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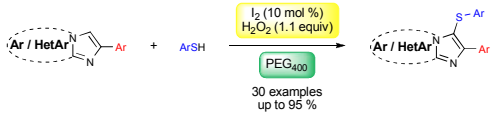

Formation of various 3-arylthioimidazoheterocycles using benign reagents and solvents with harmless by-products

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ARTICLE

Iodine-catalyzed regioselective sulfenylation of imidazoheterocycles in PEG_{400}

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M.-A. Hiebel,*[a] and S. Berteina-Raboin[a]

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An iodine-catalyzed sulfenylation of imidazo[1,2-*a*]-pyridines, -pyrimidines, and [1,2-*b*]pyridazines is herein described with various thiophenols using hydrogen peroxide as oxidizing agent in PEG_{400}. The method enabled the formation of 3-arylthioimidazoheterocycles in moderate to excellent yields using metal-free conditions. Several functional groups were well tolerated under our optimized conditions.

Introduction

Imidazo[1,2-*a*]pyridines are recognized to exhibit a broad range of biological activities.[1] They are often used as building blocks in pharmaceutical compounds, and count several commercially available drugs such as the sedative Zolpidem, the anxiolytic Alpidem or S aridipem, or the heart failure drug Olprinone (Fig 1).

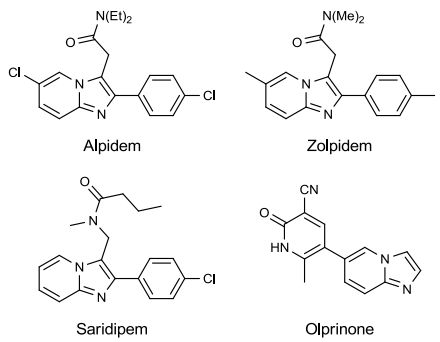


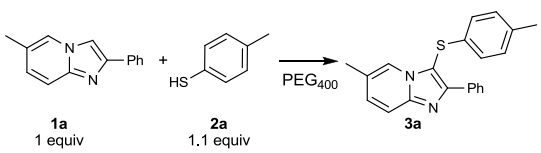
Fig 1. Examples of Imidazoheterocyclic-containing therapeutics.

In parallel, recent works exhibited the therapeutic value of sulfenylated heterocycles such as indoles.[2] Surprisingly, until lately, few methods described the introduction of sulfenyl groups on imidazo[1,2-*a*]pyridines using copper,[3] hypervalent iodine reagents,[4] strong acidic conditions,[5] ionic liquid,[6] or silica-supported $CeCl_3.7H_2O/NaI$.[7] Next, Adimurthy et *al.*[8] described the used of an excess of *N*-chlorosuccinimide with thiophenols to form *in situ* hypochlorothioite derivates,[9] which were introduced in C3 position of imidazo-[1,2-*a*]pyridines and -[2,1-*b*]thiazoles. In our effort to develop environmentally benign tools, we have continuously tried to promote the use of non-toxic media. Therefore in our approach, we focused on the potent combination of a non-toxic media, transition metal free conditions with thiophenols or disulfide species.[10] Recently, some polymer media started to be used as new solvents in organic synthesis, in particular polyethylene glycol (PEG).[11] PEG_{400} is a viscous sustainable liquid soluble in water and many organic solvents. This medium has the advantage of being non-toxic, odorless, neutral, nonvolatile, and non-irritating and is used in a variety of pharmaceuticals and medications. Herein we report the possible use of PEG_{400} as an efficient medium to introduce sulfenyl groups under transition metal free conditions.

Results and discussion

In order to achieve the optimized conditions, the sulfenylation of 6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**1a**) with 4-methylbenzenethiol (**2a**) was selected as the model reaction using standard conditions such as iodine in catalytic amount[12] with DMSO as oxidant in PEG_{400} (Table 1).[2d]

