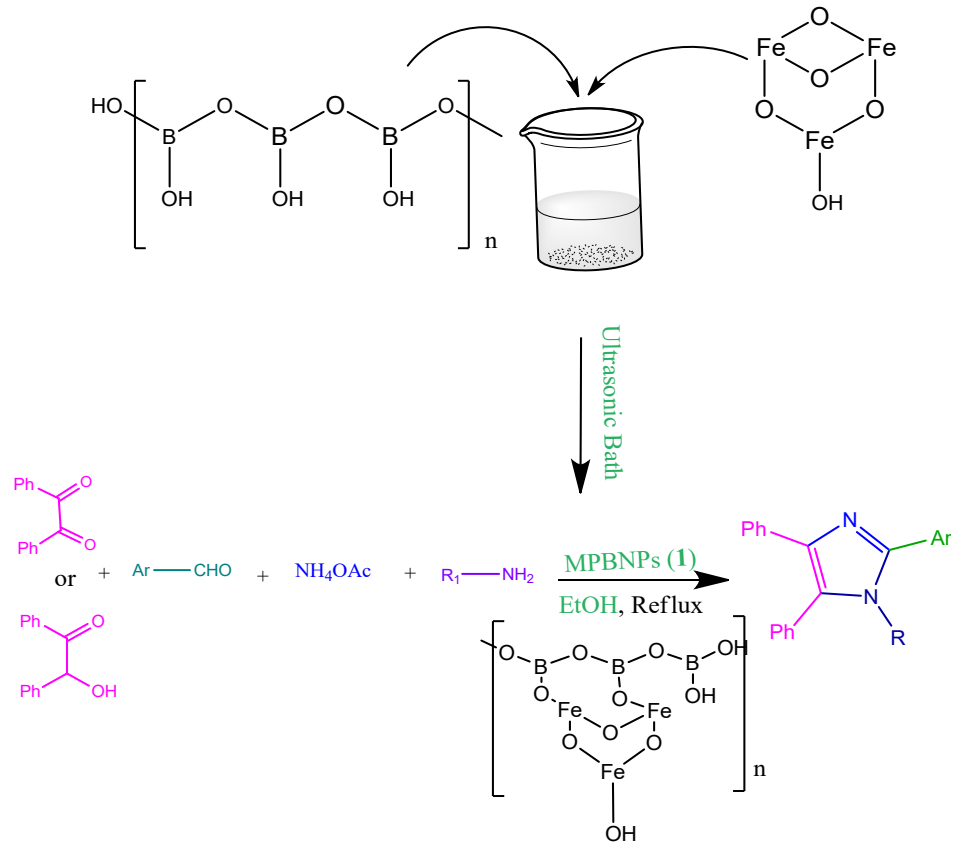
Electronic Supporting Information

Magnetic polyborate as a green and efficient catalyst for one-pot tetra-component synthesis of highly substituted imidazole derivatives

Alireza Malihishoja, Mohammad G. Dekamin*, Mohammad Eslami

[a]*Pharmaceutical and Heterocyclic Compounds Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran, 16846-13114, Iran.*

**E-mail: mdekamin@iust.ac.ir*



Scheme 1. Schematic representation of synthesis of tetra-substituted imidazoles in presence of MPBNPs catalyst (**1**).

Preparation method of polyborate

10.0 g of boric acid was heated at 200 °C while stirring for 5 h to form polyborate. Then, the obtained polyborate was converted into nanoscale by using ball milling for 20 min, and the milling frequency was set at 20 Hz. The structure of the obtained polyborate nanoparticles was confirmed by using FT-IR technique.

Preparation method of magnetic polyborate (MPBNPs, 1)

MPBNPs (**1**) were prepared from co-precipitation of ferrous and ferric salts with polyborate nanoparticles. First, $FeCl_3.6H_2O$ (4.0 mmol, 1.08 g) and $FeCl_2.4H_2O$ (2.0 mmol, 0.40 g) were dissolved in 100 ml of distilled water. Then, pH of the obtained mixture was adjusted into 4.0 from 1.5 by addition of NaOH (1.0 M). Next, another mixture containing 100 mg of polyborate dispersed in 20 ml deionized water under ultrasonic was poured into the obtained mixture by vigorous stirring. After 30 min mixing, pH of the mixture was adjusted into 10.0 using NaOH (1.0 M). Afterward, the obtained mixture was stirred for 1 hour and the nanoparticles of magnetic polyborate were washed with double distilled water (2.0 ml) three times and finally separated by using an external magnet and put into an oven at 50 °C to dry for 5 h.

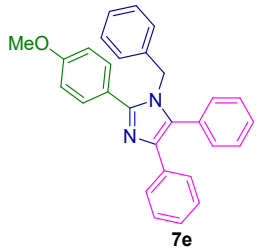
General procedure for the prepration of 1,2,4,5-tetrasubstituted imidazoles 7a-p catalyzed by the MPBNPs

10.0 mg of MPBNPs catalyst (**1**) was added to a round-bottom flask containing benzyl or benzoin (**2** or **3**, 1.0 mmol), aldehyde (**4a-p**, 1.0 mmol), primary amine (**6a**, 1.0 mmol) and ammonium acetate (**5**, 1.75 mmol) in EtOH (2.5 ml) and the obtained mixture was heated under reflux conditions. After completion of the reaction monitored by TLC, additional EtOH (2-3 ml) was used to dissolve the products and remain the insoluble MPBNPs (**1**). The obtained mixture was heated and filtered off to separate the magnetic catalyst (**1**) using an external magnet. Distilled water was added dropwise to the filtrate at 50 °C to afford pure crystals of the desired products **7a-p**. The separated magnetic catalyst (**1**) was suspended in EtOH (2 ml) and filtered off three times and then dried in an oven at 50 °C for 5 h before using in the next runs.

Spectral data of the selected derivatives of imidazoles (7e, 7h, 7k, 7l, 7m, 7r, 7w):

1-Benzyl-2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (**7e**):

Mp: 144-147 °C; White solid; FTIR (KBr; cm^{-1}): 3026, 2929, 2361, 1605, 1530, 1482, 1449; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.62 – 7.56 (m, 3H), 7.42 – 7.10 (m, 12H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.82 (dd, *J* = 7.7, 1.7 Hz, 2H), 5.09 (s, 2H), 3.88 – 3.76 (m, 3H).



