SUPPORTING INFORMATION

Hydrogen-Bonded Helical Self-Assembly of Sterically-Hindered Benzyl Alcohols: Rare Isostructurality and Synthon Equivalence Between Alcohols and Acids

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**General Aspects.** Anhyd tetrahydrofuran (THF) was freshly distilled over sodium prior to use and purged with nitrogen gas. All other solvents were distilled before use. Column chromatography was conducted with silica gel of 60-120 μ mesh.

**General Procedure for the Reduction of Substituted Aldehydes:** In a 50 mL dry two-necked round bottomed flask was taken substituted benzaldehyde (2.50 mmol) dissolved in dry THF (20 mL) under a N₂ gas atmosphere and cooled to 0 °C in an ice bath. After 15 min, NaBH₄ (3.00 mmol) was introduced in small portions. The reaction mixture was gradually allowed to attain room temperature and stirred for 3-4 h. It was then quenched with dil HCl at ice cold conditions. The THF was removed and the residue was extracted with EtOAc. The organic extract was further washed with brine, dried over anhyd Na₂SO₄, filtered and the solvent removed to yield the crude product, which was purified by silica-gel column chromatography to obtain pure substituted benzyl alcohols (8, 9, 14 and 15) in good yields (88-92%).

**Scheme S1**

![Scheme S1](image)

**General Procedure for the Hydrolysis of Substituted Benzyl Bromides:** In a 100 mL two-necked round bottomed flask was taken substituted benzyl bromide (5.00 mmol) along with CaCO₃ (25.00 mmol) in a 1:1 solvent mixture of 1,4-dioxane and H₂O (30 mL). The reaction
mixture was heated at reflux for 12-14 h. It was then cooled to room temperature and acidified with Conc HCl to yield white precipitate of benzyl alcohol. It was then extracted with EtOAc and washed with brine. The organic extract was dried over anhyd Na$_2$SO$_4$, filtered and the solvent removed to afford the crude product, which was purified by silica-gel column chromatography in a good yield (80-95%).

**Scheme S2**

![Scheme S2](image)

3,5-Dibromo-2,4,6-trimethylbenzyl Alcohol 8: Colorless solid, yield 89%; mp 191-193 °C; IR (KBr) cm$^{-1}$ 3286, 2918, 1414, 1376, 1158; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.54 (s, 6H), 2.68 (s, 3H), 4.82 (s, 2H); $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ 20.9, 26.5, 59.7, 126.1, 136.4, 136.8, 139.2; ESI-MS$^+$ $m/z$ Calcd for C$_{10}$H$_{12}$OBr$_2$ 350.9231 [M+HCOO$^-$], found 350.9238.

3,5-Dichloro-2,4,6-trimethylbenzyl Alcohol 9: Colorless solid, yield 92%; mp 174-177 °C; IR (KBr) cm$^{-1}$ 3278, 2918, 1422, 1375, 1169; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.48 (s, 6H), 2.52 (s, 3H), 4.77 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 17.0, 19.2, 60.4, 133.7, 133.9, 134.5, 136.4; ESI-MS$^+$ $m/z$ Calcd for C$_{10}$H$_{12}$OCl$_2$ 218.0265 [M], found 218.0268.
3-Bromo-2,4,5,6-tetramethylbenzyl Alcohol 10: Colorless solid, yield 80%; mp 160-162 °C;
IR (KBr) cm⁻¹ 3287, 2919, 1413, 1205, 998; ¹H NMR (400 MHz, CDCl₃) δ 2.27 (s, 3H), 2.33 (s, 3H), 2.46 (s, 3H), 2.55 (s, 3H), 4.79 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 16.2, 17.5, 20.6, 21.6, 60.6, 127.2, 134.5, 134.7, 134.8, 135.4, 136.4; EI-MS⁺ m/z Calcd for C₁₁H₁₅OBr 242.0306 [M], found 242.0307.

3-Chloro-2,4,5,6-tetramethylbenzyl Alcohol 11: Colorless solid, yield 92%; mp 151-153 °C;
IR (KBr) cm⁻¹ 3278, 2920, 1417, 1211, 999; ¹H NMR (500 MHz, CDCl₃) δ 2.24 (s, 3H), 2.35 (s, 3H), 2.39 (s, 3H), 2.49 (s, 3H), 4.78 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 16.2, 17.1, 18.0, 60.3, 132.5, 133.3, 134.1, 134.5, 134.6, 135.3; EI-MS⁺ m/z Calcd for C₁₁H₁₅OCl 198.0811 [M], found 198.0810.

