Supplementary Material

Expedient method for acylation of amines, alcohols and thiol using Trimethylsilyl acetate

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1) General methods.

Unless otherwise noted all reactions were carried out under inert atmosphere. Solvents and reagents were purchased at the highest commercial quality and used without further drying and purification respectively. Reactions were monitored by thin-layer chromatography (TLC) analysis using TLC aluminum sheets silica gel 60 F_{254}.

The $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ and DMSO-d$_6$ at 400 to 600 MHz. The chemical shifts are reported in ppm downfield to TMS (δ = 0) for $^1$H NMR and $^{13}$C NMR. Flash chromatography was carried out on silica gel (100-200 mesh) using column of the appropriate diameter and length.
2) **General procedure for acetylation:**

In a typical experimental procedure; to a mixture of amines/alcohol/phenol/thiols (1.0 mmol) and trimethylsilyl acetate (2.0 mmol) in dichloromethane solvent (10 nL), trimethylsilyl trifluoromethanesulfonate (1.0 mmol) was added at room temperature. The reaction mixture was stirred at room temperature for 24 hrs. Completion of reaction was monitored by TLC after quenching with water, separated the bottom dichloromethane layer and further extracted product into dichloromethane (1 X 10 mL). The combined organic layer was washed with saturated NaHCO₃ solution, brine solution dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. All products were characterized by means of orthogonal spectroscopic techniques.

All the products were characterized by NMR and Mass spectroscopy. All the new compounds gave satisfactory spectroscopic data in accordance with their structure.
3) Characterization of N-acetyl naphthylethylamine (3a*)

![Chemical structure of N-acetyl naphthylethylamine](image)

**Nature:** Solid

**$^1$H NMR (400 MHz, CDCl$_3$):**

$\delta$ 8.10 (1H, d), 7.87-7.78 (2H, br), 7.54-7.42 (4H, m), 5.93 (1H, m), 1.95 (3H, s), 1.66 (3H, d).

**$^{13}$C NMR (400 MHz, CDCl$_3$):**

168.9, 138.2, 133.9, 131.1, 128.8, 128.4, 126.6, 125.9, 125.2, 123.5, 122.6, 64.6, 23.4, 20.6.

**Characterization of N-acetyl morpholine (3b*):**

![Chemical structure of N-acetyl morpholine](image)

**Nature:** Liquid

**$^1$H NMR (400 MHz, CDCl$_3$):**

$\delta$ 3.78-3.44 (8H, m), 2.09 (3H, s).

**$^{13}$C NMR (400 MHz, CDCl$_3$):**

169.2, 66.9, 66.6, 66.3, 46.7, 41.8, 21.1.

**Characterization of Benzyl acetamide (3c*):**

![Chemical structure of Benzyl acetamide](image)

**Nature:** Solid

**$^1$H NMR (400 MHz, CDCl$_3$):**

$\delta$ 7.38-7.21 (5H, m), 5.88 (1H, br), 4.43 (2H, br), 2.01 (3H, s).

**$^{13}$C NMR (400 MHz, CDCl$_3$):**

170.0, 138.2, 128.7, 127.9, 127.5, 43.8, 23.2.

**Characterization of Acetanilide (3d*):**

![Chemical structure of Acetanilide](image)

**Nature:** Solid
Characterization of Benzyl acetamide (3e*):

\[ \text{Nature: Solid} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3): \delta 7.74\text{-}7.70 (2H, br), 7.61 (1H, br), 7.36\text{-}7.28 (2H, m), 2.24 (3H, s). \]

\[ ^13C \text{ NMR (400 MHz, CDCl}_3): 169.0, 138.4, 131.5, 131.1, 129.5, 125.2, 123.0, 122.5, 120.9, 116.7, 116.6, 24.4. \]

Characterization of N-(4-methoxyphenyl)acetamide (3f*):

\[ \text{Nature: Solid} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3): \delta 7.41\text{-}7.38 (2H, br), 6.96\text{-}6.80 (2H, br), 3.78 (3H, s), 2.26 (3H, s). \]

Characterization of (3s,5s,7s)-adamantan-1-yl acetate (3g*):

\[ \text{Nature: Solid} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3): \delta 2.08 (3H, s), 2.03 (6H, s), 1.89 (3H, s), 1.59 (6H, s). \]

\[ ^13C \text{ NMR (400 MHz, CDCl}_3): \delta 169.3, 79.3, 40.3, 35.2, 29.8, 21.7. \]

Characterization of O-acetyltrifloromethylphenylpropanol (3h*):
Nature: Crude Oil

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38-7.29 (4H, m), 4.02 (2H, q), 2.69 (2H, q), 1.98-1.81 (5H, m).

