Supporting Information

Pd-Catalyzed C-H Activation/Oxidative Cyclization of Acetanilide with Norbornene: Concise Access to Functionalized Indolines

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A. Optimization of Reaction Conditions

Table 1. Influence of the oxidant

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant (equiv)</th>
<th>Solvent</th>
<th>Yield (%)b</th>
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<td>1 atm O2</td>
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<td>2</td>
<td>BQ (2)</td>
<td>DMSO</td>
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<td>3</td>
<td>Ag2O (2)</td>
<td>DMSO</td>
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<td>4</td>
<td>AgOAc (2)</td>
<td>DMSO</td>
<td>15</td>
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<td>5</td>
<td>Ag2CO3 (2)</td>
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<td>6</td>
<td>Cu(OTf)2 (2)</td>
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<td>Cu(OAc)2 (2)</td>
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<td>CuBr2 (0.2) + 1 atm O2</td>
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<td>15</td>
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<td>CuBr (0.2) + 1 atm O2</td>
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<td>CuI (0.2) + 1 atm O2</td>
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<td>19</td>
<td>Cu(OAc)2 (0.2) + FePO4·4H2O (0.1) 1 atm O2</td>
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a Reaction conditions: unless otherwise noted, all reactions were performed with 1a (0.3 mmol), 2a (0.6 mmol), Pd(OAc)2 (10 mol %) in DMSO (2.0 mL) at 120 °C for 10 h. b Determined by GC based on 1a.

Table 2. Influence of the solvent

<table>
<thead>
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<th>Entry</th>
<th>Oxidant (equiv)</th>
<th>Solvent</th>
<th>Yield (%)b</th>
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<td>Cu(OAc)2 (1) + 1 atm O2</td>
<td>Toluene</td>
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<td>2</td>
<td>Cu(OAc)2 (1) + 1 atm O2</td>
<td>HOAc</td>
<td>&lt;5</td>
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<td>4</td>
<td>Cu(OAc)2 (1) + 1 atm O2</td>
<td>DCM</td>
<td>25</td>
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<td>5</td>
<td>Cu(OAc)2 (1) + 1 atm O2</td>
<td>DCE</td>
<td>63</td>
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<td>6</td>
<td>Cu(OAc)2 (1) + 1 atm O2</td>
<td>DMSO</td>
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<td>7</td>
<td>Cu(OAc)2 (1) + 1 atm O2</td>
<td>DMF</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>Cu(OAc)2 (1) + 1 atm O2</td>
<td>DMF/DMSO (10:1)</td>
<td>36</td>
</tr>
<tr>
<td>9</td>
<td>Cu(OAc)2 (1) + 1 atm O2</td>
<td>NMP</td>
<td>15</td>
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<tr>
<td>10</td>
<td>Cu(OAc)2 (1) + 1 atm O2</td>
<td>DMA</td>
<td>23</td>
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</tbody>
</table>

a Reaction conditions: unless otherwise noted, all reactions were performed with 1a (0.3 mmol), 2a (2 equiv, Pd(OAc)2 (10 mol %), NaOAc (1 equiv), Cu(OAc)2 (1 equiv) under 1 atm O2 in indicated solvent (2.0 mL) at 120 °C for 10 h. b Determined by GC based on 1a.
B. Experimental Procedures

I. General Methods

$^1$H NMR spectra were recorded in CDCl$_3$ at 400 MHz and $^{13}$C NMR spectra were recorded in CDCl$_3$ at 100 MHz respectively, and the chemical shifts (d) were referenced to TMS. GC–MS was obtained using electron ionization. HRMS was carried out on a MAT 95XP (Thermo). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF$_{254}$), and visualization was effected at 254 nm.

II. General Procedure for Synthesis of the Substrates

All the arylamines and norbornenes used were commercially available. Acetanilides were synthesized according to the reported method.$^1$

Norbornenes used in this work:

Norbornenes used in this work:

Preparation of acetanilides:$^1$

Aniline (10 mmol, 1 equiv) was added to a round-bottom flask via syringe and fitted with a rubber septum. The flask was purged with argon and dry DCM (30 mL) was added. Acetic anhydride (12 mmol, 1.2 equiv) was added and the reaction was stirred at room temperature and monitored by TLC. Upon completion the reaction mixture was washed with a saturated solution of sodium carbonate, the organic layers dried with MgSO$_4$ and the solvent removed under reduced pressure. The product was obtained in quantitative yield. In most cases analytically pure acetanilides can be obtained after extraction however if necessary purification by flash chromatography with ethyl acetate/pet. ether was used.

