Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2012, **10**, 4943

www.rsc.org/obc

PAPER

Imidazo[1,5-*a*]pyridine-1-ylalkylalcohols: synthesis *via* intramolecular cyclization of *N*-thioacyl 1,2-aminoalcohols and their silyl ethers and molecular structures†

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Received 29th February 2012, Accepted 19th April 2012
DOI: 10.1039/c2ob25438g

Iodine-mediated cyclization of *N*-thioacyl 1,2-aminoalcohols derived from aromatic aldehydes and ketones mainly produced bis(1-imidazo[1,5-*a*]pyridyl)arylmethanes, whereas the reaction of *N*-thioacyl 1,2-aminoalcohols derived from aliphatic aldehydes and *N*-thioacyl 1,2-aminoalcohols protected with a silyl group with iodine gave imidazo[1,5-*a*]pyridine-1-ylalkylalcohols as a major product.

Introduction

The design, synthesis and use of new monoanionic *N*,*O*-chelating ligands with a hydroxy group and nitrogen-containing heterocycles are intriguing topics in chemistry. The coordination of these ligands to a wide variety of metals has provided metal complexes with unique properties. Pyridinemethylalcohols,[1] 2-hydroxymethylbenzimidazoles,[2] and hydroxyquinolines[3] (Fig. 1) are major examples of the core skeletons of such ligands.

Meanwhile, imidazo[1,5-*a*]pyridines, which are nitrogen-containing 10π electron heterocycles, have recently attracted much attention because of their photophysical[4] and biological properties,[5] and due to their applicability as precursors for *N*-heterocyclic carbenes[6] and metal ligands.[7] Therefore, several new methods[8,9] have been developed for the synthesis of imidazo[1,5-*a*]pyridines. In this context, we have developed various new approaches,[10] which have enabled us to produce a wide variety of derivatives bearing unsaturated substituents at the 1- and 3-positions of imidazo[1,5-*a*]pyridyl groups. For example, the cyclization of *N*-2-pyridylmethyl thioamides **1** in the presence of iodine and pyridine is complete within several hours at room temperature and gives imidazo[1,5-*a*]pyridines **2**

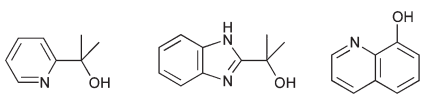

Fig. 1 Monoanionic *N*,*O*-chelating ligands.

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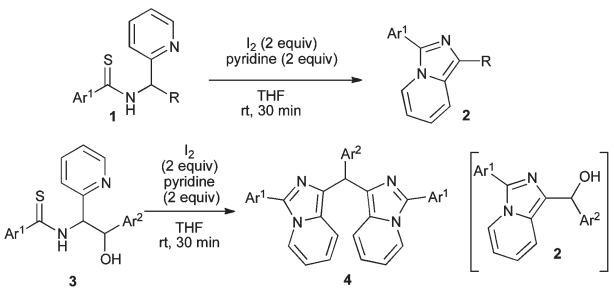
† Electronic supplementary information (ESI) available: Details on X-ray molecular structure analyses of **8a**, **2e**, and **9g**. CCDC 868371, 868372 and 868373. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25438g



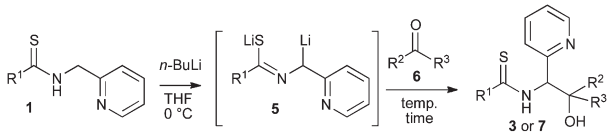
Scheme 1 Desulfurizative cyclization of *N*-2-pyridylmethyl thioamides.

(Scheme 1).[10a] Notably, application of this reaction to *N*-thioacyl 1,2-aminoalcohols **3** did not give similar products, and instead compounds bearing two imidazo[1,5-*a*]pyridyl groups **4** were obtained with high efficiency.[10d] We report here the details of the iodine-mediated cyclization of *N*-thioacyl 1,2-aminoalcohols derived from *N*-2-pyridylmethyl thioamides with aldehydes and ketones *via* thioamide dianions.[11] The distribution of the products **2** and **4** depended on the substituents on **3**, and we determined the molecular structures of some of the products. Finally, a synthetic procedure for the production of new types of monoanionic *N*,*O*-chelating ligands with a hydroxy and an imidazo-[1,5-*a*]pyridyl group is described.

Results and discussion

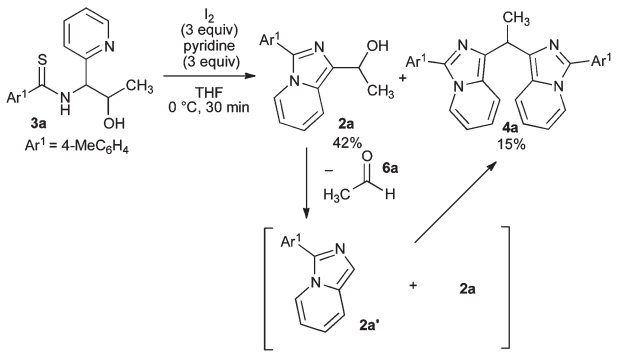
Initially, *N*-thioacyl 1,2-aminoalcohols **3** and **7** were prepared from *N*-2-pyridylmethyl thioamides **1**, which were readily obtained *via* the Willgerodt–Kindler reaction[12] of aldehydes, elemental sulfur, and 2-picolylamine. The results are shown in Table 1. Thioamide dianions **5** were generated from **1** and *n*-BuLi in THF within 10 min, and to this were then added aldehydes **6a–6f** to give *N*-thioacyl 1,2-aminoalcohols **3** as a

Table 1 Addition reaction of thioamide dianions **5** with aldehydes and ketones



Entry	1	R^1	6	R^2	R^3	T (°C)	Time (h)	3	Yield[a,b] (%)
1	**1a**	4-MeC_6H_4	**6a**	CH_3	H	0	0.5	**3a**	84 (60 : 40)
2	**1a**	4-MeC_6H_4	**6b**	*c*-Hexyl	H	0	0.5	**3b**	98 (63 : 37)
3	**1a**	4-MeC_6H_4	**6c**	*t*-Butyl	H	0	0.5	**3c**	87 (60 : 40)
4	**1b**	Ph	**6d**	2-Pyridyl	H	0–RT	3	**3d**	70 (67 : 33)
5	**1c**	2-Pyridyl	**6d**	2-Pyridyl	H	0–RT	3	**3e**	76 (60 : 40)
6	**1b**	Ph	**6e**	2-Thienyl	H	0–RT	3	**3f**	69 (63 : 37)
7	**1d**	*t*-Butyl	**6f**	Ph	H	0–RT	3	**3g**	56 (54 : 46)
8	**1a**	4-MeC_6H_4	**6g**	Ph	Ph	0	2.5	**7a**	91
9	**1e**	4-$MeOC_6H_4$	**6g**	Ph	Ph	0	2.5	**7b**	62
10	**1d**	*t*-Butyl	**6g**	Ph	Ph	0	3	**7c**	56
11	**1a**	4-MeC_6H_4	**6h**	4-ClC_6H_4	4-ClC_6H_4	0	1.5	**7d**	67
12	**1a**	4-MeC_6H_4	**6i**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	0	3	**7e**	88
13	**1a**	4-MeC_6H_4	**6k**	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	0	4	**7f**	72
14	**1a**	4-MeC_6H_4	**6l**	Fluorenone		0	3	**7g**	73

[a] Isolated yields. [b] Ratio of diastereomers is in parentheses.



Scheme 2 Cyclization of *N*-thioacyl 1,2-aminoalcohol **3a** in the presence of iodine and pyridine.

diastereomeric mixture in good to high yields (entries 1–7). Thioamides **1** with aryl, heteroaryl, and *t*-butyl groups at the carbon atom of the thiocarbonyl groups were used. The addition of thioamide dianions **5** to aliphatic aldehydes was complete within 30 min (entries 1–3), whereas the reactions with aromatic aldehydes required longer reaction times (entries 4–7). Likewise, the use of ketones **6g–6l** gave the corresponding products **7** (entries 8–14). The substituents on the aromatic rings of ketone **6**, such as chlorine, methoxy, and dimethylamino groups, had almost no effect on the efficiency of the reaction. Some of the products **7** were readily crystallized and purified.

Next, *N*-thioacyl 1,2-aminoalcohols **3** obtained from aldehydes were subjected to an iodine-mediated cyclization reaction. Treatment of **3a** with iodine (3 equiv.) and pyridine (3 equiv.) in THF gave imidazo[1,5-*a*]pyridine-1-ylethanol **2a** and bis-(imidazo[1,5-*a*]pyridyl)ethane **4a** in respective yields of 42% and 15% (Scheme 2).

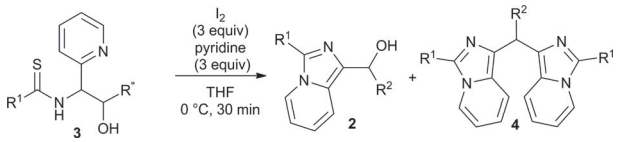
In the reaction, the elimination of aldehyde **6a** from **2a** may partially occur to generate **2a′**. A Friedel–Crafts-type condensation reaction of **2a** and **2a′** may proceed to give **4a**. In our preliminary results,[10d] *N*-thioacyl 1,2-aminoalcohols derived from aromatic aldehydes selectively led to **4**. Imidazo[1,5-*a*]-pyridine-1-ylalkylalcohols like **2a** were not formed at all. This difference may be because aromatic aldehydes are more easily eliminated from **2** than aliphatic aldehydes. A similar cyclization reaction was carried out with other derivatives **3b–3g**, and the results are listed in Table 2. Compounds with cyclohexyl and *tertiary* butyl groups **3b** and **3c** were selectively converted to the products **2b** and **2c** (entries 1 and 2), whereas the reactions of those with 2-thienyl and phenyl groups, **3f** and **3g**, gave the products **4f** and **4g** (entries 5 and 6). These differences can be understood in terms of the difference between how easily aliphatic and aromatic aldehydes are eliminated. Interestingly, however, the cyclization of *N*-thioacyl 1,2-aminoalcohols **3d** and **3e** derived from 2-pyridinecarbaldehyde (**6d**) resulted in the formation of products **2d** and **2e**, which does not involve the elimination of 2-pyridinecarbaldehyde (entries 3 and 4).

