Supporting Information for

A novel synthesis of substituted thiophenes by palladium-catalyzed cycloisomerization of (*Z*)-2-en-4-yne-1-thiols

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Experimental Section

General Methods. ^{1}H NMR spectra were run on $CDCl_3$ solutions with Me_4Si as internal standard and recorded at 300 MHz. Chemical shifts and coupling constants (J) are given in ppm (δ) and in Hz, respectively. IR spectra were taken on a FT-IR spectrometer. Mass spectra were obtained at 70 eV on a GC-MS apparatus. Microanalyses were performed at our analytical laboratory. DMA was dried over 4 Å molecular sieves and distilled under nitrogen before use. Diethyl ether and THF were dried over $LiAlH_4$ and distilled under nitrogen over $LiAlH_4$ before use. Commercial 1,2-dichloroethane was washed with a 10% KOH solution, then allowed to stand overnight over $CaCl_2$, refluxed over P_2O_5 for 5 h and eventually distilled under nitrogen over P_2O_5. All reactions were carried out under nitrogen and were monitored by TLC on silica gel 60 F_{254} or by GLC using 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.

Starting (*Z*)-2-en-4-yne-1-thiols **1** and their precursors were prepared as described below. All other materials were commercially available and were used without further purification. Known compounds 3-methylnon-1-en-4-yn-3-ol,[1] 3-methyl-5-phenylpent-1-en-4-yn-3-ol,[2] (*Z*)-5-methylhept-4-en-6-yn-3-ol,[3] (*Z*)-3-methyl-1-phenylpent-2-en-4-yn-1-ol,[3] (*Z*)-3-methylpent-2-en-4-yn-1-ol,[4] (*Z*)-2-ethylnon-2-en-4-yn-1-ol,[2] 2,3-dimethylthiophene[5], and 2-benzyl-3-methylthiophene[6] were characterized by comparison with literature data.

Preparation of substrates. (*Z*)-2-En-4-yne-1-thiols were prepared by reductive cleavage of the corresponding thioacetates with $LiAlH_4$. The latter were obtained from suitable enynol precursors following different methods depending on the substitution pattern. Thioacetates substituted at C-3 and C-5 were prepared by addition of alk-1-ynes $R^4C{\equiv}CH$ to vinyl ketones $H_2C{=}CH(CO)R^3$ to give 1-en-4-yn-3-ols, as already reported,[2] followed by reaction with AcSH in the presence of anhydrous ZnI_2.[7] This method did not work with $R^4 = H$; an alternative route involved the reaction between 3-substituted (*Z*)-2-

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[5] (a) Cagniant, M.P.; Faller, P.; Cagniant, P. *Bull. Soc. Chim. Fr.* **1961**, 2410-2417; (b) Damste, J.S.S.; Kock-van Dalen, A.C.; De Leeuw, J.W.; Schenck, P.A. *Tetrahedron Lett.* **1987**, *28*, 957-960.

[6] Hall, S.S.; Farahat, S.E. *J. Heterocycl. Chem.* **1987**, *24*, 1205-1213.

[7] Transformation of tertiary, benzylic and allylic alcohols into the corresponding thioesters by ZnI_2-catalyzed reaction with AcSH has been reported some years ago: Gauthier, J.Y.; Bourdon, F.; Young, R. N. *Tetrahedron Lett.* **1986**, *27*, 15-18. In our case, allylic isomerization occurs with exclusive formation of the most stable 2-en-4-yn rather than 4-en-1-yn derivative. This result is in agreement with the proposed S_N1 mechanism. A mixture of *Z* and *E* isomers was obtained by this method, the more thermodynamically stable *Z* isomer being the most predominant product.

en-4-yn-1-ols and AcSH under Mitsunobu conditions.[8] The latter procedure was also used for the preparation of thioacetates substituted at C-2, while the ZnI_2-catalyzed reaction was the easiest way for obtaining thioacetates substituted at C-1, starting from the corresponding (*Z*)-2-en-4-yn-1-ols.[9]