III. General Procedure for Synthesis of Indoline Products

Acetanilide 1a (0.3 mmol), norbornene 2a (2eq), Pd(OAc)$_2$ (10 mmol%), NaOAc (1eq) and Cu(OAc)$_2$ (1eq) in DMSO (2 mL) were added to a tube equipped with magnetic stirrer bar. The reaction was under 1 atm O$_2$ and the mixture was stirred at 120 °C (oil bath temperature) for the desired reaction time. After the reaction was finished (monitored by TLC), the mixture was cooled to room temperature and quenched with aqueous NaCl, and the crude product was extracted with ethyl acetate. The organic extracts were concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel with light petroleum ether/ethyl acetate as eluent to afford the desired product.

IV. Mechanistic Study

Control experiment

To gain more insight to the mechanism of these reactions, we performed deuterium competition experiment between substrate 1a and [D$_5$]-1a, and a kinetic isotope effect (KIE) of $k_H/k_D \approx 2.3$ (eqn. 3) was observed, which indicated that the C–H
activation of arenes was the rate-determining step. Further studies revealed that ortho-palladated complex of acetanilides obtained according to the reported procedure$^2$ could be transformed into 3a in 30% GC yield when refluxing with 2.0 equiv of norbornene in toluene. These results suggested that the ortho-palladated complex of acetanilide might be a key intermediate in this transformation.

**Kinetic Isotope Effect (KIE) Experiment**

\[
\begin{align*}
\text{Cu(OAc)}_2 \text{ (1 equiv)} & \quad \text{Pd(OAc)}_2 \text{ (10 mol \%)} \\
\text{NaOAc (1 equiv), DMSO} & \quad \text{1 atm O}_2, 120^\circ\text{C, 3 h} \\
K_{H}/K_{D} & = 2.3:1 \quad ^1\text{H NMR}
\end{align*}
\]

\[
\begin{align*}
[D_2]-1a + 1a & \quad \rightarrow 3a + [D_2]-3a \\
8.19 & \quad 7.26 \\
7.13 & \quad 7.12 \\
7.00 & \quad 6.98 \\
4.10 & \quad 3.40 \\
2.92 & \quad 2.48 \\
1.44 & \quad 1.46 \\
1.32 & \quad 1.46 \\
1.28 & \quad 1.46 \\
1.15 & \quad 1.15 \\
-0.05 & \quad -0.05
\end{align*}
\]

**References**


**C. Characterization Data for Compounds 3a-4f**

exo-1-(2,3,4,4a-Tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3a)

White solid; mp 99-100 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (d, $J$ = 8.1 Hz, 1H), 7.17 – 7.10 (m, 2H), 7.00 (t, $J$ = 7.4 Hz, 1H), 4.11 (d, $J$ = 7.9 Hz, 1H), 3.38 (d, $J$ = 7.8 Hz, 1H), 2.51 (s, 1H), 2.35 (s, 1H), 2.29 (s, 3H), 1.68 – 1.56 (m, 2H), 1.43 (t, $J$ = 9.9 Hz, 1H), 1.32 (d, $J$ = 10.2 Hz, 2H), 1.13 (d, $J$ = 10.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.2, 144.6, 133.6, 127.6, 124.0, 123.7, 116.6, 68.0, 50.6, 43.1, 42.8, 32.0, 28.0, 25.7, 23.7. IR (KBr, cm$^{-1}$): 2954, 2872, 1664, 1408, 1392, 1057, 855; ESI-HRMS calcd for C$_{15}$H$_{18}$NO (M + H)$^+$ 228.1383; found, 228.1388.
**exo-1-(6-Fluoro-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3b)**

