Electronic Supplementary Material (ESI) for Green Chemistry

Supplementary Information

Selective Copper Catalyzed Aromatic *N*-Arylation in Water

Jens Engel-Andreasen, Bharat Shimpukade and Trond Ulven*

Department of Physics, Chemistry and Pharmacy, University of Southern Denmark,

Campusvej 55, DK-5230 Odense M, Denmark.

E-mail: ulven@sdu.dk

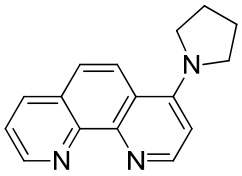
Contents

General considerations

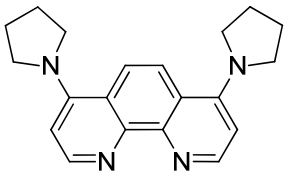
All commercial solvents and reagents were used as obtained without further purification, except for dichloromethane which was distilled before use. The reactions were monitored by TLC. Commercial reagents were used without further purification, unless otherwise stated. Water was purified by a Milli-Q system and degassed by letting through nitrogen gas. Microwave reactions were performed in an Emrys Creator microwave reactor. Flash chromatography was performed with Merck silica gel 60 (0.040–0.063 mm). All yields correspond to isolated products. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 operating at 400 MHz and 101 MHz, respectively, with chemical shifts calibrated relative to solvent residual peaks or TMS. ESI-HRMS and ESI-MS were recorded on a Bruker MicrOTOF-Q II instrument.

Synthesis of 4,7-disubstituted-1,10-phenanthrolines

Ligand **B** was synthesized as described by Feretti and co-workers.[1] Ligand **C** was synthesized as described by Altman and Buchwald.[2]



4-(Pyrrolidin-1-yl)-1,10-phenanthroline (Ligand D). 4-Chloro-1,10-phenanthroline (87 mg, 0.4 mmol) and pyrrolidine (1.5 mL, 18 mmol) were heated at reflux under a nitrogen atmosphere for 2 hours. The reaction mixture was concentrated and the brown syrup residue was washed with water (3 x 2 mL) and dried under vacuum to give a light brown powder (60 mg). The filtrate was added DIPEA until a precipitate formed. The precipitate was filtered off, washed with water (2 x 2 mL) and dried under vacuum to give an additional 30 mg light brown powder, in total 90 mg (90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (m, 1H), 8.78 (d, J = 5.5 Hz, 1H), 8.38–7.95 (m, 2H), 7.56 (m, 2H), 6.77 (d, J = 5.5 Hz, 1H), 3.70 (q, J = 6.4 Hz, 4H), 2.31–1.81 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 149.8, 149.7, 148.1, 146.7, 135.3, 127.92, 123.9, 122.7, 121.8, 119.8, 106.0, 52.5, 26.0; HRMS (ESI) calcd for $C_{16}H_{16}N_3$ ($M+H^+$) 250.1344, found 250.1344.



4,7-(Dipyrrolidin-1-yl)-1,10-phenanthroline (Ligand E). 4,7-Dichloro-1,10-phenanthroline (500 mg, 2 mmol) and pyrrolidine (3.5 mL, 42 mmol) were heated in a microwave reactor to 130 °C for 45 min. The reaction mixture was concentrated and the brown syrup residue was washed with saturated $NaHCO_3$ solution (2 x 5 mL) and ice cold water (2 mL), and dried under vacuum to give a light brown powder (617 mg, 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 5.7 Hz, 2H), 7.98 (s, 2H), 6.66 (d, J = 5.7 Hz, 2H), 3.71 (t, J = 6.4 Hz, 8H), 2.17–1.96 (t, J = 6.4 Hz, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 148.2, 145.9, 119.7, 119.0, 105.5, 52.6, 26.1; HRMS (ESI) calcd for $C_{20}H_{23}N_4$ ($M+H^+$) 319.1923, found 319.1917.

General procedure for Table 1

A reaction tube containing methyl 3-indole carboxylate (105 mg, 0.6 mmol), CuBr (3.6 mg, 0.025 mmol), ligand (**A**, **B**, **C**, **D**, **E**, **F**, **G** or **H**, 0.05 mmol) and PEG-400 (40 mg, 0.1 mmol) under nitrogen and sealed with a rubber septum was added iodobenzene (102 mg, 0.5 mmol) and aqueous 1 M KOH (1 mL) by syringe. The reaction vial was equipped with a nitrogen balloon and heated at 100 °C for 21 hours (48 hours in case of ligand **F**, **G** or **H**). The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 x 3 mL). The combined organic phases were concentrated and the residue was purified by flash chromatography (SiO_2, ethyl acetate) to give methyl 1-phenyl-1*H*-indole-3-carboxylate as a colorless oil.[3]

Synthetic procedures for Table 2

General Procedure for Table 2 (entry 1–13):

Entry 1: A reaction tube equipped with a magnetic stirring bar and charged with CuBr (3.6 mg, 0.025 mmol), DPPhen (16 mg, 0.05 mmol), imidazole (41 mg, 0.6 mmol) and PEG-400 (40 mg, 0.1 mmol) was sealed with a rubber septum, evacuated and back-filled with nitrogen three times. Iodobenzene (102 mg, 0.5 mmol) was added through the septum by syringe, followed by aqueous KOH (1 M, 1 mL). The reaction tube equipped with a N_2-balloon was heated on a preheated oil bath at 100 °C. After 21 hours, the reaction mixture was then cooled and extracted with ethyl acetate (3 x 3 mL), the combined organic phases were concentrated, and the residue was purified by flash chromatography (SiO_2, ethyl acetate) to provide 70 mg (97%) of *N*-phenylimidazole.[4]
Entries 2-15 were performed by the same procedure but with the modifications indicated in Table 2.

Procedure for larger scale reactions with low copper loading (entry 14–15)

A flask equipped with a magnetic stirring bar and charged with CuBr (7.2 mg, 0.05 mmol), DPPhen (16/32 mg, 0.05/0.1 mmol), imidazole (410 mg, 6 mmol) and PEG-400 (400 mg, 1 mmol) was sealed with a septum, evacuated and back-filled with nitrogen three times. Iodobenzene (1021 mg, 5 mmol) and aqueous KOH (1 M, 10 mL) were added sequentially by syringe. The reaction flask equipped with a N_2-balloon was heated on a preheated oil bath at 100 °C for 48 hours. The reaction mixture was then cooled to room temperature and extracted with ethyl acetate (3 x 30 mL). The combined organic phases were concentrated and purified by flash chromatography to give *N*-phenylimidazole [entry 14: 620 mg (86%), entry 15: 137 mg (19%)].

Procedure for low catalyst loading reactions in a microwave reactor (entry 16–17)

A stock solution of CuBr (2.9 mg, 0.02 mmol) and DPPhen (12.7 mg, 0.04 mmol) in aqueous KOH (1 M, 2 mL) was prepared. For entry 16 (1 mol% catalyst loading), a microwave vial containing imidazole, iodobenzene and PEG-400 under a nitrogen atmosphere was prepared as described above, and the stock solution (0.5 mL) was added by syringe and supplemented with aqueous KOH (1 M, 0.5 mL). The reaction was heated to 130 °C in a microwave reactor for 3 hours. Work-up and purification as described above yielded 69.3 mg (96%) of *N*-phenylimidazole. For entry 17 (0.1 mol% catalyst loading), the same procedure with 0.05 mL of the stock solution, 0.95 mL of 1 M KOH and 24 hours reaction time was used to yield 68 mg (94%) of *N*-phenylimidazole after work-up and purification.

Procedure for coupling with bromobenzene (entry 18-20)

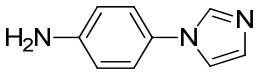
Entry 18: A reaction tube equipped with a magnetic stirring bar and charged with CuBr (7.2 mg, 0.05 mmol), DPPhen (32 mg, 0.1 mmol), imidazole (68 mg, 1.0 mmol) and PEG-400 (80 mg, 0.2 mmol) was sealed with a rubber septum, evacuated and back-filled with nitrogen three times. Bromobenzene (158 µL, 1.5 mmol) was added through the septum by syringe, followed by aqueous KOH (1 M, 2 mL). The reaction tube equipped with a N_2-balloon was heated on a preheated oil bath at 120 °C. (**CAUTION!** Pressure may form inside the reactor.)

After 48 hours, the reaction mixture was then cooled and extracted with ethyl acetate (3 x 5 mL), the combined organic phases were concentrated, and the residue was purified by flash chromatography (SiO_2, ethyl acetate) to provide 133 mg (92%) of *N*-phenylimidazole.

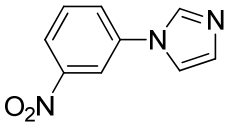
Entry 19: Reaction was performed following procedure for entry 18 using imidazole (227 mg, 3.33 mmol), bromobenzene (525 µL, 5.0 mmol), CuBr (4.8 mg, 0.033 mmol), DPPhen (21 mg, 0.067 mmol) and PEG-400 (267 mg, 0.66 mmol) to provide 433 mg (90%) of *N*-phenylimidazole.

Entry 20: A stock solution of CuBr (3.6 mg, 0.025 mmol) and DPPhen (15.9 mg, 0.05 mmol) in aqueous KOH (1 M, 25 mL) was prepared. A reaction tube equipped with a magnetic stirring bar and charged with imidazole (68 mg, 1.0 mmol), PEG-400 (80 mg, 0.2 mmol) and stock solution of catalyst (1 mL). Bromobenzene (158 µL, 1.5 mmol) was added through the septum by syringe, followed by aqueous KOH (1 M, 1 mL). The reaction tube equipped with a N_2-balloon was heated on a preheated oil bath at 135 °C. (**CAUTION!** Pressure may form inside the reactor.) After 60 hours, the reaction mixture was then cooled and extracted with ethyl acetate (3 x 5 mL), the combined organic phases were concentrated, and the residue was purified by flash chromatography (SiO_2, ethyl acetate) to provide 127 mg (88%) of *N*-phenylimidazole.

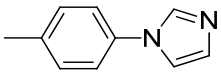
Synthetic procedures for Table 3



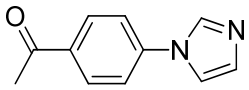
4-(1*H*-Imidazol-1-yl)aniline (Table 3, entry 1). Synthesized by the general procedure using imidazole (41 mg, 0.6 mmol) and 4-iodoaniline (109.5 mg, 0.5 mmol). Purified by flash chromatography (SiO_2, EtOAc, R_f = 0.16) to give 77 mg (97%) of the title compound as white needles.[4]



1-(3-Nitrophenyl)-1*H*-imidazole (Table 3, entry 2). Synthesized by the general procedure using imidazole (41 mg, 0.6 mmol) and 4-nitro-1-iodobenzene (124.5 mg, 0.5 mmol). Purified by flash chromatography (SiO_2, EtOAc; R_f = 0.15) to give 86 mg (91%) of the title compound as a white powder.[5]



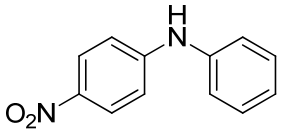
1-(*p*-Tolyl)-1*H*-imidazole (Table 3, entry 3). Synthesized by the general procedure using imidazole (41 mg, 0.6 mmol) and 4-iodotoluene (109 mg, 0.5 mmol). Purified by flash chromatography (SiO_2, EtOAc; R_f = 0.23) to give 75 mg (95%) of the title compound as a white solid.[6]



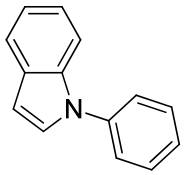
1-(4-Imidazol-1-ylphenyl)ethanone (Table 3, entry 4). Synthesized by the general procedure using imidazole (41 mg, 0.6 mmol) and 4-bromoacetophenone (99.5 mg, 0.5 mmol). Purified by flash chromatography (SiO_2, EtOAc; R_f = 0.15) to give 67.5 mg (74%) of the title compound as a white solid.[4]

General procedure for Cu/DPPhen-catalyzed *N*-arylation (Table 4)

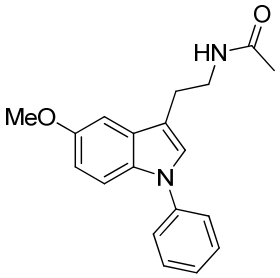
A reaction tube equipped with a magnetic stirring bar and charged with CuBr (3.6 mg, 0.025 mmol), DPPhen (**E**, 16 mg, 0.05 mmol), aryl halide (if solid, 0.5 mmol), *N*-substrate (0.6 mmol) and PEG-400 (40 mg, 0.1 mmol) was sealed with a rubber septum, evacuated and back-filled with nitrogen three times. Then aryl halide (if liquid, 0.5 mmol) was added through the septum by syringe, followed by aqueous KOH (1 M, 1 mL). The reaction tube was equipped with a N_2-balloon and heated on a preheated oil bath at 100 °C (for bromobenzene 120 °C). (**CAUTION!** Pressure may form inside the reactor.) After 21 hours (for bromobenzene 48 h), the reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 x 3 mL). The combined organic phases were concentrated and the residue was purified by flash chromatography. Known compounds exhibited ^1H and ^{13}C NMR in agreement with previously reported data cited below and ESI-MS in agreement with the predicted molecular mass.



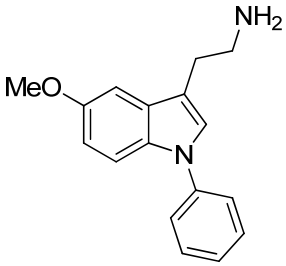
***N*-(4-Nitrophenyl)aniline (Table 4, entry 1-2).** *Entry 1:* Synthesized by the general procedure using 4-nitroaniline (82.9 mg, 0.6 mmol) and iodobenzene (102 mg, 0.5 mmol). Purified by flash chromatography (SiO_2, petroleum ether/EtOAc, 10:1; R_f = 0.17) to give 94 mg (88%) of the title compound as a yellow solid.[7] *Entry 2:* Synthesized by the general procedure using 4-nitroaniline (83 mg, 0.6 mmol) and bromobenzene (79 mg, 0.5 mmol). Purified by flash chromatography (SiO_2, petroleum ether/EtOAc, 10:1; R_f = 0.17) to give 81 mg (76%) of the title compound as a yellow solid.



