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Synthesis of thiophenes in a deep eutectic solvent: heterocyclodehydration and iodocyclization of 1-mercapto-3-yn-2-ols in a choline chloride/glycerol medium

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ABSTRACT

The heterocyclodehydration and iodocyclization of readily available 1-mercapto-3-yn-2-ols has been performed in a deep eutectic solvent (DES), that is, ChCl/Gly (1:2 molar ratio; ChCl=choline chloride, Gly=glycerol), as a non-conventional green solvent. The processes, carried out at 50 °C for 8 h in the presence of the PdI_2/KI catalytic system or at room temperature for 5 h with 1.2 equiv of I_2, led to the formation of the corresponding thiophenes and 3-iodothiophenes in good to high yields. The DES/catalytic system could be easily recycled several times without appreciable loss of activity, after extraction of the thiophene product with hexane or Et_2O. The alkynylation reaction of α-mercapto ketones, necessary for the preparation of the alkynylthiol substrates, was also successfully accomplished in the above protic eutectic mixture competitively with protonolysis.

1. Introduction

Deep eutectic solvents (DESs) are an emerging new class of unconventional solvents, characterized by low toxicity and high eco-friendliness.[1] They are increasingly being used in synthetic organic chemistry as well as in process technology, particularly for their unusual solvent properties. Emerging applications are in the field of biotransformations, organocatalysis, organometallic chemistry, and metal-catalyzed reactions.[2–4] The use of DESs as possible alternative 'green' solvents for organic transformations, while of particular importance and attractiveness, has apparently to face the issue related with the chemical inertness of DESs, which are generally less chemically inert with respect to classical organic solvents and ionic liquids,[5] so the success in using DESs in a particular chemical transformation cannot be taken for granted.

In this work, we have studied both the Pd-catalyzed heterocyclodehydration[6] and the iodocyclization[7,8] of 1-mercapto-3-yn-2-ols **1** (readily available by alkynylation of α-mercapto ketones) to give thiophene derivatives[9] in DESs as safer and greener unconventional solvents, thereby expanding the field of metal-catalyzed reactions and introducing the use of DES in iodocyclizations.

2. Results and discussion

The first heterocyclization experiments were carried out using 4-mercapto-3-methyl-1phenylpent-1-yn-3-ol **1a** as the substrate, which was allowed to react in the presence of PdI_2 (2 mol %) and KI (20 mol %) in 1:2 ChCl/urea as the solvent (ChCl=choline chloride) at 50 °C for 8 h. After cooling, the reaction mixture was extracted with hexane and analyzed by GLC and TLC, which showed the presence of the substrate almost unreacted (7% conversion). We next changed the nature of one of the component of the eutectic mixture, and conducted the same experiment in a 1:2 ChCl/Gly mixture (Gly=glycerol). We were pleased to find that, using this DES, the formation of the desired thiophene **2a** now occurred in 80% yield after 8 h at 50 °C (Table 1, entry 1, run 1). This result testifies that DESs are not interchangeable with each other and that their nature can have a profound and unpredictable influence on the outcome of a particular reaction. The process leading to **2a** may be interpreted as occurring through 5-*endo*-*dig* intramolecular

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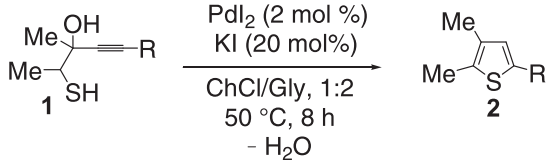
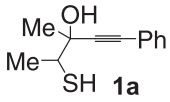
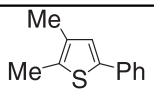
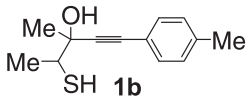
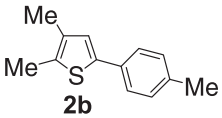
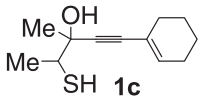
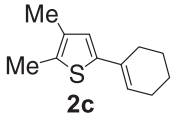
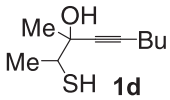
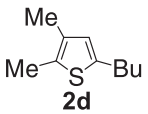
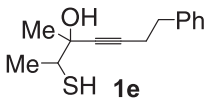
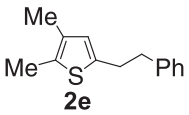
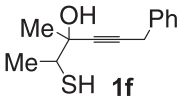
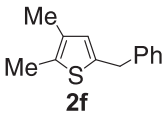
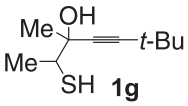
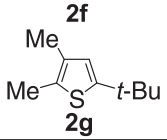
0040-4020/

