Supporting Information

Palladium-Catalyzed Cross-Coupling of Enamides with Sterically Hindered α-Bromocarbonyls

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1. General information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. $^1$H-NMR and $^{13}$C-NMR spectra were recorded at 25 ºC on Bruker Advance 400M NMR spectrometers (CDCl$_3$ as solvent). Chemical shifts for $^1$H NMR spectra are reported as $\delta$ in units of parts per million (ppm) downfield from SiMe$_4$ ($\delta$ 0.0) and relative to the signal of SiMe$_4$ ($\delta$ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and etc. Coupling constants are reported as a J value in Hz. $^{13}$C NMR spectra are reported as $\delta$ in units of parts per million (ppm) downfield from SiMe$_4$ ($\delta$ 0.0) and relative to the signal of chloroform-d ($\delta$ 77.00 triplet). High resolution mass spectral analysis (HRMS) was performed on WaterXEVOG2 Q-TOF (Waters Corporation). IR spectra were recorded on a commercial FT/IR spectrometer. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

2. Procedure for the synthesis of compound 3a – 3t, 4a – 4g.

A dry 25-mL Schlenk tube containing a magnetic stirring bar was charged with 1 (0.3 mmol), 2 (2.0 equiv), Pd(PPh$_3$)$_4$ (5 mol%, 17.3 mg, 0.015 mmol), (4-MeOPh)$_3$P (20 mol%, 21.12 mg, 0.06 mmol), AgOAc (1.5 eq, 75 mg, 0.45 mmol) and DCM (1.0 mL). Then the mixture was charged with argon and heated at 80 ºC oil bath. After finishing, the reaction mixture was concentrated on a rotary evaporator and the residue was directly subjected to flash column chromatography on silica gel with (50% EtOAc/Petroleum ether) as eluate to furnish the desired product.
3. Optimization of reaction conditions:

Table 1.

\[
\begin{align*}
\text{NHC}+ \text{BrOE} & \xrightarrow{[\text{Pd}]/\text{Ag}} \text{NHC}+\text{BrOE} \\
1 & 1 \text{Ph}_{2}P(\text{PPh}_{3})_{2} (2 \text{mol}) \quad \text{AgOAc} (1.5 \text{ eq}) \quad \text{Ph}(4\text{-MeO-Ph})_{2} (10 \text{ mol}) \quad \text{DCM} \quad 80^\circ \text{C}, 24 \text{ h} \quad \text{NP} \\
2 & 2 \text{Ph}_{2}P(\text{PPh}_{3})_{2} (5 \text{ mol}) \quad \text{AgOAc} (1.5 \text{ eq}) \quad \text{Ph}(4\text{-MeO-Ph})_{2} (20 \text{ mol}) \quad \text{DCM} \quad 80^\circ \text{C}, 24 \text{ h} \quad \text{NP} \\
3 & 3 \text{Ph}_{2}P(\text{PPh}_{3})_{2} (5 \text{ mol}) \quad \text{AgOAc} (1.5 \text{ eq}) \quad \text{Ph}(4\text{-MeO-Ph})_{2} (20 \text{ mol}) \quad \text{DCM} \quad 80^\circ \text{C}, 24 \text{ h} \quad \text{NP}
\end{align*}
\]

Table 2.

\[
\begin{align*}
\text{NHC}+ \text{BrOE} & \xrightarrow{[\text{Pd}]/\text{Ag}} \text{NHC}+\text{BrOE} \\
\text{entry} & \text{solvent} & T (^\circ \text{C}) & \text{time (h)} & \text{yield}^a \\
1 & \text{PhCF}_{3} & 80 & 12 & 63\% \\
2 & \text{dioxane} & 80 & 12 & 70\% \\
3 & \text{CH}_{3}CN & 80 & 12 & 64\% \\
4 & \text{DMF} & 80 & 12 & 52\% \\
5 & \text{toluene} & 80 & 12 & 60\%
\end{align*}
\]

*At 60 °C, †At 100 °C, ‡Isolated yield

Table 3.

\[
\begin{align*}
\text{NHC}+ \text{BrOE} & \xrightarrow{[\text{Pd}]/\text{Ag}} \text{NHC}+\text{BrOE} \\
\text{entry} & \text{additive} & \text{yield}^a \\
1 & \text{NaOAc} & \text{NP} \\
2 & \text{CuOAc}_{2} \cdot \text{H}_{2}\text{O} & 71\% \\
3 & \text{CoOAc}_{2} & 34\% \\
4 & \text{CuBr}_{2} & \text{NP}
\end{align*}
\]

\[
\begin{align*}
\text{NHC}+ \text{BrOE} & \xrightarrow{[\text{Pd}]/\text{Ag}} \text{NHC}+\text{BrOE} \\
0.3 \text{ mmol} & 0.6 \text{ mmol} \\
\text{DCM}, 60^\circ \text{C}, 15 \text{ h} & \text{35\% isolated yield}
\end{align*}
\]

eq 1

\[
\begin{align*}
\text{NHC}+ \text{BrOE} & \xrightarrow{[\text{Pd}]/\text{Ag}} \text{NHC}+\text{BrOE} \\
0.3 \text{ mmol} & 0.3 \text{ mmol} \\
\text{DCM}, 80^\circ \text{C}, 15 \text{ h} & \text{55\% isolated yield}
\end{align*}
\]

eq 2

\[
\begin{align*}
\text{NHC}+ \text{BrOE} & \xrightarrow{[\text{Pd}]/\text{Ag}} \text{NHC}+\text{BrOE} \\
0.3 \text{ mmol} & 0.45 \text{ mmol} \\
\text{DCM}, 80^\circ \text{C}, 15 \text{ h} & \text{65\% isolated yield}
\end{align*}
\]

eq 3
4. Mechanistic study of coupling reaction between enamide and α-Bromocarbonyls:

\[
\text{Pd(PPh}_3\text{)}_4 \ 5 \text{mol\%} \\
(4-\text{MeOPh})_3\text{P} \ 20 \text{mol\%} \\
\text{AgOAc} \ 1.5 \text{equiv} \\
\text{tempo} \ (2.0 \text{equiv}) \\
\text{DCM, 80 °C}
\]

\[
\text{NHAc} + \text{BrOEt} \rightarrow \text{NHAc} \text{COEt} \\
1 \text{a} \ 0.3 \text{ mmol} \quad 2 \text{a} \ 0.6 \text{ mmol}
\]

\[
\text{yield} = 50\%
\]

\[
\text{NHAc} + \text{BrOEt} \rightarrow \text{NHAc} \text{COEt} \\
1 \text{a} \ 0.3 \text{ mmol} \quad 2 \text{a} \ 0.6 \text{ mmol}
\]

\[
\text{yield} = 10\%
\]

\[
\text{NHAc} + \text{tempo} \ (2.0 \text{ equiv}) \rightarrow \text{NHAc} \text{COEt} \\
1 \text{a} \ 0.3 \text{ mmol} \quad 2 \text{a} \ 0.6 \text{ mmol}
\]

\[
\text{trace}
\]

\[
\text{Ph} + \text{NHAc} \rightarrow \text{NHAc} \text{COEt} \\
1 \text{a} \ 0.3 \text{ mmol} \quad 2 \text{a} \ 0.6 \text{ mmol}
\]

\[
\text{yield} = 20\%
\]

\[
\text{NHAc} + \text{EtO} \text{COBr} \rightarrow \text{NHAc} \text{COEt} \\
1 \text{a} \ 0.3 \text{ mmol} \quad 2 \text{i} \ 0.6 \text{ mmol}
\]

\[
\text{can not be detected}
\]

\[
\text{NHAc} + \text{EtO} \text{COBr} \rightarrow \text{NHAc} \text{COEt} \\
1 \text{a} \ 0.3 \text{ mmol} \quad 2 \text{j} \ 0.6 \text{ mmol}
\]

\[
\text{yield} = 50\% \text{ (NMR)} \\
\text{20\% isolated yield}
\]

