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Multi-redox Indenofluorene Chromophores Incorporating Dithiafulvene Donor and Ene/Enediyne Acceptor Units

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Abstract

Large donor-acceptor scaffolds derived from polycyclic aromatic hydrocarbons (PAHs) with tunable HOMO and LUMO energies are important for several applications, such as organic photovoltaics. Here we present a large selection of PAHs based on central indenofluorene (IF) or fluorene cores and containing various dithiafulvene (DTF) donor units that gain aromaticity upon oxidation, in some cases expanded by pyrrolo annelation, and a variety of acceptor units, such as vinylic diesters, enediynes, and cross-conjugated radiaannulenes (RAs) that gain aromaticity upon reduction. The optical and redox properties of these carbon-rich compounds were studied by UV-Vis absorption spectroscopy and cyclic voltammetry. Synthetically, the work explores IF

diones or fluorenone as central building blocks by subjecting the carbonyl groups to a variety of reactions; that is, phosphite- or Lawesson's reagent mediated olefination reactions (to introduce DTF motifs), Corey-Fuchs dibromoolefinations followed by Sonogashira couplings (to introduce enediynes motifs), and Knoevenagel condensations (to introduce vinylic diester motif). By a subsequent Glaser-Hay coupling reaction, a RA acceptor unit was introduced to provide an IF-DTF-RA donor-acceptor scaffold with a low-energy charge-transfer absorption and multi-redox behavior.

Keywords

Alkynes; Chromophores; Fused-ring systems; Heterocycles; Redox chemistry

Introduction

Tetrathiafulvalene (**TTF**, Figure 1) is a redox-active molecule that has been widely explored in materials and supramolecular chemistries [1-8]. **TTF** reversibly undergoes two sequential one-electron oxidations, generating first a radical cation ($\mathbf{TTF^{+\cdot}}$) and subsequently a dication ($\mathbf{TTF^{2+}}$) containing two 6π-aromatic 1,3-dithiolium rings. The redox properties and geometries of the redox states have been finely tuned by extending the conjugated system with various cores, such as polycyclic aromatic hydrocarbons (PAHs), resulting in so-called extended TTFs [9-12]. One example of this is introduction of an indeno[1,2-*b*]fluorene (**IF**) core [13], providing indenofluorene-extended TTFs (IF-TTFs) of the general structure shown in Figure 1. The π-system can be further expanded as well at the dithiole rings. For example, we have recently developed a synthetic protocol for fusing a pyrrole unit to one of the dithiole rings of an

IF-TTF, allowing for dimerization of extended TTFs *via* the nitrogen atom by different linkers [14].

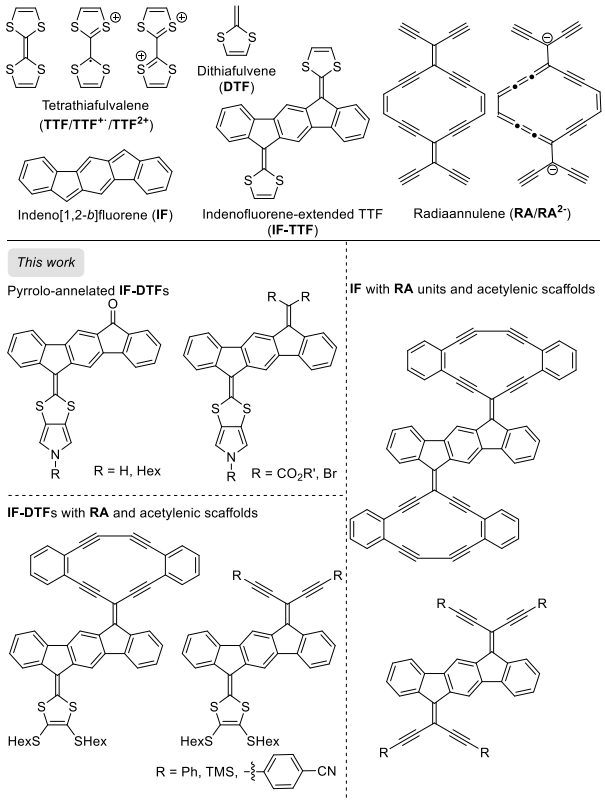


Figure 1: Overview of structural motifs.

Donor-acceptor chromophores can be obtained by replacing one of the dithiafulvene (DTF) rings of the IF-TTF by an electron acceptor. Cyclic and acyclic acetylenic scaffolds comprised of enediyne units are known to behave as good electron acceptors [15, 16], and we became interested in combining the IF-DTF scaffold with such motifs to generate novel multi-redox systems. For example, the radiaannulene moiety **RA** shown in Figure 1 (or its truncated counterpart with one of the exocyclic enediyne units removed) [17, 18] is a particularly good electron acceptor as it gains 14π-aromaticity upon reduction. In this work, we also want to further explore pyrrolo-annelated IF-DTFs with different substituents on the nitrogen atom, and the functionalization at the other

end of the IF core with electron accepting moieties. An overview of general motifs targeted in this work is shown in Figure 1.

Results and Discussion

Synthesis

The synthetic building blocks used in this work (**1**-**8**) are shown in Figure 2. The dione **1** and the ketones **4** and **6** were synthesized according to literature procedures [14, 19, 20], as were the 1,3-dithiol-2-thiones **2** and **3** [21]. Fluorenone **5** is commercially available. The new building blocks **7** and **8** were prepared according to related literature procedures [21], as described in the Supporting Information.

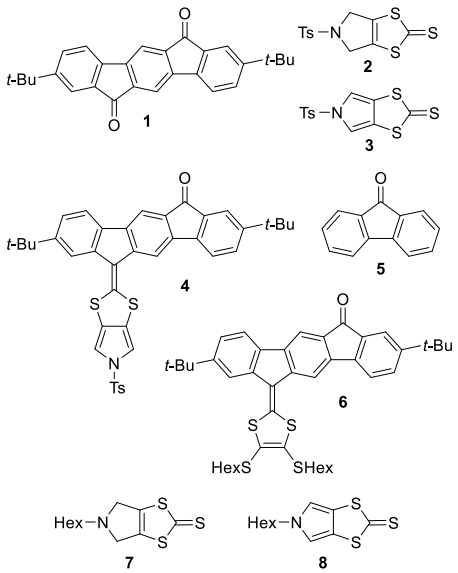
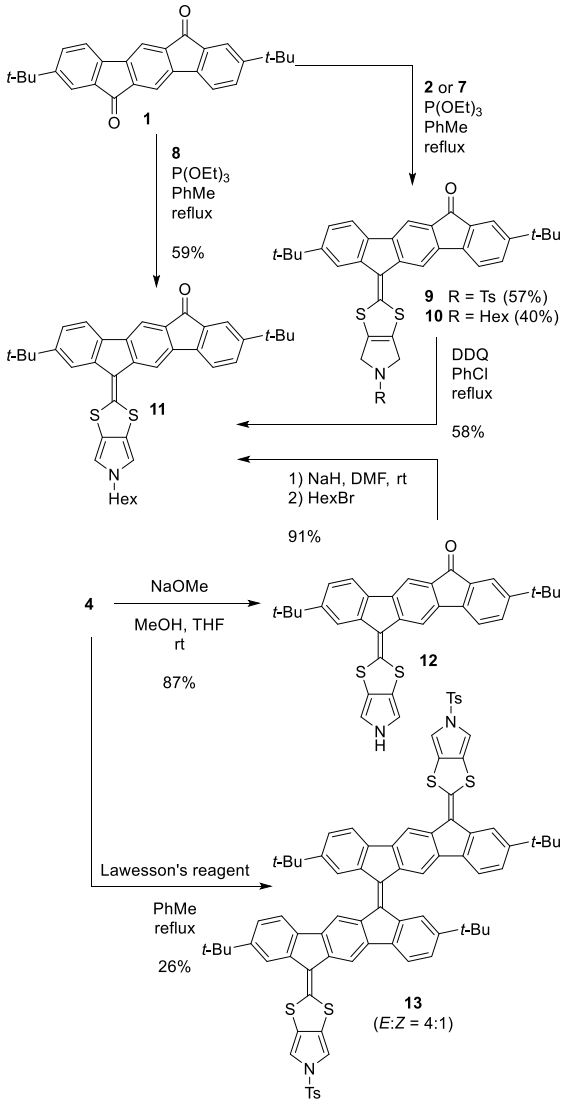


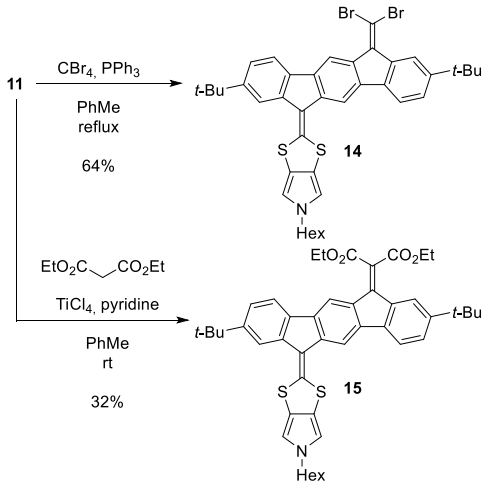
Figure 2: Dione/ketones **1**, **4**-**6** and 1,3-dithiol-2-thione compounds **2**-**3** and **7**-**8** that are building blocks used in this work.

Our first objective was to explore further annellation of dihydropyrrole and pyrrole units at the DTF moiety of an IF-DTF. A phosphite-mediated coupling of either 1,3-dithiol-2-thione **2**, **7**, or **8** with IF dione **1** afforded IF-DTFs **9**-**11**, as shown in Scheme 1.

Compound **11** was also obtained from building block **4** via the pyrrolo-annelated IF-DTF **12** by removal of the tosyl (Ts) group under alkaline conditions, followed by nucleophilic substitution to incorporate the hexyl chain on the pyrrole. Furthermore, treatment of the IF-DTF ketone **4** with Lawesson's reagent (using a recently established protocol [20]) yielded the large dimer **13** as a mixture of *E* and *Z* isomers (ca. 4:1). Further functionalization of the IF-DTF ketone **11** was obtained by Corey-Fuchs dibromo-olefination and Knoevenagel condensation to yield vinylic dibromide **14** and diester **15**, respectively, as illustrated in Scheme 2.

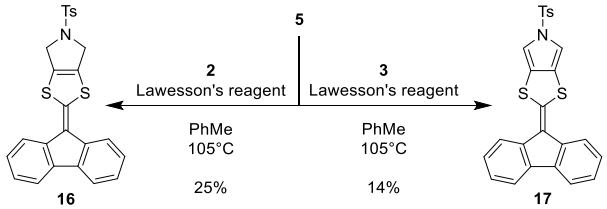


Scheme 1: Synthesis of IF-DTF ketones **9-12** and dimer **13**.



Scheme 2: Further functionalization of the IF-DTF ketone **11** via Corey-Fuchs dibromo-olefination and Knoevenagel condensation.

