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Synthesis of multicarboxylic acid appended imidazolium ionic liquids and their application in palladium-catalyzed selective oxidation of styrene

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1 Characterization data for multicarboxylic acid appended imidazolium ionic liquids

3a: ^{1}H NMR (DMSO-d_6, δ ppm): 9.34 (1H, s), 7.92 (1H, s), 7.80 (1H, s), 5.95 (1H, t, J = 7.2 Hz, CH), 5.31 (2H, s), 4.19 (4H, m, OCH_2), 4.06 (2H, q, J = 7.2 Hz, OCH_2), 3.37 (2H, m, CH_2), 1.20 (9H, m, CH_3); ^{13}C NMR (DMSO-d_6, δ ppm): 169.2, 167.1, 166.7, 138.6 123.9, 122.2, 62.7, 62.1, 61.2, 57.8, 49.9, 35.8, 14.0, 13.9; IR (KBr, cm^{-1}): 3147, 3108, 2985, 2941, 2875, 1741, 1638, 1561, 1469, 1401, 1379, 1352, 1220, 1178, 1097, 1020; ESI-MS: *m/z*, 327 $[M\text{-}Cl]^+$; Anal. Calcd. for $C_{15}H_{23}ClN_2O_6$ (362.81) (%): C 49.66, H 6.39, N 7.72; Found: C 49.72, H 6.46, N 7.79.

4a: ^{1}H NMR (DMSO-d_6, δ ppm): 9.36 (s, 1H,), 7.90 (s, 1H), 7.88 (s, 1H), 5.83 (1H, t, J = 7.2 Hz, CH), 4.27 (2H, q, J = 7.2 Hz, CH_2), 4.19 (2H, q, J = 7.0 Hz, OCH_2), 4.09 (2H, q, J = 7.1 Hz, OCH_2), 3.37 (2H, d, J = 6.4 Hz, CH_2), 1.43 (3H, t, J = 7.5 Hz, CH_3), 1.20 (3H, t, J = 7.0 Hz, CH_3), 1.16 (3H, t, J = 6.4 Hz, CH_3); ^{13}C NMR (DMSO-d_6, δ ppm): 169.6, 167.7, 137.3, 123.1, 122.7, 63.1, 61.5, 58.0, 45.1, 36.2, 15.6, 14.5, 14.4; IR (KBr, cm^{-1}): 3138, 3072, 2984, 2941, 2909, 2875, 1738, 1632, 1570, 1558, 1468, 1448, 1399, 1378, 1356, 1270, 1212, 1169, 1097, 1071, 1022; ESI-MS: *m/z*, 269 $[M\text{-}Br]^+$; Anal. calcd for $C_{13}H_{21}BrN_2O_4$ (349.22) (%): C 44.71, H 6.06, N 8.02; Found: C 44.77, H 6.12, N 8.09.

5a: ^{1}H NMR (DMSO-d_6, δ ppm): 9.18 (1H, s), 7.83 (1H, s), 7.74 (1H, s), 5.26 (2H, s), 4.47 (2H, t, J = 6.6 Hz), 4.21 (2H, q, J = 7.4 Hz), 4.06 (2H, q, J = 7.1 Hz), 2.99 (2H, t, J = 6.7 Hz), 1.24 (3H, t, J = 7.1 Hz), 1.16 (3H, t, J = 7.2 Hz); ^{13}C NMR (DMSO-d_6, δ ppm): 170.8, 167.3, 138.2, 124.3, 122.8, 62.7, 61.3, 50.1, 45.4, 34.2, 14.4; IR (KBr, cm^{-1}): 3147, 3081, 2985, 2941, 2875, 1733, 1638, 1567, 1450, 1399, 1378, 1344, 1296, 1224, 1169, 1098, 1065, 1020; ESI-MS: *m/z*, 255 $[M\text{-}Cl]^+$; Anal. calcd for $C_{12}H_{19}ClN_2O_4$ (290.75) (%): C 49.57, H 6.59, N 9.63; Found: C 49.62, H 6.66, N 9.69.

