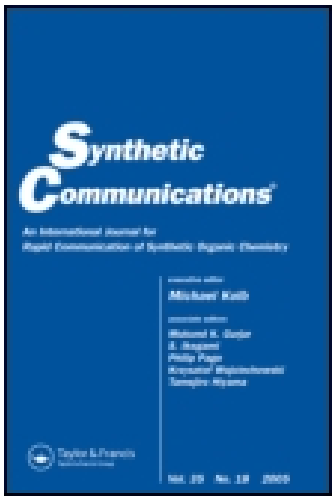

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p-Methoxy Diphenylmethanol (MDPM), p-Phenyl Diphenylmethanol (PDPM), and p-Phenylphenyl Diphenylmethanol (PPDPM)—Protecting Groups for Alcohols—Protection and Deprotection

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p-Methoxy Diphenylmethanol (MDPM), *p*-Phenyl Diphenylmethanol (PDPM), and *p*-Phenylphenyl Diphenylmethanol (PPDPM)—Protecting Groups for Alcohols—Protection and Deprotection[#]

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ABSTRACT

Two new protecting groups viz. *p*-phenyl diphenylmethanol (PDPM) and *p*-phenylphenyl diphenylmethanol (PPDPM) were prepared and utilized along with *p*-methoxy diphenylmethanol (MDPM), for the protection of alcohols in the presence of $Yb(OTf)_3$. Deprotection of the above ethers was achieved using DDQ or CF_3COOH.

Key Words: DPM; Alcohol; Protection; $Yb(OTf)_3$.

[#]IICT Communication Number: 021001.

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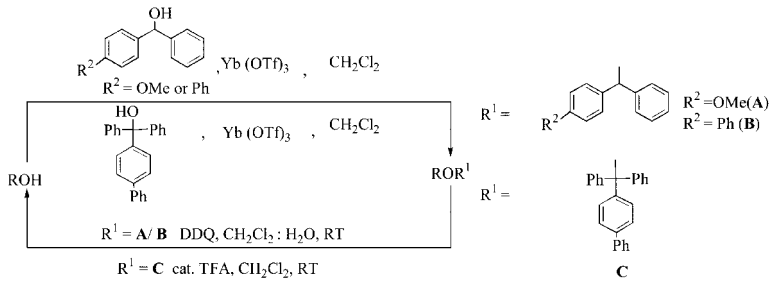
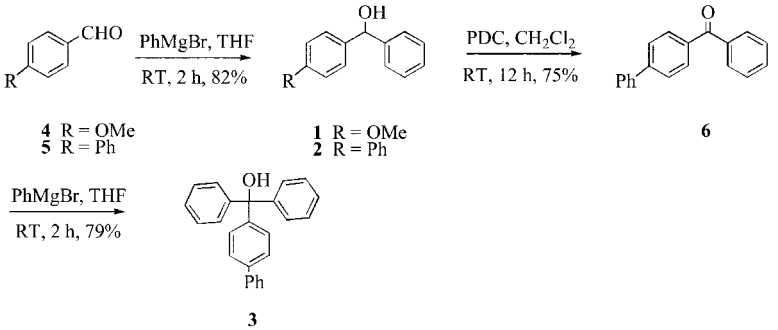
Development of new and mild reactions and reagents[1] for the protection of functional groups is of paramount research in the area of synthetic organic chemistry. A total synthesis of complex natural product always is benefited by mild reagents and efficient protocols for the protection as well as deprotection. Inspite, still there is an urge for new and specific protecting groups to realize the successful overall operation of the total synthesis. Of the several protecting groups for alcohol, benzylic groups such as triphenylmethyl (Tr), diphenylmethyl (DPM), benzyl (Bn), *p*-methoxy and *p*-phenyl benzyl (PMB and PPB) etc. enjoy a widespread appreciation, especially the PMB and PPB with oxidatively[2,3] labile groups. Hence, in this class of protecting groups, altering the reactivities of the existing protecting groups to the diversified new protecting groups in order to show specificity in their mode of introduction and removal is very essential. In continuation of our efforts in the area of masking/unmasking of functional groups[4–11] herein, we report three new reagents viz. *p*-methoxy diphenylmethanol (MDPM-**1**), *p*-phenyl diphenylmethanol (PDPM-**2**) and *p*-phenylphenyl diphenylmethanol (PPDPM-**3**) for the protection of alcohols (Equation).



