Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Preparation, characterization and application of succinimidinium hydrogensulfate ([H-Suc]HSO_4) as an efficient ionic liquid catalyst for the *N*-Boc protection of amines

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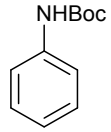
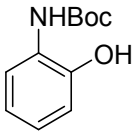
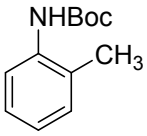


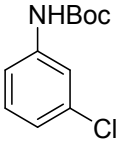
White solid, Mp: 132-133°C. IR (KBr) υ: 1689 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 1.51(s, 9H), 6.55 (bs, 1H), 6.99-7.04 (m, 1H), 7.24-7.36(m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ : 28.3, 80.4, 118.5, 122.9, 128.9, 138.3, 152.7.



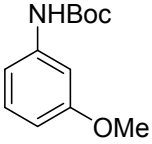
White solid, m.p. 141-143 °C dec.; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.53 (s, 9H, Boc), 6.71 (br s, 1H, NH), 6.85 (t *J*= 8.0 Hz, 1H, Ar CH), 6.96 (d *J*=8.0 Hz, 1H, Ar CH), 7.03 (t *J*= 8.0 Hz, 1H, Ar CH), 7.10 (d *J*=8.0 Hz, 1H, Ar CH) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 28.3, 82.1, 118.9, 120.7, 121.4, 125.6, 147.4, 155.0.



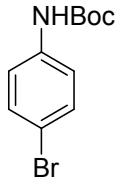
White Solid, yield 92 %; IR (KBr) :1693 cm-1; 1H NMR (CDCl3, 300 MHz) *d* : 1.52 (s,9H), 2.23 (s,3 H), 6.26 (bs, 1H), 6.95-7.06 (m, 1H), 7.11-7.20 (m, 2H), 7.78 (d, *J* =7.5 Hz, 1H).



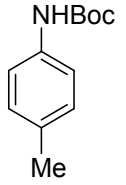
Mp: 69-70°C IR (KBr): 3368, 3306, 2987, 2938, 1695, 1592, 1519, 1400, 1268, 1237, 1178 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): d = 1.51 (s, 9H), 6.53 (br s, 1H), 7.0 (d, 1H, *J* = 6.75 Hz), 7.13–7.21 (m, 2H), 7.52 (s, 1H). 13C NMR ($CDCl_3$, 75 MHz) d = 28.29, 81.02, 116.37, 118.48, 123.02, 129.91, 134.72, 139.54, 152.43.



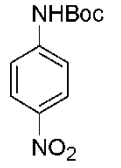
Brown solid, m.p. 54-56 °C; IR (KBr): υ 3320, 2990, 2920, 1690, 1600, 1530, 1450, 1420, 1362, 1285, 1240, 1160, 1045, 1032, 960, 870, 842 cm^{-1}; ^1H NMR (DMSO, 300 MHz): δ 1.46 (s, 9H), 3.69 (s, 3H), 6.52 (d, *J*=7.6 Hz, 1H), 6.99 (d, *J*=7.6 Hz, 1H), 7.14 (d, *J*=7.6 Hz, 2H), 9.31 (s, 1H); ^{13}C NMR (DMSO, 75 MHz): δ 28.5, 55.3, 79.4, 104.3, 107.8, 110.8, 129.8, 141.2, 153.1, 160.0.



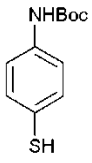
White solid, Mp: 102 °C. IR (KBr) υ: 1690 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.51 (s, 9H), 6.50 (bs, 1H), 7.25 (d, *J*= 7.53 Hz, 2H), 7.38 (d, *J* = 7.10 Hz, 2H).



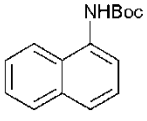
White solid, m.p. 86-87°C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.52 (s, 9H, Boc), 2.30 (s, 3H, Me), 6.57 (br s, 1H, NH), 7.09 (d, *J* = 7.6 Hz, 1H, Ar CH), 7.25 (d *J*=7.6 Hz, 2H, Ar CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 28.4, 80.2, 118.7, 129.4,132.5, 135.8, 153.0.



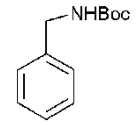
IR (neat): υ 3380, 2990, 2965, 1718, 1588, 1522, 1492, 1461, 1365, 1305, 1281, 1220, 1106, 840 cm^{-1}; ^1H NMR (90 MHZ, $CDCl_3$): δ 1.5 (s, 9H), 4.5 (bs, 1H), 6.7 (d, 2H), 8.1 (d, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 29.1 (CH3), 51.5 (C), 113.0 (CH), 125.3 (CH), 126.3 (C), 137.6 (C), 152.7 (CO).



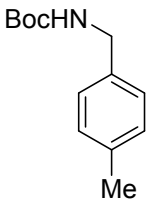
Off-white solid, Mp: 179-180° C. IR (KBr) υ 1704 cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$) δ : 1.51 (s, 9H), 4.25 (bs, 1H) 4.65 (bs, 1H), 7.19 - 7.49 (m, 4 H).



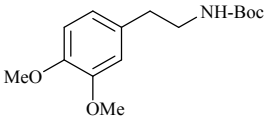
White solid, m.p. 98-99 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.57 (s, 9H, Boc), 6.89 (br s, 1H, NH), 7.42-7.55 (m, 3H, Ar CH), 7.63 (d *J*= 8.4 Hz, 1H, Ar CH), 7.80-7. 95 (m, 3H, Ar CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.4, 80.7, 118.7, 120.5, 124.5, 125.8, 126.0, 126.5, 128.7, 132.9, 134.0, 153.5.



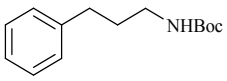
White solid, m.p. 55-57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 9H, Boc), 4.30 (s, 2H, PhC$\underline{H_2}$), 4.94 (br s, 1H, NH), 7.20-7.40 (m, 5H, Ar CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.4, 44.7, 79.5, 127.3, 127.4, 128.6, 138.9, 155.9.



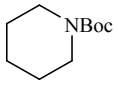
Off-white solid; m.p. 72–73 _C; IR (KBr): m = 3,395, 2,980, 2,920, 1,680, 1,600, 1,508, 1,360, 1,320, 1,295, 1,260, 1,172, 1,000, 858, 761, 694 cm^{-1}; 1H NMR ($CDCl_3$, 400 MHz): d = 1.50 (s, 9H), 2.36 (s, 3H), 4.30 (d, *J* = 5.2, 2H), 4.88 (br s, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}CNMR($CDCl_3$, 100 MHz): d =21.1, 28.4, 44.5, 79.4, 127.5, 129.3, 135.9, 137.0, 155.9 ppm



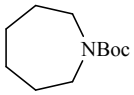
Yellow solid, m.p. 55-57 °C; IR (KBr): ν 3380, 2990, 2940, 2840, 2820, 1680, 1585, 1515, 1458, 1360, 1325, 1290, 1260, 1230, 1162, 1140, 1020, 990, 842, 808 cm^{-1}. ^{1}H NMR (DMSO, 300 MHz) δ : 1.36 (s, 9H), 2.60 (t, *J*=7.0 Hz, 2H), 3.09 (t, *J*=7.0 Hz, 2H), 3.70 (s, 3H), 3.73 (s, 3H), 6.68 (d, *J*=8.25 Hz, 1H), 6.76 (s, 1H), 6.84 (d, *J*=8.25 Hz, 2H). ^{13}C NMR (DMSO, 75 MHz) δ : 28.69, 35.49, 42.12, 55.73, 77.89, 112,26, 112.83, 120.83, 132.29, 147.58, 149.00, 155.95.



