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Copper(II) triflate-catalyzed reduction of carboxylic acids to alcohols and reductive etherification of carbonyl compounds

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ABSTRACT

A protocol is described for the reduction of carboxylic acids to primary alcohols using 1,1,3,3-tetramethyldisiloxane (TMDS) and a catalytic amount of $Cu(OTf)_2$. Aliphatic as well as aromatic carboxylic acids are reduced in high selectivity and good yields. TMDS/$Cu(OTf)_2$ has also been found to be an efficient catalytic reducing system for the preparation of symmetrical ethers from carbonyl compounds under mild conditions.

1. Introduction

Reduction of carboxylic acids to alcohols constitutes a significant position in functional group transformation.[1] Carboxylic acids are relatively resistant to basic reducing reagents, because of the formation of a carboxylate ion. Consequently, some efficient reducing systems have been developed: H_2 gas/transition metal,[2] $NaBH_4$-additive protocol,[3] borane reducing reagents such as $(BH_3)_2$,[4] $BH_3 \cdot SMe_2$,[5] 9-borabicyclo[3.3.1]nonane (9-BBN),[6] strong aluminum hydrides such as AlH_3,[7] $LiAlH_4$,[8] $Li(OMe)_3$—AlH,[9] DIBAL,[10] or $EtMe_2SiH$/ ruthenium-based catalyst,[11] etc. In most of these cases, reactions are carried out under harsh conditions, or generate stoichiometric amounts of inorganic salts.

An alternative strategy with more functionality tolerance has also been developed. It is based on the conversion of carboxylic acid into a highly reactive intermediate, which subsequently undergoes a smooth reduction under mild conditions. These intermediates include benzotriazole esters,[12] *N*-acylbenzo-triazoles,[13] acyl azides,[14] acylimidazolides,[15] arylboronic anhydrides,[16] mixed anhydrides,[17] cyanurates,[18] fluorides,[19] *O*-acyl-isoureas,[20] carbonates,[21] carboxyl methyleniminium chlorides,[22] etc. However, this strategy still has some drawbacks: two steps are necessary and the intermediates are usually reduced by dangerous hydrides such as $NaBH_4$.

During the last decade, hydrosiloxanes appear to be promising reducing reagents because of their efficiency, stability to air and water, low toxicity, and simple handling.[23] Lawrence et al. have realized the reduction of carboxylic acids to alcohols in good yields through the use of polymethylhydrosiloxane (PMHS)/tetra-*n*-butylammonium fluoride (TBAF)[24] or PMHS/$Ti(Oi\text{-}Pr)_4$.[25] Sakai et al. recently described reduction of aliphatic carboxylic acids into primary alcohols using 1,1,3,3-tetramethyldisiloxane (TMDS) in the presence of catalytic quantity of $InBr_3$.[26] Although TMDS/$InBr_3$ system was efficient with aliphatic carboxylic acids, it was completely inefficient in the reduction of aromatic acids such as benzoic acid and its derivatives.

The Williamson etherification is a classical reaction for the synthesis of ethers.[27] It is widely used in both laboratory and industrial synthesis, and remains the most popular method of preparing both symmetrical and unsymmetrical ethers. Nevertheless, Williamson ether synthesis requires strong basic nucleophiles and good leaving groups, which can lead to side reactions. Another

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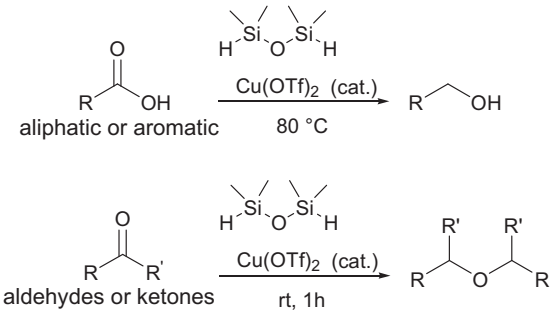
limitation arises from its sensitivity to steric bulk, which restricts the preparation of more substituted ethers. In all cases, the Williamson reaction generates stoichiometric amount of inorganic salts. Therefore, alternative methods for the synthesis of ethers have been reported,[28] including silane-reductive etherification of carbonyl compounds.[29] Hatakeyama et al. have described a TMSOTf-promoted ether synthesis from carbonyl compounds and alkoxyltrimethylsilanes via triethylsilane-reduction.[29h] However, TMSOTf is extremely moisture sensitive, difficult to handle and store. Some reported methods employ trialkylsilanes along with large excess of strong Brønsted acids.[29a] Sakai et al. have recently prepared symmetrical ethers from aliphatic ketones using silanes and 5 mol % $InBr_3$.[29g] Although these methodologies are efficient, several silanes have been proposed to be harmful since they release a dangerous, toxic, and pyrophoric SiH_4 gas.[23a] As a consequence, hydrosiloxanes are considered to be a good alternative for silanes.

For several years, our laboratory has demonstrated that two hydrosiloxanes, TMDS and PMHS, can conveniently reduce a range of functionalities including phosphine oxides,[30] nitriles,[31] amides,[32] nitro groups,[33] and acetals[34] activated by different metal catalysts, i.e., Cu, Ti, Fe, Pd, etc.

Metal triflates have been widely employed as catalysts in a large variety of organic reactions.[35] Very recently, we reported that TMDS/$Cu(OTf)_2$ reducing system efficiently promotes cleavage of one C–O bond of acetals.[36] This protocol has also been successfully applied in the regioselective ring opening of hexopyranosyl acetals to ethers.[37] As part of our continuing interest in the reduction of organic functional groups, we describe herein the use of TMDS/$Cu(OTf)_2$ system for the straightforward reduction of both aliphatic and aromatic carboxylic acids to primary alcohols as well as reduction of acids, aldehydes, and ketones to symmetrical ethers (Scheme 1). The one-step reaction avoids the drawbacks of employing dangerous hydride sources, harsh reaction conditions or generating excessive inorganic wastes.