Table 1. Optimization of the reaction conditions



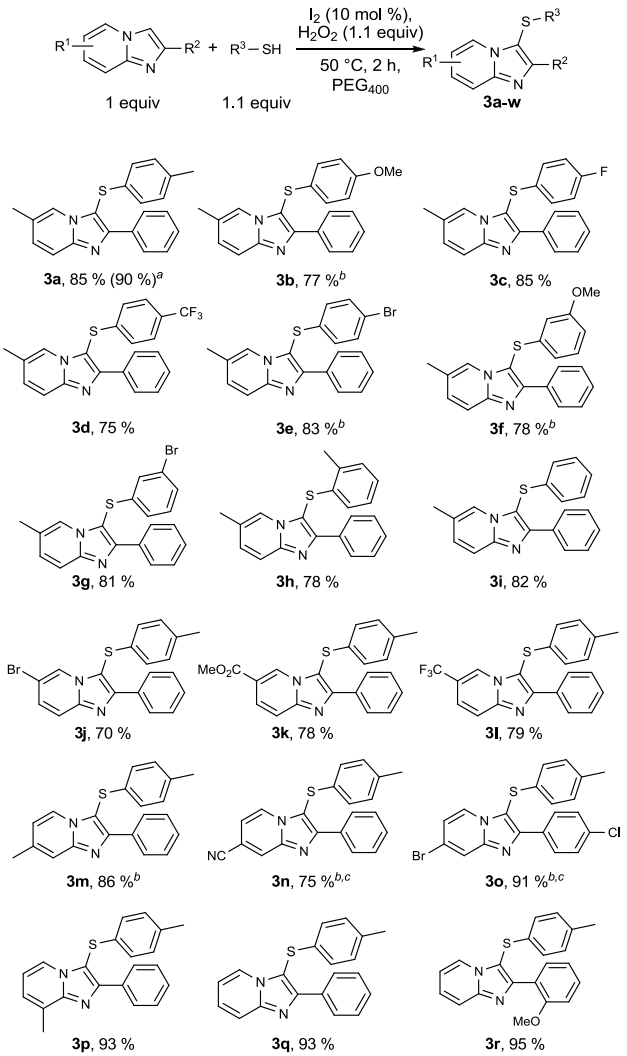
1a 1 equiv **2a** 1.1 equiv **3a**

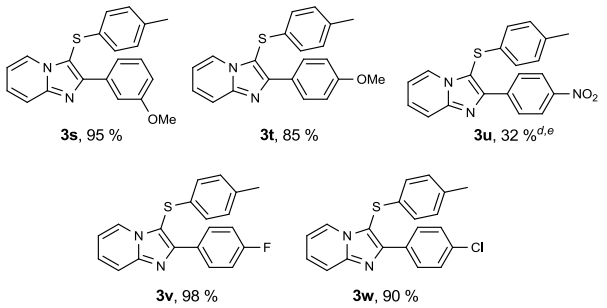
Entry	Catalyst (equiv)	Oxidant (equiv)	T (°C)	t (h)	Yield (%)[a]
1	I_2 (0.1)	DMSO (3)	135	18	62[b]
2	I_2 (0.1)	DMSO (3)	50	24	0
3	I_2 (0.1)	H_2O_2 (1.1)	50	2	85
3	I_2 (0.1)	H_2O_2 (1.1)	RT	24	77
5	I_2 (0.1)	*t*BuOOH (1.1)	50	2	80
6	I_2 (0.1)	O_2	50	2	0[c]
7	I_2 (0.1)	$K_2S_2O_8$ (1.1)	50	2	0[c]
8	KI (0.1)	H_2O_2 (1.1)	50	2	25[c]
9	NIS (0.1)	H_2O_2 (1.1)	50	2	45[c]
10	nBu_4NI (0.1)	H_2O_2 (1.1)	50	2	20[c]
11	-	H_2O_2 (1.1)	50	2	0
12	I_2 (1)	-	50	24	0

[a]Isolated yield. [b]Yield obtained with 2 equiv of 4-thiocresol.[c]Conversion estimated by 1H NMR.

The expected product **3a** was isolated in 62 % yield after 18 hours at 135 °C. Working at a lower temperature was desired however a diminution to 50 °C inhibited completely the reaction (entries 1 and 2). Other oxidants were then investigated such as *tert*butyl peroxide, potassium persulfate, oxygen, and hydrogen peroxide was found to be the most effective since **3a** was isolated after 2 hours at 50 °C in 85 % yield. Unfortunately, at room temperature the reaction was less efficient due to solubility issues of **1a** in PEG_{400} (entry 4). Different iodine sources were next investigated but **3a** was only obtained in low yields (entries 8-10). Both iodine and hydrogen peroxide are necessary since only traces of **3a** were observed when the reaction was performed in their absence (entries 11 and 12). Surprisingly even a stoichiometric amount of iodine did not provide the expected product. Hence the optimized reaction conditions were chosen as follows: **1a** (1 equiv), **2a** (1.1 equiv), hydrogen peroxide (1.1 equiv) in PEG_{400} at 50 °C for 2 hours. It should be noted that working under inert atmosphere did not improve the yield of the reaction.

In an endeavor to expand the scope of the methodology, the reactivity of various imidazo[1,2-*a*]pyridines was investigated (Scheme 1).



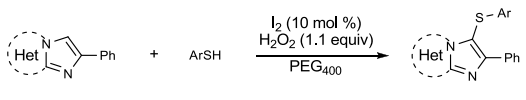


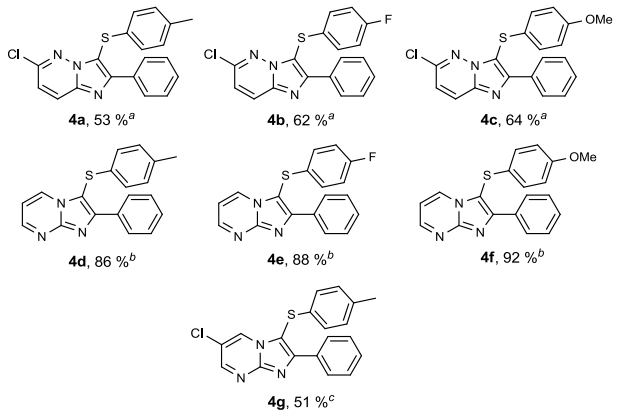
[a]Reaction performed on 5 mmol scale using 0.5 mol % I_2, 5 h at 50 °C. [b]Additional introduction of iodine (10 mol %). [c]The reaction was performed in 3 mL of PEG_{400} at 60 °C. [d]Additional introduction of iodine (2 x 10 mol %). [e]The reaction was performed in 3 mL of PEG_{400} at 100 °C.

Scheme 1. Scope of substrates

In general, the reactions were very clean and the expected products were synthetized in moderate to excellent yields. The reaction tolerates different aromatic thiols bearing electron-donating (Me, OMe) and withdrawing groups (F, Br, CF_3) in ortho, meta and para positions (**3a-i**). Apart from **3b**, **3e** and **3f**, which required an extra addition of iodine (10 mol %) to consume **1a** entirely, the corresponding sulfenated product was smoothly obtained regardless of the thiol used. Then different imidazo[1,2-*a*]pyridines substituted in positions 6, 7 and 8 were examined. As observed by the yields of **3a** and **3j-l**, the reaction showed no electronic effect from the substituent in position 6. However in position 7 for **3m-o**, a supplementary addition of iodine was required to achieve completion. Furthermore, due to solubility issue, a dilution of the medium and an increase of the temperature were necessary (**3n** and **3o**). Finally, no steric hindrance was observed when a methyl group was introduced in position 8 (**3p**). The influence of the substituents on the phenyl ring of 2-phenylimidazo[1,2-*a*]pyridines was also evaluated. Presence of moderate electron withdrawing (F, Cl) and electron donating (OMe) groups did not prevent the smooth formation of the expected products (**3r-w**) in high yields. Ortho and meta substitutions did not affect the efficiency of the reaction. Halides, esters, trifluoromethyls, cyanides substituents are well tolerated under these mild conditions, which enable further transformations. Nevertheless, nitro group gave poor results (**3u**) probably due to a combined effect of the insolubility of the corresponding starting material and its strong electron withdrawing effect, which could deactivate the C3 position. Finally, on a larger scale reaction (1 g of product), the catalyst loading could be lowered to 0.5 mol % with similar results (**3a**).

