Supporting Information

Unexpected Reactions of Push-Pull N-Heterocyclic Carbene Derived from N-(4-methoxyphenyl)-N-(4-nitrophenyl)-imidazolium Chloride

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General Methods.

All reactions were carried out under nitrogen atmosphere. All the reagents used were purchased from commercial sources and used without further purification. DMSO, xylene, and EtOAc were freshly distilled from CaH₂. 1H, 13C NMR spectra were recorded in CDCl₃, Acetone-d₆ and DMSO-d₆ on a spectrometer operating at 300 and 75 MHz, respectively. Chemical shifts are reported in parts per million relative to the appropriate standard: TMS for 1H and 13C NMR spectra. Column chromatography was carried out on silica gel H (10-40 mm).

Quaternization of 1-(4-methoxyphenyl)-imidazole: 1-(4-methoxyphenyl)-imidazole (1.74 g, 10 mmol), 1-chloro-4-nitrobenzene (1.89 g, 12 mmol) were mixed together in a dry sealed tube. To this mixture 1 ml of dry xylene were added. The mixture was heated at 160 °C for 48 h. The precipitate was filtered, washed with CHCl₃, and dried under reduced pressure to give the white powder (1) 597 mg in 18% yield.

3-(4-methoxyphenyl)-1-(4-nitrophenyl)-imidazolium chloride (1)

18%. 1H NMR (DMSO-d₆, δ): 10.56 (brs, 1 H), 8.73 (brs, 1 H), 8.59 (brs, 1 H), 8.58 (d, J = 9.1 Hz, 2 H), 8.26 (d, J = 9.1 Hz, 2 H), 7.89 (d, J = 9.1 Hz, 2 H), 7.26 (d, J = 9.1 Hz, 2 H), 3.87 (s, 3 H); 13C NMR (DMSO-d₆, δ): 160.8, 148.1, 139.7, 135.5, 128.0, 126.0, 124.0, 123.5, 122.9, 122.0, 115.6, 56.3; IR (KBr): ν = 3080, 3015, 2950, 1622, 1598, 1544, 1518, 1345, 1319, 1290, 1261, 1195, 1074, 1020, 1009, 855, 832, 747, 734, 630, 617, 524 cm⁻¹; MS (ESI, m/z): 296 [cation]⁺; Anal. Calcd for C₁₆H₁₄ClN₃O₃: C 57.93, H 4.25, N 12.67; Found: C 57.91, H 4.10, N 12.79.

General procedure for the reaction of 1 with aromatic aldehydes: A mixture of 1 (33.2 mg, 0.1 mmol), K₃PO₄ (106 mg, 0.5 mmol) and 3,4-dichlorobenzylaldehyde (87 mg, 0.5 mmol) in dried ethyl acetate was stirred at room temperature under N₂ for 8 h. The reaction mixture was passed through a short pad of Celite. After evaporation of the filtrate under reduced pressure, the residue was purified by flash column chromatography (PE/EA, 3/1 to 1/1) on silica gel to give the product 2a.

2-((3,4-dichlorophenyl)(4-nitrophenoxy)methyl)-1-(4-methoxyphenyl)-imidazole (2a)

1
81%. $^1$H NMR (Acetone-$d_6$, δ): 8.02 (d, $J = 9.3$ Hz, 2 H), 7.48 (d, $J = 2.0$ Hz, 1 H), 7.43 (d, $J = 8.4$ Hz, 1 H), 7.28 (dd, $J = 8.4$ Hz, $J = 2.0$ Hz, 1 H), 7.14 (d, $J = 1.2$ Hz, 1 H), 7.12 (d, $J = 9.0$ Hz, 2 H), 7.03 (d, $J = 9.3$ Hz, 2 H), 6.95 (d, $J = 1.2$ Hz, 1 H), 6.85 (d, $J = 9.0$ Hz, 2 H), 6.58 (s, 1 H), 3.70 (s, 3 H); $^{13}$C NMR (Acetone-$d_6$, δ): 162.0, 160.0, 144.2, 142.1, 138.2, 131.7, 131.5, 130.4, 129.7, 129.2, 128.3, 127.7, 127.2, 125.5, 123.5, 116.1, 114.3, 73.5, 55.1; IR (KBr): ν = 3140, 1609, 1590, 1520, 1494, 1475, 1383, 1344, 1299, 1242, 1171, 1129, 1110, 1032, 1009, 987, 851, 840, 776, 750, 646, 555 cm$^{-1}$; HRMS (ESI, m/z): calcd for [C$_{23}$H$_{18}$Cl$_2$N$_3$O$_4$]$^+$, 470.0669; found, 470.0678.

