

Supporting Information

Copper-Catalyzed Aerobic Oxidative Amidation of Tertiary Amines

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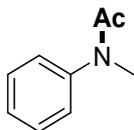
1. General Information

All manipulations were performed in air atmosphere. $\text{Cu}(\text{OAc})_2$ was purchased from J&K Scientific Co. *N,N*-Dimethylaniline (**1a**) was purchased from Heowns Chemical, dried by distillation over CaH_2 and distilled prior to use. Anilines **1b**, **1f**, **1g**, **1h** and **1j** were purchased from Heowns Chemical, and used without further purification. Other tertiary amines were prepared according to reported procedures^[1]. CH_3CN , DMA, DME, DMF, PhCl and DCE were dried by distillation over CaH_2 . THF and toluene were dried by distillation over sodium/benzophenone. ^1H NMR and ^{13}C NMR were recorded on a Bruker AVANCE AV 400 (400 MHz for ^1H , 100 MHz for ^{13}C) instrument in CDCl_3 with tetramethylsilane as an internal standard. Data were reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), integration. TLC were performed on silica gel Huanghai HSGF254 plates and visualized by quenching of UV fluorescence ($\lambda_{\text{max}} = 254 \text{ nm}$). Silica gel (200-300 mesh) was purchased from Qingdao Haiyang Chemical Co., China. Electron-impact-ionisation mass spectra (EI) were recorded with an Agilent 7890A/5975C GC-MS instrument. High resolution mass spectra (HRMS) were acquired on Varian 7.0T FTMS. FTIR spectra were obtained with a Bruker Tensor 27 instrument. All IR samples were prepared as thin films and reported in wave numbers (cm^{-1}).

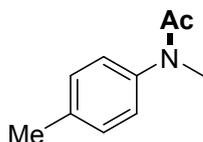
2. General Procedure for the Amides Synthesis

Typical procedure: A 25 mL Schlenk-type tube was equipped with a magnetic stir bar, and charged with $\text{Cu}(\text{OAc})_2$ (4.6 mg, 0.05 mmol). The tube was sealed, and the atmosphere was changed to O_2 with an oxygen balloon. Tertiary amines **1a** (0.5 mmol), Ac_2O (2.5 mmol) and CH_3CN (1.0 mL) were added sequentially via syringes. The mixture was stirred at reflux for 36 h. The resulting solution was then cooled to room temperature, neutralized with a saturated solution of NaHCO_3 , and extracted with EtOAc ($3 \times 25 \text{ mL}$). The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4 . The volatiles were removed under vacuum, and the residue was purified by column chromatography to give the crude product **3a** in 90% yield (67 mg, white solid).

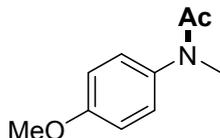
3. Characterization Data for Products 3



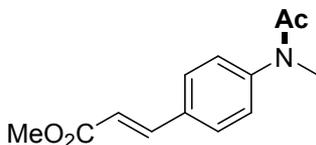
***N*-Methyl-*N*-phenylacetamide (3a):** white solid (67 mg, 90%). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.41 (t, $J=7.4$ Hz, 2H), 7.33 (t, $J=7.3$ Hz, 1H), 7.18 (d, $J=7.4$ Hz, 2H), 3.26 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.70, 144.72, 129.85, 127.83, 127.20, 37.28, 22.55. GC-MS: $m/z = 149$.



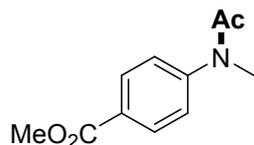
***N*-methyl-*N*-(*p*-tolyl)acetamide (3b):** white solid (68 mg, 83%), ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.21 (d, $J=8.04$ Hz, 2H), 7.07 (d, $J=8.16$ Hz, 2H), 3.24 (s, 3H), 2.38 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.86, 142.16, 137.73, 130.41, 126.92, 37.31, 22.49, 21.18. GC-MS: $m/z = 163$.