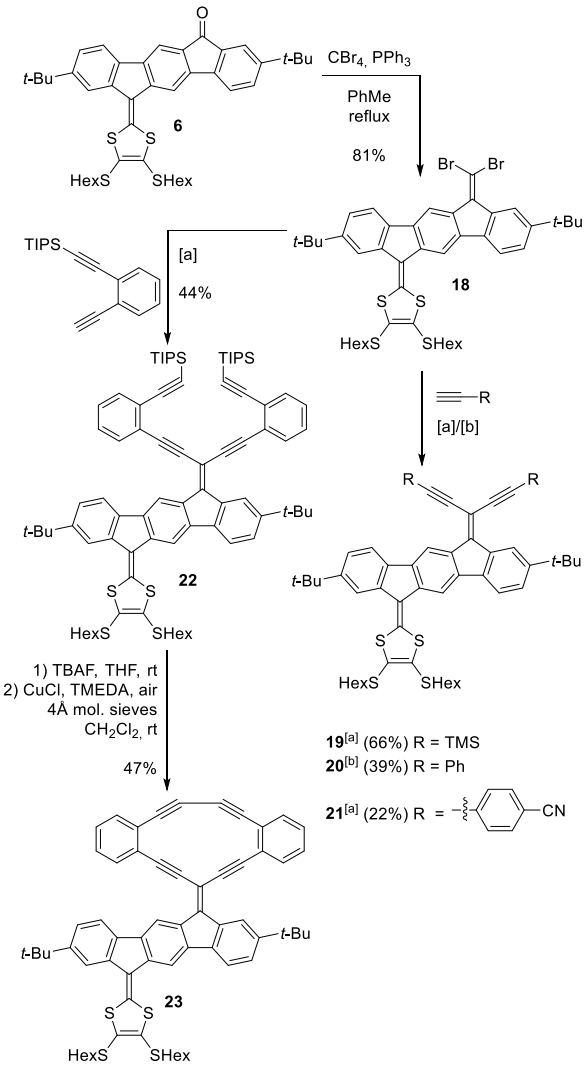
To elucidate the properties of the donor part itself of the pyrrolo-annelated IF-DTF systems, we prepared compounds **16** and **17** containing a smaller fluorene PAH. These compounds were prepared by a Lawesson's reagent promoted coupling between fluorenone **5** and the Ts-protected 1,3-dithiole-2-thione building blocks **2** and **3**, respectively, shown in Scheme 3 (albeit in modest yields). Fluorene-based DTF compounds have previously been explored in various elaborate systems [22-25].



Scheme 3. Coupling of 1,3-dithiole-2-thione building blocks **2** and **3** with fluorenone **5** to afford fluorene-extended DTFs **16** and **17**.

Next, we wanted to explore IF-DTFs as motifs for acetylenic scaffolding (Scheme 4). Starting from IF-DTF building block **6**, dibromo-olefinated compound **18** was obtained

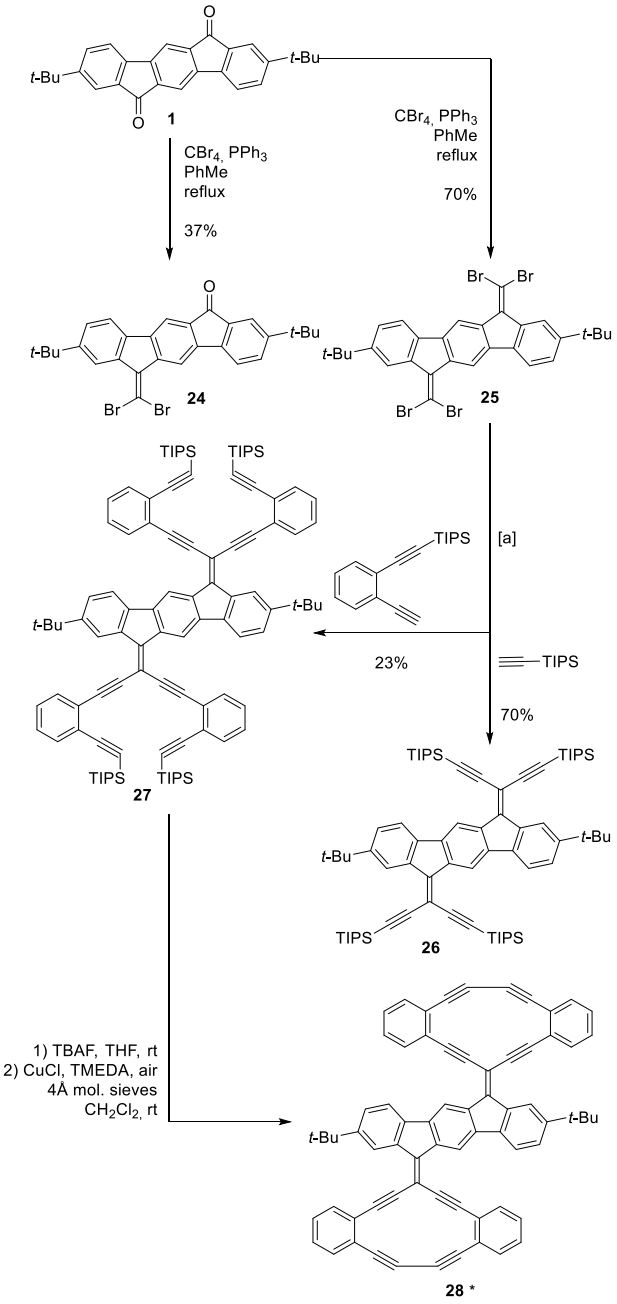
by a Corey-Fuchs reaction. Two-fold Sonogashira couplings with TMS-acetylene, ethynylbenzene, or 4-ethynylbenzonitrile yielded compounds **19**-**21**, while two-fold Sonogashira coupling with ((2-ethynylphenyl)ethynyl)-triisopropylsilane resulted in compound **22**. Desilylation of the alkynes of compound **22** with tetrabutylammonium fluoride (TBAF) and subsequent intramolecular Glaser-Hay coupling of the terminal alkynes afforded the macrocyclic IF-DTF-RA scaffold **23**. Molecular sieves (4 Å) were added to the reaction mixture as this has previously been shown to significantly promote the Glaser-Hay coupling [26]. Compounds **20** and **21** were unfortunately very sensitive compounds that were found to easily degrade, which made their characterization somewhat difficult (*vide infra*).



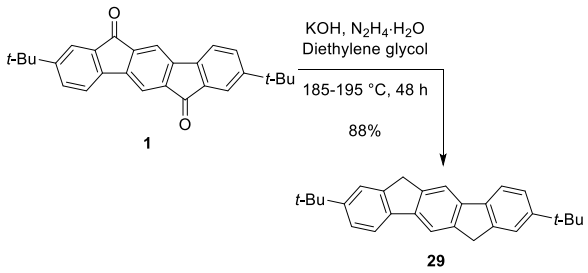
Scheme 4: Synthesis of acetylenic scaffolds based on IF-DTF. Conditions: [a] $Pd(PPh_3)_2Cl_2$, CuI, THF, Et_3N, rt. [b] Pd_2dba_2, $P(^tBu)_3$, CuI, THF, Et_3N, rt.

We also targeted other enediyne acetylenic scaffolds with IF as central core as shown in Scheme 5. Starting from IF dione **1**, compounds **24** and **25** were synthesized via Corey-Fuchs dibromo-olefinations. Four-fold Sonogashira couplings of compound **25** with TIPS-acetylene and ((2-ethynylphenyl)ethynyl)-triisopropylsilane yielded compounds **26** and **27**, respectively. A two-fold, intramolecular Glaser-Hay coupling of compound **27** (after desilylation) was attempted under the conditions that were successful in the synthesis of compound **23** (Scheme 4). A compound that may tentatively be assigned to **28** was observed by MALDI-MS analysis of the reaction mixture, but less than needed for an NMR sample was isolated. Furthermore, the isolated compound proved quite insoluble in all investigated deuterated solvents, and therefore it was not possible to determine the purity of the product by this method.

In an initial attempt to investigate other synthetic pathways to extended IF compounds, the reduced IF **29** was synthesized from IF dione **1** by a Wolff-Kishner reduction of the two ketones as shown in Scheme 6. Compound **29** could potentially after deprotonation be reacted with electrophiles as previously established [27] for the parent structure [28] without *tert*-butyl substituents.



Scheme 5: Synthesis of acetylenic scaffolds with IF as central core. *Not fully characterized due to poor solubility. Conditions: [a] $Pd(PPh_3)_2Cl_2$, CuI, THF, Et_3N, rt.



Scheme 6: Reduction of IF dione **1** to dihydro-IF **29**.

UV-Vis Absorption Spectroscopy

UV-Vis absorption spectra of the known compound **4** [14] and new compounds **9**-**13** and **15** are depicted in Figure 3, and the data are presented in Table 1. A redshift of the longest-wavelength absorption maximum is observed for all new compounds compared to that of **4**. For compounds **11** and **12**, this indicates that the inductive electron withdrawing or donating influences of the substituent group (Ts-group in **4** and Hex-group in **11**) on the nitrogen atom in the pyrrole ring have an effect on the absorption in the visible spectrum of pyrrolo-annelated IF-DTF ketones. Interestingly, the absorption of the dihydropyrrole IF-DTF **9** is redshifted relative to that of the pyrrole IF-DTF **4**, while the absorption does not change significantly when comparing IF-DTFs **10** and **11**, indicating that the extent to which the absorption changes upon oxidation from a dihydropyrrole to a pyrrole unit depends on the substituent on the N of the dihydropyrrole/pyrrole ring. Introducing the diester electron-acceptor in compound **15** does not change the absorption significantly, compared to compound **11**. When changing the solvent from PhMe to CH_2Cl_2, we observed a redshift of the longest-wavelength absorption maximum for compounds **10** and **11**, indicating some charge-transfer character of the absorption (see Figure S1 in the Supporting Information). Of all the compounds, the large dimer **13** stands out with a significantly redshifted and intense longest-wavelength absorption maximum (λ_{max} at 574 nm) expanding to ca. 680 nm.

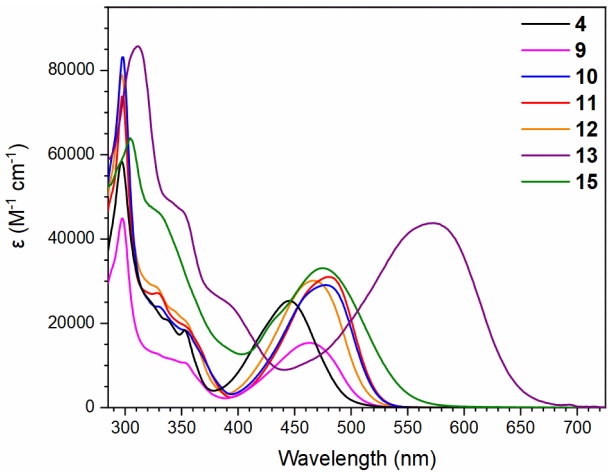


Figure 3: UV-Vis absorption spectra of compounds **4**, **9**-**13**, and **15** in PhMe at 25 °C.

Table 1: UV-Vis absorption data of compounds in PhMe or CH_2Cl_2 at 25 °C (absorption maxima λ_{max} and molar absorptivities ε).

Compound	λ_{max} [nm] (ε [10^3 M^{-1} cm^{-1}])	Compound	λ_{max} [nm] (ε [10^3 M^{-1} cm^{-1}])
4[a]	297 (58), 445 (25)	**16**[b]	297 (3.6), 395 (21)*, 409 (22)
9[a]	297 (45), 462 (20)	**17**[b]	297 (7.1), 383 (27), 393 (25)*
10[a]	298 (68), 478 (24)	**22**[b]	262 (51), 300 (55), 402 (17) (broad), 489 (27)
11[a]	298 (74), 480 (31)	**23**[b]	297 (95), 401 (21)*, 426 (24), 444 (23)*, 529 (34)
12[a]	297 (79), 466 (30)	**26**[b]	296 (76), 413 (52), 440 (70)
13[b, c]	269 (69), 312 (84), 574 (43)	**27**[b]	306 (46), 444 (24)*, 461 (25), 534 (1.8) (broad)
15[a]	304 (60), 475 (34)	**30**[b, d]	251, 400*, 412

[a]PhMe; [b]CH_2Cl_2; [c]*E*/*Z* ratio of 4:1; [d]Reference [14]; *Shoulder peak

UV-Vis absorption spectra of the known compound **30** [20] and new compounds **16** and **17** are shown in Figure 4, and the data are presented in Table 1. Compared to compound **30**, the longest-wavelength absorption maximum of compound **16** is slightly blueshifted while the absorption maximum of compound **17** is significantly blueshifted. This indicates that annelation of the dihydropyrrole ring to the DTF moiety does not change the absorption maximum significantly compared to the two SHex-substituents, while annelation of a pyrrole ring results in an absorption maximum at significantly shorter wavelength. These compounds have blueshifted longest-wavelength absorptions relative to the donor-acceptor scaffolds incorporating a pyrrolo-annelated DTF unit.

