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Zhang, Zhang and Liebeskind

Supplementary Material

The Room Temperature Ullmann

**Supplementary Material to****Ambient Temperature, Ullmann-like Reductive Coupling of Aryl, Heteroaryl, and Alkenyl Halides.**

by Shijie Zhang, Dawei Zhang and Lanny S. Liebeskind\*

**General Methods**

THF, CH<sub>3</sub>CN and Et<sub>3</sub>N were dried over 4Å molecular sieves. Anhydrous DMF and NMP were obtained from Aldrich in Sure-Seal bottles and were used without further drying. Purification by flash chromatography was performed using 32-63 μm SiO<sub>2</sub> with compressed air as a source of positive pressure. Analytical thin-layer chromatography (TLC) was performed using Merck Kieselgel 60F<sub>254</sub> and EM Science 60F<sub>254</sub> (type E) aluminum oxide plates with visualization by UV, phosphomolybdic acid or iodine stain. Melting points were obtained from recrystallized samples or samples which crystallized during concentration of the chromatography eluents; <sup>1</sup>H NMR spectra were recorded at 300 MHz and were internally referenced to CHCl<sub>3</sub> (7.26 ppm); <sup>13</sup>C NMR spectra were recorded at 75 MHz and were referenced to CDCl<sub>3</sub> (77.0 ppm) or DMSO-d<sub>6</sub> (39.7 ppm).

**Starting Materials**

Cu<sub>2</sub>O, thiophene-2-carboxylic acid, CuCl, CuBr, CuI, 1-bromo-2-nitrobenzene, 1-iodo-2-nitrobenzene, 2-iodoaniline, 2-iodoanisole, 2-iodobenzoyl chloride, 2-iodobenzyl alcohol, 2-iodobenzyl chloride, 6-iodo-2-picolin-5-ol, 2-iodothiophene, Lawesson's reagent, N,N-dimethyl carbamyl chloride, 5,5-dimethyl-1,3-cyclohexanedione, 3,4,5-trimethoxyaniline were purchased from Aldrich and used as received. Methyl 2-chlorobenzoate, methyl 2-bromobenzoate, methyl 2-iodobenzoate, 2-iodophenol, and 2-iodophenylacetonitrile were purchased from Lancaster. 2-Iodoacetanilide,<sup>1</sup> 2-iodoindole,<sup>2</sup> (*E*)- and (*Z*)-β-iodostyrene,<sup>3,4</sup>

and 3-iodo-5,5-dimethyl-2-cyclohexene-1-one,<sup>5</sup> and (*E*)-1-iodo-1-octene<sup>6</sup> were prepared according to published procedures.

### **Preparation of Copper(I) Thiophene-2-carboxylate (CuTC).**

A 500 mL round-bottomed flask was charged with thiophene-2-carboxylic acid (100 g, 780 mmol, 4 equiv), Cu<sub>2</sub>O (28 g, 196 mmol, 1 equiv) and toluene (300 mL). The flask was outfitted with a Dean-Stark trap, condenser, and magnetic stirring bar and the mixture was brought to reflux under dry N<sub>2</sub> and stirred overnight with azeotropic removal of water. The yellow/brown suspension was cooled to 60 °C and the product was collected on a medium porosity sintered-glass filter funnel. Under a stream of dry nitrogen, the filter cake was washed with de-oxygenated methanol (300 mL) then ether until the eluant was colorless, and then with a small amount of hexanes. The product was dried on the filter under a flow of nitrogen (20 min), then transferred to a flask and dried in vacuo. The product was obtained as a tan, air-stable powder that was ground with a mortar and pestle to produce a finely divided powder (69.8 g, 94%). Elemental analysis was consistent with the existence of ~5 mol % unreacted copper(I) oxide which does not affect use. NMR analysis (d<sub>6</sub>-DMSO) was uninformative because of broad signals. IR (KBr pellet, cm<sup>-1</sup>) 3096 (w), 1600 (s), 1424 (s), 1389 (s). Anal. Calcd for C<sub>5</sub>H<sub>3</sub>O<sub>2</sub>CuS(Cu<sub>2</sub>O)<sub>0.05</sub>: C, 30.40; H, 1.50; S, 16.20. Found: C, 30.35; H, 1.55; S, 16.11.

**Notes on CuTC:** The color of the product varies from yellow to tan depending on the grade of copper(I) oxide used. However, CuTC prepared from low-grade (96.4 %, Aldrich) copper oxide was equally effective as that prepared from high-grade (99.5 %, Alfa). Grinding the product using a mortar and pestle produced CuTC with higher activity. CuTC is somewhat air-sensitive while wetted by solvent, thus it is helpful to perform the filtration and washings under nitrogen. An inverted funnel with a stream of nitrogen flowing through it placed over the fritted glass funnel is sufficient. Extensive washing with ether is necessary to remove all Cu(II). It is helpful to stir the filter cake with a stirring rod occasionally during the washings.

Once the product is dry it can be stored and handled at room temperature without any special precautions.

### **Preparation of Aromatic Substrates.**

**N,N-Dimethyl 2-iodothiobenzamide.** This compound was prepared by a modification of a literature procedure.<sup>7</sup> Triethylamine (2.53 g, 25.00 mmol, 2.50 equiv) was added dropwise to a flask charged with 2-iodobenzoyl chloride (2.67 g, 10.00 mmol, 1.00 equiv) and Me<sub>2</sub>NH•HCl (0.98 g, 12.00 mmol, 1.20 equiv) in 50 mL CH<sub>2</sub>Cl<sub>2</sub> at 0 °C. After 2 h, the reaction mixture was washed with H<sub>2</sub>O (1 x 50 mL) and the aqueous layer was back extracted with ether (1 x 50 mL). The combined organic layers were dried (MgSO<sub>4</sub>) and evaporated to give 2.75 g of N,N-dimethyl-2-iodobenzamide as a white solid. The solid was dissolved in 50 mL of toluene and Lawesson's reagent (2.43 g, 6.00 mmol, 0.60 equiv) was added. After 15 h at 80 °C solvent was removed leaving a crude product that was purified by flash chromatography to yield N,N-dimethyl-2-iodothiobenzamide<sup>7</sup> (2.50 g, 8.59 mmol, 86%) as a light yellow solid. TLC (SiO<sub>2</sub>, 30% EtOAc in hexane, R<sub>f</sub> = 0.32); chromatographic purification (Flash column, SiO<sub>2</sub>, 2 x 25 mm, 600 mL of 30% CH<sub>2</sub>Cl<sub>2</sub>/hexane to remove the by-product with an R<sub>f</sub> value of 0.28 then 30% EtOAc/20% CH<sub>2</sub>Cl<sub>2</sub>/hexane to elute the desired product); mp 109.0-111.0 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>) 3046 (w), 2976 (w), 2939 (w), 1522 (s), 1461 (w), 1397 (m), 1294 (m), 1267 (s), 1145 (m), 993 (w); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.74 (d, J = 7.8 Hz, 1 H), 7.32 (dt, J = 7.5, 0.9 Hz, 1 H), 7.22 (dd, J = 7.5, 1.5 Hz, 1 H), 6.94 (dt, J = 7.5, 1.5 Hz, 1 H), 3.57 (s, 3 H), 3.07 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 200.1, 147.8, 139.0, 129.1, 128.5, 126.3, 92.2, 43.1, 42.2. Anal. Calcd for C<sub>9</sub>H<sub>10</sub>INS: C, 37.13; H, 3.46; I, 43.59; N, 4.81; S, 11.01. Found: C, 37.24; H, 3.46; I, 43.65; N, 4.73.

**N-Methyl-2-iodoacetanilide.** Lithium hexamethyldisilazide (12 mL, 1.0 M in THF, 12.00 mmol, 1.20 equiv) was added dropwise via syringe to a stirred solution of 2-iodoacetanilide (2.61 g, 10.00 mmol, 1.00 equiv) in 30 mL THF at -78 °C. After 20 min at -78 °C, MeI (1.70 g, 12.00 mmol, 1.20 equiv) was added via syringe, the cooling bath was removed, and the

reaction mixture was kept at room temperature overnight. The usual workup and purification by flash chromatography gave N-methyl-2-iodoacetanilide as a light brown solid (2.64 g, 9.60 mmol, 96%). TLC (SiO<sub>2</sub>, 30% EtOAc/hexane, R<sub>f</sub> = 0.10); chromatographic purification (Flash column, SiO<sub>2</sub>, 2 x 15 mm, 1st: 10% EtOAc/hexane 200 mL; 2nd: EtOAc); mp 62.0-64.0 °C (*mp not reported in lit.*<sup>1</sup>); IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>) 3053 (w), 2985 (w), 1663 (s), 1580 (w), 1472 (m), 1421 (m), 1382 (m), 1303 (w), 1269 (m); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.84 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.35 (dt, *J* = 7.8, 1.2 Hz, 1 H), 7.20 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.00 (dt, *J* = 7.5, 1.5 Hz, 1 H), 3.08 (s, 3 H), 1.70 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 169.9, 146.4, 140.0, 129.9, 129.6, 128.6, 99.3, 35.6, 22.3. Anal. Calcd for C<sub>9</sub>H<sub>10</sub>INO: C, 39.30; H, 3.66; I, 46.13; N, 5.09. Found: C, 39.25; H, 3.65; N, 5.01.