1-(4-methoxyphenyl)-2-((4-nitrophenoxy)(p-tolyl)methyl)-imidazole ($2b$)

96%. $^1$H NMR (Acetone-$d_6$, δ): 7.98 (d, $J = 9.3$ Hz, 2 H), 7.17 (d, $J = 8.1$ Hz, 2 H), 7.07 (d, $J = 1.2$ Hz, 1 H), 7.07 (d, $J = 8.9$ Hz, 2 H), 7.01 (d, $J = 8.1$ Hz, 2 H), 6.92 (d, $J = 9.3$ Hz, 2 H), 6.91 (d, $J = 1.2$ Hz, 1 H), 6.83 (d, $J = 8.9$ Hz, 2 H), 6.39 (s, 1 H), 3.69 (s, 3 H), 2.17 (s, 3 H); $^{13}$C NMR (Acetone-$d_6$, δ): 162.6, 159.9, 145.1, 137.8, 134.4, 130.0, 128.8, 128.2, 127.7, 127.3, 125.5, 123.0, 116.0, 114.3, 74.8, 55.1, 20.3; IR (KBr): ν = 1609, 1593, 1511, 1496, 1341, 1301, 1251, 1170, 1110, 1031, 1011, 987, 843, 773, 752, 657, 547, 491 cm$^{-1}$; HRMS (ESI, m/z): calcd for [C$_{24}$H$_{22}$N$_3$O$_4$]$^+$, 416.1605; found, 416.1614.

1-(4-methoxyphenyl)-2-((4-nitrophenoxy)(phenyl)methyl)-imidazole ($2c$)

78%. $^1$H NMR (Acetone-$d_6$, δ): 7.99 (d, $J = 9.3$ Hz, 2 H), 7.27 (dd, $J = 7.8$ Hz, $J = 1.9$ Hz, 2 H), 7.14-7.22 (m, 3 H), 7.07 (d, $J = 1.2$ Hz, 1 H), 7.05 (d, $J = 9.0$ Hz, 2 H), 6.95 (d, $J = 9.3$ Hz, 2 H), 6.92 (d, $J = 1.2$ Hz, 1 H), 6.82 (d, $J = 9.0$ Hz, 2 H), 6.45 (s, 1 H), 3.68 (s, 3 H); $^{13}$C NMR (Acetone-$d_6$, δ): 163.4, 160.8, 145.9, 142.6, 138.2, 130.8, 129.0, 128.9, 128.6, 128.1, 126.3, 124.0, 116.8, 115.1, 75.7, 55.9; IR (KBr): ν = 1609, 1593, 1511, 1494, 1342, 1298, 1249, 1170, 1111, 1031, 988, 881, 838, 751, 697, 667, 545 cm$^{-1}$; HRMS (ESI, m/z): calcd for [C$_{23}$H$_{20}$N$_3$O$_4$]$^+$, 402.1448; found, 402.1452.

