Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Decarboxylative Reduction of Free Aliphatic Carboxylic Acid by Photogenerated Cation Radical

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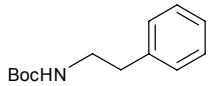
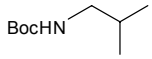
General Procedure for the Photochemical Decarboxylative Reduction

A solution of *N*-Boc amino acid **1** (0.6 mmol, 10 mM), phenanthrene (0.6 mmol, 10 mM), 1,4-dicyanobenzene (0.6 mmol, 10 mM), and *t*-dodecanethiol (1.2 mmol, 20 mM) in aqueous CH_3CN solution (CH_3CN 54 ml, H_2O 6 ml) was purged with argon for 10 min and irradiated through a Pyrex filter with a 400W high-pressure mercury lamp for 6 h. Then the solvent was evaporated, and the resulting residue was dissolved in EtOAc and washed with water, dried over Na_2SO_4, and concentrated under reduced pressure to give **2**. Similar irradiation in the presence of 1 equiv. NaOH (0.6 mmol, 10 mM) of **1**, **4**, **5** afforded the corresponding decarboxylative reduction products. These products were isolated by column chromatography on silica gel using hexane and EtOAc as eluents.

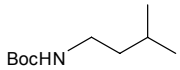
Characterization Data



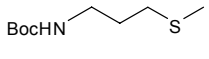
2a[1]: IR (neat, cm^{-1}) 3357, 2962 and 1701; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.18 (m, 5H), 4.55 (s (br), 1H), 3.38 (m, 2H), 2.79 (t, *J*=6.7 Hz, 2H) and 1.41 (s, 9H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 155.8, 139.0, 128.8, 128.5,126.3, 79.2, 41.7, 36.2 and 28.4; MS *m*/*z* 221 (M^+).



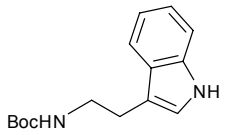
2b[2]: IR (neat, cm^{-1}) 3357, 2963 and 1700; ^1H NMR (500 MHz, $CDCl_3$) δ 4.62 (s (br), 1H), 2.95 (m, 2H), 1.78 (m, 1H), 1.44 (s, 9H) and 0.90 (d, *J*=6.7 Hz, 6H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 156.1, 78.9, 48.0, 28.8, 28.4 and 19.9; MS *m*/*z* 173 (M^+).



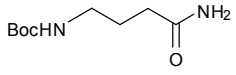
2c: IR (neat, cm^{-1}) 3348, 2962 and 1701; ^1H NMR (500 MHz, $CDCl_3$) δ 4.52 (s (br), 1H), 3.13 (m, 2H), 1.62 (m, 1H), 1.44 (s, 9H), 1.35 (m, 2H) and 0.91 (d, *J*=6.4 Hz, 6H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 156.0, 78.9, 38.9, 28.4, 25.7 and 22.4; MS *m*/*z* 187 (M^+).



2d[3]: IR (neat, cm^{-1}) 3339, 2961 and 1699; ^1H NMR (500 MHz, $CDCl_3$) δ 4.67 (s (br), 1H), 3.22 (m, 2H), 2.52 (t, *J*=7.3 Hz, 2H), 2.10 (s, 3H), 1.78 (m, 2H) and 1.44 (s, 9H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 155.9, 79.2, 39.6, 31.4, 29.3, 28.4 and 15.5; MS *m*/*z* 205 (M^+).

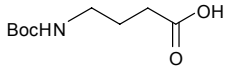


2e[4]: IR (neat, cm^{-1}) 3367, 2953 and 1696; ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (s (br), 1H), 7.59 (d, *J*=7.9 Hz, 1H), 7.32 (d, *J*=7.9 Hz, 1H), 7.19 (t, *J*=7.3 Hz, 1H), 7.10 (t, *J*=7.0 Hz, 1H), 6.97 (s (br), 1H), 4.65 (s (br), 1H), 3.45 (m, 2H), 2.95 (t, *J*=6.7 Hz, 2H) and 1.46 (s, 9H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 156.0, 136.4, 127.5, 122.1, 122.0, 119.3, 118.7, 112.9, 111.2, 79.1, 40.9, 28.4 and 25.7; MS *m*/*z* 260 (M^+).

