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Room Temperature Synthesis of Tetrasubstituted 1,3-Dithioles by Dimerizing Sulfuration of Chalcones with Elemental Sulfur

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ABSTRACT: Chalcones were found to undergo a sulfurative dimerization with elemental sulfur to tetrasubstituted 1,3-dithioles. The reaction was found to proceed at room temperature in the presence of a nitrogen base catalyst in DMSO.

Introduction

Organosulfur compounds, including sulfa heterocycles, are ubiquitous in both natural products and artificial molecules with interesting properties. Consequently, the finding of efficient and direct approaches to such molecules starting from simple starting materials and readily available in terms of both quantity and variety plays undoubtedly a central role in accelerating their research and development.

To this end, a wide range of synthetic methods has been developed to incorporate one or more sulfur atoms to the organic scaffolds using simple inorganic sulfur sources. Among these sulfur precursors, elemental sulfur is unarguably the best sulfur source. Using elemental sulfur in organic synthesis, we can benefit from its unique redox chemistry as an element, its user-friendliness along with its easy

availability. Consequently, this element has drawn the attention of chemists to develop cost-effective and environmentally friendly reactions in recent years.[1]

Among sulfa heterocycles, 1,3-dithioles are well known for a wide range of applications with some representative examples we shown in Figure 1.

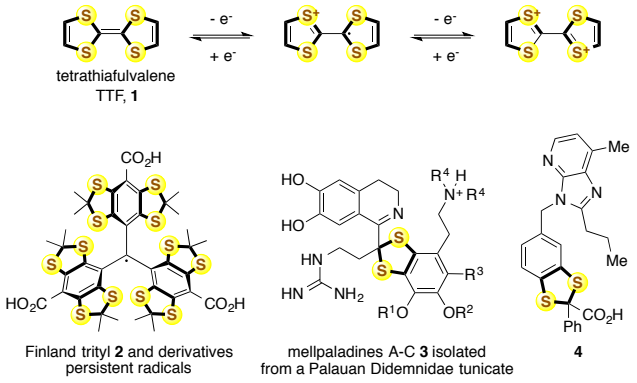


Figure 1. Selected examples of 1,3-dithioles

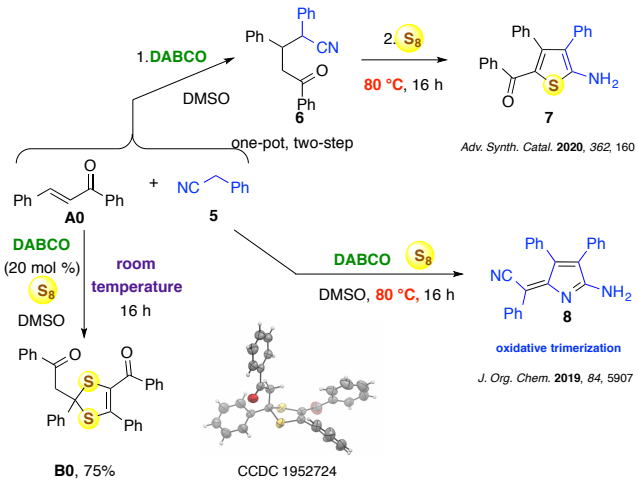
Tetrathiafulvalene (TTF) unit and derivatives are well known electron donors with three stable redox states. Thanks to their capability of forming easily charge-transfer complexes with electron acceptors, TTF is the core structure for development of organic conducting materials with over 13,000 scientific publications.[2] Interestingly, stabilized by fused 1,3-dithiole rings, tetrathiatriarylmethyl (TAM) radicals derived from the Finland trityl **2** are considerably more persistent than the Gomberg radical even under in-cell conditions. With strong EPR signals, TAM derivatives could be used for magnetic resonance imaging, dynamic nuclear polarization, and spin labeling EPR.[3] Recently, tunicate guanidine alkaloids mellpaladines A-C **3**, were found to bind to synaptic receptors, and modulated behavioral profiles of mice.[4] Furthermore, 1,3-benzodithiole-2-carboxylates **4** displayed potent binding affinity to the angiotensin II AT1 receptor.[5]

Consequently, a collection of synthetic methods of this scaffold was developed. Most of them were based on reactions of 1,2-dithiole-3-thiones or thioesters with activated acetylenes,[6] reactions involving sulfur-rich compounds[7] as well as elemental sulfur[8] as the only sulfur source. In the latter cases, most of the reactions required prolonged heating or highly reactive substrates and were applied to a very limited number of examples. If densely substituted 1,3-dithiole are of interest, synthesis of the respective precursors might be a complex and challenging multistep process.

An interesting aspect of elemental sulfur is its capability to promote oligomerization of single starting materials to provide oligomers that are much more difficult or unpractical to obtain otherwise. Via this strategy, simple and readily available starting molecules could undergo dimerization,[9] trimerization,[10] tetramerization[11] and hexamerization[12] with various degree of sulfuration.[13] Herein, we report a direct dimerization of chalcones with sulfur to provide original tetrasubstituted 1,3-dithiole scaffold. More strikingly, the reactions could be performed under simple conditions even at room temperature.[14]

Results and Discussion

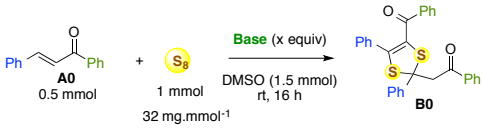
During the course of our study on new reactivities of the combination S_8/DMSO,[15] which could act as both oxidizing and sulfurating agent, we developed a three-component access to 2-aminothiophene **7** from phenylacetonitrile **5**, chalcone **A0** and elemental sulfur (Scheme 1).[16] Reasonable yield was obtained if the Michael adduct **6** between phenylacetonitrile **5** and chalcone **A0** were formed prior to the DABCO-catalyzed thiophenation with elemental sulfur. On the contrary, if three components of the reaction were mixed together in the presence of DABCO catalyst, 2-aminothiophenes **7** were formed in low yield along with pyrrole **8** from trimerization of **5**[10a] and a byproduct **B0** which could be generated in another control experiment performed without **5** (Table 1, entry 1). Interestingly, high yield of **B0** could be achieved even at rt. The exact structure of **B0** was unambiguously determined to be a tetrasubstituted dithiole by single crystal X-ray crystallographic analysis.



Scheme 1. Initial observation for the formation of dichalcone disulfide B0

Other basic additives such as liquid organic bases (triethylamine, tri-*n*-propylamine, *t*-butylamine, DIPEA, *N*-methylpiperidine, 2,2,6,6-tetramethylpiperidine, *N*-methylpyrrolidine in stoichiometric amount) (Table 1, entries 2-10) or solid inorganic base (CsF, $Na_2S•5H_2O$, K_2CO_3 in 20 mol % amount) were also found to promote this sulfurative dimerization in good yields in almost all cases (Table 1, entries 11-13).

Table 1. Screening of the reaction conditions



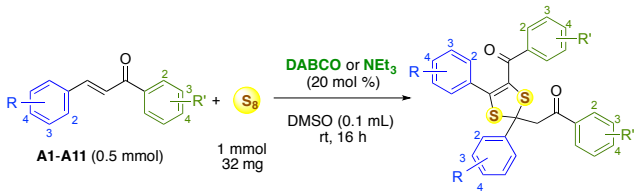
Entry[a]	Base (x equiv)	Yield (%)[b]
1	**DABCO (0.2)**	**75**
2	NEt_3 (1)	75
3	N(*n*-Pr)$_3$ (1)	70
4	*t*-BuNH_2 (1)	60
5	DIPEA (1)	71
7	*N*-methylpiperidine (1)	67
8	2,2,6,6-tetramethylpiperidine (1)	52
9	*N*-methylpyrrolidine (1)	55
10	DBU (1)	73
11	CsF (0.2)	70
12	$Na_2S•5H_2O$ (0.2)	62
13	K_2CO_3 (0.2)	55
14	**NEt_3 (0.2)**	**75**
15	NEt_3 (0.1)	47

16[c]	NEt_3 (0.2-10)	0
17[d]	NEt_3 (0.2)	50
18[e]	NEt_3 (0.2)	30

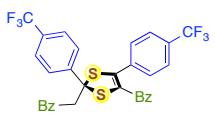
[a]Reaction conditions: chalcone A0 (0.5 mmol, 104 mg), S (1 mmol 32 mg), base (x equiv), DMSO (1.5 mmol, 0.1 mL) at rt. [b]Isolated yield. [c]Reaction performed in the absence of DMSO. [d]Reaction performed in DMF (0.1 mL) instead of DMSO. [e]Reaction performed with S (1 equiv, 0.5 mmol, 16 mg).

Comparably good yield 75% was obtained when triethylamine was used in catalytic amount (20 mol %) (entry 14). Lowering NEt_3 amount to 10 mol % resulted in lower yield (54%, entry 15). When reaction was performed in the absence of DMSO, chalcone **A0** remained unchanged regardless of NEt_3 amount (entry 16). We noted that in this case, since both chalcone **A0** and sulfur are solid at rt, their mixtures with NEt_3 remained slurry states with increasing amounts of NEt_3 (0.2-10 equiv). When DMF was used instead of DMSO (entry 17), the reaction was not complete, the expected dimer **B0** was formed in low yield along with many side-products.

