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SUPPLEMENTARY MATERIAL TO

DBUHI3 complex an efficient catalyst for the synthesis of 2-phenylbenzimidazole and benzothiazole derivatives

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EXPERIMENTAL AND ANALYTICAL DATA

General:

All local brand chemicals were purchase checked their purity by TLC and purified. The melting point were determined in open capillary and are uncorrected. For analysis technique following instruments were used.Solvents that were entirely dry and free of impurities were used. Reaction of the progress was checked on Merck TLC Silica gel 60 F254 plates using UV lamp (365 nm and 254 nm) and iodine chamber.

Sr. No.	**Analysis Type**	**Instrument**
1	HRMS	Brucker Impact HD
2	UV-visible Spectrum	shimadzuCorp, Model UV-2600
3	IR Spectrum	shimadzu Corp, FTIR-shimay, Model IR affinity

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4	FESM	FEI Nova NanoSEM 450
5	EDS	Brucker XFlash 6130
6	TGA-DTA	shimadzu Corp
7	NMR (^{1}H &^{13}C)	500MHz &125MHZ Brucker

Synthesis of amine-iodine complexes

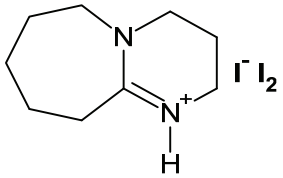
Ammonium iodide (2.8 eq.) was added to water (2 volume) has obtained clear solution in 250 mL beaker and then added iodine (1 eq). This mixture of the solution was added dropwise to a stirred solution of amine (1 eq) in water (8 Volume) in 250 mL round bottom flask. The solid product has formed during addition, stirred mixture for 15 minutes and filter off the solid product. The product was washed with cold water and dried under vacuum to provide the desired complexes and the yield of the complex was reported.

Typical Process for the synthesis of benzimidazole / benzothiazole from o-phenylenediamine/thiophenol and aldehyde.

A mixture of *o*-phenylenediamine/*o*-amino thiophenol (1 mmol) and arylaldehyde (1 mmol) was dissolved in 2 mL ethanol in 25 mL round bottom flask. The catalyst (**1a**) (15mol%) was added and the reaction mixture was stirred for 30 min. The progress of the reaction was monitored by (hexane: ethyl acetate) TLC. The TLC clearly have showed the disappearance of thestarting material. After completion of the reaction, the solvent was evaporated under vacuum. The crude solid product was extracted in ethyl acetate after the addition of 20 % sodium thiosulphate solution. The organic layer was dried over sodium sulfate and purified by

column chromatography. The structure of the compound was confirmed by the spectroscopic techniques and match with the reported.

1a. DBU-Iodine complex (Table 1, Entry 1, 1a): Greenish Yellow solid M. P. 87^0C.



M. F. = $C_9H_{17}N_2\ I^-\ I_2$ Mol. Wt. = 533.79

HRMS: Positive ion polarity: 153.138 (cal. 153.242).

Negative ion polarity: 126.904 (cal. 126.904), 380.712 (cal. 380.713).

UV-visible Spectrum(nm): 210, 307,364 (λ_{max} **=364nm**).

IR Spectrum(cm^{-1}): 530, 601, 633, 1203, 1319, 1440, 1574, 1638, 3133, 3267.

SEM: Clumpy and agrummerated morphology.

Field Emission Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy (FESEM - EDS):

Element	At. Number	Wt. %	At. %
Iodine	53	78.97	26.69
Carbon	6	17.57	62.74
Nitrogen	7	3.45	10.57
		100	100

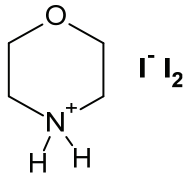
TGA: DBU-iodine complex was stable up to 200°C after that gradual weight loss start up to 380°C then fast weight loss observed and stop 410°C. After 410°Cslow weight loss starts and end by complete vanishing of complex at 500°C.

DTA: Endotherm was observed at 110°Cand exotherm at 410°C. Both peaks are very sharp.

Strong exotherm and sharp weight loss was located in graph at 410°C.

^{1}HNMR:(500 MHz,DMSO-d_6):δ9.47 (s, 1H), 3.55 (t, 2H *J*=3.55 Hz), 3.48 (t, 2H *J*=3.48 Hz), 3.24-3.26 (m, 2H), 2.63 (t, 2H *J*=2.64 Hz), 1.92(q, *J*=1.94Hz) 1.54-1.72 (m, 6H);**^{13}CNMR:(125 MHz,DMSO-d_6) δ**:165.88, 53.89, 48.38, 38.10, 32.22, 28.70, 26.38, 23.78, 19.34.

1b. Morpholine-Iodine complex (Table 1, Entry 2, 1b): Orange Yellow solid M. P. 78^{0}C.



M. F. = $C_4H_9NO\ I^-\ I_2$ Mol. Wt. = 467.73

HRMS: Positive ion polarity: 88.075 (cal. 88.126).

Negative ion polarity: 126.905 (cal. 126.904), 380.713 (cal. 380.713).

UV-visible Spectrum(nm): 210, 360, 365, 366. (λ_{max} = **360nm**).

IR Spectrum (cm^{-1}): 585, 626, 817, 859, 1006, 1033, 1083, 1159, 1243, 1295, 1357, 1438, 2858, 3183.

SEM: Clumpy and agrummerated morphology.

Field Emission Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy (FESEM - EDS):

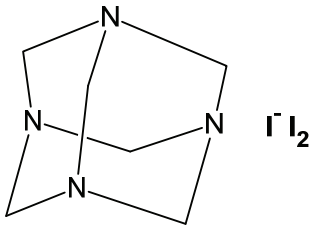
Element	At. Number	Wt. %	At. %
Iodine	53	66.21	16.45
Carbon	6	23.94	62.86
Oxygen	8	5.36	10.57
Nitrogen	7	4.49	10.11
		100	100

TGA: The morpholine-iodine complex was stable up to 150°C then underwent fast weight loss till 300°Cthen gradual weight loss observed end at 500°Cby complete disappearing complex.

