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Aryl–aryl cross-coupling constitutes one of the most widely used procedures for the synthesis of high-value materials, ranging from pharmaceuticals to organic electronics and conducting polymers. The assembly of (hetero)biaryl scaffolds generally requires multiple steps; coupling partners must be functionalized before the key bond-forming event is considered. Thus, the development of selective C–H arylation processes in arenes, that side-step the need for prefunctionalized partners, is crucial for streamlining the construction of these key architectures. Here we report an expedient, one-pot assembly of (hetero)biaryl motifs using photocatalysis and two non-prefunctionalized arene partners. The approach is underpinned by the activation of a C–H bond in an arene coupling partner using the interrupted Pummerer reaction. A unique pairing of the organic photoredox catalyst and the intermediate dibenzothiophenium salts enables highly selective reduction in the presence of sensitive functionalities. The utility of the metal-free, one-pot strategy is exemplified by the synthesis of a bioactive natural product and the modification of complex molecules of societal importance.

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Metal-Free Photoredox-Catalyzed C–H/C–H Coupling of Arenes Enabled by Interrupted Pummerer Activation

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Abstract

Aryl–aryl cross-coupling constitutes one of the most widely used procedures for the synthesis of high-value materials, ranging from pharmaceuticals to organic electronics and conducting polymers. The assembly of (hetero)biaryl scaffolds generally requires multiple steps; coupling partners must be functionalized before the key bond-forming event is considered. Thus, the development of selective C–H arylation processes in arenes, that side-step the need for prefunctionalized partners, is crucial for streamlining the construction of these key architectures. Here we report an expedient, one-pot assembly of (hetero)biaryl motifs using photocatalysis and two non-prefunctionalized arene partners. The approach is underpinned by the activation of a C–H bond in an arene coupling partner using the interrupted Pummerer reaction. A unique pairing of the organic photoredox catalyst and the intermediate dibenzothiophenium salts enables highly selective reduction in the presence of sensitive functionalities. The utility of the metal-free, one-pot strategy is exemplified by the synthesis of a bioactive natural product and the modification of complex molecules of societal importance.

Introduction

The construction of (hetero)biaryls is a key application of cross-couplings,¹ as the motif is ubiquitous amongst medicines, functional materials, and agrochemicals.^{2,3} Although powerful, traditional cross-couplings require two prefunctionalized partners and supply-risk platinum group metals. In order to streamline synthesis, it is desirable to engage non-prefunctionalized starting materials in cross-coupling processes that selectively manipulate C–H bonds in order to access novel building blocks or modify complex structures at a late-stage. Methods for accessing (hetero)biaryl motifs through selective C–H/C–H couplings have grown in sophistication in recent years,⁴

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however, methods can still require platinum group metals, high temperatures and/or suffer from the need for prefunctionalization in the form of a directing group to ensure site selective C–H functionalization.⁵ The use of photoredox catalysis has emerged as a complementary approach to (hetero)biaryls that operates under mild conditions and, in some cases, without the requirement for transition metals. While initial reports used aryl diazonium salts as substrates,^{6,7} recent progress has allowed less hazardous and more available substrates such as aryl halides to be used (Fig. 1a).^{8–13} A process that allowed the coupling of two non-prefunctionalized partners using photoredox catalysis would represent a clear advance. Here we present a general and effective photoredox-catalyzed approach to achieve the chemo- and regioselective C–H/C–H coupling of non-prefunctionalized arenes. The one-pot approach is underpinned by the selective interrupted Pummerer activation of an arene partner, using a benzothiophene S-oxide mediator, prior to catalytic cross-coupling with a second, non-prefunctionalized partner, mediated by an organic photocatalyst and visible light (Fig. 1b).

Figure 1. | Strategies for arylation of arenes. a, Photocatalytic approaches for the preparation of (hetero)biaryls. Such methods require prefunctionalized arene coupling partners, for example, aryl diazonium salts or aryl halides. **b,** Outline of a metal-free, strategy for the one-pot, photocatalytic C–H/C–H coupling of non-prefunctionalized arenes that relies on a selective, interrupted Pummerer reaction to activate one partner. LG = Leaving group.

Results and Discussion

Owing to their reactivity at both oxygen and at sulfur, and the tuneability of such reactivity, sulfoxides are attracting significant attention as selective activators of partners for cross-coupling, often at the expense of C–H bonds.^{14–36} We recently disclosed a strategy to activate the C–H bonds of nucleophilic alkenes using sulfoxides.³⁷ Sulfenylation by sulfoxide results in *in situ* polarity reversal of nucleophilic alkenes and the resultant alkenyl sulfonium salts are willing partners in nickel-catalyzed cross-couplings with organozincs that are carried out in the same pot. Herein, we report an effective, one-pot method for the selective C–H/C–H cross-coupling of non-prefunctionalized arene partners through the marriage of interrupted Pummerer activation and organophotocatalysis (Fig. 2a). Exploiting commercial dibenzothiophene S-oxide (DBTSO) as the process mediator ensures high selectivity and high reactivity in both sulfenylation and aryl radical generation, and the by-product dibenzothiophene can be easily recovered and recycled. Key to the approach is the identification of 10-phenylphenothiazine (PTH) as the optimal photocatalyst (see supporting information for full optimization studies and comparison with more conventional photoredox catalysts). The protocol involves direct reduction of the substrate by the excited catalyst and does not require super-stoichiometric quantities of electron donors (e.g. amines) to access the reactive state of the photocatalyst and enable efficient turnover.^{38–40}

Our blueprint for the process begins with sulfoxide activation of the nucleophilic arene, by an interrupted Pummerer reaction, to generate the corresponding aryldibenzothiophenium salt (Ar–DBT⁺; Fig. 2b, **A** → **B**). Single electron transfer (SET) from the excited state PTH to the Ar–DBT⁺ results in the expulsion of dibenzothiophene and concomitant formation of an aryl radical species (Fig. 2b, **B** → **C**). Sulfonium salts,^{41,42} in particular triarylsulfonium salts,^{43,33} have previously been investigated as aryl radical precursors using traditional ruthenium and iridium photocatalysts, but due to their inherent structure, they display non-selective C–S bond cleavage and radical generation. Crucially, the choice of sulfonium salts formed from dibenzothiophene S-oxide (e.g. **2**) is key as; i) SET reduction of the C–S bond is promoted by a gain in aromaticity, and; ii) SET reduction leads to selective cleavage of one of the C–S bonds. After subsequent trapping of the aryl radical (Fig. 2b, **C** → **D**), turnover of the catalytic cycle is thought to occur through oxidation of the newly formed radical adduct and aromatization delivers the product (Fig. 2b, **D** → **E** → **F**). At present, a radical chain process in which **D** reduces **B**, to generate **C** and **E**, can't be ruled out.⁴⁰ After optimisation (see supplementary information for full details), the metal-free,

one-pot process was exemplified by the C–H/C–H-type coupling of *tert*-butylbenzene **1** and *N*-methyl pyrrole to give (hetero)biaryl **3** (Fig. 2c).

Figure 2. | Mechanistic proposal for a one-pot, metal-free, photoredox-catalyzed C–H/C–H coupling of arenes, enabled by interrupted Pummerer activation. **a**, Overview of the developed sequence. **b**, Mechanistic proposal: interrupted Pummerer activation of arene **A** generates the corresponding Ar–DBT⁺ salt **B**. Single electron reduction of **B** releases aryl radical **C**, which is coupled with the arene trap to form **D**. Single electron oxidation of **D** may close the catalytic cycle and delivers the product of aryl–aryl coupling **F**. **c**, Exemplification of a one-pot, metal-free, photoredox-catalyzed C–H/C–H coupling of arenes, enabled by interrupted Pummerer-activation, using *tert*-butylbenzene and *N*-methylpyrrole. PTH, 10-phenylphenothiazine.

Mechanistic investigations. To gain support for the proposed reaction mechanism, the feasibility of the SET event was assessed using cyclic voltammetry (CV). CV analysis of a range of dibenzothiophenium salts, showed irreversible reduction profiles with $E^{\text{red}} = -1.1$ V (versus saturated calomel electrode, SCE) in DMSO (Supplementary Fig. 1, 2, and 3), significantly less negative than that determined for the excited state of PTH ($E_{1/2}^* = -2.1$ V versus SCE; Supplementary Fig. 5) in DMSO. In line with these findings, Stern-Volmer experiments confirmed that Ar-DBT⁺ salt **2** effectively quenches the excited state of the photocatalyst (Fig. 3a and Supplementary Fig. 9 and 11). Radical scavenger and radical probe experiments were also used to probe the reaction mechanism. The presence of 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) in the reaction mixture inhibited the formation of (hetero)biaryl **3** (Fig. 3b) while the addition of radical scavenger 1,1-diphenylethylene (DPE)^{11,44} gave the product of radical trapping **4** (Fig. 3c). Finally, reduction of engineered Ar-DBT⁺ salt **5**, containing an *ortho*-allyl ether moiety, gave additional support for the proposed mechanism; 5-*exo*-trig radical cyclization/addition product **6** was obtained in moderate yield (Fig. 3d).

Figure 3. | Mechanistic investigations. **a**, Fluorescence studies show the quenching of PTH upon addition of Ar-DBT⁺ salt **2**. **b**, The presence of TEMPO inhibits the photoredox C–H/C–H coupling. **c**, the postulated aryl radical intermediate can be intercepted by the radical trap 1,1-diphenylethylene to afford alkenylated product **4**. **d**, An intramolecular radical trap experiment using the allyl ether-containing substrate **5** delivers the product of radical cyclization/addition **6**. DBT⁺, dibenzothiophenium; TEMPO, 2,2,6,6-tetramethylpiperidin-1-yl)oxyl.

Evaluation of the protocol's substrate scope. Having established optimal reaction conditions and gained support for our mechanistic proposal, we set about determining the generality of the one-pot C–H/C–H coupling (Table 1). Simple, alkyl-substituted arenes were arylated with *N*-methylpyrrole in good overall yields (**3** and **7-10**). More electron-rich phenol and aniline derivatives also underwent coupling in good yields over the two stages of the process (**11-17**). To assess the compatibility of various functional groups, a range of substituted anisoles were then engaged in the arylation sequence. Substrates bearing halogens, triflyl, mesyl, keto, amido, ester, trifluoromethyl, and cyano groups all provided the desired heterobiaryls with complete chemoselectivity (**18-28**). The high chemoselectivity observed in the reduction of the Ar–DBT⁺ group is particularly noteworthy, given that PTH has previously been shown to catalyse the reduction of aryl halides^{45,46} and trifluoromethyl groups.⁴⁷ The process' tolerance of halide and triflyl functional groups signals its orthogonality with regard to traditional cross-coupling and ensures that further structural modification of products can be carried out using conventional cross-coupling processes. Furthermore, performing the preparation of **26** on a 10 mmol scale, without any alterations to the reaction conditions or set-up, revealed that the protocol is scalable.

Table 1. | Evaluation of the substrate scope in the metal-free, photoredox-catalyzed C-H/C-H coupling of arenes, enabled by interrupted Pummerer activation. a, Substrate scope with respect to the arene coupling partner. **b,** Substrate scope with respect to the (hetero)arene radical trap. All reactions were run on 0.2 mmol

scale with 20 equivalents of the trapping reagent, unless stated otherwise. ^a1 mL of radical trap used. ^bbased on recovered starting material. ^c10 equivalents of radical trap used.

We next evaluated the scope with respect to the trapping (hetero)arene. A range of substituted pyrroles (**29-32**), thiophenes (**33-35**), furans (**36-40**), benzofuran (**41**), and indole (**42**) partners was used successfully in the coupling. In the cases of 3-substituted heterocycles, complete regiocontrol was observed (**35**, **39**, and **40**). Ar-DBT⁺ salts can also engage in Minisci-type couplings (**43**). Finally, in addition to being capable of activation using the interrupted Pummerer process, arenes can also serve as radical trapping agents, thus allowing access to biaryls (**45-48**).

Application of the developed sequence. To showcase the potential of the one-pot, metal-free strategy, we have applied it to the synthesis and modification of several complex molecules. We first targeted the pseudilin marine natural products (Fig. 4a). Owing to their unusual, highly halogenated structures, pseudilins have gained attention in recent years and have been found to exhibit antibiotic, antitumor, and phytotoxic activities.⁴⁸⁻⁵⁰ Previous routes to the pseudilins have invariably used stepwise heterocycle construction from precursor benzaldehydes or phenyl ketones, with the shortest synthesis to date being seven steps in length.⁵⁰ Engaging commercial 2,4-dichloroanisole in our one-pot sequence delivered *N*-H heterobiaryl **49** after removal of the *tert*-butoxycarbonyl group. Subsequent chlorination and demethylation provided natural, pentachloropseudilin **50**, while bromination of the pyrrole ring enabled access to the dichloro-tribromopseudilin analogue **51**, both in good overall yield.

Our method is also suited to the selective modification of complex scaffolds of biological significance (Fig. 4b). Salicin pentaacetate (**52**), boscalid (**53**), fenofibrate (**54**), clofibrate (**55**), and *N*-acetylmexiletine (**56**) underwent smooth arylation using the two-stage, one-pot process. Complete chemo- and regiocontrol was observed in all cases. The structure of **53** was confirmed by X-ray crystallographic analysis.

Figure 4. | Application of the one-pot, metal-free photoredox-catalyzed C–H/C–H coupling of arenes, enabled by interrupted Pummerer activation. **a**, Concise synthesis of a bioactive pseudilin natural product and an analogue. Reaction conditions: **A**, arene (1.0 equiv.), DBTSO (2.0 equiv.), triflic anhydride (2.0 equiv.), CH_2Cl_2 (0.1 M), $-78\text{ }^\circ\text{C}$ to $-40\text{ }^\circ\text{C}$, 2 hour, *then* PTH (10 mol%), *N*-Boc pyrrole (10 equiv.), DMSO (0.2 M), blue LED irradiation, 18 hours. **B**, Sodium methoxide (30% w/w in MeOH, 10 equiv.), THF (0.14 M), $45\text{ }^\circ\text{C}$, 2 hours. **C**, chlorination: NCS (3.0 equiv.), MeCN (0.05 M), $-40\text{ }^\circ\text{C}$ to RT, 15 hours. bromination: Pyridinium tribromide (3.0 equiv.), EtOH (0.06 M), RT, 30 minutes. **D**, Boron tribromide (1.1 equiv.), CH_2Cl_2 (0.04 M), $-78\text{ }^\circ\text{C}$ to $0\text{ }^\circ\text{C}$, 2 hours. **b**, Late-stage functionalization of bioactive molecules. Reaction conditions: arene (1.0 equiv.), DBTSO (1.1 equiv.), triflic anhydride (1.2 equiv.), CH_2Cl_2 (0.1 M), $-78\text{ }^\circ\text{C}$ to RT, 2 hour, *then* PTH (10 mol%), *N*-Methyl pyrrole (20 equiv.), DMSO (0.2 M), blue LED irradiation, 18 hours.

Conclusions

We have developed a one-pot strategy for the rapid construction of (hetero)biaryl motifs from non-prefunctionalized partners using a combination of organophotocatalysis and substrate activation using the interrupted Pummerer reaction. Our C–H/C–H cross-coupling allows (hetero)biaryl carbon frameworks to be assembled under metal-free conditions, without multi-step synthesis. The marriage of the organic photoredox catalyst, 10-phenylphenothiazine, and intermediate aryldibenzothiophenium salts is unique and has led to a highly selective process that is broad in scope. The utility of the strategy has been exemplified by the synthesis of the bioactive natural product pentachloropseudilin and the modification of complex molecules of societal importance.

Methods

General Procedure for the interrupted Pummerer-enabled, photoredox-catalyzed C–H/C–H coupling of arenes.

Tf₂O (1.2 equiv.) was slowly added to a stirred solution of the arene (0.2 mmol, 1.0 equiv.) and dibenzothiophene S-oxide (1.1 equiv.) in CH₂Cl₂ (0.1 M) at –78 °C under a nitrogen atmosphere. The resulting solution was stirred at this temperature for 15 minutes before warming to room temperature. After stirring for 1 h, TLC analysis showed complete consumption of the arene starting material, at which point the solvent was removed *in vacuo*. 10-Phenyl-phenothiazine (10 mol%) was then added to the reaction vial, followed by evacuation and refilling with nitrogen (3 cycles). DMSO (0.2 M) was then added followed by the radical trap reagent. The reaction mixture was then irradiated with a Kessil 34W blue LED lamp for 18 h before quenching with aqueous saturated NaHCO₃ and dilution with EtOAc. The organic layer was washed with brine, dried using MgSO₄, filtered, and concentrated *in vacuo*, to give the crude product, which was purified by column chromatography on silica gel.

Data Availability

All data is available in the main text or the Supplementary Information. Metrical parameters for the structures of **2** and **53** (see Supplementary Information) are available free of charge from the Cambridge Crystallographic Data Centre (<https://www.ccdc.cam.ac.uk/>) under reference numbers CCDC 1922367 and 1922368.

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Supplementary Information is available in the online version of the paper.

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Author Contributions M.H.A. and D.J.P. conceived the study and co-wrote the manuscript. M.H.A. designed and performed experiments and M.S., A.W. and G.P. performed experiments.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of this article. Correspondence and requests for materials should be addressed to D. J. P. (david.j.procter@manchester.ac.uk).

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Metal-Free Photoredox-catalyzed C–H/C–H Coupling of Arenes Enabled by Interrupted Pummerer Activation

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GENERAL INFORMATION

General Experimental Information

Glassware for inert atmosphere reactions was oven-dried and cooled under a flow of nitrogen. THF was distilled over sodium wire and benzophenone. All other solvents and reagents were purchased from commercial sources and used as supplied. Photoredox reactions were subjected to irradiation from a 34W Kessil blue LED bulb, with the reaction tube placed approximately 10 cm from the bulb. Routine TLC analysis was carried out on aluminium sheets coated with silica gel, 0.20 mm (Macherey-Nagel, Polygram® Sil G/UV254). TLC plates were visualized by UV absorption, potassium permanganate, *p*-anisaldehyde, or phosphomolybdic acid solution and heating.

General Analytical Information

Novel compounds were characterized by NMR, IR spectroscopy, HRMS, and melting point. ¹H-NMR spectra were obtained on a 400 or 500 MHz Bruker spectrometer. ¹³C-NMR spectra were obtained at 100 or 125 MHz. All NMR spectra were processed using *MestReNova*® NMR software. All chemical shift values are reported in parts per million (ppm) relative to residual protio solvent and were determined in either CDCl₃, CD₃CN, or D₆-DMSO with coupling constant (*J*) values reported in Hz. The notation of signals is - Proton: δ chemical shift in ppm (number of protons, multiplicity, *J* value(s), proton assignment). Carbon: δ chemical shift in ppm (carbon assignment). If assignment is ambiguous, for example in the case of overlapping signals, a shift range is reported. Low-resolution and high-resolution mass spectra were obtained using either positive and/or negative electrospray ionisation (ES), or atmospheric-pressure chemical ionisation (APCI) techniques. IR spectra were recorded on an ATR FTIR spectrometer using neat samples. Melting points were measured on solids obtained after chromatography.

OPTIMISATION OF THE INTERRUPTED PUMMERER-ENABLED, PHOTOREDOX-CATALYZED C–H/C–H COUPLING OF ARENES

All optimization reactions were carried out on 0.2 mmol scale. The crude reaction mixtures were analyzed by ^1H -NMR with MeNO_2 as an internal standard.

Reaction Development – Photoredox Catalysis

Optimization of the visible-light-mediated direct arylation step was performed using dibenzothiophenium salt, **2**. As outlined in Table S1, the (hetero)biaryl, **S1** was formed in low yield from the reaction of **2** and furan in the presence of typical transition-metal photoredox catalysts in DMSO solvent (Entries 1 & 2). Various common organic photoredox catalysts were screened and also showed poor catalytic activity (Entries 3-7). The use of 10-phenyl phenothiazine (PTH) as the photoredox catalyst had a significant effect, providing a more efficient reaction (Entry 8). Exploring other polar solvents (required to solubilise the dibenzothiophenium salt, **2**) for the reaction showed that the chemistry is optimal when using DMSO. Increasing the amount of the furan coupling partner gave increasing yields of the desired product (Entries 17 & 18), however, as a compromise between reaction efficiency and reactant stoichiometry, 20 equivalents of radical trap was used going forward. Catalyst loading of 10 mol% was found to be optimal, as when increasing or decreasing the catalyst quantity, the yield of **S1** decreased (Entries 19 & 20). Finally, dibenzothiophenium salts proved crucial as when substituting **2** for the tetrahydrothiophenium salt **S4**, none of the desired product was detected (Entry 21).