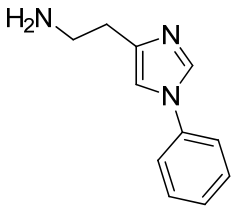
1-Phenyl-1H-indole (Table 4, entry 3-4). *Entry 3:* Synthesized by the general procedure using indole (70.3 mg, 0.6 mmol) and iodobenzene (102 mg, 0.5 mmol) and purified by flash chromatography (SiO_2, petroleum ether/EtOAc, 8:1; R_f = 0.12) to give 89 mg (93%) of the title compound as a yellow oil.[8] *Entry 4:* Synthesized by the general procedure using indole (59 mg, 0.5 mmol) and bromobenzene (79 µL, 0.75 mmol) and purified by flash chromatography (SiO_2, petroleum ether/EtOAc, 8:1; R_f = 0.12) to give 88 mg (91%) of the title compound as a yellow oil.[8]



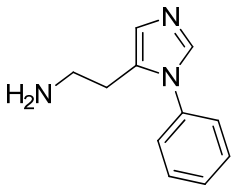
1-Phenylmelatonin (Table 4, entry 5). Synthesized by the general procedure using melatonin (139.4 mg, 0.6 mmol) and iodobenzene (102 mg, 0.5 mmol) and purified by flash chromatography (SiO_2, CH_2Cl_2/MeOH/NH_3(aq), 95:4.5:0.5; R_f = 0.20) to give 124 mg (80%) of the title compound as a white solid.[3]



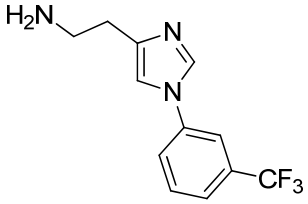
1-Phenyl-5-methoxytryptamine (Table 4, entry 6). Synthesized by the general procedure using 5-methoxytryptamine (114.2 mg, 0.6 mmol) and iodobenzene (102 mg, 0.5 mmol) and purified by flash chromatography (SiO_2, CH_2Cl_2/ MeOH/NH_3(aq), 95:4.5:0.5; R_f = 0.31) to give 125 mg (94%) of the title compound as a light brown oil.[3]



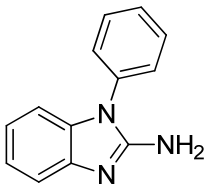
2-(1-Phenylimidazol-4-yl)ethanamine (Table 4, entry 7-8). *Entry 9:* Synthesized by the general procedure using histamine (66.7 mg, 0.6 mmol) and iodobenzene (102 mg, 0.5 mmol). Purified by flash chromatography (SiO_2, CH_2Cl_2 → CH_2Cl_2/ MeOH/NH_3(aq), 90:9:1; R_f (final eluent) = 0.12) to give 68 mg (72%) of the title compound and 15 mg (17%) of 2-(1-phenyl-1H-imidazol-5-yl)ethanamine as a by-product, both compounds as light brown oils. *Entry 10*: Synthesized by the general procedure using histamine (144 mg, 1.3 mmol) and bromobenzene (105 µL, 1.0 mmol). Purified by flash chromatography (SiO_2, CH_2Cl_2 → CH_2Cl_2/ MeOH/NH_3(aq), 90:9:1; R_f (final eluent) = 0.12) to give 110 mg (59%) of the title compound and 24 mg (13%) of 2-(1-phenyl-1H-imidazol-5-yl)ethanamine as a by-product, both compounds as light brown oils. 2-(1-Phenylimidazol-4-yl)ethanamine (major product): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 1.2 Hz, 1H), 7.47 (tt, J = 3.9, 1.9 Hz, 2H), 7.41–7.30 (m, 3H), 7.09 (s, 1H), 3.07 (t, J = 6.6 Hz, 2H), 2.78 (t, J = 6.6 Hz, 2H), 2.02 (br. s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 137.4, 135.0, 129.9, 127.2, 121.2, 115.0, 41.8, 32.2; HRMS (ESI) calcd for $C_{11}H_{14}N_3$ ($M+H^+$) 188.1188, found 188.1182.



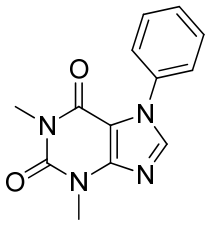
2-(1-Phenyl-1H-imidazol-5-yl)ethanamine (by-product in Table 4, entry 7-8). Yield: 15 mg (17%): R_f = 0.18 (SiO_2, CH_2Cl_2/ MeOH/NH_3(aq), 90:9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.54–7.41 (m, 3H), 7.33–7.26 (m, 2H), 6.98 (s, 1H), 2.82 (t, J = 6.9 Hz, 2H), 2.69 (t, J = 6.9 Hz, 2H), 2.03 (br. s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 136.4, 130.2, 129.6, 128.6, 127.3, 126.0, 40.9, 28.4 ppm; HRMS (ESI) calcd for $C_{11}H_{14}N_3$ ($M+H^+$) 188.1188, found 188.1187.



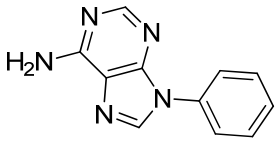
2-(1-(3-(Trifluoromethyl)phenyl)-1H-imidazol-4-yl)ethanamine (Table 4, entry 9). Synthesized by the general procedure using histamine (134 mg, 1.2 mmol) and 3-iodobenzotrifluoride (272 mg, 1.0 mmol). Purified by flash chromatography (SiO_2, CH_2Cl_2 → CH_2Cl_2/ MeOH/NH_3(aq), 90:9:1; R_f = 0.15) to give 179 mg (70%) of the title compound as light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.67–7.56 (m, 4H), 7.13 (s, 1H), 3.07 (t, J = 6.3 Hz, 2H), 2.78 (t, J = 6.5 Hz, 2H), 1.54 (br. s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 137.9, 134.9, 133.0, 132.7, 132.4, 132.0, 130.6, 124.8, 124.2, 123.9, 123.9, 123.8, 118.1, 118.0, 117.9, 117.9, 114.8, 41.7, 32.3; HRMS (ESI) calcd for $C_{12}H_{13}F_3N_3$ ($M+H^+$) 256.1056, found 256.1063.



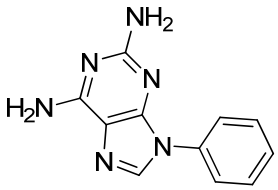
1-Phenyl-1H-benzo[d]imidazol-2-amine (Table 3, entry 10-11). *Entry 5:* Synthesized by the general procedure using 2-aminobenzimidazole (79.9 mg, 0.6 mmol) and iodobenzene (102 mg, 0.5 mmol) and purified by flash chromatography (SiO_2, EtOAc/MeOH, 50:1; R_f = 0.29) to give 92 mg (88%) of the title compound as a white solid. *Entry 6*: Synthesized by the general procedure using 2-aminobenzimidazole (160 mg, 1.2 mmol) and bromobenzene (105 µL, 1.0 mmol) and purified by flash chromatography (SiO_2, EtOAc/MeOH, 50:1; R_f = 0.29) to give 161 mg (77%) of the title compound as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, J = 7.6 Hz, 2H), 7.51–7.42 (m, 4H), 7.19–7.09 (m, 1H), 7.06–6.94 (m, 2H), 5.34 (br. s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 142.4, 135.1, 130.5, 128.9, 126.8, 122.2, 120.1, 116.4, 108.5; ESI-MS *m/z* 210.1 ($M+H^+$). (The compound is previously described, but the reported NMR data is of low resolution.[9])



7-Phenyltheophylline (Table 4, entry 12). Synthesized by the general procedure, but with a reaction time of 48 hours, using theophyilline (108 mg, 0.6 mmol), iodobenzene (102 mg, 0.5 mmol) and PEG-400 (80 mg, 0.2 mmol). The reaction mixture was diluted with ice cold water (5 mL), the solid was filtered off and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc (2 x 10 mL) and the combined organic phases were concentrated. The residue was combined with the precipitate and purified by flash chromatography (SiO_2, petroleum ether/EtOAc, 1:1) to give 83 mg (65%) of the title compound as a white solid.[10]

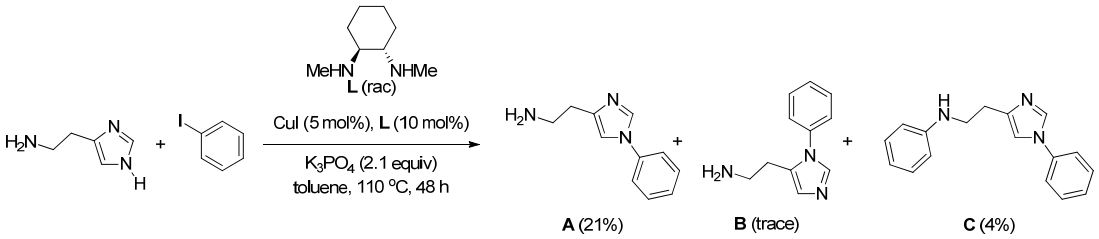


9-Phenyladenine (Table 4, entry 13). Synthesized by the general procedure, except that 100 mol% PEG-400 was required to obtain a homogenous reaction mixture, using adenine (81.1 mg, 0.6 mmol), iodobenzene (102 mg, 0.5 mmol) and PEG-400 (200 mg, 0.5 mmol). The reaction mixture was diluted with ice cold water (5 mL), the solid was filtered off and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc (2 x 10 mL) and the combined organic phases were concentrated. The residue was combined with the precipitate and purified by flash chromatography (SiO_2, EtOAc; R_f = 0.11) to give 57 mg (54%) of the title compound as a white solid.[11]



9-Phenyl-2,6-diaminopurine (Table 4, entry 14). Synthesized by the general procedure, except that 50 mol% PEG-400 was required to obtain a homogenous reaction mixture, using 2,6-diaminopurine (119.5 mg, 0.6 mmol), iodobenzene (102 mg, 0.5 mmol) and PEG-400 (100 mg, 0.25 mmol). The reaction mixture was diluted with ice cold water (5 mL), the solid was filtered off and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc (2 x 10 mL) and the combined organic phases were concentrated. The residue was combined with the precipitate and purified by flash chromatography (SiO_2, EtOAc; R_f = 0.08) to give 59 mg (52%) of the title compound as a white solid: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (s, 1H), 7.90–7.77 (d, J = 7.5, 2H), 7.53 (t, J = 7.5, 2H), 7.38 (t, J = 7.5 Hz, 1H), 6.84 (s, 2H), 5.92 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.8, 156.5, 151.5, 136.1, 135.8, 129.4, 126.8, 122.7, 113.6; HRMS (ESI) calcd for $C_{11}H_{11}N_6$ 227.1045, found 227.1065 ($M+H^+$).

Scheme S1. Coupling of histamine with iodobenzene using an established protocol.[12]



The reaction was carried out according to a previously described protocol:[12] A reaction tube equipped with a magnetic stirring bar and charged with CuI (10 mg, 0.05 mmol), histamine (134 mg, 1.2 mmol) and K_3PO_4 (446 mg, 2.1 mmol) was sealed with rubber septum. The tube was evacuated and back filled with argon (3 times). Iodobenzene (111μL, 1.0 mmol), N,N'-dimethylcyclohexane-1,2-diamine (16 μL, 0.10 mmol) and dry toluene (1.0 mL) were added successively under argon atmosphere. The tube was sealed and the contents were stirred at 110 °C for 48 h. The reaction mixture was cooled to ambient temperature, diluted with ethyl acetate and filtered through Celite. The filtrate was concentrated under vacuum. The residue was purified by flash chromatography (SiO_2, petroleum ether/EtOAc, 8:2) to give N^{τ}-phenylhistamine (39 mg, 21%, colorless oil) and N^{α},N^{τ}-diphenylhistamine (8 mg, 4%, white solid).

N^{α},N^{τ}-Diphenylhistamine (**C**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.51–7.43 (m, 2H), 7.39–7.32 (m, 3H), 7.17 (t, J = 7.9 Hz, 2H), 7.08 (s, 1H), 6.72–6.63 (m, 3H), 4.17 (br. s, 1H), 3.47 (t, J = 6.6 Hz, 2H), 2.95 (t, J = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 141.6, 137.3, 135.0, 129.9, 129.2, 127.3, 121.2, 117.2, 115.1, 112.9, 77.3, 77.0, 76.7, 43.6, 27.9.