DTA: It displaysharp endotherm at 150°C and very broad exotherm peak at 480°C.

^{1}HNMR: (500 MHz, DMSO-d_6):δ 3.66-3.77 (m, 4H), 3.35-3.41(m, 4H);**^{13}CNMR:(125 MHz, DMSO-d_6)δ**:44.09, 45.24, 64.46, 65.55.

1c. Urotropine-Iodine complex (Table 1, Entry 3, 1c): Brown Yellow solid M. P. 130^{0}C.



M. F. = $C_6H_{13}N_4$ I^- I_2 Mol. Wt. = 521.76

HRMS: Positive ion polarity: 141.113 (cal. 141.192).

Negative ion polarity: 126.905 (cal. 126.904).

UV-visible Spectrum(nm): 308, 113, 324, 369 (λ_{max} = **369nm**).

IR Spectrum (cm^{-1}): 523, 656, 705, 734, 819, 901, 991, 1028, 1230, 1250, 1381, 1455.

SEM: Clumpy and agrummerated morphology.

Field Emission Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy (FESEM - EDS):

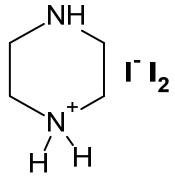
Element	At. Number	Wt. %	At. %
Iodine	53	74.50	22.60
Carbon	6	16.03	51.37
Nitrogen	7	09.47	26.03
		100	100

TGA: The complex was very stable up to 255°C after that sharp decrease in weight continue till temperature 340°C.

DTA: It show sharp three band at temperature 145°C, 255°Cand 450°C.

^{1}HNMR:(500 MHz, DMSO-d_6):δ4.73(s, 12H);**^{13}CNMR:(125 MHz, DMSO-d_6)δ**:73.85.

1d. Piperazine-Iodine complex (Table 1, Entry 4, 1d): Dark Brown Yellow Solid M. P. 346^0C.



M. F. = $C_4H_{11}N_2$ I^- I_2 Mol. Wt. = 467.74

HRMS: Positive ion polarity: 87.091(cal. 87.142).

Negative ion polarity: 126.905 (cal. 126.904).

UV-visible Spectrum(nm): 210, 306, 319, 361, 368 (λ_{max} = **368nm**).

IR Spectrum (cm^{-1}): 636, 860, 988, 1084, 1242, 1358, 1400, 1436, 3180.

SEM: Clumpy and agrummerated morphology.

Field Emission Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy (FESEM - EDS):

Element	At. Number	Wt. %	At. %
Iodine	53	89.50	45.67
Carbon	6	07.55	40.73
Nitrogen	7	02.94	13.60
		100	100

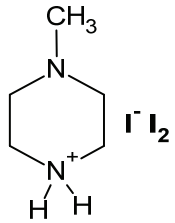
TGA: The complex show stability till temperature 115°Cafter sharp and slow weight loss continue up to 325°C.

DTA: This graph indicates one sharp exothermic band at 325°C.

^{1}HNMR: (500 MHz, DMSO-d_6): δ8.48(s, 2H), 3.81 (s, 1H), 3.22(t, 1H, *J*=3.22 Hz), 3.07 (t, 4H, *J*= 3.08Hz), 2.99 (s, 1H), 2.61-2.64 δ(q, 1H);**^{13}CNMR: (125 MHz, DMSO-d_6) δ**:47.85, 46.74, 44.28, 43.54.

1e. N-Methyl-Piperazine-Iodine complex (Table 1, Entry 5, 1e):

Pinkish Yellow solid M. P. 178^{0}C.



M. F. = $C_5H_{13}N_2$ I^- I_2 Mol. Wt. = 481.75

HRMS: Positive ion polarity: 101.107 (cal. 101.168).

Negative ion polarity: 126.905 (cal. 126.904).

UV-visible Spectrum(nm): 210, 306, 317, 365 (λ_{max} = **364nm**).

IR Spectrum (cm^{-1}): 573, 847, 893, 960, 990, 1100, 1365, 1438, 1553, 1651, 2436, 2707.

SEM: Clumpy and agrummerated morphology.

Field Emission Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy (FESEM - EDS):

Element	At. Number	Wt. %	At. %
Iodine	53	76.30	23.96
Carbon	6	18.18	60.32
Nitrogen	7	05.52	15.71
		100	100

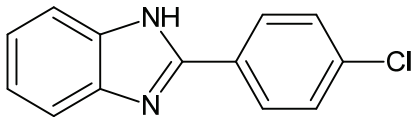
TGA: The complex was stable till 200°C above this temperature gradual weight loss till 320°C.

DTA: One sharp exothermic band observed at 320°C.

^{1}HNMR:(500 MHz, DMSO-d_6): δ8.46 (s, 2H), 2.96-3.05(m, 4H), 2.61-2.63(m, 4H), 2.35(s, 3H);**^{13}CNMR:(125 MHz, DMSO-d_6) δ**:51.47, 45.40, 43.02.

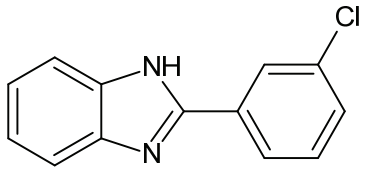
CHARACTERISATION DATA OF 2-SUBSTITUTED PHENYL BENZIMIDAZOLE.

