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Silylation of alcohols and phenols by HMDS in the presence of ionic liquid and silica-supported ionic liquids

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ABSTRACT

In this research, different alcohols and phenols are subjected to the reaction with HMDS in the presence of ionic liquid and silica-supported catalysts. Silylation was accomplished under mild reaction conditions at room temperature in short reaction times and good to excellent yields.

***Keywords**: Silylation, Hexamethyldisilazane (HMDS), Ionic Liquid, Silica-supported Catalyst, Alcohols and phenols.*

1. Introduction

Trimethylsilyl group is one of the most popular and widely used groups for the protection of hydroxyl group in the synthesis of organic compounds and sometimes is used in analytical chemistry to prepare silyl ethers as volatile derivatives of alcohols and phenols [1]. Therefore, different methods have been proposed for the silylation of alcohols and phenols in which removing ammonium salt (which is produced during this silylation reaction), stability, commercial availability, ease of handling and the cost of the reagent, acidity or basicity of the medium, the work-up of reaction and some other special precautions, have attracted considerable global attention. One of the reagent which has been used recently is 1,1,1,3,3,3-Hexamethyldisilazane (HMDS), a neutral, cheap, stable and commercially available reagent. Even though its handling does not require special precautions, and the work-up of the reaction is not time-consuming, due to the production of ammonia as by-product, it suffers from the low reactivity in silylation reaction. In order to improve the silylation power of HMDS, a variety of catalysts such as $(CH_3)_3SiCl$ [2], silica chloride [3], $ZnCl_2$ [4], zirconium sulfophenylphosphonate [5], $LiClO_4$ [6], $Fe(F_3COO_2)_3$ [7], $[ZrO(OTf)_2]$ [8], H-zeolite [9], KBr [10], tungestophosphoric acid [11], poly(*N*-bromobenzene-1,3-disulfonamide) [12], $ZrCl_4$ [13], $CuSO_4.5H_2O$ [14], $MgBr_2 \cdot OEt_2$ [15], $Al(OTf)_3$ [16], iodine [17], Tribromomelamine [18], $Cu(OTf)_2$[19], silica-supported perchloric acid [20], [bmim][BF_4] [21], sulfonic acid-functionalized silica [22], and 1,3-dibromo-5,5-diethylbarbituric acid [23] have been reported.

One the other hand, Ionic Liquids (ILs) are receiving considerable global attention because they offer a unique environment for chemistry, biocatalysts, separation science, materials synthesis, and electrochemistry which offer several interesting properties such as excellent chemical and thermal stability, good solvating capability, wide liquid range, and ease of recycling [24-25].

Recently, immobilization of acidic ionic liquids on solid supports has been designed and it can offer important advantages in handling, separation and reuse procedures. Based on economic criteria, it is desirable to minimize the amount of ionic liquid utilized in a potential process. Immobilized acidic ionic liquids have been used as novel solid catalysts, e.g., for esterification, nitration reactions [26], acetal formation [27], Baeyer-Villiger reaction [28], synthesis of α-aminonitriles [29] and bis-pyrazolones [30]. Among the various materials used as the catalyst supports, silica is of particular importance because of its abundant availability, high stability and the fact that organic groups can adjoin to the silica surface with strong connection to generate catalytic sites [31].

In continuation of our recent research using of acidic ionic liquidsin organic synthesis herein we report the

