Molecular Iodine-Catalyzed Facile Procedure for *N*-Boc Protection of Amines

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SUPPORTING INFORMATION

CONTENTS:

General Information-Experimental	S2
Experimental Procedure for <i>N</i> -Boc protection	S2
Characterization data for selected <i>N</i> -Boc protected amines	S3-S11
Copies of ¹ H NMR for Selected <i>N</i> -Boc protected compounds	S12-S26
Proof of Evidence for I ₂ -catalyzed <i>N</i> -Boc protection of amines	S27-S28

Experimental

All commercially available reagents were used without further purification unless otherwise noted. Thin layer chromatography was conducted on silica gel 60 F254 plates (250 μm thickness). The combined organic layers were dried over Na_2SO_4 . Solvents were evaporated under reduced pressure. Column chromatography was performed with silica gel (60-120 mesh). All yields given refer to as isolated yields. IR spectra were recorded on a FT-IR spectrometer. NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts are reported in ppm. Coupling constants (J values) are reported in Hertz. MS experiments were performed on a low resolution magnetic sector mass spectrometer. Optical rotations were measured on a precision automated polarimeter.

General Procedure for Preparation of *N*-Boc-Amines: To a magnetically stirred mixture of amine (1 mmol) and $(\text{Boc})_2\text{O}$ (1 mmol), a catalytic amount of iodine (10 mol%) was added under solvent-free conditions at room temperature. After stirring the reaction mixture for the specified time (Tables 2-4), diethyl ether (10 mL) was added. The reaction mixture was washed with $\text{Na}_2\text{S}_2\text{O}_3$ (5%, 5 mL) and saturated NaHCO_3 , dried over Na_2SO_4 and the solvent was rotavaped under reduced pressure and purified the residue by silica gel column chromatography (60-120, 5-15% EtOAc in hexane) to afford the corresponding pure product.

Previously reported materials were characterized by comparison of their NMR and mass spectra with those of authentic samples. All novel compounds gave satisfactory spectroscopic data in accordance to their proposed structures.

Spectral Data for Selected Compounds:

- 1. *tert*-butyl 4-methyl-1-piperazinecarboxylate (entry 5, Table 2):** IR (neat): ν 2990, 2984, 1680, 1451, 1407, 1358, 1266, 1245, 1164, 1119, 1079, 857 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.45 (s, 9H), 2.26 (s, 3H), 2.32 (t, $J=5.28$ Hz, 4H), 3.40 (t, $J=5.28$ Hz, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 28.3, 43.4, 46.0, 54.7, 79.5, 154.6; EI-MS: 200 (M^+); Analysis: $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_2$ requires C: 59.97; H: 10.06; N: 13.99 found C: 59.88; H: 10.24; N: 14.03; A copy of the ^1H NMR spectrum is provided.
- 2. *tert*-butyl 4-phenyl-1-piperazinecarboxylate (entry 6, Table 2):** IR (neat): ν 2974, 2924, 2857, 2820, 1695, 1599, 1498, 1420, 1365, 1230, 1168, 1124, 1001, 916 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 1.40 (s, 9H), 3.02 (t, $J=5.28$ Hz, 4H), 3.48 (t, $J=5.28$ Hz, 4H), 6.75-6.99 (m, 2H), 7.11-7.12 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 28.3, 49.3, 50.5, 52.7, 79.7, 116.6, 120.2, 129.1, 151.3, 154.7; EI-MS: 262 (M^+); Analysis: $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_2$ requires C: 68.67, H: 8.45, N: 10.68 found C: 68.65, H: 8.52, N: 10.71; A copy of the ^1H NMR spectrum is provided.
- 3. *tert*-butyl 4-benzyl-1-piperazinecarboxylate (entry 7, Table 2):** IR (neat): ν 2974, 2929, 2808, 1695, 1454, 1419, 1365, 1242, 1170, 1125, 1003, 866 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 1.44 (s, 9H), 2.42 (t, $J=4.68$ Hz, 4H), 3.43 (t, $J=4.68$ Hz, 4H), 3.52 (s, 2H), 7.24-7.37 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 28.1, 43.1, 52.8, 60.3, 63.0, 79.6, 127.3, 128.3, 129.3, 137.2, 154.7; EI-MS: 276 (M^+); Analysis: $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_2$ requires C: 69.53, H 8.75, N: 10.14 found C: 69.49, H 8.81, N: 10.11; A copy of the ^1H NMR spectrum is provided.
- 4. *tert*-butyl 4-(2-pyridyl)-1-piperazinecarboxylate (entry 9, Table 2):** IR (neat): ν 2997, 2980, 2914, 2837, 1690, 1593, 1481, 1434, 1241, 1164, 1125, 979, 772 cm^{-1} ; ^1H NMR

