Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information

Photocatalytic coupling of amines to imidazoles using Mo-$ZnIn_2S_4$ catalyst

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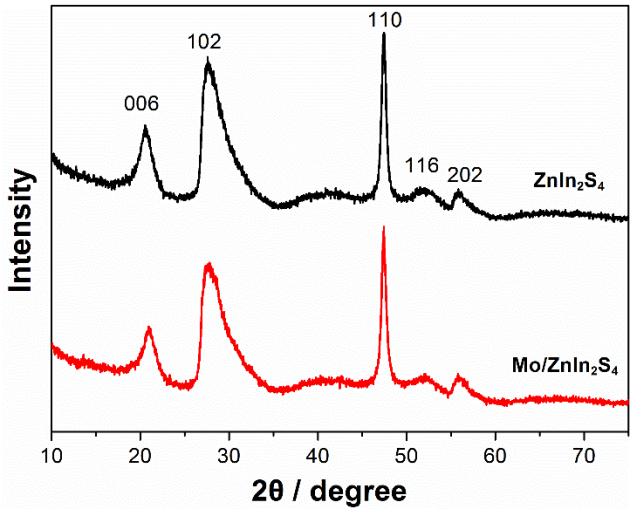


Figure S1 XRD pattern of $ZnIn_2S_4$ and Mo-$ZnIn_2S_4$

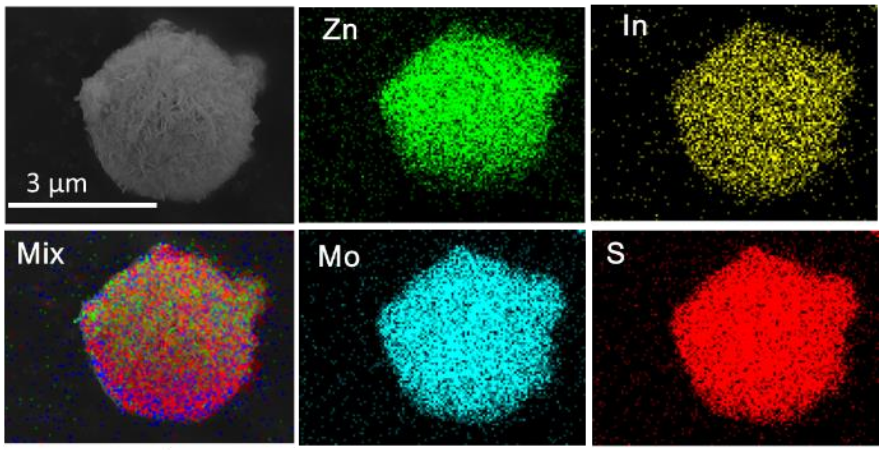


Figure S2. SEM and element mapping of Mo-$ZnIn_2S_4$.

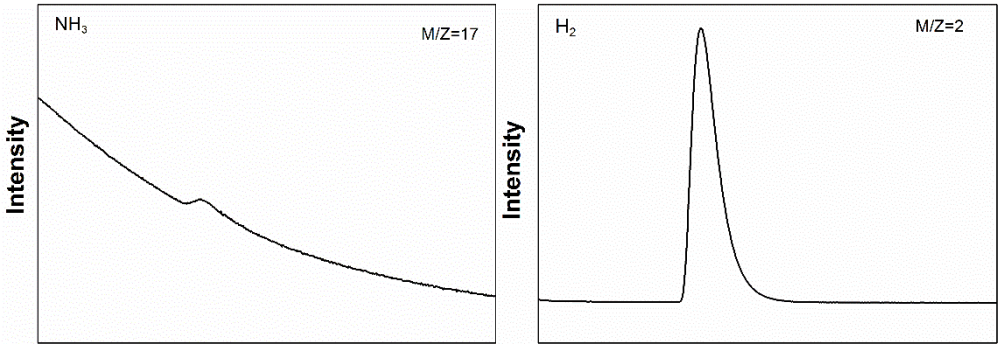


Figure S3. Mass spectrometry detection of the gas phase of photocatalyzed benzylamine self-coupling. The reaction gas was injected into the mass spectrometry, the peak of H_2 (M/Z=2) and NH_3 (M/Z=17) appeared.

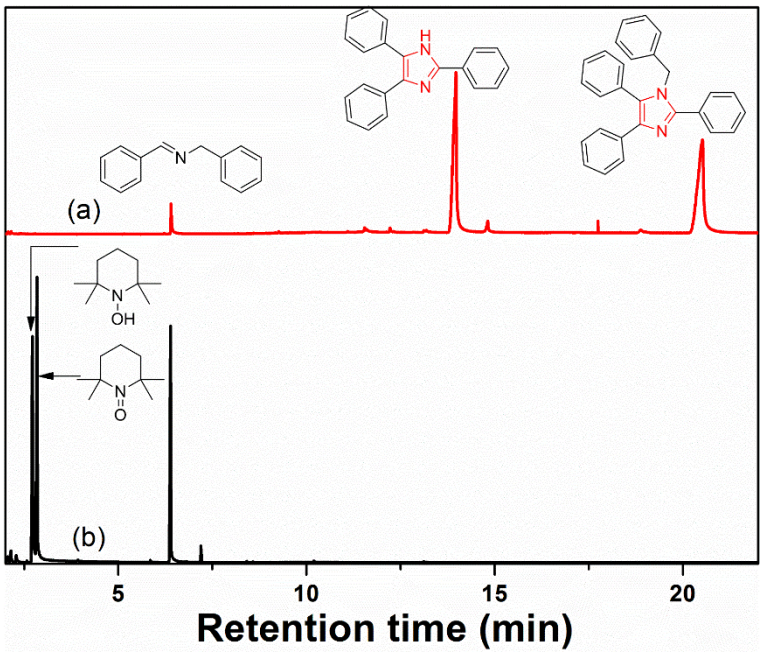


Figure S4. The photocatalytic reaction of benzylamines without (a) and in the presence of TEMPO (b). Conditions: benzylamine (0.5 mmol) and Mo/$ZnIn_2S_4$ (10 mg) were added in CH_3CN (1 mL) under Ar atmosphere and irradiation of 9.6 W blue LED (455 nm) for 6 h at rt. TEMPO (1 mmol) was added as radical scavenger.

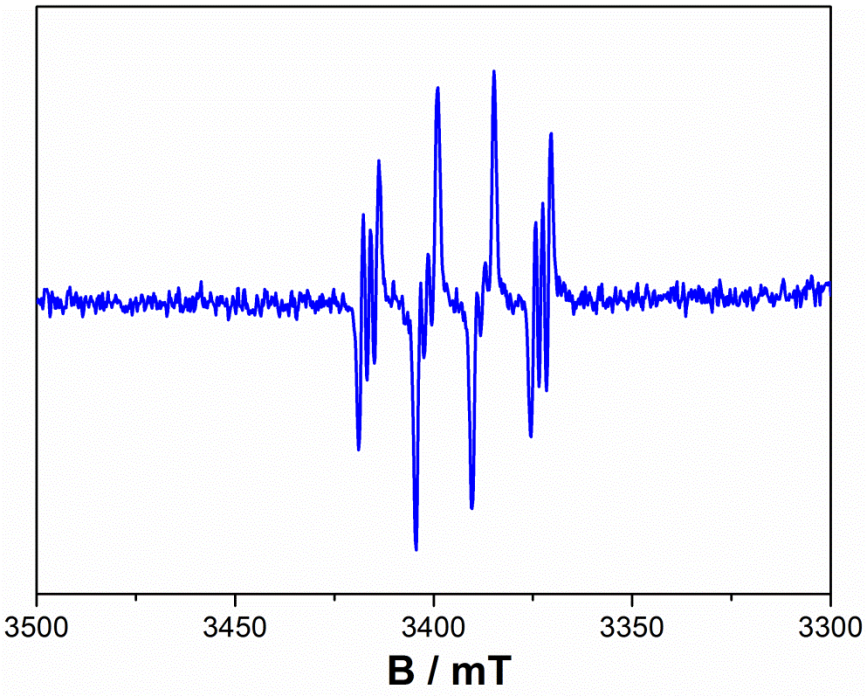


Figure S5. EPR spectrum of benzylamine under photoirridiation (455 nm) over Mo-$ZnIn_2S_4$ catalyst in the presence of dimethyl pyridine N-oxide.

