Stereoselective Synthesis of Spirocyclopentanones via N-Heterocyclic Carbene Catalyzed Reaction of Enals and Dienones

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(1) General remarks: All reactions were carried out in oven-dried glassware. Progress of reactions was monitored by Thin Layer Chromatography while purification was effected by column chromatography, using silica gel (60-120 mesh). Melting points were recorded on a Buchi melting point apparatus and are uncorrected. NMR spectra were recorded at 300 (1H) and 75 (13C) MHz respectively on a Brucker Advance DPX-300 MHz. Chemical shifts are reported in δ (ppm) relative to TMS (1H) or CDCl3 (13C) as internal standards. IR spectra were recorded on Bomem MB series FT-IR spectrometer, absorbencies are reported in cm⁻¹.

(2) General experimental procedures:

(a) Synthesis of 1,3,4-trisubstituted cyclopentene 4a and 2,3,4-trisubstituted cyclopentanone 5a:- DBU (18 mg, 12 mol %) was added to a suspension of the 1,3-dimesityl imidazolium chloride 3 (21 mg, 6 mol %) in 3 ml dry CH2Cl2 under argon atmosphere. This was followed by the addition of 4-methoxy cinnamaldehyde 1 (162 mg, 1 mmol) and dienone 2 (259 mg, 0.7 mmol) and the resulting solution was stirred for 8h at room temperature (30°C). Initial green colour of the reaction mixture gradually changed into wine red on completion of the reaction. The reaction mixture was then passed through a short pad of Celite®. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60-120 mesh) column using 95:5 hexane-ethyl acetate solvent mixture.

as eluent to afford 4a (119 mg, 32% yield, 10:1 dr2) & 5a (109 mg, 32%). CCDC file number for 5a: 638979.

(b) Synthesis of spirocyclopentanone 8a:- DBU (18 mg, 12 mol %) was added to a suspension of the 1,3-dimesityl imidazolium chloride 3 (21 mg, 6 mol %) in 3 ml dry CH2Cl2 under argon atmosphere. This was followed by the addition of cinnamaldehyde 6 (132 mg, 1 mmol) and dienone 7 (224 mg, 0.7 mmol) and the resulting solution was stirred for 8h at room temperature (30°C). Initial green colour of the reaction mixture gradually changed into wine red on completion of the reaction. The reaction mixture was then passed through a short pad of Celite®. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60-120 mesh) column using 80:20 hexane-ethyl acetate solvent mixture as eluent to afford 8a (189 mg, 60%). CCDC file number for 8a: 653444.

(3) Characterization data for selected compounds

**Compound 4a**

<table>
<thead>
<tr>
<th>Colourless viscous liquid</th>
<th>IR (Film) νmax: 3031, 2911, 2821, 1618, 1530, 1472, 1275, 1190, 1062 cm⁻¹.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H NMR: δ 7.28-7.16 (m, 4H), 6.98-6.95 (m, 3H), 6.85 (d, 1H, J = 17.1 Hz), 6.77-6.67 (m, 4H), 6.56 (d, 2H), 5.99 (s, 1H), 4.12 (s, 1H), 3.73 (s, 3H), 3.34-3.26 (m, 1H), 3.06-2.94 (m, 1H), 2.72-2.69 (m, 1H)</td>
<td></td>
</tr>
<tr>
<td>C NMR: δ 158.5, 149.0, 142.1, 140.6, 135.9, 134.2, 133.4, 131.6, 129.6, 128.5, 128.4, 127.6, 127.3, 126.9, 125.5, 125.4, 124.5, 122.5, 114.0, 60.1, 55.9, 55.0, 54.9, 54.6, 49.9, 41.5</td>
<td></td>
</tr>
<tr>
<td>HRMS (EI) for C28H22F6O: Calcd.: 488.1575, found : 488.1577</td>
<td></td>
</tr>
</tbody>
</table>

**Compound 5a**

<table>
<thead>
<tr>
<th>Yellow solid. Mp :142-144 °C</th>
<th>IR (KBr) νmax: 3658, 3032, 2931, 1741, 1640, 1629, 1578, 1510, 1457, 1308, 1245, 1117 cm⁻¹.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H NMR: δ 13.81 (s, 1H), 7.81 (d, 1H, J = 12.8 Hz), 7.69-7.53 (m, 3H), 7.42-7.35 (m, 4H), 7.16 (d, 1H, J = 7.3 Hz), 7.01 (d, 2H, J = 8.6 Hz), 6.79 (d, 2H, J = 8.6 Hz), 6.09 (d, 1H, J = 15.5 Hz), 4.60 (d, 1H, J = 3.5 Hz), 3.77 (s, 3H), 3.33-3.27 (m, 1H), 3.13 (dd, 1H, J1 = 18.4 Hz, J2 = 8.7 Hz), 2.68 (dd, 1H, J1 = 18.4 Hz, J2 = 5.3 Hz).</td>
<td></td>
</tr>
<tr>
<td>C NMR: δ 207.6, 164.6, 158.6, 139.5, 137.5, 131.4, 130.6, 130.0, 129.1, 127.9, 118.1, 117.2, 116.9, 116.7, 115.1, 114.8, 114.7, 113.5, 11.4, 113.1, 113.0, 56.1, 54.2, 52.8, 52.7, 52.3, 51.8, 44.7</td>
<td></td>
</tr>
<tr>
<td>HRMS (EI) for C29H22F6O3: Calcd. 532.1473, found : 532.1477</td>
<td></td>
</tr>
</tbody>
</table>
**Compound 4b**

![Compound 4b structure](image)

Colourless viscous liquid  
**IR** (Film) $\nu_{\text{max}}$: 3026, 2917, 2824, 1620, 1537, 1466, 1271, 1188, 1055 cm$^{-1}$.

