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Efficient Method for the Synthesis of Hetarenoindanones Based on 3-Arylhetarenes and Their Conversion into Hetarenoindenes

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Abstract: A series of hetarenoindanones have been prepared by direct double metalation of the appropriate 3-phenylhetarene with butyllithium in the presence of TMEDA followed by treatment of the resulting dilithium compound with ethyl *N*,*N*-dimethylcarbamate. All hetarenoindanones were reduced according to Wolff−Kishner by hydrazine in the presence of KOH to the corresponding hetarenoindenes.

In recent years, indene derivatives in which the cyclopentadienyl ring is annelated to a five-membered heterocycle (hetarenoindenes)[1] have found increasing application in the synthesis of ligands for transition metal complexes.[2,3]

A general method for the synthesis of hetarenoindenes is reduction of the corresponding hetarenoindanones, which usually proceeds rather smoothly and gives products in good yields. However, the main method for the synthesis of the starting hetarenoindanones consisting of intramolecular cyclization of 2-hetarylbenzoic acids and their derivatives under various conditions[4−7] (eq 1) suffers from a number of drawbacks such as low accessibility of these benzoic acids, sometimes unpredictable reaction route,[8] and relatively low yields in the case of furan derivatives.[5] According to some known methods for the synthesis of cyclic ketones, the carbonyl group is introduced by direct carbonylation. For example, a number of hetarenoindanones with various heteroatoms have been prepared by palladium-catalyzed cyclocarbonylation of phenylhetarenes containing a halogen (Br or I) either in the heterocycle or in the phenyl group[9] (eq 2) (Scheme 1).

We developed a new, efficient method for the synthesis of ketones in which readily available 3-arylhetarenes are involved in cyclocarbonylation. The essence of this method is direct double metalation of 3-arylhetarene with butyllithium in the presence of TMEDA, similar to the reaction reported for biphenyl,[10] and treatment of the resulting dilithium salt with ethyl *N*,*N*-dimethylcarbamate as a carbonylating reagent (Scheme 2). This reagent, like other *N*,*N*-disubstituted carbamates, is also employed successfully for the synthesis of acyclic dithienyl ketenes.[11] Since monometalation is apparently the rate-determining step in the preparation of the dilithium derivative of biphenyl and the heterocycle is metalated more readily than benzene,[12] we expected that the yields of the dilithium derivatives would be higher in the case of 3-phenylhetarenes than with biphenyl.

The dilithium derivatives of phenylhetarenes were prepared in situ by treatment of compounds **1a**−**e** in ether with 2 equiv of BuLi in hexane in the presence of 2 equiv of TMEDA. Treatment of a part of the reaction mixture with D_2O has shown that bimetalation of phenylhetarenes proceeds in a quantitative yield (according to ^1H and ^{13}C NMR), whereas the bimetalation of biphenyl (**1f**) and 4,4′-di-*tert*-butyl-1,1′-biphenyl (**1g**) according to a known procedure,[10] namely, by refluxing a mixture of the substrate and 2 equiv of TMEDA in a hexane solution of BuLi, occurs in a yield of only 50−60%.

The reaction of dilithium derivatives **1a**−**e** with ethyl *N*,*N*-dimethylcarbamate (eqs 3, 4) gave rise to the required hetarenoindanones **2a**−**e** (Scheme 3). The yields of ketones **2a**−**e** were 42−90%. The starting compound **1a** was synthesized by cyclization of *ω*-phenoxyacetophenone;[13] compounds **1b**−**e** were prepared by cross-coupling of 3-bromo-heterocycles with Grignard reagents in the presence of $NiCl_2$dppp as the catalyst.

The developed procedure was used to convert biphenyls **1f**,**g** into fluorenones **2f**,**g** (eq 5). The dilithium salt of biphenyl is quantitatively converted into the ketone, the yield of the product (50−60%) being determined only by the degree of bimetalation of the starting hydrocarbon (Scheme 3).

