Phase-Transfer-Catalyzed Cyclization Reaction of Nucleophilic Addition to Electron-Deficient 1,3-Conjugated Enynes for Synthesis of Functionalized 4H-Pyran

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Table of Contents

1. General Remarks  S1
2. General procedure for the preparation of 2  S1
3. References  S1
4. Characterization data of compounds 1  S1-S3
5. Characterization data of compounds 2  S3-S9
6. $^1$HNMR and $^{13}$CNMR spectra for compounds 1  S10-S15
7. $^1$HNMR and $^{13}$CNMR spectra for compounds 2  S16-S35
8. X-ray crystal of 2fb  S36
**General Remarks:**

Column chromatography was carried out on silica gel. \(^1\)H NMR spectra were recorded on 400 MHz in CDCl\(_3\) and \(^13\)C NMR spectra were recorded on 100 MHz in CDCl\(_3\) using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm\(^{-1}\). All new compounds were further characterized by element analysis; copies of their \(^1\)H NMR and \(^13\)C NMR spectra are provided. Commercially available reagents and solvents were used without further purification.

**Starting Materials:**

The preparation of the PTC 1 and PTC 2 were described in previous report,\(^1\) the starting materials 1a, 1b and 1g were prepared according to the previous literature\(^2\text{-}^5\) and the synthesis of the remaining substrates were similar.


**Typical procedure for the preparation of 2**

To a solution of 1 (0.20 mmol) in 2.0 mL of CH\(_2\)Cl\(_2\) was added Cs\(_2\)CO\(_3\) (130.3 mg, 0.40 mmol) in the reaction vessel. The mixture was allowed to stir at room temperature for 1 minute and TBAF 3H\(_2\)O (3.15 mg, 5 mol %) was added. The vessel was sealed and the resulting mixture was then heated at 60 °C. When the reaction was considered complete as determined by TLC analysis, the reaction was allowed to cool to room temperature and quenched with a saturated aqueous solution of ammonium chloride, and the mixture was extracted with EtOAc. The combined organic extracts were washed with water and saturated brine. The organic layers were dried over Na\(_2\)SO\(_4\), filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford 2.

\[
\begin{align*}
&\text{(Z)-2-benzylidene-4-(4-methoxyphenyl)but-3-ynal (1c).} \\
&\text{\(^1\)H NMR (400 MHz, CDCl\(_3\))} \\
&\text{\(\delta \) 9.62 (s, 1H), 8.14-8.11 (m, 2H), 7.54-7.45 (m, 6H), 6.91-6.89 (d, \(J = 8.4\) Hz, 2H), 3.82 (s, 3H);} \\
&\text{\(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 191.1, 160.2, 150.3, 134.2, 133.3, 131.4, 130.5, 128.7, 122.9, 114.6, 114.1, 101.2, 82.2, 55.3. IR (neat, cm\(^{-1}\)): 3367, 2198, 1692, 1508, 1250, 1027, 832, 758. Anal. Calcd for C\(_{18}\)H\(_{14}\)O\(_2\): C 82.42; H 5.38. Found: C}
\end{align*}
\]
82.49; H 5.42.

(R)-2-benzylidene-4-(4-bromophenyl)but-3-ynamide (1d). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12-8.09 (m, 2H), 7.55-7.43 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.7, 151.7, 134.0, 133.2, 131.8, 131.7, 130.6, 128.8, 123.5, 122.4, 121.4, 99.7, 84.2. IR (neat, cm$^{-1}$): 3371, 2204, 1692, 1484, 1137, 1069, 823, 756. Anal. Calcd for C$_{17}$H$_{11}$BrO: C 65.62; H 3.56. Found: C 65.68; H 3.46.

(R)-2-benzylidenehept-3-ynamide (1e). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.53 (s, 1H), 8.09-8.07 (m, 2H), 7.43-7.39 (m, 4H), 2.53-2.49 (t, $J$ = 7.2 Hz, 2H), 1.71-1.65 (t, $J$ = 7.2, 14.4 Hz, 2H), 1.09-1.05 (t, $J$ = 7.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.4, 150.7, 134.0, 131.1, 128.4, 123.3, 103.1, 74.4, 21.7, 21.7, 13.4. IR (neat, cm$^{-1}$): 3366, 2964, 1692, 1598, 1176, 758, 689. Anal. Calcd for C$_{14}$H$_{14}$O: C 84.81; H 7.12. Found: C 84.78; H 7.23.

