Supporting Information

Visible-light-induced aerobic oxidative desulfurization of 2-mercaptobenzimidazoles via sulfinyl radical

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1. General information

Reactions via general procedure were carried out under an atmosphere of oxygen unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ¹H NMR and ¹³C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using CDCl₃ or dimethyl sulfoxide- d_6 as solvent. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. All reagents obtained from commercial suppliers were used without further purification. Cyclic voltammograms were recorded with a CHI830B potentiostat at room temperature in CH₃CN. *n*-Bu₄NBF₄ (0.1 M) was used as the supporting electrolyte, and a glass carbon electrode was used as the working electrode. The auxiliary electrode was a platinum wire electrode. All potentials are referenced against the Ag/AgCl redox couple. The scan rate was 100 mV•s-1. PH is measured using a PH meter (PHS-3BW). Two standard buffer solutions with pH values of 6.86 and 4.00 at 25°C were used to calibrate the electrode system.

2. Optimization of reaction conditions

Table S1.

		N,	photocatalyst (1 mol additive (10 mol%	%))N		
		N SH	solvent, 25 °C, 48	h V		
		Н	7 W blue LED	Н		
-		1a	O ₂ (balloon)	2a		-
	Entry	PC	Additive	Solvent	Yield	
-		(1 mol%)	(10 mol%)		$(\%)^{b}$	_
	1	RB		DMF	75	
	2	[Ir]PF ₆		DMF	56	
	3	Ir(ppy) ₃		DMF	65	
	4	[Ru]		DMF	63	
	5	Eosin B		DMF	36	
	6	Eosin Y		DMF	64	
	7	4CzIPN		DMF	66	
	8			DMF	0	
	9	RB	NaCl	DMF	97 (94)	
	10	RB	NH ₄ Cl	DMF	65	
	11	RB	KCl	DMF	65	
	12	RB	LiCl	DMF	61	
	13	RB	AlCl ₃	DMF	91 (90)	
	14	RB	NaI	DMF	96 (94)	
	15	RB	NaBr	DMF	88	
	16	RB	NaCl	MeCN	68	
	17	RB	NaCl	DMSO	39	
	18	RB	NaCl	DCM	15	
	19	RB	NaCl	MeOH	69	
	20	RB	NaCl	acetone	41	
	21 ^c	RB	NaCl	DMF	69	
	22^d	RB	NaCl	DMF	80	
	23 ^e	RB	NaCl	DMF	0	
	24^{f}	RB	NaCl	DMF	0	
				O ₂ N O ₂ N	CO ₂ Na Br Br	
Rose Bengal	<pre>CF₃ [Ir]PF₆ = [Ir(dF(CF₃)pp</pre>	oy) ₂ (dtbpy)]PF ₆ Ir(ppy) ₃	∼ Ru(bpy)₃Cl₂	Eosin B	Eosin Y	4CzIPN

^{*a*} Reaction conditions: **1a** (0.2 mmol), photocatalyst (1 mol%), additive (10 mol%), O₂ balloon, solvent (2 mL), H₂O (0.2 mL), 7 W blue LED, 25 °C, 48 h. [Ir]PF₆ = [Ir(dF(CF₃)ppy)₂(dtbbpy)](PF₆), [Ru] = Ru(bpy)₃Cl₂•6H₂O. ^{*b*} NMR yield with trimethoxybenzene as the internal standard and isolated yield was given in parentheses. ^{*c*} Without additional H₂O. ^{*d*} Under air atmosphere. ^{*e*} Under Ar atmosphere. ^{*f*} Heated at 60 °C in dark.

3. General Procedures

General procedure A: 2-Mercaptobenzimidazole (0.3 mmol), NaCl (10 mol%.), Rose Bengal (1 mol%), DMF (3.0 mL), and H₂O (60 equiv) were added into a 15 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at 25 °C under the irradiation by 7 W blue LED for 48 h. The reaction was monitored by TLC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with EtOAc (3×20 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product.

General procedure B: 2-Mercaptobenzimidazole (0.3 mmol), NaCl (10 mol%.), Rose Bengal (1 mol%), dry DMF (3.0 mL), and D₂O (60 equiv) were added into a 25 mL schlenk tube successively. The atmosphere was exchanged by applying vacuum and backfilling with O_2 (this process was conducted for three times). The reaction mixture was stirred at 25 °C under the irradiation by 7 W blue LED for 48 h. The reaction was monitored by TLC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with EtOAc (3×20 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product **D-2**.

Gram-Scale Reaction for the Synthesis of 2a: 2-Mercaptobenzimidazole **1a** (9.0 mmol, 1.35 g), NaCl (5 mol%, 26.3 mg), Rose Bengal (0.3 mol%, 27.5 mg), DMF (45.0 mL), and H₂O (5.0 mL) were added into a 100 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at 25 °C under the irradiation by 3*7 W blue LED for 48 h. The reaction was monitored by TLC. After completion, the solvent was evaporated under vacuum, and the crude product was purified using column chromatography on silica gel (200-300 mesh) to obtain product **2a** in 94% yield (1.00 g).



4. Mechanistic Investigations

4.1. Control experiments

(a) The following reaction was carried out under General procedure **A**: 2-Mercaptobenzimidazole 1a (0.3 mmol), NaCl (10 mol%), Rose Bengal (1 mol%), DMF (3.0 mL), and H₂O (60 equiv), and radical inhibitor TEMPO (1.0 equiv) were added into a 15 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at 25 °C under the irradiation by 7 W blue LED for 1.5 h. After completion, TEMPO-trapped product 3 was detected by HRMS-ESI and column chromatography was performed using silica gel (200-300 mesh) to give product 2a and 3.





