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Photoredox-catalyzed indirect acyl radical generation from thioesters†

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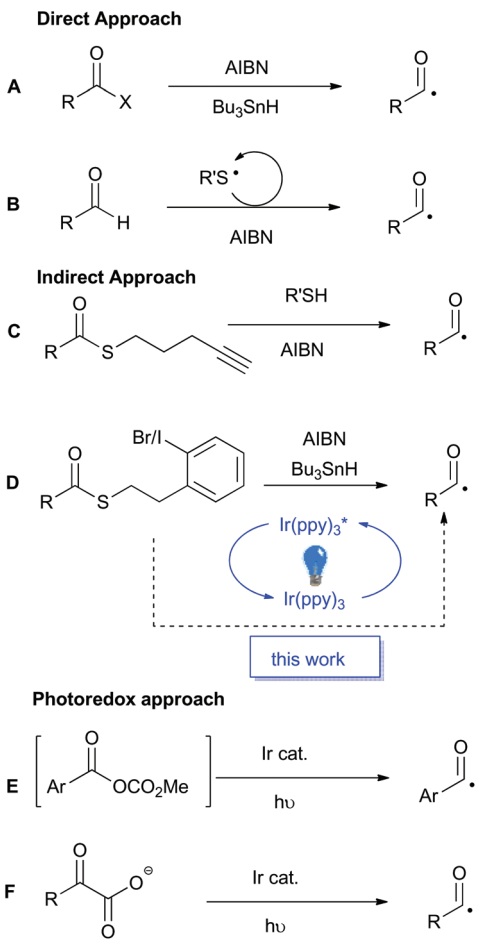
A photoredox-catalyzed method for the indirect generation of acyl radicals from stable thioesters is described. The process is applicable to both aromatic and aliphatic substrates, and the resulting acyl radicals can undergo both intermolecular and intramolecular reactions. The mild reaction conditions allow for domino photoredox-catalyzed processes to occur. To illustrate the utility of the method, the total synthesis of a pharmaceutical agent is described.

Introduction

Acyl radicals have a long history as reactive intermediates in organic chemistry, however they are seldom utilised in modern synthesis.[1–3] Traditionally, the generation of acyl radicals has relied upon the use of highly reactive acid derivatives, such as acyl chlorides, selenides and tellurides. *Direct* radical scission of the acyl–heteroatom bond in the presence of super-stoichiometric organo-tin reagents, or photolytically with high energy UV-light, reveals the desired acyl radical (Scheme 1A). The general incompatibility of these precursors with common reaction conditions, as well as the toxicity associated with both the substrates and reagents, greatly detracts from the appeal of these traditional methods and has spurred the development of alternative methods for acyl radical generation.

As potent radicalophiles, sulfur-containing functional groups have played key roles in the development of alternative acyl radical generating methods. Tomioka and co-workers established an aerobic and thiol-catalysed protocol as a *direct* route from aldehyde precursors (Scheme 1B).[4–6] In contrast, Benati, Spagnolo and co-workers described an efficient thiol–ene fragmentation reaction to liberate the desired acyl radical (Scheme 1C).[7] This *indirect* approach, where the initial radical formation is distal to the acyl centre, permits the use of a more stable precursor, namely, a thioester. Similarly, Crich and co-workers were the first to disclose this *indirect* approach utilising a pendant aryl halide (Scheme 1D).[8] Upon radical initiation, a stannyl radical abstracts the halogen to form an aryl radical which undergoes a rapid intramolecular cyclisation, releasing dihydrobenzothiophene and unveiling the desired acyl radical. Crich also reported a tin-free variant based on reduction of an aryl diazonium salt, but that reactive functional group is less well tolerated than the aryl halide.[9]



Scheme 1 Previous approaches to acyl radical generation.

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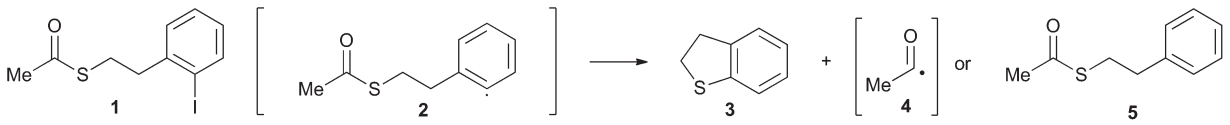
† Electronic supplementary information (ESI) available: NMR spectra for all synthesized compounds. See DOI: 10.1039/c8qo00867a

Table 1 Reaction optimization studies



Entry[a]	Ir(ppy)$_3$ loading (mol%)	Amine (equiv.)	Solvent[b]	Irradiation time (h)	Conversion into **3**[c] (%)	Conversion into **5**[c] (%)	Unreacted **1**[c] (%)
1	2.5 mol%	iPr_2NEt (10)	CH_3CN	18 h	40	6	54
2	2.5 mol%	NMM (10)	CH_3CN	18 h	33	5	62
3	2.5 mol%	HCO_2NH_4 (10)	CH_3CN	18 h	2	—	98
4	2.5 mol%	Hantzsch ester (2)	CH_3CN	18 h	—	—	100
5	2.5 mol%	Bu_3N (10)	CH_3CN	18 h	80	20	—
6	2.5 mol%	Bu_3N (10)	DMF	18 h	69	31	Trace
7	2.5 mol%	Bu_3N (10)	MeOH	18 h	10	—	90
8	2.5 mol%	Bu_3N (10)	PhMe	18 h	<10	—	>90
9	2.5 mol%	Bu_3N (10)	CH_2Cl_2	18 h	46	26	2–8
10	2.5 mol%	Bu_3N (10)	THF	18 h	12	—	88
11	1 mol%	Bu_3N (10)	CH_3CN	18 h	78	22	—
12	0.1 mol%	Bu_3N (10)	CH_3CN	18 h	78	22	—
13	2.5 mol%	Bu_3N (10) HCO_2H (10)	CH_3CN	18 h	78	22	—
14	0 mol%	Bu_3N (10)	CH_3CN	18 h	0	0	100

[a] Irradiated with a 4.5 W blue (465 nm) LED strip light. [b] Solvents were degassed. [c] Conversion by ^{1}H NMR analysis of the crude reaction mixture.

The principles of green chemistry that advocate for non-toxic reagents, catalytic processes, and energy minimisation,[10] has driven the recent upsurge in development of photoredox catalyzed processes.[11,12] In 2015 Wallentin and co-workers reported the photoredox catalyzed production of acyl radicals from *in situ* generated mixed carbonic anhydrides (Scheme 1E).[13] The process worked well for aromatic substrates but was not viable for aliphatic substrates. In the same year MacMillan and co-workers reported the photoredox catalysed decarboxylation of α-keto acids as a highly efficient method for acyl radical generation (Scheme 1F).[14] The protocol was applicable to both aromatic and aliphatic substrates, but the requisite α-keto acid precursors occur less frequently than ubiquitous carboxylic acids. MacMillan and co-workers recently reported a photocatalytic variant of Tomoika's method that utilized an aromatic thiol for the abstraction of the hydrogen atom from aldehydes.[15] Surprisingly, the combination of sulfur-containing functional groups, such as thioesters, as latent acyl radicals with photoredox-catalysis has not yet been reported. As the Crich-type thioesters are available in a single step from carboxylic acid starting materials,[8] we anticipated that the integration of those substrates into a mild photoredox catalyzed protocol would lead to a generally applicable and synthetically versatile method for acyl radical generation that would complement existing methods. The outcomes of our investigations into this integrated approach are reported below.

Optimization studies

Our studies began by identifying a suitable catalyst–thioester combination for the *indirect* transformation of haloaryl thioesters into the desired acyl radicals. The reported reduction potential of iodobenzene is −1.59 V in DMF (*vs.* SCE).[16] The reduction potential of the photo-excited state of the commercially available *fac*-Ir(ppy)$_3$ complex has been measured as −1.73 V (*vs.* SCE),[17] which suggested that the iodoaryl thioester **1** (Table 1) should be reduced by that photocatalyst under the action of blue light. As shown in Table 1, this was indeed the case.

A mixture of substrate **1**, *fac*-Ir(ppy)$_3$, and a series of amines were irradiated using a highly energy-efficient 4.5 W blue LED strip light. Reaction progress was monitored by ^{1}H NMR analysis of the crude reaction mixture, with dihydrobenzothiophene (**3**) being diagnostic of acyl radical formation. In this way tributylamine was quickly identified as the most suitable sacrificial electron donor to complete the catalyst's redox cycle (entries 1–5).[11,18] Polar aprotic solvents were well tolerated with the highest conversion being achieved in acetonitrile (entries 5–10). Given the expense of iridium-based catalysts, it was gratifying that the process suffered no loss of efficiency at catalyst loadings as low as 0.1 mol% (entries 11 and 12). And finally, the photoredox catalyzed nature of this process was confirmed by the lack of conversion in the absence of *fac*-Ir(ppy)$_3$ (entry 14).

Under the reaction conditions, some proto-dehalogenated product **5** was observed. Beckwith and Boate have measured the rate constant for the formation of dihydrobenzothiophene (**3**) by intramolecular cyclisation of an aryl radical onto a sulfide to be 5×10^7 s^{-1} at 80 °C.[19] Since Crich obtains uniformly high yields when using the tin-based reagents to generate the acyl radicals at 80 °C,[20] we attribute the relative increase in proto-dehalogenation in this instance to the lower reaction temperature. Indeed, with a view to minimizing energy consumption, all of the photoredox catalyzed reactions

in this work were performed at room temperature. Pleasingly, the presence of excess formic acid did not increase the amount of proto-dehalogenation (entry 13), even though it has previously been utilized as a hydrogen atom donor.[21] We anticipated that the ability to perform the reaction in the presence of an acid would potentially facilitate further redox processes. The conditions shown in entry 13 were adopted for subsequent reactions.

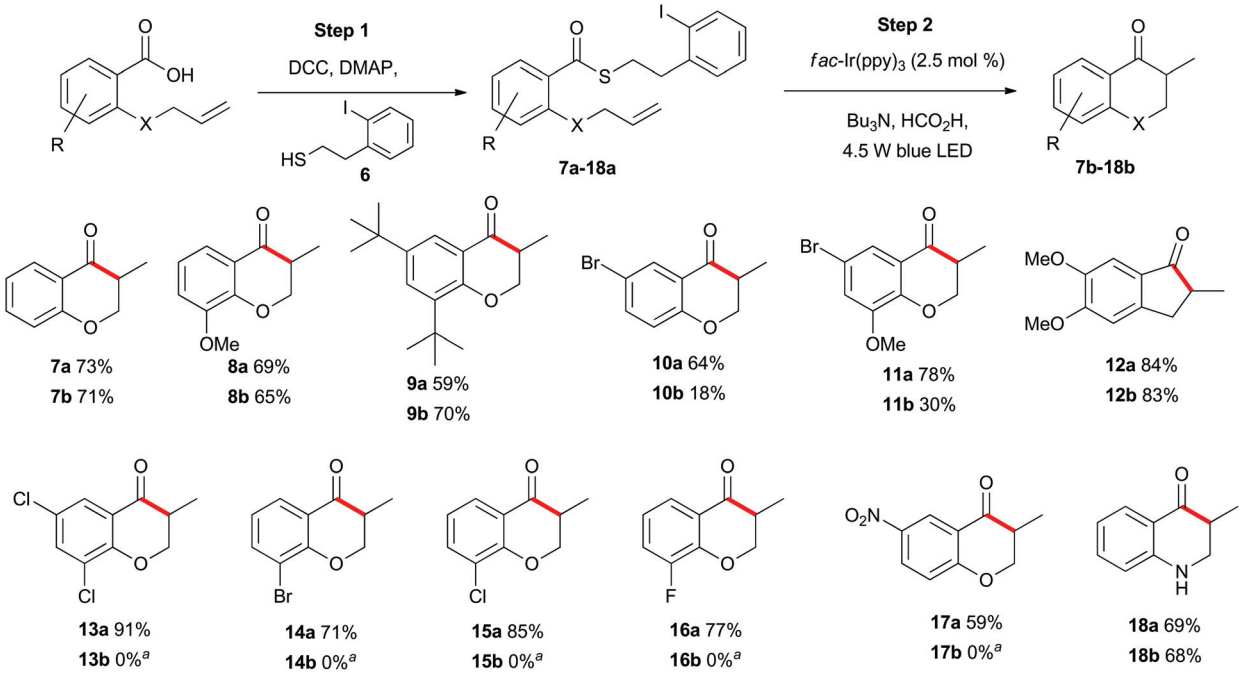
Intramolecular cyclizations

With appropriate reaction conditions in hand, we began exploring the scope of the photoredox catalysed indirect acyl radical generation through a series of intramolecular cyclisation reactions. First, we explored the reaction of aromatic substrates to generate a series of chromanone and indanone derivatives **7b–18b** (Scheme 2). Each of the allyl-containing aromatic substrates **7a–18a** was generated by a *N*,*N*′-dicyclohexylcarbodiimide (DCC) mediated coupling of the carboxylic acid with the known thiol **6** (step 1) and was then subjected to the photoredox reaction conditions (step 2). The most apparent trend in reactivity correlates with the electron-withdrawing nature of the substituents on the aromatic ring. Compound **7a** was smoothly transformed into the methylchromanone **7b** in good yield. Likewise, the relatively electron-rich compounds **8a** and **9a** also cyclized in good yield to give chromanones **8b** and **9b**. In contrast, the relatively electron-poor substrate **10a** was transformed into the bromochromanone **10b** in low yield. The yield could be rescued to some degree by inclusion of an electron-donating group, as in compound **11a**, which cyclized to give **11b** in moderate overall yield. The highest yield was obtained for the most electron-rich substrate **12a**, which cyclised to give the indanone **12b** in 83% isolated yield. When substrates **13a–17a** were subjected to the standard reaction conditions the desired chromanones **13b–17b** were not isolated (see below). The identity of the heteroatom on the allyl tether could be altered to a nitrogen with no detrimental effect and compound **18a** cyclized to give **18b** in comparable yield to the oxygen analogue **7a**.

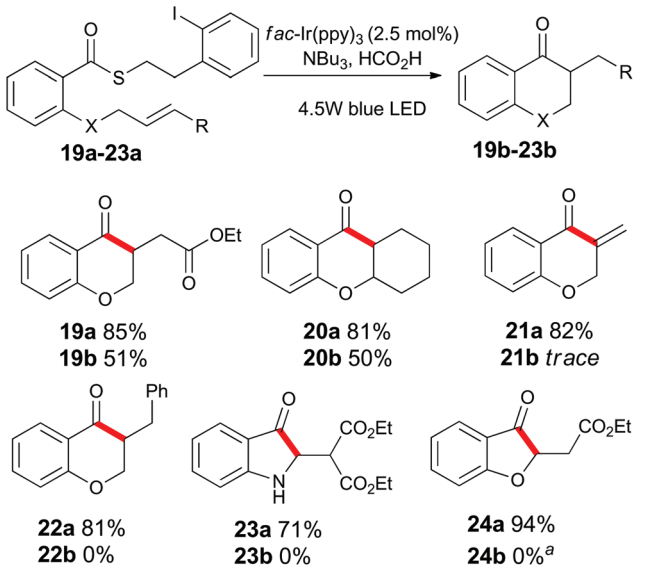
Having examined the role of the substrate, we next investigated the scope of the alkene acceptor on aromatic substrates (Scheme 3). As already demonstrated, allyl units were well tolerated. The electron-deficient acrylate substrate **19a** also cyclized to give **19b** in good yield. The pendant cyclohexene unit of substrate **20a** participated in the cyclization to give compound **20b**. The propargyl containing substrate **21a** was consumed under the standard reaction conditions, but surprisingly, product **21b** could not be isolated from the reaction mixture. The highly electron-deficient styrenyl, malonyl, and vinylogous ester derivatives **22a**, **23a** and **24a** proved to be incompatible with these standard reaction conditions (see below).

As shown in Scheme 4, the heteroaromatic substrate **25a** was transformed into the tricyclic compound **25b**, and compound **26a** which incorporated an all carbon tether and a vinylcyclopropyl unit, gave the expected ring-opened product **26b**. This result served to confirm the radical nature of the process.

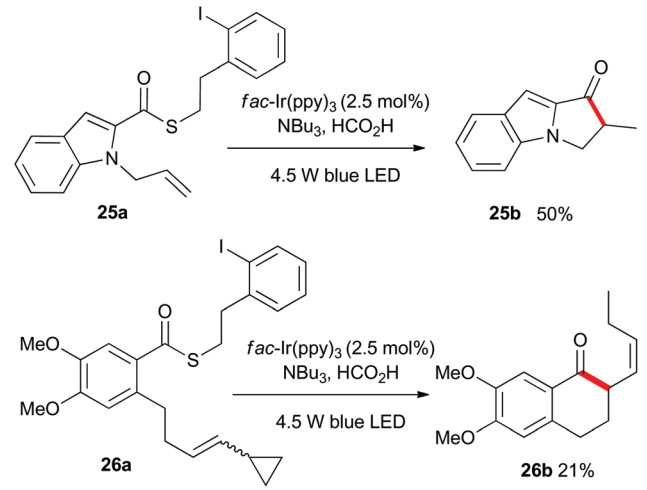
Finally, as shown in Scheme 5, we utilized substrate **27a** which contains a latent aliphatic acyl radical and a tri-substituted alkene to further explore the scope of the reaction. Pleasingly, **27a** cyclized quantitatively as monitored by ^{1}H NMR analysis and the relatively volatile menthone **27b** was isolated in 44% yield.



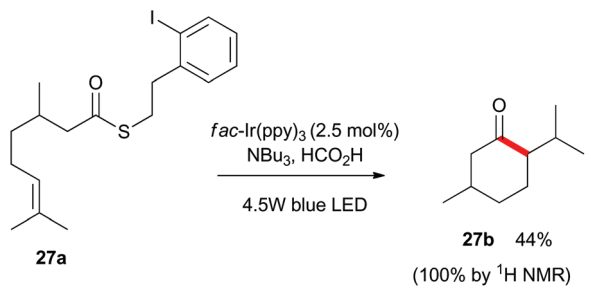
Scheme 2 Substrate scope of allyl-substituted aromatic compounds. [a] See Schemes 6 and 11 for further details.



Scheme 3 Substrate scope of alkene units on substituted aromatic compounds. [a] See Scheme 7 for further details.



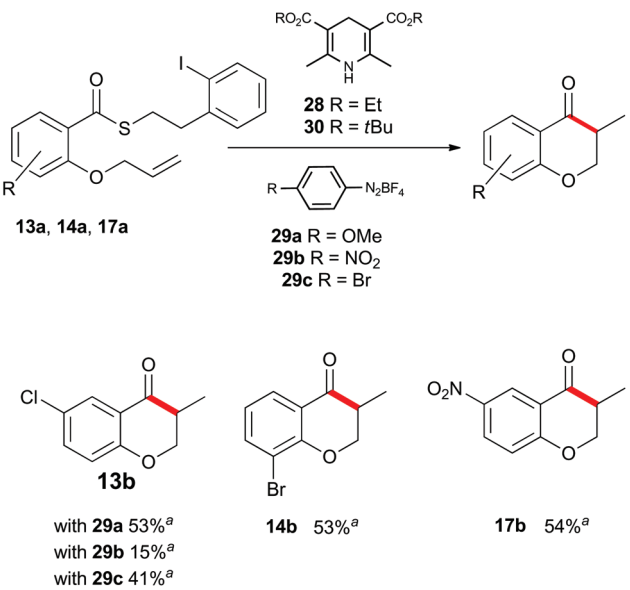
Scheme 4 Heteroaromatic acyl radical cyclization and cyclization onto a vinylcyclopropyl unit.



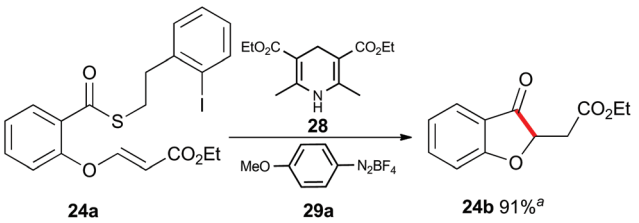
Scheme 5 Aliphatic acyl radical cyclizing onto a tri-substituted alkene.

Up to this point, the limitations on the photoredox-catalyzed indirect acyl radical generation correlated with electron deficient systems; whether it be electron deficient substrates such as **13a–17a** or electron deficient acceptors **22a–24a**. We rationalised this outcome on the basis of a preferential reaction between the photo-excited iridium catalyst and the electron-deficient unit. To overcome this shortcoming, we examined an alternative photo-induced method to reduce the aryl iodide and initiate the desired cascade. Minisci and coworkers utilized aryl radicals for the fast iodine abstraction from organic substrates containing relatively labile C(sp^3)–I bonds.[22] We examined the ability of several aryl radicals to abstract iodine from the less reactive C(sp^2)–I bond of substrate **13a** and initiate the indirect acyl radical generation sequence (Scheme 6). The required aryl radicals were generated from the corresponding diazonium salts **29a–29c** using the Hantzsch ester (**28**) and ambient light. Li and Xu have previously reported the use of Hantzsch esters as mild photo-induced single electron reductants for radical processes.[23,24] In this case, although conversions were modest (39% consumed starting material for the highest yielding example with **29a**) the desired electron deficient chromanone **13b** was isolated in a 53% yield based on recovered starting material. When compounds **13a**, **17a** and **29a** were subjected to these reaction conditions, the previously inaccessible chromanones **14b** and **17b** were produced in moderate yields (Scheme 6). The corresponding *tert*-butyl Hantzsch ester (**30**) could be employed with equal efficiency. Similarly, when substrate **24a** containing an electron-deficient alkene was subjected to these alternative photo-induced conditions, benzofuranone **24b** was isolated in a 91% yield based on recovered starting material (Scheme 7).

The use of the Hantzsch ester (**28**), a latent aryl radical (**29a**) and ambient light represents a complementary method



Scheme 6 Indirect acyl radical generation and cyclization with electron-deficient substrates. [a] Yield based on recovered starting material.



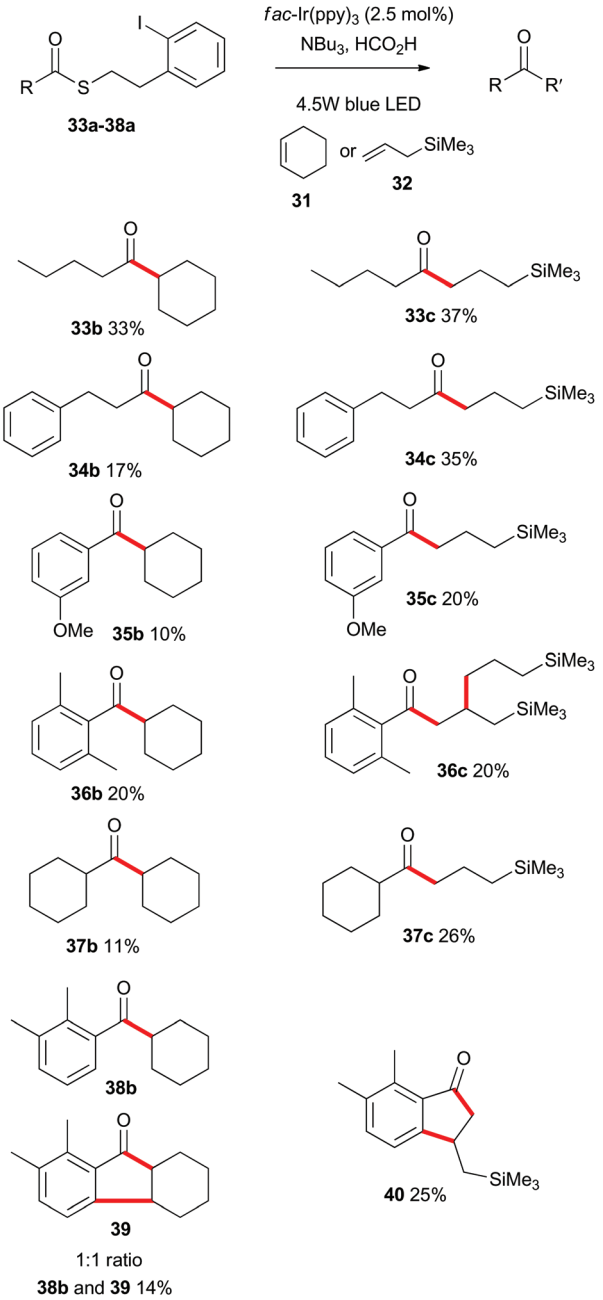
Scheme 7 Indirect acyl radical generation and cyclization with electron-defficient alkenes. [a] Yield based on recovered starting material.

that can be employed with electron deficient systems, albeit in a stoichiometric fashion.

Intermolecular additions

Having demonstrated that the photoredox-catalyzed indirect acyl radical generation and subsequent reaction onto alkenes was viable for a range of substrates in an intramolecular sense, we next explored the intermolecular variant. As shown in Scheme 8, a range of aliphatic and aromatic thioesters **33a–38a** participated in the intermolecular alkene addition with an excess of cyclohexene (**31**) or allyltrimethylsilane (**32**). As expected the overall yields of the intermolecular process were lower than the corresponding intramolecular cyclizations, with reactions involving the allylsilane **32** being consistently higher yielding. Indeed, Guindon and co-workers employed allyltrimethylsilane (**32**) as a replacement for allyltributylstannane in the allylation of β-alkoxy esters.[25] This reagent was reported to be superior due to both reduced toxicity and increased reactivity. That previous work proceeded *via* an atom transfer radical addition (ATRA) mechanism and the eliminated species was likely R_3SiX. In the present case (Scheme 8), there is no possibility to form a silyl halide and so the silicon unit is retained in the products.

Of particular interest are the reactions of substrates **36a** and **38a**. In those instances the radical intermediate generated by addition of the acyl radical onto an alkene, engaged in a secondary reaction. As such, **36a** was transformed into **36c**, and the *ortho*-substituted compound **38a** was converted into hexahydrofluorenone **39** and indanone **40**. These processes in which multiple bonds were formed under the same exceedingly mild photoredox-catalyzed reaction conditions, prompted us to explore other cascade processes.

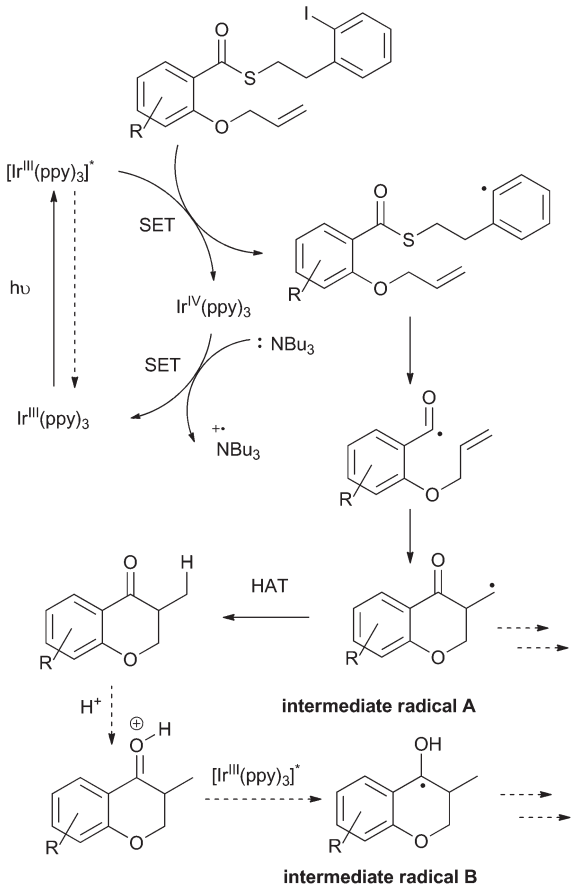


Scheme 8 Scope of the intermolecular photoredox catalysed indirect acyl radical generation, alkene addition.

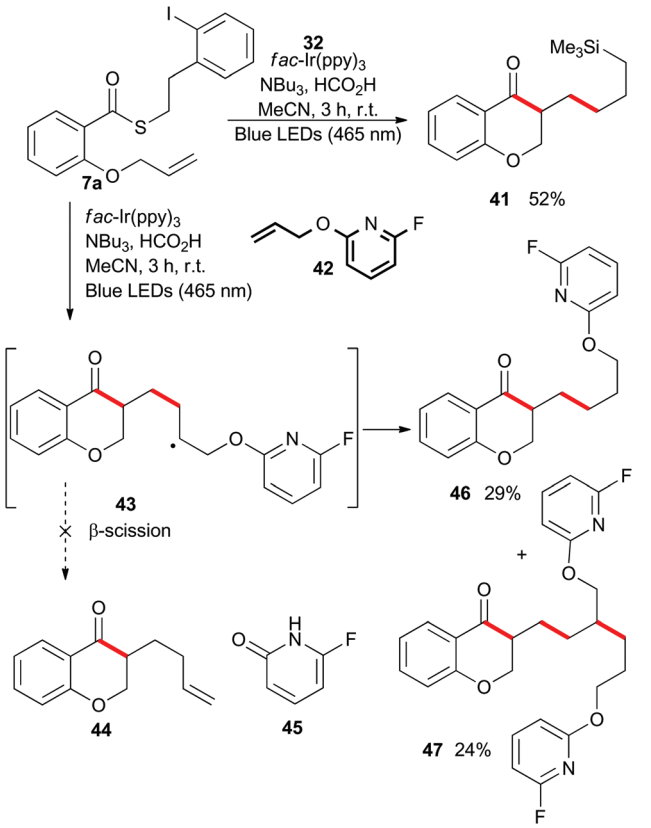
Cascade reactions

To this point, we have shown that acyl radicals can be generated from aryl and alkyl thioesters in an indirect fashion under photoredox conditions, and that they undergo addition reactions to olefins in both an intra- and intermolecular fashion. The products of those radical addition reactions subsequently underwent hydrogen atom transfer (HAT) from the oxidized tributylaminiumyl radical to give a methyl or methylene group, as shown in the plausible mechanism depicted in Scheme 9. We next explored the opportunity to engage the intermediate radical (**A**) in a subsequent alkene addition reaction to give an intra–intermolecular cascade process.