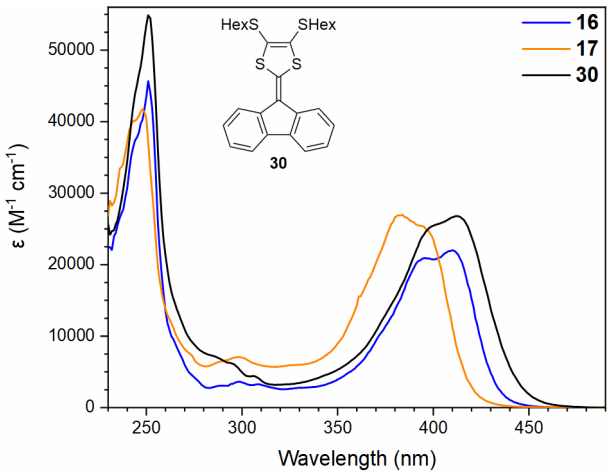


Figure 4: UV-Vis absorption spectra of compounds **16**, **17**, and **30** in CH_2Cl_2 at 25 °C.

UV-Vis absorption spectra of compounds **22**, **23**, **26**, and **27** are depicted in Figure 5. By comparing donor-acceptor chromophores **22** and **23**, it is observed that the RA moiety of IF-DTF-RA scaffold **23** induces a significant redshift, presumably due to the stronger electron-accepting character of the RA unit (and hence a lower-energy LUMO) compared to the acyclic acetylenic scaffold of compound **22** (in line with first reduction potentials, *vide infra*). For compound **27**, a shorter longest-wavelength absorption maximum at 461 nm is observed; this is a symmetric compound for which

no donor-acceptor “push-pull” system is present, in contrast to **22** and **23**. The absorption maxima of compound **26** are significantly blueshifted, presumably due to the smaller conjugated system. The same trend with a shorter longest-wavelength absorption maximum that was observed for compound **27** was also observed for this compound.

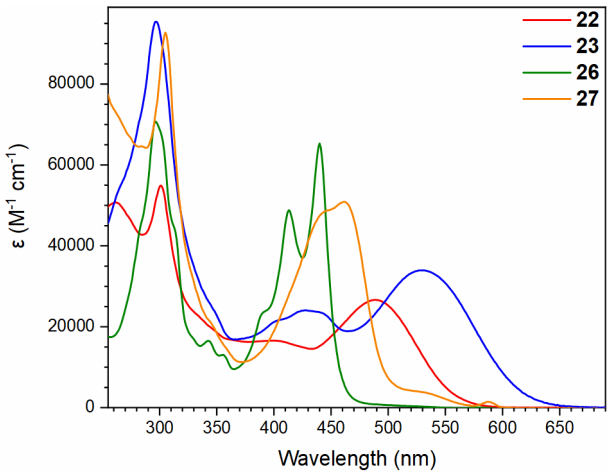


Figure 5: UV-Vis absorption spectra of compounds **22**, **23**, **26**, and **27** in CH_2Cl_2 at 25 °C.

The degradation of compound **20** in the presence of light and oxygen is visible as a color change upon leaving a sample of the compound in solution in an open vial, unshielded from light (Figure S2 in the Supporting Information). This degradation was investigated by UV-Vis absorption spectroscopy; the absorption spectrum was measured over time for three different samples, and a notable change in the longest-wavelength absorption maximum was only observed for the sample that was exposed to both light and oxygen (see Figures S3 and S4 in the Supporting Information). We speculate that this degradation is due to reaction with singlet oxygen generated by the compound as a photosensitizer; indeed, we have recently shown [29] that IF-TTF compounds are reactive towards singlet oxygen at the central fulvene bond but, in

contrast, IF-TTFs (without an acetylenic moiety as in **20**) are themselves poor photosensitizers for singlet oxygen.

Electrochemistry

Cyclic voltammograms of compounds **11**, **13**, **15**, **16**, and **17** (in MeCN for compounds **11** and **15** and in CH_2Cl_2 for compounds **13**, **16**, and **17**, all with 0.1 M Bu_4NPF_6 as supporting electrolyte) are shown in Figure 6, and potentials against ferrocene (Fc/Fc^+) (obtained from differential pulse voltammetry, see Supporting Information) are summarized in Table 2. Compounds **11** and **15** showed two irreversible first oxidations at +0.34 V and +0.38 V *vs* Fc/Fc^+, showing that replacing the ketone with the stronger electron withdrawing vinylic diester renders the first oxidation more difficult (by 40 mV). An anodic shift of 40 mV was also observed for the second oxidation. Oppositely, compound **15** underwent a significantly easier first reduction than **11** (-1.00 V *vs* -1.35 V), and it also underwent a second reduction. The pyrrolo-annelated dimer **13** showed a reversible oxidation at +0.42 V followed by an irreversible oxidation at +1.01 V, and two reversible reductions at -1.48 V and -1.81 V. Here the acceptor properties are not promoted by incorporating an acceptor unit as in **15**, but instead by the bifluorenylidene motif [30] obtained by dimerizing two pyrrolo-annelated IF-DTF units. Notably, the dimer **13** underwent a first oxidation more readily (by as much as 0.14 V) than the corresponding fluorene-DTF donor **17** (both containing the same *N*-tosylated pyrrolo-DTF unit). The low electrochemical HOMO-LUMO gap of **13** is paralleled by a low-energy longest-wavelength absorption maximum (*vide supra*, Figure 7).

A quasi-reversible first oxidation was observed at +0.47 V for the fluorene compound **16** and an irreversible oxidation at +0.99 V. Compound **17** experienced a quasi-reversible first oxidation at +0.56 V and an irreversible oxidation at +1.07 V. Thus, the

dihydropyrrolo-annelated DTF compound is more easily oxidized than the pyrrolo-annelated DTF compound. These fluorene compounds did not experience a reduction within the potential window.

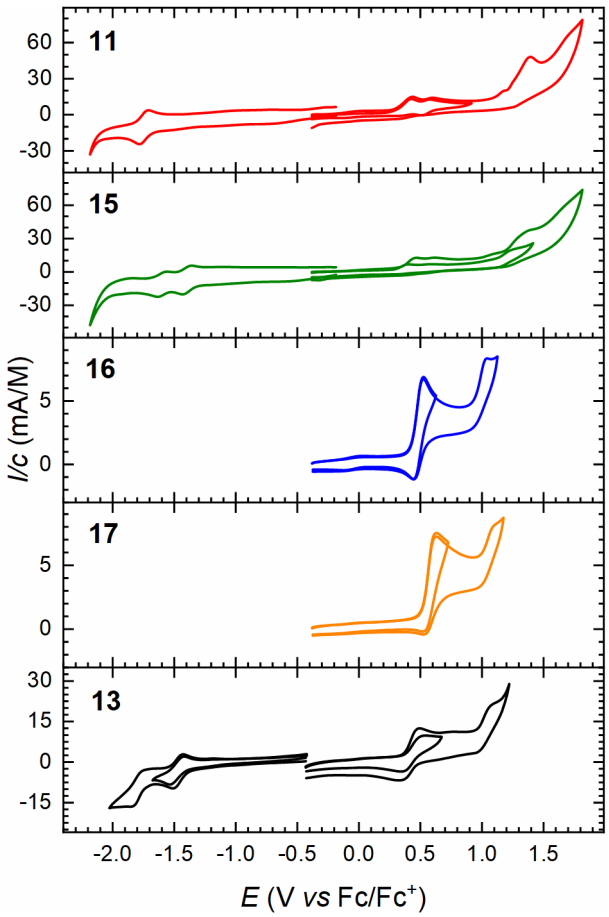


Figure 6: Cyclic voltammograms of compounds **11** (in MeCN), **13** (in CH_2Cl_2), **15** (in MeCN), **16** (in CH_2Cl_2), and **17** (in CH_2Cl_2); supporting electrolyte: 0.1 M Bu_4NPF_6, scan rate: 0.1 V/s. All potentials are depicted against the Fc/Fc^+ redox couple.

Table 2: Electrochemical data from differential pulse voltammetry of compounds in CH_2Cl_2 (with 0.1 M Bu_4NPF_6) if not otherwise stated; potentials in volts *vs* Fc/Fc^+.

Compound	E^1_{ox}	E^2_{ox}	E^1_{red}	E^2_{red}
11[a]	+0.34	+0.52	-1.35	-
13[b]	+0.42	+1.01	-1.48	-1.81
15[a]	+0.38	+0.56	-1.00	-1.21
16	+0.47	+0.99	-	-
17	+0.56	+1.07	-	-
22	+0.41	+0.76	-1.80	-
23	+0.41	+0.81	-1.50	-1.78
26	+0.84	-	-1.64	-1.98
27	+0.85	-	-1.63	-1.89

[a]In MeCN. [b]*E/Z* ratio of 4:1.

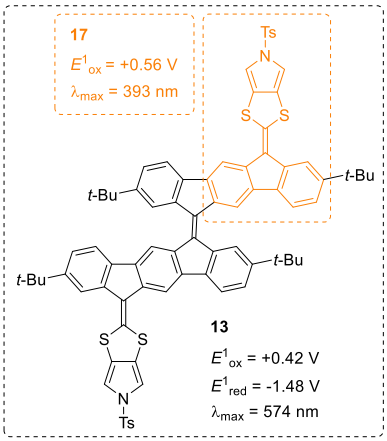


Figure 7: Comparison of properties of compounds **13** and **17**.

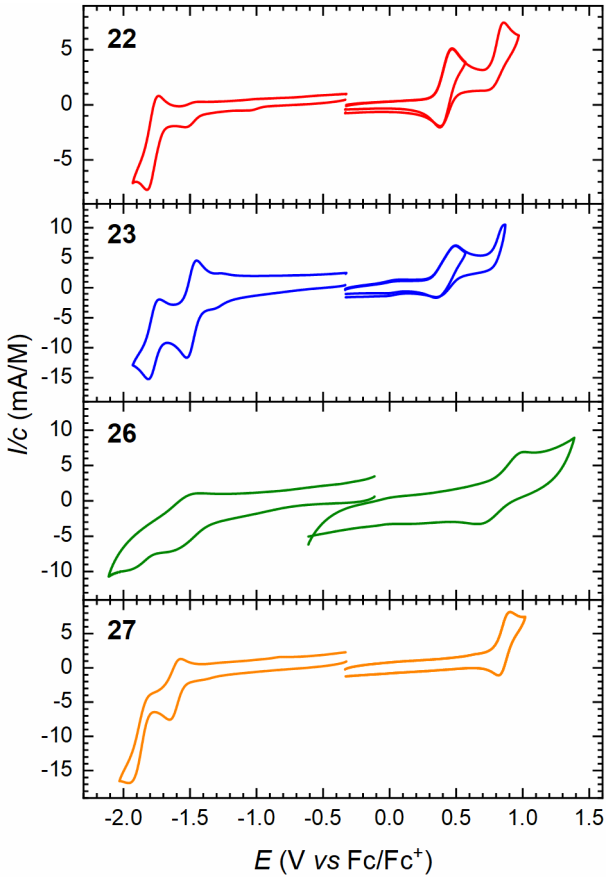


Figure 8: Cyclic voltammograms of compounds **22**, **23**, **26**, and **27** in CH_2Cl_2; supporting electrolyte: 0.1 M Bu_4NPF_6, scan rate: 0.1 V/s. All potentials are depicted against the Fc/Fc^+ redox couple.