$^1$H NMR: $\delta$ 7.43 (d, 2H, $J = 10.5$ Hz), 7.31-7.17 (m, 8H), 6.76 (d, 2H, $J = 8.7$ Hz), 6.49 (d, 1H, $J = 16.2$ Hz), 5.87 (s, 1H), 3.99 (d, 1H, $J = 6.0$ Hz), 3.73(s, 3H), 3.35-3.27 (m, 1H), 3.21-3.13 (m, 1H), 2.83-2.75 (m, 1H)

$^{13}$C NMR: $\delta$ 158.2, 145.3, 142.1, 137.4, 136.8, 133.9, 130.8, 130.0, 129.6, 128.9, 128.6, 128.4, 128.3, 128.2, 127.5, 127.3, 126.4, 126.2, 125.2, 114.1, 113.8, 113.1, 59.9, 55.1, 54.8, 40.1

HRMS (EI) for C$_{26}$H$_{24}$O: Calcd.: 352.1827, found : 352.1821

**Compound 5b**

![Compound 5b structure](image)

Yellow viscous liquid  
**IR** (Film) $\nu_{\text{max}}$: 3674, 3026, 2954, 2828, 1737, 1645, 1581, 1514, 1454, 1361, 1261, 1178 cm$^{-1}$.

$^1$H NMR: $\delta$ 13.9 (s, 1H), 7.45 (d, 1H, $J = 15.7$ Hz), 7.31-7.14 (m, 8H), 7.08-7.02 (m, 4H), 6.80 (d, 2H, $J = 8.5$ Hz), 5.99 (d, 1H, $J = 15.8$ Hz), 4.11 (d, 1H, $J = 6.89$ Hz), 3.78 (s, 3H), 3.35-3.27 (m, 1H), 2.97 (dd, 1H, $J_1 = 18.2$ Hz, $J_2 = 8.5$ Hz), 2.73 (dd, 1H, $J_1 = 18.1$ Hz, $J_2 = 8.7$ Hz)

$^{13}$C NMR: $\delta$ 207.8, 167.2, 157.9, 144.5, 139.6, 133.9, 129.9, 129.6, 128.9, 128.7, 128.6, 128.4, 128.3, 128.0, 127.7, 127.6, 127.5, 127.3, 126.8, 119.8, 113.9, 113.8, 55.8, 50.7, 44.4, 40.1

HRMS (EI) for C$_{27}$H$_{24}$O$_3$: Calcd.: 396.1725, found : 396.1729

**Compound 4c**

![Compound 4c structure](image)

Colourless viscous liquid  
**IR** (Film) $\nu_{\text{max}}$: 3033, 2911, 1607, 1518, 1457, 1301, 1224, 1171, 1101 cm$^{-1}$.

$^1$H NMR: $\delta$ 7.30 (d, 2H, $J = 8.0$ Hz), 7.12-6.97 (m, 9H), 6.79 (d, 2H, $J = 9.7$ Hz), 6.46 (d, 1H, $J = 16.1$ Hz), 5.89 (s, 1H), 3.96 (d, 1H, $J = 6.1$ Hz), 3.74 (s, 3H), 3.31-3.23 (m, 1H), 3.18 – 3.10 (m, 1H), 2.79-2.72 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H)

$^{13}$C NMR: $\delta$ 158.4, 142.5, 142.4, 137.4, 137.3, 135.7, 134.9, 13.6, 130.1, 129.9, 129.6, 129.3, 128.5, 127.5, 126.6, 124.7, 124.5, 113.9, 110.9, 60.1, 55.5, 54.7, 40.4, 21.5, 21.3

HRMS (EI) for C$_{28}$H$_{28}$O: Calcd.: 380.2140, found : 380.2135
Compound 5c

Yellow viscous liquid

**IR (Film)** $\nu_{\text{max}}$: 3668, 3022, 1685, 1641, 1612, 1582, 1513, 1461, 1372, 1247, 1181, 1036 cm$^{-1}$.

**$^1H$ NMR:** $\delta$ 13.9 (s, 1H), 7.42 (d, 2H, $J = 15.5$ Hz), 7.11-6.98 (m, 9H), 6.79 (d, 2H, $J = 8.6$ Hz), 5.96 (d, 1H, $J = 15.8$ Hz), 4.08 (d, 1H, $J = 6.7$ Hz), 3.78 (s, 3H), 3.32-3.25 (m, 1H), 2.96 (dd, 1H, $J_1 = 18.2$ Hz, $J_2 = 8.6$ Hz), 2.70 (dd, 1H, $J_1 = 18.1$ Hz, $J_2 = 8.4$ Hz), 2.33 (s, 3H), 2.30 (s, 3H)

**$^{13}C$ NMR:** $\delta$ 208.1, 167.9, 158.7, 141.9, 140.3, 139.9, 136.6, 135.7, 132.9, 132.0, 130.0, 129.8, 129.7, 129.5, 129.3, 128.9, 128.6, 128.3, 128.1, 127.8, 119.2, 114.3, 113.9, 55.4, 54.2, 50.9, 44.7, 21.8, 21.4

**HRMS (EI)** for C$_{29}$H$_{28}$O$_3$: Calcd.: 424.2038, found: 424.2045

Compound 4d

Colourless viscous liquid

**IR (Film)** $\nu_{\text{max}}$: 3034, 2908, 1604, 1508, 1462, 1300, 1228, 1190, 1047 cm$^{-1}$.

**$^1H$ NMR:** $\delta$ 7.40-7.36 (m, 2H), 7.16-7.11 (m, 2H), 7.03-6.94 (m, 7H), 6.78 (d, 2H, $J = 8.5$ Hz), 6.46 (d, 1H, $J = 16.1$ Hz), 5.86 (s, 1H), 3.92 (s, 1H), 3.76 (s, 3H), 3.33-3.25 (m, 1H), 3.19-3.11 (m, 1H), 2.78-2.70 (m, 1H)