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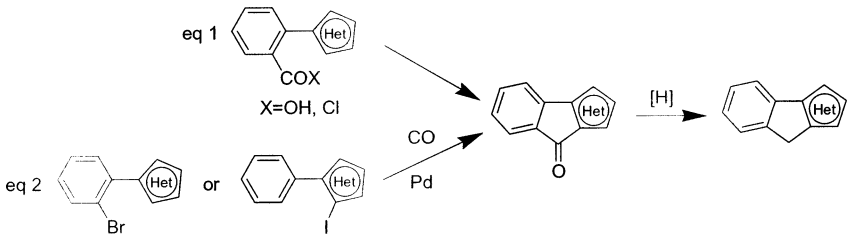
SCHEME 1



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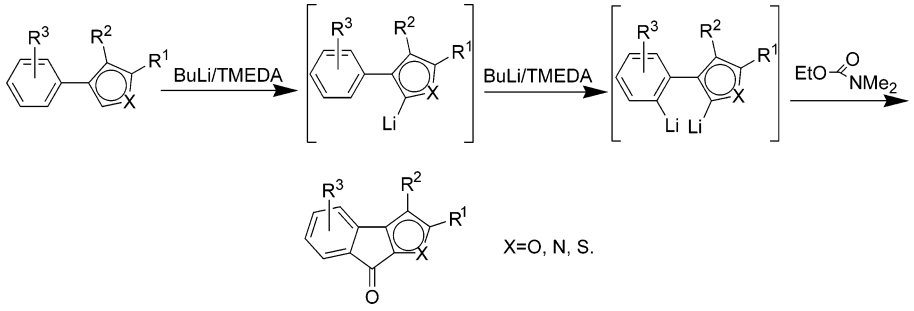

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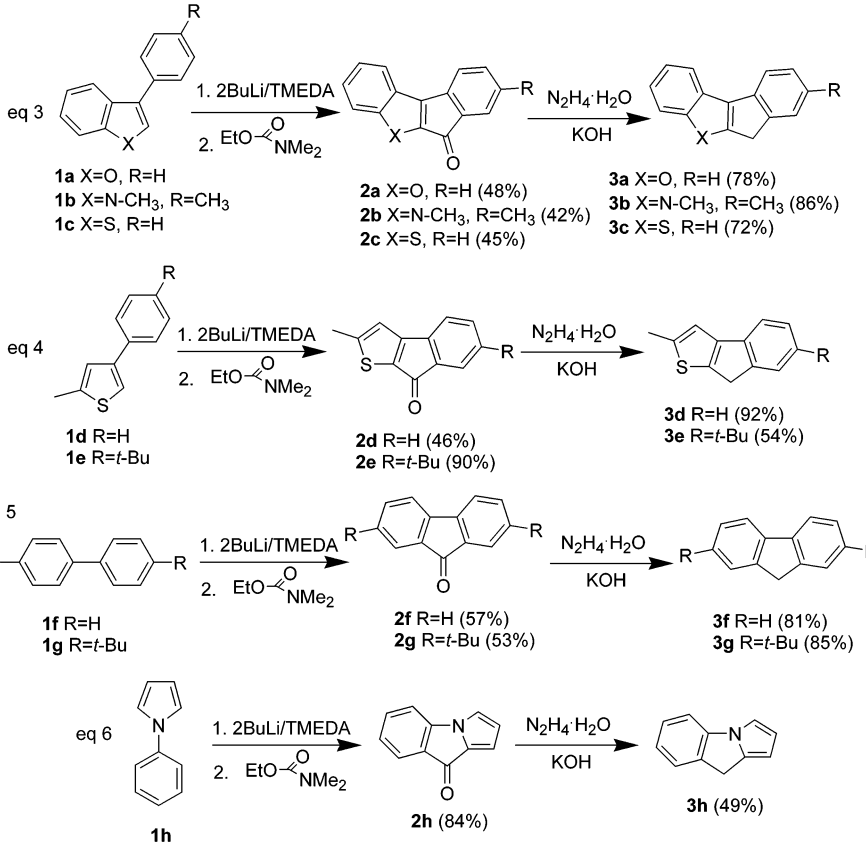

We demonstrated that our approach can be extended to *N*-arylpyrroles. 9*H*-Pyrrolo[1,2-*a*]indol-9-one (**2h**) was prepared from 1-phenyl-1*H*-pyrrole (**1h**) by the standard procedure (eq 6) (Scheme 3) .The bimetalation[14] of the latter and the reactions of its dilithium derivative[15] have been studied in detail previously.

The key method for the transformation of hetarenoindanones into hetarenoindenes is either Wolff−Kishner reduction of cyclic ketones by hydrazine in the presence of KOH[4] or reduction with the $LiAlH_4/AlCl_3$ system in ether.[16] We used both approaches; however, only the Wolff−Kishner reduction by hydrazine in the presence of KOH resulted in the desired hetarenoindenes **3a**−**h**

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(Scheme 3). The $LiAlH_4/AlCl_3$ reduction yielded the corresponding carbinol, which can further be converted into hetarenoindene by ionic hydrogenation, but only in a low yield; thus, this method is not expedient for the synthesis.