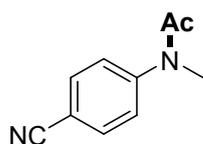
***N*-(4-methoxyphenyl)-*N*-methylacetamide (3c):** white solid (80 mg, 89%), ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.10 (d, $J=8.08$ Hz, 2H), 6.92 (d, $J=8.12$ Hz, 2H), 3.83 (s, 3H), 3.23 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 171.01, 158.86, 137.52, 128.20, 114.87, 77.48, 77.16, 76.84, 55.55, 37.36, 22.41. GC-MS: $m/z = 179$.



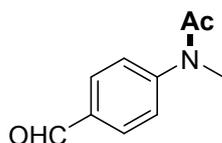
(*E*)-methyl 3-(4-(*N*-methylacetamido)phenyl)acrylate (3d): pale yellow solid (104 mg, 89%), ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.67 (d, $J=16.00$ Hz, 2H), 7.56 (d, $J=8.00$ Hz, 2H), 7.21 (d, $J=8.00$ Hz, 2H), 6.4 (d, $J=16.00$ Hz, 2H), 3.81 (s, 3H), 3.26 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.43, 167.26, 146.14, 133.83, 129.40, 127.59, 118.91, 51.95, 37.18, 22.61. IR (KBr, cm^{-1}): 1888, 1699, 1595, 1444, 1369, 935, 814, 736, 695. GC-MS: $m/z = 233$.



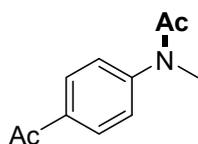
***N*-(4-Carbomethoxyphenyl)-*N*-methylacetamide (3e):** white solid (85 mg, 82%); ¹H NMR (300 MHz, CDCl₃) : δ= 8.10 (d, *J* = 8.48 Hz, 2 H), 7.29 (d, *J* = 8.48 Hz, 2 H), 3.95 (s, 3 H), 3.31 (s, 3 H), 1.94 (br s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 170.30, 166.25, 148.52, 131.17, 129.13, 126.94, 52.43, 37.20, 22.59; IR (KBr, cm⁻¹): 1721, 1664, 1602, 1509, 1275. GC-MS: *m/z* = 207.



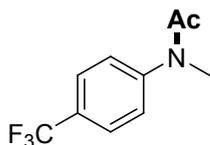
***N*-(4-Cyanophenyl)-*N*-methylacetamide (3f):** white solid (61 mg, 70%); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.73 (d, *J* = 8.44 Hz, 2H), 7.34 (d, *J* = 8.44 Hz, 2H), 3.31 (s, 3H), 1.98(s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 170.03, 148.45, 133.70, 127.68, 118.14, 37.37, 22.71. IR (KBr, cm⁻¹): 2228, 1657, 1601, 1508, 1380, 1359, 853. GC-MS: *m/z* = 174.



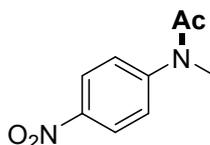
***N*-(4-Formylphenyl)-*N*-methylacetamide (3g):** white solid (46 mg, 52%); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.02 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 3.32 (s, 3H), 1.97(s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 190.9, 170.0, 149.7, 135.0, 131.0, 127.4, 37.2, 22.6. IR (KBr, cm⁻¹): 2820, 2782, 1756, 1659, 1601, 1377, 1246, 1238, 971, 865. GC-MS: *m/z* = 177.



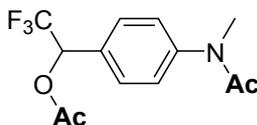
***N*-(4-acetylphenyl)-*N*-methylacetamide (3h):** white solid (81 mg, 85%); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.04(d, *J* = 8.44 Hz, 2H), 7.33(d, *J* = 8.44 Hz, 2H), 3.33(s, 3H), 2.65(s, 3H), 1.97(s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 197.02, 170.25, 148.63, 129.92, 127.08, 119.23, 37.24, 26.76, 22.65. GC-MS : *m/z* = 191.