The required new reagents **1**, **2**, and **3** were prepared from commercially available aldehydes **4** and **5**. Accordingly, **4** on reaction with PhMgBr (Sch. 1)



Scheme 1.

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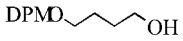
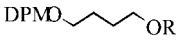
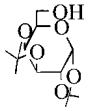
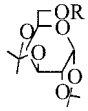
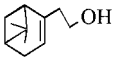
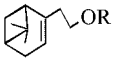
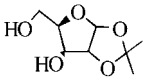
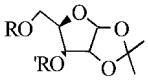
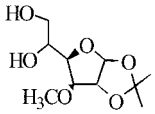
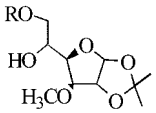
Table 1. Protection of alcohols and deprotection of ethers.

S. No	Substrate	Product	Protection of alcohols		Deprotection of ethers	
			Time	Yield (%)	Time	Yield (%)
1	$C_8H_{17}OH$	$C_8H_{17}OR$				
	7	**7a** R = A	30 min	84	12 hr[a]	70
		7b R = B	10 hr	77	7.5 hr	79
		7c R = C	15 hr	76	1.5 hr	84
2						
	8	**8a** R = A	40 min	65	12 hr[a]	75
		8b R = B	7 hr	79	7 hr	82
3						
	9	**9a** R = A	40 min	81	—	—
		9b R = B	6 hr	62	5 hr	77
		9c R = C	15 hr	78	2 hr	78
4						
	10	**10a** R = A	45 min	76	—	—
		10b R = B	9 hr	72	7 hr	75
5						
	11	**11a** R = A	30 min	76	—	—
		11b R = B	5 hr	85	7 hr	83
		11c R = C	12 hr	76	3 hr	82
6						
	12	**12a** R = A; R′ = H	40 min	59	—	—
		12a′ R = R′ = A	45 min	19	—	—
		12b R = B; R′ = H	10 hr	62	8 hr	73
		12c R = C; R′ = H	16 hr	62	2.5 hr	72
7						
	13	**13a** R = A	45 min	80	—	—

(*continued*)

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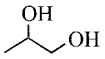
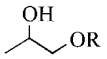
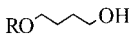
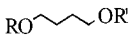
Table 1. Continued.

S. No	Substrate	Product	Protection of alcohols: Time	Protection of alcohols: Yield (%)	Deprotection of ethers: Time	Deprotection of ethers: Yield (%)
8						
	14	**14a** R = B	11.5 hr	80	7 hr	82
		14b R = C	11 hr	79	1.25 hr	85
9						
	15 R = THP	**15a** R = THP; R′ = B	8 hr	82	5 hr	83
	16 R = TBS	**16a** R = TBS; R′ = B	9 hr	81	8.5 hr	81
	17 R = Ac	**17a** R = Ac; R′ = B	8 hr	84	6 hr	72
		17b R = Ac; R′ = C	10 hr	78	1.5 hr	77

[a]Deprotection with DDQ (10 mol%) and $Mn(OAc)_3$ (3 eq).

gave the carbinol **1** (84%), while **5** gave **2** (82%). Further, oxidation of **2** with PDC followed by treatment of **6** with PhMgBr afforded **3** (79%).

Our earlier experience with active benzylic carbinols amply demonstrated that the protection can be achieved with the carbinols **1**, **2**, and **3** in the presence of Lewis acids such as $Yb(OTf)_3$. Accordingly, **7** (Table 1) was treated with MDPM-**1** and 10 mol% $Yb(OTf)_3$ in CH_2Cl_2 at room temperature for 30 min. to afford the corresponding MDPM ether **7a** (84%). Similarly, alcohol **8** on etherification with **1** and $Yb(OTf)_3$ gave ether **8a** (65%). In a further study, to establish the generality protection was extended to different alcohols such as sugar alcohols **9**, **12**, **13** and terpenes **10**, **11** using **1** and $Yb(OTf)_3$ to give the ethers **9a** to **13a** in good yields. In the case of 1,3-diol **12**, the mono- and di-protected products were obtained in 59% and 19% yields, respectively, while the 1,2-diol **13** gave **13a** as an exclusive product in 80% yield.