(b) The following reaction was carried out under General procedure **A**: 2-Mercaptobenzimidazole 1a (0.2 mmol), NaCl (10 mol%), Rose Bengal (1 mol%), DMF (2.0 mL), and H₂O (60 equiv), and radical inhibitor DABCO (1.0 equiv) were added into a 15 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at 25 °C under the irradiation by 7 W blue LED for 1.5 h. After completion, the solvent was evaporated under vacuum. Yield of 2a was determined by ¹H NMR analysis using dibromomethane as an internal standard.



The (c) following reaction was carried out under General procedure A: 2-Mercaptobenzimidazole 1a (0.2 mmol), NaCl (10 mol%.), Rose Bengal (1 mol%), DMF (2.0 mL), and H₂O (60 equiv), and radical inhibitor 1,1-Diphenylethylene (1.0 equiv) were added into a 15 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at 25 °C under the irradiation by 7 W blue LED for 1.5 h. After completion, the solvent was evaporated under vacuum. Yield of 2a was determined by ¹H NMR analysis using dibromomethane as an internal standard. 4 was determined by GC-MS.



(d) The following reaction was carried out under **General procedure A**: 2-Mercaptobenzimidazole **1a** (0.2 mmol), NaCl (10 mol%), Rose Bengal (1 mol%), DMF (2.0 mL), and H₂O (60 equiv), and radical inhibitor BHT (1.0 equiv) were added into a 15 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at 25 °C under the irradiation by 7 W blue LED for 1.5 h. After completion, the solvent was evaporated under vacuum. BHT completely quenched the formation of **2a**. **5** was determined by GC-MS.



(e) The following reaction was carried out under General procedure **A**: 2-Mercaptobenzimidazole 1a (0.3 mmol), NaCl (10 mol%), TPP (1 mol%), DMF (3.0 mL), and H₂O (60 equiv) were added into a 15 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at 25 °C under the irradiation by 7 W blue LED for 48 h. The solvent was evaporated under vacuum. Yield of 2a was determined by ¹H NMR analysis using dibromomethane as an internal standard.



(f) The following reaction was carried out under **General procedure A**: Anthracene**7a** (0.2 mmol), NaCl (10 mol%.), Rose Bengal (1 mol%), DMF (2.0 mL), and H₂O (60 equiv) were added into a 15 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at 25 °C under the irradiation by 7 W blue LED for 1.5 h. After completion, the solvent was evaporated under vacuum. **7** and **8** Were determined by GC-MS.



(g) The following reaction was carried out under General procedure **A**: 2-Mercaptobenzimidazole 1a (0.2 mmol), NaCl (10 mol%), Rose Bengal (1 mol%), DMF (2.0 mL), and H₂O (60 equiv), and Singlet oxygen scavenger Co(acac)₃ (6 mol%) were added into a 15 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at 25 °C under the irradiation by 7 W blue LED for 1.5 h. After completion, the formation of 2a was completely suppressed.



4.2. Stern-Volmer fluorescence quenching experiments

Formulation solution: 2-Mercaptobenzimidazole (7.5 mg) was dissolved in DMF in a 5 mL volumetric flask to set the concentration to be 0.01 M. Dissolve the photocatalyst Rose Bengal (2.5 mg) in DMF in a 25 mL volumetric flask, shake well, take out 5 mL of the solution and make up to volume with DMF in a 25 mL volumetric flask, setting the concentration to 0.02 mM.

Experimental procedure: The resulting 0.02 mM solution (25 µL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding DMF to prepare a 0.25 µM solution. 10.0 µL of a 2-Mercaptobenzimidazole solution was successively added and uniformly stirred, and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 521 nm. Fluorescence emission spectra of 0 µL, 10.0 µL, 20.0 µL, 30.0 µL, 40.0 µL fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn. The solution was excited at λ = 521 nm. We performed another Stern–Volmer fluorescence quenching experiment to investigate the influence of oxygen. In a typical experiment, 2.0 mL of solution of Rose Bengal in DMF was bubbled a stream of oxygen for several seconds. The solution was excited at λ = 521 nm. (a) Rose Bengal quenched by 2-Mercaptobenzimidazole in DMF.





(b) Rose Bengal quenched by NaCl in DMF.

(c) Rose Bengal quenched by O_2 in DMF.



4.3. Cyclic Voltammetry experiments

Cyclic voltammetry experiments were performed using a CHI830B potentiostat, a glassy carbon working electrode, a platinum mesh counter electrode, and a Ag/AgCl (0.01M) reference electrode. Samples were prepared with a substrate concentration of 0.1 M in a 0.1 M tetraethylammonium hexafluorophosphate in acetonitrile electrolyte solution. From the result, E $_{1/2ox}$ = 0.361 V vs SCE in CH₃CN was obtained.



4.4. Light on/off experiments



5. Characterization data of products



1H-benzo[d]imidazole (2a)^[1]

According to **General procedure A**, **2a** was obtained as white solid in 94% yield (35.4 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.46 (s, 1H), 8.20 (s, 1H), 7.63 – 7.50 (dd, 2H), 7.16 (m, *J* = 6.0, 3.2 Hz, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 142.4, 138.6, 122.2, 115.8.



5-methyl-1H-benzo[d]imidazole (2b)^[1]

According to **General procedure A**, **2b** was obtained as white solid in 69% yield (27.4 mg); using EA /PE (4:1) as eluent. prolenged reation time afforded **2b** in 98% yield (38.8 mg).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.45 (s, 1H), 7.12 (d, J = 8.2 Hz, 1H), 2.48 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 140.6, 137.5, 136.4, 132.8, 124.4, 115.5, 114.8, 21.6.



5-methoxy-1H-benzo[d]imidazole (2c)^[2]

According to **General procedure A**, **2c** was obtained as white solid in 98% yield (43.6 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 8.07 (s, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.10 (d, J = 2.4 Hz, 1H), 6.93 (dd, J = 8.8, 2.4 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 156.6, 140.7, 137.8, 133.2, 116.5, 112.7, 97.6, 55.9.