As shown in Scheme 10, irradiation of thioester **7a** under the standard reaction conditions in the presence of excess allyltrimethylsilane (**32**) resulted in isolation of the chain-extended chromanone **41**. We then attempted to perform a cascade radical allylation. Zard and co-workers developed the allyl transfer agent **42** for the production of allylated products under radical conditions.[26,27] The fluoropyridyl unit of intermediate **43** is a potent radical acceptor and is reported to undergo facile β-scission under refluxing ethyl acetate or classical radical conditions to give the corresponding alkene **44** and pyridone **45**. However, under the exceedingly mild reac-



Scheme 9 Plausible mechanism for the photoredox process.

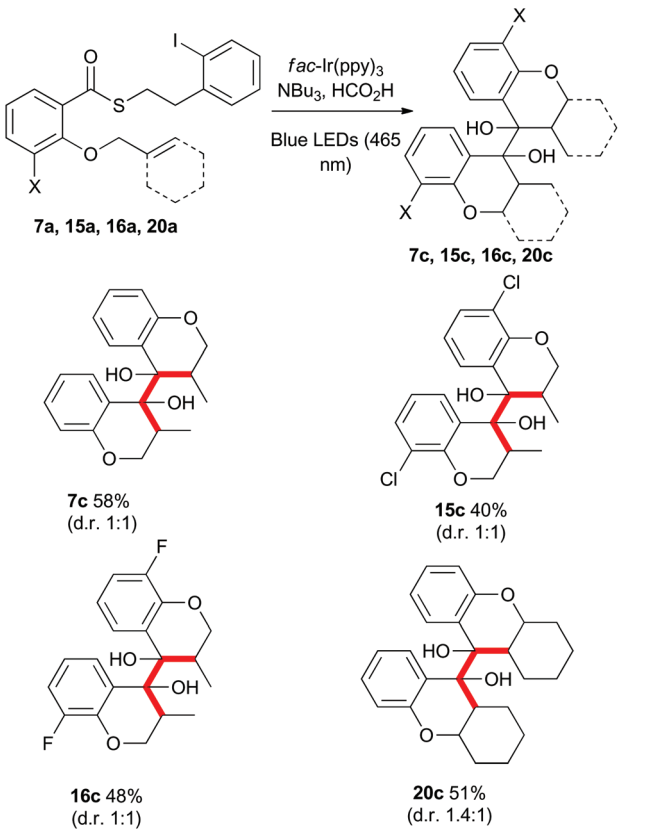


Scheme 10 Intermolecular–intramolecular radical cascade reactions.

tion conditions employed for the photoredox-catalyzed process, no β-scission was observed and compound **46** was isolated in an almost 1 : 1 mixture with the double alkene addition product **47**.

Rueping and co-workers have previously shown that acetophenones undergo photoredox catalysed dimerisations in an acid-dependent manner.[28] Our ability to conduct the photoredox-catalyzed indirect radical generation in the presence of formic acid suggested that product chromanones could be employed in a cascade reaction (Scheme 9).[29–32] The reduction potential of unsubstituted chromanone has been measured at −1.9 V (*vs.* SCE),[33,34] which lies outside the range of the photoexcited *fac*-Ir(ppy)$_3$ complex. However, in the presence of formic acid, protonation would result in a significant change in redox behaviour.[35,36] Reduction of the protonated species would give a benzylic radical (intermediate radical B) that could engage in a radical–radical dimerization reaction (colligation).

Gratifyingly, when the thioesters **7a**, **15a**, **16a** and **20a** were subjected to the standard reaction conditions, the dimeric products **7c**, **15c**, **16c**, and **20c** were isolated in good overall yield as a mixture of *meso* and racemic diastereomers (Scheme 11). The dimerization of the 3-halo thioesters (**15a** and **16a**) was particularly facile. The ease of single electron reduction of protonated chromanones bearing electron withdrawing substitu-



Scheme 11 Radical cyclization–dimerization cascade reactions.

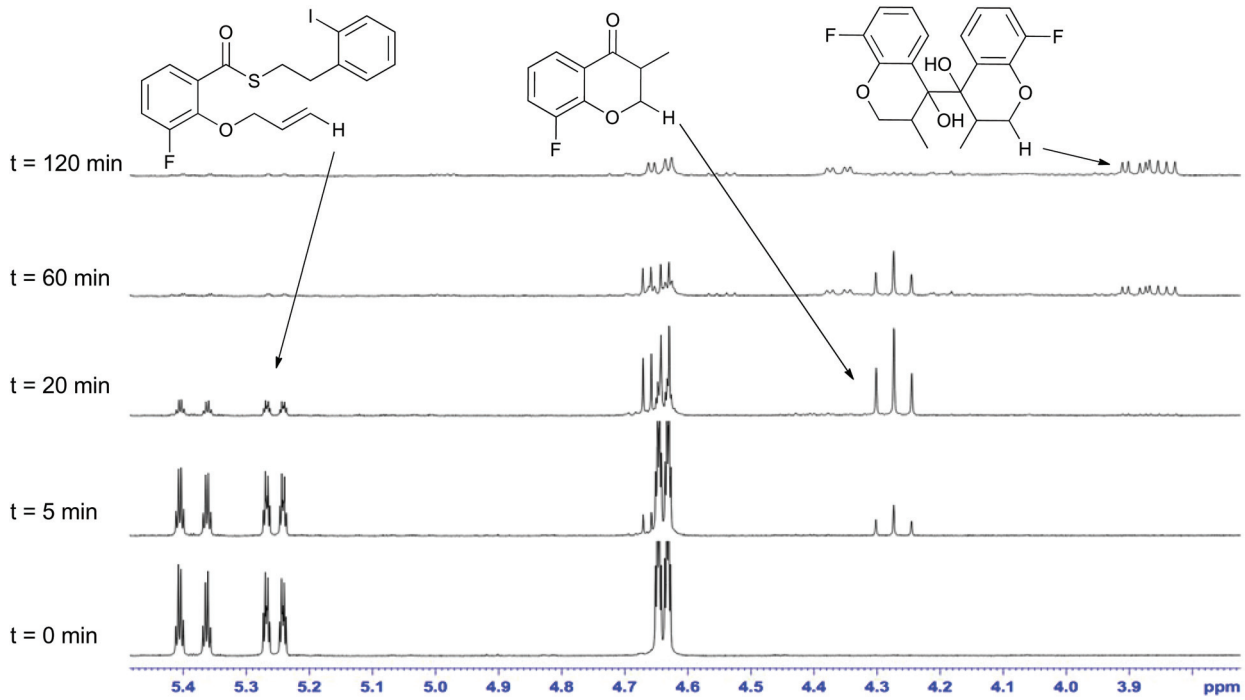
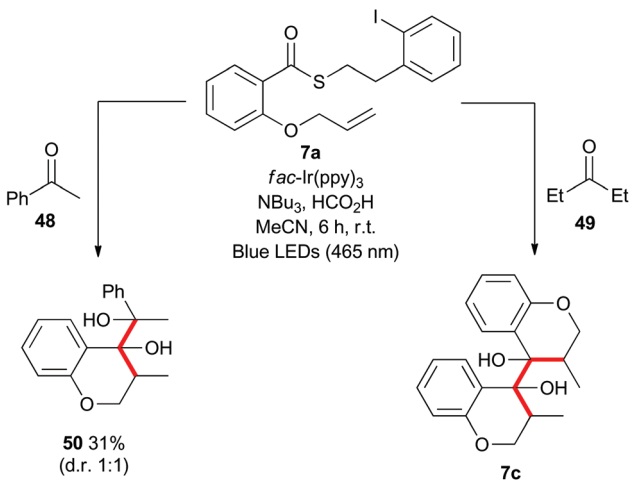


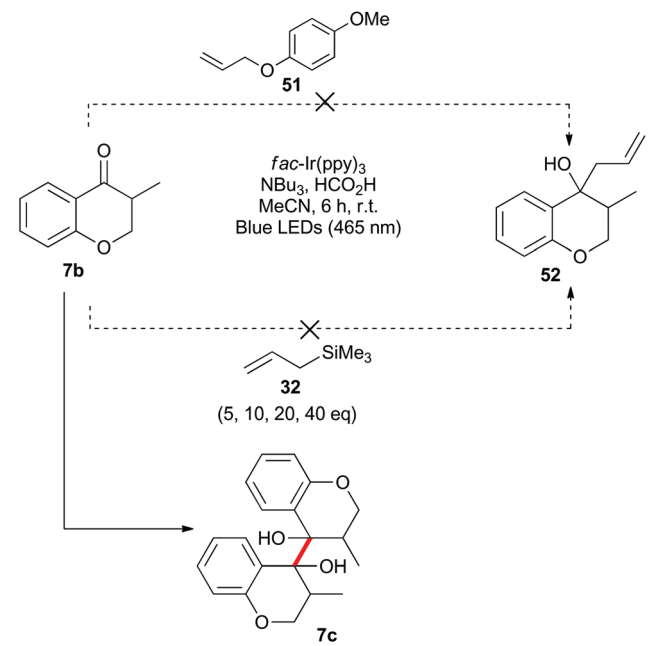
Fig. 1 *In situ* ^{1}H NMR analysis of the dimerization reaction mixture.

ents provides an explanation for the intial troubles isolating certain cyclisation products described in Scheme 2.

Mechanistically, the formation of the dimeric compounds could occur either by colligation,[37] or by addition of an initially formed radical onto an activated carbonyl unit. *In situ* ^{1}H NMR monitoring of the reaction showed that the starting materials were converted into the chromanone products before the dimeric species began to appear (Fig. 1), with no cross-reactivity between benzyl radicals and thioesters being observed. To further delineate the reaction pathway, two electronically different ketones were added to the mixture (Scheme 12). Acetophenone (**48**) is known to be reduced under photoredox conditions in an acid dependent manner,[28] but pentanone (**49**) is not reduced. If the reaction proceeds by radical addition to carbonyl, then both compounds would participate in the reaction and mixed pinacol-type products would be observed. In the event, pinacol **50** was observed in the reaction conducted in the



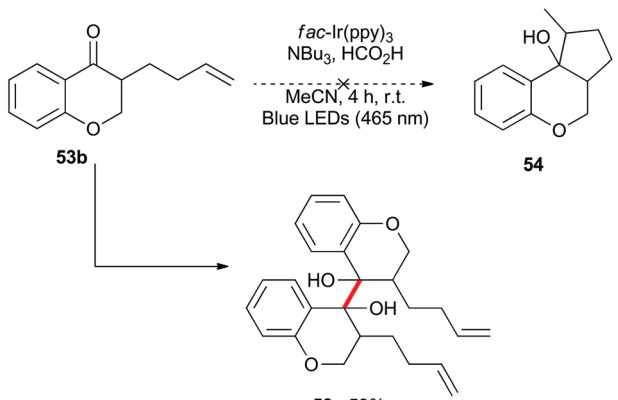
Scheme 12 Radical cyclization–dimerization with different ketones.



Scheme 13 Attempted intermolecular benzylic radical addition reactions.

presence of acetophenone (**48**). In contrast, when the reaction was conducted in the presence of pentanone (**49**), only the dimeric compound **7c** was observed. This strongly suggests that the dimerization proceeds *via* a colligation pathway.

Benzylically stabilized radicals such as intermediate B in Scheme 9 are known to be resistant to alkene addition reactions. Indeed, when pre-formed chromanone **7b** was subjected to the acidic photoredox reaction conditions in the presence of an excess of either allylmethoxyphenol **51** or allyltrimethylsilane **32**, the only observed product was the dimer **7c** (Scheme 13). We attempted to overcome the barrier to intermolecular radical addition by conducting the reaction in an intramolecular fashion (Scheme 14). As such, the alkene containing chromanone **53b** was subjected to the acidic photoredox reaction conditions. Spectacularly, the desired tricyclic compound **54** was not observed, but rather the dimeric compound **53c** was isolated in good yield.[38]



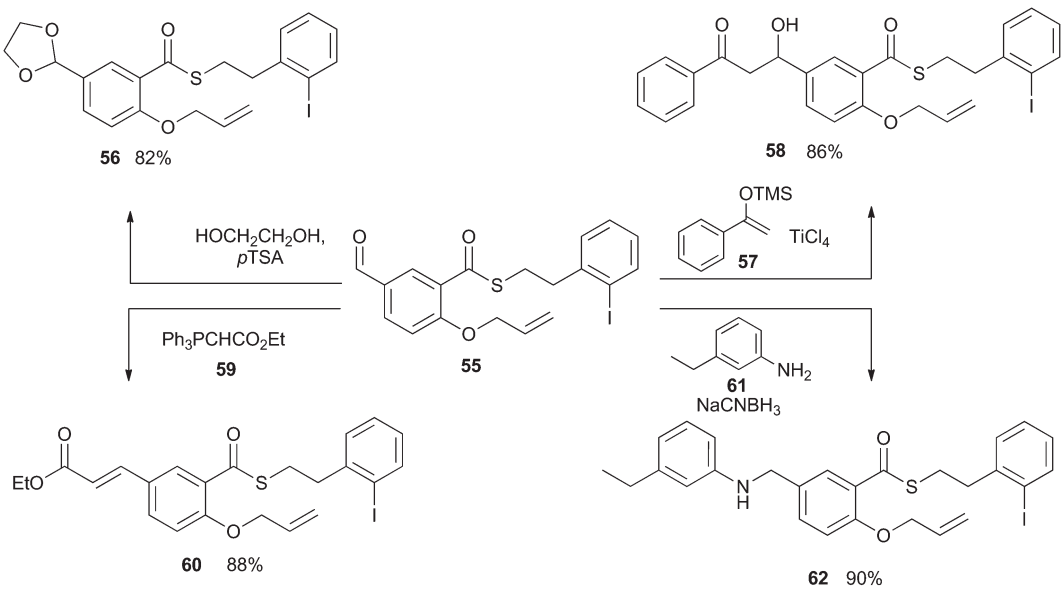
Scheme 14 Attempted intramolecular benzylic radical addition reaction.

Synthetic compatibility

The examples described above demonstrate that the iodoarene thioester can be easily generated from a range of carboxylic acids and that it can be chemoselectively engaged by the application of photoredox reaction conditions. For this indirect acyl radical generation to be generally applicable, the thioester functionality must tolerate a wide range of reaction conditions. Intuitively, we can expect that the thioester unit will be incompatible with strongly basic conditions, but the window of tolerance has not been well defined. As such, we subjected compound **55** to a range of reactions involving basic and nucleophilic reagents. As shown in Scheme 15, compound **55** was converted into acetal **56** by the action of catalytic Brønsted acid in an excess of diol. No esterification was observed. The thioester unit was similarly compatible with the Lewis acid $TiCl_4$, and underwent Mukayami aldol reaction with silyl ether **57** to give compound **58**. The thioester was also stable in the presence of the mildly basic phosphorane **59**, during the transformation of **55** into **60**. And finally, the thioester remained intact after exposure to aniline **61** and a hydride source, during the conversion of **55** into **62**. Together, these results instilled confidence that the iodoarene thioester could be carried through a practicable synthetic sequence before undergoing reaction in a chemoselective fashion.

Synthetic application

To highlight the synthetic potential of the indirect generation of acyl radicals under photoredox-catalyzed conditions, we undertook the synthesis of clinical agent donepezil (**63**) (Fig. 2). Donepezil (**63**) was disclosed by Sugimoto and coworkers in 1992 and approved by the FDA in 1996 for the treat-



Scheme 15 Synthetic compatibility of the thioester unit with common reaction conditions.

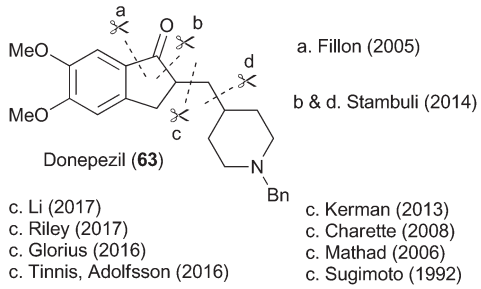


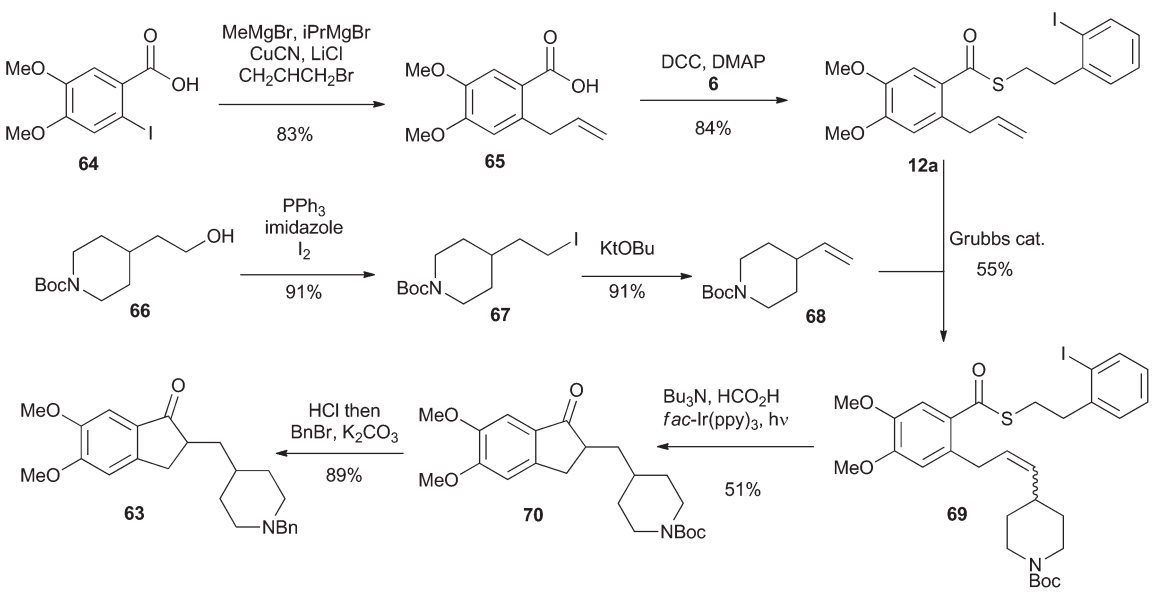
Fig. 2 Previous approaches to Donepezil.

ment of mild–severe dementia associated with Alzheimer's disease.[39] As a reversible inhibitior of acetylcholinesterase, donepezil (**63**) acts by increasing the concentration of acetylcholine in the central nervous system, thereby enhancing cholinergic function. Strictly a palliative treatment for the cognitive symptoms of the disease, donepezil (**63**) neither prevents nor slows the neurodegeneration associated with the Alzheimer's disease. Excluding the patent literature, there have been 11 previous syntheses of donepezil (**63**).[39–49] As depicted in Fig. 2, most approaches follow Sugimoto's original strategy and utilize an indanone alkylation to unite the two halves of the molecule.[39] The exceptions are Fillon's late-stage Freidel–Crafts alkylation,[46] Rao's late stage oxidation,[41] and Stambuli's palladium-catalyzed cascade construction of both the indanone and pyrrolidine connections.[44]

Our synthesis is shown in Scheme 16. The commercially available iodobenzoic acid **64** was deprotonated and then subjected to a copper-mediated allylation to give **65**. DCC-mediated coupling of **65** with thiol **6** installed the requisite thioester **12a**. Separately, the commercially available pyrrolidinyl alcohol **66** was iodinated and subjected to an elimination reaction to give the vinyl pyrrolidine **68**. Cross metathesis using Grubbs' first generation catalyst united fragments **12a** and **68** and delivered the cyclisation precursor **69**. It is noteworthy that the thioester was stable under the metathesis conditions, providing further illustration of its synthetic utility. The key photoredox-catalyzed acyl radical formation and intramolecular alkene addition was performed in the standard way and delivered compound **70** in 51% yield. The Boc unit was replaced by a benzyl group to complete the 5 step synthesis of donepezil (**63**).

Conclusions

Acyl radicals are reactive intermediates infrequently employed in organic synthesis. In an effort to increase their utility and generality, we have developed a photoredox-catalyzed process to access these useful intermediates in an *indirect* manner from thioesters. Ubiquitous carboxylic acids can be converted into relatively robust Crich-type thioesters in a single step. These aryliodide containing thioesters are stable to many common reaction conditions, including moderately basic and nucleophilic conditions. The latent acyl radical can be revealed at room temperature using the commercially available *fac*-Ir$(ppy)_3$ complex and low energy blue light. Altering the photocatalyst system to an aryldiazonium salt and the Hantzsch ester enables substrates with otherwise competing reactivity to be employed in the process. The liberated acyl radical can undergo reaction onto a variety of electronically and sterically different alkenes in both an inter- and intramolecular fashion. These include chain elongation with alkenes containing functional groups capable of β-scission reactions (no β-scission was observed), and pinacol couplings for the generation of dimeric and cross-coupled diols.



Scheme 16 Synthesis of Donepezil utilizing an indirect acyl radical generation and intramolecular cyclization reaction.

The photoredox-catalyzed *indirect* acyl radical generation has been employed for the total synthesis of the clinically used pharmaceutical, donepezil. Application of the described procedure enabled a strategically new disconnection to be envisaged for this popular synthetic target. And importantly, the short synthesis of donepezil demonstrates that this methodology is applicable to target-based synthesis.

In conclusion, we report a mild method for the generation of acyl radicals that is complementary to existing methods. The scope of the protocol both in terms of subtrates that can be employed and reactions that can be conducted, gives us confidence that this new protocol will help facilitate the increased use of acyl radicals for key bond formation during target-based synthesis.

Experimental section

General experimental

All reactions were performed under an inert atmosphere (nitrogen or argon) in oven dried glassware, unless otherwise stated. Toluene, acetonitrile, methanol, diethyl ether, dichloromethane, tetrahydrofuran and dimethylformamide were purified using an Innovative Technology, Inc., PureSolv™ solvent purification system. Tributylamine was dried over potassium hydroxide then fractionally distilled. All other solvents and reagents were used as received from commercial sources.

Melting points were determined using a Stanford Research Systems Optimelt automated melting point system and are uncorrected. Infrared spectra were acquired on a Bruker ALPHA FT-IR as thin films or neat. ^{1}H and ^{13}C NMR spectra were recorded in deuterochloroform on a Bruker AVANCE III 500, a Bruker AVANCE III 400, a Bruker AVANCE 300, or a Bruker AVANCE 200 spectrometer (^{1}H frequencies 500, 400, 300, 200 MHz; ^{13}C frequencies 125, 100, 75 and 50 MHz respectively). ^{1}H chemical shifts are expressed as parts per million (ppm) with residual chloroform (δ 7.26) as an internal reference and are reported as chemical shift (δ_H); relative integral; multiplicity (s = singlet, br = broad, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, m = multiplet); and coupling constants (J) reported in Hz. ^{13}C NMR chemical shifts are expressed as parts per million (ppm) with residual chloroform (δ 77.16) as internal reference and are reported as chemical shift (δ_C); multiplicity (assigned from DEPT or HSQC experiments). High resolution mass spectra were recorded on a Bruker Apex II Fourier Transform Ion Cyclotron Resonance mass spectrometer with a 7.0 T magnet, fitted with an off-axis Analytica electrospray source. Column chromatography was performed using 40–60 μm (230–400 mesh) silica gel using commercial solvents. Analytical thin layer chromatography was performed using preconditioned plates (Merck TLC silica gel 60 F_{254} on aluminium) and visualised using UV light (254 nm and 365 nm), ethanolic anisaldehyde, vanillin or potassium permanganate solution.

Experimental procedures

2-(2-Iodophenyl)ethan-1-ol.[50] To a solution of 2-iodophenylacetic acid (5.00 g, 19.1 mmol), in THF (45 mL) at 0 °C was added sodium borohydride (1.48 g, 39.1 mmol) in three portions. $BF_3{\cdot}OEt_2$ (4.9 mL, 39 mmol) was added dropwise over 10 min. The mixture was stirred at room temperature for 1.5 h. The reaction was quenched with methanol (25 mL) and poured onto aqueous HCl (25 mL, 1 M solution). The aqueous phase was extracted with ethyl acetate (3 × 50 mL). The organic extracts were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (20% ethyl acetate in hexanes) to give 2-(2-iodophenyl)ethan-1-ol (4.45 g, 17.9 mmol, 94%) as a yellow oil. **R_f**: 0.26 (20% ethyl acetate in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ**: 7.83 (1 H, dd, J = 7.8, 0.9 Hz, Ar–H), 7.30–7.25 (2 H, m, 2 × Ar–H), 6.91 (1 H, ddd, J = 7.9, 6.8, 2.3 Hz, Ar–H), 3.85 (2 H, t, J = 6.8 Hz, CH_2OH), 3.01 (2 H, t, J = 6.8 Hz, CH_2Ar), 1.64 (1 H, brs, OH); **^{13}C NMR (126 MHz, $CDCl_3$) δ**: 141.1 (C), 139.7 (CH), 130.3 (CH), 128.4 (CH), 128.3 (CH), 100.8 (C), 62.3 (CH_2), 43.7 (CH_2); **LRMS (APCI) m/z** 385 (67), 357 (67), 231 ($[M - OH]^+$, 100).

***S*-(2-Iodophenethyl) ethanethioate (1).**[20] To a solution of triphenylphosphine (210 mg, 0.81 mmol) in THF (2.5 mL), at 0 °C, was added DIAD (0.16 mL, 0.81 mmol). After 5 min 2-(2-iodophenyl)ethan-1-ol (100 mg, 0.40 mmol) was added as a solution in THF (1 mL) followed by thioacetic acid (60 μL, 0.81 mmol). The mixture was allowed to warm to room temperature. After 16 h the mixture was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (1% diethyl ether in hexanes) to give **1** (120 mg, 0.38 mmol, 95%) as a pale yellow oil. **R_f**: 0.44 (5% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ**: 7.80 (1 H, dd, J = 7.9, 1.2 Hz, Ar–H), 7.30–7.23 (2 H, m, 2 × Ar–H), 6.90 (1 H, ddd, J = 7.9, 6.60, 2.4 Hz, Ar–H), 3.12–3.08 (2 H, m, SCH_2), 2.99–2.95 (2 H, m, $ArCH_2$), 2.33 (3 H, s, CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) δ**: 195.6 (C), 142.6 (C), 139.7 (CH), 130.0 (CH), 128.5 (2 × CH), 100.5 (C), 40.5 (CH_2), 30.7 (CH_3), 29.2 (CH_2); **ν_{max}/cm^{-1}** 3055, 2926, 1689, 1465, 1436, 1132, 1105, 1047; **LRMS (ESI$^+$) m/z** 645 (37), 385 (47), 329 ($[M + Na]^+$, 100).

2-(2-Iodophenyl)ethane-1-thiol (6). To a solution of *S*-(2-iodophenethyl) ethanethioate (406 mg, 1.33 mmol) in MeOH (7 mL) was added a solution of NaOH (117 mg, 2.92 mmol) in water (4 mL). The mixture was stirred at room temperature for 5 min. Saturated aqueous ammonium chloride (15 mL) was added and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The organic extracts were washed with brine (50 mL), dried (Na_2SO_4) and concentrated *in vacuo* to give crude 2-(2-iodophenyl)ethane-1-thiol **6** (350 mg, 1.33 mmol, 100%) which was used without purification.

Intramolecular cyclizations

***S*-(2-Iodophenethyl) 2-(allyloxy)benzothioate (7a).**[8] To a solution of 2-(allyloxy)-benzoic acid (378 mg, 2.12 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (437 mg, 2.12 mmol) and

DMAP (28 mg, 0.23 mmol). The mixture was stirred for 5 min before a solution of 2-(2-iodophenyl)ethane-1-thiol (400 mg, 1.51 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature for 20 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (2.5–5% diethyl ether in hexanes) to give **7a** (466 mg, 1.10 mmol, 73%) as a colourless oil. **R_f:** 0.3 (5% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.83 (1 H, dd, J = 7.9, 1.3 Hz, Ar–H), 7.79 (1 H, dd, J = 7.7, 1.8 Hz, Ar–H), 7.44 (1 H, ddd, J = 8.4, 7.4, 1.8 Hz, Ar–H), 7.33 (1 H, dd, J = 7.6, 1.8 Hz, Ar–H), 7.28 (1 H, td, J = 7.4, 1.3 Hz, Ar–H), 6.99 (1 H, td, J = 7.6, 1.0 Hz, Ar–H), 6.95 (1 H, dd, J = 8.4, 1.0 Hz, Ar–H), 6.90 (1 H, ddd, J = 7.9, 7.2, 1.8 Hz, Ar–H), 6.10 (1 H, ddt, J = 17.3, 10.6, 5.1 Hz, CH=CH_2), 5.49 (1 H, dq, J = 17.3, 1.6 Hz, CH=CHH), 5.31 (1 H, dq, J = 10.5, 1.4 Hz, CH=CHH), 4.68 (2 H, dt, J = 5.1, 1.6 Hz, OCH_2), 3.28–3.24 (2 H, m, SCH_2), 3.11–3.08 (2H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.9 (C), 157.0 (C), 143.1 (C), 139.6 (CH), 133.5 (CH), 132.7 (CH), 130.2 (CH), 129.9 (CH), 128.5 (CH), 128.4 (CH), 127.5 (C), 120.7 (CH), 118.1 (CH_2), 113.6 (CH), 100.5 (C), 69.9 (CH_2), 40.5 (CH_2), 29.6 (CH_2); **ν_{max}/cm^{-1}** 3071, 2925, 2865, 1673, 1633, 1595, 1482, 1446, 1284, 1194, 1010; **LRMS (ESI$^+$) m/z** 447 ([M + Na]$^+$, 100).

