

## Supporting Information

### Copper-catalyzed synthesis of benzocarbazoles via $\alpha$ -C-arylation of ketones

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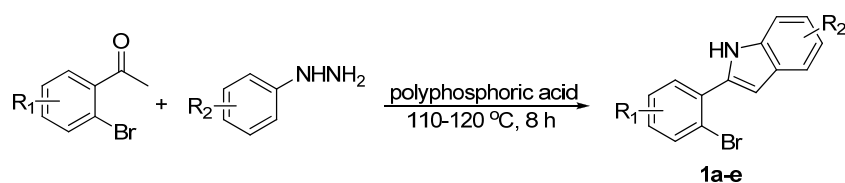
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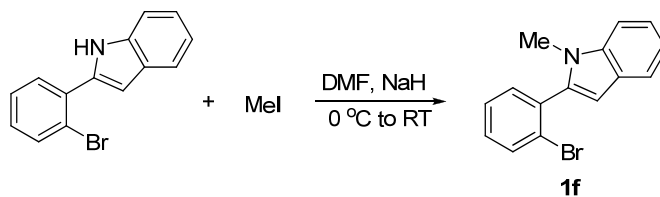
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## General experimental procedures

All reagents were weighed and handled in air at room temperature. Column chromatography was performed on silica gel (200 ~ 300 mesh). Proton magnetic resonance spectra ( $^1\text{H}$  NMR) were recorded using tetramethylsilane (TMS) (at 0.00 ppm) in the solvent, remaining  $\text{CHCl}_3$  in  $\text{CDCl}_3$  (at 7.26 ppm) or remaining DMSO in  $\text{DMSO}-d_6$  (at 2.50 ppm) as the internal standard. Carbon magnetic resonance spectra ( $^{13}\text{C}$  NMR) were recorded using  $\text{CDCl}_3$  (at 77.2 ppm) or  $\text{DMSO}-d_6$  (at 39.5 ppm) as the internal standard.



**General procedure for synthesis of compounds 1a-e.** **1a-e** were prepared according to the previous procedure.<sup>1</sup> Ketone (5 mmol) and substituted phenylhydrazine (9 mmol) were added to a flask with polyphosphoric acid (18 g), and the mixture was heated at 110-120 °C for 8 h. The resulting solution was poured into ice water (100 mL), neutralized by NaOH, and extracted with EtOAc (3 × 50 mL). The combined organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by flash chromatography to get the desired product (**1a-e**).

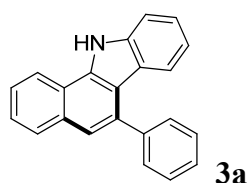


**Experimental procedure for synthesis of compound 1f.** **1f** was prepared according to the previous procedure.<sup>2</sup> To a stirred solution of indole **1a** (680 mg, 2.5 mmol) in dry DMF (6 mL), NaH (120 mg, 60% suspension in mineral oil, 3 mmol) was added portionwise under nitrogen atmosphere at 0 °C. After 30 min, MeI (426 mg, 3 mmol) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. The resulting solution was poured into cool water (50 mL), and extracted with EtOAc (3 × 50 mL). The combined organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by flash

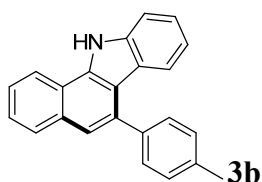
chromatography to get the desired product **1f** as a white solid. Yield 55% (393 mg). mp 88-89 °C.

