JOC The Journal of Organic Chemistry
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pubs.acs.org/joc

Synthesis of Substituted Thiophenes by Palladium-Catalyzed Heterocyclodehydration of 1-Mercapto-3-yn-2-ols in Conventional and Nonconventional Solvents

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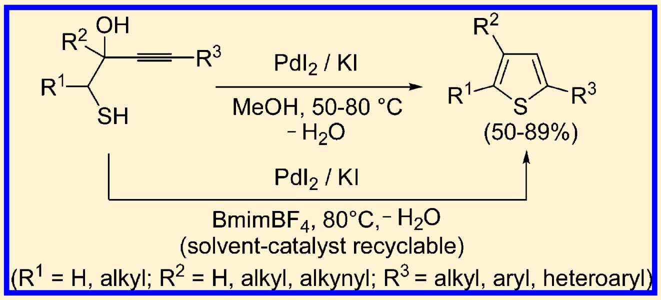
Supporting Information

ABSTRACT: A variety of readily available 1-mercapto-3-yn-2-ols **5** were conveniently converted into the corresponding thiophenes **6** in good to high yields in MeOH as the solvent at 50−100 °C in the presence of catalytic amounts (1−2%) of PdI_2 in conjunction with KI (KI:PdI_2 molar ratio = 10). The catalyst could be made recyclable employing an ionic liquid, such as $BmimBF_4$, as the solvent under suitable conditions.



Metal-catalyzed heterocyclodehydration of unsaturated substrates bearing a suitably placed nucleophilic group is a powerful methodology for the direct and atom-economical synthesis of heterocycles starting from readily available starting materials under essentially neutral conditions.[1,2] In this field, we have contributed several examples,[2] including the synthesis of quinolines from 1-(2-aminoaryl)-2-yn-1-ols[2f−h] and the synthesis of benzothiophenes from 1-(2-mercaptophenyl)-2-yn-1-ols.[2c]

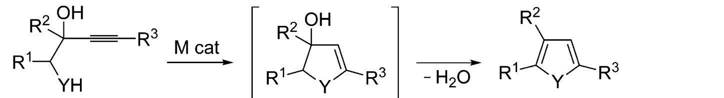
A particularly attractive process, recently developed by several research groups,[1b−e,g,j−l] including ours,[2d] consists in the formation of substituted furans **2** and pyrroles **4** by heterocyclodehydration of 3-yne-1,2-diols **1** and 1-amino-3-yn-2-ol derivatives **3**, respectively, as shown in Scheme 1. On the other hand, the analogous process starting from 1-mercapto-3-yn-2-ols **5** to obtain substituted thiophenes **6** has been reported in the literature in only one example, concerning the Au/Ag-catalyzed conversion of 1-mercapto-4-phenylbut-3-yn-2-ol to 2-phenylthiophene.[1c] In this work, we report a general method for the catalytic conversion of 1-mercapto-3-yn-2-ols **5** to substituted thiophenes **6**,[3,4] based on the use of a very simple catalytic system, consisting of PdI_2 in conjunction with an excess of KI, under neutral and mild reaction conditions.

We began our investigation with 2-mercapto-3-methylnon-4-yn-3-ol **5a**, which was initially allowed to react in MeOH (substrate concentration = 0.2 mmol of **5a** per mL of MeOH) at 80 °C in the presence of PdI_2 (1 mol %) and KI (10 mol %). After 2 h, analysis of the reaction mixture evidenced the formation of the desired 5-butyl-2,3-dimethylthiophene **6a** in 77% GLC yield. We then screened the reaction parameters, in order to find the optimal conditions for the preparation of **6a**. The specific results are reported in the Supporting Information (Table S1). From this brief optimization study, we found the best reaction conditions in term of yield of **6a**, which corresponded to the use of PdI_2 + 10KI as the catalyst, in MeOH as the solvent at 50 °C, with a substrate concentration of 0.5 mmol of **5a** per mL of MeOH. Under these optimized conditions, the reaction after 3 h led to the formation of **6a** in 88% isolated yield (Table 1, entry 1). The reaction was then applied to other differently substituted 1-mercapto-3-yn-2-ols **5b−i** (Table 1, entries 2−9).