3-Methylchroman-4-one (7b).[51] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **5** (69 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.39 mL, 1.6 mmol), formic acid (60 μL, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 1 h 15 min. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (25–35% dichloromethane in hexanes) to give **7b** (19 mg, 0.12 mmol, 71%) as a colourless oil. **R_f:** 0.2 (30% dichloromethane in hexanes). **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 7.89 (1 H, dd, J = 7.9, 1.7 Hz, Ar–H), 7.47–7.44 (1 H, m, Ar–H), 7.02–6.96 (1 H, m, Ar–H), 6.97–6.93 (1 H, m, Ar–H), 4.50 (1 H, dd, J = 11.3, 5.1 Hz, OCHH), 4.15 (1H, t, J = 11.3 Hz, OCHH), 2.89–2.82 (1 H, m, $CHCH_3$), 1.22 (3 H, d, J = 7.0 Hz, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$) δ:** 194.9 (C), 161.9 (C), 135.8 (CH), 127.5 (CH), 121.5 (CH), 120.7 (C), 117.9 (CH), 72.4 (CH_2), 40.9 (CH), 10.8 (CH_3); **ν_{max}/cm^{-1}** 2973, 2934, 2876, 1690, 1606, 1478, 1387, 1325, 1296, 1212, 1148, 1129; **LRMS (ESI$^+$) m/z** 523 (98), 347 (73), 199 (100), 185 ([M + Na]$^+$, 18).

***S*-(2-Iodophenethyl) 2-(allyloxy)-3-methoxybenzothioate (8a).** To a solution of 2-(allyloxy)-3-methoxybenzoic acid (453 mg, 2.17 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added DCC (448 mg, 2.17 mmol) and DMAP (29 mg, 0.23 mmol). The mixture was stirred for 10 min before a solution of thiol **6** (410 mg, 1.55 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature for 16 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5–8% ethyl acetate in hexanes) to give **8a** (483 mg, 1.10 mmol, 69%) as a colourless oil. **R_f:** 0.38 (10% ethyl acetate in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.82 (1 H, dd, J = 7.9, 1.1 Hz, Ar–H), 7.35–7.27 (3 H, m, 3 × Ar–H), 7.11–7.03 (2 H, m, 2 × Ar–H), 6.92 (1 H, ddd, J = 7.9, 7.1, 1.9 Hz, Ar–H), 6.13 (1 H, ddt, J = 17.2, 10.4, 6.0 Hz, CH=CHH), 5.36 (1 H, dq, J = 17.2, 1.6 Hz, CH=CHH), 5.22 (1 H, dq, J = 10.4, 1.4 Hz, CH=CHH), 4.61 (2 H, dt, J = 6.0, 1.3 Hz, OCH_2), 3.88 (3 H, s, OCH_3), 3.29–3.25 (2 H, m, SCH_2), 3.11–3.07 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 191.3 (C), 153.5 (C), 146.4 (C), 143.0 (C), 139.7 (CH), 134.1 (CH), 133.1 (C), 130.3 (CH), 128.6 (CH), 128.5 (CH), 124.0 (CH), 120.6 (CH), 118.2 (CH_2), 116.0 (CH), 100.5 (C), 74.9 (CH_2), 56.3 (CH_3), 40.5 (CH_2), 29.7 (CH_2); **ν_{max}/cm^{-1}** 2937, 1674, 1639, 1580, 1470, 1438, 1266, 1232, 1010; **LRMS (ESI$^+$) m/z** 1383 (36), 931 (100), 477 ([M + Na]$^+$, 58), 436 (14); **HRMS (ESI$^+$)** calculated for [$C_{19}H_{19}IO_3SNa$] 476.99918, found 476.99903.

8-Methoxy-3-methylchroman-4-one (8b).[8,51] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **6** (74 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.39 mL, 1.6 mmol), formic acid (60 μL, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 18 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5–10% ethyl acetate in hexanes) to give **8b** (20 mg, 0.10 mmol, 65%) as a white solid. **R_f:** 0.35 (20% ethyl acetate in hexanes). **m.p.** 82–83 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.50 (1 H, dd, J = 7.9, 1.5 Hz, Ar–H), 7.04 (1 H, dd, J = 8.0, 1.5 Hz, Ar–H), 6.95 (1 H, t, J = 7.9 Hz, Ar–H), 4.60 (1 H, dd, J = 11.3, 5.0 Hz, OCHH), 4.22 (1 H, t, J = 11.1 Hz, OCHH), 3.91 (3 H, s, OCH_3), 2.90–2.84 (1 H, m, $CHCH_3$), 1.23 (3 H, d, J = 7.0 Hz, CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 194.8 (C), 151.8 (C), 148.9 (C), 121.3 (C), 121.0 (CH), 118.7 (CH), 116.5 (CH), 72.9 (CH_2), 56.4 (CH_3), 40.7 (CH), 10.9 (CH_3); **ν_{max}/cm^{-1}** 2963, 2932, 1688, 1606, 1492, 1452, 1301, 1270, 1214, 983, 730; **LRMS (ESI$^+$) m/z** 413 (100), 393 (82), 358 (35), 273 (28), 240 (36), 215 ([M + Na]$^+$, 19), 186 (65).

***S*-(2-Iodophenethyl) 2-(allyloxy)-3,5-di-*tert*-butylbenzothioate (9a).** To a solution of 2-(allyloxy)-3,5-di-*tert*-butylbenzoic acid (540 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 10 min before a solution of compound **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature for 19.5 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (20–25% dichloromethane in hexanes) to give **9a** (420 mg, 0.78 mmol, 59%) as a colourless oil. **R_f:** 0.29 (30% dichloromethane in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.83 (1 H, dd, J = 7.9, 1.2 Hz, Ar–H), 7.49 (1 H, d, J = 2.5 Hz, Ar–H), 7.43 (1 H, d, J = 2.5 Hz, Ar–H), 7.36–7.28 (2 H, m, Ar–H),

6.95–6.90 (1 H, m, Ar–H), 6.07 (1 H, ddt, J = 17.3, 10.5, 5.3 Hz, CH=CH_2), 5.42 (1 H, dq, J = 17.3, 1.7 Hz, CH=CHH), 5.25 (1 H, dq, J = 10.5, 1.5 Hz, CH=CHH), 4.38 (2 H, dt, J = 5.3, 1.5 Hz, OCH_2), 3.30–3.26 (2 H, m, SCH_2), 3.12–3.08 (2 H, m, SCH_2CH_2), 1.41 (9 H, s, 3 × CH_3), 1.32 (9 H, s, J = 3 × CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 193.7 (C), 153.7 (C), 145.5 (C), 143.0 (C), 142.9 (C), 139.7 (CH), 133.8 (CH), 132.5 (C), 130.2 (CH), 128.60 (CH), 128.56 (CH), 128.1 (CH), 124.4 (CH), 117.4 (CH_2), 100.5 (C), 75.7 (CH_2), 40.7 (CH_2), 35.6 (C), 34.7 (C), 31.5 (3 × CH_3), 30.9 (3 × CH_3), 29.7 (CH_2); **ν_{max}/cm^{-1}** 2960, 2869, 1675, 1466, 1438, 1362, 1230, 1203, 1169, 988, 928, 829, 746; **LRMS (ESI$^+$) m/z** 559 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{26}H_{33}O_2ISNa$] 559.11382, found 559.11420.

6,8-Di-*tert*-butyl-3-methylchroman-4-one (9b).[8] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of compound **7** (79 mg, 0.15 mmol) in MeCN (2.7 mL) was added tributylamine (0.35 mL, 1.5 mmol), formic acid (50 μL, 1.5 mmol) and *fac*-Ir(ppy)$_3$ (2.4 mg, 0.32 μmol). The mixture was degassed for 30 min before irradiating with blue light (465 nm) for 10 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5–10% diethyl ether in hexanes) to give **9b** (28 mg, 0.10 mmol, 70%) as an off white solid. **R_f:** 0.26 (5% diethyl ether in hexanes); **m.p.** 101–103 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.81 (1 H, d, J = 2.5 Hz, Ar–H), 7.53 (1 H, d, J 2.5 Hz, Ar–H), 4.52 (1 H, dd, J = 11.1, 5.0 Hz, OCHH), 4.12 (1 H, dd, J = 10.9, 10.9 Hz, OCHH), 2.86–2.79 (1 H, m, OCH_2CH), 1.40 (9 H, s, 3 × CCH_3), 1.31 (9 H, s, 3 × CCH_3), 1.22 (3 H, d, J = 7.0 Hz, $CHCH_3$); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 196.0 (C), 159.0 (C), 143.3 (C), 138.3 (C), 130.5 (CH), 121.5 (CH), 120.7 (C), 71.8 (CH_2), 40.8 (CH), 35.2 (C), 34.6 (C), 31.5 (3 × CH_3), 29.8 (3 × CH_3), 11.1 (CH_3); **ν_{max}/cm^{-1}** 2958, 2870, 1688, 1604, 1478, 1444, 1244; **LRMS (ESI$^+$) m/z** 685 (32) 611 (23), 571 (100), 355 (24), 297 ([M + Na]$^+$, 37).

***S*-(2-Iodophenethyl) 2-(allyloxy)-5-bromobenzothioate (10a).** To a solution of 2-(allyloxy)-5-bromobenzoic acid (477 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 10 min before a solution of compound **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature for 15 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (20–30% dichloromethane in hexanes) to give **10a** (426 mg, 0.85 mmol, 64%) as a yellow solid. **R_f:** 0.30 (30% dichloromethane in hexanes); **m.p.** 63–65 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.88 (1 H, d, J = 2.6 Hz, Ar–H), 7.83 (1 H, dd, J = 7.9, 1.2 Hz, Ar–H), 7.52 (1 H, dd, J = 8.8, 2.6 Hz, Ar–H), 7.34 (1 H, dd, J = 7.6, 2.0 Hz, Ar–H), 7.30 (1 H, td, J = 7.3, 1.2 Hz, Ar–H), 6.92 (1 H, ddd, J = 7.9, 7.0, 2.1 Hz, Ar–H), 6.07 (1 H, ddt, J = 17.3, 10.5, 5.2 Hz, CH=CHH), 5.47 (1 H, dq, J = 17.3, 1.6 Hz, CH=CHH), 5.32 (1 H, dq, J = 10.6, 1.4 Hz, CH=CHH), 4.65 (2 H, dt, J = 5.1, 1.6 Hz, OCH_2), 3.28–3.24 (2 H, m, SCH_2), 3.10–3.07 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 189.7 (C), 156.1 (C), 142.9 (C), 139.7 (CH), 136.0 (CH), 132.4 (CH), 132.3 (CH), 130.2 (CH), 129.0 (C), 128.6 (CH), 128.5 (CH), 118.5 (CH_2), 115.5 (CH), 113.1 (C), 100.5 (C), 70.2 (CH_2), 40.4 (CH_2), 29.8 (CH_2); **ν_{max}/cm^{-1}** 2921, 1676, 1633, 1479, 1274, 1177, 1129, 1011; **LRMS (ESI$^+$) m/z** 527 ([M + Na]$^+$, 100), 525 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{18}H_{16}O_2BrISNa$] 524.89913 and 526.89704, found 524.89970 and 524.89772.

6-Bromo-3-methylchroman-4-one (10b).[51] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of *S*-(2-iodophenethyl) 2-(allyloxy)-5-bromobenzothioate (83 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.39 mL, 1.6 mmol), formic acid (60 μL, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 22 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (25–40% dichloromethane in hexanes) to give **10b** (7 mg, 0.029 mmol, 18%) as an off-white solid. **R_f:** 0.39 (40% dichloromethane in hexanes); **m.p.** 90–92 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 8.00 (1 H, d, J = 2.5 Hz, Ar–H), 7.53 (1 H, dd, J = 8.8, 2.5 Hz, Ar–H), 6.87 (1 H, d, J = 8.8 Hz, Ar–H), 4.50 (1 H, dd, J = 11.4, 5.1 Hz, OCHH), 4.14 (1 H, t, J = 11.2 Hz, OCHH), 2.85 (1 H, dqd, J = 11.0, 7.0, 5.1 Hz, $CHCH_3$), 1.22 (1 H, d, J = 7.0 Hz, $CHCH_3$); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 193.7 (C), 160.8 (C), 138.5 (CH), 129.9 (CH), 122.0 (C), 120.0 (CH), 114.2 (C), 72.4 (CH_2), 40.6 (CH), 10.7 (CH_3); **ν_{max}/cm^{-1}** 2966, 2932, 2879, 1687, 1599, 1477, 1457, 1420, 1316, 1297, 1183, 1021; **LRMS (EI$^+$) m/z** 242 ([M]$^+$, 45), 240 ([M]$^+$, 46), 200 (90), 198 (100), 172 (32), 170 (28).

***S*-(2-Iodophenethyl) 2-(allyloxy)-5-bromo-3-methoxybenzothioate (11a).** To a solution of 2-(allyloxy)-5-bromo-3-methoxybenzoic acid (533 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 10 min before a solution of compound **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature for 25 h before concentrating *in vacuo*. The residue was purified by flash chromatography on silica gel (2.5–5% diethyl ether in hexanes) to give **11a** (556 mg, 1.04 mmol, 78%) as a yellow oil. **R_f:** 0.21 (5% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.82 (1 H, dd, J = 7.9, 1.2 Hz, Ar–H), 7.41 (1 H, d, J = 2.3 Hz, Ar–H), 7.33–7.25 (2 H, m, Ar–H), 7.13 (1 H, d, J = 2.3 Hz, Ar–H), 6.91 (1 H, ddd, J = 7.9, 6.8, 2.3 Hz, Ar–H), 6.08 (1 H, ddt, J = 17.2, 10.3, 6.0 Hz, CH=CH_2), 5.34 (1 H, dq, J = 17.2, 1.6 Hz, CH=CHH), 5.22 (1 H, dq, J = 10.3, 1.3 Hz, CH=CHH), 4.58 (2 H, dt, J = 6.0, 1.3 Hz, OCH_2), 3.86 (3 H, s, OCH_3), 3.28–3.24 (2 H, m, SCH_2), 3.10–3.06 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.0 (C), 154.1 (C), 145.6 (C), 142.7 (C), 139.7 (CH), 133.9 (C), 133.6 (CH), 130.2 (CH), 128.6 (CH), 128.5 (CH), 123.0 (CH), 119.0 (CH), 118.6 (CH_2), 116.4 (C), 100.5 (C), 74.9 (CH_2), 56.5 (CH_3), 40.3 (CH_2), 29.7 (CH_2);

ν_{max}/cm^{-1} 3080, 2936, 2863, 1675, 1639, 1569, 1468, 1441, 1419, 1403, 1303, 1255, 1221, 974; **LRMS (ESI$^+$)** *m*/*z* 555 ([M + Na]$^+$, 94), 557 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{19}H_{18}O_3SIBrNa$] 554.90969 and 556.90761, found 554.91019 and 556.90817.

6-Bromo-8-methoxy-3-methylchroman-4-one (11b). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of *S*-(2-iodophenethyl) 2-(allyloxy)-5-bromo-3-methoxybenzothioate (87 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.39 mL, 1.6 mmol), formic acid (60 μL, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 18 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (2.5–5–30% diethyl ether in hexanes) to give **11b** (13 mg, 0.048 mmol, 30%) as an off-white solid. R_f: 0.17 (20% diethyl ether in hexanes); **m.p.** 98–100 °C; **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 7.61 (1 H, d, *J* = 2.3 Hz, Ar–H), 7.11 (1 H, d, *J* = 2.3 Hz, Ar–H), 4.60 (1 H, dd, *J* = 11.4, 5.0 Hz, OCHH), 4.20 (1 H, t, *J* = 11.1 Hz, OCHH), 3.90 (3 H, s, OCH_3), 2.87 (1 H, dqd, *J* = 10.9, 7.0, 5.0 Hz, CHCH$_3$), 1.22 (3 H, d, *J* = 7.0 Hz, CHCH$_3$); **^{13}C NMR (101 MHz, CDCl$_3$) δ:** 193.5 (C), 151.0 (C), 149.8 (C), 122.0 (C), 121.0 (CH), 119.5 (CH), 113.6 (C), 72.9 (CH_2), 56.7 (CH_3), 40.6 (CH), 10.8 (CH_3); ν_{max}/cm^{-1} 2967, 2933, 1694, 1486, 1578, 1486, 1460, 1440, 1294, 1263, 1248; **LRMS (ESI$^+$)** *m*/*z* 271 ([M + H]$^+$, 100), 273 ([M + H]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{11}H_{11}O_3BrNa$] 292.97838 and 294.97633, found 292.97873 and 294.97661.

***S*-(2-Iodophenethyl) 2-allyl-4,5-dimethoxybenzothioate (12a).** To a solution of 2-allyl-4,5-dimethoxybenzoic acid (310 mg, 1.39 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added DCC (359 mg, 1.74 mmol) and DMAP (32 mg, 0.26 mmol). The mixture was stirred for 5 min before a solution of compound **6** (460 mg, 1.74 mmol) in CH_2Cl_2 (3 mL) was added. The mixture was stirred at room temperature for 14 h before concentrating *in vacuo*. The residue was purified by flash chromatography on silica gel (40–60% dichloromethane in hexanes) to give **12a** (550 mg, 1.17 mmol, 84%) as a pale yellow oil. R_f: 0.36 (60% dichloromethane in hexanes); **^{1}H NMR (500 MHz, CDCl$_3$) δ:** 7.83 (1 H, dd, *J* = 8.0, 1.3 Hz, Ar–H), 7.34 (1 H, s, Ar–H), 7.34 (1 H, dd, *J* = 7.6, 1.9 Hz, Ar–H), 7.30 (1 H, td, *J* = 7.4, 1.3 Hz, Ar–H), 6.92 (1 H, ddd, *J* = 7.8, 7.2, 1.9 Hz, Ar–H), 6.74 (1 H, s, Ar–H), 5.97 (1 H, ddd, *J* = 16.9, 10.3, 6.4 Hz, CH=CH$_2$), 5.06–5.01 (2 H, m, CH=CH$_2$), 3.92 (6 H, s, 2 × OCH_3), 3.60 (2 H, dt, *J* = 6.4, 1.5 Hz, CH$_2$CH=CH$_2$), 3.29–3.25 (2 H, s, SCH_2), 3.11–3.07 (2 H, m, SCH_2CH_2); **^{13}C NMR (126 MHz, CDCl$_3$) δ:** 192.5 (C), 151.9 (C), 146.9 (C), 142.9 (C), 139.7 (CH), 137.4 (CH), 133.1 (C), 130.3 (CH), 129.5 (C), 128.6 (CH), 128.5 (CH), 115.9 (CH_2), 113.5 (CH), 112.1 (CH), 100.6 (C), 56.3 (CH_3), 56.1 (CH_3), 40.7 (CH_2), 37.6 (CH_2), 29.8 (CH_2); ν_{max}/cm^{-1} 2933, 2844, 1659, 1516, 1266, 1193, 1113; **LRMS (ESI$^+$)** *m*/*z* 491 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{20}H_{21}IO_3SNa$] 491.01483, found 491.01437.

5,6-Dimethoxy-2-methyl-2,3-dihydro-1*H*-inden-1-one (12b).[52] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of *S*-(2-iodophenethyl) 2-allyl-4,5-dimethoxybenzothioate (76 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (78 μL, 0.33 mmol), formic acid (11 μL, 0.33 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (465 nm) for 10 h min. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (30 mL, 1 M solution), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (80–100% dichloromethane in hexanes) to give **12b** (28 mg, 0.14 mmol, 83%) as a yellow solid. R_f: 0.18 (20% ethyl acetate in hexanes); **m.p.** 125–127 °C (lit.[52] 131–132 °C); **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 7.16 (1 H, s, Ar–H), 6.85 (1 H, s, Ar–H), 3.95 (3 H, s, OCH_3), 3.89 (3 H, s, OCH_3), 3.29 (1 H, dd, *J* = 16.6, 7.3 Hz, CHHCH), 2.71–2.59 (2 H, m, CHHCH), 1.28 (3 H, d, *J* = 7.4 Hz, CH_3); **^{13}C NMR (101 MHz, CDCl$_3$) δ:** 208.3 (C), 155.6 (C), 149.6 (C), 148.8 (C), 129.1 (C), 107.5 (CH), 104.6 (CH), 56.3 (CH_3), 56.2 (CH_3), 42.3 (CH), 34.9 (CH_2), 16.7 (CH_3); ν_{max}/cm^{-1} 2964, 2931, 2872, 2839, 1684, 1590, 1499, 1457, 1437, 1364, 1319, 1295, 1258, 1239, 1214, 1180, 1124, 1043, 1002; **LRMS (ESI$^+$)** *m*/*z* 435 (100), 229 ([M + Na]$^+$, 74).

***S*-(2-Iodophenethyl) 2-(allyloxy)-3,5-dichlorobenzothioate (13a).** To a solution of 2-(allyloxy)-3,5-dichlorobenzoic acid (1.61 g, 6.53 mmol) in CH_2Cl_2 (40 mL) at 0 °C was added DCC (1.35 g, 6.53 mmol) and DMAP (96 mg, 0.78 mmol). The mixture was stirred for 2 min before a solution of compound **6** (1.38 g, 5.23 mmol) in CH_2Cl_2 (12 mL) was added. The mixture was stirred at room temperature for 14 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (20–50% dichloromethane in hexanes) to give **13a** (2.35 g, 4.76 mmol, 91%) as a pale yellow oil. R_f: 0.62 (5% diethyl ether in hexanes); **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 7.84–7.82 (1 H, m, Ar–H), 7.57 (1 H, d, *J* = 2.6 Hz, Ar–H), 7.52 (1 H, d, *J* = 2.6 Hz, Ar–H), 7.32–7.30 (2 H, m, Ar–H), 6.95–6.91 (1 H, m, Ar–H), 6.09 (1 H, ddt, *J* = 17.2, 10.3, 5.9 Hz, CH=CH$_2$), 5.41 (1 H, dq, *J* = 17.2, 1.5 Hz, CH=CHH), 5.28 (1 H, dq, *J* = 10.3, 1.3 Hz, CH=CHH), 4.56 (2 H, dt, *J* = 5.9, 1.3 Hz, OCH_2), 3.32–3.28 (2 H, m, SCH_2), 3.12–3.07 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, CDCl$_3$) δ:** 189.6 (C), 151.6 (C), 142.5 (C), 139.8 (CH), 134.9 (C), 133.4 (CH), 132.8 (CH), 130.5 (C), 130.2 (CH), 129.7 (C), 128.7 (CH), 128.6 (CH), 127.6 (CH), 119.3 (CH_2), 100.5 (C), 76.0 (CH_2), 40.3 (CH_2), 29.9 (CH_2); ν_{max}/cm^{-1} 3070, 2926, 1673, 1643, 1462, 1437, 1418, 1211, 1174; **LRMS (ESI$^+$)** *m*/*z* 515 ([M + Na]$^+$, 100), 413 (42), 393 (46), 360 (16), 331 (11); **HRMS (ESI$^+$)** calculated for [$C_{18}H_{15}Cl_2IO_2SNa$] 514.91067 and 516.90770, found 514.91072 and 516.90775.

***S*-(2-Iodophenethyl) 2-(allyloxy)-3-bromobenzothioate (14a).** To a solution of 2-(allyloxy)-3-bromobenzoic acid (477 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 5 min before a solution of compound **6**

(350 mg, 1.33 mmol) in CH_2Cl_2 (3 mL) was added. The mixture was stirred at room temperature for 24 h before concentrating *in vacuo*. The residue was purified by flash chromatography on silica gel (10–20% dichloromethane in hexanes) to give **14a** (476 mg, 0.95 mmol, 71%) as a pale yellow oil. **R_f:** 0.18 (25% dichloromethane in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.83 (1 H, dd, *J* = 7.8, 1.1 Hz, Ar–H), 7.70 (1 H, dd, *J* = 8.0, 1.6 Hz, Ar–H), 7.64 (1 H, dd, *J* = 7.8, 1.7 Hz, Ar–H), 7.39–7.30 (2 H, m, Ar–H), 7.05 (1 H, t, *J* = 7.8 Hz, Ar–H), 6.93 (1 H, ddd, *J* = 7.9, 6.7, 2.3 Hz, Ar–H), 6.14 (1 H, ddt, *J* = 17.2, 10.4, 5.9 Hz, CH=CH_2), 5.43 (1 H, dq, *J* = 17.2, 1.6 Hz, CH=CHH), 5.28 (1 H, dq, *J* = 10.4, 1.3 Hz, CH=CHH), 4.57 (2 H, dt, *J* = 5.9, 1.3 Hz, OCH_2), 3.31–3.27 (2 H, m, SCH_2), 3.12–3.08 (2 H, m, SCH_2CH_2); **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 190.8 (C), 153.8 (C), 142.7 (C), 139.8 (CH), 137.1 (CH), 134.4 (C), 133.1 (CH), 130.2 (CH), 128.59 (2 × CH), 128.56 (CH), 125.3 (CH), 119.2 (C), 118.9 (CH_2), 100.5 (C), 76.0 (CH_2), 40.4 (CH_2), 29.8 (CH_2); **ν_{max}/cm^{-1}** 3064, 2927, 1677, 1640, 1437, 1417, 1229, 1179, 1134, 1010; **LRMS (ESI$^+$)** *m*/*z* 525 ([M + Na]$^+$, 100), 527 ([M + Na]$^+$, 82); **HRMS (ESI$^+$)** calculated for $[C_{18}H_{16}O_2SIBrNa]$ 524.89913 and 526.89704, found 524.89920 and 526.89719.

S*-(2-Iodophenethyl) 2-(allyloxy)-3-chlorobenzothioate (15a).** To a solution of 2-(allyloxy)-3-chlorobenzoic acid (394 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 5 min before a solution of compound **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (3 mL) was added. The mixture was stirred at room temperature for 14 h before concentrating *in vacuo*. The residue was purified by flash chromatography on silica gel (10–15% dichloromethane in hexanes) to give **15a** (516 mg, 1.12 mmol, 85%) as a yellow oil. **R_f:** 0.33 (20% dichloromethane in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.83 (1 H, dd, *J* = 7.8, 1.2 Hz, Ar–H), 7.61 (1 H, dd, *J* = 7.8, 1.7 Hz, Ar–H), 7.53 (1 H, dd, *J* = 7.9, 1.7 Hz, Ar–H), 7.34–7.30 (2 H, m, Ar–H), 7.11 (1 H, t, *J* = 7.9 Hz, Ar–H), 6.93 (1 H, ddd, *J* = 8.0, 6.8, 2.2 Hz, Ar–H), 6.13 (1 H, ddt, *J* = 17.2, 10.3, 5.9 Hz, CH=CH_2), 5.43 (1 H, dq, *J* = 17.2, 1.5 Hz, CH=CHH), 5.28 (1 H, dq, *J* = 10.3, 1.3 Hz, CH=CHH), 4.59 (2 H, dt, *J* = 5.9, 1.3 Hz, OCH_2), 3.32–3.28 (2 H, m, SCH_2), 3.12–3.08 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.7 (C), 152.8 (C), 142.7 (C), 139.7 (CH), 134.3 (C), 134.0 (CH), 133.1 (CH), 130.2 (CH), 129.6 (C), 128.6 (2 × CH), 127.7 (CH), 124.7 (CH), 118.8 (CH_2), 100.5 (C), 75.8 (CH_2), 40.3 (CH_2), 29.8 (CH_2); **ν_{max}/cm^{-1}** 3065, 2928, 1665, 1641, 1440, 1227, 1180, 1145, 978, 939, 748, 733; **LRMS (ESI$^+$)** ***m*/*z 483 ([M + Na]$^+$, 36), 481 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for $[C_{18}H_{16}O_2SI^{35}ClNa]$ 480.94964, found 480.95016; calculated for $[C_{18}H_{16}O_2SI^{37}ClNa]$ 482.94666, found 482.94720.

S*-(2-Iodophenethyl) 2-(allyloxy)-3-fluorobenzothioate (16a).** To a solution of 2-(allyloxy)-3-fluorobenzoic acid (364 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 5 min before a solution of compound **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (3 mL) was added. The mixture was stirred at room temperature for 18 h before concentrating *in vacuo*. The residue was purified by flash chromatography on silica gel (10–25% dichloromethane in hexanes) to give **16a** (453 mg, 1.02 mmol, 77%) as a colourless oil. **R_f:** 0.27 (20% dichloromethane in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 7.83 (1 H, dd, *J* = 7.9, 1.2 Hz, Ar–H), 7.50 (1 H, dd, *J* = 7.9, 1.4 Hz, Ar–H), 7.35–7.29 (2 H, m, 2 × Ar–H), 7.23 (1 H, ddd, *J* = 11.1, 8.2, 1.6 Hz, Ar–H), 7.08 (1 H, td, *J* = 8.0, 4.7 Hz, Ar–H), 6.94–6.91 (1 H, m, Ar–H), 6.13–6.07 (1 H, m, CH=CH_2), 5.39 (1 H, dq, *J* = 17.2, 1.5 Hz, CH=CHH), 5.26 (1 H, dq, *J* = 10.4, 1.2 Hz, CH=CHH), 4.69–4.67 (2 H, m, OCH_2), 3.30–3.27 (2 H, m, SCH_2), 3.12–3.08 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.3 (1 C, d, *J* = 3.3 Hz, C), 156.0 (1 C, d, *J* = 248.9 Hz, C), 144.9 (1 C, d, *J* = 12.4 Hz, C), 142.8 (C), 139.7 (CH), 133.6 (1 C, d, *J* = 1.8 Hz, C), 133.2 (CH), 130.2 (CH), 128.6 (CH), 128.5 (CH), 124.4 (1 C, d, *J* = 1.4 Hz, CH), 123.7 (1 C, d, *J* = 7.7 Hz, CH), 120.4 (1 C, d, *J* = 19.7 Hz, CH), 119.1 (CH_2), 100.5 (C), 75.7 (1 C, d, *J* = 5.8 Hz, CH), 40.4 (CH_2), 29.7 (CH_2); **^{19}F NMR (376 MHz, $CDCl_3$) δ:** −127.80; **ν_{max}/cm^{-1}** 2928, 1676, 1639, 1468, 1264, 1227, 1009; **LRMS (ESI$^+$)** ***m*/*z 465 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for $[C_{18}H_{16}O_2FSNa]$ 464.97919, found 464.97946.

