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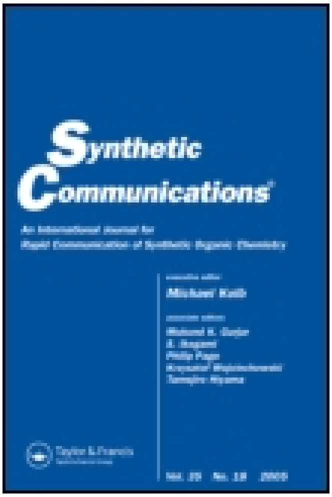

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Dowex 50WX4-100: An Efficient Catalyst for the Tetrahydropyranylation of Alcohols

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Dowex 50WX4–100: An Efficient Catalyst for the Tetrahydropyranylation of Alcohols

P. S. Poon,[1] Ajoy K. Banerjee,[1] Liadis Bedoya,[1] Manuel S. Laya,[1] Elvia V. Cabrera,[2] and Karla M. Albornoz[2]
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Abstract: The ion-exchange resin Dowex 50WX4–100 has been found to catalyze efficiently the protection reaction of a variety of alcohols with 2,3-dihydro-4H pyran (DHP) and dichloromethane at ambient conditions.

Keywords: Alcohols, reduction, tetrahydropyranylation, tetralones

INTRODUCTION

The protection of alcoholic hydroxyl groups has found application especially in the synthesis of natural products related to terpenes, steroids, sugars, and glycerids. Tetrahydropyranylation is one of the frequently used methods for the protection of alcohols and phenols because of the remarkable stability towards a variety of conditions such as reactions involving Grignard reagents and lithium alkyl and reduction with hydrides, alkylating, and acylating agents.[1,2] A variety of reagents have been developed for tetrahydropyranylation of alcohols and phenols, which include mainly protic acids,[3] Lewis acids,[4] heterogeneous catalyst,[5] and others.[6] The use of ion-exchange resins in organic synthesis has been reviewed by Gelbard.[7] Amberlyst H-15, a macroreticular

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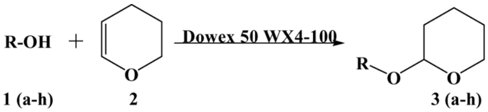
ion-exchange resin;[8] Dowex 50WX2 50–100 mesh, a strongly acidic ion-exchange resin;[9] Nafion-H, a polymeric perfluorinated resin sulfonic acid;[10] and others are notable applications for tetrahydropyranylation of alcohols. To our knowledge, no one has yet tried tetrahydropyranylation of alcohols with ion-exchange resin Dowex 50WX4–100. In this communication, we report for the first time its usefulness in the protection of alcohols as tetrahydropyranyl ethers.

RESULTS AND DISCUSSION

When a mixture of an alcohol **1** and 3,4-dihydropyran **2** in dry methylene chloride was stirred under nitrogen with a catalytic amount of activated[11] Dowex 50WX4–100 (see the Experimental Section), corresponding tetrahydropyranyl ether **3** was isolated after filtration and chromatography (Scheme 1).

The experimental procedure is quite simple, and a wide range of alcohols (**1a–h**) including primary, secondary, and cyclic alcohols underwent smooth tetrahydropyranylation in good yield (Table 1). As can be seen from Table 1, the Dowex 50WX4–100 efficiently catalyzed the protection of a variety of alcohols. It is remarkable to observe that the alcohols (entries **1a–j**) underwent protection with 2,4-dihydro-4H-pyran (DHP), producing corresponding ethers in good yield without undergoing dehydration. Tetrahydropyranylation of alcohols **1i** and **1j** was accomplished satisfactorily only after stirring for 24 h with Dowex 50WX4–100 at room temperature. The sterically hindered alcohols (e.g., triphenylmethanol) proved resistant to tetrahydropyranylation with this reagent. In addition, it has been found to be an excellent catalyst for the protection of phenolic hydroxyl group with DHP in good yield.

In conclusion, we have shown that Dowex 50WX4–100 is an excellent catalyst for the protection of a variety of alcohols. To the best of our knowledge, some of alcohols selected for tetrahydropyranylation by Dowex 50WX4–100 were not examined earlier with other catalysts. We believe that the present method for tetrahydropyranylation would constitute an important additional approach for the protection of alcohols with DHP in good yield.



