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Supporting Information

69451 Weinheim, Germany

Transition-Metal-Catalyzed Alkylations of Amines with Alkyl Halides: Photoinduced, Copper-Catalyzed Couplings of Carbazoles**

Alex C. Bissember, Rylan J. Lundgren, Sidney E. Creutz, Jonas C. Peters, and Gregory C. Fu**

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Supporting Information

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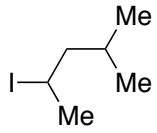
I. General Information

Unless otherwise specified, the following reagents were purchased and used as received: CuI (Aldrich), LiO*t*-Bu (Alfa Aesar), carbazole (Aldrich; recrystallized), 4-iodotetrahydro-2*H*-pyran (Aldrich), *tert*-butyl 4-iodopiperidine-1-carboxylate (Aldrich), 3-ethyl-9*H*-carbazole (Aldrich), and 3-methoxy-9*H*-carbazole (Matrix Scientific). Iodocyclohexane (Aldrich), 2-iodobutane (Aldrich), and neopentyl iodide (Aldrich) were filtered through an acrodisc prior to use, in order to remove copper stabilizers. Acetonitrile was deoxygenated and dried by sparging with nitrogen followed by passage through an activated alumina column (S. G. Water) prior to use.

Unless otherwise specified, reactions were conducted with magnetic stirring in oven-dried glassware under an inert atmosphere.

Elemental analysis was performed by Robertson Microlit Laboratories (Ledgewood, NJ). Fluorescence measurements (excitation and emission spectra) were taken in dry, degassed acetonitrile in a 1 cm quartz cuvette using a Horiba Jobin Yvon Fluorolog-3 instrument in the Beckmann Institute Laser Resource Center at Caltech.

II. Preparation of Substrates



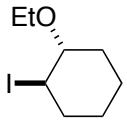
2-Iodo-4-methylpentane. A mixture of 4-methylpentan-2-ol (10.0 mL, 78.5 mmol), iodine (23.9 g, 94.2 mmol), and PPh_3 (24.7 mg, 94.2 mmol) in CH_2Cl_2 (150 mL) was heated at reflux. After 24 h, the mixture was allowed to cool to r.t., and then $Na_2S_2O_3$ (saturated aqueous solution; 20 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic phases were dried (MgSO), filtered, and concentrated under reduced pressure. Pentane (80 mL) was then added, and the resulting mixture was stirred for 0.5 h, filtered through Celite™, and then concentrated under reduced pressure. After vacuum distillation, the title compound was obtained as a clear, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.25–4.18 (m, 1H), 1.93 (d, 3H, J = 7.0 Hz), 1.90–1.84 (m, 1H), 1.82–1.74 (m, 1H), 1.33–1.28 (m, 1H), 0.94 (d, 3H, J = 7.0 Hz), 0.86 (d, 3H, J = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 52.0, 29.2, 29.1, 28.6, 22.4, 21.2.

FT-IR (neat) 3368, 1070 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_6H_{13}I$: 212, found: 212.



***trans*-1-Ethoxy-2-iodocyclohexane.** *trans*-1-Ethoxy-2-iodocyclohexane was prepared as a single diastereoisomer from cyclohexene, according to a literature procedure.[1]

III. Photoinduced, Copper-Catalyzed N-Alkylations

General Procedure (Iodides). The carbazole (1.00 mmol), Li*O*t-Bu (152 mg, 1.90 mmol), and CuI (19.5 mg, 0.10 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. The test tube was fitted with a rubber septum, the joint was wrapped with electrical tape, and the test tube was evacuated and backfilled with nitrogen (3 cycles). Acetonitrile (4.0 mL) and the alkyl iodide (1.90 mmol) were added in turn via syringe, and then the test tube was detached from the nitrogen line, and the puncture holes of the septum were covered with vacuum grease. The resulting mixture was stirred for 5 min, and then the test tube was suspended in an ice-filled dewar. The stirred mixture was irradiated with a 100-watt Hg lamp, positioned directly above the dewar, for 10 h. Next, the mixture was passed through a long plug of silica gel (eluant: hexanes; monitored by TLC), the solvent was removed, and the residue was loaded onto a silica gel column using hexanes and purified by chromatography.

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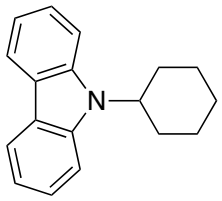
(1) Sanseverino, A. M.; de Mattos, M. C. S. *Synthesis* **1998**, 1584–1586.



9-Cyclohexyl-9*H*-carbazole (Table 2, entry 1) [5599-62-2]. Purified by chromatography (hexanes). Colorless solid. Run 1: 167 mg (67%). Run 2: 172 mg (69%).[2]

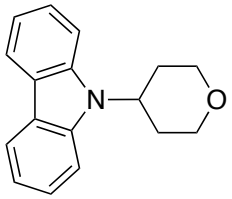
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, 2H, *J* = 8.0 Hz), 7.56 (d, 2H, *J* = 8.0 Hz), 7.43 (td, 2H, *J* = 1.5, 8.0 Hz), 7.21 (td, 2H, *J* = 1.0, 8.0 Hz), 4.50 (tt, 1H, *J* = 4.0, 13.0 Hz), 2.40 (td, 2H, *J* = 2.0, 12.5 Hz), 2.00 (t, 4H, *J* = 16.5 Hz), 1.86 (d, 1H, *J* = 13.0 Hz), 1.60–1.50 (m, 2H), 1.40 (qt, 1H, *J* = 3.0, 13.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 125.2, 120.2, 118.4, 110.3, 55.4, 30.7, 26.5, 25.7.

FT-IR (neat) 2927, 2852, 1482, 1452, 1328, 1219 cm^{-1}.

MS (ESI) *m*/*z* (M^+) calcd for $C_{18}H_{19}N$: 249, found: 249.

Gram-scale reaction. Carbazole (1.34 g, 8.00 mmol), LiO*t*-Bu (1.22 mg, 15.2 mmol), and CuI (156 mg, 0.80 mmol) were added to an oven-dried 40-mL borosilicate vial that contained a stir bar. The vial was capped with a PTFE-lined septum cap, the joint was wrapped with electrical tape, and the vial was evacuated and backfilled with nitrogen (3 cycles). Acetonitrile (32.0 mL) and cyclohexyl iodide (1.97 mL, 15.2 mmol) were added in turn via syringe, and then the vial was detached from the nitrogen line, and the puncture holes of the septum were covered with vacuum grease. The resulting mixture was stirred for 5 min, and then the test tube was suspended in a water-filled dewar. The stirred mixture was irradiated with a 100-watt Hg lamp, positioned directly above the dewar, for 10 h (the temperature of the water bath rose from r.t. to ~35 °C during the course of the reaction). Next, the reaction mixture was concentrated, the residue was loaded onto a silica gel column using CH_2Cl_2, and then it was purified by chromatography (hexanes; two times), which yielded the coupling product (1.15 g, 58%).



