Supporting Information for

Cationic Iridium Complex-Catalyzed Intermolecular Hydroalkylation of Unactivated Alkenes with 1,3-Diketones

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1. General Methods and Materials

$^1$H and $^{13}$CNMR spectra were measured on JEOL ECX 500II spectrometers using TMS as an internal standard. Samples were dissolved in CDCl$_3$. GC analyses were performed on a Shimadzu GC-14B or a Shimadzu GC-2014 using 3.2 mm x 2 m glass columns packed with 5\% OV-17 on 60/80 mesh Chromosorb WAW-DMCS. The products were purified by column chromatography on 63-210 mesh silica gel (Kanto Kagaku; Silica Gel 60N). High-resolution mass spectra were obtained with a JEOL Mstation JMS-700. IR spectra were measured on a JASCO FTIR-4100A spectrometer. All solvents were dried and distilled before use by the usual procedures. $[\text{Ir}($cod$)_2]\text{SbF}_6$ was prepared as described in the literature. Alkenes 1a-g, i-j, n were purchased. Alkene 1k was prepared according to the literature. Alkene 1l was prepared according to the literature. Alkene 1m was prepared according to the literature. Diketones 2a-h were purchased. Diketones 2i-k were prepared according to the literature. 6-Bromo-1-hexene was purchased.

2. Preparation of Alkene 1h

A flask was charged with NaH (744.2 mg, 31.00 mmol), and then evacuated and filled with argon. To the flask was added THF (20 mL). The mixture was stirred under argon for 2 h. To the flask were added $n$-hexanol (1566.5 mg, 15.33 mmol) dropwise. 6-Bromo-1-hexene (4833.0 mg, 29.64 mmol) was then added to the mixture dropwise. The mixture was stirred under reflux for 48 h. After the reaction was complete, a saturated aqueous solution of NH$_4$Cl (7.5 mL) was added. The aqueous layer was extracted two times with ether (10 mL). The combined organic layer was dried with MgSO$_4$. The solvent was evaporated in vacuo. Column chromatography of the residue gave 4a ($n$-hexane/AcOEt = 98/2, 1628.9mg, 8.84 mmol, 58\% yield).

6-(Hexyloxy)-1-hexene (1h) Pale yellow oil, Yield 58\%, 1628.9 mg, $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 0.89 (t, $J$ = 6.9 Hz, 3H), 1.25-1.37 (m, 6H), 1.42-1.48 (m, 2H), 1.53-1.64 (m, 4H), 2.07 (q, $J$ = 7.3 Hz, 2H), 3.37-3.42 (m, 4H), 4.93-4.95 (m, 1H), 4.98-5.02 (m, 1H), 5.77-5.85 (m, 1H); $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 14.0, 22.6, 25.5, 25.9, 29.2, 29.7, 31.7, 33.6, 70.7, 71.0, 76.8, 77.0, 77.3, 114.4, 138.8; IR (neat, cm$^{-1}$) 3075, 2932, 2857, 1458, 1375, 1115; HRMS (EI$^+$) m/z [M$^+$] calcd for C$_{12}$H$_{24}$O 184.1827; found 184.1825.

3. General Procedure for the Reaction of Alkene 1 with 1,3-Dione 3.
Representative Procedure for the Reaction of Alkene (1) with 1,3-Diketone (2).
A flask was charged with [Ir(cod)$_2$]SbF$_6$ (32.7 mg, 0.05 mmol). The flask was evacuated and filled with argon. To the flask were added 1,2-dichloroethane (2 mL) and acetylacetone (2a) (102.3 mg, 1.02 mmol). 1-Octene (1a) (333.9 mg, 2.98 mmol) was added to the reaction mixture. The mixture was stirred at reflux temperature for 3 h. The progress of the reaction was monitored by GLC. After the reaction was complete, the solvent was evaporated in vacuo. Column chromatography of the residue gave 3aa ($n$-hexane/AcOEt = 9/1, 191.1 mg, 0.90 mmol, 88% yield).


Synthesis of Isoxazole 4aa from 3aa.

\[
\begin{align*}
\text{3aa} & \quad \xrightarrow{\text{H$_2$NOH.HCl}} \quad \text{EtOH, reflux, 21 h} \quad \text{4aa} & \quad \text{Yield 84%}
\end{align*}
\]
A flask was charged with H$_2$NOH.HCl (107.5 mg, 1.55 mmol). The flask was evacuated and filled with argon. To the flask were added EtOH (5 mL) and 3aa (183.7 mg, 0.87 mmol). The mixture was stirred at reflux temperature for 21 h. After the reaction was complete, the solvent was evaporated in vacuo. Column chromatography of the residue gave 4aa ($n$-hexane/AcOEt = 9/1, 151.8 mg, 0.73 mmol, 84% yield).

