Electronic Supplementary Material (ESI) for RSC Advances.

A facile one-step approach for the synthesis of uniform spherical Cu/Cu_2O nano and microparticles with high catalytic activity in Buchwald-Hartwig amination reaction

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Supporting information

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(Prof. B. M. Bhanage).

1) General information

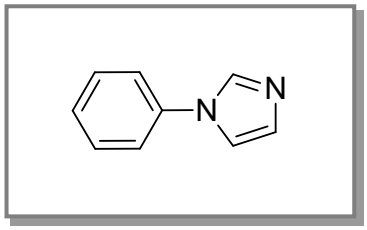
All chemicals and reagents were purchased from commercial suppliers and used as received without further purification. The reaction progress was monitored by gas chromatograph (Perkin Elmer Clarus 400 GC) equipped with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). GC-MS analysis was performed with a Shimadzu GCMS-QP 2010 instrument (Rtx-17, 30 m × 25mmID, film thickness 0.25 μm df) (column flow- 2 mL/min, 80 °C to 240 °C at 10°/min rise.

2) General experimental procedure for the reaction

Typical experimental procedure for Buchwald-Hartwig amination reaction:- In a 25 mL seal tube containing a magnetic stir bar was charged with iodobenzene (1 mmol) and imidazole (1.2 mmol), Cu/Cu_2O NMPs (0.1 mmol, 10 mol%) as nanocatalyst, KOH (2 mmol) as base and DMSO (2 mL) solvent under N_2 atmosphere. The reaction mixture was stirred for 24 h at 80 °C. After completion of the reaction, the reaction mixture was poured into 15 ml water and the product was extracted with ethyl acetate (3 × 10 mL). The reaction solvent was dried over Na_2SO_4 and evaporated under vacuum. All products are well known in the literature and were confirmed by GC-MS analysis by the comparison with those of literature data.

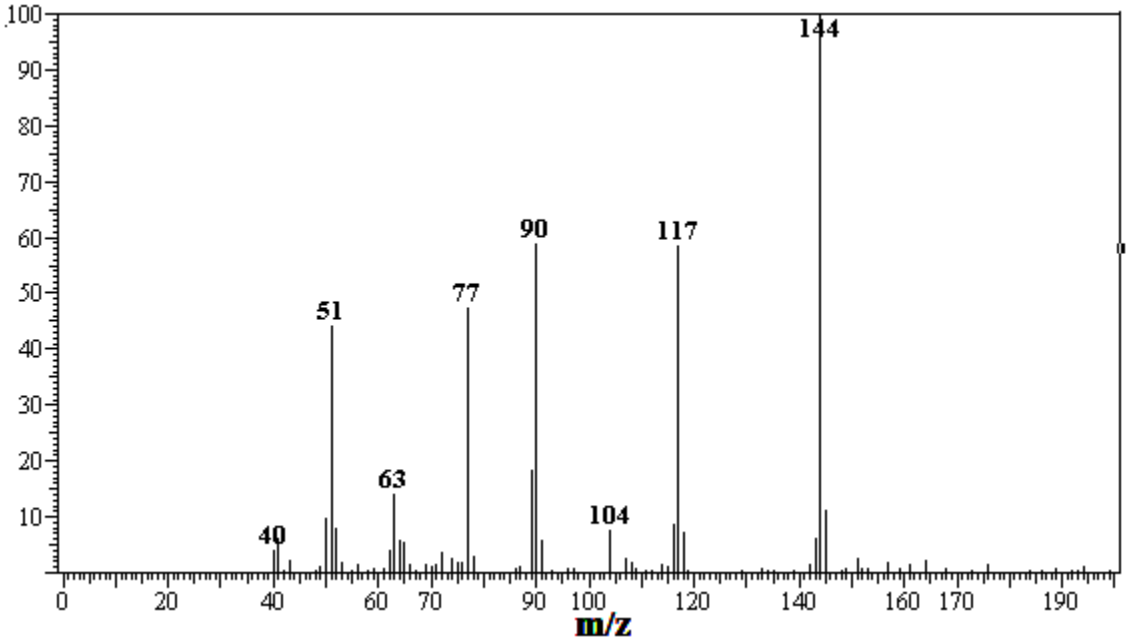
3) GC-MS data for products

1-phenyl-1H-imidazole (Table 3 Entries 1 and 8–10)



The title compound was synthesized according to the general experimental procedure from iodobenzene (204 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and imidazole (82 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

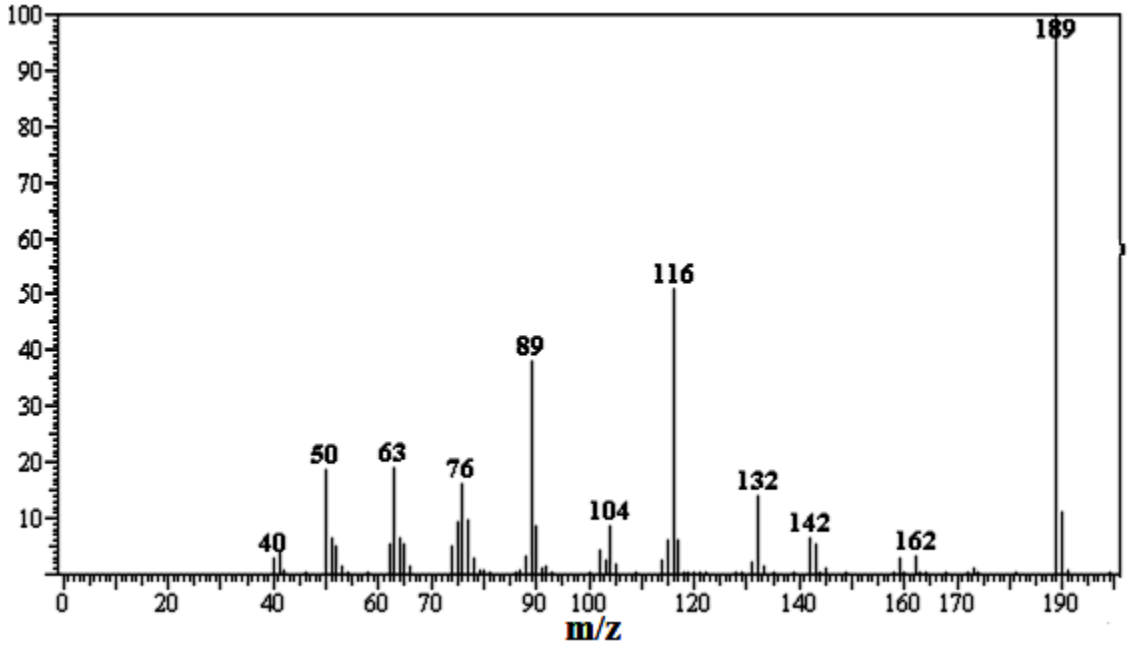
GC-MS (EI, 70 eV) t_R = 9.32 min; m/z (%) = 144 (100) [M^+], 117 (59), 90 (56.9), 104 (5.4), 77 (48.4), 63 (11.1), 51 (40), 44 (16.8).



