Synthesis of Benzimidazole-Fused Heterocycles by Intramolecular Oxidative C–N Bond Formation Using Hypervalent Iodine Reagents

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Abstract: A straightforward approach by dehydrogenative C–N coupling between aryl C–H and N–H bonds using a hypervalent iodine reagent under mild conditions offers a versatile and convenient method for synthesizing various benzimidazole-fused heterocycles.

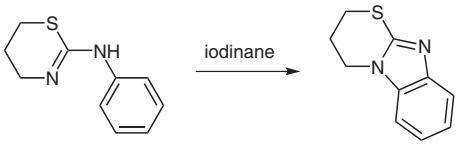
Key words: hypervalent iodine reagent, C–N bond forming cyclization, benzimidazole-fused heterocycles, straightforward synthesis, mild conditions

For the synthesis of aza-heterocycles, oxidative intramolecular C–N bond-forming cyclization is one of the most straightforward methods. In the last decade,[1] since Breslow reported the first intramolecular catalytic nitrene C–H insertion, one such type cyclization,[1a] hypervalent iodine-mediated reaction, has attracted considerable attention because of its low toxicity, high chemoselectivity, and mild conditions. For example, Du Bois et al. pioneered intramolecular oxidative C–N bond formation to afford oxazolidinones[1b] and cyclic sulfamates[1c] from a combination of $PhI(OAc)_2$, magnesium oxide, and a rhodium(II) catalyst. Togo et al. reported the synthesis of 2,1-benzothiazine derivatives from sulfonamides with PhI(OH)OTs.[1d] Nishiyama et al. demonstrated the synthesis of azaspiro- or quinolinone-type products from $PhI(OCH_2CF_3)_2$ generated electrochemically from iodobenzene.[1e]

Benzimidazole-fused heterocycles have appealing biological and pharmaceutical properties.[2] To date, however, very little is known about their systematic synthesis. We describe herein the synthesis of various benzimidazole-fused heterocycles from *N*-(1-azaheterocycle-2-yl)aniline derivatives via oxidative intramolecular C–N bond formation using hypervalent iodine reagents.

Initially, we examined the efficiency of various hypervalent iodine reagents for the synthesis of 3,4-dihydro-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (**2a**) from 2-anilino-4*H*-5,6-dihydro-1,3-thiazine (**1a**). For treatment of **1a** with a reagent (1.1 equiv) in acetonitrile from 0 °C to room temperature for three hours to give **2a**, best results were obtained using the reagent PhI(OH)OTs (Table 1, entry 4, 82%). On the other hand, use of PhI=NTs (1.1 equiv) gave no reaction (Table 1, entry 5). However, intriguingly, satisfactory results were obtained using a combination of reagent PhI=NTs (1.1 equiv) and a catalytic amount of $Cu(OTf)_2$ (5 mol%) (Table 1, entry 6, 74%).[3] Moreover, satisfactory results were obtained using two equivalents of reagent such as $PhI(OCOCF_3)_2$ (Table 1, entry 3, 80%), and unsatisfactory results were obtained using iodosobenzene and $PhI(OAc)_2$ (Table 1, entries 1 and 2).

Table 1 Screening of Hypervalent Iodine Reagents



1a **2a**

Entry	Reagent (equiv)		Conditions	Yield (%)
1	PhI=O (2)		CH_2Cl_2 r.t., 43 h	5
2	$PhI(OAc)_2$ (2)		CH_2Cl_2 r.t., 45 h	51
3	$PhI(OCOCF_3)_2$ (2)	**A**	CH_2Cl_2 0 °C to r.t., 43 h	80
4	PhI(OH)OTs (1.1)	**B**	MeCN 0 °C to r.t., 3 h	82
5	PhI=NTs (1.1)		CH_2Cl_2 0 °C to r.t., 52 h	0
6	PhI=NTs (1.1) $Cu(OTf)_2$ (5 mol%)	**C**	CH_2Cl_2 –40 to 0 °C, 5 h	74

To confirm the generality of this hypervalent iodine-mediated reaction, various *N*-dihydrothiazin-2-yl anilines **1** and *N*-dihydrothiazol-2-yl anilines **3** were examined under three reagent conditions: using 2.0 equivalents of the reagent $PhI(OCOCF_3)_2$ (reagent condition **A**), 1.1 equivalents of the reagent PhI(OH)OTs (reagent condition **B**), and 1.1 equivalents of the reagent PhI=NTs and a catalytic amount of $Cu(OTf)_2$ (reagent condition **C**) (Table 2).