Synthesis of Pyrazole 5aa from 3aa

\[
\begin{align*}
\text{3aa} & \quad \xrightarrow{\text{PhNHNH$_2$}} \quad \text{EtOH, reflux, 74 h} \quad \text{5aa} & \quad \text{Yield 75%}
\end{align*}
\]
A flask was charged with PhNHNH$_2$ (218.5 mg, 2.02 mmol). The flask was evacuated and filled with argon. To the flask were added EtOH (5 mL) and 3aa (215.5 mg, 1.02 mmol). Conc. HCl (8 drops) was added to the reaction mixture. The mixture was stirred at reflux temperature for 74 h. After the reaction was complete, the solvent was evaporated in vacuo. Column chromatography of the residue gave 5aa ($n$-hexane/AcOEt = 8/2, 217.7 mg, 0.77 mmol, 75% yield).

A flask was charged with [Ir(cod)\(_2\)]SbF\(_6\) (193.6 mg, 0.30 mmol). The flask was evacuated and filled with argon. To the flask were added 1,2-dichloroethane (12 mL) and acetylacetone (2a) (627.7 mg, 6.27 mmol). 1-Octene (1a) (2.0813 g, 18.55 mmol) was added to the reaction mixture. The mixture was stirred at reflux temperature for 6 h. After the reaction was complete, the solvent was evaporated in vacuo. Column chromatography of the residue gave 3aa (n-hexane/AcOEt = 9/1, 1.2271 g, 5.78 mmol, 92% yield).

6. Characterization of 3, 4 and 5.

**3-(n-Octan-2-yl)pentane-2,4-dione (3aa)**

Yellow oil, Yield 88%, 191.1 mg, \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.87 (d, \(J = 7.0\) Hz, 3H), 0.88 (t, \(J = 6.5\) Hz, 3H), 1.04–1.10 (m, 1H), 1.19–1.36 (m, 9H), 2.17 (s, 6H), 2.32–2.39 (m, 1H), 3.52 (d, \(J = 10.5\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 14.0, 16.9, 22.5, 26.4, 29.2, 29.6, 29.7, 31.7, 33.8, 34.3, 76.5, 204.5, 204.6; IR (Zn/Se-ATR, neat) 2958, 2928, 2857, 1697, 1466, 1421, 1357, 1267, 1196, 1156 cm\(^{-1}\); HRMS (FAB) \(m/z\) [M+H]\(^+\) calcd for C\(_{13}\)H\(_{25}\)O\(_2\) 213.1855; found 213.1853.

**3-(n-Hexan-2-yl)pentane-2,4-dione (3ba)**

Yellow oil, Yield 86%, 171.8 mg, \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.880 (d, \(J = 6.5\) Hz, 3H), 0.883 (t, \(J = 7.0\) Hz, 3H), 1.05–1.11 (m, 1H), 1.18–1.37 (m, 5H), 2.17 (s, 6H), 2.32–2.41 (m, 1H), 3.53 (d, \(J = 10\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 13.9, 16.8, 22.6, 28.6, 29.5, 29.6, 33.7, 34.0, 76.4, 204.4, 204.5; IR (Zn/Se-ATR, neat) 2959, 2931, 2861, 1697, 1467, 1421, 1383, 1357, 1276, 1191, 1158 cm\(^{-1}\); HRMS (FAB) \(m/z\) [M+H]\(^+\) calcd for C\(_{11}\)H\(_{21}\)O\(_2\) 185.1542; found 185.1536.
3-\((n\text{-Decan-2-yl})pentane\)-2,4-dione (3ca)

Yellow oil, Yield 83\%, 202.1 mg. \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.87 (d, \(J = 7.0\) Hz, 3H), 0.89 (t, \(J = 6.5\) Hz, 3H), 1.04-1.10 (m, 1H), 1.19-1.36 (m, 13H), 2.17 (s, 6H), 2.34-2.39 (m, 1H), 3.52 (d, \(J = 10.5\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 14.0, 15.2, 16.9, 22.6, 26.4, 29.2, 29.4, 29.5, 29.6, 31.8, 33.8, 34.3, 76.5, 204.5, 204.6; IR (Zn/Se-ATR, neat) 2957, 2925, 2855, 1697, 1466, 1420, 1380, 1357, 1271, 1193, 1155 cm\(^{-1}\); HRMS (FAB) \(m/z\) [M+H\(^+\)] calecd for C\(_{15}\)H\(_{29}\)O\(_2\) 241.2168; found 241.2167.

