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WITTIG REARRANGEMENT OF ALLYL 2-THIOPHENEMETHYL ETHERS: FACILE SYNTHESIS OF THIOPHENEMETHANOL AND -ETHANOL DERIVATIVES

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Abstract – Wittig rearrangement of allyl 2-thiophenemethyl ethers was studied. Deprotonation of allyl 2-thiophenemethyl ethers (**1a-d**) occurred preferentially either the α- or the α'-position, depending on three kinds of BuLi. Thiophenemethanol and -ethanol derivatives were obtained as products of [2,3] and [1,2] sigmatropic rearrangements, respectively.

INTRODUCTION

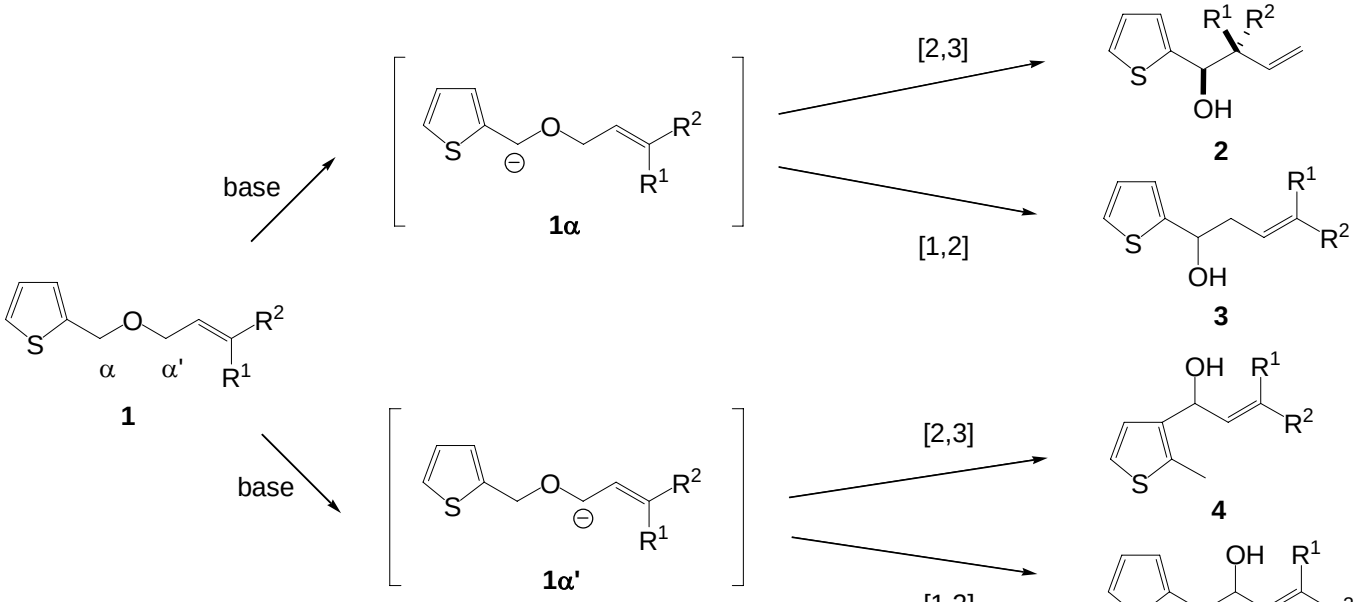
A variety of naturally occurring thiophene derivatives such as propynylthiophenes and polythiophenes have been isolated from plants and fungi.[1] The polythiophenes show interesting biological activities,[2] for instance α-terthienyl displays an array of cytotoxic properties which are all light-dependent.[3] Thiophenes are very important because of their role as versatile intermediates for natural product synthesis,[4] essential pharmacore elements for drugs,[5] and functional materials.[6] Numerous efforts have been devoted to the preparation of thiophenes and functionalization of the thiophene ring.[7]

We have found that the Wittig rearrangement of 2- and 3-furylmethyl ethers provides an efficient method for the preparation of 2-furylmethanol derivatives.[8] Recently, we have successfully applied this rearrangement to the stereoselective synthesis of furanocyclic diterpene skeleton[9a] and steroidal side chain.[9b] In this regard, we have been interested in the Wittig rearrangement[10] of thiophenemethyl ethers. Here we report a facile synthesis of thiophenemethanols and thiopheneethanols based on [2,3] and [1,2] Wittig rearrangement of allyl 2-thiophenemethyl ethers.