**$^{13}C$ NMR:** $\delta$ 164.2, 163.3, 160.9, 160.1, 158.6, 142.1, 141.1, 141.0, 136.7, 134.1, 133.8, 133.7, 129.8, 129.1, 128.9, 128.8, 128.1, 128.0, 125.1, 116.0, 115.7, 115.6, 115.3, 114.1, 60.3, 55.4, 40.3

**HRMS (EI)** for C$_{26}$H$_{22}$F$_2$O: Calcd.: 388.1639, found: 388.1620

Compound 5d

Yellow viscous liquid

**IR (Film)** $\nu_{\text{max}}$: 3674, 3041, 2964, 1671, 1645, 1598, 1511, 1464, 1373, 1306, 1239, 1179, 1157, 1032 cm$^{-1}$.

**$^1H$ NMR:** $\delta$ 13.94 (s, 1H), 7.43 (d, 1H, $J = 15.7$ Hz), 7.13-6.91 (m, 10 H), 6.81 (d, 2H, $J = 8.5$ Hz), 5.88 (d, 1H, $J = 15.8$ Hz), 4.1 (d, 1H, $J = 7.0$ Hz), 3.78 (s, 3H), 3.27-3.18 (m, 1H), 2.94 (dd, 1H, $J_1 = 18.0$ Hz, $J_2 = 8.4$ Hz), 2.73 (dd, 1H, $J_1 = 18.2$ Hz, $J_2 = 9.1$ Hz)

**$^{13}C$ NMR:** $\delta$ 207.6, 167.2, 158.6, 140.2, 138.6, 134.5, 131.4, 129.6, 129.5, 129.0, 128.9, 128.1, 119.3, 116.1, 115.9, 115.8, 115.6, 115.4, 114.3, 55.2, 53.6, 51.0, 44.4

**HRMS (EI)** for C$_{27}$H$_{22}$F$_2$O$_3$: Calcd.: 432.1537, found: 432.1555
**Compound 4e**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Colourless viscous liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IR</strong> (Film) $\nu_{\text{max}}$: 3037, 2910, 1606, 1510, 1465, 1302, 1230, 1190, 1060 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td><strong>$^1$H NMR</strong>: $\delta$ 7.15-7.05 (m, 4H), 6.97-6.94 (m, 2H), 6.89-6.87 (m, 1H), 6.82-6.79 (m, 3H), 6.73-6.62 (m, 2H), 5.84 (s, 1H), 3.99 (d, $J = 7.3$ Hz), 3.77 (s, 3H), 3.59 (m, 1H), 3.23-3.15 (m, 1H), 2.83-2.75 (m, 1H)</td>
<td></td>
</tr>
<tr>
<td><strong>$^{13}$C NMR</strong>: $\delta$ 158.4, 148.2, 142.9, 141.4, 135.9, 133.7, 129.5, 128.5, 127.6, 126.6, 125.9, 124.5, 124.3, 123.6, 122.9, 113.8, 113.2, 60.1, 55.1, 50.2, 4.07</td>
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<tr>
<td><strong>HRMS (EI)</strong> for C$<em>{22}$H$</em>{20}$O$_3$S$_2$: Calcd.: 364.0956, found : 364.0952</td>
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</table>

**Compound 5e**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Yellow viscous liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IR</strong> (Film) $\nu_{\text{max}}$: 3674, 3070,2963, 1670, 1633, 1609, 1583, 1513, 1424, 1366, 1301, 1247, 1180, 1033 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td><strong>$^1$H NMR</strong>: $\delta$ 13.8 (s, 1H), 7.62 (d, $J = 15.4$ Hz), 7.26 (d, $J = 18.2$ Hz), 7.18 (d, 1H, $J = 4.9$ Hz), 7.09-7.06 (m, 3H), 6.97-6.90 (m, 2H), 6.83-6.80 (m, 3H), 6.02 (d, 1H, $J = 15.4$ Hz), 4.35 (d, 1H, $J = 5.8$ Hz), 3.78 (s, 3H), 3.44-3.37 (m, 1H), 3.01 (dd, 1H, $J_1 = 18.2$ Hz, $J_2 = 7.6$ Hz), 2.69 (dd, 1H, $J_1 = 18.2$ Hz, $J_2 = 7.6$ Hz)</td>
<td></td>
</tr>
<tr>
<td><strong>$^{13}$C NMR</strong>: $\delta$ 206.7, 167.5, 158.5, 148.7, 141.0, 134.9, 132.6, 130.3, 130.1, 128.3, 128.1, 127.9, 126.8, 124.5, 124.3, 118.4, 114.5, 114.1, 113.6, 55.1, 50.9, 49.3, 43.9</td>
<td></td>
</tr>
<tr>
<td><strong>HRMS (EI)</strong> for C$<em>{23}$H$</em>{20}$O$_3$S$_2$: Calcd.: 408.0854, found : 408.0870</td>
<td></td>
</tr>
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</table>