Third, *N*-thioacyl 1,2-aminoalcohols obtained from ketones **7** were subjected to an iodine-mediated cyclization reaction.

As shown in Scheme 3, the cyclization of **7a**, **7b**, and **7g** was complete within 5 min at room temperature, but the distribution of the products was dependent on the substituents on the thiocarbonyl carbon atom and on the carbon atom α to the hydroxy group. The reaction of **7a** readily gave the product **8a**, despite the fact that four aromatic substituents are introduced to a quaternary carbon atom of **8a**, along with the formation of **2a′** and ketone **6g**, whereas **7b** was converted to **9b** along with the formation of **8b**. The reaction of **7g** mainly gave **2a′** and **6l**, and the product **9g**, which retained a fluorenyl group, was obtained in up to 26% yield along with some impurities.

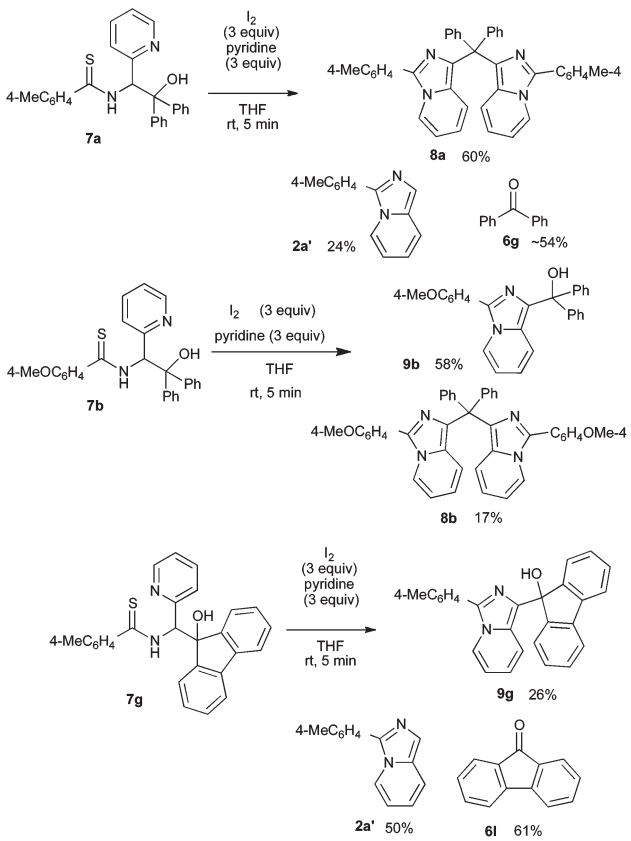
The molecular structures of some of the products were confirmed by X-ray structure analyses. A single crystal of **9g** contained one molecule of CH_2Cl_2. ORTEP drawings of **8a**, **2e**, and **9g** are shown in Fig. 2–4, respectively.

Table 2 Cyclization of *N*-thioacyl 1,2-aminoalcohols derived from aldehydes **3** in the presence of iodine and pyridine[a]



Entry	3	R^1	R^2	*T* (°C)	Time (h)	Yield[a] (%) 2		4	
1	**3b**	4-MeC_6H_4	*c*-Hexyl	0	0.5	**2b**	84	**4b**	—
2	**3c**	4-MeC_6H_4	*t*-Butyl	0	0.5	**2c**	93	**4c**	—
3	**3d**	Ph	2-Pyridyl	RT	0.67	**2d**	69	**4d**	—
4	**3e**	2-Pyridyl	2-Pyridyl	RT	0.67	**2e**	82	**4e**	—
5	**3f**	Ph	2-Thienyl	RT	0.5	**2f**	—	**4f**	86
6	**3g**	*t*-Butyl	Ph	RT	0.5	**2g**	—	**4g**	60

[a] Isolated yields.



Scheme 3 Cyclization of *N*-thioacyl 1,2-aminoalcohols **7a**, **7b** and **7g** in the presence of iodine and pyridine.

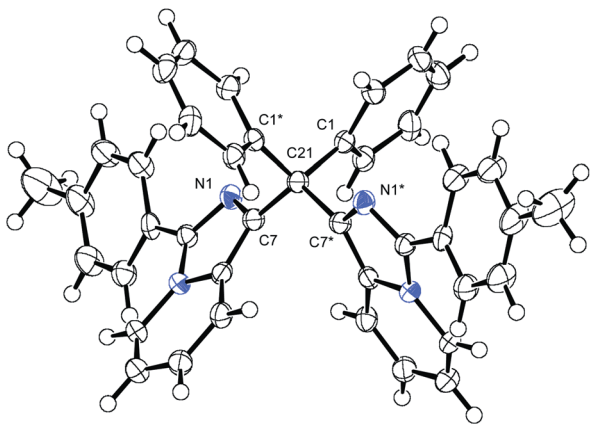


Fig. 2 An ORTEP drawing of **8a**. Selected bond angles (°) and dihedral angles (°): C7–C21–C7* = 112.4(4), C7–C21–C1 = 133.39(19), C7*–C21–C1 = 103.46(18), C7–C21–C1* = 103.46(18), C7*–C21–C1* = 113.38(19), C1–C21–C1* = 111.0(4), C1*–C21–C7–N1 = 85.1(4), C7*–C21–C7–N1 = −152.2(4), C1–C21–C7–N1 = −35.3(4).

The central quaternary carbon atom of **8a** shows slightly distorted tetrahedral structures. The two imidazopyridyl groups in **8a** are aligned in nearly the same plane, but are oriented in opposite directions. For imidazopyridylmethylalcohols **2e** and **9g**, the carbon atoms with hydroxy groups have a tetrahedral geometry. In the former case, the carbon atom is present in the bisected conformation toward the imidazopyridyl ring, whereas the carbon atom in the latter exists in an eclipsed conformation. The pyridyl group at C13 in **2e** is in nearly the same plane as that of the imidazopyridyl group, whereas the *p*-tolyl group at C20 in **9g** is twisted toward the imidazopyridyl group.

Finally, to establish an efficient synthetic route to these new types of monoanionic ligands, the protection of a hydroxy group in *N*-thioacyl 1,2-aminoalcohols **7** and cyclization of the resulting products were examined. Among them, the silylation of **7g** with chlorotrimethylsilane in the presence of imidazole was complete within 2 h to give **10g** quantitatively (Scheme 4).

The iodine-mediated cyclization of the product **10g** went to completion within 5 min in the presence of pyridine to give imidazopyridylmethylalcohol silyl ether **11g** with high efficiency. The deprotection of **11g** led to the desired alcohol **9g**. A similar reaction was carried out with other silylated compounds **10** (Table 3). Unlike in the silylation of **7g**, the reactions of **7e** and **7f** with chlorotrimethylsilane required longer reaction times, and those of **7a** and **7d** required longer reaction times,

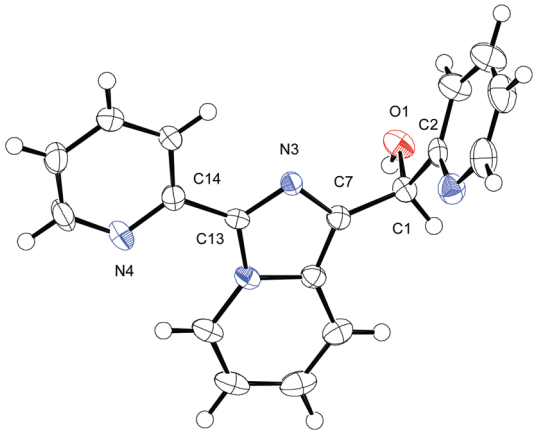


Fig. 3 An ORTEP drawing of **2e**. Selected bond angles (°) and dihedral angles (°): O1–C1–C7 = 111.0(2), C7–C1–C2 = 113.6(3), O1–C1–C2 = 107.0(3), C2–C1–C7–N3 = 45.3(4), O1–C1–C7–N3 = −75.4(4), N3–C13–C14–N4 = 173.6(3).

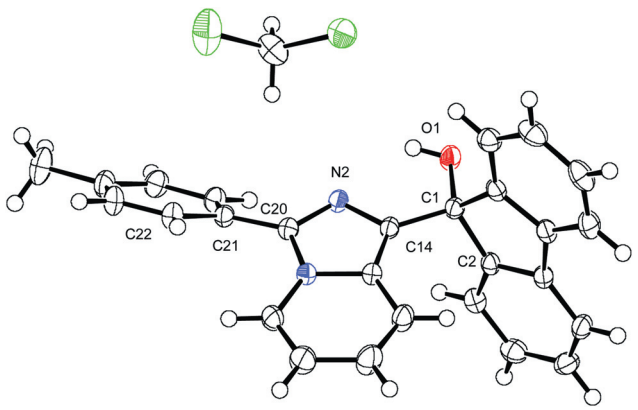
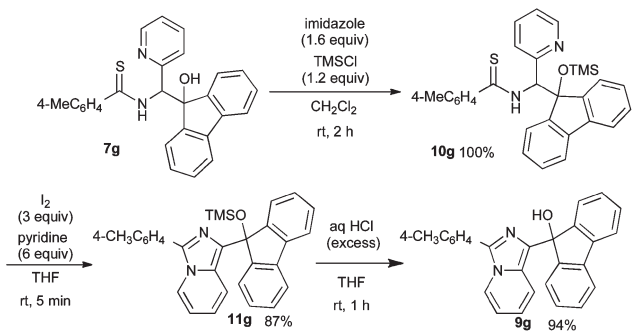


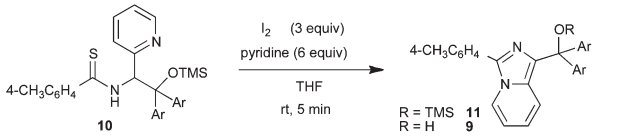
Fig. 4 An ORTEP drawing of **9g**·CH_2Cl_2. Selected bond angles (°) and dihedral angles (°): O1–C1–C14 = 109.49(14), C14–C1–C2 = 112.90(14), O1–C1–C2 = 110.84(14), C2–C1–C14–N2 = 127.75(17), O1–C1–C14–N2 = 3.7(2), N2–C20–C21–C22 = 145.59(19).



