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Application of a recyclable fluorous oxime in the convenient synthesis of 3-amino-1,2-benzisoxazoles and 4-amino-1*H*-2,3-benzoxazines†

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A microwave-assisted, fluorous synthetic route to 3-amino-1,2-benzisoxazoles and 4-amino-1*H*-2,3-benzoxazines has been developed. The strategy comprises linking the respective 2-fluorobenzonitrile or 2-(bromomethyl)benzonitrile to a fluorous oxime tag to give an aryloxime intermediate which then undergoes cyclization with concomitant cleavage of the substrate-tag in acidic conditions to provide the desired product in good to moderate yields. In addition, the aryloxime intermediate could be subjected to further reactions to expand the compound library. The product could be easily separated using fluorous solid-phase extraction (F-SPE) and the fluorous ketone recovered could be converted back to the fluorous oxime and reused in the next run of the synthesis.

Introduction

In recent years, molecular tagging strategies, which aim to facilitate purification by changing the physical properties or partitioning behaviour of the compound through the attachment of a suitable tag, have been introduced. The compounds which are commonly tagged are the substrate, reagent, catalyst or scavenger. The tags that are typically used are either the polymer- or fluorous-support. In polymer-supported reactions,[1] the heterogeneous reaction mixture eases product separation but causes disadvantages such as slow reaction rates and the need to use a large excess of the reagent. In fluorous synthesis, perfluoroalkyl chains are used as tags. The high solubility of the fluorous tags in organic solvents results in the reaction occurring in a homogeneous reaction mixture with solution-phase reaction kinetics and the distinct physical properties of the fluorous compounds enable easy separation, *via* fluorous liquid–liquid extraction or fluorous solid-phase extraction (F-SPE), from the non-fluorous species. The potential of the fluorous tagging strategy has thus inspired the development of many fluorous reagents, catalysts and scavengers to facilitate chemical synthesis.[2] As a result, a wide variety of recyclable fluorous catalysts,[3] oxidants,[4] chlorinating agents,[5] lithium amides[6] and borane carriers[7] have been recently reported. Our interest in the development of environmentally friendly reagents[8] has led us to explore the possibility of a recyclable fluorous oxime tag **1**[8a] for the synthesis of two series of compound libraries carrying 3-amino-1,2-benzisoxazoles **2** and 4-amino-1*H*-2,3-benzoxazines **3**, respectively, as the core structures (Fig. 1).

Fluorous oxime tag **1** is classified as a "light fluorous" compound (fluorine content <60%).[9] "Light fluorous" compounds have lower toxicity and persistence compared to "heavy fluorous" ones. The high chemical and thermal stability of fluorous tags also allows the reactions to be carried out under microwave irradiation. Fluorous oxime tag **1** is soluble in common organic solvents. Products derived from **1** can be separated from the non-fluorous compounds using fluorous silica gel eluted with THF–H_2O, which eliminates the use of environmentally persistent perfluorinated solvents.[10] In addition, the fluorous silica gel can be reused multiple times after washing with THF and acetone.[11] Thus, compared to conventional column chromatography, this technique reduces the volume of solvent used and also the waste generated.

Compound **2** constitutes an important class of heterocycles because they are found in many pharmacologically active substances. The scaffold has been integrated into the structure of

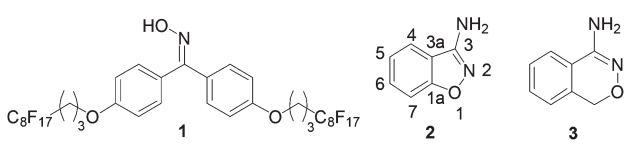

Fig. 1 Structures of **1–3**.

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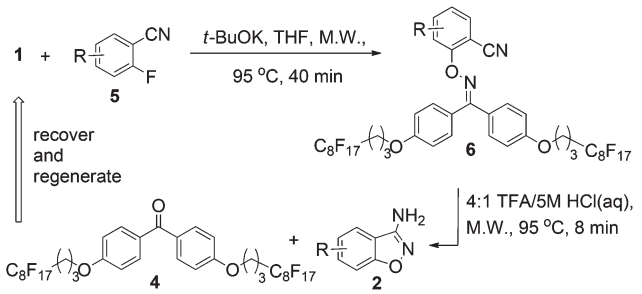
†Electronic supplementary information (ESI) available: Full spectroscopic data for all compounds. See DOI: 10.1039/c3gc36966h



Scheme 1 Synthetic route towards compound **2**, in which compound **4** could be recycled.