5-(tert-butyl)-1H-benzo[d]imidazole (2d)

According to **General procedure A**, **2d** was obtained as white solid in 83% yield (43.3 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.22 (s, 1H), 8.13 (s, 1H), 7.68 (s, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.39 (dd, *J* = 8.6, 1.8 Hz, 1H), 1.38 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 146.4, 140.9, 137.5, 136.1, 121.1, 115.2, 111.4, 34.9, 31.9. HRMS (ESI) m/z calcd for C₁₁H₁₅N₂⁺ (M+H)⁺ 175.12297, found 175.12273.



5-(difluoromethoxy)-1H-benzo[d]imidazole (2e)

According to **General procedure A**, **2e** was obtained as white solid in 87% yield (44.4 mg), using EA /PE (4:1) as eluent. mp: 76 - 78 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.09 (m, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.44 (s, 1H), 7.11 (dd, J = 8.7, 2.3 Hz, 1H), 6.52 (t, J = 74.2 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 147.1 (t, J = 2.8 Hz), 142.1, 137.8, 135.5, 116.3 (t, J = 258.1 Hz), 116.2, 116.1, 106.8. HRMS (ESI) m/z calcd for C₈H₇F₂N₂O⁺ (M+H)⁺ 185.05210, found 185.05182.



5-(trifluoromethyl)-1H-benzo[d]imidazole (2f)^[1]

According to **General procedure A**, **2f** was obtained as white solid in 46% yield (25.7 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 8.32 (s, 1H), 7.99 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 142.7, 139.1 (q, *J* = 3.4 Hz), 137.6 (q, *J* = 4.7 Hz), 125.5 (q, *J* = 32.1 Hz), 124.6 (q, *J* = 270.1 Hz), 120.0 (q, *J* = 3.5 Hz), 115.5, 113.7(q, *J* = 2.8 Hz).



5-fluoro-1H-benzo[d]imidazole (2g)^[1]

According to **General procedure A**, **2g** was obtained as white solid in 83% yield (33.9 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.53 (s, 1H), 8.23 (s, 1H), 7.56 (s, 1H), 7.45 – 7.32 (m, 1H), 7.03 (t, *J* = 8.5 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 159.7 (q, *J* = 237.4 Hz), 141.9, 137.7 (q, *J* = 237.4 Hz), 134.5 (q, *J* = 5.9 Hz), 116.2 (q, *J* = 8.5 Hz), 111.4 (q, *J* = 25.4 Hz), 101.3 (q, *J* = 26.3 Hz).



5-chloro-1H-benzo[d]imidazole (2h)^[1]

According to **General procedure A**, **2h** was obtained as white solid in 92% yield (42.1 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.65 (d, J = 2.0 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H), 7.27 (dd, J = 8.4, 2.1 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 141.9, 138.5, 136.4, 128.7, 123.6, 116.3, 115.4.



5-bromo-1H-benzo[d]imidazole (2i)^[1]

According to **General procedure A**, **2i** was obtained as white solid in 90% yield (53.2 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.68 (s, 1H), 8.14 (s, 1H), 7.81 (d, J = 1.8 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 7.40 (dd, J = 8.6, 1.8 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 141.7, 139.0, 136.6, 126.2, 118.4, 116.7, 116.0.



(1H-benzo[d]imidazol-5-yl)(phenyl)methanone (2j)^[1]

According to **General procedure A**, **2j** was obtained as white solid in 86% yield (49.0 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 8.14 (s, 1H), 7.81 – 7.77 (m, 3H), 7.67 (d, J = 8.5 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.45 (dd, J = 8.3, 7.0 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 197.4, 143.2, 138.1, 132.4, 132.4, 130.1, 128.3, 125.3.



methyl 1H-benzo[d]imidazole-5-carboxylate (2k)^[3]

According to **General procedure A**, **2k** was obtained as white solid in 85% yield (44.9 mg), using EA/PE (4:1) as eluent.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.81 (s, 1H), 8.40 (s, 1H), 8.20 (s, 1H), 7.82 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 3.84 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.2, 145.0, 138.1, 128.4, 123.6, 123.3, 118.0, 115.1, 52.4.



1H-benzo[d]imidazole-5-carbonitrile (21)^[3]

According to **General procedure A**, **2l** was obtained as white solid in 65% yield (27.9 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.46 (s, 1H), 8.14 (s, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.56 (dd, *J* = 8.3, 1.6 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 145.6, 125.7, 120.4, 104.2.



tert-butyl (1H-benzo[d]imidazol-5-yl)carbamate (2m)

According to **General procedure A**, **2m** was obtained as white solid in 44% yield (30.8 mg), using EA /PE (4:1) as eluent. mp: 197 - 199 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.27 (s, 1H), 8.08 (s, 1H), 7.79 (s, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.18 (dd, *J* = 8.7, 2.0 Hz, 1H), 1.46 (s, 9H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 153.5, 142.1, 140.2, 137.3, 134.9, 116.5, 114.6, 103.7, 79.2, 28.7. HRMS (ESI) m/z calcd for C₁₂H₁₆N₃O₂⁺ (M+H)⁺ 234.12370, found 234.12358.



7-methyl-1H-benzo[d]imidazole (2n)^[2]

According to General procedure A, 2n was obtained as white solid in 60% yield (23.8 mg),

using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.02 (s, 1H), 8.14 (s, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.21 (t, J = 7.7 Hz, 1H), 7.11 (d, J = 7.3 Hz, 1H), 2.63 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 140.5, 137.7, 137.18, 125.9, 123.3, 122.9, 112.7, 17.3.

6-methoxy-3H-imidazo[4,5-b]pyridine (20)

According to **General procedure A**, **20** was obtained as white solid in 36% yield (16.1 mg); using EA /PE (4:1) as eluent. prolenged reation time afforded **20** in 70% yield (29.8 mg). mp: 160 - 162 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.30 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 1H), 3.86 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 161.8, 146.9, 139.9, 128.5, 126.7, 106.8, 53.9. HRMS (ESI) m/z calcd for C₇H₈N₃O⁺ (M+H)⁺ 150.06619, found 150.06581.