Scheme 4 Cyclization of **10g** in the presence of iodine and pyridine.

higher temperatures, and dichloroethane as a solvent. However, in all cases, the silylated products could be isolated in good yields. The cyclization of silyl ethers **10a** and **10d** proceeded similarly to that of **10g**, but silyl ethers **11** as well as small amounts of desilylated alcohols **9** were also formed (entries 1 and 2). Nevertheless, the desired alcohols **9a** and **9d** were

Table 3 Cyclization of **10** in the presence of iodine and pyridine



Entry	No.	Ar	Yield[a] (%)	**11** : **9**
1	**10a**	Ph	88	99 : 6
2	**10d**	C_6H_4Cl-4	95	98 : 2
3	**10e**	C_6H_4OMe-4	54	67 : 33
4[b]	**10e**	C_6H_4OMe-4	73	59 : 41
5	**10f**	$C_6H_4NMe_2$-4	0	—

[a] Isolated yields. [b] Pyridine (12 equiv.) was used.

obtained in high yields by the desilylation of **11a** and **11d**. In contrast, the cyclization of **10e** gave a mixture of **11e** and **9e** in moderate yield (entry 3). Prolonging the reaction time of **10e** did not improve the yields of **11e** and **9e**, and instead **2a′** and the ketone **6i** were formed. The use of a large excess of pyridine gave a mixture of **11e** and **9e** in higher yields (entry 4). In contrast to these successful results, attempts to cyclize silyl ether **10f** to produce **11f** and/or **9f** failed, even with excess pyridine (entry 5). The product **2a′** and ketone **6k** were mainly formed as products.

Conclusions

In summary, the details of the iodine-mediated cyclization of *N*-thioacyl 1,2-aminoalcohols and their silyl ethers in the presence of pyridine were presented. The reaction of alcohols derived from aromatic aldehydes was complete within 30 min and gave products with two imidazopyridyl groups, except for the alcohols with two 2-pyridyl groups. The reactions of alcohols derived from ketones showed three reaction pathways to the products, depending on the substituents on the carbon atom α to the hydroxy group. The first pathway involves the formation of products with two imidazopyridyl groups on the quaternary carbon atom. The second is accompanied by the elimination of ketones to give imidazo[1,5-*a*]pyridines without substituents at their 3-positions. The third involves the formation of the desired products, which are available as monoanionic *N*,*O*-chelating ligands, particularly in the reaction of *N*-thioacyl 1,2-aminoalcohol silyl ethers. The formation and application of metal complexes with imidazo[1,5-*a*]pyridine-1-ylalkylalcohols are currently being studied.

Experimental section

General remarks

Characterization. The IR spectra were obtained on a JASCO FT-IR 410 spectrophotometer. ^{1}H NMR (399.7 MHz), ^{13}C (100.4 MHz) NMR spectra were measured on a JNM-α400 spectrometer. ^{1}H and ^{13}C chemical shifts are reported in δ values referred to tetramethylsilane or $CDCl_3$ as an internal standard, respectively. All spectra were acquired in the proton-decoupled mode. The mass spectra (MS) and high resolution mass spectra

(HRMS) were taken on JMS-700 mass spectrometers. Melting points were determined by using a Yanaco MP-S2 micro melting point apparatus and are uncorrected. Elemental analyses were carried out by Elemental Analysis Center of Kyoto University.

Materials. Dichloromethane (CH_2Cl_2), and 1,2-dichloroethane ($ClCH_2CH_2Cl$) were distilled over phosphorus pentoxide (P_2O_5). Tetrahydrofuran (THF) dehydride, pyridine, chloroform, *p*-tolualdehyde, Et_2O and iodine (I_2) were purchased from Kanto Chemical Co., Ltd, and used without purification. Benzophenone, hydrochloric acid (HCl), triethylamine, 2-pyridinecarboxaldehyde, and 2-thiophenecarboxaldehyde were purchased from Nacalai Tesque Inc., and used without further purification. Imidazole, 2-picolylamine, 9-fluorenone, cyclohexanecarbaldehyde, 4,4′-bis(dimethylamino)benzophenone, 4,4′-dichlorobenzophenone, and 4,4′-dimethoxybenzophenone were purchased from Tokyo Chemical Industry Co., Ltd, and used without further purification. Benzaldehyde, trimethylacetaldehyde were purchased from Aldrich Chemical Company, Inc., and used without further purification. Acetaldehyde was purchased from Merck Ltd, and used without further purification. *n*-BuLi 15 w/w% in hexane was purchased from Mitsuwa Chemicals Co., Ltd, and used without further purification. Flash column chromatography was run on silica gel 60N (Spherical, Neutral, 40–50 μm) from Kanto Chemical Co., Ltd. All manipulations were carried out under an argon atmosphere.

General procedure for the preparation of *N*-thioacyl 1,2-aminoalcohols 3 and 7 from thioamides 1 and carbonyl compounds 6 as an example leading to 3a

To a THF solution (12.5 mL) of *N*-2-pyridylmethyl-4-methylbenzenecarbothioamide (**1a**) (1.2 g, 5.0 mmol) was added *n*-BuLi (1.6 M solution in hexane, 6.8 mL, 10 mmol) at 0 °C. The mixture was stirred at 0 °C for 10 min. Then, acetaldehyde (**6a**) (0.42 mL, 7.5 mmol) was added to the reaction mixture at 0 °C, and the solution was stirred at 0 °C for 30 min. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane–EtOAc = 3 : 1) to give *N*-(2-hydroxy-2-methyl-1-pyridin-2-ylethyl)-4-methylbenzenecarbothioamide (**3a**) (1.2 g, 4.2 mmol, 84% (major : minor = 60 : 40)) as a yellow solid.

***N*-(2-Hydroxy-2-methyl-1-pyridin-2-ylethyl)-4-methylbenzenecarbothioamide (3a).** A yellow solid; m.p. 154–155 °C; IR (KBr) 3282, 3057, 2932, 1599, 1571, 1536, 1506, 1442, 1369, 1319, 1230, 1127, 1064, 1007, 930, 822, 665, 564 cm^{-1}; MS (EI) *m*/*z* 286 (M^+); HRMS calcd for $C_{16}H_{18}N_2OS$: 286.1140, found: 286.1147; Diastereomer major: ^1H NMR ($CDCl_3$) δ 1.04 (d, J = 6.8 Hz, 3H), 2.26 (s, 3H), 4.28 (qd, J = 6.8 Hz, 2.9 Hz, 1H), 4.79 (br, 1H), 5.76 (dd, J = 7.6 Hz, 2.9 Hz, 1H), 7.09 (d, J = 8.3 Hz, 2H), 7.19 (ddd, J = 7.8 Hz, 4.9 Hz, 1.5 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.65 (td, J = 7.8 Hz, 1.5 Hz, 1H), 8.45 (d, J = 4.4 Hz, 1H), 9.06 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.1, 21.2, 62.5, 70.6, 123.2, 125.2, 126.9, 128.9, 137.0, 138.5, 141.7, 148.8, 156.5, 198.0; Diastereomer minor: ^1H NMR ($CDCl_3$) δ 1.32 (d, J = 6.3 Hz, 3H), 2.36 (s, 3H), 4.52 (qd, J = 6.3 Hz, 2.0 Hz, 1H), 5.11 (br, 1H, OH), 5.87 (dd, J = 8.5 Hz, 2.0 Hz, 1H), 7.18 (d, J = 8.3 Hz, 2H), 7.27 (ddd, J = 7.8 Hz, 4.9 Hz, 1.5 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.72 (td, J = 7.8 Hz, 1.5 Hz, 1H), 8.52 (d, J = 4.9 Hz, 1H), 8.76 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.4, 21.3, 62.1, 69.1, 123.4, 124.4, 126.8, 129.0, 137.3, 138.6, 141.8, 148.7, 158.4, 198.8.

***N*-(2-Hydroxy-2-cyclohexyl-1-pyridin-2-ylethyl)-4-methylbenzenecarbothioamide (3b).** A yellow solid; IR (KBr) 3313, 2924, 2846, 1596, 1570, 1529, 1504, 1438, 1369, 1226, 1205, 1185, 1077, 955, 822, 757, 719, 676, 632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–2.11 (m, 11H), 2.36 (s, 1.9H, major), 2.37 (s, 1.1H, minor), 3.76 (d, J = 3.9 Hz, 0.65H, major), 3.95 (d, J = 8.6 Hz, 0.35H, minor), 5.30 (br, 1H), 5.99 (dd, J = 8.1 Hz, 3.9 Hz, 0.65H, major), 6.03 (d, J = 8.6 Hz, 0.35H, minor), 7.16 (d, J = 8.3 Hz, 1.4H, major), 7.18 (d, J = 7.8 Hz, 0.6H, minor), 7.25–7.30 (m, 1H), 7.66–7.72 (m, 3.3H), 7.74 (d, J = 7.8 Hz, 1.5 Hz, 0.7H major), 8.49–8.52 (m, 1H), 8.69 (d, J = 8.6 Hz, 0.35H minor), 8.96 (d, J = 8.1 Hz, 0.65H major); ^{13}C NMR ($CDCl_3$) δ 21.2, 25.5, 25.6, 25.8, 25.9, 26.2, 28.9, 28.9, 29.4, 29.5, 40.4 (minor), 41.3 (major), 58.4 (minor), 59.0 (major), 77.7, 78.8, 123.2, 124.5, 125.7, 126.8, 128.9, 129.0, 137.1, 137.3, 138.5, 138.6, 141.6, 141.7, 148.6, 148.7, 157.4, 159.1, 197.3 (C═S, major), 197.8 (C═S, minor); MS (EI) *m*/*z* 354 (M^+); HRMS calcd for $C_{21}H_{26}N_2OS$: 354.1766, found: 354.1768.

