Supporting Information

Iron Phthalocyanine as an Efficient and Versatile Catalyst for *N*-alkylation of Heterocyclic Amines with Alcohols: One-pot Synthesis of 2-Substituted Benzimidazoles, Benzothiazoles and Benzoxazoles

Manju Bala,[a,b] Praveen Kumar Verma,[a,b] Upendra Sharma,[b,c] Neeraj Kumar[b] and Bikram Singh*[a,b]

[a]*Academy of Scientific & Innovative Research; CSIR-Institute of Himalayan Bioresource Technology, Palampur, Himachal Pradesh-176 061, INDIA*

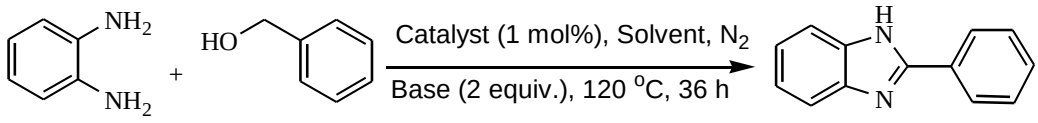
[b]*CSIR-Institute of Himalayan Bioresource Technology, Palampur, Himachal Pradesh 176 061, India*

[c]*Present address: Indian Institute of Technology Bombay, Powai 400 076, India.*

E-mail: bikram_npp@rediffmail.com

Table of Contents:

Table S1 Optimization of reaction conditions for the synthesis of 2-arylbenzazoles.[a]



Entry	Catalyst	Solvent	Base	Yield (%)[b]
1	-	Toluene	NaO*t*Bu	7
2	Iron metal	Toluene	NaO*t*Bu	77
3	$Fe(OAc)_2$	Toluene	NaO*t*Bu	65
4	$FeSO_4$	Toluene	NaO*t*Bu	50
5	$FeCl_3$	Toluene	NaO*t*Bu	76
6	**Fe(II)Pc**	**Toluene**	**NaO*t*Bu**	**92**
7	$K_3Fe(CN)_6$	Toluene	NaO*t*Bu	51
8	Fe(II)Pc	DMF	NaO*t*Bu	71
9	Fe(II)Pc	H_2O	NaO*t*Bu	No Reaction
10	Fe(II)Pc	EtOH	NaO*t*Bu	20
11	Fe(II)Pc	1,4-dioxane	NaO*t*Bu	5
12	Fe(II)Pc	PEG-400	NaO*t*Bu	7
13	Fe(II)Pc	Toluene	NaOH	3
14	Fe(II)Pc	Toluene	K_2CO_3	No Reaction
15	Fe(II)Pc	Toluene	Cs_2CO_3	72
16	Fe(II)Pc	Toluene	K_3PO_4	32
17	Fe(II)Pc	Toluene	DBACO	1
18	-	Toluene	NaO*t*Bu	83[c]

[a] Reaction conditions: 2-aminobenzothiazole (1 mmol), benzyl alcohol (1 mmol), catalyst(1 mol%), base (2 equiv.), solvent (5 mL), 120°C, 36 h. [b] GC-MS yield. [c] reaction with benzaldehyde (1 mmol).

General Information:

Metal salts used were purchased from Merck, Germany. Iron phthalocyanines, amines, alcohols, and benzothiazoles were purchased from Sigma-Aldrich USA. Silica gel (60-120 mesh) used for column chromatography was purchased from Sisco Research Laboratories Pvt. Ltd. India and all other chemicals were purchased from Spectrochem, India, Merck, Germany, and Sigma-Aldrich, USA and were used without further purification. NMR spectra were recorded on a Bruker Avance-300 spectrometer. Mass spectra were recorded on QTOF-Micro of Waters Micromass.

The GC-MS analysis was carried out on a Shimadzu (QP 2010) series Gas Chromatogram-Mass Spectrometer (Tokyo, Japan), AOC-20i auto-sampler coupled, and a DB-5MS capillary column, (30 m x 0.25 mm *i.d.*, 0.25µm). The initial temperature of column was 70 °C held for 4 min. and was programmed to 230 °C at 4 °C/min., then held for 15 min. at 230 °C; the sample injection volume was 2 µL in GC grade dichloromethane. Helium was used as carrier gas at a flow rate of 1.1 mL min^{-1} on split mode (1: 50). Melting points were determined on a Barnstead Electrothermal 9100.

General experimental procedure for *N*-alkylation of aminobenzothiazoles:

To a stirred suspension of FePc (1 mol%) and NaO*t*Bu (2 mmol) in toluene (5 mL) were added alcohols (1.0 mmol), aminobenzothiazoles (1.0 mmol) at room temperature and then temperature was raised to 100 ^{o}C for 12 h. On completion of the reaction (as monitored by TLC), reaction mixture was filtered and passed through anhydrous Na_2SO_4 and dried under vacuum. The crude product was analysed by GC-MS or purified by column chromatography over silica-gel (60-120) with appropriate mixture of *n*-hexane and ethyl acetate. The GC-MS yields of products were calculated on the basis of aminobenzothiazole reactants.

General experimental procedure for *N*-alkylation of aminopyridines and aminopyrimidines:

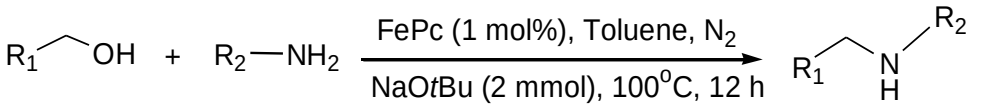
To a stirred suspension of FePc (1 mol%) and NaO*t*Bu (2 mmol) in toluene (5 mL) were added alcohols (1.0 mmol), pyridines or pyrimidines (1.0 mmol) at room temperature and then temperature was raised to 100 ^{o}C for 12 h. On completion of the reaction (as monitored by TLC), reaction mixture was filtered and passed through anhydrous Na_2SO_4 and dried under vacuum. The crude product was analysed by GC-MS or purified by column chromatography over silica-

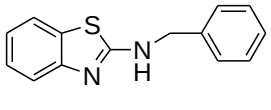
gel (60-120) with appropriate mixture of *n*-hexane and ethyl acetate. The GC-MS yields of products were calculated on the basis of amine reactants.