**N-(Trifluoroacetyl)-2-iodoaniline.** Trifluoroacetic anhydride (1.26 g, 6.00 mmol, 1.20 equiv) was added slowly via syringe to a 50 mL round-bottomed flask charged with 2-iodoaniline (1.10 g, 5.02 mmol, 1.00 equiv), K<sub>2</sub>CO<sub>3</sub> (3.46 g, 25.00 mmol, 4.98 equiv) and 30 mL ether at 0 °C. The reaction mixture was kept at 0 °C for 1 h, and then quenched with H<sub>2</sub>O (50 mL) and diluted with diethyl ether (50 mL). The organic layer was separated from the aqueous layer, and the later was extracted with 50 mL ether. The combined ether layers were dried (MgSO<sub>4</sub>), concentrated, and the solid purified by flash chromatography to give N-trifluoroacetyl-2-iodoaniline as an off-white solid (1.50 g, 4.76 mmol, 95%). TLC (SiO<sub>2</sub>, 30% EtOAc in hexane, R<sub>f</sub> = 0.32); chromatographic purification (Flash column, SiO<sub>2</sub>, 2 x 15 mm, 10% EtOAc in hexane); mp 104.0-106.0 °C (*lit.*<sup>8</sup> *mp* 102 °C); IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>) 3364 (br, m), 3057 (w), 2987 (w), 1742 (s), 1590 (m), 1540 (m), 1462 (w), 1440 (m), 1281 (m), 1197 (m), 1168 (m), 1152 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.29 (br s, 1 H), 8.20 (d, *J* = 8.4 Hz, 1 H), 7.84 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.41 (t, *J* = 7.8 Hz, 1 H), 6.98 (dt, *J* = 7.8, 1.2 Hz, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 154.7 (q, 37.9 Hz), 139.1, 135.6, 129.5, 127.8, 122.1, 115.6 (q, 289.0 Hz), 90.3. Anal. Calcd for C<sub>8</sub>H<sub>5</sub>F<sub>3</sub>INO: C, 30.50; H, 1.60; F, 18.09; I, 40.28; N, 4.45. Found: C, 30.35; H, 1.59; I, 40.21; N, 4.40.

**3,4,5-Trimethoxyacetanilide.** Acetic anhydride (4.59 g, 45.00 mmol, 1.50 equiv) was added slowly to a flask charged with 3,4,5-trimethoxyaniline (5.50 g, 30.02 mmol, 1.00 equiv),  $K_2CO_3$  (12.44 g, 90.01 mmol, 3.00 equiv) and  $CH_2Cl_2$  (80 mL) at rt. The mixture was stirred for 1.5 h, diluted with EtOAc (500 mL), and the solution was filtered through a plug of silica gel.

Evaporation of solvent gave a crude product which was washed with 50% ether in hexane (10 mL) to yield 3,4,5-trimethoxyacetanilide (6.535 g, 29.01 mmol, 97%) as a white solid. TLC ( $SiO_2$ , EtOAc,  $R_f = 0.32$ ); mp 110.0-112.0 °C (*lit.*<sup>9</sup> mp 128-139 °C); IR ( $CH_2Cl_2$ , KCl,  $cm^{-1}$ ) 3435 (m), 3338 (br, w), 3063 (w), 3008 (w), 2968 (w), 2942 (w), 2833 (w), 1690 (s), 1607 (s), 1527 (m), 1508 (s), 1464 (m), 1452 (m), 1410 (s), 1300 (w), 1234 (s), 1133 (s), 1020 (w), 1004 (w);  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.20 (br s, 1 H), 6.80 (s, 2 H), 3.83 (s, 6 H), 3.81 (s, 3 H), 2.16 (s, 3 H);  $^{13}C$  NMR ( $(CD_3)_2SO$ , 75.5 MHz)  $\delta$  168.7, 153.0, 136.0, 133.6, 97.2, 60.5, 56.0, 24.4. Anal. Calcd for  $C_{11}H_{15}NO_4$ : C, 58.66; H, 6.71; N, 6.22. Found: C, 58.81; H, 6.72; N, 6.15.

**2-Iodo-3,4,5-trimethoxyacetanilide.** This compound was prepared by a standard iodination method.<sup>10</sup> Silver trifluoroacetate (3.31 g, 15.00 mmol, 3.00 equiv) was ground with a mortar and pestle and added in three portions to a flask charged with N-acetyl-3,4,5-trimethoxyaniline (1.13 g, 5.00 mmol, 1.00 equiv) and iodine (1.27 g, 5.00 mmol, 1.00 equiv) in chloroform (150 mL). The red color disappeared within 30 min of addition of  $CF_3COOAg$ .  $K_2CO_3$  (3 g) was then added and the mixture was stirred for 30 min. The mixture was filtered and evaporation of the solvent gave a dark brown viscous oil which was purified by chromatography to yield 2-iodo-3,4,5-trimethoxyacetanilide (1.46 g, 4.16 mmol, 83%) as an off-white solid. TLC ( $SiO_2$ , EtOAc,  $R_f = 0.50$ ); chromatographic purification (Flash column,  $SiO_2$ , 2 x 15 mm, 1:1:1 of EtOAc/ $CH_2Cl_2$ /hexane); mp 123.5-124.5 °C; IR ( $CH_2Cl_2$ , KCl,  $cm^{-1}$ ) 3391 (br, m), 3050 (w), 3008 (w), 2975 (w), 2942 (w), 2855 (w), 2831 (w), 1700 (s), 1580 (s), 1512 (s), 1475 (m), 1465 (w), 1448 (m), 1424 (w), 1390 (s), 1344 (w), 1235 (m), 1202 (w), 1108 (s);  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.86 (s, 1 H), 7.49 (br s, 1 H), 3.88 (s, 3 H), 3.88 (s, 3 H), 3.84 (s, 3 H), 2.23 (s, 3 H);  $^{13}C$  NMR ( $CDCl_3$ , 75.5 MHz)  $\delta$  168.3, 153.8, 152.6,

138.7, 134.4, 101.9, 101.8, 60.9, 60.7, 56.0, 24.7. Anal. Calcd for  $C_{11}H_{14}INO_4$ : C, 37.63; H, 4.02; I, 36.14; N, 3.99. Found: C, 37.67; H, 4.01; I, 36.10; N, 4.01.

**2-Iodophenyl-N,N-dimethyl carbamate.**<sup>11</sup> A flask charged with NaH (0.22 g, 9.00 mmol, 1.50 equiv) in THF (20 mL) was cooled to 0 °C, and 2-iodophenol (1.32 g, 6.00 mmol, 1.00 equiv) dissolved in THF (10 mL) was added slowly. After 1 h at rt, dimethylcarbamyl chloride (0.68 g, 6.30 mmol, 1.05 equiv) was added dropwise and stirred for 5 h. The reaction mixture was quenched with satd  $NaHCO_3$  (20 mL) and after the usual workup and flash chromatography 2-iodophenyl-N,N-dimethyl carbamate was isolated as a colorless viscous oil (1.31 g, 4.50 mmol, 75%): TLC ( $SiO_2$ , 30% EtOAc/hexane,  $R_f$  = 0.44); chromatographic purification (Flash column,  $SiO_2$ , 2 x 15 mm, 10% EtOAc/hexane); IR ( $CH_2Cl_2$ , KCl,  $cm^{-1}$ ) 3063 (w), 3052 (w), 2941 (w), 1728 (s), 1466 (m), 1388 (s), 1265 (m), 1218 (s), 1164 (s);  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.78 (dd,  $J$  = 7.8, 1.5 Hz, 1 H), 7.33 (dt,  $J$  = 7.8, 1.2 Hz, 1 H), 7.18 (dd,  $J$  = 8.1, 1.5 Hz, 1 H), 6.91 (app t,  $J$  = 7.5 Hz, 1 H), 3.16 (s, 3 H), 3.01 (s, 3 H);  $^{13}C$  NMR ( $CDCl_3$ , 75.5 MHz)  $\delta$  153.4, 151.4, 138.8, 129.0, 126.8, 123.2, 90.6, 36.6, 36.5. Anal. Calcd for  $C_9H_{10}NIO_2$ : C, 37.14; H, 3.46; N, 4.81; I, 43.60. Found: C, 37.12; H, 3.42; N, 4.75.

