Supporting Information for

A novel self-terminated Prins strategy for the synthesis of tetrahydropyran-4-one derivatives and their behavior in Fisher indole synthesis

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Table of Contents

1. Experimental procedure for Prins cyclization .................................................S2-S2
2. Characterization data of products ..........................................................S2- S10
3. 1H and 13C NMR spectra of products ..................................................S11- S54
4. X-ray crystallography ..............................................................................S55- S55
1. Experimental Section

IR spectra were measured with a Thermo Nicolet Nexus 670 spectrometer. $^1$H-NMR spectra were measured with Bruker-400 and Bruker Avance 700 spectrometer. All signals are expressed as ppm downfield from tetramethylsilane used as an internal standard ($\delta$ value). $^{13}$C NMR spectra were recorded on the instruments operating at 75 MHz or 125 MHz with CDCl$_3$ as a solvent with internal standard ($\delta$ 77.0) Mass spectra were taken with Finnigan MAT1020B or JEOL. Column chromatography was performed using E. Merck 100-200, mesh silica gel.

**Typical procedure**

To a mixture of (3-(phenylthio)but-3-en-1-ol (0.5 mmol) and aldehyde/ketone (0.6 mmol) in anhydrous DCM (5 mL) was added Sc(OTf)$_3$ (5 mol%) at 0 °C. The resulting mixture was allowed to stir at room temperature for the specified time. After completion of the reaction, the reaction mixture was quenched with water. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2x5 mL). The combined organic phases were washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The resulting crude product was purified by silica gel column chromatography (100-200 mesh) using ethyl acetate/hexane gradient mixture to afford the pure product 3.

2. Characterization data of products

3-(Phenylthio)but-3-en-1-ol (1)

![3-(Phenylthio)but-3-en-1-ol (1)](image)

$^1$H NMR (500 MHz, CDCl$_3$, $\delta$ ppm): 7.41-7.45 (m, 2H), 7.25-7.36 (m, 3H), 5.24 (s, 1H), 5.00 (s, 1H), 3.77 (t, $J = 6.2$ Hz, 2H), 2.48 (t, $J = 6.0$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$, $\delta$ ppm): 142.1, 133.1, 132.4, 129.1, 127.9, 115.0, 60.7, 39.5; IR (neat) $\nu_{\text{max}}$/cm$^{-1}$: 3369, 2927, 1609, 1583, 1475, 1439, 1144, 1046, 846, 748, 691; ESI-HRMS calcd for C$_{10}$H$_{13}$OS (M+H)$^+$ 181.0682, found 181.0684.
2-Phenyldihydro-2\(H\)-pyran-4(3\(H\))-one (3a):

![Chemical Structure](image)

\(^1\)H NMR (500 MHz, CDCl\(_3\), δ ppm): 7.25-7.29 (m, 3H), 7.19-7.22 (m, 2H), 4.53 (dd, \(J = 8.5, 5.8\) Hz, 1H), 4.32 (ddd, \(J = 11.6, 7.5, 1.5\) Hz, 1H), 3.73 (td, \(J = 23.8, 2.9\) Hz, 1H), 2.57-2.65 (m, 1H), 2.52-2.55 (m, 2H), 2.32 (dt, \(J = 14.6, 1.4\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), δ ppm): 206.2, 140.5, 128.6, 128.0, 125.5, 79.7, 66.6, 49.8, 42.1; IR (neat) \(\nu_{\text{max}}/\text{cm}^{-1}\): 3419, 2974, 2930, 1721, 1453, 1350, 1254, 1156, 1144, 1057, 755, 699; ESI-HRMS calcd for: C\(_{11}\)H\(_{13}\)O\(_2\) (M+H\(^+\)) 177.0910, found 177.0912.