Table 1
Synthesis of substituted thiophenes **2** by PdI_2/KI-catalyzed heterocyclization of 1-mercapto-3-alkyn-2-ols **1** in ChCl/Gly (1:2) as the solvent and recycling experiments[a]

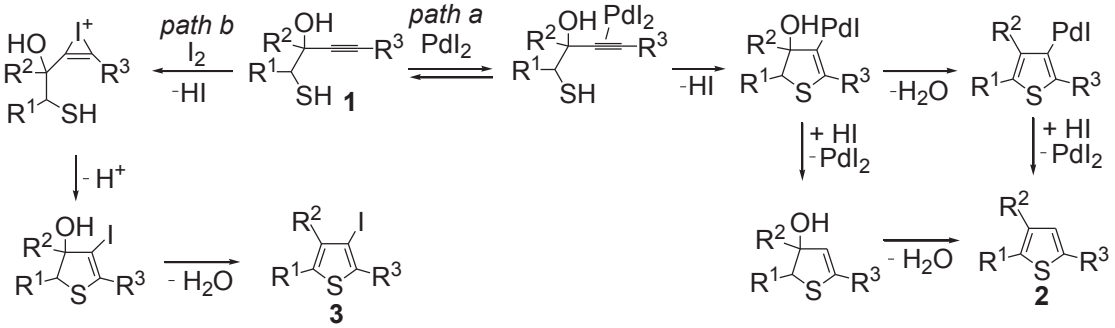


Entry	1	2	Yield of 2[b,c] (%)					
			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
1	 1a	 2a	80	80	79	80	79	78
2	 1b	 2b	80	79	79	78	78	79
3	 1c	 2c	69	68	68	67	69	67
4	 1d	 2d	78	77	76	76	75	77
5	 1e	 2e	83	82	82	83	82	82
6	 1f	 2f	73	73	72	73	73	72
7	 1g	 2g	65	63	64	64	63	64

[a] All reactions were carried out at 50 °C for 8 h in 1:2 ChCl/Gly mixture (ChCl=choline chloride; Gly=glycerol) as the solvent (0.20 mmol of starting **1** per mL of DES) in the presence of PdI_2 (2 mol %) in conjunction with KI (20 mol %). Conversion of **1** was quantitative in all cases.
[b] Isolated yield based on starting **1**.
[c] Run 1 corresponds to the first experiment, the next runs to recycles. See text for details.

attack of the mercapto group to the triple bond coordinated to the metal center, followed by protonolysis and dehydrative aromatization or vice versa (Scheme 1, path *a*; anionic iodide ligands are omitted for clarity).

We next verified the possibility of recycling the catalyst/solvent system, by adding fresh substrate to the residue obtained after extraction of the thiophene product with hexane and repeating the catalytic procedure. After 8 h, **2a** was formed again with the same



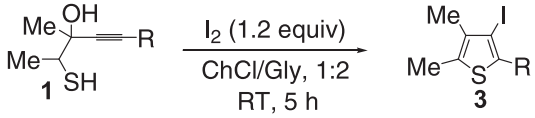
Scheme 1. Formation of substituted thiophenes **2** and 3-iodothiophenes **3** from 1-mercapto-3-yn-2-ols by PdI_2-catalyzed heterocyclodehydration (path *a*) or iodocyclization (path *b*), respectively.