**Compound 4f**

<table>
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<th>Structure</th>
<th>Colourless viscous liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IR</strong> (Film) $\nu_{\text{max}}$: 3019, 2914, 2831, 1617, 1542, 1474, 1269, 1168, 1061 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td><strong>$^1$H NMR</strong>: $\delta$ 7.35 (d, $J = 8.7$ Hz), 7.23-7.19 (m, 3H), 7.12-7.06 (m, 4H), 6.93 (d, 1H, $J = 16.1$ Hz), 6.86-6.78 (m, 4H), 6.46 (d, 1H, $J = 16.1$ Hz), 5.84 (s, 1H), 3.98 (d, $J = 5.9$ Hz), 3.80 (s, 3H), 3.77 (s, 3H), 3.31-3.26 (m, 1H), 3.19-3.11 (m, 1H), 2.80-2.75 (m, 1H)</td>
<td></td>
</tr>
<tr>
<td><strong>$^{13}$C NMR</strong>: $\delta$ 159.1, 158.0, 144.9, 142.6, 137.4, 132.4, 130.2, 129.6, 129.3, 128.8, 128.4, 128.2, 127.6, 127.4, 126.3, 123.2, 114.1, 113.8, 112.9, 60.7, 55.2, 53.9, 40.3</td>
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</tr>
<tr>
<td><strong>HRMS (EI)</strong> for C$<em>{27}$H$</em>{26}$O$_2$: Calcd.: 382.1933, found : 382.1940</td>
<td></td>
</tr>
</tbody>
</table>
**Compound 5f**

Yellow viscous liquid

**IR** (Film) ν<sub>max</sub>: 3662, 3026, 2954, 2828, 1737, 1645, 1514, 1454, 1361, 1246, 1178 cm<sup>-1</sup>.

**<sup>1</sup>H NMR**:

δ 14.03 (s, 1H), 7.43 (d, 1H, J = 15.7 Hz), 7.27-7.22 (m, 3H), 7.14-7.05 (m, 6H), 6.82 (d, 2H, J = 8.6 Hz), 6.75 (d, 2H, J = 8.7 Hz), 5.90 (d, 1H, J = 15.7 Hz), 4.11 (d, 1H, J = 6.4 Hz), 3.77 (s, 6H), 3.33-3.25 (m, 1H), 2.97 (dd, 1H, J₁ = 14.8 Hz, J₂ = 8.3 Hz), 2.72 (dd, 1H, J₁ = 18.1 Hz, J₂ = 8.2 Hz)

**<sup>13</sup>C NMR**:

δ 207.2, 168.2, 161.0, 158.5, 143.5, 139.5, 136.7, 129.5, 128.7, 128.5, 128.1, 127.1, 126.8, 117.4, 114.2, 113.3, 113.1, 55.2, 53.4, 51.4, 44.2

**HRMS (EI)** for C<sub>28</sub>H<sub>26</sub>O<sub>4</sub>: Calcd.: 426.1831, found: 426.1825

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**Compound 4g**

Colourless viscous liquid

**IR** (Film) ν<sub>max</sub>: 3021, 2917, 1611, 1521, 1443, 1308, 1227, 1173, 1109 cm<sup>-1</sup>.

**<sup>1</sup>H NMR**:

δ 7.41 (d, 2H, J = 7.7 Hz), 7.32-7.19 (m, 10H), 7.09-6.97 (m, 4H), 6.50 (d, 1H, J = 16.1 Hz), 5.9 (s, 1H), 4.04 (d, 1H, J = 5.8 Hz), 3.37-3.32 (m, 1H), 3.24-3.15 (m, 1H), 2.85-2.78 (m, 1H)

**<sup>13</sup>C NMR**:

δ 145.3, 144.7, 142.4, 141.5, 137.4, 133.5, 130.1, 128.7, 128.6, 128.5, 128.4, 127.7, 127.5, 127.4, 127.3, 126.4, 126.3, 125.8, 125.1, 60.7, 54.6, 40.2

**HRMS (EI)** for C<sub>25</sub>H<sub>22</sub>: Calcd.: 322.1721, found: 322.1718

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**Compound 5g**

Yellow viscous liquid

**IR** (Film) ν<sub>max</sub>: 3654, 3060, 3031, 1925, 1679, 1610, 1581, 1494, 1455, 1367, 1236, 1118 cm<sup>-1</sup>.

**<sup>1</sup>H NMR**:

δ 13.88 (s, 1H), 7.29-7.07 (m, 16H), 5.99 (d, 1H, J = 15.8 Hz), 4.17 (d, 1H, J = 6.6 Hz), 3.39-3.31 (m, 1H), 3.04-2.95 (m, 1H), 2.81-2.72 (m, 1H)

**<sup>13</sup>C NMR**:

δ 207.8, 167.4, 144.5, 143.1, 139.8, 135.2, 129.7, 129.1, 128.9, 128.7, 128.5, 128.3, 127.8, 127.5, 127.1, 126.9, 126.8, 126.4, 119.8, 113.6, 54.1, 51.3, 44.3

**HRMS (EI)** for C<sub>26</sub>H<sub>22</sub>O<sub>2</sub>: Calcd.: 366.1620, found: 366.1618
Compound 4h

Colourless viscous liquid

**IR (Film)** $\nu_{\text{max}}$: 3022, 2911, 2832, 1614, 1472, 1269, 1179, 1062 cm$^{-1}$.  

$^{1}H$ **NMR**: $\delta$ 7.35-6.99 (m, 14H), 6.47 (d, 1H, $J = 16.1$ Hz), 5.86 (s, 1H), 4.01 (d, 1H, $J = 6.0$ Hz), 3.35-3.28 (m, 1H), 3.20-3.12 (m, 1H), 2.81-2.74 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H)

$^{13}C$ **NMR**: $\delta$ 144.9, 142.6, 142.3, 137.2, 135.6, 134.7, 133.0, 130.0, 129.4, 129.1, 128.8, 128.3, 128.2, 127.7, 127.4, 127.2, 126.3, 124.3, 60.6, 54.3, 40.3, 21.3, 21.1