**N,N-Dimethyl-2-iodobenzylamine.**<sup>12</sup> A sealed bottle charged with 2-iodobenzyl chloride (1.26 g, 5.00 mmol, 1.00 equiv) and dimethylamine (25% aqueous, 3.61 g solution, 10.00 mmol, 2.00 equiv) was kept at 140 °C for 5 h. After cooling to rt, the reaction mixture was diluted with  $Et_2O$  (50 mL) and was washed with 1M NaOH (20 mL). The aqueous layer was extracted with  $Et_2O$  (20 mL) and the combined organic layers were dried (anhydrous  $K_2CO_3$ ) and evaporated to give N,N-dimethyl-2-iodobenzylamine as a light yellow oil (1.25 g, 4.79 mmol, 96%). No further purification was conducted. TLC ( $SiO_2$ , 20% EtOAc/hexane,  $R_f$  = 0.10); IR ( $CH_2Cl_2$ , KCl,  $cm^{-1}$ ) 3049 (w), 2978 (m), 2945 (m), 2861 (w), 2822 (s), 2776 (s), 1563 (w), 1457 (m), 1437 (m), 1362 (m), 1035 (m), 1012 (s), 910 (m);  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.83 (d,  $J$  = 7.8 Hz, 1 H), 7.38 (dd,  $J$  = 7.8, 1.2 Hz, 1 H), 7.30 (t,  $J$  = 7.5 Hz, 1 H), 6.93 (dt,  $J$  = 7.5, 1.2 Hz, 1 H), 3.46 (s, 2 H), 2.30 (s, 6 H);  $^{13}C$  NMR ( $CDCl_3$ , 75.5 MHz)  $\delta$

141.0, 139.3, 130.2, 128.5, 127.9, 100.6, 67.8, 45.4. Anal. Calcd for  $C_9H_{12}NI$ : C, 41.40; H, 4.63; N, 5.36; I, 48.60. Found: C, 41.44; H, 4.58; N, 5.31; I, 48.58

**N-Methyl 2-bromobenzylamine.**<sup>13</sup> A glass bottle was charged with 2-bromobenzyl bromide (3.75 g, 15.00 mmol, 1.00 equiv) and methylamine (2.33 g, 75.02 mmol, 5.00 equiv) while stirring vigorously, then sealed and heated at 70 °C for 2 h to ensure complete reaction. After cooling to rt, the mixture was diluted with  $Et_2O$  (100 mL), washed with satd  $NaHCO_3$ , dried over  $K_2CO_3$ , and the solvent evaporated to give an oil which was purified by chromatography to yield N-methyl 2-bromobenzylamine (1.20 g, 6.00 mmol, 40%) as a yellow oil. TLC ( $SiO_2$ , 30% EtOAc in hexane,  $R_f = 0.04$ ); chromatographic purification (Flash column,  $SiO_2$ , 2 x 10 mm, 1st: 5% EtOAc in hexane, 300 mL; 2nd: 30% EtOAc/5%  $Et_3N$ /hexane); IR ( $CH_2Cl_2$ , KCl,  $cm^{-1}$ ) 3333 (br, w), 3073 (w), 3044 (m), 2975 (m), 2940 (m), 2852 (m), 2799 (m), 1568 (w), 1472 (s), 1441 (s), 1355 (w), 1132 (w), 1100 (m), 1026 (s);  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.50 (dd,  $J = 7.8, 0.9$  Hz, 1 H), 7.33 (dd,  $J = 7.5, 1.5$  Hz, 1 H), 7.23 (dt,  $J = 7.5, 0.9$  Hz, 1 H), 7.07 (dt,  $J = 7.5, 1.5$  Hz, 1 H), 3.78 (s, 2 H), 2.41 (s, 3 H), 1.43 (br s, 1 H);  $^{13}C$  NMR ( $CDCl_3$ , 75.5 MHz)  $\delta$  138.8, 132.6, 130.1, 128.4, 127.2, 123.8, 55.5, 35.6. Anal. Calcd for  $C_8H_{10}BrN$ : C, 48.02; H, 5.04; Br, 39.94; N, 7.00. Found: C, 48.25; H, 5.15; Br, 39.66; N, 6.84.

**2-(2'-Iodophenyl)-N-methylacetamide.** This compound was prepared by a modification of the literature method.<sup>14</sup> Methyl triflate (1.64 g, 10.00 mmol, 2.00 equiv) and 2-iodophenylacetonitrile (1.22 g, 5.00 mmol, 1.00 equiv) were heated at 70 °C for 2 h under  $N_2$ , and then  $H_2O$  (10 mL) was added cautiously. After the usual workup and flash chromatographic purification, 2-(2'-iodophenyl)-N-methylacetamide was isolated as a white solid (0.50 g, 1.82 mmol, 36%). TLC ( $SiO_2$ , EtOAc,  $R_f = 0.32$ ); chromatographic purification (Flash column,  $SiO_2$ , 2 x 15 mm, 1st: EtOAc/ $CH_2Cl_2$ / $Et_3N$ /hexane (10:20:68:2), 400 mL; 2nd: EtOAc/ $Et_3N$ /hexane (40:2:58); mp 138.0-139.0 °C; IR ( $CH_2Cl_2$ , KCl,  $cm^{-1}$ ) 3446 (m), 3337 (br, m), 3052 (m), 2984 (w), 2945 (w), 1670 (s), 1524 (s), 1464 (w), 1436 (w), 1414 (m), 1014 (m);  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.87 (d,  $J = 8.1$  Hz, 1 H), 7.35 (app d,  $J = 4.2$  Hz, 2 H), 7.02-6.96 (m, 1 H), 5.37 (br s, 1 H), 3.72 (s, 2 H), 2.78 (d,  $J = 4.8$  Hz, 3 H);  $^{13}C$  NMR ( $CDCl_3$ ,

75.5 MHz)  $\delta$  170.0, 139.5, 138.3, 130.6, 128.8, 128.6, 101.1, 48.1, 26.4. Anal. Calcd for  $C_9H_{10}INO$ : C, 39.30; H, 3.66; I, 46.13; N, 5.09. Found: C, 39.30; H, 3.64; I, 46.24; N, 5.02.

**Bis-(2-Iodobenzyl)-methylamine.** 2-Iodobenzyl chloride (1.52 g, 6.00 mmol, 1.00 equiv) and methylamine (2.33 g 40% aqueous solution, 30.01 mmol, 5.00 equiv) were heated in a sealed bottle at 120 °C for 3 hr. The workup described above for N,N-dimethyl-2-iodobenzylamine was applied. 2-Iodobenzyl chloride (1.52 g, 6.00 mmol, 1.00 equiv) was added to the crude product obtained, and the mixture was again heated in a sealed bottle at 120 °C for 3 hr.

After cooling to room temperature, 50% aqueous dimethylamine (3 mL) was added and the sealed bottle was placed in an oil bath at 120 °C for 1 h. After repeating the workup, bis-(2-iodobenzyl)methylamine was obtained as a light yellow viscous oil (2.581 g, 5.570 mmol, 93%): TLC (silica gel, 20% EtOAc/hexane,  $R_f$  = 0.57); IR ( $CH_2Cl_2$ , KCl,  $cm^{-1}$ ): 3067 (w), 3048 (w), 2951 (w), 2942 (s), 2795 (s), 1586 (w), 1562 (w), 1461 (s), 1437 (m), 1363 (m), 1340 (w), 1020 (s).  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  7.86 (d,  $J$  = 7.8 Hz, 2 H), 7.56 (d,  $J$  = 7.8 Hz, 2 H), 7.35 (t,  $J$  = 7.5 Hz, 2 H), 6.96 (app t,  $J$  = 7.8 Hz, 2 H), 3.69 (s, 4 H), 2.28 (s, 3 H).  $^{13}C$  NMR ( $CDCl_3$ , 75.5 MHz):  $\delta$  141.1, 139.3, 130.4, 128.6, 128.0, 100.4, 65.8, 41.9. Anal. Calcd for  $C_{15}H_{15}NI_2$ : C, 38.90; H, 3.26; N, 3.02; I, 54.81. Found: C, 39.00; H, 3.25; N, 2.99; I, 54.73.