***N*-(2-Hydroxy-3,3-dimethyl-1-pyridin-2-ylpropyl)-4-methylbenzenecarbothioamide (3c).** A yellow solid; IR (KBr) 3345, 3204, 3024, 2953, 2868, 1593, 1542, 1474, 1440, 1371, 1310, 1233, 1188, 1081, 1017, 1004, 981, 897, 755 cm^{-1}; MS (EI) *m*/*z* 328 (M^+); HRMS calcd for $C_{19}H_{24}N_2OS$: 328.1609, found: 328.1583; Diastereomer major: ^1H NMR ($CDCl_3$) δ 0.77 (s, 9H), 2.35 (s, 3H), 3.84 (d, J = 2.4 Hz, 1H), 6.03 (br, 1H), 6.05 (dd, J = 8.3 Hz, 2.4 Hz, 1H), 7.15 (d, J = 8.3 Hz, 2H), 7.28 (ddd, J = 7.8 Hz, 4.9 Hz, 1.5 Hz, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 7.8 Hz, 1H), 7.74 (td, J = 7.8 Hz, 1.5 Hz, 1H), 8.50 (d, J = 4.9 Hz, 1H), 8.80 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 21.3, 26.4, 35.3, 58.1, 82.7, 123.5, 126.0, 126.9, 129.0, 137.4, 138.7, 141.7, 148.6, 158.2, 197.0; Diastereomer minor: ^1H NMR ($CDCl_3$) δ 1.08 (s, 9H), 2.35 (s, 3H), 3.88 (s, 1H), 5.24 (br, 1H), 6.12 (d, J = 8.3 Hz, 1H), 7.16 (d, J = 8.3 Hz, 2H), 7.25 (ddd, J = 7.8 Hz, 4.9 Hz, 1.7 Hz, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 7.8 Hz, 1H), 7.71 (td, J = 7.8 Hz, 1.7 Hz, 1H), 8.50 (d, J = 4.9 Hz, 1H), 8.78 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 21.3, 26.5, 34.9, 57.8, 80.1, 123.2, 123.8, 126.7, 129.0, 137.3, 138.4, 141.6, 148.9, 159.8, 196.3.

***N*-(2-Hydroxy-1,2-dipyridin-2-ylethyl)benzenecarbothioamide (3d).** A yellow solid; IR (KBr) 3330, 3261, 3055, 2927, 1593, 1571, 1528, 1508, 1472, 1439, 1358, 1230, 1045, 1034, 999, 955, 775, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.52 (d, J = 2.9 Hz, 0.3H, minor), 5.66 (d, J = 3.4 Hz, 0.7H, major), 6.27 (dd, J = 7.3 Hz, 3.4 Hz, 0.7H, major), 6.39 (dd, J = 8.1 Hz, 2.9 Hz, 0.3H, minor), 6.65 (d, J = 7.8 Hz, 0.7H, major), 7.16–7.12 (m, 2H), 7.37–7.55 (m, 4.3H), 7.62–7.80 (m, 2.5H), 7.89–7.91 (m, 1.5H), 8.45–8.56 (m, 2H), 9.59 (d, J = 8.1 Hz, 0.3H minor), 9.65 (d, J = 7.3 Hz, 0.7H, major); ^{13}C NMR ($CDCl_3$) δ 62.6 (minor), 64.1 (major), 74.1 (minor), 74.3 (major), 121.2, 121.3,

122.75, 122.81, 122.9, 123.0, 123.6, 126.9, 127.0, 128.5, 131.2, 136.4, 136.9, 137.1, 141.5, 148.1, 148.5, 148.7, 154.8, 158.4, 198.1; MS (EI) *m/z* 335 (M^+); HRMS calcd for $C_{19}H_{17}N_3OS$: 335.1092, found: 335.1068.

***N*-(2-Hydroxy-1,2-dipyridin-2-ylethyl)2-pyridinecarbothioamide (3e).** A yellow solid; IR (KBr) 3245, 3052, 3006, 1592, 1502, 1436, 1328, 1150, 1071, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.52 (br, 0.6H, major), 5.58 (d, J = 2.7 Hz, 0.4H, minor), 5.59 (d, J = 3.4 Hz, 0.6H, major), 6.11 (br, 0.4H, minor), 6.35 (dd, J = 8.3 Hz, 3.4 Hz, 0.6H, major), 6.39 (dd, J = 8.8 Hz, 2.7 Hz, 0.4H, minor), 6.92 (d, J = 7.8 Hz, 0.6H, major), 7.12–7.17 (m, 1.6H), 7.22 (dd, J = 7.6 Hz, 4.9 Hz, 0.4H, minor), 7.40 (dd, J = 7.3 Hz, 4.6 Hz, 0.4H, minor), 7.43 (dd, J = 7.3 Hz, 4.6 Hz, 0.6H, major), 7.47 (dd, J = 7.8 Hz, 7.6 Hz, 0.6H, major), 7.47–7.53 (m, 1.4H), 7.62 (dd, J = 7.8 Hz, 7.6 Hz, 0.4H, minor), 7.63 (dd, J = 8.1 Hz, 7.6 Hz, 0.6H, major), 7.65 (dd, J = 8.1 Hz, 7.8 Hz, 0.4H, minor), 7.77 (dd, J = 7.8 Hz, 7.6 Hz, 0.4H, minor), 7.81 (dd, J = 7.8 Hz, 7.6 Hz, 0.6H, major), 8.47–8.49 (m, 1H), 8.54–8.60 (m, 2.4H), 8.68 (d, J = 8.1 Hz, 0.6H major), 11.35 (d, J = 8.8 Hz, 0.4H, minor), 11.52 (d, J = 8.3 Hz, 0.6H, major); ^{13}C NMR ($CDCl_3$) δ 62.3 (minor), 62.9 (major), 74.5 (minor), 74.7 (major), 120.9, 121.2, 122.2, 122.4, 122.6, 122.8, 123.2, 124.0, 124.9, 124.9, 125.9, 125.9, 136.4, 136.5, 136.6, 136.9, 136.9, 137.0, 147.2, 147.2, 148.1, 148.3, 148.4, 148.7, 151.1, 151.3, 155.7, 157.5, 158.7, 159.0, 190.5 (C═S major), 191.3 (C═S minor); MS (EI) *m/z* 302 ($M^+ - H_2S$); HRMS calcd for $C_{18}H_{16}N_4OS$: 336.1045, found: 336.1039.

***N*-(2-Hydroxy-2-thienyl-1-pyridin-2-ylethyl)benzenecarbothioamide (3f).** A yellow solid; IR (KBr) 3324, 3056, 2933, 1597, 1571, 1484, 1448, 1435, 1355, 1223, 1072, 1030, 1009, 950, 709, 683 cm^{-1}; MS (EI) *m/z* 340 (M^+); HRMS calcd for $C_{18}H_{16}N_2OS_2$: 340.0704, found: 340.0706; Diastereomer major: m.p. 139–142 °C; ^1H NMR ($CDCl_3$) δ 5.71 (d, J = 3.4 Hz, 1H), 5.80 (br, 1H), 6.22 (dd, J = 8.3 Hz, 3.4 Hz, 1H), 6.84 (d, J = 3.4 Hz, 1H), 6.89 (dd, J = 4.9 Hz, 3.4 Hz, 1H), 7.14 (d, J = 4.9 Hz, 1H), 7.28 (ddd, J = 7.8 Hz, 4.9 Hz, 1.5 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.39 (dd, J = 8.3 Hz, 7.3 Hz, 2H), 7.47 (t, J = 7.3 Hz, 1H), 7.63 (td, J = 7.8 Hz, 1.5 Hz, 1H), 7.80 (d, J = 8.3 Hz, 2H), 8.51 (d, J = 4.9 Hz, 1H), 9.11 (d, J = 7.8 Hz, 1H); ^{13}C NMR δ 63.0, 73.3, 123.5, 123.9, 124.7, 125.3, 126.7, 126.9, 128.5, 131.4, 137.2, 141.3, 144.5, 158.6, 155.7, 198.7; Diastereomer minor: m.p. 152–153 °C; ^1H NMR ($CDCl_3$) δ 5.75 (d, J = 2.4 Hz, 1H), 5.78 (br, 1H), 6.23 (dd, J = 8.1 Hz, 2.4 Hz, 1H), 6.96 (dd, J = 4.9 Hz, 3.4 Hz, 1H), 7.03 (d, J = 3.4 Hz, 1H), 7.26 (d, J = 4.9 Hz, 1H), 7.31 (ddd, J = 7.8 Hz, 4.9 Hz, 1.7 Hz, 1H), 7.35 (dd, J = 8.3 Hz, 7.3 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H), 7.70–7.73 (m, 3H), 7.75 (td, J = 7.8 Hz, 1.7 Hz, 1H), 8.53 (d, J = 4.9 Hz, 1H), 8.88 (d, J = 8.1 Hz, 1H); ^{13}C NMR δ 62.5, 71.8, 123.6, 124.2, 124.8, 125.2, 126.7, 126.9, 128.4, 131.2, 137.4, 141.4, 143.2, 148.7, 157.7, 199.1.