9-(Tetrahydro-2*H*-pyran-4-yl)-9*H*-carbazole (Table 2, entry 2). Purified by chromatography (5% EtOAc/hexanes). Colorless solid. Run 1: 157 mg (62%). Run 2: 155 mg (62%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, 2H, *J* = 7.5 Hz), 7.59 (d, 2H, *J* = 8.0 Hz), 7.46 (t, 2H, *J* = 7.5 Hz), 7.24 (d, 2H, *J* = 8.0 Hz), 4.75 (tt, 1H, *J* = 4.5, 12.5 Hz), 4.24 (d, 2H, *J* = 14.0 Hz), 3.70 (td, 2H, *J* = 2.0, 12.5 Hz), 2.80 (td, 2H, *J* = 4.5, 12.5 Hz), 1.87 (dt, 2H, *J* = 2.0, 14.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 125.4, 123.3, 120.3, 118.8, 109.9, 67.9, 52.2, 30.4.

FT-IR (neat) 2964, 1483, 1455, 1340, 1238, 1147, 1088 cm^{-1}.

MS (ESI) *m*/*z* (M^+) calcd for $C_{17}H_{17}NO$: 251, found: 251.

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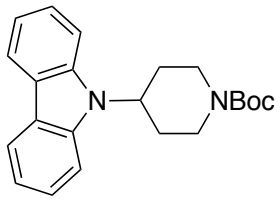
(2) Kitawaki, T.; Hayashi, Y.; Ueno. A.; Chida, N. *Tetrahedron* **2006**, *62*, 6792–6801.



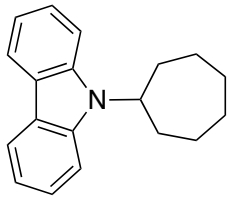
***tert*-Butyl 4-(9*H*-carbazol-9-yl)piperidine-1-carboxylate (Table 2, entry 3).** Purified by chromatography (10% EtOAc/hexanes). Colorless solid. Run 1: 215 mg (61%). Run 2: 215 (61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, 2H, *J* = 7.5 Hz), 7.51 (d, 2H, *J* = 8.5 Hz), 7.44 (dt, 2H, *J* = 1.5, 7.5 Hz), 7.23 (td, 2H, *J* = 1.0, 8.5 Hz), 4.64 (tt, 1H, *J* = 4.5, 12.5 Hz), 4.40 (d, 2H, *J* = 11.5 Hz), 2.96 (t, 2H, *J* = 14.5 Hz), 2.60 (td, 2H, *J* = 5.0, 12.5 Hz), 1.92 (d, 2H, *J* = 11.5 Hz), 1.54 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 139.2, 125.3, 123.2, 120.2, 118.7, 109.8, 79.8, 53.3, 43.8, 29.4, 28.3.

FT-IR (neat) 2974, 1696, 1482, 1453, 1419, 1241, 1157, 1133 cm^{-1}.

MS (ESI) *m*/*z* (M^+) calcd for $C_{22}H_{26}N_2O_2$: 350, found: 350.



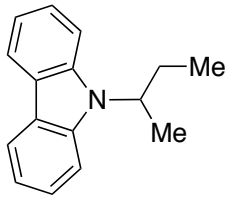
9-Cycloheptyl-9*H*-carbazole (Table 2, entry 4). Purified by chromatography (hexanes). Colorless solid. Run 1: 179 mg (68%). Run 2: 187 (71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, 2H, *J* = 1.0, 8.0 Hz), 7.51 (d, 2H, *J* = 8.0 Hz), 7.43 (td, 2H, *J* = 1.0, 8.0 Hz), 7.21 (d, 2H, *J* = 8.0 Hz), 4.68 (tt, 1H, *J* = 4.5, 11.0 Hz), 2.52–2.44 (m, 2H), 2.09–2.04 (m, 2H), 1.95–1.89 (m, 2H), 1.84–1.76 (m, 2H), 1.74–1.64 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 125.2, 123.1, 120.2, 118.4, 109.8, 57.3, 33.1, 27.8, 26.4.

FT-IR (neat) 2919, 1482, 1451, 1328, 1224 cm^{-1}.

MS (ESI) *m*/*z* (M^+) calcd for $C_{19}H_{21}N$: 263, found: 263.



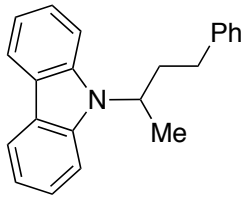
9-(*sec*-Butyl)-9*H*-carbazole (Table 2, entry 5). Purified by chromatography (hexanes). Colorless solid. Run 1: 151 mg (68%). Run 2: 153 (69%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, 2H, *J* = 7.5 Hz), 7.51 (d, 2H, *J* = 8.5 Hz), 7.43 (t, 2H, *J* = 7.5 Hz), 7.22 (t, 2H, *J* = 7.5 Hz), 4.73–4.66 (m, 1H), 2.36–2.27 (m, 1H), 2.06–1.98 (m, 1H), 1.69 (d, 3H, *J* = 7.0 Hz), 0.80 (t, 3H, *J* = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 125.3, 120.3, 118.5, 110.0, 52.9, 28.1, 19.1, 11.6.2.

FT-IR (neat) 2966, 1594, 1482, 1453, 1332, 1317, 1236, 1223, 1154 cm^{-1}.

MS (ESI) *m*/*z* (M^+) calcd for $C_{16}H_{17}N$: 223, found: 223.



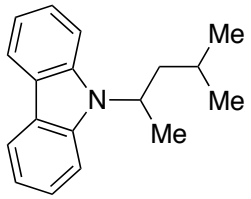
9-(4-Phenylbutan-2-yl)-9*H*-carbazole (Table 2, entry 6). Purified by chromatography (hexanes). Light-yellow oil. Run 1: 231 mg (77%). Run 2: 249 mg (83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, 2H, *J* = 8.0 Hz), 7.43 (t, 2H, *J* = 7.0 Hz), 7.26–7.21 (m, 6H), 7.18–7.14 (m, 1H), 7.02 (d, 2H, *J* = 7.0 Hz), 4.82–4.75 (m, 1H), 2.74–2.57 (m, 1H), 2.55–2.41 (m, 2H), 2.34–2.27 (m, 1H), 1.69 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 128.3, 125.9, 125.3, 120.3, 118.6, 110.1, 50.5, 36.5, 32.9, 19.2.

FT-IR (neat) 2929, 1594, 1482, 1453, 1332, 1225, 1158 cm^{-1}.

MS (ESI) *m*/*z* (M^+) calcd for $C_{22}H_{21}N$: 299, found: 299.



