

1. Experimental

1.1. Material

Unless specified, all chemicals were analytical grade and purchased from Merck, Aldrich and Fluka Chemical Companies and used without further purification. Products were characterized by their physical constant and comparison with authentic samples. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates.

1.2. Instrumentation

The purity determination of the products was accomplished by GC-MS on an Agilent GC-Mass-6890 instrument under 70 eV conditions. The IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer using KBr pellets for solid and neat or CCl₄ for liquid samples in the range of 4000-400 cm⁻¹. The UV spectra were recorded on an Agilent 8453 UV-vis spectrophotometer at room temperature. In all the cases the ¹H NMR spectra were recorded with Bruker Avance 400 or 300 MHz instrument using. ¹³C NMR data were collected on Bruker Avance 100 or 75 MHz instrument. All chemical shifts are quoted in parts per million (ppm) relative to TMS using deuterated solvent. Microanalyses were performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

1.3. Preparation of Poly(*N*-vinylimidazole) (PVI_m)

Poly(*N*-vinylimidazole) (PVI_m) was obtained by free radical polymerization of *N*-vinylimidazole in benzene under nitrogen atmosphere with azoisobutyronitrile (AIBN) as initiator. The polymer was precipitated as a white powder. The solid was separated by filtration and dried at 40°C. PVI_m was purified by dissolving in methanol and precipitating using acetone twice. Finally, the polymer was dialyzed against distilled water using dialysis tubing. PVI_m was isolated by lyophilization and dried over P₄O₁₀ in vacuum at room temperature. The molecular weight of the PVI_m sample was determined by viscometry using the Mark-Houwink-Sakurada equation with parameters taken from the literature [28].

$$[\mu] = K(M_v)^a$$

where $K = 122 \times 10^{-3}$ mL/g and $a = 0.51$ in 0.1 M NaCl at 25°C.

The M_v value of PVI_m was found to be 305,000 g/mol.

1.4. General procedure for *N*-Boc protection of amines

Amine (1 mmol) was added to the mixture of (Boc)₂O (1 mmol) and PVIm (50 mg) with constant stirring at room temperature. After completion of the reaction (monitored by TLC), ethyl acetate (3×5 mL) was added to the reaction mixture and the catalyst was decanted and washed with ethyl acetate (2×5 mL) and dried. The product was purified by column chromatography, using ethyl acetate-petroleum ether (2:8) eluent. The physical and spectral data of known compounds were in agreement with those reported in the literature [13,14,29-31].

1.5. Spectral data of new products

Table 2, entry 8: Brown solid, m.p. 52-54 °C; IR (KBr): $\nu = 3320, 2990, 2920, 1690, 1600, 1530, 1450, 1420, 1362, 1285, 1240, 1160, 1045, 1032, 960, 870, 842 \text{ cm}^{-1}$; ¹H NMR (CDCl₃, 400 MHz): $\delta = 1.55 \text{ (s, 9H)}, 3.82 \text{ (s, 3H)}, 6.61 \text{ (dd, J=8.0 and 8.4 Hz, 1H)}, 6.64 \text{ (br s, 1H)}, 6.87 \text{ (d, J= 8.0 Hz, 1H)}, 7.14 \text{ (s, 1H)}, 9.19 \text{ (dd, J= 8.0 and 8.4 Hz, 1H)}$ ppm; ¹³C NMR (CDCl₃, 100 MHz): $\delta = 28.4, 55.3, 80.5, 104.1, 108.9, 110.7, 129.7, 139.7, 152.7, 160.3$ ppm.

Table 2, entry 13: White solid, m.p. 99-101°C; IR (KBr): $\nu = 3310, 3300, 3110, 3090, 2990, 1773, 1710, 1650, 1540, 1446, 1278, 1250, 1222, 1150, 1112, 1080, 1045 \text{ cm}^{-1}$; ¹H NMR (DMSO-*d*₆, 300 MHz): $\delta 1.63 \text{ (s, 9H)}, 7.31\text{-}7.52 \text{ (m, 4H)}, 11.7 \text{ (s, 1H)}$ ppm; ¹³C NMR (DMSO-*d*₆, 75 MHz): $\delta 28.3, 87.8, 113.4, 123.5, 125.1, 127.9, 133.8, 147.7, 161.5, 167.5$ ppm.

Table 2, entry 15: Off-White solid; m.p. 72-73 °C; IR (KBr): $\nu = 3395, 2980, 2920, 1680, 1600, 1508, 1360, 1320, 1295, 1260, 1172, 1000, 858, 761, 694 \text{ cm}^{-1}$; ¹H NMR (CDCl₃, 400 MHz): $\delta = 1.50 \text{ (s, 9H)}, 2.36 \text{ (s, 3H)}, 4.30 \text{ (d, J= 5.2, 2H)}, 4.88 \text{ (br s, 1H)}, 7.16 \text{ (d, J= 7.6 Hz, 2H)}, 7.20 \text{ (d, J= 8.0 Hz, 2H)}$ ppm; ¹³C NMR (CDCl₃, 100 MHz): $\delta = 21.1, 28.4, 44.5, 79.4, 127.5, 129.3, 135.9, 137.0, 155.9$ ppm.