2-(4-Bromophenyl)tetrahydro-4\(H\)-pyran-4-one (3b):

![Chemical Structure](image)

\(^1\)H NMR (500 MHz, CDCl\(_3\), δ ppm): 7.51 (d, \(J = 8.5\) Hz, 2H), 7.25 (d, \(J = 8.5\) Hz, 2H), 4.61 (dd, \(J = 11.0, 3.0\) Hz, 1H), 4.43 (ddd, \(J = 11.6, 7.3, 1.4\) Hz, 1H), 3.84 (td, \(J = 23.9, 2.9\) Hz, 1H), 2.68-2.76 (m, 1H), 2.54-2.66 (m, 2H), 2.42-2.46 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), δ ppm): 205.7, 139.6, 131.7, 127.2, 121.9, 79.0, 66.7, 49.8, 42.0; IR (neat) \(\nu_{\text{max}}/\text{cm}^{-1}\): 3419, 2968, 2858, 1719, 1369, 1247, 1152, 1057, 1025, 756, 699; ESI-HRMS calcd for C\(_{11}\)H\(_{12}\)BrO\(_2\) (M+H\(^+\)) 255.0015, found 255.0016.

2-(4-Chlorophenyl)tetrahydro-4\(H\)-pyran-4-one (3c):

![Chemical Structure](image)

\(^1\)H NMR (500 MHz, CDCl\(_3\), δ ppm): 7.22-7.41 (m, 4H), 4.62 (d, \(J = 7.9\) Hz, 1H), 4.43 (t, \(J = 8.4\) Hz, 1H), 3.83 (t, \(J = 11.3\) Hz, 1H), 2.35-2.82 (m, 4H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), δ ppm): 205.7, 139.0, 133.7, 128.7, 126.9, 78.9, 66.6, 49.8, 42.0; IR (neat) \(\nu_{\text{max}}/\text{cm}^{-1}\): 3418, 2863, 2822, 2856, 1719, 1461,
1367, 1367, 1245, 1165, 1077, 1029, 778, 700; ESI-HRMS calcd for C_{11}H_{11}ClO_2 (M+H)^+ 211.0526, found 211.03338.

2-(p-Tolyl)dihydro-2H-pyran-4(3H)-one (3d):

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
\]

^{1}H NMR (500 MHz, CDCl₃, δ ppm): 7.24 (d, J=8.0 Hz, 2H), 7.19 (d, J=7.8, Hz, 2H), 4.16 (dd, J = 9.1, 4.8 Hz, 1H), 4.42 (ddd, J = 11.4, 7.3, 1.5 Hz, 1H), 3.83 (td, J = 12.2, 2.8 Hz, 1H), 2.67-2.77 (m, 1H), 2.60-2.66 (m, 1H), 2.40-2.44 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl₃, δ ppm): 206.4, 137.6, 129.2, 125.6, 79.7, 66.2, 49.9, 42.1, 21.0; IR (neat) ν_{max}/cm⁻¹: 2963, 2922, 2856, 1719, 1367, 1245, 1077, 778, 700; ESI-HRMS calcd for C_{12}H_{15}O_2 (M+H)^+ 191.1072 found 191.1066.

2-(m-Tolyl)tetrahydro-4H-pyran-4-one (3e):

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
\]

^{1}H NMR (500 MHz, CDCl₃, δ ppm): 7.27 ( t, J = 5.5 Hz, 1H), 7.20 (s, 1H), 7.11-7.18 (m, 2H), 4.61 (dd, J = 7.9, 6.2 Hz, 1H), 4.44 (ddd, J = 11.5, 7.4, 1.3 Hz, 1H), 3.84 (td, J = 11.7, 2.8 Hz, 1H'), 2.59-2.80 (m, 3H), 2.39-2.47 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl₃, δ ppm): 206.4, 140.5, 138.4, 128.9, 128.6, 126.3, 122.7, 79.9, 66.8, 49.9, 42.2, 21.4; IR (neat) ν_{max}/cm⁻¹: 3418, 2922, 2856, 1719, 1607, 1367, 1245, 1165, 1077, 778, 700; ESI-HRMS calcd for C_{12}H_{15}O_2 (M+H)^+ 191.1067 found 191.1068.

