A Simple and Useful Synthetic Protocol for Selective Deprotection of *tert*-Butyldimethylsilyl (TBS) Ethers

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A wide variety of *tert*-butyldimethylsilyl ethers **1** can be easily cleaved to the corresponding parent hydroxyl compound **2** in the presence of 5 mol % of acetonyltriphenylphosphonium bromide (ATPB) at room temperature. In addition, *tert*-butyldiphenylsilyl ethers can also be cleaved by using 20 mol % of the same catalyst. Alkyl *tert*-butyldimethylsilyl ethers can be deprotected to the hydroxyl compounds chemoselectively in the presence of aryl *tert*-butyldimethylsilyl ethers. Some of the major advantages are mild reaction conditions, no aqueous workup, high efficiency and chemoselectivity and compatibility with other protecting groups; no brominations occur in the aromatic ring under these experimental conditions.

Introduction

Protection and deprotection strategies are very common features of the manipulation of other functional groups in multi-step natural and non-natural product synthesis. Among the various functional groups, the protection of a hydroxyl group as a *tert*-butyldimethylsilyl (TBS) ether or *tert*-butyldiphenylsilyl (TBDPS) ether, first introduced by Corey and co-workers,[1] plays a key role in carbohydrate and nucleoside chemistry due to its ease of preparation and inherent stability under basic and mildly acidic conditions. Although a wide variety of reagents and recipes have been developed over the years for their removal,[2] there still is a need to find better alternatives that might work under milder reaction conditions with less-expensive reagents. The usual procedure for deprotection of *tert*-butyldimethylsilyl (TBS) ethers and *tert*-butyldiphenylsilyl (TBDPS) ethers involves the use of tetrabutylammonium fluoride.[1,3] However, this method has some serious drawbacks, such as high cost as well as incompatibility with base-sensitive substrates due to the basic nature of the fluoride ion, which causes side reactions.[4] Since then many other protocols have been developed that use other fluoro compounds such as, for example, boron trifluoride etherate,[5a] hydrofluoric acid,[5b] flurosilicic acid,[5c] ammonium fluoride,[5d] silicon fluoride,[5e] *O*-(benzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium tetrafluoroborate (TBTU),[5f] lithium tetrafluoroborate,[5g] and zinc tetrafluoroborate.[5h] However, these methods have some disadvantages, such as incompatibility with acid-sensitive groups,[5a−5c] and require relatively long reaction times[5g][5h] and harsh reaction conditions.[5g] Various methods have also been reported in the literature for the deprotection of TBS ethers with chloro compounds, such as cerium(III) chloride in combination with sodium iodide,[6a] cerium(III) chloride alone,[6b] LiCl in DMF,[6c] TMSCl in H_2O,[6d] $ZrCl_4$,[6e] and CH_3COCl.[6f] Likewise, a few methods have also been reported with TMSOTf,[7a] $Sc(OTf)_3$,[7b] I_2,[7c] oxone in aqueous methanol,[7d] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[7e] decaborane,[7f] 1,1,3,3-tetramethylguanidine,[7g] and Cs_2CO_3.[7h] Moreover, the deprotection of TBS ethers has also been reported with several bromo compounds, for example CBr_4,[8a] $BiBr_3$,[8b] acetyl bromide,[8c] tetrabutylammonium tribromide,[8d] molecular bromine,[8e] and IBr.[8f] Unfortunately, some of these procedures have disadvantages such as relatively harsh reaction conditions,[7a−7c,8a] failure to deprotect aryl *tert*-butyldimethylsilyl ethers,[6c,7c,8b] require longer reaction times[6,7a−7d,8d] and much more expensive reagents,[6a,6b,8d] incompatibility with other protecting groups such as thioketals[8] or a thio group at the anomeric position of the carbohydrate compounds,[8f] difficulty in maintaining a stoichiometric ratio, difficult to handle,[7a,8e] over oxidation,[7e] unwanted product (acetate instead of alcohol),[8c] or require an excess amount of reagent.[7a−7c] Therefore, there is a need to develop other alternatives. As part of our ongoing research project to develop new synthetic methodologies, particularly in protection and deprotection chemistry,[9] we envisioned that acetonyltriphenylphosphonium bromide, which can generate HBr in situ on reaction with an alcohol,[10a] might be a useful catalyst for the deprotection of *tert*-butyldimethylsilyl ethers and *tert*-butyldiphenylsilyl ethers. So far acetonyltriphenylphosphonium bromide has been utilized mainly as a Wittig salt,[10b] for the tetrahydropyranylation/depyranylation of alcohols,[10c] and for the cyclotrimerization of aldehydes.[10d] However, the full

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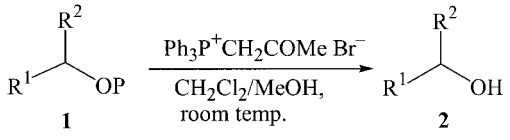
versatility of this reagent has not been investigated. Very recently, we demonstrated the utility of bromodimethylsulfonium bromide for the tetrahydropyranylation/depyranylation of alcohols and phenols and the thioacetalization of carbonyl compounds.[11] These results prompted us to investigate whether acetonyltriphenylphosphonium bromide could be used for the deprotection of TBS ethers or not. In this paper, we report for the first time a simple and useful synthetic protocol for the cleavage of various TBS ethers that involves acetonyltriphenylphosphonium bromide (ATPB) as a new pre-catalyst (Scheme 1).



R^1 = alkyl/aryl/sugar residue/nucleoside residue;
R^2 = H, alkyl; P = TBS/TBDPS

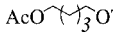
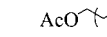
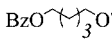
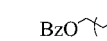
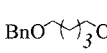
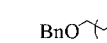
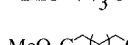
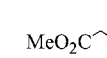
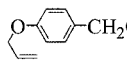
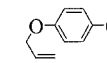
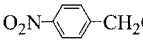
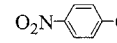
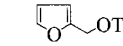
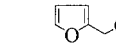
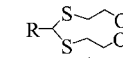
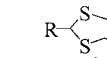
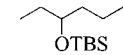
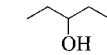
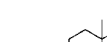
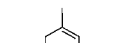
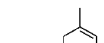
Scheme 1

