Solar Photochemistry: Optimisation of the Photo Friedel-Crafts Acylation of Naphthoquinones

Lorna J. Mitchell, William Lewis and Christopher J. Moody*

Supplementary Information

Table of Contents

Experimental Details for the Preparation of Starting Materials S2
X-Ray Crystallographic Data S11
Copies of $^1$H and $^{13}$C NMR Spectra S12
Selected HMBC Spectra for Regiochemical Assignments S90
Wavelength Emission Spectra S94
References S97

*School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K; Fax: (+44) 115 951 3564; E-mail: c.j.moody@nottingham.ac.uk
**Experimental Details for the Preparation of Starting Materials**

**Preparation of Functionalised Aldehydes**

**4-Chlorobutanal**

\[
\begin{align*}
\text{Cl} & \quad \text{OH} & \quad \rightarrow & \quad \text{Cl} & \quad \text{O} \\
\end{align*}
\]

The reaction was carried out according to the procedure in Snyder et al.\(^1\) with minor modifications. To 4-chloro-1-butanol (2.80 mL, 28.2 mmol) in dichloromethane (100 mL) was added PCC (7.30 g, 33.9 mmol) and silica gel (7.30 g) and the reaction mixture was stirred at ambient temperature for 16 h. The resulting black slurry was filtered through a short column of florasil, washed with ether (3 × 100 mL) and concentrated in vacuo. The **title compound** (2.17 g, 73%) was isolated as a colourless oil which was used in the next step without further purification; \(\delta_H\) (400 MHz; CDCl\(_3\)) 9.79 (1 H, s, CH), 3.57 (2 H, t, \(J 6.50\), CH\(_2\)), 2.65 (2 H, td, \(J 7.0, 0.8\), CH\(_2\)CO), 2.08 (2 H, pent, \(J 6.5\), CH\(_2\)); \(\delta_C\) (100 MHz; CDCl\(_3\)) 200.9 (CHO), 44.0 (CH\(_2\)), 40.8 (CH\(_2\)), 24.8 (CH\(_2\)). Data are consistent with those reported in the literature.\(^2\)

**3-(t-Butyldimethylsiloxy)propanal**

\[
\begin{align*}
\text{OH} & \quad \rightarrow & \quad \text{OTBDMS} & \quad \rightarrow & \quad \text{OTBDMS} \\
\end{align*}
\]

The reaction was carried out according to the procedure in McDougal et al.\(^3\) with minor modifications. Sodium hydride (2.63 g, 65.7 mmol) was washed with pentane (3 × 10 mL) and dried under argon. THF (125 mL) was added followed by subsequent slow addition of the propane-1,3-diol (5.00 g, 65.7 mmol) and the reaction mixture was stirred at ambient temperature. After 45 min, TBDMS-Cl (9.90 g, 65.7 mmol) was added and the reaction mixture was stirred for a further 45 min. The reaction was diluted with ether (200 mL) and washed with sodium carbonate solution (200 mL), brine (200 mL),
dried (MgSO₄), filtered and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (light petroleum → 70:30 light petroleum/ethyl acetate) to afford product (10.6 g, 85%) as a colourless oil; δₜₕ (400 MHz; CDCl₃) 3.73 (1 H, td, J 6.1, 1.5, CH₂), 3.68 (1 H, td, J 5.8, 1.8, CH₂), 3.14 (1 H, s, OH), 1.69 (1 H, quint., J 5.6, CH₂), 0.83 (9 H, d, J 0.6, 3 × CH₃), 0.00 (6 H, d, J 1.6, 2 × CH₃); δₜₖ (100 MHz; CDCl₃) 62.0 (CH₂), 61.2 (CH₂), 34.4 (CH₂), 25.7 (CH₃), 18.0 (C), -5.67 (CH₃). Data are consistent with those reported in the literature.

The next step was carried out according to the procedure by Grünanger et al. Oxalyl chloride (1.04 mL, 12.2 mmol) in dichloromethane (27 mL) was cooled to -60 °C and DMSO (1.8 mL, 25.2 mmol) in dichloromethane (5 mL) was added and the reaction mixture stirred. After 5 min, 3-(t-butyldimethylsiloxy)propan-1-ol (2.00 g, 10.5 mmol) was added dropwise, followed by further dropwise addition of triethylamine (7.38 mL, 53.2 mmol). The reaction mixture was stirred whilst being gradually warmed to ambient temperature. After 1 h, water (50 mL) was added and the phases separated. The aqueous phase was back-extracted with further dichloromethane (50 mL) and the combined organic layers were washed with brine (100 mL), water (50 mL) and further brine (50 mL), dried (MgSO₄), filtered and concentrated in vacuo. The residue was dissolved in ether, filtered through Celite and concentrated in vacuo to afford the title compound (1.69 g, 86%) as a colourless oil; δₜₕ (400 MHz; CDCl₃) 9.79 (1 H, t, J 2.3, CH), 3.98 (2 H, t, J 6.0, CH₂), 2.59 (2 H, td, J 6.0, 2.2, CH₂), 0.87 (9 H, s, 3 × CH₃), 0.05 (6 H, s, 2 × CH₃); δₜₖ (100 MHz; CDCl₃) 201.9 (CH), 57.4 (CH₂), 46.5 (CH₂), 25.8 (CH₃), 18.2 (C), -5.5 (CH₃). Data are consistent with those previously reported.