In conclusion, we have developed a general method for the synthesis of ketones, which allows one to prepare both hetarenoindanones with various heteroatoms (O, N, S) and fluorenones. All these can be easily reduced to hetarenoindenes or fluorenes. By using various Grignard reagents in the synthesis of the starting phenylhetarenes **1**, one can prepare ketones **2** (and, hence, hetarenoindenes **3**) with required substituents.

Experimental Section

Typical Procedure for Cross-Coupling of 3-Bromoheterocycle with Grignard Reagent Exemplified by the Synthesis of 1-Methyl-3-(4-methylphenyl)-1*H*-indole (1b). A solution of (4-methylphenyl)magnesiumbromide in ether (prepared from 0.6 g of Mg (0.025 mol) and 4.21 g of 1-bromo-4-methylbenzene (0.024 mol) in 40 mL of ether) was added with stirring to a mixture of 4.31 g (0.02 mol) of 3-bromo-l-methyl-l-*H*-indole and 0.22 g (0.0004 mol) of $NiCl_2$dppp in 20 mL of ether. The reaction mixture was stirred overnight and then treated with 10% aqueous NH_4Cl. The organic layer was separated, washed with 10% aqueous NH_4Cl, and dried over anhydrous Na_2SO_4. The solution was concentrated to give an oil that crystallized. The product was washed with methanol and dried. The yield was 2.2 g (49%) of a colorless crysalline solid. ^{1}H NMR ($CDC1_3$, 25 °C), δ: 8.14 (d, 1H, J = 8.2 Hz); 7.75 (d, 2H, J = 7.8 Hz); 7.50 (t, 1H, J = 8.2 Hz); 7.46−7.42 (m, 3H); 7.38 (t, 1H, J = 8.2 Hz); 7.31 (s, 1H); 3.90 (s, 3H); 2.58 (s, 3H). ^{13}C NMR ($CDC1_3$, 25 °C), δ: 137.3, 135.1, 132.6, 129.3, 127.1, 126.6, 126.1, 121.7, 119.8, 119.6, 116.5, 109.3, 32.5, 21.0. Anal. Calcd for $C_{16}H_{15}N$ (%): 86.84 C; 6.83 H; 6.33 N. Found (%): 86.75 C; 6.77 H; 6.48 N. Mp: 65−68 °C (lit.[17] 63 °C).

Typical Procedure of Carbonylation of 3-Phenyl-heterocycle Exemplified by the Synthesis of 5,8-Dimethylindeno[2,l-*b*]indol-6(5*H*)-one (2b). A solution of 2.19 g (0.00991 mol) of l-methyl-3-(4-methylphenyl)-1-*H*-indole **1b** and 3.24 mL (0.0218 mol) of TMEDA in 30 mL of ether was treated with 13.6 mL (0.0218 mol) of 1.6 M BuLi in hexane under stirring at −40 °C. Then, the reaction mixture was allowed to warm to room temperature, stirred for 4 h, cooled to −70 °C, and treated with 1.16 g (0.00991 mol) of ethyl *N*,*N*-dimethylcarbamate in 5 mL of ether. Then, the reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting mixture was treated with 50 mL of 10% aqueous NH_4Cl The violet precipitate was separated, washed twice with water, and dried. The yield was 1.04 g (42%). ^{1}H NMR ($CDC1_3$, 25 °C), δ: 7.58 (d, 1H J = 8.2 Hz); 7.27 (t, 1H J = 8.2 Hz); 7.22 (d, 1H J = 8.2 Hz); 7.14 (t, 1H J = 8.2 Hz); 7.09 (s, 1H); 6.98 (d, 1H J = 7.5 Hz); 6.92 (d, 1H J = 7.5 Hz); 3.80 (s, 3H); 2.26 (s, 3H). ^{13}C NMR ($CDC1_3$, 25 °C), δ: 184.7, 143.7, 137.3, 137.2, 136.7, 136.0, 133.6, 133.3, 125.6, 124.5, 121.5, 121.5, 120.9, 118.6, 111.2, 30.3, 21.1. Anal. Calcd for $C_{17}H_{13}N$ (%): 82.57 C; 5.30 H; 5.66 N. Found (%): 82.50 C; 5.41 H; 5.69 N. Mp: 145 °C.