(R)-2-benzylidene-4-(trimethylsilyl)but-3-ynamide (1f). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.52 (s, 1H), 8.12-8.10 (m, 2H), 7.48 (s, 1H), 7.44-7.42 (m, 3H), -0.30 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.5, 152.1, 133.7, 131.5, 130.5, 128.4, 122.2, 107.5, 98.4, -0.59. IR (neat, cm$^{-1}$): 3367, 2960, 1692, 1596, 1158, 891, 759, 689. Anal. Calcd for C$_{14}$H$_{16}$OSi: C 73.63; H 7.06. Found: C 73.69; H 7.15.

(R)-2-benzylidene-4-phenyl-1-$p$-tolylbut-3-ynamide (1h). $^1$H NMR (400 MHz,
CDCl$_3$ $\delta$ 8.09-8.07 (d, $J = 6.8$ Hz, 2H), 7.94-7.92 (d, $J = 8.4$ Hz, 2H), 7.57 (s, 1H), 7.42-7.37 (m, 5H), 7.29-7.23 (m, 5H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.7, 144.5, 143.3, 134.8, 134.2, 131.2, 130.3, 130.1, 130.0, 129.8, 128.7, 128.4, 128.3, 122.8, 121.0, 106.6, 87.2, 21.5. IR (neat, cm$^{-1}$): 3058, 2921, 1659, 1603, 1264, 1179, 757, 689. Anal. Calcd for C$_{24}$H$_{18}$O: C 89.41; H 5.63. Found: C 89.50; H 5.53.

![Diagram](Image)

(?)-4-benzylidene-6-phenylhex-5-yn-3-one (1i). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10-8.08 (dd, $J = 2.0$ Hz, 7.2 Hz, 2H), 7.85 (s, 1H), 7.56-7.54 (m, 2H), 7.44-7.39 (m, 6H), 3.08-3.02 (dd, $J = 7.2$ Hz, 14.4 Hz, 2H), 1.22-1.19 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.9, 142.6, 134.6, 131.3, 130.7, 130.6, 128.9, 128.6, 128.5, 122.8, 119.6, 99.0, 86.7, 33.7, 8.2. IR (neat, cm$^{-1}$): 3376, 2934, 1696, 1141, 755, 689. Anal. Calcd for C$_{19}$H$_{16}$O: C 87.66; H 6.19. Found: C 87.58; H 6.10.

![Diagram](Image)

Methyl 1-benzyl-5,6,7,8-tetrahydro-3-methyl-8-oxo-4a/?-isochromene-4-carboxylate (2aa). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.21 (m, 5H), 3.87-3.83 (d, $J = 14.0$ Hz, 1H), 3.75-3.68 (m, 4H), 3.49-3.45 (dd, $J = 4.0$, 12.0 Hz, 1H), 2.56-2.51 (m, 1H), 2.49-2.35 (m, 1H), 2.17-2.11 (m, 4H), 1.91-1.84 (m, 2H), 1.61-1.51 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.4, 167.5, 157.2, 153.3, 137.2, 128.9, 128.3, 126.5, 113.7, 106.5, 51.3, 40.9, 35.9, 33.3, 31.7, 21.3, 18.5. IR (neat, cm$^{-1}$): 3298, 2928, 1708, 763, 700. Anal. Calcd for C$_{19}$H$_{20}$O$_4$: C 73.06; H 6.45. Found: C 73.15; H 6.36.

![Diagram](Image)

Ethyl 1-benzyl-5,6,7,8-tetrahydro-3-methyl-8-oxo-4a/?-isochromene-4-carboxylate (2ab). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33-7.21 (m, 5H), 4.25-4.16 (m, 2H), 3.86-3.83 (d, $J = 14.0$ Hz, 1H), 3.72-3.69 (d, $J = 14.0$ Hz, 1H), 3.50-3.47 (m, 1H), 2.56-2.49 (m, 2H), 2.44-1.90 (m, 4H), 1.88-1.85 (m, 2H), 1.62-1.55 (m, 1H), 1.30-1.26 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.4, 167.1, 156.8, 153.5, 137.3, 129.0, 128.3, 126.5, 113.7, 106.8, 60.2, 41.0, 36.0, 33.3, 31.7, 21.3, 18.5, 14.2. IR (neat, cm$^{-1}$): 3394, 2938, 1740, 1681, 1163, 736, 702. Anal. Calcd for C$_{20}$H$_{22}$O$_4$: C 73.60; H
6.79. Found: C 73.69; H 6.69.

