1494, 1452, 1412, 1388, 1364, 1333, 1260, 1097, 1029, 702 cm^{-1}; MS (CI, methane), m/z (relative intensities) 29.0 (72.8), 31.9 (21.3), 40.9 (13.1), 85.1 (6.9), 91.0 (60.3), 92.0 (5.2), 107.0 (3.9), 119.0 (1.7), 131.0 (0.8), 145.0 (0.9), 175.1 (1.1), 181.0 (1.1), 213.1 (0.8) [M + 1]; HRMS (EI, 17 eV), exact mass calcd for $C_{12}H_{17}FO_2$ 212.1208, found 212.1244.

4-(Benzyloxy)-2-fluoro-2-methylbutan-1-ol (3f): 0.69 g (31%); R_f 0.15 (hexanes/ethyl acetate, 3:1); ^1H NMR (90 MHz, $CDCl_3$) δ 1.34 (3 H, d, $J_{H,F}$ = 21.3 Hz, H at C2′), 1.98 (2 H, dt, $J_{H,F}$ = 17.7 Hz, $J_{H,H}$ = 6.0 Hz, H at C3), 2.70 (1 H, s (br), OH), 3.40–3.73 (4 H, m, H at C1 and C4), 4.83 (2 H, H at benzyl C), 7.28 (5 H, s, H at phenyl C's); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.49 (d, $J_{C,F}$ = 23.8 Hz), 36.85 (d, $J_{C,F}$ = 22.4 Hz), 65.80 (d, $J_{C,F}$ = 7.3 Hz), 67.91 (d, $J_{C,F}$ = 27.5 Hz), 73.57, 96.81 (d, $J_{C,F}$ = 168.7 Hz), 128.16, 128.24, 128.89, 138.00; ^{19}F NMR (282 MHz, $CDCl_3$) δ −155.04 (1 F, m (8 lines), $J_{H,F}$ = 19.6 Hz); IR (CCl_4) 3605, 3450, 3080, 3060, 3014, 2972, 2920, 2860, 1494, 1480, 1452, 1377, 1364, 1100, 1062, 1030, 887, 730, 702 cm^{-1}; MS (CI, methane), m/z (relative intensities) 29.0 (5.4), 85.1 (24.4), 91.0 (20.6), 107.0 (2.3), 181.0 (5.9), 193.1 (3.4), 213.1 (23.0) [M + 1]; HRMS (EI, 17 eV), exact mass calcd for $C_{12}H_{17}FO_2$ 212.1208, found 212.1200.

Fluorohydrins from 1-(Benzyloxy)-4,5-epoxypentane (1g). 1-(Benzyloxy)-4,5-epoxypentane (**1g**) (1.50 g, 7.80 mmol) was treated with diisopropylamine trihydrofluoride (3.35 g, 20.80 mmol) at 110 °C for 6 h. Following workup and separation of isomers by flash chromatography (hexanes/ethyl acetate/chloroform, 1:1:1) two colorless oils were obtained.

5-(Benzyloxy)-1-fluoropentan-2-ol (2g): 1.05 (63%); R_f 0.31 (hexanes/ethyl acetate/chloroform, 1:1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 1.43–1.93 (4 H, m, H at C3 and C4), 2.95 (1 H, s (br), OH), 3.53 (2 H, t, $J_{H,H}$ = 5.8 Hz, H at C5), 3.80 (1 H, m, H at C2), 4.29 (1 H, ddd, $J_{H,F}$ = 47.8 Hz, $J_{H,H}$ = 9.3 Hz, $J_{H,H}$ = 6.4 Hz, H at C1), 4.38 (1 H, ddd, $J_{H,F}$ = 47.1 Hz, $J_{H,H}$ = 9.4 Hz, $J_{H,H}$ = 3.7 Hz, H at C1), 4.52 (2 H, s, H at benzyl C), 7.33 (5 H, s, H at phenyl C's); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.92, 29.55 (d, $J_{C,F}$ = 6.4 Hz), 70.09 (d, $J_{C,F}$ = 14.9 Hz), 86.81 (d, $J_{C,F}$ = 169.2 Hz), 127.76, 128.47, 137.97; ^{19}F NMR (282 MHz, $CDCl_3$) δ −230.72 (1 F, td, $J_{H,F}$ = 47.5 Hz, $J_{H,F}$ = 18.1 Hz); IR (CCl_4) 3589, 3410, 3075, 3053, 3020, 2935, 2850, 1489, 1448, 1354, 1266, 1197, 1090, 1021, 903, 784, 727, 692 cm^{-1}; HRMS (EI, 17 eV), exact mass calcd for $C_{12}H_{17}FO_2$ 212.1208, found 212.1210.

