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An eco-compatible pathway to the synthesis of mono and bis-multisubstituted imidazoles over novel reusable ionic liquids: an efficient and green sonochemical process

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Experimental

Chemical reagents in high purity were obtained commercially and were used without further purification. Melting points were determined in open capillaries using an Electrothermal IA9100 melting point apparatus (UK). ^{1}H and ^{13}C NMR spectra were recorded using a Bruker UltraShield spectrometer at 400 and 100 MHz, respectively. High resolution mass spectra (HRMS) were performed utilizing a Bruker Daltonics microTOF spectrometer. FT-IR spectra were obtained with potassium bromide pellets in the range of 400–4000 cm^{-1} using a Perkin-Elmer Spectrum One spectrometer. Ultrasonication was done in a SY5200DH-T ultrasound cleaner.

Synthesis of the catalysts [DABCO-DOL][X] (3a–c):

A mixture of 1,4-diazobicyclo[2.2.2]octane (DABCO) (0.224 g, 2 mmol) and 2-chloro-1,3-propandiol (0.22 g, 2 mmol) in EtOH (15 mL) was sonicated for 3 h (TLC). Then, the solvent was removed under reduced pressure to afford compound (**2**). Then, NaOAc (0.164 g, 2 mmol), KPF_6 (0.368 g, 2 mmol) and/or $NaBF_4$ (0.22 g, 2mmol) was appended to the residue **2** (0.444 g, 2 mmol) in EtOH (20 mL). The resulting solution was sonicated for 2 h and then, the solvent was evaporated in vacuo to afford the corresponding ILs (**3a–c**) in quantitative yields.

General procedure for the preparation of imidazoles 6a–p and bis-imidazoles 10a–f.

A 25 mL Erlenmeyer flask was charged with aldehydes, **4a–p**, (1 mmol) and/or dialdehyde, **9a–f**, (0.5 mmol), benzil (1 mmol in case of **4a–p**, and 2 mmol in case of **9a–f**), NH_4OAc (2.5 mmol in case of **4a–p**, and 4.5 mmol in case of **9a–f**), and **3a** (5% mol in case of **4a–p**, and 8% mol in case of **9a–f**) in 5 mL water. The reaction vessel was placed in the ultrasonic bath, where the surface of solution is

slightly lower than the water level, the reaction mixture was exposed to ultrasound irradiation at 60 °C for appropriated time. After completion of reaction (confirmed by TLC, eluent: MeOH/DCM = 1 : 4 vol.), the solid that separated out was filtered washed with H_2O, dried and recrystallized from a proper solvent to afford the analytically pure product. The catalyst was recovered from the aqueous layer under vacuum, washed with ethyl acetate and reused for the next reactions. All known products were confirmed by comparing their melting points and NMR spectra (see SI).

General procedure for the synthesis of imidazoles 8a–j and bis-imidazoles 11a–f.

A 25 mL Erlenmeyer flask was charged with aldehydes (**4a–p**, 1 mmol) and/or dialdehyde (**9a–f**, 0.5 mmol), benzil (1 mmol in case of **4a–p**, and 2 mmol in case of **9a–f**), ammonium acetate (1mmol in case of **4a–p**, and 2 mmol in case of **9a–f**), amines (**7a–e**, 1 mmol, in case of **4a–p**) and/or aniline (1 mmol, in case of **9a–f**) and **3a** (5% mol in case of **4a–p** and 8 mmol in case of **9a–f**) in 5 mL water. The reaction flask was located in the ultrasonic bath, where the surface of reactants is slightly lower than the level of the water, the reaction mixture was exposed to ultrasound irradiation at 60 °C for appropriated time. After completion of reaction (confirmed by TLC, eluent: MeOH/DCM = 1 : 3 vol.), the solid that separated out was filtered washed with water, dried and recrystallized from dioxane containing few drops of DMF to afford the analytically pure product.

Ionic liquid [DABCO-DOL][AcO] (3a)

Yield 99%; colorless liquid; ^{1}H NMR (400 MHz, DMSO): δ 4.64-4.61 (m, 2H, 2OH), 3.80-3.56 (m, 11H, CH_2), 3.42-3.20 (m, 6H, CH_2), 1.56 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO): δ 175.8 (CO), 77.3, 66.9, 63.4, 47.8, 26.4; IR (KBr, cm^{-1}): ν_{max} 3216 (OH), 1681 (C=O); Anal. Calcd. for $C_{11}H_{22}N_2O_4$: C, 53.64; H, 9.00; N, 11.37. Found: C, 53.60; H, 9.08; N, 11.29%.

Ionic liquid [DABCO-DOL][BF_4] (3b)

Yield 96%; colorless liquid; ^{1}H NMR (400 MHz, DMSO): δ 4.64-4.61 (m, 2H, 2OH), 3.85-3.68 (m, 6H, CH_2), 3.17-3.16 (m, 11H, CH_2); ^{13}C NMR (100 MHz, DMSO): δ 77.5, 67.1, 64.1, 47.2; IR (KBr, cm^{-1}): ν_{max} 3328 (OH); Anal. Calcd. for $C_9H_{19}BF_4N_2O_2$: C, 39.44; H, 6.99; N, 10.22. Found: C, 39.37; H, 7.07; N, 10.17%.

Ionic liquid [DABCO-DOL][PF_6] (3c)

Yield 98%; colorless liquid; ^{1}H NMR (400 MHz, DMSO): δ 4.66-4.64 (m, 2H, 2OH), 4.12-4.10 (m, 11H, CH_2), 3.78-3.73 (m, 6H, CH_2); ^{13}C NMR (100 MHz, DMSO): δ 77.7, 67.4, 64.3, 47.6; IR (KBr, cm^{-1}): ν_{max} 3338 (OH); Anal. Calcd. for $C_9H_{19}F_6N_2O_2P$: C, 32.54; H, 5.76; N, 8.43. Found: C, 32.50; H, 5.82; N, 8.37%.

General procedure for the synthesis of imidazoles 6a-j and bis-imidazoles 10a-f.

A 25 mL Erlenmeyer flask was charged with benzil (1 mmol), aldehydes (1 mmol) and/or dialdehyde (0.5 mmol), ammonium acetate (3 equiv), and **3a** (5% mol) in 5 mL water. The reaction flask was located in the ultrasonic bath, where the surface

of reactants is slightly lower than the level of the water, the reaction mixture was exposed to ultrasound irradiation at 60 °C for appropriated time. After completion of reaction (confirmed by TLC, eluent: MeOH/DCM = 1 : 4 vol.), the solid separated out was filtered washed with water, dried and recrystallized from dioxane to afford the analytically pure product. Aqueous layer containing catalyst was recovered under reduced pressure, washed with DCM and reused for subsequent reactions. All known products were confirmed by comparing their melting points and NMR spectra. The spectral data for newly synthesized compounds were given below.

General procedure for the synthesis of imidazoles 8a-j and bis-imidazoles 11a-f.

A 25 mL Erlenmeyer flask was charged with benzil (1 mmol), aldehydes (1 mmol) and/or dialdehyde (0.5 mmol), ammonium acetate (1 mmol), aniline (1 mmol) and **3a** (10% mol) in 8 mL water. The reaction flask was located in the ultrasonic bath, where the surface of reactants is slightly lower than the level of the water, the reaction mixture was exposed to ultrasound irradiation at 60 °C for appropriated time. After completion of reaction (confirmed by TLC, eluent: MeOH/DCM = 1 : 3 vol.), the solid separated out was filtered washed with water, dried and recrystallized from dioxane containing few drops of DMF to afford the analytically pure product. Aqueous layer containing catalyst was recovered under reduced pressure, washed with DCM and reused for subsequent reactions.

2,4,5-Triphenyl-1*H*-imidazole (6a)

Yield 99%; white solid; mp 272-273 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.71 (s, 1H, NH), 8.08 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.54-7.22 (m, 13H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 145.8, 137.6, 135.4, 131.5, 130.8, 129.3, 128.8, 128.5,

128.2, 127.4, 127.0, 125.5; Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.13; H, 5.42; N, 9.39.

2-(4-Methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (6b)

Yield 99%; white solid; mp 230-232 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.50 (s, 1H, NH), 8.00 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.55-7.21 (m, 10H, Ar-H), 7.04 (d, *J* = 8.2 Hz, 2H, Ar-H), 3.81 (s, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6): δ 159.6, 146.1, 129.3, 128.6,128.3, 128.0, 127.4, 127.1, 126.7, 123.5, 114.3, 55.4. Anal. Calcd for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58. Found: C, 80.90; H, 5.59; N, 8.49.

4-(4,5-Diphenyl-1*H*-imidazol-2-yl)phenol (6c)

Yield 98%; white solid; mp 234-236 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.40 (s, 1H, NH), 9.74 (br, 1H, OH), 7.90 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.52-7.15 (m, 10H, Ar-H), 6.85 (d, *J* = 8.3 Hz, 2H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 158.1, 146.4, 137.2, 135.7, 131.9, 129.1, 128.9, 128.3, 128.1, 127.6, 127.1, 126.8, 126.3, 121.7, 116.2. Anal. Calcd for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.79; H, 5.11; N, 8.94.

4-(4,5-Diphenyl-1*H*-imidazol-2-yl)-*N*,*N*-dimethylaniline (6d)

Yield 97%; white solid; mp 255-227 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.47 (s, 1H, NH), 7.89-7.88 (m, 1H, Ar-H); 7.52-7.50 (m, 2H, Ar-H); δ 7.27-7.36 (m, 10H, Ar-H); δ 6.80-6.79 (m, 1H, Ar-H); δ 3.51 (s, 6H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6): δ 149.9, 146.4, 127.7, 126.1, 125.5, 117.8, 111.6, 39.6; Anal. Calc. for $C_{23}H_{21}N_3$: C, 81.38; H, 6.24; N, 12.38. Found: C, 81.41; H, 6.21; N, 12.35.

2-(4,5-diphenyl-1*H*-imidazol-2-yl)phenol (6e)

Yield 95%; white solid; mp 202-204 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.04 (s, 1H, NH), 13.02 (s, 1H, OH), 8.04 (d, *J* = 7.3 Hz, 1H, Ar-H), 7.53-7.23 (m, 11H, Ar-H), 7.01-6.90 (m, 2H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 157.1, 146.2, 134.6, 134.2, 130.3, 129.5, 128.6, 127.4, 125.1, 119.3, 117.2, 113.0; Anal. Calcd for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.73; H, 5.15; N, 8.90.