7e

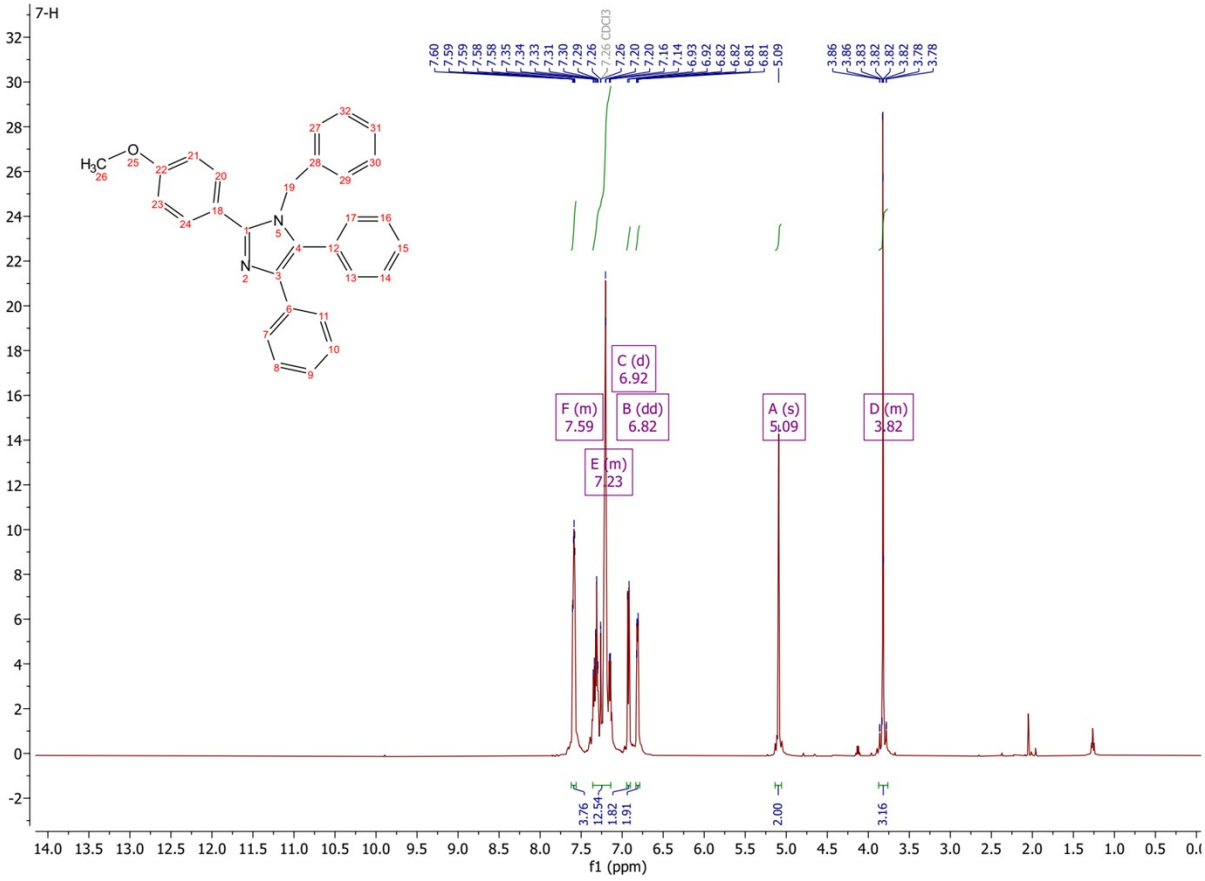


Figure S1. ^{1}H NMR spectra of 1-benzyl-2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (**7e**).

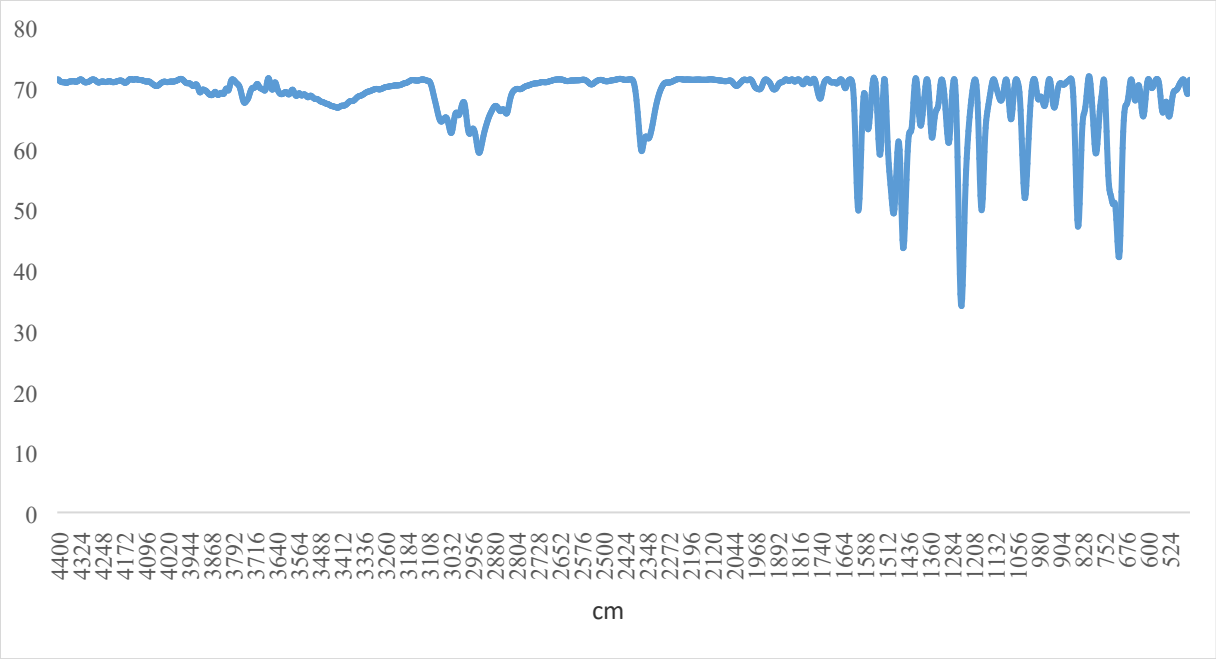
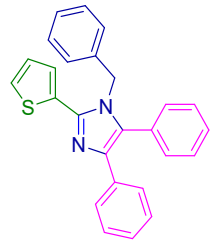


Figure S2. FT-IR spectra of 1-benzyl-2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (**7e**).

1-Benzyl-4,5-diphenyl-2-(thiophen-2-yl)-1*H*-imidazole (**7h**):

Mp: 160-161 °C; Yellow solid; FTIR (KBr; cm^{-1}): 3427, 3050, 2376, 1598, 1496, 1444; ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.61 (dt, J = 7.0, 1.5 Hz, 1H), 7.50 – 7.39 (m, 6H), 7.34 – 7.12 (m, 8H), 7.06 (m, 1H), 6.92 (d, J = 7.6 Hz, 2H), 5.26 (s, 2H).