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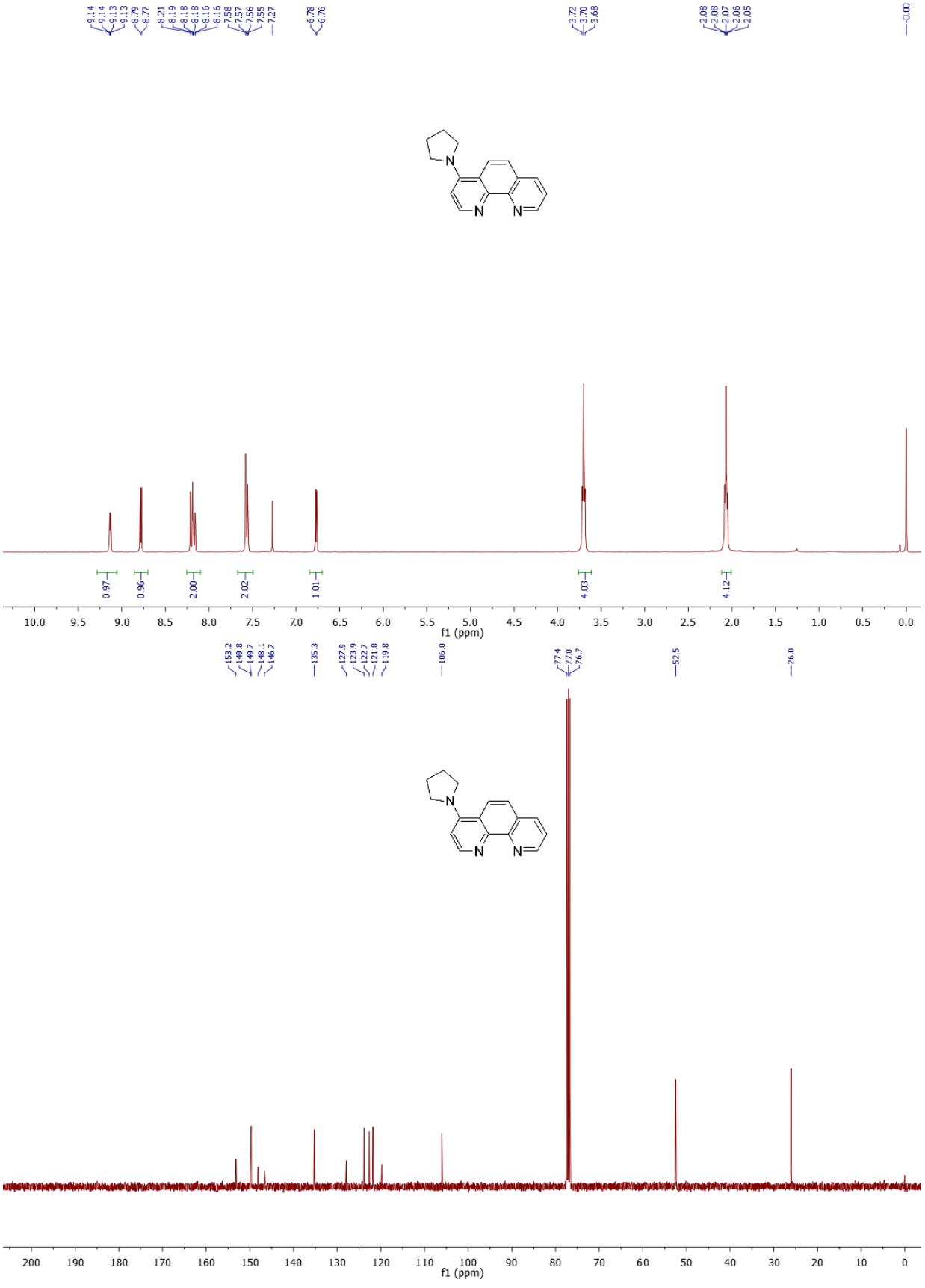
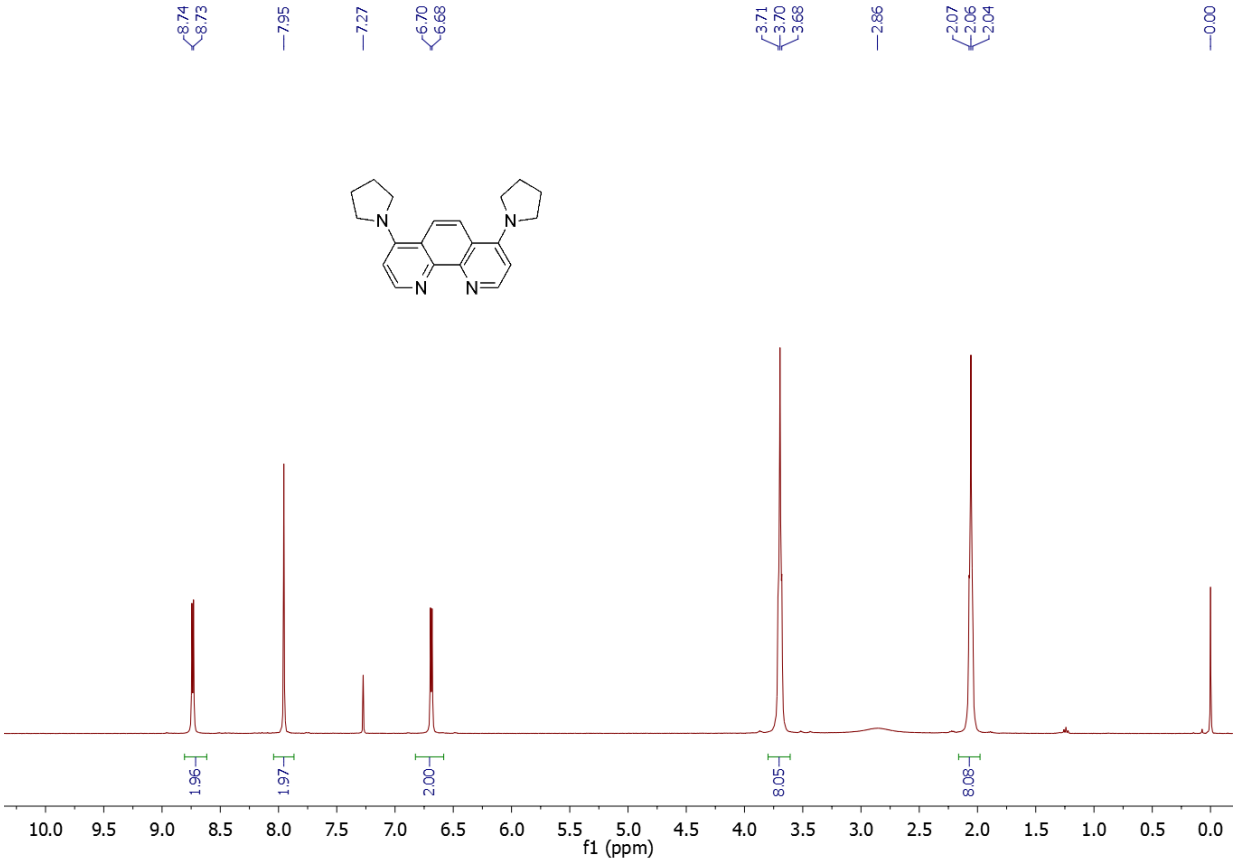
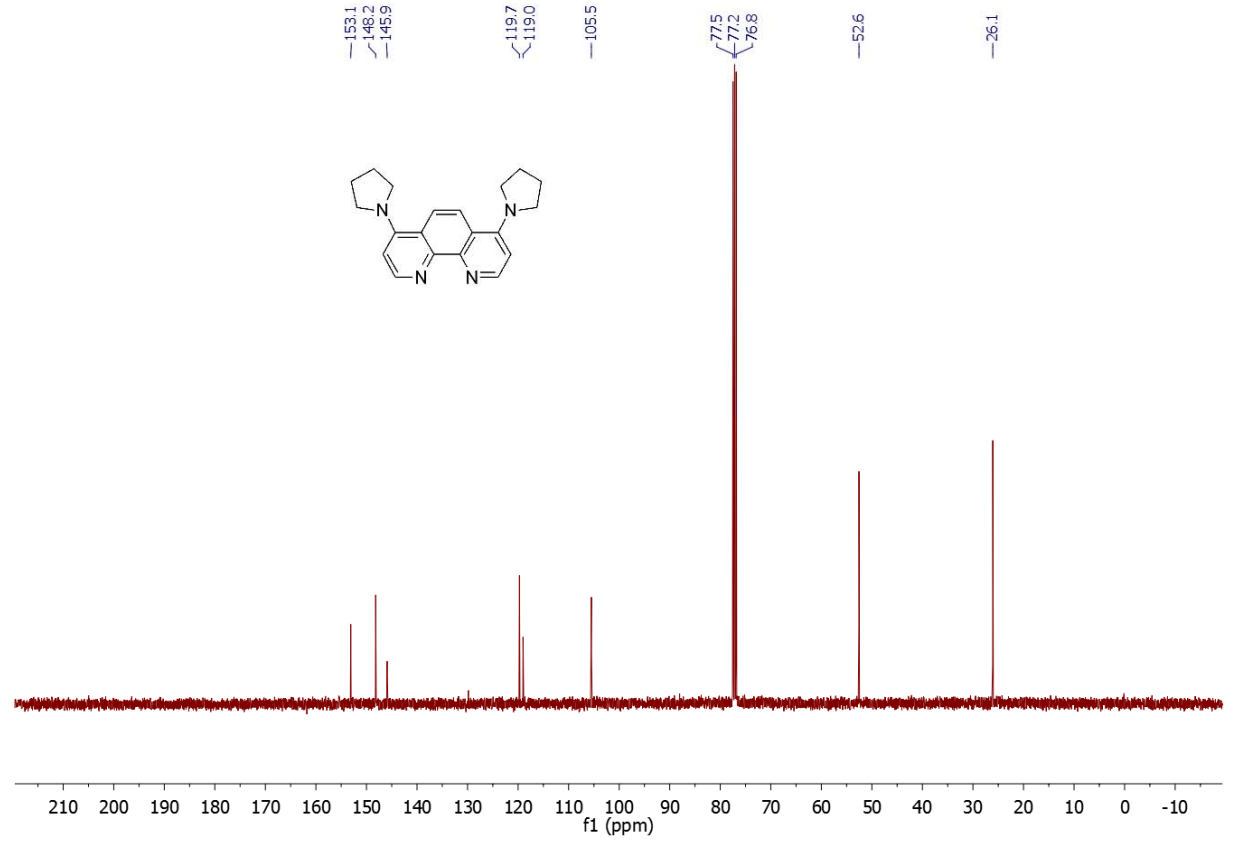
4-(Pyrrolidin-1-yl)-1,10-phenanthroline (Ligand D)

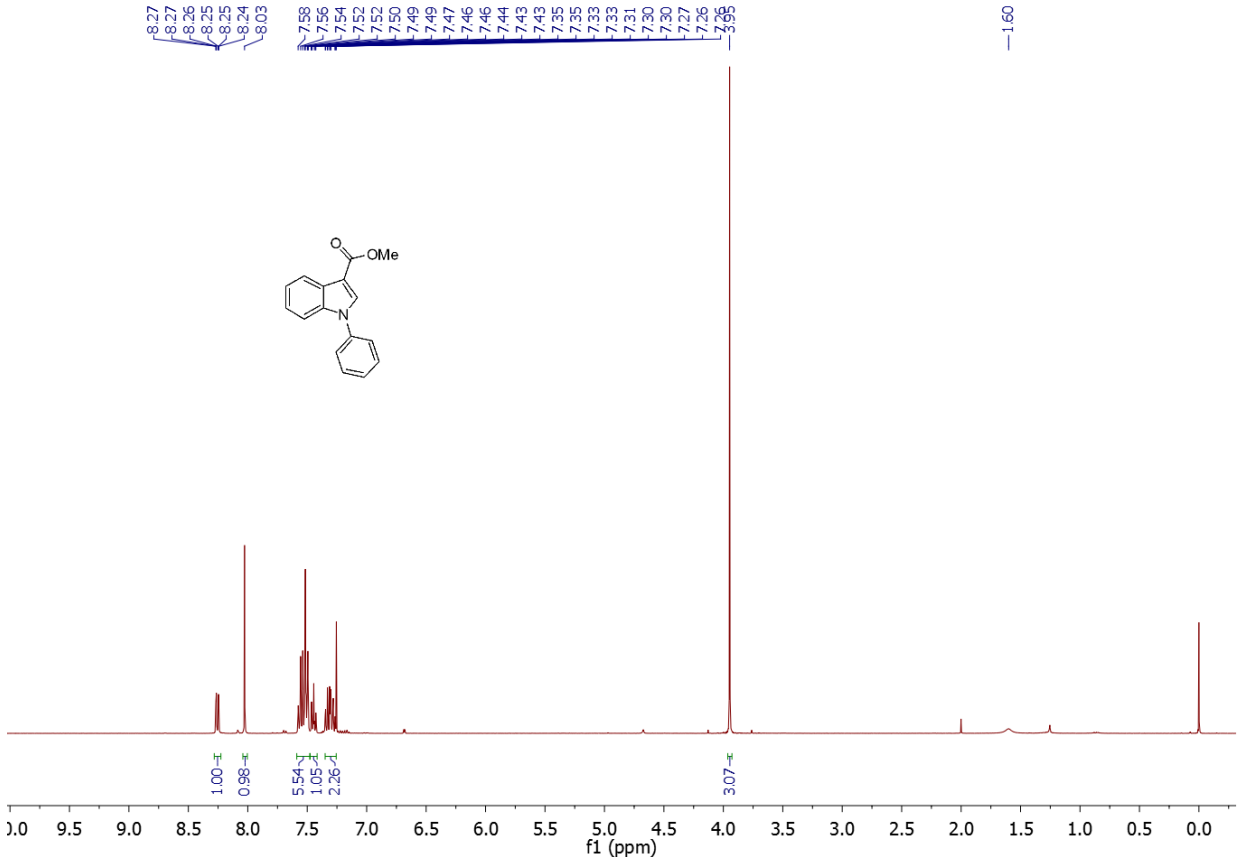


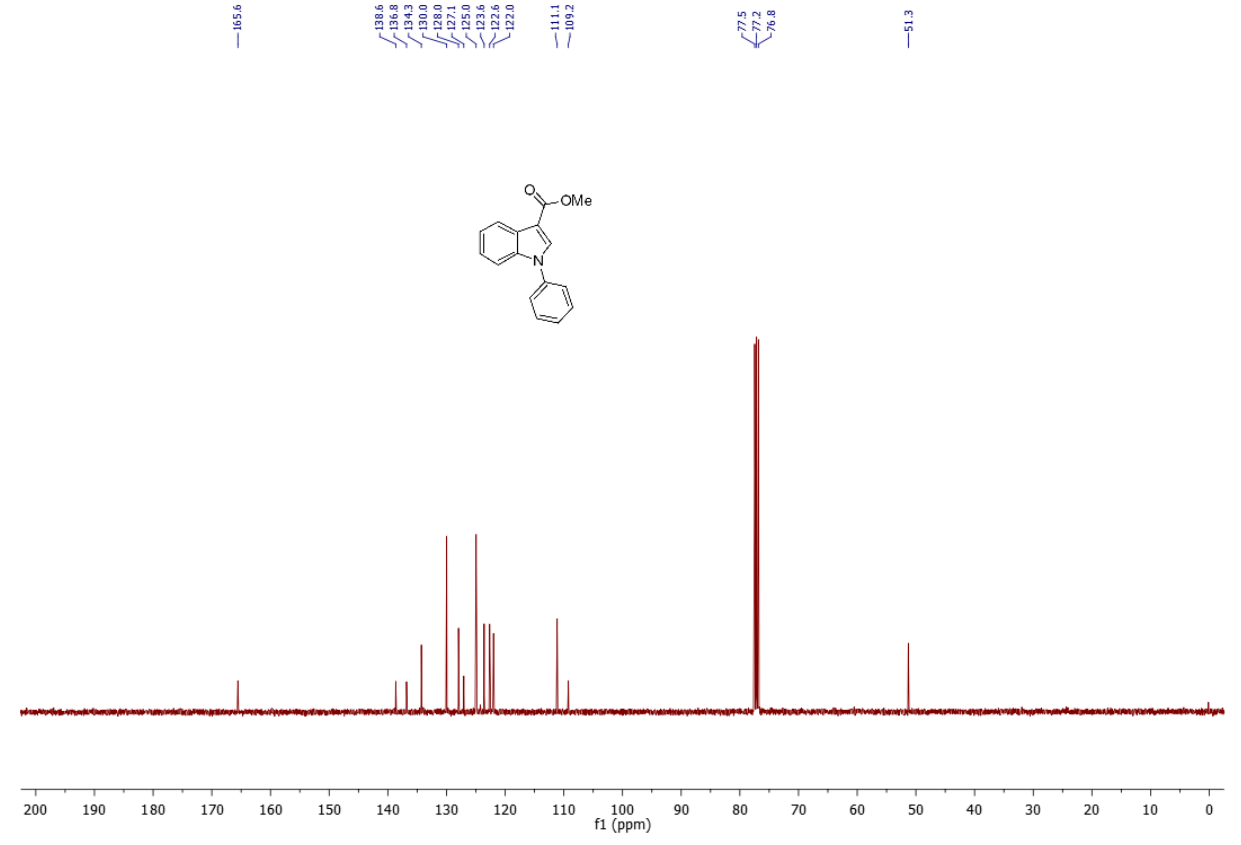
4,7-(Dipyrrolidin-1-yl)-1,10-phenanthroline (Ligand E, DPPhen)