Yellow oli; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.14 (dd, $J$ = 8.7, 5.0 Hz, 1H), 6.89 – 6.75 (m, 2H), 4.14 (d, $J$ = 7.9 Hz, 1H), 3.36 (d, $J$ = 7.8 Hz, 1H), 2.52 (d, $J$ = 3.5 Hz, 1H), 2.35 (s, 1H), 2.27 (s, 3H), 1.70 – 1.58 (m, 2H), 1.42 (dd, $J$ = 11.0, 8.9 Hz, 1H), 1.32 (d, $J$ = 10.1 Hz, 2H), 1.16 (d, $J$ = 10.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.8, 159.4 (d, $J$ = 240.4 Hz), 140.8, 135.7 (d, $J$ = 7.9 Hz), 117.4 (d, $J$ = 7.9 Hz), 113.8 (d, $J$ = 22.4 Hz), 111.1 (d, $J$ = 23.4 Hz), 68.5, 50.6, 43.2, 42.7, 32.1, 28.0, 25.7, 23.6. IR (KBr, cm$^{-1}$): 2958, 2873, 1662, 1606, 1483, 1389, 1212, 821; ESI-HRMS caleld for C$_{15}$H$_{17}$FNO (M + H)$^+$ 246.1289; found, 246.1292.

**exo-1-(6-Chloro-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3c)**

White solid; mp 103-105 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 (d, $J$ = 8.6 Hz, 1H), 7.11 (d, $J$ = 8.7 Hz, 1H), 7.07 (s, 1H), 4.13 (t, $J$ = 7.9 Hz, 1H), 3.35 (d, $J$ = 7.9 Hz, 1H), 2.51 (s, 1H), 2.34 (s, 1H), 2.28 (s, 3H), 1.63 (dd, $J$ = 23.3, 11.5 Hz, 2H), 1.42 (t, $J$ = 9.9 Hz, 1H), 1.30 (d, $J$ = 9.7 Hz, 2H), 1.16 (d, $J$ = 10.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.2, 143.3, 135.7, 128.5, 127.6, 124.2, 117.6, 68.4, 50.5, 43.2, 42.8, 32.1, 27.9, 25.7, 23.6. IR (KBr, cm$^{-1}$): 2952, 1771, 1475, 1384, 1247, 1060, 913, 745; ESI-HRMS caleld for C$_{15}$H$_{17}$ClNO (M + H)$^+$ 262.0993; found, 262.1001.

**exo-1-(6-Bromo-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3d)**

White solid; mp 116-117 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, $J$ = 8.6 Hz, 1H), 7.27 – 7.21 (m, 2H), 4.12 (d, $J$ = 7.7 Hz, 1H), 3.35 (d, $J$ = 7.9 Hz, 1H), 2.51 (s, 1H), 2.35 (s, 1H), 2.27 (s, 3H), 1.67 – 1.60 (m, 2H), 1.42 (t, $J$ = 9.7 Hz, 1H), 1.34 – 1.28 (m, 2H), 1.16 (d, $J$ = 10.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.2, 143.8, 136.1, 130.5, 127.1, 118.0, 116.0, 68.3, 50.4, 43.2, 42.8, 32.1, 27.9, 25.7, 23.7. IR (KBr, cm$^{-1}$): 2955, 2872, 1665, 1472, 1383, 1250, 820; ESI-HRMS caleld for C$_{15}$H$_{17}$BrNO (M + H)$^+$ 306.0488; found, 306.0482.

**exo-1-(6-Methyl-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3e)**

White solid; mp 113-115 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J$ = 8.2 Hz, 1H), 6.97 – 6.91 (m, 2H), 4.09 (d, $J$ = 7.8 Hz, 1H), 3.33 (d, $J$ = 7.8 Hz, 1H), 2.49 (s, 1H), 2.34 (s, 1H), 2.29 (s, 3H), 2.27 (s, 3H), 1.71 – 1.56 (m, 2H), 1.40 (d, $J$ = 9.2 Hz, 1H), 1.30 (t, $J$ = 10.1 Hz, 2H), 1.12 (d, $J$ = 10.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.8, 142.4, 133.7, 133.3, 128.1, 124.6, 116.3, 68.2, 50.7, 43.1, 42.8, 32.1, 28.0, 25.7, 23.7. IR (KBr, cm$^{-1}$): 2956, 2872, 1757, 1658, 1488, 1389, 1256, 820; ESI-HRMS caleld for C$_{16}$H$_{20}$NO (M + H)$^+$ 242.1539; found, 242.1546.

