Borate Esters as Convenient Reagents for Direct Amidation of Carboxylic Acids and Transamidation of Primary Amides

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Table of Contents

1 General S2
2 Procedures S2
2.1 Tris(2,2,2-trifluoroethyl) Borate S2
2.2 Direct Carboxamidations S3
2.3 Transamidations S9
3 References S10
4 Spectra S13
1 General

All chemicals were used as supplied. Amidations and transamidations were performed on 0.5–3.0 mmol scale. Chromatographic separations were performed on silica gel (VWR/BDH Prolabo® (40–63 μm) and Merck Silica gel 60 (40–63 μm). Thin-layer chromatography was performed on Merck TLC Silica gel 60 F254 and visualised by UV (254 nm) and/or 10% PMA ethanolic solution (PMA = phosphomolybdic acid). Melting points were determined using a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on Perkin–Elmer Spectrum 100 FTIR ATR spectrometer and are quoted in cm⁻¹. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 600, ¹¹B NMR on Bruker Avance 500 and ¹⁹F on Bruker 300 spectrometers. Residual solvent peak was used as an internal standard[1]. Chemical shifts are quoted in ppm using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qn quintet; sext sextet; non nonet, m multiplet; br, broad; or a combination thereof. The coupling constants J are measured in Hz. Mass spectra were recorded in the Department of Chemistry, University College London.

2 Procedures

2.1 Tris(2,2,2-trifluoroethyl) Borate

\[
\text{B(OCH}_2\text{CF}_3)_3
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2,2,2-Trifluoroethanol (42.7 mL, 586 mmol, 3.0 equiv) was added via syringe pump over 30 min to neat BBr₃ (48.9 g, 195 mmol, 1.0 equiv) at −78 °C and the mixture was allowed to warm up to RT overnight under argon flow. The mixture was heated for 1 h at 70 °C under argon before being distilled (120–123 °C; 760 Torr) to give the product as a colourless liquid (54.0 g, 90%).

Tris(2,2,2-trifluoroethyl)borate can also be prepared from BCl₃,[2,3] B₂O₃,[4] B(OH)₃[5] and BH₃·THF.[6]

**Tris(2,2,2-trifluoroethyl) borate:**[2,3]

Colourless liquid. Lit Bp 77 ºC (200 Torr)[3]

¹H NMR (CDCl₃, 600 MHz) δ 4.22 (q, 6H, J = 8.4, CH₂CF₃).

¹³C NMR (CDCl₃, 150 MHz) δ 123.3 (q, J = 278), 61.9 (q, J = 36).

¹⁹F NMR (CDCl₃, 282 MHz) δ −77.2.

¹¹B NMR (CDCl₃, 160 MHz) δ 15.3.

IR ν 2974, 1429, 1390, 1264, 1161, 1079, 964, 907, 840, 731.

HRMS for C₆H₇O₃F₉B [M]+ found 309.03461, calc. 309.03445.
2.2 Direct Carboxamidation

Representative Procedure: Borate (2 equiv) was added to a solution/suspension of carboxylic acid (1 equiv) and amine (1 equiv) in MeCN (0.5 M) and the mixture was heated at 80 °C. After 15 h, the solvent was removed under reduced pressure. The residue was redissolved in DCM and washed with NaHCO₃ (1 M) and HCl (1 M) aqueous solutions, dried over MgSO₄, filtered and concentrated under reduced pressure to give the clean amide product.

N-Benzyl-2-phenylacetamide.⁷
Colourless solid. Mp 118–120 °C (DCM). Lit Mp 118–119 °C (PE/EtOAc).⁷

¹H NMR (CDCl₃, 600 MHz) δ 7.36–7.32 (m, 2H, ArH), 7.32–7.22 (m, 6H, ArH), 7.19–7.15 (d, 2H, J = 7.1, ArH), 5.79 (br s, 1H, NH), 4.41 (d, 2H, J = 5.8, CH₂NH), 3.63 (s, 2H, CH₂CO).

¹³C NMR (CDCl₃, 150 MHz) δ 171.1, 138.2, 134.9, 129.6, 129.2, 128.8, 127.61, 127.56, 127.55, 43.9, 43.7.

¹H NMR (DMSO-d₆, 600 MHz) δ 8.56 (br t, 1H, J = 5.5, NH), 7.33–7.26 (m, 6H, ArH), 7.25–7.20 (m, 4H, ArH), 4.26 (d, 2H, J = 6.0, CH₂NH), 3.47 (s, 2H, CH₂CO).