Scheme 1. Tetrahydropyranylation of alcohols catalyzed by Dowex 50WX4-100.

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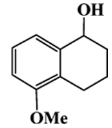
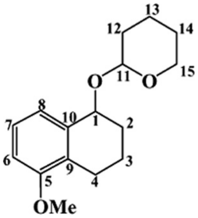
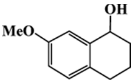
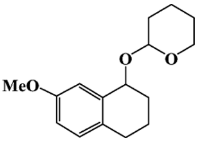
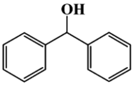
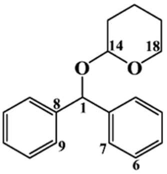
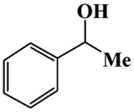
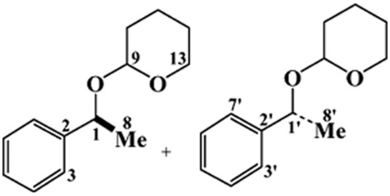
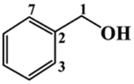
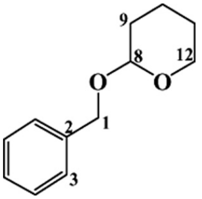
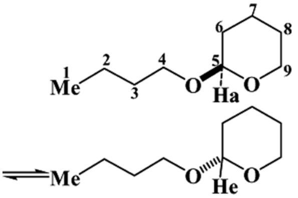
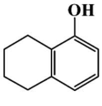
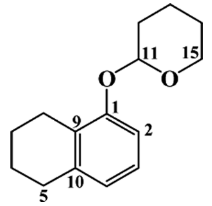
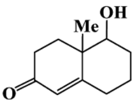
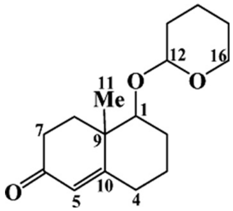
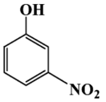
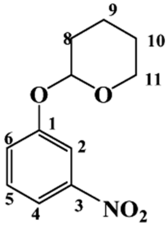
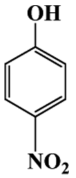
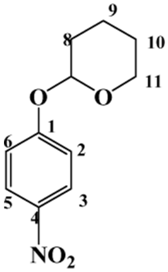
Table 1. Protection of alcohols with DHP (2) catalyzed by Dowex 50WX4–100

Entry	Alcohol (1)	THP ether (3)	Yield (%)	Time (min)
a			97	15
b			95	10
c			90	30
d			95	10
e			98	7
f	Me(CH$_2$)$_3$OH		94	1

(*Continued*)

Table 1. Continued

Entry	Alcohol (1)	THP ether (3)	Yield (%)	Time (min)
g			90	5
h			88	15
I			75	1440
J			75	1440

EXPERIMENTAL

Unless otherwise stated, infrared (IR) spectra were taken on a Nicolet Fourier transform (FT) instrument, and NMR spectra recorded on a Bruker AM-300 spectrometer in $CDCl_3$. Mass spectra (MS) were determined on a Dupont 21–492B. Column chromatography was carried out on silica gel 60 (Merck). Thin-layer chromatographic (TLC) plates were

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coated with silica gel, and the spots were located by exposure to ultraviolet (UV) light.

Preparation of Activated Ion-Exchange Resin

The Dowex 50WX4–100 (10 g) (Aldrich) was put in a chromatography column and washed with 2 L hydrochloric acid (6 M HCl). The excess acid was washed from the column with distilled water until the washings showed no reaction with silver nitrate, and then it was washed with methanol. The washed resin was dried in a furnace at 60°C.

Preparation of Alcohols from Ketones

A suspension of sodium borohydride ($NaBH_4$) was added to the commercially available ketones (5-methoxy, 7-methoxy α-tetralone, Wieland–Miescher ketone, benzophenone, and acetophenone) dissolved in ethanol (analytic grade) and stirred for 1–2 h at room temperature. After acidification with acetic acid, the product was extracted with dichoromethane, and the extract was washed, dried over $MgSO_4$, and evaporated to obtain the alcohols (**1a–f**). Acetophenone on reduction afforded a mixture of alcohols (**1d**). The benzyl alcohol (**1e**) and n-butano (**1f**) are commercially available. Tetrahydonaphthol (**1g**) was obtained by catalytic hydrogenation of the α-naphthol. The alcohol (**1h**) was prepared by the published procedure.[12] The term H_a and H_e indicate that hydrogen is axial and equatorial respectively.