**exo-1-(6-Methoxy-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3f)**

Yellow oli; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.17 – 8.00 (m, 1H), 6.69 (dd, $J$ = 6.0, 2.7 Hz, 2H), 4.10 (d, $J$ = 7.8 Hz, 1H), 3.77 (s, 3H), 3.35 (d, $J$ = 7.8 Hz, 1H), 2.50 (d, $J$ = 3.7 Hz, 1H), 2.25 (d, $J$ = 2.8 Hz, 1H), 2.26 (s, 3H), 1.68 – 1.55 (m, 2H), 1.45 – 1.38 (m, 1H), 1.35 – 1.27 (m, 2H), 1.13 (d, $J$ = 10.5 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.4, 156.4, 138.5, 135.3, 117.2, 112.0, 110.2, 68.3, 55.6, 50.8, 43.2, 42.7, 32.1, 28.0, 25.7, 23.5. IR (KBr, cm$^{-1}$): 2954, 2871, 1651, 1591, 1487, 1388, 1282, 1251, 804; ESI-HRMS caleld for C$_{16}$H$_{20}$NO$_2$ (M + H)$^+$ 258.1489; found, 258.1494.

**exo-1-(6-Phenoxy-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3g)**
White solid; mp 96-98 °C; ^1H NMR (400 MHz, CDCl$_3$) δ 8.15 (d, $J$ = 8.5 Hz, 1H), 7.30 (t, $J$ = 7.9 Hz, 2H), 7.06 (t, $J$ = 7.4 Hz, 1H), 6.96 (d, $J$ = 8.0 Hz, 2H), 6.87 – 6.73 (m, 2H), 4.13 (d, $J$ = 7.8 Hz, 1H), 3.35 (d, $J$ = 7.8 Hz, 1H), 2.52 (s, 1H), 2.32 (s, 1H), 2.28 (s, 3H), 1.67 – 1.56 (m, 2H), 1.40 – 1.25 (m, 4H), 1.16 (d, $J$ = 10.4 Hz, 1H); ^13C NMR (100 MHz, CDCl$_3$) δ 168.8, 157.9, 153.1, 140.6, 135.6, 129.6, 122.7, 118.3, 118.1, 117.4, 115.2, 68.4, 50.7, 43.2, 42.7, 32.1, 27.9, 25.7, 23.6. IR (KBr, cm$^{-1}$): 2953, 2872, 1659, 1590, 1477, 1389, 1246, 693; ESI-HRMS calcd for C$_{21}$H$_{20}$NO$_2$ (M + H)$^+$ 320.1645; found, 320.1652.

**exo-1-(6-(Trifluoromethoxy)-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3h)**

White solid; mp 86-87 °C; ^1H NMR (400 MHz, CDCl$_3$) δ 8.19 (d, $J$ = 8.7 Hz, 1H), 7.06 – 6.93 (m, 2H), 4.16 (d, $J$ = 7.9 Hz, 1H), 3.85 (s, 3H), 3.39 (d, $J$ = 7.8 Hz, 1H), 2.53 (d, $J$ = 7.9 Hz, 1H), 2.20 (s, 4H), 1.65 – 1.48 (m, 2H), 1.39 (dd, $J$ = 13.1, 5.7 Hz, 2H), 1.03 (s, 2H); ^13C NMR (100 MHz, CDCl$_3$) δ 172.0, 147.8, 138.6, 132.6, 125.5, 117.1, 111.6, 68.7, 55.4, 50.3, 42.7, 42.6, 32.3, 27.9, 23.8. IR (KBr, cm$^{-1}$): 2956, 2871, 1653, 1590, 1486, 1372, 761; ESI-HRMS calcd for C$_{16}$H$_{17}$F$_3$NO$_2$ (M + H)$^+$ 312.1206; found, 312.1218.