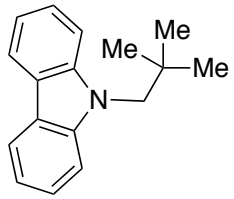
9-(4-Methylpentan-2-yl)-9*H*-carbazole (Table 2, entry 7). Purified by chromatography (hexanes). Colorless solid. Run 1: 160 mg (64%). Run 2: 158 (63%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, 2H, *J* = 8.0 Hz), 7.50 (br s, 2H), 7.44 (t, 2H, *J* = 7.5 Hz), 7.22 (d, 2H, *J* = 8.0 Hz), 4.92–4.85 (m, 1H), 2.36–2.30 (m, 1H), 1.79–1.73 (m, 1H), 1.65 (d, 3H, *J* = 7.0 Hz), 1.39–1.31 (m, 1H), 0.93 (d, 3H, *J* = 7.0 Hz), 0.82 (d, 3H, *J* = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 125.3, 122.7, 120.3, 118.5, 110.0, 49.2, 43.9, 25.3, 23.0, 22.4, 19.5.

FT-IR (neat) 2953, 2359, 1653, 1559, 1482, 1453, 1330, 1221 cm^{-1}.

MS (ESI) *m*/*z* (M^+) calcd for $C_{18}H_{21}N$: 251, found: 251.



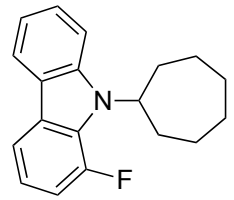
9-Neopentyl-9*H*-carbazole (Table 2, entry 8). Purified by chromatography (hexanes). Colorless solid. Run 1: 146 mg (61%). Run 2: 146 (61%).[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, 2H, J = 7.5 Hz), 7.47–7.42 (m, 4H), 7.26–7.22 (td, 2H, J = 1.5, 8.0 Hz), 4.11 (s, 2H), 1.11 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 125.3, 122.9, 120.0, 118.8, 109.9, 54.8, 35.8, 29.1.

FT-IR (neat) 2952, 1482, 1457, 1327, 1240, 1188 cm^{-1}.

MS (ESI) m/z (M^+) calcd for $C_{17}H_{19}N$: 237, found: 237.



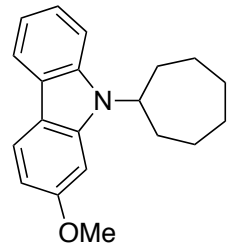
9-Cycloheptyl-1-fluoro-9*H*-carbazole (Table 3, entry 1). Performed on 0.50 mmol of the carbazole. Purified by chromatography (hexanes → 40:1 hexanes/EtOAc). Colorless oil. Run 1: 58 mg (41%). Run 2: 68 mg (48%).

^{1}H NMR (400 MHz, C_6D_6; 343 K) δ 7.98 (d, 1H, J = 7.8 Hz), 7.74 (d, 1H, J = 7.7 Hz), 7.43–7.32 (m, 2H), 7.18 (d, 1H, J = 7.8 Hz), 7.06 (dd, 1H, J = 13.6, 7.9 Hz), 6.95 (td, 1H, J = 7.8, 4.3 Hz), 4.96 (br s, 1H), 2.35–2.25 (m, 2H), 1.90–1.78 (m, 2H), 1.66–1.37 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$; 343 K) δ 125.8, 120.4, 119.1, 118.9 (d, J_{CF} = 6.9 Hz), 115.8, 111.7 (d, J_{CF} = 21 Hz), 33.5, 27.5, 26.1.

FT-IR (neat) 3057, 2926, 2856, 1632, 1601, 1575, 1500, 1455, 1434, 1330, 1241, 1220, 1158, 1100, 1064, 785, 741 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{19}H_{21}FN$ (M+H): 282.2, found 282.2.



9-Cycloheptyl-2-methoxy-9*H*-carbazole (Table 3, entry 2). Performed on 0.44 mmol of the carbazole. Purified by chromatography (0.5% Et_2O/hexanes). Light-yellow oil. Run 1: 93 mg (72%). Run 2: 94 mg (73%).

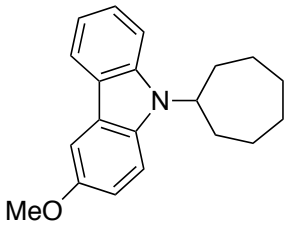
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, 1H, J = 7.5 Hz), 7.97 (d, 1H, J = 8.5 Hz), 7.46 (d, 1H, J = 8.0 Hz), 7.36 (t, 1H, J = 8.0 Hz), 7.18 (d, 1H, J = 7.5 Hz), 6.98 (br s, 1H), 6.83 (dd, 1H, J = 2.5, 8.5

Hz), 4.64–4.56 (m, 1H), 3.95 (s, 3H), 2.49–2.42 (m, 2H), 2.09–2.04 (m, 2H), 1.94–1.88 (m, 2H), 1.82–1.65 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 124.0, 120.9, 119.4, 118.6, 106.2, 57.3, 55.8, 32.9, 27.8, 26.5.

FT-IR (neat) 2924, 2855, 1628, 1599, 1497, 1462, 1345, 1205, 1121, 1039 cm^{-1}.

MS (ESI) *m*/*z* (M^+) calcd for $C_{20}H_{23}NO$: 293, found: 293.



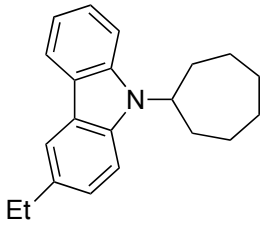
9-Cycloheptyl-3-methoxy-9*H*-carbazole (Table 3, entry 3). Purified by chromatography (0.5% Et_2O/hexanes). Light-yellow oil. Run 1: 161 mg (55%). Run 2: 186 mg (63%).

H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, 1H, *J* = 8.0 Hz), 7.58 (d, 1H, *J* = 7.5 Hz), 7.47 (d, 1H, *J* = 8.5 Hz), 7.43–7.39 (m, 2H), 7.17 (td, 1H, *J* = 1.0, 8.0 Hz), 7.07 (dd, 1H, *J* = 2.5, 9.0 Hz), 4.62 (tt, 1H, *J* = 4.0, 11.0 Hz), 3.93 (s, 3H), 2.48–2.40 (m, 2H), 2.08–2.02 (m, 2H), 1.93–1.87 (m, 2H), 1.83–1.63 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 125.2, 120.2, 117.9, 114.5, 103.1, 57.4, 56.1, 33.2, 27.7, 26.4.

FT-IR (neat) 2933, 1482, 1453, 1328, 1219, 1103, 1060 cm^{-1}.

MS (ESI) *m*/*z* (M^+) calcd for $C_{20}H_{23}NO$: 293, found: 293.