3b: ^{1}H NMR (DMSO-d_6, δ ppm): 10.50-11.00 (broad signal, 3H), 9.29 (s, 1H), 7.88 (1H, s), 7.75 (1H, s), 5.75 (1H, t, J = 7.4 Hz, CH), 5.18 (2H, s), 3.27 (2H, d, J = 7.4 Hz, CH_2). ^{13}C NMR (DMSO-d_6, δ ppm): 171.0, 170.0, 169.0, 138.4, 123.7, 122.2, 58.1, 50.0, 35.9; IR (KBr, cm^{-1}): 3151, 3132, 3104, 3065, 2975, 1726, 1634, 1563, 1487, 1384, 1256, 1166, 1090, 1031; ESI-MS: *m/z*, 243 $[M\text{-}Cl]^+$; Anal. calcd for $C_9H_{11}ClN_2O_6$ (278.65) (%): C 38.79, H 3.98, N 10.05; Found: C 38.83, H 4.02, N 10.11.

4b: ^{1}H NMR (DMSO-d_6, δ ppm): 10.50-11.00 (broad signal, 2H), 9.39 (1H, s), 7.91 (1H, s), 7.87 (1H, s), 5.66 (1H, t, J = 7.6 Hz, CH), 4.27 (2H, q, J = 7.4 Hz, CH_2), 3.28 (2H, d, J = 6.7 Hz, CH_2), 1.42 (3H, t, J = 7.3 Hz, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 171.3, 169.4, 137.2, 123.2, 122.4, 58.5, 45.0, 36.3, 15.6; IR (KBr, cm^{-1}): 3152, 3133, 3106, 2990, 2949, 1732, 1633, 1559, 1410, 1356, 1269, 1228, 1166, 1116, 1029; ESI-MS: *m/z*, 213 $[M\text{-}Br]^+$; Anal. calcd for $C_9H_{13}BrN_2O_4$ (293.12) (%): C 36.88, H 4.47, N 9.56; Found: C 36.93, H 4.52, N 9.63.

5b: ^{1}H NMR (DMSO-d_6, δ ppm): 10.50-11.00 (broad signal, 3H), 9.38 (1H, s), 7.86 (1H, s), 7.79 (1H, s), 5.21 (2H, s, CH_2), 4.40 (2H, q, J = 6.7 Hz, CH_2), 2.90 (2H, d, J = 6.8 Hz, CH_2); ^{13}C NMR (DMSO-d_6, δ ppm): 172.0, 168.4, 138.1, 124.3, 122.6, 50.3, 45.5, 34.5; IR (KBr, cm^{-1}): 3141, 3114, 3082, 2990, 2954, 1723, 1632, 1567, 1456, 1409, 1341, 1295, 1220, 1191, 1168, 1113, 1062, 1029, 1019; ESI-MS: *m/z*, 199 $[M\text{-}Cl]^+$; Anal. calcd for $C_8H_{11}ClN_2O_4$ (234.64) (%): C 40.95, H 4.73, N 11.94; Found: C 41.01, H 4.79, N 12.02.

3c: ^{1}H NMR (D_2O, δ ppm): 8.79 (1H, s), 7.45 (1H, s), 7.41 (1H, s), 5.30 (1H, t, J = 7.4 Hz, CH), 5.09 (2H, s, CH_2), 3.18 (2H, d, J = 7.2 Hz, CH_2). ^{13}C NMR (D_2O, δ ppm): 176.8, 175.2, 174.6, 139.5, 124.9, 123.5, 67.1, 47.2, 38.7; IR (KBr, cm^{-1}): 3150, 3112, 2976, 2941, 1623, 1585, 1484,

1362, 1220, 1170; ESI-MS: *m/z*, 243 $[M+H]^+$; Anal. calcd for $C_9H_{10}N_2O_6$ (242.19) (%): C 44.63, H 4.16, N 11.57; Found: C 44.68, H 4.19, N 11.65.