7h

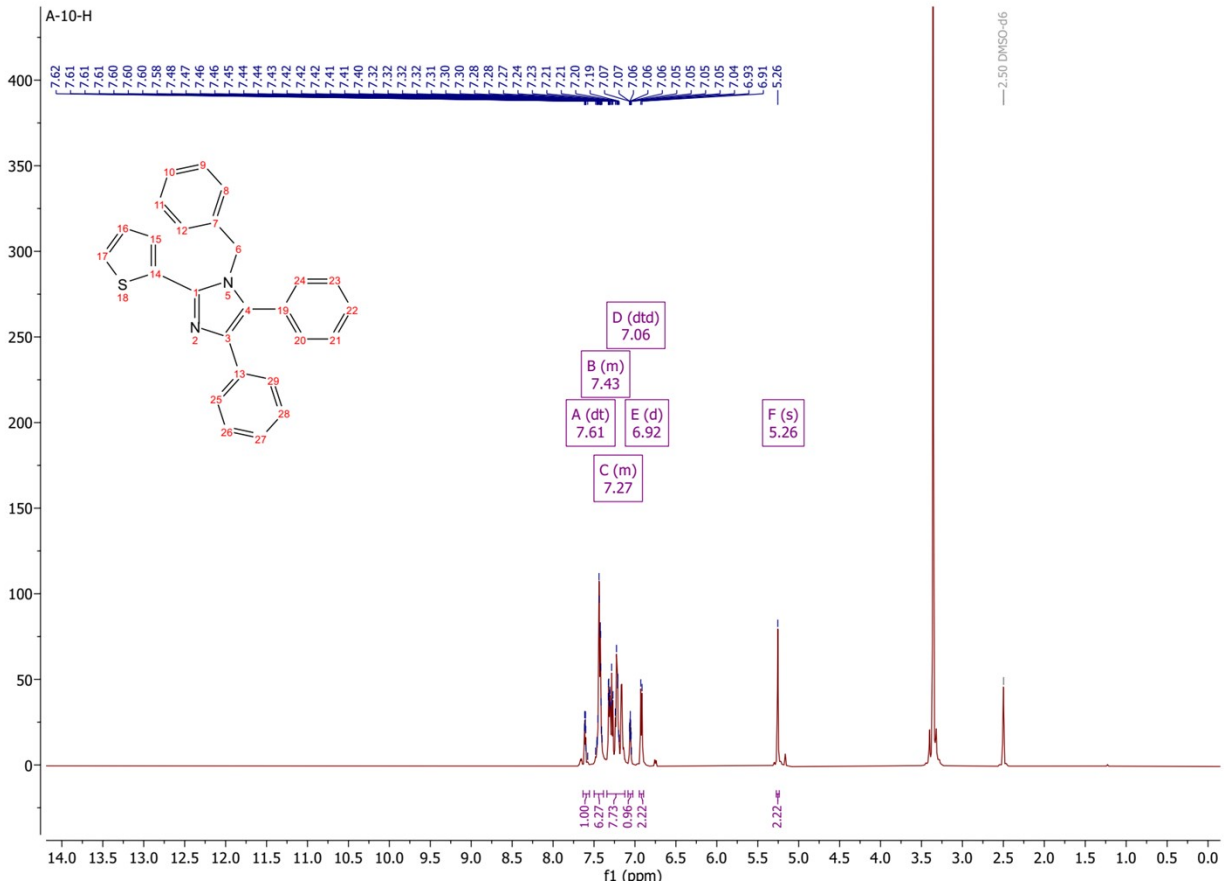


Figure S3. ^{1}H NMR spectra of 1-benzyl-4,5-diphenyl-2-(thiophen-2-yl)-1*H*-imidazole (**7h**).

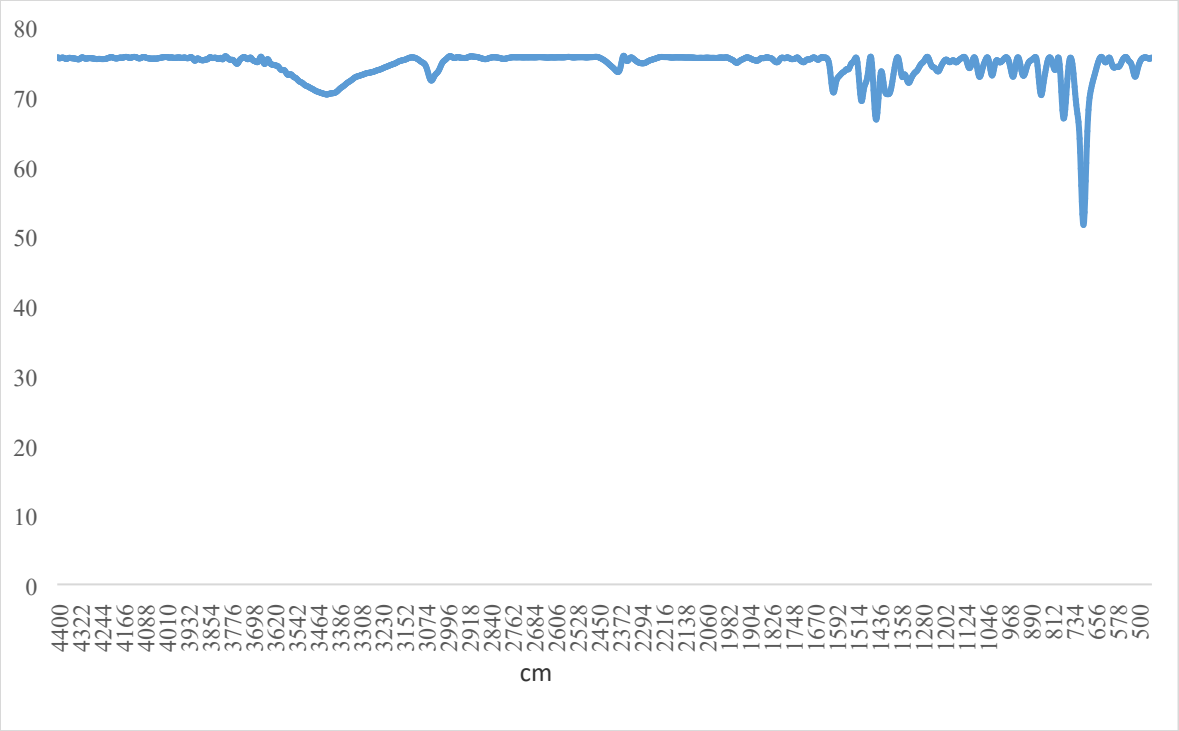
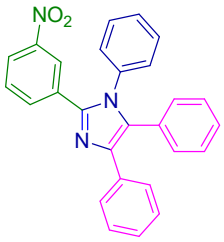


Figure S4. FT-IR spectra of 1-benzyl-4,5-diphenyl-2-(thiophen-2-yl)-1*H*-imidazole (**7h**).

2-(3-Nitrophenyl)-1,4,5-triphenyl-1*H*-imidazole (**7k**):

Mp: 258-259 °C; Yellow solid; FTIR (KBr; cm^{-1}): 3427, 1525, 1344, 766, 697; ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 8.96 (s, 1H), 8.52 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.18 – 8.10 (m, 1H), 7.78 (td, J = 8.2, 1.7 Hz, 1H), 7.62 – 7.19 (m, 14H).