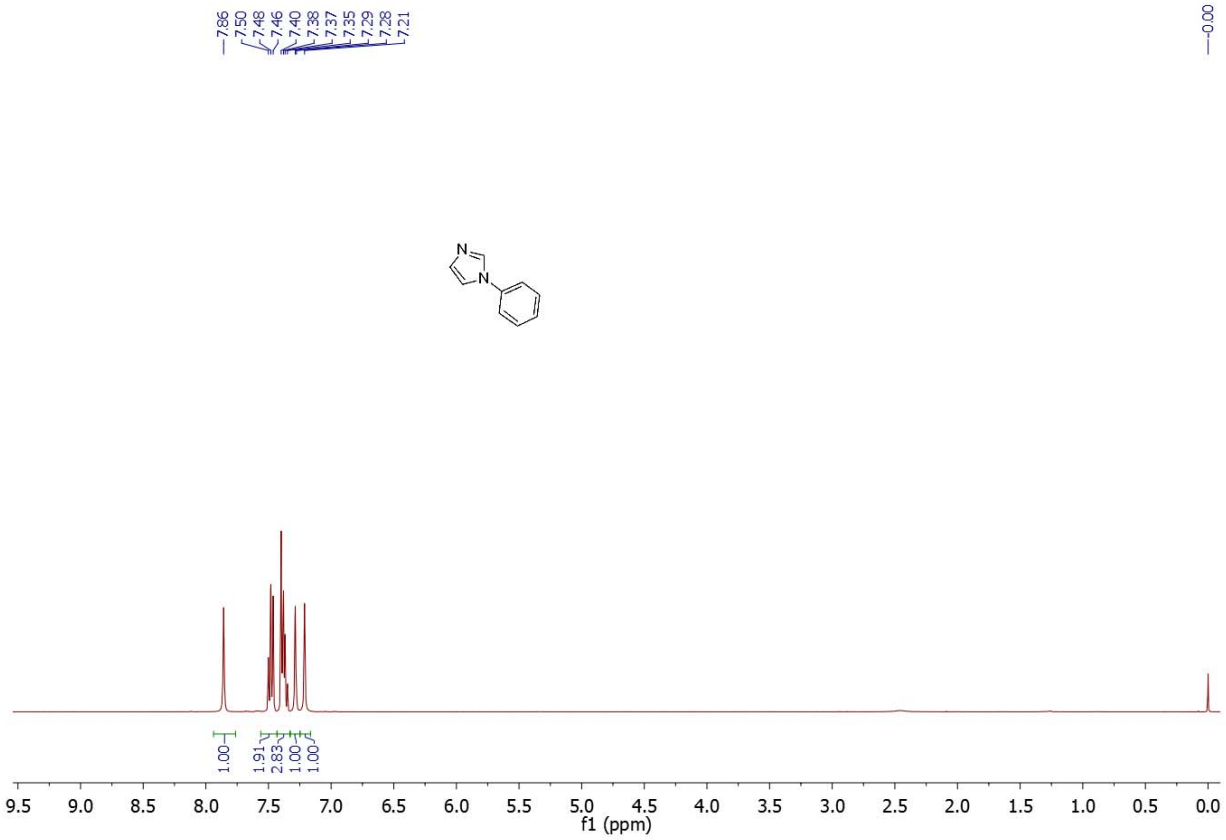


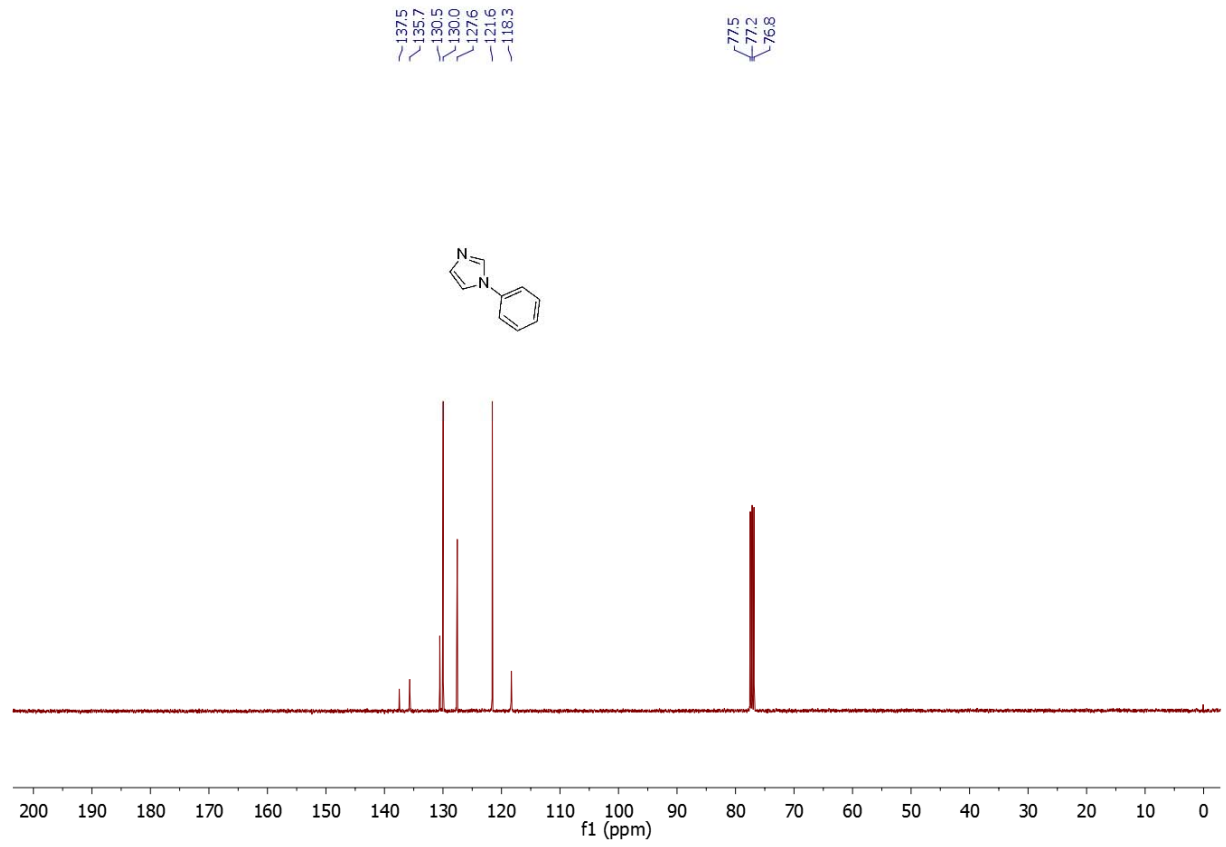
Methyl 1-phenyl-1*H*-indole-3-carboxylate (Table 1)



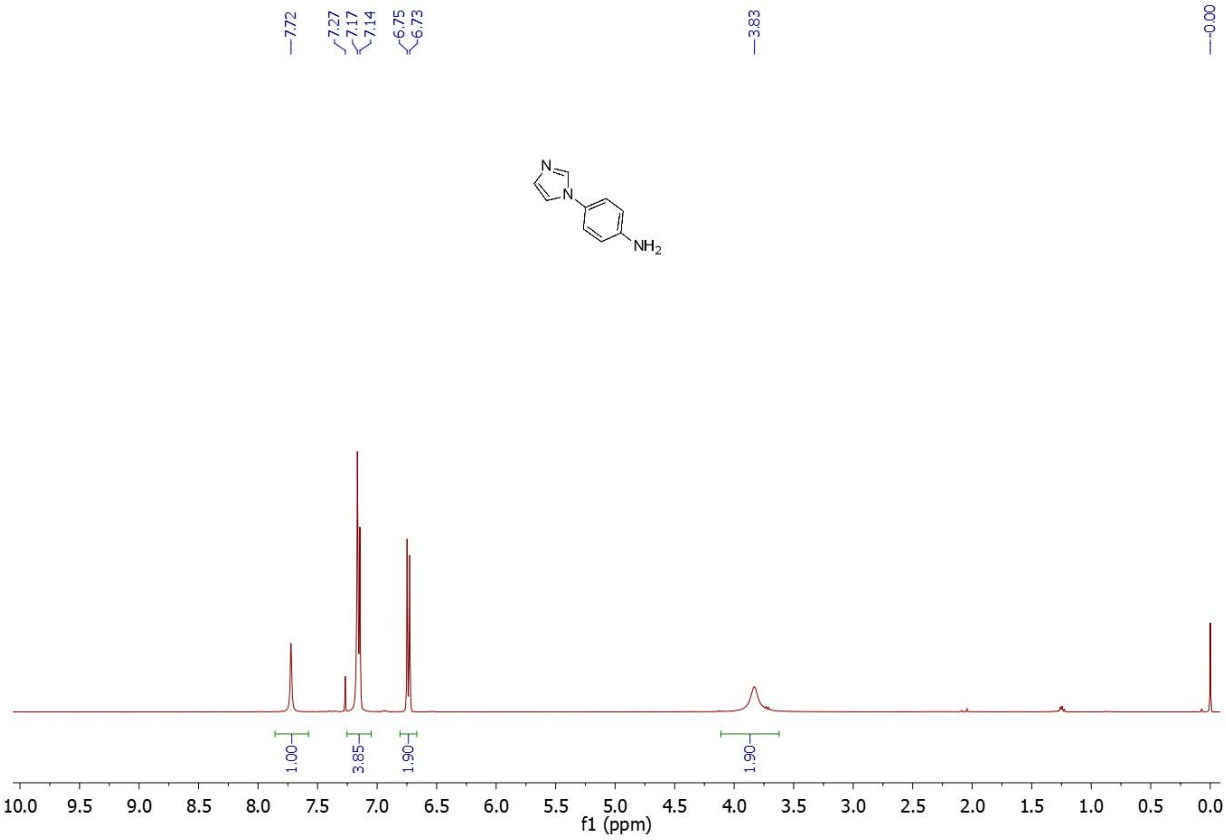


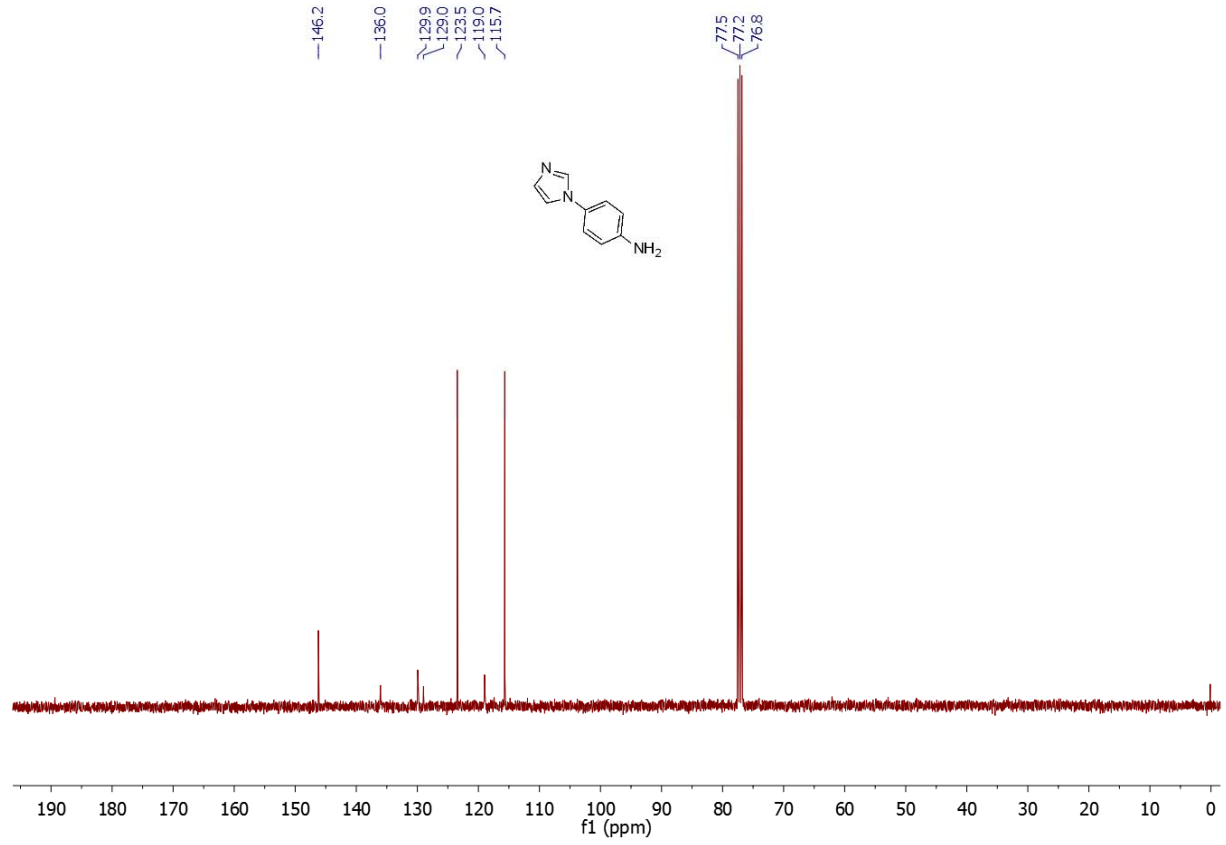
_N_-Phenylimidazole (Table 2)