The results reported in Table 1 illustrate that the R^3 substituent could be an alkyl as well an aryl group and that the heterocyclodehydration process was slower when the R^3 group was an aromatic ring substituted with an electron-releasing group at the *para* position (as in the case of 4-mercapto-3-methyl-1-*p*-tolylpent-1-yn-3-ol **5c**, entry 3) or a π-excessive heteroaromatic substituent (as in the case of 4-mercapto-3-methyl-1-(thiophen-3-yl)pent-1-yn-3-ol **5e**, entry 5). On the other hand, a *para*-electron-withdrawing group on R^3 caused an augmentation of the reaction rate, as shown by the results obtained with 4-mercapto-3-methyl-1-(4-nitrophenyl)-pent-1-yn-3-ol **5d** (entry 4). These results show that the heterocyclodehydration process is quite sensitive to the electrophilicity of the coordinated triple bond undergoing the intramolecular nucleophilic attack by the mercapto group, which leads to the formation of a vinylpalladium species as intermediate **I** (Scheme 2; anionic iodide ligands are omitted for clarity). The latter then undergoes protonolysis followed by dehydration or vice versa to give the final product with regeneration of PdI_2 (Scheme 2). When R^1 was hydrogen, as in the case of 1-mercapto-4-phenylbut-3-yn-2-ol **5f**, longer reaction times were required, and the product yield was

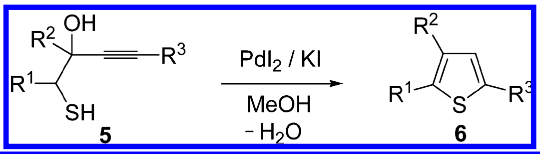
Received: September 7, 2012
Published: October 8, 2012

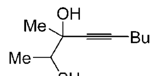
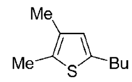
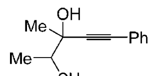
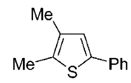
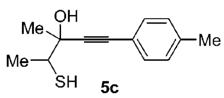
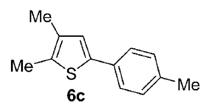
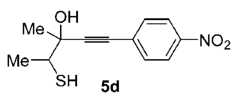
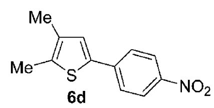
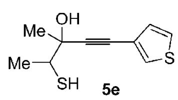
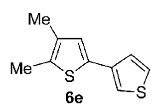
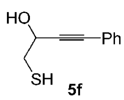
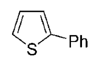
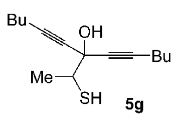
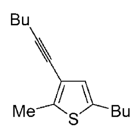
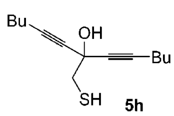
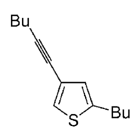
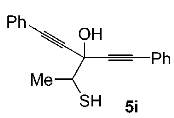
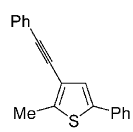
Scheme 1. Formation of Substituted Furans (2), Pyrroles (4), and Thiophenes (6) by Heterocyclodehydration of 3-Yne-1,2-diols (1), 1-Amino-3-yn-2-ol Derivatives (3), and 1-Mercapto-3-yn-2-ols (5), Respectively



1 (Y = O); **3** (Y = NR); **5** (Y = S) **2** (Y = O); **4** (Y = NR); **6** (Y = S)

Table 1. Synthesis of Substituted Thiophenes 6 by PdI_2/KI-Catalyzed Heterocyclodehydration of 1-Mercapto-3-yn-2-ols 5 in MeOH[a]