The deprotection of MDPM ethers was attempted under oxidative conditions. Accordingly, **7a** and **8a** were treated (Table 1) with DDQ in CH_2Cl_2–H_2O (19 : 1) to successfully furnish the alcohols **7** (75%) and **8** (78%), respectively. It is well documented in the literature that PMB group undergoes cleavage under acidic conditions.[11] To check the stability of the MDPM ether towards acid hydrolysis, **7a** was treated independently with (a) 60% aq. AcOH at 60°C and (b) TFA (cat.) in CH_2Cl_2 at room temperature to give **7** in 4 hr and 1.5 hr respectively. Thus, it was amply indicated that MDPM ethers, like PMB

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ethers are labile to acids. Earlier, we have demonstrated *p*-phenylbenzyl (PPB) group, unlike PMB, is not labile to acids. Hence, to avoid the acid hydrolysis, encountered with the corresponding MDPM ethers, in the present study a new reagent, *p*-phenyl diphenylmethanol (PDPM-**2**) was prepared and used for the protection of alcohols.

Accordingly, alcohol **7** was subjected to reaction with **2** using 10 mol% of $Yb(OTf)_3$ in CH_2Cl_2 to afford the ether **7b** (77%). Encouraged by the result, the study was extended to other alcohols **7**–**12** and **14**–**17** to afford the corresponding ethers as shown in the Table 1. The unsymmetrical diol **12** with **2** furnished **12b** (62%) as an exclusive product unlike with the corresponding MDPM alcohol **1**. Similarly alcohols **15** and **16** having acid sensitive THP and TBS groups also underwent facile protection with **2** to afford **15a** (82%) and **16a** (81%), respectively, while alcohol **17** having a base sensitive group gave **17a** (84%).

As demonstrated earlier,[11] the *p*-phenyl group facilitates the removal of the groups such as **2** under oxidative conditions. Hence, the thus made ethers were subjected to DDQ mediated oxidative deprotection to afford the corresponding alcohols as indicated in the Table 1.

In a further study, acid catalysed hydrolysis of **7b** with (a) 60% aq. AcOH at 60°C and (b) catalytic TFA in CH_2Cl_2 at room temperature, even after 24 hr, did not show any traces of hydrolyzed products, thus indicating, unlike the MDPM ethers, the PDPM ethers are stable to the acidic hydrolysis.

Similarly, the newly prepared trityl analogue, PPDPM-**3**, was also successfully utilized for the protection of alcohols **7**, **9**, **11**, **12**, **14**, and **17** as indicated in Table 1. *p*-Phenyl group, as evidenced from the above study, facilitates the removal of such groups under oxidative conditions, while it would enhance the rate of acid catalyzed hydrolysis in PPDPM ethers. Indeed, hydrolysis of **7c** with CF_3COOH (10 mol%) in CH_2Cl_2 gave **7** in 84% yield in 1.5 hr, while the corresponding trityl ether of **7** required 2.5 hr, thus indicating the enhanced rate of hydrolysis for PDPM ethers over triyl ethers. Similarly hydrolysis of **9c**, **11c**, **12c**, **14b** to **17b** gave the respective alcohols very efficiently in 1 to 3 hr time (Table 1).

Thus, in conclusion, in the present study, protection of alcohols is achieved with MDPM **1** and newly prepared reagents PDPM **2** and PPDPM **3** alcohols under acid catalyzed conditions using $Yb(OTf)_3$. Oxidative and acid catalyzed deprotective methods were efficiently utilized for the deprotection of MDPM, PDPM, and PPDPM ethers, wherein MDPM ethers were found to be sensitive to the acid hydrolysis unlike PDPM ethers. Thus, the two new reagents PDPM and PPDPM, with their inherent qualities for the protection and deprotection under mild conditions could find immense use when compared to the related existing reagents.

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GENERAL EXPERIMENTAL PROCEDURE

The ^{1}H NMR spectra were recorded on Varian Gemini 200 MHz spectrometer using TMS as an internal standard. Mass spectra were recorded on a VG micromass 70-70H mass spectrometer and IR spectra were recorded on Nicolet FT IR-740.

Protection of Alcohols with 1, 2, and 3

A mixture of alcohol (1 mmol) and **1**, **2**, or **3** (1 mmol) was treated with $Yb(OTf)_3$ (0.1 mmol) in CH_2Cl_2 (10 mL) at room temperature or reflux temperature (for **3**). The reaction mixtures were diluted with excess CH_2Cl_2 (20 mL) and washed with sat. aq. $NaHCO_3$ (10 mL). The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure. The crude residue was purified by column chromatography (Silicagel, hexane–EtOAc) to afford the ethers.

