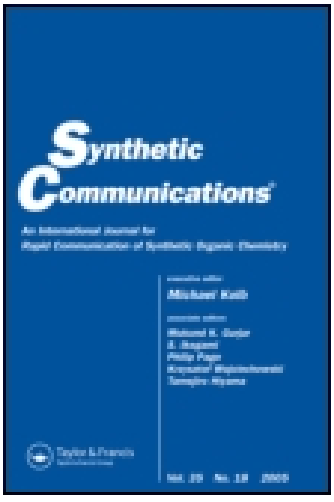

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Alternative Reagents for the Tritylation of Alcohols

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Alternative Reagents for the Tritylation of Alcohols

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Abstract: Two new tritylation reagents [viz. *p*-methoxybenzyl trityl ether (*p*-MBTE) and prenyl trityl ether (PTE)] were prepared. These two new reagents were utilized efficiently for the tritylation of alcohols, using DDQ or 20 mol% DDQ–3 eq. $Mn(OAc)_3$.

Keywords: *p*-methoxybenzyl trityl ether (*p*-MBTE), prenyl trityl ether (PTE)

INTRODUCTION

Discriminative reaction of functional groups of comparable reactivity by selective protection[1] plays a prominent role in a multistep synthesis of complex natural products, and seletion of the most suitable protecting group for each hydroxy function sometimes holds the key to success. The trityl group, among the several protecting groups that are available, is one of the most advantageous not only because of its selectivity but because of the ease of its formation and cleavage. The trityl protecting function is normally introduced with TrCl in presence of amine;[2] however, several other reagents such as TrOTMS–TMSTf,[3] tritylated pyridones,[4] BnOTr–DDQ,[5] TrODT–TrATC15,[6] and AgoTf–TrCl [7] are also available. Recently we have reported[8] the tritylation of alcohols with a new tritylating agent, *p*-methoxybenzyl trityl ether (*p*-MBTE)–DDQ, in the high yields and

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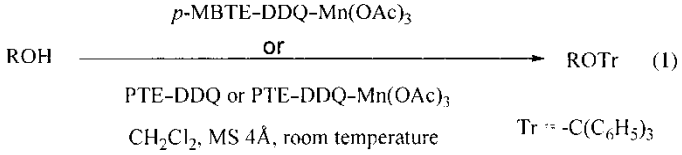
shorter reaction times, which was found to be better than several existing methods.

Herein, we report a full account of *p*-MBTE (**1**)–DDQ–$Mn(OAc)_3$, an improved tritylating agent, and prenyl trityl ether (PTE **2**)–DDQ– or PTE–DDQ–$Mn(OAc)_3$–mediated tritylation of alcohols [Eq. (1)].



RESULTS AND DISCUSSION

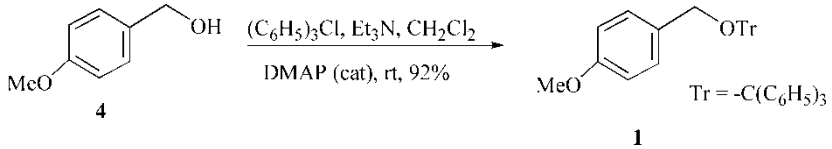
Preparation of *p*-Methoxybenzyl Trityl Ether (*p*-MBTE 1) and Use as New Tritylating Reagent With DDQ–$Mn(OAc)_3$

Keeping in mind the oxidation potential of *p*-methoxybenzyl alcohol[9–11] and hence its reactivity toward DDQ,[12] *p*-MBTE **1** was prepared by the tritylation of *p*-methoxybenzyl alcohol (**4**) in the presence of Et_3N in CH_2Cl_2 in 93% yield as a solid, mp 132–134°C (Scheme 1).

Method A: *p*-MBTE–DDQ-$Mn(OAc)_3$–Mediated Tritylation of Alcohols

Even though tritylation of alcohols with **1** offers many advantages, the main drawbacks in the protocol were a) the use of DDQ in stoichiometric quantity and b) generation of 2,3-dichloro-5,6-dicyanohydrobenzoquinol (HDDQ) as a side product. To circumvent both these problems, regeneration of DDQ was felt to be the best alternative. In the present study on the tritylation of alcohols with **1**, we have utilized a DDQ regeneration technique, developed by us earlier[13] using $Mn(OAc)_3$, a transition-metal oxide,[14] as a mild and potential reoxidant.