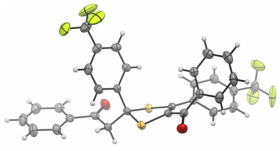
When only 1 equiv sulfur was used in the reaction, i.e. to provide exactly two sulfur atoms in dimer product **B0**, a sharp drop lower yield occurred along with the formation of unidentified products (entry 18). Since the expected sulfurative dimerization reaction required the removal of one hydrogen atom per each consumed chalcone, it is clear that sulfur acted also as a dehydrogenative agent.



B1, R = 4-*i*Pr, **DABCO**, 56%
B2, R = 3,4-(MeO)$_2$, **DABCO**,51%
B3, R = 3-MeO, **DABCO**, 52%
B4, R' = 4-MeO, **DABCO**,45%
B5, R = R' = 4-MeO, **DABCO**,47%
B6, R = 4-F, **NEt$_3$**, 58%
B7, R = 4-Br, **NEt$_3$**,50%
B8, R = 4-Cl, **DABCO**,49%
B9, R' = 4-Cl, **DABCO**,52%
B10, R = 3-Br, **NEt$_3$**,43%
B11, R = 4-CF_3, **NEt$_3$**,57%



B11



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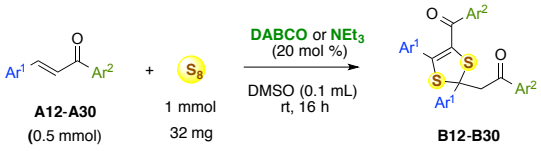
Scheme 2.

Gratifyingly, the dimer **B0** could be readily precipitated as a bright yellow solid by simply diluting the reaction mixtures with methanol and thus readily isolated by filtration.To further demonstrate the efficiency of this procedure, we explored the reaction with chalcones **A1-A11** (Scheme 2).

Two sets of optimized conditions involving either DABCO (entry 1) or NEt_3 (entry 14) in 20 mol % amount were employed. A wide range of functional substituents (alkyl **A1**, alkoxy **A2-A5**, halogen **A6-A10**, trifluoromethyl **A11**) in either or both aromatic rings were shown to be compatible with the reaction conditions. The structure of disulfide dimers **B11** was determined by X-ray diffraction, confirming again the common 1,3-dithiole scaffold of all products obtained by our reaction.

Next, a series of naphthalene and heterocyclic chalcones **A12-A30** was tested and these substrates gave moderate yields ranging from 40% to 59% (Scheme 3). Chalcones bearing naphthyl substituents **A12-A21** as well as heterocyclic ring such as thienyls (**A21-A24**), benzothienyl (**A25**), pyridyls (**A26-A29**) and furyl (**A30**) displayed good reactivity, providing the corresponding disulfurative dimeric products **B12-B30**.

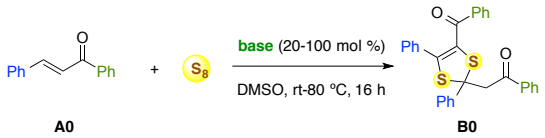


B12, Ar^1 = Ph, Ar^2 = 1-Naphthyl, **NEt_3**, 52%
B13, Ar^1 = 4-FC_6H_4, Ar^2 = 1-Naphthyl, **NEt_3**, 57%
B14, Ar^1 = 3-FC_6H_4, Ar^2 = 1-Naphthyl, **NEt_3**, 55%
B15, Ar^1 = 4-BrC_6H_4, Ar^2 = 1-Naphthyl, **NEt_3**, 47%
B16, Ar^1 = Ph, Ar^2 = 2-Naphthyl, **NEt_3**, 53%
B17, Ar^1 = 4-FC_6H_4, Ar^2 = 2-Naphthyl, **NEt_3**, 50%
B18, Ar^1 = 4-BrC_6H_4, Ar^2 = 2-Naphthyl, **NEt_3**, 43%
B19, Ar^1 = 2-Naphthyl, Ar^2 = Ph, **NEt_3**, 48%
B20, Ar^1 = 2-Naphthyl, Ar^2 = 1-Naphthyl, **NEt_3**, 46%
B21, Ar^1 = 2-Naphthyl, Ar^2 = 2-Thienyl, **NEt_3**, 42%
B22, Ar^1 = 3-Thienyl, Ar^2 = Ph, **DABCO**, 56%
B23, Ar^1 = Ph, Ar^2 = 2-Thienyl, **DABCO**,59%
B24, Ar^1 = 4-FC_6H_4, Ar^2 = 2-Thienyl, **NEt_3**, 46%
B25, Ar^1 = 4-FC_6H_4, Ar^2 = 2-Benzothienyl, **NEt_3**, 39%
B26, Ar^1 = 4-Pyridyl, Ar^2 = Ph, **NEt_3**, 43%
B27, Ar^1 = 3-Pyridyl, Ar^2 = Ph, **NEt_3**,48%
B28, Ar^1 = 2-Pyridyl, Ar^2 = Ph, **NEt_3**, 56%
B29, Ar^1 = 4-FC_6H_4, Ar^2 = 3-Pyridyl, **NEt_3**, 46%
B30, Ar^1 = 4-BrC_6H_4, Ar^2 = 2-Furyl, **NEt_3**,40%

Scheme 3.

We emphasized that the best yield was obtained with the most simple chalcone **A0**, which could be readily crystalized out from its reactions mixture by simply diluting with methanol, whereas other dimers **B1**-**B30** were shown to be much more soluble than in this solvent and thus could not be efficiently isolated by this manner. It is possible that the higher crystallinity of **B0** allowed this dimer to be separated from the reaction mixture when it was formed and thus avoided other side reactions that could lower the global yields.

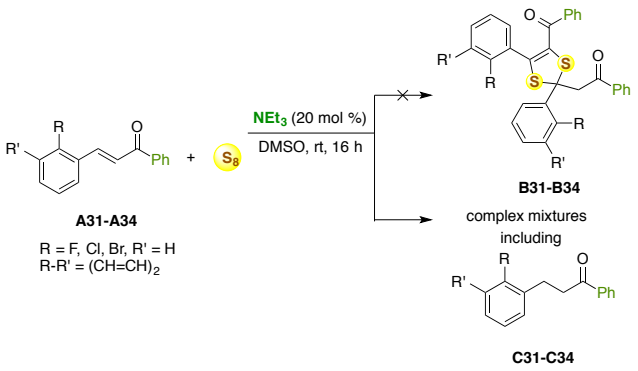
To gain further insight into the reaction mechanism, several control experiments were performed. First, NEt_3 (pK_b 3.25) was replaced by a weaker base in stoichiometric amount (1 equiv) such as *N*-methylmorpholine (pK_b 6.62) and pyridine (pK_b 8.75) (Scheme 4). Chalcone **A0** was converted only partially to dimer **B0** (30% conversion) with *N*-methylmorpholine (1 equiv) at rt and remained unchanged with the lower loading of this base (20 mol %) or with pyridine (1 equiv) even upon heating up to 80 ºC, indicating that the formation of sulfur-base adduct via ring opening of S_8 by the base was a key step in initiating the reaction. This step depended on both basicity and concentration of the base.



conditions	yield (%)
***N*-Methylmorpholine** (20 mol %), rt	0
***N*-Methylmorpholine**(100 mol %), rt	30
Pyridine (100 mol %, 80 °C	0

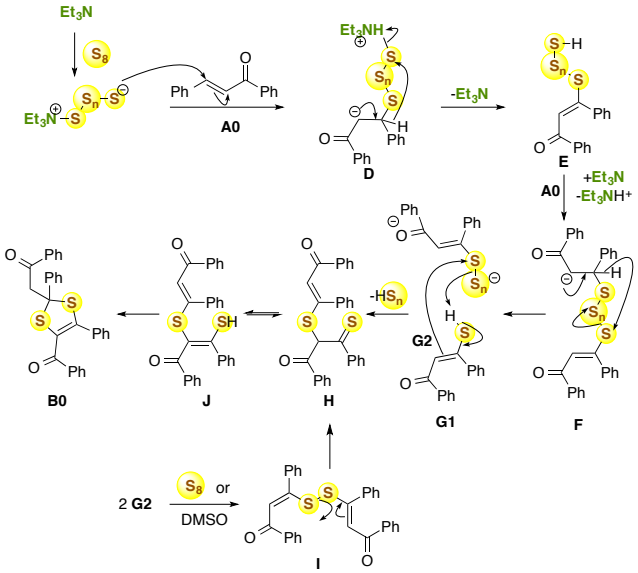
Scheme 4. Control experiment with weaker bases additives

Second, we found that chalcone substrates bearing a 2-substituent such as 2-fluoro-, 2-chloro-, 2-bromo-chalcones **A31**-**A33** or 1-naphthyl analog **A34** did not undergo the expected sulfurative dimerization (Scheme 5). Their reactions under the same conditions led to complex mixtures in which we could detect easily the presence of dihydrochalcone issued from reduction of the olefin based on their ^{1}H NMR signals of aliphatic protons. This side reaction was previously observed with *o*-halochalcones.[17a] From our previous studies on sulfur-chalcone reactions,[15f,17] we speculated that the reaction pathway should be initiated by a Michael nucleophilic addition reaction to the chalcone and an *ortho* substituent on the ring B of chalcone substrate would slower or even inhibit the reaction.