### **Preparation of Heteroaromatic Substrates.**

**N-Carboethoxy-2-iodoindole.** To a stirred solution of 2-iodoindole (2.43 g, 10.00 mmol, 1.00 equiv) in DMF (20 mL) at rt under nitrogen NaH (0.26 g, 11.00 mmol, 1.10 equiv) was cautiously added. After 30 min, ethyl chloroformate (1.19 g, 11.00 mmol, 1.10 equiv) was added via syringe, and the mixture stirred for 1 h. The usual workup and flash chromatographic purification gave N-carboethoxy-2-iodoindole as a light yellow solid (2.90 g, 9.20 mmol, 92%). TLC ( $SiO_2$ , 20% EtOAc/hexane,  $R_f$  = 0.46); chromatographic purification (Flash column,  $SiO_2$ , 2 x 15 mm, 5% EtOAc/hexane); mp 65-67 °C; IR ( $CH_2Cl_2$ , KCl,  $cm^{-1}$ ): 3072 (w), 3051 (w), 2986 (w), 1743 (s), 1468 (w), 1440 (m), 1397 (w), 1376 (m), 1318 (s),

1300 (m), 1286 (w), 1229 (w), 1203 (m), 1134 (w), 1050 (m), 811 (w).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.10 (app d,  $J = 8.4$  Hz, 1 H), 7.47-7.45 (m, 1 H), 7.27-7.18 (m, 2 H), 7.02 (s, 1 H), 4.55 (q,  $J = 7.2$  Hz, 2 H), 1.54 (t,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  150.4, 137.1, 130.9, 124.2, 122.8, 122.2, 119.2, 115.3, 74.5, 63.4, 14.1. Anal. Calcd for  $\text{C}_{11}\text{H}_{10}\text{INO}_2$ : C, 41.93; H, 3.20; I, 40.27; N, 4.44. Found: C, 41.98; H, 3.24; I, 40.37; N, 4.27.

### **Preparation of Alkenyl Substrates.**

**(E)-3-Bromo- $\beta$ -iodostyrene.** This compound was prepared according to a modification of the Takai procedure.<sup>4</sup> THF (250 mL) was added to a 500 mL 2-necked round-bottomed flask charged  $\text{CrCl}_3$  (17.12 g, 108.10 mmol). The mixture was cooled to 0 °C and then LAH pellets (2.05 g, 54.00 mmol) were added slowly. The resultant mixture was stirred under nitrogen for 4 h, then iodoform (21.28 g, 54.04 mmol) was added cautiously. After 20 min, 3-bromobenzaldehyde was added slowly and the mixture stirred at 0 °C for 1 h. The mixture was then diluted with hexanes (200 mL) and filtered through a plug of alumina. The filtrate was washed with 1.2 N HCl (2 x 200 mL) and brine (200 mL) and the organic layer was dried over  $\text{K}_2\text{CO}_3$  and treated with charcoal. After filtration through Celite, the solvents were removed under reduced pressure. The product was purified by chromatography to give (E)-3-bromo- $\beta$ -iodostyrene as a yellow oil (7.88 g, 94%). Chromatographic purification (gravity column,  $\text{SiO}_2$ , 2 x 15 cm, hexanes); IR ( $\text{CH}_2\text{Cl}_2$ , KCl,  $\text{cm}^{-1}$ ) 3066 (w), 3045 (w), 1591 (s), 1559 (s), 1474 (m), 1206 (m), 1180 (m), 1067.622 (m), 945 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 360 MHz)  $\delta$  7.44 (s, 1 H), 7.42 (d,  $J = 6.7$  Hz, 1 H), 7.36 (d,  $J = 14.6$  Hz, 1 H), 7.21 (app s, 2 H), 6.90 (d,  $J = 14.6$  Hz, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta$  143.4 (s,  $\underline{\text{C}}\text{H}=\text{CHI}$ ), 139.5 (s, C1), 131.3 (s, C4), 130.2 (s, C5), 128.9 (s, C2), 124.7 (s, C6), 122.9 (s, C3), 79.0 (s,  $\text{CH}=\underline{\text{C}}\text{HI}$ ). Anal. Calcd for  $\text{C}_8\text{H}_6\text{BrI}$ : C, 31.10; H, 1.96. Found: C, 30.88; H, 1.88.

**(E)-2-(2-Iodovinyl)-5-bromothiophene.** Prepared from 5-bromo-2-thiophenecarboxaldehyde (10.00 g, 52.35 mmol) according to the above procedure. Tan crystals (3.42 g, 21%); mp 66-68 °C (hexanes); IR ( $\text{CH}_2\text{Cl}_2$ , KCl,  $\text{cm}^{-1}$ ) 3049(w), 1428 (s), 1266 (m), 1222 (m), 966 (m),

932 (m);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 360 MHz)  $\delta$  7.36 (d,  $J = 14.7$  Hz, 1 H), 6.93 (d,  $J = 3.7$  Hz, 1 H), 6.69 (d,  $J = 3.7$  Hz, 1 H), 6.57 (d,  $J = 14.7$  Hz, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta$  144.1 (s, CH=CHI), 137.0 (s, C2), 130.3 (s, C4), 125.9 (s, C3), 112.4 (s, C5), 75.4 (s, CH=C $\underline{\text{H}}$ I).

Anal. Calcd for  $\text{C}_6\text{H}_4\text{BrIS}$ : C, 22.88; H, 1.28. Found: C, 22.93; H, 1.34.

**Ethyl (Z)-3-iodopropenoate.** A 100 mL Schlenk flask was cooled in a 0 °C bath and charged with ethyl propiolate (10.00 g, 101.94 mmol) and hydroiodic acid (21 mL, 47% aq. solution). The solution was stirred at 0 °C for 2 h and then at 23 °C for 16 h. GLC analysis showed no starting material with only a trace of the (*E*)-isomer. The resultant solution was diluted with ether (200 mL) and washed with water (200 mL), satd sodium thiosulfate (200 mL), and brine (200 mL). The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and solvents were removed under reduced pressure to give ethyl (*Z*)-3-iodopropenoate<sup>3,5</sup> containing 2% (*E*)-ethyl 3-iodopropenoate as a pale yellow oil (20.00 g, 87%). No further purification was necessary.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 360 MHz)  $\delta$  7.45 (d,  $J = 8.6$  Hz, 1 H), 6.90 (d,  $J = 8.6$  Hz, 1 H), 4.26 (q,  $J = 7.3$  Hz, 2 H), 1.33 (t,  $J = 7.3$  Hz, 3 H).

## Copper(I) Thiophene-2-carboxylate Mediated Reductive Coupling

**2,2'-Dicarbomethoxybiphenyl (2a).** Methyl 2-iodobenzoate (0.52 g, 2.00 mmol, 1.00 equiv) was added to a slurry of CuTC (0.95 g, 5.00 mmol, 2.50 equiv) in NMP (8 mL). The reaction mixture was stirred for 1 h at room temperature then diluted with  $\text{Et}_2\text{O}$  (15 mL), passed through a plug of  $\text{SiO}_2$  using  $\text{Et}_2\text{O}$  as eluent and washed with of water (100 mL). The aqueous layer was back extracted with of  $\text{Et}_2\text{O}$  (40 mL) and the  $\text{Et}_2\text{O}$  layers were combined, washed with water (2 x 50 mL), dried ( $\text{MgSO}_4$ ), and filtered. The solvent was removed under reduced pressure to give 2,2'-dicarbomethoxybiphenyl as a white solid (0.262 g, 0.97 mmol, 96%). No further purification was conducted. TLC ( $\text{SiO}_2$ , 20% EtOAc/hexane,  $R_f = 0.30$ ); mp 69.5-71.0 °C (*lit.*<sup>15</sup> mp 72-73 °C); IR ( $\text{CH}_2\text{Cl}_2$ , KCl,  $\text{cm}^{-1}$ ) 3065 (w), 3002 (w), 2953 (w), 1728 (s), 1682 (m), 1434 (m), 1294 (s), 1136 (m), 1085 (w);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300

MHz)  $\delta$  8.00 (dd,  $J = 7.5, 1.2$  Hz, 2 H), 7.52 (dt,  $J = 7.5, 1.5$  Hz, 2 H), 7.41 (dt,  $J = 7.5, 1.2$  Hz, 2 H), 7.20 (dd,  $J = 7.5, 0.9$  Hz, 2 H), 3.60 (s, 6 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta$  167.1, 143.0, 131.2, 130.0, 129.6, 129.1, 126.9, 51.5. Anal. Calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_4$ : C, 71.10; H, 5.22. Found: C, 71.04; H, 5.23.

