Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

For

Cu(I) based catalysts derived from bidentate ligands and studies on the effect of substituents for N-arylation of benzimidazoles and indoles

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Table S1 Crystal data of complex **C1.**

Empirical formula	C36 H30 Cl Cu N3 P
Formula weight ($gmol^{-1}$)	634.60
Space group	P 31
Temperature /K	293(2)
λ (Å) (Mo-Kα)	0.71073
Crystal system	Hexagonal
a (Å)	10.2089(3)
b (Å)	10.2089(3)
c (Å)	26.3489(10)
α(˚)	90.00
γ (˚)	120.00
β(˚)	90.00
V ($Å^3$)	2378.21(17)
Z	3
$\rho_{calc}(gcm^{-3})$	1.329
Crystal size (mm)	0.23x 0.23x 0.23
F(000)	984.0
Theta range for data collection	2.46−27.13
Index ranges	−11<h < 11, −11<k <11, −29<l <29.
Data/restraints/parameters	4852/1/380
GOF[a] on F^2	1.030
R1[b] [I > 2σ(I)]	0.0336
R1[all data]	0.0365
wR2[c] [I > 2σ(I)]	0.0710
wR2 [all data]	0.0720

[a]$GOF = [\Sigma[w(F_o^2 - F_c^2)^2] / M - N]^{1/2}$ (M = number of reflections, N = number of parameters refined).
[b]$R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [c]$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [(F_o^2)^2]]^{1/2}$.

Table S2 Bond distances and bond angles of complex **C1**.

Bond distance (Aº)			
Cu(1)-Cl(1)	2.2787(19)	Cu(1)-N(3)	2.182(6)
Cu(1)-N(1)	2.067(6)	Cu(1)-P(1)	2.1889(17)
N(2)-N(3)	1.384(8)		
Bond angle(º)			
N(1)-Cu(1)-N(3)	77.1(2)	N(1)-Cu(1)-P(1)	117.32(18)
N(1)-Cu(1)-Cl(1)	106.84(17)	N(3)-Cu(1)-Cl(1)	117.15(15)
P(1)-Cu(1)-Cl(1)	121.46(7)		

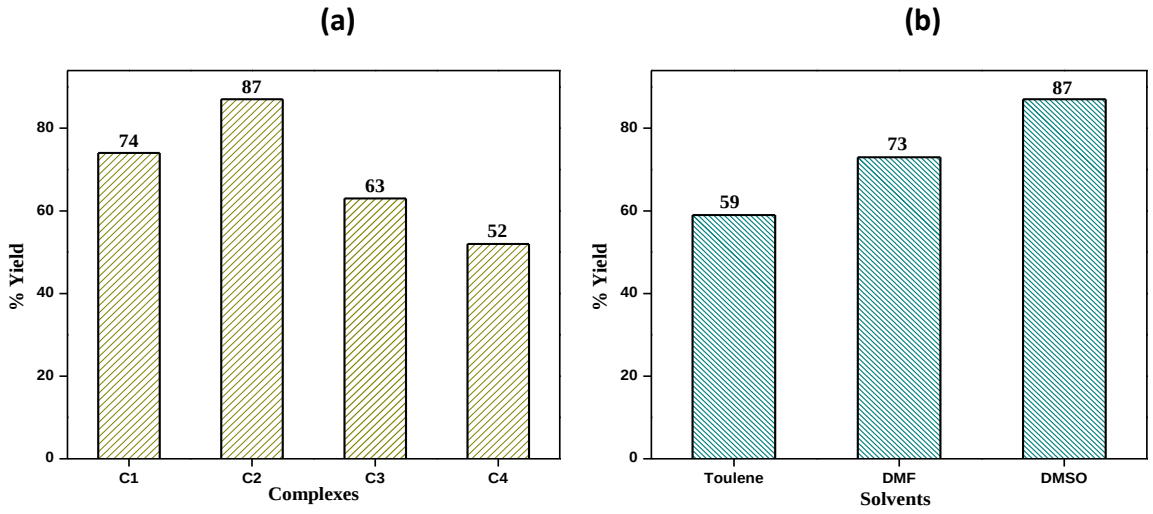

Figure S1 : Effect of (a) catalysts (**C1-C4**) and (b) solvents on N-arylation of indole using iodobenzene to synthesize (1-phenyl-1H-indole).

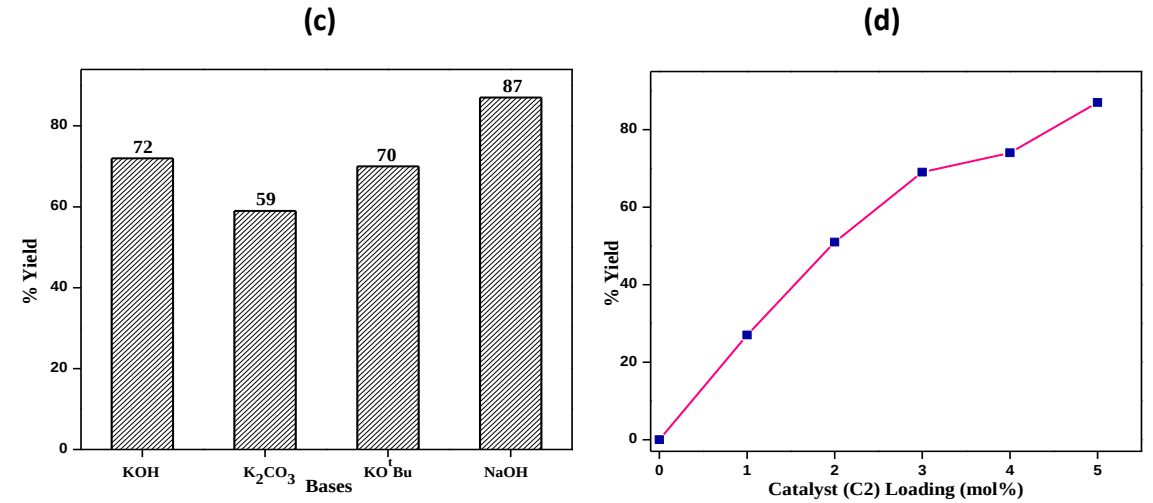

Figure S2 : Effect of (a) bases and (b) catalyst loading (**C2**) on N-arylation of indole using iodobenzene to synthesize (1-phenyl-1H-indole).

Table S3 Optimization table for N-arylation of benzimidazole to synthesize 1-phenyl-1H-benzo[d]imidazole.

S. No	Catalyst	Heterocycle	Haloarene	Base	Solvent	Product	% Yield[a]
				Effect of Catalysts			
1.	C1	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	74
2.	C2	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	89
3.	C3	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	68
4.	C4	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	61
				Effect of Solvents			
5.	C2	Benzimidazole	Iodobenzene	NaOH	Toulene	1-phenyl-1H-benzo[d]imidazole	69
6.	C2	Benzimidazole	Iodobenzene	NaOH	DMF	1-phenyl-1H-benzo[d]imidazole	77
7.	C2	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	89
				Effect of Bases			
8.	C2	Benzimidazole	Iodobenzene	KOH	DMSO	1-phenyl-1H-benzo[d]imidazole	76
9.	C2	Benzimidazole	Iodobenzene	K_2CO_3	DMSO	1-phenyl-1H-benzo[d]imidazole	68
10.	C2	Benzimidazole	Iodobenzene	KO^tBu	DMSO	1-phenyl-1H-benzo[d]imidazole	72
11.	C2	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	89
				Effect of Catalyst Loading			
12.	C2 (0mol%)	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	0
13.	C2 (1mol%)	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	30
14.	C2 (2mol%)	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	55
15.	C2 (3mol%)	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	67
16.	C2 (4mol%)	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	74
17.	C2 (5mol%)	Benzimidazole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-benzo[d]imidazole	89

[a] represents the isolated yield.

Table S4 Optimization table for N-arylation of indole to synthesize 1-phenyl-1H-indole.

S.No	Catalyst	Heterocycle	Haloarene	Base	Solvent	Product	% Yield[a]
			Effect of Catalysts				
1.	C1	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	74
2.	C2	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	87
3.	C3	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	63
4.	C4	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	52
			Effect of Solvents				
5.	C2	Indole	Iodobenzene	NaOH	Toulene	1-phenyl-1H-indole	59
6.	C2	Indole	Iodobenzene	NaOH	DMF	1-phenyl-1H-indole	73
7.	C2	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	87
			Effect of Bases				
8.	C2	Indole	Iodobenzene	KOH	DMSO	1-phenyl-1H-indole	72
9.	C2	Indole	Iodobenzene	K_2CO_3	DMSO	1-phenyl-1H-indole	59
10.	C2	Indole	Iodobenzene	KO^tBu	DMSO	1-phenyl-1H-indole	70
11.	C2	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	87
			Effect of Catalyst Loading				
12.	C2 (0 mol%)	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	0
13.	C2 (1 mol%)	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	27
14.	C2 (2 mol%)	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	51
15.	C2 (3 mol%)	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	69
16.	C2 (4 mol%)	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	74
17.	C2 (5 mol%)	Indole	Iodobenzene	NaOH	DMSO	1-phenyl-1H-indole	87

[a] represents the isolated yield.

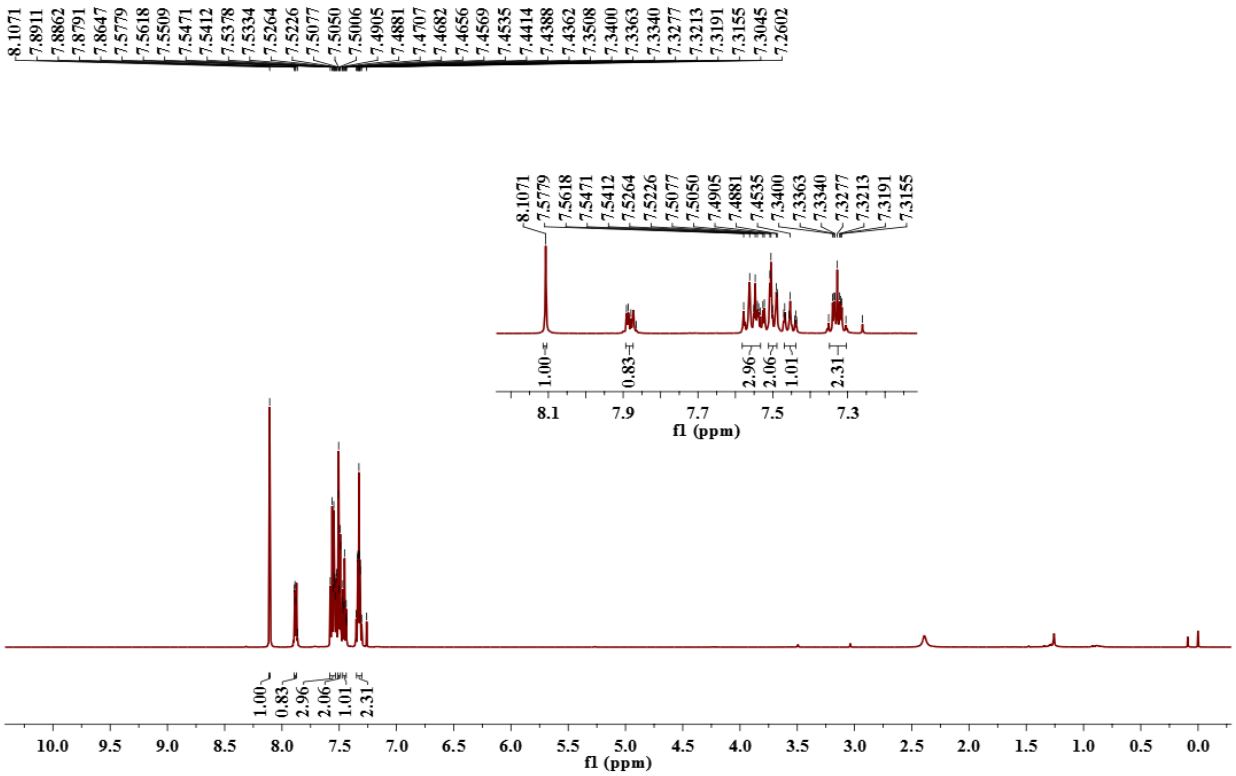

Figure S3 [1]HNMR spectrum of **R1** (1-phenyl-1H-benzo[d]imidazole {$C_{13}H_{10}N_2$}) in $CDCl_3$.