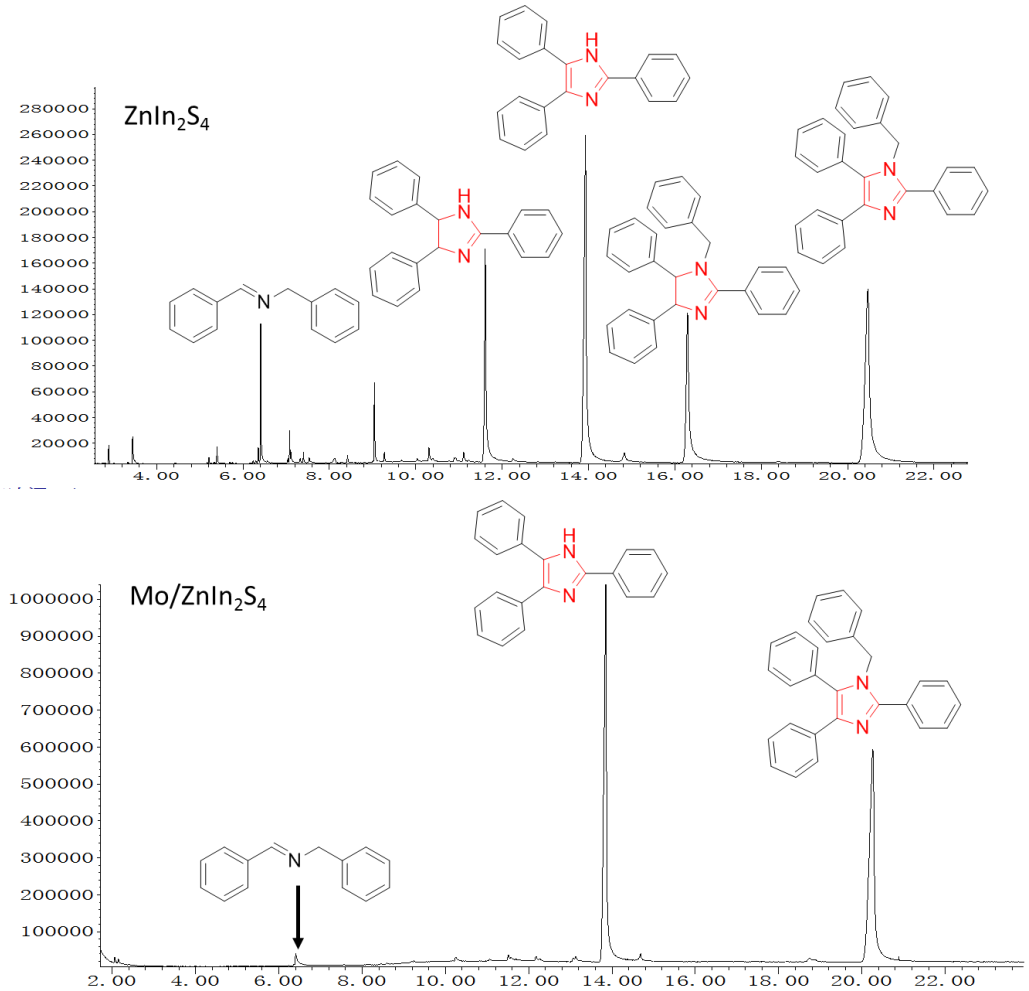
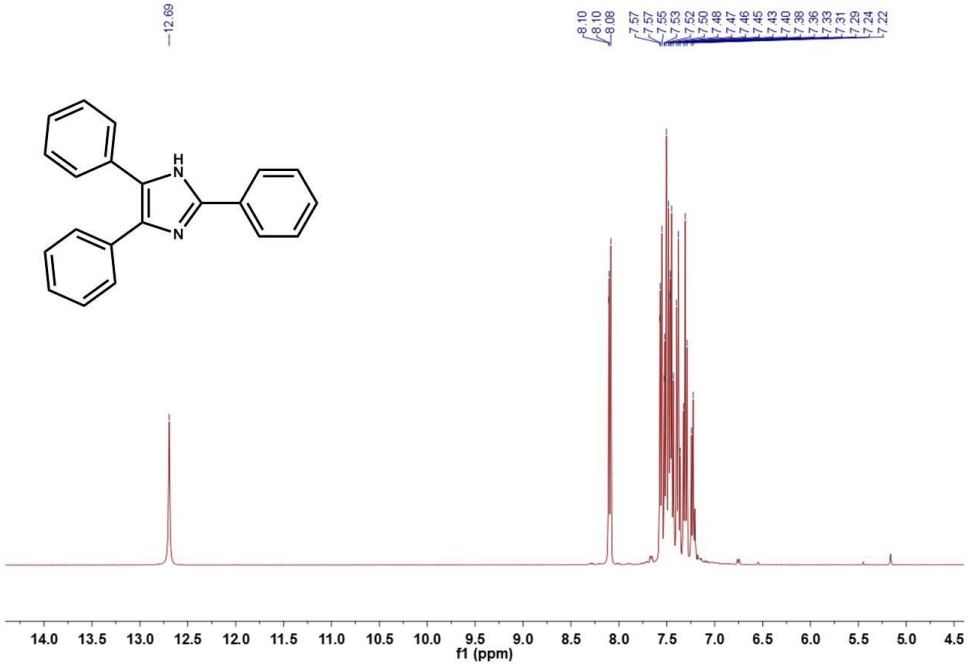


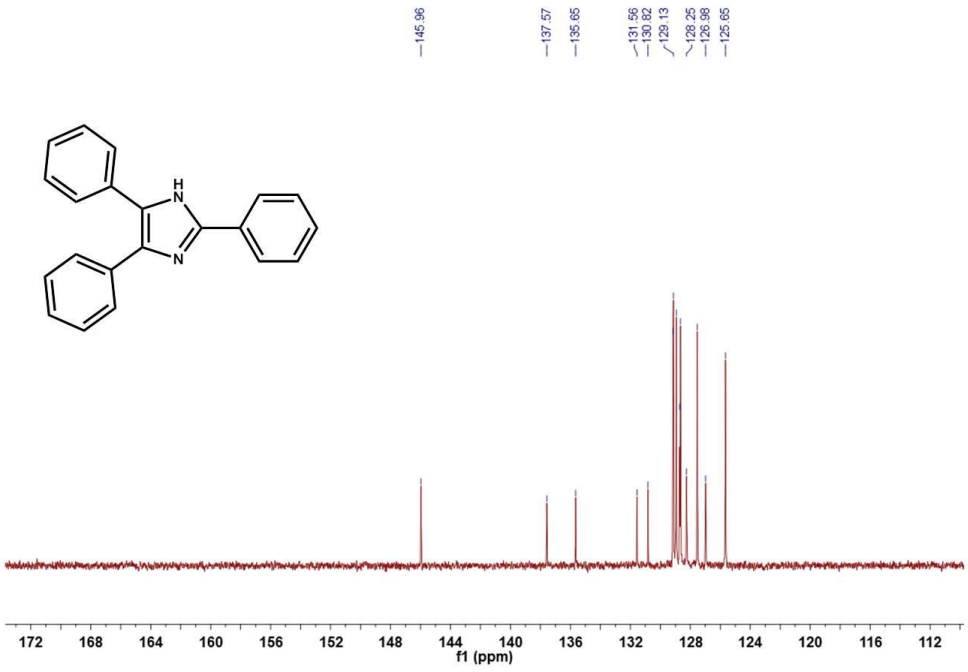
Figure S6. The photocatalytic reaction of benzylamines $ZnIn_2S_4$ (top) and Mo-$ZnIn_2S_4$ (bottom). Conditions: benzylamine (0.5 mmol) and Mo-$ZnIn_2S_4$ (10 mg) were added in CH_3CN (1 mL) under Ar atmosphere and irradiation of 9.6 W blue LED (455 nm) for 12 h at rt.

H-NMR and ^{13}C-NMR of the isolated products

2,4,5-triphenyl-1H-imidazole

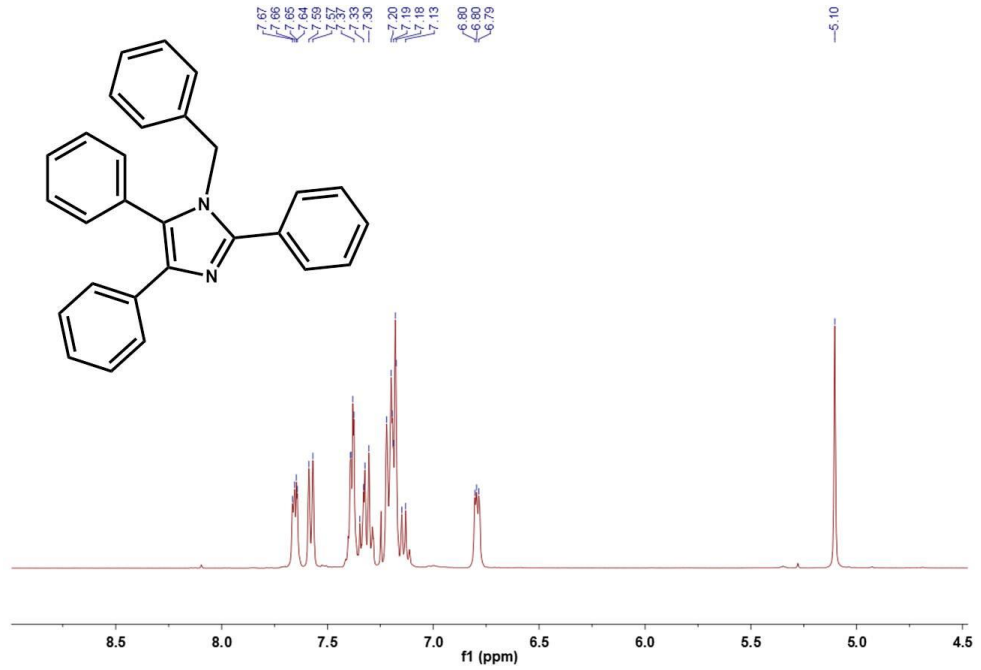
^{1}H NMR (400 MHz, d_6-DMSO) δ = 12.69 (s, 1H), 8.10 (m, 2H), 7.56 (m, 2H), 7.48 (ddd, *J*=14.5, 10.6, 4.5, 6H), 7.38 (t, *J*=7.3, 2H), 7.31 (t, *J*=7.4, 2H), 7.22 (t, *J*=7.3, 1H). ^{13}C NMR (101 MHz, d_6-DMSO) δ = 145.96, 137.57, 135.65, 131.56, 130.82, 129.15, 129.13, 128.94, 128.71, 128.65, 128.25, 127.53, 126.98, 125.65.