**2,2'-Dinitrobiphenyl (2b).** *From 2-iodonitrobenzene.* 1-Iodo-2-nitrobenzene (0.498g, 2.00 mmol, 1.00 equiv) was added to a slurry of CuTC (0.953 g, 5.00 mmol, 2.50 equiv) in NMP (8 mL). The mixture was stirred for 30 min and then diluted with  $\text{Et}_2\text{O}$  (15 mL). The resulting slurry was filtered through a plug of  $\text{SiO}_2$  using  $\text{Et}_2\text{O}$  as eluent and the solution was washed with of 5% aqueous  $\text{NH}_3$  (100 mL). The aqueous layer was back extracted with  $\text{Et}_2\text{O}$  (40 mL) and the combined  $\text{Et}_2\text{O}$  layers were washed with water (2 x 50 mL), dried ( $\text{MgSO}_4$ ) and filtered. The solvent was removed under reduced pressure to give 2,2'-dinitrobiphenyl as a yellow solid (0.225 g, 0.92 mmol, 92%): mp 124-125 °C (*Aldrich catalog mp 124-126 °C*).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are consistent with those in the Aldrich file. *From 2-bromonitrobenzene.* 1-Bromo-2-nitrobenzene (0.404 g, 2.00 mmol, 1.00 equiv) and CuTC (1.144 g, 6.00 mmol, 3.00 equiv) in NMP (8 mL) at 70 °C for 2 h gave 2,2'-dinitrobiphenyl as a yellow solid (0.21 g, 0.86 mmol, 86%) after workup as above and chromatographic purification (Flash column,  $\text{SiO}_2$ , 2 x 15 mm, 1st: 5% EtOAc/hexane; 2nd: 30% EtOAc/hexane). All data are consistent with Aldrich file. Nitrobenzene (4%) was isolated as a by-product.

**N,N,N',N'-Tetramethyl-2-2'-diaminothiocarbonyl biphenyl (2c).** N,N'-Dimethyl-2-iodothiobenzamide (0.58 g, 2.00 mmol, 1.00 equiv) was added to a slurry of CuTC (1.14 g, 6.00 mmol, 3.00 equiv) in NMP (8 mL). After stirring for 48 h at rt, the reaction mixture was diluted with EtOAc (100 mL) and sufficient 15% aqueous  $\text{NH}_3$  was added to produce a clear, deep blue aqueous layer. Water (50 mL) was added and the reaction mixture was extracted with EtOAc (2 x 40 mL). The organic layers were combined, evaporated under reduced pressure, and the crude product dissolved in  $\text{Et}_2\text{O}$  (100 mL). The solution was washed with water (2 x 40 mL), dried ( $\text{K}_2\text{CO}_3$ ), filtered, and evaporated under reduced pressure to give N,N,N',N'-tetramethyl-2-2'-diaminothiocarbonyl biphenyl as a yellow solid (0.31 g, 0.94 mmol,

94%) after chromatography: TLC (SiO<sub>2</sub>, 30% EtOAc/hexane, R<sub>f</sub> = 0.12); chromatographic purification (Flash column, SiO<sub>2</sub>, 2 x 15 mm, 10% EtOAc/2% Et<sub>3</sub>N/hexane); mp 235.0-237.0 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>) 3047 (w), 2973 (w), 2936 (w), 1520 (s), 1467 (w), 1407 (w), 1394 (m), 1290 (m), 1266 (m), 1260 (w), 1144 (m), 990 (w); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.42-7.24 (m, 8 H), 3.43 (s, 6 H), 3.10 (s, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 199.8, 142.0, 133.7, 129.7, 127.9, 127.7, 127.6, 44.8, 42.6. Anal. Calcd for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>S<sub>2</sub>: C, 65.81; H, 6.14; N, 8.53; S, 19.52. Found: C, 65.85; H, 6.16; N, 8.60.

**2,2'-Biacetanilide (2d).** CuTC (0.953 g, 5.00 mmol, 2.50 equiv) was added in one portion to 2-iodoacetanilide (0.522 g, 2.00 mmol, 1.00 equiv) in NMP (8 mL) under nitrogen. After stirring at rt for 30 min, 15 mL EtOAc was added and the resulting slurry was filtered through a plug of SiO<sub>2</sub> using EtOAc (120 mL) as eluent. The solution was washed with dilute aqueous NH<sub>3</sub> (100 mL) and the aqueous layer was extracted with EtOAc (2 x 40 mL). The combined EtOAc layers were washed with water (50 mL) and the aqueous layer was back extracted with EtOAc (30 mL). The combined EtOAc layers were dried (MgSO<sub>4</sub>), filtered, evaporated, and the solid product was recrystallized from Et<sub>2</sub>O/hexane to give 2,2'-biacetanilide as a white solid (0.242 g, 0.90 mmol, 90%): TLC (SiO<sub>2</sub>, EtOAc, R<sub>f</sub> = 0.14); mp 158.0-160.0 °C (*lit.*<sup>16</sup> mp 161 °C) (CH<sub>2</sub>Cl<sub>2</sub>); IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>) 3416 (w), 3055 (m), 2987 (w), 1695 (s), 1581 (w), 1521 (s), 1470 (w), 1447 (m), 1436 (m), 1269 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.92 (br d, *J* = 8.1 Hz, 2 H), 7.37 (dt, *J* = 7.5, 1.5 Hz, 2 H), 7.24 (br s, 2 H), 7.23-7.13 (m, 4 H), 1.88 (s, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 169.2, 135.3, 130.4, 129.9, 129.0, 125.2, 123.8, 23.8. Anal. Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.32; H, 6.04; N, 10.40.

**N,N'-Dimethyl-2,2'-biacetanilide (2e).** Following the procedure used for **2d**, N-methyl-2-iodoacetanilide (0.55 g, 2.00 mmol, 1.00 equiv) and CuTC (1.14 g, 6.00 mmol, 3.00 equiv) in NMP (8 mL) at 70 °C for 24 h gave N,N'-dimethyl-2,2'-biacetanilide as a white solid (0.246 g, 0.83 mmol, 83%): TLC (SiO<sub>2</sub>, EtOAc, R<sub>f</sub> = 0.08); mp 171.0-173.0 °C (Et<sub>2</sub>O); IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>) 3054 (w), 2986 (w), 1656 (s), 1596 (w), 1475 (m), 1438 (m), 1421 (m), 1376 (s), 1353

(m), 1304 (w), 1143 (w);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.44-7.38 (m, 4 H), 7.30-7.20 (m, 4 H), 2.92 (s, 1.5 H), 2.71 (s, 4.5 H), 1.95 (s, 4.5 H), 1.80 (s, 1.5 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz, *data in parentheses are for the minor rotamer*)  $\delta$  171.0, 141.9 (142.2), 131.2 (132.5), 129.25 (129.32), 129.1 (129.0), 128.2, 128.0, 35.4 (36.7), 22.6 (22.7). Anal. Calcd for  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2$ : C, 72.95; H, 6.80; N, 9.45. Found: C, 72.89; H, 6.81; N, 9.51.

**N,N'-Di-(trifluoroacetyl)-2,2'-diaminobiphenyl (2f).** Following the procedure used for **2a**, N-trifluoroacetyl-2-iodoaniline (0.63 g, 2.00 mmol, 1.00 equiv) and CuTC (1.14 g, 6.00 mmol, 3.00 equiv) in NMP (8 mL) for 20 h at rt gave N,N'-di-(trifluoroacetyl)-2,2'-diaminobiphenyl as a white solid (0.297 g, 0.79 mmol, 79%; 0.072 g, 11%, starting material also recovered): TLC ( $\text{SiO}_2$ , 30% EtOAc/hexane,  $R_f = 0.24$ ); chromatographic purification (Flash column,  $\text{SiO}_2$ , 2 x 15 mm, 10% EtOAc/hexane); mp 160.0-162.0 °C (*lit.*<sup>17</sup> mp 161-162 °C); IR ( $\text{CH}_2\text{Cl}_2$ , KCl,  $\text{cm}^{-1}$ ) 3402 (m), 3060 (w), 2987 (w), 1736 (s), 1585 (w), 1532 (m), 1446 (w), 1196 (m), 1165 (s), 1153 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.99 (d,  $J = 8.1$  Hz, 2 H), 7.93 (br s, 2 H), 7.52 (dt,  $J = 7.8, 1.2$  Hz, 2 H), 7.39 (dt,  $J = 7.5, 1.2$  Hz, 2 H), 7.24 (dd,  $J = 7.5, 1.2$  Hz, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta$  155.4 (q,  $J = 36.6$  Hz), 132.5, 130.0, 130.2 (2 carbon), 127.4, 124.1, 115.5 (q,  $J = 290.5$  Hz). Anal. Calcd for  $\text{C}_{16}\text{H}_{10}\text{F}_6\text{N}_2\text{O}_2$ : C, 51.08; H, 2.68; F, 30.30; N, 7.45. Found: C, 51.15; H, 2.72; N, 7.43.