Preparation of Functionalised Naphthoquinones

5-Methoxy-1,4-naphthoquinone 8b
The reaction was carried out according to the procedure in Tietze et al.,\textsuperscript{6} with minor modifications. To 5-hydroxy-1,4-naphthoquinone 8a (100 mg, 0.57 mmol) and silver(I) oxide (100 mg, 0.46 mmol) in dichloromethane (2 mL) was added iodomethane (0.07 mL, 1.12 mmol) and the mixture stirred at ambient temperature. After 20 h further iodomethane (0.03 mL, 0.46 mmol) and silver(I) oxide (100 mg, 0.46 mmol) were added and the reaction mixture stirred for a further 3 h. The reaction mixture was filtered through Celite, washed (dichloromethane) and concentrated \textit{in vacuo}. The residue was purified by flash chromatography on silica gel (light petroleum → 8:2 light petroleum: ethyl acetate) to give the \textit{title compound} 8b (96 mg, 90%) as fine orange crystals; mp 180-183 °C (lit.,\textsuperscript{7} mp 180-185 °C); δ\textsubscript{H} (400 MHz; CDCl\textsubscript{3}) 7.72 (2 H, m, ArH), 7.32 (1 H, dd, J 8.2, 1.0, ArH), 6.87 (2 H, app. br s, CH), 4.02 (3 H, s, OMe); δ\textsubscript{C} (100 MHz; CDCl\textsubscript{3}) 185.1 (C), 184.3 (C), 159.6 (C), 140.8 (CH), 136.1 (CH), 134.9 (CH), 134.0 (C), 119.6 (C), 119.1 (CH), 117.9 (CH), 56.4 (CH\textsubscript{3}). Data are consistent with those reported in the literature.\textsuperscript{6,7}

\textbf{5-Ethoxy-1,4-naphthoquinone 8c}

To 5-hydroxy-1,4-naphthoquinone 8a (100 mg, 0.57 mmol) and silver(I) oxide (100 mg, 0.46 mmol) in dichloromethane (2 mL) was added iodoethane (0.09 mL,
1.12 mmol) and the reaction mixture was stirred at ambient temperature. After 16 h further silver(I) oxide (100 mg, 0.46 mmol) and iodoethane (0.04 mL, 0.46 mmol) were added and the reaction mixture was stirred for a further 4 h. The reaction mixture was concentrated in vacuo and the product was crystallised from the minimum volume of hot toluene/light petroleum to yield the title compound 8c (114 mg, 99%) as a brown solid; mp 78-79 °C; (Found: C, 71.28; H, 4.98; C_{12}H_{10}O_{3} requires C, 71.32; H, 5.18%); (Found: M+Na^+, 225.0521. C_{12}H_{10}O_{3}Na^+ requires 225.0522); \( \lambda_{\text{max}} \) (CH_{2}Cl_{2})/nm 274 (log \( \varepsilon \) 5.71), 400 (4.37); \( \nu_{\text{max}} \) (CHCl_{3})/cm\(^{-1}\) 3686, 3012, 2415, 1521, 1239; \( \delta \)H (400 MHz; CDCl_{3}) 7.69 (1 H, dd, \( J \) 7.6, 1.4, ArH), 7.63 (1 H, app. br t, \( J \) 8.3, ArH), 7.27 (1 H, dd, \( J \) 8.3, 1.4, ArH), 6.83 (2 H, app. br s, CH), 4.20 (2 H, q, \( J \) 7.0, CH_{2}), 1.53 (3 H, t, \( J \) 7.0, CH_{3}); \( \delta \)C (100 MHz; CDCl_{3}) 185.3 (C), 184.2 (C), 159.0 (C), 140.9 (CH), 136.1 (CH), 134.8 (CH), 134.0 (C), 119.8 (C), 119.1 (CH), 119.0 (CH), 65.1 (CH_{2}), 14.6 (CH_{3}); m/z (ESI) 225 (M+Na^+, 100%), 103 (M+H^+, 5).

