TFP as Ligand in Au(I)-catalyzed Dihydropyran Synthesis.  
Unprecedented Rearrangement of Dihydropyrans into Cyclopentenones

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Supporting information

General Methods
All reagents were purchased from Sigma-Aldrich. CH₂Cl₂ was distilled from CaH₂, THF was distilled from sodium and benzophenone, MeOH was distilled over 3A molecular sieves. Silica gel 60 (Merck) was used for column chromatography. TLC was performed on Silica gel 60 F₂₅₄ aluminum sheets (Merck).

¹H and ¹³C NMR spectra were recorded on a VNMR S500 and a VARIAN MERCURY Vx BB 300 spectrometers. Chemical shifts were recorded as δ values in parts per million (ppm), and were indirectly referenced to tetramethylsilane (TMS) via the solvent signal (3.30 ppm for ¹H and 49.0 ppm for ¹³C). Coupling constants (J) are given in Hz. Melting points
were determined on a Büchi B-545 apparatus without correction. Mass spectra were recorded on a ZAB-SEQ (VG-Analytical) and a LCMS Agilent 500 instruments. Infrared spectra were recorded on a NICOLET 6700 FT-IR/ATR-Ge spectrometer and are reported in wave numbers (cm\(^{-1}\)). Elemental analyses were recorded on a CHNS-OCE Fisons EA 1110 instrument.

**Preparation of Gold Catalyst**

**Chloro(tetrahydrothiophene)gold(I)** was prepared according to a literature procedure.\(^1\)

Tetrahydrothiophene \((0.19 \text{ ml, 2.1 mmol})\) was added dropwise to a solution of H\(\text{AuCl}_3 \cdot 3\text{H}_2\text{O}\) \((394 \text{ mg, 1 mmol})\) in a mixture of water \((0.7 \text{ ml})\) and ethanol \((3.3 \text{ ml})\). The reaction mixture was stirred for 30 min at room temperature until the yellow precipitate was transformed to a white solid. The resulting white precipitate was filtered, washed with ethanol and vacuum dried. Yield 95%.

**Chloro(trifurylphosphine)gold(I)** was prepared according to a literature procedure.\(^2\)

\((\text{tht})\text{AuCl}\) \((64 \text{ mg, 0.2 mmol})\) and trifurylphosphine \((47 \text{ mg, 0.2 mmol})\) were stirred together in CH\(_2\)Cl\(_2\) \((3 \text{ ml})\) at room temperature for 1 hour. The solvent was removed, the resulting powder dissolved in a minimum amount of CH\(_2\)Cl\(_2\), and precipitated by petroleum ether. The precipitate was filtered, washed with petroleum ether and vacuum dried. Yield 90%.

The spectral data of the catalyst were identical with those reported in the literature.\(^3\)

**Formation of Propargylic Alcohols.** 3-Phenylprop-2-yn-1-ol, oct-2-yn-1-ol, but-2-yn-1-ol, 4-phenylbut-3-yn-2-ol, hex-5-en-2-yn-1-ol and hex-2-yn-1-ol were obtained commercially from Sigma-Aldrich.

3-(Naphthalen-1-yl)prop-2-yn-1-ol, 3-(thienphen-3-yl)prop-2-yn-1-ol, 4-phenylbut-2-yn-1-ol, 3-(4-methoxyphenyl)prop-2-yn-1-ol and 4-(3-hydroxyprop-1-ynyl)benzonitrile were synthesized from the corresponding alkynes: generally, an alkyne \((5 \text{ mmol})\) was dissolved in anhydrous THF \((10 \text{ ml})\) under argon atmosphere and cooled to -78 °C. Then butyllithium \((2 \text{ ml of 2.5 M solution in hexanes, 5 mmol})\) was added dropwise and after 30 min of stirring at

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this temperature, paraformaldehyde (275 mg, 5 mmol) was added. The reaction mixture was warmed to room temperature and stirred for approx. 2 hours until a dissolution of paraformaldehyde was observed. The mixture was diluted with ethyl acetate and washed with a saturated aqueous NH₄Cl solution. The organic layer was dried with anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

4-(Benzyloxy)but-2-yn-1-ol was prepared by the protection of but-2-yn-1,4-diol according to a literature procedure.⁴

**General Procedure for the Addition of Propargylic Alcohols to Methyl Propiolate.**

Methyl propiolate (0.09 ml, 1 mmol) and triethylamine (0.42 ml, 3 mmol) were added to a solution of propargylic alcohol (1 mmol) in 5 ml of anhydrous CH₂Cl₂ under argon atmosphere. The reaction mixture was stirred at room temperature for approx. 0.5 - 2 hours (conversion was monitored by TLC analysis). The mixture was diluted with ethyl acetate and washed with a saturated aqueous NH₄Cl solution. The organic layer was dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

![Structure of (E)-Methyl 3-(3-phenylprop-2-ynloxy)acrylate](image.png)

**(E)-Methyl 3-(3-phenylprop-2-ynloxy)acrylate 3a:** Prepared according to general procedure in 99 % yield, purified by column chromatography (petroleum ether/ethyl acetate 9:1), yellow oil.

**¹H NMR** (300 MHz, CDCl₃) δ 7.65 (d, J = 12.6 Hz, 1H, H3), 7.47-7.43 (m, 2H, Ar), 7.36-7.30 (m, 3H, Ar), 5.39 (d, J = 12.6 Hz, 1H, H2), 4.75 (s, 2H, OCH₂), 3.72 (s, 3H, OCH₃); **¹³C NMR** (75 MHz, CDCl₃) δ 167.8, 160.9, 131.9, 129.0, 128.3, 121.7, 98.0, 88.4, 81.8, 59.1, 51.2; **IR** νₘₐₓ [cm⁻¹] 2952, 2230, 1711, 1644, 1626, 1491, 1441, 1377, 1329, 1190, 1190, 1129; **MS (TOF CI)** m/z (relative intensity) 217.1 [M+H]+ (48), 185.1 (49), 157.1 (18), 115.1

(E)-Methyl 3-(oct-2-ynyloxy)acrylate 3b: Prepared according to general procedure in 98 % yield, purified by column chromatography (petroleum ether/ethyl acetate 98:2), yellowish oil. 

\[ \text{HRMS (TOF CI) } m/z \ \text{calcd. for } C_{13}H_{13}O_3: 217.0865, \text{ found: } 217.0858. \]

\[ \text{IR } \nu_{\max } [\text{cm}^{-1}] 2933, 2861, 2229, 1715, 1646, 1626, 1461, 1379, 1327, 1286, 1258, 1188, 1159, 1126; \text{ MS (TOF CI) } m/z \ (\text{relative intensity}) 211.1 [M+H]^+ (100), 179.1 (24), 151.1 (10), 125.1 (6), 109.1 (27), 103.0 (19), 67.1 (12); \text{ HRMS (TOF CI) } m/z \ \text{calcd. for } C_{12}H_{19}O_3: 211.1334, \text{ found: } 211.1327. \]

(E)-Methyl 3-(but-2-ynyloxy)acrylate 3c: Prepared according to general procedure in 99 % yield, purified by column chromatography (petroleum ether/ethyl acetate 85:15), white amorphous solid.

\[ \text{HRMS (TOF CI) } m/z \ (\text{relative intensity}) 155.0 [M+H]^+ (100), 140.2 (18), 123.1 (40), 102.4 (20), 84.9 (31), 52.6 (19). \]
(E)-Methyl 3-(3-(naphthalen-1-yl)prop-2-ynyloxy)acrylate 3d: Prepared according to general procedure in 96 % yield, purified by column chromatography (petroleum ether/ethyl acetate 9:1), yellow solid, mp 39.4 °C.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.13-8.08 (m, 1H, Ar), 7.71-7.69 (m, 2H, Ar), 7.58-7.51 (d, $J = 12.6$ Hz, m, 2H, H3, Ar, overlapped), 7.43-7.34 (m, 2H, Ar), 7.30-7.24 (m, 1H, Ar), 5.32 (d, $J = 12.6$ Hz, 1H, H2), 4.73 (s, 2H, OCH$_2$), 3.56 (s, 3H, OCH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.7, 160.9, 133.2, 133.0, 131.0, 129.5, 128.3, 127.0, 126.5, 125.9, 125.1, 119.3, 98.1, 86.7, 86.6, 59.2, 51.2; IR $\nu_{\text{max}}$ [cm$^{-1}$] 3088, 3057, 3044, 2947, 2237, 1703, 1640, 1435, 1397, 1339, 1230, 1196, 1169, 1138; MS (TOF EI) m/z (relative intensity) 266.1 [M]$^+$ (57), 250.1 (44), 234.1 (100), 218.1 (16), 206.1 (76), 190.1 (18), 125.0 (10), 79.0 (18); HRMS (ESI) m/z calcd. for C$_{17}$H$_{15}$O$_3$: 267.1016, found: 267.1016.

(E)-Methyl 3-(3-(thiophen-3-yl)prop-2-ynyloxy)acrylate 3e: Prepared according to general procedure in 99 % yield, purified by column chromatography (petroleum ether/ethyl acetate 9:1), yellowish solid, mp 35.0 °C.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J = 12.6$ Hz, 1H, H3), 7.53-7.50 (m, 1H, Ar), 7.49-7.46 (m, 1H, Ar), 7.37 (d, $J = 12.6$ Hz, 1H, H2), 4.73 (s, 2H, OCH$_2$), 3.72 (s, 3H, OCH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.7, 160.9, 130.1, 129.8, 125.5, 120.7, 98.0, 83.6, 81.6, 59.1, 51.2; IR $\nu_{\text{max}}$ [cm$^{-1}$] 3107, 2950, 2228, 1708, 1647, 1625, 1434, 1372, 1328, 1257, 1188, 1125; MS (TOF EI) m/z (relative intensity) 222.0 [M]$^+$ (6), 207.0 (6), 193.0 (15), 163.0 (92), 134.0 (17), 121.0 (100), 111.0 (10), 63.0 (13); HRMS (TOF EI) m/z calcd. for C$_{11}$H$_{10}$O$_3$S: 222.0351, found: 222.0357.

