Supporting Information

(Experimental Part)

A general arene C–H functionalization strategy via electron donor-acceptor complex photoactivation

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Table of Contents

General Experimental Information

All experiments were performed under an atmosphere of nitrogen, using anhydrous solvents, unless otherwise stated. Glassware for inert atmosphere reactions was oven-dried and cooled under a flow of nitrogen. Solvents and reagents were purchased from commercial sources and used as supplied. Photochemical reactions were subjected to irradiation from a 34W Kessil blue LED bulb, with the reaction tube placed approximately 2 cm from the bulb. Routine TLC analysis was carried out on aluminium sheets coated with silica gel 60 F254, 0.2 mm thickness. Plates were viewed under a 254 nm UV lamp or visualised by staining with potassium permanganate, *p*-anisaldehyde or vanillin followed by heating. Column chromatography was carried out using 35-70 μ, 60 Å silica gel.

General Analytical Information

Novel compounds were characterized by NMR, IR spectroscopy, HRMS, and melting point. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using 400 and 500 MHz spectrometers, with chemical shift values being reported in parts per million (ppm) relative to the corresponding residual solvent signal. All coupling constants (*J*) are reported in Hertz (Hz). Splitting patterns are assigned s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br. = broad. Mass spectra were obtained using positive and/or negative electrospray (ESI±), atmospheric-pressure chemical ionisation (APCI) or gas chromatography (GC) techniques. IR spectra were recorded on an ATR FTIR spectrometer using neat samples. Melting points were measured on a Stuart Digital SMP10 melting point apparatus and are uncorrected.

General Procedures

General Procedure A: Synthesis of Sulfoxides

Sulfide (1.0 equiv.), was dissolved in CH_2Cl_2 (0.1 M) and cooled to 0 °C. *m*-CPBA (1.05 equiv.) was added portionwise over 30 minutes at 0 °C and the resulting suspension

stirred for 2 h. The reaction mixture was quenched with sat. aq. $NaHCO_3$ and the aqueous layer extracted with CH_2Cl_2 (x 2). The combined organic layers were washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography or by recrystallization from refluxing EtOAc.

General procedure B: Synthesis of (hetero)aryl silyl enol ethers

An oven-dried flask was charged with sodium iodide (dried under vacuum for 1 h, 3.60 g, 24 mmol) and ketone precursor (20 mmol), under nitrogen atmosphere. The materials were suspended in anhydrous CH_3CN (25 mL) and the resulting mixture was stirred for 5 minutes. Anhydrous triethylamine (4.18 mL, 30 mmol) and chlorotrimethylsilane (3.05 mL, 24 mmol) were sequentially added to the mixture dropwise, and the reaction was stirred for 13 hours at room temperature. The reaction was quenched by addition of sat. aq. of NH_4Cl (50 mL) and the crude mixture was extracted with pentane (50 mL **X** 3). The combined organic layers were washed with H_2O (50 mL) and sat. aq. NH_4Cl (50 mL), dried over $MgSO_4$ and filtered. Evaporation of the solvents under reduced pressure delivered the desired silyl enol ether product. Unless otherwise stated, these materials were used in the photochemical protocol without any further purification.

General Procedure C: Synthesis of Triarylamine Donors

Diaryl amine (2.0 mmol, 1.0 equiv.), iodo/bromoarene (if solid) (2.4 mmol, 1.2 equiv.), $Pd_2(dba)_3$ (0.110 g, 0.12 mmol, 0.06 equiv.) and KO*t*-Bu (0.292 g, 2.6 mmol, 1.3 equiv.) were taken in an oven-dried reaction tube equipped with a magnetic stirring bar and the tube was sealed with a crimp cap. The solid mixture was put under high vacuum for 15 minutes and subsequently flushed with N_2. Next, bromoarene (if liquid) (2.4 mmol, 1.2 equiv.), (t-Bu)$_3$P (1.0 M in toluene) (0. 24 mL, 0.24 mmol, 0.12 equiv.) and dry toluene (3.7 mL) were added under N_2. The resulting mixture was stirred at 110 °C for 18 h. After cooling to room temperature, the mixture was filtered through a plug of Celite, the filtrate was concentrated under vacuum and the desired product was isolated from the crude mixture by column chromatography.

General Procedure D: Synthesis of Aryl Sulfonium Salts from Simple Arenes

Tf_2O (1.2 equiv.) was slowly added to a stirred solution of the arene (1.0 equiv.) and the S-oxide (1.1 equiv.) in dry CH_2Cl_2 (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, the reaction was quenched with the addition of methanol which removed the dark colour of the reaction mixture. At this point, the solvent was removed under vacuum while keeping the water bath at 30 °C. The sulfonium salt was then precipitated by the addition of cold Et_2O to the mixture while stirring (occasionally vigorous stirring was needed). The Et_2O was then decanted off and the resulting solid was washed with further portions of Et_2O. In case of an unsuccessful precipitation, the desired sulfonium salt was purified from the crude mixture by column chromatography (CH_2Cl_2:Methanol).

General Procedure E: Synthesis of Aryl Sulfonium Salts from Amide-containing and Complex Arenes

Tf_2O (1.2 equiv.) was slowly added to a stirred solution of the S-oxide (1.1 equiv.) in dry CH_2Cl_2 (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 amide-containing or complex arene (1.0 equiv.) and stirring was continued for a further 15 minutes. The solution was then warmed to room temperature. After stirring for 1 h, the reaction was quenched with the addition of methanol which removed the dark colour of the reaction mixture. At this point, the solvent was removed under vacuum while keeping the water bath at 30 °C. The sulfonium salt was then precipitated by the addition of cold Et_2O to the mixture while stirring (occasionally vigorous stirring was needed). The Et_2O was then decanted off and the resulting solid was washed with further portions of Et_2O. In case of an unsuccessful precipitation, the desired sulfonium salt was purified from the crude mixture by column chromatography (CH_2Cl_2:Methanol).

General procedure F: One-pot Photochemical Arylation of Silyl Enol Ethers

An oven-dried microwave tube was charged with dibenzothiophene sulfoxide **SO1** (0.22 mmol, 44.1 mg) under nitrogen atmosphere (evacuated and back-filled with N_2 three times). Anhydrous CH_2Cl_2 (0.45 mL) and arene (0.20 mmol) were sequentially added via syringe to the vessel. The reaction mixture was cooled to -78 ºC and Tf_2O (0.24 mmol, 0.04 mL) was added dropwise. The reaction mixture was stirred at -78 ºC for 15 minutes then allowed to warm to RT and stirred for 1 h. 2,6-Lutidine (0.3 mmol, 34.8 µL) was added to the vessel via syringe and the mixture stirred for 15 min. *N*-(4-Chlorophenyl)-*N*-phenylnaphthalen-1-amine (0.02 mmol, 6.6 mg) was added as a solution in anhydrous CH_2Cl_2 (0.05 mL) followed by silyl enol ether (1.00 mmol). The reaction mixture was placed at 2 cm away from a blue LED Kessil lamp (λ centred at 456 nm, 100% irradiance), and stirred at ambient temperature (~40 °C, without the use of a cooling fan) for 12 hours. After this time, the volatiles were removed under reduced pressure, and the crude mixture purified by column chromatography on silica gel [*gradient* from hexane to 5% ether in hexane] to provide the desired arylation product.

General procedure G: Photochemical Arylation of Silyl Enol Ethers

An oven-dried microwave tube was charged with aryl sulfonium salt (0.20 mmol) and *N*-(4-chlorophenyl)-*N*-phenylnaphthalen-1-amine (0.02 mmol, 6.6 mg), under nitrogen atmosphere (evacuated and back-filled with N_2 three times). Anhydrous 1,2-DCE (0.5 mL) and silyl enol ether (1.00 mmol) were sequentially added via syringe to the vessel. The reaction mixture was placed at 2 cm away from a blue LED Kessil lamp (λ centred at 456 nm, 100% irradiance), and stirred at ambient temperature (~40 °C, without the use of a cooling fan) for 12 hours. After this time, the volatiles were removed under reduced pressure, and the crude mixture purified by column chromatography on silica gel [*gradient* from CH_2Cl_2 to 1% MeOH in CH_2Cl_2] to provide the desired arylation product.

General Procedure H: Photochemical Cyanation of Aryl Sulfonium Salts

Aryl sulfonium salt (0.20 mmol, 1.0 equiv.), donor **I** (24.1 mg, 0.05 mmol, 0.25 equiv.) and NaOAc (32.8 mg, 0.4 mmol, 2.0 equiv.) were taken in an oven-dried reaction tube equipped with a magnetic stirring bar and the tube was sealed with a crimp cap. The solid mixture was put under high vacuum for 15 minutes and subsequently flushed with N_2. Next, dry DMSO (0.5 mL) was added under N_2 followed by *t*-BuNC (68 mL, 0.6 mmol, 3.0 equiv.). The crimp cap was sealed with parafilm. After irradiating with a blue LED Kessil lamp (λ centred at 456 nm, 100% irradiance) at 2 cm away for 20 h under a cooling fan (ambient temperature ~60 °C), the reaction mixture was quenched by addition of dist. H_2O (2.5 mL) and extracted with EtOAc (2 x 3 mL). The organic layer was passed through a short plug of $MgSO_4$ and concentrated under vacuum. The desired product was isolated from the crude mixture by column chromatography.

General Procedure I: One-pot Photochemical C-H Cyanation of Simple Arenes via the Formation of Aryl Sulfonium Salts

Tf_2O (1.2 equiv.) was slowly added to a stirred solution of the arene (0.20 mmol, 1.0 equiv.) and the S-oxide (1.1 equiv.) in dry CH_2Cl_2 (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, solvent was removed under vacuum while keeping the water bath at 30 °C. To the resulting crude mixture were added donor **I** (24.1 mg, 0.05 mmol, 0.25 equiv.) and NaOAc (49.2 mg, 0.6 mmol, 3.0 equiv.) and the reaction tube was sealed with a crimp cap. The mixture was put under high vacuum for 15 minutes and subsequently flushed with N_2. Next, dry DMSO (0.5 mL) was added under N_2 followed by *t*-BuNC (68 mL, 0.6 mmol, 3.0 equiv.). The crimp cap was sealed with parafilm. After irradiating with a blue LED Kessil lamp (λ centred at 456 nm, 100% irradiance) at 2 cm away for 20 h under a cooling fan (ambient temperature ~60 °C), the reaction mixture was quenched by addition of dist. H_2O (2.5 mL) and extracted with EtOAc (2 x 3 mL). The organic layer

was passed through a short plug of $MgSO_4$ and concentrated under vacuum. The desired product was isolated from the crude mixture by column chromatography.

General Procedure J: One-pot Photochemical C-H Cyanation of Amide-containing and Complex Arenes via the Formation of Aryl Sulfonium Salts

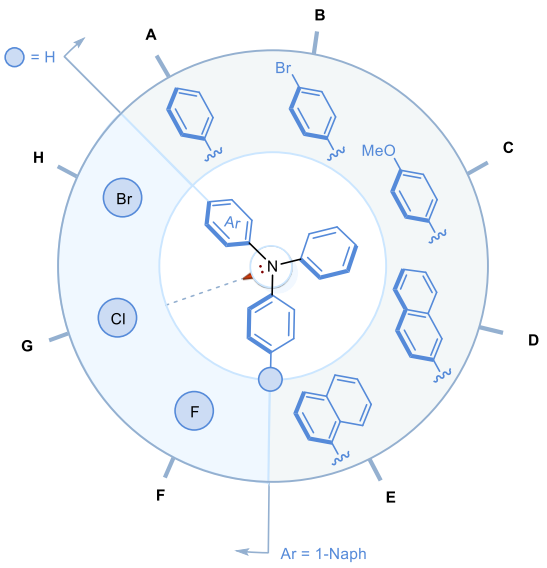
Tf_2O (1.2 equiv.) was slowly added to a stirred solution the S-oxide (1.1 equiv.) in dry CH_2Cl_2 (0.1 M) at −78 °C under a nitrogen atmosphere. The resulting solution was stirred at this temperature for 1 hour before the addition of the amide-containing or complex arene (0.20 mmol, 1.0 equiv.) and stirring was continued for a further 15 minutes. The solution was then warmed to room temperature. After stirring for 1 h, solvent was removed under vacuum while keeping the water bath at 30 °C. To the resulting crude mixture were added donor **I** (24.1 mg, 0.05 mmol, 0.25 equiv.) and NaOAc (49.2 mg, 0.6 mmol, 3.0 equiv.) and the reaction tube was sealed with a crimp cap. The mixture was put under high vacuum for 15 minutes and subsequently flushed with N_2. Next, dry DMSO (0.5 mL) was added under N_2 followed by *t*-BuNC (68 mL, 0.6 mmol, 3.0 equiv.). The crimp cap was sealed with parafilm. After irradiating with a blue LED Kessil lamp (λ centred at 456 nm, 100% irradiance) at 2 cm away for 20 h under a cooling fan (ambient temperature ~60 °C), the reaction mixture was quenched by addition of dist. H_2O (2.5 mL) and extracted with EtOAc (2 x 3 mL). The organic layer was passed through a short plug of $MgSO_4$ and concentrated under vacuum. The desired product was isolated from the crude mixture by column chromatography.

Optimization

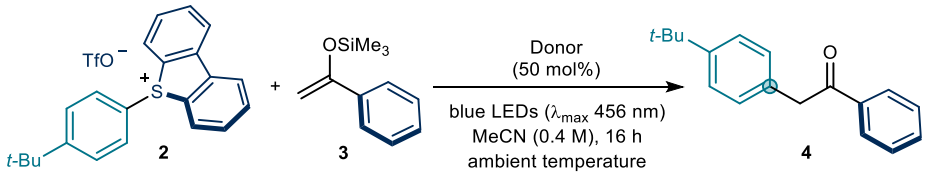
Optimization of the photochemical route to α-aryl carbonyls using EDA complexes of aryl sulfonium salts.

All optimization reactions were carried out on a 0.20 mmol scale. The crude reaction mixtures were analysed by ^{1}H-NMR with mesitylene as internal standard.

Optimization of the visible-light-mediated alpha arylation step was performed using dibenzothiophenium salt, **2**. As outlined in Supplementary Table 1, alpha arylated carbonyl, **4** was formed in low yield from the reaction of **2** and silyl enol ether **3** in the presence of triphenylamine EDA donor **A** in anhydrous EtOAc solvent (Entry 1). Various triarylamine catalysts were screened and also showed poor to moderate catalytic activity (Entries 2-5). The use of naphthyl containing triarylamines as catalysts had a significant effect, providing a more efficient reaction (Entry 5). A range of these naphthyl containing donors was then synthesised and trialled in the reaction (Entries E-H). Using Donor E, other solvents were screened for the reaction, showing that the chemistry is optimal when using 1,2-DCE (Entries 9-17). To ensure this was the case for the best donor, a few of the better solvents were retrialled using Donor **G** again finding 1,2-DCE to be optimal (Entries 18-21). Varying the amount of the radical trap **3** gave varying yields of the desired product (Entries 22-26), however, as a compromise between reaction efficiency and reactant stoichiometry, 5 equivalents of radical trap was used going forward. Lowering catalyst loading led to diminished yields but yield remained high using 10 mol% and this was found to be optimal (Entries 27, 28). Finally, the concentration was varied, finding yields were higher at higher concentrations, but this distinction was negligible when the donor loading was decreased (Entries 29-33).



Supplementary Table 1. Optimization of the photochemical α-arylation reaction conditions



Entry	Donor	Solvent	eq. **3**	Donor loading	Conc (M)	Yield (%)[a]
1	A	EtOAc	5	50 mol%	0.4	13
2	B	EtOAc	5	50 mol%	0.4	12
3	C	EtOAc	5	50 mol%	0.4	46
4	D	EtOAc	5	50 mol%	0.4	23
5	E	EtOAc	5	50 mol%	0.4	47
6	F	EtOAc	5	50 mol%	0.4	51
7	G	EtOAc	5	50 mol%	0.4	61
8	H	EtOAc	5	50 mol%	0.4	49
9	E	CH_2Cl_2	5	50 mol%	0.4	47
10	E	CH_3CN	5	50 mol%	0.4	43
11	E	1,2-DCE	5	50 mol%	0.4	54
12	E	DMA	5	50 mol%	0.4	47
13	E	DMF	5	50 mol%	0.4	45
14	E	DMSO	5	50 mol%	0.4	18
15	E	Acetone	5	50 mol%	0.4	13
16	E	THF	5	50 mol%	0.4	35
17	E	$CHCl_3$	5	50 mol%	0.4	12
18	G	1,2-DCE	5	50 mol%	0.4	70
19	G	DMA	5	50 mol%	0.4	53
20	G	DME	5	50 mol%	0.4	61
21	G	CH_2Cl_2	5	50 mol%	0.4	62
22	G	1,2-DCE	1	50 mol%	0.4	11
23	G	1,2-DCE	2	50 mol%	0.4	20
24	G	1,2-DCE	3	50 mol%	0.4	37

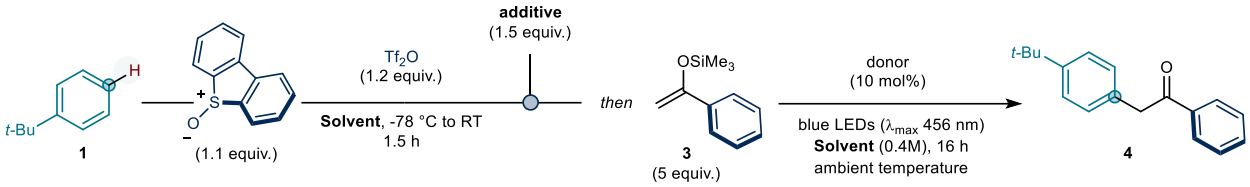
25	G	1,2-DCE	4	50 mol%	0.4	56
26	G	1,2-DCE	10	50 mol%	0.4	75
27	G	1,2-DCE	5	25 mol%	0.4	59
28	G	1,2-DCE	5	10 mol%	0.4	57
29	G	1,2-DCE	5	50 mol%	0.1	51
30	G	1,2-DCE	5	50 mol%	0.2	56
31	G	1,2-DCE	5	50 mol%	0.8	67
32	G	1,2-DCE	5	25 mol%	0.8	59
33	G	1,2-DCE	5	10 mol%	0.8	56

[a]Determined by ^{1}H NMR using mesitylene as internal standard.

Reaction Development – One-Pot route to α-aryl carbonyls exploiting EDA complexes of sulfonium salts

A short optimization was necessary to facilitate the one-pot process (Supplementary Table 2). Early trials were done using a solvent swap procedure previously employed in the group[1] by which the CH_2Cl_2 used for the formation of the dibenzothiophenium salt **2**, was removed in vacuo followed by the addition of the donor as a solid. The reaction vessel was then sealed and evacuated and flushed with nitrogen before addition of 1,2-DCE and radical trap **3**. Early trials however gave low yields (Entry 1). We hypothesised that these poor yields were a result of remaining TfOH in the reaction mixture following the sulfonium salt formation which could quench the amine donor and/or the silyl enol ether. A range of basic additives were trialled to quench this excess TfOH in-situ, finding that the addition of 2,6-lutidine after the completion of the salt formation yielded the best results (Entries 2-5). Once the reaction using pre-formed salt had been fully optimised, further work was done to investigate the one-pot procedure in an attempt to avoid the need for a solvent swap. Although 1,2-DCE is the optimal solvent for the photochemical reaction, it was a poor solvent for the salt formation reaction due to its higher melting point preventing the salt formation from being performed at -78°C, instead it was found optimal to run the reaction in CH_2Cl_2 throughout (Entries 6-9).

Supplementary Table 2. Optimization of the one-pot sequence



Entry	Solvent	Donor	Additive	Notes	Yield (%)[a]
1	CH_2Cl_2/CH_3CN	E	None	-	3
2	CH_2Cl_2/CH_3CN	E	None	Attempted to remove TfOH by high vac for 10 min	16
3	CH_2Cl_2/CH_3CN	E	K_2CO_3		17
4	CH_2Cl_2/CH_3CN	E	2,6-lutidine	Added before reaction	15
5	CH_2Cl_2/CH_3CN	E	2,6-lutidine	Added after salt formation	37
6	1,2-DCE	G	2,6-lutidine	Set to -78°C then RT	43
7	1,2-DCE	G	2,6-lutidine	Set to -30°C then RT	43
8	CH_2Cl_2/1,2-DCE	G	2,6-lutidine	Solvent swap	50
9	CH_2Cl_2	G	2,6-lutidine	-	56

[a]Determined by ^{1}H NMR using mesitylene as internal standard.

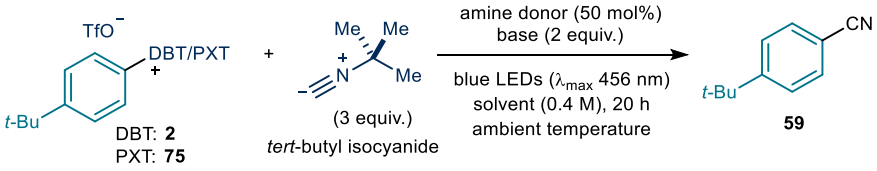
Optimization of the photochemical formal C-H cyanation of arenes using EDA complexes of aryl sulfonium salts.

All optimization reactions were carried out on a 0.20 mmol scale. The crude reaction mixtures were analysed by ^{1}H-NMR with dibromomethane (CH_2Br_2) as internal standard.

The optimization of the visible-light-mediated C-H cyanation reaction started with subjecting a dibenzothiophenium (DBT) salt **2** and a phenoxathiinium (PXT) salt **75** under identical reaction conditions comprising of an amine donor **B**, Na_2CO_3 as base and *tert*-butyl isocyanide as the cyanating agent in DMSO, where the PXT salt outperformed the DBT salt with a promising 48% NMR yield of the 4-*tert*-butyl benzonitrile (**59**) (Supplementary Table 3, entries 1-2). Before varying other

parameters, we sought out the optimum solvent for this reaction. However, only CH_3CN (Entry 5) gave a comparable result (45%), among an array of solvents that we tested (Entries 3-10). Therefore, DMSO remained as our optimum solvent. Other triarylamine donors also furnished the desired product mostly in the range of 40%s (Entries 11-16), however, while analyzing the ^1H NMR of the reaction with donor **D** (Entry 13), we observed that our reference aromatic signal of the product coincides with one of the aromatic signals of the donor. This rendered the *t*-Bu-salt **75** incompatible for a ^1H NMR analysis-based screening of triarylamine donors. So we were prompted to change our model salt to **40**. The methoxy group of **40** provided a reliable option to analyze the reactions with quantitative ^1H NMR analysis of the crude reaction mixtures (Supplementary Table 4).

Supplementary Table 3. Optimization of the photochemical C-H cyanation reaction conditions with **75** as substrate



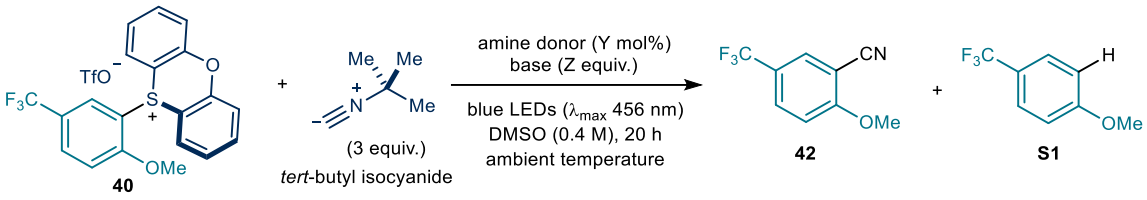
Entry	S-handle	Donor	Solvent	Base	Yield (%)[a]
1	DBT	B	DMSO	Na_2CO_3	41
2	PXT	B	DMSO	Na_2CO_3	48
3	PXT	B	DMF	Na_2CO_3	25
4	PXT	B	DMA	Na_2CO_3	23
5	PXT	B	CH_3CN	Na_2CO_3	45
6	PXT	B	DCE	Na_2CO_3	27
7	PXT	B	1,4-dioxane	Na_2CO_3	23
8	PXT	B	DCM	Na_2CO_3	18
9	PXT	B	THF	Na_2CO_3	15
10	PXT	B	Acetone	Na_2CO_3	38
11	PXT	A	DMSO	Na_2CO_3	47

12	PXT	C	DMSO	Na_2CO_3	41
13	PXT	D	DMSO	Na_2CO_3	N.D.[b]
14	PXT	F	DMSO	Na_2CO_3	42
15	PXT	G	DMSO	Na_2CO_3	40
16	PXT	I	DMSO	Na_2CO_3	57

[a]Determined by ^{1}H NMR using CH_2Br_2 as internal standard; [b]Not determined, as aromatic signals of the donor coincided with the reference aromatic signals of the cyanated product **59**.

When we reacted **40** with *t*-BuNC in presence of triphenylamine and its 4-Br and 4-OMe derivative **B** and **C**, the cyanated product was observed in ^{1}H NMR spectra from 47-51% yields (Entries 1-3). The 2-naphthyl congener **D** did not show much improvement, whereas the 1-naphthyl variant **E** showed a significant increase of the yield to 56% (Entries 4-5). Along these lines, the halo substituted *N*,*N*-diphenylnaphthalen-1-amines **F**, **G** and **H** furnished the product **42** in similar or slightly better yields (56-60%) (Entries 6-8). Pleasingly, commercially available tris(4-bromophenyl)amine **I** worked with equal efficiency and gave an NMR yield of 58%, with lesser hydrogenated side-product **S1** (Entry 9). Therefore, the rest of the screening was continued with donor **I**. Increasing the loading of the base (3 equiv), donor **I** (100 mol%) and *t*-BuNC (6 equiv) did not have any impact on the reaction outcome (Entries 10-12). Therefore, we proceeded to screen a variety of bases. Unfortunately, organic bases did not improve the efficiency of the reaction (Entries 13-20), additionally the ones containing labile aliphatic C-H bonds, caused significant formation of **S1** via a HAT mechanism. So, we tested a few more inorganic bases (Entries 21-27) and to our delight, NaOAc gave a substantially improved NMR yield of 69%. The cyanated arene **42** was isolated in 63% yield from this reaction mixture (Entry 25). Surprisingly, we observed that lowering the donor loading to 25 mol% gave a higher isolated yield of 71% and lowering it further to 10 mol% did not compromise the efficiency of the reaction (70%) (Entries 28-29).

Supplementary Table 4. Optimization of the photochemical C-H cyanation reaction conditions with **40** as substrate



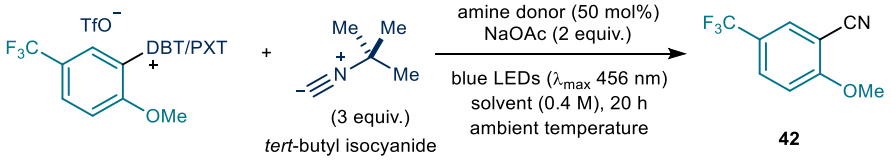
Entry	Donor (mol%)	Base (equiv)	Yield (%)[a]
1	A (50)	Na_2CO_3 (2)	**42** (47) + **S1** (5)
2	B (50)	Na_2CO_3 (2)	**42** (47) + **S1** (trace)
3	C (50)	Na_2CO_3 (2)	**42** (51) + **S1** (6)
4	D (50)	Na_2CO_3 (2)	**42** (47) + **S1** (trace)
5	E (50)	Na_2CO_3 (2)	**42** (56) + **S1** (10)
6	F (50)	Na_2CO_3 (2)	**42** (58) + **S1** (7)
7	G (50)	Na_2CO_3 (2)	**42** (56) + **S1** (7)
8	H (50)	Na_2CO_3 (2)	**42** (60) + **S1** (7)
9	I (50)	Na_2CO_3 (2)	**42** (58) + **S1** (trace)
10	I (50)	Na_2CO_3 (3)	**42** (60) + **S1** (6)
11	I (100)	Na_2CO_3 (2)	**42** (56) + **S1** (7)
12	I (50)	Na_2CO_3 (2)	**42** (58) + **S1** (trace)[b]
13	I (50)	DBU (2)	**42** (25) + **S1** (37)
14	I (50)	DABCO (2)	**42** (14) + **S1** (5)
15	I (50)	2,6-Lutidine (2)	**42** (58) + **S1** (13)
16	I (50)	2,6-Di-*t*-Bu pyridine (2)	**42** (25) + **S1** (5)
17	I (50)	TMG (2)	**42** (35) + **S1** (28)
18	I (50)	BTMG (2)	**42** (30) + **S1** (30)
19	I (50)	DMAP (2)	**42** (44) + **S1** (25)
20	I (50)	1-*t*-Bu-1H-imidazole (2)	**42** (43) + **S1** (4)
21	I (50)	K_2CO_3 (2)	**42** (58) + **S1** (5)
22	I (50)	K_3PO_4 (2)	**42** (51) + **S1** (6)
23	I (50)	KO*t*-Bu (2)	Messy reaction
24	I (50)	CsF (2)	**42** (53) + **S1** (7)
25	I (50)	NaOAc (2)	**42** [69(63[c])] + **S1** (5)
26	I (50)	$NaHCO_3$ (2)	**42** (60) + **S1** (6)

27	I (50)	Na_2HPO_4 (2)	**42** (49) + **S1** (6)
28	I (25)	NaOAc (2)	**42** (71[c])
29	I (10)	NaOAc (2)	**42** (70[c])

[a]Determined by ^1H NMR using CH_2Br_2 as internal standard; [b]6 equiv of *t*-BuNC was used; [c]Isolated yield.

Before proceeding with the scope, we wanted to compare the cyanation system with the α-arylation system in terms of S-handle and the donor. Therefore, we conducted a set of four reactions by reacting each of the DBT and PXT-salt with donors **I** and **G**. Interestingly, the combination of the PXT-salt and **I** proved to be the best choice for the C-H cyanation process (64%) (Entry 1). The optimized combination for the α-arylation (DBT-salt + **G**) gave a lower yield of 57% (Entry 4).

Supplementary Table 5. Extended optimization of the photochemical C-H cyanation



Entry	S-handle	Donor	Yield (%)[a]
1	PXT	I	64
2	PXT	G	57
3	DBT	I	55
4	DBT	G	57

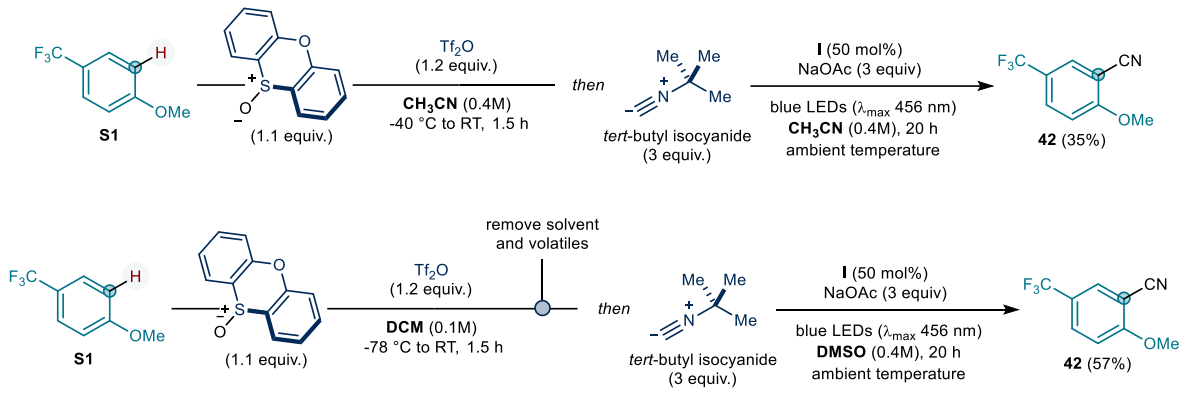
[a]Isolated yield.

Reaction Development – One-Pot formal C-H cyanation of arenes exploiting EDA complexes of aryl sulfonium salts.

Next, we wanted to establish a procedure for a one-pot formal C-H cyanation via sequential sulfonium salt formation and photochemical cyanation, preferably conducting both reactions in the same solvent. DMSO itself being a sulfoxide, is not a prefered solvent for the salt-formation step. Since DCM and DCE did not perform well in the cyanation reaction (Supplementary Table 3, entries 6 and 8), we decided

to conduct the one-pot reaction in CH_3CN (second best solvent for cyanation) and hoped to obtain a reasonably good salt formation reaction in it. However, this trial yielded only 35% of the desired product. Therefore, we attempted a reaction sequence of standard salt-formation in DCM followed by removal of volatiles and finally, photochemical cyanation in DMSO with the concentrated crude mixture. This one-pot procedure furnished the desired product **42** in 57% isolated yield. Notably, 3 equivalents of NaOAc was used with the extra one equivalent to neutralize the TfOH formed in the first step.

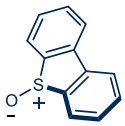
Supplementary Table 6. Optimization of the one-pot sequence



Compound Characterisation

Synthesis of starting materials.

