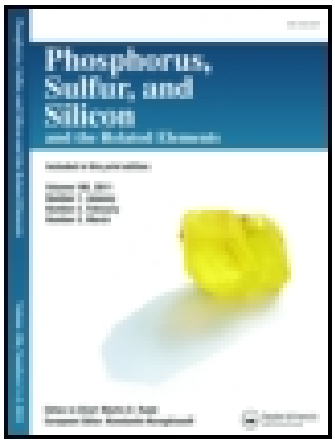

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SILICA SULFURIC ACID; AN EFFICIENT AND REUSABLE CATALYST FOR REGIOSELECTIVE RING OPENING OF EPOXIDES BY ALCOHOLS AND WATER

Peyman Salehi [a] , Minoo Dabiri [a] , Ali Zolfigol [b] & Ali Bodaghi Fard [a]

[a] Shahid Beheshti University , Tehran, Iran

[b] Bu-Ali Sina University , Hamadan, Iran

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SILICA SULFURIC ACID; AN EFFICIENT AND REUSABLE CATALYST FOR REGIOSELECTIVE RING OPENING OF EPOXIDES BY ALCOHOLS AND WATER

Peyman Salehi,[a] *Minoo Dabiri,*[a] *Mohammad Ali Zolfigol,*[b] *and Mohammad Ali Bodaghi Fard*[a]
Shahid Beheshti University, Tehran, Iran[a] *and Bu-Ali Sina University, Hamadan, Iran*[b]

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The nucleophilic ring opening reactions of epoxides by aliphatic alcohols and water are achieved efficiently in the presence of catalytic amounts of silica sulfuric acid with high degree of regioselectivity. The catalyst is reusable and can be applied several times without any decrease in the yield of reactions.

Keywords: β-Alkoxy alcohols; alcoholysis; epoxides; hydrolysis; silica sulfuric acid; vicinal-diols

Epoxides are valuable intermediates in organic synthesis because their nucleophilic ring opening is a powerful tool to access at many important 1,2-difunctionalized compounds.[1,2]

β-Alkoxy alcohols constitute an important class of organic compounds both because this type of functionality is often present in naturally occurring compounds and because their oxidation is the easiest way to the synthesis of α-alkoxy aldehydes and ketones or α-alkoxy acids.[3] The more common protocol for the synthesis of β-alkoxy alcohols is the alcoholysis of epoxides under acidic conditions.[4–15] However the yields are not always satisfactory and in some cases a mixture of regioisomers are obtained.

We recently have reported the preparation of silica sulfuric acid and some of its applications in synthetic methodology.[16–19] In this article we report on a very efficient method for regioselective ring opening of

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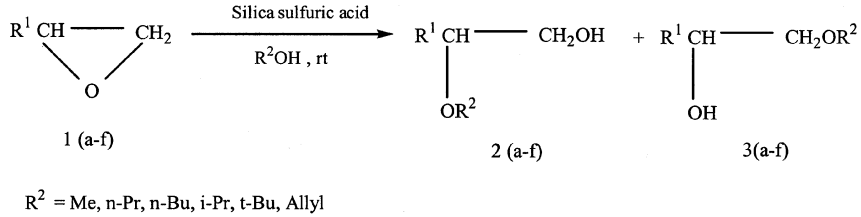
Address correspondence to Peyman Salehi, Department of Photochemistry, Medicinal Plants Research Institute, Shahid Beheshti University, Evin, Tehran, PO Box 19835 389, Iran. E-mail: p-salehi@cc.sbu.ac.ir

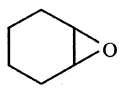
epoxides by alcohols and water in the presence of catalytic amounts of silica sulfuric acid.

RESULTS AND DISCUSSION

The reaction of epoxides with primary, secondary, and tertiary alcohols in the presence of 0.01–0.2 molar equivalents of silica sulfuric acid was investigated and the corresponding β-alkoxy alcohols were obtained in good to excellent yields with high degree of regio- and chemoselectivity (Scheme 1, Table I).