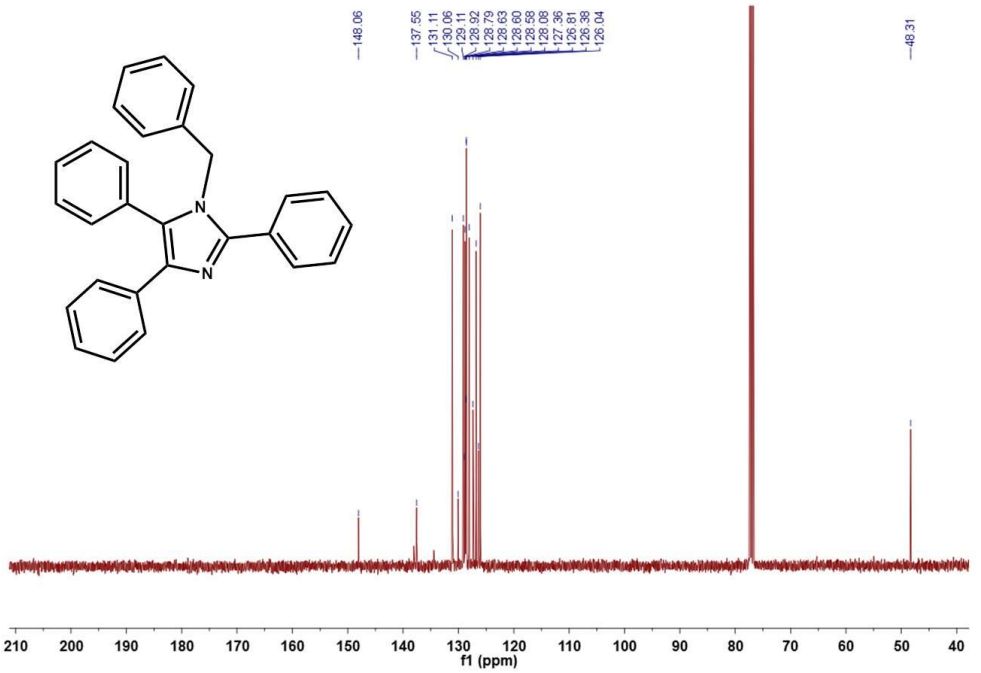




1-benzyl-2,4,5-triphenyl-1H-imidazole

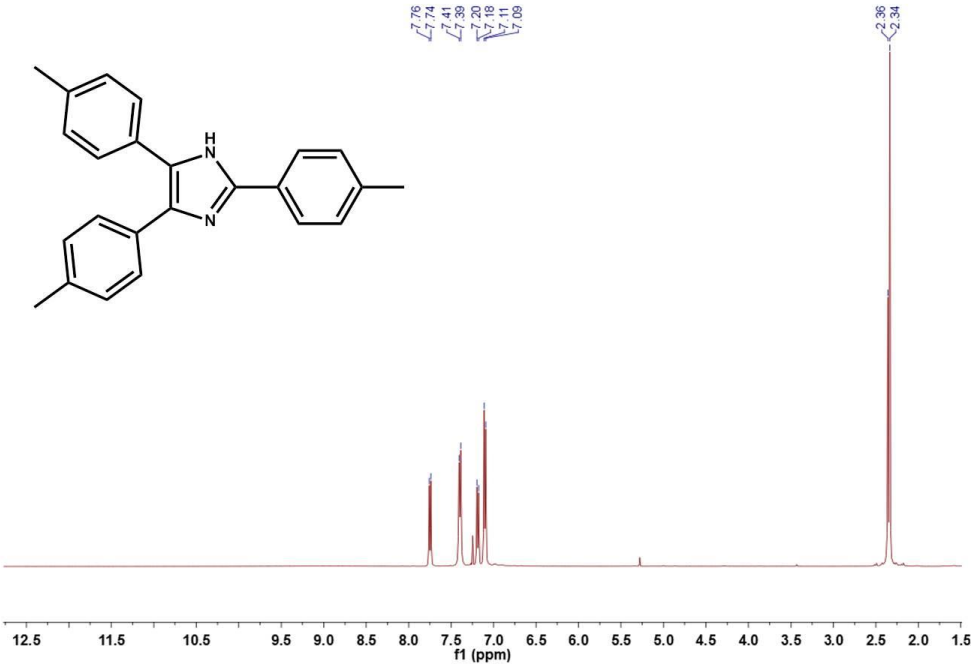
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (dd, *J*=6.5, 3.0, 2H), 7.58 (d, *J*=7.3, 2H), 7.35 (ddd, *J*=17.1, 7.4, 4.5, 6H), 7.18 (ddd, *J*=19.6, 14.4, 7.9, 8H), 6.79 (m, 2H), 5.10 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.06, 137.55, 131.11, 130.06, 129.11, 128.92, 128.79, 128.63, 128.60, 128.58, 128.08, 127.36, 126.81, 126.38, 126.04, 48.31.