2-(3,4-Dimethoxyphenyl)-4,5-diphenyl-1*H*-imidazole (6f)

Yield 98%; white solid; mp 214-216 °C; ^{1}H NMR(400 MHz, DMSO-d_6): δ 12.55 (s, 1H, NH), 8.07-8.04 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.66-7.31 (m, 10H, Ar-H), 7.01-6.99 (d, *J* = 8.7 Hz, 1H, Ar-H), 3.89 (s, 6H, C*H*$_3$); ^{13}C NMR (100MHz, DMSO-d_6): δ 150.6, 148.4, 145.1, 133.1, 129.4, 129.2, 129.0, 128.6, 128.7, 127.4, 124.5, 121.4, 115.6, 111.9, 56.3; Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86. Found: C, 77.48; H, 5.69; N, 7.78.

4,5-Diphenyl-2-(*p*-tolyl)-1*H*-imidazole (6g)

Yield 95%; white solid: mp: 230–232 °C; ^{1}H NMR(400 MHz, DMSO-d_6): δ 12.57 (s, 1H, NH), 8.06-8.03 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.55-7.23 (m, 10H, Ar-H), 7.07-7.04 (d, *J* = 8.2 Hz, 2H, Ar-H), 2.31 (s, 3H, CH_3); ^{13}C NMR (100MHz, DMSO-d_6): δ 145.9, 137.3, 137.1, 135.5, 131.8, 129.3, 128.7, 128.1, 127.9, 127.6, 127.2, 126.9, 126.5, 125.2, 21.3; Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.03. Found: C, 85.10; H, 5.89; N, 8.88.

2-(4-Fluorophenyl)-4,5-diphenyl-1*H*-imidazole (6h)

Yield 96%; white solid; mp: 260–262 °C; ^{1}H NMR(400 MHz, DMSO-d_6): δ 12.70 (s, 1H, NH), 8.16-8.13 (d, *J* = 8.2 Hz, 2H, Ar-H), 8.11-8.06 d, *J* = 8.2 Hz, 2H, Ar-H), 7.58-7.54 (t, *J* = 7.9 Hz, 4H, Ar-H), 7.41-7.21 (m, 6H, Ar-H); ^{13}C NMR (100MHz, DMSO-d_6): δ 146.5, 130.6, 130.3, 129.6, 129.1, 128.4, 127.6, 127.3,

126.5, 125.5, 125.4, 123.7, 116.0; Anal. Calcd for $C_{21}H_{15}FN_2$: C, 80.24; H, 4.81; N, 8.91. Found: C, 80.20; H, 4.89; N, 8.86.

2-(4-Bromophenyl)-4,5-diphenyl-1*H*-imidazole (6i)

Yield 98%; white solid; mp: 265–266 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.77 (s, 1H, NH), 8.01 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.67 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.50 (d, *J* = 7.5 Hz, 4H, Ar-H), 7.34 (m, 6H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.9, 137.6, 135.3, 133.3, 131.4, 129.5, 128.7, 128.2, 128.0, 127.6, 127.4, 127.1 Anal. Calcd for $C_{21}H_{15}N_2Br$: C, 67.21; H, 4.03; N, 7.47. Found: C, 67.23; H, 4.01; N, 7.41.

2-(2-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole (6j)

Yield 98%; white solid; mp: 192–193 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H, NH), 7.8-7.20 (m, 14 H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.9, 137.1, 135.2, 132.4, 131.3, 130.9, 130.5, 129.0, 128.5, 128.2, 128.0, 127.7, 127.2. Anal. Calcd for $C_{21}H_{15}N_2Cl$: C, 76.24; H, 4.57; N, 8.47. Found: C, 76.29; H, 4.50; N, 8.40.

2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole (6k)

Yield 98%; white solid; mp: 263-265 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.72 (s, 1H, NH), 8.10 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.55-7.30 (m, 12H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 145.1, 137.6, 135.5, 133.8, 131.3, 129.9, 129.7, 129.3, 128.7, 128.3, 128.0, 127.6, 126.4. Anal. Calcd for $C_{21}H_{15}N_2Cl$: C, 76.24; H, 4.57; N, 8.47. Found: C, 76.28; H, 4.52; N, 8.41.

2-(2,4-dichlorophenyl)-4,5-diphenyl-1*H*-imidazole (6l)

Yield 96%; white solid; mp: 171-173 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.70 (s, 1H, NH), 7.64-7.19 (m, 13H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 141.0, 136.9, 136.4, 135.3, 132.6, 131.7, 130.4, 129.5, 128.7, 128.3, 128.0, 127.8, 127.7, 127.4, 127.0. Anal. Calcd for $C_{21}H_{14}N_2Cl_2$: C, 69.05; H, 3.86; N, 7.67. Found: C, 69.01; H, 3.89; N, 7.61.

2-(4-Nitrophenyl)-4,5-diphenyl-1*H*-imidazole (6m)

Yield 96%; light yellow; mp: 242–243°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.95 (s, 1H, NH), 8.01 (d, J = 7.8 Hz, 1H, Ar-H), 7.90 (d, J = 7.7 Hz, 1H, Ar-H), 7.76 (t, J = 7.7 Hz, 1H, Ar-H), 7.69 (t, J = 7.8 Hz, 1H, Ar-H), 7.49-7.35 (m, 10H, Ar-H). Anal. Calcd for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31. Found: C, 73.93; H, 4.40; N, 12.28.

4,5-Diphenyl-2-(thiophen-2-yl)-1*H*-imidazole (6n)

Yield 99%; light yellow; mp: 255-257 °C; ^{1}H NMR (DMSO-d_6): δ 12.79 (s, 1H, NH), 7.70 (dd, 1H, J = 1.5, 1.1 Hz, thienyl-H3), 7.55 (dd, 1H, J = 1.1 Hz, thienyl-H5), 7.51-7.23 (m, 10H, Ar-H), 7.17 (t, 1H, J = 4.4Hz, thienyl-H); Anal. Calcd for $C_{19}H_{14}N_2S$: C, 75.47; H, 4.67; N, 9.26. Found: C, 75.40; H, 4.71; N, 9.21.

2-(Furan-2-yl)-4,5-diphenyl-1*H*-imidazole (6o)

Yield 98%; white; mp: 201–202 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.22 (s, 1H, NH), 7.57-7.44 (m, 3H, Ar-H), 7.15-7.6 (m, 10H, Ar-H); ^{13}C NMR (101MHz, DMSO-d_6): δ 148.8, 143.7, 140.0, 138.6, 130.4, 129.5, 128.5, 127.7, 127.6, 127.3, 124.2, 123.3, 118.0, 112.4, 108.5; Anal. Calcd for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93; N, 9.78. Found: C, 79.74; H, 4.90; N, 9.75.

2-Methyl-4,5-diphenyl-1*H*-imidazole (6p)

Yield 99%; white; mp: 244-246 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.0 (s, 1H, NH), 8.12-7.27 (m, 10H, Ar-H), 2.36 (s, 3H, CH_3); ^{13}C NMR (101MHz, DMSO-d_6): δ 150.6, 133.1, 128.3, 128.3, 127.5, 127.3, 17.7; Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.06; H, 5.96; N, 11.91.

1,2,4,5-Tetraphenyl-1*H*-imidazole (8a)

Yield 98%; light yellow; mp: 220–222 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.63 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.44 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.27-7.21 (m, 12H, Ar-H), 7.14 (d, *J* = 7.1 Hz, 2H, Ar-H), 7.06 (d, *J* = 7.1 Hz, 2H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 146.7, 138.1, 137.2, 134.4, 131.1, 130.9, 130.7, 130.4, 129.2, 128.8, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.3, 126.8; Anal. Calcd for $C_{27}H_{20}N_2$: C, 87.07; H, 5.41; N, 7.52. Found: C, 87.04; H, 5.49; N, 7.48.

1,4,5-Triphenyl-2-(*p*-tolyl)-1*H*-imidazole (8b)

Yield 96%; white; mp: 188-189 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.60 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.31-7.02 (m, 17H, Ar-H), 2. 31 (s, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6): δ 147.2, 138.6, 137.3, 134.3, 131.5, 130.7, 130.1, 129.4, 128.8, 128.4, 128.2, 128.0, 127.8, 127.3, 127.1, 126.5, 21.3; Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.09; H, 5.70; N, 7.19.

2-(4-Methoxyphenyl)-1,4,5-triphenyl-1*H*-imidazole (8c)

Yield 96%; white; mp: 183-185 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.60-7.03 (m, 17H, Ar-H), 6.74 (d, *J* = 8.1 Hz, 2H, Ar-H), 3.78 (s, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6): δ 159.4, 146.7, 137.6, 137.0, 134.4, 131.3, 130.1, 129.2, 128.7, 128.3, 128.0, 127.8, 127.1, 126.4, 123.1, 113.5, 55.2. Anal. Calcd for $C_{28}H_{22}N_2$: C, 83.56; H, 5.51; N, 6.96. Found: C, 83.50; H, 5.58; N, 7.03.

2-(4-Chlorophenyl)-1,4,5-triphenyl-1*H*-imidazole (8d)

Yield 95%; white; mp: 161-162 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.59 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.35 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.31-7.20 (m, 11H, Ar-H), 7.11 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.04 (d, *J* = 7.6 Hz, 2H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 145.6, 138.4, 136.8, 134.0, 131.3, 130.2, 130.2, 129.5, 129.0, 128.4, 128.4, 128.6, 128.1, 127.3, 126.6. Anal. Calcd for $C_{27}H_{19}ClN_2$: C, 79.70; H, 4.71; N, 6.88. Found: C, 79.78; H, 4.67; N, 6.80.

2-(4-Bromophenyl)-1,4,5-triphenyl-1*H*-imidazole (8e)

Yield 96%; white; mp: 209-211°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.60 (d, *J* = 9.3 Hz, 2H, Ar-H), 7.39-7.03 (m, 17H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 145.5, 138.6, 136.9, 134.1, 131.0, 131.5, 131.2, 130.6, 130.3, 129.6, 129.1, 128.5, 128.3, 128.1, 128.0, 127.7, 126.7, 122.2. Anal. Calcd for $C_{27}H_{19}BrN_2$: C, 71.85; H, 4.24; N, 6.21. Found: C, 71.89; H, 4.20; N, 6.18.