$^{13}$C NMR (400 MHz, CDCl$_3$): 171.1, 142.2, 131.8, 131.2, 130.9, 130.2, 128.9, 128.3, 125.6, 125.0, 123.0, 122.9, 120.2, 63.5, 32.0, 30.0, 20.8.

Characterization of (1$^R$,2$^S$,5$^R$)-2-isopropyl-5-methylcyclohexyl acetate (3i*):

Nature: Crude Oil

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.63-4.57 (1H, td, $J = 4.4$ Hz), 195 (3H, s), 1.93-1.90 (1H, m), 1.83-1.75 (1H, m), 1.62-1.57 (2H, m), 1.45-1.37 (1H, m), 1.32-1.18 (1H, m), 1.03-0.87 (2H, m), 0.83-0.82 (6H, d, $J = 6.52$ Hz), 0.70-0.68 (3H, d, $J = 6.96$ Hz).

$^{13}$C NMR (400 MHz, CDCl$_3$): 170.6, 74.1, 47.0, 40.9, 34.2, 31.3, 26.3, 23.5, 22.0, 21.3, 20.7, 16.4.

$[\alpha]_D^{25}$: + 77 (c 1.0, CHCl$_3$)

Characterization of Benzyl acetate (3j*):

Nature: Crude Oil

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-7.29 (5H, m), 5.08 (2H, s), 2.06 (3H, s).

$^{13}$C NMR (400 MHz, CDCl$_3$): 170.8, 136.0, 128.6, 128.3, 66.3, 21.0.

EI-Mass: $m/z$ 151 [M+H]+.

Characterization of Allyl acetate (3k*):

Nature: Crude Oil

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-7.29 (5H, m), 5.08 (2H, s), 2.06 (3H, s).

$^{13}$C NMR (400 MHz, CDCl$_3$): 170.8, 136.0, 128.6, 128.3, 66.3, 21.0.

EI-Mass: $m/z$ 151 [M+H]+.
Nature: Crude oil.

$^1$H NMR (400 MHz, CDCl$_3$): $^6$ 5.95-5.87 (1H, m), 5.34-5.21 (2H, dd, $J$ = 17.2, 17.6 Hz), 4.58-4.56 (2H, m), 2.08 (3H, s).

$^{13}$C NMR (400 MHz, CDCl$_3$): $^6$ 170.6, 132.2, 118.1, 65.1, 20.8.

Characterization of Phenyl acetate (3l*):

Nature: Crude Oil.

$^1$H NMR (400 MHz, CDCl$_3$): $^6$ 7.36-7.32 (2H, t, $J$ = 7.40 Hz), 7.20-7.16 (1H, t, $J$ = 7.44 Hz), 7.07-7.05 (2H, d, $J$ = 8.56 Hz), 2.23 (3H, s).

$^{13}$C NMR (400 MHz, CDCl$_3$): 169.5, 150.8, 129.5, 125.8, 121.6, 21.1.

EI-Mass: $m/z$ 137 [M+H]$^+$.  

Characterization of 4-Nitrophenyl acetate (3m*):

Nature: Solid

$^1$H NMR (400 MHz, CDCl$_3$): $^6$ 8.20-8.17 (2H, d, $J$ = 9.12 Hz), 7.22-7.19 (2H, d, $J$ = 9.12 Hz), 2.27 (3H, s).

$^{13}$C NMR (400 MHz, CDCl$_3$): 168.4, 155.4, 155.3, 125.2, 122.4, 21.1.

EI-Mass: $m/z$ 182 [M+H]$^+$.  