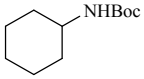
^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.3 (6H, s, CH_3), 2.43 (3H, s, SCH_3), 4.92 (1H, s), 7.18 (4H, s), 7.25 (2H, t, *J* = 7.31 Hz), 7.44 (4H, t, *J* = 7.82 Hz), 7.70 (4H, d, *J* = 7.82 Hz), 13.92 (2H, brs, OH) ppm.



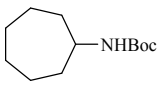
Colorless oil; IR (neat) υ; 2990, 2840, 1678, 1520, 1450, 1360, 1272, 1238, 1170, 1050, 898 cm^{-1}. ^{1}H NMR (DMSO, 300 MHz): δ 1.36-1.57 (m, 15H), 1.44 (s, 9H), 3.29-3.34 (m, 4H); ^{13}C NMR (DMSO, 75 MHz): δ 24.3, 25.5, 28.2, 46.6, 77.6, 157.3.



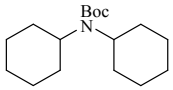
Colorless oil; IR (neat) υ; 2996, 2890, 1680, 1525, 1458, 1250 1178, 1015, 883 cm^{-1}. ^{1}H NMR (DMSO, 300 MHz): δ 1.32-1.39 (m, 9H), 1.42-1.57 (m, 4H), 1.70-1.73 (m, 4H), 2.91-2.93 (m, 2H), 3.34 (m, 2H); ^{13}C NMR (DMSO, 75 MHz): δ 24.1, 28.2, 35.0, 52.6, 78.6, 157.4.



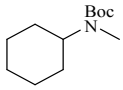
Colorless solid, mp 65-67°C , IR (CCl_4) υ: 3364, 2973, 2934, 2854, 1681, 1520 1448, 1366, 1315, 1251, 1233, 1168 cm^{-1}. ^{1}H NMR (300 MHz; $CDCl_3$) δ : 1.04-1.15 (m, 3H), 1.26-1.34 (m, 2H), 1.44 (s, 9H), 1.57- 1.71 (m, 3H), 1.90-1.93 (m, 2H), 3.43 (bs, 1H), 4.43 (bs, 1H).



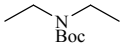
Out-white solid, m.p. 57-59 °C; IR (KBr): υ 3320, 2910, 2860, 1680, 1520, 1450, 1360, 1317, 1248, 1170, 1010, 875 cm^{-1}; ^{1}H NMR (DMSO, 300 MHz): δ 1.32-1.39 (m, 10H), 1.42-1.57 (m, 8H), 1.70-1.73 (m, 2H), 3.34 (bs, 1H), 6.72 (d, *J*=7.7 Hz, 1H). ^{13}C NMR (DMSO, 75 MHz): δ 24.1, 28.2, 28.7, 35.0, 51.6, 77.6, 155.1.



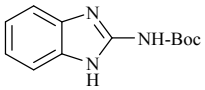
Colorless solid, mp 58 -59 °C. IR (CCl_4) υ: 2929, 2854, 1686, 1436, 1365, 1295, 1177, 1159 cm^{-1}. ^{1}H NMR (300 MHz; $CDCl_3$) δ : 1.04-1.12 (m, 3H), 1.2-1.3 (m, 5H), 1.47-1.58 (m, 18H), 1.74-1.78 (m, 5H) ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 25.5 , 26.2, 28.5, 31.2, 54.6, 78.8, 155.3.



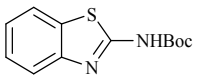
Colorless oil; IR (neat) υ; 2900, 2860, 1678, 1520, 1448, 1362, 1317, 1272 1160, 1020, 900 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.06-1.21 (m, 2H), 1.36 (s, 9H), 1.58-1.71 (m, 8H), 3.10 (s, 3H), 3.50 (s, 1H); ^{13}C NMR (DMSO, 75 MHz): δ 24.9, 27.9, 28.6, 31.0, 32.4, 54.4, 77.9, 156.9.



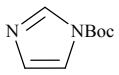
Colorless oil; IR (neat): m = 2,900, 2,860, 1,678, 1,520, 1,448, 1,362, 1,317, 1,272 1,160, 1,020, 900 cm-1; 1H NMR ($CDCl_3$, 400 MHz): d = 1.12 (t, *J* = 7.2 Hz, 6H), 1.48 (s, 9H), 3.24 (m, 4H) ppm; 13C NMR ($CDCl_3$, 100 MHz): d = 13.84, 28.44, 41.32, 78.90, 155.34 ppm.



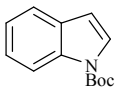
White solid; Mp 210°C; IR (neat): ν 3425, 3307, 2982, 1729, 1663, 1460, 1342, 11546, 840, 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.73 (s, 9H), 6.22 (br s, 1H, NH), 6.95-7.18 (d, *J*=7.81 HZ, 2H), 7.44-7.55 (d, *J*=7.81 HZ, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.1, 85.8, 113.9, 116.3, 120.6, 124.3, 130.3, 142.2, 150.7, 154.0.



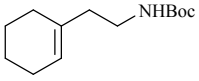
White solid; m.p. 99-101°C; IR (KBr): υ 3310, 3300, 3110, 3090, 2990, 1773, 1710, 1650, 1540, 1446, 1278, 1250, 1222, 1150, 1112, 1080, 1045 cm^{-1}. ^1H NMR (DMSO, 300 MHz): δ 1.63 (s, 9H), 7.31-7.52 (m, 4H), 11.7(s, 1H). ^{13}C NMR (DMSO, 75 MHz): δ 28.3, 87.8, 113.4, 123.5, 125.1, 127.9, 133.8, 147.7, 161.5, 167.5.



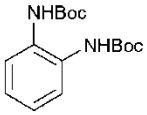
White solid, m.p. 42-45 °C; IR (KBr): 3365, 2975, 2930, 1725, 1700, 1502, 1308, 1165, 1070, 1015cm^{-1}; ^1H NMR (300MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.36 (s, 1H), 7.00 (s, 1H), 1.62 (s, 9H, Boc).