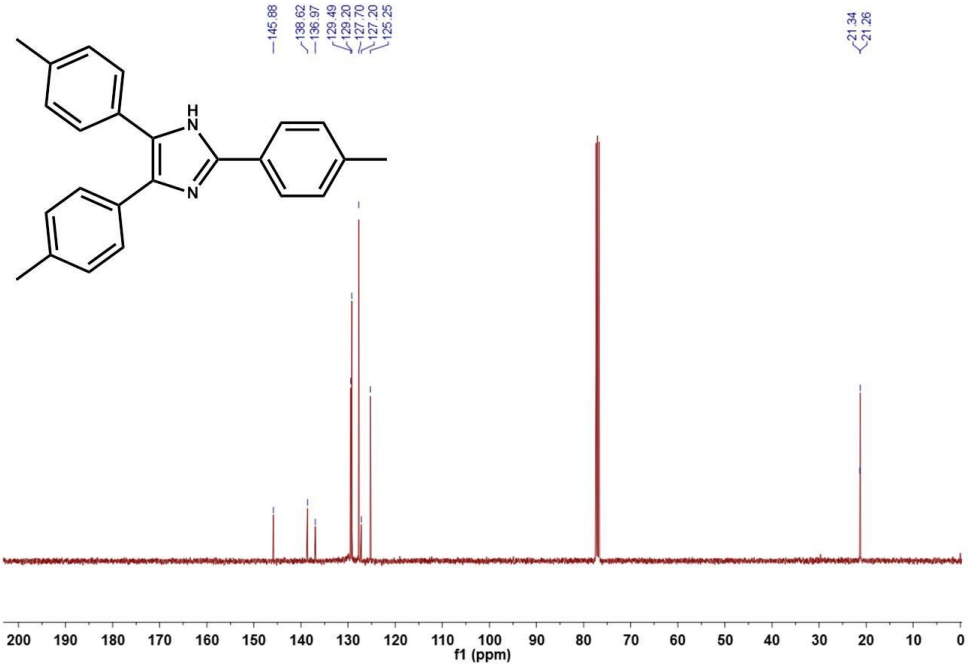




2,4,5-tri-p-tolyl-1H-imidazole

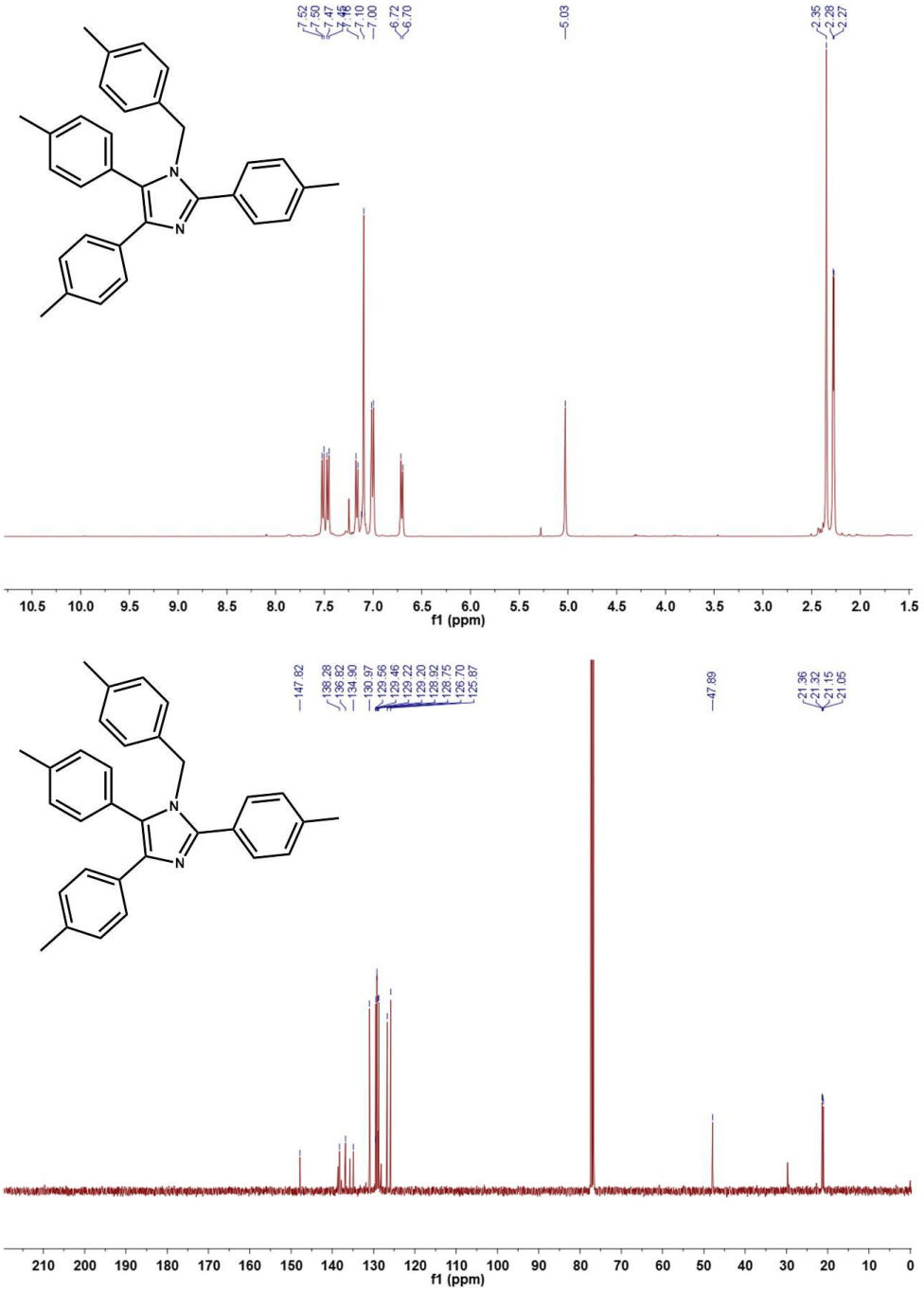
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J*=8.1, 2H), 7.40 (d, *J*=7.8, 4H), 7.19 (d, *J*=8.0,2H), 7.10 (d, *J*=7.9, 4H), 2.35 (d, *J*=9.3, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.88, 138.62, 136.97, 129.49, 129.20, 127.70, 127.20, 125.25, 21.34, 21.26.





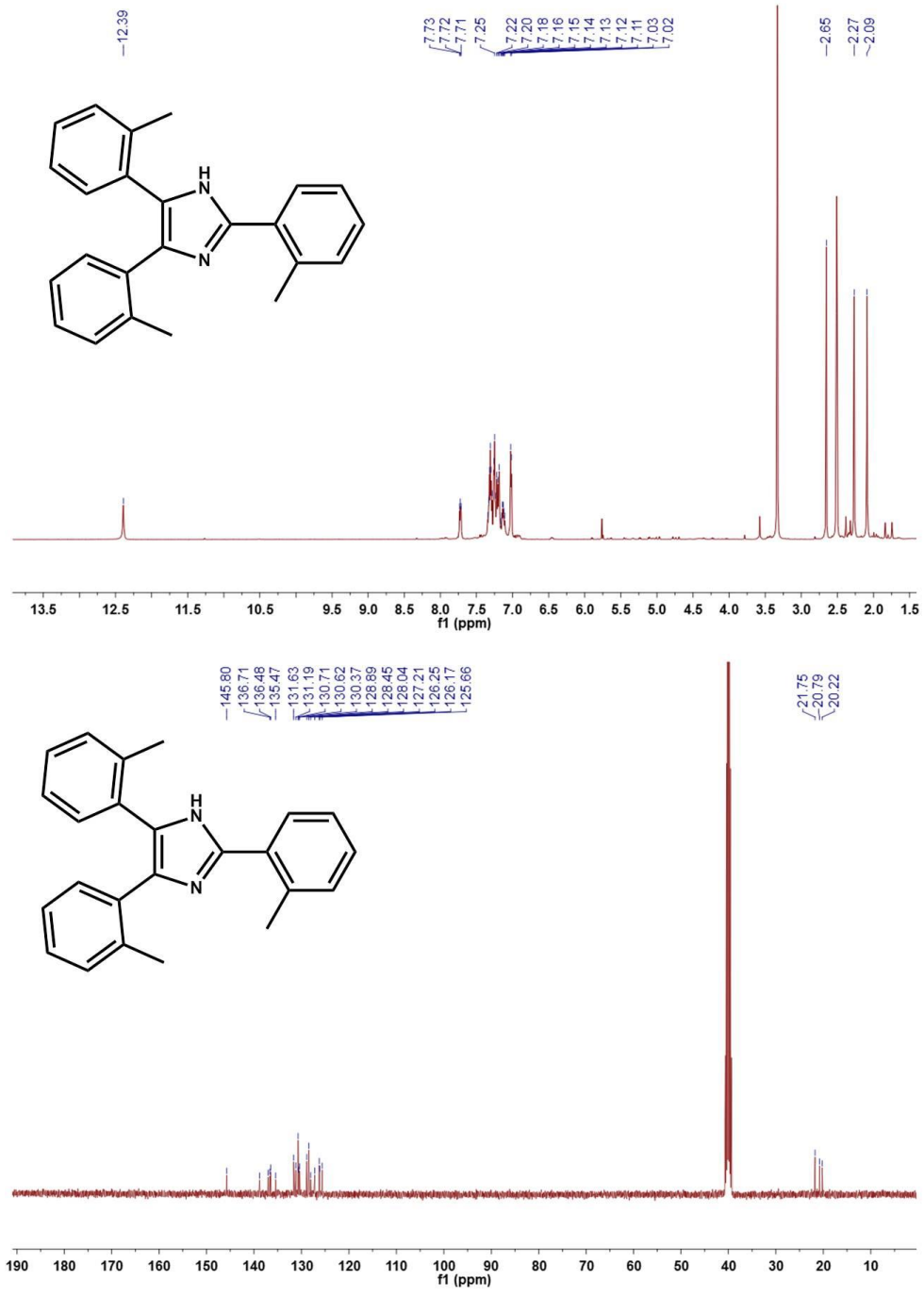
1-(4-methylbenzyl)-2,4,5-tri-p-tolyl-1H-imidazole

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (d, *J*=8.0, 2H), 7.46 (d, *J*=8.1, 2H), 7.17 (d, *J*=7.9, 2H), 7.11 (d, *J*=8.8, 4H), 7.01 (d, *J*=7.9, 4H), 6.71 (d, *J*=7.9, 2H), 5.03 (s, 2H), 2.35 (s, 6H), 2.28 (d, *J*=4.0, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.82, 138.28, 136.82, 134.90, 130.97, 129.56, 129.46, 129.22, 129.20, 128.92, 128.75, 126.70, 125.87, 47.89, 21.36, 21.32, 21.15, 21.05.