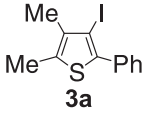
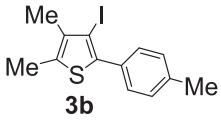
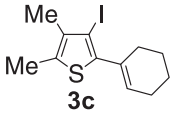
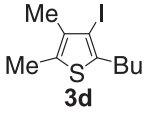
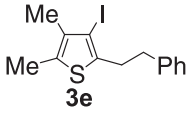
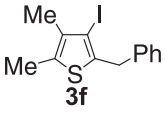
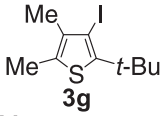
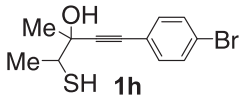
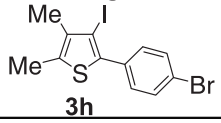
yield as that of the first experiment (Table 1, entry 1, run 2). The recycling procedure was repeated for additional four runs, with **2a** being consistently obtained in 78–80% yields (Table 1, entry 1, runs 3–6). The generality of the process was then assessed, by varying the nature of the substituent on the triple bond. As can be seen from the results reported in Table 1 (entries 2–7), satisfactory yields were obtained with all the substrates tested, bearing a *p*-tolyl (entry 2), a cyclohexen-1-yl (entry 3), or an alkyl substituent (entries 4–7) on the triple bond (including a sterically demanding *tert*-butyl group, entry 7). In all cases, the recyclability of the DES/catalyst system could be successfully achieved.

I_2 and in the absence of base, the iodocyclization of **1** proceeded smoothly under mild conditions (room temperature) to afford the corresponding 3-iodothiophenes in good yields (up to 80%) and with an excellent recyclability of the solvent (up to 5 additional runs, Table 2). The iodocyclization process may occur through the formation of an iodonium cation intermediate followed by cyclization and dehydration (Scheme 1, path *b*). As far as we know, this reaction represents the first example in the literature of an iodocyclization reaction carried out in a DES as the reaction medium.

In order to increase the green merit of the overall trans-

Table 2
Base-free synthesis of 3-iodothiophenes **3** by iodocyclization of 1-mercapto-3-alkyn-2-ols **1** in ChCl/Gly (1:2) as the solvent and recycling experiments[a]



Entry	1	2	Yield of 3[b,c] (%)					
			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
1	**1a**	 **3a**	79	80	80	79	79	79
2	**1b**	 **3b**	78	77	75	75	74	76
3	**1c**	 **3c**	69	68	68	67	69	67
4	**1d**	 **3d**	72	72	71	73	71	72
5	**1e**	 **3e**	76	74	75	74	76	75
6	**1f**	 **3f**	76	73	74	74	76	75
7	**1g**	 **3g**	65	63	64	63	62	63
8	 **1h**	 **3h**	62	62	60	61	60	61

[a] All reactions were carried out with I_2 (1.2 equiv) at 25 °C for 5 h in a 1:2 Chl/Gly (ChCl=choline chloride; Gly=glycerol) mixture as the solvent (0.20 mmol of starting **1** per mL of DES). Conversion of **1** was quantitative in all cases.
[b] Isolated yield based on starting **1**.
[c] Run 1 corresponds to the first experiment, the next runs to recycles. See text for details.

Considering the good results obtained in the Pd-catalyzed heterocyclization of 1-mercapto-3-yn-2-ols **1**, we next studied the reactivity of the same substrates under iodocyclization conditions in 1:2 ChCl/Gly as the reaction medium. With 1.2 equiv of

formation from commercially available α-mercapto ketones to the final thiophenes, and in consideration of the fact that nucleophilic additions to carbonyl compounds promoted by Grignard and organolithium reagents have been proved to be effective in

DESs,[3b,4d–f] we have also investigated the possibility of carrying out the alkynylation reactions for the preparation of 1-mercapto-3-yn-2-ols **1** in such unconventional solvents. Thus, we first subjected a cyclopentyl methyl ether (CPME) solution of phenylacetylene **4a** (1.2 mmol) to lithiation with *n*-BuLi (1.5 mmol). The resulting solution of the putative lithiated intermediate **4a**-**Li** was then added to a solution of 3-mercaptobutan-2-one **5** (0.6 mmol) in a 1:2 ChCl–Gly eutectic mixture (1 g) in the presence of 0.6 mmol of LiBr at room temperature and under air. Pleasingly, the corresponding alkynylation product **1a** was recovered with a yield of 50% after 10 min reaction time (Table 3, entry 1). When performed in other different eutectic mixtures, the reaction proved to be less effective, and afforded lower yields of **1a** (up to 28%, Table 3, entries 2–4). The nucleophilic addition of other lithium acetylides, bearing a *p*-tolyl (**4b**) or a butyl (**4d**) group, run in the above ChCl/Gly (1:2) eutectic mixture, furnished the expected 1-mercapto-3-yn-2-ols **1b** and **1d** in 61% and 41% yield, respectively (Table 3, entries 5 and 6). Although these yields are overall lower than those obtained in THF at low temperature,[7a] these results testify that alkynylation reactions of α-mercaptoketones can also be alternatively run in DESs as unconventional solvents, at RT under air, and competitively with protonolysis.

