Supplementary Material

Application of intramolecular carbonyl-ene reaction towards the synthesis of idarubicinone scaffold

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Spectra S2
References S28
$^1$H, $^{13}$C NMR spectra of synthesized compounds:

17 ($^1$H NMR, 400 MHz, CDCl$_3$)

17 ($^{13}$C NMR, 100 MHz, CDCl$_3$)
18 $^1$H NMR, 400 MHz, CDCl$_3$

18 $^{13}$C NMR, 100 MHz, CDCl$_3$
19 ($^1$H NMR, 400 MHz, CDCl$_3$)

19 ($^{13}$C NMR, 100 MHz, CDCl$_3$)
20 (¹H NMR, 400 MHz, CDCl₃)

20 (¹³C NMR, 100 MHz, CDCl₃)
21 ($^1$H NMR, 400 MHz, CDCl$_3$)

21 ($^{13}$C NMR, 100 MHz, CDCl$_3$)
23 ($^1$H NMR, 200 MHz, CDCl$_3$)

23 ($^{13}$C NMR, 50 MHz, CDCl$_3$)
24 (\textsuperscript{1}H NMR, 200 MHz, CDCl\textsubscript{3})

24 (\textsuperscript{13}C NMR, 50 MHz, CDCl\textsubscript{3})
25 ($^1$H NMR, 200 MHz, CDCl$_3$)

25 ($^{13}$C NMR, 50 MHz, CDCl$_3$)
2-methoxy-7-methyl-7,8-dihydr-o-naphthylacetate
($^1$H NMR, 600 MHz, CDCl$_3$)

D Mal
dm /sb / 277-cl-acetate - 1h

2-methoxy-7-methyl-7,8-dihydr-o-naphthylacetate
($^1$H NMR, 600 MHz, CDCl$_3$)

D Mal
dm /sb / 277-cl-acetate - 13c

2-methoxy-7-methyl-7,8-dihydr-o-naphthylacetate
($^1$C NMR, 150 MHz, CDCl$_3$)
26 ($^1$H NMR, 200 MHz, CDCl$_3$)

26 ($^1$C NMR, 50 MHz, CDCl$_3$)
31 32
(\textsuperscript{1}H NMR, 400 MHz, CDCl\textsubscript{3})

31 32
(\textsuperscript{13}C NMR, 100 MHz, CDCl\textsubscript{3})
$\text{31} \quad ^{11}\text{B NMR, 128 MHz, CDCl}_3$

$\text{32} \quad ^{11}\text{B NMR, 128 MHz, CDCl}_3$

$\text{33} \quad ^1\text{H NMR, 200 MHz, CDCl}_3$
33 ($^{13}$C NMR, 50 MHz, CDCl$_3$)

34 ($^1$H NMR, 100 MHz, CDCl$_3$)
38 ($^1$H NMR, 400 MHz, CDCl$_3$)

38 ($^{13}$C NMR, 100 MHz, CDCl$_3$)
$^{37}$ (H NMR, 400 MHz, CDCl$_3$)

$^{37}$ (13C NMR, 100 MHz, CDCl$_3$)
39 ($^1$H NMR, 400 MHz, CDCl$_3$)

39 ($^1$C NMR, 100 MHz, CDCl$_3$)
11 (\textsuperscript{1}H NMR, 400 MHz, CDCl\textsubscript{3})

11 (\textsuperscript{13}C NMR, 100 MHz, CDCl\textsubscript{3})
**41 (±) $^{13}$C NMR, 100 MHz, acetone-$d_6$**

**42 (±) $^1$H NMR, 400 MHz, CDCl$_3$**
42 (±) $^1$H NMR, 400 MHz, acetone-$d_6$}

42 (±) $^{13}$C NMR, 100 MHz, acetone-$d_6$
X-ray Crystallography
Suitable single crystals of compound 42 for X-ray diffraction studies were obtained by slow evaporation of a solution of 42 in CHCl₃. Single crystal X-ray diffraction data collections for the compound was performed at room temperature using Bruker-APEX-II CCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by SIR-92¹ or SHELXS-97 available in WinGX, which successfully located most of the non-hydrogen atoms. Subsequently, least square refinements were carried out on F² using SHELXL-97 (WinGX version)²,³ to locate the remaining non-hydrogen atoms. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically on calculated positions using riding models. These hydrogen atoms were located from the difference Fourier map and then refined isotropically with the thermal parameters equivalent to 1.2 times the thermal parameter value of the atom to which hydrogen atoms are bonded.

Figure S₄₂. ORTEP diagram of 42 with 30% probability ellipsoids.
Table S1. Crystallographic Data for Compound 42

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{11}H_{12}O_{3}</td>
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<tr>
<td>Formula weight</td>
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<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
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<tr>
<td>Temperature (K)</td>
<td>293(2)</td>
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<tr>
<td>Crystal system</td>
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<tr>
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<td>Dark Green, block</td>
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<tr>
<td>Space group</td>
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<tr>
<td>a/Å</td>
<td>5.2277(9)</td>
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<tr>
<td>b/Å</td>
<td>21.884(4)</td>
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<tr>
<td>c/Å</td>
<td>8.4573(15)</td>
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<tr>
<td>α/degree</td>
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<tr>
<td>β/degree</td>
<td>95.533(6)</td>
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<tr>
<td>γ/degree</td>
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<tr>
<td>Volume (Å³)</td>
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<tr>
<td>Z</td>
<td>4</td>
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<tr>
<td>D_{calcd}, g cm⁻³</td>
<td>1.326</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.096</td>
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<tr>
<td>F(000)</td>
<td>408</td>
</tr>
</tbody>
</table>
Crystal size/mm  0.23×0.17×0.13

θ range (degree)  1.86 to 26.52

Limiting indices

-6<=h<=6,
-26<=k<=27,
-10<=l<=10

Total/unique no. of reflns.  12183/ 1994

R_{int}  0.0940

Data / restr./params.  1994 / 0 / 127

GOF (F^2)  0.691

R1, wR2  0.0629, 0.1832

R indices (all data) R1, wR2  0.1359, 0.2739

Largest different peak and hole (e Å^-3)  0.188 and -0.189
43 (1H NMR, 400 MHz, acetone-\(d_6\))

43 (13C NMR, 100 MHz, acetone-\(d_6\))
47 (1H NMR, 600 MHz, CDCl₃)

47 (13C NMR, 150 MHz, CDCl₃)
References