Reactions of **1b** having an *o*-toluidine group (R^1 = Me; R^2 = R^3 = H) by reagent conditions **A**, **B**, and **C** gave 3,4-dihydro-9-methyl-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (**2b**) in high yields (Table 2, entries 1–3). On the other hand, cyclization reactions of **1c–e** having a methyl, methoxy, and fluoro group at the *meta*-position (R^2 = Me, OMe, F; R^1 = R^3 = H) gave **2** and/or **2′** (Table 2, entries 4–12). Moreover, reactions of **1f** and **1g** having a *para* sub-

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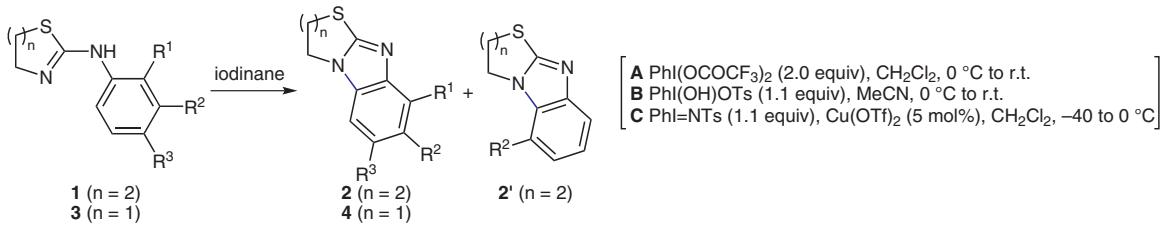
Table 2 Reaction of *N*-Dihydrothiazin-2-yl Anilines **1** and *N*-Dihydrothiazol-2-yl Anilines **3**



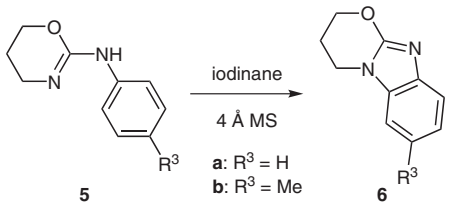
Entry	Substrate	R^1	R^2	R^3	Method	Time (h)	Yield (%)		
							2/4	**2′**	**1/3** (recovered)
1	**1b**	Me	H	H	A	6	79		
2	**1b**	Me	H	H	B	1	91		
3	**1b**	Me	H	H	C	6	81		
4	**1c**	H	Me	H	A	29	26	21	19
5	**1c**	H	Me	H	B	4	24	20	
6	**1c**	H	Me	H	C	4	38	38	
7	**1d**	H	OMe	H	A	21	32	29	
8	**1d**	H	OMe	H	B	10	23		47
9	**1d**	H	OMe	H	C	9	18	16	
10	**1e**	H	F	H	A	26	21	13	17
11	**1e**	H	F	H	B	20	trace	trace	61
12	**1e**	H	F	H	C	20	22	22	
13	**1f**	H	H	Me	A	67	60		
14	**1f**	H	H	Me	B	5	66		
15	**1f**	H	H	Me	C	3	64		
16	**1g**	H	H	OMe	A	4	44		
17	**1g**	H	H	OMe	B	7	55		
18	**1g**	H	H	OMe	C	4	24		
19	**3a**	H	H	H	A	47	34		17
20	**3a**	H	H	H	B	8	78		
21	**3a**	H	H	H	C	22	40		
22	**3b**	H	H	Me	A	91	52		
23	**3b**	H	H	Me	B	20	71		
24	**3b**	H	H	Me	C	30	67		

stituent (R^3 = Me, OMe; $R^1 = R^2$ = H) gave **2f** and **2g** in moderate yields (Table 2, entries 13–18). Similarly, reactions of *N*-dihydrothiazol-2-yl anilines **3a** and **3b** gave the corresponding **4a** and **4b**, respectively (Table 2, entries 19–24).