**General procedure for synthesis of 11H-benzo[a]carbazoles compounds 3a-z.**

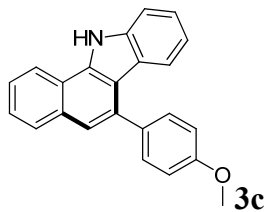
Substituted 2-(2-bromophenyl)-1H-indole (0.5 mmol), ketone (1.0 mmol), CuBr (0.05 mmol, 7 mg for entries 1-13 and 15-27 in Table 2) or CuI (0.05 mmol, 9 mg for entry 14 in Table 2), L-proline (0.1 mmol, 12 mg), Cs<sub>2</sub>CO<sub>3</sub> (1.0 mmol, 326 mg for entries 1-6 and 9-26 in Table 2) or K<sub>2</sub>CO<sub>3</sub> (1.0 mmol, 138 mg for entries 7 and 8 in Table 2 in Text), dry DMSO (2.0 mL for entries 1-13 and 15-26 in Table 2) or dry DMF (2.0 mL for entry 14 in Table 2) were added to a 25 mL Schlenk tube with a magnetic stirrer under nitrogen atmosphere. The mixture was allowed to stir under nitrogen atmosphere at 80 °C (for entries 1-18 and 20-26 in Table 2) or 90 °C (for entry 19 in Table 2) for 24 h. After cooled to room temperature, the resulting solution was concentrated via rotary evaporation, and the residue was purified by column chromatography on silica gel using petroleum/ ethyl acetate as eluent to provide the desired product (**3**). Several impure products were further purified by recrystallization in *n*-hexane-ethanol mixed solvent.



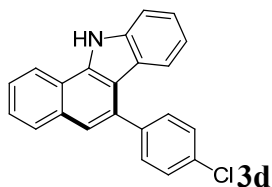
**6-Phenyl-11H-benzo[a]carbazole (3a).**<sup>3</sup> Eluent: petroleum/ethyl acetate (30:1). Yield 77% (113 mg). Pale yellow solid, mp 162-164 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.85 (br s, 1H), 8.13-8.10 (m, 1H), 8.04-8.01 (m, 1H), 7.75-7.72 (m, 2H), 7.62-7.49 (m, 8H), 7.40 (td, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 7.10 (td, *J* = 7.2 Hz, *J* = 1.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 141.3, 138.8, 136.7, 135.4, 132.2, 129.5, 129.0, 128.5, 127.7, 125.8, 125.6, 124.8, 124.0, 122.2, 121.0, 120.5, 120.3, 120.0, 116.8, 111.0. ESI-MS [M+H]<sup>+</sup> *m/z* 294.1.



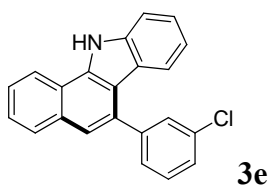
**6-*p*-Tolyl-11*H*-benzo[*a*]carbazole (3b).**<sup>3</sup> Eluent: petroleum/ethyl acetate (30:1). Yield 64% (99 mg). Pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.89 (br s, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.61-7.51 (m, 7H), 7.45-7.36 (m, 3H), 7.06 (t, *J* = 7.8 Hz, 1H), 2.52 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 138.8, 138.4, 137.4, 136.7, 135.4, 132.3, 129.3, 129.2, 129.0, 125.7, 125.4, 124.7, 124.1, 122.3, 121.0, 120.4, 119.7, 116.9, 111.0, 21.5. ESI-MS [M+H]<sup>+</sup> *m/z* 308.1.



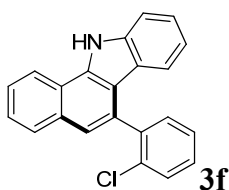
**6-(4-Methoxyphenyl)-11*H*-benzo[*a*]carbazole (3c).**<sup>3</sup> Eluent: petroleum/ethyl acetate (20:1). Yield 64% (104 mg). Snow white solid, mp 162-163 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.88 (br s, 1H), 8.14-8.11 (m, 1H), 8.02-7.98 (m, 1H), 7.65-7.54 (m, 6H), 7.51 (s, 1H), 7.39 (td, *J* = 7.2 Hz, *J* = 1.0 Hz, 1H), 7.13-7.06 (m, 3H), 3.96 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 159.3, 138.8, 136.4, 135.4, 133.8, 132.3, 130.6, 128.9, 125.8, 125.4, 124.7, 124.1, 122.2, 121.0, 120.4, 120.2, 119.7, 117.1, 113.9, 111.0, 55.5. ESI-MS [M+H]<sup>+</sup> *m/z* 324.1, [M+Na]<sup>+</sup> *m/z* 346.0.