7k

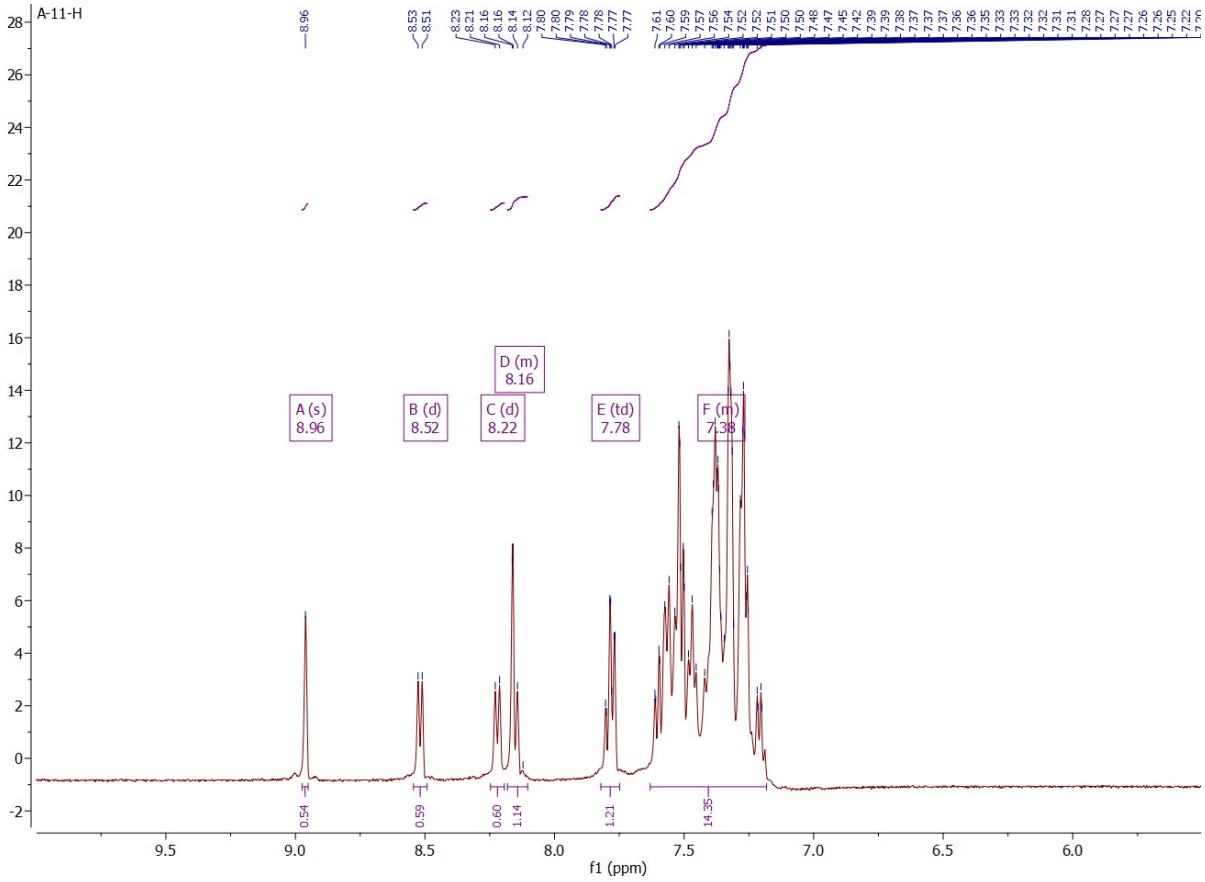


Figure S5. ^{1}H NMR spectra of 2-(3-nitrophenyl)-1,4,5-triphenyl-1*H*-imidazole (**7k**).

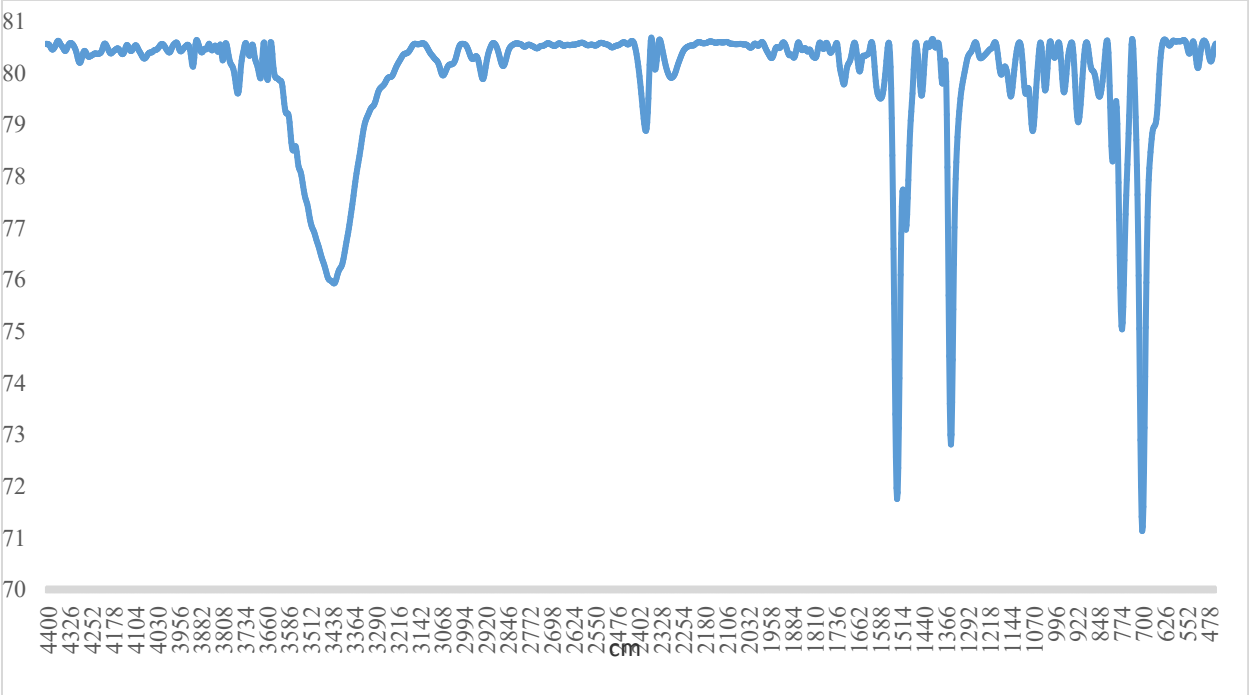


Figure S6. FT-IR spectra of 2-(3-nitrophenyl)-1,4,5-triphenyl-1*H*-imidazole (**7k**).

1,2,4,5-Tetraphenyl-1*H*-imidazole (**7l**):

Mp: 219-221 °C; White solid; FTIR (KBr; cm^{-1}): 3048, 2360, 1596, 1498, 770, 692; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.62 (s, 5H), 7.45 (s, 5H), 7.14 (s, 5H), 7.05 (s, 5H).