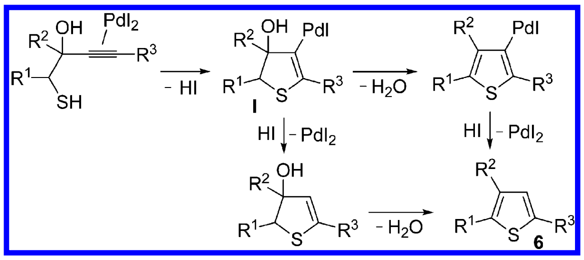
entry	5	PdI_2 (mol %)	T (°C)	t (h)	6	yield of 6[b] (%)
1	 5a	1	50	3	 6a	88
2	 5b	1	80	1	 6b	89
3	 5c	2	50	12	 6c	75
4	 5d	1	50	1	 6d	80
5	 5e	1	50	24	 6e	78
6	 5f	2	100	6	 6f	50
7	 5g	1	50	8	 6g	85
8	 5h	1	50	8	 6h	52[c]
9	 5i	2	80	3	 6i	85

[a]All heterocyclodehydration reactions were carried out in MeOH as the solvent (0.5 mmol of starting thiol **5** per mL of MeOH) in the presence of PdI_2 and KI (KI:PdI_2 molar ratio = 10). Conversion of thiol **5** was quantitative. [b]Isolated yield based on starting thiol **5**. [c]Substrate conversion was 74%.

somewhat lower (Table 1, entry 6). This result clearly shows that the reactive rotamer effect[5,6] is at work under our conditions.

We also tested the reactivity of 1-mercapto-2,2-dialkynyl-2-ols **5g–i**, bearing an additional alkynyl substituent at C-2. The results, reported in Table 1, entries 7–9, show that these substrates could be converted into the corresponding thiophenes **6g–i** in good yields without affecting the alkynyl substituent. As expected in view of the reactive rotamer effect, a substrate lacking an alkyl substituent at C-1, such as 7-

Scheme 2. Proposed Mechanism for the PdI_2/KI-Catalyzed Heterocyclodehydration of 1-Mercapto-3-yn-2-ols 5 to Substituted Thiophenes 6



(mercaptomethyl)trideca-5,8-diyn-7-ol **5h**, was less reactive than 1-mercapto-2,2-dialkynyl-2-ols **5g** and **5i**, bearing a secondary thiol group.

In order to verify the possibility to recycle the catalytic system, we also carried out the heterocyclodehydration reaction of **5** in an ionic liquid (IL) as the solvent.[7] We chose mercaptoalkynol **5b** as model substrate for testing the feasibility of the process in an IL. The results obtained by employing some ILs, with 1 mol % of catalyst at 80 °C for 24 h and with a substrate concentration of 0.2 mmol of **5b** per mL of IL, are shown in the Supporting Information (Table S2). The best result in terms of product yield (82%) was obtained with $BmimBF_4$, which was accordingly chosen as the reference IL solvent for the next experiments, aimed at assessing the recyclability of the catalyst-IL system. The results of these experiments, reported in the Supporting Information (Table S3), show that the catalyst-IL system could be recycled sixth times with comparable yields in several examples.

In conclusion, we have reported a convenient and general method for the heterocyclodehydration of readily available 1-mercapto-3-yn-2-ols **5** to substituted thiophenes **6**. The process is catalyzed by a simple catalytic system, consisting of PdI_2 in conjunction with an excess of KI, under mild reaction conditions (MeOH as the solvent at 50−80 °C) and can be applied to a variety of substrates, including 1-mercapto-2,2-dialkynyl-2-ols. The latter were converted into the corresponding thiophene derivatives without affecting the additional alkynyl substituent, which would allow further functionalization at the thiophene ring. Moreover, the catalytic method has been made recyclable using a suitable ionic liquid as the solvent, such as $BmimBF_4$.