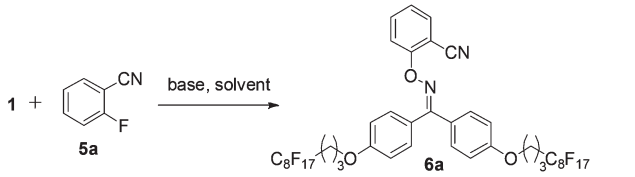
a potent LTB_4 receptor antagonist[12] and various analogs of **2** are known to possess anti-thrombin activities.[13] Furthermore, they are key intermediates in the synthesis of compounds exhibiting dual inhibition of acetylcholinesterase (AChE) and monoamine-oxidase (MAO), and are potential therapeutic agents for the treatment of senile dementia of the Alzheimer type (SDAT).[14] Because of their interesting biological properties, various synthetic routes to compound **2** have been reported. The three most common methods used are *via* the formation of the 1–1a or 1–2 bond or through the simultaneous formation of the 1–1a and 3–3a bonds.[15] The solution-phase synthesis of **2** *via* the formation of the 2–3 bond is less commonly reported.[16] Nevertheless, there is one earlier report on the synthesis of **2** *via* the formation of the 2–3 bond using a Kaiser oxime resin.[16c] However, no attempts were made to recycle the resin. In this paper, we present fluorous oxime tag **1** as a convenient and regenerable substrate-tag for the synthesis of **2** and **3**. We also demonstrate a greener procedure to synthesize fluorous oxime tag **1** from its precursor fluorous ketone **4** as well as a procedure that enables the spent fluorous-tag to be readily recovered in stoichiometric amounts, regenerated and reused (Scheme 1). In addition, this protocol is highly atom economical as the *N–O* moiety in compounds **2** and **3** is derived from the hydroxylamine.

Results and discussion

Previously, the synthesis of fluorous oxime tag **1** was achieved by refluxing **4** with $H_2NOH{\cdot}HCl$ and TEA in a benzene–EtOH mixture for 16 h.[8a] Since benzene is carcinogenic, we decided to explore a greener approach to prepare fluorous oxime tag **1** from fluorous ketone **4**. We found that by using NaOH as the base and ethanol–water as the solvent under microwave irradiation at 100 °C for 15 min, fluorous oxime tag **1** could be smoothly prepared in 91% yield.

In our initial studies on the synthesis of **2**, the key intermediate **6a** was synthesized and isolated using a conventional heating procedure[16c] that involved treating fluorous oxime tag **1** with 2-fluorobenzonitrile **5a** and *t*-BuOK in DMF at 55 °C. The reaction was monitored by TLC, was found to be completed after 12 h and provided intermediate **6a** in 45% yield (Table 1, entry 1). Subsequent treatment of intermediate **6a**

Table 1 Optimization of the nucleophilic aromatic substitution reaction



Entry	Solvent	Base	Reaction condition[a]	Yield of **6a**[b] (%)
1	DMF	*t*-BuOK	A	45
2	CH_2Cl_2	*t*-BuOK	A	79
3	THF	*t*-BuOK	A	90
4	THF	LiHMDS	A	10
5	THF	DBU	A	43
6	THF	*t*-BuOK	M.W., 75 °C, 115 min	90
7	THF	*t*-BuOK	M.W., 85 °C, 70 min	88
8	THF	*t*-BuOK	M.W., 95 °C, 40 min	96
9	CH_2Cl_2	*t*-BuOK	M.W., 95 °C, 70 min	84
10	DMF	*t*-BuOK	M.W., 95 °C, 50 min	58

[a] Condition A: conventional heating at 55 °C for 12 h. [b] Isolated yields.

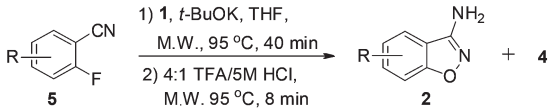
with 4 : 1 TFA–aqueous 5 M HCl at 55 °C for 2 h gave the product **2a** in 95% yield. To optimize the nucleophilic aromatic substitution reaction, we first varied the solvent and found that the reaction proceeded most efficiently in THF (Table 1, entries 1–3). Next, we explored different bases. Non-nucleophilic bases such as LiHMDS and DBU were shown to afford **6a** in lower yields than *t*-BuOK (Table 1, entries 3–5).