1-(4-methoxyphenyl)-2-((4-nitrophenoxy)(3-nitrophenyl)methyl)-imidazole ($2d$)

73%. $^1$H NMR (Acetone-$d_6$, δ): 8.12 (t, $J = 1.9$ Hz, 1 H), 7.98-8.08 (m, 3 H), 7.74 (d, $J = 7.9$ Hz, 1 H), 7.52 (t, $J = 7.9$ Hz, 1 H), 7.13 (d, $J = 1.2$ Hz, 1 H), 7.09 (d, $J = 9.0$ Hz, 2 H), 7.07 (d, $J = 9.3$ Hz, 2 H),
6.94 (d, J = 1.2 Hz, 1 H), 6.81 (d, J = 9.0 Hz, 2 H), 6.75 (s, 1 H), 3.67 (s, 3 H); 13C NMR (Acetone-d6, δ): 162.2, 160.2, 148.4, 144.5, 139.8, 133.7, 129.9, 128.5, 128.0, 125.8, 123.9, 123.2, 122.2, 116.4, 114.5, 74.0, 55.3; IR (KBr): ν = 3088, 1610, 1593, 1520, 1493, 1342, 1299, 1244, 1170, 1112, 1030, 1004, 987, 866, 850, 838, 789, 753, 725, 678, 659, 611, 553 cm⁻¹; HRMS (ESI, m/z): calcd for [C23H19N4O6]+, 447.1299; found, 447.1310.

2-((4-fluorophenyl)(4-nitrophenoxy)methyl)-1-(4-methoxyphenyl)-imidazole (2e)

83%. 1H NMR (Acetone-d6, δ): 8.02 (d, J = 9.3 Hz, 2 H), 7.33-7.41 (m, 2 H), 7.07-7.13 (m, 3 H), 6.94-7.03 (m, 5 H), 6.86 (d, J = 8.9 Hz, 2 H), 6.51 (s, 1 H), 3.71 (s, 3 H); 19F NMR (Acetone-d6, δ): -113.6 (m, 1 F); 13C NMR (75.4 MHz, Acetone-d6, δ): 163.7, 162.4, 161.3, 160.0, 144.9, 141.9, 133.5, 129.9, 129.5, 129.4, 128.2, 127.7, 125.5, 123.2, 116.0, 115.1, 114.8, 114.3, 74.2, 55.1; IR (KBr): ν = 1702, 1608, 1591, 1516, 1494, 1343, 1299, 1250, 1172, 1160, 1112, 1032, 990, 887, 838, 787, 752, 690, 655, 612, 552 cm⁻¹; HRMS (ESI, m/z): calcd for [C23H19FN3O4]+, 420.1354; found, 420.1351.

2-((4-chlorophenyl)(4-nitrophenoxy)methyl)-1-(4-methoxyphenyl)-imidazole (2f)

79%. 1H NMR (Acetone-d6, δ): 7.99 (d, J = 9.3 Hz, 2 H), 7.31 (d, J = 8.6 Hz, 2 H), 7.22 (d, J = 8.6 Hz, 2 H), 7.05-7.11 (m, 3 H), 6.96 (d, J = 9.3 Hz, 2 H), 6.92 (d, J = 1.2 Hz, 1 H), 6.83 (d, J = 8.9 Hz, 2 H), 6.50 (s, 1 H), 3.69 (s, 3 H); 13C NMR (75.4 MHz, Acetone-d6, δ): 162.3, 160.0, 144.6, 136.8, 131.2, 129.9, 129.3, 128.2, 127.7, 125.5, 123.3, 121.7, 116.0, 114.3, 74.2, 55.1; IR (KBr): ν = 1609, 1593, 1511, 1494, 1342, 1301, 1249, 1170, 1107, 1032, 1012, 989, 895, 846, 835, 775, 751, 732, 642, 550, 496, 466 cm⁻¹; HRMS (ESI, m/z): calcd for [C23H19ClN3O4]+, 436.1059; found, 436.1063.

2-((4-bromophenyl)(4-nitrophenoxy)methyl)-1-(4-methoxyphenyl)-imidazole (2g)