5-Isopropoxy-1,4-Naphthoquinone 8d

To 5-hydroxy-1,4-naphthoquinone 8a (200 mg, 1.15 mmol) and silver(I) oxide (220 mg, 0.96 mmol) in dichloromethane (2 mL) was added 2-iodopropane (0.12 mL, 2.29 mmol) and the reaction mixture was stirred at ambient temperature. After 16 h further silver(I) oxide (440 mg, 1.92 mmol) and 2-iodopropane (0.4 mL, 9.20 mmol) were added and the reaction mixture was stirred for a further 4 h. The reaction mixture was concentrated in vacuo to yield the title compound 8d (248 mg, 100%) as a dark green solid; mp 89-90 °C; (Found: M+Na^+, 239.0669. C_{13}H_{12}O_{3}Na^+ requires 239.0679);
\[ \lambda_{\text{max}} (\text{CH}_2\text{Cl}_2)/\text{nm} \ 275 \ (\log \varepsilon 4.40), \ 322 \ (2.91), \ 403 \ (3.46); \ \nu_{\text{max}} (\text{CH}_2\text{Cl}_2)/\text{cm}^{-1} \ 2983, 1662, 1585, 1464, 1298, 1251; \ \delta_{\text{H}} (400 \text{ MHz; CDCl}_3) \ 7.70 \ (1 \text{ H, dd, } J 7.6, 1.2, \text{ ArH}), \ 7.63 \ (1 \text{ H, app. br t, } J 8.3, \text{ ArH}), \ 7.30 \ (1 \text{ H, app. br d, } J 8.3, \text{ ArH}), \ 6.85 \ (2 \text{ H, app. br s, CH}), \ 4.69 \ (1 \text{ H, sept, } J 6.2, \text{ CH}), \ 1.45 \ (6 \text{ H, d, } J 6.2, \text{ CH}_3); \ \delta_{\text{C}} (100 \text{ MHz; CDCl}_3) \ 185.3 \ (\text{C}), \ 184.0 \ (\text{C}), \ 158.3 \ (\text{C}), \ 141.0 \ (\text{CH}), \ 136.0 \ (\text{CH}), \ 134.5 \ (\text{CH}), \ 134.2 \ (\text{C}), \ 121.3 \ (\text{CH}), \ 120.8 \ (\text{C}), \ 119.1 \ (\text{CH}), \ 72.3 \ (\text{CH}), \ 22.0 \ (\text{CH}_3); \ m/z \ (\text{ESI}) \ 239 \ (\text{M}+\text{Na}^+, \ 100\%).

5-Methoxymethoxy-1,4-naphthoquinone 8e

The reaction was carried out according to the procedure in Nandaluru et al.\textsuperscript{8} with minor modifications. To 5-hydroxy-1,4-naphthoquinone 8a (200 mg, 1.15 mmol) and MOM-Cl (0.23 mL, 2.87 mmol) in dichloromethane (3 mL) at 0 °C was added DIPEA (0.40 mL, 2.30 mmol) dropwise over 5 min and the reaction mixture was stirred at ambient temperature for 16 h. To the reaction mixture was added saturated ammonium chloride solution (50 mL) and the phases separated. The aqueous layer was washed with dichloromethane (50 mL), and the organic layers combined, dried (MgSO\textsubscript{4}), filtered and concentrated \textit{in vacuo}. The residue was purified by flash chromatography on silica gel (4:1 light petroleum: ethyl acetate) to afford the \textit{title compound} 8e (179 mg, 79%) as an orange solid; mp 98-100 °C (lit.,\textsuperscript{8} mp 98-101 °C); (Found: C, 66.00; H, 4.67; \text{C}_{12}\text{H}_{10}\text{O}_4 \text{ requires C, 66.05; H, 4.62 %); (Found: M}+\text{Na}^+, 241.0467. \text{C}_{12}\text{H}_{10}\text{O}_4\text{Na}^+ \text{ requires 241.0471);} \lambda_{\text{max}} (\text{CH}_2\text{Cl}_2)/\text{nm} \ 246 \ (\log \varepsilon 5.16), \ 380 \ (4.28); \ \nu_{\text{max}} (\text{CHCl}_3)/\text{cm}^{-1} \ 3012, 1663, 1587, 1335, 994; \ \delta_{\text{H}} (400 \text{ MHz; CDCl}_3) \ 7.75 \ (1 \text{ H, dd, } J 7.5, 1.0, \text{ ArH}), \ 7.63
(1 H, app. b. t, J 8.3, ArH), 7.51 (1 H, dd, J 8.3, 1.0, ArH), 6.85 (2 H, app. br. s, CH), 5.33 (2 H, s, CH₂), 3.52 (3 H, s, OCH₃); δ_C (100 MHz; CDCl₃) 184.8 (C), 184.0 (C), 157.0 (C), 140.6 (CH), 136.2 (CH), 134.6 (CH), 133.8 (C), 122.2 (CH), 120.5 (C), 120.3 (CH), 95.0 (CH₂), 56.5 (CH₃); m/z (ESI) 241 (M+Na⁺, 100%)

6-Hydroxy-1,4-naphthoquinone 12a

A stirred solution of 1,6-dihydroxynapthalene 11 (5.00 g, 31.2 mmol) and salcomine (507 mg, 1.56 mmol) in DMF (33 mL) was bubbled rapidly with oxygen at ambient temperature. After 16 h, ether (200 mL) and brine (200 mL) were added and phases separated. The aqueous layer was back-extracted with further ether (10 × 200 mL) and the organic layers combined, dried (Na₂SO₄), filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (7:3 light petroleum: ethyl acetate) to give the title compound 12a (2.50 g, 46%) as a bright orange solid; mp 170-171 °C (decomp) (lit.,⁹ mp 170 °C); (Found: C, 68.67; H, 3.42; C₁₀H₆O₃ requires C, 68.97; H, 3.47 %); (Found: M-H⁺, 173.0238. C₁₀H₅O₃⁻ requires 173.0244); λ_max (CH₂Cl₂)/nm 274 (log ε 5.26), 385 (3.26); ν_max (CHCl₃)/cm⁻¹ 3689, 3607, 3045, 1602, 1523, 1240; δ_H (400 MHz; MeOD) 7.92 (1 H, d, J 8.5, ArH), 7.34 (1 H, d, J 2.6, ArH), 7.13 (1 H, dd, J 8.5, 2.6, ArH), 6.90 (2 H, d, J 2.1, CH); δ_C (100 MHz; MeOD) 186.7 (C), 185.6 (C), 164.6 (C), 140.3 (CH), 139.5 (CH), 135.6 (C), 130.2 (CH), 125.8 (C), 121.9 (CH), 113.2 (CH); m/z (ESI) 173 (M-H⁺, 100%).
6-Methoxy-1,4-naphthoquinone 12b