**N,N'-Diacetyl-6,6'-diamino-2,3,4,2',3',4'-hexamethoxybiphenyl (2g).** CuTC (1.14 g, 6.00 mmol, 3.00 equiv) was added in one portion to 2-iodo-3,4,5-trimethoxyacetanilide (0.70 g, 2.00 mmol, 1.00 equiv) in NMP (8 mL) under nitrogen. After stirring at rt for 1 h, the reaction mixture was diluted with EtOAc (15 mL) and the resulting slurry was passed through a short plug of  $\text{SiO}_2$  using EtOAc (150 mL) as eluent. The EtOAc was removed under reduced pressure and the majority of the NMP by vacuum distillation. Residual NMP was removed in vacuo overnight at room temperature. The crude product was dissolved in  $\text{CH}_2\text{Cl}_2$  (4 mL) and  $\text{Et}_2\text{O}$  (10 mL), the volume of solvents reduced in half by evaporation, and hexane (2 mL) was added. On standing in a freezer, N,N'-diacetyl-6,6'-diamino-2,3,4,2',3',4'-hexamethoxybiphenyl was formed as an off-white solid (0.38 g, 0.85 mmol, 85%). Traces of

3,4,5-trimethoxyacetanilide (~4% from crude NMR) were removed during recrystallization. TLC (SiO<sub>2</sub>, EtOAc, R<sub>f</sub> = 0.10); mp 149.0-151.0 °C (ether/hexane); IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>) 3410 (br, m), 3062 (w), 3003 (w), 2971 (w), 2942 (m), 2850 (w), 1691 (s), 1601 (s), 1507 (s), 1466 (m), 1456 (m), 1410 (w), 1392 (m), 1339 (w), 1234 (m), 1200 (w), 1133 (w), 1108 (s), 1007 (m); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.49 (s, 2 H), 7.08 (s, 2 H), 3.88 (s, 6 H), 3.84 (s, 6 H), 3.62 (s, 6 H), 1.91 (s, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 168.8, 153.5, 151.2, 139.1, 132.4, 111.5, 103.2, 61.0, 60.9, 55.9, 24.2. Anal. Calcd for C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>8</sub>: C, 58.91; H, 6.29; N, 6.25. Found: C, 59.00; H, 6.29; N, 6.23.

**Biphenyl-N,N,N',N'-tetramethyldicarbamate (2h).** Following the procedure used for **2a**, 2-iodophenyl-N,N-dimethylcarbamate (1.02 g, 3.50 mmol, 1.00 equiv) and CuTC (2.67 g, 14.00 mmol, 4.00 equiv) in NMP (20 mL) at rt for 12 h gave 2,2'-biphenyl-N,N,N',N'-tetramethyldicarbamate as a light yellow viscous oil (0.236 g, 0.72 mmol, 41%; 0.50 g, 50% starting material also recovered) after flash chromatography: TLC (SiO<sub>2</sub>, 30% EtOAc/hexane, R<sub>f</sub> = 0.10); chromatographic purification (Flash column, SiO<sub>2</sub>, 2 x 15 mm, 1st: 20% EtOAc/hexane, 300 mL; 2nd: 50% EtOAc/2% Et<sub>3</sub>N/hexane); IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>) 3056 (w), 2939 (w), 1721 (s), 1474 (w), 1440 (w), 1390 (m), 1205 (m), 1168 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.38-7.18 (m, 8 H), 2.81 (s, 6 H), 2.71 (s, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 154.1, 148.8, 130.7, 130.6, 128.4, 124.8, 122.4, 36.4, 35.9. Anal. Calcd for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.93; H, 6.17; N, 8.45.

**2,2'-Biphenyldimethanol (2i).** CuTC (2.29 g, 12.00 mmol, 3.00 equiv) was added in one portion to 2-iodobenzyl alcohol (0.94 g, 4.00 mmol, 1.00 equiv) in NMP (20 mL) under nitrogen. After 24 h at 70 °C, 15 mL EtOAc was added and the resulting slurry was filtered through a plug of SiO<sub>2</sub> using EtOAc (150 mL) as eluent. The EtOAc was removed at reduced pressure and most of NMP in vacuo. The residue was diluted with Et<sub>2</sub>O (100 mL) and the solution was washed with dilute aqueous NH<sub>3</sub> (40 mL). The aqueous layer was back extracted with Et<sub>2</sub>O (2 x 20 mL) and the combined ether layers were dried (MgSO<sub>4</sub>) and filtered. The solvents were removed under reduced pressure to give a solid that was purified

by chromatography followed by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane to give 2,2'-biphenyldimethanol as a white solid (0.21 g, 0.97 mmol, 48%; 38% starting material, 0.36 g, also recovered): TLC ( $\text{SiO}_2$ , 60% EtOAc/hexane,  $R_f = 0.30$ ); chromatographic purification (Flash column,  $\text{SiO}_2$ , 20% EtOAc/hexane, 2 x 15 mm); mp 109.0-111.0 °C ( $\text{CH}_2\text{Cl}_2$ /hexane) (*lit.*<sup>18</sup> mp 112 °C); IR ( $\text{CH}_2\text{Cl}_2$ , KCl,  $\text{cm}^{-1}$ ) 3596 (m), 3437 (br, s), 3064 (w), 3051 (w), 2947 (w), 1658 (m), 1477 (m), 1442 (m), 1383 (w), 1200 (m), 1007 (s), 950 (m);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.44-7.29 (m, 6 H), 7.12 (d,  $J = 6.9$  Hz, 2 H), 4.24 (s, 4 H), 3.80 (br s, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta$  139.9, 138.5, 129.5, 129.4, 127.9, 127.4, 62.4. Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_2$ : C, 78.48; H, 6.59. Found: C, 78.53; H, 6.63.

**2,2'-Di(N,N-dimethylaminomethyl)biphenyl (2j).**<sup>19</sup> CuTC (1.14 g, 6.00 mmol, 3.00 equiv) was added in one portion to N,N-dimethyl-2-iodobenzylamine (0.52 g, 2.00 mmol, 1.00 equiv) in NMP (8 mL) under nitrogen. After 1h at rt, the reaction mixture was diluted with EtOAc (100 mL) and sufficient 15% aqueous  $\text{NH}_3$  was added to produce a clear, deep blue aqueous layer. Water (50 mL) was added and the reaction mixture was extracted with EtOAc (2 x 40 mL). The organic layers were combined, evaporated at reduced pressure, and the crude product dissolved in  $\text{Et}_2\text{O}$  (100 mL). The solution was washed with water (2 x 40 mL), dried ( $\text{K}_2\text{CO}_3$ ) and filtered. Removal of solvent under reduced pressure gave 2,2'-di(N,N-dimethylaminomethyl)biphenyl as a light yellow oil (0.259 g, 0.96 mmol, 97%). No purification was necessary. TLC (alumina, 30% EtOAc/hexane,  $R_f = 0.40$ ); IR ( $\text{CH}_2\text{Cl}_2$ , KCl,  $\text{cm}^{-1}$ ) 3034 (w), 2978 (m), 2945 (m), 2860 (m), 2820 (s), 2773 (s), 1469 (m), 1457 (m), 1442 (w), 1362 (m), 1137 (w), 1025 (m), 851 (m);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.56 (d,  $J = 7.5$  Hz, 2 H), 7.34 (dt,  $J = 7.5, 0.9$  Hz, 2 H), 7.24 (t,  $J = 7.5$  Hz, 2 H), 7.07 (dd,  $J = 7.5, 0.9$  Hz, 2 H), 3.16 (d,  $J = 13.5$  Hz, 2 H), 3.04 (d,  $J = 13.5$  Hz, 2 H), 2.09 (s, 12 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta$  140.6, 137.1, 129.5, 128.5, 127.1, 125.9, 60.8, 45.3. Anal. Calcd for  $\text{C}_{18}\text{H}_{24}\text{N}_2$ : C, 80.55; H, 9.01; N, 10.44. Found: C, 80.52; H, 9.04; N, 10.42.