Deprotection of Ethers with DDQ

A mixture of MDPM or PDPM ether (1 mmol) and DDQ (1 mmol) was stirred in CH_2Cl_2 (10 mL) at room temperature. The reaction mixture was quenched with aq. $NaHCO_3$ (10 mL) solution and diluted with excess CH_2Cl_2 (10 mL). The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure. The crude residue was purified was purified by column chromatography (Silicagel, hexane–EtOAc) to afford the alcohols.

Deprotection with TFA

A mixture of PPDPM ether (1 mmol) and TFA (0.1 mmol) was stirred in CH_2Cl_2 (10 mL) at room temperature. The reaction mixture was quenched with aq. $NaHCO_3$ (10 mL) solution and diluted with excess CH_2Cl_2 (10 mL). The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure. The crude residue was purified was purified by column chromatography (Silicagel, hexane–EtOAc) to afford the alcohols.

Spectral Data

7a: IR (neat): 700, 770, 1100, 1460, 2950 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.92 (t, $J = 5.82$, 16.4 Hz, 3H), 1.30 (s, 10H), 1.65 (t, $J = 8.32$, 16.6 Hz, 2H), 3.45 (t, $J = 8.32$, 16.6 Hz, 2H), 3.82 (s, 3H), 5.46 (s, 1H), 6.82

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(d, $J = 9.0$ Hz, 2H), 7.15–7.40 (m, 7H); FABMS (m/z, %): 326 (M^+, 26), 259 (15), 243 (100), 105 (40), 57 (30); analysis calcd. for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26; found: C, 80.82; H, 9.18. **7b**: IR (neat): 700, 760, 1100, 1480, 2940 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.90 (t, $J = 5.83$, 16.6 Hz, 3H), 1.30 (s, 10H), 1.64 (t, $J = 8.33$, 16.6 Hz, 2H), 3.45 (t, $J = 8.33$, 16.6 Hz, 2H), 5.30 (s, 1H), 7.15–7.40 (m, 10H), 7.42–7.60 (m, 4H); FABMS (m/z, %): 259 (16), 243 (100), 105 (44), 91 (20), 57 (30); analysis calcd. for $C_{27}H_{32}O$: C, 87.05; H, 8.66; found: C, 87.00; H, 8.52. **7c**: IR (neat): 680, 750, 1040, 1450, 2900 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.09 (t, $J = 8.0$, 16.0 Hz, 3H), 1.30 (s, 10H), 1.65 (t, $J = 6.4$, 12.0 Hz, 2H), 3.08 (t, $J = 8.0$, 16.0 Hz, 2H), 7.10–7.26 (m, 8H), 7.28–7.60 (m, 11H); FABMS (m/z, %): 319 (74), 259 (54), 241 (82), 183 (56), 105 (100); analysis calcd. for $C_{33}H_{36}O$: C, 88.35; H, 8.09; found: C, 80.28; H, 8.00. **8a**: IR (neat): 680, 750, 1040, 