JOC*Note*

Poly(ethylene Glycol) (400) as Superior Solvent Medium against Ionic Liquids for Catalytic Hydrogenations with PtO_2

Srivari Chandrasekhar,* Samala Jaya Prakash, and Chennamaneni Lohitha Rao

Organic Division-1, Indian Institute of Chemical Technology, Hyderabad 500007, India

srivaric@iict.res.in

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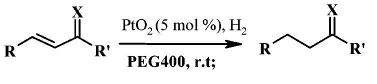
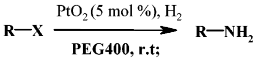
Scheme 1



R = H, alkyl, aryl; X = O, H_2
R' = alkyl, aryl, OEt, OH

Scheme 2

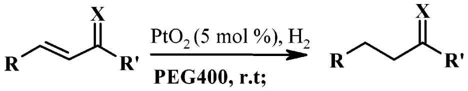


R = alkyl, aryl ; X = NO_2, N_3

Adams' catalyst in poly(ethylene glycol) (PEG) (400) has been found to be a superior solvent over the ionic liquids by severalfold in promoting the hydrogenation of various functional groups. Both the catalyst and PEG were recycled efficiently over 10 runs without loss of activity, and substrate cross contamination was not observed despite a change in the substrate four times.

Catalysis and atom efficiency go hand in hand for efficient organic synthesis.[1] Recovery of materials used in the reaction and purification difficulties limit the yield and utility of a particular organic reaction in a multistep synthesis. Enormous efforts continue in this direction, and already several protocols are being practiced as efficient alternatives to the "not so efficient" methods of older times. The major/bulk waste created in most reactions is the solvent medium, and new nonvolatile ionic liquids (IL),[2] $scCO_2$,[3] and fluorous[4] solvents have come into the limelight. These can be recycled more vigorously compared to conventional solvents, thus minimizing the solvent waste. Keeping in mind the challenges posed by traditional solvents and also the limitation of nonconventional solvents (ionic liquids, $scCO_2$ etc.), a program was initiated by our group[5] and later by others[6] where the biologically compatible poly(ethylene glycol) (PEG)[7] was demonstrated to be a recyclable solvent for various transformations. In these studies, the catalysts used (viz., palladium and osmium) were also efficiently recycled for 5−10 runs without loss of activity. Several other groups[8] have utilized ionic liquids as solvent, which are relatively expensive[9] compared to PEG for recycling similar metal catalysts as well as solvent. The $scCO_2$[10] and fluorous[11] solvents were also popularized for various transformations with claims of eco-compatibility and recyclability. An ambitious exercise has been taken up to develop recyclable solvent medium for Adams' catalyst[12] (PtO_2), one of the most expensive[9] metal catalysts that richly deserves recyclability. The study taken up by us unambiguously proved that PEG is a superior solvent over the ionic liquids by severalfold in promoting the hydrogenation of various functional groups (Schemes 1 and 2) using the catalyst. The details are presented in this Note.

SCHEME 1



R = H, alkyl, aryl; X = O, H_2
R' = alkyl, aryl, OEt, OH

In the first instance, cinnamyl alcohol **1a** (entry 1, Table 1) was subjected to PtO_2-catalyzed hydrogenation at atmospheric pressure with the aid of a balloon to observe clean formation of 3-phenyl-*n*-propanol **1b** in greater than 95% yield in less

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(1) (a) Trost, B. M. *Science* **1991**, *254*, 1471. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259. (c) Perkas, N.; Wang, Y.; Koltypin, Y.; Gedanken, A. Chandrasekaran, S. *Chem. Commun.* **2001**, 988. (d) Sheldon, R. A.; Sawyer, D. T.; Martell, A. E. In *Industrial Environmental Chemistry*; Plenum: New York 1992; pp 99−119. (e) Sheldon, R. A. *Pure Appl. Chem.* **2000**, *72*, 1233.

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(4) (a) Studer, A.; Hadida, S.; Ferritto, R.; Kim, S. Y.; Jeger, P.; Wipf, P.; Curran, D. P. *Science* **1997**, *275*, 823. (b) Horvath, I. T.; Rabai, J. *Science* **1994**, *266*, 72. (c) Foster, D. F.; Adams, D. J.; Gudmunsen, D.; Stuart, A. M.; Hope, E. G.; Cole-Hamilton, D. J. *Chem. Commun.* **2002**, 722. (d) Perperi, E.; Huang, Y. L.; Angeli, P.; Manos, G.; Mathison, C. R.; Cole-Hamilton, D. J.; Adams, D. J.; Hope, E. G. *J. Chem. Soc., Dalton Trans.* **2004**, 2062.