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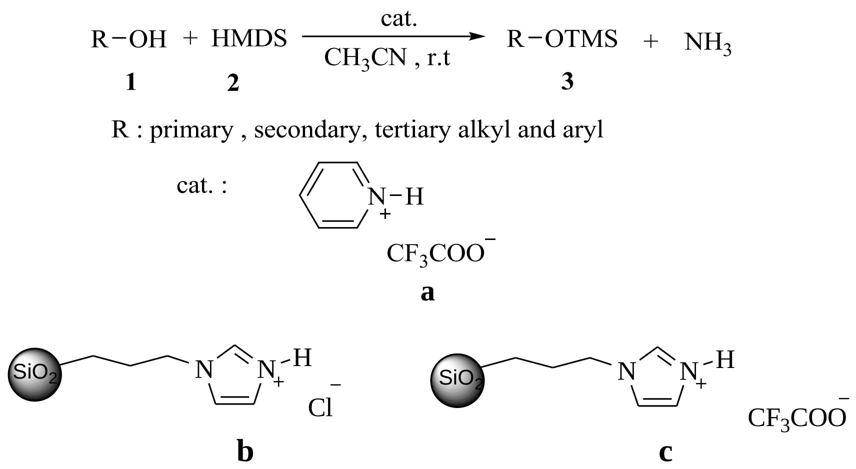


Scheme 1. Silylation of alcohols and phenlos by HMDS in the presence of ionic liquid and silica-supported ionic liquids.

silylation of different alcohols and phenols by HMDS in the presence of pyridinium 2,2,2-trifluoracatate ([py][Tfa]) as ionic liquid and also two other imidazolium ionic liquids supported on SiO_2 (Scheme 1) [32-37].

2. Experimental

2.1. General

Chemicals were purchased from the Fluka, Merck and Aldrich chemical companies. IR spectra were run on a Shimadzu Infrared Spectroscopy IR-470. The ^{1}H NMR spectroscopy was conducted using a Bruker Avance DRX (500 MHz). With TLC using silica gel SILG/UV 256 plates the progress of reaction was followed. All the products are known compounds and were characterized by comparison of their spectral (IR, ^{1}H-NMR), TLC and physical data with the data previously reported in the literature.

2.2. General procedure for silylation of hydroxyl groups

In the presence of ionic liquid **a**: To a stirred solution of alcohols/phenols (1 mmol) and HMDS (1 mmol) in acetonitrile (2 mL), [py][Tfa] (0.2 mol%) was added and the mixture was stirred at room temperature for the times mentioned in Table 2. After completion of the reaction (monitored by TLC, *n*-hexane/ EtOAc, 9:1), the mixture was washed with diethyl ether (2 × 10 mL) in order to remove ionic liquid. The organic phase was washed with water (2×10 mL) and dried over anhydrous calcium chloride. Evaporation of the solvent under reduced pressure gave the pure product.

In the presence of catalysts **b** and **c**: To a stirred solution of alcohols/phenols (1 mmol) and HMDS (1 mmol) in acetonitrile (2 mL), catalyst (0.005 g, 0.13 mol%) was added and the mixture was stirred at room temperature for the times mentioned in Table 2. After completion of the reaction (monitored by TLC, *n*-hexane/ EtOAc, 9:1), CH_2Cl_2 was added (10 mL) and the catalyst was removed by filtration. The solvent was evaporated and the trimethylsilyl ether was isolated almost as a pure crude product.

Ionic liquid **a** and catalyst **b** were prepared according to the previously reported procedures [38-39].

Preparation of catalyst **c**: Into the three-necked round bottom flask equipped with stirrer, ice bath condenser, and thermometer 3g of silica-propyl imidazolium chloride([Sipim]Cl) was suspended in 20 cm^3 of dry CH_2Cl_2. During vigorous stirring 2.9 mmol of concentrated CF_3COOH was introduced dropwise at 0˚C. Then the mixture was warm up to the room temperature, and then refluxed for 48 h. When the formed HCl was completely distilled off the condenser the solution was cooled and the CH_2Cl_2 was removed under vacuum. To remove the remaining water from the reaction mixture, 10 ml of benzene was added to the crude catalyst and stirred for 3 h by magnetic stirrer at 50˚C. The azeotrope formed was distilled off yielding silica propyl-imidazoliumtrifuoro acetate ([Sipim]Tfa) in %91 yield [40].