5,6-difluoro-1H-benzo[d]imidazole (2p)^[7]

According to **General procedure A**, **2p** was obtained as white solid in 94% yield (46.5 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.30 (s, 1H), 7.63 (t, J = 9.2 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 147.1 (q, J = 238.1 Hz), 144.5, 143.9, 103.4 (q, J = 9 Hz).

5,6-dichloro-1H-benzo[d]imidazole (2q)^[3]

According to **General procedure A**, **2q** was obtained as white solid in 98% yield (55.0 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.73 (s, 1H), 8.32 (s, 1H), 7.85 (s, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 145.1, 124.7.

Br Br

5,6-dibromo-1H-benzo[d]imidazole (2r)

According to **General procedure A**, **2r** was obtained as white solid in 56% yield (46.4 mg), using EA /PE (4:1) as eluent. mp: 234 - 235 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.29 (s, 1H), 7.99 (s, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 144.9, 116.4. HRMS (ESI) m/z calcd for $C_7H_5N_2Br_2^+$ (M+H)⁺ 274.88140, found 274.88181.



5,6-Dimethylbenzimidazole (2s)^[3]

According to **General procedure A**, **2s** was obtained as white solid in 87% yield (38.2 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.44 (s, 2H), 2.37 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 140.0, 136.3, 131.8, 115.5, 20.3.



1H-naphtho[2,3-d]imidazole (2t)^[7]

According to **General procedure A**, **2t** was obtained as white solid in 54% yield (27.2 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.50 (s, 1H), 8.12 (s, 2H), 7.99 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.35 (dd, *J* = 6.5, 3.2 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 146.9, 139.0, 130.1, 128.2, 123.8, 111.7.



1H-imidazo[4,5-b]phenazine (2u)

According to **General procedure A**, **2u** was obtained as yellow solid in 43% yield (28.4 mg), using EA /PE (4:1) as eluent. mp: 267 – 268 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.76 (s, 1H), 8.40 (s, 2H), 8.21 (dd, *J* = 6.8, 3.5 Hz, 2H), 7.87 (dd, *J* = 6.8, 3.5 Hz, 2H). 13C NMR (100 MHz, DMSO-d6) δ 151.5, 143.6, 142.2, 139.9, 130.3, 129.4, 111.4. HRMS (ESI) m/z calcd for C₁₃H₉N₄⁺ (M+H)⁺ 221.08217, found 221.08177.

1-methyl-1H-benzo[d]imidazole (2v)^[4]

According to **General procedure A**, **2v** was obtained as colorless liquid in 55% yield (21.8 mg); using EA /PE (1:1) as eluent. prolenged reation time afforded **2o** in 70% yield (27.7 mg). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.15 (s, 1H), 7.65 – 7.60 (m, 1H), 7.54 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.22 – 7.15 (m, 1H), 3.81 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 143.7, 143.5, 134.5, 122.9, 122.1, 120.2, 109.4, 31.0.



1-ethyl-1H-benzo[d]imidazole (2w)

According to **General procedure A**, **2w** was obtained as colorless liquid in 65% yield (28.5 mg), using EA /PE (1:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.82 – 7.77 (m, 1H), 7.42 – 7.37 (m, 1H), 7.31 – 7.24 (m, 2H), 4.21 (q, J = 7.3 Hz, 2H), 1.51 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 143.9, 142.4, 133.6, 122.8, 122.1, 120.4, 109.6, 39.9, 15.3. HRMS (ESI) m/z calcd for C₉H₁₁N₂⁺ (M+H)⁺ 147.09167, found 147.09135.



1-isopropyl-1H-benzo[d]imidazole (2x)^[4]

According to **General procedure A**, **2x** was obtained as colorless liquid in 83% yield (39.8 mg), using EA /PE (1:1) as eluent.

¹H NMR (400 MHz, DMSO- d_6) δ 8.31 (s, 1H), 7.62 (dd, J = 10.9, 8.3 Hz, 2H), 7.25 – 7.14 (m, 2H), 4.72 (hept, J = 6.7 Hz, 1H), 1.51 (d, J = 6.7 Hz, 6H). ¹³C NMR (100 MHz, DMSO- d_6) δ



1-butyl-1H-benzo[d]imidazole (2y)

According to **General procedure A**, **2y** was obtained as colorless liquid in 80% yield (41.8 mg), using EA /PE (1:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.81 (dd, J = 6.4, 2.3 Hz, 1H), 7.40 (dd, J = 6.6, 2.3 Hz, 1H), 7.32 – 7.26 (m, 2H), 4.17 (t, J = 7.1 Hz, 2H), 1.87 (p, J = 8.2, 7.8 Hz, 2H), 1.42 – 1.31 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 143.9, 142.9, 133.8, 122.8, 122.0, 120.4, 109.7, 44.8, 31.9, 20.0, 13.6. HRMS (ESI) m/z calcd for C₁₁H₁₅N₂⁺ (M+H)⁺ 175.12297, found 175.12267.





According to **General procedure A**, **2z** was obtained as colorless liquid in 72% yield (43.6 mg), using EA /PE (1:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.81 (dd, J = 6.7, 2.1 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.32 – 7.24 (m, 2H), 4.14 (t, J = 7.2 Hz, 2H), 1.86 (p, J = 6.6 Hz, 2H), 1.28 (h, J = 7.3, 6.7 Hz, 6H), 0.89 – 0.82 (m, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 143.6, 143.0, 133.8, 122.9, 122.2, 120.3, 109.8, 45.2, 31.3, 29.8, 26.5, 22.5, 14.0.