To 6-hydroxy-1,4-naphthoquinone 12a (100 mg, 0.57 mmol) and silver(I) oxide (200 mg, 0.92 mmol) in CH₂Cl₂ (2 mL) was added iodomethane (0.1 mL, 1.60 mmol) and the mixture stirred at ambient temperature for 3 d. The reaction mixture was filtered through Celite, washed with dichloromethane (50 mL) and concentrated in vacuo to afford the title compound 12b (107 mg, 100%) as a fine yellow solid; mp 132–133 °C (lit.,¹⁰ mp 133-135 °C); (Found: C, 69.82; H, 4.22; C₁₁H₈O₃ requires C, 70.21; H, 4.29 %); (Found: M+H⁺, 189.0546. C₁₁H₈O₃⁺ requires 189.0546); λ max (CH₂Cl₂)/nm 261 (log ε 4.91), 382 (3.89); ν max (CHCl₃)/cm⁻¹; 3012, 1667, 1593, 131, 1292; δH (400 MHz; CDCl₃) 8.02 (1 H, d, J 8.6, ArH), 7.50 (1 H, d, J 2.7, ArH), 7.21 (1 H, dd, J 8.6, 2.7, ArH), 6.92 (2 H, app br. s, CH), 3.95 (3 H, s, OCH₃); δC (100 MHz; CDCl₃) 185.2 (C), 184.1 (C), 164.1 (C), 139.0 (CH), 138.2 (CH), 133.9 (C), 128.9 (CH), 125.5 (C), 120.5 (CH), 109.6 (CH), 55.9 (CH₂); m/z (ESI) 399 (2M+Na⁺, 100%), 211 (M+Na⁺, 98), 189 (M+H⁺, 47).

6-Ethoxy-1,4-naphthoquinone 12c

To 6-hydroxy-1,4-naphthoquinone 12a (50 mg, 0.29 mmol) and silver(I) oxide (106 mg, 0.46 mmol) in CH₂Cl₂ (1 mL) was added iodoethane (0.06 mL, 0.81 mmol) and the
mixture stirred at ambient temperature for 16 h. The reaction mixture was filtered through Celite, washed with dichloromethane (50 mL) and concentrated \textit{in vacuo} to afford the \textit{title compound} \textit{12c} (44 mg, 76%) as a fine yellow solid; mp 116-117 °C; (Found: C, 71.07; H, 4.99; \( \text{C}_{13}\text{H}_{12}\text{O}_3 \) requires C, 71.28; H, 4.98%); (Found: M+Na\(^{+} \), 225.0522. \( \text{C}_{12}\text{H}_{10}\text{O}_3\text{Na}^{+} \) requires 225.0522); \( \lambda_{\text{max}} \) \((\text{CH}_2\text{Cl}_2)/\text{nm} 255 \) (log \( \varepsilon \) 4.37), 263 (4.39), 383 (3.27), 386 (3.20); \( \nu_{\text{max}} \) \((\text{CHCl}_3)/\text{cm}^{-1} \); 3012, 2415, 1666, 1595, 1333, 1239, 965; \( \delta_{\text{H}} \) (400 MHz; CDCl\(_3\)) 8.02 (1 H, d, \( J \) 8.6, ArH), 7.50 (1 H, d, \( J \) 2.7, ArH), 7.20 (1 H, dd, \( J \) 8.6, 2.7, ArH), 6.92 (2 H, app br. s, CH), 4.19 (2 H, q, \( J \) 6.9, CH\(_2\)), 1.48 (3 H, t, \( J \) 7.0, CH\(_3\)); \( \delta_{\text{C}} \) (100 MHz; CDCl\(_3\)) 185.2 (C), 184.1 (C), 163.6 (C), 139.0 (CH), 138.2 (CH), 133.9 (C), 128.9 (CH), 125.3 (C), 120.8 (CH), 110.1 (CH), 64.4 (CH\(_2\)), 14.6 (CH\(_3\)); \( m/z \) (ESI) 225 (M+Na\(^{+} \), 100%), 203 (M+H\(^{+} \), 35).