Procedure for Tetrahydropyranylation

A mixture of alcohol (**1a–h**) (10 mmol), 3,4-dihydropyran **2** (11 mmol), Dowex 50WX4–100 (0.5 mmol), and dichloromethane (20 ml) was stirred at room temperature, and the progress of the reaction was monitored by TLC. After completion, the reaction mixture was filtered off, and the residue was washed with methylene chloride. The filtrate was concentrated, and the residue was purified over a column of silica gel (eluant hexane–ether 9:1) to obtain the tetrahydropyranyl ethers (**3a–j**) (Table 1).

Data

Compound **3a**

IR ν_{max} (cm^{-1}): 3069, 2939, 1586, 1471, 1439, 1339, 1255, 1201; MS (m/z): 262 (M^+) (3%), 162 $(M^+ - C_5H_9O_2)^+$ (100%), 85 (C_5H_9O)

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(10%), ^{1}H $\delta_{(ppm)}$: 1.58–2.07 (m, 10H), (2 × CH_2 at C-2, C-3, C-12, C-13, C-14), 2.45–2.65 (m, 1H_e), 2.70–2.90 (m, 1H_a) (CH_2 at C-4), 3.55–3.68 (m, 1H_a), 3.97–4.15 (m, 1H_e) (CH_2 at C-15), 3.83 (s, 3H, 0Me), 4.73 (dd, $J = 5.6$ Hz, $J = 4.05$ Hz) (1H at C-1), 4.89 (dd, 1H, $J = 3.26$) (1H at C-11), 6.77 (dd, 1H, $J = 8.09$ Hz, $J = 1.55$ Hz) (1H at C-6), 6.94 (d, 1H, $J = 7.67$ Hz) (1H at C-8), 7.12–7.31 (m, 1H) (1H at C-7); ^{13}C $\delta_{(ppm)}$: 157.17 (C-5), 137.90 (C-9), 126.57 (C-10), 125.78 (C-7), 121.23 (C-8), 108.65 (C-6), 98.84 (C-11), 73.66 (C-1), 62.60 (C-15), 55.23 (C-11), 31.08 (C-13), 30.12 (C-2), 25.60 (C-15), 22.75 (C-4), 19.82 (C-14), 18.17 (C-3).

Compound **3b**

IR ν_{max} (cm^{-1}): 2939, 2868, 1460, 1260, 1233; MS(m/z) 162 ($(M^+ - C_5H_9O_2)^+$, 85 ($C_5H_9O_2$); ^{1}H $\delta_{(ppm)}$ 1.42–1.90 (m, 8H) (2 × CH_2 at C-3, C-12, C-13, C-14), 1.92–2.08 (m, 2H) (CH_2 at C-2), 2.56–2.85 (m, 2H) (CH_2 at C-4), 3.48–3.60 (m, 1H_a), 3.90–4.08 (m, 1H_e) (CH_2 at C-16), 3.77 (s, 3H, OCH_3), 4.64 (dd, 1H, $J = 1.04$ Hz, $J = 0.56$ Hz) (1H at C-1), 4.81–4.91 (m, 1H) (1H at C-11), 6.75 (dd, 1H, $J = 8.35$ Hz, $J = 2.76$ Hz) (1H at C-6), 6.83 (d, 1H, $J = 2.7$ Hz) (1H at C-8), 7.01 (d, 1H, $J = 8.3$ Hz) (1H at C-5); ^{13}C $\delta_{(ppm)}$: 19.30 (C-13), 19.82 (C-3), 25.50 (C-14), 28.03 (C-4), 30.59 (C-12), 31.07 (C-2), 55.24 (OMe), 62.71 (C-15), 74.36 (C-1), 99.29 (C-11), 113.51 (C-6), 113.59 (C-8), 129.70 (C-10), 129.86 (C-5), 137.93 (C-9), 157.41 (C-7).