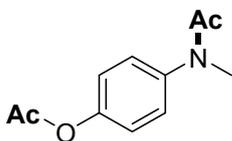
***N*-methyl-*N*-(4-(trifluoromethyl)phenyl)acetamide (3i)**: white solid (65 mg, 60%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.71(d, $J = 8.24$ Hz, 2H), 7.34(d, $J = 8.24$ Hz, 2H), 3.30(s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.10, 147.67, 129.82, 127.44, 126.87, 123.81(q, $J = 273.70$ Hz), 37.14, 22.49. ^{19}F NMR (400 MHz, CDCl_3) δ (ppm): -62.6 (s, 3F); IR (KBr, cm^{-1}): 1660, 1610, 1382, 1324, 1119, 1156, 1119, 1066, 859. GC-MS: $m/z = 217$.



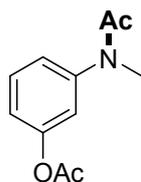
***N*-methyl-*N*-(4-nitrophenyl)acetamide (3j)**: yellow solid (49 mg, 50%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.30(d, $J = 8.68$ Hz, 2H), 7.40(d, $J = 8.68$ Hz, 2H), 3.35(s, 3H), 2.03(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.02, 154.36, 149.78, 127.49, 125.17, 37.52, 22.80. GC-MS : $m/z = 194$.



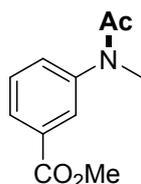
2,2,2-trifluoro-1-(4-(*N*-methylacetamido)phenyl)ethyl acetate (3k) : white solid (115 mg, 80%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.52 (d, $J = 8.18$ Hz, 2H), 7.25 (d, $J = 8.18$ Hz, 2H), 6.16 (q, $J = 6.83$ Hz, 1H), 3.27 (s, 3H), 2.22 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.39, 168.68, 145.99, 130.77, 129.55, 127.48, 123.04(q, $J = 278.85$ Hz), 71.35(q, $J = 33.20$ Hz), 37.15, 22.58, 20.66. IR (KBr, cm^{-1}): 1767, 1651, 1609, 1514, 1215, 1171, 1129, 1056, 866. GC-MS : $m/z = 289$. HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_3$ [$\text{M}+\text{Na}$] $^+$: 312.0818; found: 312.0822.



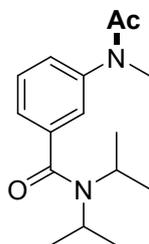
4-(*N*-methylacetamido)phenyl acetate (3l): white solid (92 mg, 89%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.20 (d, $J = 8.68$ Hz, 2H), 7.14 (d, $J = 8.68$ Hz, 2H), 3.25 (s, 3H), 2.32 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.36, 168.95, 149.62, 141.82, 127.96, 122.74, 36.99, 22.23, 20.89; IR (KBr, cm^{-1}): 1760, 1658, 1638, 1509, 1378, 1198, 913, 861; GC-MS: $m/z = 207$.



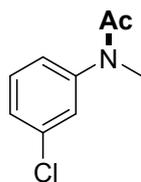
3-(*N*-methylacetamido)phenyl acetate (3m): white solid (99 mg, 96%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.41-7.44(m, 1H), 6.97-7.28(m, 3H), 3.27(s, 3H), 2.33(s, 3H), 1.91(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.60, 169.21, 151.54, 145.52, 130.48, 124.57, 121.16, 120.85, 37.22, 22.59, 21.23. GC-MS : $m/z = 207$.



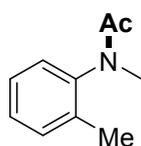
Methyl 3-(*N*-methylacetamido)benzoate (3n): white solid (88 mg, 85%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.03(d, $J = 7.63$ Hz, 1H), 8.02(s, 1H), 7.50-7.89(t, $J = 7.78$ Hz, 1H), 7.41(d, $J = 7.72$ Hz, 1H), 3.95(s, 3H), 3.29(s, 3H), 1.89(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.46, 166.16, 144.85, 132.03, 131.71, 130.01, 128.93, 128.31, 52.56, 37.25, 22.58. IR (KBr, cm^{-1}): 1726, 1670, 1415, 1381, 1314, 1248, 991, 758, 698. GC-MS : $m/z = 207$.