Scheme 5. Failed reactions with *o*-substituted chalcones

Based on the obtained results, the above-mentioned control experiments, and the precedent literature,[18] a plausible reaction mechanism is outlined in Scheme 6.



Scheme 6. Plausible reaction mechanism

The reaction was initiated by a Michael addition of NEt_3-sulfur adduct to chalcone **A0**. The resulting adduct **D** underwent a disproportionation in which the sulfurated chalcone moiety was oxidized and the terminal N-S bond was reduced, leading to polysulfane **E**. Subsequent addition of **E** to another molecule of chalcone **A1**, followed by fragmentation of the resulting adduct **F** would give two fragments **G1** and **G2**, different only in the number of sulfur atom and interconvertible. The transformation of **G2** into thioketone **H** could proceed by combining with **G1** with the simultaneous extrusion of hydropolysulfide

or by S_8- or DMSO- promoted oxidative dimerization into **I** then rearrangement.[18] Cyclization of enethiol **J**, which is a tautomer of **H**, would finally provide the dithiole **B0**.

In conclusion, we explored the reactivity of elemental sulfur on chalcones and developed an efficient strategy for the construction of tetrasubstituted 1,3-dithiole compounds using NEt_3 in DMSO as a promoter. The reaction went through a sulfurative dimerization of chalcone under mild conditions with broad substrate scope. Densely substituted 1,3-dithioles were obtained in reasonable yields for the majority of tested substrates. The result presented here confirms once again the very rich organic chemistry of elemental sulfur even under very simple conditions. Since chalcones are readily available in a wide range of structures from both commercial suppliers and syntheses, our method opens a new and convenient access to a large collection of original structures for bioactive screening. Further experiments on the mechanism as well as synthetic application are currently ongoing in our laboratory.

Experimental Section

General Information

Reagents were obtained from commercial supplier and used without further purification. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or $KMnO_4$ or vanilline stains. Flash column chromatography was carried out using kieselgel 35-70 μm particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in (δ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference ($CDCl_3$, δ 7.26 ppm for ^1H and δ 77.0 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Mass spectra were obtained using electron spray ionization (ESI). The HRMS data were measured on MALDI-TOF instrument.

General procedure

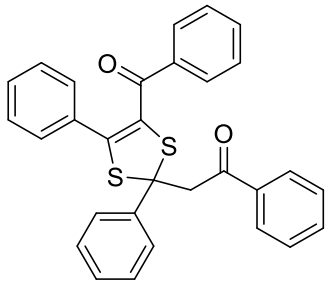
A mixture of chalcone A (0.5 mmol, 1 equiv), S (32 mg, 1 mmol, 2 equiv), triethylamine or DABCO (0.1 mmol) in 0.1 mL of DMSO in a 7-mL test-tube closed with a septum was stirred at rt for 16 h. In case of A0, upon dilution with MeOH (2-4 mL), dimer B0 was precipitated as a bright yellow solid, which was filtered, washed with MeOH (2 mL x 3) and dried in vacuo to give pure B0. In cases of chalcones A1-A30, due to higher solubilities of the corresponding dimers B1-B30, the crude mixture

was diluted with MeOH:CH_2Cl_2 (4 mL, v:v 1:1) and filtered over Celite. After removal of volatiles in vacuo, the residue was purified by column chromatography (hexane/ethyl acetate: 19/1 to 9/1) to give the dimer product a bright yellow solid.

Large-scale synthesis of **B0**: A mixture of chalcone **A0** (5.20 g, 25 mmol), S (1.60 g, 50 mmol), and DABCO (560 mg, 5 mmol) in 5.0 mL of DMSO in a 25-mL round-bottom flask closed with a septum was stirred at rt for 16 h. Dilution of the reaction mixture with MeOH (20 mL) precipitated the yellow product, which was filtered and washed with MeOH (2 mL x 5). The yellow powder was dried in vacuo (4.18 g, 70%).

Characterization of the products

2-(4-Benzoyl-2,5-diphenyl-1,3-dithiol-2-yl)-1-phenylethan-1-one (B0)



Upon dilution with MeOH (2-4 mL), the product was precipitated as a bright yellow solid, which was filtered, washed with MeOH (2 mL x 3) and dried in vacuo to give pure **B0**.

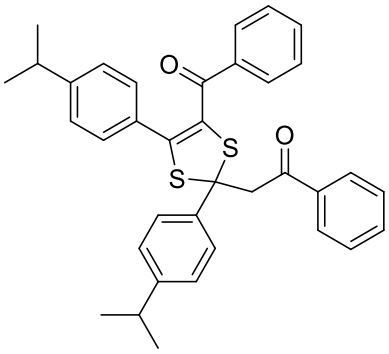
Bright yellow solid (90 mg, 75%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.0 (d, *J* = 7.7 Hz, 2H), 7.9 (d, *J* = 7.9 Hz, 2H), 7.6 (t, *J* = 7.4 Hz, 1H), 7.6 – 7.4 (m, 3H), 7.4 (t, *J* = 7.6 Hz, 2H), 7.4 – 7.2 (m, 4H), 7.2 – 7.0 (m, 5H), 4.5 (s, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.7, 190.4, 144.5, 142.2, 136.7, 136.2, 133.7, 132.5, 132.1, 129.9, 129.5, 129.3, 128.8, 128.4, 128.2, 128.1, 128.0, 127.9, 126.5, 66.4 (CS_2), 51.2.

HRMS m/z calculated for $[M+Na]^+$ $C_{30}H_{22}NaO_2S_2$ 501.0959. Found 601.0963.

2-(4-Benzoyl-2,5-bis(4-isopropylphenyl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B1)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

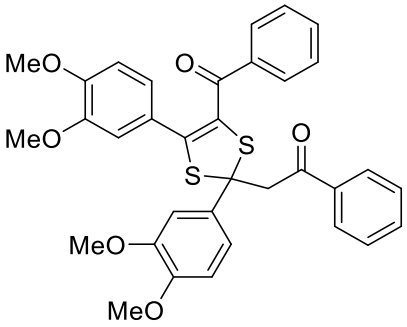
Bright yellow solid (79 mg, 56%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.0 – 7.9 (m, 2H), 7.8 – 7.7 (m, 2H), 7.6 – 7.5 (m, 1H), 7.5 – 7.4 (m, 4H), 7.2 – 7.2 (m, 2H), 7.1 (td, *J* = 6.2, 1.7 Hz, 2H), 7.1 – 7.0 (m, 1H), 6.9 (d, *J* = 8.2 Hz, 2H), 4.5 (s, 2H), 2.9 (p, *J* = 6.9 Hz, 1H), 2.7 (p, *J* = 6.9 Hz, 1H), 1.2 (d, *J* = 6.9 Hz, 6H), 1.1 (d, *J* = 6.9 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.9, 190.5, 150.5, 148.4, 145.6, 139.3, 136.9, 133.6, 132.1, 130.0, 129.2, 128.7, 128.1, 127.8, 127.7, 127.7, 126.4, 66.0, 51.2, 33.8, 33.6, 23.8, 23.6.

HRMS m/z calculated for $[M+Na]^+$ $C_{36}H_{34}NaO_2S_2$ 585.1898. Found 585.1996.

2-(4-Benzoyl-2,5-bis(3,4-dimethoxyphenyl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B2)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

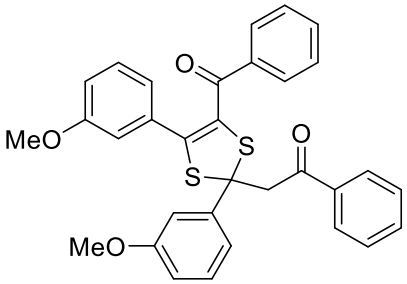
Bright yellow solid (76 mg, 51%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.0 (d, *J* = 7.3 Hz, 3H), 7.6 – 7.4 (m, 9H), 7.3 – 7.2 (m, 3H), 7.2 – 7.1 (m, 3H), 6.9 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.8 (d, *J* = 8.5 Hz, 1H), 6.6 (t, *J* = 2.5 Hz, 1H), 6.6 (d, *J* = 8.4 Hz, 1H), 4.5 (s, 2H), 3.9 (s, 3H), 3.9 (s, 3H), 3.8 (s, 3H), 3.7 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 195.0, 190.6, 150.1, 148.6, 148.5, 148.2, 145.0, 136.8, 136.3, 134.4, 133.7, 132.6, 129.2, 128.8, 128.6, 128.1, 128.0, 125.2, 124.7, 123.2, 118.6, 113.0, 110.7, 110.6, 110.5, 65.6, 56.0, 55.9, 55.7, 50.9.

HRMS m/z calculated for $[M+Na]^+$ $C_{34}H_{30}NaO_6S_2$ 621.1381. Found 621.1387.