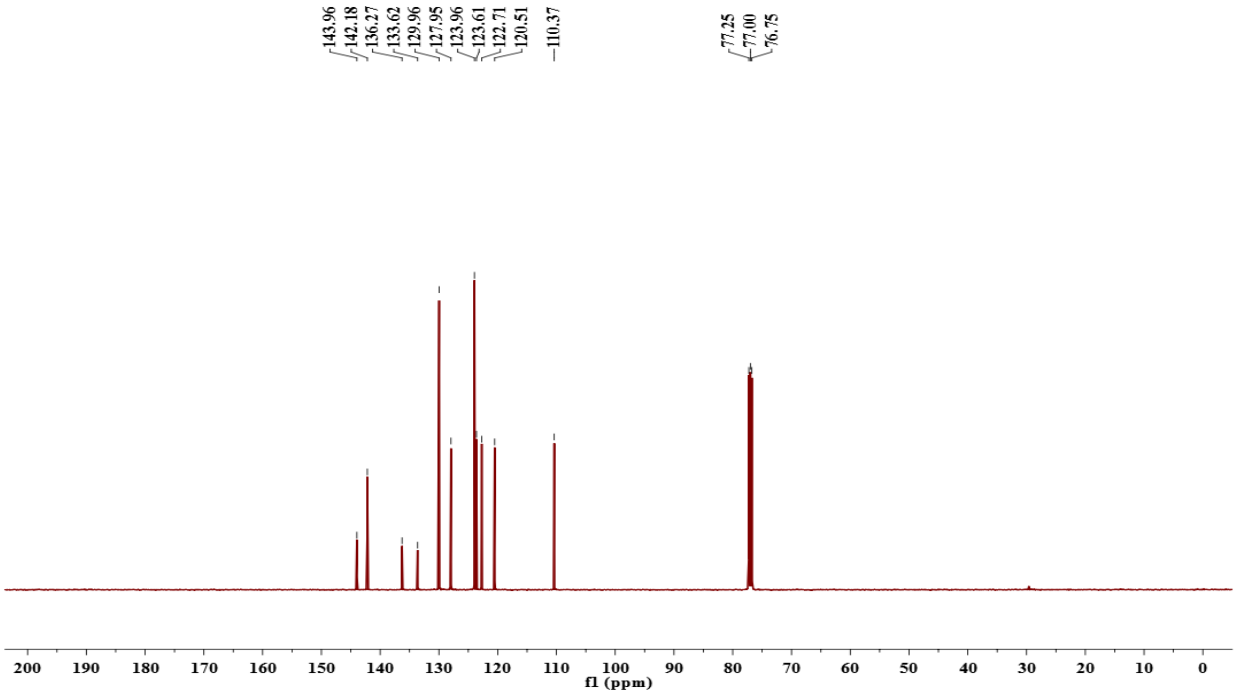

Figure S4 [13]C NMR spectrum of **R1** (1-phenyl-1H-benzo[d]imidazole {$C_{13}H_{10}N_2$}) in $CDCl_3$.

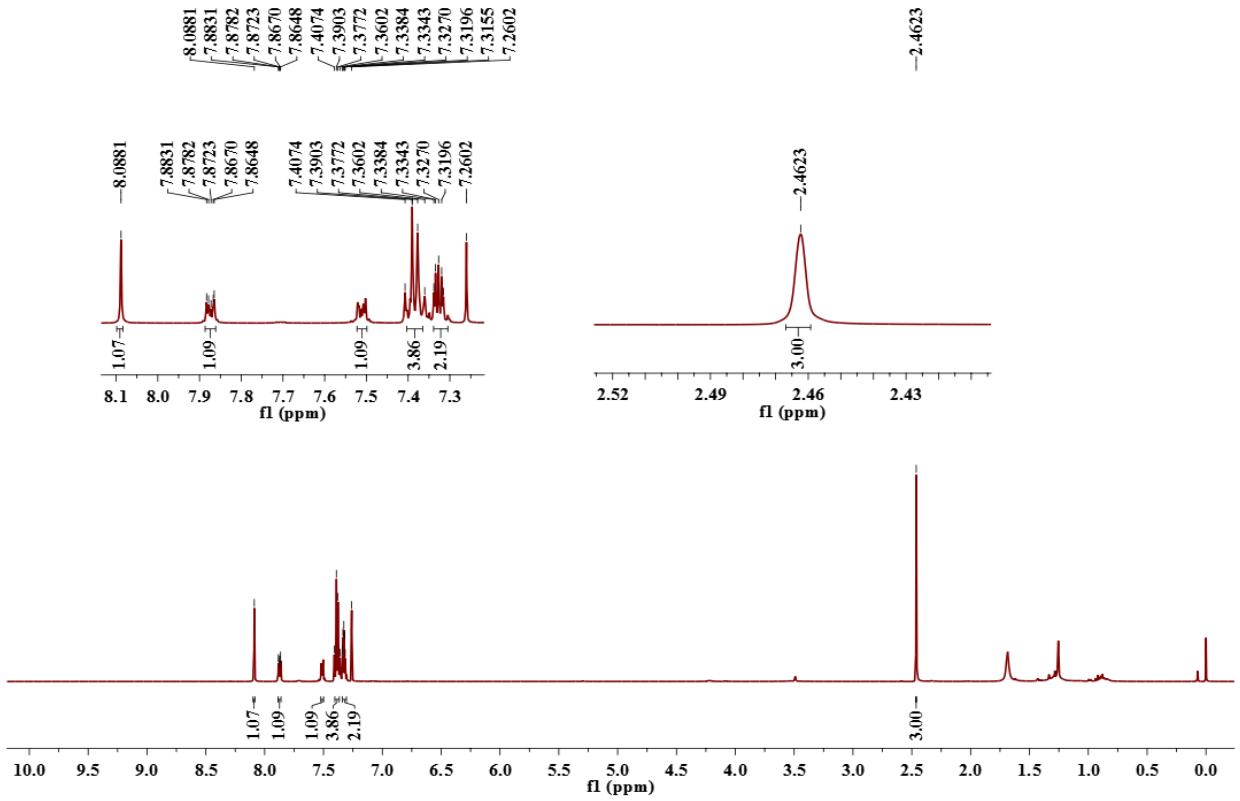

Figure S5 ^{1}H NMR spectrum of **R2** (1-(p-tolyl)-1H-benzo[d]imidazole {$C_{14}H_{12}N_2$}) in $CDCl_3$.

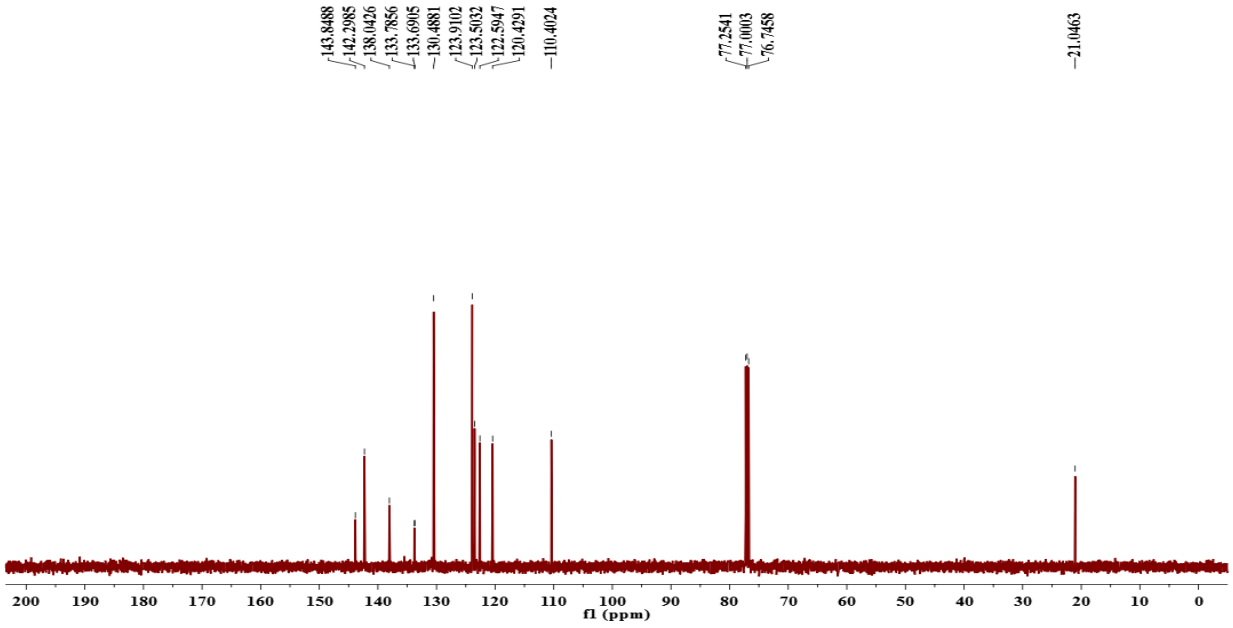

Figure S6 ^{13}C NMR spectrum of **R2** (1-(p-tolyl)-1H-benzo[d]imidazole {$C_{14}H_{12}N_2$}) in $CDCl_3$.

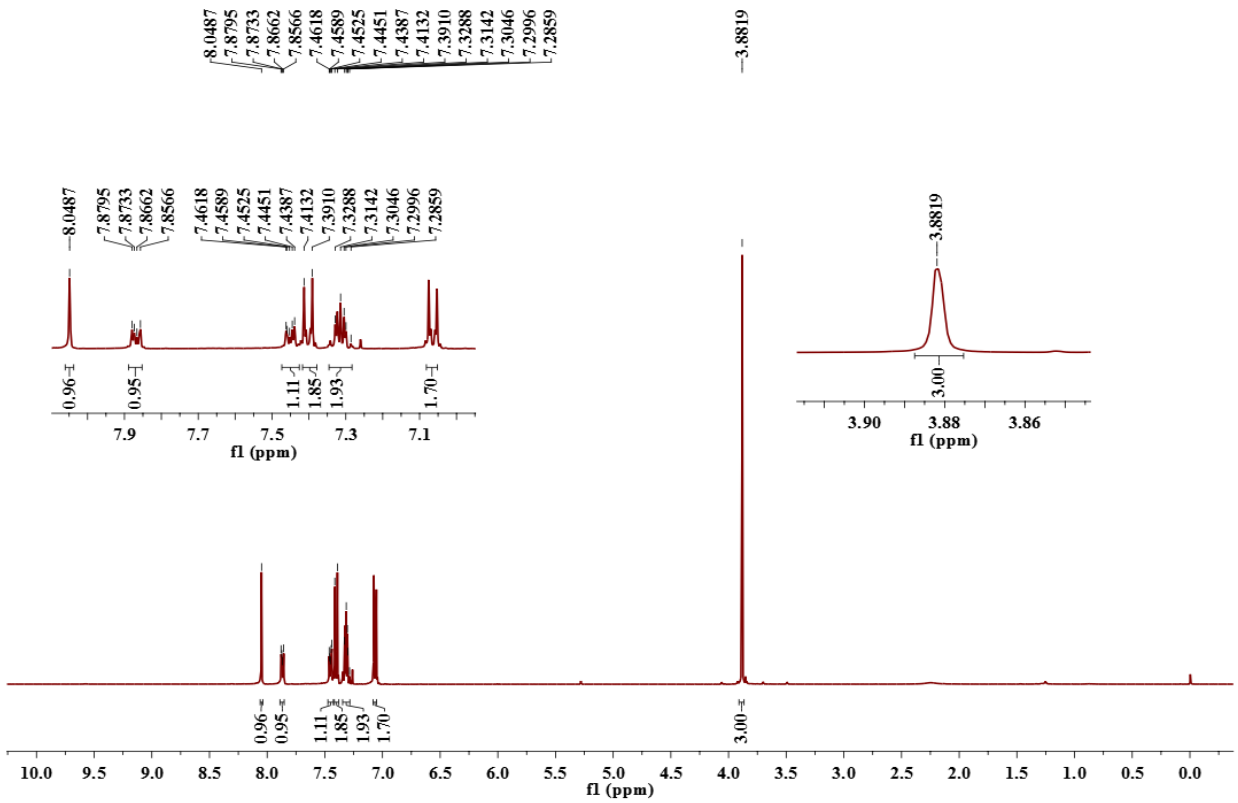

Figure S7 ^{1}H NMR spectrum of **R3** (1-(4-methoxyphenyl)-1H-benzo[d]imidazole {$C_{14}H_{12}N_2O$}) in $CDCl_3$.