4c: ^{1}H NMR (D_2O, δ ppm): 8.81 (1H, s), 7.46 (1H, s), 7.42 (1H, s), 5.22 (1H, t, J = 7.4 Hz, CH), 4.15 (2H, q, J = 7.3 Hz, CH_2), 3.19 (2H, q, J = 16.6, 7.6 Hz, CH_2), 1.40 (3H, t, J = 7.3 Hz, CH_3). ^{13}C NMR (D_2O, δ ppm): 176.6, 175.0, 138.3, 124.7, 124.4, 63.2, 47.7, 39.9, 17.0; IR (KBr, cm^{-1}): 3151, 3133, 3106, 3066, 2992, 2976, 2940, 1675, 1563, 1430, 1341, 1258, 1166; ESI-MS: *m/z*, 213 $[M+H]^+$; Anal. calcd for $C_9H_{12}N_2O_4$ (212.21) (%): C 50.94, H 5.70, N 13.20; Found: C 50.98, H 5.76, N 13.32.

5c: ^{1}H NMR (D_2O, δ ppm): 8.75 (1H, s, H-2), 7.47 (1H, s), 7.38 (1H, s), 4.77 (2H, s), 4.43 (2H, t, J = 6.8 Hz, CH_2), 2.90 (2H, t, J = 6.9 Hz, CH_2); ^{13}C NMR (D_2O, δ ppm): 177.1, 173.5, 139.2, 125.3, 124.8), 53.4, 48.7, 37.4; IR (KBr, cm^{-1}): 3163, 3132, 3098, 3042, 3003, 2953, 1625, 1560, 1435, 1338, 1255, 1168; ESI-MS: *m/z*, 199 $[M+H]^+$; Anal. calcd for $C_8H_{10}N_2O_4$ (198.18) (%): C 48.49, H 5.09, N 14.14; Found: C 48.55, H 5.16, N 14.23.

3d: ^{1}H NMR (DMSO-d_6, δ ppm): 9.21 (1H, s), 7.85 (1H, s), 7.70 (1H, s), 5.73 (1H, t, J = 7.3 Hz, CH), 5.16 (2H, s, CH_2), 3.24 (2H, d, J = 7.4 Hz, CH_2). ^{13}C NMR (DMSO-d_6, δ ppm): 170.8, 168.6, 168.0, 138.4, 123.6, 122.2, 58.1, 50.0, 35.9; IR (KBr, cm^{-1}): 3120, 3080, 3036, 3003, 1722, 1633, 1589, 1487, 1382, 1216, 1166, 1150, 1067, 1032; ESI-MS: *m/z*, 243 $[M-BF_4]^+$; Anal. calcd for $C_9H_{11}BF_4N_2O_6$ (330.00) (%): C 32.76, H 3.36, N 8.49; Found: C 32.80, H 3.40, N 8.53.

3e: ^{1}H NMR (DMSO-d_6, δ ppm): 9.18 (1H, s), 7.82 (1H, s), 7.68 (1H, s), 5.70 (1H, t, J = 7.1 Hz, CH), 5.14 (2H, s, CH_2), 3.24 (2H, d, J = 7.3 Hz, CH_2). ^{13}C NMR (DMSO-d_6, δ ppm): 170.4, 168.2, 167.5, 137.9, 123.3, 121.8, 57.8, 49.7, 35.6; IR (KBr, cm^{-1}): 3151, 3132, 3104, 3065, 2975, 2939, 1723, 1637, 1548, 1489, 1379, 1254, 1168, 1058, 967; ESI-MS: *m/z*, 243 $[M-PF_6]^+$; Anal. calcd for $C_9H_{11}PF_6N_2O_6$ (388.16) (%): C 27.85, H 2.86, N 7.22; Found: C 27.90, H 2.91, N 7.28.