(E)-Methyl 3-(hex-5-en-2-ynyloxy)acrylate 3f: Prepared according to general procedure in 87 % yield, purified by column chromatography (petroleum ether/ethyl acetate 9:1), colourless oil.
\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.58\) (d, \(J = 12.6\) Hz, 1H, H3), 5.84-5.72 (m, 1H, H5'), 5.37-5.25 (m, 2H, H2, H6', overlapped), 5.13 (m, 1H, H6'), 4.54 (s, 2H, OCH\(_2\)), 3.70 (s, 3H, OCH\(_3\)), 3.04-2.98 (m, 2H, H4'); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 167.8, 160.9, 131.5, 116.6, 97.8, 86.2, 75.4, 58.9, 51.2, 23.0\); IR \(\nu_{\text{max}}\) [cm\(^{-1}\)] 2951, 2240, 1712, 1645, 1626, 1436, 1328, 1287, 1259, 1188, 1158, 1127; MS (TOF EI) m/z (relative intensity) 280.1 [M]\(^+\) (4), 165.1 (2), 151.1 (12), 139.0 (9), 121.1 (14), 111.0 (10), 93.1 (7), 77.0 (100), 51.0 (9); HRMS (ESI) m/z calcd. for C\(_{10}\)H\(_{13}\)O\(_3\): 181.0859, found: 181.0857.

(E)-Methyl 3-(4-phenylbut-2-ynyloxy)acrylate 3g: Prepared according to general procedure in 31 % yield, purified by column chromatography (petroleum ether/ethyl acetate 9:1), yellow oil.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.56\) (d, \(J = 12.6\) Hz, 1H, H3), 7.31-7.16 (m, 5H, Ar), 5.30 (d, \(J = 12.6\) Hz, 1H, H2), 4.52 (t, \(J = 2.2\) Hz, 2H, OCH\(_2\)), 3.66 (s, 3H, OCH\(_3\)), 3.61 (t, \(J = 2.2\) Hz, 2H, CH\(_2\)); \(^1^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 167.8, 160.9, 135.8, 128.6, 127.8, 126.8, 97.8, 87.1, 75.2, 58.9, 51.2, 25.1\); IR \(\nu_{\text{max}}\) [cm\(^{-1}\)] 2950, 1712, 1646, 1625, 1495, 1453, 1436, 1328, 1288, 1258, 1188, 1128; MS (TOF EI) m/z (relative intensity) 230.1 [M]\(^+\) (2), 201.1 (15), 170.1 (14), 141.1 (24), 128.1 (100), 115.1 (7), 102.0 (5); HRMS (ESI) m/z calcd. for C\(_{14}\)H\(_{15}\)O\(_3\): 231.1016, found: 231.1015.

(E)-Methyl 3-(4-(benzyloxy)but-2-ynyloxy)acrylate 3h: Prepared according to general procedure in 98 % yield, purified by column chromatography (petroleum ether/ethyl acetate 9:1), colourless amorphous solid.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.59\) (d, \(J = 12.6\) Hz, 1H, H3), 7.37-7.27 (m, 5H, Ar), 5.35 (d, \(J = 12.6\) Hz, 1H, H2), 4.60-4.57 (m, 4H, OCH\(_2\)), 4.22 (t, \(J = 1.8\) Hz, 2H, OCH\(_2\)), 3.71 (s, 3H, OCH\(_3\)); \(^1^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 167.7, 160.7, 137.1, 128.4, 128.1, 127.9, 98.0, 84.9,
79.5, 71.8, 58.5, 57.1, 51.2; IR νmax [cm⁻¹] 2950, 1711, 1645, 1626, 1437, 1329, 1288, 1259, 1188, 1129; MS (TOF EI) m/z (relative intensity) 260.1 [M]+ (1), 186.1 (21), 155.0 (36), 127.0 (23), 116.0 (48), 111.0 (32), 98.0 (16), 85.0 (100), 71.0 (21), 59.0 (48); HRMS (ESI) m/z caled. for C₁₅H₁₇O₄: 261.1121, found: 261.1121.

(E)-Methyl 3-(3-(4-methoxyphenyl)prop-2-ynyloxy)acrylate 3i: Prepared according to general procedure in 95 % yield, purified by column chromatography (petroleum ether/ethyl acetate 85:15), yellowish solid, mp 39.9 °C.

1H NMR (300 MHz, CDCl₃) δ 7.64 (d, J = 12.6 Hz, 1H, H3), 7.41-7.36 (m, 2H, AA', BB', Ar), 6.86-6.80 (m, 2H, AA', BB', Ar), 5.38 (d, J = 12.6 Hz, 1H, H2), 4.73 (s, 2H, OCH₂), 3.80 (s, 3H, OCH₃), 3.71 (s, 3H, COOCH₃); 13C NMR (75 MHz, CDCl₃) δ 167.8, 161.0, 160.1, 133.4, 114.0, 113.7, 97.9, 88.5, 80.5, 59.3, 55.3, 51.2; IR νmax [cm⁻¹] 2956, 2840, 2233, 1706, 1626, 1605, 1443, 1433, 1379, 1335, 1294, 1246, 1227, 1186, 1177, 1142; LRMS (APCI) m/z (relative intensity) 246.8 [M+H]+ (100), 219.6 (30), 216.6 (6), 205.6 (16), 187.6 (6), 168.1 (65), 145.3 (13).

(E)-Methyl 3-(hex-2-ynyloxy)acrylate 3j: Prepared according to general procedure in 95 % yield, purified by column chromatography (petroleum ether/ethyl acetate 95:5), colourless oil.

1H NMR (300 MHz, CDCl₃) δ 7.59 (d, J = 12.6 Hz, 1H, H3), 5.31 (d, J = 12.6 Hz, 1H, H2), 4.50 (t, J = 2.2 Hz, 2H, OCH₂), 3.70 (s, 3H, OCH₃), 2.20 (tt, J = 7.0 Hz, J = 2.2 Hz, 2H, CH₂), 1.60-1.47 (m, 2H, CH₂), 0.97 (t, J = 7.4 Hz, 3H, CH₃); 13C NMR (75 MHz, CDCl₃) δ 167.9, 161.0, 97.6, 89.7, 73.2, 59.1, 51.2, 21.7, 20.7, 13.4; IR νmax [cm⁻¹] 2964, 2874, 2232, 1713, 1645, 1626, 1438, 1380, 1328, 1286, 1259, 1189, 1159, 1128; LRMS (APCI) m/z (relative intensity) 382.8 [M+H]+ (100), 168.9 (12), 164.2 (14), 152.5 (8), 142.5 (7), 131.7 (7), 124.4 (15), 104.9 (9), 91.9 (11).
\(\text{(E)-Methyl 3-(3-(4-cyanophenyl)prop-2-ynlyoxy)acrylate 3i:}\) Prepared according to general procedure in 95 % yield, purified by column chromatography (petroleum ether/ethyl acetate 8:2), yellow solid, mp 107.6 °C.

\[\text{\textsuperscript{1}H NMR (300 MHz, CDCl}_3\text{) }\delta 7.64-7.59 (m, 3H, H3, AA', BB', Ar, overlapped), 7.55-7.50 (m, 2H, AA', BB', Ar), 5.38 (d, } J = 12.6 \text{ Hz, 1H, H2), 4.76 (s, 2H, OCH}_2\text{), 3.71 (s, 3H, OCH}_3\text{);}\]
\[\text{\textsuperscript{13}C NMR (75 MHz, CDCl}_3\text{) }\delta 167.5, 160.6, 132.3, 132.0, 126.5, 118.1, 112.5, 98.2, 86.5, 86.1, 58.7, 51.3;\]
\[\text{IR }\nu_{\text{max}} [\text{cm}^{-1}] 2222, 1706, 1618, 1503, 1430, 1338, 1325, 1231, 1191, 1146;\]
\[\text{LRMS (APCI) } m/z \text{ (relative intensity) 242.3 [M+H]}^+ (80), 228.5 (7), 210.4 (18), 140.4 (100), 87.5 (34), 75.5 (18), 59.3 (13).\]

\(\text{(E)-Methyl 3-(4-phenylbut-3-yn-2-lyoxy)acrylate 6:}\) Prepared according to general procedure in 99 % yield, purified by column chromatography (petroleum ether/ethyl acetate 9:1), yellowish oil.

\[\text{\textsuperscript{1}H NMR (300 MHz, CDCl}_3\text{) }\delta 7.68 (d, } J = 12.4 \text{ Hz, 1H, H3), 7.46-7.41 (m, 2H, Ar), 7.35-7.29 (m, 3H, Ar), 5.43 (d, } J = 12.4 \text{ Hz, 1H, H2), 4.91 (q, } J = 6.6 \text{ Hz, 1H, CH), 3.71 (s, 3H, OCH}_3\text{), 1.65 (d, } J = 6.6 \text{ Hz, 3H, CH}_3;\]
\[\text{\textsuperscript{13}C NMR (75 MHz, CDCl}_3\text{) }\delta 168.1, 160.3, 131.8, 128.9, 128.3, 121.7, 98.6, 87.1, 86.1, 68.0, 51.1, 21.9;\]
\[\text{IR }\nu_{\text{max}} [\text{cm}^{-1}] 2991, 2950, 2229, 1712, 1644, 1624, 1491, 1436, 1330, 1191, 1138, 1111;\]
\[\text{MS (TOF CI) } m/z \text{ (relative intensity) 253.1 [M+Na]}^+ (1), 239.1 (4), 227.1 (12), 199.1 (100), 171.1 (45), 143.1 (5), 131.1 (4), 77.0 (1);\]
\[\text{HRMS (ESI) } m/z \text{ calcd. for C}_{14}H_{14}O_3Na: 253.0835, \text{ found: 253.0834.}\]

Addition of Propargylic Alcohol to 3,3,3-Trifluoroprop-1-yne.
**Preparation of Methyl 3-(Boc-indol-5-yl-prop-2-ynyloxy)acrylate.**

**tert-Butyl 5-iodo-1H-indole-1-carboxylate:** Prepared from 5-iodo-1H-indole according to literature procedure.\(^5\) Yield 100%, white solid, mp 51.0 °C.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.95-7.88 (m, 2H, Ar), 7.60-7.53 (m, 2H, Ar), 6.50-6.47 (m, 1H, Ar), 1.67 (s, 9H, CH\(_3\)); \(^1\)C NMR (75 MHz, CDCl\(_3\)) δ 180.6, 149.4, 134.4, 132.6, 129.7, 126.6, 117.0, 106.2, 86.6, 84.1, 28.1; IR ν\(_{max}\) [cm\(^{-1}\)] 3163, 2982, 1734, 1531, 1443, 1367, 1362, 1341, 1325, 1276, 1249, 1200, 1184, 1157, 1130, 1084.