\textbf{6-Isopropoxy-1,4-naphthoquinone 12d}

To 6-hydroxy-1,4-naphthoquinone \textit{12a} (100 mg, 0.57 mmol) and silver(I) oxide (110 mg, 0.48 mmol) in dichloromethane (1 mL) was added 2-iodopropane (0.1 mL, 1.12 mmol) and the mixture stirred at ambient temperature. After 16 h further silver(I) oxide (220 mg, 0.96 mmol) and 2-iodopropane (0.2 mL, 2.2 mmol) was added and the reaction mixture was stirred for a further 4 h. The reaction mixture was concentrated \textit{in vacuo} to yield the \textit{title compound} \textit{12d} (123 mg, 100%) as a pale green solid; mp 111-113 °C; (Found: M+Na\(^{+} \), 239.0671. \( \text{C}_{13}\text{H}_{12}\text{O}_3\text{Na}^{+} \) requires 239.0679); \( \lambda_{\text{max}} \) \((\text{CH}_2\text{Cl}_2)/\text{nm} 257 \) (log \( \varepsilon \) 4.54), 264 (4.56), 330 (2.96), 390 (3.54); \( \nu_{\text{max}} \) \((\text{CHCl}_3)/\text{cm}^{-1} \); 2983, 1665, 1592, 1491, 1316, 1110, 1045, 961; \( \delta_{\text{H}} \) (400 MHz; CDCl\(_3\)) 8.02 (1 H, d, \( J \) 8.6, ArH), 7.48
(1 H, d, J 2.6, ArH), 7.17 (1 H, dd, J 8.6, 2.7, ArH), 6.92 (2 H, app. br. s, CH), 4.76 (1 H, sept, J 6.0, CH), 1.40 (6 H, d, J 6.0, CH₃); δ_C (100 MHz; CDCl₃) 185.3 (C), 184.1 (C), 162.7 (C), 139.0 (CH), 138.2 (CH), 133.9 (C), 129.0 (CH), 125.0 (C), 121.7 (CH), 111.0 (CH), 70.8 (CH), 21.8 (CH₃); m/z (ESI) 239 (M+Na⁺, 100%), 217 (M+H⁺, 11).

6-Methoxymethoxy-1,4-naphthoquinone 12e

To 6-hydroxy-1,4-naphthoquinone 12a (100 mg, 0.57 mmol) and MOM-Cl (0.12 mL, 1.44 mmol) in dichloromethane (2 mL) at 0 °C was added DIPEA (0.2 mL, 1.15 mmol) dropwise over 5 min and the reaction mixture was stirred at ambient temperature for 16 h. To the reaction mixture was added saturated ammonium chloride solution (50 mL) and the phases separated. The aqueous layer was washed with dichloromethane (50 mL) and the organic layers combined, dried (MgSO₄), filtered and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (4:1 light petroleum: ethyl acetate) to afford the title compound 12e (82 mg, 66%) as an orange solid; mp 110-112 °C; (Found: M+Na⁺, 241.0468. C₁₂H₁₀O₄Na⁺ requires 241.0471); λ_max (CH₂Cl₂)/nm 254 (log ε 4.69), 260 (4.69), 372 (3.69); ν_max (CHCl₃)/cm⁻¹; 3012, 1668, 1595, 1312, 988; δ_H (400 MHz; CDCl₃) 8.00 (1 H, d, J 8.6, ArH), 7.62 (1 H, d, J 2.6, ArH), 7.32 (1 H, dd, J 8.6, 2.6, ArH), 6.91 (2 H, app br. s, CH), 5.29 (2 H, s, CH₂), 3.48 (3 H, s, CH₃); δ_C (100 MHz; CDCl₃) 184.8 (C), 184.0 (C), 161.6 (C), 138.8 (CH), 138.3 (CH), 133.8 (C), 128.8 (CH), 126.1 (C), 121.5 (CH), 112.5 (CH), 94.1 (CH₂), 56.4 (CH₃); m/z (ESI) 241 (M+Na⁺, 100%), 219 (M+H⁺, 17).
**X-Ray Crystallographic Studies**

All data sets were collected either with a SuperNova Cu diffractometer or a GV1000 diffractometer. The crystal was kept at 120(2)K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimisation. Crystal structure data and details are listed in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>9e</th>
<th>10c</th>
<th>13b</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC</td>
<td>952123</td>
<td>952121</td>
<td>952122</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{16}$H$</em>{18}$O$_{5}$</td>
<td>C$<em>{16}$H$</em>{18}$O$_{4}$</td>
<td>C$<em>{15}$H$</em>{16}$O$_{4}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>290.30</td>
<td>274.30</td>
<td>260.28</td>
</tr>
<tr>
<td>Crystal size/mm$^3$</td>
<td>$0.51 \times 0.0864 \times 0.0426$</td>
<td>$0.126 \times 0.1016 \times 0.0629$</td>
<td>$0.1243 \times 0.0791 \times 0.0316$</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2$_1$/c</td>
<td>P2$_1$/n</td>
<td>Pbca</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a/$\text{Å}$</td>
<td>15.7243(11)</td>
<td>7.7968(2)</td>
</tr>
<tr>
<td></td>
<td>b/$\text{Å}$</td>
<td>5.0123(3)</td>
<td>21.1512(5)</td>
</tr>
<tr>
<td></td>
<td>c/$\text{Å}$</td>
<td>18.5815(12)</td>
<td>9.1046(3)</td>
</tr>
<tr>
<td></td>
<td>$\alpha$/°</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>$\beta$/°</td>
<td>107.285</td>
<td>114.189</td>
</tr>
<tr>
<td></td>
<td>$\gamma$/°</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume/$\text{Å}^3$</td>
<td>1398.35(17)</td>
<td>1369.64(7)</td>
<td>2483.67(15)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>5181</td>
<td>12604</td>
<td>13106</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2731 [R(int) = 0.0207]</td>
<td>2766 [R(int) = 0.0207]</td>
<td>2494 [R(int) = 0.0371]</td>
</tr>
<tr>
<td>Final R indexes R[I&gt;=2$\sigma$(I)]</td>
<td>R$_1$ = 0.0362, wR$_2$ = 0.0987</td>
<td>R$_1$ = 0.0329, wR$_2$ = 0.0900</td>
<td>R$_1$ = 0.0438, wR$_2$ = 0.1128</td>
</tr>
<tr>
<td>Final R indexes (all data)</td>
<td>R$_1$ = 0.0362, wR$_2$ = 0.0987</td>
<td>R$_1$ = 0.0378, wR$_2$ = 0.0941</td>
<td>R$_1$ = 0.0525, wR$_2$ = 0.1191</td>
</tr>
</tbody>
</table>
4-Chlorobutanal