Ethyl 2-methyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate

\[^1\text{H NMR (400 MHz, chloroform-}d\text{)} \delta 4.16 \ (q, \text{ } J = 7.1 \text{ Hz, } 2\text{H}), 1.54 – 1.34 \ (\text{m, } 11\text{H}), 1.28 \ (\text{m, } 4\text{H}), 1.14 \ (\text{s, } 6\text{H}), 0.99 \ (\text{s, } 6\text{H}). \] \[^13\text{C NMR (100 MHz, chloroform-}d\text{)} \delta 176.22, 81.24, 60.72, 59.68, 40.76, 33.59, 24.62, 20.61, 17.22, 14.30.

HRMS (ESI, m/z): calcd for C\text{13}H\text{29}NO\text{3}[\text{M}+\text{H}]^+ 272.2226, found: 272.2218.
Ethyl 2,2-dimethyl-4,4-diphenylbut-3-enoate
$^1$H NMR (400 MHz, chloroform-$d$) δ 7.35 – 7.26 (m, 3H), 7.25 – 7.17 (m, 5H), 7.15 – 7.11 (m, 2H), 6.09 (s, 1H), 3.73 (q, $J = 7.2$ Hz, 2H), 1.29 (s, 6H), 1.13 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, chloroform-$d$) δ 176.49, 143.48, 141.62, 139.43, 134.29, 130.24, 128.17, 127.96, 127.37, 127.35, 127.24, 60.55, 44.18, 27.90, 14.08. HRMS (ESI, m/z): calculated for C$_{20}$H$_{22}$O$_2$Na [M+Na]$^+$ 317.1517, found: 317.1519
Ethyl 2-bromo-2-cyclopropylpropanoate

$^1$H NMR (400 MHz, chloroform-d) $\delta$ 4.25 (q, $J = 7.1$ Hz, 2H), 1.71 (s, 3H), 1.64 (tt, $J = 8.2$, 6.0 Hz, 1H), 1.32 (t, $J = 7.1$ Hz, 3H), 0.76 – 0.53 (m, 4H). $^{13}$C NMR (100 MHz, chloroform-d) $\delta$ 171.17, 63.29, 62.19, 25.13, 21.58, 14.06, 5.57, 4.55.
(E)-ethyl 5-bromo-2-methylpent-2-enoate

$^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 6.76 – 6.65 (m, 1H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.44 (t, $J = 6.9$ Hz, 2H), 2.77 (dddd, $J = 8.1, 7.1, 6.1, 1.0$ Hz, 2H), 1.86 (q, $J = 1.1$ Hz, 3H), 1.30 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, chloroform-$d$) $\delta$ 167.84, 137.68, 130.61, 60.83, 32.09, 30.76, 14.40, 12.84.

5. Unsuccessful substrates in coupling reaction between enamides and \( \alpha \)-bromocarboxyls.

![Chemical structures](image)

6. Procedure for the synthesis of compound 5a – 5j.

![Chemical structures](image)

3a (0.3 mmol, 86.4 mg) dissolved in EtOH (2.0 mL) was added 48% aqueous solution of HBr (1.0 mL). The mixture was stirred at 80 °C for 10 hours. After finishing, then the reaction was quenched by addition of saturated aqueous NaHCO\(_3\) at 0 °C. The reaction mixture was allowed to warm to room temperature and was extracted with CH\(_2\)Cl\(_2\). The organic layer was washed with brine and dried over anhydrous MgSO\(_4\). After filtration, the organic solvent was removed under reduced pressure on a rotary evaporator. Then the crude product was purified by column chromatography on silica gel (with 5% EtOAc/Petroleum ether) to afford the desired compound 5a (61.9 mg, yield = 84%).
3j (0.3 mmol, 82.8 mg) dissolved in EtOH (2.0 mL) was added 48% aqueous solution of HBr (1.0 mL). The mixture was stirred at 50 °C for 10 hours. then the reaction was quenched by addition of saturated aqueous NaHCO₃ at 0 °C. The reaction mixture was allowed to warm to room temperature and was extracted with CH₂Cl₂. The organic layer was washed with brine and dried over anhydrous MgSO₄. After filtration, the organic solvent was removed under reduced pressure on a rotary evaporator. Then the crude product was purified by chromatography on silica gel (with 5% EtOAc/Petroleum ether) to afford the desired compound 5b. Yield (61.3 mg, 87%).

3a (0.1 g) and Pd/C catalyst (10%, 0.01 g) were added to the MeOH (25 mL) solution in a two-neck round-bottom flask under hydrogen atmosphere. The mixture was stirred for 6 hours and was filtered. The filtrate was evaporated under reduced pressure to give a white solid of 5e without further purification. Yield (0.093 g, 93%).

3j (0.2 g) and Pd/C catalyst (10%, 0.02 g) were added to the MeOH (25 mL) solution in a two-neck round-bottom flask under hydrogen atmosphere. The mixture was stirred for 6 hours and was filtered. The filtrate was evaporated under reduced pressure to give a white solid of 5f without further purification. Yield (0.183 g, 91%).
4e (0.2075 g) and Pd/C catalyst (10%, 0.02 g) were added to the MeOH (25 mL) solution in a two-neck round-bottom flask under hydrogen atmosphere. The mixture was stirred for 6 hours and was filtered. The filtrate was evaporated under reduced pressure, then the crude product was purified by chromatography on silica gel (with 0% - 8% MeOH/CHCl$_3$) to give a white solid of 5c. Yield (0.1309 g, 85%).

4f (0.0668 g) and Pd/C catalyst (10%, 0.01 g) were added to the MeOH (25 mL) solution in a two-neck round-bottom flask under hydrogen atmosphere. The mixture was stirred for 6 hours and was filtered. The filtrate was evaporated under reduced pressure, then the crude product was purified by chromatography on silica gel (with 0% - 8% MeOH/CHCl$_3$) to give a white solid of 5d. Yield (0.04 g, 81%).