Reaction between 1-en-4-yn-3-ols or (*Z*)-2-en-4-yn-1-ols and thioacetic acid in the presence of ZnI_2. The procedure described by Gauthier [5] was employed. To a solution of enynol (50 mmol) in anhydrous 1,2-dichloroethane (100 mL) was added anhydrous ZnI_2 (8.0 g, 25 mmol) and the resulting mixture was stirred at rt for 15 min. Thioacetic acid (4.6 g, 60 mmol) was then added followed by stirring for 30 min. The reaction mixture was quenched with water, extracted with CH_2Cl_2 and the combined organic layers were dried over $CaCl_2$ and evaporated. Products were purified by column chromatography [thioacetic acid (*Z*)-*S*-(3-methylnon-2-en-4-ynyl) ester, hexane/AcOEt = 9:1, 75%; thioacetic acid (*Z*)-*S*-(3-methyl-5-phenylpent-2-en-4-ynyl) ester, hexane/AcOEt = 98:2, 60%; thioacetic acid (*Z*)-*S*-(1-ethyl-3-methylpent-2-en-4-ynyl) ester, hexane/AcOEt = 99:1, 59%; thioacetic acid (*Z*)-*S*-(3-methyl-1-phenylpent-2-en-4-ynyl) ester, hexane-AcOEt = 98:2, 76%].

Reaction between (*Z*)-2-en-4-yn-1-ols and AcSH under Mitsunobu conditions. The method of Volante [8] was employed. To a cooled (0 °C) solution of PPh_3 (26.2 g, 100 mmol) in anhydrous THF (280 mL) was added dropwise DEAD (17.4 g, 100 mmol) and the resulting mixture was allowed to stir at 0 °C until the formation of a white precipitate was observed (typically, 15-30 min.). A solution of the enynol (50 mmol) and AcSH (7.6 g, 100 mmol) in anhydrous THF (140 mL) was added dropwise at

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[8] Transformation of alcohols into thioesters under Mitsunobu conditions has been reported: Volante, R.P. *Tetrahedron Lett.* **1981**, *22*, 3119-3122.

0 °C followed by stirring at 0 °C for 1 h and at 25 °C for 1 h. The solvent was removed by distillation at atmospheric pressure (R^1 = R^2 = R^4 = H, R^3 = Me) or by rotary evaporation (R^1 = R^3 = H, R^2 = Et, R^4 = Bu) and the residue was purified by column chromatography [thioacetic acid (*Z*)-*S*-(3-methylpent-2-en-4-ynyl) ester, hexane/AcOEt = 85:15, 81%; thioacetic acid (*Z*)-*S*-(2-ethylnon-2-en-4-ynyl) ester, hexane/AcOEt = 98:2, 59%].

Reductive cleavage of thioacetic acid (*Z*)-*S*-(2-en-4-ynyl) esters into (*Z*)-2-en-4-yne-1-thiols with $LiAlH_4$. The procedure decribed by Volante [8] was employed. To a cooled (– 30 °C) suspension of $LiAlH_4$ (550 mg, 14.5 mmol) in anhydrous ether (25 mL) was added dropwise a solution of the thioacetic ester (29 mmol) in anhydrous ether (46 mL) with stirring. After being stirred at rt for 30 min., the reaction mixture was quenched with 10% HCl, extracted with ether and the combined organic layers washed with water and dried over Na_2SO_4. After the solvent was removed by distillation at atmospheric pressure (**1a**, **1b**) or in vacuo (**1c**, **1d**, **1e**, **1f**), products were purified by distillation (**1a**, bp 40 °C/10 mmHg, 46%; **1b**, bp 27°C/4 mmHg, 61%) or column chromatography (**1c**, hexane, 48%; **1d**, hexane, 50%; **1e**, hexane, 58%; **1f**, hexane/AcOEt = 98:2, 89%).