1-benzyl-1H-benzo[d]imidazole (2aa)^[4]

According to **General procedure A**, **2aa** was obtained as white solid in 97% yield (60.5 mg), using EA /PE (1:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.85 – 7.81 (m, 1H), 7.35 (d, *J* = 5.7 Hz, 1H), 7.32 (t, *J* = 1.9 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.20 – 7.16 (m, 2H), 5.35 (s, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 144.0, 143.2, 135.5, 134.0, 129.1, 128.3, 127.1, 123. 1, 122.3, 120.5, 110.0, 48.9.



1-Phenyl-1H-benzo[d]imidazole (2ab)^[1]

According to **General procedure A**, **2ab** was obtained as colorless liquid in 88% yield (51.2 mg), using EA/PE (1:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.91 – 7.85 (m, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.34 (q, *J* = 5.5, 3.8 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 144.0, 142.2, 136.3, 133.6, 130.0, 128.0, 124.0, 123.65, 122.8, 120.5, 110.4.



1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole (2ac)

According to **General procedure A**, **2ac** was obtained as colorless liquid in 88% yield (62.3 mg), using EA/PE (1:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.83 – 7.80 (m, 1H), 7.53 (dt, *J* = 7.0, 2.8 Hz, 1H), 7.36 – 7.28 (m, 2H), 5.52 (d, *J* = 1.9 Hz, 2H), 3.52 – 3.47 (m, 2H), 0.92 – 0.87 (m, 2H), -0.06 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 143.9, 143.0, 133.6, 123.4, 122.6, 120.3, 110.2, 74.2, 66.4, 17.6, -1.5. HRMS (ESI) m/z calcd for C₁₃H₂₁N₂OSi⁺ (M+H)⁺ 249.14177, found 249.14159.



tert-butyl 1H-benzo[d]imidazole-1-carboxylate (2ad)

According to General procedure A, **2ad** was obtained as white solid in 53% yield (34.7 mg), using EA /PE (1:1) as eluent. mp: 111 - 113 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 7.99 (d, J = 7.5 Hz, 1H), 7.78 (dd, J = 7.5, 1.6 Hz, 1H), 7.37 (pd, J = 7.3, 1.5 Hz, 2H), 1.70 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 148.1, 144.1, 142.1, 131.4 125.2, 124.3, 120.6, 114.4, 85.6, 28.1. HRMS (ESI) m/z calcd for C₁₂H₁₅N₂O₂⁺ (M+H)⁺ 219.11280, found 219.11235.



1-allyl-1H-benzo[d]imidazole (2ae)^[5]

According to **General procedure A**, **2ae** was obtained as colorless liquid in 72% yield (34.1 mg), using EA /PE (1:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.81 (dd, J = 6.6, 2.6 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.28 (dd, J = 5.7, 3.5 Hz, 2H), 6.05 – 5.93 (m, 1H), 5.28 (d, J = 10.3 Hz, 1H), 5.17 (d, J = 17.1 Hz, 1H), 4.76 (d, J = 5.4 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 143.8, 142.9, 133.8, 131.8, 122.9, 122.1, 120.3, 118.6, 109.9, 47.3.



1-(but-3-en-1-yl)-1H-benzo[d]imidazole (2af)^[6]

According to **General procedure A**, **2af** was obtained as colorless liquid in 87% yield (44.9 mg), using EA /PE (1:1) as eluent.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.18 (s, 1H), 7.60 (t, *J* = 8.7 Hz, 2H), 7.26 – 7.14 (m, 2H), 5.83 – 5.69 (m, 1H), 5.01 – 4.90 (m, 2H), 4.30 (t, *J* = 6.9 Hz, 2H), 2.54 (q, *J* = 6.9 Hz, 2H). ¹³C NMR

(100 MHz, DMSO-*d*₆) δ 144.5, 143.9, 135.2, 134.2, 122.7, 121.8, 119.9, 118.0, 110.9, 43.8, 34.1.



1-(pent-4-en-1-yl)-1H-benzo[d]imidazole (2ag)^[6]

According to **General procedure A**, **2ag** was obtained as colorless liquid in 61% yield (34.0 mg), using EA /PE (1:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.83 – 7.78 (m, 1H), 7.41 – 7.36 (m, 1H), 7.32 – 7.26 (m, 2H), 5.77 (ddt, J = 16.4, 9.8, 6.5 Hz, 1H), 5.10 – 5.00 (m, 2H), 4.16 (t, J = 7.0 Hz, 2H), 2.07 (q, J = 7.0 Hz, 2H), 1.97 (p, J = 7.0 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 143.7, 142.9, 136.6, 133.66, 122.8, 122.0, 120.3, 116.2, 109.6, 44.2, 30.5, 28.6.



1-(but-2-yn-1-yl)-1H-benzo[d]imidazole (2ah)

According to **General procedure A**, **2ah** was obtained as yellow liquid in 85% yield (43.4 mg), using EA/PE (1:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.81 (dd, *J* = 6.5, 2.1 Hz, 1H), 7.47 (dd, *J* = 6.6, 2.0 Hz, 1H), 7.31 (tt, *J* = 7.3, 5.6 Hz, 2H), 4.86 (q, *J* = 2.5 Hz, 2H), 1.85 (t, *J* = 2.5 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 143.9, 142.4, 133.5, 123.1, 122.4, 120.4, 109.8, 82.9, 71.5, 35.1, 3.6. HRMS (ESI) m/z calcd for C₁₁H₁₁N₂⁺ (M+H)⁺ 171.09167, found 171.09158.



1-(2-phenoxyethyl)-1H-benzo[d]imidazole (2ai)

According to **General procedure A**, **2ai** was obtained as white solid in 65% yield (46.4 mg), using EA/PE (1:1) as eluent. mp: 102 - 103 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.82 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.31 (qd, *J* = 7.4, 1.4 Hz, 2H), 7.28 – 7.21 (m, 3H), 4.55 (t, *J* = 5.2 Hz, 2H), 4.28 (t, *J* = 5.2 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 157.9, 143.6, 143.5, 133.8, 129.6, 123.1, 122.3, 121.6, 120.5, 114.5, 109.5, 66.0, 44.5. HRMS (ESI) m/z calcd for C₁₅H₁₅N₂O⁺ (M+H)⁺ 239.11789, found 239.11746.