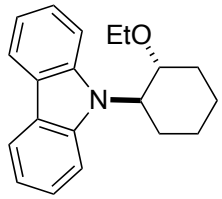
9-Cycloheptyl-3-ethyl-9*H*-carbazole (Table 3, entry 4). Purified by chromatography (hexanes). Colorless oil. Run 1: 201 mg (69%). Run 2: 189 mg (65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, 1H, *J* = 8.0 Hz), 7.92 (s, 1H), 7.47 (d, 1H, *J* = 8.5 Hz), 7.44–7.39 (m, 2H), 7.28 (dd, 1H, *J* = 3.0, 8.0 Hz), 7.18 (t, 1H, *J* = 8.0 Hz), 4.65 (tt, 1H, *J* = 4.0, 11.0 Hz), 2.83 (q, 2H, *J* = 7.5 Hz), 2.49–2.42 (m, 2H), 2.08–2.03 (m, 2H), 1.94–1.87 (m, 2H), 1.82–1.64 (m, 6H), 1.34 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 134.2, 125.3, 124.8, 119.9, 118.8, 117.9, 109.6, 65.6, 57.1, 32.8, 28.6, 27.5, 26.2, 16.3, 15.0.

FT-IR (neat) 3368, 2925, 2855, 1487, 1458, 1332, 1225, 1153, 1060 cm^{-1}.

MS (ESI) *m*/*z* (M^+) calcd for $C_{21}H_{25}N$: 291, found: 291.



9-(2-Ethoxycyclohexyl)-9*H*-carbazole (eq 4). Purified by chromatography (0.5% Et_2O/hexanes). Yellow solid. Run 1: 166 mg (57%). Run 2: 159 mg (54%).

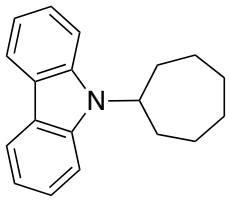
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, 2H, J = 7.5 Hz), 7.58 (br s, 2H), 7.47 (t, 2H, J = 7.5 Hz), 7.21 (td, 2H, J = 1.0, 7.5 Hz), 4.43 (td, 1H, J = 4.5, 13.0 Hz), 4.15–4.10 (m, 1H), 3.16–3.10 (m, 1H), 2.68–2.62 (m, 1H), 2.52–2.48 (m, 2H), 2.32–2.28 (m, 1H), 2.00–1.92 (m, 2H), 1.52–1.47 (m, 3H), 0.54 (t, 3H, J = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 125.1, 119.9, 118.5, 111.5, 109.0, 77.4, 65.4, 60.5, 33.3, 29.7, 25.7, 24.7, 15.4.

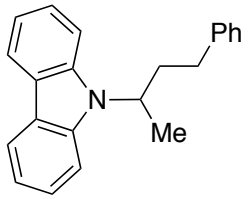
FT-IR (neat) 2924, 2854, 1487, 1459, 1323, 1288, 1204, 1171, 1060 cm^{-1}.

MS (ESI) m/z (M^+) calcd for $C_{20}H_{23}NO$: 293, found: 293.

General Procedure (Bromides). Carbazole (167 mg, 1.00 mmol), LiO*t*-Bu (120 mg, 1.50 mmol), and CuI (19.1 mg, 0.10 mmol) were added to a 20-mL borosilicate vial that contained a stir bar. The vial was capped with a PTFE-lined septum cap, the joint was wrapped with electrical tape, and the vial was evacuated and backfilled with nitrogen (3 cycles). Acetonitrile (4.0 mL) and the alkyl iodide (1.50 mmol) were added in turn via syringe, and then the vial was detached from the nitrogen line, and the puncture holes of the septum were covered with vacuum grease. The resulting mixture was stirred vigorously for 5 min, and then the vial was suspended in a water-filled dewar. The stirred mixture (the vial was tilted to increase the exposure to light) was irradiated with a 100-watt Hg lamp, positioned 20 cm above the dewar, for 12 h (the water bath was maintained at 30 °C). Next, the mixture was concentrated, and the was dissolved in EtOAc and passed through a short pad of silica gel (eluant: EtOAc). The solvent was removed, and the residue was purified by chromatography.



9-Cycloheptyl-9*H*-carbazole (eq 5). Purified by chromatography (50:1 hexanes/benzene → 50:1:2.5 hexanes/benzene/EtOAc). White solid. Run 1: 154 mg (58%). Run 2: 165 mg (62%).



9-(4-Phenylbutan-2-yl)-9*H*-carbazole (eq 6). Purified by chromatography (hexanes → 20:1 hexanes/EtOAc). Viscous, pale-yellow oil. Run 1: 265 mg (89%). Run 2: 259 mg (86%).

IV. Synthesis and Characterization of [Cu(carbazolide)$_2$]Li

The yields have not been optimized.

Synthesis of [Cu(carbazolide)$_2$][Li(CH$_3$CN)$_4$] (4). This synthesis was performed in a nitrogen atmosphere in a glovebox. Lithium carbazolide (364 mg, 2.10 mmol), prepared by treatment of carbazole with *n*-butyllithium at –78 °C in Et_2O, was dissolved in acetonitrile (10 mL) and added to a suspension of CuI (200 mg, 1.05 mmol) in acetonitrile (1 mL) at room temperature. The resulting mixture, which darkened to a dark-green color due to the formation of a fine black precipitate, was stirred for 30 min, and then it was filtered through Celite, giving a bright orange-yellow filtrate.

This filtrate was concentrated to a viscous orange solid, which was dried under vacuum for 2 h. This material was then dissolved in benzene (1 mL), and pentane was added (2 mL) to precipitate a sticky yellow-white solid. The supernatant was then decanted from the sticky solid. This procedure (dissolve the solid in benzene, add pentane to precipitate a sticky mass, and then decant the supernatant) was repeated three times until the solid no longer dissolved in benzene, instead forming a free-flowing, off-white powder. This powder was isolated atop a sintered glass frit and washed with benzene (3 x 5 mL) and pentane (3 x 5 mL), giving the title compound (240 mg; 45%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.07 (d, 4H, *J* = 8 Hz), 7.86 (d, 4H, *J* = 8 Hz), 7.36 (t, 4H, *J* = 8 Hz), 7.06 (t, 4H, *J* = 8 Hz), 1.88 (s, 12H).

ESI-MS (negative ion mode) *m*/*z*: 395.2, 397.2 ([Cu(carbazolide)$_2$]$^-$).