![Structure 1]

4-Acetyl-1-benzyl-4a,5,6,7-tetrahydro-3-methylisochromen-8-one (2ae). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.21 (m, 5H), 3.88-3.84 (d, $J = 14.0$ Hz, 1H), 3.70-3.67 (d, $J = 14.0$ Hz, 1H), 3.56-3.53 (m, 1H), 2.58-2.37 (m, 2H), 2.24 (s, 3H), 1.99 (s, 3H), 1.95-1.86 (m, 3H), 1.64-1.58 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.9, 199.9, 153.8, 153.3, 137.1, 128.9, 128.3, 126.5, 115.7, 113.4, 41.0, 36.0, 33.8, 32.1, 29.2, 21.5, 18.3. IR (neat, cm$^{-1}$): 3384, 2931, 1717, 1678, 1176, 1083, 701. Anal. Calcd for C$_{19}$H$_{20}$O$_3$: C 77.00; H 6.80. Found: C 77.09; H 6.77.

![Structure 2]

6-Benzyl-3,4,8,9,10,10a-hexahydro-2H-benzo[a]chromene-1,7-dione (2ad). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.26 (m, 5H), 3.86-3.82 (d, $J = 14.0$ Hz, 1H), 3.74-3.70 (d, $J = 14.0$ Hz, 1H), 3.42-3.38 (m, 1H), 2.59-2.30 (m, 7H), 1.97-1.90 (m, 4H), 1.48-1.42 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.8, 197.6, 165.2, 152.8, 137.0, 129.0, 128.4, 126.6, 115.7, 114.1, 41.3, 37.1, 35.9, 31.0, 30.7, 27.1, 21.7, 20.1. IR (neat, cm$^{-1}$): 3306, 2947, 1699, 1657, 1170, 1133, 724. Anal. Calcd for C$_{20}$H$_{22}$O$_3$: C 77.90; H 6.54. Found: C 77.79; H 6.46.

![Structure 3]

6-Benzyl-3,4,8,9,10,10a-hexahydro-3,3-dimethyl-2H-benzo[a]chromene-1,7-dione (2ae). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.20 (m, 5H), 3.86 -3.82 (d, $J = 14.0$ Hz, 1H), 3.74-3.70 (d, $J = 14.0$ Hz, 1H), 3.43-3.39 (m, 1H), 2.59-2.52 (m, 2H), 2.43-2.37 (m, 1H), 2.36-2.18 (m, 4H), 1.96-1.88 (m, 2H), 1.48-1.43 (m, 1H), 1.01 (s, 3H), 1.00 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.8, 197.5, 163.4, 152.4, 137.1, 128.9, 128.3, 126.6, 115.6, 112.8, 51.0, 41.2, 40.7, 35.9, 31.7, 30.9, 30.5, 28.5, 27.9, 21.6. IR (neat, cm$^{-1}$): 3305, 2958, 1700, 1387, 1162, 913, 728. Anal. Calcd for C$_{28}$H$_{24}$O$_3$: C 78.54; H 7.19. Found: C 78.61; H 7.25.
5-Acetyl-2-benzyl-6-methyl-4-phenyl-4/H-pyran-3-carbaldehyde (2ba). $^1$H NMR (400 MHz, CDCl$_3$) δ 10.0, 7.34-7.22 (m, 10H), 4.86 (s, 1H), 4.05-4.02 (d, J = 15.2 Hz, 1H), 3.93-3.90 (d, J = 15.2 Hz, 1H), 2.34 (s, 3H), 2.15 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.9, 187.8, 164.4, 157.3, 143.3, 135.4, 128.8, 128.6, 128.4, 128.3, 127.3, 127.1, 118.8, 115.8, 35.9, 34.8, 29.6, 18.7. IR (neat, cm$^{-1}$): 3313, 3029, 1663, 1160, 949, 702. Anal. Calcd for C$_{22}$H$_{20}$O$_3$: C 79.50; H 6.06. Found: C 79.60; H 6.15.

Methyl 6-benzyl-5-formyl-2-methyl-4-phenyl-4/H-pyran-3-carboxylate (2bb). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.98, 7.34-7.13 (m, 10H), 4.85 (s, 1H), 4.03-3.99 (d, J = 14.8 Hz, 1H), 3.95-3.91 (d, J = 14.8 Hz, 1H), 3.59 (s, 3H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 187.8, 166.5, 164.3, 144.1, 135.5, 128.7, 128.4, 128.1, 128.1, 127.2, 126.7, 118.4, 108.8, 51.4, 35.2, 34.7, 18.3. IR (neat, cm$^{-1}$): 3427, 1714, 1699, 1161, 1087, 700. Anal. Calcd for C$_{22}$H$_{20}$O$_4$: C 75.84; H 5.79. Found: C 75.80; H 5.71.