5-(Benzyloxy)-2-fluoropentan-1-ol (3g): 0.10 g (6%); R_f 0.25 (hexanes/ethyl acetate/chloroform, 1:1:1); ^1H NMR (90 MHz, $CDCl_3$) δ 1.39–1.95 (4 H, m, H at C3 and C4), 2.30 (1 H, s (br), OH), 3.39–3.62 (2 H, m, H at C5), 3.65 (2 H, dm $J_{H,F}$ = 20.7 Hz, H at C1), 4.47 (2 H, H at benzyl C), 4.52 (1 H, dm, $J_{H,F}$ = 48 Hz, H at C2), 7.29 (5 H, s, H at phenyl C's); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.17 (d, $J_{C,F}$ = 4.6 Hz), 27.78 (d, $J_{C,F}$ = 20.7 Hz), 64.78 (d, $J_{C,F}$ = 22.0 Hz), 69.70, 72.93, 94.45 (d, $J_{C,F}$ = 168.2 Hz), 127.61 127.87, 128.39, 138.32; ^{19}F NMR (282 MHz, $CDCl_3$) δ −192.58 (1 F, m) IR (CCl_4) 3595, 3420, 3075, 3055, 3020, 2935, 2848, 1488, 1436, 1354, 1198, 1090, 1062, 1023, 903, 722, 692 cm^{-1}; HRMS (EI, 17 eV), exact mass calcd for $C_{12}H_{17}FO_2$ 212.1208, found 212.1197.

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Registry No. **1a**, 2930-05-4; *trans*-**1b**, 80374-37-4; *cis*-**1b**, 80374-36-3; **1c**, 71312-15-7; **1d**, 112482-34-5; **1e**, 94426-72-9; **1f**, 107127-75-3; **1g**, 112482-35-6; **2a**, 112482-36-7; **2b**, 112482-38-9; **2c**, 112482-40-3; **2d**, 112482-42-5; **2e**, 112482-44-7; **2f**, 112482-47-0; **2g**, 112482-49-2; **3a**, 112482-37-8; **3b**, 112482-39-0; **3c**, 112482-41-4; **3d**, 112482-43-6; **3e**, 112482-45-8; **3f**, 112482-48-1; **3g**, 112482-50-5; $((H_3C)_2CH)_2NH{\cdot}3HF$, 112482-51-6; $H_2C{=}CHCH_2OBn$, 14593-43-2; (*E*)-$BnOCH_2CH{=}CHCH_3$, 27299-30-5; (*Z*)-$BnOCH_2CH{=}CHCH_3$, 27299-31-6; $H_3CC(CH_3){=}CHCH_2OBn$, 22089-60-7; $H_2C{=}CHC(CH_3)_2OBn$, 112482-46-9; $H_2C{=}CH(CH_2)_2OBn$, 70388-33-9; $H_2C{=}C(CH_3)(CH_2)_2OBn$, 58558-53-5; $H_2C{=}CH(CH_2)_3OBn$, 81518-74-3; $((H_3C)_2CH)_2NH$, 108-18-9.

p,p′-Dinitrobenzhydryl Ethers, Acid and Base Stable Protecting Groups, Which Are Readily Removable in the Presence of Benzyl and Monomethoxytrityl Functions

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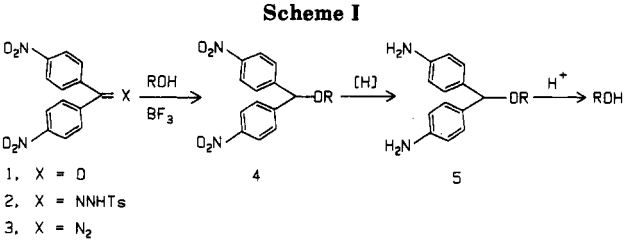
BF_3-catalyzed reaction of alcohols with bis(*p*-nitrophenyl)diazomethane gave the corresponding DNB ethers, from which blocking groups were selectively removed by catalytic hydrogenation using platinum or nickel boride or by chemical reduction, followed by mild acid hydrolysis (e.g., pH 4).

In connection with the synthesis of goniothalenol,[1] we required a protecting group that would survive strongly acidic (HCOOH, $ZnCl_2$/EtSH) and basic (PhMgBr) conditions, yet would be removable in the presence of a secondary benzyl group. As it happened, the protecting group we report on can also be removed in the presence of a monomethoxytrityl ether, which may make it useful as a carbohydrate or nucleotide protecting group.