4-Bromo-2,3,5,6-tetramethylbenzyl Alcohol 12: Colorless solid, yield 95%; mp 164-165 °C;
IR (KBr) cm⁻¹ 3251, 2920, 1446, 1423, 1382, 989; ¹H NMR (400 MHz, CDCl₃) δ 2.40 (s, 6H), 2.44 (s, 6H), 4.76 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 17.0, 21.3, 59.9, 129.6, 134.3, 134.7, 135.4; ESI-MS⁺ m/z Calcd for C₁₁H₁₅OBr 265.0204 [M+Na⁺], found 265.0207.

4-Chloro-2,3,5,6-tetramethylbenzyl Alcohol 13: Colorless solid, yield 84%; mp 144-147 °C;
IR (KBr) cm⁻¹ 3257, 2920, 1446, 1382, 1308, 993; ¹H NMR (400 MHz, CDCl₃) δ
2.37 (s, 12H), 4.77 (s, 2H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 16.5, 17.7, 59.8, 132.4, 134.6, 134.7, 135.4; EI-MS\(^+ \) m/z Calcd for C\(_{11}\)H\(_{15}\)OCl 198.0811 [M], found 198.0812.

2,3,4,5,6-Pentamethylbenzyl Alcohol 14: Colorless solid, yield 88%; mp 143-146 °C; IR (KBr) cm\(^{-1}\) 3269, 2916, 1444, 1383, 1306, 991; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 2.24 (s, 6H), 2.25 (s, 3H), 2.37 (s, 6H), 4.79 (s, 2H); \( ^{13} \)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 16.2, 16.7, 16.9, 60.1, 132.8, 132.9, 133.9, 135.2; ESI-MS\(^+ \) m/z Calcd for C\(_{12}\)H\(_{18}\)O 161.1330 [M+H-H\(_2\)O], found 161.1341.

2,4,6-Trimethylbenzyl Alcohol 15: Colorless solid, yield 91%; mp 67-69 °C; IR (KBr) cm\(^{-1}\) 3269, 2916, 1444, 1383, 1306, 991; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 2.24 (s, 6H), 2.25 (s, 3H), 2.37 (s, 6H), 4.79 (s, 2H); \( ^{13} \)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 16.2, 16.7, 16.9, 60.1, 132.8, 132.9, 133.9, 135.2; ESI-MS\(^+ \) m/z Calcd for C\(_{10}\)H\(_{14}\)O 151.1123 [M+H], found 151.1127.
Figure S1. $^1$H NMR (400 MHz) spectrum of 3,5-dibromo-2,4,6-trimethylbenzyl alcohol 8 in CDCl$_3$. 
Figure S2. $^{13}$C NMR (125 MHz) spectrum of 3,5-dibromo-2,4,6-trimethylbenzyl alcohol 8 in DMSO-$d_6$. 
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Figure S10. $^{13}$C NMR (100 MHz) spectrum of 4-bromo-2,3,5,6-tetramethylbenzyl alcohol 12 in CDCl$_3$. 
Figure S11. $^1$H NMR (400 MHz) spectrum of 4-chloro-2,3,5,6-tetramethylbenzyl alcohol 13 in CDCl$_3$. 
Figure S12. $^{13}$C NMR (100 MHz) spectrum of 4-chloro-2,3,5,6-tetramethylbenzyl alcohol 13 in CDCl$_3$. 
Figure S13. $^1$H NMR (500 MHz) spectrum of 2,3,4,5,6-pentamethylbenzyl alcohol 14 in CDCl$_3$. 
Figure S14. $^{13}$C NMR (125 MHz) spectrum of 2,3,4,5,6-pentamethylbenzyl alcohol 14 in CDCl$_3$. 
Figure S15. $^1$H NMR (500 MHz) spectrum of 2,4,6-trimethylbenzyl alcohol 15 in CDCl$_3$. 
Figure S16. $^{13}$C NMR (125 MHz) spectrum of 2,4,6-trimethylbenzyl alcohol 15 in CDCl$_3$. 