Results and Discussion

In order to verify our proposal we had to prepare a wide variety of *tert*-butyldimethylsilyl (TBS) ethers as well as *tert*-butyldiphenylsilyl (TBDPS) ethers by following the reported procedure.[1,2] Next, we prepared the reagent acetonyltriphenylphosphonium bromide (ATPB) by reaction of triphenylphosphane with bromoacetone in benzene at room temperature following the literature procedure.[10d] The solid ATPB (m.p. 221−223 °C, ref. m.p. 221−223 °C) was obtained by quick filtration followed by washing with benzene to remove the unchanged triphenylphosphane. First, we attempted the reaction of *tert*-butyldimethylsilyl ether **1a** (1 equiv.) with 0.05 equivalents of acetonyltriphenylphosphonium bromide in dichloromethane/methanol (5:2) at room temperature. We noticed that the reaction was complete within three minutes and the pure product 5-acetoxy-1-pentanol (**2a**) was obtained in 70% yield by passing the crude mixture through a silica gel column. The product was characterized by recording IR and ^{1}H NMR spectra, which were then compared with the spectra of an authentic sample. We found that various *tert*-butyldimethylsilyl ethers, such as **1b**−**d**, containing benzoyl, benzyl and ester groups, respectively, were smoothly deprotected to the corresponding alcohols **2b**−**d** in good yields, without affecting these groups, under identical reaction conditions. All the products were characterized in a similar manner. It is worthwhile to mention that our protocol is more efficient in terms of reaction time than a recently reported procedure.[8d] Similarly, other TBS ethers such as **1e**−**g** were converted into the corresponding alcohols **2e**−**g** in good yield by following the same procedure. It is interesting to note that no bromination occurs at the double bond or even in the furan ring under these experimental conditions. Likewise, the TBS ether **1h** was easily transformed into the corresponding alcohol **2h** without disturbing the thioketal group. Interestingly, the thioketal group is also cleaved when the same reaction is carried out with other bromo compounds such as tetrabutylammonium tribromide (TBATB), CBr_4 and molecular bromine. This result clearly indicates that our methodology has some additional advantages compared to the other reported procedures, especially those based on bromo reagents. In addition, various TBS ethers **1i**−**j**, which are derived from secondary alcohols, were also cleaved to the corresponding alcohols **2i**−**j** in good yields under identical reaction conditions. Again, we noticed that it took much less time for deprotection of **1j** than the earlier procedures.[8b] Moreover, by using our protocol, TBS ether **1k** and an acetylenic TBS ether **1l** were also deprotected to the desired alcohols **2k** and **2l** without bromination either at the double or at the triple bond. Remarkably, a highly acid-sensitive TBS ether such as **1m** can be cleaved to the corresponding alcohol **2m** without losing the isopropylidene group.

We also decided to study whether the same reagent can be employed for deprotection of aryl TBS ethers or not. We observed that various phenolic TBS ethers **1n**−**q** can be converted into the respective phenolic compounds **2n**−**q** without affecting a thioketal group. It is important to men-

Table 1. Deprotection of various TBS ethers **1** to the parent hydroxyl compounds **2** in the presence of a catalytic amount of acetonyltriphenylphosphonium bromide (ATPB) in dichloromethane/methanol

Entry	Substrate (1)	Time	Product[a] (2)	Yield[b][c] [%]
a		3 min		70
b		15 min		88
c		10 min		92
d		15 min		92[6f]
e		7 min		91[11a]
f		2 h		94[12]
g		10 min		83[12]
h	 R = *p*-methoxyphenyl	20 min	 R = *p*-methoxyphenyl	81
i		22 min		91[12]
j		2.5 h		90[12]
k		5 min		95[12]

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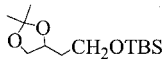
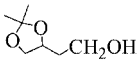
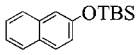
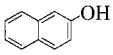
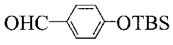
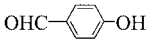
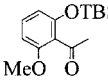
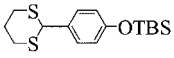
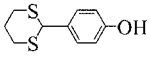
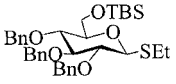
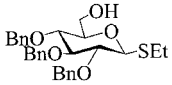
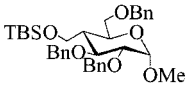
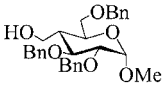
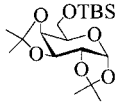
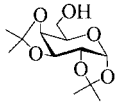
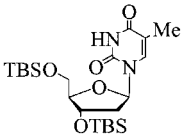
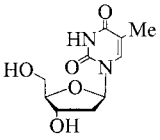
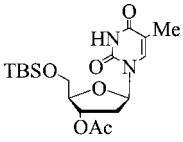
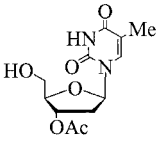
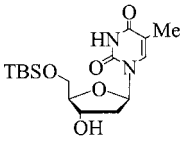
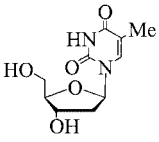
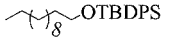
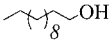
m		15 min		72[12]
n		6 h		81[12]
o		5 h		71[12]
p		3 h		91[12]
q		4 h		85
r		50 min		88[6f]
s		2 h		82
t		30 min		80[6f]
u		6 h		75[12]
v		3 h		87
w		3 h		87[12]
x		5 h		88[12]

[a] All starting materials and final products were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy, and elemental analysis. [b] Isolated yield.

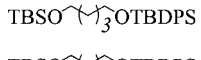
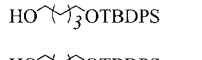
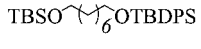
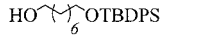
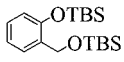
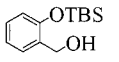
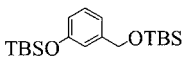
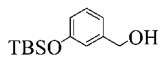
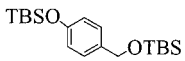
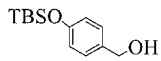
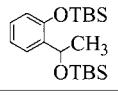
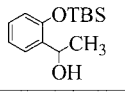
tion that no α-bromination was observed in the case of compound **1p**, and neither was any cyclotrimerization observed in the case of the aromatic aldehyde **1o**. The reactions with aryl TBS ethers take slightly longer than those with alcoholic TBS ethers. All the deprotected alcohols were characterized fully by IR and ^{1}H NMR spectroscopy and by elemental analysis; the spectra were compared with those of authentic samples.

We then turned our attention to whether this methodology could be further extended for deprotection of TBS ethers of carbohydrates and nucleosides. We found that various TBS ethers **1r**−**w** can be cleaved easily to the corresponding parent hydroxyl compounds **2r**−**w** in good yields under identical reaction conditions. Importantly, a thio group at the anomeric position usually affected by the earlier reported procedures.[8f] An OMe ether or an isopropylidene group at the anomeric position also survived under the experimental conditions. The reaction times and yields of all the products are summarized in Table 1.

These results further encouraged us to study whether our methodology could be extended to the deprotection of *tert*-butyldiphenyl silyl (TBDPS) ethers. We found that a TBDPS ether of 1-dodecanol (**1x**) was also converted into the corresponding alcohol **2x** in 88% yield in the presence of 0.2 equivalents of the same pre-catalyst although with a longer reaction time. The product was characterized as above.