■ EXPERIMENTAL SECTION

General Experimental Methods. Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ solutions at 300 and 75 MHz, respectively, with Me_4Si as an internal standard. Chemical shifts (δ) and coupling constants (J) are given in ppm and Hz, respectively. IR spectra were taken with an FT-IR spectrometer. Mass spectra were obtained using a GC−MS apparatus at 70 eV ionization voltage. All reactions were analyzed by TLC on silica gel 60 F_{254} or on neutral alumina and by GLC using a gas chromatograph and capillary columns with polymethylsilicone + 5% phenylsilicone as the stationary phase. Column chromatography was performed on silica gel 60 (70−230 mesh). Evaporation refers to the removal of solvent under reduced pressure.

Preparation of 1-Mercapto-3-alkyn-2-ols 5a−f. Substrates **5a**, **5b**, **5c**, and **5e** were prepared as we previously reported.[8] 1-Mercapto-4-phenylbut-3-yn-2-ol **5f** was prepared as described in the literature.[1c] 4-Mercapto-3-methyl-1-(4-nitrophenyl)pent-1-yn-3-ol **5d** was prepared as described below.

*Preparation of 4-Mercapto-3-methyl-1-(4-nitrophenyl)pent-1-yn-3-ol (**5d**).* To a cooled (−78 °C), stirred solution of BuLi (1.6 M in hexane) (28 mL, 44.8 mmol) in anhydrous THF (16 mL), maintained under nitrogen, was added dropwise a solution of *p*-nitrophenylacetylene (6.55 g, 44.5 mmol) in anhydrous THF (6 mL). To the resulting mixture was added, at the same temperature under nitrogen, a solution of LiBr (1.56 g, 18 mmol) in anhydrous THF (6 mL). After additional stirring for 0.5 h, a solution of 3-mercapto-2-butanone (1.77 g, 17.0 mmol) in anhydrous THF (5 mL) was added, at the same temperature under nitrogen. The resulting mixture was stirred for additional 2 h at −78 °C and then allowed to warm to room temperature. Saturated NH_4Cl (20 mL) and 1 N HCl (10 mL) were added, and the mixture was extracted with Et_2O (3 × 50 mL). The collected organic phases were washed with brine (40 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvent, the crude product was purified by column chromatography using 95:5 hexane/AcOEt as eluent, to give pure **5d** as a mixture of diastereoisomers A + B, A:B ratio = 3.0, determined by ^1H NMR. Yield: 4.06 g, starting from 1.77 g of 3-mercapto-2-butanone (95%). Yellow oil. IR (film) ν 3393 (m, br), 2975 (m), 2930 (m), 2870 (w), 2566 (vw), 2197 (vw), 1592 (m), 1510 (m), 1342 (s), 1108 (m), 854 (m), 752 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.28−8.21 [B (m, 2 H)], 8.17−8.09 [A (m, 2 H)], 7.65−7.59 [A (m, 2 H)], 7.55−7.49 [B (m, 2 H)], 4.11 [B (q, J = 7.2, 1 H)], 3.77 [A (q, J = 7.0, 1 H)], 1.47 [A (d, J = 7.0, 3 H)], 1.44 [A (s, 3 H) + B (s, 3 H)], 1.42 [B (distorted d, J = 7.2, 3 H)], 1.26 [B (d, J = 7.2, 1 H)], 1.24 [A (d, J = 7.0, 1 H)]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 140.4, 130.7, 129.2, 127.0, 126.6, 123.65, 123.59, 86.7, 84.2, 56.9, 55.2, 23.6, 18.6, 14.8, 12.3; GC−MS m/z 251 (absent) [M^+], 234 (14), 233 (100), 218 (56), 203 (11), 186 (14), 172 (36), 171 (36), 153 (12), 152 (11), 128 (9), 115 (13). Anal. Calcd for $C_{12}H_{13}NO_3S$ (251.30): C, 57.35; H, 5.21; N, 5.57; S, 12.76. Found: C, 57.41; H, 5.20; S, 12.74.

