

Supporting Information

BINAP-Copper Supported by Hydrotalcite as Efficient Catalysts for Borrowing Hydrogen Reaction

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Table of contents

I. General Methods and Materials.....	S2-S4
II. Compounds Characterization.....	S5-S23
III. References.....	S24

I . General Methods and materials:

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 400 or 101 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ = 7.26 ppm) for ^1H NMR and CDCl_3 (δ = 77.0 ppm) for ^{13}C NMR. Flash column chromatography was performed on 230- 430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer.

1.1 Representative procedure for the preparation of $[\text{Cu}(\text{binap})\text{I}]_2$ complex

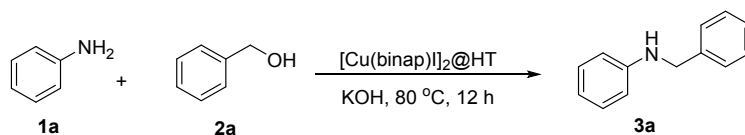
The complex $[\text{Cu}(\text{binap})\text{I}]_2$ was synthesized according to the known literature.^[1b] BINAP (311 mg, 0.5 mmol) was dissolved in CH_3CN (10 mL) in a 100 mL schlenk tube under a nitrogen atmosphere. Subsequently, CuI (95 mg, 0.5 mmol) was added. After the mixture react for 1 h at room temperature under stirring, yellow precipitate was filtered off and washed with EtOH and ether 3 times. The yellow solid was obtained with 95% yield.

1.2 Representative procedure for the preparation of $[\text{Cu}(\text{binap})\text{I}]_2@HT$

$[\text{Cu}(\text{binap})\text{I}]_2$ complex (50 mg) was dissolved in DMSO (10 mL) in a 100 mL Schlenk tube under a nitrogen atmosphere at 160 $^\circ\text{C}$. After the complex completely dispersed and dissolved in solution, Hydrotalcite (1.0 g) was added to the solution with vigorous stirring. The mixture was continuously stirred for 12 h. Subsequently, deionized water (5 mL) was added to precipitate more solids. After cooling to ambient temperature, the precipitate were collected by centrifugation and washed with

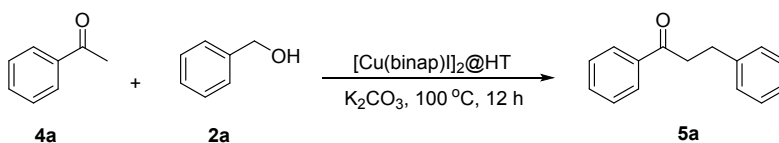
deionized water and ethanol for several times, followed by vacuum freeze-drying for 24 h.

1.3 Representative procedure for the preparation of 3a



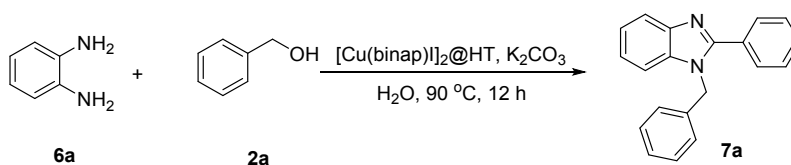
The mixture of $[\text{Cu}(\text{binap})\text{I}]_2@HT$ (2 mol%Cu), amine (2.0 mmol), alcohol (4.0 mmol) and KOH (1.0 mmol) was stirred in 20 mL colorimetric tube under $80\text{ }^\circ\text{C}$ for 12 h. The reaction mixture was removed the solvents to give the residue after cooling down to the room temperature. The residue was then directly purified by column chromatography with petroleum ether/ethyl acetate (petroleum ether /ethyl acetate = 40:1) as eluent to give the desired product (**3a**).

1.4 Representative procedure for the preparation of 5a



The mixture of $[\text{Cu}(\text{binap})\text{I}]_2@HT$ (2 mol%Cu), ketone (2.0 mmol), alcohol (4.0 mmol) and K_2CO_3 (1.0 mmol) was stirred in 20 mL colorimetric tube under $100\text{ }^\circ\text{C}$ for 8 h. The reaction mixture was removed the solvents to give the residue after cooling down to the room temperature. The residue was then directly purified by column chromatography with petroleum ether/ethyl acetate (petroleum ether /ethyl acetate = 40:1) as eluent to give the desired product (**5a**).

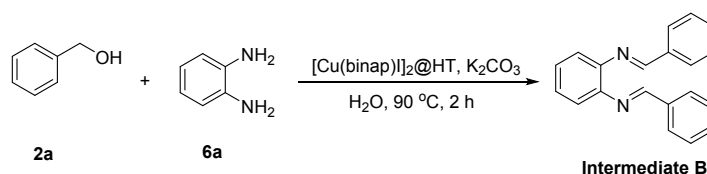
1.5 Representative procedure for the preparation of 7a



The mixture of $[\text{Cu}(\text{binap})\text{I}]_2@HT$ (2 mol%Cu), H_2O (2 mL), diamine (0.5 mmol),

alcohol (1.1 mmol) and K_2CO_3 (0.75 mmol) was stirred in 20 mL colorimetric tube under 90 °C for 12 h. The reaction mixture was removed the solvents to give the residue after cooling down to the room temperature. The residue was directly extracted by ethyl acetate and then purified by column chromatography with petroleum ether/ethyl acetate (petroleum ether /ethyl acetate = 10:1) as eluent to give the desired product (**7a**).

The separation of intermediate **B**



The mixture of $[\text{Cu}(\text{binap})\text{I}]_2@HT$ (2 mol%Cu), H_2O (2 mL), diamine (0.5 mmol), alcohol (1.1 mmol) and K_2CO_3 (0.75 mmol) was stirred in 20 mL colorimetric tube under 90 °C for 2 h. The reaction mixture was removed the solvents to give the residue after cooling down to the room temperature. The residue was directly extracted by ethyl acetate and then purified by column chromatography with petroleum ether/ethyl acetate/ triethylamine (petroleum ether /ethyl acetate/ triethylamine = 10:1:0.01) as eluent to give the intermediate **B**.

II. Compounds Characterization

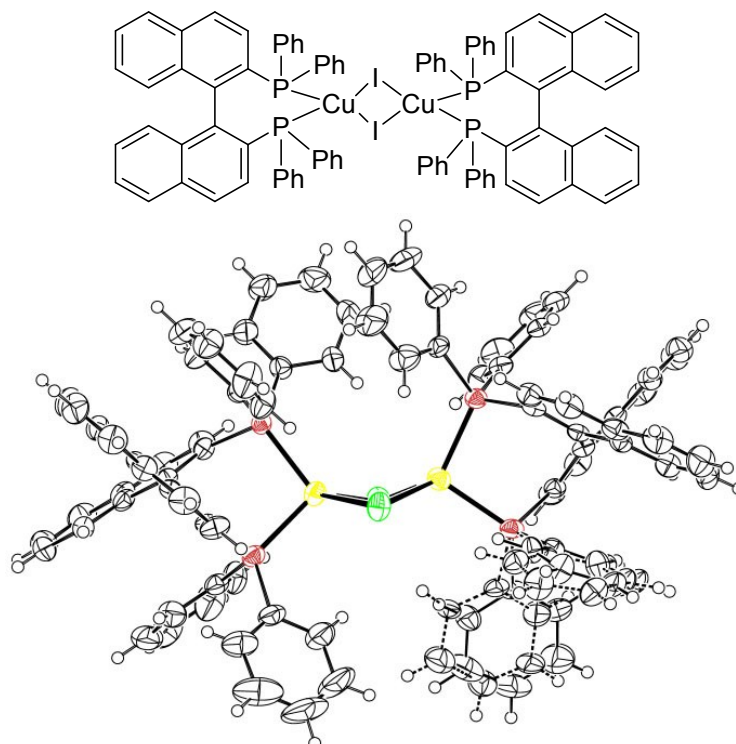


Figure S1. ORTEP diagram of $[\text{Cu}(\text{binap})\text{I}]_2$ with thermal ellipsoids shown at the 30% probability level.

CIF files giving crystallographic data for $[\text{Cu}(\text{binap})\text{I}]_2$.

The molecular structure of $[\text{Cu}(\text{binap})\text{I}]_2$, determined by X-ray diffraction was shown in Fig.S1.

CCDC number: 1547694.

Table S1. Crystallographic data for complexes $[\text{Cu}(\text{binap})\text{I}]_2$

Complex	$[\text{Cu}(\text{binap})\text{I}]_2$
Formula	$\text{C}_{88}\text{H}_{64}\text{Cu}_2\text{I}_2\text{P}_4$
M_w	1626.15
Color	yellow
Crystal system	hexagonal
Space group	Pbca
$a/\text{\AA}$	25.9178(15)
$b/\text{\AA}$	25.9178(15)
$c/\text{\AA}$	18.7806(12)
$\alpha /^\circ$	90.00

$\beta/^{\circ}$	90.00
$\gamma/^{\circ}$	120.00
$V/\text{\AA}^3$	10925.4(14)
Z	6
$D_c/\text{g cm}^{-3}$	1.483
μ/mm^{-1}	1.566
$F(000)$	4896
Crystal size/mm	0.501 x 0.443 x 0.327 mm
2θ range/ $^{\circ}$	2.931 - 27.521
	-33 $\leq h \leq$ 33
Index range	-33 $\leq k \leq$ 33
	-24 $\leq l \leq$ 24
No. of reflns	170536
collected No. of indep. reflns. (R_{int})	16754 (0.1374)
R , w $R2$ ($I > 2\sigma(I)$)	0.0525, 0.0767
R , w $R2$ (all data)	0.1269, 0.1443
Goodness of fit, F^2	1.073
Data/restraints/params.	16754 / 1.070 / 969
Largest diff. peak, hole/ $\text{\AA}^3$	1.227, -1.043

Table S2. Significant bond lengths ($\text{\AA}$) for complexes $[\text{Cu}(\text{binap})\text{I}]_2$

	Bond lengths ($\text{\AA}$)
I1-Cu1	2.6866(14)
I1-Cu2	2.6565(14)
I2-Cu1	2.6453(14)
I2-Cu2	2.6858(14)
Cu1-P1	2.289(2)
Cu1-P2	2.299(2)
Cu2-P3	2.291(2)
Cu2-P4	2.301(2)
P1-C1	1.816(9)