¹³C NMR (DMSO-d₆, 150 MHz) δ 170.1, 139.5, 136.4, 129.0, 128.3, 128.2, 127.2, 126.8, 126.4, 42.4, 42.2.

IR ν 3286, 1637, 1551.

HRMS for C₁₅H₁₅NO [M]+ found 225.11483, calc. 225.11482.

N-Butyl-2-phenylacetamide.⁸
Colourless solid. Mp 49–50 °C (DCM). Lit Mp 49 °C.⁸

¹H NMR (CDCl₃, 600 MHz) δ 7.34–7.30 (m, 2H, ArH), 7.30–7.21 (m, 3H, ArH), 5.71 (br s, 1H, NH), 3.53 (s, 2H, CH₂CO), 3.17 (q, 2H, J = 6.5, NHCH₂), 1.38 (qn, 2H, J = 6.5, CH₂Et), 1.23 (sx, 2H, J = 7.3, CH₂CH₃), 0.85 (t, 3H, J = 7.3, CH₃).

¹³C NMR (CDCl₃, 150 MHz) δ 170.1, 139.5, 136.4, 129.0, 128.3, 128.2, 127.2, 126.8, 126.4, 42.4, 42.2.

IR ν 3294, 1642, 1551.

HRMS for C₁₂H₁₇NO [M]+ found 191.12961, calc. 191.13047.
N-Benzyl-3-methylbutanamide: [9]
$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.34–7.29 (m, 2H, Ar$H$), 7.28–7.23 (m, 3H, Ar$H$), 5.97 (br s, 1H, NH), 4.41 (d, 2H, $J$ = 5.7, CH$_2$NH), 2.13 (non, 1H, $J$ = 6.7, CHMe$_2$), 2.06 (d, 2H, $J$ = 7.1, CH$_3$CO), 0.94 (d, 6H, $J$ = 6.6, CH$_3$).
$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 172.5, 138.5, 128.8, 127.9, 127.6, 46.2, 43.6, 26.3, 22.6.
IR $\nu$ 3289, 1635, 1543.
HRMS for C$_{12}$H$_{17}$NO $[M]^+$ found 191.13126, calc. 191.13047.

N-Butyl-3-methylbutanamide: [10]
Colourless oil.
$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 5.79 (br s, 1H, CONH), 3.20 (q, 2H, $J$ = 6.7, NHCH$_2$), 2.07 (non, 1H, $J$ = 6.7, CH(CH$_3$)$_3$), 1.99 (d, 2H, $J$ = 6.7, CH$_2$CO), 1.44 (qn, 2H, $J$ = 7.2, NHCH$_2$CH$_2$), 1.30 (sx, 2H, $J$ = 7.2, CH$_2$CH$_3$), 0.90 (d, 6H, $J$ = 6.7, CH(CH$_3$)$_3$), 0.88 (t, 3H, $J$ = 7.2, CH$_2$CH$_3$).
$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 172.7, 46.3, 39.2, 31.9, 26.3, 22.5, 20.2, 13.9.
IR $\nu$ 3284, 2957, 2871, 1641, 1550, 1465, 1368.
HRMS for C$_9$H$_{20}$NO $[M+H]^+$ found 158.15521, calc. 157.15449.

N-Benzylpivalamide: [11]
$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.36–7.30 (m, 2H, Ar$H$), 7.30–7.23 (m, 3H, Ar$H$), 5.92 (br s, 1H, NH), 4.43 (d, 2H, $J$ = 5.6, CH$_2$NH), 1.22 (s, 9H, CH$_3$).
$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 178.5, 138.7, 128.8, 127.8, 127.6, 43.7, 38.8, 27.7.
IR $\nu$ 3293, 1634, 1540.
HRMS for C$_{12}$H$_{17}$NO $[M]^+$ found 191.12954, calc. 191.13047.
**N-Benzylbenzamide**[^1]

Colourless solid. Mp 100–101 °C (DCM). Lit Mp 98–100 °C (H₂O/EtOH).

[^1] H NMR (CDCl₃, 600 MHz) δ 7.90–7.76 (m, 2H, Ar H), 7.52–7.46 (m, 1H, ArH), 7.45–7.39 (m, 2H, ArH), 7.37–7.32 (m, 4H, ArH), 7.32–7.26 (m, 1H, ArH), 6.56 (br s, 1H, NH), 4.63 (d, 2H, J = 5.1, CH₂CO).