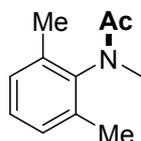
***N,N*-diisopropyl-3-(*N*-methylacetamido)benzamide (3o)**: white solid (110 mg, 80%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.45 (t, $J = 7.72$ Hz, 1H), 7.32-7.25 (m, 1H), 7.21 (d, $J = 7.92$ Hz, 1H), 7.17 (s, 1H), 3.79 (s, 1H), 3.55 (s, 1H), 3.27 (s, 3H), 1.90 (s, 3H), 1.54 (s, 6H), 1.16 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.48, 169.69, 144.81, 140.61, 130.14, 128.89, 127.45, 124.96, 124.53, 51.05, 46.03, 37.25, 22.53, 20.76. IR (KBr, cm^{-1}): 2967, 1672, 1630, 1453, 1378, 1343, 1213, 1041, 815, 716. GC-MS : $m/z = 276$.



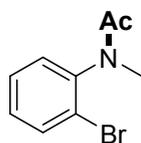
***N*-(3-chlorophenyl)-*N*-methylacetamide (3p)**: pale yellow solid (78 mg, 85%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.34-7.36(m, 2H), 7.22(s, 2H), 7.10(d, $J = 7.92$ Hz, 1H), 3.26(m, 3H), 1.90(m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.30, 145.78, 135.17, 130.77, 128.06, 127.55, 125.49, 37.18, 22.48. IR(KBr, cm^{-1}): 3051, 2930, 2359, 1667, 1593, 1572, 1477, 1418, 1383, 1294, 1144, 1105, 1087, 974, 910, 797, 773, 707, 675, 411. GC-MS : $m/z = 183$.



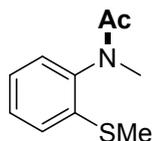
***N*-methyl-*N*-(*o*-tolyl)acetamide (3q)**: white solid (57 mg, 70%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.25-7.31(m, 3H), 7.11-7.13(m, 1H), 3.19(s, 3H), 2.24(s, 3H), 1.78(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.89, 143.16, 135.42, 131.55, 128.46, 127.94, 127.59, 35.95, 22.02, 17.39. IR (KBr, cm^{-1}): 1654, 1493, 1377, 1142, 1038, 776, 730. GC-MS : $m/z = 163$.



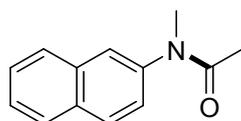
***N*-(2,6-dimethylphenyl)-*N*-methylacetamide (3r)**: white solid (74 mg, 84%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.11-7.29(m, 3H), 3.14(m, 3H), 2.22(m, 6H), 1.74(m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.90, 141.76, 135.62, 128.99, 128.17, 34.26, 21.31, 17.64. GC-MS : $m/z = 177$.



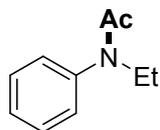
***N*-(2-bromophenyl)-*N*-methylacetamide (3s)**: white solid (102 mg, 90%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.69(d, $J = 7.9$ Hz, 1H), 7.40(t, $J = 7.43$ Hz, 1H), 7.24-7.31(m, 2H), 3.20(s, 3H), 1.81(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.54, 143.27, 134.00, 129.88, 129.76, 129.15, 123.45, 35.80, 22.23. IR (KBr, cm^{-1}): 1662, 1485, 1374, 1304, 1142, 1086, 1018, 841, 736, 723. GC-MS : $m/z = 227$.