Aqueous lithium hydroxide (1 M, 2 mL) was added to the solution of 5e (0.0893 g, 0.308 mmol) in THF (2 mL). The mixture was stirred at 60 °C for 10 hours. After finishing, the mixture was diluted with ethyl acetate (10 mL). After separation, the aqueous phase was extracted twice with ethyl acetate (3×10 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The organic solvent was removed under reduced pressure, and the crude product was purified by chromatography on silica gel (with 20% - 60% EtOAc/Petroleum ether) to afford the desired compound 5i. Yield (0.061 g, 92%).

Aqueous lithium hydroxide (1 M, 3 mL) was added to the solution of 5f (0.148 g, 0.53 mmol) in THF (3 mL). The mixture was stirred at 80 °C for 10 hours. After finishing, the mixture was diluted with ethyl acetate (10 mL). After separation, the aqueous
phase was extracted twice with ethyl acetate (3×10 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The organic solvent was removed under reduced pressure, and the crude product was purified by chromatography on silica gel (with 20% - 60% EtOAc/Petroleum ether) to afford the desired compound 5g. Yield (0.0808 g, 81%).

Diisobutylaluminum hydride solution (1.0 M in hexane, 0.9 mL, 0.9 mmol) was added dropwise to the solution of 5e (0.058 g, 0.2 mmol) in dichloromethane (2 mL) at -78 °C. After stirring for 10 minutes at the same temperature, the reaction mixture was warmed to 0 °C and stirred for an additional 30 minutes. The methanol (1 mL) and hydrochloric acid (3 M, 3 mL) were successively added. The reaction mixture was partitioned by dichloromethane, and then the aqueous phase was extracted twice with dichloromethane (3×10 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by flash column chromatography on silica gel to give 5j (0.025 g, 51%)

Diisobutylaluminum hydride solution (1.0 M in hexane, 0.9 mL, 0.9 mmol) was added dropwise to a solution of 5f (0.0576 g, 0.208 mmol) in dichloromethane (2 mL) at -78 °C. After stirring for 10 minutes at the same temperature, the reaction mixture was warmed to 0 °C and stirred for an additional 30 minutes. The methanol (1 mL) and hydrochloric acid (3 M, 3 mL) were successively added. The reaction mixture was partitioned by dichloromethane, and then the aqueous phase was extracted twice with dichloromethane (3×10 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by flash column chromatography on silica gel to give 5h (0.020 g, 43%)

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7. NMR data and spectra of the products:

**Ethyl 2-(3-acetamido-1H-inden-2-yl)-2-methylpropanoate (3a)**

\[
\begin{align*}
\text{NHAc} & \quad \text{OEt} \\
\text{OAc} & \quad \text{OEt}
\end{align*}
\]

$^1$H NMR (400 MHz, DMSO-$d_6$) \( \delta \) 9.00 (s, 1H), 7.44 (d, \( J = 7.2 \) Hz, 1H), 7.24 (dd, \( J = 7.4, 1.3 \) Hz, 1H), 7.21 – 7.14 (m, 1H), 7.09 – 7.03 (m, 1H), 4.07 (q, \( J = 7.1 \) Hz, 2H), 3.54 – 3.44 (m, 2H), 2.04 (s, 3H), 1.46 (s, 6H), 1.19 (t, \( J = 7.1 \) Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) \( \delta \) 176.35, 169.65, 144.10, 144.06, 140.92, 133.55, 126.74, 125.38, 124.33, 119.79, 61.26, 44.12, 37.58, 26.34, 23.44, 14.82.

HRMS (ESI, m/z): calculated for C$_{17}$H$_{21}$NO$_3$ [M+Na]$^+$ 310.1419, found: 310.1416.

**Ethyl 2-(3-acetamido-5-methyl-1H-inden-2-yl)-2-methylpropanoate (3b)**

\[
\begin{align*}
\text{Me} & \quad \text{NHAc} & \quad \text{OEt} \\
\text{OAc} & \quad \text{OEt}
\end{align*}
\]

$^1$H NMR (400 MHz, DMSO-$d_6$) \( \delta \) 8.95 (s, 1H), 7.31 (d, \( J = 7.5 \) Hz, 1H), 7.01 (d, \( J = 7.5 \) Hz, 1H), 6.88 (d, \( J = 3.0 \) Hz, 1H), 4.07 (q, \( J = 7.1 \) Hz, 2H), 3.43 (s, 2H), 2.34 (s, 3H), 2.04 (d, \( J = 2.2 \) Hz, 3H), 1.45 (d, \( J = 2.3 \) Hz, 6H), 1.19 (t, \( J = 7.1 \) Hz, 2H). $^{13}$C NMR (101 MHz, DMSO) \( \delta \) 176.35, 169.62, 144.35, 144.31, 138.02, 135.72, 133.50, 126.16, 124.04, 120.21, 61.22, 44.15, 37.18, 26.31, 23.45, 22.08, 14.81.

HRMS (ESI, m/z): calculated for C$_{18}$H$_{23}$NO$_3$ [M+Na]$^+$ 324.1576, found: 324.1573.

**Ethyl 2-(3-acetamido-6-chloro-1H-inden-2-yl)-2-methylpropanoate (3c)**

\[
\begin{align*}
\text{Cl} & \quad \text{NHAc} & \quad \text{OEt} \\
\text{OAc} & \quad \text{OEt}
\end{align*}
\]

$^1$H NMR (400 MHz, DMSO-$d_6$) \( \delta \) 9.05 (s, 1H), 7.50 (d, \( J = 2.0 \) Hz, 1H), 7.31 (dd, \( J = 8.2, 2.0 \) Hz, 1H), 7.05 (d, \( J = 8.1 \) Hz, 1H), 4.06 (q, \( J = 7.1 \) Hz, 2H), 3.53 (s, 2H), 2.04 (s, 3H), 1.45 (s, 6H), 1.18 (t, \( J = 7.1 \) Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) \( \delta \) 176.16,
169.71, 144.81, 143.06, 142.96, 132.95, 130.14, 126.84, 124.55, 121.19, 61.33, 44.16, 37.57, 26.26, 23.41, 14.80.

HRMS (ESI, m/z): calculated for C_{17}H_{20}NCIO_{3} [M+Na]^+ 344.1029, found: 344.1014.

**Ethyl 2-(3-acetamido-5-fluoro-1H-inden-2-yl)-2-methylpropanoate (3d)**

\[
\text{\begin{center}
\begin{tabular}{c}
\text{F} \\
\text{NHAc} \\
\text{\textbf{O}} \\
\text{\textbf{Et}} \\
\end{tabular}
\end{center}
}\]

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.05 (s, 1H), 7.43 (dd, \(J = 8.2, 5.1\) Hz, 1H), 7.00 (ddd, \(J = 9.9, 8.2, 2.5\) Hz, 1H), 6.83 (dd, \(J = 9.2, 2.5\) Hz, 1H), 4.07 (q, \(J = 7.1\) Hz, 2H), 3.49 (s, 2H), 2.05 (s, 3H), 1.45 (s, 6H), 1.18 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 176.16, 169.78, 162.44 ( \(J = 242\) Hz), 146.74, 146.31 ( \(J = 9\) Hz), 136.62, 133.12, 125.57 ( \(J = 9\) Hz), 111.98 ( \(J = 23\) Hz), 106.79 ( \(J = 24\) Hz), 61.33, 44.24, 37.09, 26.28, 23.43, 14.80.