Compound **3c**

IR ν_{max} (cm^{-1}): 30.27, 2941, 2901, 1490, 1452, 1452, 1199, 1120; MS (m/z): 167 (M^+ – OTHP) (100%), 184 (M^+ – THP)$^{+1}$ (25%), 105 (Ph_2CO) (6%); ^{1}H $\delta_{(ppm)}$: 1.51–1.62 (m, 4H) (2 × CH_2 at C-15, C-17), 1.63–1.75 (m, 1H) (1H_a at C-16), 1.82–2.05 (m, 1H) (1H_e at C-16), 3.45–3.56 (m, 1H) (1 H_a at C-18), 3.89 (ddd, 1H, $J = 11$ Hz, $J = 4.5$ Hz, $J = 3.5$ Hz) (1H_e at C-18), 4.62–4.73 (m, 1H) (1H at C-14), 5.81 (s, 1H) (1H at C-1), 7.18–7.38 (m, 10H) (aromatic protons); ^{13}C $\delta_{(ppm)}$: 19.0 9 (C-16), 25.49 (C-17), 30.25 (C-15), 61.91 (C-18), 78.04 (C-1), 95.37 (C-14), 126.76) (C-3, C-7), 126.97 (C-5), 127.51 (C-11), 127.62 (C-9, C-13), 128.11 (C-4, C-6), 128.39 (C-10, C-12), 141.69 (C-2), 142.62 (C-8).

Compound **3d**

IR ν_{max} (cm^{-1}) 3029, 2934, 2869, 1492, 1448, 1375, 1319, 1282, 1204, 11.21, 1076; MS (m/z): 105 ($M^+ - C_5H_9O_2$) (100%), 85 (THP) (55%);

^{1}H $\delta_{(ppm)}$: 1.37–1.92 (m, 18 H) (9 × CH_2 at C-8, C-8′, C-10, C-10′, C-11, C-11′, C-12, C-12′), 3.23–3.54 (m, 4H) (2 × CH_2 at C-13, C-13′), 3.90–4.01 (m, 1H) (C-1′), 4.32–4.60 (m, 1H) (C-1), 4.75–4.91 (m, 2H) (C-9, C-9′), 7.21–7.42 (m, 10H) (aromatic protons); ^{13}C $\delta_{(ppm)}$: 19.22 (C-11′), 19.78 (C-11), 21.90 (C-8, C-8′), 24.29 (C-12′), 25.47 (C-12), 30.79 (C-10, C-10′), 61.79 (C-13′), 62.67 (C-13), 73.01 (C-1′), 73.17 (C-1), 96.03 (C-9), 96.17 (C-9′), 125.95 (C-4′, C-6′), 126.37 (C-4, C-6), 126.90 (C-5′), 127.32 (C-5), 128.12 (C-3′, C-7′), 128.33 (C-3, C-7), 143 (C-2), 144.47 (C-2′).

Compound **3e**

IR ν_{max} (cm^{-1}): 3063, 3031, 2942, 2870, 1496, 1454, 1261, 1078; MS (m/z): 85 ($M^+ - PhCH_2O$) (100%), 108 ($M^+ - C_5H_9O)^+$ (8%); ^{1}H $\delta_{(ppm)}$: 1.50–1.92 (m, 6H) (3 × CH_2 at C-10, C-9, C-11), 3.50–3.62 (m, 1H_a) (C-12), 3.95 (ddd, 1H_e, $J = 11$ Hz, $J = 3.38$ Hz, $J = 3.50$) (C-12), 4.50 (d, 1H_a, $J = 12.03$ Hz) (C-1), 4.71 (t, 1H, $J = 4$ Hz) (C-8), 4.79 (d, 1H_e, $J = 12.24$ Hz) (C-1), 7.25–7.45 (m, 5H) (aromatic protons); ^{13}C $\delta_{(ppm)}$: 19.31 (C-10), 25.45 (C-11), 30.54 (C-9), 62.05 (C-12), 68.76 (C-1), 97.68 (C-8), 127.44 (C-5), 127.75 (C-3, C-7), 128.31 (C-4, C-6), 138.28 (C-2).