Dibenzo[b,d]thiophene 5-oxide, **SO1**

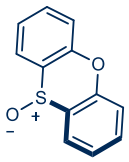


Prepared as described in General Procedure A: Dibenzothiophene (5.40 g, 29.0 mmol) was used as the substrate. Purification by column chromatography on silica gel [*gradient* from hexane to 10% EtOAc in hexane], afforded the desired product (4.15 g, 20.7 mmol, 71%) as a white solid; δ_H (400 MHz, $CDCl_3$) 7.96 (dd, *J* = 7.7, 0.9 Hz, 2H, Ar *H*), 7.77 (dd, *J* = 7.7, 0.9 Hz, 2H, Ar *H*), 7.57 (td, *J* = 7.6, 1.2 Hz, 2H, Ar *H*), 7.47 (td, *J* = 7.6, 1.2 Hz, 2H, Ar *H*); δ_C (101 MHz,

$CDCl_3$) 145.3 (Ar *C*), 137.3 (Ar *C*), 132.7 (Ar *C*H), 129.7 (Ar *C*H), 127.7 (Ar *C*H), 122.1 (Ar *C*H).

The data are in accordance with the literature.[1]

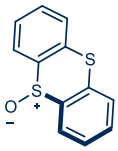
Phenoxathiine 10-oxide, **SO2**



Prepared as described in General Procedure A: phenoxathiin (1.87 g, 9.34 mmol) was used as the substrate. Purification was performed by recrystallisation from refluxing EtOAc, affording the desired compound (1.55 g, 7.2 mmol, 77%) as a white solid; δ_H (400 MHz, $CDCl_3$) 7.93 (dd, *J* = 7.8, 1.7 Hz, 2H, Ar *H*), 7.63 (dd, *J* = 8.6, 7.3 Hz, 2H, Ar *H*), 7.44 (dd, *J* = 8.3, 1.2 Hz, 2H, Ar *H*), 7.38 (td, *J* = 7.5, 1.1 Hz, 2H, Ar *H*); δ_C (101 MHz, $CDCl_3$) 149.6 (Ar *C*), 133.9 (Ar *C*H), 131.2 (Ar *C*H), 125.0 (Ar *C*H), 123.8 (Ar *C*), 118.9 (Ar *C*H).

The data are in accordance with the literature.[2]

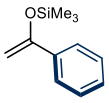
Thianthrene 5-oxide, **SO3**



Prepared as described in General Procedure A: Thianthrene (1.08 g, 5.0 mmol) was used as the substrate. Purification by column chromatography on silica gel [*gradient* from hexane to 10% EtOAc in hexane], afforded the desired compound (764 mg, 3.3 mmol, 66%) as a white solid; δ_H (400 MHz, $CDCl_3$) 7.93 (d, *J* = 7.7 Hz, 2H, Ar *H*), 7.63 (d, *J* = 7.7 Hz, 2H, Ar *H*), 7.56 (t, *J* = 7.6 Hz, 2H, Ar *H*), 7.43 (t, *J* = 7.6 Hz, 2H, Ar *H*); δ_C (101 MHz, $CDCl_3$) 141.5 (Ar *C*), 130.0 (Ar *C*H), 129.2 (Ar *C*H), 128.6 (Ar *C*H), 124.6 (Ar *C*H).

The data are in accordance with the literature.[3]

Trimethyl((1-phenylvinyl)oxy)silane, **3**

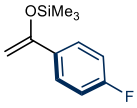


Prepared as described in General Procedure B, acetophenone (2.40 g, 20.0 mmol) was used as the substrate and the reaction yielded the desired product (3.38 g, 17.6 mmol, 88%) as a colourless liquid: δ_H (400 MHz, $CDCl_3$) 7.61 (dd, *J* = 8.2, 1.5 Hz, 2H, Ar *H*), 7.36 - 7.29 (m, 3H, Ar *H*), 4.93 (d, *J* = 1.7 Hz, 1H, CH_2), 4.45

(d, *J* = 1.7 Hz, 1H, C*H*$_2$), 0.29 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 155.8 (*C*-O), 137.7 (Ar *C*), 128.4 (Ar *C*H), 128.2 (Ar *C*H), 125.4 (Ar *C*H), 91.2 (*C*H$_2$), 0.3 (*C*H$_3$); HRMS (APCI) $C_{11}H_{17}OSi$ $[M+H]^+$: Expected 193.1043, Found 193.1039.

The data are in accordance with the literature.[4]

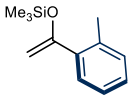
((*1-(4-Fluorophenyl)vinyl)oxy)trimethylsilane,* ***SE1***



Prepared as described in General Procedure B, 1-(4-fluorophenyl)ethan-1-one (2.76 g, 20.0 mmol) was used as the substrate and the reaction yielded the desired product (4.00 g, 19.0 mmol, 95%) as a colourless liquid; δ_H (400 MHz, $CDCl_3$) 7.56 (dd, *J* = 8.7, 5.5 Hz, 2H, Ar *H*), 7.00 (t, *J* = 8.7 Hz, 2H, Ar *H*), 4.84 (d, *J* = 1.5 Hz, 1H, C*H*$_2$), 4.41 (d, *J* = 1.5 Hz, 1H, C*H*$_2$), 0.28 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 163.0 (d, $^1J_{C-F}$ = 247.0 Hz, Ar *C*), 155.0 (*C*-O), 133.8 (d, $^4J_{C-F}$ = 3.0 Hz, Ar *C*), 127.1 (d, $^3J_{C-F}$ = 7.9 Hz, Ar *C*H), 115.0 (d, $^2J_{C-F}$ = 21.6 Hz, Ar *C*H), 90.8 (*C*H$_2$), 0.2 (*C*H$_3$); HRMS (APCI) $C_{11}H_{16}OFSi$ $[M+H]^+$: Expected 211.0949, Found 211.0940.

The data are in accordance with the literature.[4]

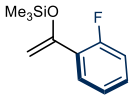
Trimethyl((*1-(o-tolyl)vinyl)oxy)silane,* ***SE2***



Prepared as described in General Procedure B, 1-(*o*-tolyl)ethan-1-one (2.68 g, 20.0 mmol) was used as the substrate and the reaction yielded the desired product (3.57 g, 17.3 mmol, 87%) as a colourless liquid; δ_H (400 MHz, $CDCl_3$) 7.32 (d, *J* = 7.6 Hz, 1H, Ar *H*), 7.23-7.11 (m, 3H, Ar *H*), 4.54 (d, *J* = 0.6 Hz, 1H, C*H*$_2$), 4.40 (d, *J* = 0.6 Hz, 1H, C*H*$_2$), 2.40 (s, 3H, C*H*$_3$), 0.20 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 157.9 (*C*-O), 139.1 (Ar *C*), 136.0 (Ar *C*), 130.5 (Ar *C*H), 128.8 (Ar *C*H), 128.2 (Ar *C*H), 125.5 (Ar *C*H), 95.0 (*C*H$_2$), 20.6 (*C*H$_3$), 0.2 (*C*H$_3$); HRMS (APCI) $C_{12}H_{19}OSi$ $[M+H]^+$: Expected 207.1200, Found 207.1196.

The data are in accordance with the literature.[5]

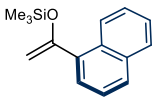
((*1-(2-Fluorophenyl)vinyl)oxy)trimethylsilane,* ***SE3***



Prepared as described in General Procedure B, 1-(2-fluorophenyl)ethan-1-one (2.76 g, 20.0 mmol) was used as the substrate and the reaction yielded the desired product (3.73 g, 17.7 mmol, 89%) as a colourless liquid; δ_H (400 MHz, $CDCl_3$) 7.56 (td, *J* = 7.9, 1.8 Hz, 1H, Ar *H*), 7.28 - 7.21 (m, 1H, Ar *H*), 7.12 (td, *J* = 7.6, 1.2 Hz, 1H, Ar *H*), 7.04 (ddd, *J* = 11.7, 8.2, 1.2 Hz, 1H, Ar *H*), 5.03 - 5.02 (m, 1H, C*H*$_2$), 4.70 - 4.69 (m, 1H, C*H*$_2$), 0.26 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 160.2 (d, $^1J_{C-F}$ = 251.2 Hz, Ar *C*), 150.5 (d, $^3J_{C-F}$ = 3.8 Hz, *C*-O), 129.5 (d, $^3J_{C-F}$ = 8.7 Hz, Ar *C*H), 129.0 (d, $^4J_{C-F}$ = 2.6 Hz, Ar *C*H), 125.8 (d, $^2J_{C-F}$ = 11.0 Hz, Ar *C*), 123.9 (d, $^3J_{C-F}$ = 3.7 Hz, Ar *C*H), 116.1 (d, $^2J_{C-F}$ = 23.5 Hz, Ar *C*H), 97.4 (d, $^4J_{C-F}$ = 11.1 Hz, *C*H$_2$), 0.2 (*C*H$_3$); HRMS (APCI) $C_{11}H_{16}OFSi$ $[M+H]^+$: Expected 211.0949, Found 211.0942.

The data are in accordance with the literature.[6]

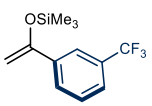
Trimethyl((*1-(naphthalen-1-yl)vinyl)oxy)silane,* ***SE4***



Prepared as described in General Procedure B, 1-(naphthalen-1-yl)ethan-1-one (3.40 g, 20.0 mmol) was used as the substrate and the reaction yielded the desired product (4.01 g, 16.5 mmol, 83%) as a colourless liquid; δ_H (400 MHz, $CDCl_3$) 8.32 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 7.86 - 7.79 (m, 2H, Ar-*H*), 7.55 - 7.40 (m, 4H, Ar-*H*), 4.76 (d, *J* = 0.5 Hz, 1H, C*H*$_2$), 4.63 (d, *J* = 0.5 Hz, 1H, C*H*$_2$), 0.16 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 157.1 (*C*-O), 137.4 (Ar *C*), 133.8 (Ar *C*), 131.1 (Ar *C*), 128.8 (Ar *C*H), 128.3 (Ar *C*H), 126.4 (Ar *C*H), 126.3 (Ar *C*H), 126.1 (Ar *C*H), 125.8 (Ar *C*H), 125.2 (Ar *C*H), 96.8 (*C*H$_2$), 0.3 (*C*H$_3$); HRMS (APCI) $C_{15}H_{19}OSi$ $[M+H]^+$: Expected 243.1200, Found 243.1190.

The data are in accordance with the literature.[5]

Trimethyl((*1-(3-(trifluoromethyl)phenyl)vinyl)oxy)silane,* ***SE5***



Prepared as described in General Procedure B, 1-(3-trifluoromethylphenyl)ethan-1-one (1.88 g, 10.0 mmol) was used as the substrate and the reaction yielded the desired product (2.17 g, 8.35 mmol, 84%) as a colourless liquid; δ_H (400 MHz, $CDCl_3$) 7.83 (s, 1H, Ar *H*), 7.77 (d, *J* = 7.9 Hz, 1H, Ar *H*),

7.54 (d, *J* = 7.7 Hz, 1H, Ar *H*), 7.44 (t, *J* = 7.8 Hz, 1H, Ar *H*), 4.98 (d, *J* = 2.0 Hz, 1H, CH_2), 4.51 (d, *J* = 2.0 Hz, 1H, CH_2), 0.28 (s, 9H, CH_3); δ_C (101 MHz, $CDCl_3$) 154.4 (*C*-O), 138.5 (Ar *C*), 130.6 (q, $^2J_{C-F}$ = 33.6 Hz, Ar *C*), 128.7 (Ar *C*H), 128.5 (Ar *C*H), 124.9 (q, $^3J_{C-F}$ = 3.8 Hz, Ar *C*H), 124.3 (q, $^1J_{C-F}$ = 267.4 Hz, *C*F_3), 122.1 (q, $^3J_{C-F}$ = 3.9 Hz, Ar *C*H), 92.3 (*C*H_2), 0.2 (*C*H_3); HRMS (APCI) $C_{12}H_{16}OF_3Si$ $[M+H]^+$: Expected 261.0917, Found 261.0913.

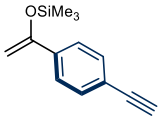
The data are in accordance with the literature.[4]

((*1-(3-Methoxyphenyl)vinyl)oxy)trimethylsilane,* ***SE6***

Prepared as described in General Procedure B, 1-(3-methoxyphenyl)ethan-1-one (1.50 g, 10.0 mmol) was used as the substrate and the reaction yielded the desired product (1.65 g, 7.43 mmol, 74%) as a colourless liquid; δ_H (400 MHz, $CDCl_3$) 7.27-7.17 (m, 2H, Ar *H*), 7.13 (t, *J* = 1.8 Hz, 1H, Ar *H*), 6.84 (d, *J* = 7.7 Hz, 1H, Ar *H*), 4.92 (d, *J* =1.6 Hz, 1H, CH_2), 4.44 (d, *J* =1.6 Hz, 1H, CH_2), 3.82 (s, 3H, CH_3), 0.27 (s, 9H, CH_3); δ_C (101 MHz, $CDCl_3$) 159.6 (Ar *C*), 155.5 (*C*-O), 139.2 (Ar *C*), 129.2 (Ar *C*H), 117.9 (Ar *C*H), 113.7 (Ar *C*H), 111.1 (Ar *C*H), 91.6 (*C*H_2), 55.3 (*C*H_3), 0.2 (*C*H_3); HRMS (APCI) $C_{12}H_{19}O_2Si$ $[M+H]^+$: Expected 223.1149, Found 223.1140.

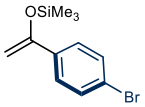
The data are in accordance with the literature.[5]

((*1-(4-Ethynylphenyl)vinyl)oxy)trimethylsilane,* ***SE7***



Prepared as described in General Procedure B, 1-(4-ethynylphenyl)ethan-1-one (360.4 mg, 2.50 mmol) was used as the substrate and the reaction yielded the desired product (466 mg, 2.16 mmol, 86%) as a pale yellow liquid; δ_H (400 MHz, $CDCl_3$) 7.54 (d, *J* = 8.4 Hz, 2H, Ar *H*), 7.44 (d, *J* = 8.4 Hz, 2H, Ar *H*), 4.94 (d, *J* = 1.9 Hz, 1H, CH_2), 4.48 (d, *J* = 1.9 Hz, CH_2), 3.07 (s, 1H, *C*H) , 0.26 (s, 9H, CH_3); δ_C (101 MHz, $CDCl_3$) 155.0 (*C*-O), 138.0 (Ar *C*), 132.0 (Ar *C*H), 125.2 (Ar *C*H), 121.9 (Ar *C*), 92.2 (*C*H_2), 83.8 (*C*-CH), 78.0 (*C*H), 0.2 (*C*H_3); HRMS (APCI) $C_{13}H_{17}OSi$ $[M+H]^+$: Expected 217.1043, Found 217.1036.

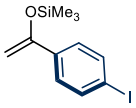
((*1-(4-Bromophenyl)vinyl)oxy)trimethylsilane,* ***SE8***



Prepared as described in General Procedure B, 1-(4-bromophenyl)ethan-1-one (3.18 g, 20.0 mmol) was used as the substrate and the reaction yielded the desired product (3.98 g, 14.7 mmol, 73%) as a pale yellow liquid; δ_H (400 MHz, $CDCl_3$) 7.48 - 7.42 (m, 4H, Ar *H*), 4.90 (d, *J* = 1.9 Hz, 1H, C*H*$_2$), 4.44 (d, *J* = 1.9 Hz, 1H, C*H*$_2$), 0.27 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 154.8 (*C*-O), 136.6 (Ar *C*), 131.3 (Ar *C*H), 127.0 (Ar *C*H), 122.4 (Ar *C*), 91.6 (*C*H$_2$), 0.2 (*C*H$_3$); HRMS (APCI) $C_{11}H_{16}OBrSi$ $[M+H]^+$: Expected 271.0148, Found 271.0143.

The data are in accordance with the literature.[4]

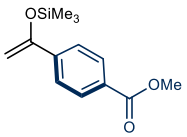
((*1-(4-Iodophenyl)vinyl)oxy)trimethylsilane,* ***SE9***



Prepared as described in General Procedure B, 1-(4-iodophenyl)ethan-1-one (2.46 g, 10.0 mmol) was used as the substrate and the reaction yielded the desired product (2.92 g, 9.18 mmol, 92%) as a pale yellow liquid; δ_H (400 MHz, $CDCl_3$) 7.64 (d, *J* = 8.6 Hz, 2H, Ar *H*), 7.32 (d, *J* = 8.6 Hz, 2H, Ar *H*), 4.91 (d, *J* = 1.9 Hz, 1H, C*H*$_2$), 4.43 (d, *J* = 1.9 Hz, 1H, C*H*$_2$), 0.26 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 154.9 (*C*-O), 137.3 (Ar *C*H), 137.2 (Ar *C*), 127.2 (Ar *C*H), 94.1 (Ar *C*), 91.7 (*C*H$_2$), 0.2 (*C*H$_3$); HRMS (APCI) $C_{11}H_{16}OISi$ $[M+H]^+$: Expected 319.0010, Found 318.9999.

The data are in accordance with the literature.[5]

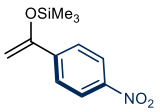
Methyl 4-(1-((trimethylsilyl)oxy)vinyl)benzoate, ***SE10***



Prepared as described in General Procedure B, methyl-4-acetylbenzoate (1.78 g, 10.0 mmol) was used as the substrate and the reaction yielded the desired product (2.10 g, 8.38 mmol, 84%) as a colourless liquid; δ_H (400 MHz, $CDCl_3$) 7.99, (d, *J* = 8.5 Hz, 2H, Ar *H*), 7.65 (d, *J* = 8.5, 2H, Ar *H*), 5.02 (d, *J* = 1.9 Hz, 1H, C*H*$_2$), 4.54 (d, *J* = 1.9 Hz, 1H, C*H*$_2$), 3.91 (s, 3H, C*H*$_3$), 0.27 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 167.0 (*C*=O), 154.9 (*C*-O), 142.0 (Ar *C*), 129.8 (Ar *C*), 129.6 (Ar *C*H), 125.2 (Ar *C*H), 93.3 (*C*H$_2$), 52.2 (*C*H$_3$), 0.2 (*C*H$_3$); HRMS (APCI) $C_{13}H_{19}O_3Si$ $[M+H]^+$: Expected 251.1098, Found 251.1086.

The data are in accordance with the literature.[7]

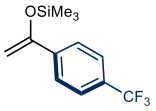
Trimethyl((*1-(4-nitrophenyl)vinyl)oxy)silane, **SE11**



Prepared as described in General Procedure B, 1-(4-nitrophenyl)ethan-1-one (3.30 g, 20.0 mmol) was used as the substrate and the reaction yielded the desired product (3.80 g, 16.0 mmol, 80%) as a pale yellow liquid; δ_H (400 MHz, $CDCl_3$) 8.17 (d, *J* = 8.7 Hz, 2H, Ar *H*), 7.73 (d, *J* = 8.7 Hz, 2H, Ar *H*), 5.08 (d, *J* = 2.1 Hz, 1H, C*H*$_2$), 4.62 (d, *J* = 2.1 Hz, 1H, C*H*$_2$), 0.29 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) δ 153.9 (*C*-O), 147.6 (Ar *C*), 143.8 (Ar *C*), 126.0 (Ar *C*H), 123.6 (Ar *C*H), 94.6 (*C*H$_2$), 0.2 (*C*H$_3$); HRMS (APCI) $C_{11}H_{16}O_3NSi$ $[M+H]^+$: Expected 238.0894, Found 238.0887.

The data are in accordance with the literature.[8]

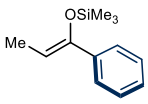
Trimethyl((*1-(4-(trifluoromethyl)phenyl)vinyl)oxy)silane, **SE12**



Prepared as described in General Procedure B, 1-(4-trifluoromethylphenyl)ethan-1-one (3.76 g, 20.0 mmol) was used as the substrate and the reaction yielded the desired product (4.72 g, 18.1.00 mmol, 91%) as a colourless liquid; δ_H (400 MHz, $CDCl_3$) 7.69 (d, *J* = 8.3 Hz, 2H, Ar *H*), 7.57 (d, *J* = 8.3 Hz, 2H, Ar *H*), 5.00 (d, *J* = 1.9 Hz, 1H, C*H*$_2$), 4.53 (d, *J* = 1.9 Hz, 1H, C*H*$_2$), 0.28 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 154.6 (*C*-O), 141.1 (Ar *C*), 130.2 (q, $^2J_{C\text{-}F}$ = 32.6 Hz, Ar *C*), 125.6 (Ar *C*H), 125.3 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, Ar *C*H), 124.3 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, *C*F$_3$), 93.0 (*C*H$_2$), 0.2 (*C*H$_3$); HRMS (APCI) $C_{12}H_{16}OF_3Si$ $[M+H]^+$: Expected 261.0917, Found 261.0914.

The data are in accordance with the literature.[9]

Trimethyl((1-phenylprop-1-en-1-yl)oxy)silane, **SE13**

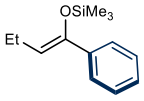


Prepared as described in General Procedure B, propiophenone (1.34 g, 10.0 mmol) was used as the substrate and the reaction yielded the desired product (1.78 g, 8.63 mmol, 86%) as a colourless liquid: δ_H (400 MHz, $CDCl_3$)

7.34 – 7.29 (m 2H, Ar *H*), 7.17 - 7.06 (m, 3H, Ar *H*), 5.19 (q, *J* = 6.9 Hz, 1H, C*H*), 1.60 (d, *J* = 6.9 Hz, 3H, CH_3), 0.00 (s, 9H, CH_3); δ_C (101 MHz, $CDCl_3$) 150.0 (*C*-O), 139.3 (Ar *C*), 128.1 (Ar *C*H), 127.4 (Ar *C*H), 125.3 (Ar *C*H), 105.5 (*C*H), 11.8 (*C*H_3), 0.3 (*C*H_3); HRMS (APCI) $C_{12}H_{19}OSi$ $[M+H]^+$: Expected 207.1200, Found 207.1194.

The data are in accordance with the literature.[10]

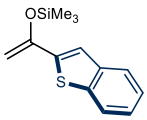
Trimethyl((1-phenylbut-1-en-1-yl)oxy)silane, ***SE14***



Prepared as described in General Procedure B, butyrophenone (1.48 g, 10.0 mmol) was used as the substrate and the reaction yielded the desired product (2.01 g, 9.13 mmol, 91%) as a colourless liquid: δ_H (400 MHz, $CDCl_3$) 7.50 – 7.45 (m, 2H, Ar *H*), 7.32 - 7.21 (m, 3H, Ar *H*), 5.25 (t, *J* = 7.1 Hz, 1H, C*H*), 2.27 – 2.19 (m, 2H, CH_2), 1.05 (t, *J* = 7.5 Hz, 3H, CH_3), 0.14 (s, 9H, CH_3); δ_C (101 MHz, $CDCl_3$) 148.5 (*C*-O), 139.4 (Ar *C*), 128.1 (Ar *C*H), 127.4 (Ar *C*H), 125.4 (Ar *C*H), 113.5 (*C*H), 19.7 (*C*H_2), 14.4 (*C*H_3), 0.6 (*C*H_3); HRMS (APCI) $C_{13}H_{21}OSi$ $[M+H]^+$: Expected 221.1356, Found 221.1353.

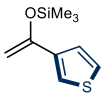
The data are in accordance with the literature.[10]

((*1-(Benzo[b]thiophen-2-yl)vinyl)oxy)trimethylsilane,* ***SE15***



Prepared as described in General Procedure B, 1-(benzo[b]thiophen-2-yl)ethan-1-one (1.76 g, 10.0 mmol) was used as the substrate and the reaction yielded the desired product (2.19 g, 8.83 mmol, 88%) as a yellow liquid; δ_H (400 MHz, $CDCl_3$) 7.78 – 7.69 (m, 2H, Ar *H*), 7.38 (s, 1H, Ar *H*), 7.35 - 7.27 (m, 2H, Ar *H*), 4.93 (d, *J* = 2.1 Hz, 1H, CH_2), 4.48 (d, *J* = 2.1 Hz, 1H, CH_2), 0.32 (s, 9H, CH_3); δ_C (101 MHz, $CDCl_3$) 151.1 (*C*-O), 142.4 (Ar *C*), 140.1 (Ar *C*), 139.7 (Ar *C*), 124.8 (Ar *C*H), 124.5 (Ar *C*H), 123.9 (Ar *C*H), 122.3 (Ar *C*H), 120.9 (Ar *C*H), 93.2 (*C*H_2), 0.2 (*C*H_3); HRMS (APCI) $C_{13}H_{17}OSSi$ $[M+H]^+$: Expected 249.0764, Found 249.0753; ν_{max} (thin film/cm^{-1}) 725, 743, 840, 1010, 1040, 1180, 1250, 1300, 1670, 2899, 2959, 3059.

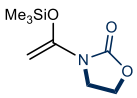
Trimethyl((*1-(thiophen-3-yl)vinyl)oxy)silane,* ***SE16***



Prepared as described in General Procedure B, 1-(thiophen-3-yl)ethan-1-one (1.26 g, 10.0 mmol) was used as the substrate and the reaction yielded the desired product (1.70 g, 8.59 mmol, 86%) as a yellow liquid; δ_H (400 MHz, $CDCl_3$) 7.37 (dd, *J* = 3.0, 1.2 Hz, 1H, Ar *H*), 7.24 (dd, *J* = 5.1, 3.0 Hz, 1H, Ar *H*), 7.20 (dd, *J* = 5.1, 1.2 Hz, 1H, Ar *H*), 4.76 (d, *J* = 1.6 Hz, 1H, C*H*$_2$), 4.38 (d, *J* = 1.6 Hz, 1H, C*H*$_2$), 0.27 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 152.3 (*C*-O), 140.5 (Ar *C*), 125.7 (Ar *C*H), 125.4 (Ar *C*H), 121.9 (Ar *C*H), 91.0 (*C*H$_2$), 0.2 (*C*H$_3$); HRMS (APCI) $C_9H_{15}OSSi$ $[M+H]^+$: Expected 199.0607, Found 199.0605.

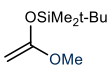
The data are in accordance with the literature.[11]

3-(1-((Trimethylsilyl)oxy)vinyl)oxazolidin-2-one, ***SE17***



Sodium bis(trimethylsilyl)amide (2.0 M in THF, 1.65 mL, 3.30 mmol) was added to a stirred solution of 3-acetyloxazolidin-2-one (387 mg, 3.00 mmol) in THF (10 mL) at –78 °C and stirred for 30 minutes. Trimethylsilyl chloride (0.53 mL, 4.2 mmol) was added dropwise at −78 °C and then the reaction mixture was allowed to warm to RT and stirred for 1 hour. Volatiles were then removed in vacuo and the resulting residue dried under a reduced pressure (2 mbar) for 30 minutes. Et_2O was then added to the residue and the resulting suspension was filtered quickly through Celite. The filtrate was concentrated in vacuo to yield the desired product (329 mg, 1.64 mmol, 55%) as a colourless liquid.; δ_H (400 MHz, $CDCl_3$) 4.54 (d, *J* = 2.5 Hz, 1H, C*H*$_2$), 4.30 (t, *J* = 8.0 Hz, 2H, C*H*$_2$), 3.91 (d, *J* = 2.5 Hz, 1H, C*H*$_2$), 3.82 (t, *J* = 8.0 Hz, 2H, C*H*$_2$), 0.27 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 154.6 (*C*=O), 146.4 (*C*-O), 78.6 (*C*H$_2$), 61.4 (*C*H$_2$), 44.3 (*C*H$_2$), -0.1 (*C*H$_3$); HRMS (ESI^+) $C_8H_{15}O_3NNaSi$ $[M+Na]^+$: Expected 224.0713, Found 224.0706; ν_{max} (thin film/cm^{-1}) 757, 840, 1035, 1309, 1397, 1649, 1760, 2913, 2960.

tert-Butyl((1-methoxyvinyl)oxy)dimethylsilane, ***SE18***



Under a positive pressure of N_2, n-BuLi (2.5 M in THF, 11.2 mL, 28.0 mmol) was added dropwise to a solution of diisopropylamine (4.23 mL, 30.0

mmol) in anhydrous THF (20 mL) at -78 °C. The mixture was allowed to heat to 0 °C and stirred for 20 min. The mixture was cooled back to -78 °C and methyl acetate (1.59 mL, 20.0 mmol) was added dropwise before stirring for 1 h. DMPU (3.14 mL, 26.0 mmol) was added dropwise followed by a solution of TBDMSCl (3.62 g, 24.0 mmol) in anhydrous THF (5 mL) and the mixture stirred at -78 °C for 30 min. The reaction mixture was allowed to heat to RT and stirred for 1 h. The reaction mixture was concentrated in vacuo and redissolved in pentane (50 mL), washed with water (25 mL), $NaHCO_3$ (25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated to yield the desired product (3.16 g, 16.8 mmol, 83%) as a pale yellow liquid; δ_H (400 MHz, $CDCl_3$) 3.53 (s, 3H, C*H*$_3$), 3.23 (d, *J* = 2.6 Hz, 1H, C*H*$_2$), 3.10 (d, *J* = 2.6 Hz, 1H, C*H*$_2$), 0.93 (s, 9H, 3 x C*H*$_3$), 0.17 (s, 6H, 2 x C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 162.4 (*C*-O), 60.2 (*C*H_2), 55.2 (O*C*H_3), 25.7 (*C*H_3), 18.3 (q*C*), -4.6 (*C*H_3); HRMS (APCI) $C_9H_{21}O_2Si$ $[M+H]^+$: Expected 189.1305, Found 189.1301.

The data are in accordance with the literature.[12]

((*3,3-Dimethylbut-1-en-2-yl)oxy)trimethylsilane,* ***SE19***

Prepared as described in General Procedure B, 3,3-dimethylbutan-2-one (1.00 g, 10.0 mmol) was used as the substrate and the reaction yielded the desired product (1.04 g, 6.04 mmol, 60%) as a colourless liquid; δ_H (400 MHz, $CDCl_3$) 4.08 (d, *J* = 1.0 Hz, 1H, C*H*$_2$), 3.93 (d, *J* = 1.0 Hz, 1H, C*H*$_2$), 1.04 (s, 9H, C*H*$_3$), 0.21 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 167.4 (*C*-O), 85.9 (*C*H_2), 36.5 (*C*-CH_3), 28.2 (*C*H_3), 0.3 (*C*H_3); HRMS (APCI) $C_{19}H_{21}OSi$ $[M+H]^+$: Expected 173.1356, Found 173.1349.

The data are in accordance with the literature.[4]

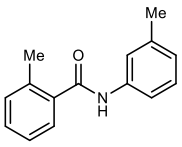
Trimethyl(prop-1-en-2-yloxy)silane, ***SE20***

Prepared as described in General Procedure B, acetone (1.16 g, 20.0 mmol) was used as the substrate and the reaction yielded the desired product (2.48

g, 19.0 mmol, 95%) as a colourless liquid; δ_H (400 MHz, $CDCl_3$) 4.06 (s, 1H, C*H*$_2$), 4.05 (s, 1H, C*H*$_2$), 1.78 (s, 3H, C*H*$_3$), 0.21 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 156.1 (*C*-O), 91.4 (*C*H_2), 23.0 (*C*H_3), 0.3 (*C*H_3).

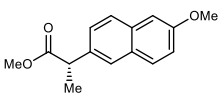
The data are in accordance with the literature.[13]

2-Methyl-N-(m-tolyl)benzamide, **S2**



A solution of sodium hydroxide (800 mg, 20.0 mmol) in deionised water (7.5 mL) was added to *m*-toluidine (2.15 mL, 20.0 mmol) in acetone (5 mL). To this mixture was slowly added *o*-methylbenzoyl chloride (2.61 mL, 20.0 mmol). The reaction was stirred at RT for 1 h, before cooling to 0 ºC. The resulting crystals were collected by vacuum filtration and washed with methanol/water (4:1, 5 mL x 2) and dried under vacuum yielding the desired product (3.87 g, 17.2 mmol, 86%) as a white crystalline solid: m.p. (recrystallized from CH_2Cl_2) 150 – 152 °C ; δ_H (400 MHz, $CDCl_3$) 7.50 (brs, 2H, Ar *H*, N*H*), 7.45 (d, *J* = 7.5 Hz, 1H, Ar *H*), 7.40 – 7.33 (m, 2H, Ar *H*), 7.28 – 7.21 (m, 3H, Ar *H*), 6.97 (d, *J* = 7.6 Hz, 1H, Ar *H*), 2.49 (s, 3H, C*H*$_3$), 2.37 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 168.2 (*C*=O), 139.2 (Ar *C*), 138.0 (Ar *C*), 136.6 (Ar *C*), 136.5 (Ar *C*), 131.4 (Ar *C*H), 130.3 (Ar *C*H), 129.0 (Ar *C*H), 126.7 (Ar *C*H), 126.0 (Ar *C*H), 125.5 (Ar *C*H), 120.6 (Ar *C*H), 117.1 (Ar *C*H), 21.6 (*C*H_3), 19.9 (*C*H_3); HRMS (ESI$^+$) $C_{15}H_{15}ONNa$ $[M+Na]^+$: Expected 248.1046, Found 248.1037 ; ν_{max} (thin film/cm^{-1}) 782, 1268, 1303, 1420, 1546, 1589, 1643, 2923, 2959, 3074, 3147, 3251.

Methyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate,

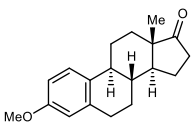


To a stirring solution of (S)-2-(6-methoxynaphthalen-2-yl)propanoic acid (461 mg, 2.00 mmol) in toluene/MeOH (3:2, 20 mL) was added an etheric solution of $TMSCHN_2$ dropwise until a yellow colour persisted (~ 3 mmol). The mixture was stirred for 30 minutesat RT and concentrated under vacuum. The crude product was purified by column chromatography (10% EtOAc in Hexane) yielding the desired product (480 mg, 1.96 mmol, 98%) as a white

crystalline solid: δ_H (400 MHz, $CDCl_3$) 7.70 (d, *J* = 8.6 Hz, 2H, Ar *H*), 7.66 (d, *J* = 1.5 Hz, 1H, Ar *H*), 7.40 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar *H*), 7.14 (dd, *J* = 8.8, 2.5 Hz, 1H, Ar *H*), 7.11 (d, *J* = 2.5 Hz, 1H, Ar *H*), 3.91 (s, 3H, C*H*$_3$), 3.86 (q, *J* = 7.2 Hz, 1H, C*H*), 3.66 (s, 3H, C*H*$_3$), 1.57 (d, *J* = 7.2 Hz, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 175.3 (*C*=O), 157.8 (Ar *C*), 135.8 (Ar *C*), 133.8 (Ar *C*), 129.4 (Ar *C*H), 129.1 (Ar *C*), 127.3 (Ar *C*H), 126.3 (Ar *C*H), 126.1 (Ar *C*H), 119.1 (Ar *C*H), 105.7 (Ar *C*H), 55.5 (*C*H$_3$), 52.2 (*C*H$_3$), 45.5 (*C*H), 18.7 (*C*H$_3$); HRMS (APCI) $C_{15}H_{16}O_3$ $[M+H]^+$: Expected 244.1094, Found 244.1089.

The data are in accordance with the literature.[14]

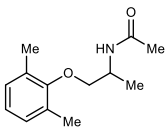
(8R,9S,13S,14S)-3-Methoxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one,



A mixture of (8R,9S,13S,14S)-3-hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (676 mg, 2.50 mmol) and tetrabutylammonium iodide (46 mg, 0.13 mmol) was suspended in CH_2Cl_2 (10 mL). Methyl iodide (623 µL, 10.0 mmol) was added followed by an aqueous 10% NaOH solution (10 mL) before stirring at reflux for 3 h. The reaction mixture was extracted with CH_2Cl_2 (25 mL x 3) and the combined organic layers washed with brine (25 mL), dried over Mg_2SO_4, filtered and concentrated. The crude product was purified by column chromatography (5% MeOH in CH_2Cl_2) to yield the desired product (588 mg, 2.07 mmol, 83%) as a white crystalline solid: δ_H (400 MHz, $CDCl_3$) 7.20 (d, *J* = 8.6 Hz, 1H, Ar *H*), 6.72 (dd, *J* = 8.6, 2.6 Hz, 1H, Ar *H*), 6.65 (d, *J* = 2.7 Hz, 1H, Ar *H*), 3.78 (s, 3H, C*H*$_3$), 2.93 – 2.87 (m, 2H, C*H*$_2$), 2.54 – 2.46 (m, 1H, C*H*$_2$), 2.43 – 2.37 (m, 1H, C*H*$_2$), 2.30 – 2.22 (m, 1H, C*H*), 2.19 - 1.92 (m, 4H, 4 x C*H*$_2$) 1.75 – 1.38 (m, 6H, 4 x C*H*$_2$, 2 x C*H*), 0.90 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 221.1 (*C*=O), 157.7 (Ar *C*), 137.9 (Ar *C*), 132.1 (Ar *C*), 126.5 (Ar *C*H), 114.0 (Ar *C*H), 111.7 (Ar *C*H), 55.3 (*C*H$_3$), 50.5 (*C*H), 48.1 (q*C*), 44.1 (*C*H), 38.5 (*C*H), 36.0 (*C*H$_2$), 31.7 (*C*H$_2$), 29.8 (*C*H$_2$), 26.7 (*C*H$_2$), 26.0 (*C*H$_2$), 21.7 (*C*H$_2$), 14.0 (*C*H$_3$); HRMS (ESI^+) $C_{19}H_{24}O_2Na$ $[M+Na]^+$: Expected 307.1669, Found 307.1654.

The data are in accordance with the literature.[15]

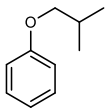
N-(1-(2,6-Dimethylphenoxy)propan-2-yl)acetamide,



To a mixture of 1-(2,6-dimethylphenoxy)propan-2-amine (647 mg, 3.00 mmol) and triethylamine (836 µL, 6.00 mmol) in CH_2Cl_2 (50 mL) was added acetyl chloride (285 µL, 4.00 mmol). The mixture was stirred ar RT for 16 h. The crude product was concentrated and purified by column chromatography (*gradient* from hexane to 1:1 EtOAc:Hexane) to yield the desired product (569 mg, 2.57 mmol, 86%) as a white powder: δ_H (400 MHz, $CDCl_3$) 7.01 (d, *J* = 7.4 Hz, 2H, Ar *H*), 6.93 (dd, *J* = 8.5, 6.3 Hz, 1H, Ar *H*), 5.92 (brd, *J* = 6.2 Hz, 1H, N*H*), 4.40 – 4.30 (m, 1H, C*H*), 3.80 (dd, *J* = 9.1, 3.9 Hz, 1H, CH_2), 3.71 (dd, *J* = 9.1, 3.1 Hz, 1H, CH_2), 2.29 (s, 6H, 2 x CH_3), 2.03 (s, 3H, CH_3), 1.41 (d, *J* = 6.9 Hz, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 169.6 (*C*=O), 155.0 (Ar *C*), 130.9 (Ar *C*), 129.2 (Ar *C*H), 124.3 (Ar *C*H), 74.0 (*C*H_2), 45.6 (*C*H), 23.6 (*C*H_3), 17.9 (*C*H_3), 16.3 (2 x *C*H_3); HRMS (ESI$^+$) $C_{13}H_{19}O_2NNa$ $[M+Na]^+$: Expected 244.1308, Found 244.1301.

The data are in accordance with the literature.[1]

Isobutoxybenzene,

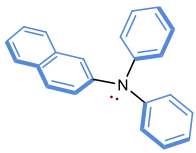


To a suspension of NaH (800 mg, 20.0 mmol) in DMF (30 mL) was added 2-methyl-propan-1-ol (1.18 mL, 20.0 mmol) and the mixture was stirred for 10 minutes. Fluorobenzene (0.94 mL, 10.0 mmol) was added slowly to the reaction mixture and the solution was stirred at 100 °C overnight. The reaction was diluted with water (25 mL) and extracted with EtOAc (3 x 25 mL), the combined organic layers were washed with water (25 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography over silica gel support [10% Et_2O in hexane] to yield the product as a colourless oil (907 mg, 6.04 mmol, 60%); δ_H (400 MHz, $CDCl_3$) 7.33 – 7.21 (m, 2H, Ar H), 6.97 – 6.86 (m, 3H, Ar H), 3.72 (d, J = 6.5 Hz, 2H, CH_2), 2.09 (sept, J = 6.7 Hz, 1H, CH), 1.03 (d, J = 6.7 Hz, 6H, CH_3); δ_C (101 MHz, $CDCl_3$) 159.4 (Ar C), 129.5 (Ar CH), 120.6 (Ar CH), 114.7 (Ar CH), 74.5 (CH_2), 28.4 (CH), 19.4 (CH_3); HRMS (ESI+) $C_{10}H_{14}O$ [M+H]+: Expected 150.1039, Found 150.1040.

The data are in accordance with the literature.[35]

Synthesis of Triarylamine Donors.

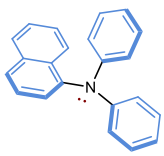
N,N-Diphenylnaphthalen-2-amine, ***D***



Prepared as described in General Procedure C: N-dipheny amine (169 mg, 1.00 mmol), 2-bromonaphthalene (248 mg, 1.20 mmol), after purification by column chromatography (Hexane) gave the desired product (249 mg, 0.84 mmol, 84%) as an off-white solid; δ_H (400 MHz, $CDCl_3$) 7.75 (d, *J* = 7.9 Hz, 1H, Ar *H*), 7.72 (d, *J* = 8.9 Hz, 1H, Ar *H*), 7.59 (d, *J* = 7.9 Hz, 1H, Ar *H*), 7.44 – 7.32 (m, 3H, Ar *H*), 7.30 – 7.24 (m, 5H, Ar *H*), 7.14 (d, *J* = 7.7 Hz, 4H, Ar *H*), 7.04 (t, *J* = 7.3 Hz, 2H, Ar *H)*; δ_C (101 MHz, $CDCl_3$) 147.9 (Ar *C*), 145.6 (Ar *C*), 134.6 (Ar *C*), 130.1 (Ar *C*), 129.4 (Ar *C*H), 129.0 (Ar *C*H), 127.7 (Ar *C*H), 127.1 (Ar *C*H), 126.4 (Ar *C*H), 124.6 (Ar *C*H), 124.55 (Ar *C*H), 124.5 (Ar *C*H), 123.0 (Ar *C*H), 120.3 (Ar *C*H); HRMS (ESI^+) $C_{22}H_{18}N$ $[M+H]^+$: Expected 296.1434, Found 296.1431.

The data are in accordance with the literature.[16]

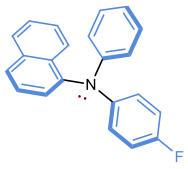
N,N-Diphenylnaphthalen-1-amine, ***E***



Prepared as described in General Procedure C: *N*-dipheny amine (338 mg, 2.00 mmol), 1-bromonaphthalene (0.34 mL, 2.40 mmol), after purification by column chromatography (Hexane) gave the desired product (581 mg, 1.97 mmol, 98%) as an off-white solid; δ_H (500 MHz, $CDCl_3$) 7.96 (d, *J* = 8.5 Hz, 1H, Ar *H*), 7.89 (d, *J* = 8.2 Hz, 1H, Ar *H*), 7.78 (d, *J* = 8.2 Hz, 1H, Ar *H*), 7.51 – 7.43 (m, 2H, Ar *H*), 7.39 – 7.32 (m, 2H, Ar *H*), 7.20 (t, *J* = 7.6 Hz, 4H, Ar *H*), 7.04 (dt, *J* = 8.6, 1.1 Hz, 4H, Ar *H*), 6.94 (td, *J* = 7.4, 1.2 Hz, 2H, Ar *H*); δ_C (126 MHz, $CDCl_3$) 148.6 (Ar *C*), 143.7 (Ar *C*), 135.4 (Ar *C*), 131.4 (Ar *C*), 129.2 (Ar *C*H), 128.5 (Ar *C*H), 127.4 (Ar *C*H), 126.6 (Ar *C*H), 126.51 (Ar *C*H), 126.48 (Ar *C*H), 126.3 (Ar *C*H), 124.4 (Ar *C*H), 122.0 (Ar *C*H), 121.8 (Ar *C*H).

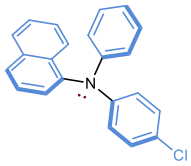
The data are in accordance with the literature.[16]

N-(4-Fluorophenyl)-N-phenylnaphthalen-1-amine, ***F***



Prepared as described in General Procedure C: N-phenylnaphthalen-1-amine (219 mg, 1.00 mmol), 1-bromo-4-fluorobenzene (121 µL, 1.20 mmol), after purification by column chromatography (Hexane) gave the desired product (239 mg, 0.76 mmol, 76%) as an off-white solid; m.p. (recrystallized from CH_2Cl_2) 133 – 135 °C ; δ_H (500 MHz, $CDCl_3$) 7.92 (d, *J* = 8.5 Hz, 1H, Ar *H*), 7.88 (d, *J* = 8.2 Hz, 1H, Ar *H*), 7.76 (d, *J* = 8.2 Hz, 1H, Ar *H*), 7.49 – 7.44 (m, 2H, Ar *H*), 7.39 – 7.34 (m, 1H, Ar *H*), 7.29 (dd, *J* = 7.3, 1.2 Hz, 1H, Ar *H*), 7.22 – 7.14 (m, 2H, Ar *H*), 7.06 – 7.00 (m, 2H, Ar *H*), 6.97 – 6.93 (m, 2H, Ar *H*), 6.93 – 6.87 (m, 3H, Ar *H*); δ_C (126 MHz, $CDCl_3$) 158.5 (d, $^1J_{C\text{-}F}$ = 241.6 Hz, Ar *C*), 148.9 (Ar *C*), 144.7 (d, $^4J_{C\text{-}F}$ = 2.6 Hz, Ar *C*), 143.7 (Ar *C*) 135.4 (Ar *C*), 131.2 (Ar *C*), 129.3 (Ar *C*H), 128.6 (Ar *C*H), 127.1 (Ar *C*H), 126.6 (Ar *C*H), 126.5 (Ar *C*H), 126.5 (Ar *C*H), 126.3 (Ar *C*H), 124.3 (Ar *C*H), 124.2 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, Ar *C*H), 121.5 (Ar *C*H), 121.2 (Ar *C*H), 116.0 (d, $^2J_{C\text{-}F}$ = 22.5 Hz, Ar *C*H); δ_F (376 MHz, $CDCl_3$) -121.11 - -121.21 (m); HRMS (ESI$^+$) $C_{22}H_{17}NF$ $[M+H]^+$: Expected 314.1340, Found 314.1330; ν_{max} (thin film/cm^{-1}) 693, 749, 774, 1215, 1273, 1307, 1390, 1491, 1500, 1588, 3054.

N-(4-Chlorophenyl)-N-phenylnaphthalen-1-amine, ***G***

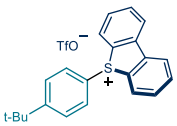


Prepared as described in General Procedure C: N-phenylnaphthalen-1-amine (439 mg, 2.00 mmol), 1-bromo-4-chlorobenzene (498 mg, 2.60 mmol), after purification by column chromatography (Hexane) gave the desired product (556 mg, 1.69 mmol, 84%) as a white solid; m.p. (recrystallized from CH_2Cl_2) 118 – 120 °C; δ_H (400 MHz, $CDCl_3$) 7.88 (d, *J* = 8.0 Hz, 2H, Ar *H*), 7.77 (d, *J* = 8.2 Hz, 1H, Ar *H*), 7.46 (t, *J* = 7.9 Hz, 2H, Ar *H*), 7.38 – 7.34 (m, 1H, Ar *H*), 7.29 (d, *J* = 7.3 Hz, 1H, Ar *H*), 7.20 (t, *J* = 8.7 Hz, 2H, Ar *H*), 7.12 (dd, *J* = 8.7, 1.8 Hz, 2H, Ar *H*), 7.02 (d, *J* = 8.0 Hz, 2H, Ar *H*), 6.98 – 6.90 (m, 3H, Ar *H*); δ_C (101 MHz, $CDCl_3$) 148.2 (Ar *C*), 147.3 (Ar *C*), 143.3 (Ar *C*), 135.5 (Ar *C*), 131.2 (Ar *C*), 129.4 (Ar *C*H), 129.2 (Ar *C*H), 128.6 (Ar *C*H), 127.3 (Ar *C*H), 126.9 (Ar *C*H), 126.7 (Ar *C*H), 126.5 (Ar *C*H), 126.4 (Ar *C*H), 124.2 (Ar *C*H), 122.7 (Ar *C*H), 122.4 (Ar *C*H), 122.3 (Ar *C*H); HRMS (ESI$^+$)

$C_{22}H_{17}NCl$ $[M+H]^+$: Expected 330.1044, Found 330.1036; ν_{max} (thin film/cm^{-1}) 695, 754, 774, 1250, 1273, 1288, 1392, 1487, 1587, 3058.

Synthesis of Sulfonium salts.

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

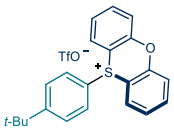


Prepared as described in General Procedure D, *tert*-butyl benzene (771 µL, 5.00 mmol) and dibenzo[b,d]thiophene 5-oxide (1.10 g, 5.50 mmol) were used as substrates and the reaction yielded the desired product (2.07 g, 4.44 mmol, 89%) as an off white solid: δ_H (400 MHz, $CDCl_3$) 8.19 (d, *J* = 7.8 Hz, 2H, Ar *H*), 8.13 (d, *J* = 8.0 Hz, 2H, Ar *H*), 7.84 (t, *J* = 7.6 Hz, 2H, Ar *H*), 7.62 (t, *J* = 7.8 Hz, 2H, Ar *H*), 7.58 (d, *J* = 8.8 Hz, 2H, Ar *H*), 7.51 (d, *J* = 8.8 Hz, 2H, Ar *H*), 1.26 (s, 9H, CH_3); δ_C (101 MHz, $CDCl_3$) 159.5 (Ar *C*), 139.0 (Ar *C*), 134.4 (Ar *C*H), 132.4 (Ar *C*), 131.8 (Ar *C*H), 130.7 (Ar *C*H), 129.0 (Ar *C*H), 128.9 (Ar *C*H), 124.1 (Ar *C*H), 122.4 (Ar *C*), 120.8 (q, $^1J_{C-F}$ = 320.6 Hz, CF_3), 35.6 (q*C*), 30.9 (CH_3); δ_F (376 MHz, $CDCl_3$) -79.30 (s); HRMS (ESI^+) $C_{22}H_{21}S$ $[M]^+$: Expected 317.1358, Found 317.1354.

The data are in accordance with the literature.[1]

2 was further characterised by X-ray crystallographic analysis. CCDC : 2120242.

10-(4-(tert-Butyl)phenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate, ***75***

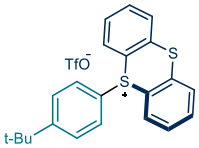


Prepared as described in General Procedure D: *tert*-butyl benzene (0.69 mL, 4.45 mmol), phenoxathiine S-oxide (1.06 g, 4.90 mmol), Tf_2O (0.90 mL, 5.34 mmol), after precipitation from cold Et_2O yielded the desired product (2.10 g, 4.35 mmol, 98%) as an off-white solid; m.p. (recrystallized from CH_2Cl_2/Et_2O) 164 – 166 °C; δ_H (400 MHz, CD_3CN) 8.02 (dd, *J* = 8.1, 1.5 Hz, 2H, Ar *H*), 7.89 (ddd, *J* = 8.7, 7.4, 1.6 Hz, 2H, Ar *H*), 7.68-7.61 (m, 4H, Ar *H*), 7.58-7.53 (m, 4H, Ar *H*), 1.24 (s, 9H, CH_3); δ_C (101 MHz, CD_3CN) 159.9 (Ar *C*), 152.3 (Ar *C*), 137.9 (Ar *C*H), 132.3 (Ar *C*H), 129.8 (Ar *C*H), 129.7 (Ar *C*H), 129.0 (Ar *C*), 128.3 (Ar *C*H), 121.5 (Ar *C*H), 106.7 (Ar *C*), 36.0 (q*C*), 30.9 (CH_3); δ_F (376 MHz, CD_3CN) -79.28; HRMS (ESI^+)

$C_{22}H_{21}OS^+$ (M^+) Expected 333.1308, Found 333.1296; ν_{max} (thin film/cm^{-1}) 637, 757, 887, 1031, 1256, 1327, 1465, 1583, 2962.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

5-(4-(tert-Butyl)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate, ***76***

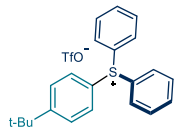


Prepared as described in General Procedure D, *tert*-butyl benzene (154 µL, 1.00 mmol) and thianthrene 5-oxide (256 mg, 1.10 mmol) were used as substrates and the reaction yielded the desired product (312 mg, 0.62 mmol, 62%) as an off white solid: δ_H (400 MHz, $CDCl_3$) 8.61 (dd, *J* = 7.6, 1.7 Hz, 2H, Ar *H*), 7.86 – 7.71 (m, 6H, Ar *H*), 7.43 (d, *J* = 8.8 Hz, 2H, Ar *H*), 7.14 (d, *J* = 8.8 Hz, 2H, Ar *H*), 1.24 (s, 9H, CH_3); δ_C (101 MHz, $CDCl_3$) 157.4 (Ar *C*), 136.6 (Ar *C*), 135.5 (Ar *C*H), 134.8 (Ar *C*H), 130.3 (Ar *C*H), 130.2 (Ar *C*H), 128.1 (Ar *C*), 128.0 (Ar *C*H), 120.5 (Ar *C*), 119.2 (Ar *C*), 35.3 (q*C*), 31.0 (CH_3); δ_F (376 MHz, $CDCl_3$) -78.15 (s); HRMS (ESI^+) $C_{22}H_{21}S_2$ $[M]^+$: Expected 349.1079, Found 349.1066.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

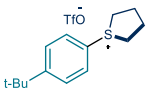
The data are in accordance with the literature.[17]

(4-(tert-Butyl)phenyl)diphenylsulfonium trifluoromethanesulfonate, ***77***



Prepared as described in General Procedure D, *tert*-butyl benzene (352 µL, 2.27 mmol) and diphenylsulfoxide (505.6 mg, 2.5 mmol) were used as the substrates and the reaction yielded the desired product (1.07 g, 2.27 mmol, 100%) as a pale yellow oil: δ_H (400 MHz, $CDCl_3$) 8.09 – 7.21 (m, 14H, Ar *H*), 1.30 (s, 9H, CH_3); δ_C (101 MHz, $CDCl_3$) 159.1 (Ar *C*), 134.6 (Ar *C*), 131.6 (Ar *C*H), 131.1 (Ar *C*H), 130.9 (Ar *C*H), 128.9 (Ar *C*H), 124.6 (Ar *C*H), 120.9 (q, $^1J_{C\text{-}F}$ = 320.9 Hz, CF_3), 120.4 (Ar *C*), 35.5 (q*C*), 30.8 (CH_3); δ_F (376 MHz, $CDCl_3$) -78.10 (s); HRMS (ESI^+) $C_{22}H_{23}S$ $[M]^+$: Expected 319.1515, Found 319.1509; ν_{max} (thin film/cm^{-1}) 636, 732, 1029, 1149, 1223, 1257, 1447, 2872, 2966, 3062.

1-(4-(tert-Butyl)phenyl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate, ***78***

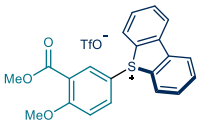


Prepared as described in General Procedure D, *tert*-butyl benzene (352 µL, 2.27 mmol) and tetrahydrothiophene 1-oxide (225 µL, 2.50 mmol) were used as the substrates and the reaction yielded the desired product (797 mg, 2.15 mmol, 95%) as an off white solid: δ_H (400 MHz, $CDCl_3$) 7.70 (d, *J* = 8.5 Hz, 2H, Ar *H*), 7.63 (d, *J* = 8.5 Hz, 2H, Ar *H*), 4.25 – 4.04 (m, 2H, C*H*$_2$), 3.72 – 3.55 (m, 2H, C*H*$_2$), 2.66 – 2.45 (m, 4H, C*H*$_2$), 1.32 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 158.6 (Ar *C*), 129.7 (Ar *C*H), 128.6 (Ar *C*H), 122.4 (Ar *C*), 48.8 (*C*H$_2$), 35.5 (q*C*), 31.0 (*C*H$_3$), 29.3 (*C*H$_2$); δ_F (376 MHz, $CDCl_3$) -78.31 (s); HRMS (ESI$^+$) $C_{14}H_{21}S$ $[M]^+$: Expected 221.1358, Found 221.1352.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

The data are in accordance with the literature.[1]

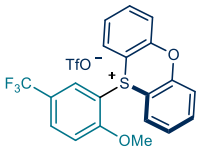
5-(4-Methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate, ***SS1***



Prepared as described in General Procedure D, methyl 2-methoxybenzoate (721 µL, 5.0 mmol) and dibenzo[b,d]thiophene 5-oxide (1.10 g, 5.50 mmol) were used as the substrates and the reaction yielded the desired product (2.14 g, 4.29 mmol, 86%) as an off white solid: δ_H (400 MHz, $CDCl_3$) 8.24 - 14 (m, 3H, Ar *H*), 8.12 (d, *J* = 7.8 Hz, 2H, Ar *H*), 7.85 (td, *J* = 7.7, 1.1 Hz, 2H, Ar *H*), 7.72 – 7.56 (m, 3H, Ar *H*), 7.20 (d, *J* = 9.1 Hz, 1H, Ar *H*), 3.93 (s, 3H, C*H*$_3$), 3.79 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 164.3 (*C*=O), 164.0 (Ar *C*), 138.8 (Ar *C*), 138.0 (Ar *C*H), 134.6 (Ar *C*H), 133.3 (Ar *C*H), 132.1 (Ar *C*), 132.0 (Ar *C*H), 128.7 (Ar *C*H), 124.3 (Ar *C*H), 123.6 (Ar *C*), 120.9 (q, $^1J_{C\text{-}F}$ = 320.4 Hz, *C*F$_3$), 115.2 (Ar *C*H), 115.1 (Ar *C*), 57.0 (*C*H$_3$), 52.8 (*C*H$_3$); δ_F (376 MHz, CD_3CN) -78.20 (s); HRMS (ESI$^+$) $C_{21}H_{17}O_3S$ $[M]^+$: Expected 349.0893, Found 349.0886.

The data are in accordance with the literature.[1]

10-(2-Methoxy-5-(trifluoromethyl)phenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate, ***40***

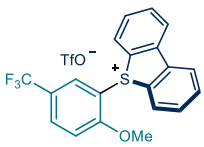


Prepared as described in General Procedure D: 4-trifluoromethyl anisole (0.64 mL, 4.50 mmol), phenoxathiine S-oxide (1.07 g, 4.95 mmol), Tf_2O (0.91 mL, 5.40 mmol), after precipitation from cold Et_2O gave (2.17 g, 4.14 mmol, 92%) as an off-white solid; m.p. (recrystallized from CH_2Cl_2/Et_2O) 214 – 216 °C; δ_H (400 MHz, CD_3CN) 8.00-7.96 (m, 3H, Ar *H*), 7.89 (ddd, *J* = 8.8, 7.4, 1.6 Hz, 2H, Ar *H*), 7.64 (dd, *J* = 8.5, 1.3 Hz, 2H, Ar *H*), 7.56-7.52 (m, 3H, Ar *H*), 7.33 (d, *J* = 8.9 Hz, 1H, Ar *H*), 3.95 (s, 3H, OCH_3); δ_C (101 MHz, CD_3CN) 161.8 (Ar *C*), 153.5 (Ar *C*), 138.0 (Ar *C*H), 135.4 (q, *J* = 3.3 Hz, Ar *C*H), 132.6 (Ar *C*H), 128.8 (q, *J* = 3.9 Hz, Ar *C*H), 127.9 (Ar *C*H), 124.4 (q, *J* = 34.2 Hz, Ar *C*(CF_3)), 124.2 (q, *J* = 271.0 Hz, *C*F_3), 120.9 (Ar *C*H), 118.5 (Ar *C*), 115.9 (Ar *C*H), 103.6 (Ar *C*), 58.4 (OCH_3); δ_F (376 MHz, CD_3CN) -62.60, -79.32; HRMS (ESI^+) $C_{20}H_{14}O_2F_3S^+$ (M^+) Expected 375.0661, Found 375.0650 ; ν_{max} (thin film/cm^{-1}) 637, 758, 1005, 1032, 1224, 1272, 1327, 1466, 1507, 1584, 1612, 2961, 3067, 3093.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

40 was further characterised by X-ray crystallographic analysis. CCDC : 2122516.

5-(2-Methoxy-5-(trifluoromethyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate, ***41***

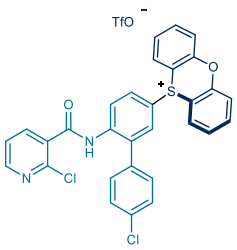


Prepared as described in General Procedure D: 4-trifluoromethyl anisole (0.33 mL, 2.30 mmol), dibenzothiophene S-oxide (0.51 g, 2.53 mmol), Tf_2O (0.46 mL, 2.76 mmol), after precipitation from cold Et_2O gave (1.00 g, 1.97 mmol, 85%) as a white solid; During m.p. (recrystallized from CH_2Cl_2/Et_2O) measurement, decomposition was observed at 260 – 262 °C; δ_H (400 MHz, CD_3CN) 8.34 (dd, *J* = 7.8, 1.2 Hz, 2H, Ar *H*), 8.11 (dd, *J* = 8.1, 1.0 Hz, 2H, Ar *H*), 8.03 (dd, *J* = 8.9, 2.3 Hz, 1H, Ar *H*), 7.96 (td, *J* = 7.7, 1.1 Hz, 2H, Ar *H*), 7.74 (td, *J* = 7.8,

1.2 Hz, 2H, Ar *H*), 7.55 (d, *J* = 2.4 Hz, 1H, Ar *H*), 7.40 (d, *J* = 8.9 Hz, 1H, Ar *H*), 3.90 (s, 3H, OC*H*$_3$); δ_C (101 MHz, CD_3CN) 162.8 (Ar *C*), 141.1 (Ar *C*), 135.5 (Ar *C*H), 135.3 (q, $^3J_{C-F}$ = 3.5 Hz, Ar *C*H), 132.5 (Ar *C*H), 129.8 (Ar *C*), 129.5 (q, $^3J_{C-F}$ = 4.1 Hz, Ar *C*H), 129.0 (Ar *C*H), 125.5 (Ar *C*H), 124.8 (q, $^2J_{C-F}$ = 34.2 Hz, Ar *C*), 121.7 (q, $^1J_{C-F}$ = 225.7 Hz, Ar *C*), 116.0 (Ar *C*H), 115.2 (Ar *C*), 58.6 (*C*H$_3$); δ_F (376 MHz, CD_3CN) -62.58, -79.32; HRMS (ESI$^+$) $C_{20}H_{14}F_3OS^+$ (M^+) Expected 359.0712, Found 359.0700; ν_{max} (thin film/cm^{-1}) 638, 740, 922, 1029, 1046, 1223, 1290, 1432, 1507, 1574, 1609, 3094.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

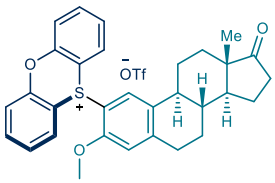
10-(4'-Chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate, ***SS2***



Prepared as described in General Procedure E: 2-chloro-N-(4'-chlorobiphenyl-2-yl)nicotinamide (343 mg, 1.00 mmol), phenoxathiine S-oxide (238 mg, 1.10 mmol), Tf_2O (0.20 mL, 1.20 mmol), the crude salt was purified by column chromatography [*gradient* from CH_2Cl_2 to 2% MeOH in CH_2Cl_2] yielding the desired product (366 mg, 0.53 mmol, 53%) as an off-white solid; m.p. (recrystallized from CH_2Cl_2/Et_2O) 156 – 158 °C; δ_H (400 MHz, CD_3CN) 8.50 (brs, 1H, N*H*), 8.42 – 8.38 (m, 2H, Ar *H*), 8.01 (dd, *J* = 8.1, 1.5 Hz, 2H, Ar *H*), 7.90 (ddd, *J* = 8.7, 7.4, 1.6 Hz, 2H, Ar *H*), 7.82 (dd, *J* = 7.6, 1.9 Hz, 1H, Ar *H*), 7.68 – 7.65 (m, 3H, Ar *H*), 7.61 (dd, *J* = 8.9, 2.6 Hz, 1H, Ar *H*), 7.57 (ddd, *J* = 8.2, 7.5, 1.2 Hz, 2H, Ar *H*), 7.49 (d, *J* = 8.6 Hz, 2H, Ar *H*), 7.39 – 7.33 (m, 3H, Ar *H*); δ_C (101 MHz, CD_3CN) 165.1 (*C*=O), 152.2 (Ar *C*), 152.0 (Ar *C*H), 147.6 (Ar *C*), 141.4 (Ar *C*), 139.1 (Ar *C*H), 137.9 (Ar *C*H), 136.4 (Ar *C*), 135.6 (Ar *C*), 135.3 (Ar *C*), 132.7 (Ar *C*), 132.4 (Ar *C*H), 132.3 (Ar *C*H), 132.0 (Ar *C*H), 130.3 (Ar *C*H), 130.2 (Ar *C*H), 128.3 (Ar *C*H), 127.4 (Ar *C*), 126.4 (Ar *C*H), 123.8 (Ar *C*H), 121.5 (Ar *C*H), 106.3 (Ar *C*); δ_F (376 MHz, CD_3CN) -79.31; HRMS (ESI$^+$) $C_{30}H_{19}O_2N_2Cl_2S$ $[M]^+$: Expected 541.0539, Found 541.0535; ν_{max} (thin film/cm^{-1}) 636, 734, 757, 1029, 1151, 1257, 1270, 1400, 1464, 1509, 1572, 1676, 3018, 3062, 3084, 3380.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

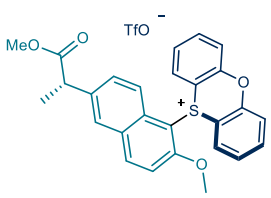
10-((8R,9S,13S,14S)-3-methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate, ***SS3***