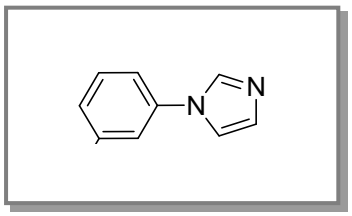
1-(4-nitrophenyl)-1H-imidazole (Table 3 Entry 2, 11 and 12)

The title compound was synthesized according to the general experimental procedure from 1-iodo-4-nitrobenzene (249 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and imidazole (82 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 13.73 min; m/z (%) = 189 (100) [M^+], 162 (3.6), 143 (6.9), 132 (14.4), 116 (51.7), 104 (8.7), 89 (38.9), 76 (16.4), 63 (19.8), 50 (19.6), 44 (7.7).

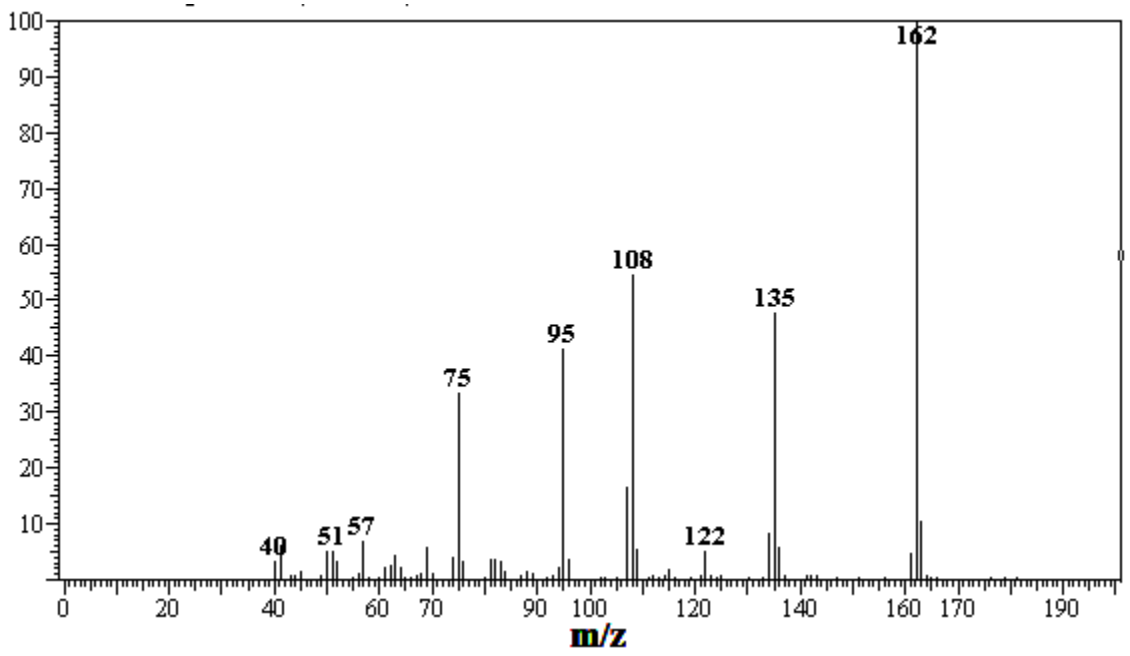


1-(3-fluorophenyl)-1H-imidazole (**Table 3 Entry 3**)

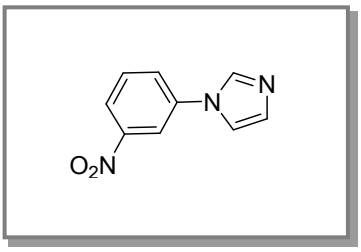


The title compound was synthesized according to the general experimental procedure from 1-fluoro-3-iodobenzene (222 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and imidazole (82 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 8.35 min; m/z (%) = 162 (100) [M^+], 135 (48.9), 122 (5.3), 108 (54.2), 95 (42.8), 75 (34.2), 57 (8.6), 51 (5.6), 44 (9.7).