Synthesis of [Cu(carbazolide)$_2$][Li(12-crown-4)$_2$] (5). This synthesis was performed in a nitrogen atmosphere in a glovebox. Lithium carbazolide (200 mg, 1.13 mmol), prepared by treatment of carbazole with *n*-butyllithium at –78 °C in Et_2O, was dissolved in acetonitrile (5 mL) and added to a suspension of CuI (107 mg, 0.56 mmol) in acetonitrile (1 mL) at room temperature. The resulting mixture, which darkened to a green-yellow color, was stirred for 30 min, and then it was filtered through Celite, giving a bright orange-yellow filtrate. 1,4,7,10-Tetraoxacyclododecane (12-crown-4; 200 mg, 1.13 mmol) was dissolved in acetonitrile (1 mL) and added to the filtrate while stirring, resulting in the immediate precipitation of [Cu(carbazolide)$_2$][Li(12-crown-4)$_2$] as a white solid. This solid was collected on a sintered glass frit and washed with acetonitrile (2 x 1 mL) and then with Et_2O (~5 mL x2), which provided 288 mg (68%) of the title complex. Crystals suitable for X-ray diffraction were grown by layering Et_2O over a saturated THF solution of **5** at room temperature.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.04 (d, 4H, *J* = 8 Hz), 7.87 (d, 4H, *J* = 8 Hz), 7.32 (t, 4H, *J* = 8 Hz), 6.99 (t, 4H, *J* = 8 Hz), 3.38 (s, 32H).

ESI-MS (negative ion mode) *m*/*z*: 395.2, 397.2 ($[Cu(carbazolide)_2]^-$).

Anal. Calcd for $C_{40}H_{48}N_2O_8CuLi$: C, 63.61; H, 6.41; N, 3.71. Found: C, 62.85; H, 6.42; N, 3.71.

X-ray diffraction studies were carried out at the Caltech Division of Chemistry and Chemical Engineering X-ray Crystallography Facility on a Bruker three-circle SMART diffractometer with a SMART 1K CCD detector. Data were collected at 100 K using Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[3] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 times the U_{eq} of the atoms to which they are bonded.

Table 1. Crystal data and structure refinement for **5**.

Empirical formula	C_{40} H_{48} Cu Li N_2 O_8	
Formula weight	755.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.5707(7) Å	a= 74.875(3)°.
	b = 11.7449(7) Å	b= 74.832(3)°.
	c = 14.2319(9) Å	g = 89.728(3)°.
Volume	1797.83(19) Å^3	
Z	2	
Density (calculated)	1.395 Mg/m^3	
Absorption coefficient	0.664 mm^{-1}	
F(000)	796	
Crystal size	0.31 x 0.18 x 0.04 mm^3	
Theta range for data collection	1.80 to 28.19°.	
Index ranges	-15<=h<=15, -15<=k<=15, -18<=l<=18	
Reflections collected	60607	
Independent reflections	8130 [R(int) = 0.0543]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9739 and 0.8205	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8130 / 0 / 469	
Goodness-of-fit on F^2	1.140	
Final R indices [I>2sigma(I)]	R1 = 0.0765, wR2 = 0.2213	
R indices (all data)	R1 = 0.0863, wR2 = 0.2262	
Largest diff. peak and hole	2.711 and -0.747 e*Å^{-3}	

(3) Sheldrick, G. M. *SHELXTL 2000*; Universität Göttingen: Göttingen, Germany, 2000.

V. Emission and Excitation Data

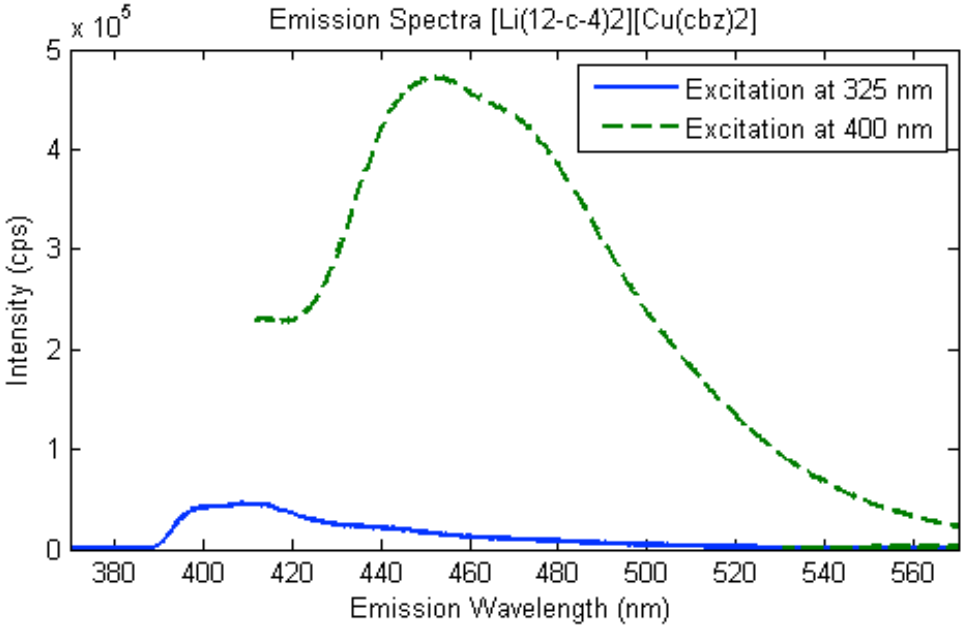


Figure 1. Additional emission data for copper complex **4**. Emission profiles for the two excitation wavelengths are to scale. The emission and excitation monochromator bandwidths are 2 nm.

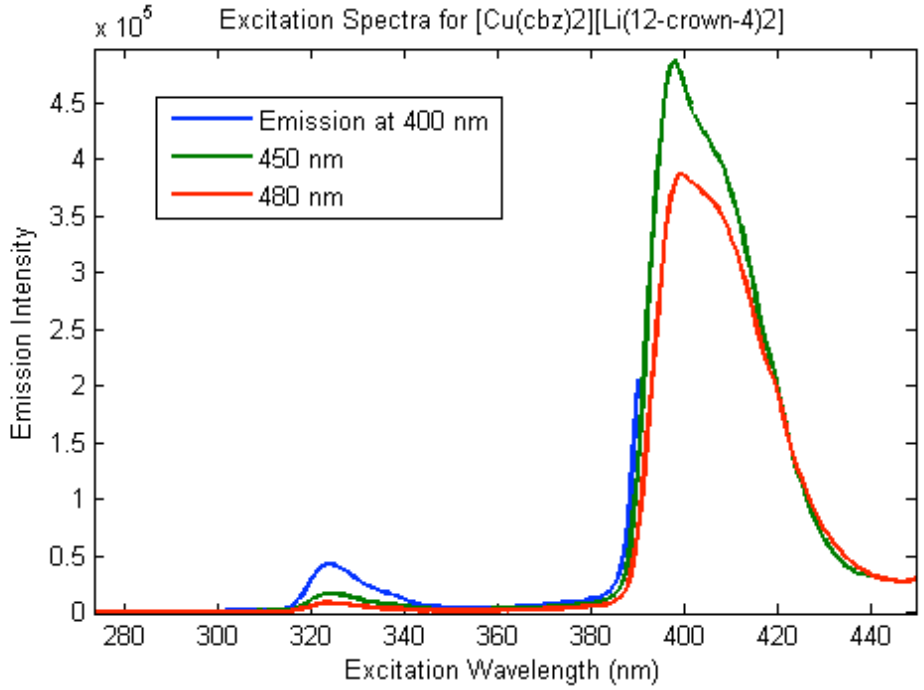


Figure 2. Additional excitation data for copper complex **4** (all traces to scale), monitoring different emission wavelengths. The emission and excitation monochromator bandwidths are 2 nm.