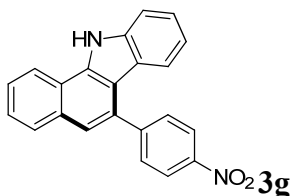
**6-(4-Chlorophenyl)-11*H*-benzo[*a*]carbazole (3d).**<sup>3</sup> Eluent: petroleum/ethyl acetate (30:1). Yield 80% (131 mg). Pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.76 (br s, 1H), 8.08-7.97 (m, 2H), 7.64-7.39 (m, 10H), 7.14 (td, *J* = 7.3 Hz, *J* = 1.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 139.8, 138.8, 135.4, 135.3, 133.7, 132.1, 130.9, 129.0, 128.7, 126.0, 125.8, 124.9, 123.7, 122.0, 121.1, 120.5, 120.4, 119.9, 116.5, 111.2. ESI-MS [M+H]<sup>+</sup> *m/z* 328.1.



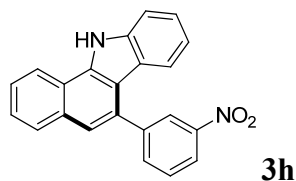
**6-(3-Chlorophenyl)-11H-benzo[a]carbazole (3e).** Eluent: petroleum/ethyl acetate (30:1). Yield 80% (132 mg). Pale yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.92 (br s, 1H), 8.16 (d,  $J = 7.9$  Hz, 1H), 8.00 (d,  $J = 7.2$  Hz, 1H), 7.70 (s, 1H), 7.64-7.36 (m, 9H), 7.08 (t,  $J = 7.9$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  143.1, 138.8, 135.4, 135.1, 134.4, 132.1, 129.8, 129.5, 129.1, 127.8, 127.8, 126.0, 125.8, 124.9, 123.7, 122.0, 121.1, 120.5, 120.0, 116.4, 111.2. HRMS (ESI) Calcd for  $(\text{C}_{22}\text{H}_{14}\text{ClN}-\text{H})^-$ : 326.0737; Found: 326.0736.



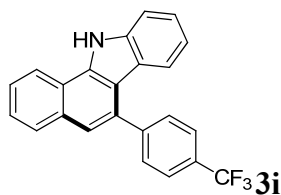
**6-(2-Chlorophenyl)-11H-benzo[a]carbazole (3f).** Eluent: petroleum/ethyl acetate (30:1). Yield 70% (114 mg). Pale yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.92 (br s, 1H), 8.19 (d,  $J = 8.3$  Hz, 1H), 8.02 (d,  $J = 7.6$  Hz, 1H), 7.66-7.34 (m, 9H), 7.04 (d,  $J = 3.8$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  140.0, 138.6, 135.0, 134.1, 133.4, 132.0, 131.7, 129.7, 129.3, 129.2, 127.0, 125.8, 125.8, 124.8, 123.9, 121.4, 120.9, 120.6, 120.6, 120.1, 117.3, 111.0. HRMS (ESI) Calcd for  $(\text{C}_{22}\text{H}_{14}\text{ClN}-\text{H})^-$ : 326.0737; Found: 326.0735.



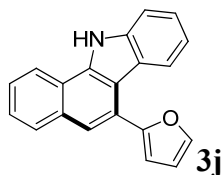
**6-(4-Nitrophenyl)-11H-benzo[a]carbazole (3g).** Eluent: petroleum/ethyl acetate (8:1). Yield 78% (132 mg). Yellow solid, mp 276-277 °C.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 300 MHz)  $\delta$  12.52 (br s, 1H), 8.61 (d,  $J = 8.0$  Hz, 1H), 8.45 (d,  $J = 8.6$  Hz, 2H), 8.10 (d,  $J = 8.0$  Hz, 1H), 7.98-7.95 (m, 2H), 7.74-7.60 (m, 3H), 7.56 (s, 1H), 7.42-7.33 (m, 2H), 7.04 (t,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , 75 MHz)  $\delta$  148.2, 147.6, 139.6, 136.5, 134.2, 131.9, 130.9, 129.3, 126.7, 126.5, 125.1, 124.3, 122.7, 122.3, 121.4, 121.4, 120.8, 119.7, 114.8, 112.2. HRMS (ESI) Calcd for  $(\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_2-\text{H})^-$ : 337.0977; Found: 337.0976.