General procedure for cycloisomerization reactions and separation of products. Reactions were carried out on a 5-10 mmol scale based on (*Z*)-enynethiol **1**. Solvent, substrate : PdI_2 molar ratio, reaction temperature and time, yield of thiophenes **2** are indicated in Table 1. In a typical experiment, PdI_2 and KI (2 mol per mol of palladium) were added to pure **1** or to a solution of **1** in dry DMA in a Schlenk flask with cooling. The resulting mixture was stirred at the temperature and for the time required to

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[9] Starting (*Z*)-2-en-4-yn-1-ols were prepared according to ref. 2.

obtain a satisfactory conversion, as shown by GLC and/or TLC analysis (Table 1). Low-boiling thiophenes **2a**, **2b** were purified by transfer distillation, all other products by column chromatography using hexane (**2c**, **2d**, **2e**) or hexane/AcOEt = 95:5 (**2f**) as eluent.

Characterization of products

Thioacetic acid (*Z*)-*S*-(3-methylpent-2-en-4-ynyl) ester. Yellow oil. IR (neat) 3287 (s), 2977 (w), 2951 (w), 2923 (w), 1687 (s), 1435 (m), 1354 (m), 1237 (w), 1136 (s), 957 (m), 627 (m) cm^{-1}; ^{1}H NMR δ 5.82-5.74 (m, 1 H, =CH), 3.74 (dq, J = 7.7, 0.9, 2 H, CH_2), 3.22-3.21 (m, 1 H, ≡CH), 2.33 [s, 3 H, CH_3(CO)], 1.88-1.85 (m, 3 H, CH_3C=) MS *m/e* 154 (4, M$^+$), 139 (28), 112 (14), 111 (75), 97 (20), 79 (26), 78 (13), 77 (57), 53 (14), 51 (28). Anal. Calcd for $C_8H_{10}OS$: C, 62.30; H, 6.54; S, 20.79. Found C, 61.68; H, 6.41; S, 21.35.

Thioacetic acid (*Z*)-*S* (1-ethyl-3-methylpent-2-en-4-ynyl) ester. Yellow oil. IR (neat) 3288 (m), 2967 (m), 2931 (w), 2875 (w), 1691 (s), 1457 (w), 1353 (w), 1114 (m), 952 (m), 630 (m) cm^{-1}; ^{1}H NMR δ 5.68-5.62 (m, 1 H, =CH), 4.52-4.42 (m, 1 H, C*H*CH_2), 3.25-3.24 (m, 1 H ≡CH), 2.31 [s, 3 H, CH_3(CO)], 1.89 (d, J = 1.5, 3 H, CH_3C=), 1.84-1.58 (m, 2 H, CH_2), 0.95 (t, J = 7.6, 3 H, CH_2CH_3); MS *m/e* 182 (M$^+$, 3), 167 (11), 153 (9), 140 (11), 139 (53), 125 (16), 111 (29), 107 (18), 105 (24), 92 (15), 91 (100), 79 (41), 77 (33), 65 (24), 53 (16), 51 (21). Anal. Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74; S, 17.59. Found C, 64.90; H, 7.61; S, 18.16.

Thioacetic acid (*Z*)-*S*-(3-methyl-1-phenylpent-2-en-4-ynyl) ester. Yellow oil. IR (neat) 3283 (m), 3059 (w), 3027 (w), 2920 (w), 1693 (s), 1493 (w), 1448 (w), 1352 (w), 1129 (s), 953 (m), 873 (w), 697 (w), 627 (m) cm^{-1}; ^{1}H NMR δ7.41-7.18 (m, 5 H on phenyl ring), 6.01-5.94 (m, 1 H, =CH), 5.79 (distorted d, *J* = 5.8, 1 H, CHS), 3.33-3.32 (m, 1 H, ≡CH), 2.31 [s, 3 H, CH_3(CO)], 1.91-1.89 (m, 3H, CH_3C=); MS *m/e* 230 (1, M$^+$), 187 (11), 156 (13), 155 (100), 154 (23), 153 (38), 152 (18), 129 (20), 128 (21), 127 (14), 115 (22), 77 (15), 51 (16). Anal. Calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13; S, 13.92. Found C, 71.55; H, 6.22; S, 14.17.