2.4. Spectroscodic Data of the products

Trimethyl(benzyloxy)silane (3a) [20]:Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.19 (s, 9H), 4.72 (s, 2H), 7.35-7.36 (m, 5H).IR (CCl_4): 2957, 1496, 1454, 1377, 1250, 1207, 1096, 1027, 842, 727, 695 cm^{-1}.

Trimethyl(4-methoxybenzyloxy)silane (3b) [20]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.18 (s, 9H) 3.81 (s, 3H), 4.66 (s, 2H), 6.91 (d, 2H, J =8.5 Hz), 7.44 (d, 2H, J =8.4 Hz).^{13}C NMR ($CDCl_3$, 125 MHz): δ: 0.30, 55.21, 64.41, 113.75, 128.13, 133.16, 158.90. IR (CCl4): 2999, 2959, 2901, 2836, 1613, 1587, 1512, 1464, 1376, 1300, 1284, 1171, 1085, 1037, 840, 751, 688 cm^{-1}.

Trimethyl(4-bromobenzyloxy)silane (3c) [17]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz, ppm): δ: 0.17 (s, 9H), 4.65 (s, 2H), 7.20 (d, 2H, J =8.4 Hz), 7.46 (d, 2H, J =8.6 Hz).

Trimethyl(4-nitrobenzyloxy)silane (3d) [28]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.22 (s, 9H), 4.83 (s, 2H), 7.52 (d, 2H, J =8.8 Hz), 8.22 (d, 2H, J =8.4 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ: 0.10, 63.95, 123.95, 127.00, 147.49, 149.16.

Trimethyl(3-methoxybenzyloxy)silane (3e) [31]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.2 (s, 9H), 3.84 (s, 3H), 4.71 (s, 2H), 6.82-6.98 (m, 3H), 7.29 (dd, 1H, J_1= 13.85 Hz, J_2= 6.93 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ: 0.045, 55.64, 64.95, 119.17, 119.52, 129.71, 130.01, 143.10, 160.13.

Trimethyl(2-phenylethoxy)silane (3f) [20]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.11 (s, 9H), 2.87 (t, 2H, J =7.3 Hz), 3.81 (t, 2H, J= 7.3 Hz), 7.23-7.33 (m, 5H); IR (CCl_4): 3064, 3028, 2955, 2899, 1604, 1479, 1474, 1454, 1383, 1250, 1207, 1094, 1030, 928, 842, 740, 698 cm^{-1}.

Trimethyl(3-phenylpropyloxy)silane (3g) [28]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.22 (s, 9H), 1.92-1.98 (m, 2H), 2.77 (t, 2H, J= 7.8 Hz), 3.70 (t, 2H, J =6.4 Hz), 7.26-7.29 (m, 3H), 7.35-7.38 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ: 0.03, 32.60, 34.70, 62.36, 126.17, 128.75, 128.91, 142.58.

Trimethyl(3-phenoxybenzyloxy)silane (3h): Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.17 (s, 9H), 4.70 (s, 2H), 6.92 (dd, 1H, J_1= 6.2 Hz, J_2= 1.51 Hz), 7.03-7.14 (m, 5H), 7.29-7.38 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ: 0.04, 64.67, 117.86, 119.36, 121.59, 123.60, 129.99, 130.12, 143.63, 157.

Trimethyl(phenoxy)silane (3i) [20]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.34 (s, 9H), 6.92 (d, 2H, J= 7.8 Hz), 7.02 (t, 1H, J= 7.3 Hz), 7.31 (t, 1H, J=8.0 Hz). IR (CCl_4): 3039, 2960, 1596, 1492, 1252, 1164, 1070, 1024, 1002, 918, 843, 759, 692. cm^{-1}.

Trimethyl(4-methylphenoxy)silane (3j) [20]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.32 (s, 9H), 2.33 (s, 3H), 6.80 (d, 2H, J= 8.1 Hz), 7.08 (d, 2H, J= 8.0 Hz). IR(CCl_4):2960, 1613, 1509, 1251, 1168, 1103, 916, 846, 754 cm^{-1}.