Scheme 1. $Cu(OTf)_2$-catalyzed reduction of carboxylic acids to primary alcohols and reductive etherification of carbonyl compounds with TMDS.

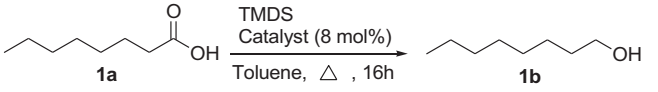
To the best of our knowledge, metal triflates have never been used with hydrosiloxanes to transform carbonyl compounds to ethers.

2. Results and discussion

Octanoic acid **1a** was selected for model studies. We started our investigation by screening catalysts and then optimized the reaction conditions (Table 1).

First, a set of metal triflates (8 mol %) were employed with TMDS (10 equiv, 20 Si–*H* mol/mol substrate) in toluene at 110 °C. No conversion of **1a** was detected when $Fe(OTf)_2$ was used (Table 1, entry 1). $Bi(OTf)_3$ and Ce_xOTf (19–23% Ce basis) provided low-to-moderate yields of octan-1-ol **1b** (Table 1, entries 2 and 3). The best results were obtained with $Cu(OTf)_2$, in the same conditions as described before. In this case, alcohol **1b** was gained with 99% yield (Table 1, entry 4). The amount of TMDS could be reduced to 8 Si–*H* mol/mol substrate (4 equiv) in the presence of 8 mol % $Cu(OTf)_2$, without affecting neither the conversion nor the selectivity of the reduction reaction (Table 1, entry 5). Further decrease of the amount of either TMDS or $Cu(OTf)_2$ afforded moderate conversion of **1a**. Finally, the reaction temperature was optimized to 80 °C. In this case, alcohol **1b** was isolated with 91% yield (Table 1, entry 6). At 60 °C, no conversion of acid **1a** was observed (Table 1, entry 7).

Table 1
Screening the reaction conditions for the reduction of aliphatic carboxylic acid **1a**



Entry	TMDS (Si–*H* equiv)	Catalyst	*T* (°C)	Conv. (%)	Yield[a] (%)
1	20	$Fe(OTf)_2$	110	—	—
2	20	$Bi(OTf)_3$	110	79	21
3	20	Ce_xOTf[b]	110	68	66
4	20	$Cu(OTf)_2$	110	>99	>99
5	8	$Cu(OTf)_2$	110	98	93
6	8	$Cu(OTf)_2$	80	95	91
7	8	$Cu(OTf)_2$	60	—	—

[a] Isolated yields.
[b] 19–23% Ce basis.

Although TMDS/$Cu(OTf)_2$ reducing system was efficient with aliphatic carboxylic acids [8 equiv TMDS, 16 Si–*H* mol/mol substrate, 8 mol % $Cu(OTf)_2$, toluene, 80 °C], reduction of benzoic acid **2a** didn't occur under this reaction condition. In this case, the only observed products were diphenylmethane derivatives **2c** (Table 2, entry 1). These products were isolated as a mixture of two isomers, with 87% overall yield. The ratio between *para* and *meta* isomers was 3:2 (mol/mol). In view of this result, we assume that isomers **2c** were generated via deoxygenation of benzoic acid followed by a substitution reaction with toluene. Sakai et al. have also observed the formation of diphenylmethane derivatives while studying the reduction of aromatic carboxylic acids using $PhSiH_3$ and $InBr_3$.[26] It should be noted that the authors did not succeed to reduce aromatic carboxylic acids to alcohols with their system. Since the observed by-products were generated through reaction with toluene, we further explored the reduction of aromatic carboxylic acids employing the same amount of reagents as described before, but in different solvents (Table 2).

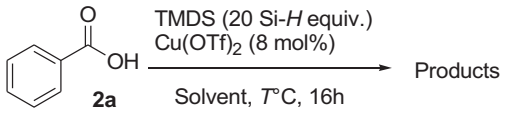
Benzoic acid **2a** remained sluggish in CH_2Cl_2 and $ClCH_2CH_2Cl$ (Table 2, entries 2 and 3). The target compound, benzyl alcohol **2b** was afforded when THF and 1,4-dioxane were used. In these cases, incomplete conversion of benzoic acid **2a** led to moderate yields of benzyl alcohol **2b** (Table 2, entries 4 and 5). It is probably because of the low solubility of starting material in these solvents. When 2-methyl THF was employed, benzoic acid **2a** was successfully reduced to the corresponding benzyl alcohol **2b** with 86% isolated yield (Table 2, entry 6). The amounts of TMDS and $Cu(OTf)_2$ were then decreased to 4 equiv (8 Si–*H* mol/mol substrate) and 5 mol %, without influencing the high conversion and yield of the target alcohol (Table 2, entry 7). Finally, when $InBr_3$ (5 mol %) was tried as catalyst, with TMDS (4 equiv) in 2-methyl THF, at 80 °C, many unknown products were detected after reaction.

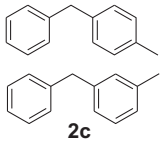
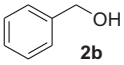
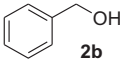
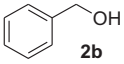
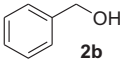
We then proceeded to investigate the scope of our reaction under the optimized conditions (Table 3).

In entries 1–12, aliphatic carboxylic acids were reduced using 4 equiv TMDS (8 Si–*H* mol/mol substrate), 8 mol % $Cu(OTf)_2$ in toluene at 80 °C for 16 h.