Compound **3f**

IR ν_{max} (cm^{-1}): 2963, 2868, 1440, 1199, 1076; MS (m/z): 101 ($M^+ - C_4H_9$) (100%) (57 ($M^+ - C_5H_9O_2$ (25%); ^{1}H $\delta_{(ppm)}$: 1.20–1.91 (m, 13H) (CH_3 at C-1) (6 × CH_2 at C-2, C-3, C-6, C-7, C-8), 3.20–3.52 (m, 2H) (CH_2 at C-4), 3.50–4.01 (m, 2H) (CH_2 at C-9), 4.65–4.70 (m, 1H_a) (C-5), 4.75–4.82 (m, 1H_e) (C-5); ^{13}C $\delta_{(ppm)}$: 19.49 (C-1), 19.57 (C-2), 25.17 (C-7), 25.28 (C-8), 30.46 (C-6), 30.75 (C-3), 62.56 (C-9), 63.05 (C-1), 98.28 (C-5$_a$), 94.23 (C-5$_e$).

Compound **3g**

IR ν_{max} (cm^{-1}): 3029, 2933, 2857, 1462, 1333, 1247; MS (m/z): 232 (M^+) (25%), 148 $(M^+ - C_5H_9O)^{+1}$ (100%), 85 ($M^+ - C_{10}H_{11}O$) (51%); ^{1}H $\delta_{(ppm)}$: 1.51–1.90 (m, 9H) (4 × CH_2 1H) (C-13, C-14, C-6, C-7, C-12–1$_{Ha}$), 2.58–2.78 (m, 4H) (2 × CH_2 at C-5, C-8), 3.55–3.63 (m, 1$_{Ha}$) (C-15), 3.85–3.97 (m, 1$_{He}$) (C-15), 5.39–5.41 (m, 1$_{Ha}$) (C-11), 6.71 (d, 1H, $J = 8$ Hz) (C-4), 6.88 (d, 1H, $J = 7$ Hz) (C-2), 7.02 (dd, 1H, $J = 8$ Hz, $J = 7$ Hz); ^{13}C $\delta_{(ppm)}$: 18.95 (C-13), 22.87 (C-6, C-7), 23.25 (C-8), 25.34

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(C-14), 29.66 (C-5), 30.62 (C-12), 61.94 (C-15), 95.89 (C-11), 110.75 (C-2), 122.17 (C-4), 125.65 (C-3), 126.59 (C-9), 138.50 (C-10), 154.65 (C-4).

Compound **3h**

IR ν_{max} (cm^{-1}): 2941, 2856, 1671 (CO), 1447, 1350; MS (m/z): 264 $(M^{+})^{+1}$ (20%), 180 $(M^{+} - 85)^{+1}$, (100%); ^{1}H $\delta_{(ppm)}$: 1.20–2.01 (m, 12H) ($2 \times CH_2$ at C-13, C-14, C-15, C-2, C-3, C-4), 3.34–3.46 (m, 2H) (C-16), 3.79–3.90 (m, 1H) (C-1), 4.52–4.56 (m, 1H) (C-12), 5.72 (s, 1H) (C-5); ^{13}C $\delta_{(ppm)}$: 18.96 (C-19), 22.89 (C-14), 29.07 (C-3), 30.64 (C-15), 31.96 (C-2), 32.13 (C-13), 33.76 (C-4), 34.36 (C-8), 34.57 (C-7), 43.56 (C-9), 66.39 (C-16), 86.70 (C-1), 98.83 (C-12), 125.17 (C-5), 168.64 (C-12), 199.63 (C-6).