General experimental procedure for the synthesis of *ortho*-substituted benzazoles:

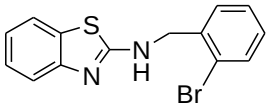
To a stirred suspension of FePc (1 mol%) and NaO*t*Bu (2 mmol) in toluene (5 mL) were added alcohols (1.5 mmol), *o*-substituted anilines (1.0 mmol) at room temperature and then temperature was raised to 120 ^{o}C for 36 h. On completion of the reaction (as monitored by TLC), reaction mixture was filtered and passed through anhydrous Na_2SO_4 and dried under vacuum. The crude product was analysed by GC-MS or purified by column chromatography over silica-gel (60-120) with appropriate mixture of *n*-hexane and ethyl acetate. The GC-MS yields of products were calculated on the basis of amine reactants.

Table S2 *N*-alkylation of aminobenzothiazoles with alcohols.[a,b,c]

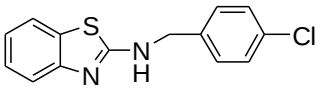




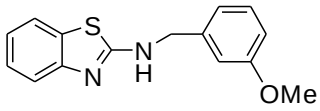
4a
Conv. = >99%
Yield = 92% (87%)



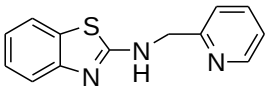
4b
Conv. = 81%
Yield = 79% (74%)



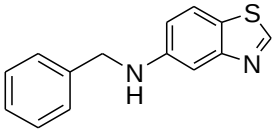
4c
Conv. = 61%
Yield = 55% (52%)



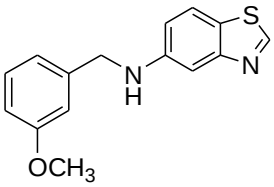
4d
Conv. = 90%
Yield = 85% (81%)



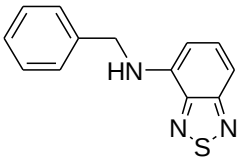
4e
Conv. = 88%
Yield = 88% (80%)



4f
Conv. = 88%
Yield = 67% (63%)



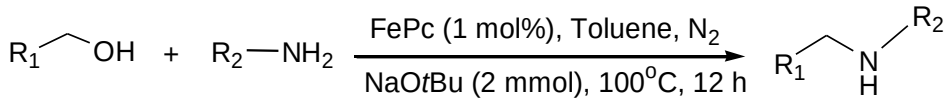
4g
Conv. = 91%
Yield = 86% (83%)

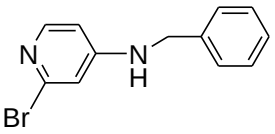


4h
Conv. = 79%
Yield = 75% (72%)

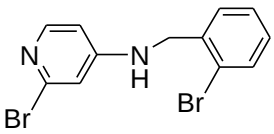
[a] Reaction conditions: amine (1 mmol), alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 mmol), toluene (5 mL) at 100 °C for 12 h. [b] Isolated yields are given in parenthesis. [c] Conv. on the basis of amine reactant.

Table S3 *N*-alkylation of aminopyridines and aminopyrimidines with alcohols.[a,b,d]

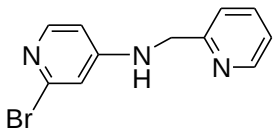




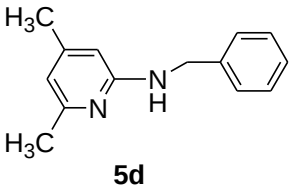
5a
Conv. = 75%
Yield = 72%



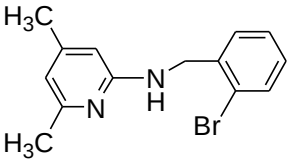
5b
Conv. = 59%
Yield = 52%



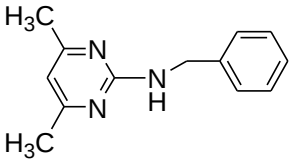
5c
Conv. = 76%
Yield = 71% (68%)



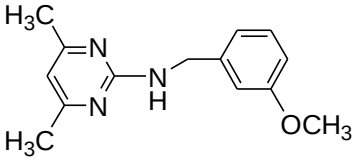
5d
Conv. = 72%
Yield = 57% (52%)



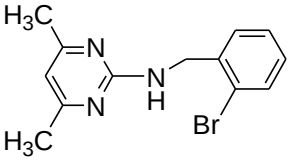
5e
Conv. = 88%
Yield = 80% (77%)



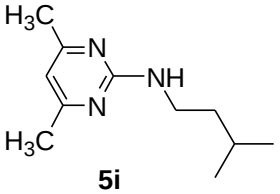
5f
Conv. = 95%
Yield = 95% (90%)



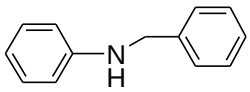
5g
Conv. = 98%
Yield = 92% (90%)



5h
Conv. = 80%
Yield = 80% (76%)



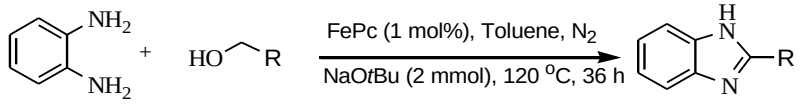
5i
Conv. = 26%
Yield = 24% (20%)

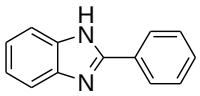


5j
Conv. = 90%
Yield = (86%)[c]

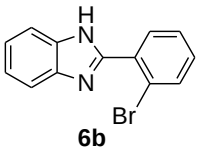
[a] Reaction conditions: amine (1 mmol), alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 mmol), toluene (5 mL) at 100 °C for 12 h. [b] Isolated yields are given in parenthesis. [c] Reaction temperature 140 °C. [d] Conv. on the basis of amine reactant.

Table S4 *N*-alkylation of *o*-phenylenediamine with alcohols.[a,b,c]

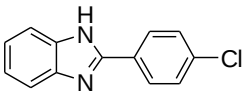




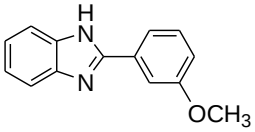
6a
Conv. = >99%
Yield = 89% (84%)



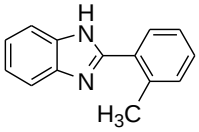
6b
Conv. = 89%
Yield = 79% (75%)



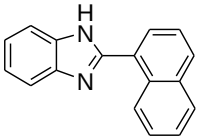
6c
Conv. = 95%
Yield = (81%)



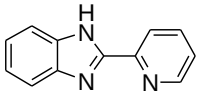
6d
Conv. = 75%
Yield = 70%



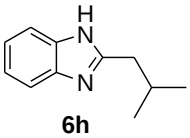
6e
Conv. = > 99%
Yield = (94%)



6f
Conv. = > 99%
Yield = 92% (89%)



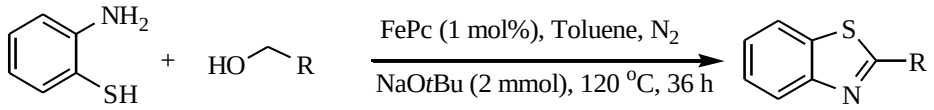
6g
Conv. = 92%
Yield = 69% (66%)

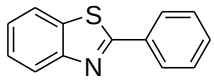


6h
Con. = 45%
Yield = 41%

[a] Reaction conditions: *o*-phenylenediamine (1 mmol), alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 mmol), toluene (5 mL) at 120 °C for 36 h. [b] Isolated yields are given in parenthesis. [c] Conv. on the basis of amine reactant.