Table S1. Optimization of the Reaction Conditions

Entry	Photocatalyst	Solvent	X (eq)	Yield (%) ^a
1	Ir(ppy) ₃	DMSO	10	34
2	Ru(bpy) ₃ Cl ₂	DMSO	10	19
3	Eosin Y	DMSO	10	5
4	Acr-BF ₄	DMSO	10	10
5	Rhodamine B	DMSO	10	N.D.
6	Fluorescein	DMSO	10	15
7	TXO	DMSO	10	30
8	PTH	DMSO	10	51
9	MTH	DMSO	10	37
10	PTH	NMP	10	8
11	PTH	DMF	10	20
12	PTH	DMA	10	24
13	PTH	MeCN	10	N.D.
14	PTH	MeOH	10	N.D.
15	PTH	Acetone	10	N.D.
16	PTH	CH ₂ Cl ₂	10	N.D.
17	PTH	DMSO	20	63 (58) ^e
18	PTH	DMSO	69	76
19 ^b	PTH	DMSO	20	35
20 ^c	PTH	DMSO	20	46
21 ^d	PTH	DMSO	20	N.D.

^a Determined by ¹H NMR using a MeNO₂ internal standard. ^b 5 mol% PTH added. ^c 20 mol% PTH added.

^d Tetrahydrothiophenium salt **S4** was used in place of **2** ^e Isolated yield.

Acr = 9-mesityl-10-methylacridinium. TXO = thioxanthen-9-one. PTH = 10-phenyl-phenothiazine. MTH = 10-methyl-phenothiazine.

Reaction Development – One-Pot Sequence

A short optimization was necessary to facilitate the one-pot process (Table S2). Dichloromethane is the optimal solvent for the interrupted Pummerer (IP) chemistry, however, from previous optimization studies (*vide supra*), dichloromethane was an unsatisfactory solvent for the direct arylation step. Addition of a solution of the radical trap and PTH to the reaction mixture after sulfenylation provided the desired product, but in low yield (Entry 1). Removing the dichloromethane solvent *in vacuo* before adding the components for the second step delivered the desired product **S1** in comparable yield to that obtained starting from dibenzothiophenium salt **2** (Entry 2). One equivalent of triflic acid is generated in the IP activation step and we hypothesized that the presence of acid may lead to degradation of the heterocyclic radical trap and/or the coupling product. However, the use of two equivalents of anhydrous potassium carbonate gave a lower yield (Entry 3).

Table S2. Optimization of the One-Pot Sequence

Entry	Yield(%) ^a	Notes
1	36	Direct addition
2	60	Solvent swap
3 ^b	34	Solvent swap

^a Determined by ¹H NMR using a MeNO₂ internal standard. ^b 2 eq. K₂CO₃ added.

Reaction Development – Control Experiments

Control experiments were conducted (Table S3). When performing the reaction in the absence of PTH a small amount of the arylated product is formed, presumably from direct excitation of the dibenzothiophenium salt **2** (Entry 1). Running the reaction in the dark led to complete recovery of the dibenzothiophenium salt **2** (Entry 2). When the reaction was carried out open to air, the yield of the product **S1** dropped significantly, (Entry 3). Finally, the addition of water to the reaction medium had little effect on the yield (Entry 4).

Table S3. Control Experiments

Entry	Yield(%) ^a	Notes
1	9 (91 salt)	Without PTH
2	>95 salt	Without light
3	21 (36 salt)	Open to air
4	58	1 eq. H ₂ O added

^a Determined by ¹H NMR using a MeNO₂ internal standard.

ELECTROCHEMICAL STUDIES

General Experimental Details

Cyclic voltammetry was conducted on an EmStat (PalmSens) potentiostat using a 3-electrode cell configuration. A glassy carbon working electrode was employed alongside a platinum wire counter electrode and a Ag/AgCl reference electrode. All the solutions were degassed by bubbling N₂ prior to measurements. 5 mM solutions of the desired compounds were freshly prepared in dry DMSO along with 0.1 M of tetrabutylammonium hexafluorophosphate as supporting electrolyte and were examined at a scan rate of 0.1 V s⁻¹. Ferrocene ($E_{1/2} = +0.435$ V vs SCE)¹ was added at the end of the measurements as an internal standard to determine the precise potential scale. Potential values are given versus the saturated calomel electrode (SCE). Irreversible reduction waves were obtained in all cases; therefore, the reduction potentials were obtained from the maximum, $E_{p\max}$.

Electrochemical Potentials & Cyclic Voltammograms

Electrochemical studies were conducted to identify the reduction potentials of the dibenzothiophenium salts. Attempts to determine the reduction potentials in acetonitrile gave inconsistent and non-reproducible results, likely due to decomposition on the electrode surface. As a result, reduction potentials were determined in DMSO. The excited state reduction potential of PTH was also determined in DMSO.

Sulfonium Salts

Figure S1. Cyclic voltammogram of **2**

Figure S2. Cyclic voltammogram of **S2**

Figure S3. Cyclic voltammogram of **S3**

Figure S4. Cyclic voltammogram of **S4**

10-Phenylphenothiazine

Figure S5. Cyclic voltammogram of PTH

Figure S6. Normalized emission spectrum of PTH in DMSO (0.17 mM)

The photoluminescence maximum was estimated to be 448 nm (Figure S6). Using the photoluminescence maximum and $E_{1/2}^{ox}$, the excited state reduction potential was determined for PTH ($E_{1/2}(PTH^{+•}/PTH^*) = -2.05$ V) according to the following equations:

$$E_{1/2}(PTH^{+•}/PTH^*) = E^{ox} - E_{0,0}$$

$$\text{where } E_{0,0} = hc/\lambda = 1240 \text{ nm}/\lambda_{max}$$

STERN-VOLMER FLUORESCENCE QUENCHING STUDY

General Experimental Details

Emission spectra were recorded on an Edinburgh Instrument FP920 Phosphorescence Lifetime Spectrometer equipped with a 450 watt xenon lamp (with single 300 mm focal length excitation and emission monochromators in Czerny Turner configuration) and a red sensitive photomultiplier in a Peltier (air-cooled) housing, (Hamamatsu R928P). All spectra are an average of three spectra and the same excitation and emission slits were used throughout. All spectra were corrected for the excitation source and the detector response using the correction files provided in the software.

Fluorescence Quenching Experiments

To evaluate the role of PTH in the process, we performed Stern-Volmer fluorescence quenching experiments, according to the procedure described by Read De Alaniz² and Jui³. The quenching of PTH was conducted in DMSO, with a catalyst concentration of 0.17 mM in a quartz cell with a 1 cm path length and an excitation wavelength of 350 nm used. The emission of PTH was measured with varying amounts of dibenzothiophenium salt, **2** (0.24, 0.50, & 2.0 M solutions in DMSO), furan (1.0 M in DMSO) and neat pyrrole to minimise the total volume change. All spectra were corrected for small changes in volume upon addition of the substrates. As demonstrated in Figure S7, the emission intensity decreased with increasing amounts of **2**, providing evidence for the direct substrate reduction by photoexcited PTH (PTH*). No significant quenching was observed in similar experiments using the radical traps *N*-methylpyrrole (Figure S9), whereas furan exhibited a small degree of quenching (Figure S11).

Figure S7. Emission spectra of PTH in DMSO (0.17 mM) with varying concentrations of dibenzothiophenium salt, **2**, normalized to PTH with no dibenzothiophenium salt added.

Figure S8. Stern-Volmer plot for PTH in DMSO (0.17 mM) with varying dibenzothiophenium salt, **2**.
K_{Sv} = 58.3

Figure S9. Emission spectra of PTH in DMSO (0.17 mM) with varying concentrations of *N*-methylpyrrole, normalized to PTH with no *N*-methylpyrrole added.

Figure S10. Stern-Volmer plot for PTH in DMSO (0.17 mM) with varying *N*-methylpyrrole.
K_{Sv} = 0.10

Figure S11. Emission spectra of PTH in DMSO (0.17 mM) with varying concentrations of furan, normalized to PTH with no furan added.

Figure S12. Stern-Volmer plot for PTH in DMSO (0.17 mM) with varying furan.
K_{Sv} = 3.3

SYNTHETIC PROCEDURES & COMPOUND CHARACTERISATION

General Procedures

General Procedure A: Interrupted Pummerer Reactions of Arenes

Tf₂O (1.2 equiv.) was slowly added to a stirred solution of the corresponding arene (0.2 mmol, 1.0 equiv.) and dibenzothiophene S-oxide (1.1 equiv.) in CH₂Cl₂ (0.1 M) at -78 °C under a nitrogen atmosphere. The resulting solution was stirred at this temperature for 15 minutes before warming to room temperature. After stirring for 1 h, TLC analysis showed complete consumption of the arene starting material, at which point the solvent was removed *in vacuo*. The sulfonium salt was then precipitated by the addition of Et₂O. The Et₂O was then decanted off and the crude product was washed with further portions of Et₂O. The pure product was obtained by recrystallization (CH₂Cl₂/Et₂O).

General Procedure B: Photoredox-Catalyzed C–H/C–H Coupling of Arenes

The dibenzothiophenium salt (0.2 mmol, 1.0 equiv.) and 10-phenyl-phenothiazine (10 mol%) were added to a reaction vial under a nitrogen atmosphere. DMSO (0.2 M) was then added followed by the corresponding radical trap reagent. The reaction mixture was then irradiated with a Kessil 34W blue LED lamp for 18 h before quenching with aqueous saturated NaHCO₃ and dilution with EtOAc. The organic layer was washed with brine, dried using MgSO₄, filtered, and concentrated *in vacuo*, to give the crude product, which was purified by column chromatography on silica gel.

General Procedure C: Interrupted Pummerer-enabled, Photoredox-Catalyzed C–H/C–H Coupling of Arenes

Tf₂O (1.2 equiv.) was slowly added to a stirred solution of the arene (0.2 mmol, 1.0 equiv.) and dibenzothiophene S-oxide (1.1 equiv.) in CH₂Cl₂ (0.1 M) at -78 °C under a nitrogen atmosphere. The resulting solution was stirred at this temperature for 15 minutes before warming to room temperature. After stirring for 1 h, TLC analysis showed complete consumption of the arene starting material, at which point the solvent was removed *in vacuo*. 10-Phenyl-phenothiazine (10 mol%) was then added to the reaction vial, followed by evacuation and refilling with nitrogen (3 cycles). DMSO (0.2 M) was then added followed by the radical trap reagent. The reaction mixture was then irradiated with a Kessil 34W blue LED lamp for 18 h before quenching with aqueous saturated NaHCO₃ and dilution with EtOAc. The organic layer was washed with brine, dried using MgSO₄, filtered, and concentrated *in vacuo*, to give the crude product, which was purified by column chromatography on silica gel.

General Procedure D: Interrupted Pummerer-enabled, Photoredox-Catalyzed C–H/C–H Coupling of Anilines & Amide-Containing Substrates

Tf₂O (1.2 equiv.) was slowly added to a stirred solution of dibenzothiophene S-oxide (1.1 equiv.) in CH₂Cl₂ (0.1 M) at –78 °C under a nitrogen atmosphere. The resulting solution was stirred at this temperature for 1 hour before the addition of the aniline (0.2 mmol, 1.0 equiv.) and a further 15 minutes of stirring. The solution was then warmed to room temperature. After stirring for 1 h, TLC analysis showed complete consumption of the arene starting material, at which point the solvent was removed *in vacuo*. 10-Phenyl-phenothiazine (10 mol%) was then added to the reaction vial, followed by evacuation and refilling with nitrogen (3 cycles). DMSO (0.2 M) was then added followed by the corresponding radical trap reagent. The reaction mixture was then irradiated with a Kessil 34W blue LED lamp for 18 h before quenching with aqueous saturated NaHCO₃ and dilution with EtOAc. The organic layer was washed with brine, dried using MgSO₄, filtered, and concentrated *in vacuo*, to give the crude product, which was purified by column chromatography on silica gel.

Preparation of Starting Materials

Catalyst Preparation

10-Phenyl-10H-phenothiazine, **S5**²

Phenothiazine (1.99 g, 10.0 mmol, 1.00 equiv.), sodium *tert*-butoxide (2.88 g, 30.0 mmol, 3.00 equiv.), and Pd(dba)₂ (0.29 g, 0.5 mmol, 0.05 equiv.) were added to a 50 mL round-bottom flask. The flask was fitted with a reflux condenser and sealed with a septum. The atmosphere was exchanged by applying vacuum and backfilling with nitrogen (3 cycles). Iodobenzene (1.1 mL, 10 mmol, 1.00 equiv.), tri-*tert*-butylphosphine (1.0 mL, 1 M in toluene, 1.00 mmol, 0.10 equiv.), and toluene (10 mL) were added by syringe. The reaction mixture was then heated to 110 °C and stirred at this temperature for 16 h. After cooling to room temperature, the reaction mixture was diluted with CH₂Cl₂ and washed with H₂O. The organic layer was dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (10% CHCl₃ in hexane), to give **S5** (2.46 g, 8.93 mmol, 89%) as a pale yellow solid; δ_{H} (400 MHz, DMSO-*d*₆) 6.16 (dd, *J* = 8.0, 1.3 Hz, 2H, Ar *H*), 6.86 (td, *J* = 7.4, 1.3 Hz, 2H, Ar *H*), 6.93 (td, *J* = 8.0, 1.7 Hz, 2H, Ar *H*), 7.08 (dd, *J* = 7.4, 1.7 Hz, 2H, Ar *H*), 7.42 (d, *J* = 7.6 Hz, 2H, Ar *H*), 7.54 (d, *J* = 7.6 Hz, 1H, Ar *H*), 7.67 (t, *J* = 7.6 Hz, 2H, Ar *H*); δ_{C} (100 MHz, DMSO-*d*₆) 116.1 (Ar CH), 119.4 (Ar C), 122.7 (Ar CH), 126.7 (Ar CH), 127.3 (Ar CH), 128.4 (Ar CH), 130.3 (Ar CH), 131.0 (Ar CH), 140.3 (Ar C), 143.6 (Ar C).

The data is in accordance with the literature.²

Substrate Preparation

Dibenzo[*b,d*]thiophene 5-oxide, **S6**⁵

Dibenzothiophene (9.2 g, 50.0 mmol, 1.0 equiv.) was dissolved in CH₂Cl₂ (250 mL) in a 500 mL round-bottom flask and cooled to 0 °C. *m*-CPBA (11.2 g, 77% in H₂O, 50.0 mmol, 1.0 equiv.) was added portionwise over 30 minutes and the resulting suspension was stirred for a further 30 minutes. The

reaction was then quenched with aqueous saturated NaHCO_3 (150 mL) and the organic layer was extracted using CH_2Cl_2 (3×100 mL). The combined organic layers were washed with aqueous saturated NaHCO_3 (3×150 mL) and brine (150 mL), dried over MgSO_4 , filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (10% EtOAc in CHCl_3), to give **S6** (8.6 g, 42.9 mmol, 86%) as a white solid; δ_{H} (400 MHz, CDCl_3) 7.51 (t, $J = 7.6$ Hz, 2H, Ar H), 7.61 (t, $J = 7.6$ Hz, 2H, Ar H), 7.82 (d, $J = 7.6$ Hz, 2H, Ar H), 8.00 (d, $J = 7.6$ Hz, 2H, Ar H); δ_{C} (100 MHz, CDCl_3) 122.0 (Ar CH), 127.7 (Ar CH), 129.7 (Ar CH), 132.7 (Ar CH), 137.2 (Ar C), 145.3 (Ar C).

The data is in accordance with the literature.⁵

5-(4-(*tert*-Butyl)phenyl)-5H-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate, 2

Prepared as described in General Procedure A: *tert*-butyl benzene (0.78 mL, 5.00 mmol), dibenzothiophene *S*-oxide (1.10 g, 5.50 mmol), Tf_2O (1.00 mL, 6.00 mmol), after purification by recrystallization gave **2** (2.04 g, 4.38 mmol, 88%) as an off-white solid; m.p. (recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$) 184 – 186 °C; δ_{H} (400 MHz, CDCl_3) 1.26 (s, 9H, CH_3), 7.47 – 7.55 (m, 2H, Ar H), 7.56 – 7.66 (m, 4H, Ar H), 7.84 (td, $J = 7.8, 1.1$ Hz, 2H, Ar H), 8.15 (d, $J = 8.2$ Hz, 2H, Ar H), 8.19 (dd, $J = 7.8, 1.1$ Hz, 2H, Ar H); δ_{C} (100 MHz, CDCl_3) 30.9 (CH_3), 35.6 (CH_3C), 120.9 (q, $J = 320.6$ Hz, CF_3), 122.4 (Ar C), 124.2 (Ar CH), 128.7 (Ar CH), 129.0 (Ar CH), 130.7 (Ar CH), 131.8 (Ar CH), 132.2 (Ar C), 134.5 (Ar CH), 139.0 (Ar C), 159.6 (Ar C); δ_{F} (376 MHz, CDCl_3) -78.2; ν_{max} (thin film/ cm^{-1}) 736, 761, 783, 837, 1005, 1027, 1162, 1222, 1254, 1448, 2871, 2907, 2966, 3062, 3087; MS (ES^+) m/z 317.1 (M^+); HRMS $\text{C}_{22}\text{H}_{21}^+$ (M^+) Expected 317.1358, Found 317.1352.

2 was further characterized by X-ray crystallographic analysis. CCDC: 1922367.

5-Phenyl-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate, S2

Prepared as described in General Procedure A: benzene (0.09 mL, 1.00 mmol), dibenzothiophene S-oxide (0.22 g, 1.10 mmol), Tf₂O (0.20 mL, 1.20 mmol), after purification by recrystallization gave **S2** (0.35 g, 0.84 mmol, 84%) as an off-white solid; m.p. (recrystallized from CH₂Cl₂/Et₂O) 177 – 179 °C; δ_H (400 MHz, CDCl₃) 7.48 – 7.56 (m, 2H, Ar H), 7.59 – 7.68 (m, 5H, Ar H), 7.85 (td, *J* = 7.8, 0.9 Hz, 2H, Ar H), 8.14 (d, *J* = 8.2 Hz, 2H, Ar H), 8.19 (d, *J* = 7.8 Hz, 2H, Ar H); δ_C (100 MHz, CDCl₃) 120.8 (q, *J* = 320.2 Hz, CF₃), 124.2 (Ar CH), 126.6 (Ar C), 128.9 (Ar CH), 130.8 (Ar CH), 131.7 (Ar CH), 131.9 (Ar CH), 132.0 (Ar C), 134.6 (Ar CH), 135.1 (Ar CH), 139.1 (Ar C); δ_F (376 MHz, CDCl₃) -78.2; ν_{max} (thin film/cm⁻¹) 734, 755, 997, 1026, 1049, 1222, 1251, 1448, 3011, 3062, 3088; MS (ES⁺) *m/z* 261.0 (M⁺); HRMS C₁₈H₁₃S⁺ (M⁺) Expected 261.0724, Found 261.0720.

5-(4-Methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate, S3

Prepared as described in General Procedure A: methyl 2-methoxybenzoate (0.14 mL, 1.00 mmol), dibenzothiophene S-oxide (0.22 g, 1.10 mmol), Tf₂O (0.20 mL, 1.20 mmol), after purification by recrystallization gave **S3** (0.46 g, 0.93 mmol, 93%) as an off-white solid; m.p. (recrystallized from CH₂Cl₂/Et₂O) 162 – 164 °C; δ_H (400 MHz, CDCl₃) 3.79 (s, 3H, OCH₃), 3.95 (s, 3H, OCH₃), 7.21 (d, *J* = 9.1 Hz, 1H, Ar H), 7.60 (d, *J* = 2.7 Hz, 1H, Ar H), 7.62 – 7.68 (m, 2H, Ar H), 7.86 (td, *J* = 7.9, 1.1 Hz, 2H, Ar H), 8.14 (d, *J* = 7.9 Hz, 2H, Ar H), 8.18 (d, *J* = 7.9 Hz, 2H, Ar H), 8.28 (dd, *J* = 9.1, 2.7 Hz, 1H, Ar H); δ_C (100 MHz, CDCl₃) 52.9 (OCH₃), 57.0 (OCH₃), 115.2 (Ar CH), 120.9 (q, *J* = 320.2 Hz, CF₃), 123.7 (Ar C), 124.1 (Ar CH), 128.8 (Ar CH), 132.0 (Ar CH), 132.3 (Ar C), 132.3 (Ar C), 133.2 (Ar CH), 134.6 (Ar CH), 138.5 (Ar CH), 138.8 (Ar C), 164.0 (Ar C), 164.4 (C=O); δ_F (376 MHz, CDCl₃) -78.2; ν_{max} (thin film/cm⁻¹) 734, 759, 1028, 1080, 1155, 1223, 1250, 1449, 1488, 1591, 1728, 2953, 3013, 3087; MS (ES⁺) *m/z* 349.1 (M⁺); HRMS C₂₁H₁₇O₃S⁺ (M⁺) Expected 349.0893, Found 349.0876.