3f: ^{1}H NMR (DMSO-d_6, δ ppm): 9.27 (1H, s), 7.86 (1H, s), 7.72 (1H, s), 5.72 (1H, t, J = 7.4 Hz, CH), 5.16 (2H, s, CH_2), 3.26 (2H, d, J = 7.4 Hz, CH_2). ^{13}C NMR (DMSO-d_6, δ ppm): 170.8,

168.6, 168.0, 164.9, 138.3, 123.7, 122.2, 119.1(CF_3), 58.1, 50.0, 35.9; IR (KBr, cm^{-1}): 3142, 3102, 2975, 2940, 1723, 1635, 1488, 1383, 1246, 1176, 1111, 1061; ESI-MS: *m/z*, 243 $[M\text{-}CF_3CO_2]^+$; Anal. calcd for $C_{11}H_{11}F_3N_2O_8$ (356.21) (%): C 37.09, H 3.11, N 7.86; Found: C 37.09, H 3.14, N 7.87.

3g: ^{1}H NMR (DMSO-d_6, δ ppm): 9.26 (1H, s), 7.85 (1H, s), 7.71 (1H, s), 5.73 (1H, t, J = 7.3 Hz, CH), 5.15 (2H, s, CH_2), 3.25 (2H, d, J = 7.3 Hz, CH_2). ^{13}C NMR (DMSO-d_6, δ ppm): 170.8, 168.5, 168.0, 138.2 (CF_3), 138.0, 123.7, 122.2, 58.1, 50.0, 35.9; IR (KBr, cm^{-1}): 3143, 3077, 2979, 1726, 1637, 1545, 1490, 1382, 1379, 1261, 1165, 1061, 1031; ESI-MS: *m/z*, 243 $[M\text{-}CF_3SO_3]^+$; Anal. calcd for $C_{10}H_{11}F_3N_2O_9S$ (392.27) (%): C 30.62, H 2.83, N 7.14; Found: C 30.61, H 2.89, N 7.16.

4d: ^{1}H NMR (DMSO-d_6, δ ppm): 9.30 (1H, s), 7.88 (1H, s), 7.82 (1H, s), 5.64 (1H, t, J = 7.6 Hz, CH), 4.25 (2H, q, J = 7.0 Hz, CH_2), 3.25 (2H, d, J = 7.0 Hz, CH_2), 1.41 (3H, t, J = 7.0 Hz, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 171.3, 169.3, 137.1, 123.2, 122.4, 58.5, 45.0, 36.3, 15.6; IR (KBr, cm^{-1}): 3145, 3123, 3074, 2990, 2976, 1723, 1633, 1564, 1487, 1378, 1252, 1164, 1150, 1072, 1060, 1031; ESI-MS: *m/z*, 213 $[M\text{-}BF_4]^+$; Anal. calcd for $C_9H_{13}BF_4N_2O_4$ (300.02) (%): C 36.03, H 4.37, N 9.34; Found: C 36.08, H 4.42, N 9.41.

4e: ^{1}H NMR (DMSO-d_6, δ ppm): 9.28 (1H, s), 7.85 (1H, s), 7.80 (1H, s), 5.61 (1H, t, J = 7.6 Hz, CH), 4.23 (2H, q, J = 7.0 Hz, CH_2), 3.24 (2H, d, J = 7.0 Hz, CH_2), 1.40 (3H, t, J = 7.0 Hz, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 170.9, 168.9, 136.7, 122.8, 122.0, 58.2, 44.7, 36.0, 15.2; IR (KBr, cm^{-1}): 3152, 3133, 3106, 2990, 2949, 1732, 1636, 1566, 1488, 1376, 1254, 1166, 1116, 1057, 959, 831; ESI-MS: *m/z*, 213 $[M\text{-}PF_6]^+$; Anal. calcd for $C_9H_{13}F_6N_2O_4P$ (358.18) (%): C 30.18, H 3.66, N 7.82; Found: C 30.23, H 3.71, N 7.89.