Table S3. Significant bond angles ($^{\circ}$) for complexes $[\text{Cu}(\text{binap})\text{I}]_2$

	Bond angles ($^{\circ}$)
Cu2-I1-Cu1	74.15(4)
Cu1-I2-Cu2	74.34(4)
P1-Cu1-P2	98.88(8)
P1-Cu1-I2	111.37(7)
P2-Cu1-I2	120.72(7)

P1-Cu1-I1	122.61(7)
P2-Cu1-I1	101.83(7)
I2-Cu1-I1	102.46(3)
P3-Cu2-P4	99.67(8)
P3-Cu2-I1	113.68(8)
P4-Cu2-I1	115.61(7)
P3-Cu2-I2	106.54(7)
I1-Cu2-I2	102.18(3)
P4-Cu2-I2	119.30(7)

IR, SEM/EDX , TEM, BET, TG and XRD Studies

The FTIR spectra of Hydrotalcite and $[\text{Cu}(\text{binap})\text{I}]_2@\text{HT}$ are presented in Figure S2, The strong absorption peak at around 3450 cm^{-1} in two spectrums is ascribed to the stretching vibration of -OH groups from interlayer water molecules and brucite layers. In Figure S2(b), a new peak was seen in the range of $3000\text{--}3100\text{ cm}^{-1}$ attributed to the bending vibrations of =C-H bonds from the $[\text{Cu}(\text{binap})\text{I}]_2$. In addition, the peaks at 694 cm^{-1} and 748 cm^{-1} are due to the bending vibrations of C-H bonds on benzene ring. Moreover, the bands at 1618 cm^{-1} and 1463 cm^{-1} corresponding to $\nu_{\text{C}=\text{C}}$ vibrations on benzene ring confirmed the presence of $[\text{Cu}(\text{binap})\text{I}]_2$.

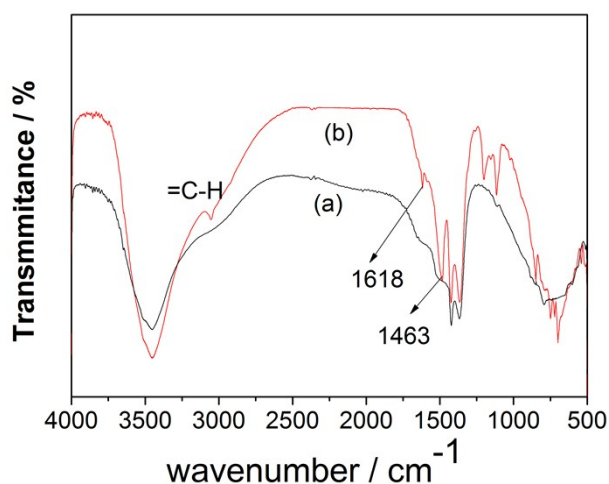
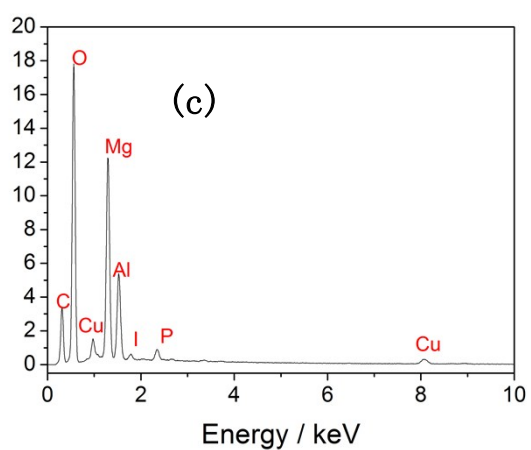
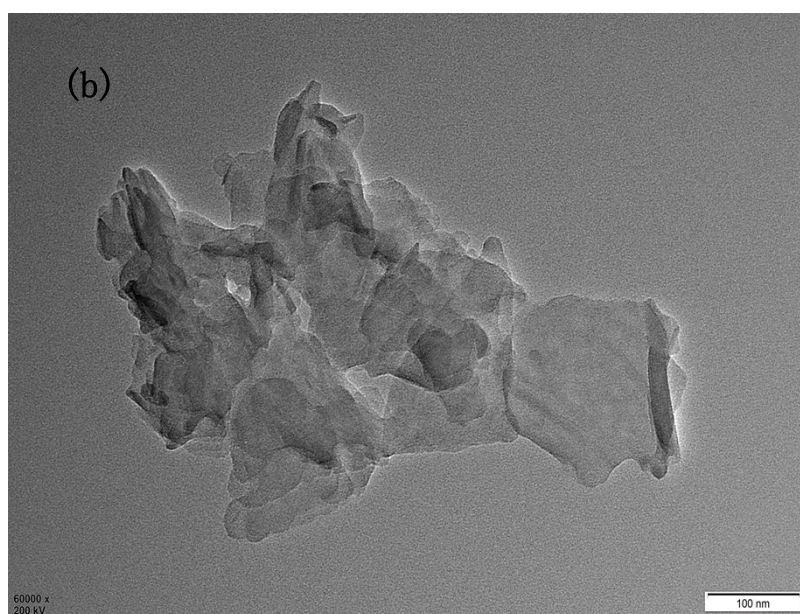
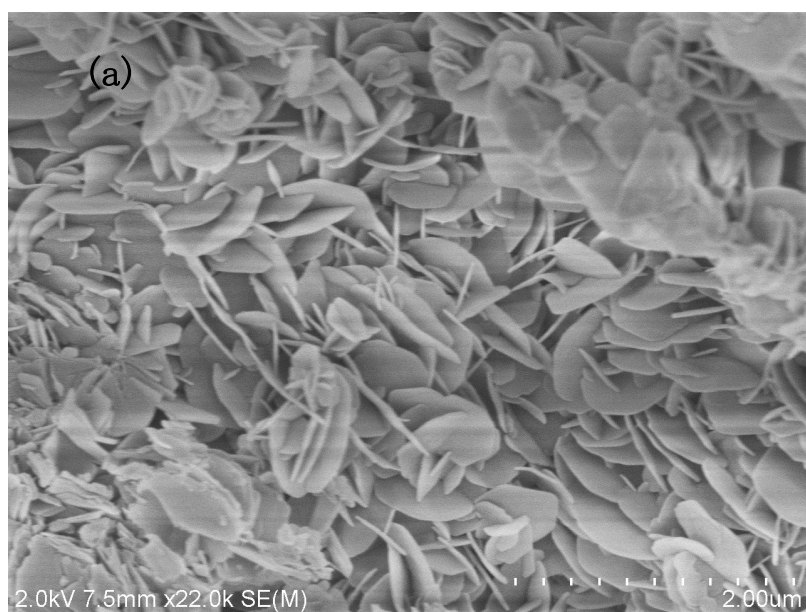


Figure S2. FT-IR spectra of (a) HT, (b) $[\text{Cu}(\text{binap})\text{I}]_2@\text{HT}$.



Element	Wt%	At%
CK	12.52	27.32
OK	34.03	36.45
MgK	22.31	15.12
AlK	7.55	5.30
PK	5.33	4.95
IL	4.24	3.54
CuK	10.01	7.32

Figure S3. The enlarged images (a) SEM images of HT, (b) TEM micrographs of HT, (c) EDX data of the $[\text{Cu}(\text{binap})\text{I}]_2@\text{HT}$.

The N_2 adsorption and desorption isotherms of hydrotalcite and $[Cu(binap)I]_2@HT$ indicate that both samples are of type IV isotherm, which characterizes mesoporous materials, as delineated in Figure S4.(A). It appears that there are two steps in the adsorption curves of hydrotalcite. At first step ($P/P_0 = 0-0.5$), the adsorption capacity remains stable with the increase of P/P_0 . Nevertheless, the adsorption quantity of N_2 has a sharp augment along with continues increase of pressure ($P/P_0 = 0.5-1.0$). The BJH method was conducted to calculate the size of the mesoporous, as shown in Figure S4.(B). Similarly, both samples curves are showed an sharp-pointed peak centered at 10-20 nm with a relatively consistent trend. After the hydrotalcite loaded with $[Cu(binap)I]_2$, It is important to note that the specific surface area and pore volume has a dramatic decline and the bore diameter decreased, either, implying that $[Cu(binap)I]_2$ is well embedded into hydrotalcite interlayer without damage of ordered structure.

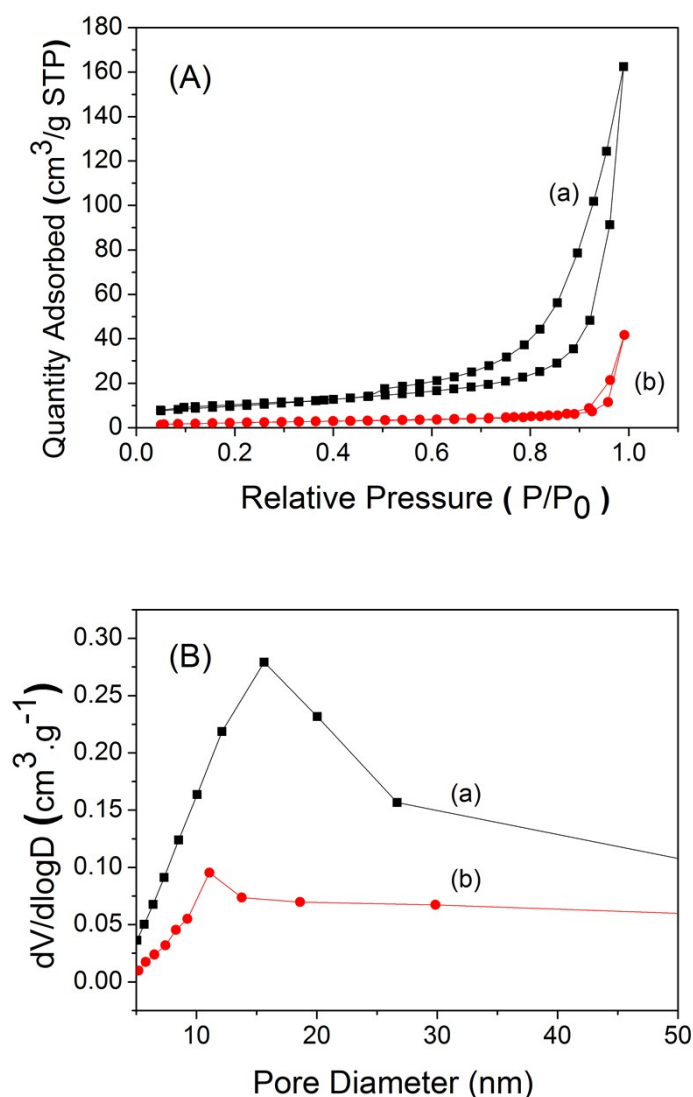


Figure S4. (A) N_2 adsorption–desorption isotherms, (B) BJH adsorption pore size distribution: (a) Hydrotalcite and (b) $[Cu(binap)I]_2@HT$.

