  = 7.0 Hz, 2H), 3.34 (t,  $J$  = 7.0 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  139.6, 137.8, 132.0, 131.3, 128.8, 128.6, 124.3, 123.1, 101.2, 45.6, 29.1;

IR (neat):  $\nu$  3902, 3820, 3748, 3433, 2965, 2361, 1634, 1045, 873, 768, 746, 670 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>11</sub>H<sub>10</sub>BrN<sub>2</sub>: 249.0022; found: 249.0017;

#### 8-methyl-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3da)



Colorless oil, isolated yield 94% (34 mg);

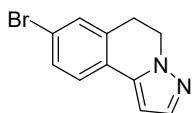
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 (d,  $J$  = 2.0 Hz, 1H), 7.54 (d,  $J$  = 7.8 Hz, 1H), 7.12-7.08 (m, 2H), 6.50 (d,  $J$  = 2.0 Hz, 1H), 4.34 (t,  $J$  = 6.9 Hz, 2H), 3.16 (t,  $J$  = 7.0 Hz, 2H), 2.36 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  139.1, 138.8, 138.0, 131.6, 128.8, 128.0, 124.3, 123.9, 100.0, 46.2, 29.2, 21.3;

IR (neat):  $\nu$  3838, 3748, 3673, 3651, 3444, 2973, 2361, 1735, 1649, 1256, 1051, 748 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>: 185.1073; found: 185.1070;

### 8-bromo-5,6-dihydropyrazolo[5,1-a]isoquinoline (3ea)



Yellow solid, isolated yield 68% (34 mg);

mp: 64.3-65.1 °C;

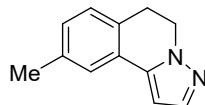
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 (s, 1H), 7.42-7.39 (m, 3H), 6.55 (s, 1H), 4.35 (t,  $J$  = 6.8 Hz, 2H), 3.18 (t,  $J$  = 6.7 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  139.4, 133.6, 131.2, 130.5, 126.0, 125.4, 121.6, 100.92, 100.86, 45.9, 28.9;

IR (neat):  $\nu$  3904, 3805, 3749, 3425, 2971, 2902, 2362, 1651, 1463, 1245, 1041, 876 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>11</sub>H<sub>10</sub>BrN<sub>2</sub>: 249.0022; found: 249.0016;

### 9-methyl-5,6-dihydropyrazolo[5,1-a]isoquinoline (3fa)



Yellow oil, isolated yield 92% (34 mg);

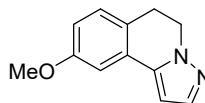
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 (d,  $J$  = 1.8 Hz, 1H), 7.36 (s, 1H), 7.15 (d,  $J$  = 7.7 Hz, 1H), 7.06 (d,  $J$  = 7.7 Hz, 1H), 6.52 (d,  $J$  = 1.7 Hz, 1H), 4.34 (t,  $J$  = 6.9 Hz, 2H), 3.16 (t,  $J$  = 6.9 Hz, 2H), 2.37 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  139.1, 138.8, 137.0, 128.8, 128.7, 128.0, 126.8, 124.5, 100.3, 46.3, 28.8, 21.1;

IR (neat):  $\nu$  3904, 3755, 3653, 3432, 2967, 2921, 2372, 1657, 1493, 1257, 1052, 770 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>: 185.1073; found: 185.1070;

### 9-methoxy-5,6-dihydropyrazolo[5,1-a]isoquinoline (3ga)



Colorless oil, isolated yield 95% (38 mg);

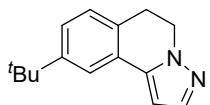
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.52 (d,  $J$  = 1.6 Hz, 1H), 7.17 (d,  $J$  = 8.4 Hz, 1H), 7.06 (d,  $J$  = 2.6 Hz, 1H), 6.80 (dd,  $J$  = 8.4, 2.6 Hz, 1H), 6.53 (d,  $J$  = 1.9 Hz, 1H), 4.34 (t,  $J$  = 6.9 Hz, 2H), 3.84 (s, 3H), 3.13 (t,  $J$  = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  158.9, 139.1, 138.6, 129.2, 127.9, 123.9, 113.7, 109.2, 100.6, 55.4, 46.5, 28.4;

IR (neat):  $\nu$  3855, 3752, 3630, 2971, 2366, 1685, 1499, 1406, 1259, 1049, 879, 800 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>O: 201.1022; found: 201.1018;

### 9-(*tert*-butyl)-5,6-dihydropyrazolo[5,1-a]isoquinoline (3ha)



Yellow oil, isolated yield 77% (36 mg);

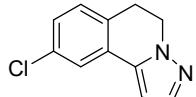
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.56 (d, *J* = 1.7 Hz, 1H), 7.53 (d, *J* = 1.7 Hz, 1H), 7.30 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 1.8 Hz, 1H), 4.35 (t, *J* = 6.9 Hz, 2H), 3.17 (t, *J* = 6.9 Hz, 2H), 1.35 (s, 9H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  150.4, 139.1, 139.0, 128.8, 127.9, 126.6, 125.2, 120.8, 100.2, 46.3, 34.6, 31.3, 28.7;

IR (neat):  $\nu$  3902, 3855, 3751, 3467, 2977, 2360, 2086, 1638, 1406, 1259, 1045, 668 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>: 227.1543; found: 227.1538;

#### 9-chloro-5,6-dihydropyrazolo[5,1-a]isoquinoline (3ia)



Yellow oil, isolated yield 60% (24 mg);

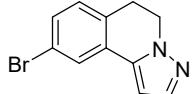
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 (d, *J* = 1.8 Hz, 1H), 7.51 (s, 1H), 7.20 (m, 2H), 6.54 (d, *J* = 1.9 Hz, 1H), 4.35 (t, *J* = 6.9 Hz, 2H), 3.17 (t, *J* = 7.0 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  139.4, 137.5, 133.1, 129.9, 129.5, 128.6, 127.8, 123.9, 101.1, 46.0, 28.7;

IR (neat):  $\nu$  3904, 3749, 3653, 3432, 2969, 23669, 1650, 1405, 1258, 1049, 876, 800 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>11</sub>H<sub>10</sub>ClN<sub>2</sub>: 205.0527; found: 205.0523;

#### 9-bromo-5,6-dihydropyrazolo[5,1-a]isoquinoline (3ja)



Yellow solid, isolated yield 80% (40 mg);

mp: 70.4-71.3 °C;

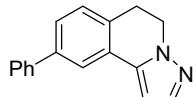
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.66 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.36 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.14 (dd, *J* = 8.1 Hz, 1H), 6.54 (d, *J* = 2.0 Hz, 1H), 4.35 (t, *J* = 6.9 Hz, 2H), 3.15 (t, *J* = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  139.4, 137.3, 130.7, 130.4, 129.8, 128.9, 126.8, 121.0, 101.1, 46.0, 28.7;

IR (neat):  $\nu$  3902, 3749, 3434, 2977, 2901, 2360, 1644, 1406, 1259, 1047, 879, 668 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>11</sub>H<sub>10</sub>BrN<sub>2</sub>: 249.0022; found: 249.0016;

#### 9-phenyl-5,6-dihydropyrazolo[5,1-a]isoquinoline (3ka)



Colorless oil, isolated yield 90% (44 mg);

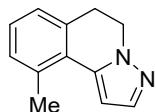
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (s, 1H), 7.63 (s, 1H), 7.61 (s, 1H), 7.56 (s, 1H), 7.49-7.45 (m, 3H), 7.40-7.34 (m, 2H), 6.62 (s, 1H), 4.40 (t, *J* = 6.8 Hz, 2H), 3.25 (t, *J* = 6.7 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  140.6, 140.5, 139.3, 130.6, 128.8, 128.6, 127.5, 127.4, 127.0, 126.8, 122.7, 111.4, 100.8, 46.2, 28.9;

IR (neat):  $\nu$  3856, 3748, 2924, 2364, 1700, 1542, 1468, 1408, 1259, 1044, 758, 668 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>: 247.1230; found: 247.1225;

**10-methyl-5,6-dihdropyrazolo[5,1-*a*]isoquinoline (3la)<sup>[4]</sup>**



Yellow solid, isolated yield 85% (32 mg);

mp: 45.4-46.3 °C;

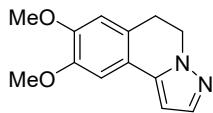
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.57 (d, *J* = 2.0 Hz, 1H), 7.17-7.12 (m, 3H), 6.59 (d, *J* = 2.0 Hz, 1H), 4.36 (t, *J* = 6.9 Hz, 2H), 3.16 (t, *J* = 6.8 Hz, 2H), 2.54 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 138.4, 137.1, 134.5, 133.2, 130.1, 127.6, 126.2, 126.0, 105.0, 46.3, 30.3, 22.2;

IR (neat): ν 3902, 3856, 3748, 3652, 3568, 2921, 2363, 1650, 1510, 1258, 1072, 780 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>: 185.1073; found: 185.1071;

**8,9-dimethoxy-5,6-dihdropyrazolo[5,1-*a*]isoquinoline (3ma)**



Colorless oil, isolated yield 85% (38 mg);

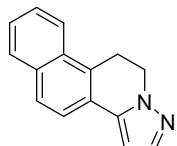
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.50 (d, *J* = 1.8 Hz, 1H), 7.01 (s, 1H), 6.76 (s, 1H), 6.44 (d, *J* = 1.8 Hz, 1H), 4.33 (t, *J* = 7.0 Hz, 2H), 3.93 (s, 3H), 3.91 (s, 3H), 3.13 (t, *J* = 7.0 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 148.9, 148.2, 139.1, 138.7, 124.4, 119.7, 111.2, 107.1, 99.5, 56.1, 56.0, 46.2, 28.8;

IR (neat): ν 3934, 3746, 3569, 3449, 2971, 2371, 1654, 1406, 1261, 1066, 879, 795 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>: 231.1128; found: 231.1123;

**10,11-dihydrobenzo[f]pyrazolo[5,1-*a*]isoquinoline (3na)**



Yellow solid, isolated yield 81% (36 mg);

mp: 104.4-105.2 °C;

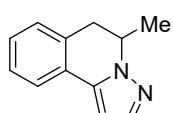
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 1.8 Hz, 1H), 7.57-7.55(m, 1H), 7.52-7.48 (m, 1H), 6.63 (d, *J* = 1.9 Hz, 1H), 4.49 (t, *J* = 7.2 Hz, 2H), 3.60 (t, *J* = 7.2 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 139.4, 139.0, 133.1, 131.2, 128.8, 127.7, 126.9, 126.8, 125.9, 124.1, 123.3, 122.1, 101.2, 45.7, 24.6;

IR (neat): ν 3905, 3855, 3713, 3434, 2979, 2369, 1639, 1508, 1406, 1046, 879, 850 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>: 221.1073; found: 221.1069;

**5-methyl-5,6-dihdropyrazolo[5,1-*a*]isoquinoline (3oa)**



Yellow oil, isolated yield 90% (44 mg);

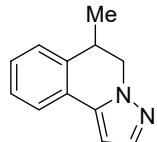
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.55-7.54 (m, 2H), 7.31-7.28 (m, 3H), 6.56 (s, 1H), 4.58 (q, *J* = 6.2 Hz, 1H), 3.32 (dd, *J* = 15.8, 5.4 Hz, 1H), 2.94 (dd, *J* = 15.7 Hz, 1H), 1.51 (d, *J* = 6.5 Hz, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 139.2, 138.1, 130.9, 128.5, 128.0, 127.2, 126.7, 123.8, 100.7, 52.3, 36.6, 19.5;

IR (neat): ν 3910, 3855, 3673, 2972, 2361, 1735, 1538, 1459, 1397, 1256, 1052, 880 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>: 185.1073; found: 185.1070;

#### 6-methyl-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3pa)



Yellow solid, isolated yield 60% (22 mg);

mp: 44.5-45.3 °C;

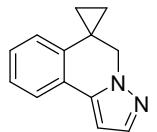
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.57-7.53 (m, 2H), 7.32-7.28 (m, 3H), 6.55 (d, *J* = 2.0 Hz, 1H), 4.37 (dd, *J* = 5.2, 5.2 Hz, 1H), 4.15 (dd, *J* = 5.2, 5.2 Hz, 1H), 3.36-3.28 (m, 1H), 1.32 (d, *J* = 7.0 Hz, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 139.2, 138.1, 137.0, 128.3, 127.3, 126.8, 126.1, 124.1, 100.4, 52.3, 33.9, 19.0;

IR (neat): ν 3837, 3673, 3651, 2971, 2362, 1699, 1538, 1459, 1396, 1052, 880, 798 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>: 185.1073; found: 185.1070;

#### 5'H-spiro[cyclopropane-1,6'-pyrazolo[5,1-*a*]isoquinoline] (3qa)



Yellow oil, isolated yield 85% (34 mg);

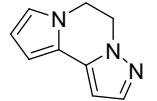
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.60-7.58 (m, 1H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.30-7.25 (m, 2H), 6.97-6.95 (m, 1H), 6.60 (d, *J* = 1.9 Hz, 1H), 4.14 (s, 2H), 1.15-1.12 (m, 2H), 1.05-1.02 (m, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 139.1, 138.9, 136.1, 128.4, 127.6, 126.7, 124.1, 121.9, 100.5, 54.8, 19.5, 14.7;

IR (neat): ν 3856, 3838, 3651, 3444, 2971, 2362, 1650, 1538, 1459, 1398, 1049, 754 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>: 197.1073; found: 197.1070;

#### 5,6-dihydropyrazolo[1,5-*a*]pyrrolo[2,1-*c*]pyrazine (3ra)



Blue oil, isolated yield 70% (22 mg);

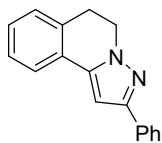
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.48 (s, 1H), 6.72 (s, 1H), 6.42 (d, *J* = 2.7 Hz, 1H), 6.32 (s, 1H), 6.24-6.23 (m, 1H), 4.48 (t, *J* = 5.6 Hz, 2H), 4.31 (t, *J* = 6.3 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 139.6, 134.2, 122.6, 121.0, 109.6, 105.7, 99.2, 46.4, 44.3;

IR (neat): ν 3856, 3748, 3616, 3029, 2924, 2365, 1737, 1542, 1486, 1099, 760, 693 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>9</sub>H<sub>10</sub>N<sub>3</sub>: 160.0869; found: 160.0867;

#### 2-phenyl-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3ab)<sup>[5]</sup>



Yellow oil, isolated yield 93% (46 mg);

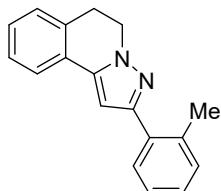
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.87-7.85 (m, 2H), 7.61 (d,  $J$  = 7.5 Hz, 1H), 7.44-7.40 (m, 2H), 7.34-7.27 (m, 4H), 6.86 (s, 1H), 4.41 (t,  $J$  = 6.9 Hz, 2H), 3.25 (t,  $J$  = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  151.3, 140.0, 133.4, 131.6, 128.6, 128.2, 128.1, 127.6, 127.4, 126.9, 125.4, 124.0, 97.6, 46.2, 29.1;

IR (neat):  $\nu$  3854, 3735, 3650, 2972, 2360, 1654, 1540, 1394, 1250, 1066, 879, 788 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>: 247.1230; found: 247.1226;

### 3-(*o*-tolyl)-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3ac)<sup>[5]</sup>



Yellow solid, isolated yield 80% (42 mg);

mp: 92.4-92.9 °C;

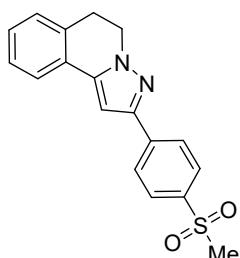
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.63-7.58 (m, 2H), 7.34-7.24 (m, 6H), 6.70 (s, 1H), 4.42 (t,  $J$  = 7.0 Hz, 2H), 3.26 (t,  $J$  = 6.9 Hz, 2H), 2.53 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  151.5, 139.1, 135.9, 133.3, 131.6, 130.7, 129.2, 128.2, 128.0, 127.6, 127.3, 127.0, 125.8, 123.9, 100.7, 46.2, 29.2, 21.2;

IR (neat):  $\nu$  3856, 3748, 3673, 3565, 2970, 2363, 1736, 1649, 1258, 1050, 799, 758 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>: 261.1386; found: 261.1383;

### 2-(4-(methylsulfonyl)phenyl)-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3ad)



Yellow solid, isolated yield 92% (60 mg);

mp: 145.2-146.1 °C;

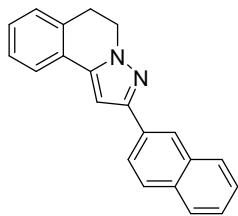
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.04 (d,  $J$  = 8.1 Hz, 2H), 7.97 (d,  $J$  = 8.2 Hz, 2H), 7.60 (d,  $J$  = 7.3 Hz, 1H), 7.37-7.30 (m, 3H), 6.93 (s, 1H), 4.42 (t,  $J$  = 6.9 Hz, 2H), 3.26 (t,  $J$  = 6.9 Hz, 2H), 3.09 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  149.1, 140.5, 138.9, 138.8, 131.6, 128.5, 128.3, 127.8, 127.5, 126.4, 126.0, 124.0, 98.3, 46.4, 44.6, 29.0;

IR (neat):  $\nu$  3904, 3871, 3751, 3676, 3650, 3567, 2971, 2361, 1734, 1260, 1066, 669 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>S: 325.1005; found: 325.1000;

### 2-(naphthalen-2-yl)-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3ae)<sup>[6]</sup>



Yellow solid, isolated yield 92% (54 mg);

mp: 140.1-140.7 °C;

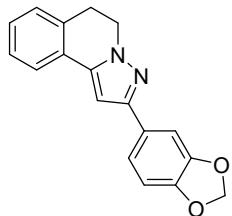
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.32 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.51-7.45 (m, 2H), 7.37-7.33 (m, 1H), 7.30-7.29 (m, 2H), 7.00 (s, 1H), 4.46 (t, *J* = 6.9 Hz, 2H), 3.27 (t, *J* = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 151.2, 140.2, 133.6, 133.0, 131.6, 130.8, 128.3, 128.23, 128.19, 128.16, 127.7, 127.4, 126.8, 126.2, 125.7, 124.0, 123.92, 123.89, 97.8, 46.3, 29.2;

IR (neat): ν 3902, 3748, 3673, 3615, 2972, 2362, 1650, 1538, 1397, 1254, 1052, 756 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>: 297.1386; found: 297.1382;

#### 2-(benzo[d][1,3]dioxol-5-yl)-5,6-dihdropyrazolo[5,1-a]isoquinoline (3af)



Yellow solid, isolated yield 87% (50 mg);

mp: 71.4-72.2 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.35-7.28 (m, 5H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 5.99 (s, 2H), 4.38 (t, *J* = 6.9 Hz, 2H), 3.23 (t, *J* = 6.8 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 151.0, 147.9, 147.2, 140.0, 131.6, 128.2, 128.1, 127.8, 127.4, 126.9, 123.9, 119.1, 108.4, 106.1, 101.0, 97.2, 46.2, 29.2;

IR (neat): ν 3983, 3922, 3690, 3621, 2988, 2901, 1559, 1066, 1027, 893, 867, 794 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>: 291.1128; found: 291.1122;

#### 2-(thiophen-2-yl)-5,6-dihdropyrazolo[5,1-a]isoquinoline (3ag)<sup>[7]</sup>



Yellow oil, isolated yield 95% (48 mg);

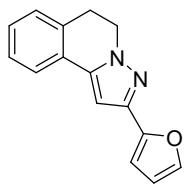
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.57 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 3.2 Hz, 1H), 7.34-7.27 (m, 3H), 7.26-7.25 (m, 1H), 7.07 (t, *J* = 4.2 Hz, 1H), 6.76 (s, 1H), 4.38 (t, *J* = 7.0 Hz, 2H), 3.22 (t, *J* = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 146.5, 140.0, 136.8, 131.7, 128.3, 128.2, 127.44, 127.38, 126.6, 124.3, 124.0, 123.4, 97.5, 46.2, 29.1;

IR (neat): ν 3854, 3735, 3567, 2988, 2360, 1772, 1684, 1541, 1457, 1250, 1066, 892 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>S: 253.0794; found: 253.0791;

#### 2-(furan-2-yl)-5,6-dihdropyrazolo[5,1-a]isoquinoline (3ah)



Yellow oil, isolated yield 78% (36 mg);

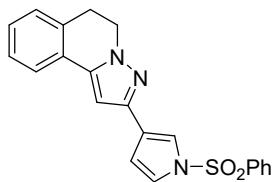
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.77 (s, 1H), 7.35-7.27 (m, 3H), 6.77 (s, 1H), 6.70 (d, *J* = 3.0 Hz, 1H), 6.48 (s, 1H), 4.39 (t, *J* = 6.9 Hz, 2H), 3.23 (t, *J* = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 148.9, 143.7, 141.7, 139.8, 131.7, 128.3, 128.2, 127.4, 126.6, 124.1, 111.3, 105.5, 97.4, 46.3, 29.1;

IR (neat): ν 3857, 3749, 3674, 2923, 2369, 1790, 1717, 1454, 1260, 1015, 798, 752 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>O: 237.1022; found: 237.1019;

### 2-(1-(phenylsulfonyl)-1H-pyrrol-3-yl)-5,6-dihdropyrazolo[5,1-a]isoquinoline (3ai)



Colorless oil, isolated yield 80% (60 mg);

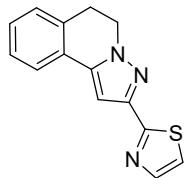
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.59-7.48 (m, 5H), 7.32-7.27 (m, 3H), 7.21 (s, 1H), 6.70 (s, 1H), 6.63 (s, 1H), 4.34 (t, *J* = 6.9 Hz, 2H), 3.20 (t, *J* = 6.8 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 145.5, 139.9, 138.9, 133.9, 131.6, 129.4, 128.23, 128.21, 127.4, 126.9, 126.7, 124.0, 123.1, 121.5, 116.7, 112.4, 97.8, 46.1, 29.1;

IR (neat): ν 3857, 3748, 3673, 3651, 2971, 2362, 1700, 1650, 1255, 1060, 893, 798 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>18</sub>N<sub>3</sub>O<sub>2</sub>S: 376.1114; found: 376.1107;

### 2-(5,6-dihdropyrazolo[5,1-a]isoquinolin-2-yl)thiazole (3aj)



Colorless oil, isolated yield 88% (44 mg);

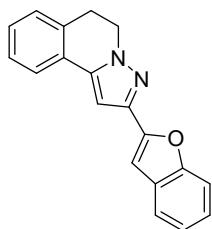
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.85 (d, *J* = 3.1 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.34-7.29 (m, 4H), 7.13 (s, 1H), 4.42 (t, *J* = 7.0 Hz, 2H), 3.25 (t, *J* = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 162.1, 146.6, 143.1, 140.4, 131.6, 128.6, 128.2, 127.6, 126.4, 124.2, 118.3, 98.6, 46.5, 29.0;

IR (neat): ν 3904, 3854, 3650, 3567, 2972, 2361, 1734, 1654, 1599, 1259, 1066, 761 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>S: 254.0746; found: 254.0743;

### 2-(benzofuran-2-yl)-5,6-dihdropyrazolo[5,1-a]isoquinoline (3ak)



Yellow solid, isolated yield 91% (52 mg);

mp: 86.5-87.4 °C;

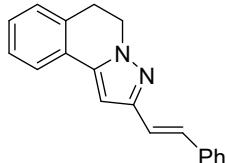
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.62-7.56 (m, 3H), 7.37-7.27 (m, 4H), 7.24-7.22 (m, 1H), 7.05 (s, 1H), 6.95 (s, 1H), 4.45 (t, *J* = 7.0 Hz, 2H), 3.25 (t, *J* = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 154.6, 150.8, 143.2, 140.0, 131.6, 128.9, 128.5, 128.2, 127.5, 126.5, 124.2, 124.1, 122.9, 120.9, 111.3, 101.8, 98.5, 46.4, 29.0;

IR (neat): ν 3946, 3858, 3741, 3464, 2982, 2571, 1550, 1438, 1359, 1298, 1049, 754 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>O: 287.1179; found: 287.1174;

#### (E)-2-styryl-5,6-dihdropyrazolo[5,1-a]isoquinoline (3al)



Yellow oil, isolated yield 60% (32 mg);

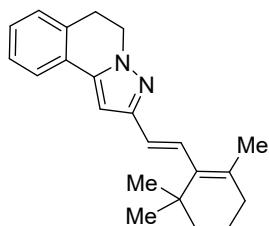
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.38-7.27 (m, 6H), 7.16 (s, 2H), 6.76 (s, 1H), 4.37 (t, *J* = 6.5 Hz, 2H), 3.23 (t, *J* = 6.8 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 150.4, 139.8, 137.2, 131.7, 129.6, 128.7, 128.2 (2C), 127.6, 127.4, 126.7, 126.4, 124.0, 120.6, 97.6, 46.2, 29.1;

IR (neat): ν 3854, 3752, 2988, 2361, 1717, 1654, 1541, 1457, 1394, 1250, 1066, 892 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub>: 273.1386; found: 273.1381;

#### (E)-2-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)vinyl)-5,6-dihdropyrazolo[5,1-a]isoquinoline (3am)



Yellow oil, isolated yield 68% (44 mg);

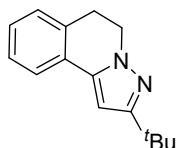
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.33-7.26 (m, 3H), 6.74 (d, *J* = 16.5 Hz, 1H), 6.67 (s, 1H), 6.38 (d, *J* = 16.5 Hz, 1H), 4.33 (t, *J* = 6.9 Hz, 2H), 3.20 (t, *J* = 6.8 Hz, 2H), 2.04 (t, *J* = 5.8 Hz, 2H), 1.79 (s, 3H), 1.67-1.61 (m, 2H), 1.51-1.48 (m, 2H), 1.79 (s, 6H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 151.1, 139.6, 137.2, 131.7, 129.9, 128.8, 128.2, 128.1, 127.3, 126.9, 124.7, 124.0, 96.8, 46.1, 39.6, 34.2, 33.0, 29.1, 28.9, 21.7, 19.2;

IR (neat): ν 3901, 3855, 3802, 3649, 3444, 2972, 2361, 1649, 1538, 1397, 1049, 757 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>27</sub>N<sub>2</sub>: 319.2169; found: 319.2161;

#### 2-(tert-butyl)-5,6-dihdropyrazolo[5,1-a]isoquinoline (3an)



Yellow oil, isolated yield 85% (38 mg);

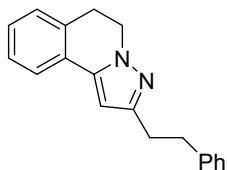
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.52 (d,  $J$  = 7.6 Hz, 1H), 7.30-7.27 (m, 1H), 7.24-7.20 (m, 2H), 6.41 (s, 1H), 4.30 (t,  $J$  = 6.8 Hz, 2H), 3.18 (t,  $J$  = 6.8 Hz, 2H), 1.36 (s, 9H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  162.0, 138.9, 131.6, 128.1, 127.7, 127.2 (2C), 123.8, 96.8, 45.9, 32.1, 30.7, 29.2;

IR (neat):  $\nu$  3946, 3838, 3677, 3546, 2971, 2562, 1678, 1536, 1460, 1408, 1066, 669 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>: 227.1543; found: 227.1547;

### 2-phenethyl-5,6-dihydropyrazolo[5,1-a]isoquinoline (3ao)



Yellow solid, isolated yield 99% (54 mg);

mp: 72.4-73.3 °C;

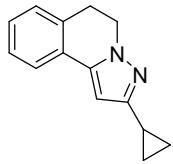
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.50 (d,  $J$  = 7.4 Hz, 1H), 7.34-7.27 (m, 5H), 7.24-7.22 (m, 3H), 6.35 (s, 1H), 4.32 (t,  $J$  = 6.9 Hz, 2H), 3.20 (t,  $J$  = 6.9 Hz, 2H), 3.05-2.97 (m, 4H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  152.4, 141.9, 139.3, 131.6, 128.4, 128.3, 128.1, 127.9, 127.3, 127.1, 125.9, 123.8, 99.2, 45.9, 36.1, 30.4, 29.2;

IR (neat):  $\nu$  3904, 3751, 3650, 3567, 2988, 2360, 1772, 1734, 1394, 1250, 1066, 892 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>19</sub>N<sub>2</sub>: 275.1543; found: 275.1535;

### 2-cyclopropyl-5,6-dihydropyrazolo[5,1-a]isoquinoline (3ap)



Yellow oil, isolated yield 95% (40 mg);

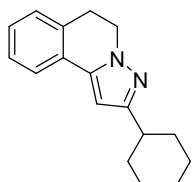
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.48 (d,  $J$  = 7.4 Hz, 1H), 7.29-7.26 (m, 1H), 7.23-7.20 (m, 2H), 6.21 (s, 1H), 4.26 (t,  $J$  = 6.9 Hz, 2H), 3.17 (t,  $J$  = 6.9 Hz, 2H), 2.00-1.93 (m, 1H), 0.96-0.92 (m, 2H), 0.79-0.75 (m, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  155.1, 139.3, 131.6, 128.1, 127.9, 127.2, 127.0, 123.8, 96.7, 45.9, 29.2, 9.2, 7.9;

IR (neat):  $\nu$  3904, 3855, 3752, 3677, 3650, 3568, 2971, 2364, 2344, 1654, 1050, 758 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>: 211.1230; found: 211.1226;

### 2-cyclohexyl-5,6-dihydropyrazolo[5,1-a]isoquinoline (3aq)



Colorless oil, isolated yield 93% (46 mg);

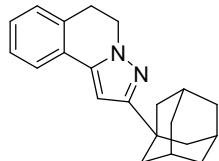
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.29-7.26 (m, 1H), 7.23-7.2 (m, 2H), 6.35 (s, 1H), 4.29 (t, *J* = 6.9 Hz, 2H), 3.18 (t, *J* = 6.9 Hz, 2H), 2.70-2.64 (m, 1H), 2.03 (d, *J* = 11.7 Hz, 2H), 1.84 (d, *J* = 11.9 Hz, 2H), 1.73 (d, *J* = 12.6 Hz, 1H), 1.52-1.35 (m, 5H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 158.4, 139.0, 131.6, 128.1, 127.8, 127.21, 127.17, 123.8, 97.3, 45.9, 37.7, 33.4, 29.2, 26.4, 26.1;

IR (neat): ν 3902, 3820, 3651, 3395, 2975, 2898, 2362, 1650, 1453, 1083, 1047, 879 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>: 253.1699; found: 253.1695;

### 2-((3*r*,5*r*,7*r*)-adamantan-1-yl)-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3ar)



Yellow solid, isolated yield 80% (48 mg);

mp: 98.8-99.6 °C;

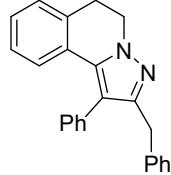
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.51 (d, *J* = 7.4 Hz, 1H), 7.29-7.26 (m, 1H), 7.23-7.21 (m, 2H), 6.39 (s, 1H), 4.30 (t, *J* = 6.8 Hz, 2H), 3.18 (t, *J* = 6.8 Hz, 2H), 2.08 (s, 3H), 2.00 (s, 6H), 1.79 (s, 6H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 162.4, 138.8, 131.6, 128.1, 127.7, 127.25, 127.19, 123.8, 96.3, 46.0, 42.8, 36.8, 34.0, 29.2, 28.7;

IR (neat): ν 3857, 3820, 3673, 3565, 2972, 2903, 2362, 1736, 1538, 1397, 1052, 893 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>25</sub>N<sub>2</sub>: 305.2012; found: 305.2006;

### 2-benzyl-1-phenyl-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3as)



Yellow solid, isolated yield 99% (68 mg);

mp: 82.9-83.7 °C;

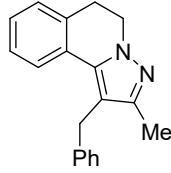
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.40-7.35 (m, 3H), 7.24-7.12 (m, 9H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.00 (s, 1H), 4.36 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 2H), 3.22 (t, *J* = 6.8 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 149.4, 140.2, 135.1, 133.8, 132.5, 130.4, 128.59, 128.58, 128.18, 128.15, 127.6, 127.3, 127.1, 126.9, 125.8, 124.2, 117.6, 46.3, 32.5, 29.6;

IR (neat): ν 3904, 3854, 3751, 3567, 3446, 2988, 2363, 1653, 1558, 1457, 1066, 668 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>21</sub>N<sub>2</sub>: 337.1699; found: 337.1696;

### 1-benzyl-2-methyl-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3at)



Yellow oil, isolated yield 92% (50 mg);

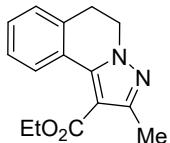
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.40 (d, *J* = 7.2 Hz, 1H), 7.30-7.28 (m, 2H), 7.26-7.25 (m, 1H), 7.21-7.17 (m, 5H), 4.32 (t, *J* = 6.7 Hz, 2H), 4.11 (s, 2H), 3.16 (t, *J* = 6.7 Hz, 2H), 2.21 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  147.8, 140.0, 135.8, 132.7, 128.5, 128.3, 127.9, 127.7, 127.5, 127.3, 126.0, 123.9, 112.4, 46.1, 29.9, 29.8, 11.7;

IR (neat):  $\nu$  3854, 3751, 3650, 2972, 2360, 1558, 1541, 1507, 1457, 1419, 1050, 668 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>19</sub>N<sub>2</sub>: 275.1543; found: 275.1538;

**ethyl 2-methyl-5,6-dihydropyrazolo[5,1-*a*]isoquinoline-1-carboxylate (3au)**



Yellow solid, isolated yield 98% (50 mg);

mp: 63.2-64.1 °C;

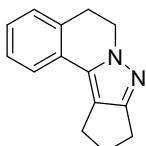
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.40 (d,  $J$  = 8.9 Hz, 1H), 7.36-7.25 (m, 3H), 4.35 (q,  $J$  = 7.1 Hz, 2H), 4.24 (t,  $J$  = 6.7 Hz, 2H), 3.12 (t,  $J$  = 6.8 Hz, 2H), 2.48 (s, 3H), 1.39 (t,  $J$  = 7.1 Hz, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  164.6, 151.2, 140.7, 133.5, 129.2, 128.0, 127.7, 127.1, 126.1, 108.0, 60.1, 46.3, 29.6, 14.8, 14.3;

IR (neat):  $\nu$  3904, 3854, 3751, 3567, 3274, 2971, 2360, 1654, 1558, 1541, 1049, 669 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>: 257.1285; found: 257.1280;

**5,9,10,11-tetrahydro-6H-cyclopenta[3,4]pyrazolo[5,1-*a*]isoquinoline (5aa)**



Yellow oil, isolated yield 60% (24 mg);

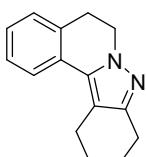
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.44 (d,  $J$  = 7.5 Hz, 1H), 7.30-7.21 (m, 3H), 4.30 (t,  $J$  = 6.9 Hz, 2H), 3.18 (t,  $J$  = 6.9 Hz, 2H), 2.86 (t,  $J$  = 6.9 Hz, 2H), 2.75 (t,  $J$  = 7.2 Hz, 2H), 2.54-2.46 (m, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  161.1, 132.7, 131.9, 128.1, 127.8, 127.4, 127.2, 124.1, 120.9, 46.6, 30.2, 29.6, 24.5, 23.9;

IR (neat):  $\nu$  3838, 3748, 3423, 2972, 2361, 1649, 1397, 1258, 1048, 879, 774, 689 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>: 211.1230; found: 211.1226;

**5,6,9,10,11,12-hexahydroindazolo[3,2-*a*]isoquinoline (5ab)**



Yellow oil, isolated yield 94% (42 mg);

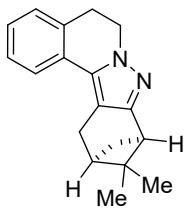
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 (d,  $J$  = 7.6 Hz, 1H), 7.31-7.28 (m, 1H), 7.25-7.19 (m, 2H), 4.28 (t,  $J$  = 6.8 Hz, 2H), 3.16 (t,  $J$  = 6.8 Hz, 2H), 2.83-2.81 (m, 2H), 2.72-2.70 (m, 2H), 1.85-1.84 (m, 4H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  148.9, 133.9, 132.1, 128.3, 128.2, 127.2, 127.1, 123.8, 112.2, 46.1, 29.7, 23.6 (2C), 23.1, 22.3;

IR (neat):  $\nu$  3838, 3748, 3444, 2974, 2361, 1649, 1396, 1255, 1050, 879, 692, 668 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>: 225.1386; found: 225.1381;

**(9*R*,11*R*)-10,10-dimethyl-5,6,9,10,11,12-hexahydro-9,11-methanoindazolo[3,2-*a*]isoquinoline (5ac)**



Yellow oil, isolated yield 60% (32 mg);

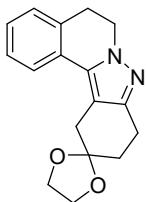
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 (d,  $J$  = 7.6 Hz, 1H), 7.32-7.27 (m, 1H), 7.25-7.20 (m, 2H), 4.32-4.21 (m, 2H), 3.26-3.17 (m, 2H), 3.03-2.87 (m, 3H), 2.78-2.72 (m, 1H), 2.37-2.32 (m, 1H), 4.14-4.12 (m, 4H), 0.75 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  159.1, 134.3, 132.1, 128.2 (2C), 127.3, 127.1, 124.0, 108.6, 46.0, 41.8, 41.3, 41.1, 32.6, 29.7, 26.4, 26.0, 21.5;

IR (neat):  $\nu$  3901, 3855, 3747, 3673, 3615, 2922, 2361, 1699, 1649, 1257, 1052, 763 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>: 265.1699; found: 265.1694;

#### 5,9,10,12-tetrahydro-6H-spiro[indazolo[3,2-a]isoquinoline-11,2'-[1,3]dioxolane] (5ad)



Yellow oil, isolated yield 95% (54 mg);

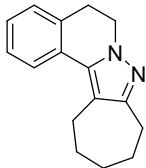
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.45 (d,  $J$  = 7.6 Hz, 1H), 7.30-7.26 (m, 1H), 7.25-7.20 (m, 2H), 4.28 (t,  $J$  = 6.8 Hz, 2H), 4.06 (s, 4H), 3.15 (t,  $J$  = 6.8 Hz, 2H), 3.05 (s, 2H), 2.92 (t,  $J$  = 6.6 Hz, 2H), 2.03 (t,  $J$  = 6.6 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  147.0, 134.6, 132.2, 128.2, 127.9, 127.4, 127.1, 123.6, 110.2, 108.9, 64.7, 46.2, 33.3, 31.7, 29.6, 21.3;

IR (neat):  $\nu$  3903, 3856, 3749, 3652, 3449, 2919, 2365, 1650, 1260, 1058, 798, 671 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>: 283.1141; found: 283.1143;

#### 5,9,10,11,12,13-hexahydro-6H-cyclohepta[3,4]pyrazolo[5,1-a]isoquinoline (5ae)



Yellow solid, isolated yield 93% (44 mg);

mp: 41.3-42.1 °C;

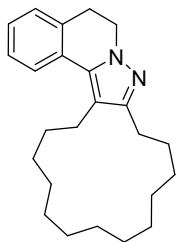
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.64 (d,  $J$  = 7.7 Hz, 1H), 7.30-7.28 (m, 2H), 7.24-7.20 (m, 1H), 4.22 (t,  $J$  = 6.6 Hz, 2H), 3.11 (t,  $J$  = 6.6 Hz, 2H), 2.90 (t,  $J$  = 5.4 Hz, 2H), 2.80 (t,  $J$  = 5.4 Hz, 2H), 1.87-1.86 (m, 2H), 1.73-1.72 (m, 4H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  153.6, 134.3, 133.2, 128.6, 128.3, 127.2, 127.1, 124.2, 117.0, 45.9, 32.1, 30.1, 29.4, 29.0, 27.5, 25.4;

IR (neat):  $\nu$  3837, 3801, 3747, 3444, 2975, 2903, 2360, 1649, 1556, 1252, 1051, 879 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>: 239.1543; found: 239.1537;

#### 5,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23-hexadecahydro-6H-cycloheptadeca[3,4]pyrazolo[5,1-a]isoquinoline (5af)



Yellow solid, isolated yield 75% (56 mg);

mp: 84.1–84.9 °C;

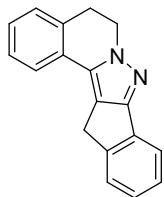
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.25–7.20 (m, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 3.13 (t, *J* = 6.5 Hz, 2H), 2.68–2.58 (m, 4H), 1.73–1.30 (m, 20H), 1.05–0.83 (m, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 151.4, 134.6, 132.7, 128.3 (2C), 127.23, 127.15, 123.6, 115.4, 46.1, 29.9, 29.7, 28.8, 28.7, 27.4, 27.3, 26.8, 26.7, 26.5, 25.9, 25.8, 25.2, 25.0, 24.1;

IR (neat): ν 3854, 3650, 3434, 2988, 2360, 1654, 1541, 1458, 1396, 1045, 692, 669 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>35</sub>N<sub>2</sub>: 351.2795; found: 351.2788;

#### 5,13-dihydro-6H-indeno[1',2':3,4]pyrazolo[5,1-*a*]isoquinoline (5ag)



Yellow oil, isolated yield 55% (28 mg);

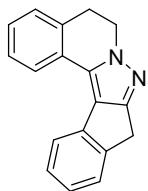
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.80 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.39–7.35 (m, 2H), 7.31–7.28 (m, 3H), 4.47 (t, *J* = 6.8 Hz, 2H), 3.96 (s, 2H), 3.28 (t, *J* = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 159.3, 148.1, 134.9, 133.4, 132.0, 128.3, 127.9, 127.5, 127.3, 127.0, 126.4, 125.8, 124.5, 119.8, 119.7, 46.9, 29.5, 29.4;

IR (neat): ν 3878, 3855, 3621, 3444, 2960, 2365, 1688, 1588, 1449, 1368, 1069, 669 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>: 259.1230; found: 259.1226;

#### 5,9-dihydro-6H-indeno[2',1':3,4]pyrazolo[5,1-*a*]isoquinoline (5ah)



Yellow oil, isolated yield 70% (36 mg);

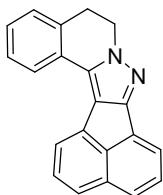
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.47–7.43 (m, 1H), 7.39–7.29 (m, 3H), 7.24–7.20 (m, 1H), 4.43 (t, *J* = 6.6 Hz, 2H), 3.80 (s, 2H), 3.24 (t, *J* = 6.6 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 159.7, 145.4, 136.3, 132.7, 131.9, 128.3, 128.0, 127.8, 127.4, 126.9, 125.7, 125.3, 124.9, 122.3, 120.7, 46.9, 30.4, 29.8;

IR (neat): ν 3856, 3837, 3748, 3564, 3444, 2975, 2361, 1649, 1556, 1397, 1048, 670 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>: 259.1230; found: 259.1225;

#### 9,10-dihydroacenaphtho[1',2':3,4]pyrazolo[5,1-*a*]isoquinoline (5ai)



Colorless oil, isolated yield 70% (42 mg);