2-(4-Benzoyl-2,5-bis(3-methoxyphenyl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B3)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

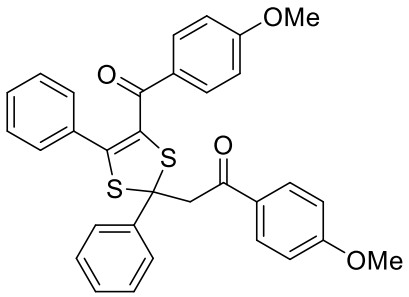
Bright yellow solid (70 mg, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.9 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.6 – 7.5 (m, 3H), 7.5 – 7.4 (m, 3H), 7.4 (ddd, *J* = 7.9, 2.0, 0.9 Hz, 1H), 7.3 – 7.3 (m, 2H), 7.2 – 7.1 (m, 2H), 7.0 (t, *J* = 7.9 Hz, 1H), 6.9 – 6.8 (m, 1H), 6.8 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 6.7 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.7 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 194.8, 190.4, 159.6, 159.1, 144.1, 143.9, 136.8, 136.3, 133.8, 133.3, 132.6, 129.5, 129.3, 129.2, 128.8, 128.2, 128.0, 126.6, 122.5, 118.7, 115.8, 115.0, 113.2, 113.0, 66.2, 55.4, 55.3, 51.3.

HRMS m/z calculated for $[M+Na]^+$ $C_{32}H_{26}NaO_4S_2$ 561.1170. Found 561.1175.

2-(4-(4-Methoxybenzoyl)-2,5-diphenyl-1,3-dithiol-2-yl)-1-(4-methoxyphenyl)ethan-1-one (B4)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

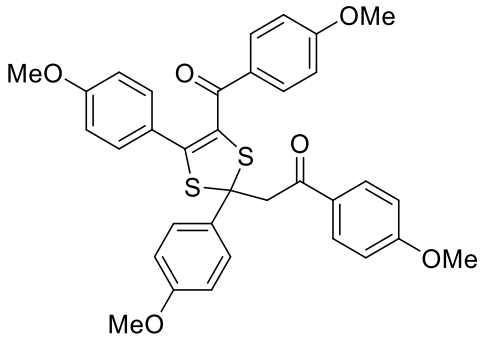
Bright yellow solid (61 mg, 45%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.0 – 7.9 (m, 4H), 7.6 (d, *J* = 9.1 Hz, 2H), 7.4 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.3 (ddd, *J* = 7.5, 4.8, 1.7 Hz, 2H), 7.1 (td, *J* = 5.9, 2.8 Hz, 2H), 6.9 (d, *J* = 8.4 Hz, 2H), 6.7 (d, *J* = 10.2 Hz, 2H), 4.5 (s, 2H), 3.9 (s, 3H), 3.7 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 192.2, 188.2, 162.9, 162.2, 141.5, 140.7, 131.3, 130.7, 129.4, 128.7, 128.2, 128.2, 127.3, 127.1, 126.7, 126.6, 125.4, 125.0, 112.8, 112.3, 112.2, 65.9, 54.5, 54.3, 49.6.

HRMS m/z calculated for $[M+Na]^+$ $C_{32}H_{26}NaO_4S_2$ 561.1170. Found 561.1175.

2-(4-(4-Methoxybenzoyl)-2,5-bis(4-methoxyphenyl)-1,3-dithiol-2-yl)-1-(4-methoxyphenyl)ethan-1-one (B5)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

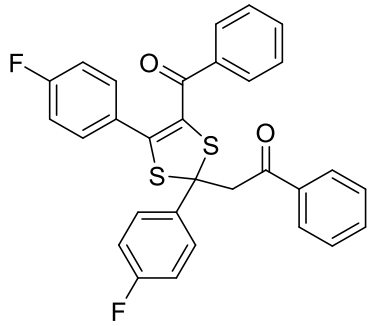
Bright yellow solid (70 mg, 47%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.9 (d, *J* = 8.9 Hz, 2H), 7.8 (d, *J* = 8.9 Hz, 2H), 7.6 (d, *J* = 8.8 Hz, 2H), 7.2 (d, *J* = 8.8 Hz, 2H), 6.9 (dd, *J* = 11.9, 8.9 Hz, 4H), 6.6 (t, *J* = 8.9 Hz, 3H), 4.4 (s, 2H), 3.9 (s, 3H), 3.8 (s, 3H), 3.8 (s, 3H), 3.7 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.4, 189.5, 163.9, 163.2, 160.3, 158.9, 142.4, 134.4, 131.7, 131.6, 131.3, 131.1, 131.0, 130.5, 130.4, 130.3, 130.1, 129.4, 129.3, 129.2, 129.1, 129.0, 127.9, 124.9, 124.6, 113.9, 113.6, 113.4, 113.3, 66.2, 55.5, 55.4, 55.3, 55.2, 50.4.

HRMS m/z calculated for $[M+Na]^+$ $C_{34}H_{30}NaO_6S_2$ 621.1381. Found 621.1392.

2-(4-Benzoyl-2,5-bis(4-fluorophenyl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B6)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

Bright yellow solid (75 mg, 58%).

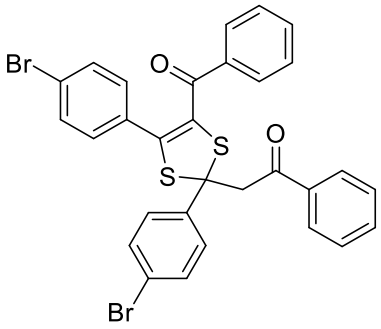
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.9 (d, *J* = 8.2 Hz, 2H), 7.9 – 7.8 (m, 2H), 7.6 (t, *J* = 7.4 Hz, 1H), 7.5 (t, *J* = 7.9 Hz, 3H), 7.3 (t, *J* = 7.4 Hz, 1H), 7.2 – 7.2 (m, 1H), 7.1 (t, *J* = 7.9 Hz, 2H), 7.1 (t, *J* = 8.5 Hz, 2H), 6.8 (t, *J* = 8.6 Hz, 2H), 4.5 (s, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.7, 190.2, 163.6 (d, *J* = 132.1 Hz), 161.6 (d, *J* = 129.2 Hz), 143.1, 138.2, 136.5, 136.0, 133.9, 132.8, 131.8, 131.7, 129.2, 128.8, 128.5 (d, *J* = 8.1 Hz), 128.1 (d, *J* = 4.3 Hz), 115.3 (d, *J* = 4.3 Hz), 115.2 (d, *J* = 4.3 Hz), 65.9, 51.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -110.2, -114.2.

HRMS m/z calculated for $[M+Na]^+$ $C_{30}H_{20}F_2NaO_2S_2$ 537.0770. Found 537.0775.

2-(4-Benzoyl-2,5-bis(4-bromophenyl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B7)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

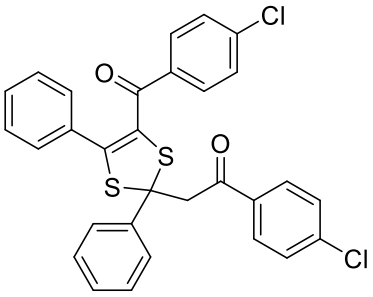
Bright yellow solid (80 mg, 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.43 (m, 5H), 7.38 – 7.31 (m, 1H), 7.25 – 7.10 (m, 4H), 7.08 (d, *J* = 8.5 Hz, 1H), 4.45 (s, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.5, 190.0, 142.3, 141.6, 136.4, 135.9, 134.0, 132.9, 131.5, 131.4, 131.2, 130.8, 129.2, 128.8, 128.3, 128.2, 128.1, 127.0, 123.9, 122.1, 66.2, 51.0.

HRMS m/z calculated for $[M+Na]^+$ $C_{30}H_{20}Br_2NaO_2S_2$ 656.9169. Found 656.9176.

2-(4-(4-Chlorobenzoyl)-2,5-diphenyl-1,3-dithiol-2-yl)-1-(4-chlorophenyl)ethan-1-one (B8)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

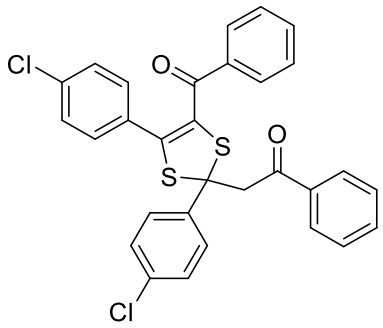
Bright yellow solid (67 mg, 49%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.9 – 7.8 (m, 5H), 7.4 – 7.4 (m, 5H), 7.4 (d, *J* = 8.0 Hz, 2H), 7.3 – 7.3 (m, 1H), 7.2 – 7.2 (m, 2H), 7.2 – 7.1 (m, 1H), 7.1 (d, *J* = 8.4 Hz, 2H), 7.1 (d, *J* = 9.4 Hz, 2H), 4.4 (s, 2H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 193.6, 189.1, 145.0, 142.1, 140.4, 138.9, 135.1, 134.5, 131.9, 130.6, 129.9, 129.8, 129.6, 129.1, 128.5, 128.3, 128.1, 126.5, 126.2, 66.5, 51.2

HRMS m/z calculated for $[M+Na]^+$ $C_{30}H_{20}Cl_2NaO_2S_2$ 569.0179. Found 569.0184.