4f: ^{1}H NMR (DMSO-d_6, δ ppm): 9.37 (1H, s), 7.89 (1H, s), 7.84 (1H, s), 5.63 (1H, t, J = 7.0 Hz, CH), 4.25 (2H, q, J = 7.0 Hz, CH_2), 3.27 (2H, d, J = 7.0 Hz, CH_2), 1.41 (3H, t, J = 7.0 Hz, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 171.3, 169.3, 164.8, 137.1, 123.2, 122.4, 119.1(CF_3), 58.5, 45.0, 36.3, 15.6; IR (KBr, cm^{-1}): 3163, 3135, 3114, 3004, 2990, 2943, 1722, 1624, 1560, 1428, 1314, 1278, 1246, 1199, 1137, 1116, 1036, 707; ESI-MS: *m/z*, 213 $[M\text{-}CF_3CO_2]^+$; Anal. calcd for $C_{11}H_{13}F_3N_2O_6$ (326.23) (%): C 40.50, H 4.02, N 8.59; Found: C 40.61, H 4.00, N 8.57.

4g: ^{1}H NMR (DMSO-d_6, δ ppm): 9.36 (1H, s), 7.88 (1H, s), 7.83 (1H, s), 5.64 (1H, t, J = 7.6 Hz, CH), 4.24 (2H, q, J = 7.3 Hz, CH_2), 3.26 (2H, d, J = 7.0 Hz, CH_2), 1.40 (3H, t, J = 7.0 Hz, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 171.3, 169.2, 137.0, 123.2, 122.4, 138.2 (CF_3), 58.5, 45.0, 36.3, 15.6; IR (KBr, cm^{-1}): 3144, 3105, 3078, 2989, 1724, 1637, 1490, 1441, 1383, 1262, 1227, 1165, 1066, 1032, 757; ESI-MS: *m/z*, 213 $[M\text{-}CF_3SO_3]^+$; Anal. calcd for $C_{10}H_{13}F_3N_2O_7S$ (362.28) (%): C 33.15, H 3.62, N 7.73; Found: C 33.20, H 3.60, N 7.69.

5d: ^{1}H NMR (DMSO-d_6, δ ppm): 9.29 (1H, s), 7.83 (1H, s), 7.74 (1H, s), 5.19 (2H, s, CH_2), 4.38 (2H, q, J = 7.0 Hz, CH_2), 2.87 (2H, d, J = 7.0 Hz, CH_2); ^{13}C NMR (DMSO-d_6, δ ppm): 172.0, 168.3, 138.1, 124.2, 122.6, 50.3, 45.5, 34.5; IR (KBr, cm^{-1}): 3151, 3105, 2980, 2904, 1723, 1631, 1568, 1416, 1356, 1248, 1164, 1150, 1113, 1062; ESI-MS: *m/z*, 199 $[M\text{-}BF_4]^+$; Anal. calcd for $C_8H_{11}BF_4N_2O_4$ (285.99) (%): C 33.60, H 3.88, N 9.80; Found: C 33.66, H 3.93, N 9.85.

5e: ^{1}H NMR (DMSO-d_6, δ ppm): 9.27 (1H, s), 7.80 (1H, s), 7.72 (1H, s), 5.16 (2H, s), 4.36 (2H, q, J = 7.0 Hz, CH_2), 2.86 (2H, d, J = 7.0Hz, CH_2); ^{13}C NMR (DMSO-d_6, δ ppm): 171.6, 167.9, 137.6, 123.9, 122.2, 50.1, 45.2, 34.2; IR (KBr, cm^{-1}): 3152, 3114, 3083, 2990, 2950, 1723, 1634, 1567, 1461, 1413, 1354, 1249, 1166, 1115, 1058, 959, 831; ESI-MS: *m/z*, 199 $[M\text{-}PF_6]^+$; Anal. calcd for $C_8H_{11}F_6N_2O_4P$ (344.15) (%): C 27.92, H 3.22, N 8.14; Found: C 27.99, H 3.28, N 8.22.