3-(1-Cyclohexylethyl)pentane-2,4-dione (3da)

Yellow oil, Yield 25\%, 53.6 mg. \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.78 (d, \(J = 6.9\) Hz, 3H), 0.94-0.99 (m, 1H), 1.04-1.24 (m, 5H), 1.48-1.55 (m, 2H), 1.64-1.66 (m, 1H), 1.73-1.75 (m, 2H), 2.166 (s, 3H), 2.170 (s, 3H), 2.29-2.37 (m, 1H), 3.75 (d, \(J = 11.5\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 12.4, 26.4, 26.5, 26.7, 29.4, 29.8, 31.8, 39.0, 39.9, 77.2, 77.4, 204.8, 204.9; IR (Zn/Se-ATR, neat) 2925, 2853, 1696, 1449, 1421, 1357, 1267, 1199, 1155 cm\(^{-1}\); HRMS (EI) \(m/z\) [M\(^+\)] calecd for C\(_{13}\)H\(_{22}\)O\(_2\) 210.1620; found 210.1623.

3-(1-Cyclohexylpropan-2-yl)pentane-2,4-dione (3ea)

Yellow oil, Yield 68\%, 160.9 mg. \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.72-0.94 (m, 4H), 0.98–1.01 (m, 2H), 1.11-1.34 (m, 5H), 1.55–1.58 (m, 1H), 1.63–1.72 (m, 3H), 1.81–1.84 (m, 1H), 2.16 (s, 3H), 2.17 (s, 3H), 2.42–2.51 (m, 1H), 3.47 (d, \(J = 10.0\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 16.9, 25.9, 26.2, 26.3, 29.3, 29.8, 30.9, 31.7, 34.3, 34.5, 42.1, 76.6,
204.4, 204.5; IR (Zn/Se-ATR, neat) 2922, 2849, 1696, 1448, 1357, 1194, 1150 cm\(^{-1}\); HRMS (FAB) \(m/z\) [M+H]\(^+\) calcd for C\(_{14}\)H\(_{25}\)O\(_2\) 225.1855; found 225.1853.

3-(6-Bromohexan-2-yl)pentane-2,4-dione (3fa)

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

Dark orange oil, Yield 54%, 139.7 mg, \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.89 (d, \(J = 6.5\) Hz, 3H), 1.07-1.15 (m, 1H), 1.25-1.32 (m, 1H), 1.35-1.44 (m, 1H), 1.50-1.57 (m, 1H), 1.76-1.89 (m, 2H), 2.17 (s, 3H), 2.18 (s, 3H), 2.35-2.41 (m, 1H), 3.37-3.44 (m, 2H), 3.54 (d, \(J = 10.0\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 16.8, 25.0, 29.6, 29.8, 32.4, 33.3, 33.4, 33.6, 76.2, 204.2, 204.4; IR (Zn/Se-ATR, neat) 2965, 2938, 2868, 1696, 1462, 1421, 1357, 1250, 1196, 1151 cm\(^{-1}\); HRMS (EI) \(m/z\) [M]\(^+\) calcd for C\(_{11}\)H\(_{19}\)BrO\(_2\) 262.0568; found 262.0562.

3-(6-Chlorohexan-2-yl)pentane-2,4-dione (3ga)

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

Dark yellow oil, Yield 70%, 158.2 mg, \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.89 (d, \(J = 7.0\) Hz, 3H), 1.07–1.15 (m, 1H), 1.26–1.32 (m, 1H), 1.35-1.43 (m, 1H), 1.50-1.58 (m, 1H), 1.68–1.81 (m, 2H), 2.168 (s, 3H), 2.174 (s, 3H), 2.35-2.41 (m, 1H), 3.51-3.55 (m, 3H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 16.8, 23.7, 29.6, 29.8, 32.3, 33.5, 44.7, 76.2, 204.2, 204.4; IR (Zn/Se-ATR, neat) 2965, 2938, 2868, 1696, 1421, 1358, 1266, 1195, 1151 cm\(^{-1}\); HRMS (FAB) \(m/z\) [M+H]\(^+\) calcd for C\(_{11}\)H\(_{20}\)ClO\(_2\) 219.1152; found 219.1148.