(2R,3R,4R,5R)-2-(acetoxymethyl)-5-(5,6-dichloro-1H-benzo[d]imidazol-1-yl)tetrahydrofuran -3,4-diyl diacetate (2aj)^[9]

According to **General procedure A**, **2aj** was obtained as colorless liquid in 80% yield (103.5 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.90 (s, 1H), 7.77 (s, 1H), 7.26 (s, 1H), 6.01 (d, J = 6.2 Hz, 1H), 5.50 (t, J = 5.9 Hz, 1H), 5.41 (dd, J = 5.7, 3.6 Hz, 1H), 4.51 – 4.46 (m, 2H), 4.40 – 4.35 (m, 1H), 2.22 (s, 3H), 2.16 (s, 3H), 2.08 (s, 3H), 1.75 (s, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 170.2, 169.5, 169.2, 143.6, 142.5, 131.4, 127.8, 127.4, 121.8, 112.4, 87.1, 80.5, 72.7, 70.0, 62.8, 20.8, 20.5, 20.3.



(2R,3R,4S,5R)-2-(5,6-dichloro-1H-benzo[d]imidazol-1-yl)-5-(hydroxymethyl)tetrahydrofura n-3,4-diol (2ak)^[9]

According to **General procedure A**, **2ak** was obtained as white solid in 49% yield (44.9 mg), using EA /PE (4:1) as eluent.

¹H NMR (400 MHz, DMSO- d_6) δ 8.57 (s, 1H), 8.22 (s, 1H), 7.96 (s, 1H), 5.87 (d, J = 6.3 Hz, 1H), 5.50 (d, J = 6.5 Hz, 1H), 5.23 (t, J = 5.3 Hz, 2H), 4.29 (q, J = 6.1 Hz, 1H), 4.09 (td, J = 4.9, 3.1 Hz,

1H), 3.98 (t, J = 3.2 Hz, 1H), 3.64 (m, 2H). ¹³C NMR (100 MHz, DMSO- d_6) δ 145.4, 143.8, 132.5, 125.6, 125.1, 121.1, 114.1, 89.4, 86.2, 74.1, 70.4, 61.4.



1H-benzo[d]imidazole-2-d (D-2a)

According to **General procedure B**, **D-2a** was obtained as white solid in 97% yield (34.6 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 95%. mp: 170 - 171 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 12.45 (s, 1H), 8.20 (s, 0.05H), 7.57 (dd, J = 5.8, 3.3 Hz, 2H), 7.16 (dd, J = 6.0, 3.2 Hz, 2H).



5-methyl-1H-benzo[d]imidazole-2-d (D-2b)

According to **General procedure B**, **D-2b** was obtained as white solid in 87% yield (34.7 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 91%. mp: 106 - 108 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 8.12 (s, 0.09H), 7.44 (d, J = 8.1 Hz, 1H), 7.34 (s, 1H), 6.98 (d, J = 8.1 Hz, 1H), 2.38 (s, 3H).



5-methoxy-1H-benzo[d]imidazole-2-d (D-2c)

According to **General procedure B**, **D-2c** was obtained as white solid in 93% yield (34.7 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 94%. mp: 126 - 127 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.09 (s, 0.06H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.75 (s, 3H).



5-(tert-butyl)-1H-benzo[d]imidazole-2-d (D-2d)

According to **General procedure B**, **D-2d** was obtained as white solid in 99% yield (52.0 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 92%. mp: 136 - 138 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 8.14 (s, 0.08H), 7.53 – 7.44 (m, 2H), 7.25 (dd, J = 8.5, 1.9 Hz,



5-(difluoromethoxy)-1H-benzo[d]imidazole-2-d (D-2e)

According to **General procedure B**, **D-2e** was obtained as white solid in 90% yield (49.4 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 92%. mp: 80 -82 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.26 (s, 0.08H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 2.3 Hz, 1H), 7.18 (t, *J* = 74.8 Hz, 1H), 7.02 (dd, *J* = 8.7, 2.4 Hz, 1H).



5-(trifluoromethyl)-1H-benzo[d]imidazole-2-d (D-2f)

According to **General procedure B**, **D-2f** was obtained as white solid in 85% yield (49.4 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 96%. mp: $105 - 106^{\circ}$ C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.44 (s, 0.04H), 7.95 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H).

5-fluoro-1H-benzo[d]imidazole-2-d (D-2g)

According to General procedure B, D-2g was obtained as white solid in 87% yield (35.5 mg),

using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 93%. mp: 113 – 114 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.53 (s, 1H), 8.23 (s, 0.07H), 7.56 (dd, *J* = 8.8, 4.9 Hz, 1H), 7.37 (dd, *J* = 9.6, 2.5 Hz, 1H), 7.02 (m, 1H).



5-chloro-1H-benzo[d]imidazole-2-d (D-2h)

According to **General procedure B**, **D-2h** was obtained as white solid in 54% yield (24.9 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 95%. mp: 98 - 100 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 8.44 (s, 0.05H), 7.95 (s, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7.50 (d, J = 8.5 Hz, 1H).



5-bromo-1H-benzo[d]imidazole-2-d (D-2i)

According to **General procedure B**, **D-2i** was obtained as white solid in 85% yield (35.5 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 93%. mp: 118 - 121 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.25 (s, 0.07H), 7.78 (d, *J* = 1.9 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.30 (dd, *J* = 8.5, 1.9 Hz, 1H).



(1H-benzo[d]imidazol-5-yl-2-d)(phenyl)methanone (D-2j)

According to **General procedure B**, **D-2j** was obtained as white solid in 72% yield (48.2 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 94%. mp: 131 - 133 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.43 (s, 0.06H), 7.96 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 3H), 7.69 – 7.61 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 2H).



methyl 1H-benzo[d]imidazole-5-carboxylate-2-d (D-2k)

According to **General procedure B**, **D-2k** was obtained as white solid in 80% yield (42.5 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 92%. mp: 114 - 115 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.80 (s, 1H), 8.39 (s, 0.08H), 8.20 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.6 Hz, 1H), 3.84 (s, 3H).