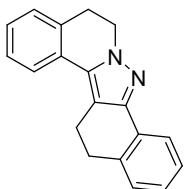
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.02 (d,  $J$  = 7.6 Hz, 1H), 7.95 (d,  $J$  = 6.9 Hz, 1H), 7.91 (d,  $J$  = 6.8 Hz, 1H), 7.82 (d,  $J$  = 8.2 Hz, 1H), 7.75 (d,  $J$  = 8.3 Hz, 1H), 7.64-7.58 (m, 2H), 7.52-7.48 (m, 1H), 7.37-7.36 (m, 2H), 4.51 (t,  $J$  = 6.8 Hz, 2H), 3.31 (t,  $J$  = 6.7 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  158.0, 136.5, 133.2, 132.8, 131.0, 130.6, 130.0, 128.41, 128.38, 127.71, 127.66, 127.5, 127.3, 126.8, 125.5, 125.3, 120.2, 120.1, 120.0, 47.0, 29.6;

IR (neat):  $\nu$  3902, 3856, 3802, 3673, 3566, 2973, 2362, 1736, 1700, 1539, 1052, 893 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>15</sub>N<sub>2</sub>: 295.1230; found: 295.1225;

### 5,6,13,14-tetrahydrobenzo[6,7]indazolo[3,2-a]isoquinoline (5aj)



Yellow oil, isolated yield 92% (50 mg);

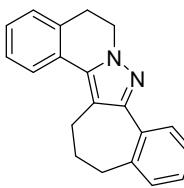
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.87 (d,  $J$  = 7.4 Hz, 1H), 7.61 (d,  $J$  = 7.6 Hz, 1H), 7.36-7.28 (m, 4H), 7.25-7.24 (m, 2H), 4.40 (t,  $J$  = 6.8 Hz, 2H), 3.21 (t,  $J$  = 6.8 Hz, 2H), 3.09-3.03 (m, 4H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  147.6, 136.0, 133.9, 132.4, 129.9, 128.3, 128.2, 128.0, 127.5, 127.3, 127.2, 126.8, 124.0, 121.9, 112.4, 46.5, 29.7, 29.5, 20.2;

IR (neat):  $\nu$  3838, 3748, 3444, 2983, 2361, 1649, 1556, 1397, 1252, 1050, 877, 769 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub>: 273.1386; found: 273.1381;

### 5,13,14,15-tetrahydro-6H-benzo[6',7']cyclohepta[1',2':3,4]pyrazolo[5,1-a]isoquinoline (5ak)



Colorless oil, isolated yield 87% (50 mg);

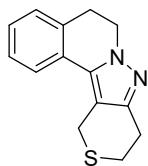
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.06 (d,  $J$  = 8.6 Hz, 1H), 7.71 (d,  $J$  = 7.6 Hz, 1H), 7.36-7.28 (m, 3H), 7.25-7.18 (m, 3H), 4.41 (t,  $J$  = 6.7 Hz, 2H), 3.21 (t,  $J$  = 6.8 Hz, 2H), 3.06 (t,  $J$  = 6.8 Hz, 2H), 2.90-2.87 (m, 2H), 2.21-2.15 (m, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  149.0, 141.0, 135.2, 133.1, 132.7, 129.2, 128.34, 128.29, 127.4, 127.21, 127.20, 127.1, 126.3, 123.9, 114.9, 46.5, 34.7, 29.9, 27.8, 26.5;

IR (neat):  $\nu$  3902, 3856, 3748, 3615, 2923, 2368, 1650, 1541, 1459, 1260, 1027, 762 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>19</sub>N<sub>2</sub>: 287.1543; found: 287.1536;

### 5,9,10,12-tetrahydro-6H-thiopyrano[4',3':3,4]pyrazolo[5,1-a]isoquinoline (5al)



Yellow oil, isolated yield 72% (34 mg);

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.48 (d,  $J$  = 7.6 Hz, 1H), 7.34-7.27 (m, 2H), 7.25-7.23 (m, 1H), 4.29 (t,  $J$  = 6.8 Hz, 2H), 3.96 (s, 2H), 3.17 (t,  $J$  = 6.6 Hz, 2H), 3.05-3.02 (m, 2H), 2.97-2.94 (m, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  147.1, 133.6, 132.4, 128.4, 127.7, 127.6, 127.3, 123.8, 108.4, 46.2, 29.7, 26.2, 25.8, 23.9;

IR (neat):  $\nu$  3904, 3854, 3650, 3567, 2972, 2364, 1869, 1654, 1541, 1457, 1066, 668 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>S: 243.0951; found: 243.0944;

#### **benzyl 5,9,10,12-tetrahydropyrido[4',3':3,4]pyrazolo[5,1-a]isoquinoline-11(6H)-carboxylate (5am)**



Yellow oil, isolated yield 80% (38 mg);

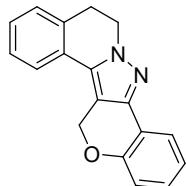
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.39-7.27 (m, 9H), 5.20 (s, 2H), 4.83-4.82 (m, 2H), 4.30 (t,  $J$  = 6.8 Hz, 2H), 3.90-3.76 (m, 2H), 3.18 (t,  $J$  = 6.8 Hz, 2H), 2.82-2.81 (m, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  155.7, 146.0, 136.7, 133.5, 132.0, 128.5, 128.3, 128.0, 127.9, 127.8, 127.4, 124.1, 123.9, 109.0, 67.3, 46.2, 41.9, 29.5, 24.0, 23.7;

IR (neat):  $\nu$  3855, 3752, 3650, 3630, 2923, 2364, 1700, 1458, 1419, 1227, 1108, 763 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>: 360.1707; found: 360.1704;

#### **11,12-dihydro-6H-chromeno[4',3':3,4]pyrazolo[5,1-a]isoquinoline (5an)**



Yellow solid, isolated yield 90% (50 mg);

mp: 125.7-126.4 °C;

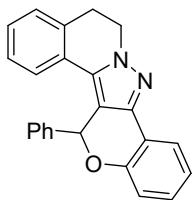
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (dd,  $J$  = 7.6, 1.5 Hz, 1H), 7.36-7.28 (m, 3H), 7.24-7.18 (m, 2H), 7.03-6.96 (m, 2H), 5.57 (s, 2H), 4.40 (t,  $J$  = 6.8 Hz, 2H), 3.23 (t,  $J$  = 6.8 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  153.8, 142.9, 133.3, 132.4, 129.2, 128.5, 128.2, 127.5, 126.9, 124.3, 122.0, 121.8, 118.3, 117.0, 107.8, 64.0, 46.5, 29.5;

IR (neat):  $\nu$  3874, 3588, 3431, 3244, 2887, 2562, 1750, 1488, 1459, 1378, 1059, 668 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>O: 275.1179; found: 275.1174;

#### **5-phenyl-11,12-dihydro-6H-chromeno[4',3':3,4]pyrazolo[5,1-a]isoquinoline (5ao)**



Colorless oil, isolated yield 60% (42 mg);

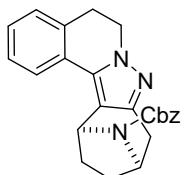
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.79 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.29-7.26 (m, 3H), 7.23-7.21 (m, 2H), 7.18-7.12 (m, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.74 (s, 1H), 4.57-4.39 (m, 2H), 3.35-3.18 (m, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  152.1, 142.9, 139.5, 134.2, 132.4, 129.3, 128.6, 128.5, 128.4, 128.2, 127.8, 127.5, 126.6, 124.5, 122.0, 121.7, 118.3, 117.8, 109.8, 75.4, 46.6, 29.5;

IR (neat):  $\nu$  3904, 3654, 3752, 3676, 3630, 2971, 2360, 1654, 1559, 1395, 1066, 668 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>19</sub>N<sub>2</sub>O: 351.1492; found: 351.1489;

#### Benzyl-5,9,10,11,12,13-hexahydro-6H-10,13-epiminocyclohepta[3,4]pyrazolo[5,1-*a*]isoquinoline-14-carboxylate (5ap)



Yellow oil, isolated yield 98% (76 mg);

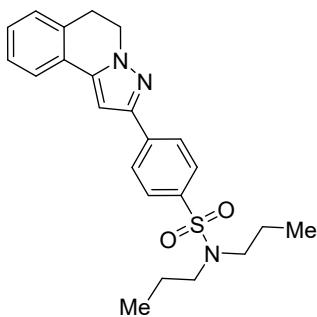
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.52-7.27 (m, 6H), 7.26-7.21 (m, 3H), 5.56-5.40 (m, 1H), 5.16-5.01 (m, 2H), 4.78-4.58 (m, 1H), 4.44-4.11 (m, 2H), 3.50-3.01 (m, 3H), 2.60 (d, *J* = 15.9 Hz, 1H), 2.46-2.16 (m, 2H), 2.05-1.97 (m, 1H), 1.78-1.72 (m, 1H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  153.8, 144.7, 136.7, 132.34, 132.31, 131.9, 128.4, 128.3, 127.9, 127.8, 127.7, 127.4, 124.3, 117.0, 66.9, 52.1, 51.8, 46.2, 34.8, 32.4, 29.5, 29.2;

IR (neat):  $\nu$  3855, 3752, 3650, 3630, 2923, 2364, 1700, 1458, 1419, 1227, 1108, 763 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>24</sub>N<sub>3</sub>O<sub>2</sub>: 386.1863; found: 386.1854;

#### 4-(5,6-dihydropyrazolo[5,1-*a*]isoquinolin-2-yl)-N,N-dipropylbenzenesulfonamide (7aa)



Yellow oil, isolated yield 67% (54 mg);

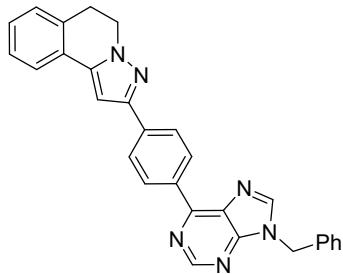
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.96 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.36-7.26 (m, 3H), 6.90 (s, 1H), 4.41 (t, *J* = 6.9 Hz, 2H), 3.24 (t, *J* = 6.9 Hz, 2H), 3.10 (t, *J* = 7.6 Hz, 4H), 1.54 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  149.5, 140.4, 138.7, 137.3, 131.6, 128.4, 128.3, 127.5, 127.4, 126.5, 125.7, 124.0, 98.1, 49.8, 46.4, 29.0, 21.9, 11.2;

IR (neat):  $\nu$  3903, 3856, 3748, 3673, 2923, 2369, 1650, 1557, 1459, 1421, 1090, 745 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>23</sub>H<sub>28</sub>N<sub>3</sub>O<sub>2</sub>S: 410.1897; found: 410.1892;

**2-(4-(9-benzyl-9H-purin-6-yl)phenyl)-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (7ab)**



Yellow solid, isolated yield 75% (68 mg);

mp: 201.2-201.8 °C;

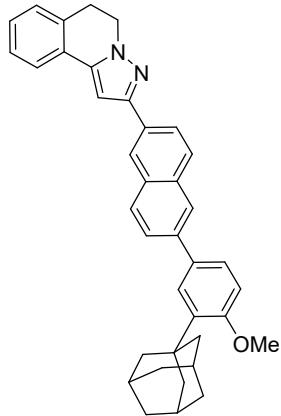
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.06 (s, 1H), 8.91 (d, *J* = 8.4 Hz, 2H), 8.11 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.37-7.31 (m, 6H), 7.28-7.26 (m, 2H), 6.95 (s, 1H), 5.49 (s, 2H), 4.44 (t, *J* = 6.9 Hz, 2H), 3.25 (t, *J* = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 154.5, 152.6, 152.5, 150.6, 144.0, 140.2, 135.9, 135.2, 134.7, 131.6, 130.8, 130.2, 129.1, 128.5, 128.2 (2C), 127.8, 127.4, 126.7, 125.6, 124.0, 98.1, 47.2, 46.3, 29.7;

IR (neat): ν 3972, 3899, 3685, 3566, 2970, 1394, 1249, 1066, 891, 754, 720, 679 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>29</sub>H<sub>23</sub>N<sub>6</sub>: 455.1979; found: 455.1971;

**2-(6-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (7ac)**



Yellow solid, isolated yield 62% (66 mg);

mp: 135.7-136.4 °C;

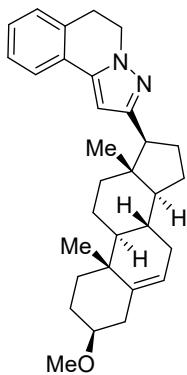
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.32 (s, 1H), 8.05-7.93 (m, 4H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.67-7.60 (m, 2H), 7.55 (d, *J* = 10.1 Hz, 1H), 7.39-7.29 (m, 3H), 7.00 (d, *J* = 8.9 Hz, 2H), 4.46 (t, *J* = 6.9 Hz, 2H), 3.90 (s, 3H), 3.27 (t, *J* = 6.9 Hz, 2H), 2.20 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 158.5, 151.3, 140.2, 138.9, 138.8, 133.4, 133.1, 132.4, 131.7, 130.5, 128.5, 128.4, 128.24, 128.19, 127.4, 126.9, 126.0, 125.9, 125.8, 125.5, 124.8, 124.2, 124.0, 123.7, 112.0, 97.8, 55.1, 46.3, 40.6, 37.1, 29.2, 29.1;

IR (neat): ν 3968, 3878, 3654, 3523, 2954, 2346, 1738, 1652, 1545, 1290, 1058, 669 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>38</sub>H<sub>37</sub>N<sub>2</sub>O: 537.2900; found: 537.2893;

**2-(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-methoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (7ad)**



Yellow solid, isolated yield 80% (72 mg);

mp: 41.4-42.3 °C;

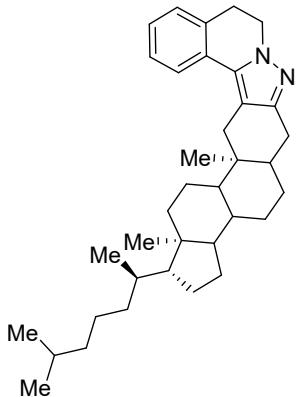
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.52 (d, *J* = 8.9 Hz, 1H), 7.29-7.20 (m, 3H), 6.37 (s, 1H), 5.39-5.37 (m, 1H), 4.30 (t, *J* = 6.7 Hz, 2H), 3.36 (s, 3H), 3.18 (t, *J* = 6.8 Hz, 2H), 3.10-3.03 (m, 1H), 2.73 (t, *J* = 7.1 Hz, 2H), 2.43-2.38 (m, 1H), 2.20-2.00 (m, 4H), 1.94-1.78 (m, 4H), 1.65-1.16 (m, 9H), 1.00 (s, 3H), 0.59 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 153.2, 140.9, 138.8, 131.6, 128.1, 127.7, 127.2 (2C), 123.7, 121.5, 99.4, 80.3, 56.1, 55.6, 50.4, 50.3, 45.9, 43.5, 38.6, 37.8, 37.2, 37.0, 32.3, 31.9, 29.2, 27.9, 26.5, 24.6, 20.8, 19.4, 13.0;

IR (neat): ν 3904, 3854, 3650, 3567, 2971, 2360, 1734, 1654, 1558, 1259, 1066, 669 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>31</sub>H<sub>41</sub>N<sub>2</sub>O: 457.3213; found: 457.3207;

**(1*R*,15a*S*,17a*R*)-15a,17a-dimethyl-1-((*R*)-6-methylheptan-2-yl)2,3,3a,3b,4,5,5a,6,9,10,15,15a,15b,16,17,17a-hexadecahydro-1H-cyclopenta[5',6']naphtho[1',2':5,6]indazolo[3,2-*a*]isoquinoline (7ae)**



Yellow oil, isolated yield 55% (56 mg);

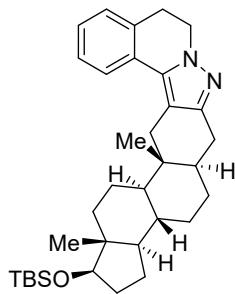
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.29-7.27 (m, 1H), 7.24-7.18 (m, 2H), 4.41-4.36 (m, 1H), 4.07-3.99 (m, 1H), 3.32-3.23 (m, 1H), 2.96-2.90 (m, 2H), 2.71-2.54 (m, 2H), 2.29-2.25 (m, 1H), 1.99-1.71 (m, 5H), 1.55-1.30 (m, 12H), 1.12 (s, 3H), 1.04-0.84 (m, 17H), 0.66 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 149.2, 134.5, 133.1, 128.6, 127.8, 127.0, 126.7, 126.0, 115.6, 56.23, 56.21, 46.4, 42.4, 41.8, 40.8, 40.1, 39.5, 36.1, 35.8, 35.4, 34.9, 34.5, 30.2, 28.2, 28.0, 27.7, 24.2, 23.9, 23.8, 22.8, 22.5, 22.3, 21.7, 19.7, 18.6, 11.9;

IR (neat): ν 3904, 3854, 3735, 3650, 3567, 2966, 2360, 1654, 1559, 1541, 1507, 669 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>36</sub>H<sub>53</sub>N<sub>2</sub>: 513.4203; found: 513.4205;

**(1*R*,3a*R*,3b*S*,5a*R*,15a*R*,15b*R*,17a*R*)-1-((*tert*-butyldimethylsilyl)oxy)-15a,17a-dimethyl-2,3,3a,3b,4,5,5a,6,9,10,15,15a,15b,16,17,17a-hexadecahydro-1H-cyclopenta[5',6']naphtho[1',2':5,6]indazolo[3,2-*a*]isoquinoline (7af)**



Yellow solid, isolated yield 55% (56 mg);

mp: 44.2-45.1 °C;

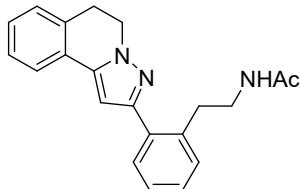
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.50 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.25-7.20 (m, 2H), 4.39-4.33 (m, 1H), 4.23-4.16 (m, 1H), 3.58 (t, *J* = 8.3 Hz, 1H), 3.29-3.21 (m, 1H), 3.07 (dt, *J* = 15.7, 4.8 Hz, 1H), 2.87 (d, *J* = 15.2 Hz, 1H), 2.63 (dd, *J* = 16.4, 4.7 Hz, 1H), 2.37-2.30 (m, 2H), 1.94-1.72 (m, 4H), 1.53-1.04 (m, 12H), 0.89 (s, 9H), 0.80 (s, 3H), 0.74 (s, 3H), -0.03 (s, 3H), -0.02 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  147.8, 134.4, 132.2, 128.3, 128.2, 127.1, 123.8, 111.8, 81.9, 54.3, 50.6, 46.2, 43.2, 42.1, 37.3, 36.7, 36.4, 35.8, 31.4, 30.9, 29.8, 29.3, 27.6, 25.9, 23.6, 20.9, 18.1, 11.8, 11.3, -4.5, -4.8;

IR (neat):  $\nu$  3901, 3837, 3747, 3673, 3615, 2922, 2361, 1699, 1649, 1538, 1397, 881 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>34</sub>H<sub>51</sub>N<sub>2</sub>OSi: 531.3765; found: 531.3757;

#### N-(2-(5,6-dihydropyrazolo[5,1-a]isoquinolin-2-yl)phenethyl)acetamide (11)



Yellow oil, isolated yield 60% (40 mg);

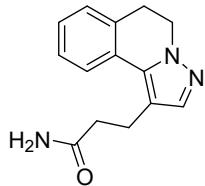
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.92 (s, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.36-7.27 (m, 6H), 6.68 (s, 1H), 4.41 (t, *J* = 6.9 Hz, 2H), 3.60-3.56 (m, 2H), 3.29 (t, *J* = 6.8 Hz, 2H), 3.02 (t, *J* = 12.3 Hz, 2H), 1.91 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  170.4, 151.7, 139.7, 137.8, 133.4, 131.5, 130.4, 130.0, 128.44, 128.37, 128.3, 127.5, 126.52, 126.45, 124.1, 100.8, 46.2, 42.1, 31.4, 29.0, 23.1;

IR (neat):  $\nu$  3904, 3854, 3735, 3650, 3567, 3274, 2971, 2360, 1654, 1049, 760, 669 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>22</sub>N<sub>3</sub>O: 332.1757; found: 332.1753;

#### 3-(5,6-dihydropyrazolo[5,1-a]isoquinolin-1-yl)propanamide (13)



Yellow solid, isolated yield 60% (30 mg);

mp: 228.2-229.1 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.54 (s, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.35-7.28 (m, 3H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.20 (t, *J* = 6.8 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  170.6, 148.2, 134.4, 132.4, 128.5, 128.2, 127.3, 127.1, 124.0, 97.5, 45.9, 31.6, 29.5, 17.8;

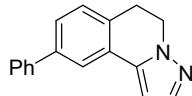
IR (neat):  $\nu$  3904, 3854, 3650, 3567, 2972, 2360, 1654, 1541, 1419, 1339, 1066, 669 cm<sup>-1</sup>;

HRMS (ESI): m/z [M - H]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>O: 240.1131; found: 240.1128;

#### Procedure for synthesis of 3ka

To a solution of **3ja** (24.8 mg, 0.1 mmol, 1.0 equiv), S-PHOS (4.7 mg, 0.01 mmol, 10 mol %), PhB(OH)<sub>2</sub> (27.5 mg, 0.2 mmol, 2.0 equiv), anhydrous K<sub>3</sub>PO<sub>4</sub> (47.7 mg, 0.2 mmol, 2.0 equiv) in toluene (2 mL) was added Pd(OAc)<sub>2</sub> (2.4 mg, 0.01 mmol, 10 mol %) at room temperature. The resulting mixture was degassed with N<sub>2</sub> and heated to 100 °C for 24 h. After cooling to room temperature, the reaction mixture was directly charged to column chromatography on silica gel (Hexanes:EtOAc = 6:1) to afford the product (23 mg, 93% yield);

#### 9-phenyl-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (3ka)



Colorless oil;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.75 (s, 1H), 7.63 (s, 1H), 7.61 (s, 1H), 7.56 (s, 1H), 7.49–7.45 (m, 3H), 7.40–7.34 (m, 2H), 6.62 (s, 1H), 4.40 (t, *J* = 6.8 Hz, 2H), 3.25 (t, *J* = 6.7 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 140.6, 140.5, 139.3, 130.6, 128.8, 128.6, 127.5, 127.4, 127.0, 126.8, 122.7, 111.4, 100.8, 46.2, 28.9;

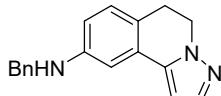
IR (neat): ν 3856, 3748, 2924, 2364, 1700, 1542, 1468, 1408, 1259, 1044, 758, 668 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>: 247.1230; found: 247.1225;

#### Procedure for synthesis of 14

To a solution of **3ja** (24.8 mg, 0.1 mmol, 1.0 equiv), benzylamine (64 μL, 0.5 mmol, 5.0 equiv), 'BuOK (95%, 40.0 mg, 0.3 mmol, 3.0 equiv) and *o*-P(*t*-Bu)<sub>2</sub>-biphenyl (6.0 mg, 0.02 mmol, 20 mol %) in toluene (2 mL) was added Pd(OAc)<sub>2</sub> (2.6 mg, 0.01 mmol, 10 mol %) at room temperature. The resulting mixture was degassed with N<sub>2</sub>. The mixture was stirred at 110 °C for 24 h. After cooling to room temperature, the reaction mixture was directly charged to column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to afford the product (26 mg, 95% yield);

#### 5-N-benzyl-5,6-dihydropyrazolo[5,1-*a*]isoquinolin-9-amine (14)



Yellow oil;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 2.0 Hz, 1H), 7.40–7.34 (m, 4H), 7.32–7.27 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 6.56 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.45 (d, *J* = 1.9 Hz, 1H), 4.37 (s, 2H), 4.31 (t, *J* = 6.9 Hz, 2H), 3.08 (t, *J* = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.0, 138.6, 134.5, 129.7, 129.1 (2C), 129.0, 128.7 (2C), 128.3, 127.9, 127.7, 100.6, 50.1, 46.5, 28.4;

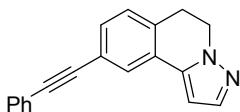
IR (neat): ν 3867, 3757, 3661, 3421, 2927, 2407, 1740, 1654, 1513, 1458, 1029, 746 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>3</sub>: 276.1495; found: 276.1497;

#### Procedure for synthesis of 15

To a solution of **3ja** (24.8 mg, 0.1 mmol, 1.0 equiv), phenylacetylene (16 μL, 0.150 mmol, 1.5 equiv), Cs<sub>2</sub>CO<sub>3</sub> (107.0 mg, 0.3 mmol, 3 equiv) and S-PHOS (18.6 mg, 0.03 mmol, 30 mol %) in anhydrous acetonitrile (2 mL) was added PdCl<sub>2</sub>(MeCN)<sub>2</sub> (3.3 mg, 0.01 mmol, 10 mol %) at room temperature. The resulting mixture was degassed with N<sub>2</sub> and then heated to 90 °C for 3 h. The reaction was cooled down to room temperature the solvent was removed in vacuo. The crude mixture was purified by flash column chromatography (Hexanes:EtOAc = 6:1) to afford the product (26 mg, 95% yield);

#### 6-9-(phenylethynyl)-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (15)



Yellow oil;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 1.4 Hz, 1H), 7.57–7.54 (m, 3H), 7.43 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.38–7.35 (m, 3H), 7.27 (s, 1H), 6.59 (d, *J* = 2.0 Hz, 1H), 4.38 (t, *J* = 6.9 Hz, 2H), 3.22 (t, *J* = 6.9 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.4, 138.0, 131.8, 131.6, 131.0, 128.41, 128.38, 128.3, 127.2, 126.9, 123.0, 122.4, 100.9, 89.7, 88.7, 46.0, 29.2;

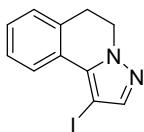
IR (neat): *v* 3867, 3819, 3686, 3668, 2995, 2908, 1410, 1253, 1077, 1068, 758, 659 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>: 271.1230; found: 271.1234;

#### Procedure for synthesis of 16

A mixture of **3aa** (291 mg, 1.7 mmol, 1.0 equiv), iodine (522 mg, 2.04 mmol, 1.2 equiv) and CAN (1.128 g, 2.04 mmol, 1.2 equiv) in anhydrous acetonitrile (17 mL) was stirred at 90 °C for 3 h. The solvent was then evaporated in vacuo and the resulting residue was dissolved in EtOAc (40 mL). The resulting organic solution was washed with an aqueous solution of NaHSO<sub>3</sub> (5%), and finally dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent in vacuo gave a crude mixture that was purified by column chromatography (petroleum ether:EtOAc = 5:1) to afford the product (468 mg, 93% yield);

#### 1-iodo-5,6-dihydropyrazolo[5,1-a]isoquinoline (16)



Yellow oil;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.41 (d, *J* = 7.6 Hz, 1H), 7.53 (s, 1H), 7.37–7.32 (m, 1H), 7.30–7.23 (m, 2H), 4.34 (t, *J* = 6.7 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.3, 136.3, 128.6, 128.2, 127.0, 126.5, 124.0 (2C), 52.9, 47.0, 29.7;

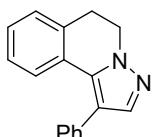
IR (neat): *v* 3862, 3756, 3681, 3659, 3452, 2927, 2366, 1739, 1702, 1024, 914, 746 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>11</sub>H<sub>10</sub>IN<sub>2</sub>: 296.9883; found: 296.9883;

#### Procedure for synthesis of 17

To a solution of **16** (29.6 mg, 0.1 mmol, 1.0 equiv) in toluene (2 mL) was added phenylboronic acid (24.4 mg, 0.2 mmol, 2.0 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (11.6 mg, 0.01 mmol, 10 mol %). Absolute EtOH (2.0 mL) and aqueous NaHCO<sub>3</sub> (2.0 mL) was then added to the reaction mixture. The resulting mixture was degassed with N<sub>2</sub> and then heated to 110 °C for 12 h. After cooling to room temperature, the organic layer was separated and the aqueous fraction was extracted with EtOAc. The organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvents in vacuo gave a crude mixture that was purified by column chromatography (Hexanes:EtOAc = 6:1) to afford the product (23 mg, 92% yield);

#### 6-1-phenyl-5,6-dihydropyrazolo[5,1-a]isoquinoline (17)



Yellow solid;

mp: 93.4–93.9 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 (s, 1H), 7.49–7.47 (m, 2H), 7.44–7.39 (m, 3H), 7.36–7.32 (m, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.21 (td, *J* = 7.4, 1.2 Hz, 1H), 7.11–7.07 (m, 1H), 4.38 (t, *J* = 6.7 Hz, 2H), 3.23 (t, *J* = 6.8 Hz, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.3, 134.0, 133.8, 132.7, 128.9, 128.6, 128.2, 127.9, 127.3, 126.94, 126.93, 124.4, 119.4, 46.6, 29.7;

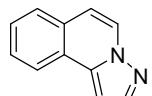
IR (neat): ν 3865, 3700, 3685, 3668, 2995, 2979, 2908, 1409, 1253, 1068, 1017, 894 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>: 247.1230; found: 247.1232;

### Procedure for synthesis of 18

A mixture of **3aa** (34 mg, 0.20 mmol, 1.0 equiv) and activated MnO<sub>2</sub> (173.8 mg, 2 mmol, 10.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was refluxed for 36 h. After cooling to room temperature, the mixture was passed through a pad of Celite and evaporated in vacuo. The residue was purified by column chromatography (Hexanes:EtOAc = 6:1) to afford the product (31 mg, 92%);

#### pyrazolo[5,1-*a*]isoquinoline (18)<sup>[7]</sup>



Yellow solid;

mp: 33.4–33.9 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, J = 7.4 Hz, 1H), 8.10–8.08 (m, 1H), 7.97 (d, J = 2.1 Hz, 1H), 7.72–7.70 (m, 1H), 7.59–7.51 (m, 2H), 6.99–6.98 (m, 2H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.2, 138.3, 128.6, 127.8, 127.6, 127.1, 126.4, 124.5, 123.6, 112.0, 97.5;

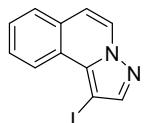
IR (neat): ν 3862, 3756, 3452, 2927, 2368, 1739, 1702, 1653, 1462, 1024, 914, 747 cm<sup>-1</sup>;

HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>11</sub>H<sub>9</sub>N<sub>2</sub>: 169.0760; found: 169.0761;

### Procedure for synthesis of 19

To a solution of **18** (50.5 mg, 0.3 mmol, 1.0 equiv) in DMF (1.5 mL) was added *N*-iodosuccinimide (74.4 mg, 0.33 mmol) at room temperature. The resulting mixture was stirred at room temperature overnight. The reaction was quenched with an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and NaHCO<sub>3</sub>. The mixture was extracted with Et<sub>2</sub>O, and the resulting organic solution was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent in vacuo gave a crude mixture that was purified by column chromatography (petroleum ether:EtOAc = 10:1) to afford the product (25 mg, 85%);

#### 1-iodopyrazolo[5,1-*a*]isoquinoline (19)



White solid;

mp: 65.4–65.9 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.22 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 7.4 Hz, 1H), 7.98 (s, 1H), 7.73 (dd, J = 7.7, 1.2 Hz, 1H), 7.66–7.56 (m, 2H), 7.02 (d, J = 7.4 Hz, 1H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 147.5, 134.8, 129.3, 128.4, 127.3, 127.2, 126.5, 124.7, 123.0, 113.0, 48.3;

IR (neat): ν 3976, 3658, 2864, 2564, 1682, 1542, 1365, 1307, 1258, 1136, 1008, 668 cm<sup>-1</sup>;

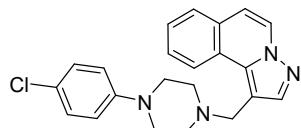
HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>11</sub>H<sub>8</sub>IN<sub>2</sub><sup>+</sup>: 294.9727; found: 294.9731;

### Procedure for synthesis of III

To a solution of **19** (25 mg, 0.1 mmol, 1.0 equiv) in THF (1 mL) was added isopropylmagnesium chloride (0.4 mL, 0.8 mmol, 2.0 M in THF, 8.0 equiv) at 0 °C. The resulting solution was warmed up to room temperature and stirred for 30 min. DMF (29 mg, 0.4 mmol, 4.0 equiv) was added and the mixture was stirred at room temperature overnight. The reaction was quenched with an aqueous solution of NH<sub>4</sub>Cl. The mixture was

extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the resulting organic solution was washed with brine and finally dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL), and to this solution was added 1-(4-chlorophenyl)piperazine (20 mg, 0.1 mmol, 1.0 equiv) and acetic acid (1.2 mg, 0.02 mmol, 0.2 equiv). The resulting mixture was stirred at room temperature for 30 min, then sodium triacetoxyborohydride (64 mg, 0.3 mmol, 3.0 equiv) was added. The reaction was stirred at room temperature for 18 h and was quenched with an aqueous solution of NaHCO<sub>3</sub>. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the resulting organic solution was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent in vacuo gave a crude mixture that was purified by column chromatography (petroleum ether:EtOAc = 5:1) to afford the product (30 mg, 80%);

**1-((4-(4-chlorophenyl)piperazin-1-yl)methyl)pyrazolo[5,1-*a*]isoquinoline (III)**



White solid;

mp: 107.6-107.9 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.59 (d, *J* = 7.7 Hz, 1H), 8.25 (d, *J* = 7.4 Hz, 1H), 7.89 (s, 1H), 7.73-7.71 (m, 1H), 7.61-7.52 (m, 2H), 7.20-7.16 (m, 2H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.84-6.80 (m, 2H), 3.91 (s, 2H), 3.17-3.15 (m, 4H), 2.74-2.71 (m, 4H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 150.0, 143.0, 135.7, 129.4, 128.9, 127.6, 127.5, 127.0, 126.7, 125.8, 125.5, 124.4, 117.2, 112.4, 111.1, 53.8, 52.8, 49.2;

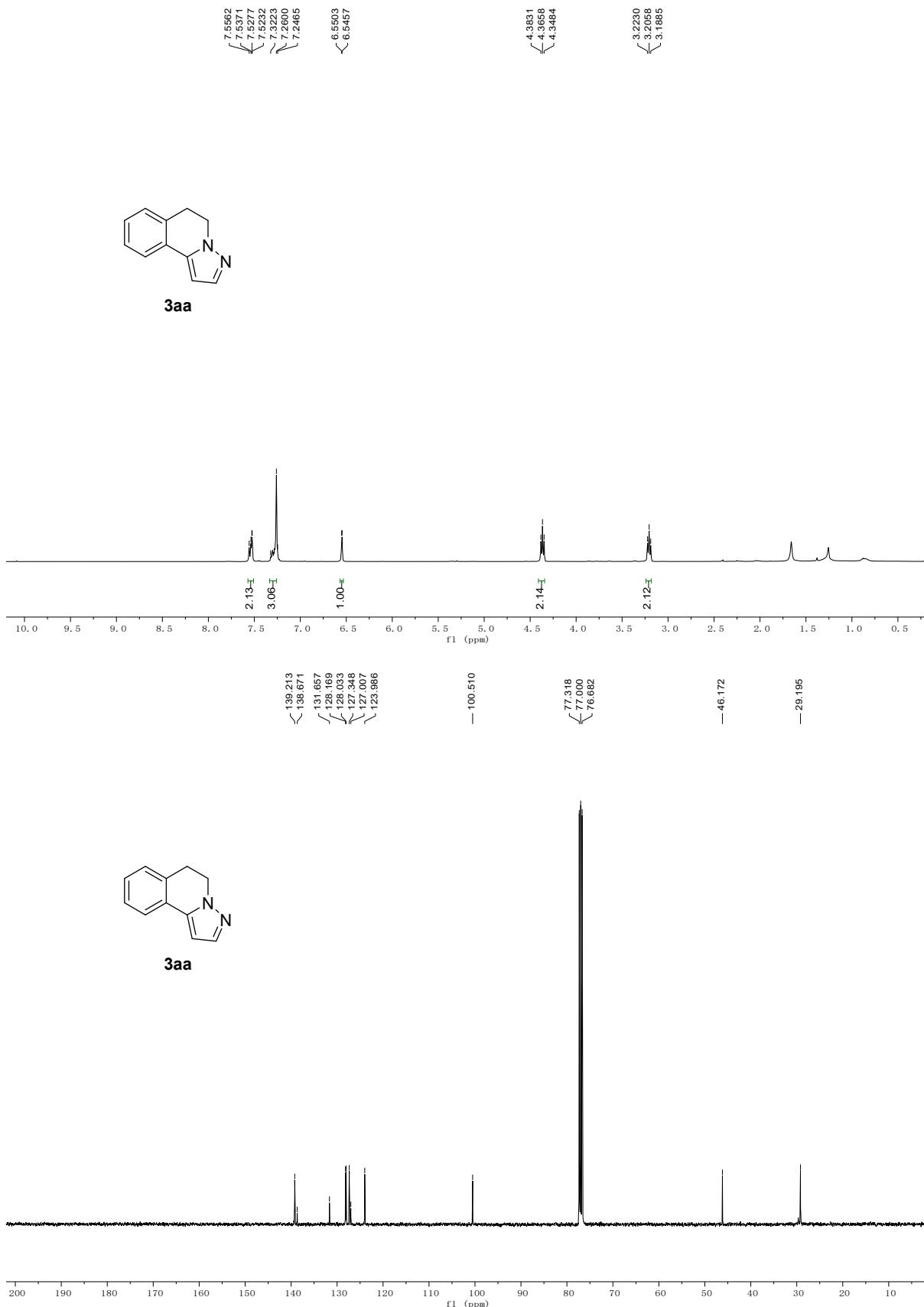
IR (neat): ν 3942, 2862, 2936, 2568, 1856, 1652, 1632, 1406, 1269, 1002, 788, 668 cm<sup>-1</sup>;

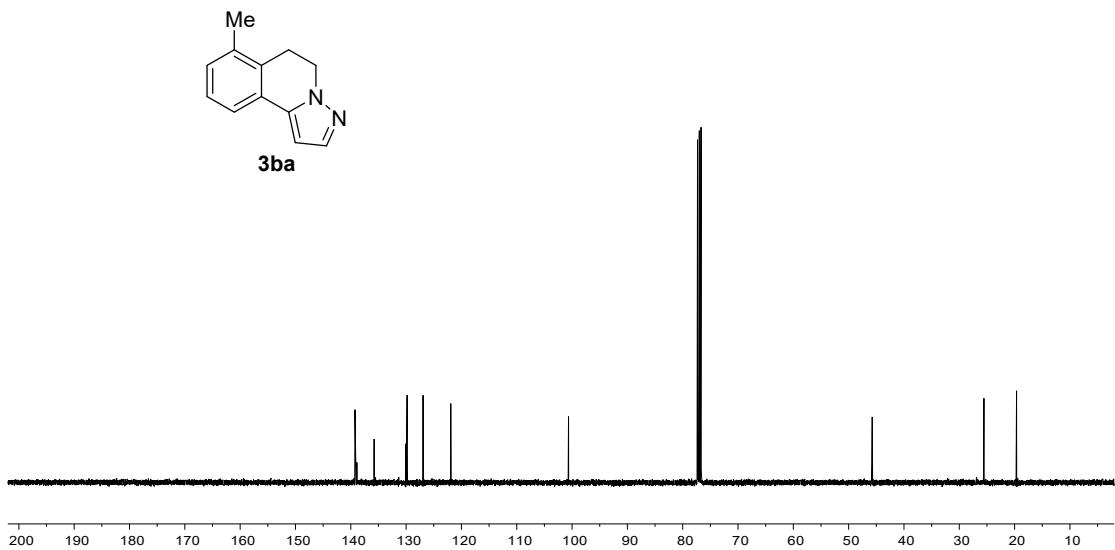
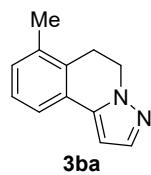
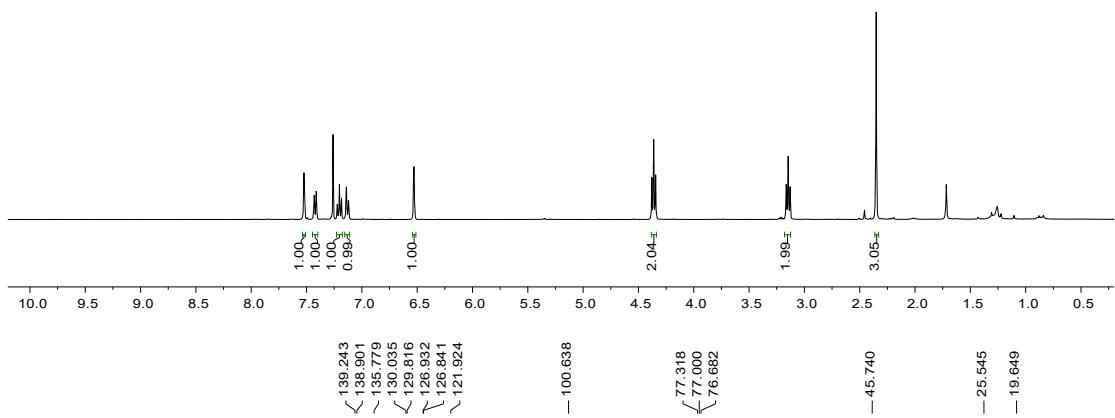
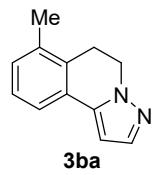
HRMS (ESI): m/z [M + H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>22</sub>ClN<sub>4</sub>: 377.1528; found: 377.1523;

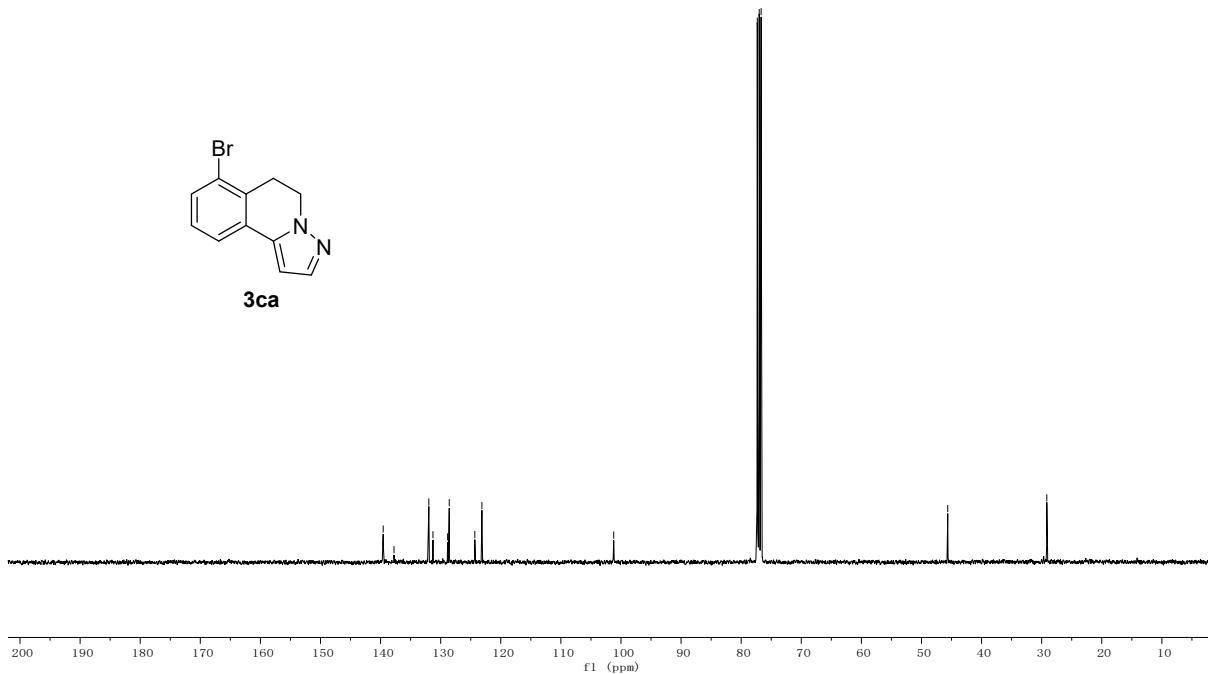
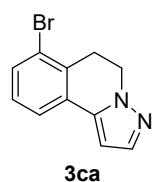
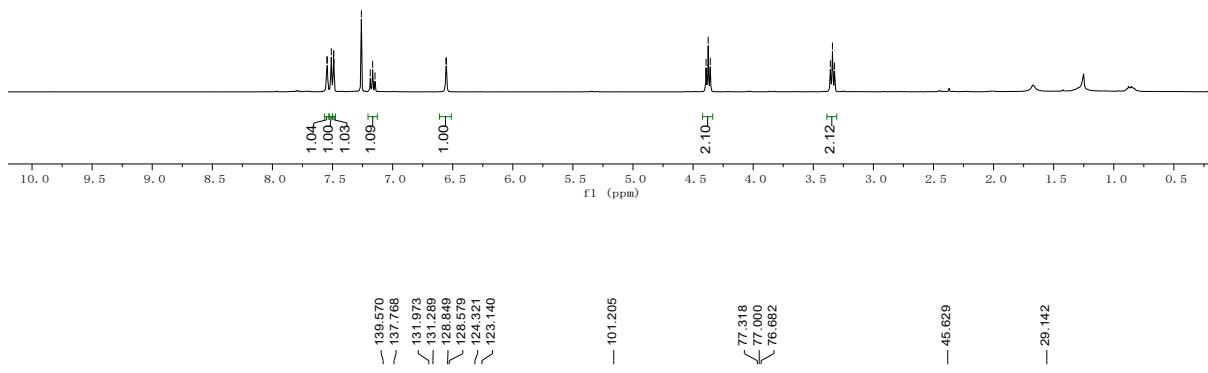
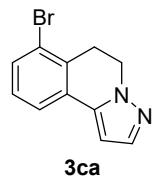
### 3. References

- [1] W. B. Cao, S. J. Li, M. M. Xu, H. Li, X. P. Xu, Y. Lan and S. J. Ji, *Angew. Chem. Int. Ed.*, 2020, **59**, 21425-21430.
- [2] (a) Z. H. Guan, Z. Y. Zhang, Z. H. Ren, Y. Y. Wang and X. M. Zhang, *J. Org. Chem.*, 2011, **76**, 339-341; (b) J. T. Reeves, Z. L. Tan, Z. S. Han, G. S. Li, Y. D. Zhang, Y. B. Xu, D. C. Reeves, N. C. Gonnella, S. L. Ma, H. Lee, B. Z. Lu and C. H. Senanayake, *Angew. Chem. Int. Ed.*, 2012, **51**, 1400-1404; (c) M. J. Burk, G. Casy and N. B. Johnson, *J. Org. Chem.*, 1998, **63**, 6084-6085; (d) M. G. Barthakur, M. Borthakur and R. C. Boruah, *Steroids*, 2008, **73**, 1137-1142.
- [3] Z. Li, H. Yu, H. L. Liu, L. Zhang, H. Jiang, B. Wang and H. C. Guo, *Chem. Eur. J.*, 2014, **20**, 1731-1736.
- [4] C. Blaszykowski, E. Aktoudianakis, C. Bressy, D. Alberico and M. Lautens, *Org. Lett.*, 2006, **8**, 2043-2045.
- [5] H. Ortega, S. Ahmed and H. Alper, *Synthesis*, 2007, **23**, 3683-3691.
- [6] Z. H. Qu, F. Zhang, G. J. Deng and H. W. Huang, *Org. Lett.*, 2019, **21**, 8239-8243.
- [7] M. Kobayashi, K. Kondo and T. Aoyama, *Tetrahedron Lett.*, 2007, **48**, 7019-7021.