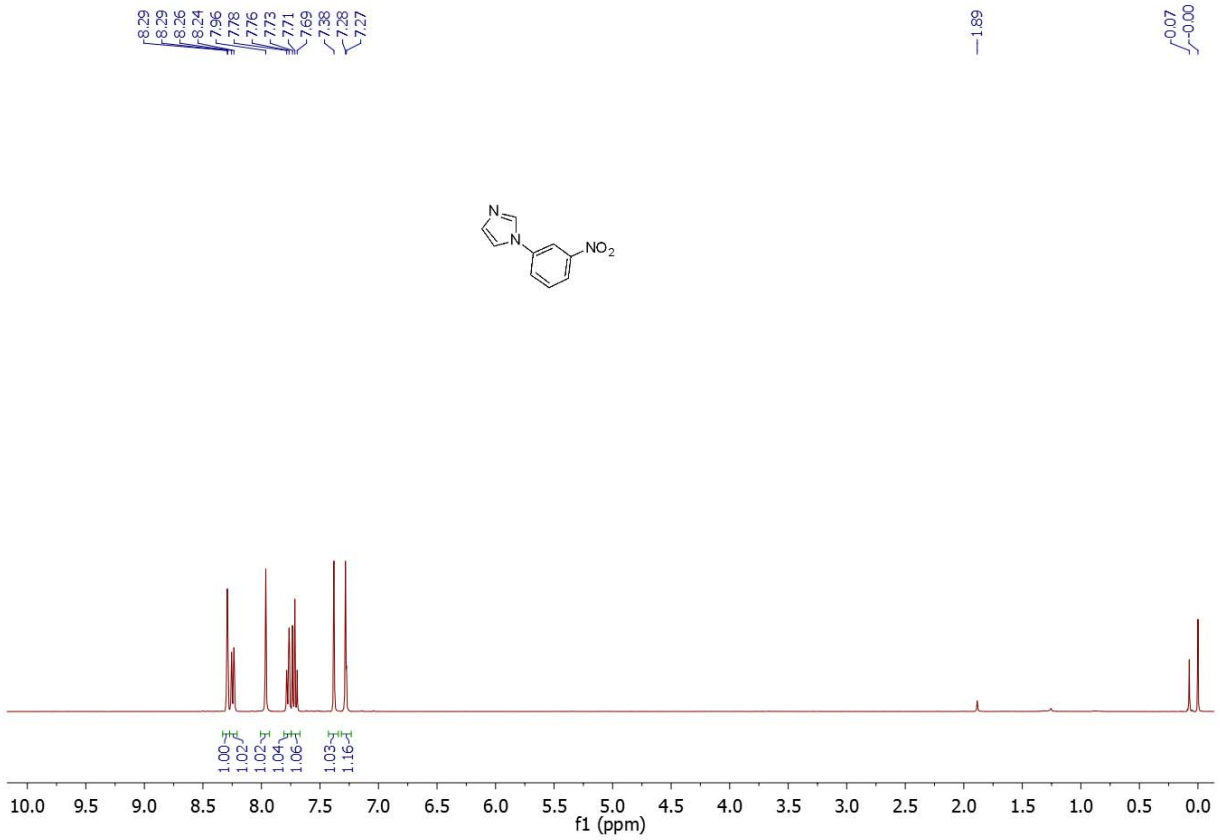


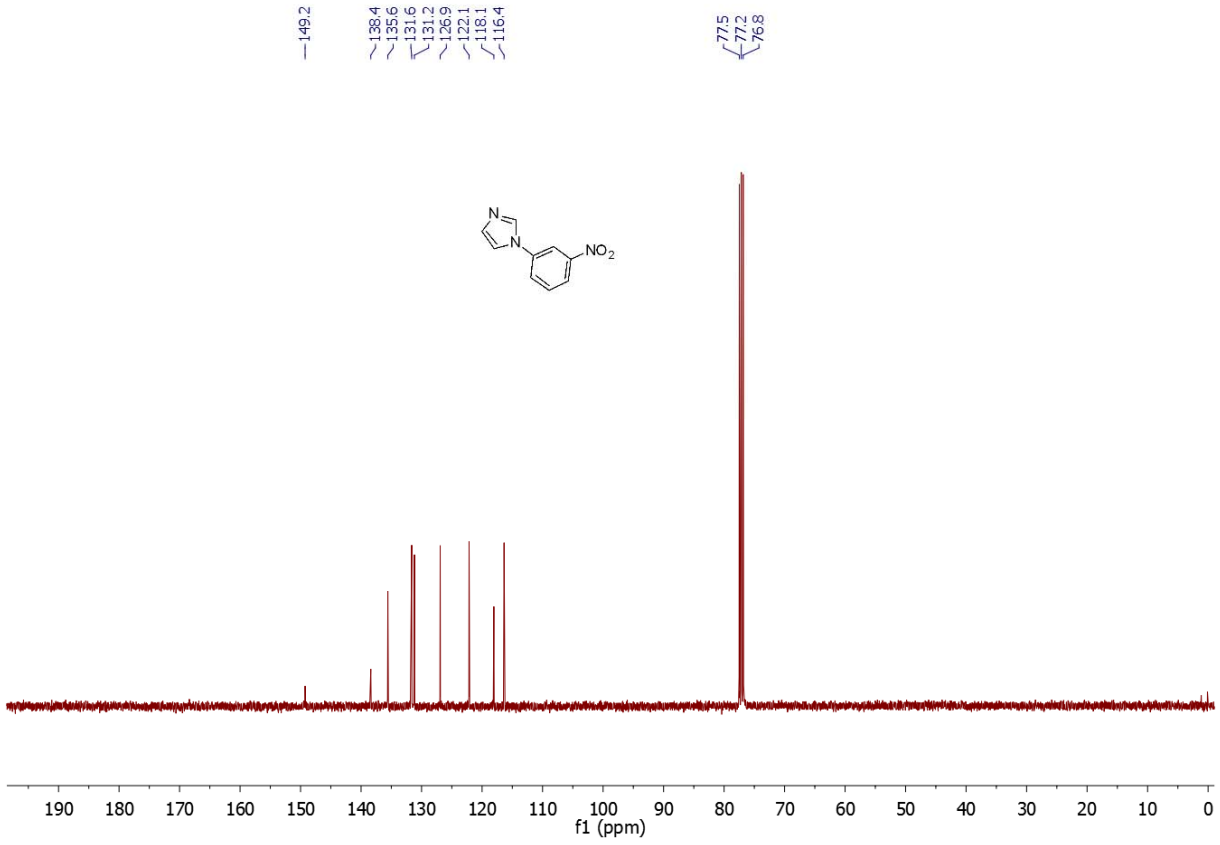
4-(1*H*-Imidazol-1-yl)aniline (Table 3, entry 1)



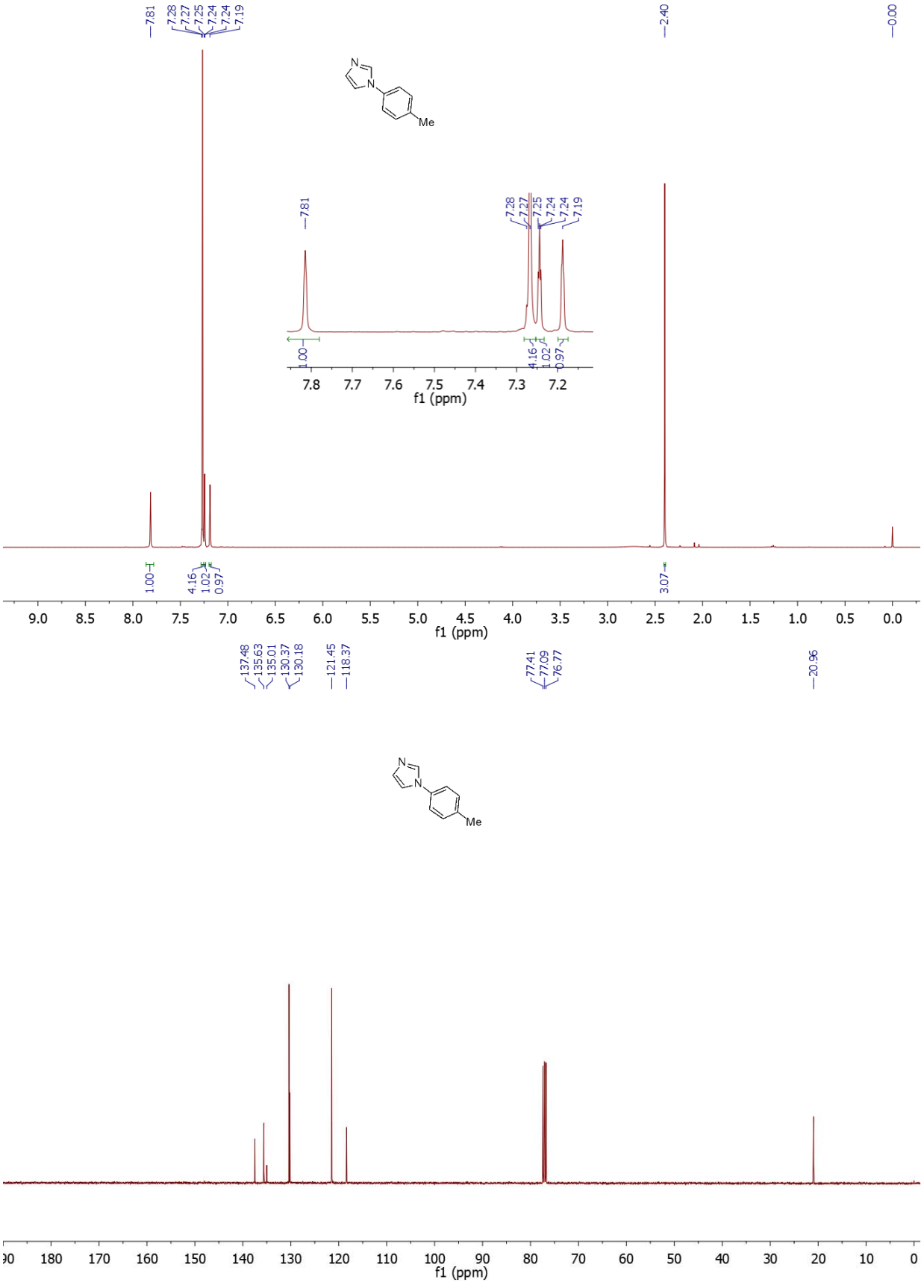


1-(3-Nitrophenyl)-1*H*-imidazole (Table 3, entry 2)

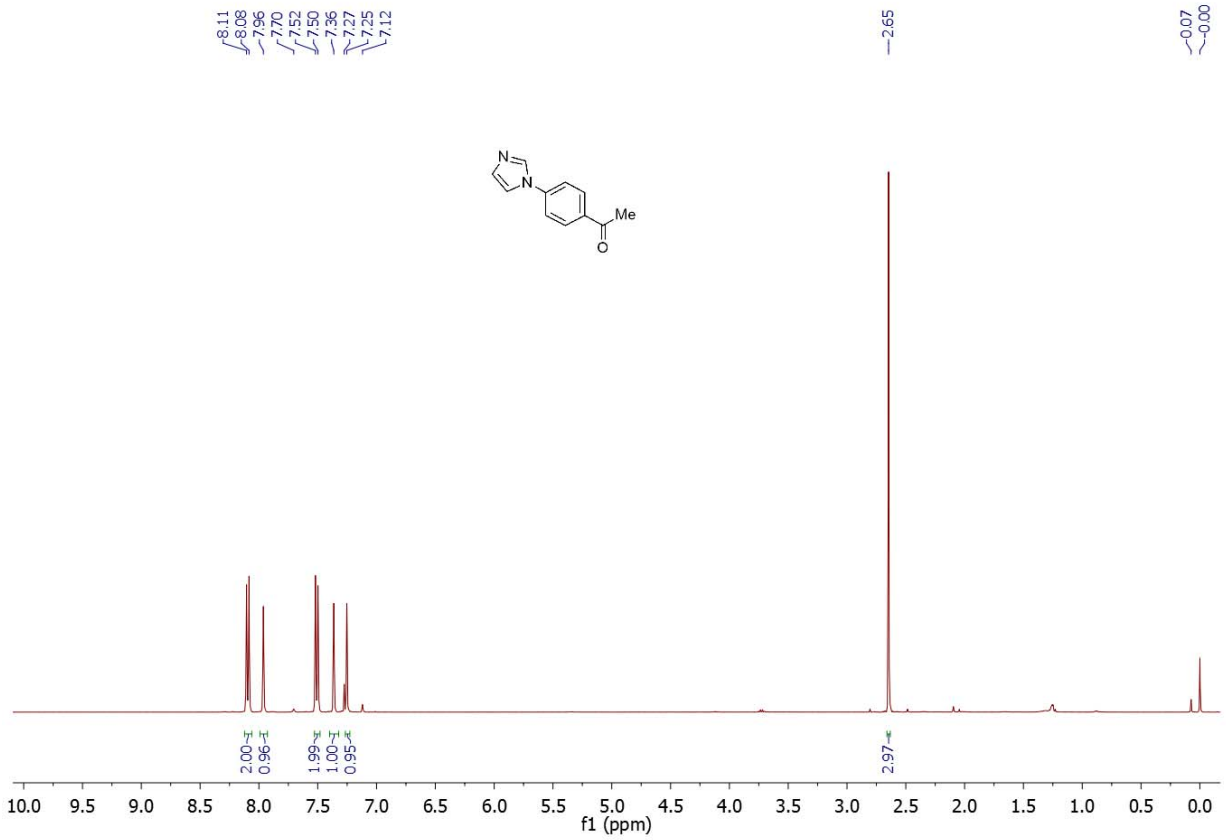


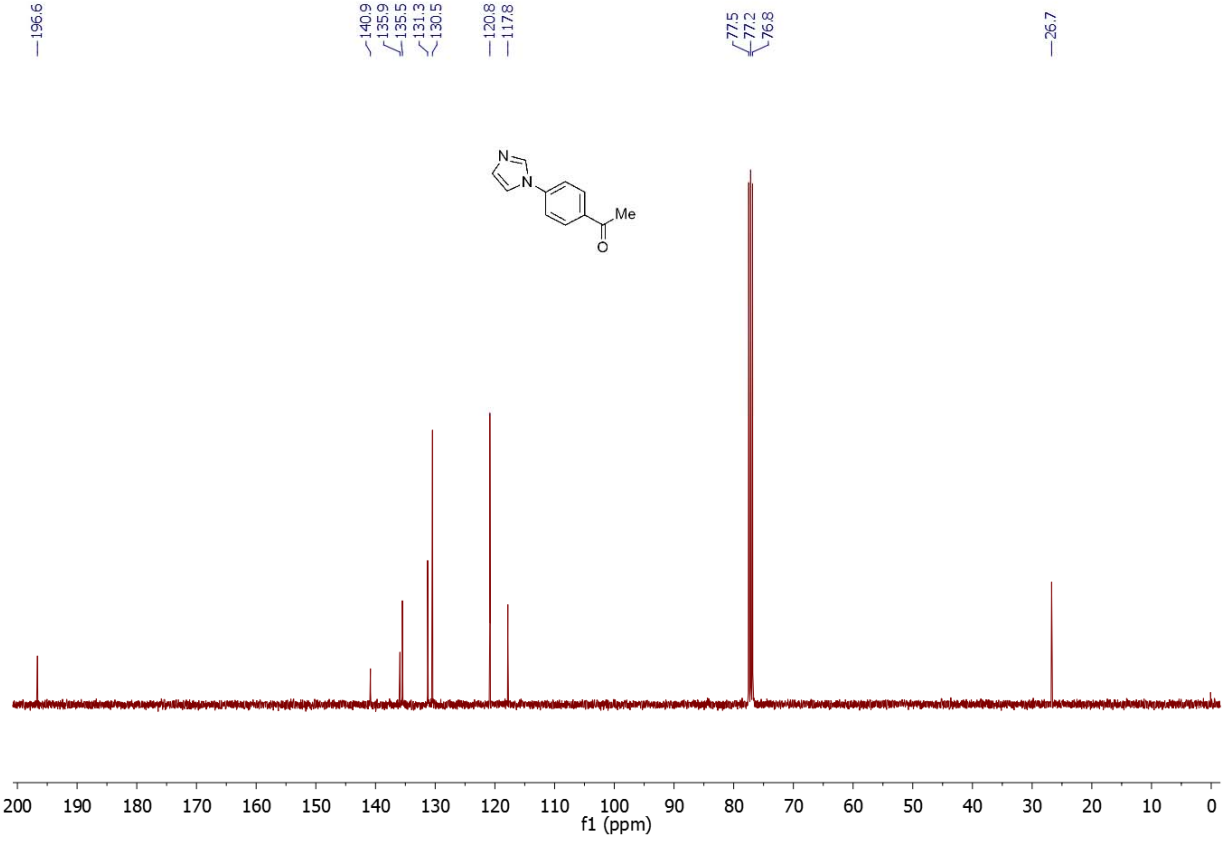


1-(p-Tolyl)-1*H*-imidazole (Table 3, entry 3)

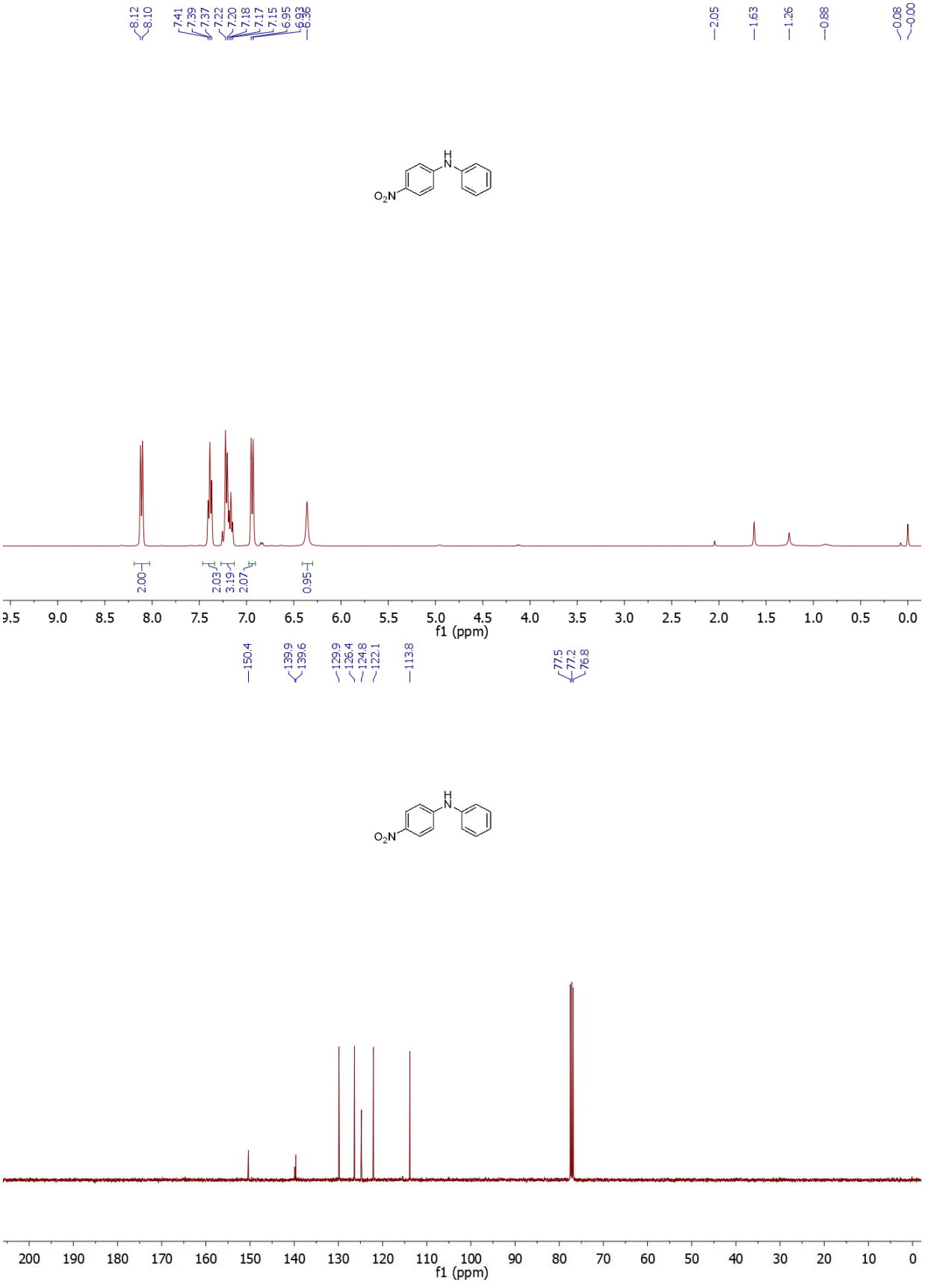


1-(4-(1*H*-Imidazol-1-yl)phenyl)ethanone (Table 3, entry 4)