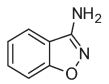
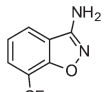
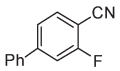
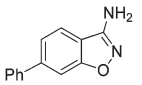
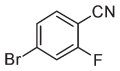
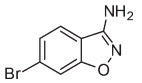
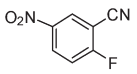
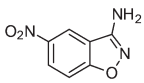
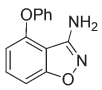
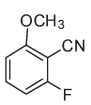
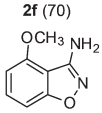
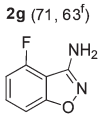
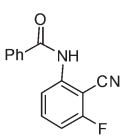
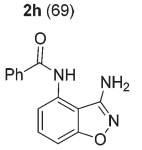
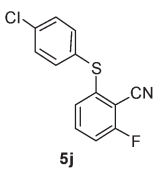
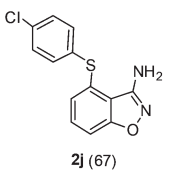
To facilitate a rapid synthesis of **2a**, we explored microwave irradiation (Table 1, entries 6–10) and found that compound **6a** was obtained in the highest yield (96%) when the reaction was performed in THF at 95 °C for 40 min (Table 1, entry 8). Subsequent reaction of **6a** with 4 : 1 TFA–aqueous 5 M HCl under microwave irradiation at 95 °C for 8 min resulted in the cyclization of **6a** with concomitant cleavage of the fluorous-tag to give product **2a** and fluorous ketone **4** (Scheme 1), which could be easily separated using F-SPE to provide pure **2a** in quantitative yield. Not only is the overall yield of **2** obtained under microwave synthesis higher than that achieved *via* conventional heating, it also offered a much more efficient protocol in terms of time consumed.

Since microwave irradiation conditions could be applied to both steps of the synthesis, we further explored the possibility of synthesizing compound **2a** directly from **5a** without isolating and purifying intermediate **6a**. Gratifyingly, this methodology proceeded efficiently and provided compound **2a** in comparable yield (Table 2, entry 1) to the two-step microwave irradiation procedure. Using the optimized reaction conditions, we extended the reaction to various substituted *o*-fluorobenzonitriles **5** which gave the respective compound **2** in moderate to good yields (Table 2). It is worth noting that a comparison of fluorous oxime tag **1** with its Kaiser oxime resin counterpart showed that **1** provided **2** in higher yields (Table 2, entries 1–2 and 4–5). In addition, ketone **4** was also recoverable by F-SPE in very good yield (Table 2).

Next, we proceeded to investigate the reuse of fluorous oxime tag **1**. Compound **5a** was used for the model recycling

Table 2 Synthesis of the compound **2** library[a]

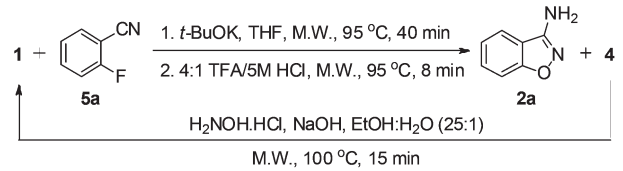


Entry	Substrate	Yield of 2[b] (%)	Recovered 4[c] (%)
1	 **5a**	 **2a** (94, 86[d], 49[e])	97
2	 **5b**	 **2b** (80, 72[d], 51[e])	95
3	 **5c**	 **2c** (76)	97
4	 **5d**	 **2d** (71, 49[e])	96
5	 **5e**	 **2e** (86, 78[d], 67[e])	96
6	 **5f**	 **2f** (70)	96
7	 **5g**	 **2g** (71, 63[f])	97
8	 **5h**	 **2h** (69)	97
9	 **5i**	 **2i** (79)	98
10	 **5j**	 **2j** (67)	97

[a] Intermediate **6** was not isolated. [b] Isolated yields over two steps. [c] *Via* F-SPE. [d] Conventional heating conditions: (1) 55 °C, 12 h; (2) 55 °C, 2 h. [e] Using Kaiser oxime resin reaction conditions.[16c] [f] Conventional heating conditions: (1) 55 °C, 15 h; (2) 55 °C, 2 h.

study under the optimized reaction conditions. The recycling experiments were carried out over 4 runs which provided compound **2a** in 91–94% overall yields (Table 3). The amount of

Table 3 Regeneration of **1** under microwave irradiation



Run	Yield of 2a[a] (%)	Recovered 4[b] (%)
1	94	97
2	92	95
3	92	96
4	91	96

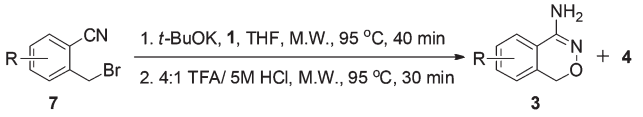
[a] Isolated yields over two steps. [b] Recovered *via* F-SPE.