1H-benzo[d]imidazole-5-carbonitrile-2-d (D-2l)

According to **General procedure B**, **D-21** was obtained as white solid in 47% yield (20.3 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 93%. mp: 244 - 248 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.98 (s, 1H), 8.46 (s, 0.07H), 8.15 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H).



tert-butyl (1H-benzo[d]imidazol-5-yl-2-d)carbamate (D-2m)

According to **General procedure B**, **D-2m** was obtained as white solid in 70% yield (42.5 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 93%. mp: 205 - 206 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 12.27 (s, 1H), 9.29 (s, 1H), 8.09 (s, 0.07H), 7.79 (s, 1H), 7.44 (d, J = 8.7 Hz, 1H), 7.18 (d, J = 8.5 Hz, 1H), 1.46 (s, 9H).



7-methyl-1H-benzo[d]imidazole-2-d (D-2n)

According to General procedure B, D-2n was obtained as white solid in 43% yield (17.2 mg),

using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 95%. mp: 124 – 127 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 8.18 (s, 0.05H), 7.37 (d, J = 8.0 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 7.1 Hz, 1H), 2.49 (s, 3H).

6-methoxy-3H-imidazo[4,5-b]pyridine-2-d (D-2o)

According to **General procedure B**, **D-2o** was obtained as white solid in 47% yield (21.2 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 94%. mp: 162 - 163 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 12.75 (s, 1H), 8.20 (s, 0.06H), 7.90 (d, J = 8.5 Hz, 1H), 6.65 (d, J = 8.6 Hz, 1H), 3.85 (s, 3H).



5,6-difluoro-1H-benzo[d]imidazole-2-d (D-2p)

According to **General procedure B**, **D-2p** was obtained as white solid in 98% yield (45.0 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 96%. mp: 189–191 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 12.62 (s, 1H), 8.26 (s, 0.04H), 7.62 (d, J = 34.5 Hz, 2H).



5,6-dichloro-1H-benzo[d]imidazole-2-d (D-2q)

According to **General procedure B**, **D-2q** was obtained as white solid in 80% yield (44.9 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 92%. mp: 248 - 249 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.74 (s, 1H), 8.33 (s, 0.08H), 7.85 (s, 2H).

5,6-dibromo-1H-benzo[d]imidazole-2-d (D-2r)

According to General procedure B, D-2r was obtained as white solid in 35% yield (29.1 mg),

using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 92%. mp: 230 - 232 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.89 (s, 1H), 8.29 (s, 0.08H), 7.99 (s, 2H).



5,6-Dimethylbenzimidazole-2-d₁ (D-2s)

According to **General procedure B**, **D-2s** was obtained as white solid in 82% yield (36.2 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 97%. mp: 193 - 195 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.19 (s, 1H), 8.03 (s, 0.03H), 7.32 (s, 2H), 2.27 (s, 6H).



1H-naphtho[2,3-d]imidazole-2-d (D-2t)

According to **General procedure B**, **D-2t** was obtained as white solid in 79% yield (40.1 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 95%. mp: 144 - 145 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 8.47 (s, 0.05H), 8.10 (s, 2H), 7.98 (dd, J = 6.4, 3.3 Hz, 2H), 7.35 (dd, J = 6.5, 3.2 Hz, 2H).



1-methyl-1H-benzo[d]imidazole-2-d (D-2v)

According to **General procedure B**, **D-2v** was obtained as colorless liquid in 65% yield (25.9 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 92%.. ¹H NMR (400 MHz, DMSO- d_6) δ 8.16 (s, 0.08H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.21 – 7.16 (m, 1H), 3.81 (s, 3H).



1-ethyl-1H-benzo[d]imidazole-2-d (D-2w)

According to **General procedure B**, **D-2w** was obtained as colorless liquid in 85% yield (37.5 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 93%. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 0.07H), 7.83 – 7.78 (m, 1H), 7.42 – 7.37 (m, 1H), 7.29 (m, 2H), 4.21 (q, *J* = 7.3 Hz, 2H), 1.53 (t, *J* = 7.3 Hz, 3H).



1-isopropyl-1H-benzo[d]imidazole-2-d (D-2x)

According to **General procedure B**, **D-2x** was obtained as colorless liquid in 97% yield (46.9 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 94%. ¹H NMR (400 MHz, DMSO- d_6) δ 8.31 (s, 0.06H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.20 (dt, *J* = 20.5, 7.5 Hz, 2H), 4.73 (m, 1H), 1.51 (dd, *J* = 6.8, 2.2 Hz, 6H)



1-butyl-1H-benzo[d]imidazole-2-d (D-2y)

According to **General procedure B**, **D-2y** was obtained as colorless liquid in 99% yield (52.0 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 95%. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 0.05H), 7.80 (dd, *J* = 6.9, 2.2 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.31 – 7.24 (m, 2H), 4.14 (t, *J* = 7.1 Hz, 2H), 1.84 (p, *J* = 7.3 Hz, 2H), 1.34 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).



1-hexyl-1H-benzo[d]imidazole-2-d (D-2z)

According to **General procedure B**, **D-2z** was obtained as colorless liquid in 68% yield (41.4 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 93%.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 0.07H), 7.80 (dd, *J* = 6.4, 2.4 Hz, 1H), 7.39 (dd, *J* = 6.3, 2.1 Hz, 1H), 7.32 – 7.26 (m, 2H), 4.15 (t, *J* = 7.2 Hz, 2H), 1.87 (p, *J* = 7.0 Hz, 2H), 1.29 (d, *J* = 9.1 Hz, 6H), 0.89 – 0.84 (m, 3H).