Prepared as described in General Procedure E: Estrone methyl ether (284.4 mg, 1.00 mmol), phenoxathiine S-oxide (238 mg, 1.10 mmol), Tf_2O (0.20 mL, 1.20 mmol), after purification by column chromatography [CH_2Cl_2:MeOH = 96:4] yielded the desired product (587 mg, 0.93 mmol, 93%) as a yellowish solid; m.p. (recrystallized from CH_2Cl_2/Et_2O) 123 – 125 °C; δ_H (500 MHz, CD_3CN) 7.90 (dd, *J* = 8.1, 1.6 Hz, 1H, Ar *H*), 7.88 (dd, *J* = 7.9, 1.6 Hz, 1H, Ar *H*), 7.86 – 7.82 (m, 2H, Ar *H*), 7.60 (dd, *J* = 5.0, 1.2 Hz, 1H, Ar *H*), 7.59 (dd, *J* = 5.0, 1.2 Hz, 1H, Ar *H*), 7.52-7.47 (m, 2H, Ar *H*), 7.21 (s, 1H, Ar *H*), 6.91 (s, 1H, Ar *H*), 3.79 (s, 3H, OCH_3), 2.92-2.88 (m, 2H, Bn *C*H, Bn CH_2), 2.42 (dd, *J* = 18.8, 8.5 Hz, 1H, Bn CH_2), 2.09-1.96 (m, 4H, Alk *C*H & CH_2), 1.83-1.80 (m, 1H, Alk *C*H), 1.63 – 1.44 (m, 4H, Alk *C*H & CH_2), 1.43 – 1.33 (m, 3H, Alk *C*H & CH_2), 0.84 (s, 3H, CH_3); δ_C (126 MHz, CD_3CN) 220.7 (*C*=O), 156.8 (Ar *C*), 153.2 (Ar *C*), 153.0 (Ar *C*), 149.5 (Ar *C*), 137.5 (Ar *C*H), 137.4 (Ar *C*H), 135.9 (Ar *C*), 132.2 (Ar *C*H), 132.1 (Ar *C*H), 128.7 (Ar *C*H), 127.7 (Ar *C*H), 127.7 (Ar *C*H), 120.7 (Ar *C*H), 120.6 (Ar *C*H), 115.1 (Ar *C*H), 114.3 (Ar *C*), 105.2 (Ar *C*), 104.8 (Ar *C*), 57.4 (OCH_3), 50.8 (*C*H), 48.5 (q*C*), 44.2 (*C*H), 38.2 (*C*H), 36.3 (CH_2), 32.2 (CH_2), 30.5 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 22.1 (CH_2), 14.1 (CH_3); δ_F (471 MHz, CD_3CN) -79.29; HRMS (ESI$^+$) $C_{31}H_{31}O_3S^+$ [M]$^+$: Expected 483.1988, Found 483.1976 ; ν_{max} (thin film/cm^{-1}) 636, 761, 1029, 1145, 1257, 1467, 1730, 2859, 2929.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

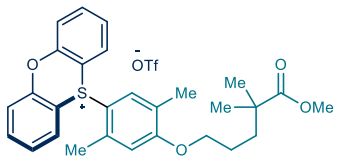
(S)-10-(2-Methoxy-6-(1-methoxy-1-oxopropan-2-yl)naphthalen-1-yl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate, ***SS4***



Prepared as described in General Procedure E: methyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (244 mg, 1.00 mmol), phenoxathiine S-oxide (238 mg, 1.10 mmol), Tf_2O (0.20 mL, 1.20 mmol), after purification by column chromatography [*gradient* from CH_2Cl_2 to 2% MeOH in CH_2Cl_2] yielded the desired product (400 mg, 0.67 mmol, 67%) as an off-white solid; m.p. (recrystallized from CH_2Cl_2/Et_2O) 110 – 112 °C; δ_H (400 MHz, CD_3CN) 8.85 (d, *J* = 8.8 Hz, 1H, Ar *H*), 8.32 (d, *J* = 9.2 Hz, 1H, Ar *H*), 7.94 (s, 1H, Ar *H*), 7.90 (dd, *J* = 8.8, 1.6 Hz, 1H, Ar *H*), 7.78 (t, *J* = 7.3 Hz, 2H, Ar *H*), 7.62 (d, *J* = 8.0 Hz, 2H, Ar *H*), 7.56 (d, *J* = 8.4 Hz, 2H, Ar *H*), 7.38 (d, *J* = 9.3 Hz, 1H, Ar *H*), 7.34 (t, *J* = 7.8 Hz, 2H, Ar *H*), 4.03 (q, *J* = 7.1 Hz, 1H, C*H*), 3.73 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 1.58 (d, *J* = 7.1 Hz, 3H, CH_3); δ_C (101 MHz, CD_3CN) 175.3 (*C*=O), 161.9 (Ar *C*), 153.0 (Ar *C*), 140.4 (Ar *C*H), 139.5 (Ar *C*), 137.0 (Ar *C*H), 133.4 (Ar *C*), 131.9 (Ar *C*H), 131.2 (Ar *C*H), 129.9 (Ar *C*), 128.5 (Ar *C*H), 127.3 (Ar *C*H), 122.7 (Ar *C*H), 120.0 (Ar *C*H), 115.5 (Ar *C*H), 109.0 (Ar *C*), 103.3 (Ar *C*), 57.8 (OCH_3), 52.7 (OCH_3), 45.6 (*C*H), 18.8 (CH_3); δ_F (376 MHz, CD_3CN) -79.34; HRMS (ESI$^+$) $C_{27}H_{23}O_4S$ $[M+H]^+$: Expected 443.1312, Found 443.1297; ν_{max} (thin film/cm^{-1}) 636, 755, 888, 1028, 1143, 1256, 1466, 1593, 1730, 2850, 2925, 3079.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

10-(4-((5-Methoxy-4,4-dimethyl-5-oxopentyl)oxy)-2,5-dimethylphenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate, ***SS5***

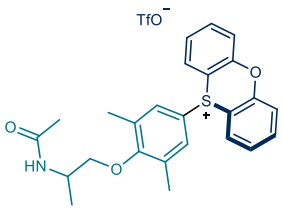


Prepared as described in General Procedure E: methyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (264 mg, 1.00 mmol), phenoxathiine S-oxide (238 mg, 1.10 mmol), Tf_2O (0.20 mL, 1.20 mmol), after purification by column chromatography [CH_2Cl_2:MeOH = 98:2] yielded the desired product (487 mg, 0.79 mmol, 79%) as an yellowish solid; m.p. (recrystallized from CH_2Cl_2/Et_2O) 115 – 117 °C; δ_H (400 MHz, CD_3CN) 7.84 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 2H, Ar *H*), 7.79 (dd, *J* = 8.2, 1.5 Hz, 2H, Ar *H*),

7.63 (dd, *J* = 8.5, 1.2 Hz, 2H, Ar *H*), 7.49 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 2H, Ar *H*), 6.97 (s, 1H, Ar *H*), 6.94 (s, 1H, Ar *H*), 4.01 (t, *J* = 5.8 Hz, 2H, OCH_2), 3.55 (s, 3H, OCH_3), 2.84 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.72-1.60 (m, 4H, CH_2), 1.14 (s, 6H, gem di-CH_3); δ_C (101 MHz, CD_3CN) 178.7 (*C*=O), 163.1 (Ar *C*), 152.0 (Ar *C*), 142.5 (Ar *C*), 137.3 (Ar C*H*), 132.2 (Ar *C*H), 131.7 (Ar C*H*), 130.7 (Ar *C*), 128.1 (Ar *C*H), 121.4 (Ar *C*H), 119.8 (Ar *C*), 115.3 (Ar *C*H), 107.2 (Ar *C*), 69.9 (OCH_2), 52.2, (OCH_3), 42.7 (q*C*), 37.4 (Alk *C*H_2), 25.4 (Alk *C*H_2 & C(*C*H_3)$_2$), 20.2 (*C*H_3), 15.9 (*C*H_3); δ_F (376 MHz, CD_3CN) -79.31; HRMS (ESI$^+$) $C_{28}H_{31}O_4S$ $[M]^+$: Expected 463.1938, Found 463.1925 ; ν_{max} (thin film/cm^{-1}) 635, 761, 884, 1028, 1142, 1249, 1464, 1724, 2873, 2952, 3064.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

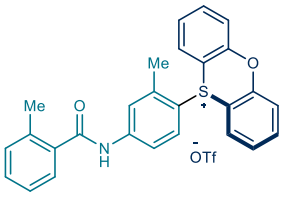
10-(4-(2-Acetamidopropoxy)-3,5-dimethylphenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate, ***SS6***



Prepared as described in General Procedure E: methyl N-(1-(2,6-dimethylphenoxy)propan-2-yl)acetamide (221 mg, 1.00 mmol), phenoxathiine S-oxide (238 mg, 1.10 mmol), Tf_2O (0.20 mL, 1.20 mmol), after purification by column chromatography [*gradient* from CH_2Cl_2 to 2% MeOH in CH_2Cl_2] yielded the desired product (297 mg, 0.52 mmol, 52%) as an off-white solid; m.p. (recrystallized from CH_2Cl_2/Et_2O) 93 – 95 °C; δ_H (400 MHz, CD_3CN) 7.94 – 7.85 (m, 4H, Ar *H*), 7.65 (d, *J* = 8.4 Hz, 2H, Ar *H*), 7.53 (t, *J* = 7.7 Hz, 2H, Ar *H*), 7.33 (s, 2H, Ar *H*), 6.53 (brd, *J* = 7.4 Hz, 1H, N*H*), 4.23 – 4.12 (m, 1H, C*H*), 3.70 (d, *J* = 4.9 Hz, 2H, CH_2), 2.21 (s, 6H, 2 x CH_3), 1.83 (s, 3H, CH_3) 1.21 (d, *J* = 6.8 Hz, 3H, CH_3); δ_C (101 MHz, CD_3CN) 170.5 (*C*=O), 161.9 (Ar *C*), 152.0 (Ar *C*), 137.7 (Ar *C*H), 136.5 (Ar *C*), 132.0 (Ar *C*H), 130.7 (Ar *C*H), 128.2 (Ar *C*H), 125.8 (Ar *C*), 121.5 (Ar *C*H), 106.6 (Ar *C*), 75.4 (*C*H_2), 46.1 (*C*H), 23.0 (*C*H_3), 17.2 (*C*H_3), 16.6 (*C*H_3); δ_F (376 MHz, CD_3CN) -79.32; HRMS (ESI$^+$) $C_{25}H_{26}O_3SN$ $[M]^+$: Expected 420.1628, Found 420.1623 ; ν_{max} (thin film/cm^{-1}) 638, 1030, 1157, 1224, 1272, 1466, 1595, 1654, 1664, 2922, 2986, 3088, 3335.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

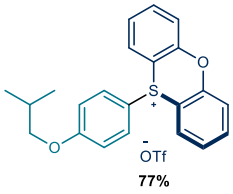
10-(2-Methyl-4-(2-methylbenzamido)phenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate, ***SS7***

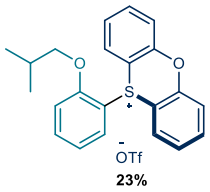


Prepared as described in General Procedure E: 2-methyl-*N*-(*m*-tolyl)benzamide (225 mg, 1.00 mmol), phenoxathiine S-oxide (238 mg, 1.10 mmol), Tf_2O (0.20 mL, 1.20 mmol), after purification by column chromatography [CH_2Cl_2:MeOH = 98:2] yielded the desired product (535 mg, 0.93 mmol, 93%) as a yellowish solid; m.p. (recrystallized from CH_2Cl_2/Et_2O) 101 – 103 °C; δ_H (400 MHz, CD_3CN) 8.94 (brs, N*H*), 7.91-7.85 (m, 5H, Ar *H*), 7.67 (dd, *J* = 8.5, 1.2 Hz, 2H, Ar *H*), 7.64 (dd, *J* = 9.0, 2.4 Hz, 1H, Ar *H*), 7.55-7.51 (m, 2H, Ar *H*), 7.46 (dd, *J* = 7.6, 1.5 Hz, 1H, Ar *H*), 7.38 (td, *J* = 7.5, 1.5 Hz, 1H, Ar *H*), 7.29-7.24 (m, 2H, Ar *H*), 7.21 (d, *J* = 9.0 Hz, 1H, Ar *H*), 2.89 (s, 3H, C*H*$_3$), 2.37 (s, 3H, C*H*$_3$); δ_C (101 MHz, CD_3CN) 169.6 (*C*=O), 152.5 (Ar *C*), 145.7 (Ar *C*), 142.8 (Ar *C*), 137.6 (Ar *C*H), 137.4 (Ar *C*), 136.5 (Ar *C*), 132.3 (Ar *C*H), 131.9 (2 x Ar *C*H), 131.5 (Ar *C*H), 128.3 (2 x Ar *C*H), 126.7 (Ar *C*H), 124.0 (Ar *C*), 123.2 (Ar *C*H), 121.5 (Ar *C*H), 121.3 (Ar *C*H), 106.8 (Ar *C*), 20.6 (*C*H$_3$), 19.9 (*C*H$_3$); δ_F (376 MHz, CD_3CN) -79.30; HRMS (ESI$^+$) $C_{27}H_{22}O_2NS$ $[M]^+$: Expected 424.1366, Found 424.1351; ν_{max} (thin film/cm^{-1}) 635, 758, 884, 1028, 1152, 1246, 1465, 1522, 1593, 1676, 3024, 3080, 3247, 3303.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

10-(4-Isobutoxyphenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (major), ***SS8***





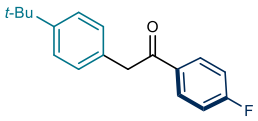
Prepared as described in General Procedure D: isobutoxybenzene (150 mg, 1.00 mmol), phenoxathiine S-oxide (238 mg, 1.10 mmol), Tf_2O (0.20 mL, 1.20 mmol), after purification by column chromatography [*gradient* from 1% MeOH to 4% MeOH in CH_2Cl_2] yielded the desired product (495 mg, 0.99 mmol, 99%) as a yellowish oil and as a regioisomeric mixture (*p*:*o* = 77:23); δ_H (400 MHz, CD_3CN) 7.93 (dd, *J* = 8.2, 1.5 Hz, 2H, Ar *H* of *p*-isomer), 7.90-7.84 (m, 3H, Ar *H* of *p*- and *o*-isomer), 7.73-7.60 (m, 5H, Ar *H* of *p*- and *o*-isomer), 7.56-7.42 (m, 3H, Ar *H* of *p*- and *o*-isomer), 7.21 (dd, *J* = 8.5, 1.0 Hz, 1H, Ar *H* of *o*-isomer), 7.14-7.05 (m, 3H, Ar *H* of *p*- and *o*-isomer), 3.96 (d, *J* = 6.9 Hz, 2H, OC*H*$_2$ of *o*-isomer), 3.79 (d, *J* = 6.5 Hz, 2H, OC*H*$_2$ of *p*-isomer), 2.26-2.18 (m, 1H, C*H* of *o*-isomer), 2.06-1.96 (m, 1H, C*H* of *p*-isomer), 1.03 (d, *J* = 6.7 Hz, 6H, C*H*$_3$ of *o*-isomer), 0.96 (d, *J* = 6.7 Hz, 6H, C*H*$_3$ of *p*-isomer); δ_C (101 MHz, CD_3CN) 165.3 (Ar *C*, *p*), 158.5 (Ar *C*, *o*), 153.4 (Ar *C*, *o*), 152.0 (Ar *C*, *p*), 138.1 (Ar *C*H, *o*), 137.6 (Ar *C*, *p*), 137.6 (Ar *C*H, *p*), 132.9 (Ar *C*H, *p*), 132.3 (Ar *C*H, *o*), 132.0 (Ar *C*H, *p*), 131.0 (Ar *C*H, *o*), 128.2 (Ar *C*H, *p*), 128.0 (Ar *C*H, *o*), 123.8 (Ar *C*, *o*), 123.5 (Ar *C*H, *o*), 121.7 (Ar *C*H, *o*), 121.4 (Ar *C*H, *p*), 121.2 (Ar *C*H, *o*), 115.7 (Ar *C*H, *o*), 107.3 (Ar *C*, *p*), 105.3 (Ar *C*, *o*), 77.5 (O*C*H$_2$, *o*), 76.0 (O*C*H$_2$, *p*), 28.8 (*C*H, *p*), 28.7 (*C*H, *o*), 19.3 (*C*H$_3$, *o*), 19.1 (*C*H$_3$, *p*); δ_F (376 MHz, CD_3CN) -79.28; HRMS (APCI) $C_{22}H_{21}O_2S^+$ $[M]^+$: Expected 349.1257, Found 349.1246; ν_{max} (thin film/cm^{-1}) 637, 764, 886, 1029, 1067, 1224, 1268, 1417, 1439, 1585, 2873, 2929, 2962, 3091, 3566.

One Ar *C*H (*p*) signal is hidden underneath the CD_3CN signal at 118.3 ppm.

The quaternary carbon corresponding to the CF_3 in the triflate counter anion was not observed, though its presence was confirmed by ^{19}F NMR.

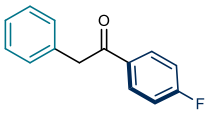
Photochemical synthesis of α-aryl carbonyls using EDA complexes of aryl sulfonium salts.

2-(4-(tert-Butyl)phenyl)-1-(4-fluorophenyl)ethan-1-one, ***5***



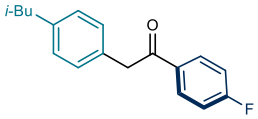
Prepared as described in General Procedure F, using *tert*-butylbenzene (31.0 μL, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a pale yellow crystalline solid (27.9 mg, 0.10 mmol, 52% yield); m.p. (recrystallized from $CHCl_3$) 68 – 70 °C; δ_H (400 MHz, $CDCl_3$) 8.05 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar *H*), 7.35 (d, *J* = 8.3 Hz, 2H, Ar *H*), 7.20 (d, *J* = 8.3 Hz, 2H, Ar *H*), 7.12 (t, *J* = 8.6 Hz, 2H, Ar *H*), 4.23 (s, 2H, CH_2), 1.31 (s, 9H, CH_3); δ_C (101 MHz, $CDCl_3$) 196.5 (*C*=O), 165.9 (d, $^1J_{C\text{-}F}$ = 255.2 Hz, Ar *C*), 149.9 (Ar *C*), 133.2 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, Ar *C*), 131.4 (d, $^3J_{C\text{-}F}$ = 9.6 Hz, Ar *C*H), 131.3 (Ar *C*), 129.1 (Ar *C*H), 125.8 (Ar *C*H), 115.9 (d, $^2J_{C\text{-}F}$ = 21.6 Hz, Ar *C*H), 45.1 (CH_2), 34.6 (CCH_3), 31.4 (CH_3); δ_F (376 MHz, $CDCl_3$) -105.09 - -105.18 (m); HRMS (ESI$^+$) $C_{18}H_{19}OFNa$ $[M+Na]^+$: Expected 293.1312, Found 293.1302; ν_{max} (thin film/cm^{-1}) 834, 1156, 1230, 1269, 1410, 1506, 1598, 1682, 2904, 2963, 3063.

1-(4-Fluorophenyl)-2-phenylethan-1-one, ***6***



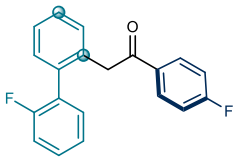
Prepared as described in General Procedure F, using benzene (17.8 μL, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [toluene], afforded the title compound as an off-white crystalline solid (20.4 mg, 0.10 mmol, 48% yield); m.p. (recrystallized from $CHCl_3$) 81 – 83 °C; δ_H (400 MHz, $CDCl_3$) 8.04 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar *H*), 7.37 – 7.30 (m, 2H, Ar *H*), 7.29 – 7.23 (m, 3H, Ar *H*), 7.12 (t, *J* = 8.6 Hz, 2H, Ar *H*), 4.26 (s, 2H, CH_2); δ_C (101 MHz, $CDCl_3$) 196.2 (*C*=O), 165.9 (d, $^1J_{C\text{-}F}$ = 255.0 Hz, Ar *C*), 134.5 (Ar *C*), 133.1 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, Ar *C*), 131.4 (d, $^3J_{C\text{-}F}$ = 9.0 Hz, Ar *C*H), 129.5 (Ar *C*H), 128.9 (Ar *C*H), 127.1 (Ar *C*H), 115.9 (d, $^2J_{C\text{-}F}$ = 21.6 Hz, Ar *C*H), 45.7 (CH_2); δ_F (376 MHz, $CDCl_3$) -105.0 - -105.1 (m); HRMS (ESI$^+$) $C_{14}H_{11}OFNa$ $[M+Na]^+$: Expected 237.0686, Found 237.0680; ν_{max} (thin film/cm^{-1}) 728, 828, 1154, 1214, 1506, 1598, 1687, 2901, 2931, 3069.

1-(4-Fluorophenyl)-2-(4-isobutylphenyl)ethan-1-one, ***7***



Prepared as described in General Procedure F, using *iso*-butylbenzene (31.5 µL, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 30% CH_2Cl_2 in hexane], afforded the title compound as a colourless crystalline solid (21.6 mg, 0.08 mmol, 40% yield); m.p. (recrystallized from $CHCl_3$) 62 – 64°C; δ_H (400 MHz, $CDCl_3$) 8.04 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar *H*), 7.18 – 7.08 (m, 6H, Ar *H*), 4.22 (s, 2H, C*H*$_2$), 2.44 (d, *J* = 7.2 Hz, 2H, C*H*$_2$), 1.90 – 1.79 (m, 1H, C*H*), 0.89 (d, *J* = 6.6 Hz, 6H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 196.4 (*C*=O), 165.8 (d, $^1J_{C\text{-}F}$ = 255.2 Hz, Ar *C*), 140.6 (Ar *C*), 133.2 (d, $^4J_{C\text{-}F}$ = 3.0 Hz, Ar *C*), 131.6 (Ar *C*), 131.4 (d, $^3J_{C\text{-}F}$ = 9.2 Hz, Ar *C*H), 129.6 (Ar *C*H), 129.2 (Ar *C*H), 115.8 (d, $^2J_{C\text{-}F}$ = 22.0 Hz, Ar *C*H), 45.3 (*C*H$_2$), 45.2 (*C*H$_2$), 30.3 (*C*H), 22.5 (*C*H$_3$); δ_F (376 MHz, $CDCl_3$) -105.14 - -105.23 (m); HRMS (ESI$^+$) $C_{18}H_{19}OFNa$ [M+Na]$^+$: Expected 293.1312, Found 293.1301; ν_{max} (thin film/cm^{-1}) 769, 833, 1158, 1238, 1332, 1506, 1599, 1686, 2844, 2870, 2906, 2955.

2-(2'-Fluoro-[1,1'-biphenyl]-2-yl)-1-(4-fluorophenyl)ethan-1-one, ***8***



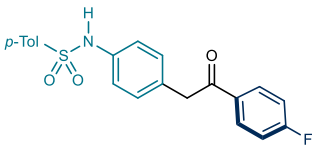
Prepared as described in General Procedure F, using 2-fluoro-1,1'-biphenyl (34.4 mg, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 5% Et_2O in hexane], afforded the desired compound as a yellow amorphous solid (31.4 mg, 0.10 mmol, 51% yield) as a 1.3:1 mixture of regioisomers;

MAJOR δ_H (400 MHz, $CDCl_3$) 7.77 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar *H*), 7.39 – 7.27 (m, 5H, Ar *H*), 7.25 – 7.17 (m, 1H, Ar *H*), 7.14 – 7.07 (m, 1H, Ar *H*), 7.02 (t, *J* = 8.6 Hz, 2H, Ar *H*), 7.05 – 6.99 (m, 1H, Ar *H*), 4.16 (s, 2H, C*H*$_2$); δ_C (101 MHz, $CDCl_3$) 196.3 (*C*=O), 165.7 (d, $^1J_{C\text{-}F}$ = 255.0 Hz, Ar *C*), 159.6 (d, $^1J_{C\text{-}F}$ = 245.7 Hz, Ar *C*), 136.0 (Ar *C*), 133.5 (Ar *C*), 133.2 (d, $^4J_{C\text{-}F}$ = 3.1 Hz, Ar *C*), 132.0 (d, $^4J_{C\text{-}F}$ = 3.5 Hz, Ar *C*H), 131.0 (d, $^3J_{C\text{-}F}$ = 9.4 Hz, Ar *C*H), 130.8 (Ar *C*H), 130.5 (Ar *C*H), 129.7 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, Ar *C*H), 128.7 (d, $J_{C\text{-}F}$ = 17.9 Hz, Ar*C*), 128.5 (Ar *C*H), 127.3 (Ar *C*H), 124.4 (d, $^4J_{C\text{-}F}$ = 3.7 Hz, Ar *C*H), 115.8 (d,

$^{2}J_{C\text{-}F}$ = 22.5 Hz, Ar *C*H), 115.7 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, Ar *C*H), 43.2 (*C*H$_2$); δ_F (376 MHz, CDCl$_3$) -114.67 - -114.74 (m), -105.32 - -105.41 (m); HRMS (ESI$^+$) $C_{20}H_{14}OF_2Na$ [M+Na]$^+$: Expected 331.0905, Found 331.0894; ν_{max} (thin film/cm^{-1}) 757, 835, 993, 1156, 1211, 1226, 1484, 1506, 1596, 1683, 2924, 3031, 3066.

MINOR δ_H (400 MHz, CDCl$_3$) 8.07 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar *H*), 7.53 (dd, *J* = 8.2, 1.6 Hz, 2H, Ar *H*), 7.43 (td, *J* = 7.8, 1.8 Hz, 1H, Ar *H*), 7.39 – 7.27 (m, 3H, Ar *H*), 7.25 – 7.17 (m, 1H, Ar *H*), 7.15 (t, *J* = 8.7 Hz, 2H, Ar *H*), 7.14 – 7.07 (m, 1H, Ar *H*), 4.31 (s, 2H, C*H*$_2$); δ_C (101 MHz, CDCl$_3$) 196.0 (*C*=O), 166.0 (d, $^{1}J_{C\text{-}F}$ = 255.2 Hz, Ar *C*), 159.9 (d, $^{1}J_{C\text{-}F}$ = 249.5 Hz, Ar *C*), 134.7 (Ar *C*), 133.9 (Ar *C*), 133.1 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz, Ar *C*), 131.4 (d, $^{3}J_{C\text{-}F}$ = 9.6 Hz, Ar *C*H), 130.8 (Ar *C*H), 129.6 (Ar *C*H), 129.5 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz, Ar *C*H), 129.1 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz, Ar *C*H), 128.5 (d, $J_{C\text{-}F}$ = 17.9 Hz, Ar*C*), 124.5 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz, Ar *C*H), 116.2 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz, Ar *C*H), 116.0 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, Ar *C*H), 45.3 (*C*H$_2$); δ_F (376 MHz, CDCl$_3$) -117.92 - -118.01 (m), -104.79 - -104.88 (m).

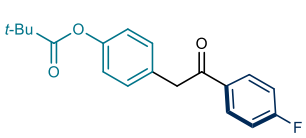
N-(4-(2-(4-Fluorophenyl)-2-oxoethyl)phenyl)-4-methylbenzenesulfonamide, ***9***



Prepared as described in General Procedure F, using 4-methyl-N-phenylbenzenesulfonamide (49.5 mg, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from toluene to 10% MeCN in toluene], afforded the title compound as an off-white amorphous solid (44.7 mg, 0.12 mmol, 58% yield); δ_H (400 MHz, CDCl$_3$) 8.99 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar *H*), 7.63 (d, *J* = 8.2 Hz, 2H, Ar *H*), 7.21 (d, *J* = 8.1 Hz, 2H, Ar *H*), 7.15 – 7.09 (m, 4H, Ar *H*), 7.01 (d, *J* = 8.5 Hz, 2H, Ar *H*), 6.58 (bs, 1H, N*H*), 4.18 (s, 2H, C*H*$_2$), 2.37 (s, 3H, C*H*$_3$); δ_C (101 MHz, CDCl$_3$) 195.9 (*C*=O), 166.0 (d, $^{1}J_{C\text{-}F}$ = 255.4 Hz, Ar *C*), 144.1 (Ar *C*), 136.3 (Ar *C*), 135.5 (Ar *C*), 133.0 (d, $^{4}J_{C\text{-}F}$ = 3.9 Hz, Ar *C*), 131.6 (Ar *C*), 131.3 (d, $^{3}J_{C\text{-}F}$ = 9.6 Hz, Ar *C*H), 130.5 (Ar *C*H), 129.8 (Ar *C*H), 127.4 (Ar *C*H), 122.1 (Ar *C*H), 116.0 (d, $^{2}J_{C\text{-}F}$ = 22.2 Hz, Ar *C*H), 44.8 (*C*H$_2$), 21.7 (*C*H$_3$); δ_F (376 MHz, CDCl$_3$) -104.61 - -104.69 (m); HRMS (ESI$^+$) $C_{21}H_{18}O_3FNaS$ [M+Na]$^+$: Expected 406.0884, Found

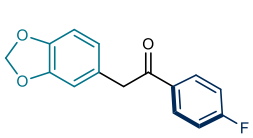
406.0878; ν_{max} (thin film/cm^{-1}) 815, 835, 916, 1091, 1157, 1229, 1335, 1508, 1597, 1677, 2926, 3062, 3258.

4-(2-(4-Fluorophenyl)-2-oxoethyl)phenyl pivalate, ***10***



Prepared as described in General Procedure F, using phenyl pivalate (36.1 µL, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from toluene to 5% MeCN in toluene], afforded the title compound as an off-white crystalline solid (29.1 mg, 0.09 mmol, 46% yield); m.p. (recrystallized from $CHCl_3$) 146 – 148 °C; δ_H (400 MHz, $CDCl_3$) 8.02 (dd, *J* = 8.8, 5.4 Hz, 2H, Ar *H*), 7.26 (d, *J* = 8.4 Hz, 2H, Ar *H*), 7.12 (t, *J* = 8.6 Hz, 2H, Ar *H*), 7.02 (d, *J* = 8.5 Hz, 2H, Ar *H*), 4.24 (s, 2H, C*H*$_2$), 1.34 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 196.0 (*C*=O), 177.2 (*C*=O), 165.9 (d, $^1J_{C\text{-}F}$ = 255.0 Hz, Ar *C*), 150.2 (Ar *C*), 133.0 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, Ar *C*), 131.7 (Ar *C*), 131.4 (d, $^3J_{C\text{-}F}$ = 9.6 Hz, Ar *C*H), 130.4 (Ar *C*H), 121.9 (Ar *C*H), 115.9 (d, $^2J_{C\text{-}F}$ = 22.2 Hz, Ar *C*H), 44.9 (*C*H$_2$), 39.2 (*C*CH$_3$), 27.2 (*C*H$_3$); δ_F (376 MHz, $CDCl_3$) -104.80 - -104.89 (m); HRMS (ESI$^+$) $C_{19}H_{19}O_3FNa$ $[M+Na]^+$: Expected 337.1210, Found 337.1204; ν_{max} (thin film/cm^{-1}) 840, 902, 1117, 1236, 1510, 1599, 1681, 1748, 2935, 2976, 3022.

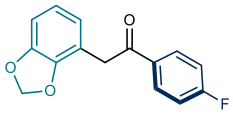
2-(Benzo[d][1,3]dioxol-5-yl)-1-(4-fluorophenyl)ethan-1-one, ***11***



Prepared as described in General Procedure F, using benzo[*d*][1,3]dioxole (23.0 µL, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 30% CH_2Cl_2 in hexane], afforded the title compound as a brown amorphous solid (27.3 mg, 0.11.00 mmol, 53% yield); δ_H (400 MHz, $CDCl_3$) 8.02 (dd, *J* = 8.9, 5.5 Hz, 2H, Ar *H*), 7.12 (t, *J* = 8.7 Hz, 2H, Ar *H*), 6.78 – 6.68 (m, 3H, Ar *H*), 5.93 (s, 2H, C*H*$_2$), 4.16 (s, 2H, C*H*$_2$); δ_C (101 MHz, $CDCl_3$) 196.2 (*C*=O), 165.9 (d, $^1J_{C\text{-}F}$ = 255.2 Hz, Ar *C*), 148.0 (Ar *C*), 146.8 (Ar *C*), 133.0 (d, $^4J_{C\text{-}F}$ = 3.0 Hz, Ar *C*), 131.4 (d, $^3J_{C\text{-}F}$ = 9.6 Hz, Ar *C*H), 128.0 (Ar *C*), 122.6 (Ar *C*H), 115.9 (d, $^2J_{C\text{-}F}$ = 22.2 Hz, Ar *C*H), 109.9 (Ar *C*H), 108.6 (Ar *C*H), 101.2

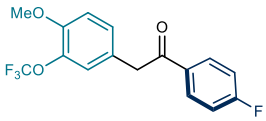
(CH_2), 45.2 (CH_2); δ_F (376 MHz, $CDCl_3$) -104.91 - -105.00 (m); HRMS (ESI^+) $C_{15}H_{11}O_3FNa$ $[M+Na]^+$: Expected 281.0584, Found 281.0577; ν_{max} (thin film/cm^{-1}) 787, 836, 928, 1038, 1156, 1247, 1445, 1490, 1504, 1597, 1683, 2904, 3077.

Product contains minor regioisomer identified by selected signals only (10%):



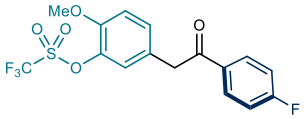
δ_H (400 MHz, $CDCl_3$) 5.96 (s, 2H, CH_2), 4.29 (s, 2H, CH_2); δ_C (101 MHz, $CDCl_3$) 147.7 (Ar *C*), 147.0 (Ar *C*), 131.1 (d, $^3J_{C-F}$ = 9.1 Hz, Ar *C*H), 116.0 (d, $^2J_{C-F}$ = 21.9 Hz, Ar *C*H), 111.0 (Ar *C*H), 110.0 (Ar *C*H), 102.0 (CH_2), 43.0 (CH_2); δ_F (376 MHz, CDCl3) -105.33 - -105.41 (m).