75%. 1H NMR (Acetone-d6, δ): 7.99 (d, J = 9.3 Hz, 2 H), 7.38 (d, J = 8.5 Hz, 2 H), 7.24 (d, J = 8.5 Hz, 2 H), 7.08 (d, J = 8.8 Hz, 2 H), 6.96 (d, J = 9.3 Hz, 2 H), 6.92 (d, J = 1.2 Hz, 1 H), 6.83 (d, J = 8.8 Hz, 2 H), 6.48 (s, 1 H), 3.68 (s, 3 H); 13C NMR (75.4 MHz, Acetone-d6, δ): 162.3, 160.0, 144.6, 141.9, 136.3, 133.5, 129.9, 129.0, 128.3, 127.7, 125.5, 123.3, 116.0, 114.3, 74.1, 55.1; IR (KBr): ν = 1610, 1591, 1519,
1495, 1441, 1343, 1302, 1249, 1172, 1109, 1071, 1034, 1009, 990, 896, 853, 840, 777, 751, 732, 619, 547, 491 cm\(^{-1}\); HRMS (ESI, m/z): calcd for [C\(_{23}\)H\(_{19}\)BrN\(_3\)O\(_4\)]\(^+\), 480.0554; found, 480.0563.

2-((3-bromophenyl)(4-nitrophenoxy)methyl)-1-(4-methoxyphenyl)-imidazole (2h)

68%. \(^1\)H NMR (Acetone-\(d_6\), \(\delta\)): 8.00 (d, \(J = 9.3\) Hz, 2 H), 7.42 (t, \(J = 1.6\) Hz, 1 H), 7.34 (dt, \(J = 7.9\) Hz, \(J = 1.6\) Hz, 1 H), 7.26 (d, \(J = 7.9\) Hz, 1 H), 7.15 (t, \(J = 7.9\) Hz, 1 H), 7.09 (d, \(J = 1.2\) Hz, 1 H), 7.05 (d, \(J = 9.0\) Hz, 2 H), 7.00 (d, \(J = 9.3\) Hz, 2 H), 6.92 (d, \(J = 1.2\) Hz, 1 H), 6.82 (d, \(J = 9.0\) Hz, 2 H), 6.52 (s, 1 H), 3.68 (s, 3 H); \(^{13}\)C NMR (75.4 MHz, Acetone-\(d_6\), \(\delta\)): 163.0, 160.8, 145.4, 142.8, 140.7, 131.9, 131.0, 130.8, 130.6, 129.0, 128.6, 126.9, 126.4, 124.3, 122.6, 116.9, 115.1, 74.9, 55.9; IR (KBr): \(v = 1609, 1591, 1514, 1493, 1342, 1329, 1249, 1170, 1111, 1031, 838, 769, 751, 547\) cm\(^{-1}\); HRMS (ESI, m/z): calcd for [C\(_{23}\)H\(_{19}\)BrN\(_3\)O\(_4\)]\(^+\), 480.0554; found, 480.0555.

2-((3,5-dimethoxyphenyl)(4-nitrophenoxy)methyl)-1-(4-methoxyphenyl)-imidazole (2i)

72%. \(^1\)H NMR (Acetone-\(d_6\), \(\delta\)): 8.00 (d, \(J = 9.2\) Hz, 2 H), 7.08 (d, \(J = 8.8\) Hz, 2 H), 7.07 (s, 1 H), 6.98 (d, \(J = 9.2\) Hz, 2 H), 6.93 (s, 1 H), 6.84 (d, \(J = 8.8\) Hz, 2 H), 6.42 (d, \(J = 2.2\) Hz, 2H), 6.40 (s, 1 H), 6.28 (t, \(J = 2.2\) Hz, 1 H), 3.70 (s, 3 H), 3.58 (s, 6 H); \(^{13}\)C NMR (75.4 MHz, Acetone-\(d_6\), \(\delta\)): 162.8, 161.1, 160.1, 145.1, 142.0, 139.7, 130.2, 128.3, 128.0, 125.7, 123.4, 116.2, 114.5, 105.4, 99.9, 75.2, 55.3, 54.9; IR (KBr): \(v = 1610, 1593, 1519, 1474, 1428, 1341, 1311, 1251, 1212, 1159, 1112, 1035, 1023, 924, 867, 835, 752, 725, 678, 659, 611, 553\) cm\(^{-1}\); HRMS (ESI, m/z): calcd for [C\(_{25}\)H\(_{24}\)N\(_3\)O\(_6\)]\(^+\), 462.1660; found, 462.1669.