Dedicated to the memory of the late Professor Kenji Koga.

RESULTS AND DISCUSSION

2-Thiophenemethyl ethers (**1a-d**) were prepared from by reaction of 2-thiophenemethanol with the corresponding allylic halides in DMF using 1.5 equiv. of NaH. Wittig rearrangement of allyl 2-thiophenemethyl ether (**1**) could lead to both 2,3-rearrangement products (**2** and **4**) and 1,2-rearrangement products (**3** and **5**) *via* anions (**1α** and **1α'**) generated by deprotonation (Scheme 1). The Wittig rearrangement of allyl 2-thiophenemethyl ethers (**1a-d**) was investigated under the same condition reported previously,[8b, 11] the results are shown in Table 1.



Scheme 1

Table 1 Wittig rearrangement of 2-thiophenemethyl ethers (**1a-d**)[a]

Substrate	Base[c]	Yield (%)	Product Distribution[b] (%)			
			2	**3**	**4**	**5**
1a $R^1 = R^2 = H$	*n*-BuLi	78	7		51	42
	s-BuLi	74	-		61	39
	t-BuLi	84	44		25	31
1b $R^1 = H$	*n*-BuLi	94	17 (47/53)[d]	6	53	24
$R^2 = CH_3$	*s*-BuLi	96	18 (56/44)[d]	-	33	49
	t-BuLi	88	68 (47/53)[d]	-	10	22
1c $R^1 = CH_3$	*n*-BuLi	71	14 (100/0)[d]	28	15 (20/80)[e]	43 (33/67)[e]
$R^2 = H$	*s*-BuLi	96	-	-	39 (18/82)[e]	61 (51/49)[e]
	t-BuLi	82	52 (100/0)[d]	10	8 (25/75)[e]	30 (66/34)[e]
1d $R^1 = R^2 = CH_3$	*n*-BuLi	82	42	17	-	41
	s-BuLi	73	26	-	-	74
	t-BuLi	82	76	4	-	20

[a] Reactions were carried out with base in THF at -78°C. In case of *n*-BuLi used, reaction was allowed to warm to 0 °C. [b] Determined by 270 MHz NMR analysis of the crude products. [c] *n*-BuLi (10 equiv.), *s*-BuLi (3 equiv.), and *t*-BuLi (5 equiv.) were employed. [d] In parentheses; the ratio of the *syn* to the *anti* product. [e] In parentheses; the ratio of the *(E)* to the *(Z)* alkene.

Treatment of **1a** with either *n*- or *s*-BuLi brought about selective deprotonation at α' position to afford both α'[2,3] product (**4a**), 3-(2-methylthiophenemethyl)vinylcarbinol, and α'[1,2] product (**5a**), 2-thiophenemethylvinylcarbinol. In contrast, reaction of **1a** with *t*-BuLi underwent deprotonation at α and α' positions to give 2-thiophenemethylallylcarbinol [**2a**(=**3a**)], **4a**, and **5a** in a ratio of 44 : 25 : 31, respectively. The similar tendency of product distribution was observed for Wittig rearrangement of (*E*)- and (*Z*)-crotyl ethers (**1b,c**). As expected, α[2,3] products (**2b,c**) became major isomers when **1b,c** were treated with *t*-BuLi. Remarkable diastereoselectivity was observed with (*Z*)-substrate (**1c**), whereas disappointingly lower stereoselectivity was observed with (*E*)-substrate (**1b**). This findings are in accordance with that most Wittig rearrangement of (*Z*)-crotyl aryl ethers exhibit higher diastereoselectivities.[8b,12] α'[2,3] And α'[1,2] products (**4b** and **5b**), obtained from **1b**, have (*E*) geometries at olefins, while the corresponding α' products (**4c** and **5c**), derived from **1c**, contain mixtures of (*E*) and (*Z*) geometries. The observed partial isomerization can be explained by relaxation of $A^{1,3}$ strain in (*Z*)-allylic anion intermediate (**1cα'**). Prenyl ether (**1d**) underwent [2,3] Wittig rearrangement on treatment with either *n*- or *t*-BuLi to give **2d** as a major product in moderate yield. Although α'[1,2] product (**5d**) was produced from **1d**, none of **4d** was isolated. This observation can be speculated that envelope transition state suffers from steric repulsion between thiophene ring and terminal dimethyl groups.