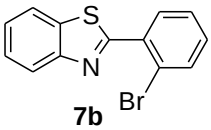
Table S5 *N*-alkylation of 2-aminothiophenol with alcohols.[a,b,c]





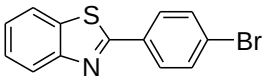
7a

Conv. = >99%
Yield = 94% (90%)



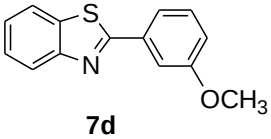
7b

Conv. = 96%
Yield = 96% (90%)



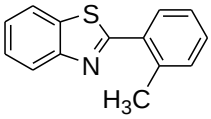
7c

Conv. = >99%
Yield = 99% (96%)



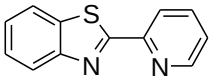
7d

Conv. = >99%
Yield = 99% (92%)



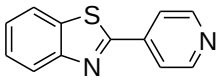
7e

Conv. = 93%
Yield = 73% (70%)



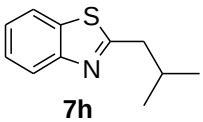
7f

Conv. = >99%
Yield = 99%



7g

Conv. = >99%
Yield = 99%

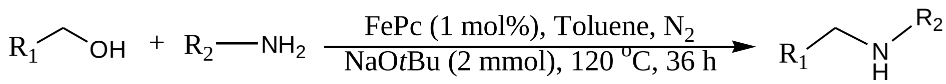


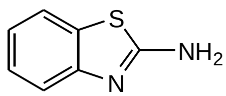
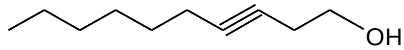
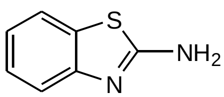
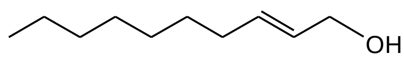
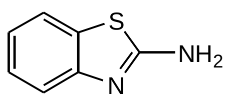
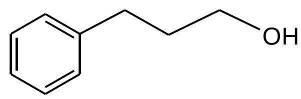
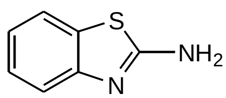
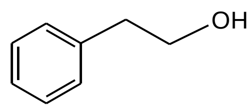
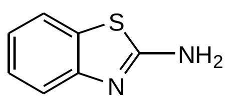
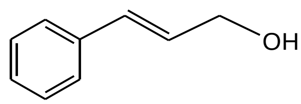
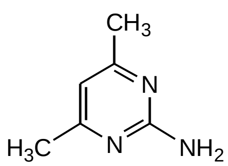
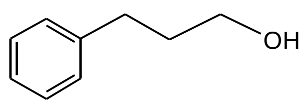
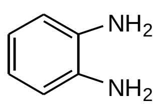
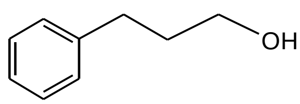
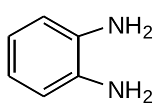
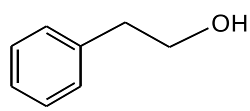
7h

Conv. = 66%
Yield = 44%

[a] Reaction conditions: 2-aminothiophenol (1 mmol), alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 mmol), toluene (5 mL) at 120 °C for 36 h. [b] Isolated yields are given in parenthesis. [c] Conv. on the basis of amine reactant.

Table S6. Reaction of amines with aliphatic alcohols[a].

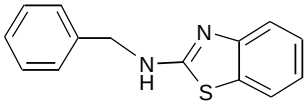


Amine	Alcohol	Yield (%)[b]
		NR[c]
		NR[c]
		NR[c]
		NR[c]
		NR[c]
		NR[c]
		NR[c]
		NR[c]

[a] Reaction conditions: amine (1 mmol), alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 mmol), toluene (5 mL) at 120 °C for 36 h.
[b] Yields on the basis of amine reactant. [c] Reactants were remains as such.

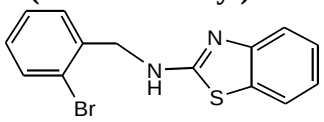
Characterization data of compounds:

***N*-Benzylbenzo[d]thiazol-2-amine (Table 4, entry 4a)[1,7]**



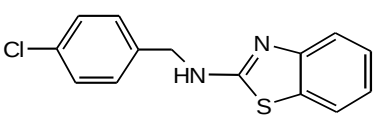
Following the general experimental procedure with 2-aminobenzothiazole (1 mmol), benzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (87 %) as off white crystalline powder; GC-MS yield = 92%; mp 162-164 ^{o}C (Lit[1] mp = 164-165 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.66 (s, 2H), 7.08-7.13 (m, 1H), 7.28-7.31 (m, 1H), 7.33-7.43 (m, 5H), 7.52 (d, 1H, J = 8.0 Hz), 7.59 (d, 1H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 49.8, 119.3, 121.2, 122.0, 126.3, 128.0, 128.2, 129.2, 130.8, 137.8, 152.6, 167.8; HRESIMS calcd for $C_{14}H_{13}N_2S$ $[M+H]^+$ 241.0799, found 241.0758. GC-MS (EI): *m/z* 240 $[M]^+$, 136, 106, 91, 65.

***N*-(2-Bromobenzyl)benzo[d]thiazol-2-amine (Table 4, entry 4b)**



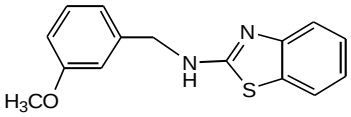
Following the general experimental procedure with 2-aminobenzothiazole (1 mmol), 2-bromobenzylalcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (74 %) as yellow crystalline powder; GC-MS yield = 79%; mp 128-130 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.71 (s, 2H), 7.07-7.12 (m, 1H), 7.14-7.20 (m, 1H), 7.26-7.31 (m, 2H), 7.42-7.46 (m, 1H), 7.52-7.54 (m, 1H), 7.57-7.63 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 49.9, 119.1, 121.5, 122.8, 123.9, 126.4, 128.1, 129.2, 129.7, 130.7, 133.3, 137.0, 152.5, 168.2; HRESIMS calcd for $C_{14}H_{12}BrN_2S$ $[M+H]^+$ 318.9905, found 318.9915.

