Supporting Information

Copper-Catalyzed [2 + 3]-Annulation of N-H Imines with Vinyl Azides: Access to Polyaryl 2H-imidazoles

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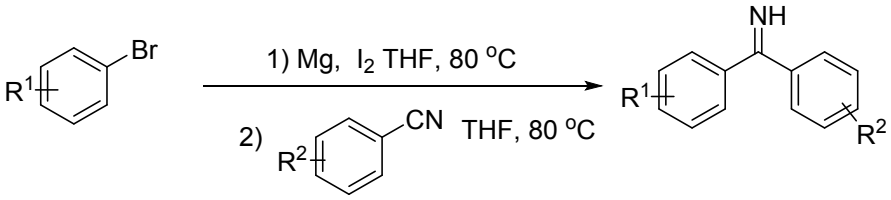
A. General information

Melting points were measured with a melting point instrument and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a 400/500 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. GC-MS was obtained using electron ionization. HRMS was obtained with a LCMS-IT-TOF mass spectrometer. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. High-resolution mass spectra (ESI) were obtained with a LCMS-IT-TOF mass spectrometer.

B. Typical procedure for preparation of N-H imines

General Procedure for the Preparation of N-H Diaryl Imines [1]:



In an oven-dried flask with three necks equipped with a magnetic stir bar was added magnesium turnings (0.583 g, 24.0 mmol, 1.2 equiv.) and suspended in THF (20.0 mL) under N_2 atmosphere. A few drops of bromobenzene and a crystal of iodine were added, placed into a preheated oil bath (80 ˚C) to initiate the exothermic reaction. A solution of bromobenzene (22.0 mmol, 1.1 equiv.) diluted in THF (5.0 mL) was added dropwise to maintain a gentle reflux for 2 hours; the solution colour changed from yellow to brown. The reaction mixture was cooled to room temperature and aryl nitrile (20.0 mmol, 1 equiv.) diluted in THF (5 mL) was added dropwise to form a viscous pale brown slurry. It was then placed in a preheated oil bath (80 ˚C), refluxed for 5 hours and stirred at room temperature overnight. MeOH (10 mL) was added in an ice-bath (with caution, exothermic) to give a red solution and yellow precipitate. The resulting mixture was stirred at room temperature for 30 min, and after this time the volatile materials were evaporated under reduced pressure. The residue was re-dissolved into ethyl acetate. Further purification was achieved by flash-column chromatography, with 1.5 mL of Et_3N added into every 100 mL of the solvent

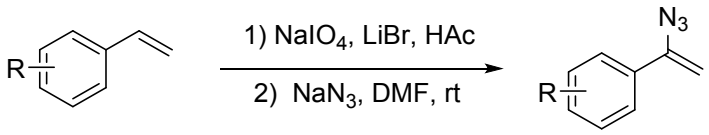
mixture EA/PE.

General Procedure for the Preparation of N-H Aryl Alkyl Imines [1]:

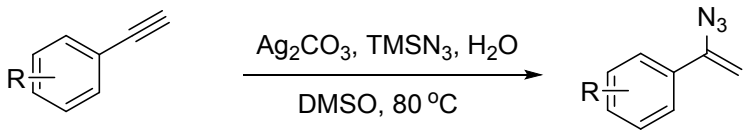
A stirred solution of the aryl nitrile (20 mmol) in THF (20 mL) under a positive atmosphere of N_2 was cooled to -78 °C and the alkyllithium reagent (32 mmol) was added dropwise over 0.5 h. The mixture was stirred at -78 °C for 2 h, quenched with anhydrous MeOH (5 mL) and then stirred at room temperature for 2 h. The resulting suspension was filtrated through Celite and the solvent was removed by rotary evaporation. The residue was purified by vacuum distillation.

1-(3,5-Dimethylphenyl)pentan-1-imine (1ar): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (d, J = 87.4 Hz, 1H), 7.48 (s, 1H), 7.06 (t, J = 6.1 Hz, 2H), 2.7-.67 (m, 2H), 2.35 (d, J = 5.3 Hz, 6H), 1.67-1.56 (m, 2H), 1.45-1.37 (m, 2H), 0.99 – 0.92 (m, 3H)； ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.9, 178.8, 140.1, 138.6, 138.3, 137.8, 132.0, 131.5, 124.8, 123.4, 37.9, 37.0, 28.9, 28.1, 22.6, 22.3, 21.3, 14.0, 13.9.

C. Typical procedure for preparation of azidovinyl benzenes [2]

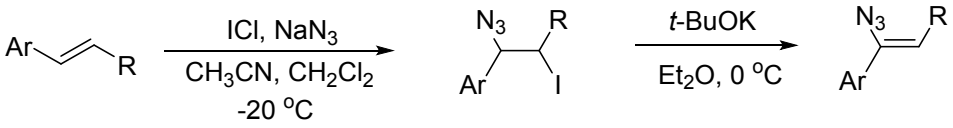


Method A for azidovinyl benzenes: To a solution of substituted-styrene (5 mmol) and LiBr (12 mmol) in acetic acid (8 mL) was added $NaIO_4$ (2.6 mmol) portionwise during 15 min. After the reaction mixture was stirred at room temperature for 5 h, then diluted with water, the product was extracted with CH_2Cl_2. The organic layer was washed with saturated aq. $NaHCO_3$, $Na_2S_2O_3$, and brine. It was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give dibromide. To a solution of dibromide in dry DMF (20 mL) was added NaN_3 (15 mmol). The mixture was stirred for 24 h at room temperature, then diluted with water and extracted with diethyl ether. The combined organic layers were washed with water (3 × 10 mL) and dried with anhydrous Na_2SO_4. After removal of the solvent, the crude residue was purified by column chromatography using silica gel with hexanes as the eluent to afford vinyl azides **2**.



Method B for azidovinyl benzenes: In a flask with a magnetic bar, Ag_2CO_3 (0.2 mmol) was suspended in DMSO (4 ml). Aryl acetylene (2 mmol), $TMSN_3$ (4 mmol) and H_2O (4 mmol) were added to flask, respectively. Then the mixture was heat to 80 °C. After 1 h, the mixture was partitioned between Et_2O and H_2O, and the organic phase was separated, dried (Na_2SO_4), and concentrated. The residue was chromatographed with petroleum as eluent to afford the **2** in 50-85% yield. [3]

Method C for azidovinyl benzenes:



To a suspension of NaN_3 (812.5 mg, 12.5 mmol, 2.5 equiv) in acetonitrile (3 mL) was added dropwise a solution of iodine monochloride (1214.0 mg, 7.5 mmol, 1.5 equiv) in CH_2Cl_2 (5 mL) at -20°C, and the mixture was stirred at the same temperature. After 30 min, a solution of vinylbenzene (5 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added slowly, and the mixture was stirred for 1 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$, and the organic materials were extracted two times with Et_2O. The combined extracts were washed with brine and dried over $MgSO_4$. After evaporation of solvents, the resulting crude materials were used immediately for the next step without any further purification. To a solution of the obtained compounds above in Et_2O (10 mL) was added *t*-BuOK (672.0mg, 6 mmol, 1.2 equiv) at 0 °C, and the mixture was stirred for 1.5 h at the same temperature. The reaction was quenched by adding NH_4HCO_3 saturated solution, and the organic materials were extracted with ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the resulting crude materials were purified by flash column chromatography (silica gel; pure petroleum ether) to give azidovinyl benzenes as a yellow liquid.

D. Typical procedure for preparation of 3-phenyl-2*H*-azirine 4a

To a solution of (1-azidovinyl) benzene (**2a**) (2 mmol) and diazabicyclo [2.2.2] octan (0.2 mmol) in dry toluene (6 mL) stirred 50 min at 110 ^{o}C. Upon completion of the reaction as indicated by TLC, the solvent was removed and concentrated under reduced pressure to give crude raffinate. The crude raffinate was purified by column chromatography using silica gel with eluent (petroleum ether: EtOAc = 10 : 1) to afford azirines **4a** as a light yellow oil (198.5 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.4 Hz, 1H), 7.63 – 7.52 (m, 2H), 1.80 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 132.9, 129.6, 129.1, 125.5, 19.7.

E. Typical procedure for preparation of 2*H*-imidazoles

N-H imines **1** (0.3 mmol), azidovinyl benzene **2** (0.36 mmol), CuCl (3.0 mg, 0.03 mmol), and 2 mL of dry CH_3CN were added to a 10 mL screw-capped tube under O_2 atmosphere. The reaction vessel was closed with the cap and the reaction mixture was stirred at 80 ^{o}C (oil bath) for 8 h. The crude product was cooled to room temperature and concentrated in vacuum to give a residue, which was purified by flash column chromatography to afford the 2*H*-imidazoles **3** .

Typical procedure for preparation of 2-butyl-2,4-diphenyl-2,5-dihydro-1*H*-imidazole 5aq

To a solution of 2-butyl-2,4-diphenyl-2*H*-imidazole (**3aq**) (1 mmol), dry THF (3 mL) and $LiAlH_4$ (114 mg, 3 equiv) were added to a 10 mL screw-capped tube under N_2 atmosphere stirred at 0 ^{o}C. Upon completion of the reaction as indicated by TLC, the solvent was removed and concentrated under reduced pressure to give crude raffinate. The crude raffinate was purified by column chromatography using silica gel with eluent (petroleum ether: EtOAc = 5 : 1) to afford **5aq** as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.43 (d, *J* = 7.7 Hz, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 6.5 Hz, 1H), 4.26 (d, *J* = 15.9 Hz, 1H), 4.09 (d, *J* = 15.9 Hz, 1H), 2.39 (s, 1H), 2.11 – 1.98 (m, 2H), 1.33 – 1.22 (m, 4H), 0.84 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 145.8, 130.9, 128.6, 128.2, 128.0, 127.1, 125.9, 97.5, 55.3, 43.3, 26.5, 23.0, 14.1.

F. Typical procedure for preparation of 6, 7, 8

Typical procedure for preparation of 6

To a solution of 2*H*-imidazoles **3** (2.0 mmol), dry CH_3CN (4 mL) and *m*-CPBA (688 mg, 2.0 equiv) were added to a 10 mL screw-capped tube at 80 ^oC. Upon completion of the reaction as indicated by TLC, the solvent was removed and concentrated under reduced pressure to give crude raffinate. The crude raffinate was purified by column chromatography using silica gel with eluent (petroleum ether: EtOAc = 4 : 1) to afford **6**.

2,2,5-Triphenyl-2,3-dihydro-4*H*-imidazol-4-one (6aa), ^1H NMR (500 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.56 – 8.49 (m, 2H), 7.56 – 7.52 (m, 1H), 7.52 – 7.47 (m, 6H), 7.33 (dt, *J* = 13.9, 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 160.9, 141.3, 131.9, 130.3, 128.8, 128.6, 128.6, 128.3, 126.8, 87.5.

2-(3-Bromophenyl)-2-methyl-5-phenyl-2,3-dihydro-4*H*-imidazol-4-one (6bj), ^1H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.51 (d, *J* = 7.3 Hz, 2H), 7.84 (s, 1H), 7.57 (dd, *J* = 7.4, 5.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.25 (m, 1H), 1.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 161.2, 143.2, 132.0, 131.3, 130.3, 130.2, 129.1, 128.7, 128.6, 124.4, 122.8, 83.6, 29.0.

2-(3-Bromophenyl)-2,5-diphenyl-2,3-dihydro-4*H*-imidazol-4-one (6bk), ^1H NMR (500 MHz, $CDCl_3$) δ 10.86 (s, 1H), 8.63 – 8.50 (m, 2H), 7.78 (t, *J* = 1.8 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.52 (t, *J* = 7.4 Hz, 3H), 7.47 – 7.43 (m, 1H), 7.35 (ddd, *J* = 8.3, 7.7, 3.6 Hz, 3H), 7.22 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 161.3, 143.7, 140.9, 132.1, 131.4, 130.2, 130.2, 130.0, 128.9, 128.8, 128.7, 128.5, 126.7, 125.5, 122.8, 87.3.

Typical procedure for preparation of 7

To a solution of **6** (1.0 mmol), pyridine (3.0 mL), and phosphorus pentasulfide (0.29g, 1.5 mmol) were added to a 25 mL screw-capped tube at 120 °C for 1 h. Ammonia (7 M in methanol) (8 mL, 56mmol) and *tert*-butyl hydroperoxide (2.2 mL, 15.6 mmol) were added, and the mixture was stirred at room temperature for 16 h. The solvents were evaporated, and the crude raffinate was purified by column chromatography using silica gel with eluent (petroleum ether: EtOAc = 2 : 1) and repurified through reversed phase preparative-HPLC to afford **7**.

2-(3-Bromophenyl)-2-methyl-5-phenyl-2*H*-imidazol-4-amine (**7aj**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (t, *J* = 1.7 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.64 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 3H), 7.40 – 7.36 (m, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 4.88 (s, 2H), 1.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 158.3, 144.7, 131.2, 130.9, 130.3, 129.9, 129.8, 129.2, 127.9, 125.5, 122.3, 99.3, 28.5.

2-(3-Bromophenyl)-2,5-diphenyl-2*H*-imidazol-4-amine (**7bk**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 13.4, 7.0 Hz, 3H), 7.62 (dd, *J* = 13.6, 7.7 Hz, 3H), 7.55 – 7.49 (m, 3H), 7.37 – 7.35 (m, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 1H), 5.27 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7, 158.6, 145.2, 142.5, 131.1, 131.0, 130.5, 130.4, 129.7, 129.2, 128.3, 128.1, 127.5, 127.4, 126.4, 122.2, 102.8.

Typical procedure for preparation of 8

A portion of **7** (0.3 mmol), boronic acid (0.60 mmol), and bis(triphenylphosphine)palladium(II) chloride (42 mg, 60 µmol) was taken up in DME (4 mL) and water (2 mL). Sodium carbonate (1 M in water) (0.6 mmol) was added, and the mixture was heated at 80 °C for 2 h. The solvents were evaporated and extracted with ethyl acetate. The crude raffinate was purified by column chromatography using silica gel with eluent (0:1 → 1:10, MeOH/ EtOAc) and repurified through reversed phase preparative-HPLC to afford **8.**

2-Methyl-5-phenyl-2-(3-(pyridin-3-yl)phenyl)-2*H*-imidazol-4-amine (**8a**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.1 Hz, 1H), 8.54 (s, 1H), 7.98 – 7.88 (m, 2H), 7.81 – 7.70 (m, 3H), 7.56 – 7.43 (m, 5H), 7.35 (d, *J* = 2.4 Hz, 1H), 3.82 (s, 2H), 1.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 157.9, 149.3, 148.3, 148.2, 142.7, 137.8, 134.6, 131.2, 130.7, 129.3, 129.1, 128.0, 126.6, 126.3, 125.5, 123.6, 99.1, 28.7.

2-Methyl-5-phenyl-2-(3-(pyrimidin-5-yl)phenyl)-2*H*-imidazol-4-amine (**8b**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.98 (s, 2H), 7.94 (s, 1H), 7.83 (d, *J* = 5.3 Hz, 1H), 7.77 (d, *J* = 6.9 Hz, 2H), 7.56 – 7.45 (m, 5H), 4.58 (s, 2H), 1.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 155.0, 154.9, 143.4, 134.4, 134.2, 131.9, 131.2, 130.8, 129.4, 129.3, 128.0, 127.5, 126.1, 125.4, 77.3, 28.7.

2,5-Diphenyl-2-(3-(pyridin-3-yl)phenyl)-2*H*-imidazol-4-amine (8c) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.54 (s, 1H), 7.91 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.50 (q, *J* = 6.3 Hz, 3H), 7.43 (dt, *J* = 15.2, 7.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 3H), 7.23 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 158.6, 148.4, 148.4, 144.0, 142.7, 137.7, 136.7, 134.5, 131.2, 131.0, 129.2, 128.9, 128.3, 128.1, 127.5, 127.5, 126.3, 126.1, 123.5, 122.8, 103.3.

2,5-Diphenyl-2-(3-(pyrimidin-5-yl)phenyl)-2*H*-imidazol-4-amine (8d) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.92 (s, 2H), 7.90 (s, 1H), 7.80 (dd, *J* = 10.4, 5.4 Hz, 3H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.55 – 7.50 (m, 3H), 7.48 – 7.42 (m, 3H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 158.4, 157.4, 155.0, 144.2, 142.3, 134.1, 132.1, 132.1, 131.2, 130.9, 129.3, 129.3, 128.4, 128.3, 128.1, 127.7, 127.4, 126.1, 126.0, 102.9.

G. Spectroscopic data for 2*H*-imidazoles

2,2,4-Triphenyl-2*H*-imidazole (3aa) as a yellow solid (72.1 mg, 82% yield); mp 99.3-100.3 ^{o}C R_f = 0.5 (PE: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.06 (d, *J* = 4.9 Hz, 2H), 7.69 (d, *J* = 6.3 Hz, 4H), 7.45 (s, 3H), 7.27 (d, *J* = 6.9 Hz, 4H), 7.22 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 163.3, 155.1, 148.7, 140.9, 133.6, 131.6, 131.5, 131.0, 129.6, 129.1, 128.6, 128.4, 127.8, 126.5, 112.7; HRMS (ESI) m/z: calcd for $C_{21}H_{17}N_2$ $[M+H]^+$ 297.1386; found 297.1383.

2,4-Diphenyl-2-(*p*-tolyl)-2*H*-imidazole (3ab): as a brown solid (84.0 mg, 82% yield); mp 102.4-103.6 ^{o}C; R_f = 0.5 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.17-8.15 (m, 2H), 7.78-7.73 (m, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 7.0 Hz, 3H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.33-7.29 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 155.0, 140.9, 137.9, 137.6, 131.6, 131.0, 129.1, 129.1, 128.6, 128.4, 127.8, 127.7, 127.6, 112.6, 21.2; HRMS (ESI) m/z: calcd for $C_{22}H_{19}N_2$ $[M+H]^+$ 311.1543; found 311.1538.

2-([1,1'-Biphenyl]-4-yl)-2,4-diphenyl-2*H*-imidazole (3ac): as a yellow solid (85.1 mg, 76% yield); mp 160.4-161.6 ^{o}C; R_f = 0.7 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.18 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.87-7.81 (m, 4H), 7.63-7.60 (m, 4H), 7.56 (dd, *J* = 4.8, 2.5 Hz, 3H), 7.47 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.43-7.37 (m, 3H), 7.36-7.32

(m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 155.2, 140.8, 140.8, 140.7, 139.9, 131.7, 131.0, 129.2, 128.9, 128.6, 128.5, 128.2, 127.9, 127.8, 127.4, 127.2, 127.2, 112.6; HRMS (ESI) m/z: calcd for $C_{27}H_{21}N_2$ $[M+H]^+$ 373.1699; found 373.1694.

2-(4-Methoxyphenyl)-2,4-diphenyl-2*H*-imidazole (3ad): as a yellow soild (69.6 mg, 61% yield); mp 110.1-111.0 °C;R_f = 0.3 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.15 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.76-7.70 (m, 2H), 7.69-7.64 (m, 2H), 7.56 (t, *J* = 6.0 Hz, 3H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 6.96-6.86 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 159.1, 154.9, 141.0, 133.0, 131.6, 131.0, 129.1, 129.0, 128.6, 128.4, 127.8, 127.7, 113.7, 112.4, 55.3; HRMS (ESI) m/z: calcd for $C_{22}H_{19}N_2O$ $[M+H]^+$ 327.1492; found 327.1497.

2-(4-Fluorophenyl)-2,4-diphenyl-2H-imidazole (3ae): as a yellow soild (62.0 mg, 66% yield); mp 102.9-104.0 °C; R_f = 0.4 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.15-8.10 (m, 2H), 7.72-7.67 (m, 4H), 7.56-7.51 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 162.3 (d, *J* = 248.2 Hz), 155.2, 140.6, 136.7 (d, *J* = 3.8 Hz) 131.8, 130.8, 129.5 (d, *J* = 8.8 Hz), 129.2, 128.6, 128.5, 127.9, 127.6, 115.2 (d, *J* = 21.4 Hz), 112.1; HRMS (ESI) m/z: calcd for $C_{21}H_{16}FN_2$ $[M+H]^+$ 315.1292; found 315.1289.

2-(4-Chlorophenyl)-2,4-diphenyl-2*H*-imidazole (3af): as a brown solid (60.8 mg, 62% yield); mp 119.5-121.7 °C; R_f = 0.5 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.16 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.77-7.72 (m, 4H), 7.56 (d, *J* = 7.6 Hz, 3H), 7.42-7.33 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 155.4, 140.6, 139.5, 133.7, 131.8, 130.8, 129.2, 129.2, 128.6, 128.5, 128.0, 127.7, 112.1; HRMS (ESI) m/z: calcd for $C_{21}H_{16}ClN_2$ $[M+H]^+$ 331.0997; found 331.0992.

2-(4-Bromophenyl)-2,4-diphenyl-2*H*-imidazole (3ag): as a light yellow solid (68.0 mg, 61% yield); mp 130.5-131.7 °C; R_f = 0.6 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.0 Hz, 1H), 8.14-8.08 (m, 2H), 7.70-7.65 (m, 2H), 7.61-7.57 (m, 2H), 7.56-7.51 (m, 3H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35-7.30 (m, 2H), 7.28 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 155.3, 140.4, 139.9, 131.8, 131.4, 130.7, 129.5, 129.2, 128.6, 128.5, 128.0, 127.6, 121.9, 112.1; HRMS (ESI) m/z: calcd for $C_{21}H_{16}BrN_2$ $[M+H]^+$ 375.0491; found 375.0488.

2,4-Diphenyl-2-(4-(trifluoromethyl)phenyl)-2*H*-imidazole (3ah): as a light yellow solid (66.5 mg, 61% yield); mp 147.4-148.5 °C R_f = 0.4, (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, *J* = 0.9 Hz, 1H), 8.17 (d, *J* = 7.6 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.54 (m, 3H), 7.39 (dd, *J* = 11.3, 4.1 Hz, 2H), 7.36 – 7.29 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 155.6, 144.8, 140.3, 131.9, 130.6，129.9 (q, *J* = 32.7 Hz), 128.6, 128.6, 128.2, 128.1, 127.7, 127.1, 125.3 (q, *J* = 3.6), (q, *J* = 278.5) 120.9, 112.1; HRMS (ESI) m/z: calcd for $C_{22}H_{16}F_3N_2$ $[M+H]^+$ 365.1260; found 365.1255.

2-(4-Nitrophenyl)-2,4-diphenyl-2*H*-imidazole (3ai): as a yellow solid (67.9 mg, 66% yield); mp 134.1-135.0 °C; R_f = 0.3, (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.19-8.10 (m, 4H), 7.96 – 7.92 (m, 2H), 7.72-7.67 (m, 2H), 7.55 (dt, *J* = 14.0, 5.9 Hz, 3H), 7.36-7.32 (m, 2H), 7.30 (dd, *J* = 4.8, 3.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 155.9, 147.9, 147.2, 139.9, 132.1, 130.4, 129.3, 128.7, 128.7, 128.3, 127.6, 123.6, 111.8; HRMS (ESI) m/z: calcd for $C_{21}H_{16}N_3O_2$ $[M+H]^+$ 342.1237; found 342.1234.

2,4-Diphenyl-2-(*o*-tolyl)-2*H*-imidazole (3aj): as a light yellow solid (70.4 mg, 76% yield); mp 100.1-101.9 °C; R_f = 0.5 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.19-8.14 (m, 2H), 7.80-7.75 (m, 2H), 7.59-7.56 (m, 5H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.34-7.26 (m, 2H), 7.15 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 155.1, 140.9, 140.7, 138.0, 131.7, 131.0, 129.1, 128.6, 128.6, 128.4, 128.3, 127.8, 127.8, 124.9, 21.6; HRMS (ESI) m/z: calcd for $C_{22}H_{19}N_2$ $[M+H]^+$ 311.1543; found 311.1540.

2,4-Diphenyl-2-(*m*-tolyl)-2*H*-imidazole (3ak): as a white solid (68.4 mg, 74% yield); mp 109.4-110.7 °C; R_f = 0.4 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 2H), 7.82 – 7.74 (m, 2H), 7.59 (s, 2H), 7.55 (d, *J* = 7.0 Hz, 3H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.23, 155.13, 155.07, 140.94, 140.74, 138.05, 131.65, 129.13, 128.65, 128.61, 128.42, 128.41, 128.32, 127.82, 127.79, 124.91, 21.65; HRMS (ESI) m/z: calcd for $C_{22}H_{19}N_2$ $[M+H]^+$ 311.1543; found 311.1542.

2,4-Diphenyl-2-(3-(trifluoromethyl)phenyl)-2*H*-imidazole (3al): as a yellow solid (49.2 mg, 45% yield); mp 133.5-134.5 °C; R_f = 0.3 (PE: EA = 10:1); ^{1}H NMR (500 MHz,

$CDCl_3$) δ 8.67 (s, 1H), 8.14 (d, J = 6.6 Hz, 2H), 7.98 (s, 2H), 7.95 (d, J = 7.9 Hz, 2H), 7.57 (ddd, J = 14.3, 11.6, 9.4 Hz, 6H), 7.46 (t, J = 7.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 156.1, 141.3, 132.2, 131.7 (q, J = 33.0 Hz), 131.3, 130. 9, 130.6, 130.3, 129.3, 129.2, 129.0, 128.7, 125.0 (q, J = 3.5 Hz), 124.2 (q, J = 3.6 Hz), 123.9 (q, J = 272.3 Hz), 111.2; HRMS (ESI) m/z: calcd for $C_{22}H_{16}F_3N_2$ $[M+H]^+$ 365.1260; found 365.1258.

4-Phenyl-2,2-di-*p*-tolyl-2*H*-imidazole (3am): as a gray solid (73.1 mg, 76% yield); mp 112.5-113.5 °C; R_f = 0.5 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.21-8.14 (m, 2H), 7.69 (d, J = 8.2 Hz, 4H), 7.59-7.54 (m, 3H), 7.23 (d, J = 8.1 Hz, 4H), 2.40 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 155.0, 138.1, 137.5, 131.6, 131.6, 131.1, 129.1, 128.6, 127.7, 112.6, 21.2; HRMS (ESI) m/z: calcd for $C_{23}H_{21}N_2$ $[M+H]^+$ 325.1699; found 325.1696.

2,2-Bis(4-fluorophenyl)-4-phenyl-2*H*-imidazole (3an): as a yellow solid (40.1 mg, 56% yield); mp89.5-91.5 °C; R_f = 0.5 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.13-8.09 (m, 2H), 7.66-7.62 (m, 4H), 7.56-7.51 (m, 3H), 7.03-6.98 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 162.3 (d, J = 247.1 Hz), 155.2, 136.5 (d, J = 3.1 Hz), 131.9, 130.7, 129.4 (d, J = 8.3 Hz), 129.2, 128.6, 115.2 (d, J = 21.3 Hz), 111.5; HRMS (ESI) m/z: calcd for $C_{21}H_{15}Cl_2N_2$ $[M+H]^+$ 365.0607; found 365.0605.

2,2-Bis(4-chlorophenyl)-4-phenyl-2*H*-imidazole (3ao): as a yellow solid (66.5 mg, 61% yield); mp 102.6-102.6 °C; R_f = 0.4 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.15-8.13 (m, 2H), 7.68-7.64 (m, 4H), 7.59-7.54 (m, 3H), 7.35-7.31 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 155.6, 139.0, 133.9, 132.0, 130.6, 129.2, 129.1, 128.6, 128.6, 111.5; HRMS (ESI) m/z: calcd for calcd for $C_{21}H_{15}Cl_2N_2$ $[M+H]^+$ 365.0607; found 365.0605.

2,2-Bis(4-bromophenyl)-4-phenyl-2*H*-imidazole (3ap): as a yellow solid (66.5 mg, 61% yield); mp 115.9-117.3 °C; R_f = 0.5 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.11-8.08 (m, 2H), 7.56-7.50 (m, 7H), 7.46-7.41 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 155.6, 139.5, 132.0, 131.5, 130.5, 129.3, 129.2, 128.6, 122.2, 111.5; HRMS (ESI) m/z: calcd for $C_{21}H_{15}Br_2N_2$ $[M+H]^+$ 452.9597; found 452.9592.

2-**Butyl-2,4-diphenyl-2*H*-imidazole** (**3aq**): as a yellow oil; R_f = 0.6 (PE: EA = 10:1);

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.09-8.04 (m, 2H), 7.77-7.73 (m, 2H), 7.53-7.49 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 2.24-2.19 (m, 2H), 1.25-1.19 (m, 4H), 1.16-1.09 (m, 2H), 0.80(t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 154.6, 140.2, 131.4, 131.2, 129.1, 128.3, 128.2, 127.6, 127.5, 111.8, 40.6, 26.2, 22.7, 13.9; HRMS (ESI) m/z: calcd for $C_{19}H_{21}N_2$ $[M+H]^+$ 277.1699; found 277.1697.

2-Butyl-2-(3,5-dimethylphenyl)-4-phenyl-2H-imidazole (3ar), as a yellow oil; R_f = 0.5 (PE: EA = 10:1); ^{1}H NMR (500 MHz, Chloroform-d) δ 8.51 (s, 1H), 8.10-8.05 (m, 2H), 7.56-7.51 (m, 4H), 7.39 (d, J = 1.6 Hz, 2H), 7.29 (s, 1H), 6.94 (s, 1H), 2.35 (s, 6H), 2.28-2.24 (m, 2H), 1.31-1.24 (m, 4H), 1.15-1.10 (m, 2H), 0.83 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 154.5, 140.1, 137.7, 131.3, 131.3, 129.2, 129.1, 128.3, 125.3, 111.9, 40.6, 26.1, 22.7, 21.4, 13.9; HRMS (ESI) m/z: calcd for $C_{21}H_{25}N_2$ $[M+H]^+$ 305.2012; found 305.2008.

2,2-Diphenyl-4-(*p*-tolyl)-2*H*-imidazole (3as): as a yellow solid (56.0 mg, 76% yield); mp 105.9-107.1 °C; R_f = 0.4 (PE: EA= 10: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.87-7.84 (m, 2H), 7.60-7.55 (m, 4H), 7.20-7.15 (m, 6H), 7.13-7.09 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 155.2, 142.1, 141.0, 129.8, 128.6, 128.3, 127.8, 127.7, 21.7; HRMS (ESI) m/z: calcd for $C_{22}H_{19}N_2$ $[M+H]^+$, 311.1543; found 311.1541.

4-(4-Ethylphenyl)-2,2-diphenyl-2*H*-imidazole (3at): as a gray solid (69.8 mg, 72% yield); R_f = 0.4 (PE: EA= 10: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 4H), 7.16 (t, *J* = 7.4 Hz, 6H), 7.10 (d, *J* = 7.2 Hz, 2H), 2.55 (d, *J* = 7.6 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 155.2, 148.4, 141.0, 128.7, 128.7, 128.6, 128.4, 127.8, 127.8, 112.6, 29.0, 15.5; HRMS (ESI) m/z: calcd for $C_{23}H_{21}N_2$ $[M+H]^+$ 325.1699; found 325.1698.

4-(4-Butylphenyl)-2,2-diphenyl-2*H*-imidazole (**3au**): as a gray solid (74.9 mg, 71% yield); R_f = 0.5 (PE: EA= 10: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.57 (s, 4H), 7.16 (t, *J* = 7.1 Hz, 6H), 7.09 (d, *J* = 7.0 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H), 1.51-1.45 (m, 2H), 1.25-1.19 (m, 2H), 0.80 (d, *J* = 2.8 MR (100 MHz, $CDCl_3$) δ 164.2, 155.2, 147.1, 141.1, 129.2, 128.6, 128.6, 128.4, 127.8, 127.8, 126.9, 123.9, 35.8, 33.4, 22.4, 14.0; HRMS (ESI) m/z: calcd for $C_{25}H_{25}N_2$ $[M+H]^+$ 353.2012; found 353.2014.

4-(4-Ethoxyphenyl)-2,2-diphenyl-2*H*-imidazole (3av): as a light yellow solid (68.3 mg, 67% yield); mp 124.6-125.6 °C; R_f = 0.35 (PE: EA= 10: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 4H), 7.36 (t, *J* = 7.5 Hz, 4H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 4.13 (q, *J* = 6.9 Hz, 2H), 1.49 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.8, 155.1, 141.2, 130.3, 128.3, 127.8, 127.7, 123.5, 115.0, 112.4, 77.5, 77.1, 76.8, 63.7, 14.7; HRMS (ESI) m/z: calcd for $C_{23}H_{21}N_2O$ $[M+H]^+$ 341.1648; found 341.1642.

4-(4-Fluorophenyl)-2,2-diphenyl-2*H*-imidazole (3aw): as a white solid (66.8 mg, 71% yield); mp 104.5-105.5 °C; R_f = 0.4 (PE: EA= 10: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.98-7.95 (m, 2H), 7.57 (d, *J* = 7.5 Hz, 4H), 7.19 (t, *J* = 7.4 Hz, 4H), 7.13 (d, *J* = 7.0 Hz, 2H), 7.04 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (t, *J* = 251.3 Hz), 163.1, 154.7, 140.8, 130.8, 130.7, 128.4, 127.8, 127.7, 116.3 (d, *J* = 27.5 Hz), 112.8; HRMS (ESI) m/z: calcd for $C_{21}H_{16}FN_2$ $[M+H]^+$ 315.1292; found 315.1290.

4-(4-Chlorophenyl)-2,2-diphenyl-2*H*-imidazole (3ax): as a yellow solid (66.3 mg, 67% yield); mp 102.5-104.5 °C; R_f = 0.4 (PE: EA= 10: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.78-7.70 (m, 4H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.41-7.34 (m, 4H), 7.34-7.28 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 154.7, 140.6, 137.9, 129.8, 129.4, 129.4, 128.4, 127.9, 127.7, 112.8; HRMS (ESI) m/z: calcd for $C_{21}H_{16}ClN_2$ $[M+H]^+$ 331.0997; found 331.1000.

4-(4-Bromophenyl)-2,2-diphenyl-2*H*-imidazole (3ay): as a gray solid (75.3 mg, 68% yield); mp 104.5-105.5 °C; R_f = 0.4 (PE: EA= 10: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.68-7.60 (m, 6H), 7.30 (dd, *J* = 8.1, 6.7 Hz, 4H), 7.25 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 154.6, 140.5, 132.4, 130.0, 129.8, 128.41, 127.9, 127.7, 126.3; HRMS (ESI) m/z: calcd for $C_{21}H_{16}BrN_2$ $[M+H]^+$ 375.0491; found 375.0487.