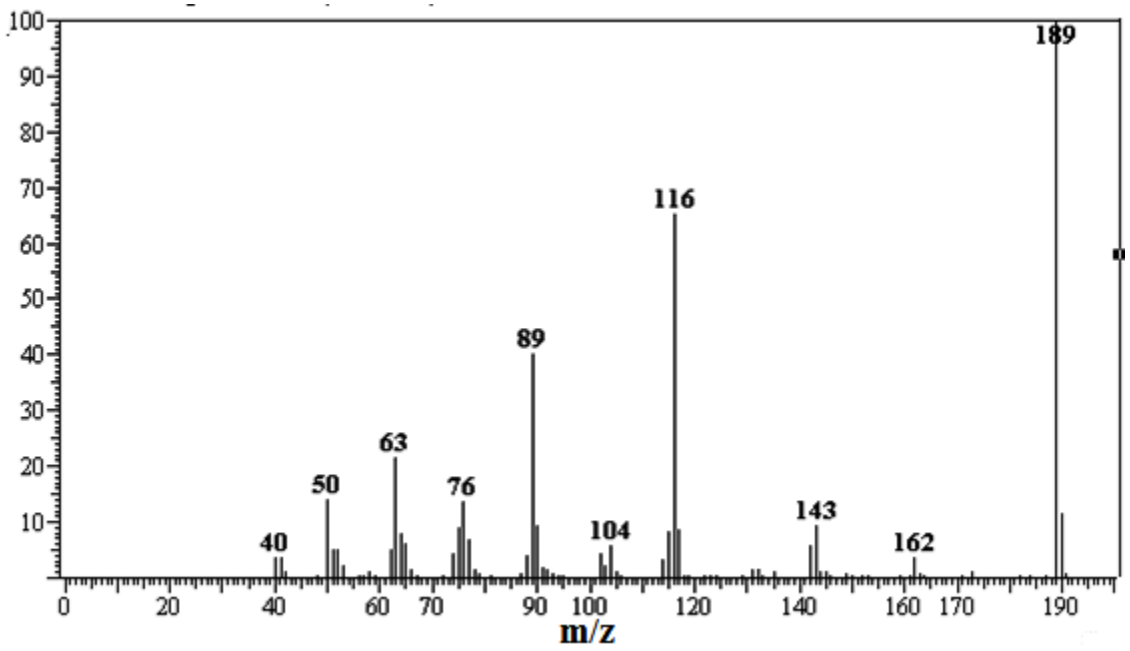


1-(3-nitrophenyl)-1H-imidazole (Table 3 Entry 4)

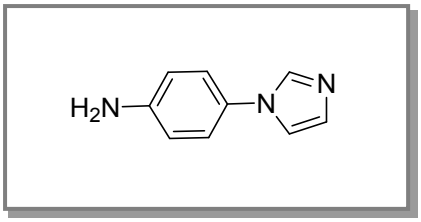


The title compound was synthesized according to the general experimental procedure from 1-iodo-3-nitrobenzene (249 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and imidazole (82 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 13.27 min; m/z (%) = 189 (100) [M^+], 143 (9.7), 116 (64.9), 104 (5.9), 89 (40.3), 76 (13.5), 63 (22.2), 50 (14.6), 44 (6.2).

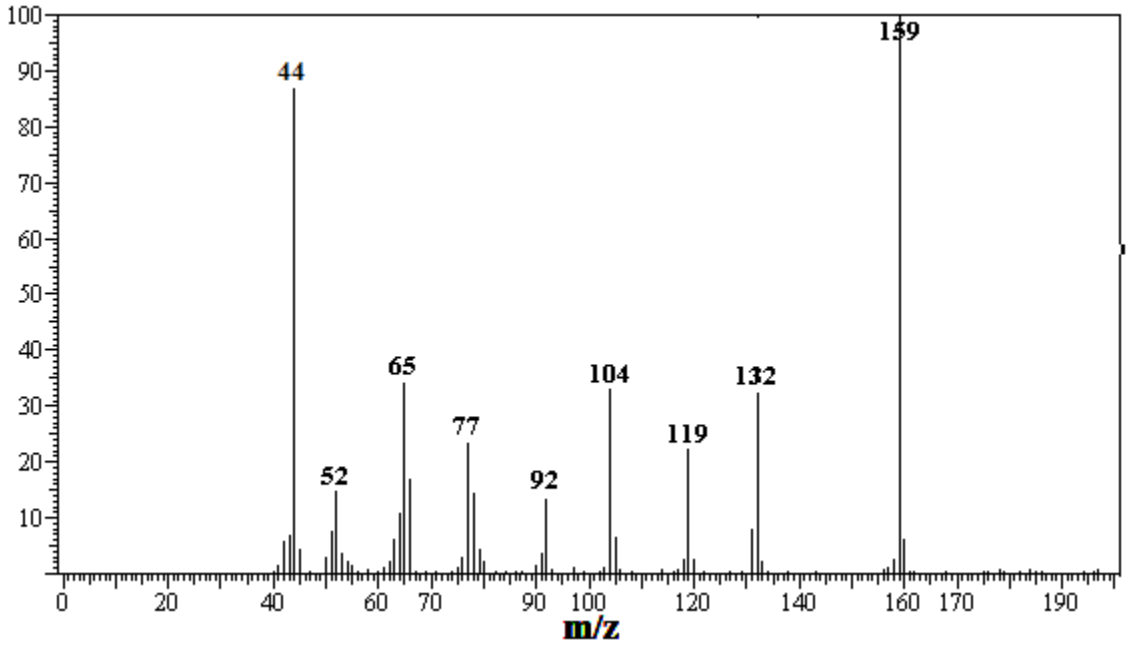


4-(1H-imidazol-1-yl) aniline (Table 3 Entry 5)

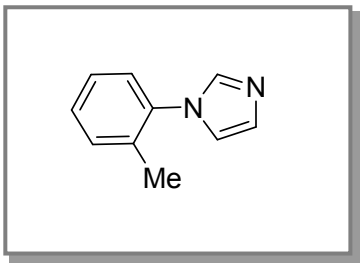


The title compound was synthesized according to the general experimental procedure from 4-iodoaniline (219 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and imidazole (82 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 14.24 min; m/z (%) = 159 (100) [M^+], 132 (31.2), 119 (22.3), 104 (33.6), 92 (14.1), 77 (23.8), 73 (25.9), 65 (32.8), 52 (14.8), 44 (87.8).