1450, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.45–2.0 (m, 4H), 3.48 (t, $J = 6.75$ Hz, 2H), 3.64 (t, $J = 6.75$ Hz, 2H), 5.32 (s, 1H), 6.82 (d, $J = 9.0$ Hz, 2H) 7.15–7.45 (m, 17H); FABMS (m/z, %): 452 (M^+, 12), 213 (15), 197 (100), 137 (5), 55 (10); analysis calcd. for $C_{31}H_{32}O_3$: C, 82.27; H, 7.13; found: C, 82.19; H, 7.10. **8b**: IR (neat): 700, 760, 1060, 1450, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.46–2.02 (m, 4H), 3.48 (t, $J = 6.74$ Hz, 2H), 3.66 (t, $J = 6.74$ Hz, 2H), 5.32 (s, 1H), 5.54 (s, 1H), 6.81 (d, $J = 9.2$ Hz, 2H), 7.15–7.42 (m, 17H), 7.45–7.60 (m, 4H); FABMS (m/z, %): 213 (20), 197 (100), 137 (15), 55 (20); analysis calcd. for $C_{36}H_{34}O_2$: C, 86.71; H, 6.87; found: C, 86.68; H, 6.76. **9a**: IR (neat): 720, 760, 1050, 1460, 2900 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.34, 1.40, 1.54 (3s, 12H, 4 CH_3), 3.60 (t, 2H, $J = 6.75$ Hz), 3.80 (s, 3H), 4.05 (m, 1H), 4.22–4.40 (m, 2H), 4.53–4.65 (m, 1H), 5.50 (s, 1H), 5.52 (d, $J = 4.95$ Hz, 1H), 6.82 (d, $J = 8.65$ Hz, 2H), 7.15–7.45 (m, 7H); FABMS: (m/z, %): 441 (M^+, −15, 10), 197 (100), 91 (25), 69 (30), 57 (10); analysis calcd. for $C_{26}H_{32}O_7$: C, 71.34; H, 7.54; found: C, 71.23; H, 7.42. **9b**: IR (KBr): 750, 1050, 1210, 1300, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.36 (s, 6H), 1.45 (s, 3H), 1.60 (s, 3H), 3.58–3.65 (m, 2H), 4.05 (t, $J = 8.0$, 16.0 Hz, 1H), 4.25–4.38 (m, 2H), 4.60 (d, $J = 8.0$ Hz, 1H), 5.50 (d, $J = 4.0$ Hz, 2H), 7.20–7.40 (m, 10H), 7.44–7.60 (m, 4H); FABMS (m/z, %): 525 (M^+, +23), 259 (18), 243 (44), 241 (100), 91 (16); analysis calcd. for $C_{31}H_{34}O_6$: C, 76.77; H, 7.25; found: C, 76.59; H, 7.16. **9c**: IR (KBr): 720, 1020, 1050, 1200, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.38 (s, 6H), 1.45 (s, 3H), 1.60 (s, 3H), 3.30–3.45 (m, 2H), 4.00 (t, $J = 8.0$, 16.0 Hz, 1H), 4.25–4.40 (m, 2H), 4.60 (d, $J = 8.0$ Hz, 1H), 5.50 (d, $J = 4.0$ Hz, 1H), 7.20–7.42 (m, 8H), 7.46–7.62 (m, 11H); FABMS (m/z, %): 601 (M^+, +23, 24), 578 (M^+, 20), 319 (100), 241 (24), 154 (30); analysis calcd. for $C_{37}H_{38}O_6$: C, 79.14; H, 6.99; found: C, 79.01; H, 6.85. **10a**: IR (neat): 700, 740, 1050, 1450, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.45 (d, $J = 3.2$ Hz, 3H), 0.8–1.02 (m, 8H), 1.20–1.50