Typical Procedure of Reduction of Hetarenoindanone to Hetarenoindene Exemplified by the Synthesis of 5,8-Dimethyl-5,6-dihydroindeno[2,l-*b*]indole (3b). A mixture of 1.04 g (0.0042 mol) of 5,8-dimethylindeno[2,l-*b*]indol-6(5*H*)-one **2b** and 1.12 mL (0.0224 mol) of hydrazine monohydrate in 20 mL of diethylene glycol was stirred at 80 °C for 1 h and then refluxed for 1 h. The resulting mixture was cooled to room temperature, treated with a solution of 1.2 g (0.0214 mol) of KOH in 5 mL of water, and refluxed for 2 h. The resulting mixture was poured into 100 mL of water, and the precipitate was filtered off, washed five times with 50 mL of water, and dried. The yield was 0.84 g (86%) of a greenish solid. ^{1}H NMR ($CDC1_3$, 25 °C), δ: 7.88 (m, 1H); 7.55 (d, 1H J = 7.4 Hz); 7.36 (m, 1H); 7.26 (m, 3H); 7.18 (d, 1H J = 7.4 Hz); 3.77 (s, 3H); 3.64 (s, 2H); 2.44 (s, 3H). ^{13}C NMR ($CDC1_3$, 25 °C), δ: 148.2, 142.4, 141.0, 137.5, 131.4, 127.4, 125.7, 121.8, 120.6, 119.8, 119.7, 119.1, 117.8, 109.7, 31.0, 29.9, 21.3. Anal. Calcd for $C_{17}H_{15}N$ (%): 87.52 C; 6.48 H; 6.00 N. Found (%): 87.48 C; 6.49 H; 6.03 N. Mp: 142−143 °C.

3-Phenyl-1-benzofuran (1a). ^{1}H NMR ($CDCl_3$, 25 °C) δ: 7.93 (d, 1H J = 7.4 Hz); 7.85 (s, 1H); 7.72 (d, 2H J = 6.9 Hz); 7.63 (d, 1H J = 7.4 Hz); 7.55 (t, 2H J = 6.9 Hz); 7.42−7.35 (m, 3H). Anal. Calcd for $C_{14}H_{10}O$ (%): 86.57 C; 5.19 H. Found (%): 86.52 C; 5.23 H. Taken from ref 1 in Supporting Information.

3-Phenyl-1-benzothiophene (1c). ^{1}H NMR ($CDCl_3$, 30 °C) δ: 7.37−7.42 (4H, m); 7.48 (2H, t, J = 7.5 Hz); 7.58 (2H, d, J = 7.8 Hz); 7.90−7.92 (2H, m). ^{13}C NMR ($CDCl_3$, 30 °C) δ: 140.7. 138.1, 137.9, 136.0, 128.7, 127.5, 124.4, 124.3, 123.4, 122.9. Anal. Calcd for $C_{14}H_{10}S$ (%): 79.69 C; 4.79 H. Found (%): 79.66 C; 4.81 H. Taken from ref 2 in Supporting Information.

2-Methyl-4-phenylthiophene (1d). ^{1}H NMR ($CDCl_3$, 30 °C) δ: 7.66 (d, 2H, J = 7.5 Hz), 7.47 (t, 2H, J = 7.5 Hz), 7.37 (t, 1H, J = 7.5 Hz), 7.28 (d, 1H J = 7.5 Hz), 7.16 (s, 1H), 2.61 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 30 °C) δ: 141.9, 140.3, 136.0, 128.6, 126.8, 126.1, 124.5, 117.9, 15.3. Anal. Calcd for $C_{11}H_{10}S$ (%): 75.82 C; 5.78 H. Found (%): 75.84 C; 5.79 H. Mp: 75−77 °C.

4-(4-*tert*-Butylphenyl)-2-methylthiophene (1e). ^{1}H NMR ($CDCl_3$, 30 °C) δ: 7.55 (d, 2H, J = 8.1 Hz), 7.46 (d, 2H, J = 8.1 Hz), 7.21 (s, 1H), 7.10 (s, 1H), 2.57 (s, 3H), 1.40 (s, 9H). ^{13}C NMR ($CDCl_3$, 30 °C) δ: 149.8, 141.9, 140.1, 133.3, 125.8, 125.5, 124.6, 117.4, 34.4, 31.2, 15.3. Anal. Calcd for $C_{15}H_{18}S$ (%): 78.21 C; 7.88 H. Found (%): 78.29 C; 7.92 H. Mp: 58−59 °C.