Figure S5 shows TGA and DTG curves of Hydrotalcite and $[\text{Cu}(\text{binap})\text{I}]_2@HT$, respectively. As depicted in Figure 6a, there are two decomposition stages. The first mass loss (11.25 %) region ((162 to 225) K; $T_1 = 208$ K) was as a result of the elimination of interlayer water molecules. In the second stage, the mass loss (31.70 %) region ((257 to 534) K corresponds to the decomposing of Mg and Al mixed oxides. There were no distinct differences for two samples in these two stages. Nevertheless, a new decomposition stage was seen in Figure S5(b), a prodigious decrease (19.45 %) in residual weight was noticed from approximately 520°C to the end of heating process, due to the decomposition of $[\text{Cu}(\text{binap})\text{I}]_2$ complex.

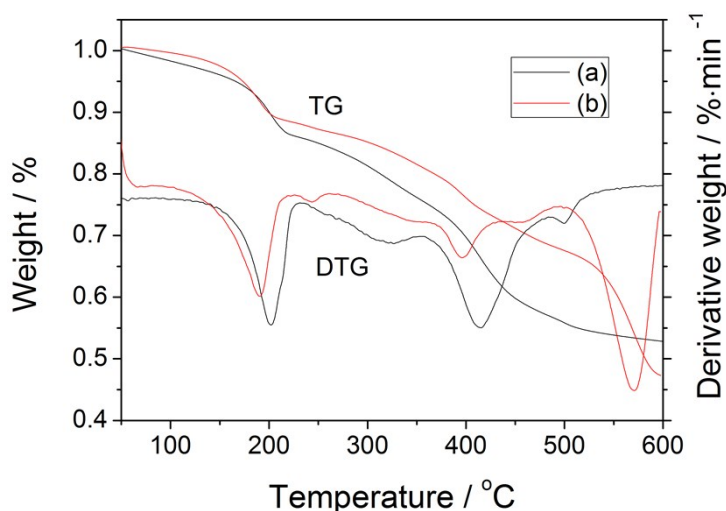


Figure S5. TG and DTG curves of (a) Hydrotalcite and (b) $[\text{Cu}(\text{binap})\text{I}]_2@HT$.

X-ray diffraction (XRD) was conducted to verify the crystallinity and phase composition of the as-synthesized catalyst. The Figure S6(a) displayed the typical hydrotalcite reflections with six characteristic peaks ($2\theta = 11.5^\circ, 23.2^\circ, 34.7^\circ, 39.3^\circ, 46.8^\circ, 62.1^\circ$). Two weak diffraction peaks at 46.8° and 62.1° are ascribed to the characteristic of MgO. Meanwhile, three diffraction bands at $23.2^\circ, 34.7^\circ$ and 62.1° are consistent with the presence of Mg and Al mixed oxides. As shown in Figure S6(b), the intensity of peaks at 23.2° and 46.8° have a significantly decrease resulting from the entering of $[\text{Cu}(\text{binap})\text{I}]_2$ molecules into the hydrotalcite interlayer space. Besides, new ordered peaks were seen at $6.7^\circ, 8.4^\circ$ and 9.4° due to the loading of $[\text{Cu}(\text{binap})\text{I}]_2$.

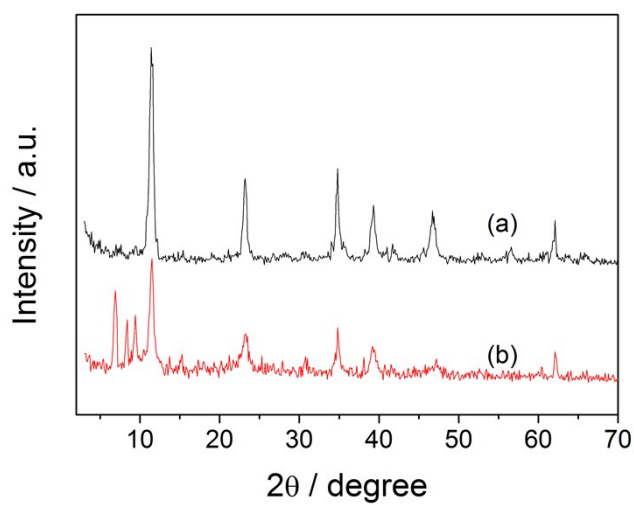


Figure S6. XRD diffractograms: (a) Hydrotalcite, (b) [Cu(binap)I]₂@HT.

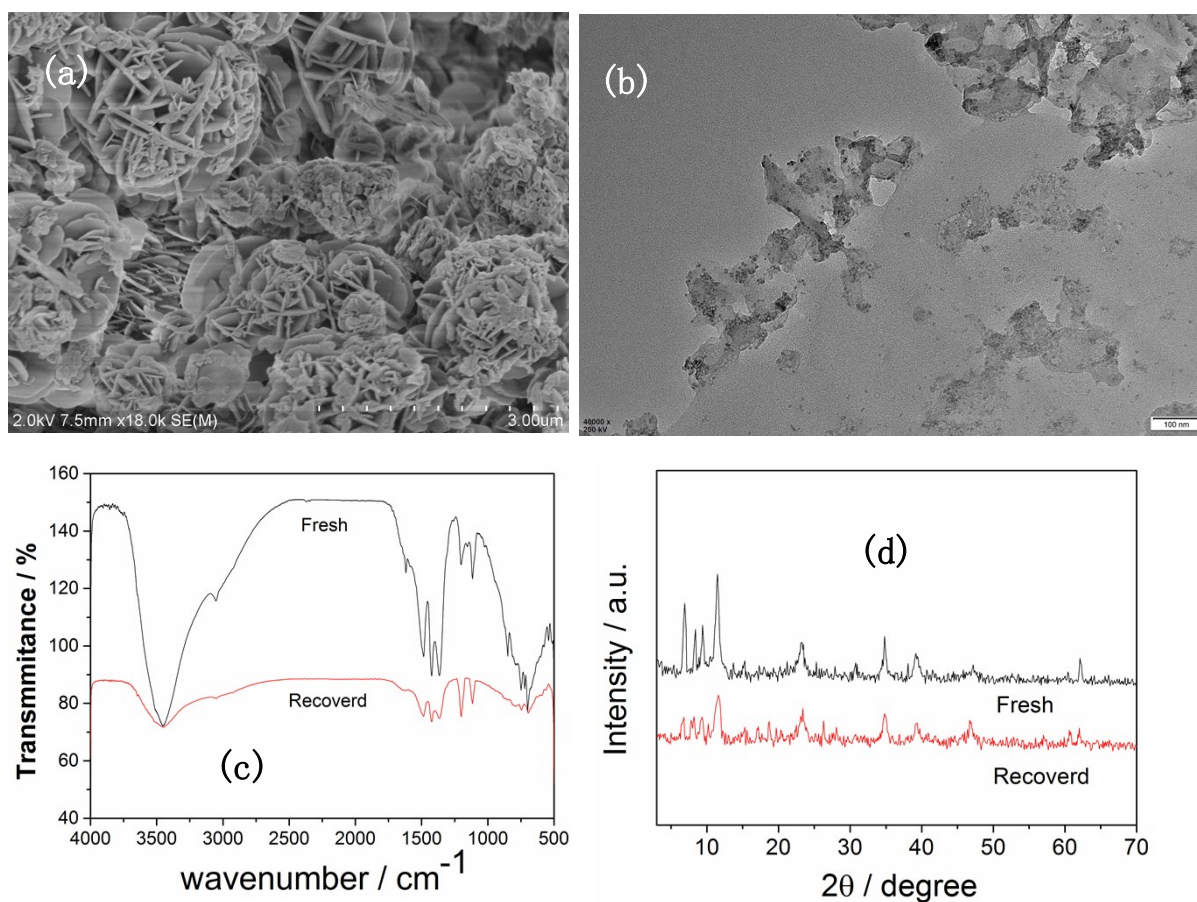
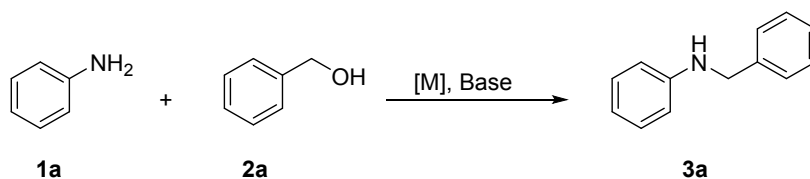


Figure S7. SEM(a) and TEM(b) image, FTIR graphs(c), XRD patterns (d) of the fifth recycled catalyst.

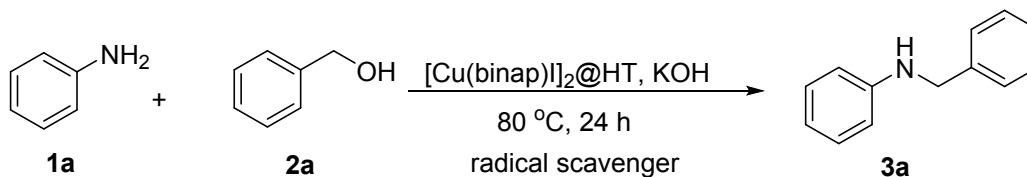
Table S4. Screening of reaction conditions with [Cu(binap)I]₂^a



Entry	Catalyst	Base	Yield[%] ^b
1	[Cu(binap)I] ₂	Na ₂ CO ₃	<5
2	[Cu(binap)I] ₂	Cs ₂ CO ₃	38
3	[Cu(binap)I] ₂	K ₂ CO ₃	23
4	[Cu(binap)I] ₂	<i>t</i> BuOK	47
5	[Cu(binap)I] ₂	NEt ₃	<5
6	[Cu(binap)I] ₂	K ₃ PO ₄	16
7	[Cu(binap)I]₂	KOH	51

^aReagents and conditions: **1a** (2.0 mmol), **2a** (4.0 mmol), catalyst (2 mol% Cu), base (1.0 mmol), 100 °C, 12 h, under solvent-free conditions.^b Isolated yield.