***N*-(2-Hydroxy-2-benzene-1-pyridin-2-ylethyl)-2,2-dimethylthiopropionamide (3g).** IR (KBr) 3375, 3084, 2961, 1597, 1524, 1477, 1441, 1382, 1355, 1057, 1005, 768, 744, 703, 615 cm^{-1}; MS (EI) *m/z* 280 ($M^+ - H_2S$); HRMS calcd for $C_{18}H_{22}N_2OS$: 314.1453, found: 314.1444; Diastereomer major: a yellow solid; m.p. 130–131 °C; ^1H NMR ($CDCl_3$) δ 1.39 (s, 9H), 5.16 (br, 1H), 5.48 (d, J = 3.0 Hz, 1H), 6.08 (dd, J = 7.3 Hz, 2.9 Hz, 1H), 6.95 (d, J = 7.8 Hz, 1H), 7.14 (d, J = 7.8 Hz, 2H), 7.19–7.26 (m, 4H), 7.51–7.57 (m, 1H), 8.52 (d, J = 4.9 Hz, 1H), 9.11 (d, 1H); ^{13}C NMR δ 29.9, 44.8, 63.2, 76.2, 123.1, 124.5, 125.7, 127.4, 127.9, 136.7, 140.2, 148.4, 155.3, 213.1; Diastereomer minor: yellow oil; ^1H NMR ($CDCl_3$) δ 1.19 (s, 9H), 5.35 (d, J = 3.1 Hz, 1H), 5.51 (br, 1H), 5.98 (dd, J = 7.3 Hz, 3.1 Hz, 1H), 7.15–7.25 (m, 6H), 7.43 (d, J = 7.8 Hz, 1H), 7.61 (td, J = 7.8 Hz, 1.5 Hz, 1H), 8.45 (d, J = 4.9 Hz, 1H), 8.70 (d, J = 7.3 Hz, 1H); ^{13}C NMR δ 29.8, 44.7, 62.6, 74.8, 123.2, 124.6, 125.9, 127.6, 128.1, 136.9, 139.8, 148.5, 157.3, 213.5.

***N*-(2-Hydroxy-2,2-diphenyl-1-pyridin-2-ylethyl)-4-methylbenzenecarbothioamide (7a).** A yellow solid; m.p. 179–180 °C; IR (KBr) 3356, 3289, 3057, 3024, 1595, 1571, 1488, 1448, 1351, 1258, 1187, 1174, 1061, 978, 820, 749, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.29 (s, 3H), 6.87 (d, J = 8.2 Hz, 1H), 7.01 (t, J = 7.3 Hz, 1H), 7.04 (d, J = 8.2 Hz, 2H), 7.10 (ddd, J = 7.6 Hz, 5.0 Hz, 1.5 Hz, 1H), 7.12 (t, J = 7.8 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.32 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.56 (td, J = 7.6 Hz, 1.5 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.5 Hz, 2H), 7.91 (br, 1H), 8.37 (d, J = 5.0 Hz, 1H), 8.75 (d, J = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 62.3, 81.2, 123.2, 125.2, 125.3, 126.6, 126.7, 126.9, 127.2, 128.1, 128.5, 128.9, 137.1, 138.8, 141.6, 143.9, 144.9, 148.1, 157.5, 197.9; MS (EI) *m/z* 424 (M^+); HRMS calcd for $C_{27}H_{24}N_2OS$: 424.1609, found: 424.1603.

***N*-(2-Hydroxy-2,2-diphenyl-1-pyridin-2-ylethyl)-4-methoxybenzenecarbothioamide (7b).** A yellow solid; m.p. 126–127 °C; IR (KBr) 3293, 3056, 2967, 2867, 1605, 1505, 1448, 1439, 1376, 1254, 1173, 1065, 1025, 969, 834, 755, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.77 (s, 3H), 6.75 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.1 Hz, 1H), 7.01 (t, J = 7.3 Hz, 1H), 7.11 (ddd, J = 7.8 Hz, 4.9 Hz, 1.5 Hz, 1H), 7.12 (t, J = 7.8 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.33 (t, J = 7.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 4H), 7.56 (td, J = 7.8 Hz, 1.5 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 8.8 Hz, 2H), 7.92 (br, 1H), 8.37 (d, J = 4.9 Hz, 1H), 8.69 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.4, 62.3, 81.2, 113.5, 123.1, 125.20, 125.24, 126.6, 126.9, 127.2, 128.1, 128.5, 128.6, 134.0, 137.1, 143.9, 144.9, 148.1, 157.5, 162.1, 197.0; MS (EI) *m/z* 406 ($M^+ - H_2S$); HRMS calcd for $C_{27}H_{24}N_2O_2S$: 440.1558, found: 440.1537.

***N*-(2-Hydroxy-2,2-diphenyl-1-pyridin-2-ylethyl)-2,2-dimethylthiopropionamide (7c).** A yellow solid; m.p. 127–128 °C; IR (KBr) 3389, 3192, 3084, 2953, 1595, 1571, 1501, 1475, 1450, 1377, 1349, 1057, 1008, 757, 744, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (s, 9H), 6.73 (d, J = 7.8 Hz, 1H), 6.91 (t, J = 7.3 Hz, 1H), 6.99 (ddd, J = 7.8 Hz, 4.9 Hz, 1.5 Hz, 1H), 7.02 (dd, J = 8.3 Hz, 7.3 Hz, 2H), 7.10 (t, J = 7.3 Hz, 1H), 7.21 (dd, J = 8.3 Hz, 7.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.45 (td, J = 7.8 Hz, 1.5 Hz, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 7.8 Hz, 1H), 7.83 (br, 1H), 8.26 (d, J = 4.9 Hz, 1H), 8.51 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.5, 44.3, 61.6, 81.0, 122.9, 125.0, 125.1, 126.5, 126.7, 126.9, 127.9, 128.1, 137.0, 143.8, 144.8, 147.9, 157.3, 212.1; MS (EI) *m/z* 390 (M^+); HRMS calcd for $C_{24}H_{26}N_2OS$: 390.1766, found: 390.1775.

***N*-(2-Hydroxy-2,2-bis(4-chlorophenyl)-1-pyridin-2-ylethyl)-4-methylbenzenecarbothioamide (7d).** A yellow solid; m.

p. 134–135 °C; IR (KBr) 3308, 3101, 2923, 1598, 1570, 1488, 1437, 1406, 1369, 1349, 1090, 1078, 1012, 971, 817 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H), 6.88 (d, J = 8.3 Hz, 1H), 7.08 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 7.16 (ddd, J = 7.8 Hz, 4.9 Hz, 1.7 Hz, 1H), 7.27 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.62 (td, J = 7.8 Hz, 1.7 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 8.08 (br, 1H), 8.38 (d, J = 4.9 Hz, 1H), 8.66 (d, J = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 61.7, 80.7, 123.6, 126.6, 126.7, 126.7, 126.8, 128.4, 128.7, 129.0, 132.7, 133.3, 137.7, 138.4, 142.0, 142.1, 143.3, 148.0, 156.9, 198.0; MS (EI) m/z 458 ($M^+ - H_2S$); HRMS calcd for $C_{27}H_{22}Cl_2N_2OS$: 492.0830, Found: 492.0827.

***N*-(2-Hydroxy-2,2-bis(4-methoxyphenyl)-1-pyridin-2-ylethyl)-4-methylbenzenecarbothioamide (7e).** A yellow solid; m.p. 133–136 °C; IR (KBr) 3310, 3293, 2953, 2833, 1608, 1509, 1251, 1174, 1034, 822 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.29 (s, 3H), 3.64 (s, 3H), 3.72 (s, 3H), 6.63 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.5 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 7.10 (ddd, J = 7.6 Hz, 4.9 Hz, 1.2 Hz, 1H), 7.29 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.55 (dt, J = 7.8 Hz, 1.7 Hz, 1H), 7.58 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 7.8 Hz, 1H), 7.78 (br, 1H), 8.36 (d, J = 4.9 Hz, 1H), 8.76 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.2, 55.0, 55.1, 62.5, 80.7, 113.3, 113.7, 123.1, 126.3, 126.7, 126.8, 128.9, 136.5, 137.0, 137.5, 138.7, 141.6, 148.1, 157.6, 157.9, 158.4, 197.7; MS (EI) m/z 484 (M^+); HRMS calcd for $C_{29}H_{28}N_2O_3S$: 484.1821, found: 484.1829.

***N*-(2-Hydroxy-2,2-bis(4-dimethylaminophenyl)-1-pyridin-2-ylethyl)4-methylbenzenecarbothioamide (7f).** A yellow solid; m.p. 193–194 °C (decomp.); IR (KBr) 3351, 3196, 2882, 2792, 1614, 1521, 1490, 1360, 1224, 1063, 814 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.29 (s, 3H), 2.79 (s, 6H), 2.87 (s, 6H), 6.46 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.1 Hz, 1H), 6.67 (d, J = 8.8 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 7.08 (dd, J = 7.3 Hz, 4.9 Hz, 1H), 7.18 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.53 (dd, J = 7.8 Hz, 7.3 Hz, 1H), 7.55 (br, 1H), 7.61 (d, J = 7.8 Hz, 1H), 8.37 (d, J = 4.9 Hz, 1H), 8.82 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 40.4, 40.5, 62.8, 80.7, 112.0, 112.5, 122.8, 125.9, 126.0, 126.8, 127.0, 128.9, 132.7, 133.6, 136.8, 138.9, 141.4, 148.0, 148.7, 149.3, 158.0, 197.4; MS (EI) m/z 510 (M^+); HRMS calcd for $C_{31}H_{34}N_4OS$: 510.2453, Found: 510.2423.