4-(4-Nitrophenyl)-2,2-diphenyl-2*H*-imidazole (3az): as a light yellow solid (67.5 mg, 66% yield); mp 195.5-196.5 °C; R_f = 0.2 (PE: EA= 10: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.40 (d, *J* = 8.8 Hz, 2H), 8.32 (d, *J* = 8.8 Hz, 2H), 7.77 -7.68 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 4H), 7.32-7.28 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5, 154.1, 149.5,

140.2, 136.6, 129.5, 128.5, 128.1, 127.7, 124.3, 113.4; HRMS (ESI) m/z: calcd for $C_{21}H_{16}N_3O_2$ $[M+Na]^+$ 342.1237; found 342.1235.

2,2-Diphenyl-4-(*o*-tolyl)-2*H*-imidazole (3ba): as a light yellow solid (70.5 mg, 76% yield); mp 110.3-111.7; R_f = 0.5 (PE: EA= 10: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 4H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.37-7.27 (m, 7H), 7.22 (t, *J* = 7.3 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 156.8, 141.0, 138.9, 131.8, 130.6, 130.4, 129.8, 128.4, 127.7, 126.1, 113.2, 21.8; HRMS (ESI) m/z: calcd for $C_{22}H_{19}N_2$ $[M+H]^+$ 311.1543; found 311.1541.

4-(3-Fluorophenyl)-2,2-diphenyl-2*H*-imidazole (3bb): as a yellow solid (60.8 mg, 65% yield); mp 129.5-130.9 ^{o}C; R_f = 0.4 (PE: EA= 10: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.83 (t, *J* = 8.9 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 4H), 7.43 (dd, *J* = 7.3, 6.1 Hz, 1H), 7.34-7.27 (m, 4H), 7.26-7.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 163.2 (d, *J* = 246.2), 154.6, 140.6, 133.2 (d, *J* = 7.6), 130.8 (d, *J* = 8.0), 128.4, 127.9, 127.8, 124.3 (d, *J* = 3.0), 118.7 (d, *J* = 21.3), 115.5 (d, *J* = 22.5), 112.9; HRMS (ESI) m/z: calcd for $C_{21}H_{15}FN_2$ $[M+H]^+$, 315.1292; found 315.1289.

4-(3-Chlorophenyl)-2,2-diphenyl-2*H*-imidazole (3bc): as a yellow solid (62.2 mg, 63% yield); mp 132.0-133.0 ^{o}C; R_f = 0.4 (PE: EA= 10: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.16 (s, 1H), 7.95 (s, 1H), 7.72 (d, *J* = 7.3 Hz, 4H), 7.51-7.48 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 4H), 7.29 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 154.5, 140.6, 135.3, 132.7, 131.6, 130.3, 128.6, 128.4, 127.9, 127.8, 126.6, 112.9; HRMS (ESI) m/z: calcd for $C_{21}H_{15}ClN_2$ $[M+H]^+$ 331.0997; found 331.0994.

4-(Naphthalen-2-yl)-2,2-diphenyl-2*H*-imidazole (**3bd)** as a white solid (63.3 mg, 61% yield); mp 167.3-168.3 ^{o}C; R_f = 0.3 (PE: EA= 10: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.48 (s, 1H), 8.34-8.25 (m, 1H), 7.96 (d, *J* = 8.6 Hz, 2H), 7.88 (s, 1H), 7.82-7.74 (m, 4H), 7.60-7.55 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 4H), 7.31 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3, 155.2, 140.9, 134.9, 133.0, 129.2, 129.2, 128.9, 128.4, 128.0, 127.9, 127.9, 127.8, 127.0, 125.0, 112.8.; HRMS (ESI) m/z: calcd for $C_{25}H_{19}N_2$ $[M+H]^+$, 347.1543; found 347.1539.

4-Benzyl-2,2-diphenyl-2*H*-imidazole (3be): as a white solid (68.1 mg, 73% yield); mp 91.3-92.3 ^{o}C; R_f = 0.5 (PE: EA= 10: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.69-

7.61 (m, 4H), 7.39-7.31 (m, 7H), 7.30-7.25 (m, 4H), 4.16 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 157.2, 140.5, 135.2, 129.1, 129.1, 128.3, 127.8, 127.6, 127.3, 112.2, 36.5; HRMS (ESI) m/z: calcd for $C_{22}H_{19}N_2$ $[M+H]^+$, 311.1543; found 311.1539.

4-Phenethyl-2,2-diphenyl-2*H*-imidazole (3bf): as a white solid (74.0 mg, 76% yield); mp; 87.3-88.6 °C; R_f = 0.5 (PE: EA= 10: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 0H), 7.64-7.57 (m, 2H), 7.36-7.29 (m, 4H), 7.27-7.21 (m, 2H), 3.19-3.16 (m, 2H), 3.13-3.09 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 157.3, 140.5, 140.3, 128.7, 128.5, 128.3, 127.7, 127.7, 126.4, 112.0, 32.8, 31.7; HRMS (ESI) m/z: calcd for $C_{23}H_{21}N_2$ $[M+H]^+$, 325.1699; found 325.1696.

2,2-Diphenyl-4-(3-phenylpropyl)-2*H*-imidazole (3bg): as a white solid (79.0 mg, 78% yield); mp 89.3-99.3 °C; R_f = 0.5 (PE: EA= 10: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.62-7.59 (m, 3H), 7.30-7.21 (m, 6H), 7.20-7.08 (m, 5H), 2.69-2.64 (m, 4H), 2.11-2.03 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 157.6, 141.5, 140.9, 128.7, 128.6, 128.4, 127.8, 127.7, 126.3, 112.1, 35.5, 29.4, 28.3; HRMS (ESI) m/z: calcd for $C_{24}H_{23}N_2$ $[M+H]^+$, 339.1856; found 339.1854.

4-Methyl-2,2,5-triphenyl-2*H*-imidazole (**3bh**) as a white solid (69.0 mg, 74% yield); mp 123.3-124.3 °C; R_f = 0.5 (PE: EA= 10: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, J = 7.8, 1.7 Hz, 2H), 7.71-7.67 (m, 4H), 7.51 – 7.46 (m, 3H), 7.33 – 7.28 (m, 4H), 7.26 – 7.23 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 164.4, 141.3, 132.1, 130.6, 128.7, 128.6, 128.3, 127.7, 127.6, 107.7, 17.7; HRMS (ESI) m/z: calcd for $C_{22}H_{19}N_2$ $[M+H]^+$, 311.1543; found 311.1533.

2,2,4,5-Tetraphenyl-2*H*-imidazole (3bi): as a white solid (74.8 mg, 67% yield); mp 140.3-141.9 °C; R_f = 0.6 (PE: EA= 10: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.62 – 7.55 (m, 2H), 7.45 (d, J = 7.5 Hz, 1H), 7.39 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H);^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 141.4, 132.5, 130.4, 129.2, 129.3, 128.4, 128.3, 127.9, 127.7, 108.4; HRMS (ESI) m/z: calcd for $C_{27}H_{21}N_2$ $[M+H]^+$, 373.1699; found 373.1690.

2-(3-Bromophenyl)-2-methyl-4-phenyl-2*H*-imidazole (3bj): as a gray oil (1443 mg, 46% yield); R_f = 0.4 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.05 (dd, J = 7.8, 1.7 Hz, 2H), 7.89 (t, J = 1.8 Hz, 1H), 7.68 (dd, J = 4.6, 3.5 Hz, 1H), 7.54 – 7.49 (m,

3H), 7.41 (dd, *J* = 5.0, 4.0 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 154.8, 142.3, 131.7, 130.8, 130.2, 129.9, 129.2, 128.4, 125.8, 122.4, 108.5, 27.16; MS (EI) m/z 108, 285, 314.1.

2-(3-Bromophenyl)-2,4-diphenyl-2*H*-imidazole (3bk): as a gray solid (2361 mg, 63% yield); mp 120.3-131.5 °C; R_f = 0.5 (PE: EA = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 0.5 Hz, 1H), 8.13 (dd, *J* = 7.1, 1.0 Hz, 2H), 7.98 – 7.89 (m, 1H), 7.76 – 7.70 (m, 3H), 7.55 – 7.50 (m, 3H), 7.41 (dd, *J* = 4.9, 4.1 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.21 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 155.4, 143.1, 140.4, 131.8, 130.9, 130.8, 130.7, 129.9, 129.2, 128.6, 128.5, 128.1, 127.7, 126.6, 122.4, 111.9; MS (EI) m/z 295.3, 347.1, 376.1.

H. Crystal data and structure refinement for compound 3bb (CCDC: 1920440)

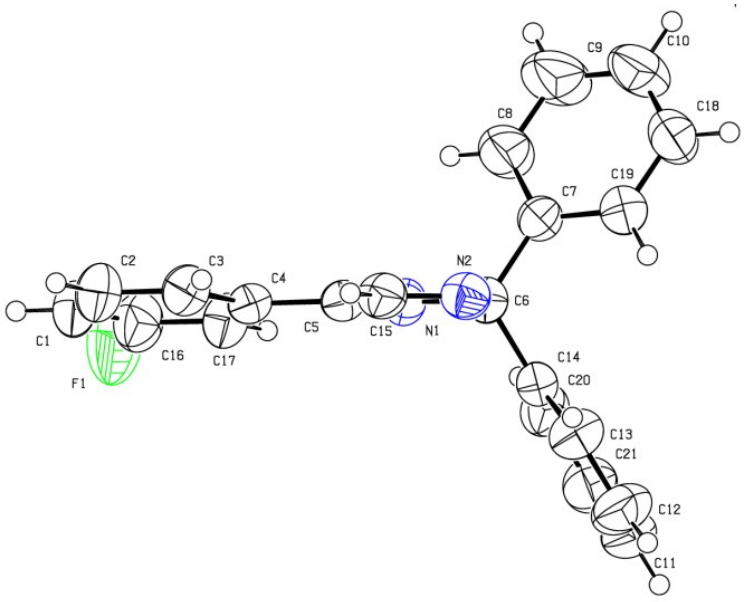


Figure 1. ORTEP drawing of **3bb** with the numbering scheme.

Table S1. Crystal data and structure refinement for **3bb**.

Identification code	**3bb**	
Empirical formula	$C_{21}H_{15}FN_2$	
Formula weight	314.12	
Temperature	296.0 K	
Wavelength	0.71073 Å	
Unit cell dimensions	a = 8.768(7) Å	α= 89.574(9)°.
	b = 9.173(7) Å	β= 84.573(9)°
	c =10.452(8) Å	γ = 78.861(9)°.
Volume	821.0(11) Å^3	

Z	2
Mu (mm-1)	0.083
F000	328.0
F000’	328.14
h,k,lmax	11,11,13
Nref	3614
Tmin,Tmax	0.550,0.746
Correction method= # Reported T Limits:	Tmin=0.550 Tmax=0.746
AbsCorr = MULTI-SCAN	
Data completeness= 0.966	Theta(max)= 27.408

Reference:

(1) D. J. Power, K. D. Jones, S. S. Kampmann, G. R. Flematti and S. S, *Asian J. Org. Chem*. 2017, **6**, 1794-1799; (2) R. He, Z.-T. Huang, Q.-Y. Zheng and C. Wang, *Angew. Chem*. 2014, **126**, 5050-5053; H. Wang, Y. Man, K. Wang, X. Wan, L. Tong N. Li, and B. Tang, *Chem. Commun*. 2018, **54**, 10989-10992.

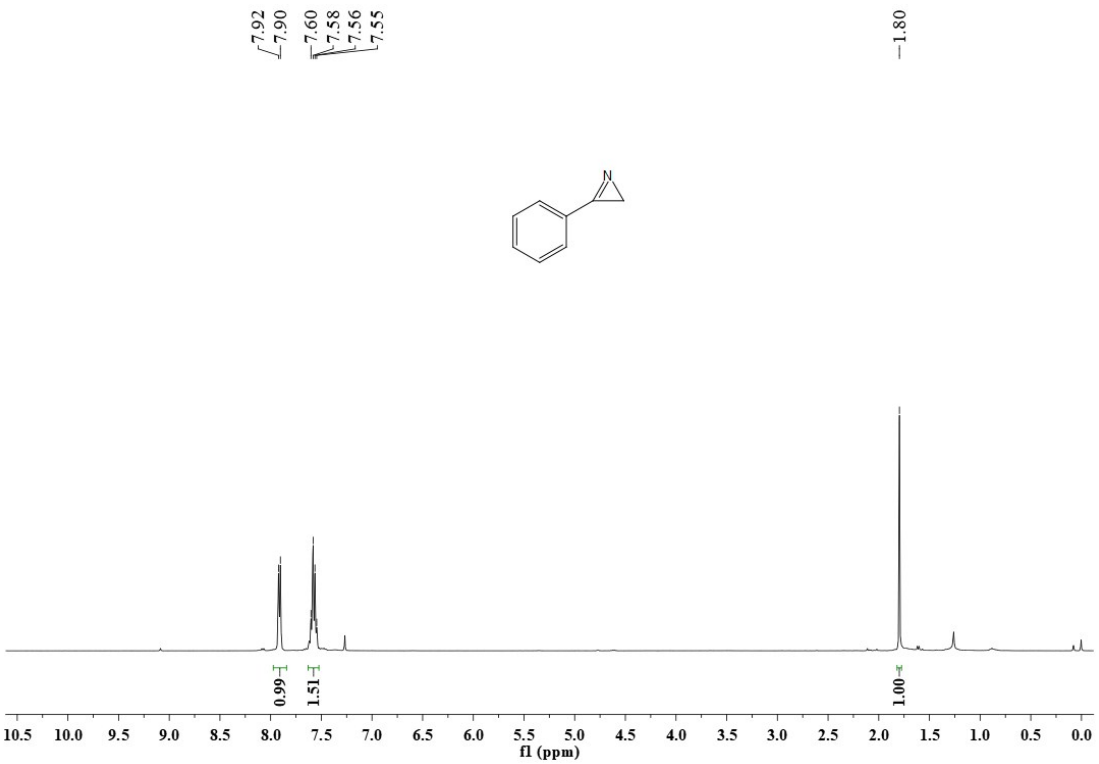
(2) S. Chiba, Y.-F. Wang, G. Lapointe and K. Narasaka, *Org. Lett*. 2008, **10**, 313-316; (b)Y.-F. Wang, K.-K. Toh, , S. Chiba, K. Narasaka, *Org. Lett*. 2008, **10**, 5019-5022

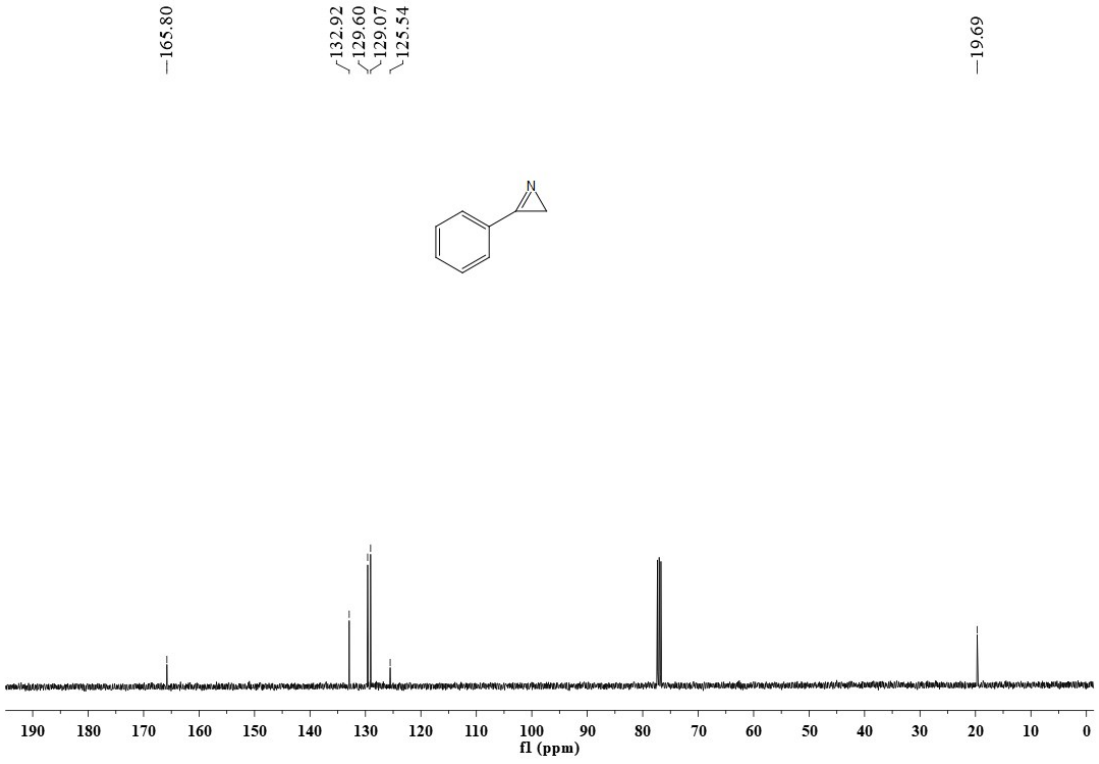
(3) Z. Liu, P. Liao, X. Bi, *Org. Lett*. 2014, **16**, 3668-3671.

I. Copies of ^{1}H and ^{13}C NMR spectra:

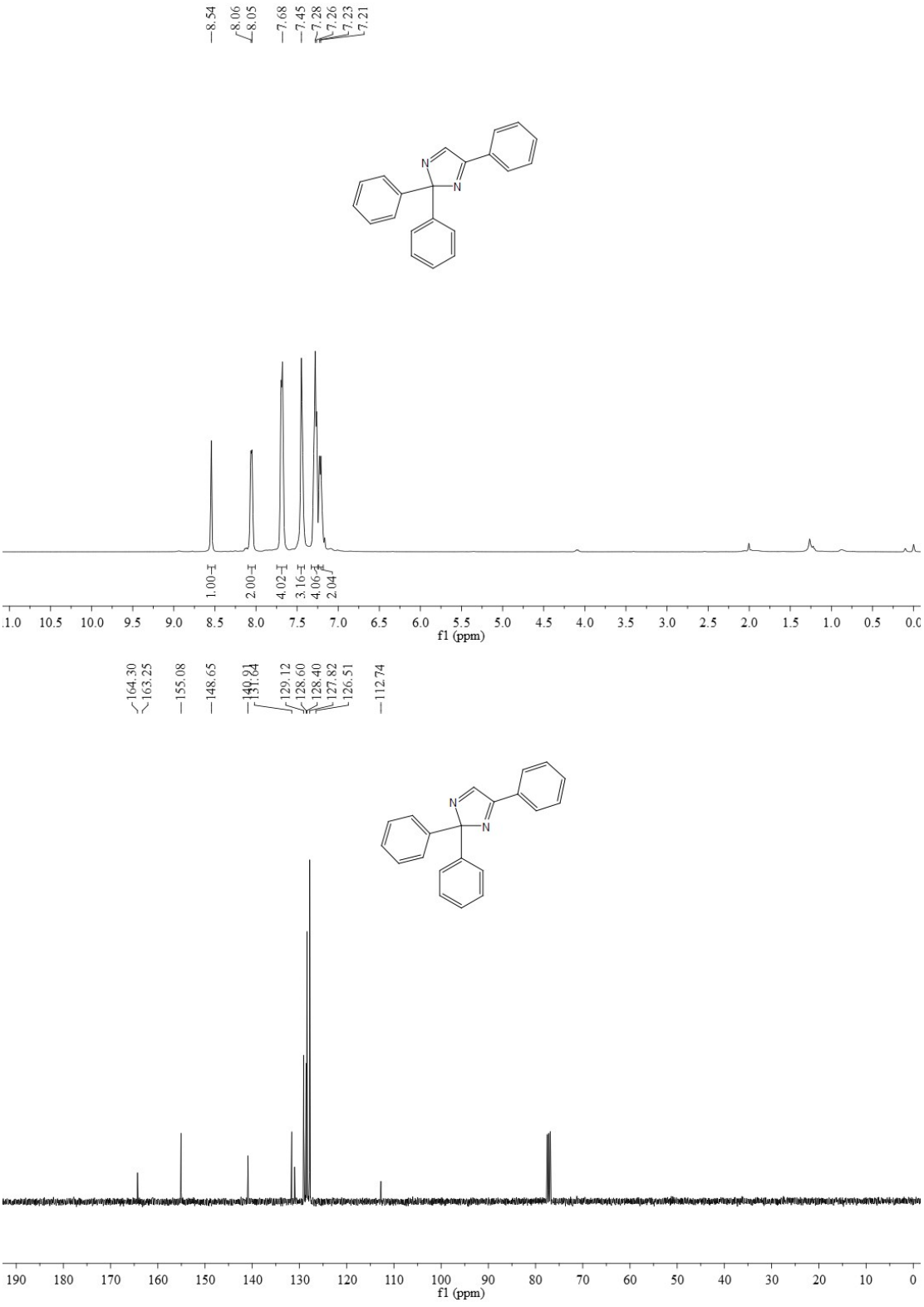
^{1}H NMR and ^{13}C NMR of 1-(3,5-dimethylphenyl)pentan-1-iminee (**1ar**)

^{1}H NMR and ^{13}C NMR of 3-phenyl-2H-azirine (4a)

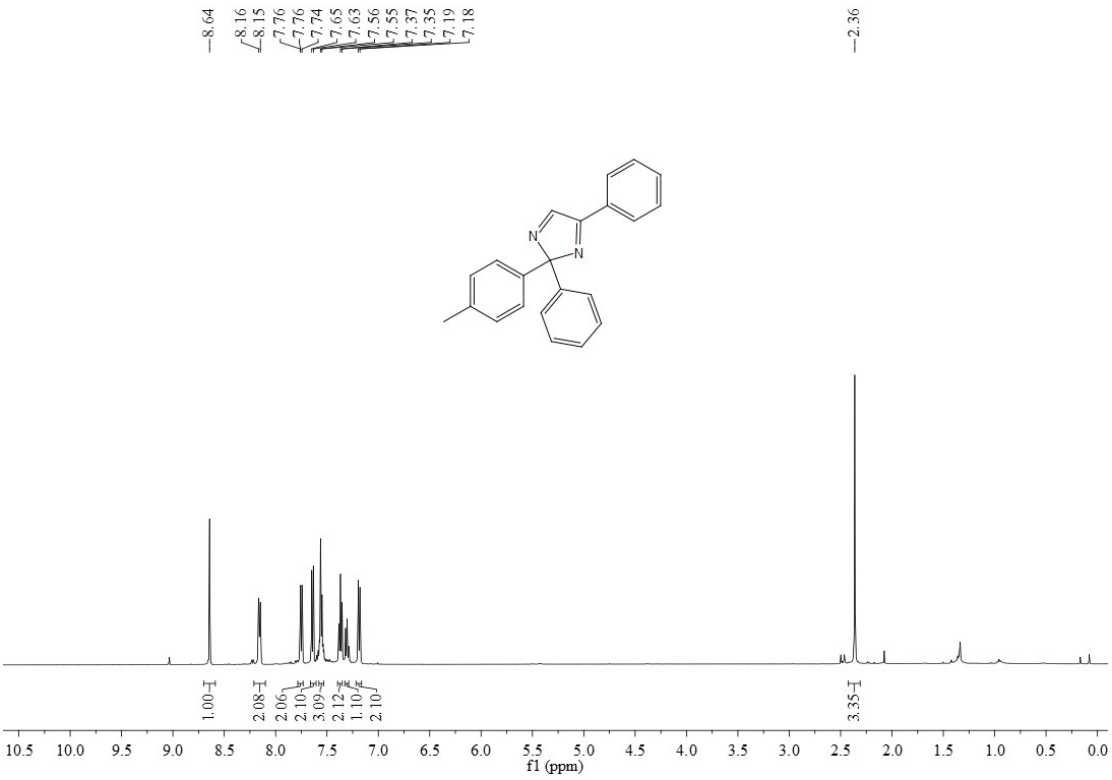


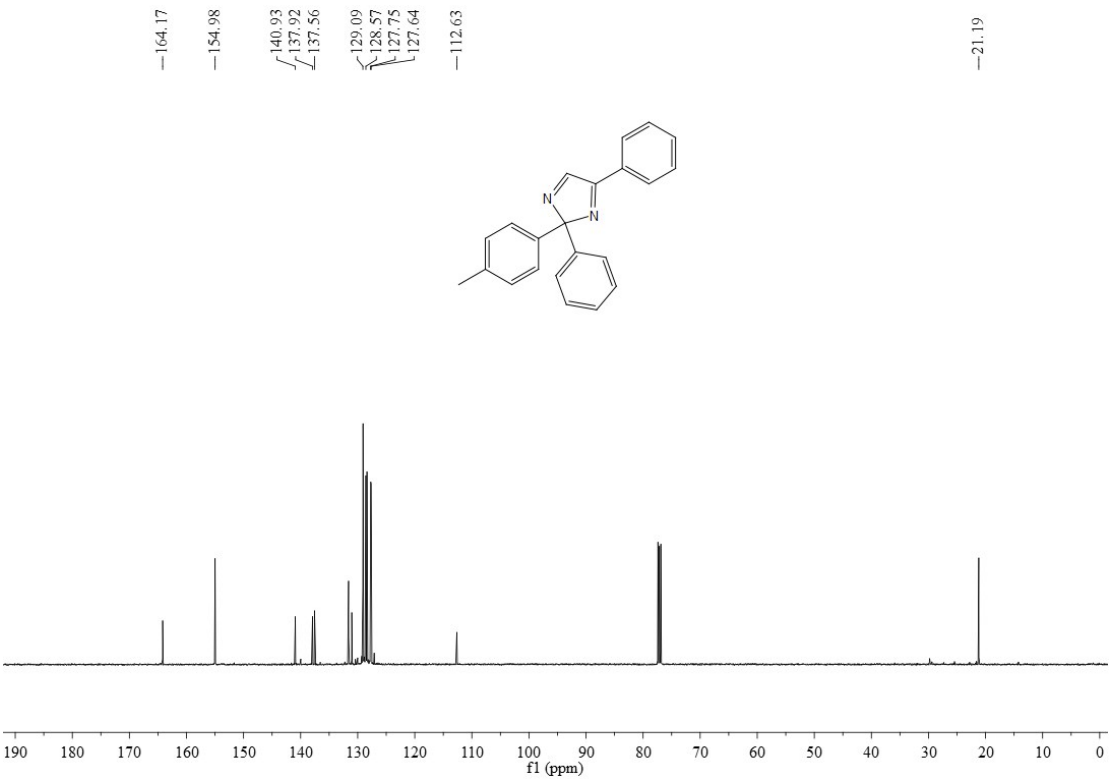


^{1}H NMR and ^{13}C NMR of 2,2,4-triphenyl-2*H*-imidazole (3aa)

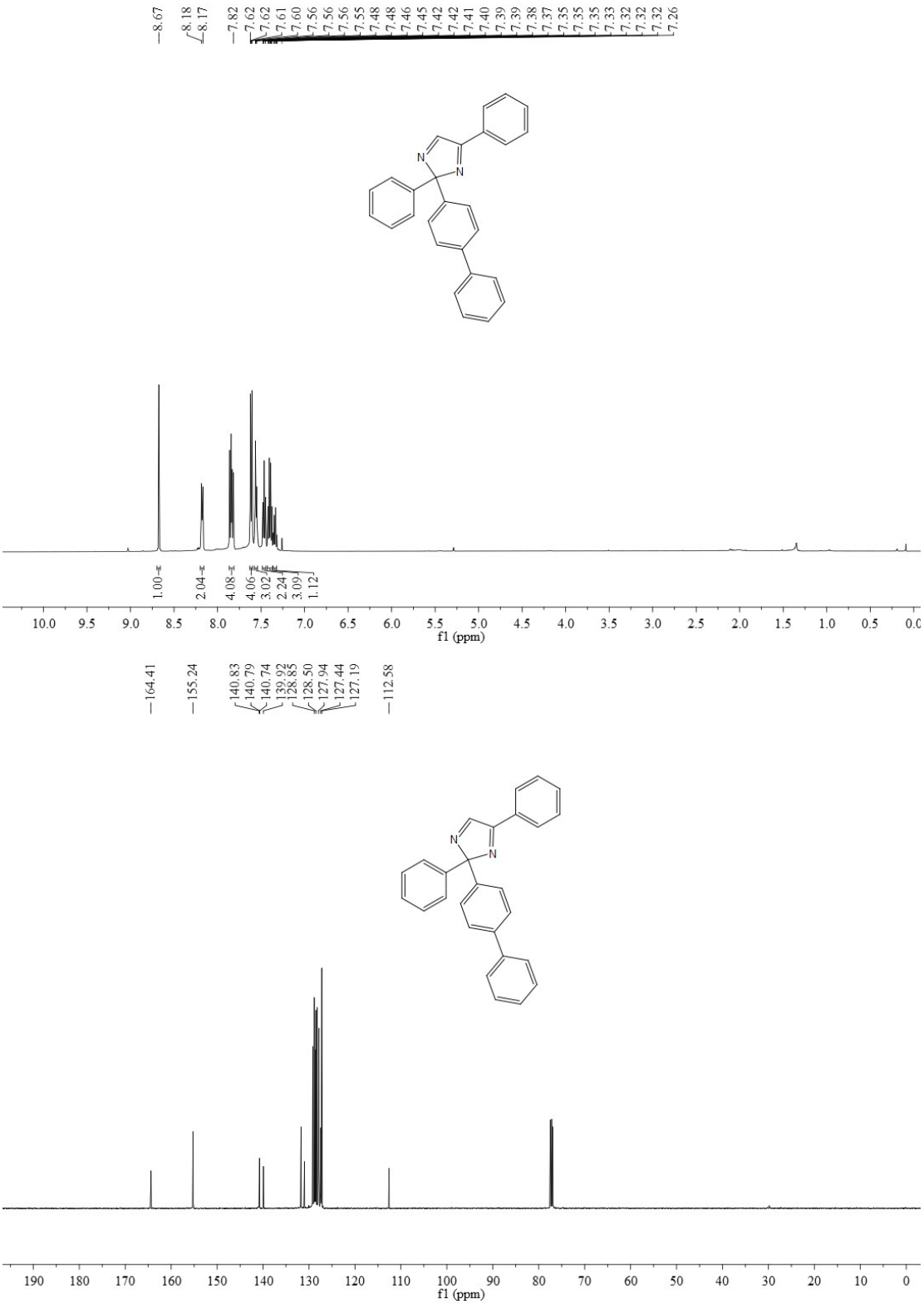


^{1}H NMR and ^{13}C NMR of 2,4-diphenyl-2-(*p*-tolyl)-2*H*-imidazole (3ab)

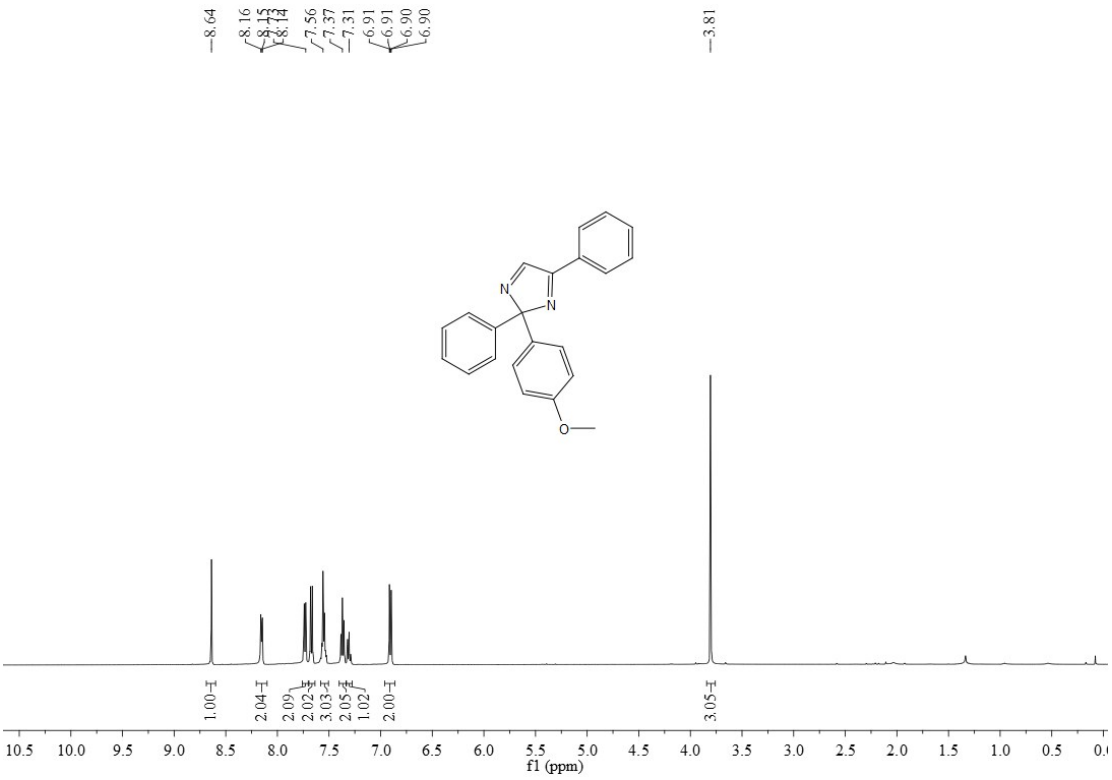


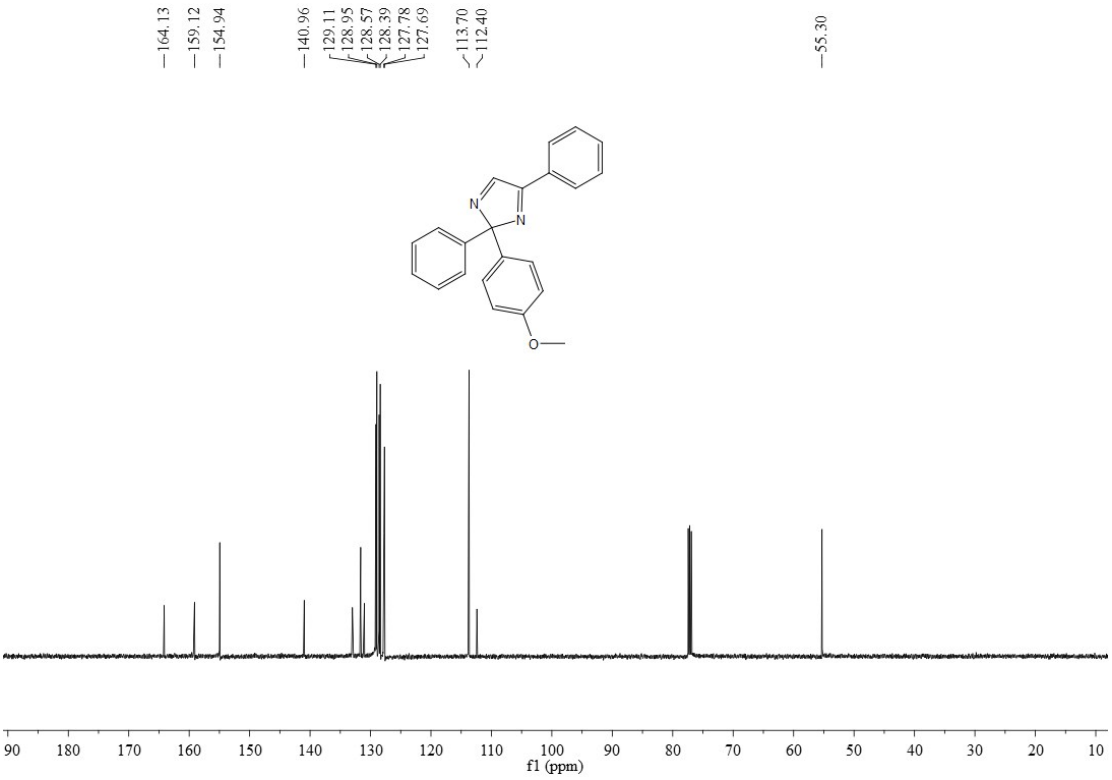


^{1}H NMR and ^{13}C NMR of 2-([1,1'-biphenyl]-4-yl)-2,4-diphenyl-2*H*-imidazole (3ac)