Benzyl or benzhydryl ethers fulfill the stability conditions listed. It occurred to us that a *p,p′*-dinitrobenzhydryl (DNB) ether should be equally stable, yet be transformed by chemical or catalytic reduction to a very acid-labile diaminobenzhydryl ether (**4** to **5**, Scheme I).

Scheme I



Results and Discussion

Since the reaction of a sodium alkoxide with the known *p,p′*-dinitrobenzhydryl chloride[2] did not proceed in a

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Table I. Results from the Cleavage of DNB Ethers

entry	substrates (DNBOR)	reagents	solvents	products[a] (ROH)	yields,[b] %
1	**6a**	H_2/PtO_2	MeOH–THF	**6**	89
2	**7a**	H_2/Ni_2B[c]	MeOH–THF	**7**	81
3	**8a**	$Fe_3(CO)_{12}$[d]	toluene	**8**	85
4	**11**	H_2/PtO_2	MeOH–THF	**11a**	84
5	**12a**	H_2/PtO_2	MeOH–THF	**12**	82
6	**13a**	H_2/PtO_2	MeOH–H_2O	**13**[e]	84
7	**14a**	H_2/PtO_2	MeOH–H_2O	**14b**	85
8	**15a**	H_2/PtO_2	THF–MeOH–H_2O	**15**	90

[a] All products were identified by comparison with authentic samples. [b] Isolated yields. [c] Generated from $NaBH_4$ and $Ni(OAc)_2$. [d] Reaction was carried out under argon with 1.5 equiv of $Fe_3(CO)_{12}$ and 5 equiv of $PhEt_3NOH$ (40% in MeOH) at room temperature for 2 h, and then, after extractive workup, the mixture was acidified with silica gel. [e] Obtained directly after hydrogenation.

Table II. Various Conditions[a] for Acid Hydrolysis of p,p'-Diaminobenzhydryl Cholestanyl[b] Ether to Cholestanol 6

reagents	pH 2	pH 3	pH 4	pH 5	HCl[c]	TFA[d]	AcOH[e]	resin[f]
$t_{1/2}$, h[g]	4	7	10	n/r	0.5	<0.1	3	3

[a] All reactions were carried out in MeOH–THF (1:1 v/v) with same amount of starting material. [b] Obtained from DNB ether **6a** after hydrogenation (H_2/PtO_2) in MeOH–THF (1:1 v/v). [c] 0.03 M HCl. [d] 0.05% trifluoroacetic acid (TFA). [e] 0.05% AcOH. [f] Amberlite resin IRC-50 (H) from BDH. [g] Monitored by TLC, half life ($t_{1/2}$) was obtained approximately from reaction time required for completion.

satisfactory manner, perhaps because of the acidity of the α-hydrogen, we investigated the usefulness of bis(*p*-nitrophenyl)diazomethane (**3**) as a protecting agent. It was synthesized as a red solid from reaction of sodium hydroxide with *p,p'*-dinitrobenzophenone tosylhydrazone (**2**)[3] (Scheme I) and found to be stable over months at room temperature when kept in the dark under nitrogen.

The conversion of an alcohol to its DNB ether was best carried out by mixing 1 equiv of alcohol in methylene chloride with 1.2–1.5 equiv of bis(*p*-nitrophenyl)diazomethane (**3**) at temperatures ranging from −20 to 25 °C, followed by 0.5–1.05 equiv of $BF_3{\cdot}Et_2O$. The reaction was usually complete in a few hours. Thus, the DNB ethers of cholestanol (**6**), cholesterol (**7**), nonynol (**8**), and lactone **9** were prepared in 91–96% isolated yield. Interestingly, the protection of the 3-OH of 1,2:5,6-di-*O*-isopropylidene-D-glucose (**10**) did not proceed in the expected way. Instead $BF_3{\cdot}Et_2O$-catalyzed rearrangement of the isopropylidene group at O-5,6 to O-3,5 followed by etherification at O-6 occurred cleanly in good yield. Thus, only the ether **11** was isolated in 94% yield by quenching the reaction with dry triethylamine. If quenching was carried with water or dilute sodium bicarbonate solution, the diol **10a** was obtained in 89% yield. Similarly, treatment of the DNB ether **11** with 70% acetic acid at 40 °C gave the diol **10a**, which was characterized by its diacetate derivative; the ^1H NMR spectrum showed the typical downfield shifts for only C_3-H (5.36 ppm, d) and C_5-H (5.21 ppm, m). In order to test the selectivity of the reagent for primary versus secondary alcohols, the easily obtained 3-*O*-*tert*-butyldiphenylsilyl derivative of the monoisopropylideneglucose **12**[4] was treated with the reagent **3**. Only the ether **12a**, obtained from monoderivatization of the primary alcohol, was formed in 82% yield. 2,3,4-Tri-*O*-benzyl-D-ribose diethyl dithioacetal (**13**)[5] was transformed to its DNB ether **13a** in 97% yield. Hydrolysis of the dithioacetal function ($HgCl_2/CdCO_3$) and reduction of the resulting aldehyde with sodium borohydride gave the D-ribitol **14** in 84% yield. It was converted by standard methods[6] to its monomethoxytrityl ether **14a**. Finally, the etherification of the tertiary alcohol of 1-adamantanol (**15**) in moderate yield (80%) is notable (Chart I).