_N_-(4-Chlorobenzyl)benzo[d]thiazol-2-amine (Table 4, entry 4c)[1]



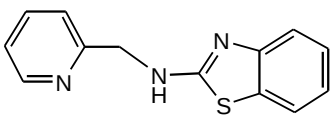
Following the general experimental procedure with 2-aminobenzothiazole (1 mmol), 4-chlorobenzylalcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (52%) as off white amorphous powder, GC-MS yield = 55%; mp 184-186 ^{o}C (Lit[1] mp = 188-189 °C); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.62 (s, 2H), 7.05-7.07 (m, 1H), 7.23-7.27 (m, 1H), 7.34-7.35 (m, 2H), 7.37-7.39 (m, 2H), 7.42-7.43 (m, 1H), 7.57-7.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 48.3, 119.2, 121.9, 122.9, 126.9, 129.7, 130.2, 131.4, 134.2, 138.6, 153.2, 169.2; HRESIMS calcd for $C_{14}H_{12}ClN_2S$ $[M+H]^+$ 275.0410, found 275.0438. GC-MS (EI): *m/z* 274 $[M]^+$, 140, 127, 125, 99, 89, 63.

_N_-(3-Methoxybenzyl)benzo[d]thiazol-2-amine (Table 4, entry 4d)



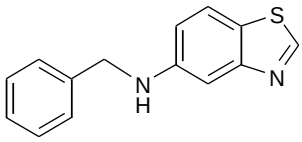
Following the general experimental procedure with 2-aminobenzothiazole (1 mmol), 3-methoxybenzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification afforded the desired product (81%), GC-MS yield = 85%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.79 (s, 2H), 4.61 (s, 2H), 6.85-6.86 (m, 1H), 6.94 (s, 1H), 6.98 (d, 1H, J = 7.8 Hz), 7.09 (t, 1H, J = 7.8 Hz), 7.26-7.31 (m, 2H), 7.53 (d, 1H, J = 7.8 Hz), 7.58 (d, 1H, J = 7.8 Hz); HRESIMS calcd for $C_{15}H_{15}N_2OS$ $[M+H]^+$ 271.0905, found 271.0922. GC-MS (EI): *m/z* 270 $[M]^+$, 255, 136, 121, 105, 91, 77, 65, 51.

_N_-(Pyridin-2-ylmethyl)benzo[d]thiazol-2-amine (Table 4, entry 4e)[1]



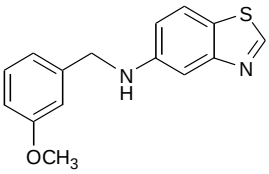
Following the general experimental procedure with 2-aminobenzothiazole (1 mmol), 2-pyridylmethanol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (80 %) as brownish powder; GC-MS yield = 88%; mp 158-160 ^{o}C (Lit[1] mp = 156-158 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.82 (s, 2H), 7.07-7.33 (m, 3H), 7.37 (d, 1H, J = 7.8 Hz), 7.57-7.59 (m, 2H), 7.68 (m, 1H), 8.57 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 49.6, 119.4, 121.2, 122.0, 122.2, 122.9, 126.2, 131.1, 137.2, 149.4, 152.8, 156.3, 167.1; HRESIMS calcd for $C_{13}H_{12}N_3S$ $[M+H]^+$ 242.0752, found 242.0736; GC-MS (EI): *m/z* 241 $[M]^+$, 213, 163, 136, 120, 107, 93, 79, 65, 51.

_N_-Benzylbenzothiazol-6-amine (Table 4, entry 4f)



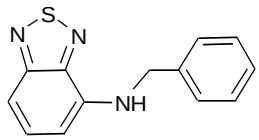
Following the general experimental procedure with 6-aminobenzothiazole (1 mmol), benzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (63 %) as brownish viscous liquid; GC-MS yield = 67%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.42 (s, 2H), 6.85-6.89 (m, 1H), 7.07 (s, 1H), 7.28-7.30 (m, 1H), 7.32-7.43 (m, 4H), 7.91 (m, 1H), 8.68 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 48.9, 102.5, 115.1, 124.2, 127.8, 129.1, 136.2, 139.1, 146.4, 146.9, 149.6; HRESIMS calcd for $C_{14}H_{13}N_2S$ $[M+H]^+$ 241.0799, found 241.0772; GC-MS (EI): *m/z* 240 $[M]^+$, 163, 134, 91, 63.

***N*-(3-Methoxybenzyl)benzothiazol-6-amine (Table 4, entry 4g)**



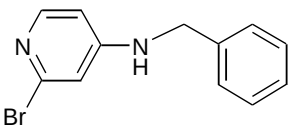
Following the general experimental procedure with 6-aminobenzothiazole (1 mmol), 3-methoxybenzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification afforded the desired product (83%), GC-MS yield = 86%; ^{1}H NMR (CD_3COCD_3, 600 MHz) δ 3.75 (s, 3H), 4.42 (s, 2H), 5.89 (brs, 1H), 6.79-6.81 (m, 1H), 6.97-7.01 (m, 1H), 7.15 (s, 1H), 7.22-7.23 (m, 1H), 7.75-7.77 (m, 1H), 8.77 (s, 1H); ^{13}C NMR (CD_3COCD_3, 150 MHz) δ 48.7, 55.9, 103.1, 113.5, 114.3, 116.0, 120.8, 124.7, 130.8, 137.2, 142.9, 147.2, 148.8, 149.9, 161.5; GC-MS (EI): *m/z* 270 $[M]^+$, 163, 134, 121, 91, 77, 63.

***N*-benzylbenzothiadiazol-4-amine (Table 4, entry 4h)**



Following the general experimental procedure with 4-aminobenzothiadiazole (1 mmol), benzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification (72%) afforded the desired product, GC-MS yield = 75%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.54 (s, 2H), 5.66 (brs, 1H), 6.35-6.36 (m, 1H), 7.26-7.27 (m, 1H), 7.30-7.33 (m, 1H), 7.35-7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 47.7, 101.9, 108.6, 127.4, 127.5, 128.8, 131.7, 138.1, 140.0, 147.8, 155.7; HRESIMS calcd for $C_{13}H_{12}N_3S$ $[M+H]^+$ 242.0752, found 242.0733; GC-MS (EI): *m/z* 241 $[M]^+$, 162, 91, 77, 65, 51.