S*-(2-Iodophenethyl) 2-(allyloxy)-5-nitrobenzothioate (17a).** To a solution of 2-(allyloxy)-5-nitrobenzoic acid (414 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 10 min before a solution of compound **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature for 14 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (30–40% diethyl ether in hexanes and 40–50% dichloromethane in hexanes) to give **17a** (365 mg, 0.78 mmol, 59%) as a brown solid. **R_f:** 0.21 (50% dichloromethane in hexanes); **m.p.** 81–83 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 8.65 (1 H, d, *J* = 2.8 Hz, Ar–H), 8.33 (1 H, dd, *J* = 9.2, 2.9 Hz, Ar–H), 7.84 (1 H, dd, *J* = 8.0, 1.0 Hz, Ar–H), 7.35–7.29 (2 H, m, 2 × Ar–H), 7.05 (1 H, d, *J* = 9.2 Hz, Ar–H), 6.94 (1 H, ddd, *J* = 7.9, 6.8, 2.2 Hz, Ar–H), 6.08 (1 H, ddt, *J* = 17.3, 10.6, 5.2 Hz, CH=CHH), 5.50 (1 H, dq, *J* = 17.3, 1.6 Hz, CH=CHH), 5.38 (1 H, dq, *J* = 10.6, 1.3 Hz, CH=CHH), 4.78 (1 H, dt, *J* = 5.1, 1.5 Hz, OCH_2), 3.33–3.29 (2 H, m, SCH_2), 3.13–3.09 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 189.2 (C), 161.2 (C), 142.6 (C), 141.2 (C), 139.8 (CH), 131.3 (CH), 130.2 (CH), 128.7 (CH), 128.64 (CH), 128.63 (CH), 127.8 (C), 125.9 (CH), 119.3 (CH_2), 113.3 (CH), 100.5 (C), 70.5 (CH_2), 40.3 (CH_2), 29.9 (CH_2); **ν_{max}/cm^{-1}** 3084, 1637, 1608, 1563, 1342, 1276, 1086; **LRMS (ESI$^+$)** ***m*/*z 492 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for $[C_{18}H_{16}NO_4SINa]$ 491.97369, found 491.97428.

***S*-(2-Iodophenethyl) 2-(allylamino)benzothioate (18a).** To a solution of 2-(allylamino) benzoic acid (329 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 10 min before a solution of compound **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature for 20 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (0–5% diethyl ether in

hexanes) to give **18a** (390 mg, 0.92 mmol, 69%) as a yellow oil. R_f: 0.5 (5% diethyl ether in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 8.15 (1 H, brs, NH), 7.95 (1 H, dd, J = 8.1, 1.6 Hz, Ar–H), 7.84 (1 H, dd, J = 7.9, 1.3 Hz, Ar–H), 7.37–7.29 (3 H, m, 3 × Ar–H), 6.93 (1 H, ddd, J = 7.8, 7.3, 1.9 Hz, Ar–H), 6.69 (1 H, dd, J = 8.6, 0.8 Hz, Ar–H), 6.62 (1 H, ddd, J = 8.1, 7.0, 1.1 Hz, Ar–H), 5.96 (1 H, ddt, J = 17.2, 10.3, 5.1 Hz, CH=CHH), 5.31 (1 H, dq, J = 17.2, 1.7 Hz, CH=CHH), 5.21 (1 H, dq, J = 10.3, 1.6 Hz, CH=CHH), 3.89 (2 H, tt, J = 5.4, 1.8 Hz, NCH_2), 3.27–3.24 (2 H, m, SCH_2), 3.10–3.07 (2 H, m, SCH_2CH_2); **^{13}C NMR (126 MHz, $CDCl_3$) δ:** 193.1 (C), 149.0 (C), 143.0 (C), 139.7 (CH), 135.0 (CH), 134.4 (CH), 130.9 (CH), 130.2 (CH), 128.54 (CH), 128.46 (CH), 118.0 (C), 116.4 (CH_2), 115.0 (CH), 112.1 (CH), 100.6 (C), 45.3 (CH_2), 40.9 (CH_2), 29.0 (CH_2); **ν_{max}/cm^{-1}** 3476, 3359, 3059, 2925, 1694, 1630, 1582, 1516, 1447, 1197, 1162, 1011; **LRMS (ESI$^+$) m/z** 522 (42), 424 ([M + H]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{18}H_{18}INOSNa$] 446.00460, found 446.00472.

3-Methyl-2,3-dihydroquinolin-4(1*H*)-one (18b). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of compound **18a** (68 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.39 mL, 1.6 mmol), formic acid (60 μL, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (465 nm) for 18 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5–10–20% ethyl acetate in hexanes) to give **18b** (17.5 mg, 0.109 mmol, 68%) as a yellow solid. R_f: 0.16 (30% diethyl ether in hexanes); **m.p.** 88–89 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.86 (1 H, dd, J = 7.9, 1.6 Hz, Ar–H), 7.28 (1 H, ddd, J = 8.3, 6.9, 1.5 Hz, Ar–H), 6.73 (1 H, ddd, J = 8.1, 7.1, 1.1 Hz, Ar–H), 6.65 (1 H, dd, J = 8.3, 1.3 Hz, Ar–H), 4.44 (1 H, brs, NH), 3.55 (1 H, dd, J = 11.7, 5.3 Hz, NHCHH), 3.27 (1 H, t, J = 11.6 Hz, NHCHH), 2.74–2.64 (1 H, m, $CHCH_3$), 1.22 (3 H, d, J = 6.9 Hz, CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 196.6 (C), 151.8 (C), 134.9 (CH), 128.0 (CH), 118.9 (C), 118.0 (CH), 115.7 (CH), 48.9 (CH_2), 41.2 (CH), 12.7 (CH_3); **ν_{max}/cm^{-1}** 3348, 2964, 2930, 2872, 2815, 1656, 1611, 1512, 1365, 1343, 1237, 1155; **LRMS (ESI$^+$) m/z** 393 (84), 345 (100), 184 ([M + Na]$^+$, 71); **HRMS (ESI$^+$)** calculated for [$C_{10}H_{11}NONa$] 184.07329, found 184.07325.

Ethyl (*E*)-4-(2-(((2-iodophenethyl)thio)carbonyl)phenoxy)but-2-enoate (19a). To a solution of (*E*)-2-((4-ethoxy-4-oxobut-2-en-1-yl)oxy)benzoic acid (464 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 5 min before a solution of compound **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (3 mL) was added. The mixture was stirred at room temperature for 16 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (30–35% diethyl ether in hexanes) to give **19a** (559 mg, 1.13 mmol, 85%) as a yellow oil. R_f: 0.38 (50% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.83 (1 H, dd, J = 7.9, 1.3 Hz, Ar–H), 7.77 (1 H, dd, J = 7.8, 1.8 Hz, Ar–H), 7.43 (1 H, ddd, J = 8.4, 7.4, 1.8 Hz, Ar–H), 7.35 (1 H, dd, J = 7.6, 1.8 Hz, Ar–H), 7.29 (1 H, td, J = 7.4, 1.3 Hz, Ar–H), 7.09 (1 H, dt, J = 15.7, 4.0 Hz, CH_2CH=CH), 7.03 (1 H, td, J = 7.6, 1.0 Hz, Ar–H), 6.93–6.88 (2 H, m, 2 × Ar–H), 6.32 (1 H, dt, J = 15.7, 2.1 Hz, CH_2CH=CH), 4.80 (2 H, dd, J = 4.0, 2.1 Hz, $ArOCH_2$), 4.21 (2 H, q, J = 7.1 Hz, CO_2CH_2), 3.30–3.25 (2 H, m, SCH_2), 3.13–3.07 (2 H, m, SCH_2CH_2), 1.28 (3 H, t, J = 7.1 Hz, CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.7 (C), 166.1 (C), 156.1 (C), 142.9 (C), 141.6 (CH), 139.6 (CH), 133.6 (CH), 130.2 (CH), 129.9 (CH), 128.5 (CH), 128.4 (CH), 127.8 (C), 122.7 (CH), 121.3 (CH), 113.3 (CH), 100.5 (C), 67.6 (CH_2), 60.7 (CH_2), 40.5 (CH_2), 29.6 (CH_2), 14.3 (CH_3); **ν_{max}/cm^{-1}** 2980, 2935, 1718, 1669, 1637, 1596, 1484, 1443, 1288, 1180, 1039; **LRMS (ESI$^+$) m/z** 514 (100), 497 ([M + H]$^+$, 40); **HRMS (ESI$^+$)** calculated for [$C_{21}H_{21}O_4ISNa$] 519.00974, found 519.00972.

Ethyl 2-(4-oxochromn-3-yl)acetate (19b).[53] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of compound **19a** (81 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.4 mL, 1.6 mmol), formic acid (60 μL, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.4 μmol). The mixture was degassed for 30 min before irradiating with blue light (465 nm) for 1 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5–10% ethyl acetate in hexanes) to give **19b** (19 mg, 0.082 mmol, 51%) as a yellow oil. R_f: 0.26 (20% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.89 (1 H, dd, J = 7.9, 1.8 Hz, Ar–H), 7.50–7.45 (1 H, m, Ar–H), 7.04–7.00 (1 H, m, Ar–H), 6.97 (1 H, dd, J = 8.4, 1.2 Hz, Ar–H), 4.60 (1 H, dd, J = 11.2, 5.3 Hz, ArOCHH), 4.30 (1 H, dd, 11.9, 11.2 Hz, ArOCHH), 4.19 (2 H, qd, J = 7.2, 2.0 Hz, CO_2CH_2), 3.33 (1 H, dddd, J = 11.9, 8.3, 5.1, 5.1 Hz, ArCOCH), 2.93 (1 H, dd, J = 16.9, 4.8 Hz, $CHHCO_2Et$), 2.41 (1 H, dd, J = 16.9, 8.2 Hz, $CHHCO_2Et$), 1.28 (3 H, t, J = 7.2 Hz, CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 192.7 (C), 171.5 (C), 161.9 (C), 136.1 (CH), 127.5 (CH), 121.7 (CH), 120.7 (C), 118.0 (CH), 70.4 (CH_2), 61.1 (CH_2), 42.7 (CH), 30.5 (CH_2), 14.3 (CH_3); **ν_{max}/cm^{-1}** 2980, 2927, 1730, 1688, 1605, 1479, 1298, 1213, 1175, 1128, 1035, 1012; **LRMS (ESI$^+$) m/z** 682 (29), 491 (24), 420 (100), 403 (43), 257 (49), 234 (M$^+$, 33).

***S*-(2-Iodophenethyl) 2-(cyclohex-2-en-1-yloxy)benzothioate (20a).** To a solution of 2-(cyclohex-2-en-1-yloxy)benzoic acid (335 mg, 1.53 mmol) in CH_2Cl_2 (8 mL) at 0 °C was added DCC (316 mg, 1.53 mmol) and DMAP (21 mg, 0.17 mmol). The mixture was stirred for 5 min before a solution of compound **6** (300 mg, 1.14 mmol) in CH_2Cl_2 (3 mL) was added. The mixture was stirred at room temperature for 16 h before concentrating *in vacuo*. The residue was purified by flash chromatography on silica gel (2.5–5% diethyl ether in hexanes) to give **20a** (426 mg, 0.917 mmol, 81%) as an off white solid. R_f: 0.37 (20% diethyl ether in hexanes); **m.p.** 65–68 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.83–7.80 (2 H, m, 2 × Ar–H), 7.43 (1 H, ddd, J = 8.4,

7.3, 1.8 Hz, Ar–H), 7.35 (1 H, dd, *J* = 7.6, 1.8 Hz, Ar–H), 7.29 (1 H, td, *J* = 7.4, 1.3 Hz, Ar–H), 7.02 (1 H, d, *J* = 9.0 Hz, Ar–H), 7.00–6.96 (1 H, m, Ar–H), 6.93–6.89 (1 H, m, Ar–H), 6.00–5.91 (2 H, m, CH=CH), 4.94–4.88 (1 H, m, OCH), 3.26–3.22 (2 H, m, SCH_2), 3.10–3.06 (2 H, m, SCH_2CH_2), 2.22–2.11 (1 H, m, OCHCHH), 2.06–1.95 (4 H, m, OCHCHHCH$_2$CHH), 1.68–1.65 (1 H, m, OCHCHHCH$_2$CHH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.9 (C), 156.8 (C), 143.2 (C), 139.6 (CH), 133.5 (CH), 132.6 (CH), 130.2 (CH), 130.0 (CH), 128.4 (CH), 128.3 (CH), 128.0 (C), 125.8 (CH), 120.4 (CH), 114.5 (CH), 100.5 (C), 72.7 (CH), 40.5 (CH_2), 29.6 (CH_2), 28.5 (CH_2), 25.2 (CH_2), 19.2 (CH_2); **ν_{max}/cm^{-1}** 3029, 2932, 2865, 1676, 1631, 1593, 1478, 1447, 1282, 1239, 1190, 1009; **LRMS (ESI$^+$) *m*/*z*** 619 (100), 487 ([M + Na]$^+$, 78), 321 (47); **HRMS (ESI$^+$)** calculated for $[C_{21}H_{21}O_2ISNa]$ 487.01991, found 487.02033.

1,2,3,4a,9a-Hexahydro-9*H*-xanthen-9-one (20b).[54] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of compound **20a** (76 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.39 mL, 1.6 mmol), formic acid (60 μL, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (465 nm) for 1 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5–10% ethyl acetate in hexanes) to give **20b** (15 mg, 0.074 mmol, 50%) as a colourless oil. **R_f:** 0.24 (10% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.88 (1 H, ddd, *J* = 7.8, 1.8, 0.5 Hz, Ar–H), 7.47 (1 H, ddd, *J* = 8.3, 7.2, 1.8 Hz, Ar–H), 7.01–6.96 (2 H, m, 2 × Ar–H), 4.60–4.57 (1 H, m, OCH), 2.57–2.53 (1 H, m, COCH), 2.13–2.09 (1 H, m, CH), 1.79–1.58 (6 H, m, 6 × CH), 1.47–1.37 (1 H, m, CH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 195.9 (C), 161.4 (C), 136.0 (CH), 127.5 (CH), 121.2 (CH), 119.8 (C), 118.0 (CH), 76.3 (CH), 48.1 (CH), 29.5 (CH_2), 24.13 (CH_2), 24.06 (CH_2), 20.6 (CH_2); **ν_{max}/cm^{-1}** 2934, 2860, 1685, 1605, 1461, 1306, 1229, 1150, 1121; **LRMS (APCI) *m*/*z*** 389 (30), 203 ([M + H]$^+$, 100).

S*-(2-Iodophenethyl) 2-(prop-2-yn-1-yloxy)benzothioate (21a).** To a solution of 2-(prop-2-yn-1-yloxy)benzoic acid (327 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 10 min before a solution of compound **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature for 24 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5–10% diethyl ether in hexanes) to give **21a** (462 mg, 1.09 mmol, 82%) as a colourless oil. **R_f:** 0.38 (20% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.83 (1 H, dd, *J* = 7.8, 1.2 Hz, Ar–H), 7.79 (1 H, dd, *J* = 7.8, 1.8 Hz, Ar–H), 7.48 (1 H, ddd, *J* = 8.4, 7.3, 1.8 Hz, Ar–H), 7.36 (1 H, dd, *J* = 7.6, 1.9 Hz, Ar–H), 7.30 (1 H, td, *J* = 7.4, 1.3 Hz, Ar–H), 7.15 (1 H, dd, *J* = 8.4, 0.9 Hz, Ar–H), 7.06 (1 H, td, *J* = 7.6, 0.9 Hz, Ar–H), 6.94–6.90 (1 H, m, Ar–H), 4.82 (2 H, d, *J* = 2.4 Hz, OCH_2), 3.29–3.25 (2 H, m, SCH_2), 3.12–3.08 (2 H, m, SCH_2CH_2), 2.55 (1 H, t, *J* = 2.4 Hz, CH_2CCH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.8 (C), 155.8 (C), 143.0 (C), 139.7 (CH), 133.5 (CH), 130.3 (CH), 130.0 (CH), 128.6 (CH), 128.5 (CH), 128.1 (C), 121.6 (CH), 114.2 (CH), 100.5 (C), 78.1 (C), 76.4 (CH), 56.8 (CH_2), 40.5 (CH_2), 29.7 (CH_2); **ν_{max}/cm^{-1}** 3291, 3059, 2923, 1669, 1634, 1596, 1482, 1447, 1286, 1260, 1011; **LRMS (ESI$^+$) *m*/*z 445 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for $[C_{18}H_{15}O_2SINa]$ 444.97296, found 444.97346.

S*-(2-Iodophenethyl) 2-(cinnamyloxy)benzothioate (22a).** To a solution of 2-(cinnamyloxy)benzoic acid (332 mg, 1.30 mmol) in CH_2Cl_2 (8 mL) at 0 °C was added DCC (269 mg, 1.30 mmol) and DMAP (18 mg, 0.15 mmol). The mixture was stirred for 5 min before a solution of compound **6** (265 mg, 1.00 mmol) in CH_2Cl_2 (2 mL) was added. The mixture was stirred at room temperature for 16 h before concentrating *in vacuo*. The residue was purified by flash chromatography on silica gel (5–10% diethyl ether in hexanes) to give **22a** (407 mg, 0.813 mmol, 81%) as a pale yellow oil. **R_f:** 0.34 (20% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.83–7.80 (2 H, m, 2 × Ar–H), 7.46 (1 H, ddd, *J* = 8.4, 7.4, 1.8 Hz, Ar–H), 7.44–7.41 (2 H, m, 2 × Ar–H), 7.36–7.28 (3 H, m, 3 × Ar–H), 7.28–7.24 (2 H, m, 2 × Ar–H), 7.05–7.00 (2 H, m, 2 × Ar–H), 6.90 (1 H, ddd, *J* = 7.8, 7.4, 1.8 Hz, Ar–H), 6.80 (1 H, dt, *J* = 16.0, 1.6 Hz, CHPh), 6.45 (1 H, dt, *J* = 16.0, 5.7 Hz, CH=CHPh), 4.85 (2 H, dd, *J* = 5.6, 1.6 Hz, OCH_2), 3.30–3.26 (2 H, m, SCH_2), 3.12–3.08 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.9 (C), 157.1 (C), 143.1 (C), 139.6 (CH), 136.5 (C), 133.6 (CH), 133.3 (CH), 130.2 (CH), 129.9 (CH), 128.7 (2 × CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 127.6 (C), 126.8 (2 × CH), 124.0 (CH), 120.9 (CH), 113.8 (CH), 100.6 (C), 69.9 (CH_2), 40.5 (CH_2), 29.7 (CH_2); **ν_{max}/cm^{-1}** 3057, 3025, 2924, 2863, 1671, 1633, 1594, 1482, 1446, 1285, 1241, 1193, 1162, 1111; **LRMS (ESI$^+$) *m*/*z 523 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for $[C_{24}H_{21}O_2ISNa]$ 523.01991, found 523.02024.

Diethyl 2-(((2-(((2-iodophenethyl)thio)carbonyl)phenyl)amino)methylene)-malonate (23a). To a solution of 2-((3-ethoxy-2-(ethoxycarbonyl)-3-oxoprop-1-en-1-yl)amino)benzoic acid (570 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DMAP (24 mg, 0.20 mmol) and DCC (383 mg, 1.86 mmol). The mixture was stirred for 10 min before a solution of compound **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature for 15 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (10–30% ethyl acetate in hexanes) to give **23a** (520 mg, 0.94 mmol, 71%) as a yellow solid. **R_f:** 0.5 (30% ethyl acetate in hexanes); **m.p.** 76–78 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 12.41 (1 H, d, 13.5 Hz, NH), 8.55 (1 H, d, *J* = 13.5 Hz, C=CH), 8.07 (1 H, dd, *J* = 8.0, 1.4 Hz, Ar–H), 7.83 (1 H, dd, *J* = 7.8, 1.0 Hz, Ar–H), 7.60–7.55 (1 H, m, Ar–H), 7.40 (1 H, d, *J* = 8.1 Hz, Ar–H), 7.34–7.28 (2 H, m, Ar–H), 7.16 (1 H, ddd, *J* = 7.3, 7.1, 0.9 Hz, Ar–H), 6.93 (1 H, ddd, *J* = 7.8, 6.7, 2.3 Hz, Ar–H), 4.43 (2 H, q, *J* = 7.1 Hz, CH_2CH_3), 4.27 (2 H, q, *J* = 7.1 Hz, CH_2CH_3), 3.40–3.36 (2 H, m, SCH_2), 3.14–3.10 (2 H, m, CH_2Ar), 1.41 (3 H, t, *J* = 7.1 Hz, CH_3), 1.34 (3 H, t, *J* = 7.1 Hz, CH_3);

^{13}C NMR (101 MHz, $CDCl_3$) δ: 193.4 (C), 167.0 (C), 166.2 (C), 149.7 (CH), 142.6 (C), 139.8 (CH), 139.3 (C), 134.7 (CH), 130.7 (CH), 130.2 (CH), 128.62 (CH), 128.56 (CH), 124.5 (C), 123.5 (CH), 115.9 (CH), 100.6 (C), 97.3 (C), 60.7 (CH_2), 60.5 (CH_2), 40.3 (CH_2), 29.6 (CH_2), 14.62 (CH_3), 14.56 (CH_3); ν_{max}/cm^{-1} 2978, 2928, 1716, 1693, 1656, 1610, 1589, 1225, 1191, 1170; **LRMS (ESI$^+$)** *m*/*z* 576 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{23}H_{24}NO_5SINa$] 576.03121, found 576.03198.

Ethyl (*E*)-3-(2-(((2-iodophenethyl)thio)carbonyl)phenoxy) acrylate (24a). To a solution of *S*-(2-iodophenethyl) 2-hydroxybenzothioate (350 mg, 0.91 mmol) in MeCN (4.5 mL) was added ethyl propiolate (0.12 mL, 1.1 mmol) and *N*-methylmorpholine (20 mL, 0.2 μmol). The mixture was stirred at room temperature for 18 h. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The organic extracts were washed with aqueous HCl (30 mL, 1 M solution), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5–15% diethyl ether in hexanes) to give **24a** (413 mg, 0.86 mmol, 94%) as a white solid. **R_f:** 0.16 (10% diethyl ether in hexanes); **m.p.** 70–71 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.84 (1 H, dd, *J* = 7.8, 1.7 Hz, Ar–H), 7.83 (1 H, dd, *J* = 7.8, 1.3 Hz, Ar–H), 7.74 (1 H, d, *J* = 12.3 Hz, OCH=CH), 7.55 (1 H, ddd, *J* = 8.2, 7.5, 1.7 Hz, Ar–H), 7.33–7.28 (3 H, m, 3 × Ar–H), 7.14 (1 H, dd, *J* = 8.2, 0.9 Hz, Ar–H), 6.93 (1 H, ddd, *J* = 7.9, 6.7, 2.3 Hz, Ar–H), 5.57 (1 H, d, *J* = 12.2 Hz, OCH=CH), 4.20 (2 H, q, *J* = 7.1 Hz, OCH_2), 3.30–3.26 (2 H, m, SCH_2), 3.11–3.07 (2 H, m, SCH_2CH_2), 1.28 (3 H, t, *J* = 7.1 Hz, CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 189.8 (C), 166.9 (C), 158.9 (CH), 153.2 (C), 142.6 (C), 139.7 (CH), 133.8 (CH), 130.2 (CH), 130.0 (CH), 129.5 (C), 128.6 (2 × CH), 125.4 (CH), 119.8 (CH), 103.4 (CH), 100.5 (C), 60.3 (CH_2), 40.3 (CH_2), 29.7 (CH_2), 14.4 (CH_3); ν_{max}/cm^{-1} 3056, 2978, 1712, 1646, 1479, 1446, 1225, 1199, 1123, 1046; **LRMS (ESI$^+$)** *m*/*z* 505 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{20}H_{19}IO_4SNa$] 504.99409, found 504.99422.

***S*-(2-Iodophenethyl) 1-allyl-1*H*-indole-2-carbothioate (25a).** To a solution of 1-allyl-1*H*-indole-2-carboxylic acid (373 mg, 1.86 mmol) in CH_2Cl_2 (8 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 5 min before a solution of **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature for 24 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (10–20% dichloromethane in hexanes) to give **25a** (470 mg, 1.1 mmol, 79%) as a white solid. **R_f:** 0.29 (25% dichloromethane in hexanes); **m.p.** 80–81 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.85 (1 H, dd, *J* = 7.9, 1.2 Hz, Ar–H), 7.70 (1 H, dt, *J* = 8.1, 1.1 Hz, Ar–H), 7.46 (1 H, s, Ar–H), 7.37–7.31 (4 H, m, Ar–H), 7.20–7.16 (1 H, m, Ar–H), 6.93 (1 H, ddd, 8.0, 7.0, 2.1 Hz, Ar–H), 6.00 (1 H, ddt, *J* = 17.1, 10.3, 5.0 Hz, CH=CH_2), 5.17 (2 H, dt, *J* = 5.0, 1.7 Hz, NCH_2), 5.12 (1 H, dq, *J* = 10.3, 1.5 Hz, CH=CHH), 4.92 (1 H, dq, *J* = 17.1, 1.6 Hz, CH=CHH), 3.33–3.29 (2 H, m, SCH_2), 3.13–3.10 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 184.4 (C), 142.8 (C), 139.7 (CH), 139.5 (C), 133.83 (C), 133.77 (CH), 130.3 (CH), 128.5 (2 × CH), 126.2 (C), 126.0 (CH) 123.0 (CH), 121.2 (CH), 116.4 (CH_2), 110.9 (CH), 110.8 (CH), 100.6 (C), 47.2 (CH_2), 40.8 (CH_2), 28.9 (CH_2); ν_{max}/cm^{-1} 3058, 2926, 1640, 1510, 1454, 1154, 1131, 1010; **HRMS (ESI$^+$)** calculated for [$C_{20}H_{18}NOISNa$] 470.00460, found 470.00477.

2-Methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-one (25b).[7,55] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of compound **25a** (73 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.39 mL, 1.6 mmol), formic acid (60 μL, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (465 nm) for 1 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5–10% ethyl acetate in hexanes) to give **25b** (15 mg, 0.082 mmol, 50%) as a white solid. **R_f:** 0.33 (40% diethyl ether in hexanes); **m.p.** 114–115 °C (lit. 100–102 °C,[55] 108–110 °C);[7] **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.77 (1 H, ddd, *J* = 8.2 Hz, 1.0, 1.0 Hz, Ar–H), 7.42 (1 H, dddd, *J* = 8.4, 1.0, 1.0, 1.0 Hz, Ar–H), 7.36 (1 H, ddd, *J* = 8.4, 6.8, 1.1 Hz, Ar–H), 7.19 (1 H, ddd, *J* = 8.2, 6.8, 1.2 Hz, Ar–H), 7.02 (1 H, d, *J* = 0.9 Hz, Ar–H), 4.68 (1 H, dd, *J* = 10.8, 8.0 Hz, NCHH), 3.98 (1 H, dd, *J* = 10.8, 4.8 Hz, NCHH), 3.32–3.27 (1 H, m, NCH_2CH), 1.46 (3 H, d, *J* = 7.5 Hz, CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 196.2 (C), 135.3 (C), 135.2 (C), 132.3 (C), 125.2 (CH), 124.3 (CH), 121.6 (CH), 110.6 (CH), 99.4 (CH), 48.0 (CH_2), 45.6 (CH), 15.7 (CH_3); ν_{max}/cm^{-1} 3077, 2972, 2882, 1711, 1539, 1348, 1232, 1166; **LRMS (ESI$^+$)** *m*/*z* 238 (77), 234 (30), 214 (32), 200 (40), 186 ([M + H]$^+$, 100).

***S*-(2-Iodophenethyl) 2-(4-cyclopropylbut-3-en-1-yl)-4,5-dimethoxy benzothioate (26a).** To a solution of 2-(4-cyclopropylbut-3-en-1-yl)-4,5-dimethoxybenzoic acid (499 mg, 1.81 mmol) in CH_2Cl_2 (12 mL) at 0 °C was added DCC (389 mg, 1.89 mmol) and DMAP (29 mg, 0.24 mmol). The mixture was stirred for 5 min before a solution of compound **6** (415 mg, 1.57 mmol) in CH_2Cl_2 (4 mL) was added. The mixture was stirred at room temperature for 6 h before concentrating *in vacuo*. The residue was purified by flash chromatography on silica gel (10–20% diethyl ether in hexanes) to give a 2.7 : 1 diasteteromeric mixture of **26a** (670 mg, 1.28 mmol, 82%) as a colourless oil. **R_f:** 0.19 (10% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.84–7.82 (1 H + 0.6 × 1 H, m, Ar–H), 7.35–7.28 (3 H + 0.6 × 3 H, m, 3 × Ar–H), 6.94–6.90 (1 H + 0.6 × 1 H, m, Ar–H), 6.75 (1 H, s, Ar–H), 6.70 (0.6 × 1 H, s, Ar–H), 5.54 (0.6 × 1 H, dt, *J* = 15.0, 7.0 Hz, CH_2CH=CH), 5.35 (1 H, dtd, 10.7, 7.4, 0.8 Hz, CH_2CH=CH), 4.99 (0.6 × 1 H, ddt, *J* = 15.2, 8.5, 1.3 Hz, CH_2CH=CH), 4.78–4.73 (1 H, m, CH_2CH=CH), 3.92 (3 H, s, $ArOCH_3$), 3.91 (0.6 × 3 H, s, $ArOCH_3$), 3.91 (3 H, s, $ArOCH_3$), 3.91 (0.6 × 3 H, s, $ArOCH_3$), 3.29–3.25 (2 H + 0.6 × 2 H, m, SCH_2), 3.11–3.07 (2 H + 0.6 × 2 H, m, SCH_2CH_2), 2.93–2.89 (2 H, m, $ArCH_2$), 2.87–2.83 (0.6 × 2 H, m, $ArCH_2$), 2.48–2.46 (2 H, m, CH_2CH=CH), 2.27–2.25 (0.6 × 2 H, m, CH_2CH=CH), 1.56–1.47 (1 H, m, CH=CHCH), 1.38–1.29 (1 H, m, CH=CHCH), 0.68–0.63 (2 H + 0.6 × 2 H, m, 2 × $CH(CHH)_2$), 0.31–0.26 (2 H + 0.6 × 2 H, m, 2 × $CH(CHH)_2$);

^{13}C NMR (101 MHz, $CDCl_3$) δ: 192.39 (C), 192.35 (C), 151.64 (C), 151.60 (C), 146.63 (C), 146.59 (C), 142.84 (C), 142.83 (C), 139.7 (CH + CH), 135.49 (C), 135.46 (C), 134.9 (CH), 134.6 (CH), 130.18 (CH), 130.17 (CH), 129.4 (C), 129.3 (C), 128.51 (CH + CH), 128.49 (CH + CH), 127.3 (CH), 127.1 (CH), 113.74 (CH), 113.69 (CH), 112.14 (CH), 112.08 (CH), 100.63 (C), 100.60 (C), 56.24 (CH_3), 56.22 (CH_3), 56.08 (CH_3), 56.06 (CH_3), 40.70 (CH_2), 40.67 (CH_2), 34.6 (CH_2), 33.8 (CH_2), 33.7 (CH_2), 29.8 (CH_2), 29.7 (CH_2 + CH_2), 13.6 (CH), 9.7 (CH), 7.0 (2 × CH_2), 6.5 (2 × CH_2); **ν_{max}/cm^{-1}** 3001, 2934, 1661, 1516, 1464, 1265, 1193, 1111; **LRMS (ESI$^+$)** ***m*/*z*** 545 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for $[C_{24}H_{27}O_3SINa]$ 545.06178, found 545.06249.