2-(4-Isopropylphenyl)dihydro-2H-pyran-4(3H)-one (3f):

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
\]

^{1}H NMR (500 MHz, CDCl₃, δ ppm): 7.29, (d, J = 8.1 Hz, 2H), 7.24, (d, J = 8.1 Hz, 2H), 4.61 (dd, J = 9.9, 4.0 Hz, 1H), 4.41 (dd, J = 11.4, 7.3 Hz, 1H), 3.79-3.86 (m, 1H'), 2.91 (sep, J = 6.9 Hz, 1H),
2.61-2.75 (m, 3H), 2.42 (d, $J = 14.6$ Hz, 1H'); $^{13}$C NMR (125 MHz, CDCl$_3$, δ ppm): 206.4, 148.9, 137.8, 126.6, 125.7, 79.7, 66.6, 49.7, 42.1, 33.8, 29.6, 23.8; IR (neat) $\nu_{\text{max}}$/cm$^{-1}$: 3420, 2961, 2926, 2857, 1720, 1463, 1367, 1248, 1152, 1024, 829. ESI-HRMS calcd for C$_{14}$H$_{19}$O$_2$ (M+H)$^+$ 219.1380, found 219.1381.

2-(Naphthalen-2-yl)dihydro-2H-pyran-4(3H)-one (3g):

$^1$H NMR (500 MHz, CDCl$_3$, δ ppm): 8.02 (d, $J = 8.4$ Hz, 1H), 7.89 (dd, $J = 7.9$, 1.5 Hz, 1H), 7.83 (d, $J = 8.2$ Hz, 1H), 7.66 (d, $J = 7.2$ Hz, 1H), 7.55 (dd, $J = 8.2$, 1.5 Hz, 1H), 7.50 (d, $J = 7.2$ Hz, 1H), 5.40 (dd, $J = 10.2$, 3.8 Hz, 1H), 4.50 (dd, $J = 11.7$, 7.3, 2.0 Hz, 1H), 4.00 (td, $J = 23.5$, 3.0 Hz, 1H), 2.78-2.90 (m, 3H), 2.51-2.56 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$, δ ppm): 206.6, 135.9, 133.7, 129.9, 128.9, 128.7, 126.3, 125.7, 125.4, 123.1, 122.8, 76.9, 66.7, 49.1, 42.3; IR (neat) $\nu_{\text{max}}$/cm$^{-1}$: 3398, 2891, 1701, 1594, 1255, 1063, 1008, 793, 773. ESI-HRMS calcd for C$_{15}$H$_{15}$O$_2$ (M+H)$^+$ 227.1066, found 227.1070.

(E)-2-Styryldihydro-2H-pyran-4(3H)-one (3h):

$^1$H NMR (500 MHz, CDCl$_3$, δ ppm): 7.39 (dd, $J = 8.7$, 1.5 Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.24-7.28 (m, 1H), 6.65 (d, $J = 16.0$ Hz, 1H), 6.23 (dd, $J = 16.0$, 5.9 Hz, 1H), 4.37 (ddd, $J = 11.4$, 7.2, 1.7 Hz, 1H), 4.29-4.34 (m, 1H), 3.79 (td, $J = 23.6$, 3.0 Hz, 1H), 2.62-2.69 (m, 1H), 2.50-2.59 (m, 2H), 2.37-2.43 (m, 1H'); $^{13}$C NMR (125 MHz, CDCl$_3$, δ ppm): 206.1, 136.0, 131.6, 128.5, 127.9, 126.5, 78.1, 66.3, 48.1, 42.1; IR (neat) $\nu_{\text{max}}$/cm$^{-1}$: 3420, 3026, 2962, 2921, 2852, 1718, 1366, 1246, 1079, 749. ESI-HRMS calcd for: C$_{13}$H$_{13}$O$_2$ (M-H)$^-$ 201.0908 found 201.0910.