With pentanoic acid **3a** as starting material, pentan-1-ol **3b** was obtained with 71% isolated yield and 100% selectivity. In this case, the low boiling point of pentan-1-ol **3b** resulted in partial loss of product in the reduced pressure evaporation during the reaction treatment (Table 3, entry 1). Acids with longer alkyl chain length (C6–C18) were transformed into the corresponding alcohols in

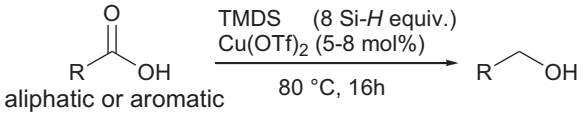
Table 2
Screening the reaction conditions for the reduction of aromatic carboxylic acid **2a**



Entry	Solvent	T (°C)	Product	Yield[a] (%)
1	Toluene	110	 **2c**	87[b]
2	CH_2Cl_2	39	—	—
3	$ClCH_2CH_2Cl$	82	—	—
4	THF	66	 **2b**	47
5	1,4-Dioxane	101	 **2b**	54
6	2-Me THF	80	 **2b**	86
7[c]	2-Me THF	80	 **2b**	84

[a] Isolated yields.
[b] The ratio between *para* and *meta* was 3:2 (mol/mol).
[c] TMDS (4 equiv, 8 Si–*H* mol/mol substrate) and 5 mol% $Cu(OTf)_2$ were used.

Table 3
$Cu(OTf)_2$-catalyzed reduction of aliphatic and aromatic carboxylic acids to alcohols using TMDS



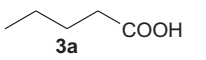
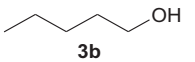
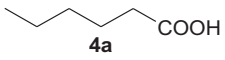
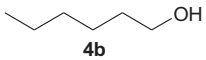
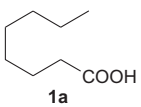
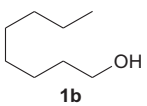
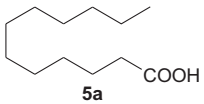
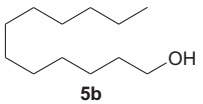
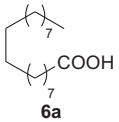
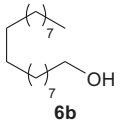
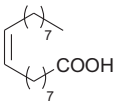
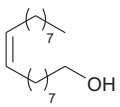
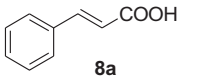
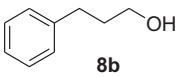
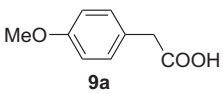
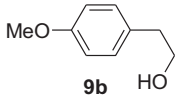
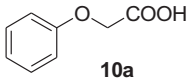
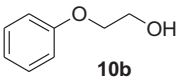
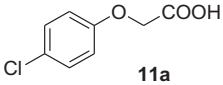
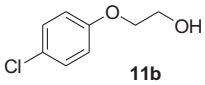
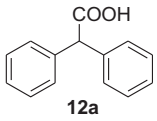
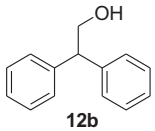
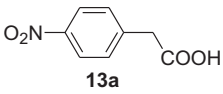
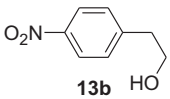
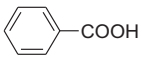
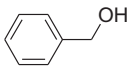
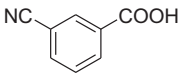
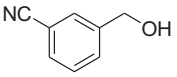
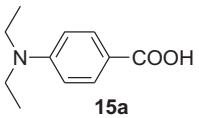
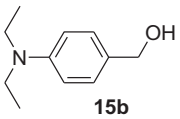
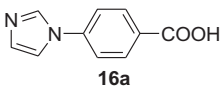
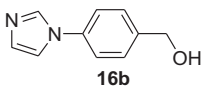
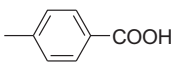
Entry	Carboxylic acid	Alcohol	Yield[a] (%)
1[b]	 **3a**	 **3b**	71
2	 **4a**	 **4b**	94
3	 **1a**	 **1b**	91
4	 **5a**	 **5b**	95
5	 **6a**	 **6b**	96
6	 Oleic acid **7a**	 **7b**	32

Table 3 (*continued*)

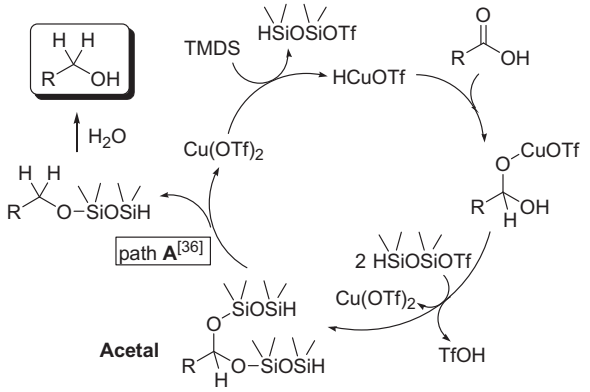
Entry	Carboxylic acid	Alcohol	Yield[a] (%)
7	 **8a**	 **8b**	76
8	 **9a**	 **9b**	63
9	 **10a**	 **10b**	88
10	 **11a**	 **11b**	43
11	 **12a**	 **12b**	86
12	 **13a**	 **13b**	—
13[c]	 **2a**	 **2b**	84
14	 **14a**	 **14b**	—
15	 **15a**	 **15b**	—
16	 **16a**	 **16b**	—
17	 **17a**	**17b**	73
18	**18a**	**18b**	82

[a] Isolated yields.
[b] For aliphatic carboxylic acids (entries 1–12): 8 Si–*H* equiv TMDS, 8 mol% $Cu(OTf)_2$, toluene, 80 °C, 16 h.
[c] For aromatic carboxylic acids (entries 13–18): 8 Si–*H* equiv TMDS, 5 mol% $Cu(OTf)_2$, 2-Me THF, 80 °C, 16 h.

quantitative isolated yields (Table 3, entries 2–5). When oleic acid **7a** was reduced, oleyl alcohol **7b** was obtained as the major product in 32% yield (Table 3, entry 6). The cis configuration of the double bond remained unchanged. However, the conjugated trans double bond of cinnamic acid **8a** was reduced under the same condition (Table 3, entry 7). Carboxylic acids bearing aromatic ethers furnished the desired alcohols in moderate-to-good yields (Table 3, entries 8–10). Steric hindrance in carboxylic acid **12a** didn't affect its high conversion into the corresponding alcohol (Table 3, entry 11).