1. 2-(4-chlorophenyl)-*1H*-benzimidazole (Table 5, Entry 1, 4a): Yellow solid M. P. 290-293°C (290-292°C)[1]



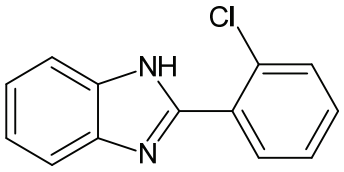
^{1}HNMR: (500 MHz, DMSO-d_6): **δ** 12.98 (s, 1H), 8.17-8.20 (m, 2H), 7.73 (d, 1H, *J*=7.73 Hz), 7.64-7.68 (m, 1H), 7.63 (t, 1H, *J*= 7.62 Hz), 7.61 δ (d, 1H *J*= 7.60 Hz), 7.20-7.36 (m, 2H); **^{13}CNMR: (125 MHz, DMSO-d_6)δ**: 150.61, 144.20, 135.48, 134.95, 129.54, 129.27, 128.60, 123.24, 122.31, 119.43, 111.88.

2. 2-(3-chlorophenyl)-1*H*-benzimidazole (Table 5, Entry 2, 4b): Brown solid M. P. 228-230°C (227-229°C)[2]



^{1}HNMR: (500 MHz, DMSO-d_6): **δ** 13.04 (s, 1H), 8.23 (t, 1H *J*= 8.22 Hz), 8.17 (t, 1H *J*= 8.17 Hz), 8.15 (t, 1H, *J*= 8.13 Hz) 7.57-7.66 (m, 1H), 7.55 (t, 1H, *J*= 7.54 Hz), 7.30 (q, 1H), 7.20 – 7.27 δ (m, 2H); **^{13}CNMR: (125 MHz, DMSO-d_6)δ**: 150.19, 144.11, 135.45, 134.23, 132.67, 131.42, 130.01, 126.48, 125.48, 123.43, 122.41, 119.56, 111.98.

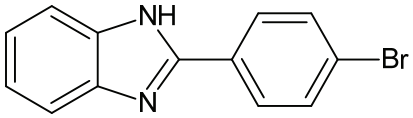
3. 2-(2-chlorophenyl)-*1H*-benzimidazole (Table 5, Entry 3, 4c):Yellow solid M. P. 232-234°C (231-233^{0}C)[1]



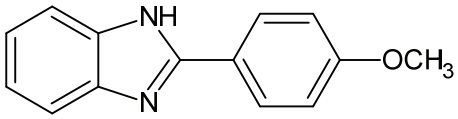
^{1}HNMR: (500 MHz, DMSO-d_6): δ 12.73 δ (s, 1H), 7.90-7.91 (m, 1H), 7.66 (d, 1H, *J*= 7.65 Hz), 7.65 (d, 2H, *J*=7.65 Hz), 7.50-7.56 (m, 2H),

7.22-7.26 (m, 2H); **^{13}CNMR: (125 MHz, DMSO-d_6)δ** :149.55, 132.56, 132,09, 131.68, 130.82, 130.43, 127.91, 122.72, 120.07.

4. 2-(4-bromophenyl)-*1H*-benzimidazole (Table 5, Entry 4, 4d):Yellow solid M. P. 286-290°C (292-293°C)[1]

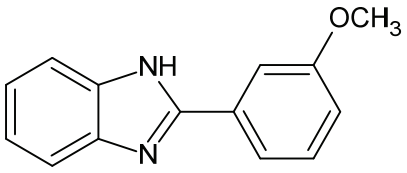


5. 2-(4-Methoxyphenyl)-*1H*-benzimidazole (Table 5, Entry 5, 4e):White solid M. P. 223-225°C (222-223°C)[3]

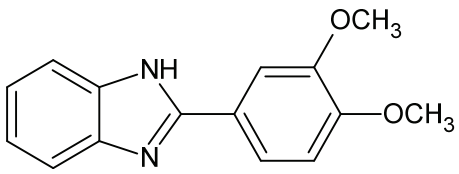


^{1}HNMR: (500 MHz, DMSO-d_6): δ 12.73 (s, 1H), 8.10 - 8.12 (m, 2H), 7.61 (d, 1H, *J*= 7.60 Hz), 7.48 (d, 1H, *J*=7.48 Hz), 7.17 (t, 2H, *J*= 7.16 Hz) 7.13 (d 1H *J*=7.13 Hz) 7.11 (d, 1H *J*=7.10 Hz) 3.84 (s, 3H); **^{13}CNMR: (125 MHz, DMSO-d_6)δ**: 161.05, 151.79, 144.34, 135.43, 128.45, 123.15, 122.53, 121.90, 118.95, 114.83, 111.49.

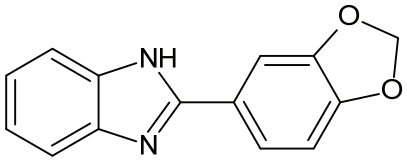
6. 2-(3-methoxyphenyl)-1*H*-benzimidazole (Table 5, Entry 6, 4f):Yellow solid M. P. 202-205°C (200-202°C)[1]



7. 2-(3,4-dimethoxyphenyl)-*1H*-benzimidazole (Table 5, Entry 7, 4g): White solid M. P. 225-227°C (223-226°C)[4]

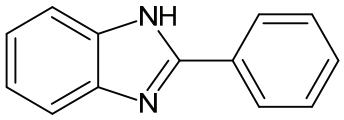


8. 2-(2H-1,3-benzodioxol-5-yl)-*1H*-benzimidazole (Table 5, Entry 8, 4h):Yellow solid 238-240°C (239-241°C)[3]



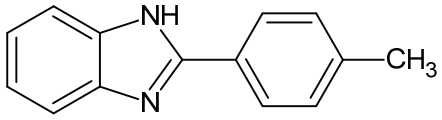
^{1}HNMR: (500 MHz, DMSO-d_6): δ 12.80 (s, 1H), 7.67 (q, 1H, *J*= 7.66 Hz), 7.45-7.47 (m, 1H), 7.27 (d, 1H, *J*= 7.26 Hz), 7.21-7.23 (m, 3H), 6.59(d, 1H, *J*= 6.58 Hz), 5.96 (s, 2H); **^{13}CNMR: (125 MHz, DMSO-d_6)δ**: 153.50, 148.07, 147.04, 143.02, 136.25, 124.22, 123.00, 122.60, 119.85, 119.55, 111.53, 108.91, 107.22, 101.58.