Cyclic voltammograms of the acetylenic scaffolds **22**, **23**, **26**, and **27** (in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte) are shown in Figure 8. Quasi-reversible one-electron oxidations of the two DTF-functionalized compounds **22** and **23** are observed at +0.41 V followed by irreversible oxidations at +0.76 V (**22**) and +0.81 V (**23**), respectively. One reversible oxidation at +0.84 V and one reversible reduction at -1.64 V were observed for compound **26**, along with one irreversible reduction at -1.98 V. These oxidation and reduction potentials are not significantly different from the potentials observed for compound **27**, namely one quasi-reversible oxidation at +0.85 V and two one-electron reductions at -1.63 V and -1.89 V, indicating that the larger

conjugated system of compound **27** does not significantly change the redox properties of the compound. Compounds **26** and **27** lack the DTF donor part and are hence oxidized at significantly higher potentials than the other compounds. On the other hand, they are stronger acceptors than the acetylenic scaffold **22** containing the DTF donor. We have previously [31] studied a related compound in which all four TIPS-ethynyl substituents of **26** are replaced by cyano groups; this compound showed superior acceptor properties, being reduced at -0.81 V and -1.09 V *vs* Fc/Fc^+ (similar conditions), but no donor properties (thereby contrasting **26** and **27**).

Of the acetylenic scaffolds studied, IF-DTF-RA **23** containing an RA moiety is the strongest acceptor, which we ascribe to gain of $14\pi_z$-aromaticity of the cyclic moiety of the reduced species (in line with previously studied RA scaffolds [17, 18, 32]). Indeed, it is reduced more easily by as much as 0.3 V than its corresponding acyclic counterpart, compound **22**, although it contains a π-system of the same size, and it is even reduced more easily by 0.13 V than the acetylenic scaffold **27** containing acetylenic acceptor motifs at both ends of the IF core and hence no DTF donor unit. Compound **23** also undergoes a reversible, second reduction to form the dianion. This compound should gain aromaticity upon either reduction or oxidation as illustrated in Figure 9.

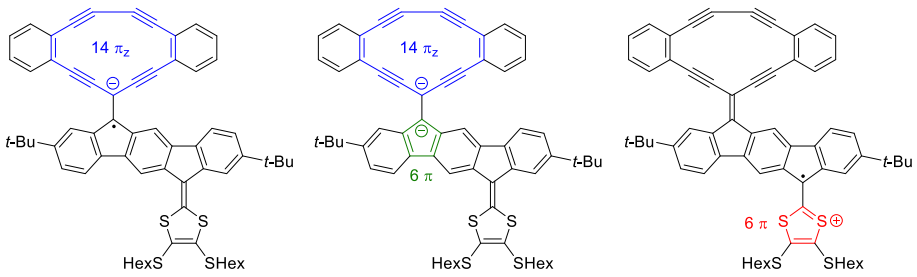


Figure 9: Radical anion (left), dianion (middle), and radical cation (right) of compound **23**; the radical anion has a $14\pi_z$-aromatic ring (highlighted in blue; only counting 2 π-

electrons of each triple bond, here defined as those in π_z orbitals), the dianion has an additional 6π-aromatic cyclopentadienyl anion (highlighted in green), while the cation has a 6π-aromatic 1,3-dithiolium ring (highlighted in red).

X-Ray Crystallographic Analysis

Crystals suitable for single-crystal X-ray diffraction studies were obtained for compounds **25**, **26**, and **29**. Their structures are shown in Figure 10, top, and their respective crystal packings below. All three compounds pack in a herringbone manner in the crystal structure, with the major difference that compound **29** is perpendicular with respect to the herringbone pattern and the related structures (see Figure 10, bottom). Compound **25** packs with an intramolecular distance of 3.41 Å between the planes of the π-systems. Neither compound **26** nor **29** shows π-π interactions in the crystal packing. The large bulkiness of the TIPS groups along with the *tert*-butyl groups in compound **26** prevent these interactions, while for compound **29**, the lack of π-π interactions can be ascribed to the methylene bridges as the hydrogens along with the *tert*-butyl groups prevent good overlap of the π-systems.

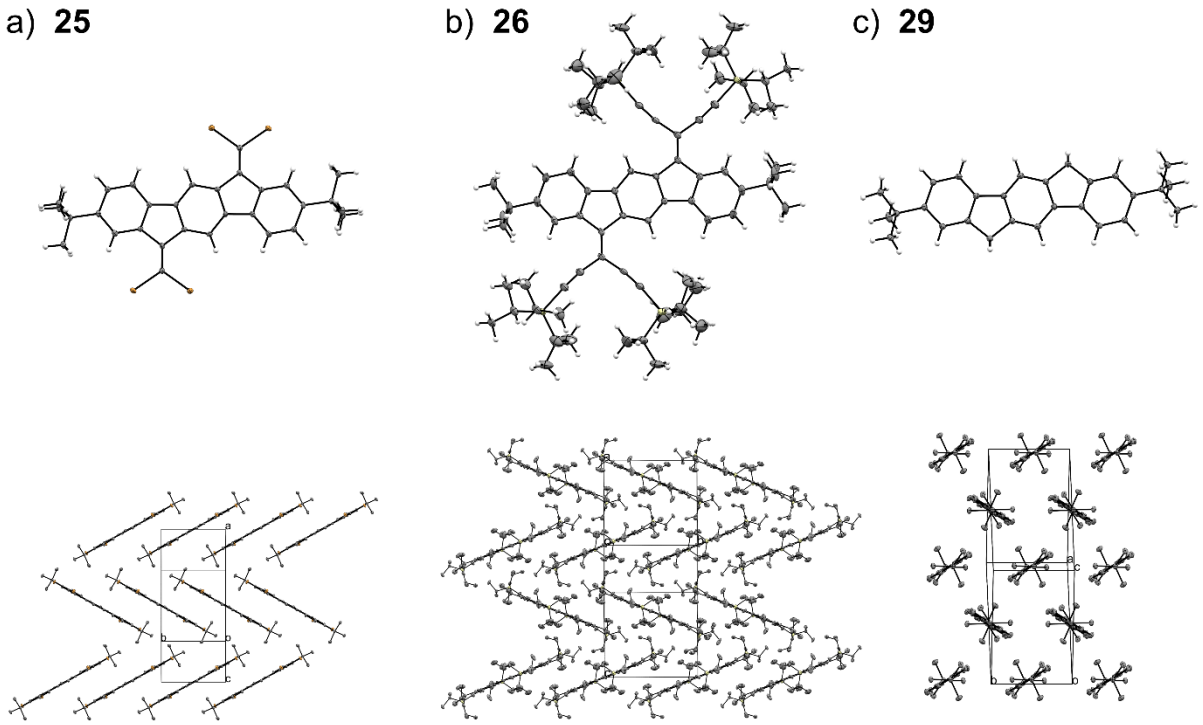


Figure 10. ORTEP plots (50% probability) and crystal packing of compounds a) **25**, b) **26**, and c) **29**. The respective crystal packing of each compound is shown below, in which the hydrogen atoms are omitted for clarity.

Conclusion

In summary, various redox-active chromophores based on the indenofluorene scaffold were synthesized, incorporating different dithiafulvenes and acetylenic scaffolds, such as acetylenic radiaannulenes. The compounds have strong absorptions in the visible region and undergo reversible (or quasi-reversible) oxidations and reductions. We have also presented two new fluorene-extended dithiafulvenes, which also absorb strongly in the visible region and undergo one reversible oxidation, while no reductions were observed for these compounds. Systematic studies show that by small structural modifications, the optical and electrochemical HOMO-LUMO gaps can be finely tuned – with first oxidations and reductions that can be adjusted by several hundreds of millivolts for donor-acceptor IF scaffolds. Introduction of both the dithiafulvene and

radiaannulene units along the indenofluorene scaffold provided a donor-acceptor compound covering a particularly broad absorption profile and with a redshifted longest-wavelength absorption maximum relative to most of the compounds (529 nm in dichloromethane), which can be related to the fact that it is both a good donor and a good acceptor as shown electrochemically. This compound stands out as gaining aromaticity in one of its appendages along the IF core upon either reduction (generation of 14π_z-aromatic ring) or oxidation (generation of 1,3-dithiolium ring).

Synthetically, the work relies on using indenofluorene diones as key building blocks for performing olefination reactions, such as phosphite or Lawesson's reagent mediated couplings, Corey-Fuchs dibromoolefinations, and Knoevenagel condensations. In particular, the acetylenic scaffolds presented in this work may be useful precursors for even more elaborate, conjugated and carbon-rich structures in future work.

Experimental

Anhydrous MeOH was obtained by distillation from activated Mg and stored over 3 Å molecular sieves, or by drying over 3 Å molecular sieves. All remaining anhydrous solvents were obtained from a solvent drying tower (IT model PS-MD-05). HPLC grade solvents were used unless otherwise specified. Purification by chromatography was performed using silica gel (flash: 40-63 μm, Sepacore® Flash Systems X10/X50: 40-63 μm). TLC was performed using aluminum sheets covered with silica gel coated with fluorescent indicator. NMR spectra were recorded on Bruker instrument at 500 MHz and 126 MHz for ^{1}H and ^{13}C NMR, respectively. Deuterated chloroform ($CDCl_3$, ^{1}H = 7.26 ppm, ^{13}C = 77.16 ppm), deuterated CH_2Cl_2 (CD_2Cl_2, ^{1}H = 5.32 ppm, ^{13}C = 54.00 ppm), deuterated DMSO ($(CD_3)_2SO$, ^{1}H = 2.50 ppm, ^{13}C = 39.53 ppm), deuterated

acetone ($(CD_3)_2CO$, ^1H = 2.05 ppm, ^{13}C = 29.84 ppm), or deuterated benzene (C_6D_6, ^1H = 7.16 ppm, ^{13}C = 128.39 ppm) were used as solvents and internal references. Chemical shift values are referenced to the ppm scale and coupling constants are expressed in Hertz (Hz). HRMS analysis was performed on a Bruker SolariX XR MALDI-FT-ICR instrument with dithranol as matrix. Melting points are not corrected.

UV-Vis absorption spectroscopy

UV-Vis absorption spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer scanning between 800 and 200 nm. All spectra were recorded with baseline correction in CH_2Cl_2 or toluene (HPLC grades) at 25 °C in a quartz cuvette with a 10 mm path length.

Electrochemistry

Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were obtained using an Autolab PGSTAT12 instrument and Nova 1.11 software with a scan rate of 0.1 V/s for the CVs. Ag/AgCl was used as the reference electrode, a Pt wire was used as the counter electrode, and a glassy-carbon disk electrode (3 mm) was used as the working electrode. The reference electrode was separated from the solution containing the substrate by a ceramic frit. Measured potentials were referenced to ferrocene/ferrocenium (Fc/Fc^+) redox couple, measured before and after the experiment. A 0.1 M solution of NBu_4PF_6 was used as electrolyte. All solutions were purged with Ar prior to measurements.