2-(4-Methoxyphenyl)dihydro-2H-pyran-4(3H)-one (3i)
2-(3,4,5-Trimethoxyphenyl)dihydro-2H-pyran-4(3H)-one (3j):

\[\text{IR (neat) } \nu_{\text{max}}/\text{cm}^{-1}: 2984, 2881, 1740, 1594, 1378, 1255, 773; \text{ ESI-HRMS calcd for } C_{12}H_{15}O_{3} (M+H)^{+} 207.1021, \text{ found 207.1013.}\]

2-(4-(Benzyloxy)-3-methoxyphenyl)dihydro-2H-pyran-4(3H)-one (3k):

\[\text{IR (neat) } \nu_{\text{max}}/\text{cm}^{-1}: 3389, 2947, 2857, 1714, 1524, 1460, 1369, 1234, 1129, 1061, 708. \text{ ESI-HRMS calcd for } C_{14}H_{19}O_{5} (M+H)^{+} 267.1227, \text{ found 267.1228.}\]
56.0, 49.9, 42.1; IR (neat) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3420, 2961, 2926, 2857, 1720, 1463, 1367, 1248, 1152, 1086, 1024, 829. ESI-HRMS calcd for \( \text{C}_{19}\text{H}_{21}\text{O}_{4} \) (M+H)\(^+\) 313.1434, found 313.1435.

2-Butyltetrahydro-4\(H\)-pyran-4-one (3l)

\[
\begin{align*}
\text{O} \\
\text{O} \\
\text{1} \\
\end{align*}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\), \( \delta \) ppm): 4.29 (dd, \( J = 11.4, 7.3 \text{ Hz, 1H} \), 3.65 (td, \( J = 11.6, 2.9 \text{ Hz, 1H} \), 3.54-3.60 (m, 1H), 2.54-2.64 (m, 1H), 2.40 (d, \( J = 14.3 \text{ Hz, 1H} \), 2.25-2.35 (m, 2H), 1.61-1.72 (m, 1H), 1.29-1.58 (m, 6H), 0.91 (t, \( J = 7.2 \text{ Hz, 3H} \)); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), \( \delta \) ppm): 207.3, 78.0, 66.4, 48.3, 42.2, 36.0, 27.2, 22.5, 13.9; IR (neat) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3444, 2956, 2926, 1716, 1584, 1464, 1361, 1150, 739, 691; ESI-HRMS calcd for \( \text{C}_{9}\text{H}_{15}\text{O}_{2} \) (M-H)\(^+\) 155.1066, found 155.1065.

2-Isobutyldihydro-2\(H\)-pyran-4(3\(H\))-one (3m)

\[
\begin{align*}
\text{O} \\
\text{O} \\
\text{1} \\
\end{align*}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\), \( \delta \) ppm): 4.29 (ddd, \( J = 11.5, 7.5, 1.3 \text{ Hz, 1H} \), 3.59-3.72 (m, 2H), 2.52-2.66 (m, 1H), 2.16-2.43 (m, 3H), 1.73-1.90 (m, 1H), 1.57-1.70 (m, 1H), 1.20-1.35 (m, 1H), 0.92 (dd, \( J = 6.6, 5.8 \text{ Hz, 6H} \)); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), \( \delta \) ppm): 207.1, 76.3, 66.5, 48.8, 45.4, 42.2, 24.2, 23.0, 22.1; IR (neat) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3425, 2958, 2928, 2868, 1721, 1468, 1376, 1250, 1161, 1087, 769; ESI HRMS calcd for \( \text{C}_{9}\text{H}_{17}\text{O}_{2} \) (M-H)\(^+\) 157.1224, found 157.12234.