1-(4-Fluorophenyl)-2-(4-methoxy-3-(trifluoromethoxy)phenyl)ethan-1-one, ***12***



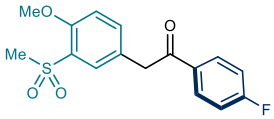
Prepared as described in General Procedure F, using 1-methoxy-2-(trifluoromethoxy)benzene (34.9 µL, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [toluene], afforded the title compound as a pale orange amorphous solid (41.7 mg, 0.13 mmol, 64% yield); δ_H (400 MHz, $CDCl_3$) 8.02 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar *H*), 7.18 – 7.10 (m, 4H, Ar *H*), 6.96 (d, *J* = 9.0 Hz, 1H, Ar *H*), 4.21 (s, 2H, CH_2), 3.86 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 195.6 (*C*=O), 166.0 (d, $^1J_{C-F}$ = 255.5 Hz, Ar *C*), 151.1 (Ar *C*), 138.1 (Ar *C*), 132.9 (d, $^4J_{C-F}$ = 3.2 Hz, Ar *C*), 131.3 (d, $^3J_{C-F}$ = 9.5 Hz, Ar *C*H), 129.0 (Ar *C*H), 126.8 (Ar *C*), 124.3 (Ar *C*H), 120.8 (q, $^1J_{C-F}$ = 257.9 Hz CF_3), 116.0 (d, $^2J_{C-F}$ = 21.9 Hz, Ar *C*H), 113.2 (Ar *C*H), 56.2 (CH_3), 44.3 (CH_2); δ_F (376 MHz, $CDCl_3$) -58.17 (s), -104.58 - -104.67 (m); HRMS (ESI^+) $C_{16}H_{12}O_3F_4Na$ $[M+Na]^+$: Expected 351.0615, Found 351.0605; ν_{max} (thin film/cm^{-1}) 741, 817, 835, 854, 1128, 1157, 1208, 1515, 1599, 1686, 2845, 2940, 3081.

5-(2-(4-Fluorophenyl)-2-oxoethyl)-2-methoxyphenyl trifluoromethanesulfonate, ***13***



Prepared as described in General Procedure F, using 2-methoxyphenyl trifluoromethanesulfonate (36.1 µL, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 30% EtOAc in hexane], afforded the title compound as a yellow amorphous solid (45.1 mg, 0.12 mmol, 57% yield); δ_H (400 MHz, $CDCl_3$) 8.02 (dd, *J* = 8.9, 5.3 Hz, 2H, Ar *H*), 7.20 (dd, *J* = 8.5, 2.1 Hz, 1H, Ar *H*), 7.18 – 7.12 (m, 3H, Ar *H*), 7.00 (d, *J* = 8.5 Hz, 1H, Ar *H*), 4.23 (s, 2H, C*H*$_2$), 3.90 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 195.3 (*C*=O), 166.1 (d, $^1J_{C\text{-}F}$ = 255.4 Hz, Ar *C*), 150.5 (Ar *C*), 138.7 (Ar *C*), 132.8 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, Ar *C*), 131.2 (d, $^3J_{C\text{-}F}$ = 9.3 Hz, Ar *C*H), 130.4 (Ar *C*H), 127.2 (Ar *C*), 123.8 (Ar *C*H), 118.9 (q, $^1J_{C\text{-}F}$ = 320.7 Hz, *C*F$_3$), 116.1 (d, $^2J_{C\text{-}F}$ = 21.7 Hz, Ar *C*H), 113.4 (Ar *C*H), 56.4 (*C*H$_3$), 44.1 (*C*H$_2$); δ_F (376 MHz, $CDCl_3$) -73.83 (s), -104.32 - -104.41 (m); HRMS (ESI$^+$) $C_{16}H_{12}O_5F_4NaS$ [M+Na]$^+$: Expected 415.0234, Found 415.0223; ν_{max} (thin film/cm^{-1}) 769, 836, 962, 1097, 1139, 1206, 1422, 1515, 1600, 1691, 2848, 2940, 3080.

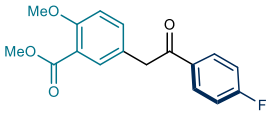
1-(4-Fluorophenyl)-2-(4-methoxy-3-(methylsulfonyl)phenyl)ethan-1-one, ***14***



Prepared as described in General Procedure F, using 1-methoxy-2-(methylsulfonyl)benzene (37.3 mg, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from toluene to 10% MeCN in toluene], afforded the title compound as an off-white crystalline solid (38.4 mg, 0.12 mmol, 60% yield); m.p. (recrystallized from $CHCl_3$) 129 – 131 °C; δ_H (400 MHz, $CDCl_3$) 8.03 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar *H*), 7.84 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.48 (dd, *J* = 8.5, 2.3 Hz, 1H, Ar *H*), 7.15 (t, *J* = 8.6 Hz, 2H, Ar *H*), 7.04 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.27 (s, 2H, C*H*$_2$), 3.99 (s, 3H, C*H*$_3$), 3.21 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 195.4 (*C*=O), 166.1 (d, $^1J_{C\text{-}F}$ = 256.0 Hz, Ar *C*), 156.4 (Ar *C*), 136.8 (Ar *C*H), 132.8 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, Ar *C*), 131.2 (d, $^3J_{C\text{-}F}$ = 9.6 Hz, Ar *C*H), 130.8 (Ar *C*H), 128.4 (Ar *C*), 127.0 (Ar *C*), 116.1 (d, $^2J_{C\text{-}F}$ = 21.9 Hz, Ar *C*H), 112.8 (Ar *C*H), 56.6 (*C*H$_3$), 44.0 (*C*H$_2$), 43.0 (*C*H$_3$); δ_F (376 MHz, $CDCl_3$) -104.26 - -104.34 (m); HRMS (ESI$^+$) $C_{16}H_{15}O_4FNaS$ [M+Na]$^+$:

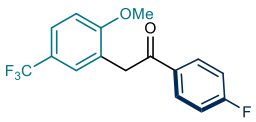
Expected 345.0567, Found 345.0560; ν_{max} (thin film/cm^{-1}) 770, 836, 961, 1017, 1140, 1229, 1297, 1410, 1496, 1597, 1687, 2844, 2929, 3011, 3072.

Methyl 5-(2-(4-fluorophenyl)-2-oxoethyl)-2-methoxybenzoate, ***15***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a yellow crystalline solid (51.3 mg, 0.17 mmol, 85% yield); m.p. (recrystallized from $CHCl_3$) 92 – 94 °C; δ_H (400 MHz, $CDCl_3$) 8.02 (dd, *J* = 8.9, 5.3 Hz, 2H, Ar *H*), 7.69 (d, *J* = 2.4 Hz, 1H, Ar *H*), 7.35 (dd, *J* = 8.6, 2.4 Hz, 1H, Ar *H*), 7.13 (t, *J* = 8.6 Hz, 2H, Ar *H*), 6.95 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.21 (s, 2H, C*H*$_2$), 3.88 (s, 3H, C*H*$_3$), 3.87 (s, 3H, *H*$_3$); δ_C (101 MHz, $CDCl_3$) 195.9 (*C*=*O*), 166.5 (*C*=O), 165.9 (d, $^1J_{C\text{-}F}$ = 255.3 Hz, Ar *C*), 158.4 (Ar *C*), 134.7 (Ar *C*H), 132.9 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, Ar *C*), 132.8 (Ar *C*H), 131.3 (d, $^3J_{C\text{-}F}$ = 9.5 Hz, Ar *C*H), 126.0 (Ar *C*), 120.1 (Ar *C*), 115.9 (d, $^2J_{C\text{-}F}$ = 22.2 Hz, Ar *C*H), 112.6 (Ar *C*H), 56.2 (*C*H$_3$), 52.1 (*C*H$_3$), 44.2 (*C*H$_2$); δ_F (376 MHz, $CDCl_3$) -104.7 - -104.8 (m); HRMS (ESI$^+$) $C_{17}H_{15}O_4F$ [M+Na]$^+$: Expected 325.0847, Found 325.0838; ν_{max} (thin film/cm^{-1}) 788, 835, 1084, 1156, 1211, 1257, 1504, 1597, 1688, 1726, 2839, 2908, 2951, 3011.

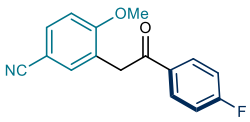
1-(4-Fluorophenyl)-2-(2-methoxy-5-(trifluoromethyl)phenyl)ethan-1-one, ***16***



Prepared as described in General Procedure F, using 1-methoxy-4-(trifluoromethyl)benzene (28.3 µL, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 5% ether in hexane], afforded the title compound as a yellow amorphous solid (36.3 mg, 0.12 mmol, 58% yield); δ_H (400 MHz, $CDCl_3$) 8.06 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar *H*), 7.54 (dd, *J* = 8.6, 1.9 Hz, 1H, Ar *H*), 7.43 (d, *J* = 2.1 Hz, 1H, Ar *H*), 7.15 (t, *J* = 8.6 Hz, 2H, Ar *H*), 6.94 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.28 (s, 2H, C*H*$_2$), 3.82 (s, 3H, C*H*$_3$); δ_C (101 MHz,

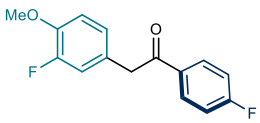
$CDCl_3$) 195.4 (*C*=O), 165.9 (d, $^1J_{C\text{-}F}$ = 254.6 Hz, Ar *C*), 159.8 (Ar *C*), 133.3 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, Ar *C*), 131.1 (d, $^3J_{C\text{-}F}$ = 9.0 Hz, Ar *C*H), 128.4 (q, $^3J_{C\text{-}F}$ = 3.5 Hz, Ar *C*H), 126.2 (q, $^3J_{C\text{-}F}$ = 3.9 Hz, Ar *C*H), 124.5 (q, $^1J_{C\text{-}F}$ = 271.3 Hz, *C*F_3) 124.3 (Ar *C*), 122.9 (q, $^2J_{C\text{-}F}$ = 32.7 Hz, Ar *C*), 115.9 (d, $^2J_{C\text{-}F}$ = 21.5 Hz, Ar *C*H), 110.4 (Ar *C*H), 55.8 (*C*H_3), 39.9 (*C*H_2); δ_F (376 MHz, $CDCl_3$) -61.41 (s), -105.03 - -105.12 (m); HRMS (ESI$^-$) $C_{16}H_{11}O_2F_4$ [M-H]$^-$: Expected 311.0701, Found 311.0687; ν_{max} (thin film/cm^{-1}) 820, 835, 997, 1116, 1156, 1331, 1507, 1597, 1691, 2845, 2916, 2940, 3077.

3-(2-(4-Fluorophenyl)-2-oxoethyl)-4-methoxybenzonitrile, ***17***



Prepared as described in General Procedure F, using 4-methoxybenzonitrile (26.6 mg, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 30% EtOAc in hexane], afforded the title compound as a yellow amorphous solid (28.6 mg, 0.11.00 mmol, 53% yield); δ_H (400 MHz, $CDCl_3$) 8.05 (dd, *J* = 8.8, 5.4 Hz, 2H, Ar *H*), 7.59 (dd, *J* = 8.5, 2.1 Hz, 1H, Ar *H*), 7.44 (d, *J* = 2.1 Hz, 1H, Ar *H*), 7.16 (t, *J* = 8.6 Hz, 2H, Ar *H*), 6.93 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.25 (s, 2H, *C*H_2), 3.83 (s, 3H, *C*H_3); δ_C (101 MHz, $CDCl_3$) 194.9 (*C*=O), 166.0 (d, $^1J_{C\text{-}F}$ = 255.2 Hz, Ar *C*), 160.8 (Ar *C*), 134.9 (Ar *C*H), 133.6 (Ar *C*H), 133.1 (d, $^4J_{C\text{-}F}$ = 3.0 Hz, Ar *C*), 131.1 (d, $^3J_{C\text{-}F}$ = 9.3 Hz, Ar *C*H), 125.2 (Ar *C*), 119.2 (*C*N), 115.9 (d, $^2J_{C\text{-}F}$ = 22.1 Hz, Ar *C*H), 111.0 (Ar *C*H), 104.1 (Ar *C*), 55.9 (*C*H_3), 39.6 (*C*H_2); δ_F (376 MHz, $CDCl_3$) -104.63 - -104.73 (m); HRMS (APCI) $C_{16}H_{13}O_2FN$ [M+H]$^+$: Expected 270.0925, Found 270.0912; ν_{max} (thin film/cm^{-1}) 835, 1024, 1156, 1263, 1500, 1597, 1689, 2224, 2845, 2925, 3073.

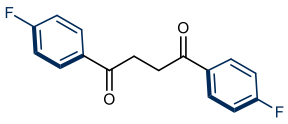
2-(3-Fluoro-4-methoxyphenyl)-1-(4-fluorophenyl)ethan-1-one, ***18***



Prepared as described in General Procedure F, using 1-fluoro-2-methoxybenzene (22.4 µL, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [toluene], afforded the title compound as a pale yellow amorphous solid (29.2 mg, 0.11.00 mmol, 56% yield); δ_H

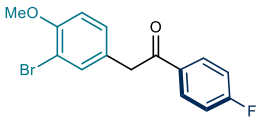
(400 MHz, $CDCl_3$) 8.02 (dd, *J* = 8.9, 5.2 Hz, 2H, Ar *H*), 7.13 (t, *J* = 8.6 Hz, 2H, Ar *H*), 7.02 – 6.89 (m, 3H, Ar *H*), 4.18 (s, 2H, CH_2), 3.87 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 195.8 (*C*=O), 166.0 (d, $^1J_{C-F}$ = 255.3 Hz, Ar *C*), 152.4 (d, $^1J_{C-F}$ = 245.9 Hz, Ar *C*), 146.8 (d, $^2J_{C-F}$ = 10.6 Hz, Ar *C*), 132.9 (d, $^4J_{C-F}$ = 3.0 Hz, Ar *C*), 131.3 (d, $^3J_{C-F}$ = 9.0 Hz, Ar *C*H), 127.2 (d, $^3J_{C-F}$ = 6.8 Hz, Ar *C*), 125.3 (d, $^4J_{C-F}$ = 3.7 Hz, Ar *C*H), 117.4 (d, $^2J_{C-F}$ = 18.7 Hz, Ar *C*H), 116.0 (d, $^2J_{C-F}$ = 22.2 Hz, Ar *C*H), 113.7 (d, $^3J_{C-F}$ = 1.9 Hz, Ar *C*H), 56.4 (CH_3), 44.5 (CH_2); δ_F (376 MHz, $CDCl_3$) -104.68 - -104.77 (m), -134.76 - -134.83 (m); HRMS (ESI+) $C_{15}H_{12}O_2F_2Na$ [M+Na]+: Expected 285.0698, Found 285.0692; ν_{max} (thin film/cm^{-1}) 786, 835, 997, 1027, 1157, 1226, 1273, 1507, 1518, 1598, 1685, 2841, 2904, 2957, 3034.

Product contains minor inseparable impurity identified by selected signals only (9%):



δ_H (400 MHz, $CDCl_3$) 8.06 (dd, *J* = 8.9, 5.4 Hz, 4H, Ar *H*), 3.43 (s, 4H, 2 x CH_2); δ_C (101 MHz, $CDCl_3$) 197.1 (*C*=O), 130.9 (d, $^3J_{C-F}$ = 9.0 Hz, Ar *C*H), 115.9 (d, $^2J_{C-F}$ = 21.9 Hz, Ar *C*H), 32.6 (CH_2); δ_F (376 MHz, $CDCl_3$) -105.05 - -105.13 (m).

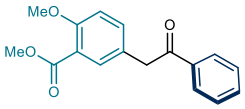
2-(3-Bromo-4-methoxyphenyl)-1-(4-fluorophenyl)ethan-1-one, ***19***



Prepared as described in General Procedure F, using 1-bromo-2-methoxybenzene (24.9 µL, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 30% EtOAc in hexane], afforded the title compound as a pale yellow amorphous solid (32.9 mg, 0.10 mmol, 51% yield); δ_H (400 MHz, $CDCl_3$) 8.02 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar *H*), 7.44 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.18 – 7.10 (m, 3H, Ar *H*), 6.86 (d, *J* = 8.4 Hz, 1H, Ar *H*), 4.18 (s, 2H, CH_2), 3.88 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 195.8 (*C*=O), 166.0 (d, $^1J_{C-F}$ = 255.3 Hz, Ar *C*), 155.1 (Ar *C*), 134.3 (Ar *C*H), 132.9 (d, $^4J_{C-F}$ = 3.0 Hz, Ar *C*), 131.3 (d, $^3J_{C-F}$ = 9.0 Hz, Ar *C*H), 129.6 (Ar *C*H), 127.9 (Ar *C*), 116.0 (d, $^2J_{C-F}$ = 21.6 Hz, Ar *C*H), 112.2 (Ar *C*H), 111.9 (Ar *C*), 56.4 (CH_3), 44.1 (CH_2); δ_F (376 MHz, $CDCl_3$) -104.62 - -104.71 (m); HRMS (ESI^+) $C_{15}H_{12}O_2BrFNa$ $[M+Na]^+$: Expected 344.9897, Found

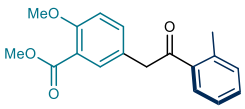
344.9892; ν_{max} (thin film/cm^{-1}) 785, 835, 995, 1054, 1156, 1228, 1257, 1410, 1497, 1596, 1683, 2838, 2905,2965, 3074.

Methyl 2-methoxy-5-(2-oxo-2-phenylethyl)benzoate, ***20***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and trimethyl((1-phenylvinyl)oxy)silane **3** (192 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a brown amorphous solid (45.6 mg, 0.16 mmol, 80% yield); δ_H (400 MHz, $CDCl_3$) 8.00 (d, *J* = 8.6, 2H, Ar *H*), 7.71 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.56 (tt, *J* = 7.4, 1.8 Hz, 1H, Ar *H*), 7.46 (t, *J* = 7.4 Hz, 2H, Ar *H*), 7.36 (dd, *J* = 8.6, 2.3 Hz, 1H, Ar *H*), 6.95 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.25 (s, 2H, CH_2), 3.88 (s, 3H, CH_3), 3.87 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 197.4 (*C*=O), 166.5 (*C*=O), 158.3 (Ar *C*), 136.5 (Ar *C*), 134.7 (Ar *C*H), 133.4 (Ar *C*H), 132.9 (Ar *C*H), 128.8 (Ar *C*H), 128.6 (Ar *C*H), 126.2 (Ar *C*), 120.1 (Ar *C*), 112.5 (Ar *C*H), 56.2 (CH_3), 52.1 (CH_3), 44.2 (CH_2); HRMS (APCI) $C_{17}H_{17}O_4$ $[M+H]^+$: Expected 285.1121, Found 285.1113; ν_{max} (thin film/cm^{-1}) 691, 753, 1083, 1180, 1213, 1255, 1501, 1687, 1725, 2838, 2905, 2949, 3003.

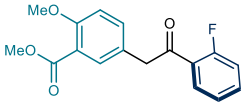
Methyl 2-methoxy-5-(2-oxo-2-(o-tolyl)ethyl)benzoate, ***21***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and trimethyl((1-(*o*-tolyl)vinyl)oxy)silane (206 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a brown amorphous solid (40.7 mg, 0.14 mmol, 68% yield); δ_H (400 MHz, $CDCl_3$) 8.63 (dd, *J* = 7.8, 0.8 Hz, 1H, Ar *H*), 7.68 (d, *J* = 2.4 Hz, 1H, Ar *H*), 7.39 - 7.32 (m, 2H, Ar *H*), 7.29 - 7.21 (m, 2H, Ar *H*), 6.94 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.16 (s, 2H, CH_2), 3.88 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 2.45 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 201.2 (*C*=O), 166.5 (*C*=O), 158.3 (Ar *C*), 138.7 (Ar *C*), 137.4 (Ar *C*), 134.8 (Ar *C*H), 132.9 (Ar *C*H), 132.2 (Ar *C*H),

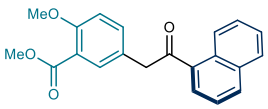
131.6 (Ar *C*H), 128.7 (Ar *C*H), 126.2 (Ar *C*), 125.8 (Ar *C*H), 120.0 (Ar *C*), 112.4 (Ar *C*H), 56.2 (*C*H$_3$), 52.1 (*C*H$_3$), 47.1 (*C*H$_2$), 21.4 (*C*H$_3$); HRMS (APCI) $C_{18}H_{19}O_4$ $[M+H]^+$: Expected 299.1278, Found 299.1267; ν_{max} (thin film/cm^{-1}) 756, 1025, 1083,1206, 1257, 1436, 1502, 1688, 1727, 2839, 2950, 3014, 3063.

methyl 5-(2-(2-fluorophenyl)-2-oxoethyl)-2-methoxybenzoate, ***22***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and ((1-(2-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a pale orange amorphous solid (48.1 mg, 0.16 mmol, 80% yield); δ_H (400 MHz, $CDCl_3$) 8.85 (td, *J* = 7.6, 1.8 Hz, 1H, Ar *H*), 7.69 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.55 - 7.48 (m, 1H, Ar *H*), 7.35 (dd, *J* = 8.6, 1.3 Hz, 1H, Ar *H*), 7.22 (td, *J* = 7.6, 0.9 Hz, 1H , Ar *H*), 7.14 (dd, *J* = 10.9, 8.6 Hz, 1H, Ar *H*), 6.94 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.24 (d, *J* = 2.6 Hz, 2H, C*H*$_2$), 3.88 (s, 3H, C*H*$_3$), 3.86 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 196.0 (d, $^3J_{C-F}$ = 4.4 Hz, *C*=O), 166.5 (*C*=O), 161.9 (d, $^1J_{C-F}$ = 254.1 Hz, Ar *C*), 158.4 (Ar *C*), 135.0 (Ar *C*H), 134.9 (Ar *C*H), 133.1 (Ar *C*H), 131.1 (d, $^3J_{C-F}$ = 2.5 Hz, Ar *C*H), 125.8 (Ar *C*), 125.4 (d, $^2J_{C-F}$ = 13.2 Hz, Ar *C*), 124.7 (d, $^4J_{C-F}$ = 3.6 Hz, Ar *C*H), 119.9 (Ar *C*), 116.8 (d, $^2J_{C-F}$ = 23.6 Hz, Ar *C*H) 112.3 (Ar *C*H), 56.2 (*C*H$_3$), 52.1 (*C*H$_3$), 48.8 (*C*H$_2$); δ_F (376 MHz, $CDCl_3$) -108.9 (m); HRMS (APCI) $C_{17}H_{16}O_4F$ $[M+H]^+$: Expected 303.1027, Found 303.1018; ν_{max} (thin film/cm^{-1}) 763, 824, 1024, 1083, 1199, 1256, 1451, 1502, 1609, 1689, 1726, 2839, 2951, 3078.

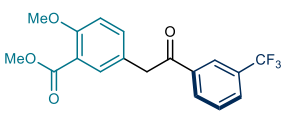
Methyl 2-methoxy-5-(2-(naphthalen-1-yl)-2-oxoethyl)benzoate, ***23***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and trimethyl((1-(naphthalen-1-yl)vinyl)oxy)silane (242 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a brown amorphous solid (44.7 mg, 0.13 mmol, 67%

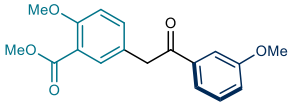
yield); δ_H (400 MHz, $CDCl_3$) 8.57 (d, *J* = 8.4 Hz, 1H, Ar *H*), 7.99 (d, *J* = 8.2 Hz, 1H, Ar *H*), 7.95 (d, *J* = 7.2 Hz, 1H, Ar *H*), 7.87 (d, *J* = 7.7 Hz, 1H, Ar *H*), 7.75 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.59 - 7.47 (m, 3H, C Ar *H*), 7.40 (dd, *J* = 8.6, 2.3 Hz, 1H, Ar *H*), 6.94 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.33 (s, 2H, C*H*$_2$), 3.88 (s, 3H, C*H*$_3$), 3.87 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 201.3 (*C*=O), 166.5 (*C*=O), 158.3 (Ar *C*), 135.4 (Ar *C*), 134.7 (Ar *C*H), 134.1 (Ar *C*), 133.1 (Ar *C*H), 132.9 (Ar *C*H), 130.5 (Ar *C*), 128.5 (Ar *C*H), 128.2 (Ar *C*H), 128.0 (Ar *C*H), 126.6 (Ar *C*H), 126.3 (Ar *C*), 125.9 (Ar *C*H), 124.4 (Ar *C*H), 120.0 (Ar *C*), 112.5 (Ar *C*H), 56.2 (*C*H$_3$), 52.1 (*C*H$_3$), 47.6 (*C*H$_2$); HRMS (APCI) $C_{21}H_{19}O_4$ $[M+H]^+$: Expected 335.1278, Found 335.1265; ν_{max} (thin film/cm^{-1}) 784, 1023, 1084, 1202, 1261, 1436, 1501, 1692, 1727, 2839, 2950, 3010.

Methyl 2-methoxy-5-(2-oxo-2-(3-(trifluoromethyl)phenyl)ethyl)benzoate, ***24***



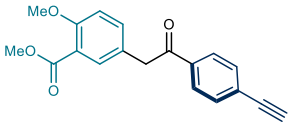
Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and trimethyl((1-(3-(trifluoromethyl)phenyl)vinyl)oxy)silane (260 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a brown amorphous solid (49.5 mg, 0.14 mmol, 70% yield); δ_H (400 MHz, $CDCl_3$) 8.25 (s, 1H, Ar *H*), 8.16 (d, *J* = 7.8 Hz, 1H, Ar *H*), 7.82 (d, *J* = 7.8 Hz, 1H, Ar *H*), 7.71 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.61 (t, *J* = 7.8 Hz, 1H, Ar *H*), 7.36 (dd, *J* = 8.6, 2.3 Hz, 1H, Ar *H*), 6.96 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.27 (s, 2H, C*H*$_2$), 3.89 (s, 3H, C*H*$_3$), 3.87 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 196.1 (*C*=O), 166.5 (*C*=O), 158.5 (Ar *C*), 137.0 (Ar *C*), 134.7 (Ar *C*H), 132.9 (Ar *C*H), 131.7 (Ar *C*H), 131.5 (q, $^2J_{C\text{-}F}$ = 32.9 Hz, Ar *C*), 129.8 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, Ar *C*H), 129.5 (Ar *C*H), 125.4 (Ar *C*), 125.4 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, Ar *C*H), 123.7 (d, $^1J_{C\text{-}F}$ = 272.6 Hz, *C*F$_3$), 120.2 (Ar *C*), 112.6 (Ar *C*H), 56.2 (*C*H$_3$), 52.2 (*C*H$_3$), 44.4 (*C*H$_2$); δ_F (376 MHz, $CDCl_3$) -62.8 (s); HRMS (APCI) $C_{18}H_{16}O_4F_3$ $[M+H]^+$: Expected 353.0995, Found 353.0985; ν_{max} (thin film/cm^{-1}) 695, 782, 817, 1025, 1124, 1255, 1325, 1437, 1502, 1611, 1695, 1727, 2841, 2906, 2952, 3011.

Methyl 2-methoxy-5-(2-(3-methoxyphenyl)-2-oxoethyl)benzoate, ***25***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and ((1-(3-methoxyphenyl)vinyl)oxy)trimethylsilane (222 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a yellow amorphous solid (38.8 mg, 0.12 mmol, 62% yield); δ_H (400 MHz, $CDCl_3$) 8.72 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.59 (d, *J* = 7.7 Hz, 1H, Ar *H*), 7.54 (t, *J* = 1.9 Hz, 1H, Ar *H*), 7.40 - 7.34 (m, 2H Ar *H*), 7.11 (dd, *J* = 8.2, 2.6 Hz, 1H, Ar *H*), 6.95 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.23 (s, 2H, C*H*$_2$), 3.89 (s, 3H, C*H*$_3$), 3.87 (s, 3H, C*H*$_3$), 3.84 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 197.3 (*C*=O), 166.5 (*C*=O), 160.0 (Ar *C*), 158.5 (Ar *C*), 137.9 (Ar *C*), 134.7 (Ar *C*H), 132.9 (Ar *C*H), 129.8 (Ar *C*H), 126.3 (Ar *C*), 121.2 (Ar *C*H), 120.1 (Ar *C*), 119.9 (Ar *C*H), 112.8 (Ar *C*H), 112.5 (Ar *C*H), 56.2 (*C*H$_3$), 55.5 (*C*H$_3$), 52.1 (*C*H$_3$), 44.4 (*C*H$_2$); HRMS (APCI) $C_{18}H_{19}O_5$ $[M+H]^+$: Expected 315.1227, Found 315.1215; ν_{max} (thin film/cm^{-1}) 786, 1028, 1083, 1257, 1583, 1597, 1689, 1728, 2836, 2948, 2999.

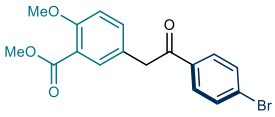
Methyl 5-(2-(4-ethynylphenyl)-2-oxoethyl)-2-methoxybenzoate, ***26***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and ((1-(4-ethynylphenyl)vinyl)oxy)trimethylsilane (215 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as an off white amorphous solid (20.6 mg, 0.07 mmol, 34% yield); δ_H (400 MHz, $CDCl_3$) 8.95 (d, *J* = 8.4 Hz, 2H, Ar *H*), 7.69 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.57 (d, *J* = 8.4 Hz, 2H, Ar *H*), 7.35 (dd, *J* = 8.6, 2.3 Hz, 1H, Ar *H*), 6.95(d, *J* = 8.6 Hz, 1H, Ar *H*), 4.23 (s, 2H, C*H*$_2$), 3.88 (s, 3H, C*H*$_3$), 3.87 (s, 3H, C*H*$_3$), 3.26 (s, 1H, C*H*); δ_C (101 MHz, $CDCl_3$) 196.7 (*C*=O), 166.5 (*C*=O), 158.4 (Ar *C*), 136.2 (Ar *C*), 134.7 (Ar *C*H), 132.9 (Ar *C*H), 132.5 (Ar *C*H), 128.5 (Ar *C*H), 127.2 (Ar *C*), 125.9 (Ar *C*), 120.2 (Ar *C*), 112.6 (Ar *C*H), 82.8 (*C*CH), 80.7 (*C*H), 56.2 (*C*H$_3$), 52.2 (*C*H$_3$), 44.3 (*C*H$_2$); HRMS (APCI)

$C_{19}H_{15}O_4$ [M-*H*]$^-$: Expected 307.0965, Found 307.0964; ν_{max} (thin film/cm^{-1})827, 1085, 1177, 1214, 1259, 1436, 1501, 1602, 1686, 1723, 2110, 2839, 2951, 3257.

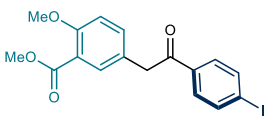
Methyl 5-(2-(4-bromophenyl)-2-oxoethyl)-2-methoxybenzoate, ***27***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and ((1-(4-bromophenyl)vinyl)oxy)trimethylsilane (271 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as an off-white crystalline solid (63.7 mg, 0.18 mmol, 88% yield); m.p. (recrystallized from hexane) 97 – 99 °C; δ_H (400 MHz, $CDCl_3$) 8.84 (d, *J* = 8.5 Hz, 2H, Ar *H*), 7.68 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.59 (d, *J* = 8.5 Hz, 2H, Ar *H*), 7.33 (dd, *J* = 8.6, 2.3 Hz, 1H, Ar *H*), 6.94 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.20 (s, 2H, C*H*$_2$), 3.87 (s, 3H, C*H*$_3$), 3.86 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 196.4 (*C*=O), 166.5 (*C*=O), 158.4 (Ar *C*), 135.2 (Ar *C*), 134.6 (Ar *C*H), 132.8 (Ar *C*H), 132.1 (Ar *C*H), 130.1 (Ar *C*H), 128.6 (Ar *C*), 125.8 (Ar *C*), 120.1 (Ar *C*), 112.6 (Ar *C*H), 56.2 (*C*H$_3$), 52.2 (*C*H$_3$), 44.2 (*C*H$_2$); HRMS (APCI) $C_{17}H_{16}O_4Br$ [M+H]$^+$: Expected 363.0226, Found 363.0225; ν_{max} (thin film/cm^{-1}) 788, 818, 996, 1083, 1205, 1256, 1435, 1501, 1583, 1683, 1725, 2838, 2949, 2998, 3086.

27 was further characterised by X-ray crystallographic analysis. CCDC : 2120244.

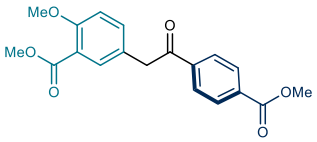
Methyl 5-(2-(4-iodophenyl)-2-oxoethyl)-2-methoxybenzoate, ***28***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and ((1-(4-iodophenyl)vinyl)oxy)trimethylsilane (318 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a yellow amorphous solid (48.0 mg, 0.12 mmol, 59% yield); δ_H (400 MHz, $CDCl_3$) 8.82 (d, *J* = 8.3 Hz, 2H, Ar *H*), 7.72 - 7.67 (m, 3H, Ar *H*), 7.34 (dd, *J* =

8.5, 2.2 Hz, 1H, Ar *H*), 6.94 (d, *J* = 8.5 Hz, 1H, Ar *H*), 4.19 (s, 2H, CH_2), 3.88 (s, 3H, CH_3), 3.87 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 196.8 (*C*=O), 166.5 (*C*=O), 158.4 (Ar *C*), 138.1 (Ar *C*H), 135.7 (Ar *C*), 134.6 (Ar *C*H), 132.8 (Ar *C*H), 130.0 (Ar *C*H), 125.8 (Ar *C*), 120.1 (Ar *C*), 112.6 (Ar *C*H), 101.5 (Ar *C*), 56.2 (*C*H_3), 52.2 (*C*H_3), 44.2 (*C*H_2); HRMS (APCI) $C_{17}H_{14}O_4I$ $[M\text{-}H]^-$: Expected 408.9942, Found 408.9932; ν_{max} (thin film/cm^{-1}) 814, 994, 1059, 1259, 1435, 1501, 1580, 1683, 1725, 2838, 2948, 3011.