Interestingly, our protocol can also be further extended to the chemoselective deprotection of TBS ethers in the presence of a TBDPS ether or an aryl TBS ether. 1-*tert*-Butyldimethylsilyl-5-*tert*-butyldiphenylsilyl diether (**1a′**) and 1-*tert*-butyldimethylsilyl-8-*tert*-butyldiphenylsilyl diether (**1b′**) were smoothly converted into the corresponding mono TBDPS ethers chemoselectively, as shown in Table 2. Likewise, various alkyl *tert*-butyldimethylsilyl ethers **1c′**−**f′** were converted into the desired mono aryl *tert*-butyldimethylsilyl ethers **2c′**−**f′** in good yields. Moreover, the secondary TBS ether was also cleaved faster than the aryl TBS ether, as shown in Table 2. All the products were characterized by the usual spectroscopic techniques.

Table 2. Deprotection of various TBS ethers **1** to the parent hydroxyl compounds **2** in the presence of a catalytic amount of acetonyltriphenylphosphonium bromide (ATPB) in dichloromethane/methanol

Entry	Substrate (1)	Time	Product[a] (2)	Yield[b] [%]
a′		35 min		78
b′		12 min		81
c′		10 min		77
d′		6 min		86
e′		15 min		87
f′		45 min		76

[a] All starting materials and final products were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy, and elemental analysis. [b] Isolated yield.

The formation of the products can be rationalized as follows. We believe that HBr, generated in the reaction medium from the reaction of acetonyltriphenylphosphonium bromide with methanol, catalyzes the deprotection of TBS ethers to the corresponding alcohols. However, the same reaction failed when it was carried out with benzyltriphenylphosphonium bromide instead of acetonyltriphenylphosphonium bromide. This indicates that ATPB generates HBr much more easily than the other alkylphosphonium bromide.

Conclusion

In summary, we have devised a new, efficient, and regioas well as chemoselective protocol for the deprotection of TBS ethers and TBDPS ethers using a catalytic amount of acetonyltriphenylphosphonium bromide in dichloromethane/methanol at room temperature under very mild conditions. The significant features of the present method include the ease of operation, high efficiency, mild conditions and chemoselectivity, which may be useful in organic synthesis. In addition, the selective deprotection of alkyl *tert*-butyldimethylsilyl ether can be achieved in the presence of aryl-*tert*-butyldimethylsilyl ethers. We have found that a wide variety of other protecting groups, such as acetyl, benzyl, benzoyl, thioketals, esters and isopropylidene survive under the present experimental conditions.

Experimental Section

Melting points were recorded on a Büchi B-545 melting point apparatus and are uncorrected. IR spectra were recorded in KBr or neat on a Nicolet Impact 410 spectrophotometer. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker 200, Bruker 300 or Jeol 400 MHz spectrometer in $CDCl_3$ using TMS as internal reference. Elemental analyses were carried out with a Perkin−Elmer 2400 automatic carbon, hydrogen, nitrogen and sulfur analyzer. Column chromatographic separations were done on SRL silica gel (60−120 mesh).

General Procedure for the Deprotection: A catalytic amount of acetonyltriphenylphosphonium bromide (20 mg, 0.05 mmol) was added to a well-stirred solution of *tert*-butyldimethylsilyl ether **1** (1 mmol) in 2 mL of dichloromethane/methanol mixture (5:2) at room temperature (except for **1x**) and the mixture kept stirring. After completion of the reaction, as monitored by TLC, it was concentrated on a rotary evaporator. The crude residue was subjected to silica gel column chromatography to isolate the desired alcohols **2** in good yields.

Compound 1a: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2960, 2935, 2868, 1747, 1475, 1373, 1250, 1112, 1045, 840, 779 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 [s, 6 H, $Si(CH_3)_2$], 0.85 [s, 9 H, $SiC(CH_3)_3$], 1.36 (m, 2 H, CH_2), 1.50 (m, 2 H, CH_2), 1.60 (m, 2 H, CH_2), 1.99 (s, 3 H, $COCH_3$), 3.57 (t, *J* = 6.3 Hz, 2 H, CH_2OTBS), 4.01 (t, *J* = 6.6 Hz, 2 H, $AcOCH_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.4, 18.3, 20.9, 22.2, 25.9, 28.3, 32.3, 62.9, 64.5, 171.2 ppm. $C_{13}H_{28}O_3Si$ (260.45): calcd. C 59.95, H 10.83; found C 59.72, H 10.75.

Compound 1b: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2940, 2858, 1721, 1583, 1429, 1337, 1301, 1112, 943 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.02 [s, 6 H, $Si(CH_3)_2$], 0.83 [s, 9 H, $SiC(CH_3)_3$], 1.47 (m, 2 H, CH_2), 1.54 (m, 2 H, CH_2), 1.74 (m, 2 H, CH_2), 3.57 (t, *J* = 6.3 Hz, 2 H, CH_2OTBS), 4.26 (t, *J* = 6.6 Hz, 2 H, $PhCOOCH_2$), 7.39 (t, *J* = 7.8 Hz, 1 H, ArH), 7.44 (t, *J* = 7.8 Hz, 1 H, ArH), 7.54 (m, 1 H, ArH), 8.00 (dd, *J* = 1.2, *J* = 7.3 Hz, 1 H, ArH), 8.09 (dd, *J* = 1.2, *J* = 7.1 Hz, 1 H, ArH) ppm. $C_{18}H_{30}O_3Si$ (322.52): calcd. C 67.03, H 9.38; found C 66.91, H 9.25.

Compound 1c: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2960, 2935, 2858, 1506, 1470, 1460, 1368, 1255, 1102, 1009, 840 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.01 [s, 6 H, $Si(CH_3)_2$], 0.83 [s, 9 H, $SiC(CH_3)_3$], 1.50 (m, 6 H, CH_2), 3.43 (t, *J* = 6.5 Hz, 2 H, CH_2OTBS), 3.57 (t, *J* = 6.4 Hz, 2 H, $PhCH_2OCH_2$), 4.46 (s, 2 H, OCH_2Ph), 7.31 (m, 5 H, ArH) ppm. $C_{17}H_{32}O_2Si$ (296.52): calcd. C 68.86, H 10.88; found 68.79, H 10.80.

Compound 1e: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2955, 2929, 2863, 1655, 1615, 1516, 1470, 1250, 1096, 1034, 855 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 [s, 6 H, $Si(CH_3)_2$], 0.93 [s, 9 H, $SiC(CH_3)_3$], 4.52 (d, *J* = 1.2 Hz, 2 H, $OCH_2CH=CH_2$), 4.66 (s, 2 H, CH_2OTBS), 5.27 (dd, *J* = 1.0, *J* = 10.5 Hz, 1 H, $OCH_2CH=CH_2$), 5.40 (dd, *J* = 1.4, *J* = 15.8 Hz, 1 H, $OCH_2CH=CH_2$), 6.06 (m, 1 H, $OCH_2CH=CH_2$), 6.88 (d, *J* = 8.6 Hz, 2 H, ArH), 7.22 (d, *J* = 8.3 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.2, 18.4, 25.9, 64.7, 68.9, 114.5, 117.6, 127.5, 133.4, 133.8, 157.7 ppm. $C_{16}H_{26}O_2Si$ (278.47): calcd. C 69.01, H 9.41; found C 68.82, H 9.47.