Compound **3i**

MS (m/z): 168 $(M^{+} - C_4H_7)$, 111 $(M^{+} - C_4H_6\text{-NO-CO})$, 85 $(C_5H_9O^{+})$; ^{1}H $\delta_{(ppm)}$: 1.40–1.93 (m, 6H, CH_2 at C-8, C-9, C-10), 3.38–3.53 (m, 2H) (C-11), 5.42 (t, 1H, $J = 3.1$ Hz) (C-7), 7.29 (ddd, 1H, $J = 7.8$ Hz, $J = 2.3$ Hz, $J = 1.6$ Hz) (C-6), 7.34 (ddd, 1H, $J = 7.8$ Hz, $J = 7.8$ Hz, $J = 0.5$ Hz) (C-5), 7.73 (ddd, 1H, $J = 7.8$ Hz, $J = 2.3$ Hz, $J = 1.6$ Hz) (C-4), 7.83 (ddd, 1H, $J = 2.3$ Hz, $J = 2.3$ Hz, $J = 0.5$ Hz) (C-2); ^{13}C $\delta_{(ppm)}$: 18.31 (C-9), 24.89 (C-10), 30.06 (C-8), 61.89 (C-11), 98.35 (C-7), 111.30 (C-2), 116.23 (C-4), 122.72 (C-6), 129.70 (C-5), 149.03 (C-3), 157.46 (C-1).

Compound **3j**

MS (m/z): 168 $(M^{+} - C_4H_7)$, 85 $(C_5H_9O^{+})$; ^{1}H $\delta_{(ppm)}$: 1.36–1.70 (m, 6H, CH_2 at C-8, C-9, C-10), 3.31–3.34 (m, 2H) (C-11), 5.36 (t, 1H, $J = 3.0$ Hz) (C-7), 6.94 (d, 2H, $J = 9.3$ Hz) (C-6, C-2), 7.98 (d, 2H, $J = 9.3$ Hz) (C-5, C-3); ^{13}C $\delta_{(ppm)}$: 18.06 (C-9), 24.74 (C-10), 30.74 (C-8), 61.72 (C-11), 96.17 (C-7), 116.01 (C-2, C-6), 125.37 (C-3, C-5), 141.69 (C-4), 161.97 (C-1).

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REFERENCES

1. Kocienski, P. J. In *Protecting Groups*; D. Ender, R. Nayori, B. Trost (Eds.); Georg Thieme Verlag: Stuttgart, 1994.

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2. Greene, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Synthesis,* 3rd ed.; John Wiley and Sons: New York, 1991.
3. Kunz, H.; Waldmann, H. In *Comprensive Organic Synthesis*; B. M. Trost, I. Fleming (Eds.); Pergamon Press: Oxford, 1992; vol. 6, p. 631.
4. Nishiguchi, T.; Kawamine, K. J. Selective monoetherification of 1,N-diols catalyzed by aluminum sulfate supported on silica gel. *J. Chem. Soc., Chem. Commun.* **1990**, 1776.
5. Hoyer, S.; Laszlo, P.; Orlovic, M.; Polla, E. Catalysis by acidic clay of the protective tetrahydropyranylation of alcohols and phenols. *Synthesis* **1986**, 655.
6. Pore, D. M.; Desai, U.V.; Mane, R. B.; Wadgaonkar, P. P. Chemoselective tetrahydropyranylation of alcohols and their detetrahydropyranylation using silica sulphuric acid as a reusable catalyst. *Synth. Commun.* **2004**, *34*, 2135, and references cited therein.
7. Gelbard, G. Organic synthesis by catalysis with ion-exchange resins. *Ind. Eng. Chem. Res.* **2005**, *44*, 8468.
8. Bongini, A.; Cardillo, G.; Orena, M.; Sandri, S. A simple and practical method for tetrahydropyranylation of alcohols and phenols. *Synthesis* **1979**, 618.
9. Nishiguchi, T.; Kuroda, M.; Saitoh, M.; Nishida, A.; Fujisaki, S. Highly selective monotetrahydropyranylation of symmetrical diols catalyzed by a strongly acidic ion-exchange resin. *J. Chem. Soc., Chem. Commun.* **1995**, 2491.
10. Olah, G. A.; Husain, A.; Singh, B. P. Catalysis by solid superacids, 19: Simplified and improved polymeric perfluorinated resin sulfonic acid (Nafion-H) catalyzed protection–deprotection reactions. *Synthesis* **1983**, 892.
11. Beier, R.; Mundy, B. P. A facile removal of the tetrahydropyranyl protecting group from alcohol derivatives. *Synth. Commun.* **1979**, *9*, 271.
12. Boyce, C. B. C.; Whitehurst, J. S. Reduction of 9-methyl-Δ-5(10)-octalin-1,6-dione. *J. Chem. Soc.* **1960**, 2680.

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