Thus, we have disclosed Wittig rearrangement of 2-thiophenemethyl ethers leading to thiophene-methanol and –ethanol derivatives. Employing *t*-BuLi reaction of 2-thiophenemethyl ethers preferentially underwent [2,3] Wittig rearrangement of α anions to give 2-thiophenemethanols, in contrast treatment with *s*-BuLi brought about deprotonation at α' positions to afford [2,3] and [1,2] rearrangement products, such as 3-thiophenemethanols and 2-thiopheneethanols. Studies on the synthesis of natural product using the Wittig rearrangement of 2-thiophenemethyl ethers are underway.

EXPERIMENTAL

IR spectra were obtained using a JASCO FT/IR-200 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were obtained on a JEOL JNM-LA270 (^{1}H-NMR: 270 MHz, ^{13}C-NMR: 67.8 MHz) instrument for solutions in $CDCl_3$, and chemical shifts are reported on the δ scale using TMS as an internal standard of δ 0.00 for ^{1}H NMR spectra and $CDCl_3$ as an internal standard of δ 77.00 for ^{13}C NMR spectra, respectively. MS spectra were measured with a JEOL JMS-600 spectrometer. Elemental analyses were performed on a Yanaco-MT5.

General procedure for etherification of thiophenemethanol

To a solution of allylic halide (87.6 mmol) and 2-thiopehenemethanol (5 g, 43.8 mmol) in DMF (130 mL)

was added NaH (*ca*. 60 % purity, 2.63 g, *ca*. 65.7 mmol) at 0°C and stirring was continued for 30 min at rt. The reaction was carefully quenched with sat. aq. NH_4Cl solution in ice bath. The reaction mixture was extracted with Et_2O and CH_2Cl_2 (v/v, 2:1), and the combined organic layer was washed with brine. The organic layer was dried over Na_2SO_4 and evaporated to give a residue, which was chromatographed on silica gel (100 g, *n*-hexane/Et_2O=95:5) to afford 2-thiophenemethyl ether as a colorless oil.

Allyl 2-thiophenemethyl ether (**1a**)[13]

87 % yield; bp 65.0 °C (5 mmHg).

(*E*)-Crotyl 2-thiophenemethyl ether (**1b**)

60 % yield; bp 76.0 °C (5 mmHg). IR 2850, 1670 cm^{-1}; ^{1}H-NMR δ 1.72 (3H, dd, *J*=1.0 and 6.1 Hz, CH_3), 3.95 (2H, dq, *J*=6.1 and 1.0 Hz, CHC*H*$_2$O), 4.64 (2H, s, thienyl-CH_2), 5.54-5.80 (2H, m, C*H*=C*H*), 6.94-7.00 (2H, m, 3-H and 4-H), 7.24-7.26 (1H, m, 5-H); ^{13}C-NMR δ 17.7, 66.1, 70.4, 125.6, 126.2, 126.5, 127.2, 130.0, 141.2; MS (EI): 168 (M^+); HRMS (CI) calcd for $C_9H_{12}OS$+H: 169.0687. Found: 169.0692. Anal. Calcd for $C_9H_{12}OS \cdot 0.1H_2O$: C, 63.57; H, 7.23. Found: C, 63.27; H, 7.19.

(*Z*)-Crotyl 2-thiophenemethyl ether (1c)

52 % yield; bp 75.0 °C (5 mmHg). IR 2860, 1080 cm^{-1}; ^{1}H-NMR δ 1.65 (3H, ddt, *J*=5.8, 0.7 and 1.5 Hz, CH_3), 4.09 (2H, dq, *J*=5.3 and 0.7 Hz, CHC*H*$_2$O), 4.67 (2H, s, thienyl-CH_2), 5.54-5.74 (2H, m, C*H*=C*H*), 6.96-7.02 (2H, m, 3-H and 4-H), 7.29 (1H, dd, *J*=1.5 and 5.0 Hz, 5-H); ^{13}C-NMR δ 13.2, 65.0, 66.3, 125.7, 126.3, 126.5, 126.6, 128.3, 141.2; MS (EI): 168 (M^+); HRMS (EI) calcd for $C_9H_{12}OS$: 168.0609. Found: 168.0621. Anal. Calcd for $C_8H_{10}OS$: C, 64.25; H, 7.19. Found: C, 64.40; H, 7.37.