DNB ethers, similar to benzyl and nitrobenzyl ethers, are stable under a wide variety of conditions including strong base, strong acid, organometallic reagents, oxidizing agents, and some reducing agents (e.g., $NaBH_4$). Selective cleavage of DNB ether is possible in the presence of acetals, thioacetals, ketals, esters as well as allyl, benzyl, THP, MEM, MTM, silyl, and trityl ethers. Conversely, most of these protecting units may be selectively removed in the presence of a DNB ether. The cleavage of DNB ethers to form the corresponding alcohols is best effected in most cases by catalytic hydrogenation (H_2/PtO_2) of the ethers in aqueous methanol with or without other cosolvent (e.g., THF) at 25 °C under ambient pressure for a few hours. The resulting intermediate diaminobenzhydryl ethers were then hydrolyzed by treatment with mild acid, such as a pH 3 or pH 4 buffer solution. Thus, the DNB ethers **6a**, **11**, **12a**, **13a**, **14a**, and **15a** were cleaved to give the corresponding alcohols **6**, **11a**, **12**, **13**, **14b**,[5] and **15** in good yields (Table I). It is possible to cleave the DNB ethers having alkenyl or alkynyl functionalities such as **7a** and **8a** by using a different catalyst or a chemical reduction. Thus, the ether **7a** was cleaved by nickel boride [$Ni(OAc)_2/NaBH_4$]-catalyzed hydrogenation[7] followed by mild acid hydrolysis (Table I, entry 2). The ether **8a** was cleaved with $Fe_3(CO)_{12}$[8] in toluene–methanol, followed by treatment with silica gel to afford the alcohol **8** (Table I, entry 3).

In order to study of the stability of the intermediate, diaminobenzhydryl ether, toward acid hydrolysis, various conditions for hydrolysis of *p,p'*-diaminobenzhydryl cholestanyl ether, obtained after hydrogenation of the DNB ether **6a** in neutral medium, were tested (Table II). It was found to be stable at pH 5 but rapidly hydrolyzed in 0.05% trifluoroacetic acid or 0.03 M hydrogen chloride solution. Acidic resin and 0.05% acetic acid or pH 4 buffer solution provided moderate acidic media, and the hydrolysis reaction was over in about 6–8 h at room temperature. A very mild condition was found to be a pH 3 and pH 4 buffer, in which the intermediate was hydrolyzed smoothly

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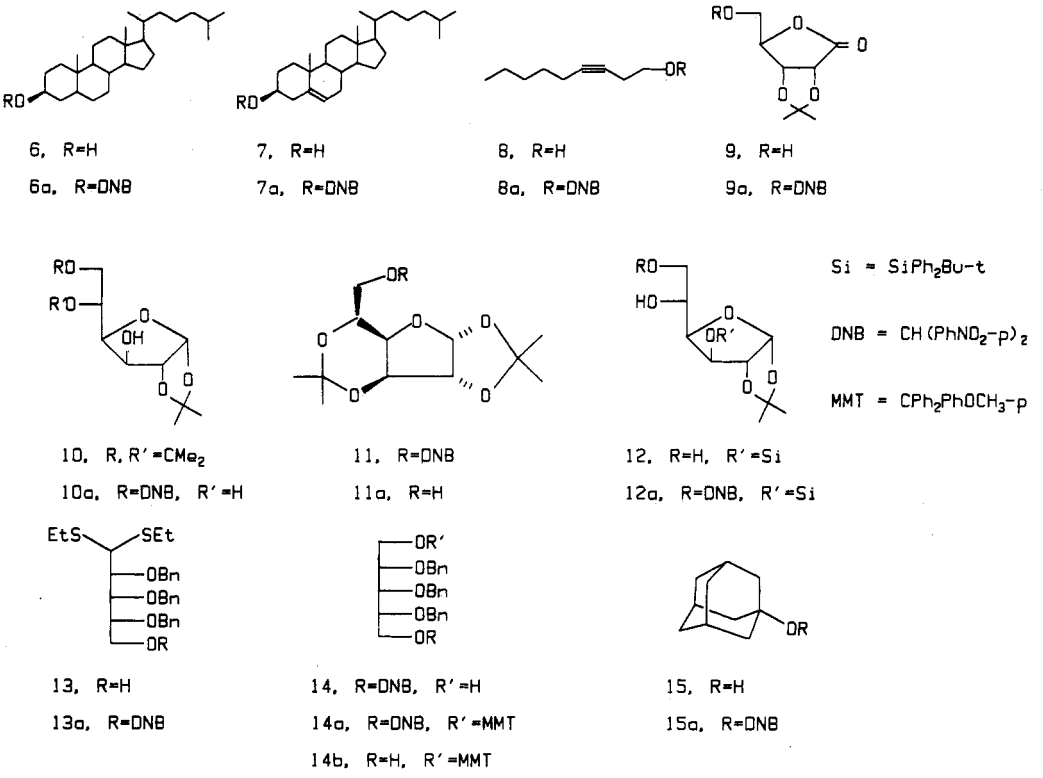
Chart I