3-(6-(\(\alpha\)-Hexyloxy)hexan-2-yl)pentane-2,4-dione (3ha)

\[
\begin{align*}
\end{align*}
\]

Yellow oil, Yield 58%, 169.5 mg, \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.87-0.90 (m, 6H), 1.08-1.12 (m, 1H), 1.24-1.36 (m, 8H), 1.43-1.60 (m, 5H), 2.16 (s, 6H), 2.32–2.39 (m, 1H), 3.37-3.39 (m, 4H), 3.52 (d, \(J = 10.0\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 14.0, 16.8,
22.6, 23.2, 25.8, 29.6, 29.65, 29.66, 31.7, 33.7, 34.1, 70.5, 71.0, 76.4, 204.4, 204.5; IR (Zn/Se-ATR, neat) 2932, 2859, 1697, 1464, 1420, 1358, 1245, 1157, 1112 cm\(^{-1}\); HRMS (FAB) \(m/z\) [M+H]\(^+\) calcd for C\(_{17}\)H\(_{33}\)O\(_3\) 285.2430; found 285.2416.

6-Acetyl-5-methyl-7-oxooctyl acetate (3ia)

Yellow oil, Yield 76%, 187.0 mg, \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta 0.88\) (d, \(J = 6.5\) Hz, 3H), 1.09-1.13 (m, 1H), 1.26-1.33 (m, 1H), 1.42-1.47 (m, 1H), 1.53-1.65 (m, 2H), 2.05 (s, 3H), 2.169 (s, 3H), 2.173 (s, 3H), 2.33-2.42 (m, 1H), 3.53 (d, \(J = 10.0\) Hz, 1H), 4.05 (t, \(J = 6.5\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta 16.7, 20.9, 22.9, 28.5, 29.6, 29.7, 33.5, 33.9, 64.1, 76.3, 171.0, 204.2, 204.3; IR (Zn/Se-ATR, neat) 2941, 2871, 1735, 1696, 1423, 1360, 1239, 1199, 1157, 1037 cm\(^{-1}\); HRMS (FAB) \(m/z\) [M-H]\(^+\) calcd for C\(_{13}\)H\(_{21}\)O\(_4\) 241.1440; found 241.1448.

Ethyl 11-acetyl-10-methyl-12-oxotridecanoate (3ja)

Yellow oil, Yield 73%, 252.0 mg, \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta 0.87\) (d, \(J = 7.0\) Hz, 3H), 1.03-1.09 (m, 1H), 1.18-1.35 (m, 14H), 1.58-1.64 (m, 2H), 2.17 (s, 6H), 2.28 (t, \(J = 7.5\) Hz, 2H), 2.33-2.38 (m, 1H), 3.52 (d, \(J = 10.0\) Hz, 1H), 4.13 (q, \(J = 7.0\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta 14.2, 16.9, 24.9, 26.4, 29.0, 29.1, 29.3, 29.5, 29.6, 29.7, 33.8, 34.30, 34.32, 60.1, 76.5, 173.8, 204.5, 204.6; IR (Zn/Se-ATR, neat) 2976, 2928, 2855, 1733, 1697, 1465, 1421, 1357, 1249, 1181, 1158, 1112, 1033 cm\(^{-1}\); HRMS (El) \(m/z\) [M]\(^+\) calcd for C\(_{18}\)H\(_{32}\)O\(_4\) 312.2301; found 312.2307.

11-Acetyl-10-methyl-12-oxotridecyl 4-methylbenzenesulfonate (3ka)

Dark orange oil, Yield 75%, 349.6 mg, \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta 0.87\) (d, \(J = 6.5\) Hz, 3H), 1.00-1.09 (m, 1H), 1.21-1.34 (m, 13H), 1.60-1.66 (m, 2H), 2.16 (s, 6H), 2.31-2.39
(m, 1H), 2.45 (s, 3H), 3.52 (d, J = 10.5 Hz, 1H), 4.02 (t, J = 6.5 Hz, 2H), 7.43-7.36 (m, 2H), 7.78-7.80 (m, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 16.9, 21.6, 25.2, 26.4, 28.7, 28.8, 29.2, 29.3, 29.5, 29.67, 29.71, 33.8, 34.3, 70.6, 76.5, 127.8, 129.7, 133.2, 144.6, 204.5, 204.6; IR (Zn/Se-ATR, neat) 2927, 2855, 1696, 1598, 1465, 1421, 1357, 1188, 1175, 1097 cm$^{-1}$; HRMS (EI) $m/z$ [M]$^+$ calcd for C$_{23}$H$_{36}$O$_5$S 424.2283; found 424.2275.