Thioacetic acid (*Z*)-*S*-(3-methylnon-2-en-4-ynyl) ester. Yellow oil. IR (neat) 2959 (m), 2933 (m), 2873 (w), 1695 (s), 1375 (w), 1355 (w), 1228 (m), 1135 (m), 956 (w), 628 (m) cm^{-1}; ^{1}H NMR δ5.63 (tq, *J* = 7.4, 1.5, 1 H, =CH), 3.72 (dq, *J* = 7.4, 1.0, 2 H, CH_2S), 2.39-2.30 (m, 2 H, CH_2C≡), 2.33 [s, 3 H CH_3(CO)], 1.84-1.82 (m, 3 H, CH_3C=), 1.60-1.35 (m, 4 H, CH_2C$H_2$$CH_3$), 0.93 (t, *J* = 7.3, 3 H, CH_2CH_3); MS *m/e* 210 (3, M$^+$), 168 (9), 167 (49), 135 (40), 125 (25), 111 (40), 107 (14), 105 (15), 99 (11), 97 (12), 93 (55), 92 (12), 91 (70), 81 (14), 79 (42), 78 (11), 77 (57), 69 (11), 67 (13), 65 (25), 63 (11), 55 (40), 53 (17), 51 (20). Anal. Calcd for $C_{12}H_{18}OS$: C, 68.53; H, 8.63; S, 15.24. Found C, 67.50; H, 8.80; S, 15.56.

Thioacetic acid (*Z*)-*S*-(3-methyl-5-phenylpent-2-en-4-ynyl) ester. Yellow oil. IR (neat) 2975 (vw), 2921 (vw), 1693 (s), 1490 (w), 1443 (w), 1355 (w), 1134 (m), 956 (w), 756 (m), 691 (m), 628 (m) cm^{-1}; ^{1}H NMR δ7.53-7.37 (m, 2 H on phenyl ring), 7.37-7.27 (m, 3 H on phenyl ring), 5.77 (tq, *J* = 7.8, 1.5, 1 H, =CH), 3.82 (d, *J* = 7.8, CH_2S), 2.34 [s, 3 H CH_3(CO)], 1.95 (d, *J* =1.5, 3 H, CH_3C=); MS *m/e* = 230 (M$^+$, 10), 215 (10), 188 (23), 187 (100), 173 (13), 171 (13), 155 (81), 154 (21), 153 (31), 152 (17), 128 (21), 127 (18), 115 (70), 77 (24), 51 (14). Anal. Calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13; S, 13.92. Found C, 74.20; H, 6.28; S, 13.73.

Thioacetic acid (*Z*)-*S*-(2-ethylnon-2-en-4-ynyl) ester. Yellow oil. IR (neat) 2961 (m), 2933 (m), 2873 (w), 1695 (s), 1459 (w), 1429 (w), 1353 (w), 1135 (m), 1106 (m), 957 (m), 851 (w), 629 (m) cm^{-1}; ^1H NMR δ 5.39-5.36 (m, 1 H, =CH), 3.87 (s, 2 H, CH_2S), 2.35 (td, *J* = 6.8, 2.2, 2 H, $CH_2C\equiv$), 2.35 [s, 3 H $CH_3(CO)$], 2.12 (qd, *J* = 7.3, 1.0, 2 H, $CH_3CH_2C=$), 1.58-1.36 (m, 4 H, $CH_2CH_2CH_3$), 1.03 (t, *J* = 7.3, 3 H, $CH_3CH_2C=$), 0.92 (t, *J* = 7.1, 3 H, $CH_2CH_2CH_3$); MS *m/e* 224 (10, M^+), 182 (23), 181 (43), 153 (18), 139 (28), 125 (41), 111 (12), 107 (10), 105 (15), 97 (12), 93 (17), 91 (44), 79 (31), 77 (25), 65 (14), 55 (17), 53 (11), 51 (13). Anal. Calcd for $C_{13}H_{20}OS$: C, 69.59; H, 8.98; S, 14.29. Found C, 70.42; H, 8.85; S, 14.60.