2-(4-Benzoyl-2,5-bis(4-chlorophenyl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B9)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

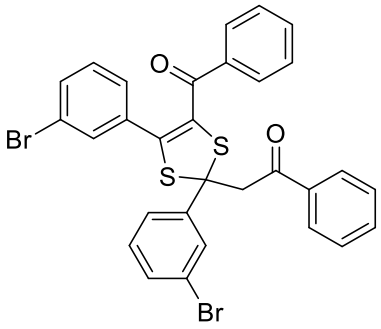
Bright yellow solid (71 mg, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.9 (d, *J* = 6.3 Hz, 2H), 7.8 (d, *J* = 8.7 Hz, 2H), 7.6 (t, *J* = 7.7 Hz, 1H), 7.5 (d, *J* = 7.1 Hz, 2H), 7.5 (t, *J* = 7.8 Hz, 2H), 7.4 – 7.3 (m, 3H), 7.2 – 7.1 (m, 4H), 7.1 (d, *J* = 8.5 Hz, 2H), 4.5 (s, 2H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 194.6, 190.2, 142.5, 141.1, 136.5, 135.9, 135.6, 134.0, 133.9, 133.0, 131.1, 130.4, 129.8, 129.6, 129.3, 129.1, 128.9, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.0, 66.1, 51.1.

HRMS m/z calculated for $[M+Na]^+$ $C_{30}H_{20}Cl_2NaO_2S_2$ 569.0179. Found 569.0188.

2-(4-Benzoyl-2,5-bis(3-bromophenyl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B10)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

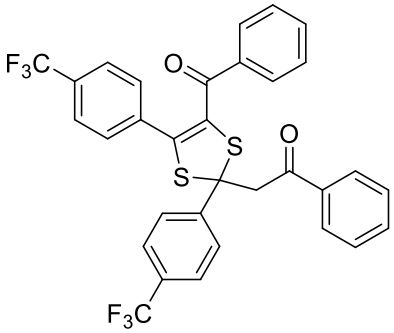
Bright yellow solid (68 mg, 43%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (t, *J* = 2.0 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.69 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.41 (dd, *J* = 8.2, 6.7 Hz, 5H), 7.35 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.27 (d, *J* = 1.9 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.20 – 7.15 (m, 3H), 7.12 – 7.05 (m, 3H), 6.86 (t, *J* = 7.9 Hz, 1H), 4.40 (d, *J* = 1.5 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.4, 190.0, 144.8, 141.9, 136.5, 135.8, 134.0, 133.6, 132.9, 132.7, 132.5, 131.1, 130.0, 129.8, 129.6, 129.1, 128.9, 128.3, 128.2, 127.7, 125.0, 122.7, 122.1, 65.8, 51.1.

HRMS m/z calculated for $[M+Na]^+$ $C_{30}H_{20}Br_2NaO_2S_2$ 656.9169. Found 656.9174.

2-(4-Benzoyl-2,5-bis(4-(trifluoromethyl)phenyl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B11)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

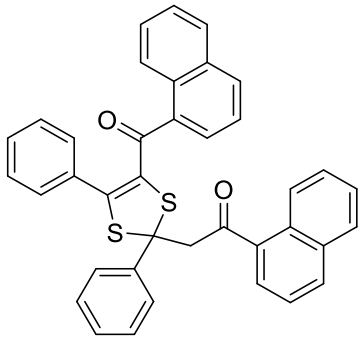
Bright yellow solid (87 mg, 57%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.0 (d, *J* = 8.2 Hz, 2H), 8.0 (d, *J* = 7.6 Hz, 2H), 7.7 (d, *J* = 8.3 Hz, 2H), 7.6 (d, *J* = 7.9 Hz, 1H), 7.6 – 7.5 (m, 4H), 7.4 – 7.3 (m, 6H), 7.2 (t, *J* = 7.0 Hz, 2H), 4.6 (s, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.4, 189.7, 146.5, 141.3, 136.2, 135.6, 135.3, 134.1, 133.2, 130.0, 129.1, 128.9, 128.3, 128.1, 127.0, 125.5 (d, *J* = 3.8 Hz), 125.1 (d, *J* = 4.1 Hz), 66.5, 51.2.

HRMS m/z calculated for $[M+Na]^+$ $C_{32}H_{20}F_6NaO_2S_2$ 637.0707. Found 637.0712.

2-(4-(1-Naphthoyl)-2,5-diphenyl-1,3-dithiol-2-yl)-1-(naphthalen-1-yl)ethan-1-one (B12)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

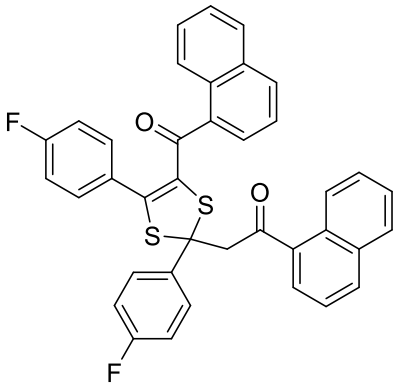
Bright yellow solid (75 mg, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 – 8.32 (m, 1H), 8.20 – 8.10 (m, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.88 – 7.81 (m, 2H), 7.64 (dd, *J* = 6.2, 3.3 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.45 – 7.38 (m, 4H), 7.33 (dd, *J* = 8.8, 7.1 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.1 Hz, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 4.61 (d, *J* = 17.4 Hz, 1H), 4.56 (d, *J* = 17.3 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 198.8, 190.7, 148.8, 142.8, 135.4, 134.9, 133.9, 133.4, 133.2, 131.6, 131.6, 130.6, 130.0, 129.7, 129.3, 129.1, 128.5, 128.4, 128.3, 128.2, 128.0, 128.0, 127.8, 127.3, 127.2, 126.7, 126.0, 125.6, 125.3, 124.3, 124.0, 77.3, 77.0, 76.8, 65.5, 54.3.

HRMS m/z calculated for $[M+Na]^+$ $C_{38}H_{26}NaO_2S_2$ 601.1272. Found 601.1278.

2-(4-(1-Naphthoyl)-2,5-bis(4-fluorophenyl)-1,3-dithiol-2-yl)-1-(naphthalen-1-yl)ethan-1-one (B13)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

Bright yellow solid (87 mg, 57%).

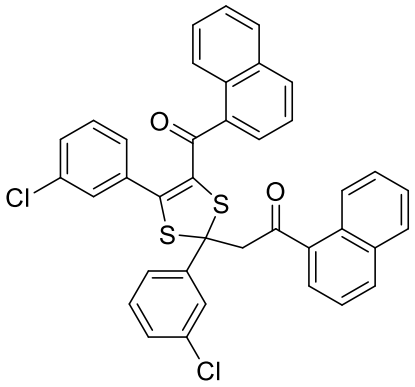
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 – 8.36 (m, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.97 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.85 (dd, *J* = 8.5, 6.0 Hz, 2H), 7.68 (d, *J* = 6.8 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.53 (td, *J* = 5.5, 4.8, 3.2 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.45 – 7.35 (m, 2H), 7.31 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.10 (dt, *J* = 15.1, 8.1 Hz, 3H), 6.93 (dd, *J* = 8.6, 5.4 Hz, 2H), 6.38 (t, *J* = 8.6 Hz, 2H), 4.56 (d, *J* = 17.4 Hz, 1H), 4.52 (d, *J* = 17.4 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 198.6, 190.5, 163.5 (d, *J* = 76.9 Hz), 161.5 (d, *J* = 74.5 Hz), 147.3, 138.9 (d, *J* = 3.2 Hz), 135.3, 134.5, 133.7, 133.2, 131.7, 131.1 (d, *J* = 8.5 Hz), 130.5, 130.1, 130.0, 128.7 (d, *J* = 8.2 Hz), 128.5, 128.3, 128.2 (d, *J* = 5.1 Hz), 128.0, 127.5, 127.5, 126.8, 126.2, 125.5, 125.0, 124.3, 124.1, 115.3 (d, *J* = 21.9 Hz), 114.4 (d, *J* = 22.0 Hz), 65.0, 54.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -110.52, -114.05.

HRMS m/z calculated for $[M+Na]^+$ $C_{38}H_{24}F_2NaO_2S_2$ 637.1083. Found 637.1085.

2-(4-(1-Naphthoyl)-2,5-bis(3-chlorophenyl)-1,3-dithiol-2-yl)-1-(naphthalen-1-yl)ethan-1-one (B14)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

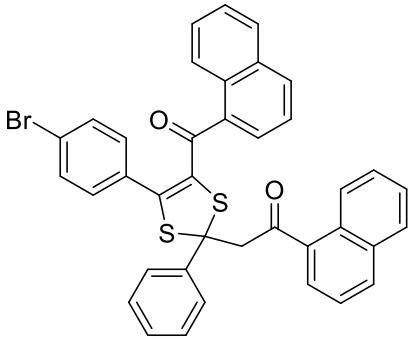
Bright yellow solid (84 mg, 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.4 (d, *J* = 8.4 Hz, 1H), 8.1 (d, *J* = 9.5 Hz, 1H), 8.0 – 8.0 (m, 2H), 7.9 – 7.8 (m, 2H), 7.8 (d, *J* = 7.8 Hz, 1H), 7.7 – 7.7 (m, 1H), 7.6 (d, *J* = 8.2 Hz, 1H), 7.6 – 7.5 (m, 4H), 7.4 (qd, *J* = 7.0, 3.6 Hz, 2H), 7.4 – 7.3 (m, 4H), 7.1 (t, *J* = 7.6 Hz, 1H), 6.9 (s, 1H), 6.8 (d, *J* = 8.1 Hz, 2H), 6.6 (t, *J* = 7.9 Hz, 1H), 4.6 (d, *J* = 17.6 Hz, 1H), 4.5 (d, *J* = 17.6 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 198.3, 190.3, 146.3, 145.3, 135.2, 134.6, 134.2, 134.0, 133.8, 133.5, 133.2, 132.8, 131.9, 130.9, 130.4, 130.0, 129.8, 129.2, 129.2, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.5, 127.3, 127.2, 126.8, 126.3, 125.5, 125.0, 124.7, 124.3, 124.1, 64.9, 54.0.