Compound 1f: Yellowish liquid. IR (neat): $\tilde{\nu}$ = 2955, 2935, 2863, 1614, 1521, 1475, 1352, 1265, 1102, 1020, 856 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13 [s, 6 H, Si $(CH_3)_2$], 0.96 [s, 9 H, $SiC(CH_3)_3$], 4.83 (s, 2 H, CH_2OTBS), 7.49 (d, *J* = 8.7 Hz, 2 H, ArH), 8.20 (d, *J* = 9.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.4, 18.3, 25.8, 64.0, 123.5, 126.3, 146.0, 149.0 ppm. $C_{13}H_{21}NO_3Si$ (267.40): calcd. C 58.39, H 7.92, and N 5.24; found C 58.15, H 7.84, N 5.08.

Compound 1g: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2960, 2935, 2863, 1603, 1506, 1470, 1255, 1158, 1076, 1015, 840 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 [s, 6 H, $Si(CH_3)_2$], 0.88 [s, 9 H, $SiC(CH_3)_3$], 4.62 (s, 2 H, CH_2OTBS), 6.14 (d, *J* = 3.2 Hz, 1 H, 3-H), 6.23 (dd, *J* = 1.7, *J* = 3.2 Hz, 1 H, 4-H), 7.28 (dd, *J* = 0.9, *J* = 1.7 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.3, 18.4, 25.9, 58.1, 107.2, 110.2, 142.0, 154.3 ppm. $C_{11}H_{20}O_2Si$ (212.36): calcd. C 62.22, H 9.49; found C 61.97, H 9.42.

Compound 1h: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2955, 2930, 2863, 1609, 1516, 1470, 1255, 1091, 1040, 902, 840 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 [s, 12 H, 2 × $Si(CH_3)_2$], 0.84 [s, 18 H, 2 × $SiC(CH_3)_3$], 2.54−2.61 (m, 4 H, SCH_2), 3.66 (m, 4 H, OCH_2), 3.76 (s, 3 H, OCH_3), 5.01 (s, 1 H, SCHS), 6.82 (d, *J* = 9.5 Hz, 2 H, ArH), 7.33 (d, *J* = 9.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.3, 18.3, 25.9, 34.6, 53.4, 55.3, 63.2, 113.9, 128.9, 132.5, 159.2 ppm. $C_{24}H_{46}O_3S_2Si_2$ (502.93): calcd. C 57.32, H 9.22, S, 12.75; found C 57.08, H 9.15, S 12.63.

Compound 1i: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2960, 2940, 2863, 1475, 1378, 1255, 1132, 1061, 835 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 [s, 6 H, $Si(CH_3)_2$], 0.83 (t, *J* = 7.6 Hz, 6 H, 2 × CH_3), 0.85 [s, 9 H, $SiC(CH_3)_3$], 1.22−1.30 (m, 6 H, CH_2), 1.34−1.43 (m, 4 H, CH_2), 3.53 (quin., *J* = 5.9 Hz, 1 H, CH_2CHCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.5, −4.5, 9.6, 14.0, 18.1, 22.6, 25.0, 25.9, 29.7, 32.0, 36.5, 73.5 ppm.

$C_{14}H_{32}OSi$ (244.49): calcd. C 68.78 H, 13.19; found C 68.91, H 13.06.

Compound 1j: White solid; m.p. 151−153 °C. IR (KBr): $\tilde{\nu}$ = 2930, 2858, 1665, 1460, 1378, 1255, 1112 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 3 H, $SiCH_3$), 0.12 (s, 3 H, $SiCH_3$), 0.82 (s, 6 H, 2 × CH_3), 0.83 [s, 9 H, $SiC(CH_3)_3$], 0.85 (d, *J* = 6.3 Hz, 3 H, $CHCH_3$), 0.94 (s, 6 H, 2 × CH_3), 1.00−1.50 (m, 22 H, CH and CH_2), 1.75 (m, 2 H, CH_2), 1.94 (m, 2 H, CH_2), 2.12 (m, 1 H, CH), 2.20 (m, 1 H, CH), 3.42 (q, *J* = 6.0 Hz, 1 H, OCH), 5.25 (m, 1 H, =CH) ppm. $C_{33}H_{60}OSi$ (500.92): calcd. C 79.13, H 12.07; found C 79.09, H 12.11.

Compound 1k: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2955, 2930, 2858, 1665, 1465, 1383, 1255, 1096, 1061, 835 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.01 [s, 6 H, $Si(CH_3)_2$], 0.84 [s, 9 H, $SiC(CH_3)_3$], 1.53 [s, 6 H, $C(CH_3)_3$], 1.61 (s, 3 H, CH_3), 1.88−2.03 (m, 4 H, $CHCH_2$), 3.54−3.59 (m, 1 H, OCH_2), 4.12−4.13 (m, 1 H, OCH_2), 5.01−5.05 (m, 1 H, CH), 5.22−5.25 (m, 1 H, CH) ppm. $C_{16}H_{32}OSi$ (268.51): calcd. C 71.57, H 12.01; found C 71.75, H 12.09.

Compound 1l: Yellowish liquid. IR (neat): $\tilde{\nu}$ = 2955, 2934, 2863, 1465, 1357, 1255, 1137, 1070, 840 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.12 [s, 12 H, 2 × Si $(CH_3)_2$], 0.91 [s, 18 H, 2 × SiC $(CH_3)_3$], 4.34 (s, 4 H, OCH2) ppm. $C_{16}H_{34}O_2Si_2$ (314.61): calcd. C 61.08, H 10.89; found C 61.10, H 10.85.

Compound 1m: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2945, 2863, 1460, 1378, 1255, 1148, 1107, 846, 784 cm^{-1}. $C_{10}H_{26}O_3Si$ (222.40): calcd. C 54.01, H 11.78; found C 54.12, H 11. 83.

Compound 1n: Colourless liquid. IR (neat): $\tilde{\nu}$ = 3058, 2966, 2940, 2863, 1634, 1603, 1506, 1470, 1363, 1260, 1230, 1173, 1132, 1015, 933, 851 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.25 [s, 6 H, $Si(CH_3)_2$], 1.02 [s, 9 H, $SiC(CH_3)_3$], 7.07 (dd, *J* = 3.2, *J* = 8.7 Hz, 1 H, 3-ArH), 7.19 (d, *J* = 2.4 Hz, 1 H, 1-ArH), 7.30 (t, *J* = 7.0 Hz, 1 H, 6-ArH), 7.38 (t, *J* = 7.0 Hz, 1 H, 7-ArH), 7.68 (d, *J* = 8.7 Hz, 1 H, ArH, 4-ArH), 7.72 (d, *J* = 9.0 Hz, 1 H, 5-ArH), 7.76 (d, *J* = 8.1 Hz, 1 H, 8-ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.3, 18.3, 25.7, 114.9, 122.1, 123.7, 126.1, 126.7, 127.6, 129.3, 134.6, 153.5 ppm. $C_{16}H_{22}OSi$ (258.43): calcd. C 74.36, H 8.58; found C 74.10, H 8.50.