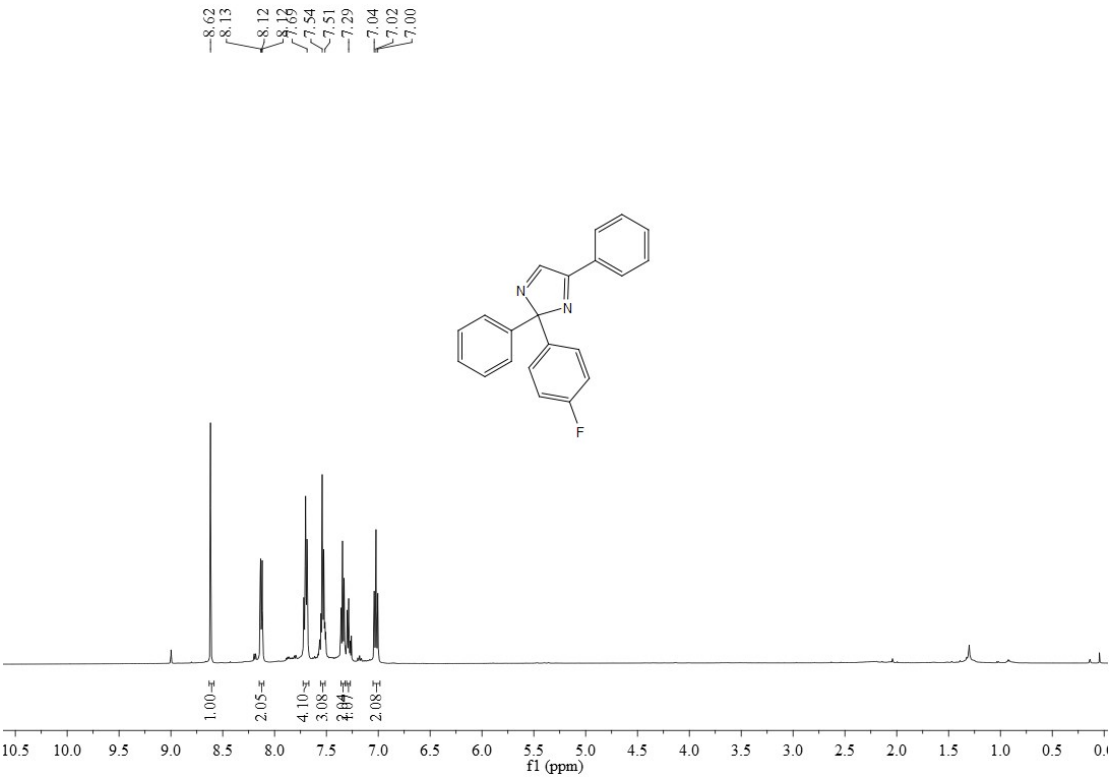


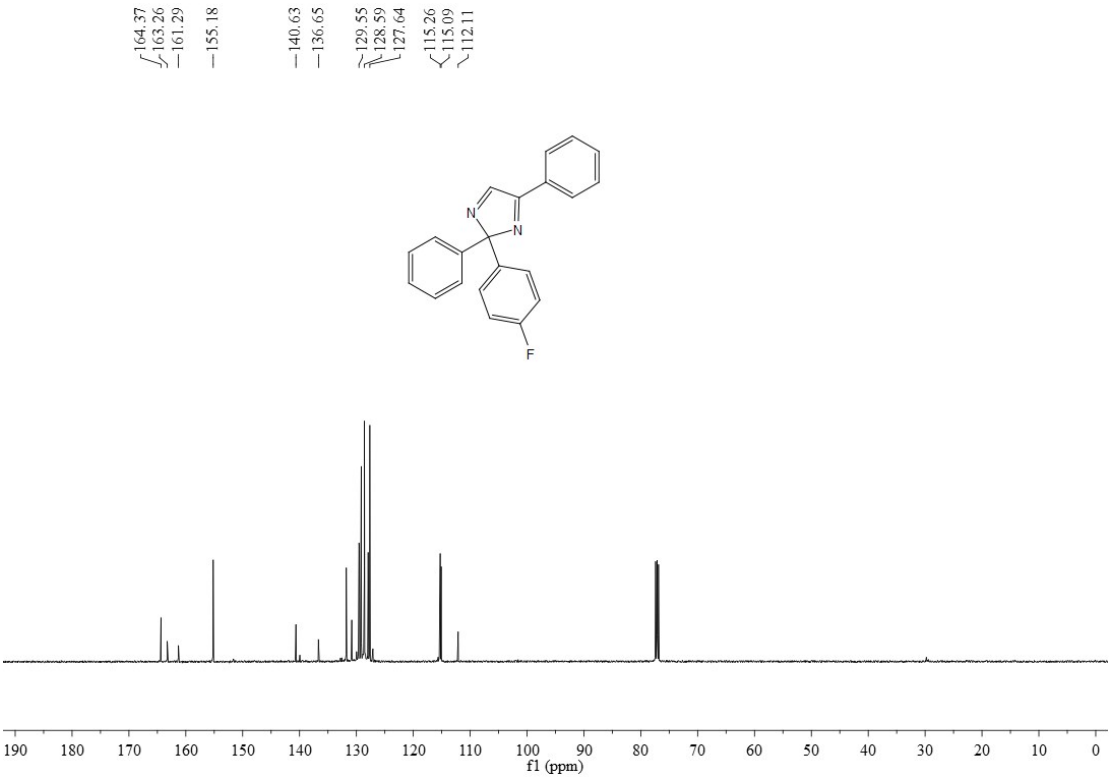
^{1}H NMR and ^{13}C NMR of 2-(4-methoxyphenyl)-2,4-diphenyl-2*H*-imidazole (3ad)



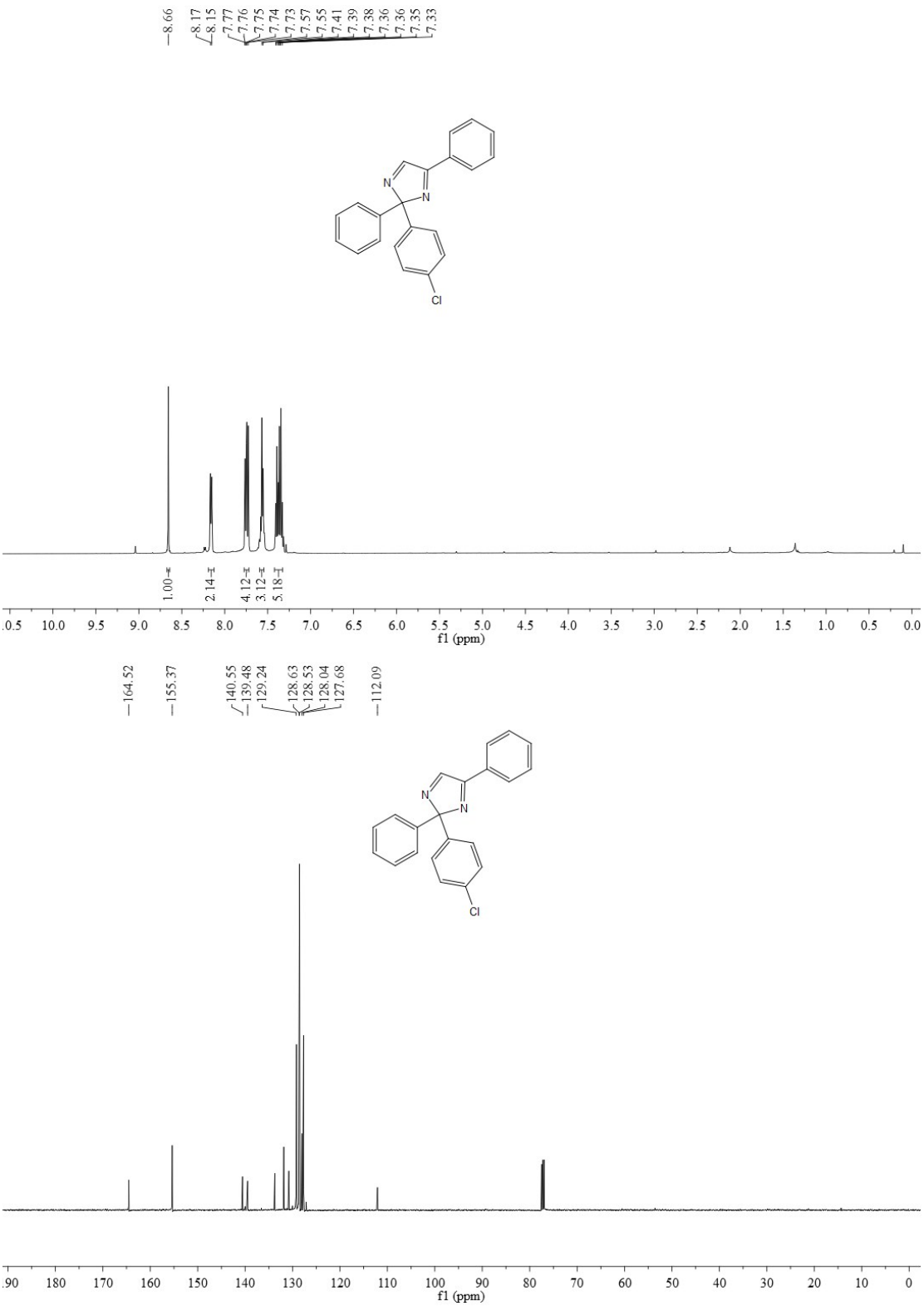


^{1}H NMR and ^{13}C NMR of 2-(4-fluorophenyl)-2,4-diphenyl-2*H*-imidazole (3ae)

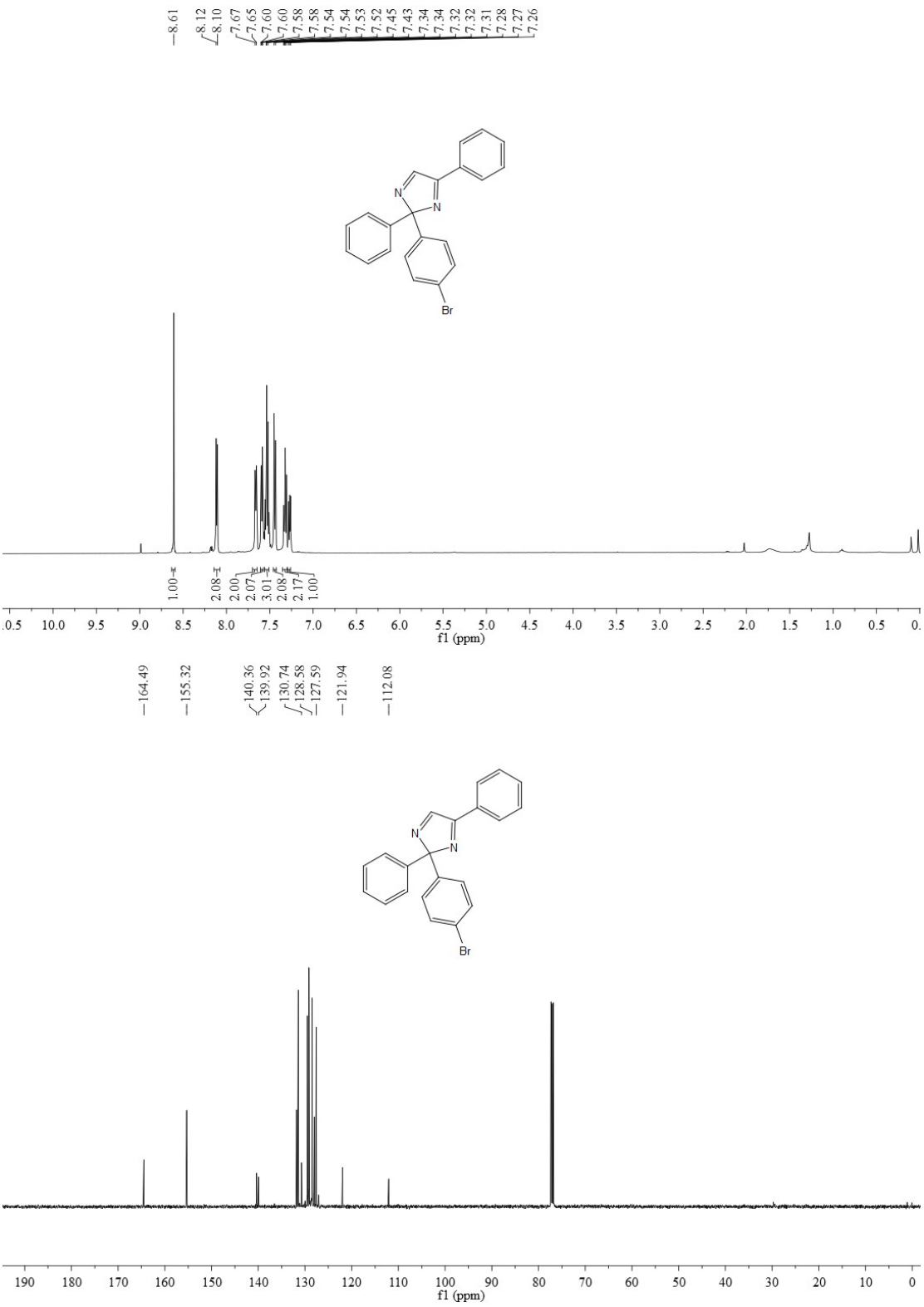




^{1}H NMR and ^{13}C NMR of 2-(4-chlorophenyl)-2,4-diphenyl-2*H*-imidazole (3af)

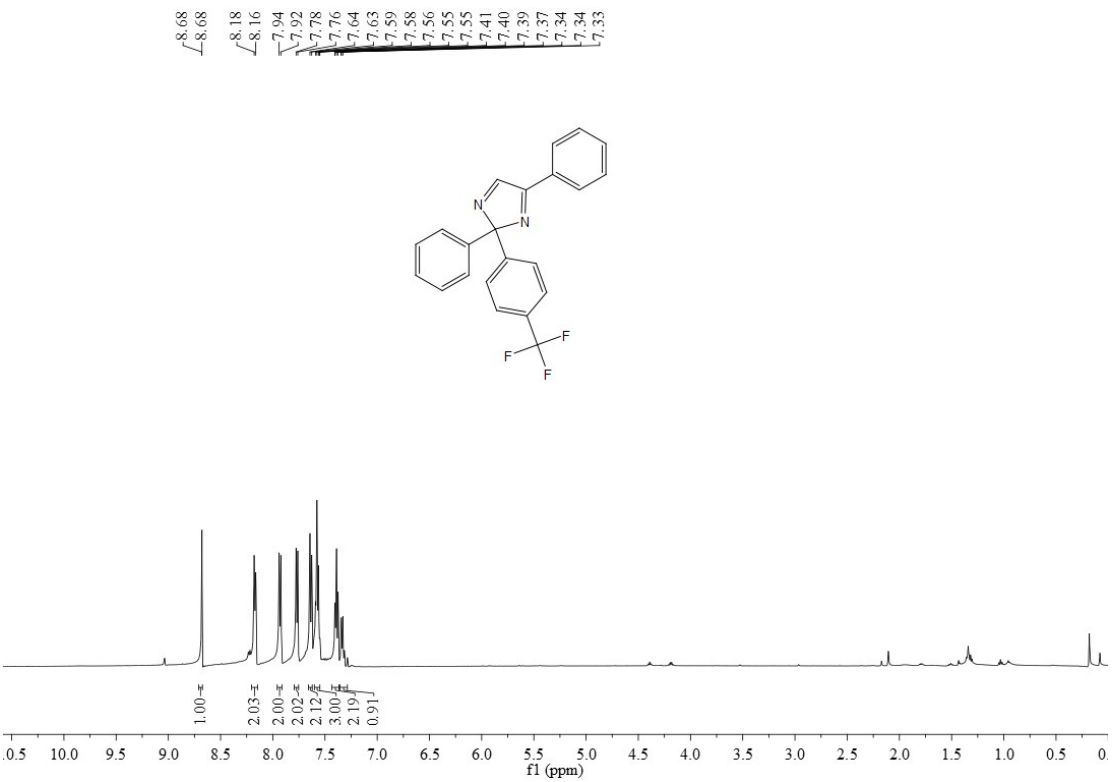


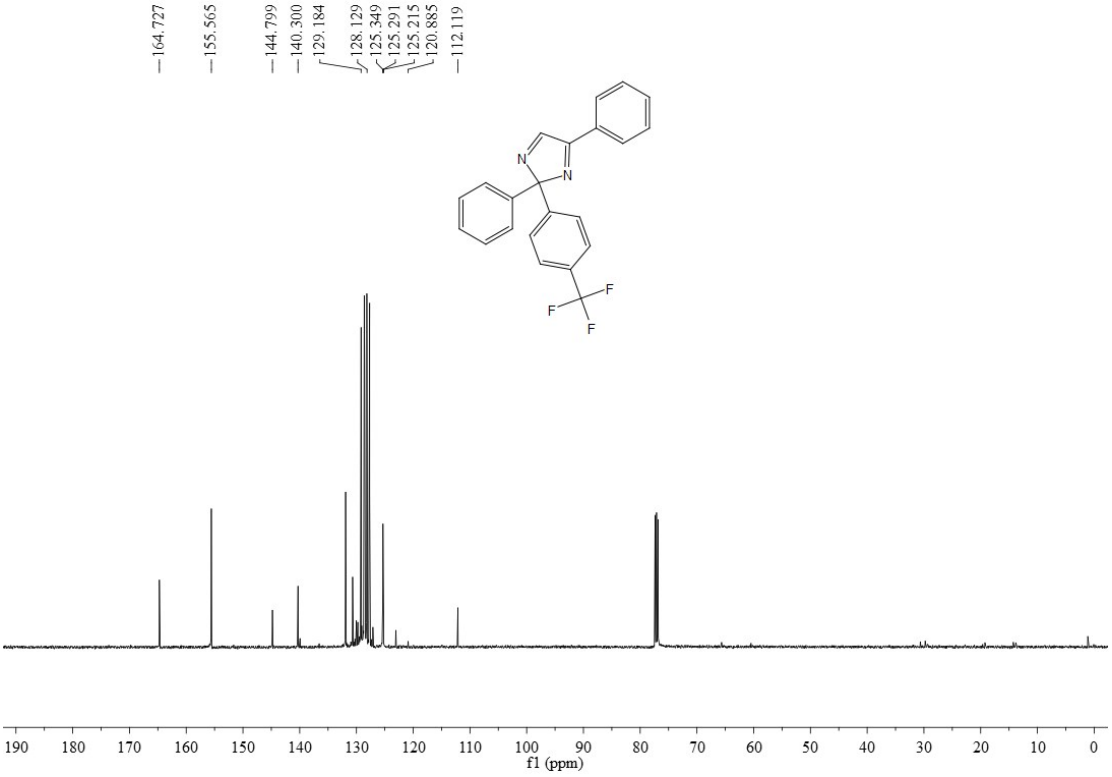
^{1}H NMR and ^{13}C NMR of 2-(4-bromophenyl)-2,4-diphenyl-2*H*-imidazole (3ag)



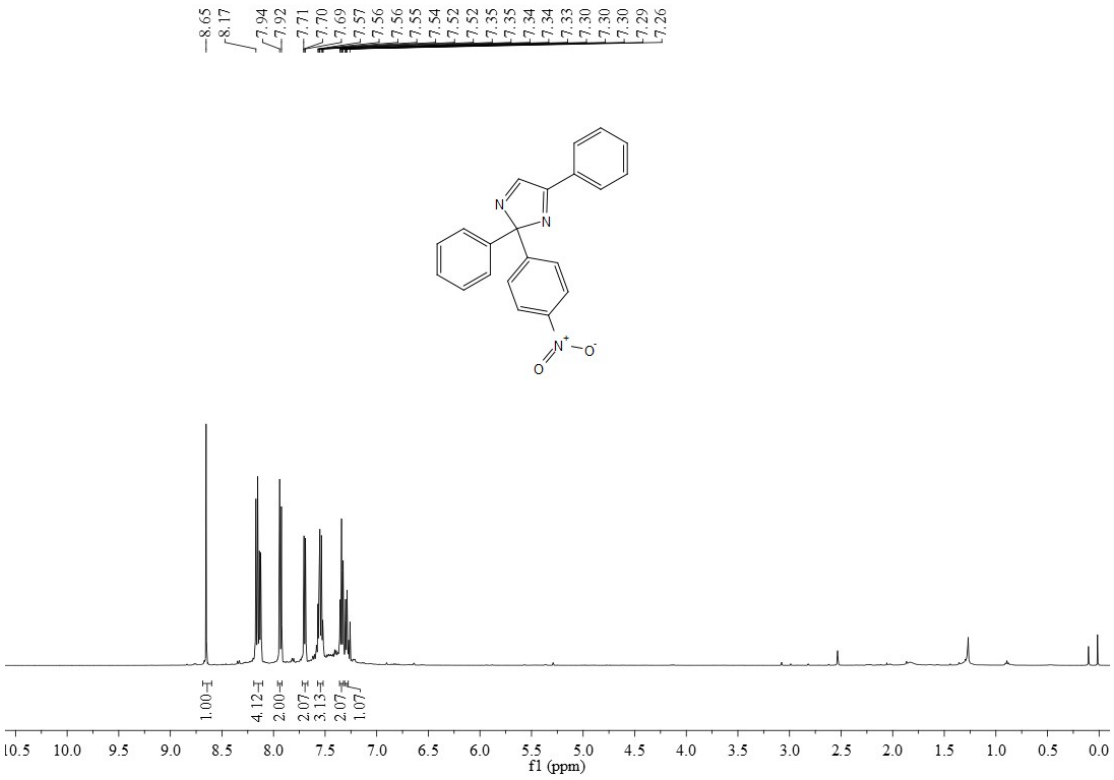
^{1}H NMR and ^{13}C NMR of 2,4-diphenyl-2-(4-(trifluoromethyl)phenyl)-2*H*-imidazole

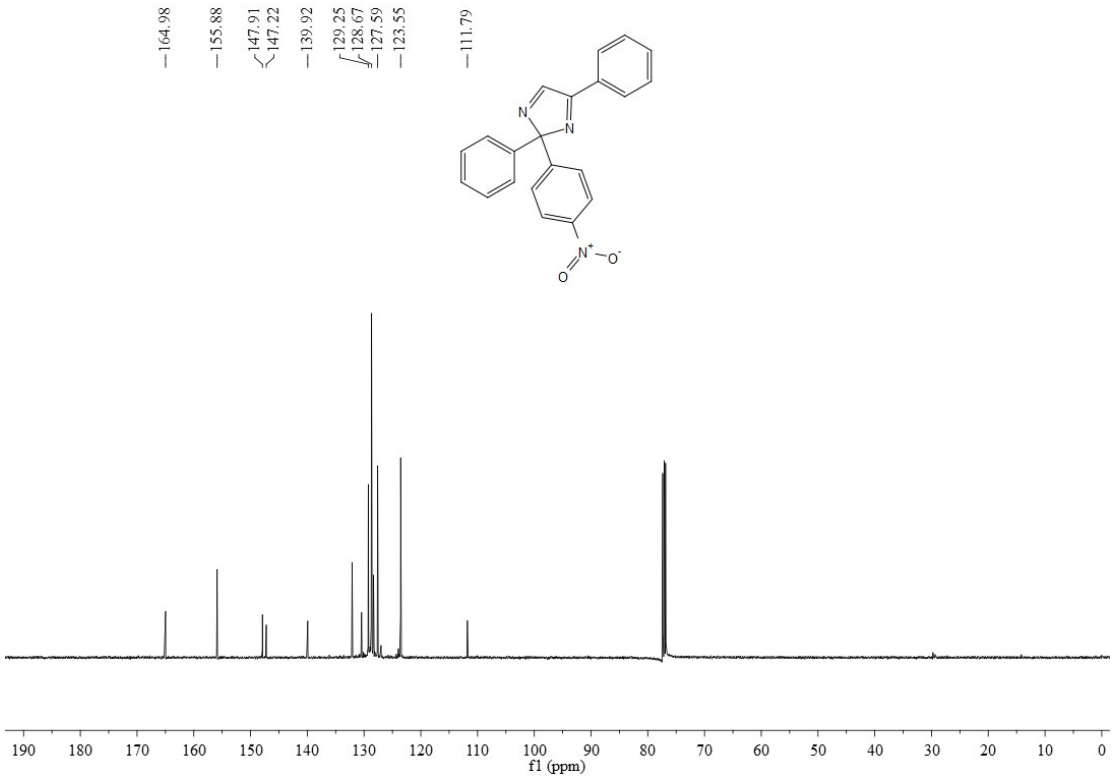
(3ah)



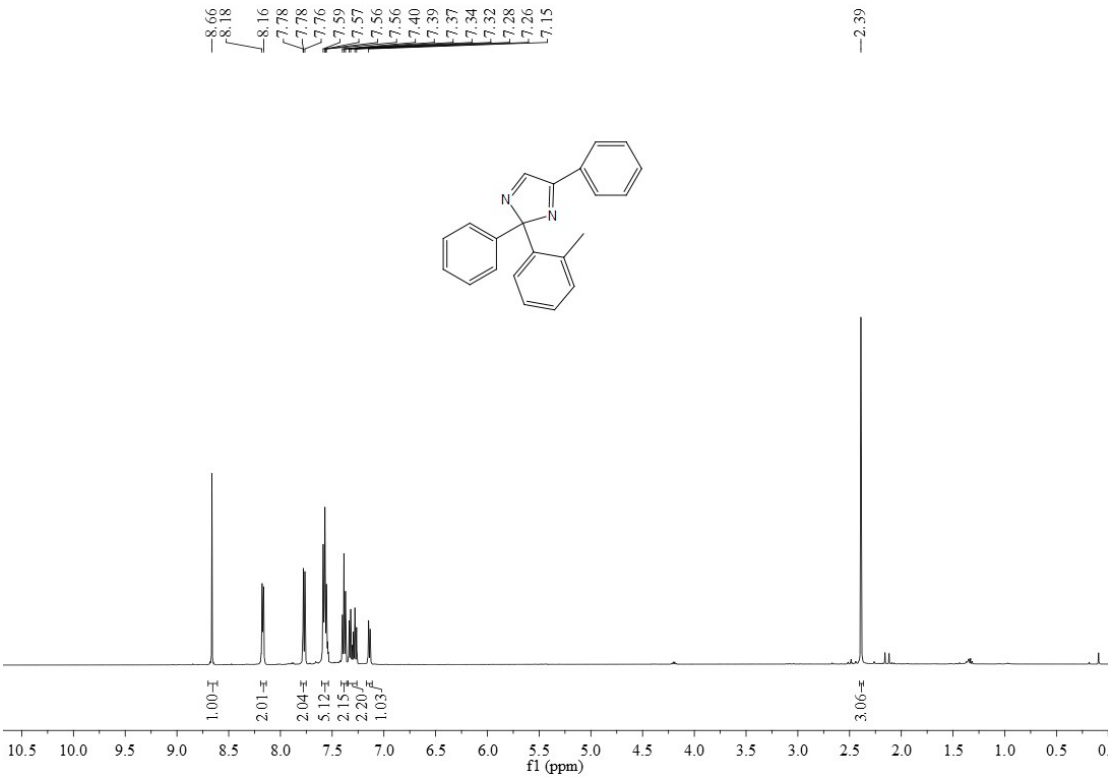


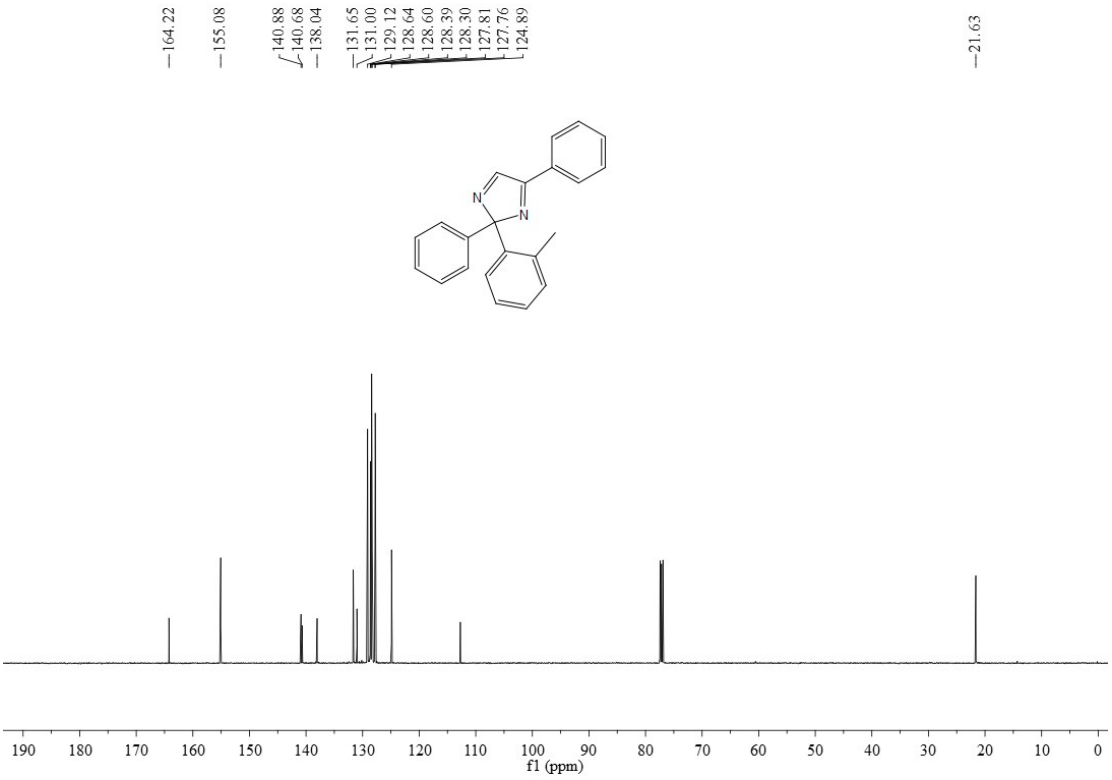
^{1}H NMR and ^{13}C NMR of 2-(4-nitrophenyl)-2,4-diphenyl-2*H*-imidazole (3ai)