1-(4-(*tert*-Butyl)phenyl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate, **S4**

Prepared as described in General Procedure A: *tert*-butyl benzene (0.78 mL, 5.00 mmol), tetrahydrothiophene-S-oxide (0.50 mL, 5.50 mmol), Tf₂O (1.00 mL, 6.00 mmol), after purification by recrystallization (CH₂Cl₂/Et₂O), gave **S4** (1.46 g, 3.95 mmol, 79%) as a grey solid; m.p. (recrystallized from CH₂Cl₂/Et₂O) 106 – 108 °C; δ_H (400 MHz, CDCl₃) 1.33 (s, 9H, CH₃), 2.49 – 2.63 (m, 4H, CH₂), 3.57 – 3.70 (m, 2H, CH₂), 4.16 – 4.29 (m, 2H, CH₂), 7.60 – 7.69 (m, 2H, Ar H), 7.66 – 7.74 (m, 2H, Ar H); δ_C (100 MHz, CDCl₃) 29.3 (CH₂), 31.0 (CH₃), 35.5 (CH₃C), 48.8 (CH₂), 120.8 (q, *J* = 320.4 Hz, CF₃), 122.5 (Ar C), 128.7 (Ar CH), 129.7 (Ar CH), 158.7 (Ar C); δ_F (376 MHz, CDCl₃) -78.3; ν_{max} (thin film/cm⁻¹) 735, 843, 871, 1030, 1158, 1250, 1266, 2873, 2908, 2961, 3025; MS (ES⁺) *m/z* 221.1 (M⁺); HRMS C₁₄H₂₁⁺ (M⁺) Expected 221.1358, Found 221.1355.

Phenyl pivalate, **S7**⁶

Triethylamine (2.20 mL, 15.9 mmol, 2.0 equiv.) and pivaloyl chloride (1.10 mL, 8.77 mmol, 1.1 equiv.) were added sequentially to a stirred solution of phenol (0.75 g, 7.97 mmol, 1.0 equiv.) in THF (10 mL) at 0 °C. After 15 minutes, the reaction mixture was warmed to ambient temperature and was stirred for a further 18 hours, before removal of the solvent *in vacuo*. The crude product was purified by column chromatography on silica gel (1% EtOAc in hexanes), to give **S7** (1.21 g, 6.77 mmol, 85%) as a colourless oil; δ_H (400 MHz, CDCl₃) 1.37 (s, 9H, CH₃), 7.03 – 7.09 (m, 2H, Ar H), 7.18 – 7.25 (m, 1H, Ar H), 7.34 – 7.42 (m, 2H, Ar H); δ_C (100 MHz, CDCl₃) 27.3 (CH₃), 39.2 (CH₃C), 121.6 (Ar CH), 125.7 (Ar CH), 129.5 (Ar CH), 151.3 (Ar C), 177.2 (C=O).

The data is in accordance with the literature.⁷

N,N-Diethyl-2-methoxybenzamide, **S8**⁸

Dimethyl sulfate (0.32 mL, 3.3 mmol, 1.1 equiv.) was added to a stirred solution of *N,N*-diethyl-2-hydroxybenzamide (0.58 g, 3.0 mmol, 1.0 equiv.) and K₂CO₃ (0.46 g, 3.3 mmol, 1.1 equiv.) in acetone (15 mL) at ambient temperature. The reaction mixture was stirred for 18 hours, before removal of the solvent *in vacuo*. The crude residue was then diluted with CH₂Cl₂ (25 mL), washed with water (2 × 25 mL) and brine (25 mL), dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (40% EtOAc in hexanes), to give **S8** (0.61 g, 2.95 mmol, 98%) as a white solid; δ_{H} (400 MHz, CDCl₃) 1.02 (t, *J* = 7.1 Hz, 3H, CH₃), 1.24 (t, *J* = 7.1 Hz, 3H, CH₃), 3.14 (q, *J* = 7.1 Hz, 2H, CH₂), 3.46 – 3.69 (m, 2H, CH₂), 3.81 (s, 3H, OCH₃), 6.89 (dd, *J* = 8.4, 0.9 Hz, 1H, Ar *H*), 6.96 (td, *J* = 7.4, 0.9 Hz, 1H, Ar *H*), 7.18 (dd, *J* = 7.4, 1.7 Hz, 1H, Ar *H*), 7.31 (ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H, Ar *H*); δ_{C} (100 MHz, CDCl₃) 13.0 (CH₃), 14.1 (CH₃), 38.9 (CH₂), 42.9 (CH₂), 55.6 (OCH₃), 111.1 (Ar CH), 120.9 (Ar CH), 127.2 (Ar C), 127.6 (Ar CH), 130.0 (Ar CH), 155.3 (Ar C), 168.9 (Ar C=O).

The data is in accordance with the literature.⁹

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(Acetoxymethyl)-6-(2-(acetoxymethyl)phenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate, **S9**¹⁰

Acetic anhydride (9.50 mL, 100 mmol, 10 equiv.) was added to a stirred solution of salicin (2.86 g, 10 mmol, 1.0 equiv.) and K₂CO₃ (2.76 g, 20 mmol, 2.0 equiv.) in dioxane (40 mL) at ambient temperature. The resulting suspension was then heated to 60 °C for 16 hours before removing the solvent *in vacuo*. The crude residue was then diluted with EtOAc (50 mL), washed with water (2 × 50 mL) and brine (50 mL), dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude product was purified by recrystallization (1:1 EtOAc/hexanes), to give **S9** (4.62 g, 9.3 mmol, 93%) as a white solid; δ_{H} (400 MHz, CDCl₃) 2.03 (s, 3H, CH₃), 2.04 (s, 3H, CH₃), 2.06 (s, 3H, CH₃), 2.09 (s, 6H, CH₃), 3.85 (ddd, *J* = 10.0, 5.3, 2.5 Hz, 1H, Alk CH), 4.18 (dd, *J* = 12.3, 2.5 Hz, 1H, Alk CH₂), 4.27 (dd, *J* = 12.3, 5.3 Hz, 1H, Alk CH₂), 5.01 – 5.22 (m, 4H, Alk CH & Bn CH₂), 5.25 – 5.35 (m, 2H, Alk CH), 7.08 (t, *J* = 7.7 Hz,

2H, Ar H), 7.24 – 7.30 (m, 1H, Ar H), 7.34 (dd, $J = 7.7, 1.5$ Hz, 1H, Ar H); δ_c (100 MHz, CDCl₃) 20.7 (CH₃), 20.7 (CH₃), 20.7 (CH₃), 20.8 (CH₃), 21.1 (CH₃), 61.2 (Bn CH₂), 62.0 (Alk CH₂), 68.4 (Alk CH), 71.1 (Alk CH), 72.1 (Alk CH), 72.8 (Alk CH), 99.5 (Alk CH), 116.0 (Ar CH), 123.7 (Ar CH), 126.4 (Ar C), 129.5 (Ar CH), 129.7 (Ar CH), 154.7 (Ar C), 169.4 (C=O), 169.5 (C=O), 170.3 (C=O), 170.7 (C=O), 170.8 (C=O).

The data is in accordance with the literature.¹⁰

N-(1-(2,6-Dimethylphenoxy)propan-2-yl)acetamide, **S10**¹¹

Acetyl chloride (0.50 mL, 6.95 mmol, 1.5 equiv.) was slowly added to a stirred suspension of mexiletine hydrochloride (1.00 g, 4.64 mmol, 1.0 equiv.) in EtOAc (5 mL) and 5N NaOH (5 mL) at 0 °C. After the addition, the reaction mixture was warmed to ambient temperature and stirred for 1 hour. The mixture was then added to water (10 mL) and the organic layer was extracted using EtOAc (3 × 15 mL). The combined organic layers were washed with aqueous saturated NaHCO₃ (3 × 15 mL) and brine (15 mL), dried over MgSO₄, filtered, and concentrated *in vacuo*, to give **S10** (0.99 g, 4.50 mmol, 97%) as a white solid; δ_H (400 MHz, CDCl₃) 1.41 (d, $J = 6.9$ Hz, 3H, CH₃), 2.03 (s, 3H, CH₃), 2.26 (s, 6H, CH₃), 3.71 (dd, $J = 9.1, 3.5$ Hz, 1H, CH₂), 3.80 (dd, $J = 9.1, 3.5$ Hz, 1H, CH₂), 4.24 – 4.44 (m, 1H, Alk CH), 5.91 (br s, 1H, NH), 6.93 (dd, $J = 8.4, 6.5$ Hz, 1H, Ar H), 6.99 – 7.03 (m, 2H, Ar H); δ_c (100 MHz, CDCl₃) 16.3 (CH₃), 17.9 (CH₃), 23.6 (CH₃), 45.6 (Alk CH), 74.0 (CH₂), 124.3 (Ar CH), 129.2 (Ar CH), 130.8 (Ar C), 155.0 (Ar C), 169.5 (C=O).

The data is in accordance with the literature.¹¹

Interrupted Pummerer-Enabled, Photoredox-Catalyzed C–H/C–H Coupling of Arenes

Substrate Scope

2-(4-(*tert*-Butyl)phenyl)furan, **51**¹²

Prepared as described in General Procedure C: *tert*-butyl benzene (31 μ L, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), TiF_4 (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), furan (0.29 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% CHCl_3 in hexanes), gave **51** (23.2 mg, 0.12 mmol, 58%) as a white solid; δ_{H} (500 MHz, CDCl_3) 1.34 (s, 9H, CH_3), 6.46 (dd, $J = 3.3, 1.8$ Hz, 1H, Ar H), 6.60 (dd, $J = 3.3, 0.8$ Hz, 1H, Ar H), 7.41 (d, $J = 8.5$ Hz, 2H, Ar H), 7.45 (dd, $J = 1.8, 0.8$ Hz, 1H, Ar H), 7.61 (d, $J = 8.5$ Hz, 2H, Ar H); δ_{C} (125 MHz, CDCl_3) 31.4 (CH_3), 34.8 (CH_3C), 104.5 (Ar CH), 111.7 (Ar CH), 123.7 (Ar CH), 125.7 (Ar CH), 128.4 (Ar C), 141.9 (Ar CH), 150.5 (Ar C), 154.3 (Ar C).

The data is in accordance with the literature.¹²

1-Methyl-2-phenyl-1H-pyrrole, **7**¹³

Prepared as described in General Procedure C: benzene (18 μ L, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), TiF_4 (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (1.0 mL, 11.3 mmol, 56 equiv.), after purification by column chromatography on silica gel (20% CHCl_3 in hexanes), gave **7** (15.4 mg, 0.10 mmol, 49%) as an off-white solid; δ_{H} (400 MHz, CDCl_3) 3.68 (s, 3H, CH_3), 6.22 (dd, $J = 3.6, 2.6$ Hz, 1H, Ar H), 6.24 (dd, $J = 3.6, 1.9$ Hz, 1H, Ar H), 6.73 (dd, $J = 2.6, 1.9$ Hz, 1H, Ar H), 7.28 – 7.35 (m, 1H, Ar H), 7.37 – 7.44 (m, 4H, Ar H); δ_{C} (100 MHz, CDCl_3) 35.2 (CH_3), 107.9 (Ar CH), 108.8 (Ar CH), 123.8 (Ar CH), 126.9 (Ar CH), 128.5 (Ar CH), 128.8 (Ar CH), 133.5 (Ar C), 134.7 (Ar C).

The data is in accordance with the literature.¹³

2-(4-Ethylphenyl)-1-methyl-1H-pyrrole, 8

Prepared as described in General Procedure C: ethylbenzene (25 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), TiF_4 (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% CHCl_3 in hexanes), gave **8** (19.2 mg, 0.10 mmol, 52%) as a colourless oil; δ_{H} (400 MHz, CDCl_3) 1.28 (td, $J = 7.6, 0.8$ Hz, 3H, CH_3), 2.69 (q, $J = 7.6$ Hz, 2H, CH_2), 3.67 (s, 3H, NCH_3), 6.18 – 6.23 (m, 2H, Ar *H*), 6.68 – 6.73 (m, 1H, Ar *H*), 7.24 (d, $J = 8.1$ Hz, 2H, Ar *H*), 7.33 (d, $J = 8.1$ Hz, 2H, Ar *H*); δ_{C} (100 MHz, CDCl_3) 15.6 (CH_3), 28.7 (CH_2), 35.1 (NCH_3), 107.8 (Ar CH), 108.5 (Ar CH), 123.4 (Ar CH), 128.0 (Ar CH), 128.8 (Ar CH), 130.8 (Ar C), 134.8 (Ar C), 143.0 (Ar C); ν_{max} (thin film/ cm^{-1}) 834, 909, 982, 1057, 1089, 1242, 1308, 1414, 1475, 2871, 2929, 2962; MS (GCMS) m/z 185.1 (M); HRMS $\text{C}_{13}\text{H}_{16}\text{N}^+$ ($\text{M}+\text{H}^+$) Expected 186.1277, Found 186.1276.

2-(4-Isopropylphenyl)-1-methyl-1H-pyrrole, 9

Prepared as described in General Procedure C: cumene (28 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), TiF_4 (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% CHCl_3 in hexanes), gave **9** (19.4 mg, 0.10 mmol, 49%) as a colourless oil; δ_{H} (400 MHz, CDCl_3) 1.30 (d, $J = 6.9$ Hz, 6H, CH_3), 2.95 (hept, $J = 6.9$ Hz, 1H, Alk CH), 3.67 (s, 3H, NCH_3), 6.16 – 6.26 (m, 2H, Ar *H*), 6.67 – 6.77 (m, 1H, Ar *H*), 7.27 (d, $J = 8.2$ Hz, 2H, Ar *H*), 7.34 (d, $J = 8.2$ Hz, 2H, Ar *H*); δ_{C} (100 MHz, CDCl_3) 24.1 (CH_3), 34.0 (Alk CH), 35.2 (NCH_3), 107.8 (Ar CH), 108.5 (Ar CH), 123.4 (Ar CH), 126.5 (Ar CH), 128.8 (Ar CH), 131.0 (Ar C), 134.8 (Ar C), 147.5 (Ar C); ν_{max} (thin film/ cm^{-1}) 835, 909, 982, 1058, 1241, 1309, 1361, 1458, 1475, 2867, 2926, 2957; MS (GCMS) m/z 199.1 (M); HRMS $\text{C}_{14}\text{H}_{18}\text{N}^+$ ($\text{M}+\text{H}^+$) Expected 200.1434, Found 200.1432.

2-(4-(*tert*-Butyl)phenyl)-1-methyl-1H-pyrrole, **3**¹⁴

Prepared as described in General Procedure C: *tert*-butyl benzene (31 μ L, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), TiF_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% CHCl_3 in hexanes), gave **3** (21.8 mg, 0.10 mmol, 51%) as a colourless oil; Reaction with excess *N*-methylpyrrole (1.0 mL, 11.3 mmol, 56 equiv.), gave **3** (28.5 mg, 0.13 mmol, 67%); δ_{H} (400 MHz, CDCl_3) 1.37 (s, 9H, CH_3), 3.68 (s, 3H, NCH_3), 6.19 – 6.25 (m, 2H, Ar *H*), 6.69 – 6.75 (m, 1H, Ar *H*), 7.36 (d, $J = 8.5$ Hz, 2H, Ar *H*), 7.44 (d, $J = 8.5$ Hz, 2H, Ar *H*); δ_{C} (100 MHz, CDCl_3) 31.5 (CH_3), 34.7 (CH_3C), 35.2 (NCH_3), 107.8 (Ar CH), 108.5 (Ar CH), 123.4 (Ar CH), 125.4 (Ar CH), 128.5 (Ar CH), 130.6 (Ar C), 134.7 (Ar C), 149.8 (Ar C).

The data is in accordance with the literature.¹⁴

2-(2,4-Dimethylphenyl)-1-methyl-1H-pyrrole, **10**

Prepared as described in General Procedure C: *meta*-xylene (25 μ L, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), TiF_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% CHCl_3 in hexanes), gave **10** (isolated as a 15:1 mixture with **10'**, 13.3 mg, 0.10 mmol, 51%) as a colourless oil; **10** δ_{H} (400 MHz, CDCl_3) δ 2.17 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.41 (s, 3H, NCH_3), 6.05 (dd, $J = 3.5, 1.8$ Hz, 1H, Ar *H*), 6.21 (dd, $J = 3.5, 2.7$ Hz, 1H, Ar *H*), 6.71 (dd, $J = 2.7, 1.8$ Hz, 1H, Ar *H*), 7.01 – 7.07 (m, 1H, Ar *H*), 7.11 (s, 1H, Ar *H*), 7.14 (d, $J = 7.7$ Hz, 1H, Ar *H*); **10** δ_{C} (100 MHz, CDCl_3) 20.1 (CH_3), 21.3 (CH_3), 34.2 (NCH_3), 107.3 (Ar CH), 108.5 (Ar CH), 121.6 (Ar CH), 126.3 (Ar CH), 130.3 (Ar CH), 130.9 (Ar CH), 131.3 (Ar C), 133.4 (Ar C), 137.8 (Ar C), 138.2 (Ar C); ν_{max} (thin film/ cm^{-1}) 821, 883, 981, 1036, 1051, 1087, 1233, 1242, 1357, 1408, 1467, 2859, 2918, 3003; MS (GCMS) m/z 185.1 (M^+); HRMS $\text{C}_{13}\text{H}_{16}\text{N}^+$ ($\text{M}+\text{H}^+$) Expected 186.1277, Found 186.1277.

2-(Benzo[d][1,3]dioxol-5-yl)-1-methyl-1H-pyrrole, **11**

Prepared as described in General Procedure C: 1,3-Benzodioxole (23 μ L, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), Ti_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% CHCl_3 in hexanes), gave **11** (24.9 mg, 0.12 mmol, 62%) as a colourless oil; δ_{H} (400 MHz, CDCl_3) 3.64 (s, 3H, CH_3), 6.00 (s, 2H, CH_2), 6.16 (dd, $J = 3.6, 1.9$ Hz, 1H, Ar *H*), 6.19 (dd, $J = 3.6, 2.7$ Hz, 1H, Ar *H*), 6.69 (dd, $J = 2.7, 1.9$ Hz, 1H, Ar *H*), 6.85 – 6.87 (m, 2H, Ar *H*), 6.88 – 6.89 (m, 1H, Ar *H*); δ_{C} (100 MHz, CDCl_3) 35.0 (CH_3), 101.2 (CH_2), 107.7 (Ar CH), 108.4 (Ar CH), 108.4 (Ar CH), 109.5 (Ar CH), 122.5 (Ar CH), 123.3 (Ar CH), 127.4 (Ar C), 134.4 (Ar C), 146.8 (Ar C), 147.7 (Ar C); ν_{max} (thin film/ cm^{-1}) 781, 811, 868, 987, 1036, 1124, 1221, 1242, 1305, 1331, 1435, 1450, 2777, 2888; MS (GCMS) m/z 201.1 (M^+); HRMS $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}^+$ ($\text{M}+\text{H}^+$) Expected 202.0863, Found 202.0863.

1-Methyl-2-(4-phenoxyphenyl)-1H-pyrrole, **12**

Prepared as described in General Procedure C: diphenyl ether (32 μ L, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), Ti_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% CHCl_3 in hexanes), gave **12** (isolated as an 11:1 mixture with **12'**, 33.4 mg, 0.13 mmol, 67%) as a colourless oil; **12** δ_{H} (400 MHz, CDCl_3) 3.67 (s, 3H, CH_3), 6.22 (d, $J = 2.3$ Hz, 2H, Ar *H*), 6.72 (t, $J = 2.3$ Hz, 1H, Ar *H*), 7.05 (d, $J = 8.7$ Hz, 2H, Ar *H*), 7.06 – 7.10 (m, 2H, Ar *H*), 7.12 – 7.18 (m, 1H, Ar *H*), 7.33 – 7.42 (m, 4H, Ar *H*); **12** δ_{C} (100 MHz, CDCl_3) 35.1 (CH_3), 107.8 (Ar CH), 108.5 (Ar CH), 118.7 (Ar CH), 119.2 (Ar CH), 123.5 (Ar CH), 123.6 (Ar CH), 128.5 (Ar C), 129.9 (Ar CH), 130.2 (Ar CH), 134.1 (Ar C), 156.5 (Ar C), 157.1 (Ar CH); ν_{max} (thin film/ cm^{-1}) 839, 868, 982, 1022, 1056, 1166, 1228, 1308, 1475, 1487, 1588, 2922, 3038; MS (GCMS) m/z 249.1 (M^+); HRMS $\text{C}_{17}\text{H}_{16}\text{ON}^+$ ($\text{M}+\text{H}^+$) Expected 250.1226, Found 250.1223.

4-(1-Methyl-1H-pyrrol-2-yl)phenyl pivalate, 13

Prepared as described in General Procedure C: **57** (36 mg, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (70% CHCl₃ in hexanes), gave **13** (26.2 mg, 0.10 mmol, 51%) as a white gum; δ_{H} (400 MHz, CDCl₃) 1.38 (s, 9H, CH₃), 3.66 (s, 3H, NCH₃), 6.17 – 6.25 (m, 2H, Ar H), 6.68 – 6.75 (m, 1H, Ar H), 7.10 (d, *J* = 8.6 Hz, 2H, Ar H), 7.40 (d, *J* = 8.6 Hz, 2H, Ar H); δ_{C} (100 MHz, CDCl₃) 27.3 (CH₃), 35.1 (NCH₃), 39.3 (CH₃C), 107.9 (Ar CH), 108.9 (Ar CH), 121.5 (Ar CH), 123.8 (Ar CH), 129.7 (Ar CH), 131.0 (Ar C), 133.9 (Ar C), 150.1 (Ar C), 177.3 (C=O); ν_{max} (thin film/cm⁻¹) 710, 780, 851, 942, 1014, 1028, 1112, 1165, 1198, 1277, 1309, 1476, 1501, 1546, 1745, 2873, 2932, 2972; MS (GCMS) *m/z* 257.1 (M⁺); HRMS C₁₆H₂₀O₂N⁺ (M+H⁺) Expected 258.1489, Found 258.1488.

