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Homoconjugated and Spiro Push–Pull Systems: Cycloadditions of Naphto- and Anthra-diquinones with Electron-Rich Alkynes

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Homoconjugated and Spiro Push–Pull Systems: Cycloadditions of Naphto- and Anthra-diquinones with Electron-Rich Alkynes

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Abstract

We report the synthesis and characterization of three new classes of push–pull chromophores using [2+2] cycloaddition reactions of electron-rich alkynes and electron-poor alkenes. Previous investigations have focused on the reactions of cyano-substituted electron acceptors. This study demonstrates that cyano-free electron acceptors, naphto- and anthra-diquinones, can also be used to access extended push–pull systems. The effects of the structural changes on the spectroscopic and electronic properties were investigated by UV/Vis spectroscopy. Structures were confirmed by X-ray and NMR analysis in solution.

Keywords

Homoconjugation, cycloadditon, push–pull, quinones, spirocycles

Introduction

Planar and non-planar push–pull chromophores are of continuing interest as a result of their optoelectronic properties.[1] A major challenge to use these chromophores in optoelectronical devices is the control of their film morphology. The improved solubility, processability, and reduction of self-quenching displayed by structurally rigid non-planar chromophores offer distinct advantages over planar counterparts on thin film preparations.[2] The [2+2] cycloaddition–retroelectrocyclization (CA–RE) reactions represent an efficient route to the synthesis of these materials from readily accessible electron-rich alkynes and electron-deficient alkenes.[3] Extensive research efforts have been invested in development of these transformations because of their atom-economic, high-yielding characteristics which meet the prerequisites of click-type reactions.[4] The most investigated reactions have focused on cyano-substituted electron acceptors such as tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ), and 6,6-dicyanopentafulvenes.[1c,3,5] Recently, Diederich,[6] Tromifov,[7] and Shoji[8] have demonstrated the [2+2] cycloadditions of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with variety of electron-rich alkynes to give homoconjugated push–pull chromophores. Results in those reports indicated that the adducts produced in the cycloadditions were not suitable to undergo simple retroelectrocyclization. Specifically, the cycloadducts transform into donor–acceptor (D–A)-substituted spiro compounds instead of CA–RE products.[6b] These results indicated that even when the CA–RE reaction pathway was not accessible, structurally

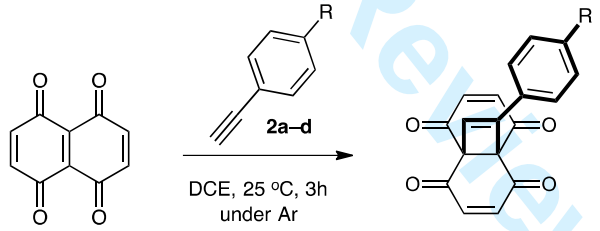
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demanding chromophores could still be obtained, which further heightened our interest in exploring the reactions between electron-rich alkynes and electron-poor alkenes. Almost all electron acceptors, used for the CA–RE reactions, possess activating cyano substituents. There are only a few investigations of cyano-free electron acceptors in these transformations.[9, 10] In all reported cases,[9, 10] elevated temperatures were required and low yields were observed due to the formation of significant amount of decomposition products. In the present work, we expand the scope of formal [2+2] cycloadditions by introducing new electron-acceptors, naphto- and anthra-diquinones as alternatives to the commonly used cyano-substituted electron-deficient olefins. We describe the synthesis and the electronic properties of new series of homoconjugated push–pull chromophores **3a**–**d**, **5a**–**d** and (D–A)-substituted spiro systems **6a**–**c**. We also demonstrated that the cyano-free electron acceptors react efficiently with dialkylanilino (DAA) acetylenes and the structures of the three new chromophores were confirmed by X-ray analysis.

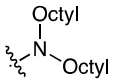
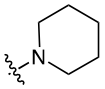
Results and Discussion

A series of electron-rich alkynes were tested for [2+2] cycloadditions with electron-poor diquinones (Figure S1 in the Supporting Information (SI)). Based on these initial results, diquinone **1**[11] and electron-rich alkynes **2b**–**d** [12] were identified for investigations and we prepared these compounds following the literature procedures. Push–pull chromophores **3a**–**d** were obtained by one-step method using various alkynes **2a**–**d** and electron-poor diquinone **1**. Upon addition of diquinone **1**, the color of the alkyne solutions in 1,2-dichloroethane changed from colorless to dark orange, and compounds **3a**–**d** were obtained in yields of 23–35% (Table 1).

Table 1. Synthesis of homoconjugated chromophores **3a**–**d**. DCE = 1,2-dichloroethane



1 **3a–d**

Substrate	R	Product	Yield (%)
2a		**3a**	35%
2b		**3b**	23%
2c		**3c**	29%
2d		**3d**	27%

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Homoconjugated chromophores **3a**–**d** are dark-orange colored solids that are stable at room temperature. The formation of compounds **3a**–**d** was accompanied by very small amount of dark colored, unstable side products. Unfortunately, our attempts to purify these species failed due to their fast decomposition during crystallization or column chromatography on aluminum oxide (neutral, and basic) and silica gel. However, the formation of these species was not responsible for the low yields obtained for **3a**–**d.** Rather, we also observed substantial amount of insoluble material formation, similar to the earlier reports for the reactions of DDQ and electron-rich acetylenes.[6b] The structure of chromophore **3a** was unambiguously confirmed by X-ray diffraction analysis (Figure 1).

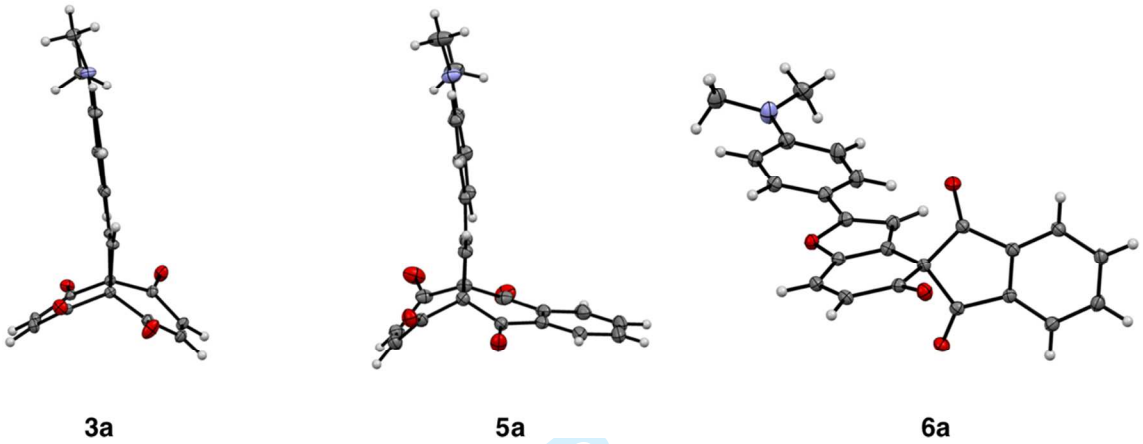
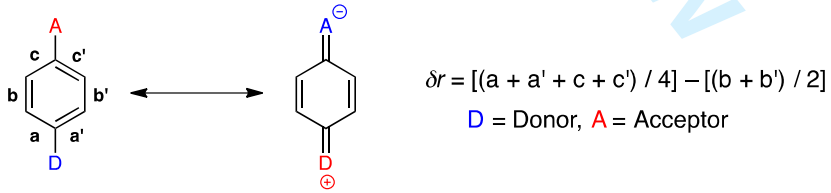


Figure 1. ORTEP plots of **3a**, **5a**, and **6a**. Atomic displacement parameters are drawn at 50% probability level.

Bond-length alternation in the DAA moiety can be described by the quinoid character (δr) and δr is a good description for the ground state charge-transfer (CT) from the DAA group to π-conjugated or homoconjugated acceptor units (See Scheme 1 and ref. 13 for δr value calculations). The δr value in the DAA moiety for compound **3a** was calculated to be 0.021 by using the experimental bond lengths in the X-ray structure (Figure S2 in the SI). This value is comparable to those obtained for the similar push–pull chromophores in the literature.[6b, 10]



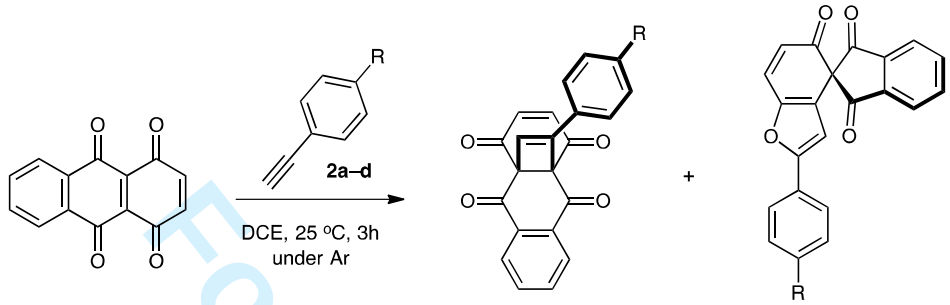
Scheme 1. General scheme for quinoid character calculations of DAA-substituted push–pull chromophores (for benzene, $\delta r = 0$; for fully quinoid rings, $\delta r = 0.08 – 0.10$ Å).

After successful synthesis of chromophores **3a**–**d,** we turned our attention to the reactions of diquinone **4** with electron-rich alkynes **2a**–**d**. Dark-orange chromophores **5a**–**d** were obtained in yields of 26–39% (Table 2). Similar to the reactions of diquinone **1**, the formation of dark-colored side products was observed. For three of the four reactions, these products could be identified as the spiro compounds **6a**–**c** in 4–5% yield. Isolation was thought to be possible due

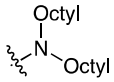
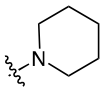
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to their relative stability resulting from the additional aromatic unit. Although we observed the formation of a similar spot on TLC that is likely attributable to **6d**, multiple attempts to isolate it failed due to decomposition issues similar to the reactions of quinone **1**, which could not be avoided.

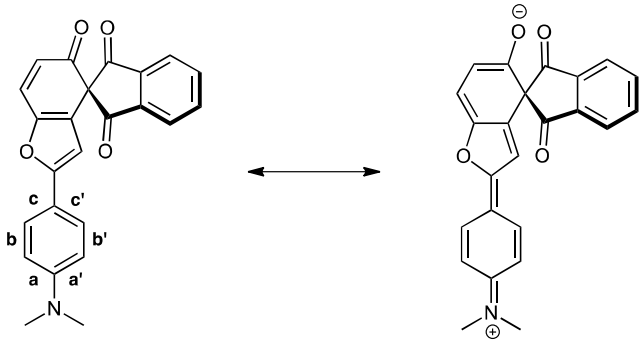
Table 2. Synthesis of homoconjugated **5a**–**d** and spiro push–pull chromophores **6a**–**c**.



4 **5a–d** **6a–d**

Substrate	R	Products	Yield (%) **5a**–**d**	Yield (%) **6a**–**d**
2a		**5a**,**6a**	39%	5%
2b		**5b**,**6b**	26%	4%
2c		**5c**,**6c**	34%	4%
2d		**5d**,**6d**	34%	–

Single crystals of **5a** and **6a** were obtained by slow diffusion of *n*-hexane into CH_2Cl_2 solutions of compounds (Figure 1). The calculated δr values of DAA units for compounds **5a** and **6a** are 0.023 and 0.020 respectively (Scheme 2, see also Figure S3 and S4 for experimental bond lengths).

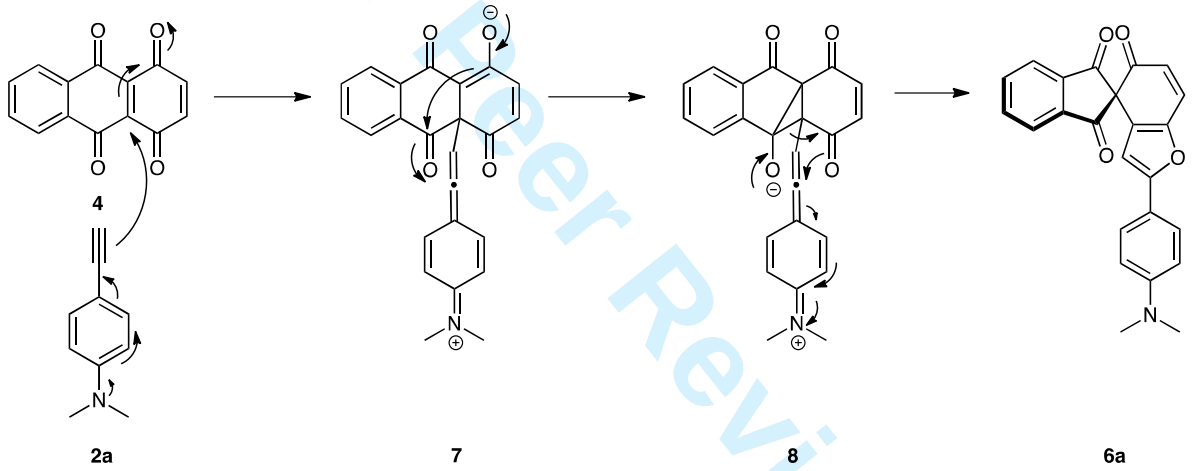


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Scheme 2. Resonance structures of chromophore **6a** that highlight the interconnection between BLA and charge-transfer interactions. (See also Scheme 1 for δr value calculations)

The δr values of homoconjugated chromophores **3a**, **5a** and spirocyclic chromophore **6a** suggested that there is almost no meaningful difference in between these values although it should be expected higher values for the spiro system **6a** because of the direct π-conjugated CT pathway. This unexpected observation can be explained by the substantial deconjugation due to non-planarity, as shown by the large dihedral angle between the donor and the acceptor units (**3a**: 4.2(2)° / δr = 0.021, **5a**: -8.1(2)° / δr = 0.023, and **6a**: 16.7(2)° / δr = 0.020, Figures S2, S3, and S4 in the SI).

We propose a mechanism outlined in Scheme 3 for the transformation to the spirocyclic push–pull chromophore **6a**. The cascade mechanism starts with the initial regioselective conjugate addition of electron-rich alkyne **2a** to 1,4-dihydroxyanthraquinone **4** to form zwitterionic intermediate **7**. The formed intermediate **7** undergoes intramolecular cyclization to give intermediate **8**. The final step of the mechanism is the charge neutralization to give spirocycle **6a**.



Scheme 3. Proposed mechanism for the formation of spirocyclic chromophore **6a**.

The UV/Vis spectra acquired from three representative push–pull chromophores **3a**, **5a**, and **6a** are shown in Figure 2 (See Figures S6, S7, and S8 in the SI for the electronic absorption spectra of all chromophore series). The orange-colored homoconjugated chromophores **3a** and **5a** display weak intramolecular CT bands (453 nm (2.74 eV), ε = 2400 M^{-1} cm^{-1}, **3a** and 411 nm (3.02 eV), ε = 3400 M^{-1} cm^{-1}, **5a**). The CT bands of chromophores are bathochromically shifted with increasing donor strength (Figures S6 and S7 in the SI).[14] The spiro compound **6a** displays relatively stronger CT band because of the linear CT pathway (480 nm (2.58 eV), ε = 12500 M^{-1} cm^{-1}, **6a**). In all cases, low-energy transfer bands can be explained as intramolecular CT interactions which includes transfer of electron density from the DAA donor to the rest of the molecule according to the HOMO, LUMO orbital depictions (See Figure S13 in the SI).[15] The structural complexity of the spiro compound **6a** creates other CT pathways (See Tables S1–S3 in the SI for TD-DFT calculations). For example, Intramolecular CT might arise from the transition between electron-rich furan ring and carbonyl group. The other possibility is the CT between spiro rings *via* homoconjugation. In summary, the strong CT band of spirocycle **6a** is an overlap of several transitions.

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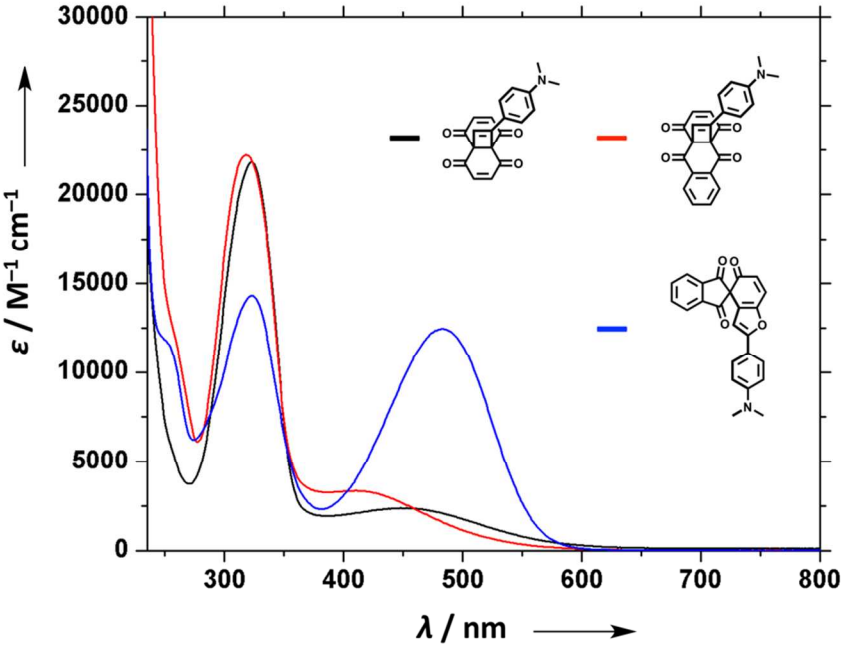


Figure 2. UV/Vis spectra of selected compounds **3a** (black line), **5a** (red line), and **6a** (blue line) in CH_2Cl_2 at 298 K.

The spiro compound **6a** displays positive solvatochromism which further support the intramolecular CT interactions (Figure S9). In addition to this observation, the selected compounds **3a**, **5a**, and **6a** were subjected to protonation experiments. Upon treatment with trifluoroacetic acid (TFA), the longest wavelength absorption band disappeared because of the quaternization of DAA moieties. The re-neutralization with trimethylamine (TEA) provided full recovery of the CT bands (Figures S10–S12 in the SI).