(*Z*)-2-(But-1-en-1-yl)-6,7-dimethoxy-3,4-dihydronaphthalen-1(2*H*)-one (26b). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **26a** (85 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (78 μL, 0.33 mmol), formic acid (11 μL, 0.33 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 10 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (30–50% diethyl ether in hexanes) to give **26b** (9.0 mg, 0.035 mmol, 21%) as a yellow solid. **R_f:** 0.16 (30% diethyl ether in hexanes); **m.p.** 57–59 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.52 (1 H, s, Ar–H), 6.66 (1 H, s, Ar–H), 5.65 (1 H, dtd, *J* = 10.8, 7.2, 1.0 Hz, CH=CHCH$_2$), 5.50 (1 H, ddt, *J* = 10.8, 8.8, 1.6 Hz, CH=CHCH$_2$), 3.93 (3 H, s, OCH$_3$), 3.91 (3 H, s, OCH$_3$), 3.44 (1 H, dddd, *J* = 10.9, 8.8, 4.6, 1.0 Hz, CHCH=CH), 3.04–2.92 (2 H, m, ArCH$_2$), 2.21–1.97 (4 H, m, CHCH$_2$ + CH$_2$CH$_3$), 1.03 (3 H, t, *J* = 7.5 Hz, CH$_2$CH$_3$); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 197.6 (C), 153.6 (C), 148.1 (C), 138.8 (C), 135.1 (CH), 126.1 (CH), 125.8 (C), 110.3 (CH), 109.1 (CH), 56.20 (CH_3), 56.16 (CH_3), 46.2 (CH), 30.8 (CH_2), 28.3 (CH_2), 21.3 (CH_2), 14.4 (CH_3); **ν_{max}/cm^{-1}** 2959, 2932, 2867, 1670, 1599, 1511, 1265, 1146; **LRMS (ESI$^+$)** ***m*/*z*** 543 (100), 283 ([M + Na]$^+$, 80); **HRMS (ESI$^+$)** calculated for $[C_{16}H_{20}O_3Na]$ 283.13047, found 283.13072.

S*-(2-Iodophenethyl) 3,7-dimethyloct-6-enethioate (27a).** To a solution of citronellic acid (316 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added DCC (383 mg, 1.86 mmol) and DMAP (24 mg, 0.20 mmol). The mixture was stirred for 10 min before a solution of compound **6** (350 mg, 1.33 mmol) in CH_2Cl_2 (7 mL) was added. The mixture was stirred at room temperature for 24 h. The white solid was removed by filtration and the filtrate concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (10–20% CH_2Cl_2 in hexanes) to give **27a** (400 mg, 0.96 mmol, 72%) as a colourless oil. **R_f:** 0.52 (30% dichloromethane in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.83–7.80 (1 H, m, Ar–H), 7.29–7.27 (2 H, m, Ar–H), 6.93–6.89 (1 H, m, Ar–H), 5.10–5.07 (1 H, m, C=CH), 3.14–3.10 (2 H, m, SCH$_2$), 3.01–2.97 (2 H, m, SCH$_2$CH$_2$), 2.56 (1 H, dd, *J* = 14.5, 5.9 Hz, CHHCO), 2.37 (1 H, dd, *J* = 14.5, 8.2 Hz, CHHCO), 2.07–1.95 (3 H, m, CH$_2$CH$_2$CH), 1.70 (3 H, d, *J* = 1.1 Hz, (H$_3$C)$_2$C), 1.60 (3 H, s, (H$_3$C)$_2$C), 1.39–1.32 (1 H, m, CH$_2$CHHCH), 1.27–1.20 (1 H, m, CH$_2$CHHCH), 0.94 (3 H, d, *J* = 6.7 Hz, H$_3$CCH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 199.0 (C), 142.8 (C), 139.7 (CH), 131.8 (C), 130.2 (CH), 128.53 (CH), 128.51 (CH), 124.3 (CH), 100.5 (C), 51.5 (CH_2), 40.8 (CH_2), 36.8 (CH_2), 30.9 (CH), 29.0 (CH_2), 25.9 (CH_3), 25.5 (CH_2), 19.6 (CH_3), 17.8 (CH_3); **ν_{max}/cm^{-1}** 2963, 2926, 1688, 1465, 1436, 1010; **LRMS (ESI$^+$)** ***m*/*z 471 (100), 455 (66), 439 ([M + Na]$^+$, 93); **HRMS (ESI$^+$)** calculated for $[C_{18}H_{25}OISNa]$ 439.05630, found 439.05665.

Menthone (27b).[4] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **27a** (68 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (78 μL, 0.32 mmol), formic acid (11 μL, 0.32 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 15 min before irradiating with blue light (465 nm) for 3 h. The mixture was concentrated *in vacuo* and the residue purified by flash chromatography on silica gel (0–5% diethyl ether in hexanes) to give **27b** (11 mg, 0.071 mmol, 44%) as a colourless oil. **R_f:** 0.32 and 0.44 (10% diethyl ether in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 2.35 (1 H, ddd, *J* = 13.0, 4.0, 2.2 Hz, CHHCO), 2.31–2.28 (1 H, m, CHHCO), 2.19–1.66 (13 H, m, 2 × CHHCO, 2 × CHCH$_2$CO, 2 × CH$_3$CHCHH, 2 × CH$_3$CHCH$_2$CHH, CH$_3$CHCH$_2$CHH, 2 × CHCO, 2 × (CH$_3$)$_2$CH), 1.51–1.32 (3 H, m, 2 × CH$_3$CHCHH, CH$_3$CHCH$_2$CHH), 1.00 (3 H, d, *J* = 6.4 Hz, CHCH$_3$), 0.98 (3 H, d, *J* = 6.7 Hz, CHCH$_3$), 0.93 (3 H, d, *J* = 6.6 Hz, H$_3$CCHCH$_3$), 0.91 (3 H, d, *J* = 6.9 Hz, H$_3$CCHCH$_3$), 0.85 (3 H, d, *J* = 6.8 Hz, H$_3$CCHCH$_3$), 0.84 (3 H, d, *J* = 6.6 Hz, H$_3$CCHCH$_3$); **^{13}C NMR (126 MHz, $CDCl_3$) δ:** 214.7 (C), 212.6 (C), 57.3 (CH), 56.1 (CH), 51.0 (CH_2), 48.2 (CH_2), 35.6 (CH), 34.5 (CH), 34.1 (CH_2), 29.6 (CH_2), 28.0 (CH_2), 27.1 (CH_2), 27.0 (CH), 26.0 (CH), 22.4 (CH_3), 21.6 (CH_3), 21.4 (CH_3), 21.0 (CH_3), 20.0 (CH_3), 18.8 (CH_3); **ν_{max}/cm^{-1}** 2955, 2926, 2871, 1708, 1456, 1368, 1203, 1116.

Alternative photo-induced cyclizations

4-Methoxybenzenediazonium tetrafluoroborate (29a).[56] To a solution of 4-methoxyaniline (1.00 g, 8.12 mmol) in H_2O (1.8 mL) and HBF_4 (4.1 mL, 35 wt% aqueous solution, 16 mmol) at 0 °C was added dropwise a solution of $NaNO_2$ (589 mg, 8.53 mmol) in H_2O (1.3 mL). The mixture was stirred for 30 min and the precipitate was collected by filtration. The solid was washed with diethyl ether (20 mL) and dried *in vacuo* to give **29a** (1.68 g, 7.57 mmol, 93%) as a purple solid. No purification was required. **^{1}H NMR (500 MHz, CD_3CN) δ:** 8.42–8.40 (2 H, m, 2 × Ar–H), 7.35–7.34 (2 H, m, 2 × Ar–H), 4.06 (3 H, s, OCH$_3$); **^{13}C NMR (126 MHz, CD_3CN) δ:** 171.2 (C), 136.7 (2 × CH), 118.8 (2 × CH), 102.5 (C), 58.4 (CH_3); **^{19}F NMR (471 MHz, CD_3CN) δ:** −151.7; **^{11}B NMR (160 MHz, CD_3CN) δ:** −1.15; **ν_{max}/cm^{-1}** 3120, 2252, 1583, 1569, 1291, 1051, 1002; **LRMS (ESI$^+$)** ***m*/*z*** 357 (100), 135 (M$^+$, 56).

4-Nitrobenzenediazonium tetrafluoroborate (29b).[56] To a solution of 4-nitroaniline (1.10 g, 8.0 mmol) in H_2O (5 mL) and HBF_4 (4.0 mL, 35 wt% aqueous solution, 16 mmol) at 0 °C was added dropwise a solution of $NaNO_2$ (577 mg, 8.36 mmol) in H_2O (1.3 mL). The mixture was stirred for 30 min and the

precipitate was collected by filtration. The solid was washed with diethyl ether (20 mL) and dried *in vacuo* to give **29b** (1.22 g, 5.15 mmol, 65%) as a yellow solid. No purification was required. **^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ:** 9.19–9.17 (2 H, m, 2 × Ar–H), 8.87–8.84 (2 H, m, 2 × Ar–H); **^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ:** 155.1 (C), 135.9 (2 × CH), 127.4 (2 × CH), 122.5 (C); **^{19}F NMR (471 MHz, $(CD_3)_2CO$) δ:** −150.7; **^{11}B NMR (160 MHz, $(CD_3)_2CO$) δ:** −0.96; **ν_{max}/cm^{-1}** 3119, 3106, 2307, 1539, 1359, 1317, 1040; **LRMS (ESI$^+$) *m*/*z*** 387 (45), 150 (M^+, 100).

4-Bromobenzenediazonium tetrafluoroborate (29c).[56] To a solution of 4-bromoaniline (1.40 g, 8.14 mmol) in H_2O (1.8 mL) and HBF_4 (4.1 mL, 35 wt% aqueous solution, 16 mmol) at 0 °C was added dropwise a solution of $NaNO_2$ (589 mg, 8.53 mmol) in H_2O (1.3 mL). The mixture was stirred for 30 min and the precipitate was collected by filtration. The solid was washed with diethyl ether (20 mL) and dried *in vacuo* to give **29c** (1.94 g, 7.16 mmol, 88%) as an off-white solid. No purification was required. **^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ:** 8.76–8.73 (2 H, m, 2 × Ar–H), 8.32–8.29 (2 H, m, 2 × Ar–H); **^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ:** 138.4 (C), 135.9 (2 × CH), 134.9 (2 × CH), 115.5 (C); **^{19}F NMR (471 MHz, $(CD_3)_2CO$) δ:** −150.8; **^{11}B NMR (160 MHz, $(CD_3)_2CO$) δ:** −0.94; **ν_{max}/cm^{-1}** 3103, 2287, 1556, 1041, 1009; **LRMS (ESI$^-$) *m*/*z*** 455 (100), 185 (M^+, 79) 183 (M^+, 79), 157 ($[M–N_2]^+$, 79), 155 ($[M–N_2]^+$, 79).

6,8-Dichloro-3-methylchroman-4-one (13b). To a solution of *S*-(2-iodophenethyl) 2-(allyloxy)-3,5-dichlorobenzothioate (200 mg, 0.41 mmol) in DMSO (4.5 mL) was added 4-methoxybenzenediazonium tetrafluoroborate (100 mg, 0.45 mmol). The mixture was stirred for 2 min. Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (140 mg, 0.54 mmol) was added and the mixture stirred at room temperature for 30 min. H_2O (10 mL) was added and the aqueous phase was extracted with ethyl acetate/diethyl ether (1 : 1, 3 × 15 mL). The organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (1–5% diethyl ether in hexanes) to give **13b** (19 mg, 0.082 mmol, 20%) as a dark yellow solid and recovered starting material (122 mg, 0.25 mmol, 61%). **R_f:** 0.38 (10% diethyl ether in hexanes); **m.p.** 84–86 °C: **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.77 (1 H, d, *J* = 2.6 Hz, Ar–H), 7.53 (1 H, d, *J* = 2.6 Hz, Ar–H), 4.63 (1 H, dd, *J* = 11.5, 5.1 Hz, OCHH), 4.23 (1 H, t, *J* = 11.3 Hz, OCHH), 2.89 (1 H, dqd, *J* = 11.2, 7.0, 5.1 Hz, CHCH$_3$), 1.23 (3 H, d, *J* = 7.0 Hz, CH$_3$); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 192.9 (C), 156.0 (C), 135.4 (CH), 126.8 (C), 125.6 (CH), 123.8 (C), 122.2 (C), 72.9 (CH_2), 40.5 (CH), 10.6 (CH_3); **ν_{max}/cm^{-1}** 3074, 2989, 2932, 2879, 1694, 1591, 1469, 1435, 1372, 1291, 1245, 1205, 1183, 1012; **HRMS (ESI$^+$)** calculated for $[C_{10}H_9Cl_2O_2]$ 230.99741 and 232.99446, found 230.99739 and 232.99445.

8-Bromo-3-methylchroman-4-one (14b). To a solution of *S*-(2-iodophenethyl) 2-(allyloxy)-3-bromobenzothioate (102 mg, 0.203 mmol) in DMSO (2.5 mL) was added 4-methoxybenzenediazonium tetrafluoroborate (50 mg, 0.23 mmol). The mixture was stirred for 2 min. Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (68 mg, 0.27 mmol) was added and the mixture stirred at room temperature for 30 min. H_2O (10 mL) was added and the aqueous phase was extracted with ethyl acetate/diethyl ether (1 : 1, 3 × 15 mL). The organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (2–5% diethyl ether in hexanes) to give **14b** (9.0 mg, 0.037 mmol, 18%) as a pale yellow oil and recovered starting material (67 mg, 0.13 mmol, 66%). **R_f:** 0.33 (10% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.86 (1 H, dd, *J* = 7.9, 1.6 Hz, Ar–H), 7.72 (1 H, dd, *J* = 7.7, 1.6 Hz, Ar–H), 6.92 (1 H, t, *J* = 7.8 Hz, Ar–H), 4.64 (1 H, dd, *J* = 11.4, 5.1 Hz, OCHH), 4.24 (1 H, t, *J* = 11.3 Hz, OCHH), 2.90 (1 H, dqd, *J* = 11.1, 7.0, 5.1 Hz, CHCH$_3$), 1.23 (3 H, d, *J* = 7.0 Hz, CH$_3$); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 194.0 (C), 158.2 (C), 139.1 (CH), 126.9 (CH), 122.2 (CH), 121.9 (C), 111.5 (C), 72.9 (CH_2), 40.5 (CH), 10.7 (CH_3); **ν_{max}/cm^{-1}** 2975, 2932, 2875, 1693, 1594, 1468, 1439, 1288, 1259, 1221, 1071; **LRMS (ESI$^+$) *m*/*z*** 283 (59), 243 ($[M + Na]^+$, 100), 241 ($[M + Na]^+$, 100); **HRMS (ESI$^+$)** calculated for $[C_{10}H_{10}O_2Br]$ 240.98587 and 242.98382, found 240.98591 and 242.98384.

3-Methyl-6-nitrochroman-4-one (17b). To a solution of *S*-(2-iodophenethyl) 2-(allyloxy)-5-nitrobenzothioate (74 mg, 0.16 mmol) in DMSO (1.8 mL) was added 4-methoxybenzenediazonium tetrafluoroborate (39 mg, 0.18 mmol). The mixture was stirred for 2 min. Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (53 mg, 0.21 mmol) was added and the mixture stirred at room temperature for 30 min. H_2O (10 mL) was added and the aqueous phase was extracted with ethyl acetate/diethyl ether (1 : 1, 3 × 15 mL). The organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (60–80% dichloromethane in hexanes) to give **17b** (6.0 mg, 0.029 mmol, 18%) as a white solid and recovered starting material (49 mg, 0.10 mmol, 66%). **R_f:** 0.23 (20% diethyl ether in hexanes); **m.p.** 123–125 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 8.79 (1 H, d, *J* = 2.9 Hz, Ar–H), 8.32 (1 H, dd, *J* = 9.2, 2.9 Hz, Ar–H), 7.10 (1 H, d, *J* = 2.9 Hz, Ar–H), 4.64 (1 H, dd, *J* = 11.5, 5.3 Hz, OCHH), 4.26 (1 H, t, *J* = 11.4 Hz, OCHH), 2.95 (1 H, dqd, *J* = 11.4, 7.0, 5.2 Hz, CHCH$_3$), 1.26 (3 H, t, *J* = 7.0 Hz, CH$_3$); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 192.7 (C), 165.8 (C), 142.4 (C), 130.2 (CH), 124.1 (CH), 120.3 (C), 119.3 (CH), 72.8 (CH_2), 40.6 (CH), 10.5 (CH_3); **ν_{max}/cm^{-1}** 3089, 2926, 2889, 2852, 1699, 1616, 1519, 1484, 1437, 1343, 1296, 1263, 1133, 1008; **LRMS (ESI$^+$) *m*/*z*** 413 (59), 362 (62), 301 (79), 230 ($[M + Na]^+$, 100); **HRMS (ESI$^+$)** calculated for $[C_{10}H_{10}NO_4]$ 208.06043, found 208.06048.

Ethyl 2-(3-oxo-2,3-dihydrobenzofuran-2-yl)acetate (24b).[57] To a solution of ethyl (*E*)-3-(2-(((2-iodophenethyl)thio)-carbonyl) phenoxy) acrylate (98 mg, 0.20 mmol) in DMSO (2.3 mL) was added 4-methoxybenzenediazonium tetrafluoroborate (50 mg, 0.23 mmol). The mixture was stirred for 2 min. Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (69 mg, 0.27 mmol) was added and the mixture stirred at room temperature for 30 min. H_2O (10 mL) was added and the aqueous phase was extracted with ethyl acetate/diethyl ether (1 : 1, 3 × 15 mL). The organic extracts were washed with brine (20 mL),

dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (50–100% dichloromethane in hexanes – 1% diethyl ether in dichloromethane) to give **24b** (15 mg, 0.072 mmol, 36%) as a yellow oil and recovered starting material (60 mg, 0.12 mmol, 61%). **R_f**: 0.25 (20% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.68 (1 H, ddd, J = 7.7, 1.4, 0.6 Hz, Ar–H), 7.62 (1 H, ddd, J = 8.4, 7.1, 1.5 Hz, Ar–H), 7.14–7.08 (2 H, m, 2 × Ar–H), 4.88 (1 H, dd, J = 7.6, 3.8 Hz, OCHCH$_2$), 4.19–4.11 (2 H, m, OCH$_2$), 3.07 (1 H, dd, J = 17.0, 3.8 Hz, OCHCHH), 2.82 (1 H, dd, J = 17.0, 7.6 Hz, OCHCHH), 1.18 (3 H, t, J = 7.1 Hz, CH$_3$); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 200.5 (C), 172.7 (C), 169.5 (C), 138.2 (CH), 124.4 (CH), 122.3 (CH), 121.1 (C), 113.7 (CH), 81.2 (CH), 61.4 (CH_2), 36.2 (CH_2), 14.1 (CH_3); **ν_{max}/cm^{-1}** 2981, 2926, 1718, 1650, 1614, 1464, 1326, 1192, 1026.

Intermolecular additions

***S*-(2-Iodophenethyl) pentanethioate (33a).** To a solution of pentanoic acid (0.65 mL, 5.9 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added DCC (1.2 g, 5.9 mmol) and DMAP (72 mg, 0.59 mmol). The mixture was mixture was stirred for 5 min before a solution of compound **6** (1.0 g, 3.9 mmol) in CH_2Cl_2 (10 mL) was added. The mixture was stirred at room temperature for 16 h. The white solid was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (10% CH_2Cl_2 in hexanes) to give **33a** (950 mg, 2.7 mmol, 70%) as a pale yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 7.80 (1 H, dd, J = 8.0, 0.9 Hz), 7.30–7.24 (2 H, m), 6.92–6.88 (1 H, m), 3.12–3.10 (2 H, m), 2.99–2.95 (2 H, m), 2.55 (2 H, t, J = 7.5 Hz), 1.68–1.60 (2 H, m), 1.39–1.31 (2 H, m), 0.90 (3 H, t, J = 7.4 Hz); **^{13}C NMR(101 MHz; $CDCl_3$) δ:** 199.5 (C), 142.8 (C), 139.7 (CH), 130.2 (CH), 128.53 (CH), 128.52 (CH) 100.5 (C), 44.0 (CH_2), 40.7 (CH_2), 28.9 (CH_2), 27.8 (CH_2), 22.2 (CH_2), 13.9 (CH_3); **ν_{max}/cm^{-1}**: 2956, 1685, 1465, 1117, 1009; ***m*/*z* HRMS (ESI$^+$)** calcd for $C_{13}H_{17}IOSNa$ ([M + Na]$^+$): 370.99370; found: 370.99387.

1-Cyclohexylpentan-1-one (33b).[58] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **33a** (50 mg, 0.14 mmol) in MeCN (2.6 mL) was added tributylamine (65 μL, 0.28 mmol), cyclohexene (0.72 mL, 7.2 mmol), and *fac*-Ir(ppy)$_3$ (1.8 mg, 0.0028 mmol). The mixuture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 20. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting with 1–2% ether in hexanes) to give **33b** (8.2 mg, 0.048 mmol, 33%) as a yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 2.42 (2 H, t, J = 7.4), 2.36–2.29 (1 H, m), 1.83–1.76 (4 H, m), 1.57–1.49 (2 H, m), 1.37–1.17 (8 H, m), 0.89 (3 H, t, J = 7.3); **^{13}C NMR (101 MHz; $CDCl_3$) δ:** 214.6 (C), 51.0 (CH), 40.5 (CH_2), 28.7 (2 × CH_2), 26.04 (CH_2), 26.01 (CH_2), 25.9 (2 × CH_2), 22.6 (CH_2), 14.0 (CH_3). **ν_{max}/cm^{-1}**: 2928, 2855, 1707, 1450, 1408, 1376, 1257, 1147, 1126, 1055, 1009.

1-(Trimethylsilyl)octan-4-one (33c). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **33a** (100 mg, 0.29 mmol) in MeCN (5.3 mL) was added tributylamine (0.14 mL, 0.47 mmol), allyltrimethylsilane (2.3 mL, 14 mmol), and *fac*-Ir(ppy)$_3$ (3.8 mg, 0.0057 mmol). The mixuture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 20. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting with 1–2% ether in hexanes) to give **33c** (21 mg, 0.10 mmol, 37%) as a yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 2.42–2.35 (4 H, m), 1.63–1.50 (4 H, m), 1.35–1.25 (2 H, m) 0.90 (3 H, t, J = 7.3), 0.48–0.43 (2 H, m) 0.023 (9 H, s); **^{13}C NMR (101 MHz; $CDCl_3$) δ:** 211.8 (C), 46.6 (CH_2), 42.7 (CH_2), 26.1 (CH_2), 22.5 (CH_2), 18.7 (CH_2), 16.7 (CH_2), 14.0 (CH_2), −1.5 (3 × CH_3); **ν_{max}/cm^{-1}**: 2954, 1713, 1247; ***m*/*z* HRMS (ESI):** calcd for $C_{11}H_{24}OSiNa$ ([M + Na]$^+$): 223.14886; found: 223.14905.

***S*-(2-Iodophenethyl) 3-phenylpropanethioate (34a).** To a solution of 3-phenylpropanoic acid (440 mg, 3 mmol) in CH_2Cl_2 (13 mL) at 0 °C was added DCC (610 mg, 3 mmol) and DMAP (36 mg, 0.3 mmol). The mixture was stirred for 5 min before the solution of compound **6** (500 mg, 2 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 16 h. The white solid was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting with 20% CH_2Cl_2 in hexanes) to give the **34a** (800 mg, 2.0 mmol, 95%) as a pale yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 7.82 (1 H, dd, J = 7.9, 1.0 Hz), 7.32–7.19 (7 H, m), 6.92 (1 H, td, J = 7.6, 1.7 Hz), 3.15–3.11 (2 H, m), 3.01–2.96 (4 H, m), 2.90–2.86 (2 H, m); **^{13}C NMR(101 MHz; $CDCl_3$) δ:** 198.4 (C), 142.7 (C), 140.2 (C), 139.7 (CH), 130.2 (CH), 128.7 (CH), 128.53 (CH), 128.47 (CH), 126.5 (CH), 100.5 (C), 45.6 (CH_2), 40.6 (CH_2), 31.6 (CH_2), 29.0 (CH_2); **ν_{max}/cm^{-1}**: 3059, 3027, 2925, 2861, 1687, 1466, 1046, 1011; ***m*/*z* HRMS (ESI$^+$):** calcd for $C_{17}H_{17}IOSNa$ ([M + Na]$^+$): 418.99370; found: 418.99405.

1-Cyclohexyl-3-phenylpropan-1-one (34b).[59] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **34a** (53 mg, 0.13 mmol) in MeCN (2.5 mL) was added tributylamine (63 μL, 0.27 mmol), cyclohexene (0.7 mL, 6.7 mmol), and *fac*-Ir(ppy)$_3$ (1.7 mg, 0.0027 mmol). The mixuture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 20. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting with 20–30% CH_2Cl_2 in hexanes) to give the **34b** (5.0 mg, 0.023 mmol, 17%) as a yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 7.29–7.25 (2 H, m), 7.20–7.16 (3 H, m), 2.90–2.86 (2 H, m), 2.77–2.73 (2 H, m), 2.33–2.27 (1 H, m),

1.82–1.75 (4 H, m), 1.67–1.63 (1 H, m), 1.36–1.16 (5 H, m); **^{13}C NMR (101 MHz; $CDCl_3$) δ:** 213.3 (C), 114.6 (C), 128.6 (2 × CH), 128.5 (2 × CH), 126.2 (CH), 51.3 (CH), 42.4 (CH_2), 29.9 (CH_2), 28.6 (2 × CH_2), 26.0, (CH_2), 25.8 (2 × CH_2); **ν_{max}/cm^{-1}:** 2929, 2855, 2239, 2231, 2120, 1067, 1044, 1015, 991; ***m*/*z* HRMS (ESI):** calcd for $C_{15}H_{21}O$ ($[M + H]^+$): 217.15847; found: 217.15869.

1-Phenyl-6-(trimethylsilyl)hexan-3-one (34c). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **34a** (53 mg, 0.13 mmol) in MeCN (2.5 mL) was added tributylamine (63 μL, 0.27 mmol), allyltrimethylsilane (1.0 mL, 6.7 mmol), and *fac*-Ir(ppy)$_3$ (1.7 mg, 0.0027 mmol). The mixuture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 20. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting with 20–30% CH_2Cl_2 in hexanes) to give **34c** (11.3 mg, 0.44 mmol, 35%) as a yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 7.29–7.26 (2 H, m), 7.20–7.17 (3 H, m), 2.91–2.87 (2 H, m), 2.73–2.70 (2 H, m), 2.40 (2 H, t, *J* = 7.30), 1.60–1.52 (2 H, m), 0.46–0.41 (2 H, m), 0.03 (9 H, s); **^{13}C NMR (101 MHz; $CDCl_3$) δ:** 210.5 (C), 141.4 (C), 128.6 (CH), 128.5 (CH), 126.2 (2 × CH), 46.9 (CH_2), 44.5 (CH_2), 29.9 (CH_2), 18.7 (CH_2), 16.6 (CH_2), −1.6 (3 × CH_3); **ν_{max}/cm^{-1}:** 3064, 3028, 2952, 2928, 2894, 2009, 1928, 1713, 1604, 1496, 1454, 1409, 1367, 1296, 1247, 1180, 1085, 1030, 972; **HRMS (ESI$^+$):** calcd for ($[M + H]^+$): 249.16678; found: 249.16692.

***S*-(2-Iodophenethyl) 3-methoxybenzothioate (35a).** To a solution of 3-methoxybenzoic acid (310 mg, 1.8 mmol) in CH_2Cl_2 (8 mL) at 0 °C was added DCC (360 mg, 1.8 mmol) and DMAP (22 mg, 0.18 mmol). The mixture was stirred for 5 min before a solution of compound **6** (310 mg, 1.2 mmol) in CH_2Cl_2 (3 mL) was added. The mixture was stirred at room temperature for 16 h. The white solid was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting 30% CH_2Cl_2 in hexanes) to give the **35a** (320 mg, 0.8 mmol, 68%) as a pale yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 7.84 (1 H, dd, *J* = 7.9, 1.1 Hz), 7.58 (1 H, ddd, *J* = 7.7, 1.6, 1.0 Hz), 7.48 (1 H, dd, *J* = 2.6, 1.6 Hz), 7.38–7.28 (3 H, m), 7.12 (1 H, ddd, *J* = 8.3, 2.7, 1.0 Hz), 6.93 (1 H, ddd, *J* = 7.9, 6.9, 2.2 Hz), 3.86 (3 H, s), 3.33–3.29 (2 H, m), 3.12–3.08 (2 H, m); **^{13}C NMR(101 MHz; $CDCl_3$) δ:** 191.8 (C), 159.9 (C), 142.8 (C), 139.8 (CH), 138.6 (C), 130.3 (CH), 129.8 (CH), 128.63 (CH), 128.59 (CH), 120.0 (2 × CH), 111.6 (CH), 100.5 (C), 55.6 (CH_3), 40.7 (CH_2), 29.2 (CH_2); **ν_{max}/cm^{-1}:** 3057, 2934, 1657, 1595, 1581, 1562, 1445, 1327, 1287, 1102, 1009, 969; ***m*/*z* HRMS (ESI$^+$):** calcd for $C_{16}H_{15}IOSNa$ ($[M + Na]^+$): 420.97296; found: 420.97291.