Table S5. Effect of inhibitor concentration on reaction ^a



Entry	Radical scavenger	Equiv.	Yield[%] ^b
1	TEMPO	0.2 eq	85
2	TEMPO	0.4 eq	78
3	TEMPO	0.8 eq	81
4	TEMPO	1.0 eq	83
5	BHT	0.2 eq	82
6	BHT	0.4 eq	79
7	BHT	0.8 eq	82
8	BHT	1.0 eq	78
9	-	-	84

^aReagents and conditions: **1a** (2.0 mmol), **2a** (4.0 mmol), catalyst (2 mol% Cu, 5 % loading, w/w), base (1.0 mmol), 80 °C, 24 h, under solvent-free conditions.^b Isolated yield.

¹H NMR and ¹³C NMR Spectra

N-benzylaniline (3a). ^[1] Following the general procedure, **3a** was obtained as a white solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.45 – 7.38 (m, 4H), 7.37 – 7.31 (m, 1H), 7.27 – 7.21 (m, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.70 (dd, *J* = 8.5, 1.0 Hz, 2H), 4.38 (s, 2H), 4.11 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ = 148.22, 139.46, 129.31, 128.65, 127.54, 127.26, 117.60, 112.92, 48.40.

N-(2-fluorobenzyl)aniline (3b). ^[2] Following the general procedure, **3b** was obtained as a yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.50 – 7.41 (m, 1H), 7.33 – 7.28 (m, 1H), 7.25 – 7.20 (m, 2H), 7.15 – 7.07 (m, 2H), 6.80 – 6.73 (m, 1H), 6.71 (dt, *J* = 8.8, 1.5 Hz, 2H), 4.45 (s, 2H), 4.10 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ = 162.19, 159.75, 147.86, 129.53, 129.48, 129.34, 128.89, 128.81, 126.46, 126.31, 124.27, 124.23, 117.84, 115.50, 115.29, 113.02, 41.93, 41.89.

N-(4-fluorobenzyl)aniline (3c). ^[3] Following the general procedure, light orange liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.45 – 7.33 (m, 2H), 7.31 – 7.17 (m, 2H), 7.12 – 7.01 (m, 2H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.69 (dd, *J* = 8.5, 1.0 Hz, 2H), 4.34 (s, 2H), 4.10 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ = 163.32, 160.88, 147.97, 135.17, 135.14, 129.34, 129.09, 129.01, 117.80, 115.62, 115.36, 112.93, 47.71.

N-(2-chlorobenzyl)aniline (3d). ^[3] Following the general procedure, white solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.53 – 7.45 (m, 2H), 7.30 – 7.16 (m, 4H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 4.51 (s, 2H), 4.24 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ = 147.83, 136.72, 133.29, 129.57, 129.33, 129.10, 128.40, 127.03, 117.81, 113.04, 45.99.

N-(3-chlorobenzyl)aniline (3e). ^[4] Following the general procedure, light yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.41 (s, 1H), 7.40 – 7.29 (m, 3H), 7.25 – 7.20 (m, 2H), 6.80 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 8.6, 2H), 4.35 (s, 2H), 4.13 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ = 147.81, 141.79, 134.56, 129.97, 129.34, 127.50, 127.42, 125.44, 117.95, 112.99, 47.85.

N-(4-chlorobenzyl)aniline (3f). ^[1] Following the general procedure, yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.45 – 7.29 (m, 4H), 7.25 – 7.19 (m, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 8.6, 2H), 4.34 (s, 2H), 4.09 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ = 147.90, 138.11, 132.94, 129.34, 128.81, 128.71, 117.89, 112.96, 47.63.

N-(4-methylbenzyl)aniline (3g). ^[1] Following the general procedure, white solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.31 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.16 (m, 4H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.5, 2H), 4.34 (s, 2H), 4.07 (s, 1H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 148.29, 136.90, 136.46, 129.34, 129.33, 127.60, 117.59, 112.90, 48.17, 21.14.

N-(thiophen-2-ylmethyl)aniline (3h). ^[5] Following the general procedure, yellow solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.31 – 7.20 (m, 3H), 7.11 – 7.04 (m, 1H), 7.03 (d, *J* = 5.0, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 8.6, 2H), 4.54 (s, 2H), 4.10 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ = 147.66, 142.94, 129.32, 126.89, 125.07, 124.60, 118.14, 113.26, 43.55.

N-(2-bromobenzyl)aniline (3i). ^[3] Following the general procedure, light yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.66 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.46 (dd, *J* =

7.8, 1.4 Hz, 1H), 7.32 (t, $J = 7.5$, 1H), 7.27 – 7.15 (m, 3H), 6.80 (t, $J = 7.4$ Hz, 1H), 6.68 (d, $J = 8.5$, 2H), 4.48 (s, 2H), 4.23 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 147.81$, 138.25, 132.86, 129.38, 129.21, 128.73, 127.62, 123.33, 117.84, 113.05, 48.46.

methyl 4-((phenylamino)methyl)benzoate (3j). ^[6] Following the general procedure, colorless liquid; ^1H NMR (400 MHz, CDCl_3) $\delta = 8.06$ (d, $J = 8.4$, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.25 – 7.13 (m, 2H), 6.79 (t, $J = 7.4$ Hz, 1H), 6.65 (d, $J = 8.5$, 2H), 4.42 (s, 2H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) $\delta = 167.00$, 147.83, 145.08, 130.01, 129.35, 129.12, 127.16, 117.90, 112.99, 52.07, 48.01.

N-(2,4-dichlorobenzyl)aniline (3k). Following the general procedure, white solid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.36$ (d, $J = 8.1$ Hz, 2H), 7.29 – 7.17 (m, 3H), 6.84 – 6.77 (m, 3H), 4.63 (s, 2H), 4.05 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 147.78$, 136.15, 134.66, 129.39, 129.27, 128.59, 118.18, 113.57, 44.00. HRMS (ESI) Calculated for $\text{C}_{13}\text{H}_{11}\text{Cl}_2\text{N}$ $[\text{M}+\text{H}]^+$ 252.0347, found 252.0349.

N-(4-(trifluoromethyl)benzyl)aniline (3l). ^[6] Following the general procedure, light yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.65$ (d, $J = 8.1$ Hz, 2H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.31 – 7.19 (m, 2H), 6.84 – 6.76 (m, 1H), 6.66 (dd, $J = 8.6$, 1.0 Hz, 2H), 4.46 (s, 2H), 4.21 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 147.69$, 143.79, 129.37, 127.47, 125.64, 125.60, 125.57, 118.01 (s), 112.95, 47.82.

N-benzyl-4-methoxyaniline (3m). ^[1] Following the general procedure, orange solid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.51$ – 7.41 (m, 4H), 7.38 – 7.32 (m, 1H), 6.87 ((d, $J = 9.8$, 2H), 6.67 (d, $J = 9.8$, 2H), 4.35 (s, 2H), 3.95 – 3.33 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 152.31$, 142.59, 139.89, 128.71, 127.63, 127.28, 115.07, 114.20, 55.90, 49.31.

N-benzyl-2-methoxyaniline (3n). ^[2] Following the general procedure, orange liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.60$ – 7.43 (m, 4H), 7.42 – 7.38 (m, 1H), 7.00 (t, $J = 7.6$, 1H), 6.95 (d, $J = 7.9$, 1H), 6.86 (t, $J = 7.7$, 1H), 6.75 (d, $J = 7.8$, 1H), 4.81 (s, 1H), 4.50 (s, 2H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 147.01$, 139.88, 138.36, 128.76, 127.66, 127.30, 121.54, 116.85, 110.30, 109.67, 55.56, 48.23.

N-benzyl-3-chloroaniline (3o). ^[1] Following the general procedure, yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.53$ – 7.32 (m, 5H), 7.15 (t, $J = 8.1$ Hz, 1H), 6.81 (dd, $J = 7.9$, 1.9, 1H), 6.70 (t, $J = 2.0$ Hz, 1H), 6.57 (dd, $J = 8.2$, 2.3 Hz, 1H), 4.38 (s, 2H), 4.15 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 149.42$, 138.99, 135.15, 130.40, 128.89, 127.57, 117.55, 112.70, 111.30, 48.16.

N-benzyl-4-chloroaniline (3p). ^[1] Following the general procedure, yellow solid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.50$ – 7.24 (m, 5H), 7.21 – 7.10 (m, 2H), 6.65 (d, $J = 9.6$, 2H), 4.34 (s, 2H), 4.10 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 146.80$, 139.09, 129.15, 128.83, 127.55, 127.48, 122.15, 114.07, 48.41.

N-benzyl-4-fluoroaniline (3q). ^[1] Following the general procedure, yellow solid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.53$ – 7.29 (m, 5H), 7.05 – 6.90 (m, 2H), 6.68 – 6.57 (m, 2H), 4.34 (s, 2H), 4.10 – 3.45 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 157.17$, 154.83, 144.63, 144.61, 139.39, 128.77, 127.59, 127.41, 115.88, 115.64, 113.82, 113.74, 48.95.

N-benzyl-naphthalen-1-amine (3r). ^[1] Following the general procedure, orange solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.89 – 7.85 (m, 2H), 7.56 – 7.20 (m, 9H), 6.70 (d, *J* = 7.5 Hz, 1H), 4.83 (s, 1H), 4.54 (s, 2H). ¹³C NMR (101 MHz, CDCl₃): δ = 143.18, 139.11, 134.33, 128.75, 127.80, 127.42, 126.64, 125.79, 124.81, 123.49, 119.93, 117.78, 104.94, 48.77.