(*Z*)-3-Methylpent-2-en-4-yne-1-thiol 1a. Colorless oil. IR (neat) 3286 (s), 2976 (w), 2921 (m), 2560 (vw), 1434 (m), 1376 (w), 1233 (w), 1011 (m), 854 (w), 643 (m) cm^{-1}; ^1H NMR δ 5.93-5.85 (m, 1 H, =CH), 3.35 (tq, *J* = 7.9, 0.9, 2 H, CH_2SH), 3.20-3.19 (m, 1 H, $\equiv$CH), 1.89-1.87 (m, 3 H, $CH_3C=$), 1.56 (t, *J* = 7.9, SH); MS *m/e* 112 (27, M^+), 111 (20), 97 (32), 79 (46), 78 (20), 77 (100), 63 (12), 53 (28), 52 (13), 51 (43). Anal. Calcd for C_6H_8S: C, 64.24; H, 7.19; S, 28.58. Found C, 63.78; H, 7.25; 29.01.

(*Z*)-5-Methylhept-4-en-6-yne-3-thiol 1b. Colorless oil. IR (neat) 3293 (s), 2966 (s), 2930 (m), 2876 (m), 2563 (vw), 1455 (m), 1379 (w), 1217 (w), 866 (w), 640 (s) cm^{-1}; ^1H NMR δ 5.71-5.65 (m, 1 H, =CH), 3.99-3.88 (m, 1 H, CHSH), 3.18-3.17 (m, 1 H, $\equiv$CH), 1.88-1.86 (m, 3 H, $CH_3C=$), 1.69 (d, *J* = 5.4, 1 H, SH), 1.69-1.57 (m, 2 H, CH_2CH_3), 0.96 (t, *J* = 7.3, 3 H, CH_2CH_3); MS *m/e* 140 (17, M^+), 111 (26), 107 (29), 105 (21), 92 (16), 91 (100), 79 (39), 78 (10), 77 (41), 67 (13), 65 (27), 63 (11), 53 (19), 51

(32). Anal. Calcd for $C_8H_{12}S$: C, 68.52; H, 8.62; S, 22.86. Found C, 67.75; H, 8.78; 23.34.

(*Z*)-3-Methyl-1-phenylpent-2-en-4-yne-1-thiol 1c. Pale yellow oil. IR (neat) 3289 (s), 3029 (w), 2921 (m), 2853 (w), 2561 (vw), 1599 (w), 1491 (m), 1452 (m), 1072 (w), 868 (m), 758 (w), 697 (m), 626 (m) cm^{-1}; ^{1}H NMR δ 7.44-7.21 (m, 5 H on phenyl ring), 6.09 (dq, *J* = 10.3, 1.5, 1 H, =CH), 5.31 (dd, *J* = 10.3, 4.9, 1 H, C*H*SH), 3.26 (s, 1 H, ≡CH), 2.19 (d, *J* = 4.9, 1 H, SH), 1.88 (d, *J* = 1.5, 3 H, Me); MS *m/e* 188 (11, M$^+$), 173 (13), 156 (13), 155 (100), 154 (23), 153 (39), 152 (18), 139 (11), 129 (22), 128 (26), 127 (16), 115 (25), 77 (15), 63 (10), 51 (16). Anal. Calcd for $C_{12}H_{12}S$: C, 76.55; H, 6.42; S, 17.03. Found C, 77.69; H, 6.38; S, 16.82.