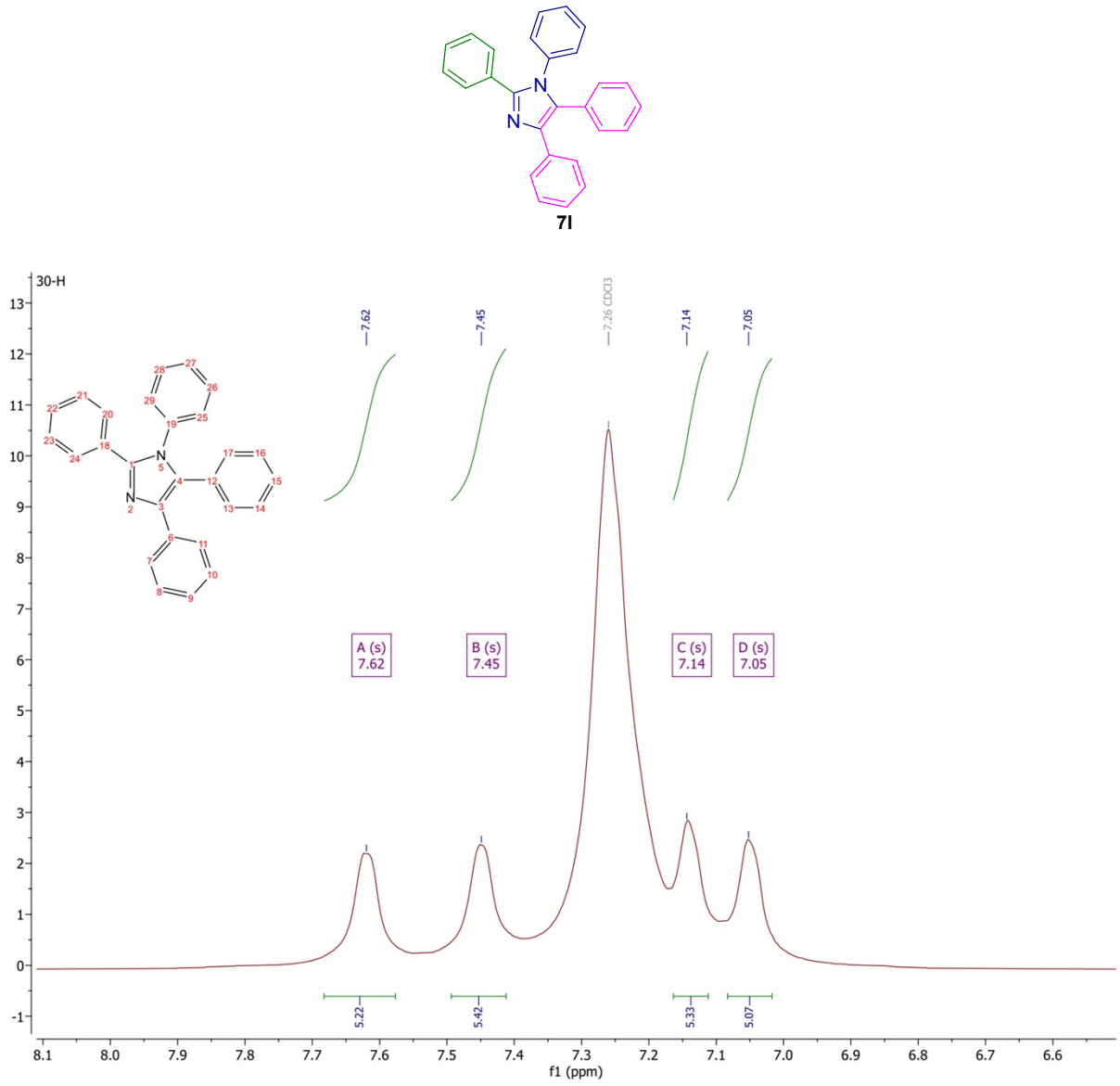


Figure S7. ^1H NMR spectra of 1,2,4,5-tetraphenyl-1*H*-imidazole (**7l**).

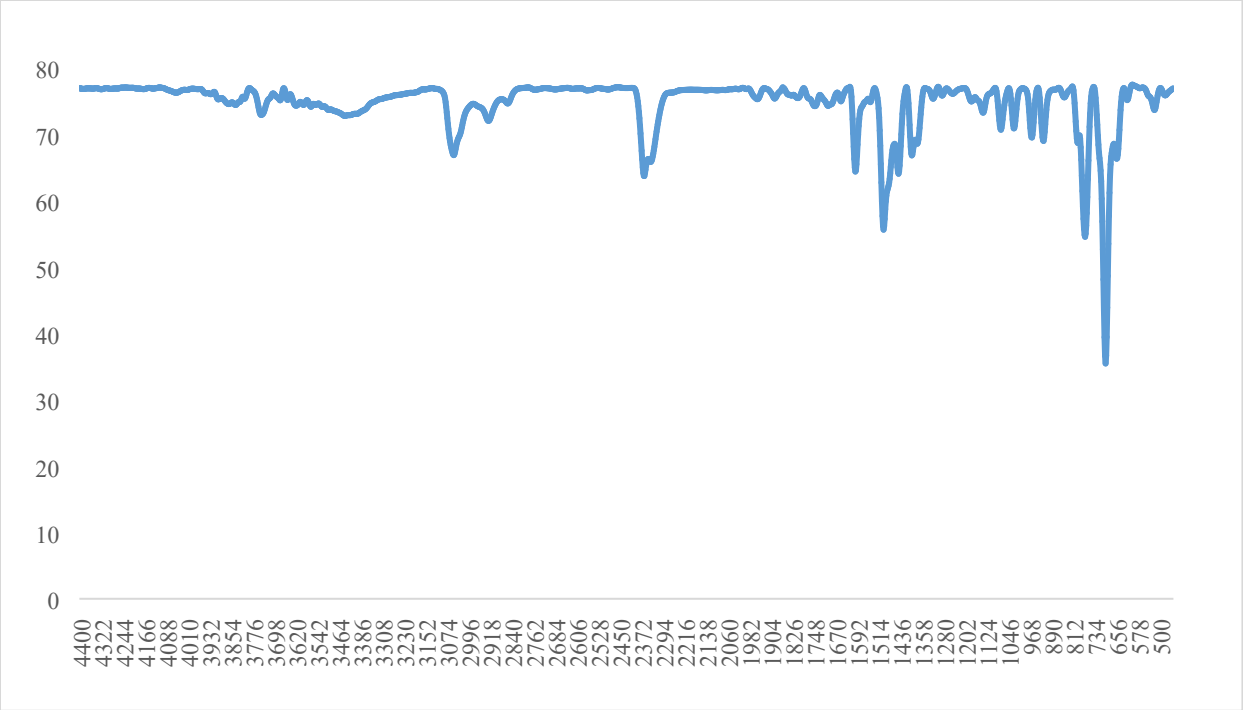
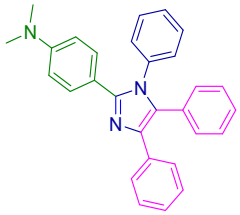


Figure S8. FT-IR spectra of 1,2,4,5-tetraphenyl-1*H*-imidazole (**7l**).

N,*N*-Dimethyl-4-(1,4,5-triphenyl-1*H*-imidazol-2-yl)aniline (**7m**):

Mp: 206-2027 °C; Brown solid; FTIR (KBr; cm^{-1}): 3422, 2926, 2364, 1722, 1612, 1488, 1442, 1370, 816, 694; ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.60 – 7.50 (m, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.35 – 7.30 (m, 6H), 7.21 (m, 10H), 6.57 (d, J = 8.5 Hz, 2H), 2.88 (s, 6H).