Accordingly, reaction of **5** with **1** (1.1 eq) in the presence of 20 mol% DDQ–3 eq. of $Mn(OAc)_3$ in CH_2Cl_2 containing molecular sieves 4 Å



4 **1**

Scheme 1.

indeed afforded the expected ether **5a** in 84% yield, albeit in 6 h. The study was then extended to other substrates, and the results are tabulated in Table 1.

Having established **1** and 20 mol% DDQ–3 eq. of $Mn(OAc)_3$ in CH_2Cl_2 as a better tritylating reagent, the study was then extended to variety of alcohols, the results of which are shown in Table 1. Thus, compounds **7**, **8**, and **11**, having primary alcohol groups, underwent tritylation and gave **7a**, **8a**, and **11a** respectively. Similarly, compounds **6** and **10** with secondary alcohol groups on tritylation with **1** gave **6a** (78%) and **10a** (81%), respectively. Discriminative tritylation of unsymmetrical diol **9** gave the monotritylated ether **9a** (92%) in 10 min, while reaction of symmetrical diol **12** with **1** gave **12a** (50%) and **12b** (30%) in 20 min. Alcohols **13**, **14**, and **15** with different protecting groups (THP, TBS, benzylidene) gave **13a** (74%) and **14a** (75%) in 10 min and **15a** (67%) in 15 min, respectively. Similarly, amino alcohol **16** and amino acid derivative **17** gave **16a** (71%) and **17a** (75%) respectively in 20 min.

The plausible mechanism[15] of DDQ regeneration is illustrated in Scheme 2. Accordingly, 2 mol of $Mn(OAc)_3$ is reacted with HDDQ and thus formed intermediate **A**, leading to DDQ and $Mn(OAc)_2$ by one electron transfer mechanism.

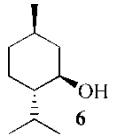
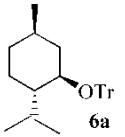
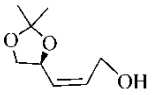
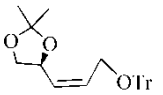
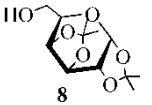
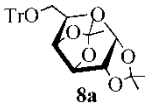
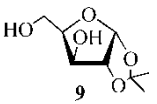
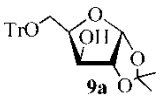
Thus, in the alternate protocol, regeneration of DDQ using $Mn(OAc)_3$ as reoxidant solved the problems associated with DDQ and HDDQ. Although the tritylation reactions with **1** went at a very fast rate and in high yields irrespective of the nature of alcohols, the main disadvantage associated with *p*-MBTE is the formation of anisaldehyde as a by-product. It is well documented in the literature[16] that allylic double bonds behave similar to benzylic systems toward oxidation with DDQ. Keeping this in mind, it was planned to prepare a new tritylating reagent such as prenyl trityl ether (PTE **2**) for the first time. The prenyl group on oxidation produces a low-boiling traceless counterpart, such as prenal, as a by-product.

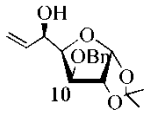
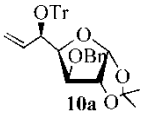
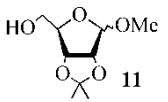
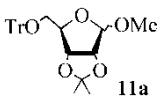
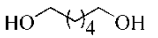
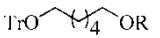
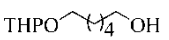
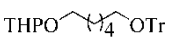
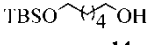
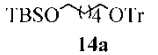
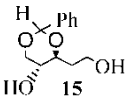
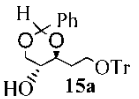
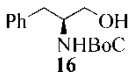
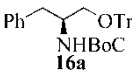
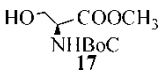
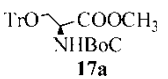
Accordingly, prenyl trityl ether (PTE, **2**) was prepared by reaction of prenyl alcohol (**13**) with TrCl (Scheme 3) in the presence of Et_3N and DMAP (cat.) in CH_2Cl_2 for 12 h in 65% yield as a colorless syrup, which was characterized by ^1H NMR, IR, and mass spectrometry and used as a new tritylating reagent for alcohols.