N-benzyl-2-methylaniline (3s). ^[3] Following the general procedure, white solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.55 – 7.29 (m, 5H), 7.22 – 7.14 (m, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 4.45 (s, 2H), 3.96 (s, 1H), 2.25 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 146.01, 139.54, 130.13, 128.70, 127.61, 127.27, 127.19, 122.02, 117.26, 110.08, 48.37, 17.55.

N-benzyl-2,5-dimethylaniline (3t). Following the general procedure, light brown liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.57 – 7.28 (m, 5H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.65 – 6.57 (m, 2H), 4.44 (s, 2H), 3.96 (s, 1H), 2.35 (s, 3H), 2.25 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 146.05, 139.62, 136.83, 130.05, 128.73, 127.70, 127.30, 119.05, 117.97, 110.99, 48.50, 21.65, 17.18. HRMS (ESI) Calculated for C₁₅H₁₇N [M+H]⁺ 212.1439, found 212.1445.

3-chloro-N-(2-methylbenzyl)aniline (3u). Following the general procedure, yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.35 (d, *J* = 7.0 Hz, 1H), 7.33 – 7.24 (m, 3H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.67 (s, 1H), 6.55 (d, *J* = 8.2, 1H), 4.28 (s, 2H), 3.96 (s, 1H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 149.43, 136.40, 135.15, 130.60, 130.29, 128.31, 127.73, 126.27, 117.36, 112.35, 111.09, 46.25, 18.97. HRMS (ESI) Calculated for C₁₄H₁₄ClN [M+H]⁺ 232.0893, found 232.0895.

3-chloro-N-(thiophen-2-ylmethyl)aniline (3v). Following the general procedure, light yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.29 (d, *J* = 5.0, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.07 – 7.02 (m, 2H), 6.82 – 6.73 (m, 1H), 6.70 (t, *J* = 2.0 Hz, 1H), 6.56 (dd, *J* = 8.1, 2.2 Hz, 1H), 4.54 (s, 2H), 4.15 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ = 148.75, 142.19, 135.09, 130.30, 127.01, 125.35, 124.82, 117.99, 112.91, 111.45, 43.30. HRMS (ESI) Calculated for C₁₁H₁₀ClNS [M+H]⁺ 224.0301, found 224.0300.

3-chloro-N-(4-fluorobenzyl)aniline (3w). Following the general procedure, light yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.38 – 7.31 (m, 2H), 7.13 – 7.04 (m, 3H), 6.72 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.63 (t, *J* = 2.1 Hz, 1H), 6.51 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.30 (s, 2H), 4.15 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ = 163.41, 160.93, 149.01, 135.10, 134.43, 130.23, 129.04, 117.66, 115.70, 115.44, 112.61, 111.25, 47.44. HRMS (ESI) Calculated for C₁₃H₁₁ClFN [M+H]⁺ 236.0642, found 236.0647.

3-chloro-N-(4-methylbenzyl)aniline (3x). Following the general procedure, light yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.85 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.74 (t, *J* = 2.1 Hz, 1H), 6.61 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.35 (s, 2H), 4.14 (s, 1H), 2.52 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 149.51, 137.22, 135.92, 135.16, 130.38, 129.59, 127.65, 117.46, 112.72, 111.30, 47.97, 21.28. HRMS (ESI) Calculated for C₁₄H₁₄ClN [M+H]⁺ 232.0893, found 232.0896.

1,3-diphenylpropan-1-one (5a). ^[21] Following the general procedure, white solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.99 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.49

(t, $J = 7.5$ Hz, 2H), 7.35 – 7.28 (m, 4H), 7.25 – 7.22 (m, 1H), 3.35 (t, $J = 7.6$ Hz, 2H), 3.13 (t, $J = 7.6$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 199.28, 141.30, 136.90, 133.05, 126.13, 40.47, 30.14$.

1-phenyl-3-(p-tolyl)propan-1-one (5b). ^[7] Following the general procedure, light yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.02$ (d, $J = 7.2$ Hz, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 2H), 7.22 – 7.16 (m, 4H), 3.33 (t, $J = 7.5$ Hz, 2H), 3.09 (t, $J = 7.5$ Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 199.35, 138.22, 136.99, 135.61, 133.07, 129.24, 128.60, 128.33, 128.10, 40.61, 29.79, 21.05$.

3-(4-chlorophenyl)-1-phenylpropan-1-one (5c). ^[8] Following the general procedure, light yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.97$ (d, $J = 7.2$ Hz, 2H), 7.59 (d, $J = 7.4$ Hz, 1H), 7.48 (d, $J = 7.5$ Hz, 2H), 7.31 – 7.27 (m, 2H), 7.22 (d, $J = 8.5$ Hz, 2H), 3.35 – 3.29 (m, 2H), 3.05 (t, $J = 7.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 198.85, 139.73, 136.80, 133.17, 129.88, 128.63, 128.60, 128.00, 40.15, 29.40$.

3-(4-iodophenyl)-1-phenylpropan-1-one (5d). Following the general procedure, 5 light yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.99$ – 7.95 (m, 2H), 7.65 – 7.56 (m, 3H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.03 (d, $J = 8.2$ Hz, 2H), 3.31 (t, $J = 7.4$ Hz, 2H), 3.05 (t, $J = 7.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 198.77, 141.02, 137.53, 136.77, 133.20, 130.63, 128.66, 128.05, 40.01, 29.55$. HRMS (ESI) Calculated for $\text{C}_{15}\text{H}_{13}\text{IO}$ $[\text{M}+\text{H}]^+$ 337.0089, found 337.0090.

1-phenyl-3-(thiophen-2-yl)propan-1-one (5e). ^[7] Following the general procedure, light yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.01$ (d, $J = 5.2$, 2H), 7.62 – 7.57 (m, 1H), 7.50 (t, $J = 7.5$ Hz, 2H), 7.17 (d, $J = 5.1$, 1H), 6.96 – 6.94 (m, 1H), 6.88 (d, $J = 3.3$, 1H), 3.42 – 3.38 (m, 2H), 3.36 – 3.31 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 198.60, 143.92, 136.81, 133.17, 128.66, 128.07, 126.88, 124.63, 123.36, 40.55, 24.0$.

3-(2-bromophenyl)-1-phenylpropan-1-one (5f). Following the general procedure, yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.02$ – 8.00 (m, 2H), 7.61 – 7.57 (m, 2H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.36 – 7.33 (m, 1H), 7.29 – 7.25 (m, 1H), 7.14 – 7.09 (m, 1H), 3.37 – 3.33 (m, 2H), 3.24 – 3.20 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 198.95, 140.62, 136.79, 133.13, 132.90, 130.88, 128.65, 128.10, 128.00, 127.69, 124.43, 38.62, 30.88$. HRMS (ESI) Calculated for $\text{C}_{15}\text{H}_{13}\text{BrO}$ $[\text{M}+\text{H}]^+$ 289.0228, found 289.0227.

3-(4-methoxyphenyl)-1-phenylpropan-1-one (5g). ^[9] Following the general procedure, white solid; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.01$ – 7.99 (m, 2H), 7.56 (t, $J = 7.0$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 6.91 – 6.88 (m, 2H), 3.82 (s, 3H), 3.32 – 3.28 (m, 2H), 3.05 (t, $J = 7.5$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 199.31, 158.10, 137.05, 133.39, 133.08, 129.44, 128.67, 128.10, 114.08, 55.29, 40.69, 29.32$.

3-phenyl-1-(p-tolyl)propan-1-one (5h). ^[10] Following the general procedure, light yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.88$ (d, $J = 8.1$ Hz, 2H), 7.35 – 7.23 (m, 7H), 3.34 – 3.29 (m, 2H), 3.11 – 3.07 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 198.94, 143.80, 141.46, 134.47, 129.30, 128.56, 128.47, 128.19, 126.14, 40.33, 30.27, 21.60$.

1-(4-methoxyphenyl)-3-phenylpropan-1-one (5i). ^[10] Following the general procedure, white solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (dt, *J* = 14.2, 7.0 Hz, 2H), 7.36 – 7.24 (m, 5H), 6.96 (dt, *J* = 14.2, 7.0 Hz, 2H), 3.89 (s, 3H), 3.30 – 3.26 (m, 2H), 3.12 – 3.08 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ = 197.80, 163.55, 141.51, 130.36, 130.05, 128.57, 128.50, 126.11, 113.79, 55.49, 40.10, 30.36.

1-(4-methoxyphenyl)-3-(o-tolyl)propan-1-one (5j). Following the general procedure, light yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ = 8.02 – 7.98 (m, 2H), 7.25 – 7.15 (m, 4H), 6.99 – 6.96 (m, 2H), 3.90 (s, 3H), 3.27 – 3.23 (m, 2H), 3.11 – 3.07 (m, 2H), 2.41 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 197.92, 163.51, 139.59, 136.05, 130.38, 130.33, 130.07, 128.79, 126.74, 126.30, 113.79, 55.45, 38.76, 27.75, 19.33. HRMS (ESI) Calculated for C₁₇H₁₈O₂ [M+H]⁺ 255.1385, found 255.1386.

3-(2-bromophenyl)-1-(4-methoxyphenyl)propan-1-one (5k). ^[8] Following the general procedure, white solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (d, *J* = 8.0, 2H), 7.56 (d, *J* = 8.0, 1H), 7.34 (d, *J* = 7.6, 1H), 7.28 – 7.24 (m, 1H), 7.10 (t, *J* = 7.7, 1H), 6.96 – 6.93 (m, 2H), 3.87 (s, 3H), 3.30 – 3.26 (m, 2H), 3.21 – 3.17 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ = 197.53, 163.55, 140.72, 132.83, 130.79, 130.33, 129.91, 127.92, 127.66, 124.36, 113.75, 55.43, 38.29, 31.03.

3-(4-chlorophenyl)-1-(4-methoxyphenyl)propan-1-one (5l). ^[8] Following the general procedure, white solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.95 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.26 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 3.23 (t, *J* = 7.5 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ = 197.39, 163.53, 139.91, 131.80, 130.30, 129.91, 129.88, 128.58, 113.77, 55.49, 39.79, 29.55.