9. 2-phenyl-*1H*-benzimidazole (Table 5, Entry 9, 4i): Brown solid M. P. 243-245°C (242-244°C)[2]

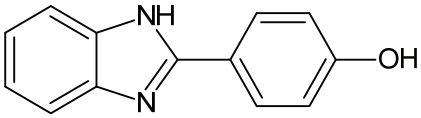


^{1}HNMR: (500 MHz, DMSO-d_6): δ 12.91 (s, 1H), 8.19 (t, 2H *J*=8.18 Hz), 7.67 (d, 1H, *J*=7.67 Hz), 7.53-7.57 (m, 3H), 7.50 (t, 1 H *J*=7.48 Hz) 7.18-7.24 (m, 2H); **^{13}CNMR: (125 MHz, DMSO-d_6)δ**: 151.68, 144.28, 135.47, 130.64, 130.30, 129.41, 129.25, 127.09, 126.90, 122.99, 122.13, 119.34, 111.78.

10. 2-(4-methylphenyl)-*1H*-benzimidazole (Table 5, Entry 10, 4j):Brown Solid M. P. 216-219°C (214-216°C)[2]

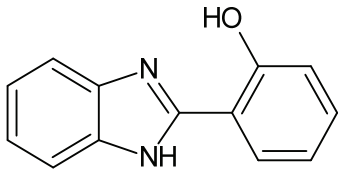


11. 4-(*1H*-benzimidazole-2-yl) phenol (Table 5, Entry 11, 4k): White solid M. P. 252-254°C (254-255°C)[1]



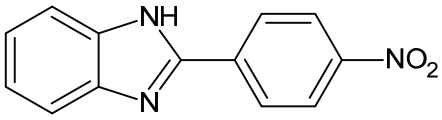
^{1}HNMR: (500 MHz, DMSO-d_6): δ 15.33 (s, 1H), 10.87 (s, 1H), 8.25 (d, 2H *J*= 8.24 Hz) 7.77-7.81 (m, 2H), 7.51-7.54 (m, 2H), 7.09-7.11 (d, 2H, *J*=7.09 Hz); **^{13}CNMR: (125 MHz, DMSO-d_6)δ**: 162.86, 149.60, 132.12, 130.74, 125.97, 116.98, 114.04, 113.78.

12. 2-(*1H*-benzimidazole-2yl) phenol (Table 5, Entry 12, 4l):Brown solid 204-206°C (205-206°C)[5]

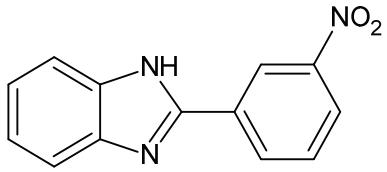


^{1}HNMR: (500 MHz, DMSO-d_6): δ 13.29 (s, 1H), 13.09 (s, 1H), 8.06 (d, 1H, *J*=8.05 Hz), 7.94-7.97 (m, 2H), 7.90 (d, 1H, *J*=7.89Hz), 6.61-7.64 (m, 2H), 7.48-7.51(m, 1H), 7.38-7.41(m, 1H); **^{13}CNMR: (125 MHz, DMSO-d_6)δ**: 156.85, 152.58, 142.33, 131.85, 128.83, 127.16, 123.10, 122.99, 119.50, 116.88, 115.50, 111.29.

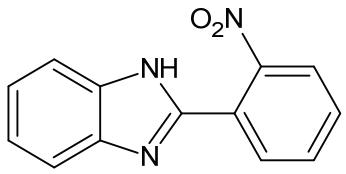
13. 2-(4-nitrophenyl)-*1H*-benzimidazole (Table 5, Entry 13 4m):Yellow solid M. P. 301-303°C (300°C)[6]



14. 2-(3-nitrophenyl)-*1H*-benzimidazole (Table 5, Entry 14, 4n):Yellow solid M. P. 196-198°C (199°C)[6]

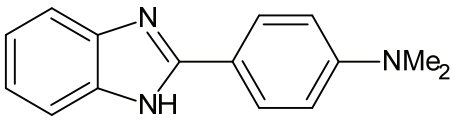


15. 2-(2-nitrophenyl)-*1H*-benzimidazole (Table 5, Entry 15, 4o):Yellow solid M. P. 229-231°C (230°C)[6]



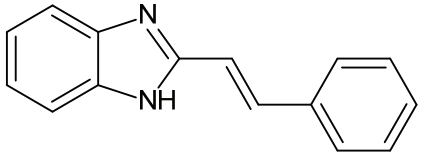
^{1}HNMR: (500 MHz, DMSO-d_6): δ 13.06 (s, 1H), 8.03 (dd, 1H, *J*=8.02 Hz), 7.98 δ (dd, 1H, *J*=7.97 Hz) 7.85-7.88 (m, 1H), 7.74-7.77 (m, 1H) 7.69 (d, 1H, *J*=7.65 Hz), 7.57 (d, 1H *J*=7.56 Hz) 7.20-7.29 (m, 2H); 13**CNMR: (125 MHz, DMSO-d_6)δ**:149.42, 147.76, 144.05, 135.07, 133.12, 131.38, 124.77, 124.67, 123.56, 122.36, 119.71, 112.14.