3. Conclusions

In conclusion, we have reported the S-heterocyclization and iodocyclization of 1-mercapto-3-yn-2-ols in choline chloride/glycerol both run in the deep eutectic solvent ChCl/Gly (1:2) as a non-conventional, safe, inexpensive and 'green' reaction medium. Substituted thiophenes **2** and 3-iodothiophenes **3** were efficiently obtained starting from readily available 1-mercapto-3-alkyne-2-ols **1**, which, in turn, could also be synthesized by carrying out the alkynylation of commercially available α-mercaptoketone **5** in the above DES. The heterocyclodehydration of **1** to thiophenes **2** was carried out using a simple catalytic system, consisting of PdI_2 in conjunction with 10 equiv of KI, which could be conveniently recycled together with the DES several times without loss of activity. The DES solvent could also be easily recycled in the iodocyclization process leading to 3-iodothiophenes **3**.

4. Experimental section

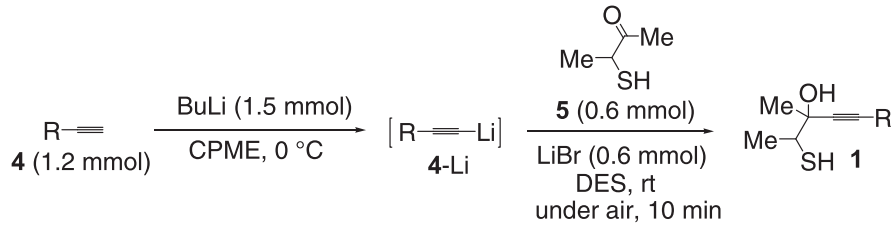
4.1. General experimental methods

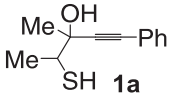
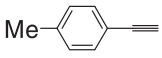
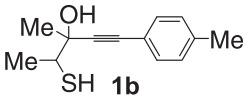
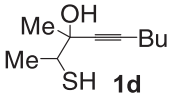
Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ solutions with a Bruker DPX Avance 300 spectrometer operating at 300 MHz and 75 MHz, respectively, with Me_4Si as internal standard. Chemical shifts (δ) and coupling constants (J) are given in ppm and in Hz, respectively. IR spectra were taken with a JASCO FTIR 4200 spectrometer. Mass spectra were obtained using a Shimadzu QP-2010 GC–MS apparatus at 70 eV ionization voltage. Microanalyses were carried out with a Thermo-Fischer Elemental Analyzer Flash 2000. All reactions were analyzed by TLC on silica gel 60 F_{254} (Merck) or on neutral alumina (Merck) and by GLC using a Shimadzu GC-2010 gas chromatograph and capillary columns with polymethylsilicone +5% polyphenylsilicone as the stationary phase (HP-5). Column chromatography was performed on silica gel 60 (Merck, 70–230 mesh). Evaporation refers to the removal of solvent under reduced pressure.

4.2. Preparation of substrates

Starting 1-mercapto-3-alkyne-2-ols **1a**–**h** were prepared as we already reported.[7a] Substrates **1a**, **1b**, and **1d** were also prepared by alkynylation of commercially available 3-mercaptobutan-2-one **5** in the ChCl/Gly (1:2) eutectic mixture (Table 3), as described below. All other materials were commercially available and were used without further purification.