Characterization of 4-Bromohenyl acetate (3n*):

Nature: Crude Oil
\( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta 7.48-7.46 \) (2H, d, \( J = 8.8\) Hz), 6.98-6.96 (2H, d, \( J = 8.88\) Hz), 2.27 (3H, s) \\
\( ^{13}\)C NMR (400 MHz, CDCl\(_3\)): 169.1, 149.7, 132.5, 123.4, 118.9, 21.1. \\
EI-Mass: \( m/z\) 215 \([\text{M+H}]^+\)

Characterization of 4-Methoxyphenyl acetate (3o\(^*\)):

\[
\begin{array}{c}
\text{O} \\
\text{OAc}
\end{array}
\]

Nature: Crude Oil;  \\
\( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta 6.99-6.97 \) (2H, d, \( J = 9.16\) Hz), 6.87-6.85 (2H, d, \( J = 9.16\) Hz), 3.75 (3H, s), 2.24 (3H, s). \\
\( ^{13}\)C NMR (400 MHz, CDCl\(_3\)): 169.9, 157.3, 144.2, 122.3, 114.4, 55.5, 21.0. \\
EI-Mass: \( m/z\) 167 \([\text{M+H}]^+\)

Characterization of (S)-1-(3,5-bis(trifluoromethyl)phenyl)ethyl acetate (3p\(^*\)):

\[
\begin{array}{c}
\text{F}_{\text{CF}}
\end{array}
\]

Nature: Crude Oil  \\
\( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta 7.81 \) (3H, s), 5.98-5.93 (1H, q, \( J = 6.68, 6.64\) Hz), 2.12 (3H, s), 1.58-1.57 (3H, d, \( J = 6.64\) Hz). \\
\( ^{13}\)C NMR (400 MHz, CDCl\(_3\)): 170.0, 144.4, 132.4, 126.3, 124.5, 121.9, 7.9, 22.2, 21.0. \\
EI-Mass: \( m/z\) 301 \([\text{M+H}]^+\)

Characterization of p-tolyl acetate (3q\(^*\)):

\[
\text{OAc}
\]

\( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta 7.19-7.10 \) (2H, br), 6.98-6.90 (2H, br), 2.39 (3H, s), 2.26 (3H, s)
Characterization of \((S)-5\)-carbamoyl-10,11-dihydro-5H-dibenzo[b,f]azepin-10-yl acetate (3r*):

\[\text{Nature: Solid;}\]

\[\text{\(^{1}H\) NMR (400 MHz, CDCl}_{3}\):} \delta 7.47-7.42 (2H, m), 7.32-7.23 (6H, m) 6.40-5.99 (1H, b), 5.03(2H, br), 3.61-3.58 (1H, d, J = 13.48 Hz), 3.19-3.05 (1H, dd, J = 13.48, 4.09 Hz), 2.09 (3H, s);

\[\text{\(^{13}C\) NMR (400 MHz, CDCl}_{3}\):} \delta 170.7, 170.2, 157.0, 156.7, 141.3, 140.6, 139.1, 134.4, 133.5, 131.0, 129.3, 128.9, 128.3, 128.1, 128.0, 127.8, 72.3, 70.1, 36.0, 35.8, 21.1.

HRMS calc for C_{17}H_{16}N_{2}O_{3} : 297.1239, found: 297.124;

IR (KBr): 3476, 3361, 2934, 1726, 1653, 1411, 1254 cm\(^{-1}\).

\([\alpha]\) D\(^{25}\): 21.0 (c =1, pyridine).

Characterization of \((3S,10R,13S)-10,13\)-dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (3s*):

\[\text{Nature: Solid;}\]

\[\text{\(^{1}H\) NMR (400 MHz, CDCl}_{3}\):} \delta 5.34-5.33 (1H, d, J = 5.12 Hz), 4.56-4.49 (1H, m), 2.42-2.35 (1H, dd J = 8.4 Hz), 2.28-2.24 (2H, m), 2.06-1.97 (2H, m), 1.96 (3H, s), 1.91-1.85 (3H, m), 1.63-1.39 (6H, m), 1.26-1.18 (2H, m), 1.11-1.05 (1H, m), 0.98-0.93 (4H, m), 0.81 (3H, s).

\[\text{\(^{13}C\) NMR (400 MHz, CDCl}_{3}\):} \delta 221.0, 170.5, 139.9, 121.9, 73.7, 51.7, 50.1, 47.5, 38.1, 36.9, 36.7, 35.8, 31.5, 31.4, 30.8, 27.7, 21.9, 21.4, 20.3, 19.3, 13.5
IR (KBr): 1240.0, 1734.6, 1460.7, 1434.4, 1369.7, 2949.3, 1023.7 cm⁻¹

EI-Mass: \( m/z \) 348.4 [M+NH₄]⁺.