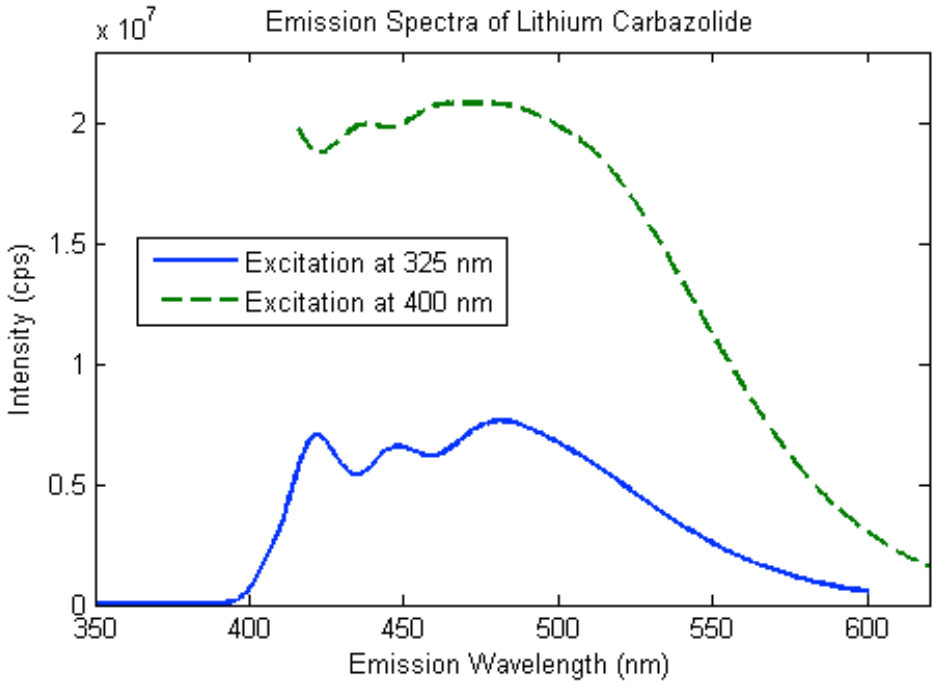


Figure 3. Emission spectra for lithium carbazolide in acetonitrile with different excitation wavelengths. The emission and excitation monochromator bandwidths are 5 nm.

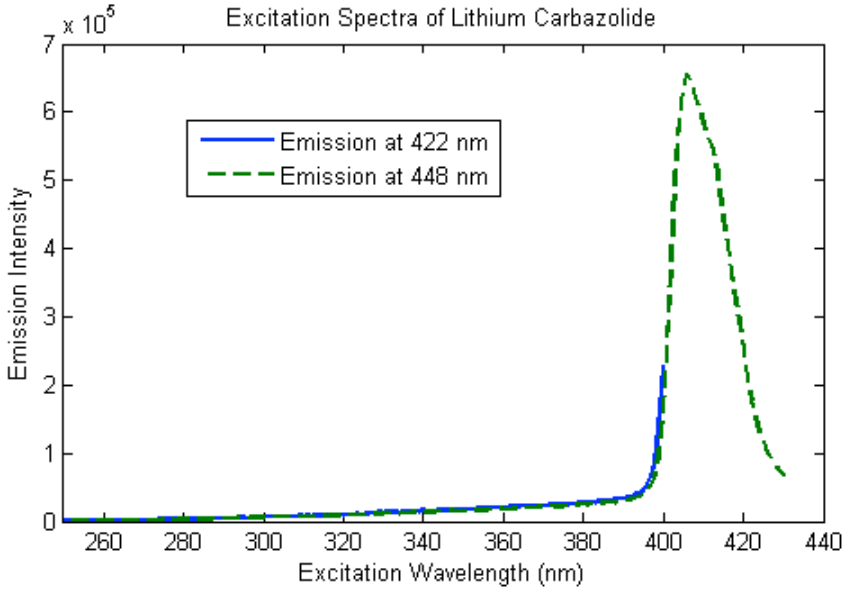
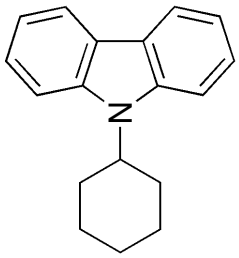


Figure 4. Excitation spectra for lithium carbazolide in acetonitrile with different emission wavelengths. The emission and excitation monochromator bandwidths are 5 nm.