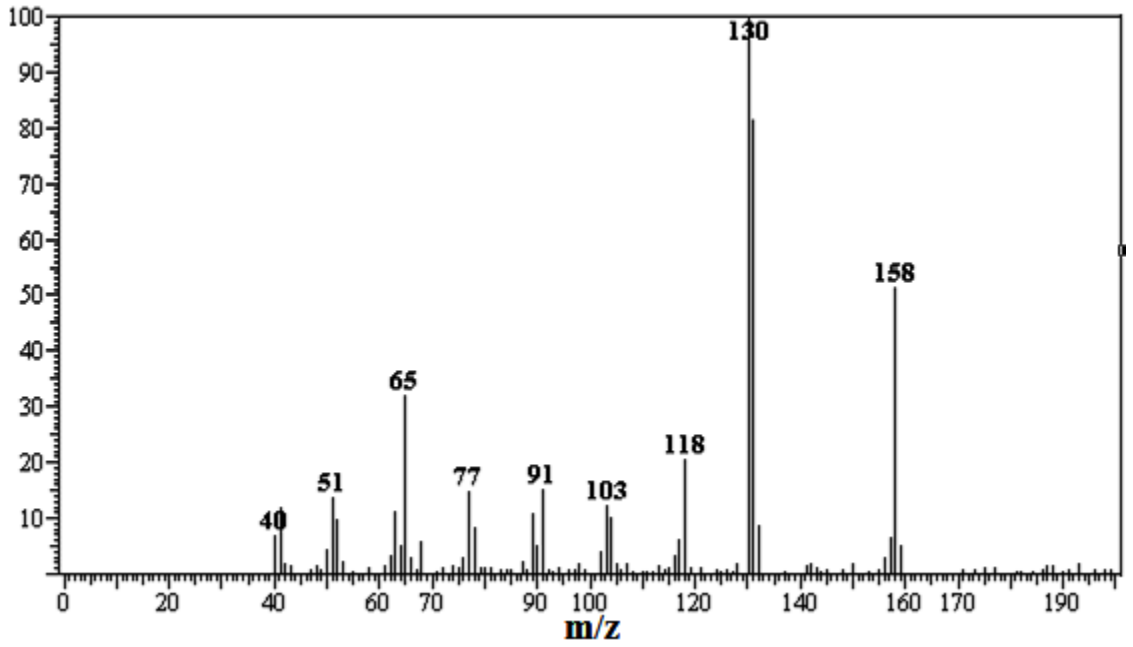


1-(o-tolyl)-1H-imidazole (Table 3 Entry 6)

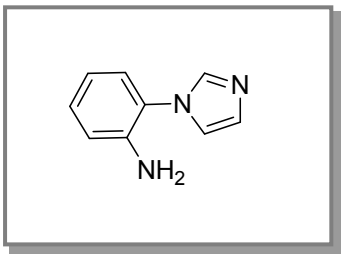


The title compound was synthesized according to the general experimental procedure from 2-methyl iodobenzene (218 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and imidazole (82 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 8.85 min; m/z (%) = 158 (51.7) [M^+], 130 (100), 118 (19.4), 103 (13.3), 91 (16.6), 77 (18.2), 65 (33.4), 51 (15.1), 44 (23.2).

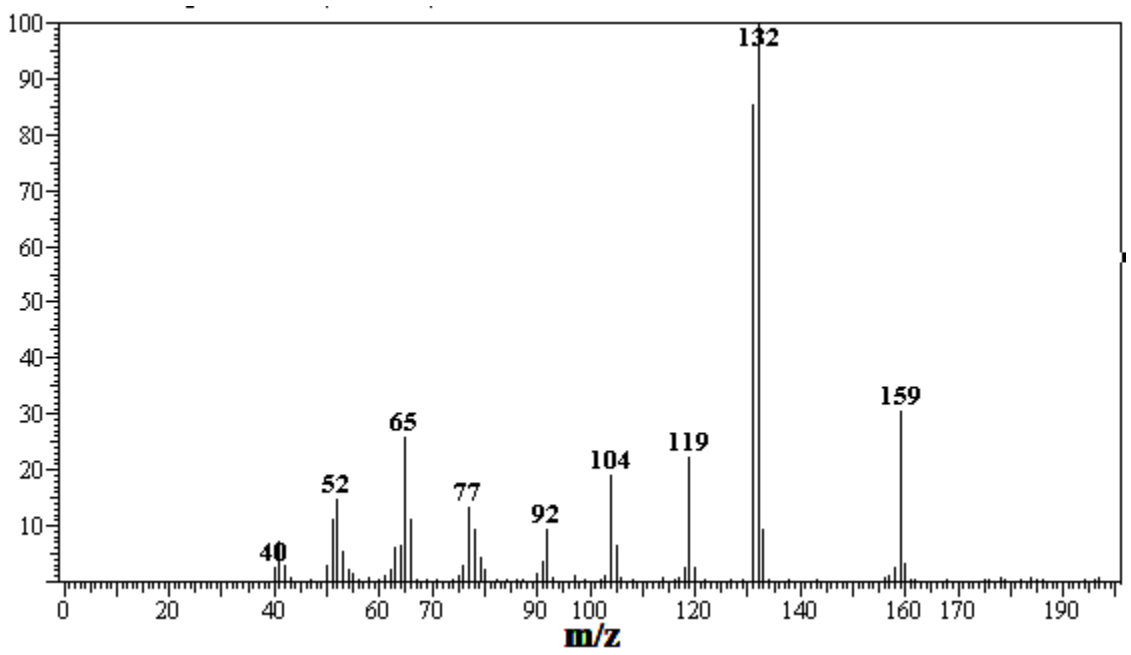


2-(1H-imidazol-1-yl) aniline (Table 3 Entry 7)

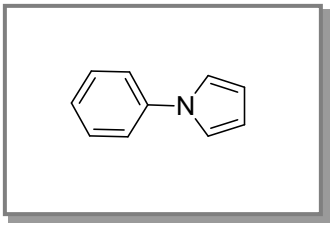


The title compound was synthesized according to the general experimental procedure from 2-iodoaniline (219 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and imidazole (82 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 10.85 min; m/z (%) = 159 (13.7) [M^+], 132 (100), 119 (21.5), 104 (19.5), 92 (10.1), 77 (14.6), 65 (25), 52 (15), 40 (19.8).