***N*-methyl-*N*-(2-(methylthio)phenyl)acetamide (3t)**: yellow solid (84 mg, 86%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.36(t, $J = 7.42$ Hz, 1H), 7.16-7.22 (m, 2H), 7.12-7.14(m, 1H), 3.18(s, 3H), 2.45(s, 3H), 1.81(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 171.07, 140.89, 138.59, 129.02, 128.25, 125.54, 124.91, 35.18, 21.92, 14.15. IR (KBr, cm^{-1}): 1659, 1470, 1421, 1375, 1300, 1142, 1060, 970, 778, 741. GC-MS : $m/z = 195$.



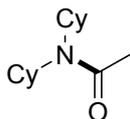
***N*-methyl-*N*-(naphthalen-2-yl)acetamide (4a)**: white solid (95 mg, 95%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.83-7.91(m, 3H), 7.66(s, 1H), 7.53-7.55(m, 2H), 7.30(d, $J = 8.54$ Hz, 1H), 3.35(m, 3H), 1.92(m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.79, 141.98, 133.71, 132.39, 129.96, 127.90, 127.86, 126.99, 126.76, 125.57, 125.20, 37.35, 22.66. GC-MS : $m/z = 199$.



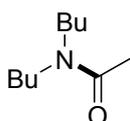
***N*-ethyl-*N*-phenylacetamide (4b)**: white solid (77 mg, 94%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.40 (t, $J = 7.52$ Hz, 2H), 7.32 (t, $J = 7.31$ Hz, 1H), 7.13 (d, $J = 7.31$ Hz, 2H), 3.72 (q, $J = 7.22$ Hz, 2H), 1.79 (s, 3H), 1.08 (t, $J = 7.22$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 169.9, 142.8, 129.6, 128.1, 127.8, 43.7, 22.8, 13.0. IR (KBr, cm^{-1}): 2983, 2938, 1654, 1597, 1496, 1401, 1298, 769, 711. GC-MS: $m/z = 163$.



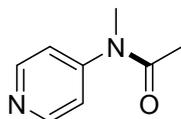
***N*-benzyl-*N*-phenylacetamide (4c)**: white solid (90 mg, 80%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.20-7.31(m, 8H), 6.98-6.99(m, 2H), 4.89(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.68, 144.59, 133.09, 130.03, 129.75, 128.35, 127.74, 127.09, 126.75, 37.20, 22.42. GC-MS: $m/z = 225$.



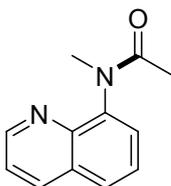
***N,N*-Dicyclohexylacetamid (4d)**: white solid (83 mg, 74%); ^1H NMR (400 MHz, DMSO) δ (ppm): 2.29(s, 2H), 1.97(s, 3H), 1.76-1.03(m, 20H). ^{13}C NMR (100 MHz, DMSO) δ (ppm): 168.65, 57.91, 54.41, 30.70, 29.83, 25.95, 25.46, 25.16, 24.75, 23.74. GC-MS: $m/z = 223$.



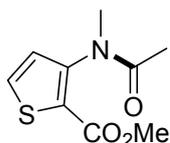
***N,N*-dibutylacetamide (4e)**: colorless liquid (79 mg, 92%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 3.30(t, $J = 7.58$ Hz, 2H), 3.21(t, $J = 7.58$ Hz, 2H), 2.07(s, 3H), 1.46-1.58(m, 4H), 1.26-1.38(m, 4H), 0.94(m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.16, 48.68, 45.58, 31.14, 29.98, 21.58, 20.33, 20.16, 13.96, 13.88. GC-MS: $m/z = 171$.



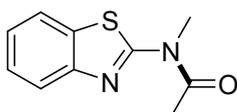
***N*-methyl-*N*-(pyridin-4-yl)acetamide (4f)**: white solid (39 mg, 51%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.61(d, $J = 5.86$ Hz, 2H), 7.16(d, $J = 5.86$ Hz, 2H), 3.29(s, 3H), 2.04(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.09, 151.70, 151.03, 120.95, 36.87, 22.80. GC-MS : $m/z = 150$.