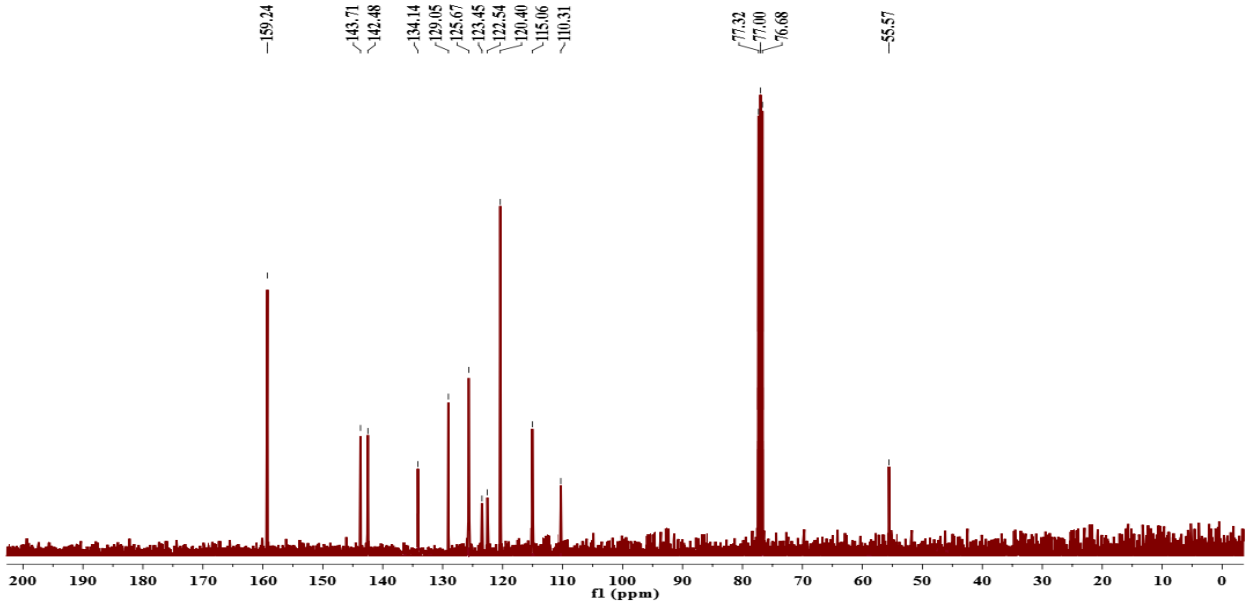

Figure S8 ^{13}C NMR spectrum of **R3** (1-(4-methoxyphenyl)-1H-benzo[d]imidazole {$C_{14}H_{12}N_2O$}) in $CDCl_3$.

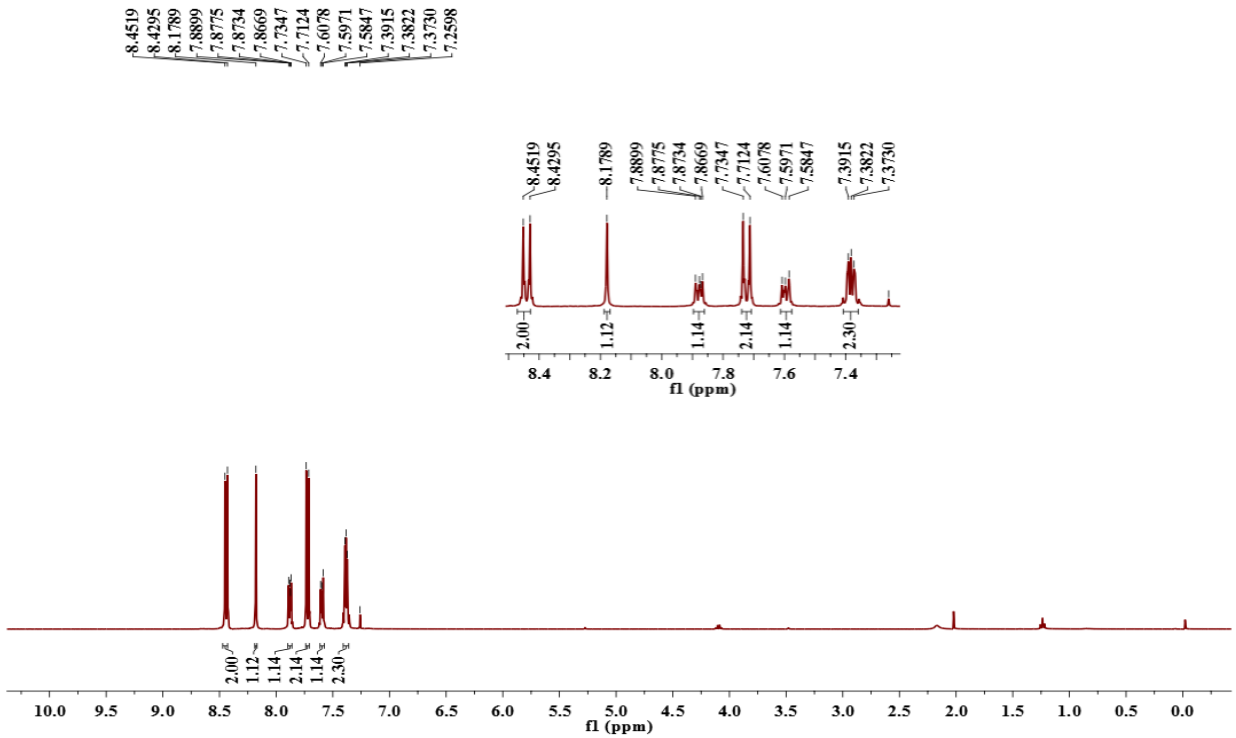

Figure S9 ^{1}H NMR spectrum of **R4** (1-(4-nitrophenyl)-1H-benzo[d]imidazole {$C_{13}H_9N_3O_2$}) in $CDCl_3$.

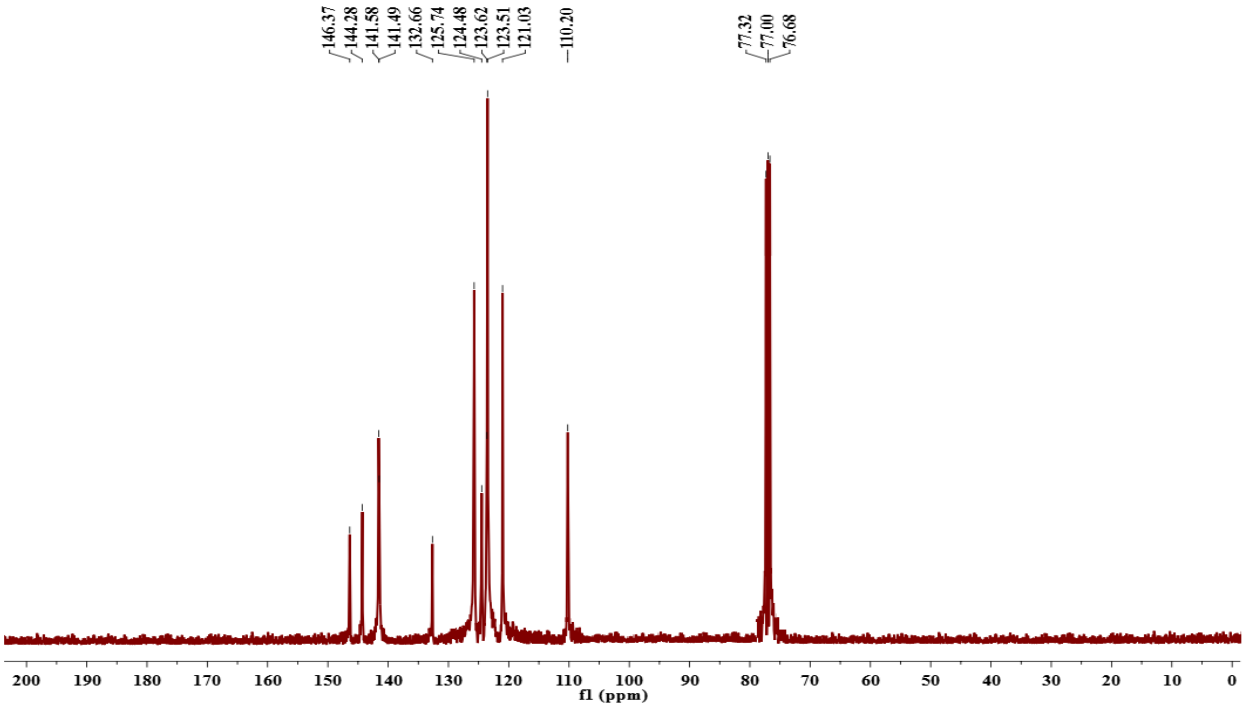

Figure S10 ^{13}C NMR spectrum of **R4** (1-(4-nitrophenyl)-1H-benzo[d]imidazole {$C_{13}H_9N_3O_2$}) in $CDCl_3$.

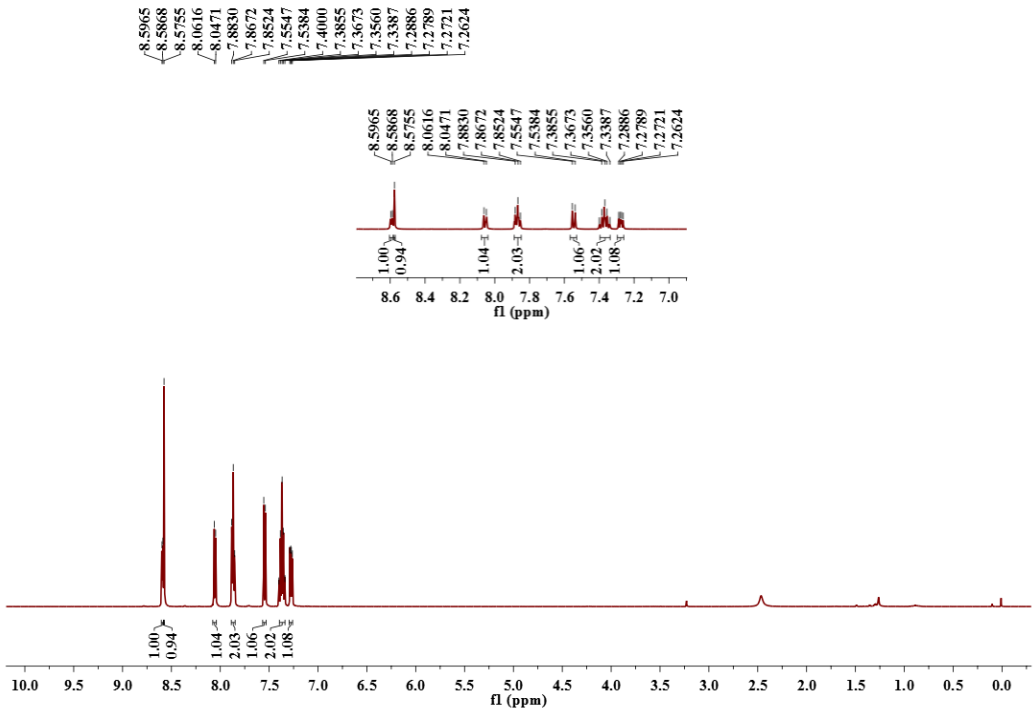

Figure S11 ^{1}H NMR spectrum of **R5** (1-(pyridin-2-yl)-1H-benzo[d]imidazole {$C_{12}H_9N_3$}) in $CDCl_3$.