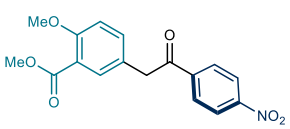
Methyl 2-methoxy-5-(2-(4-(methoxycarbonyl)phenyl)-2-oxoethyl)benzoate, ***29***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and methyl 4-(1-((trimethylsilyl)oxy)vinyl)benzoate (250 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as an off-white crystalline solid (49.4 mg, 0.14 mmol, 72% yield); m.p. (recrystallized from hexane) 114 – 116 °C; δ_H (400 MHz, $CDCl_3$) 8.11 (d, *J* = 8.5 Hz, 2H, Ar *H*), 8.03 (d, *J* = 8.5 Hz, 2H, Ar *H*), 7.69 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.35 (dd, *J* = 8.6, 2.3 Hz, 1H, Ar *H*), 6.95(d, *J* = 8.6 Hz, 1H, Ar *H*), 4.26 (s, 2H, CH_2), 3.93 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 3.86 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 197.0 (*C*=O), 166.5 (*C*=O), 166.2 (*C*=O), 158.4 (Ar *C*), 139.7 (Ar *C*), 134.7 (Ar *C*H), 134.1 (Ar *C*), 132.9 (Ar *C*H), 130.0 (Ar *C*H), 128.5 (Ar *C*H), 125.6 (Ar *C*), 120.2 (Ar *C*), 112.6 (Ar *C*H), 56.2 (*C*H_3), 52.6 (*C*H_3), 52.2 (*C*H_3), 44.3 (*C*H_2); HRMS (ESI^+) $C_{19}H_{18}O_6Na$ $[M+Na]^+$: Expected 365.0996, Found 365.0986; ν_{max} (thin film/cm^{-1}) 765, 999, 1083, 1107, 1209, 1258, 1277, 1435, 1501, 1692, 1721, 2840, 2904, 2951, 2998.

29 was further characterised by X-ray crystallographic analysis. CCDC : 2120243.

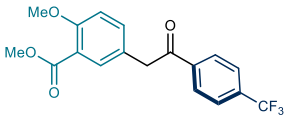
Methyl 2-methoxy-5-(2-(4-nitrophenyl)-2-oxoethyl)benzoate, ***30***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7

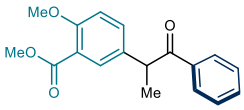
mg, 0.20 mmol) and trimethyl((1-(4-nitrophenyl)vinyl)oxy)silane (237 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a yellow amorphous solid (30.2 mg, 0.09 mmol, 46% yield); δ_H (400 MHz, $CDCl_3$) 8.30 (d, *J* = 8.9 Hz, 2H, Ar *H*), 8.13 (d, *J* = 8.9 Hz, 2H, Ar *H*), 7.70 (d, *J* = 2.4 Hz, 1H, Ar *H*), 7.35 (dd, *J* = 8.6, 2.4 Hz, 1H, Ar *H*), 6.97 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.29 (s, 2H, C*H*$_2$), 3.90 (s, 3H, C*H*$_3$), 3.88 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 195.9 (*C*=O), 166.5 (*C*=O), 158.6 (Ar *C*), 150.5 (Ar *C*), 141.0 (Ar *C*), 134.6 (Ar *C*H), 132.9 (Ar *C*H), 129.7 (Ar *C*H), 125.0 (Ar *C*), 124.1 (Ar *C*H), 120.4 (Ar *C*), 112.7 (Ar *C*H), 56.3 (*C*H$_3$), 52.3 (*C*H$_3$), 44.9 (*C*H$_2$); HRMS (APCI) $C_{17}H_{16}O_6N$ $[M+H]^+$: Expected 330.0972, Found 330.0967; ν_{max} (thin film/cm^{-1}) 854, 1085, 1204, 1259, 1343, 1521, 1598, 1694, 1725, 2840, 2951, 3078, 3108.

Methyl 2-methoxy-5-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)benzoate, ***31***



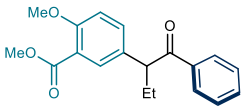
Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and trimethyl((1-(4-(trifluoromethyl)phenyl)vinyl)oxy)silane (260 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as an off-white amorphous solid (43.4 mg, 0.12 mmol, 62% yield); δ_H (400 MHz, $CDCl_3$) 8.09 (d, *J* = 8.2 Hz, 2H, Ar *H*), 7.72 (d, *J* = 8.2 Hz, 2H, Ar *H*), 7.70 (d, *J* = 2.4 Hz, 1H, Ar *H*), 7.35 (dd, *J* = 8.6, 2.4 Hz, 1H, Ar *H*), 6.96 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.26 (s, 2H, C*H*$_2$), 3.88 (s, 3H, C*H*$_3$), 3.87 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 196.5 (*C*=O), 166.5 (*C*=O), 158.5 (Ar *C*), 139.2 (Ar *C*), 134.7 (Ar *C*H), 134.7 (q, $^2J_{C\text{-}F}$ = 32.7 Hz, Ar *C*), 132.9 (Ar *C*H), 128.9 (Ar *C*H), 125.9 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, Ar *C*H), 125.4 (Ar *C*), 125.0 (q, $^1J_{C\text{-}F}$ = 272.8 Hz, *C*F$_3$), 120.2 (Ar *C*), 112.6 (Ar *C*H), 56.2 (*C*H$_3$), 52.2 (*C*H$_3$), 44.6 (*C*H$_2$); δ_F (376 MHz, $CDCl_3$) -63.16 (s); HRMS (APCI) $C_{18}H16O_4F_3$ $[M+H]^+$: Expected 353.0995, Found 353.0984; ν_{max} (thin film/cm^{-1}) 789, 831, 1016, 1066, 1125, 1166, 1258, 1322, 1502, 1694, 1727, 2841, 2911, 2952.

Methyl 2-methoxy-5-(1-oxo-1-phenylpropan-2-yl)benzoate, ***32***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and trimethyl((1-phenylprop-1-en-1-yl)oxy)silane (206 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a yellow amorphous solid (25.1 mg, 0.08 mmol, 42% yield); δ_H (400 MHz, $CDCl_3$) 8.93 (d, *J* = 7.4 Hz, 2H, Ar *H*), 7.74 (d, *J* = 2.4 Hz, 1H, Ar *H*), 7.49 (t, *J* = 7.4 Hz, 1H, Ar *H*), 7.42 - 7.34 (m, 3H, Ar *H*), 6.90 (d, *J* = 8.7 Hz, 1H, Ar *H*), 4.67 (q, *J* = 6.9 Hz, 1H, C*H*), 3.87 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 1.51 (d, *J* = 6.9 Hz, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 200.3 (*C*=O), 166.6 (*C*=O), 158.2 (Ar *C*), 136.4 (Ar *C*), 133.2 (Ar *C*), 133.1 (Ar *C*H), 132.7 (Ar *C*H), 131.2 (Ar *C*H), 128.8 (Ar *C*H), 128.7 (Ar *C*H), 120.4 (Ar *C*), 112.8 (Ar *C*H), 56.2 (*C*H_3), 52.2 (*C*H_3), 46.7 (*C*H), 19.7 (*C*H_3); HRMS (APCI) $C_{18}H_{19}O_4$ $[M+H]^+$: Expected 299.1278, Found 299.1267; ν_{max} (thin film/cm^{-1}) 742, 1084, 1181, 1215, 1260, 1302, 1435, 1499, 1681, 1728, 1838, 2950, 2973.

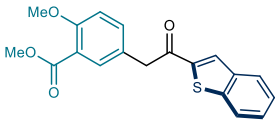
Methyl 2-methoxy-5-(1-oxo-1-phenylbutan-2-yl)benzoate, ***33***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and trimethyl((1-phenylbut-1-en-1-yl)oxy)silane (220 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a pale orange amorphous solid (25.5 mg, 0.08 mmol, 41% yield); δ_H (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H, Ar *H*), 7.74 (d, *J* = 2.4 Hz, 1H, Ar *H*), 7.49 (tt, *J* = 7.4, 1.3 Hz, 1H, Ar *H*), 7.43 - 7.37 (m, 3H, Ar *H*), 6.90 (d, *J* = 8.7 Hz, 1H, Ar *H*), 4.43 (t, *J* = 7.3 Hz, 1H, C*H*), 3.87 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 2.23 - 2.11 (m, 1H, CH_2), 1.88 - 1.79 (m, 1H, CH_2), 0.89 (t, *J* = 7.4 Hz, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 200.2 (*C*=O), 166.6 (*C*=O), 158.3 (Ar *C*), 136.9 (Ar *C*), 133.2 (Ar *C*H), 133.1 (Ar *C*H), 131.7 (Ar *C*H), 131.4 (Ar *C*), 128.7 (2 x Ar *C*H), 120.3 (Ar *C*), 112.7 (Ar *C*H), 56.2 (*C*H_3), 54.2 (*C*H), 52.2 (*C*H_3), 27.3 (*C*H_2), 12.4 (*C*H_3); HRMS (ESI$^+$) $C_{19}H_{20}O_4Na$ $[M+Na]^+$: Expected

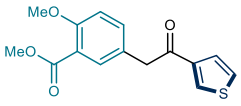
335.1254, Found 335.1242; ν_{max} (thin film/cm^{-1}) 1024, 1084, 1181, 1209, 1260, 1300, 1436, 1499, 1679, 1729, 2839, 2874, 2963.

Methyl 5-(2-(benzo[b]thiophen-2-yl)-2-oxoethyl)-2-methoxybenzoate, ***34***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol), *N*-(4-chlorophenyl)-*N*-phenylnaphthalen-1-amine (50 mol%, 0.10 mmol) and ((1-(benzo[b]thiophen-2-yl)vinyl)oxy)trimethylsilane (248 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as an off white crystalline solid (32.6 mg, 0.10 mmol, 48% yield); m.p. (recrystallized from $CHCl_3$) 135 – 138 °C; δ_H (400 MHz, $CDCl_3$) 8.02 (s, 1H, Ar *H*), 7.88 (dd, *J* = 15.0, 7.9 Hz, 2H, Ar *H*), 7.77 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.49 - 7.35 (m, 3H, Ar *H*), 6.96 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.26 (s, 2H, C*H*$_2$), 3.89 (s, 3H, C*H*$_3$), 3.88 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 191.9 (*C*=O), 166.5 (*C*=O), 158.5 (Ar *C*), 143.2 (Ar *C*), 142.8 (Ar *C*), 139.2 (Ar *C*), 134.7 (Ar *C*H), 132.8 (Ar *C*H), 129.9 (Ar *C*H), 127.7 (Ar *C*H), 126.2 (Ar *C*H), 125.8 (Ar *C*), 125.2 (Ar *C*H), 123.1 (Ar *C*H), 120.2 (Ar *C*), 112.6 (Ar *C*H), 56.3 (*C*H$_3$), 52.2 (*C*H$_3$), 45.0 (*C*H$_2$); HRMS (APCI) $C_{19}H_{15}O_4S$ [M-*H*]$^-$: Expected 339.0697, Found 339.0687; ν_{max} (thin film/cm^{-1}) 727, 751, 785, 1024, 1084, 1157, 1261, 1435, 1502, 1667, 1726, 2837, 2948, 2999, 3057.

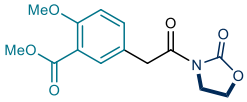
Methyl 2-methoxy-5-(2-oxo-2-(thiophen-3-yl)ethyl)benzoate, ***35***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and trimethyl((1-(thiophen-3-yl)vinyl)oxy)silane (198 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a brown amorphous solid (14.6 mg, 0.05 mmol, 25% yield); δ_H (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 2.8, 1.1 Hz, 1H, Ar *H*), 7.71 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.56 (dd, *J* = 5.1, 1.0 Hz, 1H, Ar *H*), 7.38 (dd, *J* = 8.5, 2.4 Hz, 1H, Ar *H*), 7.32 (dd, *J* = 5.1, 2.9 Hz, 1H, Ar *H*), 6.95 (d, *J* = 8.6 Hz, 1H, Ar

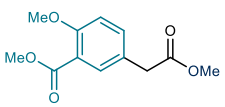
H), 4.14 (s, 2H, C*H*$_2$), 3.89 (s, 3H, C*H*$_3$), 3.87 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 191.7 (*C*=O), 166.6 (*C*=O), 158.4 (Ar *C*), 141.8 (Ar *C*), 134.7 (Ar *C*H), 132.82 (Ar *C*H), 132.76 (Ar *C*H), 127.4 (Ar *C*H), 126.7 (Ar *C*H), 126.1 (Ar *C*), 120.1 (Ar *C*), 112.6 (Ar *C*H), 56.3 (*C*H$_3$), 52.2 (*C*H$_3$), 45.6 (*C*H$_2$); HRMS (APCI) $C_{15}H_{15}O_4S$ $[M+H]^+$: Expected 291.0686, Found 291.0682; ν_{max} (thin film/cm^{-1}) 1024, 1084, 1260, 1436, 1502, 1674, 1725, 2949, 2986, 3054.

Methyl 2-methoxy-5-(2-oxo-2-(2-oxooxazolidin-3-yl)ethyl)benzoate, ***36***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and 3-(1-((trimethylsilyl)oxy)vinyl)oxazolidin-2-one (201 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 60% EtOAc in hexane], afforded the title compound as a colourless oil (26.6 mg, 0.09 mmol, 45% yield); δ_H (400 MHz, $CDCl_3$) 8.73 (d, *J* = 2.4 Hz, 1H, Ar *H*), 7.42 (dd, *J* = 8.6, 2.4 Hz, 1H, Ar *H*), 6.94 (d, *J* = 8.6 Hz, 1H, Ar *H*), 4.41 (t, *J* = 8.1 Hz, 2H, C*H*$_2$), 4.23 (s, 2H, C*H*$_2$), 4.02 (t, *J* = 8.1 Hz, 2H, C*H*$_2$), 3.89 (s, 3H, C*H*$_3$), 3.87 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 171.3 (*C*=O), 166.5 (*C*=O), 158.5 (Ar *C*), 153.6 (*C*=O), 135.0 (Ar *C*H), 132.9 (Ar *C*H), 125.3 (Ar *C*), 120.1 (Ar *C*), 112.3 (Ar *C*H), 62.2 (*C*H$_2$), 56.2 (*C*H$_3$), 52.2 (*C*H$_3$), 42.8 (*C*H$_2$) 40.1 (*C*H$_2$); HRMS (ESI^+) $C_{14}H_{15}O_6NNa$ $[M+Na]^+$: Expected 316.0797, Found 316.0792; ν_{max} (thin film/cm^{-1}) 759, 1022, 1084, 1263, 1366, 1387, 1502, 1698, 1724, 1774, 2840, 2952.

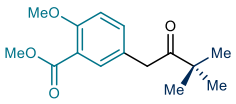
Methyl 2-methoxy-5-(2-methoxy-2-oxoethyl)benzoate, ***37***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and tert-butyl((1-methoxyvinyl)oxy)dimethylsilane (188 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a brown amorphous solid (12.6 mg, 0.05 mmol, 26% yield); δ_H (400 MHz, $CDCl_3$) 8.74 (d, *J* = 2.4 Hz, 1H, Ar *H*), 7.41 (dd, *J* = 8.6, 2.4 Hz, 1H, Ar *H*), 6.96 (d, *J* = 8.6 Hz, 1H, Ar

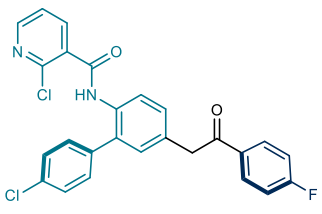
H), 3.91 (s, 3H, C*H*$_3$), 3.90 (s, 3H, C*H*$_3$), 3.71 (s, 3H, C*H*$_3$), 3.60 (s, 2H, C*H*$_2$); δ_C (101 MHz, $CDCl_3$) 172.0 (*C*=O), 166.5 (*C*=O), 158.4 (Ar *C*), 134.4 (Ar *C*H), 132.6 (Ar *C*H), 125.8 (Ar *C*), 120.0 (Ar *C*), 112.4 (Ar *C*H), 56.2 (*C*H$_3$), 52.2 (*C*H$_3$), 52.1 (*C*H$_3$), 40.0 (*C*H$_2$); HRMS (APCI) $C_{12}H_{15}O_5$ $[M+H]^+$: Expected 239.0914, Found 239.0913; ν_{max} (thin film/cm^{-1}) 824, 1024, 1084, 1201, 1257, 1436, 1501, 1728, 2840, 2998.

Methyl 5-(3,3-dimethyl-2-oxobutyl)-2-methoxybenzoate, ***38***



Prepared as described in General Procedure G, using 5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (99.7 mg, 0.20 mmol) and ((3,3-dimethylbut-1-en-2-yl)oxy)trimethylsilane (172.3 mg, 1.00 mmol). Purification by column chromatography on silica gel [*Standard conditions*], afforded the title compound as a pale yellow oil (31.2 mg, 0.12 mmol, 59% yield); δ_H (400 MHz, $CDCl_3$) 8.60 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.29 (dd, *J* = 8.6, 2.3 Hz, 1H, Ar *H*), 6.93 (d, *J* = 8.6 Hz, 1H, Ar *H*), 3.88 (s, 3H, C*H*$_3$), 3.87 (s, 3H, C*H*$_3$), 3.76 (s, 2H, C*H*$_2$), 1.20 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 212.9 (*C*=O), 166.7 (*C*=O), 158.2 (Ar *C*), 134.9 (Ar *C*H), 132.9 (Ar *C*H), 126.7 (Ar *C*), 119.8 (Ar *C*), 112.3 (Ar *C*H), 56.2 (*C*H$_3$), 52.1 (*C*H$_3$), 44.7 (*CC*H$_3$), 42.1 (*C*H$_2$), 26.5 (*C*H$_3$); HRMS (ESI$^+$) $C_{15}H_{20}O_4Na$ $[M+Na]^+$: Expected 287.1254, Found 287.1249; ν_{max} (thin film/cm^{-1}) 1025, 1084, 1202, 1261, 1304, 1436, 1502, 1709, 1729, 2834, 2891, 2956, 2980.

2-Chloro-N-(4'-chloro-5-(2-(4-fluorophenyl)-2-oxoethyl)-[1,1'-biphenyl]-2-yl)nicotinamide, ***62***

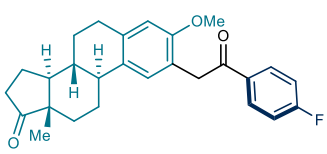


Prepared as described in General Procedure G, using 10-(4'-chloro-6-(2-chloronicotinamido) [1,1'-biphenyl]-3-yl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (138 mg, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from 1% NEt_3 in hexane to 1% NEt_3 and 40% EtOAc in hexane], afforded the title compound as a yellow crystalline solid (48.9 mg, 0.10 mmol, 51% yield); m.p.

(recrystallized from hexane) 164 – 166 °C; δ_H (400 MHz, $CDCl_3$) 8.45 (dd, *J* = 4.7, 1.8 Hz, 1H, Ar *H*), 8.40 (d, *J* = 8.4 Hz, 1H, Ar *H*), 8.13 (bs, 1H, N*H*), 8.12 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar *H*), 8.05 (dd, *J* = 8.7, 5.4 Hz, 2H, Ar *H*), 7.42 (d, *J* = 8.4 Hz, 2H, Ar *H*), 7.37 – 7.31 (m, 4H, Ar *H*), 7.17 – 7.12 (m, 3H, Ar *H*), 4.29 (s, 2H, CH_2); δ_C (101 MHz, $CDCl_3$) 195.8 (*C*=O), 166.0 (d, $^1J_{C-F}$ = 255.3 Hz, Ar *C*), 162.6 (*C*=O), 151.5 (Ar *C*H), 146.8 (Ar *C*), 140.4 (Ar *C*H), 136.0 (Ar *C*), 134.7 (Ar *C*), 133.5 (Ar *C*), 133.0 (d, $^4J_{C-F}$ = 3.3 Hz, Ar *C*), 132.6 (Ar *C*), 131.5 (Ar *C*), 131.3 (d, $^3J_{C-F}$ = 9.3 Hz, Ar *C*H), 131.3 (Ar *C*H), 131.1 (Ar *C*), 130.9 (Ar *C*H), 130.1 (Ar *C*H), 129.5 (Ar *C*H), 123.1 (Ar *C*H), 122.4 (Ar *C*H), 116.0 (d, $^2J_{C-F}$ = 22.0 Hz, Ar *C*H), 44.9 (CH_2); δ_F (376 MHz, $CDCl_3$) -104.49 - -104.58 (m); HRMS (ESI^+) $C_{26}H_{17}O_2N_2Cl_2FNa$ $[M+Na]^+$: Expected 501.0543, Found 501.0531; ν_{max} (thin film/cm^{-1}) 737, 836, 1090, 1156, 1230, 1300, 1399, 1508, 1517, 1596, 1675, 3051, 3067, 3261, 3391.

62 was further characterised by X-ray crystallographic analysis. CCDC : 2120245.

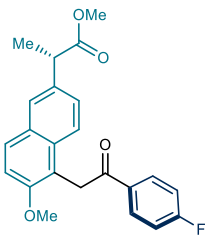
(13S)-2-(2-(4-Fluorophenyl)-2-oxoethyl)-3-methoxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one, ***64***



Prepared as described in General Procedure G, using 10-((8R,9S,13S,14S)-3-methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-4-yl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (126 mg, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from toluene to 5% MeCN in toluene], afforded the title compound as a brown amorphous solid (43.8 mg, 0.10 mmol, 52% yield); δ_H (400 MHz, $CDCl_3$) 8.07 (dd, *J* = 8.5, 5.6 Hz, 2H, Ar *H*), 7.12 (t, *J* = 8.9 Hz, 2H, Ar *H*), 7.09 (s, 1H, Ar *H*), 6.61 (s, 1H, Ar *H*), 4.25 (d, *J* = 16.0 Hz, 1H, CH_2), 4.15 (d, *J* = 16.0 Hz, 1H, CH_2), 3.76 (s, 3H, CH_3), 2.94 – 2.88 (m, 2H, CH_2), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H, CH_2), 2.40 – 2.33 (m, 1H, CH_2), 2.29 – 2.20 (m, 1H, CH_2), 2.19 – 1.90 (m, 4H, 4 x CH_2), 1.68 – 1.39 (m, 6H, 4 x CH_2, 2 x C*H*), 0.89 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 221.1 (*C*=O), 196.8 (*C*=O), 165.8 (d, $^1J_{C-F}$ = 254.3 Hz, Ar *C*), 155.2 (Ar

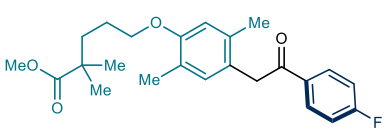
C), 136.8 (Ar *C*), 133.5 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz, Ar *C*), 131.9 (Ar *C*), 131.2 (d, $^{3}J_{C\text{-}F}$ = 9.4 Hz, Ar *C*H), 128.2 (Ar *C*H), 120.8 (Ar *C*), 115.7 (d, $^{2}J_{C\text{-}F}$ = 21.7 Hz, Ar *C*H), 111.2 (Ar *C*H), 55.6 (*C*H$_3$), 50.5 (*C*H), 48.1 (q*C*), 44.0 (*C*H), 39.8 (*C*H$_2$), 38.4 (*C*H), 36.0 (*C*H$_2$), 31.7 (*C*H$_2$), 29.8 (*C*H$_2$), 26.7 (*C*H$_2$), 26.0 (*C*H$_2$), 21.7 (*C*H$_2$), 14.0 (*C*H$_3$); δ_F (376 MHz, CDCl$_3$) -105.67 - -105.77 (m); HRMS (ESI$^+$) $C_{27}H_{29}O_3FNa$ [M+Na]$^+$: Expected 443.1993, Found 443.1982; ν_{max} (thin film/cm^{-1}) 724, 835, 904, 1156, 1226, 1507, 1599, 1686, 1734, 2253, 2859, 2933.

Methyl (S)-2-(5-(2-(4-fluorophenyl)-2-oxoethyl)-6-methoxynaphthalen-2-yl)propanoate, ***66***



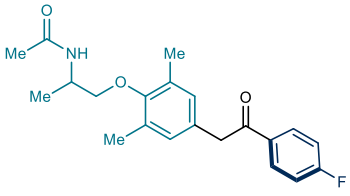
Prepared as described in General Procedure G, using (S)-10-(3-methoxy-7-(1-methoxy-1-oxopropan-2-yl)naphthalen-2-yl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (118 mg, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 30% EtOAc in hexane], afforded the title compound as a yellow amorphous solid (48.7 mg, 0.13 mmol, 64% yield); δ_H (400 MHz, CDCl$_3$) 8.14 (dd, *J* = 8.4, 5.6 Hz, 2H, Ar *H*), 7.79 (d, *J* = 9.1, 1H, Ar *H*), 7.74 (d, *J* = 8.8, 1H, Ar *H*), 7.70 (s, 1H, Ar *H*), 7.41 (d, *J* = 8.8, 1H, Ar *H*), 7.29 (d, *J* = 9.0, 1H, Ar *H*), 7.14 (t, *J* = 8.6 Hz, 2H, Ar *H*), 4.72 (s, 2H, C*H*$_2$), 3.90 (s, 3H, OC*H*$_3$), 3.85 (q, *J* = 7.1 Hz, 1H, C*H*), 3.66 (s, 3H, OC*H*$_3$), 1.57 (d, *J* = 7.1, 3H, C*H*$_3$); δ_C (101 MHz, CDCl$_3$) 196.6 (*C*=O), 175.1 (*C*=O), 165.8 (d, $^{1}J_{C\text{-}F}$ = 254.6 Hz, Ar *C*), 154.8 (Ar *C*), 135.5 (Ar *C*), 133.5 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz, Ar *C*), 132.8 (Ar *C*), 131.1 (d, $^{3}J_{C\text{-}F}$ = 9.2 Hz, Ar *C*H), 129.3 (Ar *C*), 129.1 (Ar *C*H), 126.9 (Ar *C*H), 126.8 (Ar *C*H), 123.7 (Ar *C*H), 116.4 (Ar *C*), 115.7 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, Ar *C*H), 113.5 (Ar *C*H), 56.6 (OCH$_3$), 52.1 (OCH$_3$), 45.3 (*C*H), 35.9 (*C*H$_2$), 18.6 (*C*H$_3$); δ_F (376 MHz, CDCl$_3$) -107.35 - -107.45 (m); HRMS (ESI$^+$) $C_{23}H_{21}O_4FNa$ [M+Na]$^+$: Expected 403.1316, Found 403.1304; ν_{max} (thin film/cm^{-1}) 730, 804, 832, 991, 1090, 1156, 1207, 1254, 1597, 1689, 1733, 2841, 2950, 2978, 3074.

Methyl 5-(4-(2-(4-fluorophenyl)-2-oxoethyl)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate, ***68***



Prepared as described in General Procedure G, using 10-(4-((5-methoxy-4,4-dimethyl-5-oxopentyl)oxy)-2,5-dimethylphenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (122 mg, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 20% ether in hexane], afforded the title compound as a brown amorphous solid (55.9 mg, 0.14 mmol, 70% yield); δ_H (400 MHz, $CDCl_3$) 8.04 (dd, *J* = 8.8, 5.4 Hz, 2H, Ar *H*), 7.13 (t, *J* = 8.6 Hz, 2H, Ar *H*), 6.86 (s, 1H, Ar *H*), 6.63 (s, 1H, Ar *H*), 4.17 (s, 2H, C*H*$_2$), 3.91 (t, *J* = 5.0 Hz, 2H, OC*H*$_2$), 3.66 (s, 1H, OC*H*$_3$), 2.20 (s, 3H, C*H*$_3$), 2.15 (s, 3H, C*H*$_3$), 1.73 – 1.69 (m, 4H, 2 x C*H*$_2$), 1.22 (s, 6H, 2 x C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 196.6 (*C*=O), 178.5 (*C*=O), 165.8 (d, $^1J_{C\text{-}F}$ = 254.4 Hz, Ar *C*), 156.3 (Ar *C*), 135.1 (Ar *C*), 133.5 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, Ar *C*), 132.5 (Ar *C*H), 131.1 (d, $^3J_{C\text{-}F}$ = 9.0 Hz, Ar *C*H), 124.5 (Ar *C*), 124.4 (Ar *C*), 115.8 (d, $^2J_{C\text{-}F}$ = 21.9 Hz, Ar *C*H), 113.3 (Ar *C*H), 68.1 (OCH$_2$), 51.9 (OCH$_3$), 42.8 (*C*H$_2$), 42.2 (q*C*), 37.2 (*C*H$_2$), 25.3 (*C*H$_2$, 2 x *C*H$_3$), 20.0 (*C*H$_3$), 15.8 (*C*H$_3$); δ_F (376 MHz, $CDCl_3$) -105.27 - -105.36 (m); HRMS (APCI) $C_{24}H_{30}O_4F$ $[M+H]^+$: Expected 401.2123, Found 401.2105; ν_{max} (thin film/cm^{-1}) 836, 1095, 1155, 1198, 1229, 1274, 1508, 1598, 1689, 1729, 2873, 2926, 2951.

N-(1-(4-(2-(4-Fluorophenyl)-2-oxoethyl)-2,6-dimethylphenoxy)propan-2-yl)acetamide, ***70***

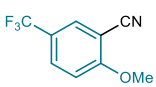


Prepared as described in General Procedure G, using 10-(4-(2-acetamidopropoxy)-3,5-dimethylphenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (113 mg, 0.20 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (210 mg, 1.00 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 80% EtOAc in hexane],

afforded the title compound as a pale yellow amorphous solid (35.2 mg, 0.10 mmol, 49% yield); δ_H (400 MHz, $CDCl_3$) 8.02 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar *H*), 7.11 (t, *J* = 8.6 Hz, 2H, Ar *H*), 6.88 (s, 2H, Ar *H*), 6.00 (bd, *J* = 7.9 Hz, 1H, N*H*), 4.37 – 4.28 (m, 1H, C*H*), 4.13 (s, 2H, CH_2), 3.76 (dd, *J* = 9.1, 4.0 Hz, 1H, OCH_2), 3.68 (dd, *J* = 9.1, 3.2 Hz, 1H, OCH_2), 2.22 (s, 6H, 2 x CH_3), 2.02 (s, 3H, CH_3), 1.38 (d, *J* = 6.9 Hz, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 196.4 (*C*=O), 169.7 (*C*=O), 165.9 (d, $^1J_{C-F}$ = 255.2 Hz, Ar *C*), 154.0 (Ar *C*), 133.1 (d, $^4J_{C-F}$ = 2.9 Hz, Ar *C*), 131.4 (d, $^3J_{C-F}$ = 9.2 Hz, Ar *C*H), 130.0 (Ar *C*H), 129.9 (Ar *C*), 115.9 (d, $^2J_{C-F}$ = 22.2 Hz, Ar *C*H), 74.0 (O*C*H$_2$), 45.6 (*C*H), 44.9 (*C*H$_2$), 23.5 (*C*H$_3$), 17.8 (*C*H$_3$), 16.3 (*C*H$_3$); δ_F (376 MHz, $CDCl_3$) -104.95 - -105.04 (m); HRMS (ESI$^+$) $C_{21}H_{24}O_3NFNa$ [M+Na]$^+$: Expected 380.1632, Found 380.1620; ν_{max} (thin film/cm^{-1}) 733, 836, 1028, 1154, 1206, 1506, 1597, 1652, 1731, 2923, 2971, 3067, 3293, 3367.

Synthesis of Cyanated Arenes.

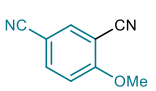
2-Methoxy-5-(trifluoromethyl)benzonitrile, ***42***



Prepared as described in General Procedure I, using 1-methoxy-4-(trifluoromethyl)benzene (28.0 µL, 0.20 mmol). Purification by column chromatography on silica gel [5% Et_2O in Hexane], afforded the title compound as an pale yellow liquid (22.8 mg, 0.113 mmol, 57% yield); δ_H (400 MHz, $CDCl_3$) 7.83 (d, *J* = 2.3 Hz, 1H, Ar *H*), 7.80 (dd, *J* = 9.7, 1.6 Hz, 1H, Ar *H*), 7.08 (d, *J* = 8.8 Hz, 1H, Ar *H*), 4.00 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 163.5, 131.7 (q, $^3J_{C-F}$ = 3.5 Hz), 131.3 (q, $^3J_{C-F}$ = 3.7 Hz), 123.7 (q, $^2J_{C-F}$ = 34.2 Hz), 123.3 (q, $^1J_{C-F}$ = 271.7 Hz), 115.1, 111.8, 102.7, 56.7; δ_F (376 MHz, $CDCl_3$) -62.09 (s); HRMS (APCI$^+$) $C_9H_7ONF_3$ [M+H]$^+$: Expected 202.0474, Found 202.0468.