**6-(3-Nitrophenyl)-11H-benzo[a]carbazole (3h).** Eluent: petroleum/ethyl acetate (8:1). Yield 82% (138 mg). Yellow solid, mp 219-221 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz) δ 12.47 (br s, 1H), 8.57 (d, *J* = 7.8 Hz, 1H), 8.44-8.38 (m, 2H), 8.15 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.88 (t, *J* = 7.8 Hz, 1H), 7.70-7.60 (m, 4H), 7.35 (t, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz) δ 148.4, 142.8, 139.6, 136.5, 136.3, 133.8, 132.0, 130.7, 129.2, 126.6, 126.5, 125.1, 123.9, 123.2, 122.7, 122.3, 121.4, 121.2, 120.9, 119.7, 115.0, 112.2. HRMS (ESI) Calcd for (C<sub>22</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>-H)<sup>-</sup>: 337.0977; Found: 337.0981.

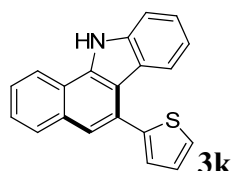


**6-(4-(Trifluoromethyl)phenyl)-11H-benzo[a]carbazole (3i).**<sup>3</sup> Eluent: petroleum/ethyl acetate (20:1). Yield 78% (140 mg). Pale yellow solid, mp 138-139 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.94 (br s, 1H), 8.17 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.82-7.38 (m, 7H), 7.50 (s, 1H), 7.42-7.38 (m, 2H), 7.09 (t, *J* = 7.7 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 145.0, 138.8, 135.5, 135.0, 132.0, 129.9 (q, *J* = 32.5 Hz), 129.8, 129.1, 126.0, 125.9, 125.5 (q, *J* = 3.6 Hz), 125.0, 124.6 (q, *J* = 272.3 Hz), 123.6, 121.9, 121.3, 120.5, 112.0, 116.2, 111.2. ESI-MS [M+H]<sup>+</sup> *m/z* 362.1.

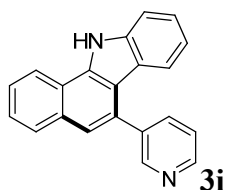


**6-(Furan-2-yl)-11H-benzo[a]carbazole (3j).** Eluent: petroleum/ethyl acetate (30:1). Yield 64% (91 mg). Pale yellow solid, mp 143-144 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.71 (br s, 1H), 8.05-7.90 (m, 3H), 7.72-7.67 (m, 2H), 7.53-7.44 (m, 3H), 7.38 (td, *J* = 7.9 Hz, *J* = 1.0 Hz, 1H), 7.19 (td, *J* = 8.1 Hz, *J* = 1.0 Hz, 1H), 6.79 (d, *J* = 3.1 Hz, 1H),

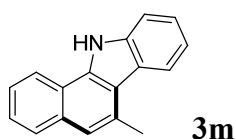
6.64-6.63 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  154.3, 142.3, 138.8, 135.7, 131.9, 129.1, 126.0, 125.9, 125.0, 123.6, 122.6, 120.8, 120.5, 120.1, 116.1, 111.8, 111.0, 108.7. HRMS (ESI) Calcd for  $(\text{C}_{20}\text{H}_{13}\text{NO}-\text{H})^-$ : 282.0919; Found: 282.0924.



**6-(Thiophen-2-yl)-11H-benzo[a]carbazole (3k).** Eluent: petroleum/ethyl acetate (30:1). Yield 58% (87 mg). Pale yellow solid, mp 143-144 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.84 (br s, 1H), 8.09 (d,  $J$  = 8.0 Hz, 1H), 7.97 (d,  $J$  = 8.0 Hz, 1H), 7.70-7.36 (m, 8H), 7.26-7.23 (m, 1H), 7.11 (t,  $J$  = 7.2 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  142.2, 138.7, 135.3, 131.9, 129.1, 128.7, 127.4, 127.1, 125.9, 125.6, 125.0, 123.8, 122.6, 122.1, 120.7, 120.4, 119.9, 117.2, 111.0. HRMS (ESI) Calcd for  $(\text{C}_{20}\text{H}_{13}\text{NS}-\text{H})^-$ : 298.0690; Found: 298.0702.

