***N*- Heterocyclic Carbene Catalyzed Reaction of Chalcones and Enals *via* Homoenolate: An Efficient Synthesis of 1,3,4-trisubstituted Cyclopentenones**

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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 Bruker 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:

Synthesis of 3,4-trans-1- aryl cyclopentene:- DBU (18 mg, 12 mol%) was added to a suspension of the 1,3-dimesityl imidazolium chloride¹ **3** (21 mg, 6 mol%) in 2 ml dry THF under argon atmosphere. This was followed by the addition of 4-methoxy cinnamaldehyde **1** (162 mg, 1 mmol) and chalcone **2** (204 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 dark blue

¹Arduengo, A. J. III.; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, 55, 14523.

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 98:2 hexane-ethyl acetate solvent mixture as eluent to afford **4a** (258 mg, 90%) white crystalline solid. **CCDC** file number for **4a**: 603422.

(3) Characterization data

Compound 4a:

<p>White crystalline solid Mp. 125-126°C. IR (KBr) $\nu_{\max}$: 3047, 2931, 1608, 1517, 1400, 1300, 1248, 1093, 735 cm^{-1}.</p> <p>^1H NMR: δ 7.91-7.82 (m, 2H), 7.70 (d, J = 7.0 Hz, 1H), 7.46-7.36 (m, 6H), 7.31 (d, J = 9.0 Hz, 2H), 7.06 (d, J = 9.0 Hz, 2H), 6.77 (d, J = 9.0 Hz, 2H), 6.30 (s, 1H), 4.33-4.32 (m, 1H), 4.15-4.10 (m, 1H), 3.75 (s, 3H), 3.50-3.41 (m, 1H), 3.11-3.03 (m, 1H)</p> <p>^{13}C NMR: 158.4, 141.3, 140.9, 137.1, 134.4, 134.2, 133.3, 131.6, 129.2, 128.6, 128.3, 127.1, 125.7, 125.5, 123.9, 114.0, 96.2, 59.0, 55.1, 50.3, 41.6.</p> <p>FAB-LRMS for $\text{C}_{28}\text{H}_{23}\text{ClO}$: calcd. ($\text{M}^+$): 410.14, found: 410.14.</p>
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Compound 4b:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 2932, 1600, 1492, 1461, 1288, 1160, 1105, 1030, 780, 753 cm^{-1}.</p> <p>^1H NMR: δ 7.38 (d, J = 9.0 Hz, 2H), 7.26 (d, J = 9.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.05-7.03 (m, 1H), 6.89-6.78 (m, 4H), 6.13 (s, 1H), 4.55-4.52 (m, 1H), 3.80-3.69 (m, 4H), 3.29-3.20 (m, 1H), 2.97-2.91 (m, 1H).</p> <p>^{13}C NMR: 157.5, 149.6, 140.9, 134.7, 133.2, 132.0, 129.0, 128.7, 128.5, 127.9, 127.1, 126.5, 125.7, 124.4, 123.3, 122.8, 122.6, 120.8, 120.1, 110.8, 110.0, 55.4, 54.0, 48.0, 42.0, 41.6.</p> <p>FAB-LRMS for $\text{C}_{22}\text{H}_{19}\text{ClOS}$: calcd. ($\text{M}^+$): 366.08, found: 366.05.</p>
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Compound 4c:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 3041, 1597, 1491, 1448, 1402, 1263, 1169, 1094, 1012, 818, 778 cm^{-1}.</p> <p>^1H NMR: δ 7.87-7.82 (m, 2H), 7.46-7.13 (m, 14H), 6.32 (s, 1H), 4.38-4.37 (m, 1H), 4.19-4.12 (m, 1H), 3.51-3.45 (m, 1H), 3.12-3.05 (m, 1H).</p> <p>^{13}C NMR: 145.0, 141.3, 134.4, 133.3, 129.0, 128.9, 128.6, 128.1, 127.4, 127.1, 127.0, 126.6, 125.7, 125.5, 125.4, 124.0, 123.7, 59.7, 50.1, 41.7.</p> <p>FAB-LRMS for $\text{C}_{27}\text{H}_{21}\text{Cl}$: calcd. ($\text{M}^+$): 380.13, found: 380.04.</p>