The data are in accordance with the literature.[18]

4-Methoxyisophthalonitrile, ***43***

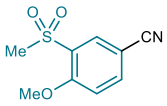


Prepared as described in General Procedure I, using 4-methoxybenzonitrile (26.6 mg, 0.20 mmol). Purification by column chromatography on silica gel [20% EtOAc in Hexane], afforded the title compound as

a white solid (14.2 mg, 0.09 mmol, 45% yield); δ_H (400 MHz, $CDCl_3$) 7.86 (d, *J* = 2.0 Hz, 1H), 7.83 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 4.02 (s, 3H).); δ_C (101 MHz, $CDCl_3$) 164.0, 138.3, 137.7, 117.1, 114.3, 112.5, 105.2, 103.8, 56.9; HRMS (APCI) $C_9H_7ON_2$ $[M+H]^+$: Expected 159.0553, Found 159.0551.

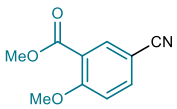
The data are in accordance with the literature.[18]

4-Methoxy-3-(methylsulfonyl)benzonitrile, ***44***



Prepared as described in General Procedure I, using *1-methoxy-2-(methylsulfonyl)benzene* (37.2 mg, 0.20 mmol). Purification by column chromatography on silica gel [40% EtOAc in Hexane], afforded the title compound as a white solid (24.2 mg, 0.114 mmol, 57% yield); m.p. (recrystallized from $CHCl_3$) 160 – 161 °C; δ_H (400 MHz, $CDCl_3$) 8.27 (d, *J* = 2.2 Hz, 1H, Ar *H*), 7.88 (dd, *J* = 8.7, 2.2 Hz, 1H, Ar *H*), 7.16 (d, *J* = 8.7 Hz, 1H, Ar *H*), 4.08 (s, 3H, C*H*$_3$), 3.22 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 160.3 (Ar *C*), 139.4 (Ar *C*H), 134.2 (Ar *C*H), 129.9 (Ar *C*), 117.4 (*C*N), 113.4 (Ar *C*H), 105.0 (Ar *C*), 57.2 (*C*H$_3$), 43.0 (*C*H$_3$); HRMS (APCI$^+$) $C_9H_9O_3NNaS$ $[M+Na]^+$: Expected 234.0195, Found 234.0191; ν_{max} (thin film/cm^{-1}) 773, 1010, 1142, 1285, 1306, 1491, 1603, 2230, 2851, 2930, 3011.

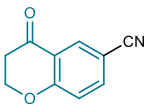
Methyl 5-cyano-2-methoxybenzoate, ***45***



Prepared as described in General Procedure I, using methyl 2-methoxybenzoate (29.0 µL, 0.20 mmol). Purification by column chromatography on silica gel [10% EtOAc in Hexane], afforded the title compound as an off white solid (18.4 mg, 0.096 mmol, 48% yield); δ_H (400 MHz, $CDCl_3$) 8.09 (d, *J* = 2.2 Hz, 1H, Ar *H*), 7.75 (dd, *J* = 8.8, 2.2 Hz, 1H, Ar *H*), 7.05 (d, *J* = 8.8 Hz, 1H, Ar *H*), 3.97 (s, 3H, C*H*$_3$), 3.90 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 164.8, 162.2, 137.3, 136.1, 121.3, 118.3, 112.9, 104.0, 56.6, 52.6; HRMS (APCI$^+$) $C_{10}H_{10}O_3N$ $[M+H]^+$: Expected 192.0655, Found 192.0649.

The data are in accordance with the literature.[19]

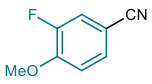
4-Oxochromane-6-carbonitrile, ***46***



Prepared as described in General Procedure J, using 4-chromanone (29.6 mg, 0.20 mmol). Purification by column chromatography on silica gel [10% EtOAc in Hexane], afforded the title compound as a off white amorphous solid (14.2 mg, 0.082 mmol, 41% yield); δ_H (400 MHz, $CDCl_3$) 8.22 (d, *J* = 2.0 Hz, 1H, Ar *H*), 7.70 (dd, *J* = 8.7, 2.2 Hz, 1H, Ar *H*), 7.08 (d, *J* = 8.7 Hz, 1H, Ar *H*), 4.65-4.61 (m, 2H, OCH_2), 2.89-2.86 (m, 2H, CH_2); δ_C (101 MHz, $CDCl_3$) 189.6, 164.5, 138.4, 132.6, 121.7, 119.7, 118.1, 105.5, 67.5, 37.4; HRMS (APCI) $C_{10}H_8O_2N$ $[M+H]^+$: Expected 174.0550, Found 174.0547.

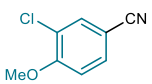
The data are in accordance with the literature.[20]

3-Fluoro-4-methoxybenzonitrile, ***47***



Prepared as described in General Procedure I, using 1-fluoro-2-methoxybenzene (23.0 µL, 0.20 mmol). Purification by column chromatography on silica gel [10% Et_2O in hexane], afforded the title compound as a pale yellow solid (19.5 mg, 0.13 mmol, 65% yield); m.p. (recrystallized from $CHCl_3$) 105 – 107 °C; δ_H (400 MHz, $CDCl_3$) 7.43 (ddd, *J* = 8.5, 2.0, 1.4 Hz, 1H, Ar *H*), 7.36 (dd, *J* = 10.6, 2.0 Hz, 1H, Ar *H*), 7.01 (t, *J* = 8.4 Hz, 1H, Ar *H*), 3.95 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 151.9 (d, J_{C-F} = 10.4 Hz, Ar *C*), 151.8 (d, J_{C-F} = 250.3 Hz, Ar *C*), 129.7 (d, J_{C-F} = 3.9 Hz, Ar *C*H), 119.6 (d, J_{C-F} = 21.4 Hz, Ar *C*H), 118.0 (d, J_{C-F} = 2.5 Hz, *C*N), 113.6 (d, J_{C-F} = 2.5 Hz, Ar *C*H), 104.0 (d, J_{C-F} = 8.3 Hz, Ar *C*), 56.4 (*C*H_3); δ_F (376 MHz, $CDCl_3$) -131.83 – -132.09 (m); HRMS ($APCI^+$) C_8H_7ONF $[M+H]^+$: Expected 152.0506, Found 152.0506; ν_{max} (thin film/cm^{-1}) 760, 816, 1126, 1281, 1516, 1615, 2228, 2599, 2852, 2926, 3064.

3-Chloro-4-methoxybenzonitrile, ***48***

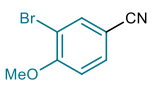


Prepared as described in General Procedure I, using 1-chloro-2-methoxybenzene (25.0 µL, 0.20 mmol). Purification by column chromatography on silica gel [7% Et_2O in hexane], afforded the title compound as a white solid (19.2 mg, 0.114 mmol, 57% yield); δ_H (400 MHz, $CDCl_3$) 7.65 (d, *J* = 2.0 Hz,

1H, Ar *H*), 7.55 (dd, *J* = 8.6, 2.1 Hz, 1H, Ar *H*), 6.98 (d, *J* = 8.5 Hz, 1H, Ar *H*), 3.96 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 158.7, 133.7, 132.6, 123.7, 118.0, 112.3, 104.9, 56.6; HRMS (APCI$^+$) C_8H_7ONCl $[M+H]^+$: Expected 168.0211, Found 168.0205.

The data are in accordance with the literature.[21]

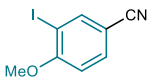
3-Bromo-4-methoxybenzonitrile, ***49***



Prepared as described in General Procedure I, using 1-bromo-2-methoxybenzene (25.0 µL, 0.20 mmol). Purification by column chromatography on silica gel [8% Et_2O in hexane], afforded the title compound as an off white solid (26.5 mg, 0.125 mmol, 62% yield); δ_H (400 MHz, $CDCl_3$) 7.76 (d, *J* = 2.0 Hz, 1H, Ar *H*), 7.53 (dd, *J* = 8.6, 2.1 Hz, 1H, Ar *H*), 6.88 (d, *J* = 8.6 Hz, 1H, Ar *H*), 3.89 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 159.6, 136.8, 133.3, 117.9, 112.5, 112.0, 105.4, 56.7, 29.8; HRMS (APCI$^+$) C_8H_7ONBr $[M+H]^+$: Expected 211.9706, Found 211.9699.

The data are in accordance with the literature.[22]

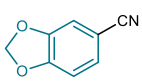
3-Iodo-4-methoxybenzonitrile, ***50***



Prepared as described in General Procedure I, using 1-iodo-2-methoxybenzene (26.0 µL, 0.20 mmol). Purification by column chromatography on silica gel [6% Et_2O in hexane], afforded the title compound as a pale yellow solid (17.1 mg, 0.066 mmol, 33% yield); δ_H (400 MHz, $CDCl_3$) 8.04 (d, *J* = 2.1 Hz, 1H, Ar *H*), 7.63 (dd, *J* = 8.6, 2.0 Hz, 1H, Ar *H*), 6.85 (d, *J* = 8.6 Hz, 1H, Ar *H*), 3.95 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 161.7, 142.9, 134.2, 117.7, 110.8, 106.0, 86.2, 56.9; HRMS (APCI$^+$) C_8H_7ONI $[M+H]^+$: Expected 259.9567, Found 259.9559.

The data are in accordance with the literature.[23]

Benzo[d][1,3]dioxole-5-carbonitrile, ***51***

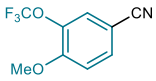


Prepared as described in General Procedure I, using benzo[d][1,3]dioxole (23.0 µL, 0.20 mmol). Purification by column chromatography on silica gel [5% Et_2O in hexane], afforded the title compound as a pale yellow solid (16.4 mg,

0.111 mmol, 56% yield); δ_H (400 MHz, $CDCl_3$) 7.21 (dd, *J* = 8.1, 1.6 Hz, 1H, Ar *H*), 7.03 (d, *J* = 1.6 Hz, 1H, Ar *H*), 6.86 (d, *J* = 8.1 Hz, 1H, Ar *H*), 6.07 (s, 2H, CH_2); δ_C (101 MHz, $CDCl_3$) 151.7, 148.2, 128.4, 119.0, 111.6, 109.3, 105.1, 102.3; HRMS (APCI$^+$) $C_8H_6O_2N$ $[M+H]^+$: Expected 148.0393, Found 148.0387.

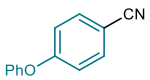
The data are in accordance with the literature.[24]

4-Methoxy-3-(trifluoromethoxy)benzonitrile, ***52***



Prepared as described in General Procedure I, using 1-methoxy-2-(trifluoromethoxy)benzene (38.4 mg, 0.20 mmol). Purification by column chromatography on silica gel [10% Et_2O in hexane], afforded the title compound as a white solid (28.0 mg, 0.129 mmol, 64% yield); m.p. (recrystallized from $CHCl_3$) 56 – 58 °C; δ_H (400 MHz, $CDCl_3$) 7.59 (dd, *J* = 8.6, 2.0 Hz, 1H, Ar *H*), 7.52 (dd, *J* = 2.1, 1.1 Hz, 1H, Ar *H*), 7.06 (d, *J* = 8.6 Hz, 1H, Ar *H*), 3.95 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 156.0 (Ar *C*), 138.1 (q, $^3J_{C-F}$ = 2.1 Hz, Ar *C*), 132.9 (Ar *C*H), 126.7 (Ar *C*H), 120.6 (q, $^1J_{C-F}$ = 259.2 Hz, CF_3) 117.9 (*C*N), 113.5 (Ar *C*H), 104.2 (Ar *C*), 56.5 (CH_3); δ_F (376 MHz, $CDCl_3$) -58.52 (s); HRMS (APCI$^+$) $C_9H_6O_2NF_3Na$ $[M+Na]^+$: Expected 240.0243, Found 240.0243; ν_{max} (thin film/cm^{-1}) 824, 1022, 1173, 1216, 1510, 1610, 2229, 2592, 2857, 2964, 3062.

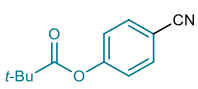
4-Phenoxybenzonitrile, ***53***



Prepared as described in General Procedure I, using oxydibenzene (34.0 mg, 0.20 mmol). Purification by column chromatography on silica gel [3% Et_2O in hexane], afforded the title compound as a pale yellow oil (19.0 mg, 0.097 mmol, 49% yield); δ_H (400 MHz, $CDCl_3$) 7.60 (d, *J* = 8.8 Hz, 2H, Ar *H*), 7.42 (dd, *J* = 8.5, 7.4 Hz, 2H, Ar *H*), 7.23 (t, *J* = 7.4 Hz, 1H, Ar *H*), 7.07 (dd, *J* = 8.6, 1.1 Hz, 2H, Ar *H*), 7.00 (d, *J* = 8.9 Hz, 2H, Ar *H*); δ_C (101 MHz, $CDCl_3$) 161.8, 154.9, 134.3, 130.4, 125.3, 120.6, 119.0, 118.0, 105.9; HRMS (APCI$^+$) $C_{13}H_1ON$ $[M+H]^+$: Expected 196.0757, Found 196.0748.

The data are in accordance with the literature.[25]

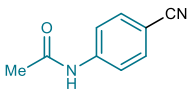
4-Cyanophenyl pivalate, ***54***



Prepared as described in General Procedure I, using phenyl pivalate (35.6 mg, 0.20 mmol). Purification by column chromatography on silica gel [10% Et_2O in hexane], afforded the title compound as a pale yellow oil (9.5 mg, 0.046 mmol, 23% yield); δ_H (400 MHz, $CDCl_3$) 7.70-7.67 (m, 2H), 7.22-7.18 (m, 2H), 1.36 (s, 9H, CH_3); δ_C (101 MHz, $CDCl_3$) 176.4, 154.6, 133.8, 122.8, 118.5, 109.7, 39.4, 27.2; HRMS (APCI) $C_{12}H_{14}O_2N$ $[M+H]^+$: Expected 204.1019, Found 204.1015.

The data are in accordance with the literature.[26]

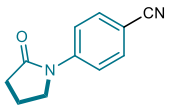
N-(4-Cyanophenyl)acetamide, ***55***



Prepared as described in General Procedure J, using N-phenylacetamide (27.0 mg, 0.20 mmol). Purification by column chromatography on silica gel [30% EtOAc in hexane], afforded the title compound as a white solid (15.5 mg, 0.096 mmol, 48% yield); δ_H (400 MHz, MeOD) 7.75 (d, J = 8.7 Hz, 2H, Ar H), 7.65 (d, J = 8.8 Hz, 2H, Ar H), 2.15 (s, 3H, CH_3); δ_C (101 MHz, MeOD) 172.0, 144.4, 134.2, 120.7, 119.8, 107.5, 24.0; HRMS (ESI^+) $C_9H_9ON_2$ $[M+H]^+$: Expected 161.0709, Found 161.0704.

The data are in accordance with the literature.[27]

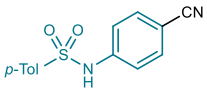
4-(2-Oxopyrrolidin-1-yl)benzonitrile, ***56***



Prepared as described in General Procedure J, using 1-phenylpyrrolidin-2-one (32.2 mg, 0.20 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 25% EtOAc in hexane], afforded the title compound as a off white solid (14.6 mg, 0.078 mmol, 39% yield); δ_H (400 MHz, $CDCl_3$) 7.78 (d, J = 9.2 Hz, 2H, Ar H), 7.63 (d, J = 9.0 Hz, 2H, Ar H), 3.87 (t, J = 7.0 Hz, 2H, CH_2), 2.64 (t, J = 8.1 Hz, 2H, CH_2), 2.26 – 2.14 (m, 2H, CH_2); δ_C (101 MHz, $CDCl_3$) 174.9, 143.3, 133.1, 119.3, 119.0, 107.2, 48.4, 32.9, 17.9; HRMS ($APCI^+$) $C_{11}H_{11}ON_2$ $[M+H]^+$: Expected 187.0866, Found 187.0861;

The data are in accordance with the literature.[28]

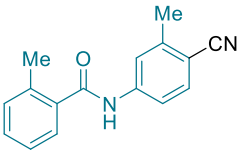
N-(4-Cyanophenyl)-4-methylbenzenesulfonamide, ***57***



Prepared as described in General Procedure J, using 4-methyl-N-phenylbenzenesulfonamide (51.0 mg, 0.20 mmol). Purification by column chromatography on silica gel [*gradient* from hexane to 20% EtOAc in hexane], afforded the title compound as a off white solid (28.1 mg, 0.103 mmol, 52% yield); δ_H (400 MHz, $CDCl_3$) 7.75 (d, *J* = 8.4 Hz, 2H, Ar *H*), 7.56 (br s, 1H, N*H*), 7.52 (d, *J* = 8.9 Hz, 2H, Ar *H*), 7.28 (d, *J* = 8.0 Hz, 2H, Ar *H*), 7.17 (d, *J* = 8.9 Hz, 2H, Ar *H*), 2.40 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 145.0, 141.1, 135.6, 133.7, 130.2, 127.4, 119.4, 118.6, 107.8, 21.8; HRMS (ESI$^-$) $C_{14}H_{11}O_2N_2S$ $[M-H]^-$: Expected 271.0547, Found 271.0544;

The data are in accordance with the literature.[29]

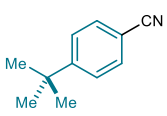
N-(4-Cyano-3-methylphenyl)-2-methylbenzamide, ***58***



Prepared as described in General Procedure J, using 10-(2-methyl-4-(2-methylbenzamido)phenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (574 mg, 1.0 mmol), the crude product was purified by column chromatography [*gradient* from hexane to 20% EtOAc in Hexane] yielding the desired product (128 mg, 0.51 mmol, 51%) as an pale yellow crystalline solid; m.p. (recrystallized from CH_2Cl_2/Et_2O) 182 – 183 °C; δ_H (400 MHz, $CDCl_3$) 7.78 (brs, 1H, N*H*), 7.71 (s, 1H, Ar *H*), 7.58 (d, *J* = 8.4 Hz, 1H, Ar *H*), 7.54 – 7.46 (m, 2H, Ar *H*), 7.41 (t, *J* = 7.5 Hz, 1H, Ar *H*), 7.33 – 7.24 (m, 2H, Ar *H*), 2.56 (s, 3H, C*H*$_3$), 2.51 (s, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 168.4 (*C*=O), 143.7 (Ar *C*), 142.0 (Ar *C*), 136.9 (Ar *C*), 135.7 (Ar *C*), 133.7 (Ar *C*H), 131.6 (Ar *C*H), 131.0 (Ar *C*H), 126.7 (Ar *C*H), 126.1 (Ar *C*H), 120.7 (Ar *C*H), 118.3 (*C*N), 117.2 (Ar *C*H), 108.0 (Ar *C*), 20.8 (*C*H$_3$), 20.0 (*C*H$_3$); HRMS (ESI$^+$) $C_{16}H_{14}ON_2Na$ $[M+Na]^+$: Expected 273.0998, Found 273.0992; ν_{max} (thin film/cm^{-1}) 657, 739, 1252, 1316, 1520, 1583, 1664, 2220, 2926, 2962, 3100, 3297.

58 was further characterised by X-ray crystallographic analysis. CCDC : 2122517.

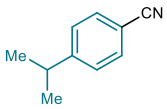
4-(tert-Butyl)benzonitrile, ***59***



Prepared as described in General Procedure I, using *tert*-butylbenzene (31.0 µL, 0.20 mmol). Purification by column chromatography on silica gel [1% Et_2O in hexane], afforded the title compound as a pale yellow oil (16.5 mg, 0.104 mmol, 52% yield); δ_H (400 MHz, $CDCl_3$) 7.59 (d, *J* = 8.6 Hz, 2H, Ar *H*), 7.48 (d, *J* = 8.6 Hz, 2H, Ar *H*), 1.33 (s, 9H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 156.8, 132.1, 126.3, 119.3, 109.4, 35.4, 31.1; HRMS (APCI$^+$) $C_{11}H_{14}N$ $[M+H]^+$: Expected 160.1121, Found 160.1115.

The data are in accordance with the literature.[30]

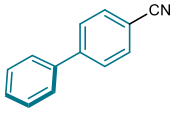
4-iso-Propylbenzonitrile, ***60***



Prepared as described in General Procedure I, using cumene (28.0 µL, 0.20 mmol). Purification by column chromatography on silica gel [1% Et_2O in hexane], afforded the title compound as a colourless oil (12.9 mg, 0.088 mmol, 44% yield); δ_H (500 MHz, $CDCl_3$) 7.58 (d, *J* = 8.4 Hz, 2H, Ar, *H*), 7.32 (d, *J* = 8.1 Hz, 2H, Ar *H*), 2.96 (hept, *J* = 7.0 Hz, 1H, C*H*), 1.26 (d, *J* = 6.9 Hz, 6H, 2 x C*H*$_3$); δ_C (126 MHz, $CDCl_3$) 154.5, 132.4, 127.4, 119.3, 109.8, 34.5, 23.7; HRMS (APCI$^+$) $C_{10}H_{12}N$ $[M+H]^+$: Expected 146.0964, Found 146.0961.

The data are in accordance with the literature.[31]

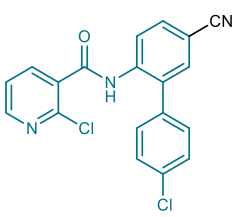
[1,1'-Biphenyl]-4-carbonitrile, ***61***



Prepared as described in General Procedure I, using 1,1'-biphenyl (31.0 mg, 0.20 mmol). Purification by column chromatography on silica gel [1% Et_2O in hexane], afforded the title compound as a white solid (15.3 mg, 0.085 mmol, 43% yield); δ_H (400 MHz, $CDCl_3$) 7.73 (d, *J* = 8.6 Hz, 2H, Ar *H*), 7.69 (d, *J* = 8.6 Hz, 2H, Ar *H*), 7.59 (d, *J* = 6.9 Hz, 2H, Ar *H*), 7.53 – 7.45 (m, 2H, Ar *H*), 7.53 – 7.39 (m, 1H, Ar *H*); δ_C (101 MHz, $CDCl_3$) 145.8, 139.3, 132.7, 129.3, 128.8, 127.9, 127.4, 119.1, 111.1; HRMS (APCI$^+$) $C_{13}H_{10}N$ $[M+H]^+$: Expected 180.0808, Found 180.0801.

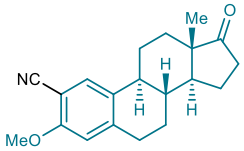
The data are in accordance with the literature.[32]

2-Chloro-N-(4'-chloro-5-cyano-[1,1'-biphenyl]-2-yl)nicotinamide, ***63***



Prepared as described in General Procedure H, using 10-(4'-chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (138 mg, 0.20 mmol), the crude product was purified by column chromatography [*gradient* from hexane to 40% EtOAc in Hexane] yielding the desired product (31.7 mg, 0.09 mmol, 43%) as an pale yellow amorphous solid; δ_H (400 MHz, $CDCl_3$) 8.74 (d, *J* = 8.6 Hz, 1H, Ar *H*), 8.47 (dd, *J* = 4.7, 1.9 2H, Ar *H,* N*H*), 8.21 (dd, *J* = 7.7, 1.9 Hz, 2H, Ar *H*), 7.73 (dd, *J* = 8.6, 1.9 Hz, 2H, Ar *H*), 7.54 (d, *J* = 1.9 Hz, 1H, Ar *H*), 7.50 (d, *J* = 8.4 Hz, 2H, Ar *H*), 7.39 (dd, *J* = 7.7, 4.7 Hz, 1H, Ar *H*), 7.32 (d, *J* = 8.3 Hz, 2H, Ar *H*); δ_C (101 MHz, $CDCl_3$) 162.6 (*C*=O), 152.1 (Ar *C*H), 146.6 (Ar *C*), 140.9 (Ar *C*H), 138.9 (Ar *C*), 135.9 (Ar *C*), 133.9 (Ar *C*H), 133.1 (Ar *C*H), 132.1 (Ar *C*), 130.8 (Ar *C*H), 130.3 (Ar *C*), 130.0 (Ar *C*H), 123.3 (Ar *C*H), 121.4 (Ar *C*H), 118.5 (*C*N), 108.3 (Ar *C*); HRMS (APCI) $C_{19}H_{12}ON_3Cl_2$ $[M+H]^+$: Expected 368.0352, Found 368.0357; ν_{max} (thin film/cm^{-1}) 732, 835, 1091, 1310, 1400, 1513, 1581, 1681, 2229, 2853, 2926, 3066, 3273, 3370.

(8R,9S,13S,14S)-2-Isocyano-3-methoxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one, ***65***

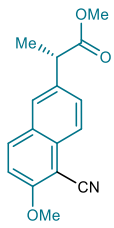


Prepared as described in General Procedure H, using 10-((8R,9S,13S,14S)-3-methoxy-13-methyl-17-oxo-7, 8, 9, 11, 12, 13, 14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (127 mg, 0.20 mmol), the crude product was purified by column chromatography [*gradient* from hexane to 15% EtOAc in Hexane] yielding the desired product (19.6 mg, 0.063 mmol, 32%) as an light brown amorphous solid; δ_H (400 MHz, $CDCl_3$) 7.44 (s, 1H, Ar *H*), 6.67 (s, 1H, Ar *H*), 3.88 (s, 3H, OCH_3), 2.96-2.93 (m, 2H, Alk CH_2), 2.51 (ddd, *J* = 19.0, 8.8, 0.9 Hz, 1H, Alk C*H*), 2.37-2.33 (m, 1H, Alk C*H*), 2.26-1.96 (m, 5H, Alk CH_2 & Alk C*H*), 1.67-1.40 (m,

6H, Alk CH_2 & Alk CH), 0.91 (s, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 220.3, 159.0, 144.1, 132.8, 130.7, 117.0, 111.5, 99.1, 55.9, 50.3, 47.9, 43.5, 37.9, 35.8, 31.4, 30.2, 26.1, 25.7, 21.5, 13.8; HRMS (ESI$^+$) $C_{20}H_{23}O_2NNa$ $[M+Na]^+$: Expected 332.1621, Found 332.1606.

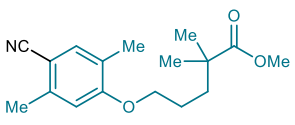
The data are in accordance with the literature.[33]

Methyl (S)-2-(5-cyano-6-methoxynaphthalen-2-yl)propanoate, ***67***



Prepared as described in General Procedure H, using (*S*)-10-(2-methoxy-6-(1-methoxy-1-oxopropan-2-yl)naphthalen-1-yl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (119 mg, 0.20 mmol), the crude product was purified by column chromatography [15% EtOAc in Hexane] yielding the desired product (24.2 mg, 0.09 mmol, 45%) as a pale yellow liquid; δ_H (400 MHz, $CDCl_3$) 8.03 (ddd, *J* = 20.5, 9.1, 0.8 Hz, 2H, Ar *H*), 7.73 (d, *J* = 1.8 Hz, 1H, Ar *H*), 7.60 (dd, *J* = 8.7, 1.8 Hz, 1H, Ar *H*), 7.27 (d, *J* = 9.2 Hz, 1H, Ar *H*), 4.06 (s, 3H, CH_3), 3.88 (q, *J* = 7.1 Hz, 1H, C*H*), 3.68 (s, 3H, CH_3), 1.59 (d, *J* = 7.2 Hz, 3H, CH_3); δ_C (101 MHz, $CDCl_3$) 174.7 (*C*=O), 161.6 (Ar *C*), 137.4 (Ar *C*), 134.9 (Ar *C*H), 132.8 (Ar *C*), 129.3 (Ar *C*H), 128.1 (Ar *C*), 126.6 (Ar *C*H), 124.6 (Ar *C*H), 115.6 (*C*N), 112.4 (Ar *C*H), 95.2 (Ar *C*), 56.7 (*C*H_3), 52.2 (*C*H_3), 45.2 (*C*H), 18.5 (*C*H_3), HRMS (ESI$^+$) $C_{16}H_{15}O_3NNa$ $[M+Na]^+$: Expected 292.0944, Found 292.0934; ν_{max} (thin film/cm^{-1}) 808, 828, 1037, 1087, 1159, 1261, 1281, 1596, 1733, 2221, 2852, 2925, 2979.

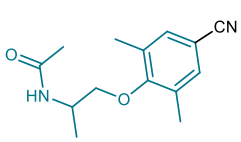
Methyl 5-(4-cyano-2,5-dimethylphenoxy)-2,2-dimethylpentanoate, ***69***



Prepared as described in General Procedure H, using 10-(4-((5-methoxy-4,4-dimethyl-5-oxopentyl)oxy)-2,5-dimethylphenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (123 mg, 0.20 mmol), the crude product was purified by column chromatography [*gradient* from Hexane to 10% EtOAc in hexane] yielding the desired product (32.1 mg, 0.09 mmol, 44%) as a colourless amorphous solid; δ_H (400 MHz, $CDCl_3$) 7.31 (s, 1H, Ar *H*), 6.64 (s, 1H, Ar *H*), 3.95 (t, *J* = 5.9 Hz, 2H, CH_2), 3.66 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 1.81 – 1.66 (m, 4H, 2 x CH_2), 1.22 (s,

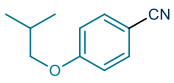
6H, 2 x C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 178.2 (*C*=O), 160.4 (Ar *C*), 141.9 (Ar *C*), 134.1 (Ar *C*H), 125.4 (Ar *C*), 119.0 (*C*N), 112.2 (Ar *C*H), 103.6 (Ar *C*), 68.3 (*C*H$_2$), 51.9 (*C*H$_2$), 42.2 (q*C*), 37.0 (C*H*$_2$), 25.3 (C*H*$_3$), 25.0 (*C*H$_2$), 20.7 (*C*H$_3$), 15.7 (*C*H$_3$); HRMS (APCI) $C_{17}H_{24}O_3N$ $[M+H]^+$: Expected 290.1751, Found 290.1744 ; ν_{max} (thin film/cm^{-1}) 847, 1090, 1146, 1209, 1259, 1324, 1610, 1729, 2217, 2874, 2928, 2951.

N-(1-(4-Cyano-2,6-dimethylphenoxy)propan-2-yl)acetamide, ***71***



Prepared as described in General Procedure H, using 10-(4-(2-acetamidopropoxy)-3,5-dimethylphenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate (114 mg, 0.20 mmol) the crude product was purified by column chromatography [*gradient* from 50% EtOAc in Hexane to EtOAc] yielding the desired product (20.7 mg, 0.08 mmol, 42%) as an off-white amorphous solid; δ_H (400 MHz, $CDCl_3$) 7.31 (s, 2H, Ar *H*), 5.85 (brd, *J* = 6.7 Hz, 3H, N*H*), 4.41 – 4.30 (m, 2H, C*H*), 3.80 (dd, *J* = 9.0, 4.3 Hz, 1H, C*H*$_2$), 3.74 (dd, *J* = 9.0, 3.2 Hz, 1H, C*H*$_2$), 2.27 (s, 6H, 2 x C*H*$_3$), 2.02 (s, 3H, C*H*$_3$), 1.39 (d, *J* = 6.9 Hz, 3H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 169.7 (*C*=O), 159.0 (Ar *C*), 133.1 (Ar *C*H), 132.6 (Ar *C*), 119.0 (*C*N), 107.8 (Ar *C*), 74.3 (*C*H$_2$), 45.5 (*C*H), 23.5 (*C*H$_3$), 17.7 (*C*H$_3$), 16.2 (*C*H$_3$); HRMS (APCI) $C_{14}H_{19}O_2N_2$ $[M+H]^+$: Expected 247.1441, Found 247.1441 ; ν_{max} (thin film/cm^{-1}) 882, 1010, 1141, 1221, 1303, 1544, 1652, 2224, 2878, 2930, 2975, 3067, 3291.

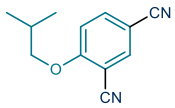
4-Isobutoxybenzonitrile, ***73***



Prepared as described in General Procedure H, using Sulfonium salt mixture **SS8** (*p:o* = 77:23) (100 mg, 0.20 mmol), the crude product was purified by column chromatography [5% EtOAc in Hexane] yielding the desired product (15.9 mg, 0.09 mmol, 45%) as an colorless oil; δ_H (400 MHz, $CDCl_3$) 7.59-7.55 (m, 2H, Ar *H*), 6.95-6.91 (m, 2H, Ar *H*), 3.76 (d, *J* = 6.5 Hz, 2H, OC*H*$_2$), 2.17-2.03 (m, 1H, C*H*), 1.03 (d, *J* = 6.7 Hz, 6H, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 162.7 (Ar *C*), 134.1 (Ar *C*H), 119.5 (*C*N), 115.3 (Ar *C*H), 103.8 (Ar *C*), 74.8 (O*C*H$_2$), 28.3 (*C*H), 19.3 (*C*H$_3$); HRMS

(ESI$^+$) $C_{11}H_{13}ONNa$ $[M+Na]^+$: Expected 198.0889, Found 198.0881; ν_{max} (thin film/cm^{-1}) 752, 832, 998, 1020, 1169, 1254, 1298, 1469, 1507, 1604, 2223, 2874, 2927, 2960.

4-Isobutoxyisophthalonitrile, ***74***



Prepared as described in General Procedure I, using *4-isobutoxybenzonitrile* (35 mg, 0.20 mmol), the crude product was purified by column chromatography [20% EtOAc in Hexane] yielding the desired product (13.6 mg, 0.07 mmol, 34%) as an off white solid; δ_H (400 MHz, $CDCl_3$) 7.85 (d, *J* = 2.0 Hz, 1H, Ar *H*), 7.79 (dd, *J* = 8.9, 2.1 Hz, 1H, Ar *H*), 7.04 (d, *J* = 8.9 Hz, 1H), 3.91 (d, *J* = 6.4 Hz, 2H, OC*H*$_2$), 2.26-2.16 (m, 1H, C*H*), 1.08 (d, *J* = 6.8 Hz, 6H); δ_C (101 MHz, $CDCl_3$) 163.7, 138.2, 137.7, 117.2, 114.3, 113.2, 104.8, 103.9, 76.2, 28.2, 19.1; HRMS (APCI) $C_{12}H_{13}ON_2$ $[M+H]^+$: Expected 201.1022, Found 201.1018.