2-(11-Acetyl-10-methyl-12-oxotridecyl)isoindoline-1,3-dione (3la)

![Structure of 2-(11-Acetyl-10-methyl-12-oxotridecyl)isoindoline-1,3-dione (3la)](image)

White solid, mp 53.3–55.1 ºC, Yield 73%, 305.8 mg, $^1$H NMR (CDCl$_3$, 500 MHz) δ 0.86 (d, J = 6.5 Hz, 3H), 1.05-1.07 (m, 1H), 1.20-1.32 (m, 13H), 1.64–1.71 (m, 2H), 2.16 (s, 6H), 2.33–2.37 (m, 1H), 3.51 (d, J = 10.5 Hz, 1H), 3.67 (t, J = 7.5 Hz, 2H), 7.70-7.73 (m, 2H), 7.82–7.85 (m, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 16.9, 26.4, 26.8, 28.5, 29.1, 29.3, 29.5, 29.65, 29.69, 33.8, 34.3, 38.0, 76.6, 123.1, 132.1, 133.8, 168.4, 204.58, 204.62; IR (Zn/Se-ATR, neat) 2965, 2925, 2852, 1698, 1467, 1434, 1399, 1359, 1335, 1276, 1190, 1142, 1053 cm$^{-1}$; HRMS (EI) $m/z$ [M]$^+$ calcd for C$_{24}$H$_{33}$NO$_4$ 399.2410; found 399.2410.

11-Acetyl-10-methyl-12-oxotridecyl thiophene-2-carboxylate (3ma)

![Structure of 11-Acetyl-10-methyl-12-oxotridecyl thiophene-2-carboxylate (3ma)](image)

Yellow oil, Yield 70%, 278.9 mg, $^1$H NMR (CDCl$_3$, 500 MHz) δ 0.87 (d, J = 6.0 Hz, 3H), 1.02-1.10 (m, 1H), 1.18-1.44 (m, 13H), 1.71-1.77 (m, 2H), 2.16 (s, 6H), 2.31-2.39 (m, 1H), 3.52 (d, J = 10.0 Hz, 1H), 4.29 (q, J = 8.0 Hz, 2H), 7.09–7.11 (m, 1H), 7.54-7.56 (m, 1H), 7.79-7.80 (m, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 16.9, 25.8, 26.4, 28.6, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 33.8, 34.3, 65.2, 76.5, 127.6, 132.1, 133.2, 134.0, 162.3, 204.5, 204.6; IR (Zn/Se-ATR, neat) 2927, 2854, 1697, 1525, 1466, 1419, 1357, 1258, 1225, 1153, 1095 cm$^{-1}$; HRMS (EI) $m/z$ [M]$^+$ calcd for C$_{21}$H$_{32}$O$_4$S 380.2021; found 380.2023.

4-(n-Octan-2-yl)heptane-3,5-dione (3ab)

![Structure of 4-(n-Octan-2-yl)heptane-3,5-dione (3ab)](image)
Yellow oil, Yield 82%, 207.1 mg, $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 0.83 (d, $J = 6.5$ Hz, 3H), 0.87 (t, $J = 7.0$ Hz, 3H), 1.00-1.07 (m, 7H), 1.17-1.34 (m, 9H), 2.36-2.55 (m, 5H), 3.53 (d, $J = 10.0$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 7.40, 7.43, 14.0, 17.0, 22.5, 26.5, 29.2, 34.0, 35.6, 35.8, 75.2, 207.08, 207.12; IR (Zn/Se-ATR, neat) 2958, 2928, 2874, 2857, 1697, 1460, 1379, 1345, 1276, 1156, 1101, 1022 cm$^{-1}$; HRMS (FAB) $m/z$ [M+H]$^+$ calcd for C$_{15}$H$_{29}$O$_2$ 241.2168; found 241.2167.

2,6-Dimethyl-4-(octan-2-y1)heptane-3,5-dione (3ac)

Yellow oil, Yield 48%, 126.3 mg, $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 0.84 (d, $J = 7.0$ Hz, 3H), 0.87 (t, $J = 7.0$ Hz, 3H), 1.01-1.08 (m, 13H), 1.19 (s, 9H), 1.20-1.32 (m, 10H), 2.36-2.43 (m, 1H), 2.75-2.84 (m, 2H), 3.76 (d, $J = 10.5$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 14.0, 17.2, 18.1, 18.2, 18.6, 22.5, 26.6, 29.2, 31.7, 34.0, 34.7, 39.9, 40.1, 72.9, 210.4, 210.6; IR (Zn/Se-ATR, neat) 2966, 2930, 2873, 2853, 1727, 1693, 1467, 1383, 1343, 1291, 1024 cm$^{-1}$; HRMS (FAB) $m/z$ [M+H]$^+$ calcd for C$_{17}$H$_{33}$O$_2$ 269.2481; found 269.2487.