Cyclohexyl(3-methoxyphenyl)methanone (35b). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **35a** (50 mg, 0.13 mmol) in MeCN (2.5 mL) was added tributylamine (60 μL, 0.26 mmol), cyclohexene (0.65 mL, 6.5 mmol), and *fac*-Ir(ppy)$_3$ (1.6 mg, 0.0057 mmol). The mixuture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 20. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting with 1–2% ether in hexanes) to give **35b** (2.4 mg, 0.0073 mmol, 10%) as a yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 7.52 (1 H, d, *J* = 7.7), 7.48–7.47 (1 H, m), 7.36 (1 H, t, *J* = 7.9), 7.10–7.08 (1 H, m), 3.86 (3 H, s), 3.23 (1 H, tt, *J* = 11.4, 3.1), 1.90–1.82 (4 H, m), 1.76–1.72 (1 H, m), 1.54–1.33 (5 H, m); **^{13}C NMR (101 MHz; $CDCl_3$) δ:** 203.9 (C), 160.1 (C), 138.0 (C), 129.7 (CH), 120.9 (CH), 119.2 (CH), 112.9 (CH), 55.6 (CH_3), 46.0 (CH), 29.6 (2 × CH_2), 26.1 (CH_2), 26.0 (2 × CH_2); **ν_{max}/cm^{-1}:** 2930, 1678, 1581, 1485, 1450, 1260, 1166, 1039, 988; ***m*/*z* HRMS (ESI):** calcd for $C_{14}H_{18}O_2$ ($[M + Na]^+$): 241.11990; found: 241.12006.

1-(3-Methoxyphenyl)-4-(trimethylsilyl)butan-1-one (35c). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **35a** (50 mg, 0.13 mmol) in MeCN (2.5 mL) was added tributylamine (60 μL, 0.26 mmol), allyltrimethylsilane (1.0 mL, 6.5 mmol), and *fac*-Ir(ppy)$_3$ (1.6 mg, 0.0026 mmol). The mixuture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 20. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting with 2% ether in hexane) to give **35c** (6.2 mg, 0.025 mmol, 20%) as a yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 7.58–7.46 (2 H, m), 7.36 (1 H, dd, *J* = 7.9, 7.9), 7.10 (1 H, ddd, *J* = 8.2, 2.6, 0.9), 3.86 (3 H, s), 2.97 (2 H, t, *J* = 7.3), 1.78–1.70 (2 H, m), 0.59–0.55 (2 H, m), 0.00 (9 H, s); **^{13}C NMR (101 MHz; $CDCl_3$) δ:** 200.6 (C), 160.0 (C), 138.7 (C), 129.7 (CH), 120.9 (CH), 119.5 (CH), 112.4 (CH), 55.6 (CH_3), 42.6 (CH_2), 19.9 (CH_2), 16.8 (CH_2), −1.6 (3 × CH_3); **ν_{max}/cm^{-1}:** 2970, 1684, 1247; ***m*/*z* HRMS (ESI):** calcd for $C_{14}H_{22}O_2SiNa$ ($[M + Na]^+$): 273.12813; found: 273.12820.

***S*-(2-Iodophenethyl) 2,6-dimethylbenzothioate (36a).** To a solution of 2,6-dimethylbenzoic acid (290 mg, 1.9 mmol) in CH_2Cl_2 (8.5 mL) at 0 °C was added DCC (400 mg, 1.9 mmol) and DMAP (24 mg, 0.19 mmol). The mixture was stirred for 5 min before the solution of compound **6** (340 mg, 1.2 mmol) in CH_2Cl_2 (3.5 mL). The mixture was stirred at room temperature for 16 h. The white solid was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting 20% CH_2Cl_2 in hexanes) to give the **36a** (220 mg, 0.56 mmol, 43%) as a white solid. **m.p.** 75–78 °C; **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 7.84 (1 H, dd, *J* = 7.9, 1.0 Hz), 7.36 (1 H, dd, *J* = 7.6, 1.9 Hz), 7.31 (1 H, td, *J* = 7.1, 1.2), 7.18 (1 H, t, *J* = 7.64 Hz), 7.02 (2 H, d, *J* = 7.6 Hz), 6.93 (1 H, td, *J* = 7.5, 1.9 Hz), 3.35–3.1 (2 H, m), 3.15–3.11 (2 H, m), 2.3 (6 H, s); **^{13}C NMR(101 MHz; $CDCl_3$) δ:** 197.6 (C), 142.5 (C), 140.3 (C), 139.8 (CH), 133.8 (2 × C), 130.2 (CH), 129.5 (CH),

128.62 (CH), 128.61 (CH), 127.8 (2 × CH), 100.5 (C), 40.8 (CH_2), 29.4 (CH_2), 19.2 (2 × CH_3); ν_{max}/cm^{-1}: 2920, 1796, 1672, 1465, 1196, 1009, 968; ***m*/*z* HRMS (ESI$^+$):** calcd for $C_{17}H_{17}IOSNa$ ($[M + Na]^+$): 418.99370; found: 418.99387.

Cyclohexyl(2,6-dimethylphenyl)methanone (36b). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **36a** (47 mg, 0.11 mmol) in MeCN (2.2 mL) was added tributylamine (55 μL, 0.23 mmol), cyclohexene (0.60 mL, 5.9 mmol), and *fac*-Ir(ppy)$_3$ (1.6 mg, 0.0023 mmol). The mixuture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 20. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting with 1–2% ether in hexanes) to give **36b** (5.0 mg, 0.023 mmol, 20%) as a yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) *δ*:** 7.17–7.13 (1 H, m), 7.02–7.00 (2 H, m), 2.68 (1 H, tt, *J* = 11.7, 3.4), 2.22 (6 H, s), 1.95–1.92 (2 H, m), 1.85–1.81 (2 H, m), 1.71–1.67 (1 H, m), 1.48–1.38 (2 H, m), 089–0.83 (3 H, m); **^{13}C NMR (101 MHz; $CDCl_3$) *δ*:** 213.6 (C), 142.0 (C), 133.4 (CH), 128.6 (2 × C), 128.0 (2 × CH), 52.3 (CH), 29.9 (2 × CH_2), 28.3 (2 × CH_2), 26.1 (CH_2), 19.9 (2 × CH_3); ν_{max}/cm^{-1}: 2928, 1675, 1465, 1197, 970; ***m*/*z* HRMS (ESI):** calcd for $C_{15}H_{22}O$ ($[M + Na]^+$): 239.14064; found: 239.14083.

1-(2,6-Dimethylphenyl)-6-(trimethylsilyl)-3-((trimethylsilyl)-methyl) hexan-1-one (36c). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **36a** (47 mg, 0.11 mmol) in MeCN (2.2 mL) was added tributylamine (55 μL, 0.23 mmol), allyltrimethylsilane (0.94 mL, 5.9 mmol), and *fac*-Ir(ppy)$_3$ (1.6 mg, 0.0023 mmol). The mixuture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 20. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting with 1–2% ether in hexanes) to give the **36c** (8.0 mg, 0.022 mmol, 20%) as a yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) *δ*:** 7.16–7.12 (2 H, m), 7.00–6.98 (1 H, m), 2.75 (1 H, dd, *J* = 18.6, 6.8), 2.60 (1 H, dd, *J* = 18.6, 5.9), 2.2 (6 H, s), 1.52–1.28 (5 H, m), 0.90–0.81 (2 H, m), 0.63 (2 H, d *J* = 6.8), 0.50–0.46 (2 H, m), 0.04 (9 H, s), −0.02 (9 H, m); **^{13}C NMR (101 MHz; $CDCl_3$) *δ*:** 210.1 (C), 142.7 (C), 132.5 (CH), 128.5 (2 × C), 127.9 (2 × CH), 52.5 (CH_2), 40.9 (CH_2), 29.1 (CH_2), 22.3 (CH), 20.9 (CH_2), 19.3 (2 × CH_3), 17.0 (CH_2), −0.4 (3 × CH_3), −1.5 (3 × CH_3); ν_{max}/cm^{-1}: 2952, 1700, 1247; ***m*/*z* HRMS (ESI):** calcd for $C_{21}H_{38}OSi_2Na$ ($[M + Na]^+$): 385.23534; found: 385.23556.

***S*-(2-Iodophenethyl) cyclohexanecarbothioate (37a).** To a solution of hexahydrobenzoic acid (370 mg, 3 mmol) in CH_2Cl_2 (13 mL) at 0 °C was added DCC (610 mg, 3 mmol) and DMAP (35 mg, 0.3 mmol). The mixture was stirred for 5 min before a solution of compound **6** (510 mg, 2 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature for 16 h. The white solid was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting with 20% CH_2Cl_2 in hexanes) to give **37a** (700 mg, 1.9 mmol, 95%) as a pale yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) *δ*:** 7.80 (1 H, dd, *J* = 7.9, 1.0 Hz), 7.28–7.24 (2 H, m), 6.92–6.88 (1 H, m), 3.10–3.06 (2 H, m), 2.98–2.94 (2 H, m), 2.47 (1 H, tt, *J* = 11.4, 3.5 Hz), 1.92–1.88 (2 H, m), 1.80–1.76 (2 H, m), 1.66–1.63 (1 H, m), 1.49–1.40 (2 H, m), 1.32–1.14 (3 H, m); **^{13}C NMR(101 MHz; $CDCl_3$) *δ*:** 202.9 (C), 142.8 (C), 139.7 (CH), 130.2 (CH), 128.50 (CH), 128.48 (CH), 100.5 (C), 52.9 (CH_2), 40.8 (CH_2), 29.7 (CH_2), 28.5 (2 × CH_2), 25.8 (2 × CH_2), 25.7 (CH_2); ν_{max}/cm^{-1}: 2929, 2853, 1686, 1965, 1447, 1011, 971; ***m*/*z* HRMS (ESI$^+$):** calcd for $C_{15}H_{19}IOSNa$ ($[M + Na]^+$): 397.00935; found: 397.00962.

Dicyclohexylmethanone (37b). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **37a** (53 mg, 0.14 mmol) in MeCN (2.5 mL) was added tributylamine (65 μL, 0.28 mmol), cyclohexene (0.7 mL, 6.9 mmol), and *fac*-Ir(ppy)$_3$ (1.7 mg, 0.0028 mmol). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The crude mixture was purified by flash chromatography on silica gel (eluting with 20–30% CH_2Cl_2 in hexanes) to give **37b** as a yellow oil (3.0 mg, 11%). **^{1}H NMR (400 MHz; $CDCl_3$) *δ*:** 2.51–2.44 (2 H, m) 1.78–1.75 (8 H, m) 1.41–1.21 (12 H, m); ν_{max}/cm^{-1}: 2926, 2852, 1705, 1608, 1449, 1378, 1325, 1260, 1230, 1150, 1094, 1023, 998, 914; **^{13}C NMR (101 MHz; $CDCl_3$) *δ*:** 217.3 (C), 49.4 (2 × CH), 28.8 (4 × CH_2), 26.0 (2 × CH_2), 25.9 (4 × CH_2); **HRMS (ESI$^+$):** calcd for ($[M + H]^+$): 195.17354; found: 195.17434.

1-Cyclohexyl-4-(trimethylsilyl)butan-1-one (37c). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **37a** (52 mg, 0.14 mmol) in MeCN (2.5 mL) was added tributylamine (65 μL, 0.28 mmol), allyltrimethylsilane (1.1 mL, 6.9 mmol), and *fac*-Ir(ppy)$_3$ (1.8 mg, 0.0028 mmol). The mixuture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 20. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The crude mixture was purified by flash chromatography on silica gel (eluting with 20–30% CH_2Cl_2 in hexanes) to give **37c** (8.2 mg, 0.036 mmol, 26%) as a yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) *δ*:** 2.45 (2 H, t, *J* = 7.3 Hz), 2.34–2.27 (1 H, m), 1.83–1.76 (4 H, m), 1.36–1.28 (4 H, m), 0.47–0.43 (2 H, m), 0.018 (9 H, s). **^{13}C NMR (101 MHz; $CDCl_3$) *δ*:** 214.7 (C), 51.0 (CH_2), 44.5 (CH_2), 28.6 (2 × CH_2), 26.0 (CH_2), 25.8 (2 × CH_2), 18.6 (CH_2), 16.7 (CH_2), −1.6 (2 × CH_3); ν_{max}/cm^{-1}: 2927, 2854, 1708, 1450, 1374, 1247, 1179, 1149, 1081, 1013, 988; **HRMS (ESI):** calcd for $C_{13}H_{26}OSiNa$ ($[M + Na]^+$): 249.16451; found: 249.16477.

***S*-(2-Iodophenethyl) 2,3-dimethylbenzothioate (38a).** To a solution of 2,3-dimethylbenzoic acid (290 mg, 1.9 mmol) in CH_2Cl_2 (8.5 mL) at 0 °C was added DCC (400 mg, 1.9 mmol)

and DMAP (24 mg, 0.19 mmol). The mixture was stirred for 5 min before a solution of compound **6** (340 mg, 1.2 mmol) in CH_2Cl_2 (3.5 mL) was added. The mixture was stirred at room temperature for 16 h. The white solid was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting 30% CH_2Cl_2 in hexanes) to give **38a** (490 mg, 1.3 mmol, 96%) as a pale yellow oil. **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 7.86 (1 H, dd, *J* = 7.9, 1.1 Hz), 7.49 (1 H, d, *J* = 7.6 Hz), 7.36–7.28 (3 H, m), 7.14 (1 H, t, *J* = 7.6 Hz), 6.93 (1 H, td, *J* = 7.5, 2.0 Hz), 3.31–3.28 (2 H, m), 3.12–3.10 (2 H, m), 2.32 (3 H, s), 2.31 (3 H, s); **^{13}C NMR(101 MHz; $CDCl_3$) δ:** 195.5 (C), 142.8 (C), 139.7 (CH), 139.1 (C), 138.3 (C), 134.4 (CH), 132.9 (C), 130.3 (CH), 128.6 (2 × CH), 125.8 (CH), 125.4 (CH), 100.6 (C), 40.7 (CH_2), 29.9 (CH_2), 20.5 (CH_3), 16.4 (CH_3); **ν_{max}/cm^{-1}**: 2996, 1663, 1464, 1226, 1081, 1009; ***m*/*z* HRMS (ESI$^+$):** calcd for $C_{17}H_{17}IOSNa$ ($[M + Na]^+$): 418.99370; found: 418.99380.

Cyclohexyl(2,3-dimethylphenyl)methanone (38b) and 7,8-dimethyl-1,2,3,4,4a,9a-hexahydro-9*H*-fluoren-9-on (39). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **38a** (50 mg, 0.13 mmol) in MeCN (2.5 mL) was added tributylamine (60 μL, 0.26 mmol), cyclohexene (0.63 mL, 6.3 mmol), and *fac*-Ir(ppy)$_3$ (1.6 mg, 0.0026 mmol). The mixuture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 20. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The crude mixture was purified by flash chromatographyon silica gel (eluting with 1–2% ether in hexane) to give **38b** (1 mg, 7%) as a yellow oil. **ν_{max}/cm^{-1}**: 2926, 2853, 17 084, 1602, 1585, 1327, 1258, 1157, 1018; **^{1}H NMR (400 MHz; $CDCl_3$) δ:** 7.19–7.17 (3 H, m), 2.93 (1 H, ttt, *J* = 11.2, 3.2), 2.30 (3 H, s), 2.22 (3 H, s), 1.90–1.84 (2 H, m), 1.83–1.77 (2 H, m), 1.45–1.40 (2 H, m), 1.32–1.28 (4 H, m); **^{13}C NMR (101 MHz; $CDCl_3$) δ:** 210.7 (C), 141.1 (C), 138.1 (C), 134.4 (C), 131.6 (CH), 125.3 (CH), 124.2 (CH), 50.2 (CH), 29.8 (CH_2), 28.7 (2 × CH_2), 26.1 (CH_2), 25.9 (CH_2), 20.4 (CH_3), 16.6 (CH_3); ***m*/*z* HRMS (ESI):** calcd for $C_{15}H_{20}ONa$ ($[M + Na]^+$): 239.14064; found: 239.14086; and compound **39** (2 mg, 7%) as a yellow oil. **ν_{max}/cm^{-1}**: 2926, 2853, 17 084, 1602, 1585, 1327, 1258, 1157, 1018; **^{1}H-NMR (400 MHz; $CDCl_3$) δ:** 7.31 (1 H, d, *J* = 7.7), 7.16 (1 H, d, *J* = 7.6), 3.29–3.23 (1 H, m), 2.71 (1 H, td, *J* = 6.9, 4.4), 2.59 (3 H, s), 2.30 (3 H, s), 2.16–2.04 (3 H, m), 1.74–1.65 (2 H, m), 1.58–1.48 (2 H, m), 1.26–1.24 (1 H, m); **^{13}C NMR (101 MHz; $CDCl_3$) δ:** 209.1 (C), 157.0 (C), 137.5 (C), 136.3 (C), 135.3 (CH), 133.1 (C), 121.8 (CH), 49.5 (CH), 38.0 (CH), 32.1 (CH_2), 23.4 (CH_2), 23.1 (CH_2), 22.7 (CH_2), 19.2 (CH_3), 13.9 (CH_3); ***m*/*z* HRMS (ESI):** calcd for $C_{15}H_{18}ONa$ ($[M + Na]^+$): 237.12499; found: 237.12521.

6,7-Dimethyl-3-((trimethylsilyl)methyl)-2,3-dihydro-1*H*-inden-1-one (40). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **38a** (50 mg, 0.13 mmol) in MeCN (2.5 mL) was added tributylamine (60 μL, 0.26 mmol), allyltrimethylsilane (1.0 mL, 6.3 mmol), and *fac*-Ir(ppy)$_3$ (1.6 mg, 0.0026 mmol). The mixuture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 20. Water (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluting with 1–2% ether in hexanes) to give **40** (8.0 mg, 0.032 mmol, 25%) as a yellow oil. **^{1}H-NMR (400 MHz; $CDCl_3$) δ:** 7.35 (1 H, d, *J* = 7.8), 7.21 (1 H, d, *J* = 7.8), 2.88 (1 H, dd, *J* = 18.5, 7.6), 2.59 (3 H, s), 2.30 (3 H, s), 2.25 (1 H, dd, *J* = 18.5, 4.0), 1.27 (1 H, dd, *J* = 14.6, 2.9), 0.71 (1 H, dd, *J* = 14.6, 12.0), −0.08 (9 H, s); **^{13}C NMR (101 MHz; $CDCl_3$) δ:** 207.8 (C), 160.5 (C), 136.9 (C), 136.1 (C), 136.0 (CH), 133.4 (C), 122.2 (CH), 46.8 (CH_2), 33.2 (CH), 25.0 (CH_2), 19.1 (CH_3), 13.8 (CH_3), −0.7 (3 × CH_3); **ν_{max}/cm^{-1}**: 2952, 1703, 1478, 1249; ***m*/*z* HRMS (ESI):** calcd for $C_{15}H_{22}OSiNa$ ($[M + Na]^+$): 269.13321; found: 269.13337.

Cascade intramolecular cyclization – intermolecular addition

3-(4-(Trimethylsilyl)butyl)chroman-4-one (41). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **7a** (69 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (78 μL, 0.32 mmol), formic acid (12 μL, 0.32 mmol), trimethylallylsilane (1.0 mL, 6.5 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 15 min at 0 °C before irradiating with blue light (465 nm) for 3 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (30 mL, 1 M solution), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (0–5% diethyl ether in hexanes) to give **41** (20 mg, 0.072 mmol, 44%) as a colourless oil. **R_f:** 0.45 (10% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.89 (1 H, ddd, *J* = 7.8, 1.7, 0.4 Hz, Ar–H), 7.46 (1 H, ddd, *J* = 8.3, 7.1, 1.8 Hz, Ar–H), 7.01 (1 H, ddd, *J* = 7.8, 7.1, 1.1 Hz, Ar–H), 6.95 (1 H, d, *J* = 8.3 Hz, Ar–H), 4.52 (1 H, dd, *J* = 11.4, 4.4 Hz, OCHH), 4.28 (1 H, dd, *J* = 11.4, 8.4 Hz, OCHH), 2.66–2.63 (1 H, m, OCH_2CH), 1.91–1.84 (1 H, m, $CHCH_2CHHCH_2$), 1.57–1.28 (5 H, m, $CHCH_2CHHCH_2$), 0.55–0.47 (2 H, m, $CH_2Si(CH_3)_3$) −0.03 (9 H, s, $Si(CH_3)_3$); **^{13}C NMR (126 MHz, $CDCl_3$) δ:** 194.8 (C), 161.6 (C), 135.8 (CH), 127.6 (CH), 121.5 (CH), 120.8 (C), 117.8 (CH), 70.6 (CH_2), 46.1 (CH), 31.0 (CH_2), 26.2 (CH_2), 24.1 (CH_2), 16.6 (CH_2), −1.6 (3 × CH_3); **ν_{max}/cm^{-1}** 2951, 2922, 2858, 1691, 1606, 1478, 1246; **LRMS (ESI$^+$) *m*/*z*** 435 (100), 344 (45), 299 ($[M + Na]^+$, 40), 254 (44), 186 (54), 130 (50); **HRMS (ESI$^+$)** calculated for $[C_{16}H_{24}O_2SiNa]$ 299.14378, found 299.14386.

2-(Allyloxy)-6-fluoropyridine. To a solution of allyl alcohol (0.68 mL, 10 mmol) and 2,6-difluoropyridine (1.0 mL, 11 mmol) in DMSO (10 mL) at 0 °C was added sodium hydride (520 mg, 60% dispersion in mineral oil, 13.0 mmol) in three portions. The mixture was stirred at 60 °C for 16 h. H_2O (30 mL) was added and the aqueous phase was extracted with diethyl ether (3 × 50 mL). The organic extracts were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*.

The residue was purified by flash chromatography on silica gel (5–15% dichloromethane in hexanes) to give 2-(allyloxy)-6-fluoropyridine (1.26 g, 8.23 mmol, 82%) as a colourless oil. **R_f:** 0.32 (15% CH_2Cl_2 in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.94 (1 H, q, J = 8.1 Hz, Ar–H), 6.63 (1 H, dd, J = 8.2, 1.5 Hz, Ar–H), 6.46 (1 H, dd, J = 7.8, 2.5 Hz, Ar–H), 6.07 (1 H, ddt, J = 17.2, 10.5, 1.5 Hz, CH_2CH), 5.40 (1 H, dq, J = 17.2, 1.6 Hz CH=CHH), 5.27 (1 H, dq, J = 10.4, 1.4 Hz, CH=CHH), 4.80 (2 H, dt, J = 5.6, 1.4 Hz, OCH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 162.7 (1 C, d, J = 13.6 Hz, C), 162.3 (1 C, d, J = 240.4 Hz, C), 142.7 (1 C, d, J = 8.0 Hz, CH), 133.0 (CH), 118.1 (CH_2), 107.4 (1 C, d, J = 5.1 Hz, CH), 100.2 (1 C, d, J = 35.5 Hz, CH), 67.3 (CH_2); **^{19}F NMR (376 MHz, $CDCl_3$) δ:** −70.25; **ν_{max}/cm^{-1}** 2952, 2923, 1614, 1576, 1467, 1440, 1422, 1317, 1230, 1030; **LRMS (ESI$^+$) m/z** 441 (67), 301 (100), 214 (33), 176 ([M + Na]$^+$, 39).

3-(4-((6-Fluoropyridin-2-yl)oxy)butyl)chroman-4-one (46) and 47. MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **7a** (69 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (78 μL, 0.32 mmol), formic acid (12 μL, 0.32 mmol), 2-(allyloxy)-6-fluoropyridine (250 mg, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 15 min at 0 °C before irradiating with blue light (465 nm) for 1 h 15 min. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (30 mL, 1 M solution), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (10–20% diethyl ether in hexanes) to give **46** (14.6 mg, 0.046 mmol, 29%) as a colourless oil. **R_f:** 0.15 (10% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.89 (1 H, dd, J = 7.9, 1.8 Hz, Ar–H), 7.62 (1 H, q, J = 8.2 Hz, Ar–H), 7.46 (1 H, ddd, J = 8.4, 7.2, 1.8 Hz, Ar–H), 7.02 (1 H, ddd, J = 7.9, 7.1, 1.0 Hz, Ar–H), 6.96 (1 H, dd, J = 8.3, 0.8 Hz, Ar–H), 6.58 (1 H, dd, J = 7.9, 1.4 Hz, Ar–H), 6.44 (1 H, dd, J = 7.8, 2.5 Hz, Ar–H), 4.53 (1 H, dd, J = 11.4, 4.4 Hz, OCHHCH), 4.29 (1 H, dd, J = 11.4, 8.5 Hz, OCHHCH), 4.28 (2 H, t, J = 6.6 Hz, OCH_2CH_2), 2.72–2.64 (1 H, m, OCHHCH), 2.03–1.89 (1 H, m, COCHCHH), 1.87–1.77 (2 H, m, OCH_2CH_2), 1.69–1.52 (3 H, m, COCHCHHCH_2); **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 194.5 (C), 163.2 (1 C, d, J = 13.7 Hz, C), 162.4 (1 C, d, J = 240.1 Hz, C), 161.6 (1 C, d, J = 8.1 Hz, CH), 135.9 (CH), 127.6 (CH), 121.5 (CH), 120.8 (C), 117.8 (CH), 107.3 (1 C, d, J = 5.1 Hz, CH), 99.9 (1 C, d, J = 35.6 Hz, CH), 70.6 (CH_2), 66.4 (CH_2), 46.1 (CH), 29.0 (CH_2), 26.3 (CH_2), 23.8 (CH_2); **^{19}F NMR (376 MHz, $CDCl_3$) δ:** −70.21; **ν_{max}/cm^{-1}** 2925, 2857, 1689, 1606, 1574, 1478, 1453, 1439, 1322, 1229, 1016; **LRMS (ESI$^+$) m/z** 653 (41), 531 (13), 338 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{18}H_{18}FNO_3Na$] 338.11629, found 338.11674; and **47** (18.0 mg, 0.038 mmol, 24%) as an inseparable mixture of diastereomers isolated as a pale yellow oil. **R_f:** 0.09 (10% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.89–7.87 (1 H, m, Ar–H), 7.63–7.59 (2 H, m, 2 × Ar–H), 7.48–7.44 (1 H, m, Ar–H), 7.02–6.99 (1 H, m, Ar–H), 6.96–6.94 (1 H, m, Ar–H), 6.59–6.55 (2 H, m, 2 × Ar–H), 6.45–6.41 (2 H, m, 2 × Ar–H), 4.53–4.50 (1 H, m, OCHHCHC(O)), 4.31–4.19 (5 H, m, $OCH_2CHCH_2CH_2CH_2$ + OCHHCHC(O)), 2.68–2.61 (1 H, m, C(O)CH), 1.98–1.78 (4 H, m, C(O)CHCHHCH_2CHCH_2CH_2), 1.59–1.56 (5 H, m, C(O)CHCHHCH_2CHCH_2); **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 194.5, 163.57, 163.56, 163.38, 163.32, 163.25, 163.2, 161.6, 161.2, 142.7, 142.62, 142.60, 142.5, 135.9, 127.6, 121.5, 120.7, 117.8, 107.32, 107.31, 107.27, 107.26, 100.2, 100.1, 99.8, 99.7, 70.6, 68.9, 68.82, 68.76, 46.4, 46.2, 37.7, 37.6, 29.1, 28.9, 27.9, 27.7, 26.34, 26.30, 23.9, 23.8; **^{19}F NMR (376 MHz, $CDCl_3$) δ:** −70.18, −70.23; **ν_{max}/cm^{-1}:** 2920, 2843, 1684, 1621, 1580, 1490, 1470, 1450, 1210, 1012; **LRMS (ESI$^+$) m/z** 491 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{26}H_{27}N_2O_4F_2$] 469.19334, found 469.19324.

