Supplementary Material

Generation and reversible cyclisation of furfurylic radicals

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$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{)} \]

\[ \text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3\text{)} \]
\({}^1\text{H} \text{NMR (400 MHz, CDCl}_3\)}

\(13\text{C NMR (101 MHz, CDCl}_3\)}

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

21 (contains ~30% pyridine)

$^{13}$C NMR (101 MHz, CDCl$_3$)

21 (contains ~30% pyridine)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$\text{H NMR (500 MHz, C}_6\text{D}_6)$

$\text{C NMR (126 MHz, C}_6\text{D}_6)$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, C$_6$D$_6$)

$^{13}$C NMR (126 MHz, C$_6$D$_6$)
$^1$H NMR (400 MHz, C$_6$D$_6$)

$^{13}$C NMR (101 MHz, C$_6$D$_6$)
Issue in honor of Professor Samir Zard

$^1$H NMR (400 MHz, C$_6$D$_6$)

$^1$C NMR (101 MHz, C$_6$D$_6$)
$^1$H NMR (400 MHz, C$_6$D$_6$)

$^1$C NMR (101 MHz, C$_6$D$_6$)
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$^1$H NMR (400 MHz, CDCl$_3$)

31
(+ C=C regioisomers)

$^{13}$C NMR (101 MHz, CDCl$_3$)

31
(+ C=C regioisomers)

Inset taken from a more concentrated, impure sample of compound 31.
32 – by hydrogenation
(dr ~ 90:10, cis/trans)

**1H NMR (500 MHz, C₆D₆)**

**13C NMR (126 MHz, C₆D₆)**
$^1$H NMR (500 MHz, C$_6$D$_6$)

32 – from selenide 33
(dr ~ 55:45, trans/cis)

$^{13}$C NMR (126 MHz, C$_6$D$_6$)

32 – from selenide 33
(dr ~ 55:45, trans/cis)
$^1$H NMR (400 MHz, C$_6$D$_6$)

$^{13}$C NMR (101 MHz, C$_6$D$_6$)
$^{1}H$ NMR (400 MHz, C$_6$D$_6$)

$^{13}$C NMR (101 MHz, C$_6$D$_6$)
1H NMR (500 MHz, C₆D₆)

(dr = 85:15, cis/trans)

13C NMR (126 MHz, C₆D₆)

(dr = 85:15, cis/trans)
$^2$H NMR (92 MHz, C$_6$H$_6$ spiked with C$_6$D$_6$)
Figure S1: $^1$H–$^1$H NOESY (500 MHz, C$_6$D$_6$) spectrum of compound 22 ($dr = 52:48$, trans/cis) from radical cyclisation. Green arrows indicate observed correlations; red arrows indicate those not observed; blue arrow is an ambiguous correlation.
**Figure S2** $^1$H–$^1$H NOESY (500 MHz, C$_6$D$_6$) spectrum of compound **32** ($dr = 90:10$, **cis**/**trans**) prepared by hydrogenation. Green arrows indicate observed correlations; red arrows indicate those not observed.
DFT calculations

Energy calculations for trans- and cis-22' 

(a) A conformer distribution was obtained within Spartan’20 using molecular mechanics (MMFF, MonteCarlo) to generate 38 conformations for trans-22' and 24 for cis-22'; the methyl ester was used here to keep the number of conformations to a manageable level.

(b) The low-lying conformations, representing ~95% of the conformational space, were retained: 17 for trans-22', 13 for cis-22'.

(c) DFT (B3LYP/6-31G*) equilibrium geometry calculations of the 30 separate conformations were used to obtain a Boltzmann-weighted average energy for each diastereomer leading to the values presented in Figure 1 of the main text.

Transition state calculations for the cyclisation of methyl (E)-7-(2-furyl)hept-2-enoate (7-yl radical) (S6) 

(a) Transition states were computed within Spartan’20 for the cyclisation of 6-hexenyl radical in both anti (‘chair’) and gauche (‘boat’) conformations as defined in Table 1 of the main text.

(b) These were then used to build the substituted radical S6 in anti and gauche conformations, each configured to lead to either cis or trans disubstituted cyclopentane.

(c) For each of the four so-generated transition state approximations, a conformer distribution was obtained (MMFF, MonteCarlo) with the hexenyl radical core frozen (Table S1).

(d) DFT (B3LYP/6-31G*) equilibrium geometry calculations of the 28 separate radical conformations, with the cores unfrozen, were used to obtain an energy-weighted conformer distribution within each parent.

(e) In all cases, based on the Boltzmann weightings, just one or two low-lying conformations accounted for 83–90% of the conformational space; these were selected for DFT (B3LYP/6-31G*) transition state calculations with all constraints removed, leading to the energies presented in Table 1 of the main text.

Table S1. Numbers of conformations taken through each stage of the transition state calculations.

<table>
<thead>
<tr>
<th>Conformation</th>
<th>MMFF conformers</th>
<th>Number selected for TS calcns</th>
</tr>
</thead>
<tbody>
<tr>
<td>anti-cis</td>
<td>4</td>
<td>1 (83%)</td>
</tr>
<tr>
<td>anti-trans</td>
<td>5</td>
<td>2 (83%)</td>
</tr>
<tr>
<td>gauche-cis</td>
<td>9</td>
<td>1 (86%)</td>
</tr>
<tr>
<td>gauche-trans</td>
<td>10</td>
<td>2 (90%)</td>
</tr>
</tbody>
</table>