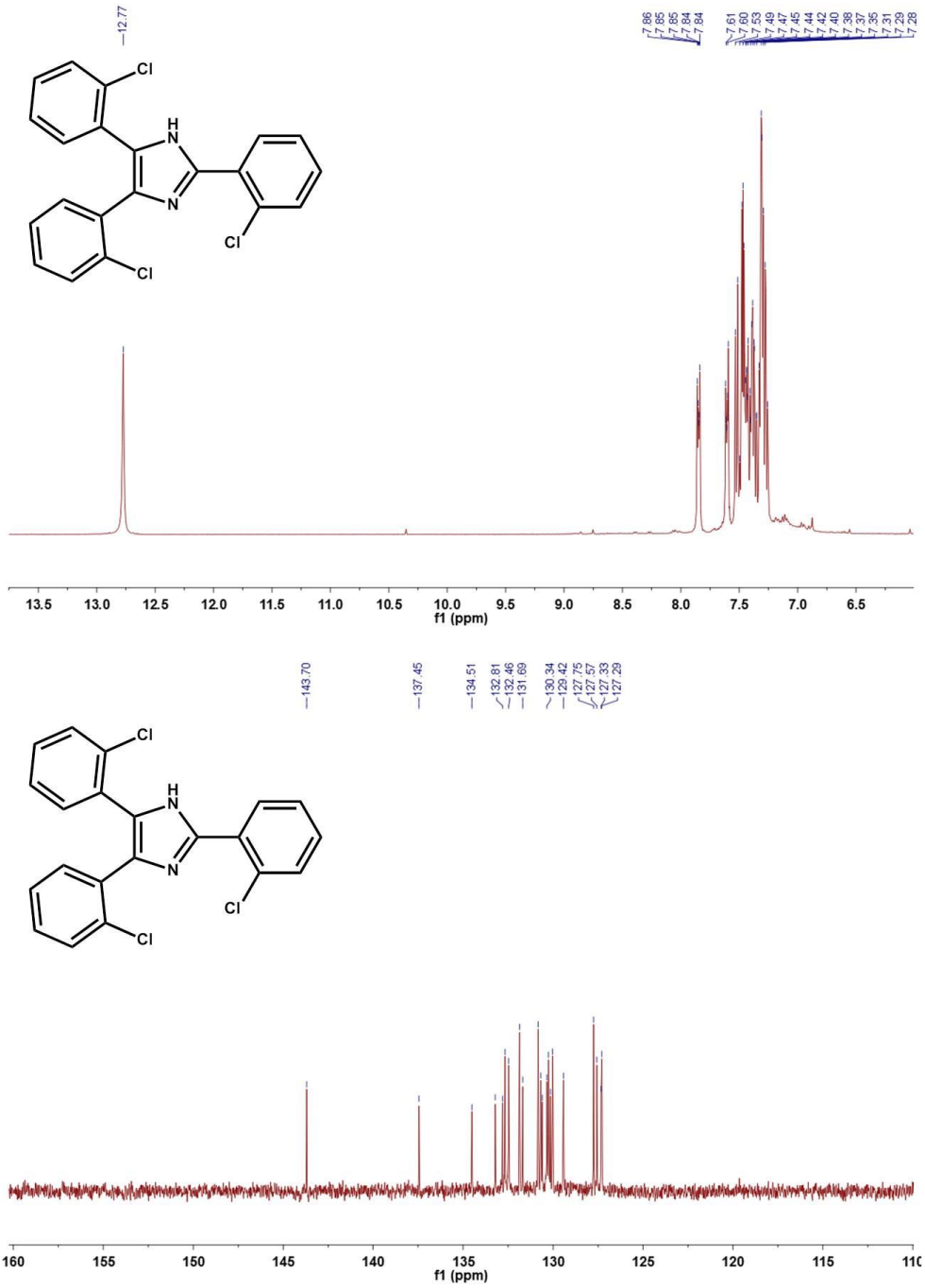
2,4,5-tri-o-tolyl-1H-imidazole

^{1}H NMR (400 MHz, d_6-DMSO) δ = 12.39 (s, 1H), 7.72 (m, 1H), 7.31 (dt, *J*=9.2, 5.2, 3H), 7.18 (m, 6H), 7.02 (d, *J*=4.1, 2H), 2.65 (s, 3H), 2.27 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ = 145.80, 138.81, 137.05, 136.71, 136.48, 135.47, 131.63, 131.19, 130.71, 130.62, 130.37, 128.89, 128.45, 128.04, 127.21, 126.25, 126.17, 125.66, 21.75, 20.79, 20.22.



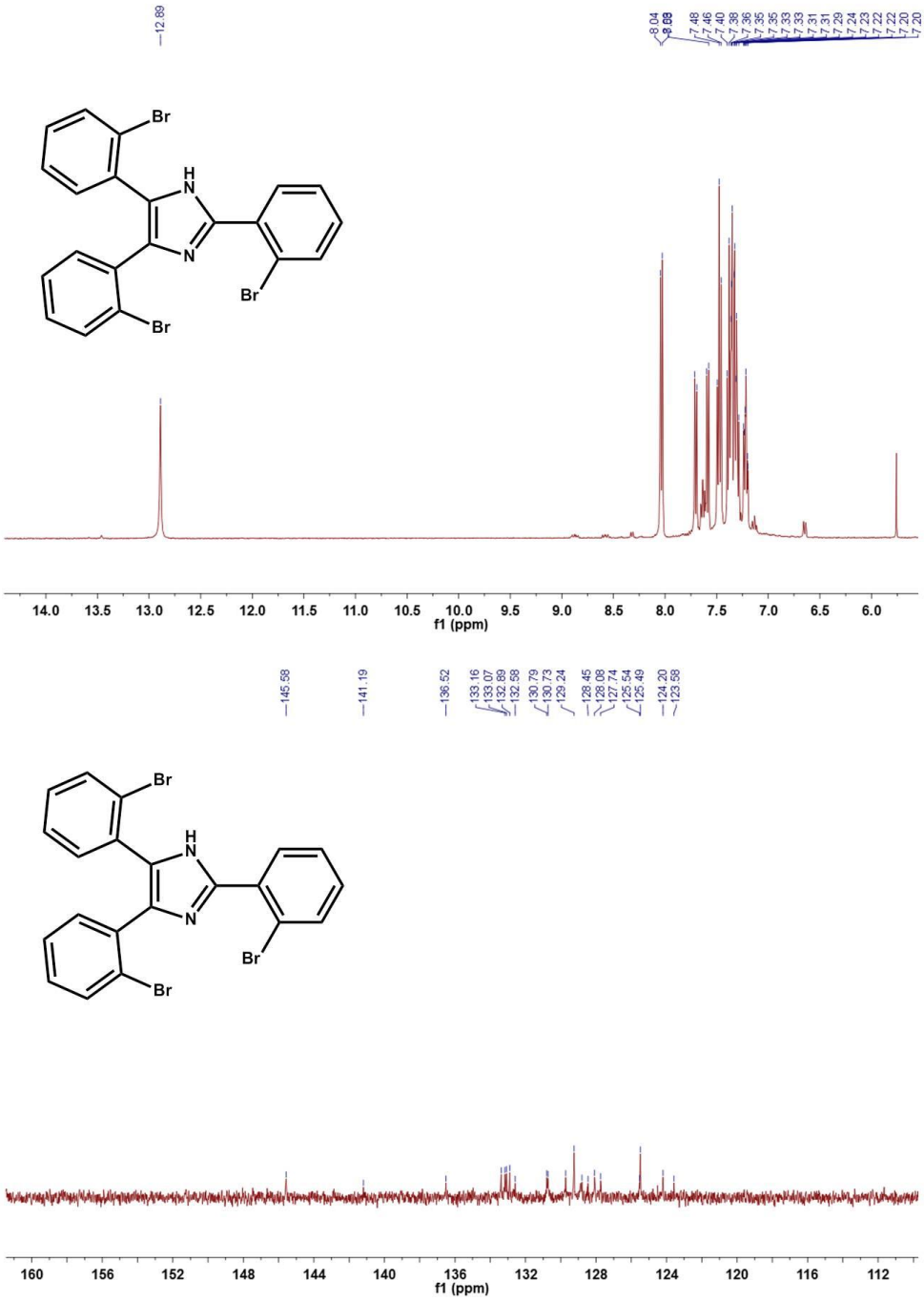
2,4,5-tris(2-chlorophenyl)-1H-imidazole

^{1}H NMR (400 MHz, d_6-DMSO) δ = 12.77 (s, 1H), 7.85 (m, 1H), 7.61 (m, 1H), 7.52 (d, *J*=7.9, 1H), 7.38 (m, 9H). ^{13}C NMR (101 MHz, d_6-DMSO) δ = 143.70, 137.45, 134.51, 133.21, 132.81, 132.68, 132.46, 131.87, 131.69, 130.83, 130.68, 130.61, 130.34, 130.25, 130.14, 130.02, 129.42, 127.75, 127.57, 127.33, 127.29.