In summary, we have demonstrated the synthesis of three new push–pull chromophore types starting from cyano-free electron acceptors.[16] Despite the observed modest yields, the short synthetic method facilitates the formation of these interesting chromophores. The simplicity of the method will enable us to design new chromophores for desired optoelectronic applications.

Acknowledgment

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Supporting Information for this article is available online at http://

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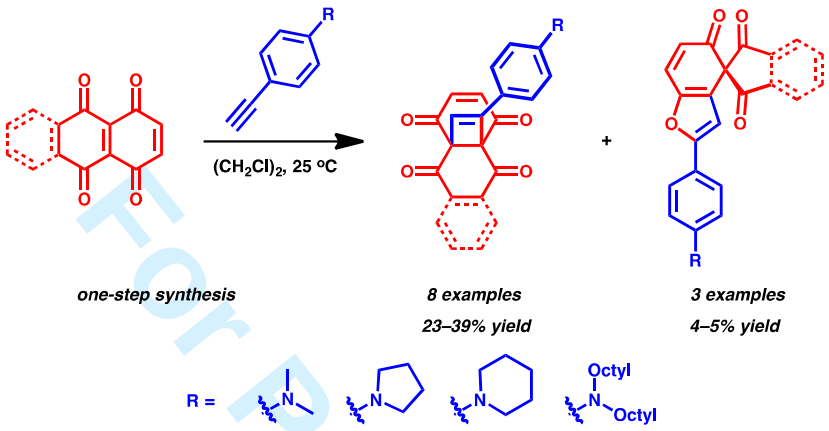
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[15] Frisch, M. J. et al. Gaussian 03, revision E.01, Gaussian, Inc., Wallingford CT, 2004. See the Supporting Information for the full list of the authors.
[16] **General procedure for the synthesis of homoconjugated and spiro push–pull systems:** Diquinone (1 equiv) was added under Ar to a solution of electron rich alkyne (1 equiv) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated and spirocyclic products.
3a: Naphthazarin **1** (100 mg, 0.532 mmol) was added under Ar to a solution of electron rich alkyne **2a** (77 mg, 0.532 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (FCC), (SiO_2, $CHCl_3$) to give homoconjugated chromophore **3a** (62 mg, 35%) as a dark-orange solid. R_f = 0.13 (SiO_2; $CHCl_3$); m.p. 215 – 218 °C ; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.99 (s, 6 H), 6.43 (s, 1 H), 6.65 (quasi d, J = 9.0 Hz, 2 H), 6.80 (s, 4 H), 7.63 ppm (quasi d, J = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 189.0, 187.6, 151.5, 150.7, 140.3, 139.7, 128.4, 123.7, 117.3, 111.6, 68.7, 64.6, 40.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 453 (2400), 323 nm (21800 M^{-1} cm^{-1}); HR-ESI-MS: found 334.1076 ([M + H]$^+$, calcd for $C_{20}H_{15}NO_4^+$: 334.1074).
5a and 6a: Quinizarin **4** (50 mg, 0.210 mmol) was added under Ar to a solution of electron rich alkyne **2a** (31 mg, 0.210 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **5a** (31mg, 39%) and **6a** (4 mg, 5%) as a dark-orange solids. **5a**: R_f = 0.13 (SiO_2; $CHCl_3$); m.p. 125 – 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.99 (s, 6 H), 6.53 (s, 1 H), 6.66 (quasi d, J = 8.9 Hz, 2 H), 6.83 (s, 2 H), 7.67 (quasi d, J = 8.9 Hz, 2 H), 7.73 – 7.80 (m, 2 H), 8.03 – 8.12 ppm (m, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 189.9, 188.5, 188.4, 187.3, 151.4, 150.9, 140.7, 139.9, 135.04, 134.96, 134.7, 134.2, 128.41, 128.39, 128.1, 124.2, 117.7, 111.6, 69.5, 65.5, 40.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 411 (3400), 318 nm (22200 M^{-1} cm^{-1}); HR-ESI-MS: found 384.1220 ([M + H]$^+$, calcd for $C_{24}H_{17}NO_4^+$: 384.1230). **6a**: R_f = 0.26 (SiO_2; $CHCl_3$); m.p. 144 – 147 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.00 (s, 6 H), 5.79 (d, J = 10.0 Hz, 1 H), 6.17 (s, 1 H), 6.68 (quasi d, J = 9.0 Hz, 2 H), 7.50 (quasi d, J = 9.0 Hz, 2 H), 7.53 (d, J = 10.0 Hz, 1 H), 7.93 (dd, J = 5.7, 3.1 Hz, 2 H), 8.13 (dd, J = 5.7, 3.1 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 193.3 (2 x C=O) 159.9, 150.8, 147.5, 144.4, 136.2, 134.7, 126.9, 126.0, 125.1, 118.6, 117.6, 112.2, 103.0, 73.2, 40.4 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 480 (12500), 323 nm (14300 M^{-1} cm^{-1}); HR-ESI-MS: found 384.1227 ([M + H]$^+$, calcd for $C_{24}H_{17}NO_4^+$: 384.1230).

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Graphical Abstract



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Supporting Information

Homoconjugated and Spiro Push–Pull Systems: Cycloadditions of Naphto- and Anthra-diquinones with Electron-Rich Alkynes

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S1. Experimental Section

General Methods and Materials:

Materials: All reactions were carried out under argon. All solvents were of ACS reagent grade or better. Silica gel (40 μm) was purchased from SiliCycle Inc. All reagent grade materials were purchased from Alfa Aesar, Strem and Sigma-Aldrich and used without further purification Compounds **1**[1], **2b–d**[2] and **4**[1] were prepared according to the procedures described in literature.

NMR Spectroscopy: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz, proton-decoupled) spectra were acquired in $CDCl_3$ on a Bruker Avance III HD Spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to residual NMR $CDCl_3$ peaks. ($CDCl_3$: δ 7.26 ppm for ^{1}H, 77.16 for ^{13}C).

Mass Spectrometry: High-resolution mass spectra (HR-MS) were obtained at the MIT Department of Chemistry Instrumentation Facility with electrospray ionization (ESI).

Absorption and Emission Spectroscopy: Ultraviolet-visible absorption spectra were measured with an Agilent Cary 4000 UV/Vis spectrophotometer and corrected for background signal with a solvent-filled cuvette.

Additional Characterizations: Thermogravimetric analyses (TGA) were performed with a TGA Q50 apparatus (TA Instruments). Experiments were carried out under nitrogen. Samples were heated 20 °C/min from 30 °C to 800 °C.

Experimental Data:

Compound 3a

Naphthazarin **1** (100 mg, 0.532 mmol) was added under Ar to a solution of electron rich alkyne **2a** (77 mg, 0.532 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (FCC), (SiO_2, $CHCl_3$) to give homoconjugated chromophore **3a** (62 mg, 35%) as a dark-orange solid. R_f = 0.13 (SiO_2; $CHCl_3$); m.p. 215 – 218 °C ; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.99 (s, 6 H), 6.43 (s, 1 H), 6.65 (quasi d, J = 9.0 Hz, 2 H), 6.80 (s, 4 H), 7.63 ppm (quasi d, J = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 189.0, 187.6, 151.5, 150.7, 140.3, 139.7, 128.4, 123.7, 117.3, 111.6, 68.7, 64.6, 40.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 453 (2400), 323 nm (21800 M^{-1} cm^{-1}); HR-ESI-MS: found 334.1076 ($[M + H]^+$, calcd for $C_{20}H_{15}NO_4^+$: 334.1074).

Compound 3b

Naphthazarin **1** (100 mg, 0.532 mmol) was added under Ar to a solution of electron rich alkyne **2b** (182 mg, 0.532 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3

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hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **3b** (65 mg, 23%) as a dark-orange viscous foam. R_f = 0.16 (SiO_2; $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.88 (t, J = 6.8 Hz, 6 H) 1.20 – 1.35 (m, 20 H), 1.49 – 1.63 (m, 4 H), 3.26 (quasi t, J = 7.7 Hz, 4 H), 6.38 (s, 1 H), 6.57 (quasi d, J = 9.0 Hz, 2 H), 6.79 (s, 4 H), 7.58 ppm (quasi d, J = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 189.1, 187.7, 150.7, 149.4, 140.3, 139.6, 128.6, 122.8, 116.2, 111.0, 68.7, 64.6, 51.1, 31.9, 29.6, 29.4, 27.3, 27.2, 22.8, 14.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 465 (1400), 331 nm (13700 M^{-1} cm^{-1}); HR-ESI-MS: found 530.3271 ($[M + H]^+$, calcd for $C_{34}H_{43}NO_4^+$: 530.3265).

Compound 3c

Naphthazarin **1** (100 mg, 0.532 mmol) was added under Ar to a solution of electron rich alkyne **2c** (91 mg, 0.532 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **3c** (56 mg, 29%) as a dark-orange solid. R_f = 0.08 (SiO_2; $CHCl_3$); m.p. 210 – 213 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.98 – 2.04 (m, 4 H), 3.28 – 3.34 (m, 4 H), 6.40 (s, 1 H), 6.50 (quasi d, J = 8.9 Hz, 2 H), 6.80 (s, 4 H), 7.61 ppm (quasi d, J = 8.9 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 189.1, 187.7, 150.9, 149.1, 140.3, 139.7, 128.5, 122.9, 116.6, 111.4, 68.7, 64.6, 47.6, 25.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 462 (2600), 329 nm (25200 M^{-1} cm^{-1}); HR-ESI-MS: found 360.1227 ($[M + H]^+$, calcd for $C_{22}H_{17}NO_4^+$: 360.1230).

Compound 3d

Naphthazarin **1** (100 mg, 0.532 mmol) was added under Ar to a solution of electron rich alkyne **2d** (99 mg, 0.532 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **3d** (54 mg, 27%) as a dark-orange solid. R_f = 0.08 (SiO_2; $CHCl_3$); m.p. 220 – 223 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.58 – 1.70 (m, 6 H), 3.20 – 3.30 (m, 4 H), 6.46 (s, 1 H), 6.80 (s, 4 H), 6.84 (quasi d, J = 9.0 Hz, 2 H), 7.61 ppm (quasi d, J = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 188.8, 187.5, 152.7, 150.4, 140.4, 139.6, 128.3, 124.6, 118.9, 114.6, 68.7, 64.7, 49.2, 25.5, 24.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 431 (2400), 322 nm (21600 M^{-1} cm^{-1}); HR-ESI-MS: found 374.1372 ($[M + H]^+$, calcd for $C_{23}H_{19}NO_4^+$: 374.1387).

Compounds 5a and 6a

Quinizarin **4** (50 mg, 0.210 mmol) was added under Ar to a solution of electron rich alkyne **2a** (31 mg, 0.210 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **5a** (31mg, 39%) and **6a** (4 mg, 5%) as a dark-orange solids. **5a**: R_f = 0.13 (SiO_2; $CHCl_3$); m.p. 125 – 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.99 (s, 6 H), 6.53 (s, 1 H), 6.66 (quasi d, J = 8.9 Hz, 2 H), 6.83 (s, 2 H), 7.67 (quasi d, J = 8.9 Hz, 2 H), 7.73 – 7.80 (m, 2 H), 8.03 – 8.12 ppm (m, 2 H); ^{13}C NMR (100 MHz, CDCl3,

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298 K): δ = 189.9, 188.5, 188.4, 187.3, 151.4, 150.9, 140.7, 139.9, 135.04, 134.96, 134.7, 134.2, 128.41, 128.39, 128.1, 124.2, 117.7, 111.6, 69.5, 65.5, 40.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 411 (3400), 318 nm (22200 M^{-1} cm^{-1}); HR-ESI-MS: found 384.1220 ($[M + H]^+$, calcd for $C_{24}H_{17}NO_4^+$: 384.1230).

6a: R_f = 0.26 (SiO_2; $CHCl_3$); m.p. 144 – 147 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.00 (s, 6 H), 5.79 (d, J = 10.0 Hz, 1 H), 6.17 (s, 1 H), 6.68 (quasi d, J = 9.0 Hz, 2 H), 7.50 (quasi d, J = 9.0 Hz, 2 H), 7.53 (d, J = 10.0 Hz, 1 H), 7.93 (dd, J = 5.7, 3.1 Hz, 2 H), 8.13 (dd, J = 5.7, 3.1 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 193.3 (2 x C=O) 159.9, 150.8, 147.5, 144.4, 136.2, 134.7, 126.9, 126.0, 125.1, 118.6, 117.6, 112.2, 103.0, 73.2, 40.4 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 480 (12500), 323 nm (14300 M^{-1} cm^{-1}); HR-ESI-MS: found 384.1227 ($[M + H]^+$, calcd for $C_{24}H_{17}NO_4^+$: 384.1230).

Compounds 5b and 6b

Quinizarin **4** (50 mg, 0.210 mmol) was added under Ar to a solution of electron rich alkyne **2b** (72 mg, 0.210 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **5b** (32 mg, 26%) and **6b** (5 mg, 4%) as a dark-orange viscous foams. **5b**: R_f = 0.21 (SiO_2; $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.88 (quasi t, J = 6.8 Hz, 6 H), 1.20 – 1.35 (m, 20 H), 1.50 – 1.63 (m, 4 H), 3.26 (quasi t, J = 7.7 Hz, 4 H), 6.46 (s, 1 H), 6.57 (quasi d, J = 8.8 Hz, 2 H), 6.82 (s, 2 H), 7.62 (quasi d, J = 8.8 Hz, 2 H), 7.71 – 7.78 (m, 2 H), 8.02 – 8.11 ppm (m, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 190.0, 188.6, 188.5, 187.3, 150.9, 149.3, 140.7, 139.9, 135.0, 134.9, 134.6, 134.2, 128.5, 128.4, 128.0, 123.3, 116.5, 111.0, 69.4, 65.4, 51.1, 31.9, 29.6, 29.4, 27.3, 27.2, 22.8, 14.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 411 (5900), 328 nm (19000 M^{-1} cm^{-1}); HR-ESI-MS: found 580.3420 ($[M + H]^+$, calcd for $C_{38}H_{45}NO_4^+$: 580.3421).

6b: R_f = 0.45 (SiO_2; $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.88 (quasi t, J = 6.7 Hz, 6 H), 1.20 – 1.37 (m, 20 H), 1.52 – 1.64 (m, 4 H), 3.27 (quasi t, J = 7.8 Hz, 4 H), 5.78 (d, J = 10.0 Hz, 1 H), 6.13 (s, 1 H), 6.58 (quasi d, J = 8.6 Hz, 2 H), 7.45 (quasi d, J = 8.6 Hz, 2 H), 7.52 (d, J = 10.0 Hz, 1 H), 7.93 (dd, J = 5.6, 3.1 Hz, 2 H), 8.13 (dd, J = 5.6, 3.1 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 193.3 (2 x C=O) 160.1, 148.7, 147.2, 144.4, 136.2, 134.8, 127.1, 126.2, 125.1, 118.3, 116.4, 111.5, 102.6, 73.2, 51.1, 32.0, 29.6, 29.4, 27.4, 27.3, 22.8, 14.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 498 (16800), 330 nm (18600 M^{-1} cm^{-1}); HR-ESI-MS: found 580.3419 ($[M + H]^+$, calcd for $C_{38}H_{45}NO_4^+$: 580.3421).

Compounds 5c and 6c

Quinizarin **4** (50 mg, 0.210 mmol) was added under Ar to a solution of electron rich alkyne **2c** (36 mg, 0.210 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **5c** (29 mg, 34%) and **6c** (3 mg, 4%) as a dark-orange solids. **5c**: R_f = 0.13 (SiO_2; $CHCl_3$); m.p. 127 – 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.96 – 2.04 (m, 4 H), 3.26 – 3.34 (m, 4 H), 6.49 (s, 1 H), 6.50 (quasi d, J = 8.8 Hz, 2 H), 6.83 (s, 2 H), 7.65 (quasi d, J = 8.8 Hz, 2 H), 7.71 – 7.82 (m, 2 H), 8.04 – 8.12 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 190.0, 188.54, 188.53, 187.4, 151.1, 149.0, 140.7, 139.9,

135.0, 134.9, 134.7, 134.3, 128.5, 128.4, 128.1, 123.5, 117.0, 111.4, 69.5, 65.5, 47.6, 25.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 427 (3750), 327 nm (21000 M^{-1} cm^{-1}); HR-ESI-MS: found 410.1392 ($[M + H]^+$, calcd for $C_{26}H_{19}NO_4^+$: 410.1387).

6c: R_f = 0.24 (SiO_2; $CHCl_3$); m.p. 142 – 145 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.98 – 2.04 ppm (m, 4 H), 3.28 – 3.35 ppm (m, 4 H), 5.78 (d, J = 10.0 Hz, 1 H), 6.15 (s, 1 H), 6.52 (quasi d, J = 8.9 Hz, 2 H), 7.49 (quasi d, J = 8.9 Hz, 2 H), 7.52 (d, J = 10.0 Hz, 1 H), 7.93 (dd, J = 5.7, 3.1 Hz, 2 H), 8.13 (dd, J = 5.7, 3.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 193.3 (2 x C=O) 160.2, 151.3,148.3, 144.4, 136.2, 134.8, 127.6, 126.1, 125.1, 118.3, 116.7, 111.8, 102.7, 70.5, 47.7, 25.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 498 (16800), 328 nm (14350 M^{-1} cm^{-1}); HR-ESI-MS: found 410.1386 ($[M + H]^+$, calcd for $C_{26}H_{19}NO_4^+$: 410.1387).