Table 3
Addition reaction of various lithium acetylides **4**-Li to 3-mercaptobutan-2-one **5** in DES mixtures[a]



Entry	4	DES	1	Yield of **1** (%)
1	 **4a**	ChCl/Gly (1:2)	 **1a**	50[b]
2	**4a**	ChCl/urea (1:2)	**1a**	8[c]
3	**4a**	ChCl/D-sorbitol (1:1)	**1a**	28[c]
4	**4a**	ChCl/D-fructose (1:1)	**1a**	23[c]
5	 **4b**	ChCl/Gly (1:2)	 **1b**	61[b]
6	 **4d**	ChCl/Gly (1:2)	 **1d**	41[b]

[a] 1 g of DES per 1.2 mmol of **4**.
[b] Isolated yield based on **5**.
[c] Determined by ^{1}H NMR analysis of the crude reaction mixture.

4.3. Preparation of DESs

Eutectic mixtures of solvents [ChCl–Gly (1:2 mol/mol); ChCl/D-fructose (1:1 mol/mol); ChCl–urea (1:2 mol/mol); ChCl/D-sorbitol (1:1 mol/mol)] were prepared by heating with stirring up to 90 °C for 10–30 min the corresponding individual components until a clear solution was obtained.

4.4. Preparation of 1-mercapto-3-alkyne-2-ols 1a, 1b, and 1d in DES

A solution of the desired lithium acetylide was initially prepared by adding, at 0 °C and under nitrogen, 0.6 mL of a 2.5 M solution of *n*-BuLi in hexanes (1.5 mmol) to a stirred solution of the 1-alkyne **4** [1.2 mmol; phenylacetylene (**4a**) 124 mg; *p*-tolylacetylene (**4b**), 140 mg; 1-hexyne (**4d**), 100 mg] dissolved in cyclopentyl methyl ether (1 mL). To a stirred solution of commercially available 3-mercapto-2-butanone **5** (63 mg, 0.60 mmol) and LiBr (52 mg, 0.6 mmol) in ChCl–Gly (1:2) (1.0 g) was added, at RT and under air, a solution of the above alkynyllithium reagent (1.2 mmol). After stirring for 10 min, the reaction was quenched by adding a saturated aqueous solution of NH_4Cl and 1 N HCl (2 mL). The mixture was then extracted with Et_2O (3×10 mL), and the collected organic phases were washed with brine and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by column chromatography on silica gel (95:5 hexane/AcOEt as the eluent), to give the pure product as a ca. 1:1 mixture of diastereoisomers: 4-mercapto-3-methyl-1-phenylpent-1-yn-3-ol **1a** was a yellow oil (62 mg, 50%); 4-mercapto-3-methyl-1-*p*-tolylpent-1-yn-3-ol **1b** was a yellow oil (82 mg, 61%); 2-mercapto-3-methylnon-4-yn-3-ol **1d** was a yellow oil (46 mg, 41%). The spectroscopic properties agreed with those previously reported.[7a]

4.5. General procedure for the synthesis of substituted thiophenes 2 by PdI_2/KI-catalyzed heterocyclization of 1-mercapto-3-alkyn-2-ols 1 in ChCl/Gly (1:2) as the solvent (Table 1)

To a solution of **1** (0.42 mmol) (**1a**, 87 mg; **1b**, 93 mg; **1c**, 88 mg; **1d**, 78 mg; **1e**, 99 mg; **1f**, 93 mg; **1g**, 78 mg) in ChCl/Gly (1:2; 2 mL) were added PdI_2 (3.0 mg, 8.3×10^{-3} mmol) and KI (13.8 mg, 8.3×10^{-2} mmol) in this order under nitrogen in a Schlenk flask. The mixture was allowed to stir at 50 °C for 8 h. After cooling, the product was extracted with hexane (6×5 mL), and the residue (still containing the catalyst dissolved in the DES) was used as such for the next recycle (see below). The hexane phases were collected and, after evaporation of the solvent, products **2a**–**g** were purified by column chromatography on silica gel using 99: 1 hexane–AcOEt as the eluent: 2,3-dimethyl-5-phenylthiophene **2a** was a yellowish solid, mp 49–50 °C (yield: 63 mg, 80%); 2,3-dimethyl-5-*p*-tolylthiophene **2b** was a yellow solid, mp 47–49 °C (68 mg, 80%); 5-cyclohexenyl-2,3-dimethylthiophene **2c** was a yellow oil (56 mg, 69%); 5-butyl-2,3-dimethylthiophene **2d** was a yellow oil (55 mg, 78%); 2,3-dimethyl-5-phenethylthiophene **2e** was a yellow solid, mp=28–30 °C (75 mg, 83%); 5-benzyl-2,3-dimethylthiophene **2f** was a yellow solid, mp 38–39 °C (62 mg, 73%); 5-*tert*-butyl-2,3-dimethylthiophene **2g** was a yellow oil (46 mg, 65%). R_f values were as follows (pure hexane): **2a**, 0.54; **2b**, 0.51; **2c**, 0.75; **2d**, 0.75; **2e**, 0.43; **2f**, 0.52; **2g**, 0.72.