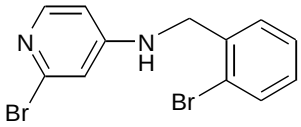
***N*-Benzyl-4amino-2-bromopyridine (Table 5, entry 5a)**



Following the general experimental procedure with 4-amino-2-bromo-pyridine (1 mmol), benzyl alcohol (1 mmol), Fe(II)Pc (1 mol%),

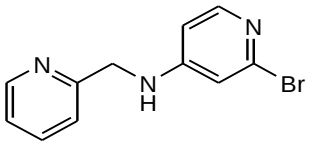
NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate afforded the desired product, GC-MS yield = 72%; GC-MS (EI): *m/z* 262 $[M]^+$, 91, 77, 65, 51.

_N_-(2-Bromobenzyl)-4-amino-2-bromopyridine (Table 5, entry 5b)



Following the general experimental procedure with 4-amino-2-bromopyridine (1 mmol), 2-bromobenzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate afforded the desired product, GC-MS yield = 52%; GC-MS (EI): *m/z* 340 $[M]^+$, 259, 179, 153, 129, 102, 89, 77, 63, 51.

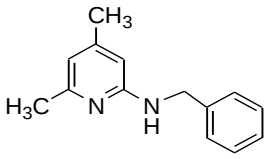
_N_-(Pyridine-2-methyl)-4-amino-2-bromopyridine (Table 5, entry 5c)



Following the general experimental procedure with 4-amino-2-bromopyridine (1 mmol), 2-pyridylmethanol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (68%) as brownish viscous liquid; GC-MS yield = 71%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.45 (s, 2H), 5.88 (brs, 1H), 6.49 (d, 1H, J = 5.7 Hz), 6.71 (s, 1H), 7.23-7.29 (m, 2H), 7.64-7.73 (m, 1H), 7.93 (d, 1H, J = 5.7 Hz), 8.60 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 47.5, 108.3, 110.6, 122.1, 123.1, 137.3, 143.3, 149.5, 149.9, 155.0, 155.9; HRESIMS calcd for $C_{11}H_{11}BrN_3$ $[M+H]^+$ 264.0136, found 264.0124; GC-MS (EI): *m/z* 263 $[M]^+$, 247, 185, 155, 131, 107, 92, 79, 65, 51.

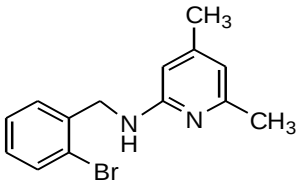
_N_-Benzyl-2-amino-4,6-dimethylpyridine (Table 5, entry 5d)

Following the general experimental procedure with 2-amino-4,6-dimethylpyridine (1 mmol), benzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12



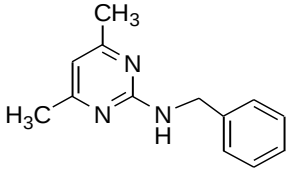
h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (52%) as light yellow crystalline powder, GC-MS yield = 57%; mp 58-61 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.19 (s, 3H), 2.36 (s, 3H), 4.47 (s, 2H), 4.99 (brs, 1H), 6.03 (s, 1H), 6.35 (s, 1H), 7.25-7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 24.4, 47.0, 103.6, 114.5, 127.5, 127.7, 128.9, 139.6, 149.4, 156.9, 158.9; HRESIMS calcd for $C_{14}H_{17}N_2$ $[M+H]^+$ 213.1392, found 213.1356; GC-MS (EI): *m/z* 212 $[M]^+$, 135, 106, 91, 79, 65.

_N_-(2-Bromobenzyl)-2-amino-4,6-dimethylpyridine (Table 5, entry 5e)



Following the general experimental procedure with 2-amino-4,6-dimethylpyridine (1 mmol), 2-bromobenzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification (77%) afforded the desired product, GC-MS yield = 80%. ^{1}H NMR (CD_3COCD_3, 600 MHz) δ 2.04 (s, 3H), 2.22 (s, 3H), 4.61 (s, 2H), 6.07 (brs, 1H), 6.18 (s, 1H), 6.27 (s, 1H), 7.16 (t, 1H, J = 7.8 Hz), 7.29 (t, 1H, J = 7.8 Hz), 7.46 (d, 1H, J = 7.2 Hz), 7.57 (d, 1H, J = 8.4 Hz); ^{13}C NMR (CD_3COCD_3, 150 MHz) δ 21.4, 24.8, 46.6, 106.1, 114.5, 124.2, 128.8, 129.8, 130.7, 133.8, 141.1, 149.3, 157.4, 159.9.

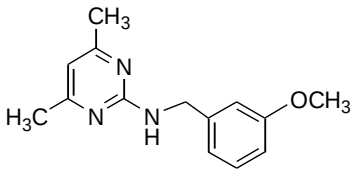
_N_-Benzyl-2-amino-4,6-dimethylpyrimidine (Table 5, entry 5f)



Following the general experimental procedure with 2-amino-4,6-dimethylpyrimidine (1 mmol), benzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification,

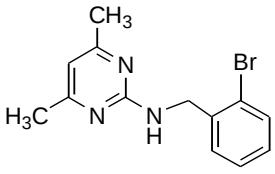
afforded the desired product (90%) as brownish liquid, GC-MS yield = 95%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.3 (s, 6H), 4.67 (s, 2H), 5.39 (brs, 1H), 6.35 (s, 1H), 7.26-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.3, 45.8, 110.4, 127.4, 127.9, 128.8, 159.9, 162.6, 167.9; HRESIMS calcd for $C_{13}H_{16}N_3$ $[M+H]^+$ 214.1344, found 214.1318; GC-MS (EI): *m/z* 213 $[M]^+$, 136, 106, 91, 79, 65, 51.