2-Pentyldihydro-2\(H\)-pyran-4(3\(H\))-one (3n):

\[
\begin{align*}
\text{O} \\
\text{O} \\
\text{1} \\
\end{align*}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\), \( \delta \) ppm): 4.26 (ddd, \( J = 11.6, 7.5, 1.4 \text{ Hz, 1H} \), 3.63 (td, \( J = 23.8, 2.9 \text{ Hz, 1H} \), 3.52-3.57 (m, 1H), 2.52-2.60 (m, 1H), 2.37 (dt, \( J = 14.3, 2.4 \text{ Hz, 1H} \), 2.23-2.32 (m, 2H), 1.60-1.67 (m, 1H), 1.38-1.52 (m, 2H), 1.22-1.35 (m, 6H), 0.87 (t, \( J = 7.0 \text{ Hz, 3H} \)); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), \( \delta \) ppm): 207.1, 78.1, 66.4, 48.3, 42.2, 36.2, 31.6, 24.7, 22.4, 13.9; IR (neat) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3422,
2929, 2857, 1718, 1463, 1378, 1219, 1087, 770. ESI-HRMS calcd for C₁₀H₁₉O₂ (M+H)⁺ 171.1379, found 171.1382.

2-(4-hydroxyphenyl)dihydro-2H-pyran-4(3H)-one (3o):

\[\text{O} \]
\[\text{O} \]
\[\text{H} \]
\[\text{1} \]
\[\text{H} \]
\[\text{NMR (500 MHz, CDCl}_3, \delta \text{ ppm): } 7.24 \text{ (d, } J = 8.3 \text{ Hz, 2H), 6.83 \text{ (d, } J = 8.5 \text{ Hz, 2H), 5.48 (br s, 1H, -OH), 4.59 (dd, } J = 9.6, 4.3 \text{ Hz, 1H), 4.40 (dd, } J = 11.5, 7.4 \text{ Hz, 1H), 3.83 (td, } J = 23.8, 3.0 \text{ Hz, 1H), 2.58-2.78 (m, 3H), 2.43 (dt, } J = 14.5, 1.1 \text{ Hz, 1H); }^{13}\text{C NMR (125 MHz, CDCl}_3, \delta \text{ ppm): 207.0, 155.7, 132.5, 127.3, 115.4, 79.5, 66.5, 49.7, 42.1; IR (neat) } \nu_{\text{max}}/\text{cm}^{-1}: 3241, 2925, 2855, 1698, 1517, 1460, 1367, 1263, 1150, 823. \text{ESI-HRMS calcd for: C}_{11}\text{H}_{13}\text{O}_3 (M+H)⁺ 193.0859, found 193.0862.\]

2-(Furan-2-yl)dihydro-2H-pyran-4(3H)-one (3p):

\[\text{O} \]
\[\text{O} \]
\[\text{1} \]
\[\text{H} \]
\[\text{NMR (500 MHz, CDCl}_3, \delta \text{ ppm): } 7.43 \text{ (dd, } J = 1.9, 0.9 \text{ Hz, 1H), 6.36 \text{ (dd, } J = 3.2, 1.7 \text{ Hz, 1H), 6.33 (dt, } J = 3.4, 0.7 \text{ Hz, 1H), 4.82 (dd, } J = 10.0, 3.8 \text{ Hz, 1H), 4.19-4.27 (m, 1H), 3.81-3.90 (m, 1H), 2.88 \text{ (ddd, } J = 14.7, 9.8, 1.1 \text{ Hz, 1H), 2.59-2.73 (m, 2H), 2.42-2.50 (m, 1H); }^{13}\text{C NMR (125 MHz, CDCl}_3, \delta \text{ ppm): 205.5, 152.1, 142.9, 110.2, 108.2, 72.2, 65.5, 45.3, 42.0; IR (neat) } \nu_{\text{max}}/\text{cm}^{-1}: 3121, 2925, 2854, 1725, 1462, 1261, 1078, 1018, 800. \text{ESI-HRMS calcd for: C}_9\text{H}_{11}\text{O}_3 (M+H)⁺ 167.0703, found 167.0705\]