**HRMS (EI)** for C$_{27}$H$_{26}$: Calcd.: 350.2034, found: 350.2032

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Compound 5h

Yellow viscous liquid

**IR (Film)** $\nu_{\text{max}}$: 3654, 3060, 3031, 1925, 1679, 1610, 1581, 1494, 1455, 1367, 1236, 1118 cm$^{-1}$.  

$^{1}H$ **NMR**: $\delta$ 13.93 (s, 1H), 7.41 (d, 1H, $J = 15.7$ Hz), 7.26-7.21 (m, 3H), 7.13-6.99 (m, 10 H), 5.95 (d, 1H, $J = 15.8$ Hz), 4.12 (d, 1H, $J = 6.3$ Hz), 3.35-3.28 (m, 1H), 2.97 (dd, 1H, $J_1 = 18.1$ Hz, $J_2 = 8.1$ Hz), 2.72 (dd, 1H, $J_1 = 18.2$ Hz, $J_2 = 8.1$ Hz), 2.31 (s, 3H), 2.28 (s, 3H)

$^{13}C$ **NMR**: $\delta$ 207.8, 167.9, 143.7, 141.8, 140.2, 139.9, 136.5, 132.9, 129.8, 129.7, 129.3, 128.9, 128.7, 128.1, 127.7, 127.2, 119.1, 113.7, 53.9, 51.5, 44.5, 21.7, 21.3

**HRMS (EI)** for C$_{28}$H$_{26}$O$_2$: Calcd.: 394.1933, found: 394.1927
**$^{1}$H nOe Studies of compound 4a**

The relative stereochemistry of C3-H and C4-H is established from $^{1}$H nOe studies. Irradiation of C3-H ($\delta$ 4.12) causes an nOe enhancement of 1.8% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

**$^{1}$H nOe Studies of compound 4b**

The relative stereochemistry of C3-H and C4-H is established from $^{1}$H nOe studies. Irradiation of C3-H ($\delta$ 3.99) causes an nOe enhancement of 1.5% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

**$^{1}$H nOe Studies of compound 4c**

The relative stereochemistry of C3-H and C4-H is established from $^{1}$H nOe studies. Irradiation of C3-H ($\delta$ 3.96) causes an nOe enhancement of 1.9% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.
**1H nOe Studies of compound 4d**

![Diagram of compound 4d](image)

The relative stereochemistry of C3-H and C4-H is established from 1H nOe studies. Irradiation of C3-H (δ 3.92) causes an nOe enhancement of 1.5% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

**1H nOe Studies of compound 4e**

![Diagram of compound 4e](image)

The relative stereochemistry of C3-H and C4-H is established from 1H nOe studies. Irradiation of C3-H (δ 3.99) causes an nOe enhancement of 1.8% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

**1H nOe Studies of compound 4f**

![Diagram of compound 4f](image)

The relative stereochemistry of C3-H and C4-H is established from 1H nOe studies. Irradiation of C3-H (δ 3.98) causes an nOe enhancement of 1.7% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.
**$^1$H nOe Studies of compound 4g**

The relative stereochemistry of C3-H and C4-H is established from $^1$H nOe studies. Irradiation of C3-H (δ 4.04) causes an nOe enhancement of 1.6% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

**$^1$H nOe Studies of compound 4h**

The relative stereochemistry of C3-H and C4-H is established from $^1$H nOe studies. Irradiation of C3-H (δ 4.01) causes an nOe enhancement of 1.8% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.
Supplementary Material (ESI) for Chemical Communications
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**Compound 8a**

Yellow solid. Mp : 169-171 °C

**IR (KBr) ν max:** 3024, 2914, 1741, 1689, 1614, 1587, 1512, 1457, 1303, 1257, 1170, 1078 cm⁻¹.

**¹H NMR:** δ 7.47–7.42 (m, 3H), 7.32-7.22 (m, 5H), 7.16 (d, 1H, J = 7.2 Hz), 7.03 (d, 2H, J = 8.6 Hz), 6.94-6.88 (m, 2H), 6.71 (d, 2H, J = 8.6 Hz), 4.42 (d, 1H, J = 12.2 Hz), 3.83 (s, 3H), 3.70-3.67 (m, 4H), 3.09-2.86 (m, 2H), 2.77-2.71 (m, 1H), 2.67-2.56 (m, 1H), 2.19-2.16 (m, 1H), 1.66-1.62 (m, 1H)

**¹³C NMR:** 213.5, 204.4, 160.9, 158.5, 140.7, 135.2, 134.6, 133.3, 133.1, 132.7, 132.5, 129.9, 129.1, 128.8, 128.7, 128.1, 127.5, 126.9, 114.3, 114.2, 113.8, 70.1, 55.3, 54.9, 54.3, 47.9, 43.5, 27.1.

**HRMS (EI) for C₃₀H₂₈O₄ Calcd:** 452.1988, found: 452.1976

**Compound 8b**

White solid. Mp : 172-174 °C

**IR (KBr) ν max:** 3027, 2925, 1740, 1684, 1618, 1588, 1490, 1301, 1248, 1181, 1095 cm⁻¹.

**¹H NMR:** δ 7.48-7.46 (m, 3H), 7.37-7.26 (m, 4H), 7.16-7.09 (m, 6H), 6.85-6.79 (m, 2H), 4.64 (d, 1H, J = 12.7 Hz), 4.19-4.17 (m, 1H), 3.86 (s, 3H), 3.06-2.96 (m, 2H), 2.59-2.48 (m, 2H), 2.18-2.17 (m, 1H), 1.65-1.60 (m, 1H).

**¹³C NMR:** 214.1, 204.9, 157.5, 137.2, 135.8, 135.3, 134.3, 130.8, 129.6, 128.7, 128.6, 128.4, 127.7, 127.1, 126.9, 120.9, 110.4, 69.9, 55.3, 52.7, 46.5, 35.6, 27.0.