MS spectra were identical with literature.\(^6\)

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(E)-tert-Butyl 5-(3-(3-methoxykarbonylprop-1-enyloxy)prop-1-ynyl)-1H-indole-1-carboxylate 3k: To a solution of tert-butyl 5-iodo-1H-indole-1-carboxylate (344 mg, 1 mmol) in anhydrous THF (7.5 mL) (PPh₃)₂PdCl₂ (35 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol), triethylamine (1.4 mL, 10 mmol) and (E)-methyl 3-(prop-2-ynyloxy)acrylate (155 mg, 1.1 mmol) were added. The reaction mixture was stirred at room temperature for 20 hours. The mixture was diluted with ethyl acetate and washed with a saturated aqueous NH₄Cl solution. The organic layer was dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 9:1). Yield 49 %, brown oil.

¹H NMR (300 MHz, CDCl₃) δ 8.13-8.06 (m, 1H, Ar), 7.70-7.64 (m, 2H, CH, Ar, overlapped), 7.63-7.59 (m, 1H, Ar), 7.42-7.36 (m, 1H, Ar), 6.55-6.52 (m, 1H, Ar), 5.41 (d, J = 12.6 Hz, 1H, CH), 4.77 (s, 2H, OCH₂), 3.72 (s, 3H, OCH₃), 1.67 (s, 9H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 180.6, 167.8, 161.0, 149.4, 130.4, 127.8, 126.9, 124.9, 115.7, 115.2, 107.0, 97.9, 89.2, 84.1, 80.5, 59.3, 51.2, 28.1; IR νₘₐₓ [cm⁻¹] 2980, 2229, 1732, 1645, 1625, 1468, 1437, 1366, 1331, 1286, 1257, 1231, 1154, 1132, 1084; LRMS (APCI) m/z (relative intensity) 355.8 [M+H]+ (100), 327.9 (15), 299.8 (24), 253.7 (28), 199.4 (11).

General Procedure for Gold(I)-Catalyzed Cyclisation to Dihydropyrans. (TFP)AuCl (23 mg, 0.05 mmol) and AgBF₄ (10 mg, 0.05 mmol) were placed into a dry flask under argon atmosphere and 10 mL of anhydrous CH₂Cl₂ and 0.13 mL of anhydrous methanol (3 mmol) were added. Subsequently, a solution of propargyl vinyl ether (1 mmol) in anhydrous CH₂Cl₂ (6.5 mL) was added. The reaction mixture was stirred at room temperature for approx. 0.5 - 4 hours (conversion was monitored by TLC analysis). The mixture was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.
Methyl 3,6-dihydro-2-methoxy-4-phenyl-2H-pyran-3-carboxylate 4a: Prepared according to general procedure in 98 % yield (66 % trans, 32 % cis), purified by column chromatography (petroleum ether/ethyl acetate 9:1), yellowish amorphous solid.

**trans isomer:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.36-7.22 (m, 5H, Ar), 6.22 (t, $J = 3.0$ Hz, 1H, H5), 5.15 (d, $J = 2.2$ Hz, 1H, H2), 4.38 (t, $J = 2.2$ Hz, 2H, H6), 3.73-3.69 (m, 1H, H3), 3.63 (s, 3H, COOCH$_3$), 3.51 (s, 3H, OCH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.9, 139.1, 130.1, 128.4, 127.5, 125.2, 123.7, 98.6, 60.7, 55.8, 52.3, 48.0; IR $\nu_{\text{max}}$ [cm$^{-1}$] 2926, 2851, 1723, 1652, 1598, 1496, 1437, 1364, 1240, 1194, 1136, 1093, 1072; MS (TOF EI) m/z (relative intensity) 248.1 [M]$^+$ (4), 216.1 (15), 184.1 (15), 157.1 (100), 129.1 (68), 115.1 (19), 77 (10); HRMS (ESI) m/z calcd. for C$_{14}$H$_{16}$O$_4$Na: 271.0946, found: 271.0941; Anal calcd. for C$_{14}$H$_{16}$O$_4$: C, 67.7; H, 6.6; O, 25.7 %.

**cis isomer:** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.33-7.22 (m, 5H, Ar), 6.24-6.21 (m, 1H, H5), 4.98 (d, $J = 4.2$ Hz, 1H, H2), 4.54 (dt, $J = 17.0$ Hz, $J = 2.6$ Hz, 1H, H6), 4.32 (dt, $J = 17.0$ Hz, $J = 2.6$ Hz, 1H, H6), 3.98-4.00 (m, 1H, H3), 3.59 (s, 3H, COOCH$_3$), 3.52 (s, 3H, OCH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.0, 139.1, 131.2, 128.5, 127.5, 124.8, 124.2, 98.5, 62.0, 56.4, 52.2, 47.5; IR $\nu_{\text{max}}$ [cm$^{-1}$] 2936, 2838, 1730, 1654, 1492, 1446, 1438, 1366, 1249, 1238, 1206, 1135, 1101, 1079; MS (TOF CI) m/z (relative intensity) 249.1 [M+H]$^+$ (3), 231.1 (6), 217.1 (37), 189.1 (100), 157.1 (23), 129.1 (4); HRMS (TOF CI) m/z calcd. for C$_{14}$H$_{17}$O$_4$: 249.1127, found: 249.1124; Anal calcd. for C$_{14}$H$_{16}$O$_4$: C, 67.7; H, 6.5; O, 25.8; found: C, 67.9; H, 6.65; O, 25.5 %.

Methyl 3,6-dihydro-2-methoxy-4-pentyl-2H-pyran-3-carboxylate 4b: Prepared according to general procedure in 83 % yield (62 % trans, 21 % cis), purified by column chromatography (petroleum ether/ethyl acetate 98:2), colourless oil.
**trans isomer:** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.63-5.53 (m, 1H, H5), 4.94 (d, $J = 2.8$ Hz, 1H, H2), 4.21-4.13 (m, 2H, H6), 3.72 (s, 3H, COOCH$_3$), 3.45 (s, 3H, OCH$_3$), 3.08-3.05 (m, 1H, H3), 2.08-1.90 (m, 2H, CH$_2$), 1.48-1.19 (m, 6H, CH$_2$), 0.87 (t, $J = 7.0$ Hz, 3H, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.3, 130.9, 120.6, 98.9, 60.9, 55.8, 52.1, 49.2, 35.2, 31.4, 26.5, 22.4, 14.0; IR $\nu_{max}$ [cm$^{-1}$] 2953, 2929, 2857, 1736, 1435, 1383, 1312, 1244, 1193, 1138, 1118, 1097, 1069; MS (TOF CI) m/z (relative intensity) 243.2 [M+H]$^+$ (6), 225.1 (8), 211.1 (100), 193.1 (32), 183.1 (27), 179.1 (13), 151.1 (28); HRMS (TOF CI) m/z calcd. for C$_{13}$H$_{23}$O$_4$: 243.1596, found: 243.1599; Anal calcd. for C$_{13}$H$_{22}$O$_4$: C, 64.4; H, 9.15; O, 26.4; found: C, 64.5; H, 9.3; O, 26.2 %.

**cis isomer:** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.62-5.59 (m, 1H, H5), 4.80 (d, $J = 4.3$ Hz, 1H, H2), 4.31 (d, $J = 16.1$ Hz, 1H, H6), 4.07 (d, $J = 16.1$ Hz, 1H, H6), 3.70 (s, 3H, COOCH$_3$), 3.48 (s, 3H, OCH$_3$), 3.34-3.30 (m, 1H, H3), 2.05 (t, $J = 7.7$ Hz, 2H, CH$_2$), 1.40-1.18 (m, 6H, CH$_2$), 0.84 (t, $J = 7.0$ Hz, 3H, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.1, 131.7, 121.3, 98.3, 61.4, 56.1, 51.9, 48.3, 34.8, 31.3, 26.7, 22.4, 13.9; IR $\nu_{max}$ [cm$^{-1}$] 2953, 2929, 2857, 1750, 1677, 1435, 1382, 1306, 1270, 1246, 1193, 1139, 1119, 1090, 1059; LRMS (APCI) m/z (relative intensity) 243.1 [M+H]$^+$ (6), 224.8 (30), 212.4 (48), 210.8 (100), 192.9 (25), 183.8 (8), 162.7 (9), 151.0 (14), 134.7 (12), 121.7 (9); Anal calcd. for C$_{13}$H$_{22}$O$_4$: C, 64.4; H, 9.15; O, 26.4; found: C, 64.2; H, 9.1; O, 26.7 %.