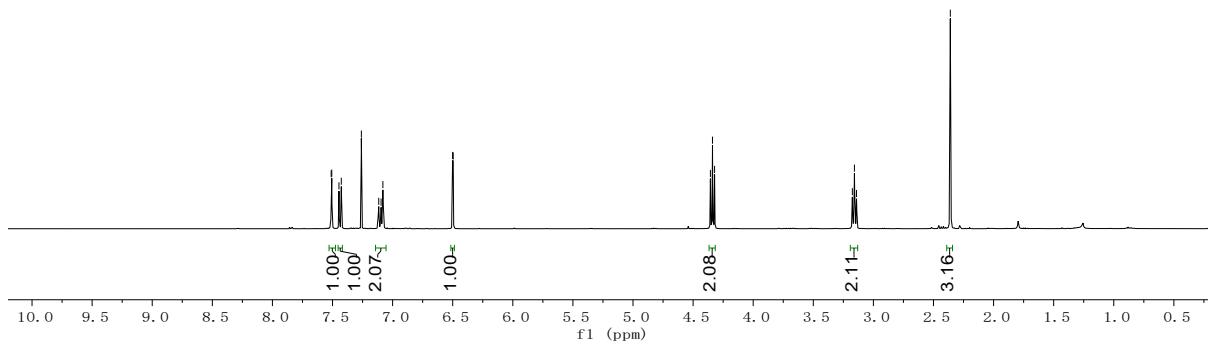
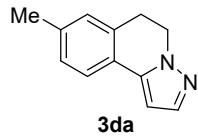
#### 4. Copies of NMR spectra



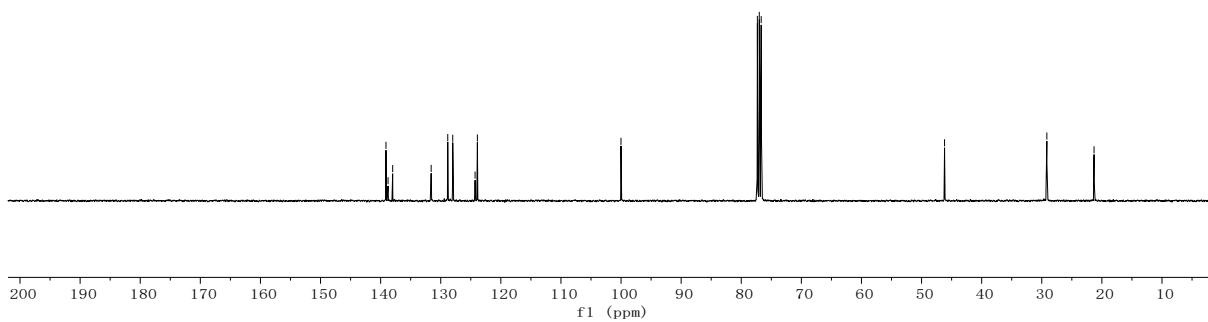
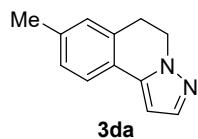


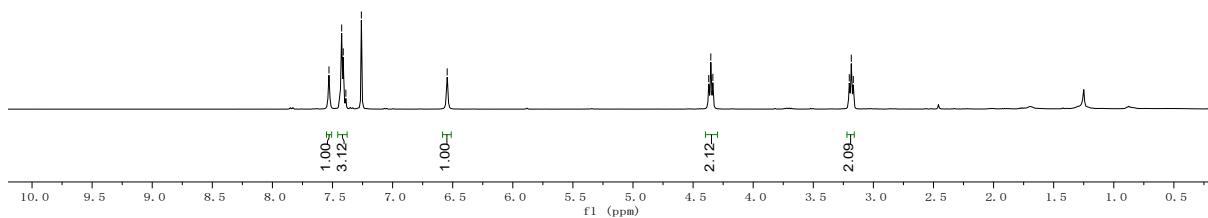
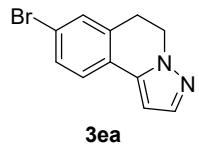


7.5111  
 7.5062  
 7.4464  
 7.4270  
 7.2800  
 7.1155  
 7.0960  
 7.0810  
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 6.4960

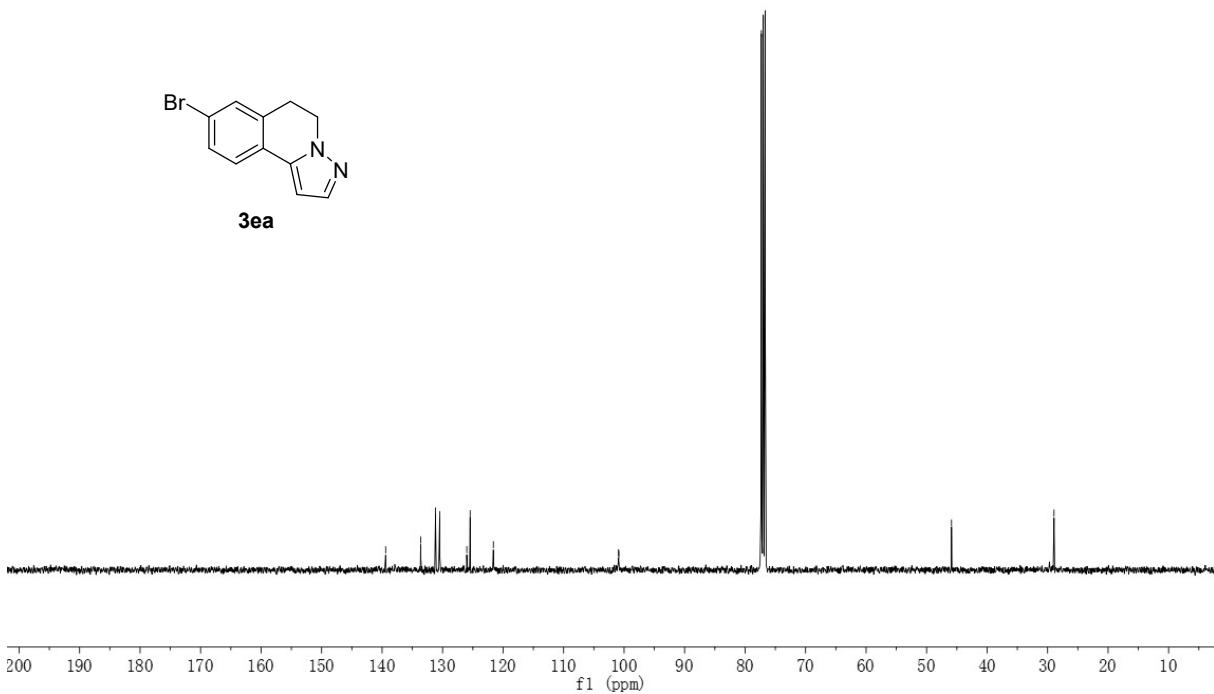
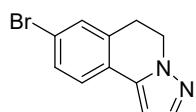


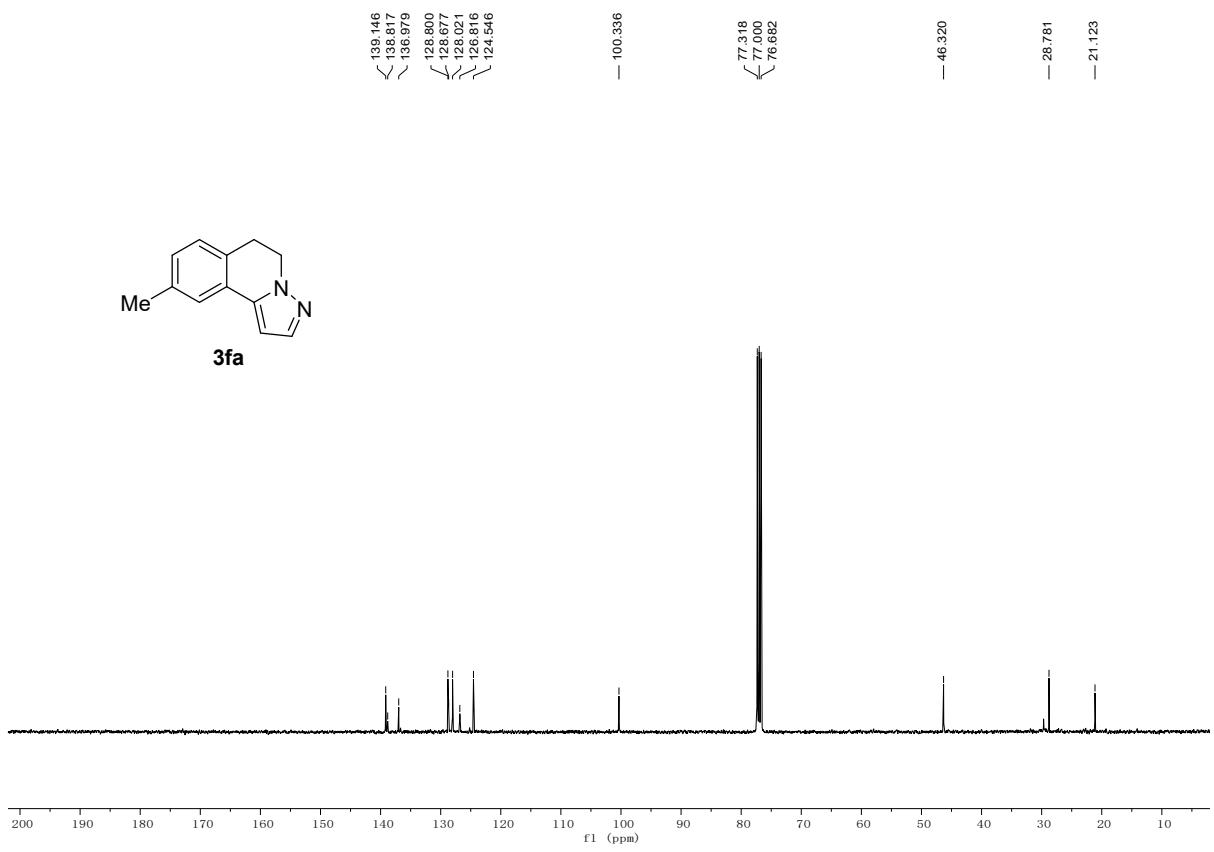
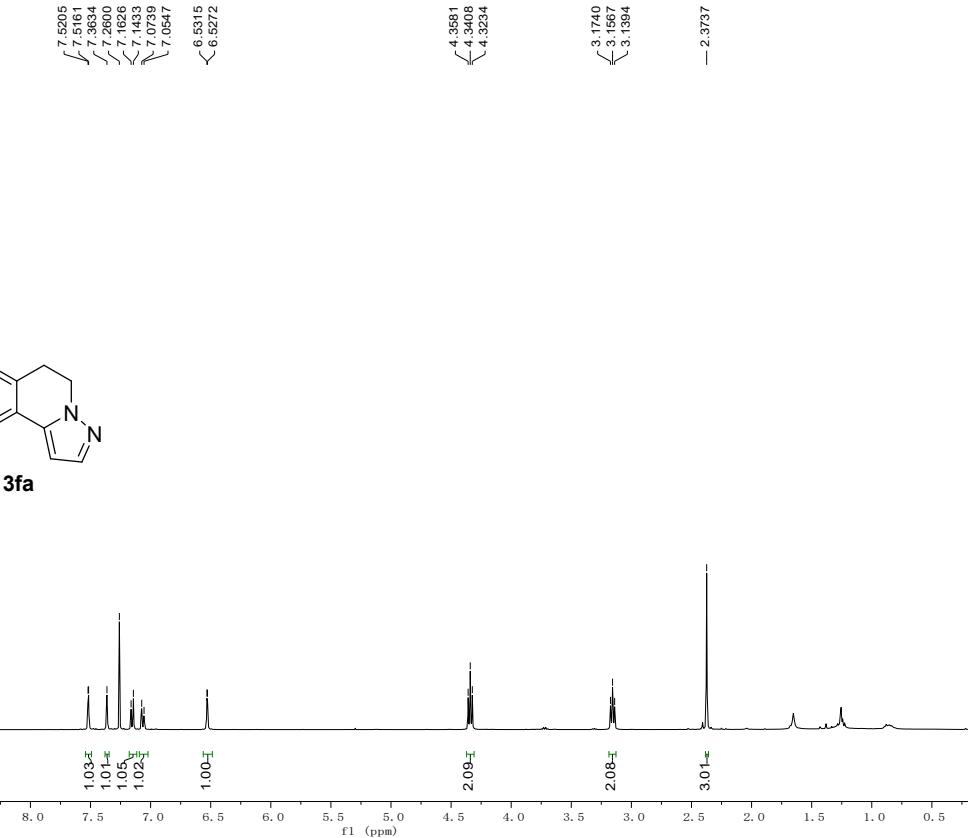
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 123.903

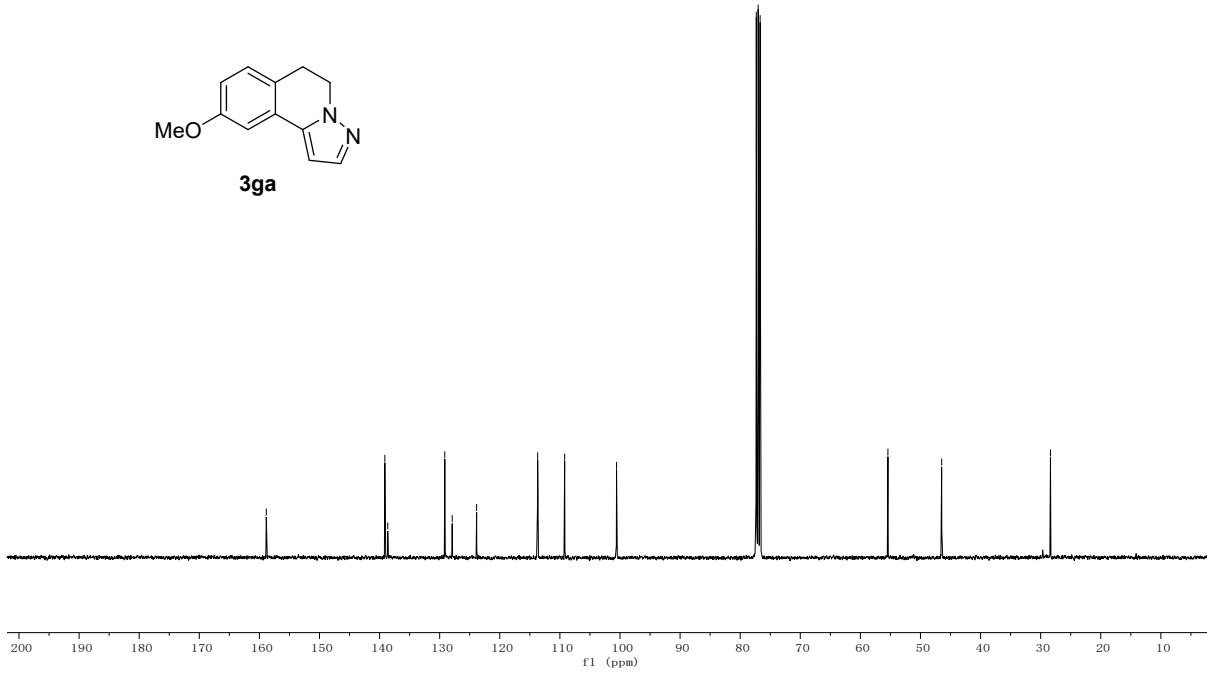
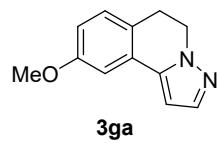
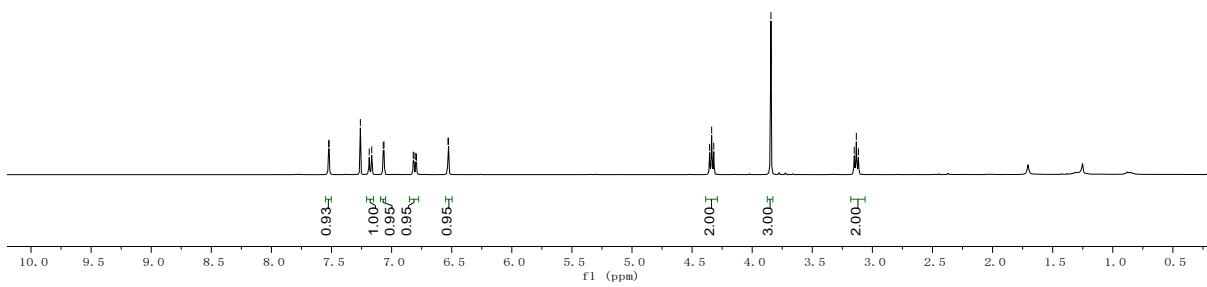
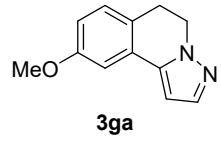


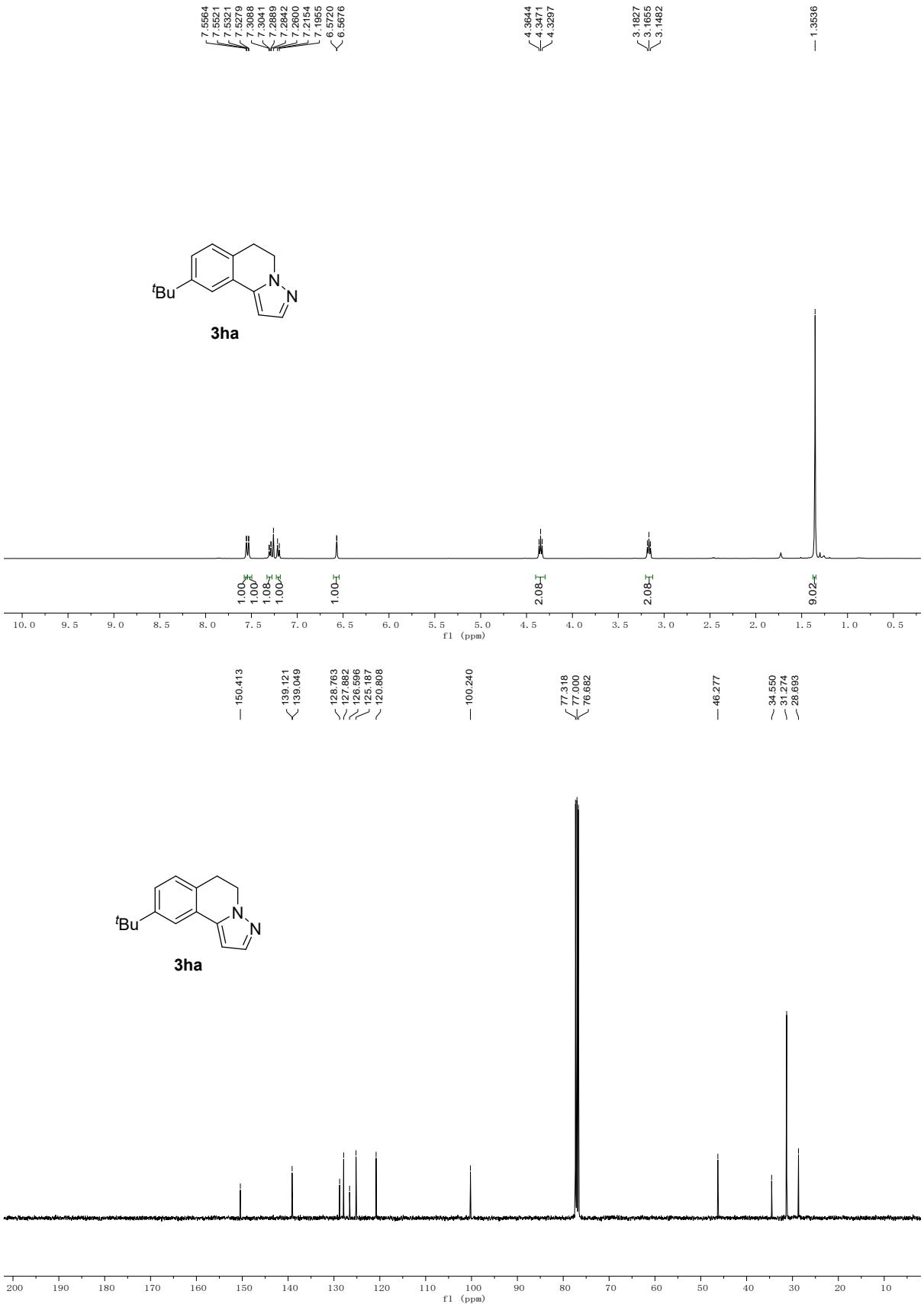


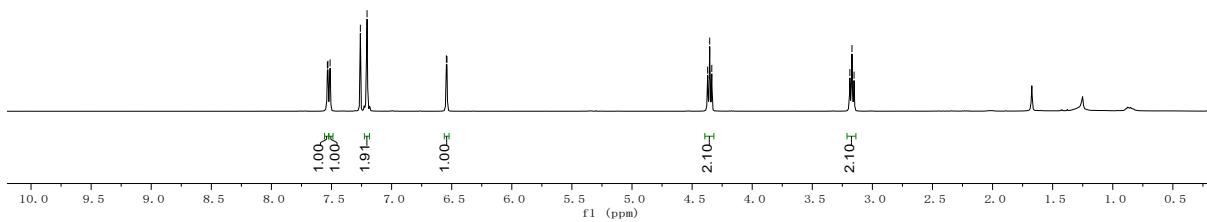
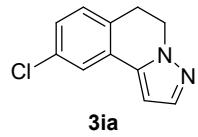
— 139.413  
— 133.618  
✓ 131.189  
✓ 130.464  
✓ 126.002  
✓ 125.443  
✓ 121.607  
✓ 100.918  
✓ 100.858  
✓ 77.318  
✓ 77.000  
✓ 76.682  
— -45.882  
— -28.940











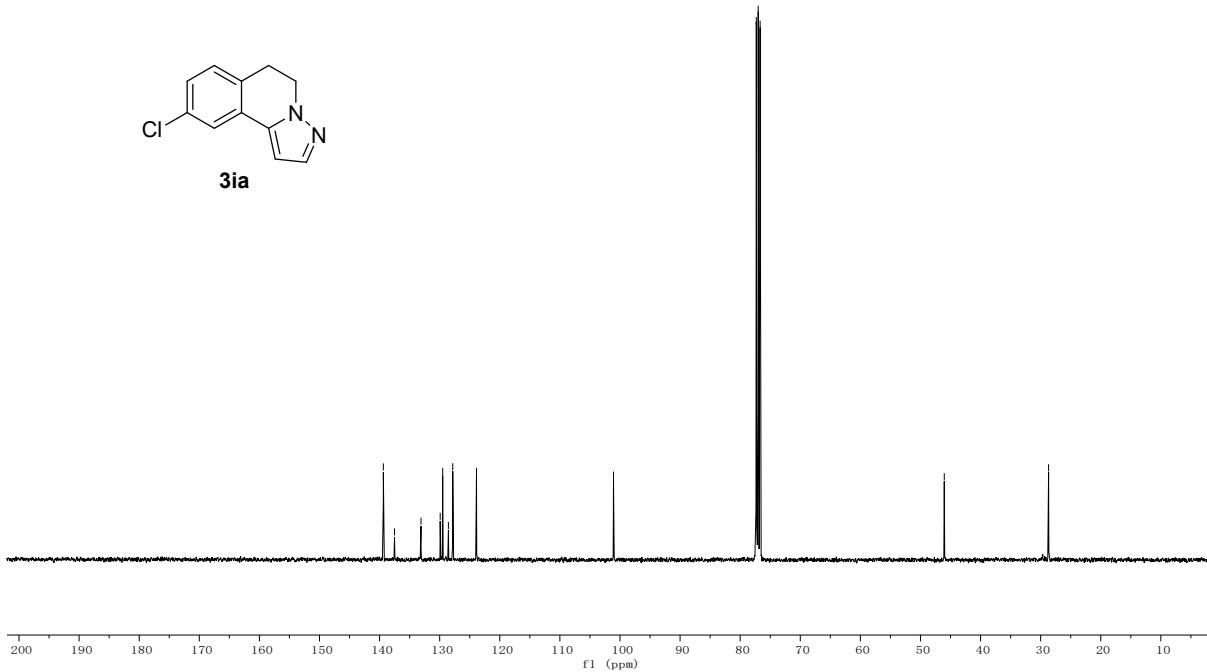
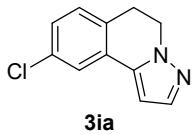
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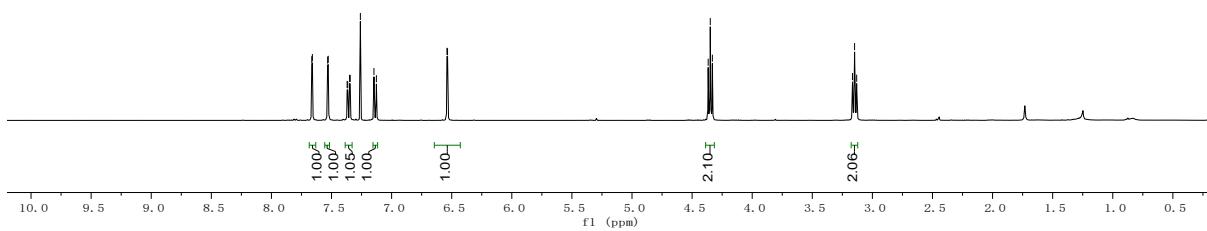
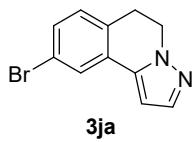
— 101.077

— 77.318  
 $\nearrow$  77.000  
 $\searrow$  76.682

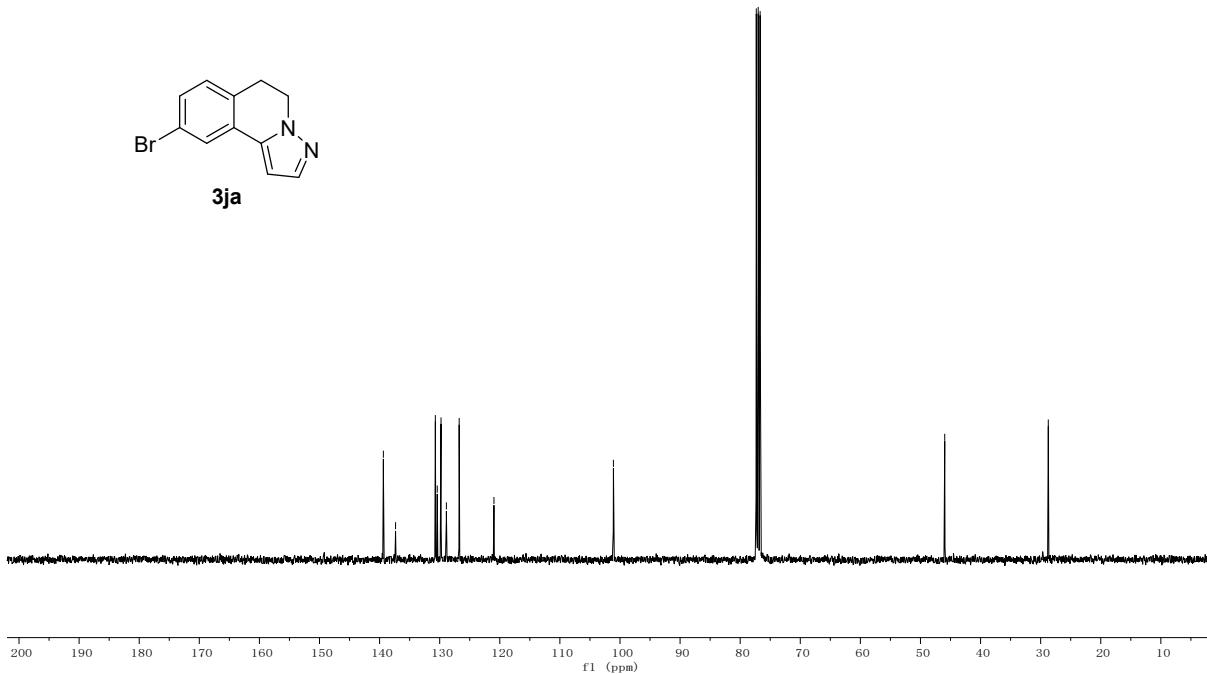
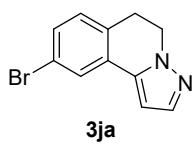
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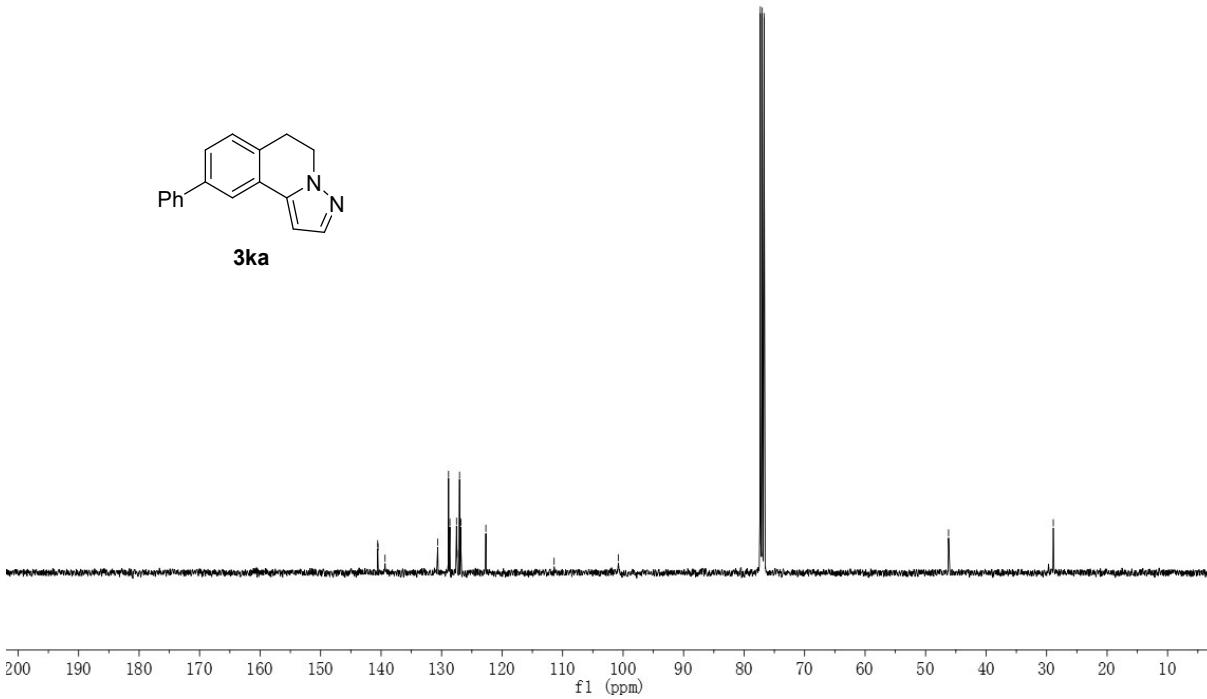
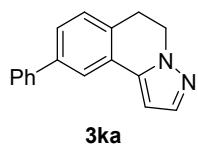
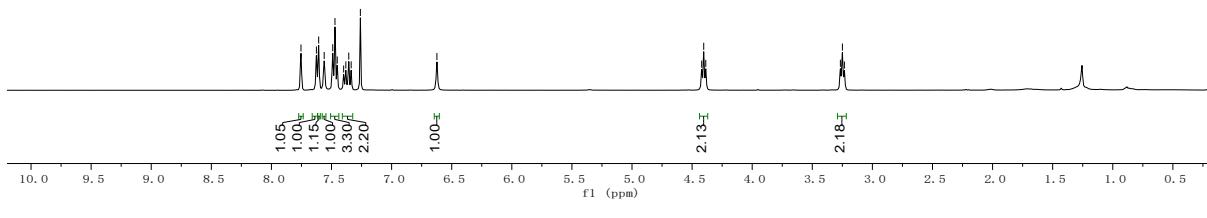
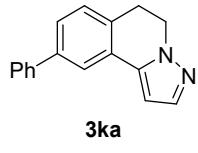
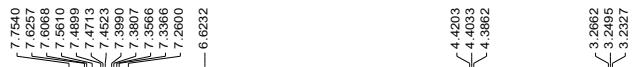
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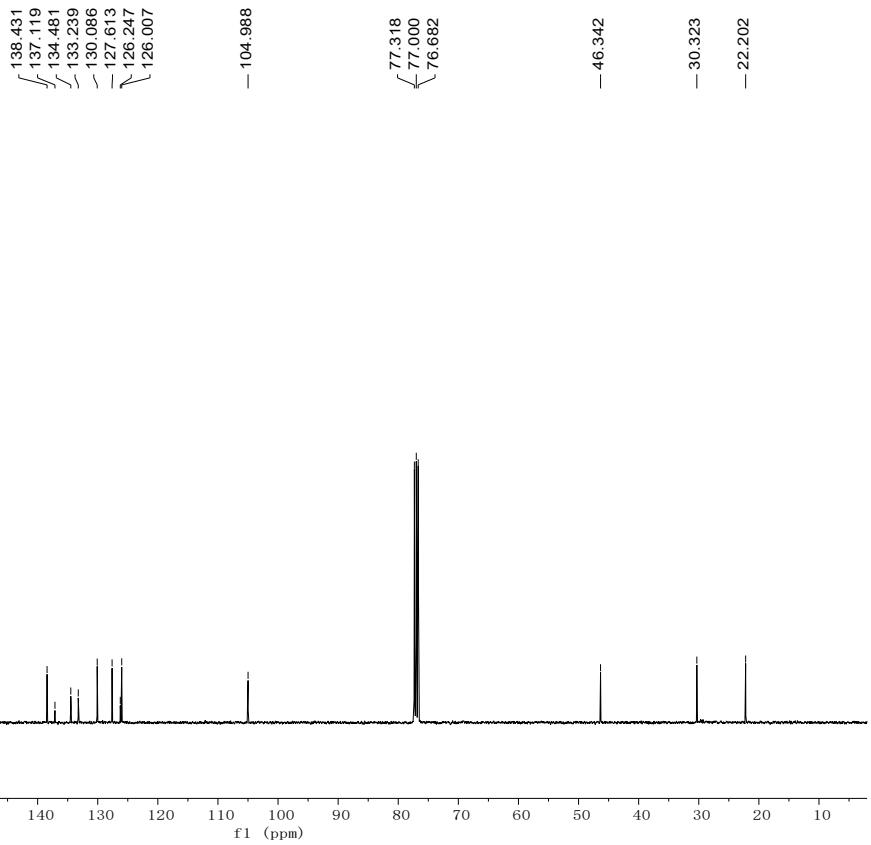
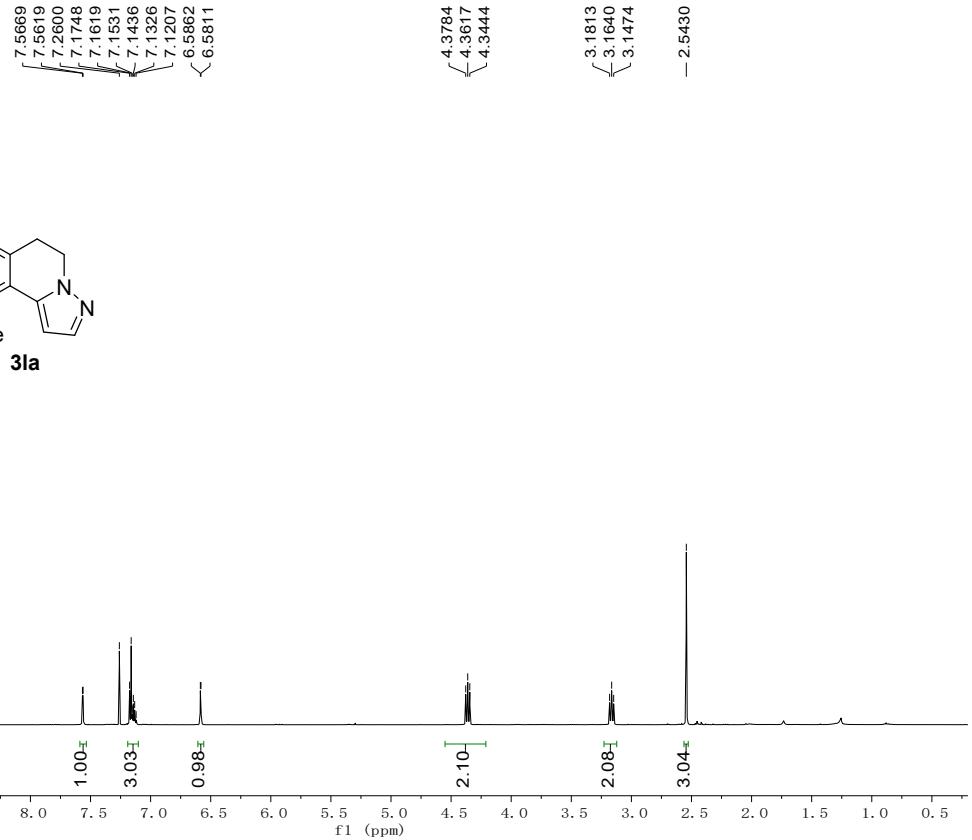