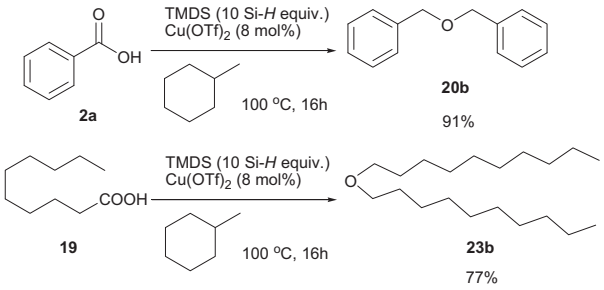
Reduction of aromatic carboxylic acids was conducted using 4 equiv TMDS (8 Si–*H* mol/mol substrate), 5 mol % $Cu(OTf)_2$ in 2-methyl THF at 80 °C for 16 h (Table 3, entries 13–18). Aromatic alcohols **2b**, **17b**, and **18b** were afforded in good yields starting from aromatic acids **2a**, **17a**, and **18a**, respectively (Table 3, entries 13, 17, and 18). Nitrogen containing substrates remained inactive under these reaction conditions (Table 3, entries 12, 14–16).

A plausible mechanism for the reduction of carboxylic acids to alcohols is shown in Scheme 2. Similar to silyl halides,[26] we believe that siloxyl triflate serves as a promoter for the reduction reaction. First, TMDS reacts with $Cu(OTf)_2$ to generate HCuOTf. Hydrocopperation of carboxylic acid furnishes a hemiketal, which undergoes a substitution reaction with siloxyl triflate to afford disiloxylated acetal intermediate.[38] Then, the disiloxylated acetal is further reduced to a siloxylated ether in a similar pathway A as described in our previous publication.[36] The corresponding alcohol is obtained after hydrolysis and $Cu(OTf)_2$ is regenerated. At the beginning of the reaction pathway, formation of a siloxylated ester intermediate also seems possible. Extraction of an acidic proton in the carboxylic acid by a siloxane proceeds in the presence of a Lewis acid.



Scheme 2. Presumed reaction pathway for $Cu(OTf)_2$-catalyzed reduction of carboxylic acids by TMDS.

$Cu(OTf)_2$-catalyzed reductive etherification of carboxylic acids with TMDS was further explored (Scheme 3). Sakai et al. reported a two-step preparation of symmetrical ethers from carboxylic acids via an ester intermdiate.[39] When we screened solvent to reduce benzoic acid **2a**, symmetrical ether **20b** was obtained in quantitative yield in methyl cyclohexane using 5 equiv TMDS (10 Si–*H* mol/mol substrate) and 8 mol % $Cu(OTf)_2$ at 100 °C. Decanoic acid **19** also afforded symmetrical ether **23b** in good yield under the same reaction condition. This one-step methodology was successfully applied to reduce both aliphatic and aromatic carboxylic acids to ethers.



Scheme 3. $Cu(OTf)_2$-catalyzed reduction of carboxylic acids to symmetrical ethers with TMDS.

We then continued our study in the reductive etherification of aldehydes and ketones. Benzaldehyde **20a** was initially selected as model. In the presence of 1 mol % $Cu(OTf)_2$, and 0.6 equiv TMDS (1.2 Si–*H* mol/mol substrate) in CH_2Cl_2 at room temperature, the reaction was complete within 1 h. Dibenzyl ether **20b** was obtained as the desired product in 95% isolated yield (Table 4, entry 1). In view of this good result, the same reaction conditions were applied with other aromatic and aliphatic aldehydes (Table 4, entries 2–5). In these cases, the corresponding substituted aromatic ethers and aliphatic ethers with different alkyl chain length were afforded in good-to-excellent yields (85–96%). When substrates were changed to ketones (Table 4, entries 6–9), the same reaction conditions were employed. Symmetrical ethers were formed in excellent isolated yields ranging from 82 to 97%. Compared with Sakai's method to synthesize symmetrical ethers[29g] (4 equiv $PhSiH_3$ or Et_3SiH, and 5 mol % $InBr_3$), much less amount of safer reducing agent and catalyst was used for TMDS/$Cu(OTf)_2$ system. In entries 6–8, the products were produced as diastereomeric mixtures. Ratios of the diastereoisomers were determined by NMR or GC–MS spectra. With dialdehyde **29a** as starting material, 3 equiv TMDS (6 Si–*H* mol/mol substrate) and 5 mol % $Cu(OTf)_2$ were added. A macrocyclic ether **29b** was furnished in 81% isolated yield (Table 4, entry 10). Komatsu et al. prepared similar products using Et_3SiH in the presence of Me_3SiOTf or $BiBr_3$.[40] All products prepared in this paper were analyzed by ^1H, ^{13}C NMR, and mass spectroscopy.

We here propose a mechanism using TMDS/$Cu(OTf)_2$ reducing system (Scheme 4). First, reaction between TMDS and $Cu(OTf)_2$ generates HCuOTf. After hydrocopperation of the carbonyl compound, the formed intermediate reacts with siloxyl triflate to furnish a siloxylated ether. This ether attacks another $Cu(OTf)_2$-activated carbonyl compound to afford a siloxylated acetal. The corresponding symmetrical ether is then obtained after desiloxylation through pathway A as described in our previous paper.[36]

3. Conclusion

In summary, we described herein a safe and non-toxic siloxane/$Cu(OTf)_2$ reducing system for the direct reduction of both aliphatic and aromatic carboxylic acids to primary alcohols. The obtained results remain unprecedented since 1,1,3,3-tetramethyldisiloxane (TMDS) has been reported to be inefficient to reduce aromatic carboxylic acids.[26]

Moreover, the described reducing system also furnishes symmetrical ethers from various carbonyl compounds in good-to-excellent yields. Key features of this protocol are the mild reaction conditions and the relatively small amount of both catalyst and reductant.