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Compound 4d:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 2925, 1609, 1510, 1302, 1247, 1173, 1037, 810 cm^{-1}.</p> <p>^1H NMR: δ 7.35 (d, J = 8.0 Hz, 2H), 7.12-7.05 (m, 5H), 6.86-6.71 (m, 4H), 6.09 (s, 1H), 4.04-4.02 (m, 1H), 3.72 (s, 3H), 3.65-3.58 (m, 1H), 3.33-3.25 (m, 1H), 3.01-2.93 (m, 1H), 2.32 (s, 3H).</p> <p>^{13}C NMR: δ 158.5, 148.5, 141.7, 137.3, 136.4, 133.2, 129.7, 129.3, 128.7, 127.6, 126.8, 125.8, 123.8, 123.0, 114.0, 60.4, 55.2, 50.4, 42.7, 29.9, 21.4.</p> <p>FAB-LRMS for $\text{C}_{23}\text{H}_{22}\text{OS}$: calcd. ($\text{M}^+$): 346.14, found: 346.10.</p>
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Compound 4e:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 2932, 2226, 1604, 1510, 1250, 1177, 1034, 830. cm^{-1}.</p> <p>^1H NMR: δ 7.57 (d, J = 8.0 Hz, 2H), δ 7.45 (d, J = 9.0 Hz, 2H), 7.33-7.29 (m, 4H), 6.99 (d, J = 9.0 Hz, 2H), 6.19 (s, 1H), 4.05-3.99 (m, 1H), 3.77 (s, 3H), 3.44 (dd, J = 15Hz, J = 8Hz), 3.44-3.26 (m, 1H), 2.98-2.89 (m, 1H).</p> <p>^{13}C NMR: 158.6, 150.5, 140.6, 135.6, 133.9, 132.3, 131.4, 129.4, 129.1, 128.7, 128.2, 128.1, 127.0, 118.7, 114.0, 113.4, 110.4, 60.1, 55.1, 54.8, 41.0.</p> <p>FAB-LRMS for $\text{C}_{25}\text{H}_{20}\text{ClNO}$: calcd. ($\text{M}^+$): 385.12, found: 385.05.</p>
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Compound 4f:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 2930, 1608, 1510, 1453, 1300, 1248, 1174, 1033, 830 cm^{-1}.</p> <p>^1H NMR: δ 7.49 (d, J = 8.0 Hz, 2H), δ 7.45 (d, J = 9.0 Hz, 2H), 7.33-7.29 (m, 4H), 6.99 (d, J = 9.0 Hz, 2H), 6.19 (s, 1H), 4.05-3.99 (m, 1H), 3.77 (s, 3H), 3.44 (dd, J = 15Hz, J = 8Hz), 3.44-3.26 (m, 1H), 2.98-2.89 (m, 1H).</p> <p>^{13}C NMR: 158.4, 141.3, 140.9, 137.1, 134.4, 134.2, 133.3, 131.6, 129.2, 128.6, 128.3, 127.1, 125.7, 125.5, 123.9, 114.0, 96.2, 59.0, 55.1, 50.3, 41.6.</p> <p>FAB-LRMS for $\text{C}_{24}\text{H}_{22}\text{O}$: calcd. ($\text{M}^+$): 326.17, found: 326.11.</p>
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Compound 4g:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 2931, 1599, 1495, 1243, 1107, 1029, 819, 754 cm^{-1}.</p> <p>^1H NMR: δ 7.51-7.49 (m, 2H), 7.35-7.10 (m, 13H), 6.23 (s, 1H), 4.11 (s, 1H), 3.43-3.28 (m, 2H), 3.02-2.98 (m, 1H).</p> <p>^{13}C NMR: 145.5, 145.0, 142.4, 136.1, 128.6, 128.2, 127.8, 127.6, 127.5, 126.6, 126.4, 125.9, 61.0, 54.7, 42.1.</p> <p>FAB-LRMS for $\text{C}_{23}\text{H}_{20}$: calcd. ($\text{M}^+$): 296.16, found: 296.04.</p>
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Compound 4h:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 2931, 1606, 1512, 1463, 1301, 1175, 1092, 1037, 820 cm^{-1}.</p> <p>^1H NMR: δ 7.38 (d, J = 9.0 Hz, 2H), 7.28 (d, J = 9.0 Hz, 2H), 7.15-7.10 (m, 2H), 7.00-6.90 (m, 4H), 6.77 (d, J = 9.0 Hz, 2H), 6.16 (s, 1H), 3.98-3.95 (m, 1H), 3.74 (s, 3H), 3.38-3.18 (m, 2H), 2.90-2.84 (m, 1H).</p> <p>^{13}C NMR: δ 163.3, 160.1, 158.6, 140.9, 140.7, 136.5, 134.4, 133.4, 129.9, 129.2, 128.9, 128.4, 127.2, 115.6, 115.3, 114.4, 113.5, 60.4, 55.3, 54.4, 42.0.</p> <p>FAB-LRMS for $\text{C}_{24}\text{H}_{20}\text{ClFO}$: calcd. ($\text{M}^+$): 378.12, found: 378.05.</p>
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Compound 4i:

<p>Viscous liquid. 128-129°C. IR (KBr) $\nu_{\max}$: 2930, 1610, 1510, 1402, 1247, 1176, 1093, 1011, 819 cm^{-1}.</p> <p>^1H NMR: δ 7.39 (d, J = 9.0 Hz, 2H), 7.28 (d, J = 9.0 Hz, 2H), 7.21 (d, J = 9.0 Hz, 2H), 7.10 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 6.77 (d, J = 9.0 Hz, 2H), 6.16 (s, 1H), 3.98-3.95 (m, 1H), 3.74 (s, 3H), 3.35-3.19 (m, 2H), 2.92-2.85 (m, 1H).</p> <p>^{13}C NMR: δ 158.6, 143.5, 140.9, 136.4, 134.5, 133.5, 132.3, 129.9, 129.2, 128.8, 128.4, 128.1, 127.5, 127.2, 114.7, 60.4, 55.3, 41.9.</p> <p>FAB-LRMS for $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{O}$: calcd. ($\text{M}^+$): 394.09, found: 394.98.</p>
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Compound 4j:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 2928, 1610, 1510, 1439, 1303, 1248, 1175, 1108, 1035, 832, 756 cm^{-1}.</p> <p>^1H NMR: δ 7.47 (d, J = 8.0 Hz, 2H), 7.34-7.29 (m, 2H), 7.24 (d, J = 7 Hz, 1H), 7.11-7.08 (m, 2H), 6.88-6.85 (m, 1H), 6.80 (d, J = 8 Hz, 2H), 6.74-6.73 (m, 1H), 6.17 (s, 1H), 4.05 (d, J = 7 Hz, 1H), 3.75 (s, 3H), 3.69-3.61 (m, 1H), 3.37-3.29 (m, 1H), 3.05-2.97 (m, 1H).</p> <p>^{13}C NMR: δ 158.6, 148.5, 141.9, 136.3, 129.8, 128.8, 128.6, 127.9, 127.27, 126.8, 125.9, 124.8, 123.9, 123.3, 114.1, 113.5, 109.7, 60.6, 55.3, 50.5, 42.7, 40.3.</p> <p>FAB-LRMS for $\text{C}_{24}\text{H}_{20}\text{OS}$: calcd. ($\text{M}^+$): 332.12, found: 332.15.</p>
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Compound 4k:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 2952, 1612, 1462, 1333, 1298, 1175, 1090, 1009, 816, 732. cm^{-1}.</p> <p>^1H NMR: δ 7.38 (d, J = 9.0 Hz, 2H), 7.31-7.26 (m, 3H), 7.07 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 9.0 Hz, 2H), 6.26-6.24 (m, 1H), 6.13 (s, 1H), 5.99 (d, J = 3 Hz, 1H), 4.15-4.12 (m, 1H), 3.75 (s, 3H), 3.43 (q, J = 17 Hz, J = 9 Hz, 1H), 3.19-3.11 (m, 1H), 3.04-2.96 (m, 1H).</p> <p>^{13}C NMR: δ 158.6, 157.3, 141.4, 140.8, 136.4, 134.6, 133.4, 129.4, 129.1, 128.8, 128.6, 127.1, 114.1, 110.3, 105.1, 56.9, 55.3, 48.0, 39.1, 32.2, 31.7, 30.5, 29.9, 22.9.</p> <p>FAB-LRMS for $\text{C}_{22}\text{H}_{19}\text{ClO}_2$: calcd. ($\text{M}^+$): 350.11, found: 350.15.</p>
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Compound 4l:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 2952, 1611, 1509, 1245, 1176, 1038, 824, 749 cm^{-1}.</p> <p>^1H NMR: δ 7.31-7.26 (m, 2H), 7.22-7.17 (m, 1H), 7.11 (d, $J = 9.0$ Hz, 2H), 6.81 (d, $J = 9.0$ Hz, 2H), 6.10 (s, 1H), 3.76 (s, 3H), 3.49-3.46 (m, 1H), 3.04-2.96 (m, 1H), 2.44-2.37 (m, 1H), 2.27-2.23 (m, 1H), 1.19 (d, $J = 7.0$ Hz, 3H).</p> <p>^{13}C NMR: δ 158.4, 142.5, 137.7, 136.6, 129.4, 128.6, 127.4, 125.8, 114.0, 59.6, 55.3, 44.4, 41.6, 32.2, 31.8, 30.4, 29.9, 22.9, 19.9, 14.4.</p> <p>FAB-LRMS for $\text{C}_{19}\text{H}_{19}\text{ClO}$: calcd. ($\text{M}^+$): 298.11, found: 298.15.</p>
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Compound 4m:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 3042, 2957, 1623, 1593, 1403, 1370, 1241, 1092, 1011, 814 cm^{-1}.</p> <p>^1H NMR: δ 7.37-7.20 (m, 4H), 7.12-7.08 (m, 1H), 6.93-6.83 (m, 2H), 6.04 (s, 1H), 3.33-3.25 (m, 1H), 3.20-3.12 (m, 1H), 2.99-2.82 (m, 2H), 1.21 (d, $J = 7.0$ Hz, 3H).</p> <p>^{13}C NMR: δ 148.5, 139.0, 134.5, 132.9, 131.1, 128.5, 127.1, 126.7, 124.4, 123.4, 122.8, 114.7, 49.8, 48.4, 44.6, 43.6, 42.7, 39.1, 19.5.</p> <p>FAB-LRMS for $\text{C}_{16}\text{H}_{15}\text{ClS}$: calcd. ($\text{M}^+$): 274.06, found: 274.94.</p>
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Compound 6:

<p>Viscous liquid. IR (KBr) $\nu_{\max}$: 2952, 1611, 1443, 1300, 1245, 1176, 1038, 824 cm^{-1}.</p> <p>^1H NMR: δ 7.61-7.59 (m, 1H), 7.18-7.06 (m, 6H), 6.89-6.86 (m, 1H), 6.77 (d, $J = 9.0$ Hz, 2H), 6.70-6.69 (m, 1H), 6.10 (s, 1H), 4.07 (d, $J = 9.5$ Hz, 1H), 3.74 (s, 3H), 3.15 (t, $J = 9.6$ Hz), 3.06-2.98 (m, 1H), 2.93-2.83 (m, 2H), 2.21-2.17 (m, 1H), 1.65-1.56 (m, 1H).</p> <p>^{13}C NMR: 158.6, 146.0, 141.7, 137.2, 136.2, 131.4, 129.4, 128.8, 127.8, 127.0, 126.3, 124.8, 124.7, 124.0, 123.2, 114.0, 59.3, 59.2, 55.3, 32.2, 30.6, 29.9, 29.6, 29.2, 22.9.</p> <p>FAB-LRMS for $\text{C}_{24}\text{H}_{22}\text{OS}$: calcd. ($\text{M}^+$): 358.14, found: 358.13.</p>
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¹H NOE Studies of compound 6

The relative stereochemistry of compound **6** is obtained from ¹H NOE studies. The irradiation of C4-H signal (δ 1.65-1.56) of compound **6**, enhanced the C3-H signal (δ 3.15), thus confirming their *cis* relationship. In addition, irradiation of the C2-H (δ 4.07) did not show any enhancement of the signal due to C3-H and C4-H thus indicating the *trans* relationship of C2-H with these protons.

Figure S1. X-ray crystal structure of **4a**

FT-IR Studies on β -lactone formation:
Scheme S1.

The enal **1** (1.0 equiv), chalcone **7** (1.0 equiv) and IMes-Cl (6 mol%) were introduced to an oven dried vial. 1 ml dry THF² and 6 mol% DBU were added to this mixture and stirred for 2 hours. After 2 hours, 0.05 ml of the reaction mixture was taken and smeared on a sodium chloride pellet, Infrared spectrum was recorded and it displayed a peak at 1822 cm^{-1} corresponding to β -lactone carbonyl stretching. IR measurements were repeated at regular intervals of time, to understand the stability of the intermediate β -lactone. A progressive decrease in the intensity of lactone carbonyl peak indicated elimination of carbon dioxide leading to the formation of cyclopentene. The time-dependent change in the expanded region (1750-1950 cm^{-1}) of the IR-spectrum is shown in Figure S2.

Figure S2. Time dependent IR spectral changes of β -lactone intermediate.

² Reaction can also be conducted in dry toluene or dry benzene

Identification of β -lactone by ^{13}C NMR experiment:

Enal **1** (1.0 equiv), chalcone **7** (1.0 equiv) and IMes (6 mol%) were taken in an NMR tube. To this mixture was added 1 ml deuteriated THF and 6 mol% DBU. After 2 hours, ^{13}C NMR (75 MHz) spectrum was recorded it showed a peak at δ 176.9 diagnostic for β -lactone carbonyl group (Figure S3).

Figure S3. ^{13}C NMR spectra of β -lactone intermediate

Compound : 4a

Compound : 4a

Compound : 4b

Compound : 4b

Compound : 4c

Compound : 4c

Compound : 4d

Compound : 4d

Compound : 4e

Compound : 4e

Compound : 4f

Compound : 4f

Compound : 4g

Compound : 4g

Compound : 4h

Compound : 4h

Compound : 4i

Compound : 4i

Compound : 4j

Compound : 4j

Compound : 4k

Compound : 4k

Compound : 4l

Compound : 4l

Compound : 4m

Compound : 4m

Compound : 6

Compound : 6