1-Oxaspiro[5.5]undecan-4-one (3q):

\[\text{O} \]
\[\text{O} \]
\[1 \]
\[\text{H} \]
\[\text{NMR (500 MHz, CDCl}_3, \delta \text{ ppm): } 3.92-3.98 (m, 2H), 2.37-2.42 (m, 2H), 2.30 (s, 2H), 1.68-1.77 (m,2H), 1.48-1.62 (m, 3H), 1.16-1.45 (m, 5H); }^{13}\text{C NMR (125 MHz, CDCl}_3, \delta \text{ ppm): 207.6, 76.6,
59.8, 52.9, 41.7, 35.0, 25.2, 21.1; IR (neat) $v_{\text{max}}$/cm$^{-1}$: 3419, 2931, 2858, 1718, 1446, 1374, 13.8, 1263, 1075, 962, 746; ESI HRMS calcd for C$_{10}$H$_{17}$O$_2$ (M-H)$^+$ 169.1223, found 167.10661

**Experimental procedure for the Fischer indole product**

Phenylhydrazine hydrochloride (0.25 g, 1.62 mmol) and 2-substituted tetrahydropyran-4-one (0.14 g, 1.62 mmol) were added to glacial acetic acid (2 g, 0.03 mol) and the mixture was refluxed for 6h with stirring. The mixture was then cooled and neutralized with 1 M NaOH, then diluted with water (100 mL) and extracted with CHCl$_3$ (3 × 100 mL). Following the drying of the organic layer over Na$_2$SO$_4$, the solvent was removed under vacuum and the residue was passed through a short plug of silica gel to afford the pure product.

1-(1-Phenyl-3,4-dihydropyrano[4,3-b]indol-5(1H)-yl)ethanone 7a (major):

![Chemical structure of 1-(1-Phenyl-3,4-dihydropyrano[4,3-b]indol-5(1H)-yl)ethanone 7a](image)

$^1$H NMR (500 MHz, CDCl$_3$, δ ppm): 7.24-7.37 (m, 7H), 7.13-7.16 (m, 2H), 6.38 (s, 1H), 4.42 (t, $J$ = 6.8 Hz, 2H), 3.07 (t, $J$ = 7.0 Hz, 2H), 2.09 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, δ ppm): 171.1, 149.8, 143.8, 139.9, 130.5, 128.6, 128.4, 128.1, 127.2, 125.1, 107.0, 63.7, 29.6, 27.8 ppm; IR (neat) $v_{\text{max}}$/cm$^{-1}$: 3449, 3059, 2925, 2854, 1738, 1597, 1502, 1239, 1035, 764, 696; HRMS (ESI) calcd for C$_{19}$H$_{17}$NO$_2$: 291.1259 found : 291.1141.

2-(1,5-Diphenyl-4,5-dihydro-1H-pyrazol-3-yl)ethanol 8a (minor):

![Chemical structure of 2-(1,5-Diphenyl-4,5-dihydro-1H-pyrazol-3-yl)ethanol 8a](image)
\[^1\text{H NMR (500 MHz, CDCl}_3, \delta \text{ ppm): 7.23-7.36 (m, 5H), 7.14 (t, } J = 7.1 \text{ Hz, 2H), 6.91 (d, } J = 7.9 \text{ Hz, 2H), 6.76 (t, } J = 7.3 \text{ Hz, 1H), 5.01 (dd, } J = 11.5, 8.5 \text{ Hz, 1H), 3.99 (t, } J = 5.6 \text{ Hz, 2H), 3.45 (dd, } J = 17.5, 12.0 \text{ Hz, 1H), 2.77 (dd, } J = 17.5, 8.2 \text{ Hz, 1H), 2.57 (t, } J = 5.4 \text{ Hz, 2H); } ^{13}\text{C NMR (125 MHz, CDCl}_3, \delta \text{ ppm): 150.4, 145.7, 142.6, 129.0, 128.9, 127.5, 125.9, 118.9, 113.1, 64.2, 59.7, 47.1, 32.8 \text{ ppm; IR (neat) } \nu_{\text{max}}/\text{cm}^{-1}: 3386, 2925, 1598, 1499, 1050, 751, 697; HRMS (ESI) calcd for C}_{17}\text{H}_{19}\text{ON}_2 = 267.1491. \text{ found: 267.1483.}
\]