to the alcohol and most other acid-labile groups, such as monomethoxytrityl unit, were not cleaved.

In conclusion, DNB ether has similar stabilities as benzyl or nitrobenzyl ether and can be selectively cleaved in the presence of many other protecting groups.

Experimental Section

General Methods. Melting points (mp) were measured on a Gallenkamp block and are uncorrected. Thin-layer chromatography (TLC) was performed on Merck silica gel $60F_{254}$ aluminum-backed plates. Flash chromatography was done on silica gel 60 (32–63 nm) from BDH. Infrared (IR) spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained in chloroform-*d* solution at 200 MHz on a Varian XL-200 FT NMR spectrometer; the 7.24 ppm resonance of residual chloroform in $CDCl_3$ was used as internal reference and chemical shifts are reported in δ units downfield from tetramethylsilane. The followed abbreviations are used to describe peak patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Low- and high-resolution mass spectra (MS and HRMS) were obtained on HP 5984A or LKB 9000 spectrometers.

Methylene chloride was distilled from phosphorus pentoxide immediately prior to use. pH buffer solutions were prepared from hydrion buffers (Aldrich).

***p,p'*-Dinitrobenzophenone Tosylhydrazone (2).** A solution of bis(*p,p'*-dinitrobenzophenone) (1; 185 g, 0.68 mol) and *p*-toluenesulfonohydrazide (190 g, 1.02 mol) in THF–ethanol (1:1 v/v, 2 L) was refluxed for 18 h. The solvents were then removed at reduced pressure, the residue was filtered, and yellow solids were collected on the filter funnel. After the residue was washed with ethanol several times, the tosylhydrazone 3 was obtained as pale yellow powder (262 g, 88%). Recrystallization of an analytical sample from toluene gave pale yellow crystals: mp 179–180 °C; IR (CH_2Cl_2, cm^{-1}) 1600, 1525, 1340, 1160; ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 3 H, CH_3), 7.38, 7.41, 7.56, 7.86, 8.17 and 8.43 (d, 12 H, Ar H), 7.70 (s, 1 H, NH); MS (DCI, NH_3), *m/e* (relative intensity) 441 (M + H^+, 29.3), 257 (M + H^+ – NNHTs, 100).

Bis(*p*-nitrophenyl)diazomethane (3). A suspension of the tosylhydrazone 2 (3.0 g, 6.8 mmol) in 1 M sodium hydroxide (100 mL) was vigorously stirred at 75 °C for 3 h. After being cooled to room temperature, the resulting dark orange suspension solution was extracted with methylene chloride (3 × 100 mL). The extracts were then washed with saturated sodium chloride solution (3 × 50 mL) and dried over anhydrous sodium sulfate. After removal of solvent at reduced pressure, the desired diazo compound 3 was obtained as a dark orange solid: 1.85 g (98%); mp 137–138 °C (dec, benzene); IR (CH_2Cl_2, cm^{-1}) 2040, 1525; ^{1}H NMR ($CDCl_3$) δ 7.43 (d, 4 H, J = 9.3 Hz, $C_{2',6'}$-H), 8.29 (d, 4 H, J = 9.3 Hz, $C_{3',5'}$-H).