Next, to demonstrate the generality of this methodology the reaction conditions were applied to other imidazoheterocyclic compounds (Scheme 2).



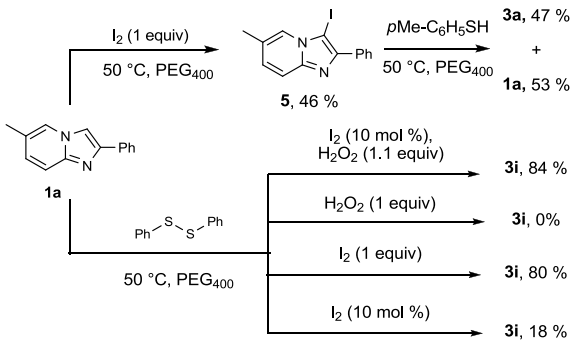


[a]The reaction was performed at 80 °C in 2 mL of PEG_{400} for 24 h, after 12 h, I_2 (10 mol %) and H_2O_2 (1.1 equiv) were added. [b]The reaction was performed at 50 °C in 1 mL of PEG_{400} for 4 h. [c]The reaction was performed at 80 °C in 3 mL of PEG_{400} for 24 h, after 12 h, I_2 (10 mol %) and H_2O_2 (1.1 equiv) were added.

Scheme 2. Extension to imidazo-pyrimidine and -pyridazine compounds

First, imidazopyridazines were submitted to our experimental conditions and we noticed that working at a higher temperature was necessary to solubilize the starting material. Despite an increased reaction time and an additional amount of iodine and hydrogen peroxide, unreacted 6-chloro-2-phenylimidazo[1,2-*b*]pyridazine was always recovered. Nonetheless the corresponding sulfenated products (**4a-c)** were isolated in moderate to good yields with thiophenols bearing electron withdrawing and donating groups. Then the imidazopyrimidine scaffold was studied. Fortunately, without any substituent on the pyrimidine ring, the reaction proceeded smoothly under the optimal conditions. The desired products were obtained in high yields (**4d-f**). However, for 6-chloro-2-phenylimidazo[1,2-*b*]pyridazine, a loss of reactivity was observed probably due to the insolubility of the compound in the reaction medium. Increase of the temperature and of the dilution enabled to obtain **4g** in 51 % yield along with unreacted 6-chloro-2-phenylimidazo[1,2-*b*]pyridazine.

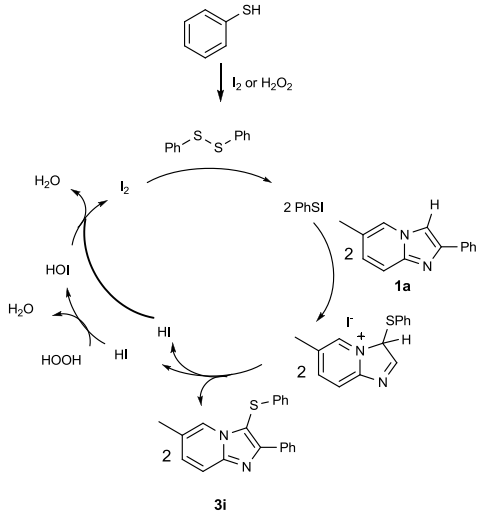
To get some insight into the reaction mechanism, some control experiments were performed (Scheme 3).



Scheme 3. Control experiments

In the literature, iodination of the C3 position of imidazo[1,2-*a*]pyridines are reported to be fast with high yields.[13] In PEG_{400}, the reaction was not complete and **5** was only obtained in a moderate yield after 24 h. Surprisingly, when *p*-thiocresol was next introduced, **3a** was isolated along with dehalogenated product **1a**. The low efficiency of this pathway made us consider the possible formation of disulfide intermediates. Indeed, iodine or hydrogen peroxide is known to oxidize thiols into disulfides.[14] **1a** and phenyl disulfide was then submitted to our experimental conditions and **3i** was easily isolated after 4 h. No reaction occurred upon treatment of **1a** and phenyl disulfide in the absence of I_2 illustrating that the transformation may not proceed *via* a radical pathway.[15] The reactivity was recovered when 1 equivalent of iodine was introduced. The oxidative role of H_2O_2 was underlined when I_2 was introduced in a catalytic amount, as expected the reaction did not reach completion.

Based on literature reports and our observations, a plausible mechanism has been proposed (Scheme 4). Initially, phenyl disulfide is generated from thiophenol in the presence of I_2 or H_2O_2. Then the electrophilic PhSI may be formed by interaction of the disulfide derivates with I_2.[2e] An electrophilic attack of PhSI on the C3 position of **1a** can occur leading to an imidazolenium intermediate. Releasing hydroiodic acid forms **3i**. Then, part of HI can be oxidized by H_2O_2 into hypoiodous acid.[16] Reaction between another portion of HI and HOI regenerates I_2 with the formation of water.[17]



Scheme 4. Plausible mechanism

Conclusions

In summary, we have developed a simple, benign and efficient method to introduce various aromatic thiols on imidazo[1,2-*a*]-pyridines, -pyrimidines and [1,2-*b*]pyridazines, and without any transition-metal catalysts in a non toxic medium which was able to solubilize a large variety of substrates. After optimization, it was found that iodine worked as a proficient catalyst easily regenerated by hydrogen peroxide. Various functional groups were tolerated under our conditions demonstrating the generality of our method.

