Action of Bisnucleophiles on \((E)-3-[3-(2-Hydroxyphenyl)-3-oxoprop-1-en-1-yl]chromones: Versatile Transformations to \(O\)- and \(N\)-Containing Heterocycles

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Supplementary Material

Table of Contents:

**Figure 1.** \(^1\)H NMR spectrum of compound \(2\text{a}\) (300.13 MHz) 2
**Figure 2.** \(^{13}\)C NMR spectrum of compound \(2\text{a}\) (75.47 MHz) 2
**Figure 3.** HMBC NMR spectrum of compound \(2\text{a}\) 3
**Figure 4.** Partial HMBC NMR spectrum of compound \(2\text{a}\) 3
**Figure 5.** \(^1\)H NMR spectrum of compound \(2\text{b}\) (300.13 MHz) 4
**Figure 6.** \(^{13}\)C NMR spectrum of compound \(2\text{b}\) (75.47 MHz) 4
**Figure 7.** \(^1\)H NMR spectrum of compound \(3\text{aa}\) (300.13 MHz) 5
**Figure 8.** \(^{13}\)C NMR spectrum of compound \(3\text{aa}\) (75.47 MHz) 5
**Figure 9.** HMBC NMR spectrum of compound \(3\text{aa}\) 6
**Figure 10.** Partial HMBC NMR spectrum of compound \(3\text{aa}\) 6
**Figure 11.** \(^1\)H NMR spectrum of compound \(3\text{ab}\) (300.13 MHz) 7
**Figure 12.** \(^{13}\)C NMR spectrum of compound \(3\text{ab}\) (75.47 MHz) 7
**Figure 13.** \(^1\)H NMR spectrum of compound \(4\text{a}\) (300.13 MHz) 8
**Figure 14.** \(^{13}\)C NMR spectrum of compound \(4\text{a}\) (75.47 MHz) 8
**Figure 15.** \(^1\)H NMR spectrum of compound \(4\text{b}\) (300.13 MHz) 9
**Figure 16.** \(^{13}\)C NMR spectrum of compound \(4\text{b}\) (75.47 MHz) 9
**Figure 17.** HMBC NMR spectrum of compound \(4\text{b}\) 10
**Figure 18.** Partial HMBC NMR spectrum of compound \(4\text{b}\) 10

Single-Crystal X-ray Diffraction Studies for compounds \(2\text{a}, 3\text{aa}\) and \(4\text{b}\) 11

References 12
Figure 1. $^1$H NMR spectrum of compound 2a (300.13 MHz)

Figure 2. $^{13}$C NMR spectrum of compound 2a (75.47 MHz)
Figure 3. HMBC NMR spectrum of compound 2a

Figure 4. Partial HMBC NMR spectrum of compound 2a
Figure 5. $^1$H NMR spectrum of compound 2b (300.13 MHz)

Figure 6. $^{13}$C NMR spectrum of compound 2b (75.47 MHz)
Figure 7. $^1$H NMR spectrum of compound 3aa (300.13 MHz)

Figure 8. $^{13}$C NMR spectrum of compound 3aa (75.47 MHz)
Figure 9. HMBC NMR spectrum of compound 3aa

Figure 10. Partial HMBC NMR spectrum of compound 3aa
Figure 11. $^1$H NMR spectrum of compound 3ab (300.13 MHz)

Figure 12. $^{13}$C NMR spectrum of compound 3ab (75.47 MHz)
Figure 13. $^1$H NMR spectrum of compound 4a (300.13 MHz)

Figure 14. $^{13}$C NMR spectrum of compound 4a (75.47 MHz)
Figure 15. $^1$H NMR spectrum of compound 4b (300.13 MHz)

Figure 16. $^{13}$C NMR spectrum of compound 4b (75.47 MHz)
Figure 17. HMBC NMR spectrum of compound 4b

Figure 18. Partial HMBC NMR spectrum of compound 4b
Single-Crystal X-ray Diffraction Studies for compounds 2a, 3aa and 4b

Single crystals of compounds 2a, 3aa and 4b were manually harvested from the crystallization vials and immersed in highly viscous FOMBLIN Y perfluoropolyether vacuum oil (LVAC 140/13, Sigma-Aldrich) to avoid degradation caused by the evaporation of the solvent.1 Crystals were mounted on Hampton Research CryoLoops with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses. X-ray diffraction data for 2a and 4b were collected on a Bruker D8 QUEST equipped with Mo Kα sealed tube (λ = 0.71073 Å), a multilayer TRIUMPH X-ray mirror, a PHOTON 100 CMOS detector, and a Oxford Instruments Cryostrem 700+ Series low temperature device. Crystal data for 3aa were instead collected on a Bruker X8 Kappa APEX II CCD area-detector diffractometer (Mo Kα graphite-monochromated radiation, λ = 0.71073 Å) controlled by the APEX2 software package2 and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely using the software interface Cryopad.3 All crystal data were collected at 180(2) K.

Diffraction images were processed using the software package SAINT+;4 and data were corrected for absorption by the multiscan semi-empirical method implemented in SADABS.5 All structures were solved using the algorithm implemented in SHELXT-2014,6 which allowed the immediate location of almost all of the heaviest atoms composing the molecular unit of the three compounds. The remaining missing and misplaced non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least-squares refinement cycles on \(F^2\) using the latest SHELXL from the 2014 release.7 All structural refinements were performed using the graphical interface ShelXle.8

Hydrogen atoms bound to carbon were placed at their idealized positions using appropriate HFIX instructions in SHELXL: 43 (aromatic carbon atoms), 13 (tertiary carbon atoms), 23 (–CH₂– carbon atoms) or 137 (for the terminal methyl group). These hydrogen atoms were included in subsequent refinement cycles with isotropic thermal displacements parameters (\(U_{iso}\)) fixed at 1.2 (for the three former families of hydrogen atoms) or 1.5×\(U_{eq}\) (solely for those associated with the methyl group) of the parent carbon atoms.

In compounds 2a and 3aa the vast majority of the hydrogen atoms attached to both nitrogen and oxygen atoms could be were directly located from difference Fourier maps. These hydrogen atoms were, in this fashion, included in the final structural model with the N–H and O–H distances restrained to to 0.95(1) Å. For the case of the amino group in compound 3aa the H⋯H distance was further restrained to 1.55(1) Å in order to ensure a chemically reasonable geometry for this terminal chemical moiety. The exception concerns the hydroxyl group in compound 3aa for which the hydrogen atom was added geometrically using the HFIX 147 instruction in SHELXL. In all cases the isotropic thermal displacements parameters (\(U_{iso}\)) of these hydrogen atoms were fixed at 1.5×\(U_{eq}\) of the parent atoms.
The last difference Fourier map synthesis showed: for **2a**, the highest peak (0.388 eÅ⁻³) and the deepest hole (-0.154 eÅ⁻³) located at 0.67 and 0.49 Å from C5 and H2, respectively; for **3aa**, the highest peak (0.232 eÅ⁻³) and the deepest hole (-0.209 eÅ⁻³) located at 0.71 and 0.60 Å from C2 and C18, respectively; for **4b**, the highest peak (0.989 eÅ⁻³) and the deepest hole (-0.332 eÅ⁻³) located at 0.95 and 0.39 Å from C10 and H10, respectively. Structural drawings have been created using the software package Crystal Impact Diamond.⁹

Crystallographic data (including structure factors) for the crystal structure of compound **3a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-1050452. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, U.K. FAX: (+44) 1223 336033. E-mail: deposit@ccdc.cam.ac.uk.

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