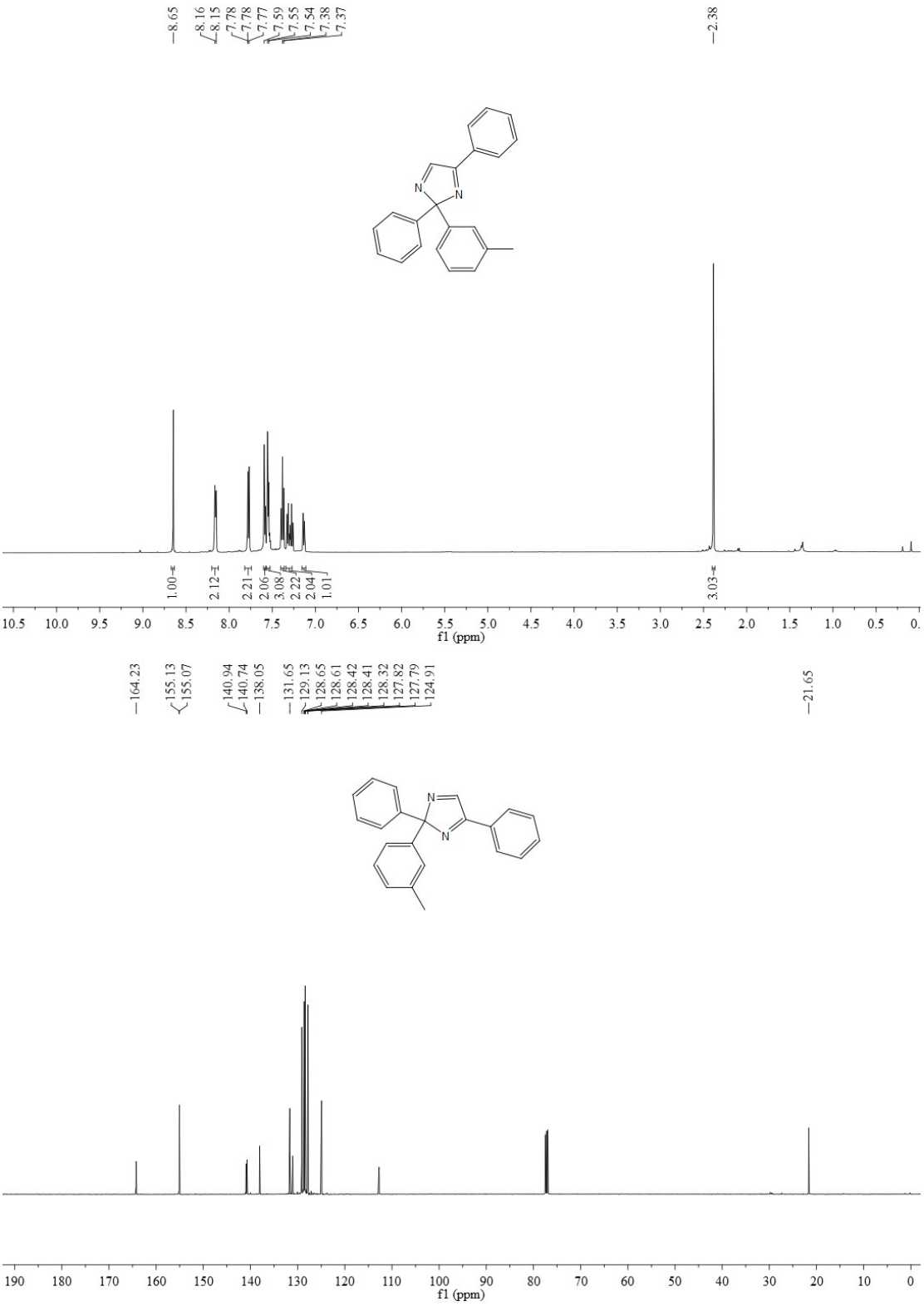


^{1}H NMR and ^{13}C NMR of 2,4-diphenyl-2-(*o*-tolyl)-2*H*-imidazole (3aj)



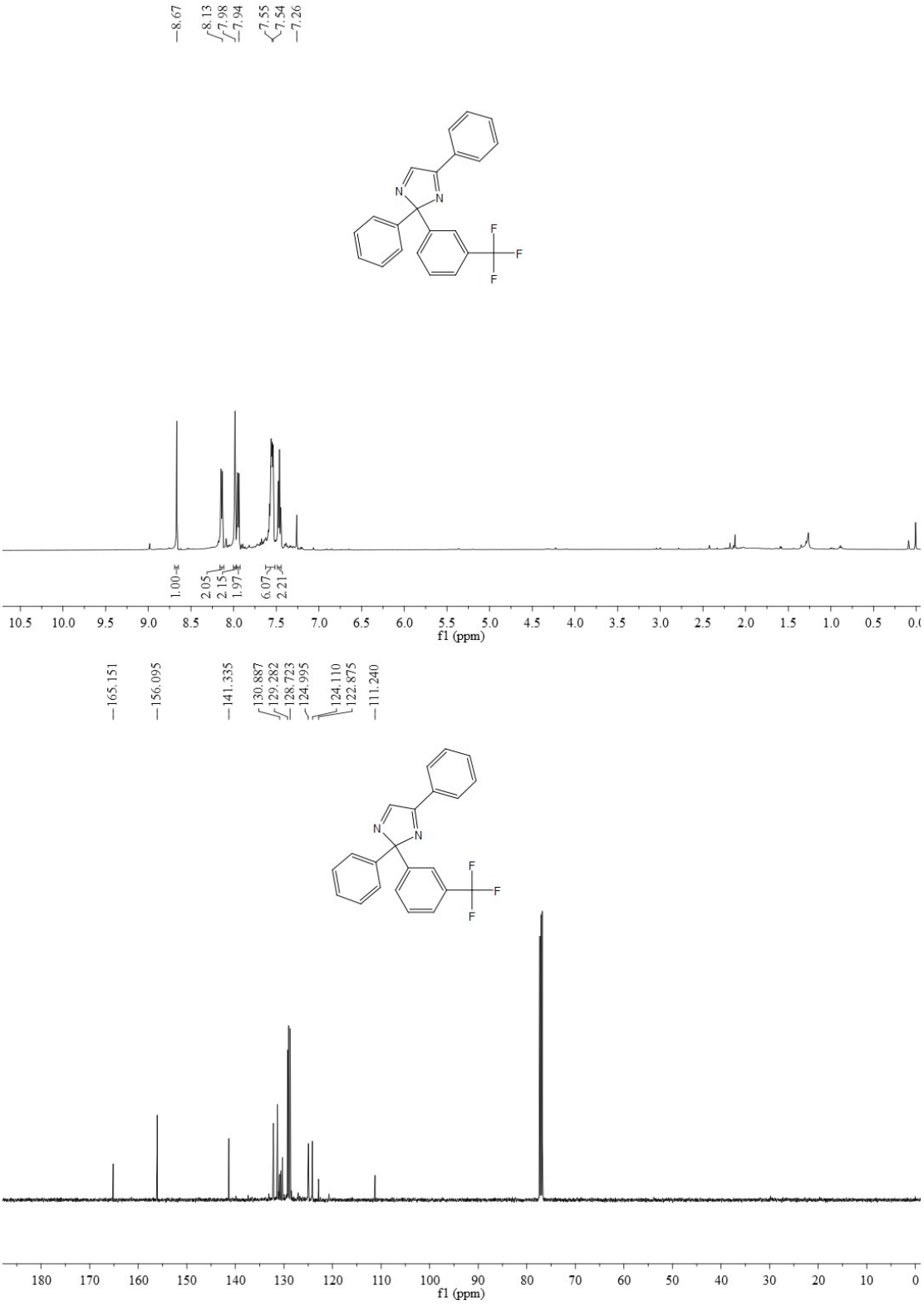


^{1}H NMR and ^{13}C NMR of 2,4-diphenyl-2-(*m*-tolyl)-2*H*-imidazole (3ak)

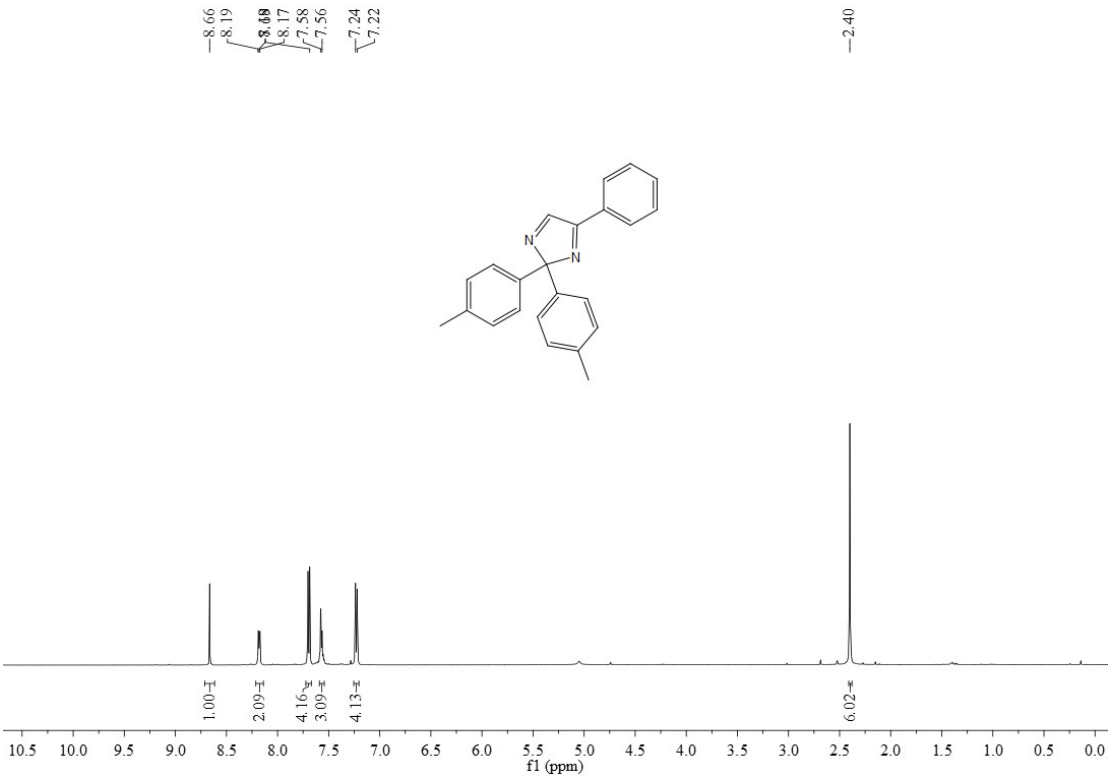


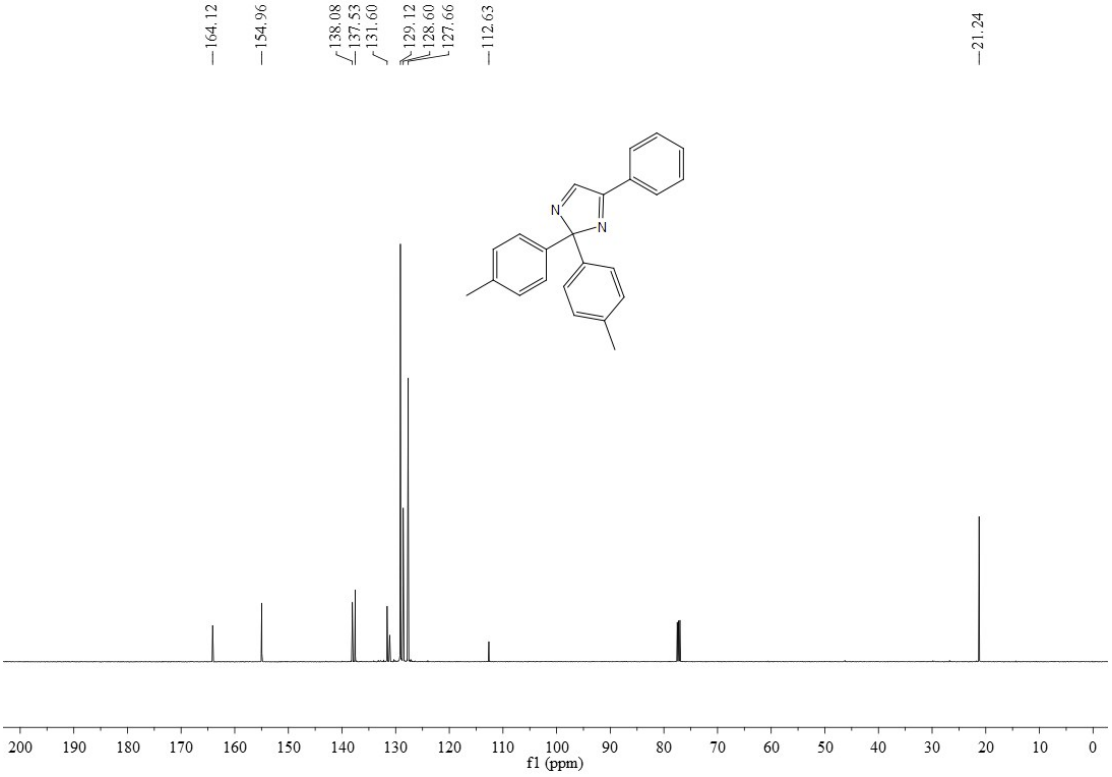
^{1}H NMR and ^{13}C NMR of 2,4-diphenyl-2-(3-(trifluoromethyl)phenyl)-2*H*-imidazole

(3al)

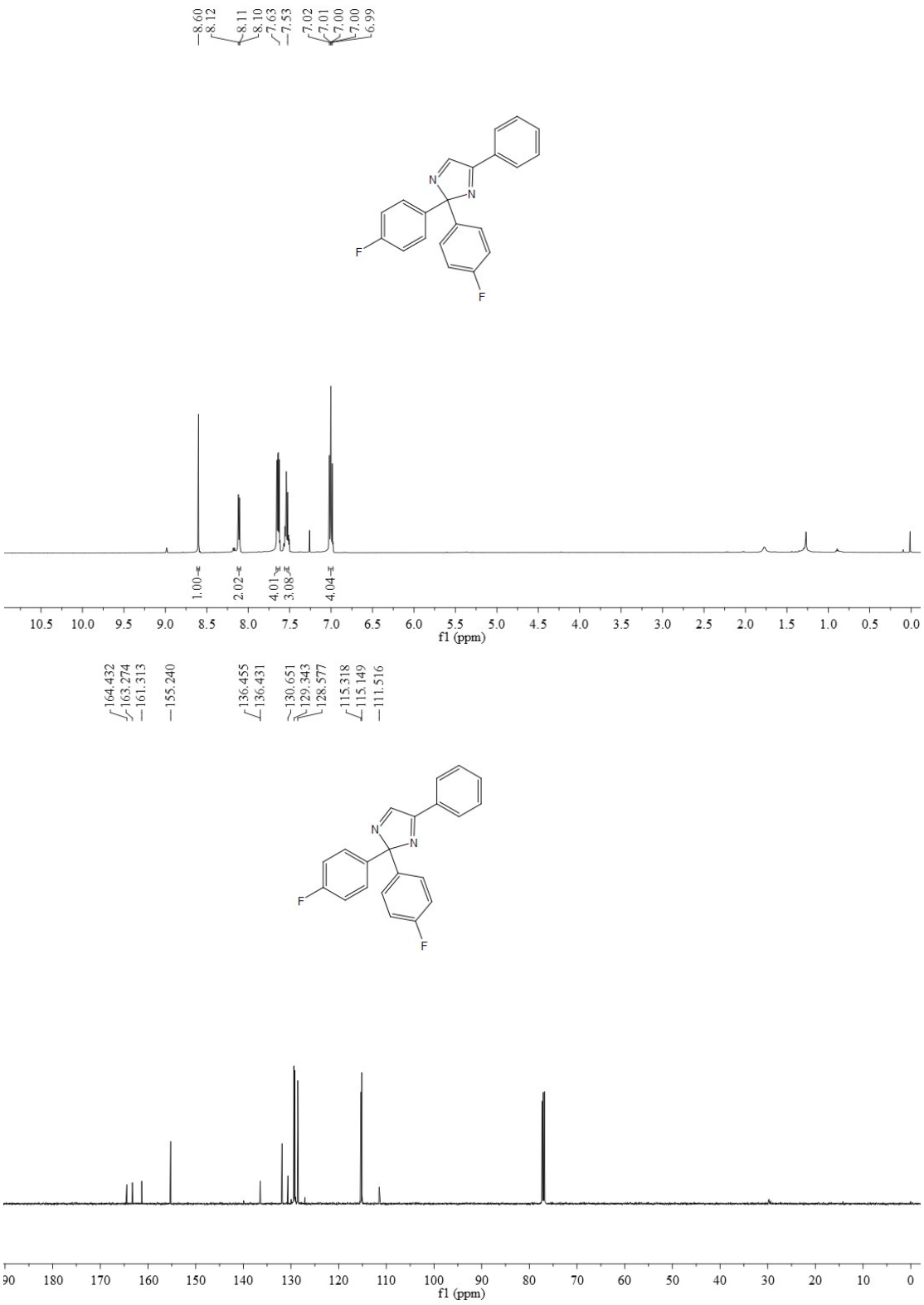


^{1}H NMR and ^{13}C NMR of 4-phenyl-2,2-di-*p*-tolyl-2*H*-imidazole (3am)

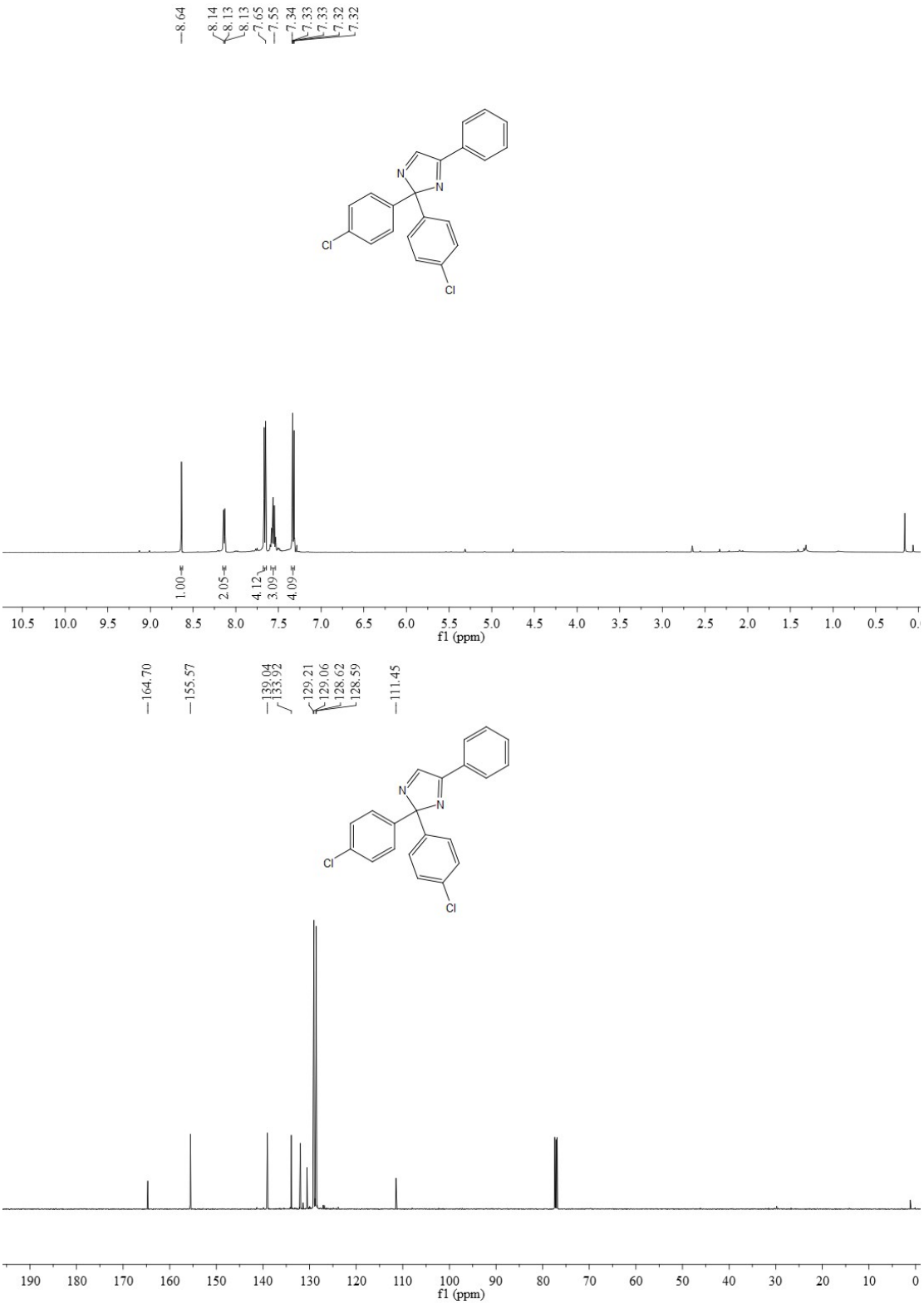




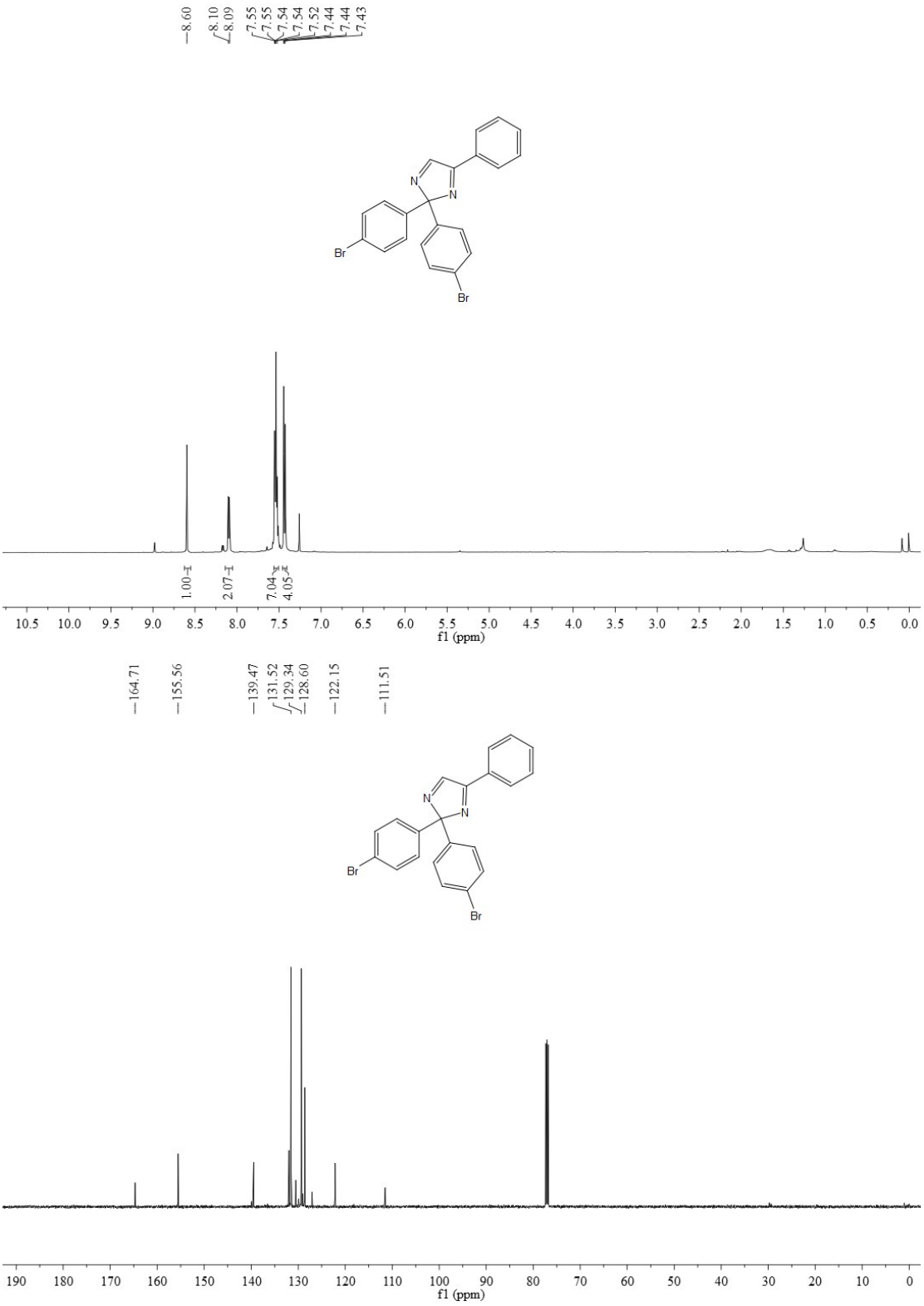
^{1}H NMR and ^{13}C NMR of 2,2-bis(4-fluorophenyl)-4-phenyl-2*H*-imidazole (3an)



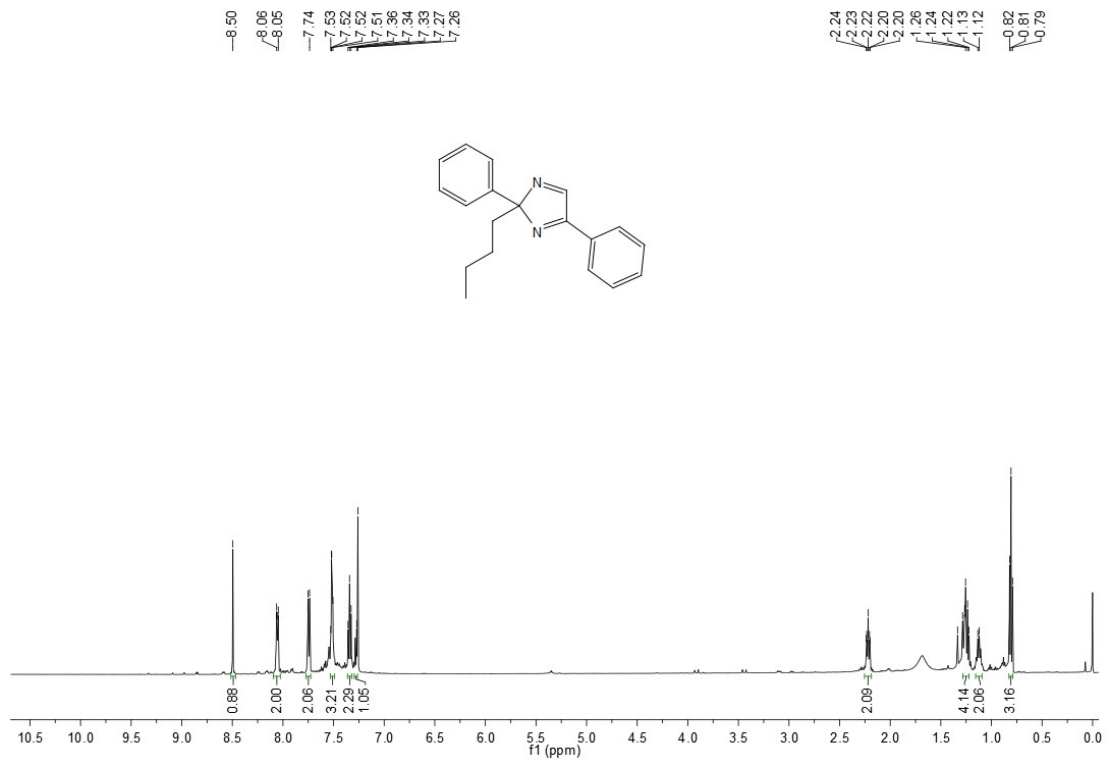
^{1}H NMR and ^{13}C NMR of 2,2-bis(4-chlorophenyl)-4-phenyl-2*H*-imidazole (3ao)

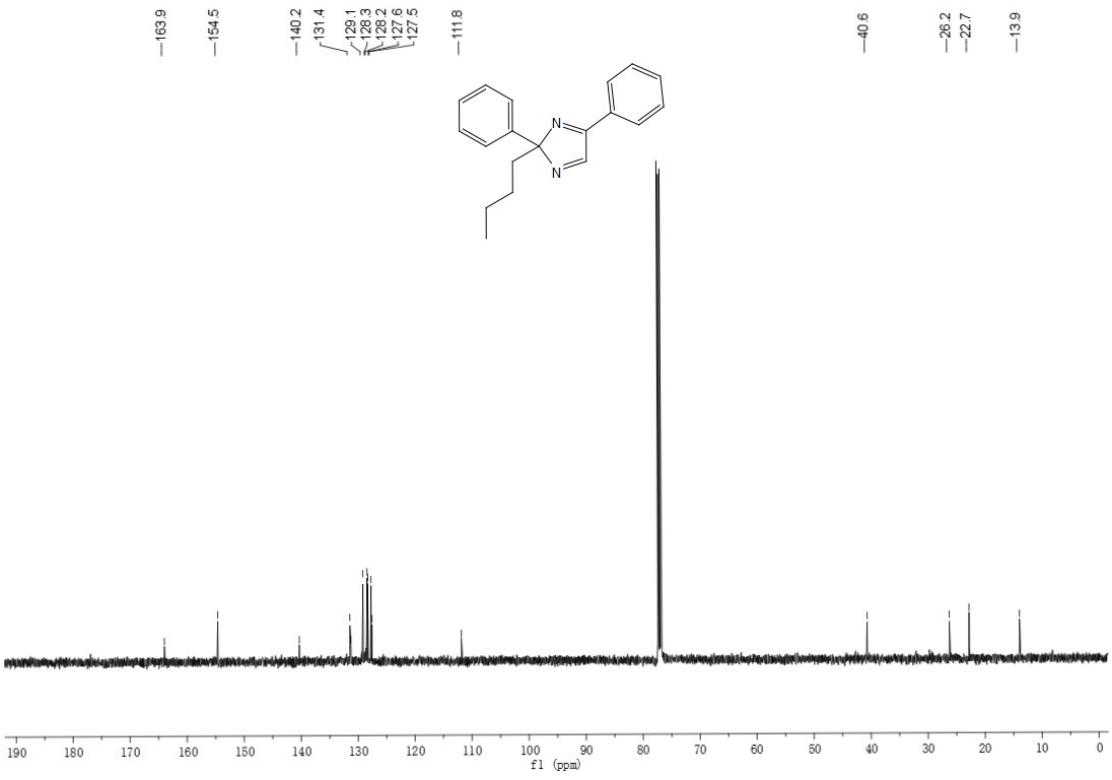


^{1}H NMR and ^{13}C NMR of 2,2-bis(4-bromophenyl)-4-phenyl-2*H*-imidazole (3ap)

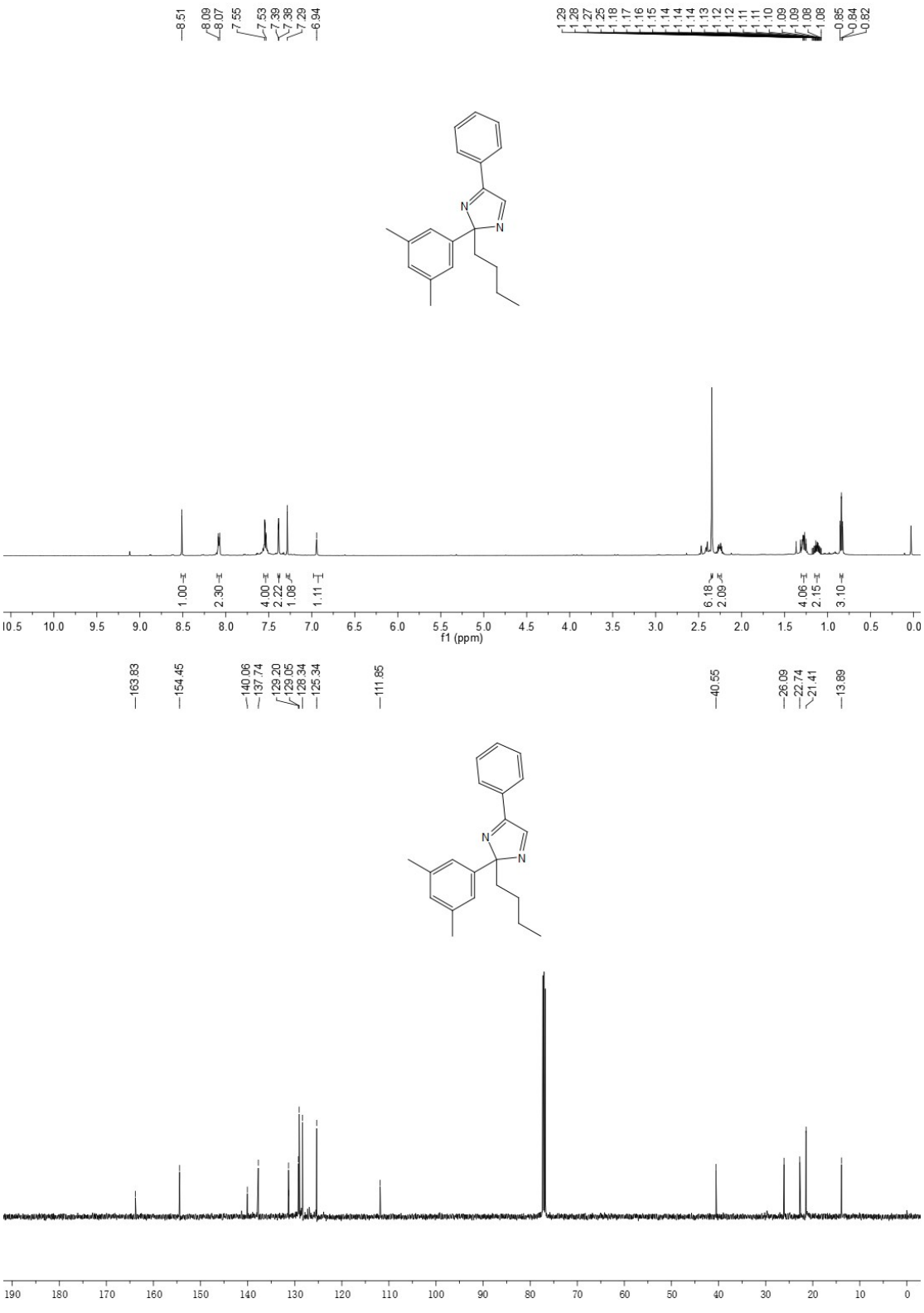


^{1}H NMR and ^{13}C NMR of 2-butyl-2,4-diphenyl-2*H*-imidazole (3aq)