1-Benzyl-2,4,5-triphenyl-1*H*-imidazole (8f)

Yield 98%; white; mp: 160-164 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.66 (dd, *J* = 3.9, 7.5 Hz, 2H, Ar-H), 7.57-7.55 (m, 2H, Ar-H), 7.40 (t, *J* = 5.7 Hz, 2H, Ar-H), 7.38-7.26 (m, 4H, Ar-H), 7.23-7.11 (m, 8H, Ar-H), 6.78 (dd, *J* = 7.1, 3.4, Hz, 2H, Ar-H), 5.10 (s, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 148.1, 137.5, 131.1, 130.0, 129.1, 128.9, 128.7, 128.5, 128.0, 127.3, 126.8, 126.3, 126.0, 48.3; Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.91; H, 5.79; N, 7.20.

1-(4-Methoxybenzyl)-2,4,5-triphenyl-1*H*-imidazole (8g)

Yield 98%; white; mp: 150-153 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.67-7.65 (m, 2H, Ar-H), 7.58-7.55 (m, 2H, Ar-H), 7.45-7.42 (m, 2H, Ar-H), 7.38-7.34 (m,

4H, Ar-H), 7.19-7.13 (m, 5H, Ar-H), 6.76-6.66 (m, 4H, Ar-H), 5.04 (s, 2H, CH_2), 3.78 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.3, 158.5, 147.6, 138.2, 134.3, 131.5, 130.7, 130.3, 129.4, 129.0, 128.7, 128.5, 128.3, 128.0, 127.4, 126.5, 126.4, 114.3, 55.2, 47.7; Anal. Calcd for $C_{29}H_{24}N_2O$: C, 83.63; H, 5.81; N, 6.73. Found: C, 83.60; H, 5.77; N, 6.69.

1-(4-Methylbenzyl)-4,5-diphenyl-2-*p*-tolyl-1*H*-imidazole (8h):

Yield 98%; white; mp: 132-135 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 7.58-7.55 (m, 4H, Ar-H), 7.36-7.34 (m, 2H, Ar-H), 7.24-7.19 (m, 8H, Ar-H), 7.01 (d, *J* = 7.7 Hz, 2H, Ar-H), 6.71 (d, *J* = 7.9 Hz, 2H, Ar-H), 5.07 (s, 2H, CH_2), 2.41 (s, 3H, CH_3), 2.30 (s, 3H, CH_3); 147.8, 138.6, 137.5, 136.2, 134.0, 133.7, 130.5, 130.4, 129.6, 129.1, 128.7, 128.5, 128.3, 128.2, 128.0, 127.6, 127.4, 126.7, 126.1, 125.4, 47.7, 21.0, 20.5; Anal. Calcd for $C_{30}H_{26}N_2$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.88; H, 6.37; N, 6.70.

1-(4-Fluorobenzyl)-2-(4-fluorophenyl)-4,5-diphenyl-1*H*-imidazole (8i)

Yield 96%; white; mp: 158-161 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 7.64-7.55 (m, 4H, Ar-H), 7.42-7.33 (m, 4H, Ar-H), 7.25-7.16 (m, 4H, Ar-H), 7.19-7.09 (m, 2H, Ar-H), 6.90 (t, *J* = 8.8 Hz, 2H, Ar-H), 6.71 (dd, *J* = 8.8, 4.7 Hz, 2H, Ar-H), 5.04 (s, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 131.3, 131.1, 129.9, 128.6, 128.6, 128.0, 127.6, 127.3, 126.6, 126.4, 115.7, 115.3, 115.0, 114.8, 47.5; Anal. Calcd for $C_{28}H_{20}F_2N_2$: C, 79.60; H, 4.77; N, 6.63. Found: C, 79.66; H, 4.71; N, 6.60.

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (8j)

Yield 96%; white; mp: 152-154 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 7.55 (t, *J* = 8.8 Hz, 4H, Ar-H), 7.39-7.26 (m, 4H, Ar-H), 7.23-7.14 (m, 4H, Ar-H), 6.90 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.77-6.65 (m, 4H, Ar-H), 5.04 (s, 2H, CH_2), 3.81 (s, 3H, CH_3),

3.76 (3H, s, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.2, 158.6, 147.5, 134.7, 131.0, 130.9, 130.6, 129.7, 128.9, 128.4, 128.1, 127.4, 126.7, 126.3, 123.5, 114.3, 114.0, 55.4, 55.0, 47.5; Anal. Calcd for $C_{30}H_{26}N_2O_2$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.74; H, 5.81; N, 6.22.

2,6-*bis*(4,5-Diphenyl-1*H*-imidazol-2-yl)-4-methylphenol (10a) [1]

Yield 98%; yellow solid; mp = 210–212 ^oC; ^1H NMR (400 MHz, DMSO-d_6): δ 14.10 (s, 1H, OH); 12.54 (s, 2H, NH); 7.96 (s, 2H, Ar-H); 7.55 (d, *J* = 7.2 Hz, 8H, Ar-H); 7.37-7.29 (m, 12H, Ar-H); 2.41 (s, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.0, 148.4, 137.8, 136.3, 134.1, 130.8, 129.2, 128.4, 128.2, 127.6, 127.2, 125.4, 115.1, 21.7; IR (KBr, cm^{-1}): ν_{max} 3401-3059 (NH + OH), 1611 (C=N), 1595 (C=C); MS (ESI) *m/z* (%): 544.22 (M^+, 2.9%), 103 (100); Anal. Calc. for $C_{37}H_{28}N_4O$: C, 81.59; H, 5.13; N, 10.29%. Found: C, 81.47; H, 5.11; N, 10.24%

4-Bromo-2,6-*bis*(4,5-diphenyl-1*H*-imidazol-2-yl)phenol (10b)

Yield 95%; yellow solid; mp = 264–266 ^oC; ^1H NMR (400 MHz, DMSO-d_6): δ 13.01 (s, 1H, OH), 12.52 (s, 2H, NH), 8.01 (d, *J* = 8.1 Hz, 4H, Ar-H), 7.54-7.20 (m, 14H, Ar-H), 7.03 (d, *J* = 8.1 Hz, 4H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.2, 146.7, 137.6, 129.1, 128.8, 128.4, 128.0, 127.3, 127.0, 126.4, 123.9; IR (KBr, cm^{-1}): ν_{max} 3376-3138 (OH and NH), 1642 (C=N), 1606 (C=C); HRMS: *m*/*z* $[M]^+$ calcd: 608.1213, found 608.1209; Anal. Calc. for $C_{36}H_{25}BrN_4O$: C, 70.94; H, 4.13; N, 9.19 %. Found: C, 71.02; H, 4.09; N, 9.12%.

3,5-*bis*(4,5-Diphenyl-1*H*-imidazol-2-yl)-4-hydroxybenzoic acid (10c)

Yield 89%; yellow solid; mp = 289–291 ^oC; ^1H NMR (400 MHz, DMSO-d_6): δ 13.05 (s, 2H, OH), 13.00 (s, 2H, NH), 8.05 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.52-7.24 (m, 17H, Ar-H), 6.99-6.92 (m, 3H, Ar-H); ^{13}C NMR (101 MHz, DMSO-d_6) δ

169.1, 157.9, 145.0, 137.8, 133.3, 131.5, 129.7, 129.3, 129.1, 128.9, 128.7, 128.4, 127.6, 122.4; IR (KBr, cm^{-1}): ν_{max} 3416-3138 (OH and NH), 1669 (C=O), 1638 (C=N), 1597 (C=C); HRMS: *m*/*z* $[M - H]^+$ calcd: 573.1926, found 573.1928; Anal. Calc. for $C_{37}H_{26}N_4O_3$: C, 77.34; H, 4.56; N, 9.75%. Found: C, 77.29; H, 4.58; N, 9.68%.

1,4-*bis*(4,5-Diphenyl-1*H*-imidazol-2-yl)benzene (10d) [2]

Yield 97%; yellow solid; mp = 234–237 ^oC (lit., mp = 232–235); ^1H NMR (400 MHz, DMSO): δ 12.74 (s, 2H, NH), 8.18 (s, 4H, Ar–H), 7.58–7.53 (m, 8H, Ar–H), 7.51–7.47 (m, 6H, Ar–H), 7.44–7.23 (m, 6H, Ar–H); ^{13}C NMR (100 MHz, DMSO): δ 145.2, 135.0, 131.2, 128.6, 128.5, 128.2, 127.7, 127.2, 126.6, 125.3; IR (KBr, cm^{-1}): ν_{max} 3413-3124 (NH), 1638 (C=N), 1616 (C=C); HRMS: *m*/*z* $[M + H]^+$ calcd: 515.2237, found 515.2234; Anal. Calc. for $C_{36}H_{26}N_4$: C, 84.02; H, 5.09; N, 10.89%. Found: C, 83.97; H, 5.14; N, 10.80%.

2,2'-(1*H*-Pyrazole-3,5-diyl)*bis*(4,5-diphenyl-1*H*-imidazole) (10e)

Yield 92%; yellow solid; mp = 361–363 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ 12.96 (s. 2H, NH), 12.64 (s, 1H, NH), 7.55 (br, 6H, Ar-H), 7.42-7.22 (m, 14H, Ar-H), 6.80 (s, 1H, pyrazole-H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.3, 137.5, 132.0, 129.0, 128.6, 128.2, 127.5, 106.6; IR (KBr, cm^{-1}): ν_{max} 3223-3168 (NH), 1636 (C=N), 1604 (C=C); HRMS: *m*/*z* $[M + H]^+$ calcd: 505.2140, found 505.2138; Anal. Calc. for $C_{33}H_{24}N_6$: C, 78.55; H, 4.79; N, 16.66%. Found: C, 78.51; H, 4.84; N, 16.58%.