Compound 1o: Yellowish liquid. IR (neat): $\tilde{\nu}$ = 2945, 2858, 1705, 1603, 1511, 1270, 1157, 912, 845 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.25 [s, 6 H, $Si(CH_3)_2$], 0.99 [s, 9 H, $SiC(CH_3)_3$], 6.95 (d, *J* = 8.4 Hz, 2 H, ArH), 7.81 (d, *J* = 8.4 Hz, 2 H, ArH), 9.89 (s, 1 H, CHO) ppm. $C_{13}H_{20}O_2Si$ (236.39): calcd. C 66.06, H 8.53; found C 65.37, H 8.58.

Compound 1p: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2966, 2935, 2863, 1711, 1593, 1470, 1255, 1107, 974, 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.19 [s, 6 H, $Si(CH_3)_2$], 0.94 [s, 9 H, $SiC(CH_3)_3$], 2.47 (s, 3 H, $COCH_3$), 3.77 (s, 3 H, OCH_3), 6.37 (d, *J* = 8.3 Hz, 1 H, ArH), 6.51 (d, *J* = 8.3 Hz, 1 H, ArH), 7.15 (t, *J* = 8.3 Hz, 1 H, ArH) ppm. $C_{15}H_{24}O_3Si$ (280.44): calcd. C 64.24, H 8.63; found C 64.45, H 8.58.

Compound 1q: White solid; m.p. 82.6 °C. IR (neat): $\tilde{\nu}$ = 2955, 2929, 2893, 2852, 1608, 1511, 1470, 1419, 1255, 1168, 912, 845 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.09 [s, 6 H, Si $(CH_3)_2$], 0.97 [s, 9 H, $SiC(CH_3)_3$], 1.84−1.88 (m, 1 H, SCH_2CH_2), 1.91−1.97 (m, 1 H, SCH_2CH_2), 2.85−2.92 (m, 2 H, SCH_2CH_2), 2.99−3.09 (m, 2 H, SCH_2CH_2), 5.12 (s, 1 H, CH), 6.79 (d, *J* = 8.4 Hz, 2 H, ArH), 7.32 (d, *J* = 8.4 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.5, 18.1, 25.0, 25.6, 32.1, 50.8, 120.1, 128.8, 131.8, 155.7 ppm. $C_{16}H_{26}OS_2Si$ (326.60): calcd. C 58.84, H 8.02; found C 58.72, H 8.09.

Compound 1r: Colourless liquid. IR (neat): $\tilde{\nu}$ = 3037, 2960, 2930, 2873, 1619, 1496, 1460, 1255, 1158, 1096, 846, 707 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.01 [s, 3 H, $Si(CH_3)_2$], 0.02 [s, 3 H, $Si(CH_3)_2$], 0.85 [s, 9 H, $SiC(CH_3)_3$], 1.25 (t, *J* = 7.3 Hz, 3 H, SCH_2CH_3), 2.63−2.71 (m, 2 H, SCH_2CH_3), 3.21−3.24 (m, 1 H, H-5), 3.46 (t, *J* = 9.0 Hz, 1 H, H-3), 3.56 (t, *J* = 9.3 Hz, 1 H, H-2), 3.61 (t, *J* = 9.0 Hz, 1 H, H-4), 3.75 (dd, *J* = 3.8, *J* = 11.2 Hz, 1 H, H-6), 3.80 (dd, *J* = 2.0, *J* = 11.7 Hz, 1 H, H-6′), 4.38 (d, *J* = 9.8 Hz, 1 H, H-1), 4.62 (d, *J* = 10.2 Hz, 1 H, $OCHPh$), 4.68 (d, *J* = 10.2 Hz, 1 H, $OCHPh$), 4.79 (dd, *J* = 4.6, *J* = 10.7 Hz, 2 H, OCH_2Ph), 4.85 (dd, *J* = 4.0, *J* = 10.3 Hz, 2 H, OCH_2Ph), 7.19−7.33 (m, 15 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.4, −5.0, 15.2, 18.3, 24.3, 25.9, 62.3, 75.1, 75.5, 75.9, 77.7, 80.0, 81.8, 84.4, 86.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5, 138.2, 138.3, 138.5 ppm. $C_{35}H_{48}O_5SSi$ (608.91): calcd. C 69.04, H 7.95, S 5.27; found C 69.22, H 7.87, S 5.12.

Compound 1s: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2929, 2858, 1603, 1459, 1362, 1260, 1106, 1060, 845, 742, 701 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = −0.12 (s, 3 H, $SiCH_3$), −0.05 (s, 3 H, $SiCH_3$), 0.83 [s, 9 H, Si $(CH_3)_3$], 1.86 (t, *J* = 10.8 Hz, 1 H, H-4), 3.38 (s, 3 H, OCH_3), 3.39−3.44 (m, 1 H, H-1), 3.53−3.66 (m, 3 H, CH_2 & H-2), 3.88 (dd, *J* = 1.8, *J* = 10.5 Hz, 1 H, H′- 6), 3.95 (d, *J* = 10.8 Hz, 1 H H-5), 4.06 (t, *J* = 9.9 Hz, 1 H, H-3), 4.43 (d, *J* = 12.3 Hz, 1 H, OCH_2), 4.61 (m, 3 H, OCH_2 & H-6), 4.65 (d, *J* = 12.6 Hz, 1 H, OCH_2), 4.77 (d, *J* = 12.0 Hz, 1 H, OCH_2), 5.01 (d, *J* = 12.0 Hz, 1 H, OCH_2), 7.26−7.37 (m, 15 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.8, −5.5, 18.1, 25.8, 44.8, 55.0, 58.3, 68.3, 69.3, 73.0, 73.4, 75.3, 75.7, 81.7, 98.5, 127.6, 127.7, 127.8, 127.9, 128.2, 128.4, 138.2, 138.4, 139.1 ppm. $C_{35}H_{48}O_6Si$ (592.84): calcd. C 70.91, H 8.16; found C 70.68, H 8.24.