2,2,6,6-Tetramethyl-4-(octan-2-y1)heptane-3,5-dione (3ad)

Yellow oil, Yield 23%, 69.4 mg, $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 0.87 (t, $J = 7.0$ Hz, 3H), 0.97 (d, $J = 7.0$ Hz, 3H), 1.14 (s, 9H), 1.18 (s, 9H), 1.22-1.38 (m, 10H), 2.15-2.21 (m, 1H), 4.49 (d, $J = 6.0$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125.0 MHz) $\delta$ 14.0, 16.9, 22.6, 27.2, 27.4, 27.7, 29.3, 31.7, 34.4, 35.7, 44.98, 45.0, 61.3, 210.8, 211.0; IR (Zn/Se-ATR, neat) 2957, 2926, 2870, 1718, 1679, 1479, 1394, 1365, 1291, 1227, 1194, 1126, 1054, 1003 cm$^{-1}$; HRMS (FAB) $m/z$ [M+H]$^+$ calcd for C$_{19}$H$_{37}$O$_2$ 297.2794; found 297.2792.

3-Methyl-3-(n-octan-2-y1)pentane-2,4-dione (3ae)

Yellow oil, Yield 26%, 56.8 mg, $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 0.78 (d, $J = 7.0$ Hz, 3H), 0.88 (d, $J = 6.5$ Hz, 3H), 0.92-0.99 (m, 1H), 1.03-1.08 (m, 1H), 1.20-1.32 (m, 10H), 1.38-1.43 (m, 1H), 2.07 (s, 3H), 2.08 (s, 3H), 2.56-2.63 (m, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz)
δ 12.5, 14.0, 14.6, 26.7, 27.9, 29.4, 31.8, 32.5, 36.1, 72.5, 207.2, 207.4; IR (Zn/Se-ATR, neat) 2954, 2928, 2861, 1696, 1459, 1421, 1380, 1356, 1197, 1128 cm\(^{-1}\); HRMS (FAB) \(m/z\) [M+H]\(^+\) calcd for C\(_{14}\)H\(_{27}\)O\(_2\) 227.2011; found 227.2016.

2-Acetyl-2-(\(n\)-octan-2-yl)cyclopentanone (3af)

Yellow oil, Yield 89%, 206.2 mg, \(^1\)H NMR (500MHz, CDCl\(_3\), the mixture of two diastereoisomers) δ 0.73 (d, \(J = 6.9\) Hz 3H), 0.82 (d, \(J = 6.4\) Hz 3H) 0.88 (t, \(J = 6.9\) Hz 3H + 3H), 1.00-1.42 (m, 10H + 10H), 1.66-1.74 (m, 2H+2H), 1.89-1.90 (m, 1H + 1H), 2.04-2.13 (m, 1H + 1H), 2.21 (s, 3H+3H), 2.26-2.28 (m, 1H + 1H), 2.42-2.45 (m, 1H+1H), 2.60-2.64 (m, 1H+1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), the mixture of two diastereoisomers) δ 14.0, 14.0, 14.6, 15.2, 19.5, 19.6, 22.6, 24.7, 24.9, 25.0, 25.2, 27.2, 27.9, 29.2, 29.3, 31.7, 31.7, 32.4, 32.8, 32.8, 37.3, 37.7, 39.9, 40.1, 75.3, 75.4, 203.9, 216.4, 216.4; IR (Zn/Se-ATR, neat) 2958, 2928, 2857, 1737, 1701, 1465, 1440, 1406, 1384, 1356, 1199, 1146, 1124 cm\(^{-1}\); HRMS (FAB) \(m/z\) [M+H]\(^+\) calcd for C\(_{15}\)H\(_{27}\)O\(_2\) 239.2011; found 239.2001.