(200 MHz, CDCl₃): δ 1.47 (s, 9H), 2.96 (t, $J=5.28$ Hz, 4H), 3.47 (t, $J=5.28$ Hz, 4H), 6.54-6.61 (m, 2H), 7.40-7.46 (m, 1H), 8.11-8.14 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 28.2, 44.8, 45.1, 79.6, 107.0, 113.4, 137.3, 137.4, 147.7, 154.6, 159.1; EI-MS: 263 (M⁺); Analysis: C₁₄H₂₁N₃O₂ requires C: 63.85, H: 8.04, N: 15.96 found C: 63.80, H: 8.12, N: 16.01; Copies of the ¹H and ¹³C NMR spectra are provided.

5. ***tert*-butyl 4-(2-pyrimidinyl)-1-piperazinecarboxylate (entry 10, Table 2):** IR (neat): ν 2988, 2922, 2851, 2717, 1737, 1646, 1586, 1549, 1493, 1445, 1358, 1272, 1262, 981, 799 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 1.48 (s, 9H), 3.47 (t, $J=5.28$ Hz, 4H), 3.79 (t, $J=5.28$ Hz, 4H), 6.45 (m, 1H), 8.27 (d, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 28.7, 43.9, 46.1, 45.0, 80.3, 110.5, 155.2, 158.1, 162.0; EI-MS: 264 (M⁺); Analysis: C₁₃H₂₀N₄O₂ requires C: 59.07, H: 7.63, N: 21.20 found C: 59.04, H: 7.72, N: 21.18; A copy of the ¹H NMR spectrum is provided.

6. ***tert*-butyl *N*-undecylcarbamate (entry 2, Table 3):** IR (neat): ν 3378, 2919, 2851, 1688, 1522, 1474, 1364, 1174, 868, 761, 583 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 0.88 (t, $J=6.79$ Hz, 3H), 1.27-1.43 (m, 18H), 1.53 (s, 9H), 3.09 (q, $J=6.79$ Hz, 2H), 4.38 (br s, 1H, NH); ¹³C NMR (75 MHz, CDCl₃): δ 14.0, 22.6, 26.8, 27.4, 28.4, 29.3, 29.5, 29.6, 29.8, 30.1, 31.8, 53.6, 78.9, 156.0; EI-MS: 271(M⁺); Analysis: C₁₆H₃₃NO₂ requires C: 70.80, H: 12.25, N: 5.16 found C: 70.74, H: 12.36, N: 5.11; A copy of the ¹H NMR spectrum is provided.

7. ***tert*-butyl *N*-allyl carbamate (entry 3, Table 3):** IR (neat): ν 3415, 2923, 2853, 2361, 1750, 1435, 1369, 1246, 1170, 1074, 761 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 1.42 (s, 9H), 3.69-3.73 (m, 2H), 4.49 (br s, 1H), 5.07 (d, $J=11.71$ Hz, 2H), 5.74-5.87 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 28.3, 43.1, 79.4, 115.6, 134.9, 155.7; EI-MS: 157 (M⁺);

Analysis: C₈H₁₅NO₂ requires C: 61.12, H: 9.62, N: 8.91 found C: 61.09, H: 9.68, N: 8.88;

A copy of the ¹H NMR spectrum is provided.