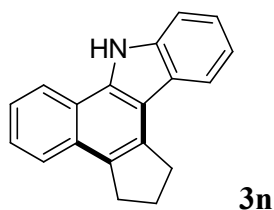


**6-(Pyridin-3-yl)-11H-benzo[a]carbazole (3i).** Eluent: petroleum/ethyl acetate (5:1). yield 65% (96 mg). Yellow solid, mp 262-263 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  9.29 (br s, 1H), 9.00 (s, 1H), 8.80 (d,  $J$  = 3.8 Hz, 1H), 8.21 (d,  $J$  = 7.9 Hz, 1H), 8.06-8.01 (m, 2H), 7.66-7.36 (m, 7H), 7.38 (t,  $J$  = 7.6 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  150.0, 148.9, 138.8, 137.1, 137.0, 135.6, 132.6, 132.0, 129.1, 126.0, 125.0, 123.5, 123.4, 121.7, 121.5, 120.7, 120.6, 120.0, 116.4, 111.2. HRMS (ESI) Calcd for  $(\text{C}_{21}\text{H}_{14}\text{N}_2-\text{H})^-$ : 293.1079; Found: 293.1083.

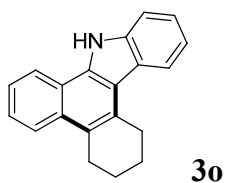


**6-Methyl-11H-benzo[a]carbazole (3m).**<sup>4</sup> Eluent: petroleum/ethyl acetate (30:1). Yield 71% (82 mg). Snow white solid, mp 189-191 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$

8.72 (br s, 1H), 8.27 (d,  $J = 7.9$  Hz, 1H), 8.06-8.02 (m, 1H), 7.97-7.92 (m, 1H), 7.60-7.32 (m, 6H), 3.00 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  138.6, 134.9, 132.5, 132.3, 128.2, 125.4, 124.7, 124.4, 122.2, 120.4, 120.1, 120.0, 119.8, 118.2, 111.1, 21.4. ESI-MS  $[\text{M}+\text{H}]^+$   $m/z$  232.1.

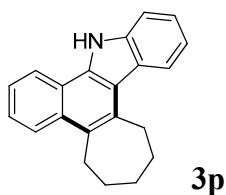


**1,2,3,8-Tetrahydrobenzo[a]cyclopenta[c]carbazole (3n).** Eluent: petroleum/ethyl acetate (30:1). The crude product was further purified by recrystallization in *n*-hexane-ethanol mixture. Yield 59% (76 mg). Snow white solid, mp 234-235 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.76 (br s, 1H), 8.16-8.12 (m, 2H), 7.97-7.94 (m, 1H), 7.61-7.53 (m, 3H), 7.43 (td,  $J = 6.9$  Hz,  $J = 1.0$  Hz, 1H), 7.32-7.27 (m, 1H), 3.60 (t,  $J = 7.2$  Hz, 2H), 3.36 (t,  $J = 7.6$  Hz, 2H), 2.49-2.40 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , 75 MHz)  $\delta$  139.2, 135.6, 135.4, 130.3, 129.1, 125.8, 125.6, 124.8, 124.6, 123.6, 122.8, 121.3, 120.9, 119.6, 115.2, 111.8, 33.1, 30.8, 24.6. HRMS (ESI) Calcd for  $(\text{C}_{19}\text{H}_{15}\text{N}-\text{H})^-$ : 256.1126; Found: 256.1125.

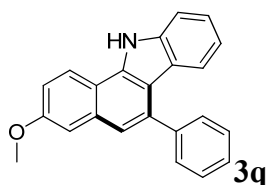


**2,3,4,9-Tetrahydro-1H-dibenzo[a,c]carbazole (3o).** Eluent: petroleum/ethyl acetate (30:1). Yield 87% (118 mg). Snow white solid, mp 183-184 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.74 (br s, 1H), 8.25 (d,  $J = 8.2$  Hz, 1H), 8.14-8.09 (m, 2H), 7.60-7.55 (m, 3H), 7.41 (t,  $J = 7.6$  Hz, 1H), 7.30-7.25 (m, 1H), 3.49 (s, 2H), 3.21 (s, 2H), 2.06-2.04 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  138.6, 133.5, 131.5, 131.4, 125.4, 124.8, 124.4, 124.1, 123.5, 122.7, 120.8, 119.9, 119.8, 117.6, 111.0, 29.1, 26.3, 23.3, 23.0. HRMS (ESI) Calcd for  $(\text{C}_{20}\text{H}_{17}\text{N}-\text{H})^-$ : 270.1283; Found: 270.1283.