Prenyl 2-thiophenemethyl ether (**1d**)

99 % yield; bp 80.0 °C (5 mmHg). IR 2850, 1670 cm^{-1}; ^{1}H-NMR δ 1.66 and 1.76 (each 3H, each d, *J*=1.5 Hz, $(CH_3)_2$), 4.00 (2H, d, *J*=6.9 Hz, CHC*H*$_2$O), 4.66 (2H, s, thienyl-CH_2), 5.38 (1H, t septet, *J*=6.9 and 1.5 Hz, C=CH), 6.87-7.01 (2H, m, 3-H and 4-H), 7.26-7.29 (1H, m, 5-H); ^{13}C-NMR δ 20.0, 25.7, 66.0, 66.1, 120.7, 125.6, 156.2, 126.5, 137.5, 141.4; MS (EI): 182 (M+); HRMS (EI) calcd for $C_{10}H_{14}OS$: 182.0765. Found: 182.0779. Anal. Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74. Found: C, 65.89; H, 7.76.

General procedure for Wittig rearrangement of 2-thiophenemethyl ether (1a-d)

To a solution of 2-thiophenemethyl ether (**1a-d**) (1.0 mmol) in THF (10 mL) was added dropwise a base (*n*-BuLi 1.6 M in hexane, 6.25 mL, 10 mmol; *s*-BuLi 1M in cyclohexane, 3.0 mL, 3.0 mmol; *t*-BuLi 1.6 M in pentane, 3.1 mL, 5.0 mmol) at -78 °C under Ar. After stirring for 1 h (the reaction mixture was allowed to warm to 0°C in the cases of *n*-BuLi), the reaction mixture was quenched with sat. aq. NH_4Cl solution, and the solvent was removed under vacuum. The residue was extracted with pentane-Et_2O (1:1, v/v). The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was chromatographed on silica gel (50 g, *n*-hexane/AcOEt=95:5) to afford rearrangement products,

respectively. Yields and the ratio of product distribution are shown in Table 1. All the rearranged products were isolated by either careful column chromatography or derivatization.

2-(1'-Hydroxy-3'-buten-1'-yl)thiophene (**2a**)[14]

Colorless oil; IR 3480, 2930, 2360, 700 cm^{-1}; ^{1}H-NMR δ 2.34 (1H, s, OH), 2.61 (2H, t, *J*=6.3 Hz, 2'-H_2), 4.97 (1H, t, *J*=6.3 Hz, C*H*OH), 5.22 (2H, m, CH_2=CH), 5.74-5.91 (1H, m, CH_2=C*H*), 6.86-6.97 (2H, m, 3-H and 4-H), 7.23 (1H, dd, *J*=2.1 and 4.3 Hz, 5-H); ^{13}C-NMR δ 43.7, 69.3, 118.7, 123.6, 124.5, 126.6, 133.8, 147.8; MS (EI): 154 (M^+); HRMS (CI) calcd for $C_8H_{10}OS$+H: 155.0515. Found; 155.0531.

3-(1'-Hydroxy-2'-propen-1'-yl)-2-methylthiophene (**4a**)

Colorless oil; IR 3340, 2920, 1040 cm^{-1}; ^{1}H-NMR δ 2.09 (1H, br s, OH), 2.42 (3H, s, CH_3), 5.16 (1H, dt, *J*=1.3 and 10.4 Hz, CH*H*=CH), 5.24-5.32 (2H, m, C*H*H=CHC*H*), 6.03 (1H, ddd, *J*=5.0, 10.4 and 17.0 Hz, CH_2=C*H*), 6.95 (1H, d, *J*=5.2 Hz, 4-H), 7.02 (1H, d, *J*=5.2 Hz, 5-H); ^{13}C-NMR δ 12.9, 69.4, 114.5, 121.8, 126.4, 135.1, 138.4, 139.3; MS (EI): 154 (M^+); HRMS (EI) calcd for $C_8H_{10}OS$: 154.0452. Found; 154.0427.