1-(1-Phenyl-3,4-dihydropyran[4,3-b]indol-5(1H)-yl)ethanone 7c (major):

\[^1\text{H NMR (500 MHz, CDCl}_3, \delta \text{ ppm): 7.25-7.35 (m, 7H), 7.22 (dd, } J = 5.4, 2.1 \text{ Hz, 1H), 6.38 (s, 1H), 4.43 (t, } J = 7.0 \text{ Hz, 2H), 3.08 (t, } J = 7.0 \text{ Hz, 2H), 2.09 (s, 3H); } ^{13}\text{C NMR (125 MHz, CDCl}_3, \delta \text{ ppm): 171.1, 149.9, 142.5, 139.7, 134.2, 129.8, 129.0, 128.7, 127.5, 125.1, 107.1, 63.6, 27.8, 21.1 \text{ ppm; IR (neat) } \nu_{\text{max}}/\text{cm}^{-1}: 3420, 2907, 1702, 1597, 1500, 1323, 1163, 1091, 1063, 820, 743, 691 \text{ cm}^{-1}; HRMS (ESI) calcd for C}_{19}\text{H}_{15}\text{ClNO}_2: 324.0797 \text{ found: 324.1431.}
\]

2-(1,5-Diphenyl-4,5-dihydro-1H-pyrazol-3-yl)ethanol 8c (minor):

\[^1\text{H NMR (500 MHz, CDCl}_3, \delta \text{ ppm): 7.31 (d, } J = 8.5 \text{ Hz, 2H), 7.24 (d, } J = 8.5 \text{ Hz, 2H), 7.15 (td, } d, J = 14.3, 1.9 \text{ Hz, 2H), 6.88 (dd, } J = 8.8, 1.0 \text{ Hz, 2H), 6.78 (t, } J = 7.3 \text{ Hz, 1H), 4.99 (dd, } J = 11.9, 8.2 \text{ Hz, 1H), 3.99 (dd, } J = 10.6, 5.3 \text{ Hz, 2H), 3.46 (dd, } J = 17.5, 12.0 \text{ Hz, 1H), 2.74 (dd, } J = 17.5, 8.2 \text{ Hz, 1H), 2.58 (t, } J = 5.4 \text{ Hz, 2H); } ^{13}\text{C NMR (125 MHz, CDCl}_3, \delta \text{ ppm): 150.4, 145.5, 141.1, 133.2, 129.2, 128.9, 127.3 119.3, 113.9, 63.6, 59.7, 47.0, 32.8 \text{ ppm; IR (neat) } \nu_{\text{max}}/\text{cm}^{-1}: 3450, 2927, 1602, 1462, 1429, 1366, 1153, 1034, 789. \text{ HRMS (ESI) calcd for C}_{17}\text{H}_{18}\text{ON}_2\text{Cl: 301.1108 found: 301.1101.}
\]
3. $^1$H and $^{13}$C NMR spectra of products

$^1$H NMR spectrum of compound 1
$^{13}$C NMR spectrum of compound 1
$^1$H NMR spectrum of compound 3a
$^{13}$C NMR spectrum of compound 3a