4,4'-Methylene*bis*(2-(4,5-diphenyl-1*H*-imidazol-2-yl)phenol) (10f)

Yield 94%; yellow solid; mp = 348–351 ^oC; ^1H NMR (400 MHz, DMSO-d_6): δ 12.44 (s, 2H, NH), 9.32 (s, 2H, OH), 7.64 (s, 2H, Ar-H), 7.52-7.19 (m, 20H, Ar-

H), 6.86 (d, *J* = 8.1 Hz, 4H, Ar-H), 3.85 (s, 2H, CH_2); ^{13}C NMR (101 MHz, DMSO-d_6): δ 152.4, 148.1, 137.5, 136.5, 130.5, 129.8, 129.1, 128.8, 128.6, 127.5, 118.8, 116.0, 56.1; IR (KBr, cm^{-1}): ν_{max} 3230-3173 (NH), 1641 (C=N), 1616 (C=C); HRMS: *m*/*z* $[M - H]^+$ calcd: 635.2446, found 635.2449; Anal. Calc. for $C_{43}H_{32}N_4O_2$: C, 81.11; H, 5.07; N, 8.80%. Found: C, 81.18; H, 5.01; N, 8.77%.

4-Methyl-2,6-bis(1,4,5-triphenyl-1*H*-imidazol-2-yl)phenol (11a)

Yield 95%; yellow solid; mp = 377–380 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H, OH), 7.60 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.33-7.22 (m, 17H, Ar-H), 7.19-7.04 (m, 13H, Ar-H), 2.31 (s, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6): δ 151.6, 147.0, 138.1, 137.2, 134.5, 131.1, 130.7, 130.6, 129.0, 128.8, 128.4, 128.3, 128.1, 127.8, 127.6, 127.4, 126.5, 119.0, 21.2; IR (KBr, cm^{-1}): ν_{max} 3378-3102 (OH), 1632 (C=N), 1609 (C=C); HRMS: *m*/*z* $[M + H]^+$ calcd: 697.2968, found 697.2965; Anal. Calc. for $C_{49}H_{36}N_4O$: C, 84.46; H, 5.21; N, 8.04%. Found: C, 84.51; H, 5.19; N, 7.94%.

4-Bromo-2,6-bis(1,4,5-triphenyl-1*H*-imidazol-2-yl)phenol (11b)

Yield 93%; yellow solid; mp > 400 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H, OH), 7.79-7.21 (m, 32 H, Ar-H); IR (KBr, cm^{-1}): ν_{max} 3411-3174 (OH), 1627 (C=N), 1613 (C=C); HRMS: *m*/*z* $[M + H]^+$ calcd: 761.1916, found 761.1919; Anal. Calc. for $C_{48}H_{33}N_4O$: C, 75.69; H, 4.37; N, 7.36%. Found: C, 75.72; H, 4.9; N, 7.30%.

4-Hydroxy-3,5-bis(1,4,5-triphenyl-1*H*-imidazol-2-yl)benzoic acid (11c)

Yield 96%; yellow solid; mp = 382–385 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (s, 2H, Ar-H), 7.57 (d, *J* = 7.7 Hz, 6H, Ar-H), 7.36-7.20 (m, 17H, Ar-H), 7.12 (d, *J* = 7.6 Hz, 4H, Ar-H), 7.03 (d, *J* = 7.7 Hz, 3H, Ar-H); ^{13}C NMR (101 MHz,

DMSO-d_6): δ 167.8, 157.4, 145.7, 138.4, 136.9, 134.2, 131.1, 130.1, 129.1, 129.0, 128.5, 128.3, 128.2, 128.0, 127.3, 126.7, 123.7, 121.7; IR (KBr, cm^{-1}): ν_{max} 3211-3054 (OH), 1612 (C=N), 1589 (C=C); HRMS: *m*/*z* $[M - H]^+$ calcd: 725.2554, found 725.2551; Anal. Calc. for $C_{49}H_{34}N_4O_3$: C, 80.97; H, 4.72; N, 7.71%. Found: C, 80.91; H, 4.66; N, 7.68%.

1,4-bis(1,4,5-Triphenyl-1*H*-imidazol-2-yl)benzene (11d)

Yield 96%; yellow solid; mp = 380–383 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 (d, *J* = 9.3 Hz, 4H, Ar-H), 7.39-7.02 (m, 30H, Ar-H); IR (KBr, cm^{-1}): ν_{max} 1649 (C=N), 1617 (C=C); HRMS: *m*/*z* $[M + Na]^+$ calcd: 689.2682, found 689.2679; Anal. Calc. for $C_{48}H_{34}N_4$: C, 86.46; H, 5.14; N, 8.40%. Found: C, 86.51; H, 5.09; N, 8.35%.

2,2'-(1*H*-Pyrazole-3,5-diyl)bis(1,4,5-triphenyl-1*H*-imidazole) (11e)

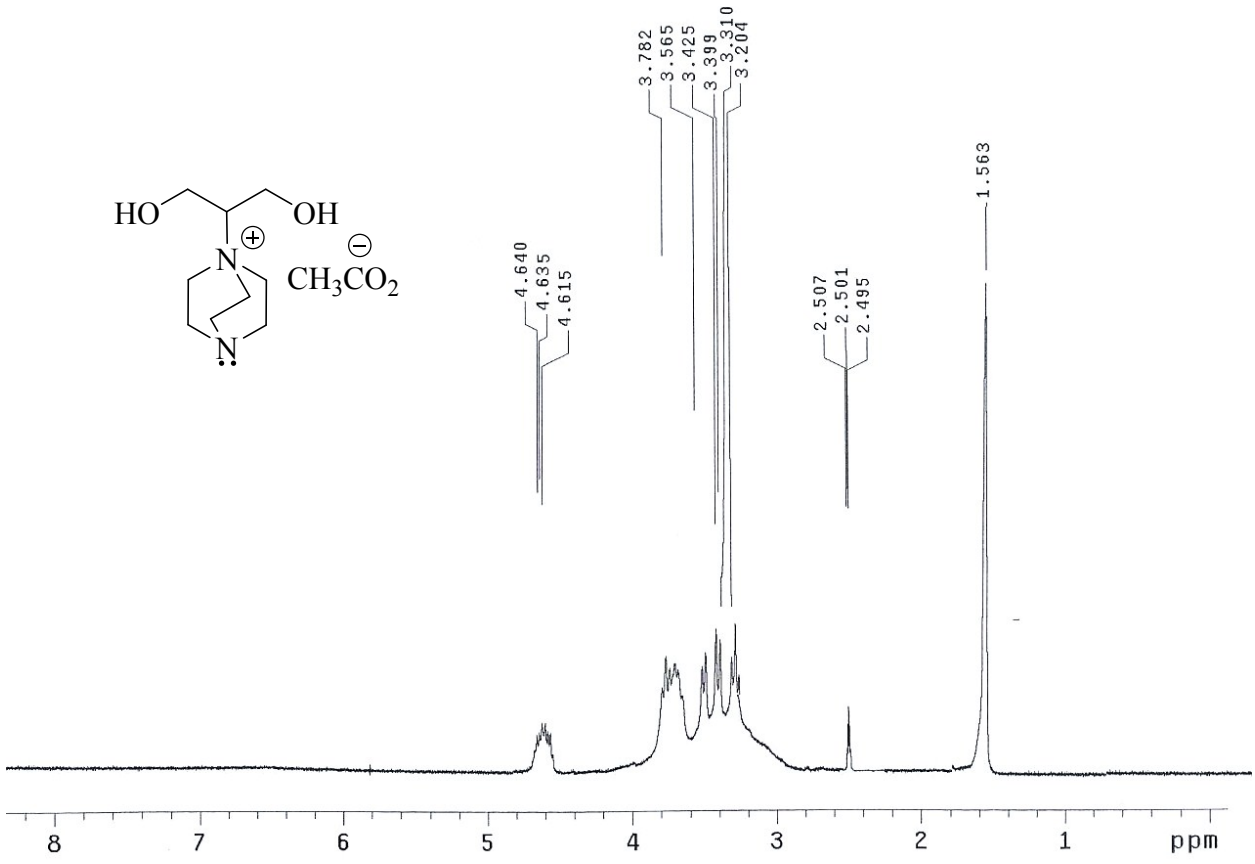
Yield 94%; yellow solid; mp > 400 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61 (d, *J* = 7.6 Hz, 4H, Ar-H), 7.30-7.08 (m, 26H, Ar-H), 6.66 (s, 1H); IR (KBr, cm^{-1}): ν_{max} 3214-3199 (NH), 1617 (C=N), 1580 (C=C); HRMS: *m*/*z* $[M + H]^+$ calcd: 657.2768, found 657.2765; Anal. Calc. for $C_{45}H_{32}N_6$: C, 82.29; H, 4.91; N, 12.80%. Found: C, 82.22; H, 4.98; N, 12.75%.

4,4'-Methylenebis(2-(1,4,5-triphenyl-1*H*-imidazol-2-yl)phenol) (11f)

Yield 94%; yellow solid; mp > 400 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (d, *J* = 8.5 Hz, 4H, Ar-H), 7.53-7.17 (m, 28H, Ar-H), 6.84 (d, *J* = 8.5 Hz, 4H, Ar-H), 3.82 (s, 2H, CH_2); IR (KBr, cm^{-1}): ν_{max} 3322-3086 (NH), 1633 (C=N), 1603 (C=C); HRMS: *m*/*z* $[M + H]^+$ calcd: 789.3228, found 789.3231; Anal. Calc. for $C_{55}H_{40}N_4O_2$: C, 83.73; H, 5.11; N, 7.10%. Found: C, 83.67; H, 5.19; N, 7.06%.

References

1. A.O. Eseola, O. Adepitan, H. Gorls and Wi. Plass, *New J. Chem.*, 2012, **36**, 891–902.
2. A. Hariharasubramanian and Y. D. Ravichandran, *RSC Adv.*, 2014, **4**, 54740– 54746.