2-(2'-Hydroxy-3'-buten-1'-yl)thiophene (**5a**)[15]

Colorless oil; IR 3480, 3080, 2920, 2360 cm^{-1}; ^{1}H-NMR δ 1.85 (1H, br s, OH), 3.00 (1H, dd, *J*=7.6 and 14.8 Hz, 1'-C*H*H), 3.1 (1H, dd, *J*=4.9 and 14.8 Hz, 1'-CH*H*), 4.36 (1H, brd, *J*=4.9 Hz, C*H*OH), 5.17 (1H, dt, *J*=10.4 and 1.3 Hz, C*H*H=CH), 5.30 (1H, td, *J*=1.3 and 17.1 Hz, CH*H*=CH), 5.94 (1H, ddd, *J*=5.8, 10.4 and 17.1 Hz, CH_2=C*H*), 6.89-6.98 (2H, m, 3-H and 4-H), 7.17-7.19 (1H, m, 5-H); ^{13}C-NMR δ 57.8, 73.3, 115.5, 124.3, 126.3, 126.9, 139.5, 139.6; MS (EI): 154 (M^+); HRMS (EI) calcd for $C_8H_{10}OS$: 154.0452. Found; 154.0467.

(1'*R, 2'*R**)-2-(1'-Hydroxy-2'-methyl-3'-buten-1'-yl)thiophene** (**2b**)[16]

Colorless oil; IR 3410, 2970, 1640 cm^{-1}; ^{1}H-NMR δ 1.09 (3H, d, *J*=6.9 Hz, 2'-CH_3), 2.29 (1H, d, *J*=2.1 Hz, OH), 2.54 (1H, distorted sextet, *J*=7.8 Hz, CH_2=CHC*H*), 4.66 (1H, dd, *J*=2.1 and 7.8 Hz, C*H*OH), 5.20 (1H, dd, *J*=1.3 and 10.2 Hz, C*H*H=CH), 5.23 (1H, dd, *J*=1.3 and 17.3 Hz, CH*H*=CH), 5.94 (1H, ddd, *J*=7.8, 10.2 and 17.3 Hz, CH_2=C*H*), 6.95-7.00 (2H, m, 3-H and 4-H), 7.23-7.29 (1H, m, 5-H); ^{13}C-NMR δ 16.5, 46.7, 73.8, 100.5, 117.3, 124.7, 124.8, 126.4, 140.1; MS (EI): 168 (M^+); HRMS (EI) calcd for $C_9H_{12}OS$: 168.0609. Found: 168.0607.

(*E*)-2-(1'-Hydroxy-3'-penten-1'-yl)thiophene (**3b**)

Colorless oil; IR 3370, 2920, 1440 cm^{-1}; ^{1}H-NMR δ 1.64 (3H, dd, *J*=0.8 and 6.8 Hz, CH_3), 2.20 (1H, br s, OH), 2.56-2.68 (2H, m, 2'-H_2), 4.97 (1H, dd, *J*=6.1 and 7.1 Hz, C*H*OH), 5.39-5.49 (1H, m, CH_3-C*H*=CH-CH_2), 5.61-5.71 (1H, m, CH_3-CH=C*H*-CH_2), 6.95-6.98 (2H, m, 3-H and 4-H), 7.25 (1H, dd, *J*=1.3 and 4.5 Hz, 5-H); ^{13}C-NMR δ 13.0, 36.9, 69.9, 123.6, 124.5, 125.1, 126.6, 128.0, 148.0; MS (CI): 169 (M+H); HRMS (CI) calcd for $C_9H_{12}OS$+H: 169.0687. Found: 169.0667.

(*E*)-3-(1'-Hydroxy-2'-buten-1'-yl)-2-methylthiophene (**4b**)

Colorless oil; IR 3460, 2920, 1440 cm^{-1}; ^{1}H-NMR δ 1.75 (3H, dd, *J*=0.7, 6.0 Hz, C*H*$_3$CH=CH), 1.89 (1H, br s, OH), 2.42 (3H, s, 2-CH_3), 5.21 (1H, d, *J*=2.6 Hz, C*H*OH), 5.73-5.68 (2H, m, C*H*=C*H*CH), 6.98-7.03 (2H, m, 4-H and 5-H); ^{13}C-NMR δ 12.9, 17.6, 69.5, 121.7, 126.3, 126.9, 132.6, 134.5, 139.2; MS (EI): 168 (M^+); HRMS (EI) calcd for $C_9H_{12}OS$: 168.0609. Found: 168.0603.