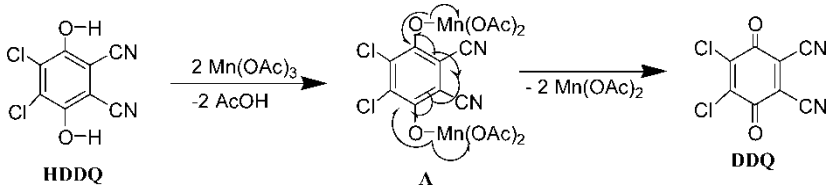
Method C: PTE–DDQ–Mediated Tritylation of Alcohols

Initially, **5** was treated with **2** and DDQ in the presence of activated MS 4 Å in CH_2Cl_2 [Eq. (1)] for 20 min to give trityl ether **5a** in 88% yield. Encouraged by this expected result, this study was extended to various alcohols. Thus, menthol **6** underwent tritylation in 40 min with 80% yield to give **6a**, while sugar derivatives **8**–**11** on tritylation gave the products **8a** (79%), **9a** (81%), **10a** (89%), and **11a** (84%) in 20–40 min. Symmetric diol **12** on reaction with **2** gave **12a** (80%) and **12b** (8%) in 15 min, whereas unsymmetric diol **9** gave **9a** (81%) as an

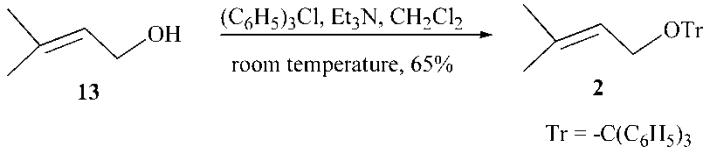
Table 1. Tritylation of alcohols with different reagents

Entry no.	Starting materials	Products	Method A		Method B		Method C	
			Time (h)	Yield (%)	Time (min)	Yield (%)	Time (h)	Yield (%)
1	$Ph(CH_2)_4OH$ **5**	$Ph(CH_2)_4OTr$ **5a**	6	84	20	88	8	74
2	 **6**	 **6a**	14	78	40	80	8	75
3	 **7**	 **7a**	4.5	82	10	84	—	—
4	 **8**	 **8a**	5	86	20	79	6	76
5	 **9**	 **9a**	4	79	20	81	5	74

6	 **10**	 **10a**	18	81	40	89	—	—
7	 **11**	 **11a**	8	80	20	84	8	79
8	 **12**	 **12 a** = H **12 b** = Tr	6	50 30	15	80 8	5	75 10
9	 **13**	 **13a**	6	74	20	84	7	74
10	 **14**	 **14a**	6	75	20	83	7	75
11	 **15**	 **15a**	4	67	20	76	3	67
12	 **16**	 **16a**	8	71	30	81	8	78
13	 **17**	 **17a**	8	75	30	80	8	72



Scheme 2. Preparation of prenyl trityl ether (PTE-2) and use as new tritylating reagent.



Scheme 3.

exclusive product in 20 min. Alcohols **13**, **14**, and **15** with acid-sensitive protecting groups (THP, TBS, benzylidene) gave **13a** (84%), **14a** (83%), and **15a** (76%), respectively, in 20 min, whereas aminol **16** and amino acid derivative **17** afforded **16a** (81%) and **17a** (80%) in 30 min, respectively.

Method D: PTE–DDQ $Mn(OAc)_3$–Mediated Tritylation of Alcohols

Thus, even though the reactivity of the new tritylating reagent **2** was found to be comparable to **1** and formation of anisaldehyde could successfully be avoided, still it utilizes a stoichiometric quantity of DDQ and generates 2,3-dichloro-5,6-dicyanohydrobenzoquinol (HDDQ) as by-product. To improve the usability of **2** for the tritylation and to circumvent this problem, the tritylation in the present study was also achieved with 20 mol% DDQ–3 eq. $Mn(OAc)_3$ by a regeneration technique.