General Procedure for the Preparation of DNB Ether. To a 0.01 M solution of the alcohol (6; 0.20 g, 0.52 mmol) and diazo agent 3 (0.25 g, 0.88 mmol) in methylene chloride, under nitrogen at –20 °C, was added 0.5–2.0 equiv of freshly distilled BF_3·Et_2O (0.13 mL, 1.0 mmol) dropwise. The reaction mixture was stirred at –20 °C for a few hours and saturated sodium bicarbonate solution (25 mL) was added. After being warmed to room temperature, the mixture was partitioned, and the aqueous phase was extracted with methylene chloride (2 × 50 mL). The combined organic phases were washed with saturated sodium chloride solution (2 × 50 mL) and dried over anhydrous sodium sulfate. After removal of solvent at reduced pressure, the orange residue was purified by flash chromatography (15% ether in hexanes) to give the desired DNB ether (**6a**; 0.33 g, 98%).

DNB ether 6a: white crystals (98%); mp 118–120 °C; ^{1}H NMR ($CDCl_3$) δ 0.50–2.00 (br m, 46 H), 3.30 (m, 1 H, C_3-H), 5.69 [s, 1 H, $CH(PhNO_2)_2$], 7.51 (d, 4 H, J = 8.6 Hz, $C_{2',6'}$-H), 8.19 (d, 4 H, J = 8.6 Hz, $C_{3',5'}$-H); MS (Cl, NH_3), *m/e* (relative intensity) 662 (M + NH_4^+, 1.6), 644 ($M^{\cdot+}$, 13.7).

DNB ether 7a: white crystals (95%); mp 158–159 °C; ^{1}H NMR ($CDCl_3$) δ 0.63–2.06 (br m, 41 H), 2.31–2.40 (m, 2 H, C_4-H), 3.25 (m, 1 H, C_3-H), 5.31 (br d, 1 H, C_6-H), 5.70 [s, 1 H, $CH(PhNO_2)_2$], 7.53 (d, 4 H, J = 8.8 Hz, $C_{2',6'}$-H on $PhNO_2$), 8.20 (d, 4 H, J = 8.8 Hz, $C_{3',5'}$-H on $PhNO_2$); MS (Cl, NH_3), *m/e* (relative intensity) 369 [$M^{\cdot+}$ – $OCH(PhNO_2)_2$, 100]; HRMS (Cl, NH_3, *m/z*) for $C_{40}H_{54}N_2O_5$ ($M^{\cdot+}$) calcd 642.4033, found 642.4032.

DNB ether 8a: oil (91%); ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 3 H, C_9-H), 1.20–1.48 (m, 6 H, C_6–$_8$-H), 2.08 (m, 2 H, C_5-H), 2.47 (m, 2 H, C_2-H), 3.52 (t, 2 H, C_1-H), 5.52 [s, 1 H, $CH(PhNO_2)_2$], 8.14 (d, 4 H, J = 9.2 Hz, $C_{2',6'}$-H on $PhNO_2$), 8.14 (d, 4 H, J = 9.2 Hz, $C_{3',5'}$-H on $PhNO_2$); MS (Cl, NH_3), *m/e* (relative intensity) 414 (M + NH_4^+, 100), 396 ($M^{\cdot+}$, 22.9); HRMS (Cl, NH_3, *m/z*) for $C_{22}H_{28}N_3O_5$ (M + NH_4^+) calcd 414.2030, found 414.2030.

DNB ether 9a: yellow foam (90%); ^{1}H NMR ($CDCl_3$) δ 1.39 and 1.49 (2 s, 6 H, CMe_2), 3.78 (t, 2 H, C_5-H), 4.71 (t, 1 H, C_4-H), 4.77 (s, 2 H, $C_{2,3}$-H), 5.57 [s, 1 H, $CH(PhNO_2$-*p*$)_2$], 7.45 (m, 4 H,

$C_{2',6'}$-H on $PhNO_2$), 8.24 (m, 4 H, $C_{3',5'}$-H on $PhNO_2$); MS (Cl, NH_3), m/e (relative intensity) 462 ($M + NH_4^+$, 100); HRMS (Cl, NH_3, m/z) for $C_{21}H_{21}N_2O_9$ ($M + H^+$) calcd 445.1247, found 445.1248.