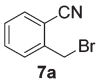
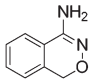
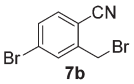
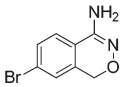
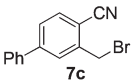
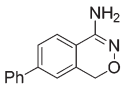
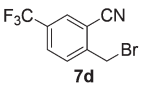
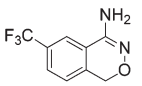
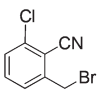
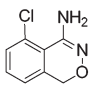
fluorous ketone **4** recovered after each run was also consistently very high (95–97%).

Encouraged by these results, we extended our studies to the synthesis of 4-amino-1*H*-2,3-benzoxazines **3**, a class of compounds which have previously been demonstrated to possess hypotensive, myorelaxant, anti-inflammatory and sedative activities.[17] Compound **3** is typically prepared *via* a multi-step synthesis which first involves the cyclization of α-aminoxy-*o*-toluic acid to yield 1*H*-2,3-benzoxazine-4(3*H*)-one.[18] The latter compound was then chlorinated with phosphorus pentachloride to give 4-chloro-1*H*-2,3-benzoxazine[19] which was then treated with ammonium acetate to facilitate a nucleophilic substitution reaction to provide compound **3**.[17] Herein we applied the reaction condition used for the synthesis of **2** to 2-(bromomethyl)benzonitrile **7a** and fluorous oxime tag **1**. The first *O*-benzylation step went well under microwave conditions. However, the second cyclization and hydrolytic step proceeded more slowly than in the synthesis of compound **2** and required 30 min to complete. Compound **3a** was obtained in 61% yield and fluorous ketone **4** was recovered in 95% yield (Table 4, entry 1). To demonstrate the versatility of this procedure, we have applied it to other analogs of 2-(bromomethyl)benzonitrile which gave the corresponding compound **3** derivatives in good to moderate yields (Table 4, entries 2–5). It should be emphasized that the newly developed synthetic route to compound **3** presented here not only is shorter and more convenient, but also offers much more sense of green chemistry as compared to the previous methods.

Since the fluorous aryloxime intermediate **6**, unlike its Kaiser oxime resin counterpart, could be isolated and purified using F-SPE, this prompted us to examine the possibility of subjecting **6** to further reactions before cyclization and release of fluorous ketone **4**. First, we explored the application of the Suzuki coupling reaction on the aryloxime intermediate **6**. As a model study, the aryloxime intermediate of 4-bromo-2-fluoronitrile **5d** was coupled with phenylboronic acid using Pd $(PPh_3)_4$ as the catalyst and under microwave irradiation at 95 °C for 60 min. Subsequent cyclization and release of fluorous ketone **4** afforded the biaryl product **2c** in 47% overall yield (over 3 steps) (Table 5, entry 1). The Suzuki coupling

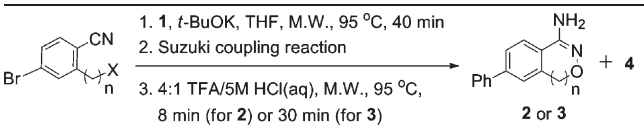
Table 4 Synthesis of the compound **3** library

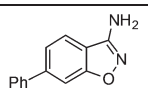
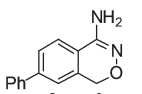


Entry	Substrate	Yield of **3**[a] (%)	Recovered **4**[b] (%)
1	 **7a**	 **3a** (61)	96
2	 **7b**	 **3b** (64)	98
3	 **7c**	 **3c** (71)	97
4	 **7d**	 **3d** (79)	97
5	 **7e**	 **3e** (69)	96

[a] Isolated yields over two steps. [b] *Via* F-SPE.