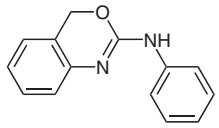
To extend the generality of this reaction, the syntheses of other benzimidazole-fused heterocycles were investigated. Hypervalent iodine-mediated reactions of *N*-oxazin-2-yl anilines **5** gave the corresponding benzimidazoles **6** (Table 3). The addition of 4 Å molecular sieves facilitated the reactions of **5a** and **5b** to give higher yields of **6a** and **6b**, which were sensitive to acid (Table 3, entries 3, 4),[4] but did not affect the reactions of **5c** (Table 3, entries 8–10).

The reactions of compounds **7** having a pyridine-modified substituent were also examined (Table 4). Pyrido[1,2-*a*]benzimidazole derivatives **8a**,**b** and dipyrido[1,2-*a*:2′,3′-*d*]imidazole **8c** were obtained in moderate yields (Table 4, entries 1–9).

Table 3 Reaction of *N*-Oxazin-2-yl Anilines **5**



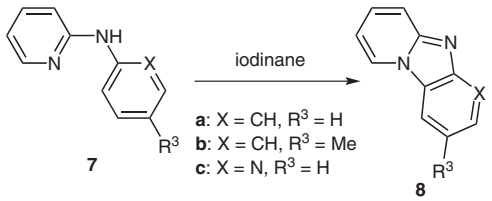
5 **6**

Entry	Substrate	Method	Time (h)	Yield (%)
1	**5a**	A	43	0[a]
2	**5a**	B	27	76
3	**5a**	C	5	54
4	**5a**	C[b]	17	13
5	**5b**	A	32	33
6	**5b**	B	3	86
7	**5b**	C	9	54
8		A[b]	25	34[c]
9		B[b]	3	79
10		C[b]	7	46

5c

[a] Substrate **5a** was recovered (91%).
[b] Without 4 Å molecular sieves.
[c] Substrate **5c** was recovered (40%).

Table 4 Reaction of Pyridine-Modified Compounds **7**



7 **8**

Entry	Substrate	Method	Time (h)	Yield (%)
1	**7a**	A	6	33
2	**7a**	B	2	52
3	**7a**	C	6	30
4	**7b**	A	4	62
5	**7b**	B	2	73
6	**7b**	C	4	44
7	**7c**	A	28	65
8	**7c**	B	4	74
9	**7c**	C	24	44

In conclusion, we have achieved the synthesis of benzimidazole-fused heterocycles using hypervalent iodine reagents. The PhI(OH)OTs-mediated condition (reagent condition **B**) tends to be efficient depending on the substrate. We are extending this work by investigating hypervalent iodine-mediated oxidative intramolecular C–N bond-forming cyclization.

All melting points were determined on a Yanaco melting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi 270-30 or a Horiba FT-710 model spectrophotometer. ^{1}H and ^{13}C NMR spectral data were recorded on a Bruker AV 600, a Jeol JNM-EX 500, or a Jeol JNM-EX 300 instrument. Chemical shifts (δ) are quoted in ppm using TMS (δ = 0 ppm) as internal standard for ^{1}H NMR spectroscopy, and $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR spectroscopy. Mass spectra were measured on a Bruker Daltonics microTOF or a Hitachi double-focusing M-80B spectrometer. Elemental analyses were performed with a Yanaco CHN-Coder MT-6 model analyzer. Column chromatography was conducted on silica gel (Kanto Chemical Co. or Merck Co. Ltd). All reactions were performed under an argon atmosphere.

The starting materials **1**, **3**, and **5** were prepared from the corresponding amino alcohol derivatives and isothiocyanates by Loev's protocol[5a] or Heinelt's protocol.[5b] Preparation and/or analytical data for known compounds have been reported.[6]

Compounds 1 and 3; 2-Anilino-4*H*-5,6-dihydro-1,3-thiazine (1a);[5a] Typical Procedure

A mixture of 3-aminopropan-1-ol (0.61 mL, 8.0 mmol) and phenyl isothiocyanate (1.0 mL, 8.4 mmol) in THF (20 mL) was stirred at r.t. for 2 h. After evaporation, the residual crystals were collected by suction filtration. The thiourea derivative was dissolved in concd HCl (3.0 mL) and then heated at 80 °C for 3 h. After cooling to r.t., the mixture was made alkaline by the addition of aq 2.5 M NaOH (15 mL) and then filtered by suction to afford **1a** (1.3 g, 82% over 2 steps).