16. 4-(*1H*-benzimidazole-2-yl)-N, N-dimethylaniline (Table 5, Entry 16,4p):Yellow solid M. P. 280-283°C (277-279°C)[1]

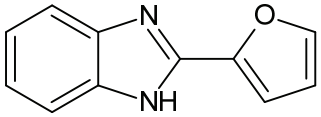


^{1}HNMR: (500 MHz, $CDCl_3$): 12.51 (s, 1H), 7.61-7.64 (m, 1H), 7.23-7.26 (m, 1H), 7.15-7.20 (m, 1H), 7.01 (d, 1H, *J*=7.01 Hz), 6.67-6.74 (m, 2H), 3.00 (m, 3H), 2.92 (m, 3H); **^{13}CNMR: (125 MHz, $CDCl_3$)δ**: 155.04, 149.98, 143.30, 136.38, 130.31, 126.94, 124.34, 122.16, 119.26, 117.39, 112.81, 111.81, 110.40, 40.57, 40.23.

17. 2-[(*E*)-2-phenylethenyl]-*1H*-benzimidazole (Table 5, Entry 17 4q):Yellow solid M. P. 270-273°C (164-166°C)[2]

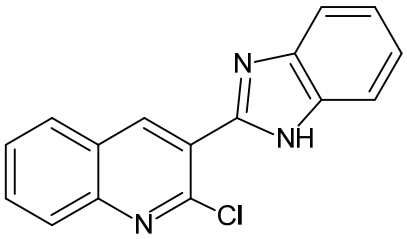


18. 2-(furan-2-yl)-*1H*-benzimidazole (Table 5, Entry 18, 4r):Brown solid M. P. 226-228°C(221-223°C)[2]



^{1}HNMR: (500 MHz, DMSO-d_6): δ 12.95(m, 1H), 7.96(dd, *J*=1.71&0.90Hz, 1H), 7.57(d, *J*=7.11Hz, 1H), 7.51 (d, *J*=7.15Hz, 1H) 7.17-7.22 (m, 3H), 6.72(dd, *J*=3.4 Hz &0.95 Hz, 1H); **^{13}CNMR: (125 MHz, DMSO-d_6) δ**:147.12, 143.37, 135.00, 134.44, 129.02, 128.68, 127.15, 123.01, 121.90, 117.81, 112.59.

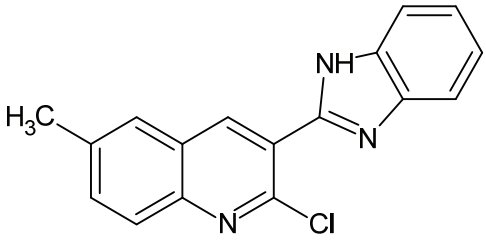
19. 3-(*1H*-benzimidazole-2-yl)2-chloroquinoline (Table 5, Entry 19, 4s):Yellow solid M. P. 219-222°C (202°C)[7]



^{1}HNMR: (500 MHz, DMSO-d_6): δ 10.41 (s, 1H), 9.34 (s, 1H), 8.08 (d, 1H, *J*=8.06 Hz), 8.06 (d, 1H, *J*=8.05Hz), 7.98-8.00 (m, 1H), 7.81-7.85 (m, 1H), 7.35-7.60 (m, 2H); **^{13}CNMR: (125 MHz, DMSO-d_6) δ**: 147.57,

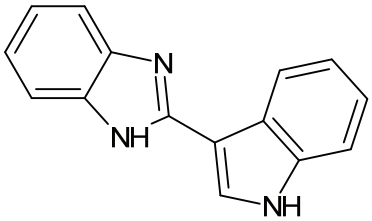
147.02, 145.58, 143.07, 141.48, 133.96, 131.98, 128.41, 128.30, 128.09, 127.05, 124,12, 123.22, 122,74, 119.86, 111.29.

20. 3-(*1H*-benzimidazol-2-yl)-2-chloro-6-methylquinoline (Table 5, Entry 20, 4t):White solid M. P. 221-224°C (220°C)[7]



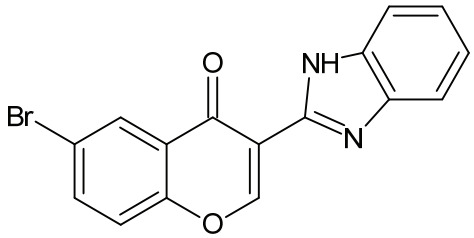
[1]HNMR: (500 MHz, DMSO-*d*$_6$): δ 12.94 (s, 1H), 8.87 (s, 1H), 8.59 (s, 1H), 7.75-7.78 (m, 2H), 7.61-7.74 (m, 2H), 7.28-7.59 (m, 2H), 2.63 (s, 3H); **[13]CNMR: (125 MHz, DMSO-*d*$_6$) δ**: 148.31, 146.73, 145.95, 141.20, 138.32, 134.71, 127.93, 127.60, 126.83, 124.87, 123.53, 122.41, 119.66, 112.32, 21.64.

21. 2-(1*H*-indol-2-yl)-*1H*-benzimidazole (Table 5, Entry 21, 4u):Black solid 220-223°C (226-227°C)[17]



[1]HNMR:(500 MHz DMSO-*d*$_6$): **δ** 12.59 (s, 1H), 11.66 (s, 1H), 8.49 (t, 1H, *J*= 8.48 Hz), 8.14 (d, 1H, *J*=8.13 Hz), 7.49-7.55 (m, 2H), 7.54-7.55 (m, 2H), 7.49-7.50 (q, 1H), 7.19-7.21 (m, 1H), 7.13-7.16 (m, 1H); **[13]CNMR:**(125 MHz DMSO-*d*$_6$) δ: 149.84, 136.96, 126.77, 125.54, 122.73, 121.78, 120.78, 112.41, 106.74.

22. 3-(*1H*-benzimidazol-2-yl)-6-bromo-4*H*-1-benzopyran-4-one (Table 5, Entry 22, 4v): Yellow solid M. P. 269-271°C.