5f: ^{1}H NMR (DMSO-d_6, δ ppm): 9.36 (1H, s), 7.84 (1H, s), 7.76 (1H, s), 5.18 (2H, s), 4.38 (2H, q, J = 7.0 Hz, CH_2), 2.89 (2H, d, J = 7.0 Hz, CH_2); ^{13}C NMR (DMSO-d_6, δ ppm): 172.0, 168.3, 164.7, 138.0, 124.3, 122.6, 119.2(CF_3),50.3, 45.5, 34.5; IR (KBr, cm^{-1}): 3151, 2945, 1718, 1566, 1418, 1163, 1062, 707; ESI-MS: *m/z*, 199 $[M\text{-}CF_3CO_2]^+$; Anal. calcd for $C_{10}H_{11}F_3N_2O_6$ (312.20) (%): C 38.47, H 3.55, N 8.97; Found: C 38.68, H 3.57, N 8.96.

5g: ^{1}H NMR (DMSO-d_6, δ ppm): 9.35 (1H, s), 7.83 (1H, s), 7.75 (1H, s), 5.19 (2H, s), 4.37 (2H, q, J = 7.0 Hz), 2.88 (2H, d, J = 7.0 Hz); ^{13}C NMR (DMSO-d_6, δ ppm): 172.0, 168.2, 138.2 (CF_3), 137.9, 124.3, 122.6, 50.3, 45.5, 34.5; IR (KBr, cm^{-1}): 3164, 2990, 1728, 1662, 1436, 1175, 1168, 1113, 1062, 1029, 707; ESI-MS: *m/z*, 199 $[M\text{-}CF_3SO_3]^+$; Anal. calcd for $C_9H_{11}F_3N_2O_7S$ (348.26) (%): C 31.04, H 3.18, N 8.04; Found: C 31.05, H 3.19, N 8.05.