8. *tert*-butyl *N,N*-diallyl carbamate (entry 4, Table 3): IR (neat): ν 2987, 2921, 1745, 1642, 1443, 1256, 1077, 757 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 1.45 (s, 9H), 3.77 (m, 4H), 5.09 (d, J =8.31 Hz, 4H), 5.73 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 28.6, 48.7, 79.5, 116.3, 134.0, 155.4; EI-MS: 197 (M⁺); Analysis: C₁₁H₁₉NO₂ requires C: 66.97, H: 9.71, N: 7.10 found C: 66.84, H: 9.79, N: 7.04; A copy of the ¹H NMR spectrum is provided.

9. *tert*-butyl *N*-(2-hydroxyethyl)carbamate (entry 5, Table 3): IR (neat): ν 3357, 2976, 2933, 1690, 1525, 1366, 1279, 1251, 1171, 1068, 864 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 1.44 (s, 9H), 3.25 (distorted triplet, J =3.77 Hz, 2H), 3.64 (distorted triplet, J =3.77 Hz, 2H), 5.16 (br s, 1H, NH); ¹³C NMR (75 MHz, CDCl₃): δ 28.3, 43.0, 61.9, 79.5, 156.4; EI-MS: 161 (M⁺); Analysis: C₇H₁₅NO₃ requires C: 52.16, H: 9.38, N: 8.69 found C: 52.11, H: 9.42, N: 8.64; A copy of the ¹H NMR spectrum is provided.

10. *tert*-butyl *N*-benzylcarbamate (entry 8, Table 3): IR (neat): ν 3338, 2978, 2925, 1691, 1440, 1230, 1158, 876 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 1.50 (s, 9H), 4.24 (d, J =5.84 Hz, 2H), 4.85 (br s, 1H), 7.17-7.26 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ 28.3, 44.5, 127.2, 127.3, 128.4, 138.8, 155.8; EI-MS: 207 (M⁺); Analysis: C₁₂H₁₇NO₂ requires C: 69.54, H: 8.27, N: 6.76 found C: 69.49, H: 8.34, N: 6.73; A copy of the ¹H NMR spectrum is provided.

11. *tert*-butyl *N,N*-dibenzylcarbamate (entry 9, Table 3): IR (neat): ν 2921, 1685, 1445, 1401, 1228, 1160, 1112, 870 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 1.51 (s, 9H), 4.48 (br s, 4H), 7.30-7.72 (m, 10H); ¹³C NMR (75 MHz, CDCl₃): δ 28.1, 48.9, 80.1, 127.4, 127.9,

128.7, 138.2, 156.3; EI-MS: 297 (M^+); Analysis: $C_{19}H_{23}NO_2$ requires C: 76.74, H: 7.79, N: 4.71 found C: 76.71, H: 7.85, N: 4.68.

12. *tert*-butyl *N*-(4-methoxyphenyl)carbamate (entry 12, Table 3): IR (neat): ν 3434, 2925, 2360, 1704, 1625, 1525, 1238, 1158, 1055, 1021, 762 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 1.49 (s, 9H), 3.76 (s, 3H), 6.27 (br s, 1H), 6.75 (d, $J=8.76$ Hz, 2H), 7.23 (d, $J=12.42$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.3, 55.5, 80.2, 114.2, 120.8, 131.4, 153.3, 155.7; EI-MS: 223 (M^+); Analysis: $C_{12}H_{17}NO_3$ requires C: 64.56, H: 7.67, N: 6.27 found C: 64.49, H: 7.75, N: 6.22; A copy of the 1H NMR spectrum is provided.

13. *tert*-butyl *N*-(4-nitrophenyl)carbamate (entry 14, Table 3): IR (neat): ν 3380, 2990, 2965, 1718, 1588, 1522, 1492, 1461, 1365, 1305, 1281, 1220, 1106, 840 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 1.53 (s, 9H), 4.29 (br s, 1H), 6.63 (d, $J=9.36$ Hz, 2H), 8.05 (d, $J=8.57$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.1, 51.5, 113.0, 125.3, 126.3, 137.6, 152.7; EI-MS: 238 (M^+); Analysis: $C_{11}H_{14}N_2O_4$ requires C: 55.46, H: 5.92, N: 11.76 found C: 55.42; H: 5.89; N: 11.81; A copy of the 1H NMR spectrum is provided.