$^1$H NMR spectrum of compound 3b
$^{13}$C NMR spectrum of compound 3b
$^1$H NMR spectrum of compound 3c
$^{13}$C NMR spectrum of compound 3c
^1H NMR spectrum of compound 3d
$^{13}$C NMR spectrum of compound 3d
$^1$H NMR spectrum of compound 3e
$^{13}$C NMR spectrum of compound 3e
\(^1\text{H NMR spectrum of compound 3f}\)
$^{13}$C NMR spectrum of compound 3f
$^1$H NMR spectrum of compound 3g
$^{13}$C NMR spectrum of compound $3g$
$^1$H NMR spectrum of compound 3h
$^{13}$C NMR spectrum of compound 3h
$^1$H NMR spectrum of compound 3i
$^{13}$C NMR spectrum of compound 3i
$^1$H NMR spectrum of compound 3j
$^{13}$C NMR spectrum of compound 3j
$^1$H NMR spectrum of compound 3k
$^{13}$C NMR spectrum of compound 3k
\(^1\text{H NMR spectrum of compound 31}\)
$^{13}$C NMR spectrum of compound 3l
$^1$H NMR spectrum of compound 3m
$^{13}$C NMR spectrum of compound 3m
$^1$H NMR spectrum of compound 3n
$^{13}$C NMR spectrum of compound 3n
$^1$H NMR spectrum of compound 3o
$^{13}$C NMR spectrum of compound 3o
$^1$H NMR spectrum of compound 3p
$^{13}$C NMR spectrum of compound 3p
$^1$H NMR spectrum of compound 3q
$^{13}$C NMR spectrum of compound 3q
$^1$H NMR spectrum of compound 7a (major)
$^{13}$C NMR spectrum of compound 7a (major)
$^1$H NMR spectrum of compound 8a (minor)
$^{13}$C NMR spectrum of compound 8a (minor)
\(^1\)H NMR spectrum of compound 7c (major)
$^{13}$C NMR spectrum of compound 7c (major)
$^1$H NMR spectrum of compound 8c (minor)
$^{13}$C NMR spectrum of compound 8c (minor)
4. X-ray Crystallography

X-ray data for the compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (\(\lambda=0.71073\text{Å}\)) with \(\omega\)-scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data was accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS [2] and refinement was carried out by full-matrix least-squares technique using SHELXL [2]. Anisotropic displacement parameters were included for all non-hydrogen atoms. O-bound and C-bound H atoms were located in a difference density map but were positioned geometrically and included as riding atoms, with O-H distance = 0.82 Å and C—H distance = 0.93 -0.97 Å and with \(U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C \text{ and } O)\) and \(1.2U_{\text{eq}}(C)\) for the other H atoms.

The methyl groups were allowed to rotate but not to tip. Owing to the poor quality and diffraction ability of the crystal, the data set contains a large number of weak high-angle reflections, which accounts for the high K values in the analysis of variance. Hence, the SHEL command was used to cut off the weak high-angle reflections.

**Crystal Data for 8c:** \(\text{C}_{17}\text{H}_{17}\text{N}_{2}\text{OCl} (M=300.79)\): triclinic, space group P-1 (no. 2), \(a = 5.479(3)\ \text{Å}, b = 7.926(4)\ \text{Å}, c = 18.296(9)\ \text{Å}, \alpha = 78.658(8)^\circ, \beta = 86.196(8)^\circ, \gamma = 79.757(8)^\circ, V = 766.2(6)\ \text{Å}^3, Z = 2, T = 294.15 \text{ K}, \mu(\text{MoKα}) = 0.250\ \text{mm}^{-1}, D_{\text{calc}} = 1.3036\ \text{g/mm}^3, 8327\ \text{reflections measured (}4.54 \leq 2\Theta \leq 56.66\text{), 3488 unique (}R_{\text{int}} = 0.0934\text{) which were used in all calculations. The final } R_1 \text{ was 0.1306 (I>2}\sigma(I)\text{) and } wR_2 \text{ was 0.2288 (all data). CCDC 1440304 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk.}