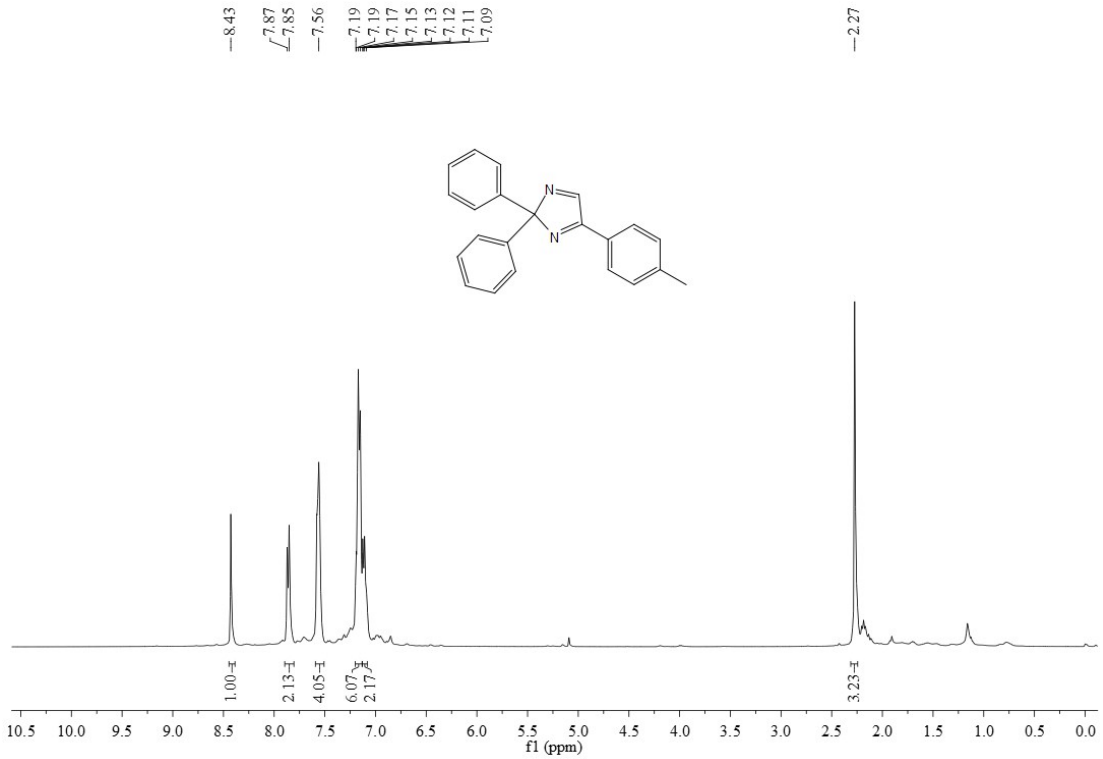


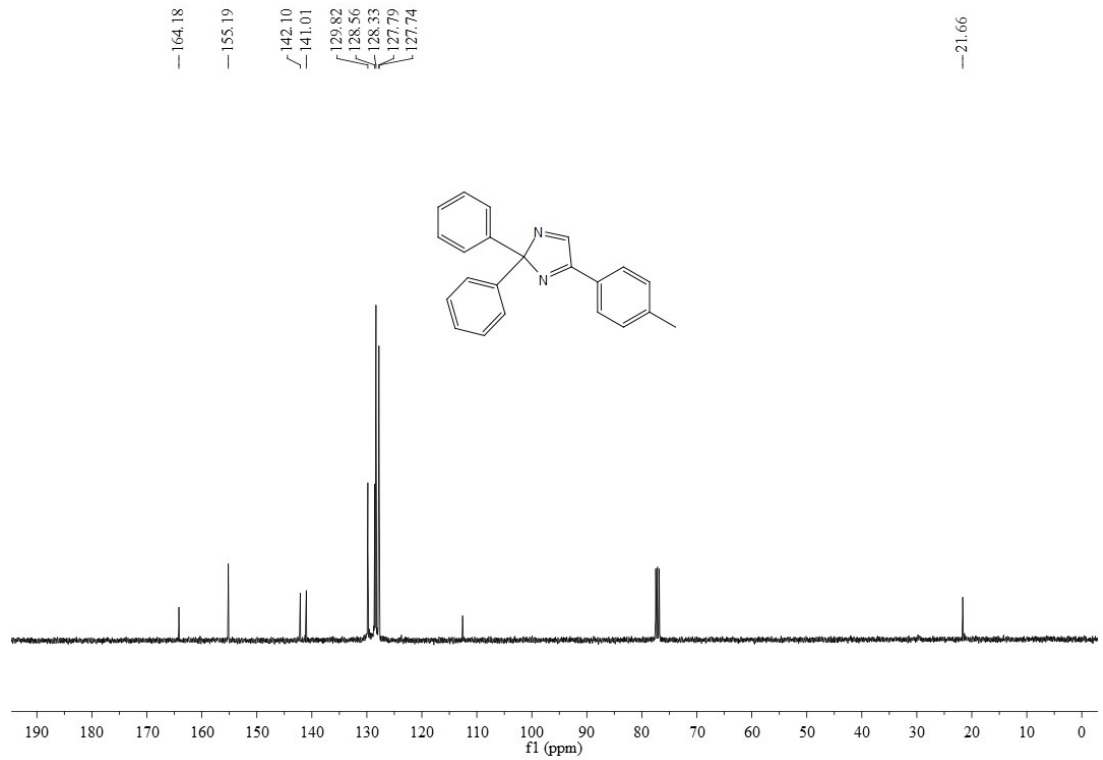


^{1}H NMR and ^{13}C NMR of 2,2-diphenyl-4-(*p*-tolyl)-2*H*-imidazole (3ar)

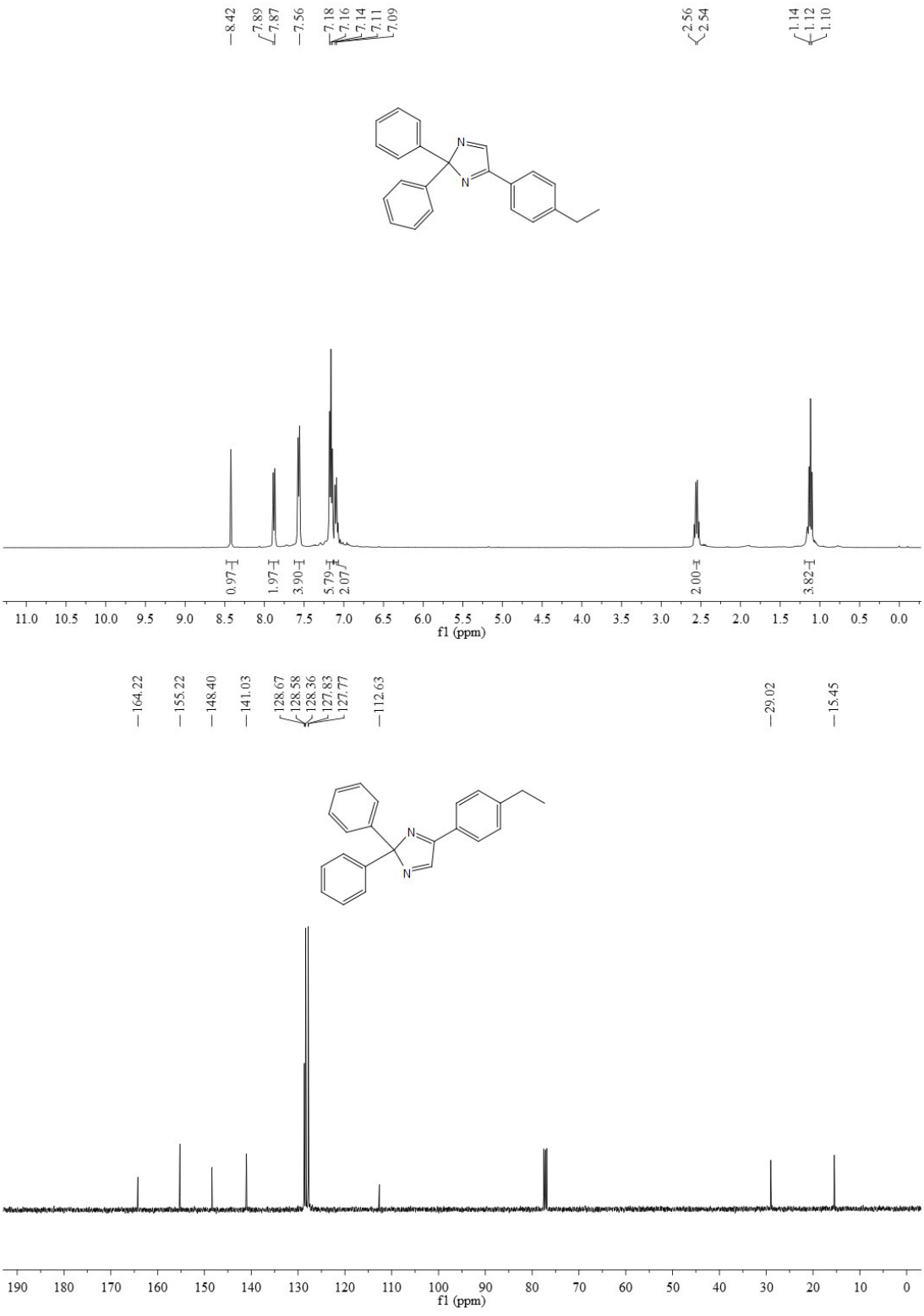


^{1}H NMR and ^{13}C NMR of 2,2-diphenyl-4-(*p*-tolyl)-2*H*-imidazole (3as)

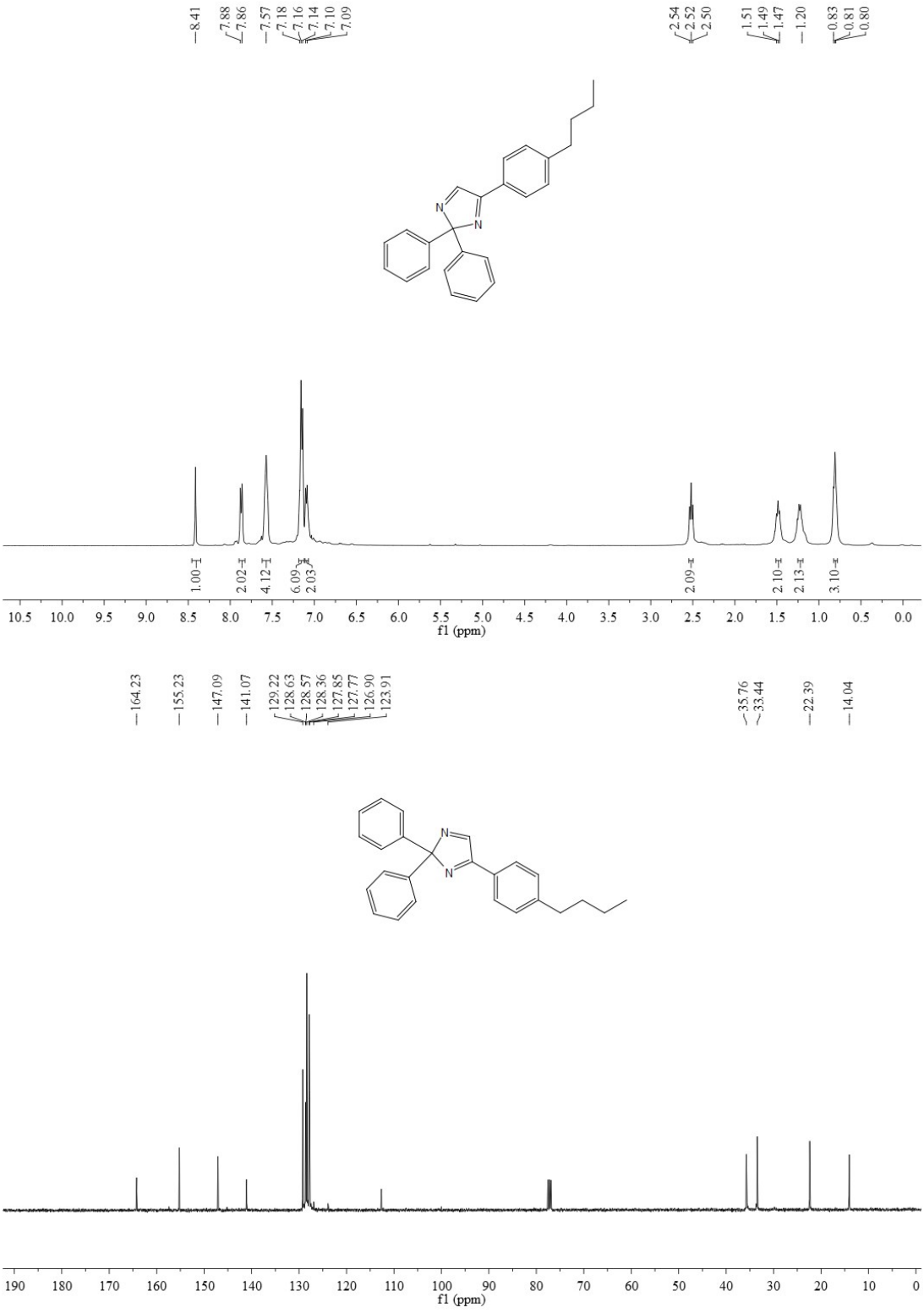




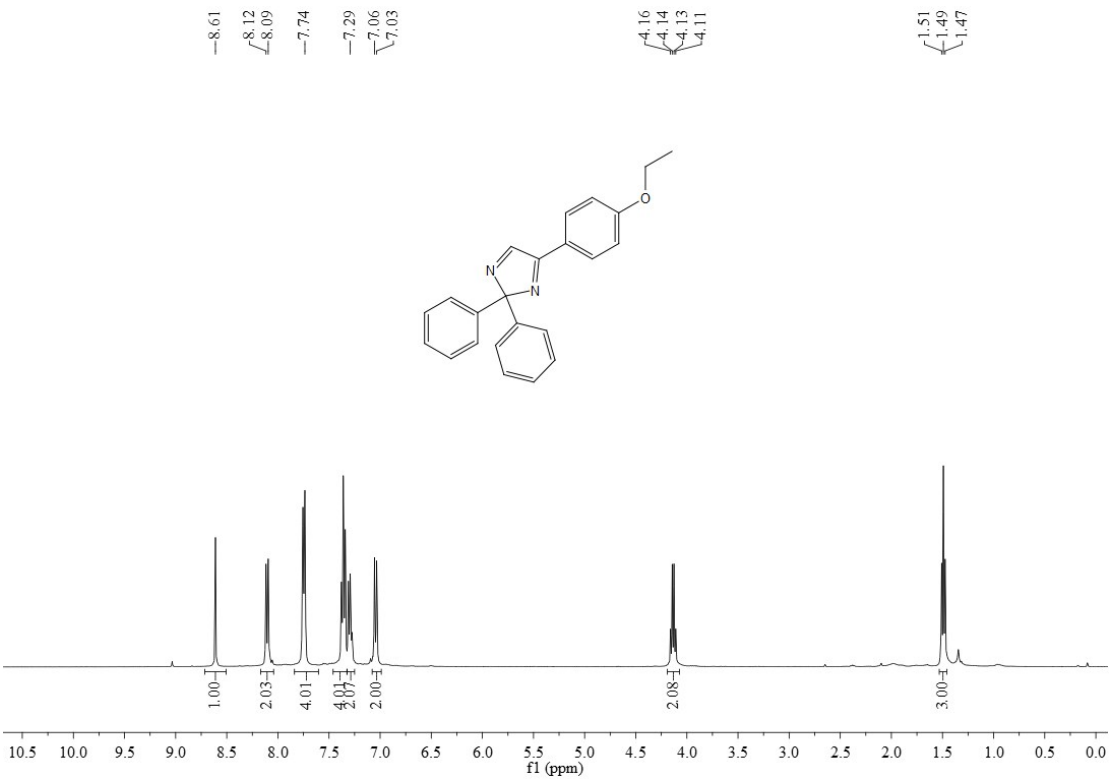
^{1}H NMR and ^{13}C NMR of 4-(4-ethylphenyl)-2,2-diphenyl-2*H*-imidazole (3at)

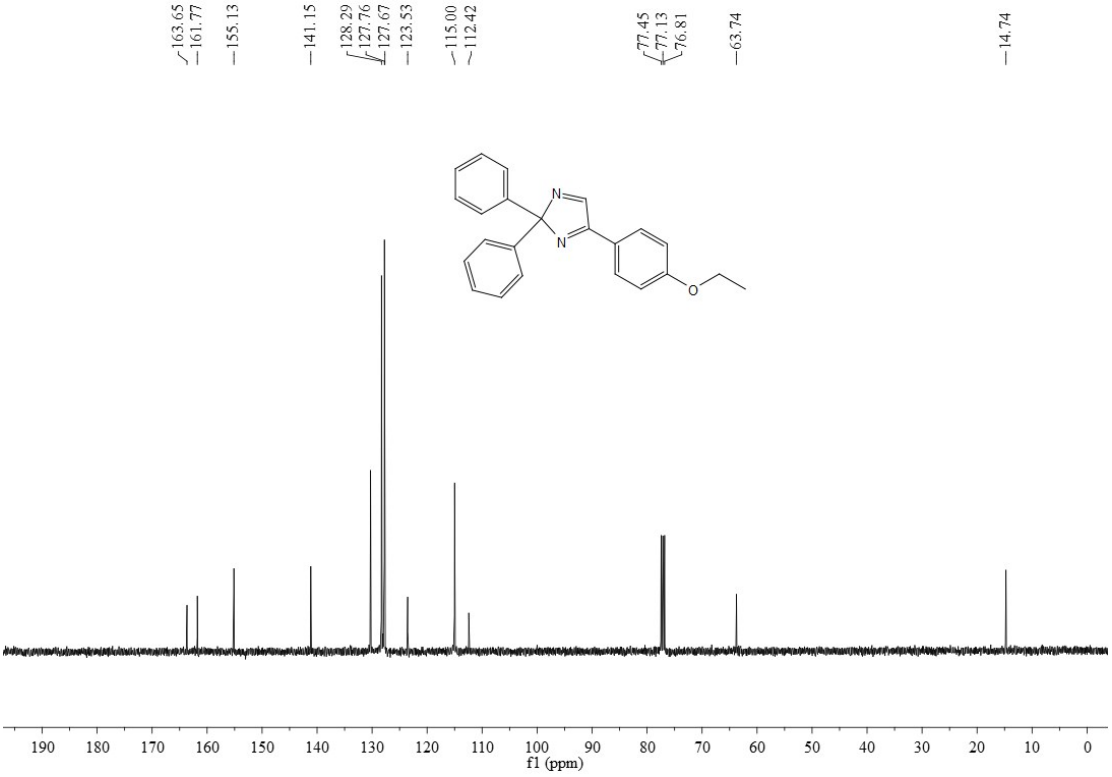


^{1}H NMR and ^{13}C NMR of 4-(4-butylphenyl)-2,2-diphenyl-2*H*-imidazole (3au)

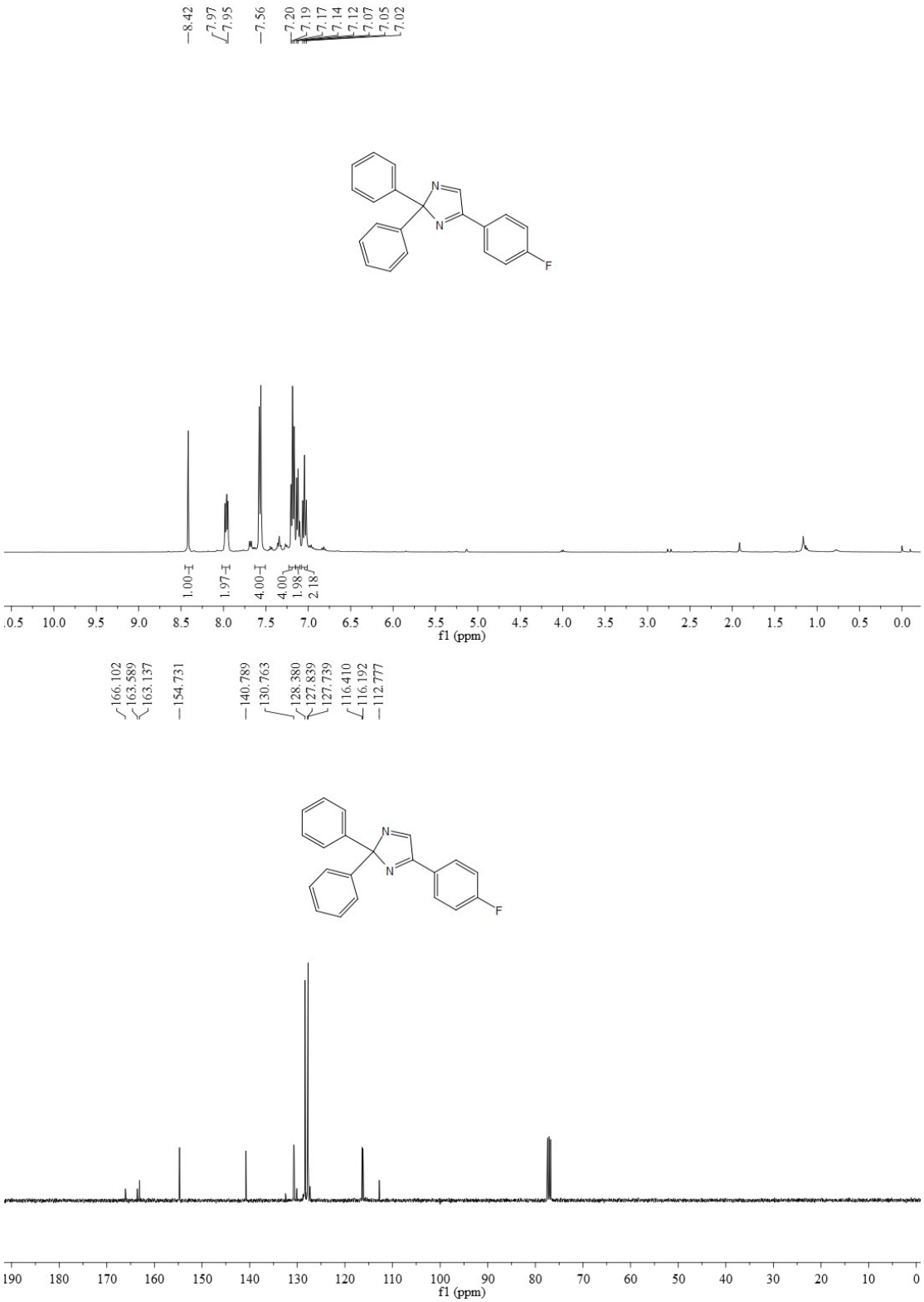


^{1}H NMR and ^{13}C NMR of 4-(4-ethoxyphenyl)-2,2-diphenyl-2*H*-imidazole (3av)

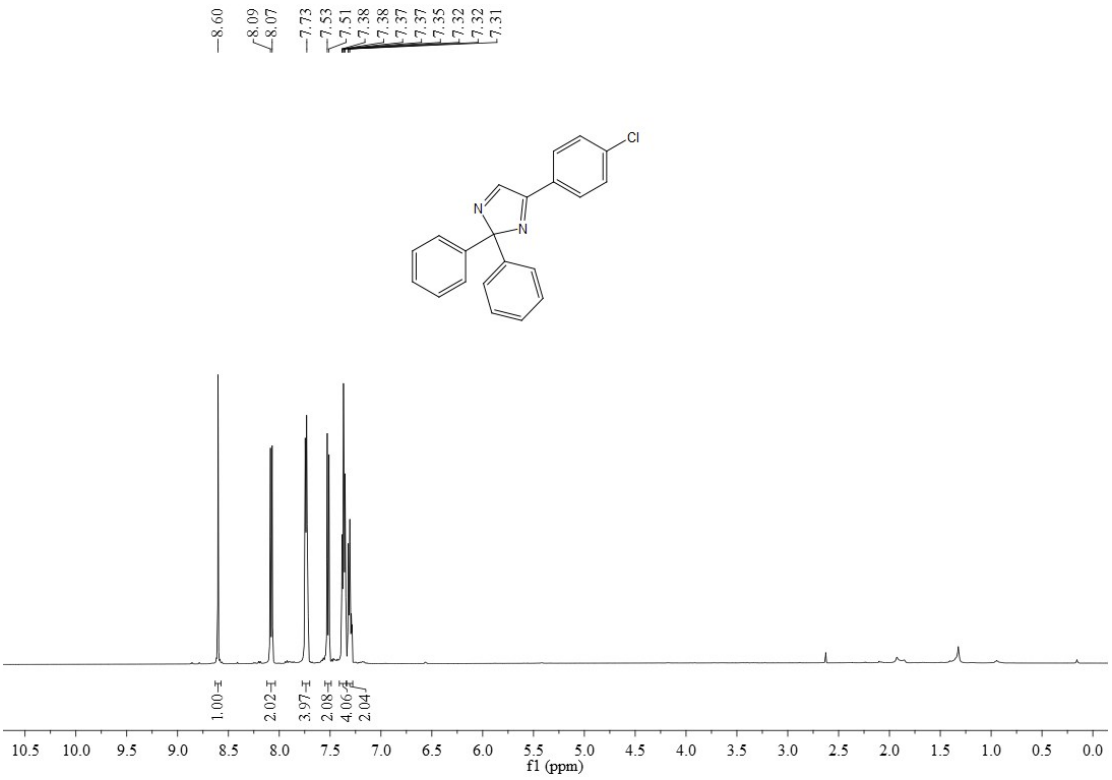


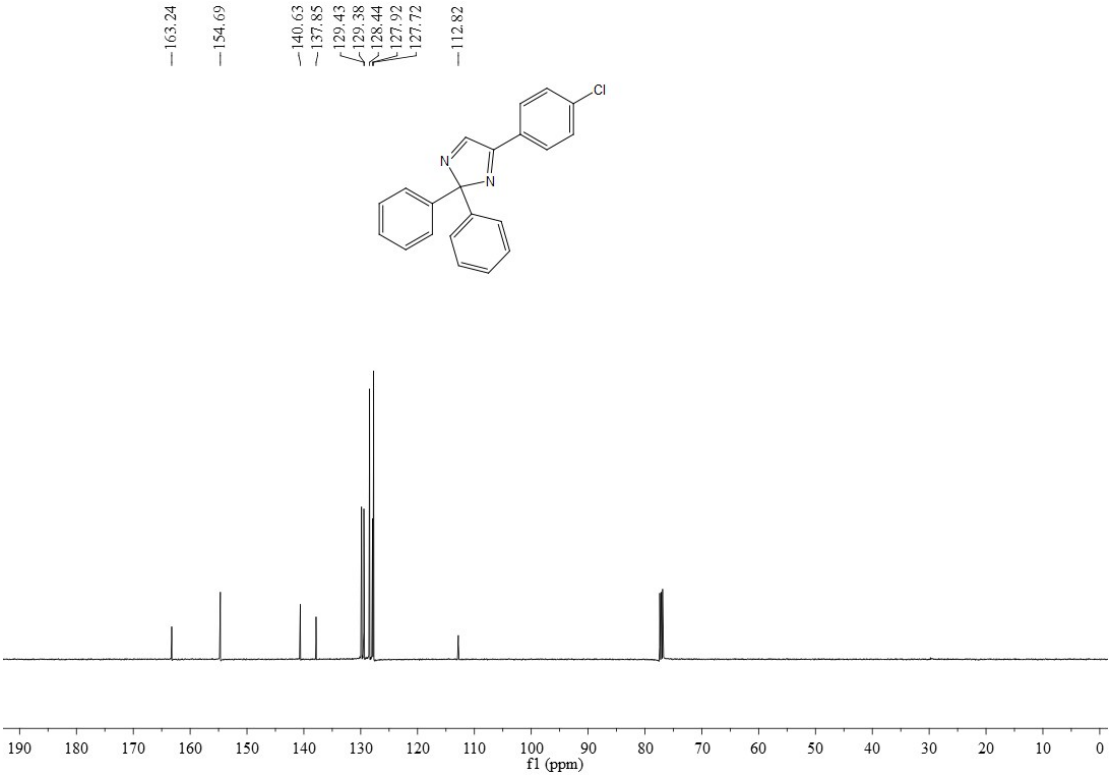


^{1}H NMR and ^{13}C NMR of 4-(4-fluorophenyl)-2,2-diphenyl-2*H*-imidazole (3aw)

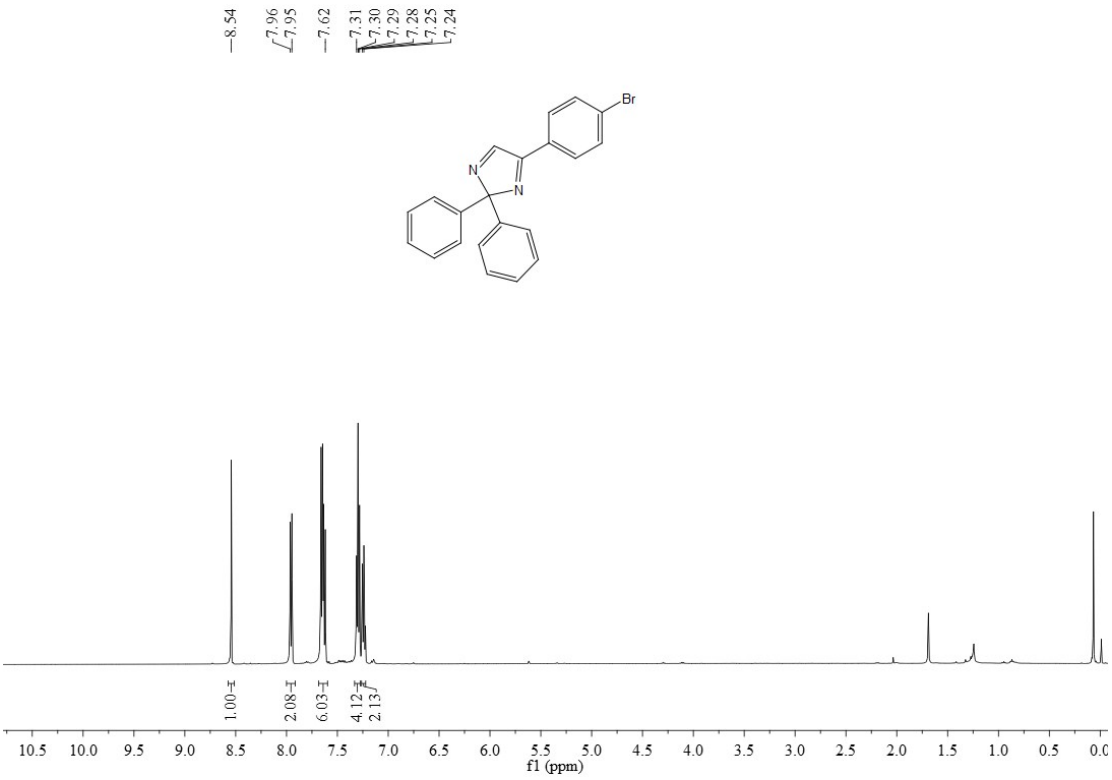


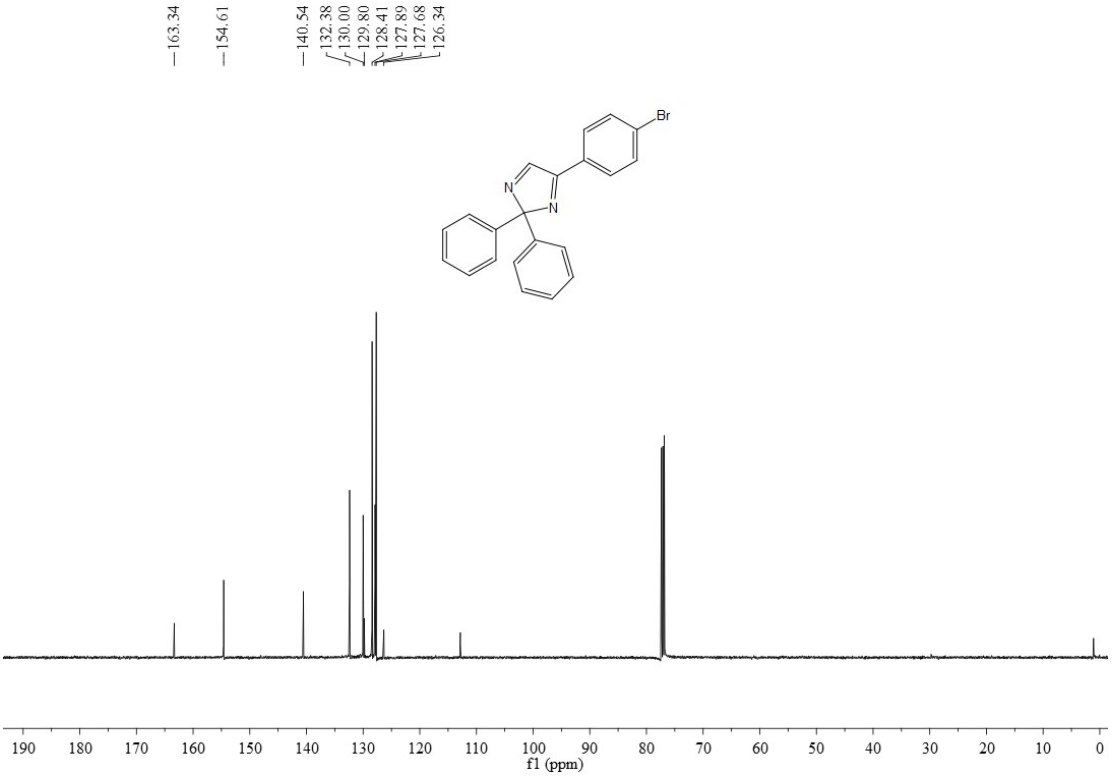
^{1}H NMR and ^{13}C NMR of 4-(4-chlorophenyl)-2,2-diphenyl-2*H*-imidazole (3ax)