![](image)

**Methyl 3,6-dihydro-2-methoxy-4-methyl-2H-pyran-3-carboxylate 4c:** Prepared according to general procedure in 70 % yield (57 % trans, 13 % cis), purified by column chromatography (petroleum ether/ethyl acetate 95:5), yellowish oil.

**trans isomer:** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.60-5.57 (m, 1H, H5), 4.96 (d, $J = 2.7$ Hz, 1H, H2), 4.16-4.11 (m, 2H, H6), 3.71 (s, 3H, COOCH$_3$), 3.44 (s, 3H, OCH$_3$), 2.98 (s, 1H, H3), 1.73-1.75 (m, 3H, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.0, 126.6, 121.7, 98.6, 60.6, 55.8, 52.1, 50.2, 22.0; IR $\nu_{max}$ [cm$^{-1}$] 2918, 2848, 1736, 1436, 1388, 1325, 1306, 1194, 1157, 1137, 1110, 1082, 1073; MS (TOF CI) m/z (relative intensity) 209.1 [M+Na]$^+$ (3), 183.1 (22), 169.0 (100), 155.1 (1), 141.1 (3), 112.1 (3); HRMS (ESI) m/z calcd. for C$_9$H$_{14}$O$_4$Na: 209.0784, found: 209.0784; Anal calcd. for C$_9$H$_{14}$O$_4$: C, 58.05; H, 7.6; O, 34.4; found: C, 58.1; H, 7.7; O, 34.2 %.
cis isomer: 

\[ \text{H NMR} \ (500 \text{ MHz, CDCl}_3) \delta 5.65-5.62 \ (m, 1H, H5), 4.87 \ (d, J = 4.4 \text{ Hz, 1H, H2}), 4.32-4.25 \ (m, 1H, H6), 4.07-4.01 \ (m, 1H, H6), 3.72 \ (s, 3H, COOCH}_3, 3.45 \ (s, 3H, OCH}_3, 3.33-3.28 \ (m, 1H, H3), 1.76 \ (s, 3H, CH}_3; \]  

\[ \text{13C NMR} \ (125 \text{ MHz, CDCl}_3) \delta 170.0, 127.4, 122.3, 98.0, 60.8, 56.1, 52.0, 49.5, 21.3; \]  

\[ \text{LRMS (APCI)} \ m/z \ \text{(relative intensity)} \ 187.2 \ [\text{M+H}^+] \ (1), 169.2 \ (100), 155.2 \ (21), 141.3 \ (15), 128.2 \ (9), 111.9 \ (6); \]  

\[ \text{Anal calcd. for } C_9H_{14}O_4: \ C, 58.05; H, 7.6; O, 34.4; \text{ found: C, 58.3; H, 7.5; O, 34.2 \%}. \]

Methyl 3,6-dihydro-2-methoxy-4-(naphthalen-1-yl)-2H-pyran-3-carboxylate 4d:

Prepared according to general procedure in 84 % yield (61 % trans, 23 % cis), purified by column chromatography (gradient elution, petroleum ether/ethyl acetate 95:5 – 9:1), yellowish solid, mp 110.5 °C (trans), 95.0 °C (cis).

trans isomer: 

\[ \text{H NMR} \ (500 \text{ MHz, CDCl}_3) \delta 8.18-8.14 \ (m, 1H, Ar), 7.87-7.83 \ (m, 1H, Ar), 7.81-7.86 \ (m, 1H, Ar), 7.52-7.35 \ (m, 4H, Ar), 5.98-5.96 \ (m, 1H, H5), 5.24-5.22 \ (m, 1H, H2), 4.47-4.43 \ (m, 2H, H6), 3.70-3.66 \ (m, 1H, H3), 3.61 \ (s, 3H, COOCH}_3, 3.50 \ (s, 3H, OCH}_3; \]  

\[ \text{13C NMR} \ (125 \text{ MHz, CDCl}_3) \delta 170.6, 138.4, 133.6, 131.4, 130.1, 128.2, 127.7, 127.2, 126.1, 126.0, 125.7, 125.4, 125.2, 98.5, 60.6, 55.9, 52.0, 50.4; \]  

\[ \text{IR } \nu_{\text{max}} \ [\text{cm}^{-1}] \ 3061, 3003, 2945, 2917, 2856, 1732, 1591, 1506, 1441, 1360, 1321, 1274, 1218, 1190, 1136, 1069; \]  

\[ \text{MS (TOF EI)} \ m/z \ \text{(relative intensity)} \ 298.1 \ [\text{M}]^+ \ (19), 266.1 \ (7), 234.1 \ (20), 207.1 \ (98), 195.1 \ (17), 179.1 \ (100), 165.1 \ (32), 152.1 \ (28), 127.1 \ (3), 89.0 \ (7); \]  

\[ \text{HRMS (TOF EI)} \ m/z \ \text{calcd. for } C_{18}H_{18}O_4: 298.1205, \text{ found: 298.1200}; \]  

\[ \text{Anal calcd. for } C_{18}H_{18}O_4: \ C, 72.5; H, 6.1; O, 21.45; \text{ found: C, 72.2; H, 6.2; O, 21.6 \%}. \]

cis isomer: 

\[ \text{H NMR} \ (500 \text{ MHz, CDCl}_3) \delta 8.09-8.03 \ (m, 1H, Ar), 7.86-7.82 \ (m, 1H, Ar), 7.79-7.75 \ (m, 1H, Ar), 7.51-7.39 \ (m, 3H, Ar), 7.32-7.28 \ (m, 1H, Ar), 6.02-6.00 \ (m, 1H, H5), 5.11 \ (d, J = 4.1 \text{ Hz, 1H, H2}), 4.65 \ (dt, J = 16.7 \text{ Hz, } J = 2.3 \text{ Hz, 1H, H6}), 4.41-4.35 \ (dt, J = 16.7 \text{ Hz, } J = 2.3 \text{ Hz, 1H, H6}), 3.98-3.94 \ (m, 1H, H3), 3.58 \ (s, 3H, COOCH}_3, 3.49 \ (s, 3H, OCH}_3; \]  

\[ \text{13C NMR} \ (125 \text{ MHz, CDCl}_3) \delta 169.5, 138.0, 133.8, 131.3, 130.8, 128.3, 128.1, 127.7, 126.0, 125.7, 125.3, 125.2, 125.1, 98.7, 62.1, 56.4, 51.9, 50.0; \]  

\[ \text{IR } \nu_{\text{max}} \ [\text{cm}^{-1}] \ 3042, 3006, 2928, 2831, 1739, 1506, 1442, 1384, 1358, 1259, 1244, 1211, 1193, 1156, 1137, 1110, 1102; \]  

\[ \text{MS (TOF EI)} \ m/z \ \text{(relative intensity)} \ 298.1 \ [\text{M}]^+ \ (9), 266.1 \ (4), 234.1 \ (7), 207.1 \ (100), \]
195.1 (8), 179.1 (75), 165.1 (22), 152.1 (17), 127.1 (2), 89.0 (5); **HRMS (TOF EI) m/z** calcd. for \( \text{C}_{18}\text{H}_{18}\text{O}_4 \): 298.1205, found: 298.1193; **Anal** calcd. for \( \text{C}_{18}\text{H}_{18}\text{O}_4 \): C, 72.5; H, 6.1; O, 21.45; found: C, 72.7; H, 6.0; O, 21.3 %.

**Crystallographic data for trans-4d**

Molecular structure of 4d, an ORTEP view, 50% probability level.

4d crystallizes in orthorhombic centrosymmetric space group \( \text{Pbca} \). The molecular structure of 4d consists of two ring systems where one is the planar aromatic naphthyl moiety and the second one is the skewed partially saturated six membered heterocycle. All interatomic distances are in line with the standard single and double bond distances.\(^7\)

The X-ray data for colourless crystals of 4d were obtained at 150K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with MoK\( \alpha \) radiation (\( \lambda = 0.71073 \) Å), a graphite monochromator, and the \( \phi \) and \( \chi \) scan mode. Data reductions were performed with DENZO-SMN.\(^8\) The absorption was corrected by integration methods.\(^9\) Structures were solved by direct methods (Sir92)\(^{10}\) and refined by full matrix least-square

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based on $F^2$ (SHELXL97).\textsuperscript{11} Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2 \, U_{eq}(pivot \, atom)$ or of $1.5\, U_{eq}$ for the methyl moiety with C-H = 0.96, 0.97, 0.98 and 0.93 Å for methyl, methylene, methine and hydrogen atoms in aromatic rings or unsaturated carbon atom, respectively.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Crystallographic data for 4d: $C_{18}H_{18}O_4$, M = 298.32, orthorhombic, $Pbca$, $a = 12.9230(7)$, $b = 7.4390(12)$, $c = 30.766(2)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $Z = 8$, $V = 2957.7(6)$ Å$^3$, $D_c = 1.340 \text{ g.cm}^{-3}$, $\mu = 0.094 \text{ mm}^{-1}$, $T_{min} = 0.977$, $T_{max} = 0.986$; 16499 reflections measured ($\theta_{max} = 27.5^\circ$), 16377 independent ($R_{int} = 0.0567$), 3373 with $I > 2\sigma(I)$, 199 parameters, $S = 1.140$, $R_1$ (obs. data) = 0.0548, $wR_2$ (all data) = 0.1065; max., min. res. El. density = 0.356, -0.239 e Å$^{-3}$.

CCDC Deposition number: 829174.

Methyl 3,6-dihydro-2-methoxy-4-(thiophen-3-yl)-2$H$-pyran-3-carboxylate 4e: Prepared according to general procedure in 87% yield (61% trans, 26% cis), purified by column chromatography (petroleum ether/ethyl acetate 95:5), yellowish solid, mp 82.5 °C (trans), yellowish amorphous solid (cis).