14. *tert*-butyl *N*-(1-naphthyl)carbamate (entry 15, Table 3): IR (neat): ν 3262, 2974, 2928, 1692, 16292, 1536, 1513, 1498, 1449, 1365, 1240, 1248, 1157, 996, 765 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 1.55 (s, 9H), 6.81 (br s, 1H, NH), 7.41-7.89 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.3, 80.7, 118.7, 120.5, 124.5, 126.0, 128.7, 133.0, 134.1, 153.6; EI-MS: 243 (M^+); Analysis: $C_{15}H_{17}NO_2$ requires C: 74.05, H: 7.04, N: 5.76 found C: 73.99, H: 7.11, N: 5.72.

15. *tert*-butyl *N*-(2-aminophenyl)carbamate (entry 16, Table 3): IR (neat): ν 3445, 3350, 3300, 3120, 2975, 1677, 1622, 1587, 1513, 1484, 1444, 1365, 1294, 1248, 1159, 1049, 740 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 1.51 (s, 9H), 3.28 (br s, 2H), 6.24 (br s, 1H),

6.61-6.73 (m, 2H), 7.19–7.30 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 28.0, 80.4, 117.8, 119.8, 124.9, 125.0, 126.0, 139.7, 154.2; EI-MS: 208 (M^+); Analysis: $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2$ requires C: 63.44, H: 7.74, N: 13.45 found C: 63.39, H: 7.61, N: 13.62; A copy of the ^1H NMR spectrum is provided.

16. *tert*-butyl *N*-(2-hydroxyphenyl)carbamate (entry 17, Table 3): IR (neat): ν 3423, 3286, 3300, 2982, 2926, 1689, 1622, 1612, 1523, 1455, 1444, 1325, 1151, 1054, 749 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.52 (s, 9H), 6.71-7.42 (m, 4H), 6.58 (br s, 1H), 8.00 (br s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 28.5, 82.0, 118.5, 120.7, 121.2, 125.4, 147.3, 154.9; EI-MS: 209 (M^+); Analysis: $\text{C}_{11}\text{H}_{15}\text{NO}_3$ requires C: 63.14, H: 7.23, N: 6.69 found C: 63.09, H: 7.25, N: 6.72.

17. *tert*-butyl *N*-(2-sulfanyphenyl)carbamate (entry 18, Table 3): IR (neat): ν 3381, 2977, 2931, 1805, 1713, 1576, 1509, 1431, 1156, 752 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.49 (s, 9H), 4.27 (br s, 1H, NH), 7.21-7.55 (m, 3H), 8.23 (d, J = 6.79 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 28.2, 80.8, 118.7, 119.8, 123.1, 131.7, 136.6, 139.9, 152.7; EI-MS: 225 (M^+); Analysis: $\text{C}_{11}\text{H}_{15}\text{NO}_2\text{S}$ requires C: 58.64, H: 6.71, N: 6.22 found C: 58.60, H: 6.77, N: 6.18.

18. *tert*-butyl 1*H*-1-imidazolecarboxylate (entry 20, Table 3): IR (neat): ν 3364, 2975, 2930, 1725, 1699, 1502, 1308, 1165, 1070, 1015 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.63 (s, 9H), 7.02 (s, 1H), 7.33 (s, 1H), 8.04 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 27.6, 85.6, 117.2, 130.3, 137.2, 147.4; EI-MS: 168 (M^+); Analysis: $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2$ requires C: 57.13, H: 7.19, N: 16.66 found C: 57.11, H: 7.12, N: 16.69; A copy of the ^1H NMR spectrum is provided.