DNB ether 10a: oil (89%); ^1H NMR ($CDCl_3$–D_2O) δ 1.31 and 1.46 [2 s, 6 H, $C(CH_3)_2$], 3.67 (dd, 1 H, $J_{6,6'}$ = 10 Hz, $J_{6,5}$ = 5.4 Hz, $C_{6'}$-H), 3.78 (dd, 1 H, $J_{6,6'}$ = 10 Hz, $J_{6',5}$ = 3.2 Hz, C_6-H), 4.20–4.28 (m, 1 H, C_5-H), 4.34 (d, 1 H, J = 2.6 Hz, C_3-H), 4.52 (d, 1 H, J = 3.4 Hz, C_2-H), 5.62 [s, 1 H, $CH(PhNO_2)_2$], 5.93 (d, 1 H, J = 3.4 Hz, C_1-H), 7.53 (d, 4 H, J = 8.2 Hz, $C_{2,6}$-H on $PhNO_2$), 8.21 (d, 4 H, J = 8.2 Hz, $C_{3,5}$-H on $PhNO_2$); MS (Cl, NH_3), m/e (relative intensity), 494 ($M + NH_4^+$, 16.1), 476 ($M^{\bullet+}$, 3.2); HRMS (Cl, NH_3, m/z) for $C_{22}H_{25}N_2O_{10}$ ($M + H^+$) calcd 477.1510, found 477.1509.

DNB ether 11: oil (94%); ^1H NMR ($CDCl_3$) δ 1.31–1.44 [4 s, 12 H, 2 $C(CH_3)_2$], 3.63–3.68 (m, 2 H, $C_{6,6'}$-H), 3.75–3.80 (m, 1 H, C_5-H), 4.21 (d, 1 H, J = 3.8 Hz, C_3-H), 4.27 (dd, 1 H, C_4-H), 4.65 (d, 1 H, J = 3.9 Hz, C_2-H), 5.61 [s, 1 H, $CH(PhNO_2)_2$], 5.98 (d, 1 H, J = 3.4 Hz, C_1-H), 7.51 (d, 4 H, J = 8.1 Hz, $C_{2,6}$-H on $PhNO_2$), 8.21 (d, 4 H, J = 8.1 Hz, $C_{3,5}$-H) on $PhNO_2$); MS (Cl, NH_3), m/e (relative intensity) 534 ($M + NH_4^+$, 14.5), 5.17 ($M + H^+$, 43.2), 476 ($M + NH_4^+ - 58$, 100); HRMS (Cl, NH_3, m/z) for $C_{25}H_{28}N_2O_{10}$ ($M + H^+$) calcd 517.1822, found 517.1821.

DNB ether 12a: oil (82%); ^1H NMR ($CDCl_3$) δ 1.09 [s, 9 H, $C(CH_3)_3$], 1.14 and 1.37 [2 s, 6 H, $C(CH_3)_2$], 1.95 (br s, 1 H, OH), 3.67 (dd, 1 H, $J_{6,6'}$ = 9.8 Hz, $J_{6,5}$ = 4.4 Hz, C_6-H), 3.79 (dd, 1 H, $J_{6',6}$ = 9.8 Hz, $J_{6',5}$ = 1.8 Hz, $C_{6'}$-H), 4.09–4.15 (m, 2 H, $C_{4,5}$-H), 4.26 (d, 1 H, J = 3.8 Hz, C_2-H), 4.50 (d, 1 H, J = 1.8 Hz, C_3-H), 5.61 [s, 1 H, $CH(PhNO_2)_2$], 5.83 (d, 1 H, J = o.8 Hz, C_1-H), 7.40–8.35 (m, 14 H, Ar H); HRMS (Cl, NH_3, m/z) for $C_{38}H_{43}N_2O_{10}Si$ ($M + H^+$) calcd 715.2689, found 715.2689.

DNB ether 13a: oil (97%); ^1H NMR ($CDCl_3$) δ 1.15 and 1.17 (2 t, 6 H, SCH_2CH_3), 2.63 and 2.65 (2 q, 4 H, SCH_2CH_3), 3.62 (d, 2 H, C_5-H), 3.96 (dd, 1 H, C_2-H), 4.15 (m, 2 H, $C_{3,4}$-H), 4.21 (d, 1 H, C_1-H), 4.54–4.95 (m, 6 H, CH_2Ph), 5.87 [s, 1 H, $CH(PhNO_2)_2$], 7.22–7.40 (m, 19 H, Ar H), 8.07 (m, 4 H, $C_{3',5'}$-H on $PhNO_2$); MS (DCI, NH_3), m/e (relative intensity) 721 ($M^{\bullet+}$ – SEt, 0.42); HRMS (DCI, NH_3, m/z) for $C_{43}H_{46}N_2O_8S_2$ ($M^{\bullet+}$ – SEt) calcd 721.2584, found 721.2586.