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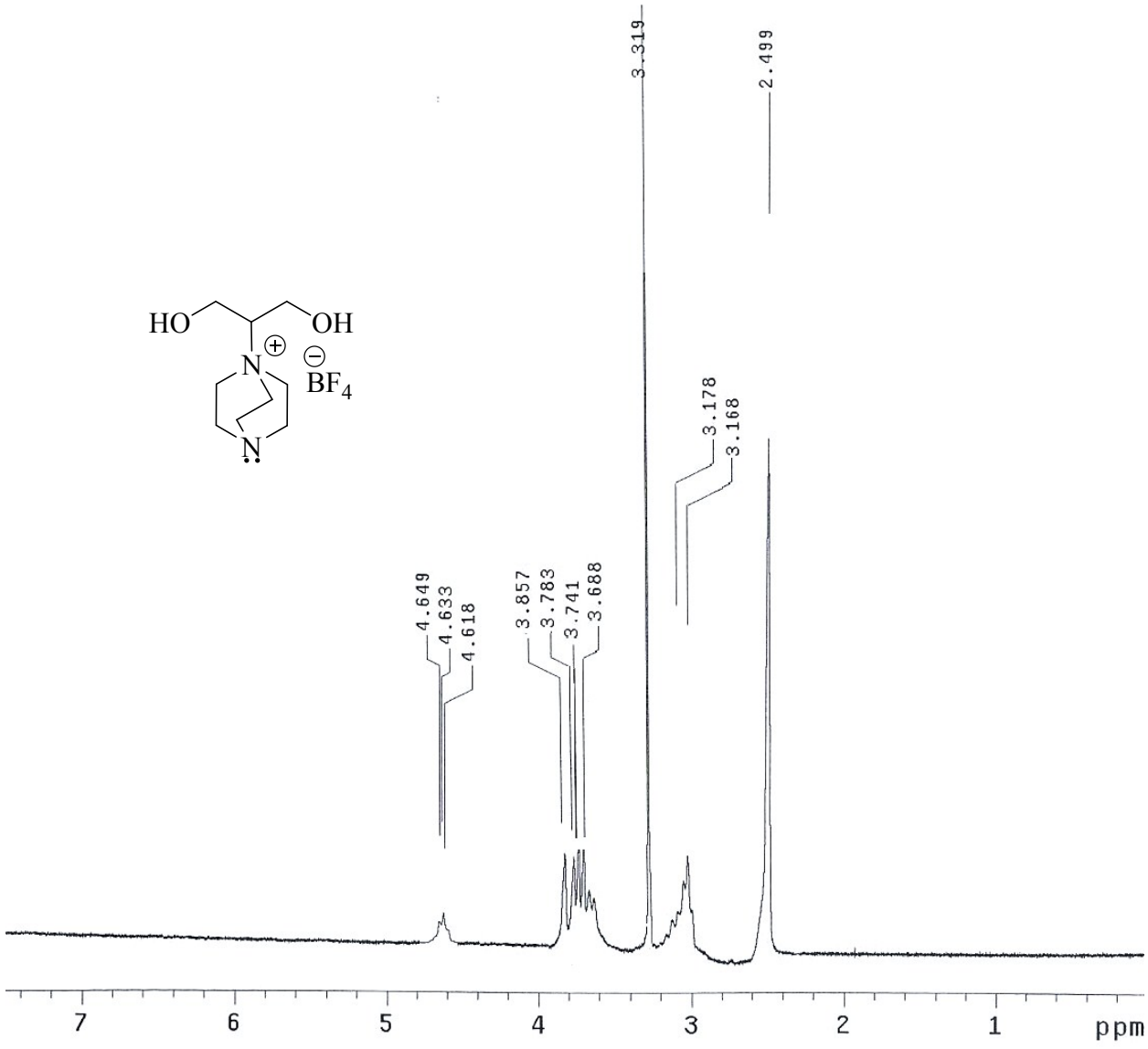

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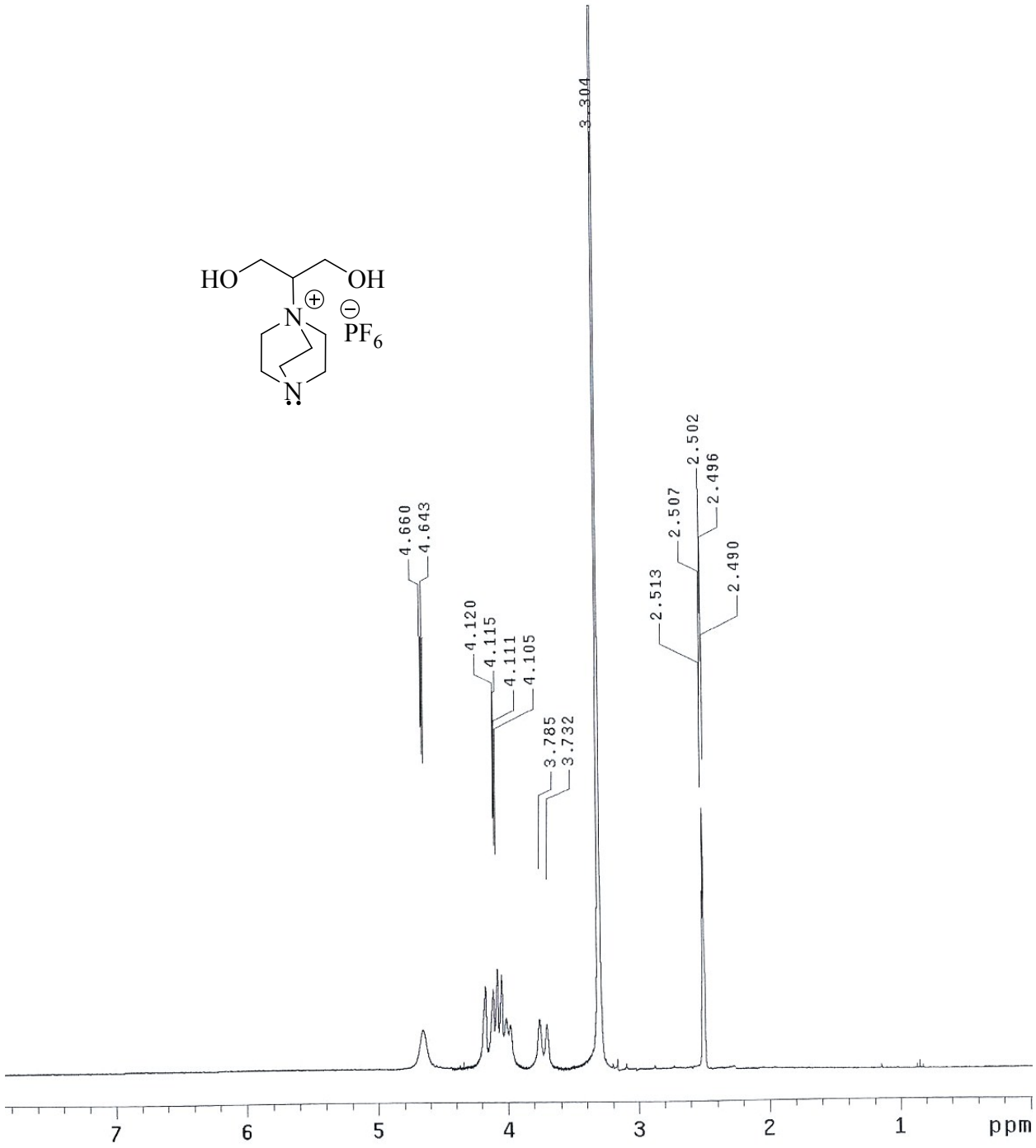
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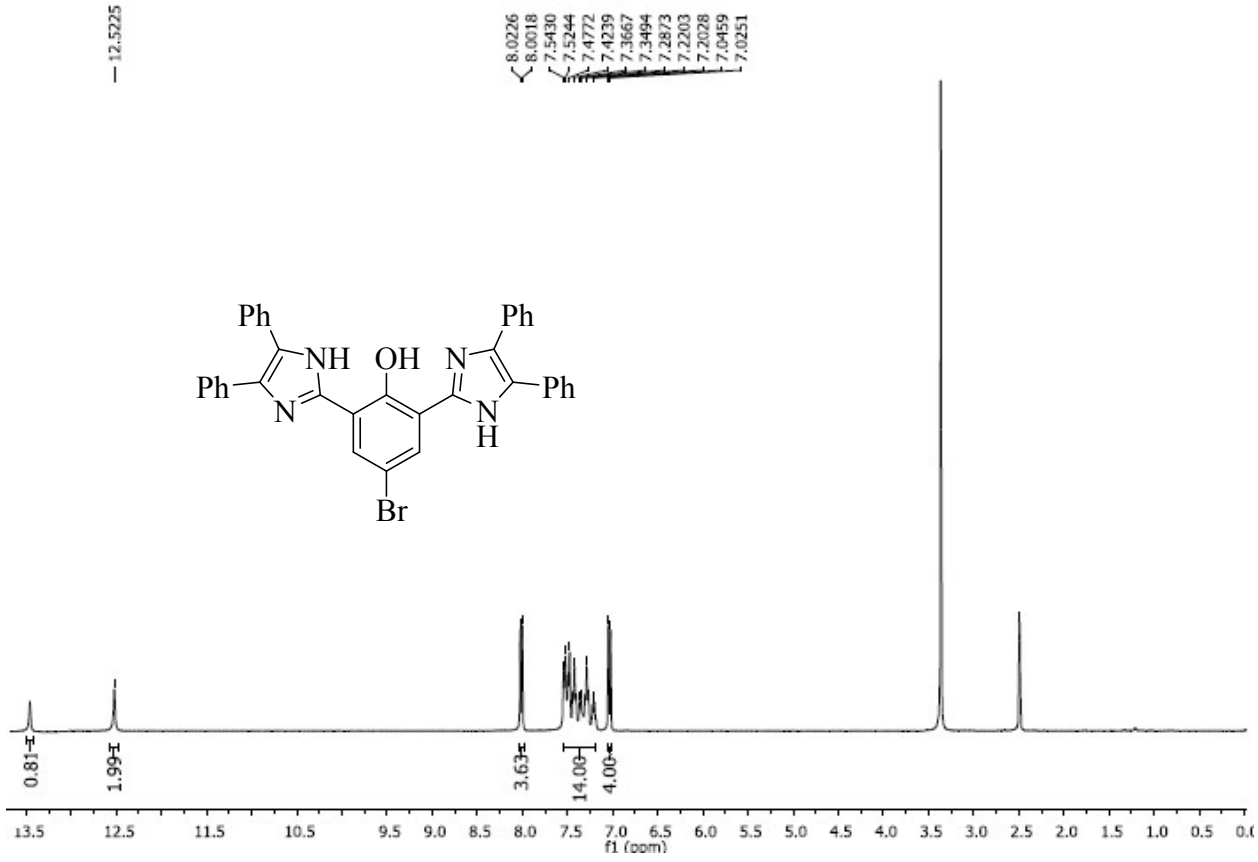
^{1}H NMR spectrum of IL 3c