_N_-(3-Methoxybenzyl)-2-amino-4,6-dimethylpyrimidine (Table 5, entry 5g)



Following the general experimental procedure with 2-amino-4,6-dimethylpyrimidine (1 mmol), 3-methoxybenzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification (90%) afforded the desired product, GC-MS yield = 92%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.28 (s, 6H), 3.78 (s, 3H), 4.62 (s, 2H), 5.43 (brs, 1H), 6.33 (s, 1H), 6.78-7.79 (m, 1H), 6.91-6.94 (m, 2H), 7.22-7.24 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 22.6, 45.4, 55.2, 110.0, 112.6, 113.0, 119.8, 129.5, 141.2, 159.8, 162.2, 167.5; HRESIMS calcd for $C_{14}H_{18}N_3O$ $[M+H]^+$ 244.3123, found 244.3108; GC-MS (EI): *m/z* 243 $[M]^+$, 228, 212, 136, 121, 108, 91, 77, 65.

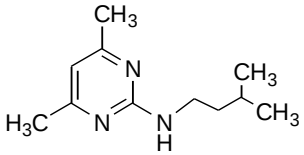
_N_-(2-Bromobenzyl)-2-amino-4,6-dimethylpyrimidine (Table 5, entry 5h)



Following the general experimental procedure with 2-amino-4,6-dimethylpyrimidine (1 mmol), 2-bromobenzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (76%) as light brown powder, GC-MS yield = 80%; mp 134-137 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.29 (s, 6H), 4.74 (s, 2H), 5.55 (brs, 1H), 6.34 (s, 1H), 7.12-

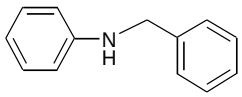
7.28 (m, 2H), 7.46-7.57 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.3, 45.8, 110.5, 124.1, 124.8, 127.7, 129.0, 130.2, 133,0, 139.0, 162.4, 167.9; HRESIMS calcd for $C_{13}H_{15}N_3Br$ $[M+H]^+$ 292.1807, found 292.1807; GC-MS (EI): *m/z* 291 $[M]^+$, 212, 184, 107, 90, 65.

_N_-(3-Methylbutane)-2-amino-4,6-dimethylpyrimidine (Table 5, entry 5i)



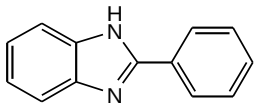
Following the general experimental procedure with 2-amino-4,6-dimethylpyrimidine (1 mmol), 3-methylbutanol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate afforded the desired product (20%), GC-MS yield = 24%; ^{1}H NMR (CD_3OD, 600 MHz) δ 0.92-0.95 (m, 6H), 1.58-1.59 (m, 1H), 2.26 (s, 6H), 3.31-3.40 (m, 2H), 4.88 (s, 2H), 6.38 (s, 1H); ^{13}C NMR (CD_3OD, 150 MHz) δ 22.8, 23.5, 26.8, 30.5, 39.6, 40.3, 109.9, 163.3, 168.9; HRESIMS calcd for $C_{11}H_{20}N_3$ $[M+H]^+$ 194.1657, found 194.1631; GC-MS (EI): *m/z* 193 $[M]^+$, 150, 136, 123, 108, 96, 67.

_N_-Benzylaniline (Table 5, entry 5j)



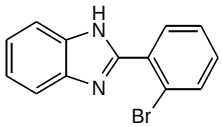
Following the general experimental procedure with aniline (1 mmol), 2-benzyl alcohol (1 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 140 °C for 12 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (86%) as colorless oil, GC-MS yield = 98%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.40 (s, 2H), 6.71–6.84 (m, 3H), 7.23–7.45 (m, 7H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 48.8, 113.3, 118.1, 127.7, 127.9, 129.1, 129.7, 139.9, 148.7. MS (EI): *m/z* 183 $[M]^+$, 106, 91, 77, 65, 51.

2-Phenylbenzimidazole (Table 6, entry 6a, CAS No.: 716-79-0)[4,5]



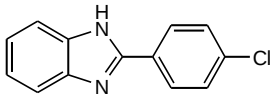
Following the general experimental procedure with *o*-phenylenediamine (1 mmol), benzyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (84%) as colorless solid, GC-MS yield = 89%; mp 294-297 ^{o}C (Lit[4] mp = 294-295 °C; Lit[5] mp = 288-289 °C); ^{1}H NMR (CD_3OD, 600 MHz) δ 7.24-7.25 (m, 2H), 7.46-7.53 (m, 3H), 7.59-7.60 (m, 2H), 8.07-8.08 (m, 2H); ^{13}C NMR (CD_3OD, 150 MHz) δ 114.5, 122.6, 126.4, 128.7, 129.6, 130.0, 151.9; HRESIMS calcd for $C_{13}H_{11}N_2$ $[M+H]^+$ 195.0922, found 195.0907; GC-MS (EI): *m/z* 194 $[M]^+$, 166, 90, 77, 63.

2-(2-Bromophenyl)-benzo[d]imidazole (Table 6, entry 6b, CAS No.: 13275-42-8)



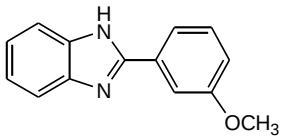
Following the general experimental procedure with *o*-phenylenediamine (1 mmol), 2-bromobenzyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (75%) as colorless solid, GC-MS yield = 79%; ^{1}H NMR (CD_3OD, 600 MHz) δ 7.30-7.31 (m, 2H), 7.43-7.46 (m, 1H), 7.51-7.54 (m, 1H), 7.64 (s, 2H), 7.72 (d, 1H, *J* = 7.8 Hz), 7.79 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (CD_3OD, 150 MHz) δ 123.5, 124.3, 129.1, 132.9, 133.5, 133.8, 134.9, 152.6; HRESIMS calcd for $C_{13}H_{10}BrN_2$ $[M+H]^+$ 273.0027, found 273.0066; GC-MS (EI): *m/z* 272 $[M]^+$, 193, 166, 139, 102, 90, 83, 63, 51.

2-(4-Chlorophenyl)-benzo[d]imidazole (Table 6, entry 6c, CAS No.: 1019-85-8)[4]



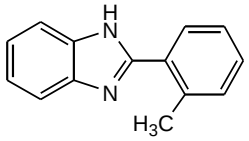
Following the general experimental procedure with *o*-phenylenediamine (1 mmol), 4-chlorobenzyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (81%) as white solid, mp 289-290 ^{o}C (Lit[4] mp = 290-291 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.02-7.05 (m, 1H), 7.29-7.35 (m, 5H), 7.43-7.46 (m, 1H), 7.58-7.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 110.7, 120.5, 123.5, 123.9, 127.7, 128.6, 129.0, 129.6, 129.8, 130.8, 153.3.