R^2 = Me, n-Pr, n-Bu, i-Pr, t-Bu, Allyl

R^1 or Epoxide		R^1	
1a	Ph -	1d	n-BuO-CH_2 -
1b		1e	PhO-CH_2 -
1c	CH_2=CH-CH_2O-CH_2 -	1f	ClCH_2 -

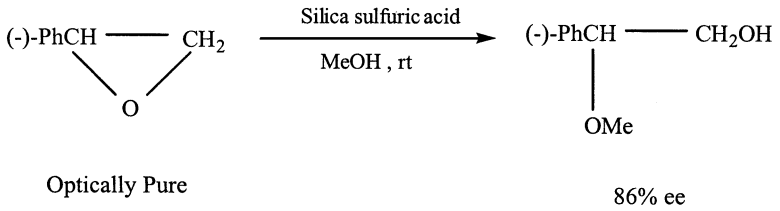
SCHEME 1

In the case of styrene oxide the attack of nucleophile to the more hindered carbon showed that electronic effect controlled the course of the reactions. Methanolysis of optically active styrene oxide in the presence of the catalyst ended up with the formation of the corresponding β-methoxy alcohol with nearly 93% inversion of configuration (Scheme 2).

This showed that attack of nucleophile and ring opening of epoxide almost occurred simultaneously. Similar behavior was also observed in the case of cyclohexene oxide which was transformed only to the trans vicinal alkoxy alcohols (Table I, entries 5–8).

TABLE I The Reaction of Epoxides with Aliphatic Alcohols in the Presence of Silica Sulfuric Acid at Room Temperature

Entry	R^1	Cat./Sub. (mole ratio)	Time (min)[hr]	Yield (%)	R^2	Product
1	1a	0.02	(1)	98	Me	2a
2	1a	0.02	(3)	97	n-Pr	2a
3	1a	0.05	(5)	97	i-Pr	2a
4	1a	0.05	(3)	96	Allyl	2a
5	1b	0.05	(2)	96	Me	
6	1b	0.05	(25)	87	n-Pr	
7	1b	0.05	[1]	86	i-Pr	
8	1b	0.05	(10)	90	Allyl	
9	1c	0.1	(20)	96	Me	3c
10	1c	0.1	(45)	95	n-Pr	3c
11	1c	0.15	[1.5]	96	i-Pr	3c
12	1c	0.15	[3]	88	t-Bu	3c
13	1c	0.1	(50)	94	Allyl	3c
14	1d	0.1	(30)	96	Me	3d
15	1d	0.1	[1]	94	n-Pr	3d
16	1d	0.1	[1.2]	92	n-Bu	3d
17	1d	0.1	[1]	92	i-Pr	3d
18	1d	0.1	[1.5]	90	t-Bu	3d
19	1d	0.1	(45)	94	Allyl	3d
20	1e	0.05	[1.5]	96	Me	3e
21	1e	0.2	[2]	97	n-Pr	3e
22	1e	0.2	[2]	94	n-Bu	3e
23	1e	0.2	[2]	94	i-Pr	3e
24	1e	0.2	[5.5]	92	t-Bu	3e
25	1e	0.2	[3]	95	Allyl	3e
26	1f	0.15	[2]	92	Me	3f
27	1f	0.15	[1.3]	92	n-Pr	3f
28	1f	0.15	[5]	90	i-Pr	3f
29	1f	0.15	[9]	88	t-Bu	3f
30	1f	0.15	[3.5]	92	Allyl	3f



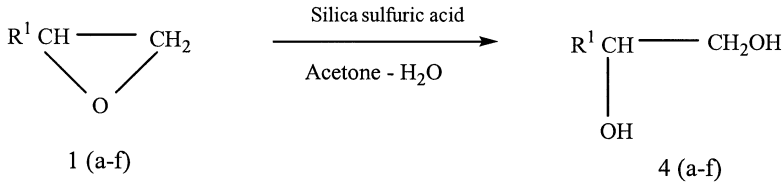
SCHEME 2

In other model compounds that electron withdrawing groups were attached to the epoxide ring, the electronic and steric effects acted in the same direction and the products of the attack of nucleophiles to the less hindered carbon atoms were obtained (Table I, entries 9–30). The reactions were chemoselective and cleavage of other carbon-oxygen and carbon-halogen bonds was not observed in any case. Also the double bond in allyl glycidyl ether remained intact under the reaction conditions.

In some representative reactions, after isolation of the products, the solid catalyst was washed and reloaded with fresh reagents for further runs. No decrease in the yield was observed after several runs, demonstrating that silica sulfuric acid can be reused in these reactions with no discharge to the environment.