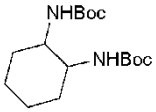
White solid; Mp 150°C; IR (neat): ν 2982, 1729, 1663, 1460, 1342, 11546, 840, 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.73 (s, 9H), 6.38-7.89 (m, 6H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.1, 85.8, 113.9, 116.3, 120.6, 124.3, 130.3, 142.2, 150.7, 154.0



Colorless oil; IR (neat): m = 2,912, 2,858, 1,680, 1,518, 1,442, 1,366, 1,275, 1,158, 1,010, 904 cm-1; 1HNMR ($CDCl_3$, 400 MHz) d = 1.40 (s, 9H), 1.48–1.57 (m, 4H), 1.87–1.94 (m, 4H), 2.05–2.07 (m, 2H), 3.14–3.15 (m, 2H), 4.60 (br s, 1H), 5.40 (s, 1H) ppm; 13C NMR ($CDCl_3$, 100 MHz) d = 28.4, 28.5, 31.1, 38.0, 38.2, 38.3, 78.9, 123.2, 146.7, 155.9 ppm.



White solid, m.p. 104-106 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.49 (s, 18H, Boc), 6.89 (br s, 2H, NH), 7.06 (m, 2H, Ar CH), 7.43 (m, 2H, Ar CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 80.7, 124.1, 125.2, 130.2, 153.9.



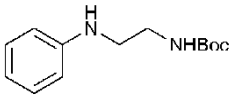
IR (KBr): υ 3380, 2920, 2850, 1680, 1517, 1450, 1360, 1245, 1178, 1050, 1004 cm^{-1}. ^1H NMR (DMSO, 300 MHz): δ 1.02-1.21 (m, 6H), 1.36 (s, 27H), 1.57-1.75 (m, 6H), 3.11 (s, 2H), 6.34 (d, J= 5.89Hz, 1H), 6.47 (d, J= 6.38Hz, 1.5H). ^{13}C NMR (DMSO, 75 MHz): δ 24.9, 28.6, 32.5, 54.3, 77.9, 78.1, 155.5, 156.1.

$BocHN(CH_2)_2NHBoc$

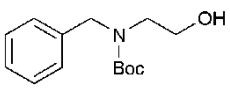
Out-white solid, m.p.144 °C; IR (KBr, cm^{-1}): 3379, 2985, 1685, 1164; ^1H-NMR (400 MHz, $CDCl_3$): 1.45 (s, 18H), 3.24 (s, 4H), 4.89 (s, NH) ppm, ^{13}C-NMR (100 MHz, $CDCl_3$): 28.38, 40.83, 79.45, 155.11 ppm.

$BocHN(CH_2)_6NHBoc$ (ee)

: White solid, m.p. 97 °C; IR (KBr, cm^{-1}): 3373, 2979, 1689, 1172; ^1H-NMR (400 MHz, $CDCl_3$) : 1.32-1.50 (m, 26H), 3.07-3.13 (m, 4H), 4.57 (s, NH) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): 26.34, 28.43, 29.99, 40.38, 79.06, 156.02 ppm.

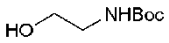


Off-White solid, m.p. 79-80 °C; IR (KBr): ν 3395, 2980, 2920, 1680, 1600, 1508, 1360, 1320, 1295, 1260, 1172, 1000, 858, 761, 694 cm^{-1}; ^1H NMR (300 MHz, DMSO): δ = 1.38 (s, 9H), 3.03- 3.09 (m, 4H), 5.56 (bs, 1H), 6.49–6.56 (m, 3H), 6.88 (bs, 1H), 7.03-7.08 (m, 2H); ^{13}C NMR (75 MHz, DMSO): δ = 28.68 (CH_3), 43.18 (CH_2), 78.14 (C), 112.28 (CH), 116.08 (CH), 129.38 (CH), 149.07 (C) 156.20 (C=O).

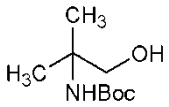


^1H NMR (500 MHz, $CDCl_3$): δ = 1.51 (s, 9H), 2.18 (br s, 1H, OH), 3.44 (m, 2H), 3.74 (m, 2H), 4.50 (s, 2H), 7.27–7.32 (m, 3H), 7.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.8 (CH_3), 50.12 (CH_2), 52.40 (CH_2), 62.2 (CH_2), 80.94 (C), 128.0 (CH), 128.9 (CH), 138.68 (CH),

147.19 (C) 157.64 (C=O).



IR (neat): ν 3357, 2976, 2933, 1690, 1525, 1366, 1279, 1251, 1171, 1068, 864 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.3, 43.0, 61.9, 79.5, 156.4.



Colorless solid, m.p. 50-52 °C IR (neat): 3490, 3300, 2994, 2930, 1696, 1680, 1540, 1520, 1362, 1300, 1250, 1170, 1080, 1040 cm^{-1}. ^{1}H NMR (DMSO, 300 MHz) δ = 1.12 (s, 6H), 1.35 (s, 9H), 3.28 (s, 2H), 4.72 (bs, 1H), 6.11 (s, 1H). ^{13}C NMR (DMSO, 75 MHz) δ = 23.98, 28.72, 53.51, 68.18, 77.67, 154.86..