19. *tert*-butyl *N*-(2-pyridyl)carbamate (entry 24, Table 3): IR (neat): ν 3215, 2981, 1713, 1580, 1538, 1471, 1435, 1307, 1231, 1150, 773 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.51 (s, 9H), 6.94 (m, 1H), 7.64 (dd, $J=7.88$, 8.59 Hz, 1H), 7.93 (d, $J=8.59$ Hz, 2H), 8.33 (d, $J=4.68$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 28.5, 80.8, 112.6, 118.1, 138.7, 147.7, 152.9, 153.2; EI-MS: 194 (M^+); Analysis: $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$ requires C: 61.84, H: 7.26, N: 14.42 found C: 61.79, H: 7.32, N: 14.37.

20. *tert*-butyl *N*-(1*H*-benzo[d]imidazol-2-yl)carbamate (entry 25, Table 3): IR (neat): ν 3425, 3307, 2982, 1729, 1663, 1460, 1342, 11546, 840, 746 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.73 (s, 9H), 6.22 (br s, 1H, NH), 6.95-7.18 (d, $J=7.81$ Hz, 2H), 7.44-7.55 (d, $J=7.81$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 28.1, 85.8, 113.9, 116.3, 120.6, 124.3, 130.3, 142.2, 150.7, 154.0; EI-MS: 233 (M^+); Analysis: $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_2$ requires C: 61.79, H: 6.48, N: 18.01 found C: 61.71, H: 6.52, N: 17.98.

21. *tert*-butyl *N*-(1*H*-1,2,3,4-tetraazol-5-yl)carbamate (entry 27, Table 3): IR (neat): ν 3380, 2981, 2929, 2361, 1805, 1758, 1581, 1459, 1371, 1259, 1119, 1071, 798 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.53 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 28.2, 79.8, 153.2, 160.8; EI-MS: 185 (M^+); Analysis: $\text{C}_6\text{H}_{11}\text{N}_5\text{O}_2$ requires C: 38.92, H: 5.99, N: 37.82 found C: 38.74, H: 6.05, N: 37.91.

22. *tert*-butyl *N*-[(1*R*)-1-phenylethyl]carbamate (entry 28, Table 3):^{6b,c} IR (neat): ν 3387, 3028, 1686, 1663, 1507, 1443, 1389, 1365, 1305, 1244, 1168, 1069, 747 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.43 (s, 9H), 1.39 (s, 3H), 4.78 (br s, 1NH and CH, 2H), 7.19-7.35 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 22.6, 28.1, 50.2, 79.6, 125.8, 127.1, 128.5, 144.0, 155.3; EI-MS: 221 (M^+); Analysis: $\text{C}_{13}\text{H}_{19}\text{NO}_2$ requires C: 70.56, H: 8.65, N: 6.33 found

C: 70.49, H: 8.71, N: 6.35; $[\alpha]_D^{25}$: + 29.1 (c = 10, EtOH), after deprotection and comparing with literature value; Optical purity: 97%.^{11c}

23. *tert*-butyl 2-(2-phenylacetyl)-1-hydrazinecarboxylate (entry 29, Table 3): IR (neat): ν 3469, 3197, 2981, 2928, 1717, 1677, 1657, 1535, 1250, 1166, 724 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.52 (s, 9H), 3.58 (s, 2H), 6.52 (1H, NHCO), 7.17-7.32 (m, 5H), 7.52 (1H, NH); ^{13}C NMR (75 MHz, CDCl_3): δ 28.0, 46.2, 80.9, 126.1, 128.9, 129.4, 129.8, 155.5, 166.3; EI-MS: 250 (M^+); Analysis: $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_3$ requires C: 62.38, H: 7.25, N: 11.19 found C: 62.29, H: 7.21, N: 11.28.

24. *N*-(*tert*-butoxy carbonyl)-4-methyl-1-benzenesulfonamide (entry 31, Table 3): IR (neat): ν 3360, 3338, 3123, 2991, 1798, 1755, 1448, 1370, 1302, 1208, 1150, 1066, 768, 660 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.50 (s, 9H), 2.21 (s, 3H), 5.19 (br s, 1H, NH), 7.29 (d, 2H), 7.79 (d, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.5, 27.4, 85.1, 126.4, 129.4, 139.2, 143.5, 146.7; EI-MS: 271 (M^+); Analysis: $\text{C}_{12}\text{H}_{17}\text{NO}_4\text{S}$ requires C: 53.12, H: 6.31, N: 5.16 found C: 53.09, H: 6.42, N: 5.11.