Compounds 5d

Quinizarin **4** (50 mg, 0.210 mmol) was added under Ar to a solution of electron rich alkyne **2d** (39 mg, 0.210 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **5d** (30 mg, 34%). **5d**: R_f = 0.11 (SiO_2; $CHCl_3$); m.p. 115 – 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.54 – 1.71 (m, 6 H), 3.25 (t, J = 5.0 Hz, 4 H), 6.56 (s, 1 H), 6.83 (s, 2 H), 6.84 (quasi d, J = 8.4 Hz, 2 H), 7.66 (quasi d, J = 8.4 Hz, 2 H), 7.73 – 7.83 (m, 2 H), 8.02 – 8.14 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 189.7, 188.4, 188.3, 187.2, 152.7, 150.7, 140.8, 140.0, 135.1, 135.0, 134.7, 134.2, 128.5, 128.4, 128.1, 125.1, 119.3, 114.7, 69.5, 65.6, 49.2, 25.6, 24.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 408 (3300), 318 nm (19300 M^{-1} cm^{-1}); HR-ESI-MS: found 424.1553 ($[M + H]^+$, calcd for $C_{27}H_{21}NO_4^+$: 424.1543).

The R_f that was thought to correspond to compound **6d** was 0.21 (SiO_2; $CHCl_3$). However, isolation and characterization could not be achieved.

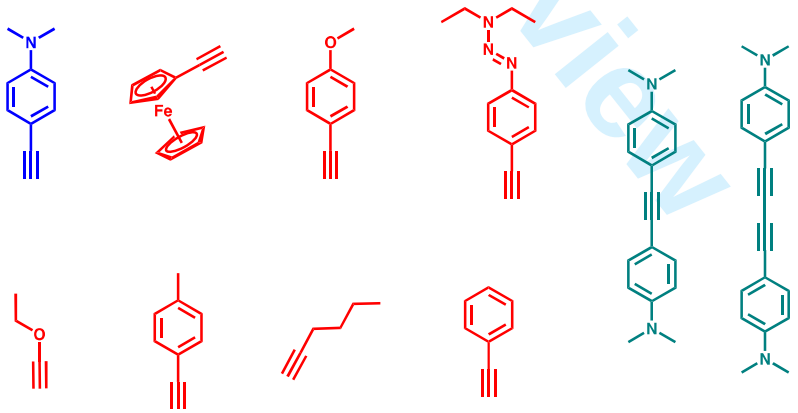


Figure S1. Alkynes screened for [2+2] cycloadditions. Compound with the blue color undergo [2+2] cycloadditions. Compounds with the red color show no reaction with electron-poor diquinones. Compounds with the green color show no reactivity towards [2+2] cycloadditions but they aromatize electron-poor diquinones through electron donation.[1]

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S2. X-ray analysis

The supplementary crystallographic data for this paper can be found using the following deposition numbers: CCDC 1525643 (**3a**), 1525645 (**5a**), and 1525644 (**6a**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk), or via www.ccdc.cam.ac.uk/data_request/cif.

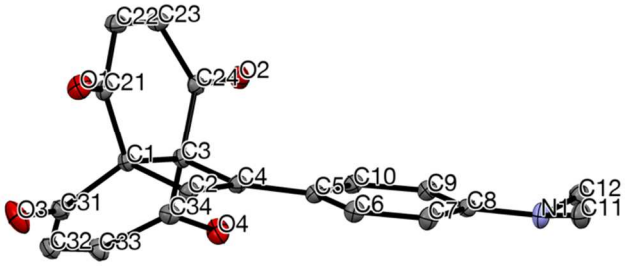


Figure S2. ORTEP plot of **3a**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters are drawn at 50% probability level. Selected bond length (Å) and torsional angles (°): C12–N1 1.4552(13), N1–C8 1.3822(13), C8–C9 1.4112(13), C9–C10 1.3910(14), C10–C5 1.4039(13), C5–C6 1.4085(13), C6–C7 1.3877(14), C7–C8 1.4185(14), C5–C4 1.4571(14), C4–C2 1.3515(13), C2–C1 1.5275(13), C1–C3 1.5795(13), C3–C4 1.5505(13), C3–C24 1.5317(13), C24–O2 1.2187(12), C24–C23 1.4783(14), C23–C22 1.3387(14), C22–C21 1.4695(14), C21–O1 1.2203(12), C21–C1 1.5278(13), C21-C1-C31 109.55(8), C2-C4-C5-C6 -4.2(2).

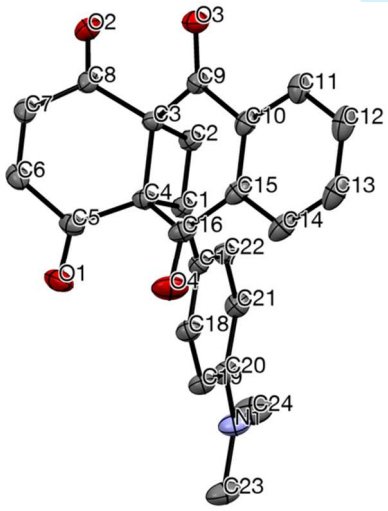


Figure S3. ORTEP plot of **5a**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters at are drawn at 50% probability level. Selected bond length (Å) and torsional angles (°): C24–N1 1.4399(17), N1–C20 1.3753(15), C20–C21 1.4146(16), C21–C22 1.3833(15), C22–C17 1.4033(14), C17–C18 1.4004(14), C18–C19 1.3869(15), C19–C20 1.4126(16), C17–C1 1.4548(14), C1–C2 1.3445(14), C2–C3 1.5251(14), C3–C4 1.5746(14), C4–C1 1.5449(14), C3–C8 1.5237(14), C8–O2 1.2157(14), C8–C7 1.4723(16), C7–C6 1.3382(16), C6–C5 1.4700(16), C5–O1 1.2118(14), C5–C4 1.5200(15), C3–C9 1.5290(15), C9–O3 1.2130(13), C9–C10 1.4866(15), C10–C15 1.4014(16), C15–C16 1.4836(17), C16–O4 1.2155(14), C16–C4 1.5310(15), C10–C11 1.3975(16), C11–C12 1.3884(17), C12–C13 1.390(2), C13–C14 1.383(2), C14–C15 1.4025(15), C5-C4-C16 110.42(9), C18-C17-C1-C4 -8.1(2).

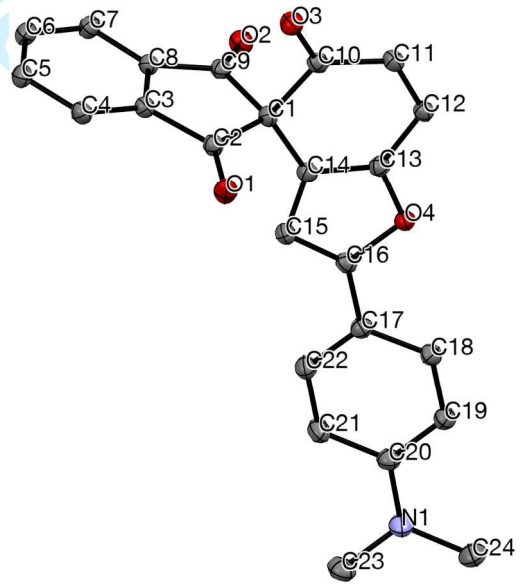


Figure S4. ORTEP plot of **6a**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters are drawn at 50% probability level. Selected bond length (Å) and torsional angles (°): C24–N1 1.4483(17), N1–C20 1.3786(15), C20–C21 1.4142(17), C21–C22 1.3812(17), C22–C17 1.3988(17), C17–C18 1.4005(16), C18–C19 1.3896(16), C19–C20 1.4075(17), C17–C16 1.4525(15), C16–C15 1.3788(16), C15–C14 1.4240(16), C14–C13 1.3651(16), C13–O4 1.3703(13), O4–C16 1.3802(14), C13–C12 1.4229(16), C12–C11 1.3565(15), C11–C10 1.4585(16), C10–O3 1.2250(14), C10–C1 1.5553(16), C1–C14 1.4906(15), C14–C13 1.3651(16), C1–C9 1.5634(15), C9–O2 1.2070(14), C9–C8 1.4791(16), C8–C3 1.3932(15), C3–C2 1.4811(15), C2–O1 1.2086(14), C2–C1 1.5469(16), C8–C7 1.3938(15), C7–C6 1.3904(17), C6–C5 1.4029(17), C5–C4 1.3934(16), C4–C3 1.3916(16), C9-C1-C10 105.33(8), C22-C17-C16-C15 16.7(2).

Additional Characterization:

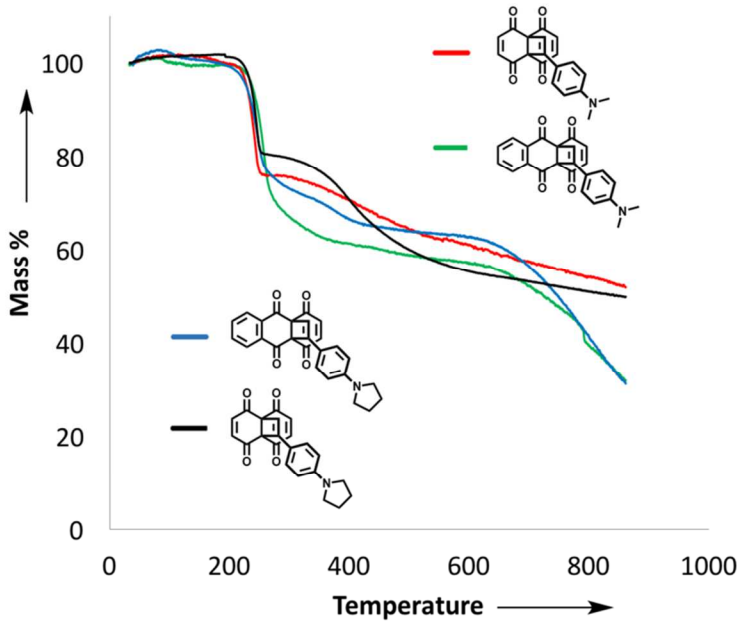


Figure S5. Thermal stability of a selection of the synthesized compounds as demonstrated by thermogravimetric analysis (TGA) of compounds **3a** (red line), **5a** (green line) **3c** (black line), and **5c** (blue line).

In Review

S3. UV/Vis Spectra

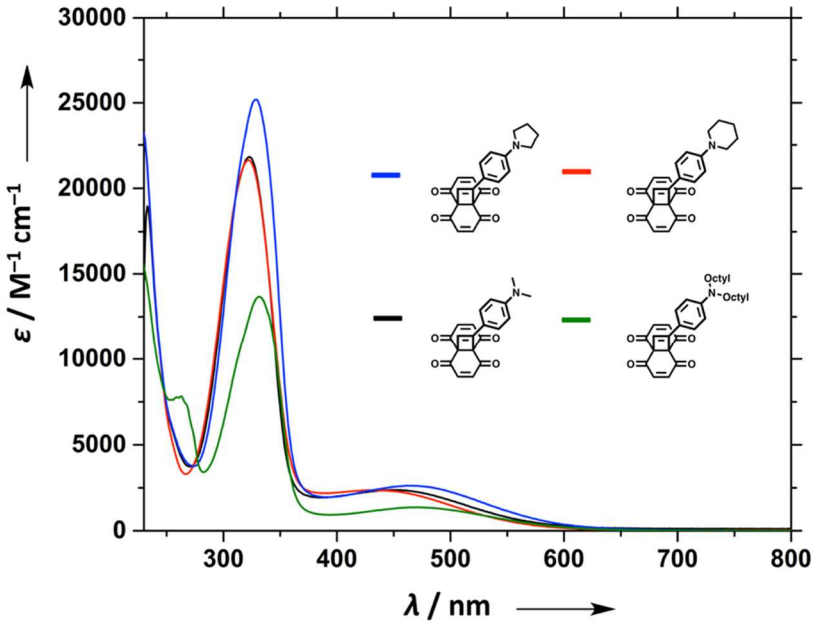


Figure S6. UV/Vis spectra of compounds **3a** (black line), **3b** (green line), **3c** (blue line), and **3d** (red line) in CH_2Cl_2 at 298 K.

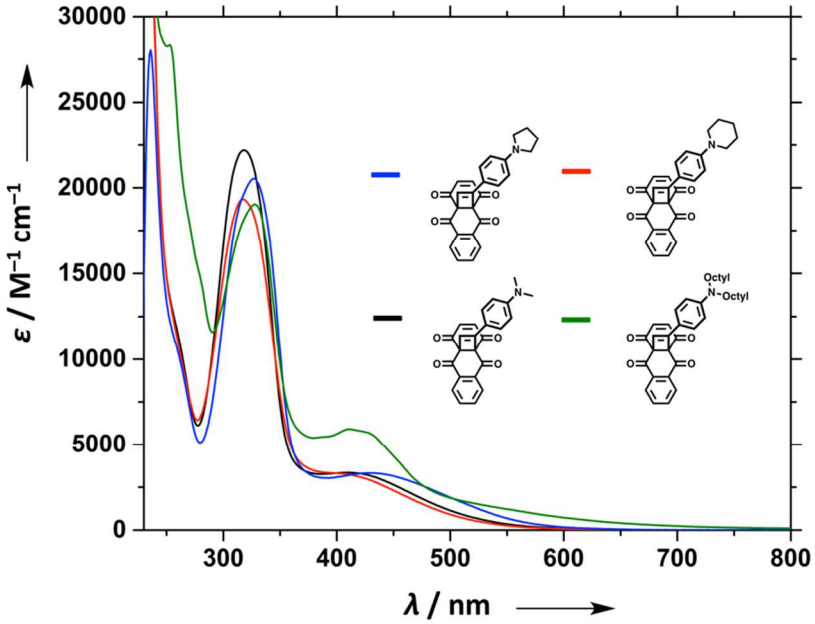


Figure S7. UV/Vis spectra of compounds **5a** (black line), **5b** (green line), **5c** (blue line), and **5d** (red line) in CH_2Cl_2 at 298 K.

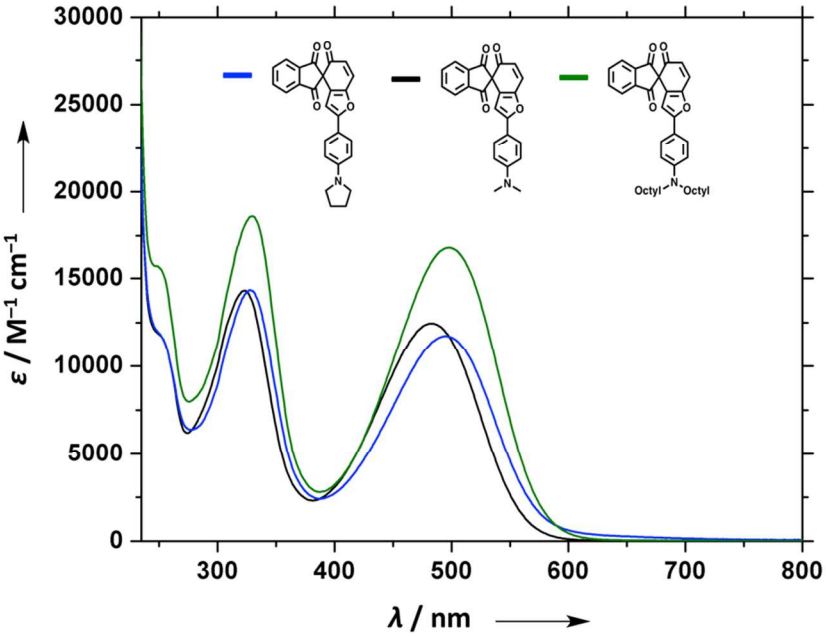


Figure S8. UV/Vis spectra of compounds **5a** (black line), **5b** (green line), and **5c** (blue line) in CH_2Cl_2 at 298 K.

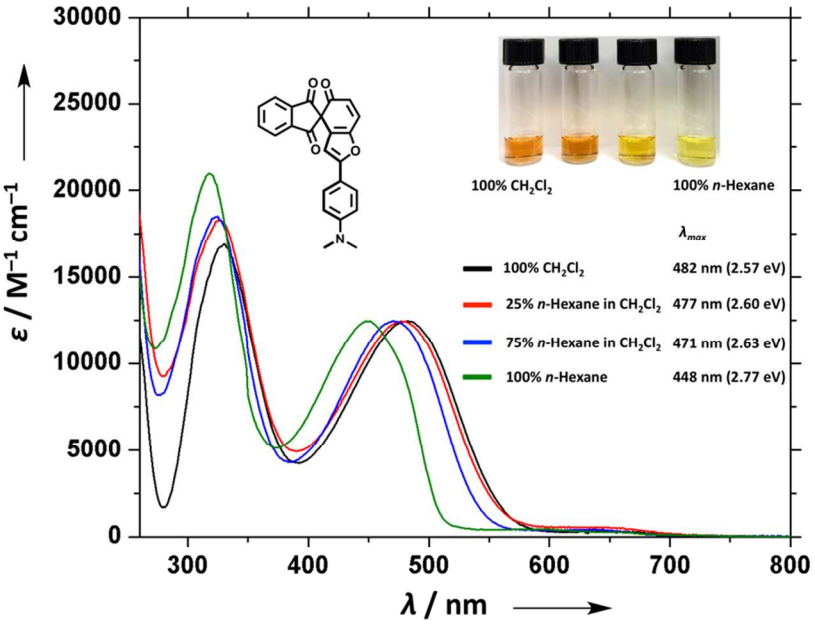


Figure S9. UV/Vis spectra of chromophore **6a** in CH_2Cl_2/*n*-hexane mixtures at 298 K.