\textbf{trans isomer:} $^1H$ NMR (500 MHz, CDCl$_3$) $\delta$ 7.27-7.24 (m, 1H, Ar), 7.21-7.18 (m, 1H, Ar), 7.10-7.08 (m, 1H, Ar), 6.24 (t, $J = 2.9$ Hz, 1H, H5), 5.11 (d, $J = 1.7$ Hz, 1H, H2), 4.37-4.34 (m, 2H, H6), 3.69 (s, 3H, COOCH$_3$), 3.62-3.59 (m, 1H, H3), 3.49 (s, 3H, OCH$_3$); $^{13}C$ NMR (125 MHz, CDCl$_3$) $\delta$ 170.9, 140.8, 125.8, 125.1, 124.7, 122.3, 119.4, 98.2, 60.1, 55.8, 52.5, 48.2; IR $\nu_{\text{max}}$ [cm$^{-1}$] 3104, 2950, 2842, 1729, 1435, 1386, 1364, 1321, 1246, 1197, 1165,

\textsuperscript{11} G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, 1997.
Methyl 4-allyl-3,6-dihydro-2-methoxy-2H-pyran-3-carboxylate 4f: Prepared according to general procedure in 67 % yield (52 % trans, 15 % cis), purified by column chromatography (petroleum ether/ethyl acetate 98:2), colourless oil.

cis isomer: \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.29-7.25 (m, 1H, Ar), 7.21-7.13 (m, 2H, Ar), 6.27 (t, \(J = 2.5\) Hz, 1H, H5), 4.85 (d, \(J = 3.9\) Hz, 1H, H2), 4.63 – 4.57 (m, 1H, H6), 4.39-4.33 (m, 1H, H6), 3.84-3.81 (m, 1H, H3), 3.69 (s, 3H, COOCH\(_3\)), 3.54 (s, 3H, OCH\(_3\)); \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)) \(\delta\) 170.2, 140.3, 126.9, 126.0, 124.5, 122.9, 119.5, 98.9, 63.1, 56.5, 52.3, 48.0; IR \(\nu_{\text{max}}\) [cm\(^{-1}\)] 3103, 2952, 2923, 2851, 1724, 1428, 1380, 1370, 1251, 1238, 1203, 1136, 1108, 1076; MS (TOF EI) \(m/z\) (relative intensity) 254.1 [M]\(^+\) (5), 222.0 (12), 195.0 (13), 179.0 (12), 163.0 (100), 139.0 (47), 121.0 (7), 109.0 (10), 91.1 (13); HRMS (ESI) \(m/z\) calcd. for C\(_{12}\)H\(_{14}\)O\(_4\)Na: 235.0941, found: 235.0940; Anal calcd. for C\(_{11}\)H\(_{16}\)O\(_4\): C, 62.25; H, 7.6; O, 30.15; found: C, 62.4; H, 7.6; O, 30.0 %. 

trans isomer: \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 5.80-5.69 (m, 1H, H2'), 5.63 (s, 1H, H5), 5.09-5.04 (m, 2H, H3'), 5.02-4.95 (m, 1H, H2), 4.18-4.14 (m, 2H, H6), 3.70 (s, 3H, COOCH\(_3\)), 3.43 (s, 3H, OCH\(_3\)), 3.06 (s, 1H, H3), 2.86-2.71 (m, 2H, CH\(_2\)); \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)) \(\delta\) 171.0, 134.6, 128.9, 122.2, 117.3, 98.5, 60.4, 55.7, 52.1, 48.5, 39.7; IR \(\nu_{\text{max}}\) [cm\(^{-1}\)] 2951, 2847, 1737, 1638, 1435, 1385, 1364, 1312, 1257, 1194, 1171, 1136, 1107, 1080, 1070; MS (TOF EI) \(m/z\) (relative intensity) 212.1 [M]\(^+\) (1), 180.1 (19), 171.1 (7), 152.1 (50), 139.0 (53), 121.1 (100), 91.0 (79), 77.0 (47), 65.0 (13), 59.0 (12); HRMS (ESI) \(m/z\) calcd. for C\(_{11}\)H\(_{16}\)O\(_4\)Na: 235.0941, found: 235.0940; Anal calcd. for C\(_{12}\)H\(_{14}\)O\(_4\): C, 56.7; H, 5.55; O, 25.2; S, 12.6; found: C, 56.7; H, 5.7; O, 25.3; S, 12.3 %. 

Electronic Supplementary Material (ESI) for Chemical Communications
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39.4; IR ν max [cm⁻¹] 2951, 2926, 2854, 1749, 1435, 1383, 1362, 1312, 1267, 1191, 1170, 1136, 1087, 1059; LRMS (APCI) m/z (relative intensity) 213.0 [M+H]⁺ (4), 181.0 (30), 153.1 (41), 140.0 (38), 121.9 (91), 92.0 (100), 78.0 (5), 60.0 (7); Anal calcd. for C₁₁H₁₆O₄: C, 62.25; H, 7.6; O, 30.15; found: C, 61.9; H, 7.9; O, 30.2 %.

**Methyl 4-benzyl-3,6-dihydro-2-methoxy-2H-pyran-3-carboxylate 4g:** Prepared according to general procedure in 75 % yield (57 % trans, 18 % cis), purified by column chromatography (petroleum ether/ethyl acetate 98:2), colourless oil.

**trans isomer:** H NMR (500 MHz, CDCl₃) δ 7.34-7.16 (m, 5H, Ar), 5.52 (s, 1H, H5), 5.00 (d, J = 2.2 Hz, 1H, H2), 4.20-4.16 (m, 2H, H6), 3.68 (s, 3H, COOCH₃), 3.47-3.32 (m, 5H, OCH₃, CH₂), 3.04 (bs, 1H, H3); IR ν max [cm⁻¹] 3027, 2930, 2848, 1736, 1602, 1495, 1435, 1384, 1364, 1311, 1255, 1195, 1168, 1134, 1107, 1081, 1070; MS (TOF EI) m/z (relative intensity) 262.1 [M]⁺ (1), 230.1 (21), 202.1 (92), 171.1 (100), 143.1 (96), 139.0 (61), 128.1 (79), 115.1 (42), 91.1 (49), 65.0 (15), 59.0 (6); HRMS (ESI) m/z calcd. for C₁₅H₁₉O₄: 263.1278, found: 263.1278; Anal calcd. for C₁₅H₁₈O₄: C, 68.7; H, 6.9; O, 24.4; found: C, 68.8; H, 6.8; O, 24.4 %.

**cis isomer:** H NMR (500 MHz, CDCl₃) δ 7.32-7.13 (m, 5H, Ar), 5.69-5.65 (m, 1H, H5), 4.83 (d, J = 4.4 Hz, 1H, H2), 4.39-4.30 (m, 1H, H6), 4.14-4.07 (m, 1H, H6), 3.72-3.70 (m, 5H, COOCH₃, CH₂, overlapped), 3.45 (s, 3H, OCH₃), 3.28-3.25 (m, 1H, H3); IR ν max [cm⁻¹] 2954, 2923, 2853, 1739, 1642, 1494, 1462, 1378, 1364, 1312, 1248, 1189, 1161, 1136, 1112, 1083, 1061; MS (TOF EI) m/z (relative intensity) 262.1 [M]⁺ (1), 230.1 (19), 202.1 (89), 171.1 (98), 143.1 (100), 139.0 (60), 128.1 (75), 115.1 (38), 91.1 (44), 65.0 (15), 59.0 (7); HRMS (ESI) m/z calcd. for C₁₅H₁₉O₄: 263.1278, found: 263.1278; Anal calcd. for C₁₅H₁₈O₄: C, 68.7; H, 6.9; O, 24.4; found: C, 69.0; H, 6.65; O, 24.3 %.
Methyl 4-((benzyloxy)methyl)-3,6-dihydro-2-methoxy-2H-pyran-3-carboxylate 4h:
Prepared according to general procedure in 70% yield (49% trans, 21% cis), purified by column chromatography (petroleum ether/ethyl acetate 95:5), colourless amorphous solid. 

**trans isomer:** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38-7.27 (m, 5H, Ar), 5.93-5.90 (m, 1H, H5), 5.08 (d, $J = 2.0$ Hz, 1H, H2), 4.51 (d, $J = 11.7$ Hz, 1H, OCH$_2$), 4.41 (d, $J = 11.7$ Hz, 1H, OCH$_2$), 4.24-4.21 (m, 2H, OCH$_2$), 4.12-4.08 (m, 1H, H6), 3.99-3.94 (m, 1H, H6), 3.68 (s, 3H, COOCH$_3$), 3.47 (s, 3H, OCH$_3$), 3.28-3.25 (m, 1H, H3); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.7, 138.1, 128.3, 127.8, 127.5, 124.6, 98.3, 72.0, 71.7, 60.0, 55.8, 52.2, 46.2; IR $\nu_{max}$ [cm$^{-1}$] 2923, 2853, 1737, 1496, 1453, 1356, 1311, 1259, 1196, 1156, 1136, 1082; LRMS (APCI) m/z (relative intensity) 293.4 [M+H]$^+$ (2), 261.4 (100), 243.4 (30), 229.4 (38), 211.4 (28), 183.4 (38), 153.4 (7), 129.4 (11), 91.4 (20); Anal calcd. for C$_{16}$H$_{20}$O$_5$: C, 65.7; H, 6.9; O, 27.2 %.

