Supplementary Materials: Regioselective Benzoylation of Diols and Carbohydrates by Catalytic Amounts of Organobase

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Contents

1. Characterization of Important Known Compounds

Methyl 6-O-benzoyl-α-D-glucopyranoside (**2**): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.05–7.98 (m, 2H), 7.53–7.50 (m, 1H), 7.39 (m, 2H), 4.78 (d, *J* = 3.4 Hz, 1H, H_1), 4.67 (dd, *J* = 12.1, 4.8 Hz, 1H), 4.54 (d, *J* = 11.8 Hz, 1H), 3.86 (dd, *J* = 9.6, 3.2 Hz, 2H), 3.80 (t, *J* = 8.9 Hz, 1H), 3.56 (d, *J* = 6.2 Hz, 1H), 3.48 (d, *J* = 9.5 Hz, 1H), 3.43 (s, 3H, OMe) [1].

2-Hydroxy-2-phenylethyl benzoate (**4a**): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.11–8.03 (m, 2H), 7.64–7.54 (m, 1H), 7.45 (dd, *J* = 10.7, 4.7 Hz, 4H), 7.41–7.35 (m, 3H), 5.12 (d, *J* = 8.1 Hz, 1H), 4.54 (dd, *J* = 11.6, 3.5 Hz, 1H), 4.43 (dd, *J* = 11.6, 8.2 Hz, 1H) [2].

1-Phenylethane-1,2-diyl dibenzoate (**4b**): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.19–8.12 (m, 2H), 8.08–8.00 (m, 2H), 7.66–7.55 (m,4H), 7.52–7.36 (m, 7H), 6.47 (dd, *J* = 8.2, 3.7 Hz, 1H), 4.80 (dd, *J* = 11.9, 8.2 Hz, 1H), 4.72 (dd, *J* = 11.9, 3.7 Hz, 1H) [3].

2-Hydroxy-3-methoxypropyl benzoate (**6a**): ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.09–8.03 (m, 2H, Ph), 7.60–7.55 (m, 1H, Ph), 7.48–7.41 (m, 2H, Ph), 4.45–4.36 (m, 2H, C*H*$_2$OCOPh), 4.19–4.12 (m, 1H, C*H*OH), 3.59–3.47 (m, 2H, C*H*$_2$OCH$_3$), 3.42 (s, 3H, OC*H*$_3$) [4].

3-Methoxypropane-1,2-diyl dibenzoate (**6b**): ^{1}H-NMR (500 MHz,$CDCl_3$) δ 8.13–8.04 (m, 4H, Ph), 7.64–7.57 (m, 2H, Ph), 7.51–7.44 (m, 4H, Ph), 5.68–5.62 (m, 1H, C*H*OCOPh), 4.74–4.62 (m,2H, C*H*$_2$OCOPh), 3.84–3.76 (m, 2H, C*H*$_2$OCH$_3$), 3.48 (s, 3H, OC*H*$_3$) [4].

3-(Allyloxy)-2-hydroxypropyl benzoate (**8a**): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.3–8.07 (m, 2H, Ph), 7.64–7.59 (m, 1H, Ph), 7.53–7.45 (m, 2H, Ph), 6.01–5.90 (m, 1H), 5.37–5.22 (m, 2H), 4.52–4.41 (m, 2H), 4.27–4.18 (m, 1H), 4.15–4.07 (m, 2H), 3.63 (ddd, *J* = 15.8, 9.7, 5.2 Hz, 2H) [3].

3-Phenoxypropyl benzoate (**10a**): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.17–8.06 (m, 2H), 7.69–7.59 (m, 1H), 7.56–7.45 (m, 2H), 7.40–7.32 (m, 2H), 7.10–7.00 (m, 1H), 7.02–6.92 (m, 2H), 4.67–4.55 (m, 2H), 4.48–4.40 (m, 1H), 4.17 (qd, *J* = 9.5, 5.2 Hz, 2H) [5].

3-Phenoxypropane-1,2-diyl dibenzoate (**10b**): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.08 (dt, *J* = 12.2, 6.1 Hz, 4H), 7.61 (dd, *J* = 13.6, 7.3 Hz, 2H), 7.48 (dd, *J* = 13.8, 7.6 Hz, 4H), 7.40–7.32 (m, 2H), 7.09–6.95 (m, 3H), 5.88–5.78 (m, 1H), 4.92–4.75 (m, 2H), 4.48–4.33 (m, 2H) [5].