(5) (a) Chandrasekhar, S.; Narsihmulu, Ch.; Sultana, S. S.; Reddy, N. R. *Org. Lett.* **2002**, *4*, 4399. (b) Chandrasekhar, S.; Narsihmulu, Ch.; Sultana, S. S.; Reddy, N. R. *Chem. Commun.* **2003**, 1716.

(6) (a) Li, J.-H.; Zhu, Q.-M.; Liang, Y.; Yang, D. *J. Org. Chem.* **2005**, *70*, 5347. (b) Li, J.-H.; Liu, W.-J.; Xie, Y.-X. *J. Org. Chem.* **2005**, *70*, 5409. (c) Huaxing, Z.; Yuhong, Z.; Leifang, L.; Hailiang, X.; Yanguang, W. *Synthesis* **2005**, *13*, 2129. (d) Zhang, Z.-H.; Yin, L.; Wang, Y.-M.; Liu, J.-Y.; Li, Y. *Green Chem.* **2004**, *6*, 563.

(7) Harris, J. M.; Zalipsky, S. *Poly(ethylene Glycol): Chemistry and Biological Applications*; American Chemical Society: Washington, DC, 1997.

(8) (a) Baan, Z.; Finta, Z.; Keglevich, G.; Hermecz, I. *Tetrahedron Lett.* **2005**, *46*, 6203. (b) Mo, J.; Xu, L.; Xiao, J. *J. Am. Chem. Soc.* **2005**, *127*, 751. (c) Xie, X.; Chen, B.; Lu, J.; Han, J.; She, X.; Pan, X. *Tetrahedron Lett.* **2004**, *45*, 6235. (d) Chhikara, B. S.; Chandra, R.; Tandon, V. *Tetrahedron Lett.* **2004**, *45*, 7585. (e) Ranu, B. C.; Banerjee, S. *J. Org. Chem.* **2005**, *70*, 4517. (f) Yao, Q. *Org. Lett.* **2002**, *4*, 2197. (g) Teo, Y.-C.; Goh, E.-L.; Loh, T.-P. *Tetrahedron Lett.* **2005**, *46*, 4573. (h) Yadav, J. S.; Reddy, B. V. S.; Baishya, G.; Harshavardhan, S. J.; Chary, C. J.; Gupta, M. K. *Tetrahedron Lett.* **2005**, *46*, 3569.

(9) Ionic liquids cost 60−400 USD/50 g, compared to PEG (400), which costs 23 USD/500 g. Platinum(IV) oxide costs 60 USD/1 g (Aldrich 2005−2006).

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(11) (a) Nakamur, H.; Usui, T.; Kuroda, H.; Ryu, I.; Matsubara, H.; Yasuda, S.; Curran, D. P. *Org. Lett.* **2003**, *5*, 1167. (b) Crich, D.; Zou, Y. *Org. Lett.* **2004**, *6*, 775.

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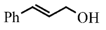
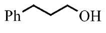
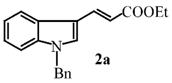
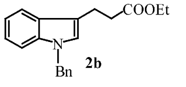
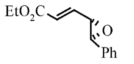
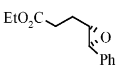
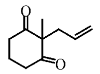
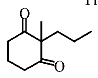
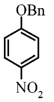
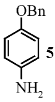
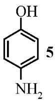
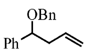
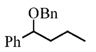
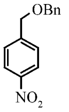
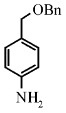
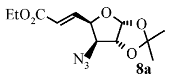
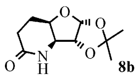
10.1021/jo052604x CCC: \$33.50

SCHEME 2

$$R{-}X \xrightarrow[\textbf{PEG400, r.t;}]{PtO_2\,(5\ mol\ \%),\ H_2} R{-}NH_2$$

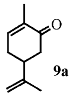
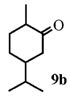
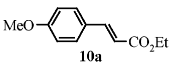
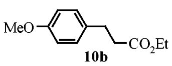
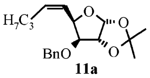
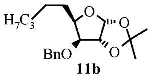
R = alkyl, aryl ; X = NO_2, N_3