***N*-(2-Pyridylmethyl-9*H*-fluoren-9-ol)-4-methylbenzenecarbothioamide (7g).** A yellow solid; m.p. 122–124 °C; IR (KBr) 3346, 3245, 3048, 3015, 2932, 1590, 1480, 1354, 1209, 1092, 1065, 824, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (s, 3H), 6.37 (d, J = 8.5 Hz, 1H), 6.99 (d, J = 7.8 Hz, 1H), 7.08 (d, J = 7.3 Hz, 1H), 7.13–7.19 (m, 6H), 7.28–7.32 (m, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.47 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 8.52 (d, J = 8.5 Hz, 1H), 8.59 (d, J = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 63.8, 85.4, 119.7, 120.1, 123.3, 123.8, 124.5, 124.7, 126.8, 127.9, 129.1, 129.3, 129.6, 137.1, 138.4, 139.5, 140.2, 142.0, 145.6, 145.7, 148.1, 156.8, 199.2; MS (EI) m/z 422 (M^+); HRMS calcd for $C_{27}H_{22}N_2OS$: 422.1453, found: 422.1430.

General procedure for the cyclization of *N*-thioacyl 1,2-aminoalcohols 3 to imidazo[1,5-*a*]pyridine-1-ylethanols as an example leading to 2b

To a THF solution (2 mL) of *N*-(2-hydroxy-2-cyclohexyl-1-pyridine-2-ylethyl)-4-methylbenzenecarbothioamide (**1b**) (0.17 g, 0.5 mmol) was added iodine (0.38 g, 1.5 mmol) and pyridine (0.12 mL, 1.0 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 min. To the reaction mixture was then added an aqueous solution of sodium thiosulfate, and the aqueous layer was extracted with dichloromethane. The organic layer was washed with water, and dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane–EtOAc = 8 : 1–1 : 1) to give (3-(4-methylphenyl)imidazo[1,5-*a*]pyridine-1-yl)cyclohexylmethanol (**2b**) as a brown oil.

1-(3-(4-Methylphenyl)imidazo[1,5-*a*]pyridine-1-yl)ethanol (2a). A brown oil; IR (neat) 3343, 2973, 2924, 1750, 1711, 1633, 1530, 1466, 1364, 1313, 1112, 1074, 1040, 1007, 886, 825, 721, 502 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (d, J = 6.3 Hz, 3H), 2.40 (s, 3H), 3.29 (br, 1H), 5.29 (q, J = 6.3 Hz, 1H), 6.32–6.48 (m, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 10.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) d 21.3, 23.9, 64.8, 112.9, 118.0, 118.5, 121.3, 126.7, 127.1, 127.9, 129.6, 135.5, 136.8, 138.5; MS (EI) m/z 252 (M^+); HRMS calcd for $C_{16}H_{16}N_2O$: 252.1263, found: 252.1243.

(3-(4-Methylphenyl)imidazo[1,5-*a*]pyridine-1-yl)cyclohexylmethanol (2b). A brown oil; IR (KBr) 3394, 2923, 2849, 1750, 1632, 1528, 1463, 1447, 1364, 1313, 1262, 1082, 1021, 999, 950, 823, 751, 471 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87–2.01 (m, 11H), 2.29 (s, 3H), 3.45 (br, 1H), 4.65 (d, J = 7.3 Hz, 1H), 6.36 (dd, J = 7.3 Hz, 6.3 Hz, 1H), 6.50 (dd, J = 9.3 Hz, 6.3 Hz, 1H), 7.16 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 9.3 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H), 8.00 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 25.9, 26.0, 26.4, 29.0, 29.3, 44.7, 73.1, 112.9, 117.9, 118.6, 121.2, 127.1, 127.7, 127.9, 129.5, 133.9, 136.9, 138.5; MS (EI) m/z 320 (M^+); HRMS calcd for $C_{21}H_{24}N_2O$: 320.1889, found: 320.1906.

(3-(4-Methylphenyl)imidazo[1,5-*a*]pyridine-1-yl)-2,2-dimethylpropanol (2c). A brown soild; m.p. 47–48 °C; IR (KBr) 3253, 2950, 2865, 1633, 1529, 1463, 1361, 1314, 1240, 1185, 1113, 1082, 1058, 1011, 964, 898, 823, 739, 716, 499 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (s, 9H), 2.26 (s, 3H), 3.66 (br, 1H), 4.59 (s, 1H), 6.32 (dd, J = 7.3 Hz, 6.3 Hz, 1H), 6.46 (dd, J = 9.3 Hz, 6.3 Hz, 1H), 7.13 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 9.3 Hz, 1H), 7.47 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5, 26.3, 37.3, 76.7, 112.9, 118.0, 119.4, 121.3, 127.4, 128.1, 128.2, 129.7, 133.3, 136.7, 138.5; MS (EI) m/z 294 (M^+); HRMS calcd for $C_{19}H_{22}N_2O$: 294.1732, found: 294.1743.

(3-Phenylimidazo[1,5-*a*]pyridine-1-yl)-2-pyridine-1-ylmethanol (2d). A brown oil; IR (neat) 3265, 3064, 1634, 1591, 1571, 1519, 1461, 1435, 1367, 1317, 1148, 1077, 1033, 1001, 961, 916, 849, 774, 740, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.62 (br, 1H), 6.28 (s, 1H), 6.47 (dd, J = 7.3 Hz, 6.3 Hz, 1H), 6.58 (dd, J = 9.3 Hz, 6.3 Hz, 1H), 7.17 (dd, J = 7.3 Hz, 5.1 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.41 (d, J = 9.3 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.48 (d, J = 7.8 Hz, 1H), 7.62 (td, J = 7.8 Hz, 1.5

Hz, 1H), 7.73 (d, J = 7.3 Hz, 2H), 8.13 (d, J = 7.3 Hz, 1H), 8.56 (d, J = 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 70.7, 113.1, 118.5, 118.8, 121.1, 121.4, 122.2, 128.0, 128.1, 128.5, 128.8, 130.0, 133.2, 136.7, 136.9, 147.6, 160.6; MS (EI) m/z 301 (M^+); HRMS calcd for $C_{19}H_{15}N_3O$: 301.1215, found: 301.1204.

(3-(2-Pyridin-1-yl)imidazo[1,5-*a*]pyridin-1-yl)-2-pyridin-1-ylmethanol (2e). A yellow solid; m.p. 130–134 °C; IR (KBr) 3293, 3134, 1587, 1499, 1426, 1342, 1030, 755, 737 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.43 (br, 1H), 6.28 (s, 1H), 6.69 (dd, J = 7.3 Hz, 6.6 Hz, 1H), 6.77 (dd, J = 9.0 Hz, 6.6 Hz, 1H), 7.19 (dd, J = 6.3 Hz, 4.9 Hz, 1H), 7.22 (dd, J = 6.8 Hz, 4.9 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 7.64 (dd, J = 7.8 Hz, 7.6 Hz, 1H), 7.77 (dd, J = 8.1 Hz, 7.6 Hz, 1H), 8.35 (d, J = 8.1 Hz, 1H), 8.63–8.60 (m, 2H), 9.90 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 70.8, 113.7, 118.1, 120.0, 121.5, 122.0, 122.4, 125.9, 129.6, 133.6, 134.0, 136.4, 136.8, 147.7, 148.1, 150.9, 160.5; MS (EI) m/z 302 (M^+); HRMS calcd for $C_{18}H_{14}N_4O$: 302.1168, found: 302.1160.

General procedure for the cyclization of *N*-thioacyl 1,2-aminoalcohols 3 to imidazo[1,5-*a*]pyridinylethanols as an example leading to 4f

To a THF solution (4 mL) of *N*-(2-hydroxy-2-thienyl-1-pyridin-2-ylethyl)benzenecarbothioamide (**3f**) (0.17 g, 0.50 mmol) was added I_2 (0.38 g, 1.5 mmol) and pyridine (0.12 mL, 1.5 mmol) at room temperature. The mixture was stirred at room temperature for 30 min. The reaction mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$ and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane–EtOAc = 6 : 1) to give 0.10 g (0.22 mmol, 86% per 0.25 mmol) of bis-(3-phenylimidazo[1,5-*a*]pyridine-1-yl)-2-thiophen-1-ylmethane (**4f**) as a yellow solid.

Bis-(3-(4-methylphenyl)imidazo[1,5-*a*]pyridine-1-yl)ethane (4a). A brown solid; m.p. 110–111 °C; IR (KBr) 3432, 3026, 2970, 2922, 2859, 1630, 1527, 1458, 1362, 1312, 1248, 1111, 1023, 954, 824, 732, 717 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.01 (d, J = 7.3 Hz, 3H), 2.42 (s, 6H), 5.02 (q, J = 7.3 Hz, 1H), 6.42 (dd, J = 7.3 Hz, 6.3 Hz, 2H), 6.51 (dd, J = 9.3 Hz, 6.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 4H), 7.56 (d, J = 9.3 Hz, 2H), 7.68 (d, J = 8.0 Hz, 4H), 8.11 (d, J = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) 20.7, 21.4, 33.2, 122.8, 117.0, 199.4, 121.0, 127.1, 127.7, 128.0, 129.6, 136.0, 136.1, 138.3; MS (EI) m/z 442 (M^+); HRMS calcd for $C_{30}H_{26}N_4$: 442.2157, found: 442.2162.

Bis-(3-phenylimidazo[1,5-*a*]pyridine-1-yl)-2-thiophen-1-ylmethane (4f). A yellow solid; m.p. 87–88 °C; IR (KBr) 3063, 3037, 2960, 2924, 1632, 1602, 1519, 1460, 1404, 1364, 1315, 1274, 1073, 1002, 961, 859, 772, 731, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.31 (dd, J = 7.3 Hz, 6.4 Hz, 2H), 6.44 (s, 1H), 6.45 (dd, J = 9.3 Hz, 6.4 Hz, 2H), 6.80 (dd, J = 4.9 Hz, 3.4 Hz, 1H), 6.93 (d, J = 3.4 Hz, 1H), 7.05 (d, J = 4.9 Hz, 1H), 7.24 (t, J = 7.6 Hz, 2H), 7.34 (dd, J = 7.6 Hz, 7.3 Hz, 4H), 7.53 (d, J = 9.3 Hz, 2H), 7.65 (d, J = 7.3 Hz, 4H), 8.01 (d, J = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 40.6, 112.9, 117.8, 119.5, 121.0, 124.1, 125.5, 126.2, 128.0, 128.1, 128.2, 128.7, 130.4, 133.6, 136.4, 147.1; MS (EI) m/z 482 (M^+); HRMS calcd for $C_{31}H_{22}N_4S$: 482.1565, found: 482.1557.

