Supporting Information

MgBr₂·OEt₂ – A Lewis Acid Catalyst for the *O*- and *N*-Boc Protection of Phenols and Amines

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General Considerations

Unless noted otherwise, all reagents and solvents were used as purchased without further purification. All reactions were carried out open to the atmosphere. For analytical TLC silica gel 60 F 254(Merck 1.05715) was used. Flash column chromatography was performed on silica gel 60 (230–400 mesh) with reagent grade solvents. ¹H and ¹³C NMR spectra were recorded on a Bruker 300 MHz spectrometer at ambient temperature. All ¹H chemical shifts are reported in ppm (δ) relative to TMS; ¹³C shifts are reported relative to the corresponding NMR solvent. IR spectra were recorded on a Thermo Nicolet 380 Ft-IR spectrometer (ATR). HRMS data was collected from a Thermo Scientific Orbitrap Qexactive mass spectrometer.

Spectral Data obtained for compounds 2-9, 11, and 14-19 were identical to spectral data previously published.^{1, 2, 3}

***p*-Nitrophenoxy 2,2-dimethylpropionate 2**

¹H NMR (300 MHz, CDCl₃) δ ppm 1.53 (s, 9 H) 7.33 (d, *J*=9.33 Hz, 2 H) 8.21 (d, *J*=9.06 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ ppm 27.9, 85.08, 122.26, 125.50, 145.48, 150.87, 156.10.

Phenoxy 2,2-dimethylpropionate 3

¹H NMR (300 MHz, CDCl₃) δ ppm 1.59 (s, 9 H) 7.10 - 7.30 (m, 3 H) 7.30 - 7.48 (m, 2 H)
¹³C NMR (75 MHz, CDCl₃) δ ppm 28.11, 83.85, 121.67, 126.11, 129.78, 151.54, 152.34.

Methyl *p*-(*tert*-butoxycarbonyloxy)benzoate 4

¹H NMR (300 MHz, CDCl₃) δ ppm 1.51 (s, 9 H) 3.85 (s, 3 H) 7.21 (d, *J*=8.78 Hz, 2 H) 8.02 (d, *J*=8.78 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ ppm 27.99, 52.47, 84.34, 121.49, 127.91, 131.48, 151.44, 155.03, 166.57.

***p*-Bromophenoxy 2,2-dimethylpropionate 5**

¹H NMR (300 MHz, CDCl₃) δ ppm 1.56 (s, 9 H) 7.08 (d, *J*=8.51 Hz, 2 H) 7.49 (d, *J*=8.51 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ ppm 28.07, 84.25, 119.11, 123.47, 132.79, 150.59, 151.82.

***tert*-Butoxy *p*-anisate 6**

^1H NMR (300 MHz, CDCl_3) δ ppm 1.57 (s, 9 H) 3.78 (s, 3 H) 6.89 (d, $J=9.06$ Hz, 2 H) 7.10 (d, $J=9.06$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 28.09, 55.94, 83.61, 114.77, 122.48, 145.14, 152.73, 157.63.

1-Naphthyloxy 2,2-dimethylpropionate 7

^1H NMR (300 MHz, CDCl_3) δ ppm 1.68 (s, 9 H) 7.40 - 7.47 (m, 1 H) 7.49 - 7.67 (m, 3 H) 7.80 (d, $J=7.96$ Hz, 1 H) 7.89 - 7.97 (m, 1 H) 8.07 - 8.15 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 28.19, 84.05, 118.30, 121.61, 125.89, 126.49, 126.94, 127.00, 127.46, 128.49, 135.17, 147.48, 152.55.

***p*-Acetylphenoxy 2,2-dimethylpropionate 8**

^1H NMR (300 MHz, CDCl_3) δ ppm 1.49 (s, 9 H) 2.49 (s, 3 H) 7.19 (d, $J=8.78$ Hz, 2 H) 7.90 (d, $J=8.78$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 26.84, 27.97, 84.36, 121.63, 130.23, 134.91, 151.38, 155.03, 196.98.

***tert*-Butoxy *p*-formylbenzoate 9**

^1H NMR (300 MHz, CDCl_3) δ ppm 1.51 (s, 9H) 7.30 (d, $J=8.78$ Hz, 2 H) 7.85 (d, $J=8.78$ Hz, 2 H) 9.92 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 27.97, 84.62, 122.23, 131.52, 134.22, 151.25, 156.02, 191.19.

***tert*-Butoxy *p*-cyanobenzoate 11**

^1H NMR (300 MHz, CDCl_3) δ ppm 1.53 (s, 9 H) 7.18 - 7.36 (m, 2 H) 7.56 - 7.74 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 27.97, 84.94, 109.90, 118.56, 122.64, 134.00, 151.05, 154.65.

***tert*-Butyl 3*H*-imidazole-1-carboxylate 14**

^1H NMR (300 MHz, CDCl_3) δ ppm 1.56 (s, 9 H) 6.96 (s, 1 H) 7.31 (s, 1 H) 8.01 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 28.21, 85.95, 117.47, 130.51, 137.41, 147.44.

Benzylamino 2,2-dimethylpropionate 15

^1H NMR (300 MHz, CDCl_3) δ ppm 1.47 (s, 9 H) 4.29 (br. s., 2 H) 5.09 (br. s., 1 H) 7.15 - 7.40 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 28.82, 45.06, 127.66, 128.96, 139.47, 156.38.