2-(\(n\)-Octan-2-yl)-1,3-diphenylpropane-1,3-dione (3ag)

Yellow oil, Yield 95%, 318.5 mg, \(^1\)H NMR (CDCl\(_3\), 500 MHz) δ 0.84 (t, \(J = 6.5\) Hz, 3H), 0.99 (d, \(J = 6.5\) Hz, 3H), 1.17-1.29 (m, 8H), 1.34–1.46 (m, 2H), 2.74-2.82 (m, 1H), 5.20 (d, \(J = 9.0\) Hz, 1H), 7.42–7.44 (m, 4H), 7.51–7.53 (m, 2H), 7.98-8.01 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) δ 14.0, 17.6, 22.5, 26.9, 29.2, 31.7, 34.9, 35.1, 63.8, 128.6, 128.7, 128.8, 133.3, 195.7, 195.8; IR (Zn/Se-ATR, neat) 3063, 2956, 2926, 2856, 1696, 1663, 1596, 1579, 1447, 1320, 1279, 1197, 1180, 1076 cm\(^{-1}\); HRMS (FAB) \(m/z\) [M]\(^+\) calcd for C\(_{23}\)H\(_{28}\)O\(_2\) 336.2089; found 336.2080.

1,3-Bis(4-methoxyphenyl)-2-(\(n\)-octan-2-yl)propane-1,3-dione (3ah)
Yellow oil, Yield 90\%, 180.2 mg, $^1$H NMR (CDCl$_3$, 500 MHz) δ 0.84 (t, $J = 7.0$ Hz, 3H), 0.96 (d, $J = 7.0$ Hz, 3H), 1.16-1.25 (m, 8H), 1.36-1.42 (m, 2H), 2.75-2.80 (m, 1H), 3.83 (s, 3H), 3.84 (s, 3H), 4.99 (d, $J = 9.0$ Hz, 1H), 6.88–6.91 (m, 2H), 7.99–8.02 (m, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 14.0, 17.6, 22.5, 26.9, 29.2, 31.7, 34.6, 35.2, 55.4, 64.4, 113.8, 130.2, 131.05, 131.13, 163.6, 194.3, 194.4; IR (Zn/Se ATR, neat) 2957, 2928, 2855, 1685, 1654, 1598, 1574, 1510, 1461, 1419, 1313, 1257, 1166, 1116, 1028 cm$^{-1}$; HRMS (FAB) m/z [M+H]$^+$ calcd for C$_{25}$H$_{33}$O$_4$ 397.2379; found 397.2375.

1,3-Bis(4-chlorophenyl)-2-(n-octan-2-yl)propane-1,3-dione (3ai)

Dark orange oil, Yield 76\%, 153.3 mg, $^1$H NMR (CDCl$_3$, 500 MHz) δ 0.85 (t, $J = 6.5$ Hz, 3H), 0.96 (d, $J = 7.0$ Hz, 3H), 1.17–1.25 (m, 8H), 1.35-1.39 (m, 2H), 2.72–2.80 (m, 1H), 4.99 (d, $J = 9.5$ Hz, 1H), 7.40–7.42 (m, 4H), 7.92-7.94 (m, 4H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 14.0, 17.6, 22.5, 26.8, 29.2, 31.7, 34.8, 35.1, 64.8, 129.2, 130.06, 130.11, 135.18, 135.23, 140.10, 140.12, 194.4, 194.5; IR (Zn/Se ATR, neat) 2956, 2927, 2856, 1695, 1663, 1587, 1571, 1487, 1466, 1399, 1281, 1197, 1176, 1092, 1011 cm$^{-1}$; HRMS (FAB) m/z [M+H]$^+$ calcd for C$_{23}$H$_{27}$Cl$_2$O$_2$ 405.1388; found 405.1400.

1,3-Bis(4-(trifluoromethyl)phenyl)-2-(n-octan-2-yl)propane-1,3-dione (3aj)

Yellow oil, Yield 22\%, 105.6 mg, $^1$H NMR (CDCl$_3$, 500 MHz) δ 0.85 (d, $J = 7.0$ Hz, 3H), 0.99 (d, $J = 7.0$ Hz, 3H), 1.19-1.25 (m, 8H), 1.38–1.41 (m, 2H), 2.76-2.81 (m, 1H), 5.11 (d, $J = 8.5$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 14.0, 17.6, 22.5, 26.9, 29.1, 31.7,
34.9, 35.1, 64.9, 123.4 \( (J = 270.6 \text{ Hz}) \), 126.0 \( (J = 3.6 \text{ Hz}) \), 129.0 \( (J = 5.9 \text{ Hz}) \), 134.8 \( (J = 32.3 \text{ Hz}) \), 139.5 194.7; IR (Zn/Se-ATR, neat) 2961, 2930, 2858, 1703, 1670, 1581, 1510, 1467, 1410, 1323, 1283, 1170, 1130, 1114, 1066, 1014 \( \text{cm}^{-1} \); HRMS (FAB) \( m/z \) [M+H]\(^{+}\) calcd for C\(_{25}\)H\(_{27}\)F\(_{6}\)O\(_{4}\) 473.1915; found 473.1894.