(*Z*)-3-Methylnon-2-en-4-yne-1-thiol 1d. Colorless oil. IR (neat) 2958 (s), 2931 (s), 2872 (m), 2563 (vw), 1456 (m), 1432 (w), 1377 (w), 1243 (w), 837 (w) cm^{-1}; ^{1}H NMR δ 5.72 (tq, *J* = 7.8, 1.5, 1 H, =CH), 3.32 (tq, *J* = 7.8, 1.0, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{SH}$), 2.36 (t, *J* = 6.8, 2 H, $\mathrm{CH_2C}$≡), 1.84-1.82 (m, 3 H, $\mathrm{CH_3C}$=), 1.61-1.38 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_3$), 1.55 (t, *J* = 7.8, 1 H, SH), 0.94 (t, *J* = 7.1, 3 H, $\mathrm{CH_2CH_2C}\mathit{H}_3$); MS *m/e* = 168 (2, M$^+$), 167 (5), 153 (16), 135 (37), 125 (55), 111 (33), 107 (14), 105 (17), 93 (59), 92 (18), 91 (100), 81 (16), 79 (52), 78 (14), 77 (80), 67 (14), 65 (33), 63 (16), 55 (43), 53 (20), 51 (27). Anal. Calcd for $C_{10}H_{16}S$: C, 71.37; H, 9.58; S, 19.05. Found C, 70.51; H, 9.48; S, 19.45.

(*Z*)-3-Methyl-5-phenypent-2-en-4-yne-1-thiol 1e. Pale yellow oil. IR (neat) 2920 (w), 2568 (vw), 1596 (w), 1489 (m), 1442 (m), 755 (s), 690 (s) cm^{-1}; ^{1}H NMR δ 7.48-7.16 (m, 5 H on phenyl ring), 5.87 (tq, *J* = 7.8, 1.5, 1 H, =CH), 3.42 (tq, *J* = 7.8, 1.0, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{SH}$), 1.96-1.94 (m, 3 H, $\mathrm{CH_3C}$=), 1.61 (t, *J* = 7.8, 1 H, SH), MS *m/e* 188 (21, M$^+$), 173 (7), 156 (13), 155 (100), 154 (12), 153 (18), 152 (11), 129 (10), 128 (15), 127 (13), 115 (55), 77 (17), 63 (9), 51 (10). Anal. Calcd for $C_{12}H_{12}S$: C, 76.55; H, 6.42, S, 17.03. Found C, 77.26; H, 6.29; S, 16.74.

(*Z*)-2-Ethylnon-2-en-4-yne-1-thiol 1f. Pale yellow oil. IR (neat) 2961 (s), 2932 (s), 2873 (m), 2566 (vw), 1459 (m), 1428 (w), 848 (m) cm^{-1}; ^1H NMR δ 5.29-5.25 (m, 1 H, =CH), 3.37 (d, *J* = 8.3, 2 H, C*H*$_2$SH), 2.36 (td, *J* = 6.8, 2.0, 2 H, $CH_2C\equiv$), 2.26 (qd, *J* = 7.3, 1.0, 2 H, =CC*H*$_2$CH$_3$), 1.69 (t, *J* = 8.3, 1 H, SH), 1.60-1.38 (m, 4 H, C*H*$_2$C*H*$_2$CH$_3$), 1.05 (t, *J* = 7.3, 3 H, =CCH$_2$C*H*$_3$), 0.93 (t, *J* = 7.1, 3 H, CH$_2$CH$_2$C*H*$_3$); MS *m/e* 182 (4, M^+), 181 (15), 167 (3), 153 (46), 139 (82), 125 (29), 111 (38), 107 (35), 105 (34), 97 (24), 93 (44), 91 (100), 79 (73), 77 (55), 65 (29), 55 (23), 51 (28). Anal. Calcd for $C_{11}H_{18}S$: C, 72.47; H, 9.95, S, 17.58. Found C, 71.33; H, 10.03; S, 18.03.

2,3-Dimethyl-5-ethylthiophene 2b. Colorless oil. IR (neat) 2967 (s), 2919 (s), 2861 (m), 1456 (m), 1384 (w), 1149 (w), 830 (m), 602 (w) cm^{-1}; ^1H NMR δ 6.46 (s, 1 H, H-4), 2.72 (q, *J* = 7.3, C*H*$_2$CH$_3$), 2.28 (s, 3 H, Me at C-2), 2.06 (s, 3 H, Me at C-3), 1.25 (t, *J* = 7.3, 3 H, CH$_2$C*H*$_3$); MS *m/e* 140 (29, M^+), 125 (100), 97 (6), 91 (13), 77 (6), 65 (6), 59 (15), 53 (6), 51 (9). Anal. Calcd for $C_8H_{12}S$: C, 68.52; H, 8.62; S, 22.86. Found C, 69.31; H, 8.55; S, 22.33.