Crystallography

All single crystal X-ray diffraction diffraction data for compound **9** were collected on a Bruker D8 VENTURE diffractometer equipped with a Mo Kα X-ray (λ = 0.71073 Å). The data collections were done at 100 K. All data were integrated with SAINT and a

multi-scan absorption correction using SADABS was applied [33, 34]. The structure was solved by direct methods using SHELXT and refined by full-matrix least-squares methods against F_2 by SHELXL-2019/2 [35, 36]. The data for the compounds have been deposited with the Cambridge Crystallographic Data Centre [37]. The CIF-files and reports found in the Supporting Information were generated using FinalCIF [38].

Synthesis

Compounds **1** [19], **2** [21], **3** [21], **4** [14], and **6** [20] were synthesized according to literature procedures, and compounds **7** and **8** were synthesized according to modified literature procedures [21].

Compound 9

A solution of **1** (139 mg, 352 μmol) and **2** (176 mg, 534 μmol) in anhydrous toluene (5 mL) and $P(OEt)_3$ (10 mL) was heated to reflux for 5 h, resulting in a color change from orange to dark red. The reaction mixture was then allowed to cool to rt before it was concentrated under reduced pressure. The resulting dark red solid was purified by flash column chromatography (SiO_2, 20% EtOAc/heptane), and recrystallization from CH_2Cl_2/MeOH followed by centrifugation yielded **9** (136 mg, 57%) as an orange solid. R_f = 0.18 (70% CH_2Cl_2/heptane). M.p.: 178-181 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.76 (s, 1H), 7.72 - 7.71 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.44 (m, 2H), 7.44 – 7.35 (m, 3H), 4.50 (s, 4H), 2.44 (s, 3H), 1.43 (s, 9H), 1.36 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 152.5, 150.8, 147.7, 144.4, 143.2, 142.1, 142.0, 138.5, 136.9 135.2, 134.8, 133.4, 132.1, 131.2, 130.1, 128.9, 128.5, 127.4, 123.7, 123.2, 121.4, 119.8, 119.4, 119.3, 115.5, 114.2, 52.4, 35.1, 35.0, 31.6, 31.1, 21.5 ppm; one sp^3-C signal missing, presumably due to overlap. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 676.2019 [M + H$^+$], calcd for ($C_{40}H_{38}NOS_3^+$) = 676.2008.

Compound 10

A solution of **1** (85 mg, 223 μmol) and **7** (92 mg, 354 μmol) in anhydrous toluene (5 mL) and $P(OEt)_3$ (10 mL) was heated to reflux for 5 h, resulting in a color change from red to dark red. The reaction mixture was then allowed to cool to rt before it was concentrated under reduced pressure. The resulting dark red solid was purified by flash column chromatography using Sepacore® Flash Systems X10/X50 (SiO_2, 1%-10% EtOAc/heptane), and recrystallization from CH_2Cl_2/MeOH followed by centrifugation yielded **10** (54 mg, 40%) as a dark red solid. R_f = 0.32 (20% EtOAc/heptane). M.p.: 180-182 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.02 (d, *J* = 0.8 Hz, 1H), 7.94 (d, *J* = 0.8 Hz, 1H), 7.87 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.42 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.91 (s, 2H), 2.80 (t, *J* = 7.4 Hz, 2H), 1.53 (s, 9H), 1.45 (s, 9H), 1.59 – 1.54 (m, 2), 1.42 – 1.33 (m, 6H), 0.92 (t, *J* = 7.1, 3H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 193.9, 152.8, 151.2, 143.5, 142.7, 142.6, 138.4, 137.7, 135.9, 134.9, 132.6, 132.3, 131.9, 131.7, 123.6, 121.8, 121.5, 120.2, 119.9, 119.7, 115.7, 114.7, 57.5, 57.4, 57.0, 35.5, 35.4, 32.2, 31.9, 31.4, 29.2, 27.3, 23.1, 14.3 ppm; one sp^2-C signal missing, presumably due to overlap. HRMS ($MALDI^+$, FT-ICR, dithranol) *m/z* = 606.2866 [M + H^+], calcd for ($C_{39}H_{44}NOS_2^+$) = 606.2859.

Compound 11

*Method 1 – from IF dione **1***

A solution of **1** (89 mg, 226 μmol) and **8** (95 mg, 350 μmol) in anhydrous toluene (5 mL) and $P(OEt)_3$ (10 mL) was heated to reflux for 5 h, resulting in a color change from orange to dark red. The reaction mixture was then allowed to cool to rt before it was concentrated under reduced pressure. The resulting dark red solid was purified by flash column chromatography (SiO_2, 20% EtOAc/heptane), and recrystallization from CH_2Cl_2/MeOH followed by centrifugation yielded **11** (74 mg, 59%) as a red solid.

*Method 2 – from **10***

To a solution of **10** (50 mg, 83 μmol) in PhCl (10 mL) was added DDQ (49 mg, 216 μmol), before it was heated to reflux for 4 h. The reaction mixture was then allowed to cool to rt before it was filtered through a silica plug (SiO_2, CH_2Cl_2) and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 10% EtOAc/heptane), and recrystallization from CH_2Cl_2/MeOH followed by centrifugation yielded **11** (29 mg, 58%) as a red solid.

*Method 3 – from **12***

A solution of **12** (22.0 mg, 42.3 μmol) in anhydrous DMF (4 mL) was degassed with Ar for 15 min before NaH (60% in mineral oil suspension, 19.3 mg, 483 μmol) was added, and the reaction mixture was stirred at rt for 15 min resulting in a color change from dark red to dark blue. Then, 1-bromohexane (0.06 mL, 42 μmol) was added, and the reaction mixture was stirred at rt for 2 h, resulting in a color change to dark red. Brine (40 mL) was added dropwise under stirring, and the reaction mixture was extracted with CH_2Cl_2 (80 mL, then 2 x 50 mL). The combined organic phases were washed with brine (3 x 100 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 10% EtOAc/heptane), yielding **11** (20.6 mg, 91%) as a red solid. R_f = 0.28 (20% EtOAc/heptane). M.p.: 224-225 °C. ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 8.21 (s, 1H), 8.20 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 1.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.45 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.26 (d, *J* = 2.1 Hz, 1H), 7.24 (d, *J* = 2.1, 1H), 4.04 (t, *J* = 7.1 Hz, 2H), 1.76 – 1.69 (m, 2H), 1.43 (s, 9H), 1.34 (s, 9H), 1.30 – 1.25 (m, 6H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $(CD_3)_2SO$) δ 192.7, 155.12, 152.1, 150.3, 142.5, 141.8, 141.8, 137.4, 136.9, 134.6, 133.8, 131.8, 130.6, 123.0, 120.5, 120.4, 120.0, 119.7, 119.3, 116.8, 116.6,

115.8, 114.4, 114.1, 113.8, 50.3, 34.9, 34.7, 31.5, 31.0, 30.9, 30.7, 25.6, 22.0, 13.9 ppm. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 604.2723 [M + H$^+$], calcd for ($C_{35}H_{34}NOS_2^+$) = 604.2702.

Compound 12

A solution of NaOMe was prepared from Na (182 mg, 7.92 mmol) and MeOH (3 mL) and stirred for 0.5 h. It was then added dropwise to a solution of **4** (251 mg, 0.372 mmol) in anhydrous THF (35 mL) and anhydrous MeOH (35 mL), resulting in a color change from orange to dark red. The reaction mixture was stirred for 1.5 h at rt before H_2O (50 mL) followed by aqueous HCl (1 M, 8 mL) were added. The resulting suspension was extracted with CH_2Cl_2 (200 mL), and the organic phase was washed with H_2O (3 x 120 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was filtered through a silica plug (SiO_2, CH_2Cl_2) and concentrated under reduced pressure, yielding **12** (168 mg, 87%) as golden dark red crystals**.** R_f = 0.32 (30% EtOAc/heptane). M.p.: 240 °C (decomp.). The compound decomposes in $CDCl_3$. ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 11.68 (t, *J* = 2.8 Hz, 1H), 8.22 (s, 1H), 8.20 (s, 1H), 8.05 – 8.02 (m, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.65 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.45 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.25 (dd, *J* = 2.8, 1.9 Hz, 1H), 7.21 (dd, *J* = 2.8, 1.9 Hz, 1H), 1.43 (s, 9H), 1.34 (s, 9H) ppm. ^{13}C NMR (126 MHz, $(CD_3)_2SO$) δ 192.7, 155.9, 152.1, 150.3, 142.5, 141.9, 141.8, 137.4, 136.9, 134.7, 133.8, 131.8, 130.6, 123.0, 120.4, 120.0, 119.9, 119.5, 117.2, 117.3, 115.8, 114.5, 111.2, 111.0, 34.9, 34.8, 31.5, 30.9 ppm; one sp^2-C signal missing, presumably due to overlap. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 520.1760 [M + H$^+$], calcd for ($C_{35}H_{30}NOS_2^+$) = 520.1763.

Compound 13

A solution of **4** (62.0 mg, 92.0 μmol) and Lawesson's reagent (23.1 mg, 57.0 μmol) in anhydrous, N_2-degassed toluene (20 mL) was heated to reflux for 21 h. The reaction mixture was then allowed to cool to rt, diluted with toluene (50 mL), washed with 1 M NaOH (3 x 50 mL), and then with H_2O (3 x 50 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 20% EtOAc/heptane), yielding **13** (15.5 mg, 26%) as a purple solid. R_f = 0.23 (20% EtOAc/heptane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 2H), 8.50 (s, 2H), 8.12 (s, 2H), 7.96 (s, 2H), 7.83 (d, *J* = 8.4 Hz, 4H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.34 (m, 6H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.23 (s, 2H), 7.20 (s, 2H), 2.42 (s, 6H), 1.44 (s, 18H), 1.27 (s, 18H) ppm (*E*:*Z* ratio 4:1; ^{1}H NMR signals reported for the *E* isomer). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 149.9, 145.8, 143.6, 140.7, 140.5, 139.1, 139.0, 138.6, 137.9, 137.4, 137.0, 136.4, 135.5, 130.4, 127.2, 126.7, 126.6, 126.1, 125.4, 124.1, 123.7, 120.8, 119.2, 119.1, 117.9, 115.0, 111.5, 111.4, 55.7, 35.3, 35.2, 35.2, 35.1, 32.0, 31.9, 31.8, 31.7, 31.6, 29.9, 29.5, 29.1, 22.8, 21.8, 14.3 ppm (*E*:*Z* ratio 4:1; sp^2-C signals missing, presumably due to overlap). HRMS (MALDI$^+$, FT-ICR, dithranol) *m*/*z* = 1314.3631 [$M^{\cdot+}$], calcd for ($C_{80}H_{70}N_2O_4S_6^{\cdot+}$) = 1314.3654.