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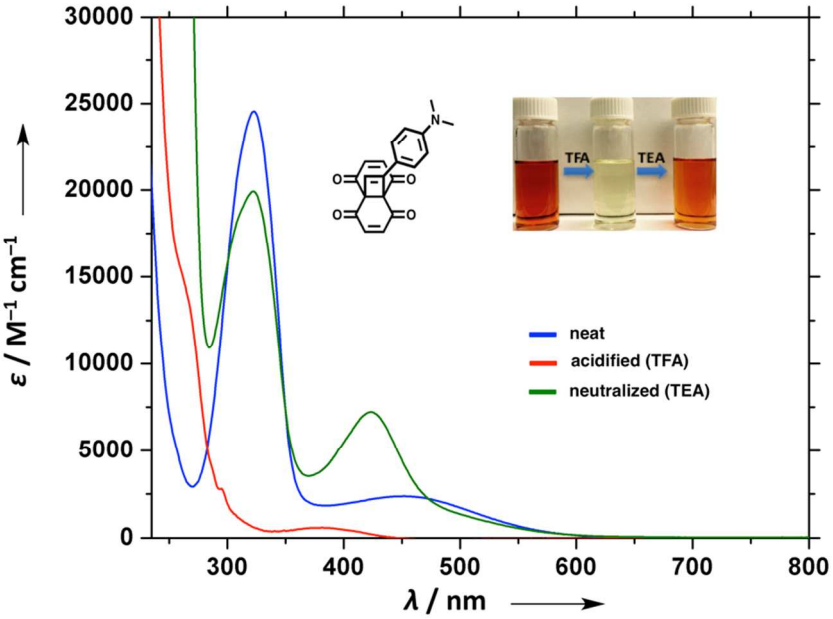


Figure S10. UV/Vis spectra of compounds **3a** in CH_2Cl_2 at 298 K recorded neat, after acidification with TFA, and after neutralization with TEA.

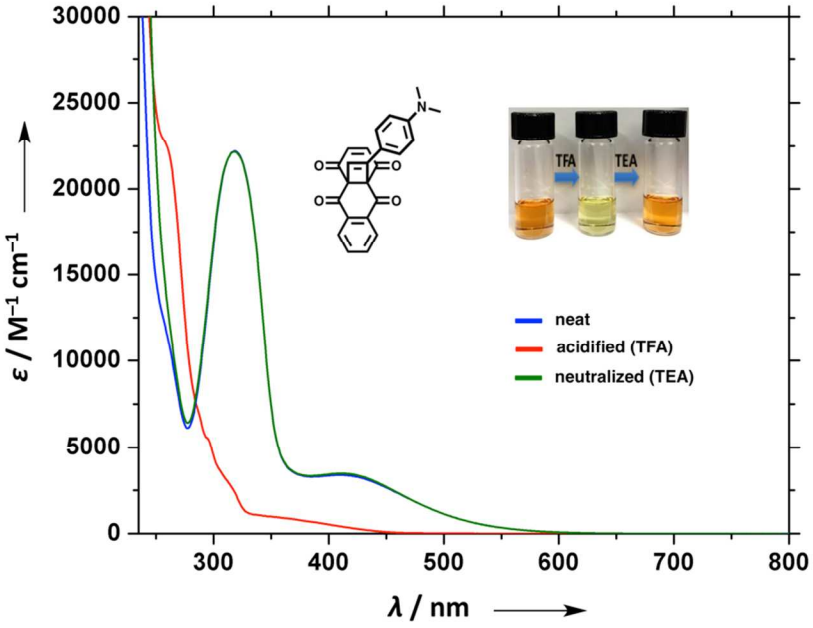


Figure S11. UV/Vis spectra of compounds **5a** in CH_2Cl_2 at 298 K recorded neat, after acidification with TFA, and after neutralization with TEA.

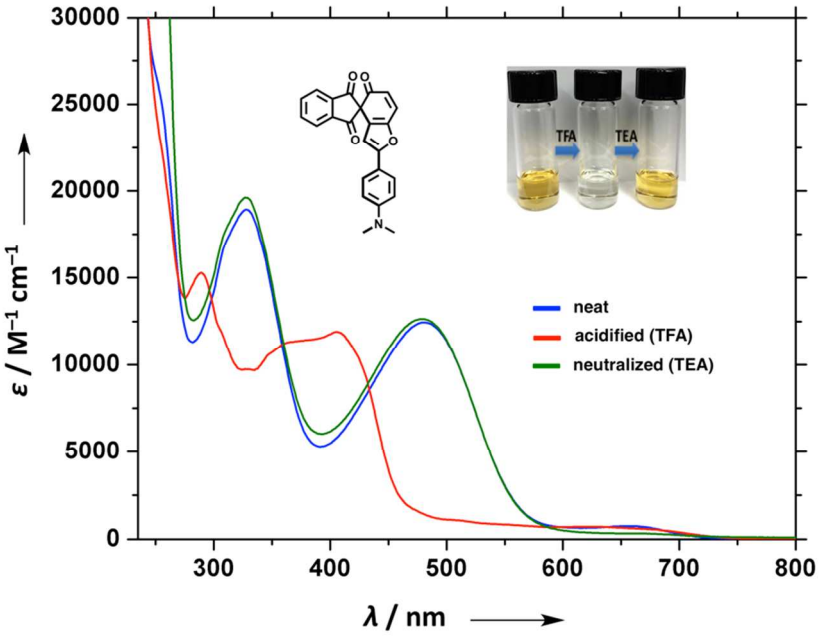


Figure S12. UV/Vis spectra of compounds **6a** in CH_2Cl_2 at 298 K recorded neat, after acidification with TFA, and after neutralization with TEA.

Peer Review

S4. Theoretical Calculations

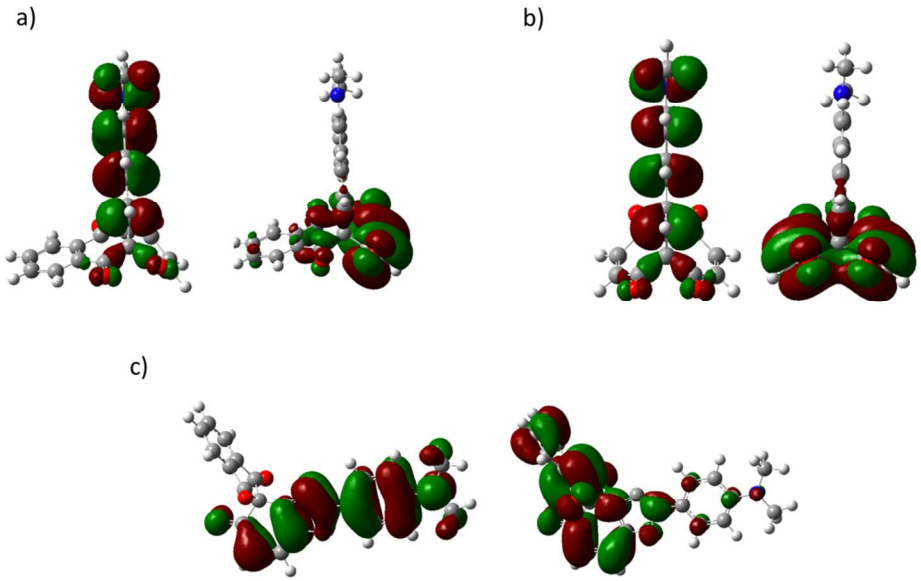


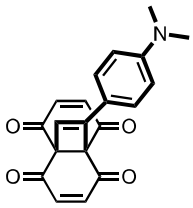
Figure S13. Molecular orbital plots of (a) **5a**, (b) **3a**, and (c) **6a** calculated by B3LYP/6-31G(d). The plots on the left represent the HOMOs, and the plots on the right represents LUMOs.

Review

Calculated Optical and Electronic Properties of 3a, 5a, and 6a

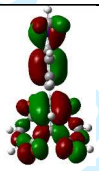
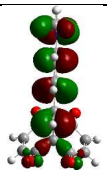
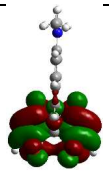
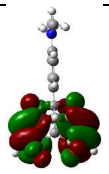
On the optimized molecular structures of **3a**, **5a**, and **6a** at the B3LYP/6-31G(d) level of theory with the CPCM solvation model in CH_2Cl_2, the vertical optical transitions were calculated by time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G(d) level of theory, again with the CPCM solvation model in CH_2Cl_2 using the software package Gaussian 03.

Table S1. Depiction of calculated HOMOs and LUMOs over optimized groundstate geometries, transition energies (*E*), and oscillator strengths (*f*) for **3a**.



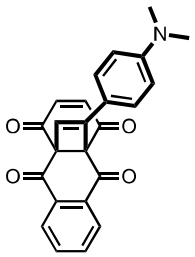
Exptl.: λ = 453 nm (in CH_2Cl_2)

Excited state	Δ*E* (eV)	*λ* (nm)	*f*	assignments
1	1.84	674	0.0245	H➔L+1
2	3.89	319	0.5601	H➔L+3, H–6➔L

Orbital		*E* (eV)
HOMO–1		–6.60
HOMO		–5.10
LUMO		–2.85
LUMO+1		–2.65

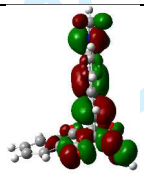
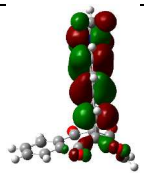
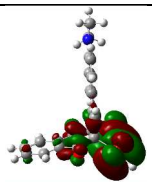
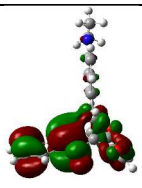
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Table S2. Depiction of calculated HOMOs and LUMOs over optimized groundstate geometries, transition energies (*E*), and oscillator strengths (*f*) for **5a**.



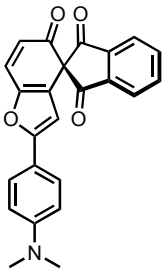
Exptl.: λ = 411 nm (in CH_2Cl_2)

Excited state	Δ*E* (eV)	*λ* (nm)	*f*	assignments
1	2.13	581	0.0527	H➔L+1
2	3.88	320	0.5036	H➔L+3, H➔L+4

Orbital		*E* (eV)
HOMO–1		–6.69
HOMO		–5.11
LUMO		–2.64
LUMO+1		–2.47

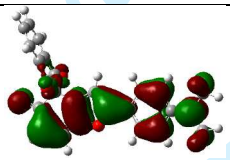
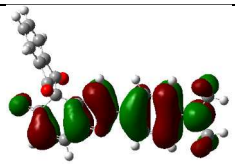
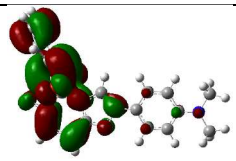
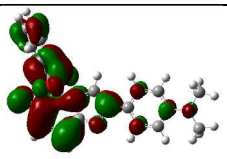
For Peer Review

Table S3. Depiction of calculated HOMOs and LUMOs over optimized groundstate geometries, transition energies (*E*), and oscillator strengths (*f*) for **6a**.



Exptl.: λ = 480 nm (in CH_2Cl_2)

Excited state	Δ*E* (eV)	*λ* (nm)	*f*	assignments
1	2.42	514	0.6149	H➔L, H➔L+1
2	3.97	312	0.6074	H➔L+3, H–4➔L+1

Orbital		*E* (eV)
HOMO–1		–6.18
HOMO		–4.94
LUMO		–2.35
LUMO+1		–2.21

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Cartesian Coordinates and Structural Parameters of the Push–Pull Chromophores

DFT calculations were performed with the Gaussian 03 program using the B3LYP functional with basis set 6-31G**.[1] Cartesian coordinates of the selected compounds **3a**, **5a** and **6a** are listed below: Atom type, (x,y,z) coordinates

Compound 3a

C	1.46183300	0.56192900	0.00420900
C	2.46855800	-0.66590700	0.00042200
C	1.22194200	-1.53523100	-0.01193100
H	1.15025800	-2.61669200	-0.02042700
C	0.33760900	-0.51346200	-0.00950400
C	-1.11133600	-0.41091100	-0.01726700
C	-1.79129500	0.82108700	-0.01661500
C	-1.89373200	-1.58309200	-0.02224600
C	-3.17775000	0.87777800	-0.02487900
H	-1.22491600	1.74442200	-0.00624400
C	-3.27706600	-1.53808600	-0.03049500
H	-1.40489500	-2.55417600	-0.01609100
C	-3.96471800	-0.29775200	-0.04022000
H	-3.65070300	1.85234000	-0.01825600
H	-3.82841800	-2.47069800	-0.02812400
C	3.34101300	-0.86906800	-1.24899300
O	3.97097500	-1.89524700	-1.42527300
C	1.47814900	1.47080600	-1.23815200
O	0.64938900	2.34791600	-1.40543700
C	3.33075200	-0.88412800	1.25394200
O	3.95076000	-1.91666800	1.42821800
C	1.46657700	1.45174500	1.25998500
O	0.62741500	2.31629400	1.44004900
C	2.53196100	1.25746700	-2.25681400
H	2.53651100	1.99565600	-3.05492300
C	3.36996600	0.20851000	-2.26415800
H	4.08340600	0.05509800	-3.07015400
C	2.52361000	1.23608100	2.27504500
H	2.52682700	1.96837100	3.07858700
C	3.36306100	0.18815400	2.27473700
H	4.07669400	0.02950500	3.07955500
N	-5.34488200	-0.24274800	-0.06797400
C	-6.12304500	-1.46483300	0.04100800
H	-7.18454100	-1.22018300	-0.02492600
H	-5.89023900	-2.15962800	-0.77602300
H	-5.95124200	-1.99028500	0.99295800
C	-6.01974200	1.03949800	0.04432200
H	-5.80076200	1.54751800	0.99573900
H	-5.73215800	1.71311000	-0.77275400
H	-7.09804100	0.88301200	-0.01794200

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Compound 5a

C	0.97133600	-0.70340000	0.57752600
C	1.94158200	-1.08609100	-0.61865300
C	0.70410200	-0.99002200	-1.49668300
H	0.61266300	-1.15187800	-2.56463100
C	-0.14899100	-0.66590100	-0.49980400
C	-1.56622800	-0.35809100	-0.41923800
C	-2.22002900	-0.08773000	0.79707200
C	-2.34349300	-0.32510100	-1.59418100
C	-3.57710800	0.19978200	0.83672700
H	-1.65996600	-0.12142800	1.72400100
C	-3.69782100	-0.04068100	-1.56626500
H	-1.87410100	-0.52937200	-2.55331100
C	-4.35805300	0.23785300	-0.34236300
H	-4.03270500	0.39061800	1.80088600
H	-4.24749200	-0.03393600	-2.49990800
C	3.01069300	-0.06074900	-1.04237200
O	3.85745000	-0.35112500	-1.86777300
C	1.16954800	0.67553000	1.24032400
O	0.55271400	0.97555200	2.24736100
C	2.56206400	-2.48568600	-0.58658300
O	2.96033300	-3.03302300	-1.59747600
C	0.81431400	-1.76925200	1.66956100
O	-0.11210300	-1.76162600	2.46043100
C	2.08212500	1.65829200	0.58805600
C	2.93673400	1.31769700	-0.47578400
C	1.84252100	-2.83543900	1.75479500
H	1.82113000	-3.41391600	2.67511400
C	2.64146800	-3.16760600	0.72691800
H	3.30084500	-4.03121000	0.76767300
N	-5.70659900	0.53756000	-0.30690000
C	-6.50572900	0.42584200	-1.51534300
H	-7.53718900	0.70121600	-1.28895500
H	-6.14372400	1.10550100	-2.29745800
H	-6.50596000	-0.59532100	-1.92617200
C	-6.37733700	0.69643500	0.97262000
H	-6.34115300	-0.21870000	1.58303400
H	-5.92995000	1.51052500	1.55643300
H	-7.42472100	0.94927000	0.79870000
C	2.08456500	2.97016500	1.08530800
H	1.42136200	3.20629500	1.91042200
C	2.92092200	3.93190000	0.52978700
H	2.91452000	4.94580000	0.92005700
C	3.78086600	2.29336200	-1.02517800
H	4.43650300	2.00283600	-1.83906600
C	3.77207500	3.59230400	-0.52900200
H	4.42821900	4.34207100	-0.96233400

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Compound 6a

C	-5.53226400	-2.84465900	0.71141100
C	-4.70799900	-1.97761600	1.42723400
C	-3.89739700	-1.10370200	0.70228100
C	-3.90295200	-1.10184400	-0.69454100
C	-4.71929600	-1.97386100	-1.41528800
C	-5.53785800	-2.84279500	-0.69520300
H	-6.18067700	-3.53493100	1.24397500
H	-4.68970700	-1.96991400	2.51259300
H	-4.70963600	-1.96332900	-2.50073300
H	-6.19050000	-3.53167000	-1.22439600
C	-2.92576200	-0.11070400	1.22343300
C	-2.93540600	-0.10743900	-1.22070400
C	-2.37927600	0.69782000	0.00010400
O	-2.60290600	0.05230500	2.37820200
O	-2.62155800	0.05838000	-2.37755700
C	-3.13886900	2.07485900	0.00583300
C	-0.89616100	0.83429600	-0.00483000
C	-0.29631000	2.07652300	-0.00011300
C	-2.35650800	3.30836800	0.01011600
H	-2.93154000	4.22798300	0.01511900
C	-0.99360500	3.31335900	0.00724600
O	-4.36465500	2.06447300	0.00715300
H	-0.42848900	4.24182300	0.01010000
C	0.18536700	-0.06227500	-0.01309000
C	1.37414000	0.62596500	-0.01275600
O	1.06837300	1.97354100	-0.00473900
C	2.76459100	0.23392900	-0.01874100
C	3.11832600	-1.12745400	-0.03259400
C	3.80545900	1.17854300	-0.00664800
C	4.44321800	-1.53089100	-0.03729000
H	2.33530400	-1.88144900	-0.03726300
C	5.13536600	0.78657200	-0.01086100
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C	5.49673000	-0.58267200	-0.03334100
H	4.66175000	-2.59181400	-0.04354700
H	5.90022800	1.55360000	0.00462100
N	6.82057400	-0.97812700	-0.05472700
C	7.15781300	-2.38845400	0.03539500
H	8.24224900	-2.50075000	-0.01089800
H	6.80592500	-2.84497000	0.97301900
H	6.72771300	-2.95589800	-0.80004700
C	7.87463900	0.01475200	0.06295300
H	8.84389400	-0.48349400	0.00803800
H	7.82815000	0.74480900	-0.75539600
H	7.82657800	0.56687300	1.01386000

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S5. ^{1}H and ^{13}C NMR spectra

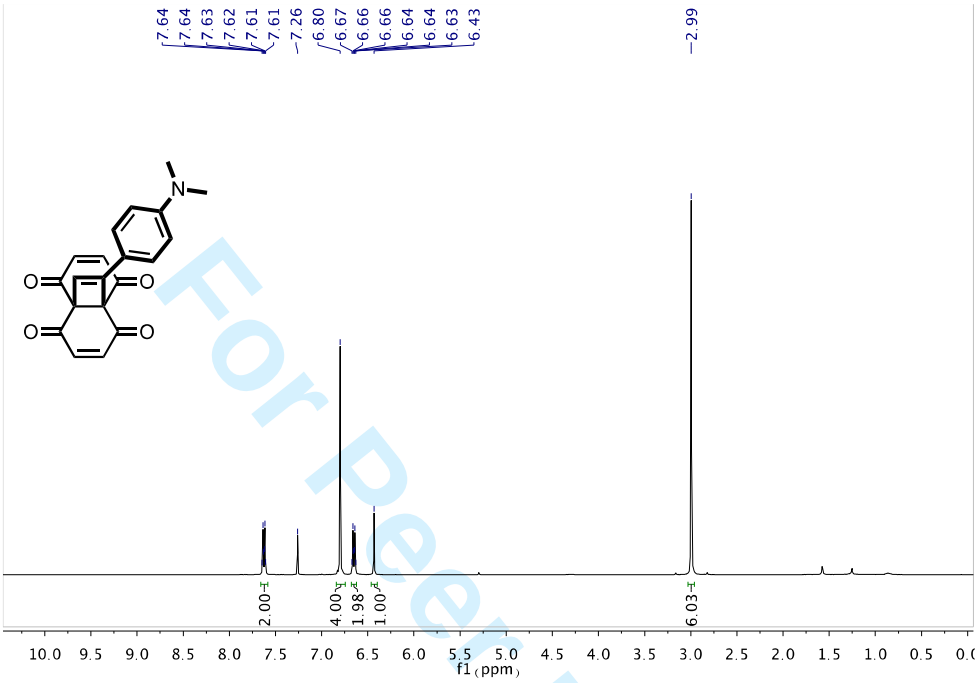


Figure S14. ^{1}H NMR spectrum of **3a** in $CDCl_3$ solution (400 MHz).