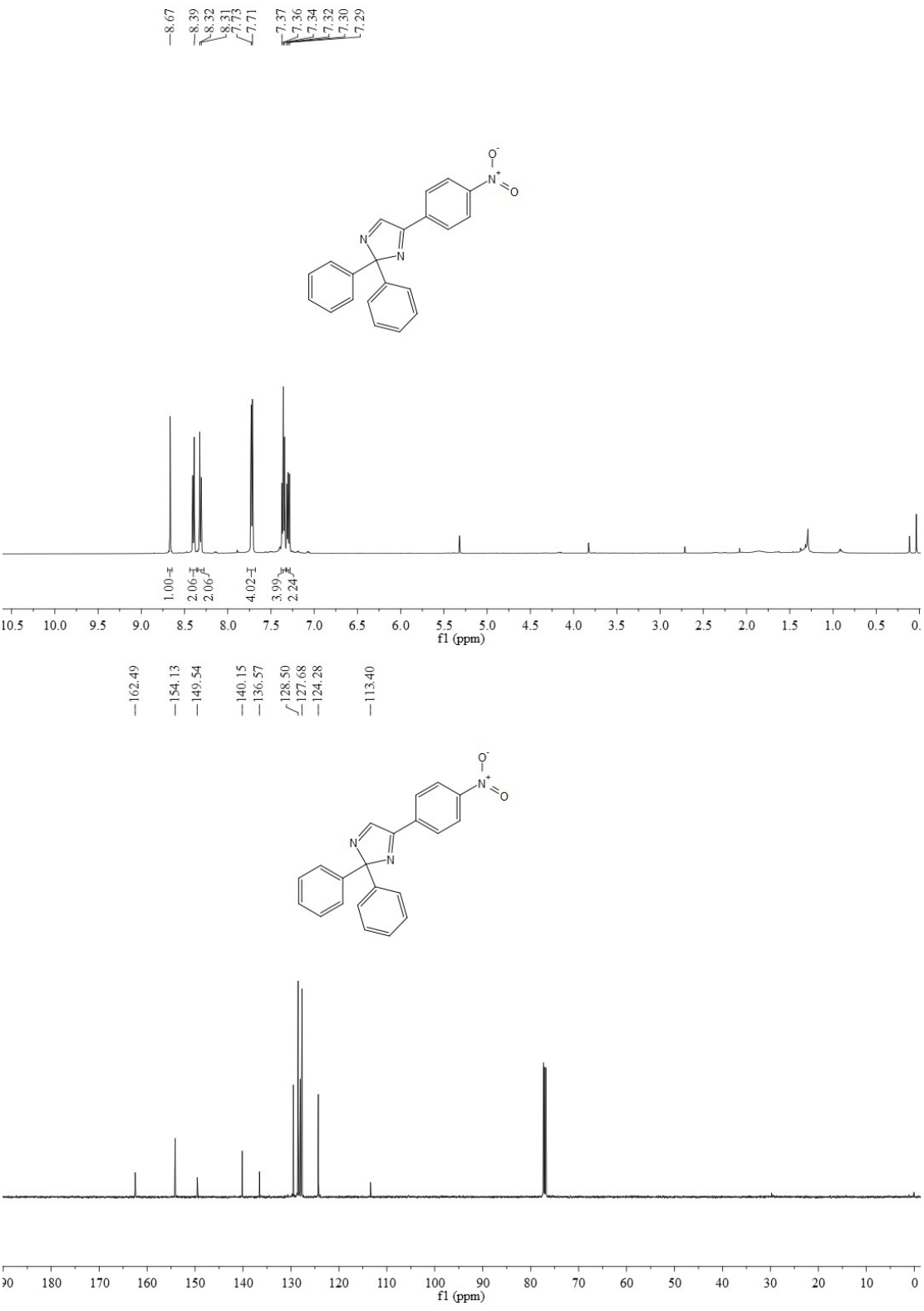


^{1}H NMR and ^{13}C NMR of 4-(4-bromophenyl)-2,2-diphenyl-2*H*-imidazole (3ay)

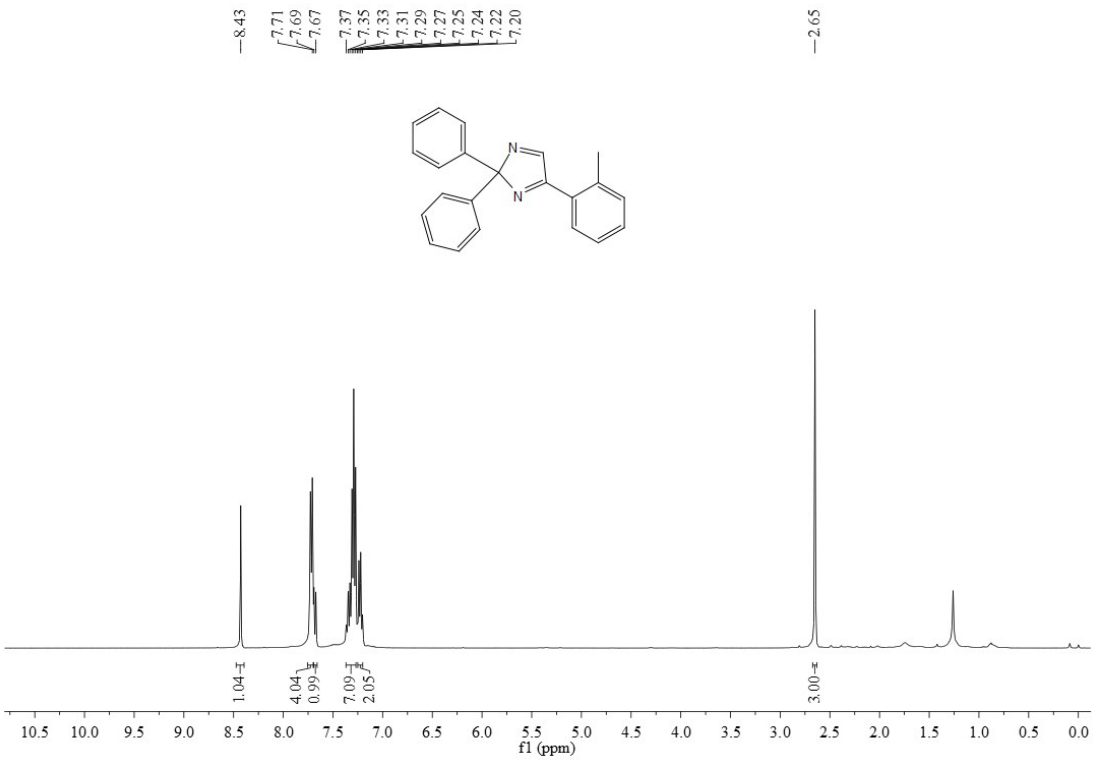


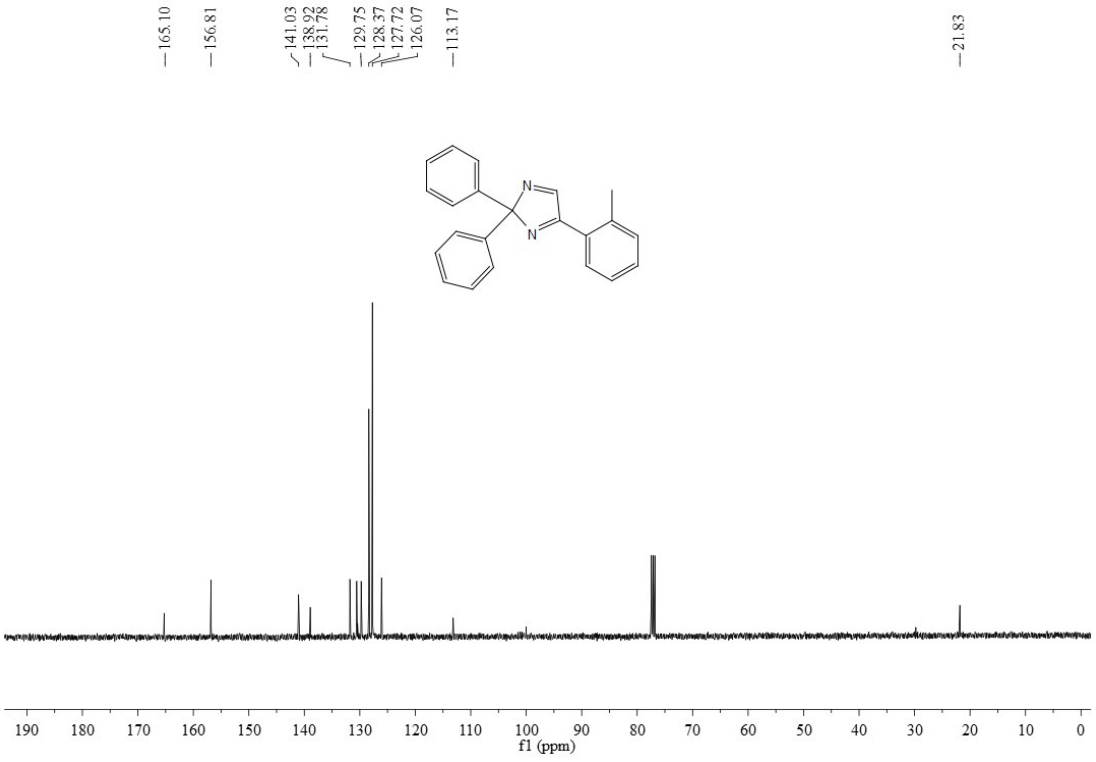


^{1}H NMR and ^{13}C NMR of 4-(4-nitrophenyl)-2,2-diphenyl-2*H*-imidazole (3az)

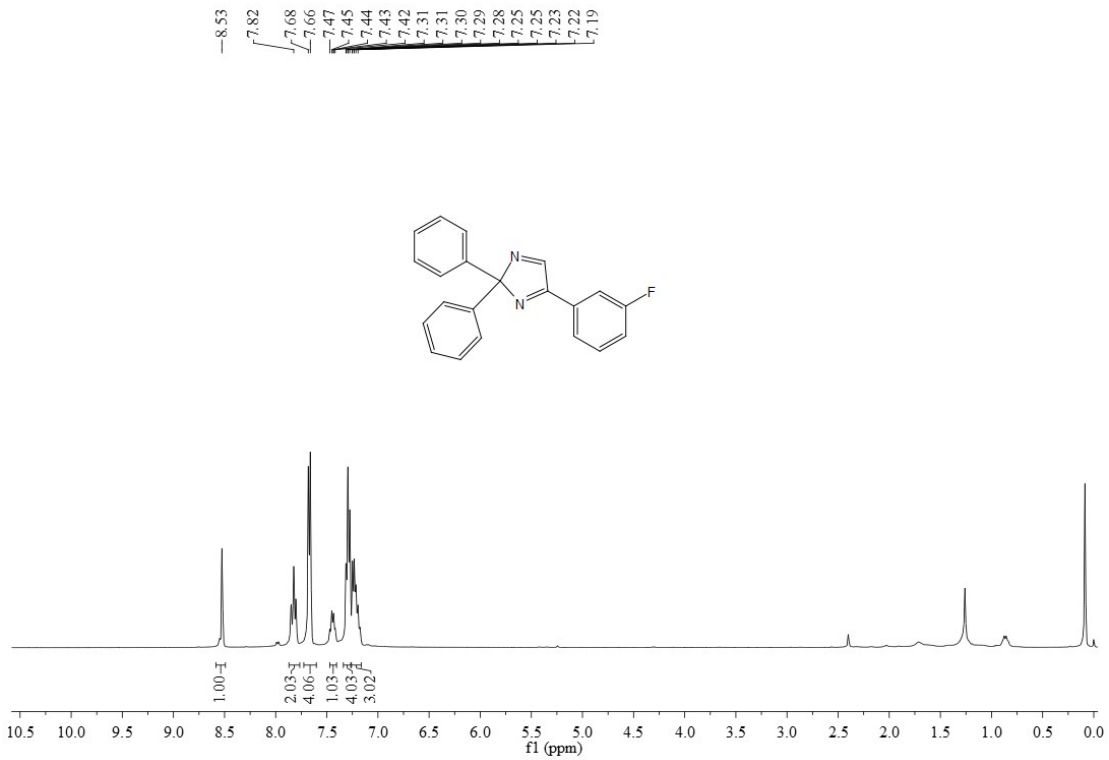


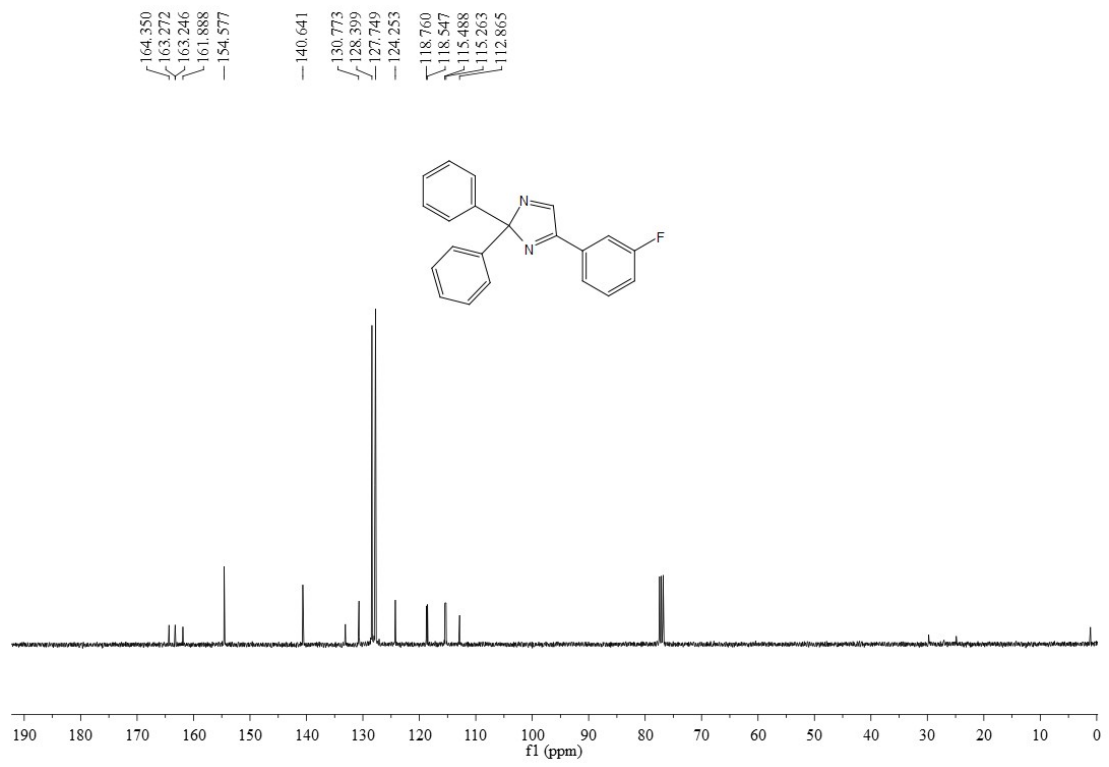
^{1}H NMR and ^{13}C NMR of 2,2-diphenyl-4-(*o*-tolyl)-2*H*-imidazole (3ba)



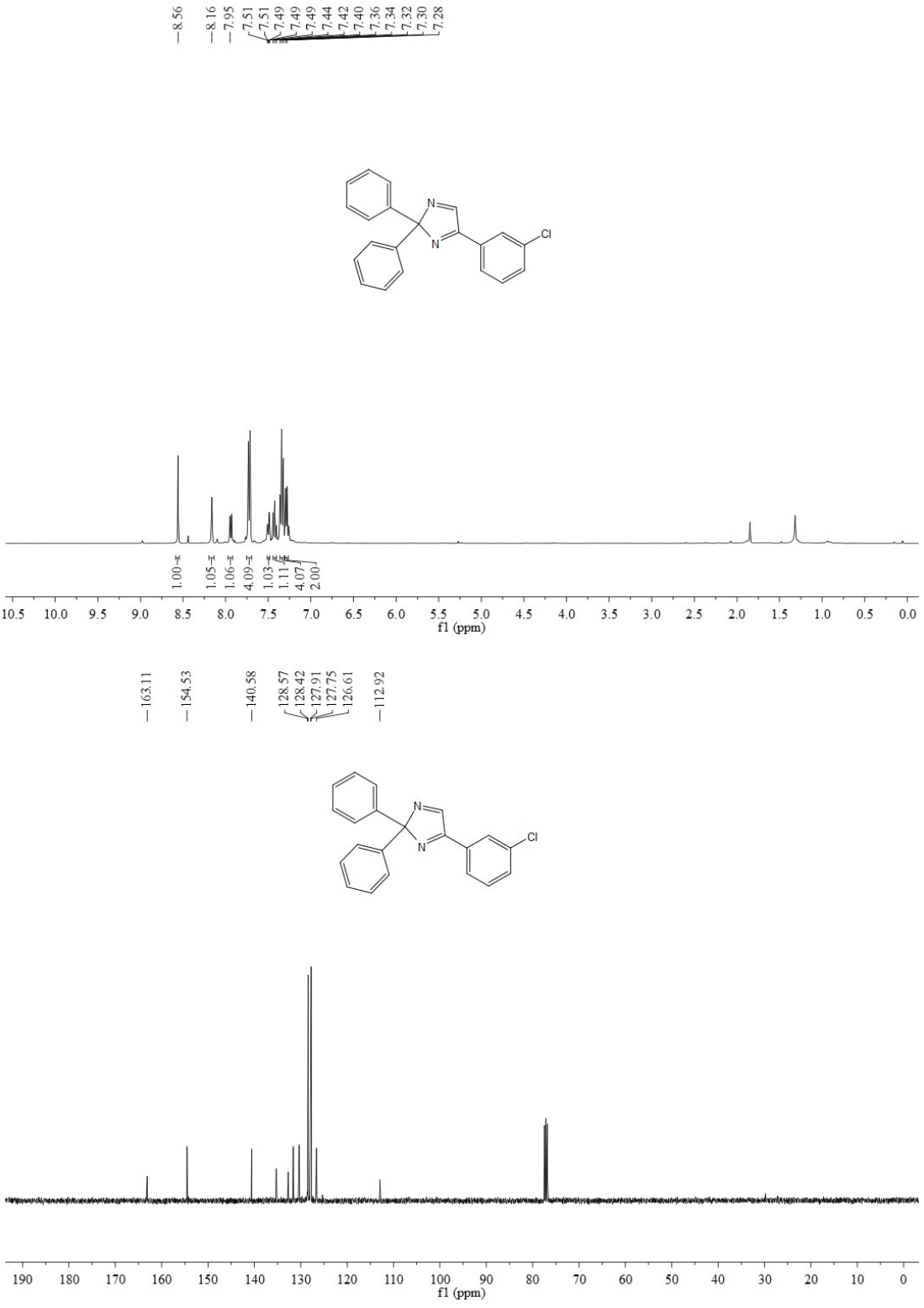


^{1}H NMR and ^{13}C NMR of 4-(3-fluorophenyl)-2,2-diphenyl-2*H*-imidazole (3bb)

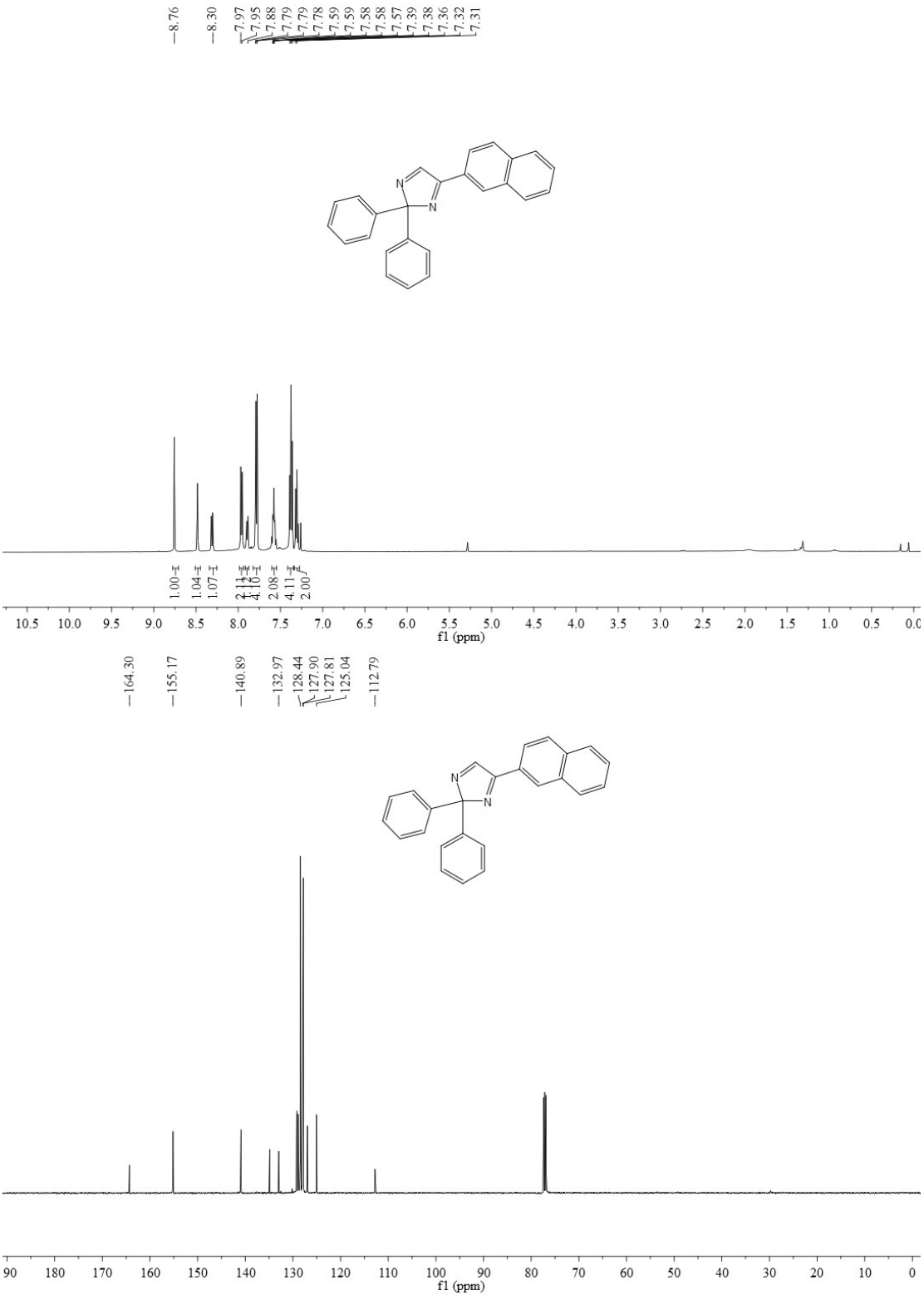




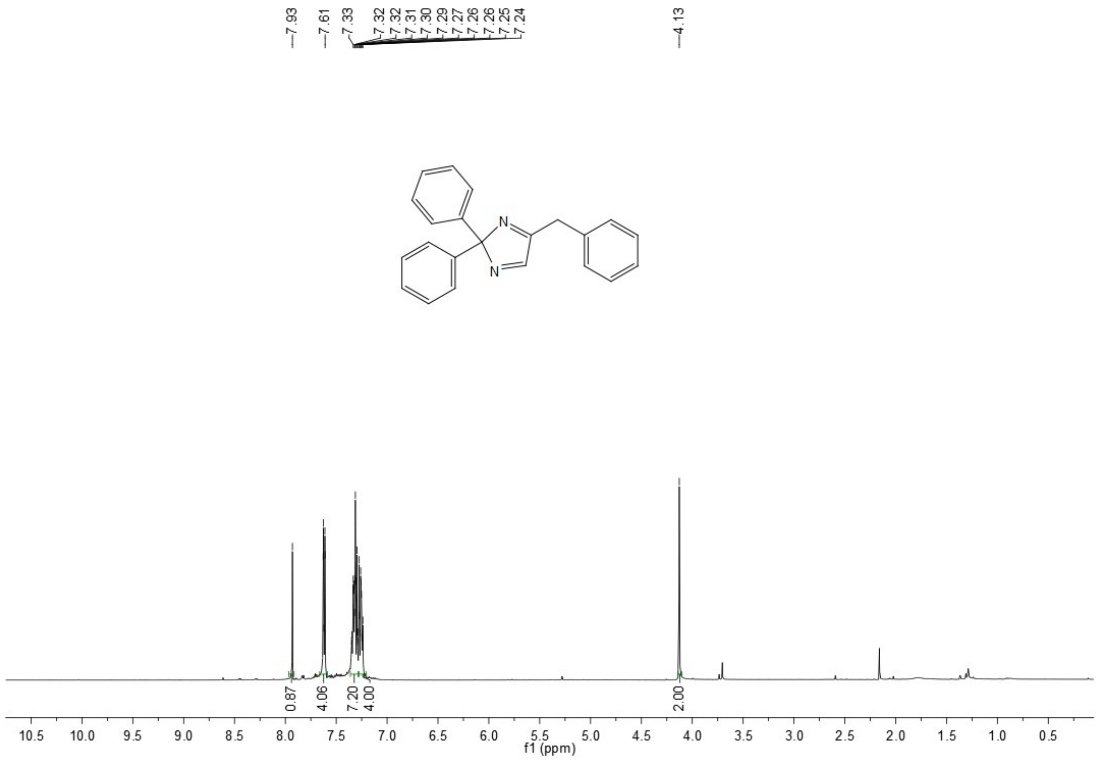
^{1}H NMR and ^{13}C NMR of 4-(3-chlorophenyl)-2,2-diphenyl-2*H*-imidazole (3bc)

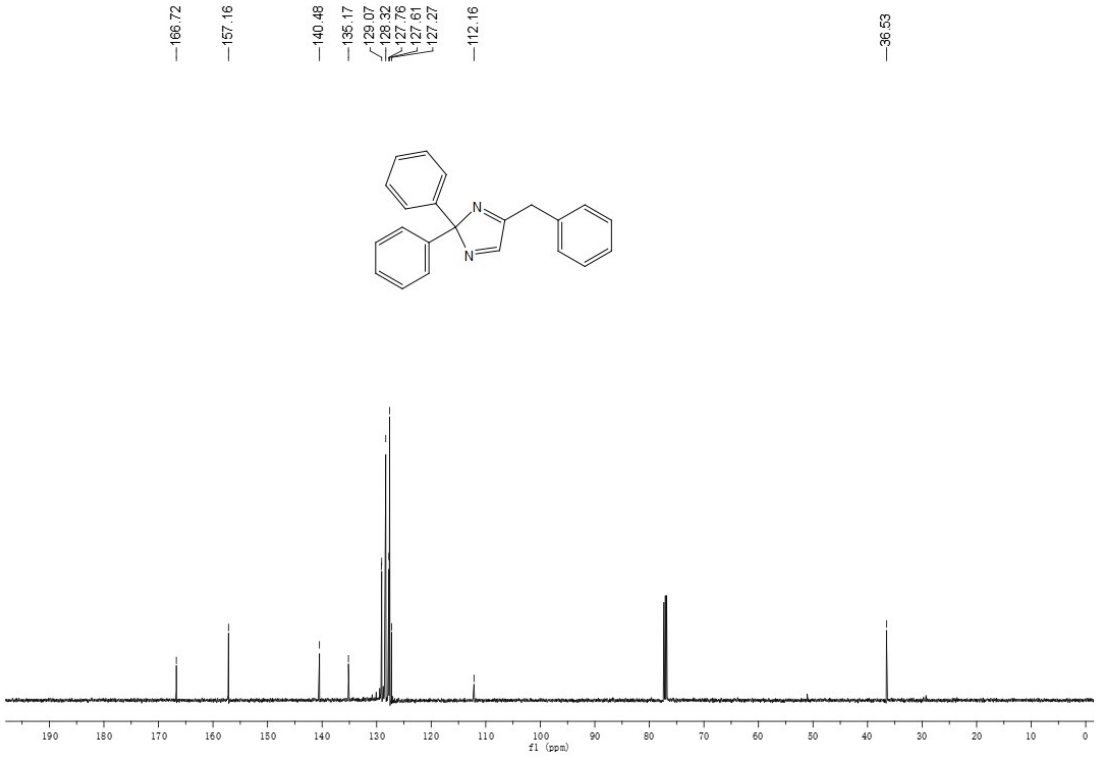


^{1}H NMR and ^{13}C NMR of 4-(naphthalen-2-yl)-2,2-diphenyl-2*H*-imidazole (3bd)

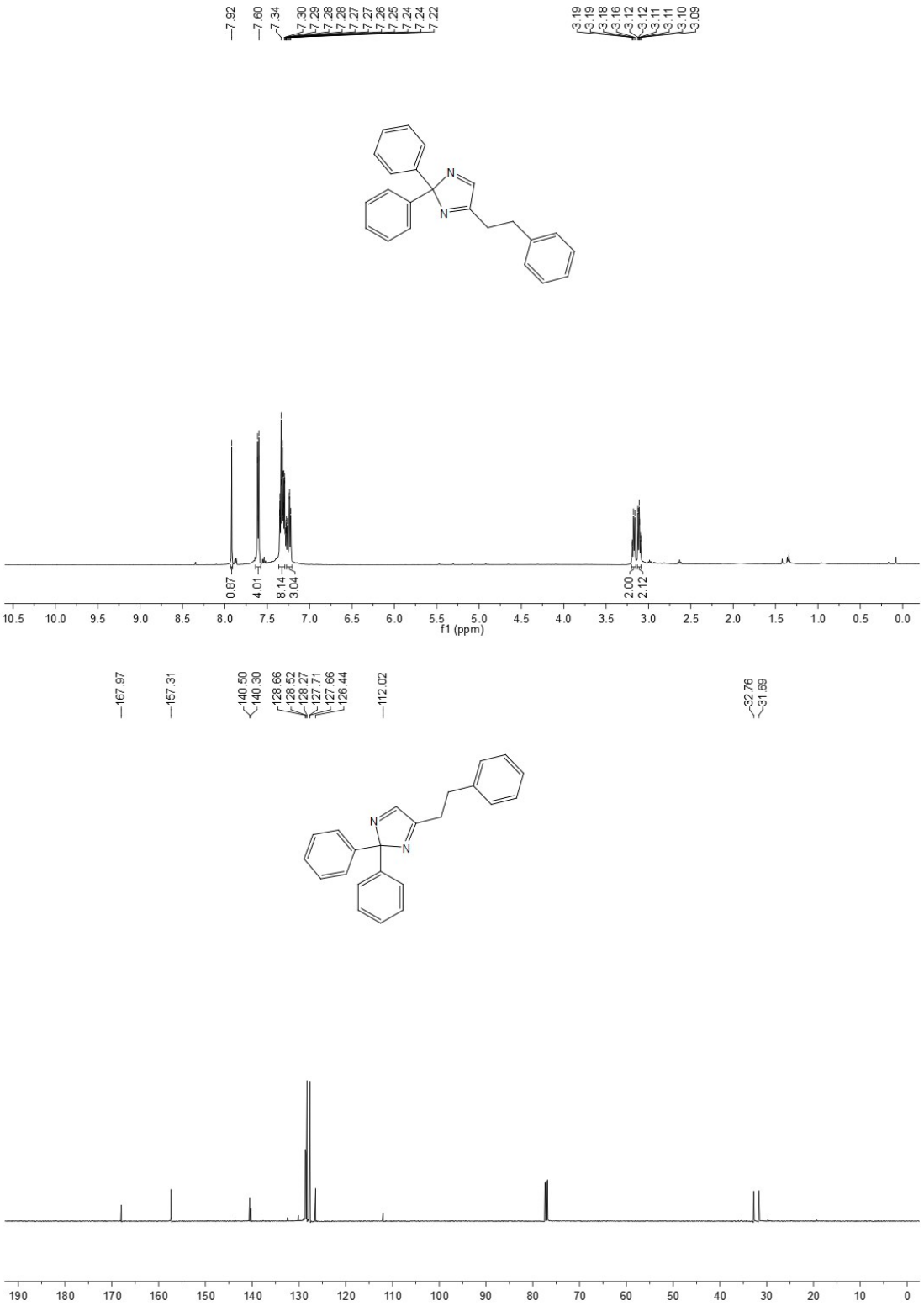


^{1}H NMR and ^{13}C NMR of 4-benzyl-2,2-diphenyl-2*H*-imidazole (3be)

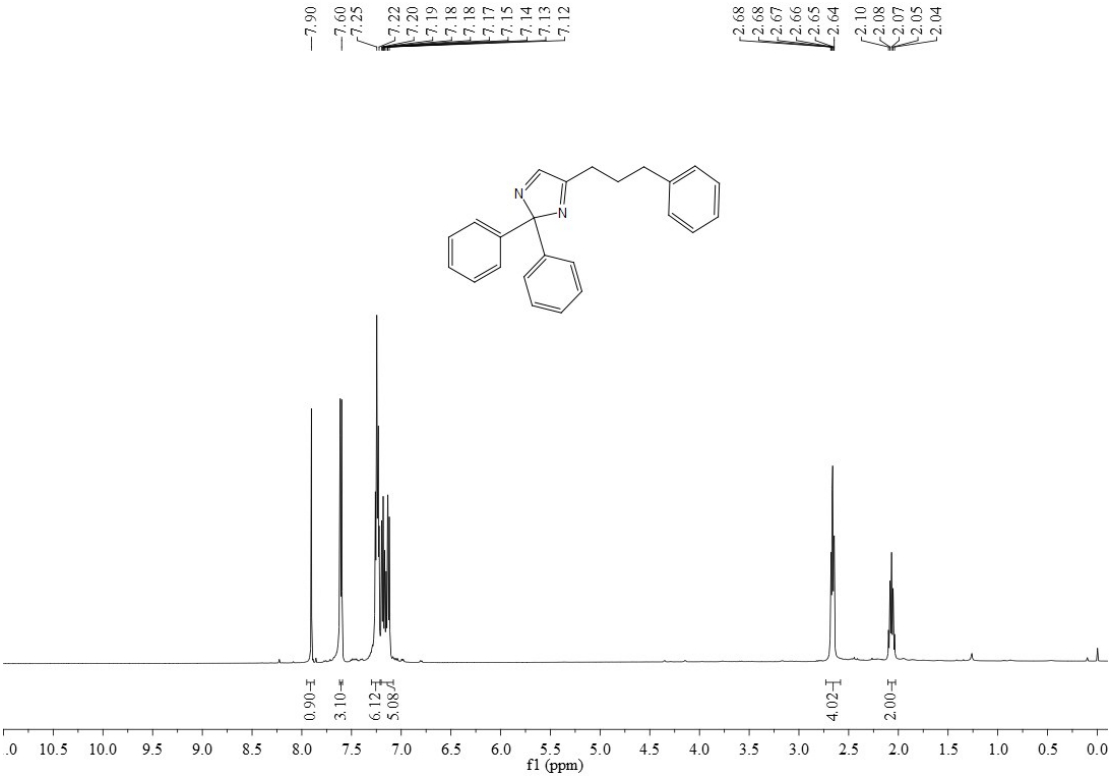


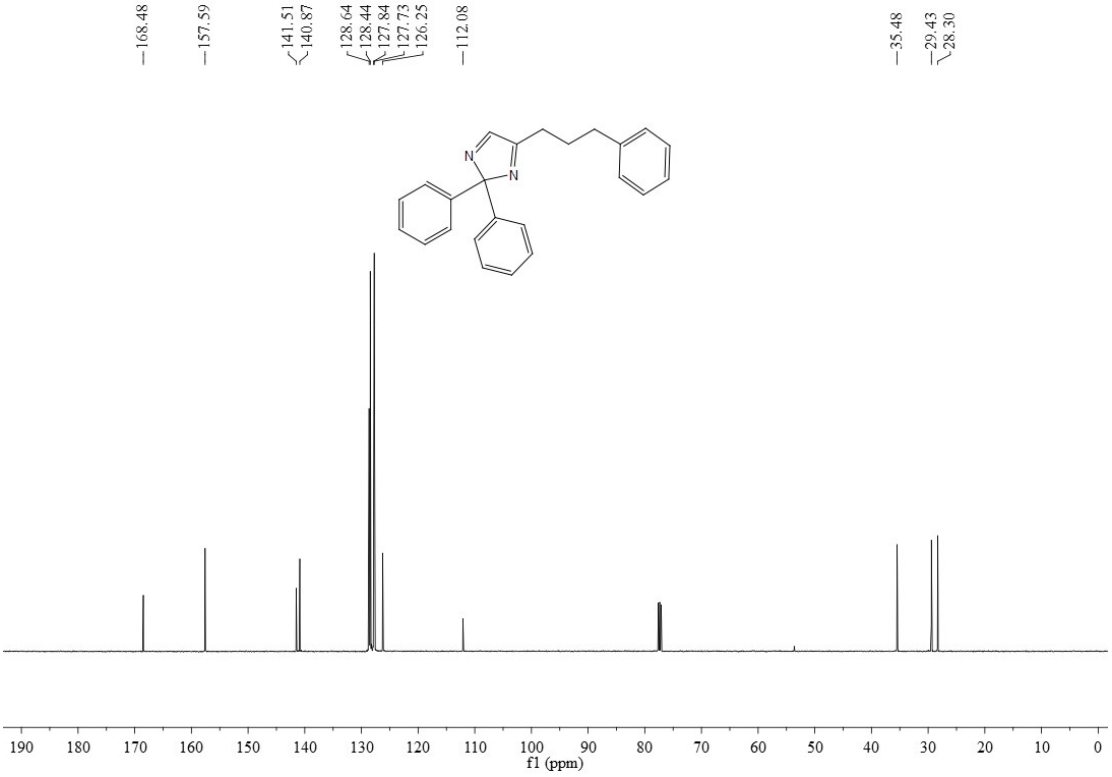


^{1}H NMR and ^{13}C NMR of 4-phenethyl-2,2-diphenyl-2*H*-imidazole (3bf)