Morpholinopropyl benzoate (**14a**): ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.12–8.09 (m, 2H, Ar*H*), 7.64–7.58 (m, 1H, Ar*H*), 7.52–7.46 (m, 2H, Ar*H*), 4.46–4.33 (m, 2H, PhCO$_2$C*H*$_2$-), 4.17–4.11 (m, 1H, PhCO$_2$CH$_2$C*H*-),3.79–3.73 (m, 4H, -C*H*$_2$OC*H*$_2$-), 2.75–2.69 (m, 2H, -C*H*$_2$CH(OH)-), 2.55(m, 2H, -C*H*$_2$CH$_2$OCH$_2$-), 2.53–2.48 (m, 2H, -CH$_2$OCH$_2$C*H*$_2$-) [6].

3-Morpholinopropane-1,2-diyl dibenzoate (**14b**): ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.12–8.04 (m, 4H), 7.67–7.57 (m, 2H), 7.55–7.41 (m, 4H), 5.66 (qd, *J* = 6.4, 3.2 Hz, 1H), 4.75 (dd, *J* = 11.9, 3.2 Hz, 1H), 4.69–4.57 (m, 1H), 3.77–3.68 (m, 4H), 2.82–2.72 (m, 2H), 2.68–2.55 (m, 4H) [7].

3-Hydroxybutyl benzoate (**16a**): ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.11–8.05 (m, 2H, Ph), 7.64–7.56 (m, 1H, Ph), 7.52–7.45 (m, 2H, Ph), 4.74–4.37 (m, 1H), 3.78 (t, *J* = 77.9, 19.7, 7.1 Hz, 1H), 2.47–2.14 (m, 1H), 2.06–1.83 (m, 1H), 1.39 (dd, *J* = 73.3, 6.3 Hz, 2H) [3].

Butane-1,3-diyl dibenzoate (**16b**): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.06–8.03 (m, 4H), 7.65–7.53 (m, 2H), 7.51–7.43 (m, 4H), 5.43 (dt, *J* = 12.7, 6.2 Hz, 1H), 4.62–4.44 (m, 2H), 2.31–2.13 (m, 2H), 1.49 (d, *J* = 6.3 Hz, 3H) [3].

3-Hydroxy-3-methylbutyl benzoate (**18**): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.07 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 4.55 (t, *J* = 6.8 Hz, 2H), 2.03 (t, *J* = 6.8 Hz, 2H), 1.37 (s, 6H) [8].

3-Hydroxyadamantan-1-yl)methyl benzoate (**20**): ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.07–8.02 (m, 2H, ph), 7.59–7.54 (m, 1H, Ph), 7.48–7.42 (m, 2H, Ph), 4.01 (s, 2H), 2.29–2.25 (m, 2H), 1.77–1.68 (m, 4H), 1.65–1.53 (m, 8H) [9].

Methyl 2,3-di-O-benzyl-6-O-benzoyl-α-D-glucopyranoside (**22**): ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.10–8.06 (m, 2H, Ph), 7.64–7.58 (m, 1H, Ph), 7.50–7.32 (m, 12H, Ph), 5.06 (d, 1H, *J* = 11.2 Hz, -C*H*$_2$Ph), 4.82 (m, 2H, -C*H*$_2$Ph), 4.76–4.64 (m, 3H, H-1, H-6), 4.59–4.53 (m, 1H, H-3), 3.97–3.85 (m, 2H, H-5,H-2), 3.61–3.54 (m, 1H, H-4), 3.45 (s, 3H, OCH_3) [10].

Methyl 2,3-di-O-benzyl-6-O-benzoyl-β-D-glucopyranoside (**24**): ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.13–8.08 (m, 2H, Ph), 7.60–7.54(m, 1H, Ph), 7.49–7.28(m, 12H, Ph), 4.98–4.91 (m, 2H, -C*H*$_2$Ph), 4.76–4.69 (m, 2H, -C*H*$_2$Ph), 4.71–4.60 (m, 2H, H-6), 4.42 (d, *J* = 7.6 Hz, 1H, H-1), 3.66–3.63(m, 1H, H-4), 3.62 (s, 3H, OCH_3), 3.60–3.58 (m, 1H, H-3), 3.57–3.51 (m, 1H, H-2), 3.50–3.44 (m, 1H, H-5) [11].

Methyl 2,3-di-O-benzyl-6-O-benzoyl-α-D-galactopyranoside (**26**): ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.09–8.05 (m, 2H, Ph), 7.64–7.58 (m, 1H, Ph), 7.51–7.31(m, 12H, Ph), 4.91–4.88(m, 1H, -C*H*$_2$Ph), 4.87 (d, *J* = 3.6 Hz, 1H, H-1), 4.79–4.70(m, 3H, -C*H*$_2$Ph), 4.63–4.51(m, 2H, H-6), 4.13–4.07(m, 2H, H-4,-H-5), 3.98–3.89 (m, 2H, H-2,H-3), 3.42 (s, 3H, OCH_3) [12].