1-(4-(1-Methyl-1H-pyrrol-2-yl)phenyl)pyrrolidin-2-one, 14

Prepared as described in General Procedure D: 1-phenyl-2-pyrrolidinone (32 mg, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% EtOAc in hexanes), gave **14** (28.8 mg, 0.12 mmol, 60%) as a white solid; m.p. (recrystallized from CHCl₃) 119 – 121 °C; δ_{H} (400 MHz, CDCl₃) 2.18 (tt, *J* = 7.7, 6.8 Hz, 2H, CH₂), 2.63 (dd, *J* = 8.5, 7.7 Hz, 2H, CH₂C(O)), 3.66 (s, 3H, CH₃), 3.85 – 3.94 (m, 2H, CH₂N), 6.17 – 6.24 (m, 2H, Ar H), 6.71 (dd, *J* = 2.6, 1.9 Hz, 1H, Ar H), 7.41 (d, *J* = 8.8 Hz, 2H, Ar H), 7.65 (d, *J* = 8.8 Hz, 2H, Ar H); δ_{C} (100 MHz, CDCl₃) 18.2 (CH₂), 32.9 (CH₂C(O)), 35.2 (CH₃), 48.9 (CH₂N), 107.9 (Ar CH), 108.7 (Ar CH), 119.9 (Ar CH), 123.7 (Ar CH), 129.1 (Ar CH), 129.6 (Ar C), 134.2 (Ar C), 138.2 (Ar C), 174.3 (C=O); ν_{max} (thin film/cm⁻¹) 838, 982, 1024, 1057, 1125, 1222, 1243, 1389, 1477, 1504, 1547, 1688, 2878, 2975, 3098; MS (GCMS) *m/z* 240.1 (M⁺); HRMS C₁₅H₁₇ON₂⁺ (M+H⁺) Expected 241.1335, Found 241.1337.

N-(4-(1-Methyl-1H-pyrrol-2-yl)phenyl)acetamide, **15**

Prepared as described in General Procedure D: *N*-acetylaniline (27 mg, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (50% EtOAc in hexanes), gave **15** (23.1 mg, 0.11 mmol, 54%) as a white solid; m.p. (recrystallized from CHCl₃) 164 – 166 °C; δ_{H} (400 MHz, CDCl₃) 2.19 (s, 3H, CH₃), 3.64 (s, 3H, NCH₃), 6.16 – 6.23 (m, 2H, Ar *H*), 6.67 – 6.73 (m, 1H, Ar *H*), 7.35 (br s, NH), 7.35 (d, *J* = 8.6 Hz, 2H, Ar *H*), 7.53 (d, *J* = 8.6 Hz, 2H, Ar *H*); δ_{C} (100 MHz, CDCl₃) 24.8 (CH₃), 35.2 (NCH₃), 107.9 (Ar CH), 108.6 (Ar CH), 120.0 (Ar CH), 123.7 (Ar CH), 129.3 (Ar CH), 129.6 (Ar C), 134.2 (Ar C), 136.7 (Ar C), 168.4 (C=O); ν_{max} (thin film/cm⁻¹) 788, 832, 966, 978, 1017, 1183, 1238, 1265, 1321, 1366, 1401, 1505, 1529, 1542, 1601, 1658, 2927, 3061, 3116, 3182, 3303; MS (GCMS) *m/z* 214.1 (M⁺); HRMS C₁₃H₁₅ON₂⁺ (M+H⁺) Expected 215.1179, Found 215.1177.

4-Methyl-*N*-(4-(1-methyl-1H-pyrrol-2-yl)phenyl)benzenesulfonamide, **16**

Prepared as described in General Procedure D: *N*-tosylaniline (50 mg, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (25% EtOAc in hexanes), gave **16** (37.9 g, 0.12 mmol, 58%) as a white solid; m.p. (recrystallized from CHCl₃) 86 – 88 °C; δ_{H} (400 MHz, CDCl₃) 2.39 (s, 3H, CH₃), 3.61 (s, 3H, NCH₃), 6.13 – 6.21 (m, 2H, Ar *H*), 6.66 – 6.72 (m, 1H, Ar *H*), 6.87 (s, 1H, NH), 7.10 (d, *J* = 8.4 Hz, 2H, Ar *H*), 7.23 – 7.31 (m, 4H, Ar *H*), 7.71 (d, *J* = 8.4 Hz, 2H, Ar *H*); δ_{C} (100 MHz, CDCl₃) 21.7 (CH₃), 35.2 (NCH₃), 108.0 (Ar CH), 108.8 (Ar CH), 121.6 (Ar CH), 124.0 (Ar CH), 127.4 (Ar CH), 129.5 (Ar CH), 129.8 (Ar CH), 130.6 (Ar C), 133.7 (Ar C), 135.2 (Ar C), 136.3 (Ar C), 144.1 (Ar C); ν_{max} (thin film/cm⁻¹) 813, 912, 1017, 1089, 1155, 1223, 1328, 1393, 1447, 1479, 1547, 1596, 2922, 3046, 3249; MS (GCMS) *m/z* 326.1 (M⁺); HRMS C₁₈H₁₉O₂N₂S⁺ (M+H⁺) Expected 327.1162, Found 327.1153.

N-(4-(1-Methyl-1H-pyrrol-2-yl)phenyl)methanesulfonamide, **17**

Prepared as described in General Procedure D: *N*-mesylaniline (34 mg, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (30% EtOAc in hexanes), gave **17** (28.0 mg, 0.11 mmol, 56%) as a colourless oil; δ_{H} (400 MHz, CDCl₃) 3.07 (s, 3H, CH₃), 3.66 (s, 3H, NCH₃), 6.17 – 6.25 (m, 2H, Ar *H*), 6.69 – 6.75 (m, 1H, Ar *H*), 6.78 (s, 1H, NH), 7.27 (d, *J* = 8.5 Hz, 2H, Ar *H*), 7.39 (d, *J* = 8.5 Hz, 2H, Ar *H*); δ_{C} (100 MHz, CDCl₃) 35.2 (NCH₃), 39.7 (CH₃), 108.0 (Ar CH), 109.0 (Ar CH), 120.9 (Ar CH), 124.1 (Ar CH), 129.9 (Ar CH), 130.9 (Ar C), 133.6 (Ar C), 135.3 (Ar C); ν_{max} (thin film/cm⁻¹) 840, 907, 966, 1058, 1090, 1147, 1222, 1322, 1391, 1504, 1546, 2849, 2927, 3012, 3257; MS (GCMS) *m/z* 250.1 (M⁺); HRMS C₁₂H₁₅O₂N₂S⁺ (M+H⁺) Expected 251.0849, Found 251.0848.

2-(3-Fluoro-4-methoxyphenyl)-1-methyl-1H-pyrrole, **18**

Prepared as described in General Procedure C: 2-fluoroanisole (23 μ L, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (30% CHCl₃ in hexanes), gave **18** (27.5 mg, 0.13 mmol, 67%) as a white solid; m.p. (recrystallized from CHCl₃) 53 – 55 °C; δ_{H} (400 MHz, CDCl₃) 3.65 (s, 3H, NCH₃), 3.93 (s, 3H, OCH₃), 6.15 – 6.23 (m, 2H, Ar *H*), 6.68 – 6.73 (m, 1H, Ar *H*), 6.95 – 7.04 (m, 1H, Ar *H*), 7.09 – 7.17 (m, 2H, Ar *H*); δ_{C} (100 MHz, CDCl₃) 35.1 (NCH₃), 56.5 (OCH₃), 107.9 (Ar CH), 108.7 (Ar CH), 113.4 (d, *J* = 2.4 Hz, Ar CH), 116.6 (d, *J* = 18.8 Hz, Ar CH), 123.7 (Ar CH), 124.6 (d, *J* = 3.4 Hz, Ar CH), 126.7 (d, *J* = 7.0 Hz, Ar C), 133.3 (d, *J* = 2.0 Hz, Ar C), 146.7 (d, *J* = 10.7 Hz, Ar C), 152.1 (d, *J* = 245.7 Hz, Ar C); δ_{F} (376 MHz, CDCl₃) -135.3; ν_{max} (thin film/cm⁻¹) 813, 874, 996, 1023, 1049, 1090, 1169, 1268, 1297, 1463, 1478, 1508, 1549, 2838, 2934, 3098; MS (GCMS) *m/z* 205.0 (M⁺); HRMS C₁₂H₁₃ONF⁺ (M+H⁺) Expected 206.0976, Found 206.0975.

2-(3-Chloro-4-methoxyphenyl)-1-methyl-1H-pyrrole, **19**

Prepared as described in General Procedure C: 2-chloroanisole (25 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Ti_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (40% CHCl_3 in hexanes), gave **19** (30.2 mg, 0.14 mmol, 68%) as an off-white solid; m.p. (recrystallized from CHCl_3) 58 – 60 $^\circ\text{C}$; δ_{H} (400 MHz, CDCl_3) 3.64 (s, 3H, NCH_3), 3.94 (s, 3H, OCH_3), 6.15 – 6.21 (m, 2H, Ar *H*), 6.67 – 6.73 (m, 1H, Ar *H*), 6.97 (d, J = 8.5 Hz, 1H, Ar *H*), 7.26 (dd, J = 8.5, 2.2 Hz, 1H, Ar *H*), 7.42 (d, J = 2.2 Hz, 1H, Ar *H*); δ_{C} (100 MHz, CDCl_3) 35.1 (NCH_3), 56.3 (OCH_3), 107.9 (Ar CH), 108.7 (Ar CH), 112.0 (Ar CH), 122.4 (Ar C), 123.6 (Ar CH), 127.0 (Ar C), 128.2 (Ar CH), 130.6 (Ar CH), 133.1 (Ar C), 154.1 (Ar C); ν_{max} (thin film/ cm^{-1}) 885, 992, 1020, 1061, 1149, 1183, 1253, 1287, 1474, 1498, 1544, 1564, 2837, 2942, 3002, 3098; MS (GCMS) m/z 221.0 (M^+); HRMS $\text{C}_{12}\text{H}_{13}\text{ONCl}^+$ ($\text{M}+\text{H}^+$) Expected 222.0680, Found 222.0681.

2-(3-Bromo-4-methoxyphenyl)-1-methyl-1H-pyrrole, **20**

Prepared as described in General Procedure C: 2-bromoanisole (25 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Ti_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (30% CHCl_3 in hexanes), gave **20** (36.6 mg, 0.14 mmol, 69%) as an off-white solid; m.p. (recrystallized from CHCl_3) 71 – 73 $^\circ\text{C}$; δ_{H} (400 MHz, CDCl_3) 3.64 (s, 3H, NCH_3), 3.93 (s, 3H, OCH_3), 6.13 – 6.22 (m, 2H, Ar *H*), 6.67 – 6.73 (m, 1H, Ar *H*), 6.94 (d, J = 8.4 Hz, 1H, Ar *H*), 7.31 (dd, J = 8.4, 2.2 Hz, 1H, Ar *H*), 7.60 (d, J = 2.2 Hz, 1H, Ar *H*); δ_{C} (100 MHz, CDCl_3) 35.0 (NCH_3), 56.4 (OCH_3), 107.9 (Ar CH), 108.7 (Ar CH), 111.6 (Ar C), 111.8 (Ar CH), 123.6 (Ar CH), 127.5 (Ar C), 128.9 (Ar CH), 132.9 (Ar C), 133.6 (Ar CH), 155.0 (Ar C); ν_{max} (thin film/ cm^{-1}) 711, 783, 812, 885, 1017, 1053, 1147, 1182, 1251, 1283, 1360, 1441, 1542, 2836, 2939, 3002; MS (GCMS) m/z 265.0 (M^+); HRMS $\text{C}_{12}\text{H}_{13}\text{ONBr}^+$ ($\text{M}+\text{H}^+$) Expected 266.0175, Found 266.0177.

2-(3-Iodo-4-methoxyphenyl)-1-methyl-1H-pyrrole, **21**

Prepared as described in General Procedure C: 2-iodoanisole (26 μ L, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), Ti_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (30% CHCl_3 in hexanes), gave **21** (40.1 mg, 0.13 mmol, 64%) as a colourless oil; δ_{H} (400 MHz, CDCl_3) 3.63 (s, 3H, NCH_3), 3.92 (s, 3H, OCH_3), 6.12 – 6.24 (m, 2H, Ar *H*), 6.67 – 6.73 (m, 1H, Ar *H*), 6.86 (d, J = 8.5 Hz, 1H, Ar *H*), 7.34 (dd, J = 8.5, 2.1 Hz, 1H, Ar *H*), 7.84 (d, J = 2.1 Hz, 1H, Ar *H*); δ_{C} (100 MHz, CDCl_3) 35.0 (NCH_3), 56.6 (OCH_3), 85.9 (Ar C), 107.8 (Ar CH), 108.7 (Ar CH), 110.7 (Ar CH), 123.6 (Ar CH), 128.1 (Ar C), 130.0 (Ar CH), 132.8 (Ar C), 139.8 (Ar CH), 157.2 (Ar C); ν_{max} (thin film/ cm^{-1}) 710, 751, 815, 886, 1014, 1037, 1144, 1180, 1239, 1279, 1427, 1461, 1490, 1540, 2835, 2937, 2959, 3002; MS (GCMS) m/z 313.0 (M^+); HRMS $\text{C}_{12}\text{H}_{13}\text{ONI}^+$ ($\text{M}+\text{H}^+$) Expected 314.0036, Found 314.0035.

2-Methoxy-5-(1-methyl-1H-pyrrol-2-yl)phenyl trifluoromethanesulfonate, **22**

Prepared as described in General Procedure C: 2-methoxyphenyl trifluoromethanesulfonate (51 mg, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), Ti_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (40% CHCl_3 in hexanes), gave **22** (57.5 mg, 0.17 mmol, 86%) as a colourless oil; δ_{H} (400 MHz, CDCl_3) 3.52 (s, 3H, NCH_3), 3.85 (s, 3H, OCH_3), 6.20 (dd, J = 3.6, 1.8 Hz, 1H, Ar *H*), 6.24 (dd, J = 3.6, 2.7 Hz, 1H, Ar *H*), 6.77 (dd, J = 2.7, 1.8 Hz, 1H, Ar *H*), 6.97 (d, J = 9.0 Hz, 1H, Ar *H*), 7.19 – 7.29 (m, 2H, Ar *H*); δ_{C} (100 MHz, CDCl_3) 34.8 (NCH_3), 56.1 (OCH_3), 108.0 (Ar CH), 110.2 (Ar CH), 111.6 (Ar CH), 118.9 (q, J = 320.9 Hz, CF_3), 121.6 (Ar CH), 123.6 (Ar CH), 124.5 (Ar C), 124.8 (Ar CH), 129.0 (Ar C), 142.8 (Ar C), 156.9 (Ar C); δ_{F} (376 MHz, CDCl_3) -72.7; ν_{max} (thin film/ cm^{-1}) 714, 878, 906, 1025, 1089, 1135, 1204, 1418, 1495, 1546, 2844, 2915, 2942, 3002; MS (GCMS) m/z 335.1 (M^+); HRMS $\text{C}_{13}\text{H}_{13}\text{O}_4\text{NF}_3\text{S}^+$ ($\text{M}+\text{H}^+$) Expected 336.0512, Found 336.0501.

2-(4-Methoxy-3-(methylsulfonyl)phenyl)-1-methyl-1H-pyrrole, 23

Prepared as described in General Procedure C: 2-mesylnisole (37 mg, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (50% EtOAc in hexanes), gave **23** (40.3 mg, 0.15 mmol, 76%) as a colourless oil; δ_{H} (400 MHz, CDCl₃) 3.25 (s, 3H, CH₃), 3.64 (s, 3H, NCH₃), 4.03 (s, 3H, OCH₃), 6.19 (dd, J = 3.6, 2.7 Hz, 1H, Ar *H*), 6.22 (dd, J = 3.6, 1.8 Hz, 1H, Ar *H*), 6.71 (dd, J = 2.7, 1.8 Hz, 1H, Ar *H*), 7.10 (d, J = 8.6 Hz, 1H, Ar *H*), 7.62 (dd, J = 8.6, 2.4 Hz, 1H, Ar *H*), 8.01 (d, J = 2.4 Hz, 1H, Ar *H*); δ_{C} (100 MHz, CDCl₃) 35.2 (NCH₃), 43.1 (CH₃), 56.6 (OCH₃), 108.0 (Ar CH), 109.2 (Ar CH), 112.7 (Ar CH), 124.2 (Ar CH), 126.6 (Ar C), 128.5 (Ar C), 129.5 (Ar CH), 132.3 (Ar C), 135.5 (Ar CH), 156.0 (Ar C); ν_{max} (thin film/cm⁻¹) 719, 749, 831, 911, 958, 1015, 1064, 1139, 1281, 1301, 1429, 1475, 1492, 1543, 1568, 2844, 2942, 3019; MS (GCMS) m/z 265.0 (M⁺); HRMS C₁₃H₁₆O₃NS⁺ (M+H⁺) Expected 266.0845, Found 266.0845.

6-(1-Methyl-1H-pyrrol-2-yl)chroman-4-one, 24

Prepared as described in General Procedure C: chroman-4-one (30 mg, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% EtOAc in hexanes), gave **24** (21.9 mg, 0.10 mmol, 48%) as a pale yellow oil; δ_{H} (400 MHz, CDCl₃) 2.84 (t, J = 6.3 Hz, 2H, CH₂C(O)), 3.65 (s, 3H, NCH₃), 4.57 (t, J = 6.3 Hz, 2H, CH₂O), 6.19 (dd, J = 3.6, 2.7 Hz, 1H, Ar *H*), 6.21 (dd, J = 3.6, 1.9 Hz, 1H, Ar *H*), 6.70 (dd, J = 2.7, 1.9 Hz, 1H, Ar *H*), 7.02 (d, J = 8.6 Hz, 1H, Ar *H*), 7.53 (dd, J = 8.6, 2.4 Hz, 1H, Ar *H*), 7.91 (d, J = 2.4 Hz, 1H, Ar *H*); δ_{C} (100 MHz, CDCl₃) 35.2 (NCH₃), 37.9 (CH₂C(O)), 67.2 (CH₂O), 107.9 (Ar CH), 108.8 (Ar CH), 118.2 (Ar CH), 121.2 (Ar C), 123.8 (Ar CH), 126.5 (Ar CH), 127.0 (Ar C), 133.2 (Ar C), 136.5 (Ar CH), 160.8 (Ar C), 191.7 (C=O); ν_{max} (thin film/cm⁻¹) 713, 831, 872, 914, 927, 1028, 1063, 1133, 1172, 1236, 1279, 1403, 1461, 1491, 1615, 1687, 2878, 2923, 3054, 3098; MS (GCMS) m/z 227.1 (M⁺); HRMS C₁₄H₁₄O₂N⁺ (M+H⁺) Expected 228.1019, Found 228.1018.

N,N-Diethyl-2-methoxy-5-(1-methyl-1H-pyrrol-2-yl)benzamide, **25**

Prepared as described in General Procedure C: **S8** (42 mg, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (50% EtOAc in hexanes), gave **25** (36.7 mg, 0.13 mmol, 64%) as a white solid; m.p. (recrystallized from CHCl₃) 69 – 71 °C; δ_{H} (400 MHz, CDCl₃) 1.05 (t, J = 7.1 Hz, 3H, CH₃), 1.24 (t, J = 7.1 Hz, 3H, CH₃), 3.19 (q, J = 7.1 Hz, 2H, CH₂), 3.53 – 3.64 (m, 2H, CH₂), 3.63 (s, 3H, NCH₃), 3.85 (s, 3H, OCH₃), 6.13 – 6.21 (m, 2H, Ar H), 6.65 – 6.71 (m, 1H, Ar H), 6.94 (d, J = 8.6 Hz, 1H, Ar H), 7.22 (d, J = 2.3 Hz, 1H, Ar H), 7.34 (dd, J = 8.6, 2.3 Hz, 1H, Ar H); δ_{C} (100 MHz, CDCl₃) 13.0 (CH₃), 14.1 (CH₃), 35.1 (NCH₃), 38.9 (CH₂), 42.9 (CH₂), 55.8 (OCH₃), 107.8 (Ar CH), 108.4 (Ar CH), 111.1 (Ar CH), 123.4 (Ar CH), 126.3 (Ar C), 127.1 (Ar C), 127.9 (Ar CH), 130.3 (Ar CH), 133.8 (Ar C), 154.4 (Ar C), 168.5 (C=O); ν_{max} (thin film/cm⁻¹) 710, 781, 821, 877, 1022, 1085, 1144, 1175, 1248, 1292, 1378, 1440, 1472, 1543, 1626, 2837, 2872, 2970; MS (GCMS) m/z 286.1 (M⁺); HRMS C₁₇H₂₃O₂N₂⁺ (M+H⁺) Expected 287.1754, Found 287.1748.