2-Pyridylamino 2,2-dimethylpropionate 16

^1H NMR (300 MHz, CDCl_3) δ ppm 1.56 (s, 9 H) 6.94 (ddd, $J=6.72, 5.63, 0.82$ Hz, 1 H) 7.56 - 7.75 (m, 1 H) 8.03 (d, $J=8.51$ Hz, 1 H) 8.30 - 8.48 (m, 1 H) 10.05 (br. s., 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 28.80, 81.03, 113.05, 118.26, 138.70, 147.97, 153.41.

***tert*-Butyl 1-piperidinecarboxylate 17**

^1H NMR (300 MHz, CDCl_3) δ ppm 1.40 (s, 9 H) 1.42 - 1.56 (m, 6 H) 3.23 - 3.36 (m, 4 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 24.84, 26.09, 28.80, 45.27, 79.37, 155.25.

***p*-Acetylphenylamino 2,2-dimethylpropionate 18**

^1H NMR (300 MHz, CDCl_3) δ ppm 1.34 - 1.52 (m, 9 H) 2.51 (s, 3 H) 7.51 (d, $J=8.78$ Hz, 2 H) 7.66 (s, 1 H) 7.81 - 7.92 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 26.72, 28.64, 81.49, 117.90, 130.21, 132.02, 143.71, 152.81, 197.55.

Methyl 2-(*tert*-butoxycarbonylamino)propionate 19

^1H NMR (300 MHz, CDCl_3) δ ppm 1.25 (d, $J=7.14$ Hz, 3 H) 1.31 (s, 9 H) 3.61 (s, 3 H) 4.20 (br. s., 1 H) 5.25 (br. s., 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 18.61, 28.54, 49.46, 52.43, 79.90, 155.47, 174.14.

1. Chebolu, R.; Chankeshwara, S.V.; Chakraborti, A.K. *Synthesis*, **2008**, 1448.
2. Chebolu, R.; Chankeshwara, S.V.; Chakraborti, A.K. *J. Org. Chem.*, **2008**, 73, 8615.
3. Varala, R.; Nuvula, S.; Adapa, S.R. *J. Org. Chem.*, **2006**, 71, 8283.

***tert*-Butoxy *p*-acetylamino benzoate 10**

^1H NMR (300 MHz, CDCl_3) δ 8.43 (s, 1H), 7.42 (d, $J = 9.0$ Hz, 2H), 7.02 (d, $J = 8.9$ Hz, 2H), 2.04 (s, 3H), 1.52 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 169.47, 152.55, 147.45, 136.28, 121.85, 121.46, 84.04, 28.07, 24.51.

IR (KBr) ν : 2985, 1757, 1660, 1508, 1405, 1263, 1145, 779, 735 cm^{-1} .

HRMS (ESI) m/z : Calculated for $\text{C}_{13}\text{H}_{18}\text{NO}_4$ 252.1230 $[\text{M}+\text{H}]^+$; found 252.1227.

(*p*-Chlorophenyl)methoxy 2,2-dimethylpropionate 12

^1H NMR (300 MHz, CDCl_3) δ 7.30 (s, 4H), 5.03 (s, 2H), 1.51 (s, 10H), 1.47 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 153.69, 147.13, 134.61, 129.99, 129.09, 129.03, 128.73, 85.49, 82.81, 68.17, 28.14, 28.05, 27.80.

IR (KBr) ν : 2981, 1740, 1493, 1371, 1276, 1161, 863 cm^{-1} .

HRMS (ESI) m/z : Calculated for $\text{C}_{12}\text{H}_{15}\text{ClNaO}_3$ 265.0607 $[\text{M}+\text{Na}]^+$; found 265.0594.

Methyl 2-[(9H-fluoren-9-yl)methoxycarbonylamino]-3-[*p*-(*tert*-butoxycarbonyloxy)phenyl]propionate 13

^1H NMR (300 MHz, CDCl_3) δ 7.83 – 7.75 (m, 2H), 7.61 (d, $J = 7.5$ Hz, 2H), 7.48 – 7.28 (m, 4H), 7.13 (s, 3H), 5.41 (d, $J = 8.2$ Hz, 1H), 4.69 (q, $J = 6.5$ Hz, 1H), 4.44 (ddd, $J = 29.5, 10.6, 7.0$ Hz, 2H), 4.24 (t, $J = 6.9$ Hz, 1H), 3.74 (s, 3H), 3.13 (d, $J = 6.3$ Hz, 2H), 1.77 – 1.41 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 172.18, 156.00, 152.21, 150.65, 144.26, 144.17, 141.73, 133.71, 130.64, 128.13, 127.49, 125.53, 125.45, 121.77, 120.39, 83.92, 67.35, 55.20, 52.78, 47.60, 37.92, 28.11.

IR (KBr) ν : 2982, 1752, 1721, 1509, 1396, 1257, 1145, 735 cm^{-1}

HRMS (ESI) m/z : Calculated for $\text{C}_{30}\text{H}_{32}\text{NO}_7$ 518.2172 $[\text{M}+\text{H}]^+$; found 518.2167.

HRMS (ESI Orbitrap) Compound 8

HRMS (ESI Orbitrap) Compound 12

HRMS (ESI Orbitrap) Compound 13