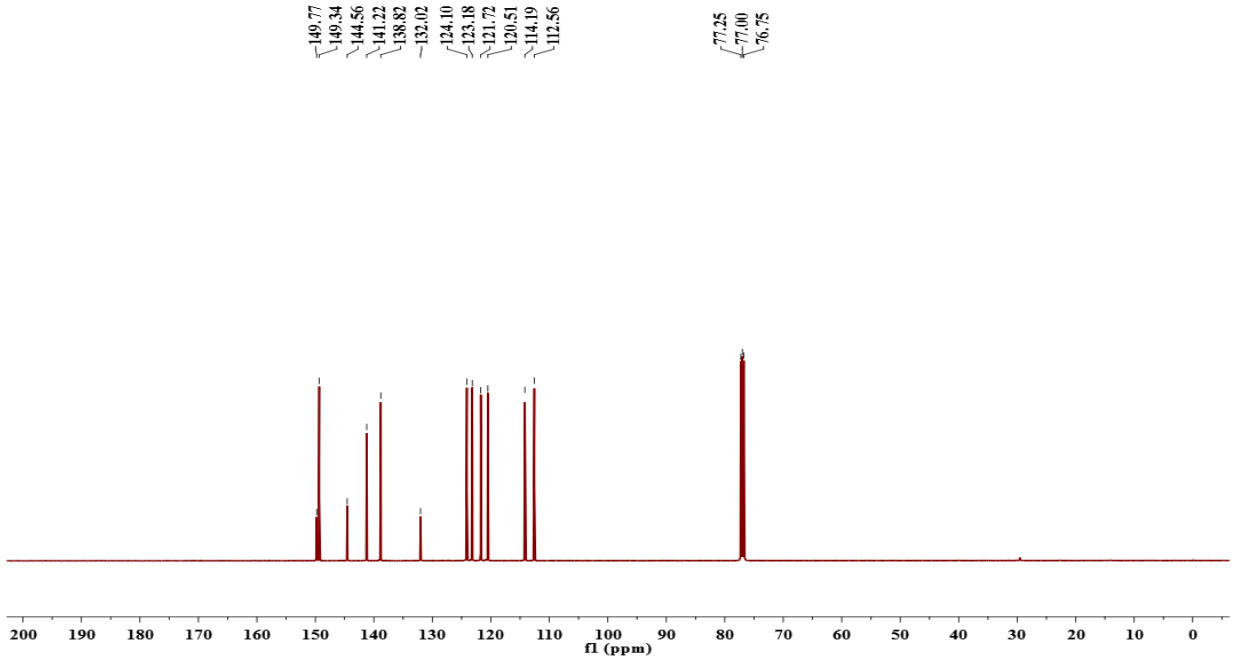

Figure S12 ^{13}C NMR spectrum of **R5** (1-(pyridin-2-yl)-1H-benzo[d]imidazole {$C_{12}H_9N_3$}) in $CDCl_3$.

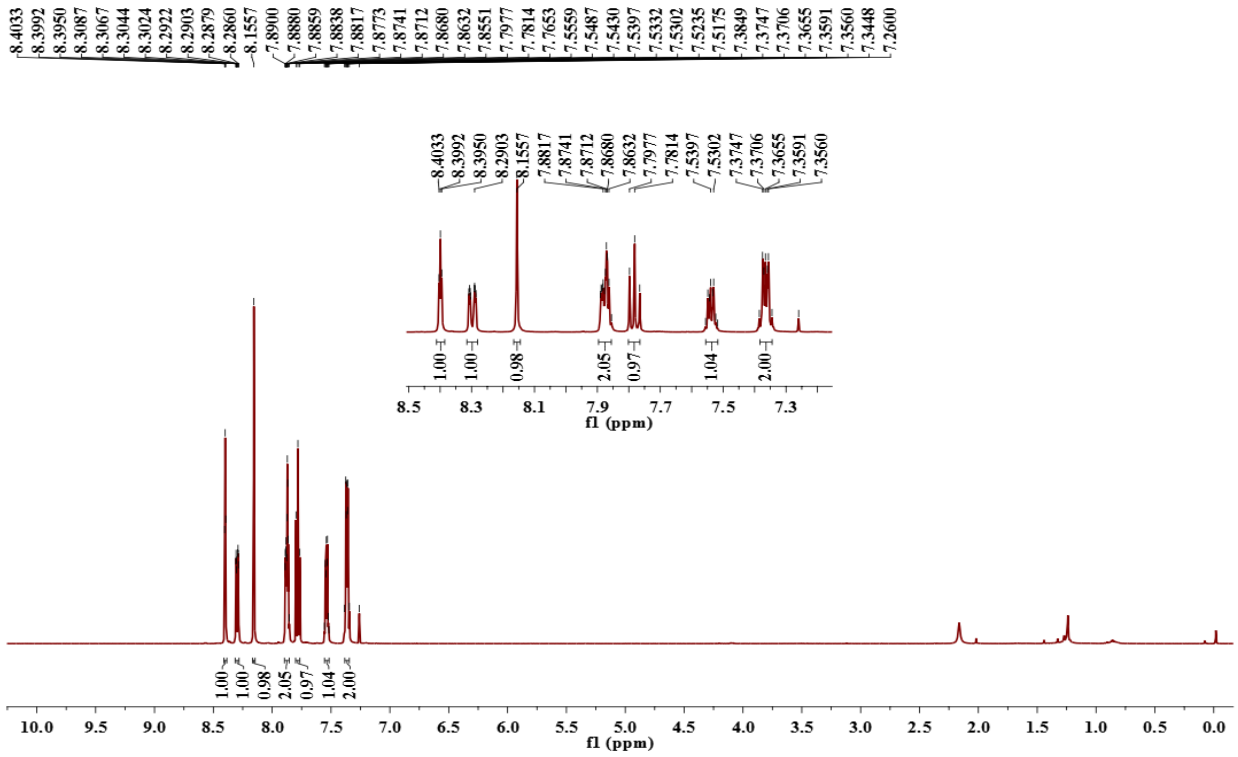

Figure S13 ^{1}H NMR spectrum of **R6** (1-(3-nitrophenyl)-1H-benzo[d]imidazole {$C_{13}H_9N_3O_2$}) in $CDCl_3$.

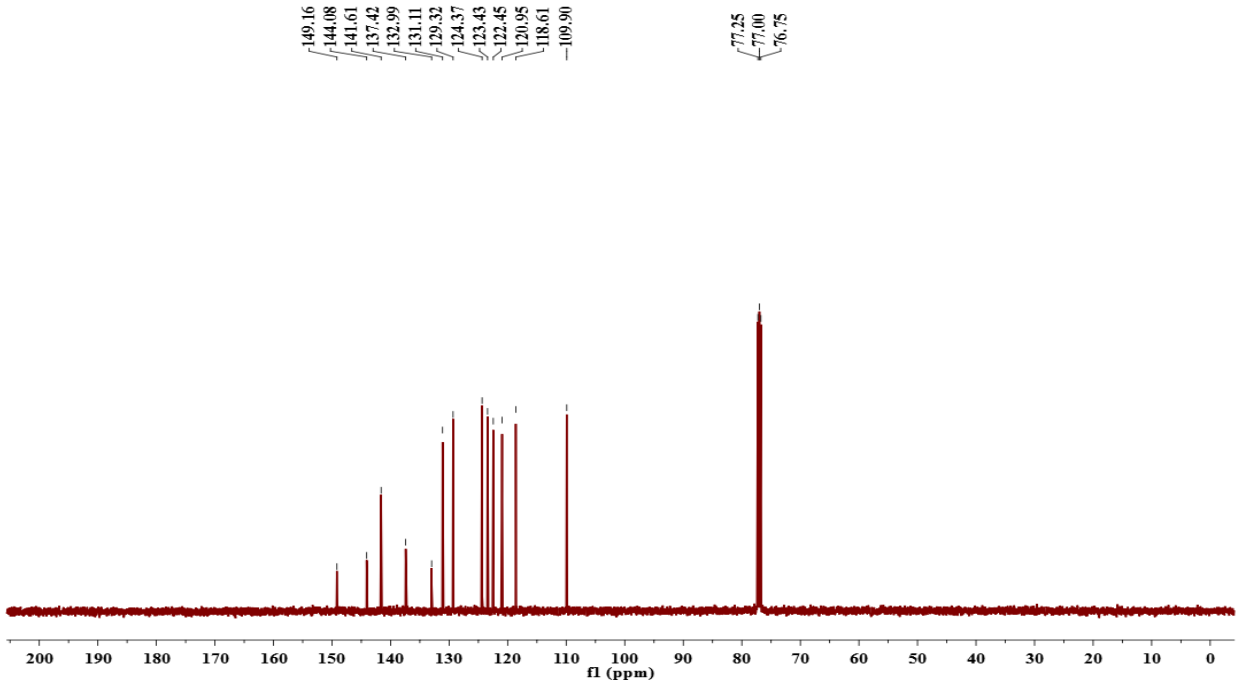

Figure S14 ^{13}C NMR spectrum of **R6** (1-(3-nitrophenyl)-1H-benzo[d]imidazole {$C_{13}H_9N_3O_2$}) in $CDCl_3$.

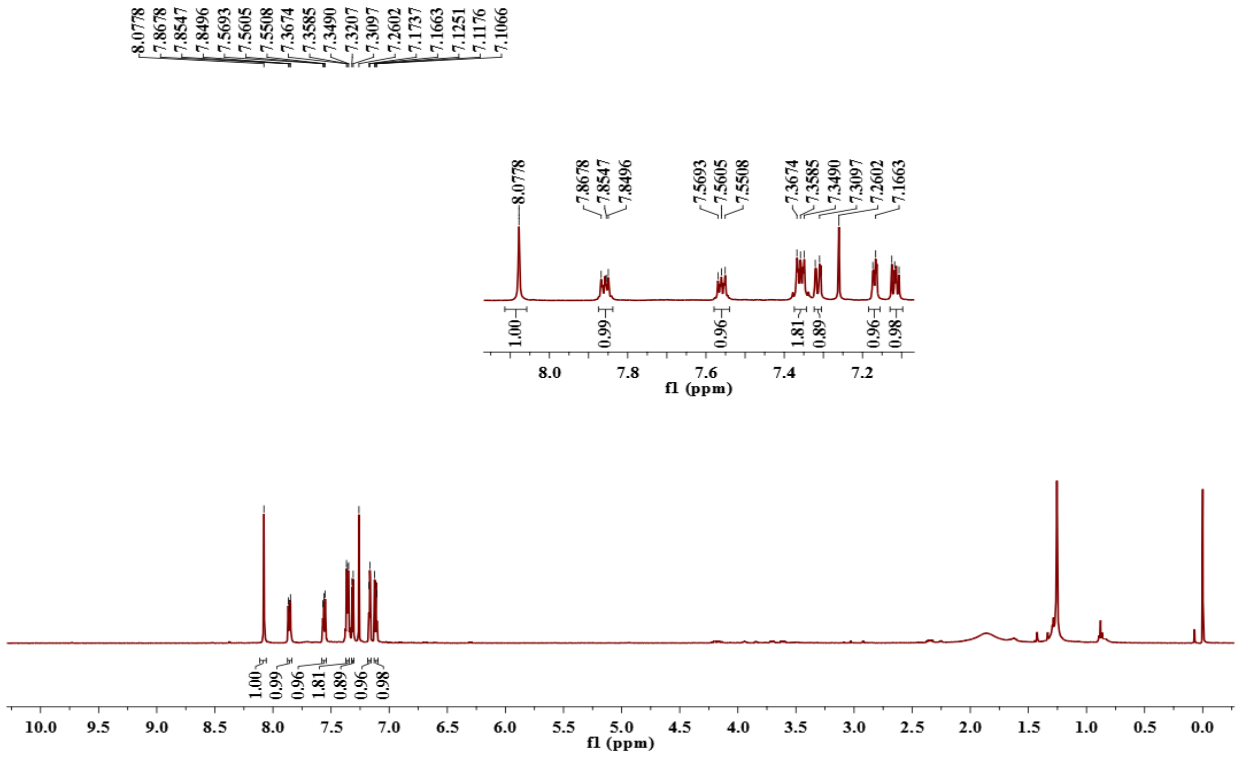

Figure S15 ^{1}H NMR spectrum of **R7** (1-(thiophen-2-yl)-1H-benzo[d]imidazole {$C_{11}H_8N_2S$}) in $CDCl_3$.