Methyl 2-methoxy-5-(1-methyl-1H-pyrrol-2-yl)benzoate, **26**

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% EtOAc in hexanes), gave **26** (32.9 mg, 0.13 mmol, 67%) as a white solid.

10 mmol scale reaction: methyl 2-methoxybenzoate (1.44 mL, 10 mmol), dibenzothiophene S-oxide (2.20 g, 11 mmol), Tf₂O (2.02 mL, 12 mmol), PTH (275 mg, 1.0 mmol), *N*-methylpyrrole (17.8 mL, 200 mmol, 20 equiv.), after purification on silica gel (20% EtOAc in hexanes), gave **26** (1.45 g, 5.9 mmol, 59%, 68% brsm) as a white solid; m.p. (recrystallized from CHCl₃) 70 – 72 °C; δ_{H} (400 MHz, CDCl₃) 3.63 (s, 3H, NCH₃), 3.90 (s, 3H, OCH₃), 3.94 (s, 3H, OCH₃), 6.15 – 6.22 (m, 2H, Ar H), 6.67 – 6.73 (m, 1H, Ar H), 7.02 (d, J = 8.6 Hz, 1H, Ar H), 7.50 (dd, J = 8.6, 2.4 Hz, 1H, Ar H), 7.84 (d, J = 2.4 Hz, 1H, Ar H); δ_{C} (100 MHz, CDCl₃) 35.0 (NCH₃), 52.2 (OCH₃), 56.3 (OCH₃), 107.8 (Ar CH), 108.6 (Ar CH), 112.2 (Ar CH), 120.0 (Ar C), 123.5 (Ar CH), 125.7 (Ar C), 132.0 (Ar CH), 133.3 (Ar C), 133.8 (Ar CH), 158.1 (Ar C),

166.6 (C=O); $\nu_{\max}$ (thin film/cm⁻¹) 712, 784, 821, 965, 1021, 1081, 1229, 1255, 1315, 1463, 1497, 1543, 1574, 1699, 1726, 2838, 2949, 3097; MS (GCMS) m/z 245.1 (M⁺); HRMS C₁₄H₁₆O₃N⁺ (M+H⁺) Expected 246.1125, Found 246.1120.

2-(2-Methoxy-5-(trifluoromethyl)phenyl)-1-methyl-1H-pyrrole, 27

Prepared as described in General Procedure C: 4-trifluoromethylanisole (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (30% CHCl₃ in hexanes), gave **27** (41.6 mg, 0.16 mmol, 82%) as a white solid; m.p. (recrystallized from CHCl₃) 67 – 69 °C; δ_{H} (400 MHz, CDCl₃) 3.50 (s, 3H, NCH₃), 3.88 (s, 3H, OCH₃), 6.20 (dd, J = 3.6, 1.8 Hz, 1H, Ar H), 6.24 (dd, J = 3.6, 2.7 Hz, 1H, Ar H), 6.73 – 6.79 (m, 1H, Ar H), 7.03 (d, J = 8.6 Hz, 1H, Ar H), 7.56 (d, J = 2.4 Hz, 1H, Ar H), 7.57 – 7.65 (m, 1H, Ar H); δ_{C} (100 MHz, CDCl₃) 34.7 (NCH₃), 55.9 (OCH₃), 107.9 (Ar CH), 109.8 (Ar CH), 110.7 (Ar CH), 123.0 (q, J = 32.8 Hz, Ar C), 123.2 (Ar C), 123.3 (Ar CH), 124.2 (q, J = 271.0 Hz, CF₃), 126.5 (q, J = 3.8 Hz, Ar CH), 129.5 (q, J = 3.6 Hz, Ar CH), 129.7 (Ar C), 159.8 (Ar C); δ_{F} (376 MHz, CDCl₃) -61.5; $\nu_{\max}$ (thin film/cm⁻¹) 711, 818, 907, 1022, 1045, 1079, 1111, 1166, 1268, 1330, 1446, 1505, 1613, 2841, 2947, 3101; MS (GCMS) m/z 255.1 (M⁺); HRMS C₁₃H₁₃ONF₃⁺ (M+H⁺) Expected 256.0944, Found 256.0939.

4-Methoxy-3-(1-methyl-1H-pyrrol-2-yl)benzonitrile, 28

Prepared as described in General Procedure C: 4-methoxybenzonitrile (26 mg, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% EtOAc in hexanes), gave **28** (30.1 mg, 0.14 mmol, 71%) as a colourless oil; δ_{H} (400 MHz, CDCl₃) 3.48 (s, 3H, NCH₃), 3.89 (s, 3H, OCH₃), 6.14 – 6.20 (m, 1H, Ar H), 6.19 – 6.26 (m, 1H, Ar H), 6.72 – 6.79 (m, 1H, Ar H), 7.01 (d, J = 8.6 Hz, 1H, Ar H), 7.56 (d, J = 2.1 Hz, 1H, Ar H), 7.65 (dd, J = 8.6, 2.1 Hz, 1H, Ar H); δ_{C} (100 MHz, CDCl₃) 34.8 (NCH₃), 56.0 (OCH₃), 104.2 (Ar C), 108.1 (Ar CH), 110.2 (Ar CH), 111.4 (Ar CH), 119.1 (C $\equiv$ N), 123.6 (Ar CH), 124.1 (Ar C), 128.7 (Ar C), 133.7 (Ar CH), 135.9 (Ar

CH), 160.7 (Ar C); $\nu_{\max}$ (thin film/cm⁻¹) 714, 817, 892, 904, 1018, 1056, 1142, 1259, 1295, 1463, 1495, 1540, 1580, 1600, 2222, 2841, 2943, 3099; MS (GCMS) m/z 212.1 (M⁺); HRMS C₁₃H₁₃ON₂⁺ (M+H⁺) Expected 213.1022, Found 213.1019.

Methyl 2-methoxy-5-(1H-pyrrol-2-yl)benzoate, 29

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-H-pyrrole (0.28 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (30% EtOAc in hexanes), gave **29** (23.9 mg, 0.10 mmol, 52%) as a white solid; m.p. (recrystallized from CHCl₃) 93 – 95 °C; δ_{H} (400 MHz, CDCl₃) 3.89 (s, 3H, OCH₃), 3.91 (s, 3H, OCH₃), 6.29 (dd, J = 3.9, 2.7 Hz, 1H, Ar H), 6.45 (dd, J = 3.9, 1.5 Hz, 1H, Ar H), 6.84 (dd, J = 2.7, 1.5 Hz, 1H, Ar H), 6.96 (d, J = 8.7 Hz, 1H, Ar H), 7.58 (dd, J = 8.7, 2.5 Hz, 1H, Ar H), 7.90 (d, J = 2.5 Hz, 1H, Ar H), 8.56 (s, 1H, NH); δ_{C} (100 MHz, CDCl₃) 52.3 (OCH₃), 56.3 (OCH₃), 105.6 (Ar CH), 110.1 (Ar CH), 112.8 (Ar CH), 118.8 (Ar CH), 120.3 (Ar C), 125.7 (Ar C), 127.2 (Ar CH), 129.3 (Ar CH), 131.1 (Ar C), 157.7 (Ar C), 166.8 (C=O); $\nu_{\max}$ (thin film/cm⁻¹) 722, 787, 820, 1020, 1060, 1085, 1182, 1234, 1255, 1315, 1434, 1462, 1498, 1564, 1578, 1709, 2839, 2948, 3001, 3098, 3356; MS (GCMS) m/z 231.1 (M⁺); HRMS C₁₃H₁₄O₃N⁺ (M+H⁺) Expected 232.0968, Found 232.0965.

Methyl 2-methoxy-5-(1-phenyl-1H-pyrrol-2-yl)benzoate, 30

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-phenylpyrrole (286 mg, 2.00 mmol, 10 equiv.), after purification by column chromatography on silica gel (20% EtOAc in hexanes), gave **30** (41.8 mg, 0.14 mmol, 68%) as a colourless oil; δ_{H} (400 MHz, CDCl₃) 3.83 (s, 3H, OCH₃), 3.86 (s, 3H, OCH₃), 6.35 (dd, J = 3.6, 2.8 Hz, 1H, Ar H), 6.41 (dd, J = 3.6, 1.8 Hz, 1H, Ar H), 6.78 (d, J = 8.7 Hz, 1H, Ar H), 6.93 (dd, J = 2.8, 1.8 Hz, 1H, Ar H), 7.09 (dd, J = 8.7, 2.4 Hz, 1H, Ar H), 7.11 – 7.20 (m, 2H, Ar H), 7.23 – 7.33 (m, 1H, Ar H), 7.29 – 7.40 (m, 2H, Ar H), 7.69 (d, J =

2.4 Hz, 1H, Ar H); δ_c (100 MHz, $CDCl_3$) 52.1 (OCH_3), 56.2 (OCH_3), 109.3 (Ar CH), 110.4 (Ar CH), 111.8 (Ar CH), 119.9 (Ar C), 124.2 (Ar CH), 125.5 (Ar C), 125.9 (Ar CH), 126.8 (Ar CH), 129.2 (Ar CH), 131.7 (Ar CH), 132.6 (Ar C), 133.3 (Ar CH), 140.4 (Ar C), 157.7 (Ar C), 166.6 ($C=O$); ν_{max} (thin film/ cm^{-1}) 764, 822, 950, 1022, 1070, 1084, 1154, 1185, 1232, 1263, 1301, 1435, 1454, 1497, 1544, 1597, 1728, 2838, 2947, 3002, 3102; MS (GCMS) m/z 307.1 (M^+); HRMS $C_{19}H_{18}O_3N^+$ ($M+H^+$) Expected 308.1281, Found 308.1276.

tert-Butyl 2-(4-methoxy-3-(methoxycarbonyl)phenyl)-1H-pyrrole-1-carboxylate, **31**

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-Boc-pyrrole (0.33 mL, 2.00 mmol, 10 equiv.), after purification by column chromatography on silica gel (20% EtOAc in hexanes), gave **31** (50.6 mg, 0.15 mmol, 76%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 1.40 (s, 9H, CH_3), 3.90 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 6.14 – 6.21 (m, 1H, Ar H), 6.20 – 6.27 (m, 1H, Ar H), 6.99 (d, J = 8.6 Hz, 1H, Ar H), 7.35 – 7.40 (m, 1H, Ar H), 7.49 (dd, J = 8.6, 2.4 Hz, 1H, Ar H), 7.83 (d, J = 2.3 Hz, 1H, Ar H); δ_c (100 MHz, $CDCl_3$) 27.8 (CH_3), 52.1 (OCH_3), 56.2 (OCH_3), 83.9 (CH_3C), 110.7 (Ar CH), 111.3 (Ar CH), 114.6 (Ar CH), 119.1 (Ar C), 122.7 (Ar CH), 126.6 (Ar C), 132.9 (Ar CH), 133.6 (Ar C), 134.3 (Ar CH), 149.4 (Ar C), 158.6 ($C=O$), 166.5 ($C=O$); ν_{max} (thin film/ cm^{-1}) 730, 771, 813, 832, 962, 1022, 1080, 1142, 1253, 1311, 1504, 1579, 1728, 2839, 2950, 2978; MS (GCMS) m/z 331.1 (M^+); HRMS $C_{18}H_{22}O_5N^+$ ($M+H^+$) Expected 332.1492, Found 332.1484.

Methyl 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-1-methyl-1H-pyrrole-2-carboxylate, **32**

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), methyl 2-pyrrolecarboxylate (0.52 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% EtOAc in hexanes), gave **32** (36.9 mg, 0.12 mmol, 61%) as a white solid; m.p. (recrystallized from $CHCl_3$) 104 – 106 $^{\circ}C$; δ_H (400 MHz, $CDCl_3$) 3.83 (s, 3H, OCH_3), 3.85 (s, 3H, NCH_3), 3.90 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 6.17 (d, J = 4.0 Hz, 1H, Ar H), 7.00 (d, J = 4.0 Hz, 1H,

Ar H), 7.05 (d, $J = 8.6$ Hz, 1H, Ar H), 7.48 (dd, $J = 8.6, 2.4$ Hz, 1H, Ar H), 7.83 (d, $J = 2.4$ Hz, 1H, Ar H); δ_c (100 MHz, $CDCl_3$) 34.4 (NCH_3), 51.2 (OCH_3), 52.3 (OCH_3), 56.3 (OCH_3), 109.2 (Ar CH), 112.3 (Ar CH), 117.8 (Ar CH), 120.3 (Ar C), 123.4 (Ar C), 124.4 (Ar C), 132.8 (Ar CH), 134.4 (Ar CH), 140.4 (Ar C), 159.0 (Ar C), 162.0 (C=O), 166.3 (C=O); ν_{max} (thin film/ cm^{-1}) 753, 785, 822, 914, 1021, 1082, 1106, 1183, 1238, 1300, 1433, 1454, 1539, 1575, 1697, 1729, 2841, 2949, 2997; MS (GCMS) m/z 303.1 (M^+); HRMS $C_{16}H_{18}O_5N^+$ ($M+H^+$) Expected 304.1179, Found 304.1176.

Methyl 2-methoxy-5-(thiophen-2-yl)benzoate, **33**

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), thiophene (0.32 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% EtOAc in hexanes), gave **33** (29.3 mg, 0.12 mmol, 59%) as a white solid; m.p. (recrystallized from $CHCl_3$) 85 – 87 $^{\circ}C$; δ_H (400 MHz, $CDCl_3$) 3.94 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 7.01 (d, $J = 8.7$ Hz, 1H, Ar H), 7.08 (dd, $J = 4.9, 3.9$ Hz, 1H, Ar H), 7.24 – 7.30 (m, 2H, Ar H), 7.71 (dd, $J = 8.7, 2.5$ Hz, 1H, Ar H), 8.05 (d, $J = 2.5$ Hz, 1H, Ar H); δ_c (100 MHz, $CDCl_3$) 52.3 (OCH_3), 56.3 (OCH_3), 112.6 (Ar CH), 120.5 (Ar C), 122.9 (Ar CH), 124.6 (Ar CH), 127.1 (Ar C), 128.2 (Ar CH), 129.3 (Ar CH), 131.0 (Ar CH), 143.2 (Ar C), 158.6 (Ar C), 166.5 (C=O); ν_{max} (thin film/ cm^{-1}) 814, 858, 956, 1008, 1025, 1081, 1207, 1234, 1263, 1306, 1432, 1493, 1574, 1610, 1727, 2837, 2947, 3002; MS (GCMS) m/z 248.0 (M^+); HRMS $C_{13}H_{12}O_3S^+$ (M^+) Expected 248.0502, Found 248.0510.

Methyl 5-(3,4-dibromothiophen-2-yl)-2-methoxybenzoate, **34**

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), 3,4-dibromothiophene (0.44 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (15% EtOAc in hexanes), gave **34** (50.4 mg, 0.12 mmol, 62%) as a white solid; m.p. (recrystallized from $CHCl_3$) 126 – 128 $^{\circ}C$; δ_H (400 MHz, $CDCl_3$) 3.91 (s, 3H, OCH_3), 3.95 (s,

3H, OCH₃), 7.05 (d, *J* = 8.7 Hz, 1H, Ar *H*), 7.35 (s, 1H, Ar *H*), 7.72 (dd, *J* = 8.7, 2.5 Hz, 1H, Ar *H*), 8.02 (d, *J* = 2.5 Hz, 1H, Ar *H*); δ_c (100 MHz, CDCl₃) 52.4 (OCH₃), 56.3 (OCH₃), 111.6 (Ar C), 112.3 (Ar CH), 114.8 (Ar C), 120.4 (Ar C), 122.2 (Ar CH), 125.1 (Ar C), 132.5 (Ar CH), 134.1 (Ar CH), 138.3 (Ar C), 159.5 (Ar C), 166.1 (C=O); $\nu_{\max}$ (thin film/cm⁻¹) 751, 824, 839, 881, 967, 1008, 1014, 1026, 1120, 1157, 1262, 1313, 1398, 1433, 1485, 1521, 1609, 1710, 1734, 2839, 2942, 3003, 3132; MS (GCMS) *m/z* 403.2 (M⁺); HRMS C₁₃H₁₁O₃Br₂S⁺ (M+H⁺) Expected 404.8790, Found 404.8793.

Methyl 5-(4-acetylthiophen-2-yl)-2-methoxybenzoate, 35

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), 3-acetylthiophene (505 mg, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (30% EtOAc in hexanes), gave **35** (37.6 mg, 0.13 mmol, 65%) as a white solid; m.p. (recrystallized from CHCl₃) 86 – 88 °C; δ_H (400 MHz, CDCl₃) 2.26 (s, 3H, CH₃), 3.89 (s, 3H, OCH₃), 3.95 (s, 3H, OCH₃), 7.03 (d, *J* = 8.6 Hz, 1H, Ar *H*), 7.23 (d, *J* = 5.3 Hz, 1H, Ar *H*), 7.43 (d, *J* = 5.3 Hz, 1H, Ar *H*), 7.58 (dd, *J* = 8.6, 2.4 Hz, 1H, Ar *H*), 7.90 (d, *J* = 2.4 Hz, 1H, Ar *H*); δ_c (100 MHz, CDCl₃) 30.1 (CH₃), 52.3 (OCH₃), 56.3 (OCH₃), 112.1 (Ar CH), 120.0 (Ar C), 124.3 (Ar CH), 125.5 (Ar C), 129.4 (Ar CH), 133.2 (Ar CH), 135.0 (Ar CH), 137.9 (Ar C), 148.4 (Ar C), 159.7 (Ar C), 166.1 (C=O), 194.5 (C=O); $\nu_{\max}$ (thin film/cm⁻¹) 737, 817, 824, 878, 959, 1011, 1024, 1081, 1139, 1182, 1246, 1270, 1305, 1431, 1493, 1572, 1608, 1673, 1727, 2840, 2948, 3001, 3107; MS (GCMS) *m/z* 290.1 (M⁺); HRMS C₁₅H₁₅O₄S⁺ (M+H⁺) Expected 291.0686, Found 291.0682.

Methyl 5-(furan-2-yl)-2-methoxybenzoate, 36

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), furan (0.29 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel

(20% EtOAc in hexanes), gave **36** (26.4 mg, 0.11 mmol, 57%) as a white solid; m.p. (recrystallized from CHCl₃) 75 – 77 °C; δ_{H} (400 MHz, CDCl₃) 3.92 (s, 3H, OCH₃), 3.93 (s, 3H, OCH₃), 6.46 (dd, J = 3.3, 1.8 Hz, 1H, Ar H), 6.58 (dd, J = 3.3, 0.8 Hz, 1H, Ar H), 7.00 (d, J = 8.7 Hz, 1H, Ar H), 7.44 (dd, J = 1.8, 0.8 Hz, 1H, Ar H), 7.76 (dd, J = 8.7, 2.4 Hz, 1H, Ar H), 8.09 (d, J = 2.4 Hz, 1H, Ar H); δ_{C} (100 MHz, CDCl₃) 52.3 (OCH₃), 56.3 (OCH₃), 104.4 (Ar CH), 111.8 (Ar CH), 112.5 (Ar CH), 120.4 (Ar C), 123.8 (Ar C), 127.4 (Ar CH), 128.9 (Ar CH), 141.9 (Ar CH), 153.0 (Ar C), 158.5 (Ar C), 166.5 (C=O); ν_{max} (thin film/cm⁻¹) 733, 785, 801, 819, 915, 1013, 1082, 1153, 1181, 1217, 1235, 1310, 1462, 1479, 1507, 1596, 1726, 2838, 2903, 2949, 3002; MS (GCMS) m/z 232.0 (M⁺); HRMS C₁₃H₁₃O₄⁺ (M+H⁺) Expected 233.0808, Found 233.0804.

Methyl 2-methoxy-5-(5-methylfuran-2-yl)benzoate, 37

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), 2-methylfuran (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (10% EtOAc in hexanes), gave **37** (25.9 mg, 0.11 mmol, 53%) as a white solid; m.p. (recrystallized from CHCl₃) 77 – 79 °C; δ_{H} (500 MHz, CDCl₃) 2.36 (s, 3H, CH₃), 3.92 (s, 3H, OCH₃), 3.92 (s, 3H, OCH₃), 6.03 (d, J = 3.2 Hz, 1H, Ar H), 6.45 (d, J = 3.2 Hz, 1H, Ar H), 6.98 (d, J = 8.8 Hz, 1H, Ar H), 7.71 (dd, J = 8.8, 2.4 Hz, 1H, Ar H), 8.04 (d, J = 2.4 Hz, 1H, Ar H); δ_{C} (125 MHz, CDCl₃) 13.8 (CH₃), 52.3 (OCH₃), 56.3 (OCH₃), 105.2 (Ar CH), 107.8 (Ar CH), 112.5 (Ar CH), 120.3 (Ar C), 124.1 (Ar C), 126.9 (Ar CH), 128.4 (Ar CH), 151.3 (Ar C), 151.9 (Ar C), 158.0 (Ar C), 166.7 (C=O); ν_{max} (thin film/cm⁻¹) 782, 819, 956, 1020, 1087, 1153, 1181, 1233, 1271, 1312, 1462, 1489, 1579, 1728, 2838, 2918, 2948, 3000; MS (GCMS) m/z 246.1 (M⁺); HRMS C₁₄H₁₅O₄⁺ (M+H⁺) Expected 247.0965, Found 247.0962.