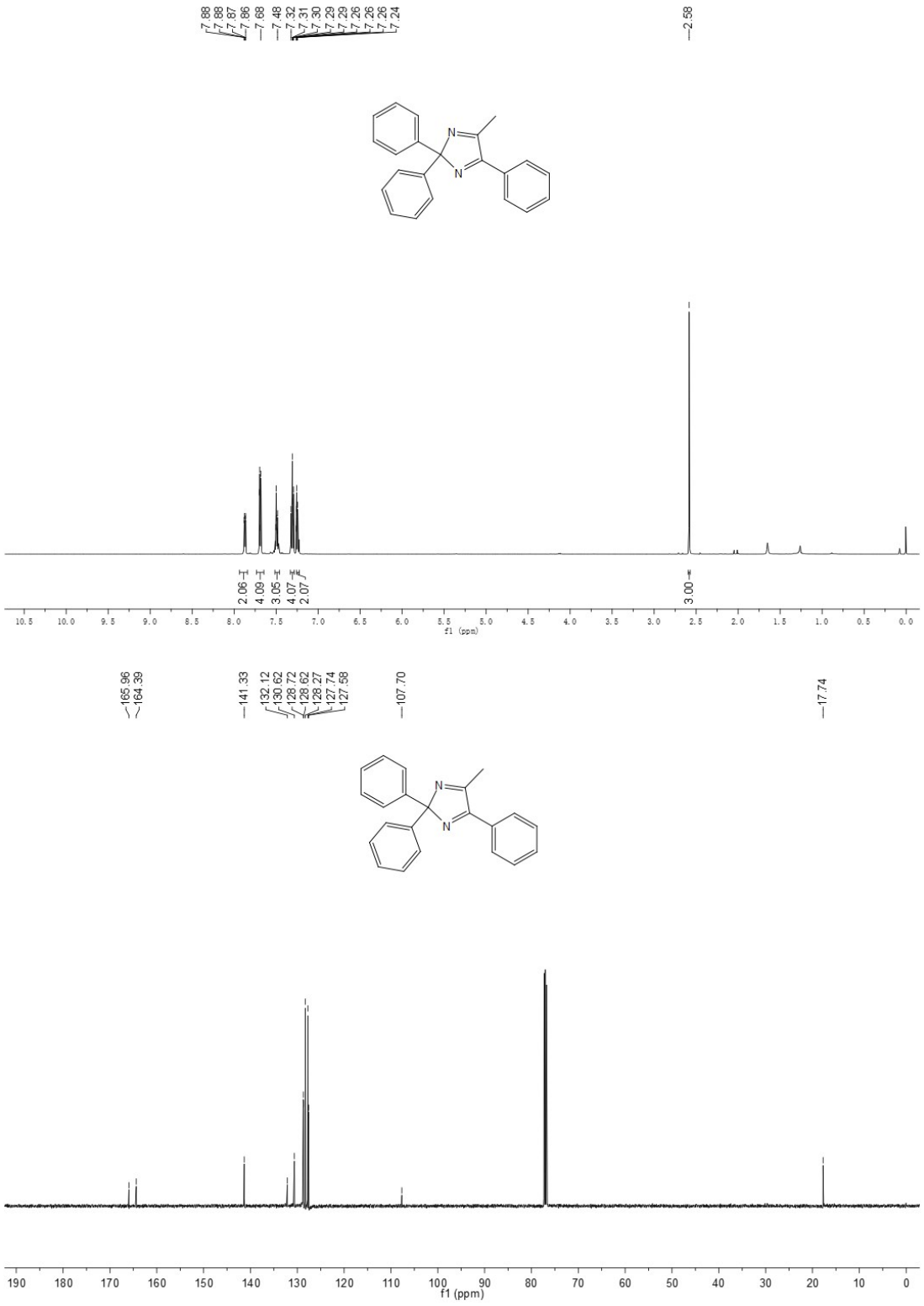


^{1}H NMR and ^{13}C NMR of 2,2-diphenyl-4-(3-phenylpropyl)-2*H*-imidazole (3bg)

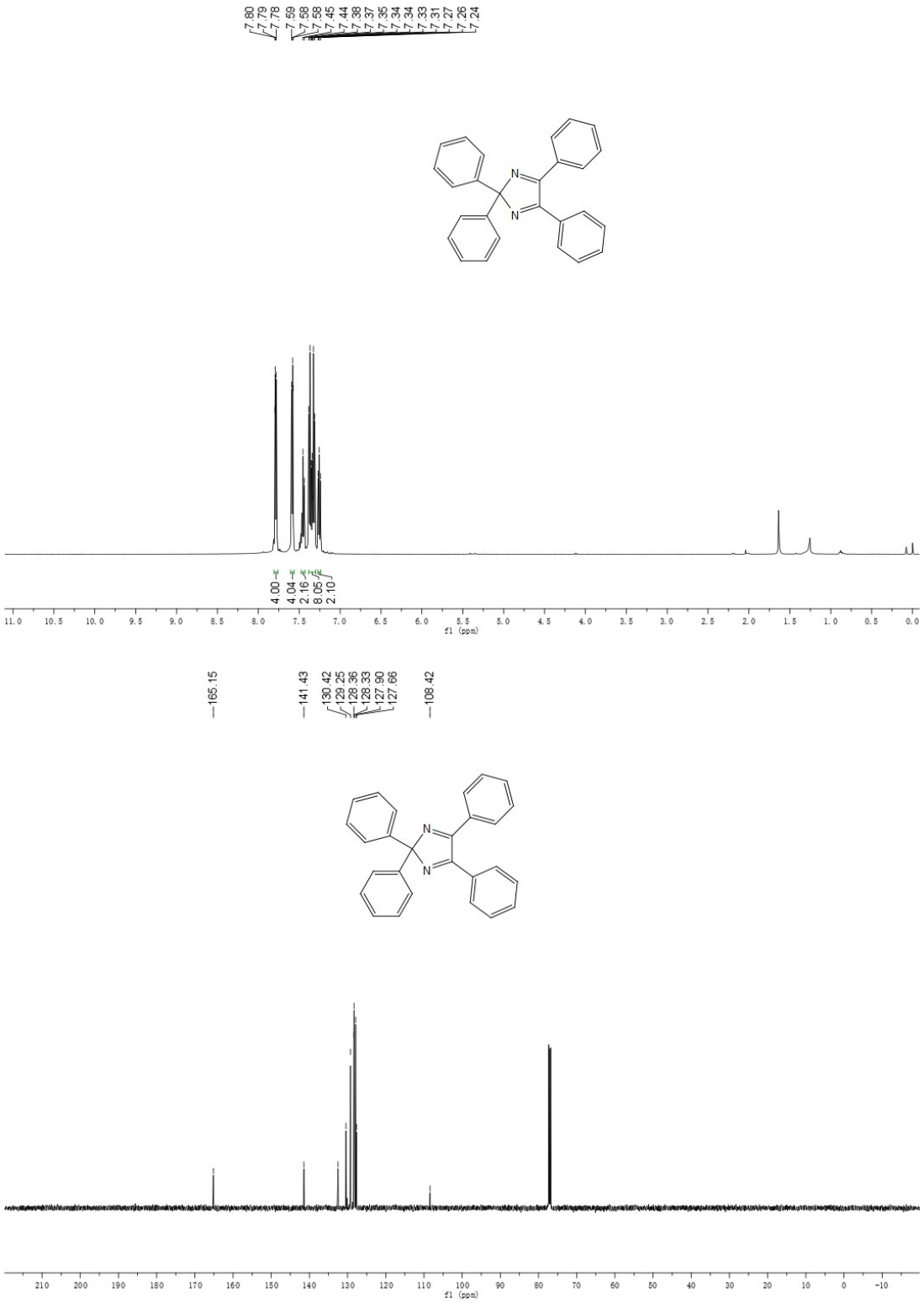




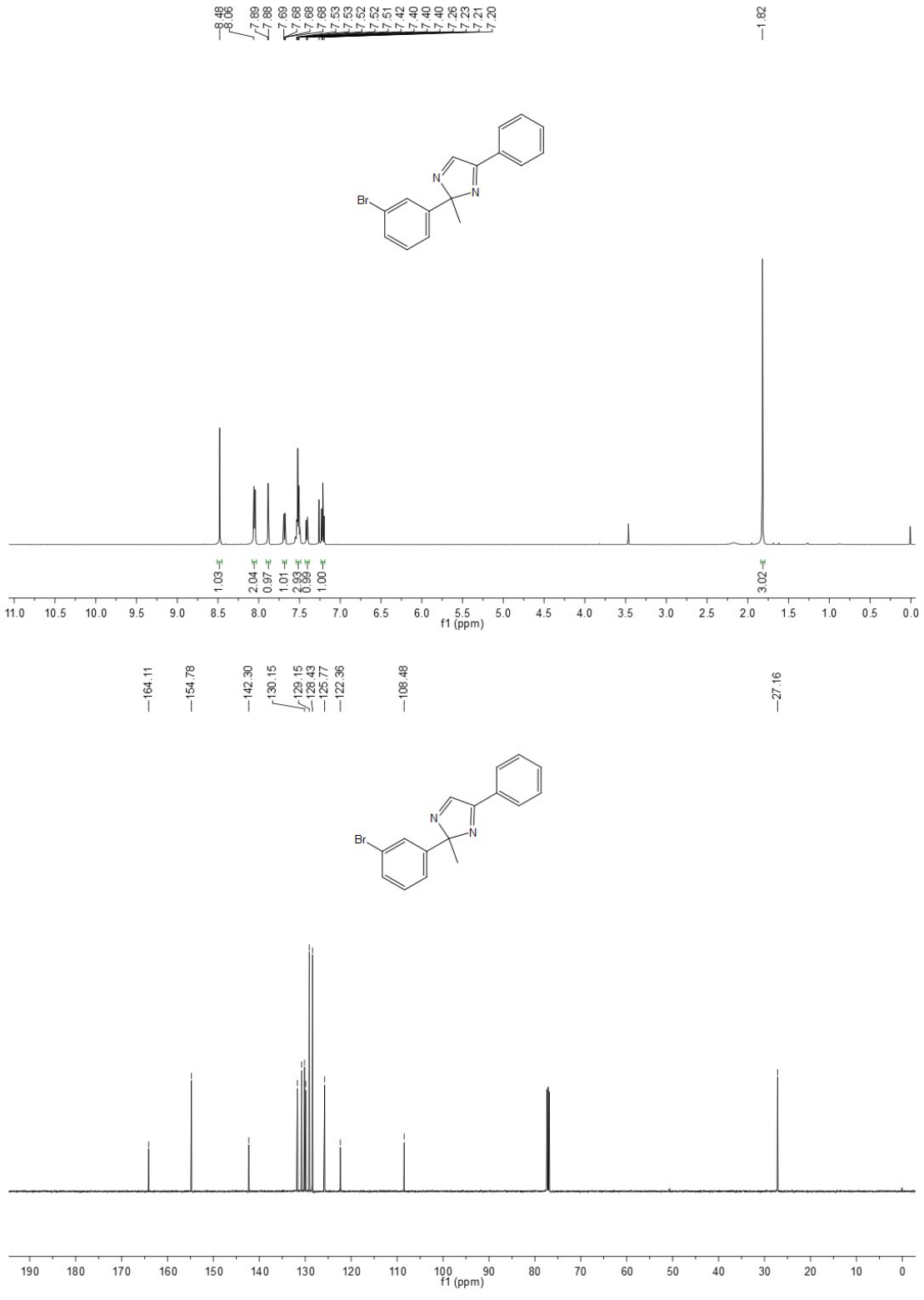
^{1}H NMR and ^{13}C NMR of 4-methyl-2,2,5-triphenyl-2*H*-imidazole (3bh)



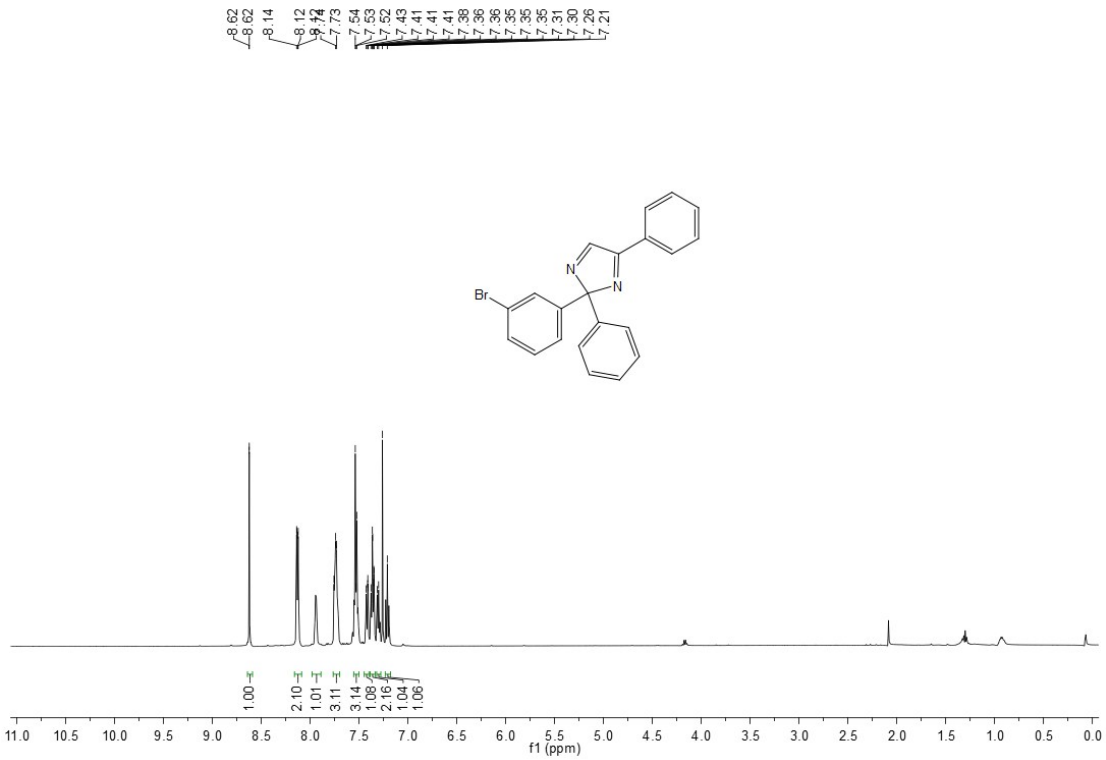
^{1}H NMR and ^{13}C NMR of 2,2,4,5-tetraphenyl-2*H*-imidazole (3bi)

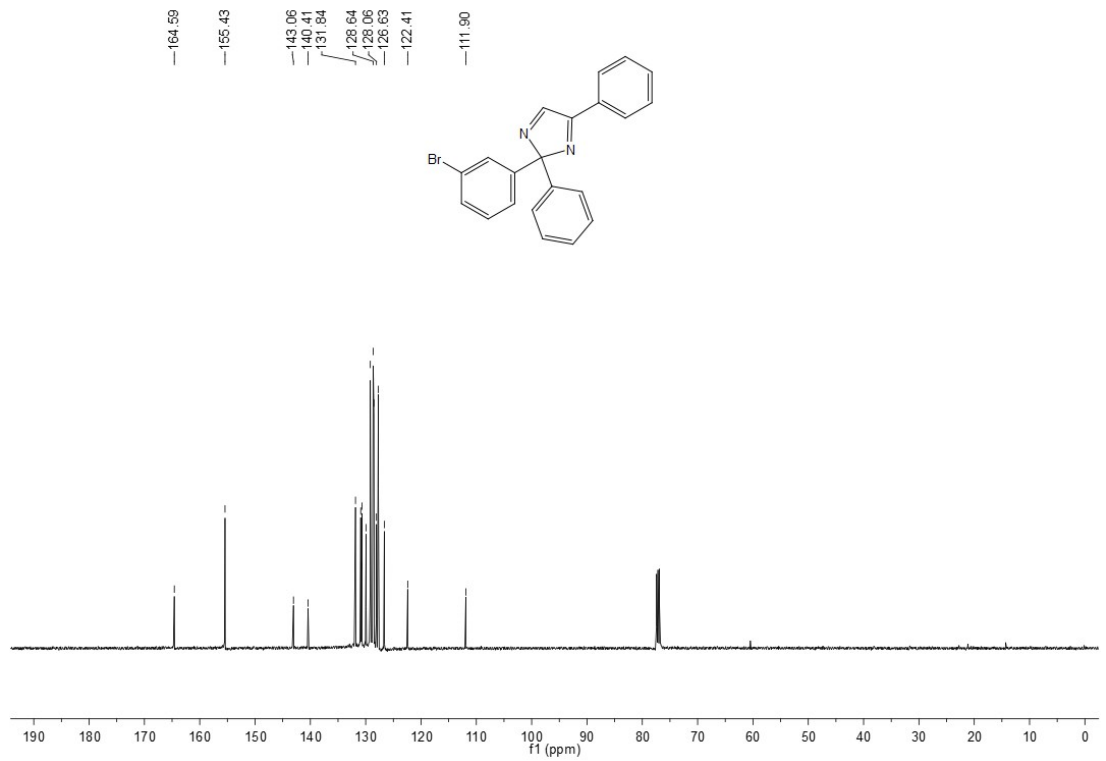


^{1}H NMR and ^{13}C NMR of 2-(3-bromophenyl)-2-methyl-4-phenyl-2*H*-imidazole (3bj)

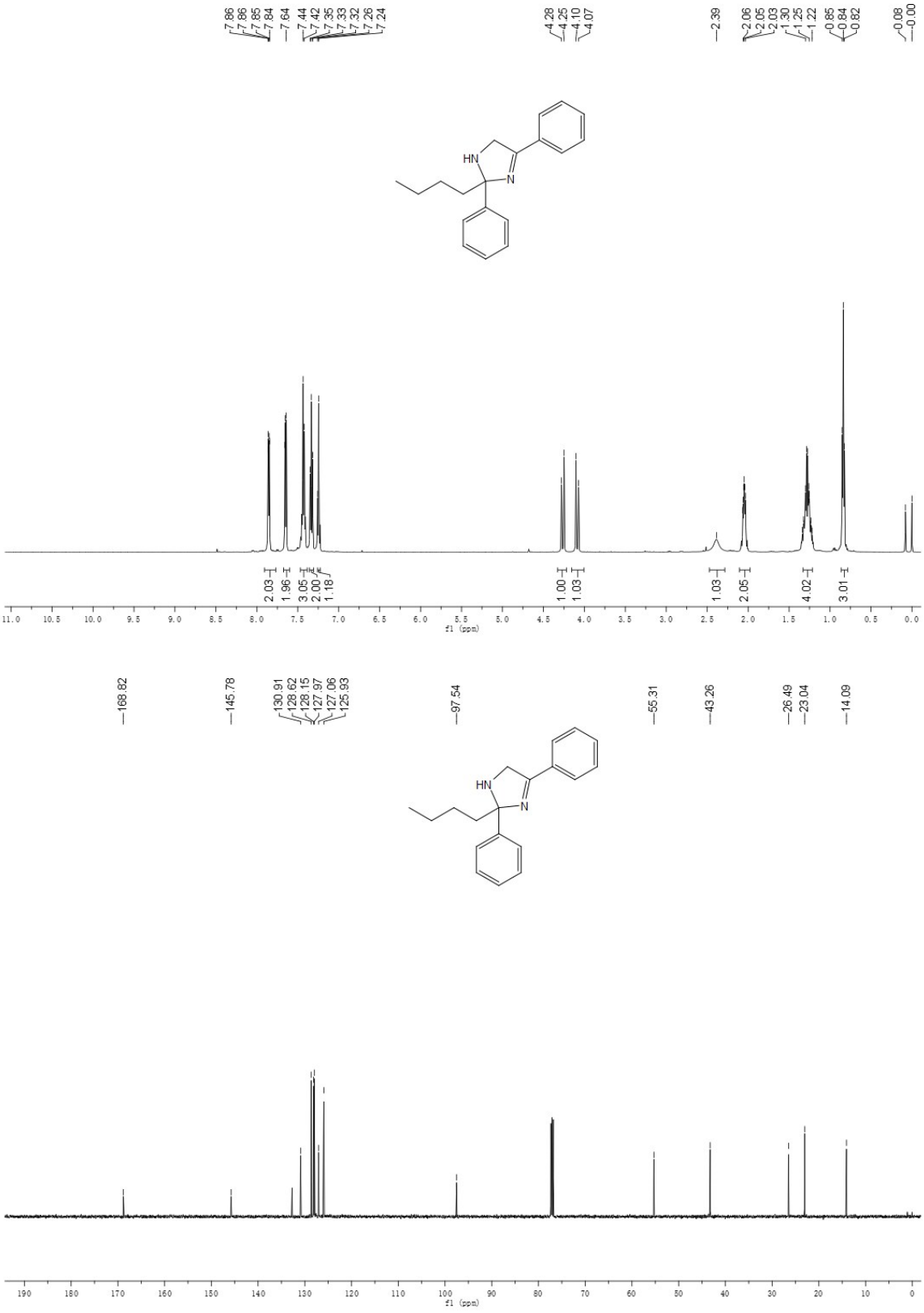


^{1}H NMR and ^{13}C NMR of 2-(3-bromophenyl)-2,4-diphenyl-2*H*-imidazole (3bk)

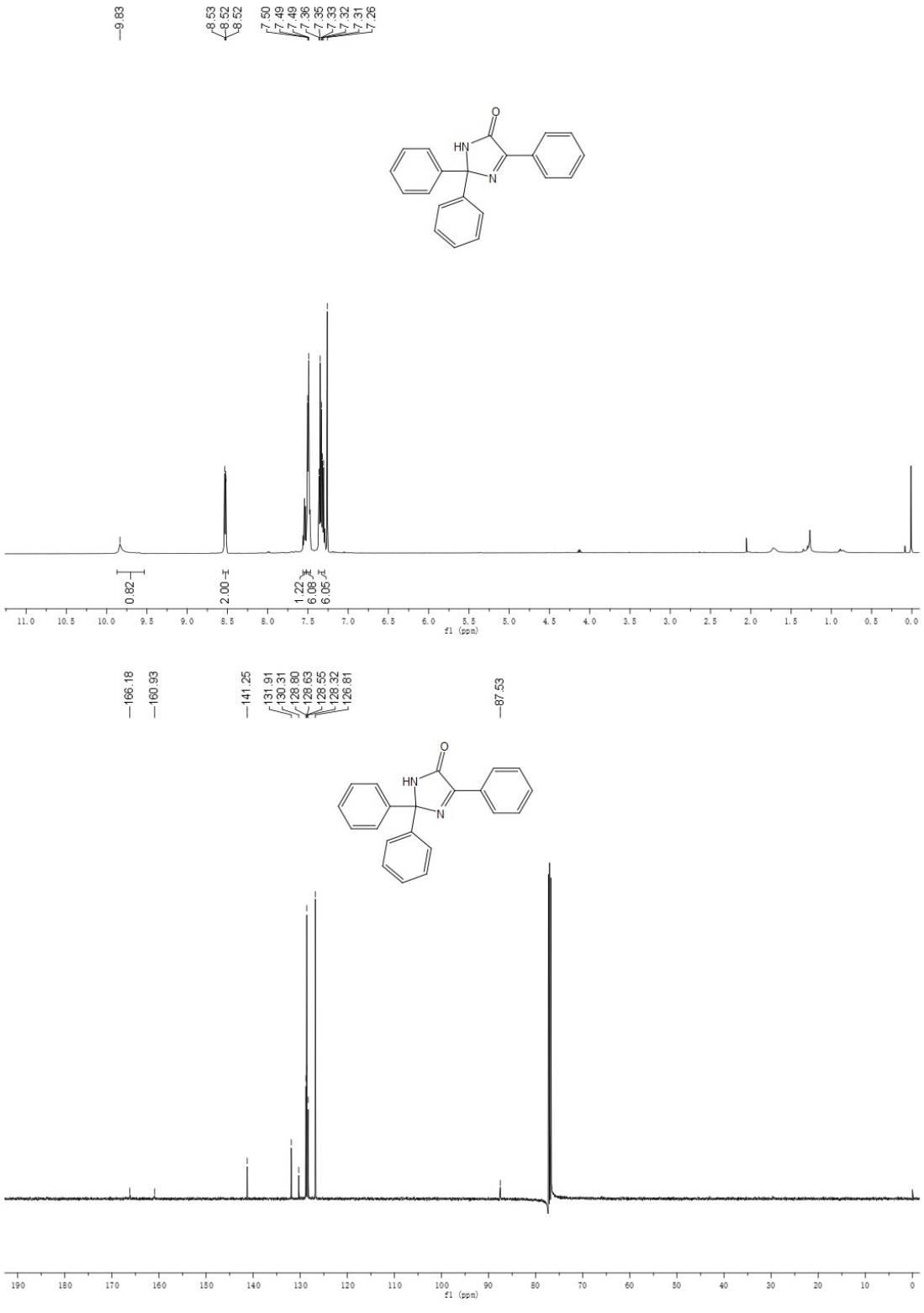




^{1}H NMR and ^{13}C NMR of 2-butyl-2,4-diphenyl-2,5-dihydro-1*H*-imidazole (5a)

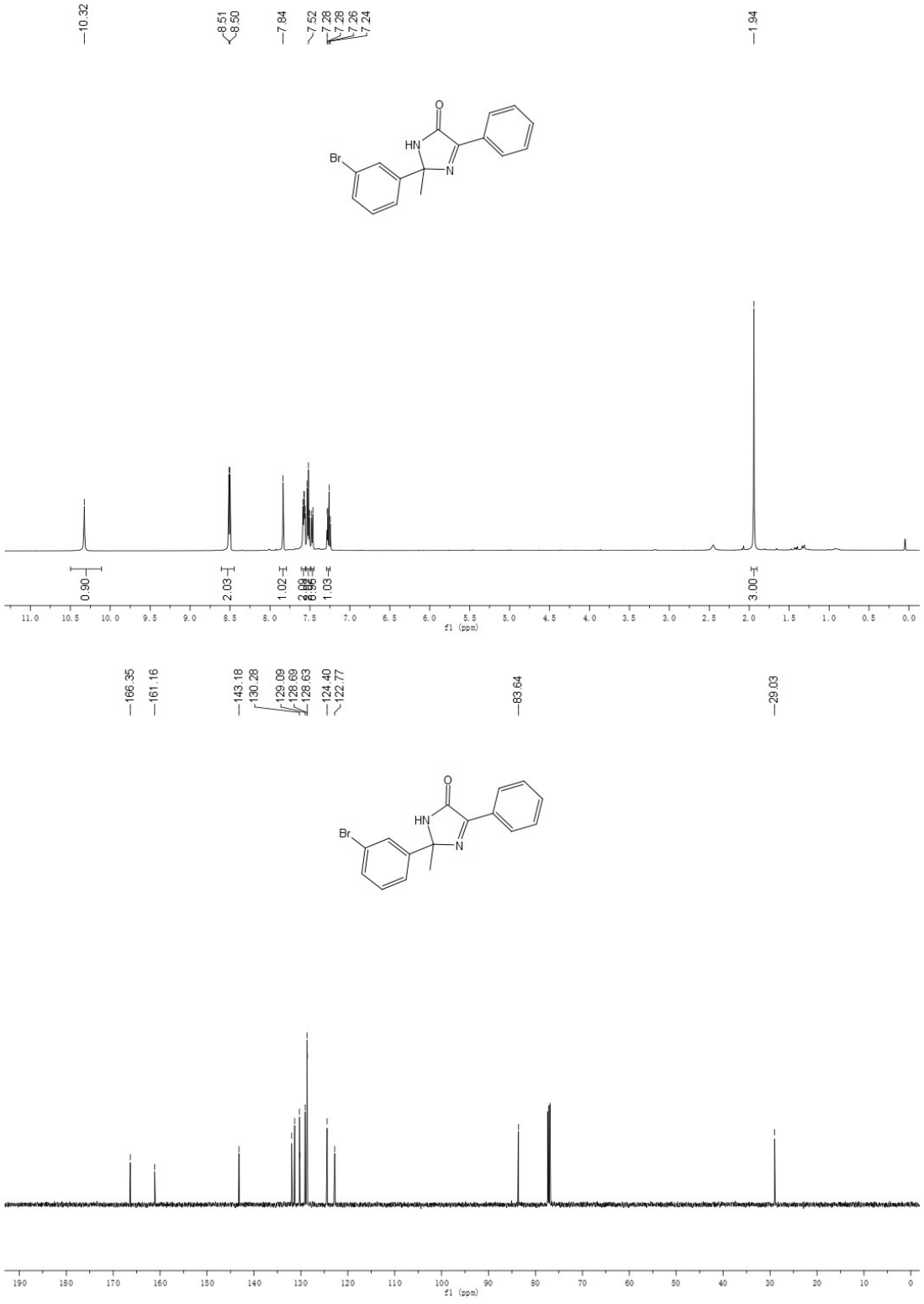


^{1}H NMR and ^{13}C NMR of 2,2,5-triphenyl-2,3-dihydro-4*H*-imidazol-4-one (6aa)

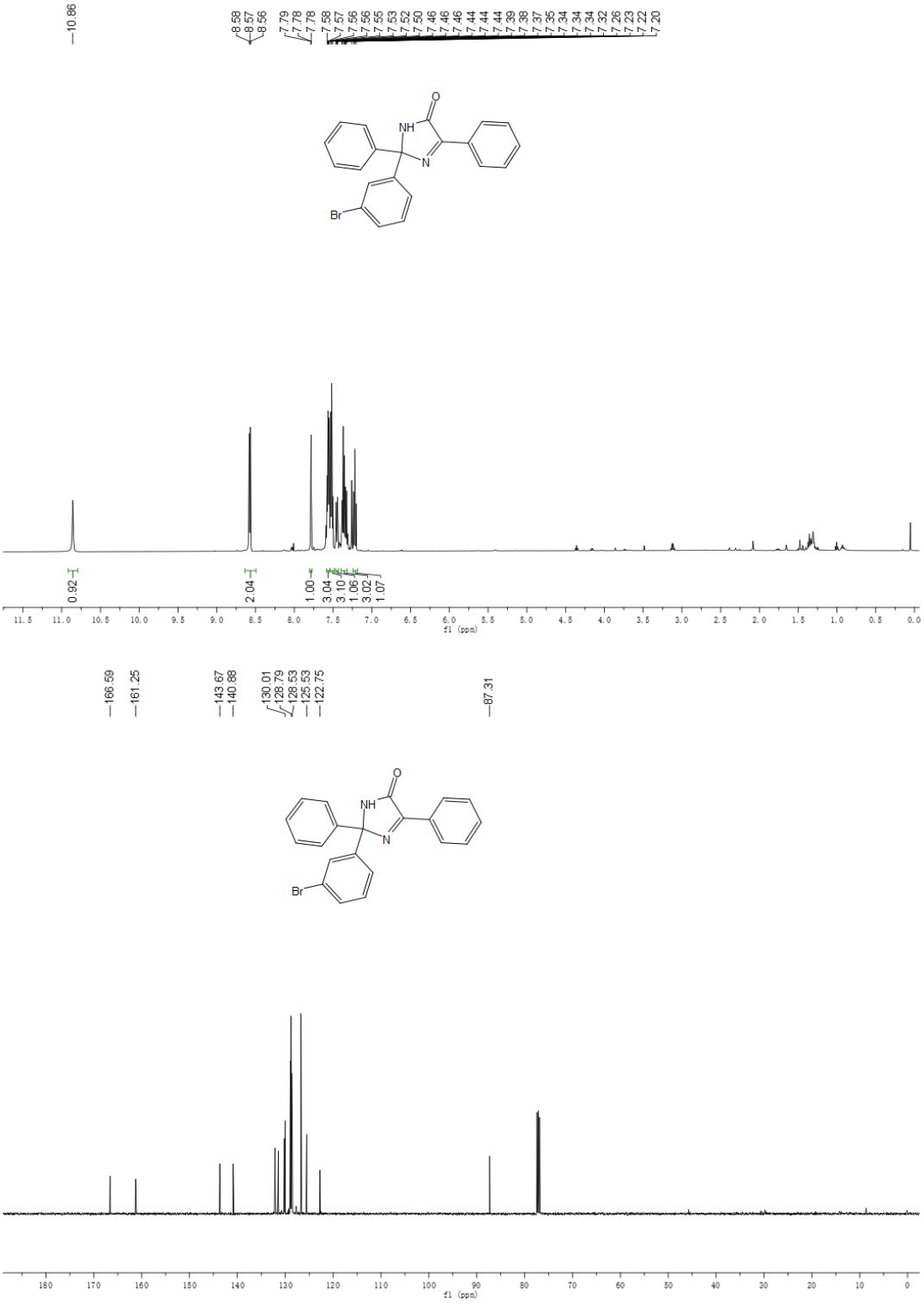


^{1}H NMR and ^{13}C NMR of 2-(3-bromophenyl)-2-methyl-5-phenyl-2,3-dihydro-4*H*-imidazol-4-one