2-(3-Methoxyphenyl)-benzo[d]imidazole (Table 6, entry 6d)



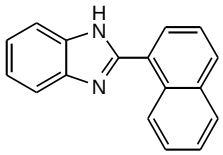
Following the general experimental procedure with *o*-phenylenediamine (1 mmol), 3-methoxybenzyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate afforded the desired product. GC-MS yield = 70%; GC-MS (EI): *m/z* 224 $[M]^+$, 195, 181, 112, 90, 77, 63.

2-(2-Methylphenyl)-benzimidazole (Table 6, entry 6e, CAS No.: 2963-64-6)[5]



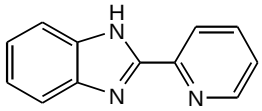
Following the general experimental procedure with *o*-phenylenediamine (1 mmol), 2-methylbenzyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (94%) as light yellow solid; mp 216-218 ^{o}C (Lit[5] mp = 218-219 °C); ^{1}H NMR (CD_3OD, 600 MHz) δ 2.49 (s, 3H), 7.26-7.36 (m, 5H), 7.61 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) *δ* 115.8, 123.69, 127.02, 130.92, 131.52, 132.05, 138.48, 153.99; GC-MS (EI): *m/z* 208 $[M]^+$, 103, 91, 77, 63.

2-(1-Naphthyl)-benzo[d]imidazole (Table 6, entry 6f, CAS No.: 2562-81-4)



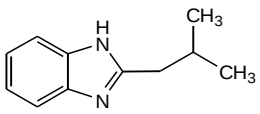
Following the general experimental procedure with *o*-phenylenediamine (1 mmol), naphthyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (89%) as colorless solid, GC-MS yield = 92%; ^{1}H NMR (CD_3OD, 600 MHz) δ 7.32-7.45 (m, 2H), 7.46-7.67 (m, 5H), 7.79-7.82 (m, 1H), 7.87-7.07 (m, 2H), 8.46 (s, 1H); ^{13}C NMR (CD_3OD, 150 MHz) *δ* 126.4, 126.9, 127.7, 128.4, 129.5, 129.7, 131.8, 132.7, 135.6, 153.5; HRESIMS calcd for $C_{17}H_{13}N_2$ $[M+H]^+$ 245.1079, found 245.1058.

2-(2-Pyridyl)-benzo[d]imidazole (Table 6, entry 6g, CAS No.: 1137-68-4)[4]



Following the general experimental procedure with *o*-phenylenediamine (1 mmol), 2-pyridylmethanol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (66%) as white solid, GC-MS yield = 69%; mp 215-217 ^{o}C (Lit[4] mp = 218-219 °C); ^{1}H NMR (CD_3OD, 600 MHz) δ 7.28-7.29 (m, 2H), 7.43-7.45 (m, 1H), 7.65 (s, 2H), 7.92-7.95 (m, 1H), 8.27-8.28 (m, 1H), 8.69-8.70 (m, 1H); ^{13}C NMR (CD_3OD, 150 MHz) *δ* 122.4, 124.2, 125.8, 138.4, 149.3, 150.7, 152.3; HRESIMS calcd for $C_{12}H_{10}N_3$ $[M+H]^+$ 196.0875, found 196.0891; GC-MS (EI): *m/z* 195 $[M]^+$, 167, 105, 90, 78, 63, 51.

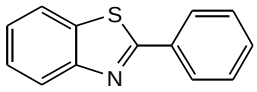
2-(3-Methylbutane)-benzo[d]imidazole (Table 6, entry 6h)



Following the general experimental procedure with *o*-phenylenediamine

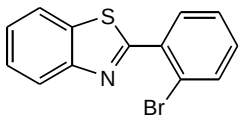
(1 mmol), 3-methylbutanol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate, afforded the desired product. GC-MS yield = 41%; GC-MS (EI): *m/z* 174 $[M]^+$, 159, 132, 104, 77, 63.

2-Phenylbenzo[d]thiazole (Table 7, entry 7a, CAS No.: 883-93-2)[2,4,6]



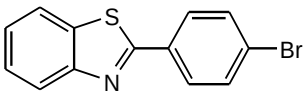
Following the general experimental procedure with 2-aminothiophenol (1 mmol), benzyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification, afforded the desired product (90%) as colorless solid, GC-MS yield = 94%; mp 97-99 ^{o}C (Lit[2] mp = 98-101 °C; Lit[4] mp = 112-114 °C); ^{1}H NMR (CD_3OD, 300 MHz) δ 6.45-6.56 (m, 6H), 6.83-6.88 (m, 3H); ^{13}C NMR (CD_3OD, 75 MHz) *δ* 113.8, 120.5, 123.3, 126.6, 138.5, 145.6; GC-MS (EI): *m/z* 211 $[M]^+$, 184, 108, 92, 82, 69, 58.

2-(2-Bromophenyl)benzo[d]thiazole (Table 7, entry 7b, CAS No.: 22901-00-4)



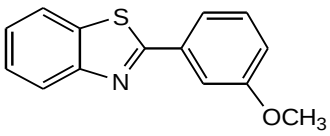
Following the general experimental procedure with 2-aminothiophenol (1 mmol), 2-bromobenzyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification (90%), afforded the desired product; GC-MS yield = 96%; ^{1}H NMR (CD_3COCD_3, 600 MHz) δ 7.24-7.26 (m, 2H), 7.44-7.47 (m, 1H), 7.52-7.54 (m, 2H), 7.66 (s, 2H), 7.78 (d, 1H, *J* = 7.8 Hz), 7.96 (d, 1H, *J* = 7.8 Hz); GC-MS (EI): *m/z* 289 $[M]^+$, 211, 179, 167, 151, 139, 105, 91, 79, 69, 50.

2-(4-Bromophenyl)benzo[d]thiazole (Table 7, entry 7c, 19654-19-4)[2]



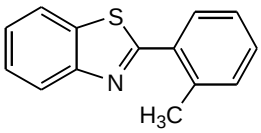
Following the general experimental procedure with 2-aminothiophenol (1 mmol), 4-bromobenzyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification (96%), afforded the desired product as colorless solid, GC-MS yield = 99%; mp 105-108 ^{o}C (Lit[2] mp = 105-107 °C); ^{1}H NMR (CD_3COCD_3, 600 MHz) δ 7.46-7.49 (m, 1H), 7.55-7.57 (m, 1H), 7.74-7.76 (m, 2H), 8.04-8.09 (m, 4H); ^{13}C NMR (CD_3COCD_3, 150 MHz) *δ* 123.0, 124.2, 125.9, 126.7, 127.6, 130.0, 133.3, 133.7, 136.1, 155.1, 167.2; HRESIMS calcd for $C_{13}H_9BrNS$ $[M+H]^+$ 289.9639, found 289.9614; GC-MS (EI): *m/z* 289 $[M]^+$, 211, 179, 167, 151, 139, 105, 91, 79, 69, 50.