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(m, 3H), 1.56–1.72 (m, 2H), 2.10–2.22 (m, 1H), 2.33 (d, $J = 10.2$ Hz, 1H), 3.12 (dt, $J = 3.8$, 10.2 Hz, 1H), 3.80 (s, 3H), 5.48 (s, 1H), 6.82 (d, $J = 9.0$ Hz, 2H), 7.15–7.40 (m, 7H); FABMS: (m/z, %): 352 (M^+, 30), 213 (10), 197 (100), 137 (10), 83 (15), 55 (10); analysis calcd. for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15; found: C, 81.62; H, 9.00. **10b**: IR (neat): 700, 760, 1060, 1450, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 0.45 (dd, $J = 10.3$ Hz, 3H), 0.8–1.02 (m, 8H), 1.20–1.42 (m, 3H), 1.56–1.70 (m, 2H), 2.10–2.25 (m, 1H), 2.30–2.45 (m, 1H), 3.10–3.22 (m, 1H), 5.54 (s, 1H), 7.15–7.42 (m, 10H), 7.45–7.60 (m, 4H); FABMS (m/z, %): 399 (M^+, +1, 10), 243 (100), 154 (10), 83 (14), 55 (12); analysis calcd. for $C_{29}H_{34}O$: C, 87.39; H, 8.60; found: C, 87.23; H, 8.46. **11a**: IR (neat): 680, 740, 1080, 1440, 2980 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.40 (s, 3H), 1.50 (m, 9H), 2.12 (t, $J = 7.0$ Hz, 2H), 3.45 (t, $J = 7.0$ Hz, 2H), 3.78 (s, 3H), 5.25 (s, 1H), 5.38–5.48 (m, 1H), 6.80 (d, $J = 8.5$ Hz, 2H), 7.15–7.40 (m, 7H); FABMS (m/z, %): 362 (M^+, 15), 345 (30), 213 (5), 197 (100), 149 (10), 93 (10), 69 (12); analysis calcd. for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34; found: C, 82.72; H, 8.23. **11b**: IR (neat): 700, 760, 1100, 1500, 2880 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.42 (s, 3H), 1.50 (m, 9H), 2.12 (t, $J = 7.2$ Hz, 2H), 3.44 (t, $J = 7.2$ Hz, 2H), 5.52 (s, 1H), 5.38–5.49 (m, 1H), 7.15–7.42 (m, 10H), 7.46–7.60 (m, 4H); FABMS (m/z, %), 431 (M^+, +23, 12), 259 (8), 243 (100), 105 (10), 91 (14); analysis calcd. for $C_{30}H_{32}O$: C, 88.19; H, 7.89; found: C, 88.00; H, 7.72. **11c**: IR (neat): 720, 760, 1040, 1500, 2900 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.42 (s, 3H), 1.50 (m, 9H), 2.11 (t, $J = 7.0$ Hz, 2H), 3.42 (t, $J = 7.0$ Hz, 2H), 5.36–5.49 (m, 1H), 7.20–7.42 (m, 8H), 7.46–7.62 (m, 11H); FABMS (m/z, %): 482 (10), 319 (100), 243 (16), 89 (64), 77 (60); analysis calcd. for $C_{36}H_{36}O$: C, 89.21; H, 7.49; found: C, 89.13; H, 7.31. **12a**: IR (neat): 700, 750, 1050, 1480, 2880 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.28, 1.43 (2s, 6H), 3.40 (dd, $J = 3.5$, 14.1 Hz, 1H), 3.78 (s, 3H), 3.85 (d, $J = 3.9$ Hz, 2H), 4.15–4.30 (m, 2H), 4.45 (d, $J = 3.7$ Hz, 1H), 5.40 (s, 1H), 5.90 (d, $J = 3.7$ Hz, 1H), 6.80 (d, $J = 9.4$ Hz, 2H), 7.10–7.40 (m, 7H); FABMS (m/z, %): 409 (M^+, +23, 12), 386 (M^+, 25), 259 (70), 243 (100), 154 (65); analysis calcd. for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78; found: C, 68.25; H, 6.68. **12a′**: IR (neat): 680, 740, 1020, 1450, 2900 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.28, 1.45 (2s, 6H), 3.60–3.85 (m, 1H), 3.9 (s, 6H), 4.10 (br.s, 2H), 4.50 (dd, $J = 3.0$, 10.0 Hz, 1H), 5.30 (m, 1H), 5.45 (2s, 2H), 5.88 (m, 1H), 6.10–6.85 (m, 4H), 7.05–7.45 (m, 14H); FABMS (m/z, %): 582 (M^+, 5), 385 (16), 258 (62), 243 (100), 154 (30); analysis calcd. for $C_{36}H_{38}O_7$: C, 74.21; H, 6.57; found: C, 74.12; H, 6.45. **12b**: IR (neat): 700, 780, 1040, 2900, 3100 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.30, 1.42 (2s, 6H), 3.34 (dd, $J = 8.69$ Hz, 1H), 3.92 (d, $J = 4.34$ Hz, 2H), 4.18–4.30 (m, 2H), 4.44 (d, $J = 4.34$ Hz, 1H), 5.50 (s, 1H), 5.92 (d, $J = 4.34$ Hz, 1H), 7.18–7.40 (m, 10H), 7.42–7.60 (m, 4H); FABMS (m/z, %): 455 (M^+, +23, 10), 431 (M^+, −1, 6), 259 (66), 243 (100), 154 (74);