2,3-Dimethyl-5-phenylthiophene 2c. White solid, mp 46-47 °C (lit[10] 41-42 °C). IR (neat) 2914 (w), 1498 (m), 1462 (m), 1072 (w), 944 (w), 902 (w), 831 (m), 753 (s), 687 (s) cm^{-1}; ^1H NMR δ 7.55-7.50 (m, 2 H on phenyl ring), 7.37-7.29 (m, 2 H on phenyl ring), 7.25-7.18 (m, 1 H on phenyl ring), 7.01 (s, 1 H, H-4), 2.36 (s, 3 H, Me at C-2), 2.14 (s, 3 H, Me at C-3); MS *m/e* 188 (64, M^+), 187 (36), 174 (13), 173 (100), 129 (9),

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[10] Eichinger, K.; Mayr, P.; Nussbaumer, P. *Synthesis* **1989**, 210-211.

128 (13), 115 (10), 77 (12), 51 (11). Anal. Calcd for $C_{12}H_{12}S$: C, 76.55; H, 6.42; S, 17.03. Found C, 77.01; H, 6.31; S, 16.79.

3-Methyl-2-pentylthiophene 2d. Colorless oil. IR (neat) 2958 (s), 2924 (s), 2853 (s), 1462 (m), 1377 (w), 801 (m) cm^{-1}; ^1H NMR δ 7.00 (d, $J = 5.1$, 1 H, H-5), 6.77 (d, $J = 5.1$, 1 H, H-4), 2.70 (t, $J = 7.6$, 2 H, $CH_2CH_2CH_2CH_2CH_3$), 2.15 (s, 3 H, Me at C-3), 1.68-1.56 (m, 2 H, $CH_2CH_2CH_2CH_2CH_3$), 1.39-1.30 (m, 4 H, $CH_2CH_2CH_2CH_2CH_3$), 0.94-0.86 (m, 3 H, $CH_2CH_2CH_2CH_2CH_3$); MS *m/e* 168 (17, M^+), 153 (1), 111 (100), 97 (6), 77 (8), 67 (5), 53 (5), 51 (4). Anal. Calcd for $C_{10}H_{16}S$: C, 71.37; H, 9.58; S, 19.05. Found C, 72.13; H, 9.32; S, 18.75.

4-Ethyl-2-pentylthiophene 2f. Pale yellow oil. IR (neat) 2960 (s), 2928 (s), 2856 (m), 1556 (w), 1458 (m), 1377 (w), 849 (w), 830 (w), 727 (w) cm^{-1}; ^1H NMR δ 6.70-6.67 (m, 1 H, H-5), 6.64-6.62 (m, 1 H, H-3), 2.76 (td, $J = 7.6$, 1.0, 2 H, $CH_2CH_2CH_2CH_2CH_3$), 2.58 (qd, $J = 7.6$, 1.0, 2 H, CH_2CH_3), 1.72-1.60 (m, 2 H, $CH_2CH_2CH_2CH_2CH_3$), 1.39-1.30 (m, 4 H, $CH_2CH_2CH_2CH_2CH_3$), 1.22 (t, $J = 7.6$, 3 H, CH_2CH_3), 0.94-0.87 (m, 3 H, $CH_2CH_2CH_2CH_2CH_3$). MS *m/e* 182 (19, M^+), 167 (2), 139 (5), 126 (23), 125 (100), 110 (7), 97 (8), 91 (6), 77 (5), 65 (4). Anal. Calcd for $C_{11}H_{18}S$: C, 72.47; H, 9.95; S, 17.58. Found C, 73.21; H, 10.11; 18.03.