SUPPORTING INFORMATION

Iodine as a very powerful catalyst for three component synthesis of protected
homoallylic amines

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CONTENTS

General remark	S2
General procedure for the synthesis of homoallylic amines	S2
Analytical data of compounds	S2
^1H and ^{13}C NMR of compounds	S6

General remark:

Iodine was purified by sublimation before use. Chemical shifts are given in δ units relative to the tetramethylsilane (TMS) signal as an internal reference in CDCl_3 . Coupling constants (J) are reported in hertz.

General procedure for iodine catalysed synthesis of homoallylic amines:

To a solution of aldehyde (1mmol) and iodine (0.1 mmol) in acetonitrile (1 ml), benzyl carbamate (1.05 mmol) was added followed by the addition of allyl trimethyl silane (1 mmol). After completion of reaction (TLC), Sodium thiosulfate (20 mg approx.) was added, the reaction mixture stirred for 20 min. The reaction mixture was taken up in ether, washed with brine, dried (Na_2SO_4) and concentrated. Purification of the crude product by flash chromatography on silica gel (230-400 mesh) with petroleum ether –EtOAc (10-20%) as eluent gave the pure product (66 – 82 %).

Analytical Data of the compounds: **N-Benzyloxycarbonyl-1-phenylbut-3-enylamine (4a)¹**

Colourless solid; mp. 67-68°C (Lit¹ mp (for R-(+)-enantiomer 68-69°C), IR (Nujol, cm^{-1}): 3056, 1714, 1423, 1262, 739. ^1H NMR (400 M Hz, CDCl_3): 7.36-7.24 (m, 5H), 7.24-7.13 (m, 5H), 5.67-5.50 (m, 1H), 5.10-4.94 (m, 5H), 4.81-4.65 (m, 1H), 2.55-2.37 (m, 2H); ^{13}C NMR (100 M Hz, CDCl_3): 155.6, 141.9, 136.4, 133.7, 128.5, 128.4, 128.1, 127.3, 126.2, 118.4, 66.7, 54.4, 41.0. MS (m/z, % rel. intensity): 240 (31), 196 (28), 129 (3), 107 (9), 104 (14), 91 (100), 77 (11), 65 (8).

N-Benzyloxycarbonyl-1-(4-nitrophenyl)but-3-enylamine(4b)

Colourless solid; mp 88-89°C IR (Nujol, cm^{-1}): 3047, 2307, 1719, 1516, 1266, 739. ^1H NMR (400 M Hz, CDCl_3): 8.1 (d, $J = 7.8$ Hz, 2H), 7.35 (d, $J = 7.6$ Hz, 2H) 7.32-6.92 (m, 5H), 5.65-5.45 (m, 1H), 5.23-4.91 (m, 5H), 4.86-4.72 (m, 1H), 2.56-2.30 (m, 2H). ^{13}C NMR (100 M Hz, CDCl_3): 155.5, 149.6, 147.1, 132.4, 128.5, 128.3, 128.2, 127.0, 123.8, 119.7, 67.7, 54.1, 40.7. MS (m/z , % rel. intensity): 285 (6), 241 (13), 191 (2), 177 (2), 152 (16), 108 (4), 91 (100), 77 (4), 65 (4). $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4$ requires C, 66.25; H, 5.56; N, 8.58 %; found: 66.29; H, 5.51; N, 8.63

N-Benzyloxycarbonyl-1-(4-bromophenyl)but-3-enylamine (4c)

Colourless solid, mp 87-88°C IR (Nujol, cm^{-1}): 3055, 1714, 1598, 1418, 1266, 748. ^1H NMR (400 M Hz, CDCl_3): 7.44 (d, $J=8.1$, 2H), 7.40-7.25 (m, 5H), 7.13 (d, $J = 7.7$ Hz, 2H), 5.72-5.54 (m, 1H), 5.22-4.96 (m, 5H), 4.82-4.65 (m, 1H), 2.60-2.36 (m, 2H). ^{13}C NMR (100 M Hz, CDCl_3): 155.6, 141.0, 136.2, 133.2, 131.6, 128.5, 128.2, 127.9, 121.1, 118.9, 66.9, 53.9, 40.8. MS (m/z , % rel. intensity): 320 (8), 274 (10), 253 (6), 185 (36), 105 (34), 91 (100), 77 (41), 65 (6). $\text{C}_{18}\text{H}_{18}\text{BrNO}_2$ requires C, 60.01; H, 5.03; N, 3.89 %; found: C, 59.97; H, 5.07; N, 3.84 %