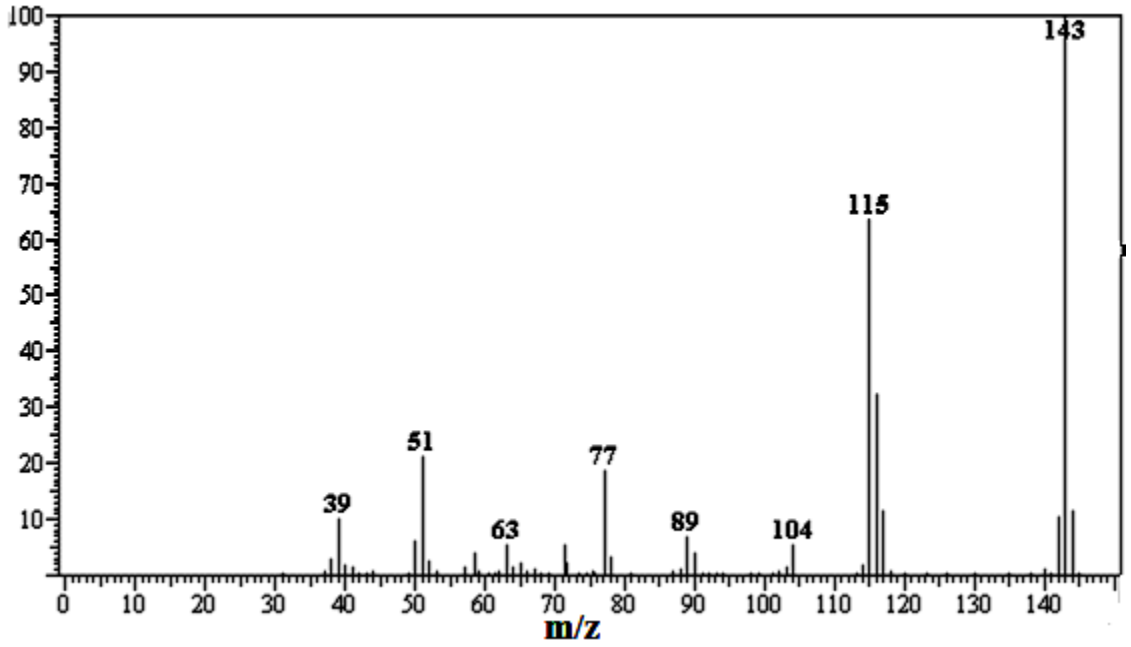


1-phenyl-1H-pyrrole (Table 3 Entry 13)

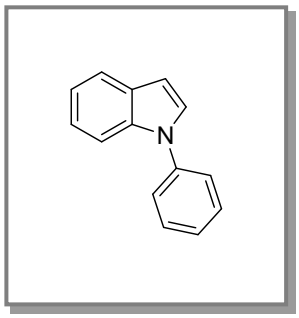


The title compound was synthesized according to the general experimental procedure from iodobenzene (204 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and pyrrole (80.4 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 9.98 min; m/z (%) = 143 (100) [M^+], 115 (63.6), 77 (19.5), 51 (21.5), 44 (11.3), 39 (10.1).

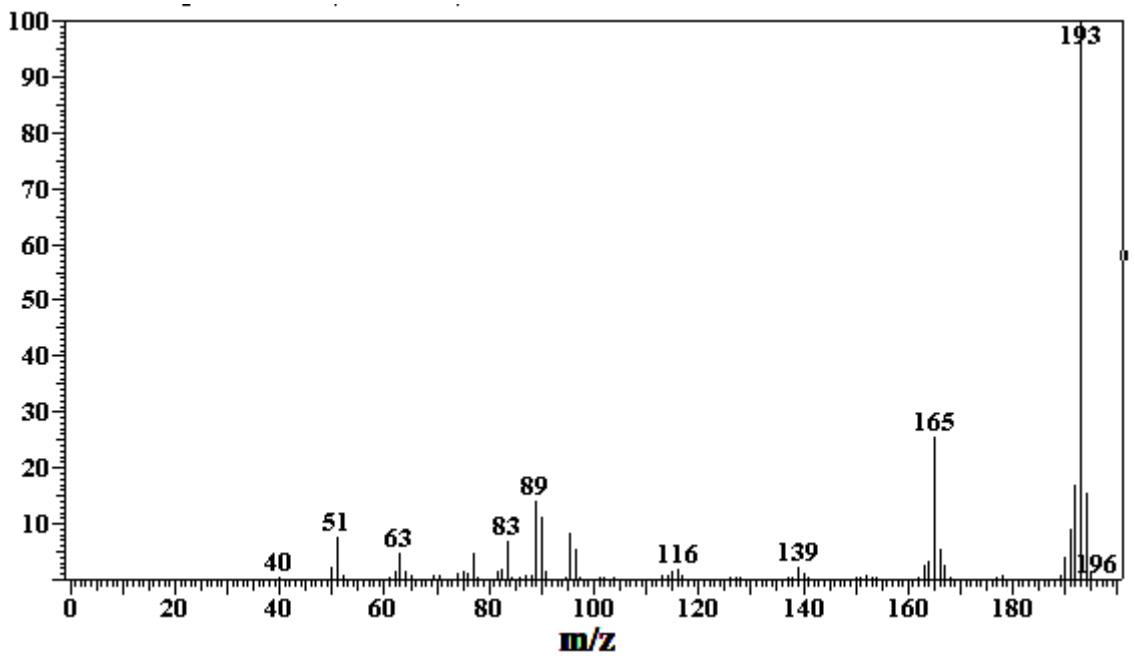


1-phenyl-1H-indole (Table 3 Entry 14)

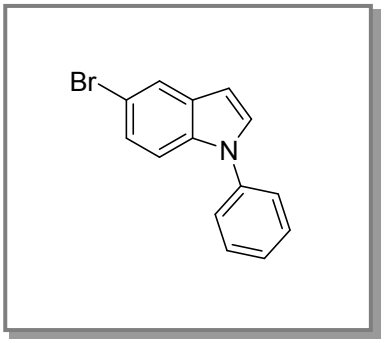


The title compound was synthesized according to the general experimental procedure from iodobenzene (204 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and indole (140.4 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 11.39 min; m/z (%) = 193 (100) [M^+], 165 (25.5), 139 (2), 116 (1.7), 95 (8.4), 89 (15.3), 83 (7.4), 77 (5.2), 63 (5.3), 51 (8.9), 40 (2.1).