1,3-Oxazin-2-amines 5; *N*-(*p*-Tolyl)-5,6-dihydro-4*H*-1,3-oxazin-2-amine (5b);[5b] Typical Procedure

A mixture of 3-aminopropan-1-ol (0.61 mL, 8.0 mmol) and 4-methylphenyl isothiocyanate (1.3 g, 8.4 mmol) in THF (20 mL) was stirred at r.t. for 2 h. After evaporation, the residual crystals were collected by suction filtration. The thiourea derivative was dissolved in THF (20 mL) and an aqueous solution of NaOH (0.80 g, 20.0 mmol) in H_2O (10 mL) was added with stirring at r.t. Then a solution of TsCl (1.9 g, 10.0 mmol) in THF (20 mL) was slowly added and the mixture was stirred at the same temperature for 3 h. After completion of the reaction, the solvent was evaporated and the mixture was extracted with EtOAc (3 × 20 mL). The combined extracts were washed with brine (20 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc–Et_3N, 100:1) to afford **5b** (0.80 g, 53% over 2 steps); colorless crystals; mp 117–118 °C.

IR (KBr): 1672, 1604, 1510, 1253 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.81–1.91 (m, 2 H), 2.25 (s, 3 H), 3.34 (dd, *J* = 6.1, 6.1 Hz, 2 H), 4.17 (dd, *J* = 5.4, 5.4 Hz, 2 H), 6.96–7.05 (m, 4 H), 7.12 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.4, 21.8, 40.1, 65.7, 120.8 (2 ×), 128.9 (2 ×), 130.7, 140.0, 150.2.

HRMS-EI: *m/z* [M]$^+$ calcd for $C_{11}H_{14}N_2O$: 190.1106; found: 190.1103.

Reagent Condition A; 3,4-Dihydro-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2a);[7] Typical Procedure (Table 1, Entry 3)
To a solution of **1a** (58 mg, 0.30 mmol) in CH_2Cl_2 (10 mL) was added $PhI(OCOCF_3)_2$ (260 mg, 0.60 mmol) at 0 °C. The reaction mixture was stirred for 1 h, then the temperature was raised slowly to r.t. After stirring for 42 h, the reaction was quenched with sat. aq $NaHCO_3$ (20 mL), and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were washed with brine (10 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc–Et_3N, 100:1) to afford **2a** (46 mg, 80%).

Reagent Condition B; 3,4-Dihydro-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2a);[7] Typical Procedure; (Table 1, Entry 4)
To a solution of **1a** (58 mg, 0.30 mmol) in MeCN (10 mL) was added PhI(OH)OTs (130 mg, 0.33 mmol) at 0 °C. The reaction mixture was stirred for 1 h, then the temperature was raised slowly to r.t. After stirring for 2 h, the reaction was quenched with sat. aq $NaHCO_3$ (20 mL), and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were washed with brine (10 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc–Et_3N, 100:1) to afford **2a** (47 mg, 82%).

Reagent Condition C; 3,4-Dihydro-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2a);[7] Typical Procedure (Table 1, Entry 6)
To a solution of **1a** (58 mg, 0.30 mmol) in CH_2Cl_2 (10 mL) were added PhI=NTs (120 mg, 0.33 mmol) and a catalytic amount of $Cu(OTf)_2$ (5.4 mg, 0.015 mmol) at –40 °C. The reaction mixture was stirred at 0 °C for 5 h. The reaction was quenched with sat. aq $NaHCO_3$ (20 mL), and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc–Et_3N, 100:1) to afford **2a** (42 mg, 74%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38–2.50 (m, 2 H), 3.19 (dd, *J* = 5.7, 5.6 Hz, 2 H), 4.14 (dd, *J* = 6.1, 6.0 Hz, 2 H), 7.16–7.26 (m, 3 H), 7.61 (d, *J* = 7.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.3, 25.7, 42.1, 107.6, 119.9, 121.3, 122.3, 135.5, 142.7, 146.8.