2-(4-Methoxybenzyl)-5-acetyl-6-methyl-4-phenyl-4/H-pyran-3-carbaldehyde (2ca). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.99 (s, 1H), 7.26-7.19 (m, 4H), 7.18-7.15 (dd, J = 4.0, 8.4 Hz, 1H), 7.13-7.11 (d, J = 8.8 Hz, 2H), 6.86-6.84 (d, J = 8.8 Hz, 2H), 4.84 (s, 1H), 3.97-3.93 (d, J = 14.8 Hz, 1H), 3.85-3.81 (d, J = 14.8 Hz, 1H), 3.79 (s, 3H), 2.32 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.9, 187.8, 164.8, 158.8, 157.2, 143.4, 129.4, 128.6, 128.3, 127.3, 127.0, 118.6, 115.8, 114.3, 55.2, 35.9, 34.0, 29.6, 18.7. IR (neat, cm$^{-1}$): 3420, 2928, 1660, 1249, 1158, 700. Anal. Calcd for C$_{23}$H$_{22}$O$_4$: C 76.22; H 6.12. Found: C 76.28; H 6.18.

Methyl 6-(4-methoxybenzyl)-5-formyl-2-methyl-4-phenyl-4/H-pyran-3-carboxylate (2cb). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.98 (s, 1H), 7.24-7.22 (d, J = 6.0 Hz, 4H), 7.15-7.14 (d, J = 8.4 Hz, 3H), 6.86-6.84 (d, J = 8.4 Hz, 2H), 4.83 (s, 1H), 3.97-3.93 (m, 2H), 3.78 (s, 3H), 3.61 (s, 3H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 187.8,
166.6, 164.8, 158.8, 158.6, 144.2, 129.4, 128.2, 128.1, 127.4, 126.6, 118.2, 114.2, 108.8, 55.2, 51.4, 35.2, 33.9, 18.4. IR (neat, cm⁻¹): 3410, 2951, 1714, 1669, 1246, 1158, 1036, 732. Anal. Calcd for C₂₃H₂₂O₅: C 73.00; H 5.86. Found: C 73.07; H 5.79.

![Image](image_url)

2-(4-Bromobenzyl)-5-acetyl-6-methyl-4-phenyl-4H-pyran-3-carbaldehyde (2da). ¹H NMR (400 MHz, CDCl₃) δ 9.96 (s, 1H), 7.46-7.43 (d, J = 8.4 Hz, 2H), 7.27-7.24 (m, 5H), 7.09-7.07 (d, J = 8.0 Hz, 2H), 4.84 (s, 1H), 3.97-3.94 (d, J = 15.2 Hz, 1H), 3.88-3.84 (d, J = 15.2 Hz, 1H), 2.31 (s, 1H), 2.13 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.7, 187.6, 163.6, 157.1, 143.2, 134.4, 131.9, 130.1, 128.6, 128.2, 127.2, 121.3, 118.9, 115.8, 35.9, 34.2, 29.6, 18.7. IR (neat, cm⁻¹): 3407, 2925, 1661, 1160, 1020, 800. Anal. Calcd for C₂₂H₁₉BrO₃: C 64.25; H 4.66. Found: C 64.28; H 4.58.

![Image](image_url)

Methyl 6-(4-bromobenzyl)-5-formyl-2-methyl-4-phenyl-4H-pyran-3-carboxylate (2db). ¹H NMR (400 MHz, CDCl₃) δ 9.95 (s, 1H), 7.47-7.44 (d, J = 8.4 Hz, 2H), 7.25-7.21 (m, 5H), 7.12-7.10 (d, J = 8.4 Hz, 2H), 4.84 (s, 1H), 3.99-3.89 (m ,2H), 3.62 (s, 3H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 187.7, 166.5, 163.5, 158.5, 144.0, 134.5, 131.9, 130.2, 128.2, 128.1, 126.8, 121.3, 118.7, 108.9, 51.5, 35.4, 34.2, 18.4. IR (neat, cm⁻¹): 3430, 2949, 1714, 1670, 1161, 1080, 733. Anal. Calcd for C₂₂H₁₉BrO₄: C 61.84; H 4.48. Found: C 64.75; H 4.41.