(*E*)-2-(2'-Hydroxy-3'-penten-1'-yl)thiophene (**5b**)

Colorless oil; IR 3440, 2970, 2930, 1440 cm^{-1}; ^{1}H-NMR δ 1.71 (3H, ddd, *J*=0.8, 1.5 and 6.3 Hz, CH_3), 2.95-3.11 (2H, m, 1'-H_2), 4.29 (1H, q, *J*=6.3 Hz, C*H*OH), 5.55 (1H, ddd, *J*=1.5, 6.3 and 15.3 Hz, CH_3CH=C*H*), 5.68-5.80 (1H, m, CH_3C*H*=CH), 6.88 (1H, d, *J*=3.5 Hz, 3-H), 6.96 (1H, dd, *J*=3.5 and 5.1 Hz, 4-H), 7.18 (1H, d, *J*=5.1 Hz, 5-H); ^{13}C-NMR δ 17.7, 38.1, 73.2, 124.3, 126.2, 126.9, 127.8, 132.6, 140.0; MS (CI): 169 (M+H); HRMS (CI) calcd for $C_9H_{12}OS$+H: 169.0687. Found: 169.0715.

(1'R*, 2'S*)-2-(1'-Hydroxy-2'-methyl-3'-buten-1'-yl)thiophene (**2c**)[16]

Colorless oil; IR 2980, 1640, 1010 cm^{-1}; ^{1}H-NMR δ 1.08 (3H, d, *J*=6.9 Hz, 2'-CH_3), 2.18 (1H, d, *J*=4.0 Hz, OH), 2.63 (1H, sextet, *J*=6.8 Hz, CH_2=CHC*H*), 4.83 (1H, dd, *J*=4.0 and 6.8 Hz, C*H*OH), 5.06-5.12 (2H, m, C*H*$_2$=CH), 5.73-5.86 (1H, m, CH_2=C*H*), 6.93-6.98 (2H, m, 3-H and 4-H), 7.23 (1H, dd, *J*=1.1 and 5.0 Hz, 5-H); ^{13}C-NMR δ 14.7, 45.0, 73.7, 116.0, 124.2, 124.4, 126.4, 139.6, 146.5; MS (EI): 168 (M^+); HRMS (EI) calcd for $C_9H_{12}OS$: 168.0609. Found: 168.0605. Anal. calcd for $C_9H_{12}OS$: C, 64.25; H, 7.19. Found: C, 64.21; H,7.21.

(*Z*)-2-(1'-Hydroxy-3'-penten-1'-yl)thiophene (**3c**)

Colorless oil; IR 2920, 2850, 2460, 1440 cm^{-1}; ^{1}H-NMR δ 1.64 (3H, dd, *J*=1.6 and 6.8 Hz, CH_3), 3.01-3.04 (2H, m, 2'-H_2), 4.68 (1H, td, *J*=6.8 and 8.2 Hz, C*H*OH), 5.47 (1H, dqt, *J*=10.9, 6.8 and 1.6 Hz, CH_3C*H*=CH), 5.56-5.68 (1H, m, CH_3CH=C*H*), 6.88 (1H, dd, *J*=1.1 and 3.5 Hz, 3-H), 6.96 (1H, dd, *J*=3.5 and 5.1 Hz, 4-H), 7.18 (1H, dd, *J*=1.1 and 5.1 Hz, 5-H); ^{13}C-NMR δ 13.3, 37.9, 68.1, 124.3, 126.1, 126.9, 127.4, 131.9, 139.8; MS (CI): 169 (M+H); HRMS (CI) calcd for $C_9H_{12}OS$+H: 169.0687. Found: 169.0670.

(*Z*)-3-(1'-Hydroxy-2'-buten-1'-yl)-2-methylthiophene (**4c**)

Colorless oil; IR 3480, 3020, 2920, 1440 cm^{-1}; ^{1}H-NMR δ 1.74 (3H, dd, *J*=1.5 and 6.8 Hz, C*H*$_3$CH), 2.45 (3H, s, 2-CH_3), 5.54-5.77 (3H, m, CH_3C*H*=C*HCH*), 7.05 (2H, s, 4-H and 5-H); ^{13}C-NMR δ 13.0, 13.2, 64.2, 122.0, 126.0, 126.3, 132.0, 134.5 139.5; MS (EI): 168 (M^+); HRMS (EI) calcd for $C_9H_{12}OS$: 168.0609. Found: 168.0601.