25. *tert*-butyl 2,2-dimethyl-1-hydrazinecarboxylate (entry 32, Table 3): IR (neat): ν 3254, 2972, 2849, 1707, 1505, 1440, 1364, 1241, 1179, 1089 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.51 (s, 9H), 2.69 (s, 6H), 5.48 (br s, 1H, NH); ^{13}C NMR (75 MHz, CDCl_3): δ 28.0, 47.5, 80.2, 154.7; EI-MS: 160 (M^+); Analysis: $\text{C}_7\text{H}_{16}\text{N}_2\text{O}_2$ requires C: 52.48, H: 10.07, N: 17.48 found C: 52.41, H: 10.11, N: 17.37.

26. *N*-(*tert*-butoxy carbonyl)-methane sulfonamide (entry 33, Table 3): IR (neat): ν 3337, 2983, 2939, 1808, 1762, 1462, 1372, 1311, 1213, 1120, 1069, 845 cm^{-1} ; ^1H -NMR (300 MHz, CDCl_3): δ 1.52 (s, 9H), 2.97 (s, 3H), 4.41 (br s, 1H, NH); ^{13}C NMR (75 MHz,

CDCl₃): δ 28.0, 46.4, 80.5, 151.2; EI-MS: 195 (M⁺); Analysis: C₆H₁₃NO₄S requires C: 36.91, H: 6.71, N: 7.17 found C: 36.88, H: 6.79, N: 7.07.

27. *tert*-butyl 2-oxo-1,3-oxazolan-3-carboxylate (entry 34, Table 3): IR (neat): ν 2922, 2852, 1685, 1526, 1458, 1314, 1263, 1169, 1010, 759 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.55 (s, 9H), 3.57-3.69 (t, J =7.81 Hz, 2H), 4.42-4.47 (t, J =7.81 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 27.3, 40.5, 64.9, 85.1, 146.6, 160.9; EI-MS: 187 (M⁺); Analysis: C₈H₁₃NO₄ requires C: 51.33, H: 6.99, N: 7.48 found C: 51.29, H: 7.02, N: 7.47.

28. *tert*-butyl *N*-[(1*S*)-1-benzyl-2-hydroxyethyl]carbamate (entry 1, Table 4): IR (neat): ν 3416, 2983, 2934, 1806, 1755, 1481 1372, 1213, 1119, 1073, 844, 770 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.43 (s, 9H), 2.83-2.86 (d, J =7.03 Hz, 2H), 3.55-3.88 (m, 1H), 4.65 (m, 2H), 7.16-7.33 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ 27.9, 56.8, 66.6, 79.9, 126.7, 127.8, 128.8, 139.8, 156.5; EI-MS: 251 (M⁺); Analysis: C₁₄H₂₁NO₃ requires C: 66.91, H: 8.42, N: 5.57 found C: 66.89, H: 8.51, N: 5.51; $[\alpha]_D^{25}$: - 26.9 (c = 1, CHCl₃).¹¹

29. *tert*-butyl *N*-[(1*S*)-1-(hydroxymethyl)-2,2-dimethylpropyl]carbamate (entry 2, Table 4): IR (neat): ν 3370, 3257, 3072, 2965, 2871, 1682, 1657, 1563, 1475, 1366, 1295, 1179, 1068, 754, 629 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 0.95 (s, 9H), 1.45 (s, 9H), 3.42-3.49 (m, 1H), 3.77-3.88 (m, 1H), 4.49-4.66 (m, 1H), 7.18 (1H, NH); ¹³C NMR (75 MHz, CDCl₃): δ 26.7, 28.3, 33.6, 60.8, 62.9, 79.5, 157.1; EI-MS: 217 (M⁺); Analysis: C₁₁H₂₃NO₃ requires C: 60.80, H: 10.67, N: 6.45 found C 60.79, H: 10.71, N: 6.48; $[\alpha]_D^{25}$: - 7.0 (c = 1, CHCl₃).¹¹