1,3-Bis(thiophen-2-yl)-2-(n-octan-2-yl)-propane-1,3-dione (3ak)

![1,3-Bis(thiophen-2-yl)-2-(n-octan-2-yl)-propane-1,3-dione (3ak)](image)

Yellow solid, mp 58.0–59.0 °C, Yield 86%, 298.9 mg, \(^1\)H NMR (CDCl\(_3\), 500 MHz) \( \delta \) 0.85 (t, \( J = 6.5 \text{ Hz} \), 3H), 0.98 (d, \( J = 6.5 \text{ Hz} \), 3H), 1.16-1.28 (m, 8H), 1.36–1.47 (m, 2H), 2.76-2.85 (m, 1H), 4.65 (d, \( J = 10.5 \text{ Hz} \), 1H), 7.10–7.13 (m, 2H), 7.64–7.66 (m, 2H), 7.90-7.93 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \( \delta \) 14.0, 17.5, 22.5, 26.6, 29.2, 31.7, 34.86, 34.93, 68.4, 128.4, 128.5, 133.3, 133.4, 144.16, 144.19, 187.8, 187.9; IR (Zn/Se-ATR, neat) 3105, 3090, 2958, 2925, 2855, 1666, 1518, 1463, 1412, 1355, 1298, 1263, 1238, 1193, 1064 \( \text{cm}^{-1} \); HRMS (FAB) \( m/z \) [M+H]\(^{+}\) calcd for C\(_{19}\)H\(_{25}\)O\(_{2}\)S\(_{2}\) 349.1296; found 349.1283.

3,5-Dimethyl-4-(n-octan-2-yl)isoazole (4aa)

![3,5-Dimethyl-4-(n-octan-2-yl)isoazole (4aa)](image)

Yellow oil, Yield 84%, 151.8 mg \(^1\)H NMR (CDCl\(_3\), 500 MHz) \( \delta \) 0.87 (t, \( J = 7.4 \text{ Hz} \), 3H), 1.16-1.30 (m, 8H), 1.19 (d, \( J = 7.4 \text{ Hz} \), 3H), 1.53 (q, \( J = 7.4 \text{ Hz} \), 2H), 2.23 (s, 3H), 2.31 (s, 3H), 2.55 (sext, \( J = 7.4 \text{ Hz} \), 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \( \delta \) 11.1, 11.4, 14.0, 20.3, 22.6, 27.8, 28.8, 29.2, 31.7, 36.1, 117.5, 159.2, 164.0; IR (neat) 2960, 2929, 2856, 1630, 1423, 1377, 1258 \( \text{cm}^{-1} \); HRMS (EI\(^{+}\)) \( m/z \) [M]\(^{+}\) calcd for C\(_{13}\)H\(_{23}\)NO 209.1780; found 209.1774.

3,5-Dimethyl-4-(n-octan-2-yl)-1-phenyl-1H-pyrazole (5aa)

![3,5-Dimethyl-4-(n-octan-2-yl)-1-phenyl-1H-pyrazole (5aa)](image)
Yellow oil, Yield 75%, 217.7 mg $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 0.87 (t, $J = 6.8$ Hz, 3H), 1.18-1.34 (m, 11H), 1.56-1.67 (m, 2H), 2.21 (s, 3H), 2.30 (s, 3H), 2.67 (sext, $J = 5.2$ Hz, 1H), 7.25-7.28 (m, 1H), 7.36-7.41 (m, 4H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 11.0, 13.1, 13.8, 20.5, 22.4, 27.9, 29.1, 29.9, 31.6, 36.3, 121.8, 124.7, 126.7, 128.6, 135.1, 139.9, 146.8; IR (neat) 3065, 2964, 2928, 1598, 1565, 1504, 1455, 1379, 1141, 1021 cm$^{-1}$; HRMS (EI$^+$) m/z [M]$^+$ calcd for C$_{19}$H$_{28}$N$_2$ 284.2252; found 284.2252.

7. References
8. $^1$H and $^{13}$C NMR Charts
Cl

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### Chart 1

- X: parts per Million - 1H
- Y: (Millions)
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### Chart 2

- X: parts per Million - 13C
- Y: (Billions)
- Data points:
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![Chemical structure of compound 5aa](image)