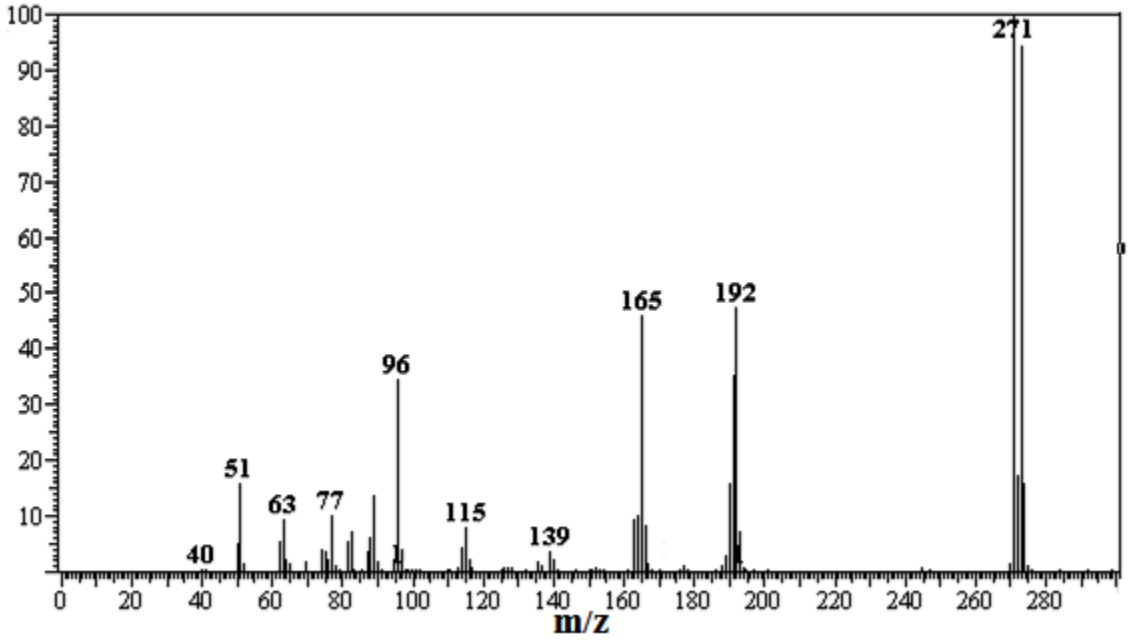


5-bromo-1-phenyl-1H-indole (Table 3 Entry 15)

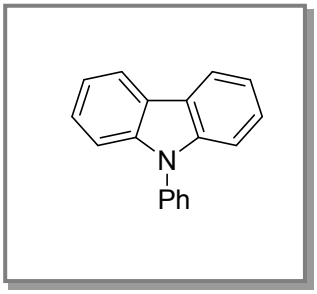


The title compound was synthesized according to the general experimental procedure from iodobenzene (204 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and 5-bromoindole (235.2 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 14.76 min; m/z (%) = 272 (100) [M^+], 192 (48.6), 165 (59), 139 (4.6), 115 (9), 96 (38.6), 89 (15.7), 77 (12.9), 63 (11.1), 51 (18.7), 40 (10.7).

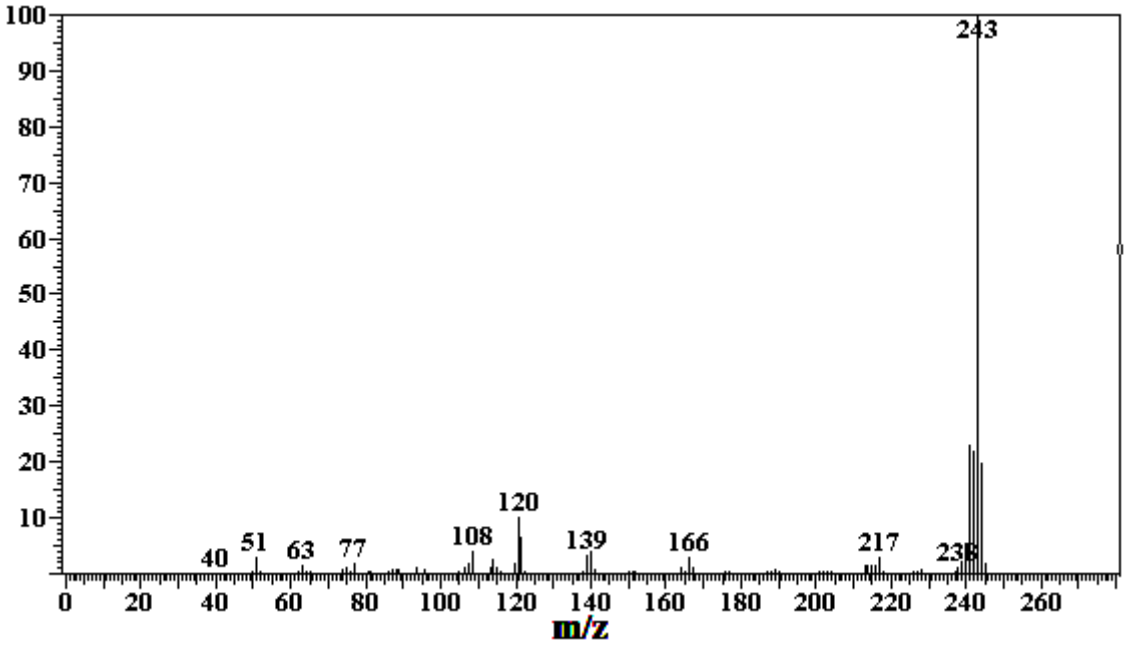


9-Phenylcarbazole (Table 3 Entry 16)

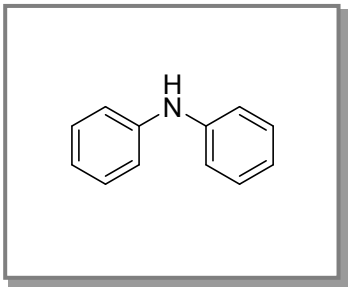


The title compound was synthesized according to the general experimental procedure from iodobenzene (204 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and carbazole (200.6 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 16.14 min; m/z (%) = 243 (100) [M^+], 217 (2.7), 166 (2.8), 139 (4.2), 120 (10.7), 108 (3.9), 77 (2.8), 63 (5.7), 51 (13.6), 40 (3.1).