Preparation of 1-Mercapto-2,2-dialkynyl-2-ols 5g−i. Substrates **5h** and **5i** were prepared as we already reported.[8] 7-(1-Mercaptoethyl)trideca-5,8-diyn-7-ol **5g** was prepared as described below.

*Preparation of 7-(1-Mercaptoethyl)trideca-5,8-diyn-7-ol **5g**.* To a suspension of Mg turnings (0.6 g, 24.7 mmol) in anhydrous THF (3 mL), maintained under nitrogen at reflux was added pure ethyl bromide (0.8 mL) to start formation of the Grignard reagent. The remaining bromide was added dropwise in THF solution (2.0 mL of EtBr in 5 mL of THF; total amount of EtBr added, 4.09 g, 37.5 mmol). The mixture was then allowed to reflux for an additional 20 min. After cooling, the resulting solution of EtMgBr was transferred under nitrogen to a dropping funnel and added dropwise under nitrogen to a solution of 1-hexyne (3.27 g, 39.8 mmol) in anhydrous THF (6 mL) at 0 °C with stirring. After additional stirring at 0 °C for 15 min, the mixture was allowed to warm to room temperature and then was heated at 45 °C and stirred for 2 h. To the hot solution of the 1-hexynylmagnesium bromide thus obtained was added, dropwise and under nitrogen, a solution of ethyl 2-mercaptopropanoate (1.33 g, 9.94 mmol) in anhydrous THF (5 mL). The resulting mixture was allowed to stir at 45 °C for 2 h. After cooling to room temperature, saturated aqueous NH_4Cl (50 mL) and Et_2O (40 mL) were sequentially added, the phases were separated, and the aqueous phase was extracted with Et_2O (3 × 50 mL). The collected organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation of the solvent, product **5g** was purified by column chromatography on silica gel using 95:5 hexane/AcOEt as the eluent. Yield: 1.13 g, starting from 1.33 g of ethyl 2-mercaptopropanoate (45%). Yellow oil. IR (film) ν 3426 (m, br), 2957 (m), 2930 (m), 2231 (w), 1458 (m), 1251 (w), 1157 (w), 1041 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.21−3.08 (m, 1 H), 2.27 (t, J = 6.9, 2 H), 2.25 (t, J = 6.9, 2 H), 1.87 (d, J = 8.5, 1 H), 1.60−1.35 (m, 8 H), 1.51 (d, J = 6.9, 3 H), 0.92 (t, J = 7.3, 3 H), 0.91 (t, J = 7.3, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 85.7, 85.2, 79.2, 78.1, 67.8, 47.8, 30.5, 30.4, 22.0, 20.4, 18.4, 13.6; GC−MS m/z 252 (absent) [M^+], 236 (3), 192 (18), 191 (100), 190 (10), 161 (12), 148 (8), 147 (13), 135 (11), 128 (14), 115 (25), 107 (14), 103 (13), 93 (12), 92 (13), 91 (49), 80 (11), 77 (40). Anal. Calcd for $C_{15}H_{24}OS$ (252.42): C, 71.37; H, 9.58; S, 12.70. Found: C, 71.42; H, 9.57; S, 12.72.