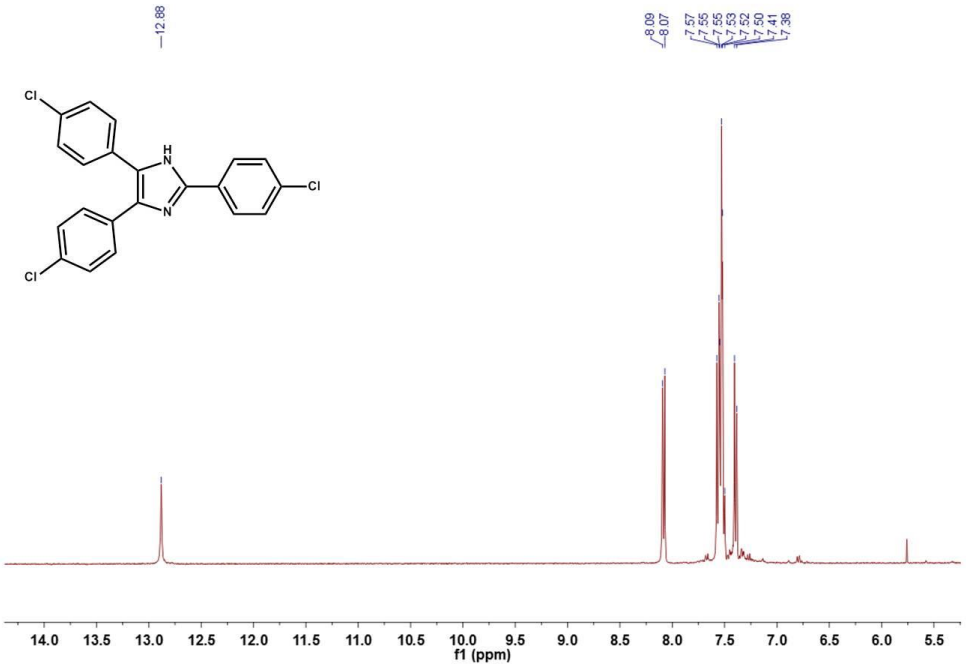
2,4,5-tris(2-bromophenyl)-1H-imidazole

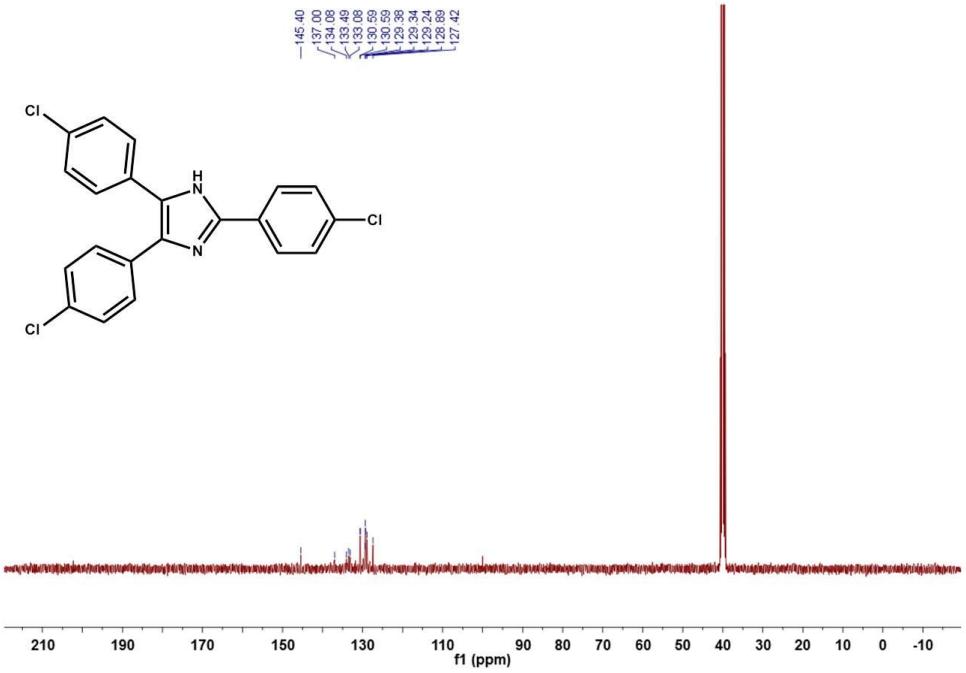
^{1}H NMR (400 MHz, d_6-DMSO) δ = 12.89 (s, 1H), 8.04 (d, *J*=7.4, 2H), 7.70 (d, *J*=8.0, 1H), 7.59 (d, *J*=7.9, 1H), 7.48 (t, *J*=7.5, 2H), 7.29 (dddd, *J*=14.6, 11.4, 10.2, 4.9, 6H). ^{13}C NMR (101 MHz, d_6-DMSO) δ = 145.58, 141.19, 136.52, 133.38, 133.16, 133.07, 132.89, 132.58, 130.79, 130.73, 129.72, 129.24, 128.80, 128.45, 128.08, 127.74, 125.54, 125.49, 124.20, 123.58.



2,4,5-tris(4-chlorophenyl)-1H-imidazole

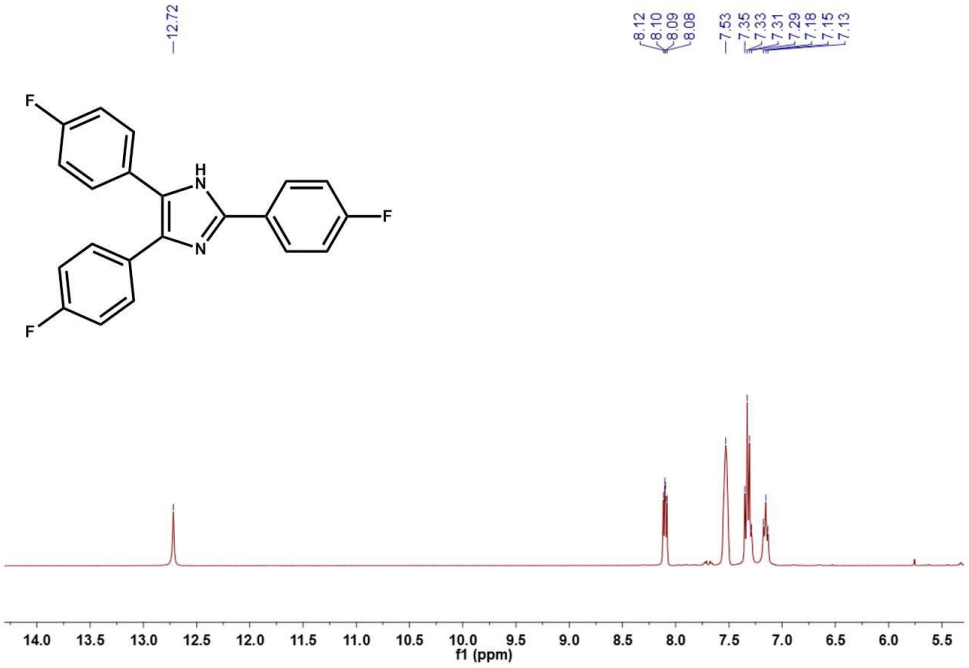
^{1}H NMR (400 MHz, d_6-DMSO) δ = 12.88 (s, 1H), 8.08 (d, *J*=8.6, 2H), 7.54 (dt, *J*=12.2, 8.7, 8H), 7.39 (d, *J*=8.5, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ = 145.40, 137.00, 134.08, 133.49, 133.08, 130.59, 130.59, 129.38, 129.34, 129.24, 128.89, 127.42.





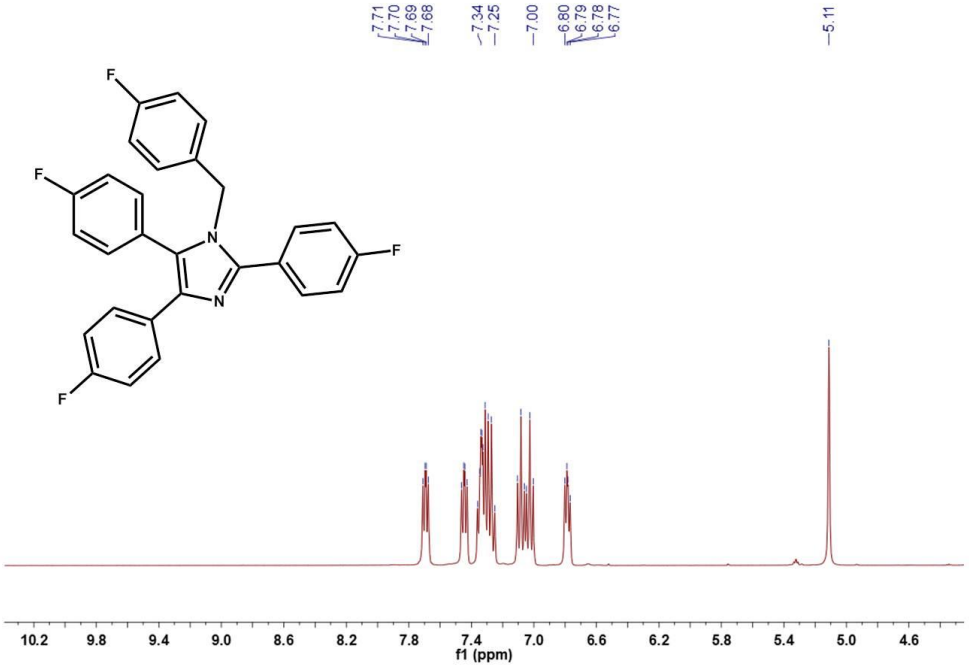
2,4,5-tris(4-fluorophenyl)-1H-imidazole

^{1}H NMR (400 MHz, d_6-DMSO) δ = 12.72 (s, 1H), 8.10 (dd, *J*=8.3, 5.6, 2H), 7.53 (s, 4H), 7.32 (m, 4H), 7.15 (t, *J*=8.5, 2H).



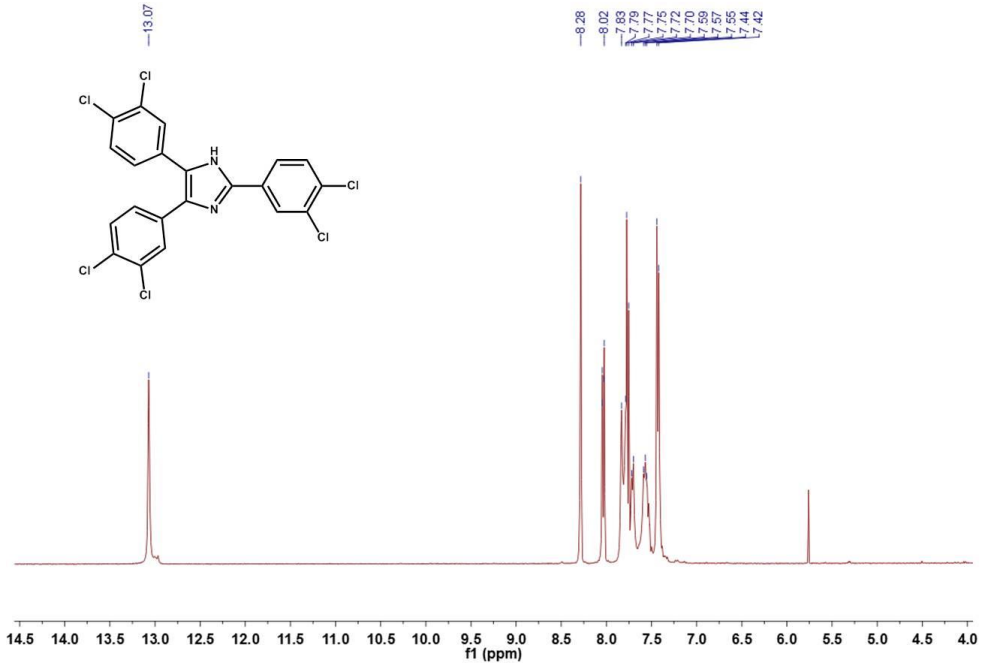
1-(4-fluorobenzyl)-2,4,5-tris(4-fluorophenyl)-1H-imidazole