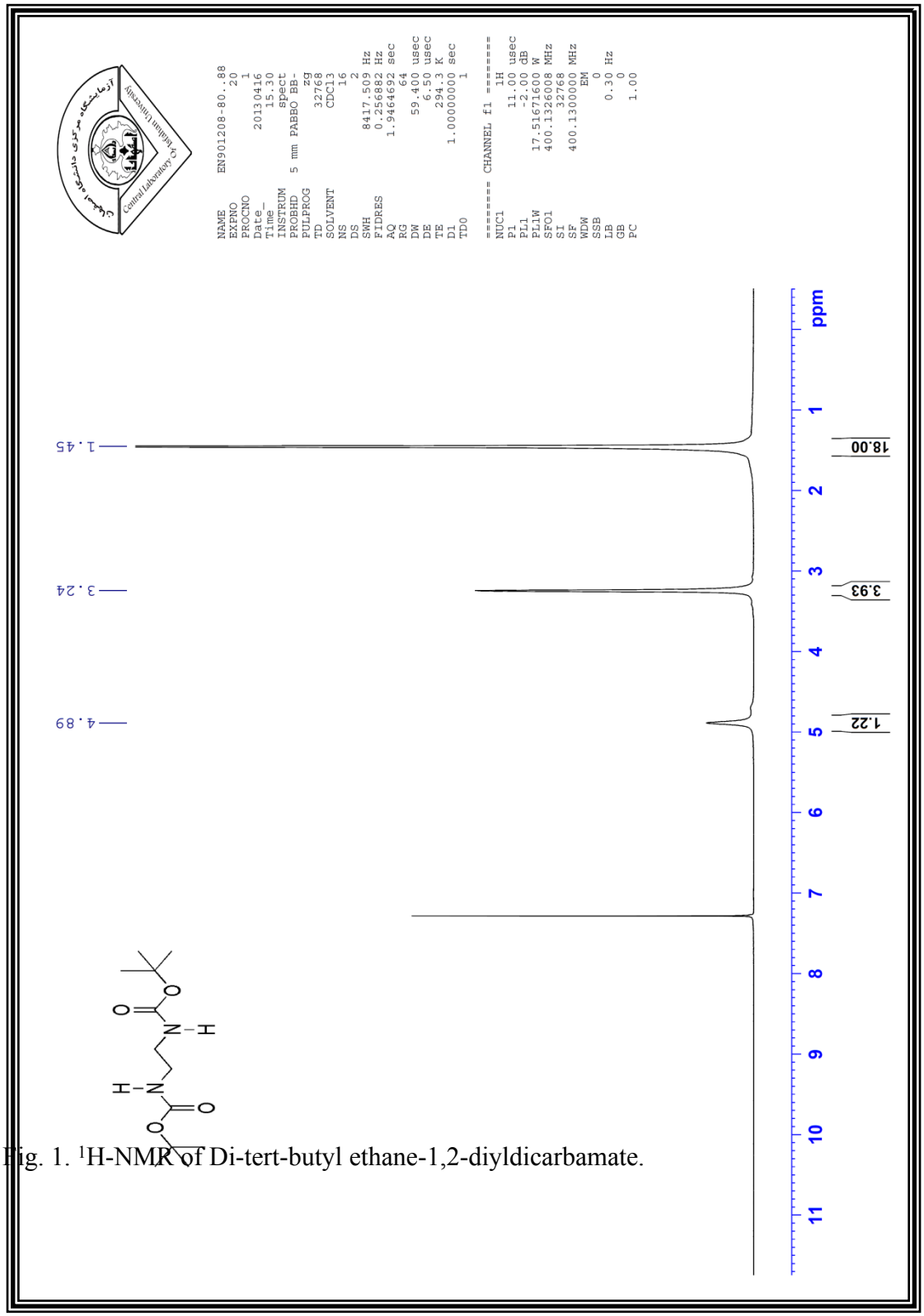


Fig. 1. ^{1}H-NMR of Di-tert-butyl ethane-1,2-diyldicarbamate.

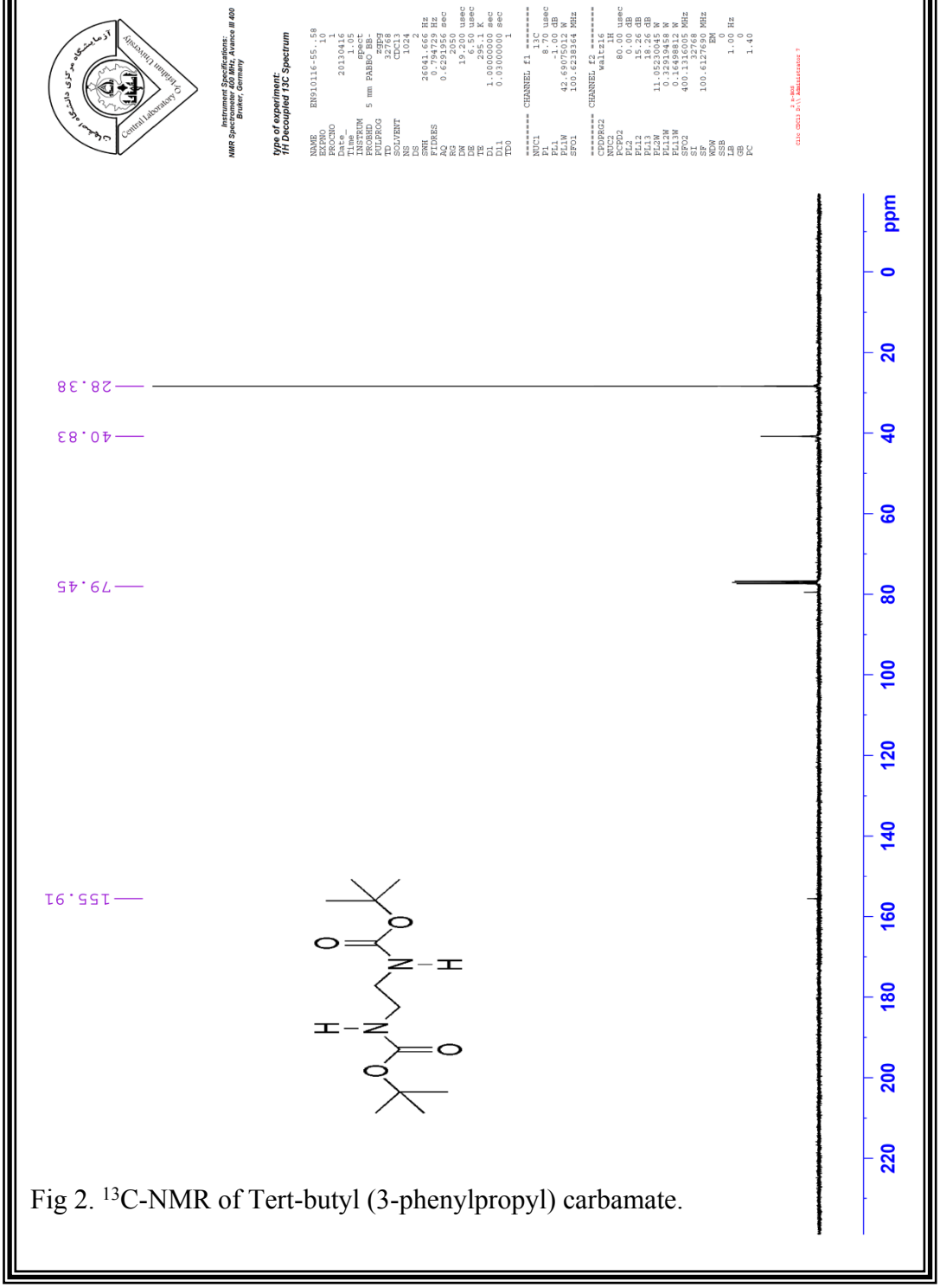


Fig 2. ^{13}C-NMR of Tert-butyl (3-phenylpropyl) carbamate.