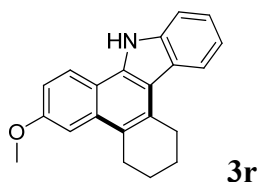




**1,2,3,4,5,10-Hexahydrobenzo[a]cyclohepta[c]carbazole (3p).** Eluent: petroleum/ethyl acetate (30:1). The crude product was further purified by recrystallization in *n*-hexane-ethanol mixture. Yield 53% (75 mg). Snow white solid, mp 233-234 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz) δ 12.12 (br s, 1H), 8.54-8.50 (m, 1H), 8.31 (d, *J* = 7.9 Hz, 1H), 8.26-8.23 (m, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.58-7.55 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 3.65-3.62 (m, 2H), 3.37-3.32 (m, 2H), 1.92-1.91 (d, 2H), 1.80-1.79 (d, 2H), 1.69-1.67 (d, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz) δ 139.7, 137.2, 134.8, 130.4, 129.9, 125.9, 124.6, 124.4, 123.8, 122.8, 122.2, 120.4, 119.5, 116.4, 111.9, 31.9, 30.6, 27.6, 27.2, 26.6. HRMS (ESI) Calcd for (C<sub>21</sub>H<sub>19</sub>N-H)<sup>+</sup>: 284.1439; Found: 284.1443.

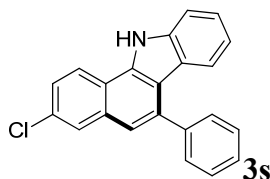


**3-Methoxy-6-phenyl-11H-benzo[a]carbazole (3q).** Eluent: petroleum/ethyl acetate (15:1). Yield 61% (98 mg). Pale yellow solid, mp 156-158 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.75 (br s, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.73-7.70 (m, 2H), 7.60-7.22 (m, 9H), 7.08-7.03 (m, 1H), 3.97 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 157.8, 141.4, 138.7, 137.3, 135.8, 133.7, 129.4, 128.5, 127.7, 124.3, 124.1, 122.1, 121.9, 120.2, 119.7, 117.5, 115.4, 115.3, 110.9, 107.8, 55.5. HRMS (ESI) Calcd for (C<sub>23</sub>H<sub>17</sub>NO-H)<sup>+</sup>: 322.1232; Found: 322.1230.

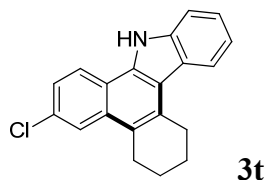


**6-Methoxy-2,3,4,9-tetrahydro-1H-dibenzo[a,c]carbazole (3r).** Eluent: petroleum/ethyl acetate (15:1). The crude product was further purified by recrystallization in *n*-hexane-ethanol mixture. Yield 82% (124 mg). Snow white solid,

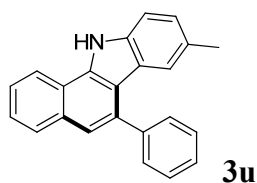
mp 189-190 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.64 (br s, 1H), 8.22 (d,  $J$  = 7.9 Hz, 1H), 8.01 (d,  $J$  = 8.9 Hz, 1H), 7.55 (d,  $J$  = 7.9 Hz, 1H), 7.43-7.36 (m, 2H), 7.29-7.20 (m, 2H), 3.98 (s, 3H), 3.48 (s, 2H), 3.13 (s, 2H), 2.07-2.05 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , 75 MHz)  $\delta$  157.7, 139.1, 134.7, 132.9, 131.8, 124.2, 123.8, 122.2, 121.7, 119.4, 115.7, 115.4, 115.2, 111.5, 104.4, 55.6, 29.0, 26.3, 23.3, 23.0. HRMS (ESI) Calcd for  $(\text{C}_{21}\text{H}_{19}\text{NO}-\text{H})^-$ : 300.1388; Found: 300.1390.