analysis calcd. for $C_{27}H_{28}O_5$: C, 74.98; H, 6.53; found: C, 74.81; H, 6.41. **12c**: IR (neat): 700, 760, 1080, 1500, 2920 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.25 (s, 3H), 1.45 (s, 3H), 3.38–3.64 (m, 2H), 4.20 (s, 2H), 4.44 (d, $J = 5.26$ Hz, 1H), 5.94 (d, $J = 5.26$ Hz, 1H), 7.20–7.40 (m, 8H), 7.46–7.62 (m, 11H); FABMS (m/z, %): 509 (M^+, +1, 12), 319 (100), 259 (6), 91 (10), 55 (18); analysis calcd. for $C_{33}H_{32}O_5$: C, 77.93; H, 6.34; found: C, 77.86; H, 6.28. **13a**: IR (neat): 680, 750, 1040, 1450, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.30, 1.50 (2s, 6H), 2.56–2.70 (br.s, 1H), 3.25 (ddd, $J = 4.7$, 16.4, and 21.1 Hz, 1H), 3.42 (s, 3H), 3.75–3.85 (m, 4H), 4.0–4.20 (m, 2H), 4.52 (d, $J = 4.7$ Hz, 1H), 5.40 (s, 1H), 5.82 (d, $J = 4.7$ Hz, 1H), 6.83 (d, $J = 9.4$ Hz, 2H), 7.15–7.40 (m, 7H); FABMS (m/z, %): 430 (M^+, +23, 10), 393 (10), 197 (100), 165 (10), 147 (15); analysis calcd. for $C_{24}H_{30}O_7$: C, 66.96; H, 7.02; found: C, 66.84; H, 6.91. **14a**: IR (neat): 710, 760, 1060, 1500, 2940 cm^{-1}; ^1H NMR ($CDCl_3$, 200 Mz): δ 1.14 (d, $J = 8.2$ Hz, 3H), 2.10 (br.s, 1H), 2.95–3.22 (m, 2H), 3.90–4.08 (m, 1H), 5.55 (s, 1H), 7.15–7.45 (m, 10H), 7.45–7.60 (m, 4H); FABMS (m/z, %): 318 (M^+, 22), 214 (8), 165 (8), 105 (32), 55 (38); analysis calcd. for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96; found: C, 82.86; H, 6.79. **14b**: IR (neat): 700, 760, 1080, 1500, 2920 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.14 (d, $J = 8.3$ Hz, 3H), 2.10 (br.s, 1H), 2.96–3.22 (m, 2H), 3.90–4.10 (m, 1H), 7.20–7.38 (m, 8H), 7.46–7.62 (m, 11H); FABMS (m/z, %): 394 (M^+, 5), 241 (10), 165 (8), 105 (20), 55 (30); analysis calcd. for $C_{28}H_{26}O_2$: C, 85.25; H, 6.64; found: C, 85.18; H, 6.49. **15a**: IR (neat): 700, 780, 1240, 1750, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.45–1.62 (m, 4H), 1.63–1.90 (m, 6H), 3.35–3.42 (m, 1H), 3.44–3.55 (m, 3H), 3.70–3.88 (m, 2H), 4.58 (s, 1H), 5.38 (s, 1H), 7.15–7.42 (m, 10H), 7.46–7.58 (m, 4H); FABMS (m/z, %): 416 (M^+, 8), 331 (10), 259 (20), 243 (100), 85 (55); analysis calcd. for $C_{28}H_{32}O_3$: C, 80.73; H, 7.74; found: C, 80.61; H, 7.64. **16a**: IR (neat): 760, 840, 1100, 1250, 2940 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.05 (s, 6H), 0.95 (s, 9H), 1.55–1.65 (m, 4H), 3.56–3.70 (m, 4H), 5.40 (s, 1H), 7.14–7.40 (m, 10H), 7.46–7.56 (m, 4H); FABMS (m/z, %): 331 (12), 259 (14), 243 (100), 136 (30), 85 (52); analysis calcd. for $C_{29}H_{38}O_2Si$: C, 77.97; H, 8.57; found: C, 77.84; H, 8.50. **17a**: IR (neat): 700, 1020, 1060, 1480, 2940 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.75 (t, $J = 8.2$, 16.14 Hz, 4H), 2.02 (s, 3H), 3.50 (t, $J = 7.4$, 14.8 Hz, 2H), 4.10 (t, $J = 7.4$, 14.8 Hz, 2H), 5.30 (s, 1H), 7.12–7.40 (m, 10H), 7.45–7.60 (m, 4H); FABMS (m/z, %): 374 (M^+, 6), 259 (14), 243 (100), 154 (14), 136 (24); analysis calcd. for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00; found: C, 80.09; H, 6.86. **17b**: IR (neat): 760, 1240, 1480, 1750, 3000 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.70 (t, $J = 8.0$, 16.0 Hz, 4H), 2.00 (s, 3H), 3.20 (t, $J = 6.0$, 12.0 Hz, 2H), 4.10 (t, $J = 6.0$, 12.0 Hz, 2H), 7.22–7.40 (m, 8H), 7.45–7.65 (m, 11H); FABMS (m/z, %): 450 (M^+, 24), 319 (100), 259 (16), 105 (42), 55 (25); analysis calcd. for $C_{31}H_{30}O_3$: C, 82.64; H, 6.71; found: C, 82.53; H, 6.68.

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