4. Experimental section

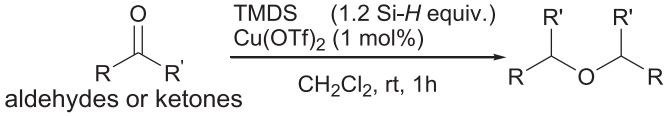
4.1. General

Products in this paper are mainly known products and have already been characterized in the literature. All purchased chemicals and reagents were of high commercially available grade. Solvents were purified by standard procedures. ^1H and ^{13}C NMR spectra were recorded on Bruker ALX-300, DRX-300 or DRX 400 spectrometer in solvents using tetramethylsilane as the internal standard (chemical shifts in parts per million). Reactions were monitored by TLC (thin-layer chromatography). GC–MS were measured with a FOCUS DSQ instrument using electronic ionization with a DBS phase; column dimensions 30 m×0.25 mm (initial temperature 70 °C; initial time 2 min; rate 15 °C/min). ESI mass spectra were recorded on Bruker MicroTOFQII or ThermoLCQ spectrometer. EI and CI mass spectra were obtained on Thermo-Finnigan MAT95XL spectrometer using standard conditions.

4.2. General procedure for reduction of aliphatic carboxylic acids to primary alcohols

In a sealed tube, 29 mg $Cu(OTf)_2$ (0.08 mmol, 8 mol %) and 0.7 mL TMDS (537 mg, 4 mmol, 8 Si–*H* mol/mol substrate) were

Table 4
$Cu(OTf)_2$-catalyzed reductive etherification of carbonyl compounds with TMDS



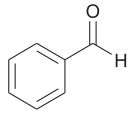
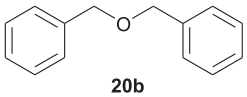
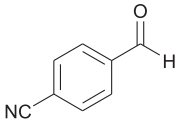
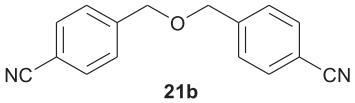
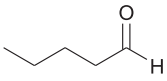
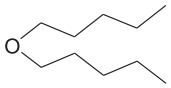
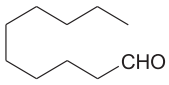
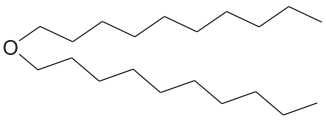
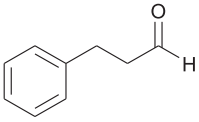
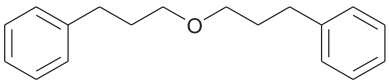
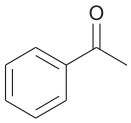
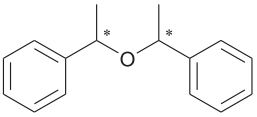
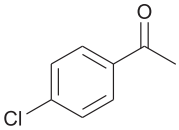
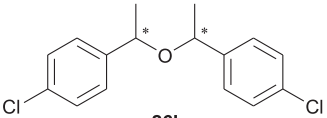
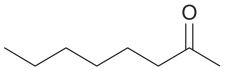
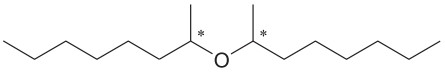
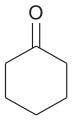
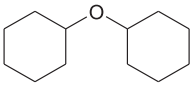
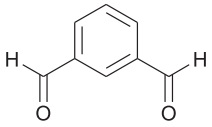
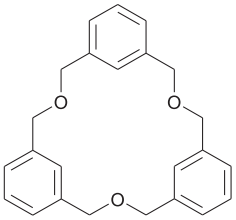
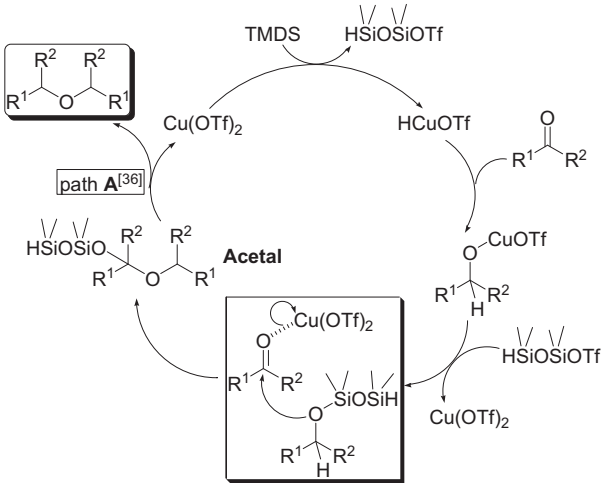
Entry	Carbonyl Compound	Ether	Conv. (%)	Isolated yield (%)
1	 **20a**	 **20b**	≥99	95
2	 **21a**	 **21b**	≥99	86
3	 **22a**	 **22b**	≥99	96
4	 **23a**	 **23b**	≥99	88
5	 **24a**	 **24b**	≥99	85
6	 **25a**	 **25b**	≥99	82[a]
7	 **26a**	 **26b**	≥99	92[b]
8	 **27a**	 **27b**	≥99	94[a]

Table 4 (*continued*)

Entry	Carbonyl Compound	Ether	Conv. (%)	Isolated yield (%)
9	 **28a**	 **28b**	≥99	97
10[c]	 **29a**	 **29b**	≥99	81

[a] The product was obtained as diastereomeric mixture in 3:1 ratio, evaluated by NMR or GC–MS.
[b] The product was obtained as diastereomeric mixture in 1:1 ratio, evaluated by NMR.
[c] TMDS (3 equiv, 6 Si–*H* mol/mol substrate) and 5 mol % $Cu(OTf)_2$ were added into reaction medium.