Compound 1t: Yellowish liquid. IR (neat): $\tilde{\nu}$ = 2986, 2935, 2858, 1475, 1378, 1312, 1255, 1214, 1112, 1071, 1004, 840 cm^{-1} ^1H NMR (300 MHz, $CDCl_3$): δ = 0.07 [s, 6 H, $Si(CH_3)_2$], 0.90 [s, 9 H, $SiC(CH_3)_3$], 1.33 (s, 6 H, 2 × CH_3), 1.44 (s, 3 H, CH_3), 1.54 (s, 3 H, CH_3), 3.70−3.86 (m, 3 H, H-2, H-3, H-5), 4.30 (dd, *J* = 2.3, *J* = 7.2 Hz, 2 H, H-4, H-6), 4.60 (dd, *J* = 1.6, *J* = 7.9 Hz, 1 H, H-6′), 5.52 (d, *J* = 4.9 Hz, 1 H, H-1) ppm. $C_{18}H_{34}O_6Si$ (374.55): calcd. C 57.72, H 9.15; found C 57.89, H 9.02.

Compound 1u: White solid; m.p. 115 °C. IR (KBr): $\tilde{\nu}$ = 3180, 3057, 2950, 2929, 2858, 1700, 1465, 1362, 1270, 1101, 1065, 1029, 835, 778 cm^{-1}.^1H NMR (300 MHz, $CDCl_3$): δ = 0.06 (s, 3 H, $SiCH_3$), 0.07 (s, 3 H, $SiCH_3$), 0.10 (s, 6 H, $SiCH_3$), 0.88 [s, 9 H, $SiC(CH_3)_3$], 0.91 [s, 9 H, $SiC(CH_3)_3$], 1.91 (s, 3 H, CH_3) 1.94−2.03 (m, 1 H, H-2), 2.21−2.28 (m, 1 H, H′-2), 3.75 (dd, *J* = 2.3, *J* = 13.7 Hz, 1 H, H-4), 3.84−3.92 (m, 2 H, OCH_2), 4.37−4.41 (m, 1 H, H-3), 6.30−6.35 (m, 1 H, H-1), 7.46 (s, 1 H, CH), 9.01 (s, 1 H, NH) ppm. $C_{22}H_{42}N_2O_5Si_2$ (470.75): calcd. C 56.13, H 8.99, N 5.95; found C 56.34, H 8.89, N 6.12.

Compound 1v: White solid; m.p. 145 °C. IR (KBr): $\tilde{\nu}$ = 3247, 3083, 2940, 2863, 1736, 1700, 1467, 1372, 1255, 1203, 1121, 1014, 835 cm^{-1}.^1H NMR (300 MHz, $CDCl_3$): δ = 0.14 (s, 6 H, Si $(CH_3)_2$), 0.93 [s, 9 H, $SiC(CH_3)_3$], 1.93 (s, 3 H, CH_3), 2.11 (s, 3 H, $COCH_3$), 2.12 (m, 2 H, H-2, H-2′), 2.41 (dd, *J* = 5.2, *J* = 13.7 Hz, 1 H), 3.92 (d, *J* = 1.8 Hz, 2 H, CH_2OTBS), 4.10 (d, *J* = 1.1 Hz, 1 H, 5.25 (d, *J* = 5.9 Hz, 1 H), 6.38 (dd, *J* = 5.2, *J* = 9.2 Hz, 1 H), 7.55 (d, *J* = 1.1 Hz, 1 H, ArH), 9.12 (s, 1 H, NH) ppm. $C_{18}H_{30}N_2O_6Si$ (398.53): calcd. C 54.25, H 7.59, N 7.03; found C 54.16, H 7.49, N 7.11.

Compound 1w: White solid. IR (KBr): $\tilde{\nu}$ = 3478, 3421, 3180, 3057, 2950, 2929, 2858, 1700, 1465, 1362, 1270, 1101, 1065, 1029, 835, 778 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.12 [s, 6 H, $Si(CH_3)_2$], 0.91 [s, 9 H, $SiC(CH_3)_3$], 1.92 (s, 3 H, CH_3), 2.01−2.04 (m, 1 H, CH_2), 2.36−2.38 (m, 1 H, CH_2), 3.14 (s, 1 H, OH), 3.85−3.88 (m, 2 H, OCH_2), 4.05−4.07 (m, 1 H, OCH), 4.46 (m, 1 H, OCH), 6.40 (m, 1 H, OCH), 7.52 (m, 1 H, =CH), 9.40 (s, 1 H, NH) ppm. $C_{16}H_{28}N_2O_5Si$ (356.491): calcd. C 53.91, H 7.92, N 7.86; found C 53.70, H 7.78, N 7.89.

Compound 1x: Colourless liquid. IR (neat): $\tilde{\nu}$ = 3063, 2925, 2858, 1460 1388, 1107, 825, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.1 Hz, 3 H, CH_3), 1.05 [s, 9 H, $SiC(CH_3)_3$], 1.06 (m, 2 H, CH_2CH_3), 1.25 (m, 16 H, CH_2), 1.55 (m, 2 H, OCH_2CH_2), 3.65 (t, *J* = 6.4 Hz, 2 H, OCH_2), 7.42 (m, 5 H, ArH), 7.66 (m, 5 H, ArH) ppm. $C_{28}H_{44}OSi$ (454.74): calcd. C 80.55, H 9.75; found C 80.63, H 9.80.

Compound 1a′: Yellowish liquid. IR (neat): $\tilde{\nu}$ = 2965, 2929, 2858, 1599, 1475, 1424, 1260, 1101, 835 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.04 [s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $SiC(CH_3)_3$], 1.04 [s, 9 H, $SiC(CH_3)_3$], 1.49 (m, 6 H, CH_2), 3.60 (t, *J* = 6.3 Hz, 2 H, OCH_2CH_2), 3.66 (t, *J* = 6.6 Hz, 2 H, OCH_2CH_2), 7.39 (m, 5 H, ArH), 7.68 (m, 5 H, ArH) ppm. $C_{27}H_{44}O_2Si_2$ (456.81): calcd. C 70.99, H 9.71; found C 70.90, H 9. 65.

Compound 1b′: Yellowish liquid. IR (neat): $\tilde{\nu}$ = 3073, 2940, 2863, 1588, 1481, 1434, 1388, 1260, 1107, 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.02 [s, 6 H, $Si(CH_3)_2$], 0.87 [s, 9 H, $SiC(CH_3)_3$], 1.02 [s, 9 H, $SiC(CH_3)_3$], 1.25 (m, 8 H, CH_2), 1.53 (m, 4 H, CH_2), 3.57 (t, *J* = 6.4 Hz, 2 H OCH_2CH_2), 3.62 (t, *J* = 6.4 Hz, 2 H OCH_2CH_2), 7.38 (m, 5 H, ArH), 7.66 (m, 5 H, ArH) ppm. $C_{30}H_{50}O_2Si_2$ (498.90): calcd. C 72.22, H 10.10; found C 72.50, H 10.22.

Compound 1c′: Yellowish liquid. IR (neat): $\tilde{\nu}$ = 2945, 2858, 1598, 1485, 1459, 1377, 1260, 1116, 1070, 932, 840 cm^{-1}. $C_{19}H_{36}O_2Si_2$ (356.66): calcd. C 64.71, H, 10.29; found C 64.80, H 10.32.