HRMS m/z calculated for $[M+Na]^+$ $C_{38}H_{24}Cl_2NaO_2S_2$ 669.0492. Found 669.0798.

2-(4-(1-Naphthoyl)-5-(4-bromophenyl)-2-phenyl-1,3-dithiol-2-yl)-1-(naphthalen-1-yl)ethan-1-one (B15)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

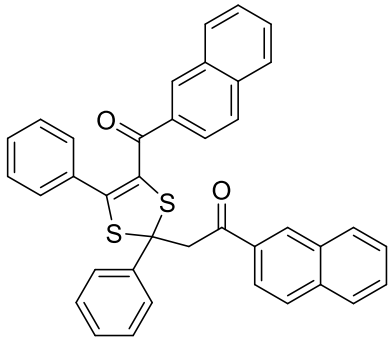
Bright yellow solid (86 mg, 47%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.4 (d, *J* = 9.5 Hz, 1H), 8.0 (d, *J* = 8.3 Hz, 3H), 7.9 (dd, *J* = 7.5, 4.1 Hz, 6H), 7.7 – 7.6 (m, 3H), 7.6 (d, *J* = 8.7 Hz, 3H), 7.5 – 7.5 (m, 4H), 7.5 – 7.4 (m, 2H), 7.4 (ddd, *J* = 8.1, 6.7, 1.4 Hz, 2H), 7.3 – 7.3 (m, 1H), 7.1 (t, *J* = 7.7 Hz, 2H), 6.8 (d, *J* = 8.5 Hz, 3H), 6.8 (d, *J* = 8.5 Hz, 3H), 4.6 (d, *J* = 17.7 Hz, 1H), 4.5 (d, *J* = 17.4 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.5, 190.1, 141.7, 141.4, 135.9, 135.5, 133.6, 133.2, 132.4, 132.2, 132.0, 131.7, 131.5, 131.5, 131.0, 130.1, 129.9, 129.7, 129.4, 129.0, 128.8, 128.7, 128.5, 128.4, 127.9, 127.7, 127.1, 126.8, 126.7, 124.3, 123.8, 123.5, 122.2, 67.2, 50.9.

HRMS m/z calculated for $[M+Na]^+$ $C_{38}H_{25}BrNaO_2S_2$ 679.0377. Found 679.0385.

2-(4-(2-Naphthoyl)-2,5-diphenyl-1,3-dithiol-2-yl)-1-(naphthalen-2-yl)ethan-1-one (B16)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

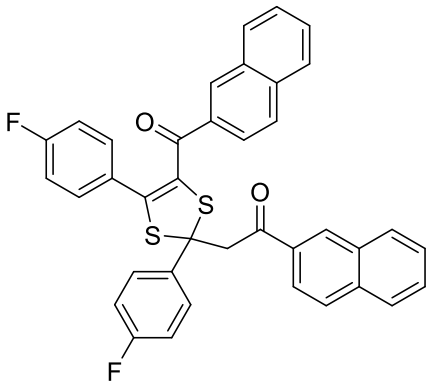
Bright yellow solid (77 mg, 53%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 1.6 Hz, 1H), 8.02 (d, *J* = 1.5 Hz, 1H), 7.99 – 7.92 (m, 4H), 7.88 (dd, *J* = 8.5, 4.6 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.54 (m, 6H), 7.53 – 7.47 (m, 1H), 7.44 – 7.38 (m, 4H), 7.34 – 7.29 (m, 3H), 6.99 (dd, *J* = 5.2, 1.9 Hz, 3H), 4.67 (s, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.7, 190.5, 143.9, 142.3, 135.8, 135.2, 133.9, 133.6, 132.4, 132.2, 132.2, 132.0, 131.6, 130.1, 129.7, 129.3, 129.3, 128.9, 128.7, 128.4, 128.3, 128.1, 128.0, 127.8, 127.6, 127.0, 126.6, 126.4, 124.6, 123.6, 67.3, 51.1.

HRMS m/z calculated for $[M+Na]^+$ $C_{38}H_{26}NaO_2S_2$ 601.1272. Found 601.1278.

2-(4-(2-Naphthoyl)-2,5-bis(4-fluorophenyl)-1,3-dithiol-2-yl)-1-(naphthalen-2-yl)ethan-1-one (B17)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

Bright yellow solid (77 mg, 50%).

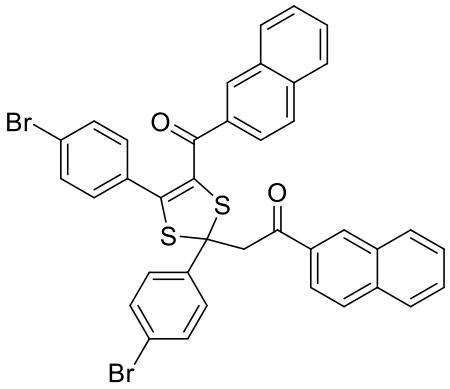
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 1.7 Hz, 1H), 8.01 (s, 1H), 7.96 (ddd, *J* = 13.8, 8.3, 3.9 Hz, 4H), 7.88 (dd, *J* = 8.3, 6.1 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.59 (m, 4H), 7.57 (s, 0H), 7.28 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 6.70 (t, *J* = 8.6 Hz, 2H), 4.63 (d, *J* = 2.7 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.6, 190.3, 163.6 (d, *J* = 107.6 Hz), 161.6 (d, *J* = 104.4 Hz), 142.4, 138.2, 135.9, 135.3, 133.7, 133.4, 132.4, 132.0, 131.6, 131.5, 131.5, 130.1, 129.7, 129.6, 129.0, 128.8, 128.7, 128.6, 128.6, 128.2, 127.9, 127.7, 127.1, 126.7, 124.5, 123.5, 115.4 (d, *J* = 8.5 Hz), 115.2 (d, *J* = 8.2 Hz), 66.8, 51.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -110.35, -114.11.

HRMS m/z calculated for $[M+Na]^+$ $C_{38}H_{24}F_2NaO_2S_2$ 637.1083. Found 637.1095.

2-(4-(2-Naphthoyl)-2,5-bis(4-bromophenyl)-1,3-dithiol-2-yl)-1-(naphthalen-2-yl)ethan-1-one (B18)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

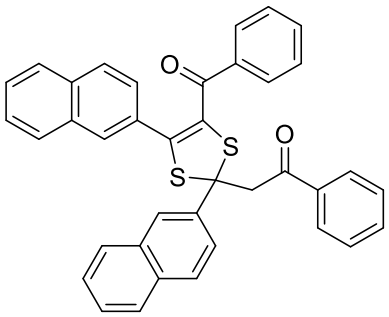
Bright yellow solid (79 mg, 43%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 1.6 Hz, 1H), 8.00 – 7.94 (m, 4H), 7.91 – 7.86 (m, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.71 – 7.61 (m, 4H), 7.60 – 7.51 (m, 6H), 7.48 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.16 (s, 4H), 4.62 (d, *J* = 2.2 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.5, 190.1, 141.7, 141.4, 135.9, 135.5, 133.6, 133.2, 132.4, 132.2, 132.0, 131.7, 131.7, 131.5, 131.5, 131.0, 130.1, 129.9, 129.7, 129.4, 129.0, 128.8, 128.7, 128.5, 128.4, 127.9, 127.7, 127.1, 126.8, 126.7, 124.3, 123.8, 123.5, 122.2, 67.2, 50.9.

HRMS m/z calculated for $[M+Na]^+$ $C_{38}H_{24}Br_2NaO_2S_2$ 756.9482. Found 756.9488.

2-(4-Benzoyl-2,5-di(naphthalen-2-yl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B19)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

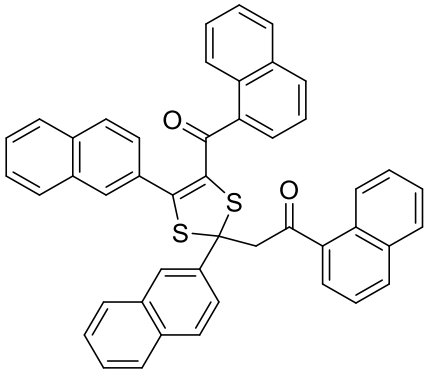
Bright yellow solid (69 mg, 48%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 2.0 Hz, 1H), 7.96 (dd, *J* = 8.6, 1.9 Hz, 3H), 7.92 – 7.85 (m, 2H), 7.85 – 7.79 (m, 2H), 7.71 – 7.62 (m, 2H), 7.61 – 7.52 (m, 3H), 7.53 – 7.38 (m, 7H), 7.29 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.7 Hz, 2H), 4.65 (s, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.8, 190.6, 144.2, 139.3, 136.8, 136.2, 133.7, 133.3, 132.8, 132.7, 132.5, 132.5, 130.0, 129.5, 129.1, 128.8, 128.5, 128.5, 128.2, 128.2, 127.9, 127.7, 127.5, 127.5, 127.0, 126.8, 126.7, 126.6, 126.5, 126.5, 126.0, 124.2, 66.6, 51.0.