[^1] C NMR (CDCl₃, 150 MHz) δ 167.5, 138.3, 134.5, 131.7, 128.9, 128.7, 128.0, 127.7, 127.1, 44.2.

IR ν 3318, 1639, 1540.

HRMS for C₁₄H₁₄NO [M+H]^+ found 212.10846, calc. 212.10754.

**N-(2-Hydroxyethyl)-2-phenylacetamide**[^12]

Colourless solid. Mp 64–66 °C. Lit Mp 65–66 °C.

[^12] H NMR (CDCl₃, 600 MHz) δ 7.38–7.25 (m, 5H, ArH), 5.98 (br s, 1H, CONH), 3.68 (t, 2H, J = 5.0, CH₂OH), 3.61 (s, 2H, PhCH₂), 3.38 (q, 2H, J = 5.0, NHCH₂), 2.46 (br s, 1H, OH).

[^12] C NMR (CDCl₃, 150 MHz) δ 172.8, 134.6, 129.6, 129.2, 127.6, 62.5, 43.7, 42.9.

IR ν 3397, 3278, 3090, 2931, 1635, 1540, 1495, 1454, 1429, 1345, 1061.

HRMS for C₁₀H₁₄NO₂ [M+H]^+ found 180.10266, calc. 180.10245.

**(R)-2-Phenyl-N-(1-phenylethyl)acetamide**[^7]


[^7] D α +3.3 (c 1.0, CHCl₃). Lit D α +3.3 (c 1.0, CHCl₃).

[^7] H NMR (CDCl₃, 600 MHz) δ 7.37–7.33 (m, 2H, ArH), 7.32–7.27 (m, 3H, ArH), 7.27–7.21 (m, 3H, ArH), 7.20–7.16 (m, 2H, ArH), 5.66 (br s, 1H, CONH), 5.12 (qn, 1H, J = 7.1, CHCH₂), 3.60(d, 1H, J = 16.3, PhCHH), 3.58 (d, 1H, J = 16.3, PhCHH), 1.39 (d, 3H, J = 7.1, CH₃).

[^7] C NMR (CDCl₃, 150 MHz) δ 170.2, 143.1, 134.9, 129.5, 129.2, 128.7, 127.5, 127.4, 126.1, 48.9, 43.9, 21.9.

IR ν 3284, 3062, 3030, 2974, 1641, 1543, 1495, 1453.

HRMS for C₁₆H₁₈NO [M+H]^+ found 240.13757, calc. 240.13884.
N-Allylhex-5-enamide:
Pale yellow oil.
$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 6.09 (bs s, 1H, CONH), 5.83–5.66 (m, 2H, 2×C=CH$_2$), 5.12 (d, 1H, $J$ = 17.2, NHCH$_2$CH=CHH-trans), 5.07 (d, 1H, $J$ = 10.4, NHCH$_2$CH=CHH-cis), 4.97 (d, 1H, $J$ = 17.2, (CH$_2$)$_2$CH=CHH-trans), 4.92 (d, 1H, $J$ = 10.4, (CH$_2$)$_2$CH=CHH-cis), 3.81 (t, 2H, $J$ = 5.6, NHCH$_2$CH=CH$_2$), 2.16 (t, 2H, $J$ = 7.6, COCH$_2$), 2.04 (q, 2H, $J$ = 7.2, CH$_2$CH=CH$_2$), 1.70 (qn, 2H, $J$ = 7.5, CH$_2$CH$_2$CH$_2$).
$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 173.0, 138.0, 134.4, 116.3, 115.4, 35.9, 33.3, 24.9.
IR $\nu$ 3289, 3077, 2927, 1640, 1543, 911.
HRMS for C$_9$H$_{14}$NO [M–H]$^+$ found 152.10643, calc. 152.10699.

N-Cyclopropylbut-3-enamide:
Yellow oil.
$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 6.53 (br s, 1H, CONH), 5.82 (ddt, 1H, $J$ = 17.1, 10.7, 7.1, C=CH$_2$), 5.10–5.05 (m, 2H, CH=C$_2$H$_2$), 2.88 (d, 2H, $J$ = 7.1, CH$_2$CO), 2.59 (tq, $J$ = 7.3, 3.7, 1H, CHN), 0.66–0.62 (m, 2H, $^3$Pr–H), 0.40 (m, 2H, $^3$Pr–H).
$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 172.5, 131.6, 119.2, 41.4, 22.7, 6.4.
IR $\nu$ 3275, 3081, 1647, 1537, 913.
HRMS for C$_7$H$_{11}$NO [M]$^+$ found 125.08291, calc. 125.08352.