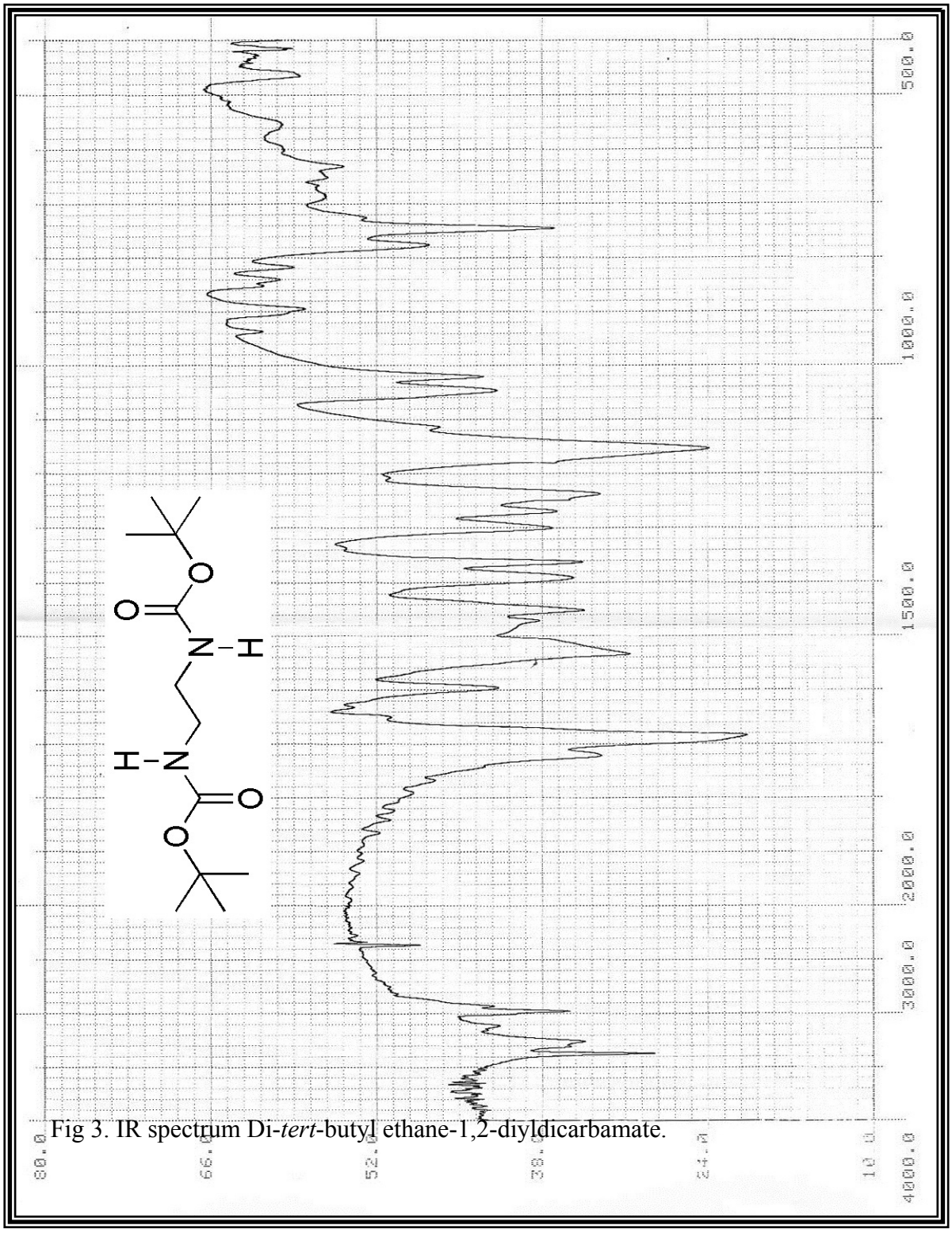


Fig 3. IR spectrum Di-*tert*-butyl ethane-1,2-diyldicarbamate.

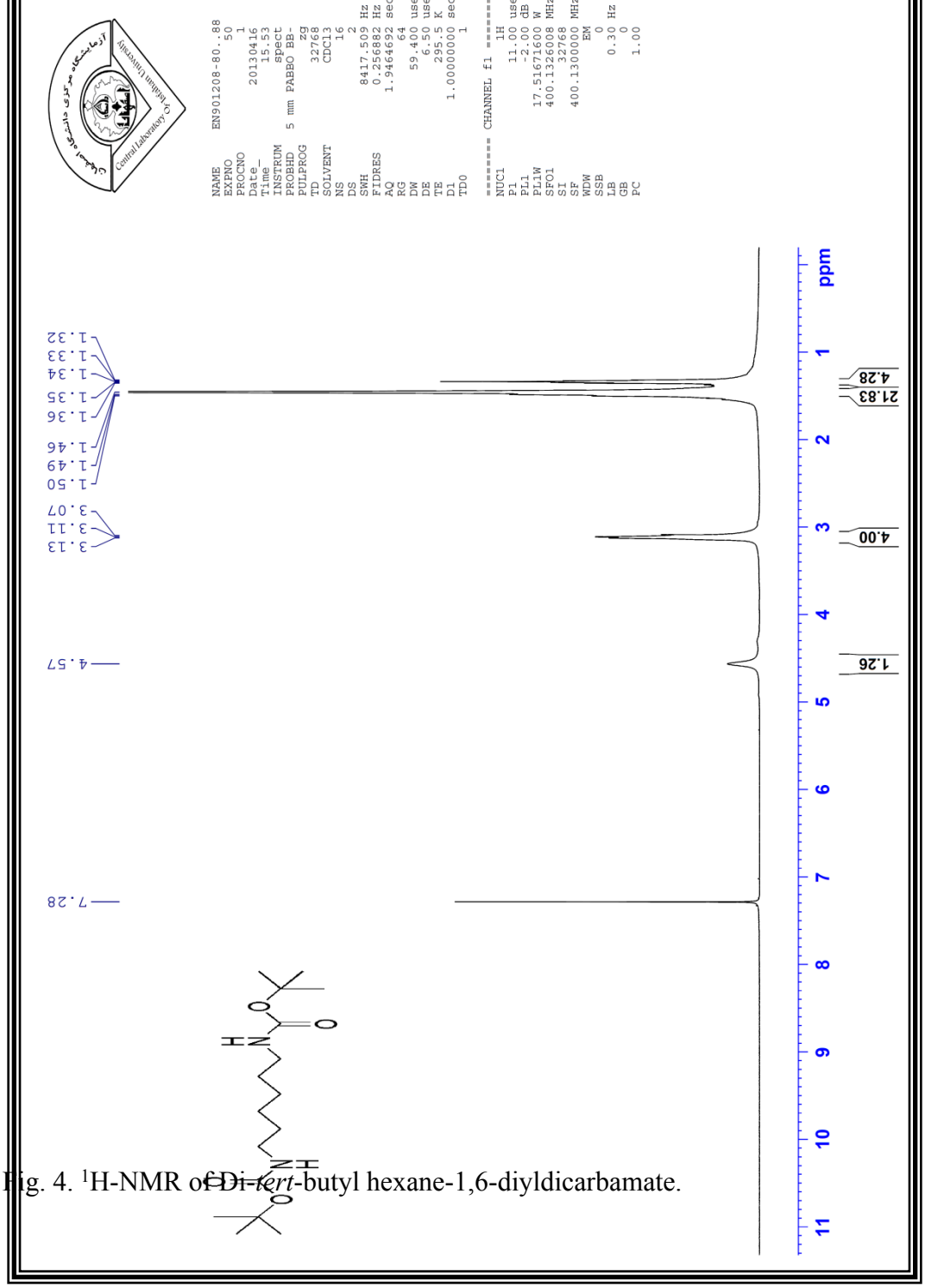


Fig. 4. [1]H-NMR of Di-*tert*-butyl hexane-1,6-diyldicarbamate.