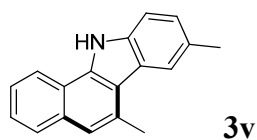
**3-Chloro-6-phenyl-11H-benzo[a]carbazole (3s).** Eluent: petroleum/ethyl acetate (30:1). Yield 44% (72 mg). Pale yellow oil.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 300 MHz)  $\delta$  12.49 (br s, 1H), 8.59 (d,  $J$  = 8.7 Hz, 1H), 8.18 (d,  $J$  = 1.8 Hz, 1H), 7.70-7.55 (m, 7H), 7.49 (s, 1H), 7.36 (t,  $J$  = 8.3 Hz, 1H), 7.28 (d,  $J$  = 7.8 Hz, 1H), 6.99 (t,  $J$  = 8.3 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  140.9, 138.8, 137.9, 135.1, 133.0, 131.4, 129.4, 128.6, 127.9, 127.8, 126.1, 125.0, 123.8, 122.2, 122.0, 120.0, 120.0, 118.5, 117.2, 111.0. HRMS (ESI) Calcd for  $(\text{C}_{22}\text{H}_{14}\text{ClN}-\text{H})^-$ : 326.0737; Found: 326.0740.



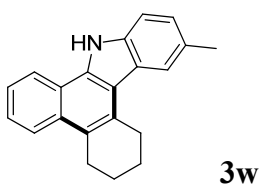
**6-Chloro-2,3,4,9-tetrahydro-1H-dibenzo[a,c]carbazole (3t).** Eluent: petroleum/ethyl acetate (30:1). The crude product was further purified by recrystallization in *n*-hexane-ethanol mixture. Yield 62% (95 mg). Snow white solid, mp 218-219 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.57 (br s, 1H), 8.21 (d,  $J$  = 8.3 Hz, 1H), 8.05 (d,  $J$  = 1.7 Hz, 1H), 7.93 (d,  $J$  = 8.6 Hz, 1H), 7.55 (d,  $J$  = 7.9 Hz, 1H), 7.48-7.40 (m, 2H), 7.32-7.26 (m, 1H), 3.42 (s, 2H), 3.09 (s, 2H), 2.04-2.00 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , 75 MHz)  $\delta$  139.4, 134.0, 132.9, 132.3, 130.7, 125.0, 124.7, 124.6, 123.8, 123.1, 122.6, 121.8, 119.7, 119.0, 117.2, 111.8, 29.0, 26.0, 23.1, 22.8. HRMS (ESI) Calcd for  $(\text{C}_{20}\text{H}_{16}\text{ClN}-\text{H})^-$ : 304.0893; Found: 304.0896.



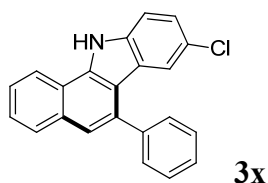
**8-Methyl-6-phenyl-11H-benzo[a]carbazole (3u).**<sup>3</sup> Eluent: petroleum/ethyl acetate (30:1). Yield 72% (110 mg). Pale yellow amorphous. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.43 (br s, 1H), 7.90-7.81 (m, 2H), 7.65-7.36 (m, 8H), 7.25-7.21 (m, 2H), 7.10 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 1H), 2.29 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 141.5, 137.2, 136.8, 135.7, 132.2, 129.6, 129.0, 129.0, 128.5, 127.8, 126.3, 125.8, 125.5, 124.2, 122.2, 120.9, 120.6, 120.4, 116.6, 110.8, 21.9. ESI-MS [M+H]<sup>+</sup> m/z 308.1.