6*H*-Indeno[2,1-*b*][1]benzofuran-6-one (2a). ^{1}H NMR ($CDCl_3$, 25 °C) δ: 7.73 (d, 1H, J = 7.8 Hz); 7.55 (d, 1H, J = 7.8 Hz); 7.46 (t, 1H, J = 7.8 Hz); 7.41−4.29 (m, 3H); 7.21−7.14 (m, 2H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 180.4, 161.4, 154.5, 141.2, 135.9, 134.8, 133.7, 128.5, 128.5, 124.6, 123.9, 121.9, 121.9, 120.1, 113.64. Anal. Calcd for $C_{15}H_8O_2$ (%): 81.81 C; 3.66 H. Found (%): 81.78 C; 3.55 H. Mp: 105−106 °C (lit. 109−110 °C (from ref 3 in Supporting Information)).

6*H*-Indeno[2,1-*b*][1]benzothiophen-6-one (2c). ^{1}H NMR ($CDCl_3$, 25 °C) δ: 7.87 (m, 1H); 7.81 (m, 1H); 7.76−7.38 (m, 3H); 7.34 (m, 2H); 7.16 (m, 1H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 186.9, 152.7, 148.2, 140.1, 137.0, 136.9, 133.6, 131.8, 127.98, 127.4, 125.7, 124.4, 123.8, 123.7, 119.5. Anal. Calcd for $C_{15}H_8OS$ (%): 76.25 C; 3.41 H. Found (%): 76.11 C; 3.49 H. Mp: 198−199 °C (lit. 194−196 °C (from ref 4 in Supporting Information)).

2-Methyl-8*H*-indeno[2,1-*b*]thiophen-8-one (2d). ^{1}H NMR ($CDCl_3$, 30 °C) δ: 7.44 (d, 1H, J = 7.5 Hz), 7.29 (t, 1H, J = 7.5 Hz), 7.14 (t, 1H, J = 7.5 Hz), 7.07 (d, 1H, J = 7.5 Hz), 6.79 (d, 1H, J = 1.0 Hz), 2.55 (d, 3H, J = 1.0 Hz). ^{13}C NMR ($CDCl_3$, 30 °C) δ: 185.2, 159.0, 156.1, 139.6, 137.4, 134.1, 133.1, 127.8, 123.3, 119.1, 118.9, 16.4. Anal. Calcd for $C_{12}H_8OS$ (%): 71.97 C; 4.03 H. Found (%): 72.88 C; 4.00 H. Mp: 125−126 °C.

6-*tert*-Butyl-2-methyl-8*H*-indeno[2,1-*b*]thiophen-8-one (2e). ^{1}H NMR ($CDCl_3$, 30 °C) δ: 7.53 (d, 1H, J = 1.9 Hz), 7.29 (dd, 1H, J = 7.5 and 1.9 Hz), 7.01 (d, 1H, J = 7.5 Hz), 6.80 (d, 1H, J = 0.9 Hz), 2.55 (d, 3H, J = 0.9 Hz), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 30 °C) δ: 185.8, 159.1, 156.0, 151.5, 137.6, 136.8, 134.0, 129.2, 121.3, 118.9, 118.8, 34.8, 30.9, 16.5. Anal. Calcd for $C_{16}H_{16}$-OS (%): 74.96 C; 6.29 H. Found (%): 75.02 C; 6.39 H.

9*H*-Pyrrolo[1,2-*a*]indol-9-one (2h). ^{1}H NMR ($CDCl_3$, 30 °C) δ: 7.58 (d, 1H, J = 6.8 Hz), 7.44 (dt, 1H, J = 6.8 Hz, and 1.3 Hz), 7.16−7.08 (m, 3H), 6.78 (d, 1H, J = 3.7 Hz), 6.32 (dd, 1H, J = 3.7 and 2.6 Hz). ^{13}C NMR ($CDCl_3$, 30 °C) δ: 179.4, 143.6, 133.9, 131.8, 130.1, 125.2, 124.3, 119.3, 115.7, 113.7, 110.1. Anal. Calcd for $C_{11}H_7NO$ (%): 78.09 C; 4.17 H; 8.28 N. Found (%): 78.18 C; 4.06 H; 8.21 N. Mp: 121−122 °C (lit. 121−122 °C (from ref 3 in Supporting Information)).