**General procedure for the reaction of 1 with acrylates:** A mixture of 1 (33 mg, 0.1 mmol), K\(_3\)PO\(_4\) (212 mg, 1 mmol), and methacrylate (0.18 ml, 2 mmol) in dried ethyl acetate was stirred at room temperature under N\(_2\) for 8 h. The reaction mixture was passed through a short pad of Celite. After evaporation of the filtrate under reduced pressure, the residue was purified by flash column chromatography (PE/EA, 2/1 to 1/1) on silica gel to give the product 3a.

Methyl 3-(1-(4-methoxyphenyl)-imidazol-2-yl)-2-(4-nitrophenyl)propanoate (3a)
79%. $^1$H NMR (CDCl$_3$, $\delta$): 8.10 (d, $J = 8.7$ Hz, 2 H), 7.36 (d, $J = 8.7$ Hz, 2 H), 7.06 (d, $J = 8.8$ Hz, 2 H), 7.03 (s, 1 H), 6.94 (d, $J = 8.8$ Hz, 2 H), 6.89 (s, 1 H), 4.53 (t, $J = 7.8$ Hz, 1 H), 3.86 (s, 3 H), 3.66 (s, 3 H), 3.43 (dd, $J = 15.5$ Hz, $J = 8.7$ Hz, 1 H), 2.95 (dd, $J = 15.5$ Hz, $J = 6.9$ Hz, 1 H); $^{13}$C NMR (CDCl$_3$, $\delta$): 172.5, 159.4, 147.2, 145.5, 144.9, 129.9, 128.8, 127.7, 127.0, 123.7, 121.2, 114.5, 55.5, 52.5, 49.3, 30.3; IR (KBr): $\nu = 3105, 2957, 2846, 1737, 1607, 1519, 1446, 1432, 1423, 1352, 1299, 1247, 1170, 1160, 1108, 1026, 862, 842, 746, 732, 618, 608, 539$ cm$^{-1}$; HRMS (ESI, m/z): calcd for [C$_{20}$H$_{20}$N$_3$O$_5$]$^+$, 382.1397; found, 382.1395.

Ethyl 3-((1-(4-methoxyphenyl)-imidazol-2-yl)-2-(4-nitrophenyl)propanoate (3b)

82%. $^1$H NMR (CDCl$_3$, $\delta$): 8.09 (d, $J = 8.3$ Hz, 2 H), 7.35 (d, $J = 8.3$ Hz, 2 H), 7.04 (d, $J = 8.7$ Hz, 2 H), 7.03 (s, 1 H), 6.93 (d, $J = 8.7$ Hz, 2 H), 6.88 (s, 1 H), 4.50 (t, $J = 7.8$ Hz, 1 H), 4.02-4.21 (m, 2 H), 3.86 (s, 3 H), 3.42 (dd, $J = 15.6$ Hz, $J = 8.2$ Hz, 1 H), 2.95 (dd, $J = 15.6$ Hz, $J = 7.3$ Hz, 1 H), 1.16 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (CDCl$_3$, $\delta$): 172.0, 159.5, 147.2, 145.7, 145.0, 130.0, 128.9, 127.8, 127.1, 123.7, 121.2, 114.6, 61.4, 55.6, 49.7, 30.4, 13.9; IR (KBr): $\nu = 2840, 1733, 1608, 1517, 1465, 1446, 1349, 1299, 1251, 1164, 1109, 1033, 912, 857, 838, 733, 612, 541$ cm$^{-1}$; HRMS (ESI, m/z): calcd for [C$_{21}$H$_{22}$N$_3$O$_5$]$^+$, 396.1554; found, 396.1555.

tert-Butyl 3-((1-(4-methoxyphenyl)-imidazol-2-yl)-2-(4-nitrophenyl)propanoate (3c)