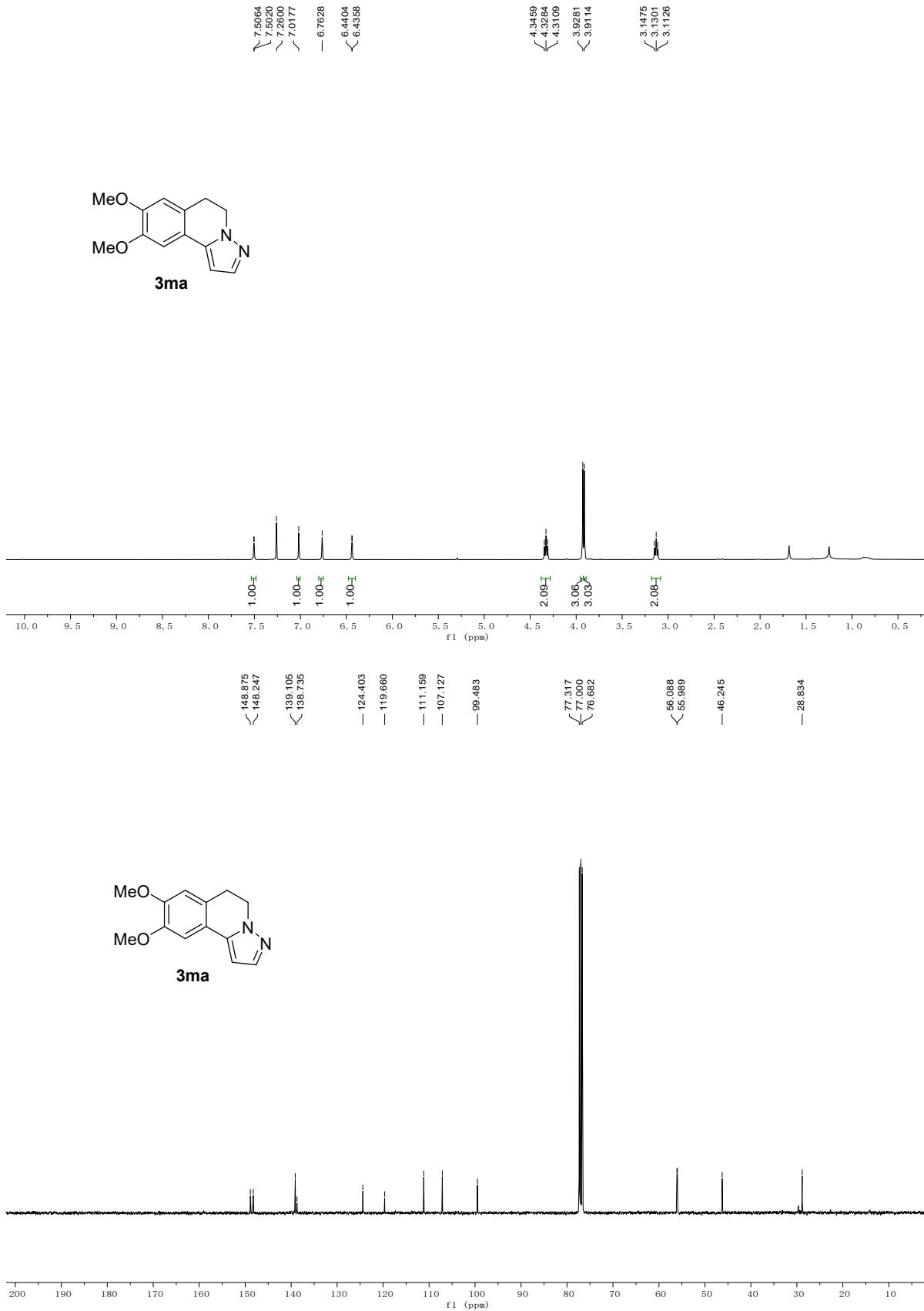


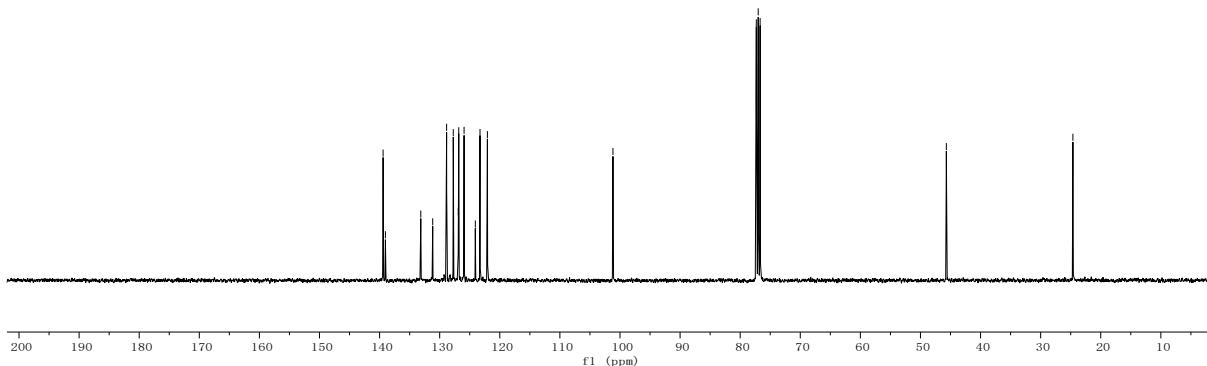
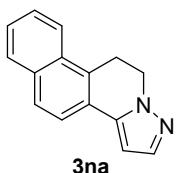
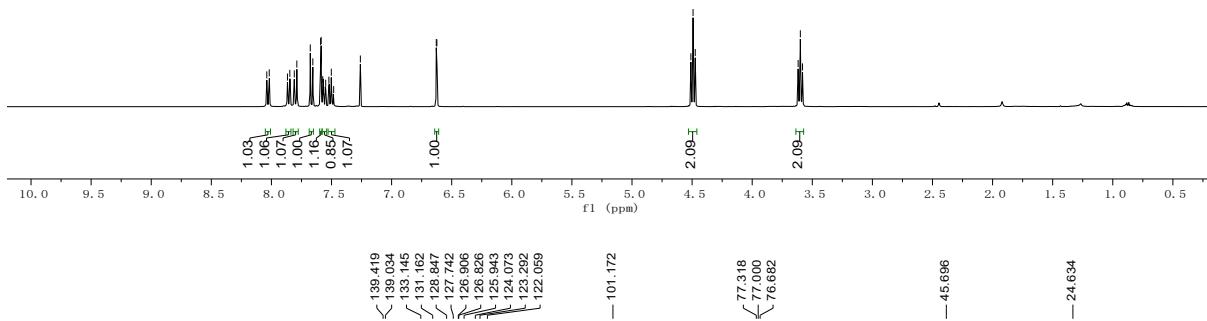
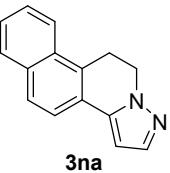
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 — 130.721  
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 — 128.887  
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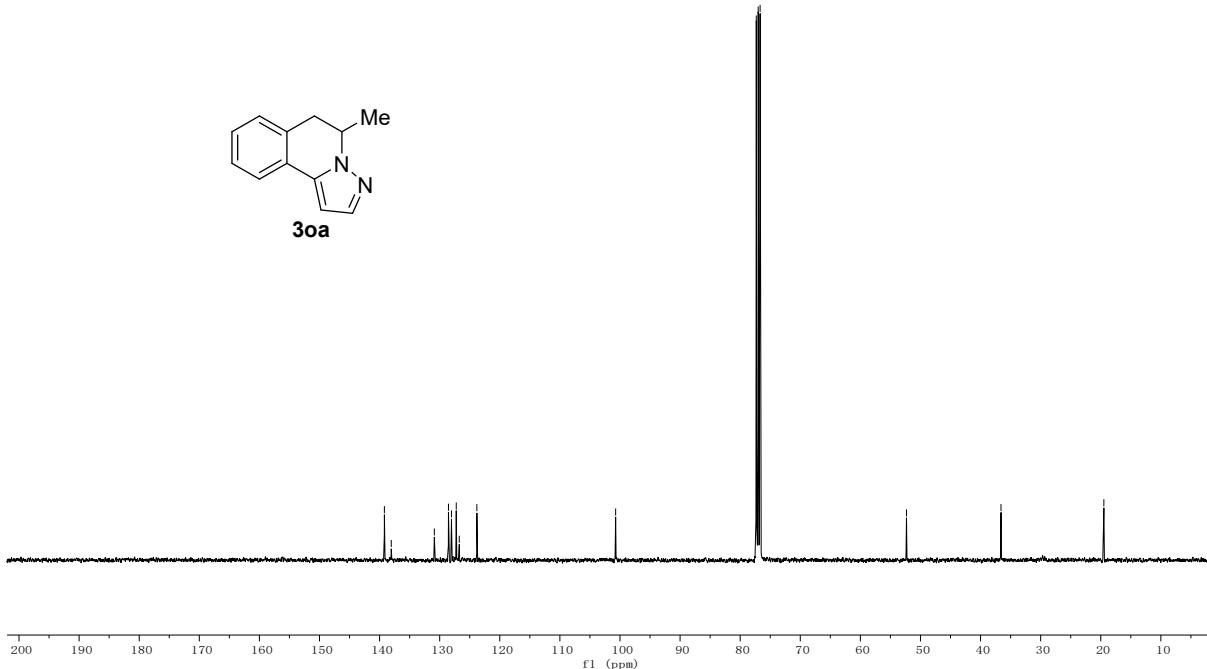
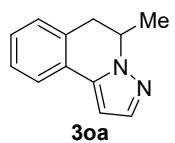
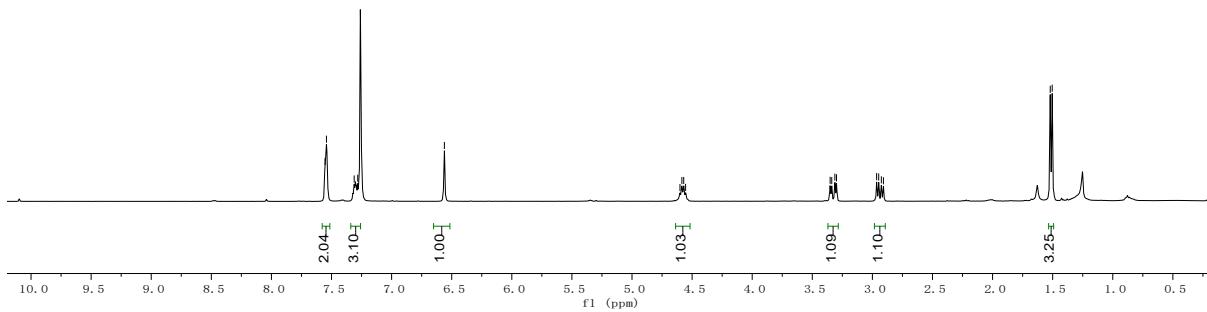
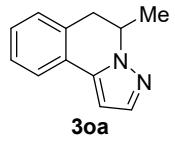
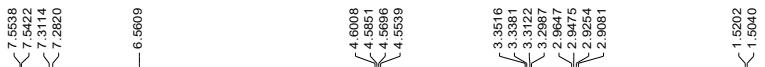


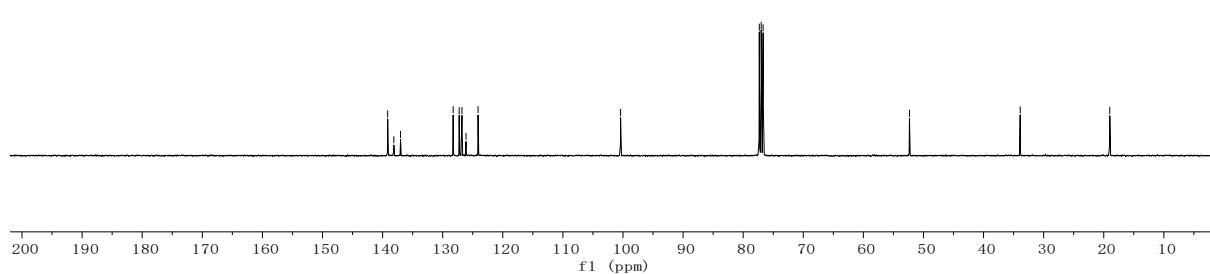
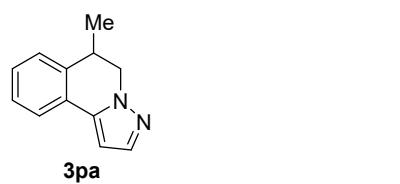
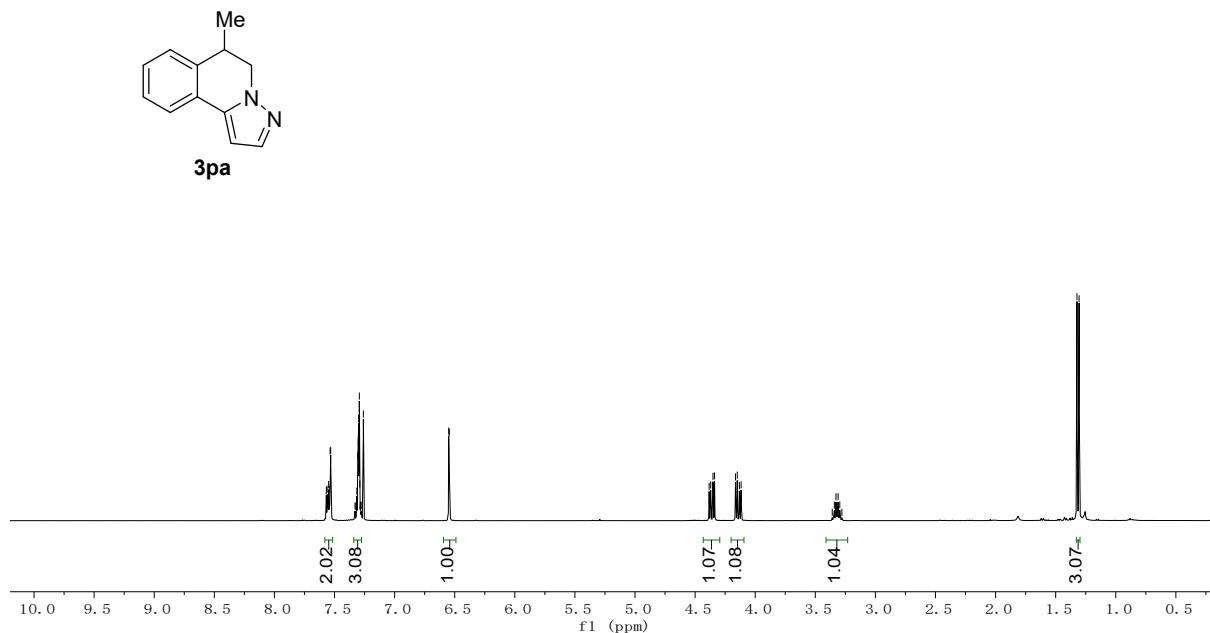








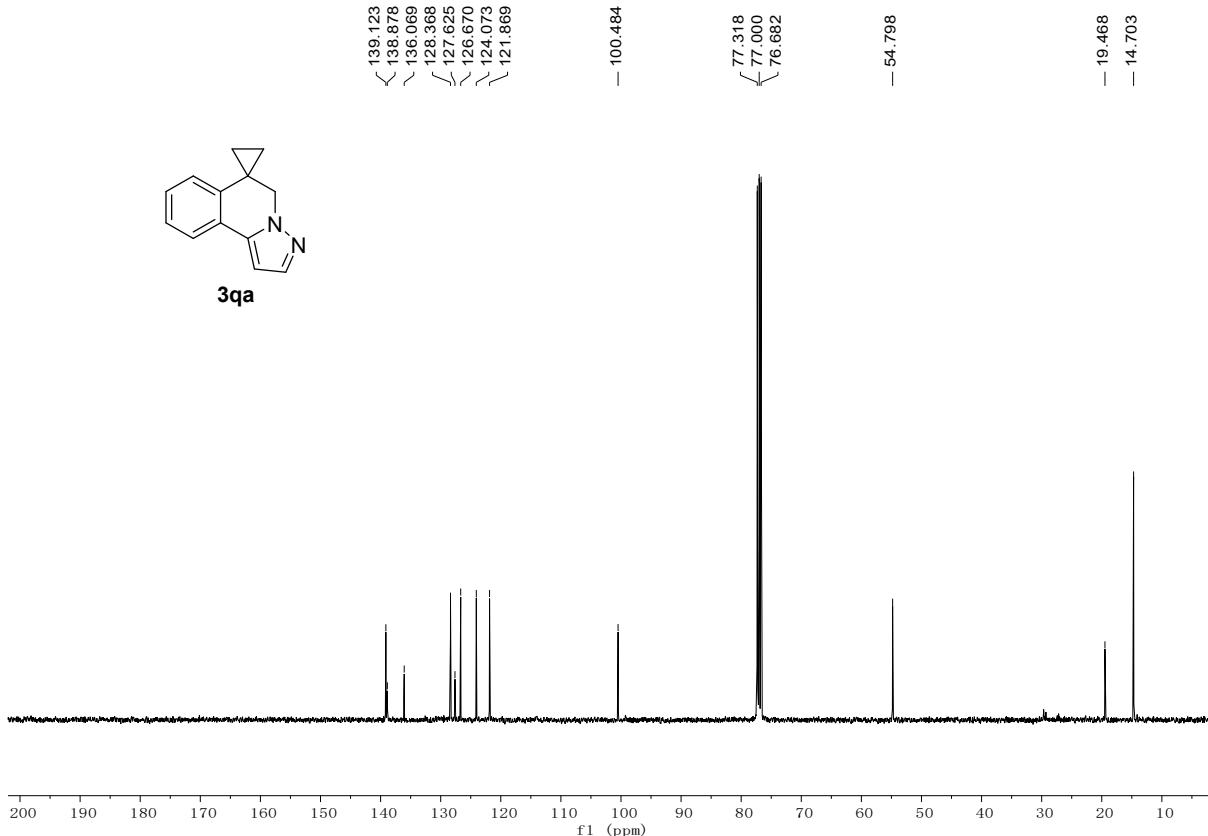
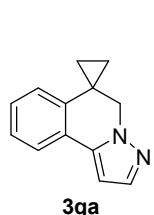
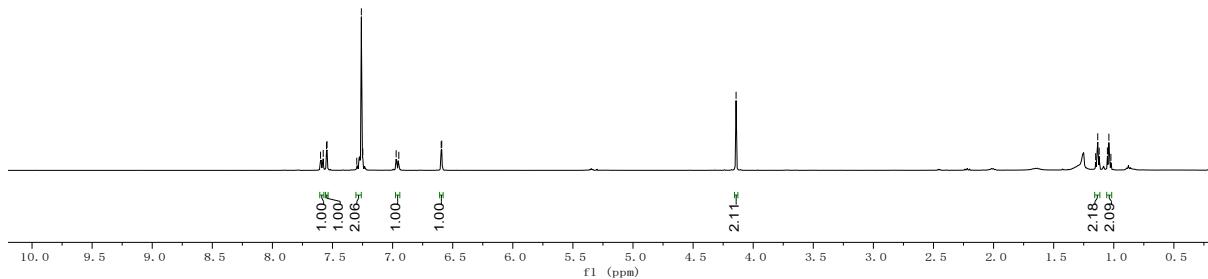
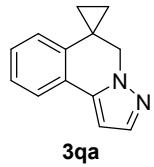


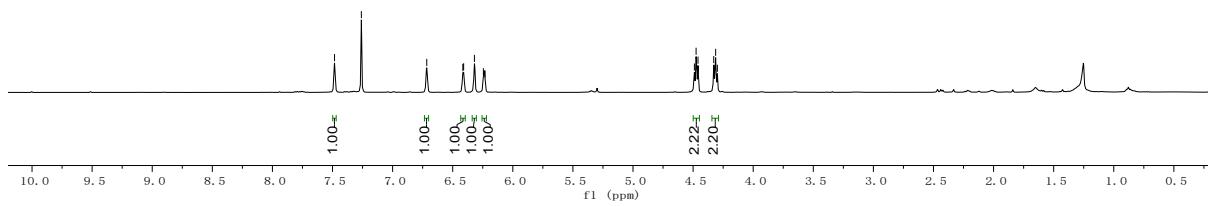
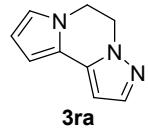


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 6.8959  
 6.8912

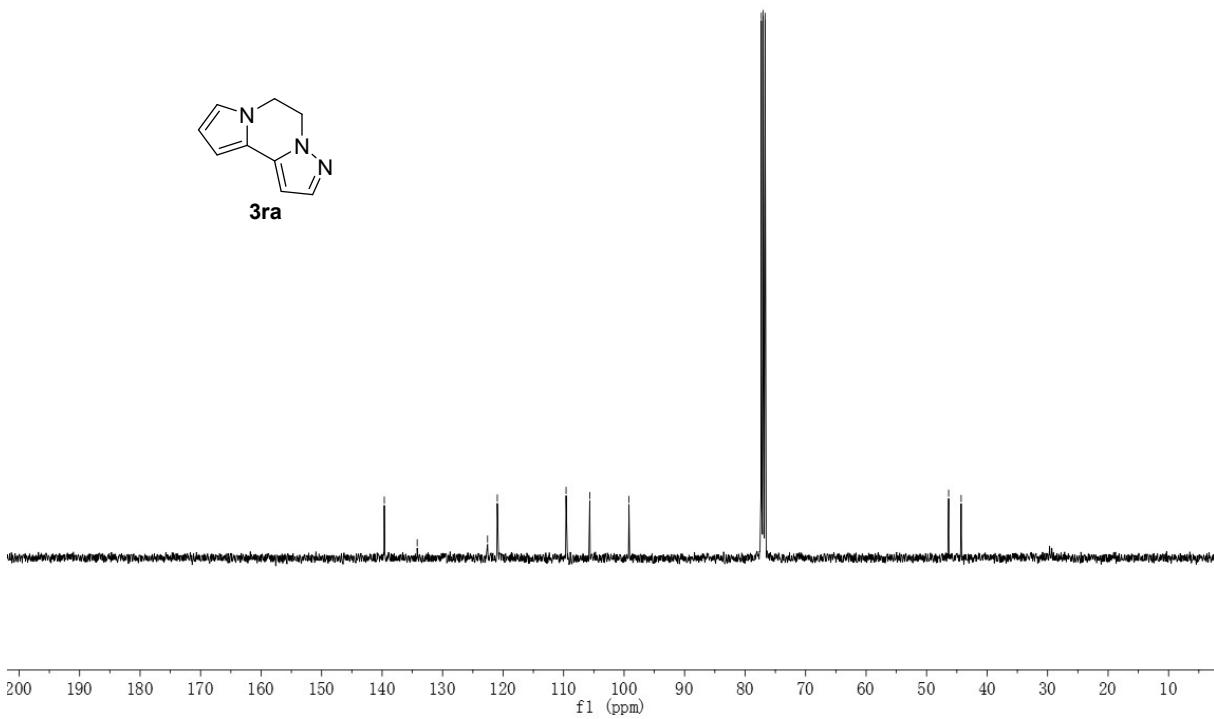
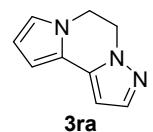
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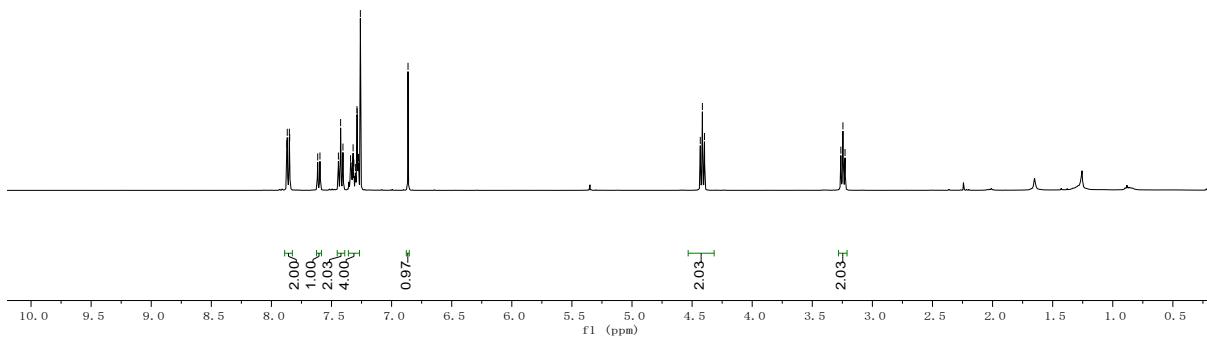
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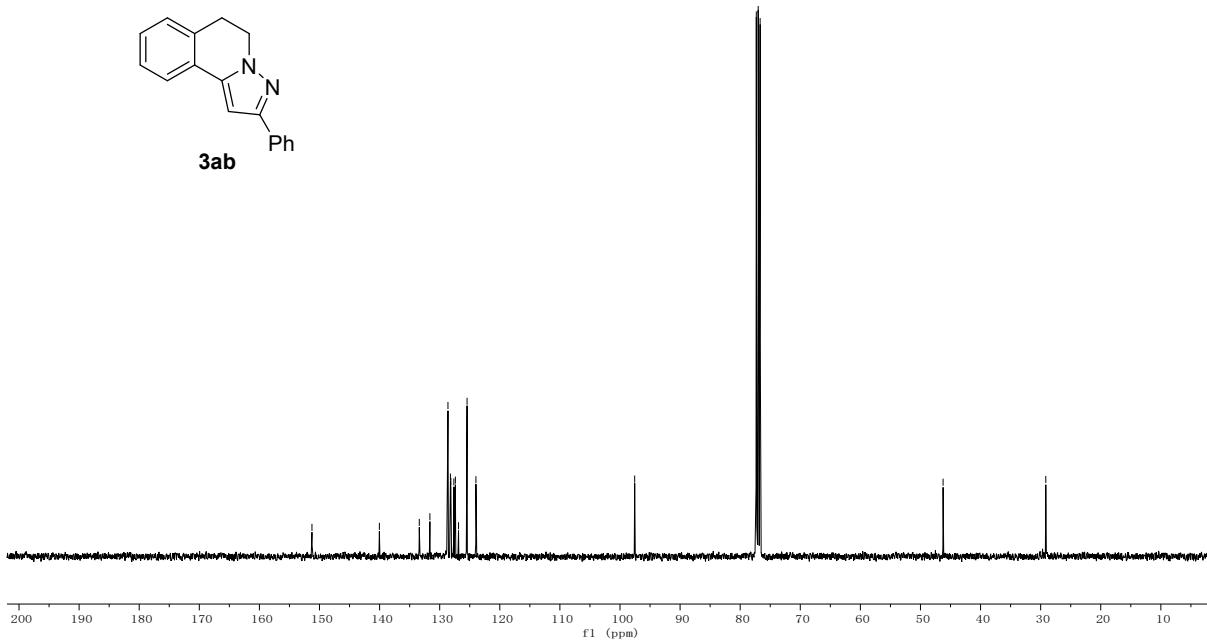


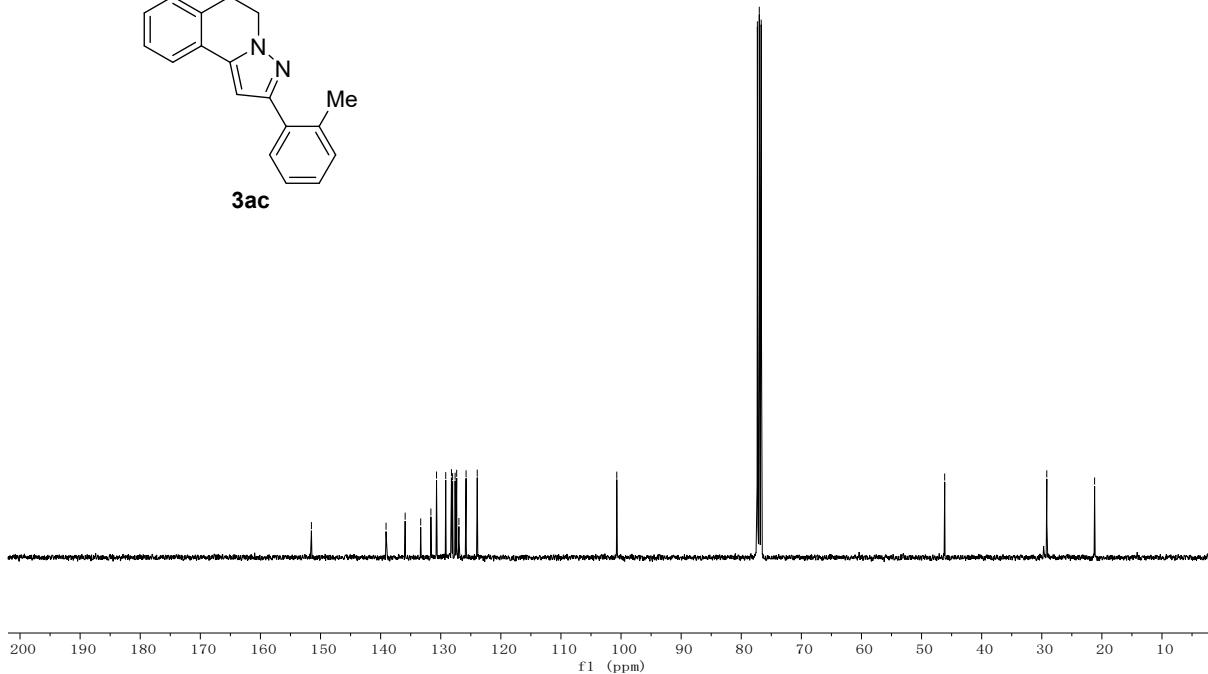
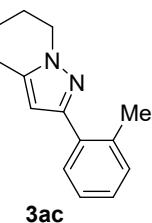
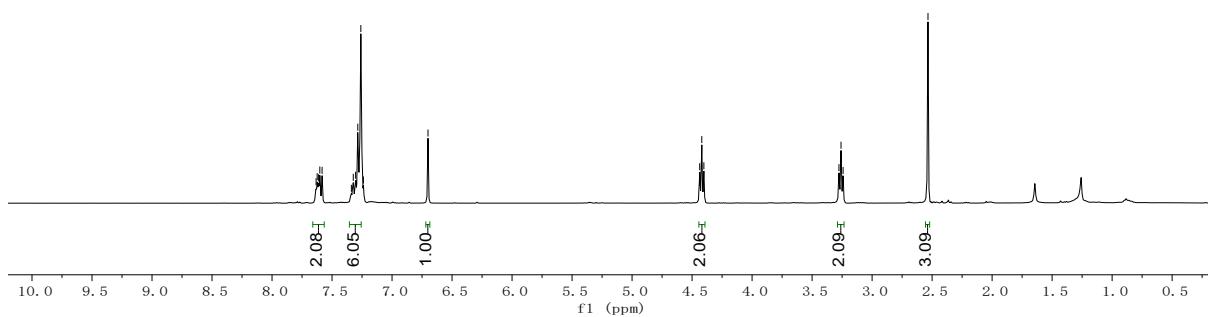
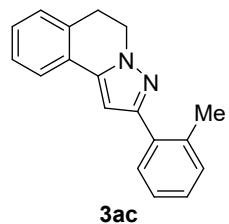
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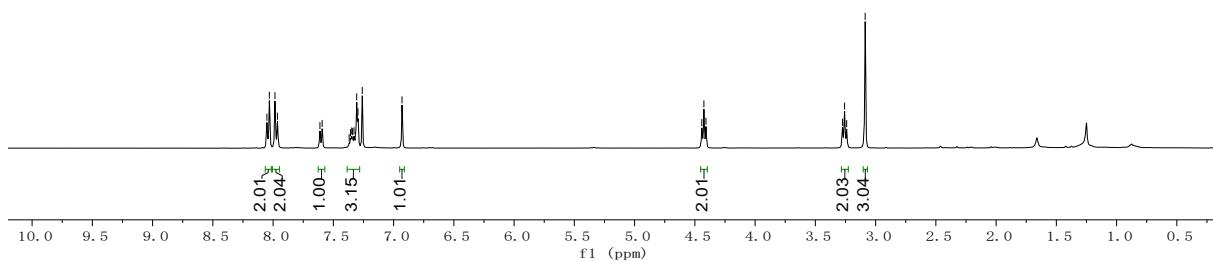
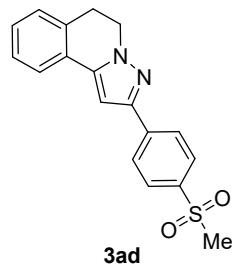


— 151.255  
— 140.036  
— 133.396  
— 131.630  
— 128.625  
— 128.214  
— 128.141  
— 127.642  
— 127.389  
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— 123.970  
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— 46.146

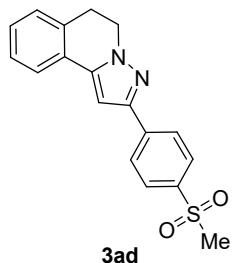




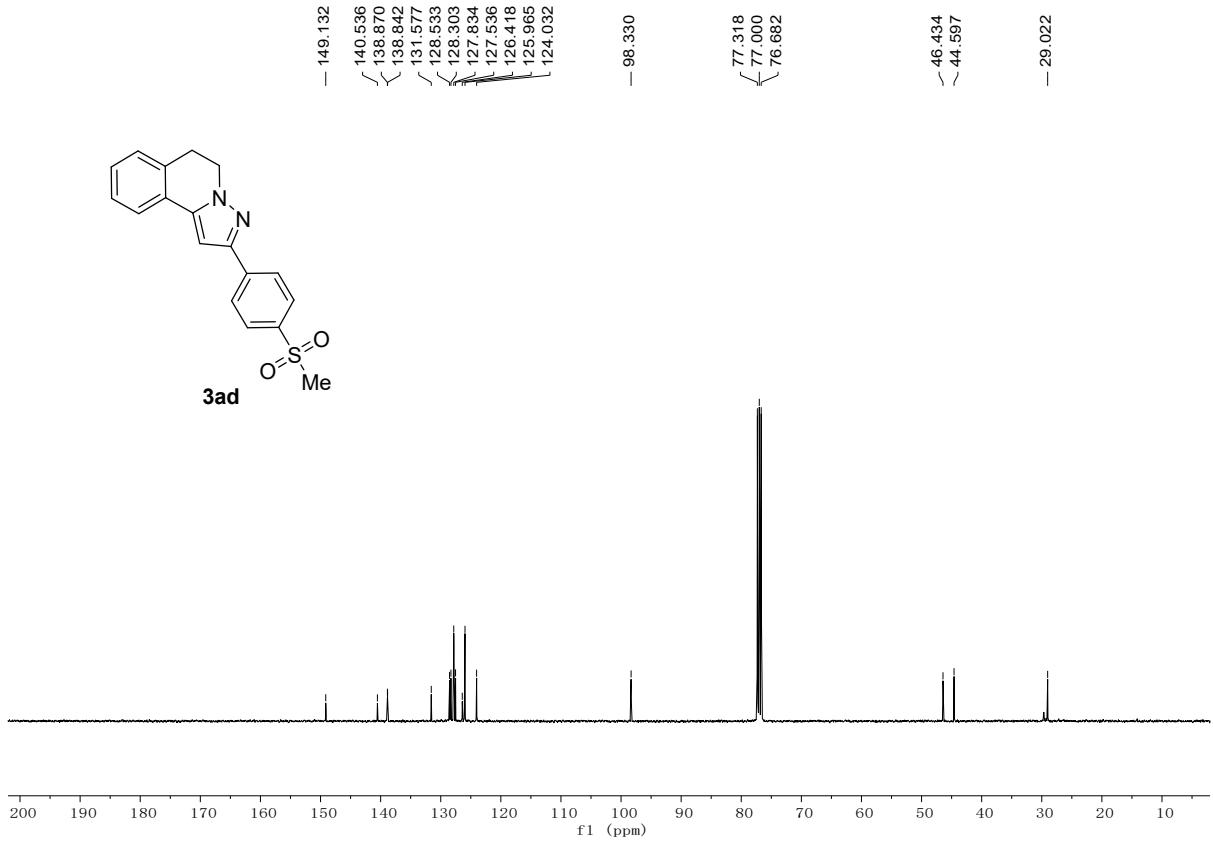
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 - 6.9301

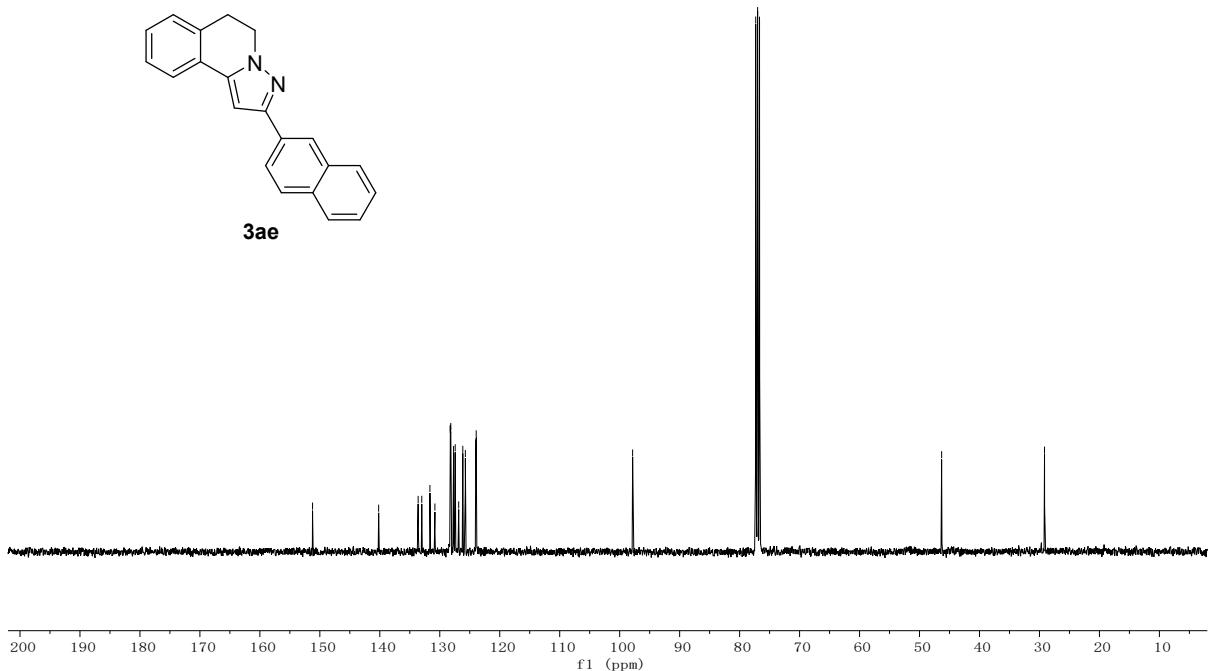
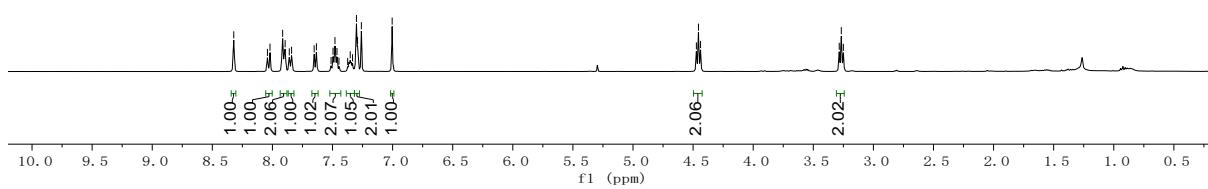


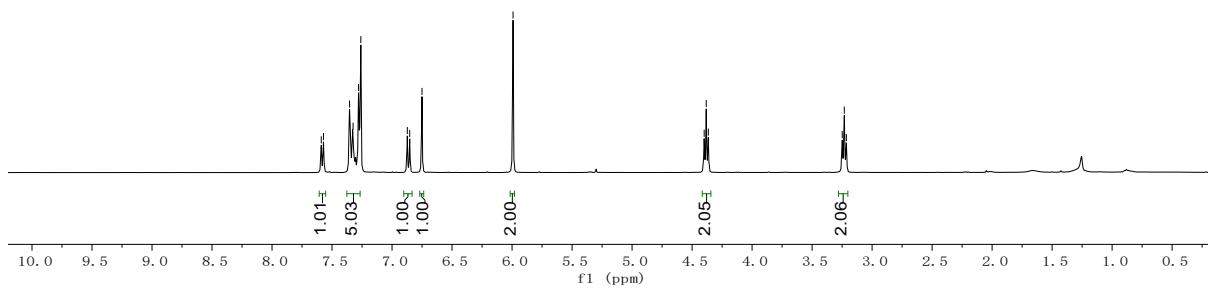
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 128.303  
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 127.536  
 126.418  
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4.4422  
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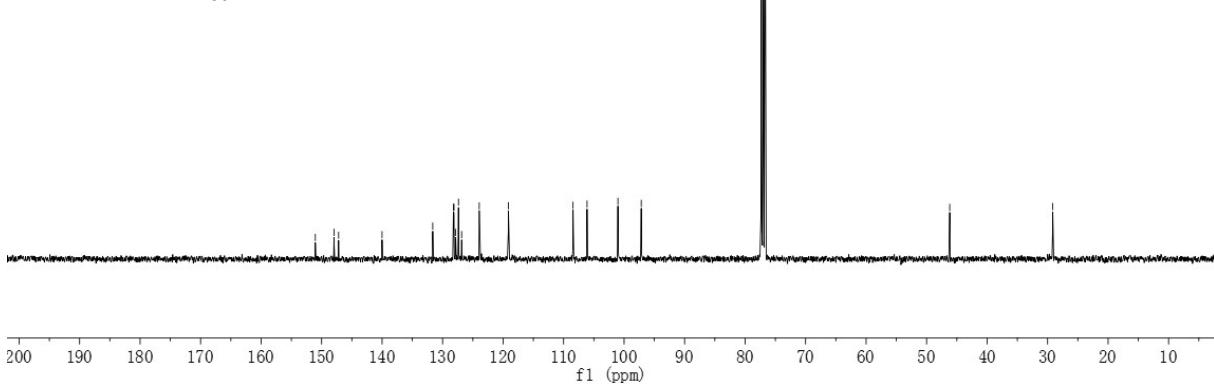
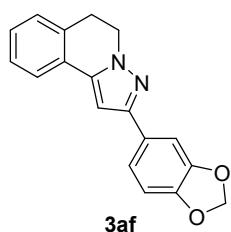


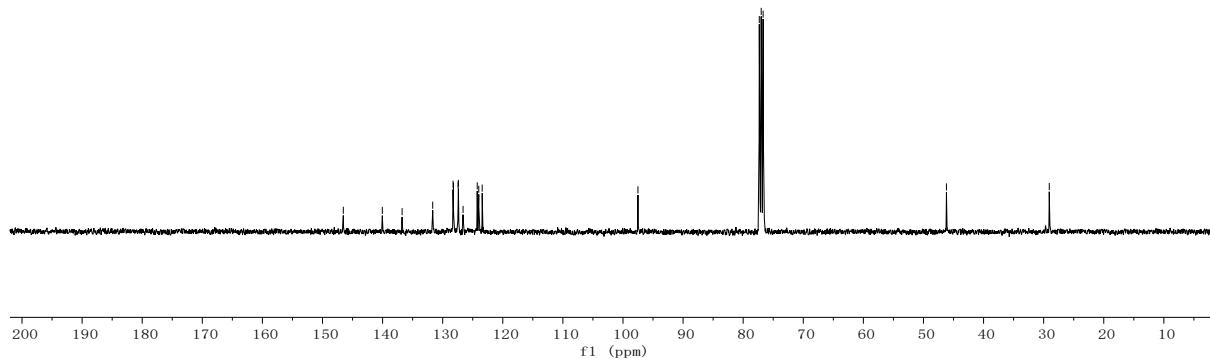
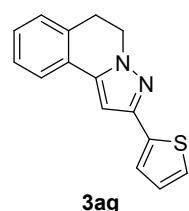
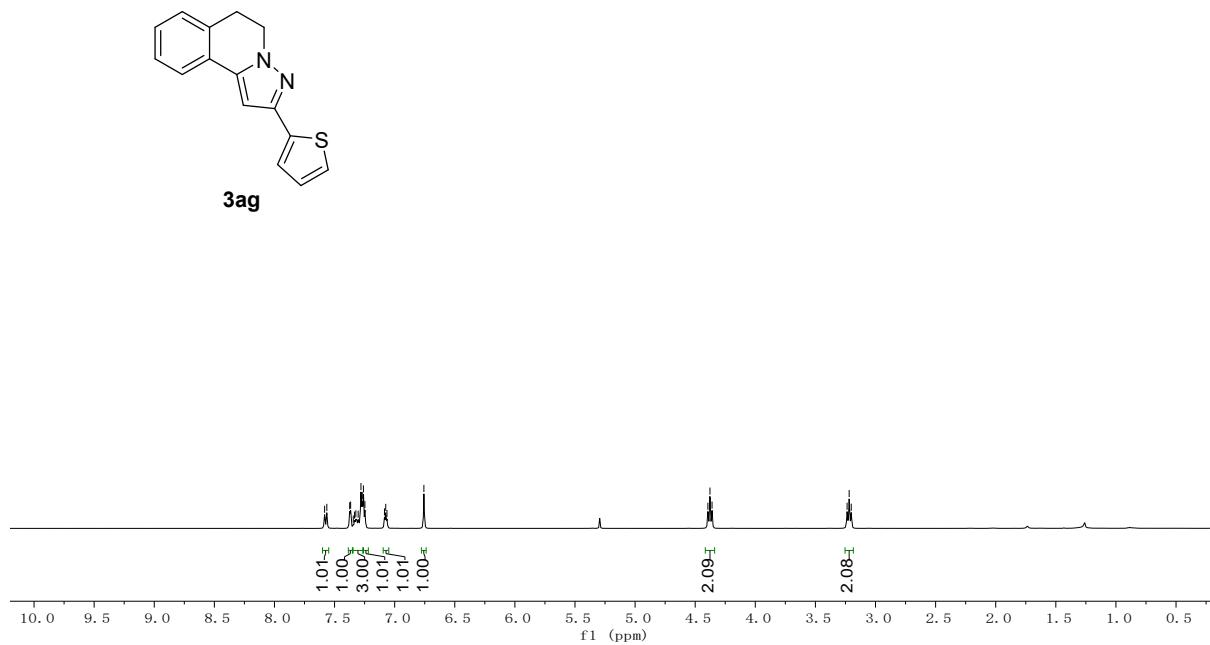