Methyl 2,3-di-O-benzyl-6-O-benzoyl-β-D-galactopyranoside (**28**): ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.06–8.02 (m, 2H, Ph), 7.57 (m, 1H, Ph), 7.47–7.27 (m, 12H, Ph), 4.90 (d, *J* = 11.1 Hz, 1H, -C*H*$_2$Ph), 4.78–4.68 (m, 3H, -C*H*$_2$Ph), 4.65–4.55 (m, 2H, H-6), 4.29 (d, *J* = 7.7 Hz, 1H, H-1), 3.99 (m, 1H, H-4), 3.76–3.72 (m, 1H, H-5), 3.68–3.62 (m,1H, H-2), 3.56 (s, 3H, OCH_3), 3.55–3.51 (m, 1H, H-3) [12].

Methyl 2,3-di-O-benzyl-6-O-benzoyl-α-D-mannopyranoside (**30**): ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.14–8.06 (m, 2H, Ph), 7.63–7.55 (m, 1H, Ph), 7.49–7.30 (m, 12H, Ph), 4.88 (d, *J* = 2.9 Hz, 1H, *H-1*), 4.72–4.65 (m, 5H,-C*H*$_2$Ph, *H*-6), 4.58–4.54 (m, 1H, *H*-6), 4.19–4.12 (m, 1H, *H*-4), 3.94–3.85 (m, 2H, *H*-5, *H*-2, 3.82–3.78 (m, 1H, *H*-3), 3.42 (s, 3H, OC*H*$_3$) [13].

6-O-Benzoyl-D-galactal (**32a**): ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.07–8.01 (m, 2H, Ph), 7.59–7.54 (m,1H, Ph), 7.47–7.41 (m,2H, Ph), 6.39 (dd, *J* = 6.4, 1.6Hz, 1H, *H*-1), 4.75–4.70 (m, 1H, *H*-2), 4.70–4.51 (m, 2H, *H*-6), 4.41 (m,1H, *H*-5), 4.22 (m, 1H, *H*-3), 4.00–3.93 (m, 1H, *H*-4) [14].

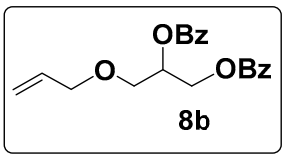
3,6-Di-O-benzoyl-D-galactal (**32b**): ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.12–8.03 (m, 4H, Ph), 7.64–7.54 (m, 2H, Ph), 7.50–7.42 (m,4H, Ph), 6.57 (dd, *J* = 6.2, 1.5 Hz, 1H, *H-1*), 5.76–5.70 (m, 1H, *H-3*), 4.89–4.84 (m, 1H, *H*-2), 4.74–4.64 (m, 2H, *H-6*), 4.51–4.33 (m, 2H, *H*-5, *H-4*) [14].

Methyl 6-O-benzoyl-β-D-glucopyranoside (**34**): ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.05–7.98 (m, 2H), 7.53–7.50 (m, 1H), 7.39 (m, 2H), 4.67–4.62 (m, 1H), 4.56–4.51 (m, 1H), 4.22 (d, *J* = 7.7 Hz, 1H, H_1), 3.63–3.59 (m, 2H), 3.55–3.51 (m, 1H), 3.48 (s, 3H, OMe), 3.44–3.38 (m, 1H) [15].

Methyl 6-O-benzoyl-α-D-galactopyranoside (**36**): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.08–8.03 (m, 2H), 7.59–7.55 (m, 1H), 7.47–7.43 (m, 2H), 4.72 (dd, *J* = 11.4, 6.8 Hz, 1H), 4.53 (dd, *J* = 11.3, 6.5 Hz, 1H), 4.21 (d, *J* = 7.4 Hz, 1H, H_1), 4.01–3.97 (m, 1H), 3.84 (d, *J* = 6.7 Hz, 1H), 3.67–3.64 (m, 2H), 3.57 (s, 3H, OMe) [16].

Methyl 6-O-benzoyl-β-D-galactopyranoside (**38**): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.08–8.03 (m, 2H), 7.59–7.55 (m, 1H), 7.47–7.43 (m, 2H), 4.76 (dd, *J* = 11.2, 6.7 Hz, 1H), 4.56 (dd, *J* = 11.2, 6.6 Hz, 1H), 4.17 (d, *J* = 7.3 H, 1H, *H-1*), 3.84 (m, 2H), 3.69–3.65 (m, 2H), 3.37 (s, 3H, OMe) [16].