2-(3-Methoxyphenyl)benzo[d]thiazole (Table 7, entry 7d)



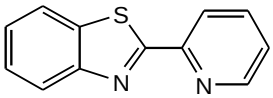
Following the general experimental procedure with 2-aminothiophenol (1 mmol), 3-methoxybenzyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification (92%), afforded the desired product as colorless solid, GC-MS yield = 99%; ^{1}H NMR (CD_3COCD_3, 600 MHz) δ 3.92 (s, 3H), 7.12-7.14 (m, 1H), 7.45-7.48 (m, 2H), 7.54-7.56 (m, 1H), 7.67-7.69 (m, 2H), 8.04-8.09 (m, 2H); ^{13}C NMR (CD_3COCD_3, 150 MHz) *δ* 56.2, 113.2, 118.3, 121.1, 123.2, 124.3, 126.7, 127.7, 131.5, 136.1, 136.2, 155.4, 161.6, 168.6; HRESIMS calcd for $C_{14}H_{12}$ NOS $[M+H]^+$ 242.0640, found 242.0619; GC-MS (EI): *m/z* 241 $[M]^+$, 211, 154, 120, 108, 82, 69, 63.

2-(*o*-Tolyl)benzo[d]thiazole (Table 7, entry 7e, CAS No.: 15903-58-9)[2]



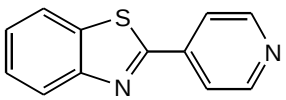
Following the general experimental procedure with 2-aminothiophenol (1 mmol), 2-methylbenzyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate and purification (70%), afforded the desired product as colorless solid, GC-MS yield = 73%; mp 55-57 ^{o}C (Lit[2] mp = 56-58 °C); ^{1}H NMR (CD_3COCD_3, 600 MHz) δ 2.34 (s, 3H), 6.49-6.51 (m, 1H), 6.58 (d, 1H, *J* = 7.8 Hz), 7.10-7.19 (m, 5H), 7.25-7.27 (m, 1H); ^{13}C NMR (CD_3COCD_3, 150 MHz) *δ* 19.5, 112.2, 117.6, 119.1, 127.3, 128.6, 128.7, 131.5, 133.4, 137.2, 138.1, 138.3, 150.8; GC-MS (EI): *m/z* 225 $[M]^+$, 108, 91, 82, 69, 63.

2-(Pyridin-2-yl)benzo[d]thiazole (Table 7, entry 7f, CAS No.: 716-80-3)[2]



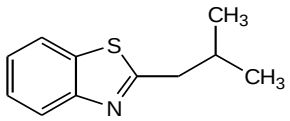
Following the general experimental procedure with 2-aminothiophenol (1 mmol), 2-pyridylmethanol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate, afforded the desired product as yellow solid, GC-MS yield = 99%; mp 130-132 ^{o}C (Lit[2] mp = 132-134 °C); C-MS (EI): *m/z* 212 $[M]^+$, 108, 82, 69, 51.

2-(Pyridin-4-yl)benzo[d]thiazole (Table 7, entry 7g, CAS No.: 51784-73-7)[4,6]



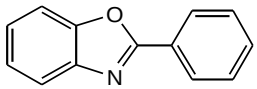
Following the general experimental procedure with 2-aminothiophenol (1 mmol), 4-pyridylmethanol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate, afforded the desired product as yellow solid, GC-MS yield = 99%; mp 131-134 ^{o}C (Lit[4] mp = 133-135 °C); GC-MS (EI): *m/z* 212 $[M]^+$, 186, 108, 82, 69.

2-(3-Methylbutane)-benzo[d]thiazole (Table 7, entry 7h)



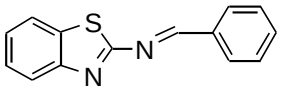
Following the general experimental procedure with 2-aminothiophenol (1 mmol), 3-methylbutanol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate, afforded the desired product as yellow solid, GC-MS yield = 44%; GC-MS (EI): *m/z* 191 $[M]^+$, 176, 149, 125, 108, 69.

2-Phenylbenzo[d]xazole (Scheme 5)[4]



Following the general experimental procedure with 2-aminophenol (1 mmol), benzyl alcohol (1.5 mmol), Fe(II)Pc (1 mol%), NaO*t*Bu (2 equiv.) in 5 mL toluene at 120 °C for 36 h. After completion of reaction (monitored by TLC), extraction with ethyl acetate afforded the desired product; GC-MS yield = 89%; mp 100-101 ^oC (Lit[2] mp = 100-104 °C); GC-MS (EI): *m/z* 195 $[M]^+$, 167, 92, 77, 63, 51.

***N*-Benzylidenebenzo[d]thiazol-2-amine (Fig. 1)**



^1H NMR ($CDCl_3$, 300 MHz) δ 7.38 (t, 1H, J = 7.8 Hz), 7.47-7.65 (m, 4H), 7.85 (d, 1H, J = 7.9 Hz), 7.99-8.06 (m, 3H), 9.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 121.3, 122.1, 123.5, 125.5, 126.4, 126.8, 129.4, 130.6, 133.6, 135.0, 135.1, 152.1, 166.5, 172.2; MS (EI): m/z 238 $[M]^+$.

References:

1. F. Li, H. Shan, Q. Kang and L. Chen, *Chem. Commun*., 2011, **47**, 5058-5060.
2. Z. Yang, X. Chen, S. Wang, J, Liu, K. Xie, A. Wang and Z. Tan, *J. Org. Chem.*, 2012, **77**, 7086-7091.

3. N. Khatun, L. Jamir, M. Ganesh and B. K. Patel, *RSC Advances*, 2012, **2**, 11557-11565.
4. T. B. Nguyen, L. Ermolenko, W. A. Dean and A. Al-Mourabit, *Org. Lett.*, 2012, **14**, 5948-5951.
5. J. Li, S. Benard, L, Neuville and J. Zhu, *Org. Lett.*, 2012, **14**, 5980-5983.
6. Y. Liao, H. Qi, S. Chen, P. Jiang, W. Zhou and G. J. Deng, *Org. Lett.*, **14**, 6004-6007.
7. Q. Li, S. Fan, Q. Sun, H. Tian, X. Yu and Q. Xu, *Org. Biomol. Chem.*, 2012, **10**, 2966-2972.