![Image](image_url)

5-Acetyl-2-butyl-6-methyl-4-phenyl-4H-pyran-3-carbaldehyde (2ea). ¹H NMR (400 MHz, CDCl₃) δ 9.83 (s, 1H), 7.26-7.17 (m, 5H), 4.80 (s, 1H), 2.69-2.58 (m, 2H), 2.39 (s, 3H), 2.14 (s, 3H), 1.66-1.60 (m, 2H), 1.39-1.34 (m, 2H), 0.94-0.91 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 187.8, 167.1, 157.2, 143.6, 128.6, 128.2, 126.9, 118.3, 115.8, 35.8, 29.9, 29.6, 28.6, 22.1, 18.8, 13.7. IR (neat, cm⁻¹): 3407, 2929, 1661, 1176, 1030, 747. Anal. Calcd for C₁₉H₂₂O₅: C 76.48; H 7.43. Found: C 76.59; H 7.49.
Methyl 6-butyl-5-formyl-2-methyl-4-phenyl-4H-pyran-3-carboxylate (2eb). 1H NMR (400 MHz, CDCl₃) δ 9.83 (s, 1H), 7.26-7.13 (m, 5H), 4.79 (s, 1H), 3.63 (s, 3H), 2.70-2.65 (m, 2H), 2.42 (s, 3H), 1.70-1.63 (m, 2H), 1.43-1.36 (m, 2H), 0.96-0.92 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl₃) δ 187.8, 167.1, 166.8, 158.5, 144.4, 128.1, 128.1, 126.6, 118.9, 51.5, 35.1, 29.9, 28.5, 22.1, 18.4, 13.7. IR (neat, cm⁻¹): 3399, 2956, 1715, 1669, 1175, 1039, 698. Anal. Calcd for C₁₉H₂₂O₃: C 76.48; H 7.43. Found: C 76.58; H 7.36.

5-Acetyl-2,6-dimethyl-4-phenyl-4H-pyran-3-carbaldehyde (2fa). 1H NMR (400 MHz, CDCl₃) δ 9.83 (s, 1H), 7.27-7.16 (m, 5H), 4.79 (s, 1H), 2.39 (s, 3H), 2.29 (s, 3H), 2.13 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 199.1, 188.1, 163.3, 157.1, 143.5, 128.6, 128.3, 127.0, 118.3, 115.8, 35.8, 29.6, 18.9, 15.4. IR (neat, cm⁻¹): 3433, 2925, 1660, 1194, 1022, 700. Anal. Calcd for C₁₆H₁₆O₃: C 74.98; H 6.29. Found: C 74.88; H 6.37.

Methyl 5-formyl-2,6-dimethyl-4-phenyl-4H-pyran-3-carboxylate (2fb). 1H NMR (400 MHz, CDCl₃) δ 9.82 (s, 1H), 7.26-7.12 (m, 5H), 4.79 (s, 1H), 3.62 (s, 3H), 2.42 (s, 3H), 2.32 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 188.1, 166.7, 163.3, 158.3, 144.3, 128.1, 126.6, 117.9, 108.9, 51.4, 35.1, 18.5, 15.3. IR (neat, cm⁻¹): 3416, 2925, 1714, 1670, 1192, 1021, 699. Anal. Calcd for C₁₆H₁₆O₄: C 70.57; H 5.92. Found: C 70.68; H 5.84.

5-Acety-2-benzyl-6-methyl-4-phenyl-4H-pyran-3-benzaldehyde (2ga). 1H NMR (400 MHz, CDCl₃) δ 7.56-7.46 (m, 3H), 7.34-7.30 (t, J = 7.6 Hz, 2H), 7.24-7.05 (m, 10 H), 4.92 (s, 1H), 3.42-3.29 (m, 2H), 2.30 (s, 3H), 2.06 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 198.9, 197.2, 158.2, 150.6, 143.3, 138.4, 136.4, 132.9, 128.9, 128.7, 128.6, 128.4, 127.7, 127.2, 126.7, 117.2, 113.8, 41.9, 37.1, 29.6, 19.1. IR (neat, cm⁻¹): 3397, 2961, 1693, 1598, 1209, 1026, 699. Anal. Calcd for C₂₉H₂₉O₃: C 82.33; H 5.92. Found: C 82.27; H 5.88.
Methyl 6-benzyl-5-benzoyl-2-methyl-4-phenyl-4/H-pyran-3-carboxylate (2gb). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60-7.58 (d, $J = 8.4$ Hz, 2H), 7.48-7.46 (d, $J = 7.6$ Hz, 1H), 7.36-7.32 (m, 2H), 7.25-7.07 (m, 10H), 4.86 (s, 1H), 3.55 (s, 3H), 3.49-3.38 (m, 2H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.9, 167.1, 159.7, 151.1, 143.9, 138.1, 136.6, 132.8, 128.8, 128.6, 128.5, 128.4, 128.3, 127.7, 126.8, 126.6, 117.1, 106.5, 51.3, 41.1, 37.0, 18.7. IR (neat, cm$^{-1}$): 3400, 3028, 1714, 1164, 1088, 698. Anal. Calcd for C$_{25}$H$_{24}$O$_3$: C 79.22; H 5.70. Found: C 79.16; H 5.66.