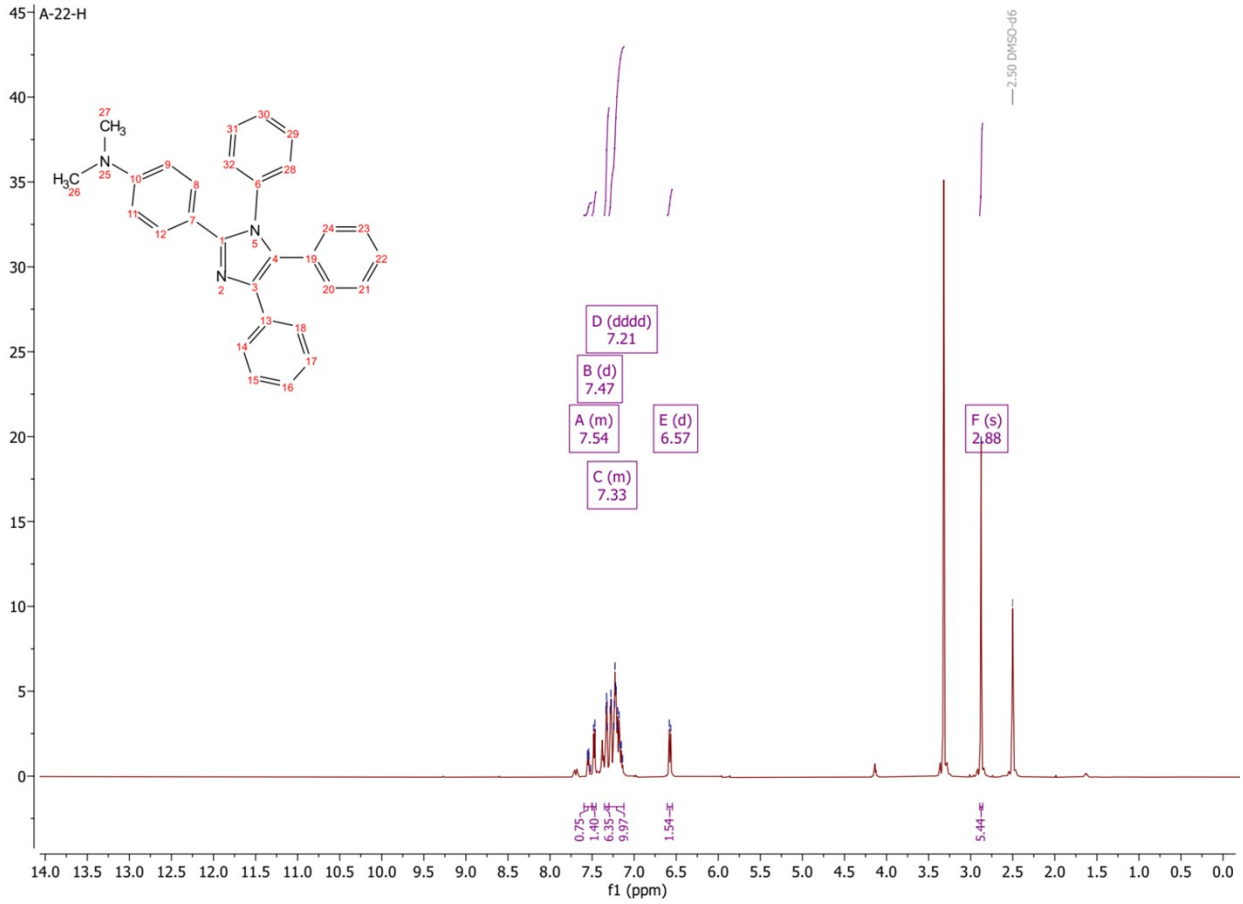


Figure S9. ^{1}H NMR spectra of *N*,*N*-dimethyl-4-(1,4,5-triphenyl-1*H*-imidazol-2-yl)aniline (**7m**).

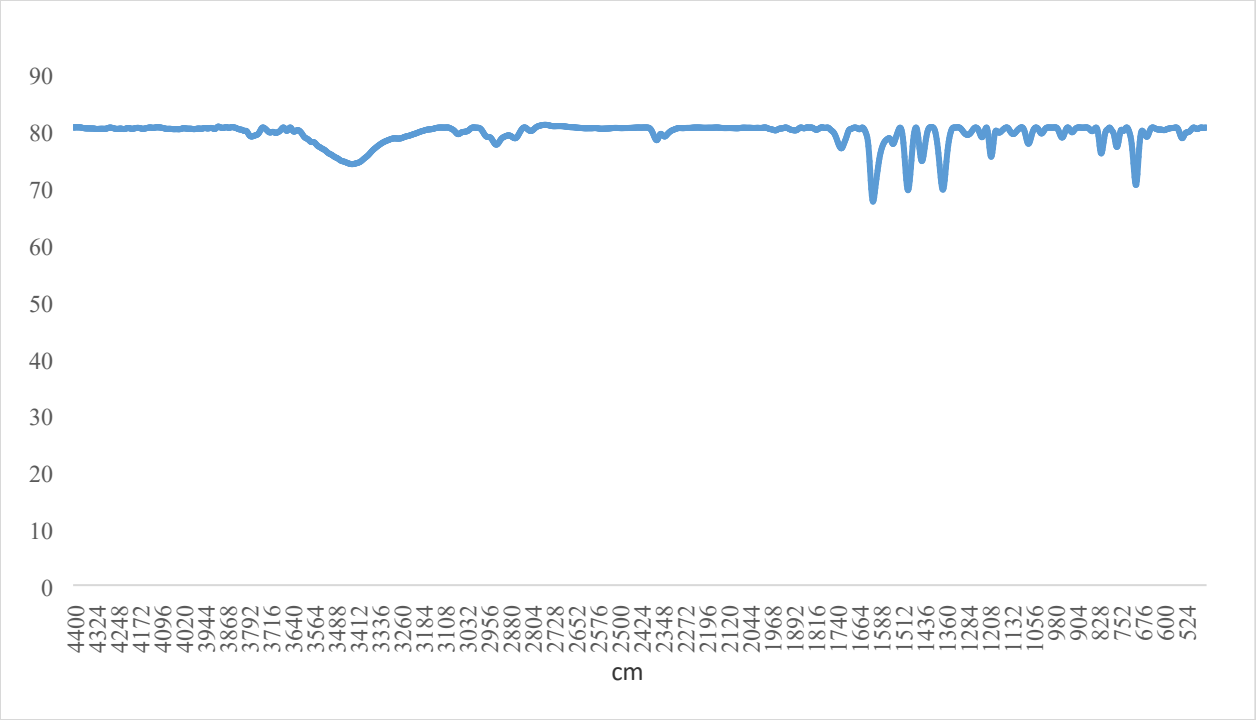
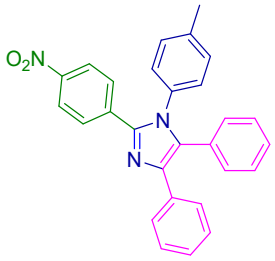


Figure S10. FT-IR spectra of *N*,*N*-dimethyl-4-(1,4,5-triphenyl-1*H*-imidazol-2-yl)aniline (**7m**).

2-(4-Nitrophenyl)-4,5-diphenyl-1-(*p*-tolyl)-1*H*-imidazole (**7r**):

Mp: 218-219 °C; Yellow solid; FTIR (KBr; cm^{-1}): 3032, 2922, 2852, 2366, 1532, 1352, 750, 694; ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.98 (s, 1H), 7.73 – 7.56 (m, 3H), 7.50 – 7.39 (m, 2H), 7.33 (dt, J = 6.0, 3.5 Hz, 3H), 7.27 – 7.21 (m, 4H), 7.20 – 7.14 (m, 1H), 7.03 (t, J = 10.5 Hz, 4H), 2.18 (s, 3H).