TABLE 1. Catalytic Hydrogenation in PEG under PtO_2

Entry	Substrate	Product	Time[a] (h)	Yield[b] (%)
1	 **1a**	 **1b**	2.5	95
2	 **2a**	 **2b**	4	92
3	 **3a**	 **3b**	5	60
4	 **4a**	 **4b**	2	93
5	 **5a**	 **5b** +  **5c**	10	88 **(5b)** + 7 **(5c)**
6	 **6a**	 **6b**	3	91
7	 **7a**	 **7b**	9	92
8	 **8a**	 **8b**	4	95

[a] Time in hours. [b] All the products were characterized by ^1H, ^{13}C NMR, IR, and mass spectra.

TABLE 2. Comparison of Catalytic Hydrogenation in PEG and IL Using PtO_2

Entry	Substrate	Product	In PEG Time[a] (h)	In PEG Yield[b] (%)	In IL Time[a] (h)	In IL Yield[b] (%)
1	 **9a**	 **9b**	3	97	23	40
2	 **10a**	 **10b**	2	93	24	15
3	 **11a**	 **11b**	4	94	25	20

[a] Time in hours. [b] All the products were characterized by ^1H, ^{13}C NMR, IR, and mass spectra.

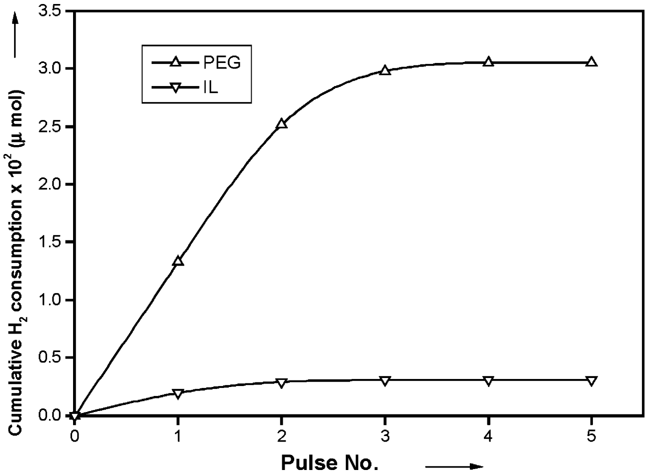


FIGURE 1. Plot of consumed volume of hydrogen versus pulse No.

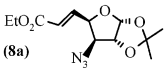
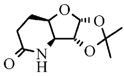
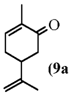
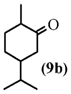
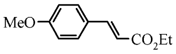
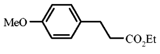
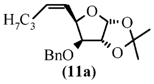
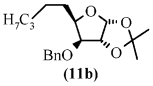
than 3 h. Similarly, ethyl-4-methoxycinnamate **10a** (entry 2, Table 2) was subjected to hydrogenation with 5 mol % PtO_2 in PEG (400 Da) for 2 h to isolate the saturated ester **10b** in greater than 93% yield and greater than 95% purity just by ethereal workup (vide infra). The same substrate (entry 2, Table 2) when subjected to hydrogenation in ionic liquid ($EMIMBF_4$) was resistant even after 24 h (15% conversion). Two other substrates, namely the carvone **9a** (entry 1, Table 2) and the sugar derivative **11a** (entry 3, Table 2), having a hydrogenation-sensitive benzyl ether were effectively saturated in greater than 90% yields in PEG. The benzyl ether cleavage was not observed even in traces. These two substrates when subjected to PtO_2-catalyzed hydrogenation in ionic liquid ($EMIMBF_4$) yielded products in poor conversion and yields (entries 2 and 3, Table 2). To understand more closely the chemisorption of Adams' catalyst in PEG over ionic liquids, quantitative adsorption of hydrogen on PtO_2 in both solvents was taken up.