N-(2-(1H-Indol-3-yl)ethyl)-4-phenylbutanamide:
Pale yellow solid. Mp 110–111 °C (PE/Et$_2$O). Lit Mp 112–113 °C (MeOH)$^{[13]}$
$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 8.59 (br s, 1H, indole-NH), 7.60 (d, 1H, $J$ = 7.9, indole-CH), 7.37 (d, 1H, $J$ = 7.9, indole-CH), 7.29–7.24 (m, 2H, ArH), 7.24–7.17 (m, 2H, indole-CH), 7.15–7.10 (m, 3H, ArH), 6.97 (s, 1H, indole-CH), 5.69 (br s, 1H, CONH), 3.59 (q, 2H, $J$ = 6.6, NHCH$_2$), 2.98 (t, 2H, $J$ = 6.6, NHCH$_2$CH$_2$), 2.60 (t, 2H, $J$ = 7.6, PhCH$_2$), 2.11 (t, 2H, $J$ = 7.6, CH$_2$CO), 1.94 (qn, 2H, $J$ = 7.6, CH$_2$CH$_2$CH$_2$).
$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 173.2, 141.6, 136.5, 128.6, 128.5, 127.5, 126.1, 122.4, 122.2, 119.5, 118.8, 112.8, 111.6, 40.0, 36.1, 35.3, 27.3, 25.4.
IR ν 3407, 3284, 2924, 1644, 1526, 1455.
HRMS for C_{20}H_{22}N_{2}O_{3}Na [M+Na]^+ found 329.1628, calc. 329.1630.

\[ \text{N-Benzylbut-2-ynamide:} \]
Pale yellow solid. Mp 114–115 °C (DCM).
Mixture of rotamers in a ratio 1:10.
$^1$H NMR (CDCl$_3$, 600 MHz) δ 7.37–7.31 (m, 2H, ArH), 7.31–7.26 (m, 3H, ArH), 6.02 (br s, 1H, CONH), 4.60/4.47 (minor/major, d, 2H, $J_{\text{minor}} = 6.5$, $J_{\text{major}} = 5.9$, CH$_2$Ph), 2.01/1.93 (minor/major, s, 3H, CH$_3$).
$^{13}$C NMR (CDCl$_3$, 150 MHz, major rotamer) δ 153.4, 137.4, 128.9, 128.0, 127.9, 83.9, 74.8, 43.9, 3.8.
IR ν 3266, 3062, 2253, 1631, 1532, 1287.
HRMS for C$_{11}$H$_{11}$NO [M]^+ found 173.08273, calc. 173.08352.

(E)-N-Benzyl-3-(3-nitrophenyl)acrylamide: \[^{[14]}\]
Pale yellow solid. Mp 185–186 °C (DCM). Lit Mp 184–185 °C. \[^{[14]}\]
$^1$H NMR (CDCl$_3$, 600 MHz) δ 8.31 (s, 1H, ArH), 8.15 (d, 1H, $J = 8.2$, ArH), 7.71 (d, 1H, $J = 7.7$, ArH), 7.66 (d, 1H, $J = 15.6$, ArCH=CH), 7.52 (t, 1H, $J = 8.2$, ArH), 7.34–7.24 (m, 5H, ArH), 6.60 (d, 1H, $J = 15.6$, ArCH=CH), 6.48 (br s, 1H, NH), 4.57 (d, 2H, $J = 5.8$, NHCH$_2$).
$^{13}$C NMR (CDCl$_3$, 150 MHz) δ 165.1, 148.7, 138.8, 138.0, 136.7, 134.1, 130.0, 128.9, 128.0, 127.8, 124.1, 123.7, 121.8, 44.8.
IR ν 3283, 1656, 1619, 1525, 1349, 1221.
HRMS for C$_{16}$H$_{15}$NO [M]^+ found 282.09909, calc. 282.09989.