Accordingly, **5**, on reaction with **2**, $Mn(OAc)_3$ (3 eq), and DDQ (20 mol%) in CH_2Cl_2, gave **5a** (74%), albeit in 8 h. similar result were obtained with all other substrates as summarized in Table 1. Thus, even though the reaction by the DDQ regeneration method was slow, the yields were good and it avoided the formation of HDDQ. Thus, the new reagent **2** is as efficient as *p*-MBTE in tritylation; although unlike **1**, the by-product prenal is traceless because it is easy to remove during workup.

CONCLUSION

The present study thus demonstrates a) the preparation of new tritylating reagent *p*-MBTE **1** and its use for the tritylation of alcohols with DDQ of DDQ–$Mn(OAc)_3$, where use of stoichiometric quantity of DDQ is avoided

in addition to the by-product quinol, and b) a modified tritylating reagent PTE **2** is synthesized and utilized under DDQ and DDQ regeneration conditions for the tritylation, wherein the formation of by-product such as anisaldehyde is also avoided. Thus, because their ease of preparation and simple and efficient reaction conditions for protection, the alternative tritylating agents could find immense use in organic systhesis.

EXPERIMENTAL

General

NMR spectra were recorded on Varian Gemini FT-200 MHz (21°C) with 7- to 10-mM solutions in appropriate solvents using TMS as internal standard. Solvents were dried over standard drying agents and were freshly distilled prior to use. IR spectra were taken with a Perkin-Elmer 1310 spectrometer. Mass spectra were recorded on CEC-21-11013 or Finnigan Mat 1210 double-focusing mass spectrometers operating at a direct inlet system, and FABMS was measured using a VG AUTOSPEC mass spectrometers at 5 or 7 K resolution using perflurokerosene as an internal reference. Nomenclature mentioned in this section was adopted from ACD/Name Version 1.0β, Advanced Chemistry Development Inc., Toronto, Canada. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40°C in vacuo. Elemental analysis was recorded on Elementar (Vario El, Germany).

Procedure for the Preparation of the Reagents

Preparation of *p*-Methoxybenzyl Trityl Ether (*p*-PMBTE **1**)

To a stirred solution of *p*-methoxybenzyl alcohol (**4**, 5.0 g, 36.2 mmol) and Et_3N (3.65 g, 36.2 mmol) in CH_2Cl_2 (50 mL) containing activated MS 4Å (1.5 g) at room temperature, trityl chloride (10.06 g, 36.2 mmol) and 4-dimethylamonopyridine (0.440 g, 3.62 mmol) were added. After 8 h, the reaction mixture was evaporated, the residue was dissolved in ethyl acetate (20 mL), and the insoluble materials were filtered. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, toluene) to afford **1** (12.8 g) in 93% yield as a white solid, mp 132–134°C. Analysis found C, 85.21; H, 6.34. $C_{27}H_{24}O_2$ requires C, 85.23; H, 6.36%. δ_H (200 MHz, $CDCl_3$) 3.8 (s, 2H, CH_2Ar), 4.18 (s, 3H, OCH_3), 7.15–7.55 (m, 19H, ArH); *m/z*: (FABMS) 243 (M^+-137).

Preparation of Prenyl Trityl Ether (PTE **2**)

To a stirred solution of prenyl alcohol (**13**, 3.0 g, 34.9 mmol) and Et_3N (3.87 g, 38.3 mmol) in CH_2Cl_2 (40 mL) containing activated MS 4Å (1.5 g) at room

temperature, trityl chloride (9.7 g, 34.9 mmol) and 4-dimethylaminopyridine (0.42 g, 3.49 mmol) were added. After 12 h, it was worked up as described for **1** and was purified by column chromatography (silica gel, EtOAc–hexane, 1:9) to afford **2** (7.41 g) in 65% yield as a colorless syrup. Analysis found C, 87.72; H, 7.34. $C_{24}H_{24}O$ requires C, 87.76; H, 7.37%. δ_H (200 MHz, $CDCl_3$) 1.50, 1.75 (2s, 6H, -CH_3), 3.55 (d, 2H, $J = 6.8$ Hz, H-1), 5.40 (t, 1H, $J = 5.9$ Hz, H-2), 7.15–7.55 (m, 15H, Ar-H), *m/z:* (FABMS) 328 (M^+).