Compound 14

A solution of **11** (100 mg, 0.166 mmol) in anhydrous toluene (6 mL) was added dropwise to an Ar-degassed solution of CBr_4 (264 mg, 0.796 mmol) and PPh_3 (406 mg, 1.55 mmol) in anhydrous toluene (10 mL). The reaction mixture was degassed with Ar for another 10 min before it was heated to reflux for 5 h, resulting in a color change from dark red to orange. Additional CBr_4 (221 mg, 0.666 mmol) and PPh_3 (402 mg, 1.53 mmol) were added, and the reaction mixture was heated to reflux for another 19

h before it was allowed to cool to rt and filtered. The filtrate was concentrated under reduced pressure, and the resulting orange/yellow solid was purified by flash column chromatography (SiO_2, 15% EtOAc/heptane). The resulting solid was triturated with heptane (4 x 2 mL) yielding **14** (72 mg, 57%) as an orange solid. The combined supernatants were concentrated under reduced pressure and the obtained orange oil solidified upon cooling in the freezer overnight. The solid was triturated with heptane (3 x 2 mL), yielding additional **14** (9 mg) as an orange solid (total yield: 81 mg, 64%). R_f = 0.30 (15% EtOAc/heptane). M.p.: 158 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.71 (d, *J* = 1.7 Hz, 1H), 8.27 (d, *J* = 1.3 Hz, 1H), 8.06 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.48 (dd, J = 8.0, 1.7 Hz, 1H), 7.38 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.96 (t, *J* = 7.3 Hz, 2H), 1.82 (p, *J* = 7.1 Hz, 2H), 1.47 (s, 9H), 1.40 (s, 9H), 1.39 – 1.28 (m, 6H), 0.90 (t, *J* = 7.1, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 150.5, 149.5, 140.2, 139.7, 139.1, 139.1, 138.3, 137.6, 136.0, 126.8, 123.4, 123.2, 122.4, 120.8, 119.2, 119.2, 119.1, 118.8, 117.4, 114.6, 112.7, 112.6, 89.0, 51.6, 35.6, 35.6, 32.2, 32.0, 31.8, 26.7, 22.9, 14.4, 1.4 ppm; two sp^2-C signals missing, presumably due to overlap. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 759.1092 [$M^{\cdot+}$], calcd for ($C_{40}H_{41}Br_2NS_2^{\cdot+}$) = 759.1021.

Compound 15

To a solution of **11** (80 mg, 0.132 mmol) in anhydrous toluene (20 mL) was added $TiCl_4$ (0.2 mL, 1.82 mmol) dropwise, resulting in a color change from dark red to black. Dropwise addition of diethyl malonate (0.2 mL, 1.32 mmol) and pyridine (0.3 mL, 3.72 mmol) resulted in another color change to dark red. The reaction mixture was stirred at rt for 20 h before additional $TiCl_4$ (0.2 mL, 1.82 mmol) and diethyl malonate (0.2 mL, 1.32 mmol) were added dropwise, and the reaction mixture was stirred for another 16 h and then filtered. The filtrate was diluted with toluene (150 mL), washed with brine (3

x 100 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting dark red oil was purified by flash column chromatography (SiO_2 neutralized with Et_3N, 35% EtOAc/heptane), yielding **15** (22 mg, 22%) as a deep red thin film after freeze-drying for five days. Minor impure fractions were combined and concentrated under reduced pressure. The obtained film was triturated with pentane (4 x 1 mL) to yield additional **15** (10 mg) as a deep red thin film (total yield: 32 mg, 32%). R_f = 0.30 (20% EtOAc/heptane). ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 8.34 (s, 1H), 8.31 (s, 1H), 8.10 (d, *J* = 1.6 Hz, 1H), 7.95 (d, *J* = 1.7 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.46 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.55 (q, *J* = 7.2 Hz, 2H), 4.48 (q, *J* = 7.2 Hz, 2H), 4.10 (t, *J* = 7.1 Hz, 2H), 1.85 (quin, *J* = 7.1 Hz, 2H), 1.46 (s, 9H), 1.44 – 1.38 (m, 6H), 1.37 (s, 9H), 1.36 – 1.25 (m, 6H), 0.88 (t, *J* = 5.0 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ 166.5, 166.4, 153.0, 151.6, 151.4, 144.6, 141.6, 140.9, 140.6, 138.9, 138.2, 137.3, 136.0, 133.7, 129.4, 124.0, 123.4, 122.0, 121.2, 120.2, 119.8, 118.7, 118.6, 118.2, 115.1, 114.4, 114.3, 62.9, 62.9, 51.8, 35.9, 35.8, 32.5, 32.3, 32.2, 32.0, 31.8, 27.1, 23.4, 14.5, 14.4 ppm; one sp^2-C signal missing, presumably due to overlap. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 745.3493 [$M^{\cdot+}$], calcd for ($C_{46}H_{51}NO_4S_2^{\cdot+}$) = 745.3254.

Compound 16

To a flame-dried vial equipped with a magnetic stirrer bar were added **2** (69 mg, 209 μmol), **5** (28 mg, 153 μmol), and Lawesson's reagent (63 mg, 155 μmol). Dry toluene (5 mL) degassed with N_2 for 15 min was added, and the solution was heated to 105 °C for 18.5 h. The reaction mixture was then allowed to cool to rt, diluted with toluene (20 mL), and washed with 1 M NaOH (3 x 20 mL), and then with H_2O (20 mL). The yellow precipitate in the aqueous phase was isolated by filtration and washed with H_2O before it was purified by flash column chromatography (SiO_2, 50%-100% CH_2Cl_2/heptane)

yielding **16** (18 mg, 39 μmol, 25%) as a yellow solid. R_f = 0.18 (50% CH_2Cl_2/heptane). M.p.: >260 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.41 (td, *J* = 7.5, 1.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.34 (td, *J* = 7.5, 1.1 Hz, 2H), 4.46 (s, 4H), 2.42 (s, 3H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 145.0, 138.5, 137.3, 134.0, 130.6, 128.8, 128.0, 127.5, 126.4, 123.4, 120.2, 21.7 ppm; two sp^2-C carbon signals missing, presumably due to overlap. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 461.0577 [$M^{\cdot+}$], calcd for ($C_{25}H_{19}NO_2S_3^{\cdot+}$) = 461.0572.

Compound 17

To a flame-dried vial equipped with a magnetic stirrer bar were added **3** (70 mg, 212 μmol), **5** (24 mg, 135 μmol), and Lawesson's reagent (63 mg, 155 μmol). Dry toluene (5 mL) degassed with N_2 for 15 min was added, and the solution was heated to 105 °C for 18.5 h. The reaction mixture was then allowed to cool to rt, diluted with toluene (10 mL), and washed with 1 M NaOH (3 x 20 mL), and then with H_2O (20 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography twice (SiO_2, 1) 1% EtOAc/heptane, 2) 50% CH_2Cl_2/heptane), yielding **17** (8.6 mg, 18 μmol, 14%) as a yellow solid. R_f = 0.18 (50% CH_2Cl_2/heptane). M.p.: 255 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.2, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.15 (s, 2H), 2.42 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 146.0 138.8, 137.5, 136.8, 135.6, 130.6, 127.4, 127.4, 126.5, 126.4, 123.9, 120.0, 111.5, 22.0 ppm. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 459.0421 [$M^{\cdot+}$], calcd for ($C_{25}H_{17}NO_2S_3^{\cdot+}$) = 459.0416.

Compound 18

To an Ar-degassed solution of PPh_3 (845 mg, 3.22 mmol) and CBr_4 (560 mg, 1.69 mmol) in anhydrous toluene (20 mL) was added **6** (250 mg, 0.351 mmol). The reaction mixture was heated to reflux and stirred under a N_2 atmosphere for 30 h before it was cooled to rt and filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated in vacuum. Flash column chromatography (10% CH_2Cl_2/heptane) yielded **18** (246 mg, 81%) as an orange solid. R_f = 0.29 (10% CH_2Cl_2/heptane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 0.7 Hz, 1H), 8.71 (d, *J* = 1.5 Hz, 1H), 7.94 (d, *J* = 0.7 Hz, 1H), 7.76 – 7.75 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.38 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.01 – 2.96 (m, 4H), 1.85 – 1.68 (m, 4H), 1.51 – 1.47 (m, 4H), 1.45 (s, 9H), 1.40 (s, 9H), 1.37 – 1.30 (m, 8H), 0.92 – 0.88 (m, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 150.4, 139.8, 139.6, 138.8, 138.5, 138.3, 138.1, 137.6, 137.3, 136.1, 135.8, 129.5, 128.4, 126.6, 123.3, 123.2, 121.4, 120.1, 119.2, 118.9, 117.3, 113.8, 89.1, 36.9, 36.8, 35.3, 35.3, 31.9, 31.7, 31.6, 31.5, 30.1, 30.0, 28.5, 22.7, 14.2, 14.2 ppm; two sp^3-C signals missing, presumably due to overlap. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 868.1287 [$M^{\cdot+}$], calcd for ($C_{44}H_{52}Br_2S_4^{\cdot+}$) = 868.1293.

Compound 19

To a N_2-degassed solution of **18** (90 mg, 0.10 mmol) in anhydrous THF (5 mL) and Et_3N (5 mL) were added N_2-degassed TMS-acetylene (0.20 mL, 1.4 mmol), $Pd(PPh_3)_2Cl_2$ (15 mg, 0.021 mmol), and CuI (5.0 mg, 0.026 mmol). The reaction mixture was stirred at rt under a N_2 atmosphere for 4 h before it was filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, 10-15% CH_2Cl_2/heptane) yielded **19** (62 mg, 66%) as a purple solid (red in solution). R_f = 0.31 (15% CH_2Cl_2/heptane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.81 (d, *J* = 1.7 Hz, 1H), 7.91 (s, 1H), 7.76 (d, *J* = 1.7 Hz,

1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.41 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.37 (dd, *J* = 8.0, 1.7 Hz, 1H), 3.01 – 2.96 (m, 4H), 1.79 – 1.72 (m, 4H), 1.54 – 1.48 (m, 4H), 1.45 (s, 9H), 1.40 (s, 9H), 1.35 – 1.32 (m, 8H), 0.92 – 0.89 (m, 6H), 0.44 (s, 9H), 0.35 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 150.2, 146.7, 139.6, 138.8, 138.3, 138.0, 137.6, 137.5, 136.0, 135.5, 129.5, 128.5, 126.9, 123.2, 123.2, 121.8, 120.1, 119.0, 118.8, 117.3, 113.9, 104.9, 104.5, 104.5, 104.3, 99.5, 36.9, 36.8, 35.3, 35.3, 31.9, 31.8, 31.6, 31.5, 30.1, 30.0, 28.5, 22.7, 22.7, 14.2, 14.2, 0.3, 0.1 ppm; one sp^2-C signal and one sp^3-C signal missing, presumably due to overlap. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 903.3985 [$M^{\cdot+}$], calcd for ($C_{54}H_{70}S_4Si_2^{\cdot+}$) = 903.3972.