3-(4-iodophenyl)-1-(4-methoxyphenyl)propan-1-one (5m). Following the general procedure, light yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.94 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 3.25 (t, *J* = 7.5 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ = 197.31, 163.55, 141.12, 137.50, 130.60, 130.30, 129.87, 113.83, 91.16, 55.51, 39.67, 29.75. HRMS (ESI) Calculated for C₁₆H₁₅IO₂ [M+H]⁺ 367.0195, found 367.0190.

1-(4-methoxyphenyl)-3-(p-tolyl)propan-1-one (5n). ^[8] Following the general procedure, white solid; ¹H NMR (400 MHz, CDCl₃): δ = 8.00 – 7.96 (m, 2H), 7.22 – 7.14 (m, 4H), 7.00 – 6.94 (m, 2H), 3.90 (s, 3H), 3.27 (t, *J* = 7.5 Hz, 2H), 3.06 (t, *J* = 7.5 Hz, 2H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 197.96, 163.43, 138.41, 135.54, 130.32, 130.08, 129.20, 128.31, 113.77, 55.48, 40.30, 29.99, 21.00.

1-(4-methoxyphenyl)-3-(thiophen-2-yl)propan-1-one (5o). Following the general procedure, light yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (d, *J* = 8.8, 2H), 7.15 (d, *J* = 5.1, 1H), 6.97 – 6.91 (m, 3H), 6.87 (d, *J* = 3.3, 1H), 3.87 (s, 3H), 3.36 – 3.28 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ = 197.11, 163.55, 144.10, 130.31, 129.89, 126.85, 124.67, 123.33, 113.77, 55.44, 40.17, 24.42. HRMS (ESI) Calculated for C₁₄H₁₄O₂S [M+H]⁺ 247.0793, found 247.0797.

1-(4-bromophenyl)-3-phenylpropan-1-one (5p). Following the general procedure, white solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, *J* = 8.4, 2H), 7.61 (d, *J* = 8.4,

2H), 7.38 – 7.31 (m, 5H), 3.31 – 7.27 (m, 2H), 3.11 (t, $J = 7.5$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 198.18, 141.02, 135.60, 133.87, 133.64, 131.95, 129.55, 128.57, 128.40, 126.23, 40.44, 30.02$. HRMS (ESI) Calculated for $\text{C}_{15}\text{H}_{13}\text{BrO}$ $[\text{M}+\text{H}]^+$ 289.0228, found 289.0226.

1-(4-bromophenyl)-3-(4-iodophenyl)propan-1-one (5q). Following the general procedure, light yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.82$ (d, $J = 8.5$ Hz, 2H), 7.66 – 7.60 (m, 4H), 7.01 (d, $J = 8.4$ Hz, 2H), 3.25 (t, $J = 7.4$ Hz, 2H), 3.04 (t, $J = 7.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 197.78, 140.70, 137.58, 135.49, 131.96, 130.55, 129.57, 128.34, 39.99, 29.45$. HRMS (ESI) Calculated for $\text{C}_{15}\text{H}_{12}\text{BrIO}$ $[\text{M}+\text{H}]^+$ 414.9194, found 414.9194.

1-(4-bromophenyl)-3-(p-tolyl)propan-1-one (5r).^[10] Following the general procedure, yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.84$ (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.18 – 7.13 (m, 4H), 3.29– 3.25 (m, 2H), 3.06 (t, $J = 7.5$ Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 198.29, 137.97, 135.79, 135.68, 131.90, 129.59, 129.27, 128.41, 128.16, 40.58, 29.66, 21.01$.

1-(4-bromophenyl)-3-(4-methoxyphenyl)propan-1-one (5s).^[11] Following the general procedure, light yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.83$ (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.20 (d, $J = 8.5$ Hz, 2H), 6.87 (d, $J = 8.5$ Hz, 2H), 3.82 (s, 3H), 3.28 – 3.23 (m, 2H), 3.02 (t, $J = 7.5$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 198.34, 158.11, 135.63, 133.09, 131.94, 129.63, 129.37, 128.19, 114.05, 55.31, 40.66, 29.20$.

1-(4-bromophenyl)-3-(4-chlorophenyl)propan-1-one (5t). Following the general procedure, yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.82$ (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.29 – 7.26 (m, 2H), 7.20 – 7.17 (m, 2H), 3.25 (t, $J = 7.4$ Hz, 2H), 3.06 (t, $J = 7.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 197.78, 139.50, 135.48, 131.99, 129.83, 129.56, 128.63, 128.31, 40.09, 29.30$. HRMS (ESI) Calculated for $\text{C}_{15}\text{H}_{12}\text{BrClO}$ $[\text{M}+\text{H}]^+$ 322.9838, found 322.9837.

3-(2-bromophenyl)-1-(4-bromophenyl)propan-1-one (5u). Following the general procedure, yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.87 – 7.84$ (m, 2H), 7.61 – 7.56 (m, 3H), 7.36 – 7.32 (m, 2H), 7.11 (t, $J = 7.7$, 1H), 3.32 – 3.26 (m, 2H), 3.22 – 3.18 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 197.89, 140.31, 135.50, 132.99, 131.95, 130.84, 129.63, 128.11, 127.69, 124.36, 38.59, 30.74$. HRMS (ESI) Calculated for $\text{C}_{15}\text{H}_{12}\text{Br}_2\text{O}$ $[\text{M}+\text{H}]^+$ 366.9333, found 366.9338.

1-benzyl-2-phenyl-1H-benzo[d]imidazole (7a).^[12] Following the general procedure, brown solid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.91$ (d, $J = 8.0$ Hz, 1H), 7.75 – 7.71 (m, 2H), 7.53 – 7.45 (m, 3H), 7.37 – 7.32 (m, 4H), 7.26 – 7.22 (m, 2H), 7.14 – 7.11 (m, 2H), 5.47 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 154.20, 143.21, 136.44, 136.09, 130.11, 129.95, 129.33, 129.11, 128.75, 127.79, 126.04, 123.08, 122.72, 120.01, 110.55, 48.39$.

1-(2-fluorobenzyl)-2-(2-fluorophenyl)-1H-benzo[d]imidazole (7b). Following the general procedure, yellow liquid; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.90$ (d, $J = 7.5$ Hz, 1H), 7.62 (t, $J = 7.5$ Hz, 1H), 7.48 – 7.43 (m, 1H), 7.26 – 7.13 (m, 6H), 7.02 – 6.91 (m, 2H), 6.76 (t, $J = 7.5$ Hz, 1H), 5.40 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 161.45, 161.36, 158.97, 158.90, 149.34, 143.33, 135.30, 132.36, 132.34, 132.28, 132.20$,

131.43, 131.34, 130.31, 130.29, 129.65, 129.57, 128.47, 128.45, 124.91, 124.75, 124.72, 124.42, 124.38, 123.36, 123.05, 122.91, 122.73, 120.14, 118.52, 118.37, 118.00, 117.89, 116.19, 115.54, 115.98, 115.54, 115.33, 110.59, 42.23. HRMS (ESI) Calculated for $C_{20}H_{14}F_2N_2$ $[M+H]^+$ 321.1203, found 321.1205.

1-(4-fluorobenzyl)-2-(4-fluorophenyl)-1H-benzo[d]imidazole (7c).^[13] Following the general procedure, white solid; 1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.1 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.37 – 7.33 (m, 1H), 7.31 – 7.22 (m, 2H), 7.21 – 7.15 (m, 2H), 7.10 – 7.02 (m, 4H), 5.41 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.05, 163.54, 162.56, 161.09, 153.06, 142.95, 142.93, 135.85, 135.83, 131.92, 131.29, 131.20, 127.69, 127.60, 126.08, 123.33, 122.98, 120.03, 116.23, 116.13, 116.02, 115.92, 110.32, 47.73.

1-(2-chlorobenzyl)-2-(2-chlorophenyl)-1H-benzo[d]imidazole (7d).^[14] Following the general procedure, white solid; 1H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, J = 8.1 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.38 – 7.27 (m, 4H), 7.24 – 7.17 (m, 2H), 7.08 (t, J = 7.1 Hz, 1H), 6.67 (d, J = 7.5 Hz, 1H), 5.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.53, 143.07, 134.80, 134.38, 133.30, 132.39, 132.15, 131.40, 129.95, 129.70, 129.63, 129.01, 127.81, 127.15, 127.00, 123.40, 122.73, 120.35, 110.55, 45.76.

1-(3-chlorobenzyl)-2-(3-chlorophenyl)-1H-benzo[d]imidazole (7e). Following the general procedure, light yellow liquid; 1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.1 Hz, 1H), 7.73 (t, J = 1.7 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 – 7.33 (m, 2H), 7.34 – 7.29 (m, 3H), 7.25 (t, J = 8.0 Hz, 1H), 7.13 (s, 1H), 6.95 (d, J = 7.0 Hz, 1H), 5.44 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.54, 143.10, 138.24, 135.99, 135.25, 135.00, 131.70, 130.54, 130.15, 130.09, 129.52, 128.31, 127.09, 126.26, 124.11, 123.67, 123.11, 120.35, 110.37, 47.96. HRMS (ESI) Calculated for $C_{20}H_{14}Cl_2N_2$ $[M+H]^+$ 353.0612, found 353.0610.

1-(4-chlorobenzyl)-2-(4-chlorophenyl)-1H-benzo[d]imidazole (7f).^[14] Following the general procedure, white solid; 1H NMR (400 MHz, DMSO): δ = 7.78 – 7.72 (m, 3H), 7.58 – 7.56 (m, 2H), 7.49 – 7.46 (m, 1H), 7.34 (d, J = 8.5 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.01 (d, J = 8.5 Hz, 2H), 5.58 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ = 152.58, 143.15, 136.33, 136.26, 135.29, 132.60, 131.59, 131.23, 129.40, 129.25, 128.45, 123.49, 122.99, 119.89, 111.53, 47.38.