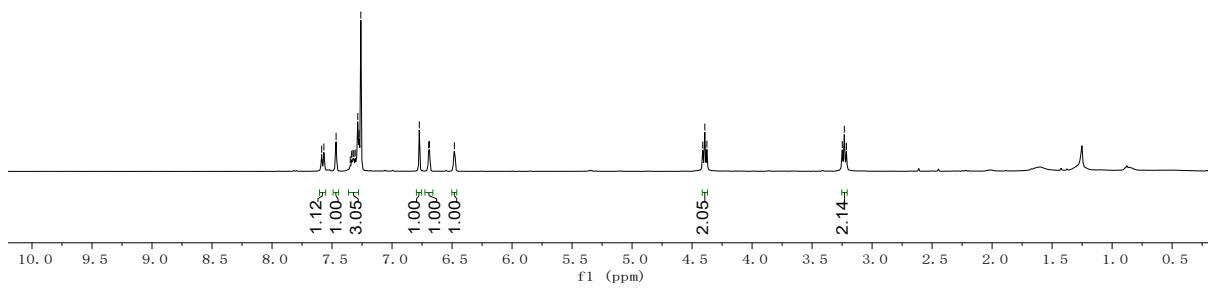
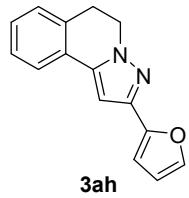
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 < 147.186  
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 / 128.202  
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 — 119.113

> 108.441  
 > 106.123  
 > 101.019  
 > 97.167

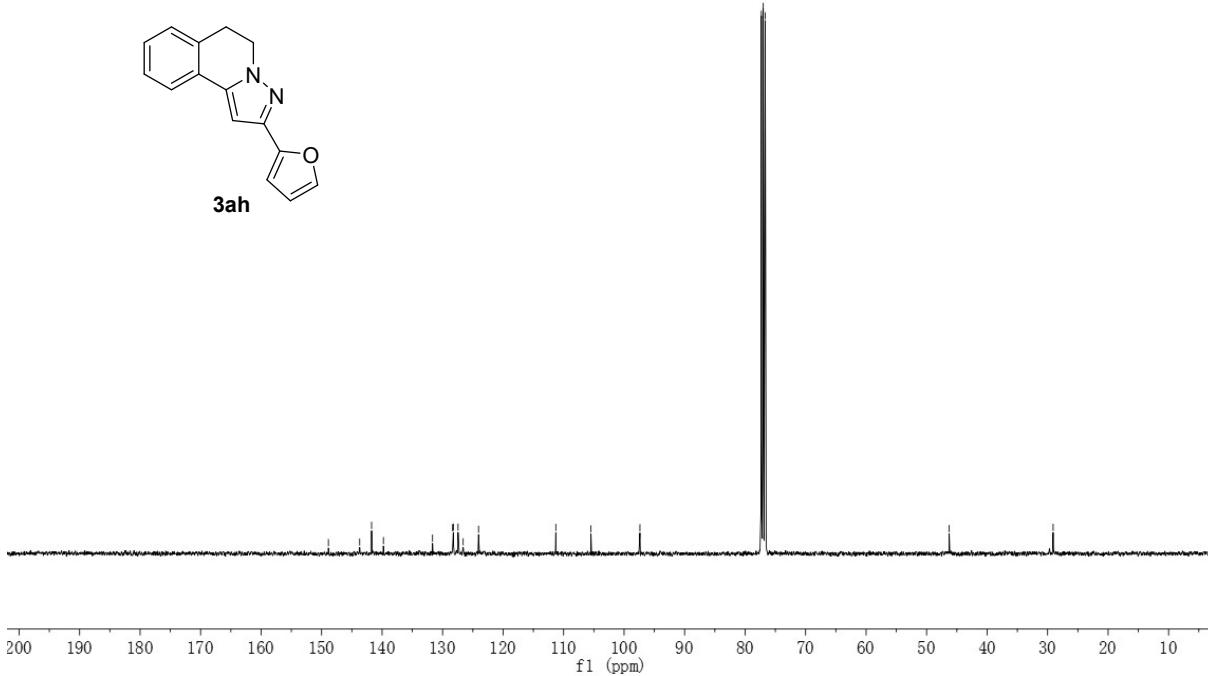
— 46.175  
 — 29.151

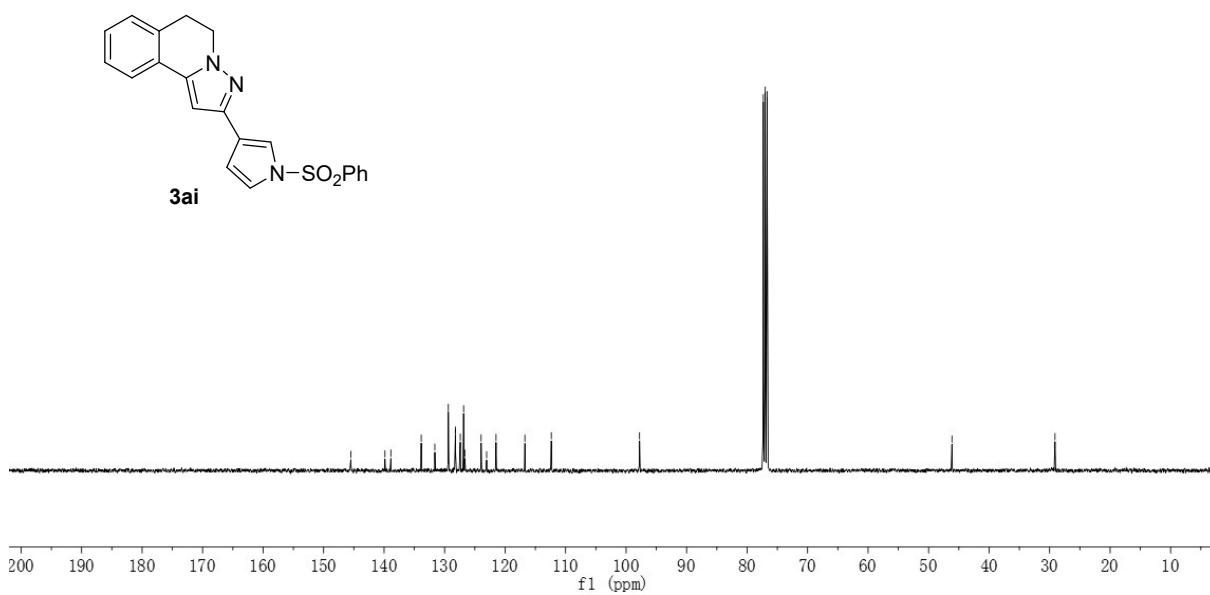
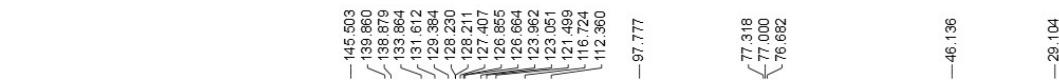
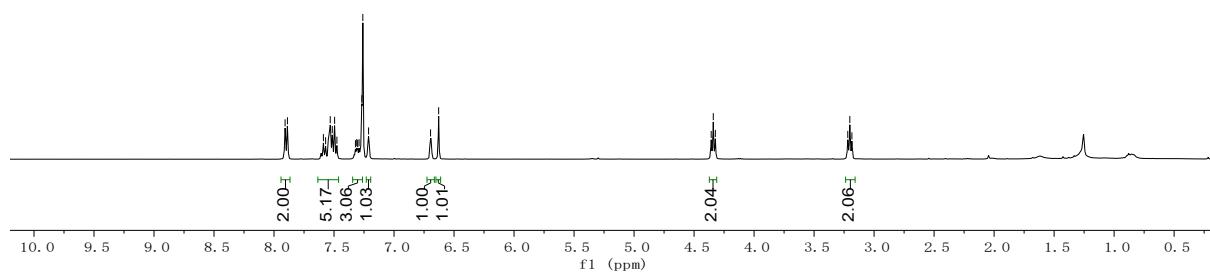


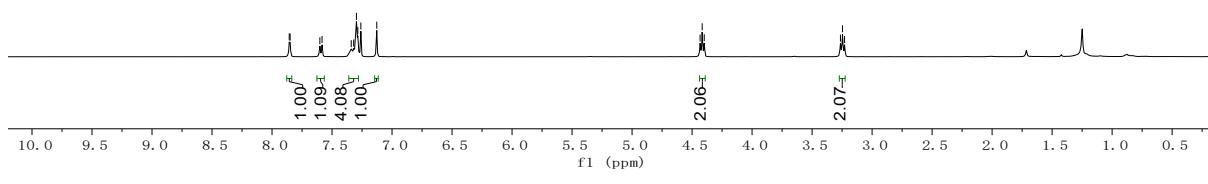
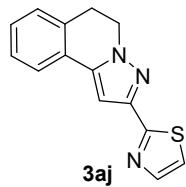




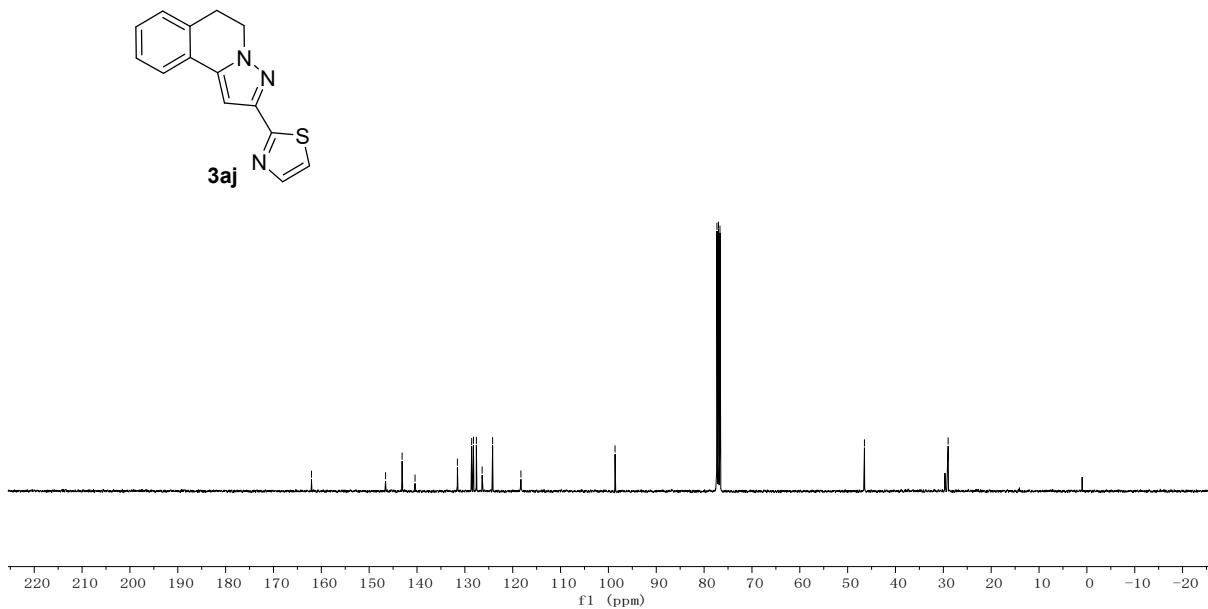
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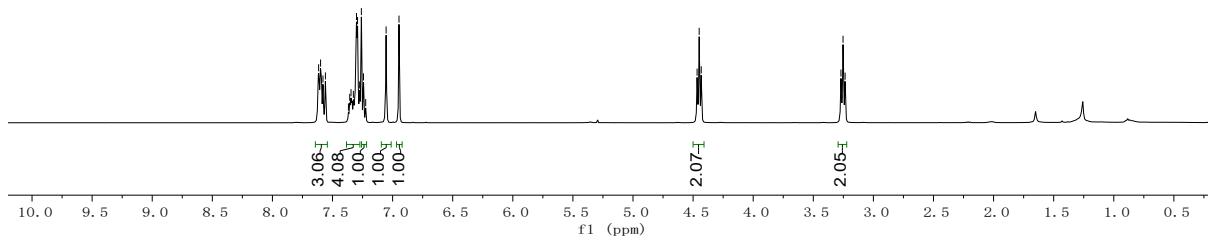
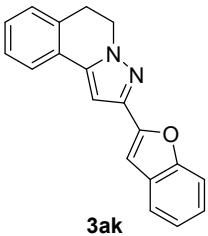






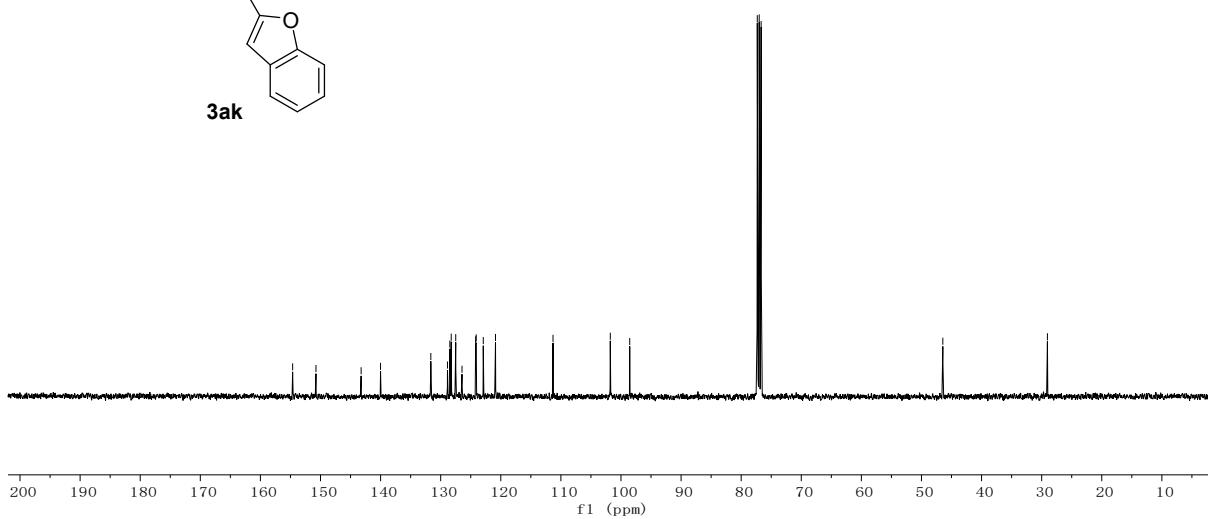
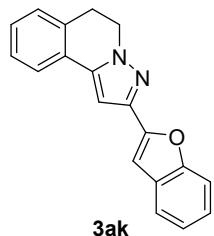
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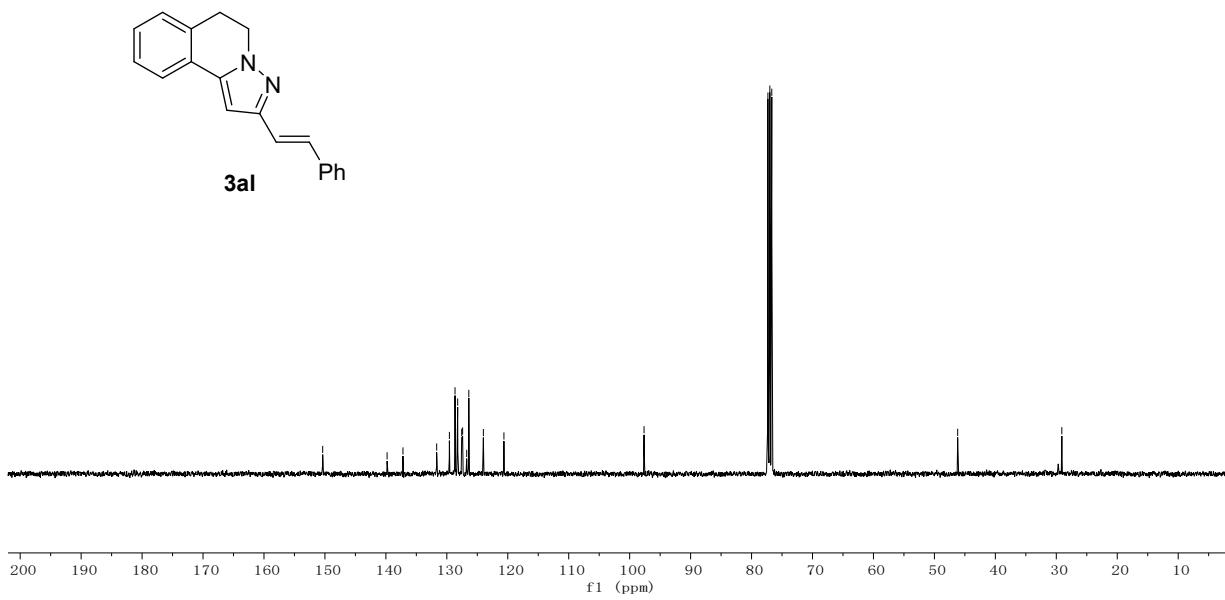
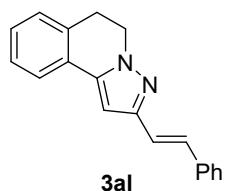
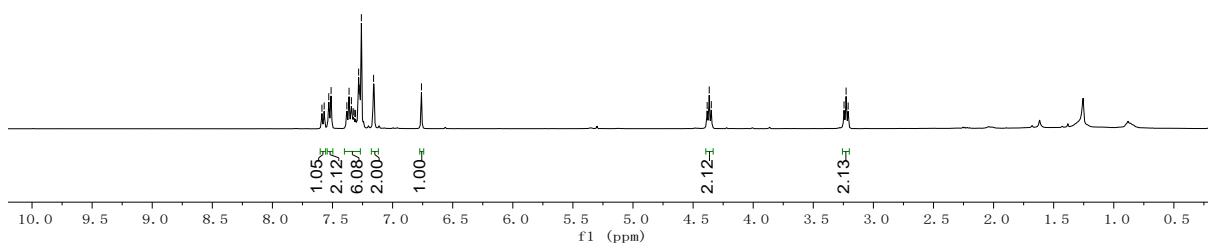
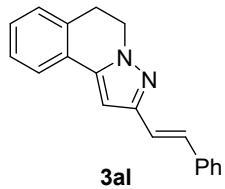


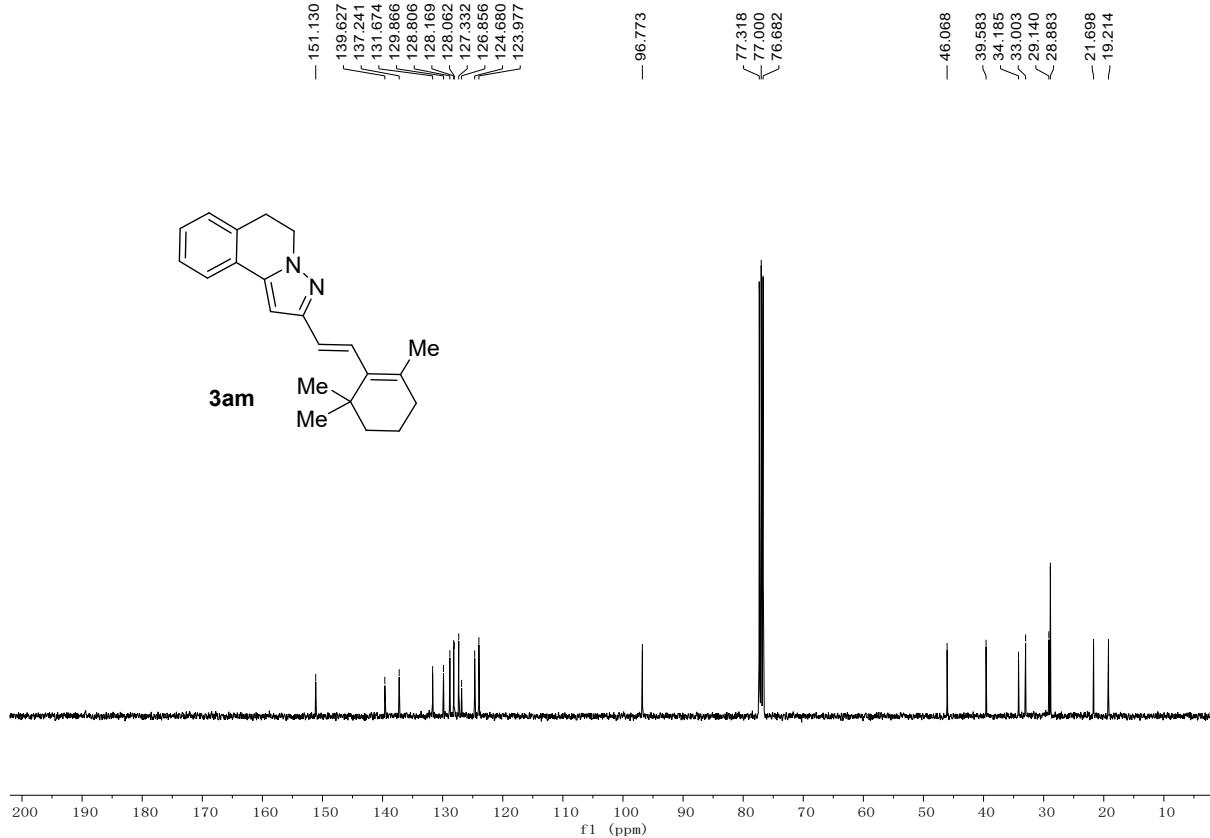
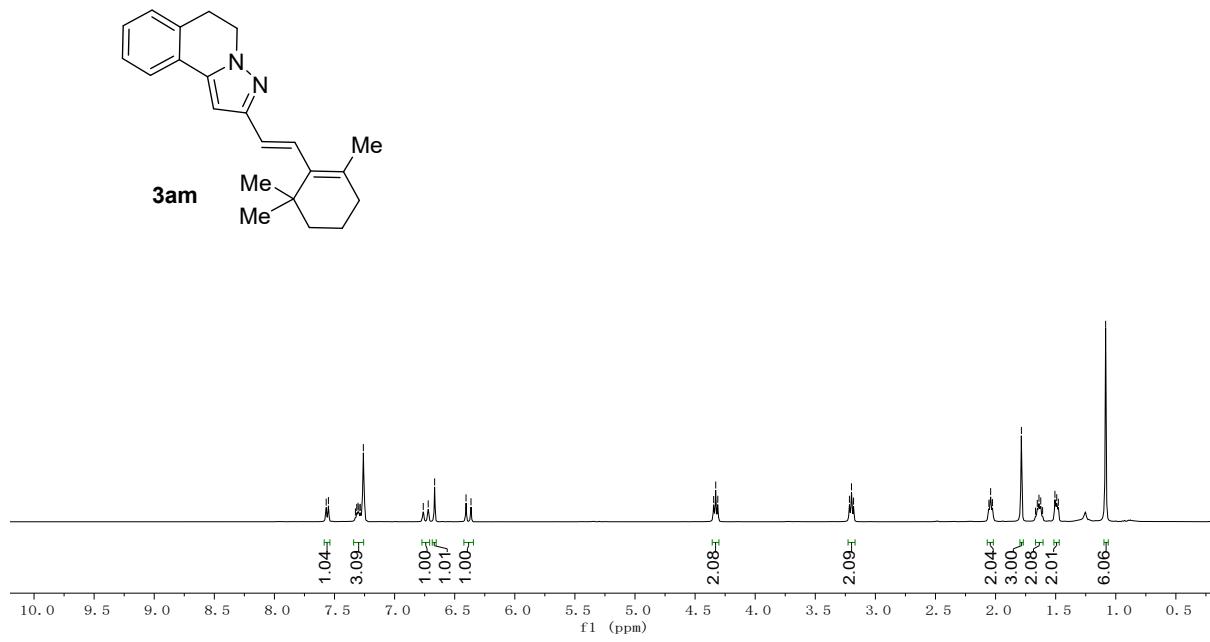
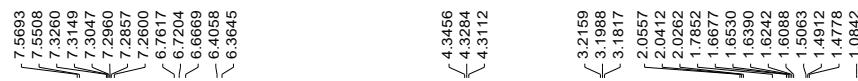


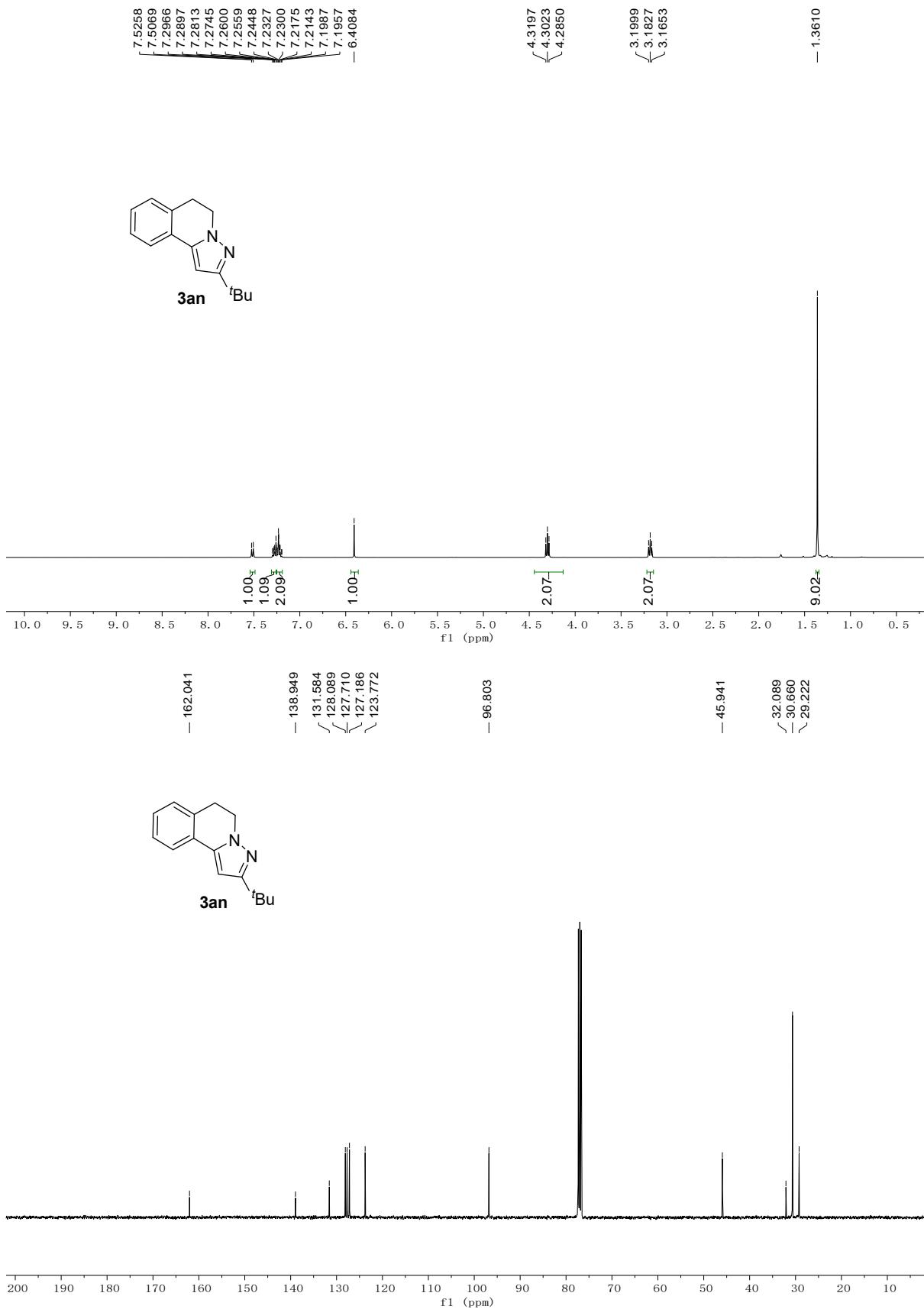
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— 150.754  
— 143.241  
— 140.009  
— 131.641  
— 128.872  
— 128.476  
— 128.248  
— 127.497  
— 126.451  
— 124.185  
— 124.092  
— 122.916  
— 120.879  
— 111.310  
— 101.779  
— 98.546

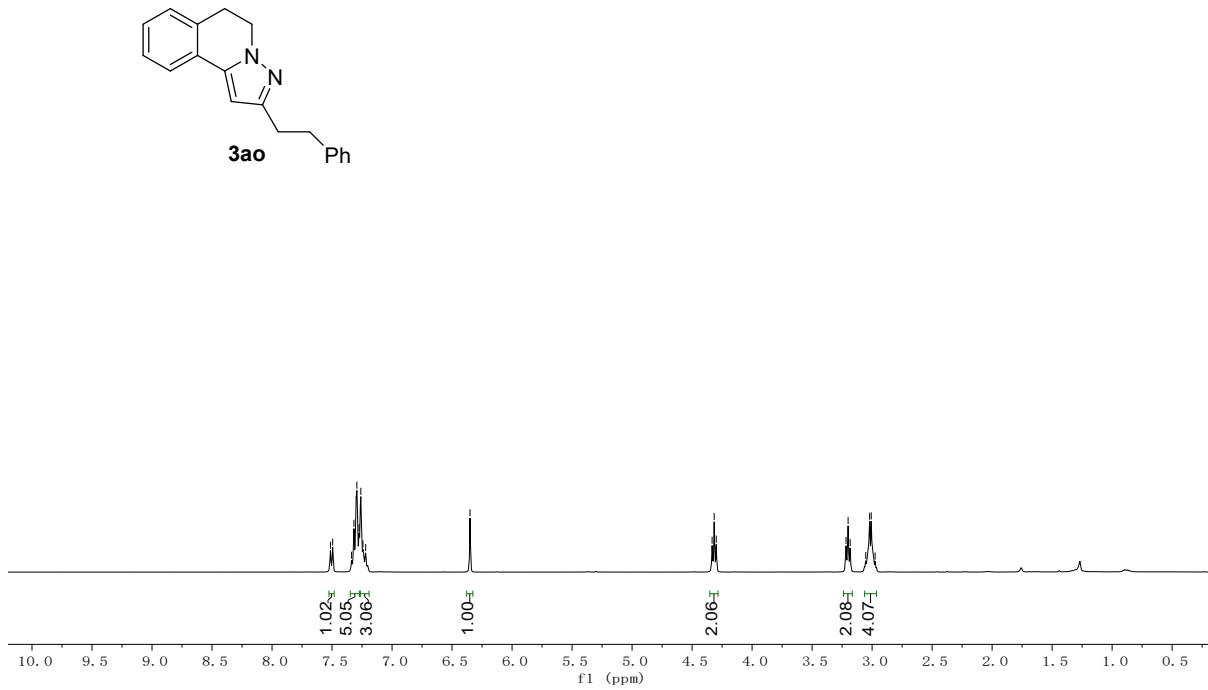
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— 29.040



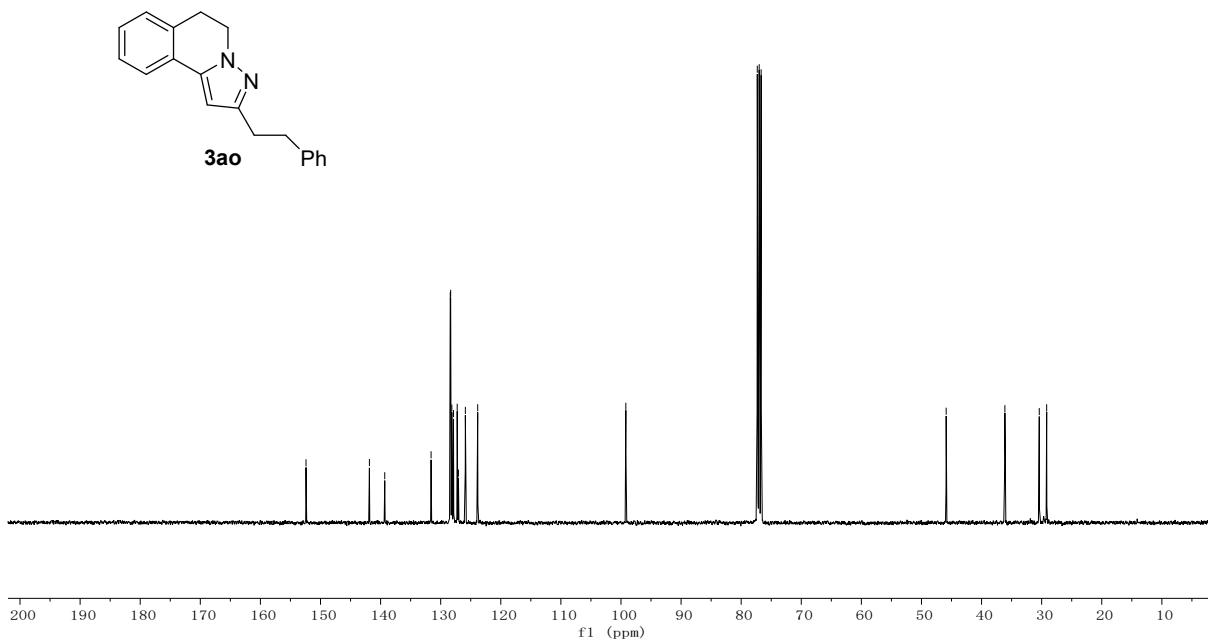


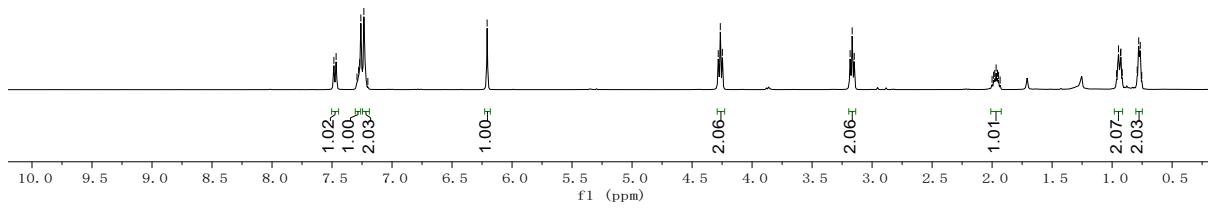
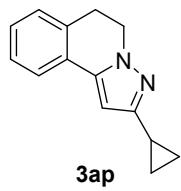




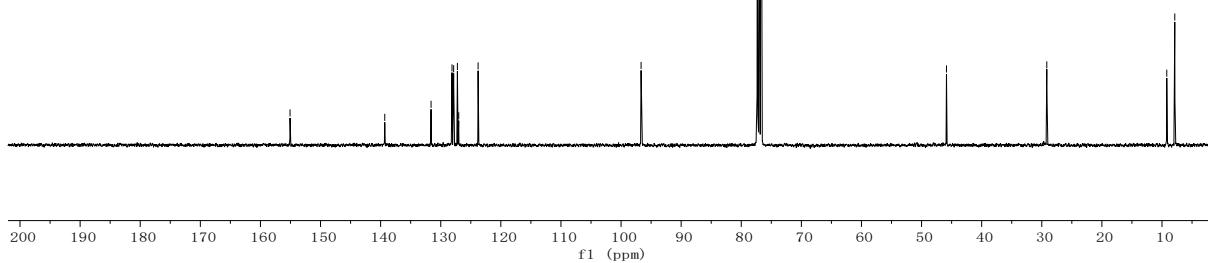
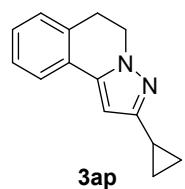


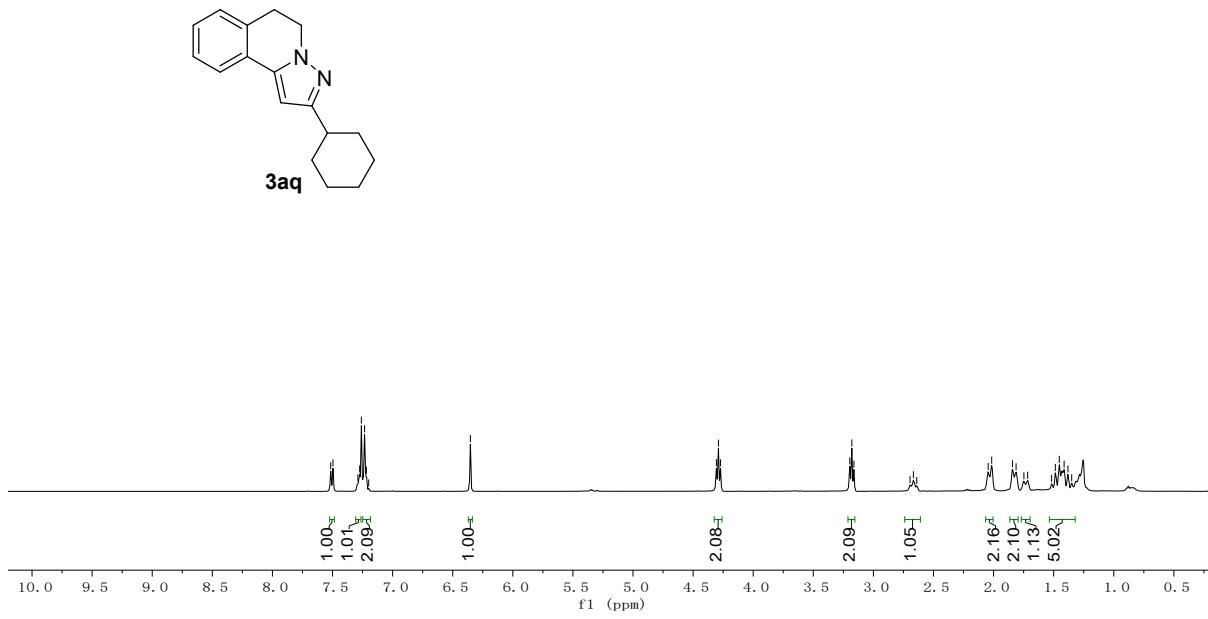
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— 141.862  
— 139.309  
— 131.598  
— 128.406  
— 128.340  
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— 127.873  
— 127.253  
— 127.051  
— 125.896  
— 123.640



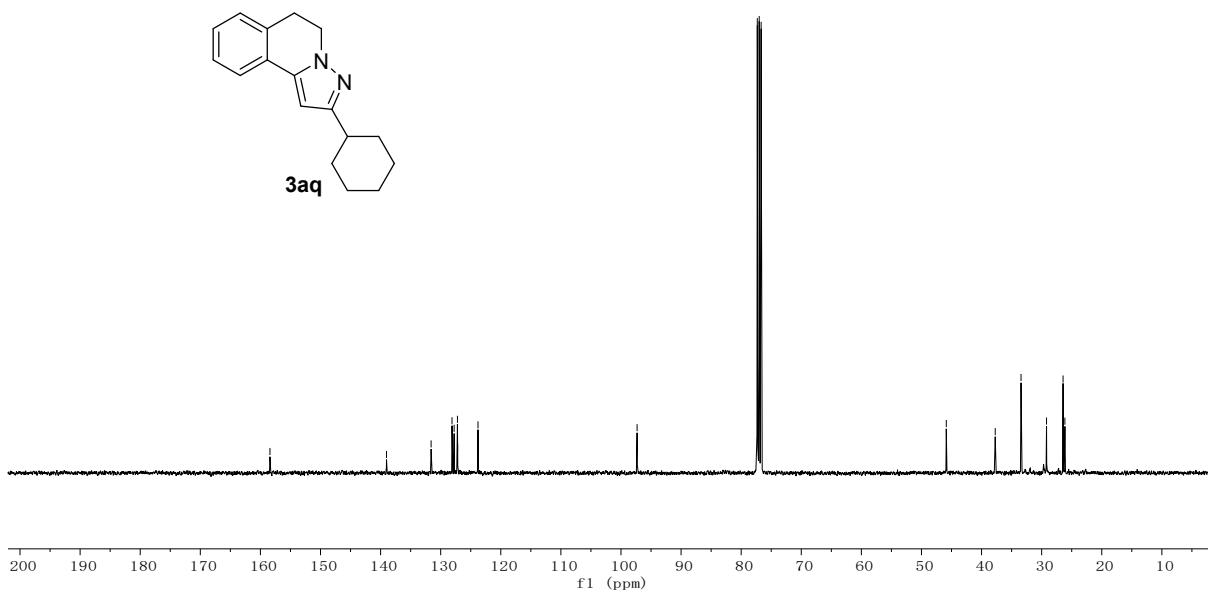


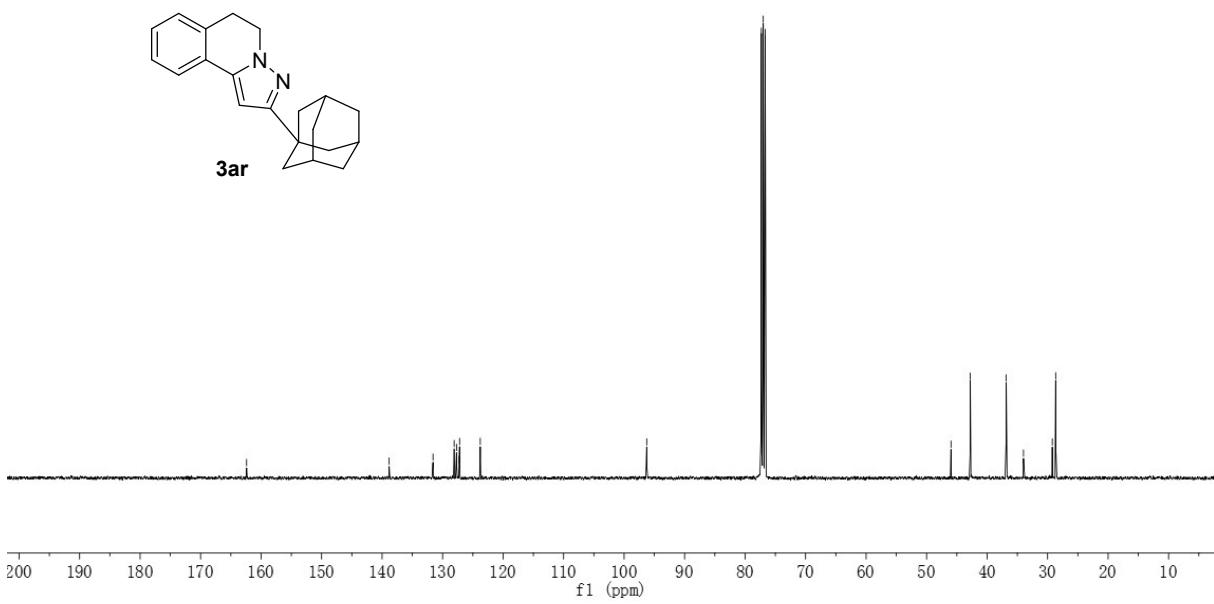
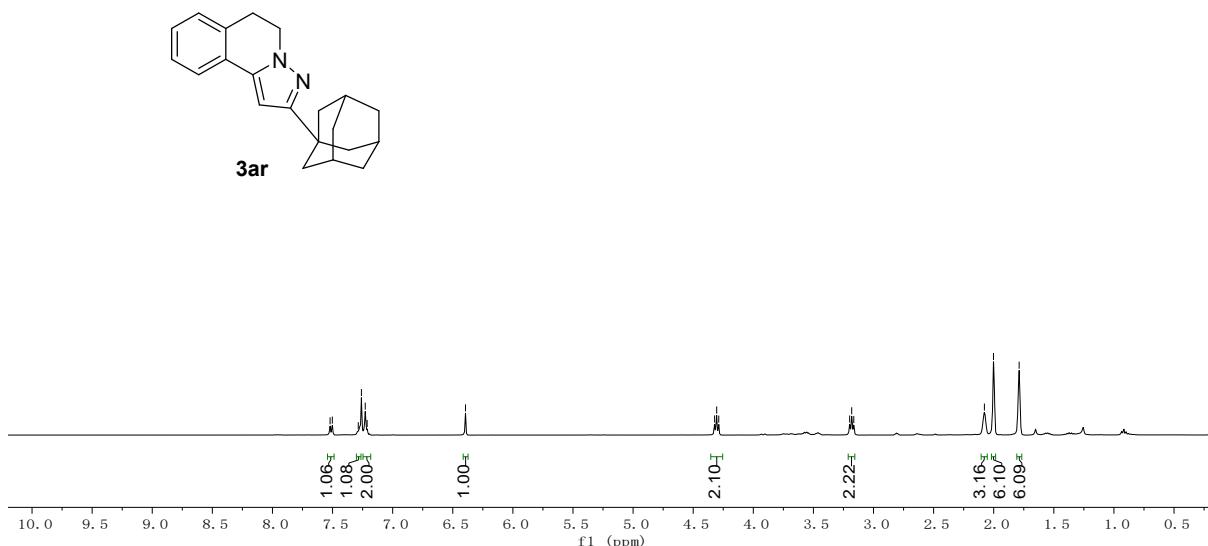
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~7.869