DNB ether 15a: white crystals (80%); mp 155.5–156.5 °C; ^1H NMR ($CDCl_3$) δ 1.60 (br s, 6 H), 1.75 (br s, 6 H), 2.12 (br s, 3 H), 5.88 [s, 1 H, $CH(PhNO_2)_2$], 7.53 (d, 4 H, J = 8.8 Hz, $C_{2',6'}$-H on $PhNO_2$), 8.16 (d, 4 H, J = 8.8 Hz, $C_{3',5'}$-H on $PhNO_2$); MS (Cl, NH_3), m/e (relative intensity) 426 ($M + NH_4^+$, 20.1), 408 ($M^{\bullet+}$, 6.6), 135 [$M^{\bullet+}$ – $OCH(PhNO_2)_2$, 100]; HRMS (Cl, NH_3, m/z) for $C_{23}H_{28}N_3O_5$ ($M + NH_4^+$) calcd 426.2029, found 426.2028.

General Procedure for the Deprotection of DNB Ether by Pt-Catalytic Hydrogenation. A suspension of PtO_2 (7 mg, 15% wt) in ethanol (5 mL) was stirred under a hydrogen atmosphere until gas uptake was complete. The DNB ether (44 mg, 0.07 mmol; **6a**) in THF (2 mL) was then added. After the required amount of hydrogen has been absorbed (about 2 h), the reaction mixture was filtered through Celite. The filtrate was stirred with a pH 3 (or pH 4) buffer solution, and the reaction was monitored by TLC (about 8 h). After the completion of hydrolysis, the solvents were then evaporated at reduced pressure to dryness, and the residue was taken up in ether (100 mL). The ethereal solution was washed with dilute HCl solution (e.g., 5%) and saturated sodium chloride solution and dried over anhydrous sodium sulfate. Removal of solvent in vacuo and chromatography of the residue afforded the desired alcohol (**6**; 23 mg, 89%).

Alcohol 11a: oil (84%); ^1H NMR ($CDCl_3$–D_2O) δ 1.30–1.47 [3 s, 12 H, 2 $C(CH_3)_2$], 3.62–3.70 (m, 2 H, $C_{6,6'}$-H), 3.76–3.83 (m, 1 H, C_5–H), 4.17 (d, 1 H, J = 3.7 Hz, C_3-H), 4.35 (dd, 1 H, J = 3.8 Hz, J = 6.7 Hz, C_2-H), 5.98 (d, 1 H, J = 3.8 Hz, C_1-H); MS (Cl, NH_3), m/e (relative intensity) 261 ($M + H^+$, 12.5); HRMS (Cl, NH_3, m/z) for $C_{12}H_{21}O_6$ ($M + H^+$) calcd 261.1338, found 261.1338.

Deprotection of the DNB Ether 8a with $Fe_3(CO)_{12}$. To a solution of the DNB ether **8a** (70 mg, 0.18 mmol) in toluene (5 mL), at room temperature under argon, was added benzyltrimethylammonium hydroxide (40% in methanol, 5 equiv, 369 mg), followed by $Fe_3(CO)_{12}$ (2 equiv, 178 mg). The resulting dark brown solution was stirred for 2 h. The reaction mixture was then diluted with methylene chloride (50 mL) and water (50 mL) and carefully acidified with dilute HCl solution (0.5 N) to pH 7. The mixture was partitioned, and the aqueous phase was extracted with methylene chloride (50 mL) once. The combined organic phase was dried over anhydrous sodium sulfate and filtered through a pad of silica gel (30 g, silica gel 60 from BDH), washed with 25% ethyl acetate in hexanes. The filtrate was concentrated in vacuo to an oil. It was then purified by flash chromatography (20% ethyl acetate in hexanes) to afford the alcohol **8** (21 mg) in 85% yield.

Deprotection of the DNB Ether 7a by Nickel Boride Catalytic Hydrogenation. The catalyst was prepared by mixing a solution of sodium borohydride (75 mg, 1.97 mmol) in ethanol (2 mL) to a suspension solution of $Ni(OAc)_2 \cdot 4H_2O$ (2.18 mmol) in EtOH-THF (1:1 v/v, 15 mL) under a hydrogen atmosphere (1 atm). After evolution of hydrogen was complete, a solution of the DNB ether **7a** (400 mg, 0.62 mmol) in THF (1 mL) was added. After completion of reaction (8 h), 5 mL of pH 3 buffer solution was added and stirring was continued for 3 h. The mixture was then filtered through Celite and washed with ether. The filtrate was concentrated at reduced pressure, and the residue was then dissolved in methylene chloride (50 mL). It was washed with 5% HCl (25 mL) and brine (25 mL) and dried over anhydrous sodium sulfate. After removal of solvent in vacuo and recrystallization of the solid residue, the alcohol **7** (195 mg) was obtained in 81% yield.

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