HRMS (ESI, m/z): calculated for C_{17}H_{20}NFO_{3} [M+Na]^+ 328.1325, found: 328.1318.

**Ethyl 2-(3-acetamido-6-bromo-1H-inden-2-yl)-2-methylpropanoate (3e)**

\[
\text{\begin{center}
\begin{tabular}{c}
\text{Br} \\
\text{NHAc} \\
\text{\textbf{O}} \\
\text{\textbf{Et}} \\
\end{tabular}
\end{center}
]\]

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.05 (s, 1H), 7.63 (d, \(J = 1.8\) Hz, 1H), 7.44 (dd, \(J = 8.1, 1.9\) Hz, 1H), 7.00 (d, \(J = 8.1\) Hz, 1H), 4.06 (q, \(J = 7.1\) Hz, 2H), 3.53 (s, 2H), 2.03 (s, 3H), 1.45 (s, 6H), 1.18 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 176.13, 169.71, 144.83, 143.45, 143.33, 133.02, 129.63, 127.36, 121.64, 118.50, 61.33, 44.14, 37.59, 26.25, 23.40, 14.80.

HRMS (ESI, m/z): calculated for C_{17}H_{20}NBrO_{3} [M+Na]^+ 388.0524, found: 388.0527.
Ethyl 2-(3-acetamido-5-methoxy-1H-inden-2-yl)-2-methylpropanoate (3f)

\[
\text{\begin{center}
\includegraphics[width=0.5\textwidth]{ethyl_2-(3-acetamido-5-methoxy-1H-inden-2-yl)-2-methylpropanoate.png}
\end{center}}
\]

\[^1H\text{ NMR (400 MHz, DMSO-}d_6\text{)} \delta 8.97 (s, 1H), 7.32 (d, } J = 8.1 \text{ Hz, 1H}, 6.77 \text{ (dd, } J = 8.1, 2.4 \text{ Hz, 1H}, 6.61 \text{ (d, } J = 2.4 \text{ Hz, 1H}, 4.07 \text{ (q, } J = 7.1 \text{ Hz, 2H}, 3.76 \text{ (s, 3H}, 3.41 \text{ (d, } J = 1.7 \text{ Hz, 2H}, 2.04 \text{ (d, } J = 2.7 \text{ Hz, 3H), 1.45 \text{ (s, 6H}, 1.19 \text{ (t, } J = 7.1 \text{ Hz, 3H).} \]

\[^{13}C\text{ NMR (101 MHz, DMSO)} \delta 176.31, 169.67, 159.27, 145.61, 145.56, 133.45, 132.95, 124.87, 111.34, 105.46, 61.25, 56.14, 44.21, 36.81, 26.29, 23.46, 14.81.

HRMS (ESI, m/z): calculated for C_{18}H_{23}NO_{4} [M+Na]^+ 340.1525, found: 340.1526.

Ethyl 2-(3-acetamido-7-acetoxy-1H-inden-2-yl)-2-methylpropanoate (3g)

\[
\text{\begin{center}
\includegraphics[width=0.5\textwidth]{ethyl_2-(3-acetamido-7-acetoxy-1H-inden-2-yl)-2-methylpropanoate.png}
\end{center}}
\]

\[^1H\text{ NMR (400 MHz, DMSO-}d_6\text{)} \delta 9.01 (s, 1H), 7.27 \text{ (t, } J = 7.8 \text{ Hz, 1H}, 6.93 \text{ (dd, } J = 12.6, 7.7 \text{ Hz, 2H}, 4.03 \text{ (q, } J = 7.1 \text{ Hz, 2H}, 3.34 \text{ (s, 2H), 2.33 \text{ (s, 3H), 2.01 \text{ (s, 3H), 1.41 \text{ (s, 6H), 1.15 \text{ (t, } J = 7.1 \text{ Hz, 3H).} \]

\[^{13}C\text{ NMR (101 MHz, DMSO)} \delta 176.15, 169.76, 169.60, 146.90, 146.36, 144.53, 133.40, 132.12, 128.47, 119.13, 117.80, 61.32, 44.09, 35.03, 26.28, 23.40, 21.66, 14.78.

HRMS (ESI, m/z): calculated for C_{19}H_{23}NO_{5} [M+Na]^+ 368.1474, found: 368.1472.

Ethyl 2-(4-acetamido-2H-chromen-3-yl)-2-methylpropanoate (3h)

\[
\text{\begin{center}
\includegraphics[width=0.5\textwidth]{ethyl_2-(4-acetamido-2H-chromen-3-yl)-2-methylpropanoate.png}
\end{center}}
\]

\[^1H\text{ NMR (400 MHz, DMSO-}d_6\text{)} \delta 8.70 (s, 1H), 7.16 (td, } J = 7.6, 1.7 \text{ Hz, 1H), 7.02 \text{ (dd, } J = 7.7, 1.7 \text{ Hz, 1H), 6.92 (td, } J = 7.5, 1.2 \text{ Hz, 1H), 6.83 (dd, } J = 8.1, 1.2 \text{ Hz, 1H), 4.85 \text{ (s, 2H), 4.09 \text{ (t, } J = 7.1 \text{ Hz, 2H), 1.97 \text{ (s, 3H), 1.32 \text{ (s, 6H), 1.22 \text{ (t, } J = 7.1 \text{ Hz, 3H).} \]

\[^{13}C\text{ NMR (101 MHz, DMSO)} \delta 176.23, 170.33, 154.48, 133.93, 129.79, 126.21, 124.18, 123.61, 122.07, 116.02, 66.26, 61.73, 45.44, 44.88, 23.33, 14.83.
Ethyl 2-((2-acetamidoacenaphthyl-1-yl)-2-methylpropanoate (3i)

\[
\text{\text{\begin{align*}
\text{H NMR (400 MHz, DMSO-d6) } & \delta 9.47 (s, 1H), 8.00 – 7.79 (m, 2H), 7.57 (t, J = 21.2 Hz, 4H), 4.11 (d, J = 6.3 Hz, 2H), 2.13 (s, 3H), 1.70 (s, 6H), 1.11 (t, J = 7.3 Hz, 3H). \\
\text{\text{\text{\text{13C NMR (101 MHz, DMSO) } & \delta 176.97, 170.35, 138.02, 137.79, 137.26, 134.65, 128.53, 128.46, 128.34, 128.06, 127.82, 126.67, 124.27, 123.35, 61.39, 44.89, 26.74, 23.71, 14.80. \\
\text{HRMS (ESI, m/z): calculated for C}_{20}\text{H}_{21}\text{O}_{3} \text{[M+Na]}^{+} 346.1419, found: 346.1415. }
\end{align*}}}
\]