2. IR spectrum of **3b**, **4b** and **5b**

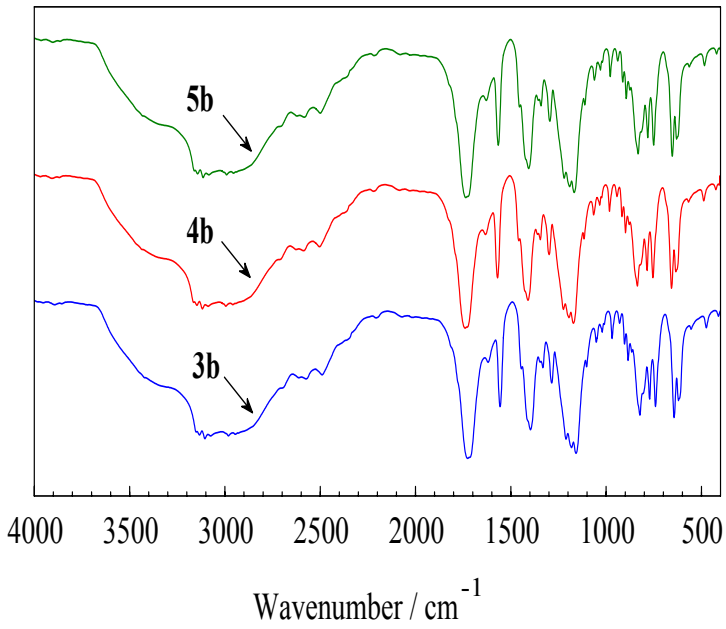

Figure S1 IR spectrum of **3b**, **4b** and **5b**

3. TG curves for **3b**, **3d**, **3e** and **3f**

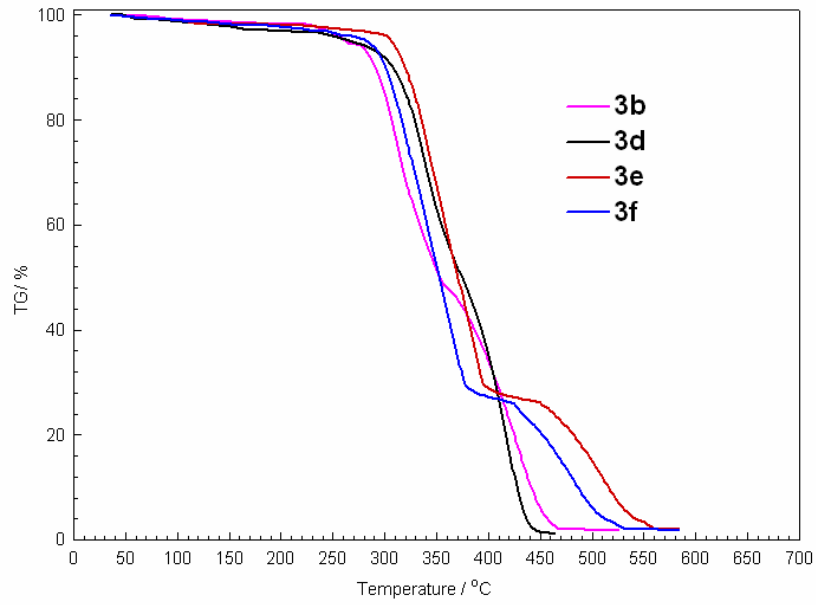

Figure S2 TG curves for **3b**, **3d**, **3e** and **3f**

4. DSC investigation of McaILs

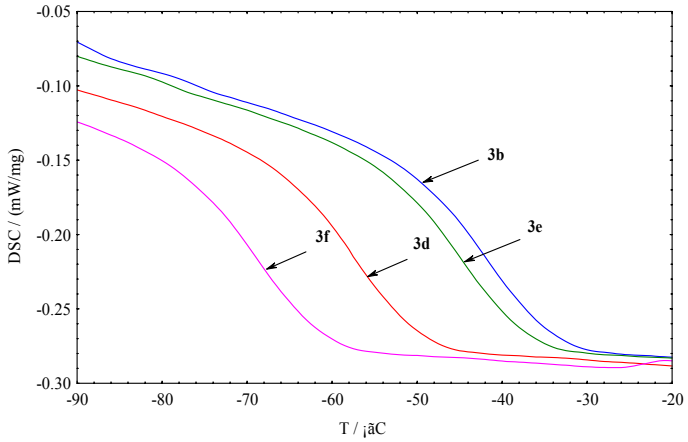

Fig.S3 DSC curves for the glass transitions of **3b, 3d~3f** at cooling stage

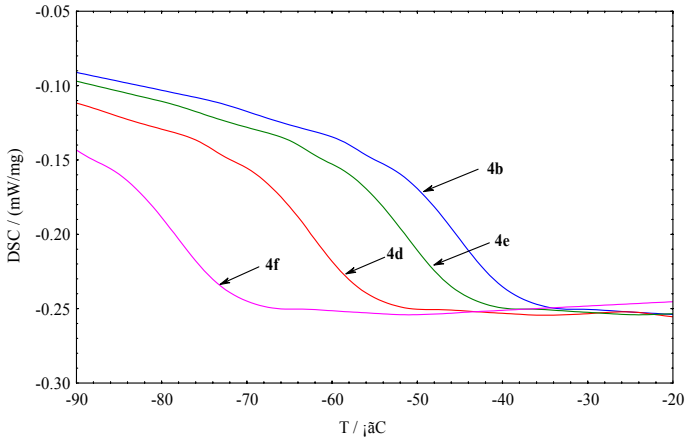