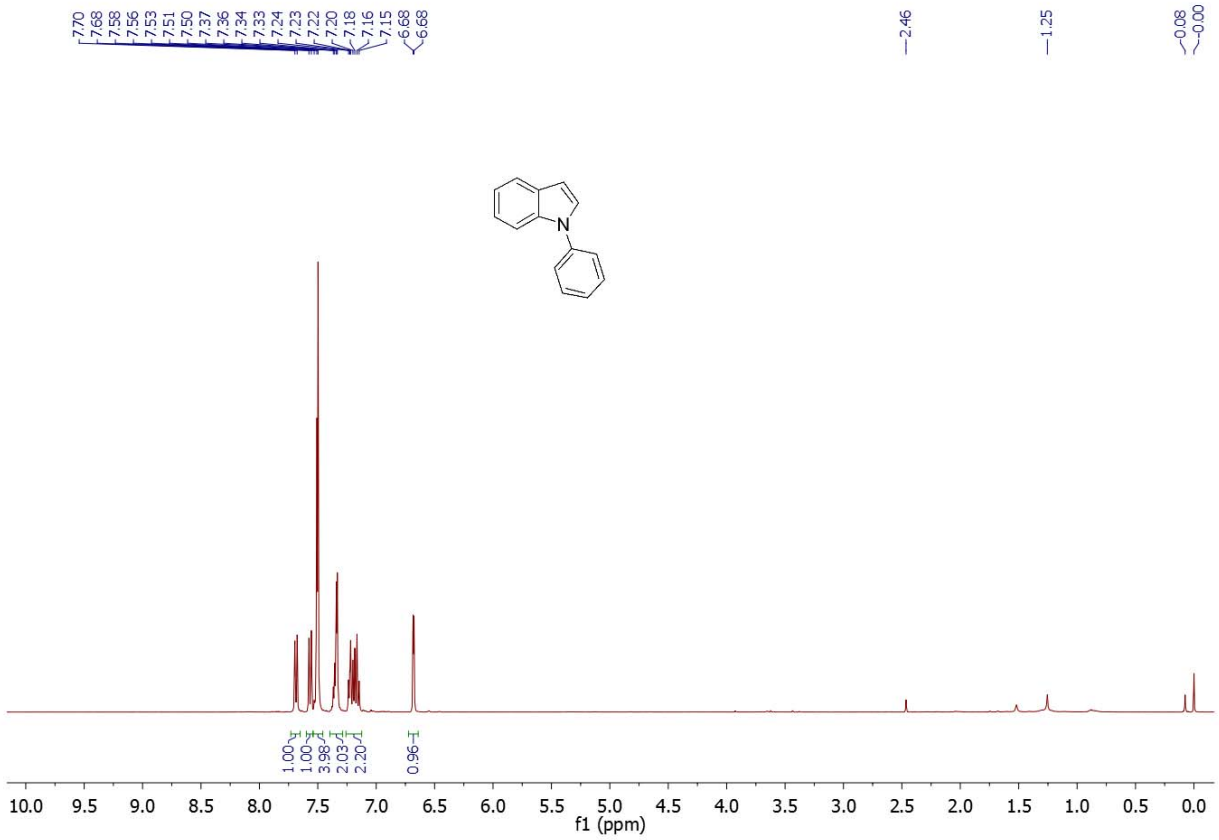


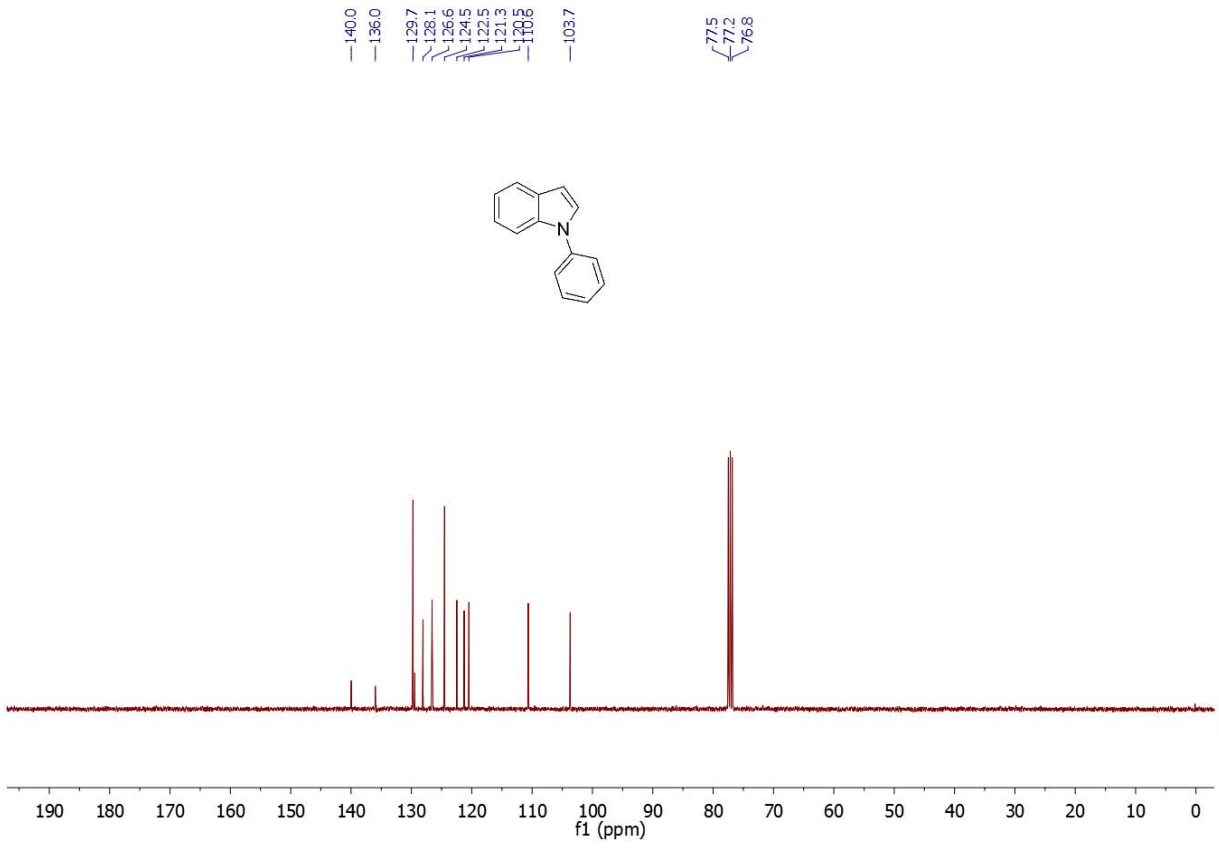


4-Nitro-*N*-phenylaniline (Table 4, entry 1–2)

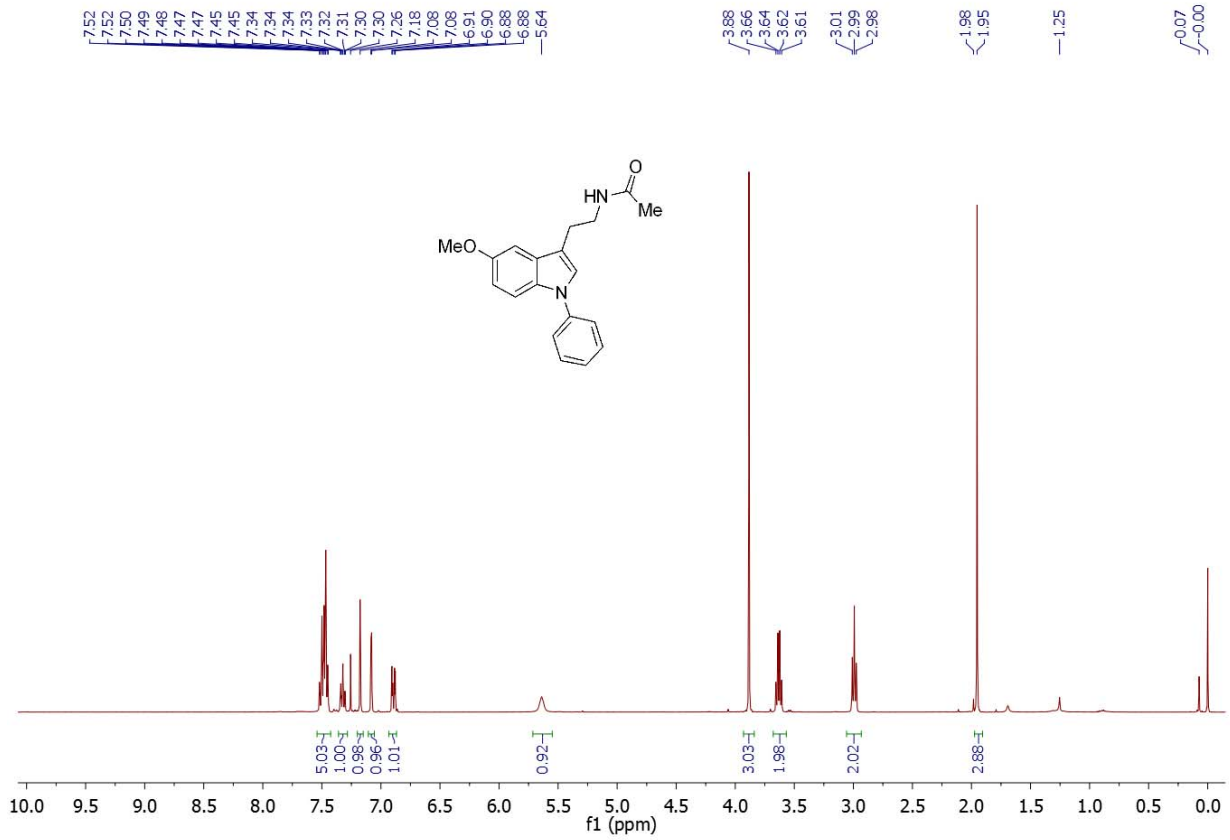


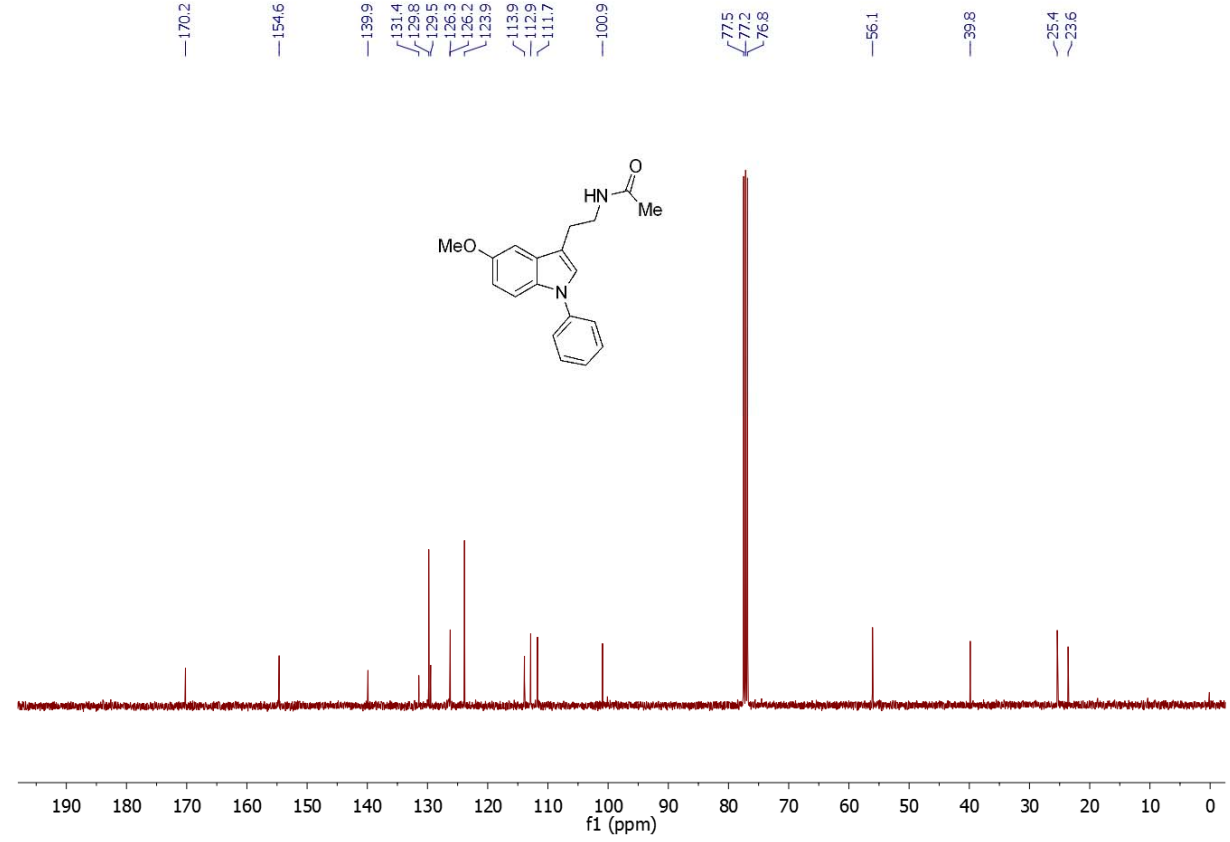
1-Phenyl-1*H*-indole (Table 4, entry 3–4)