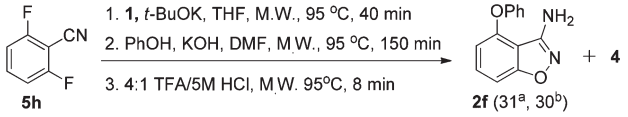
Table 5 Extension of the diversity of compounds **2** and **3** *via* the Suzuki coupling reaction



Entry	X	*n*	Yield of **2** or **3**[a] (%)	Recovered **4**[b] (%)
1	F	0	 **2c** (47[c], 38[d])	92
2	Br	1	 **3c** (34[e])	93

[a] Isolated yield. [b] *Via* F-SPE. [c] Suzuki coupling reaction: $PhB(OH)_2$, $Pd(PPh_3)_4$, 2 M Na_2CO_3, THF, M.W., 95 °C, 60 min. [d] Using Kaiser oxime resin reaction conditions.[20] [e] Suzuki coupling reaction: $PhB(OH)_2$, $Pd(PPh_3)_4$, 2 M Na_2CO_3, THF, M.W., 95 °C, 110 min.

reaction was also demonstrated with the aryloxime intermediate of 4-bromo-2-(bromomethyl)benzonitrile **7b** which afforded the biaryl product **3c** in 34% overall yield (over 3 steps). Next we assessed the compatibility of the fluorous aryloxime intermediate **6** for a second nucleophilic aromatic substitution reaction. Compound **5h** was used to prepare the aryloxime intermediate which was then subjected to the



[a] isolated yield over three steps. [b] using Kaiser oxime resin reaction condition, yield over three steps.[20]

Scheme 2 Extension of the diversity of compound **2** *via* the nucleophilic aromatic substitution reaction.

nucleophilic substitution reaction with phenol using potassium hydroxide as the base and DMF as the solvent under microwave irradiation followed by cyclization and release of fluorous ketone **4** to afford the phenoxy compound **2f** in 31% yield (over 3 steps) (Scheme 2). These results demonstrate that the fluorous aryloxime intermediate **6** could play a versatile role and have great potential in expanding the structural variation of the compound library.

Conclusions

We have developed a greener procedure for the preparation of fluorous oxime **1** and utilized it in a convenient, atom economical and environmentally friendly synthesis of 3-amino-1,2-benzisoxazoles **2** and 4-amino-1*H*-2,3-benzoxazines **3**. The by-product fluorous ketone **4** could be recovered in high yield, converted back into **1**, and reused 4 times without significant loss in quantity. In addition, the aryloxime intermediate **6** could be subjected to further reactions resulting in greater diversity of the compound library. More importantly, the sense of green chemistry offered by fluorous oxime **1** would certainly create new opportunities for those previously considered formidable reactions utilizing benzophenone oxime and make them more accessible.

Experimental

General

All chemicals purchased were used without further purification. Starting materials **5c**, **5i**, **7b**, **7c**, **7d** and **7e** were synthesized by adapting literature procedures.[8,21] Reactions were carried out under nitrogen with commercially obtained anhydrous solvents. Analytical thin-layer chromatography (TLC) was carried out on precoated F254 silica plates and visualized with UV light. F-SPF was performed with Fluoro*Flash*® silica gel (40 micron). ^1H and ^{13}C NMR spectra were recorded at 298 K. Chemical shifts are expressed in terms of ppm relative to the internal standard tetramethylsilane (TMS). Mass spectra were performed under EI and ESI mode. Microwave reactions were performed on the Biotage Initiator™ microwave synthesizer in quartz pressure tubes.

Synthesis of fluorous oxime tag 1

A mixture of fluorous ketone **4** (312 mg, 0.275 mmol), NaOH (55 mg, 1.375 mmol) and hydroxylamine hydrochloride

(30 mg, 0.43 mmol) in 25 : 1 95% EtOH–H_2O (520 μL) was heated in a pressure tube at 100 °C under microwave irradiation for 15 min. The reaction was monitored by TLC. When the reaction was complete, the reaction mixture was cooled to room temperature and concentrated to dryness. 2 M HCl was added and the resulting mixture was extracted with EtOAc. The organic phase was washed consecutively with 2 M HCl, 5% $NaHCO_3$, water and brine. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated to provide fluorous oxime tag **1** in 91% yield (296 mg).

General procedure for the synthesis of 3-amino-1,2-benzisoxazoles under microwave irradiation

A mixture of fluorous tag **1** (230 mg, 0.20 mmol), the respective *o*-fluorobenzonitriles **5** (0.20 mmol) and potassium *tert*-butoxide (27 mg, 0.24 mmol) in THF (2.60 mL) was heated in a pressure tube at 95 °C under microwave irradiation for 40 min. The reaction was monitored by TLC. When the reaction was complete, the mixture was cooled to room temperature and concentrated to dryness. The reaction mixture was diluted with ethyl acetate (20 mL) and washed with sodium bicarbonate (10 mL), water (10 mL) and brine (10 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered and concentrated. A solution of 4 : 1 TFA–5 M HCl (aq.) (5 mL) was added to the crude product and the reaction mixture was heated in a pressure tube at 95 °C under microwave irradiation for 8 min. The reaction was monitored by TLC. When the reaction was complete, the mixture was cooled to room temperature and basified with 10% NaOH. The aqueous solution was extracted with ethyl acetate (50 mL), washed with water (20 mL), dried over anhydrous $MgSO_4$, filtered, concentrated and subjected to F-SPE.