2. ^{1}H-NMR and ^{13}C-NMR Spectra



^{1}H-NMR
(500 MHz, $CDCl_3$)

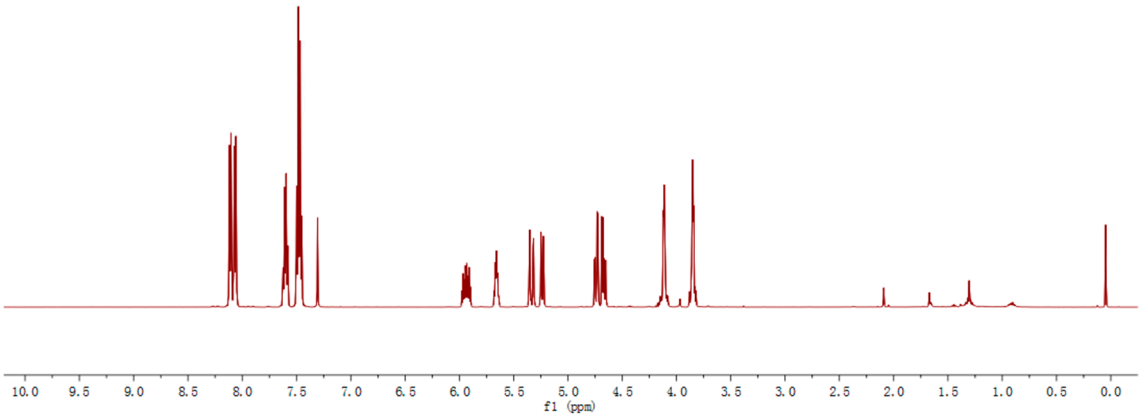
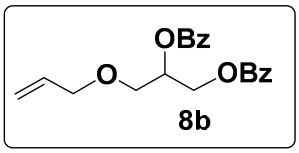


Figure S1. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **8b**.



^{13}C-NMR
(125 MHz, $CDCl_3$)

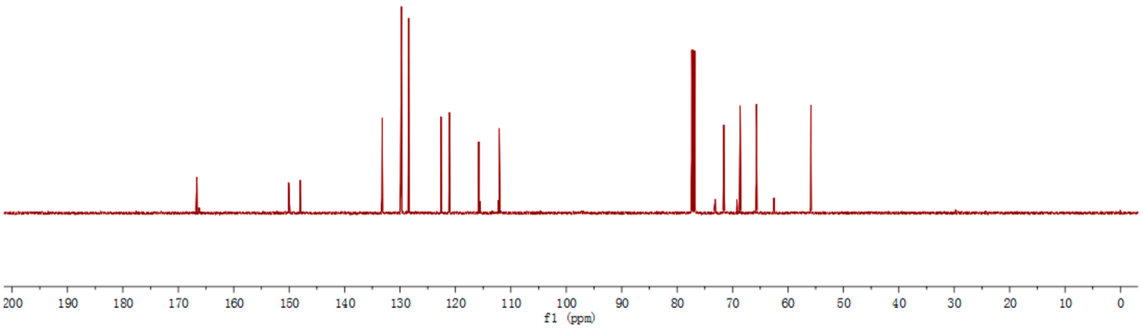
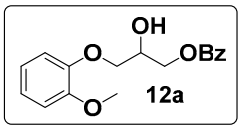


Figure S2. ^{13}C-NMR spectrum (125 MHz, $CDCl_3$) of **8b**.



^{1}H-NMR
(500 MHz, $CDCl_3$)