Experimental section

General remarks

All reagents were purchased from commercial suppliers and were used without further purification and imidazoheterocycles were synthetized following the procedure reported in the literature.[10a] The reactions were monitored by thin-layer chromatography (TLC) analysis using silica gel (60 F254) plates. Compounds were visualized by UV irradiation. Flash column chromatography was

performed on silica gel 60 (230-400 mesh, 0.040-0.063 mm). Melting points (mp [°C]) were taken on samples in open capillary tubes and are uncorrected. The infrared spectra of compounds were recorded on a Thermo Scientific Nicolet iS10. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 250 MHz (^{13}C, 62.9 MHz and ^{19}F, 235 MHz). Chemical shifts are given in parts per million from tetramethylsilane (TMS) as internal standard. All ^{19}F spectra are reported in ppm relative to hexafluorobenzene as internal standard (-164.9 ppm). The following abbreviations are used for the proton spectra multiplicities: b : broad, s: singlet, d: doublet, t: triplet, q: quartet, p: pentuplet, m: multiplet. Coupling constants (*J*) are reported in hertz (Hz). High-resolution mass spectra (HRMS (ESI)) were performed on a Maxis Bruker 4G by the "Federation de Recherche" ICOA/CBM (FR2708) platform and the monoisotopic mass was given.

General procedure for the sulfenylation of imidazoheterocycles. Imidazoheterocycles (0.5 mmol), thiophenol (0.55 mmol) were dissolved in PEG_{400} (1 mL). Hydrogen peroxide (0.55 mmol) with iodine (13 mg, 0.05 mmol) were next added before heating up to 50 °C for the required time. After completion the reaction mixture was diluted in EtOAc (20 mL). The organic phase was washed with a saturated solution of sodium carbonate (3 x 10 mL) and sodium thiosulfate (10 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel to provide the expected product.

6-methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3a) (PE/EA: 70:30) Beige solid (140 mg, 85 %). mp: 130.5-131.9 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.27-8.19 (m, 2H), 8.12 (d, *J* = 7.1 Hz, 1H), 7.52-7.31 (m, 4H), 7.00 (bd, *J* = 8.4 Hz, 2H), 6.90 (bd, *J* = 8.4 Hz, 2H), 6.64 (dd, *J* = 7.2, 2.2 Hz, 1H), 2.40 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.1, 147.4, 137.8, 135.9, 133.6, 131.9, 130.2, 128.4, 128.4, 128.3, 125.7, 123.7, 116.2, 115.6, 106.0, 21.4, 20.9; IR (ATR, cm^{-1}): 6054, 2915, 1643, 1488, 1440, 860, 701, 690; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{19}N_2S$, 331.1263 found 331.1262.

3-((4-methoxyphenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (3b) (PE/EA: 80:20) Beige solid (133 mg, 77 %); mp: 122.5-124.1 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.26-8.20 (m, 2H), 8.17 (d, *J* = 7.0 Hz, 1H), 7.48-7.32 (m, 4H), 6.98 (ddd, *J* = 9.0, 3.1, 2.3 Hz, 2H), 6.75 (ddd, *J* = 9.0, 3.1, 2.3 Hz, 2H), 6.69 (dd, *J* = 7.0, 1.6 Hz, 1H), 3.72 (s, 3H), 2.43 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 158.6, 150.9, 147.4, 137.8, 128.5, 128.5, 128.5, 128.0, 123.8, 116.3, 115.7, 115.3, 107.0, 55.5, 21.5; IR (ATR, cm^{-1}): 3057, 2952, 2832, 1646, 1488, 1463, 1239, 772, 702; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{19}N_2OS$ 347.1213, found 347.1216.

3-((4-fluorophenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (3c) (PE/EA: 70:30) Beige solid (142 mg, 85 %); mp: 178.8-179.6 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.22-8.16 (m, 2H), 8.14 (d, *J* = 6.9 Hz, 1H), 7.51-7.46 (m, 1H), 7.45-7.42 (m, 1H), 7.42-7.32 (m, 2H), 7.02-6.85 (m, 4H), 6.71 (dd, *J* = 7.0, 1.7 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 161.7 (d, *J* = 245 Hz), 151.4, 147.7, 138.1, 133.6, 130.6, 130.6, 128.7, 128.6, 128.4, 127.7, 127.6, 123.6, 116.9, 116.5, 116.4, 115.9, 105.9, 21.6; ^{19}F (235 MHz, $CDCl_3$) δ -119.4; IR (ATR, cm^{-1}): 3062, 2917, 1646, 1589, 1484, 1007, 840, 770, 690; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{20}H_{16}FN_2S$ 335.1013, found 335.1010.

6-methyl-2-phenyl-3-((4-(trifluoromethyl)phenyl)thio)imidazo[1,2-*a*]pyridine (3d) (PE/EA: 80:20) White solid (142 mg, 75 %); mp: 153.2-154.1 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.17-8.11 (m, 2H), 8.09 (bd, *J* = 6.8 Hz, 1H), 7.54-7.49 (m, 1H), 7.49-7.45 (m, 1H), 7.45-7.42 (m, 2H), 7.41-7.33 (m, 2H), 7.10-7.02 (m, 2H), 6.74 (dd, *J* = 7.0, 1.6 Hz, 1H), 2.46 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 152.1, 148.0, 141.0, 138.5, 133.3, 128.9, 128.6, 128.4, 128.3 (q, *J* = 32.8 Hz), 126.4 (q, *J* = 3.8 Hz), 125.3, 123.6, 121.9, 115.6, 116.2, 103.8, 21.6; ^{19}F (235 MHz, $CDCl_3$) δ -65.7; IR (ATR, cm^{-1}): 1645, 1602, 1495, 1012, 826, 774, 700, 689; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{16}F_3N_2S$ 385.0981, found 385.0983.