**HRMS (EI) for C₂₉H₂₆O₃ Calcd:** 422.1882, found: 422.1888

**Compound 8c**

White solid. Mp : 202-204 °C

**IR (KBr) ν max:** 3026, 2914 1732, 1695, 1624, 1602, 1494, 1301, 1244, 1176, 1099 cm⁻¹.

**¹H NMR:** δ 7.43-7.37 (m, 3H), 7.29-7.25 (m, 3H), 7.18-7.12 (m, 3H), 7.03-6.94 (m, 3H), 6.83-6.80 (m, 2H), 4.59 (d, 1H, J = 12.8 Hz), 4.15-4.13 (m, 1H), 3.88 (s, 3H), 3.03-2.95 (m, 2H), 2.57-2.47 (m, 2H), 2.37 (s, 3H), 2.21 (s, 3H), 2.17-2.16 (m, 1H), 1.66-1.62 (m, 1H).

**¹³C NMR:** 214.4, 205.1, 157.5, 139.9, 136.3, 134.8, 134.3, 134.1, 132.6, 130.9, 129.4, 129.1, 128.8, 128.6, 127.6, 127.1, 120.9, 110.3, 69.9, 55.3, 52.4, 46.6, 35.6, 26.9, 26.8, 21.5.

**HRMS (EI) for C₃₁H₃₀O₃ Calcd:** 450.2195, found: 450.2194
**Compound 8d**

White solid. Mp : 156-158 °C  
**IR (KBr) v max:** 3022, 2916, 1738, 1691, 1614, 1581, 1511, 1459, 1255, 1165, 1060 cm⁻¹.  
**¹H NMR:** δ 7.42-7.37 (m, 3H), 7.25-7.16 (m, 6H), 6.98 (s, 3H), 6.77 (d, 2H, J = 8.6 Hz), 4.38 (d, 1H, J = 12.3 Hz) 3.73 (s, 3H), 3.70-3.66 (m, 1H) 3.09-2.98 (m, 1H), 2.87 (dd, 1H, J₁ = 17.8 Hz, J₂ = 7.3 Hz), 2.68 (dd, 1H, J₁ = 17.8 Hz, J₂ = 12.6 Hz) 2.59-2.51 (m, 1H), 2.37 (s, 3H), 2.23 (s, 3H), 2.15-2.13 (m, 1H), 1.63-1.58 (m, 1H)  
**¹³C NMR:** 213.8, 203.3, 157.3, 132.8, 132.1, 130.4, 130.0, 128.6, 128.3, 115.2, 113.3, 70.3, 58.1, 56.1, 55.7, 27.2  
**HRMS (EI) for C₃₁H₃₀O₃:** Calcd: 450.2195, found: 450.2186

**Compound 8e**

White solid. Mp : 143-145 °C  
**IR (KBr) v max:** 3030, 2920, 1739, 1691, 1620, 1598, 1478, 1310, 1239, 1175, 1080 cm⁻¹.  
**¹H NMR:** δ 7.47-7.42 (m, 3H), 7.30-7.25 (m, 1H), 7.15-7.03 (m, 3H), 6.90-6.80 (m, 4H), 6.69 (d, 2H, J = 8.7 Hz), 4.57 (d, 1H, J = 12.8 Hz), 4.13-4.10 (m, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.69 (s, 3H), 3.02-2.94 (m, 2H), 2.56-2.46 (m, 2H), 2.18-2.16 (m, 1H), 1.68-1.64 (m, 1H).  
**¹³C NMR:** δ 214.8, 205.2, 161.0, 158.6, 157.7, 134.4, 133.6, 132.8, 129.9, 129.4, 128.9, 128.3, 127.8, 127.3, 121.2, 117.3, 114.4, 113.9, 113.5, 110.6, 109.8, 70.2, 55.5, 55.4, 55.1, 52.3, 46.9, 35.9, 27.1.  
**HRMS (EI) for C₃₁H₃₀O₅:** Calcd: 482.2093, found: 482.2097

**Compound 8f**

White solid. Mp : 134-136 °C  
**IR (KBr) v max:** 3025, 2918, 1741, 1696, 1617, 1592, 1492, 1306, 1241, 1176, 1093 cm⁻¹.  
**¹H NMR:** δ 7.49-7.46 (m, 3H), 7.37-7.35 (m, 3H), 7.24-7.17 (m, 5H), 7.14-7.09 (m, 3H), 6.78 (d, 2H, J = 8.6 Hz), 4.42 (d, 1H, J = 12.3 Hz), 3.73 (s, 3H), 3.72-3.65 (m, 1H), 3.12-3.01 (m, 1H), 2.89 (dd, 1H, J₁ = 17.9 Hz, J₂ = 7.3 Hz), 2.71 (dd, 1H, J₁ = 17.8 Hz, J₂ = 12.6 Hz), 2.60-2.52 (m, 1H), 2.21-2.14 (m, 1H), 1.62-1.55 (m, 1H)  
**¹³C NMR:** δ 213.1, 204.4, 158.4, 137.2, 135.4, 135.3, 134.7, 134.5, 132.4, 130.8, 129.6, 128.9, 128.5, 128.4, 127.1, 114.1, 70.1, 55.1, 54.9, 47.9, 42.5, 27.2.  
**HRMS (EI) for C₂₉H₂₆O₃:** Calcd: 422.1882, found: 422.1869
Compound 8g

White solid. Mp : 157-159 °C

IR (KBr) \( \nu \text{ max: } 3031, 2917, 1736, 1688, 1620, 1580, 1501, 1459, 1302, 1261, 1210, 1080 \text{ cm}^{-1}. \)