**cis isomer:** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38-7.26 (m, 5H, Ar), 5.93 (s, 1H, H5), 4.91 (d, $J = 4.3$ Hz, 1H, H2), 4.50-4.40 (m, 2H, OCH$_2$), 4.34 (d, $J = 16.5$ Hz, 1H, H6), 4.20 (d, $J = 12.0$ Hz, 1H, OCH$_2$), 4.14 (d, $J = 16.5$ Hz, 1H, H6), 4.00 (d, $J = 12.0$ Hz, 1H, OCH$_2$), 3.68 (s, 3H, COOCH$_3$), 3.55 (s, 1H, H3), 3.46 (s, 3H, OCH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 169.7, 138.0, 128.9, 128.3, 127.6, 127.6, 124.6, 97.9, 72.2, 71.9, 60.6, 56.1, 52.0, 45.9; IR $\nu_{max}$ [cm$^{-1}$] 2954, 2923, 2853, 1741, 1462, 1454, 1378, 1309, 1264, 1169, 1137, 1092; LRMS (APCI) m/z (relative intensity) 293.4 [M+H]$^+$ (3), 260.9 (100), 243.0 (33), 228.9 (24), 210.9 (17), 183.9 (8), 153.1 (9), 91.9 (3); Anal calcd. for C$_{16}$H$_{20}$O$_5$: C, 65.7; H, 6.9; O, 27.4 %; found: C, 66.0; H, 6.7; O, 27.3 %.

Methyl 3,6-dihydro-2-methoxy-4-(4-methoxyphenyl)-2H-pyran-3-carboxylate 4i:
Prepared according to general procedure in 89% yield (63% *trans*, 26% *cis*), purified by column chromatography (gradient elution, petroleum ether/ethyl acetate 9:1 – 8:2), white solid, mp 75.4 °C (*trans*), 127.8 °C (*cis*).

**trans isomer:**

1H NMR (300 MHz, CDCl3) δ 7.30-7.23 (m, 2H, AA', BB', Ar), 6.88-6.81 (m, 2H, AA', BB', Ar), 6.12 (t, J = 2.5 Hz, 1H, H5), 5.13-5.11 (m, 1H, H2), 4.38-4.34 (m, 2H, H6), 3.79 (s, 3H, OCH3), 3.68-3.65 (m, 1H, H3), 3.64 (s, 3H, COOCH3), 3.50 (s, 3H, OCH3);

13C NMR (75 MHz, CDCl3) δ 171.0, 159.1, 131.7, 129.5, 126.3, 122.0, 113.8, 98.7, 98.7, 60.7, 55.8, 55.2, 52.4, 48.1; IR νmax [cm⁻¹] 2943, 2843, 1722, 1608, 1515, 1439, 1367, 1302, 1272, 1238, 1181, 1138, 1095, 1072; LRMS (APCI) m/z (relative intensity) 279.1 [M+H]+ (3), 248.3 (12), 219.4 (100), 217.1 (9), 188.1 (6); Anal calcd. for C15H18O5: C, 64.7; H, 6.5; O, 28.7; found: C, 64.9; H, 6.5; O, 28.6 %.

cis isomer:

1H NMR (300 MHz, CDCl3) δ 7.29-7.23 (m, 2H, AA', BB', Ar), 6.87-6.81 (m, 2H, AA', BB', Ar), 6.17-6.12 (m, 1H, H5), 4.94 (d, J = 4.1 Hz, 1H, H2), 4.54 (dt, J = 16.9 Hz, J = 2.7 Hz, 1H, H6), 4.31 (dt, J = 16.9 Hz, J = 2.7 Hz, 1H, H6), 3.96-3.90 (m, 1H, H3), 3.79 (s, 3H, OCH3), 3.62 (s, 3H, COOCH3), 3.52 (s, 3H, OCH3);

13C NMR (75 MHz, CDCl3) δ 170.1, 159.1, 131.5, 130.7, 125.9, 122.5, 113.9, 98.7, 62.3, 56.4, 55.2, 52.2, 47.6; IR νmax [cm⁻¹] 2945, 2842, 1729, 1607, 1514, 1462, 1428, 1379, 1300, 1265, 1250, 1239, 1202, 1183, 1139, 1108, 1082; LRMS (APCI) m/z (relative intensity) 279.2 [M+H]+ (1), 260.9 (17), 248.2 (34), 219.1 (100), 217.1 (21), 188.1 (8); Anal calcd. for C15H18O5: C, 64.7; H, 6.5; O, 28.7; found: C, 64.9; H, 6.5; O, 28.7 %.

**Electronic Supplementary Material (ESI) for Chemical Communications**

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cis isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.61-5.58 (m, 1H, H5), 4.79 (d, $J = 4.3$ Hz, 1H, H2), 4.34-4.28 (m, 1H, H6), 4.10-4.04 (m, 1H, H6), 3.69 (s, 3H, COOCH$_3$), 3.43 (s, 3H, OCH$_3$), 3.33-3.29 (m, 1H, H3), 2.08-1.97 (m, 2H, CH$_2$), 1.46-1.30 (m, 2H, CH$_2$), 0.85 (t, $J = 7.3$ Hz, 3H, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.1, 131.4, 121.5, 98.3, 61.4, 56.1, 51.9, 48.2, 36.9, 20.1, 13.6; IR $\nu_{\text{max}}$ [cm$^{-1}$] 2958, 2874, 1737, 1462, 1439, 1383, 1309, 1265, 1198, 1141, 1120, 1094, 1057; LRMS (APCI) m/z (relative intensity) 215.2 [M+H]$^+$ (1), 197.4 (45), 184.2 (25), 165.2 (76), 133.2 (100), 106.0 (11); Anal calcd. for C$_{11}$H$_{18}$O$_4$: C, 61.7; H, 8.5; O, 29.9; found: C, 62.0; H, 8.2; O, 29.8 %.

tert-Butyl 5-(2-methoxy-3-(methoxycarbonyl)-3,6-dihydro-2H-pyran-4-yl)-1H-indole-1-carboxylate 4k: Prepared according to general procedure in 38 % yield (25 % trans, 13 % cis), purified by column chromatography (petroleum ether/ethyl acetate 95:5), yellowish solid, mp 115.3 °C (trans), 124.8 °C (cis)

trans isomer: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.10-8.02 (m, 1H, Ar), 7.59-7.55 (m, 1H, Ar), 7.51-7.48 (m, 1H, Ar), 7.35-7.29 (m, 1H, Ar), 6.55-6.52 (m, 1H, Ar), 6.21 (t, $J = 2.8$ Hz, 1H, H5), 5.16 (d, $J = 2.2$ Hz, 1H, H2), 4.40 (t, $J = 2.4$ Hz, 2H, H6), 3.80-3.76 (m, 1H, H3), 3.61 (s, 3H, COOCH$_3$), 3.53 (s, 3H, OCH$_3$), 1.66 (s, 9H, CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 180.6, 171.0, 149.6, 134.1, 130.7, 130.4, 126.3, 123.1, 122.0, 117.7, 115.0, 107.4, 98.8, 83.7, 60.8, 55.9, 52.3, 48.5, 28.2; IR $\nu_{\text{max}}$ [cm$^{-1}$] 2931, 2853, 1736, 1471, 1439, 1366, 1339, 1286, 1246, 1193, 1160, 1137, 1089, 1072; LRMS (APCI) m/z (relative intensity) 388.3 [M+H]$^+$ (16), 370.4 (7), 329.4 (100), 300.4 (78), 272.4 (23), 268.4 (63), 256.4 (16), 224.4 (11), 197.4 (14); Anal calcd. for C$_{21}$H$_{25}$NO$_6$: C, 65.1; H, 6.5; N, 3.6; O, 24.8; found: C, 65.0; H, 6.4; N, 3.9; O, 24.7 %.

cis isomer: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.09-8.01 (m, 1H, Ar), 7.59-7.55 (m, 1H, Ar), 7.51-7.47 (m, 1H, Ar), 7.33-7.27 (m, 1H, Ar), 6.55-6.51 (m, 1H, Ar), 6.25-6.21 (m, 1H, H5),
5.01 (d, J = 4.2 Hz, 1H, H2), 4.57 (dt, J = 16.9 Hz, J = 2.6 Hz, 1H, H6), 4.34 (dt, J = 16.9 Hz, J = 2.6 Hz, 1H, H6), 4.08-4.03 (m, 1H, H3), 3.58 (s, 3H, COOCH3), 3.54 (s, 3H, OCH3), 1.66 (s, 9H, CH3); 13C NMR (75 MHz, CDCl3) δ 180.8, 170.4, 149.9, 134.2, 131.8, 131.0, 126.6, 123.9, 121.8, 117.5, 115.4, 107.7, 98.9, 84.0, 62.4, 56.6, 52.4, 48.1, 28.4; IR νmax [cm⁻¹] 2930, 2856, 1732, 1470, 1439, 1369, 1336, 1276, 1257, 1237, 1194, 1159, 1138, 1112, 1084, 1056; LRMS (APCI) m/z (relative intensity) 388.2 [M+H]+ (9), 370.2 (12), 329.2 (100), 300.2 (53), 272.2 (18), 268.3 (70), 256.2 (8), 224.2 (18), 197.1 (6); Anal calcd. for C21H25NO6: C, 65.1; H, 6.5; N, 3.6; O, 24.8%; found: C, 64.85; H, 6.7; N, 3.7; O, 24.8 %.

Methyl 4-(4-cyanophenyl)-2-methoxy-3,6-dihydro-2H-pyran-3-carboxylate 4l: Prepared according to general procedure in 92 % yield (68 % trans, 24 % cis), purified by column chromatography (petroleum ether/ethyl acetate 9:1), white solid, mp 121.2 °C (trans), yellowish amorphous solid (cis)

**trans isomer:** 1H NMR (500 MHz, CDCl3) δ 7.63-7.58 (m, 2H, AA', BB', Ar), 7.44-7.40 (m, 2H, AA', BB', Ar), 6.35-6.31 (m, 1H, H5), 5.21-5.18 (m, 1H, H2), 4.40-4.36 (m, 2H, H6), 3.67-3.62 (m, 4H, H3, COOCH3, overlapped), 3.50 (s, 3H, OCH3); 13C NMR (125 MHz, CDCl3) δ 170.2, 143.7, 132.3, 128.9, 127.0, 125.9, 118.7, 111.0, 98.1, 60.4, 55.8, 52.5, 47.4; IR νmax [cm⁻¹] 2923, 2848, 2227, 1603, 1438, 1362, 1274, 1247, 1136, 1093, 1074; LRMS (APCI) m/z (relative intensity) 274.1 [M+H]+ (1), 256.3 (23), 243.2 (18), 210.3 (100), 215.2 (50), 183.3 (12), 154.3 (29), 75.2 (3); Anal calcd. for C15H15NO4: C, 65.9; H, 5.5; N, 5.1; O, 23.4; found: C, 65.8; H, 5.4; N, 5.1; O, 23.7 %.