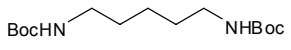


2f[5]: IR (KBr, cm^{-1}) 3358, 3200, 2972, 1696 and 1637; ^1H NMR (500 MHz, $CDCl_3$) δ 6.23 (s (br), 1H), 5.52 (s (br), 1H), 4.80 (s (br), 1H), 3.20 (m, 2H), 2.28 (t, *J*=7.0 Hz, 2H),

1.82 (m, 2H) and 1.44 (s, 9H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 175.1, 156.6, 79.4, 39.6, 32.8, 28.1 and 26.3.

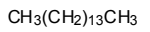


2g[5,6]: IR (neat, cm^{-1}) 3348, 2972 and 1701; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.68 (s (br), 1H), 3.20 (m, 2H), 2.39 (t, *J*=7.3Hz, 2H), 1.82 (m, 2H) and 1.44 (s, 9H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 177.9, 156.6, 79.5, 39.7, 31.2, 28.3 and 25.2.

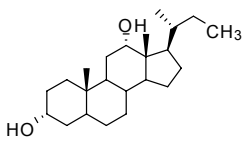


2h: IR (KBr, cm^{-1}) 3357, 2982 and 1691; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.54 (s (br), 2H), 3.11 (m, 4H), 1.55 (m, 4H), 1.44 (s (br), 18H) and 1.32 (m, 2H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 156.0, 77.2, 40.3, 29.7, 28.4 and 23.8.

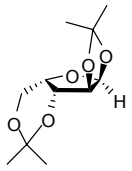
2i[7]: IR (neat, cm^{-1}) 3339, 2961 and 1699; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.30 (m, 4H), 1.82 (m, 4H) and 1.43 (s, 9H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 154.7, 78.9, 45.8, 28.5 and 25.7; MS *m*/*z* 171 (M^+).



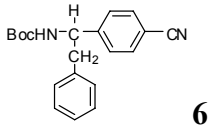
Decarboxylative reduction product of **3**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31-1.19 (m, 26H) and 0.88 (t, *J*=7.0 Hz, 6H); MS *m*/*z* 212 (M^+).



Decarboxylative reduction product of **4**[8]: IR (neat, cm^{-1}) 3397 and 2933; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.00 (t, *J*=3.0 Hz, 1H), 3.62 (m, 1H), 1.88-0.94 (m, 24H), 0.88 (s, 3H), 0.82 (m, 3H) and 0.68 (s, 3H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 73.2, 71.8, 48.2, 47.3, 46.4, 42.1, 36.7, 36.4, 36.0, 35.2, 34.1, 33.6, 30.5, 28.4, 28.1, 27.4, 27.1, 26.1, 23.6, 23.1, 17.1, 12.7 and 10.3.



Decarboxylative reduction product of **5**[9]: IR (neat, cm^{-1}) 2962; ^1H NMR (500 MHz, $CDCl_3$) δ 6.00 (d, *J*=3.6 Hz, 1H), 4.52 (d, *J*=3.9 Hz, 1H), 4.26 (s, 1H), 4.15-3.99 (m, 3H), 1.49 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H) and 1.32 (s, 3H) ; ^{13}C NMR(125 MHz, $CDCl_3$) δ 116.6, 105.2, 97.5, 84.7, 73.2, 71.6, 60.2, 28.9, 26.7, 26.1 and 18.7.



6: IR (KBr, cm^{-1}) 3387, 2982, 2232 and 1686; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J*=2.2 Hz, 2H), 7.28-7.21 (m, 5H), 7.06 (d, *J*=2.2 Hz, 2H), 4.93 (s (br), 2H), 3.01 (s (br), 2H) and 1.35 (s, 9H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 154.9, 136.2, 132.2,129.2, 128.5, 127.2, 127.1, 126.9, 118.7, 111.0, 80.1, 55.7, 42.9 and 28.2.

References

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