4.6. Recycling procedure

To the DES residue obtained as described above was added a solution of **1** (0.42 mmol) in Et_2O (3 mL). The Et_2O was removed under vacuum and then the same procedure described above was followed.

4.7. Characterization of thiophenes 2

Thiophenes **2a**, **2b**, and **2d** were characterized by spectroscopic comparison with the corresponding products obtained in our previous report.[6] All other thiophene derivatives were fully characterized by MS spectrometry, IR, ^1H NMR and ^{13}C NMR spectroscopies, and elemental analysis, as reported below.

*4.7.1. 5-Cyclohex-1-enyl-2,3-dimethylthiophene (**2c**).* Yellow oil. IR (film): ν=2957 (m), 2924 (m), 2863 (m), 1562 (w), 1456 (s), 1375 (m), 1167 (w), 1111 (w), 1007 (w), 742 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=6.60 (s, 1 H,=CH), 6.02 (s, 1 H,=CH), 2.41–2.28 (m, 1H, cyclohexenyl ring), 2.28 (s, 3H, Me), 2.18–2.08 (m, 1H, cyclohexenyl ring), 2.06 (s, 3H, Me), 1.81–1.54 (m, 4H, cyclohexenyl ring); ^{13}C NMR (75 MHz, $CDCl_3$): δ=142.0, 132.9, 131.2, 130.1, 124.2, 122.6, 27.2, 25.6, 22.8, 22.3, 13.6, 13.1; GC–MS: *m*/*z*=192 (100) [M^+], 191 (19), 178 (10), 177 (71), 164 (34), 163 (20), 149 (42), 135 (10), 125 (9), 115 (7), 91 (7), 77 (7); Anal. Calcd for $C_{12}H_{16}S$ (192.32): C, 74.94; H, 8.39; S, 16.67; found C, 74.91; H, 8.38; S, 16.69.

*4.7.2. 2,3-Dimethyl-5-phenethylthiophene (**2e**).* Yellow solid, mp 28–30 °C. IR (KBr): ν=2939 (m), 2916 (m), 2855 (m), 1492 (m), 1450 (m), 1151 (w), 1069 (w), 848 (m), 824 (m), 749 (s), 702 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=7.31–7.23 (m, 2H, aromatic), 7.22–7.13 (m, 3 H, aromatic), 6.45 (s, 1H,=CH), 3.05–2.85 (m, 4H, CH_2CH_2Ph), 2.27 (s, 3H, Me), 2.05 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$): δ=141.3, 139.6, 132.4, 130.1, 128.4, 128.3, 127.2, 126.0, 38.1, 31.9, 13.5, 12.9; GC–MS: *m*/*z*=216 (28) [M^+], 127 (7), 126 (11), 125 (100), 110 (2), 97 (3), 91 (16), 79 (2); Anal. Calcd for $C_{14}H_{16}S$ (216.34): C, 77.72; H, 7.45; S, 14.82; found C, 77.69; H, 7.48; S, 14.81.