Fig.S4 DSC curves for the glass transitions of **4b, 4d~4f** at cooling stage

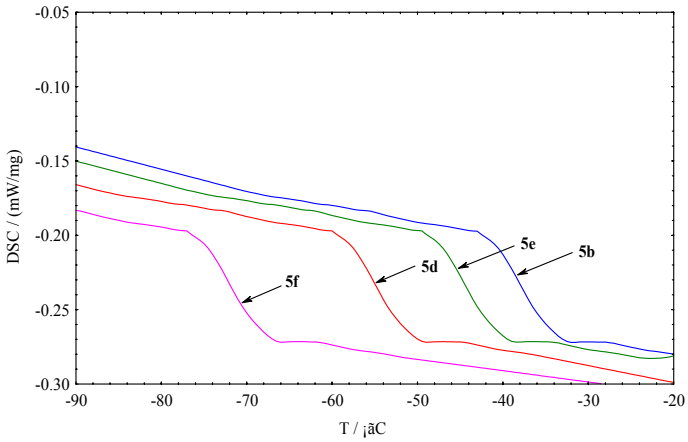

Fig.S5 DSC curves for the glass transitions of **5b, 5d~5f** at cooling stage

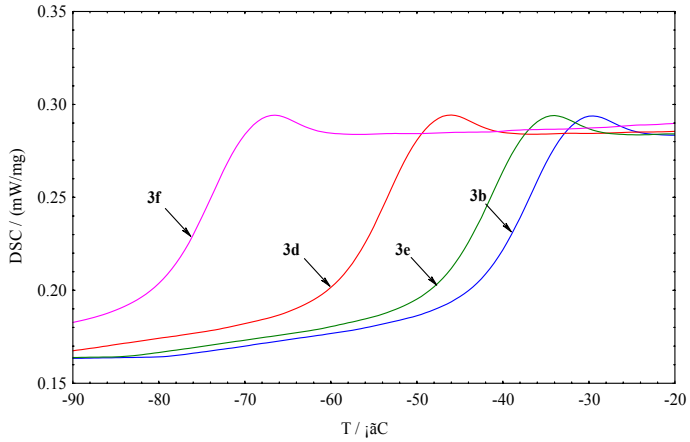

Fig.S6 DSC curves for the glass transitions of **3b, 3d~3f** at heating stage

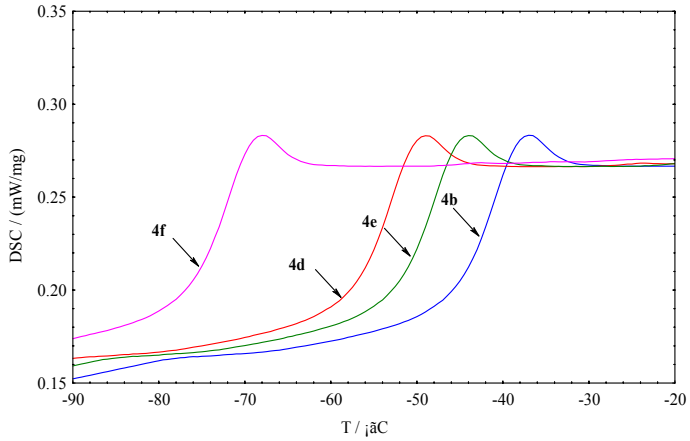

Fig.S7 DSC curves for the glass transitions of **4b, 4d~4f** at heating stage

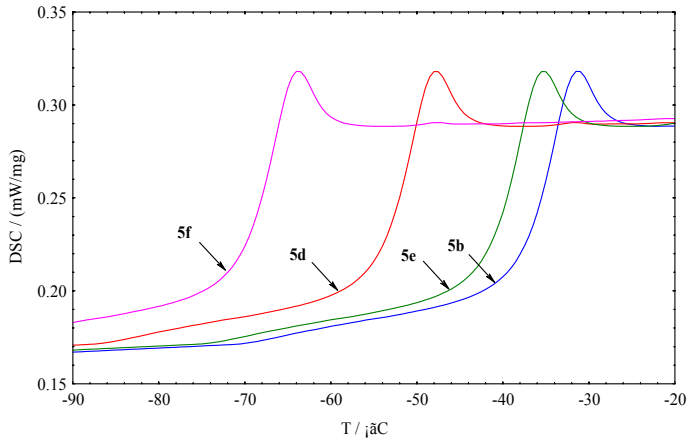

Fig.S8 DSC curves for the glass transitions of **5b, 5d~5f** at heating stage