58%. $^1$H NMR (CDCl$_3$, $\delta$): 8.08 (d, $J = 8.5$ Hz, 2 H), 7.32 (d, $J = 8.5$ Hz, 2 H), 7.03 (s, 1 H), 7.01 (d, $J = 9.0$ Hz, 2 H), 6.92 (d, $J = 9.0$ Hz, 2 H), 6.87 (s, 1 H), 4.38 (t, $J = 7.8$ Hz, 1 H), 3.86 (s, 3 H), 3.36 (dd, $J = 15.6$ Hz, $J = 7.8$ Hz, 1 H), 2.93 (dd, $J = 15.6$ Hz, $J = 7.8$ Hz, 1 H), 1.34 (s, 9 H); $^{13}$C NMR (CDCl$_3$, $\delta$): 171.1, 159.5, 147.1, 145.2, 145.0, 130.0, 128.8, 127.7, 127.0, 123.6, 121.1, 114.5, 81.6, 55.5, 50.7, 30.4, 27.8; IR (KBr): $\nu = 2984, 2937, 1725, 1608, 1518, 1422, 1369, 1348, 1299, 1251, 1153, 1110, 1030, 911, 840, 733$ cm$^{-1}$; HRMS (ESI, m/z): calcd for [C$_{23}$H$_{26}$N$_3$O$_5$]$^+$, 424.1867; found, 424.1869.
Methyl 3-(1-(4-methoxyphenyl)-imidazol-2-yl)-2-methyl-2-(4-nitrophenyl)propanoate (3d)

11% at room temperature for 8 h and 89% at 65 °C for 13 h. \(^1\)H NMR (CDCl\(_3\), \(\delta\)): 7.99 (d, \(J = 8.8\) Hz, 2 H), 7.18 (d, \(J = 8.8\) Hz, 2 H), 7.03 (s, 1 H), 6.78-6.87 (m, 5 H), 3.84 (s, 3 H), 3.68 (s, 3 H), 3.39 (s, 2 H), 1.78 (s, 3 H); \(^13\)C NMR (CDCl\(_3\), \(\delta\)): 175.3, 159.6, 150.0, 147.0, 144.0, 130.4, 128.1, 127.4, 127.3, 123.5, 121.6, 114.6, 55.8, 52.9, 51.0, 35.7, 22.8; IR (KBr): \(v = 2952, 2841, 1734, 1606, 1517, 1461, 1349, 1299, 1251, 1170, 1034, 911, 853, 838, 732, 700, 549\) cm\(^{-1}\); HRMS (ESI, m/z): calcd for [C\(_{21}\)H\(_{22}\)N\(_3\)O\(_5\)]\(^+\), 396.1554; found, 396.1560.
Single-Crystal X-ray Structure of 2a and 3a

Figure 1. Single crystal X-ray structure of 2a

Figure 2. Single crystal X-ray structure of compound 3a
The $^1$H NMR of 1

The $^{13}$C NMR of 1
The $^1$H NMR of 2a

The $^{13}$C NMR of 2a
The $^1$H NMR of 2b

The $^{13}$C NMR of 2b
The $^{1}H$ NMR of 2c

![1H NMR of 2c]

The $^{13}C$ NMR of 2c

![13C NMR of 2c]
The $^1$H NMR of 2d

The $^{13}$C NMR of 2d
The $^1$H NMR of 2e

The $^{19}$F NMR of 2e
The $^{13}$C NMR of 2e

The $^1$H NMR of 2f
The $^{13}$C NMR of $2f$

![$^{13}$C NMR spectrum of $2f$]

The $^1$H NMR of $2g$

![$^1$H NMR spectrum of $2g$]
The $^{13}$C NMR of $2g$

The $^1$H NMR of $2h$
The $^{13}$C NMR of 2h

The $^1$H NMR of 2i
The $^{13}$C NMR of 2i

The $^1$H NMR of 3a
The $^{13}$C NMR of 3a

The $^1$H NMR of 3b
The $^{13}$C NMR of $3b$

![13C NMR spectrum of 3b](image)

The $^1$H NMR of $3c$

![1H NMR spectrum of 3c](image)
The $^{13}$C NMR of $3c$

![Carbon NMR spectrum of 3c](image)

The $^1$H NMR of $3d$

![Proton NMR spectrum of 3d](image)
The $^{13}$C NMR of 3d