Ethyl (Z)-4-acetamido-2,2-dimethyl-4-phenylbut-3-enoate (3j)

\[
\text{\text{\text{\text{\text{1H NMR (400 MHz, DMSO-d6) } & \delta 8.84 (s, 1H), 7.45 – 7.26 (m, 5H), 5.98 (d, J = 1.3 Hz, 1H), 4.07 (q, J = 7.1 Hz, 2H), 1.95 (s, 3H), 1.36 (s, 6H), 1.20 (t, J = 7.1 Hz, 3H). \\
\text{\text{\text{\text{13C NMR (101 MHz, DMSO) } & \delta 176.62, 169.73, 139.30, 134.89, 131.90, 129.09, 128.41, 126.14, 61.12, 43.55, 27.10, 23.45, 14.86. \\
\text{HRMS (ESI, m/z): calculated for C}_{16}\text{H}_{21}\text{O}_{3} \text{[M+Na]}^{+} 298.1419, found: 298.1413. }
\end{align*}}}
\]

Ethyl (Z)-4-acetamido-2,2-dimethyl-4-(o-tolyl)but-3-enolate (3k)

\[
\text{\text{\text{\text{\text{1H NMR (400 MHz, DMSO-d6) } & \delta 8.85 (s, 1H), 7.22 – 7.12 (m, 4H), 5.27 (d, J = 1.2 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 1.86 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). \\
\text{\text{\text{\text{13C NMR (101 MHz, DMSO) } & \delta 176.73, 168.93, 140.78, 136.18, 134.98, 132.74, 130.90, 129.59, 127.97, 126.12, 61.15, 43.42, 26.99, 23.43, 20.97, 14.81. }
\end{align*}}}
\]
HRMS (ESI, m/z): calculated for C$_{17}$H$_{23}$NO$_3$ [M+Na]$^+$ 312.1576, found: 312.1578.

**Ethyl (Z)-4-acetamido-2,2-dimethyl-4-(m-tolyl)but-3-enoate (3l)**

![Ethyl (Z)-4-acetamido-2,2-dimethyl-4-(m-tolyl)but-3-enoate (3l)](image)

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.80 (s, 1H), 7.26 – 7.19 (m, 2H), 7.17 (d, $J$ = 7.8 Hz, 1H), 7.11 (d, $J$ = 7.4 Hz, 1H), 5.95 (d, $J$ = 1.3 Hz, 1H), 4.06 (q, $J$ = 7.1 Hz, 2H), 2.34 (s, 3H), 1.94 (s, 3H), 1.35 (s, 6H), 1.20 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 176.62, 169.69, 139.34, 138.08, 134.93, 131.74, 129.08, 128.97, 126.70, 123.38, 61.10, 43.52, 27.13, 23.46, 22.01, 14.86.

HRMS (ESI, m/z): calculated for C$_{17}$H$_{23}$NO$_3$ [M+Na]$^+$ 312.1576, found: 312.1576.

**Ethyl (Z)-4-acetamido-4-(2-methoxyphenyl)-2,2-dimethylbut-3-enoate (3m)**

![Ethyl (Z)-4-acetamido-4-(2-methoxyphenyl)-2,2-dimethylbut-3-enoate (3m)](image)

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.62 (s, 1H), 7.28 – 7.13 (m, 2H), 7.02 – 6.90 (m, 2H), 5.75 (d, $J$ = 1.3 Hz, 1H), 4.07 (q, $J$ = 7.1 Hz, 2H), 3.80 (s, 3H), 1.87 (s, 3H), 1.36 (s, 6H), 1.21 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 176.75, 169.24, 157.47, 133.67, 132.84, 130.33, 129.47, 128.91, 121.11, 112.74, 61.09, 56.59, 43.57, 27.08, 23.48, 14.88.

HRMS (ESI, m/z): calculated for C$_{17}$H$_{23}$NO$_4$ [M+Na]$^+$ 328.1525, found: 328.1520.

**Ethyl (Z)-4-acetamido-4-(4-methoxyphenyl)-2,2-dimethylbut-3-enoate (3n)**

![Ethyl (Z)-4-acetamido-4-(4-methoxyphenyl)-2,2-dimethylbut-3-enoate (3n)](image)

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.76 (s, 1H), 7.32 (d, $J$ = 8.7 Hz, 2H), 6.91 (d, $J$ = 8.8 Hz, 2H), 6.32 (s, 0H), 5.86 (d, $J$ = 1.2 Hz, 1H), 4.06 (q, $J$ = 7.1 Hz, 2H), 3.78 (s, 3H), 1.94 (s, 3H), 1.35 (s, 6H), 1.20 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO)
δ 176.71, 169.66, 159.77, 134.50, 131.74, 129.96, 127.40, 114.45, 61.07, 56.05, 43.47, 
27.19, 23.47, 14.87.

HRMS (ESI, m/z): calculated for C_{17}H_{23}NO_4 [M+Na]^+ 328.1525, found: 328.1523.

**Ethyl (Z)-4-acetamido-4-(4-fluorophenyl)-2,2-dimethylbut-3-enoate (3o)**

![Ethyl (Z)-4-acetamido-4-(4-fluorophenyl)-2,2-dimethylbut-3-enoate](image)

\[\text{H NMR (400 MHz, DMSO-}d_6\text{) } \delta 8.86 (s, 1H), 7.42 (dd, J = 8.8, 5.6 Hz, 2H), 7.18 (t, J = 8.8 Hz, 2H), 5.94 (d, J = 1.3 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 1.95 (s, 3H), 1.35 (s, 6H), 1.20 (t, J = 7.1 Hz, 3H). \]

\[\text{C NMR (101 MHz, DMSO) } \delta 176.56, 169.74, 162.58 (J = 242 Hz), 135.83, 135.80, 134.01, 131.78, 128.14 (J = 8 Hz), 115.85 (J = 22 Hz), 61.14, 43.54, 27.09, 23.44, 14.85. \]

HRMS (ESI, m/z): calculated for C_{16}H_{20}FNO_3 [M+Na]^+ 316.1325, found: 316.1326.