The pulse chemisorption of H_2 was employed to know the amount of H_2 chemisorbed on PtO_2 (catalyst) in the presence of solvent (PEG/IL). The pretreatment of catalyst was performed by passing N_2 at ambient temperature for 1 h. Then the hydrogen was chemisorbed on pretreated catalyst at room temperature in pulses through a six-port valve. In a typical experiment, 10 mg of the catalyst in 1 mL of PEG/IL was taken in a 5-mL round-bottom flask. The outlet of the reactor was connected to a microthermal conductivity detector (TCD) equipped with GC-17A (M/S Shimadzu Instruments, Japan) through a blank column. After the pretreatment of the catalyst, pulses of H_2 (purity 99.99%) were injected at room temperature through a 500-μL loop connected to the six-port valve until no further change in the intensity of the outlet H_2 (monitored by a data station with CLASS 10 GC software) was observed. The cumulative H_2 consumption was recorded against five pulses, and the data recorded (Figure 1) clearly demonstrated that the H_2 adsorption into PtO_2 in PEG is severalfold superior to ionic liquid. This is direct evidence for the efficient reduction of functional groups in PEG over the ionic liquids.

This advantage is further exploited with various substrates. For instance, in entry 2 (Table 1), the selective reduction of electron-deficient olefin was rapid while that of the N−Bn group was stable. However, partial O−Bn cleavage was observed in the 4-nitro-1-benzyloxy aryl system **5a** (entry 5, Table 1). The reduction of the nitro group was also very efficient in the case of 4-NO_2-benzyl ether **7a** (entry 7, Table 1).

Furanose derivative **8a** (entry 8, Table 1) not only allowed reduction of both azido and olefin groups but also facilitated intramolecular cyclization to furnish the tricyclic compound **8b** in 95% yield. The recyclability of both PEG as solvent and PtO_2 as catalyst was amply demonstrated in Table 3 for 10 runs, and substrate cross contamination was not observed despite a change in the substrate four times (entries 1, 4, 7, and 9 in Table 3).

TABLE 3. Recyclability of Both PEG and PtO_2 as a Solvent and Catalyst

Entry	Substrate	Product	Time[a] (h)	Yield[b] (%)
1	 **(8a)**	 **(8b)**	4	95
2	**8a**	**8b**	4	93
3	**8a**	**8b**	4	93
4	 **(9a)**	 **(9b)**	3	96
5	**9a**	**9b**	3	95
6	**9a**	**9b**	3	93
7	 **(10a)**	 **(10b)**	2	93
8	**10a**	**10b**	2	92
9	 **(11a)**	 **(11b)**	4	92
10	**11a**	**11b**	4	91

[a] Time in hours. [b] All the products were characterized by ^1H, ^{13}C NMR, IR, and mass spectra.

In conclusion, we have demonstrated that the very expensive PtO_2 can be recycled several times in PEG (400) without considerable loss of activity. Also, dissolution of H_2 in PEG and ionic liquid was studied using a gas chromatography technique to prove the fact that the H_2 dissolution plays an advantageous role in favor of PEG over ionic liquid. It is needless to mention of course that ionic liquid will be superior in catalysis of acid-catalyzed reactions where PEG may not be stable.

Experimental Section

General. The chemicals PtO_2, ionic liquid ($EMIMBF_4$), and poly(ethylene glycol) (400) were purchased from commercial suppliers and used without further purification. Diethyl ether was distilled over sodium wire. IR spectra were recorded on Perkin-Elmer 683 spectrometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Varian Gemini 200, Brucker Avance 300. Chemical shifts were reported in ppm with respect to internal TMS. Coupling constants (*J*) are quoted in Hz. Mass spectra were obtained on an Agilent Technologies LC/MSD Trap SL.

Spectroscopic (IR, ^1H, and ^{13}C NMR) data for the new compounds are presented in order of their entries in Tables 1and 2.

3-Phenyl-1-propanol (1b). Data are in accordance with the data of a commercially available sample.

Ethyl-3-(1-benzyl-1*H*-3-indolyl)-propanoate (2b): ^1H NMR (200 MHz, $CDCl_3$) δ 7.61 (d, $J = 7.55$ Hz, 1H), 7.33−7.07 (m, 8H), 6.94 (s, 1H), 5.27 (s, 2H), 4.12 (q, $J = 7.55$ Hz, 2H), 3.10 (t, $J = 7.55$ Hz, 2H), 2.70 (t, $J = 7.55$ Hz, 2H), 1.21 (t, $J = 7.55$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.4, 137.7, 136.7, 128.7, 127.9, 127.5, 126.8, 125.6, 121.8, 119.0, 118.9, 114.2, 109.7, 60.3, 49.9, 35.1, 20.6, 14.3; IR (KBr): 2980, 1729, 1467, 1177, 912, and 743 cm^{-1}; ESI (MS): 308 $[M + H]^+$, 330 $[M + 23]^+$; HRMS (ESI) Calcd for $C_{20}H_{22}NO_2$: 308.1650 $[M + H]^+$; Found: 308.1648 $[M + H]^+$.