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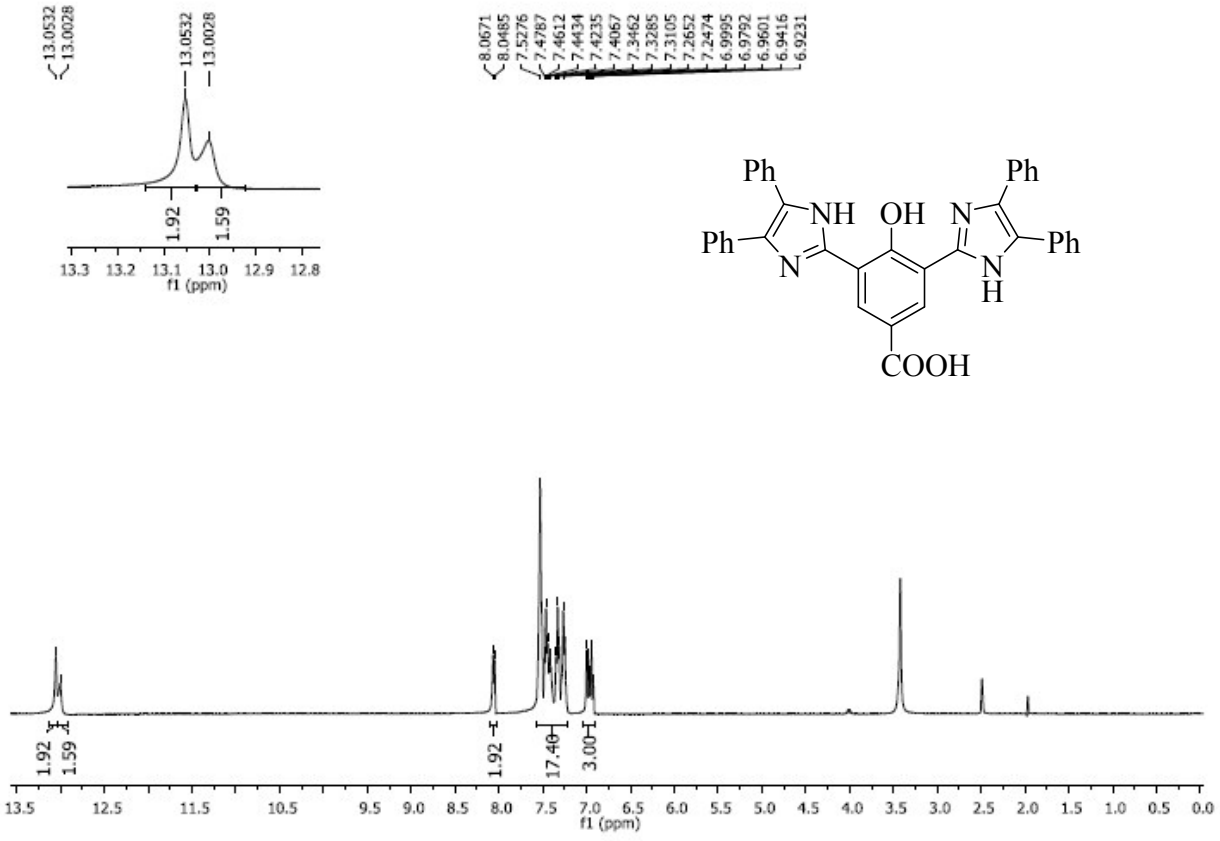

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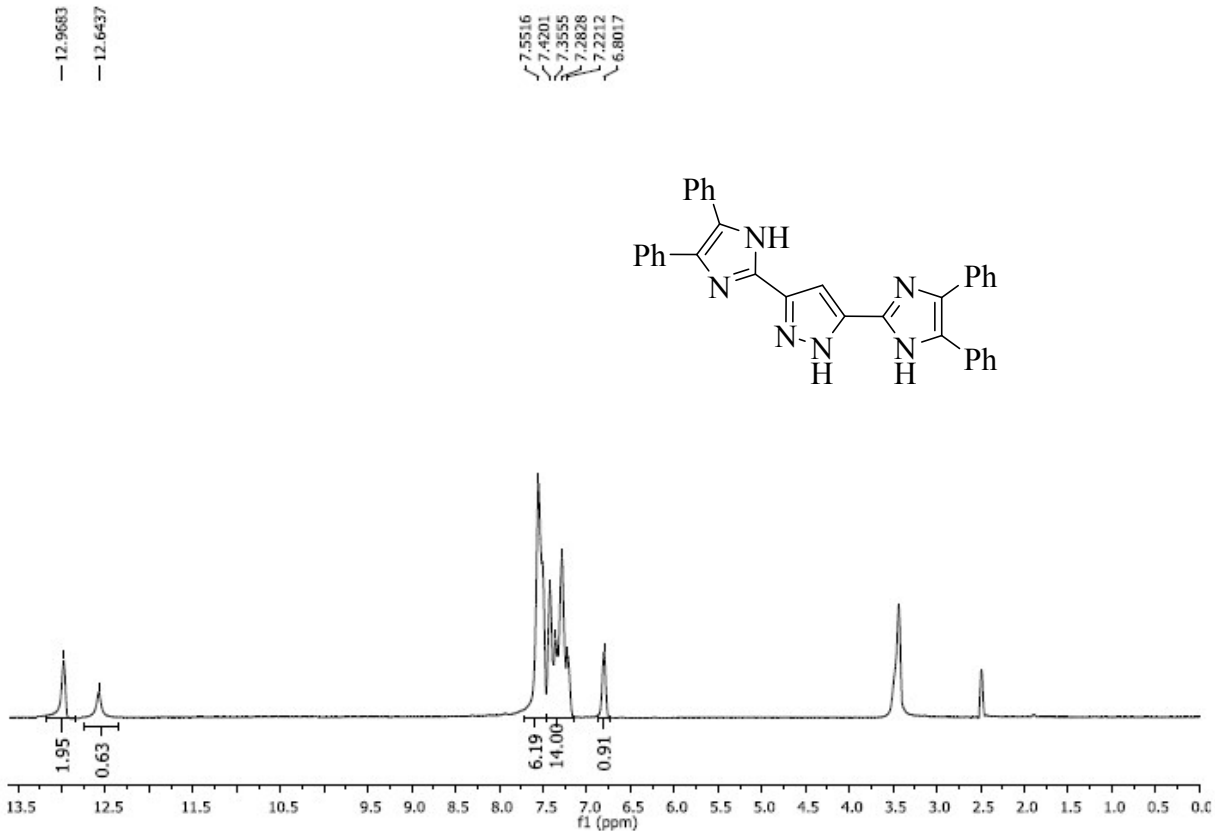

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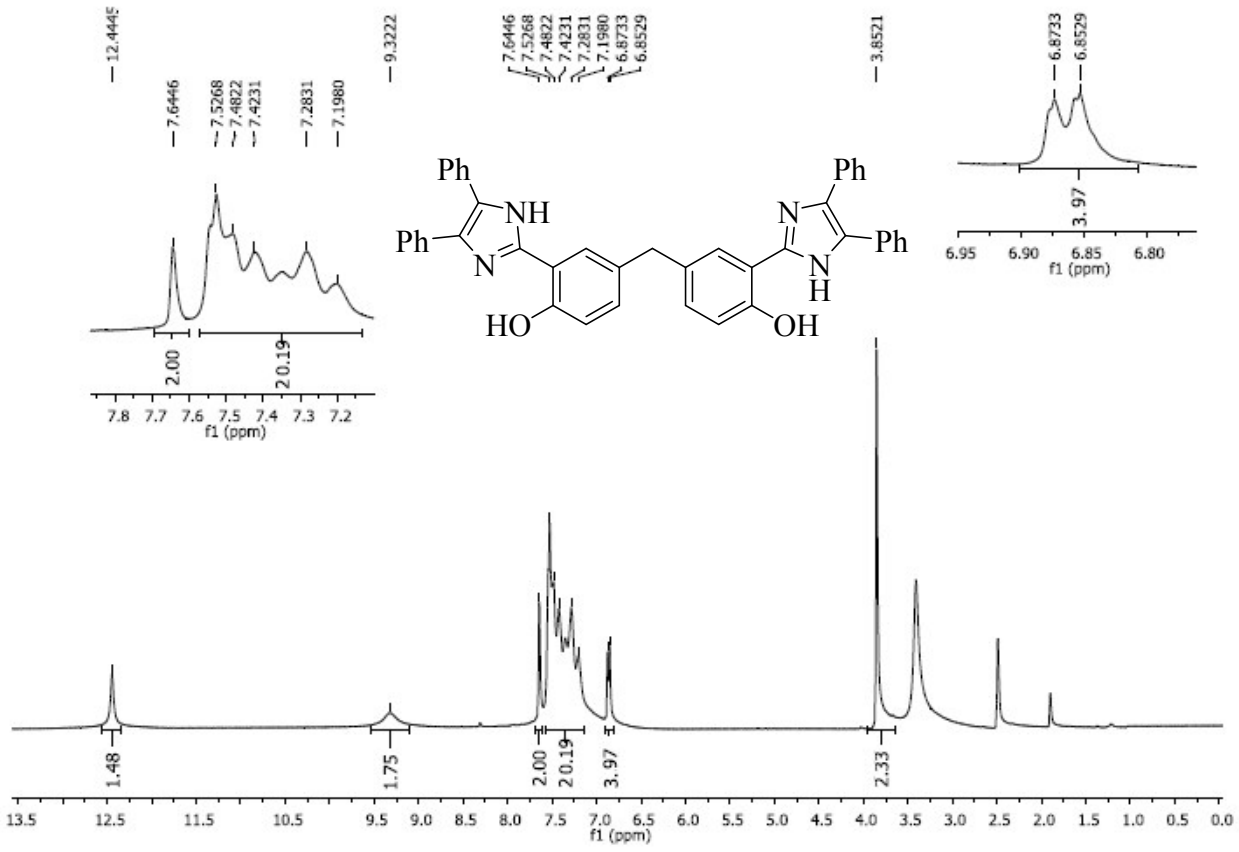