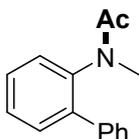
***N*-methyl-*N*-(quinolin-8-yl)acetamide (4g)**: white solid (65 mg, 65%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.99(d, $J = 2.78$ Hz, 1H), 8.24(dd, $J = 1.27$ Hz, 8.23Hz, 1H), 7.85(d, $J = 7.84$ Hz, 1H), 7.56-7.64(m, 2H), 7.48(q, $J = 4.14$ Hz, 1H), 3.40(s, 3H), 1.76(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 171.58, 151.16, 144.36, 142.09, 136.34, 129.61, 128.54, 128.39, 126.60, 121.99, 37.39, 22.33. IR (KBr, cm^{-1}): 1653, 1495, 1390, 1285, 1035, 970, 838, 801. GC-MS : $m/z = 200$. HRMS (ESI): Calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 201.1022; found: 201.1024.



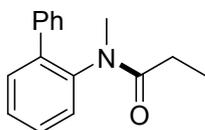
Methyl 3-(*N*-methylacetamido)thiophene-2-carboxylate (4h): white solid (68 mg, 64%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.56(d, $J = 5.20$ Hz, 1H), 6.98(d, $J = 5.20$ Hz, 1H), 3.88(s, 3H), 3.20(s, 3H), 1.85(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.41, 161.09, 147.00, 131.16, 128.30, 126.45, 52.51, 36.21, 21.96. IR (KBr, cm^{-1}): 1704, 1659, 1531, 1437, 1410, 1267, 794, 694. GC-MS : $m/z = 213$.



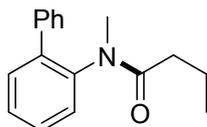
***N*-(benzo[d]thiazol-2-yl)-*N*-methylacetamide (4i)** : white solid (61 mg, 59%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.82(t, $J = 9.61$ Hz, 2H), 7.44(t, $J = 8.00$ Hz, 1H), 7.31(t, $J = 7.48$ Hz, 1H), 3.83, 2.48, 2.47. ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.90, 148.14, 133.50, 126.03, 123.95, 121.39, 121.20, 36.02, 23.71. IR (KBr, cm^{-1}): 1674, 1499, 1375, 1277, 1001, 765, 693. GC-MS : $m/z = 206$. HRMS (ESI): Calcd. for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{OS}$ [$\text{M}+\text{H}$] $^+$: 207.0587; found: 207.0589.



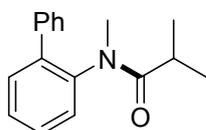
***N*-([1,1'-biphenyl]-2-yl)-*N*-methylacetamide (5a)**: white solid (107 mg, 95%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.36-7.44(m, 6H), 7.23-7.30(m, 3H), 3.00(s, 3H), 1.82(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.76, 141.99, 139.73, 138.75, 131.56, 128.91, 128.84, 128.56, 128.51, 128.43, 127.86, 37.07, 22.49. IR (KBr, cm^{-1}): 1663, 1479, 1431, 1372, 1077, 1074, 973, 781, 740, 701. GC-MS : $m/z = 225$.



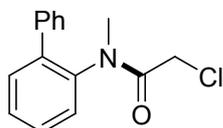
***N*-([1,1'-biphenyl]-2-yl)-*N*-methylpropionamide (5b)** : white solid (97 mg, 81%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.29-7.43(m, 6H), 7.22-7.29(m, 3H), 3.02(s, 3H), 2.07-2.17(m, 1H), 1.89-1.98(m, 1H), 0.96(t, $J = 7.43$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 173.94, 141.64, 139.80, 138.72, 131.48, 128.84, 128.74, 128.59, 128.42, 128.39, 127.76, 37.15, 27.46, 9.60. IR (KBr, cm^{-1}): 1651, 1502, 1482, 1388, 1286, 1244, 1052, 776, 745, 698. GC-MS : $m/z = 239$.