7r

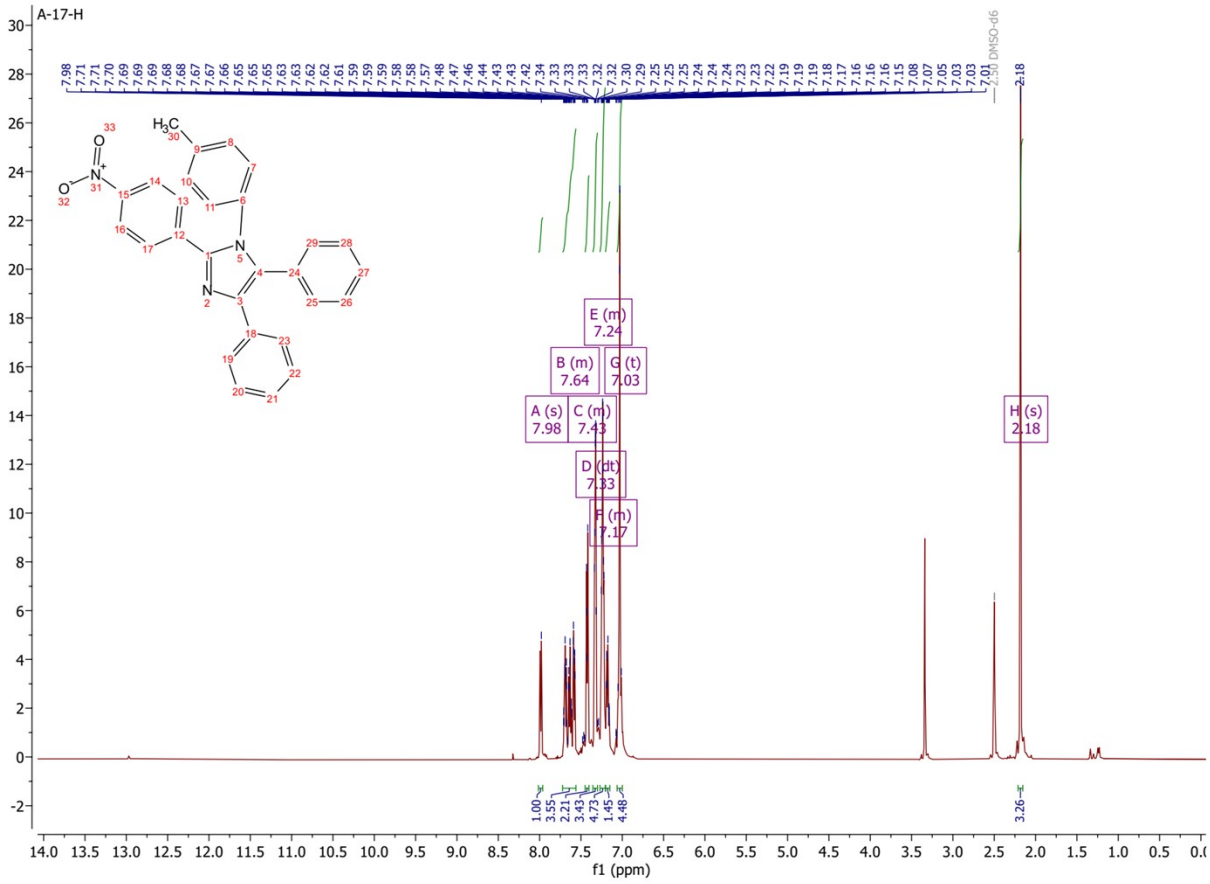


Figure S11. ^{1}H NMR spectra of 2-(4-nitrophenyl)-4,5-diphenyl-1-(*p*-tolyl)-1*H*-imidazole (**7r**).

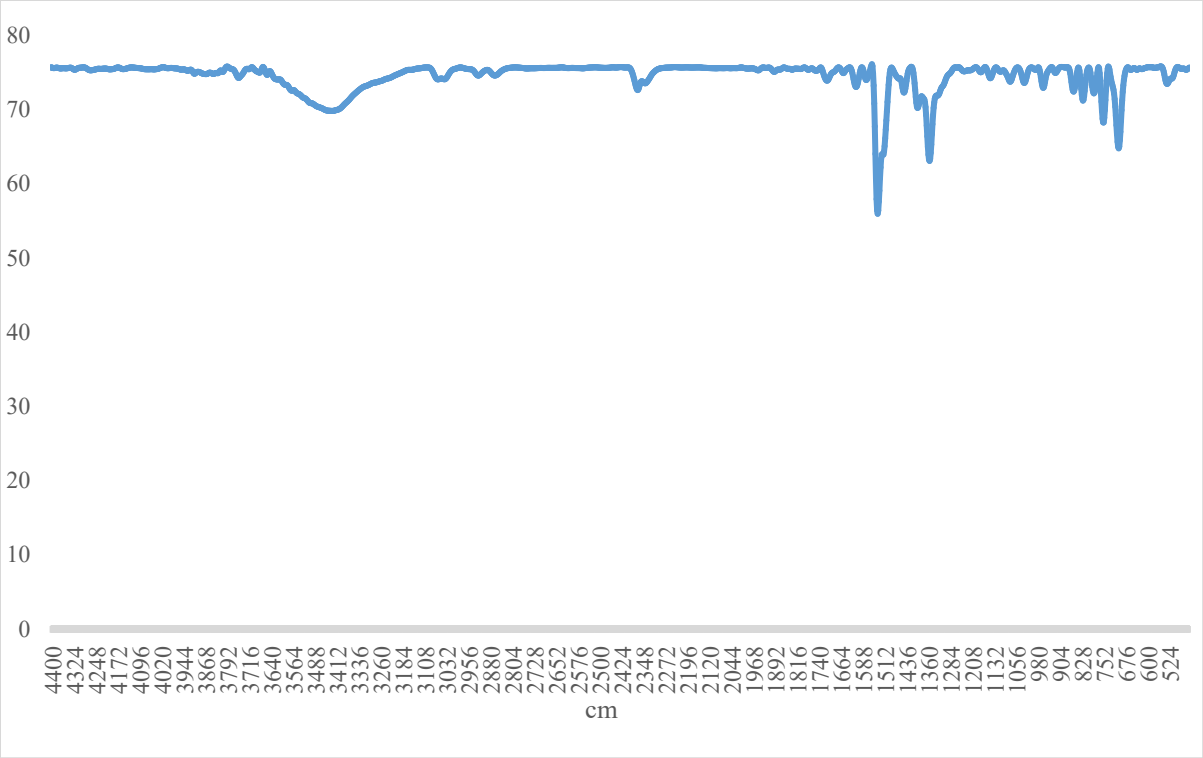


Figure S12. FT-IR spectra of 2-(4-nitrophenyl)-4,5-diphenyl-1-(*p*-tolyl)-1*H*-imidazole (**7r**).

2-(4-Methoxyphenyl)-4,5-diphenyl-1-(*p*-tolyl)-1*H*-imidazole (**7w**):

Mp: 179-180 °C; White solid; FTIR (KBr; cm^{-1}): 2922, 2376, 1606, 1514, 1438, 1368, 1022, 824, 776, 698, 526; ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 7.49 – 7.44 (m, 2H), 7.34 – 7.26 (m, 5H), 7.26 – 7.19 (m, 4H), 7.19 – 7.06 (m, 5H), 6.88 – 6.82 (m, 2H), 3.73 (s, 3H), 2.26 (s, 3H).