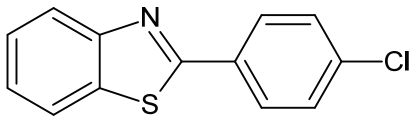


^{1}HNMR: (500 MHz, DMSO-d_6):δ 12.65 (s, 1H), 8.32 (s, 1H), 9.41 (s, 1H), 8.32 (d, 1H, *J*= 8.31 Hz), 8.06-8.09 (m, 1H), 7.67-7.70 (m, 1H), 7.62-7.66 (m, 1H), 7.18-7.22 (m, 2H); **^{13}CNMR: (125 MHz, DMSO-d_6) δ**: 174.11, 158.91, 155.05, 145.27, 142.70, 137.89, 134.93, 127.82, 125.57, 122.70, 122.40, 121.96, 119.22, 118.73, 115.03, 112.97.

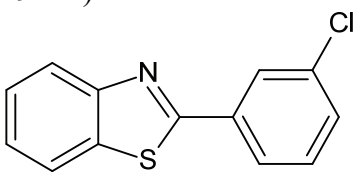
HRMS: [MF: $C_{16}H_{10}O_2N_2Br$(M+H)]: 342.99 (Calculated: 342.16)

CHARACTERISATION DATA OF 2-SUBSTITUTED PHENYL BENZOTHIAZOLE.

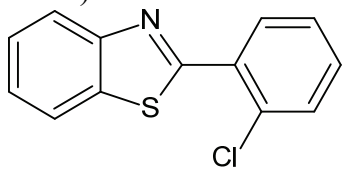
1. 2-(4-chlorophenyl)-1,3-benzothiazole (Table 6, Entry 1, 7a): White solid M. P. 115-117°C (111-112°C)[8]



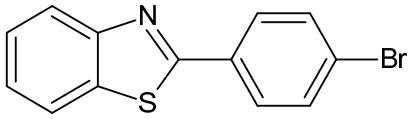
2. 2-(3-chlorophenyl)-1,3-benzothiazole (Table 6, Entry 2. 7b): White solid M. P. 94-95°C (93-94°C)[8]



3. 2-(2-chlorophenyl)-1,3-benzothiazole (Table 6, Entry 3, 7c): White solid M. P. 80-82°C (83-84°C)[8]

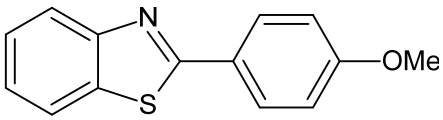


4. 2-(4-bromophenyl)-1,3-benzothiazole (Table 6, Entry 4, 7d): White Solid M. P. 127-129°C (129-131°C)[9]



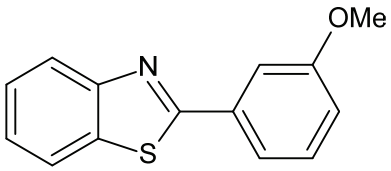
^{1}HNMR: (500 MHz, $CDCl_3$): **δ** 8.06 (d, 1H, *J*=8.05 Hz), 7.94-7.91 (m, 2H), 7.90(d, 1H, *J*= 7.89 Hz), 7.61-7.64(m, 2H), 7.48-7.51 (m, 1H), 7.38-7.41 (m, 1H); **^{13}CNMR: (125 MHz, $CDCl_3$)δ**: 166.70, 154.06, 135.03, 132.54, 132.23, 128.90, 126.51, 125.45, 125.42, 123.31, 121.67.

5. 2-(4-methoxyphenyl)-1,3-benzothiazole (Table 6, Entry 5, 7e): White Solid M. P. 120-121°C (120-122°C)[9]

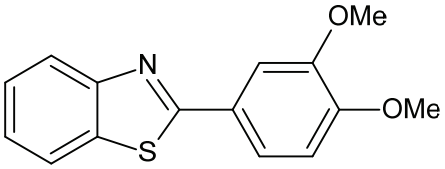


^{1}HNMR: (500 MHz, $CDCl_3$): δ 8.02-8.04 (m, 3H), 7.86 (d, 1H, *J*=7.86 Hz), 7.44-7.48 (m, 1H), 7.33-7.36 (m, 1H), 6.98-7.01 (m, 2H), 3.87 (s, 3H); **^{13}CNMR: (125 MHz, $CDCl_3$) δ**: 167.86, 161.91, 154.22, 134.85, 129.10, 126.43, 126.19, 124.78, 122.81, 121.50, 114.36, 55.46.

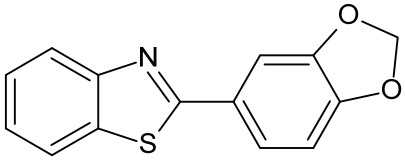
6. 2-(3-methoxyphenyl)-1,3-benzothiazole (Table 6, Entry 6, 7f): Yellow solid M. P. 99-102°C (98-100°C)[10]



7. 2-(3,4-dimethoxyphenyl)-1,3-benzothiazole (Table 6, Entry 7, 7g): Brown solid M. P. 229-231°C (230-232°C)[11]

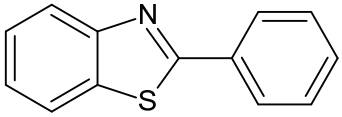


8. 2-(2*H*-1,3-benzodioxol-5-yl)-1,3-benzothiazole (Table 6, Entry 8, 7h):Yellow solid M. P. 130-132°C (128-130°C)[12]

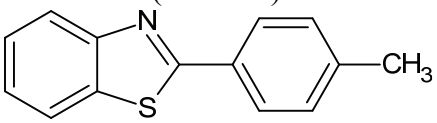


^{1}HNMR: (500 MHz, $CDCl_3$): δ 8.00 (d, 1H, *J*=7.99 Hz), 7.81 (d, 1H, *J*=7.81 Hz), 7.57 (d, 1H, *J*=7.56 Hz), 7.42-7.45 (m, 1H), 7.30-7.35 (m, 1H), 6.85 (d, 1H, *J*=6.84 Hz), 5.99 (s, 2H); **^{13}CNMR: (125 MHz, $CDCl_3$) δ**: 167.49, 154.01, 150.01, 148.29, 134.80, 127.94, 126.20, 124.89, 122.86, 122.66, 122.43, 108.56, 107.43, 101.67.