3-((4-bromophenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (3e) (PE/EA: 70:30) Beige solid (169 mg, 86 %); mp: 166.3-167.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.19-8.12 (m, 2H), 8.10 (d, *J* = 7.0 Hz, 1H), 7.51-7.47 (m, 1H), 7.47-7.35 (m, 3H), 7.35-7.28 (m, 2H), 6.90-6.80 (m, 2H), 6.71 (dd, *J* = 6.9, 1.7 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151., 147.8, 138.2, 135.0, 133.5, 132.6, 128.7, 128.6, 128.4, 127.2, 123.6, 119.8, 116.5, 116.0, 21.6; IR (ATR, cm^{-1}): 3049, 2911, 1645, 1491, 1468, 807, 770, 687; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{20}H_{16}BrN_2S$ 395.0212, found 395.0208.

3-((3-methoxyphenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (3f) (PE/EA: 70:30) Yellow solid (135 mg, 78 %); mp: 106.7-107.5 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.24-8.15 (m, 2H), 8.13 (d, *J* = 6.5 Hz, 1H), 7.54-7.30 (m, 4H), 7.11 (dd, *J* = 8.0, 7.9 Hz, 1H), 6.75-6.62 (m, 2H), 6.61-6.52 (m, 2H), 3.66 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 160.5, 151.5, 147.7, 138.0, 137.1, 133.6, 130.4, 128.6, 128.6, 128.5, 123.8, 117.8, 116.3, 115.8, 111.7, 111.2, 105.5, 55.3, 21.5; IR (ATR, cm^{-1}): 1644, 1589, 1575, 1483, 1463, 1251, 775, 750, 700, 684; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{19}N_2OS$ 347.1213, found 347.1210.

3-((3-bromophenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (3g) (PE/EA: 70:30) Beige solid (159 mg, 81 %); mp: 135.0-136.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.18-8.13 (m, 2H), 8.11 (d, *J* = 6.9 Hz, 1H), 7.52-7.48 (m, 1H), 7.48-7.32 (m, 3H), 7.29-7.22 (m, 1H), 7.18 (dd, *J* = 1.8, 1.8 Hz, 1H), 7.04 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.84 (bd, *J* = 8.0 Hz, 1H), 6.72 (dd, *J* = 7.0, 1.6 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.9, 147.8, 138.3, 138.2, 133.4, 130.8, 129.3, 128.7, 128.6, 128.5, 128.4, 128.1, 123.9, 123.6, 123.6, 116.5, 116.1, 21.6; IR (ATR, cm^{-1}): 3066, 2920, 1647, 769, 745, 697; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{20}H_{16}BrN_2S$ 395.0212, found 395.0208.

6-methyl-2-phenyl-3-(*o*-tolylthio)imidazo[1,2-*a*]pyridine (3h) (PE/EA: 75:25) White solid (129 mg, 78 %); mp: 165.5-166.1 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.18-8.11 (m, 2H), 8.05 (d, *J* = 6.9 Hz, 1H), 7.50 (bs, 1H), 7.46-7.30 (m, 3H), 7.20 (bd, *J* = 7.5 Hz, 1H), 7.04 (ddd, *J* = 7.6, 7.3, 1.0 Hz, 1H), 6.91 (bdd, *J* = 7.8, 7.4 Hz, 1H), 6.68 (bd, *J* = 6.9 Hz, 1H), 6.43 (bd, *J* = 7.8 Hz, 1H), 2.52 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.8, 147.8, 137.9, 135.0, 134.6, 133.7, 130.8, 128.6, 128.5, 128.4, 127.0, 125.7, 124.2, 123.8, 116.4, 115.8, 105.8, 21.6, 19.9; IR (ATR, cm^{-1}): 3043, 2914, 1646, 1463, 770, 752, 700. HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{19}N_2S$ 331.1263, found 331.1263.

6-methyl-2-phenyl-3-(phenylthio)imidazo[1,2-*a*]pyridine (3i)[8] (PE/EA: 70:30) White solid (130 mg, 82 %); mp: 173.3-174.1 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.12-8.06 (m, 2H), 8.04 (d, *J* = 7.0 Hz, 1H), 7.41-7.37 (m, 1H), 7.37-7.21 (m, 3H), 7.15-6.98 (m, 3H), 6.93-6.86 (m, 2H), 6.74 (dd, *J* = 7.2, 1.6 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.5, 147.7, 138.0, 135.7, 133.7, 129.5, 128.6, 128.5, 128.4, 126.1, 125.6, 123.8, 116.4, 115.8, 105.6, 21.6; IR (ATR, cm^{-1}): 1643, 1492, 1476, 1466, 855, 745, 687; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{20}H_{17}N_2S$ 317.1107, found 317.1110.