\(^1\text{H NMR: } \delta 7.43-7.24 (m, 6H), 7.18-7.12 (m, 4H), 6.99 (s, 4H), 4.44 (d, 1H, \( J = 12.3 \text{ Hz} \)), 3.75-3.71 (m, 1H), 3.08-2.99 (m, 1H), 2.90 (dd, 1H, \( J_1 = 17.8 \text{ Hz}, J_2 = 7.3 \text{ Hz} \)), 2.73 (dd, 1H, \( J_1 = 17.8 \text{ Hz}, J_2 = 12.5 \text{ Hz} \)), 2.60-2.57 (m, 1H), 2.36 (s, 3H), 2.22 (s, 3H), 2.17-2.13 (m, 1H), 1.64-1.59 (m, 1H)

\(^{13}\text{C NMR: } 213.3, 204.5, 140.7, 140.0, 136.6, 134.7, 134.5, 134.0, 132.6, 130.9, 129.4, 129.2, 128.8, 128.7, 127.5, 126.9, 70.1, 54.6, 47.9, 43.3, 27.2, 26.9, 21.6.

HRMS (EI) for C\(_{30}\)H\(_{28}\)O\(_2\): Calcd: 420.2089, Found: 420.2076

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Compound 8h

White solid. Mp : 166-168 °C

IR (KBr) \( \nu \text{ max: } 3028, 2911, 1737, 1693, 1602, 1488, 1301, 1247, 1168, 1079 \text{ cm}^{-1}. \)

\(^1\text{H NMR: } \delta 7.49-7.47 (m, 3H), 7.38-7.27 (m, 5H), 7.22-7.10 (m, 9H), 4.48 (d, 1H, \( J = 12.3 \text{ Hz} \)), 3.77-3.74 (m, 1H), 3.13-3.02 (m, 1H), 2.93 (dd, 1H, \( J_1 = 17.9 \text{ Hz}, J_2 = 7.3 \text{ Hz} \)), 2.75 (dd, 1H, \( J_1 = 17.9 \text{ Hz}, J_2 = 12.5 \text{ Hz} \)), 2.62-2.58 (m, 1H), 2.22-2.16 (m, 1H), 1.63-1.59 (m, 1H)

\(^{13}\text{C NMR: } 213.0, 204.4, 140.5, 137.1, 135.4, 134.8, 134.6, 130.7, 129.7, 128.9, 128.7, 128.5, 127.5, 127.2, 126.9, 70.0, 55.0, 47.9, 27.2.

HRMS (EI) for C\(_{28}\)H\(_{24}\)O\(_2\): Calcd: 392.1776, Found: 392.1786

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Compound 8i

White solid. Mp : 152-154 °C

IR (KBr) \( \nu \text{ max: } 3029, 2914, 1740, 1696, 1621, 1600, 1495, 1303, 1247, 1228, 1180, 1091 \text{ cm}^{-1}. \)

\(^1\text{H NMR: } \delta 7.43 (d, 3H, \( J = 8.8 \text{ Hz} \)), 7.25-7.20 (m, 2H), 7.02 (d, 2H, \( J = 8.5 \text{ Hz} \)), 6.87 (d, 2H, \( J = 8.6 \text{ Hz} \)), 6.79-6.69 (m, 4H), 4.35 (d, 1H, \( J = 12.3 \text{ z} \)), 3.80 (s, 3H), 3.71 (s, 3H), 3.68 (s, 3H), 3.65-3.63 (m, 1H), 3.06-2.95 (m, 1H), 2.86 (dd, 1H, \( J_1 = 17.8 \text{ Hz}, J_2 = 7.2 \text{ Hz} \)), 2.67 (dd, 1H, \( J_1 = 17.8 \text{ Hz}, J_2 = 12.4 \text{ Hz} \)), 2.56-2.48 (m, 1H), 2.19-2.15 (m, 1H), 1.65-1.61 (m, 1H)

\(^{13}\text{C NMR: } 213.6, 204.5, 160.8, 158.4, 158.3, 134.5, 133.0, 132.6, 132.5, 129.8, 129.1, 128.3, 128.0, 114.2, 114.0, 113.8, 70.1, 55.2, 54.9, 54.5, 48.0, 47.7, 27.1, 26.8

HRMS (EI) for C\(_{31}\)H\(_{30}\)O\(_5\): Calcd: 482.2093, Found: 482.2094
### Compound 8j

<table>
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<th>White solid. Mp : 162 -164 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR (KBr) ν max: 3031, 2901, 1738, 1691, 1625, 1588, 1497, 1309, 1236, 1221, 1158, 1084 cm⁻¹.</td>
</tr>
<tr>
<td>¹H NMR: δ 7.70 (s, 1H), 7.53 (d, 1H, J = 5.0 Hz), 7.38 (d, 1H, J = 3.6 Hz), 7.34-7.31 (m, 1H), 7.19-7.11 (m, 2H), 7.05-7.03 (m, 1H), 6.91-6.80 (m, 3H), 6.76-6.75 (m, 1H), 4.88 (d, 1H, J = 12.4 Hz), 4.08-3.97 (m, 1H), 3.90 (s, 3H), 3.01-2.93 (m, 2H), 2.70-2.50 (m, 2H), 2.25-2.18 (m, 1H), 1.86-1.75 (m, 1H)</td>
</tr>
<tr>
<td>¹³C NMR: 213.8, 203.9, 157.7, 141.0, 140.0, 133.6, 130.9, 128.6, 128.2, 127.5, 127.3, 127.0, 126.1, 124.5, 121.1, 110.7, 70.8, 55.5, 48.2, 46.4, 38.5, 26.8</td>
</tr>
<tr>
<td>HRMS (EI) for C₂₅H₂₂O₃S₂: Calcd: 434.1010, found: 434.1008</td>
</tr>
</tbody>
</table>