Cascade intramolecular cyclization – colligation

3,3′-Dimethyl-[4,4′-bichromane]-4,4′-diol (7c). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution **7a** (69 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (80 μL, 0.33 mmol), formic acid (11 μL, 0.33 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (4.5 W; 465 nm) for 16 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (25–35% dichloromethane in hexanes) to give **7c** as a mixture of diastereomers (15 mg, 0.046 mmol, 57%). **Diastereomer 1** (7.5 mg, 0.023 mmol, 29%) a colourless oil. **R_f:** 0.12 (15% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.34 (2 H, dd, J = 7.8, 1.3 Hz, 2 × Ar–H), 7.26–7.22 (2 H, m, 2 × Ar–H), 6.96–6.91 (2 H, m, 2 × Ar–H), 6.87 (2 H, dd, J = 8.2, 1.1 Hz, 2 × Ar–H), 4.41 (2 H, dd, J = 10.9, 4.1 Hz, 2 × OCHH), 3.68 (2 H, dd, J = 10.9, 7.0 Hz, 2 × OCHH), 2.62 (2 H, s, 2 × OH), 2.36 (2 H, pd, J = 6.9, 4.2 Hz, 2 × OCHHCH), 0.57 (6 H, d, J = 6.9 Hz, 2 × CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 156.1 (2 × C), 129.5 (2 × CH), 129.1 (2 × CH), 125.6 (2 × C), 120.4 (2 × CH), 116.6 (2 × CH), 76.2 (2 × C), 70.4 (2 × CH_2), 34.4 (2 × CH), 12.9 (2 × CH_3); **ν_{max}/cm^{-1}** 3473, 2960, 2925, 2855, 1606, 1580, 1486, 1448, 1221, 1046, 1023; **LRMS (ESI$^-$)** m/z 397 (71), 361 (33), 325 ([M − H]$^-$, 100); **HRMS (ESI$^+$)** calculated for [$C_{20}H_{22}O_4Na$] 349.14103, found 349.14158. **Diastereomer 2** (7.5 mg, 0.023 mmol, 29%) a colourless oil. **R_f:** 0.29 (40% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.19 (2 H, ddd, J = 8.2, 7.2, 1.7 Hz, 2 × Ar–H), 7.07 (2 H, dd, J = 7.9, 1.7 Hz, 2 × Ar–H), 6.86–6.82 (2 H, m, 2 × Ar–H), 6.76 (2 H, dd, J = 8.2, 1.3 Hz, 2 × Ar–H), 3.94 (2 H, dd, J = 11.2, 3.7 Hz, 2 × OCHH), 3.71 (2 H, dd, J = 11.2, 4.8 Hz, 2 × OCHH), 2.70–2.66 (2 H, m, 2 × OCHHCH), 2.51 (2 H, s, 2 × OH), 1.08 (6 H, d, J = 7.0 Hz, 2 × CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 155.5 (2 × C), 129.6 (2 × CH), 129.3 (2 × CH), 124.4 (2 × C), 120.6 (2 × CH), 116.6 (2 × CH), 77.7 (2 × C), 70.4 (2 × CH_2), 33.8 (2 × CH), 14.8 (2 × CH_3); **ν_{max}/cm^{-1}** 3485, 2962, 2927, 2874, 1607, 1580, 1487, 1450, 1310, 1225, 1047, 1025; **LRMS (ESI$^-$)** m/z 361 (100), 325 ([M − H]$^-$, 30); **HRMS (ESI$^+$)** calculated for [$C_{20}H_{22}O_4Na$] 349.14103, found 349.14156.

8,8′-Dichloro-3,3′dimethyl-[4,4′bichromane]-4,4′-diol (15c). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **15a** (72 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.39 mL, 1.6 mmol), formic acid (60 μL, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (465 nm) for 1 h 40 min. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (30 mL, 1 M solution), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (30–50% diethyl ether in hexanes) to give **15c** as a mixture of diastereomers. **Diastereomer 1** (6.5 mg, 0.020 mmol, 20%) a pale yellow oil. R_f: 0.24 (40% diethyl ether in hexanes); **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 7.34 (2 H, dd, J = 7.8, 1.6 Hz, 2 × Ar–H), 7.06 (2 H, dd, J = 7.9, 1.5 Hz, 2 × Ar–H), 6.82 (2 H, t, J = 7.9 Hz, 2 × Ar–H), 4.67 (2 H, dd, J = 11.0, 3.9 Hz, 2 × OCHH), 3.92 (2 H, dd, J = 11.0, 5.5 Hz, 2 × OCHH), 2.44–2.38 (4 H, m, 2 × (CHCH$_3$ and OH)), 0.71 (6 H, d, J = 6.9 Hz, 2 × CH$_3$); **^{13}C NMR (101 MHz, CDCl$_3$) δ:** 151.4 (2 × C), 130.2 (2 × CH), 127.5 (2 × CH), 126.6 (2 × C), 121.3 (2 × C), 119.9 (2 × CH), 76.5 (2 × C), 70.7 (2 × CH$_2$), 33.5 (2 × CH), 13.5 (2 × CH$_3$); **ν_{max}/cm^{-1}** 3495, 2962, 2928, 2856, 1474, 1444, 1289, 1245, 1125, 1081, 1027; **HRMS (ESI$^+$)** calculated for [$C_{10}H_{11}O_2{}^{35}Cl^{35}ClNa$] 417.06309, found 417.06300, calculated for [$C_{10}H_{11}O_2{}^{35}Cl^{37}ClNa$] 419.06014, found 419.06013; **Diastereomer 2** (6.5 mg, 0.020 mmol, 20%) a pale yellow oil. R_f: 0.19 (40% diethyl ether in hexanes); **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 7.31 (2 H, dd, J = 7.8, 1.6 Hz, 2 × Ar–H), 6.99 (2 H, dd, J = 8.0, 1.6 Hz, 2 × Ar–H), 6.80 (2 H, t, J = 7.9 Hz, 2 × Ar–H), 4.15 (2 H, dd, J = 11.3, 3.8 Hz, 2 × OCHH), 3.89 (2 H, dd, J = 11.3, 4.5 Hz, 2 × OCHH), 2.70–2.66 (2 H, m, 2 × CHCH$_3$), 2.47 (2 H, s, 2 × OH), 1.07 (6 H, d, J = 7.0 Hz, 2 × CH$_3$); **^{13}C NMR (101 MHz, CDCl$_3$) δ:** 151.2 (2 × C), 130.3 (2 × CH), 127.8 (2 × CH), 125.7 (2 × C), 121.5 (2 × C), 120.5 (2 × CH), 77.8 (2 × C), 71.0 (2 × CH$_2$), 33.6 (2 × CH), 14.8 (2 × CH$_3$); **ν_{max}/cm^{-1}** 3520, 2963, 2931, 1597, 1476, 1444, 1245, 1080; **HRMS (ESI$^+$)** calculated for [$C_{10}H_{11}O_2{}^{35}Cl^{35}ClNa$] 417.06309, found 417.06314, calculated for [$C_{10}H_{11}O_2{}^{35}Cl^{37}ClNa$] 419.06014, found 419.06019.

8,8′-Difluoro-3,3′dimethyl-[4,4′bichromane]-4,4′-diol (16c). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **16a** (72 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.39 mL, 1.6 mmol), formic acid (60 μL, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (465 nm) for 18 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (1 M; 30 mL), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (30–50% diethyl ether in hexanes) to give compound **16c** as a mixture of diastereomers. **Diastereomer 1** a pale yellow oil (7 mg, 0.020 mmol, 24%). R_f: 0.24 (40% diethyl ether in hexanes); **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 7.03 (2 H, ddd, J = 10.7, 8.0, 1.7 Hz, 2 × Ar–H), 6.86 (2 H, dt, J = 8.1, 1.5 Hz, 2 × Ar–H), 6.78 (2 H, td, J = 8.0, 5.0 Hz, 2 × Ar–H), 4.13 (2 H, dd, J = 11.3, 3.7 Hz, 2 × OCHH), 3.89 (2 H, dd, J = 11.3, 4.3 Hz, 2 × OCHH), 2.74–2.65 (2 H, m, 2 × CHCH$_3$), 2.49 (2 H, s, 2 × OH), 1.09 (6 H, d, J = 7.0 Hz, 2 × CH$_3$); **^{13}C NMR (101 MHz, CDCl$_3$) δ:** 151.3 (2 C, d, J = 245.3 Hz, 2 × C), 144.0 (2 C, d, J = 11.2 Hz, 2 × C), 126.5 (2 C, d, J = 1.0 Hz, 2 × C), 124.2 (2 C, d, J = 3.6 Hz, 2 × CH), 119.7 (2 C, d, J = 7.2 Hz, 2 × CH), 115.9 (2 C, d, J = 17.9 Hz, 2 × CH), 77.4 (2 × C), 70.9 (2 × CH$_2$), 33.5 (2 × CH), 14.8 (2 × CH$_3$); **^{19}F NMR (376 MHz, CDCl$_3$) δ:** −136.60; **ν_{max}/cm^{-1}** 3503, 2958, 2924, 2854, 1484, 1258, 1224; **HRMS (ESI$^+$)** calculated for [$C_{20}H_{20}O_4FNa$] 385.12219, found 385.12287; **Diastereomer 2** a pale yellow oil (7 mg, 0.020 mmol, 24%). R_f: 0.17 (40% diethyl ether in hexanes); **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 7.07 (2 H, ddd, J = 10.7, 8.0, 1.5 Hz, 2 × Ar–H), 6.99 (2 H, dt, J = 8.1, 1.4 Hz, 2 × Ar–H), 6.83 (2 H, td, J = 8.0, 5.0 Hz, 2 × Ar–H), 4.59 (2 H, dd, J = 11.0, 3.9 Hz, 2 × OCHH), 3.86 (2 H, dd, J = 11.0, 5.8 Hz, 2 × OCHH), 2.53 (2 H, s, 2 × OH), 2.45–2.36 (2 H, m, 2 × CHCH$_3$), 0.69 (6 H, d, J = 6.9 Hz, 2 × CH$_3$); **^{13}C NMR (101 MHz, CDCl$_3$) δ:** 151.2 (2 C, d, J = 245.5 Hz, 2 × C), 144.2 (2 C, d, J = 11.1 Hz, 2 × C), 127.7 (2 × C), 124.0 (2 C, d, J = 3.6 Hz, 2 × CH), 119.3 (2 C, d, J = 7.0 Hz, 2 × CH), 115.9 (2 C, d, J = 17.9 Hz, 2 × CH), 76.2 (2 C, d, J = 2.6 Hz, 2 × C), 70.6 (2 × CH$_2$), 33.9 (2 × CH), 13.3 (2 × CH$_3$); **^{19}F NMR (376 MHz, CDCl$_3$) δ:** −136.78; **ν_{max}/cm^{-1}** 3510, 2959, 2925, 2854, 1483, 1455, 1258, 1220; **HRMS (ESI$^+$)** calculated for [$C_{20}H_{20}O_4FNa$] 385.12219, found 385.12268.

1,1′,2,2′,3,3′,4,4a,4′,4′a,9a,9′a-Dodecahydro-9*H*,9′*H*-[9,9′-bixanthene]-9,9′-diol (20c). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **20b** (78 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.39 mL, 1.6 mmol), formic acid (60 μL, 1.6 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (465 nm) for 18 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (30 mL, 1 M solution), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (2.5–10% diethyl ether in hexanes) to give **20c**. **Diastereomer 1** (10 mg, 0.024 mmol, 30%) a colourless oil. R_f: 0.48 (25% diethyl ether in hexanes); **^{1}H NMR (500 MHz, CDCl$_3$) δ:** 7.26–7.23 (2 H, m, 2 × Ar–H), 6.88 (2 H, dd, J = 8.2, 0.9 Hz, 2 × Ar–H), 6.81–6.78 (2 H, m, 2 × Ar–H), 6.65 (2 H, dd, J = 7.8, 1.5 Hz, 2 × Ar–H), 5.09 (2 H, brs, 2 × OCH), 2.23 (2 H, ddd, J = 12.3, 4.1, 2.6 Hz, 2 × CCH), 2.18–2.15 (2 H, m, 2 × OCHCHH), 1.80 (2 H, s, 2 × OH), 1.76–1.73 (2 H, m, 2 × CCHCHHCHH), 1.70–1.65 (2 H, m, 2 × CCHCHH), 1.61–1.55 (6 H, m, 2 × OCHCHHCH$_2$), 1.36–1.29 (2 H, m, 2 × CCHCHHCHH), 0.89 (2 H, qd, J = 12.9, 3.7 Hz, 2 × CCHCHH); **^{13}C NMR (126 MHz, CDCl$_3$) δ:** 155.6 (2 × C), 129.7 (2 × CH), 128.3 (2 × CH), 122.7 (2 × C), 118.6 (2 × CH), 115.6 (2 × CH), 77.3 (2 × C), 71.1 (2 × CH), 38.4 (2 × CH), 31.2 (2 × CH$_2$), 25.1 (2 × CH$_2$), 23.0 (2 × CH$_2$), 19.9 (2 × CH$_2$); **ν_{max}/cm^{-1}** 3558, 2932, 2857, 1605, 1579, 1481, 1451, 1232;

LRMS (ESI$^+$) ***m/z*** 653 (55), 543 (26), 441 (35), 429 ([M + Na]$^+$, 26), 393 (100), 283 (35); **HRMS (ESI$^+$)** calculated for [$C_{26}H_{30}O_4Na$] 429.20363, found 429.20442; **Diastereomer 2** (7 mg, 0.0168 mmol, 21%) a colourless oil. R_f: 0.34 (30% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.18–7.15 (2 H, m, 2 × Ar–H), 6.80–6.73 (6 H, m, 6 × Ar–H), 4.33 (2 H, brs, 2 × OCH), 2.77 (2 H, s, 2 × OH), 2.42–2.38 (2 H, m, 2 × CCH), 2.00–1.97 (2 H, m, 2 × OCHCHH), 1.83–1.75 (4 H, m, 2 × CCHCHHCHHH), 1.59–1.48 (6 H, m, 2 × OCHCHHCH$_2$), 1.35–1.33 (2 H, m, 2 × CCHCHHCHH), 1.07 (2 H, qd, J = 12.8, 3.4 Hz, CCHCHH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 155.2 (2 × C), 129.5 (2 × CH), 128.8 (2 × CH), 123.7 (2 × C), 120.0 (2 × CH), 116.2 (2 × CH), 77.9 (2 × C), 72.1 (2 × CH), 39.2 (2 × CH), 31.0 (2 × CH_2), 25.4 (2 × CH_2), 23.0 (2 × CH_2), 19.7 (2 × CH_2); **ν_{max}/cm^{-1}** 3484, 2932, 2860, 1606, 1580, 1483, 1453, 1232; **HRMS (ESI$^+$)** calculated for [$C_{26}H_{30}O_4Na$] 429.20363, found 429.20435.

4-(1-Hydroxy-1-phenylethyl)-3-methylchroman-4-ol (49). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution **7b** (69 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (0.12 mL, 0.32 mmol), formic acid (16 μL, 0.32 mmol), acetophenone (0.10 mL, 0.82 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.4 μmol). The mixture was degassed for 15 min at 0 °C before irradiating with blue light (465 nm) for 6 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (30 mL, 1 M solution), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (0–5% diethyl ether in dichloromethane) to give **49** as a mixture of diastereomers. **Diastereomer 1** (6 mg, 0.022 mmol, 13%) a colourless oil. R_f: 0.16 (15% diethyl ether in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 7.64 (1 H, dd, J = 7.8, 1.7 Hz, Ar–H), 7.63–7.60 (2 H, m, 2 × Ar–H), 7.36–7.33 (2 H, m, 2 × Ar–H), 7.30–7.22 (3 H, m, 3 × Ar–H), 6.99–6.95 (1 H, m, Ar–H), 6.82 (1 H, dd, J = 8.2, 1.2 Hz, Ar–H), 4.84 (1 H, dd, J = 10.9, 3.3 Hz, OCHH), 3.81 (1 H, dd, J = 10.9, 2.3 Hz, OCHH), 2.00 (1 H, s, OH), 1.84 (1 H, qdd, J = 7.1, 3.3, 2.3 Hz, OCHHCH), 1.74 (3 H, s, CCH$_3$), 1.56 (1 H, s, OH), 0.84 (3 H, d, J = 7.1 Hz, CHCH$_3$); **^{13}C NMR (125 MHz, $CDCl_3$) δ:** 155.3 (C), 144.4 (C), 129.6 (CH), 128.7 (CH), 128.0 (2 × CH), 127.1 (CH), 126.6 (2 × CH), 123.1 (C), 119.8 (CH), 116.3 (CH), 79.7 (C), 76.3 (C), 70.0 (CH_2), 33.3 (CH), 27.2 (CH_3), 14.8 (CH_3). **Diastereomer 2** (7.5 mg, 0.026 mmol, 16%). R_f: 0.31 (2% diethyl ether in dichloromethane); **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 7.56 (1 H, dd, J = 7.9, 1.7 Hz, Ar–H), 7.26–7.18 (26 H, m, Ar–H, 2 × Ar–H, 10 × Ar–H and 10 × Ar–H), 7.13–7.12 (2 H, m, 2 × Ar–H), 7.07 (2 H, dd, J = 7.9, 1.7 Hz, 2 × Ar–H), 6.94 (1 H, ddd, J = 7.9, 7.2, 1.3 Hz, Ar–H), 6.84 (2 H, ddd, J = 7.9, 7.2, 1.3 Hz, 2 × Ar–H), 6.76 (2 H, dd, J = 8.2, 1.3 Hz, 2 × Ar–H), 6.74 (1 H, dd, J = 8.2, 1.4 Hz, Ar–H), 3.93 (2 H, dd, J = 11.2, 3.7 Hz, 2 × OCHH), 3.71 (2 H, dd, J = 11.2, 4.8 Hz, 2 × OCHH), 3.53 (1 H, dd, J = 11.5, 3.4 Hz, OCHH), 3.19 (1 H, dd, J = 11.5, 3.3 Hz, OCHH), 2.70–2.65 (2 H, m, 2 × CHCH$_3$), 2.70 (1 H, s, OH), 2.68 (1 H, s, OH), 2.57 (2 H, s, 2 × OH), 2.53 (2 H, s, 2 × OH), 2.47 (1 H, qt, J = 7.1, 3.4 Hz, CH), 2.27 (2 H, s, 2 × OH), 1.69 (3 H, s, CCH$_3$), 1.59 (6 H, s, 2 × CH$_3$), 1.51 (6 H, s, 2 × CH$_3$), 1.08 (6 H, d, J = 7.0 Hz, 2 × CH$_3$), 0.92 (3 H, d, J = 7.2 Hz, CHCH$_3$); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 155.5 (2 × C), 155.4 (C), 144.4 (C), 143.9 (2 × C), 143.6 (2 × C), 129.6 (2 × CH), 129.5 (CH), 129.3 (2 × CH), 129.0 (CH), 128.1 (CH), 127.5 (4 × CH), 127.43 (4 × CH), 127.37 (CH), 127.3 (CH and 4 × CH), 127.2 (2 × CH), 127.1 (4 × CH), 127.0 (2 × CH), 126.4 (2 × CH), 124.4 (2 × C), 123.4 (C), 120.6 (2 × CH), 120.1 (CH), 116.6 (2 × CH), 116.4 (CH), 79.8 (C), 79.0 (2 × C), 78.7 (2 × C), 77.6 (2 × C), 75.8 (C), 70.4 (2 × CH_2), 70.0 (CH_2), 33.7 (2 × CH), 32.3 (CH), 27.2 (CH_3), 25.3 (2 × CH_3), 25.1 (2 × CH_3), 14.78 (2 × CH_3), 14.77 (CH_3).

3-Methylenechroman-4-one.[60] To a solution of diisopropylamine (14 mL, 100 mmol) in Et_2O (100 mL) at 0 °C was added dropwise trifluoroacetic acid (7.7 mL, 100 mmol). After 5 min the precipitate was collected by vacuum filtration to give diisopropylammonium trifluoroacetate (21.2 g, 100 mmol, 100%) as a white solid. The product was used without further purification. To a solution of 4-chromanone (6.50 g, 43.9 mmol) in THF (43 mL) was added paraformaldehyde (5.27 g, 175 mmol), diisopropylammonium trifluoroacetate (18.9 g, 87.7 mmol) and trifluoroacetic acid (0.34 mL, 4.4 mmol). The mixture was heated at reflux for 48 h. Water (50 mL) was added and the aqueous phase extracted with diethyl ether (3 × 75 mL). The organic extracts were washed with aqueous NaOH (100 mL, 1 M solution), hydrochloric acid (100 mL, 1 M solution), brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (10–15% diethyl ether in hexanes) to give 3-methylenechroman-4-one (2.26 g, 14.1 mmol, 32%) as a white solid. R_f: 0.26 (10% diethyl ether in hexanes); **m.p.** 56–57 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.99 (1 H, dd, J = 7.9, 1.8 Hz, Ar–H), 7.49 (1 H, ddd, J = 8.4, 7.1, 1.8 Hz, Ar–H), 7.06 (1 H, ddd, J = 8.0, 7.1, 1.0 Hz, Ar–H), 6.98 (1 H, dd, J = 8.3, 1.0 Hz, Ar–H), 6.31 (1 H, t, J = 1.2 Hz, C=CHH), 5.58 (1 H, td, J = 1.7, 1.0 Hz, C=CHH), 5.01 (2 H, t, J = 1.5 Hz, OCH$_2$); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 182.1 (C), 162.1 (C), 139.0 (C), 136.1 (CH), 128.1 (CH), 122.5 (CH_2), 122.1 (CH), 122.0 (C), 118.2 (CH), 71.3 (CH_2); **ν_{max}/cm^{-1}** 2983, 2855, 1685, 1608, 1475, 1465, 1322, 1212, 1148, 1111; **LRMS (ESI$^+$)** ***m/z*** 497 (27), 479 (40), 355 (33), 321 (100), 237 (46), 161 ([M + H]$^+$, 12).

3-(But-3-en-1-yl)chroman-4-one (53b). To a solution of 3-methylenechroman-4-one (30 mg, 0.19 mmol) in CH_2Cl_2 (1.8 mL) at 0 °C was added trimethylallylsilane (0.15 mL, 0.94 mmol) and iodine (48 mg, 0.19 mmol). The mixture was stirred at room temperature for 16 h. Water (10 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic extracts were washed with saturated aqueous sodium thiosulfate (15 mL), brine (15 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5–10% diethyl ether in hexanes) to give **53b** (8 mg, 0.04 mmol, 21%) as a yellow oil. R_f: 0.36 (diethyl ether in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 7.89 (1 H, dd, J = 7.9, 1.8 Hz, Ar–H), 7.46 (1 H, ddd, J = 8.4, 7.1, 1.8 Hz, Ar–H), 7.01 (1 H, ddd, J = 7.9, 7.1, 1.0 Hz, Ar–H), 6.95 (1 H, dd, J = 8.4, 1.0 Hz, Ar–H), 5.81 (1 H, ddt, J = 17.1, 10.2, 6.6 Hz, CH=CHH), 5.08 (1 H, dq, 17.1, 1.7 Hz, CH=CHH),

5.01 (1 H, dq, J = 10.2, 1.5 Hz, CH=CHH), 4.52 (1 H, dd, J = 11.5, 4.5 Hz, OCHH), 4.27 (1 H, dd, J = 11.5, 8.7 Hz, OCHH), 2.71–2.69 (1 H, m, OCHHCH), 2.24–2.18 (2 H, m, $CH_2CH=CH_2$), 2.05–2.02 (1 H, m, OCH_2CHCHH), 1.60–1.57 (1 H, m, OCH_2CHCHH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 194.5 (C), 161.6 (C), 137.6 (CH), 135.9 (CH), 127.6 (CH), 121.5 (CH), 120.8 (C), 117.8 (CH), 115.8 (CH_2), 70.5 (CH_2), 45.3 (CH), 31.1 (CH_2), 25.6 (CH_2); ν_{max}/**cm^{-1}** 3075, 2978, 2923, 2871, 1690, 1606, 1479, 1325, 1298, 1215; **LRMS (ESI$^+$)** m/z 499 (23), 457 (38), 427 (100), 225 ([M + Na]$^+$, 35); **HRMS (ESI$^+$)** calculated for $[(C_{13}H_{14}O_2)_2Na]$ 427.18798, found 427.18771.

3,3′-Di(but-3-en-1-yl)-[4-4′-bichromane]-4,4′diol (53c). MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **53b** (32 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (78 μL, 0.32 mmol), formic acid (12 μL, 0.32 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.4 μmol). The mixture was degassed for 15 min before irradiating with blue light (465 nm) for 6 h. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (30 mL, 1 M solution), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (20% diethyl ether in hexanes) to give **53c** (19.5 mg, 0.048 mmol, 59%) as a 1 : 1 mixture of diastereomers. **Diastereomer 1**, a yellow solid. R_f: 0.22 (20% diethyl ether in hexanes); **m.p.** 76–78 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.18 (2 H, ddd, J = 8.2, 7.2, 1.7 Hz, 2 × Ar–H), 7.00 (2 H, dd, J = 7.9, 1.6 Hz, 2 × Ar–H), 6.82 (2 H, ddd, J = 8.0, 7.2, 1.3 Hz, 2 × Ar–H), 6.75 (2 H, dd, J = 8.2, 1.3 Hz, 2 × Ar–H), 5.77 (2 H, dddd, J = 17.2, 10.2, 7.1, 6.2 Hz, 2 × CH=CHH), 5.01 (2 H, dq, J = 17.2, 1.7 Hz, 2 × CH=CHH), 4.96 (2 H, ddt, J = 10.2, 2.1, 1.1 Hz, 2 × CH=CHH), 3.98 (2 H, dd, J = 11.6, 3.3 Hz, 2 × OCHH), 3.88 (2 H, dd, J = 11.6, 4.2 Hz, 2 × OCHH), 2.64 (2 H, s, 2 × OH), 2.47–2.45 (2 H, m, 2 × OCHHCH), 2.23–2.21 (2 H, m, 2 × CHHCH=CH_2), 2.09–2.06 (2 H, m, 2 × CHHCH=CH_2), 1.86–1.80 (2 H, m, 2 × OCH_2CHCHH), 1.37–1.26 (2 H, m, 2 × OCH_2CHCHH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 155.5 (2 × C), 138.4 (2 × CH), 129.6 (2 × CH), 128.9 (2 × CH), 124.8 (2 × C), 120.6 (2 × CH), 116.6 (2 × CH), 115.3 (2 × CH_2), 77.7 (2 × C), 67.0 (2 × CH_2), 38.0 (2 × CH), 31.9 (2 × CH_2), 26.8 (2 × CH_2); ν_{max}/**cm^{-1}** 3482, 3074, 2925, 2866, 1639, 1606, 1579, 1487, 1450, 1306, 1280, 1225, 1019; **LRMS (ESI$^+$)** m/z 429 ([M + Na]$^+$, 100), 393 (53); **HRMS (ESI$^+$)** calculated for $[C_{26}H_{30}O_4Na]$ 429.20363, found 429.20443. **Diastereomer 2**, a yellow solid. R_f: 0.27 (20% diethyl ether in hexanes); **m.p.** 133–135 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.24 (2 H, ddd, J = 8.2, 7.2, 1.7 Hz, 2 × Ar–H), 7.13 (2 H, dd, J = 7.7, 1.5 Hz, 2 × Ar–H), 6.92–6.86 (4 H, m, 4 × Ar–H), 5.59 (2 H, ddt, J = 17.0, 10.2, 6.7 Hz, 2 × CH=CHH), 4.95–4.88 (4 H, m, 2 × CH=CH_2), 4.61 (2 H, dd, J = 11.1, 3.6 Hz, 2 × OCHH), 3.92 (2 H, dd, J = 11.2, 5.3 Hz, 2 × OCHH), 2.48 (2 H, s, 2 × OH), 2.19–2.15 (2 H, m, 2 × OCHHCH), 2.12–2.01 (2 H, m, 2 × CHHCH=CH_2), 1.89–1.78 (2 H, m, 2 × CHHCH=CH_2), 1.36–1.29 (2 H, m, 2 × OCH_2CHCHH), 1.08–1.03 (2 H, m, 2 × OCH_2CHCHH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 155.9 (2 × C), 138.3 (2 × CH), 129.6 (2 × CH), 128.6 (2 × CH), 124.9 (2 × C), 120.0 (2 × CH), 116.5 (2 × CH), 115.1 (2 × CH_2), 76.5 (2 × C), 67.0 (2 × CH_2), 38.2 (2 × CH), 32.0 (2 × CH_2), 26.4 (2 × CH_2); ν_{max}/**cm^{-1}** 3465, 3074, 2925, 2861, 1486, 1449, 1280, 1220, 1044, 1020; **LRMS (ESI$^+$)** m/z 429 ([M + Na]$^+$, 76), 393 (100); **HRMS (ESI$^+$)** calculated for $[C_{26}H_{30}O_4Na]$ 429.20363, found 429.20446.

Thioester stability studies

***S*-(2-Iodophenethyl) 5-formyl-2-hydroxybenzothioate.** To a solution of 5-formylsalicylic acid (1.36 g, 8.38 mmol) in dichloromethane (15 mL) at 0 °C was added CDI (0.68 g, 4.19 mmol). The mixture was stirred at 0 °C for 30 min before a solution of compound **6** (0.74 g, 2.8 mmol) in dichloromethane (3 mL) was added. The reaction was heated at 40 °C for 16 hours. The mixture was cooled and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (20–25% dichloromethane in hexanes) to give *S*-(2-iodophenethyl) 5-formyl-2-hydroxybenzothioate (0.48 g, 1.2 mmol, 42%) as a white solid. R_f: 0.36 (60% dichloromethane in hexanes); **m.p.** 112–114 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 11.64 (1 H, s, OH), 9.89 (1 H, s, CHO), 8.37 (1 H, d, J = 2.0 Hz, Ar–H), 7.99 (1 H, dd, J = 8.7, 1.9 Hz, Ar–H), 7.85–7.83 (1 H, m, Ar–H), 7.32–7.30 (2 H, m, 2 × Ar–H), 7.10 (1 H, d, J = 8.7 Hz, Ar–H), 6.95 (1 H, ddd, J = 8.0, 5.3, 3.7 Hz, Ar–H), 3.38–3.35 (2 H, m, SCH_2), 3.14–3.11 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 197.3 (C), 189.7 (CH), 164.4 (C), 142.1 (C), 139.9 (CH), 135.9 (CH), 132.5 (CH), 130.2 (CH), 128.84 (CH), 128.79 (C), 128.72 (CH), 120.0 (C), 119.5 (CH), 100.5 (C), 40.3 (CH_2), 29.2 (CH_2); ν_{max}/**cm^{-1}** 3055, 2926, 2828, 1693, 1625, 1584, 1480, 1197, 1147; **LRMS (ESI$^-$)v** m/z 471 (384), 411 ([M − H]$^-$, 100); **HRMS (ESI$^+$)** calculated for $[C_{16}H_{14}O_3SI]$ 412.97028, found 412.96977.