1-(2-methylbenzyl)-2-(o-tolyl)-1H-benzo[d]imidazole (7g). Following the general procedure, light yellow liquid; 1H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.1 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.30 – 7.16 (m, 5H), 7.07 – 7.03 (m, 1H), 6.69 (d, J = 7.6 Hz, 1H), 5.24 (s, 2H), 2.31 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.97, 143.26, 138.39, 135.17, 134.89, 134.10, 130.93, 130.67, 129.91, 129.89, 127.60, 126.43, 126.15, 125.66, 122.90, 122.39, 120.06, 110.60, 45.84, 19.88, 19.11. HRMS (ESI) Calculated for $C_{22}H_{20}N_2$ $[M+H]^+$ 313.1705, found 313.1706.

1-(3-methylbenzyl)-2-(m-tolyl)-1H-benzo[d]imidazole (7h). Following the general procedure, yellow liquid; 1H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.1 Hz, 1H), 7.65 (s, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.24 – 7.20 (m, 3H), 7.10 (d, J = 7.5 Hz, 1H), 6.95 (s, 1H), 6.92 (d, J = 7.5 Hz, 1H), 5.42 (s, 2H), 2.41 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.38, 143.09, 138.75, 138.61,

136.50, 136.20, 130.71, 130.26, 129.95, 128.93, 128.55, 126.70, 126.09, 123.13, 123.02, 122.69, 119.91, 110.63, 48.40, 21.46, 21.34. HRMS (ESI) Calculated for $C_{22}H_{20}N_2 [M+H]^+$ 313.1705, found 313.1705.

1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole (7i). ^[13] Following the general procedure, light yellow liquid; ¹H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.23– 7.20 (m, 2H), 7.15 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 5.43 (s, 2H), 2.42 (s, 3H), 2.35 (s, 3H). ¹³C NMR (101 MHz, $CDCl_3$): δ = 154.36, 143.20, 140.01, 137.45, 136.11, 133.52, 129.70, 129.43, 129.19, 127.23, 125.95, 122.88, 122.55, 119.81, 110.52, 48.24, 21.45, 21.10.

2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1H-benzo[d]imidazole (7j). ^[15] Following the general procedure, brown solid; ¹H NMR (400 MHz, DMSO): δ = 7.83 (d, J = 5.0 Hz, 1H), 7.75 – 7.68 (m, 3H), 7.41 (d, J = 5.1 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.04 – 7.03 (m, 1H), 6.96 (t, J = 5.0 Hz, 1H), 5.94 (s, 2H). ¹³C NMR (101 MHz, DMSO): δ = 147.26, 142.94, 139.80, 136.31, 132.55, 130.17, 128.89, 128.35, 127.52, 126.56, 126.43, 123.39, 123.40, 123.07, 119.46, 111.29, 43.51.

1-(2-methoxybenzyl)-2-(2-methoxyphenyl)-1H-benzo[d]imidazole (7k). ^[16] Following the general procedure, white solid; ¹H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 8.8 Hz, 2H), 7.34– 7.28 (m, 1H), 7.23 – 7.21 (m, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 5.37 (s, 2H), 3.84 (s, 3H), 3.77 (s, 3H). ¹³C NMR (101 MHz, $CDCl_3$): δ = 160.90, 159.15, 154.09, 143.17, 136.09, 130.71, 128.52, 127.25, 122.73, 122.50, 119.71, 114.43, 114.20, 110.42, 55.37, 55.26, 47.85.

1-(4-bromobenzyl)-2-(4-bromophenyl)-1H-benzo[d]imidazole (7l). ^[17] Following the general procedure, light yellow liquid; ¹H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 7.9 Hz, 1H), 7.63 (t, J = 7.3 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.27 – 7.14 (m, 6H), 6.96 (dt, J = 15.1, 8.3 Hz, 2H), 6.77 (t, J = 7.5 Hz, 1H), 5.39 (s, 2H). ¹³C NMR (101 MHz, $CDCl_3$): δ = 161.45, 161.36, 158.97, 158.90, 149.35, 143.32, 135.29, 132.29 (dd, J = 10.7, 5.3 Hz), 131.38 (d, J = 8.9 Hz), 130.30 (d, J = 2.7 Hz), 129.61 (d, J = 8.1 Hz), 128.46 (d, J = 2.4 Hz), 124.82 (dd, J = 16.2, 3.0 Hz), 124.40 (d, J = 3.6 Hz), 123.36, 123.05, 122.91, 122.73, 120.15, 118.45 (d, J = 14.9 Hz), 117.95 (d, J = 10.8 Hz), 116.11 (dd, J = 21.9, 5.3 Hz), 115.54, 115.33, 110.59, 42.23 (t, J = 4.5 Hz).

1-(2-fluorobenzyl)-2-(2-fluorophenyl)-5-methyl-1H-benzo[d]imidazole (7m). Following the general procedure, brown solid; ¹H NMR (400 MHz, DMSO): δ = 7.66 – 7.51 (m, 3H), 7.44 – 7.31 (m, 3H), 7.26 (dd, J = 14.0, 7.0 Hz, 1H), 7.15 – 7.07 (m, 2H), 7.03 (dt, J = 8.5, 1.0 Hz, 1H), 6.85 – 6.75 (m, 1H), 5.44 (s, 2H), 2.42 (d, J = 5.4 Hz, 3H). ¹³C NMR (101 MHz, DMSO): δ = 161.39 (d, J = 5.0 Hz), 158.92 (dd, J = 5.3, 3.6 Hz), 148.85, 148.42, 143.61, 141.43, 135.91, 133.77, 132.91, 132.85, 132.81, 132.58, 131.85, 130.26 (dd, J = 8.2, 4.1 Hz), 129.18 (dd, J = 20.6, 3.8 Hz), 125.29, 124.96, 124.85, 124.29, 123.75 (dd, J = 14.4, 3.9 Hz), 119.60 (d, J = 8.3 Hz), 118.86 (d, J = 14.9 Hz), 116.64, 116.43, 115.94, 115.73, 111.08 (d, J = 5.9 Hz), 42.26, 42.06, 21.91, 21.57. HRMS (ESI) Calculated for $C_{21}H_{16}F_2N_2 [M+H]^+$ 335.1360, found 335.1357.

1-(4-fluorobenzyl)-2-(4-fluorophenyl)-5-methyl-1H-benzo[d]imidazole (7n).

Following the general procedure, white solid; ^1H NMR (400 MHz, CDCl_3): δ = 7.76–7.60 (m, 3H), 7.17 – 7.12 (m, 3H), 7.07 (s, 1H), 7.06 – 7.00 (m, 4H), 5.34 (s, 2H), 2.47 (d, J = 20.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 164.94, 164.91, 163.49, 162.43, 161.05, 152.99, 152.60, 143.46, 141.25, 136.21, 134.06, 133.35, 132.59, 132.14, 131.16 (dd, J = 8.5, 5.2 Hz), 127.63 (dd, J = 8.0, 5.9 Hz), 126.37 (d, J = 3.2 Hz), 124.73, 124.50, 119.82, 119.60, 116.17, 116.03, 115.96, 115.81, 110.11, 109.85, 47.61 (d, J = 12.5 Hz), 21.85, 21.53. HRMS (ESI) Calculated for $\text{C}_{21}\text{H}_{16}\text{F}_2\text{N}_2$ $[\text{M}+\text{H}]^+$ 335.1360, found 335.1357.

1-(3-chlorobenzyl)-2-(3-chlorophenyl)-5-methyl-1H-benzo[d]imidazole (7o).

Following the general procedure, yellow liquid; ^1H NMR (400 MHz, CDCl_3): δ = 7.78 – 7.66 (m, 2H), 7.50 – 7.41 (m, 2H), 7.39 – 7.34 (m, 1H), 7.30 – 7.24 (m, 2H), 7.18 – 7.02 (m, 3H), 6.94 (t, J = 5.1 Hz, 1H), 5.36 (s, 2H), 2.48 (d, J = 18.7 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 152.35, 152.00, 143.44, 141.20, 138.41, 138.37, 136.25, 135.15, 135.13, 134.92, 134.90, 134.09, 133.83, 132.88, 131.80, 130.51, 130.48, 130.05, 129.98, 129.49, 129.46, 128.25, 127.06, 126.98, 126.26, 126.18, 125.19, 124.81, 124.16, 120.07, 119.85, 110.10, 109.89, 47.89, 47.77, 21.93, 21.65. HRMS (ESI) Calculated for $\text{C}_{21}\text{H}_{16}\text{Cl}_2\text{N}_2$ $[\text{M}+\text{H}]^+$ 367.0769, found 367.0770.

1-(4-chlorobenzyl)-2-(4-chlorophenyl)-5-methyl-1H-benzo[d]imidazole (7p).

Following the general procedure, white solid; ^1H NMR (400 MHz, CDCl_3): δ = 7.77 – 7.56 (m, 3H), 7.42 – 7.40 (m, 2H), 7.33 – 7.25 (m, 2H), 7.18 – 6.98 (m, 4H), 5.35 (s, 2H), 2.46 (d, J = 21.1, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 152.77, 152.34, 143.45, 141.27, 136.27, 136.19, 136.13, 134.89, 134.86, 134.09, 133.77, 133.60, 132.72, 130.41, 130.37, 129.38, 129.36, 129.09, 128.58, 127.30, 127.27, 124.99, 124.65, 119.97, 119.69, 110.11, 109.86, 47.79, 47.65, 21.88, 21.59. HRMS (ESI) Calculated for $\text{C}_{21}\text{H}_{16}\text{Cl}_2\text{N}_2$ $[\text{M}+\text{H}]^+$ 367.0769, found 367.0768.

5-methyl-1-(2-methylbenzyl)-2-(o-tolyl)-1H-benzo[d]imidazole (7q). Following the general procedure, light yellow liquid; ^1H NMR (400 MHz, CDCl_3): δ = 7.82 – 7.72 (m, 1H), 7.62 (s, 1H), 7.45 (t, J = 5.1 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.23 – 7.10 (m, 3H), 7.08 – 7.05 (m, 1H), 6.97– 6.88 (m, 2H), 5.37 (s, 2H), 2.50 (d, J = 27.6 Hz, 3H), 2.40 (d, J = 3.1 Hz, 3H), 2.31 (d, J = 5.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 154.33, 153.95, 143.57, 141.39, 138.67 (dd, J = 16.6, 2.7 Hz), 136.76, 136.73, 136.52, 134.35, 132.96, 132.21, 130.58 (d, J = 5.0 Hz), 130.25, 130.22, 130.17, 128.95 (d, J = 3.6 Hz), 128.52, 126.64 (d, J = 9.4 Hz), 125.98 (d, J = 7.4 Hz), 124.38 (d, J = 19.8 Hz), 123.09 (d, J = 8.1 Hz), 119.75, 119.49, 110.40, 110.15, 48.32 (d, J = 14.0 Hz), 21.92, 21.51 (dd, J = 14.9, 13.0 Hz). HRMS (ESI) Calculated for $\text{C}_{23}\text{H}_{22}\text{N}_2$ $[\text{M}+\text{H}]^+$ 327.1861, found 327.1858.

