Electronic supplementary information

Water-promoted ortho-selective monohydroxymethylation of phenols in NaBO$_2$ system

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2. General Information

Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. Where necessary, organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under argon. Organic extracts were, in general, dried over anhydrous sodium sulfate (Na₂SO₄). TLC plates were visualized by exposure to ultraviolet light (UV). Chemical shifts for protons are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents (CHCl₃: δ 7.26; DMSO-d₆: δ 2.50). Chemical shifts for carbon resonances are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl₃: δ 77.0; DMSO-d₆: δ 39.43). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constant in Hz. Coupling constants (J) are reported in Hertz (Hz).
3. NMR Spectra

3a. NMR spectra of salicyl alcohol 2a–t

Salicyl alcohol 2a

$^1$H NMR (400 MHz, CDCl$_3$)
Salicyl alcohol 2a

$^{13}$C NMR (100 MHz, CDCl$_3$)
Salicyl alcohol 2b

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2b

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2c

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2e

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2d

$^1H$ NMR (300 MHz, CDCl$_3$)
Salicyl alcohol 2d

$^{13}$C NMR (75 MHz, CDCl$_3$)
Salicyl alcohol 2e

$^1$H NMR (300 MHz, CDCl$_3$)
Salicyl alcohol 2e

$^{13}$C NMR (75 MHz, CDCl$_3$)
Salicyl alcohol 2f

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2f

$^{13}$C NMR (75 MHz, CDCl$_3$)
Salicyl alcohol 2g

$^1$H NMR (300 MHz, CDCl$_3$)
Salicyl alcohol 2g

$^{13}$C NMR (75 MHz, CDCl$_3$)
Salicyl alcohol 2h

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2h

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2i

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2i

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2j

$^1$H NMR (300 MHz, CDCl$_3$)
Salicyl alcohol 2j

$^{13}$C NMR (75 MHz, CDCl$_3$)
Salicyl alcohol 2k

$^1$H NMR (300 MHz, CDCl$_3$)
Salicyl alcohol 2k

$^{13}$C NMR (75 MHz, CDCl$_3$)
Salicyl alcohol 21

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2m

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2m

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2n

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2n

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Salicyl alcohol 20

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2o

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2p

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2p

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2q

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2q

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2q

HSQC (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2q

HMBC (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2r

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2r

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2s

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2s

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2s

HSQC (100 MHz, DMSO-$d_6$)
Salicyl alcohol 2t

$^1$H NMR (400 MHz, DMSO-$d_6$)
Salicyl alcohol 2t

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
3b. NMR spectra of bishydroxymethyled product 3a

$^1$H NMR (300 MHz, CDCl$_3$)
Bishydroxymethyled product 3a

$^{13}$C NMR (75 MHz, CDCl$_3$)
3c. NMR spectra of bishydroxymethyelled product 3i

$^1$H NMR (400 MHz, DMSO-$d_6$)
Bishydroxymethyled product 3i

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
3d. NMR spectra of *para*-hydroxymethylated product 4d

$^1$H NMR (400 MHz, DMSO-$d_6$)
para-Hydroxymethyled product 4d

$^{13}$C NMR (100 MHz, DMSO-$d_6$)