30. *S*-1,5-Dimethyl-2-[(*tert*-butoxycarbonyl)amino] pentanedioate (entry 4, Table 4): IR (neat): ν 3436, 3025, 2965, 2981, 1732, 1714, 1682, 1657, 1503, 1369, 1168, 1068, 754, 629 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.43 (s, 9H), 1.85-2.00 (m, 1H), 2.10-2.25 (m,

1H), 2.34-2.45 (t, 2H), 3.62-3.78 (s, 3H), 3.80- 3.98 (s, 3H), 4.27 (dd, 1H, CH), 5.17 (br s, 1H, NH); ^{13}C NMR (75 MHz, CDCl_3): δ 27.7, 28.2, 30.0, 51.7, 52.3, 52.8, 79.9, 155.3, 172.6, 173.1; FAB-MS: 276 ($\text{M}^+ + \text{H}$); Analysis: $\text{C}_{12}\text{H}_{21}\text{NO}_6$ requires C: 52.35, H: 7.69, N: 5.09 found C: 52.26, H: 7.81, N: 5.05; $[\alpha]_{\text{D}}^{25}$: + 12.5 ($c = 2$, CHCl_3);^{11a} Optical purity: 96.89%. HPLC retention time (t_R) 4.683 min (purity (area %) 95.80 at 230 nm).

Table 1, Entry 5

Table 2, Entry 6

Table 3, Entry 7

Table 1, Entry 9

Entry 9, Table 2

Table 2, Entry 10

Table 3 Entry 2

Table 3, Entry 3

Table 3, Entry 4

Table 3, Entry 5

Table 3, Entry 8

Table 3, Entry 11

Table 3 Entry 13

Table 3, Entry 16

Table 3, Entry 19

Some preliminary experiments were carried out in order to understand the reaction mechanism for the formation of N-Boc amines:

To explore mechanism of iodine-catalyzed in N-Boc protection of amines, IR spectrum of a mixture of 1 equiv. I_2 and 1 equiv. $(Boc)_2O$ was recorded. Two frequency bands of C=O stretching vibration of carbonyl oxygen atoms were observed in the region of 1807.33 and 1761.20 cm^{-1} . Comparing the frequency of free carbonyl oxygen atoms of $(Boc)_2O$ at 1808.87 and 1761.91 cm^{-1} (as doublet due to Fermi resonance), the *shift of vibration frequency* implicated the possible coordination of I_2 with $(Boc)_2O$. The 1H NMR spectrum of the mixture of 1 equiv. I_2 and 1 equiv. $(Boc)_2O$ in $CDCl_3$ showed that the chemical shift of the proton attached to methyl protons of *t*-butyl group was 1.524. The chemical shift of the same proton in methyl protons of free $(Boc)_2O$ was 1.531.

“ Proposed Mechanism for Iodine-Catalyzed N-Boc Protection of Amines”.

The change of *chemical shift* also suggested a possible coordination of I_2 with $(Boc)_2O$. As already mentioned, the formation of N-Boc protected amine **3** (IR frequency of C=O of **3** 1688.33 cm^{-1} and 1H NMR value of **3**: 1.514) is occurring by addition of catalytic amount of I_2 with exothermicity and commencement of effervescence (evolution of CO_2 is observed-Lime water test = +ve).

¹H NMR Spectral Record (evidence)

chemical shift change of *t*-Bu protons
for a possible coordination of I₂ with (Boc)₂O

Thus, following mechanism can be proposed for the reaction. Both the carbonyl oxygen atoms of (Boc)₂O are activated by iodine (TS I, 2) initially, making the carbonyl group more susceptible to nucleophilic attack by amine 1 in one-pot. This facilitates the extrusion of *t*-butanol and carbon dioxide as leaving entities eventually leading to the formation of *N*-Boc protected amine 3.