Compound 1d′: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2959, 2934, 2860, 1597, 1479, 1370, 1282, 1163, 1104, 1015, 971, 848, 779, 705cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.10 [s, 6 H, $Si(CH_3)_2$], 0.20 [s, 6 H, $Si(CH_3)_2$], 0.85 [s, 9 H, $SiC(CH_3)_3$], 0.89 [s, 9 H, $SiC(CH_3)_3$], 4.60 (s, 2 H, CH_2OTBS), 6.51 (dd, *J* = 2.4, *J* = 7.8 Hz, 1 H, ArH), 6.65 (s, 1 H, ArH), 6.69 (d, *J* = 7.6 Hz, 1 H, ArH), 6.98 (t, *J* = 7.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.3, −4.4, 18.2, 18.4, 25.7, 25.9, 64.7, 117.6, 118.6, 118.8, 129.1, 143.1, 155.7 ppm. $C_{19}H_{36}O_2Si_2$ (352.66): calcd. C 64.71, H 10.29; found C 64.82, H 10.32.

Compound 1e′: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2960, 2945, 2899, 2868, 1614, 1516, 1475, 1255, 1091, 922, 851, 779 cm^{-1}.^1H NMR (300 MHz, $CDCl_3$): δ = 0.08 [s, 6 H, $Si(CH_3)_2$], 0.18 [s, 6 H, $Si(CH_3)_2$], 0.93 [s, 9 H, $SiC(CH_3)_3$], 0.98 [s, 9 H, $SiC(CH_3)_3$], 4.66 (s, 2 H, CH_2OTBS), 6.79 (d, *J* = 8.4 Hz, 2 H, ArH), 7.17 (d, *J* = 8.4 Hz, 2 H, ArH) ppm. $C_{19}H_{36}O_2Si_2$ (352.66): calcd. C 64.71, H 10.29; found C 64.83, H 10.3.

Compound 1f′: Colourless liquid. IR (neat): $\tilde{\nu}$ = 2960, 2935, 2863, 1609, 1588, 1496, 1470, 1368, 1260, 1107, 1086, 1040, 927, 846, 789 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.01 (s, 3 H, $SiCH_3$), 0.03 (s, 3 H, $SiCH_3$), 0.26 (s, 3 H, $SiCH_3$), 0.30 (s, 3 H, $SiCH_3$), 0.93 [s, 9 H, $SiC(CH_3)_3$], 1.05 [s, 9 H, $SiC(CH_3)_3$], 1.38 (d, *J* = 6.2 Hz, 3 H, $CHCH_3$), 5.25 (q, *J* = 6.2 Hz, 1 H, $OCHCH_3$), 6.75 (d, *J* = 8.0 Hz, 1 H, ArH), 6.96 (t, *J* = 7.6 Hz, 1 H, ArH), 7.06 (t, *J*) 7.3 Hz, 1 H, ArH), 7.55 (d, *J* = 6.9 Hz, 1 H, ArH) ppm. $C_{20}H_{38}O_2Si_2$ (366.69): calcd. C 65.51, H 10.44; found C 65.62, H 10.5.

Compound 2a: Yield: 0.102 g, 70%; colourless liquid. IR (neat): $\tilde{\nu}$ = 3447, 2935, 2868, 1742, 1465, 1404, 1368, 1235, 1045, 897, 851 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ = 1.35−1.74 (m, 7 H, CH_2 & OH), 2.05 (s, 3 H, $COCH_3$), 3.67 (t, *J* = 6.4 Hz, 2 H, CH_2OH), 4.08 (t, *J* = 6.6 Hz, 2 H, $AcOCH_2$) ppm. $C_7H_{14}O_3$ (146.18): calcd. C 57.52, H 9.65; found C 57.63, H 9.71.

Compound 2b: Yield: 0.183 g, 88%; colourless liquid. IR (neat): $\tilde{\nu}$ = 3421, 3068, 2940, 2868, 1726, 1614, 1460, 1393, 1281, 1189, 1122, 717 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.48 (m, 3 H, CH_2 & OH), 1.59 (m, 2 H, CH_2), 1.75 (m, 2 H, CH_2), 3.62 (t, *J* = 6.4 Hz, 2 H, CH_2OH), 4.27 (t, *J* = 6.6 Hz, 2 H, $PhCOOCH_2$), 7.37 (t, *J* = 7.8 Hz, 2 H, ArH), 7.49 (t, *J* = 7.6 Hz, 1 H, ArH), 7.96 (d, *J* = 7.1 Hz, 2 H ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.4, 28.6, 32.3, 62.7, 64.9, 128.3, 129.5, 130.5, 132.9, 166.7 ppm. $C_{12}H_{16}O_3$ (208.26): calcd. C 69.21, H 7.74; found C 69.32, H 7.83.

Compound 2c: Yield: 0.178 g, 92%; colourless liquid. IR (neat): $\tilde{\nu}$ = 3416, 2935, 2863, 1609, 1501, 1455, 1368, 1265, 1209, 1096, 1055, 1030, 805 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.31−1.70 (m, 7 H, CH_2 & OH), 3.47 (t, *J* = 6.4 Hz, 2 H, CH_2OH), 3.63 (t, *J* = 6.4 Hz, 2 H, $PhCH_2OCH_2$), 4.48 (s, 2 H, OCH_2Ph), 7.32 (m, 5 H, ArH) ppm. $C_{12}H_{18}O_2$ (194.27): calcd. C 74.19, H 9.34; found C 74.32, H 9.4%.

Compound 2h: Yield: 0.222 g, 81%; colourless liquid. IR (neat): $\tilde{\nu}$ = 3334, 2914, 2848, 2745, 1609, 1516, 1455, 1255, 1173, 1076, 1020, 830 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.58−2.90 (m, 6 H, SCH_2 & OH), 3.71 (m, 4 H, OCH_2), 3.80 (s, 3 H, OCH_3), 5.06 (s, 1 H, SCHS), 6.87 (d, *J* = 8.6 Hz, 2 H, ArH), 7.38 (d, *J* = 8.6 Hz, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.1, 33.2, 55.9, 99.5, 114.7, 129.5, 132.0, 160.0 ppm. $C_{12}H_{18}O_3S_2$ (274.40): calcd. C 52.53, H 6.61, S 23.37; found C 53.58, H 6.73, S 23.40.

Compound 2q: Yield: 0.180 g, 85%; White solid; m.p 155−158 °C. IR (KBr): $\tilde{\nu}$ = 3370, 2940, 2894, 1609, 1445, 1368, 1250, 1173, 1112 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.72−1.86 (m, 1 H, SCH_2CH_2), 2.02−2.07 (m, 1 H, SCH_2CH_2), 2.74−2.81 (m, 2 H, SCH_2CH_2), 2.89−2.98 (m, 2 H, SCH_2CH_2), 5.00 (s, 1 H, CH), 6.65 (d, *J* = 8.2 Hz, 2 H, ArH), 7.22 (d, *J* = 8.2 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1, 32.2, 50.7, 115.6, 129.2, 131.5, 155.6 ppm. $C_{10}H_{12}OS_2$ (212.34): calcd. C 56.57, H 5.70; found C 56.63, H 5.68.