**Ethyl (Z)-4-acetamido-4-(4-chlorophenyl)-2,2-dimethylbut-3-enoate (3p)**

![Ethyl (Z)-4-acetamido-4-(4-chlorophenyl)-2,2-dimethylbut-3-enoate](image)

\[\text{H NMR (400 MHz, DMSO-}d_6\text{) } \delta 8.88 (s, 1H), 7.41 (s, 4H), 4.06 (q, J = 7.1 Hz, 2H), 1.95 (s, 3H), 1.36 (s, 6H), 1.20 (t, J = 7.1 Hz, 3H). \]

\[\text{C NMR (101 MHz, DMSO) } \delta 176.49, 169.77, 138.25, 133.97, 132.88, 132.50, 129.06, 127.93, 61.17, 43.58, 27.05, 23.43, 14.84. \]

HRMS (ESI, m/z): calculated for C_{16}H_{20}ClNO_3 [M+Na]^+ 332.1029, found: 332.1032

**Ethyl (Z)-4-acetamido-4-(4-bromophenyl)-2,2-dimethylbut-3-enoate (3q)**

![Ethyl (Z)-4-acetamido-4-(4-bromophenyl)-2,2-dimethylbut-3-enoate](image)

\[\text{H NMR (400 MHz, DMSO-}d_6\text{) } \delta 8.89 (s, 1H), 7.54 (d, J = 8 Hz, 2H), 7.34 (d, J = 8 Hz, 2H), 6.01 (d, J = 1.3 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 1.95 (s, 3H), 1.36 (s, 6H), \]

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$^{13}$C NMR (101 MHz, DMSO) $\delta$ 176.48, 169.77, 138.65, 134.06, 132.51, 131.97, 128.27, 121.43, 61.17, 43.59, 27.04, 23.42, 14.84.

HRMS (ESI, m/z): calculated for C$_{16}$H$_{20}$BrNO$_3$ [M+Na]$^+$ 376.0524, found: 376.0526.

**Ethyl (Z)-4-acetamido-4-(furan-2-yl)-2,2-dimethylbut-3-enoate (3r)**

$^1$H NMR (400 MHz, DMSO-$_d_6$) $\delta$ 8.83 (s, 1H), 7.64 (dd, $J = 1.9$, 0.8 Hz, 1H), 6.49 (dd, $J = 3.4$, 1.8 Hz, 1H), 6.28 (dd, $J = 3.3$, 0.8 Hz, 1H), 6.04 (d, $J = 1.1$ Hz, 1H), 4.06 (q, $J = 7.1$ Hz, 2H), 1.93 (s, 3H), 1.33 (s, 6H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 176.30, 170.07, 152.72, 143.59, 129.90, 126.48, 112.46, 107.73, 61.22, 43.14, 26.95, 23.42, 14.84.

HRMS (ESI, m/z): calculated for C$_{14}$H$_{19}$NO$_4$ [M+Na]$^+$ 288.1212, found: 288.1207

**Ethyl (Z)-4-acetamido-2,2-dimethyl-4-(thiophen-2-yl)but-3-enoate (3s)**

$^1$H NMR (400 MHz, DMSO-$_d_6$) $\delta$ 8.93 (s, 1H), 7.38 (dd, $J = 4.9$, 1.4 Hz, 1H), 7.03 – 6.93 (m, 2H), 5.95 (d, $J = 1.3$ Hz, 1H), 4.03 (q, $J = 7.1$ Hz, 2H), 1.90 (s, 3H), 1.30 (s, 6H), 1.17 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 176.28, 169.85, 144.36, 130.99, 129.93, 128.46, 125.91, 124.64, 61.22, 43.49, 26.97, 23.39, 14.86.

HRMS (ESI, m/z): calculated for C$_{14}$H$_{19}$NSO$_3$ [M+Na]$^+$ 304.0983, found: 304.0982

**Ethyl (Z)-4-acetamido-2,2-dimethyl-4-(naphthalen-2-yl)but-3-enoate (3t)**

$^1$H NMR (400 MHz, DMSO-$_d_6$) $\delta$ 8.96 (s, 1H), 7.98 – 7.85 (m, 4H), 7.67 – 7.59 (m, 1H), 7.58 – 7.48 (m, 2H), 6.17 (s, 1H), 4.09 (q, $J = 7.1$ Hz, 2H), 2.02 (s, 3H), 1.41 (s,
6H), 1.22 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 176.64, 169.88, 136.75, 134.91, 133.77, 133.34, 132.62, 128.99, 128.55, 128.29, 127.21, 126.88, 124.77, 124.62, 61.18, 43.68, 27.19, 23.54, 14.88.

HRMS (ESI, m/z): calculated for C$_{20}$H$_{23}$NO$_3$ [M+Na]$^+$ 348.1576, found: 348.1577.

Diethyl 2-(3-acetamido-1H-inden-2-yl)malonate (4a)

\[
\text{NHAc} \quad \text{CO}_2\text{Et} \quad \text{CO}_2\text{Et}
\]

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 9.72 (s, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.40 – 7.24 (m, 3H), 4.83 (s, 1H), 4.19 (tq, J = 7.1, 3.0 Hz, 4H), 3.56 (s, 2H), 2.13 (s, 3H), 1.23 (t, J = 7.1 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO) δ 169.34, 168.35, 142.37, 142.00, 137.05, 127.39, 126.86, 126.28, 124.63, 120.47, 62.20, 52.53, 37.80, 23.82, 14.85.

HRMS (ESI, m/z): calculated for C$_{18}$H$_{21}$NO$_3$ [M+Na]$^+$ 354.1317, found: 354.1318.

\[N-(2-(2-methyl-3-oxobutan-2-yl)-1H-inden-3-yl)acetamide (4b)\]

\[
\text{NHAc} \quad \text{O}
\]

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 9.02 (s, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.23 (ddd, J = 15.7, 7.3, 1.3 Hz, 2H), 7.07 (dd, J = 7.0, 1.2 Hz, 1H), 3.57 (d, J = 1.7 Hz, 2H), 2.06 (s, 3H), 2.03 (s, 3H), 1.37 (s, 6H). $^{13}$C NMR (101 MHz, DMSO) δ 210.51, 169.98, 144.58, 143.98, 141.31, 134.19, 126.75, 125.43, 124.38, 119.81, 50.12, 37.77, 26.33, 25.15, 23.34.

HRMS (ESI, m/z): calculated for C$_{16}$H$_{19}$NO$_2$[M+Na]$^+$ 280.1313, found: 280.1316.

Methyl 2-(3-acetamido-1H-inden-2-yl)propanoate (4c)

\[
\text{NHAc} \quad \text{CO}_2\text{Me}
\]

$^1$H NMR (400 MHz, DMSO-d6) δ 9.50 (s, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.32 – 7.16 (m, 3H), 3.85 (q, J = 7.2 Hz, 1H), 3.63 (s, 3H), 3.47 (d, J = 22.9 Hz, 1H), 3.36 (d, J =
22.9 Hz, 1H), 2.11 (s, 3H), 1.38 (d, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, DMSO) δ 174.73, 169.38, 143.01, 141.83, 136.65, 134.45, 126.77, 125.57, 124.51, 120.12, 52.66, 38.94, 36.39, 23.71, 17.74.

HRMS (ESI, m/z): calculated for C$_{15}$H$_{17}$NO$_3$ [M+Na]$^+$ 282.1106, found: 280.1110.