1-benzyl-1H-benzo[d]imidazole-2-d (D-2aa)

According to **General procedure B**, **D-2aa** was obtained as white solid in 72% yield (45.1 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 92%. mp: 123 - 126 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s,0.08H), 7.81 (d, J = 7.8 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.25 – 7.20 (m, 2H), 7.16 (d, J = 6.3 Hz, 2H), 5.33 (s, 2H).



1-phenyl-1H-benzo[d]imidazole-2-d (D-2ab)

According to **General procedure B**, **D-2ab** was obtained as colorless liquid in 93% yield (54.4 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 94%. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 0.06H), 7.90 – 7.87 (m, 1H), 7.60 – 7.43 (m, 7H), 7.36 – 7.31 (m, 2H).



1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole-2-d (D-2ac)

According to **General procedure B**, **D-2ac** was obtained as white solid in 88% yield (54.4 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 92%.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 0.07H), 7.84 – 7.79 (m, 1H), 7.54 (dd, J = 6.3, 2.2

Hz, 1H), 7.36 – 7.28 (m, 2H), 5.53 (s, 2H), 3.53 – 3.47 (m, 2H), 0.92 – 0.86 (m, 2H), -0.06 (s, 9H).



1-allyl-1H-benzo[d]imidazole-2-d (D-2ae)

According to **General procedure B**, **D-2ae** was obtained as colorless liquid in 74% yield (35.3 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 92%.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 (s, 0.08H), 7.85 – 7.80 (m, 1H), 7.41 – 7.36 (m, 1H), 7.33 – 7.27 (m, 2H), 6.01 (m, 1H), 5.30 (d, *J* = 10.3 Hz, 1H), 5.19 (d, *J* = 17.7 Hz, 1H), 4.80 (d, *J* = 5.2 Hz, 2H).



1-(but-3-en-1-yl)-1H-benzo[d]imidazole-2-d (D-2af)

According to **General procedure B**, **D-2af** was obtained as colorless liquid in 67% yield (37.8 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 94%. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.85 (s, 0.05H), 7.80 – 7.76 (m, 1H), 7.37 (dd, *J* = 6.5, 2.4 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.26 – 7.22 (m, 1H), 5.71 (m, 1H), 5.06 – 4.96 (m, 2H), 4.17 (t, *J* = 7.0 Hz, 2H), 2.57 (q, *J* = 6.9 Hz, 2H).



1-(pent-4-en-1-yl)-1H-benzo[d]imidazole-2-d (D-2ag)

According to **General procedure B**, **D-2ag** was obtained as colorless liquid in 95% yield (48.7mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 93%. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 0.07H), 7.80 (dd, *J* = 6.0, 2.7 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.31 – 7.23 (m, 2H), 5.81 – 5.70 (m, 1H), 5.08 – 5.00 (m, 2H), 4.15 (t, *J* = 7.0 Hz, 2H), 2.06 (q, *J* = 7.0, 6.6 Hz, 2H), 1.96 (p, *J* = 7.0 Hz, 2H).



1-(but-2-yn-1-yl)-1H-benzo[d]imidazole-2-d (D-2ah)

According to **General procedure B**, **D-2ah** was obtained as yellow liquid in 91% yield (46.7 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 93%. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 0.07H), 7.81 (dd, *J* = 6.6, 2.3 Hz, 1H), 7.47 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.31 (tt, *J* = 7.3, 5.6 Hz, 2H), 4.86 (q, *J* = 2.4 Hz, 2H), 1.85 (t, *J* = 2.5 Hz, 3H).



1-(2-phenoxyethyl)-1H-benzo[d]imidazole-2-d (D-2ai)

According to **General procedure B**, **D-2ai** was obtained as white solid in 72% yield (51.6 mg), using EA /PE (1:1) as eluent. D incorporation was determined by ¹H NMR to be 94%. mp: 97 - 99 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 0.06H), 7.81 (d, *J* = 7.0 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.23 (d, *J* = 9.3 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 2H), 4.55 (t, *J* = 5.1 Hz, 2H), 4.28 (t, *J* = 5.2 Hz, 2H).



(2R,3R,4S,5R)-2-(5,6-dichloro-1H-benzo[d]imidazol-1-yl-2-d)-5-(hydroxymethyl)tetrahydrof uran-3,4-diol (D-2ak)

According to **General procedure B**, **D-2ak** was obtained as colorless liquid in 88% yield (48.7 mg), using EA /PE (4:1) as eluent. D incorporation was determined by ¹H NMR to be 86%. mp: 230 - 235 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 8.23 (s, 1H), 7.96 (s, 1H), 5.87 (d, J = 6.3 Hz, 1H), 5.55 (s, 1H), 5.33 – 5.20 (m, 2H), 4.29 (t, J = 5.7 Hz, 1H), 4.12 – 4.06 (m, 1H), 3.97 (q, J = 3.2 Hz, 1H), 3.63 (m, 2H).

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7. NMR Spectra







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)




¹H NMR spectrum of compound **2f**



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)





¹H NMR spectrum of compound **2h**







¹H NMR spectrum of compound **2i**







¹H NMR spectrum of compound **2k**



¹H NMR spectrum of compound **2**l





¹H NMR spectrum of compound **2m**









¹H NMR spectrum of compound **2p**





















S55



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)









¹H NMR spectrum of compound **2aa**



¹H NMR spectrum of compound **2ab**



¹H NMR spectrum of compound **2ac**











¹H NMR spectrum of compound **2af**











¹H NMR spectrum of compound **2ai**





¹H NMR spectrum of compound **2ak**



¹H NMR spectrum of compound **D-2a**




¹H NMR spectrum of compound **D-2e**







¹H NMR spectrum of compound **D-2i**



















S80



9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 f1 (ppm)



S82



¹H NMR spectrum of compound **D-2ab**





¹H NMR spectrum of compound **D-2ae**







¹H NMR spectrum of compound **D-2ai**