HRMS m/z calculated for $[M+Na]^+$ $C_{38}H_{26}NaO_2S_2$ 601.1272. Found 601.1278.

2-(4-(1-Naphthoyl)-2,5-di(naphthalen-2-yl)-1,3-dithiol-2-yl)-1-(naphthalen-1-yl)ethan-1-one (B20)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

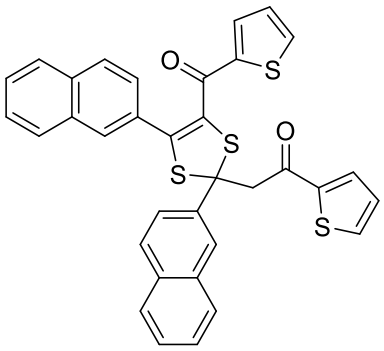
Bright yellow solid (78 mg, 46%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.6 (d, *J* = 2.0 Hz, 1H), 8.4 (d, *J* = 7.2 Hz, 1H), 8.2 – 8.2 (m, 3H), 8.1 – 8.0 (m, 3H), 8.0 (d, *J* = 8.1 Hz, 1H), 8.0 – 7.9 (m, 1H), 7.7 – 7.7 (m, 2H), 7.6 (ddd, *J* = 20.0, 14.6, 7.8 Hz, 5H), 7.5 (dd, *J* = 13.0, 7.9 Hz, 2H), 7.4 – 7.3 (m, 5H), 7.3 (dd, *J* = 11.9, 8.0 Hz, 2H), 7.1 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.9 (t, *J* = 7.6 Hz, 1H), 5.2 (d, *J* = 18.3 Hz, 1H), 5.0 (d, *J* = 18.2 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, DMSO) δ 200.2, 190.7, 148.5, 140.5, 135.6, 134.6, 133.9, 133.8, 133.1, 132.8, 132.7, 132.0, 131.6, 130.2, 129.9, 129.8, 129.7, 129.5, 129.0, 129.0, 128.9, 128.8, 128.5, 128.5, 128.4, 128.1, 127.9, 127.6, 127.6, 127.5, 127.5, 127.2, 127.2, 127.0, 126.7, 126.6, 126.4, 126.0, 125.4, 125.3, 125.2, 125.0, 124.4, 66.0, 53.4.

HRMS m/z calculated for $[M+Na]^+$ $C_{46}H_{30}NaO_2S_2$ 701.1585. Found 701.1592.

2-(2,4-Di(naphthalen-2-yl)-5-(thiophene-2-carbonyl)-1,3-dithiol-2-yl)-1-(thiophen-2-yl)ethan-1-one (B21)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

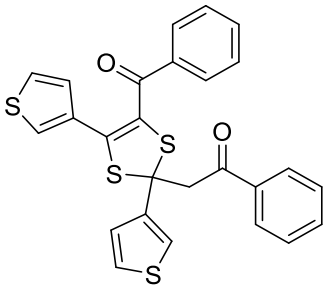
Bright yellow solid (62 mg, 42%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.4 (d, *J* = 2.1 Hz, 1H), 7.9 – 7.9 (m, 2H), 7.9 – 7.8 (m, 2H), 7.8 – 7.7 (m, 1H), 7.6 (d, *J* = 4.9 Hz, 1H), 7.6 (d, *J* = 8.5 Hz, 1H), 7.5 – 7.4 (m, 5H), 7.4 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.4 (d, *J* = 4.9 Hz, 1H), 7.3 (d, *J* = 3.8 Hz, 1H), 7.1 (t, *J* = 4.4 Hz, 1H), 6.6 (t, *J* = 4.4 Hz, 1H), 4.5 (d, *J* = 17.0 Hz, 1H), 4.5 (d, *J* = 17.1 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 187.5, 182.4, 143.5, 142.7, 142.2, 138.6, 134.6, 134.5, 133.4, 132.8, 132.5, 129.7, 129.6, 128.5, 128.5, 128.4, 128.3, 128.0, 127.7, 127.6, 127.5, 127.0, 126.7, 126.6, 126.6, 126.5, 126.1, 124.2, 67.4, 51.3.

HRMS m/z calculated for $[M+Na]^+$ $C_{34}H_{22}NaO_2S_4$ 613.0400. Found 613.0409.

2-(4-Benzoyl-2,5-di(thiophen-3-yl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B22)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

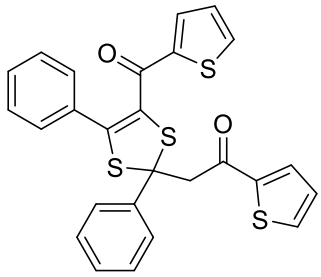
Bright yellow solid (69 mg, 56%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.0 – 7.9 (m, 2H), 7.7 – 7.6 (m, 5H), 7.5 – 7.4 (m, 2H), 7.4 – 7.4 (m, 3H), 7.3 – 7.3 (m, 2H), 7.2 (ddt, *J* = 8.1, 6.6, 1.2 Hz, 3H), 7.0 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.9 (dd, *J* = 5.0, 1.3 Hz, 1H), 4.4 (d, *J* = 17.5 Hz, 1H), 4.4 (d, *J* = 17.5 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.8, 190.5, 143.7, 136.7, 136.1, 133.8, 132.8, 132.6, 129.3, 128.8, 128.3, 128.2, 128.0, 127.4, 126.5, 126.3, 125.7, 123.2, 50.3.

HRMS m/z calculated for $[M+Na]^+$ $C_{26}H_{18}NaO_2S_4$ 513.0087. Found 513.0093.

2-(2,4-Diphenyl-5-(thiophene-2-carbonyl)-1,3-dithiol-2-yl)-1-(thiophen-2-yl)ethan-1-one (B23)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

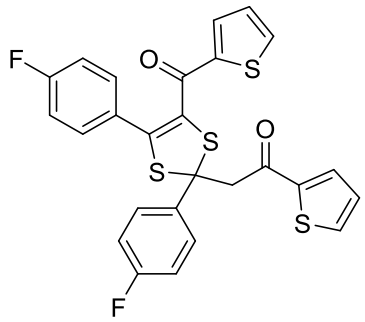
Bright yellow solid (72 mg, 59%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.9 – 7.8 (m, 2H), 7.7 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.6 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.5 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.4 (ddd, *J* = 6.2, 4.7, 2.7 Hz, 4H), 7.3 – 7.3 (m, 3H), 7.2 (tq, *J* = 4.3, 1.6 Hz, 4H), 7.1 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.8 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.5 (d, *J* = 17.1 Hz, 1H), 4.4 (d, *J* = 17.1 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 187.6, 182.3, 143.5, 143.4, 142.7, 142.4, 141.6, 134.6, 134.5, 132.6, 129.7, 129.6, 128.4, 128.4, 128.3, 128.1, 127.7, 126.6, 125.3, 67.4, 51.5.

HRMS m/z calculated for $[M+Na]^+$ $C_{26}H_{18}NaO_2S_4$ 513.0087. Found 513.0098.

2-(2,4-Bis(4-fluorophenyl)-5-(thiophene-2-carbonyl)-1,3-dithiol-2-yl)-1-(thiophen-2-yl)ethan-1-one (B24)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

Bright yellow solid (60 mg, 46%).

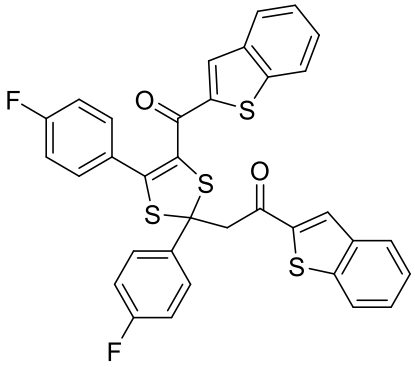
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.8 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.7 (d, *J* = 3.8 Hz, 1H), 7.7 (d, *J* = 5.0 Hz, 1H), 7.5 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.3 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.1 (t, *J* = 4.4 Hz, 1H), 7.0 (t, *J* = 8.6 Hz, 2H), 6.9 (t, *J* = 8.6 Hz, 2H), 6.8 (t, *J* = 4.4 Hz, 1H), 4.4 (d, *J* = 17.0 Hz, 1H), 4.3 (d, *J* = 17.0 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 187.4, 182.0, 163.7 (d, *J* = 127.8 Hz), 161.7 (d, *J* = 125.1 Hz), 143.3, 142.5, 141.0, 137.5 (d, *J* = 3.3 Hz), 134.8 (d, *J* = 9.8 Hz), 134.4, 132.6, 131.5 (d, *J* = 8.5 Hz), 128.5 (d, *J* = 8.1 Hz), 128.3, 127.8, 125.4, 115.6 (d, *J* = 21.9 Hz), 115.3 (d, *J* = 21.7 Hz), 66.9, 51.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -110.2, -113.9.

HRMS m/z calculated for $[M+Na]^+$ $C_{26}H_{16}F_2NaO_2S_4$ 548.9899. Found 548.9890.

1-(Benzo[b]thiophen-2-yl)-2-(4-(benzo[b]thiophene-2-carbonyl)-2,5-bis(4-fluorophenyl)-1,3-dithiol-2-yl)ethan-1-one (B25)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

Bright yellow solid (61 mg, 39%).