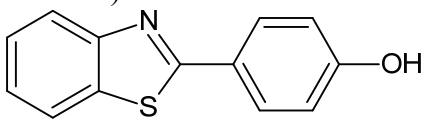
9. 2-phenyl-1,3 benzothiazole (Table 6, Entry 9, 7i): White solid M. P. 112-113°C (109-110°C)[8]



10. 2-(4-methylphenyl)-1, 3-benzothiazole (Table 6, Entry, 10, 7j): Yellow solid M. P. 85-86°C (87-88°C)[13]

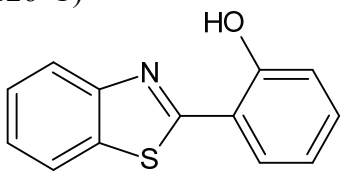


11. 4-(1,3-benzothiazol-2-yl) phenol (Table 6, Entry 11, 7k): White solid M. P. 227-229°C (225-227°C)[14]



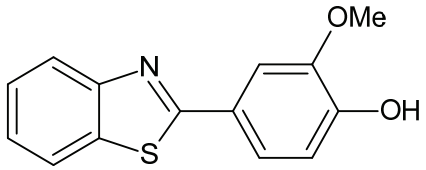
^{1}HNMR: (500 MHz DMSO-d_6): δ 10.24 (s, 1H), 8.09 (d, 1H, *J*=8.07), 8.07 (d, 1H, *J*=8.06), 7.93-7.00 (m, 2H), 7.49-7.52 (m, 1H), 7.39-7.42 (m, 1H), 6.96 (t, 2H, *J*=6.95); **^{13}CNMR: (125 MHz DMSO-d_6) δ**: 167.92, 160.99, 154.19, 134.57, 129.74, 129.51, 129.27, 126.89, 125.36, 124.50, 122.76, 122.58, 116.55.

12. 2-(1,3-benzothiazol-2-yl) phenol (Table 6, Entry 12, 7l): White solid M. P. 131-132°C (124-126°C)[14]



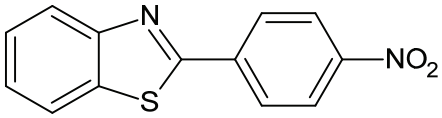
^{1}HNMR: (500 MHz, $CDCl_3$): δ 12.50 (s, 1H), 7.97 (d, 1H, *J*=7.96 Hz), 7.87 (d, 1H, *J*=7.87 Hz), 7.66-7.68 (m, 1H), 7.47-7.50 (m, 1H), 7.35-7.70 (m, 2H), 7.09-7.10 (m, 1H), 6.92-6.96 (m, 1H); **^{13}CNMR: (125 MHz, $CDCl_3$) δ**: 169.35, 157.92, 151.81, 132.73, 132.56, 128.39, 128.14, 126.66, 125.52, 122.16, 121.49, 119.53, 117.85.

13. 4-(1,3-benzothiazol-2-yl)-2-methoxyphenol (Table 6, Entry 13, 7m): White solid M. P. 160-162°C (161-163°C)[14]



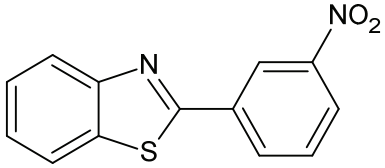
^{1}HNMR: (500 MHz, $CDCl_3$): δ 8.03 (d, 1H, *J*= 8.01 Hz), 7.86 (q, 1H), 7.71 (d, 1H, *J*= 7.70 Hz), 7.54 (q, 1H), 7.45-7.48 (m, 1H), 7.33-7.37 (m, 1H), 7.00 (q, 1H), 6.10 (s, 1H) 4.00(s, 3H); **^{13}CNMR: (125 MHz, $CDCl_3$) δ**: 168.15, 154.04, 148.52, 146.95, 134.81, 126.22, 126.17, 124.84, 122.72, 121.94, 121.51, 114.71, 109.24, 56.17.

14. 2-(4-nitrophenyl)-1,3-benzothiazole (Table 6, Entry14, 7n): Brown solid M. P. 320-322°C (228-230°C)[14]

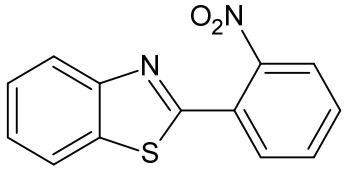


^{1}HNMR: (500 MHz, $CDCl_3$): δ 8.92 (s, 1H), 8.40 (d, 1H, *J*=8.40 Hz), 8.31 (d, 1H, *J*=8.30 Hz), 8.11 (d, 1H, *J*=8.10 Hz), 7.94 (d, 1H, *J*=7.93 Hz), 7.67 (t, 1H, *J*= 7.68 Hz), 7.56 (t, 1H, *J*=7.56 Hz), 7.45 (t, 1H, *J*=7.45 Hz); **^{13}CNMR: (125 MHz, $CDCl_3$) δ**: 164.89, 153.93, 148.74, 135.17, 133.01, 130.12, 126.85, 126.05, 125.19, 123.75, 122.69, 122.32, 121.85.