General procedure for F-SPE

The crude product was first diluted with THF–H_2O = 1 : 1 and loaded into F-SPE fluorous silica. The product was then eluted using THF–H_2O = 1 : 1 and the recovered ketone **6** was subsequently eluted with THF and concentrated. The product was then concentrated, diluted with ethyl acetate (50 mL) and washed with water (20 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered and concentrated to give the pure, desired product.

General procedure for the synthesis of 4-amino-1*H*-2,3-benzoxazines under microwave irradiation

A mixture of fluorous tag **1** (230 mg, 0.20 mmol), the respective 2-(bromomethyl)benzonitrile **7** (0.20 mmol) and potassium *tert*-butoxide (27 mg, 0.24 mmol) in THF (2.60 mL) was heated in a pressure tube at 95 °C under microwave irradiation for 40 min. The reaction was monitored by TLC. When the reaction was complete, the mixture was cooled to room temperature and concentrated to dryness. The reaction mixture was diluted with ethyl acetate (20 mL) and washed with sodium bicarbonate (10 mL), water (10 mL) and brine (10 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered and concentrated. A solution of 4 : 1 TFA–5 M HCl (aq.) (5 mL) was added to the crude product and the reaction mixture was heated in a pressure tube at 95 °C under microwave irradiation for 30 min. The reaction was monitored by TLC. When the reaction was complete, the mixture was cooled to room temperature and basified with 10% NaOH. The aqueous solution was extracted with ethyl acetate (50 mL), washed with water (20 mL), dried over anhydrous $MgSO_4$, filtered, concentrated and subjected to F-SPE.

General procedure for the Suzuki coupling reaction with fluorous-tagged aryloxime intermediate, cyclization and concomitant cleavage of the substrate-tag

A mixture of the fluorous aryloxime intermediate (0.20 mmol), phenylboronic acid (24 mg, 0.20 mmol), 5 mol% $Pd(PPh_3)_4$, and Na_2CO_3 (535 μL, 2 M in H_2O, 0.20 mmol) in THF (2.60 mL) was heated in a pressure tube at 95 °C under microwave irradiation (reaction time for **5d**: 60 min and reaction time for **7b**: 110 min). The reaction was monitored by TLC. When the reaction was complete, the mixture was cooled to room temperature and concentrated to dryness. The reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (10 mL) and brine (10 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered, concentrated and subjected to F-SPE. A solution of 4 : 1 TFA–5 M HCl (aq.) (5 mL) was added to the Suzuki coupled fluorous aryloxime intermediate and the reaction mixture was heated in a pressure tube at 95 °C under microwave irradiation for 8 min. The reaction was monitored by TLC. When the reaction was complete, the mixture was cooled to room temperature and basified with 10% NaOH. The aqueous solution was extracted with ethyl acetate (50 mL), washed with water (20 mL), dried over anhydrous $MgSO_4$, filtered, concentrated and subjected to F-SPE.

General procedure for the nucleophilic aromatic substitution reaction with the fluorous tagged aryloxime intermediate of 5h, cyclization and concomitant cleavage of the substrate-tag

A mixture of the fluorous aryloxime intermediate (0.40 mmol), phenol (38 mg, 0.40 mmol) and KOH (23 mg, 0.40 mmol) in DMF (2.60 mL) was heated in a pressure tube at 95 °C under microwave irradiation for 150 min. The reaction was monitored by TLC. When the reaction was complete, the mixture was cooled to room temperature and concentrated to dryness. The reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (10 mL) and brine (10 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered, concentrated and subjected to F-SPE. A solution of 4 : 1 TFA–5 M HCl (aq.) (5 mL) was added to the crude product and the reaction mixture was heated in a pressure tube at 95 °C under microwave irradiation for 8 min. The reaction was monitored by TLC. When the reaction was complete, the mixture was cooled to room temperature and basified with 10% NaOH. The aqueous solution was extracted with ethyl acetate (50 mL), washed with water (20 mL), dried over anhydrous $MgSO_4$, filtered, concentrated and subjected to F-SPE.

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