**2,2'-Di(N-methylaminomethyl)biphenyl (2k).** Following the procedure used for 2j, 2-bromo-N-methylbenzylamine (0.40 g, 2.00 mmol, 1.00 equiv) and CuTC (1.14 g, 6.00 mmol, 3.00

equiv) in NMP (8 mL) at rt for 12 h gave 2,2'-di(N-methylaminomethyl)biphenyl (0.237 g, 0.99 mmol, 99%) as a light yellow viscous oil. No purification was necessary. IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>) 3340 (br, w), 3250 (br, w), 3068 (w), 3045 (m), 3026 (w), 2971 (m), 2939 (s), 2874 (m), 2849 (s), 2795 (s), 1677 (w), 1650 (w), 1475 (s), 1441 (s), 1354 (w), 1131 (m), 1100 (m); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.45 (d, *J* = 7.5 Hz, 2 H), 7.33 (dt, *J* = 7.5, 1.5 Hz, 2 H), 7.26 (dt, *J* = 7.5, 1.2 Hz, 2 H), 7.11 (dd, *J* = 7.5, 1.2 Hz, 2 H), 3.49 (d, *J* = 13.2 Hz, 2 H), 3.42 (d, *J* = 13.2 Hz, 2 H), 2.25 (s, 6 H), 1.73 (br s, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 139.9, 137.5, 129.2, 128.5, 127.2, 126.2, 52.9, 35.6. HRMS (EI) Calcd for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>Li<sup>+</sup> (M+Li)<sup>+</sup>: 247.1787. Found: 247.1783. Anal. Calcd for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>: C, 79.96; H, 8.39; N, 11.66. Found: C, 78.42; H, 8.19; N, 11.28.

**α,α'-(2,2'-Biphenyl)-N,N'-dimethyl diacetamide (2l).** Following the procedure used for **2d**, 2-(2-iodophenyl)-N-methylacetamide (0.55 g, 2.00 mmol, 1.00 equiv) and CuTC (1.14 g, 6.00 mmol, 3.00 equiv) in NMP (8 mL) for 12 h at rt gave α,α'-(2,2'-biphenyl)-N,N'-dimethyl diacetamide as a white solid (0.152 g, 0.51 mmol, 51%; 18% starting material, 0.10 g, also recovered) after flash chromatography: TLC (SiO<sub>2</sub>, EtOAc, R<sub>f</sub> = 0.05); chromatographic purification (Flash column, SiO<sub>2</sub>, 2 x 15 mm, 1st: 30% EtOAc/2%Et<sub>3</sub>N/hexane, 400 mL; 2nd: 5% MeOH/2% Et<sub>3</sub>N/EtOAc); mp 202.5-204.0 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>) 3454 (w), 3330 (br, m), 3054 (m), 2986 (w), 1664 (s), 1526 (m), 1478 (w), 1421 (w); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.37-7.22 (m, 6 H), 7.06 (dd, *J* = 7.5, 1.2 Hz, 2 H), 6.40 (br s, 2 H), 3.37 (d, *J* = 15.3 Hz, 2 H), 3.28 (d, *J* = 15.3 Hz, 2 H), 2.58 (d, *J* = 4.8 Hz, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 172.0, 140.4, 133.8, 130.0, 129.8, 127.9, 126.7, 40.9, 26.2. HRMS (EI) Calcd for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>Li<sup>+</sup> (M+Li)<sup>+</sup>: 303.1685. Found: 303.1699. Anal. Calcd for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.95; H, 6.80; N, 9.45. Found: C, 71.55; H, 6.86; N, 9.22.

**2,2'-Bithiophene (4a).** Following the procedure used for **2j**, 2-iodothiophene (0.84 g, 4.00 mmol, 1.00 equiv) and CuTC (2.67 g, 14.00 mmol, 3.50 equiv) in NMP (15 mL) for 48 h at rt gave 2,2'-bithiophene as a light yellow solid (0.257 g, 1.54 mmol, 77%) after workup and

chromatographic purification (Flash column, SiO<sub>2</sub>, 2 x 15 mm, 5% EtOAc in hexane): mp 31-33 °C (Aldrich catalog mp 32-33 °C). <sup>1</sup>H and <sup>13</sup>C NMR were consistent with the Aldrich file.

**3,3'-Dihydroxy-6,6'-dimethyl-2,2'-bipyridine (4b).** CuTC (1.14 g, 6.00 mmol, 3.00 equiv) was added in one portion to 6-iodo-2-picolin-5-ol (0.47 g, 2.00 mmol, 1.00 equiv) in NMP (8 mL) under nitrogen. After 4 h at rt, EtOAc (15 mL) was added and the resulting slurry was filtered through a plug of SiO<sub>2</sub> using EtOAc (120 mL) as eluent. The solution was washed with dilute aqueous NH<sub>3</sub> (100 mL) and the aqueous layer was back extracted with EtOAc (4 x 40 mL). The combined EtOAc layers were washed with water (50 mL) and the resulting aqueous layer was back extracted with EtOAc (30 mL). The combined EtOAc layers were dried (MgSO<sub>4</sub>), filtered, and evaporated at reduced pressure. The crude product was purified by flash chromatography to give 3,3'-dihydroxy-6,6'-dimethyl-2,2'-bipyridine as a yellow-green solid (0.15 g, 0.69 mmol, 69%): TLC (SiO<sub>2</sub>, 30% EtOAc in hexane, R<sub>f</sub> = 0.50);

chromatographic purification (Flash column, SiO<sub>2</sub>, 2 x 15 mm, 15% EtOAc in hexane); mp 186.5-188.0 °C (*lit.*<sup>20</sup> mp 189-190 °C); IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>) 3274-2120 (br, s), 3051 (w), 2921 (w), 1728 (w), 1660 (w), 1584 (w), 1492 (s), 1386 (w), 1372 (w), 1320 (w), 1297 (m), 1235 (m), 1125 (w), 830 (m); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.29 (d, *J* = 8.4 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 6.03 (br s, 2 H), 2.50 (s, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 153.9, 144.6, 138.5, 126.3, 124.5, 22.7. Anal. Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 66.65; H, 5.59; N, 12.95. Found: C, 66.74; H, 5.65; N, 12.98.

**N,N'-Di-carboethoxy-2,2'-biindole (4c)** Following the procedure used for **2a**, N-carboethoxy-2-iodoindole (0.63 g, 2.00 mmol, 1.00 equiv) and CuTC (1.14 g, 6.00 mmol, 3.00 equiv) in NMP (12 mL) at 0 °C for 4 h gave N,N'-dicarboethoxy-2,2'-biindole as a white solid (0.227 g, 0.60 mmol, 60%) after chromatographic purification and recrystallization: TLC (SiO<sub>2</sub>, 20% EtOAc/hexane, R<sub>f</sub> = 0.44); chromatographic purification (Flash column, SiO<sub>2</sub>, 2 x 20 mm, 3% EtOAc/hexane); mp 136-137 °C (methylene chloride/hexane); IR (CH<sub>2</sub>Cl<sub>2</sub>, KCl, cm<sup>-1</sup>): 3072 (w), 3052 (w), 2985 (w), 2875 (w), 1739 (s), 1452 (m), 1400 (w), 1378 (m), 1333 (s), 1218 (m), 1125 (w), 1095 (w), 1047 (w), 818 (w). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.27 (d, *J*

= 8.4 Hz, 2 H), 7.59 (app d,  $J = 7.8$  Hz, 2 H), 7.38 (dt,  $J = 7.8, 1.2$  Hz, 2 H), 7.28 (app t,  $J = 7.8$  Hz, 2 H), 6.72 (s, 2 H), 4.29-4.14 (m, 4 H), 1.02 (t,  $J = 7.2$  Hz, 6 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  151.1, 136.6, 131.6, 128.7, 125.0, 123.1, 120.8, 115.6, 112.0, 62.8, 13.6. Anal. Calcd for  $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4$ : C, 70.20; H, 5.36; N, 7.44. Found: C, 69.51; H, 5.31; N, 7.34.