Scheme 4. Presumed reaction pathway for $Cu(OTf)_2$-catalyzed reductive etherification of carbonyl compounds.

introduced to a solution of aliphatic carboxylic acid (1 mmol) in 1.5 mL toluene. After stirring 16 h at 80 °C, the reaction mixture was cooled to room temperature and quenched with 4 mL H_2O. The organic layer was extracted with CH_2Cl_2, dried with anhydrous $MgSO_4$, and evaporated under reduced pressure. The crude was purified by silica gel column chromatography to obtain the alcohol.

*4.2.1. Octan-1-ol (**1b**).* Colorless oil; yield: 91%; TLC: R_f=0.53 (cyclohexane/EtOAc=3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.64 (t, J=6.7 Hz, 2H), 1.62–1.49 (m, 2H), 1.37–1.21 (m, 10H), 0.87 (t, J=6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=63.0, 32.8, 31.9, 29.5, 29.4, 25.9, 22.8, 14.2; GC–MS: t_R=5.51 min; m/z (%)=112 (2) [$M^{+\bullet}-H_2O$], 97 (5), 84 (68), 70 (71), 56 (72), 41 (100).

*4.2.2. Pentan-1-ol (**3b**).* Colorless oil; yield: 71%; TLC: R_f=0.50 (cyclohexane/EtOAc=2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.60 (t, J=6.7 Hz, 2H), 2.00 (br s, 1H), 1.65–1.42 (m, 2H), 1.40–1.22 (m, 4H), 0.88 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=63.0, 32.5, 28.0, 22.6, 14.1; GC–MS: t_R=3.81 min; m/z (%)=88 [$M^{+\bullet}$], 70 (31) [$M^{+\bullet}-H_2O$], 55 (52), 42 (100).

*4.2.3. Hexan-1-ol (**4b**).* Colorless oil; yield: 94%; TLC: R_f=0.49 (cyclohexane/EtOAc=2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.61 (t, J=6.7 Hz, 2H), 1.92 (br s, 1H), 1.62–1.44 (m, 2H), 1.39–1.21 (m, 6H), 0.87 (t, J=6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=63.1, 32.8, 31.8, 25.5, 22.7, 14.1; GC–MS: t_R=5.24 min; m/z (%)=84 (4) [$M^{+\bullet}-H_2O$], 69 (30), 56 (100), 43 (90).

*4.2.4. Dodecan-1-ol (**5b**).* White solid; yield: 95%; TLC: R_f=0.63 (cyclohexane/EtOAc=3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.64 (t, J=6.6 Hz, 2H), 1.61–1.52 (m, 2H), 1.46 (br s, 1H), 1.37–1.22 (m, 18H), 0.88 (t, J=6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=63.3, 33.0, 32.1, 29.8, 29.8, 29.8, 29.8, 29.6, 29.5, 25.9, 22.8, 14.3; MS (EI): m/z (%)= 168.1 (8) [$M^{+\bullet}-H_2O$], 140.1 (13), 125.1 (8), 111.1 (25), 97.1 (49), 83.1 (74), 69.1 (87), 55.1 (100), 43.2 (89).

*4.2.5. Octadecan-1-ol (**6b**).* White solid; yield: 96%; TLC: R_f=0.80 (cyclohexane/EtOAc=3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.61 (t, J=6.7 Hz, 2H), 2.41 (br s, 1H), 1.61–1.49 (m, 2H), 1.48–1.38 (m, 2H), 1.30–1.23 (m, 28H), 0.87 (t, J=6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=63.1, 32.9, 32.1, 29.8, 29.8, 29.8, 29.8, 29.8, 29.8, 29.8, 29.8, 29.6, 29.5, 27.0, 25.9, 22.8, 14.2; ESI MS: calcd for $C_{18}H_{37}$ ([$M-H_2O+H$]$^+$) 253.3, found 253.3.

*4.2.6. Oleyl alcohol (**7b**).* Colorless oil; yield: 32%; TLC: R_f=0.90 (cyclohexane/EtOAc=1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.42–5.27 (m, 2H), 3.63 (t, J=6.6 Hz, 2H), 2.09–1.92 (m, 4H), 1.58–1.51 (m, 2H), 1.38–1.20 (m, 22H), 0.88 (t, J=6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=130.1, 129.9, 63.2, 33.0, 32.1, 29.9, 29.9, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 27.4, 27.3, 25.9, 22.8, 14.2; GC–MS: t_R=13.47 min; m/z (%)=268 [$M^{+\bullet}$], 250 (20), 222 (4), 166 (2), 151 (3), 138 (10), 124 (15), 109 (28), 96 (79), 82 (100), 67 (61), 55 (44), 41 (80).

*4.2.7. 3-Phenyl-propan-1-ol (**8b**).* Colorless oil; yield: 76%; TLC: R_f=0.64 (cyclohexane/EtOAc=1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.27–7.16 (m, 2H), 7.16–7.02 (m, 3H), 3.59 (t, J=6.5 Hz, 2H), 2.63 (t, J=7.6 Hz, 2H), 1.91–1.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=141.9, 128.5, 128.5, 126.0, 62.4, 34.3, 32.2; GC–MS: t_R=8.01 min; m/z (%)=136 (38) [$M^{+\bullet}$], 117 (100), 91 (81), 77 (15), 65 (11), 51 (6).

*4.2.8. 2-(4-Methoxy-phenyl)-ethanol (**9b**).* Red oil; yield: 63%; TLC: R_f=0.53 (cyclohexane/EtOAc=1:1); ^{1}H NMR (300 MHz, $CDCl_3$):

δ=7.14 (d, J=8.6 Hz, 2H), 6.85 (d, J=8.6 Hz, 2H), 3.80 (t, J=6.6 Hz, 2H), 3.79 (s, 3H), 2.80 (t, J=6.6 Hz, 2H), 2.36 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=158.3, 130.5, 130.1, 114.1, 63.9, 55.4, 38.3; ESI MS: calcd for $C_9H_{13}O_2$ ($[M+H]^+$) 153.1, found 153.1.