The products in entries 16 and 22 (Table I) are known as choleretic drugs with international names Dibuprol and Febuprol respectively.[20]

We also have investigated the hydrolysis reactions of epoxides in the presence of catalytic amounts of silica sulfuric acid (Scheme 3, Table II).



SCHEME 3

The reactions were carried out in acetone-water (2/1: v/v) as solvent and the corresponding vicinal diols were obtained in excellent yields. In the case of cyclohexene oxide the trans-1,2-dihydroxy cyclohexane was obtained in 94% yield (Table II, entry 2).

TABLE II Hydrolysis of Epoxides in the Presence of Silica Sulfuric Acid

Entry	R^1	Cat./Sub. (mole ratio)	Time/Temp. (min)/[°C]	Yield (%)	Product
1	1a	0.01	(3)[rt]	98	4a
2	1b	0.01	(5)[rt]	94	Trans-1,2-cyclohexandiol
3	1c	0.05	(100)[reflux]	95	4c
4	1d	0.05	(35)[reflux]	96	4d
5	1e	0.1	(150)[reflux]	94	4e
6	1f	0.1	(120)[reflux]	92	4f

Catalytic nature of the reactions, high degree of regio- and chemoselectivity, cheapness and stability of the reagent and ease of work up procedure are among the outstanding features of this method which makes it an attractive addition to the previous reported procedures. The catalyst is recyclable and can be used for minimum four more runs in most of the reactions.

EXPERIMENTAL

General

All of the products are known compounds and were characterized by comparison of their spectral data (^{1}HNMR, IR) and physical properties with those reported in the literature.[4,6,11] ^{1}HNMR spectra were run on a Bruker Avance 500 MHz spectrometer. IR spectra were obtained by a Shimadzu 470 spectrophotometer. The reaction monitoring was accomplished by TLC on SIL G/UV 254 sheets. Optical purity determination was accomplished by HPLC on a Shimadzu SPD-6 AV instrument using a Vancomycin chiral column. Silica sulfuric acid was prepared according to our previously reported procedure.[16] All yields refer to isolated products.

General Procedure for the Alcoholysis of Epoxides

Silica sulfuric acid (equal to 0.04–0.4 mmol of H^+) was added to a solution of epoxide (2 mmol) in alcohol (7 ml). The mixture was stirred magnetically at room temperature for the appropriate period of time (Table I). The progress of the reaction was followed by TLC. After completion of the reaction, the mixture was filtered through a silica gel pad and washed with chloroform (20 ml). Evaporation of the solvent followed by purification on a silica gel column gave the desired β-alkoxy alcohols in 86–98% yields.

General Procedure for the Hydrolysis of Epoxides

To a solution of epoxide (2 mmol) in acetone-water (2/1:v/v, 7 ml), silica sulfuric acid (equal to 0.02–0.2 mmol of H^+) was added. The reaction mixture was stirred magnetically at the optimum temperature (Table II). The mixture was passed through a silica gel pad followed by washing the pad with diethyl ether. Ethereal solution was dried (Na_2SO_4) and concentrated to afford the corresponding vicinal diols in 92–98% yields.

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SUPPLEMENTARY INFORMATION

Spectral Data of the Products

2a (R^2 = Me): ^{1}HNMR ($CDCl_3$), δ(ppm): 3.3(3H, s), 3.6(1H, dd), 3.7(1H, dd), 3.8(1H, s), 4.3(1H, dd), 7.3(5H, m). IR(neat), υ(cm^{-1}): 3405(s), 3050(m), 3015(m), 2950(s), 2860(s), 2840(s), 1445(s), 1100(s), 1037(s).

2a (R^2 = n-Pr): ^{1}HNMR ($CDCl_3$), δ(ppm): 1.0(3H, t), 1.7(2H, sex), 3.4(2H, m), 3.65(1H, dd), 3.73(1H, dd), 4.0 (1H, s), 4.5 (1H, dd), 7.4(5H, m). IR(neat), υ(cm^{-1}): 3410(s), 3045(m), 3015(m), 2960(s), 2855(s), 1447(s), 1098(s), 1060(s), 1037(s).

2a (R^2 = i-Pr): ^{1}HNMR ($CDCl_3$), δ(ppm): 1.17(3H, d), 1.24(3H, d), 3.6(4H, m), 4.6(1H, dd), 7.3(5H, m). IR(neat), υ(cm^{-1}): 3425(s), 3015(m), 2930(s), 2865(s), 1435(s), 1375(s), 1085(s), 967(s).

