Supporting Information

Rh-catalyzed direct synthesis of 2,2’-dihydroxybenzophenones and xanthones

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Contents

1. Crystallographic data for Compound 2.2 (CCDC-1480785)..........................................................S2-S3
2. Copies of 1H NMR, 13C NMR and HRMS spectra of Compound 2.1 to 2.11 (Table 2)..........................S4-S36
3. Copies of 1H NMR, 13C NMR and HRMS spectra of Compound 3.1 to 3.10 (Table 3).........................S37-S66
4. Copies of 1H NMR, 13C NMR and HRMS spectra of Compound 4 (Scheme 2).................................S67-S69
1. Crystallographic data for Compound 2.2 (CCDC-1480785):

Crystal data and structure refinement for 2marb_0m.

**Identification code:** 2marb_0m  
**Empirical formula:** C15 H14 O5  
**Formula weight:** 274.26  
**Temperature:** 298(2) K  
**Wavelength:** 0.71073 Å  
**Crystal system:** Monoclinic  
**Space group:** P21/n  
**Unit cell dimensions:**  
\[ a = 3.8416(3) \text{ Å} \quad a = 90^\circ. \]  
\[ b = 25.1212(16) \text{ Å} \quad b = 92.567(2)^\circ. \]  
\[ c = 12.9636(9) \text{ Å} \quad g = 90^\circ. \]
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>1249.80(15) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.458 Mg/m³</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.110 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>576</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.16 x 0.13 x 0.12 mm³</td>
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<tr>
<td>Theta range for data collection</td>
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<tr>
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<td>-5&lt;=h&lt;=5, -33&lt;=k&lt;=33, -13&lt;=l&lt;=17</td>
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<tr>
<td>Reflections collected</td>
<td>12538</td>
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<tr>
<td>Independent reflections</td>
<td>3107 [R(int) = 0.0674]</td>
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<td>Completeness to theta = 28.35°</td>
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<tr>
<td>Absorption correction</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0581, wR2 = 0.1219</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1180, wR2 = 0.1535</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.292 and -0.362 e.Å⁻³</td>
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</table>
2. Copies of $^1$H NMR, $^{13}$C NMR and HRMS spectra of Compound 2.1 to 2.11 (Table 2):

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of bis(2-hydroxyphenyl)methanone (2.1)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of bis(2-hydroxyphenyl)methanone (2.1)
El(HRMS) spectrum of bis(2-hydroxyphenyl)methanone (2.1)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of bis(2-hydroxy-4-methoxyphenyl)methanone (2.2)
$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of bis(2-hydroxy-4-methoxyphenyl)methanone (2.2)
El(HRMS) spectrum of bis(2-hydroxy-4-methoxyphenyl)methanone (2.2)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of bis(2-hydroxy-3-methoxyphenyl)methanone (23)
$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of bis(2-hydroxy-3-methoxyphenyl)methanone (2.3)
EI(HRMS) spectrum of bis(2-hydroxy-3-methoxyphenyl)methanone (2.3)
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of bis(4-(diethylamino)-2-hydroxyphenyl)methanone (2.4)
$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of bis(4-(diethylamino)-2-hydroxyphenyl)methanone (2.4)
ESI(HRMS) spectrum of bis(4-(diethylamino)-2-hydroxyphenyl)methanone (2.4)
\(^1H\) NMR (400 MHz, CDCl\(_3\)) spectrum of bis(2-hydroxy-5-methylphenyl)methanone (2.5)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of bis(2-hydroxy-5-methylphenyl)methane (2.5)
EI(HRMS) spectrum of bis(2-hydroxy-5-methylphenyl)methanone (2.5)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of bis(2-hydroxy-3,4,5-trimethoxyphenyl)methanone (2.6)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of bis(2-hydroxy-3,4,5-trimethoxyphenyl)methanone (2.6)
EI(HRMS) spectrum of bis(2-hydroxy-3,4,5-trimethoxyphenyl)methanone (2.6)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of bis(5-fluoro-2-hydroxyphenyl)methanone (2.7)
$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of bis(5-fluoro-2-hydroxyphenyl)methanone (2.7)
EI(HRMS) spectrum of bis(5-fluoro-2-hydroxyphenyl)methanone (2.7)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of bis(3,5-dichloro-2-hydroxyphenyl)methanone (2.8)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of bis(3,5-dichloro-2-hydroxyphenyl)methanone (2.8)
EI(HRMS) spectrum of bis(3,5-dichloro-2-hydroxyphenyl)methanone (2.8)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of bis(5-bromo-2-hydroxyphenyl)methanone (2.9)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of bis(5-bromo-2-hydroxyphenyl)methanone (2.9)
ESI(HRMS) spectrum of bis(5-bromo-2-hydroxyphenyl)methanone (2.9)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of bis(5-chloro-2-hydroxyphenyl)methanone (2.10)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of bis(5-chloro-2-hydroxyphenyl)methanone (2.10)
ESI(HRMS) spectrum of bis(5-chloro-2-hydroxyphenyl)methanone (2.10)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1,1'-(3,3'-carbonylbis(4-hydroxy-3,1-phenylene))diethanone (2.11)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1,1'-((3,3'-carbonylbis(4-hydroxy-3,1-phenylene))diethanone (2.11)
ESI(HRMS) spectrum of 1,1'-((3,3'-carbonylbis(4-hydroxy-3,1-phenylene))diethanone (2.11)