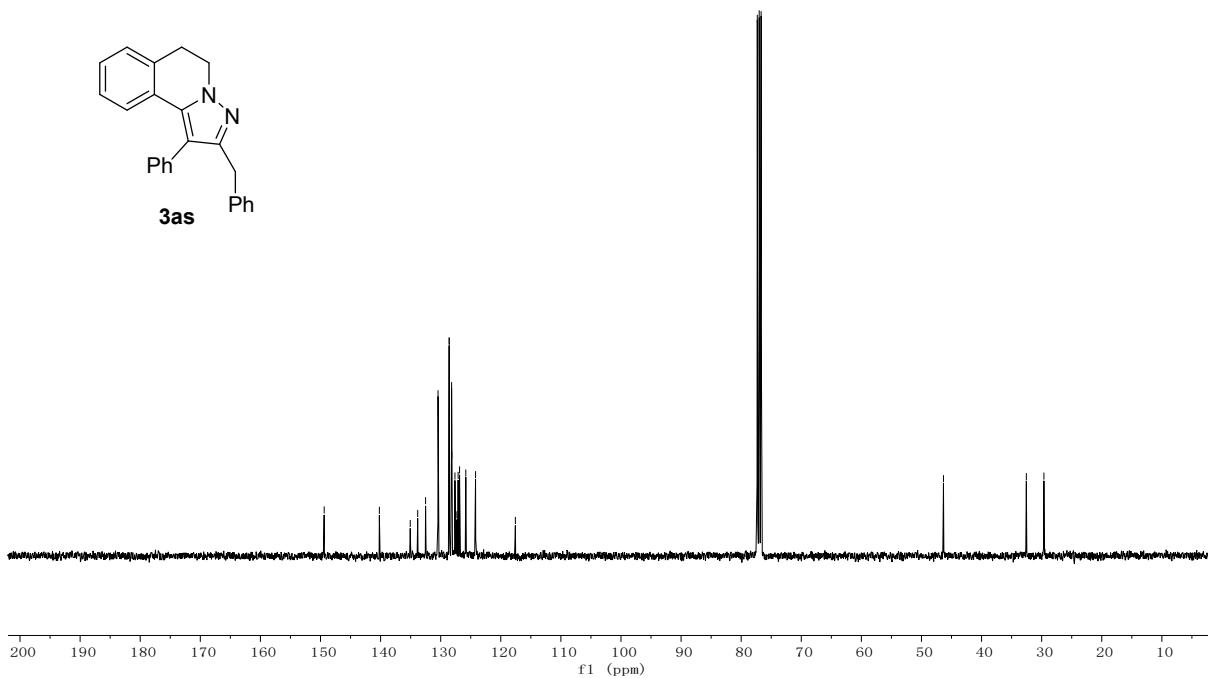
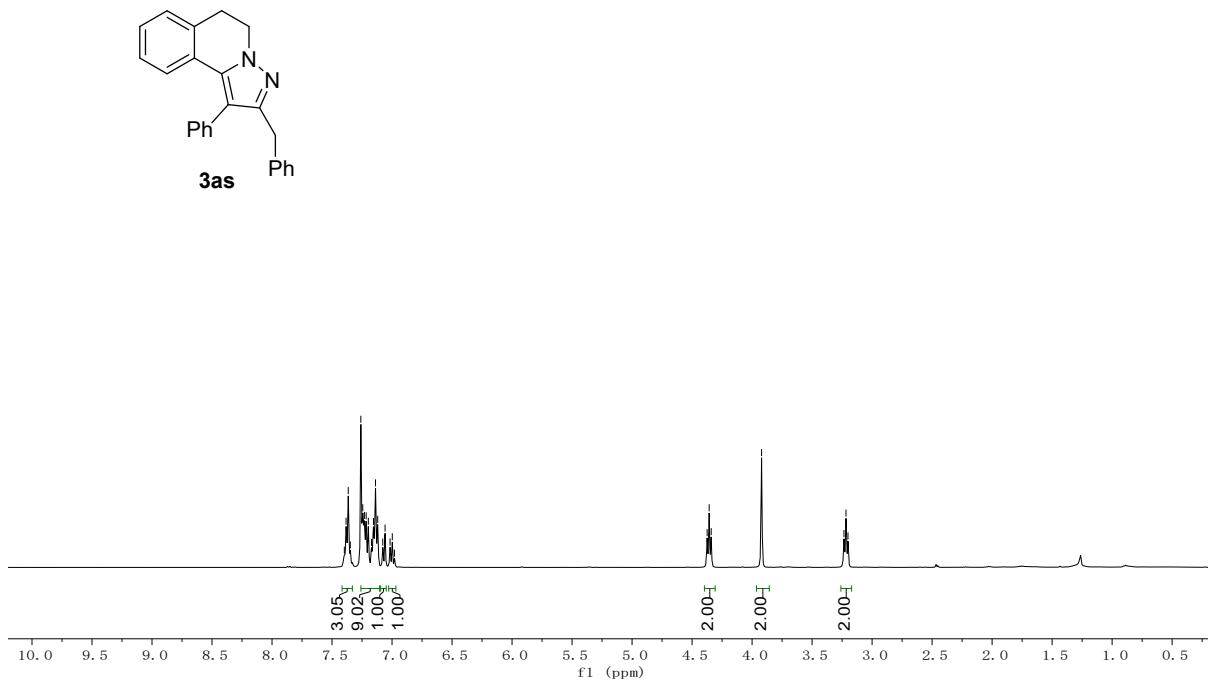


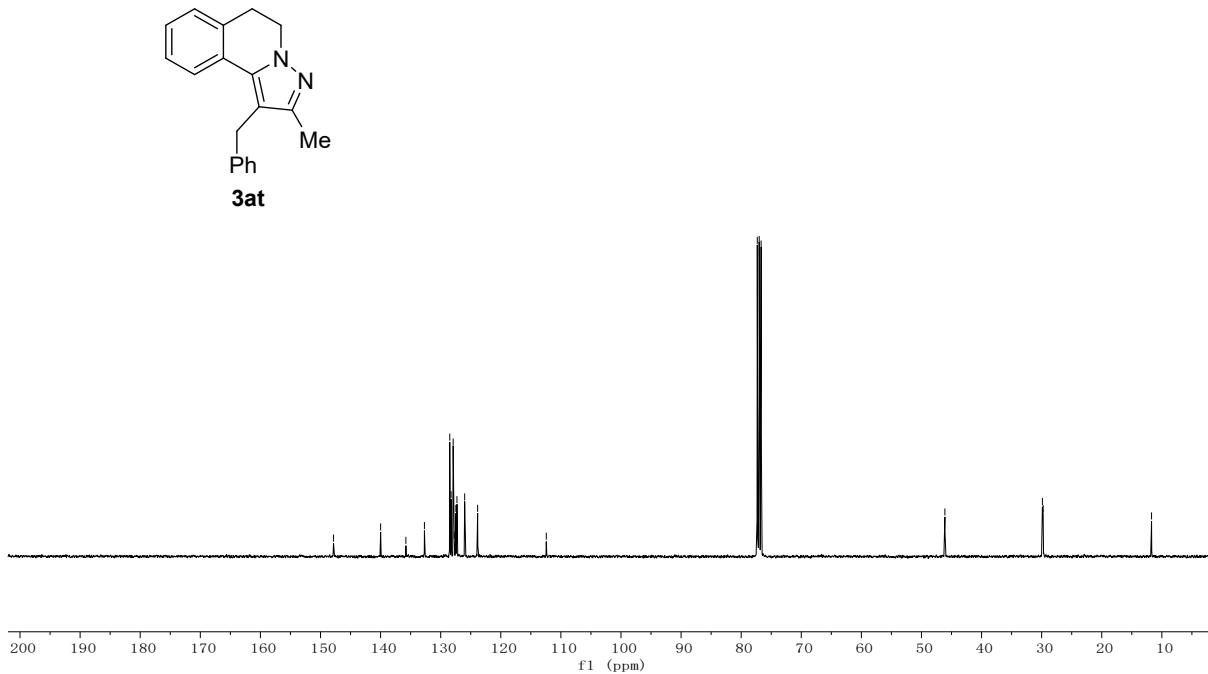
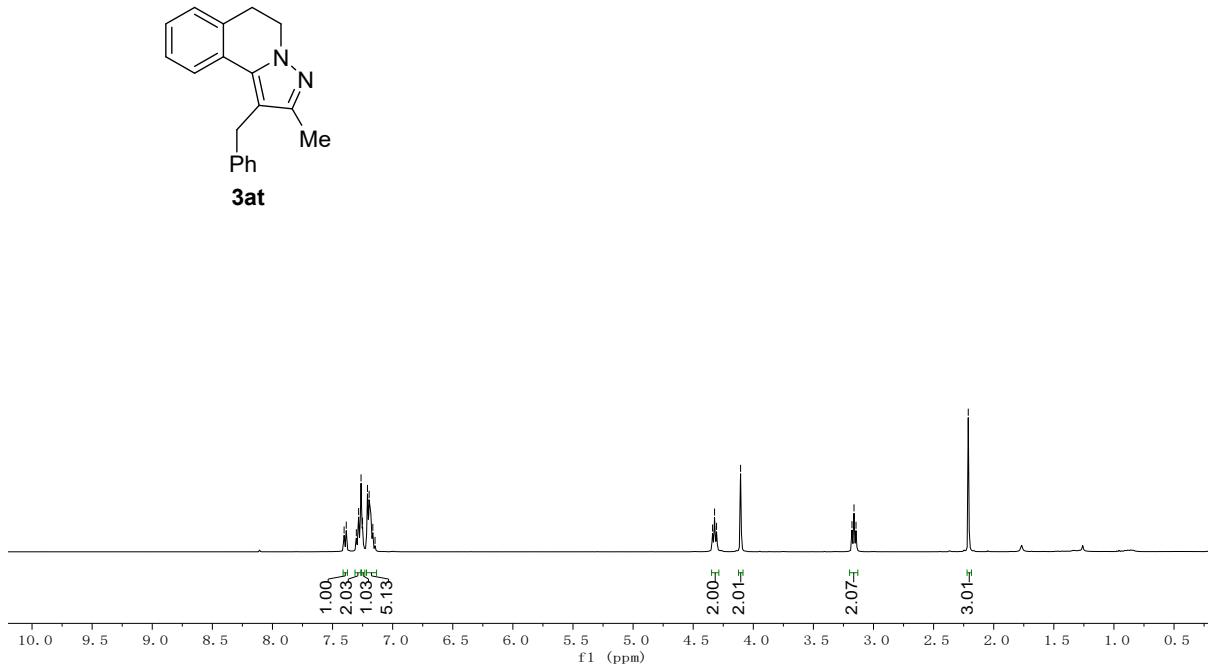
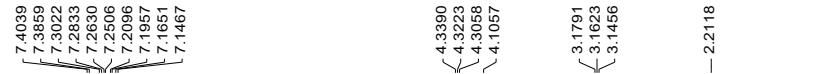


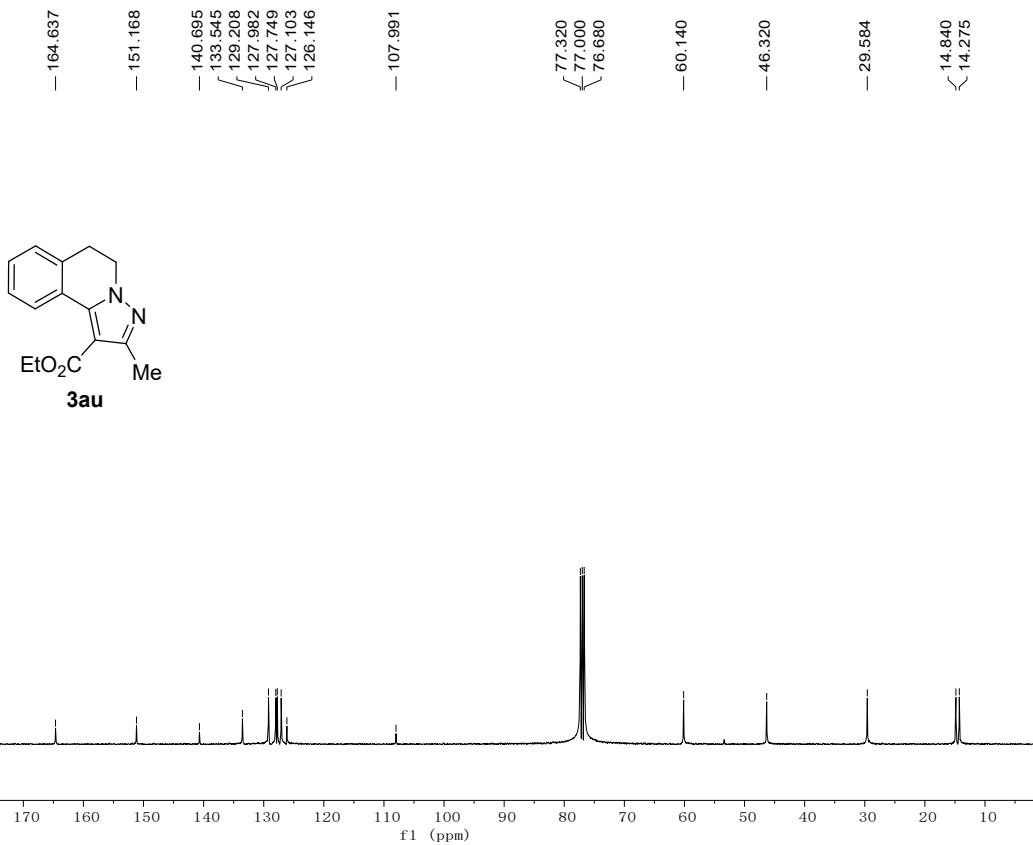
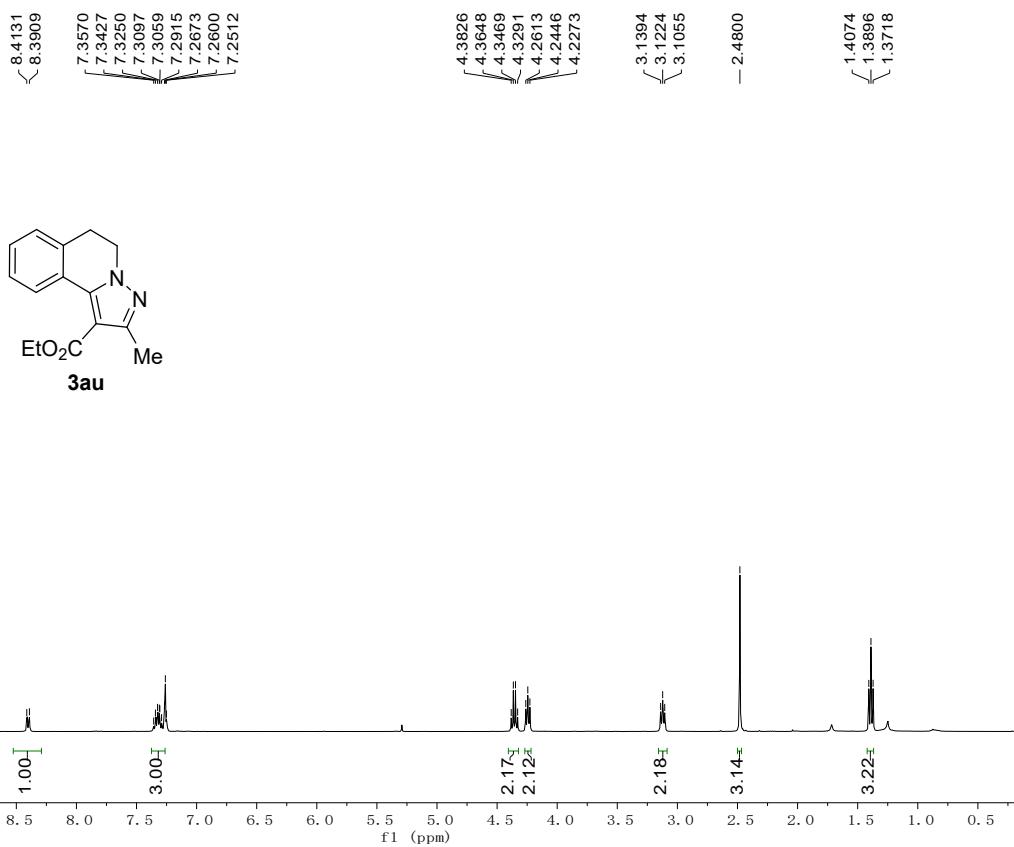
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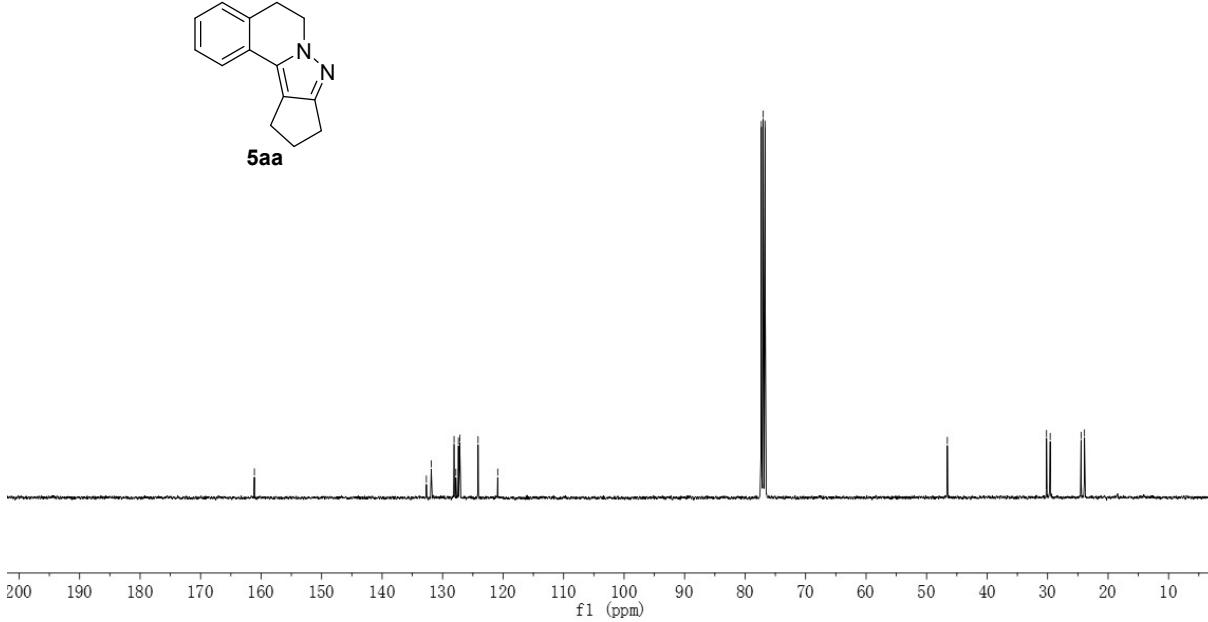
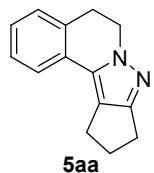
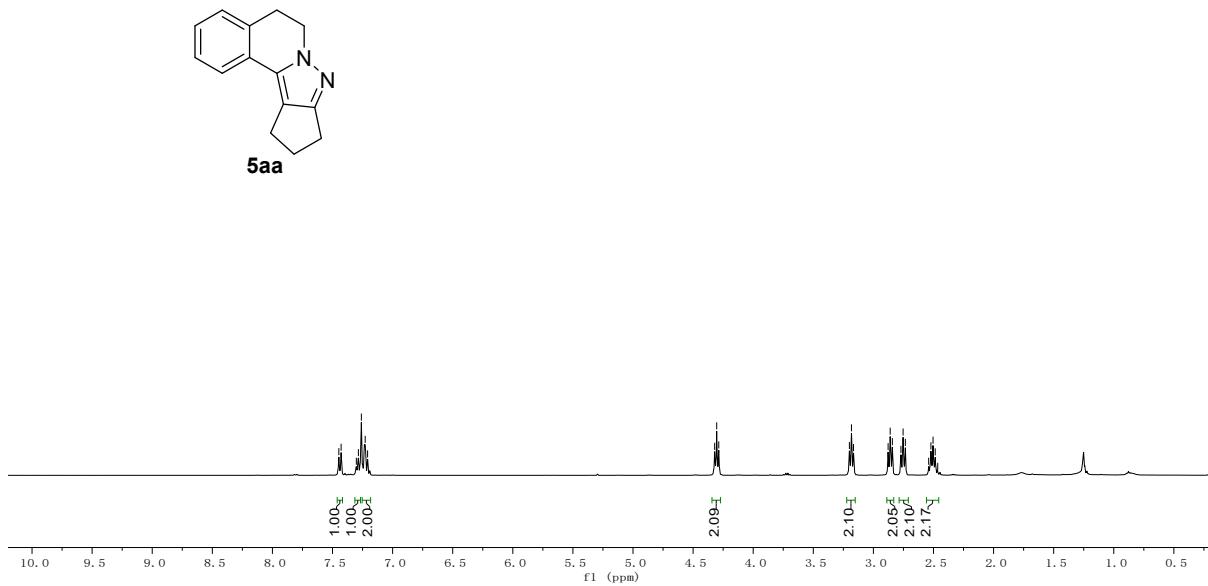


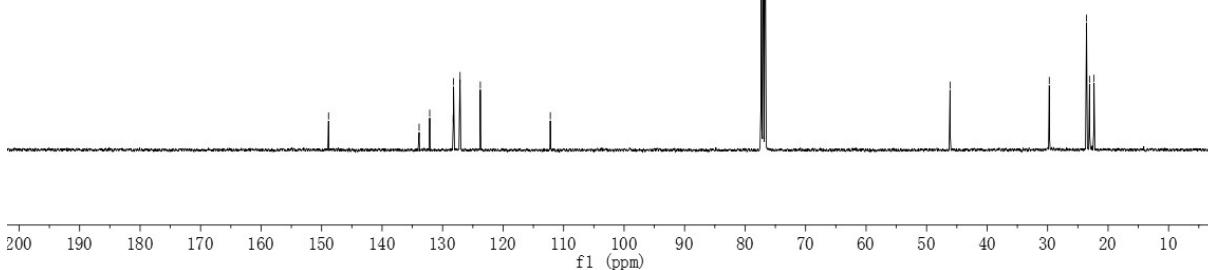
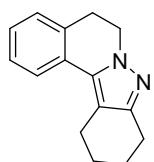
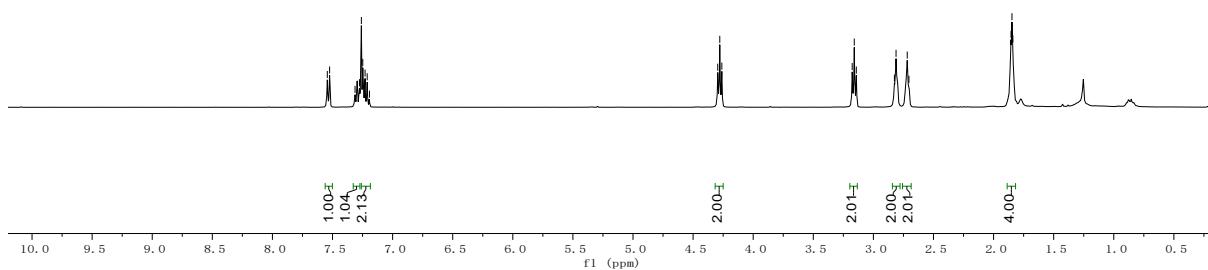
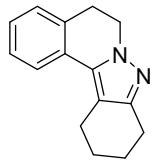


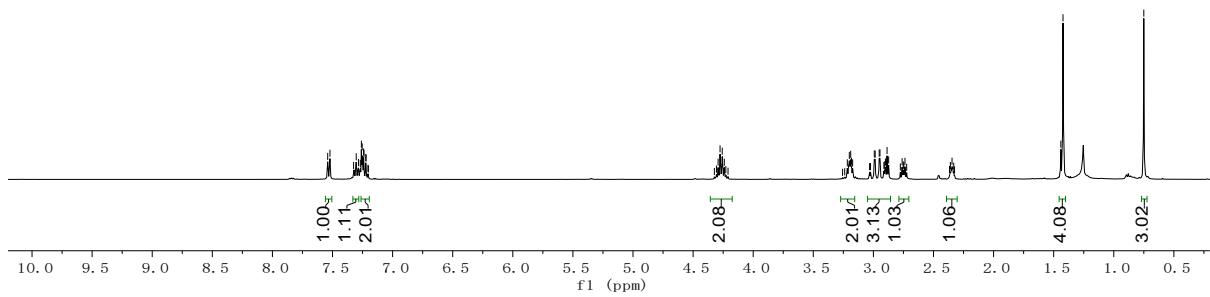
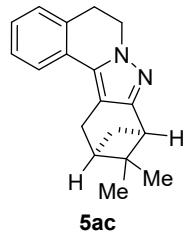




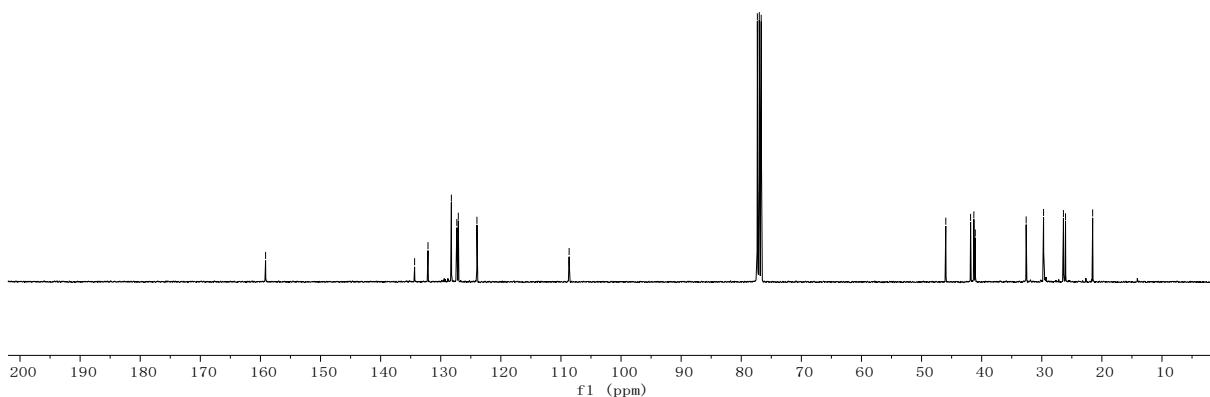
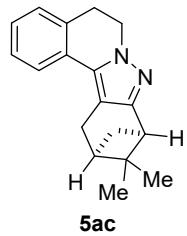




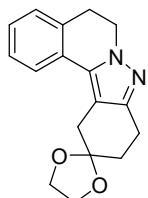




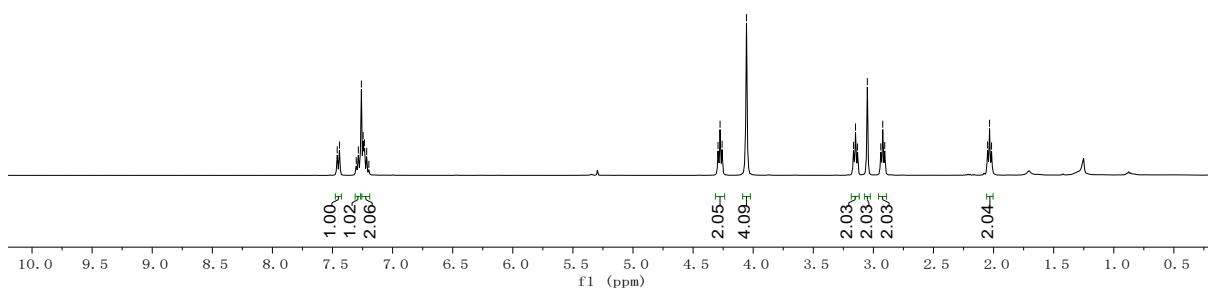
— 159.141  
— 108.640



7.4610  
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 7.2951  
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 7.2454  
 7.2345  
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 7.1978



**5ad**

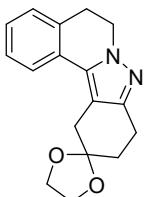


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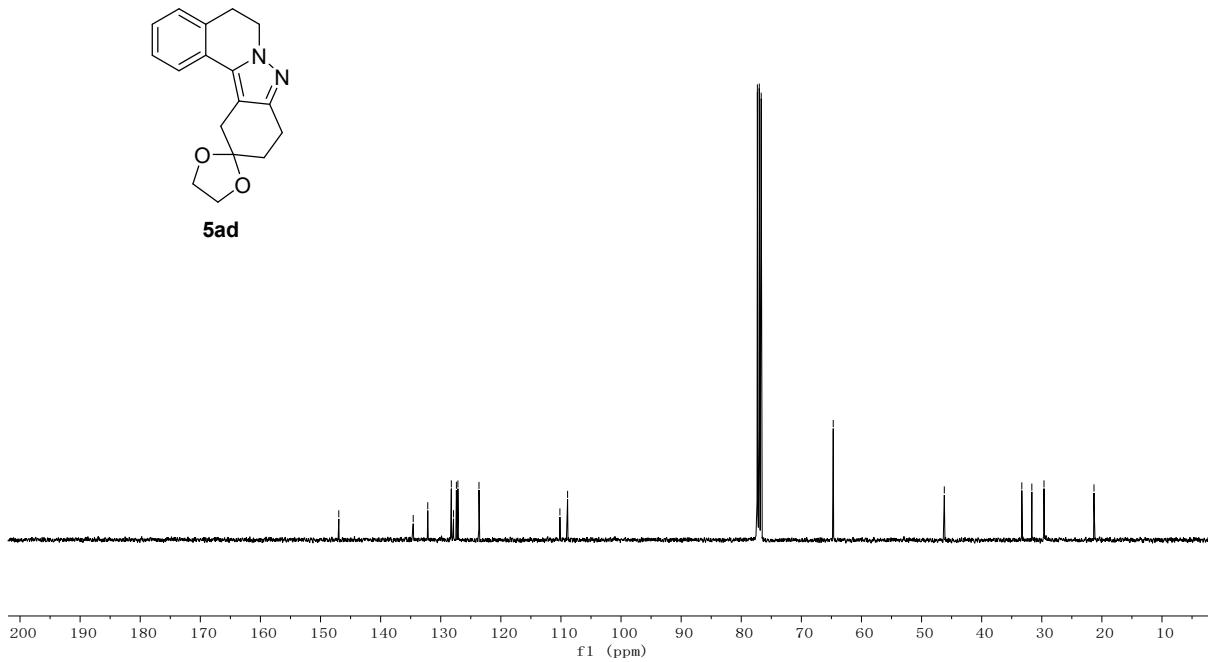
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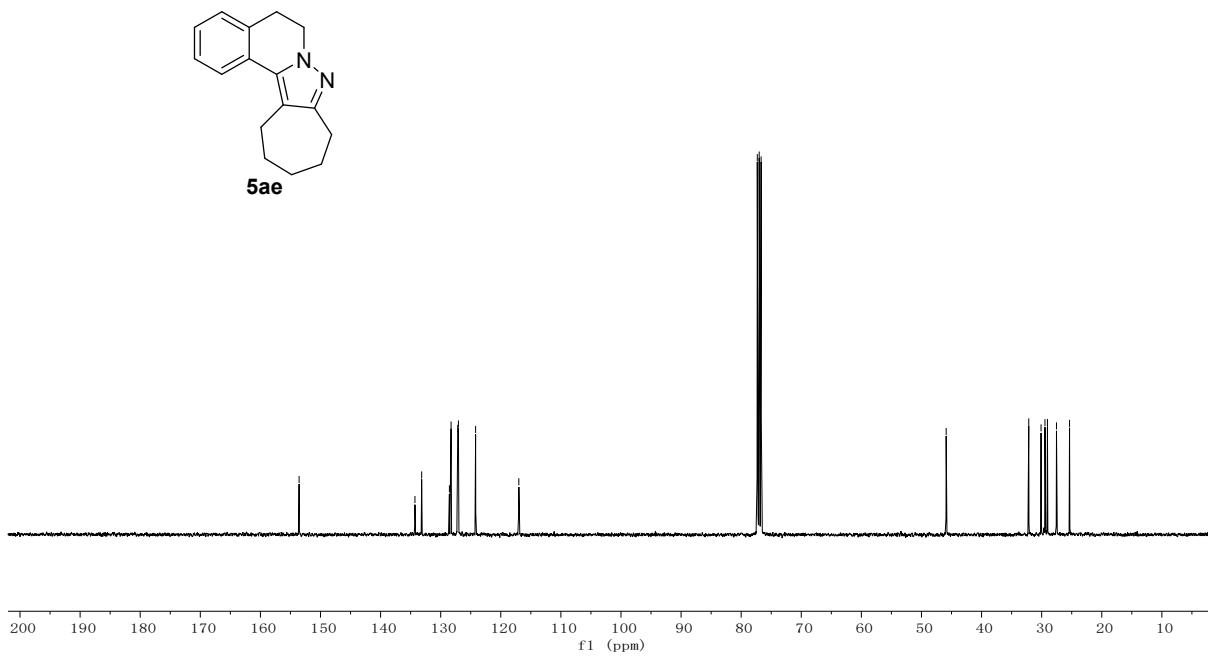
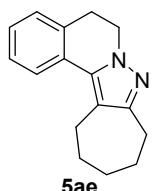
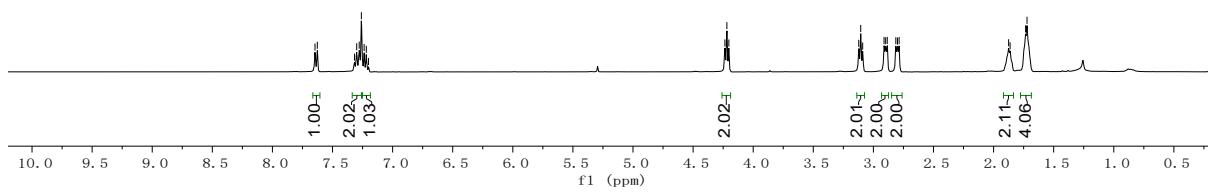
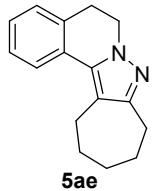
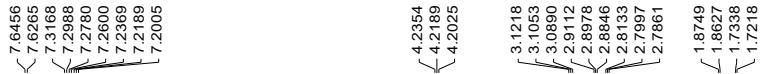
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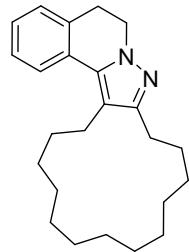
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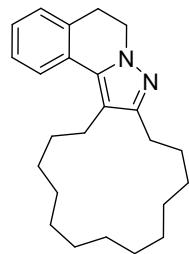
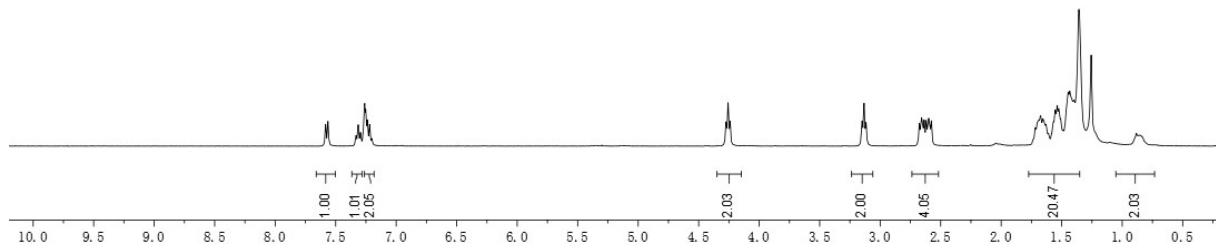
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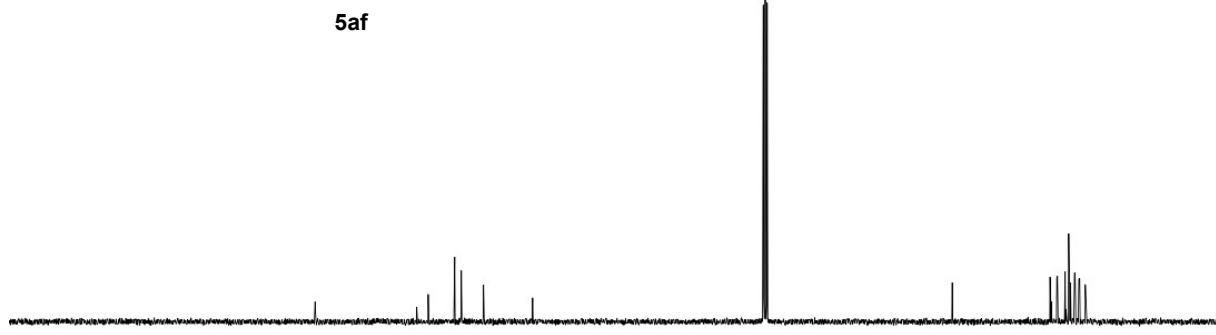


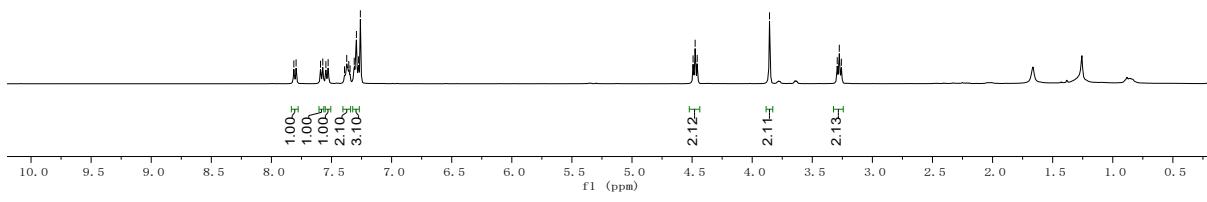
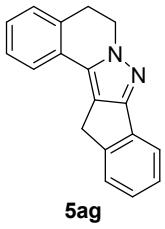


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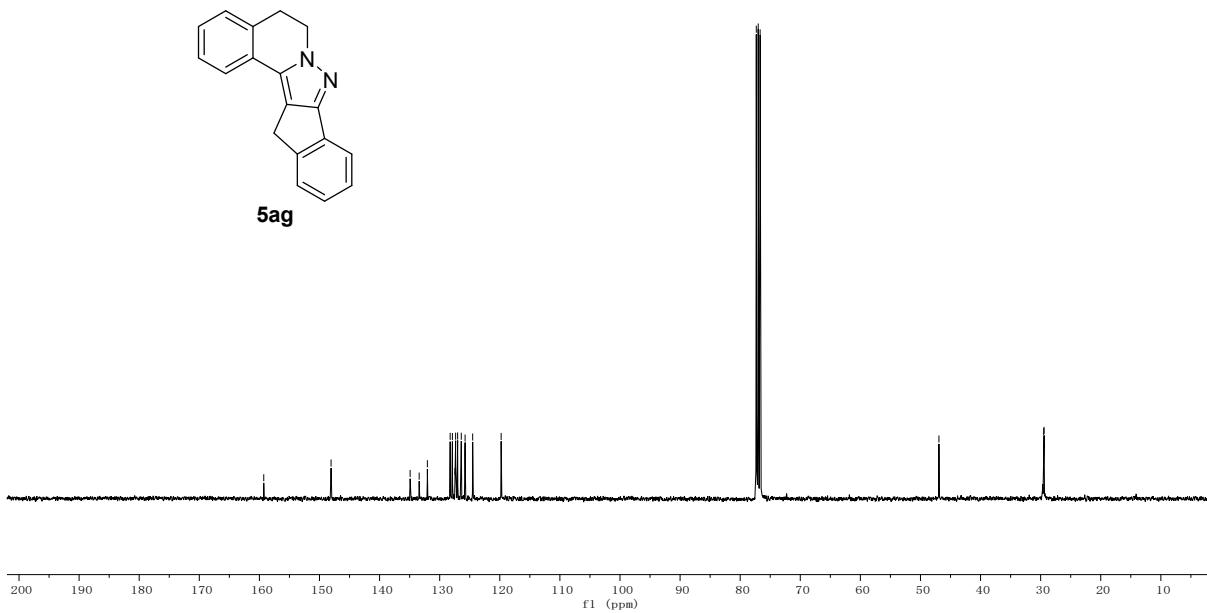
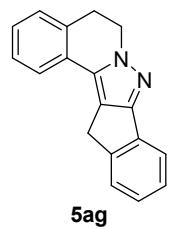


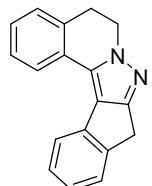
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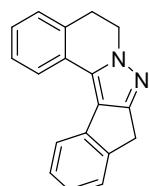
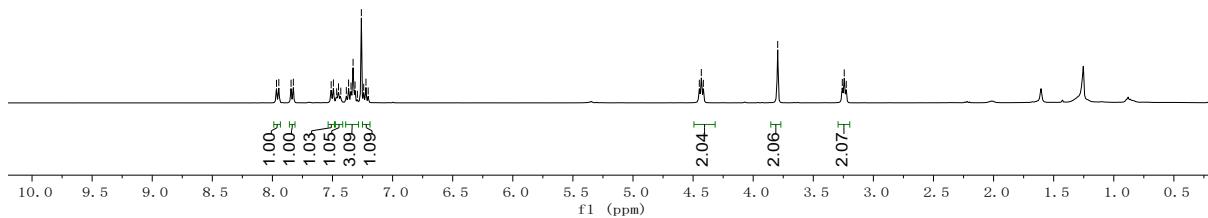


— 159.274  
— 148.073  
— 134.917  
— 133.414  
— 132.049  
— 128.256  
— 127.885  
— 127.461  
— 127.350  
— 127.014  
— 126.409  
— 125.773  
— 124.510  
— 119.774  
— 118.770  
— 4.4919  
— 4.4748  
— 4.4574  
— 3.8558  
— 3.2825  
— 3.2753  
— 3.2581  
— 2.12-T  
— 2.11-T  
— 2.13-T  
— 1.00-T  
— 1.00-T  
— 2.10-T  
— 3.10-T