Methyl 5-(5-acetylfuran-2-yl)-2-methoxybenzoate, 38

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), 2-acetylfuran (0.40 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica

gel (40% EtOAc in hexanes), gave **38** (38.4 mg, 0.14 mmol, 70%) as a white solid; m.p. (recrystallized from CHCl₃) 94 – 96 °C; δ_{H} (400 MHz, CDCl₃) 2.51 (s, 3H, CH₃), 3.92 (s, 3H, OCH₃), 3.94 (s, 3H, OCH₃), 6.70 (d, J = 3.7 Hz, 1H, Ar H), 7.03 (dd, J = 8.8, 2.2 Hz, 1H, Ar H), 7.24 (d, J = 3.7 Hz, 1H, Ar H), 7.89 (dd, J = 8.8, 2.2 Hz, 1H, Ar H), 8.17 (d, J = 2.2 Hz, 1H, Ar H); δ_{C} (100 MHz, CDCl₃) 26.1 (CH₃), 52.4 (OCH₃), 56.4 (OCH₃), 106.8 (Ar CH), 112.6 (Ar CH), 119.9 (Ar CH), 120.8 (Ar C), 122.0 (Ar C), 128.6 (Ar CH), 130.1 (Ar CH), 151.8 (Ar C), 156.9 (Ar C), 159.7 (Ar C), 166.2 (C=O), 186.2 (C=O); ν_{max} (thin film/cm⁻¹) 786, 817, 924, 971, 1018, 1074, 1088, 1156, 1182, 1233, 1273, 1311, 1409, 1434, 1475, 1581, 1613, 1727, 2839, 2949, 3002; MS (GCMS) m/z 274.1 (M⁺); HRMS C₁₅H₁₅O₅⁺ (M+H⁺) Expected 275.0914, Found 275.0910.

Methyl 5-(4-bromofuran-2-yl)-2-methoxybenzoate, 39

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), 3-bromofuran (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (10% EtOAc in hexanes), gave **39** (38.9 mg, 0.13 mmol, 63%) as a white solid; m.p. (recrystallized from CHCl₃) 67 – 69 °C; δ_{H} (500 MHz, CDCl₃) 3.92 (s, 3H, OCH₃), 3.94 (s, 3H, OCH₃), 6.52 (d, J = 1.9 Hz, 1H, Ar H), 7.04 (d, J = 8.8 Hz, 1H, Ar H), 7.39 (d, J = 1.9 Hz, 1H, Ar H), 8.07 (dd, J = 8.8, 2.4 Hz, 1H, Ar H), 8.38 (d, J = 2.4 Hz, 1H, Ar H); δ_{C} (125 MHz, CDCl₃) 52.4 (OCH₃), 56.3 (OCH₃), 95.4 (Ar C), 112.2 (Ar CH), 116.3 (Ar CH), 120.2 (Ar C), 122.4 (Ar C), 129.2 (Ar CH), 130.7 (Ar CH), 141.7 (Ar CH), 148.1 (Ar C), 158.8 (Ar C), 166.4 (C=O); ν_{max} (thin film/cm⁻¹) 738, 785, 818, 885, 950, 1022, 1084, 1183, 1226, 1265, 1309, 1462, 1483, 1511, 1572, 1615, 1727, 2838, 2906, 2948, 3001; MS (GCMS) m/z 310.0 (M⁺); HRMS C₁₃H₁₂O₄Br⁺ (M+H⁺) Expected 310.9913, Found 310.9911.

Methyl 2-methoxy-5-(5-methylfuran-2-yl)benzoate, 40

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), TiF_4 (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), methyl furan-3-carboxylate (0.43 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (30% EtOAc in hexanes), gave **40** (38.9 mg, 0.13 mmol, 67%) as a white solid; m.p. (recrystallized from CHCl_3) 89 – 91 $^\circ\text{C}$; δ_{H} (400 MHz, CDCl_3) 3.83 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 6.81 (d, $J = 2.0$ Hz, 1H, Ar H), 7.04 (d, $J = 8.8$ Hz, 1H, Ar H), 7.39 (d, $J = 2.0$ Hz, 1H, Ar H), 8.21 (dd, $J = 8.8, 2.4$ Hz, 1H, Ar H), 8.44 (d, $J = 2.4$ Hz, 1H, Ar H); δ_{C} (100 MHz, CDCl_3) 51.8 (OCH_3), 52.3 (OCH_3), 56.3 (OCH_3), 111.7 (Ar CH), 113.0 (Ar CH), 113.1 (Ar C), 119.8 (Ar C), 122.1 (Ar C), 132.0 (Ar CH), 133.7 (Ar CH), 141.1 (Ar CH), 156.7 (Ar C), 159.9 (Ar C), 164.1 (C=O), 166.3 (C=O); ν_{max} (thin film/ cm^{-1}) 745, 785, 821, 935, 1077, 1149, 1227, 1263, 1302, 1461, 1489, 1581, 1612, 1714, 2843, 2950, 3002; MS (GCMS) m/z 290.1 (M^+); HRMS $\text{C}_{15}\text{H}_{14}\text{O}_6^+$ (M^+) Expected 290.0785, Found 290.0781.

Methyl 5-(benzofuran-2-yl)-2-methoxybenzoate, 41

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), TiF_4 (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), benzofuran (0.44 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% EtOAc in hexanes), gave **41** (29.9 mg, 0.11 mmol, 53%) as a white solid; m.p. (recrystallized from CHCl_3) 110 – 112 $^\circ\text{C}$; δ_{H} (400 MHz, CDCl_3) 3.95 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 6.96 (d, $J = 1.0$ Hz, 1H, Ar H), 7.06 (d, $J = 8.8$ Hz, 1H, Ar H), 7.23 (td, $J = 7.4, 1.0$ Hz, 1H, Ar H), 7.25 – 7.30 (m, 1H, Ar H), 7.49 – 7.54 (m, 1H, Ar H), 7.54 – 7.60 (m, 1H, Ar H), 7.96 (dd, $J = 8.8, 2.4$ Hz, 1H, Ar H), 8.30 (d, $J = 2.4$ Hz, 1H, Ar H); δ_{C} (100 MHz, CDCl_3) 52.4 (OCH_3), 56.4 (OCH_3), 100.7 (Ar CH), 111.2 (Ar CH), 112.5 (Ar CH), 120.6 (Ar C), 120.9 (Ar CH), 123.1 (Ar C), 123.1 (Ar CH), 124.3 (Ar CH), 128.6 (Ar CH), 129.4 (Ar C), 130.0 (Ar CH), 154.9 (Ar C), 155.0 (Ar C), 159.4 (Ar C), 166.4 (C=O); ν_{max} (thin film/ cm^{-1}) 749, 798, 929, 1021, 1082, 1182, 1204, 1237, 1273, 1350, 1434, 1452, 1496, 1595, 1615, 1729, 2837,

2901, 2948, 3003; MS (GCMS) m/z 282.1 (M^+); HRMS $C_{17}H_{14}O_4^+$ (M^+) Expected 282.0887, Found 282.0895.

Methyl 2-methoxy-5-(3-methyl-1H-indol-2-yl)benzoate, 42

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), 3-methylindole (525 mg, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (30% EtOAc in hexanes), gave **42** (30.8 mg, 0.10 mmol, 52%) as a white solid; m.p. (recrystallized from $CHCl_3$) 131 – 133 $^{\circ}C$; δ_H (400 MHz, $CDCl_3$) 2.44 (s, 3H, CH_3), 3.93 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 7.09 (d, J = 8.7 Hz, 1H, Ar H), 7.15 (t, J = 8.0 Hz, 1H, Ar H), 7.21 (t, J = 8.0 Hz, 1H, Ar H), 7.36 (d, J = 8.0 Hz, 1H, Ar H), 7.59 (d, J = 8.0 Hz, 1H, Ar H), 7.69 (dd, J = 8.7, 2.4 Hz, 1H, Ar H), 8.01 (d, J = 2.4 Hz, 1H, Ar H), 8.02 (s, 1H, NH); δ_C (100 MHz, $CDCl_3$) 9.7 (CH_3), 52.4 (OCH_3), 56.4 (OCH_3), 108.6 (Ar C), 110.8 (Ar CH), 112.6 (Ar CH), 119.0 (Ar CH), 119.7 (Ar CH), 120.6 (Ar C), 122.4 (Ar CH), 125.7 (Ar C), 130.1 (Ar C), 130.9 (Ar CH), 132.9 (Ar CH), 133.0 (Ar C), 135.9 (Ar C), 158.5 (Ar C), 166.6 (C=O); ν_{max} (thin film/ cm^{-1}) 743, 821, 1019, 1087, 1182, 1242, 1261, 1307, 1460, 1489, 1501, 1574, 1613, 1714, 2840, 2861, 2948, 3003, 3360; MS (GCMS) m/z 295.1 (M^+); HRMS $C_{18}H_{17}O_3N^+$ (M^+) Expected 295.1203, Found 295.1206.

Methyl 2-methoxy-5-(pyrazin-2-yl)benzoate, 43

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), pyrazine (320 mg, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (50% EtOAc in hexanes), gave **43** (20.5 mg, 0.08 mmol, 42%) as a white solid; m.p. (recrystallized from $CHCl_3$) 86 – 88 $^{\circ}C$; δ_H (400 MHz, $CDCl_3$) 3.93 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 7.11 (d, J = 8.8 Hz, 1H, Ar H), 8.16 (dd, J = 8.8, 2.5 Hz, 1H, Ar H), 8.41 – 8.52 (m, 2H, Ar H), 8.59 (dd, J = 2.5, 1.5 Hz, 1H, Ar H), 9.01 (d, J = 1.5 Hz, 1H, Ar H); δ_C (100 MHz, $CDCl_3$) 52.3 (OCH_3), 56.4 (OCH_3), 112.7 (Ar CH), 120.7

(Ar C), 128.5 (Ar C), 130.4 (Ar CH), 132.0 (Ar CH), 141.7 (Ar CH), 142.8 (Ar CH), 144.2 (Ar CH), 151.6 (Ar C), 160.6 (Ar C), 166.3 (C=O); $\nu_{\max}$ (thin film/cm⁻¹) 818, 969, 1013, 1041, 1076, 1093, 1142, 1184, 1229, 1274, 1410, 1435, 1504, 1609, 1725, 2840, 2949, 3003; MS (GCMS) m/z 244.1 (M⁺); HRMS C₁₃H₁₃O₃N₂⁺ (M+H⁺) Expected 245.0921, Found 245.0917.

Methyl 5-(2,6-dimethoxypyridin-3-yl)-2-methoxybenzoate, 44

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), 2,6-dimethoxypyridine (0.53 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (20% EtOAc in hexanes), gave **44** (25.6 mg, 0.08 mmol, 42%) as a colourless oil; δ_{H} (400 MHz, CDCl₃) 3.90 (s, 3H, OCH₃), 3.93 (s, 3H, OCH₃), 3.96 (s, 3H, OCH₃), 3.96 (s, 3H, OCH₃), 6.38 (d, J = 8.0 Hz, 1H, Ar H), 7.01 (d, J = 8.7 Hz, 1H, Ar H), 7.55 (d, J = 8.0 Hz, 1H, Ar H), 7.66 (dd, J = 8.7, 2.4 Hz, 1H, Ar H), 7.94 (d, J = 2.4 Hz, 1H, Ar H); δ_{C} (100 MHz, CDCl₃) 52.2 (OCH₃), 53.6 (OCH₃), 53.8 (OCH₃), 56.3 (OCH₃), 101.2 (Ar CH), 112.0 (Ar CH), 114.4 (Ar C), 119.9 (Ar C), 129.1 (Ar C), 132.2 (Ar CH), 134.1 (Ar CH), 141.3 (Ar CH), 158.1 (Ar C), 159.3 (Ar C), 162.3 (Ar C), 166.8 (C=O); $\nu_{\max}$ (thin film/cm⁻¹) 733, 808, 911, 953, 967, 1014, 1082, 1155, 1181, 1243, 1369, 1420, 1455, 1476, 1568, 1597, 1728, 2836, 2946, 3005; MS (GCMS) m/z 303.1 (M⁺); HRMS C₁₆H₁₈O₅N⁺ (M+H⁺) Expected 304.1179, Found 304.1170.

Methyl 4-methoxy-[1,1'-biphenyl]-3-carboxylate, 45

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), benzene (1.0 mL, 11.2 mmol, 56 equiv.), after purification by column chromatography on silica gel (CHCl₃), gave **45** (26.6 mg, 0.11 mmol, 55%) as a colourless oil; δ_{H} (400 MHz, CDCl₃) 3.92 (s, 3H, OCH₃), 3.95 (s, 3H, OCH₃), 7.06 (d, J = 8.7 Hz, 1H, Ar H), 7.30 – 7.36 (m, 1H, Ar H), 7.43 (t, J = 7.6 Hz, 2H, Ar H), 7.54 – 7.59 (m, 2H, Ar H), 7.70 (dd, J = 8.7, 2.5 Hz, 1H, Ar H), 8.05 (d, J = 2.5 Hz, 1H, Ar H);

δ_{C} (100 MHz, CDCl_3) 52.3 (OCH_3), 56.3 (OCH_3), 112.6 (Ar CH), 120.4 (Ar C), 126.9 (Ar CH), 127.3 (Ar CH), 129.0 (Ar CH), 130.4 (Ar CH), 132.0 (Ar CH), 133.4 (Ar C), 139.9 (Ar C), 158.7 (Ar C), 166.8 ($\text{C}=\text{O}$); ν_{max} (thin film/ cm^{-1}) 761, 820, 968, 1019, 1082, 1153, 1181, 1228, 1272, 1312, 1433, 1484, 1583, 1611, 1699, 1726, 2838, 2949, 3002; MS (GCMS) m/z 242.1 (M^+); HRMS $\text{C}_{15}\text{H}_{15}\text{O}_3^+$ ($\text{M}+\text{H}^+$) Expected 243.1016, Found 243.1015.

Methyl 2',5'-difluoro-4-methoxy-[1,1'-biphenyl]-3-carboxylate, **46**

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μL , 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), TiF_4 (41 μL , 0.24 mmol), PTH (5.5 mg, 0.02 mmol), 1,4-difluorobenzene (1.0 mL, 9.7 mmol, 49 equiv.), after purification by column chromatography on silica gel (CHCl_3), gave **46** (31.2 mg, 0.11 mmol, 56%) as a colourless oil; δ_{H} (400 MHz, CDCl_3) 3.91 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 6.93 – 7.02 (m, 1H, Ar H), 7.06 (d, $J = 8.7$ Hz, 1H, Ar H), 7.09 – 7.16 (m, 2H, Ar H), 7.66 (dt, $J = 8.7, 2.3$ Hz, 1H, Ar H), 7.98 (dd, $J = 2.3, 1.2$ Hz, 1H, Ar H); δ_{C} (100 MHz, CDCl_3) 52.3 (OCH_3), 56.3 (OCH_3), 112.3 (Ar CH), 115.2 (dd, $J = 23.9, 8.6$ Hz, Ar CH), 116.7 (dd, $J = 24.4, 3.8$ Hz, Ar CH), 117.3 (dd, $J = 25.9, 8.8$ Hz, Ar CH), 120.3 (Ar C), 126.9 (Ar C), 129.1 (dd, $J = 15.8, 8.1$ Hz, Ar C), 132.2 (d, $J = 3.0$ Hz, Ar CH), 134.0 (d, $J = 3.9$ Hz, Ar CH), 155.8 (dd, $J = 243.4, 2.5$ Hz, Ar C), 158.9 (dd, $J = 242.6, 2.5$ Hz, Ar C), 159.2 (Ar C), 166.4 ($\text{C}=\text{O}$); δ_{F} (376 MHz, CDCl_3) -124.3, -118.9; ν_{max} (thin film/ cm^{-1}) 761, 820, 977, 1021, 1082, 1158, 1176, 1237, 1435, 1484, 1591, 1610, 1728, 2840, 2950, 3001; MS (GCMS) m/z 278.1 (M^+); HRMS $\text{C}_{15}\text{H}_{13}\text{O}_3\text{F}_2^+$ ($\text{M}+\text{H}^+$) Expected 279.0827, Found 279.0828.

Methyl 2',4,4',6'-tetramethoxy-[1,1'-biphenyl]-3-carboxylate, **47**

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μL , 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), TiF_4 (41 μL , 0.24 mmol), PTH (5.5 mg, 0.02 mmol), 1,3,5-trimethoxybenzene (673 mg, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (30% EtOAc in hexanes), gave **47** (34.7 mg, 0.10 mmol, 52%) as a white solid; m.p. (recrystallized from CHCl_3) 46 – 48 $^{\circ}\text{C}$; δ_{H} (400 MHz, CDCl_3) 3.72 (s, 6H, OCH_3), 3.86 (s, 3H,

OCH₃), 3.87 (s, 3H, OCH₃), 3.93 (s, 3H, OCH₃), 6.22 (s, 2H, Ar H), 7.00 (d, *J* = 8.6 Hz, 1H, Ar H), 7.44 (dd, *J* = 8.6, 2.3 Hz, 1H, Ar H), 7.79 (d, *J* = 2.3 Hz, 1H, Ar H); δ_c (100 MHz, CDCl₃) 52.0 (OCH₃), 55.5 (OCH₃), 56.0 (OCH₃), 56.0 (OCH₃), 56.1 (OCH₃), 91.0 (Ar CH), 111.1 (Ar C), 111.5 (Ar CH), 119.3 (Ar C), 126.1 (Ar C), 134.8 (Ar CH), 136.5 (Ar CH), 157.9 (Ar C), 158.5 (Ar C), 160.7 (Ar C), 166.9 (C=O); $\nu_{\max}$ (thin film/cm⁻¹) 733, 813, 947, 1021, 1068, 1082, 1121, 1152, 1220, 1267, 1307, 1434, 1583, 1602, 1725, 2837, 2944, 3000; MS (GCMS) *m/z* 332.2 (M⁺); HRMS C₁₈H₂₁O₆⁺ (M+H⁺) Expected 333.1333, Found 333.1327.

Methyl 2-methoxy-5-(2-methoxynaphthalen-1-yl)benzoate, 48

Prepared as described in General Procedure C: methyl 2-methoxybenzoate (29 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), 2-methoxynaphthalene (633 mg, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (CH₂Cl₂), gave **48** (25.8 mg, 0.08 mmol, 40%) as a white solid; m.p. (recrystallized from CHCl₃) 144 – 146 °C; δ_H (400 MHz, CDCl₃) 3.84 (s, 3H, OCH₃), 3.87 (s, 3H, OCH₃), 4.00 (s, 3H, OCH₃), 7.12 (d, *J* = 8.5 Hz, 1H, Ar H), 7.33 – 7.38 (m, 3H, Ar H), 7.45 – 7.52 (m, 2H, Ar H), 7.80 – 7.85 (m, 2H, Ar H), 7.88 (d, *J* = 9.1 Hz, 1H, Ar H); δ_c (100 MHz, CDCl₃) 52.1 (OCH₃), 56.3 (OCH₃), 56.9 (OCH₃), 112.1 (Ar CH), 113.8 (Ar CH), 119.9 (Ar C), 123.7 (Ar CH), 123.9 (Ar C), 125.1 (Ar CH), 126.6 (Ar CH), 128.1 (Ar CH), 128.3 (Ar C), 129.2 (Ar C), 129.4 (Ar CH), 133.8 (Ar C), 134.4 (Ar CH), 136.3 (Ar CH), 154.1 (Ar C), 158.5 (Ar C), 166.8 (C=O); $\nu_{\max}$ (thin film/cm⁻¹) 750, 809, 961, 1004, 1022, 1082, 1245, 1260, 1301, 1435, 1499, 1592, 1726, 2837, 2902, 2946, 3001; MS (GCMS) *m/z* 322.1 (M⁺); HRMS C₂₀H₁₉O₄⁺ (M+H⁺) Expected 323.1278, Found 323.1274.