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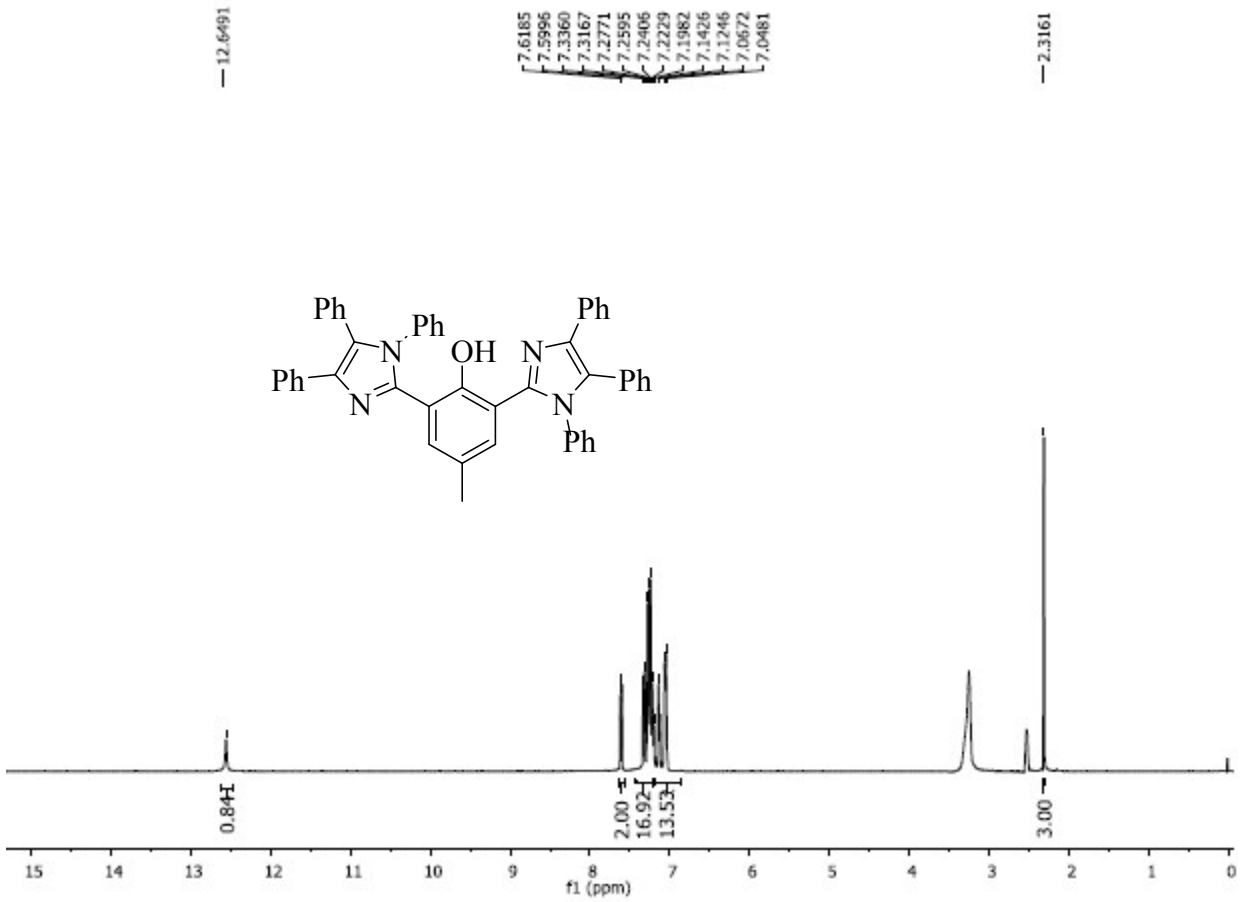

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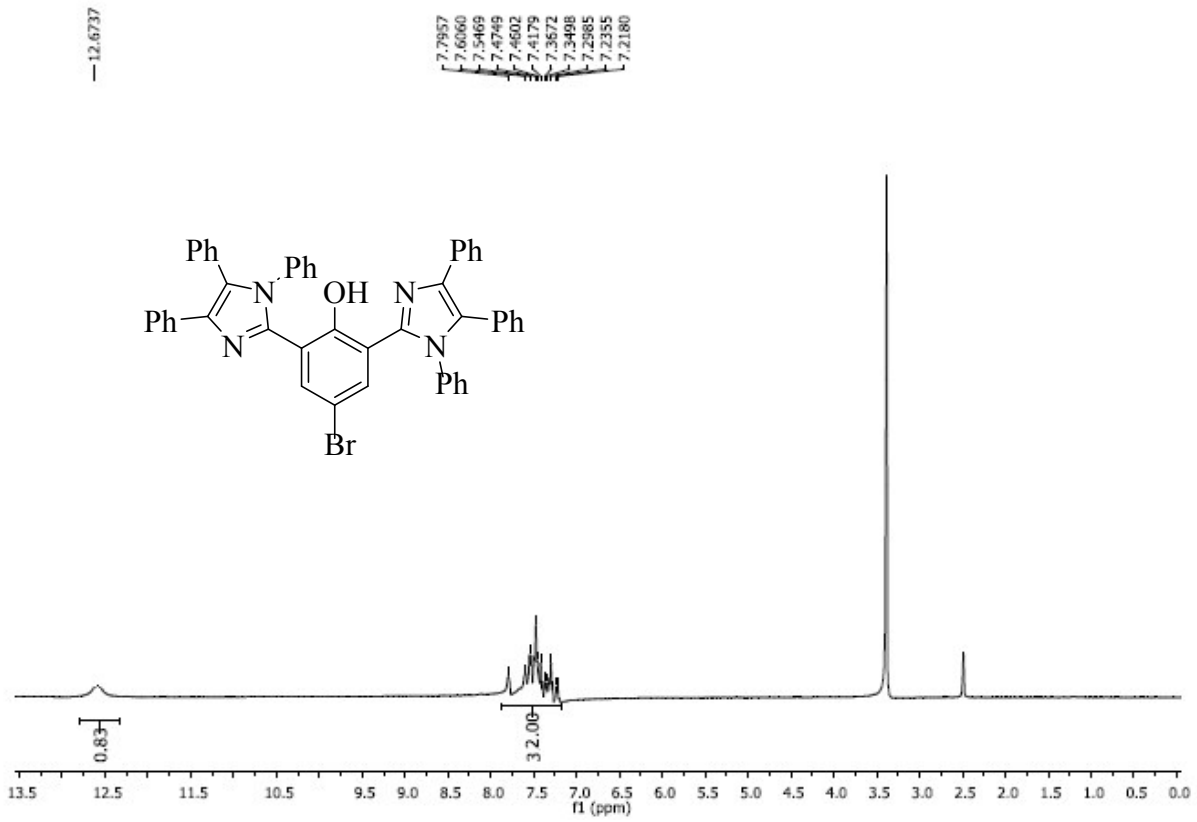

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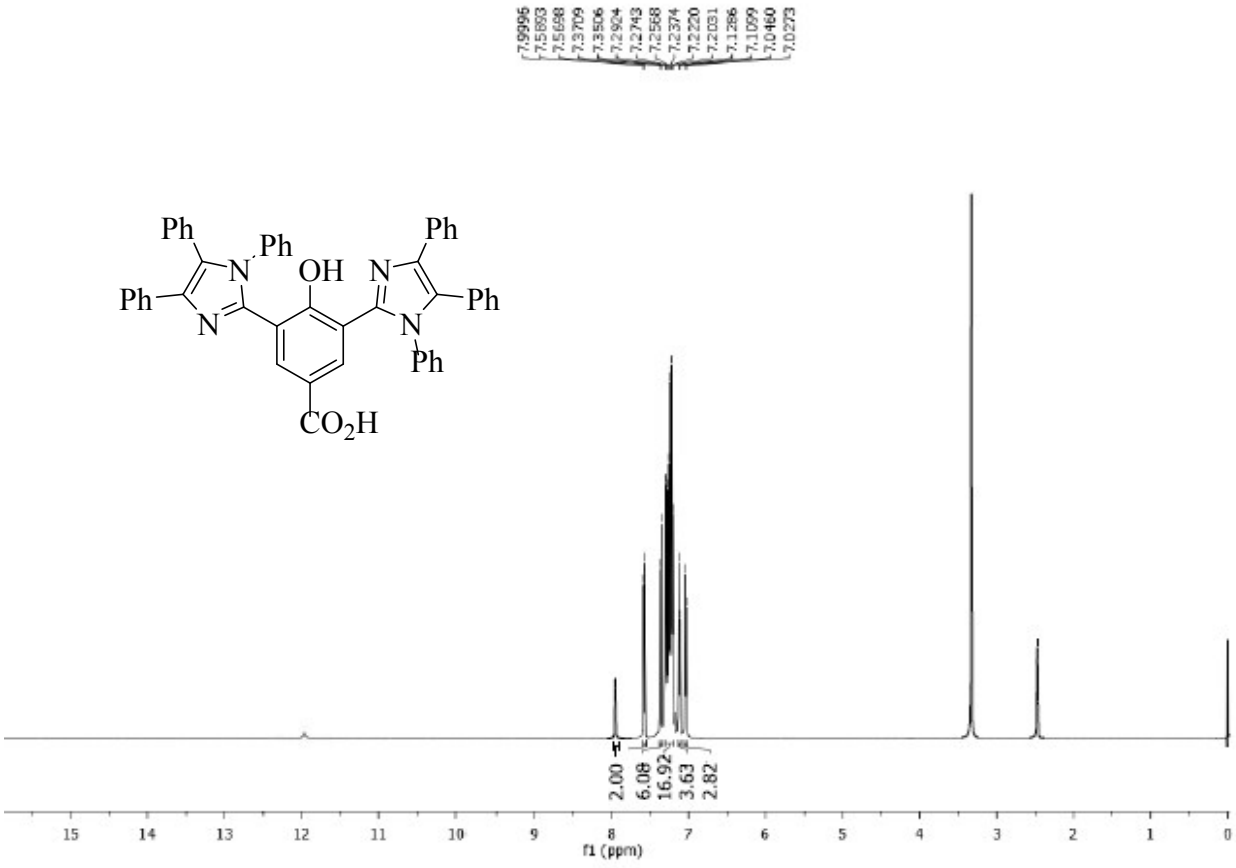