**cis isomer:** 1H NMR (500 MHz, CDCl3) δ 7.62-7.58 (m, 2H, AA', BB', Ar), 7.41-7.36 (m, 2H, AA', BB', Ar), 6.33 (s, 1H, H5), 5.09-5.05 (m, 1H, H2), 4.51 (d, J = 17.3 Hz, 1H, H6), 4.32 (d, J = 17.3 Hz, 1H, H6), 4.00 (s, 1H, H3), 3.60 (s, 3H, OCH3); 13C NMR (125 MHz, CDCl3) δ 169.4, 144.0, 132.4, 130.0, 127.4, 125.4, 118.7, 111.0, 97.8, 60.9, 56.3, 52.3, 46.9; IR νmax [cm⁻¹] 2924, 2851, 2227, 1734, 1605, 1558, 1507, 1437, 1385, 1362, 1307, 1250, 1197, 1168, 1134, 1112, 1057; LRMS (APCI) m/z (relative intensity) 274.1 [M+H]+ (3), 256.4 (100), 242.4 (98), 226.4 (28), 210.4 (29), 182.4 (41), 85.5 (9), 75.5
(14), 61.3 (6); Anal calcd. for C_{15}H_{15}NO_{4}: C, 65.9; H, 5.5; N, 5.1; O, 23.4; found: C, 66.0; H, 5.4; N, 5.3; O, 23.3 %.

3-(Trifluoromethyl)-3,6-dihydro-2-methoxy-4-phenyl-2H-pyran 7: Prepared according to general procedure in 38 % yield (20 % trans, 18 % cis), purified by column chromatography (petroleum ether/ethyl acetate 9:1), white solid, mp 82.1 °C (trans), white amorphous solid (cis).

**trans isomer:** \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.38-7.27 (m, 5H, Ar), 6.21 (t, \(J = 2.5\) Hz, 1H, H5), 5.21 (s, 1H, H2), 4.39-4.34 (m, 2H, H6), 3.51 (s, 3H, OCH\(_3\)), 3.51-3.47 (m, 1H, H3); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 139.7, 128.5, 127.7, 127.7, 127.4 (q, \(J = 2.0\) Hz), 125.7, 124.8 (q, \(J = 281.2\) Hz), 95.0 (q, \(J = 3.7\) Hz), 60.0, 55.6, 44.8 (q, \(J = 25.6\) Hz); IR \(\nu\)max [cm\(^{-1}\)] 2932, 2886, 2851, 1600, 1495, 1447, 1393, 1365, 1320, 1260, 1160, 1144, 1117, 1110, 1069; LRMS (APCI) \(m/z\) (relative intensity) 259.2 [M+H\(^+\)] (100), 241.0 (24), 208.5 (9), 190.5 (19), 185.0 (17), 85.2 (6); Anal calcd. for C\(_{13}\)H\(_{13}\)F\(_3\)O\(_2\): C, 60.5; H, 5.1; F, 22.1; O, 12.4; found: C, 60.7; H, 5.0; F, 22.2; O, 12.1 %.

**cis isomer:** \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.39-7.24 (m, 5H, Ar), 6.05 (s, 1H, H5), 4.97-4.94 (m, 1H, H2), 4.51 (dt, \(J = 17.2\) Hz, \(J = 2.4\) Hz, 1H, H6), 4.34 (dt, \(J = 17.2\) Hz, \(J = 2.4\) Hz, 1H, H6), 3.75-3.67 (m, 1H, H3), 3.59-3.57 (m, 3H, OCH\(_3\) ); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 139.5, 130.2 (q, \(J = 2.1\) Hz), 128.4, 128.2, 127.6, 126.5, 124.9 (q, \(J = 281.7\) Hz), 97.6 (q, \(J = 2.3\) Hz), 62.3, 56.6, 44.7 (q, \(J = 25.1\) Hz); IR \(\nu\)max [cm\(^{-1}\)] 2939, 2850, 1600, 1498, 1446, 1397, 1362, 1329, 1256, 1245, 1155, 1144, 1112, 1069; LRMS (APCI) \(m/z\) (relative intensity) 259.4 [M+H\(^+\)] (100), 241.3 (35), 208.4 (17), 190.3 (8), 185.4 (23), 85.2 (11); Anal calcd. for C\(_{13}\)H\(_{13}\)F\(_3\)O\(_2\): C, 60.5; H, 5.1; F, 22.1; O, 12.4; found: C, 60.8; H, 4.7; F, 22.5; O, 12.0 %.
Methyl 3,6-dihydro-2-methoxy-6-methyl-4-phenyl-2H-pyran-3-carboxylate 8: Prepared according to general procedure in 71 % yield, purified by column chromatography (gradient elution, petroleum ether/ethyl acetate 95:5 – 9:1), colourless oil. 

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.38-7.20 (m, 5H, Ar), 6.16 (d, $J = 2.0$ Hz, 1H, H5), 5.21-5.19 (m, 1H, H2), 4.50-4.44 (m, 1H, H6), 3.67-3.65 (m, 4H, COOCH$_3$, H3), 3.48 (s, 3H, OCH$_3$), 1.39 (d, $J = 6.8$ Hz, 3H, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 170.9, 139.1, 129.1, 128.4, 128.3, 127.5, 125.2, 98.7, 65.1, 55.6, 52.4, 47.7, 20.4; IR $\nu_{\text{max}}$ [cm$^{-1}$] 3025, 2977, 2951, 2951, 2838, 1744, 1728, 1600, 1496, 1445, 1435, 1347, 1313, 1246, 1192, 1155, 1118, 1070, 1045; MS (TOF CI) $m/z$ (relative intensity) 285.1 [M+Na]$^+$ (1), 261.1 (7), 249.1 (7), 245.1 (10), 231.1 (44), 221.1 (13), 203.1 (10), 189.1 (48), 171.1 (23), 105.0 (4); HRMS (ESI) $m/z$ calcd. for C$_{15}$H$_{18}$O$_4$Na: 285.1097, found: 285.1098; Anal calcd. for C$_{15}$H$_{18}$O$_4$: C, 68.7; H, 6.9; O, 24.4; found: C, 68.6; H, 6.9; O, 24.5 %.

General Procedure for the Rearrangement of Dihydropyrans to Cyclopentenones.
Methanol (0.03 ml, 0.2 mmol) and anhydrous p-toluenesulfonic acid (138 mg, 0.8 mmol) were added to a solution of dihydropyran (0.2 mmol) in toluene (1.5 ml). The reaction mixture was heated to 80 °C and stirred overnight at this temperature. The mixture was diluted with ethyl acetate and washed with a saturated aqueous NaHCO$_3$ solution. The organic layer was dried with anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

Methyl 3-oxo-2-phenylcyclopent-1-enecarboxylate 9a: Prepared according to general procedure in 69 % yield, purified by column chromatography (petroleum ether/ethyl acetate 9:1), yellow oil. The spectral data were identical with those in the literature.$^{12}$

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.43-7.28 (m, 5H, Ar), 3.74 (s, 3H, OCH$_3$), 2.98-2.91 (m, 2H, H5), 2.69-2.63 (m, 2H, H4); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 207.2, 166.2, 156.4, 146.3, 130.1, 128.9, 128.8, 127.9, 52.2, 34.5, 27.0; MS (TOF CI) $m/z$ (relative intensity) 217.1 [M+H]$^+$

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Methyl 3-oxo-2-pentylcyclopent-1-enecarboxylate 9b: Prepared according to general procedure in 20 % yield, purified by column chromatography (petroleum ether/ethyl acetate 95:5), yellow oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.85 (s, 3H, OCH$_3$), 2.78-2.72 (m, 2H, H5), 2.52 (t, $J$ = 7.7 Hz, 2H, CH$_2$), 2.48-2.43 (m, 2H, H4), 1.46-1.34 (m, 2H, CH$_2$), 1.34-1.22 (m, 4H, CH$_2$), 0.87 (t, $J$ = 6.9 Hz, 3H, CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 209.6, 165.8, 154.0, 151.8, 52.0, 34.0, 31.9, 28.1, 26.4, 24.0, 22.4, 13.9; IR $\nu_{\text{max}}$ [cm$^{-1}$] 2955, 2928, 2859, 1713, 1679, 1461, 1436, 1274, 1224, 1182, 1101; MS (TOF CI) $m/z$ (relative intensity) 211.1 [M+H]$^+$ (100), 195.1 (5), 151.1 (4); HRMS (TOF CI) $m/z$ calcd. for C$_{12}$H$_{19}$O$_3$: 211.1334, found: 211.1328.