**exo-1-(8-Methoxy-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3i)**

Yellow oil; ^1H NMR (400 MHz, CDCl$_3$) δ 7.03 (t, $J$ = 7.8 Hz, 1H), 6.79 (d, $J$ = 7.9 Hz, 2H), 4.06 (d, $J$ = 7.4 Hz, 1H), 3.48 (d, $J$ = 7.5 Hz, 1H), 2.48 (d, $J$ = 3.1 Hz, 1H), 2.26 (s, 3H), 2.22 (s, 4H), 1.40 (t, $J$ = 10.7 Hz, 1H), 1.30 (dd, $J$ = 15.3, 6.8 Hz, 1H), 1.07 (s, 2H); ^13C NMR (100 MHz, CDCl$_3$) δ 170.3, 150.0, 142.8, 135.7, 130.2, 127.4, 124.8, 121.1, 68.1, 51.1, 43.2, 42.7, 32.3, 27.8, 26.3, 23.6, 21.4. IR (KBr, cm$^{-1}$): 2954, 2871, 1677, 1589, 1460, 1386, 1228, 763; ESI-HRMS calcd for C$_{16}$H$_{20}$NO (M + H)$^+$ 258.1539; found, 242.1553.
Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.74 (s, 1H), 4.08 (d, \(J = 7.8\) Hz, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 3.81 (s, 3H), 3.37 (d, \(J = 7.8\) Hz, 1H), 2.48 (s, 2H), 2.26 (s, 3H), 1.69 – 1.55 (m, 2H), 1.45 – 1.39 (m, 1H), 1.35 (d, \(J = 10.2\) Hz, 1H), 1.31 – 1.24 (m, 1H), 1.14 (d, \(J = 10.3\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.0, 153.2, 149.1, 140.8, 138.0, 117.4, 97.1, 68.7, 60.9, 60.6, 56.2, 48.7, 43.3, 40.9, 321, 28.0, 25.6, 23.7. IR (KBr, cm\(^{-1}\)): 2954, 2871, 1659, 1392, 1127, 1051, 916; ESI-HRMS calecd for C\(_{19}\)H\(_{24}\)N\(_2\)O (M + H\(^{+}\)) = 318.1700; found, 318.1703.

**exo-1-(8,9,10,10a-Tetrahydro-6bH-7,10-methanobenz[a]carbazol-11(7H)-yl)ethanone (3m)**

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (dd, \(J = 13.4, 8.2\) Hz, 2H), 7.62 (d, \(J = 8.1\) Hz, 1H), 7.46 – 7.36 (m, 2H), 7.25 (s, 1H), 4.26 (d, \(J = 6.7\) Hz, 1H), 3.66 (d, \(J = 7.2\) Hz, 1H), 2.55 (d, \(J = 15.6\) Hz, 1H), 2.36 (s, 3H), 2.27 (s, 1H), 1.65 – 1.57 (m, 2H), 1.48 (t, \(J = 10.6\) Hz, 1H), 1.40 – 1.32 (m, 1H), 1.06 (s, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.9, 139.7, 134.0, 132.2, 128.0, 126.6, 126.2, 125.1, 124.6, 123.8, 121.8, 68.9, 51.7, 43.3, 42.1, 32.2, 28.0, 26.4, 24.0. IR (KBr, cm\(^{-1}\)): 2955, 2871, 1674, 1592, 1290, 810, 760; ESI-HRMS calecd for C\(_{16}\)H\(_{20}\)NO (M + H\(^{+}\)) = 278.1539; found, 278.1538.

**exo-1-(7-Methoxy-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3n)**

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (dd, \(J = 13.4, 8.2\) Hz, 2H), 7.62 (d, \(J = 8.1\) Hz, 1H), 7.46 – 7.36 (m, 2H), 7.25 (s, 1H), 4.26 (d, \(J = 6.7\) Hz, 1H), 3.66 (d, \(J = 7.2\) Hz, 1H), 2.55 (d, \(J = 15.6\) Hz, 1H), 2.36 (s, 3H), 2.27 (s, 1H), 1.65 – 1.57 (m, 2H), 1.48 (t, \(J = 10.6\) Hz, 1H), 1.40 – 1.32 (m, 1H), 1.06 (s, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.9, 139.7, 134.0, 132.2, 128.0, 126.6, 126.2, 125.1, 124.6, 123.8, 121.8, 68.9, 51.7, 43.3, 42.1, 32.2, 28.0, 26.4, 24.0. IR (KBr, cm\(^{-1}\)): 2955, 2871, 1674, 1592, 1290, 810, 760; ESI-HRMS calecd for C\(_{16}\)H\(_{20}\)NO (M + H\(^{+}\)) = 278.1539; found, 278.1538.