**Tert-butyl 2-(3-acetamido-1H-inden-2-yl)-2-methylpropanoate (4d)**

![](image)

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.00 (s, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.25 (td, J = 7.5, 1.2 Hz, 1H), 7.18 (td, J = 7.3, 1.3 Hz, 1H), 7.09 – 7.04 (m, 1H), 3.46 (d, J = 1.6 Hz, 2H), 2.05 (s, 3H), 1.44 (s, 6H), 1.42 (s, 9H). $^{13}$C NMR (101 MHz, DMSO) δ 175.43, 169.62, 144.21, 143.67, 140.95, 133.45, 126.68, 125.30, 124.28, 119.88, 80.71, 45.16, 37.96, 28.39, 26.42, 23.67.

HRMS (ESI, m/z): calculated for C$_{19}$H$_{25}$NO$_3$ [M+Na]$^+$ 338.1732, found: 338.1735.

**Benzyl 2-(3-acetamido-1H-inden-2-yl)-2-methylpropanoate (4e)**

![](image)

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.05 (s, 1H), 7.44 – 7.34 (m, 6H), 7.26 (td, J = 7.4, 1.2 Hz, 1H), 7.19 (td, J = 7.4, 1.3 Hz, 1H), 7.12 – 7.07 (m, 1H), 5.12 (s, 2H), 3.49 (d, J = 1.7 Hz, 2H), 2.07 (s, 3H), 1.50 (s, 6H). $^{13}$C NMR (101 MHz, DMSO) δ 176.09, 169.81, 144.09, 143.97, 140.93, 137.23, 133.70, 129.28, 128.77, 128.59, 126.77, 125.45, 124.33, 119.73, 66.71, 44.28, 37.63, 26.23, 23.46.

HRMS (ESI, m/z): calculated for C$_{22}$H$_{23}$NO$_3$ [M+Na]$^+$ 372.1576, found: 372.1578.

**Benzyl (Z)-4-acetamido-2,2-dimethyl-4-phenylbut-3-enoate (4f)**

![](image)
**1H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.91 (s, 1H), 7.44 – 7.32 (m, 10H), 6.09 – 5.97 (m, 1H), 5.11 (s, 2H), 1.98 (d, \(J = 1.6\) Hz, 3H), 1.40 (s, 6H).**

**13C NMR (101 MHz, DMSO) \(\delta\) 176.39, 169.90, 139.23, 137.41, 135.07, 131.81, 129.29, 129.11, 128.74, 128.53, 128.48, 126.15, 66.59, 43.68, 27.02, 23.49.

HRMS (ESI, m/z): calculated for C\(_{21}\)H\(_{23}\)NO\(_3\) [M+Na]\(^+\) 360.1576, found: 360.1579.

**Ethyl 2-methyl-2-(1-oxo-2,3-dihydro-1\(H\)-inden-2-yl) propanoate (5a)**

\(\text{1H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.72 (ddd, \(J = 7.6, 1.3, 0.7\) Hz, 1H), 7.57 (td, \(J = 7.5, 1.2\) Hz, 1H), 7.44 (dt, \(J = 7.6, 1.0\) Hz, 1H), 7.35 (td, \(J = 7.4, 0.9\) Hz, 1H), 4.13 (qd, \(J = 7.2, 0.7\) Hz, 2H), 3.34 – 3.22 (m, 1H), 3.04 (dd, \(J = 8.1, 4.7\) Hz, 1H), 2.90 (dd, \(J = 17.1, 4.7\) Hz, 1H), 1.90 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H), 1.18 (t, \(J = 7.1\) Hz, 3H).**

**13C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 206.36, 176.77, 152.90, 137.68, 134.71, 127.51, 126.41, 123.82, 60.89, 53.73, 44.83, 30.42, 23.45, 22.66, 14.15.

HRMS (ESI, m/z): calculated for C\(_{15}\)H\(_{18}\)O\(_3\) [M+Na]\(^+\) 269.1154, found: 269.1154.

**Ethyl 2,2-dimethyl-4-oxo-4-phenylbutanoate (5b)**
$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.96 – 7.91 (m, 2H), 7.57 – 7.53 (m, 1H), 7.48 – 7.41 (m, 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.28 (s, 2H), 1.32 (s, 6H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.77, 177.42, 137.24, 133.15, 128.66, 128.04, 60.63, 48.58, 40.21, 25.89, 14.22.

HRMS (ESI, m/z): calculated for C$_{14}$H$_{18}$O$_{3}$ [M+Na]$^+$ 257.1154, found: 257.1153

2-(1-acetamido-2,3-dihydro-1$H$-inden-2-yl)-2-methylproanoic acid (5c)

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.29 (d, $J = 7.3$ Hz, 1H), 7.24 – 7.14 (m, 3H), 6.37 (d, $J = 9.9$ Hz, 1H), 5.67 (dd, $J = 10.0$, 7.5 Hz, 1H), 3.43 (dd, $J = 16.0$, 9.9 Hz, 1H), 2.98 (dd, $J = 16.0$, 8.2 Hz, 1H), 2.69 (dt, $J = 9.5$, 7.9 Hz, 1H), 1.90 (s, 3H), 1.36 (s, 3H), 1.29 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 182.85, 170.33, 143.01, 142.60, 128.44, 127.16, 125.00, 124.75, 54.59, 51.93, 42.74, 32.85, 25.94, 25.65, 23.10.

HRMS (ESI, m/z): calculated for C$_{15}$H$_{19}$NO$_{3}$ [M+Na]$^+$ 284.1263, found: 284.1269

4-Acetamido-2,2-dimethyl-4-phenylbutanoic acid (5d)

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.29 (d, $J = 5.8$ Hz, 4H), 7.23 (dd, $J = 6.2$, 2.6 Hz, 1H), 6.48 (d, $J = 8.9$ Hz, 1H), 5.18 (ddd, $J = 11.1$, 8.9, 3.9 Hz, 1H), 2.38 (dd, $J = 14.5$, 11.1 Hz, 1H), 1.92 (s, 3H), 1.77 (dd, $J = 14.5$, 3.9 Hz, 1H), 1.28 (s, 3H), 1.25 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 182.85, 170.33, 142.96, 128.77, 127.48, 126.40, 50.66, 46.45, 41.24, 28.46, 23.17, 23.07.

HRMS (ESI, m/z): calculated for C$_{14}$H$_{19}$NO$_{3}$ [M+Na]$^+$ 272.1263, found: 272.1269
Ethyl 2-(1-acetamido-2,3-dihydro-1H-inden-2-yl)-2-methylpropanoate (5e)

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

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.38 – 7.31 (m, 1H), 7.24 – 7.15 (m, 3H), 6.19 (d, \(J = 9.8\) Hz, 1H), 5.65 (dd, \(J = 9.9, 7.6\) Hz, 1H), 4.18 – 4.02 (m, 2H), 3.46 (dd, \(J = 15.9, 9.7\) Hz, 1H), 2.97 (dd, \(J = 15.9, 8.1\) Hz, 1H), 2.63 (dt, \(J = 9.7, 7.9\) Hz, 1H), 1.90 (s, 3H), 1.35 (s, 3H), 1.30 – 1.24 (m, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 178.68, 169.08, 143.69, 142.45, 128.23, 124.95, 124.68, 60.80, 54.39, 51.95, 42.90, 33.03, 26.45, 25.47, 23.59, 14.26.