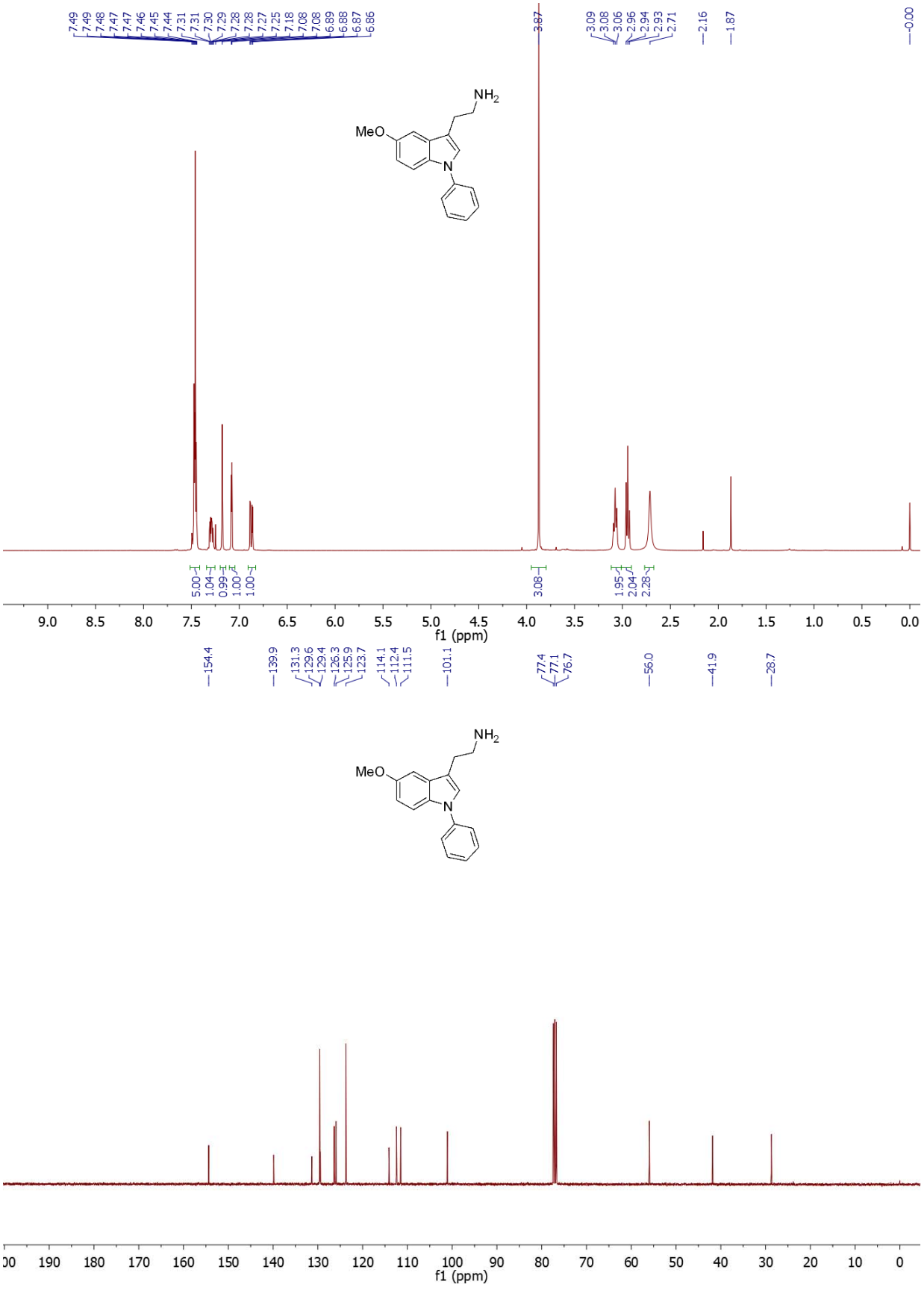


_N_-(2-(5-Methoxy-1-phenyl-1_H_-indol-3-yl)ethyl)acetamide (Table 4, entry 5)

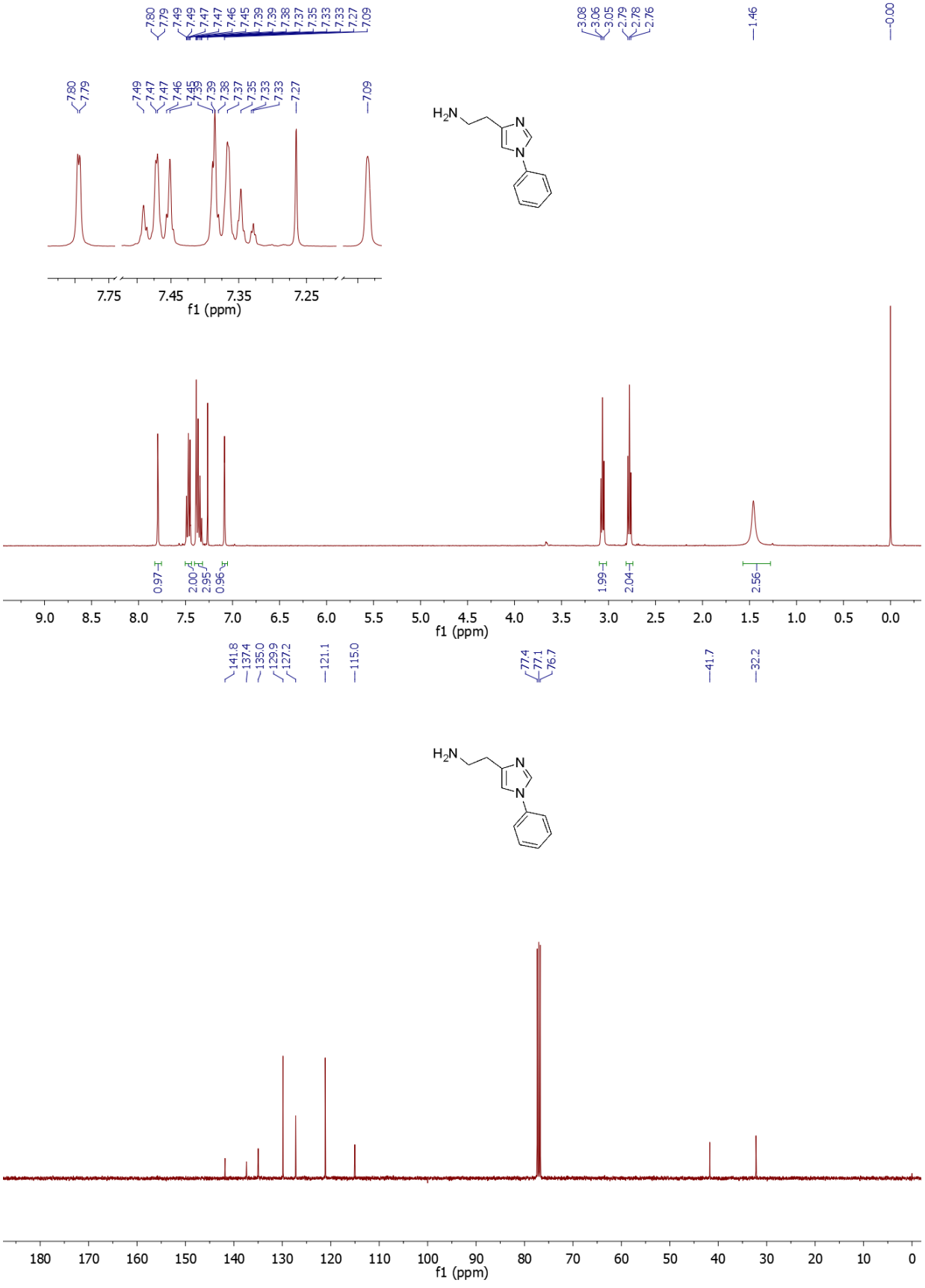




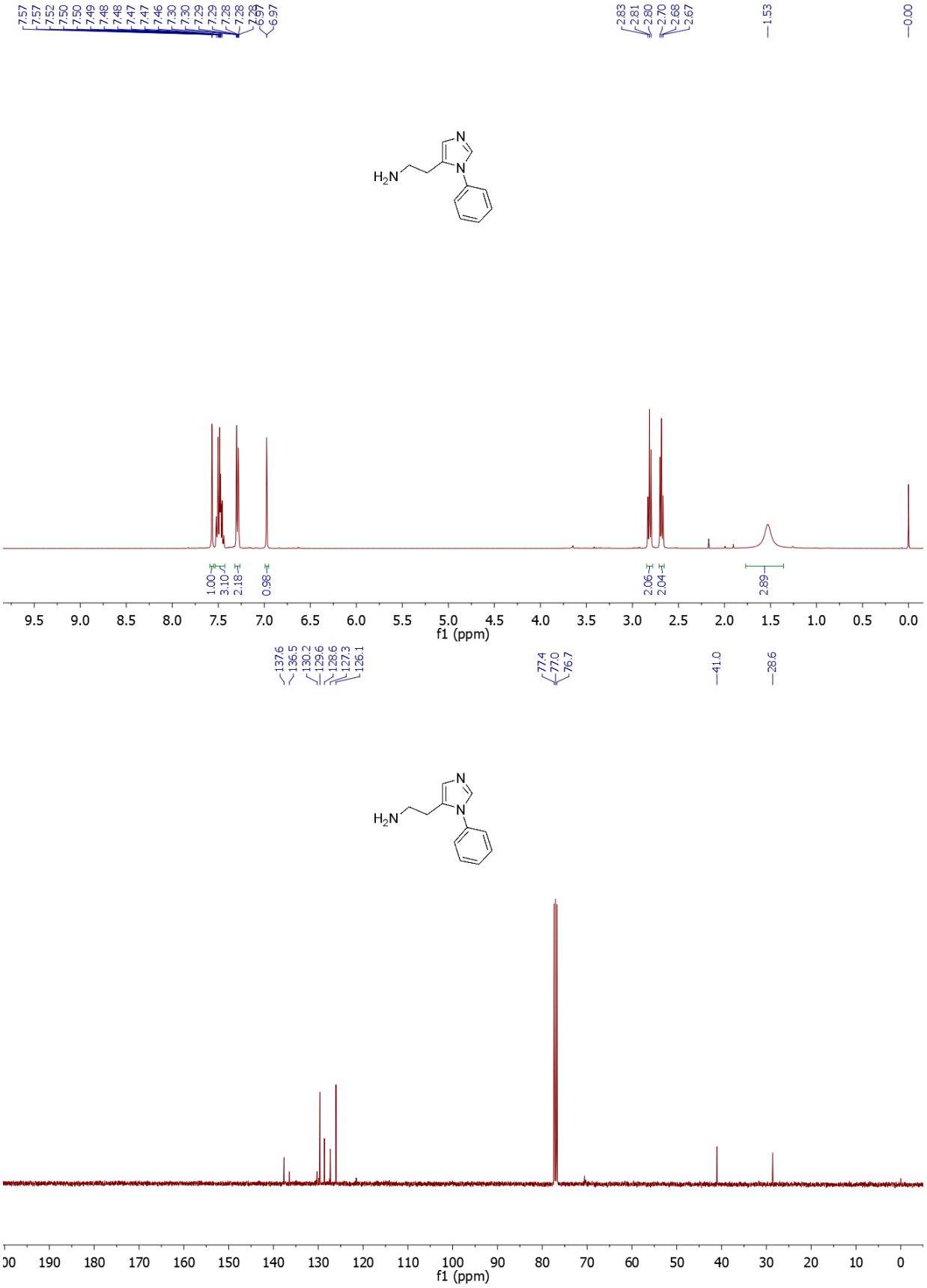
2-(5-Methoxy-1-phenyl-1*H*-indol-3-yl)ethanamine (Table 4, entry 6)



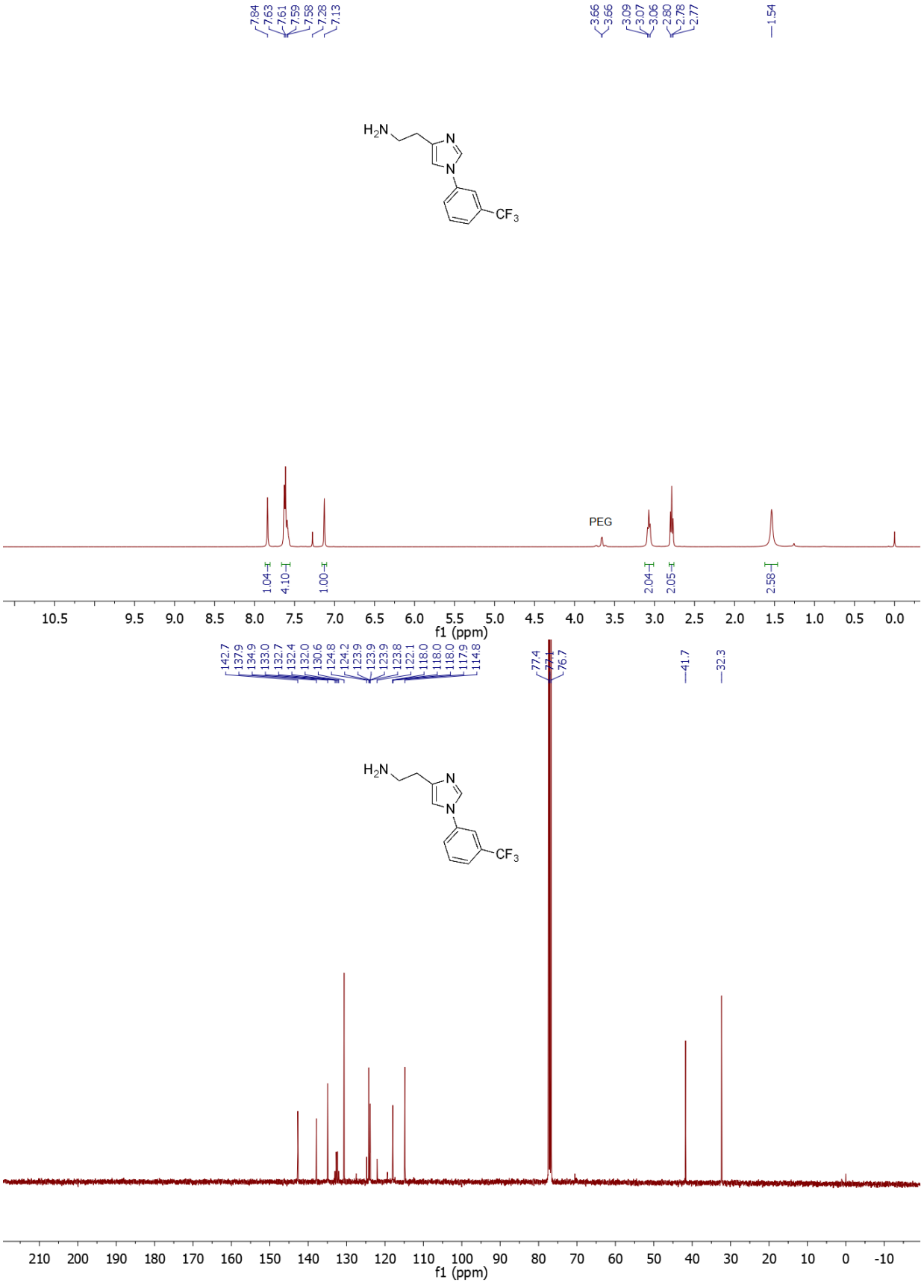
2-(1-Phenyl-1*H*-imidazol-4-yl)ethanamine (Table 4, entry 7–8)