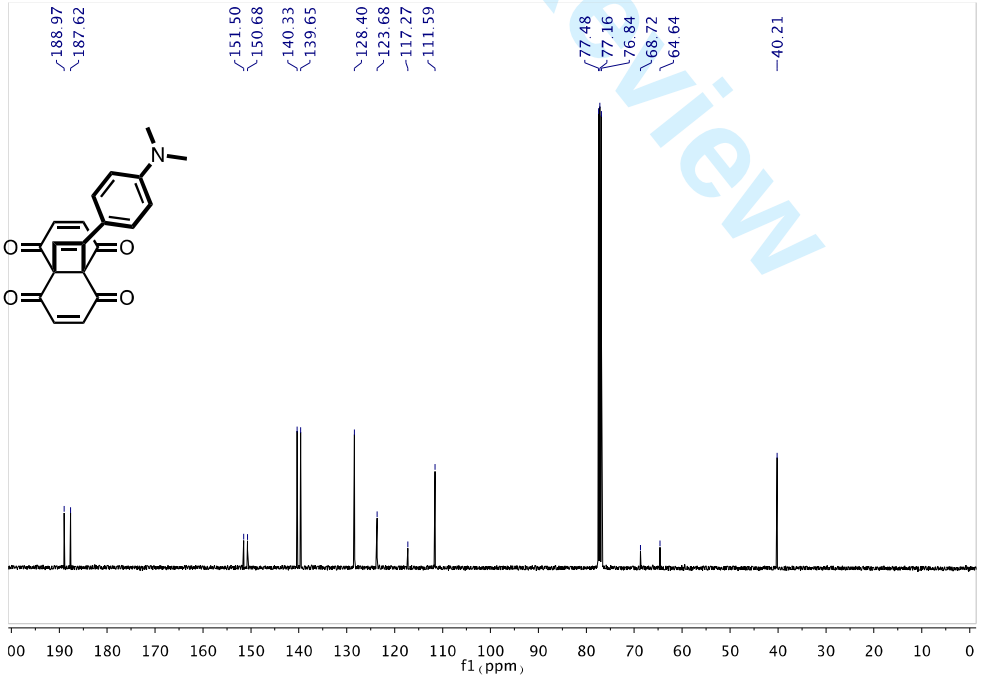


Figure S15. ^{13}C NMR spectrum of **3a** in $CDCl_3$ solution (100 MHz).

For Peer Review

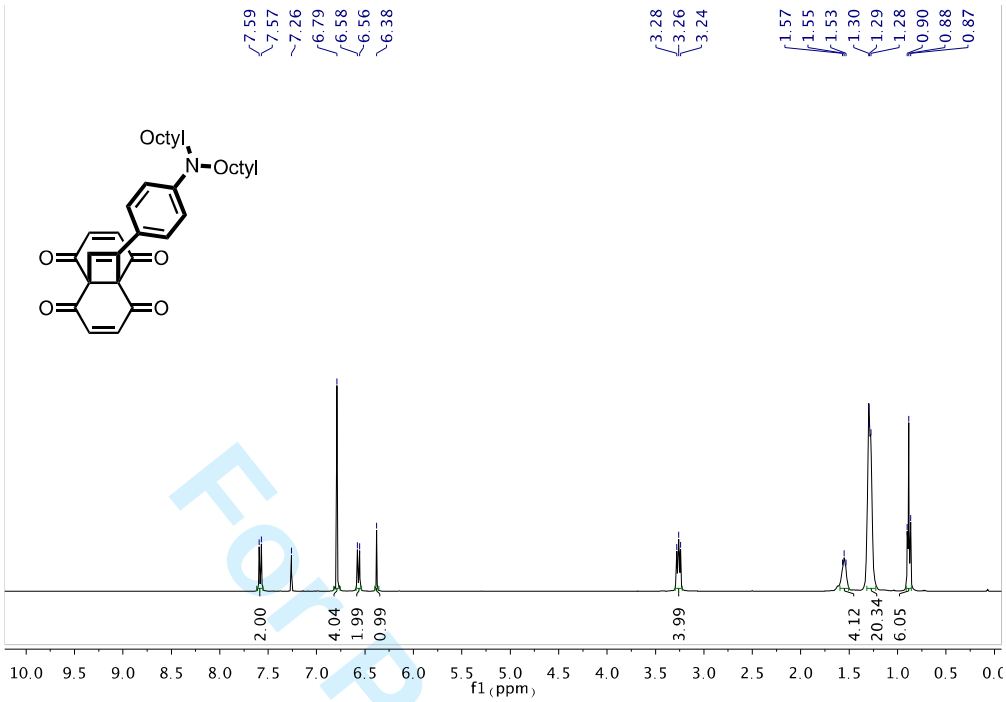


Figure S16. ^{1}H NMR spectrum of **3b** in $CDCl_3$ solution (400 MHz).

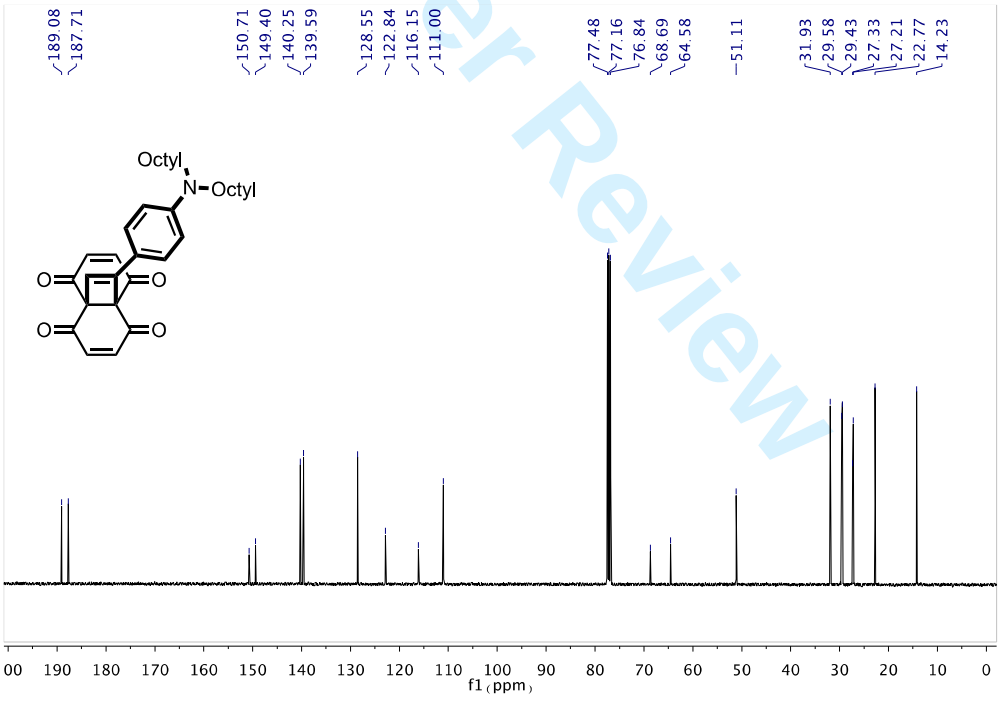


Figure S17. ^{13}C NMR spectrum of **3b** in $CDCl_3$ solution (100 MHz).

For Peer Review

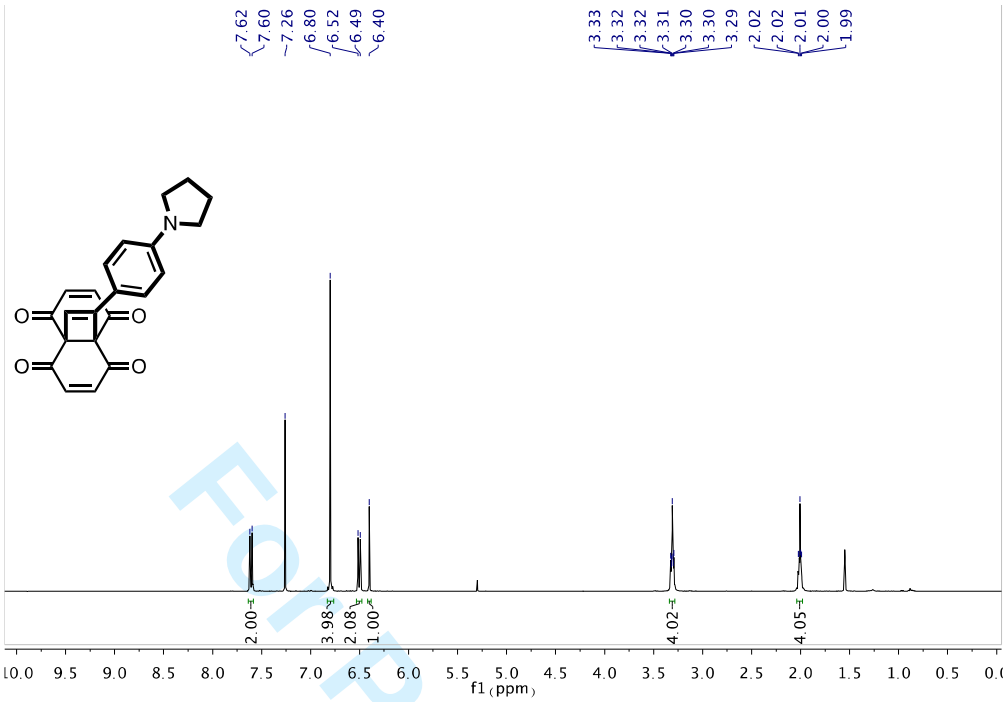


Figure S18. ^{1}H NMR spectrum of **3c** in $CDCl_3$ solution (400 MHz).

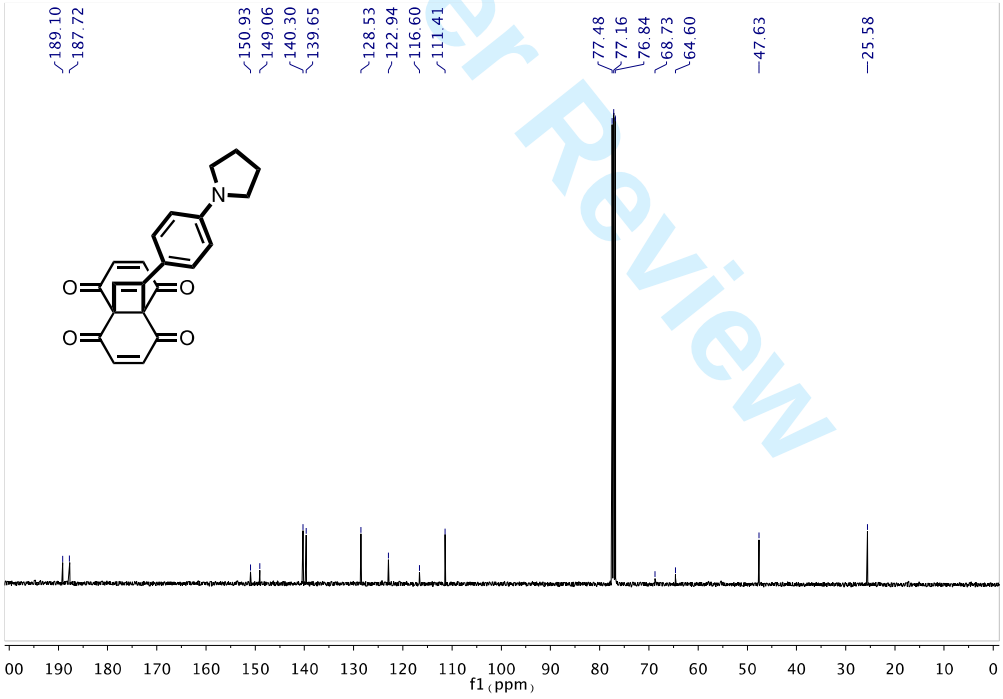


Figure S19. ^{13}C NMR spectrum of **3c** in $CDCl_3$ solution (100 MHz).

For Peer Review

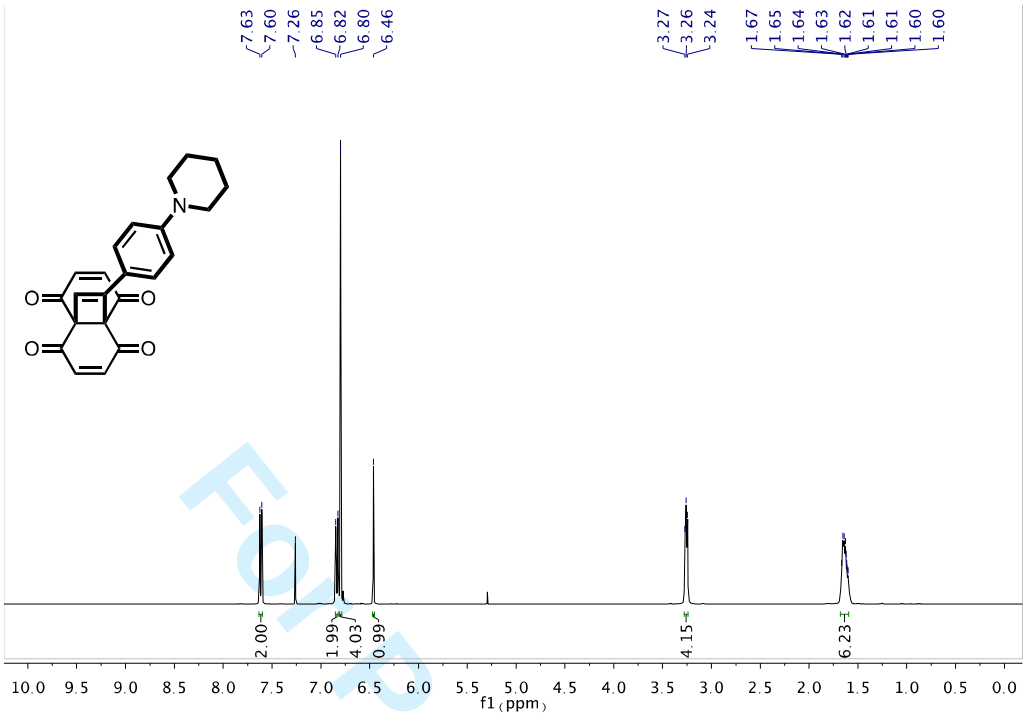


Figure S20. ^{1}H NMR spectrum of **3d** in $CDCl_3$ solution (400 MHz).

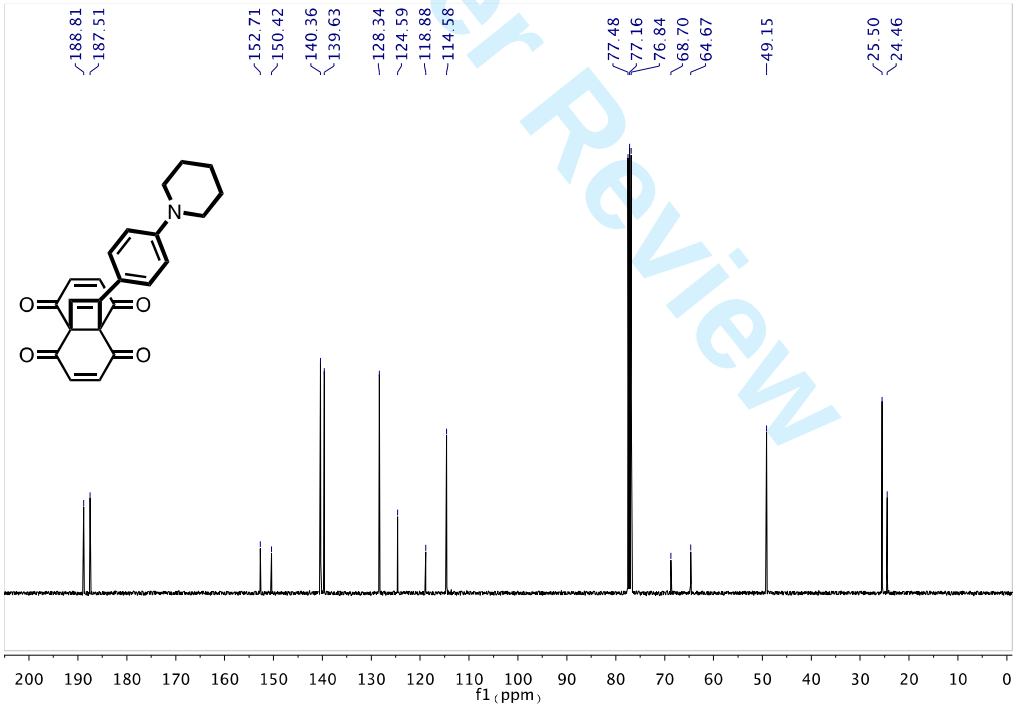


Figure S21. ^{13}C NMR spectrum of **3d** in $CDCl_3$ solution (100 MHz).