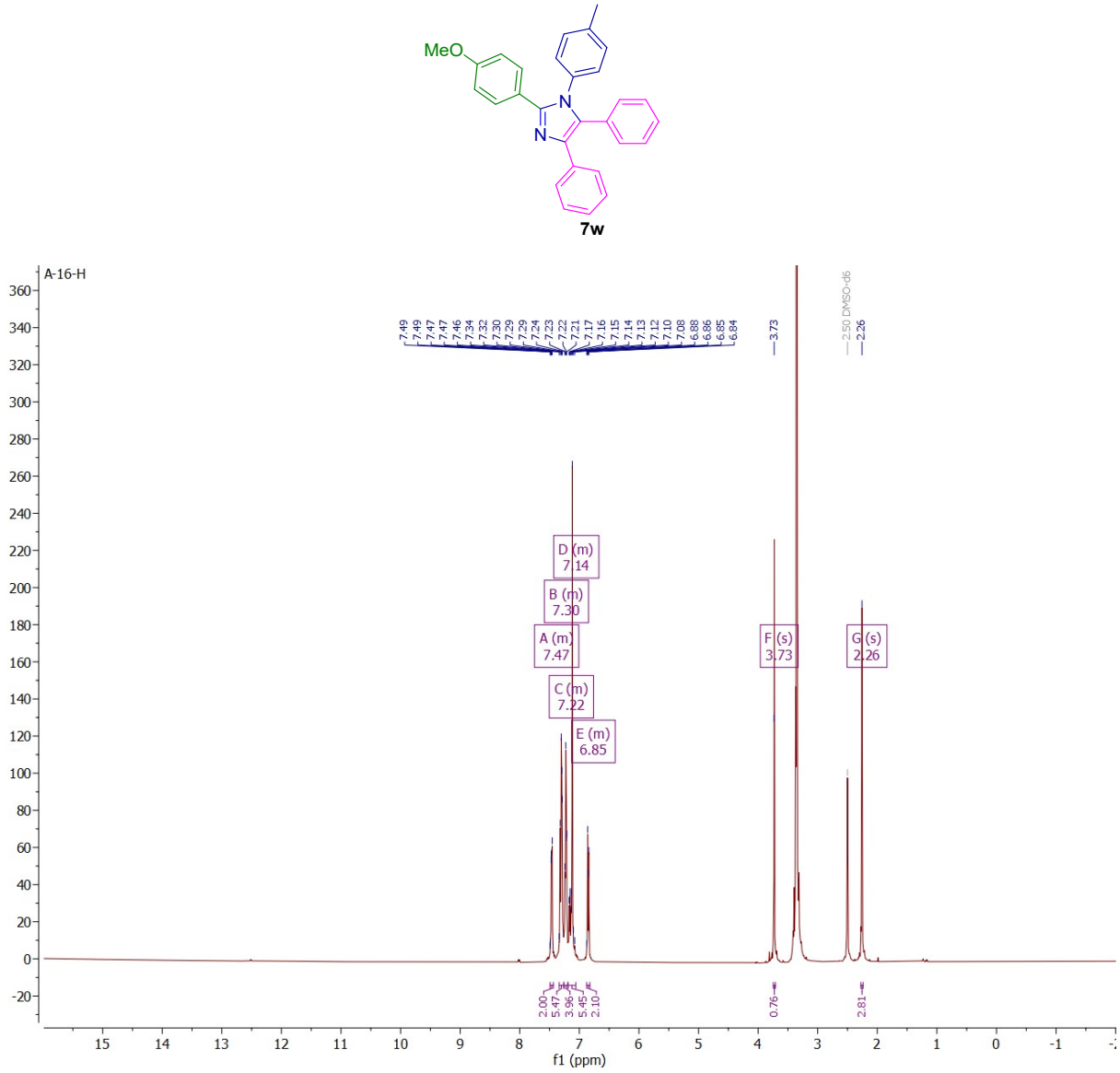


Figure 13 ^{1}H NMR spectra of 2-(4-methoxyphenyl)-4,5-diphenyl-1-(*p*-tolyl)-1*H*-imidazole (**7w**).

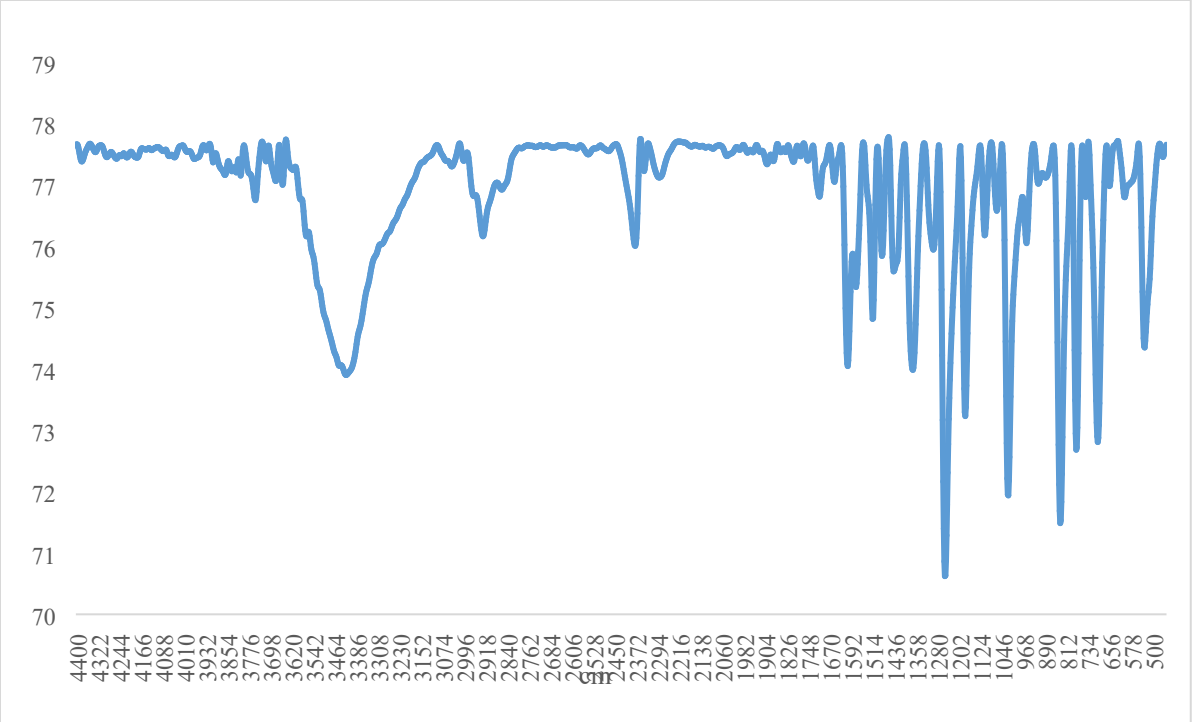


Figure S14. FT-IR spectra of 2-(4-methoxyphenyl)-4,5-diphenyl-1-(*p*-tolyl)-1*H*-imidazole (**7w**).