15. 2-(3-nitrophenyl)-1,3-benzothiazole (Table 6, Entry 15, 7o): Yellow solid M. P. 190-193°C (185-187°C)[15]

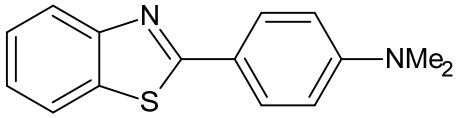


16. 2-(2-nitrophenyl)-1,3-benzothiazole (Table 6, Entry 16, 7p): Orange brown solid M. P. 195-197°C (191-193°C)[15]

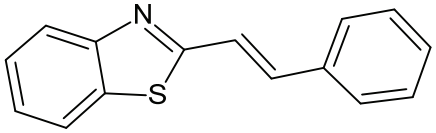


^{1}HNMR: (500 MHz, $CDCl_3$): δ 8.08 (d, 1H *J*=8.07 Hz), 7.88-7.94 (m, 2H) 7.79 (q, 1H), 7.67-7.70 (m, 1H), 7.61-7.64 (m, 1H), 7.51-7.54 (m, 1H), 7.43-7.46 (m, 1H); **^{13}CNMR: (125 MHz, $CDCl_3$) δ**: 162.40, 153.51, 148.91, 135.79, 132.39, 131.81, 130.93, 128.10, 126.59, 125.87, 124.61, 123.94, 121.58.

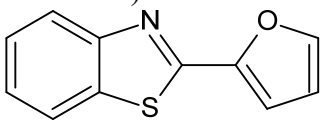
17. 4-(1,3-benzothiazol-2-yl)-*N*, *N*-dimethylaniline (Table 6, Entry 17, 7q):White solid 161-163°C (160-162°C)[14]



18. 2-[(*E*)-2-phenylethenyl]-1,3-benzothiazole (Table 6, Entry 18, 7r):White solid M. P. 107-110°C (110-112°C)[14]

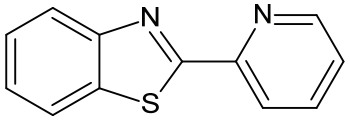


19. 2-(furan-2-yl)-1,3-benzothiazole (Table 6, Entry 19, 7s): White solid M. P. 103-104°C (101-102°C)[10]



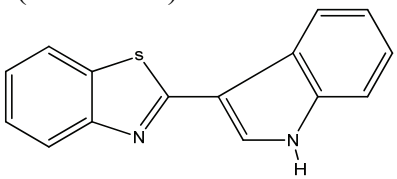
^{1}HNMR: (500 MHz, $CDCl_3$): δ 8.04 (d, 1H, *J*=8.04 Hz), 7.88 (d, 1H, *J*=7.88 Hz), 7.60 (d, 1H, *J*=7.59 Hz), 7.47-7.50 (m, 1H), 7.36-7.39 (m, 1H), 7.18 (d, 1H, *J*=7.18 Hz), 6.59-6.60 (m, 1H); **^{13}CNMR: (125 MHz, $CDCl_3$)δ**:157.56, 153.74, 148.73, 144.70, 134.26, 126.48, 125.19, 123.11, 121.57, 112.53, 111.43.

20. 2-(pyridin-2-yl)-1,3-benzothiazole (Table 6, Entry 20, 7t): Brown solid 132-134°C (130-132°C)[16]



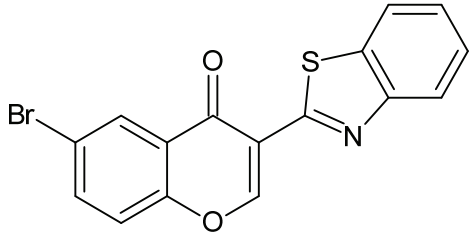
^{1}HNMR: (500 MHz, $CDCl_3$): δ 8.67-8.68 (m, 1H), 8.36 (d, 1H, *J*=8.35 Hz), 8.08 (d, 1H, *J*=8.08 Hz), 7.94 (d, 1H, *J*=7.94 Hz), 7.80-7.84 (m, 1H), 7.47-7.51 (m, 1H), 7.34-7.42 (m, 2H); **^{13}CNMR: (125 MHz, $CDCl_3$) δ**: 169.35, 154.25, 151.36, 149.63, 136.99, 136.09, 126.26, 125.63, 125.25, 123.55, 122.00, 120.73.

21. 2-(1*H*-indol-2-yl)-1,3-benzothiazole (Table 6, Entry 21, 7u):Brown solid M. P. 146-148°C (144-147°C)[16]



^{1}HNMR:(500 MHz, $CDCl_3$):δ 8.82 (s, 1H), 8.44 (d, 1H, *J*=8.43 Hz), 8.03 (d, 1H, *J*=8.03 Hz), 7.93 (d, 1H, *J*=7.92 Hz), 7.88 (d, 1H, *J*=7.87 Hz), 7.46 δ (t, 1H, *J*=7.46 Hz), 7.43 (t, 1H, *J*=7.41 Hz) 7.35-7.28 (m, 3H); **^{13}CNMR: (125 MHz, $CDCl_3$) δ**: 163.00, 153.730, 136.46, 133.84, 126.34, 126.07, 124.92, 124.23, 123.44, 122.11, 121.83, 121.30, 121.05, 112.46, 111.67.

22: 3-(1,3-benzothiazol-2-yl)-6-bromo-4*H*-1-benzopyran-4-one. (Table 6, Entry 22, 7v): Yellow solid M. P. 254-256 °C.



^{1}HNMR:(500 MHz, $CDCl_3$): **δ** 9.28 (s, 1H), 8.50 (d, 1H, *J*=8.49 Hz), 7.98-8.04 (m, 2H), 7.83 (q, 1H), 7.46-7.53 (m, 2H), 7.41 (t, 1H, *J*=7.40 Hz); **^{13}CNMR:(125 MHz, $CDCl_3$) δ:** 173.58, 158.03, 156.55, 154.69, 151.63, 137.33, 136.08, 128.98, 126.32, 125.17, 124.97, 122.57, 121.68, 120.34, 119.75, 118.52.

HRMS: [MF: $C_{16}H_9O_2NSBr(M+H)$]: 359.95 (Calculated: 359.21).

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