**exo-1-(6,7-Dimethyl-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3o)**

White solid; mp 106-107 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (s, 1H), 6.88 (s, 1H), 4.07 (d, \(J = 7.8\) Hz, 1H), 3.31 (d, \(J = 7.8\) Hz, 1H), 2.48 (d, \(J = 3.2\) Hz, 1H), 2.32 (s, 1H), 2.27 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 1.70 – 1.51 (m, 2H), 1.44 – 1.37 (m, 1H), 1.33 – 1.27 (m, 2H), 1.11 (d, \(J = 10.5\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.8, 142.8, 135.8, 131.9, 131.1, 125.0, 117.7, 68.3, 50.5, 43.1, 42.7, 32.0, 28.0, 25.8, 23.7, 20.1, 19.5. IR (KBr, cm\(^{-1}\)): 2960, 2026, 1665, 1600, 1468, 1383, 1095, 991, 639, 618; ESI-HRMS calecd for C\(_{17}\)H\(_{22}\)NO (M + H\(^{+}\)) = 256.1696; found, 256.1708.

**exo-1-(6,7-Dichloro-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3p)**

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.34 (s, 1H), 7.17 (s, 1H), 4.17 (d, \(J = 7.9\) Hz, 1H), 3.35 (d, \(J = 10.2\) Hz, 1H), 2.53 (s, 1H), 2.36 (s, 1H), 2.30 (s, 3H), 1.72 – 1.61 (m, 2H), 1.44 (t, \(J = 8.9\) Hz, 1H), 1.37 – 1.27 (m, 2H), 1.20 (d, \(J = 10.6\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.2, 144.0, 134.0, 131.1, 126.5, 125.4, 118.1, 68.7, 50.1, 43.2, 42.8, 32.1, 27.9, 25.6, 23.6. IR (KBr, cm\(^{-1}\)): 2979, 2871, 1384, 1095, 991, 618; ESI-HRMS calecd for C\(_{18}\)H\(_{18}\)Cl\(_2\)NO (M + H\(^{+}\)) = 296.0603; found, 296.0604.

**exo-1-(7-Fluoro-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3q)** and **exo-1-(5-Fluoro-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3q')**
Yellow oil (7/4 mixture of 3q and 3q' isomers); ¹H NMR (400 MHz, CDCl₃) δ 7.95 (t, J = 8.9 Hz, 1H), 7.15 – 6.99 (m, 1H), 6.69 (t, J = 8.5 Hz, 1H), 4.16 (d, J = 7.8 Hz, 1H), 3.49 – 3.34 (m, 1H), 2.56 – 2.52 (m, 1H), 2.29 (s, 3H), 1.64 – 1.62 (m, 2H), 1.43 (dd, J = 19.7, 10.4 Hz, 1H). 1.34 – 1.28 (m, 2H), 1.19 (d, J = 12.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.3, 169.2, 162.3 (d, J = 241.8 Hz), 158.8 (d, J = 244.5 Hz), 146.8 (d, J = 8.5 Hz), 145.8 (d, J = 12.5 Hz), 129.5 (d, J = 7.9 Hz), 129.1 (d, J = 10.0 Hz), 119.6 (d, J = 21.0 Hz), 112.4 (d, J = 2.9 Hz), 110.5 (d, J = 19.9 Hz), 110.1 (d, J = 22.9 Hz), 104.6 (d, J = 29.1 Hz), 68.9, 68.7, 50.0, 47.8, 43.2, 43.1, 42.8, 40.6, 32.2, 32.0, 27.9, 27.8, 25.6, 25.4, 23.7, 23.7. IR (KBr, cm⁻¹): 2957, 2873, 1689, 1462, 739; ESI-HRMS calcd for C₁₅H₁₇FNO (M + H)+ 246.1289; found, 246.1290.

**exo-1-(5a,6,6a,7,8,9,10,10a,11,11a-decahydro-5H-6,11:7,10-Dimethanobenzo[b]carbazol-5-yl)ethanone (3r)**

Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 8.1 Hz, 1H), 7.13 (t, J = 7.7 Hz, 1H), 7.07 (d, J = 7.3 Hz, 1H), 6.99 (t, J = 7.3 Hz, 1H), 4.46 (d, J = 7.5 Hz, 1H), 3.72 (d, J = 7.5 Hz, 1H), 2.53 (s, 1H), 2.36 (d, J = 12.7 Hz, 2H), 2.29 (s, 3H), 1.87 (dd, J = 10.6, 7.2 Hz, 2H), 1.62 – 1.53 (m, 3H), 1.29 (t, J = 7.3 Hz, 1H), 1.16 – 0.97 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 168.9, 145.0, 133.9, 127.4, 123.7, 123.6, 116.6, 64.2, 49.7, 49.2, 48.2, 47.6, 46.1, 36.4, 36.2, 35.4, 35.1, 31.4, 31.1, 23.7. IR (KBr, cm⁻¹): 2952, 2869, 1663, 1594, 1480, 1091, 752; ESI-HRMS calcd for C₂₀H₂₄NO (M + H)+ 294.1852; found, 294.1867.