### Compound 8k

<table>
<thead>
<tr>
<th>White solid. Mp : 157 -159°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR (KBr) ν max: 3025, 2911, 1737, 1688, 1617, 1605, 1493, 1310, 1245, 1220, 1177, 1088 cm⁻¹.</td>
</tr>
<tr>
<td>¹H NMR: δ 7.69 (s, 1H), 7.53 (d, 1H, J = 4.9 Hz), 7.38 (d, 1H, J = 3.6 Hz), 7.29 (s, 1H), 7.14-7.11 (m, 1H), 7.08 (d, 1H, J = 4.9 Hz), 6.84-6.80 (m, 3H), 6.72 (d, 1H, J = 3.4 Hz), 4.65 (d, 1H, J = 12.3 Hz), 3.76 (s, 3H), 3.62-3.51 (m, 1H), 2.99-2.83 (m, 2H), 2.70-2.60 (m, 2H), 2.24-2.17 (m, 1H), 1.85-1.75 (m, 1H)</td>
</tr>
<tr>
<td>¹³C NMR: 212.5, 203.3, 158.6, 140.6, 139.8, 133.4, 132.8, 132.2, 130.8, 128.4, 127.4, 126.9, 126.2, 124.4, 114.1, 70.7, 55.0, 50.6, 47.9, 44.8, 26.8, 26.7</td>
</tr>
<tr>
<td>HRMS (EI) for C₂₅H₂₂O₃S₂: Calcd: 434.1010, found: 434.1014</td>
</tr>
</tbody>
</table>
Compound 10

DBU (18 mg, 12 mol %) was added to a suspension of the carbene precursor 1,3-dimesityl imidazolium chloride 3 (21 mg, 6 mol %) in dry CH$_2$Cl$_2$ under argon atmosphere. This was followed by the addition of enal 6 (132 mg, 1 mmol) and dienone 9 (192 mg, 0.7 mmol) and the resulting solution was stirred for 8 h at room temperature. Removal of solvent followed by column chromatography as described in the general procedure afforded the bicyclic cyclopentene derivative 10 as a colorless viscous liquid (202 mg, 80%).

<table>
<thead>
<tr>
<th>IR (film) $\nu_{\text{max}}$: 3026, 2926, 1600, 1494, 1450 cm$^{-1}$.</th>
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<tbody>
<tr>
<td>$^1$H NMR: $\delta$ 7.31–7.06 (m, 15H), 6.78 (s, 1H), 5.87 (s, 1H), 4.06–4.03 (m, 1H), 2.99–2.85 (m, 3H), 2.29–2.25 (m, 1H), 1.97–1.81 (m, 2H), 1.42–1.27 (m, 2H).</td>
</tr>
<tr>
<td>$^{13}$C NMR: $\delta$ 146.6, 144.6, 142.5, 137.4, 136.7, 129.4, 128.5, 127.7, 126.5, 125.2, 124.0, 65.3, 58.4, 53.8, 32.3, 29.7, 25.7.</td>
</tr>
<tr>
<td>HRMS (EI) for C$<em>{28}$H$</em>{26}$: calcd.: 362.2034, found: 362.2033.</td>
</tr>
</tbody>
</table>

$^1$H nOe Studies of compound 10

1.7%

The relative stereochemistry of compound 10 is obtained from $^1$H nOe studies. The irradiation of C4-H signal ($\delta$ 2.29-2.25) causes an nOe enhancement of 1.5% to C2-H signal ($\delta$ 4.06-4.03), thus confirming their cis relationship. In addition, irradiation of the C2-H ($\delta$ 4.06-4.03) enhanced the C1-H signal ($\delta$ 5.87), but did not show any enhancement of the signal due to C3-H thus indicating the trans relationship of C3-H with these protons.
Molecular packing diagram of compound 5a

In an attempt to understand the stabilization of the enolic form of the cyclopentanone in the solid state, we have examined the molecular packing and interactions present in this compound. A view of the H-bonding interactions is given in Figure 1. There is a strong intramolecular O-H…..O interaction between the enolic hydrogen and ketonic oxygen. The exocyclic ketonic oxygen further acts as an acceptor via intermolecular C-H…..O interaction with a phenyl hydrogen which link the molecules in an infinite chain with base vector [1,-1,0]. Thus the stabilization of the enolic form cyclopentanone in the solid state is chiefly attributed to the strong intramolecular O-H...O hydrogen bonding and weak intermolecular C-H...O interactions.

Figure 1. Close up view of the O-H….O and C-H…O hydrogen bonding interactions present in the compound 5a.
Compound 4a.
Compound 4a.
Compound 5a.
Compound 5a.
Compound 4b.
Compound 4b.
Compound 5b.
Compound 5b.
Compound 4c.
Compound 4c.
Compound 5c.
Compound 5c.
Compound 4d.
Compound 4d.
Compound 5d.
Compound 5d
Compound 4e.
Compound 4e.
Compound 5e.
Compound 5e.
Compound 4f.
Compound 4f.
Compound 5f.
Compound 5f.
Compound 4g.
Compound 4g.
Compound 5g.
Compound 5g.
Compound 4h.
Compound 4h.
**Compound 5h.**
Compound 5h.
Compound 8a.
Compound 8a.
Compound 8b.
Compound 8b.
Compound 8c.
Compound 8c.
Compound 8d.
Compound 8d.
Compound 8e.
Compound 8e.
Compound 8f.
Compound 8f.
Compound 8g.
Compound 8g.
Compound 8h.
Compound 8h.
Compound 8i.
Compound 8i.
Compound 8j.
Compound 8j.
Compound 8k.
**Compound 8k.**