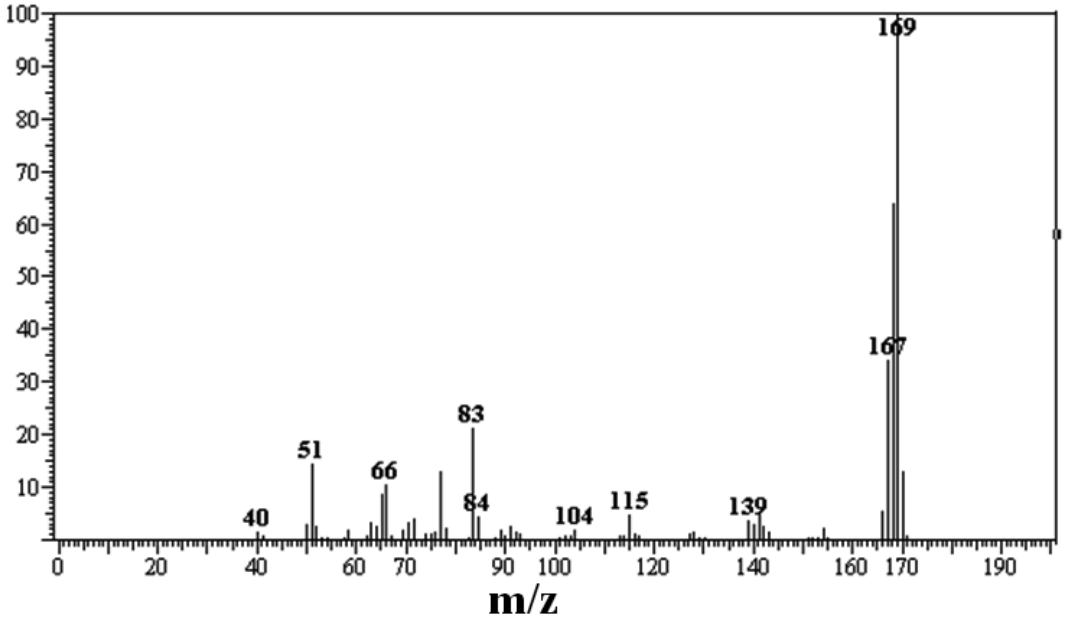


Diphenylamine (Table 3 Entry 17)

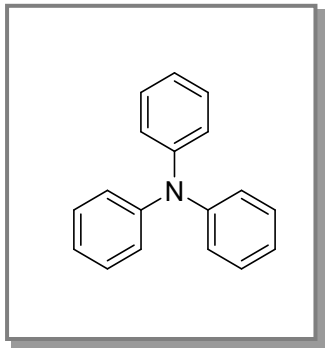


The title compound was synthesized according to the general experimental procedure from iodobenzene (204 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and aniline (111.6 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 9.93 min; m/z (%) = 169 (100) [M^+], 167 (33.5), 141 (5.1), 139 (4.6), 115 (4.5), 104 (2), 91 (10.6), 83 (19.9), 77 (13.2), 66 (10.3), 51 (14.2), 40 (5.7).

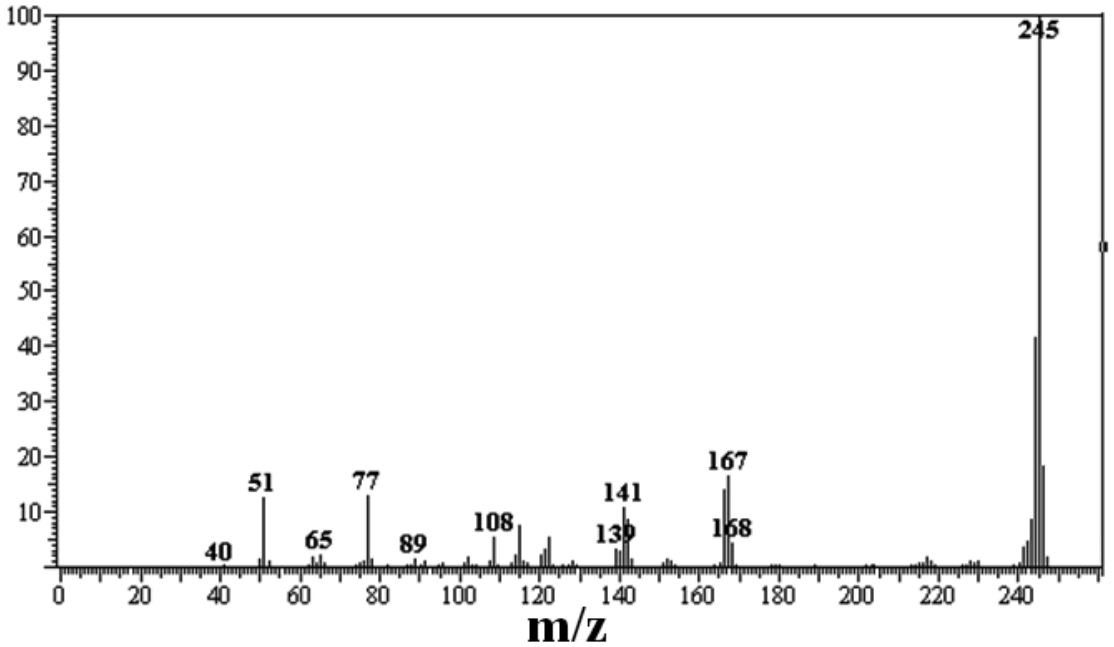


Triphenylamine (Table 3 Entry 18)

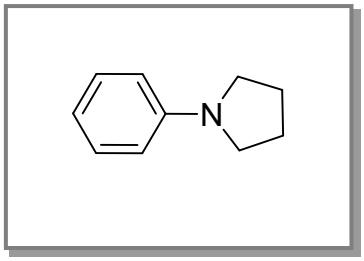


The title compound was synthesized according to the general experimental procedure from iodobenzene (204 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and diphenylamine (202.8 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 13.56 min; m/z (%) = 245 (100) [M^+], 167 (17.4), 141 (12.9), 115 (6.9), 89 (1.8), 77 (15.6), 65 (2), 51 (15.1), 40 (2).