Methyl 3-oxo-2-propylcyclopent-1-enecarboxylate 9c: Prepared according to general procedure in 44 % yield, purified by column chromatography (petroleum ether/ethyl acetate 95:5), yellow oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.85 (s, 3H, OCH$_3$), 2.78-2.72 (m, 2H, H5), 2.54-2.43 (m, 4H, H4, CH$_2$), 1.50-1.37 (m, 2H, CH$_2$), 0.90 (t, $J$ = 7.4 Hz, 3H, CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 209.6, 165.8, 154.2, 151.4, 52.0, 34.0, 26.4, 25.9, 21.8, 14.1; IR $\nu_{\text{max}}$ [cm$^{-1}$] 2958, 2929, 2872, 1712, 1693, 1462, 1439, 1366, 1256, 1237, 1207, 1190, 1179, 1129, 1100; LRMS (APCI) $m/z$ (relative intensity) 183.7 [M+H]$^+$ (100), 151.6 (5), 123.6 (13), 105.7 (4), 75.7 (5), 59.5 (3).
Methyl 2-(naphthalen-1-yl)-3-oxocyclopent-1-enecarboxylate 9d: Prepared according to general procedure in 40 % yield, purified by column chromatography (petroleum ether/ethyl acetate 9:1), brown amorphous solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.91-7.85 (m, 2H, Ar), 7.55-7.39 (m, 5H, Ar), 3.50 (s, 3H, OCH$_3$), 3.22-2.99 (m, 2H, CH$_2$), 2.83-2.75 (m, 2H, CH$_2$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 207.5, 165.4, 158.6, 147.4, 133.4, 131.1, 129.0, 128.5, 128.2, 126.7, 126.1, 125.8, 125.0, 124.7, 52.1, 34.7, 27.2; IR $\nu_{max}$ [cm$^{-1}$] 2925, 2854, 1729, 1709, 1507, 1436, 1395, 1259, 1231, 1201, 1161, 1108, 1047; LRMS (APCI) m/z (relative intensity) 267.4 [M+H]$^+$ (12), 235.5 (100), 85.5 (5), 59.1 (4).

Methyl 2-benzyl-3-oxocyclopent-1-enecarboxylate 9e: Prepared according to general procedure in 38 % yield, purified by column chromatography (petroleum ether/ethyl acetate 95:5), yellowish oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.33-7.14 (m, 5H, Ar), 3.92 (s, 2H, CH$_2$), 3.87 (s, 3H, OCH$_3$), 2.82-2.75 (m, 2H, CH$_2$), 2.50-2.44 (m, 2H, CH$_2$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 209.1, 165.6, 154.6, 149.6, 138.3, 129.0, 128.4, 126.3, 52.1, 34.0, 29.6, 26.6; IR $\nu_{max}$ [cm$^{-1}$] 2951, 2854, 1729, 1709, 1507, 1436, 1395, 1259, 1231, 1201, 1161, 1108, 1047; LRMS (APCI) m/z (relative intensity) 230.9 [M+H]$^+$ (100), 198.9 (34), 182.5 (12), 158.7 (24), 137.1 (3).
Methyl 2-(4-cyanophenyl)-3-oxocyclopent-1-enecarboxylate 9f: Prepared according to general procedure in 22 % yield, purified by column chromatography (petroleum ether/ethyl acetate 85:15), yellow oil.

$^1$H NMR (300 MHz, CDCl₃) δ 7.72-7.63 (m, 2H, AA', BB', Ar), 7.46-7.38 (m, 2H, AA', BB', Ar), 3.76 (s, 3H, OCH₃), 3.02-2.92 (m, 2H, CH₂), 2.73-2.62 (m, 2H, CH₂); $^{13}$C NMR (75 MHz, CDCl₃) δ 206.1, 165.2, 158.0, 145.1, 134.9, 131.6, 129.8, 118.5, 112.4, 52.4, 34.5, 27.2; IR ν max [cm⁻¹] 2927, 2852, 2222, 1730, 1712, 1437, 1343, 1214, 1183, 1161, 1091; LRMS (APCI) m/z (relative intensity) 242.3 [M+H]⁺ (100), 210.3 (50), 156.4 (3), 75.6 (5).

Methyl 2-(4-(methoxycarbonylphenyl)-3-oxocyclopent-1-enecarboxylate 9g: Prepared according to general procedure in 20 % yield, purified by column chromatography (petroleum ether/ethyl acetate 85:15), yellow oil.

$^1$H NMR (300 MHz, CDCl₃) δ 8.08-8.03 (m, 2H, AA', BB', Ar), 7.40-7.35 (m, 2H, AA', BB', Ar), 3.92 (s, 3H, OCH₃), 3.73 (s, 3H, OCH₃), 2.99-2.94 (m, 2H, CH₂), 2.71-2.65 (m, 2H, CH₂); $^{13}$C NMR (75 MHz, CDCl₃) δ 206.6, 166.7, 165.8, 157.5, 145.7, 134.8, 130.2, 129.1, 129.0, 52.3, 52.2, 34.6, 27.1; IR ν max [cm⁻¹] 2923, 2852, 1715, 1436, 1277, 1227, 1183, 1161, 1111; LRMS (APCI) m/z (relative intensity) 274.9 [M+H]⁺ (100), 256.9 (2), 243.9 (16), 148.5 (3).

Preparation of $^{13}$C-labelled compounds.

3-phenylprop-2-yn-1-ol-$^{13}$C: Prepared according to general procedure for formation of propargylic alcohols from alkynes in 92 % yield, purified by column chromatography (petroleum ether/ethyl acetate 8:2), colourless oil.
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.46-7.41 (m, 2H, Ar), 7.34-7.28 (m, 3H, Ar), 4.50 (d, $J$ = 7.5 Hz, 2H, OCH$_2$), 1.95 (bs, 1H, OH); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 131.6 (d, $J$ = 2.5 Hz), 128.4, 128.3, 122.5 (d, $J$ = 12.4 Hz), 87.2 ($^{13}$C), 86.4 (d, $J$ = 83.1 Hz), 51.6 (d, $J$ = 73.7 Hz).

(E)-Methyl 3-(3-phenylprop-2-ynyloxy)acrylate-2-$^{13}$C: Prepared according to general procedure for the addition of propargylic alcohols to methyl propiolate in 99 % yield, purified by column chromatography (petroleum ether/ethyl acetate 95:5), yellowish oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J$ = 12.6 Hz, 1H, H3), 7.47-7.43 (m, 2H, Ar), 7.37-7.29 (m, 3H, Ar), 5.39 (d, $J$ = 12.6 Hz, 1H, H2), 4.75 (d, $J$ = 7.9 Hz, 2H, OCH$_2$), 3.72 (s, 3H, OCH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.7, 160.9 (d, $J$ = 2.5 Hz), 131.8 (d, $J$ = 2.6 Hz), 129.0, 128.3, 121.7 (d, $J$ = 12.8 Hz), 98.0, 82.1 (d, $J$ = 92.9 Hz), 81.8 ($^{13}$C), 59.1 (d, $J$ = 79.2 Hz), 51.2.

Methyl 3,6-dihydro-2-methoxy-4-phenyl-2H-pyran-3-carboxylate-5-$^{13}$C:

Prepared according to general procedure for gold(I)-catalyzed cyclisation to dihydropyrans in 80 % yield (58 % trans, 22 % cis), purified by column chromatography (petroleum ether/ethyl acetate 95:5), white amorphous solid.

trans isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.36-7.22 (m, 5H, Ar), 6.21 (dt, $J$ = 157.9 Hz, $J$ = 2.8 Hz, 1H, H5), 5.15 (d, $J$ = 2.2 Hz, 1H, H2), 4.38 (dt, $J$ = 5.2 Hz, $J$ = 2.2 Hz, 2H, H6), 3.72-3.69 (m, 1H, H3), 3.63 (s, 3H, COOCH$_3$), 3.51 (s, 3H, OCH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.9 (d, $J$ = 2.9 Hz), 139.1, 130.1 (d, $J$ = 74.2 Hz), 128.4, 127.5, 125.2 (d, $J$ = 3.8 Hz), 123.7 ($^{13}$C), 98.6 (d, $J$ = 4.5 Hz), 60.7 (d, $J$ = 42.6 Hz), 55.8, 52.3, 48.0.

cis isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.34-7.22 (m, 5H, Ar), 6.23 (d, $J$ = 158.1 Hz, 1H, H5), 4.99 (d, $J$ = 4.2 Hz, 1H, H2), 4.55 (ddt, $J$ = 17.0 Hz, $J$ = 5.4 Hz, $J$ = 2.6 Hz, 1H, H6), 4.32 (ddt, $J$ = 17.0 Hz, $J$ = 5.4 Hz, $J$ = 2.6 Hz, 1H, H6), 4.01-3.97 (m, 1H, H3), 3.60 (s, 3H,
COOCH₃), 3.53 (s, 3H, OCH₃); $^{13}$C NMR (125 MHz, CDCl₃) δ 170.0 (d, $J = 2.7$ Hz), 139.1, 131.2 (d, $J = 74.0$ Hz), 128.5, 127.5, 124.8 (d, $J = 3.8$ Hz), 124.2 ($^{13}$C), 98.5 (d, $J = 4.8$ Hz), 62.0 (d, $J = 42.9$ Hz), 56.4, 52.2, 47.5.

Methyl 3-oxo-2-phenylcyclopent-1-enecarboxylate-3-$^{13}$C: Prepared according to general procedure for the rearrangement of dihydropyrans to cyclopentenones in 69% yield, purified by column chromatography (petroleum ether/ethyl acetate 95:5), yellow oil.

$^1$H NMR (500 MHz, CDCl₃) δ 7.44-7.27 (m, 5H, Ar), 3.74 (s, 3H, OCH₃), 2.96-2.91 (m, 2H, H5), 2.68-2.63 (m, 2H, H4); $^{13}$C NMR (125 MHz, CDCl₃) δ 207.2 ($^{13}$C), 166.2 (d, $J = 8.0$ Hz), 156.4 (d, $J = 12.0$ Hz), 146.2 (d, $J = 46.9$ Hz), 130.1 (d, $J = 2.0$ Hz), 128.9, 128.8, 127.9, 52.2, 34.5 (d, $J = 39.6$ Hz), 27.0 (d, $J = 3.3$ Hz).
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