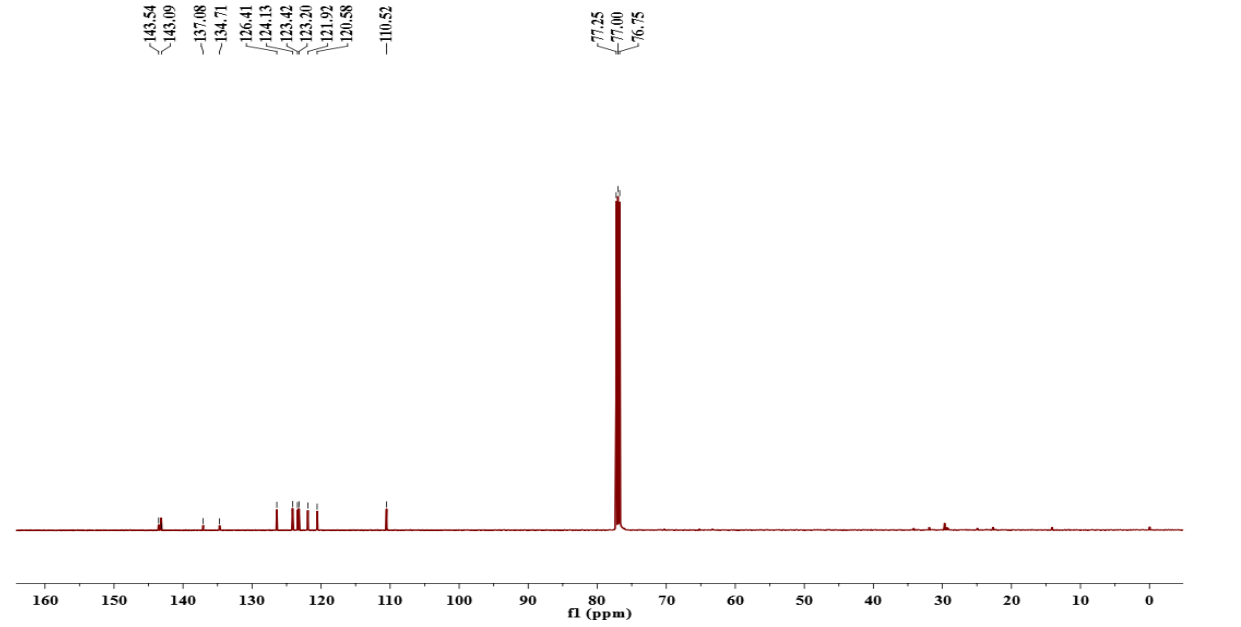

Figure S16 ^{13}C NMR spectrum of **R7** (1-(thiophen-2-yl)-1H-benzo[d]imidazole {$C_{11}H_8N_2S$}) in $CDCl_3$.

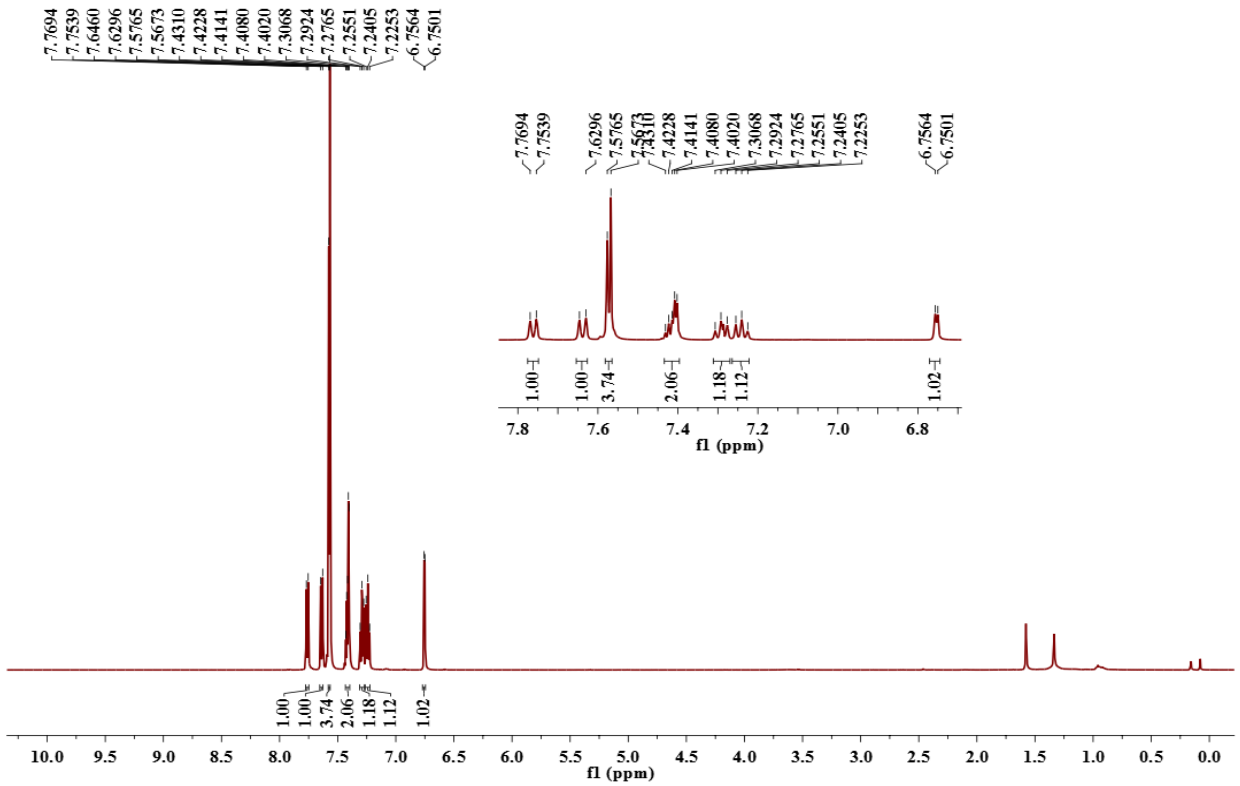

Figure S17 ^{1}H NMR spectrum of **R8** (1-phenyl-1H-indole {$C_{14}H_{11}N$}) in $CDCl_3$.

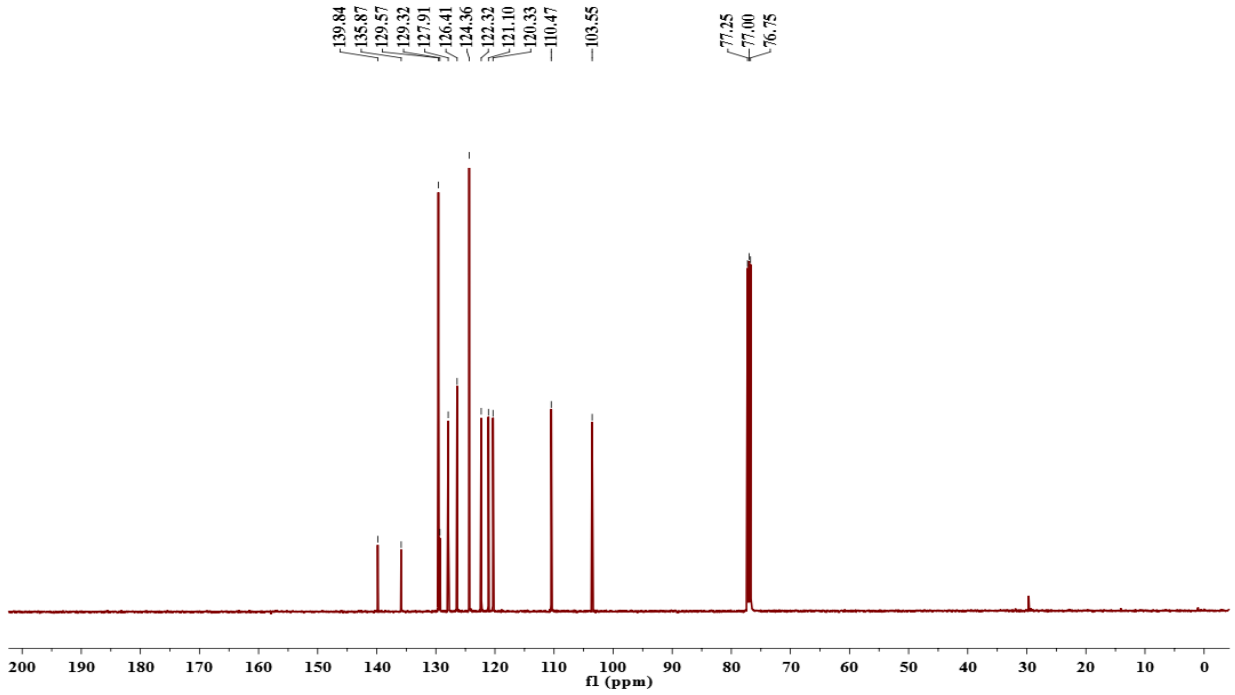

Figure S18 ^{13}C NMR spectrum of **R8** (1-phenyl-1H-indole {$C_{14}H_{11}N$}) in $CDCl_3$.