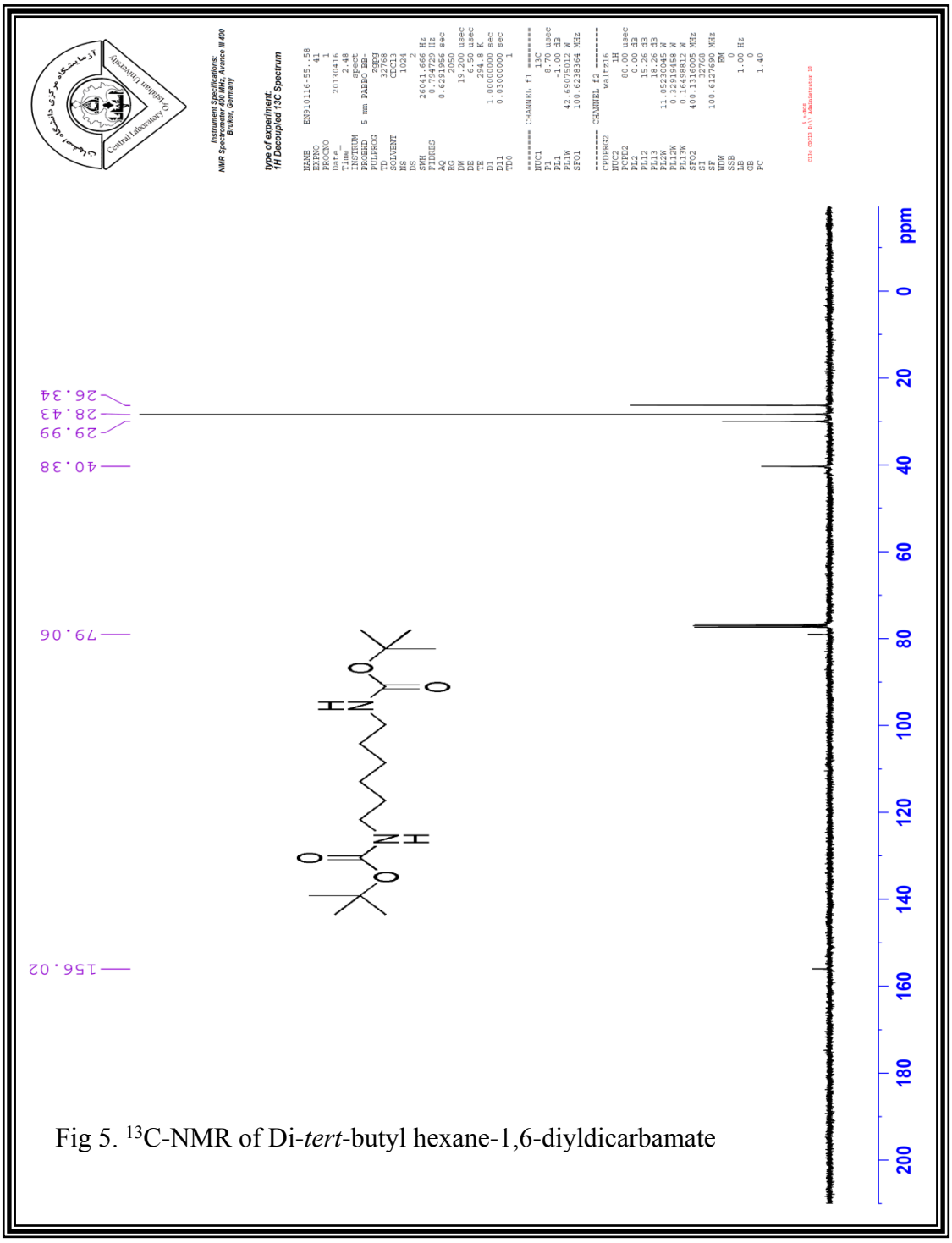


Fig 5. ^{13}C-NMR of Di-*tert*-butyl hexane-1,6-diyldicarbamate

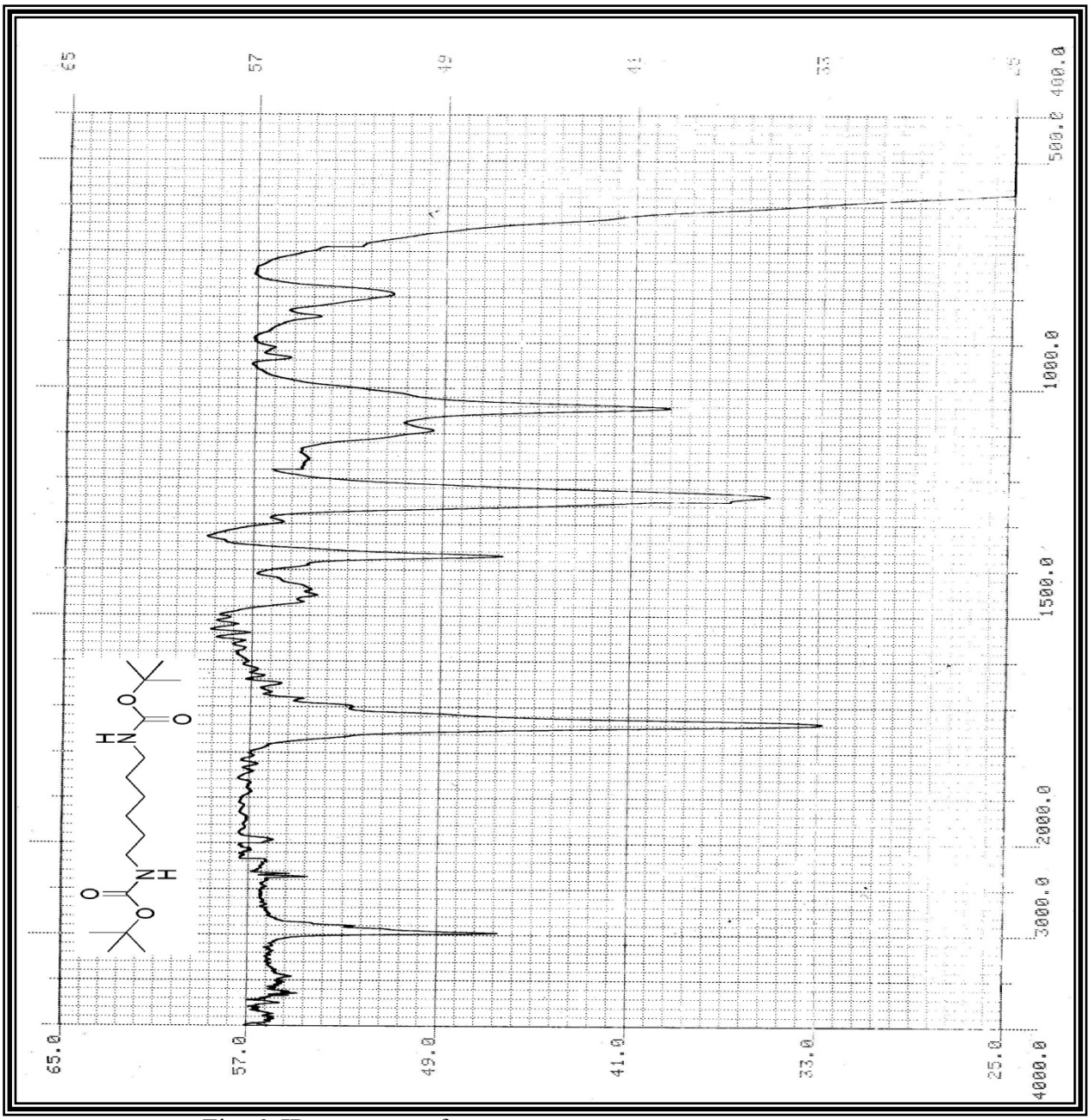