Ethyl-3-(3-phenyl-2-oxiranyl)-propanoate (3b): ^1H NMR (200 MHz, $CDCl_3$) δ 7.36−7.19 (m, 5H), 4.15 (q, $J = 7.2$ Hz, 2H), 3.61 (d, $J = 2.4$ Hz, 1H), 3.01−2.93 (m, 1H), 2.50 (t, $J = 7.2$ Hz, 2H), 2.21−2.03 (m, 1H), 2.00−1.84 (m, 1H), 1.28 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 137.3, 128.4, 128.0, 125.5, 61.6, 60.5, 58.6, 30.3, 27.5, 14.1; IR (KBr): 2981, 1732, 1179, and 699 cm^{-1}; ESI (MS): 221 $[M + H]^+$, 243 $[M + 23]^+$; HRMS (ESI) Calcd for $C_{13}H_{17}O_3$: 221.1177 $[M + H]^+$; Found: 221.1187 $[M + H]^+$.

2-Methyl-2-propyl-1,3-cyclohexanedione (4b): ^1H NMR (300 MHz, $CDCl_3$) δ 2.78−2.54 (m, 4H), 2.11−1.96 (m, 1H), 1.92−1.70 (m, 3H), 1.25−1.08 (m, 5H), 0.88 (t, $J = 7.55$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.8, 65.3, 39.4, 37.4, 18.1, 17.5, 17.2, 13.8; IR (KBr): 2963, 1695, 1618, and 1130 cm^{-1}; ESI (MS): 169 $[M + H]^+$.

4-Benzyloxyaniline (5b): ^1H NMR (300 MHz, $CDCl_3$) δ 7.42−7.28 (m, 5H), 6.78 (d, $J = 9.0$ Hz, 2H), 6.61 (d, $J = 9.0$ Hz, 2H), 4.98 (s, 2H), 1.90−1.46 (bs, 2NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.8, 140.1, 137.4, 128.4, 127.7, 127.4, 116.2, 115.9, 70.6; IR (KBr): 3416, 2220, 1618, and 618 cm^{-1}; ESI (MS): 200 $[M + H]^+$; HRMS (ESI) Calcd for $C_{13}H_{14}NO$: 200.1075 $[M + H]^+$; Found: 200.1078 $[M + H]^+$.

1-(1-Benzyloxybutyl)-benzene (6b): ^1H NMR (300 MHz, $CDCl_3$) δ 7.35−7.20 (m, 10H), 4.42 (d, $J = 12.0$ Hz, 1H), 4.25 (dd, $J = 5.2$, 7.5 Hz, 1H), 4.20 (d, $J = 12.0$ Hz, 1H), 1.89−1.77 (m, 1H), 1.66−1.54 (m, 1H), 1.52−1.40 (m, 1H), 1.34−1.23 (m, 1H), 0.89 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.6, 138.6, 128.2, 128.1, 127.6, 127.4, 127.3, 126.6, 81.1, 70.2, 40.4, 19.0, 13.8; IR (KBr): 2958, 1454, 1085, and 736 cm^{-1}; ESI (MS): 241 $[M + H]^+$; HRMS (ESI) Calcd for $C_{17}H_{24}NO$: 258.1857$[M + NH_4]^+$; Found: 258.1862 $[M + NH_4]^+$.

4-Benzyloxymethylaniline (7b): ^1H NMR (300 MHz, $CDCl_3$) δ 7.33−7.24 (m, 5H), 7.11 (d, $J = 8.1$ Hz, 2H), 6.60 (d, $J = 8.1$ Hz, 2H), 4.47 (s, 2H), 4.40 (s, 2H), 1.45−1.34 (bs, 2-NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 138.5, 129.5, 128.3, 128.1, 127.8, 127.5, 115.0, 72.0, 71.6; IR (KBr): 3458, 1619, 1359, 1067, and 742 cm^{-1}; ESI (MS): 214 $[M + H]^+$; HRMS (ESI) Calcd for $C_{14}H_{16}NO$: 214.1231 $[M + H]^+$; Found: 214.1232 $[M + H]^+$.