***S*-(2-Iodophenethyl) 2-(allyloxy)-5-formylbenzothioate (55).** To a solution of *S*-(2-iodophenethyl) 5-formyl-2-hydroxybenzothioate (100 mg, 0.24 mmol) in acetonitrile (1.5 mL) was added triethylamine (0.34 mL, 2.4 mmol) and allyl bromide (0.21 mL, 2.4 mmol). The reaction was heated at 60 °C for 72 h. The reaction was quenched with hydrochloric acid (10 mL, 1 M solution). The aquesous phase was extracted with ethyl acetate (3 × 15 mL). The organic extracts were washed with brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (30–40% diethyl ether in hexanes) to give **55** (104 mg, 0.23 mmol, 95%) as a pale yellow solid. R_f: 0.11 (20% diethyl ether in hexanes); **m.p.** 54–56 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 9.93 (1 H, s, CHO), 8.28 (1 H, d, J = 2.0 Hz, Ar–H), 8.00 (1 H, dd, J = 8.7, 1.9 Hz, Ar–H), 7.84 (1 H, d, J = 7.9 Hz, Ar–H), 7.35 (1 H, dd, J = 7.7, 1.6 Hz, Ar–H), 7.31 (1 H, t, J = 7.4 Hz, Ar–H), 7.09 (1 H, d, J = 8.7 Hz, Ar–H), 6.93 (1 H, td, J = 7.5, 1.6 Hz, Ar–H), 6.13–6.05 (1 H, m, CH=CHH); 5.52–5.48 (1 H, m, CH=CHH), 5.38–5.35 (1 H, m, CH=CHH), 4.77 (2 H, dt, J = 5.2, 1.6 Hz, OCH_2), 3.31–3.28 (2 H, m, SCH_2), 3.12–3.09 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.1 (CH), 190.0 (C), 161.3 (C), 142.8 (C), 139.7 (CH), 134.1 (CH), 132.7 (CH), 131.7 (CH), 130.2 (CH), 129.5 (C), 128.6 (CH), 128.5 (CH), 127.9 (C), 118.9 (CH_2), 113.6 (CH), 100.5 (C), 70.1 (CH_2), 40.4 (CH_2),

29.8 (CH_2); ν_{max}/cm^{-1} 2924, 1694, 1634, 1596, 1493, 1422, 1276, 1263, 1231, 1164, 1115, 1008; **LRMS (ESI$^+$)** ***m*/*z*** 475 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{19}H_{17}IO_3SNa$] 474.98353, found 474.98317.

***S*-(2-Iodophenethyl) 2-(allyloxy)-5-(1,3-dioxolan-2-yl)benzothioate (56).** To a solution of **55** (22 mg, 0.049 mmol) in dichloromethane (50 μL) and freshly distilled ethylene glycol (500 μL) was added *p*-toluenesulfonic acid monohydrate (2 mg, 0.01 mmol) and 3 Å molecular sieves. The reaction was stirred at room temperature for 16 h. Water (10 mL) was added and the aqueous phase extracted with dichloromethane (3 × 10 mL). The organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (10–20% ethyl acetate in hexanes) to give **56** (20 mg, 0.040 mmol, 82%) as a colourless oil. ***R*$_f$:** 0.15 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$) *δ*:** 7.91 (1 H, d, *J* = 2.3 Hz, Ar–H), 7.82 (1 H, dd, *J* = 7.9, 1.3 Hz, Ar–H), 7.56 (1 H, dd, *J* = 8.6, 2.4 Hz, Ar–H), 7.35 (1 H, dd, *J* = 7.6, 1.8 Hz, Ar–H), 7.30 (1 H, td, *J* = 7.4, 1.3 Hz, Ar–H), 6.97 (1 H, d, *J* = 8.6 Hz, Ar–H), 6.92 (1 H, td, *J* = 7.6, 1.8 Hz, Ar–H), 6.08 (1 H, ddt, *J* = 17.3, 10.6, 5.2 Hz, CH=CHH), 5.78 (1 H, s, ArCH), 5.47 (1 H, dq, *J* = 17.3, 1.6 Hz, CH=CHH), 5.31 (1 H, dq, *J* = 10.6, 1.4 Hz, CH=CHH), 4.68 (2 H, dt, *J* = 5.1, 1.6 Hz, CH_2CH=), 4.15–4.12 (2 H, m, OCHHCHHO), 4.04–4.01 (2 H, m, OCHHCHHO), 3.28–3.24 (2 H, m, SCH_2), 3.11–3.07 (2 H, m, SCH_2CH_2); **^{13}C NMR (126 MHz, $CDCl_3$) *δ*:** 190.6 (C), 157.7 (C), 143.1 (C), 139.7 (CH), 132.6 (CH), 131.8 (CH), 130.5 (C), 130.3 (CH), 128.6 (CH), 128.5 (2 × CH), 127.3 (C), 118.3 (CH_2), 113.5 (CH), 103.2 (CH), 100.5 (C), 70.0 (CH_2), 65.5 (2 × CH_2), 40.6 (CH_2), 29.6 (CH_2); ν_{max}/cm^{-1} 2923, 2886, 1692, 1672, 1634, 1596, 1495, 1465, 1274, 1165, 1119, 1008; **HRMS (ESI$^+$)** calculated for [$C_{21}H_{21}IO_4SNa$] 519.00974, found 519.00979.

Ethyl (*E*)-3-(4-(allyloxy)-3-(((2-iodophenethyl)thio)carbonyl)phenyl) acrylate (60). To a solution of **55** (20 mg, 0.044 mmol) in dichloromethane (0.5 mL) was added ethyl 2-(triphenyl-λ^5-phosphanylidene)acetate (17 mg, 0.049 mmol). The reaction was stirred at room temperature for 14 h. The mixture was concentrated *in vacuo* and the residue purified by flash chromatography on silica gel (20–30% diethyl ether in hexanes) to give **60** (20 mg, 0.039 mmol, 88%) as a white solid. ***R*$_f$:** 0.2 (25% diethyl ether in hexanes); **m.p.** 77–79 °C; **^{1}H NMR (500 MHz, $CDCl_3$) *δ*:** 7.95 (1 H, d, *J* = 2.4 Hz, Ar–H), 7.83 (1 H, dd, *J* = 7.9, 1.2 Hz, Ar–H), 7.63 (1 H, d, *J* = 16.0 Hz, ArCH=CH), 7.59 (1 H, dd, *J* = 8.7, 2.3 Hz, Ar–H), 7.35 (1 H, dd, *J* = 7.6, 1.9 Hz, Ar–H), 7.30 (1 H, td, *J* = 7.4, 1.3 Hz, Ar–H), 6.97 (1 H, d, *J* = 8.7 Hz, Ar–H), 6.93 (1 H, td, *J* = 7.5, 1.9 Hz, Ar–H), 6.37 (1 H, d, *J* = 16.0 Hz ArCH=CH), 6.08 (1 H, ddt, *J* = 17.3, 10.6, 5.2 Hz, CH=CHH), 5.48 (1 H, dq, *J* = 17.3, 1.6 Hz, CH=CHH), 5.33 (1 H, dq, *J* = 10.6, 1.4 Hz, CH=CHH), 4.70 (2 H, dt, *J* = 5.1, 1.6 Hz, $ArOCH_2$), 4.26 (2 H, q, *J* = 7.1 Hz, CO_2CH_2), 3.30–3.26 (2 H, m, SCH_2), 3.12–3.08 (2 H, m, SCH_2CH_2), 1.34 (3 H, t, *J* = 7.1 Hz, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$) *δ*:** 190.4 (C), 167.1 (C), 158.2 (C), 143.1 (CH), 142.9 (C), 139.7 (CH), 133.0 (CH), 132.2 (CH), 130.2 (CH), 129.6 (CH), 128.6 (CH), 128.5 (CH), 127.9 (C), 127.3 (C), 118.5 (CH_2), 117.6 (CH), 113.8 (CH), 100.5 (C), 70.0 (CH_2), 60.6 (CH_2), 40.5 (CH_2), 29.7 (CH_2), 14.5 (CH_3); ν_{max}/cm^{-1} 2979, 2929, 1708, 1636, 1598, 1495, 1260, 1166, 1120, 1010; **LRMS (ESI$^+$)** ***m*/*z*** 545 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{23}H_{23}IO_4SNa$] 545.02539, found 545.02578.

Trimethyl((1-phenylvinyl)oxy)silane (57).[61] To a solution of acetophenone (1.50 g, 12.5 mmol) in MeCN (10 mL) at 0 °C was added triethylamine (2.6 mL, 19 mmol) and chlorotrimethylsilane (2.4 mL, 19 mmol). After 5 min a solution of NaI (2.81 g, 18.7 mmol) in MeCN (21 mL) was added dropwise. The reaction was stirred at room temperature for 1 h. Water (20 mL) was added and the aqueous phase extracted with pentane (3 × 30 mL). The organic extracts were washed with sat. aq. NH_4Cl (20 mL), brine (50 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (0–10% diethyl ether in pentane) to give **57** (1.75 g, 9.10 mmol, 73%) as a colourless oil. ***R*$_f$:** 0.45 (in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 7.63–7.60 (2 H, m, 2 × Ar–H), 7.36–7.26 (3 H, m, 3 × Ar–H), 4.93 (1 H, d, *J* = 1.7 Hz, C=CHH), 4.45 (1 H, d, *J* = 1.7 Hz, C=CHH), 0.29 (9 H, s, 3 × CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) *δ*:** 155.8 (C), 137.7 (C), 128.3 (CH), 128.2 (2 × CH), 125.4 (2 × CH), 91.2 (CH_2), 0.22 (3 × CH_3); ν_{max}/cm^{-1} 2960, 1316, 1302, 1286, 1252, 1027, 1010; **LRMS (ESI$^+$)** ***m*/*z*** 295 (73), 193 ([M + H]$^+$, 100).

S*-(2-Iodophenethyl) 2-(allyloxy)-5-(1-hydroxy-3-oxo-3-phenylpropyl) benzothioate (58).** To a solution of **55** (23 mg, 0.051 mmol) and trimethyl(1-phenylvinyl)oxysilane (15 mg, 0.076 mmol) in dichloromethane (0.5 mL) at −40 °C was added $TiCl_4$ (6 μL, 0.06 mmol). The reaction was stirred at −40 °C for 3 h before quenching with sat. aq. NH_4Cl (10 mL). The aqueous phase extracted with dichloromethane (3 × 10 mL). The organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (20–30% ethyl acetate in hexanes) to give **58** (25 mg, 0.044 mmol, 86%) as a colourless oil. ***R*$_f$:** 0.14 (20% ethyl acetate in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) *δ*:** 7.97–7.95 (2 H, m, 2 × Ar–H), 7.84 (1 H, d, *J* = 2.4 Hz, Ar–H), 7.82 (1 H, dd, *J* = 7.9, 1.2 Hz, Ar–H), 7.60–7.55 (2 H, m, 2 × Ar–H), 7.49–7.45 (2 H, m, 2 × Ar–H), 7.35 (1 H, dd, *J* = 7.6, 1.8 Hz, Ar–H), 7.29 (1 H, td, *J* = 7.4, 1.2 Hz, Ar–H), 6.98 (1 H, d, *J* = 8.6 Hz, Ar–H), 6.91 (1 H, ddd, *J* = 7.8, 7.3, 1.8 Hz, Ar–H), 6.10 (1 H, ddt, *J* = 17.3, 10.6, 5.2 Hz, CH=CHH), 5.48 (1 H, dq, *J* = 17.3, 1.7 Hz, CH=CHH), 5.34–5.30 (2 H, m, CH=CHH + CHOH), 4.68 (2 H, dt, *J* = 5.1, 1.6 Hz, OCH_2), 3.66 (1 H, brs, OH), 3.38–3.35 (2 H, m, CH_2CHOH), 3.28–3.24 (2 H, m, SCH_2), 3.11–3.07 (2 H, m, SCH_2CH_2); **^{13}C NMR (101 MHz, $CDCl_3$) *δ*:** 200.2 (C), 190.9 (C), 156.6 (C), 143.1 (C), 139.7 (CH), 136.6 (C), 135.4 (C), 133.9 (CH), 132.7 (CH), 131.1 (CH), 130.2 (CH), 128.9 (2 × CH), 128.6 (CH), 128.4 (CH), 128.3 (2 × CH), 127.4 (C), 127.3 (CH), 118.2 (CH_2), 113.8 (CH), 100.5 (C), 70.1 (CH_2), 69.4 (CH), 47.2 (CH_2), 40.5 (CH_2), 29.7 (CH_2); ν_{max}/cm^{-1} 3487, 3059, 2924, 1676, 1634, 1494, 1285, 1254, 1211, 1120, 1010; **LRMS (ESI$^+$)** ***m*/*z 595 ([M + Na]$^+$, 100); **HRMS (ESI$^+$)** calculated for [$C_{27}H_{25}IO_4SNa$] 595.04104, found 595.04148.

***S*-(2-Iodophenethyl) 2-(allyloxy)-5-(((3-ethylphenyl)amino)methyl) benzothioate (62).** To a solution of **55** (20 mg,

0.044 mmol) in dichloromethane (0.75 mL) was added 3-ethylaniline (**61**) (16 mg, 0.13 mmol). The reaction was stirred at room temperature for 18 h. Sodium cyanoborohydride (14 mg, 0.22 mmol) was added and the reaction stirred at room temperature for 16 h. The mixture was concentrated *in vacuo* and the residue purified by flash chromatography on silica gel (20% diethyl ether in hexanes) to give **62** (22 mg, 0.040 mmol, 90%) as a yellow oil. R_f: 0.33 (25% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.83 (1 H, dd, J = 7.9, 1.2 Hz, Ar–H), 7.80 (1 H, d, J = 2.4 Hz, Ar–H), 7.46 (1 H, dd, J = 8.5, 2.4 Hz, Ar–H), 7.35 (1 H, dd, J = 7.6, 1.8 Hz, Ar–H), 7.29 (1 H, td, J = 7.4, 1.2 Hz, Ar–H), 7.10 (1 H, t, J = 7.7 Hz, Ar–H), 6.94 (1 H, d, J = 8.6 Hz, Ar–H), 6.94–6.92 (1 H, m, Ar–H), 6.59 (1 H, brd, J = 7.5 Hz, Ar–H), 6.49 (1 H, brt, J = 2.0 Hz, Ar–H), 6.46 (1 H, ddd, J = 8.0, 2.5, 0.8 Hz, Ar–H), 6.10 (1 H, ddt, J = 17.3, 10.6, 5.1 Hz, CH=CHH), 5.48 (1 H, dq, J = 17.2, 1.6 Hz, CH=CHH), 5.32 (1 H, dq, J = 10.6, 1.5 Hz, CH=CHH), 4.67 (2 H, dt, J = 5.1, 1.6 Hz, OCH_2), 4.29 (2 H, s, NCH_2), 4.01 (1 H, brs, NH), 3.28–3.25 (2 H, m, SCH_2), 3.11–3.08 (2 H, m, SCH_2CH_2), 2.57 (2 H, q, J = 7.6 Hz $ArCH_2$), 1.21 (3 H, t, J = 7.6 Hz, CH_3); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.9 (C), 156.3 (C), 148.1 (C), 145.6 (C), 143.1 (C), 139.7 (CH), 132.8 (CH), 132.7 (CH), 132.0 (C), 130.2 (CH), 129.4 (CH), 129.0 (CH), 128.6 (CH), 128.5 (CH), 127.5 (C), 118.2 (CH_2), 117.7 (CH), 113.9 (CH), 112.8 (CH), 110.4 (CH), 100.5 (C), 70.1 (CH_2), 47.7 (CH_2), 40.6 (CH_2), 29.7 (CH_2), 29.1 (CH_2), 15.6 (CH_3); ν_{max}/**cm^{-1}** 3408, 2962, 2928, 1667, 1633, 1604, 1493, 1284, 1268, 1164, 1122, 1010; **LRMS (ESI$^+$)** m/z 580 ($[M + Na]^+$, 100); **HRMS (ESI$^+$)** calculated for $[C_{27}H_{28}INO_2SNa]$ 580.07776, found 580.07835.

Synthesis of donepezil

2-Allyl-4,5-dimethoxybenzoic acid (65).[44] To a solution of 2-iodo-4,5-dimethoxybenzoic acid (**64**) (100 mg, 0.33 mmol) and lithium chloride (22 mg, 0.52 mmol) in THF (1 mL) at −40 °C was added methylmagnesium bromide (0.11 mL, 3 M solution in diethyl ether, 0.33 mmol). The mixture was stirred for 5 min at −40 °C. Isopropylmagnesium chloride (0.20 mL, 2 M solution in THF, 0.39 mmol) was added and the mixture stirred at −40 °C for 1.5 h. A solution of copper(I) cyanide (2 mg, 0.02 mmol) and lithium chloride (2 mg, 0.04 mmol) in THF (0.1 mL) was added and the mixture stirred at −40 °C for 1 h. Allyl bromide (0.09 mL, 1 mmol) was added and the reaction allowed to warm to room temperature overnight. The reaction was quenched with hydrochloric acid (5 mL, 1 M solution). The aqueous phase was extracted with ethyl acetate (3 × 15 mL). The organic extracts were washed with brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (10–20% ethyl acetate in hexanes) to give **65** (60 mg, 0.27 mmol, 83%) as a white solid. R_f: 0.10 (20% ethyl acetate in hexanes); **m.p.** 131–133 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 7.61 (1 H, s, Ar–H), 6.76 (1 H, s, Ar–H), 6.04 (1 H, ddt, J = 17.7, 9.5, 6.5 Hz, CH=CH_2), 5.07–5.02 (2 H, m, CH=CH_2), 3.94 (3 H, s, OCH_3), 3.92 (3 H, s, OCH_3), 3.82 (2 H, dt, J = 6.5, 1.5 Hz, CH_2); **^{13}C NMR (126 MHz, $CDCl_3$) δ:** 172.1 (C), 153.0 (C), 147.0 (C), 138.0 (C), 137.7 (CH), 119.7 (C), 115.7 (CH_2), 114.3 (CH), 113.6 (CH), 56.2 (CH_3), 56.1 (CH_3), 38.6 (CH_2); ν_{max}/**cm^{-1}** 3003, 2957, 1688, 1606, 1574, 1522, 1266, 1222, 1207, 1167; **LRMS (ESI$^-$)** m/z 465 (42), 430 (37), 221 ($[M - H]^-$, 100).

***tert*-Butyl 4-(2-iodoethyl)piperidine-1-carboxylate (67).**[62] To a solution of triphenylphosphine (5.60 g, 21.4 mmol) and imidazole (1.46 g, 21.4 mmol) in dichloromethane (120 mL) at 0 °C was added iodine (5.42 g, 21.4 mmol). The mixture was stirred at room temperature for 30 min before a solution of **66** (3.50 g, 15.3 mmol) in dichloromethane (30 mL) was added. The mixture was stirred at room temperature for 16 h. Water (200 mL) was added and the aqueous phase was extracted with diethyl ether (3 × 200 mL). The organic extracts were washed with sat. aq. $NaHCO_3$ (200 mL), aq. $Na_2S_2O_3$ (200 mL), brine (200 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (10% diethyl ether in hexanes) to give **67** (4.73 g, 13.9 mmol, 91%) as a colourless oil. R_f: 0.36 (20% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 4.08 (2 H, brs, 2 × NCHH), 3.21 (2 H, t, J = 7.2 Hz, CH_2I), 2.69 (2 H, brt, J = 12.5 Hz, 2 × NCHH), 1.77 (2 H, q, J = 7.0 Hz, CH_2CH_2I), 1.66–1.56 (3 H, m, 2 × NCH_2CHH and CH), 1.44 (9 H, s, 3 × CH_3), 1.09 (2 H, qd, J = 12.2, 4.3 Hz, 2 × NCH_2CHH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 154.9 (C), 79.5 (C), 43.9 (2 × CH_2), 40.0 (CH_2), 36.8 (CH), 31.3 (2 × CH_2), 28.6 (3 × CH_3), 4.0 (CH_2); ν_{max}/**cm^{-1}** 2973, 2925, 2848, 1687, 1447, 1364, 1277, 1223, 1161, 1111; **LRMS (ESI$^+$)** m/z 701 (55), 362 ($[M + Na]^+$, 100).

***tert*-Butyl 4-vinylpiperidine-1-carboxylate (68).**[63] To a solution of **67** (5.26 g, 15.5 mmol) in THF (78 mL) was added potassium *tert*-butoxide (3.48 g, 31.0 mmol). The mixture was stired at room temperature for 5 h. Water (100 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 150 mL). The organic extracts were washed with brine (200 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5% diethyl ether in hexanes) to give **68** (2.98 g, 14.1 mmol, 91%) as a colourless oil. R_f: 0.54 (20% diethyl ether in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 5.76 (1 H, ddd, J = 17.3, 10.6, 6.5 Hz, CH=CHH), 4.99 (1 H, dt, J = 17.3, 1.5 Hz, CH=CHH), 4.94 (1 H, dt, J = 10.4, 1.4 Hz, CH=CHH), 4.07 (2 H, brd, J = 8.3 Hz, 2 × NCHH), 2.72 (2 H, brt, J = 12.3 Hz, 2 × NCHH), 2.13–2.05 (1 H, m, $CHCH=CH_2$), 1.67 (2 H, brd, J = 13.1 Hz, 2 × NCH_2CHH), 1.44 (9 H, s, 3 × CH_3), 1.26 (2 H, qd, J = 12.3, 4.1 Hz, 2 × NCH_2CHH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 155.0 (C), 142.7 (CH), 113.1 (CH_2), 79.4 (C), 43.8 (2 × CH_2), 39.8 (CH), 31.5 (2 × CH_2), 28.6 (3 × CH_3); ν_{max}/**cm^{-1}** 2976, 2931, 2850, 1689, 1417, 1365, 1231, 1156; **LRMS (ESI$^+$)** m/z 445 (72), 234 ($[M + Na]^+$, 100); **HRMS (ESI$^+$)** calculated for $[C_{12}H_{21}NO_2Na]$ 234.14645, found 234.14665.

***tert*-Butyl (*E*)-4-(3-(2-(((2-iodophenethyl)thio)carbonyl)-4,5-dimethoxyphenyl)prop-1-en-1-yl)piperidine-1-carboxylate (69).** To a solution of **12a** (50 mg, 0.107 mmol) and **68** (113 mg, 0.534 mmol) in dichloromethane (0.8 mL) was added Grubbs' first generation catalyst (9 mg, 0.01 mmol). The mixture was heated at 40 °C for 16 h. The reaction mixture was cooled and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (15% ethyl acetate in hexanes) to

give **69** (38 mg, 0.058 mmol, 55%) as a colourless oil. R_f: 0.26 (20% ethyl acetate in hexanes); **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.82 (1 H + 0.15 × 1 H, dd, J = 7.9, 0.8 Hz, Ar–H), 7.33–7.27 (3 H + 0.15 × 3 H, m, 3 × Ar–H), 6.91 (1 H + 0.15 × 1 H, ddd, J = 7.9, 7.0, 2.1 Hz, Ar–H), 6.74 (0.15 × 1 H, s, Ar–H), 6.70 (1 H, s, Ar–H), 5.54 (1 H, dtd, J = 15.4, 6.5, 1.1 Hz, CH_2CH=CH), 5.51–5.29 (0.15 × 2 H, m, CH_2CH=CH), 5.39 (1 H, ddt, J = 15.4, 6.5, 1.3 Hz, CH_2CH=CH), 4.04 (2 H + 0.15 × 2 H, brs, 2 × NCHH), 3.90 (3 H + 0.15 × 3 H, s, OCH_3), 3.89 (3 H + 0.15 × 3 H, s, OCH_3), 3.63 (0.15 × 2 H, dd, J = 7.1, 1.4 Hz, CH_2CH=CH), 3.52 (2 H, d, J = 6.5 Hz, CH_2CH=CH), 3.26–3.22 (2 H + 0.15 × 2 H, m, SCH_2), 3.09–3.05 (2 H + 0.15 × 2 H, m, SCH_2CH_2), 2.80–2.66 (2 H + 0.15 × 2 H, m, 2 × NCHH), 2.09–2.05 (1 H + 0.15 × 1 H, CH=CHCH), 1.64–1.61 (2 H + 0.15 × 2 H, m, 2 × NCHHCHH), 1.45 (0.15 × 9 H, s, $C(CH_3)_3$), 1.43 (9 H, s, $C(CH_3)_3$), 1.28–1.19 (2 H + 0.15 × 2 H, m, 2 × NCHHCHH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 192.5 (C + C), 154.93 (C), 154.91 (C), 151.9 (C), 151.8 (C), 146.79 (C), 146.76 (C), 142.78 (C), 142.75 (C), 139.7 (CH + CH), 135.8 (CH), 135.3 (CH), 134.0 (C), 133.7 (C), 130.1 (CH + CH), 129.4 (C), 129.3 (C), 128.51 (CH + CH), 128.49 (CH + CH), 127.5 (CH), 127.3 (CH), 113.4 (CH), 112.9 (CH), 112.3 (CH), 112.1 (CH), 100.6 (C + C), 79.3 (C + C), 56.2 (CH_3 + CH_3), 56.0 (CH_3 + CH_3), 43.9 (2 × (CH_2 + CH_2)), 40.6 ((CH_2 + CH_2), 38.9 (CH), 36.3 (CH_2), 34.7 (CH), 32.0 (2 × (CH_2 + CH_2)), 31.1 (CH_2), 29.7 (CH_2 + CH_2), 28.6 (3 × (CH_3 + CH_3)); **ν_{max}/cm^{-1}** 2972, 2931, 1689, 1516, 1465, 1424, 1267, 1166, 1112; **LRMS (APCI) m/z** 674 ([M + Na]$^+$, 14), 615 (12), 543 (37), 319 (42), 295 (100); **HRMS (APCI)** calculated for $[C_{30}H_{38}INO_5SNa]$ 674.14076, found 674.14129.

***tert*-Butyl 4-((5,6-dimethoxy-1-oxo-2,3-dihydro-1*H*-inden-2-yl) methyl) piperidine-1-carboxylate (70).**[64] MeCN (10 mL) was degassed (argon sparging) for 1 h before use. To a solution of **69** (76 mg, 0.16 mmol) in MeCN (3 mL) was added tributylamine (78 μL, 0.33 mmol), formic acid (11 μL, 0.33 mmol) and *fac*-Ir(ppy)$_3$ (2.7 mg, 0.41 μmol). The mixture was degassed for 30 min before irradiating with blue light (465 nm) for 10 h min. Water (10 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with aqueous hydrochloric acid (30 mL, 1 M solution), saturated aqueous sodium bicarbonate (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (80–100% dichloromethane in hexanes) to give **70** (61 mg, 0.16 mmol, 51%) as a yellow solid; R_f: 0.36 (50% ethyl acetate in hexanes); **m.p.** 107–109 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.15 (1 H, s, Ar–H), 6.84 (1 H, s, Ar–H), 4.12–4.06 (2 H, m, 2 × NCHH), 3.94 (3 H, s, OCH_3), 3.89 (3 H, s, OCH_3), 3.24 (1 H, dd, J = 17.6, 8.3 Hz, ArCHH), 2.71–2.66 (4 H, ArCHHCH + 2 × NCHH), 1.92–1.85 (1 H, m, CHCHHCH), 1.73–1.63 (3 H, m, 2 × NCH_2CHH + NCH_2CH_2CH), 1.44 (9 H, s, $C(CH_3)_3$), 1.36–1.16 (3 H, m, 2 × NCH_2CHH + CHCHHCH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 207.6 (C), 155.7 (C), 155.0 (C), 149.6 (C), 148.8 (C), 129.4 (C), 107.5 (CH), 104.5 (CH), 79.4 (C), 56.3 (CH_3), 56.2 (CH_3), 45.3 (CH), 44.2 (2 × CH_2), 38.8 (CH_2), 34.7 (CH), 33.4 (CH_2), 32.9 (2 × CH_2), 28.6 (3 × CH_3); **ν_{max}/cm^{-1}** 2925, 2847, 1689, 1501, 1422, 1313, 1266, 1157; **LRMS (ESI$^+$) m/z** 499 (26), 412 ([M + Na]$^+$, 100).

Donepezil (63).[39] To a solution of **70** (23 mg, 0.059 mmol) in dichoromethane (0.6 mL) was added hydrochloric acid (0.22 mL, 4.0 M solution in 1,4-dioxane, 0.88 mmol). The mixture was concentrated *in vacuo* to give crude hydrochloride salt (24 mg). To a solution of crude hydrochloride salt (12 mg) in DMF (0.2 mL) was added benzyl bromide (3 μL, 0.03 mmol) and K_2CO_3 (11 mg, 0.083 mmol). The mixture was stirred at room temperature for 14 h before concentrating *in vacuo*. The residue was purified by flash chromatography on silica gel (0–5% methanol/ethyl acetate) to give **63** (10 mg, 0.026 mmol, 89%) as a colourless oil. R_f: 0.32 (ethyl acetate); **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 7.35–7.27 (5 H, m, 5 × Ar–H), 7.16 (1 H, s, Ar–H), 6.85 (1 H, s, Ar–H), 3.96 (3 H, s, OCH_3), 3.90 (3 H, s, OCH_3), 3.56 (2 H, s, CH_2Ph), 3.23 (1 H, dd, J = 17.5, 8.1 Hz, ArCHH), 2.94 (2 H, brs, 2 × NCHH), 2.71–2.67 (2 H, m, ArCHHCH), 2.03 (2 H, brs, 2 × NCHH), 1.93–1.88 (1 H, m, CHCHHCH), 1.75–1.69 (2 H, m, 2 × NCH_2CHH), 1.42–1.30 (3 H, m, 2 × NCH_2CHH + CHCHHCH); **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 207.9 (C), 155.6 (C), 149.6 (C), 148.9 (C), 138.9 (C – only observed through HMBC), 129.55 (C), 129.46 (2 × CH), 128.4 (2 × CH), 127.3 (CH), 107.5 (CH), 104.5 (CH), 63.4 (CH_2), 56.4 (CH_3), 56.2 (CH_3), 53.8 (2 × CH_2), 45.5 (CH), 38.8 (CH_2), 34.4 (CH), 33.6 (CH_2), 31.7 (2 × CH_2); **ν_{max}/cm^{-1}** 2921, 2845, 1693, 1591, 1500, 1439, 1312, 1264, 1121, 1073; **LRMS (ESI$^+$) m/z** 402 ([M + Na]$^+$, 25), 380 ([M + H]$^+$, 100).

Conflicts of interest

There are no conflicts to declare.

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