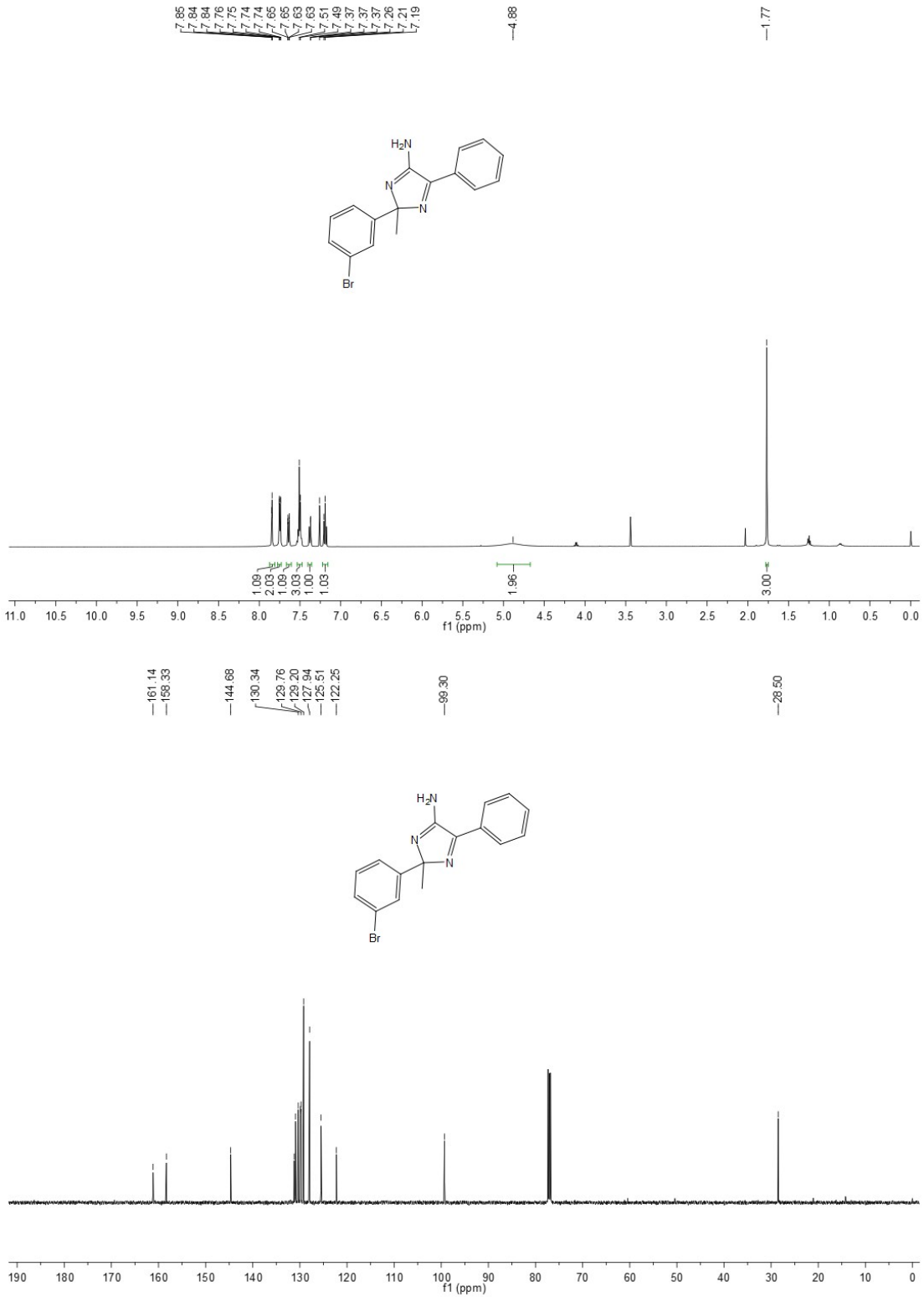
(6bj)



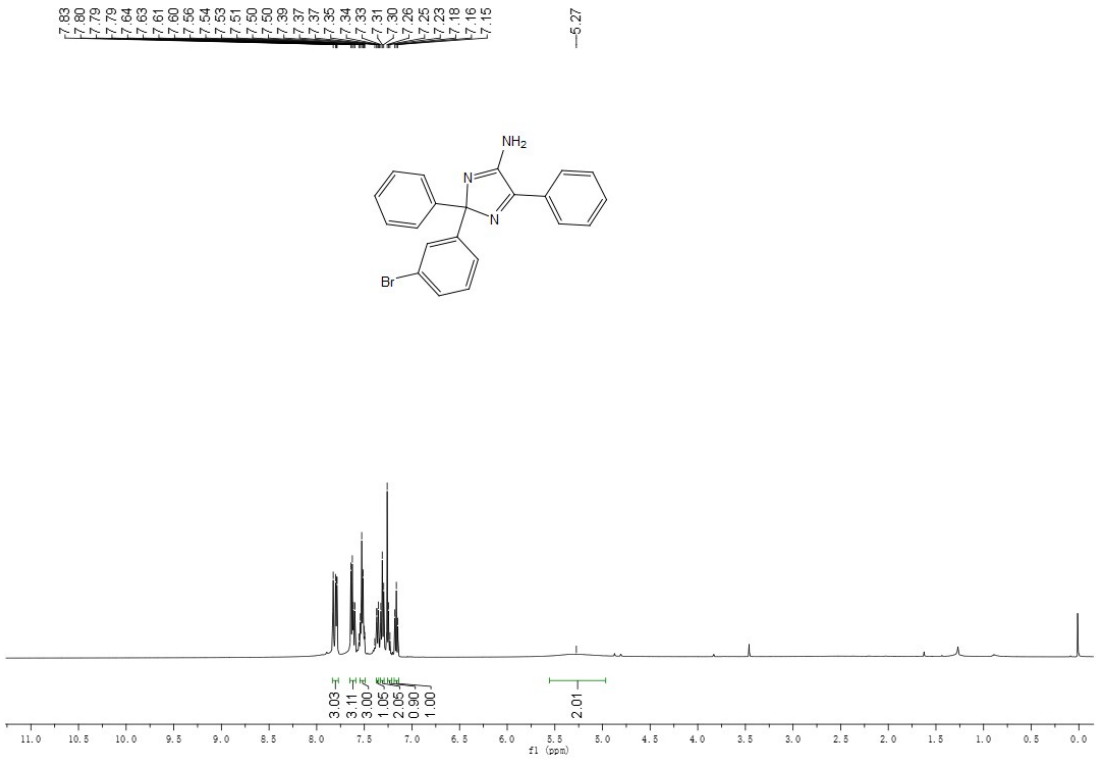
^{1}H NMR and ^{13}C NMR of 2-(3-bromophenyl)-2,5-diphenyl-2,3-dihydro-4*H*-imidazol-4-one (6bk)

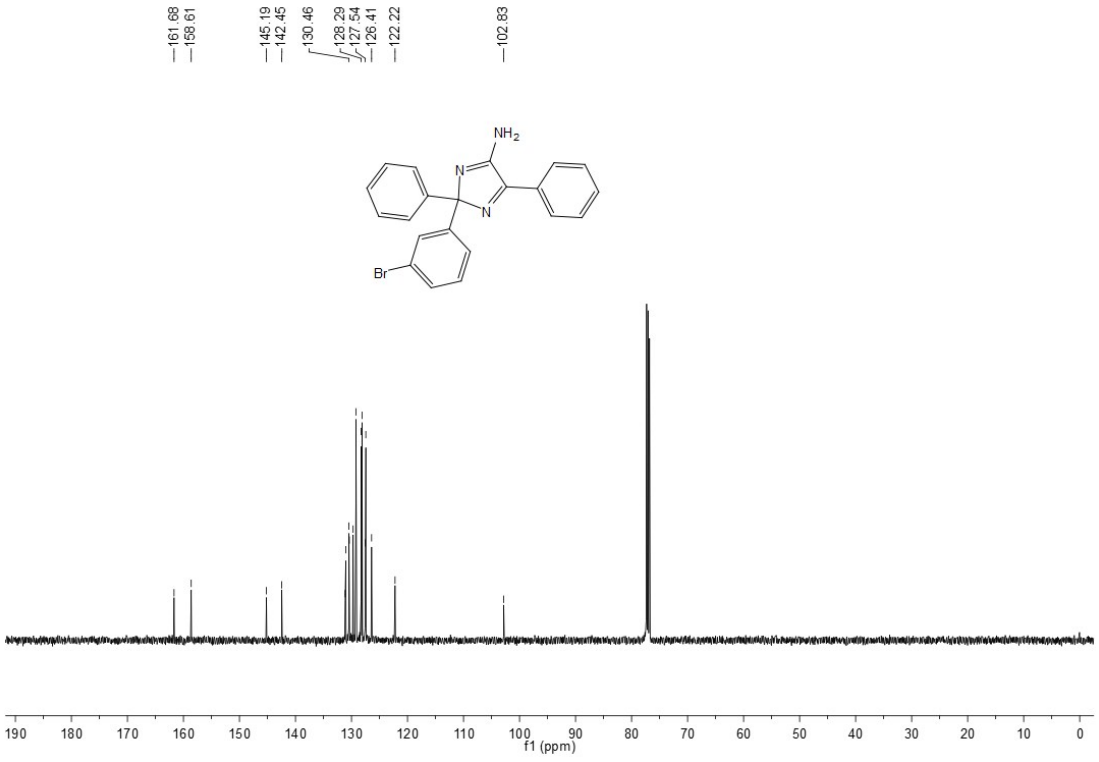


^{1}H NMR and ^{13}C NMR of 2-(3-bromophenyl)-2-methyl-5-phenyl-2*H*-imidazol-4-amine (7bj)

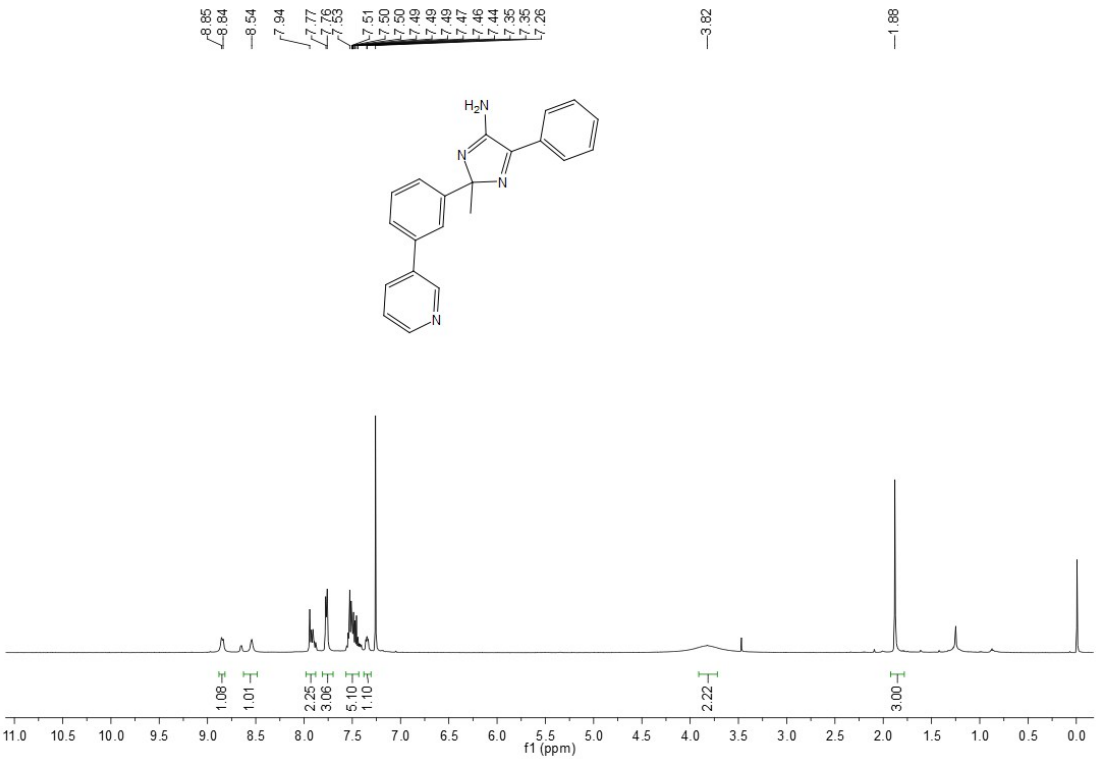


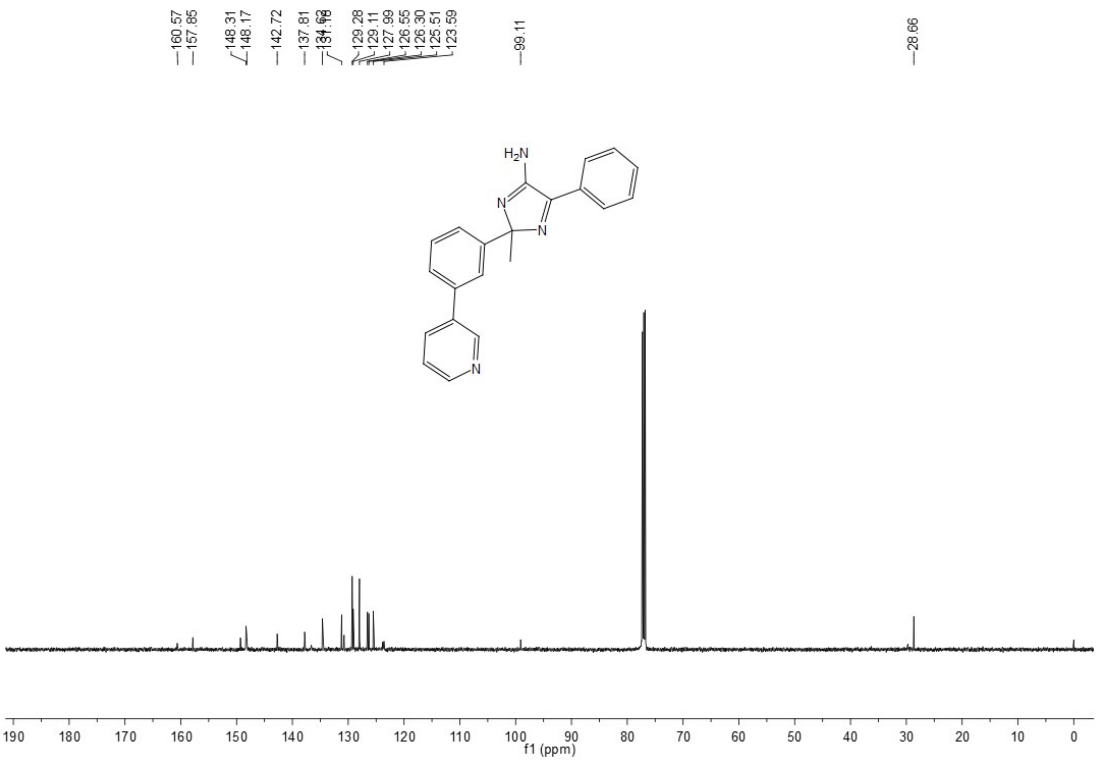
^{1}H NMR and ^{13}C NMR of 2-(3-bromophenyl)-2,5-diphenyl-2*H*-imidazol-4-amine (7bk)



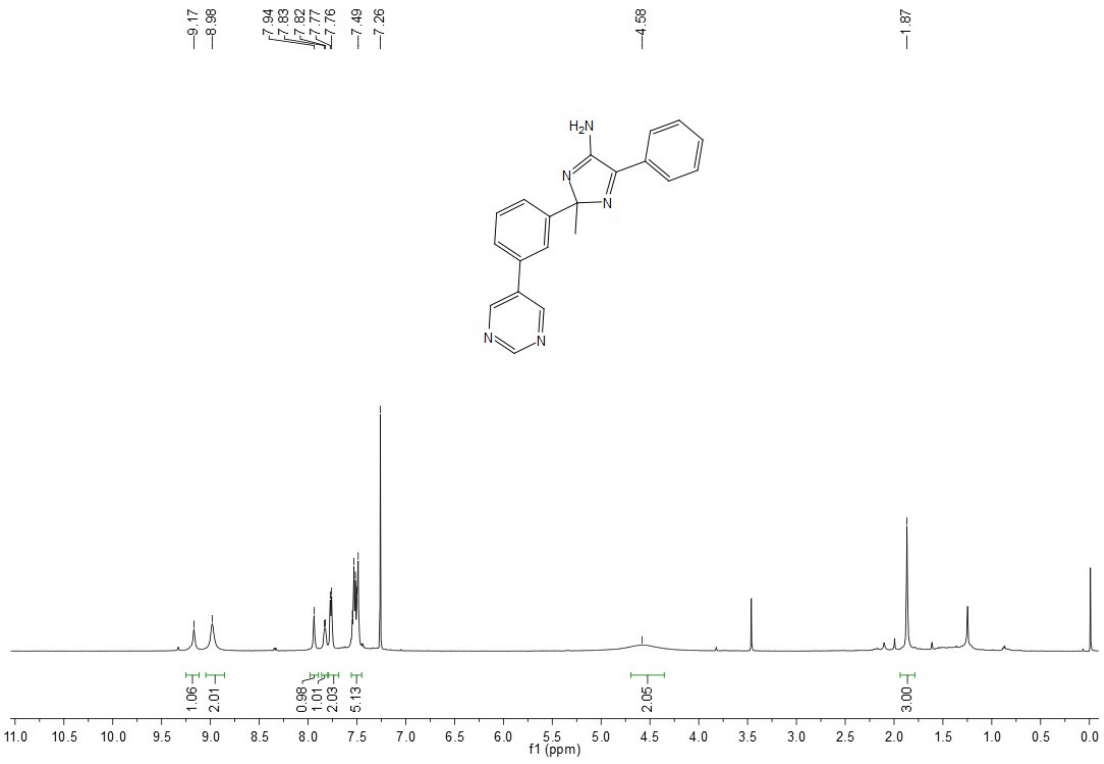


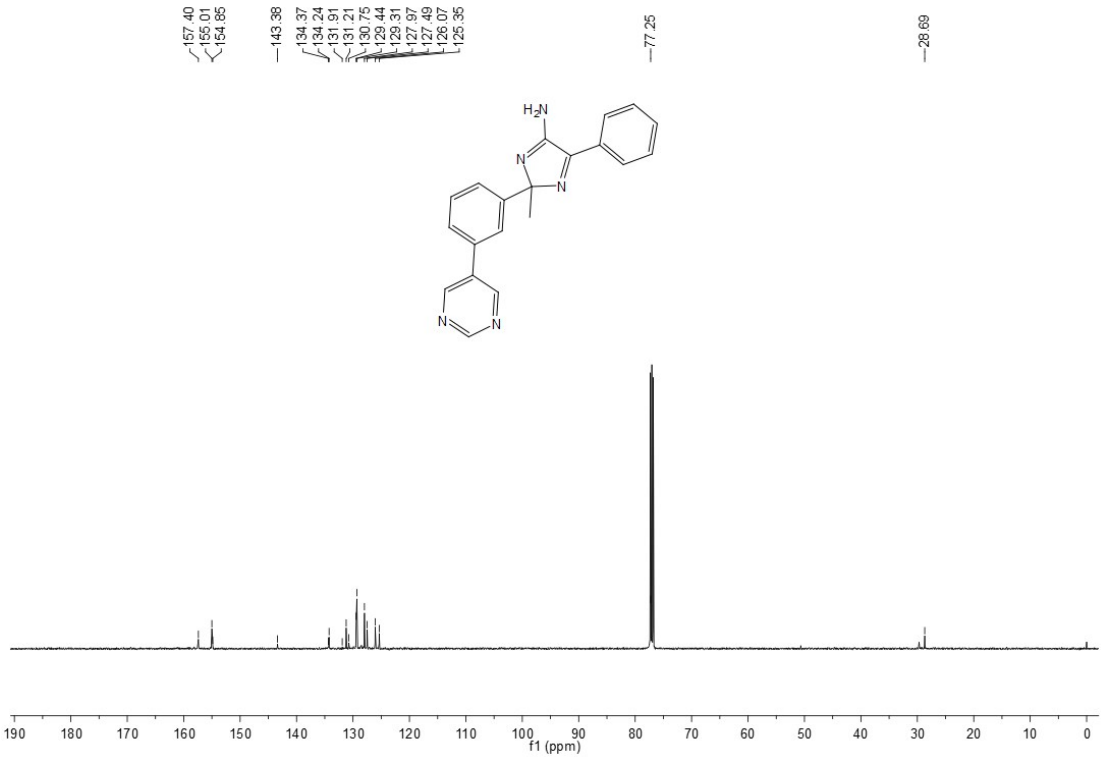
^{1}H NMR and ^{13}C NMR of 2-methyl-5-phenyl-2-(3-(pyridin-3-yl)phenyl)-2*H*-imidazol-4-amine (8a)


8.85
8.84
8.54
7.94
7.77
7.76
7.53
7.51
7.50
7.50
7.49
7.49
7.49
7.47
7.46
7.44
7.35
7.35
7.26
3.82
1.88
H2N
N
N
N
1.08
1.01
2.25
3.06
5.10
1.10
2.22
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

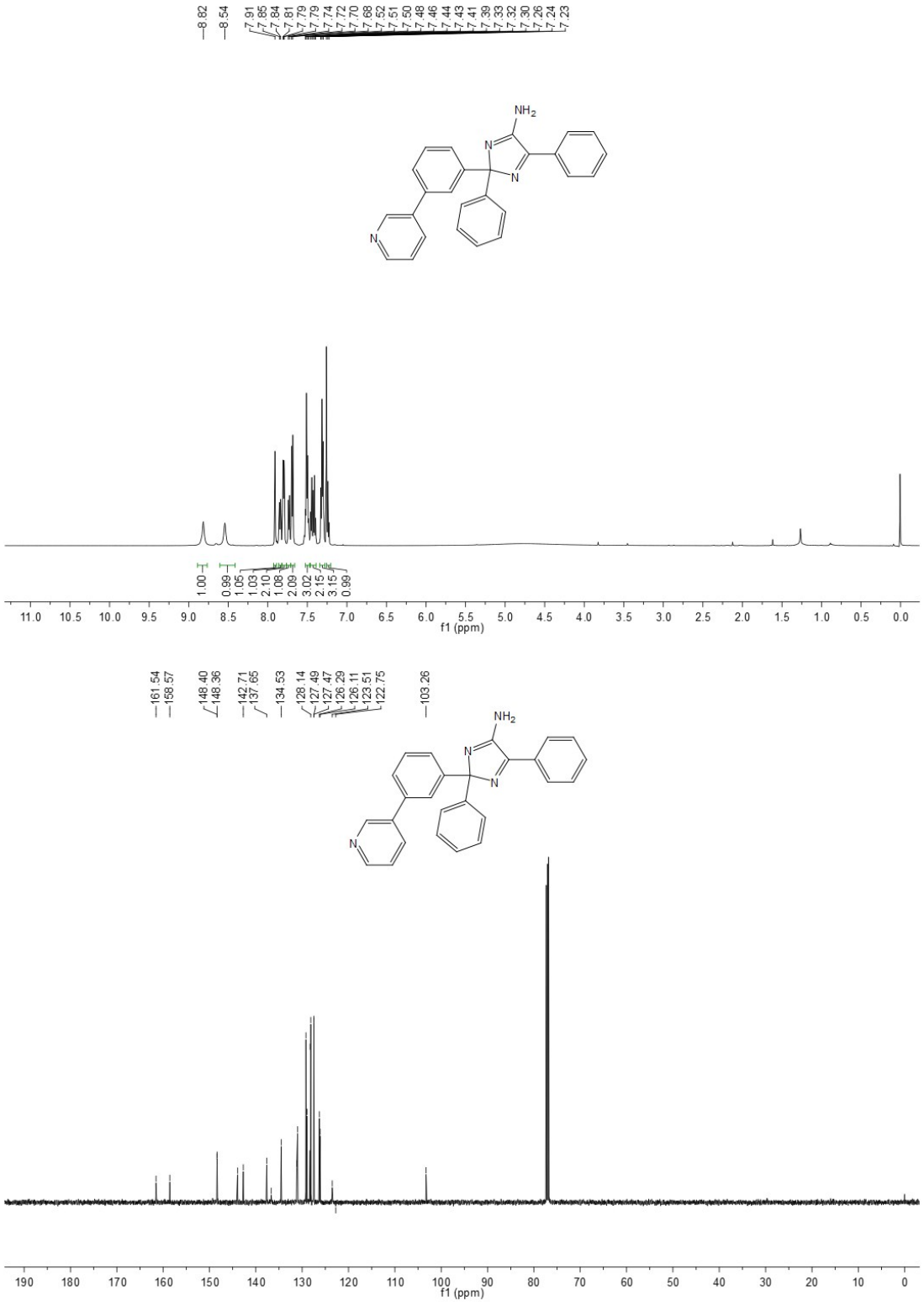

160.57
157.85
148.31
148.17
142.72
137.81
129.28
129.11
127.99
126.55
126.30
125.51
123.59
99.11
28.66
H2N
N
N
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR and ^{13}C NMR of 2-methyl-5-phenyl-2-(3-(pyrimidin-5-yl)phenyl)-2*H*-imidazol-4-amine (8b)

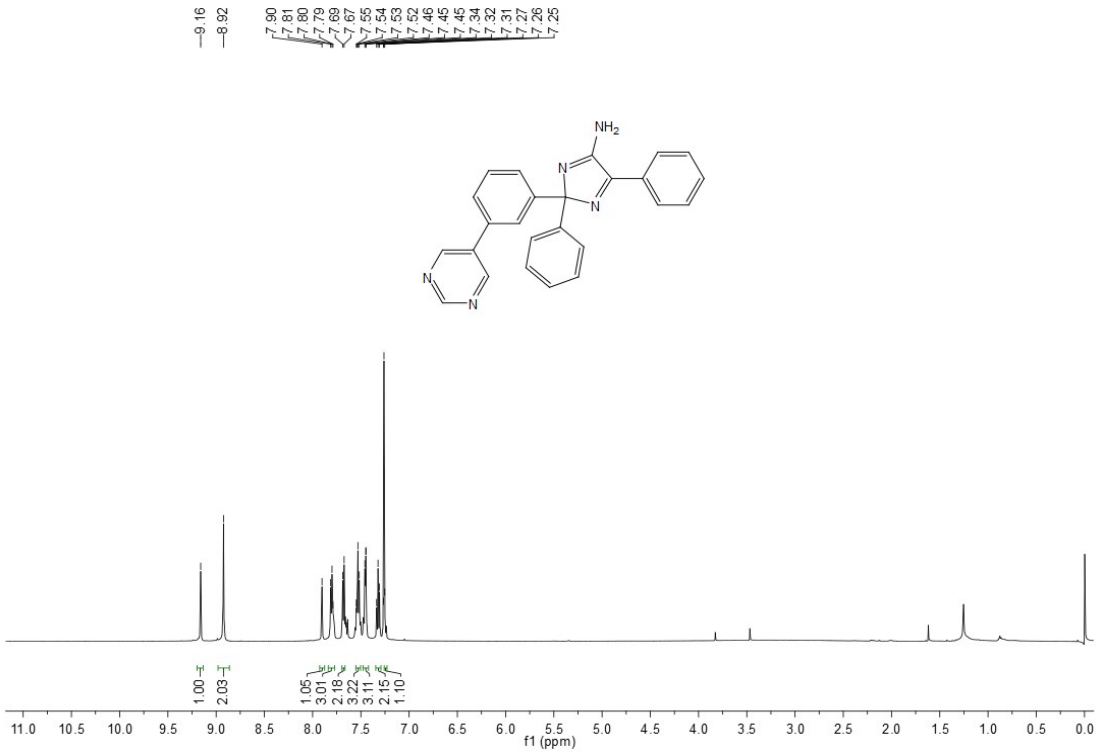


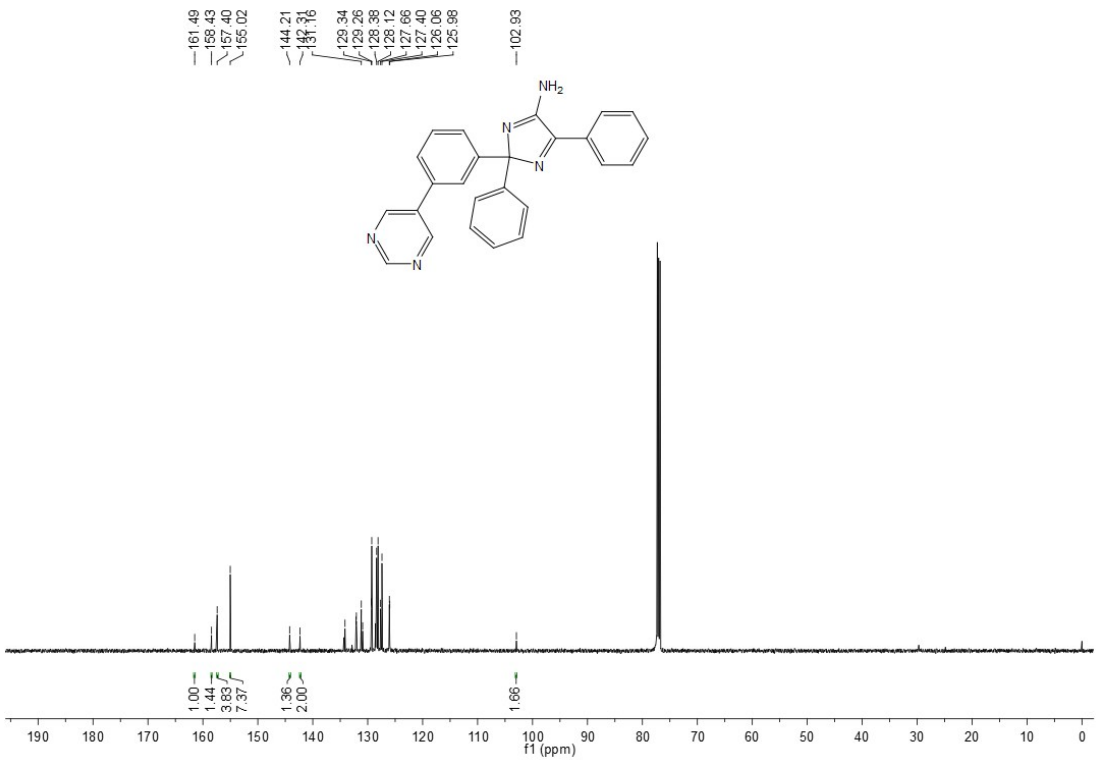


^{1}H NMR and ^{13}C NMR of 2,5-diphenyl-2-(3-(pyridin-3-yl)phenyl)-2*H*-imidazol-4-amine (8c)



^{1}H NMR and ^{13}C NMR of 2,5-diphenyl-2-(3-(pyrimidin-5-yl)phenyl)-2*H*-imidazol-4-amine (8d)

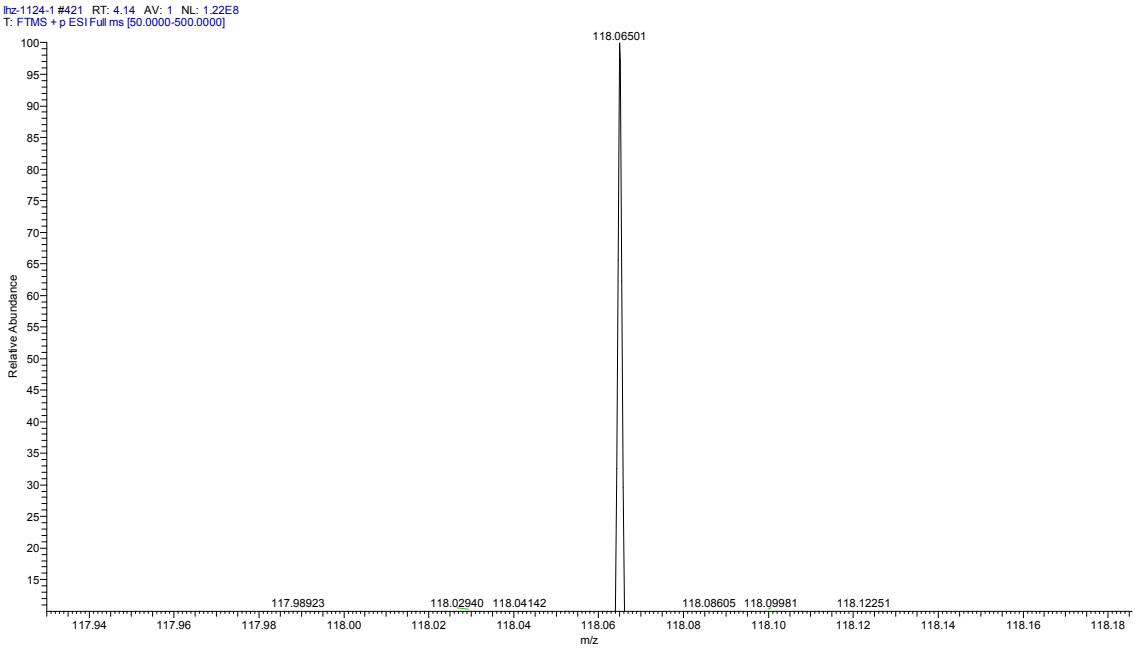




J. Copies of HRMS (ESI) of 4a and 5aa

HRMS (ESI) of 3-phenyl-2*H*-azirine 4a

calcd for C_8H_8N $[M+H]^+$, 118.0651; found 118.0650.



HRMS (ESI) of 2,2,4-triphenyl-2,5-dihydro-1*H*-imidazole 5aa

calcd for $C_{21}H_{19}N_2$ $[M+H]^+$, 299.1543; found 299.1532