2a (R^2 = allyl): ^{1}HNMR ($CDCl_3$), δ(ppm): 3.66(1H, dd), 3.75(1H, dd), 3.9(1H, dd), 4.0(1H, dd), 4.3(1H, s), 4.5(1H, dd), 5.3(2H, dd), 6.0(1H, m), 7.3(5H, m). IR(neat), υ(cm^{-1}): 3415(s), 3055(s), 3044(m), 2905(s), 1482(m), 1443(s), 1092(s), 1055(s).

Trans-2-methoxycyclohexanol: ^{1}HNMR ($CDCl_3$), δ(ppm): 0.8–2.7(10H, m), 3.2(3H, s), 4.0(1H, s). IR(neat), $\upsilon(cm^{-1})$: 3415(s), 2915(s), 2900(s), 1453(s), 1188(s), 1097(s).

Trans-2-n-propoxycyclohexanol: ^{1}HNMR ($CDCl_3$), δ(ppm): 0.9(3H, t), 1–2.3(10H, m), 3.4(1H, s), 2.9–3.8(4H, m). IR(neat), $\upsilon(cm^{-1})$: 3415(s), 2920(s), 2850(s), 1462(s), 1390(s), 1265(s), 1077(s).

Trans-2-allyloxycyclohexanol: ^{1}HNMR ($CDCl_3$), δ(ppm): 1–2.1(8H, m), 2.9–3.4(2H, m), 3.8(1H, s), 3.9(1H, dd), 4.1(1H, dd), 5.1(2H, dd), 5.9(1H, m). IR(neat), $\upsilon(cm^{-1})$: 3410(s), 3065(m), 2920(s), 2830(s), 1450(s), 1073(s), 980(s).

3c (R^2 = Me): ^{1}HNMR ($CDCl_3$), δ(ppm): 3.27(3H, s), 3.3–3.9(5H, m), 3.91(2H, d), 4.3(1H, s), 5.1(2H, dd), 5.8(1H, m). IR(neat), $\upsilon(cm^{-1})$: 3410(s), 3065(m), 2880(s), 1640(w), 1450(m), 1190(s), 1098(s), 920(s).

3c (R^2 = n-Pr): ^{1}HNMR ($CDCl_3$), δ(ppm): 0.8(3H, t), 1.5(2H, quin), 3.3–3.9(7H, m), 3.9(2H, d), 4.1(1H, s), 5.2(2H, dd), 5.8(1H, m). IR(neat), $\upsilon(cm^{-1})$: 3420(s), 3065(m), 2965(s), 2925(s), 1640(w), 1465(m), 1188(m), 1100(s).

3c (R^2 = i-Pr): ^{1}HNMR ($CDCl_3$), δ(ppm): 1.1(6H, d), 3.3–3.8(6H, m), 3.87(1H, s), 3.92(2H, d), 5.1(2H, dd), 5.8(1H, m). IR(neat), $\upsilon(cm^{-1})$: 3400(s), 3080(w), 2980(s), 2920(s), 2840(s), 1650(w), 1460(m), 1370(s), 1120(s), 1080(s).

3c (R^2 = t-Bu): ^{1}HNMR ($CDCl_3$), δ(ppm): 1.1(9H, s), 3.2–3.8(5H, m), 3.9(2H, d), 5.1(1H, s), 5.2(2H, dd), 5.8(1H, m). IR(neat), $\upsilon(cm^{-1})$: 3400(s), 3080(w), 2980(s), 2930(s), 1650(w), 1470(m), 1360(s), 1195(s), 1085(s).

3c (R^2 = allyl): ^{1}HNMR ($CDCl_3$), δ(ppm): 3.3–3.8(6H, m), 4.0(4H, d), 5.2(4H, dd), 5.9(2H, m). IR(neat), $\upsilon(cm^{-1})$: 3420(s), 3080(w), 2960(s), 2910(s), 1635(s), 1450(s), 1375(m), 1090(s).

3d (R^2 = Me): ^{1}HNMR ($CDCl_3$), δ(ppm): 0.8(3H, t), 1.2(2H, sex), 1.4(2H, quin), 3.3(3H, s), 3.3–3.9(7H, m), 4.0(1H, s). IR(neat, $\upsilon(cm^{-1})$: 3420(s), 3410(s), 2920(s), 2870(s), 1465(m), 1370(s), 1190(m), 1020(s), 1075(s).