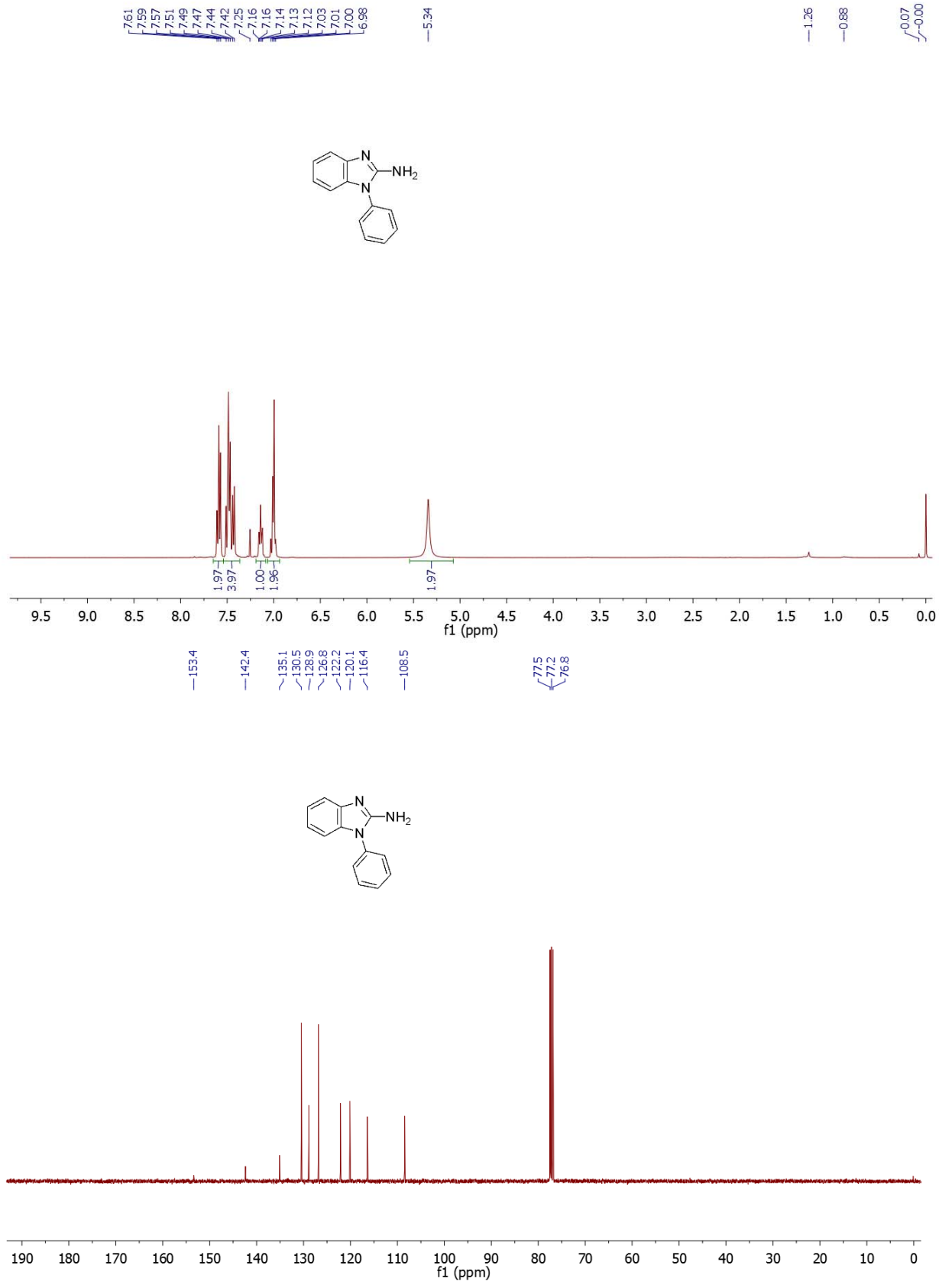
2-(1-Phenyl-1*H*-imidazol-5-yl)ethanamine (by-product from Table 3, entry 7-8)



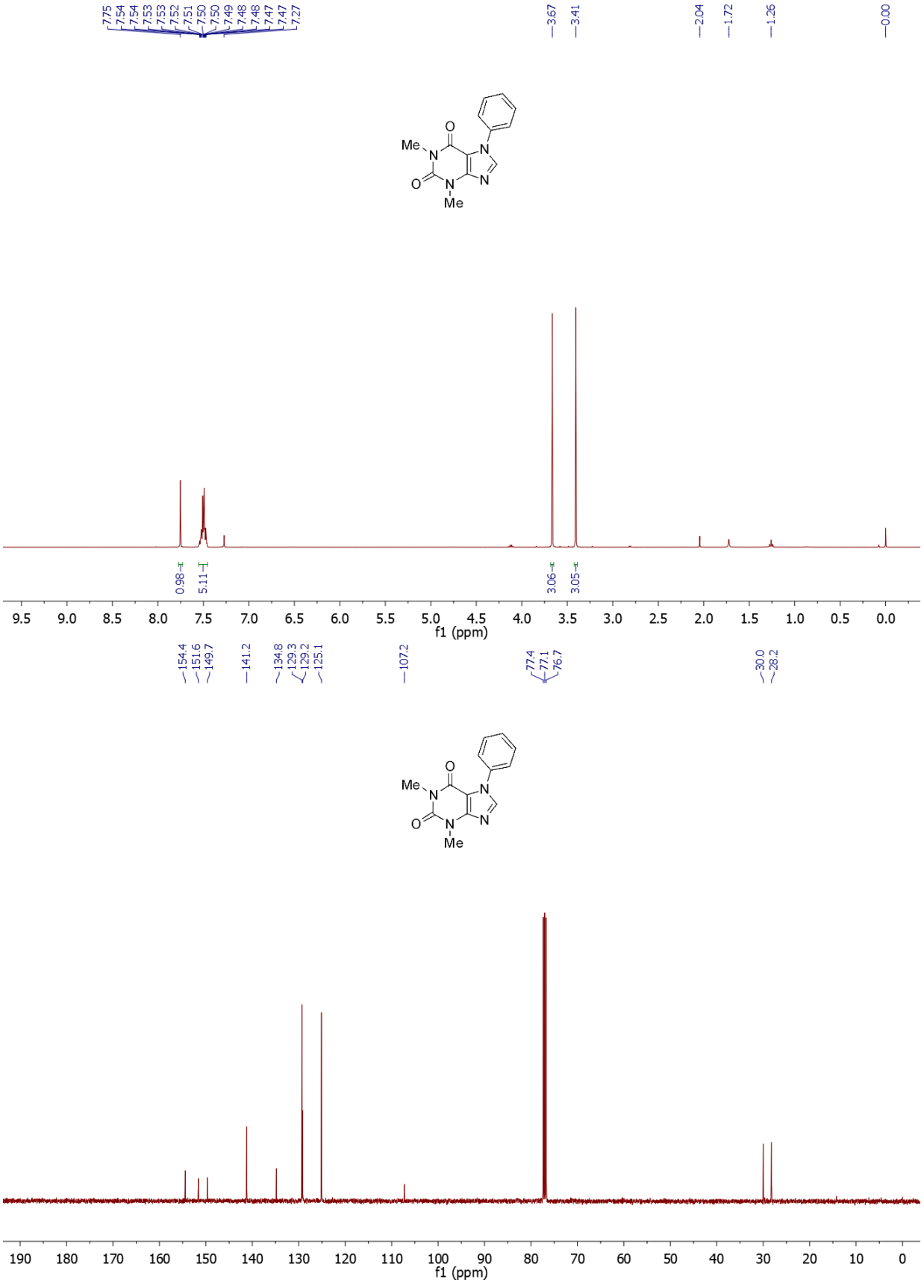
2-(1-(3-(Trifluoromethyl)phenyl)-1*H*-imidazol-4-yl)ethanamine (Table 4, entry 9)



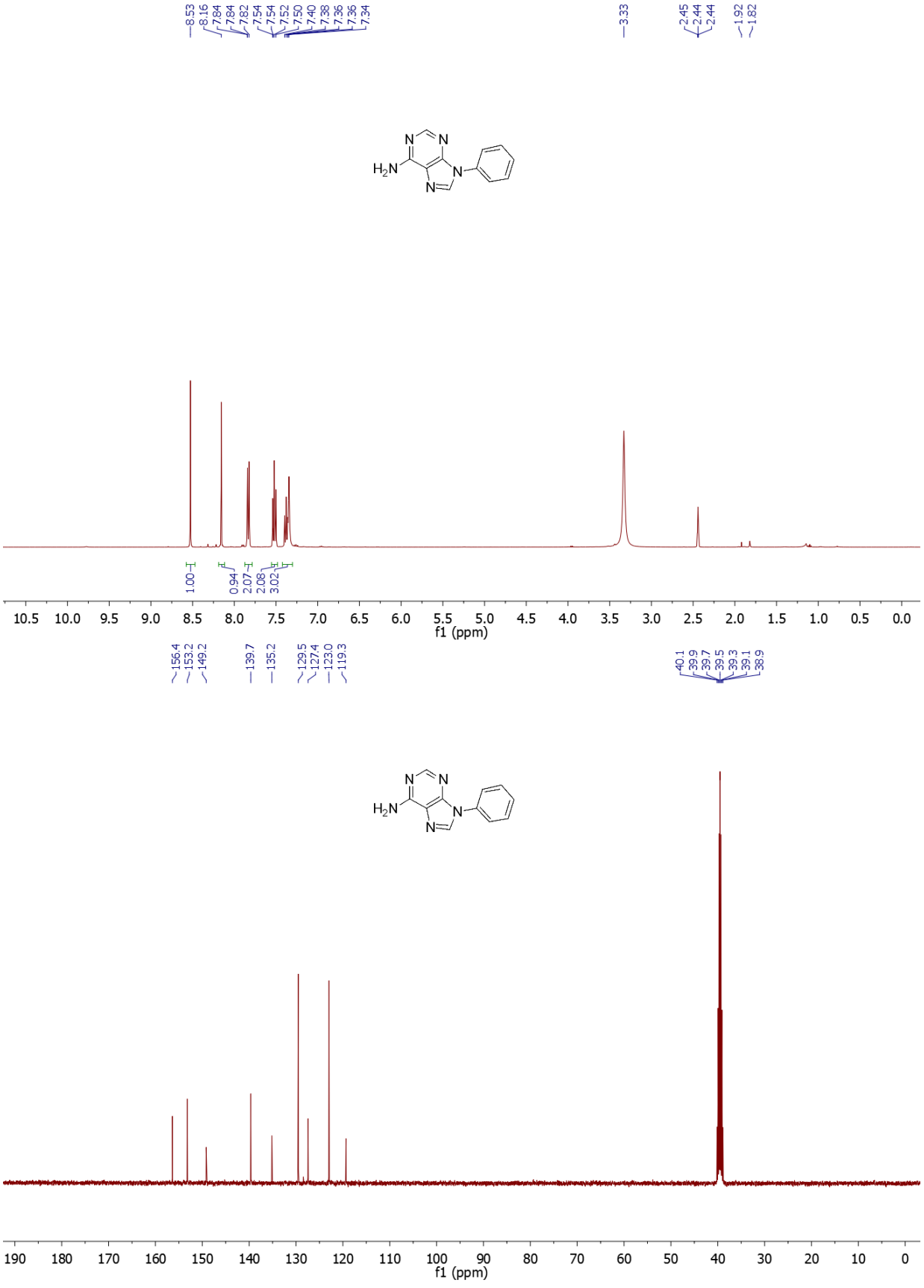
1-Phenyl-1*H*-benzo[d]imidazol-2-amine (Table 4, entry 10–11)



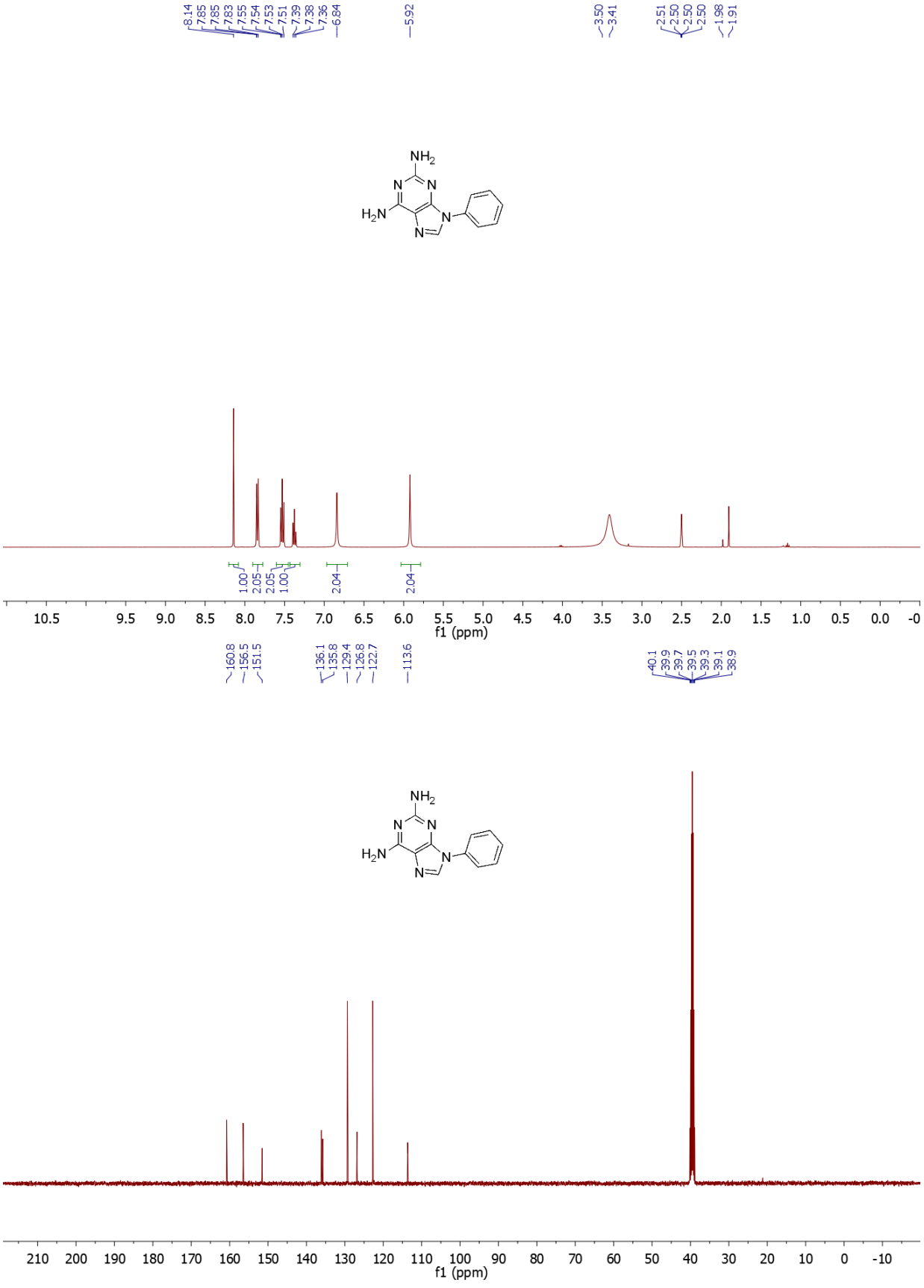
1,3-Dimethyl-7-phenyl-1*H*-purine-2,6(3*H*,7*H*)-dione (Table 4, entry 12)



9-Phenyl-9*H*-purin-6-amine (Table 4, entry 13)



9-Phenyl-9*H*-purine-2,6-diamine (Table 4, entry 14)



N^{α},N^{τ}-Diphenylhistamine (Scheme S1)