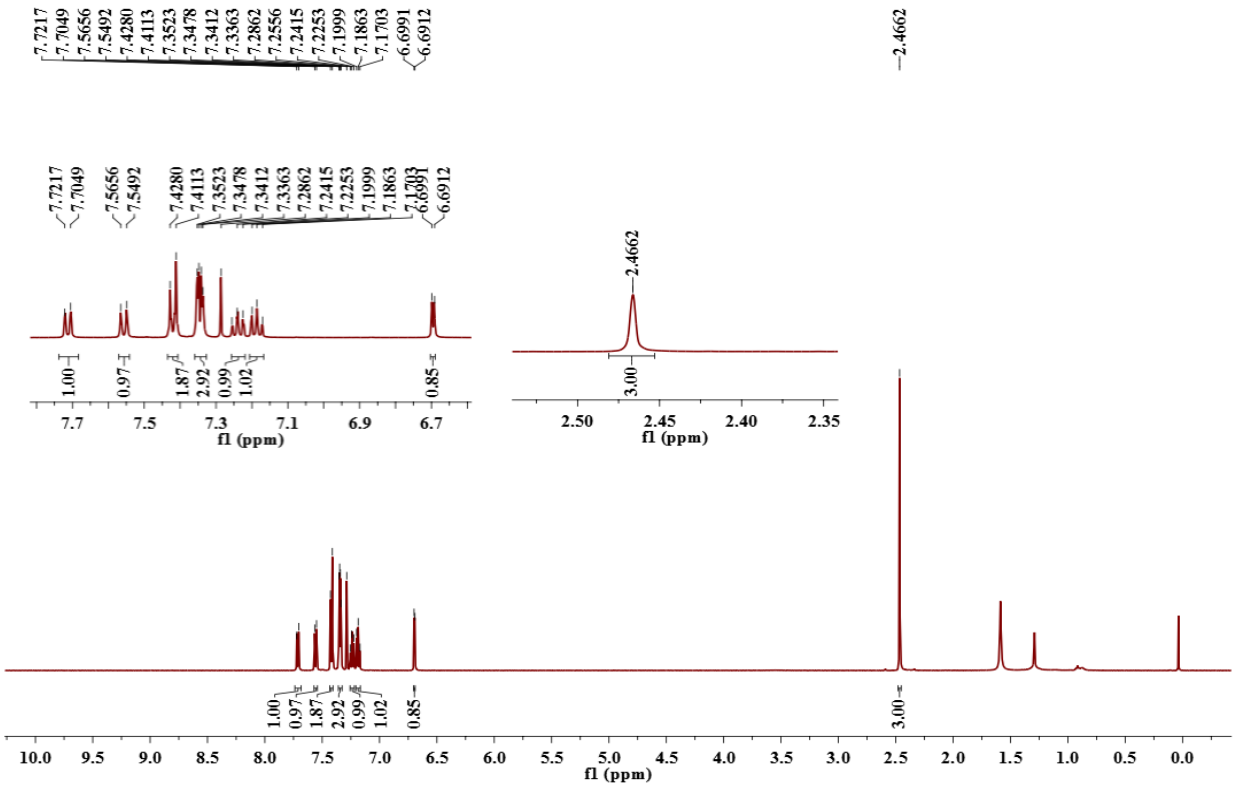

Figure S19 ^{1}H NMR spectrum of **R9** (1-(p-tolyl)-1H-indole {$C_{15}H_{13}N$}) in $CDCl_3$.

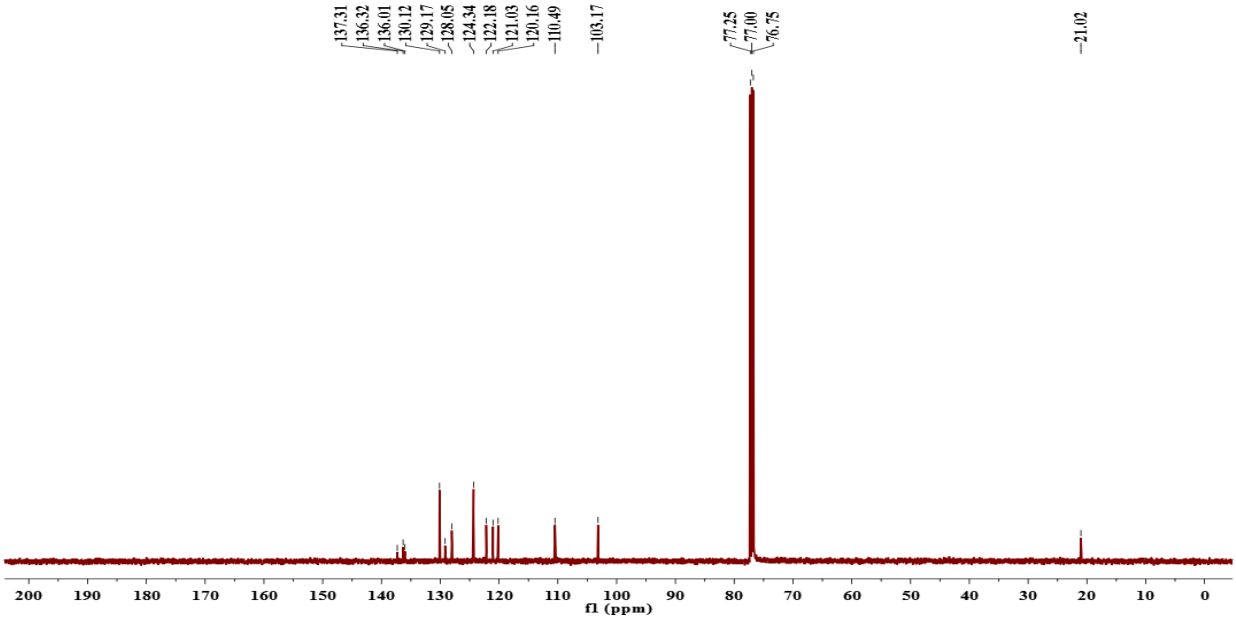

Figure S20 ^{13}C NMR spectrum of **R9** (1-(p-tolyl)-1H-indole {$C_{15}H_{13}N$}) in $CDCl_3$.

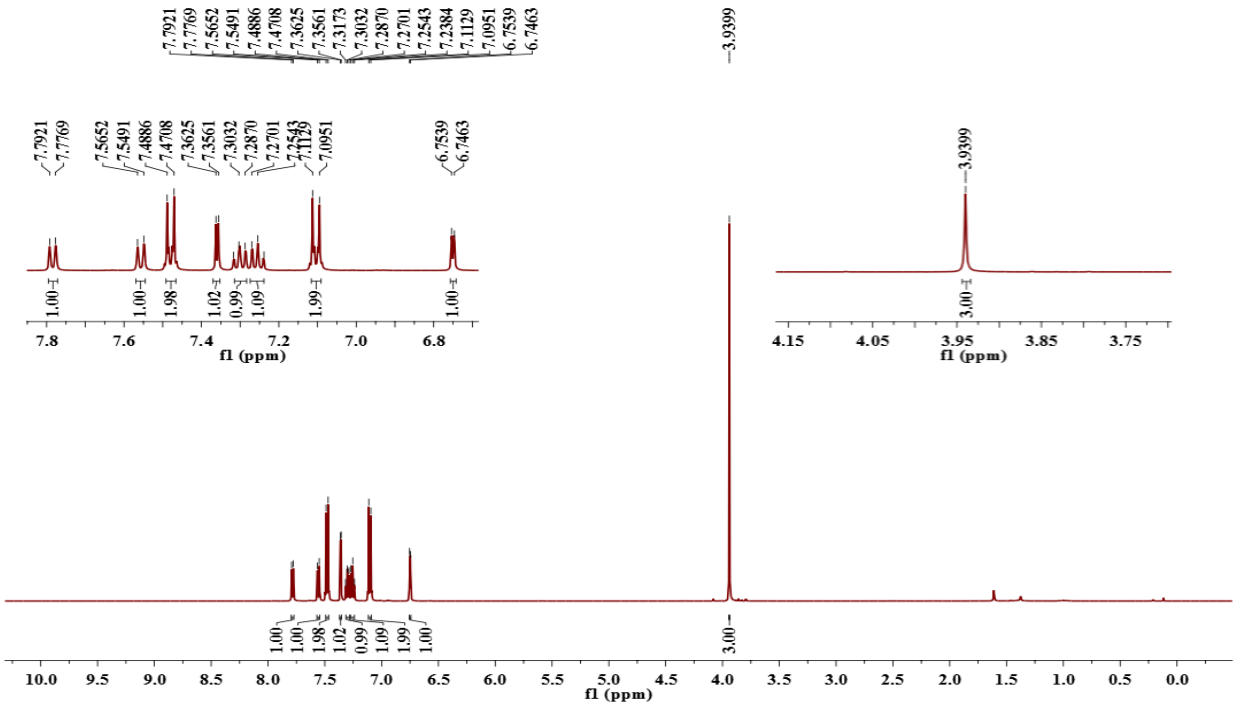

Figure S21 ^{1}H NMR spectrum of **R10** (1-(4-methoxyphenyl)-1H-indole {$C_{15}H_{13}NO$}) in $CDCl_3$.

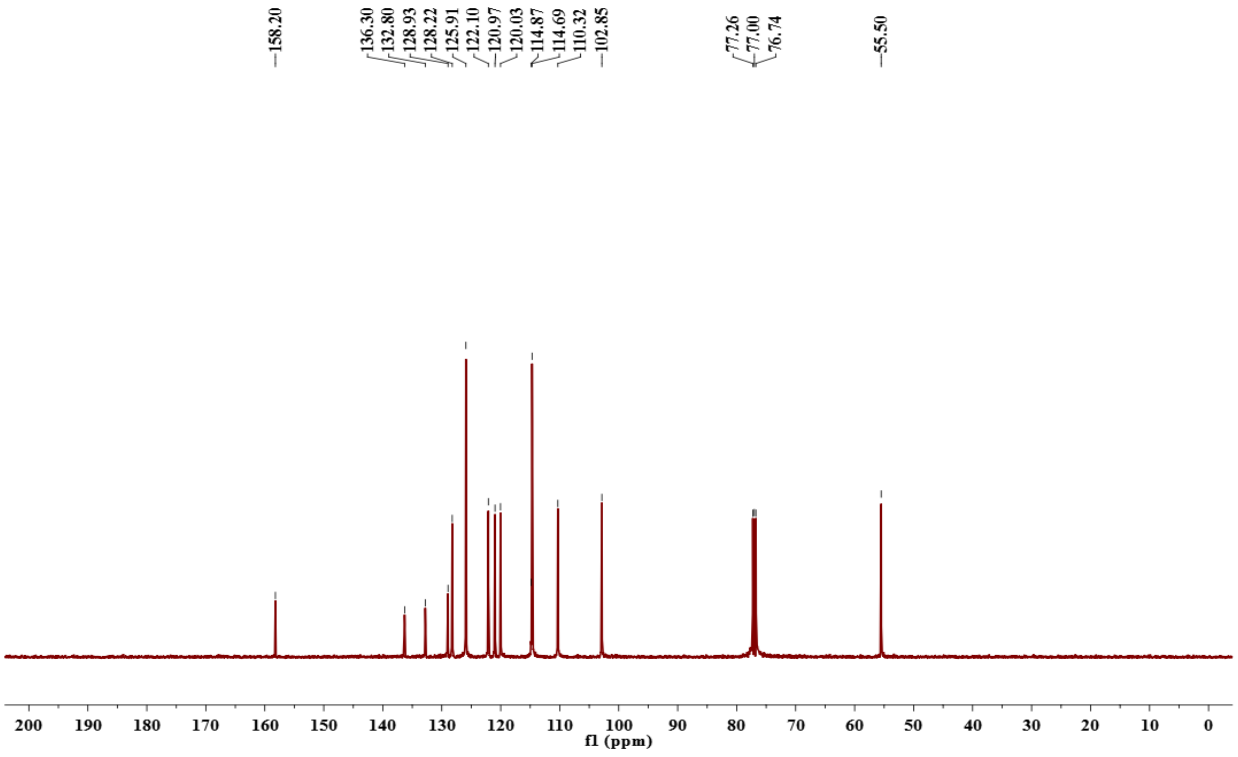

Figure S22 ^{13}C NMR spectrum of **R10** (1-(4-methoxyphenyl)-1H-indole {$C_{15}H_{13}NO$}) in $CDCl_3$.