dx.doi.org/10.1021/jo301943k | J. Org. Chem. 2012, 77, 9905−9909

General Procedure for the PdI_2-Catalyzed Heterocyclodehydration of 1-Mercapto-2,2-dialkynyl-2-ols 5 to Thiophenes 6. To a solution of **5** (1.0 mmol) (**5a**, 186 mg; **5b**, 206 mg; **5c**, 220 mg; **5d**, 251 mg; **5e**, 212 mg; **5f**, 178 mg; **5g**, 252 mg; **5h**, 292 mg, **5i**, 238 mg) in anhydrous MeOH (2 mL) was added PdI_2 (3.6 mg, 1.0×10^{-2} mmol, or 7.2 mg, 1.0×10^{-2} mmol, see Table 1) and KI (16.6 mg, 1.0×10^{-1} mmol, or 33.2 mg, 2.0×10^{-1} mmol) in this order under nitrogen in a Schlenk flask. The mixture was allowed to stir at the required temperature for the required time (see Table 1). After cooling, solvent was evaporated, and products were purified by transfer distillation (**6a**) or column chromatography on silica gel using as eluent 9:1 hexane/acetone (**6b**), 98:2 hexane/AcOEt (**6c**, **6g**), 95:5 hexane/AcOEt (**6d**, **6f**), pure hexane (**6e**, **6i**), or 98:2 hexane/acetone (**6h**).

5-Butyl-2,3-dimethylthiophene (6a).[9] Yield: 148 mg, starting from 186 mg of **5a** (88%) (Table 1, entry 1). Yellow oil. IR (film) ν 2961 (s), 2839 (w), 1464 (s), 1147 (w), 828 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.44, (s, 1 H, H-4), 2.69 (t, J = 7.7, 2 H), 2.27 (s, 3 H), 2.06 (s, 3 H), 1.66−1.53 (m, 2 H), 1.45−1.30 (m, 2 H), 0.92 (t, J = 7.3, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9, 132.3, 129.8, 126.9, 33.9, 29.6, 22.2, 13.9, 13.5, 12.9; GC−MS m/z 168 (26) [M^+], 125 (100), 111 (4), 91 (13), 77 (4). Anal. Calcd for $C_{10}H_{16}S$ (168.30): C, 71.36; H, 9.58; S, 19.05. Found: C, 71.40; H, 9.56; S, 19.04.

2,3-Dimethyl-5-phenylthiophene (6b).[10] Yield: 168 mg, starting from 206 mg of **5b** (89%) (Table 1, entry 2). Yellow amorphous solid, mp = 46−47 °C, lit.[10] 46−47 °C. IR (KBr) ν 2915 (m), 2855 (w), 1598 (w), 1502 (m), 1444 (m), 1172 (w), 755 (s), 699 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55−7.47 (m, 2 H), 7.35−7.26 (m, 2 H), 7.24−7.16 (m, 1 H), 6.99 (s, 1 H), 2.33 (s, 3 H), 2.12 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 134.7, 134.0, 131.4, 128.7, 126.8, 126.0, 125.3, 13.6, 13.1; GC−MS m/z 188 (100) [M^+], 187 (54), 173 (69), 153 (9), 128 (15), 115 (10), 102 (7), 77 (18). Anal. Calcd for $C_{12}H_{12}S$ (188.29): C, 76.55; H, 6.42; S, 17.03. Found: C, 76.60; H, 6.41; S, 16.99.

2,3-Dimethyl-5-p-tolylthiophene (6c). Yield: 152 mg, starting from 220 mg of **5c** (75%) (Table 1, entry 3). Yellow amorphous solid, mp = 46−47 °C. IR (KBr) ν 2918 (m), 1516 (m), 1447 (w), 811 (s), 757 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44−7.37 (m, 2 H), 7.16−7.08 (m, 2 H), 6.94 (s, 1 H), 2.33 (s, 3 H), 2.32 (s, 3 H), 2.12 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3, 136.6, 133.9, 132.0, 131.3, 129.4, 125.5, 125.3, 21.1, 13.6, 13.1; GC−MS m/z 202 (100) [M^+], 201 (54), 171 (5), 153 (5), 141 (4), 128 (6), 115 (6), 101 (5). Anal. Calcd for $C_{13}H_{14}S$ (202.32): C, 77.18; H, 6.97; S, 15.8. Found: C, 77.26; H, 6.95; S, 15.79.