Characterization of S-phenyl ethanethioate (3t*):

![Structure](image)

Nature: Crude Oil

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.41-7.7.37 (5H, m), 2.38 (3H, s)

\(^{13}\)C NMR (400 MHz, CDCl₃): 194.0, 134.5, 129.5, 129.2, 128.0, 30.2

EI-Mass: \( m/z \) 152 [M+H]⁺.
Figure 1: $^1$H NMR spectrum of compound 3a* in CDCl$_3$

Figure 2: $^{13}$C NMR spectrum of compound 3a* in CDCl$_3$
Figure 3: $^1$H NMR spectrum of compound 3b* in CDCl$_3$

Figure 4: $^{13}$C NMR spectrum of compound 3b* in CDCl$_3$
Figure 5: $^1$H NMR spectrum of compound 3c* in CDCl$_3$

Figure 6: $^{13}$C NMR spectrum of compound 3c* in CDCl$_3$
Figure 7: $^1$H NMR spectrum of compound 3d* in CDCl$_3$

Figure 8: $^{13}$C NMR spectrum of compound 3d* in CDCl$_3$
Figure 9: $^1$H NMR spectrum of compound 3e* in CDCl$_3$

Figure 10: $^{13}$C NMR spectrum of compound 3e* in CDCl$_3$
Figure 11: $^1$H NMR spectrum of compound 3f* in CDCl$_3$

Figure 12: $^1$H NMR spectrum of compound 3g* in CDCl$_3$
Figure 13: $^{13}$C NMR spectrum of compound 3g* in CDCl$_3$

Figure 14: ESI(+ve) mass spectrum of compound 3g*
Figure 15: $^1$H NMR spectrum of compound 3h* in CDCl$_3$

Figure 16: $^{13}$C NMR spectrum of compound 3h* in CDCl$_3$
Figure 17: $^1$H NMR spectrum of compound 3i* in CDCl$_3$

Figure 18: $^{13}$C NMR spectrum of compound 3i* in CDCl$_3$
Figure 19: $^1$H NMR spectrum of compound 3j* in CDCl$_3$

Figure 20: $^{13}$C NMR spectrum of compound 3j* in CDCl$_3$
Figure 21: $^1$H NMR spectrum of compound 3k* in CDCl$_3$

Figure 22: $^{13}$C NMR spectrum of compound 3k* in CDCl$_3$
Figure 23: $^1$H NMR spectrum of compound 3l* in CDCl$_3$

Figure 24: $^{13}$C NMR spectrum of compound 3l* in CDCl$_3$
Figure 25: $^1$H NMR spectrum of compound 3m* in CDCl$_3$

Figure 26: $^{13}$C NMR spectrum of compound 3m* in CDCl$_3$
Figure 27: $^1$H NMR spectrum of compound 3n* in CDCl$_3$

Figure 28: $^{13}$C NMR spectrum of compound 3n* in CDCl$_3$
Figure 29: $^1$H NMR spectrum of compound 3o* in CDCl$_3$

Figure 30: $^{13}$C NMR spectrum of compound 3o* in CDCl$_3$
Figure 31: $^1$H NMR spectrum of compound 3p* in CDCl$_3$

Figure 32: $^{13}$C NMR spectrum of compound 3p* in CDCl$_3$
Figure 33: $^1$H NMR spectrum of compound 3q* in CDCl$_3$

Figure 34: $^{13}$C NMR spectrum of compound 3q* in CDCl$_3$
Figure 35: $^1$H NMR spectrum of compound 3r$^*$ in CDCl$_3$

Figure 36: $^{13}$C NMR spectrum of compound 3r$^*$ in CDCl$_3$
Figure 37: FT-IR spectrum of compound 3r* 

Figure 38: $^1$H NMR spectrum of compound 3s* in CDCl$_3$
Figure 39: $^{13}$C NMR spectrum of compound 3s* in CDCl$_3$

Figure 40: FT-IR spectrum of compound 3s*
Figure 41: ES-MS/MS spectrum of compound 3s*

Figure 42: $^1$H NMR spectrum of compound 3t* in CDCl$_3$
Figure 43: $^{13}$C NMR spectrum of compound 3t* in CDCl$_3$