Fig. 6. IR spectrum of Di-*tert*-butyl hexane-1,6-diyldicarbamate.

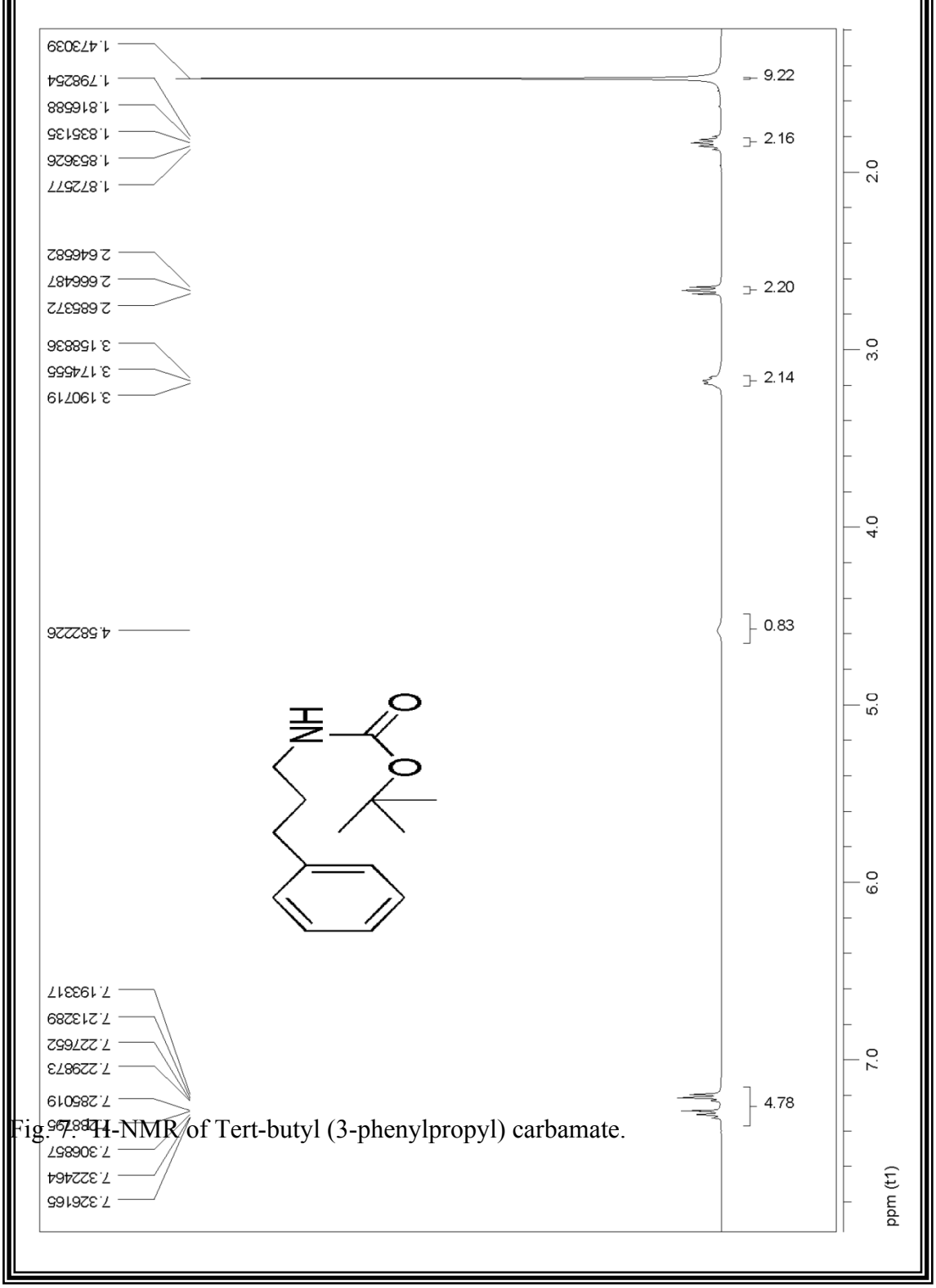


Fig. 7. ^{1}H-NMR of Tert-butyl (3-phenylpropyl) carbamate.