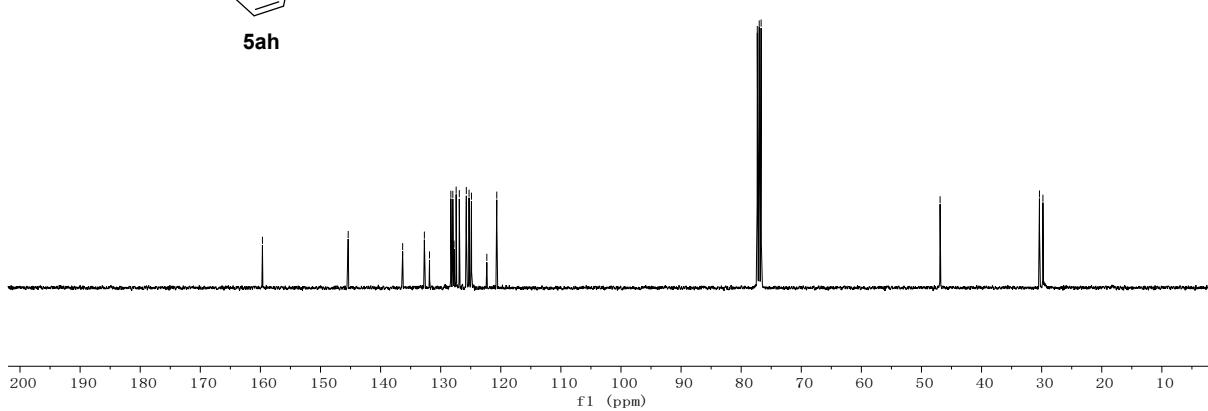




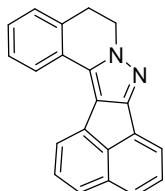
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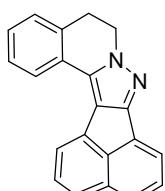
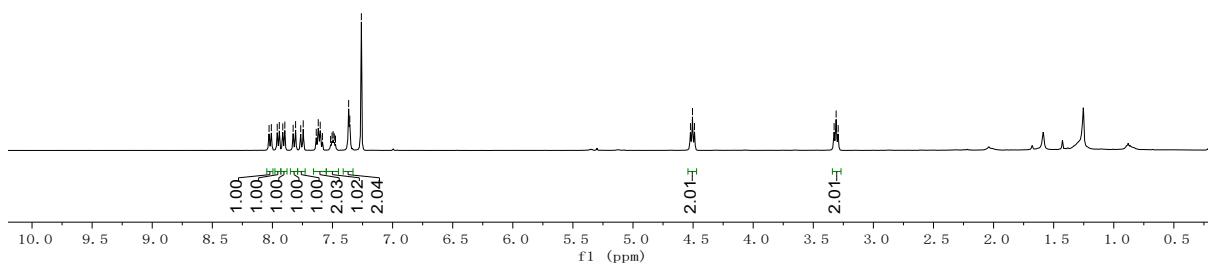
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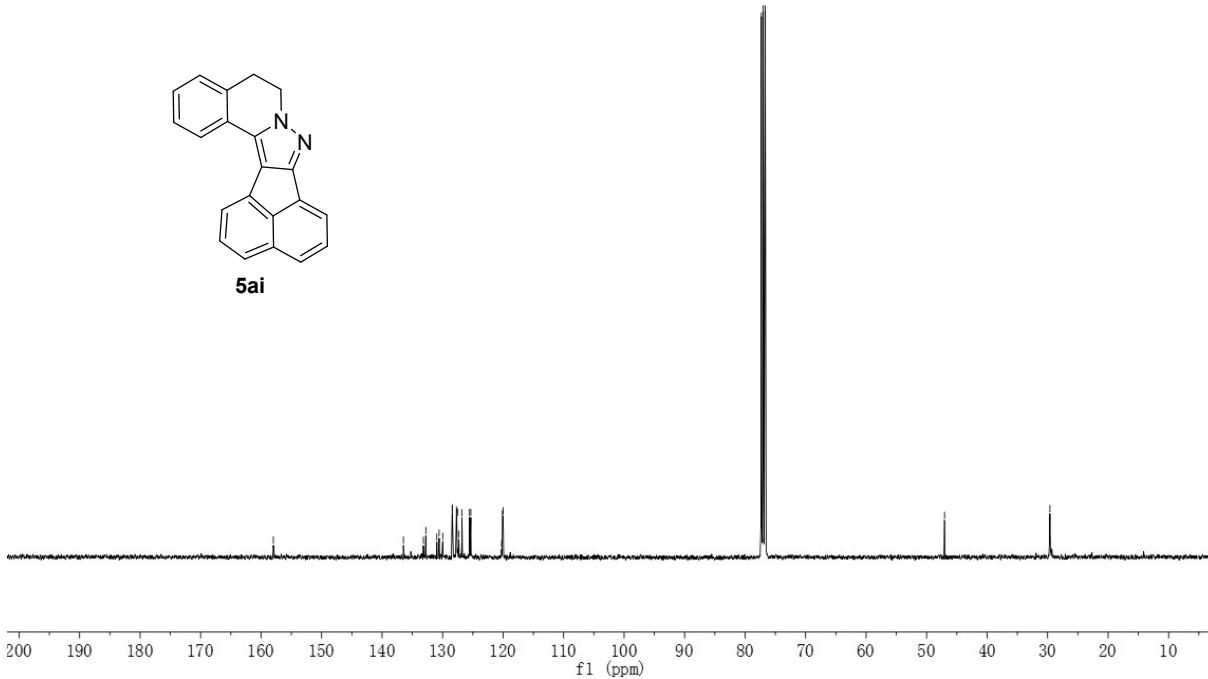
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7.8277
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7.6353
7.6188
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7.3363
7.2600

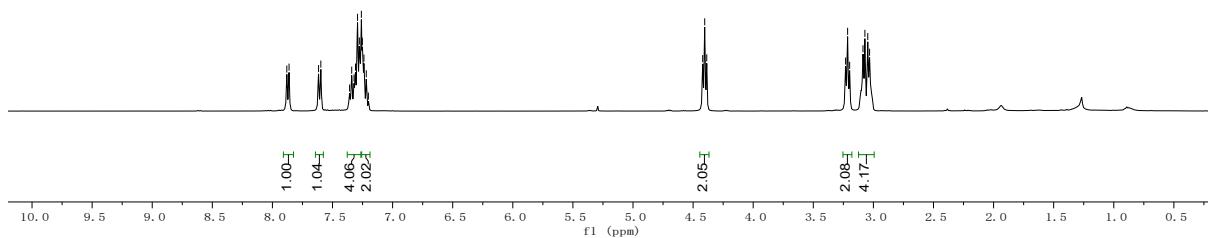


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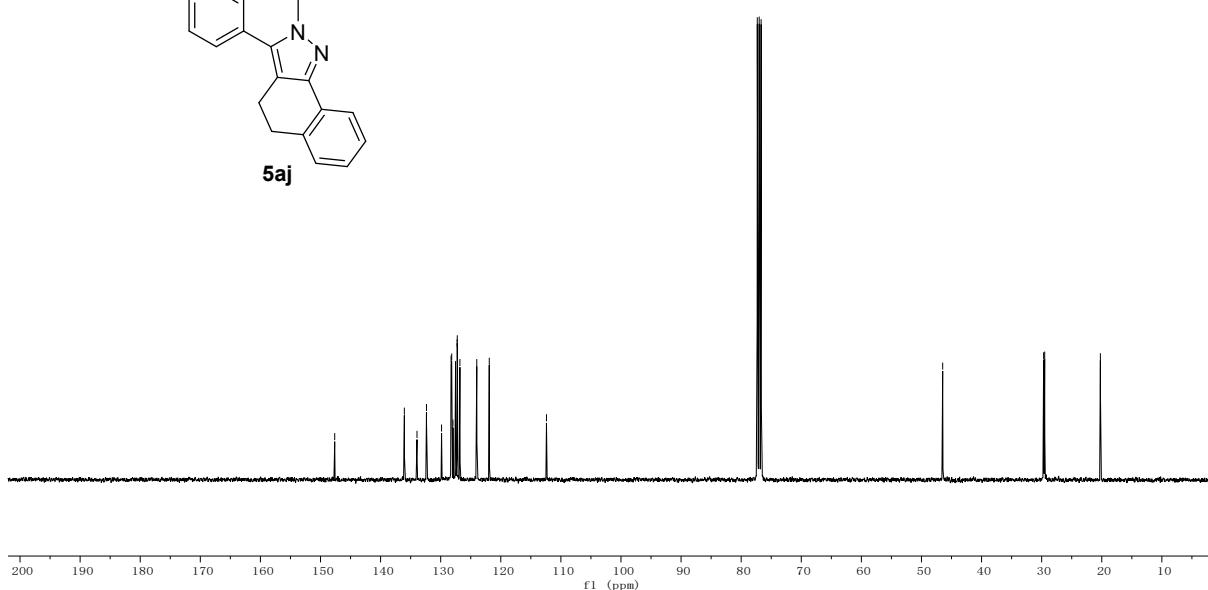
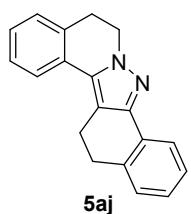
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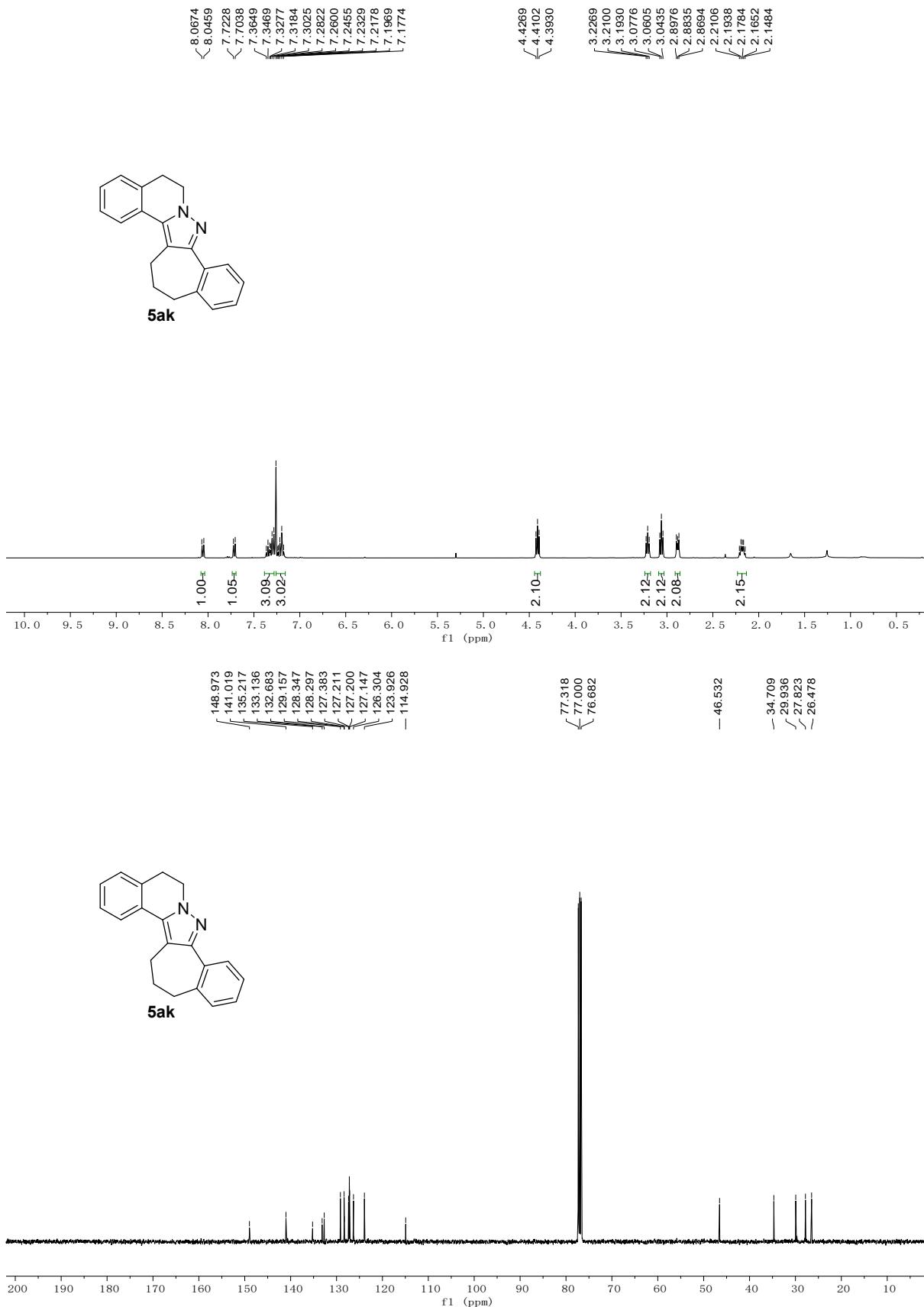


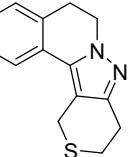


— 147.635  
— 136.047  
— 133.944  
— 132.366  
— 129.855  
— 128.273  
— 128.168  
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— 127.532  
— 127.266  
— 127.243  
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— 121.919  
— 112.396

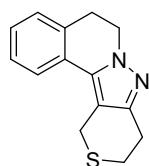
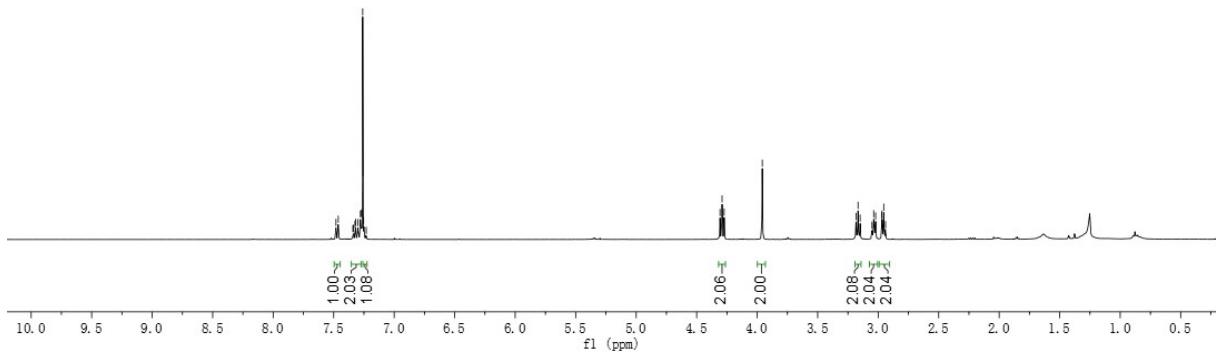
— 46.469  
— 29.495  
— 29.469  
— 20.228



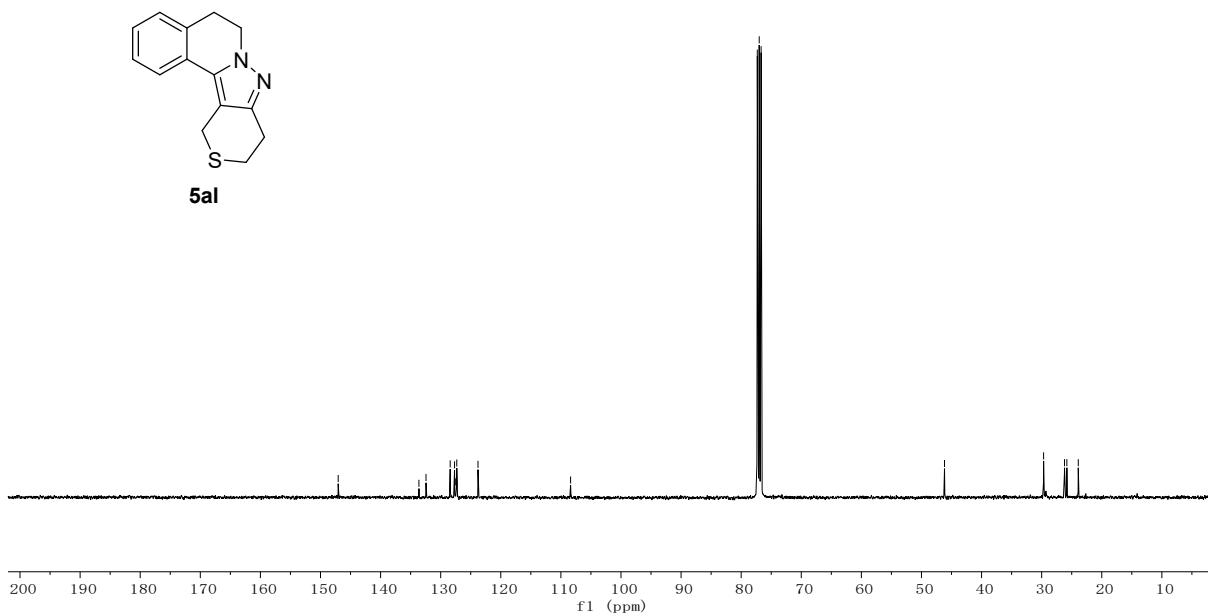




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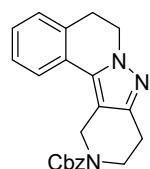
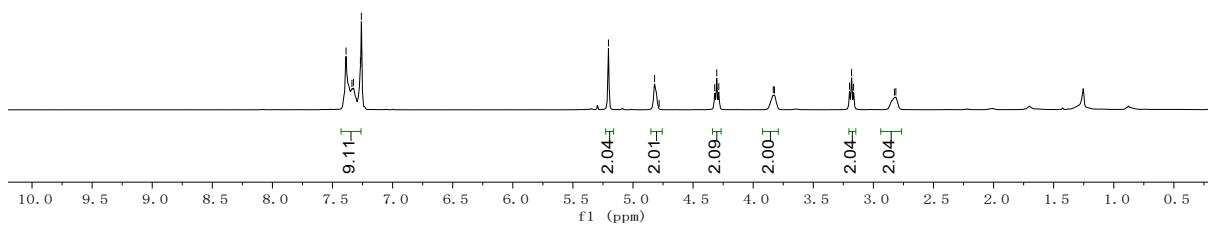


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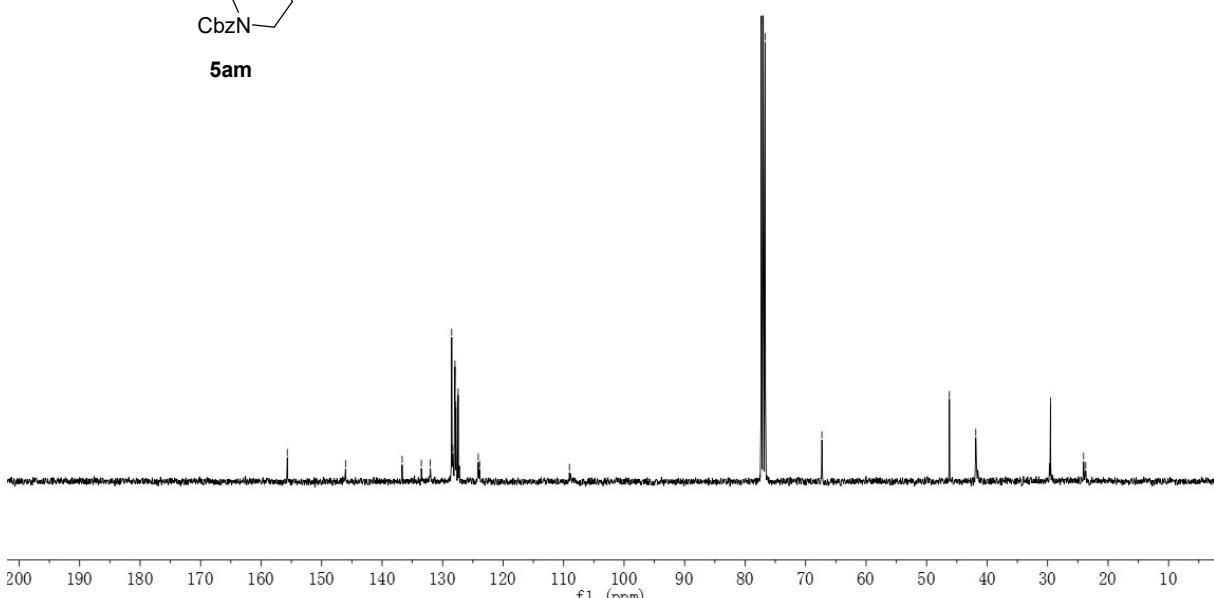


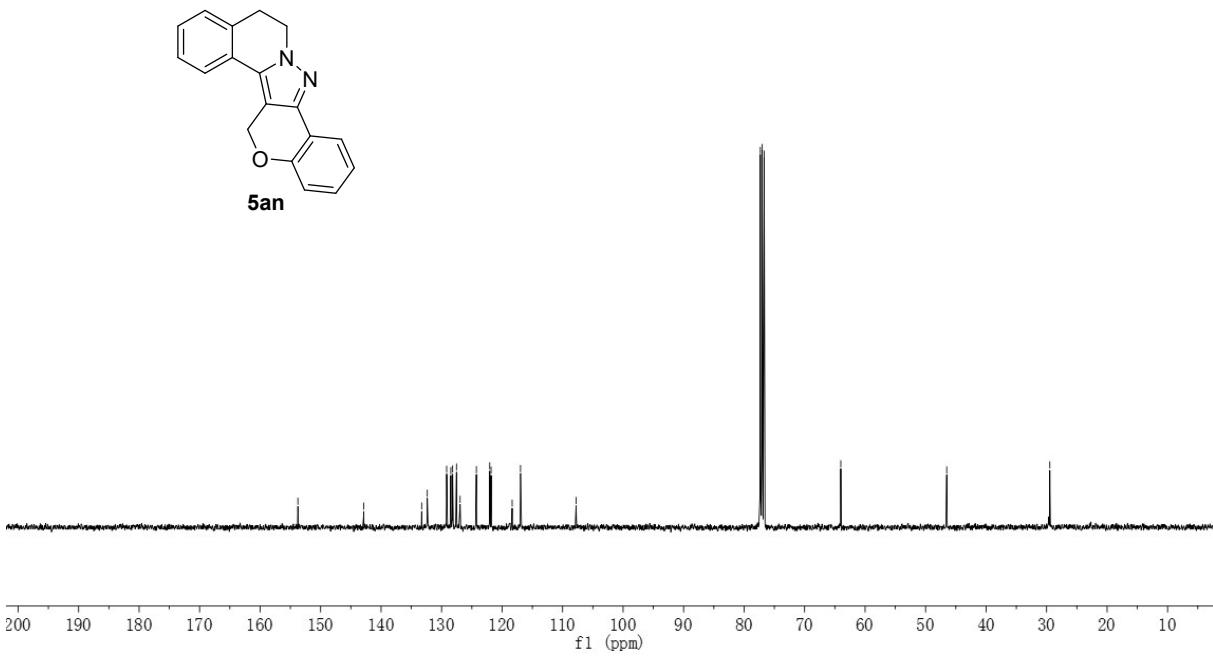
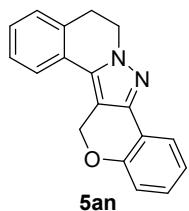
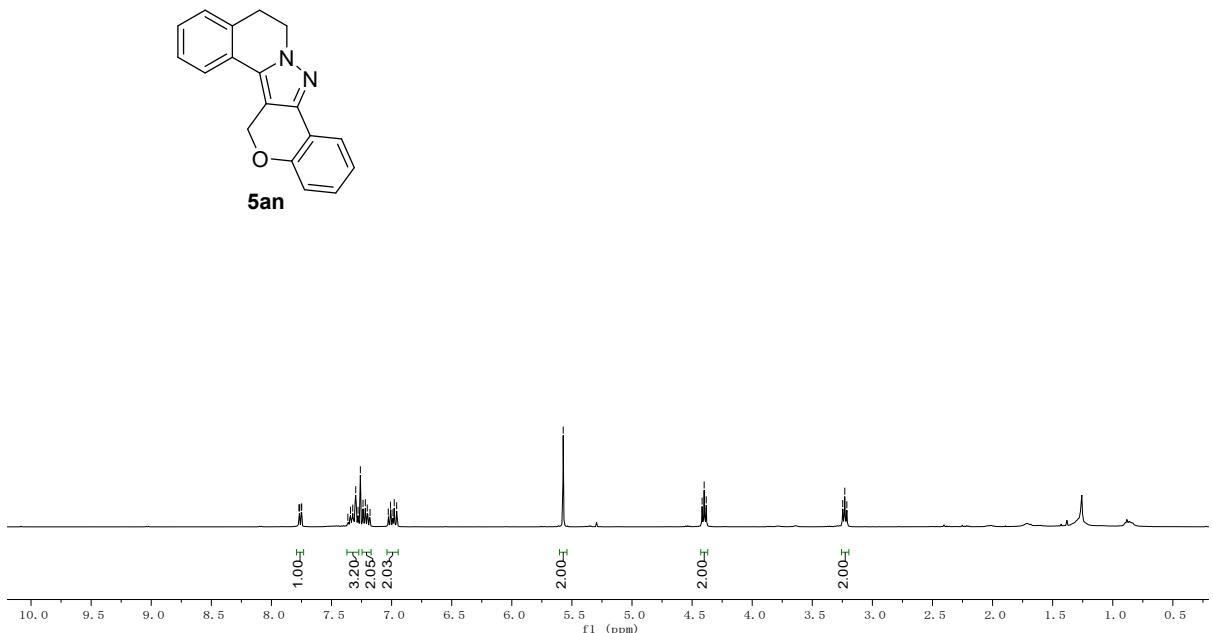


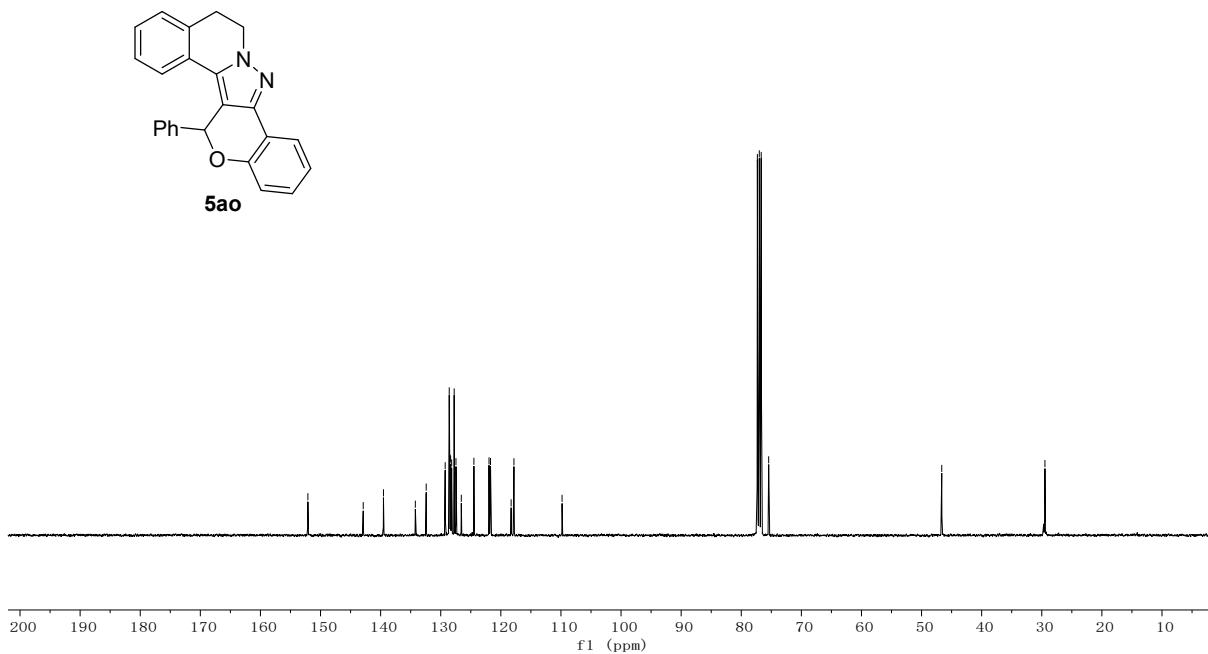
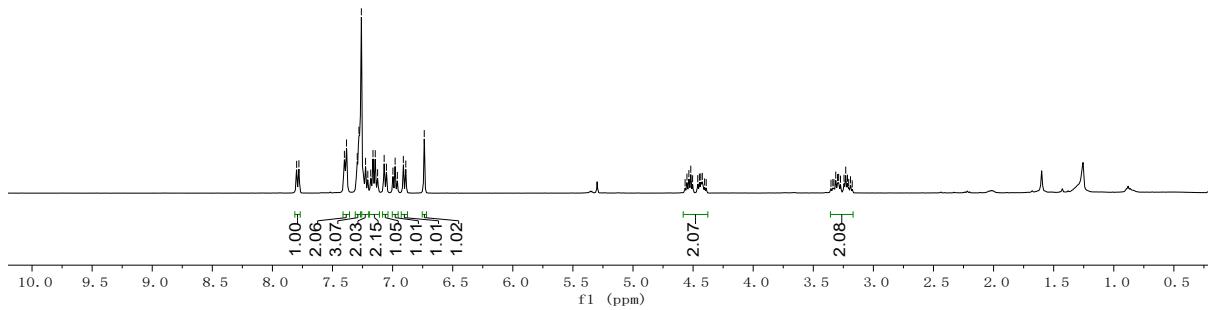
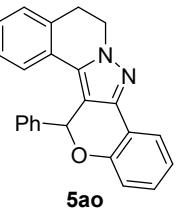
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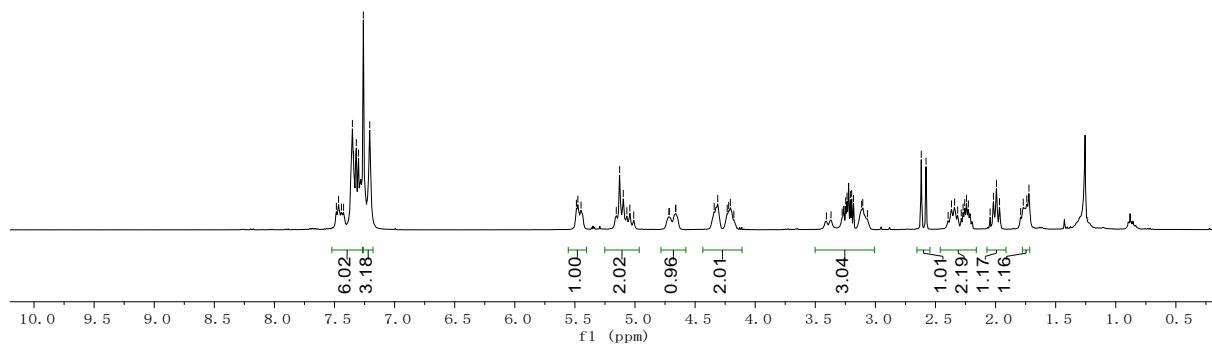
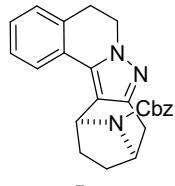


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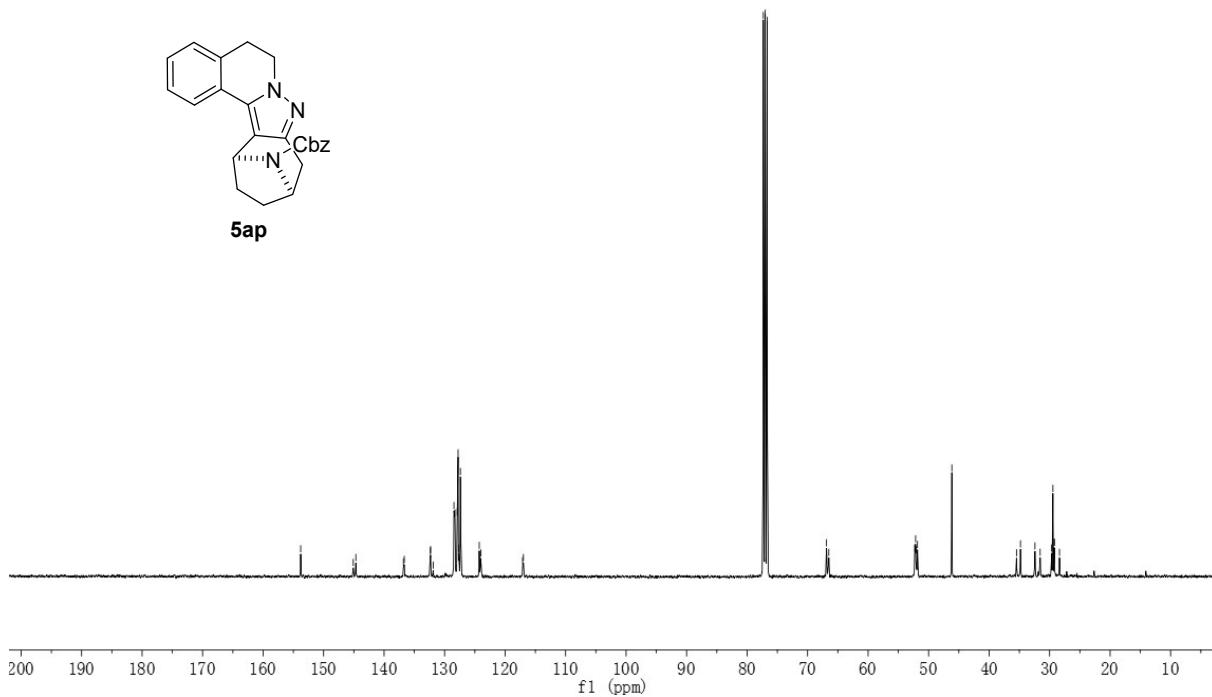
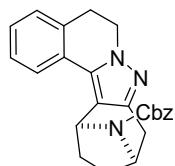


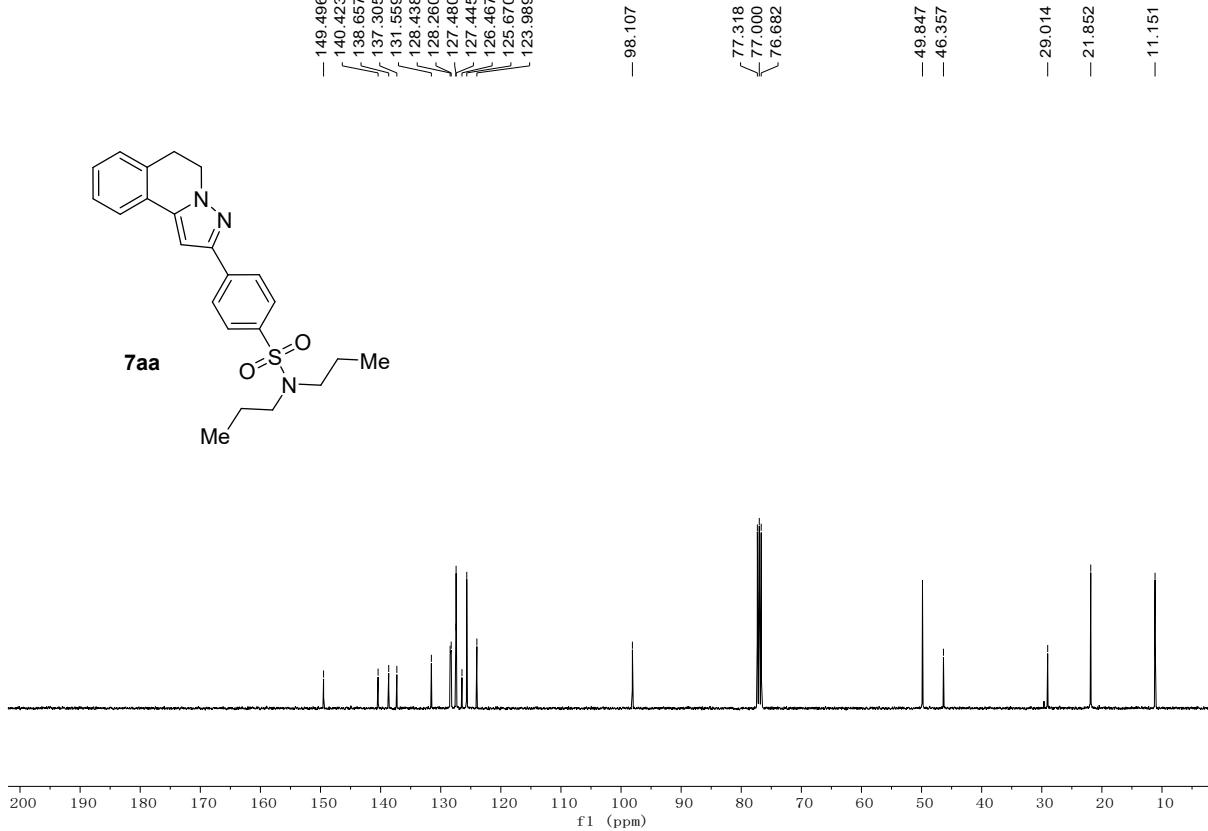
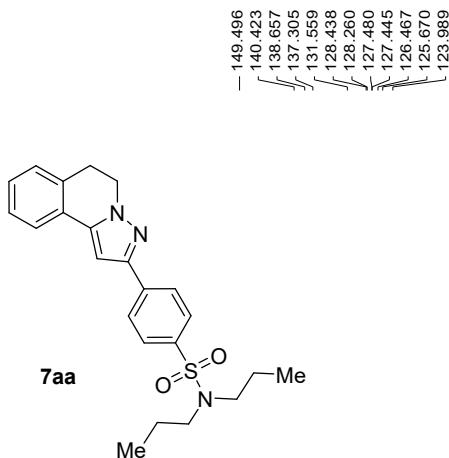
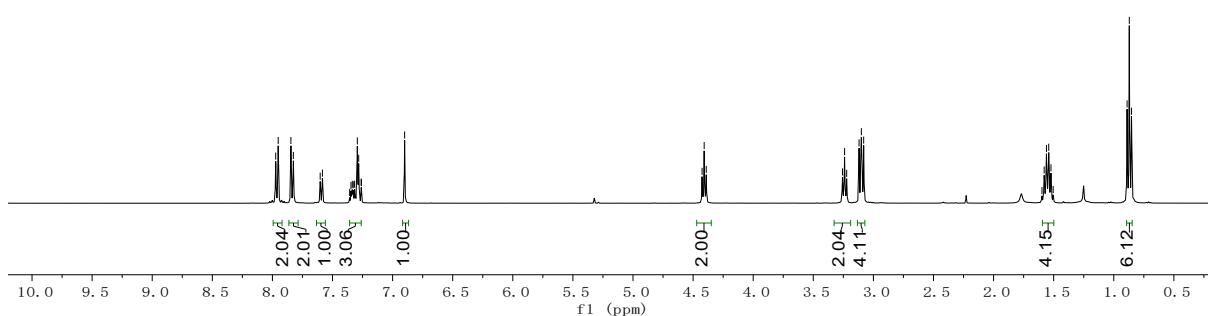
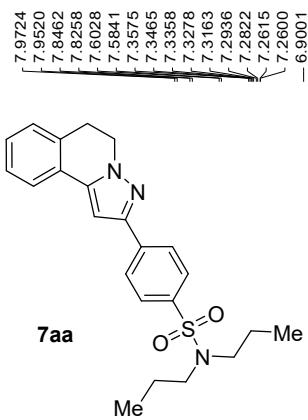


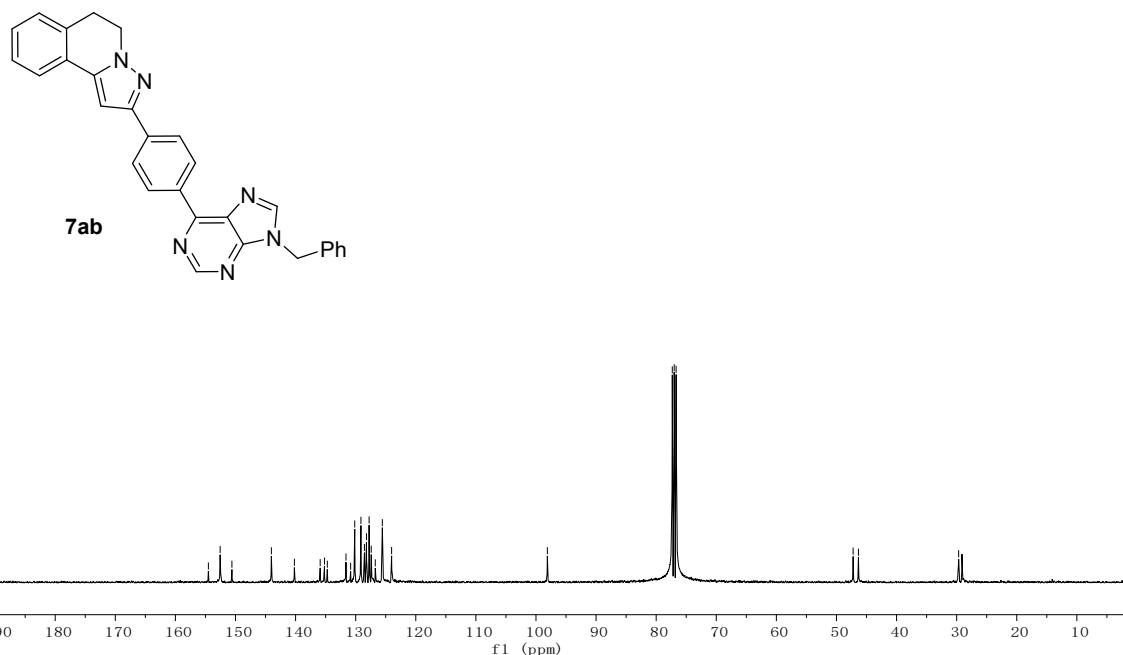
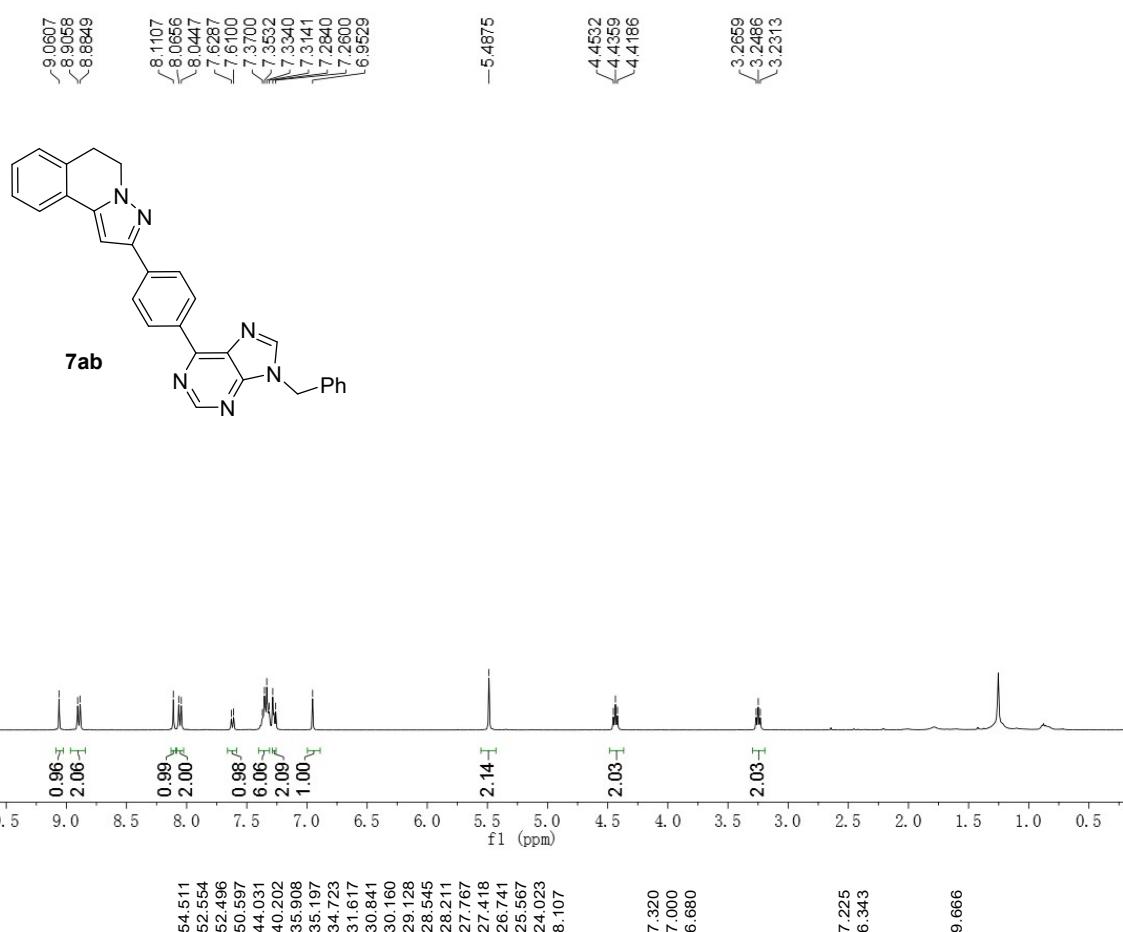