Concise Synthesis of Pseudilins

tert-Butyl 2-(3,5-dichloro-2-methoxyphenyl)-1H-pyrrole-1-carboxylate, **S11**

Tf₂O (170 μ L, 1.00 mmol, 2.0 equiv.) was slowly added to a stirred solution of 2,4-dichloroanisole (69 μ L, 0.50 mmol, 1.0 equiv.) and dibenzothiophene S-oxide (200 mg, 1.00 mmol, 2.0 equiv.) in CH₂Cl₂ (0.1 M) at -40 °C under a nitrogen atmosphere. The resulting solution was stirred at this temperature for 2 hours before warming to room temperature. The solvent was removed *in vacuo* and PTH (13.7 mg, 0.05 mmol, 10 mol%) was then added to the reaction vial, followed by evacuation and refilling with nitrogen (3 cycles). DMSO (0.2 M) was then added followed by *N*-Boc-pyrrole (835 μ L, 5.00 mmol, 10 equiv.). The reaction mixture was then irradiated with a Kessil 34W blue LED lamp for 18 h before quenching with aqueous saturated NaHCO₃ and dilution with EtOAc. The organic layer was washed with brine, dried using MgSO₄, filtered, and concentrated *in vacuo*, to give the crude product, which was purified by column chromatography (50% CHCl₃/hexanes to CHCl₃) to give **S11** (135 mg, 0.39 mmol, 79%) as a brown oil; δ_{H} (400 MHz, CDCl₃) 1.32 (d, J = 1.2, 9 H, CH₃), 3.44 (d, J = 1.2 Hz, 3 H, OCH₃), 6.19 – 6.29 (m, 2 H, Ar H), 7.20 (dd, J = 2.6, 1.1 Hz, 1 H, Ar H), 7.35 (dd, J = 2.6, 1.1 Hz, 1 H, Ar H), 7.42 (dt, J = 3.0, 1.4 Hz, 1 H, Ar H). δ_{C} (100 MHz, CDCl₃) 27.6 (CH₃), 60.3 (OCH₃), 84.1 (CH₃C), 110.6 (Ar CH), 115.2 (Ar CH), 123.2 (Ar CH), 128.1 (Ar C), 128.4 (Ar C), 128.8 (Ar CH), 128.9 (Ar C), 129.1 (Ar CH), 131.7 (Ar C), 152.8 (Ar C), C=O not observed; ν_{max} (thin film/cm⁻¹) 732, 842, 1002, 1147, 1312, 1337, 1370, 1742, 2935, 2978; MS (APCI) m/z 342.1 (M+H⁺); HRMS C₁₆H₁₈Cl₂NO₃⁺ (M+H⁺) Expected 342.0658, Found 342.0657.

2-(3,5-Dichloro-2-methoxyphenyl)-1H-pyrrole, **49**

A solution of NaOMe (1.0 mL, 30% w/w in MeOH) was added to a solution of *tert*-butyl 2-(3,5-dichloro-2-methoxyphenyl)-1H-pyrrole-1-carboxylate, **S11** (171 mg, 0.50 mmol) in anhydrous THF (3.5 mL) and the resulting mixture was heated at 45 °C for 2 hours. The reaction was allowed to cool to room temperature and was quenched by the addition of H₂O (5 mL). The mixture was extracted

with CH₂Cl₂ (2 × 5 mL), the combined organic extracts were washed with H₂O (3 × 10 mL), dried using MgSO₄, filtered, and concentrated *in vacuo*. The resulting crude pyrrole **49** (117 mg, 0.48 mmol, 97%) was used without purification; δ_{H} (500 MHz, CDCl₃) 3.78 (s, 3H, OCH₃), 6.30 (dt, *J* = 3.8, 2.6 Hz, 1H, Ar *H*), 6.61 (ddd, *J* = 3.8, 2.6, 1.5 Hz, 1H, Ar *H*), 6.92 (td, *J* = 2.8, 1.5 Hz, 1H, Ar *H*), 7.19 (d, *J* = 2.5 Hz, 1H, Ar *H*), 7.47 (d, *J* = 2.5 Hz, 1H, Ar *H*), 9.67 (s, 1H, NH); δ_{C} (125 MHz, CDCl₃) 60.9 (OCH₃), 108.6 (Ar CH), 109.7 (Ar CH), 119.9 (Ar CH), 125.4 (Ar CH), 127.1 (Ar CH), 127.2 (Ar C), 128.3 (Ar C), 129.7 (Ar C), 130.3 (Ar C), 149.9 (Ar C).

The data is in accordance with the literature.¹⁵

2,4-dichloro-6-(3,4,5-trichloro-1H-pyrrol-2-yl)phenol, 50

A solution of *N*-chlorosuccinimide (46.7 mg, 0.35 mmol, 3.0 equiv.) in MeCN (0.5 mL) was added to a solution of 2-(3,5-dichloro-2-methoxyphenyl)-1*H*-pyrrole, **49** (30.3 mg, 0.12 mmol, 1.0 equiv.) in MeCN (2 mL) at –40 °C. The reaction mixture was stirred at –40 °C for 15 min and then allowed to warm up to room temperature and was stirred for 15 hours. The solvent was removed *in vacuo* and the residue was filtered through a plug of silica, eluting with 50% CHCl₃/hexanes. The resulting crude product (0.07 mmol, 55%, yield determined by ¹H NMR analysis) was dissolved in CH₂Cl₂ (2 mL) and cooled to –78 °C. Boron tribromide (1 M in CH₂Cl₂, 70 μ L, 0.07 mmol, 1.1 equiv.) was then added and the reaction mixture was stirred at 0 °C for 2 hours. The reaction was quenched by the addition of MeOH (5 mL) and the solvent was removed *in vacuo*. To the residue was added H₂O (5 mL) and the product was extracted into Et₂O (2 × 5 mL). The combined organic extracts were dried using MgSO₄, filtered and concentrated *in vacuo*, to give the crude product which was purified by column chromatography on silica gel (20% to 40% Et₂O in hexanes), to give **50** (13.7 mg, 0.04 mmol, 64%) as a purple solid; δ_{H} (400 MHz, CDCl₃) 6.12 – 6.24 (1 H, m, OH), 7.29 (dd, *J* = 2.5, 1.3 Hz, 1 H, Ar *H*), 8.00 (dd, *J* = 2.5, 1.3 Hz, 1 H, Ar *H*), 9.57 (s, 1 H, NH); δ_{C} (100 MHz, CDCl₃) 110.6 (Ar C), 110.6 (Ar C), 112.5 (Ar C), 118.8 (Ar C), 120.7 (Ar C), 121.5 (Ar C), 126.6 (Ar CH and Ar C), 127.3 (Ar CH), 145.7 (Ar C).

The data is in accordance with the literature.¹⁵

2,3,4-tribromo-5-(3,5-dichloro-2-methoxyphenyl)-1H-pyrrole, **S12**

Pyridinium tribromide (113 mg, 0.35 mmol, 3.0 equiv.) was added to a solution of 2-(3,5-dichloro-2-methoxyphenyl)-1H-pyrrole, **49** (30.3 mg, 0.12 mmol, 1.0 equiv.) in EtOH (1 mL) at room temperature and the mixture was stirred for 30 min. The solvent was removed *in vacuo* and the residue was filtered through a plug of silica, eluting with 25% to 50% CHCl₃/hexanes, to give **S12** (39.7 mg, 0.08 mmol, 70%) as a brown oil; δ_{H} (400 MHz, CDCl₃) 3.68 (3 H, s, OCH₃), 7.35 (d, J = 2.5 Hz, 1 H, Ar H), 7.82 (d, J = 2.5 Hz, 1 H, Ar H), 9.41 – 9.64 (m, 1H, NH); δ_{C} (100 MHz, CDCl₃) 61.3 (OCH₃), 99.7 (Ar C), 101.5 (Ar C), 103.9 (Ar C), 125.2 (Ar C), 125.9 (Ar C), 127.8 (Ar CH), 129.7 (Ar CH), 129.7 (Ar C), 130.3 (Ar C), 151.3 (Ar C).

The data is in accordance with the literature.¹⁵

2,4-dichloro-6-(3,4,5-tribromo-1H-pyrrol-2-yl)phenol, **51**

Boron tribromide (1 M in CH₂Cl₂, 60 μ L, 60.0 μ mol, 1.1 equiv.) was added to a solution of 2,3,4-tribromo-5-(3,5-dichloro-2-methoxyphenyl)-1H-pyrrole, **S12** (27.0 mg, 56.3 μ mol) in CH₂Cl₂ (2 mL) at –78 °C and the reaction mixture was stirred at 0 °C for 2 h. The reaction was quenched by the addition of MeOH (5 mL) and the solvent was removed *in vacuo*. To the residue was added H₂O (5 mL) and the product was extracted into Et₂O (2 $\times$ 5 mL). The combined organic extracts were dried using MgSO₄, filtered and concentrated *in vacuo*, to give **51** (25.0 mg, 53.8 μ mol, 96%) as an off-white solid; δ_{H} (400 MHz, CDCl₃) 6.10 (1 H, s, OH), 7.31 (d, J = 2.4 Hz, 1 H, Ar H), 7.96 (d, J = 2.4 Hz, 1 H, Ar H), 9.55 (s, 1 H, NH); δ_{C} (100 MHz, CDCl₃) 99.5 (Ar C), 101.2 (Ar C), 104.1 (Ar C), 119.2 (Ar C), 121.5 (Ar C), 125.3 (Ar C), 126.3 (Ar C), 127.4 (Ar CH), 127.8 (Ar CH), 146.1 (Ar C).

The data is in accordance with the literature.¹⁵

Late-Stage Functionalization

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(Acetoxymethyl)-6-(2-(acetoxymethyl)-4-(1-methyl-1*H*-pyrrol-2-yl)phenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate, **52**

Prepared as described in General Procedure C: **S9** (99 mg, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), TiF_2O (41 μL , 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (40% EtOAc in hexanes), gave **52** (81.7 mg, 0.14 mmol, 71%) as a white gum; δ_{H} (400 MHz, CDCl_3) 2.05 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 3.62 (s, 3H, NCH_3), 3.88 (ddd, $J = 10.0, 5.3, 2.5$ Hz, 1H, Alk CH), 4.20 (dd, $J = 12.3, 2.5$ Hz, 1H, Alk CH_2), 4.29 (dd, $J = 12.3, 5.3$ Hz, 1H, Alk CH_2), 5.03 – 5.23 (m, 4H, OCHO, Alk CH & Bn CH_2), 5.27 – 5.37 (m, 2H, Alk CH), 6.14 – 6.22 (m, 2H, Ar H), 6.68 – 6.72 (m, 1H, Ar H), 7.10 (d, $J = 8.5$ Hz, 1H, Ar H), 7.30 (dd, $J = 8.5, 2.3$ Hz, 1H, Ar H), 7.37 (d, $J = 2.3$ Hz, 1H, Ar H); δ_{C} (100 MHz, CDCl_3) 20.7 (CH_3), 20.7 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 21.1 (CH_3), 35.1 (NCH_3), 61.1 (Alk CH_2), 62.0 (Bn CH_2), 68.4 (Alk CH), 71.1 (Alk CH), 72.2 (Alk CH), 72.7 (Alk CH), 99.4 (OCHO), 107.9 (Ar CH), 108.7 (Ar CH), 115.8 (Ar CH), 123.7 (Ar CH), 126.3 (Ar C), 128.9 (Ar C), 129.7 (Ar CH), 129.9 (Ar CH), 133.7 (Ar C), 153.5 (Ar C), 169.4 (C=O), 169.5 (C=O), 170.3 (C=O), 170.6 (C=O), 170.8 (C=O); ν_{max} (thin film/ cm^{-1}) 733, 833, 907, 983, 1033, 1121, 1210, 1365, 1375, 1498, 1545, 1741, 2958, 3056; MS (GCMS) m/z 575.3 (M^+); HRMS $\text{C}_{28}\text{H}_{33}\text{O}_{12}\text{NNa}^+$ ($\text{M}+\text{Na}^+$) Expected 598.1895, Found 598.1866.

2-Chloro-*N*-(4'-chloro-5-(1-methyl-1*H*-pyrrol-2-yl)-[1,1'-biphenyl]-2-yl)nicotinamide, **53**

Prepared as described in General Procedure D: boscalid (69 mg, 0.20 mmol), dibenzothiophene *S*-oxide (44 mg, 0.22 mmol), TiF_2O (41 μL , 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (40% EtOAc, 1%

Et₃N in hexanes), gave **53** (55.7 mg, 0.13 mmol, 66%) as an off-white solid; m.p. (recrystallized from CHCl₃) 145 – 147 °C; δ_{H} (400 MHz, CDCl₃) 3.71 (s, 3H, NCH₃), 6.21 (dd, J = 3.6, 2.7 Hz, 1H, Ar *H*), 6.26 (dd, J = 3.6, 1.8 Hz, 1H, Ar *H*), 6.73 (dd, J = 2.7, 1.8 Hz, 1H, Ar *H*), 7.32 (d, J = 2.1 Hz, 1H, Ar *H*), 7.33 – 7.41 (m, 3H, Ar *H*), 7.41 – 7.53 (m, 3H, Ar *H*), 8.17 (dd, J = 7.7, 2.1 Hz, 1H, Ar *H*), 8.21 (s, 1H, NH), 8.43 – 8.50 (m, 2H, Ar *H*); δ_{C} (100 MHz, CDCl₃) 35.3 (NCH₃), 108.1 (Ar CH), 109.2 (Ar CH), 122.1 (Ar CH), 123.1 (Ar CH), 124.2 (Ar CH), 128.8 (Ar CH), 129.6 (Ar CH), 130.3 (Ar CH), 130.6 (Ar CH), 130.9 (Ar C), 131.1 (Ar C), 132.4 (Ar C), 133.1 (Ar C), 133.6 (Ar C), 134.8 (Ar C), 136.2 (Ar C), 140.4 (Ar CH), 146.8 (Ar C), 151.5 (Ar CH), 162.6 (C=O); ν_{max} (thin film/cm⁻¹) 733, 831, 900, 1013, 1066, 1089, 1150, 1286, 1308, 1398, 1474, 1513, 1580, 1667, 2923, 3047, 3248, 3390; MS (GCMS) m/z 421.1 (M⁺); HRMS C₂₃H₁₈ON₃Cl₂⁺ (M+H⁺) Expected 422.0821, Found 422.0821.

53 was further characterized by X-ray crystallographic analysis. CCDC: 1922368.

Isopropyl 2-(4-(4-chlorobenzoyl)-2-(1-methyl-1H-pyrrol-2-yl)phenoxy)-2-methylpropanoate, **54**

Prepared as described in General Procedure C: fenofibrate (72 mg, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), Tf₂O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (10% EtOAc in hexanes), gave **54** (49.2 mg, 0.11 mmol, 56%) as a white solid; m.p. (recrystallized from CHCl₃) 99 – 101 °C; δ_{H} (400 MHz, CDCl₃) 1.21 (d, J = 6.3 Hz, 6H, CH₃), 1.55 (s, 6H, CH₃), 3.58 (s, 3H, NCH₃), 5.08 (hept, J = 6.3 Hz, 1H, Alk CH), 6.13 (dd, J = 3.5, 1.9 Hz, 1H, Ar *H*), 6.19 (dd, J = 3.5, 2.6 Hz, 1H, Ar *H*), 6.73 (dd, J = 2.6, 1.9 Hz, 1H, Ar *H*), 6.84 (d, J = 8.5 Hz, 1H, Ar *H*), 7.45 (d, J = 8.5 Hz, 2H, Ar *H*), 7.68 – 7.79 (m, 4H, Ar *H*); δ_{C} (100 MHz, CDCl₃) 21.7 (CH₃), 25.3 (CH₃), 35.0 (NCH₃), 69.5 (Alk CH), 80.2 (CH₃C), 107.6 (Ar CH), 109.7 (Ar CH), 115.7 (Ar CH), 123.0 (Ar CH), 125.1 (Ar C), 128.7 (Ar CH), 130.4 (Ar C), 130.5 (Ar C), 130.9 (Ar CH), 131.3 (Ar CH), 135.1 (Ar CH), 136.4 (Ar C), 138.6 (Ar C), 157.7 (Ar C), 173.2 (C=O), 194.3 (C=O); ν_{max} (thin film/cm⁻¹) 763, 847, 941, 1014, 1089, 1100, 1137, 1263, 1384, 1466, 1495, 1593, 1653, 1730, 2938, 2981; MS (GCMS) m/z 439.2 (M⁺); HRMS C₂₅H₂₇O₄NCl⁺ (M+H⁺) Expected 440.1623, Found 440.1621.

Ethyl 2-(4-chloro-2-(1-methyl-1H-pyrrol-2-yl)phenoxy)-2-methylpropanoate, 55

Prepared as described in General Procedure C: clofibrate (43 μ L, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), TiF_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (CHCl_3), gave **55** (28.3 mg, 0.09 mmol, 44%) as a colourless oil; δ_{H} (400 MHz, CDCl_3) 1.26 (t, $J = 7.1$ Hz, 4H, CH_3), 1.34 (s, 6H, CH_3), 3.55 (s, 3H, NCH_3), 4.22 (q, $J = 7.1$ Hz, 2H, CH_2), 6.11 (dd, $J = 3.6, 1.8$ Hz, 1H, Ar H), 6.18 (dd, $J = 3.6, 2.7$ Hz, 1H, Ar H), 6.71 (dd, $J = 2.7, 1.8$ Hz, 1H, Ar H), 6.88 (d, $J = 8.7$ Hz, 1H, Ar H), 7.19 (dd, $J = 8.7, 2.8$ Hz, 1H, Ar H), 7.29 (d, $J = 2.8$ Hz, 1H, Ar H); δ_{C} (100 MHz, CDCl_3) 14.2 (CH_3), 25.0 (CH_3), 35.0 (NCH_3), 61.6 (CH_2), 80.7 (CH_3C), 107.6 (Ar CH), 109.8 (Ar CH), 120.5 (Ar CH), 123.0 (Ar CH), 127.6 (Ar C), 128.3 (Ar CH), 128.7 (Ar C), 130.5 (Ar C), 132.1 (Ar CH), 152.2 (Ar C), 174.2 (C=O); ν_{max} (thin film/ cm^{-1}) 710, 886, 964, 1021, 1091, 1133, 1174, 1281, 1382, 1437, 1466, 1594, 1732, 2871, 2936, 2981; MS (GCMS) m/z 321.1 (M^+); HRMS $\text{C}_{17}\text{H}_{20}\text{O}_3\text{NClNa}^+$ ($\text{M}+\text{Na}^+$) Expected 344.1024, Found 344.1015.

N-(1-(2,6-Dimethyl-4-(1-methyl-1H-pyrrol-2-yl)phenoxy)propan-2-yl)acetamide, 56

Prepared as described in General Procedure C: **S10** (44 mg, 0.20 mmol), dibenzothiophene S-oxide (44 mg, 0.22 mmol), TiF_2O (41 μ L, 0.24 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (65% EtOAc in hexanes), gave **56** (35.6 mg, 0.12 mmol, 59%) as a colourless oil; δ_{H} (400 MHz, CDCl_3) 1.42 (d, $J = 6.9$ Hz, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.29 (s, 6H, CH_3), 3.63 (s, 3H, NCH_3), 3.75 (dd, $J = 9.1, 3.7$ Hz, 1H, CH_2), 3.84 (dd, $J = 9.1, 3.7$ Hz, 1H, CH_2), 4.31 – 4.42 (m, 1H, Alk CH), 5.89 (d, $J = 8.5$ Hz, 1H, NH), 6.14 (dd, $J = 3.6, 1.8$ Hz, 1H, Ar H), 6.14 – 6.20 (m, 1H, Ar H), 6.65 – 6.71 (m, 1H, Ar H), 7.03 (s, 2H, Ar H); δ_{C} (100 MHz, CDCl_3) 16.4 (CH_3), 17.9 (CH_3), 23.6 (CH_3), 35.1 (NCH_3), 45.6 (Alk CH), 74.2 (CH_2), 107.7 (Ar CH), 108.4 (Ar CH), 123.3 (Ar CH), 129.4 (Ar C), 129.5 (Ar CH), 130.7 (Ar C), 134.4 (Ar C), 154.1 (Ar C), 169.5 (C=O); ν_{max} (thin film/ cm^{-1}) 710, 880, 981, 1014, 1029, 1088, 1173, 1210, 1228, 1275, 1371, 1475,

1548, 1644, 2873, 2924, 2971, 3078, 3284; MS (GCMS) m/z 300.1 (M^+); HRMS $C_{18}H_{25}O_2N_2^+$ ($M+H^+$)
Expected 301.1911, Found 301.1906.

Mechanistic Studies

(2-(4-(*tert*-Butyl)phenyl)ethene-1,1-diyl)dibenzene, **4**¹⁶

Prepared as described in General Procedure B: **2** (93 mg, 0.20 mmol), PTH (5.5 mg, 0.02 mmol), 1,1-diphenylethylene (0.18 mL, 1.0 mmol, 5.0 equiv.), after purification by column chromatography on silica gel (10% CHCl₃ in hexanes), gave **4** (43.7 mg, 0.14 mmol, 70%) as a white solid; δ_{H} (500 MHz, CDCl₃) 1.18 (s, 9H, CH₃), 6.85 – 6.91 (m, 3H, C=CH & Ar H), 7.07 (d, J = 8.3 Hz, 2H, Ar H), 7.13 – 7.34 (m, 10H, Ar H); δ_{C} (125 MHz, CDCl₃) 31.4 (CH₃), 34.6 (CH₃C), 125.1 (Ar CH), 127.4 (Ar CH), 127.5 (Ar CH), 127.6 (C=CH), 128.1 (Ar CH), 128.3 (Ar CH), 128.9 (Ar CH), 129.4 (Ar CH), 130.4 (Ar CH), 134.5 (Ar C), 140.8 (C=CH), 141.7 (Ar C), 143.7 (Ar C), 150.0 (Ar C).