3d (R^2 = n-Pr): ^{1}HNMR ($CDCl_3$), δ(ppm): 0.8(6H, t), 1.3(2H, sex), 1.5(4H, m), 3.3–3.9(9H, m), 4.0(1H, s). IR(neat, $\upsilon(cm^{-1})$: 3420(s), 3065(w), 2915(s), 1450(m), 1230(m), 1190(m), 1105(s).

3d (R_2 = n-Bu): ^{1}HNMR ($CDCl_3$), δ(ppm): 0.8(6H, t), 1.3(4H, sex), 1.5(4H, quin), 3.3–4.0(9H, m), 4.4(1H, s). IR(neat), $\upsilon(cm^{-1})$: 3415(s), 2915(s), 1450(m), 1230(m), 1190(m), 1020(s).

3d (R^2 = i-Pr): ^{1}HNMR ($CDCl_3$), δ(ppm): 0.8(3H, t), 1.0(6H, d), 1.3(2H, sex), 1.4(2H, quin), 3.2–4.0(9H, m). IR(neat), $\upsilon(cm^{-1})$: 3420(s), 2955(s), 2855(s), 1465(s), 1399(s), 1250(m), 1193(s), 1110(s).

3d (R^2 = t-Bu): ^{1}HNMR ($CDCl_3$), δ(ppm): 0.9(3H, t), 1.2(9H, s), 1.3(2H, sex), 1.5(2H, quin), 3.2–4.1(8H, m). IR(neat), $\upsilon(cm^{-1})$: 3415(s),

2960(s), 2855(s), 1465(s), 1400(s), 1360(s), 1230(m), 1193(s), 1110(s), 1085(s).

3d (R^2 = allyl): ^{1}HNMR ($CDCl_3$), δ(ppm): 0.8(3H, t), 1.3(2H, sex), 1.5(2H, quin), 3.2–3.9(7H, m), 4.0(2H, d), 4.1(1H, s), 5.1(2H, dd), 5.8(1H, m). IR(neat), $\upsilon(cm^{-1})$: 3380(s), 2970(s), 1635(w), 1445(m), 1395(s), 1360(s), 1230(m), 1195(s), 1083(s).

3e (R^2 = Me): ^{1}HNMR ($CDCl_3$), δ(ppm): 3.4(3H, s), 3.5–4.3(5H, m), 4.5(1H, s), 6.9–7.4(5H, m). IR(neat), $\upsilon(cm^{-1})$: 3405(s), 3065(w), 2920(s), 2850(s), 1485(s), 1245(s), 1030(s).

3e (R^2 = n-Pr): ^{1}HNMR ($CDCl_3$), δ(ppm): 1.0(3H, t), 1.7(2H, sex), 3.5(2H, t), 3.5–4.3(5H, m), 4.5(1H, s), 6.9–7.4(5H, m). IR(neat), $\upsilon(cm^{-1})$: 3410(s), 3065(w), 2960(s), 2930(s), 2890(s), 1480(s), 1240(s), 1050(s).

3e (R^2 = n-Bu): ^{1}HNMR ($CDCl_3$), δ(ppm): 0.9(3H, t), 1.4(2H, sex), 1.6(2H, quin). 3.5–4.3(7H, m), 5.5(1H, s), 6.9–7.4(5H, m). IR(neat), $\upsilon(cm^{-1})$: 3415(s), 3070(w), 2970(s), 2935(s), 2880(s), 1490(s), 1250(s), 1060(s).

3e (R^2 = i-Pr): ^{1}HNMR ($CDCl_3$), δ(ppm): 1.2(6H, d), 3.6–4.4(6H, m), 5.1(1H, s), 6.9–7.4(5H, m). IR(neat), $\upsilon(cm^{-1})$: 3420(s), 3065(w), 2970(s), 2920(s), 1590(s), 1490(s), 1245(s), 1070(s).

3e (R^2 = t-Bu): ^{1}HNMR ($CDCl_3$), δ(ppm): 1.3(9H, s), 3.5–4.4(6H, m), 6.9–7.4(5H, m). IR(neat), $\upsilon(cm^{-1})$: 3390(s), 3040(w), 2980(s), 2920(s), 1600(s), 1495(s), 1450(s), 1390(s), 1250(s), 1190(s), 1075(s), 1040(s).