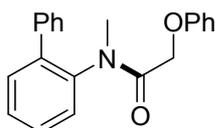
***N*-([1,1'-biphenyl]-2-yl)-*N*-methylbutyramide (5c)**: white solid (94 mg, 74%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.35-7.44(m, 6H), 7.21-7.29(m, 3H), 3.02(s, 3H), 2.04-2.10(m, 1H), 1.83-1.91(m, 1H), 1.40-1.63(m, 2H), 0.77(t, $J = 7.33$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 173.13, 141.69, 139.80, 138.76, 131.48, 128.84, 128.74, 128.68, 128.47, 128.39, 127.78, 37.16, 36.07, 18.74, 13.95. IR (KBr, cm^{-1}): 2965, 2875, 1644, 1503, 1483, 1388, 1325, 1243, 1137, 1057, 808, 786, 748, 698. GC-MS : $m/z = 253$.



***N*-([1,1'-biphenyl]-2-yl)-*N*-methylisobutyramide (5d)**: white solid (58 mg, 46%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.34-7.44(m, 6H), 7.27-7.30(m, 3H), 3.11(s, 3H), 2.35-2.42(m, 1H), 0.96(d, $J = 7.23$ Hz, 3H), 0.67(d, $J = 6.10$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 177.46, 141.76, 140.02, 138.67, 131.37, 128.89, 128.72, 128.67, 128.34, 128.31, 127.77, 37.72, 31.43, 20.33, 18.81. IR (KBr, cm^{-1}): 1647, 1483, 1427, 1387, 789, 752, 705. GC-MS: $m/z = 253$.

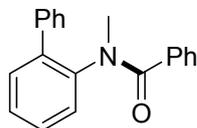


***N*-([1,1'-biphenyl]-2-yl)-2-chloro-*N*-methylacetamide (5e)**: white solid (83 mg, 64%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.37-7.46 (m, 6H), 7.29 (m, 3H), 3.88 (d, $J = 12.37$ Hz, 1H), 3.70 (d, $J = 12.37$ Hz, 1H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 166.35, 140.15, 139.77, 138.09, 131.86, 131.81, 129.25, 129.04, 128.58, 128.42, 128.19, 41.76, 38.03. IR (KBr, cm^{-1}): 1669, 1484, 1421, 1381, 1268, 1241, 782, 746, 701. GC-MS: $m/z = 259$.

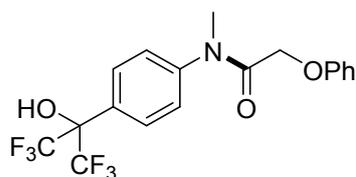


***N*-([1,1'-biphenyl]-2-yl)-*N*-methyl-2-phenoxyacetamide (5f)**: white solid (98 mg, 62%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.50-7.40 (m, 6H), 7.39-7.34 (m, 2H), 7.30 (s, 1H), 7.13 (t, $J = 8.00$ Hz, 2H), 6.88 (t, $J = 7.32$ Hz, 1H), 6.49 (d, $J = 7.20$ Hz, 2H), 4.33 (d, $J = 14.77$ Hz, 1H), 4.18 (d, $J = 14.77$ Hz, 1H), 3.20 (s, 3H). ^{13}C NMR (100 MHz,

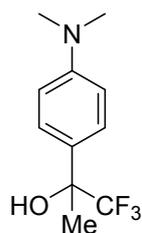
CDCl₃) δ (ppm): 167.70, 158.18, 139.89, 139.85, 138.46, 131.79, 129.39, 129.27, 129.14, 129.11, 128.65, 128.23, 128.15, 121.27, 114.69, 66.67, 38.06. IR (KBr, cm⁻¹): 3071, 2935, 1679, 1596, 1482, 1433, 1219, 1086, 778, 740, 702. GC-MS: m/z = 317. HRMS (ESI): Calcd. for C₂₁H₁₉NO₂ [M+H]⁺: 318.1489; found: 318.1491.