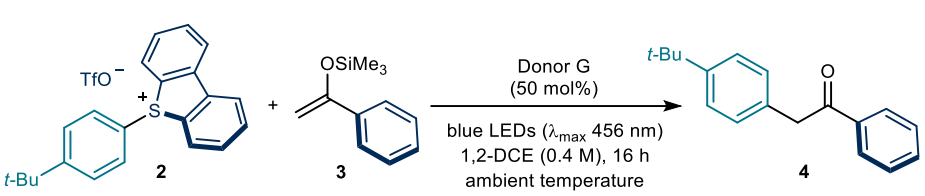
The data are in accordance with the literature.[34]

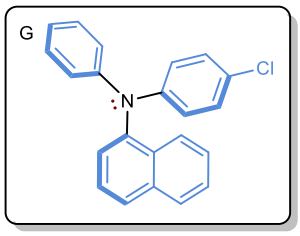
Mechanistic Studies

Control Experiments – Alpha Arylation

Control experiments were conducted (Supplementary Table 7). When performing the reaction in the absence of donor, a small amount of product formation is observed, presumably from the direct excitation of sulfonium salt **2**. This was confirmed by irradiation of a solution of the salt **2** in 1,2-DCE overnight, after which 82% of the salt **2** was recovered (Entries 1-2). Running the reaction in the dark led to no formation of the product, even at elevated temperature, with quantitative salt **2** remaining by NMR (Entries 3 - 4). When run in the presence of an excess of TEMPO free radical, a negligible amount of product formation was observed by NMR (Entry 5). When irradiated by green light (λ_{max} = 525 nm), 8% product formed after 16 h (Entry 6).

Supplementary Table 7. Control experiments for the photochemical arylation of silyl enol ethers





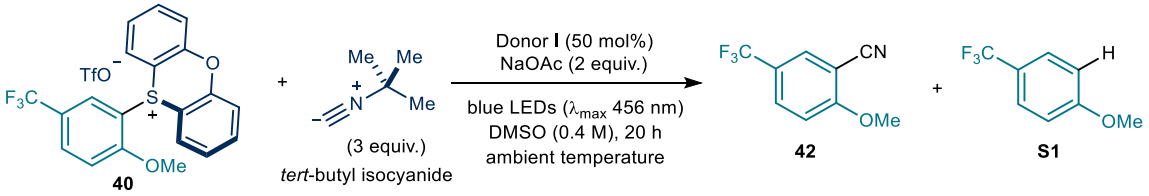
Entry	Solvent	Donor	Notes	Yield (%)[a]
1	1,2-DCE	-	Absence of Donor	34
2	1,2-DCE	-	Only **2** in 1,2-DCE	82[b]
3	1,2-DCE	G	No irradiation	-
4	1,2-DCE	G	No irradiation, 60°C	-
5	1,2-DCE	G	In precense of 2 eq. TEMPO	<5
6	1,2-DCE	G	Irradiated with Green light (λ_{max} = 525 nm)	8

[a]Determined by ^{1}H NMR using mesitylene as internal standard. [b]Recovered yield of sulfonium salt **2**.

Control Experiments – C-H Cyanation

Control experiments were conducted (Supplementary Table 8). When performing the reaction in the absence of donor, a small amount of product formation occurs, presumably from the direct excitation of sulfonium salt **40** (Entry 1). The reaction was highly inefficient in the absence of base, with the hydrogenated side-product **S1** (21%) forming as a major product compared to **42** (6%) (Entry 2). Running the reaction in the dark led to no formation of the product (Entry 3).

Supplementary Table 8. Control experiments for the photochemical C-H cyanation



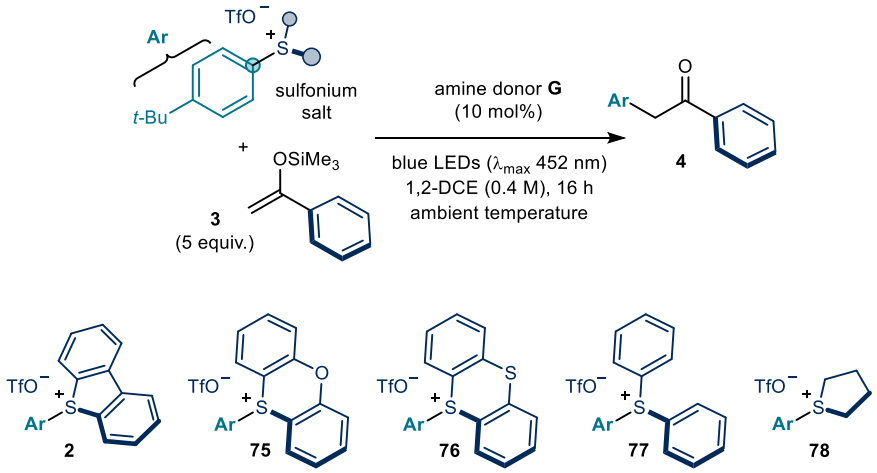
Entry	Deviation	Yield (%)[a]
1	Absence of Donor **I**	**42** (17) + **S1** (trace)
2	Absence of NaOAc	**42** (6) + **S1** (21)
3	No irradiation	-

[a]Determined by ^{1}H NMR using CH_2Br_2 as internal standard.

Different Salt trials

An array of different sulfonium salts were trialled in the arylation of silyl enol ethers to assess the effects of the salt on the reaction. It was found that non-aromatic sulfonium salt **78** and non-bridged salt **77** were poor substrates in the reaction (Entry 4-5). The salts of thianthrene **76**, dibenzothiophene **2** and phenoxathiine **75** all underwent reaction successfully (Entries 1-3) but dibenzothiophene gave the highest yield with the *tert*-butyl benzene aryl unit used to optimise the process.

Supplementary Table 9. Variation of the triarylsulfonium salt



Entry	Solvent	Donor	Sulfonium Salt	Yield (%)[a]
1	1,2-DCE	G	**2**	57 (63)
2	1,2-DCE	G	**75**	51
3	1,2-DCE	G	**76**	40
4	1,2-DCE	G	**77**	5
5	1,2-DCE	G	**78**	<5

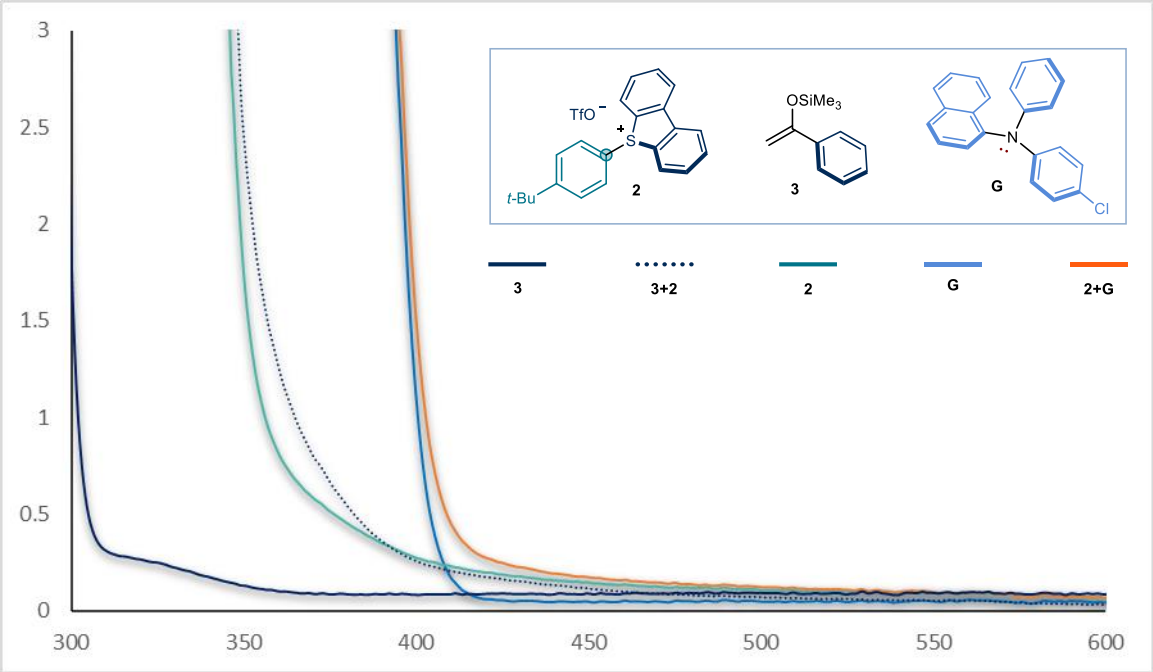
[a]Determined by ^{1}H NMR using mesitylene as internal standard. Isolated yield in parenthesis.

UV/Vis Spectroscopy

UV/Vis analyses were conducted on a Mettler Toledo UV5Bio Spectrophotometer using a 1 cm path length quartz cuvette.

Alpha Arylation of Silyl enol ethers

Absorption spectra of each of the individual components were run at a concentration of 0.04 M, followed by mixtures of different components in the reaction mixture in an attempt to show a shift in absorbance caused by the formation of an EDA complex between the sulfonium salt **2** and donor **G**.



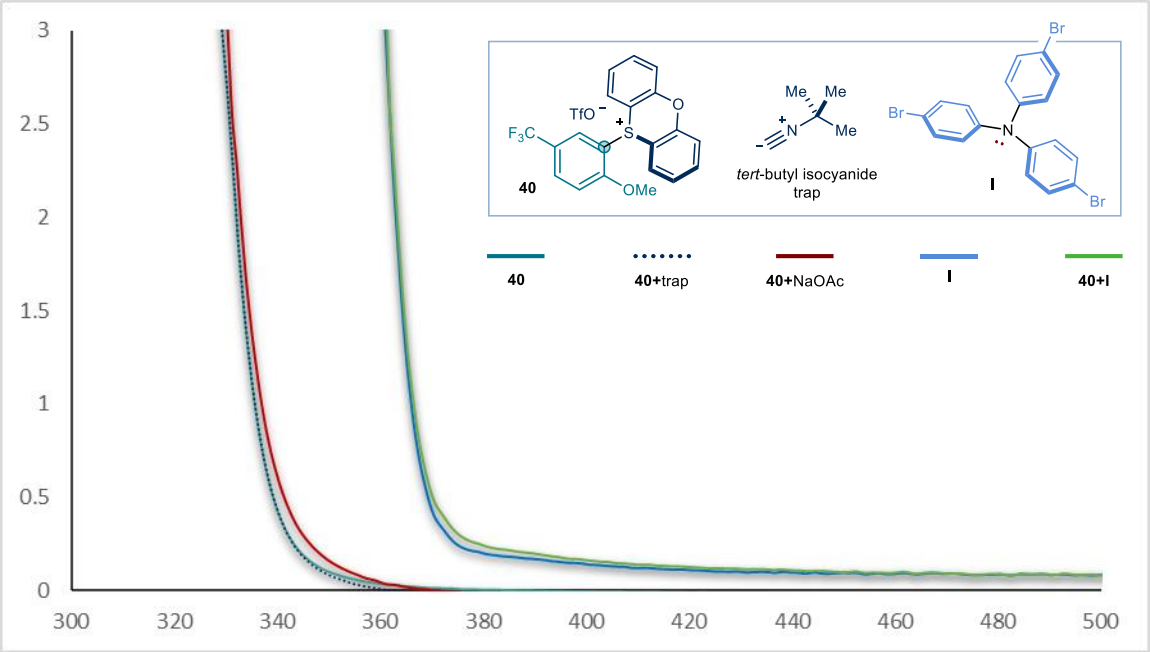
Supplementary Figure 1. UV/Vis spectra of components and mixtures of components of the photochemical alpha arylation of silyl enol ethers.

From the spectra obtained, a shift in the absorbance can be seen between 400 and 450 nm, with absorbance of the mixture of **2** and donor **G** continuing well into the visible region. It is also evident that the salt by itself can also absorb in this region to a lesser extent, which would explain the formation of a small amount of product in the absence of any donor.

C-H Cyanation

Absorption spectra of each of the individual components were run at a concentration of 0.04 M, followed by mixtures of different components in the reaction mixture in an

attempt to show a shift in absorbance caused by the formation of an EDA complex between the sulfonium salt **40** and donor **I**.



Supplementary Figure 2. UV/Vis spectra of components and mixtures of components of the photochemical C-H cyanation reaction

From the spectra obtained a slight shift in the absorbance can be seen around 370 nm, with the absorbance of the mixture of **40** and donor **I** continuing well into the visible region. In this case the salt **40** does not have any absorbance in the visible region on its own, however the donor **I** does absorb well in the region.

Quantum Yield Measurements

General Experimental Details

Samples were irradiated using a 34W Kessil blue LED bulb set to 25% intensity, with the reaction tube placed exactly 2 cm from the bulb. The quantum yield was calculated following procedures previously reported.[36,37] The ferrioxalate actinometer solution decomposes from ferric to ferrous ions upon irradiation, the ferrous ions are then complexed with 1,10-phenanthroline and the UV/Vis absorbance of the complex is monitored at 510 nm. The moles of complex formed are related to the moles of photons absorbed.

Solutions Needed

Ferrioxalate solution (A)

In a darkened room, potassium ferrioxalate ($K_3FeC_2O_4.3H_2O$, 147 mg, 0.30 mmol) was added to a 25 mL volumetric flask. H_2O (HPLC grade, 20 mL) was added followed by H_2SO_4 (95% w/w, 70 µL), H_2O was then added until the graduation mark was reached and the solution allowed to equilibrate for 30 min. The solution was wrapped in aluminium foil and stored in the dark.

Phenanthroline solution (B)

Phenanthroline (50 mg, 0.28 mmol) was added to a 25 mL volumetric flask and H_2O was added until the solution reached the graduation mark. The solution was allowed to equilibrate for 30 min.

Buffer solution (C)

NaOAc (1.24 g, 12.5 mmol) was added to a 25 mL volumetric flask. H_2O (HPLC grade, 20 mL) was added followed by H_2SO_4 (95% w/w, 250 µL), H_2O was then added until the graduation mark was reached and the solution allowed to equilibrate for 30 min.

Measurements

Photon Flux measurement/Actinometry

In a darkened room, a microwave vial was charged with 0.5 mL of solution A and irradiated for 5 s. After irradiation, the solution was immediately transferred to a 5 mL volumetric flask containing 0.25 mL solution B and 1 mL solution C. H_2O (HPLC grade) was added until the graduation mark was reached. This was repeated 2 more times, irradiating for 10 s and 15 s. A control sample was also made, where 0.5 mL solution A was added directly to a 5 mL volumetric flask containing 0.25 mL solution B and 1 mL solution C without irradiation. H_2O (HPLC grade) was added until the graduation mark was reached. The UV/Vis spectra of the samples were then taken

(blank sample = 1 mL solution C in 4 mL H_2O) and the absorbance measured at 510 nm.

Conversion was calculated using eq. 1:

$$mol\ Fe^{2+} = \frac{V\ \Delta A}{l\ \varepsilon} \qquad (1)$$

V = total volume (0.005 L)

ΔA = difference in absorbance between the irradiated and non-irradiated solutions

l = path length (1 cm)

ε = molar absorptivity at 510 nm (11100 L mol^{-1} cm^{-1})

Photon Flux was calculated using eq. 2:

$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi\ t\ f} \qquad (2)$$

Φ = quantum yield for the ferrioxalate actinometer (1.11 at 436 nm – Hatchard Parker 56)

t = time

f = fraction of light absorbed by ferrioxalate at 456 nm (0.3253, calculation shown below)

The moles of Fe^{2+} were plotted as a function of time allowing the slope of the graph to be used to represent $\frac{mol Fe^{2+}}{t}$, this was determined to be 6 x 10^{-8} mol s^{-1} (Average of three experiments). The photon flux was then calculated to be 1.66 x 10^{-7} einstein s^{-1} (Average of three experiments).

Fraction of light absorbed (f) by ferrioxalte measurement

In a darkened room, a quartz cuvette was charged with solution A directly. The UV/Vis spectrum of the sample was taken and the absorbance at 456 nm measured. The fraction of light absorbed was calculated using eq. 3:

$$fraction\ of\ light\ absorbed = 1 - 10^{-A} \quad (3)$$

A = absorbance of the actinometer at 456 nm (0.170).

Photochemical Arylation of Silyl eno ethers

The photochemical arylation was performed in a darkened room; An oven-dried microwave vial was charged with sulfonium salt **2** (93 mg, 0.20 mmol) and donor **G** (6.6 mg, 0.02 mmol) and sealed. The vial was evacuated and flushed with nitrogen x 3. Anhydrous 1,2-DCE (0.5 mL) was added under nitrogen, followed by silyl enol ether **3** (205 µL, 1.00 mmol). The reaction was placed 2 cm from a 34W Kessil blue LED bulb set to 25% intensity and irradiated for 2 h. After irradiation, the reaction was diluted with CH_2Cl_2 and concentrated in vacuo. The moles of product molecule **4** formed was quantified by ^{1}H NMR using mesitylene as an internal standard and this was used to calculate the quantum yield using a modified eq 2.

$$\Phi = \frac{mol\ product}{flux\ t\ f} \quad (2)$$

mol product = 5.33 x 10^{-5} mol (26.5% conversion, average of two experiments)

t = reaction time (7200 s)

f = fraction of light absorbed by reaction mixture at 456 nm (0.9 based on an absorbance of 1)

Φ based on this was calculated to be 0.05.

Photochemical C-H Cyanation Reaction

The photochemical cyanation reaction was performed in a darkened room; An oven-dried microwave vial was charged with sulfonium salt **40** (105 mg, 0.20 mmol) and donor **I** (16.5 mg, 0.05 mmol) and sealed. The vial was evacuated and flushed with nitrogen x 3. Anhydrous DMSO (0.5 mL) was added under nitrogen, followed by *tert*-butyl isonitrile (68 µL, 0.6 mmol) and 2,6-lutidine (46 µL, 0.4 mmol). The reaction was placed 2 cm from a 34W Kessil blue LED bulb set to 25% intensity and irradiated for 4

h. After irradiation the reaction was quenched with H_2O and extracted with EtOAc x 2. The combined organic layers were concentrated in vacuo. The moles of product formed was quantified by ^1H NMR using bromomethane as an internal standard and this was used to calculate the quantum yield using a modified eq 2.

$$\Phi = \frac{mol\ product}{flux\ t\ f} \qquad (2)$$

mol product = 6.03 x 10^{-5} mol (30.2% conversion, average of two experiments)

t = reaction time (14400 s)

f = fraction of light absorbed by reaction mixture at 456 nm (0.33 based on an absorbance of 0.174)

Φ based on this was calculated to be 0.08.

X-Ray Structures

Data Collection

X-ray data was collected at a temperature of 100 K on a Rigaku FR-X DW rotating anode diffractometer using CuKα radiation, (λ = 1.54184 Å) with an AFC-11 RINC goniometer and a Hypix 60000HE detector.

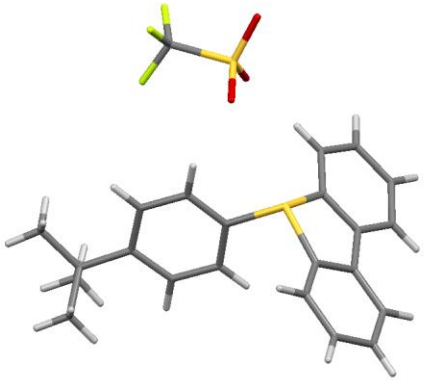
The diffractometer was equipped with an Oxford Cryosystems Cryostream 800 plus nitrogen flow gas system.

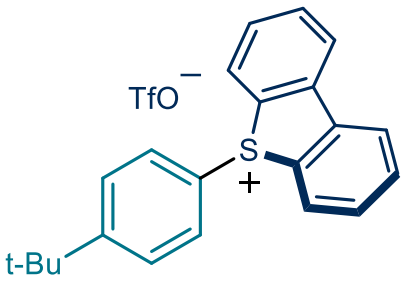
Crystal structure determinations and refinements

X-ray data were collected and reduced using CrysAlisPro v41.[38] Absorption correction was performed using empirical methods (SCALE3 ABSPACK) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles. The crystal structures were solved using ShelXT and refined against all F^2 values using the SHELXL implemented through Olex2.[39,40] 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. 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 **2** – CCDC: 2120242



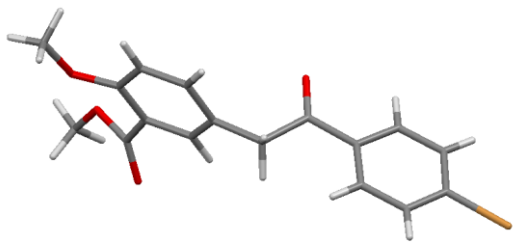


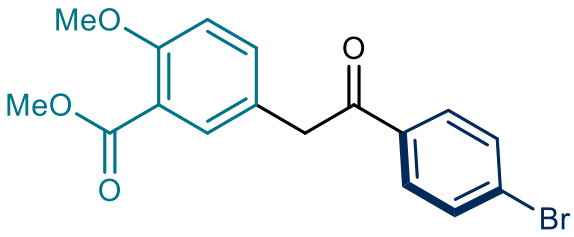
Supplementary Table 10 Crystal data and structure refinement for **2**

Identification code	*5-(4-(tert-butyl)phenyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate*
Empirical Formula	$C_{22}H_{21}F_3O_3S_2$
Formula weight	466.52
Temperature/K	100
Crystal system	Monoclinic
Space group	P 21/n
a/Å	13.9217(4)
b/Å	8.7768(2)
c/Å	19.0992(6)
α/°	90
β/°	107.872(3)
γ/°	90
Volume/Å^3	2221.11(11)
Z	4
P_{calc}g/cm^3	1.395
μ/mm^{-1}	2.598
F(000)	968.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.7018 to 151.3480
Index ranges	-17 ≤ h ≤ 16, -10 ≤ k ≤ 10, -23 ≤ l ≤ 23
Reflections collected	10642

Independent reflections	4461
Data/restraints/parameters	4461/0/283
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1= 0.0832 wR_2= 0.2311
Final R indexes [all data]	R_1= 0.0797 wR_2= 0.2252

X-ray structure of **27** – CCDC: 2120244



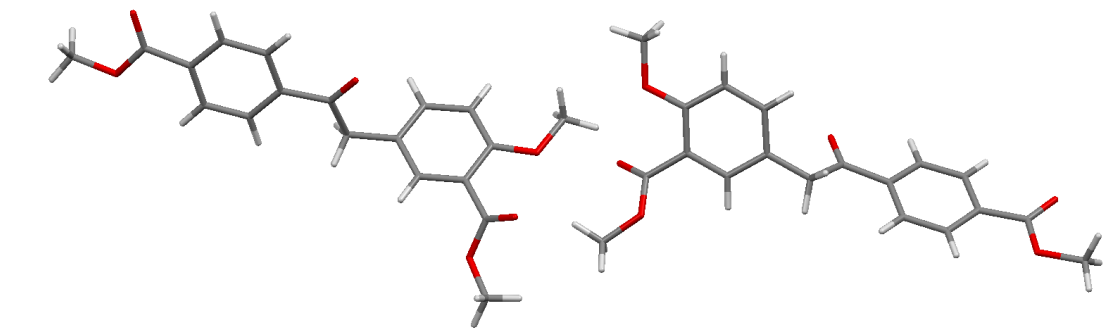


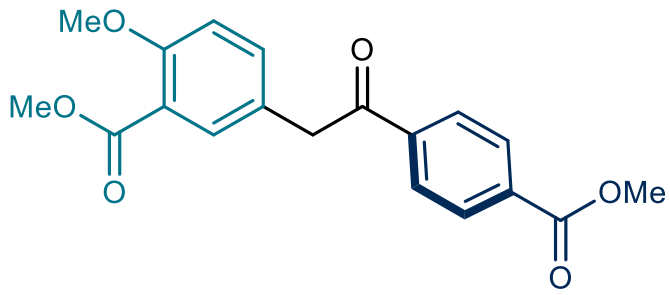
Supplementary Table 11 Crystal data and structure refinement for **27**

Identification code	*methyl 5-(2-(4-bromophenyl)-2-oxoethyl)-2-methoxybenzoate*
Empirical Formula	$C_{17}H_{15}BrO_4$
Formula weight	363.21
Temperature/K	100
Crystal system	monoclinic
Space group	P 21/c
a/Å	15.9281(5)
b/Å	12.1587(4)
c/Å	7.8047(3)
α/°	90
β/°	97.137(3)
γ/°	90
Volume/$Å^3$	1499.79(9)
Z	4
P_{calc} g/cm^3	1.609
μ/mm^{-1}	3.882
F(000)	736.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.5520 to 151.5720

Index ranges	-20 ≤ h ≤ 19, -15 ≤ k ≤ 15, 0 ≤ l ≤ 9
Reflections collected	3101
Independent reflections	2762
Data/restraints/parameters	2762/0/202
Goodness-of-fit on F^2	1.156
Final R indexes [I>=2σ (I)]	R_1= 0.0557 wR_2= 0.1482
Final R indexes [all data]	R_1= 0.0609 wR_2= 0.1509

X-ray structure of **29** – CCDC: 2120243



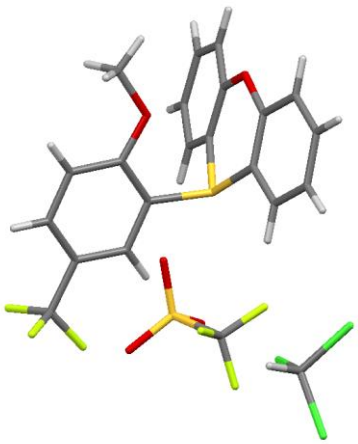


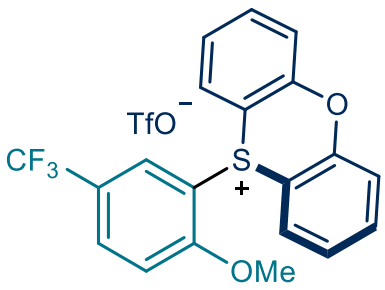
Supplementary Table 12 Crystal data and structure refinement for **29**

Identification code	*methyl 2-methoxy-5-(2-(4-(methoxycarbonyl)phenyl)-2-oxoethyl)benzoate*
Empirical Formula	$C_{19}H_{18}O_6$
Formula weight	342.33
Temperature/K	100
Crystal system	Triclinic

Space group	P -1
a/Å	8.0154(6)
b/Å	10.2380(6)
c/Å	20.2520(12)
α/°	95.642(5)
β/°	96.833(5)
γ/°	90.381(5)
Volume/Å^3	1641.83(19)
Z	4
P_{calc}g/cm^3	1.385
μ/mm^{-1}	0.863
F(000)	720.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.4140 to 148.9640
Index ranges	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -25 ≤ l ≤ 25
Reflections collected	6423
Independent reflections	4758
Data/restraints/parameters	4758/0/458
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1= 0.0946 wR_2= 0.2792
Final R indexes [all data]	R_1= 0.1144 wR_2= 0.2944

X-ray structure of **40** – CCDC: 2122516



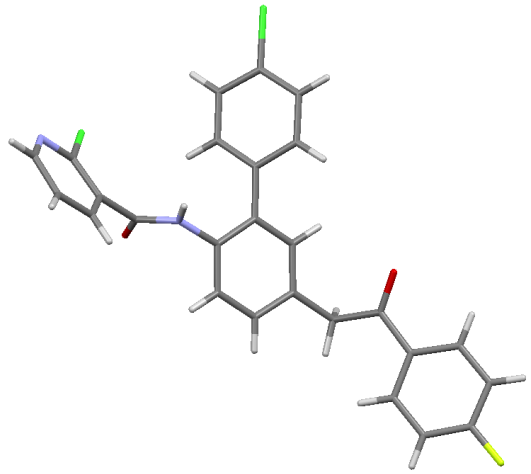


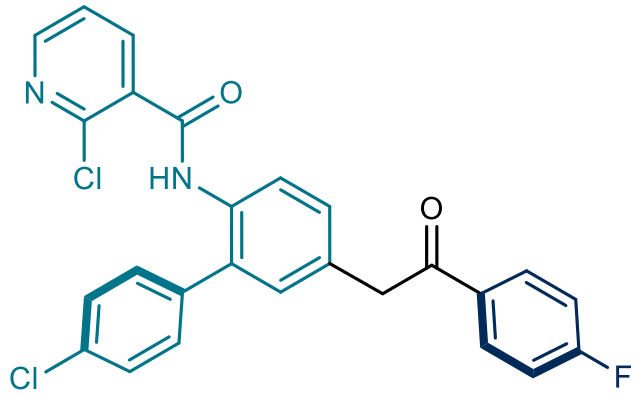
Supplementary Table 13 Crystal data and structure refinement for **40**

Identification code	*10-(2-methoxy-5-(trifluoromethyl)phenyl)-10H-phenoxathiin-10-ium trifluoromethanesulfonate*

Empirical Formula	$C_{22}H_{15}Cl_3F_6O_5S_2$
Formula weight	643.81
Temperature/K	100
Crystal system	Monoclinic
Space group	P 21/c
a/Å	8.20438(13)
b/Å	19.9465(3)
c/Å	15.5291(2)
α/°	90
β/°	98.0995(14)
γ/°	90
Volume/$Å^3$	2515.97(7)
Z	4
$P_{calc}g/cm^3$	1.700
μ/mm^{-1}	5.589
F(000)	1296
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.5680 to 151.1580
Index ranges	-10 ≤ h ≤ 10, -24 ≤ k ≤ 24, -19 ≤ l ≤ 19
Reflections collected	5244
Independent reflections	5190
Data/restraints/parameters	5190/0/344
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1= 0.0318 wR_2= 0.0785
Final R indexes [all data]	R_1= 0.0380 wR_2= 0.0817

X-ray structure of **62** – CCDC: 2120245

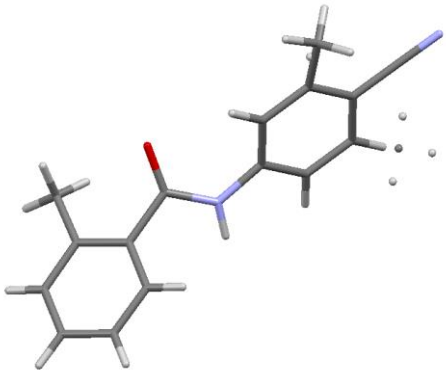


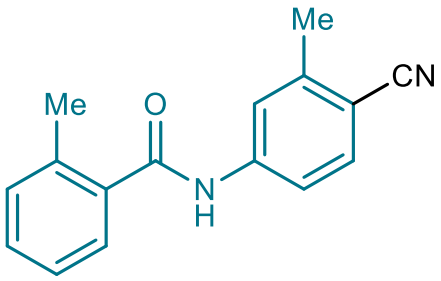


Supplementary Table 14 Crystal data and structure refinement for **62**

Identification code	*2-chloro-N-(4'-chloro-5-(2-(4-fluorophenyl)-2-oxoethyl)-[1,1'-biphenyl]-2-yl)nicotinamide*
Empirical Formula	$C_{26}H_{17}Cl_2FN_2O_2$
Formula weight	479.32
Temperature/K	100
Crystal system	monoclinic
Space group	P 21/c
a/Å	7.9730(3)
b/Å	14.1564(6)
c/Å	19.0771(7)
α/°	90
β/°	96.947(4)
γ/°	90
Volume/Å^3	2137.41(15)
Z	4
P_{calc}g/cm^3	1.490
μ/mm^{-1}	3.047
F(000)	984.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.3340 to 150.7260
Index ranges	-6 ≤ h ≤ 10, -17 ≤ k ≤ 17, -23 ≤ l ≤ 23
Reflections collected	13450
Independent reflections	4247
Data/restraints/parameters	4247/0/298
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1= 0.0425 wR_2= 0.1076
Final R indexes [all data]	R_1= 0.0607 wR_2= 0.1174

X-ray structure of **58** – CCDC: 2122517





Supplementary Table 15 Crystal data and structure refinement for **58**

Identification code	*N-(4-cyano-3-methylphenyl)-2-methylbenzamide*
Empirical Formula	$C_{16}H_{14}N_2O$
Formula weight	250.29
Temperature/K	100
Crystal system	Monoclinic
Space group	P 21/c
a/Å	10.7067(3)
b/Å	12.3629(4)
c/Å	10.0480(4)
α/°	90
β/°	93.244(3)
γ/°	90
Volume/Å^3	1327.88(8)
Z	4
P_{calc}g/cm^3	1.252
μ/mm^{-1}	0.632
F(000)	528.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.9400 to 151.8120
Index ranges	-10 ≤ h ≤ 13, -14 ≤ k ≤ 15, -12 ≤ l ≤ 11
Reflections collected	7223
Independent reflections	2663
Data/restraints/parameters	2663/0/185
Goodness-of-fit on F^2	1.082

Final R indexes [I>=2σ (I)]	R_1= 0.0448 wR_2= 0.1226
Final R indexes [all data]	R_1= 0.0529 wR_2= 0.1285

References

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