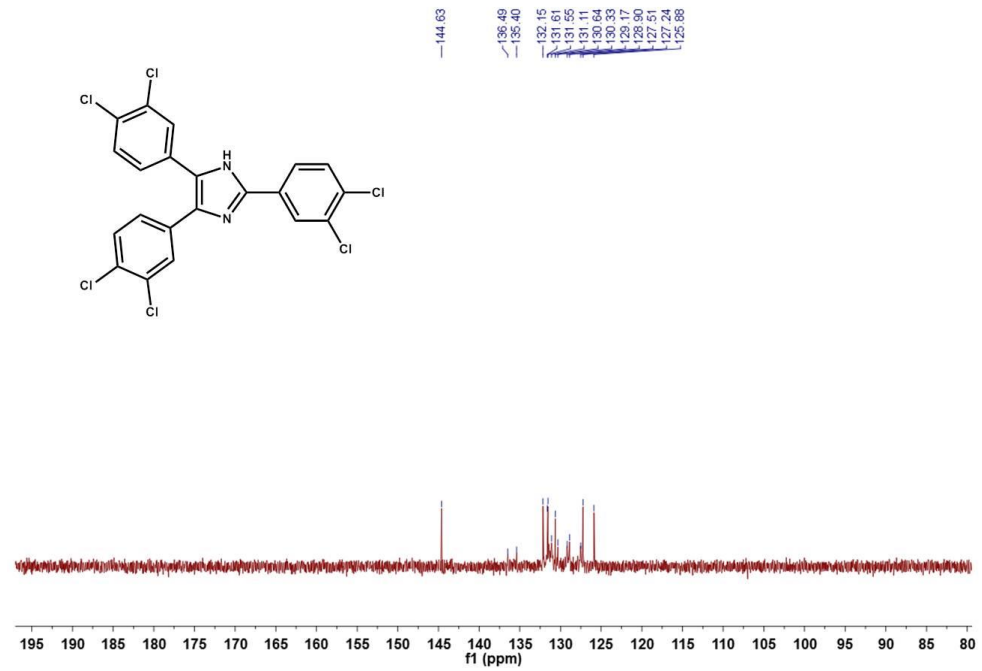
^{1}H NMR (400 MHz, d_6-DMSO) δ = 7.69 (dd, *J*=8.3, 5.6, 2H), 7.44 (dd, *J*=8.4, 5.8, 2H), 7.31 (m, 6H), 7.05 (dt, *J*=22.7, 8.8, 4H), 6.78 (dd, *J*=8.1, 5.6, 2H), 5.11 (s, 2H).



2,4,5-tris(3,4-dichlorophenyl)-1H-imidazole

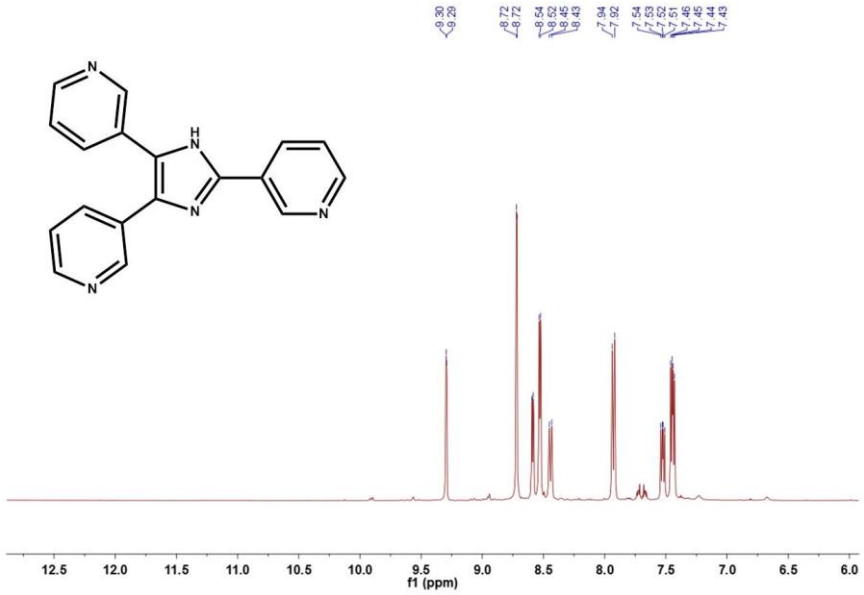
^{1}H NMR (400 MHz, d_6-DMSO) δ = 13.07 (s, 1H), 8.28 (s, 1H), 8.04 (dd, *J*=8.4, 1.6, 1H), 7.76 (m, 4H), 7.57 (m, 1H), 7.43 (d, *J*=8.3, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ = 144.63, 136.49, 135.40, 132.15, 131.61, 131.55, 131.11, 130.64, 130.33, 129.17, 128.90, 127.51, 127.24, 125.88.