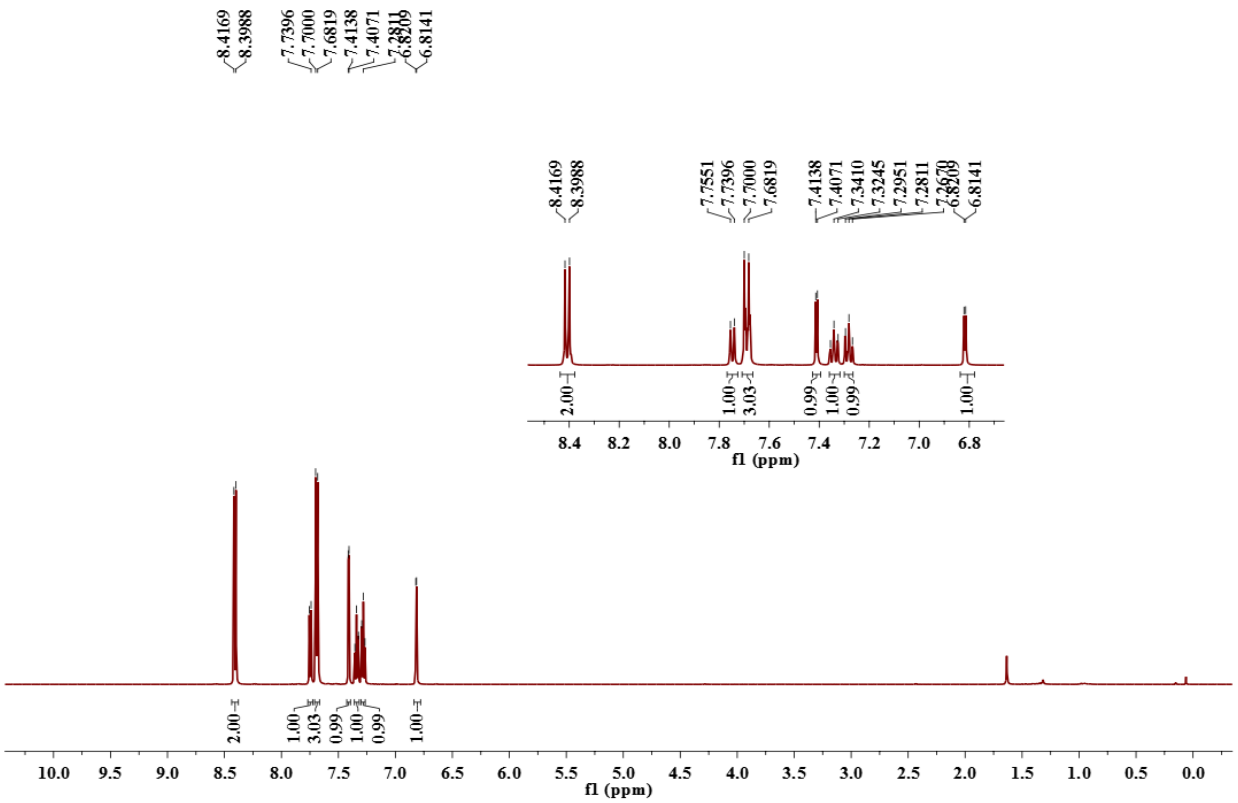

Figure S23 ^{1}H NMR spectrum of **R11** (1-(4-nitrophenyl)-1H-indole {$C_{14}H_{10}N_2O_2$}) in $CDCl_3$.

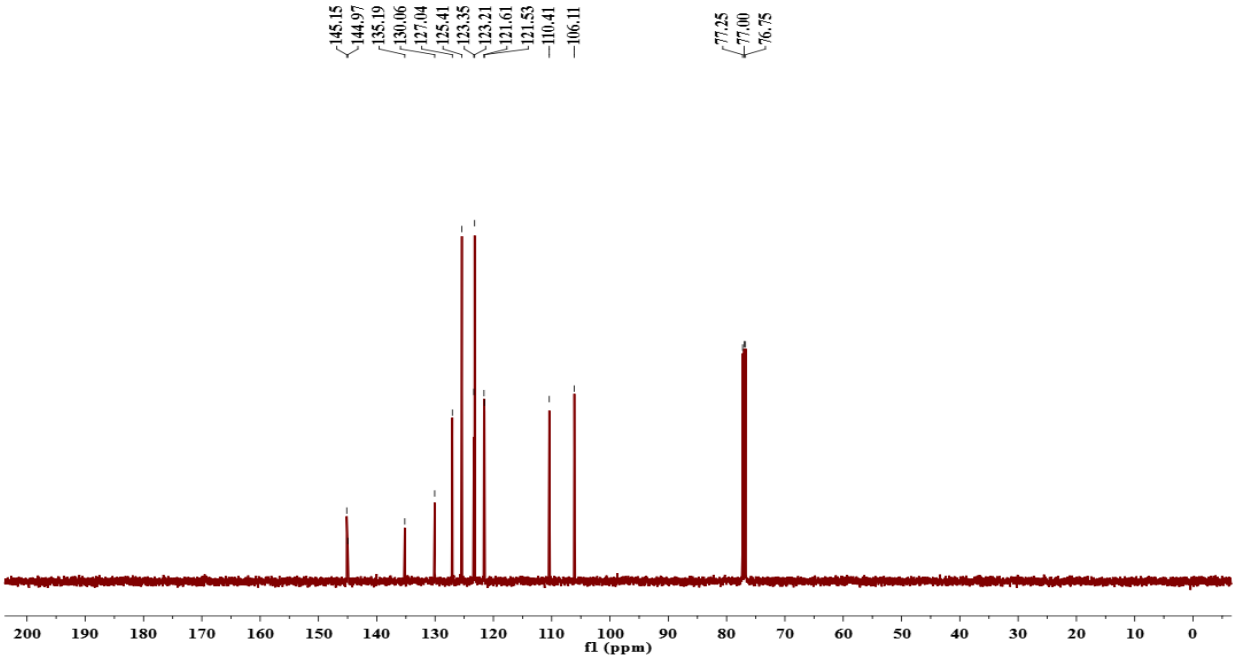

Figure S24 ^{13}C NMR spectrum of **R11** (1-(4-nitrophenyl)-1H-indole {$C_{14}H_{10}N_2O_2$}) in $CDCl_3$.

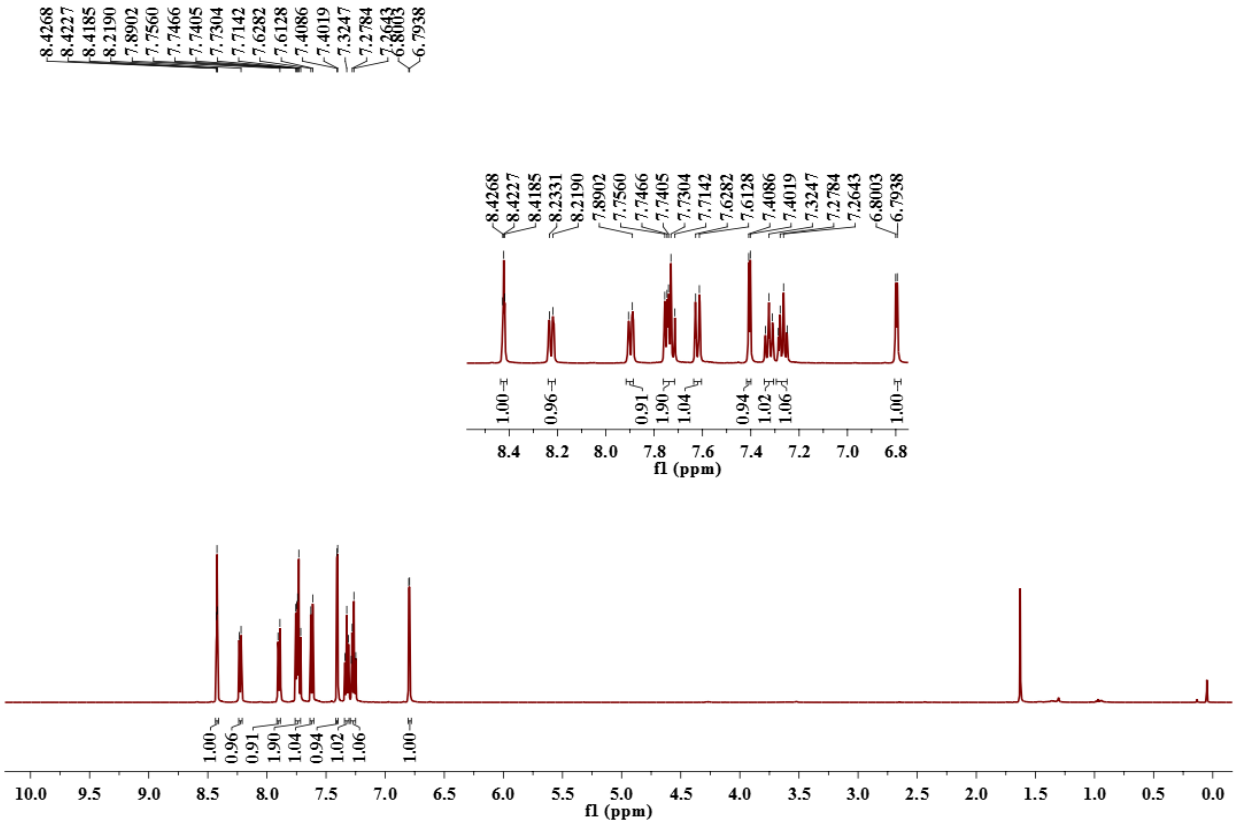

Figure S25 ^{1}H NMR spectrum of **R12** (1-(3-nitrophenyl)-1H-indole {$C_{14}H_{10}N_2O_2$}) in $CDCl_3$.

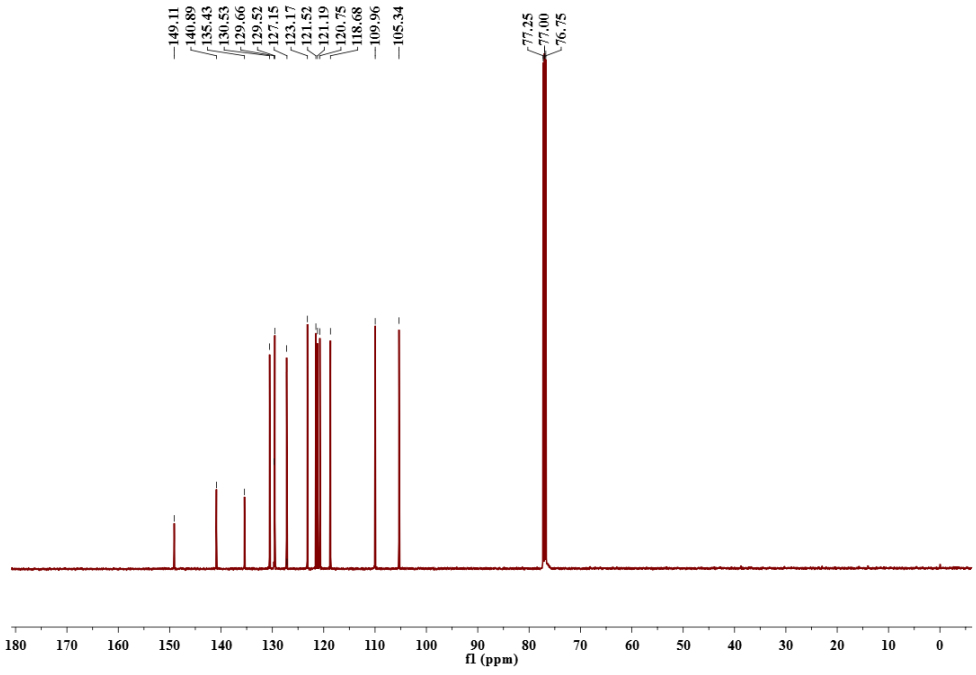

Figure S26 ^{13}C NMR spectrum of **R12** (1-(3-nitrophenyl)-1H-indole {$C_{14}H_{10}N_2O_2$}) in $CDCl_3$.