2,3-Dimethyl-5-(4-nitrophenyl)thiophene (6d). Yield: 182 mg, starting from 251 mg of **5d** (78%) (Table 1, entry 4). Yellow amorphous solid, mp = 78−79 °C. IR (KBr) ν 1594 (m), 1514 (m), 1446 (s), 1102 (w), 851 (m), 736 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.29−8.21 (m, 2 H), 7.55−7.47 (m, 2 H), 7.07 (s, 1 H), 2.42 (s, 3 H), 2.13 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5, 141.5, 135.1, 131.1, 129.3, 123.6, 120.4 (2C), 13.7, 13.0; GC−MS m/z 232 (100) [M^+], 218 (56), 203 (11), 186 (16), 172 (37), 171 (37), 153 (12), 128 (10), 115 (14). Anal. Calcd for $C_{12}H_{11}NO_2S$ (233.29): C, 61.78; H, 4.75; N, 6.00; S, 15.8. Found: C, 61.82; H, 4.73; N,6.02; S, 15.79.

2,3-Dimethyl-5-(thiophen-3-yl)thiophene (6e). Yield: 151 mg, starting from 212 mg of **5e** (78%) (Table 1, entry 5). Yellow amorphous solid, mp = 52−53 °C. IR (KBr) ν 1638 (m), 1384 (m), 1080 (w), 823 (m), 771 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28−7.19 (m, 3 H), 6.85 (s, 1 H), 2.30 (s, 3 H), 2.10 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9, 134.1, 133.6, 131.4, 126.03, 125.96, 125.8, 118.4, 13.6, 13.0; GC−MS m/z 194 (100) [M^+], 193 (58), 179 (67), 161 (15), 134 (10), 115 (9), 97 (10). Anal. Calcd for $C_{10}H_{10}S_2$ (194.32): C, 61.81; H, 5.19; S, 33.00. Found: C, 61.80; H, 5.18; S, 33.02.

2-Phenylthiophene (6f).[1c] Yield: 80 mg, starting from 178 mg of **5f** (50%) (Table 1, entry 6). Yellow solid, mp = 34−35 °C, lit.[1c] 33−34 °C. IR (KBr) ν 2924 (m), 1600 (m), 1446 (m), 1072 (m), 755 (s), 693 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63−7.54 (m, 2 H), 7.39−7.20 (m, 5 H), 7.07−7.01 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 134.4, 128.9, 128.0, 127.4, 125.9, 124.8, 123.1; GC−MS m/z 160 (100) [M^+], 128 (15), 115 (42), 102 (7), 89 (10), 77 (6), 63 (8). Anal. Calcd for $C_{10}H_8S$ (160.24): C, 74.96; H, 5.03; S, 20.01. Found: C, 74.98; H, 5.01; S, 20.01.

5-Butyl-3-hex-1-ynyl-2-methylthiophene (6g). Yield: 200 mg, starting from 252 mg of **5g** (85%) (Table 1, entry 7). Yellow oil. IR (film) ν 2964 (s), 2931 (s), 2859 (m), 2360 (vw), 1465 (m), 1378 (w), 832 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.56 (s, 1 H), 2.66 (t, J = 7.5, 2 H), 2.42 (s, 3 H), 2.39 (t, J = 6.9, 2 H), 1.65−1.28 (m, 8 H), 0.94 (t, J = 7.3, 3 H), 0.91 (t, J = 7.3, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 139.6, 126.3, 119.7, 91.7, 75.5, 33.6, 31.1, 29.6, 22.1, 22.0, 19.2, 14.2, 13.8, 13.7; GC−MS m/z 234 (19) [M^+], 205 (4), 191 (100), 177 (8), 161 (16), 147 (42), 128 (14), 115 (31), 103 (9), 91 (16), 77 (12). Anal. Calcd for $C_{15}H_{22}S$ (234.40): C, 76.86; H, 9.46; S, 13.68. Found: C, 76.88; H, 9.45; S, 13.67.