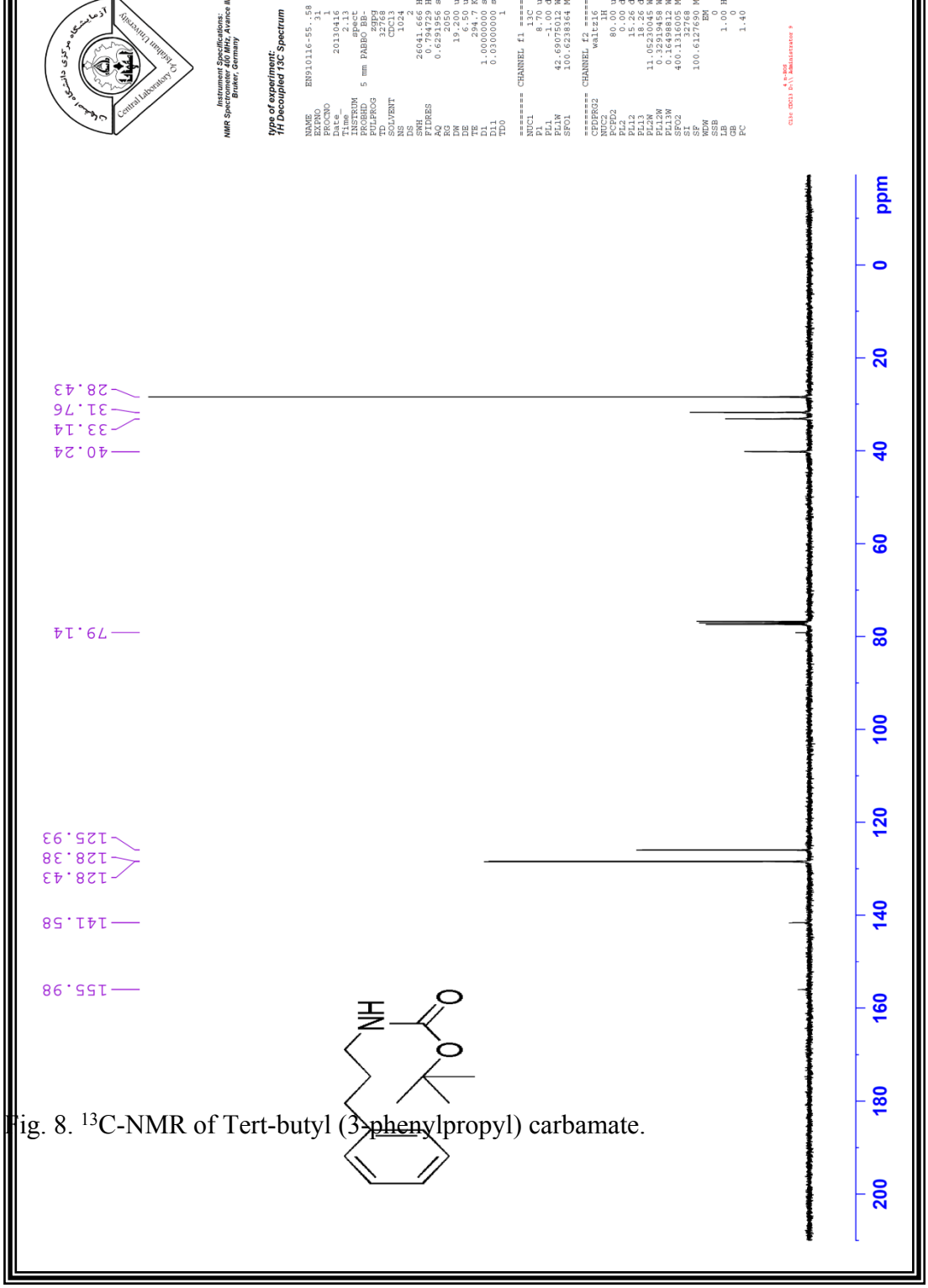


Fig. 8. ^{13}C-NMR of Tert-butyl (3-phenylpropyl) carbamate.

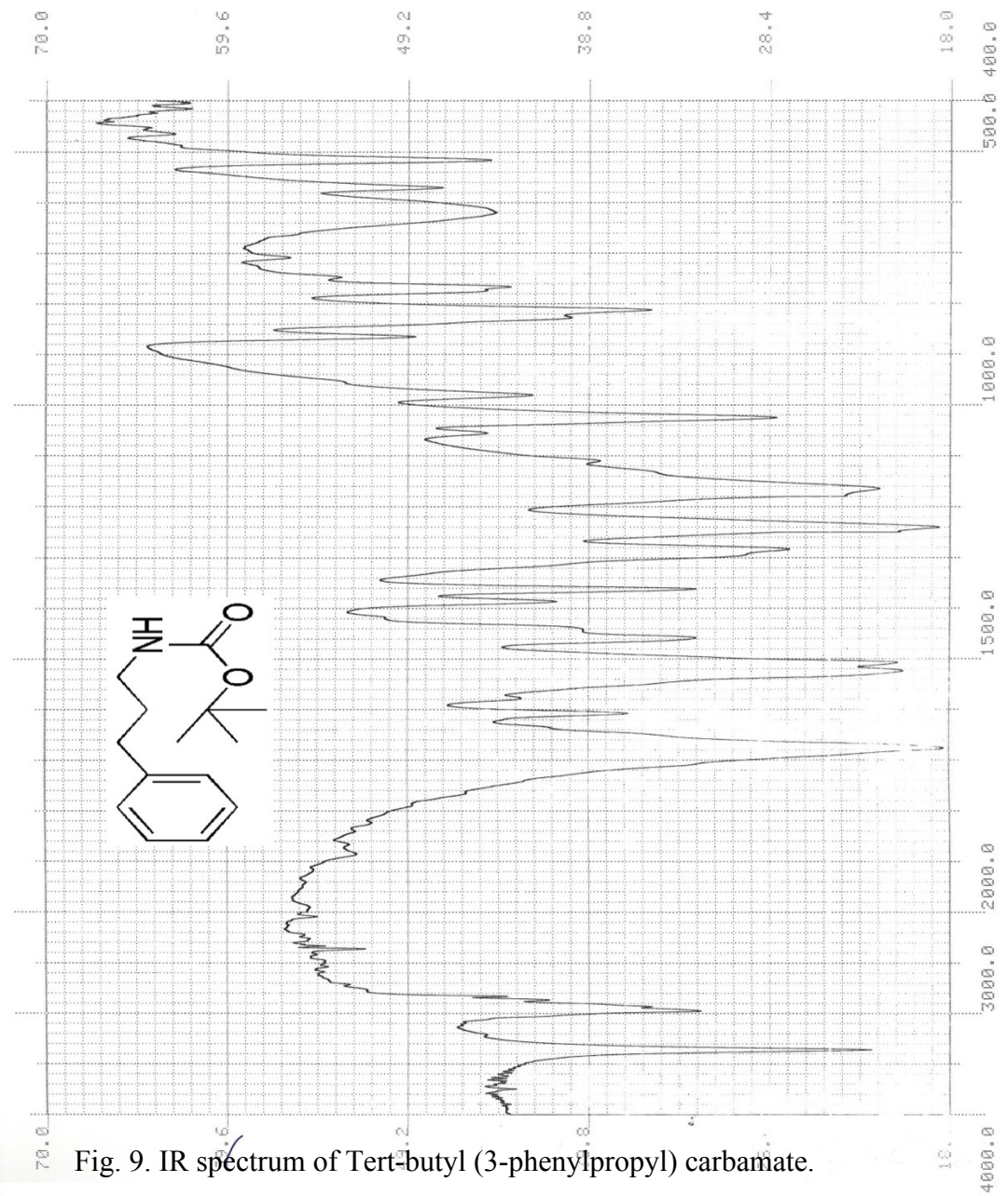


Fig. 9. IR spectrum of Tert-butyl (3-phenylpropyl) carbamate.