**exo-1-(4,4a-Dihydro-1H-1,4-methanocarbazol-9(9aH)-yl)ethanone (3s)**

Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, J = 8.0 Hz, 1H), 7.10 (dd, J = 16.9, 8.1 Hz, 2H), 6.95 (t, J = 7.3 Hz, 1H), 6.32 (s, 1H), 6.07 (s, 1H), 4.15 (d, J = 7.7 Hz, 1H), 3.46 (d, J = 7.6 Hz, 1H), 3.06 (s, 1H), 2.89 (s, 1H), 2.27 (s, 3H), 1.42 (d, J = 9.5 Hz, 1H), 1.35 (d, J = 9.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.2, 146.3, 140.3, 134.8, 132.1, 127.9, 123.8, 123.7, 117.2, 66.9, 49.0, 48.4, 48.0, 42.1, 23.8. IR (KBr, cm⁻¹): 2952, 2869, 1663, 1594, 1480, 1091, 752, 618; ESI-HRMS calcd for C₁₅H₁₆NO (M + H)+ 226.1226; found, 226.1232.

**exo-methyl 9-Acetyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole-2-carboxylate (3t) or exo-methyl 9-acetyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole-3-carboxylate (3t')**

Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 7.13 (t, J = 7.7 Hz, 1H), 7.03 (t, J = 7.3 Hz, 1H), 4.26 (d, J = 8.2 Hz, 1H), 3.79 (d, J = 5.2 Hz, 3H), 3.50 (d, J = 7.8 Hz, 1H), 2.86 (s, 1H), 2.43 (s, 1H), 2.31 (d, J = 5.3 Hz, 3H), 1.94 – 1.88 (m, 2H), 1.46 (d, J = 10.3 Hz, 1H), 1.33 – 1.26 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, major isomer) δ 174.1, 169.3, 144.7, 133.1, 127.8, 124.0, 123.9, 116.7, 63.6, 51.8, 50.5, 46.2, 43.4, 43.3, 33.5, 30.5, 23.4. IR (KBr, cm⁻¹): 2959, 2026, 1661, 1597, 1479, 1397, 1094, 752; ESI-HRMS calcd for C₁₇H₂₅NO₃ (M + H)+ 286.1438; found, 286.1438.

**exo-1-(1,4,4a,9b,10,10a-hexahydro-4,10-methanocyclopenta[b]carbazol-5(3aH)-yl)ethanone (3u) and exo-1-(3,3a,4,4a,10,10a-hexahydro-4,10-methanocyclopenta[b]carbazol-5(9bH)-yl)ethanone (3u')**
Yellow oil (3/1 mixture of 3u and 3u’ isomers); 'H NMR (400 MHz, CDCl₃) δ 8.18 (dd, J = 7.8, 4.8 Hz, 1H), 7.14 (t, J = 7.7 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 6.99 (t, J = 7.3 Hz, 1H), 5.73 (t, J = 21.3, 7.4 Hz, 1H), 3.54 – 3.34 (m, 1H), 3.23 (s, 1H), 2.75 – 2.55 (m, 1H), 2.51– 2.48 (m, 1H), 2.41 – 2.38 (m, 2H), 2.25 (d, J = 12.8 Hz, 3H), 1.46 – 1.24 (m, 3H); 'C NMR (100 MHz, CDCl₃) δ 168.9, 168.8, 145.1, 144.9, 134.3, 134.2, 132.2, 132.1, 131.0, 130.4, 127.4, 123.8, 123.7, 123.6, 116.87, 116.7, 64.7, 62.1, 52.5, 52.0, 48.06, 47.7, 46.5, 45.9, 45.7, 43.4, 41.7, 41.2, 35.3, 35.07, 32.3, 31.8, 23.9, 23.7. IR (KBr, cm⁻¹): 3018, 2961, 1688, 1386, 1095, 991, 619; ESI-HRMS calcd for C₁₈H₂₀NO (M + H)⁺ 266.1539; found, 266.1546.