VI. ^{1}H NMR Spectra

Table 2, entry 1



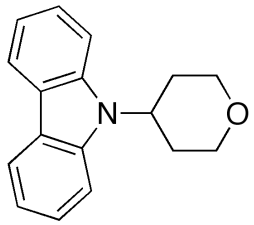
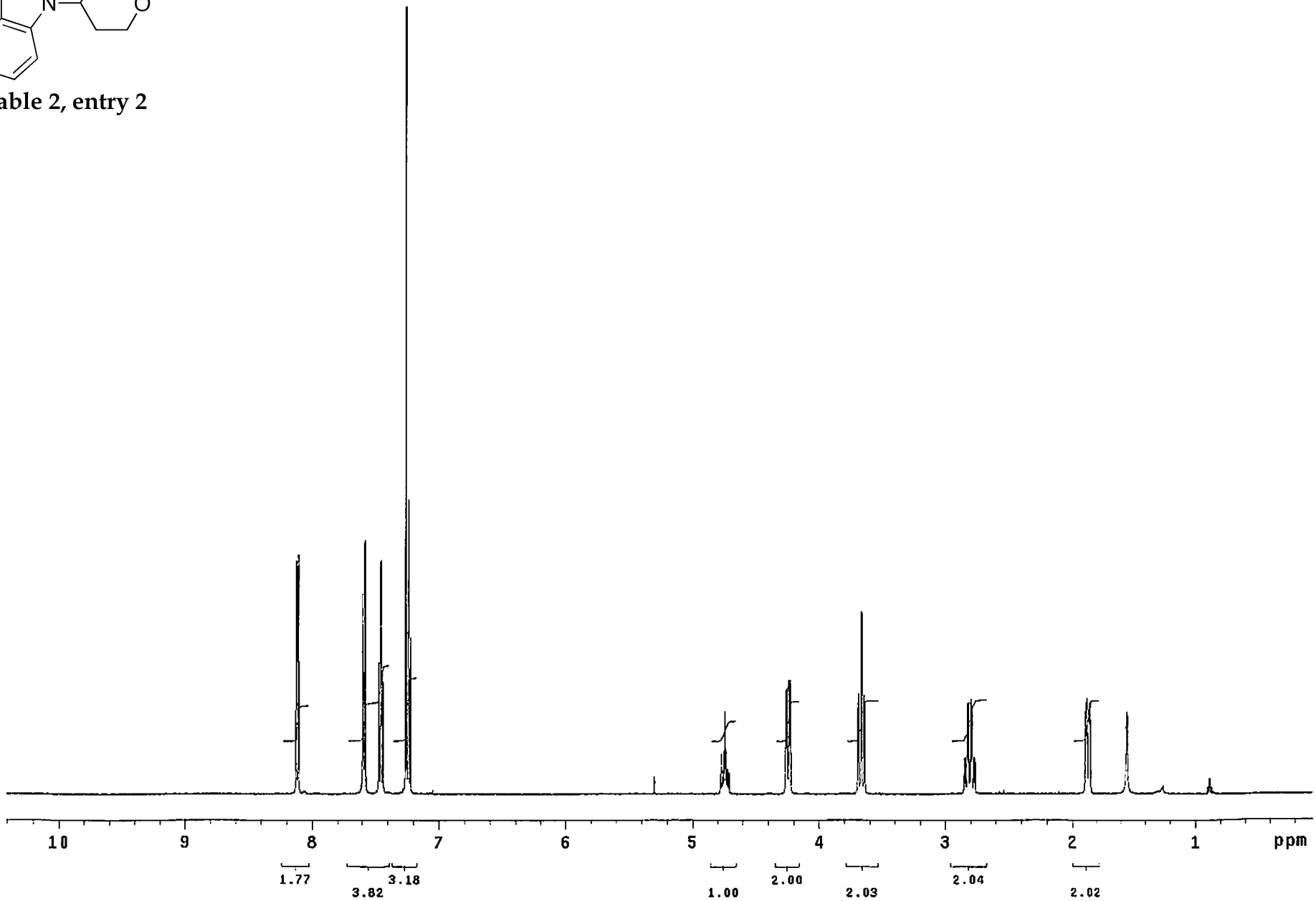
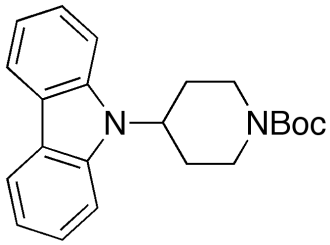


Table 2, entry 2





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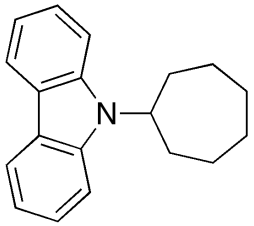

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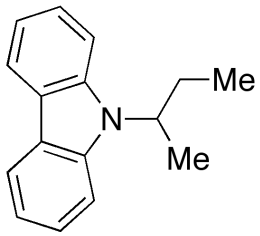

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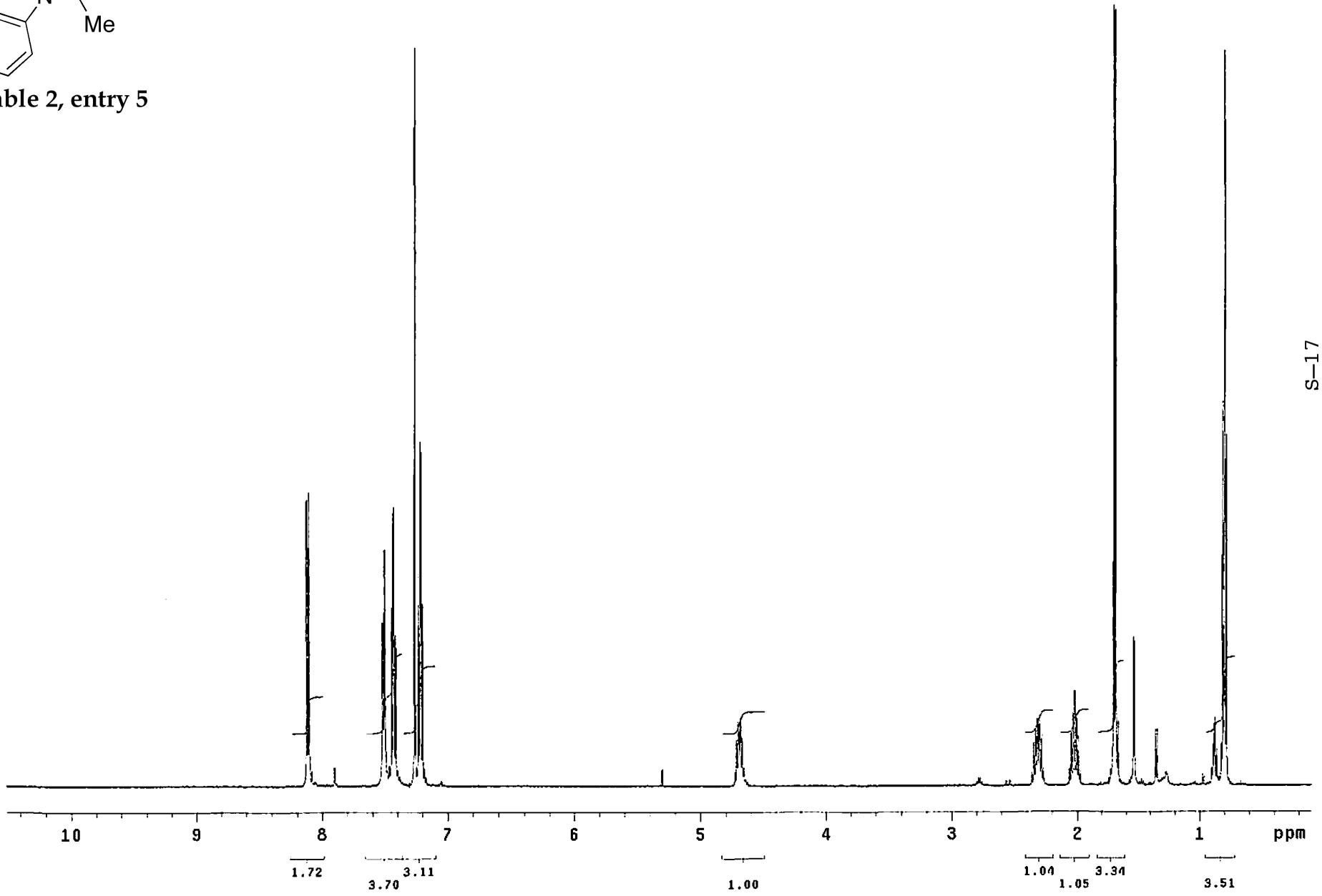