General Procedure for the Preparation of Trityl Ethers

DDQ Method

A solution of alcohol (1.0 mmol) and reagent **1** or **2** (1.1 mmol) in CH_2Cl_2 (3 mL) containing activated MS 4Å (250 mg) was treated with DDQ (1.5 mmol) and stirred at room temperature. After the completion of reaction (TLC analysis), it was quenched with saturated $NaHCO_3$ solution (10 mL) and extracted with $CHCl_3$ (3 × 10 mL). The organic layer was dried (Na_2SO_4) and evaporated and the residue was purified by column chromatography (silica gel, EtOAc in hexane) to afford trityl ethers.

DDQ–$Mn(OAc)_3$ Method

A solution of alcohol (1.0 mmol) and reagent **1** or **2** (1.1 mmol) in CH_2Cl_2 (5 mL) containing activated MS 4 Å (250 mg) and $Mn(OAc)_3$ (3.0 mmol) was treated with DDQ (0.2 mmol) and stirred at room temperature. After the completion of reaction (TLC analysis), the solid was filtered and washed with $CHCl_3$ (25 mL). The filtrate was quenched with saturated $NaHCO_3$ solution (10 mL) and extracted into $CHCl_3$ (3 × 10 mL). The organic layer was dried (Na_2SO_4) and evaporated and the residue was purified by column chromatography (silica gel, EtOAc in hexane) to afford trityl ethers.

Data

1-Trityloxy-4-phenylbutane (**5a**)

Syrup; method A: 6 h, 84%. Analysis found C, 88.75; H, 7.18. $C_{29}H_{28}O$ requires C, 88.73; H, 7.19%. γ_{max} 3400, 3100, 2920, 2850, 1800, 1500, 1050, 760 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.65–1.90 (m, 4H), 2.64 (t, 2H, $J = 7.6$ Hz), 3.12 (t, 2H, $J = 6.12$ Hz), 7.1–7.5 (m, 20H); *m/z:* (FABMS) 391 (m^+-1, 8%), 315 (m^+-77, 20%), 243 (100%); method B: 20 min, 88%; method C: 8 h, 74%.

(1S,2R,4S)-1-Isopropyl-4-methyl-2-(trityloxy) Cyclohexane (**6a**)

Semisolid; method A: 14 h, 78%. Analysis found C, 87.13; H, 8.49. $C_{29}H_{34}O$ requires C, 87.39; H, 8.60%. γ_{max} 3350, 3100, 2900, 2850, 1590, 1450, 1390, 1200, 1100, 760 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.22 (d, 2H, $J = 7.0$ Hz), 1.0–2.60 (m, 11H), 1.45–1.65 (m, 4H), 2.40–2.50 (m, 1H), 2.70–2.85 (m, 1H), 7.12–7.55 (m, 15H); *m/z:* (FABMS) 398 (M^+), 259 (10%); method B: 40 min, 80%; method C: 8 h, 75%.

(2Z,4S)-4,5-Isopropylidenedioxy-1-trityloxy-pent-4-en (**7a**)

Syrup; method A: 4.5 h, 82%. Analysis found C, 80.81; H, 7.01. $C_{27}H_{28}O_3$ requires C, 80.97, H, 7.05%. γ_{max} 3500, 2900, 2550, 2420, 1590, 1450, 1180, 1150, 1080, 900, 780 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.3, 1.38 (2s, 6H), 3.45 (t, 1H, $J = 10.2$, 9.69 Hz), 3.55–3.98 (m, 3H), 4.59 (q, 1H, $J = 9.18$, 9.69 Hz), 5.48–5.62 (m, 1H), 5.72–5.92 (m, 1H), 7.25–7.50 (m, 15H); *m/z*: (FABMS) 259 (M^+-141), 243 (100%); method B: 10 min, 84%.