Table 2, entry 16: Colorless oil; IR (KBr): $\nu = 3390, 2988, 2930, 1686, 1610, 1508, 1358, 1317, 1289, 1258, 1170, 998, 855 \text{ cm}^{-1}$; ¹H NMR (CDCl₃, 400 MHz): $\delta = 1.50 \text{ (s, 9H)}, 1.83 \text{ (qin, J =7.2, 7.6 Hz, 2H)}, 2.67 \text{ (dd, J= 7.6 and 8.0, 2H)}, 3.18 \text{ (d, J= 6.0 Hz, 2H)}, 7.22 \text{ (dd, J= 5.6 and 7.6 Hz, 3H)}, 7.32 \text{ (d, J= 8.0 Hz, 2H)}$ ppm; ¹³C NMR (CDCl₃, 100 MHz): $\delta = 28.5, 31.8, 33.2, 40.3, 125.9, 128.4, 128.4, 141.6, 156.1$ ppm.

Table 2, entry 17: Colorless solid; m.p. 65-67°C; IR (CCl₄) $\nu = 3364, 2973, 2934, 2854, 1681, 1520, 1448, 1366, 1315, 1251, 1233, 1168 \text{ cm}^{-1}$; ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.04\text{-}1.15 \text{ (m, 3H)}, 1.26\text{-}1.34 \text{ (m, 2H)}, 1.44 \text{ (s, 9H)}, 1.57\text{-}1.71 \text{ (m, 3H)}, 1.90\text{-}1.93 \text{ (m, 2H)}, 3.43 \text{ (bs, 1H)}, 4.43 \text{ (bs, 1H)}$ ppm.

Table 2, entry 18: Out-white solid; m.p. 57-59 °C; IR (KBr): $\nu = 3320, 2910, 2860, 1680, 1520, 1450, 1360, 1317, 1248, 1170, 1010, 875 \text{ cm}^{-1}$; ¹H NMR (DMSO-*d*₆, 300 MHz): $\delta = 1.32\text{-}1.39 \text{ (m, 10H)}, 1.42\text{-}1.57 \text{ (m, 8H)}, 1.70\text{-}1.73 \text{ (m, 1H)}$ ppm.

2H), 3.34 (bs, 1H), 6.72 (d, J=7.7 Hz, 1H) ppm; ^{13}C NMR (DMSO- d_6 , 75 MHz): δ 24.1, 28.2, 28.7, 35.0, 51.6, 77.6, 155.1 ppm.

Table 2, entry 19: Colorless oil; IR (neat): ν = 2912, 2858, 1680, 1518, 1442, 1366, 1275, 1158, 1010, 904 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ = 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; ^{13}C NMR (CDCl_3 , 100 MHz): δ = 28.4, 28.5, 31.1, 38.0, 38.2, 38.3, 78.9, 123.2, 146.7, 155.9 ppm.

Table 2, entry 21: Colorless oil; IR (neat) ν = 2900, 2860, 1678, 1520, 1448, 1362, 1317, 1272, 1160, 1020, 900 cm^{-1} ; ^1H 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 ppm.

Table 2, entry 22: Colorless oil; IR (neat): ν = 2916, 2862, 1682, 1525, 1450, 1360, 1314, 1275, 1164, 1024, 908 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ = 1.12 (t, J= 7.2 Hz, 6H), 1.48 (s, 9H), 3.24 (m, 4H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): δ = 13.84, 28.44, 41.32, 78.90, 155.34 ppm.

Table 2, entry 23: GC-MS (two peak with 59.32 and 40.68 %); ^1H NMR (DMSO- d_6 , 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) ppm; Isomer 59.32 %: Colorless needle; m.p. 167-169°C; IR (KBr): ν = 3380, 2920, 2850, 1680, 1517, 1450, 1360, 1245, 1178, 1050, 1004 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 1.21-1.25 (m, 3H), 1.44 (s, 9H), 1.45-1.72 (m, 4H), 2.01-2.04 (m, 1H), 3.28 (s, 1H), 4.90(s, 1H) ppm; ^{13}C NMR (DMSO- d_6 , 75 MHz): δ = 24.9, 28.6, 32.5, 54.3, 77.9, 78.1, 155.5, 156.1; GC-MS (EI) m/z: 314 (M^+), 213, 197, 185, 157, 141, 114, 97, 81, 57, 41, 29.

Table 2, entry 24: 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} ; ^1H NMR (DMSO- d_6 , 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) ppm; ^{13}C NMR (DMSO- d_6 , 75 MHz) δ = 28.7, 35.5, 42.1, 55.7, 77.9, 112.2, 112.8, 120.8, 132.3, 147.6, 149.0, 155.9 ppm.

Table 2, entry 25: White solid, m.p. 80-82 °C; IR (KBr): ν = 3414, 3395, 2980, 2920, 1680, 1600, 1508, 1360, 1320, 1295, 1260, 1172, 1000, 858, 761, 694 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ = 1.50 (s, 9H), 3.28 (t, J= 5.6 Hz, 2H), 3.39 (m, 2H), 4.02 (br s, 1H), 4.90 (br s, 1H), 6.64 (d, J= 8.0 Hz, 2H), 6.74 (dd, J= 7.2 and 7.6 Hz, 1H), 7.21 (dd, J= 7.6 and 8.0 Hz, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): δ = 28.4, 40.1, 44.4, 79.6, 112.7, 117.5, 129.3, 148.0, 156.4 ppm.

Table 2, entry 26: Colorless solid, m.p. 50-52 °C IR (neat): $\nu = 3490, 3300, 2994, 2930, 1696, 1680, 1540, 1520, 1362, 1300, 1250, 1170, 1080, 1040 \text{ cm}^{-1}$; ^1H NMR (DMSO- d_6 , 300 MHz) $\delta = 1.12$ (s, 6H), 1.35 (s, 9H), 3.28 (s, 2H), 4.72 (bs, 1H), 6.11 (s, 1H) ppm; ^{13}C NMR (DMSO- d_6 , 75 MHz) $\delta = 23.9, 28.7, 53.5, 68.2, 77.6, 154.8$ ppm.