3,4-Dihydro-9-methyl-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2b)
Colorless crystals; mp 78–79 °C.

IR (KBr): 1598, 1430, 1400, 1309 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37–2.45 (m, 2 H), 2.61 (s, 3 H), 3.17 (dd, *J* = 5.7, 5.5 Hz, 2 H), 4.10 (dd, *J* = 6.1, 5.9 Hz, 2 H), 6.70–7.09 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.6, 23.3, 25.8, 42.5, 105.2, 121.3, 122.7, 127.8, 135.3, 141.9, 145.9.

HRMS-EI: m/z $[M]^+$ calcd for $C_{11}H_{12}N_2S$: 204.0721; found: 204.0719.

3,4-Dihydro-8-methyl-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2c)
Colorless crystals; mp 129–130 °C.

IR (KBr): 1591, 1432, 1391, 1270 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.38–2.43 (m, 2 H), 2.44 (s, 3 H), 3.17 (dd, *J* = 5.6, 5.5 Hz, 2 H), 4.09 (dd, *J* = 6.1, 5.9 Hz, 2 H), 6.97 (d, *J* = 7.9 Hz, 1 H), 7.04–7.06 (m, 1 H), 7.38 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.5, 23.2, 25.0, 42.3, 117.8, 122.0, 122.5, 131.8, 133.6, 142.9, 146.5.

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{11}H_{12}N_2S$: 204.0721; found: 204.0718.

3,4-Dihydro-6-methyl-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2′c)
Colorless crystals; mp 129–130 °C.

IR (KBr): 1591, 1433, 1396, 1271 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.38–2.43 (m, 2 H), 2.63 (s, 3 H), 3.12 (dd, *J* = 5.6, 5.6 Hz, 2 H), 4.48 (dd, *J* = 5.9, 5.9 Hz, 2 H), 6.84 (d, *J* = 7.4 Hz, 1 H), 7.04–7.06 (m, 1 H), 7.42 (d, *J* = 7.9 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 18.8, 21.5, 25.7, 45.1, 107.1, 115.9, 119.9, 124.0, 134.2, 142.9, 146.5.

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{11}H_{12}N_2S$: 204.0721; found: 204.0723.

3,4-Dihydro-8-methoxy-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2d)
Colorless crystals; mp 180–181 °C.

IR (KBr): 1616, 1589, 1425, 1151 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42–2.49 (m, 2 H), 3.21 (t, *J* = 5.7 Hz, 2 H), 3.84 (s, 3 H), 4.14 (dd, *J* = 6.1, 6.0 Hz, 2 H), 6.81 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.09 (d, *J* = 8.8 Hz, 1 H), 7.12 (d, *J* = 2.4 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 23.4, 25.7, 42.5, 55.9, 101.2, 107.9, 110.6, 130.3, 143.7, 146.7, 156.3.

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{11}H_{12}N_2OS$: 220.0670; found: 220.0670.

3,4-Dihydro-6-methoxy-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2′d)
Brown crystals; mp 118–119 °C.

IR (KBr): 1610, 1587, 1423, 1282 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36–2.44 (m, 2 H), 3.17 (dd, *J* = 5.9, 5.5 Hz, 2 H), 3.90 (s, 3 H), 4.60 (dd, *J* = 5.9, 5.9 Hz, 2 H), 6.59–6.62 (m, 1 H), 7.08 (dd, *J* = 8.1, 8.1 Hz, 1 H), 7.21 (dd, *J* = 8.1, 0.9 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 23.9, 25.6, 45.5, 55.6, 102.9, 111.3, 122.3, 125.0, 144.6, 146.1, 146.5.

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{11}H_{12}N_2OS$: 220.0670; found: 220.0677.

3,4-Dihydro-8-fluoro-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2e)
Colorless solid; mp 144–145 °C.