1,2:3,4-Di-*O*-isopropylidene-6-*O*-trityl-α-D-galactopyranose (**8a**)

Syrup; method A: 5 h, 86%. Analysis found C, 74.05; H, 6.80. $C_{31}H_{34}O_6$ requires C, 74.08; H, 6.82%. γ_{max} 3400, 2860, 1800, 1550, 1450, 1200, 1150, 1080, 800, 760, 680 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.32, 1.35, 1.39, 1.56 (4s, 12H), 3.20–3.28 (m, 2H), 3.92 (t, 1H, $J = 5.72$, 6.66 Hz). 4.22–4.30 (m, 2H), 4.55 (dd, 1H, $J = 2.85$, 3.80 Hz), 5.45 (d, 1H, $J = 4.76$ Hz), 7.20–7.50 (m, 15H); *m/z*: (FABMS) 503 ($M^+ + 1$); method B: 20 min, 79%; method C: 6 h, 76%.

1,2-*O*-Isopropylidene-5-*O*-trityl-α-D-xylofuranose (**9a**)

Syrup; method A: 4 h, 79%. Analysis found C, 74.99; H, 6.55. $C_{27}H_{28}O_5$ requires C, 74.98; H, 6.53%. γ_{max} 3480, 3100, 3080, 2950, 1950, 1790, 1550, 1350, 1280, 1150, 1050, 760 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.3, 1.45 (2s, 6H), 3.10 (br, s, 1H), 3.40–3.62 (m, 2H), 4.22 (br, s, 1H), 4.98 (d, 1H, $J = 4.76$ Hz), 5.99 (d, 1H, $J = 4.76$ Hz), 5.99 (d, 1H, $J = 4.76$ Hz), 7.20–7.48 (m, 15H); *m/z*: (FABMS) 455 ($M^+ + 23$), 243 (100%); method B: 20 min, 81%; method C: 5 h, 74%.

1,2-*O*-Isopropylidene-3-*O*-benzyl-6-ene-5-*O*-trityl-α-D-xylofuranose (**10a**)

Semisolid; method A: 18 h, 81%. Analysis found C, 78.79; H, 6.63. $C_{36}H_{36}O_5$ requires C, 78.81; H, 6.61%. γ_{max} 3500, 2850, 1690, 1500, 1400, 1180, 1000, 780 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.48, 1.30 (2s, 6H), 3.72 (d, 1H, $J = 4.1$ Hz), 3.95 (dd, 1H, $J = 2.70$, 7.60 Hz), 4.74–4.32 (m, 6H),

5.62–5.42 (m, 1H), 5.85 (d, 1H, $J = 4.1$ Hz), 7.58–7.10 (m, 20H); m/z: (FABMS) 533 (M^+-15); method B: 40 min, 89%.

Methyl 2,3-*O*-Isopropylidene-5-*O*-trityl-α-D-ribofuranose (**11a**)

Semisolid; method A: 8 h, 80%. Analysis found C, 75.30; H, 6.75. $C_{28}H_{30}O_5$ requires C, 75.31; H, 6.77%. γ_{max} 3450, 2900, 1800, 1750, 1550, 1400, 1250, 1160, 1090, 1000, 890, 780 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.30, 1.48 (2s, 6H), 3.05–3.15 (m, 5H), 4.32 (t, 1H, $J = 6.9$ Hz), 4.38 (d, 1H, $J = 5.7$ Hz), 4.55 (d, 1H, $J = 5.7$ Hz), 4.88 (s, 1H), 7.15–7.55 (m, 15H); m/z: (FABMS) 431 (M^+-15); method B: 20 min, 84%; method C: 8 h, 79%.

Tritylation of 1,6-Hexandiol

Syrup; method A: 6 h, first eluted was 1-trityloxy hexane-6-ol (**12a**, 50%). Analysis found C, 83.26; H, 7.85. $C_{25}H_{28}O_2$ requires C, 83.29; H, 7.83%. γ_{max} 3400, 2860, 1620, 1580, 1350, 1210, 1100, 950, 790 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.20–1.73 (m, 8H), 3.02 (t, 2H, $J = 6.9$ Hz), 3.58 (t, 2H, $J = 6.5$ Hz), 7.12–7.48 (m, 15H), m/z: (FABMS) 383 ($M^+ + 23$); second eluted was 1,6-ditrityloxy hexane (**12b**, 30%). Analysis found C, 87.65; H, 7.01. $C_{44}H_{42}O_2$ requires C, 87.67; H, 7.02%. γ_{max} 3450, 2950, 2900, 2820, 1580, 1210, 1100, 900, 780 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.25–1.45 (m, 4H), 1.54–1.70 (m, 4H), 3.02 (t, 4H, $J = 6.9$ Hz), 7.15–7.48 (m, 30H); m/z: (FABMS) 359 (M^+-243); method B: 15 min, (**12a**, 80%), (**12b**, 8%); method C: 5 h, (**12a**, 75%), (**12b**, 10%).