3e (R^2 = allyl): ^{1}HNMR ($CDCl_3$), δ(ppm): 3.6–4.3(7H, m),5.3(2H, dd), 6.0(1H, m), 6.3(1H, s), 6.9–7.4(5H, m). IR(neat), $\upsilon(cm^{-1})$: 3405 (s), 3055(w), 2920(s), 2910(s), 1595(s), 1495(s), 1450(s), 1236(s), 1075(s), 1037(s).

3f (R^2 = Me): ^{1}HNMR ($CDCl_3$), δ(ppm): 3.36(3H, s), 3.4–4.0(5H, m), 6.5(1H, s). IR(neat), $\upsilon(cm^{-1})$: 3405(s), 2960(s), 2920(s), 2850(s), 1450(s), 1150(s), 1075(s).

3f (R^2 = n-Pr): ^{1}HNMR ($CDCl_3$), δ(ppm): 0.9(3H, t), 1.6(2H, sex), 3.4(2H, t), 3.45–4.0(5H, m), 5.0(1H, s). IR(neat), $\upsilon(cm^{-1})$: 3405(s), 2960(s), 2920(s), 2860(s), 1460(s), 1110(s), 1075(s).

3f (R^2 = i-Pr): ^{1}HNMR ($CDCl_3$), δ(ppm): 1.1(6H, d), 3.4–4.4(6H, m), 4.5(1H, s). IR(neat), $\upsilon(cm^{-1})$: 3385(s), 2965(s), 2920(s), 1585(m), 1450(m), 1395(s), 1193(s), 1080(s).

3f (R^2 = t-Bu): ^{1}HNMR ($CDCl_3$), δ(ppm): 1.2(9H, s), 3.4–4.5(6H, m). IR(neat), $\upsilon(cm^{-1})$: 3370(s), 2960(s), 2920(s), 1395(s), 1193(s), 1070(s).

3f (R^2 = allyl): ^{1}HNMR ($CDCl_3$), δ(ppm): 3.4–3.9(5H, m), 4.0(2H, d), 4.5(1H, s), 5.2(2H, dd), 5.9(1H, m). IR(neat), $\upsilon(cm^{-1})$: 3380(s), 3070(w), 2910(s), 2895(s), 1640(m), 1190(s), 1100(s), 1065(s).

4a: ^{1}HNMR ($CDCl_3$), δ(ppm): 3.2(2H, s), 3.7(2H, m), 4.8(1H, dd), 7.35(5H, m). IR(KBr), $\upsilon(cm^{-1})$: 3300(s), 3200(s), 2920(s),2910(s), 1442(s), 1335(s), 1095(s), 1045(s), 1019(s).

Trans-1,2-dihydroxy cyclohexane: ^{1}HNMR ($CDCl_3$), δ(ppm): 1.2(4H, m), 1.7(2H, m), 2.0(2H, m), 3.3(2H, m), 4.0(2H, s). IR(KBr), $\upsilon(cm^{-1})$: 3365(s), 2915(s), 2850(s), 1457(s), 1357(s), 1195(s), 1067(s), 1032(s).

4c: ^{1}HNMR ($CDCl_3$), δ(ppm): 3.4(2H, s), 3.5(2H, m), 3.58(1H, dd), 3.68(1H, dd), 3.9(1H, m), 4.0(2H, d), 5.2(2H, dd), 5.9(1H, m). IR(KBr), $\upsilon(cm^{-1})$: 3435(s), 3070(m), 2950(s), 2910(s), 1640(w), 1415(m), 1105(s), 1071(s), 1050(s).

4d: ^{1}HNMR ($CDCl_3$), δ(ppm): 0.9(3H, t), 1.2(2H, sex), 1.5(2H, quin), 3.3–3.7(7H, m), 3.8(2H, s). IR(neat), $\upsilon(cm^{-1})$: 3340(s), 3330(s), 2950(s), 2910(s), 1445(s), 1335(m), 1220(m), 1188(m), 1092(s), 1045(s), 1020(s).

4e: ^{1}HNMR ($CDCl_3$), δ(ppm): 3.2(2H, s), 3.7(1H, dd), 3.8(1H, dd), 4.0(2H, d), 4.1(1H, m), 6.9–7.4(5H, m). IR(KBr), $\upsilon(cm^{-1})$: 3435(s), 3205(s), 3095(s), 2905(s), 1590(s), 1490(s), 1450(s), 1245(s), 1165(s), 1110(s), 1060(s).