6*H*-Indeno[2,1-*b*][1]benzofuran (3a). ^{1}H NMR ($CDCl_3$, 25 °C) δ: 7.83 (d, 1H, J = 7.4 Hz); 7.67 (d, 1H, J = 7.4 Hz); 7.60 (d, 1H, J = 7.4 Hz); 7.50 (d, 1H, J = 7.4 Hz); 7.39 (m, 3H); 7.24 (t, 1H, J = 7.4 Hz); 3.81 (s, 2H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 165.4, 160.2, 141.6, 137.3, 127.0, 124.9, 124.1, 124.0, 123.6, 123.3, 123.1, 119.5, 119.3, 112.1, 31.2. Anal. Calcd for $C_{15}H_{10}O$ (%): 87.36 C; 4.89 H. Found (%): 87.25 C; 4.80 H. Mp: 95−98 °C.

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6*H*-Indeno[2,1-*b*][1]benzothiophene (3c). ^{1}H ($CDCl_3$, 25 °C) δ: 8.20 (d, 1H, J = 7.8 Hz); 7.92 (d, 1H, J = 7.8 Hz); 7.88 (d, 1H, J = 7.8 Hz); 7.56 (d, 1H, J = 7.8 Hz); 7.52 (t, 1H, J = 7.8 Hz); 7.44 (t, 1H, J = 7.8 Hz); 7.39 (t, 1H, J = 7.8 Hz); 7.27 (t, 1H, J = 7.8 Hz); 3.97 (s, 2H). ^{13}C NMR ($CDCl_3$, 25°) δ: 146.2, 145.6, 144.8, 140.9, 139.5, 133.0, 126.7, 124.5, 124.5, 124.2, 123.7, 123.5, 121.7, 118.9, 35.2. Anal. Calcd for $C_{15}H_{10}S$ (%): 81.04 C; 4.53 H. Found (%): 80.91 C; 4.58 H. Mp: 112−113 °C (lit. 111−112 °C (from ref 5 in Supporting Information)).

2-Methyl-8*H*-indeno[2,1-*b*]thiophene (3d). ^{1}H NMR ($CDCl_3$, 30 °C) δ: 7.51 (m, 2H), 7.37 (t, 1H, J = 7.9 Hz), 7.23 (t, 1H, J = 7.9 Hz), 7.01 (m, 1H), 3.81 (s, 2H), 2.61 (d, 3H, J = 0.8 Hz). ^{13}C NMR ($CDCl_3$, 30 °C) δ: 146.8, 146.2, 143.4, 141.3, 139.5, 126.5, 124.5, 123.9, 118.7, 116.6, 34.6, 16.0. Anal. Calcd for $C_{12}H_{10}S$ (%): 77.37 C; 5.41 H. Found (%): 77.26 C; 5.36 H. Mp: 77−78 °C.

6-*tert*-Butyl-2-methyl-8*H*-indeno[2,1-*b*]thiophene (3e). ^{1}H NMR ($CDCl_3$, 30 °C) δ: 7.58 (s, 1H), 7.46−7.37 (m, 2H), 6.98 (s, 1H), 3.82 (s, 2H), 2.62 (s, 3H), 1.44 (s, 9H). Anal. Calcd for $C_{16}H_{18}S$ (%): 79.29 C; 7.49 H. Found (%): 79.21 C; 7.37 H. Mp: 139−141 °C.

9*H*-Pyrrolo[1,2-*a*]indole (3h). ^{1}H NMR ($CDCl_3$, 30 °C) δ: 7.47 (d, 1H, J = 6.8 Hz), 7.41−7.32 (m, 2H), 7.22−7.12 (m, 2H), 6.54 (t, 1H, J = 3.2 Hz), 6.25 (m, 1H), 3.91 (s, 2H). ^{13}C NMR ($CDCl_3$, 30 °C) δ: 141.0, 135.2, 134.8, 128.2, 127.2, 125.6, 122.8, 113.0, 109.5, 101.5, 28.8. Anal. Calcd for $C_{11}H_9N$ (%): 85.13 C; 5.85 H; 9.03 N. Found (%): 86.02 C; 5.80 H; 8.94 N. Mp: 91−92 °C (lit. 90−91 °C (from ref 6 in Supporting Information)).

Supporting Information Available: Spectral and analytical data and literature references for **1a**, **1c**−**e**, **2a**, **2c**−**e**, **2h**, **3a**, **3c**−**e**, and **3h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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