2,2-Dimethylperhydro-[1,3]-dioxolo-[4′,5′:4,5]-furo-[3,2-b]-pyridin-7-one (8b): ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (s, 1-NH), 5.87 (d, $J = 3.7$ Hz, 1H), 4.55−4.51 (bs, 1H), 4.48 (d, $J = 3.7$ Hz, 1H), 3.81 (d, $J = 3.7$ Hz, 1H), 2.57−2.44 (m, 1H), 2.30−2.15 (m, 2H), 1.96−1.83 (m, 1H), 1.49 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 112.0, 104.9, 85.6, 71.8, 60.5, 26.7, 26.2, 25.6, 22.4; IR (KBr): 3179, 2904, 1669, 1227, 1072, and 1010 cm^{-1}; ESI (MS): 214 $[M + H]^+$, 236 $[M + 23]^+$; HRMS (ESI) Calcd for $C_{10}H_{16}NO_4$: 214.1079 $[M + H]^+$; Found: 214.1078 $[M + H]^+$.

5-Isopropyl-2-methyl-1-cyclohexanone (9b): ^1H NMR (300 MHz, $CDCl_3$) δ 2.43−2.27 (m, 2H), 2.16−1.99 (m, 1H), 1.93−1.84 (m, 1H), 1.76−1.28 (m, 5H), 1.02 (d, $J = 6.0$ Hz, 3H), 0.96−0.91 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 213.5, 46.4, 45.2, 44.7, 34.9, 32.6, 28.7, 19.4, 19.2, 14.2; IR (KBr): 2962, 1712, and 1617 cm^{-1}; ESI (MS): 155 $[M + H]^+$, 177 $[M + 23]^+$; HRMS (ESI) Calcd for $C_{10}H_{19}O$: 155.1435 $[M + H]^+$; Found: 155.1432 $[M + H]^+$.

Ethyl-3-(4-methoxyphenyl)-propanoate (10b): ^1H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, $J = 8.9$ Hz, 2H), 6.76 (d, $J = 8.9$ Hz, 2H), 4.10 (q, $J = 7.4$ Hz, 2H), 3.77 (s, 3H), 2.86 (t, $J = 7.4$ Hz, 2H), 2.55 (t, $J = 7.4$ Hz, 2H), 1.24 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.8, 157.9, 132.5, 129.1, 113.7, 60.2, 55.1, 36.1, 30.0, 14.1; IR (KBr): 2982, 1732, 1613, 1513, 1247, 1178, and 1037 cm^{-1}; ESI (MS): 209 $(M^+ + H)$, 231 $(M^+ + 23)$; HRMS (ESI) Calcd for $C_{12}H_{17}O_3$: 209.1177 $[M + H]^+$; Found: 209.1181 $[M + H]^+$.

6-Benzyloxy-2,2-dimethyl-5-pentylperhydrofuro-[2,3-d][1,3]-dioxole (11b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.25 (m, 5H), 5.83 (d, $J = 3.8$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.53 (d, $J = 4.5$ Hz, 1H), 4.45 (d, $J = 12.0$ Hz, 1H), 4.07−4.01 (m, 1H), 3.69 (d, $J = 3.0$ Hz, 1H), 1.76−1.57 (m, 2H), 1.45 (s, 3H), 1.33−1.25 (m, 9H), 0.88 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.5, 128.3, 127.8, 127.7, 111.1, 104.6, 82.1, 81.7, 80.4, 71.6, 31.9, 27.8, 26.6, 26.2, 25.7, 22.5, 14.0; IR (KBr): 2929, 1456, 1077, and 1022 cm^{-1}; ESI (MS): 321 ($M^+ + H$); HRMS (ESI) Calcd for $C_{19}H_{29}O_4$: 321.2065 $[M + H]^+$; Found: 321.2073 $[M + H]^+$.

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Supporting Information Available: General experimental procedure and copies of ^{1}H and ^{13}C NMR spectra for all new compounds **2b**, **3b**, **4b**, **5b**, **6b**, **7b**, **8b**, **9b**, **10b**, and **11b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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