Trimethyl(4-chlorobenzyloxy)silane (3k) [17]:Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.19 (s, 9H), 4.68 (s, 2H), 7.28-7.30 (m, 4H).

Trimethyl(4-fluorophenoxy)silane (3l) [20]:Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.25 (s, 9H), 6.75-6.77 (m, 2H), 6.89-6.92 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ: 0.53, 116.10, 121.26, 151.52, 159.08.

Trimethyl(2,4,6-therimethylphenoxy)silane (3m) [30]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz, ppm): δ: 0.25 (s, 9H), 2.17 (s, 6H), 2.23 (s, 3H), 6.78 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ: 1.37, 18.02, 20.94, 128.51, 129.47, 130.70, 150.63.

Trimethyl(3,5-dimethylphenoxy)silane (3n): Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.29 (s, 9H), 2.29 (s, 3H), 2.30 (s, 3H), 6.5 (d, 2H, J= 6.39 Hz), 6.63 (d, 1H, J= 6.45 Hz).). ^{13}C NMR ($CDCl_3$, 125 MHz): δ: 0.69, 21.71, 122.94, 123.63, 139.48, 155.48.

Trimethyl(3,4-dimethyl phenoxy)silane (3o): Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ:0.28 (s, 9H), 2.22 (s, 3H), 2.24 (s, 3H), 6.62 (dt, 1H, J_1= 8.00 Hz, J_2= 2.5 Hz), 6.68 (dd, 1H, J_1= 7.00 Hz, J_2= 2.31 Hz), 7.01 (d, 1H, J= 8.1 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ:0.65, 19.28, 20.32, 121.77, 129.77., 130.70, 130.89, 138.062, 153.46.

Trimethyl(4-chloro-3-methylphenoxy)silane (3p) [29]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.26 (s, 9H), 2.32 (s, 3H), 6.62 (dd, 1H, J1= 8.6 Hz, J2= 2.8 Hz), 6.72 (d, 1H, J= 2.8 Hz), 7.17 (d, 1H, J= 7.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ: 0.58, 20.60, 119.13, 122.96, 127.10, 130.03, 137.42, 154.14.

Trimethyl((benzhydryloxy)silane (3q) [20]:Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.20 (s, 9H), 5.88 (s, 1H), 7.32 (t, 2H, J= 7.3 Hz), 7.4 (t, 4H, J= 7.6 Hz), 7.46 (t, 4H, J= 7.5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ: 0.65, 77.00, 127.04, 127.53, 128.68, 145.35 . IR (CCl_4):3063, 3027, 2957, 2863, 1598, 1492, 1453, 1354, 1303, 1251, 1187, 1090, 1061, 1027, 917, 885, 740, 700, 602 cm^{-1}.

Trimethyl(2-naphtalenoxy)silane (3r) [20] :Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.41 (s, 9H), 7.18 (dd, 1H, J1= 8.8 Hz, J2= 2.3 Hz), 7.31 (d, 1H, J= 2.1 Hz), 7.41 (t, 1H, J= 7.3 Hz), 7.50 (dt, 1H, J1= 7.6 Hz, J2= 0.8 Hz), 7.77-7.85 (m, 3H). IR (CCl_4): 3057, 2959, 1631, 1598, 1508, 1468, 1349, 1254, 1173, 1122, 978, 926, 855, 746. Cm^{-1}.

Trimethyl(biphenyl-2-yloxy)silane (3s) [29]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.05 (s, 9H), 6.92 (dd, 1H, J1= 8.0 Hz, J2= 0.7 Hz),7.06 (dt, 1H, J1= 7.5, J2=0.8 Hz), 7.21-7.26 (m, 1H), 7.31 (t, 1H, J= 7.4 Hz) 7.54 (d, 2H, J= 8.3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ: 0.51, 121.03, 122.35, 127.16, 128.26, 128.81, 130.06, 133.78, 139.49, 152.73.