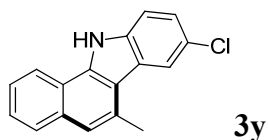
**6,8-Dimethyl-11H-benzo[a]carbazole (3v).** Eluent: petroleum/ethyl acetate (30:1). Yield 68% (83 mg). Snow white solid, mp 189-191 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.71 (br s, 1H), 8.08-8.04 (m, 2H), 7.94-7.91 (m, 1H), 7.55-7.48 (m, 3H), 7.39 (s, 1H), 7.29-7.26 (m, 1H), 3.00 (s, 3H), 2.59 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 136.1, 134.4, 131.7, 131.6, 128.5, 127.4, 125.1, 124.6, 124.2, 123.9, 121.3, 119.6, 119.1, 117.2, 109.9, 21.1, 20.8. HRMS (ESI) Calcd for (C<sub>18</sub>H<sub>15</sub>N-H)<sup>+</sup>: 244.1126; Found: 244.1135.



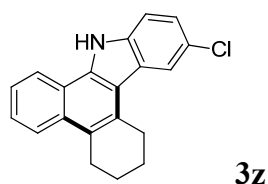
**12-Methyl-2,3,4,9-tetrahydro-1H-dibenzo[a,c]carbazole (3w).** Eluent: petroleum/ethyl acetate (30:1). Yield 93% (132 mg). Snow white solid, mp 216-217 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.52 (br s, 1H), 8.13-8.01 (m, 3H), 7.60-7.51 (m, 2H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.27-7.24 (m, 1H), 3.47 (s, 2H), 3.20 (s, 2H), 2.60 (s, 3H), 2.08-2.04 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 136.9, 133.8, 131.5, 128.9, 125.5, 125.3, 125.0, 124.3, 124.1, 123.2, 122.6, 120.8, 120.0, 117.4, 110.6, 29.1, 26.3, 23.3, 23.0, 21.9. HRMS (ESI) Calcd for (C<sub>21</sub>H<sub>19</sub>N-H)<sup>+</sup>: 284.1439; Found: 284.1442.



**8-Chloro-6-phenyl-11H-benzo[a]carbazole (3x).** Eluent: petroleum/ethyl acetate (30:1). Yield 64% (105 mg). Pale yellow solid, mp 118-120 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.92 (br s, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.68-7.31 (m, 11H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 140.7, 137.0, 136.5, 136.1, 132.4, 129.2, 129.0, 128.6, 128.0, 126.2, 125.8, 125.1, 125.0, 124.8, 121.7, 121.4, 120.4, 120.2, 116.1, 111.9. HRMS (ESI) Calcd for (C<sub>22</sub>H<sub>14</sub>ClN-H)<sup>+</sup>: 326.0737; Found: 326.0743.



**8-Chloro-6-methyl-11H-benzo[a]carbazole (3y).** Eluent: petroleum/ethyl acetate (30:1). Yield 50% (66 mg). Snow white solid, mp 195-196 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz) δ 12.44 (br s, 1H), 8.49 (d, *J* = 7.8 Hz, 1H), 8.18 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.62-7.41 (m, 4H), 2.91 (s, 3H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz) δ 137.7, 136.7, 132.7, 132.0, 128.2, 126.3, 125.4, 125.1, 124.4, 124.1, 122.2, 121.2, 120.4, 119.8, 116.7, 113.3, 21.3. HRMS (ESI) Calcd for (C<sub>17</sub>H<sub>12</sub>ClN-H)<sup>+</sup>: 264.0580; Found: 264.0582.



**12-Chloro-2,3,4,9-tetrahydro-1H-dibenzo[a,c]carbazole (3z).** Eluent: petroleum/ethyl acetate (30:1). The crude product was further purified by recrystallization in *n*-hexane-ethanol mixture. Yield 77% (117 mg). Snow white solid, mp 198-199 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.63 (br s, 1H), 8.16 (d, *J* = 1.7 Hz, 1H), 8.12-8.09 (m, 1H), 8.04-8.01 (m, 1H), 7.62-7.34 (m, 4H), 3.37 (s, 2H), 3.16 (s, 2H), 2.05-2.01 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 136.8, 134.3, 131.8, 131.1, 125.8, 125.7, 125.1, 124.6, 124.2, 124.0, 122.1, 120.7, 119.8, 117.0, 111.8, 28.8, 26.2,

23.1, 22.8. HRMS (ESI) Calcd for (C<sub>20</sub>H<sub>16</sub>ClN–H)<sup>+</sup>: 304.0893; Found: 304.0893.

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