Compound 20

To a solution of 1-phenyl-2-trimethylsilylacetylene (0.10 mL, 0.517 mmol) in anhydrous THF (25 mL) and MeOH (25 mL) was added K_2CO_3 (0.286 g, 2.07 mmol). The reaction mixture was stirred at rt for 1 h until TLC analysis showed full conversion. It was then filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated under reduced pressure until the total volume was approx. 5 mL. Et_3N (10 mL) was added to the solution, and it was concentrated under reduced pressure until the total volume was approx. 5 mL (Et_3N). The freshly prepared phenylacetylene in Et_3N (approx. 5 mL) was then added to a flask along with **18** (108 mg, 0.124 mmol), anhydrous THF (18 mL), and Et_3N (7 mL), and the solution was degassed with Ar. P(^{t}Bu)$_3$ (0.14 mL, 1.0 M in toluene), Pd_2dba_3 (17 mg, 19 μmol), and CuI (4 mg, 19 μmol) were added, and the reaction mixture was stirred at rt overnight under an Ar atmosphere. The dark brown/red reaction mixture was filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and purified by flash column chromatography (SiO_2 deactivated by 1% Et_3N, 10% CH_2Cl_2/heptane), yielding **20** as a red solid (44 mg, 0.048 mmol, 39%). R_f = 0.55 (50% CH_2Cl_2/heptane). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.10 (d, *J* = 0.8 Hz, 1H), 8.82 (d, *J* =

1.7 Hz, 1H), 7.96 (d, *J* = 0.8 Hz, 1H), 7.81 – 7.78 (m, 2H), 7.77 (d, *J* = 1.5 Hz, 1H), 7.73 – 7.69 (m, 3H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.47 – 7.44 (m, 4H), 7.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.05 – 2.97 (m, 4H), 1.79 – 1.72 (m, 4H), 1.50 – 1.46 (m, 4H), 1.44 (s, 9H), 1.36 (s, 9H), 1.35 – 1.31 (m, 8H), 0.92 – 0.88 (m, 6H) ppm. *Another ^{1}H NMR spectrum measured in C_6D_6 to disrupt π-stacking:* ^{1}H NMR (500 MHz, C_6D_6) δ 9.59 (s, 1H), 9.20 (d, *J* = 1.7 Hz, 1H), 8.32 (s, 1H), 8.06 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.65 – 7.59 (m, 4H), 7.34 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.28 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.09 – 6.99 (m, 7H), 2.75 – 2.69 (m, 4H), 1.61 – 1.54 (m, 4H), 1.42 (s, 9H), 1.32 (s, 9H), 1.29 – 1.19 (m, 8H), 1.17 – 1.11 (m, 4H), 0.88 – 0.82 (m, 6H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 151.2, 150.6, 146.2, 139.8, 139.2, 138.9, 138.5, 138.5, 137.8, 137.6, 135.9, 135.6, 132.2, 132.2, 129.8, 129.6, 129.5, 129.2, 129.0, 128.8, 127.3, 123.6, 123.4, 123.1, 122.9, 121.6, 120.3, 119.2, 117.3, 114.3, 99.9, 98.6, 98.2, 90.0, 89.2, 37.1, 37.0, 35.4, 35.4, 31.9, 31.8, 31.8, 31.8, 30.4, 30.3, 28.7, 23.0, 23.0, 14.2, 14.2 ppm; one sp^2-C signal and one sp^3-C signal missing, presumably due to overlap. *Another ^{13}C NMR spectrum measured in C_6D_6 to disrupt π-stacking could not be obtained due to low concentration of the measured sample.* HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 910.3749 [$M^{\cdot+}$], calcd for ($C_{60}H_{62}S_4^{\cdot+}$) = 910.3729.

Compound 21

To a solution of 4-[(trimethylsilyl)ethynyl]benzonitrile (0.319 g, 1.6 mmol) in anhydrous THF (25 mL) and MeOH (25 ml) was added K_2CO_3 (0.885 g, 6.4 mmol). The reaction mixture was stirred at rt for 2 h until TLC analysis showed full conversion. It was then filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated under reduced pressure until the total volume was approx. 5 mL. Et_3N (10 mL) was added to the solution, and it was concentrated under reduced pressure until the total volume was

approx. 5 mL (Et_3N). The freshly prepared 4-ethynylbenzonitrile in Et_3N (approx. 5 mL) was then added to a flask along with **18** (185 mg, 0.21 mmol) and anhydrous THF (15 mL), and the solution was degassed vigorously with Ar. $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (2 mg, 0.01 mmol) were added, and the reaction mixture was stirred at 45–50 °C overnight under a N_2 atmosphere. The dark brown/red reaction mixture was filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and purified by flash column chromatography (SiO_2, 50% CH_2Cl_2/heptane), yielding **21** as a dark red solid (45 mg, 0.05 mmol, 22%). R_f = 0.29 (100% toluene). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.60 (d, *J* = 1.7 Hz, 1H), 7.87 (s, 1H), 7.78 – 7.63 (m, 9H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.38 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.27 (dd, *J* = 8.0, 1.6 Hz, 1H), 2.96 – 2.89 (m, 4H), 1.72 – 1.65 (m, 4H), 1.44 – 1.41 (m, 3H), 1.38 (s, 9H), 1.35 – 1.27 (m, 9H), 1.27 (s, 9H), 0.86 – 0.81 (m, 6H) ppm. A ^{13}C NMR spectrum could not be obtained due to low concentration of the measured sample. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 960.3652 [$M^{\cdot+}$], calcd for ($C_{62}H_{60}N_2S_4^{\cdot+}$) = 960.3634.

Compound 22

To a solution of triisopropyl((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)silane (220 mg, 0.620 mmol) in THF (10 mL) and MeOH (10 mL) was added K_2CO_3 (180 mg, 1.30 mmol), and the suspension was stirred at rt for 1 h before it was filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated in vacuum to a volume of approx. 10 mL. Et_3N (10 mL) was added, and the solution was further concentrated to a volume of approx. 2 mL. Additional Et_3N (10 mL), anhydrous THF (10 mL), and **18** (102 mg, 0.144 mmol) were added, and the combined solution was thoroughly degassed with Ar prior to addition of $Pd(PPh_3)_2Cl_2$ (20 mg, 0.028 mmol) and CuI (5.0 mg, 0.026 mmol). The resulting reaction mixture was stirred at rt under an Ar atmosphere for 14 h before it was filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated under reduced

pressure. Flash column chromatography (SiO_2,10% CH_2Cl_2/heptane) yielded **22** (65 mg, 44%) as a red oil. R_f = 0.35 (20% CH_2Cl_2/heptane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.80 (d, *J* = 1.7 Hz, 1H), 7.95 (s, 1H), 7.75 – 7.71 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.58 – 7.54 (m, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.35 – 7.30 (m, 2H), 7.26 – 7.21 (m, 1H), 3.02 – 2.97 (m, 4H), 1.86 – 1.68 (m, 4H), 1.58 – 1.44 (m, 4H), 1.43 (s, 9H), 1.37 – 1.31 (m, 8H), 1.24 (s, 9H), 0.98 (s, 18H), 0.95 (s, 18H), 0.93 – 0.87 (m, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 150.0, 147.2, 139.6, 138.5, 138.5, 138.3, 137.6, 137.5, 137.3, 136.1, 135.8, 133.3, 133.0, 132.8, 132.3, 129.3, 128.6, 128.4, 128.2, 127.9, 126.8, 126.7, 126.3, 125.9, 123.3, 123.1, 122.0, 120.0, 119.4, 118.7, 117.5, 113.9, 105.1, 105.0, 100.1, 96.5, 96.5, 96.3, 96.1, 92.9, 92.2, 77.4, 36.9, 36.8, 35.2, 35.1, 31.9, 31.6, 31.5, 31.5, 30.1, 30.0, 28.5, 28.5, 22.7, 22.7, 18.7, 18.7, 14.2, 14.2, 11.4 ppm; one signal missing in the aromatic region and one signal missing in the aliphatic region, presumably due to overlap. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 1270.6417 [$M^{\cdot+}$], calcd for ($C_{82}H_{102}S_4Si_2^{\cdot+}$) = 1270.6397.

Compound 23

To a solution of **22** (93 mg, 0.073 mmol) in THF (10 mL) was added TBAF (1 M in THF, 0.2 mL, 0.2 mmol), and the reaction mixture was stirred at rt for 45 min before it was filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated under reduced pressure to a volume of approx. 2 mL. The resulting solution was diluted with CH_2Cl_2 (50 mL). A solution of CuCl (7.0 mg, 0.070 mmol) in CH_2Cl_2 (5 mL) and TMEDA (0.10 mL, 0.67 mmol) was added along with 4 Å molecular sieves, and the reaction mixture was stirred in an open flask at rt for 3 days before it was filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated under reduced pressure. Flash column chromatography (30% CH_2Cl_2 (technical grade stabilized with 0.2% EtOH)/heptane)

yielded **23** (33 mg, 47%) as a dark green solid. R_f = 0.20 (40% CH_2Cl_2/heptane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.83 (d, *J* = 1.7 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.88 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.28 (m, 8H), 3.02 – 2.97 (m, 4H), 1.80 – 1.73 (m, 4H), 1.52 – 1.50 (m, 4H), 1.48 (s, 9H), 1.47 (s, 9H), 1.37 – 1.32 (m, 8H), 0.96 – 0.85 (m, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 150.1, 148.3, 140.0, 139.0, 138.7, 138.7, 138.5, 137.8, 137.4, 136.0, 135.8, 131.4, 131.4, 130.6, 129.7, 129.5, 129.5, 129.0, 129.0, 128.8, 128.6, 128.6, 128.5, 127.0, 125.2, 125.0, 123.2, 123.1, 121.8, 120.2, 119.0, 117.9, 114.1, 99.6, 96.9, 95.9, 95.4, 94.5, 88.0, 87.8, 82.4, 81.2, 36.9, 36.8, 35.3, 35.2, 32.0, 31.9, 31.6, 31.5, 30.1, 30.0, 28.5, 22.7, 22.7, 14.2, 14 ppm; one signal missing in the aromatic region and one signal missing in the aliphatic region, presumably due to overlap. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 956.3620 [$M^{\cdot+}$], calcd for ($C_{82}H_{102}S_4Si_2^{\cdot+}$) = 956.3572.

Compound 24

To a N_2-degassed solution of **1** (56 mg, 0.14 mmol) in anhydrous toluene (20 mL) was added CBr_4 (191 mg, 0.576 mmol) and PPh_3 (300 mg, 1.14 mmol). The suspension was heated to reflux and stirred under a N_2 atmosphere for 4 h before it was cooled to rt, filtered through a plug of SiO_2 (CH_2Cl_2 as eluent), and concentrated under reduced pressure. Flash column chromatography (10% CH_2Cl_2/heptane) yielded **24** (29 mg, 37%) as an orange solid. R_f = 0.29 (20% CH_2Cl_2/heptane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 0.7 Hz, 1H), 8.69 (d, *J* = 1.7 Hz, 1H), 7.88 (d, *J* = 0.7 Hz, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 1.39 (s, 9H), 1.36 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 152.9, 151.4, 144.0, 143.6, 142.2, 141.6, 139.6, 138.2, 137.1, 135.5, 134.9, 131.9, 127.2, 123.2,

121.8, 119.9, 119.4, 117.7, 115.2, 93.3, 35.4, 35.2, 31.7, 31.4 ppm. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 550.0371 [$M^{\cdot+}$], calcd for ($C_{29}H_{26}Br_2O^{\cdot+}$) = 550.0325.

Compound 25

To a N_2-degassed solution of **1** (250 mg, 0.633 mmol) in anhydrous toluene (50 mL) were added CBr_4 (900 mg, 2.71 mmol) and PPh_3 (1.40 mg, 5.34 mmol). The suspension was heated to reflux and stirred under a N_2 atmosphere for 2 h before it was cooled to rt, filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated under reduced pressure. The crude material was re-dissolved in a minimum of CH_2Cl_2 (approx. 5 mL) before addition of MeOH (20 mL) led to precipitation of a yellow solid. Trituration of the solids with MeOH (3 x 10 mL) yielded **25** (314 mg, 70%) as a yellow solid. R_f = 0.21 (10% CH_2Cl_2/heptane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 2H), 8.69 (s, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 1.39 (s, 18H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 139.8, 139.6, 139.4, 138.4, 138.1, 126.8, 123.2, 119.0, 117.0, 91.0, 35.3, 31.7 ppm. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 705.8756 [$M^{\cdot+}$], calcd for ($C_{30}H_{26}Br_4^{\cdot+}$) = 705.8722.