(*Z*)-2-(2'-Hydroxy-3'-penten-1'-yl) thiophene (**5c**)

Colorless oil; IR 3480, 2920, 1440 cm^{-1}; ^{1}H-NMR δ 1.70 (3H, ddd, *J*=0.6, 0.8 and 6.6 Hz, CH_3), 2.94-3.10 (2H, m, 1'-H_2), 4.28 (1H, q, *J*=6.6 Hz, C*H*OH), 5.51-5.60 (1H, m, CH_3CH=C*H*), 5.67-5.77 (1H, m, CH_3C*H*=CH), 6.86-6.88 (1H, m, 3-H), 6.94-6.97 (1H, m, 4-H), 7.18 (1H, dd, *J*=1.2 and 5.1 Hz, 5-H);

^{13}C-NMR δ 17.7, 38.1, 73.2, 124.2, 126.1, 126.8, 127.7, 132.6, 140.0; MS (CI): 169 (M+H); HRMS (CI) calcd for $C_9H_{12}OS$+H: 169.0687. Found: 169.0674.

2-(2',2'-Dimethyl-1'-hydroxy-3'-buten-1'-yl)thiophene (**2d**)[17]

Colorless oil; IR 3460, 2920, 700 cm^{-1} ; ^{1}H-NMR δ 1.04 and 1.06 (each 3H, each s, 2'-$(CH_3)_2$), 2.16 (1H, d, *J*=3.5 Hz, OH), 4.71 (1H, d, *J*=3.5 Hz, C*H*OH), 5.12 (1H, dd, *J*=1.3 and 17.5 Hz, C*H*H=CH), 5.18 (1H, dd, *J*=1.3 and 10.9 Hz, CH*H*=CH), 5.97 (1H, dd, *J*=10.9 and 17.5 Hz, CH_2=C*H*), 6.95-6.98 (2H, m, 3-H and 4-H), 7.24 (1H, dd, *J*=1.7 and 4.8 Hz, 5-H); ^{13}C-NMR δ 21.6, 24.1, 42.1, 77.3, 114.1, 124.3, 125.3, 125.9, 144.4, 144.5; MS (CI): 183 (M+H); HRMS (CI) calcd for $C_{10}H_{14}OS$+H: 183.0844. Found: 183.0801.

2-(1'-Hydroxy-4'-methyl-3'-peneten-1'-yl)thiophene (**3d**)

Colorless oil; IR 3380, 2920 cm^{-1}; ^{1}H-NMR δ 1.64 (3H, s, CH_3), 1.73 (3H, d, *J*=1.0 Hz, CH_3), 2.18 (1H, br s, OH), 2.45-2.65 (2H, m, 2'-H_2), 4.93 (1H, t, *J*=6.3 Hz, C*H*OH), 5.14-5.21 (1H, m, 3'-H), 6.95-6.97 (2H, m, 3-H and 4-H), 7.23-7.25 (1H, m, 5-H); ^{13}C-NMR δ 18.0, 25.9, 38.2, 70.4, 119.1, 123.5, 124.4, 126.5, 136.1, 148.2; MS (EI): 182 (M^+); HRMS (EI) calcd for $C_{10}H_{14}OS$: 182.0765. Found: 182.0760.

2-(2'-Hydroxy-4'-methyl-3'-penten-1'-yl)thiophene (**5d**)

Colorless oil; IR1680, 2920, 3460 cm^{-1}; ^{1}H-NMR δ 1.65 and 1.73 (each 3H, each s, $(CH_3)_2$), 2.98 (1H, dd, *J*=6.6 and 14.5 Hz, 1'-*H*H), 3.01 (1H, dd, *J*=8.6 and 14.5 Hz, 1'-H*H*), 4.55 (1H, dt, *J*=6.6 and 8.6 Hz, C*H*OH), 5.24 (1H, d, *J*= 8.6 Hz, 3'-H), 6.86 (1H, dd, *J*=1.1 and 3.4 Hz, 3-H), 6.95 (1H, dd, *J*=3.4 and 5.0 Hz, 4-H), 7.17 (1H, dd, *J*=1.1 and 5.0 Hz, 5-H); ^{13}C-NMR δ 18.3, 25.7, 38.2, 69.3, 114.2, 126.0, 126.5, 126.6, 136.3, 140.2; MS (EI) 182(M^+); HRMS (EI) calcd for $C_{10}H_{14}OS$: 182.0765. Found: 182.0760.

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