1-Tetrahydro-2H-pyranlyoxy-6-trityloxyhexane (**13a**)

Syrup; method A: 6 h, 74%. Analysis found C, 81.02; H, 8.12. $C_{30}H_{36}O_3$ requires C, 81.04; H, 8.16%. γ_{max} 3450, 2950, 2900, 2820, 1580, 1210, 1100, 900, 780 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.2–1.85 (m, 14H), 3.05 (t, 2H, $J = 6.4$ Hz, H-1), 3.25–3.50 (m, 2H, H-6), 3.55–3.90 (m, 2H, H-5′), 4.55 (brs, 1H, H-1′), 7.1–7.50 (m, 15H, Ar-H); m/z: (FABMS) 359 (M^+-85); method B: 20 min, 84%; method C: 7 h, 74%.

1-Trityloxy-6-tert-butyldimethylsilyloxyhexane (**14a**)

Syrup; method A: 6 h, 74%. Analysis found C. 78.40; H, 8.89. $C_{31}H_{42}O_2Si$ requires C, 78.43; H, 8.92%. γ_{max} 3450, 3110, 2880, 1610, 1550, 1210, 1100, 810, 780 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.05 (s, 6H), 0.9 (s, 9H), 1.2–1.7 (m, 8H), 3.05 (t, 2H, $J = 6.0$ Hz, H-1), 3.60 (t, $J = 6.0$ Hz, H-6), 7.15–7.50 (m, 15H, Ar-H), m/z: (FABMS) 417 (M^+-57); method B: 20 min, 84%; method C: 7 h, 74%.

(2R,3S)-1,3-Benzylidenedioxy-2-hydroxy-5-trityloxy-pentane (**15a**)

Syrup; method A: 4 h, 67%. γ_{max} 3450, 3100, 2920, 2840, 1550, 1400, 1300, 1210, 1100, 900 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.75 (m, 2H), 3.16 (t, 2H, $J = 11.40$ Hz), 3.50 (m, 3H), 4.24 (m, 1H) 5.38 (s, 1H), 7.26 (m, 15H, Ar-H), 7.44 (m, 5H, Ar-H), m/z (FABMS); method B: 20 min, 76%; method C: 3 h, 67%.

tert-Butoxycarbonyl-1-phenyl-3-trityloxy-2-propanamine (**16a**)

Syrup; method A: 8 h, 71%. γ_{max} 3520, 3100, 2950, 1750, 1520, 1400, 1180, 1050, 720 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.41 (s, 9H, -BoC), 2.90 (d, 1H, $J = 8.69$ Hz), 3.07 (m, 1H), 3.70 (m, 1H), 4.74 (d, 1H, $J = 17.4$ Hz), 7.22 (m, 15H, Ar-H), 7.41 (m, 5H, Ar-H); m/z (FABMS) 380 (M^+-100); method B: 30 min, 81%; method C: 8 h, 78%.

tert-Butoxycarbonyl-2-methylamino-3-trityloxy Propanoate (**17a**)

Syrup; method A: 8 h, 75%. γ_{max} 3500, 3100, 2950, 1800, 1550, 1400, 1200, 1100, 810, 780 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.44 (s, 9H, -BoC), 3.38 (dd, 1H, $J = 7.14$, 14.28 Hz), 3.50 (dd, 1H, $J = 7.14$, 14.28 Hz), 3.72 (s, 3H, $-CH_3$), 4.38 (m, 1H, $J = 17.80$ Hz), 5.38 (d, 1H, $J = 17.80$ Hz), 7.24 (m, 15H, Ar-H); m/z (FABMS) 384 (M^+-77); method B: 30 min, 80%; method C: 8 h, 72%.

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