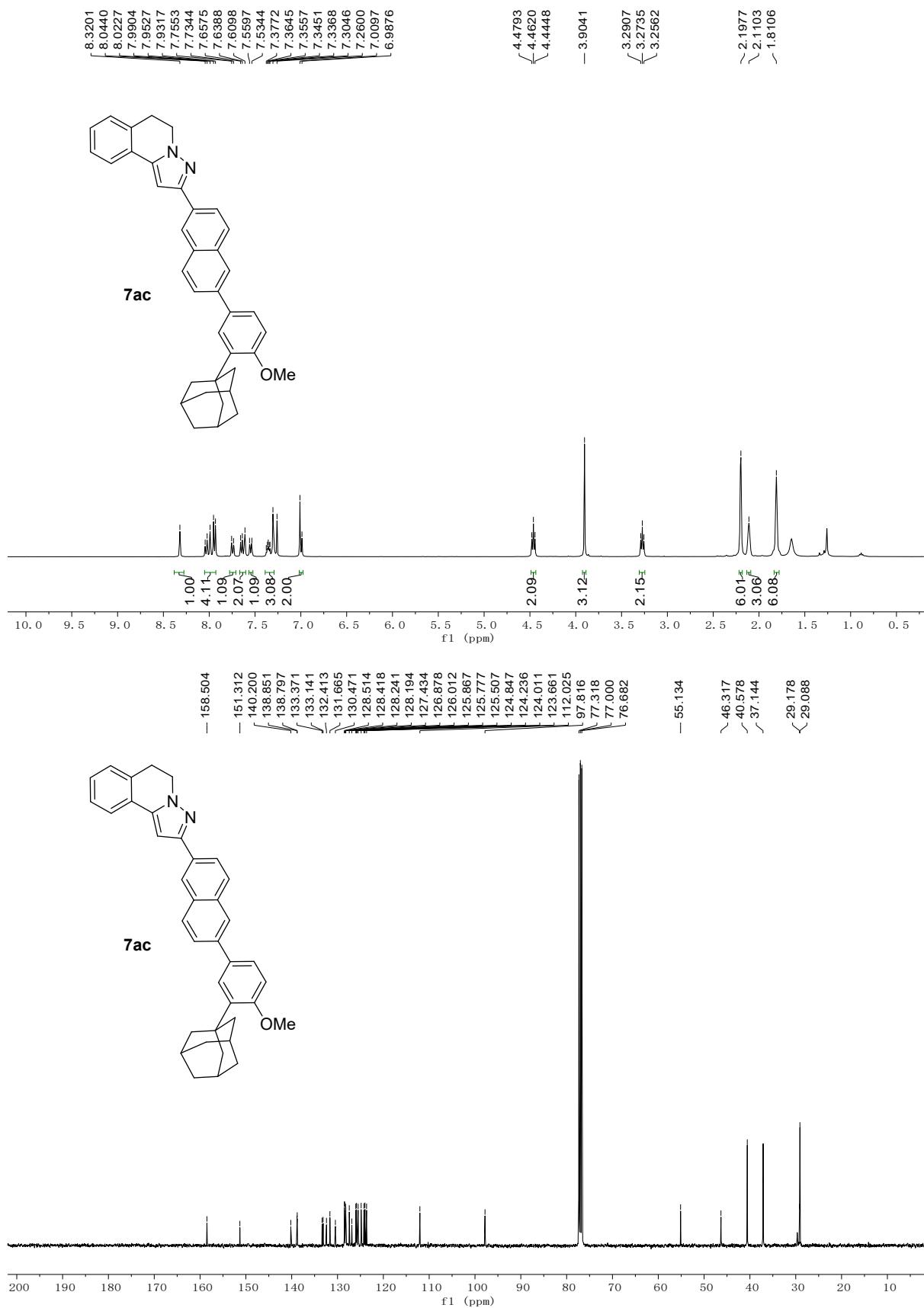


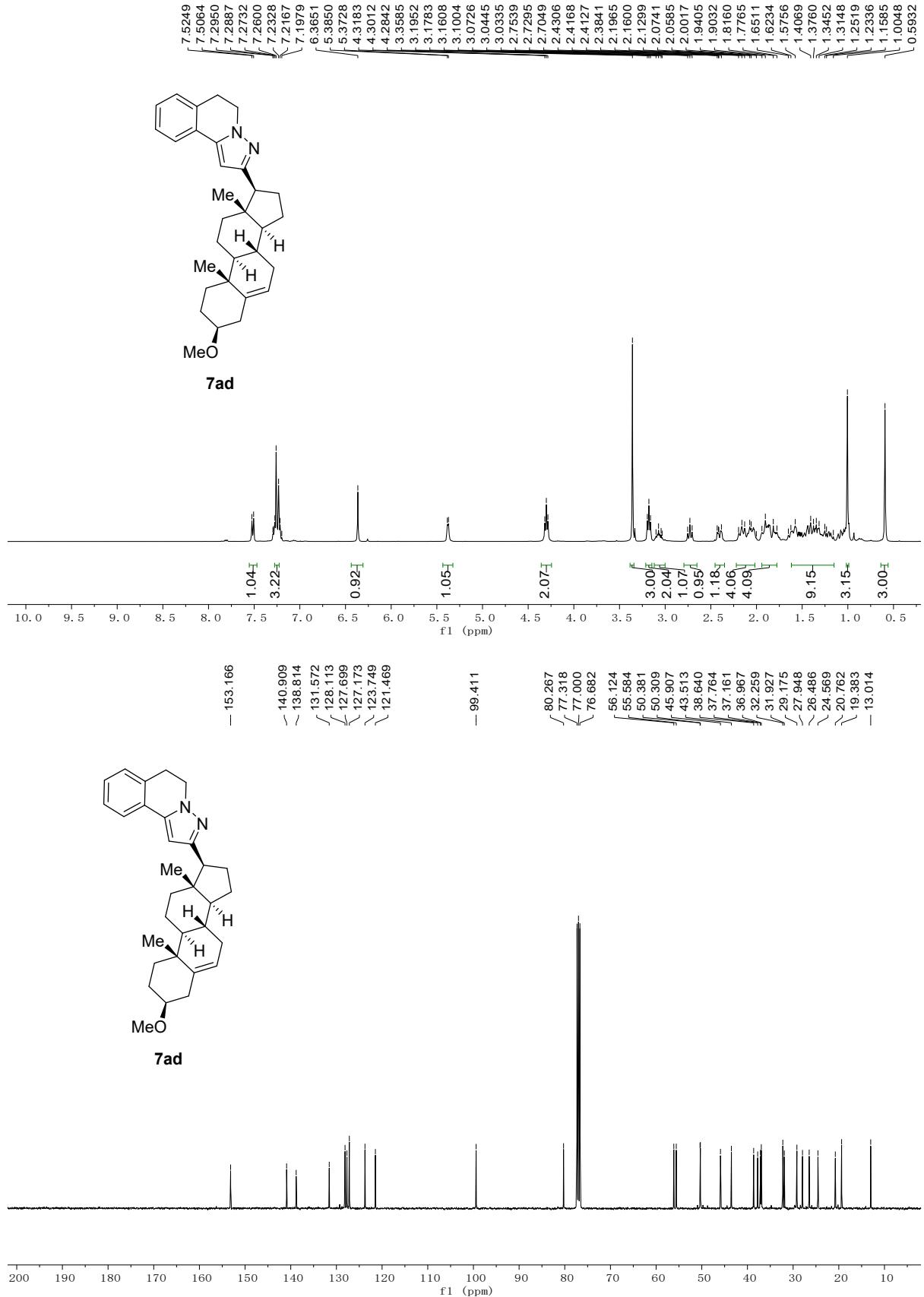
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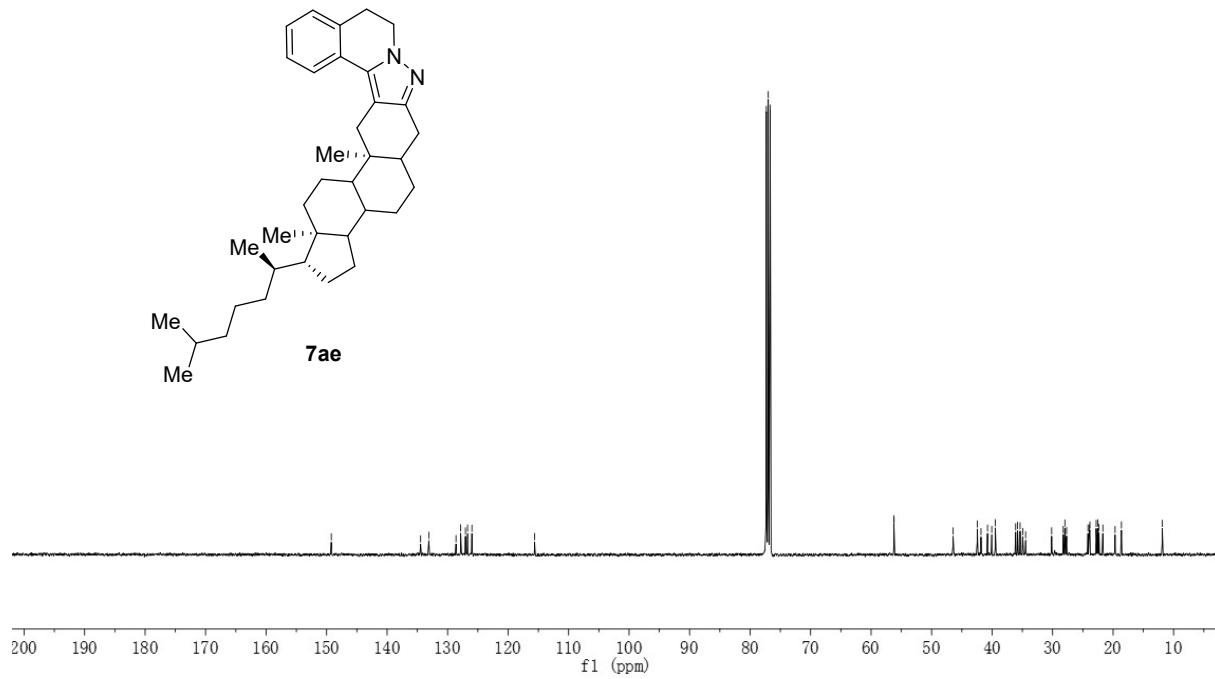
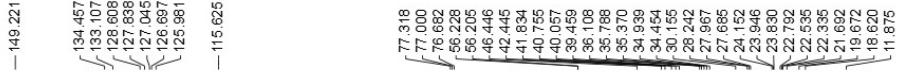
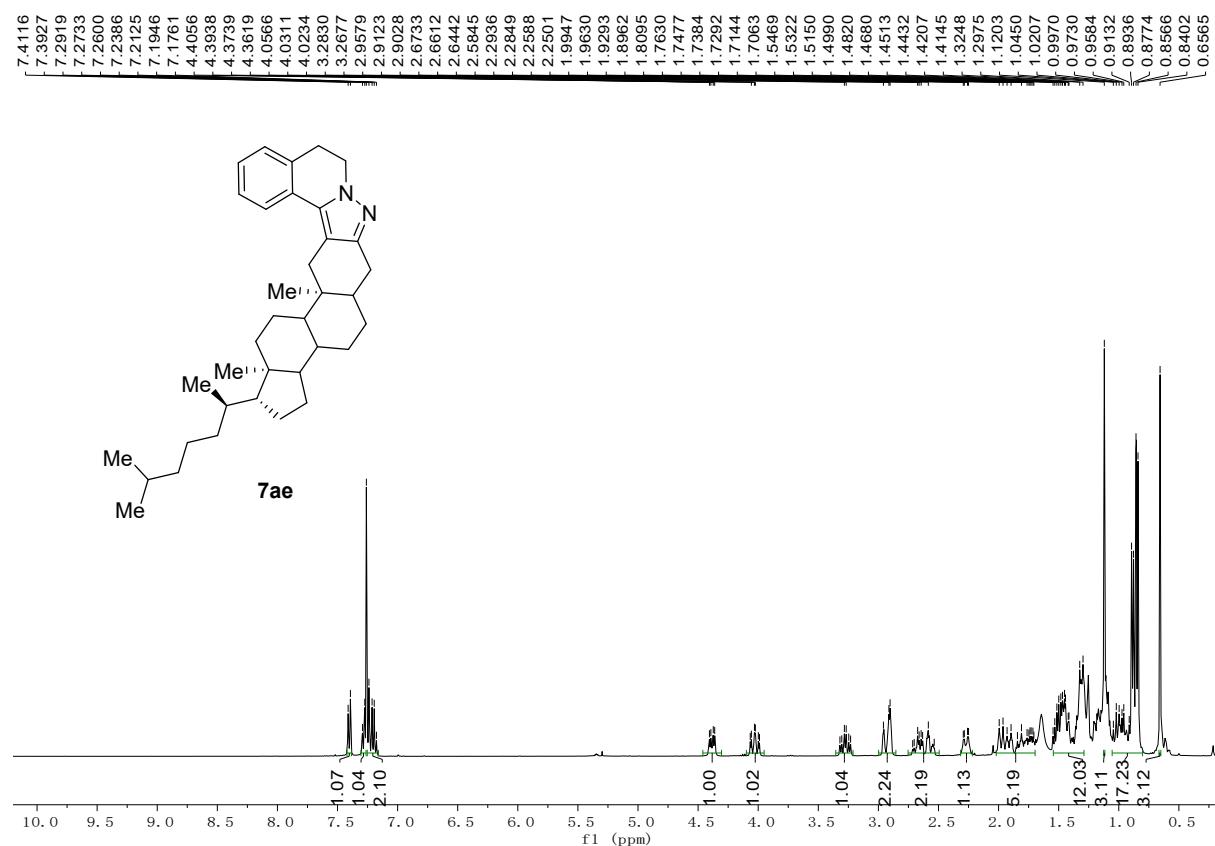




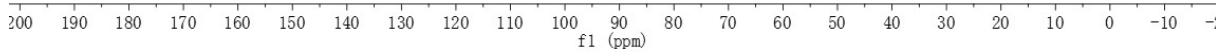
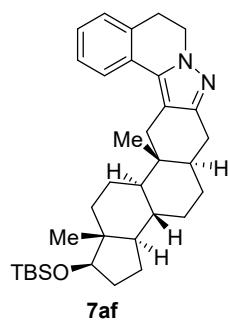
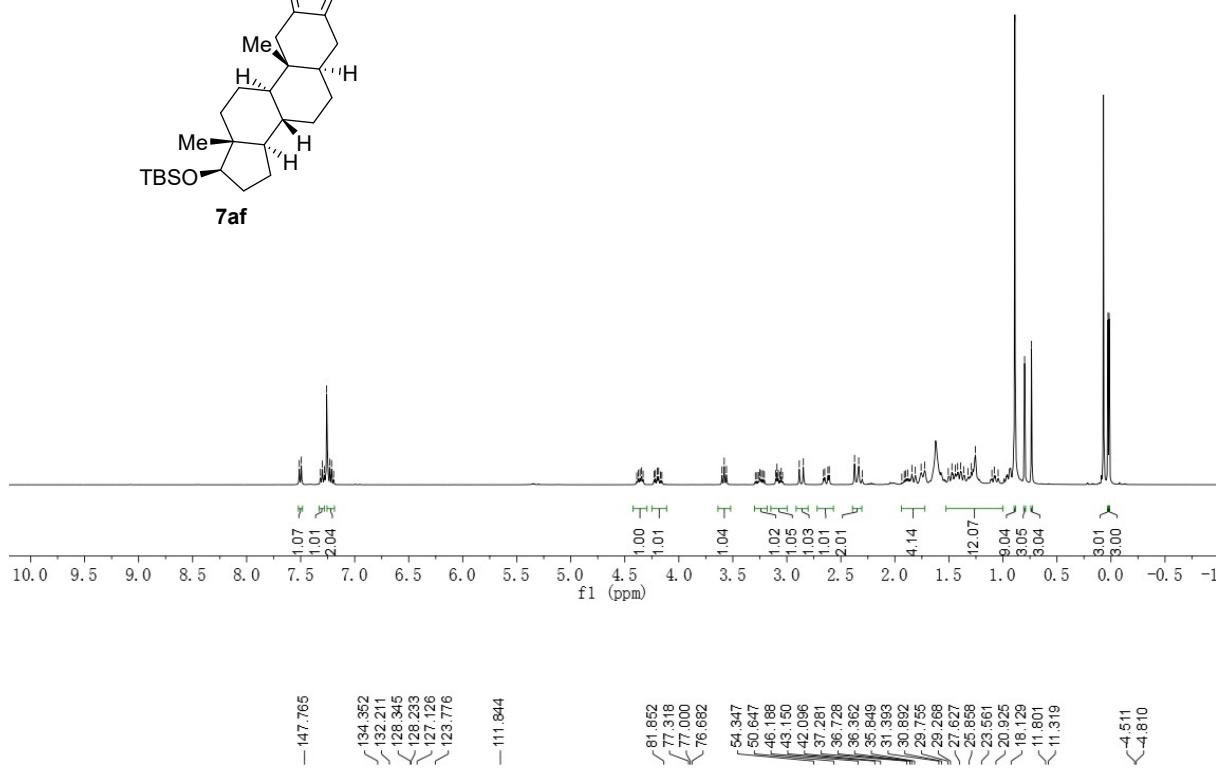
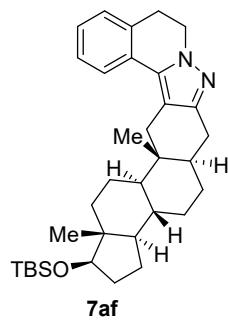


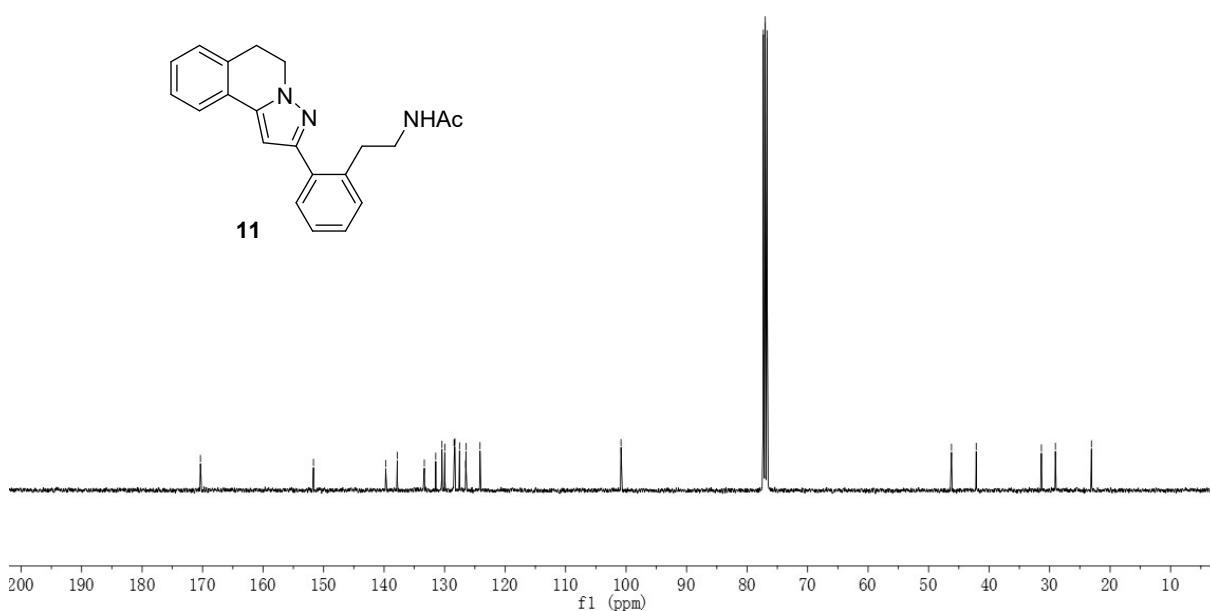
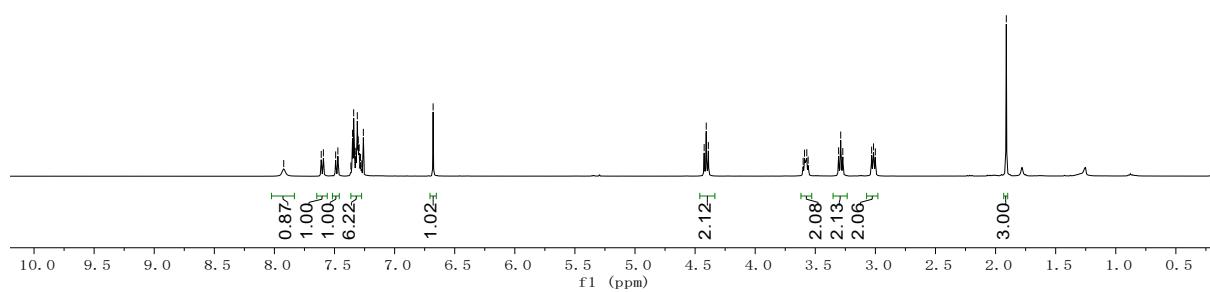


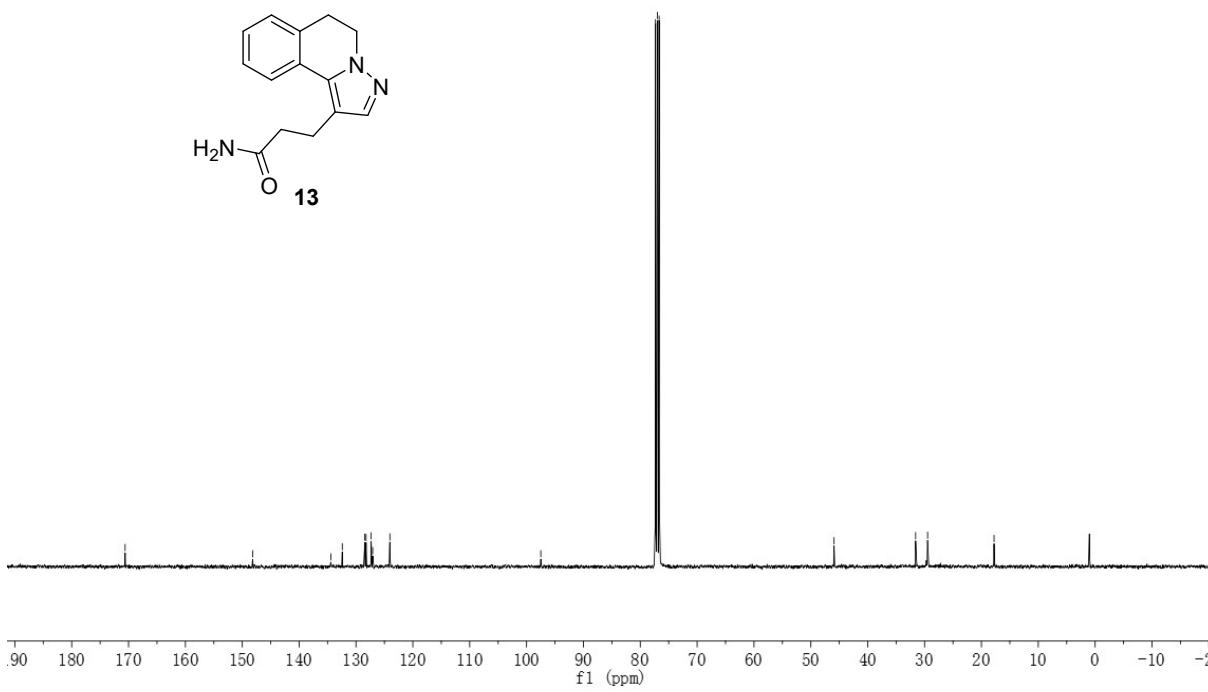
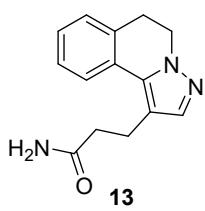
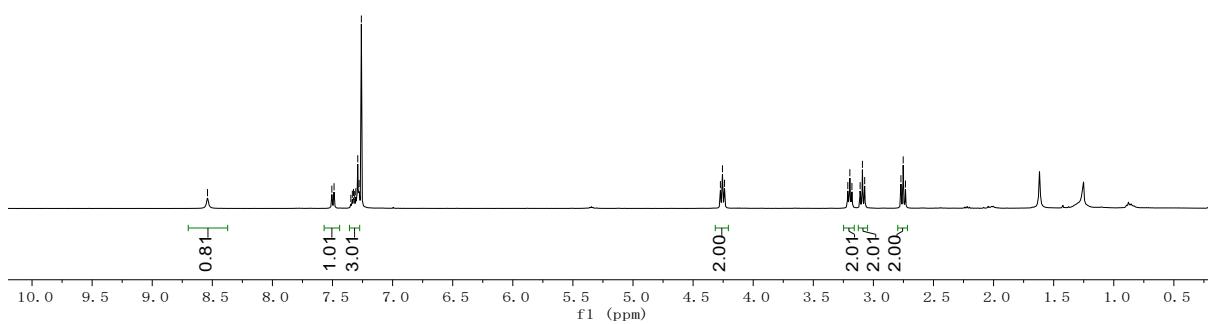


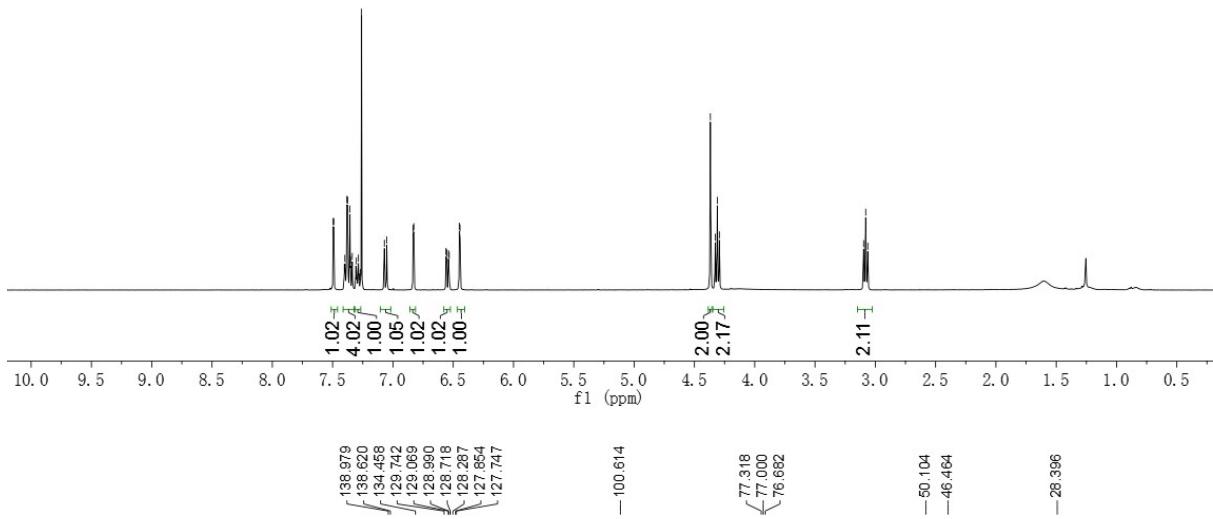
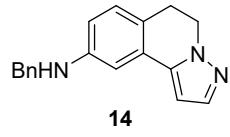
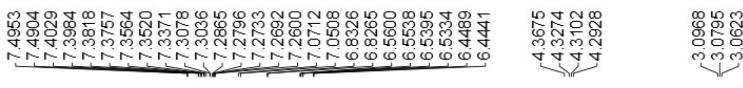


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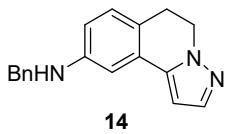


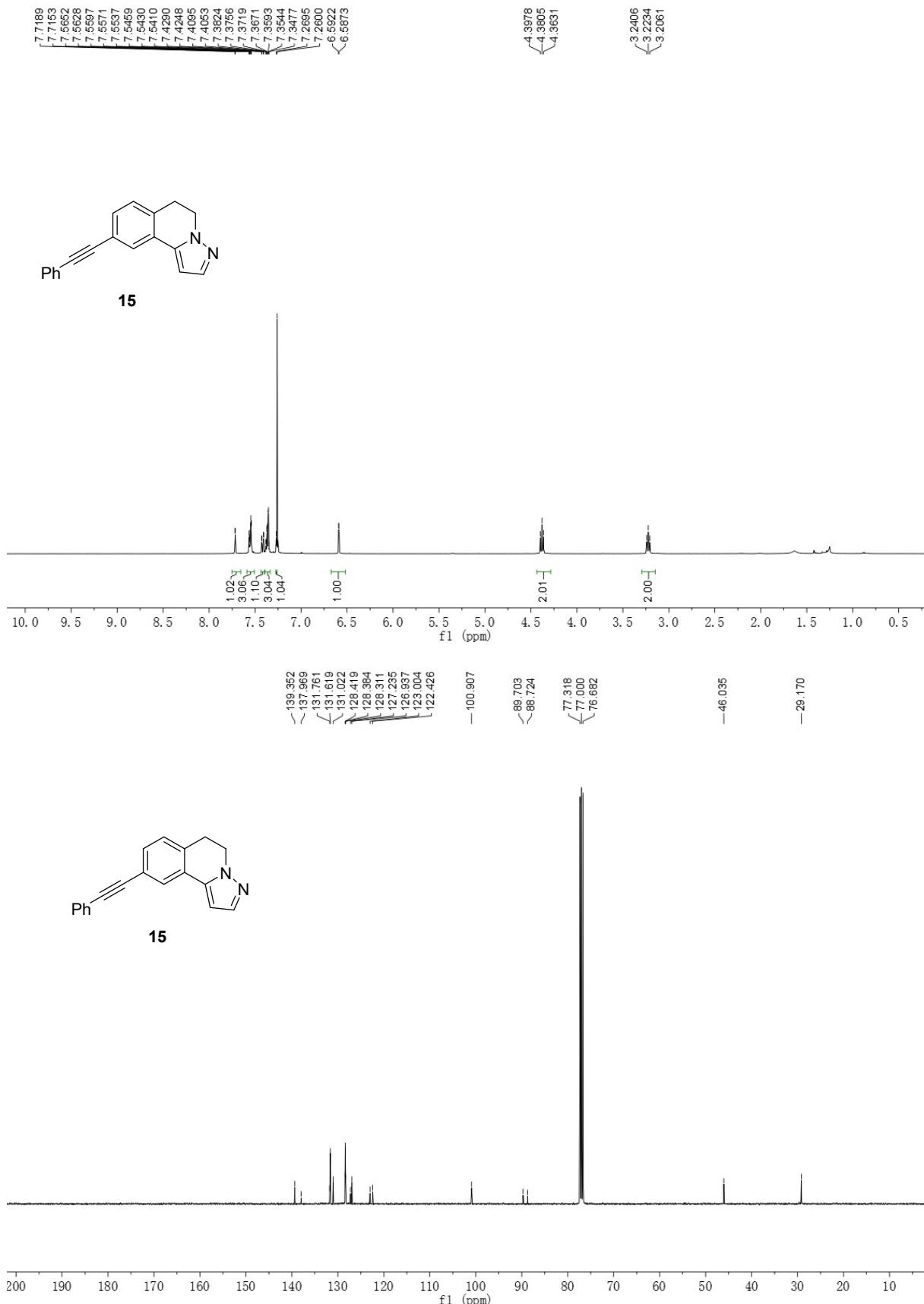


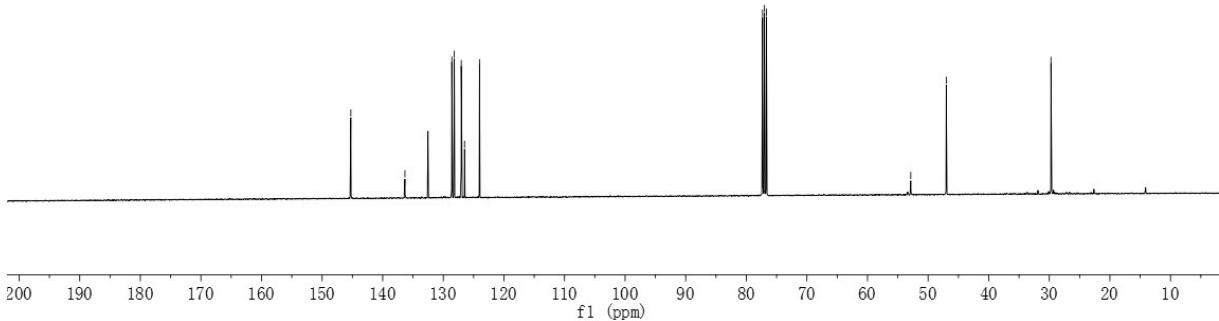
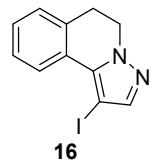
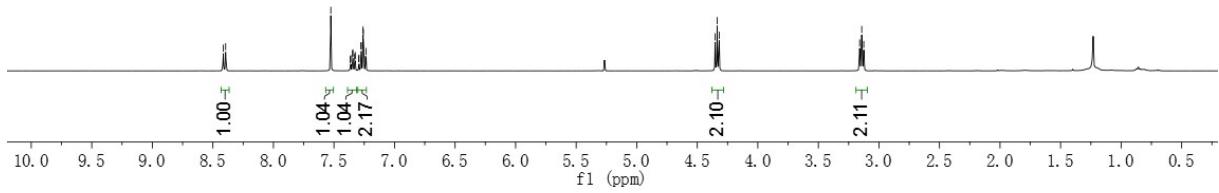
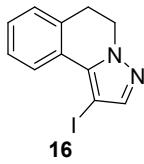
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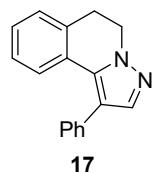
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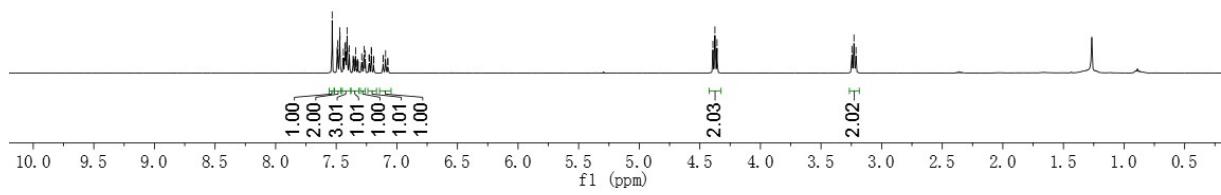




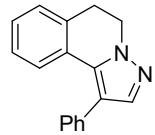
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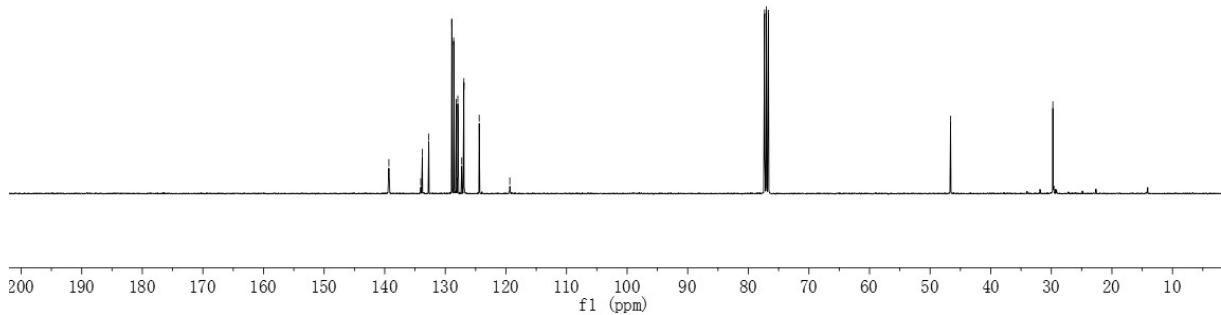
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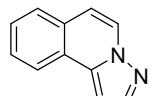
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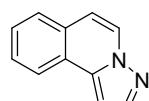
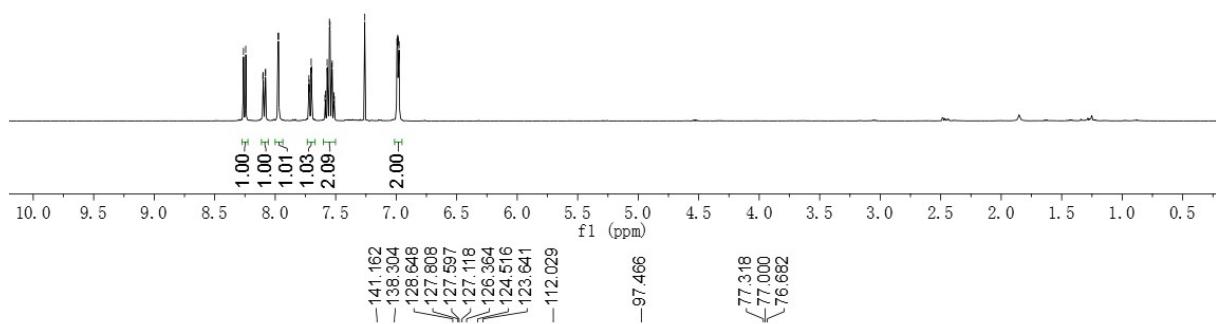
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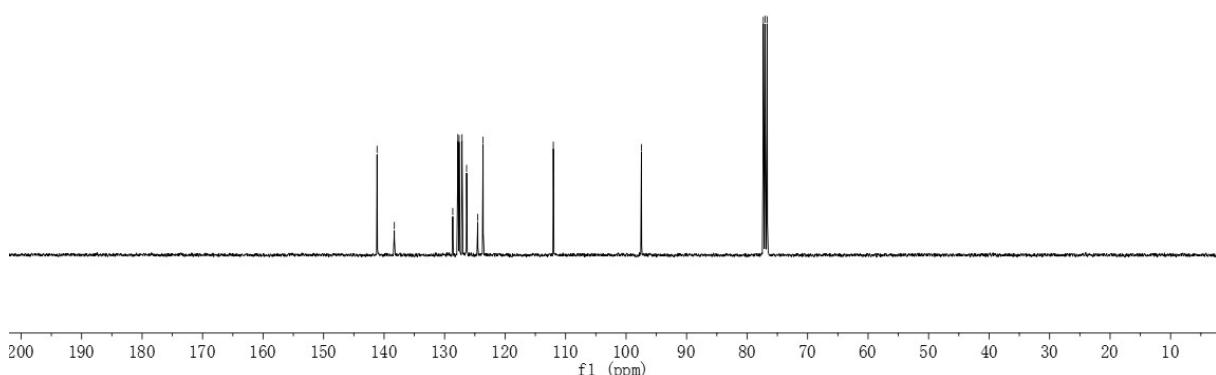
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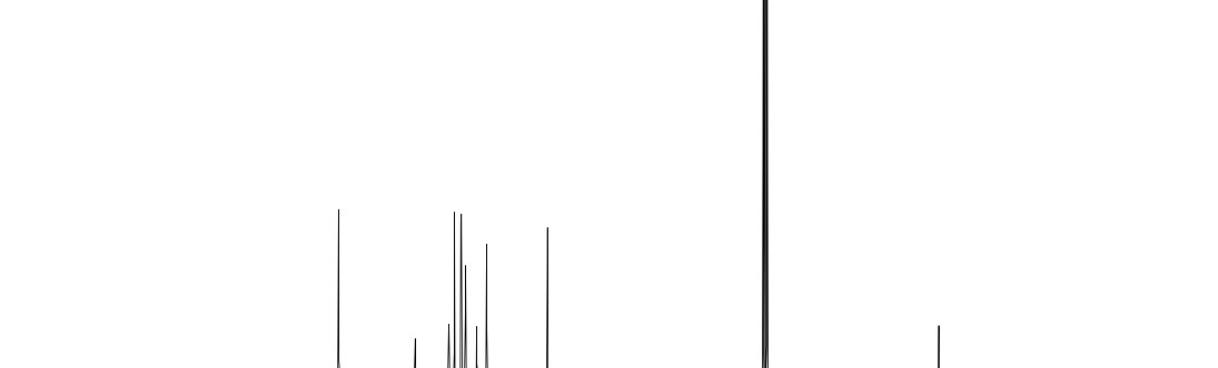
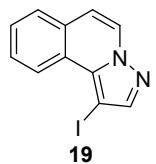
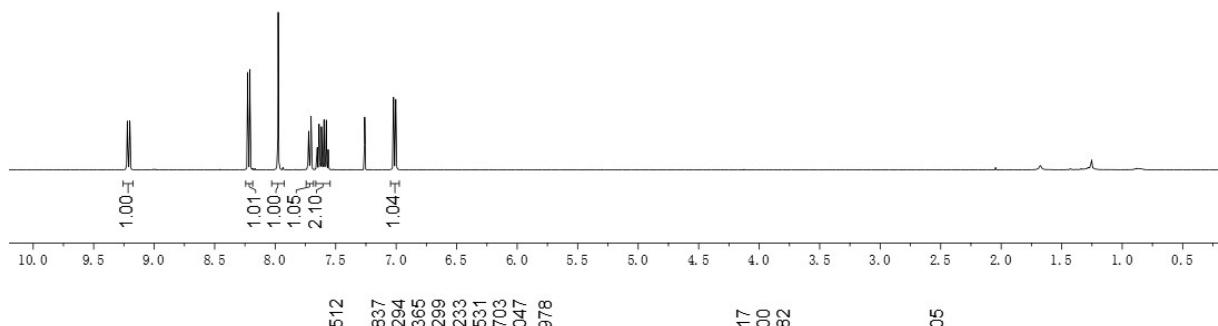
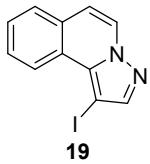
**18**



**18**



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