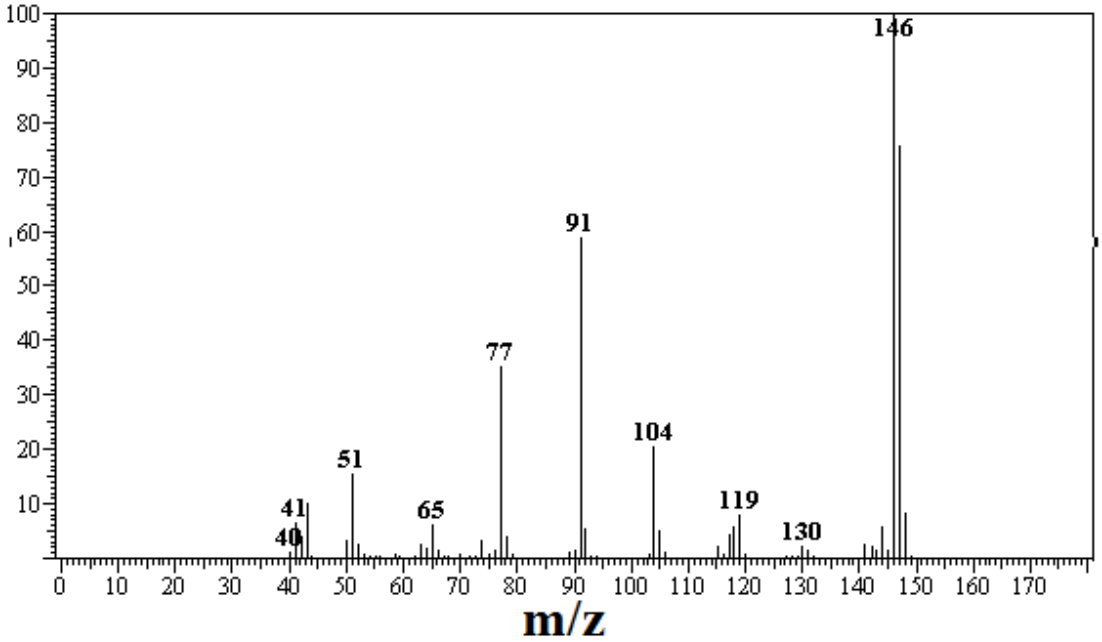


1-phenylpyrrolidine (Table 3 Entry 19)

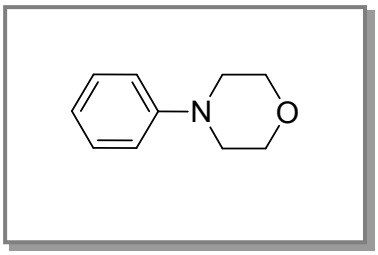


The title compound was synthesized according to the general experimental procedure from iodobenzene (204 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and pyrrolidine (85.2 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 6.90 min; m/z (%) = 147 (76.7) [M^+], 146 (100), 119 (7.8), 104 (20.4), 91 (59.9), 77 (36.2), 65 (6.4), 51 (16.2), 43 (12.3), 40 (2).

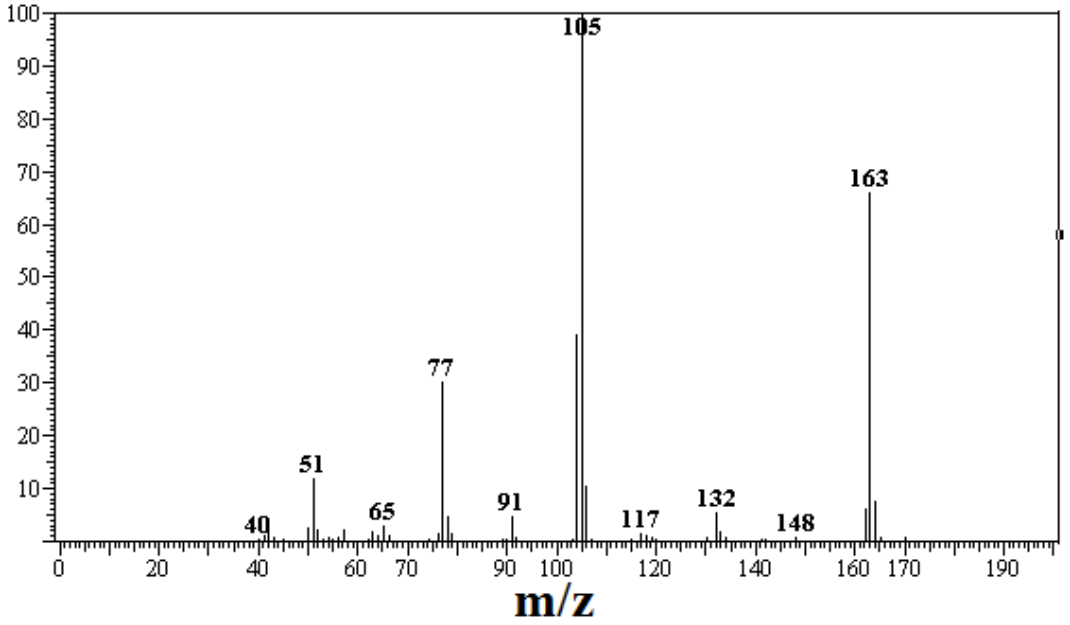


4-phenylmorpholine (Table 3 Entry 20)

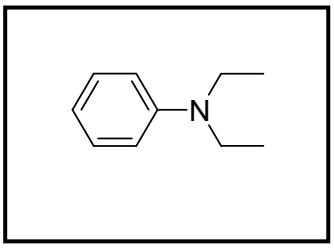


The title compound was synthesized according to the general experimental procedure from iodobenzene (204 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and morpholine (104.4 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 7.47 min; m/z (%) = 163 (64.7) [M^+], 132 (5.7), 105 (100), 91 (5.9), 77 (31.2), 65 (3.5), 51 (12.8), 44 (3.4), 40 (2).



N,N-diethylaniline (Table 3 Entry 21)



The title compound was synthesized according to the general experimental procedure from iodobenzene (204 mg, 1.0 mmol), Cu/Cu_2O NMPs (14.3 mg, 10 mol%), KOH (112 mg, 2.0 mmol) and diethylamine (87.6 mg, 1.2 mmol) with DMSO (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) t_R = 4.72 min; m/z (%) = 149 (30.8) [M^+], 134 (100), 120 (4.8), 106 (51), 91 (4.5), 79 (10), 77 (25.7), 65 (4.4), 51 (8.8), 40 (5.7).