For Peer Review

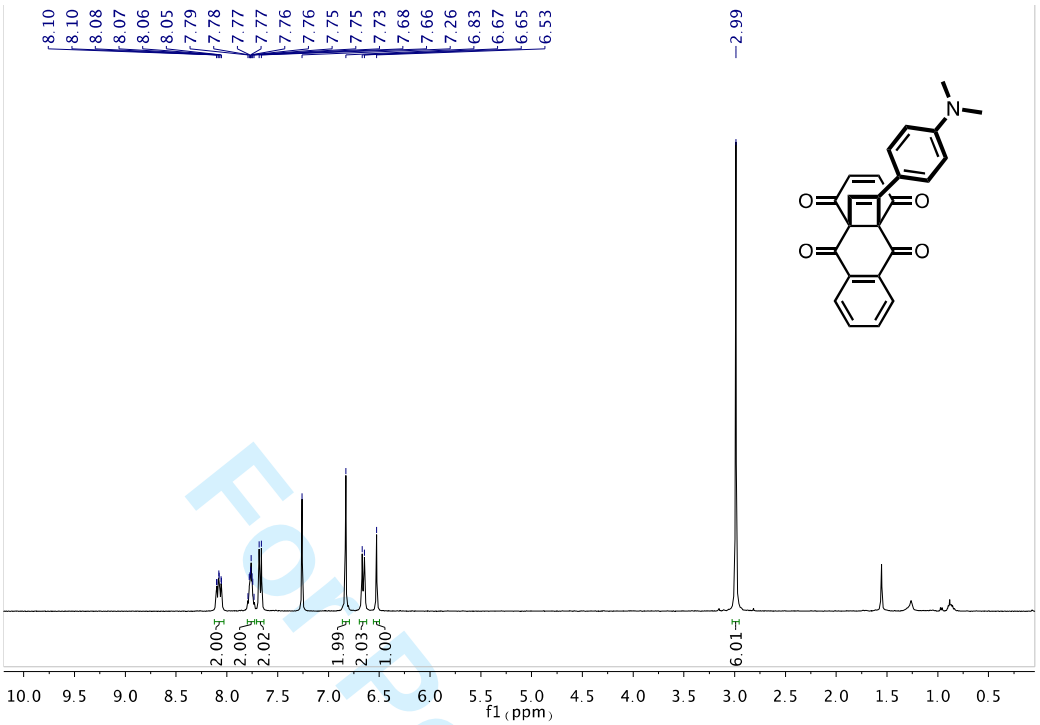


Figure S22. ^{1}H NMR spectrum of **5a** in $CDCl_3$ solution (400 MHz).

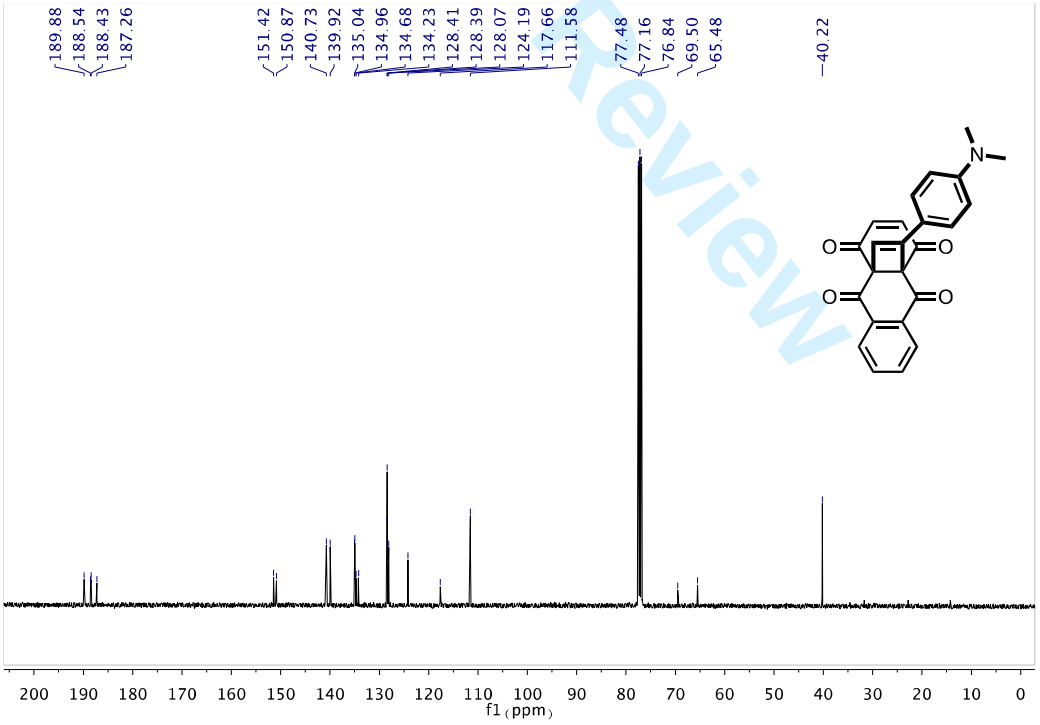


Figure S23. ^{13}C NMR spectrum of **5a** in $CDCl_3$ solution (100 MHz).

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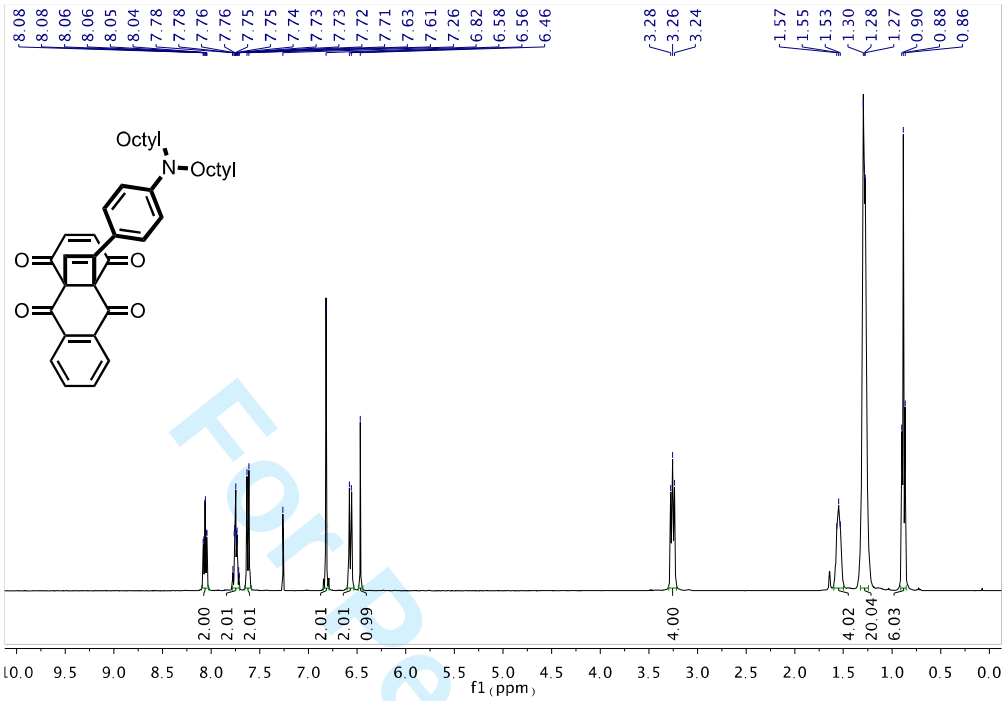


Figure S24. ^{1}H NMR spectrum of **5b** in $CDCl_3$ solution (400 MHz).

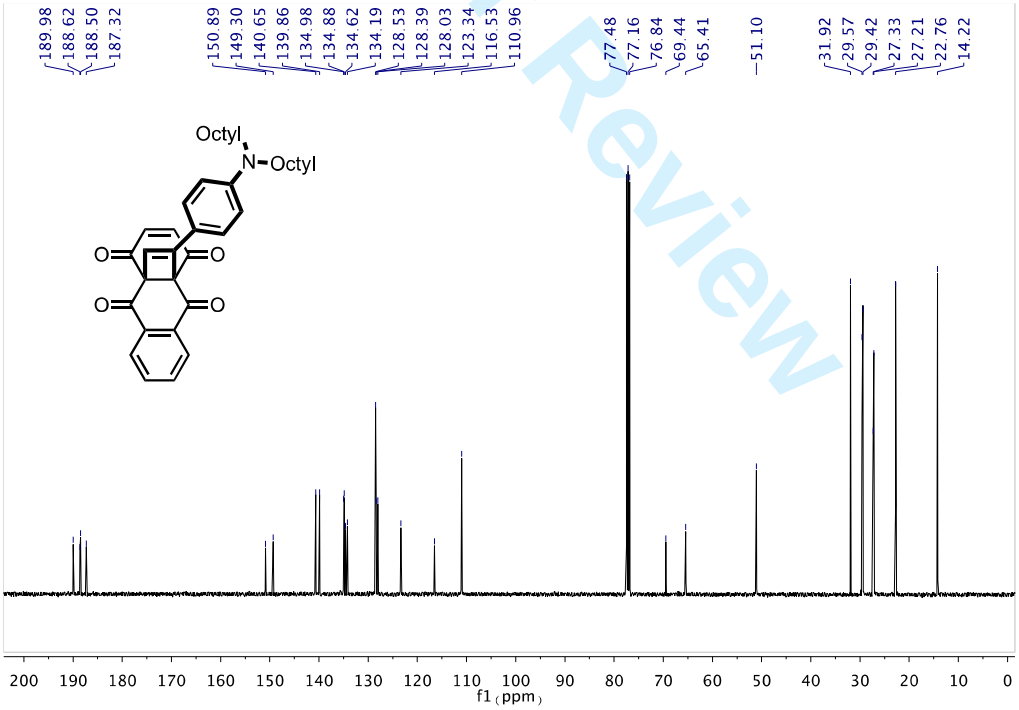


Figure S25. ^{13}C NMR spectrum of **5b** in $CDCl_3$ solution (100 MHz).

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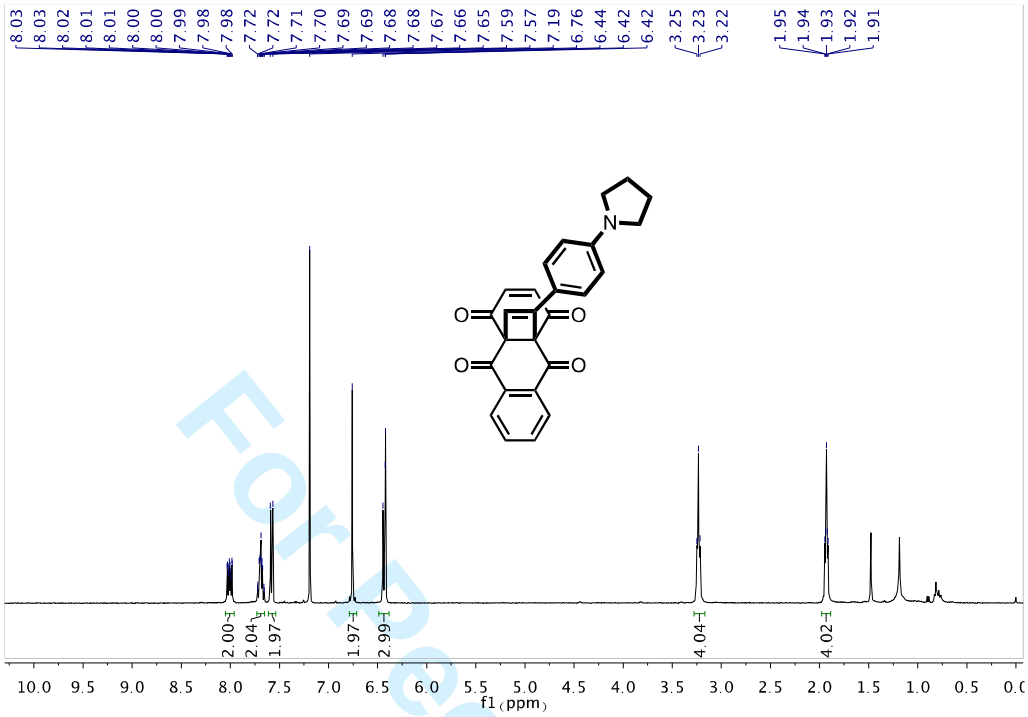


Figure S26. ^{1}H NMR spectrum of **5c** in $CDCl_3$ solution (400 MHz).

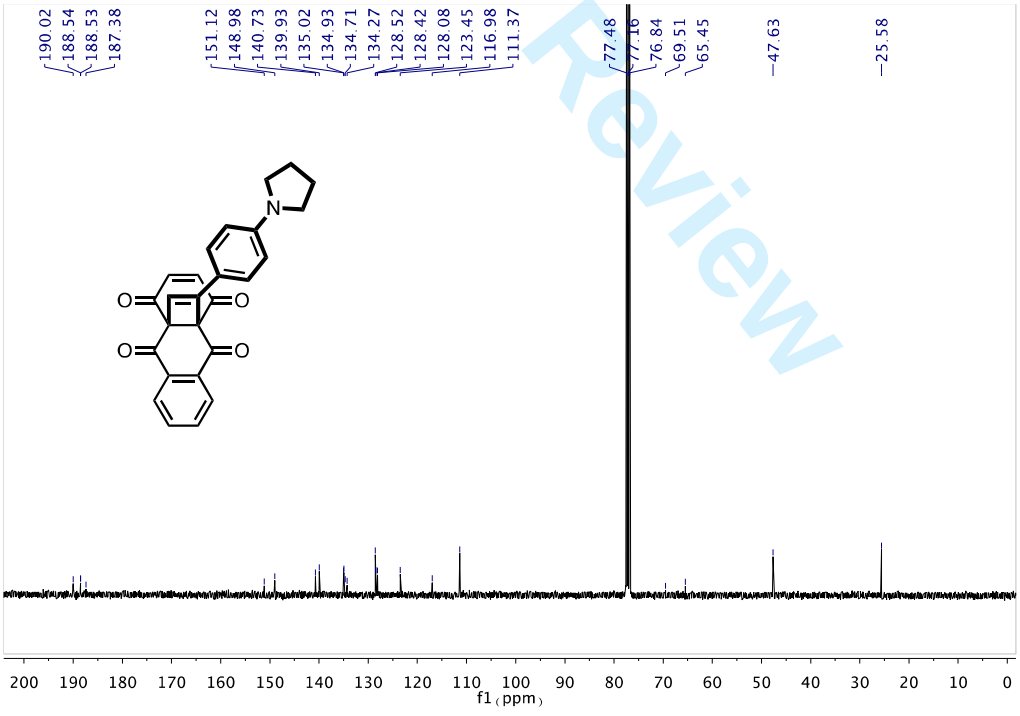


Figure S27. ^{13}C NMR spectrum of **5c** in $CDCl_3$ solution (100 MHz).

For Peer Review

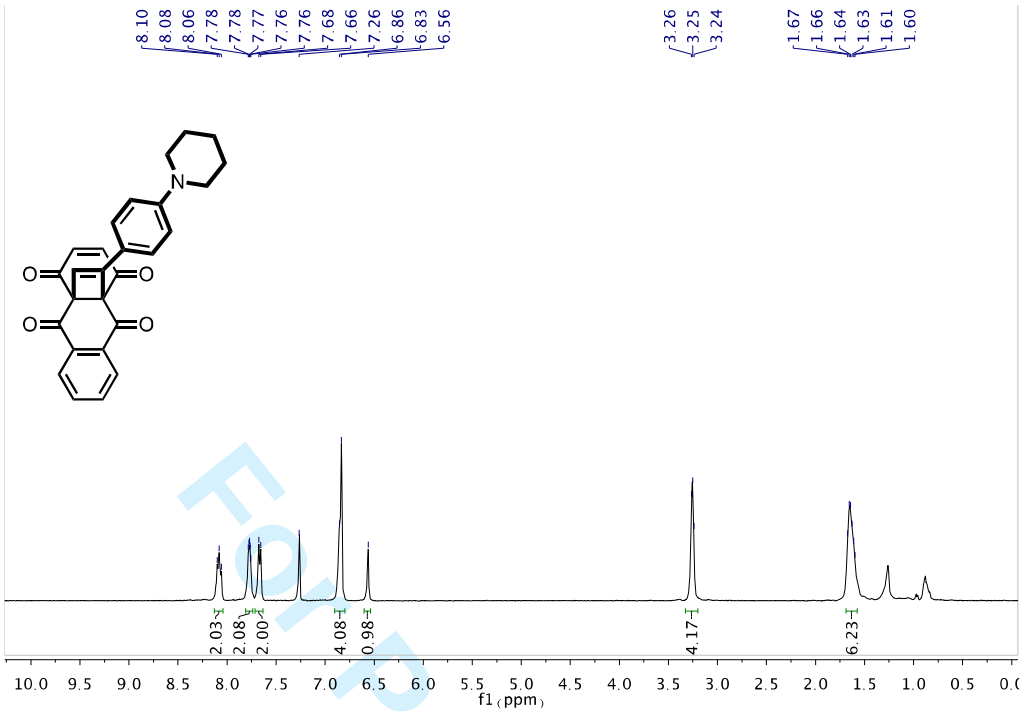


Figure S28. ^{1}H NMR spectrum of **5d** in $CDCl_3$ solution (400 MHz).