*4.2.9. 2-Phenoxy-ethanol (**10b**).* Colorless oil; yield: 88%; TLC: R_f=0.58 (cyclohexane/EtOAc=1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.24–7.11 (m, 2H), 6.94–6.72 (m, 3H), 3.94 (dd, J=5.3, 3.8 Hz, 2H), 3.83 (dd, J=5.3, 3.7 Hz, 2H), 2.68 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=158.6, 129.6, 121.1, 114.6, 69.2, 61.4; ESI MS: calcd for $C_8H_{10}NaO_2$ ($[M+Na]^+$) 161.0, found 161.0.

*4.2.10. 2-(4-Chloro-phenoxy)-ethanol (**11b**).* White solid; yield: 43%; TLC: R_f=0.68 (cyclohexane/EtOAc=1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.23 (d, J=8.8 Hz, 2H), 6.83 (d, J=8.8 Hz, 2H), 4.04 (t, J=4.0 Hz, 2H), 3.95 (t, J=4.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=157.3, 129.6, 129.5, 115.9, 69.5, 61.4; GC–MS: t_R=9.84 min; m/z (%)=172 (27) [$M^{+\bullet}$], 141 (2), 128 (100), 111 (11).

*4.2.11. 2,2-Diphenyl-ethanol (**12b**).* Colorless oil; yield: 86%; TLC: R_f=0.62 (cyclohexane/EtOAc=2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.52–6.91 (m, 10H), 4.14–3.90 (m, 3H), 1.89 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=141.6, 128.7, 128.4, 126.8, 66.0, 53.6; GC–MS: t_R=11.41 min; m/z (%)=198 (5) [$M^{+\bullet}$], 167 (100), 152 (18), 115 (3).

4.3. General procedure for reduction of aromatic carboxylic acids to primary alcohols

In a sealed tube, 18 mg $Cu(OTf)_2$ (0.05 mmol, 5 mol %) and 0.7 mL TMDS (537 mg, 4 mmol, 8 Si–*H* mol/mol substrate) were introduced to a solution of aromatic carboxylic acid (1 mmol) in 1.5 mL 2-methyl THF. After stirring for 16 h at 80 °C, the reaction mixture was cooled to room temperature and quenched with 4 mL H_2O. The organic layer was extracted with CH_2Cl_2, dried with anhydrous $MgSO_4$, and evaporated under reduced pressure. The crude was purified by silica gel column chromatography to obtain the alcohol.

*4.3.1. Benzyl alcohol (**2b**).* Colorless oil; yield: 84%; TLC: R_f=0.62 (cyclohexane/EtOAc=2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.92–7.10 (m, 5H), 4.62 (s, 2H), 2.82 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=140.9, 128.5, 127.6, 127.0, 65.1; MS (EI): m/z (%)=108.1 (97) [$M^{+\bullet}$], 91.1 (19), 79.1 (100).

*4.3.2. p-Tolyl-methanol (**17b**).* White solid; yield: 73%; TLC: R_f=0.46 (cyclohexane/EtOAc=2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.25 (d, J=8.0 Hz, 2H), 7.18 (d, J=8.0 Hz, 2H), 4.62 (s, 2H), 2.36 (s, 3H), 2.05 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=138.0, 137.4, 129.3, 127.2, 65.3, 21.2; GC–MS: t_R=6.15 min; m/z (%)=122 (100) [$M^{+\bullet}$], 107 (98), 91 (55), 79 (80), 65 (21), 51 (26).

*4.3.3. (4-Chloro-phenyl)-methanol (**18b**).* White solid; yield: 82%; TLC: R_f=0.67 (cyclohexane/EtOAc=1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.41–7.27 (m, 4H), 4.67 (s, 2H), 1.70 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=128.8, 128.4, 124.9, 124.6, 64.7; GC–MS: t_R=7.19 min; m/z (%)=142 (63) [$M^{+\bullet}$], 113 (12), 107 (74), 89 (12), 79 (100), 63 (6), 51 (45).

4.4. General procedure for reductive etherification of carboxylic acids

In a sealed tube, 29 mg $Cu(OTf)_2$ (0.08 mmol, 8 mol %) and 0.9 mL TMDS (672 mg, 5 mmol, 10 Si–*H* mol/mol substrate) were introduced to a solution of carboxylic acid (1 mmol) in 1.5 mL methyl cyclohexane. After stirring 16 h at 100 °C, the reaction mixture was cooled to room temperature and quenched with 4 mL H_2O. The organic layer was extracted with CH_2Cl_2, dried with anhydrous $MgSO_4$, and evaporated under reduced pressure. The crude was purified by silica gel column chromatography to obtain the symmetrical ether.

*4.4.1. Benzyl ether (**20b**).* Colorless oil; yield: 91%; TLC: R_f=0.52 (cyclohexane/EtOAc=16:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.69–7.36 (m, 10H), 4.74 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=138.3, 128.4, 127.7, 127.6, 72.0; ESI MS: calcd for $C_{14}H_{15}O$ ($[M+H]^+$) 199.1, found 199.1.

*4.4.2. Decanyl ether (**23b**).* Colorless oil; yield: 77%; TLC: R_f=0.46 (cyclohexane/EtOAc=20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.39 (t, J=6.7 Hz, 4H), 1.33–1.21 (m, 32H), 0.88 (t, J=6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=71.1, 32.1, 29.9, 29.8, 29.7, 29.7, 29.5, 26.4, 22.8, 14.3; GC–MS: t_R=13.46 min; m/z (%)=140 (11), 112 (12), 97 (22), 85 (52), 71 (52), 57 (63), 43 (100).