Purified by column chromatography (PE/EtOAc 1:2).
(E)-N-(4-Methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)acrylamide:
Colourless solid. Mp 191–192 °C (EtOAc/PE).
1H NMR (DMSO-d$_6$, 600 MHz) δ 10.2 (s, 1H, CONH), 7.84 (d, 2H, J = 8.5, ArH), 7.80 (d, 2H, J = 8.5, ArH), 7.66–7.60 (m, 3H, PMPH and ArCH=CH), 6.96–6.90 (m, 3H, PMPH and ArCH=CH), 3.74 (s, 3H, OC$_2$H$_3$).

13C NMR (DMSO-d$_6$, 150 MHz) δ 162.6, 155.5, 138.9, 137.9, 132.3, 129.4 (J = 32.2), 128.3, 125.9 (J = 3.9), 125.3, 124.2 (J = 271.8), 120.7, 114.0, 55.2.

IR ν 3294, 1658, 1622, 1537, 1511, 1326, 1125, 1070.

HRMS for C$_{17}$H$_{15}$F$_3$NO$_2$ [M+H]$^+$ found 322.1057, calc. 322.1055.

(R)-Methyl 3-phenyl-2-(2-phenylacetamido)propanoate:[15]

Colourless solid. Mp 93–94 °C (DCM). Lit Mp 92–94 °C (EtOAc/hexane).[15]

α$_D^{25}$ $–49.1$ (c 1.0, CHCl$_3$). Lit α$_D^{25}$ $–49.5$ (c 1.0, CHCl$_3$).[15]

1H NMR (CDCl$_3$, 600 MHz) δ 7.36.–7.27 (m, 3H, ArH), 7.21–7.16 (m, 5H, ArH), 6.90–6.85 (m, 2H, ArH), 5.80 (d, 1H, J = 6.9, CONH), 4.85 (dt, 1H, J = 7.9, 5.7, NHCH$_3$), 3.70 (s, 3H, CH$_3$), 3.56 (d, 1H, J = 15.9, PhCHHCO), 3.53 (d, 1H, J = 15.9, PhCHHCO), 3.06 (dd, 1H, J = 13.8, 5.8, CHHPh), 2.99 (dd, 1H, J = 13.8, 5.8, CHHPh).

13C NMR (CDCl$_3$, 150 MHz) δ 171.9, 170.6, 135.6, 134.5, 129.5 129.3, 129.1, 128.7, 127.5, 127.2, 53.1, 52.46, 43.8, 37.7.

IR ν 3287, 3063, 3029, 2951, 1744, 1651, 1537, 1496, 1217.

HRMS for C$_{18}$H$_{20}$NO$_3$ [M+H]$^+$ found 298.14468, calc. 298.14431.

tert-Butyl (1-(benzylamino)-1-oxopropan-2-yl)carbamate:[16]

Colourless solid. Mp 100–102 °C (DCM). Lit Mp 104–106 °C (EtOAc/hexane).[16]

α$_D^{22}$ (c 1.9, CHCl$_3$) = $–23.9$. Lit α$_D^{22}$ (c 1.9, CHCl$_3$) = $–24.5$.[16]

1H NMR (CDCl$_3$, 600 MHz) δ 7.33–7.28 (m, 2H, ArH), 7.28–7.22 (m, 3H, ArH), 6.63 (br s, 1H, CONH$_Bn$), 5.07 (m, 1H, CHCH$_3$), 4.43 (br s, 2H, CH$_2$Ph), 4.20 (br s, 1H, BocNH), 1.40 (s, 9H, C(CH$_3$)$_3$), 1.37 (3H, J = 6.8, CHCH$_3$).

13C NMR (CDCl$_3$, 150 MHz) δ 172.7, 155.7, 138.1, 128.8, 127.7, 127.6, 80.3, 50.3, 43.5, 28.4, 18.3.

IR ν 3304, 1695, 1497, 1365, 1162.

HRMS for C$_{16}$H$_{22}$N$_2$O$_3$Na [M+Na]$^+$ found 301.15319, calc. 301.15280.
2.3 Transamidations

Borate (2 equiv) was added to a solution/suspension of amide (1 equiv) and amine (1 equiv) in MeCN (0.5 M) and the mixture was heated at 100 °C in carousel tube. After 15 h, solvent was removed under reduced pressure. The residue was purified by column chromatography (EtOAc/PE 1:1) to give the product.