5-methyl-1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole (7r).^[18] Following the general procedure, gray solid; ^1H NMR (400 MHz, CDCl_3): δ = 7.82 – 7.72 (m, 1H), 7.62 (dd, J = 8.0, 3.8 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.16 – 6.99 (m, 6H), 5.35 (s, 2H), 2.46 (d, J = 31.5 Hz, 3H), 2.40 (s, 3H), 2.34 (d, J = 4.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 154.25, 153.88, 143.62, 141.47, 139.81 (d, J = 5.7 Hz), 137.31 (d, J = 1.8 Hz), 136.50, 134.31, 133.70 (d, J = 4.9 Hz), 132.79, 132.10, 129.70 (d, J = 4.2 Hz), 129.42 (d, J = 1.0 Hz), 129.14 (d, J = 5.0 Hz), 127.45, 125.90 (d, J = 7.5 Hz), 124.26 (d, J = 13.5 Hz), 119.66, 119.39, 110.34, 110.10, 48.07 (d, J = 13.4 Hz), 21.88,

21.63, 21.36, 21.08.

5-methyl-2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1H-benzo[d]imidazole (7s).

Following the general procedure, white solid; ^1H NMR (400 MHz, CDCl_3): δ = 7.75 – 7.64 (m, 1H), 7.50 – 7.43 (m, 2H), 7.25 – 7.09 (m, 4H), 6.95 – 6.92 (m, 1H), 6.84 (d, J = 3.3 Hz, 1H), 5.64 (s, 2H), 2.48 (d, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 147.49, 147.17, 143.31, 141.11, 139.03 (d, J = 3.6 Hz), 136.14, 134.08, 133.49, 132.77, 132.07 (d, J = 8.3 Hz), 128.71 (d, J = 9.8 Hz), 127.92, 127.72, 127.26 (d, J = 5.6 Hz), 125.45, 125.36, 124.77 (d, J = 18.1 Hz), 119.70, 119.45, 109.81, 109.54, 44.02 (d, J = 5.9 Hz), 21.96, 21.67. HRMS (ESI) Calculated for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$ 311.0677, found 311.0679.

1-(3,5-difluorobenzyl)-2-(3,5-difluorophenyl)-1H-benzo[d]imidazole (7t).

Following the general procedure, white solid; ^1H NMR (400 MHz, CDCl_3): δ = 7.91 (d, J = 7.7 Hz, 1H), 7.41 – 7.30 (m, 2H), 7.24 – 7.19 (m, 3H), 6.99 – 6.93 (m, 1H), 6.81 – 6.75 (m, 1H), 6.65 – 6.60 (m, 2H), 5.44 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ = 164.96, 164.83, 164.38, 164.25, 162.46, 162.36, 161.89, 161.76, 151.29, 142.97, 139.92, 135.91, 132.74, 124.15, 123.50, 120.61, 112.43, 112.16, 110.21, 109.12, 108.85, 105.65, 104.08, 103.80, 103.55, 47.69. HRMS (ESI) Calculated for $\text{C}_{20}\text{H}_{12}\text{F}_4\text{N}_2$ $[\text{M}+\text{H}]^+$ 357.1015, found 357.1016.

1-(3,4-difluorobenzyl)-2-(3,4-difluorophenyl)-1H-benzo[d]imidazole (7u).

Following the general procedure, white solid; ^1H NMR (400 MHz, CDCl_3): δ = 7.90 (d, J = 8.1 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.42 – 7.29 (m, 4H), 7.27 – 7.23 (m, 2H), 6.96 – 6.91 (m, 1H), 6.84 – 6.80 (m, 1H), 5.45 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ = 152.98, 152.86, 152.16, 152.03, 151.75, 151.64, 151.33, 151.21, 150.46, 150.34, 149.66, 149.53, 149.26, 149.13, 148.85, 142.64, 135.66, 132.89, 132.80, 126.62, 126.51, 125.60, 125.49, 123.93, 123.45, 121.94, 121.84, 120.25, 119.28, 119.09, 118.76, 118.57, 118.34, 118.16, , 117.96, 117.22, 117.04, 115.81, 115.63, 115.24, 115.08, 110.25, 47.40. HRMS (ESI) Calculated for $\text{C}_{20}\text{H}_{12}\text{F}_4\text{N}_2$ $[\text{M}+\text{H}]^+$ 357.1015, found 357.1015.

1-(4-ethylbenzyl)-2-(4-ethylphenyl)-1H-benzo[d]imidazole (7v). Following the general procedure, light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ = 7.93 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.25 – 7.18 (m, 4H), 7.05 (d, J = 8.1 Hz, 2H), 5.45 (s, 2H), 2.76 – 2.64 (m, 4H), 1.32 – 1.23 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ = 154.35, 146.27, 143.75, 143.30, 136.19, 133.75, 129.29, 128.50, 128.28, 127.55, 126.00, 122.87, 122.55, 119.88, 110.59, 48.21, 28.77, 28.43, 15.47. HRMS (ESI) Calculated for $\text{C}_{24}\text{H}_{24}\text{N}_2$ $[\text{M}+\text{H}]^+$ 341.2018, found 341.2021.

1-(4-(tert-butyl)benzyl)-2-(4-(tert-butyl)phenyl)-1H-benzo[d]imidazole (7w).^[19]

Following the general procedure, white solid; ^1H NMR (400 MHz, CDCl_3) δ = 7.91 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 8.4, 2H), 7.50 (d, J = 8.8, 2H), 7.37 – 7.31 (m, 3H), 7.25 – 7.20 (m, 2H), 7.07 (d, J = 8.4 Hz, 2H), 5.45 (s, 2H), 1.35 (d, J = 16.0 Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ = 154.34, 153.11, 150.70, 143.34, 136.19, 133.51, 129.06, 127.22, 125.97, 125.74, 122.79, 122.56, 119.84, 110.60, 48.16, 34.89, 34.54, 31.39, 31.35.

1-(4-ethylbenzyl)-2-(4-ethylphenyl)-5-methyl-1H-benzo[d]imidazole (7x).

Following the general procedure, light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ =

7.81 – 7.65 (m, 3H), 7.31 – 7.28 (m, 2H), 7.21 – 7.17 (m, 3H), 7.11 – 7.04 (m, 3H), 5.41 (s, 2H), 2.76 – 2.65 (m, 4H), 2.48 (d, $J = 27.5$ Hz, 3H), 1.31 – 1.24 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) $\delta = 154.27, 153.95, 146.11$ (d, $J = 6.5$ Hz), 143.85 – 143.46 (m), 141.41, 136.48, 134.30, 133.92 (d, $J = 5.9$ Hz), 132.85, 132.17, 129.24 (d, $J = 5.2$ Hz), 128.51 (d, $J = 3.5$ Hz), 128.23 (d, $J = 1.7$ Hz), 127.65, 125.96 (d, $J = 7.3$ Hz), 124.23 (d, $J = 12.3$ Hz), 119.68, 119.41, 110.37, 110.11, 48.15 (d, $J = 13.4$ Hz), 28.79, 28.52, 21.88, 21.64, 15.41 (d, $J = 10.1$ Hz). HRMS (ESI) Calculated for $\text{C}_{25}\text{H}_{26}\text{N}_2$ $[\text{M}+\text{H}]^+$ 355.2174, found 355.2176.

III. References:

- [1] (a) F.-X. Yan, M. Zhang, X.-T. Wang, F. Xie, M.-M. Chen, H. Jiang, *Tetrahedron* **2014**, *70*, 1193;
(b) H. Kunkely, V. Pawlowski and A. Vogler, *Inorg. Chem. Commun.* 2008, **11**, 1003.
- [2] Martinez, R.; *Org. Biomol. Chem.* **2009**, *7*(10), 2176-2181.
- [3] Zhang, M.; *Chem. Commun.* **2011**, *47*, 6605-6607.
- [4] Tajbakhsh, M.; *Synthesis* **2011**, *3*, 490-496.
- [5] Cho, B. T.; *Tetrahedron* **2005**, *61*(24), 5725-5734.
- [6] Sousa, Sara C. A.; *Adv. Synth. Catal.* **2010**, *352*(13), 2218-2226.
- [7] Osamu, K.; *Org. Biomol. Chem.* **2010**, *8*(4), 896-900.
- [8] Zhou, Y. B.; *J. Chem. Res.* **2004**, *2*, 118-119.
- [9] Gopalakrishnan, A.; *Org. Biomol. Chem.* **2011**, *9*(7), 2518-2529.
- [10] Paul, C.; *Org. Lett.* **2010**, *12*(16), 3670-3673.
- [11] Bodo, S.; *J. Org. Chem.* **2004**, *69*(11), 3943-3949.
- [12] Guru, M.M.; *J. Org. Chem.* **2011**, *76*(13), 5295-5308.
- [13] Jayabharathi, J.; *Spectrochim. Acta. A* **2012**, *95*, 143-147.
- [14] Krishnamurthy, G. N.; *Journal. Serb. Chem. Soc.* **2009**, *74*(10), 1085-1096.
- [15] Geiger, D. K.; *Acta Crystallogr. E* **2012**, *68*(2), 420.
- [16] Niknam, K.; *Syn. Commun.* **2008**, *38*(17), 2919-2928.
- [17] Yadav, J. S.; *Can. J. Chem.* **2008**, *86*(2), 124-128.
- [18] Azarifar, D.; *Heterocycles* **2010**, *81*(12), 2855-2863.
- [19] Bandyopadhyay, P.; *J. Mole. Catal. A: Chem.* **2011**, *341*, 77-82.