6-bromo-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3j) (PE/EA: 90:10) White solid (140 mg, 71 %); mp: 173.4-174.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 1.9, 0.8 Hz, 1H), 8.25-8.16 (m, 2H), 7.61 (dd, *J* = 9.4, 0.9 Hz, 1H), 7.52-7.32 (m, 4H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.9, 145.6, 136.5, 133.1, 131.1, 130.5, 130.2, 129.0, 128.6, 128.5, 126.1, 124.8, 118.4, 108.1, 107.8, 21.1; IR (ATR, cm^{-1}): 3047, 2921, 1519, 1490, 771 695, 684; HRMS

(ESI): m/z $[M+H]^+$ calc for $C_{20}H_{16}BrN_2S$ 395.0212, found 395.0208.

methyl 2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine-6-carboxylate (3k) (PE/EA: 70:30) White solid (145 mg, 78 %); mp: 153.5-154.3 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.06 (dd, *J* = 1.7, 0.9 Hz, 1H), 8.29-8.21 (m, 2H), 7.92-7.84 (m, 1H), 7.71 (dd, *J* = 9.4, 0.9 Hz, 1H), 7.52-7.34 (m, 3H), 7.03 (bd, *J* = 8.0 Hz, 2H), 6.94 (bd, *J* = 8.3 Hz, 2H), 3.93 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 165.3, 152.8, 147.7, 136.6, 133.0, 131.2, 130.5, 129.1, 128.6, 128.6, 126.4, 126.3, 120.1, 117.2, 117.1, 108.9, 52.6, 21.0; IR (ATR, cm^{-1}): 3057, 3028, 2957, 1717, 1629, 1436, 1295, 805, 765, 695; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{22}H_{19}N_2O_2S$ 375.1162, found 375.1161.

2-phenyl-3-(p-tolylthio)-6-(trifluoromethyl)imidazo[1,2-a]pyridine (3l) (PE/EA: 70:30) Beige solid (152 mg, 79 %); mp: 161.0-162.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.32-8.17 (m, 2H), 7.80 (d, *J* = 9.3 Hz, 2H), 7.56-7.38 (m, 3H), 7.05 (bd, *J* = 8.1 Hz, 2H), 6.94 (bd, *J* = 8.3 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 152.8, 146.9, 136.8, 132.8, 130.6, 129.2, 128.7, 128.5, 126.4, 125.7, 123.6 (q, *J* = 5.7 Hz), 122.6 (q, *J* = 2.9 Hz), 121.4, 118.5, 117.5 (q, *J* = 34.4 Hz), 109.4, 21.0; ^{19}F (235 MHz, $CDCl_3$) δ -65.2; IR (ATR, cm^{-1}): 3044, 1649, 1490, 1467, 1059, 800, 694, 681; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{16}F_3N_2S$ 385.0981, found 385.0978.

7-methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3m) (PE/EA: 70:30) White solid (142 mg, 86 %); mp: 131.6-133.0 °C;^{1}H NMR (250 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.5 Hz, 2H), 8.13 (d, *J* = 7.0 Hz, 1H), 7.58-7.30 (m, 4H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.67 (d, *J* = 7.0 Hz, 1H), 2.42 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.2, 147.6, 137.9, 136.0, 133.7, 132.0, 130.3, 128.5, 128.5, 128.4, 125.8, 123.8, 116.3, 115.7, 106.1, 21.5, 21.0; IR (ATR, cm^{-1}): 3049, 2915, 1645, 1489, 800, 770, 689; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{19}N_2S$ 331.1263, found 331.1261.

2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine-7-carbonitrile (3n) PE/EA: 70:30) White solid (128 mg, 75 %); mp: 218.0-219.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 7.0, 0.9 Hz, 1H), 8.23 (dd, *J* = 7.9, 1.8 Hz, 2H), 8.08 (bs, 1H), 7.55-7.37 (m, 3H), 7.09-6.97 (m, 3H), 6.90 (d, *J* = 8.2 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 153.5, 144.9, 137.0, 132.5, 130.6, 130.0, 129.8, 128.8, 128.6, 126.5, 125.5, 123.5, 117.5, 113.3, 110.8, 109.3, 21.1; IR (ATR, cm^{-1}): 3094, 3051, 2230, 801; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{16}N_3S$ 342.1059, found 342.1056.

7-bromo-2-(4-chlorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3o) (PE/EA: 90:10) White solid (190 mg, 91 %). mp: 178.2-178.8 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.88 (bs, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 150.6, 147.1, 136.7, 135.0, 131.6, 130.7, 130.5, 129.7, 128.8, 126.1, 124.9, 121.0, 120.0, 117.2, 107.9, 21.0; IR (ATR, cm^{-1}): 1621, 1512, 1490, 1459, 838, 808, 790, 779, 728; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{20}H_{15}BrClN_2S$ 428.9822, found 428.9820.

8-methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3p) (PE/EA: 70:30) White solid (154 mg, 93 %); mp: 106.7-107.3 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.25-8.18 (m, 2H), 8.15 (bdd, *J* = 6.8, 1.1 Hz, 1H), 7.50-7.31 (m, 3H), 7.11 (ddd, *J* = 7.0, 1.3, 1.1 Hz, 1H), 7.02 (bd, *J* = 8.0 Hz, 2H), 6.91 (bd, *J* = 8.0 Hz, 2H), 6.77 (ddd, *J* = 6.9, 6.7, 1 Hz, 1H), 2.71 (bs, 3H), 2.26 (bs, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.0, 147.5, 136.0, 133.9, 132.0, 130.3, 128.6, 128.5, 128.5, 127.8, 125.9, 125.4, 122.5, 113.1, 107.1, 21.0, 16.9; IR (ATR, cm^{-1}): 3029, 2918, 1622, 1489, 1466, 804, 749, 702; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{19}N_2S$ 331.1263, found 331.1261.

2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3q)[7] (PE/EA: 50:50) Beige solid (147 mg, 93 %); mp: 140.9-141.8 °C (lit: 145-147 °C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.28 (dt, *J* = 6.9, 1.2 Hz, 1H), 8.25-8.19 (m, 2H), 7.72 (dt, *J* = 9.0, 1.1 Hz, 1H), 7.50-7.28 (m, 4H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.91 (bd, *J* = 8.3 Hz, 2H), 6.85 (dd, *J* = 6.8, 1.2 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.4, 147.2, 136.2, 133.6, 131.7, 130.3, 128.7, 128.5, 128.5, 126.7, 126.0, 124.7, 117.8, 113.1, 107.0, 21.0; IR (ATR, cm^{-1}): 3063, 3035, 2915, 1648, 1631, 1489, 1465, 806, 742, 699, 688, 682; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{20}H_{17}N_2S$ 317.1107, found 317.1104.