The data is in accordance with the literature.¹⁶

5-(2-(Allyloxy)-5-(*tert*-butyl)phenyl)-5H-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate, **5**

The 2-hydroxy-5-*tert*-butylphenyl dibenzothiophenium salt was prepared as described in General Procedure A: 4-*tert*-butylphenol (451 mg, 3.0 mmol), dibenzothiophene *S*-oxide (621 mg, 3.1 mmol), Tf₂O (0.53 mL, 3.2 mmol), gave the crude salt (ca. 733 mg, 1.53 mmol, 51%) as an off-white solid, which was used in the following step without further purification; δ_{H} (400 MHz, CD₃CN) 1.13 (s, 9H, CH₃), 7.05 (d, J = 2.4 Hz, 1H, Ar H), 7.10 – 7.17 (m, 1H, Ar H), 7.61 – 7.68 (m, 1H, Ar H), 7.70 – 7.76 (m, 2H, Ar H), 7.89 – 7.98 (m, 2H, Ar H), 8.10 (dd, J = 7.9, 1.0 Hz, 2H, Ar H), 8.31 (dd, J = 7.9, 1.0 Hz, 2H, Ar H); δ_{C} (100 MHz, CD₃CN) 31.0 (CH₃), 35.2 (CH₃C), 110.8 (Ar C), 118.5 (Ar CH), 125.3 (Ar CH), 126.6 (Ar CH), 128.7 (Ar CH), 131.0 (Ar C), 132.2 (Ar CH), 135.0 (Ar C), 135.5 (Ar CH), 135.5 (Ar CH), 146.4 (Ar C), 156.7 (Ar C), CF₃ not observed; δ_{F} (376 MHz, CD₃CN) -79.3.

Allyl bromide (0.13 mL, 1.40 mmol, 1.1 equiv.) was added to a stirred suspension of the crude 2-hydroxyphenyl dibenzothiophenium salt (615 mg, 1.27 mmol, 1.0 equiv.) and K₂CO₃ (527 mg, 3.81

mmol, 3.0 equiv.) in acetone (6.4 mL) and the resulting mixture was heated to 65 °C for 12 hours. After cooling to ambient temperature, the reaction mixture was concentrated *in vacuo*, diluted with CH₂Cl₂ (25 mL), washed with water (2 × 25 mL) and brine (25 mL), dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude product was purified by recrystallization (EtOAc/hexanes), to give **5** (624 mg, 1.19 mmol, 94%) as a white solid; m.p. (recrystallized from CH₂Cl₂/Et₂O) 163 – 165 °C; δ_{H} (400 MHz, CDCl₃) 1.21 (s, 9H, CH₃), 4.36 (d, *J* = 5.8 Hz, 2H, CH₂), 5.09 (dd, *J* = 17.1, 1.3 Hz, 1H, CH=CH₂), 5.15 (dd, *J* = 10.4, 1.3 Hz, 1H, CH=CH₂), 5.44 – 5.60 (m, 1H, CH=CH₂), 6.97 (d, *J* = 8.8 Hz, 1H, Ar H), 7.56 – 7.68 (m, 4H, Ar H), 7.80 (td, *J* = 7.7, 1.1 Hz, 2H, Ar H), 7.98 – 8.09 (m, 2H, Ar H), 8.19 (dd, *J* = 7.8, 1.1 Hz, 2H, Ar H); δ_{C} (100 MHz, CDCl₃) 31.0 (CH₃), 34.8 (CH₃C), 70.7 (CH₂), 111.0 (Ar C), 114.6 (Ar CH), 120.0 (CH=CH₂), 121.0 (q, *J* = 320.9 Hz, CF₃), 124.1 (Ar CH), 128.0 (Ar CH), 129.5 (Ar CH), 129.6 (CH=CH₂), 130.7 (Ar CH), 131.2 (Ar CH), 134.1 (Ar CH), 135.0 (Ar C), 139.6 (Ar C), 146.7 (Ar C), 155.9 (Ar C); δ_{F} (376 MHz, CDCl₃) -78.2; ν_{max} (thin film/cm⁻¹) 758, 824, 939, 988, 1029, 1152, 1223, 1257, 1426, 1493, 1559, 2871, 2963, 3087; MS (ES⁺) *m/z* 373.2 (M⁺); HRMS C₂₅H₂₅OS⁺ (M⁺) Expected 373.1621, Found 373.1612.

2-((5-(*tert*-Butyl)-2,3-dihydrobenzofuran-3-yl)methyl)-1-methyl-1H-pyrrole, 6

Prepared as described in General Procedure B: **5** (105 mg, 0.20 mmol), PTH (5.5 mg, 0.02 mmol), *N*-methylpyrrole (0.36 mL, 4.00 mmol, 20 equiv.), after purification by column chromatography on silica gel (5% EtOAc in hexanes), gave **6** (11.3 mg, 0.04 mmol, 21%) as a colourless oil; δ_{H} (500 MHz, CDCl₃) 1.27 (s, 9H, CH₃), 2.84 (dd, *J* = 15.2, 8.9 Hz, 1H, Bn CH₂), 2.92 (dd, *J* = 15.2, 6.5 Hz, 1H, Bn CH₂), 3.41 (s, 3H, NCH₃), 3.64 – 3.76 (m, 1H, Bn CH), 4.32 (dd, *J* = 8.9, 5.2 Hz, 1H, OCH₂), 4.64 (t, *J* = 8.9 Hz, 1H, OCH₂), 5.89 – 5.99 (m, 1H, Ar H), 6.03 – 6.15 (m, 1H, Ar H), 6.51 – 6.61 (m, 1H, Ar H), 6.73 (d, *J* = 8.4 Hz, 1H, Ar H), 6.93 (d, *J* = 2.1 Hz, 1H, Ar H), 7.17 (dd, *J* = 8.4, 2.1 Hz, 1H, Ar H); δ_{C} (125 MHz, CDCl₃) 31.9 (CH₃), 32.1 (Bn CH₂), 33.8 (NCH₃), 34.5 (CH₃C), 42.3 (Bn CH), 77.4 (OCH₂), 106.9 (Ar CH), 106.9 (Ar CH), 108.8 (Ar CH), 121.7 (Ar CH), 121.7 (Ar CH), 125.4 (Ar CH), 129.8 (Ar C), 130.7 (Ar C), 143.5 (Ar C), 157.7 (Ar C); ν_{max} (thin film/cm⁻¹) 816, 966, 1117, 1232, 1262, 1297, 1362, 1466, 1489, 2823, 2952; MS (GCMS) *m/z* 269.1 (M⁺); HRMS C₁₈H₂₄ON⁺ (M+H⁺) Expected 270.1852, Found 270.1848.

NMR SPECTRA

S5 – ^1H NMR (400 MHz, $\text{DMSO}-d_6$)

S5 – ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$)

S6 – ^1H NMR (400 MHz, CDCl_3)

S6 – ^{13}C NMR (100 MHz, CDCl_3)

2 – ^1H NMR (400 MHz, CDCl_3)

2 – ^{13}C NMR (100 MHz, CDCl_3)

2 – ^{19}F NMR (376 MHz, CDCl_3)

S2 – ^1H NMR (400 MHz, CDCl_3)

S2 – ^{13}C NMR (100 MHz, CDCl_3)

S2 – ^{19}F NMR (376 MHz, CDCl_3)

S3 – ^1H NMR (400 MHz, CDCl_3)

S3 – ^{13}C NMR (100 MHz, CDCl_3)

S3 – ^{19}F NMR (376 MHz, CDCl_3)

S4 – ^1H NMR (400 MHz, CDCl_3)

S4 – ^{13}C NMR (100 MHz, CDCl_3)

S4 – ^{19}F NMR (376 MHz, CDCl_3)

S7 – ^1H NMR (400 MHz, CDCl_3)

S7 – ^{13}C NMR (100 MHz, CDCl_3)

S8 – ^1H NMR (400 MHz, CDCl_3)

S8 – ^{13}C NMR (100 MHz, CDCl_3)

S9 – ^1H NMR (400 MHz, CDCl_3)

S9 – ^{13}C NMR (100 MHz, CDCl_3)

S10 – ^1H NMR (400 MHz, CDCl_3)

S10 – ^{13}C NMR (100 MHz, CDCl_3)

S1 – ^1H NMR (500 MHz, CDCl_3)

S1 – ^{13}C NMR (125 MHz, CDCl_3)

7 – ^1H NMR (400 MHz, CDCl_3)

7 – ^{13}C NMR (100 MHz, CDCl_3)

8 – ^1H NMR (400 MHz, CDCl_3)

8 – ^{13}C NMR (100 MHz, CDCl_3)

9 – ^1H NMR (400 MHz, CDCl_3)

9 – ^{13}C NMR (100 MHz, CDCl_3)

3 – ^1H NMR (400 MHz, CDCl_3)

3 – ^{13}C NMR (100 MHz, CDCl_3)

10 – ^1H NMR (400 MHz, CDCl_3)

10 – ^{13}C NMR (100 MHz, CDCl_3)

11 – ^1H NMR (400 MHz, CDCl_3)

11 – ^{13}C NMR (100 MHz, CDCl_3)

12 – ^1H NMR (400 MHz, CDCl_3)

12 – ^{13}C NMR (100 MHz, CDCl_3)

13 – ^1H NMR (400 MHz, CDCl_3)

13 – ^{13}C NMR (100 MHz, CDCl_3)

14 – ^1H NMR (400 MHz, CDCl_3)

14 – ^{13}C NMR (100 MHz, CDCl_3)

15 – ^1H NMR (400 MHz, CDCl_3)

15 – ^{13}C NMR (100 MHz, CDCl_3)

16 – ^1H NMR (400 MHz, CDCl_3)

16 – ^{13}C NMR (100 MHz, CDCl_3)

17 – ^1H NMR (400 MHz, CDCl_3)

17 – ^{13}C NMR (100 MHz, CDCl_3)

18 – ^1H NMR (400 MHz, CDCl_3)

18 – ^{13}C NMR (100 MHz, CDCl_3)

18 – ^{19}F NMR (376 MHz, CDCl_3)

19 – ^1H NMR (400 MHz, CDCl_3)

19 – ^{13}C NMR (100 MHz, CDCl_3)

20 – ^1H NMR (400 MHz, CDCl_3)

20 – ^{13}C NMR (100 MHz, CDCl_3)

21 – ^1H NMR (400 MHz, CDCl_3)

21 – ^{13}C NMR (100 MHz, CDCl_3)

22 – ^1H NMR (400 MHz, CDCl_3)

22 – ^{13}C NMR (100 MHz, CDCl_3)

22 – ^{19}F NMR (376 MHz, CDCl_3)

23 – ^1H NMR (400 MHz, CDCl_3)

23 – ^{13}C NMR (100 MHz, CDCl_3)

24 – ^1H NMR (400 MHz, CDCl_3)

24 – ^{13}C NMR (100 MHz, CDCl_3)

25 – ^1H NMR (400 MHz, CDCl_3)

25 – ^{13}C NMR (100 MHz, CDCl_3)

26 – ^1H NMR (400 MHz, CDCl_3)

26 – ^{13}C NMR (100 MHz, CDCl_3)

27 – ^1H NMR (400 MHz, CDCl_3)

27 – ^{13}C NMR (100 MHz, CDCl_3)

27 – ^{19}F NMR (376 MHz, CDCl_3)

28 – ^1H NMR (400 MHz, CDCl_3)

28 – ^{13}C NMR (100 MHz, CDCl_3)

29 – ^1H NMR (400 MHz, CDCl_3)

29 – ^{13}C NMR (100 MHz, CDCl_3)

30 – ^1H NMR (400 MHz, CDCl_3)

30 – ^{13}C NMR (100 MHz, CDCl_3)

31 – ^1H NMR (400 MHz, CDCl_3)

31 – ^{13}C NMR (100 MHz, CDCl_3)

2 – ^1H NMR (400 MHz, CDCl_3)

32 – ^{13}C NMR (100 MHz, CDCl_3)

33 – ^1H NMR (400 MHz, CDCl_3)

33 – ^{13}C NMR (100 MHz, CDCl_3)

34 – ^1H NMR (400 MHz, CDCl_3)

34 – ^{13}C NMR (100 MHz, CDCl_3)

35 – ^1H NMR (400 MHz, CDCl_3)

35 – ^{13}C NMR (100 MHz, CDCl_3)

36 – ^1H NMR (400 MHz, CDCl_3)

36 – ^{13}C NMR (100 MHz, CDCl_3)

37 – ^1H NMR (500 MHz, CDCl_3)

37 – ^{13}C NMR (125 MHz, CDCl_3)

COc1ccc(cc1C(=O)c2ccoc2C=O)OC

Chemical structure of 4-(4-methoxybenzoyl)furan-2-carbaldehyde is shown above the spectrum.

¹H NMR spectrum (CDCl₃) data:

Chemical Shift (ppm)	Integration
8.17	0.94
7.91	1.04
7.90	0.98
7.88	0.99
7.88	0.97
7.24	3.04
7.23	2.76
7.04	
7.02	
6.70	
6.70	
3.94	2.93
3.92	
2.51	

Chemical structure of the compound is shown above the spectrum. The structure is 4-(4-methoxy-2-(methylcarbamoyl)phenyl)-2-methoxybenzoic acid derivative, featuring a central benzene ring substituted with a methoxy group, a methyl ester group, and a 4-methoxy-2-(methylcarbamoyl)phenyl group.

Peak list (ppm): 186.20, 166.19, 159.73, 156.86, 151.82, 130.06, 128.62, 121.99, 120.75, 119.92, 112.56, 106.82, 56.35, 52.40, 26.08.

39 – ^1H NMR (500 MHz, CDCl_3)

39 – ^{13}C NMR (125 MHz, CDCl_3)

40 – ^1H NMR (400 MHz, CDCl_3)

40 – ^{13}C NMR (100 MHz, CDCl_3)

41 – ^1H NMR (400 MHz, CDCl_3)

41 – ^{13}C NMR (100 MHz, CDCl_3)

42 – ^1H NMR (400 MHz, CDCl_3)

42 – ^{13}C NMR (100 MHz, CDCl_3)

43 – ^1H NMR (400 MHz, CDCl_3)

43 – ^{13}C NMR (100 MHz, CDCl_3)

44 – ^1H NMR (400 MHz, CDCl_3)

44 – ^{13}C NMR (100 MHz, CDCl_3)

45 – ^1H NMR (400 MHz, CDCl_3)

45 – ^{13}C NMR (100 MHz, CDCl_3)

46 – ^1H NMR (400 MHz, CDCl_3)

46 – ^{13}C NMR (100 MHz, CDCl_3)

46 – ^{19}F NMR (376 MHz, CDCl_3)

47 – ^1H NMR (400 MHz, CDCl_3)

47 – ^{13}C NMR (100 MHz, CDCl_3)

48 – ^1H NMR (400 MHz, CDCl_3)

48 – ^{13}C NMR (100 MHz, CDCl_3)

S11 – ^1H NMR (400 MHz, CDCl_3)

S11 – ^{13}C NMR (100 MHz, CDCl_3)

49 – ^1H NMR (500 MHz, CDCl_3)

49 – ^{13}C NMR (125 MHz, CDCl_3)

50 – ^1H NMR (400 MHz, CDCl_3)

50 – ^{13}C NMR (100 MHz, CDCl_3)

S12 – ^1H NMR (400 MHz, CDCl_3)

S12 – ^{13}C NMR (100 MHz, CDCl_3)

51 – ^1H NMR (400 MHz, CDCl_3)

51 – ^{13}C NMR (100 MHz, CDCl_3)

52 – ^1H NMR (400 MHz, CDCl_3)

52 – ^{13}C NMR (100 MHz, CDCl_3)

53 – ^1H NMR (400 MHz, CDCl_3)

53 – ^{13}C NMR (100 MHz, CDCl_3)

54 – ^1H NMR (400 MHz, CDCl_3)

54 – ^{13}C NMR (100 MHz, CDCl_3)

55 – ^1H NMR (400 MHz, CDCl_3)

55 – ^{13}C NMR (100 MHz, CDCl_3)

56 – ^1H NMR (400 MHz, CDCl_3)

56 – ^{13}C NMR (100 MHz, CDCl_3)

4 – ^1H NMR (500 MHz, CDCl_3)

4 – ^{13}C NMR (125 MHz, CDCl_3)

5 – ^1H NMR (400 MHz, CDCl_3)

5 – ^{13}C NMR (100 MHz, CDCl_3)

5 – ^{19}F NMR (376 MHz, CDCl_3)

6 – ^1H NMR (500 MHz, CDCl_3)

6 – ^{13}C NMR (125 MHz, CDCl_3)

X-RAY CRYSTAL STRUCTURES

Data Collection

X-ray data was collected at a temperature of 291 K on an Agilent Technologies Supernova diffractometer equipped with an Eos CCD detector with MoK α radiation, (λ = 0.71073 Å) for compound **2**.

X-ray data was collected at a temperature of 100 K on a Rigaku FR-X diffractometer with an Atlas HP6000 detector with MoK α radiation, (λ = 0.71073 Å) for compound **53**.

Both diffractometers were equipped with an Oxford Cryosystems Cobra nitrogen flow gas system. Data was measured using CrysAlisPro suite of programs.

Crystal structure determinations and refinements

X-ray data were processed and reduced using CrysAlisPro suite of programs. The crystal structures were solved and refined against all F^2 values using the SHELX and Olex 2 suite of programs.^{17,18} All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. Some carbon atoms were found disordered and modelled over two positions were possible. In such cases, C-C bond distances were restrained using DFIX and SADI commands. The atomic displacement parameters (adp) of the disordered atoms have been restrained using the RIGU command.

These data sets can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223 336033; or deposit@ccdc.cam.ac.uk).

X-ray structure of 5-(4-(*tert*-Butyl)phenyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium
trifluoromethanesulfonate **2** – CCDC: 1922367

Table A1 Crystal data and structure refinement for **2**

Identification code	5-(4-(<i>tert</i> -Butyl)phenyl)-5 <i>H</i> -dibenzo[<i>b,d</i>]thiophen-5-ium trifluoromethanesulfonate
Empirical formula	C ₂₃ H ₂₁ F ₃ O ₃ S ₂
Formula weight	466.52
Temperature/K	291
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	13.9567(6)
b/Å	8.9349(3)
c/Å	19.5441(7)
α/°	90
β/°	109.050(4)
γ/°	90
Volume/Å ³	2303.71(16)
Z	4
ρ _{calc} /g/cm ³	1.345
μ/mm ⁻¹	0.277
F(000)	968.0
Crystal size/mm ³	0.14 × 0.14 × 0.1
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.506 to 50.692
Index ranges	-16 ≤ h ≤ 16, -10 ≤ k ≤ 10, -23 ≤ l ≤ 20
Reflections collected	26063
Independent reflections	4206 [R _{int} = 0.0308, R _{sigma} = 0.0236]
Data/restraints/parameters	4206/99/340
Goodness-of-fit on F ²	1.059
Final R indexes [I > 2σ (I)]	R ₁ = 0.0473, wR ₂ = 0.1159
Final R indexes [all data]	R ₁ = 0.0614, wR ₂ = 0.1254
Largest diff. peak/hole / e Å ⁻³	0.44/-0.36

X-ray structure of 2-Chloro-*N*-(4'-chloro-5-(1-methyl-1*H*-pyrrol-2-yl)-[1,1'-biphenyl]-2-yl) nicotinamide **53** – CCDC: 1922368

Table A2 Crystal data and structure refinement for **53**

Identification code	2-Chloro- <i>N</i> -(4'-chloro-5-(1-methyl-1 <i>H</i> -pyrrol-2-yl)-[1,1'-biphenyl]-2-yl) nicotinamide
Empirical formula	C ₂₃ H ₁₇ Cl ₂ N ₃ O
Formula weight	422.29
Temperature/K	100.0(3)
Crystal system	orthorhombic
Space group	Pna2 ₁
<i>a</i> /Å	7.6043(2)
<i>b</i> /Å	13.7973(3)
<i>c</i> /Å	18.5805(4)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	1949.44(8)
<i>Z</i>	4
ρ_{calc} /g/cm ³	1.439
μ /mm ⁻¹	3.156
<i>F</i> (000)	872.0
Crystal size/mm ³	0.066 × 0.018 × 0.015
Radiation	CuK α (λ = 1.54184)
2 θ range for data collection/°	7.982 to 136.486
Index ranges	-8 ≤ <i>h</i> ≤ 9, -16 ≤ <i>k</i> ≤ 16, -20 ≤ <i>l</i> ≤ 22
Reflections collected	8626
Independent reflections	3358 [<i>R</i> _{int} = 0.0439, <i>R</i> _{sigma} = 0.0604]
Data/restraints/parameters	3358/1/263
Goodness-of-fit on <i>F</i> ²	1.080
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0426, <i>wR</i> ₂ = 0.1112
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0456, <i>wR</i> ₂ = 0.1129
Largest diff. peak/hole / e Å ⁻³	0.21/-0.44
Flack parameter	-0.001(15)

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