Trimethyl (1-phenylethoxy) silane (3t) [20]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ:0.15 (s, 9h), 1.51 (d,3H, J=6.3 Hz), 4.93 (q, 1H, J=6.3 Hz), 7.28 (t, 1H, J= 6.9 Hz), 7.34 – 7.40 (m, 4H). IR (CCl_4): 3063, 3027, 2972, 2927, 2868, 1688, 1603, 1492, 1450, 1369, 1250, 1206, 1090, 1032, 999, 959, 841, 757, 699 cm^{-1}.

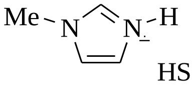
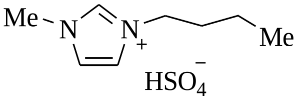
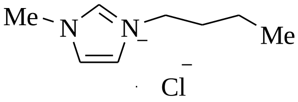
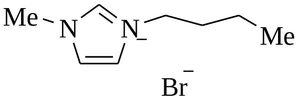
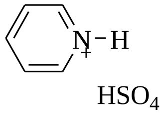
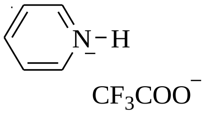
Trimethyl([1-methyl-1-(4-methyl-cyclohex-1-enyl)ethoxy]silane(3u) [27]: Colorles liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.09 (s, 9H), 0.94-2.00 (m, 16H), 5.27-5.44 (m, 1H).

Trimethyl(tert-butoxy)silane (3w) [20]: Colorless liquid ^{1}H NMR ($CDCl_3$,500MHz): δ: 0.11(s, 9H), 1.23(s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ: 58.1, 31.1, 1.4. IR (CCl_4): 2977, 1363, 1250, 1051, 794 cm^{-1}.

3. Results and Discussion

The trimethylsilylation of hydroxyl group is easily carried out at room temperature under mild condition in the presence of some ionic liquid and silica-supported catalysts (Scheme 1). Initially, several solvents were tested, it was found that acetonitrile is the best from the stand point of time and reaction conversion. Therefore, we used acetonitrile as solvent for the reactions reported here. In order to find a useful catalyst system for the silylation of alcohols and phenols some ionic liquids were tested and the best one was selected among the ionic liquids listed in Table 1.

Table 1. Silylation of *p*-methoxybenzyl alcohol by HMDS in acetonitrile as solvent at room temperature in the presence of ionic liquid as catalyst in %100 conversion.

Entry	Ionic Liquid	Time(min)
1	No catalyst	105
2		18
3		34
4		32
5		23
6		13
7		1
8	$Et_3\overset{+}{N}H.H\overset{-}{SO_4}$	6

Also, we investigated the reaction in the presence of ionic liquids supported on silica gel and the results showed that the best ones were silica-propyl imidazolium chloride([SipIm]Cl, **b**) and silica-propyl imidazoliumtriflate ([SipIm]Tfa, **c**).

Afterward, different alcohols and phenols were subjected to the reaction under three different conditions and the results are given in Table 2. As shown in Table 2, different primary, secondary, tertiary and aromatic alcohols were subjected to the reaction in the presence of the three catalysts, **a**, **b** and **c** in acetonitrile as solvent at room temperature. According to the obtained results, the three catalytic systems gave the products in short reaction times in excellent percentage of conversions. After 24 hours stirring of phenols containing electron-withdrawing groups, conversion to the corresponding trimethylsilyl ethers was not successful under similar reaction conditions (Entry **3x** Table 2), but it seemed that the best one from the stand point of generality, reaction time and reaction conversion was silica-propyl imidazoliumtriflate (Table 2).

4. Conclusions

In conclusion, we have introduced a new catalytic method for the silylation of various hydroxy compounds with HMDS under mild reaction coditions. Short reaction times, good to excellent conversions, easy work-up, stability, reusability and relatively non-toxicity of the catalyst are the main important advantages of the reported method.