N-Benzyloxycarbonyl-1-(4-methoxyphenyl)but-3-enylamine (4d)¹

Colourless solid; mp 70-71°C (Lit¹ mp (for S-(-)-enantiomer 67-68°C), IR (Nujol, cm^{-1}): 3055, 1719, 1506, 1427, 1266, 739. ^1H NMR (400 M Hz, CDCl_3): 7.41-7.29 (m, 5H), 7.19 (d, $J = 7.8$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 5.77-5.58 (m, 1H), 5.20-5.00 (m, 5H), 4.80-4.70 (m, 1H), 3.79 (s, 3H), 2.60-2.54 (m, 2H). ^{13}C NMR (100 M Hz, CDCl_3): 158.7, 155.6, 136.4, 133.9, 128.4, 128.0, 127.3, 118.2, 113.8, 86.7, 55.2, 53.9, 40.9. MS (m/z , % rel. intensity): 270 (40), 226 (54), 162 (6), 134 (6), 107 (2), 91 (100), 77 (2), 65 (4). $\text{C}_{19}\text{H}_{21}\text{NO}_3$ requires C, 73.29; H, 6.80; N, 4.50 %; found: C, 73.25; H, 6.82; N, 4.54

N-Benzyloxycarbonyl-1-(3-chlorophenyl)but-3-enylamine (4e)

Colourless solid; mp 62-63°C; IR (Nujol, cm^{-1}): 3055, 1714, 1506, 1266, 739, 702. ^1H NMR (400 M Hz, CDCl_3): 7.41 -7.17 (m, 8H), 7.12 (d, $J = 6.3$ Hz, 1H), 5.72-5.51 (m, 1H), 5.21 - 4.93 (m 5H), 4.82-4.68 (m, 1H), 2.59-2.36 (m, 2H); ^{13}C NMR (100 M Hz, CDCl_3): 155.6, 136.2, 134.4, 133.1, 129.8, 128.5, 128.2, 127.5, 126.3, 124.5, 119.0, 66.9, 53.9, 40.9. MS (m/z , % rel. intensity): 274 (12), 230(18), 166 (5), 141 (67), 113 (25), 91 (100), 77 (42), 65 (5). $\text{C}_{18}\text{H}_{18}\text{ClNO}_2$ requires C, 68.46; H, 5.74; N, 4.43 %; found: C, 68.42; H, 5.69; N, 4.48 %

N-Benzyloxycarbonyl-1-(2-furyl)but-3-enylamine (4f)

Gum; IR (Nujol, cm^{-1}): 3056, 1714, 1516, 1423, 1261, 735. ^1H NMR (400 M Hz, CDCl_3): 7.42-7.27 (m, 6H), 6.29 (dd, $J = 3.3, 1.26$ Hz, 1H), 6.21 -6.13 (m, 1H), 5.78-5.59 (m, 1H), 5.18-5.01 (m, 5H), 4.97-4.80 (m, 1H), 2.58 (t, $J = 6.6$ Hz). ^{13}C NMR (100 M Hz, CDCl_3): 155.6, 141.9, 136.3, 133.3, 128.5, 128.1, 118.6, 110.1, 106.2, 66.9, 48.7, 38.4. $\text{C}_{16}\text{H}_{17}\text{NO}_3$ requires C, 70.83; H, 6.31; N, 5.16 %; found: C, 70.85; H, 6.35; N, 5.13

N-Benzyloxycarbonyl-1-benzylbut-3-enylamine (4g)

Colourless solid; mp 86-87°C; IR (Nujol, cm^{-1}): 3065, 1701, 1520, 1446, 1252, 1040, 744. ^1H NMR (400 M Hz, CDCl_3): 7.52-7.07 (m, 10H), 5.88-5.70 (m, 1H), 5.17-5.00 (m, 4H), 4.65 (d, $J = 6.8$ Hz, 1H), 4.06-3.88 (m, 1H), 2.91 -2.68 (m, 2H), 2.36-2.23 (m, 1H), 2.21=2.04 (m, 1H). ^{13}C NMR (100 M Hz, CDCl_3): 155.7, 137.8, 136.6, 134.1, 129.4, 128.5, 128.4, 128.0, 126.4, 118.2, 66.5, 51.6, 40.4, 38.1. MS (m/z , % rel. intensity): 254 (4), 204 (19), 160 (23), 107 (8), 91 (100), 71 b(6), 65 (5). $\text{C}_{19}\text{H}_{21}\text{NO}_2$ requires C, 77.26; H, 7.17; N, 4.74 %; found: C, 77.19; H, 7.25; N, 4.79%.