2-Butyl-4-hex-1-ynylthiophene (6h). Yield: 115 mg, starting from 238 mg of **5h** (52%) (Table 1, entry 9). Yellow oil. IR (film) ν 2923 (s), 2853 (m), 2205 (vw), 1442 (m), 1384 (m), 752 (s), 686 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, J = 1.2, 1 H), 6.74−6.72 (m, 1 H), 2.74 (td, J = 7.5, 0.9, 2 H), 2.36 (t, J = 7.0, 2 H), 1.68−1.29 (m, 8 H), 0.93 (t, J = 7.3, 3 H), 0.91 (t, J = 7.3, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 126.8, 125.2, 122.3, 89.0, 76.1, 33.6, 30.9, 29.6, 22.1, 22.0, 19.1, 13.8, 13.7; GC−MS m/z 220 (45) [M^+], 205 (12), 191 (5), 177 (100), 163 (16), 147 (10), 135 (29), 115 (11), 91 (13), 77 (9). Anal. Calcd for $C_{14}H_{20}S$ (220.37): C, 76.30; H, 9.15; S, 14.55. Found: C, 76.32; H, 9.14; S, 14.54.

2-Methyl-5-phenyl-3-phenylethynylthiophene (6i). Yield: 233 mg, starting from 292 mg of **5i** (85%) (Table 1, entry 8). Yellow solid, mp = 124−125 °C. IR (KBr) ν 2957 (s), 2931 (s), 2872 (m), 2234 (vw), 1466 (m), 835 (m), 738 (m), 629 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.57−7.49 (m, 4 H), 7.39−7.23 (m, 7 H), 2.59 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 140.3, 133.9, 131.4, 128.9, 128.4, 128.1, 127.5, 125.5, 125.1, 123.4, 120.7, 91.6, 84.1, 14.6; GC−MS m/z 274 (86) [M^+], 258 (19), 239 (40), 215 (19), 197 (46), 187 (22), 171 (28), 163 (22), 152 (50), 139 (27), 121 (31), 102 (26), 89 (39), 77 (100). Anal. Calcd for $C_{19}H_{14}S$ (274.38): C, 83.17; H, 5.14; S, 11.69. Found: C, 83.15; H, 5.15; S, 11.70.

Preparation of Ionic Liquids. Ionic liquids $BmimNTf_2$[11] and BmimOTf[12] were prepared according to literature procedures. All other ionic liquids were prepared as we previously described.[2f]

General Procedure for the Recyclable PdI_2-Catalyzed Heterocyclodehydration of 1-Mercapto-2,2-dialkynyl-2-ols 5 to Thiophenes 6 in $BmimBF_4$. To a solution of **5** (0.4 mmol) (**5b**, 83 mg; **5e**, 85 mg; **5g**, 101 mg; **5h**, 95 mg) in $BmimBF_4$ (2 mL) were added PdI_2 (1.5 mg, 4.2×10^{-2} mmol) and KI (6.9 mg, 4.2×10^{-1} mmol) in this order under nitrogen in a Schlenk flask. The mixture was allowed to stir at 80 °C for 24 h. After cooling, the product was extracted with Et_2O (6 × 4 mL), and the residue (still containing the catalyst dissolved in the ionic liquid) was used as such for the next recycle (see below). The collected ethereal phases were concentrated, and products were purified as detailed in the general procedure in MeOH (see above). The isolated yields obtained in each experiment are reported in Table S3 (Supporting Information).

Recycling Procedure. To the residue obtained as described above, still containing the catalyst dissolved in the ionic liquid, was added a solution of **5** (0.4 mmol) in Et_2O (4 mL). Et_2O was removed under vacuum, and then the same procedure described above was followed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables S1−S3 and copies of ^1H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, Rome, Italy) is gratefully acknowledged (Progetto di Ricerca d'Interesse Nazionale PRIN 2008A7P7YJ). Thanks are due to the European Commission, FSE (Fondo Sociale Europeo) and Calabria Region for a fellowship grant to R.M.

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