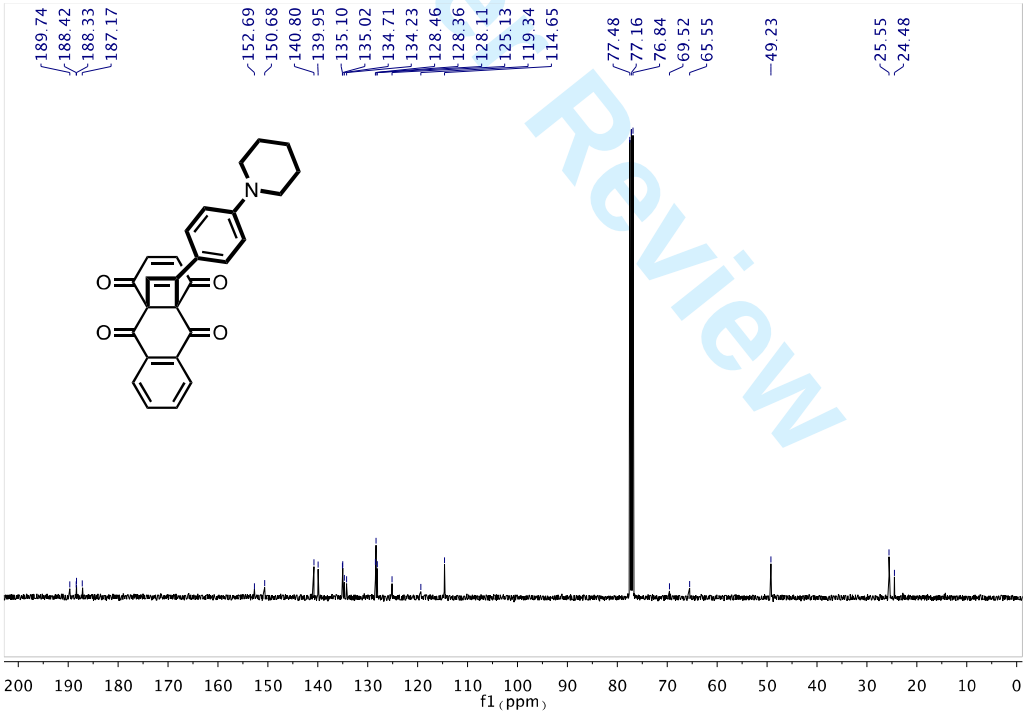


Figure S29. ^{13}C NMR spectrum of **5d** in $CDCl_3$ solution (100 MHz).

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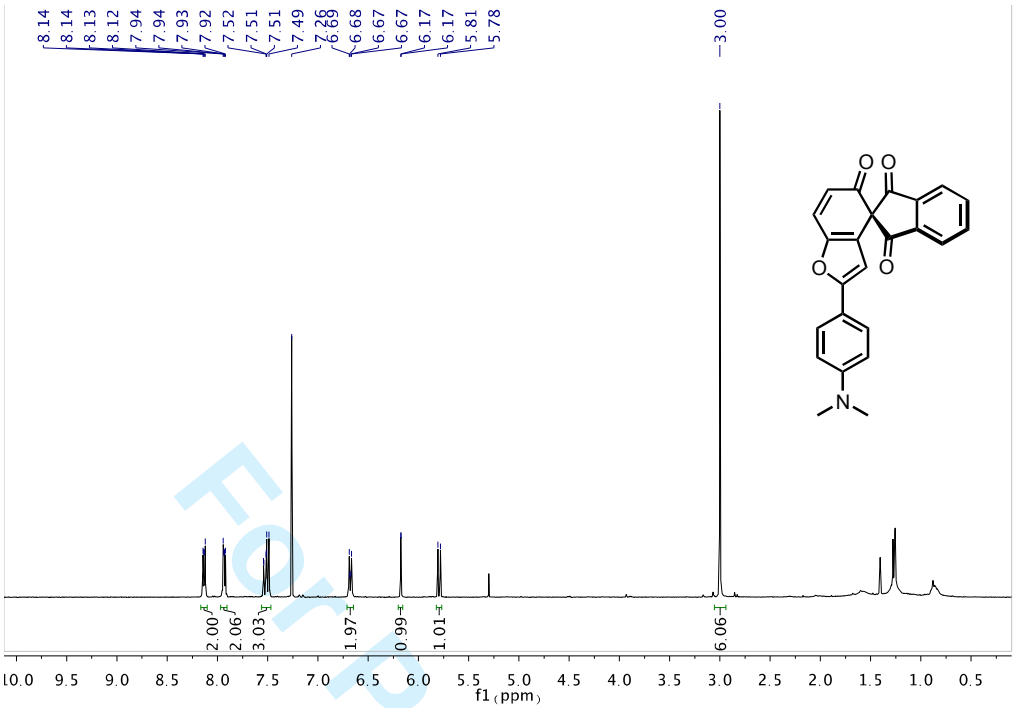


Figure S30. ^{1}H NMR spectrum of **6a** in $CDCl_3$ solution (400 MHz).

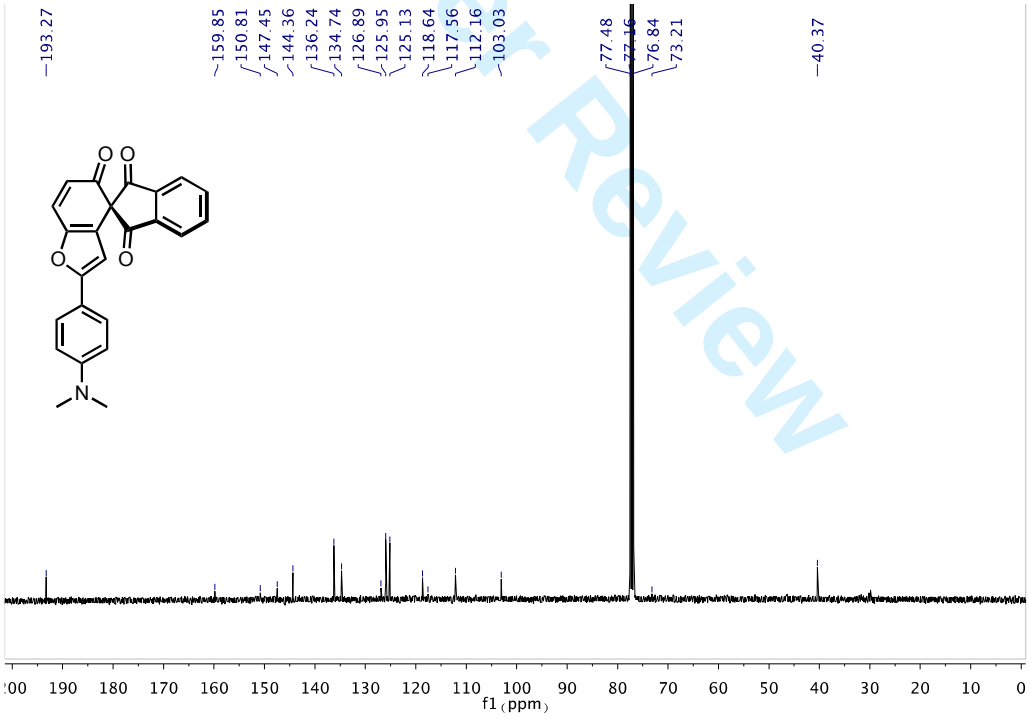


Figure S31. ^{13}C NMR spectrum of **6a** in $CDCl_3$ solution (100 MHz).

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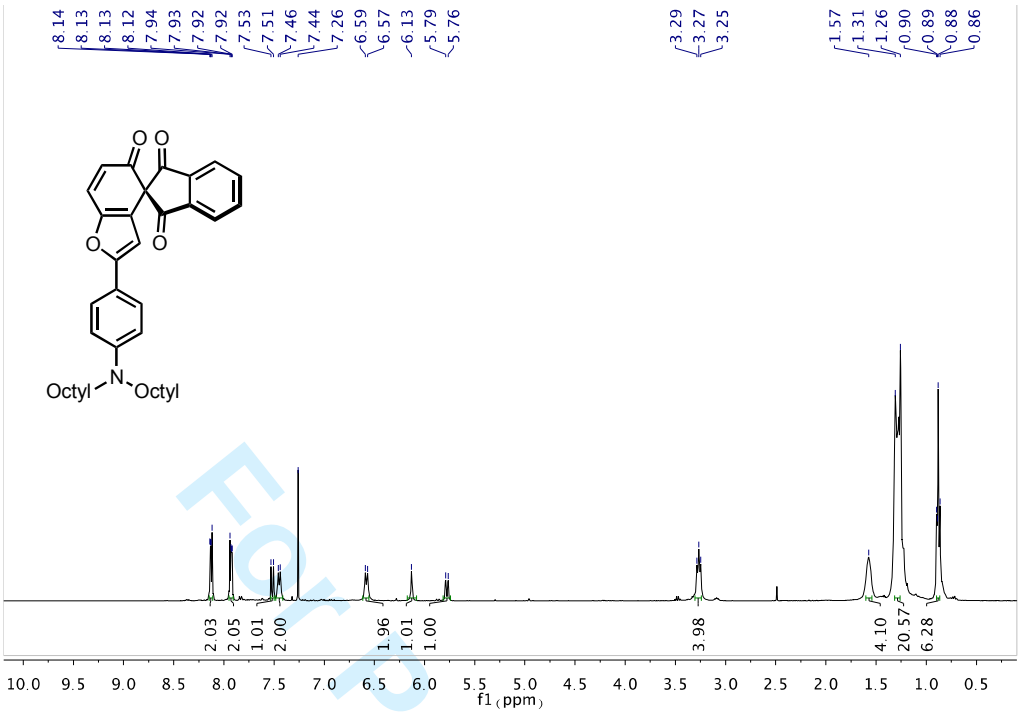


Figure S32. ^{1}H NMR spectrum of **6b** in $CDCl_3$ solution (400 MHz).

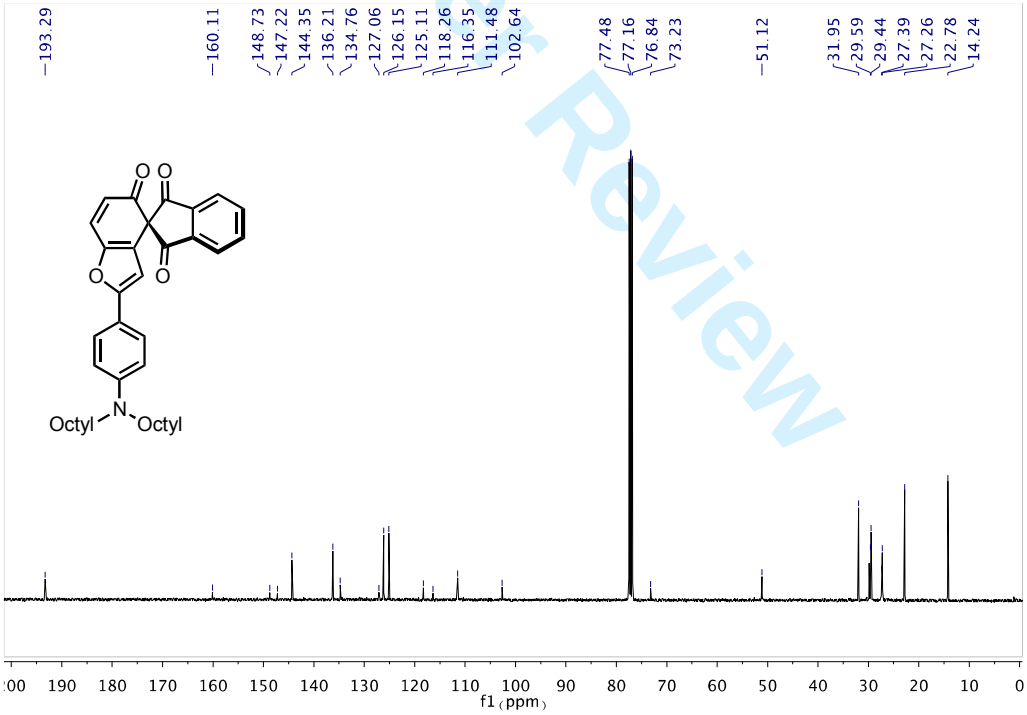


Figure S33. ^{13}C NMR spectrum of **6b** in $CDCl_3$ solution (100 MHz).

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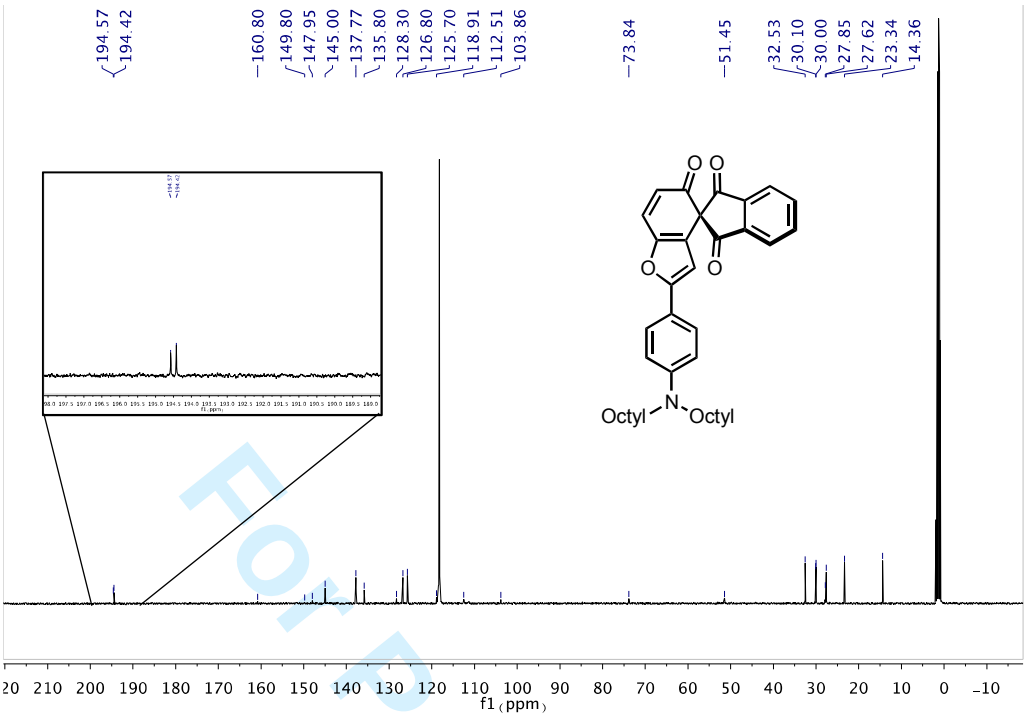


Figure S34. ^{13}C NMR spectrum of **6b** in CD_3CN solution (100 MHz).

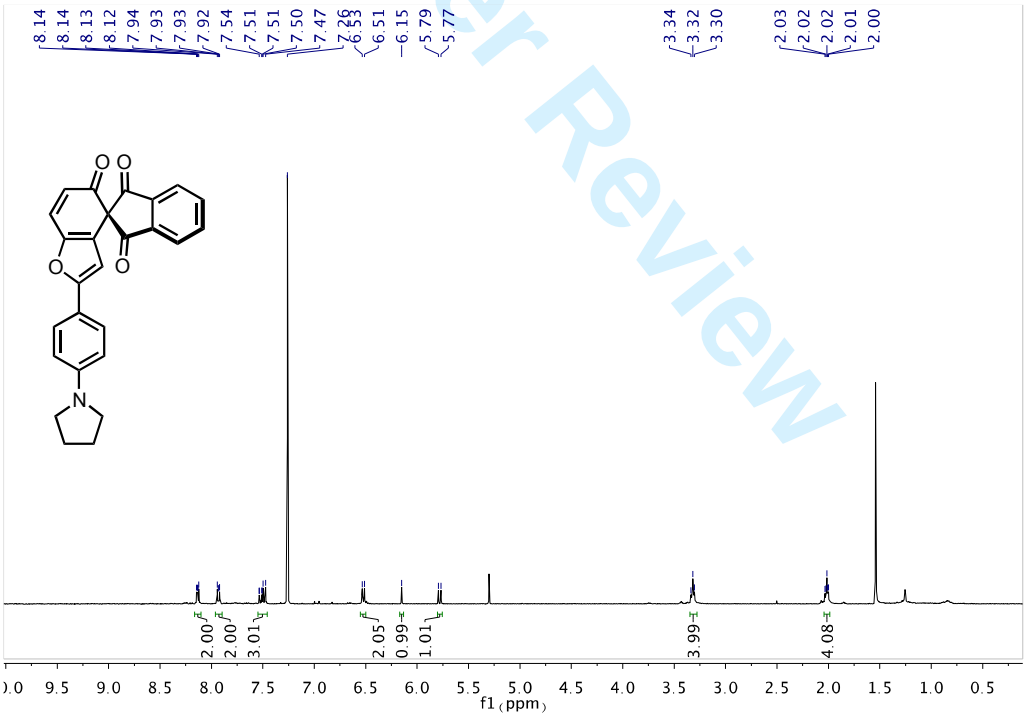


Figure S35. ^{1}H NMR spectrum of **6c** in $CDCl_3$ solution (400 MHz).