Compound 26

To a N_2-degassed solution of **25** (208 mg, 0.295 mmol) in THF (13 mL) and Et_3N (13 mL) were added Ar-degassed triisopropylsilylacetylene (1.85 mL, 1.50 g, 8.26 mmol), $Pd(PPh_3)Cl_2$ (0.0586 g, 0.0835 mmol), and CuI (0.0161 g, 0.0845 mmol). The reaction mixture was stirred for 25 h at rt under a N_2 atmosphere before it was filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated under reduced pressure. The orange residue was purified by flash column chromatography (SiO_2, 10% CH_2Cl_2/heptane), yielding **26** as red crystals (229 mg, 0.206 mmol, 70%). R_f = 0.58 (10% CH_2Cl_2/heptane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (m, 2H), 8.77 (m, 2H), 7.55

– 7.53 (d, *J* = 8 Hz, 2H), 7.34 – 7.32 (d, *J* = 8 Hz, 2H), 1.38 (s, 18H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 145.6, 139.9, 139.5, 138.2, 138.1, 126.5, 123.1, 118.9, 116.9, 106.6, 106.5, 103.5, 102.7, 101.4, 35.2, 31.8, 19.0, 11.7 ppm. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 1111.7786 [M + H$^+$], calcd for ($C_{74}H_{111}Si_4^+$) = 1111.7757. Elemental analysis: C: 79.90%, H: 10:30%; calcd for $C_{74}H_{110}Si_4$: C: 79.93%, H: 9.97%.

Compound 27

To a solution of triisopropyl((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)silane (376 mg, 1.06 mmol) in THF (10 mL) and MeOH (10 mL) was added K_2CO_3 (300 mg, 2.17 mmol). The suspension was stirred at rt for 45 min before it was filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated under reduced pressure to a volume of approx. 10 mL. Et_3N (10 mL) was added, and the solution was further concentrated to a volume of approx. 2 mL. Additional Et_3N (10 mL), anhydrous THF (10 mL), and **25** (150 mg, 0.212 mmol) were added, and the combined solution was thoroughly degassed with Ar before addition of $Pd(PPh_3)_2Cl_2$ (30 mg, 0.043 mmol) and CuI (8.0 mg, 0.042 mmol). The resulting reaction mixture was stirred at rt under an Ar atmosphere for 22 h before it was filtered through a plug of SiO_2 (CH_2Cl_2 as eluent) and concentrated under reduced pressure. Flash column chromatography (10% CH_2Cl_2/heptane) yielded **27** (75 mg, 23%) as an orange solid. R_f = 0.31 (20% CH_2Cl_2/heptane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 2H), 8.74 (d, *J* = 1.7 Hz, 2H), 7.74 – 7.67 (m, 2H), 7.65 – 7.58 (m, 4H), 7.57 – 7.52 (m, 2H), 7.43 – 7.38 (m, 4H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.24 (dd, *J* = 8.0, 1.7 Hz, 2H), 1.20 (s, 18H), 0.98 (s, 36H), 0.97 (s, 36H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 147.0, 139.9, 139.2, 138.1, 138.1, 133.3, 132.9, 132.8, 132.3, 128.7, 128.5, 128.2, 127.9, 127.0, 126.6, 126.3, 125.8, 125.8, 122.9, 119.0, 117.0, 105.0, 105.0, 101.1, 96.9, 96.9,

96.4, 96.2, 92.6, 92.0, 35.1, 31.5, 18.7, 18.7, 11.4, 11.4 ppm. HRMS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 1512.9086 [$M^{\cdot+}$], calcd for ($C_{106}H_{127}Si_4^{\cdot+}$) = 1512.9043.

Compound 29

To a 250 mL round-bottomed flask equipped with a reflux condenser and containing a magnetic stirrer bar, diethylene glycol (125 mL) and KOH (2.67 g, 47.7 mmol) were added. The solution was degassed with Ar for 30 min after which **5** (461 mg, 1.17 mmol) was added. Then, $N_2H_4 \cdot H_2O$ (2.4 mL, 50.0 mmol) was added slowly, resulting in a color change to black within 30 min. The reaction was carried out under inert N_2 atmosphere. The reaction mixture was then heated to 185-190 °C for 48 h after which it was cooled to 100 °C, poured onto ice (400 mL), and acidified with aq. HCl (20 mL, 6 M), resulting in an orange precipitate. The ice was allowed to melt, and the precipitate was filtered, washed with H_2O (100 mL), and dissolved in EtOAc (200 mL), after which the volatiles were removed under reduced pressure yielding compound **29** as a light orange crystalline solid (375 mg, 1.02 mmol, 88%). M.p.: >250°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.71 (d, *J* = 8.0, 2H), 7.59 (s, 2H), 7.42 (d, *J* = 8.0, 2H), 3.95 (s, 4H), 1.39 (s, 18H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 143.8, 142.5, 140.6, 139.5, 124.1, 122.1, 119.2, 116.3, 37.0, 35.0, 31.8 ppm. HR-MS (MALDI$^+$, FT-ICR, dithranol) *m/z* = 366.2344 [$M^{\cdot+}$], calcd for [$C_{28}H_{30}^{\cdot+}$] = 366.2342.

Supporting Information

Supporting Information File 1: UV-Vis and NMR spectra, differential pulse voltammograms, X-ray crystallographic data

Supporting Information Files 2-4: cif files of X-ray crystal structures

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References

[1] D. Canevet, M. Sallé, G. Zhang, D. Zhang and D. Zhu, *Chem. Commun.* **2009**, 2245-2269.

[2] N. Martín, *Chem. Commun.* **2013**, *49*, 7025-7027.

[3] J. J. Bergkamp, S. Decurtins and S.-X. Liu, *Chem. Soc. Rev.* **2015**, *44*, 863-874.

[4] V. A. Azov, *Tetrahedron Lett.* **2016**, *57*, 5416-5425.

[5] A. Jana, M. Ishida, J. S. Park, S. Bähring, J. O. Jeppesen, J. L. Sessler, *Chem. Rev.* **2017**, *117*, 2641-2710.

[6] A. Jana, S. Bähring, M. Ishida, S. Goeb, D. Canevet, M. Sallé, J. O. Jeppesen, J. L. Sessler, *Chem. Soc. Rev.* **2018**, *47*, 5614-5645.

[7] H. Yamada, M. Yamashita, H. Hayashi, M. Suzuki, N. Aratani, *Chem. Eur. J.* **2018**, *24*, 18601-18612.

[8] H. V. Schröder, C. A. Schalley, *Beilstein J. Org. Chem.* **2018**, *14*, 2163-2185.

[9] M. R. Bryce, *J. Mater. Chem.* **1995**, *5*, 1481-1496.

[10] J. Roncali, *J. Mater. Chem.* **1997**, *7*, 2307-2321.

[11] F. G. Brunetti, J. L. López, C. Atienza, N. Martín, *J. Mater. Chem.* **2012**, *22*, 4188-4205.

[12] O. Hammerich, M. B. Nielsen, *J. Mater. Chem. C* **2019**, *7*, 2809-2822.

[13] M. A. Christensen, C. R. Parker, T. J. Sørensen, S. de Graaf, T. J. Morsing, T. Brock-Nannestad, J. Bendix, M. M Haley, R. Rapta, A. Danilov, S. Kubatkin, O. Hammerich, M. B. Nielsen, *J. Mater. Chem. C* **2014**, *2*, 10428-10438.

[14] L. Broløs, M. B. Nielsen, *RSC Adv.* **2020**, *10*, 15030-15033.

[15] M. B. Nielsen, F. Diederich, *Chem. Rev.* **2005**, *105*, 1837-1868.

[16] M. Kivala, F. Diederich, *Adv. Mater.* **2010**, *22*, 803-812.

[17] K. Lincke, A. F. Frellsen, C. R. Parker, A. D. Bond, O. Hammerich, M. B. Nielsen, *Angew. Chem. Int. Ed.* **2012**, *124*, 6203-6206.

[18] M. D. Kilde, A. H. Murray, C. L. Andersen, F. E. Storm, K. Schmidt, A. Kadziola, K. V. Mikkelsen, F. Hampel, O. Hammerich, R. R. Tykwinski, M. B. Nielsen, *Nat. Commun.* **2019**, *10*, 3714.

[19] L. Broløs, M. D. Kilde, O. Hammerich, M. B. Nielsen, *J. Org. Chem.* **2020**, *85*, 3277-3286.

[20] V. B. R. Pedersen, J. Granhøj, A. E. Hillers-Bendtsen, A. Kadziola, K. V. Mikkelsen, M. B. Nielsen, *Chem. Eur. J.* **2021**, *27*, 8315-8324.

[21] L. J. O'Driscoll, S. S. Andersen, M. V. Solano, D. Bendixen, M. Jensen, T. Duedal, J. Lycoops, C. van der Pol, R. E. Sørensen, K. R. Larsen, K. Myntman, C. Henriksen, S. W. Hansen, J. O. Jeppesen, *Beilstein J. Org. Chem.* **2015**, *11*, 1112-1122.

[22] D. D. Mysyk, I. F. Perepichka, D. F. Perepichka, M. R. Bryce, A. F. Popov, L. M. Goldenberg, A. J. Moore, *J. Org. Chem. Chem.* **1999**, *64*, 6937-6950.

[23] S. Amriou, C. Wang, A. S. Batsanov, M. R. Bryce, D. F. Perepichka, E. Ortí, R. Viruela, J. Vidal-Gancedo, C. Rovira, *Chem. Eur. J.* **2006**, *12*, 3389-3400.

[24] E. M. Pérez, M. Sierra, L. Sánchez, M. R. Torres, R. Viruela, P. M. Viruela, E. Ortí, N. Martín, *Angew. Chem. Int. Ed.* **2007**, *46*, 1847-1851.

[25] M. Dekhtiarenko, S. Krykun, V. Carré, F. Aubriet, D. Canevet, M. Allain, Z. Voitenko, M. Sallé, S. Goeb, *Org. Chem. Front.* **2020**, *7*, 2040-2046.

[26] M. H. Vilhelmsen, J. Jensen, C. G. Tortzen, M. B. Nielsen, *Eur. J. Org. Chem.* **2013**, 701-711.

[27] G. Tan, S. Li, S. Chen, Y. Sui, Y. Zhao, X. Wang, *J. Am. Chem. Soc.* **2016**, *138*, 6735-6738.

[28] S. Merlet, M. Birau, Z. Y. Wang, *Org. Lett.* **2002**, *4*, 2157-2159.

[29] P. Henke, C. Rindom, U. K. Aryal, M. F. Jespersen, L. Broløs, M. Mansø, V. Turkovic, M. Madsen, K. V. Mikkelsen, P. R. Ogilby, M. B. Nielsen, *ChemSusChem* **2023**, *16*, e202202320.

[30] G. L. Eakins, M. W. Cooper, N. N. Gerasimchuk, T. J. Phillips, B. E. Breyfogle, C. J. Stearman, *Can. J. Chem.* **2013**, *91*, 1059-1071.

[31] D. Andersen, D. B. Nygaard, R. R. Kragh, L. Broløs, M. B. Nielsen, *Tetrahedron Lett.* **2020**, *61*, 151939.

[32] H. Jiang, V. Mazzanti, C. R. Parker, S. L. Broman, J. H. Wallberg, K. Lušpai, A. Brincko, H. G. Kjærgaard, A. Kadziola, P. Rapta, O. Hammerich, M. B. Nielsen, *Beilstein J. Org. Chem.* **2015**, *11*, 930-948.

[33] Bruker, *SAINT*, *V8.40A*, Bruker AXS Inc., Madison, Wisconsin, USA.

[34] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*, 3-10.

[35] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3-8.

[36] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8.

[37] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Cryst.* **2016**, *B72*, 171-179.

[38] D. Kratzert, *FinalCif*, *V113*, https://dkratzert.de/finalcif.html.