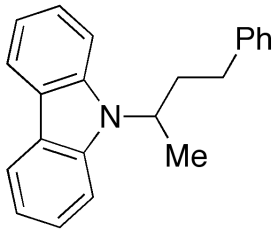

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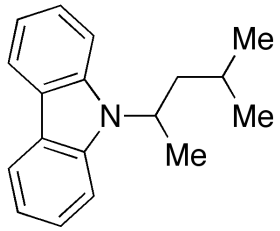

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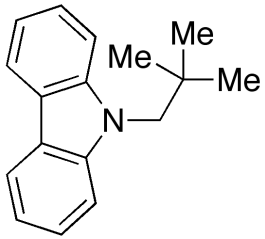
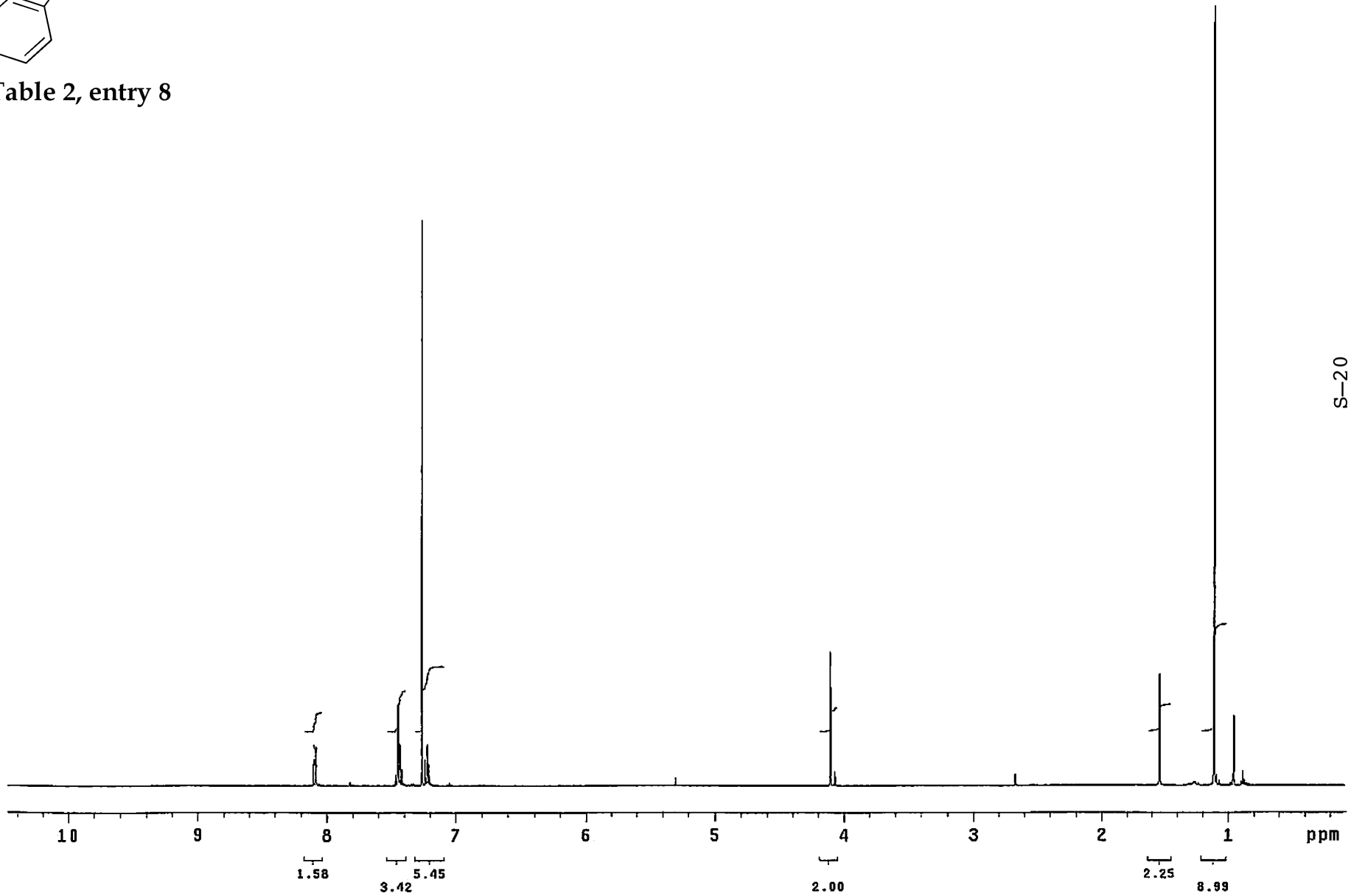


Table 2, entry 8



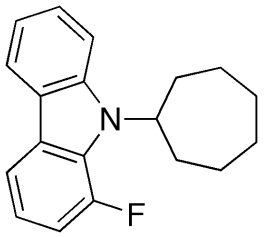
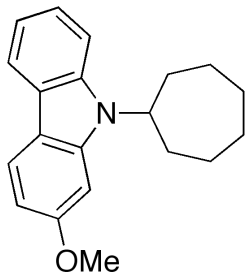


Table 3, entry 1



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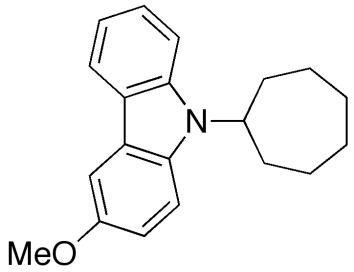

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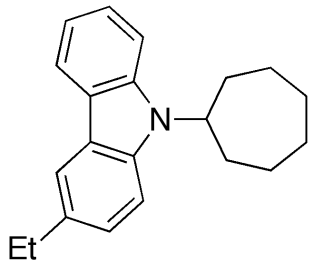
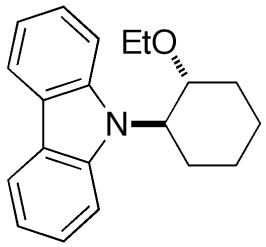


Table 3, entry 4


EtO
N

Equation 4

S-25
10
9
8
7
6
5
4
3
2
1
ppm
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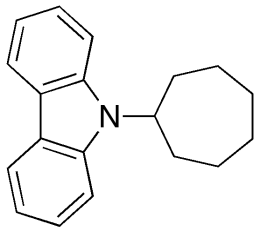
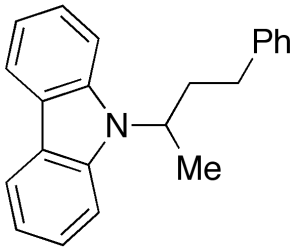
3.83
4.39
1.00
0.99
0.94
1.96
1.01
3.00
4.45
2.73



Equation 5



Equation 6