IR (KBr): 1475, 1432, 1400, 1137 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.46–2.51 (m, 2 H), 3.23 (t, *J* = 5.6 Hz, 2 H), 4.18 (dd, *J* = 6.1, 5.9 Hz, 2 H), 6.93 (ddd, *J* = 9.0, 8.9, 2.3 Hz, 1 H), 7.12 (dd, *J* = 8.9, 4.4 Hz, 1 H), 7.33 (dd, *J* = 9.5, 2.3 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 23.3, 25.7, 42.6, 104.3 (d, *J* = 24.2 Hz), 107.7 (d, *J* = 9.9 Hz), 109.2 (d, *J* = 26.4 Hz), 132.2, 143.3 (d, *J* = 13.2 Hz), 148.3, 159.5 (d, *J* = 237.1 Hz).

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{10}H_9FN_2S$: 208.0470; found: 208.0472.

3,4-Dihydro-6-fluoro-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2′e)
Colorless crystals; mp 119–120 °C.

IR (KBr): 1494, 1423, 1398, 1274 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.45–2.50 (m, 2 H), 3.23 (dd, *J* = 5.6, 5.6 Hz, 2 H), 4.51 (dd, *J* = 5.9, 5.9 Hz, 2 H), 6.85 (dd, *J* = 11.4, 8.1 Hz, 1 H), 7.09 (ddd, *J* = 8.1, 8.1, 5.0 Hz, 1 H), 7.34 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 23.6, 25.6, 45.0, 107.6 (d, *J* = 17.6 Hz), 114.1 (d, *J* = 4.4 Hz), 122.2 (d, *J* = 6.6 Hz), 123.5 (d, *J* = 9.9 Hz), 145.9 (d, *J* = 3.3 Hz), 147.5, 148.5 (d, *J* = 244.8 Hz).

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{10}H_9FN_2S$: 208.0470; found: 208.0468.

3,4-Dihydro-7-methyl-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2f)
Colorless crystals; mp 184–186 °C.

IR (KBr): 1681, 1434, 1405 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 2.37–2.48 (m, 2 H), 3.14–3.20 (m, 2 H), 4.08 (dd, *J* = 5.9, 5.9 Hz, 2 H), 6.97 (s, 1 H), 7.02 (d, *J* = 8.2 Hz, 1 H), 7.47 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 23.4, 25.7, 42.4, 107.8, 117.4, 123.6, 131.3, 135.7, 140.8, 145.9.

Anal. Calcd for $C_{11}H_{12}N_2S$: C, 64.67; H, 5.92; N, 13.71. Found: C, 64.71; H, 6.14; N, 13.31.

3,4-Dihydro-7-methoxy-2*H*-[1,3]thiazino[3,2-*a*]benzimidazole (2g)
Brown crystals; mp 169–171 °C.

IR (KBr): 1618, 1589, 1438, 1214 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.40–2.45 (m, 2 H), 3.17 (dd, *J* = 5.8, 5.5 Hz, 2 H), 3.83 (s, 3 H), 4.06 (dd, *J* = 6.1, 5.8 Hz, 2 H), 6.65 (d, *J* = 2.4 Hz, 1 H), 6.83 (dd, *J* = 8.6, 2.4 Hz, 1 H), 7.47 (d, *J* = 8.6 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.4, 25.7, 42.5, 55.8, 92.3, 110.5, 118.2, 136.0, 137.1, 145.2, 155.6.

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{11}H_{12}N_2OS$: 220.0670; found: 220.0672.

2,3-Dihydrothiazolo[3,2-*a*]benzimidazole (4a)[8]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.90 (dd, *J* = 7.3, 7.1 Hz, 2 H), 4.25 (dd, *J* = 7.3, 7.1 Hz, 2 H), 7.15–7.26 (m, 3 H), 7.58–7.62 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 34.6, 43.7, 108.7, 118.7, 121.7, 121.8, 133.7, 149.3, 158.6.

2,3-Dihydro-6-methylthiazolo[3,2-*a*]benzimidazole (4b)
Colorless crystals; mp 141–142 °C.

IR (KBr): 1614, 1477, 1392, 1251 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 3.85 (dd, *J* = 7.2, 7.2 Hz, 2 H), 4.12 (dd, *J* = 7.2, 7.2 Hz, 2 H), 6.94 (s, 1 H), 6.99 (d, *J* = 8.1 Hz, 1 H), 7.46 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 34.7, 43.7, 109.0, 118.2, 123.2, 131.6, 133.8, 147.4, 157.9.