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\text{N} \\
\text{Ph}
\]

*N-Benzylpropionamide:*\(^{[17]}\)

Colourless solid. Mp 51 °C (EtOAc/PE). Lit Mp 49–50 °C (EtOAc/hexane)\(^{[17]}\)

\(^1\)H NMR (DMSO-\(d_6\), 600 MHz) \(\delta\) 8.28 (s, 1H, CONH), 7.34–7.29 (m, 2H, ArH), 7.25–7.21 (m, 3H, ArH), 4.25 (d, 2H, \(J = 6.0\), NHCH\(_2\)\(_2\)), 2.14 (q, 2H, \(J = 7.7\), CH\(_2\)CH\(_3\)), 1.02 (t, 3H, \(J = 7.7\), CH\(_3\)).

\(^13\)C NMR (DMSO-\(d_6\), 150 MHz) \(\delta\) 172.9, 139.8, 128.3, 127.2, 126.7, 42.0, 28.5, 10.0.

IR \(\nu\) 3282, 3066, 3031, 2977, 2938, 1642, 1541, 1454, 1234, 1029.

HRMS for C\(_{10}\)H\(_{13}\)NO [M]+ found 163.09931, calc. 163.09917.

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*N-Butylpropionamide:*\(^{[18]}\)

Colourless oil.

\(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 5.55 (br s, 1H, CONH), 3.23 (q, 2H, \(J = 6.5\), NHCH\(_2\)\(_2\)), 2.18 (q, 2H, \(J = 7.5\), CH\(_2\)CO), 1.46 (qn, 2H, \(J = 7.5\), NHCH\(_2\)CH\(_2\)), 1.32 (sx, 2H, \(J = 7.5\), CH\(_2\)CH\(_2\)CH\(_3\)), 1.13 (t, 3H, \(J = 7.5\), CH\(_2\)CH\(_2\)CO), 0.90 (t, 3H, \(J = 7.5\), NH(CH\(_2\)\(_3\))=CH\(_3\)).

\(^13\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 174.2, 39.3, 31.7, 29.7, 20.1, 13.8, 10.1.

IR \(\nu\) 3292, 2960, 2933, 1644, 1550, 1464, 1236.

HRMS for C\(_7\)H\(_{15}\)NO [M]+ found 129.11468, calc. 129.11468.

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\text{H}
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*N-Benzyl-2-hydroxyacetamide:*\(^{[19]}\)

Colourless solid. Mp 102–103 °C (EtOAc/hexane). Lit Mp 102–103 °C (DCM).\(^{[19]}\)

\(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 7.35–7.30 (m, 2H, ArH), 7.29–7.24 (m, 3H, ArH), 6.99 (br s, 1H, CONH), 4.45 (d, 2H, \(J = 5.9\), NHCH\(_2\)\(_2\)), 4.09 (s, 2H, HOCH\(_2\)H), OH not observed.

\(^13\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 172.0, 137.8, 128.9, 127.9, 127.8, 62.2, 43.1.
IR ν 3317, 3208, 3058, 3031, 2933, 2857, 1633, 1562, 1453, 1424, 1342, 1082.
HRMS for C₇H₁₁NO₂ [M]+ found 165.07859, calc. 165.07843.
Purified by column chromatography (PE/EtOAc/MeOH 5:5:1).

**N-((1H-indol-3-yl)methyl)-2-hydroxyacetamide**

Colourless solid. Mp 141–142 °C (PE/MeOH).

1H NMR (DMSO-d₆, 600 MHz) δ 10.81 (s, 1H, indole-NH), 7.81 (t, 1H, J = 5.8, CONH), 7.56 (d, 1H, J = 7.9, ArH), 7.33 (d, 1H, J = 7.9, ArH), 7.16 (d, 1H, J = 2.2, ArH), 7.06 (td, 1H, J = 7.4, 0.9, ArH), 6.97 (td, 1H, J = 7.4, 0.9, ArH), 5.49 (t, 1H, J = 5.8, CH₂OH), 3.79 (d, 2H, J = 5.8, CH₂OH), 3.39 (q, 2H, J = 7.1, NHCH₂), 2.83 (t, 2H, J = 7.1, ArCH₂)

13C NMR (DMSO-d₆, 150 MHz) δ 171.6, 136.3, 127.2, 122.6, 121.0, 118.4, 118.2, 111.7, 111.4, 61.5, 38.8, 25.4.

IR ν 3391, 3301, 3260, 1644, 1619, 1543, 1455, 1353, 1223, 1072.
HRMS for C₁₂H₁₃N₂O₂ [M+H]+ found 217.0992, calc. 217.0977.