5-Acetyl-2-benzyl-6-methyl-4-phenyl-4/H-pyran-3-(4-methylbenzaldehyde) (2ha). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48-7.45 (d, $J = 8.0$ Hz, 2H), 7.25-7.18 (m, 6H), 7.15-7.05 (m, 6H), 4.91 (s, 1H), 3.43-3.28 (m, 2H), 2.35 (s, 3H), 2.29 (s, 3H), 2.06 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.9, 196.8, 158.3, 149.9, 143.9, 143.3, 136.5, 135.7, 129.3, 129.0, 128.8, 128.6, 128.3, 127.7, 127.1, 126.6, 117.2, 113.7, 41.9, 37.1, 29.6, 21.6, 19.1. IR (neat, cm$^{-1}$): 3434, 2924, 1602, 1209, 1171, 1133, 737. Anal. Calcd for C$_{29}$H$_{26}$O$_3$: C 82.44; H 6.20. Found: C 82.38; H 6.14.

Methyl 6-benzyl-5-(4-methylbenzoyl)-2-methyl-4-phenyl-4/H-pyran-3-carboxylate (2hb). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53-7.51 (d, $J = 8.0$ Hz, 2H), 7.24-7.08 (m, 12H), 4.85 (s, 1H), 3.55 (s, 3H), 3.49-3.36 (m, 2H), 2.35 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.6, 167.2, 159.8, 150.4, 143.9, 143.8, 136.7, 135.5, 129.2, 129.1, 128.7, 128.4, 128.3, 127.7, 126.9, 126.6, 117.2, 106.4, 51.2, 41.2, 37.0, 21.6, 18.7. IR (neat, cm$^{-1}$): 3409, 2981, 1685, 1179, 1044, 758. Anal. Calcd for C$_{29}$H$_{26}$O$_3$: C 79.43; H 5.98. Found: C 79.49; H 5.91.

5-Acetyl-2-benzyl-6-methyl-4-phenyl-4/H-pyran-3-propionaldehyde (2ia). $^1$H NMR
(400 MHz, CDCl₃) δ 7.31-7.18 (m, 10H), 4.85 (s, 1H), 4.03-3.92 (m, 2H), 2.60-2.53 (m, 2H), 2.45-2.39 (m, 3H), 2.22-2.21 (d, J = 7.2 Hz, 3H), 0.98-0.94 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 202.1, 198.0, 157.1, 156.0, 144.1, 137.0, 128.9, 128.8, 128.7, 128.5, 128.0, 127.1, 126.7, 117.2, 39.2, 37.1, 34.8, 30.6, 19.4, 7.9. IR (neat, cm⁻¹): 3432, 2927, 1689, 1597, 1183, 1027, 701. Anal. Calcd for C₂₄H₂₄O₃: C 79.97; H 6.71. Found: C 79.90; H 6.80.

Methyl 6-benzyl-5-propionyl-2-methyl-4-phenyl-4H-pyran-3-carboxylate (2lb). ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.17 (m, 10H), 4.81 (s, 1H), 4.07-3.98 (m, 2H), 3.67 (s, 3H), 2.65-2.55 (m, 1H), 2.42-2.32 (m, 1H), 2.25 (s, 3H), 0.97-0.94 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 201.9, 167.1, 158.7, 156.9, 144.4, 137.3, 128.9, 128.6, 128.4, 128.1, 127.0, 126.6, 116.2, 108.3, 51.4, 38.9, 37.0, 34.4, 18.8, 7.85. IR (neat, cm⁻¹): 3406, 2942, 1697, 1603, 1186, 1076, 701. Anal. Calcd for C₂₅H₂₅O₄: C 76.57; H 6.43. Found: C 76.66; H 6.50.