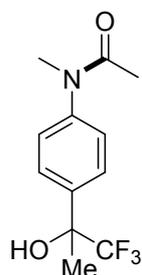
***N*-([1,1'-biphenyl]-2-yl)-*N*-methylbenzamide (5g)** : white solid (120 mg, 84%); ¹H NMR (400 MHz, DMSO) δ (ppm): 7.53(d, J = 7.76 Hz, 1H), 7.39-7.48(m, 2H), 7.29-7.34(m, 3H), 7.17-7.21(d, J = 7.52 Hz, 3H), 6.99-7.03(d, J = 7.57 Hz, 3H), 6.91-6.92(m, 2H), 6.70-6.72(d, J = 7.45Hz, 2H), 3.34(s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 168.63, 141.87, 138.62, 138.30, 135.55, 130.79, 129.26, 128.69, 128.66, 128.38, 128.31, 128.00, 127.83, 127.28, 127.00, 38.60. IR (KBr, cm⁻¹): 1637, 1479, 1367, 1299, 1095, 776, 753, 693. GC-MS : m/z = 287. HRMS (ESI): Calcd. for C₂₀H₁₇NO [M+H]⁺: 288.1383; found: 288.1385.



***N*-4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropan-2-yl)phenyl)-*N*-methyl-2-phenoxyacetamide (5h)**: white solid (146 mg, 72%); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.79(d, J = 8.38 Hz, 2H), 7.30(d, J = 8.67Hz, 2H), 7.21(t, J = 7.78 Hz, 2H), 6.94(t, J = 7.30 Hz, 1H), 6.70(s, 2H), 4.48(s, 2H), 4.14(s, 1H), 3.34(s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 168.32, 157.81, 144.12, 130.15, 129.55, 129.42, 128.68, 126.81, 122.75(q, J = 285.79 Hz), 116.06, 114.72, 66.74, 37.84. ¹⁹F NMR (376 MHz, CDCl₃) δ = -75.43. IR (KBr, cm⁻¹): 3227, 1663, 1605, 1511, 1254, 1171, 954, 934, 778, 750, 710, 688. GC-MS: m/z = 407. HRMS (ESI): Calcd. for C₁₈H₁₅F₆NO₃ [M+H]⁺: 408.1029; found: 408.1034.



2-(4-(dimethylamino)phenyl)-1,1,1-trifluoropropan-2-ol (6): white solid (565 mg, 97%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.42(d, $J = 8.32$ Hz, 1H), 6.72(d, $J = 8.32$ Hz, 1H), 2.97(s, 6H), 2.31(br s, 1H), 1.75(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 150.59, 127.04, 126.07, 125.96(q, $J = 283.53$ Hz, 1H), 112.06, 74.63(q, $J = 28.90$ Hz), 40.48, 23.63. IR (KBr, cm^{-1}): 3243, 1613, 1518, 1254, 1151, 1065, 935, 817. GC-MS: $m/z = 233$. HRMS (ESI): Calcd. for $\text{C}_{11}\text{H}_{14}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$: 234.1100; found: 234.1103.



(N-methyl-N-(4-(1,1,1-trifluoro-2-hydroxypropan-2-yl)phenyl)acetamide (7): white solid (97 mg, 74%); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.65(d, $J = 8.01$ Hz, 1H), 7.23(d, $J = 8.01$ Hz, 1H), 3.27(s, 3H), 2.80(br s, 1H), 1.89(s, 3H), 1.82(s, 3H). ^{13}C NMR (100 MHz, DMSO) δ (ppm): 169.01, 144.20, 138.82, 127.76, 126.58, 124.56(q, $J = 284.45$ Hz), 73.15(q, $J = 28.07$ Hz), 36.48, 22.83, 22.29. IR (KBr, cm^{-1}): 3346, 1646, 1511, 1379, 1292, 1152, 1061, 839. GC-MS: $m/z = 261$. HRMS (ESI): Calcd. for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{NO}_2$ $[\text{M}+\text{H}]^+$: 262.1049; found: 262.1054.

4. References

1. K. Kinashi, K.-P. Lee, S. Matsumoto, K. Ishida, Y. Ueda, *Dyes and Pigments* 2012, **92**, 783-788.

5. ^1H NMR and ^{13}C NMR Spectra of Products 3