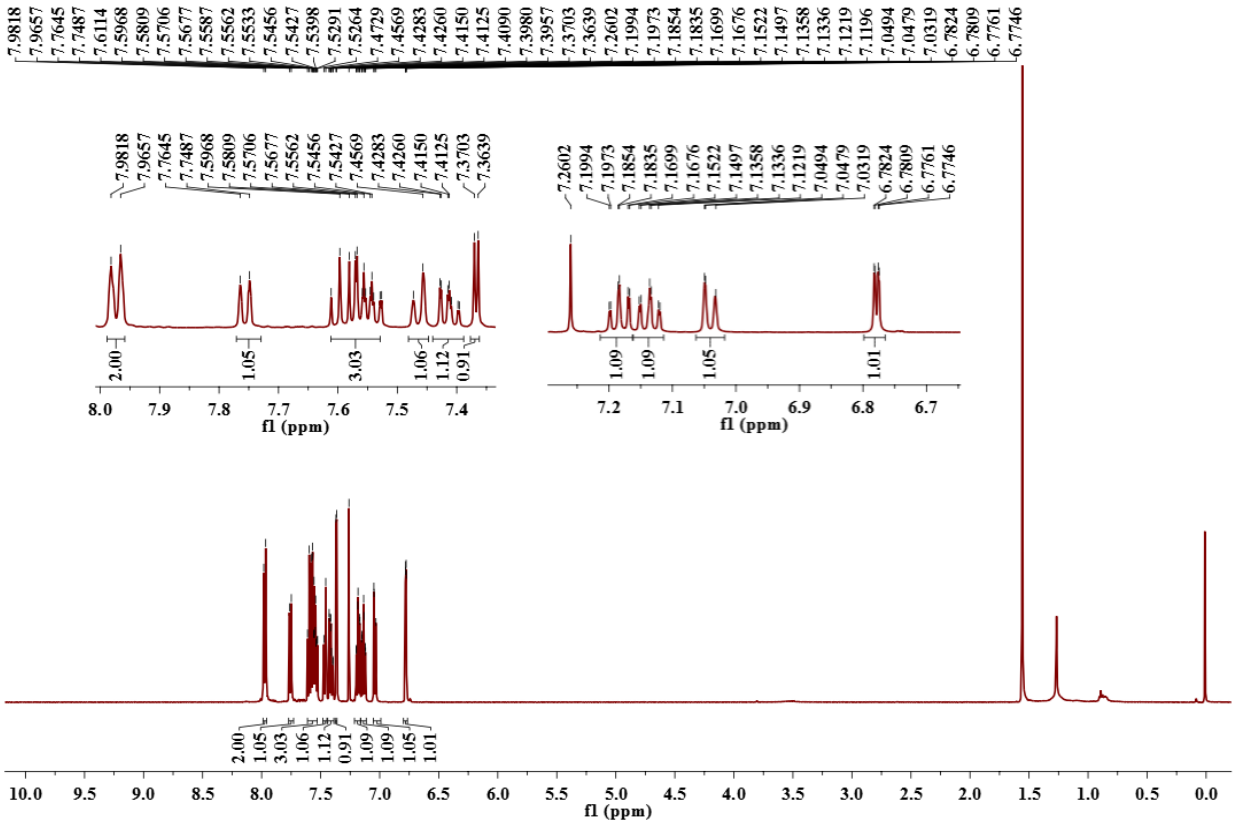

Figure S27 ^{1}H NMR spectrum of **R13** (1-(naphthalen-1-yl)-1H-indole {$C_{18}H_{13}N$}) in $CDCl_3$.

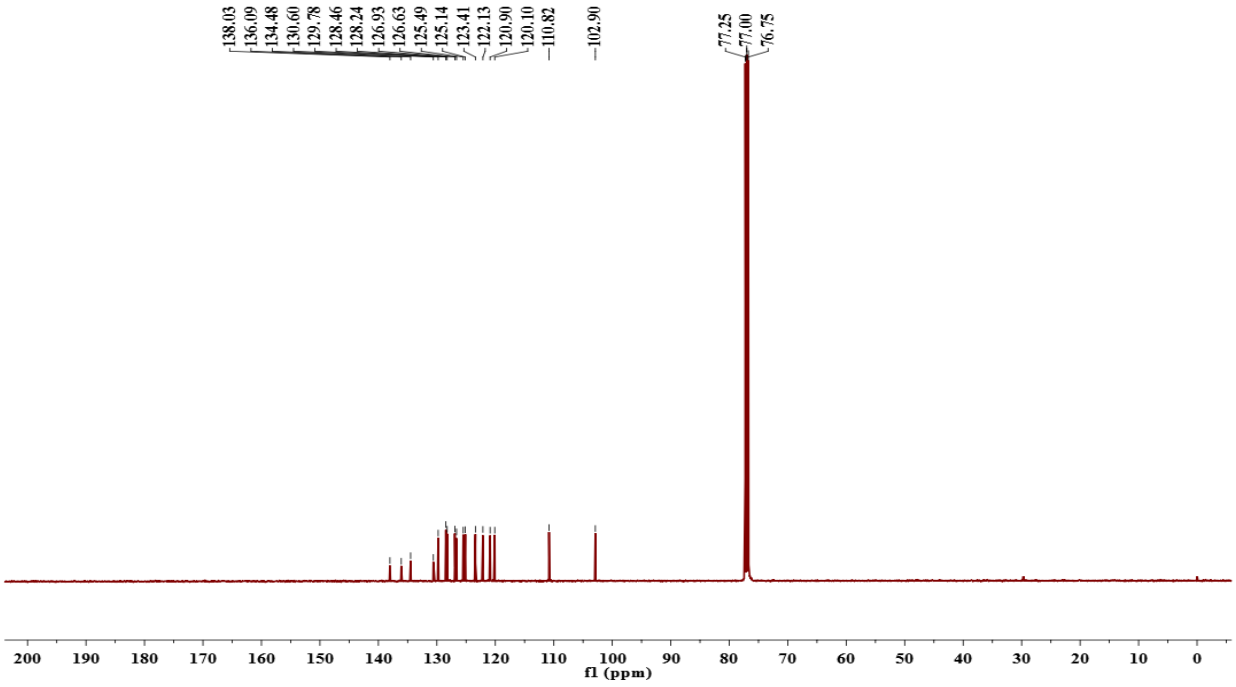

Figure S28 ^{13}C NMR spectrum of **R13** (1-(naphthalen-1-yl)-1H-indole {$C_{18}H_{13}N$}) in $CDCl_3$.

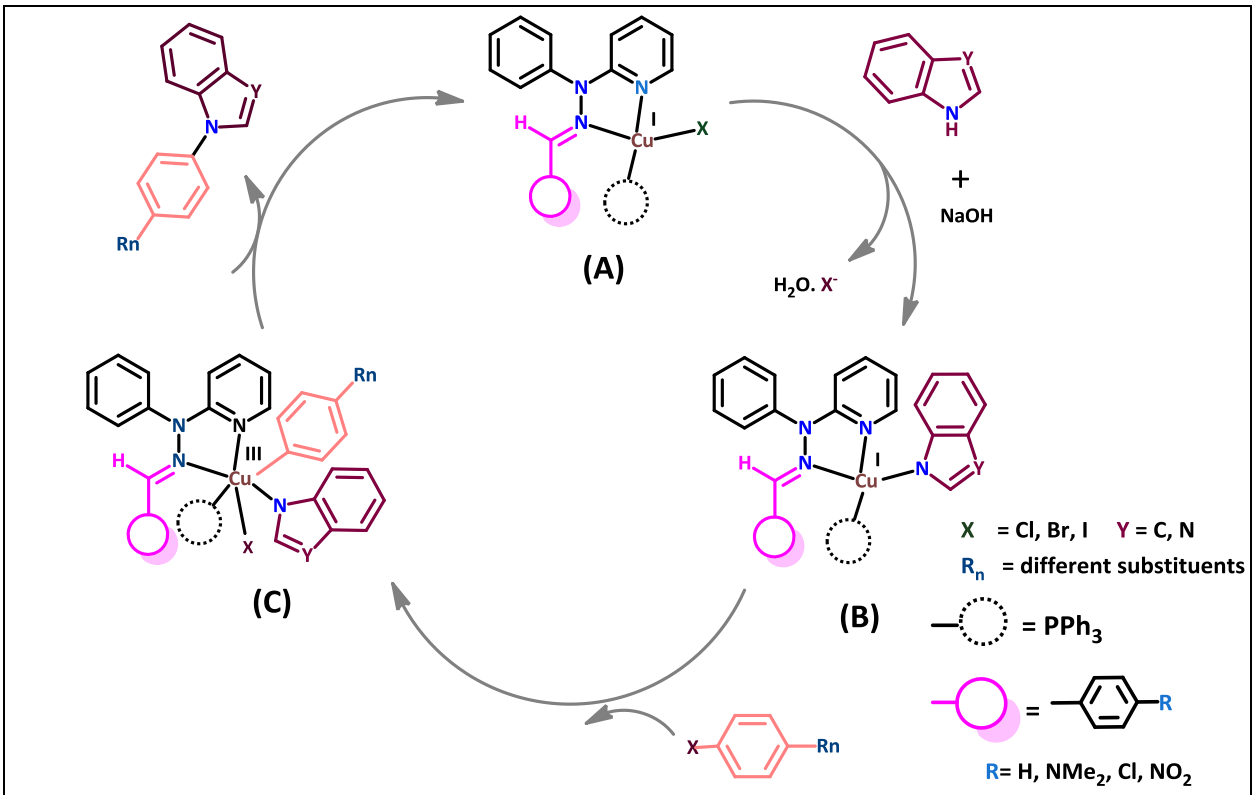

Figure S29. Plausible mechanism for N-arylation.

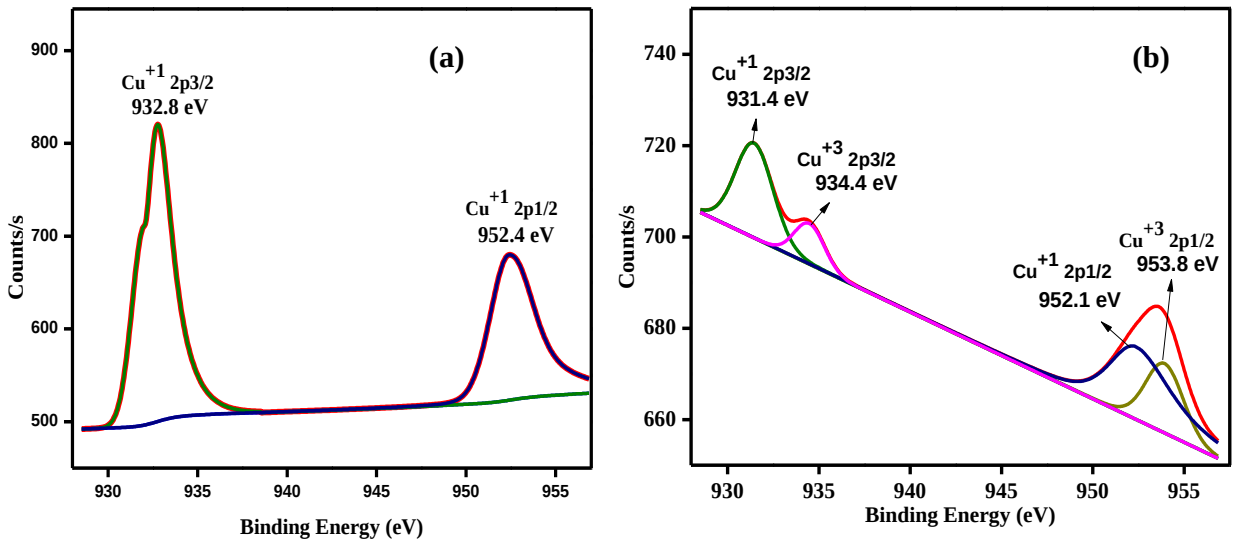

Figure S30. The XPS spectra of the 2p level of copper and deconvolution peaks of the Cu species: deconvoluted (red), Cu(I) (olive and navy blue), Cu(III) (pink and dark yellow), (a) precatalyst Cu(I) and (b) precatalyst Cu(I) after treatment with NaOH, benzimidazole and iodobenzene in DMSO at 110 °C after 30 min.