\[ [\text{M+NH}_4]^+ \text{ calcd. 316.1185} \]
3. Copies of $^1$H NMR, $^{13}$C NMR and HRMS spectra of Compound 3.1 to 3.10 (Table 3):

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 9H-xanthen-9-one (3.1)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 9H-xanthen-9-one (3.1)
ESI(HRMS) spectrum of 9H-xanthen-9-one (3.1)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2,7-dimethyl-9H-xanthen-9-one (3.2)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2,7-dimethyl-9H-xanthen-9-one (3.2)
EI(HRMS) spectrum of 2,7-dimethyl-9H-xanthen-9-one (3.2)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2,3,4,5,6,7-hexamethoxy-9H-xanthen-9-one (33)
$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 2,3,4,5,6,7-hexamethoxy-9H-xanthen-9-one (3.3)
EI(HRMS) spectrum of 2,3,4,5,6,7-hexamethoxy-9H-xanthen-9-one (3.3)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2,7-difluoro-9$H$-xanthen-9-one (3.4)
$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 2,7-difluoro-9H-xanthen-9-one (3.4)
EI(HRMS) spectrum of 2,7-difluoro-9H-xanthen-9-one (3.4)

[M]+ calcd. 232.0336
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2,7-dibromo-9$H$-xanthen-9-one (3.5)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2,7-dibromo-9H-xanthen-9-one (3.5)
EI(HRMS) spectrum of 2,7-dibromo-9H-xanthen-9-one (3.5)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2,7-dichloro-9$H$-xanthen-9-one (3.6)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2,7-dichloro-9$H$-xanthen-9-one (3.6)
EI(HRMS) spectrum of 2,7-dichloro-9H-xanthen-9-one (3.6)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1,1'-(9-oxo-9$H$-xanthene-2,7-diyl)diethanone (3.7)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1,1'$-(9$-oxo-9$H$-xanthene-2,7-diyl)diethanone (3.7)
EI(HRMS) spectrum of 1,1'-(9-oxo-9H-xanthene-2,7-diyl)diethanone (3.7)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 9-oxo-9H-xanthene-2,7-dicarbaldehyde (3.8)
$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 9-oxo-$9H$-xanthene-2,7-dicarbaldehyde (3.8)
EI(HRMS) spectrum of 9-oxo-9H-xanthene-2,7-dicarbaldehyde (3.8)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2,7-dinitro-$9H$-xanthen-9-one (3.9) (9:1)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2,7-dinitro-9H-xanthen-9-one (3.9) (9:1)
EI(HRMS) spectrum of 2,7-dinitro-9\(H\)-xanthen-9-one (3.9)
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3,6-dihydroxy-9H-xanthen-9-one (3.10)
$^{13}$C NMR (125 MHz, DMSO-$d_6$) spectrum of 3,6-dihydroxy-$9H$-xanthen-9-one (3.10)
ESI(HRMS) spectrum of 3,6-dihydroxy-9H-xanthen-9-one (3.10)
4. Copies of $^1$H NMR, $^{13}$C NMR and HRMS spectra of Compound 4 (Scheme 2):

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of (2-hydroxy-4-methoxyphenyl)(2-hydroxyphenyl)methanone (4)
"13C NMR (100 MHz, CDCl₃) spectrum of (2-hydroxy-4-methoxyphenyl)(2-hydroxyphenyl)methanone (4)"
ESI(HRMS) spectrum of (2-hydroxy-4-methoxyphenyl)(2-hydroxyphenyl)methanone (4)