Anal. Calcd for $C_{10}H_{10}N_2S$: C, 63.13; H, 5.30; N, 14.72. Found: C, 63.31; H, 5.44; N, 14.44.

3,4-Dihydro-2*H*-[1,3]oxazino[3,2-*a*]benzimidazole (6a)[9]
^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.29–2.33 (m, 2 H), 4.08 (dd, *J* = 6.4, 6.4 Hz, 2 H), 4.49 (dd, *J* = 5.3, 5.3 Hz, 2 H), 7.10–7.19 (m, 2 H), 7.27–7.29 (m, 1 H), 7.52 (d, *J* = 7.9 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 39.7, 66.7, 107.6, 118.1, 120.6, 122.2, 133.0, 140.0, 154.6.

3,4-Dihydro-7-methyl-2*H*-[1,3]oxazino[3,2-*a*]benzimidazole (6b)
Colorless crystals; mp 136–138 °C.

IR (KBr): 1625, 1546, 1498, 1309 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.17–2.26 (m, 2 H), 2.43 (s, 3 H), 4.02 (dd, *J* = 6.2, 6.2 Hz, 2 H), 4.46 (dd, *J* = 6.2, 4.2 Hz, 2 H), 6.92 (s, 1 H), 7.01 (d, *J* = 8.1 Hz, 1 H), 7.40 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 21.6, 39.5, 66.6, 107.9, 117.4, 123.2, 130.3, 133.0, 137.6, 154.2.

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{11}H_{12}N_2O$: 188.0950; found: 188.0942.

5*H*-Benzimidazo[1,2-*a*][3,1]benzoxazine (6c)
Colorless crystals; mp 88–89 °C.

IR (KBr): 1618, 1562, 1467 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.40 (s, 2 H), 7.24–7.33 (m, 4 H), 7.51 (dd, *J* = 7.9, 7.4 Hz, 1 H), 7.67 (d, *J* = 7.4 Hz, 1 H), 7.76–7.80 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 69.1, 111.4, 114.2, 119.3, 121.3, 122.3, 123.4, 125.1, 125.8, 129.8, 130.2, 133.4, 141.1, 155.1.

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{14}H_{10}N_2O$: 222.0793; found: 222.0784.

Pyrido[1,2-*a*]benzimidazole (8a)[10]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.86 (ddd, *J* = 6.9, 6.9, 0.8 Hz, 1 H), 7.35–7.45 (m, 2 H), 7.54 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1 H), 7.70 (d, *J* = 9.2 Hz, 1 H), 7.90 (d, *J* = 8.3 Hz, 1 H), 7.95 (d, *J* = 8.3 Hz, 1 H), 8.46 (d, *J* = 6.9 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 110.3, 110.4, 118.0, 119.9, 121.0, 125.2, 125.7, 129.3, 129.5, 144.4, 148.5.

8-Methylpyrido[1,2-*a*]benzimidazole (8b)[11]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.56 (s, 3 H), 6.77 (ddd, *J* = 6.7, 6.7, 1.2 Hz, 1 H), 7.31–7.37 (m, 2 H), 7.61–7.66 (m, 2 H), 7.81 (d, *J* = 8.4 Hz, 1 H), 8.33 (ddd, *J* = 6.9, 1.2, 1.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8, 110.0, 110.1, 117.9, 119.4, 125.0, 127.4, 128.7, 128.8, 131.1, 142.6, 148.2.

Dipyrido[1,2-*a*:2′,3′-*d*]imidazole (8c)[12]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93 (dt, *J* = 6.8, 0.8 Hz, 1 H), 7.26 (dd, *J* = 8.1, 4.7, 1 H), 7.50 (ddd, *J* = 9.2, 6.8, 1.2 Hz, 1 H), 7.75 (d, *J* = 9.2 Hz, 1 H), 8.22 (dd, *J* = 8.1, 1.5 Hz, 1 H), 8.50 (d, *J* = 6.8 Hz, 1 H), 8.78 (dd, *J* = 4.7, 1.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 111.2, 115.8, 118.0, 118.7, 121.0, 125.8, 130.7, 148.5, 149.4, 156.0.

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