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Table 2. Silylation of different alcohols and phenols by HMDS in the presence of different catalysts; a, b and c at room temperature in acetonitrile as solvent.[a]

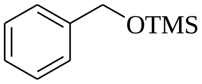
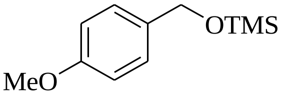
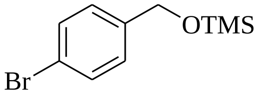
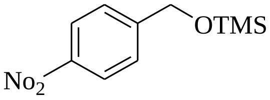
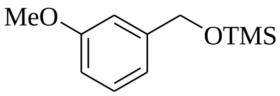
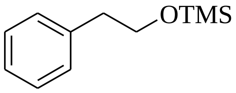
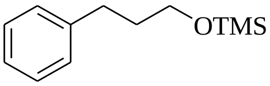
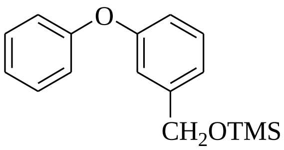
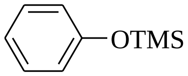
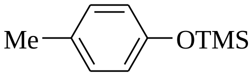
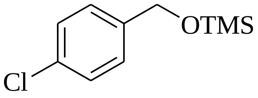
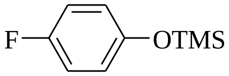
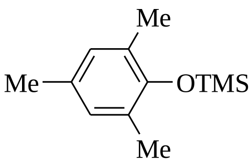
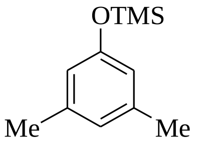
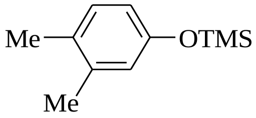
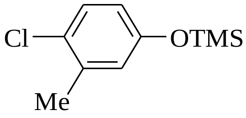
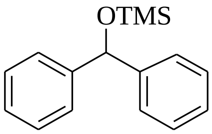
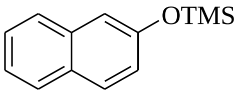
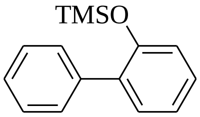
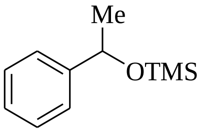
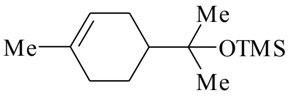
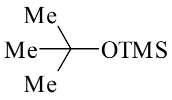
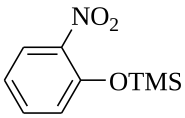
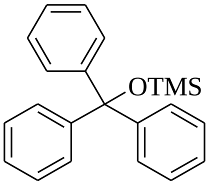
Entry	Product	Time(min)a/b/c[b]	Conversion (%) a/b/c
3a		1/1/1	100/100/100
3b		1/1/1	100/100/100
3c		4/7/1	100/100/100
3d		27/32/27	100/100/100
3e		5/1/1	100/100/100
3f		1/2/1	100/100/100
3g		2/2/1	100/100/100
3h		6/2/1	100/100/100
3i		1/1/1	100/100/100
3j		1/1/1	100/100/100
3k		14/12/21	100/100/100
3l		10/6/3	100/100/100
3m		1/2/1	100/100/100

Table 2. *(Continued).*

3n		1/1/1	100/100/100
3o		1/1/1	100/100/100
3p		15/20/11	100/100/100
3q		1/2/1	100/100/100
3r		40/52/50	100/100/100
3s		20/32/22	100/100/100
3t		2/3/3	100/100/100
3u		24[c]/24[c]/24[c]	75/30/55
3w		24[c]/24[c]/24[c]	50/0/35
3x		24[c]/24[c]/24[c]	0/0/0
3y		24[c]/24[c]/24[c]	0/<20/<25

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[a] Reaction conditions: Alcohol or phenol (1.0 mmol), catalysts a (0.4 mg 0.2 mol%), b and c(0.005g, 0.13mol%)

[b] a/b/c refer to the reaction in the presence of different catalysts a, b and c.

[c] hour

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