Compound 2v: Yield: 0.247 g, 87%; White solid; m.p 174 °C IR (KBr): $\tilde{\nu}$ = 3472, 3201, 3068, 2929, 1738, 1710, 1669, 1475, 1249, 1111, 1075, 1024, 881, 788, 576 cm^{-1}.^1H NMR (300 MHz, $CDCl_3$): δ = 1.92 (s, 3 H, CCH_3), 2.11 (s, 3 H, $COCH_3$), 2.40 (br. s, 3 H, CH_2 & OH), 3.92 (s, 2 H, OCH_2), 4.10 (br. s, 1 H, H-3), 5.36 (br. s, 1 H, H-4), 6.27 (br. s, 1 H, H-1), 7.55 (s, 1 H,= CH), 9.50 (s, 1 H, NH) ppm. $C_{12}H_{16}O_6N_2$ (284.27): calcd. C 50.70, H 5.67, N 9.85; found C 50.81, H 9.01.

Compound 2a′: Yield: 0.267 g, 78%; colourless liquid. IR (neat): $\tilde{\nu}$ = 3396, 3068, 3053, 2930, 2863, 1598, 1470, 1424, 1393, 1112, 1045, 1004, 943, 825 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.05 [s, 9 H, $SiC(CH_3)_3$], 1.56 (m, 7 H, CH_2 & OH), 3.62 (t, *J* = 6.4 Hz, 2 H OCH_2CH_2), 3.67 (t, *J* = 6.2 Hz, 2 H OCH_2CH_2), 7.40 (m, 5 H, ArH), 7.68 (m, 5 H, ArH) ppm. $C_{21}H_{30}O_2Si$ (342.55): calcd. C 73.63, H 8.8; found C 73.53, H 8.69.

Compound 2b′: Yield: 0.311 g, 81%; Yellowish liquid. IR (neat): $\tilde{\nu}$ = 3355, 3073, 3053, 2935, 2868, 1593, 1475, 1429, 1399, 1117, 835 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.02 [s, 9 H, $SiC(CH_3)_3$], 1.28 (m, 8 H, CH_2), 1.54 (m, 5 H, CH_2 & OH), 3.60 (t, *J* = 6.6 Hz, 2 H, OCH_2CH_2), 3.64 (t, *J* = 6.3 Hz, 2 H, OCH_2CH_2), 7.37 (m, 5

H, ArH), 7.67 (m, 5 H, ArH) ppm. $C_{24}H_{36}O_2Si$ (384.63): calcd. C 74.95, H 9.43; found C 74.89, H 9.48.

Compound 2c′: Yield: 0.183 g, 77%; Yellowish liquid. IR (neat): $\tilde{\nu}$ = 3370, 2976, 2940, 2873, 1609, 1588, 1491, 1460, 1393, 1368, 1265, 1194, 1117, 1040, 922, 840 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.24 [s, 6 H, $Si(CH_3)_2$], 1.00 [s, 9 H, $SiC(CH_3)_3$], 2.01 (s, 1 H, OH, D_2O exchangeable), 4.65 (s, 2 H, CH_2OH), 6.79 (d, *J* = 8.1 Hz, 1 H, ArH), 6.93 (t, *J* = 7.3 Hz, 1 H, ArH), 7.15 (t, *J* = 7.6 Hz, 1 H, ArH), 7.27 (d, *J* = 7.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.2, 18.2, 25.7, 61.9, 118.4, 121.3, 128.6, 128.8, 131.4, 153.5 ppm. $C_{13}H_{22}O_2Si$ (238.40): calcd. C 65.50, H 9.30; found C 65.54, H 9.36.

Compound 2d′: 1445, 1378, 1281, 1255, 1153, 1020, 953, 851, 784, 702 cm^{-1}.^1H NMR (400 MHz, $CDCl_3$): δ = 0.00 [s, 6 H, $Si(CH_3)_2$], 0.79 [s, 9 H, $SiC(CH_3)_3$], 1.46 (s, 1 H, OH, D_2O exchangeable), 4.44 (s, 2 H, CH_2OH), 6.56 (dd, *J* = 2.4, *J* = 8.0 Hz, 1 H, ArH), 6.66 (s, 1 H, ArH), 6.75 (d, *J* = 7.3 Hz, 1 H, ArH), 7.03 (t, *J* = 7.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.5, 18.2, 25.7, 65.2, 118.6, 119.2, 119.7, 129.5, 142.5, 155.9 ppm. $C_{13}H_{22}O_2Si$ (238.40): calcd. C 65.50, H 9.30; found C 65.55, H 9.38.

Compound 2e′: Yield: 0.207 g, 87%; colourless liquid. IR (neat): $\tilde{\nu}$ = 3365, 2970, 2945, 2863, 1618, 1521, 1485, 1260, 1019, 916, 840, 783 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.19 [s, 6 H, $Si(CH_3)_2$], 0.98 [s, 9 H, $SiC(CH_3)_3$], 1.62 (s, 1 H, OH, D_2O exchangeable), 4.60 (s, 2 H, CH_2OH), 6.82 (d, *J* = 8.4 Hz, 2 H, ArH), 7.23 (d, *J* = 8.4 Hz, 2 H, ArH) ppm. $C_{13}H_{22}O_2Si$ (238.40): calcd. C 65.50, H 9.30; found C 65.47, H 8.29.

Compound 2f′: Yield: 0.191 g, 76%; colourless liquid. IR (neat): $\tilde{\nu}$ = 3396, 2960, 2940, 2858, 1603, 1491, 1460, 1255, 1127, 1071, 1015, 927, 835, 784. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.28 [s, 6 H, $Si(CH_3)_2$], 1.02 [s, 9 H, $SiC(CH_3)_3$], 1.48 (d, *J* = 6.5 Hz, 3 H, $CHCH_3$), 2.35 (br. s, 1 H, OH, D_2O exchangeable), 5.21 [q, *J* = 6.5 Hz, 1 H, CH(OH)], 6.75 (d, *J* = 8.1 Hz, 1 H, ArH), 6.96 (t, *J* = 7.3 Hz, 1 H, ArH), 7.06 (t, *J* = 7.6 Hz, 1 H, ArH), 7.55 (d, *J* = 7.6 Hz, 1 H, ArH) ppm. $C_{14}H_{24}O_2Si$ (252.43): calcd. C 66.61, H 9.58; found C66.80, H 9.54.

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[12] ^1H NMR spectra of the products were compared with the Aldrich Spectral Library.

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