3 References


S10
http://dx.doi.org/10.1016/S0040-4039(00)74673-9

http://dx.doi.org/10.1021/ja808129p

http://dx.doi.org/10.1080/713744566


http://dx.doi.org/10.1038/nature07870

http://dx.doi.org/10.1002/adsc.200800089

http://dx.doi.org/10.1021/ol050773y


http://dx.doi.org/10.1016/j.tet.2008.08.057

http://dx.doi.org/10.1016/j.tetlet.2008.12.080

http://dx.doi.org/10.1016/j.tet.2008.09.094

http://dx.doi.org/10.1021/jo990221r

4 Spectra

Tris(2,2,2-trifluoroethyl) borate

\[ \text{B(OCH}_2\text{CF}_3)_3 \]
Tris(2,2,2-trifluoroethyl) borate (\(^{19}\text{F}\) and \(^{11}\text{B}\) NMR)

\[ \text{B(OCH}_2\text{CF}_3)_3 \]
$N$-Benzyl-2-phenylacetamide (CDCl$_3$)
N-Benzyl-2-phenylacetamide (DMSO-$d_6$)
N-Butyl-2-phenylacetamide
N-Benzyl-3-methylbutanamide (CDCl₃)
N-Butyl-3-methylbutanamide
$N$-Benzylpivalamide
**N-Benzylbenzamide**

![N-Benzylbenzamide structure](image)

1. **ppm**
   - 0.5
   - 1.0
   - 1.5
   - 2.0
   - 2.5
   - 3.0
   - 3.5
   - 4.0
   - 4.5
   - 5.0
   - 5.5
   - 6.0
   - 6.5
   - 7.0
   - 7.5

2. **Chemical Shifts**
   - 4.6269
   - 4.6349
   - 6.5643
   - 7.2855
   - 7.2917
   - 7.2990
   - 7.3056
   - 7.3425
   - 7.3494
   - 7.4023
   - 7.4147
   - 7.4272
   - 7.4805
   - 7.4928
   - 7.5050
   - 7.7840
   - 7.7963

3. **Chemical Bonding**
   - H
   - N
   - O

---

Supplementary Material (ESI) for Organic & Biomolecular Chemistry

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$N$-(2-Hydroxyethyl)-2-phenylacetamide
(R)-2-Phenyl-N-(1-phenylethyl)acetamide
N-Allylhex-5-enamide
**N-Cyclopropylbut-3-enamide**

![Chemical Structure](image)

**Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

This journal is (c) The Royal Society of Chemistry 2010
**N-(2-(1H-Indol-2-yl)ethyl)-5-phenylbutanamide**

![Chemical Structure]

**NMR Spectra**

[Detailed NMR spectra showing chemical shifts and peak assignments]
**N-Benzylbut-2-ynamide**

![Chemical structure of N-Benzylbut-2-ynamide](image)

---

**Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

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(E)-N-Benzyl-3-(3-nitrophenyl)acrylamide
(E)-N-(4-Methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)acrylamide
(R)-Methyl 3-phenyl-2-(2-phenylacetamido)propanoate
**tert-Butyl (1-(benzylamino)-1-oxopropan-2-yl)carbamate**

![Chemical Structure](image)

The spectrum shows the spectral data for the compound, indicating the presence of signals at various ppm values. The structure is depicted with the Boc protecting group and the benzylamino moiety.

---

**Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

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**tert-Butyl (1-(benzylamino)-1-oxopropan-2-yl)carbamate**

B(OCH$_2$CF$_3$)$_3$  

(S)  

![Chiral HPLC diagram](image)

BocHN\[\text{NH}O\]  

88% ee

(R)  

![Chiral HPLC diagram](image)

BocHN\[\text{NH}O\]  

>99% ee

---

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**B(OMe)$_3$**

(S)  

![Chiral HPLC diagram](image)

BocHN\[\text{NH}O\]  

>99% ee

---

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N-Benzylpropionamide
N-Butylpropionamide
N-Benzyl-2-hydroxyacetamide
**N-((1H-indol-3-yl)methyl)-2-hydroxyacetamide**

![Chemical structure](image)

**NMR Spectra**

**1H NMR (DMSO, p690)**


**13C NMR (DMSO, p690)**

- ppm values: 25.35, 38.80, 61.48, 111.38, 111.74, 118.24, 118.35, 120.96, 122.59, 127.21, 136.26, 171.62

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