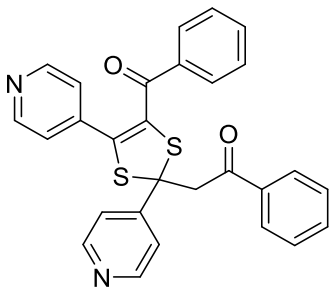
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.0 (s, 1H), 7.9 – 7.8 (m, 5H), 7.8 (d, *J* = 8.2 Hz, 1H), 7.6 (d, *J* = 8.0 Hz, 1H), 7.5 (s, 1H), 7.5 (d, *J* = 7.2 Hz, 1H), 7.4 – 7.4 (m, 4H), 7.3 (d, *J* = 7.8 Hz, 1H), 7.1 (t, *J* = 8.6 Hz, 2H), 6.9 (t, *J* = 8.6 Hz, 2H), 4.5 (d, *J* = 17.0 Hz, 1H), 4.4 (d, *J* = 16.9 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 189.0, 183.4, 164.3, 163.3, 162.3, 161.3, 142.8, 142.8, 142.7, 142.0, 141.6, 138.9, 138.5, 137.2, 137.2, 131.8, 131.5, 131.4, 130.0, 128.7, 128.6, 128.0, 127.7, 126.2, 126.0, 125.3, 125.1, 123.0, 122.8, 115.8, 115.6, 115.5, 115.3, 67.5, 51.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -109.92, -113.60.

HRMS m/z calculated for $[M+Na]^+$ $C_{34}H_{20}F_2NaO_2S_4$ 649.0212. Found 649.0218.

2-(4-Benzoyl-2,5-di(pyridin-4-yl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B26)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

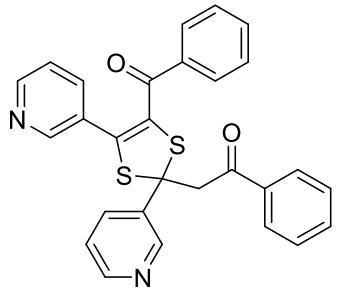
Bright yellow solid (52 mg, 43%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 5.4 Hz, 1H), 8.35 (d, *J* = 5.2 Hz, 2H), 7.90 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 6.8 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.20 (t, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 6.8 Hz, 2H), 4.49 (s, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.1, 189.5, 151.7, 150.2, 149.9, 139.2, 138.6, 135.9, 135.5, 134.2, 133.7, 129.3, 129.2, 128.9, 128.5, 128.1, 123.5, 121.1, 66.1, 50.7.

HRMS m/z calculated for $[M+Na]^+$ $C_{28}H_{20}N_2NaO_2S_2$ 503.0864. Found 503.0870.

2-(4-Benzoyl-2,5-di(pyridin-3-yl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B27)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

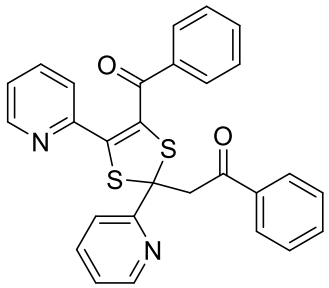
Bright yellow solid (58 mg, 48%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (d, *J* = 2.7 Hz, 1H), 8.60 – 8.50 (m, 1H), 8.45 (d, *J* = 2.4 Hz, 1H), 8.34 (dd, *J* = 4.9, 1.8 Hz, 1H), 8.26 (dt, *J* = 8.3, 2.1 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.54 – 7.45 (m, 5H), 7.37 – 7.30 (m, 2H), 7.16 (t, *J* = 7.7 Hz, 2H), 7.01 (dd, *J* = 8.0, 4.7 Hz, 1H), 4.53 (s, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.3, 189.5, 150.3, 149.9, 149.1, 147.8, 140.0, 138.5, 136.8, 136.2, 135.6, 134.5, 134.1, 133.1, 129.7, 129.2, 128.9, 128.4, 128.3, 128.1, 123.0, 122.8, 64.9, 50.9.

HRMS m/z calculated for $[M+Na]^+$ $C_{28}H_{20}N_2NaO_2S_2$ 503.0864. Found 503.0870.

2-(4-Benzoyl-2,5-di(pyridin-2-yl)-1,3-dithiol-2-yl)-1-phenylethan-1-one (B28)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

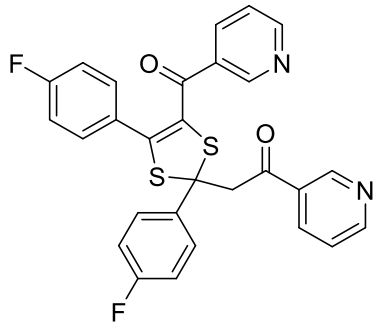
Bright yellow solid (67 mg, 56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 3.0 Hz, 0H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 3.8 Hz, 1H), 8.04 – 7.90 (m, 2H), 7.90 – 7.71 (m, 3H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.50 – 7.35 (m, 3H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.15 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.97 (dd, *J* = 7.6, 4.7 Hz, 1H), 4.78 (dd, *J* = 17.2, 3.5 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 195.8, 190.2, 161.1, 150.4, 149.0, 148.6, 137.2, 136.9, 136.8, 136.2, 136.1, 133.5, 132.9, 129.6, 129.2, 128.6, 128.3, 128.2, 123.3, 122.7, 122.3, 67.5, 51.3.

HRMS m/z calculated for $[M+Na]^+$ $C_{28}H_{20}N_2NaO_2S_2$ 503.0864. Found 503.0870.

2-(2,4-Bis(4-fluorophenyl)-5-nicotinoyl-1,3-dithiol-2-yl)-1-(pyridin-3-yl)ethan-1-one (B29)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

Bright yellow solid (62 mg, 46%).

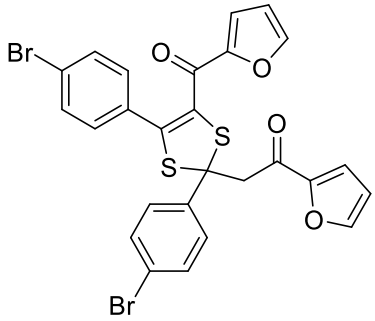
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.1 (s, 1H), 8.8 (d, *J* = 5.3 Hz, 1H), 8.6 (s, 1H), 8.5 (d, *J* = 4.9 Hz, 1H), 8.2 (d, *J* = 8.1 Hz, 1H), 7.8 (dd, *J* = 9.0, 5.0 Hz, 2H), 7.7 (d, *J* = 7.6 Hz, 1H), 7.4 (dd, *J* = 8.0, 4.5 Hz, 1H), 7.2 (dd, *J* = 8.7, 5.2 Hz, 2H), 7.1 (m, 3H), 6.8 (t, *J* = 8.5 Hz, 2H), 4.5 (s, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 193.6, 188.2, 163.8 (d, *J* = 149.7 Hz), 161.8 (d, *J* = 146.4 Hz), 145.6, 137.7 (d, *J* = 2.9 Hz), 136.0, 135.5, 132.3, 132.1 (d, *J* = 8.6 Hz), 131.3, 128.4 (d, *J* = 8.6 Hz), 127.4 (d, *J* = 3.3 Hz), 126.7, 123.8, 122.9, 115.7 (d, *J* = 21.9 Hz), 65.4, 51.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ -108.8, -113.4.

HRMS m/z calculated for $[M+Na]^+$ $C_{28}H_{18}F_2N_2NaO_2S_2$ 539.0675. Found 539.0682.

2-(2,4-Bis(4-bromophenyl)-5-(furan-2-carbonyl)-1,3-dithiol-2-yl)-1-(furan-2-yl)ethan-1-one (B30)



Eluent: hexane/ethyl acetate: 19/1 to 9/1.

Bright yellow solid (62 mg, 40%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7 (d, *J* = 8.9 Hz, 1H), 7.6 (d, *J* = 2.0 Hz, 1H), 7.5 (d, *J* = 8.9 Hz, 1H), 7.4 (s, 0H), 7.4 – 7.3 (m, 2H), 7.2 – 7.2 (m, 2H), 6.9 (d, *J* = 3.7 Hz, 1H), 6.5 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.3 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.3 (d, *J* = 1.7 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 183.5, 176.3, 152.1, 150.9, 146.9, 146.8, 142.7, 140.8, 131.9, 131.6, 131.6, 131.6, 131.5, 131.5, 131.5, 131.4, 131.3, 130.9, 130.8, 130.8, 130.1, 129.9, 128.3, 128.3, 128.3, 125.5, 123.9, 122.2, 120.0, 120.0, 120.0, 118.0, 112.7, 112.4, 66.6, 50.3.

HRMS m/z calculated for $[M+Na]^+$ $C_{26}H_{16}Br_2NaO_4S_2$ 636.8754. Found 636.8760.

ASSOCIATED CONTENT

Supporting information

The Supporting Information is available free of charge on the

ACS Publications website at DOI: 10.1021/acs.joc.xxxxxxx.

Copies of ^{1}H and ^{13}C NMR spectra data for all new compounds. X-ray crystallographic data for **B0** and **B11** (CCDC 1952724 and 1952725, respectively).

This material is available free of charge via the Internet at http://pubs.acs.org.

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