Bis-(α,α-dimethylethylimidazo[1,5-*a*]pyridine-1-yl)phenylmethane (4g). A yellow oil; IR (KBr) 2967, 2928, 2870, 1759, 1632, 1600, 1490, 1462, 1363, 1305, 1219, 1071, 1003, 865, 799, 749, 719, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 18H), 6.13 (s, 1H), 6.34 (dd, J = 7.3 Hz, 6.3 Hz, 2H), 6.42 (dd, J = 9.3 Hz, 6.3 Hz, 2H), 7.10 (t, J = 7.3 Hz, 1H), 7.18 (dd, J = 7.8 Hz, 7.3 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 9.3 Hz, 2H), 7.90 (d, J = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 28.2, 33.3, 44.7, 111.2, 115.4, 120.5, 122.4, 125.6, 127.8, 128.2, 128.5, 131.2, 143.1, 144.4; MS (EI) m/z 436 (M^+); HRMS calcd for $C_{29}H_{32}N_4$: 436.2627, found; 436.2628.

Bis-(3-(4-methylphenyl)imidazo[1,5-*a*]pyridine-1-yl)-1,1-diphenylmethane (8a). A yellow solid; m.p. 275–277 °C; IR (KBr) 3016, 2919, 1736, 1630, 1595, 1523, 1490, 1464, 1443, 1393, 1360, 1313, 1243, 1180, 1115, 1007, 961, 877, 825, 742, 716, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 6H), 6.24 (dd, J = 9.3 Hz, 6.3 Hz, 2H), 6.32 (dd, J = 7.3 Hz, 6.3 Hz, 2H), 6.36 (d, J = 9.3 Hz, 2H), 7.09–7.18 (m, 10H), 7.37 (d, J = 8.3 Hz, 4H), 7.55 (d, J = 7.8 Hz, 4H), 8.09 (d, J = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.3, 57.6, 112.5, 117.0, 121.2, 125.9, 127.2, 127.9, 128.1, 129.3, 129.4, 130.7, 135.6, 137.1, 137.9, 146.5; MS (EI) m/z 580 (M^+).

Bis-(3-(4-methoxyphenyl)limidazo[1,5-*a*]pyridine-1-yl)-1,1-diphenylmethane (8b). A brown solid; m.p. 134–135 °C; IR (KBr) 3052, 3016, 2931, 1610, 1528, 1463, 1362, 1289, 1249, 1173, 1031, 835, 745, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 6H), 6.33 (dd, J = 7.8 Hz, 6.3 Hz, 2H), 6.41 (dd, J = 9.3 Hz, 6.3 Hz, 2H), 6.42 (d, J = 9.3 Hz, 2H), 6.97 (d, J = 8.8 Hz, 4H), 7.17–7.27 (m, 6H), 7.44 (d, J = 8.8 Hz, 4H), 7.66 (d, J = 8.8 Hz, 4H), 8.14 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.3, 57.5, 112.4, 114.1, 116.8, 121.1, 123.4, 125.9, 127.1, 129.0, 129.6, 130.7, 135.4, 137.0, 146.5, 159.4; MS (EI) m/z 612 (M^+); HRMS calcd for $C_{41}H_{32}N_4O_2$: 612.2525, found: 612.2534.

General procedure for the silylation of *N*-thioacyl 1,2-aminoalcohols 7 to silyl ethers 10 as an example leading to 10a

To a $ClCH_2CH_2Cl$ solution (3 mL) of *N*-(2,2-diphenyl-2-hydroxy)-1-pyridin-2-ylethyl)-4-methylbenzenecarbothioamide (**7a**) (0.21 g, 0.50 mmol) and imidazole (68 mg, 1.0 mmol) was added chlorotrimethylsilane (0.13 mL, 1.0 mmol) at room temperature. The mixture was stirred at reflux for 12 h. The resulting mixture was poured into a saturated aqueous solution of NH_4Cl and extracted with Et_2O. The combined organic layer was washed with water. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane–ethyl acetate = 16 : 1) to give 0.20 g (0.40 mmol, 80%) of *N*-(2,2-diphenyl-1-pyridin-2-yl-2-trimethylsilyloxyethyl)-4-methylbenzenecarbothioamide (**10a**) as a yellow solid.

***N*-(2,2-Diphenyl-1-pyridin-2-yl-2-trimethylsilyloxyethyl)-4-methylbenzenecarbothioamide (10a).** A yellow solid; m.p. 117–118 °C; IR (KBr) 3392, 3060, 2957, 1492, 1250, 1102, 1073, 880, 841, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.17

(s, 9H), 2.25 (s, 3H), 6.77 (d, J = 9.8 Hz, 1H), 6.93 (dd, J = 7.3 Hz, 4.9 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 7.05 (d, J = 8.3 Hz, 2H), 7.14–7.21 (m, 8H), 7.29–7.31 (m, 2H), 7.35 (dd, J = 7.8 Hz, 7.3 Hz, 1H), 7.52 (d, J = 8.3 Hz, 2H), 8.11 (d, J = 4.9 Hz, 1H), 8.53 (d, J = 9.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.8, 21.3, 65.2, 84.6, 122.0, 125.2, 126.7, 127.7, 127.7, 127.9, 128.2, 128.8, 129.0, 134.5, 139.4, 141.4, 142.8, 143.0, 147.9, 156.6, 197.7; MS (EI) m/z 462 ($M^+ - H_2S$); HRMS calcd for $C_{30}H_{32}N_2OSSi$: 496.2005, found: 496.1995.

***N*-(2,2-Bis(4-chlorophenyl)-1-pyridin-2-yl-2-trimethylsilyloxyethyl)-4-methylbenzenecarbothioamide (10d).** A yellow solid; m.p. 66–69 °C; IR (KBr) 3380, 2955, 1591, 1490, 1361, 1253, 1092, 1013, 884, 842 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.08 (s, 9H), 2.35 (s, 3H), 6.82 (d, J = 9.9 Hz, 1H), 7.05 (dd, J = 7.6 Hz, 4.9 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.3 Hz, 4H), 7.35 (d, J = 8.8 Hz, 2H), 7.48 (dd, J = 7.8 Hz, 7.6 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 8.21 (d, J = 4.9 Hz, 1H), 8.53 (d, J = 9.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.9, 21.3, 64.7, 83.9, 122.3, 125.3, 126.7, 127.9, 128.0, 129.1, 129.5, 130.3, 133.9, 134.1, 134.8, 139.2, 141.1, 141.3, 141.8, 148.1, 156.1, 198.2; MS (EI) m/z 530 ($M^+ - H_2S$); HRMS calcd for $C_{30}H_{30}Cl_2N_2OSSi–CH_3$: 549.0990, found: 549.0993.

***N*-(2,2-Bis(4-methoxyphenyl)-1-pyridin-2-yl-2-trimethylsilyloxyethyl)-4-methylbenzenecarbothioamide (10e).** A yellow solid; m.p. 60–62 °C; IR (KBr) 3377, 2954, 2836, 1608, 1509, 1180, 1086, 1035, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.10 (s, 9H), 2.33 (s, 3H), 3.78 (s, 3H), 3.80 (s, 3H), 6.78 (d, J = 9.3 Hz, 2H), 6.78 (d, J = 9.8 Hz, 1H), 6.78 (d, J = 9.3 Hz, 2H), 7.02 (dd, J = 7.3 Hz, 4.9 Hz, 1H), 7.11 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 7.8 Hz, 1H), 7.13 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.46 (dd, J = 7.8 Hz, 7.3 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 8.21 (d, J = 4.9 Hz, 1H), 8.55 (d, J = 9.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.8, 21.3, 55.1, 65.5, 83.8, 112.8, 112.9, 122.0, 125.3, 126.7, 129.0, 129.5, 130.3, 134.5, 134.9, 135.1, 139.5, 141.4, 147.8, 156.8, 158.9, 159.1, 197.6; MS (EI) m/z 522 ($M^+ - H_2S$); HRMS calcd for $C_{32}H_{36}N_2O_3SSi–H_2S$: 522.2339, found: 522.2343.

***N*-(2,2-Bis(4-dimethylaminophenyl)-1-pyridin-2-yl-2-trimethylsilyloxyethyl)-4-methylbenzenecarbothioamide (10f).** A yellow solid; m.p. 85–89 °C (decomp.); IR (KBr) 3377, 2952, 2892, 2801, 1611, 1520, 1358, 1250, 1163, 1079, 887, 841 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.11 (s, 9H), 2.32 (s, 3H), 2.91 (s, 6H), 2.93 (s, 6H), 6.59 (d, J = 8.8 Hz, 4H), 6.75 (d, J = 9.3 Hz, 1H), 7.01 (dd, J = 7.3 Hz, 4.9 Hz, 1H), 7.04 (d, J = 8.8 Hz, 2H), 7.11 (dd, J = 8.1 Hz, 2H), 7.11 (d, J = 7.8 Hz, 1H), 7.22 (d, J = 8.8 Hz, 2H), 7.44 (dd, J = 7.8 Hz, 7.3 Hz, 1H), 7.59 (d, J = 8.1 Hz, 2H), 8.23 (d, J = 4.9 Hz, 1H), 8.53 (d, J = 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.8, 21.2, 40.3, 65.8, 83.8, 111.0, 111.1, 121.7, 125.3, 126.8, 128.8, 129.2, 130.0, 130.3, 130.5, 134.2, 139.5, 141.1, 147.6, 149.6, 149.8, 157.3, 197.1; MS (EI) m/z 582 (M^+); HRMS calcd for $C_{34}H_{42}N_4OSSi$: 582.2849, found: 582.2849.