2-(2-methoxyphenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3r) (PE/EA: 70:30) Yellow gum (164 mg, 95 %); ^{1}H NMR (250 MHz, $CDCl_3$) 8.16 (dt, *J* = 6.9, 1.2 Hz, 1H), 7.73 (dt, *J* = 9.0, 1.2 Hz, 1H), 7.52 (dd, *J* = 7.5, 1.8, Hz 1H), 7.44-7.26 (m, 2H), 7.07-6.65 (m, 4H), 6.90-6.80 (m, 3H), 3.67 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 157.6, 150.5, 147.1, 135.7, 132.1, 132.1, 130.1, 130.0, 126.2, 126.0, 124.6, 123.0, 120.5, 118.0, 113.0, 111.1, 109.5, 55.5, 21.0; IR (ATR, cm^{-1}): 1630, 1604, 1581, 1490, 1480, 1246, 751, 738; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{19}N_2OS$ 347.1213, found 347.1209.

2-(3-methoxyphenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3s) PE/EA: 70:30) Light yellow solid (165 mg, 95 %); mp: 72.4-74.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.19 (dt, *J* = 6.9, 1.2 Hz, 1H), 7.77-7.67 (m, 2H), 7.62 (dt, *J* = 9.0, 1.2 Hz, 1H), 7.307.17 (m, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.86-6.71 (m, 4H), 3.71 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 159.7, 151.0, 147.0, 136.2, 134.8, 131.6, 130.3, 129.5, 126.7, 126.0, 124.6, 121.0, 117.7, 115.1, 113.3, 113.2, 107.2, 56.4, 21.0; IR (ATR, cm^{-1}): 1631, 1602, 1578, 1490, 1478, 1461, 1341, 884, 802, 755, 737, 688; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{19}N_2OS$ 347.1213, found 347.1210.

2-(4-methoxyphenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3t) (PE/EA: 60:40) Beige solid (131 mg, 85 %); mp: 161.7-162.5 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.25 (d, *J* = 6.9 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.36-7.23 (m, 1H), 7.07-6.76 (m, 7H), 3.83 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 160.1, 151.2, 147.1, 136.1, 131.8, 130.3, 129.8, 126.5, 126.2, 125.9, 124.6, 117.5, 114.0, 112.9, 106.0, 55.4, 21.0; IR (ATR, cm^{-1}): 2949, 2831, 1610, 1247, 833, 756, 743; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{21}H_{19}N_2OS$ 347.1213, found 347.1210.

2-(4-nitrophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3u) (PE/EA: 70:30) Yellow solid (57 mg, 32 %); mp: 214.8-215.2 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.50-8.42 (m, 2H), 8.37-8.24 (m, 3H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.45-7.32 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.98-6.84 (m, 3H), 2.26 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 148.4, 147.7, 147.3, 140.0, 136.8, 130.7, 130.6, 129.0, 127.4, 126.1, 124.8, 123.8, 118.1, 113.8, 109.1, 21.0; IR (ATR, cm^{-1}): 1634, 1595, 1510, 1491, 1337, 855, 755, 705; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{20}H_{16}N_3O_2S$ 362.0958, found 362.0954.

2-(4-fluorophenyl)-3-(p-tolylthio)imidazo[1,2-a]pyridine (3v) (PE/EA: 70:30) Beige solid (168 mg, 98 %); mp: 103.5-104.8°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.33-8.15 (m, 3H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.32 (dd, *J* = 8.2, 7.5 Hz, 1H), 7.12 (dd, *J* = 8.8, 8.7 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 7.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 165.1, 161.2, 150.4, 147.1, 136.3, 131.4, 130.4, 130.3, 130.2, 129.8, 129.7, 126.8, 125.9, 124.6, 117.7, 115.6, 115.3, 113.2, 106.7, 21.0; ^{19}F (235 MHz, $CDCl_3$) δ -116.3; IR (ATR, cm^{-1}): 1632, 1474, 1220, 1014, 797, 754, 742; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{20}H_{16}FN_2S$ 335.1013, found 335.1010.

2-(4-chlorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3w) PE/EA: 50:50) Beige solid (152 mg, 90 %); mp: 132.5-133.4 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.27 (d, *J* = 6.8 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.36-7.24

(m, 1H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.93-6.81 (m, 3H), 2.25 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 150.1, 147.1, 136.4, 134.6, 132.1, 131.3, 130.4, 129.7, 128.7, 126.9, 126.0, 124.6, 117.8, 113.3, 107.2, 21.0; IR (ATR, cm^{-1}): 3030, 3029, 1630, 1489, 1462, 827, 800, 756, 743; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{20}H_{16}ClN_2S$ 351.0717, found 351.0714.

6-chloro-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*b*]pyridazine (4a) (DCM) Pale Yellow solid (93 mg, 53 %); mp: 175.2-175.8 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.30-8.23 (m, 2H), 7.92 (d, *J* = 9.3 Hz, 1H), 7.57-7.33 (m, 3H), 7.16-7.07 (m, 3H), 7.01 (d, *J* = 8.2 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 150.7, 147.4, 139.4, 136.8, 132.9, 131.0, 130.1, 129.1, 128.6, 128.4, 128.1, 126.7, 120.7, 115.2, 21.1; IR (ATR, cm^{-1}): 2919, 2850, 1524, 1491, 1465, 1100, 799, 703; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{19}H_{15}ClN_3S$ 352.0670, found 352.0669.