4.5. General procedure for reductive etherification of aldehydes and ketones

In a screw-capped vial, 3.7 mg $Cu(OTf)_2$ (0.01 mmol, 1 mol %) and 0.1 mL TMDS (80.6 mg, 0.6 mmol, 1.2 Si–*H* mol/mol substrate) were introduced to a solution of aldehyde or ketone (1 mmol) in 1.5 mL CH_2Cl_2. After stirring for 1 h at room temperature, the reaction was quenched with 4 mL H_2O. The organic layer was extracted with CH_2Cl_2, dried with anhydrous $MgSO_4$, and evaporated under reduced pressure. The crude was purified by silica gel column chromatography to obtain the symmetrical ether.

*4.5.1. 4,4′-(Oxydimethylene)dibenzonitrile (**21b**).* Yellow oil; yield: 86%; TLC: R_f=0.27 (cyclohexane/EtOAc=5:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.67–7.55 (m, 4H), 7.52–7.39 (m, 4H), 4.73 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=146.5, 132.3, 127.1, 119.0, 110.9, 64.1; ESI MS: calcd for $C_{16}H_{13}N_2O$ ($[M+H]^+$) 249.0, found 249.0.

*4.5.2. Pentyl ether (**22b**).* Colorless oil; yield: 96%; TLC: R_f=0.47 (cyclohexane/EtOAc=7:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.37 (t, J=6.7 Hz, 4H), 1.61–1.50 (m, 4H), 1.35–1.26 (m, 8H), 0.88 (t, J=6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=71.1, 29.6, 28.5, 22.7, 14.1; GC–MS: t_R=5.46 min; m/z (%)=158 [$M^{+\bullet}$], 71 (69), 43 (100).

*4.5.3. 1,1′-(Oxydi-3,1-propanediyl)dibenzene (**24b**).* Colorless oil; yield: 85%; TLC: R_f=0.60 (cyclohexane/EtOAc=8:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.24–7.12 (m, 4H), 7.12–7.01 (m, 6H), 3.31 (t, J=6.4 Hz, 4H), 2.60 (t, J=7.8 Hz, 4H), 1.90–1.70 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=142.1, 128.6, 128.4, 125.8, 70.0, 32.5, 31.4; CIMS: calcd for $C_{18}H_{23}O$ ($[M+H]^+$) 255.1, found 255.1.

*4.5.4. Methylbenzyl ether (**25b**).* Colorless oil; yield: 82%; TLC: R_f=0.67 (cyclohexane/EtOAc=16:1); *Isomer 1*: ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.31–7.03 (m, 10H), 4.16 (q, J=6.5 Hz, 2H), 1.29 (d, J=6.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=144.3, 128.6, 127.5, 126.4, 74.8, 24.8; *Isomer 2*: ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.31–7.03 (m, 10H), 4.44 (q, J=6.4 Hz, 2H), 1.37 (d, J=6.4 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=144.4, 128.4, 127.3, 126.4, 74.5, 23.1; ESI MS: calcd for $C_{16}H_{18}NaO$ ($[M+Na]^+$) 249.1, found 249.1.

*4.5.5. 1-(4-Chloro-phenyl)-ethyl ether (**26b**).* Colorless oil; yield: 92%; TLC: R_f=0.77 (cyclohexane/EtOAc=12:1); *Isomer 1*: ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.24–7.14 (m, 8H), 4.38 (q, J=6.4 Hz, 2H), 1.35 (d, J=6.4 Hz, 6H); *Isomer 2*: ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.14–7.06 (m, 8H), 4.10 (q, J=6.5 Hz, 2H), 1.26 (d, J=6.5 Hz, 6H); GC–MS: t_R=13.18 min (overlapped); m/z (%)=294 (19) [$M^{+\bullet}$], 282 (35), 155 (11), 139 (100), 103 (32), 77 (21), 43 (18).

*4.5.6. 2-[(1-Methylheptyl)oxy]-octane (**27b**).* Colorless oil; yield: 94%; TLC: R_f=0.80 (cyclohexane/EtOAc=32:1); *Isomer 1*: ^{1}H NMR

(300 MHz, $CDCl_3$): δ=3.50–3.28 (m, 2H), 1.46–1.18 (m, 20H), 1.08 (d, J=6.1 Hz, 6H), 0.87 (t, J=5.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=73.1, 37.7, 32.1, 29.6, 26.0, 22.8, 20.6, 14.2; GC–MS: t_R=9.75 min; m/z (%)= 157 (28), 113 (60), 71 (100), 57 (86), 43 (90); *Isomer 2*: ^{13}C NMR (75 MHz, $CDCl_3$): δ=73.6, 37.4, 30.3, 29.6, 27.0, 25.8, 21.2, 14.2; GC–MS: t_R=9.58 min; m/z (%)=157 (32), 113 (73), 71 (100), 57 (87), 43 (68).

*4.5.7. 1,1′-Oxybis-cyclohexane (**28b**).* Colorless oil; yield: 97%; TLC: R_f=0.75 (cyclohexane/EtOAc=15:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.35–3.12 (m, 2H), 1.88–1.74 (m, 4H), 1.72–1.59 (m, 4H), 1.54–1.40 (m, 2H), 1.27–1.04 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=74.6, 33.3, 25.9, 24.5; GC–MS: t_R=8.29 min; m/z (%)=182 (16) [$M^{+\bullet}$], 100 (100), 82 (100), 67 (34), 55 (86).

*4.5.8. 3,11,19-Trioxatetracyclo[19.3.1.15,9.113,17]heptacosa-1(25),5,7,9(27),13,15,17(26),21,23-nonaene (**29b**).* White solid; yield: 81%; TLC: R_f=0.64 (cyclohexane/EtOAc=5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.62 (s, 3H), 7.23 (dd, J=8.5, 6.4 Hz, 3H), 7.17–7.12 (m, 6H), 4.50 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=138.9, 128.3, 127.1, 127.0, 71.8; HRESI MS: calcd for $C_{24}H_{24}NaO_3$ ([M+Na]$^+$) 383.1623, found 383.1588.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.06.080. These data include MOL files and InChiKeys of the most important compounds described in this article.

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