***N*-(2-Pyridylmethyl-9*H*-fluoren-9-trimethylsilyloxy)-4-methylbenzenecarbothioamide (10g).** A yellow solid; m.p. 45–48 °C; IR (KBr) 3222, 3059, 1714, 1610, 1498, 1186, 1091, 918, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 2.61 (s, 3H), 6.86 (d, J = 7.6 Hz, 1H), 6.99 (d, J = 9.6 Hz, 1H), 7.36 (d, J = 8.3 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.52–7.59 (m, 4H), 7.64 (t, J = 7.6 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.89 (d, J = 7.3 Hz, 1H), 7.90 (d, J = 7.6 Hz, 2H), 7.96 (d, J = 7.3 Hz, 1H), 7.99 (t, J = 7.6 Hz, 1H), 8.64 (d, J = 9.6 Hz, 1H), 8.75 (d, J = 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.1, 21.2, 64.6, 85.6, 119.3, 119.7, 122.8, 125.6, 125.8, 126.6, 126.7, 127.0, 127.5, 128.7, 129.4, 129.6, 135.1, 139.4, 139.5, 140.6, 141.0, 144.1, 146.0, 147.9, 156.0, 198.4; MS (EI) m/z 460 ($M^+ - H_2S$); HRMS calcd for $C_{30}H_{30}N_2OSSi$: 494.1848, found: 494.1833.

Diphenyl-3-(4-methylphenyl)imidazo[1,5-*a*]pyridin-1-yltrimethylsilyloxymethane (11a). A yellow solid; m.p. 52–57 °C; IR (KBr) 3058, 3024, 2952, 1475, 1447, 1249, 1001, 1056, 881, 840, 746, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.16 (s, 9H), 2.40 (s, 3H), 6.38–6.45 (m, 2H), 6.68–6.73 (m, 1H), 7.20 (t, J = 7.1 Hz, 2H), 7.26 (t, J = 7.3 Hz, 4H), 7.27 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 7.3 Hz, 4H), 7.64 (d, J = 8.3 Hz, 2H), 8.12–8.16 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 1.5, 21.4, 81.8, 112.4, 117.9, 120.3, 121.3, 126.6, 127.5, 127.8, 128.1, 128.2, 129.2, 129.5, 136.2, 136.4, 138.3; MS (EI) m/z 462 (M^+); HRMS calcd for $C_{30}H_{30}N_2OSi$: 462.2127, found: 462.2150.

Bis(4-chlorophenyl)-3-(4-methylphenyl)imidazo[1,5-*a*]pyridin-1-yltrimethylsilyloxymethane (11d). A yellow solid; m.p. 70–72 °C; IR (KBr) 2954, 1590, 1486, 1250, 1091, 1054, 1013, 886, 842, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.17 (s, 9H), 2.41 (s, 3H), 6.46 (d, J = 6.8 Hz, 6.3 Hz, 1H), 6.83 (dd, J = 9.3 Hz, 6.3 Hz, 1H), 6.75 (d, J = 9.3 Hz, 1H), 7.25 (d, J = 8.3 Hz, 4H), 7.30 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.3 Hz, 4H), 7.63 (d, J = 8.3 Hz, 2H), 8.16 (d, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.4, 21.4, 80.9, 112.6, 118.5, 120.0, 121.5, 127.4, 127.8, 128.2, 129.3, 129.6, 132.6, 134.9, 136.6, 138.6, 146.0; MS (EI) m/z 530 (M^+); HRMS calcd for $C_{30}H_{28}Cl_2N_2OSi$: 530.1348, found: 530.1361.

Bis(4-methoxyphenyl)-3-(4-methylphenyl)imidazo[1,5-*a*]pyridin-1-yltrimethylsilyloxymethane (11e). A yellow solid; m.p. 51–53 °C; IR (KBr) 2952, 2834, 1606, 1507, 1249, 1173, 1089, 1035, 888, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.29 (s, 9H), 2.25 (s, 3H), 3.63 (s, 6H), 6.27 (dd, J = 6.8 Hz, 6.3 Hz, 1H), 6.31 (dd, J = 8.8 Hz, 6.3 Hz, 1H), 6.66 (d, J = 8.8 Hz, 4H), 6.76 (d, J = 8.8 Hz, 1H), 7.13 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.8 Hz, 4H), 7.49 (d, J = 8.1 Hz, 2H), 7.98 (d, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.6, 21.4, 55.1, 81.4, 112.4, 112.7, 117.7, 120.5, 121.2, 127.8, 128.2, 128.9, 129.2, 129.4, 136.3, 136.8, 138.2, 140.2, 158.2; MS (EI) m/z 522 (M^+); HRMS calcd for $C_{32}H_{34}N_2O_3Si$: 522.2339, found: 522.2314.

Diphenyl-3-(4-methylphenyl)imidazo[1,5-*a*]pyridin-1-ylmethanol (9a). A yellow solid; m.p. 176–177 °C; IR (KBr) 3466, 3023, 1446, 1367, 1006, 823, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H), 5.00 (br, 1H), 6.09 (d, J = 9.0 Hz, 1H), 6.30 (dd, J = 9.0 Hz, 6.3 Hz, 1H), 6.34 (dd, J = 7.1 Hz, 6.3 Hz, 1H), 7.17–7.25 (m, 8H), 7.30 (d, J = 7.8 Hz, 4H), 7.57 (d, J = 8.1 Hz, 2H), 8.06 (d, J = 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 78.4, 112.7, 118.7, 119.0, 121.5, 127.0, 127.4, 127.5, 127.8, 128.1, 128.2, 129.6, 136.7, 137.0, 138.8, 146.2; MS (EI) m/z 390 (M^+); HRMS calcd for $C_{27}H_{22}N_2O$: 390.1732, found: 390.1743.

Diphenyl-3-(4-methoxylphenyl)imidazo[1,5-*a*]pyridin-1-yl-methanol (9b). A yellow solid; m.p. 151–155 °C (decomp.); IR (KBr) 3444, 3003, 2961, 2934, 1609, 1530, 1375, 1252, 1035, 1013, 702, 741 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.86 (s, 3H), 5.05 (br, 1H), 6.15 (d, J = 9.3 Hz, 1H), 6.39 (d, J = 9.3 Hz, 6.3 Hz, 1H), 6.44 (dd, J = 7.3 Hz, 6.3 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H), 7.28–7.33 (m, 6H), 7.38–7.40 (m, 4H), 7.69 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.4, 78.4, 112.6, 114.4, 118.6, 119.0, 121.3, 122.3, 127.3, 127.8, 128.2, 129.6, 136.5, 136.9, 146.3, 160.0; MS (EI) m/z 406 (M^+); HRMS calcd for $C_{27}H_{22}N_2O_2$: 406.1681, found: 406.1661.

Bis(4-chlorophenyl)-3-(4-methylphenyl)imidazo[1,5-*a*]pyridin-1-ylmethanol (9d). A yellow solid; m.p. 81–84 °C (decomp.); IR (KBr) 3428, 2921, 1489, 1362, 1092, 1012, 824, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.41 (s, 3H), 5.13 (br, 1H), 6.25–6.28 (m, 1H), 6.45–6.49 (m, 2H), 7.27 (d, J = 8.8 Hz, 4H), 7.29 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.8 Hz, 4H), 7.62 (d, J = 8.3 Hz, 2H), 8.16 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 77.7, 112.9, 118.6, 119.3, 121.6, 126.7, 127.4, 128.0, 129.5, 129.7, 133.4, 135.9, 137.0, 139.0, 144.5; MS (EI) m/z 458 (M^+); HRMS calcd for $C_{27}H_{20}Cl_2N_2O$: 458.0953, Found: 458.0955.

Bis(4-methoxyphenyl)-3-(4-methylphenyl)imidazo[1,5-*a*]pyridin-1-ylmethanol (9e). A yellow solid; m.p. 62–66 °C (decomp.); IR (KBr) 3491, 2925, 2833, 1607, 1507, 1304, 1245, 1016, 1007, 828 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.42 (s, 3H), 3.80 (s, 6H), 4.95 (br, 1H), 6.23 (d, J = 8.8 Hz, 1H), 6.40–6.47 (m, 2H), 6.84 (d, J = 8.8 Hz, 4H), 7.28 (d, J = 8.8 Hz, 4H), 7.31 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 8.16 (d, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 55.2, 77.7, 112.6, 113.0, 118.6, 119.1, 121.4, 127.0, 127.4, 128.0, 129.3, 129.5, 136.6, 137.5, 138.7, 138.8, 158.7; MS (EI) m/z 450 (M^+); HRMS calcd for $C_{29}H_{26}N_2O_3$: 450.1943, Found: 450.1958.

9-(3-(4-Methylphenyl)imidazo[1,5-*a*]pyridin-1-yl)-9*H*-fluoren-9-ol (9g). A yellow solid; m.p. 159–163 °C (decomp.); IR (KBr) 3488, 3088, 1515, 1449, 1371, 1028, 826, 734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44 (s, 3H), 5.35 (br, 1H), 6.07 (d, J = 9.3 Hz, 1H), 6.25 (dd, J = 9.3 Hz, 6.3 Hz, 1H), 6.34 (d, J = 7.3 Hz, 6.3 Hz, 1H), 7.23 (dd, J = 7.8 Hz, 7.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 7.8 Hz, 2H), 7.69 (d, J = 7.3 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H), 8.08 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 79.8, 112.8, 118.1, 118.5, 120.0, 121.2, 125.0, 127.1, 127.9, 128.1, 128.9, 129.7, 133.2, 136.3, 138.8, 139.6, 149.0; MS (EI) m/z 388 (M^+); HRMS calcd for $C_{27}H_{20}N_2O$: 388.1576, found: 388.1572.

Acknowledgements

This study was supported in part by the Grant-in-Aid for Scientific Research on Innovative Areas “Organic Synthesis based on Reaction Integration. Development of New Methods and Creation of New Substances” (No. 2105).

Notes and references

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