6-chloro-3-((4-fluorophenyl)thio)-2-phenylimidazo[1,2-*b*]pyridazine (4b) (DCM) Pale pink solid (110 mg, 62 %); mp: 212.2-213.2 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.30-8.21 (m, 2H), 7.95 (d, *J* = 9.4 Hz, 1H), 7.54-7.40 (m, 3H), 7.25-7.14 (m, 3H), 6.92 (bdd, *J* = 8.7, 8.7 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 164.1, 160.2, 150.6, 147.6, 139.5, 132.8, 130.6, 130.5, 129.5, 129.5, 129.3, 128.7, 128.5, 126.8, 126.5, 120.9, 116.7, 116.3; ^{19}F (235 MHz, $CDCl_3$) δ -118.0; IR (ATR, cm^{-1}): 3093, 3062, 1526, 1488, 1465, 1219, 1099, 831, 805, 702, 690; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{18}H_{12}ClFN_3S$ 356.0419, found 356.0417.

6-chloro-3-((4-methoxyphenyl)thio)-2-phenylimidazo[1,2-*b*]pyridazine (4c) (DCM) White solid (118 mg, 64 %); mp: 160.5-161.6 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.34-8.25 (m, 2H), 7.91 (d, *J* = 9.3 Hz, 1H), 7.56-7.36 (m, 3H), 7.32-7.22 (m, 2H), 7.13 (d, *J* = 9.3 Hz, 1H), 6.81-6.71 (m, 2H), 3.73 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 159.4, 150.1, 147.3, 139.2, 133.0, 131.4, 129.1, 128.6, 128.6, 126.7, 124.7, 120.6, 116.5, 115.0, 55.4; IR (ATR, cm^{-1}): 3094, 3062, 2837, 1592, 1526, 1490, 1464, 1438, 1217, 1099, 807, 728, 689; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{19}H_{15}ClN_3OS$ 368.0619, found 368.0617.

2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyrimidine (4d) (EA/MeOH: 99:1) Beige solid (136 mg, 86 %); mp: 139.5-140.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.68-8.60 (m, 1H), 8.51 (dd, *J* = 6.7, 2.1 Hz, 1H), 8.40-8.31 (m, 2H), 7.49-7.35 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 2H),6.97-6.87 (m, 3H), 2.25 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.6, 151.6, 150.1, 136.7, 132.9, 132.2, 130.6, 130.5, 129.2, 128.7, 128.6, 126.2, 109.4, 106.1, 21.0; IR (ATR, cm^{-1}): 3060, 1604, 1488, 1341, 1212, 798, 769, 683; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{19}H_{16}N_3S$ 318.1059, found 318.1059.

2-phenyl -((4-fluorophenyl)thio)-2-phenylimidazo[1,2-*a*]pyrimidine (4e) (EA/MeOH: 99:1) Beige solid (141 mg, 88 %); mp: 153.5-154.4 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 4.2, 2.0 Hz, 1H), 8.53 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.39-8.30 (m, 2H), 7.52-7.36 (m, 3H), 7.06-6.86 (m, 5H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 163.8, 159.9, 152.9, 151.8, 150.1, 132.8, 132.1, 129.4, 129.3, 129.3, 128.7, 128.7, 128.2, 128.0, 117.1, 116.8, 109.6, 105.8; ^{19}F (235 MHz, $CDCl_3$) δ -118.4; IR (ATR, cm^{-1}): 3087, 3061, 1613, 1486, 1218, 833, 760, 714, 689; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{18}H_{13}FN_3S$ 322.0809, found 322.0809.

3-((4-methoxyphenyl)thio)-2-phenylimidazo[1,2-*a*]pyrimidine (4f) (EA) Yellow solid (153 mg, 92 %); mp: 147.5-148.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.2, 2.0 Hz, 1H), 8.55 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.42-8.35 (m, 2H), 7.52-7.36 (m, 3H), 7.05-6.97 (m, 2H), 6.92 (dd, *J* = 6.8, 4.2 Hz, 1H), 6.81-6.72 (m, 2H), 3.72 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 159.0, 152.3, 151.5, 149.9, 133.0, 132.1, 129.2, 128.8, 128.6, 128.5, 124.5, 115.4, 109.4, 107.0, 55.5; IR (ATR, cm^{-1}): 3057, 2839, 1611, 1589, 1488, 1233, 841, 810, 762, 700, 689; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{19}H_{16}N_3OS$ 334.1009, found 334.1007.

6-chloro-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyrimidine (4g) DCM) Pale Yellow solid (90 mg, 51 %); mp: 213.5-214.5 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.54 (s, 2H), 8.38-8.30 (m, 2H), 7.51-7.36 (m, 3H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 153.6, 150.8, 148.3, 137.0, 132.5, 130.6, 130.0, 129.6, 129.5, 128.7, 128.7, 126.4, 119.0, 106.9, 21.0; IR (ATR, cm^{-1}): 3078, 3051, 1519, 1476, 1440, 800, 699; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{19}H_{15}ClN_3S$ 352.0670, found 352.0669.

3-iodo-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (5) (PE/EA: 80:20) Beige solid (77 mg, 46 %); mp: 159.9-160.2 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.15-8.00 (m, 3H), 7.53-7.33 (m, 4H), 6.76 (dd, *J* = 7.0, 1.7 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 148.5, 147.9, 136.8, 133.8, 128.6, 128.4, 128.3, 125.8, 116.2, 115.9, 58.3, 21.4; IR (ATR, cm^{-1}): 3059, 2919, 1646, 1494, 1464, 1439, 767, 695; HRMS (ESI): m/z $[M+H]^+$ calc for $C_{14}H_{12}IN_2$ 335.0040, found 335.0040.

Notes and references

[a] Institut de Chimie Organique et Analytique (ICOA) Université d'Orléans UMR-CNRS 7311, BP 6759, rue de Chartres 45067 Orléans cedex 2 (France)

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