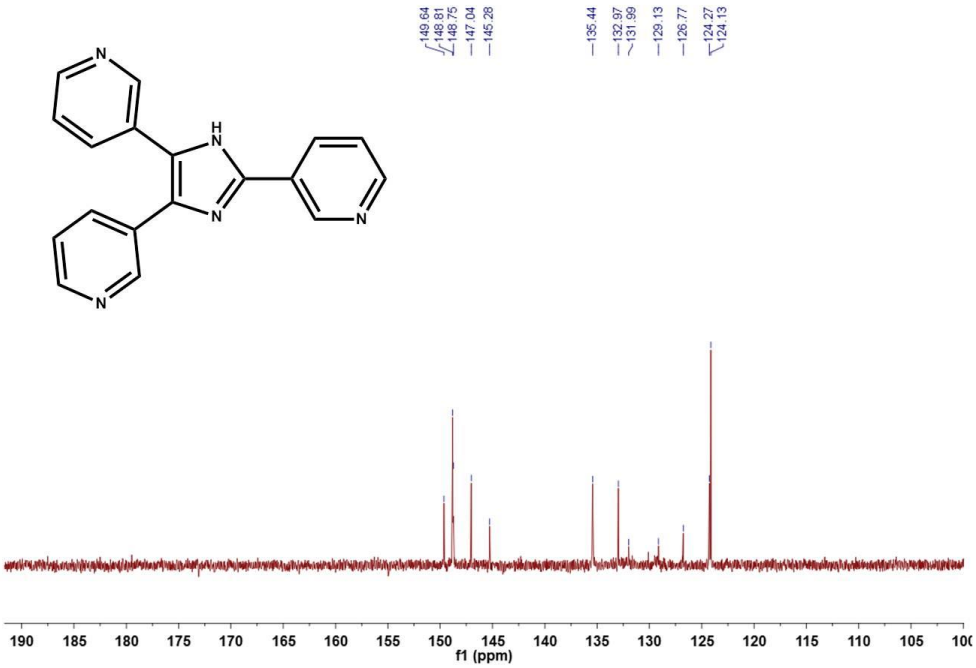




3,3',3''-(1H-imidazole-2,4,5-triyl)tripyridine

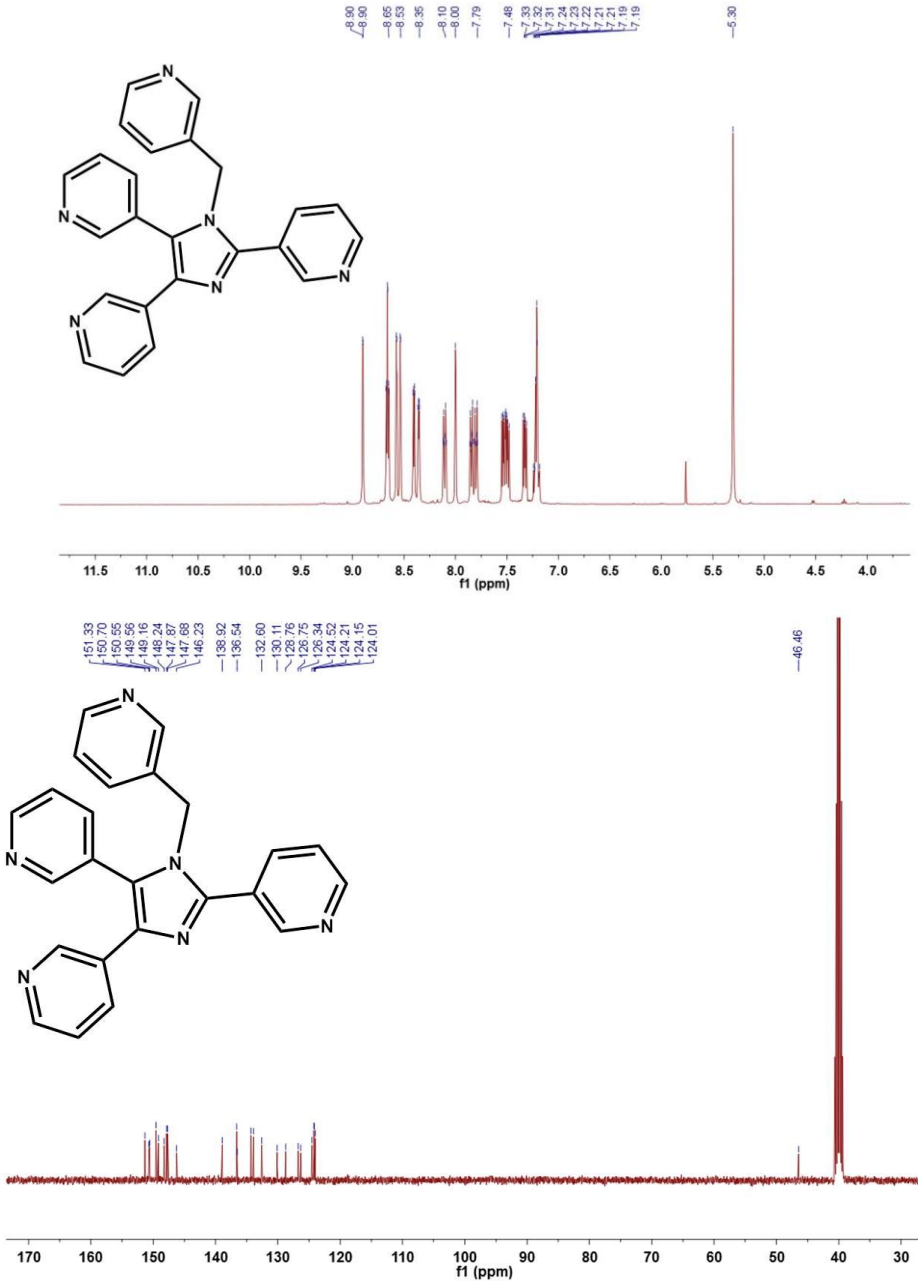
^{1}H NMR (400 MHz, d_6-DMSO) δ = 9.29 (d, *J*=1.6, 1H), 8.72 (d, *J*=2.0, 2H), 8.59 (m, 1H), 8.53 (d, *J*=4.7, 2H), 8.44 (d, *J*=8.0, 1H), 7.93 (d, *J*=7.9, 2H), 7.52 (dd, *J*=7.9, 4.8, 1H), 7.44 (dd, *J*=7.9, 4.8, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ = 149.64, 148.81, 148.75, 147.04, 145.28, 135.44, 132.97, 131.99, 129.13, 126.77, 124.27, 124.13.





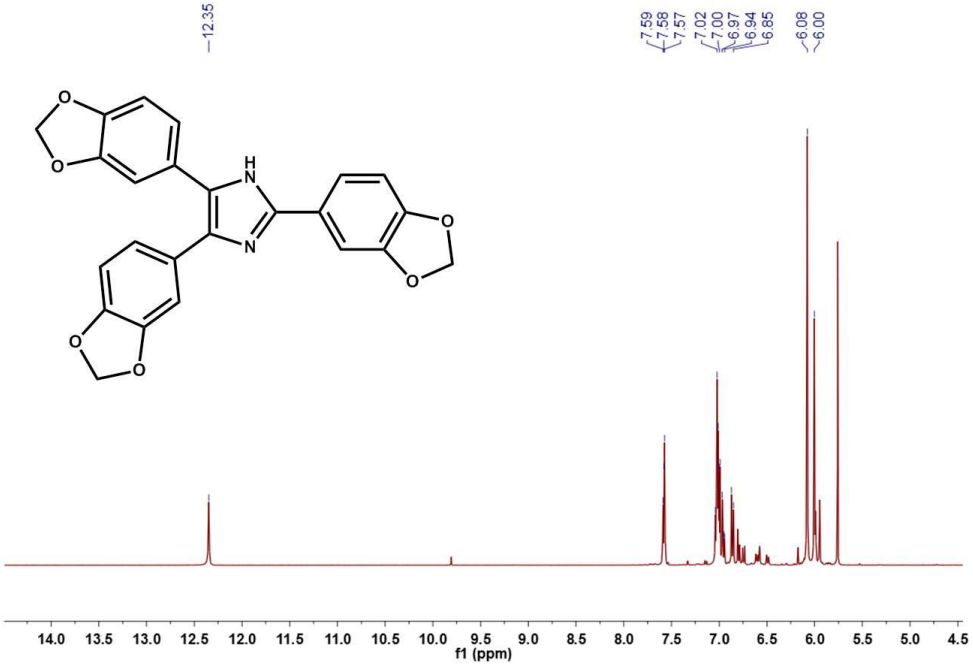
3,3',3''-(1-(pyridin-3-ylmethyl)-1H-imidazole-2,4,5-triyl)tripyridine

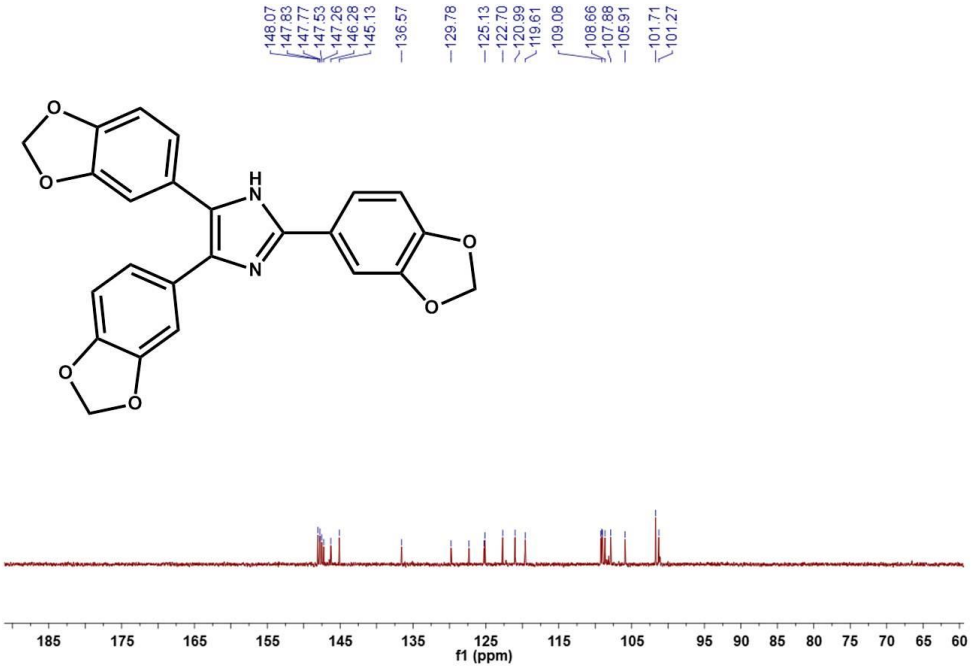
^{1}H NMR (400 MHz, d_6-DMSO) δ = 8.90 (d, *J*=2.1, 1H), 8.66 (td, *J*=4.9, 1.4, 2H), 8.57 (d, *J*=2.1, 1H), 8.54 (d, *J*=2.0, 1H), 8.40 (dd, *J*=4.7, 1.4, 1H), 8.36 (dd, *J*=4.3, 1.8, 1H), 8.10 (dt, *J*=7.9, 1.8, 1H), 8.00 (s, 1H), 7.82 (ddt, *J*=17.9, 8.0, 1.8, 2H), 7.51 (ddd, *J*=15.1, 7.9, 4.8, 2H), 7.33 (dd, *J*=8.0, 4.8, 1H), 7.21 (m, 2H), 5.30 (s, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ = 151.33, 150.70, 150.55, 149.56, 149.16, 148.24, 147.87, 147.68, 146.23, 138.92, 136.58, 136.54, 134.31, 133.92, 132.60, 130.11, 128.76, 126.75, 126.34, 124.52, 124.21, 124.15, 124.01, 46.46.



2,4,5-tris(benzo[d][1,3]dioxol-5-yl)-1H-imidazole

^{1}H NMR (400 MHz, d_6-DMSO) δ = 12.35 (s, 1H), 7.58 (m, 2H), 6.99 (m, 6H), 6.86 (d, *J*=8.5, 1H), 6.08 (s, 4H), 6.00 (s, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ = 148.07, 147.83, 147.77, 147.53, 147.26, 146.28, 145.13, 136.57, 129.78, 127.32, 125.26, 125.13, 122.70, 120.99, 119.61, 109.24, 109.08, 109.00, 108.66, 107.88, 105.91, 101.71, 101.27.





2,4,5-tris(benzo[d][1,3]dioxol-5-yl)-1-(benzo[d][1,3]dioxol-5-ylmethyl)-1H-imid

azole

^{1}H NMR (400 MHz, d_6-DMSO) δ = 7.12 (m, 2H), 6.98 (ddd, *J*=12.3, 6.9, 1.5, 4H), 6.77 (m, 4H), 6.35 (d, *J*=1.1, 1H), 6.20 (d, *J*=8.0, 1H), 6.08 (d, *J*=4.5, 4H), 5.95 (d, *J*=1.5, 4H), 5.00 (s, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ = 148.16, 148.13, 148.07, 147.90, 147.83, 147.47, 146.74, 146.67, 146.10, 136.75, 131.71, 129.27, 129.10, 125.40, 125.02, 124.31, 123.01, 120.06, 119.42, 111.33, 109.31, 109.25, 108.86, 108.71, 108.60, 106.84, 106.67, 101.91, 101.86, 101.50, 101.20, 47.73.