*4.7.3. 5-Benzyl-2,3-dimethylthiophene (**2f**).* Yellow solid, mp 38–39 °C. IR (KBr): ν=2914 (w), 2854 (w), 1498 (m), 1462 (m), 1442 (w), 1203 (w), 1072 (w), 1029 (w), 831 (m), 754 (s), 687 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=7.40–7.30 (m, 5H, aromatic), 6.45 (s, 1H,=CH), 4.01 (s, 2H, CH_2Ph), 2.25 (s, 3H, Me), 2.04 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$): δ=140.6, 139.0, 132.6, 131.1, 128.6, 128.5, 128.0, 126.3, 36.1, 13.5, 12.9; GC–MS: *m*/*z*=202 (95) [M^+], 201 (39), 188 (16), 187 (100), 172 (8), 171 (6), 153 (8), 152 (6), 141 (4), 125 (32), 115 (7), 111 (4), 91 (10), 77 (4); Anal. Calcd for $C_{13}H_{14}S$ (202.32): C, 77.18; H, 6.97; S, 15.85; found C, 77.23; H, 6.99; S, 15.88.

*4.7.4. 5-tert-Butyl-2,3-dimethylthiophene (**2g**).* Yellow oil. IR (film): ν=2923 (s), 2851 (m), 1642 (m), 1464 (m), 1215 (w), 760 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=6.48 (s, 1 H,=CH), 2.27 (s, 3 H, Me), 2.06 (s, 3 H, Me), 1.33 (s, 9 H, *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$): δ=152.4, 132.0, 129.4, 124.2, 34.1, 32.4, 13.6, 12.9; GC–MS: *m*/*z*=168 (31) [M^+], 154 (13), 153 (10), 137 (6), 125 (8), 113 (8), 105 (2), 97 (2), 91 (4), 77 (3); Anal. Calcd for $C_{10}H_{16}S$ (168.30): C, 71.36; H, 9.58; S, 19.05; found C, 71.33; H, 9.55; S, 19.10.

4.8. General procedure for the synthesis of 3-iodothiophenes 3 by iodocyclization of 1-mercapto-3-alkyn-2-ols 1 in ChCl/Gly (1:2) as the solvent (Table 2)

To a solution of **1** (0.50 mmol) (**1a**, 103 mg; **1b**, 110 mg; **1c**, 105 mg; **1d**, 93 mg; **1e**, 117 mg; **1f**, 110 mg; **1g**, 93 mg; **1h**, 143 mg) in ChCl/Gly (1:2) (2.5 mL) was added I_2 (152 mg, 0.60 mmol) under nitrogen. The mixture was allowed to stir at 25 °C for 5 h and then extracted with Et_2O (6×5 mL). After evaporation of the solvent, the products **3a**–**h** were purified by column chromatography on silica gel using 99: 1 hexane–AcOEt as the eluent: 3-iodo-4,5-dimethyl-2-phenylthiophene **3a** was a yellow oil (124 mg, 79%); 3-iodo-4,5-dimethyl-2-*p*-tolylthiophene **3b** was a yellow solid, mp 54–55 °C (128 mg, 78%); 2-cyclohex-1-enyl-3-iodo-4,5-dimethylthiophene **3c** was a yellowish solid, mp 25–26 °C (110 mg, 69%); 2-butyl-3-

iodo-4,5-dimethylthiophene **3d** was a yellow solid, mp 115–117 °C (106 mg, 72%); 3-iodo-4,5-dimethyl-2-phenethylthiophene **3e** was a yellow oil (130 mg, 76%); 2-benzyl-3-iodo-4,5-dimethylthiophene **3f** was a yellow oil (125 mg, 76%); 2-*tert*-butyl-3-iodo-4,5-dimethylthiophene **3g** was a yellow solid, mp 114–115 °C (96 mg, 65%); 2-(4-bromophenyl)-3-iodo-4,5-dimethylthiophene **3h** was a colorless solid, mp 104–105 °C (122 mg, 62%). R_f values were as follows (pure hexane): **3a**, 0.76; **3b**, 0.69; **3c**, 0.81; **3d**, 0.83; **3e**, 0.63; **3f**, 0.63; **3g**, 0.82; **3h**, 0.72.

4.9. Recycling procedure

To the DES residue obtained as described above was added a solution of **1** (0.50 mmol) and I_2 (0.60 mmol) in Et_2O (3 mL). The Et_2O was removed under vacuum and then the same procedure described above was followed.

4.10. Characterization of thiophenes 3

All thiophenes **3a**–**h** were characterized by spectroscopic comparison with the corresponding products obtained in our previous report.[7a]

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Supplementary data

Supplementary data (^1H and ^{13}C NMR spectra for all products) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.05.062.

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