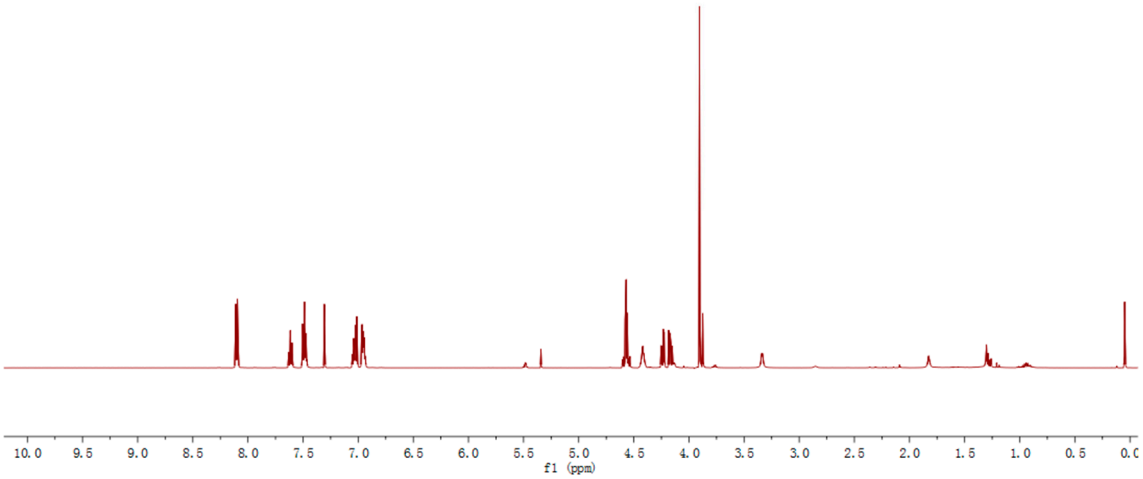
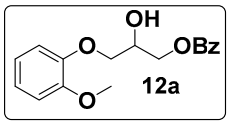
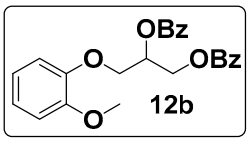


Figure S3. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **12a**.



^{13}C-NMR
(125 MHz, $CDCl_3$)

Figure S4. ^{13}C-NMR spectrum (125 MHz, $CDCl_3$) of **12a**.



^{1}H-NMR
(500 MHz, $CDCl_3$)

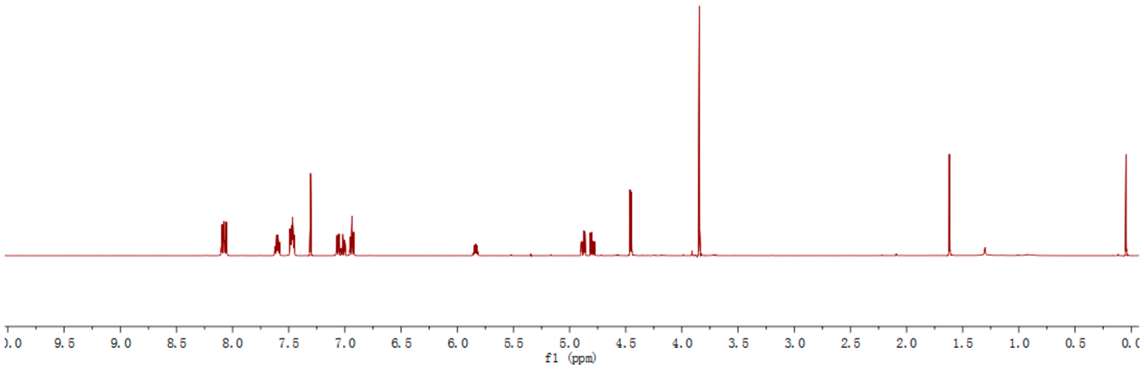
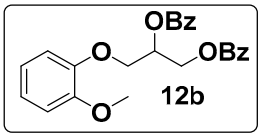


Figure S5. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **12b**.



^{13}C-NMR
(125 MHz, $CDCl_3$)

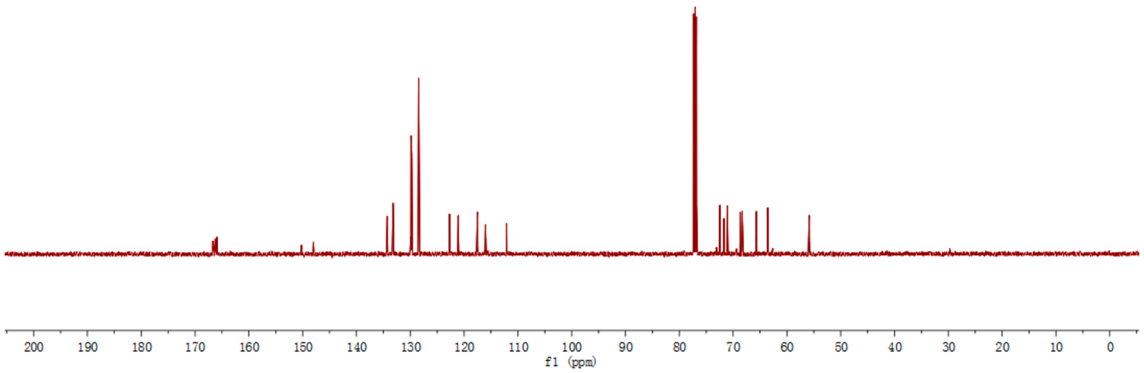


Figure S6. ^{13}C-NMR spectrum (125 MHz, $CDCl_3$) of **12b**.

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