**(E),(E)-1,4-Diphenylbuta-1,3-diene (6a).** (*E*)- $\beta$ -Iodostryene (0.51 g, 2.22 mmol, 1.00 equiv) and CuTC (1.16 g, 5.54 mmol, 2.50 equiv) in NMP (5 mL) at rt for 1 h gave product (0.19g, 0.92 mmol, 82%) as a white solid from hexane/diethyl ether (1:1). The product exhibited spectral and physical data identical to an authentic sample; mp 151-152 °C (*Aldrich catalog mp 151-153* °C).

**(Z),(Z)-1,4-Diphenylbuta-1,3-diene (6b).** (*Z*)- $\beta$ -Iodostryene (0.36 g, 1.52 mmol, 1.00 equiv) and CuTC (0.72 g, 3.78 mmol, 2.48 equiv) in NMP (5 mL) at rt for 1 h gave product (0.13 g, 0.62 mmol, 81%) as a white solid from hexane/diethyl ether (1:1): mp 69-70 °C (*Lit.*<sup>21</sup> mp 70.5 °C).

**(E,E)-1,4-Di(3-bromophenyl)-1,3-butadiene (6c).** (*E*)-3-Bromo- $\beta$ -iodostyrene (0.36 g, 1.16 mmol, 1.00 equiv) and CuTC (0.55 g, 2.88 mmol, 2.48 equiv) in NMP (5 mL) at rt for 30 min gave product (0.20 g, 0.54 mmol, 92%) as a yellow solid after crystallization: mp 139-140 °C (hexane/diethyl ether); IR ( $\text{CDCl}_3$ , KCl,  $\text{cm}^{-1}$ ) 3054 (w), 2987 (w), 1588 (w);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.56 (s, 2 H), 7.35-7.31 (m, 4 H), 7.24-7.15 (m, 2 H), 6.88 (dd,  $J = 12.0, 2.7$  Hz, 2 H), 6.57 (dd,  $J = 12.0, 2.7$  Hz, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta$  139.3, 132.1, 130.6, 130.2, 131.1, 129.2, 125.1, 122.9. Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{Br}_2$ : C, 52.78; H, 3.32; Br, 43.89. Found: C, 52.68; H, 3.36; Br, 43.96.

**(E), (E)-1,4-Di-(5-bromothiophene-2-yl)-1,3-diene, 6d.** Following the same procedure used for compound **2a**, 2-bromo-5-(2-iodovinyl)thiophene (0.63 g, 2.00 mmol, 1.00 equiv) and CuTC (1.53 g, 8.00 mmol, 4.00 equiv) in NMP (10 mL) for 2 h at rt gave (*E,E*)-1,4-di-(5-bromothiophene-2-yl)-1,3-diene as an orange solid (0.315 g, 0.84 mmol, 84%) after workup and recrystallization from  $\text{CHCl}_3$ : TLC ( $\text{SiO}_2$ , 20% EtOAc/hexane,  $R_f = 0.56$ ); mp 100 °C with decomp ( $\text{CHCl}_3$ ); IR ( $\text{CH}_2\text{Cl}_2$ , KCl,  $\text{cm}^{-1}$ ) 3054 (m), 3020 (w), 2989 (w), 1604 (w), 1512 (w),

1426 (s), 974 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  6.92 (d,  $J = 3.6$  Hz, 2 H), 6.72 (d,  $J = 3.6$  Hz, 2 H), 6.66-6.49 (m, 4 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta$  144.3, 130.6, 128.4, 126.3, 125.2, 111.4. Anal. Calcd for  $\text{C}_{12}\text{H}_8\text{Br}_2\text{S}_2$ : C, 38.32; H, 2.14; Br, 42.49; S, 17.05. Found: C, 38.24; H, 2.11; Br, 42.51.

**(*E,E*)-7,9-Hexadecadiene (6e).**<sup>22</sup> (*E*)-1-Iodo-1-octene (0.26 g, 1.10 mmol, 1.00 equiv) and CuTC (0.52 g, 2.73 mmol, 2.50 equiv) in NMP (5 mL) at rt for 1 h gave product (0.10 g, 0.44 mmol, 80%) as a colorless oil after workup and flash chromatography purification ( $\text{SiO}_2$ , hexane):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  5.99-5.96 (m, 2 H), 5.59-5.50 (m, 2 H), 2.06-2.00 (m, 4 H), 1.53-1.26 (m, 16 H), 0.86 (t,  $J = 6.6$  Hz, 6 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta$  132.4, 130.3, 32.6, 31.8, 29.4, 28.9, 22.6, 14.1.

**(*Z,Z*)-2,4-Hexadienedioic acid diethyl ester (6f).** Ethyl (*Z*)- $\beta$ -iodoacrylate (0.54 g, 2.24 mmol, 2.00 equiv) dissolved in NMP (3 mL) at rt was sparged with  $\text{N}_2$  for 0.5 h, then CuTC (0.99 g, 5.19 mmol, 4.34 equiv) was added in one portion. After 1 h, the reaction mixture was passed through a pad of neutral alumina using  $\text{Et}_2\text{O}$  as eluent. The solution was concentrated and the residue was extracted with ether (3 x 25 mL) from water (35 mL). The organic layers were combined and washed with water (3 x 15 mL). The solution was dried ( $\text{MgSO}_4$ ) and concentrated at reduced pressure to a yellow solid. Purification by crystallization gave (*Z,Z*)-2,4-hexadienedioic acid diethyl ester as a white solid (0.21 g, 1.06 mmol, 89%): mp 55-56 °C (1:1 hexane/diethyl ether); IR ( $\text{CDCl}_3$ , KCl,  $\text{cm}^{-1}$ ) 2987 (s), 2258 (s), 1715 (s), 1591 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.92 (dd,  $J = 8.1, 1.8$  Hz, 2 H), 6.14 (dd,  $J = 8.1, 1.8$  Hz, 2 H), 4.24 (q,  $J = 7.2$  Hz, 4 H), 1.36 (t,  $J = 7.2$  Hz, 6 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta$  165.6, 137.8, 124.2, 60.4, 14.2. Anal. Calcd for  $\text{C}_{10}\text{H}_{14}\text{O}_4$ : C, 60.59; H, 7.12. Found: C, 60.64; H, 7.10.

**3,3'-Bi(5,5-dimethyl-2-cyclohexen-1-one) (6g).** 5,5-Dimethyl-3-iodo-2-cyclohexen-1-one (0.38 g, 1.52 mmol, 1.00 equiv) and CuTC (0.786 g, 4.12 mmol, 2.71 equiv) in NMP (5 mL) at rt for 1 h gave product (0.146 g, 0.59 mmol, 78%) as a yellow solid after crystallization: mp 184-185 °C (1:1 ether/hexane) (*Lit.*<sup>23</sup> 184.5-185.5 °C). IR ( $\text{CDCl}_3$ , KCl,  $\text{cm}^{-1}$ ) 2964 (s), 1661

(s), 1586 (w);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  6.27 (s, 2 H), 2.38 (s, 4 H), 2.28 (s, 4 H), 1.04 (s, 12 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta$  199.9, 154.5, 126.8, 51.0, 40.1, 33.3, 28.3.

**6-Methyl-6,7-dihydro-5H-dibenzo[c,e]azepine.** Bis-(2-Iodobenzyl)methylamine (0.93 g, 2.00 mmol, 1.00 equiv) in NMP (10 mL) was added dropwise through a syringe pump to a slurry of CuTC (1.14 g, 6.00 mmol, 3.00 equiv) in NMP (15 mL) under nitrogen. After stirring 15 h at room temperature, workup as for 2,2'-biphenyl-N,N,N',N'-tetramethyldimethylamine (above), and flash chromatography (alumina, 2 x 15 mm, 1st: 200 mL hexane; 2nd: 10% EtOAc/hexane), 6-methyl-6,7-dihydro-5H-dibenzo[c,e]azepine was isolated as a viscous pink oil (0.368 g, 1.760 mmol, 88%): TLC (alumina, 30% EtOAc/hexane,  $R_f$  = 0.40); IR ( $\text{CH}_2\text{Cl}_2$ , KCl,  $\text{cm}^{-1}$ ): 3069 (w), 3037 (m), 2942 (s), 2844 (w), 2792 (s), 1480 (w), 1467 (w), 1450 (m), 1370 (w), 1078 (m), 1025 (w).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.54-7.39 (m, 8 H), 3.40 (s, 4 H), 2.48 (s, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  140.8, 134.4, 129.4, 127.8, 127.39, 127.37, 57.1, 42.9. Anal. Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}$ : C, 86.08; H, 7.22; N, 6.69. Found: C, 85.95; H, 7.23; N, 6.73.

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