N-Benzyloxycarbonyl-1-(2-phenylethyl)but-3-enylamine (4h)

Colourless solid; mp 50-51°C IR (Nujol, cm^{-1}): 3065, 1696, 1534, 1451, 1243, 1045, 739, 698. ^1H NMR (400 M Hz, CDCl_3): 7.32-7.16 (m, 7H), 7.13-7.06 (m, 3H), 5.77-5.60 (m, 1H), 5.10-4.95 (m, 4H), 4.54 (d, $J = 7.8$ Hz, 1H), 3.79-3.63 (m, 1H), 2.68-2.50 (m, 2H), 2.29-2.09 (m, 2H), 1.83-1.70 (m 1H), 1.70-1.55 (m, 1H). ^{13}C NMR (100 M Hz, CDCl_3): 156.2, 141.7, 136.6, 133.9, 128.5, 128.4, 128.3, 128.1, 125.9, 118.1, 66.6, 50.5, 39.5, 36.5, 32.3. MS (m/z , % rel. intensity): 268 (22), 224 (57), 207 (6), 181 (3), 157 (2), 132 (3), 114 (11), 91 (100), 77 (3), 65 (6).

N-Benzyloxycarbonyl-1-heptylbut-3-enylamine (4i)

Colourless solid; mp 51-52°C IR (Nujol, cm^{-1}): 3055, 1710, 1511, 1432, 1261, 739. ^1H NMR (400 M Hz, CDCl_3): 7.43-7.26 (m, 5H), 5.86-5.66 n(m, 1H), 5.19-4.97 (m, 4H), 4.63-4.47 (m, 1H), 3.81-3.56 (m, 1H), 2.34-1.99 (m, 2H), 1.5-1.18 (m, 12H), 0.87 (t, $J = 6.31$ Hz, 3H). ^{13}C NMR (100 M Hz, CDCl_3): 156.0, 136.7, 134.3, 128.5, 128.0, 117.8, 66.5, 50.7, 39.4, 34.6, 31.8, 29.4, 29.2, 25.8, 22.6, 14.0. MS (m/z , % rel. intensity): 262 (9), 218 (43), 197 (94), 154 (26), 129 (16), 103 (23), 91 (100), 86 (37), 69 (75), 55 (39), 43 (80). $\text{C}_{19}\text{H}_{29}\text{NO}_2$ requires C, 75.21; H, 9.63; N, 4.62 %; found: C, 75.27; H, 9.55; N, 4.68 %

N-Benzyloxycarbonyl-1-isopropylbut-3-enylamine (4j)¹

Colourless oil; IR (Nujol, cm^{-1}): 3074, 1696, 1534, 1248, 739. ^1H NMR (400 M Hz, CDCl_3): 7.41-7.27 (m, 5H), 5.84-5.65 (m, 1H), 5.19-4.98 (m, 4H), 4.67-4.52 (m, 1H), 3.66-3.48 (m, 1H), 2.33-2.19 (m, 1H), 2.17-2.04 (m, 1H), 1.80-1.69 (m, 1H), 0.92 (d, $J = 6.8$ Hz, 3H), 0.88 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 M Hz, CDCl_3): 156.3, 136.7, 134.7, 128.5, 128.3, 128.0, 117.4, 66.5, 55.7, 36.8, 31.4, 19.2, 17.7. MS (m/z , % rel. intensity): 206 (16), 162 (20), 107 (3), 91 (100), 77 (2), 65 (5), 43 (4). $\text{C}_{15}\text{H}_{21}\text{NO}_2$ requires C, 72.84; H, 8.56; N, 5.66 %; found: C, 72.80, H, 8.60, N, 5.61 %.

¹ Hunt, J. C. A.; Lloyd, C.; Moody, C. J.; Slawin, A. M. Z.; Takle, A. K. *J. Chem. Soc., Perkin Trans I*, **1999**, 3443