exo-1-(2,3,4,4a-Tetrahydro-1H-1,4-methanocarbazol-9(9aH)-yl)propan-1-one (4c)

White solid; mp 96-97 °C; 'H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 8.1 Hz, 1H), 7.18 – 7.10 (m, 2H), 6.99 (t, J = 7.4 Hz, 1H), 4.13 (d, J = 7.8 Hz, 1H), 3.38 (d, J = 7.8 Hz, 1H), 2.59 – 2.50 (m, 2H), 2.49 (s, 1H), 2.35 (s, 1H), 1.64 (t, J = 12.6 Hz, 2H), 1.43 (t, J = 10.0 Hz, 1H), 1.31 (d, J = 8.8 Hz, 2H), 1.25 (t, J = 7.3 Hz, 3H), 1.13 (d, J = 10.5 Hz, 1H); 'C NMR (100 MHz, CDCl₃) δ 172.7, 144.9, 133.7, 127.7, 124.0, 123.6, 116.6, 67.2, 50.8, 43.4, 42.8, 32.1, 28.6, 28.0, 25.9, 9.3. IR (KBr, cm⁻¹): 2879, 2026, 1384, 1089, 990, 618; ESI-HRMS calcd for C₁₆H₂₀NO (M + H)⁺ 242.1539; found, 242.1547.

exo-N-(Pyrimidin-2-yl)-2,3,4,4a-tetrahydro-1H-1,4-methanocarbazol-9(9aH)-amine (4e)

White solid; mp 126-127 °C; 'H NMR (400 MHz, CDCl₃) δ 8.47 (d, J = 4.6 Hz, 2H), 8.39 (d, J = 8.1 Hz, 1H), 7.17 (dd, J = 16.2, 7.7 Hz, 2H), 6.91 (t, J = 7.3 Hz, 1H), 6.65 (t, J = 4.5 Hz, 1H), 4.51 (d, J = 8.1 Hz, 1H), 3.33 (d, J = 8.1 Hz, 1H), 2.77 (s, 1H), 2.37 (s, 1H), 1.63 (t, J = 10.2 Hz, 2H), 1.44 (d, J = 8.8 Hz, 2H), 1.35 (d, J = 10.4 Hz, 1H), 1.06 (d, J = 10.3 Hz, 1H); 'C NMR (100 MHz, CDCl₃) δ 159.2, 157.2, 145.4, 134.8, 127.3, 124.2, 121.5, 115.1, 111.4, 68.0, 49.3, 43.7, 40.9, 32.1, 28.2, 25.7. IR (KBr, cm⁻¹): 2987, 2026, 1657, 1478, 1384, 1095, 991, 618; ESI-HRMS calcd for C₁₇H₁₈N₃ (M + H)⁺ 264.1495; found, 264.1498.

exo-2,3,4,4a,9,9a-Hexahydro-1H-1,4-methanocarbazole (4f)

Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 6.95 (d, J = 7.3 Hz, 1H), 6.89 (t, J = 7.6 Hz, 1H), 6.58 (t, J = 7.3 Hz, 1H), 6.46 (d, J = 7.8 Hz, 1H), 3.73 (d, J = 8.1 Hz, 1H), 3.20 (d, J = 8.1 Hz, 1H), 2.21 (s, 1H), 2.14 (s, 1H), 1.51 – 1.40 (m, 3H), 1.27 (t, J = 9.4 Hz, 1H), 1.14 (d, J = 8.5 Hz, 1H), 1.07 (d, J = 10.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 152.00, 132.16, 127.49, 124.60, 118.51, 108.73, 65.37, 52.47, 44.25, 43.17, 32.32, 28.56, 25.37. IR (KBr, cm⁻¹): 3408, 2987, 2945, 1189, 756; ESI-HRMS calcd for C₁₅H₁₈N (M + H)⁺ 186.1277; found, 186.1282.
D. NMR Spectra
E. X-Ray Crystallographic Analysis

The CCDC number of compound 3o is 988826.