$\text{^1H NMR at 400 MHz in CDCl}_3$
4-Chlorobutanal

\[ \text{Cl} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO} \]

\(^{13}\text{C}\) NMR at 100 MHz in CDCl\textsubscript{3}
$^1$H NMR at 400 MHz in CDCl$_3$
$\text{3-((t-butyldimethylsilyl)oxy)propan-1-ol}$

$^{13}\text{C NMR at 100 MHz in CDCl}_3$
3-(t-Butyldimethylsiloxy)propanal

$\text{OTBDMS}$

$\text{H NMR at 400 MHz in CDCl}_3$
3-(t-Butyldimethylsiloxy)propanal

$\text{C NMR at 100 MHz in CDCl}_3$
5-Methoxy-1,4-naphthoquinone 8b

$^1$H NMR at 400 MHz in CDCl$_3$
$\text{5-Methoxy-1,4-naphthoquinone 8b}$

\[ 13^C \text{ NMR at 100 MHz in CDCl}_3 \]
5-Ethoxy-1,4-naphthoquinone 8c

$^1$H NMR at 400 MHz in CDCl$_3$
5-Ethoxy-1,4-naphthoquinone 8c

$\text{LM-011-CARBON.ESP}$

$\text{13C NMR at 100 MHz in CDCl}_3$
$^1$H NMR at 400 MHz in CDCl$_3$
$^{13}$C NMR at 100 MHz in CDCl$_3$

5-Methoxymethoxy-1,4-naphthoquinone 8e
$^1$H NMR at 400 MHz in CDCl$_3$

**5-Methoxymethoxy-1,4-naphthoquinone 8e**
$^{13}$C NMR at 100 MHz in CDCl$_3$

6-Hydroxy-1,4-naphthoquinone 12a
$^1$H NMR at 400 MHz in MeOD

6-Hydroxy-1,4-naphthoquinone 12a
$^{13}$C NMR at 100 MHz in MeOD

6-Methoxy-1,4-naphthoquinone 12b
$^1$H NMR at 400 MHz in CDCl$_3$

6-Methoxy-1,4-naphthoquinone 12b
$^{13}$C NMR at 100 MHz in CDCl$_3$

6-Ethoxy-1,4-naphthoquinone 12c
$\text{H NMR at 400 MHz in CDCl}_3$

6-Ethoxy-1,4-naphthoquinone 12c
$^{13}$C NMR at 100 MHz in CDCl$_3$

6-Isopropoxy-1,4-naphthoquinone 12d
$^1$H NMR at 400 MHz in CDCl$_3$

**6-Isopropoxy-1,4-naphthoquinone 12d**
$^{13}$C NMR at 100 MHz in CDCl$_3$

6-(Methoxymethoxy)-1,4-naphthoquinone 12e
$^1\text{H} \text{ NMR at 400 MHz in CDCl}_3$

6-(Methoxymethoxy)-1,4-naphthoquinone 12e
$^{13}$C NMR at 100 MHz in CDCl$_3$

1-(1,4-Dihydroxy-2-naphthyl)-1-butanone 6a
$^1$H NMR at 400 MHz in $d_6$-DMSO

1-(1,4-Dihydroxy-2-naphthyl)-1-butanone 6a
$^{13}$C NMR at 100 MHz in $d_6$-DMSO

1-(1,4-Dihydroxy-2-naphthyl)-2-methyl-1-propanone 6b
$^1$H NMR at 400 MHz in d$_6$-DMSO

1-(1,4-Dihydroxy-2-naphthyl)-2-methyl-1-propanone 6b
$^{13}$C NMR at 100 MHz in $d_6$-DMSO

$1$-(1,4-Dihydroxy-2-naphthyl)-1-hexanone 6c
$^{1}$H NMR at 400 MHz in $d_6$-DMSO

1-(1,4-Dihydroxy-2-naphthyl)-1-hexanone 6c
$^{13}$C NMR at 100 MHz in $d_6$-DMSO

1-(1,4-dihydroxynaphthalen-2-yl)-3-phenylpropan-1-one 6d
$^1$H NMR at 400 MHz in d$_6$-DMSO