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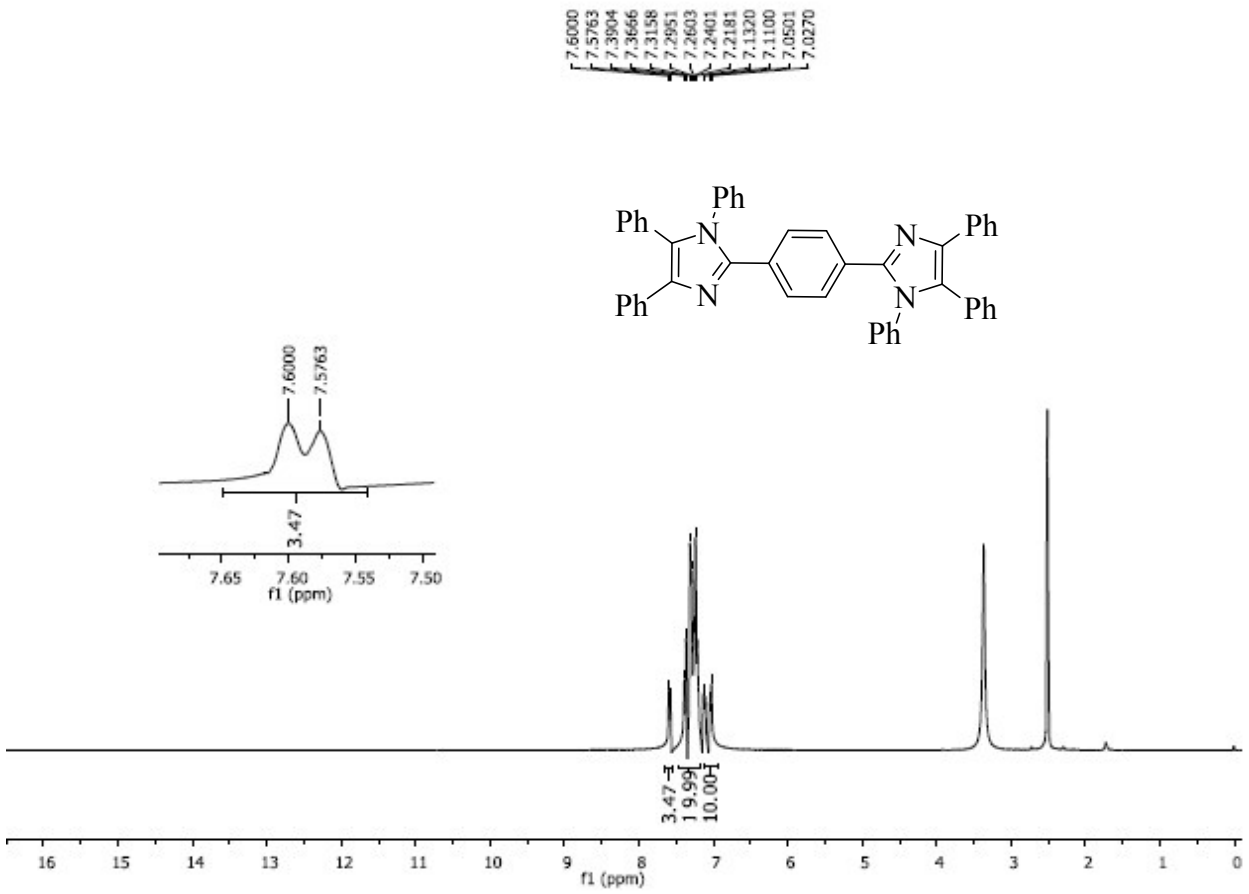
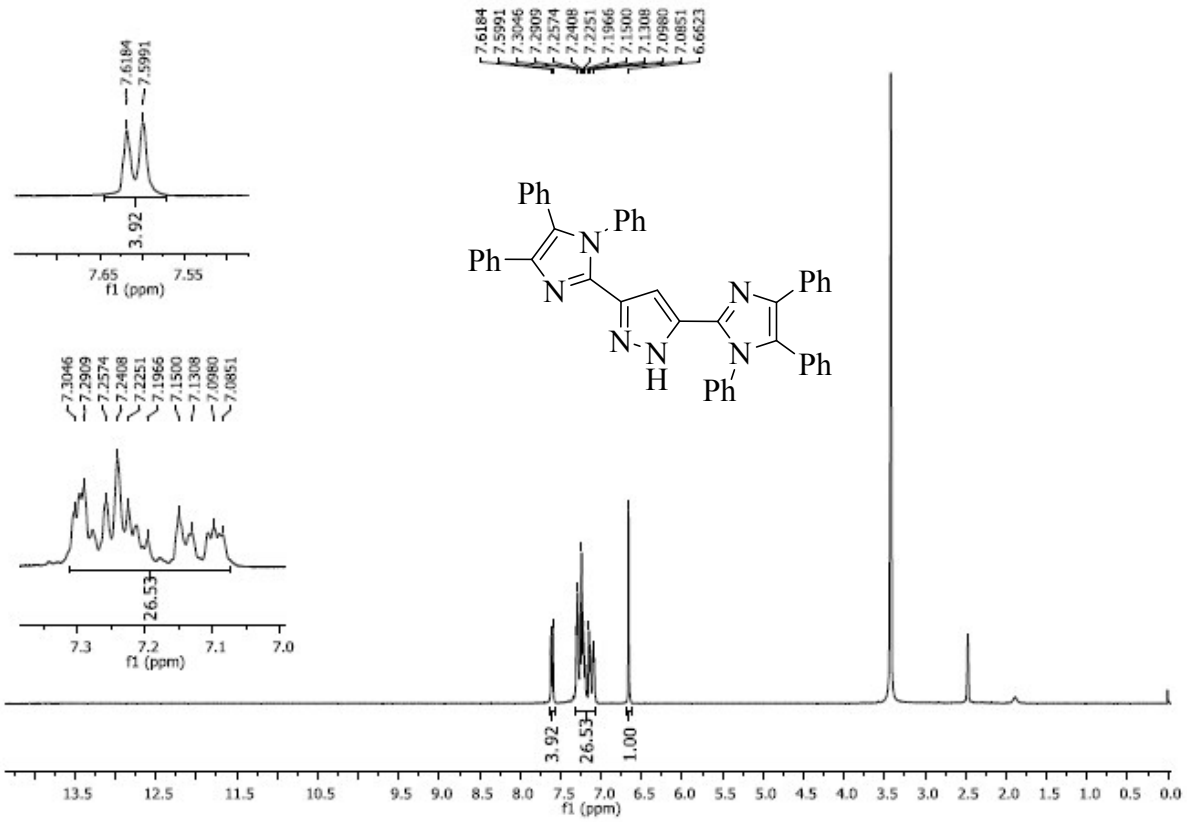


^{1}H NMR spectrum of compound 11d



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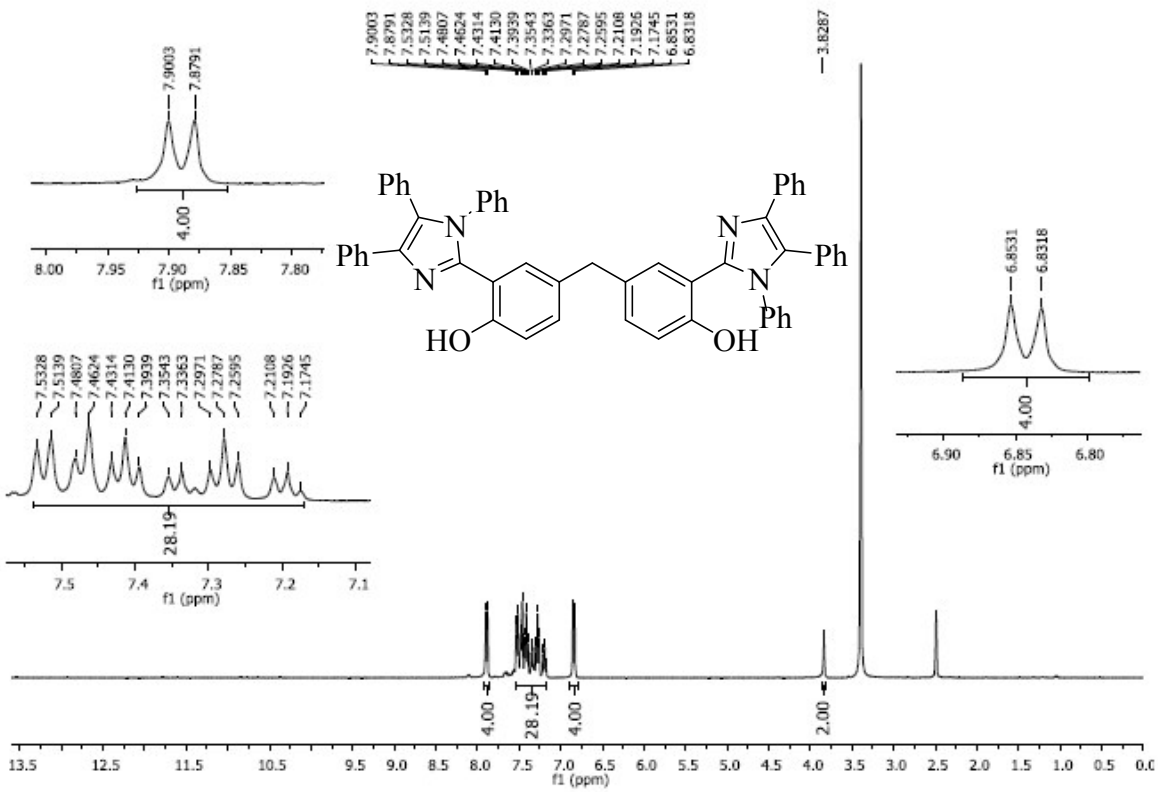

[1]H NMR spectrum of compound 11f