HRMS (ESI, m/z): calculated for C\(_{17}\)H\(_{23}\)NO\(_3\) [M+Na]\(^+\) 312.1576, found: 312.1574.

Ethyl 4-acetamido-2, 2-dimethyl-4-phenylbutanoate (5f)

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

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.36 – 7.20 (m, 5H), 6.00 (d, \(J = 8.5\) Hz, 1H), 5.09 (ddd, \(J = 10.9, 8.4, 4.4\) Hz, 1H), 4.12 – 4.01 (m, 2H), 2.38 (dd, \(J = 14.5, 10.9\) Hz, 1H), 1.90 (s, 3H), 1.75 (dd, \(J = 14.5, 4.5\) Hz, 1H), 1.29 – 1.24 (m, 6H), 1.23 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 178.87, 169.01, 143.18, 128.72, 127.39, 126.44, 60.92, 50.78, 45.94, 41.31, 28.36, 23.45, 23.39, 14.27.

HRMS (ESI, m/z): calculated for C\(_{16}\)H\(_{23}\)O\(_3\) [M+Na]\(^+\) 300.1576, found: 300.1575

N-(2-(1-hydroxy-2-methylpropan-2-yl)-2,3-dihydro-1H-inden-1-yl)acetamide (5g)

\[
\begin{align*}
\text{NHAc} & \quad \text{OH} \\
\end{align*}
\]

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.43 – 7.39 (m, 1H), 7.24 – 7.14 (m, 3H), 6.69 (s, 1H), 5.45 (t, \(J = 7.8\) Hz, 1H), 3.58 (d, \(J = 10.6\) Hz, 1H), 3.47 (d, \(J = 10.7\) Hz, 1H), 3.04 (dd, \(J = 15.5, 11.4\) Hz, 1H), 2.87 (dd, \(J = 15.5, 7.5\) Hz, 1H), 2.51 (dt, \(J = 11.4, 7.1\) Hz, 1H), 1.92 (s, 3H), 1.10 (s, 3H), 1.05 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\)
HRMS (ESI, m/z): calculated for C_{15}H_{21}O_{2} [M+Na]^+ 270.1470, found: 270.1476

N-(4-hydroxy-3,3-dimethyl-1-phenylbutyl)acetamide (5h)

\[
\begin{aligned}
\text{NHAc} & \quad \text{OH} \\
\end{aligned}
\]

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.36 – 7.21 (m, 6H), 6.44 (s, 1H), 4.91 (q, \(J = 6.6\) Hz, 1H), 3.56 (d, \(J = 10.4\) Hz, 1H), 3.23 (d, \(J = 11.5\) Hz, 2H), 1.98 (dd, \(J = 14.7, 7.1\) Hz, 1H), 1.93 (q, \(J = 0.9\) Hz, 3H), 1.72 – 1.64 (m, 1H), 0.91 (s, 3H), 0.76 (d, \(J = 1.2\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 169.82, 143.69, 128.89, 127.52, 126.84, 70.40, 51.43, 44.52, 35.44, 27.03, 23.99, 23.41.

HRMS (ESI, m/z): calculated for C_{14}H_{21}NO_{2} [M+Na]^+ 258.1470, found: 258.1475

3, 3-Dimethyl-3, 3a, 4, 8b-tetrahydroindeno[1,2-b]pyrrol-2(1H)-one (5i)

\[
\begin{aligned}
\text{NH} & \quad \text{O} \\
\end{aligned}
\]

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.34 – 7.15 (m, 4H), 6.39 (s, 1H), 4.90 (d, \(J = 6.4\) Hz, 1H), 3.06 – 2.88 (m, 3H), 1.29 (s, 3H), 1.11 (d, \(J = 1.6\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 182.15, 143.97, 141.47, 128.77, 127.06, 125.01, 124.78, 60.04, 51.25, 43.09, 33.13, 26.81, 20.69.

HRMS (ESI, m/z): calculated for C_{13}H_{15}O [M+Na]^+ 224.1051, found: 224.1051.

3,3-Dimethyl-5-phenylpyrrolidin-2-one (5j)

\[
\begin{aligned}
\text{Ph} & \quad \text{N} & \quad \text{O} \\
\end{aligned}
\]

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.40 – 7.28 (m, 5H), 5.88 (s, 1H), 4.69 (dd, \(J = 8.5, 6.9\) Hz, 1H), 2.38 (dd, \(J = 12.8, 6.9\) Hz, 1H), 1.85 (dd, \(J = 12.8, 8.6\) Hz, 1H), 1.26
(s, 3H), 1.23 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 182.92, 142.44, 129.03, 128.03, 125.89, 54.88, 47.50, 41.05, 25.23, 24.65.

HRMS (ESI, m/z): calculated for C$_{12}$H$_{15}$NO [M+Na]$^+$ 212.1051, found: 212.1050
NMR spectra

3a

NHAc

\[ \text{NMR spectra} \]

\[ \text{NHAc} \]

\[ \text{OEt} \]

\[ \begin{align*}
9.00 & \quad 7.45 \\
7.43 & \quad 7.25 \\
7.24 & \quad 7.21 \\
7.21 & \quad 7.19 \\
7.19 & \quad 7.08 \\
7.06 & \quad 4.10 \\
4.06 & \quad 4.04 \\
4.04 & \quad 3.49 \\
3.49 & \quad 3.38 \\
3.38 & \quad 2.55 \\
2.54 & \quad 2.54 \\
2.54 & \quad 2.04 \\
2.04 & \quad 1.20 \\
1.20 & \quad 1.17 \\
1.17 & \quad 0.10 \end{align*} \]

\[ \begin{align*}
1.04 & \quad 0.56 \\
0.56 & \quad 0.53 \\
0.53 & \quad 0.50 \\
0.50 & \quad 0.47 \\
0.47 & \quad 0.44 \\
0.44 & \quad 0.41 \\
0.41 & \quad 0.38 \\
0.38 & \quad 0.35 \\
0.35 & \quad 0.32 \\
0.32 & \quad 0.29 \\
0.29 & \quad 0.26 \\
0.26 & \quad 0.23 \\
0.23 & \quad 0.20 \\
0.20 & \quad 0.17 \\
0.17 & \quad 0.14 \\
0.14 & \quad 0.11 \\
0.11 & \quad 0.08 \\
0.08 & \quad 0.05 \\
0.05 & \quad 0.02 \end{align*} \]

\[ \begin{align*}
-176.35 & \quad -169.65 \\
-169.65 & \quad -163.05 \\
-163.05 & \quad -156.74 \\
-156.74 & \quad -150.33 \\
-150.33 & \quad -119.79 \\
-119.79 & \quad 44.12 \\
44.12 & \quad 40.86 \\
40.86 & \quad 39.86 \\
39.86 & \quad 29.34 \\
29.34 & \quad 23.44 \\
23.44 & \quad 14.82 \end{align*} \]