1-(1,4-dihydroxynaphthalen-2-yl)-3-phenylpropan-1-one 6d
$^{13}$C NMR at 100 MHz in $d_6$-DMSO

$1$-(1,4-Dihydroxy-2-naphthyl)-1-ethanone 6e
$^1$H NMR at 400 MHz in d$_6$-DMSO

$1$-$(1,4$-Dihydroxy-2-naphthyl)$-1$-ethanone 6e
$^{13}$C NMR at 100 MHz in $d_6$-DMSO
$^1$H NMR at 400 MHz in $d_6$-DMSO

**1-(1,4-Dihydroxy-2-naphthyl)-1-propanone 6f**
\[^{13}\text{C}\] NMR at 100 MHz in d\textsubscript{6}-DMSO
4-Chloro-1-(1,4-dihydroxynaphthalen-2-yl)butan-1-one 6g

$^1$H NMR at 400 MHz in d$_6$-DMSO
4-Chloro-1-(1,4-dihydroxynaphthalen-2-yl)butan-1-one 6g

$^{13}$C NMR at 100 MHz in $d_6$-DMSO
3-((t-Butyldimethylsilyl)oxy)-1-(1,4-dihydroxynaphthalen-2-yl)1-propanone 6h

$^1$H NMR at 400 MHz in CDCl$_3$
3-((t-Butyldimethylsilyl)oxy)-1-(1,4-dihydroxynaphthalen-2-yl)-1-propanone 6h

Chemical Shift (ppm)

13C NMR at 100 MHz in CDCl₃
1-(1,4-Dihydroxynaphthalen-2-yl)pent-4-en-1-one 6i

$^1$H NMR at 400 MHz in d$_6$-DMSO
1-(1,4-Dihydroxynaphthalen-2-yl)pent-4-en-1-one 6i

$^{13}$C NMR at 100 MHz in $d_6$-DMSO
(1,4-dihydroxynaphthalen-2-yl)(4-fluorophenyl)methanone 6j

$\text{OH}$

$\text{OH}$

$\text{F}$

$L\_\text{MIT.LM-278-PRODUCT2_001001r}$

$^1\text{H NMR at 400 MHz in } d_6\text{-acetone}$
(1,4-dihydroxynaphthalen-2-yl)(4-fluorophenyl)methanone 6j

$ ^{13}$C NMR at 100 MHz in $d_6$-acetone
(2,6-difluorophenyl)(1,4-dihydroxynaphthalen-2-yl)methanone 6k

$^{1}H$ NMR at 400 MHz in $d_6$-acetone
(2,6-difluorophenyl)(1,4-dihydroxynaphthalen-2-yl)methanone 6k

$^{13}$C NMR at 100 MHz in d$_6$-acetone
\( (1,4\text{-dihydroxynaphthalen-2-yl})(4\text{-methoxyphenyl})\text{methanone 6l} \)

\( ^{1}H \) NMR at 400 MHz in d\textsubscript{6}-acetone
(1,4-dihydroxynaphthalen-2-yl)(4-methoxyphenyl)methanone 6l

$^{13}$C NMR at 100 MHz in $d_6$-acetone
(1,4-dihydroxynaphthalen-2-yl)(thiophen-2-yl)methanone 6m

$^1$H NMR at 400 MHz in $d_6$-acetone
(1,4-dihydroxynaphthalen-2-yl)(thiophen-2-yl)methanone 6m

$^{13}$C NMR at 100 MHz in $d_6$-acetone
1-(1,4-Dihydroxy-5-methoxynaphthalen-2-yl)butan-1-one 9b

$\text{H NMR at 400 MHz in } d_6\text{-acetone}$
1-(1,4-Dihydroxy-5-methoxynaphthalen-2-yl)butan-1-one 9b

\[ \text{LM-156-P1-CARBON.ESP} \]

\[ \text{13C NMR at 100 MHz in } d_6\text{-acetone} \]
1-(1,4-Dihydroxy-8-methoxynaphthalen-2-yl)butan-1-one 10b

\[
\text{LM-156-P2-PROTON.ESP}
\]

\[\text{\textsuperscript{1}H NMR at 400 MHz in d_{6}-acetone}\]
1-(1,4-Dihydroxy-8-methoxynaphthalen-2-yl)butan-1-one 10b

$\text{OH}$

$\text{O}$

$\text{O}$

$\text{OH}$

$\text{13C NMR at 100 MHz in } d_6\text{-acetone}$
$\text{H NMR at 400 MHz in } d_6\text{-DMSO}$
1-(5-Ethoxy-1,4-dihydroxynaphthalen-2-yl)butan-1-one 9c

\[ \begin{align*}
& & & & 65.39 & & & & & & \\
& & & & 106.15 & & & & & & \\
& & & & 110.65 & & & & & & \\
& & & & 113.11 & & & & & & \\
& & & & 116.76 & & & & & & \\
& & & & 118.80 & & & & & & \\
& & & & 118.76 & & & & & & \\
& & & & 126.85 & & & & & & \\
& & & & 126.91 & & & & & & \\
& & & & 145.39 & & & & & & \\
& & & & 153.07 & & & & & & \\
& & & & 152.63 & & & & & & \\
& & & & 154.70 & & & & & & \\
\end{align*} \]

\[ \text{\textsuperscript{13}C NMR at 100 MHz in } d_6-\text{DMSO} \]
1-(8-Ethoxy-1,4-dihydroxynaphthalen-2-yl)butan-1-one 10c

$^1$H NMR at 400 MHz in $d_6$-DMSO
1-(8-Ethoxy-1,4-dihydroxynaphthalen-2-yl)butan-1-one 10c

$^{13}$C NMR at 100 MHz in d$_6$-DMSO
1-(1,4-Dihydroxy-5-isopropoxynaphthalen-2-yl)butan-1-one 9d

\[
\text{Chemical Shift (ppm)}
\]

1\(^{1}\)H NMR at 400 MHz in d\textsubscript{6}-acetone
1-(1,4-Dihydroxy-5-isopropoxynaphthalen-2-yl)butan-1-one 9d

$^{13}$C NMR at 100 MHz in d$_6$-acetone
$^1$H NMR at 400 MHz in $d_6$-acetone
$1$-(1,4-Dihydroxy-8-isopropoxynaphthalen-2-yl)butan-1-one $10d$

$^{13}$C NMR at 100 MHz in $d_6$-acetone
1-(1,4-Dihydroxy-5-(methoxymethoxy)naphthalen-2-yl)butan-1-one 9e

$^1$H NMR at 400 MHz in $d_6$-acetone
1-(1,4-Dihydroxy-5-(methoxymethoxy)naphthalen-2-yl)butan-1-one 9e

$^{13}$C NMR at 100 MHz in $d_6$-acetone
1-(1,4-Dihydroxy-8-(methoxymethoxy)naphthalen-2-yl)butan-1-one 10e

\[
\text{\textsuperscript{1}H NMR at 400 MHz in } d_6-\text{acetone}
\]
1-(1,4-Dihydroxy-8-(methoxymethoxy)naphthalen-2-yl)butan-1-one 10e

$\text{\(^{13}\text{C\ NMR at 100 MHz in } d_6\text{-acetone} \)}$
1-(1,4-Dihydroxy-6-methoxynaphthalen-2-yl)butan-1-one 13b

H NMR at 400 MHz in d₆-acetone
$1$-(1,4-Dihydroxy-6-methoxynaphthalen-2-yl)butan-1-one $13b$

$^{13}$C NMR at 100 MHz in $d_6$-acetone
$^{1}$H NMR at 400 MHz in $d_6$-acetone
$^{13}$C NMR at 100 MHz in $d_6$-acetone
1-(6-Ethoxy-1,4-dihydroxynaphthalen-2-yl)butan-1-one 13c

$^1$H NMR at 400 MHz in $d_6$-acetone
$^{13}$C NMR at 100 MHz in $d_6$-acetone
1-(7-Ethoxy-1,4-dihydroxynaphthalen-2-yl)butan-1-one 14c

$^1$H NMR at 400 MHz in d₆-acetone
$^{13}$C NMR at 100 MHz in $d_6$-acetone
1-(1,4-Dihydroxy-6-isopropoxynaphthalen-2-yl)butan-1-one 13d

$^1$H NMR at 400 MHz in d$_6$-acetone
$1'$-(1,4-Dihydroxy-6-isopropoxynaphthalen-2-yl)butan-1-one 13d

$\text{Chemical Shift (ppm)}$

$\text{13C NMR at 100 MHz in } d_6\text{-acetone}$
$1\text{-(1,4-Dihydroxy-7-isopropoxynaphthalen-2-yl)butan-1-one 14d}$

$\text{H NMR at 400 MHz in } d_6\text{-acetone}$
$^{13}$C NMR at 100 MHz in $d_6$-acetone
Key HMBC Interactions: 1-(5-Ethoxy-1,4-dihydroxynaphthalen-2-yl)butan-1-one 9c
Key HMBC Interactions: 1-(8-Ethoxy-1,4-dihydroxynaphthalen-2-yl)butan-1-one 10c
Key HMBC Interactions: 1-(6-Ethoxy-1,4-dihydroxynaphthalen-2-yl)butan-1-one 13c

LM-177-P2-HMBC.ESP
Key HMBC Interactions: 1-(7-Ethoxy-1,4-dihydroxynaphthalen-2-yl)butan-1-one 14c

Electronic Supplementary Material (ESI) for Green Chemistry
This journal is © The Royal Society of Chemistry 2013
Wavelength Emission Spectra

Wavelength Emission Spectra of the UV Sunlamp (Table 2, Entry 3)

Measured using a compact CCD (Model: CCS150) spectrometer, produced by Thorlabs
Wavelength Emission Spectra of the Halogen Floodlight (Table 2, Entry 4)

Measured using a compact CCD (Model: CCS150) spectrometer, produced by Thorlabs
Wavelength Emission Spectra of the HQI-T HID Light (Table 2, Entry 5)

Measured using a USB Miniature Fiber Optic Spectrometer, produced by Ocean Optics.
References