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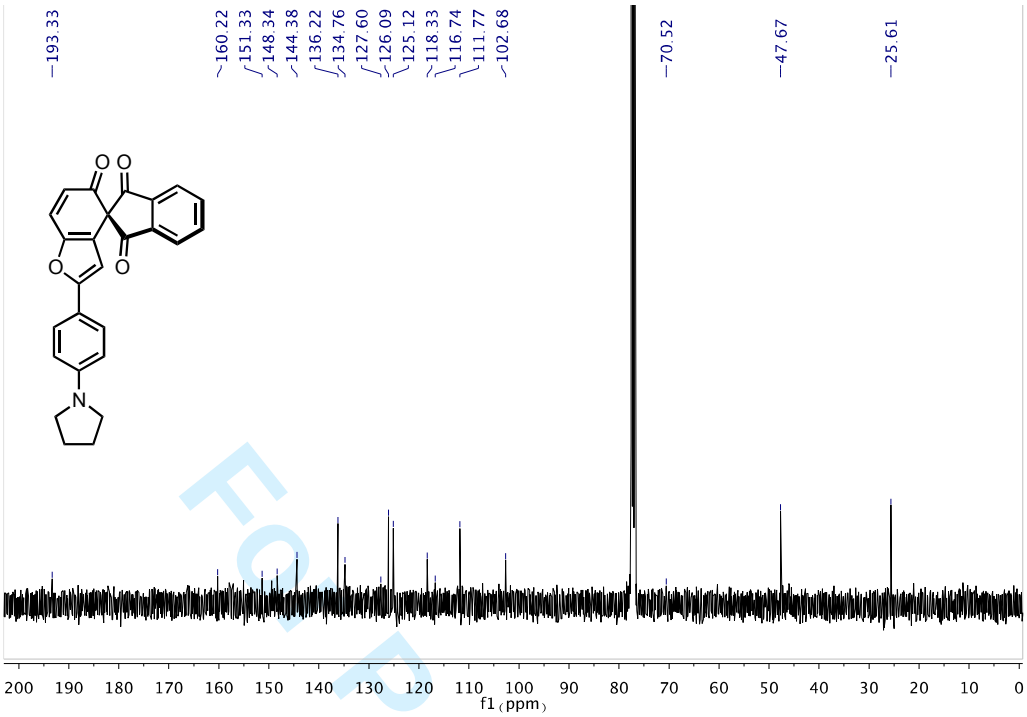


Figure S36. ^{13}C NMR spectrum of **6c** in $CDCl_3$ solution (100 MHz).

S6. References

[1] (a) Yoshino, S.; Hayakawa, K.; Kanematsu, K. *J. Org. Chem.* **1981**, *46*, 3841–3846. (b) Hayakawa, K.; Aso, M.; Kanematsu, K. *J. Org. Chem.* **1985**, *50*, 2036–2040.

[2] (a) Elangovan, A.; Chen, T.-Y.; Chen, C.-Y.; Ho, T.-I. *Chem. Commun.* **2003**, *17*, 2146–2147. (b) Huang, W.; Chen, H. *Macromolecules* **2013**, *46*, 2032–2037.

[3] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennuci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyata, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision E.01, Gaussian, Inc., Wallingford CT, 2004.

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Homoconjugated and Spiro Push–Pull Systems: Cycloadditions of Naphto- and Anthra-diquinones with Electron-Rich Alkynes

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Abstract

We report the synthesis and characterization of three new classes of push–pull chromophores using [2+2] cycloaddition reactions of electron-rich alkynes and electron-poor alkenes. Previous investigations have focused on the reactions of cyano-substituted electron acceptors. This study demonstrates that cyano-free electron acceptors, naphto- and anthra-diquinones, can also be used to access extended push–pull systems. The effects of the structural changes on the spectroscopic and electronic properties were investigated by UV/Vis spectroscopy. Structures were confirmed by X-ray and NMR analysis in solution.

Keywords

Homoconjugation, cycloadditon, push–pull, quinones, spirocycles

Introduction

Planar and non-planar push–pull chromophores are of continuing interest as a result of their optoelectronic properties.[1] A major challenge to use these chromophores in optoelectronical devices is the control of their film morphology. The improved solubility, processability, and reduction of self-quenching displayed by structurally rigid non-planar chromophores offer distinct advantages over planar counterparts on thin film preparations.[2] The [2+2] cycloaddition–retroelectrocyclization (CA–RE) reactions represent an efficient route to the synthesis of these materials from readily accessible electron-rich alkynes and electron-deficient alkenes.[3] Extensive research efforts have been invested in development of these transformations because of their atom-economic, high-yielding characteristics which meet the prerequisites of click-type reactions.[4] The most investigated reactions have focused on cyano-substituted electron acceptors such as tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ), and 6,6-dicyanopentafulvenes.[1c,3,5] Recently, Diederich,[6] Tromifov,[7] and Shoji[8] have demonstrated the [2+2] cycloadditions of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with variety of electron-rich alkynes to give homoconjugated push–pull chromophores. Results in those reports indicated that the adducts produced in the cycloadditions were not suitable to undergo simple retroelectrocyclization. Specifically, the cycloadducts transform into donor–acceptor (D–A)-substituted spiro compounds instead of CA–RE products.[6b] These results indicated that even when the CA–RE reaction pathway was not accessible, structurally

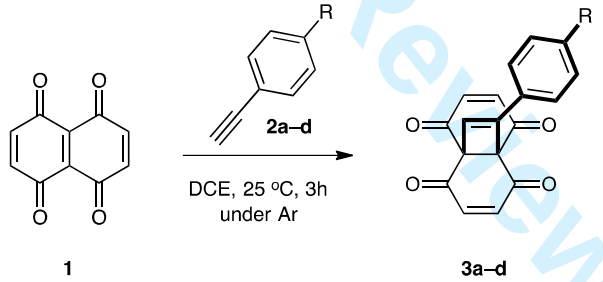
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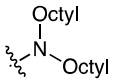
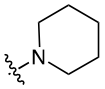
demanding chromophores could still be obtained, which further heightened our interest in exploring the reactions between electron-rich alkynes and electron-poor alkenes. Almost all electron acceptors, used for the CA–RE reactions, possess activating cyano substituents. There are only a few investigations of cyano-free electron acceptors in these transformations.[9, 10] In all reported cases,[9, 10] elevated temperatures were required and low yields were observed due to the formation of significant amount of decomposition products. In the present work, we expand the scope of formal [2+2] cycloadditions by introducing new electron-acceptors, naphto- and anthra-diquinones as alternatives to the commonly used cyano-substituted electron-deficient olefins. We describe the synthesis and the electronic properties of new series of homoconjugated push–pull chromophores **3a**–**d**, **5a**–**d** and (D–A)-substituted spiro systems **6a**–**c**. We also demonstrated that the cyano-free electron acceptors react efficiently with dialkylanilino (DAA) acetylenes and the structures of the three new chromophores were confirmed by X-ray analysis.

Results and Discussion

A series of electron-rich alkynes were tested for [2+2] cycloadditions with electron-poor diquinones (Figure S1 in the Supporting Information (SI)). Based on these initial results, diquinone **1**[11] and electron-rich alkynes **2b**–**d** [12] were identified for investigations and we prepared these compounds following the literature procedures. Push–pull chromophores **3a**–**d** were obtained by one-step method using various alkynes **2a**–**d** and electron-poor diquinone **1**. Upon addition of diquinone **1**, the color of the alkyne solutions in 1,2-dichloroethane changed from colorless to dark orange, and compounds **3a**–**d** were obtained in yields of 23–35% (Table 1).

Table 1. Synthesis of homoconjugated chromophores **3a**–**d**. DCE = 1,2-dichloroethane



Substrate	R	Product	Yield (%)
2a		**3a**	35%
2b		**3b**	23%
2c		**3c**	29%
2d		**3d**	27%

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Homoconjugated chromophores **3a**–**d** are dark-orange colored solids that are stable at room temperature. The formation of compounds **3a**–**d** was accompanied by very small amount of dark colored, unstable side products. Unfortunately, our attempts to purify these species failed due to their fast decomposition during crystallization or column chromatography on aluminum oxide (neutral, and basic) and silica gel. However, the formation of these species was not responsible for the low yields obtained for **3a**–**d.** Rather, we also observed substantial amount of insoluble material formation, similar to the earlier reports for the reactions of DDQ and electron-rich acetylenes.[6b] The structure of chromophore **3a** was unambiguously confirmed by X-ray diffraction analysis (Figure 1).

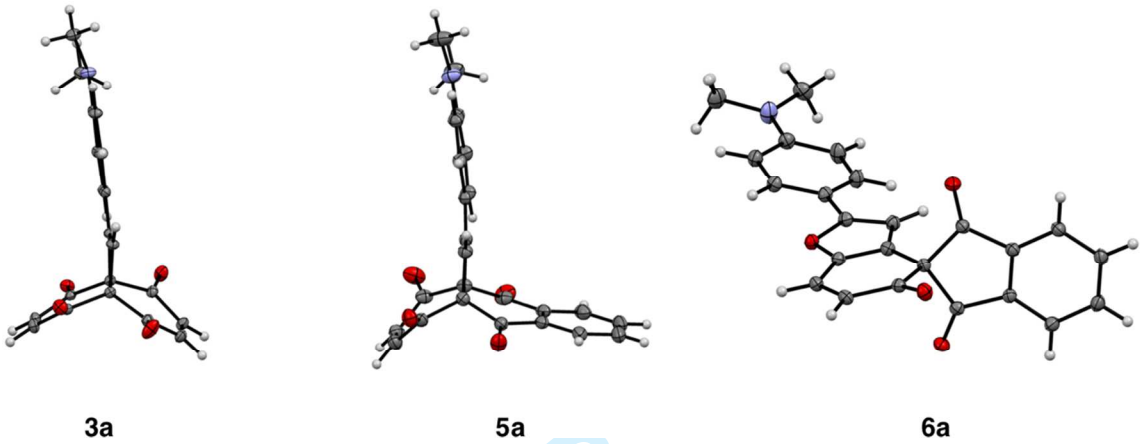
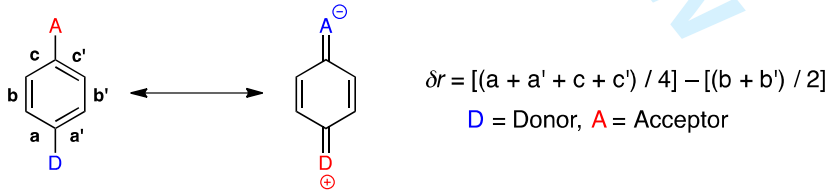


Figure 1. ORTEP plots of **3a**, **5a**, and **6a**. Atomic displacement parameters are drawn at 50% probability level.

Bond-length alternation in the DAA moiety can be described by the quinoid character (δr) and δr is a good description for the ground state charge-transfer (CT) from the DAA group to π-conjugated or homoconjugated acceptor units (See Scheme 1 and ref. 13 for δr value calculations). The δr value in the DAA moiety for compound **3a** was calculated to be 0.021 by using the experimental bond lengths in the X-ray structure (Figure S2 in the SI). This value is comparable to those obtained for the similar push–pull chromophores in the literature.[6b, 10]



Scheme 1. General scheme for quinoid character calculations of DAA-substituted push–pull chromophores (for benzene, $\delta r = 0$; for fully quinoid rings, $\delta r = 0.08 – 0.10$ Å).

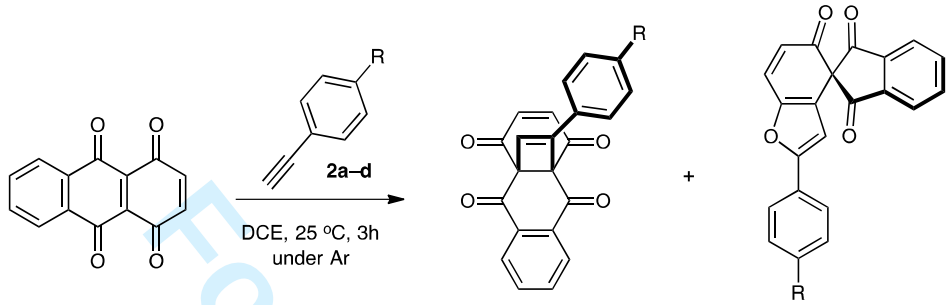
After successful synthesis of chromophores **3a**–**d,** we turned our attention to the reactions of diquinone **4** with electron-rich alkynes **2a**–**d**. Dark-orange chromophores **5a**–**d** were obtained in yields of 26–39% (Table 2). Similar to the reactions of diquinone **1**, the formation of dark-colored side products was observed. For three of the four reactions, these products could be identified as the spiro compounds **6a**–**c** in 4–5% yield. Isolation was thought to be possible due

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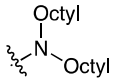
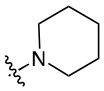
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to their relative stability resulting from the additional aromatic unit. Although we observed the formation of a similar spot on TLC that is likely attributable to **6d**, multiple attempts to isolate it failed due to decomposition issues similar to the reactions of quinone **1**, which could not be avoided.

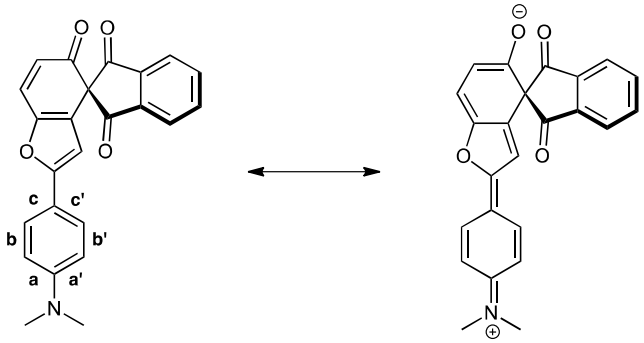
Table 2. Synthesis of homoconjugated **5a**–**d** and spiro push–pull chromophores **6a**–**c**.



4 **5a–d** **6a–d**

Substrate	R	Products	Yield (%) **5a**–**d**	Yield (%) **6a**–**d**
2a		**5a**,**6a**	39%	5%
2b		**5b**,**6b**	26%	4%
2c		**5c**,**6c**	34%	4%
2d		**5d**,**6d**	34%	–

Single crystals of **5a** and **6a** were obtained by slow diffusion of *n*-hexane into CH_2Cl_2 solutions of compounds (Figure 1). The calculated δr values of DAA units for compounds **5a** and **6a** are 0.023 and 0.020 respectively (Scheme 2, see also Figure S3 and S4 for experimental bond lengths).

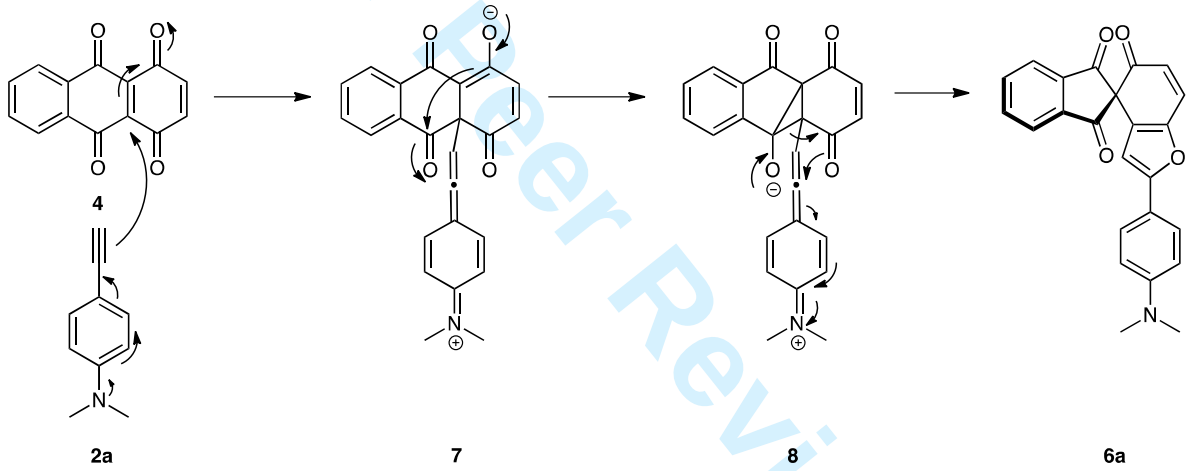


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Scheme 2. Resonance structures of chromophore **6a** that highlight the interconnection between BLA and charge-transfer interactions. (See also Scheme 1 for δr value calculations)

The δr values of homoconjugated chromophores **3a**, **5a** and spirocyclic chromophore **6a** suggested that there is almost no meaningful difference in between these values although it should be expected higher values for the spiro system **6a** because of the direct π-conjugated CT pathway. This unexpected observation can be explained by the substantial deconjugation due to non-planarity, as shown by the large dihedral angle between the donor and the acceptor units (**3a**: 4.2(2)° / δr = 0.021, **5a**: -8.1(2)° / δr = 0.023, and **6a**: 16.7(2)° / δr = 0.020, Figures S2, S3, and S4 in the SI).

We propose a mechanism outlined in Scheme 3 for the transformation to the spirocyclic push–pull chromophore **6a**. The cascade mechanism starts with the initial regioselective conjugate addition of electron-rich alkyne **2a** to 1,4-dihydroxyanthraquinone **4** to form zwitterionic intermediate **7**. The formed intermediate **7** undergoes intramolecular cyclization to give intermediate **8**. The final step of the mechanism is the charge neutralization to give spirocycle **6a**.



Scheme 3. Proposed mechanism for the formation of spirocyclic chromophore **6a**.

The UV/Vis spectra acquired from three representative push–pull chromophores **3a**, **5a**, and **6a** are shown in Figure 2 (See Figures S6, S7, and S8 in the SI for the electronic absorption spectra of all chromophore series). The orange-colored homoconjugated chromophores **3a** and **5a** display weak intramolecular CT bands (453 nm (2.74 eV), ε = 2400 M^{-1} cm^{-1}, **3a** and 411 nm (3.02 eV), ε = 3400 M^{-1} cm^{-1}, **5a**). The CT bands of chromophores are bathochromically shifted with increasing donor strength (Figures S6 and S7 in the SI).[14] The spiro compound **6a** displays relatively stronger CT band because of the linear CT pathway (480 nm (2.58 eV), ε = 12500 M^{-1} cm^{-1}, **6a**). In all cases, low-energy transfer bands can be explained as intramolecular CT interactions which includes transfer of electron density from the DAA donor to the rest of the molecule according to the HOMO, LUMO orbital depictions (See Figure S13 in the SI).[15] The structural complexity of the spiro compound **6a** creates other CT pathways (See Tables S1–S3 in the SI for TD-DFT calculations). For example, Intramolecular CT might arise from the transition between electron-rich furan ring and carbonyl group. The other possibility is the CT between spiro rings *via* homoconjugation. In summary, the strong CT band of spirocycle **6a** is an overlap of several transitions.

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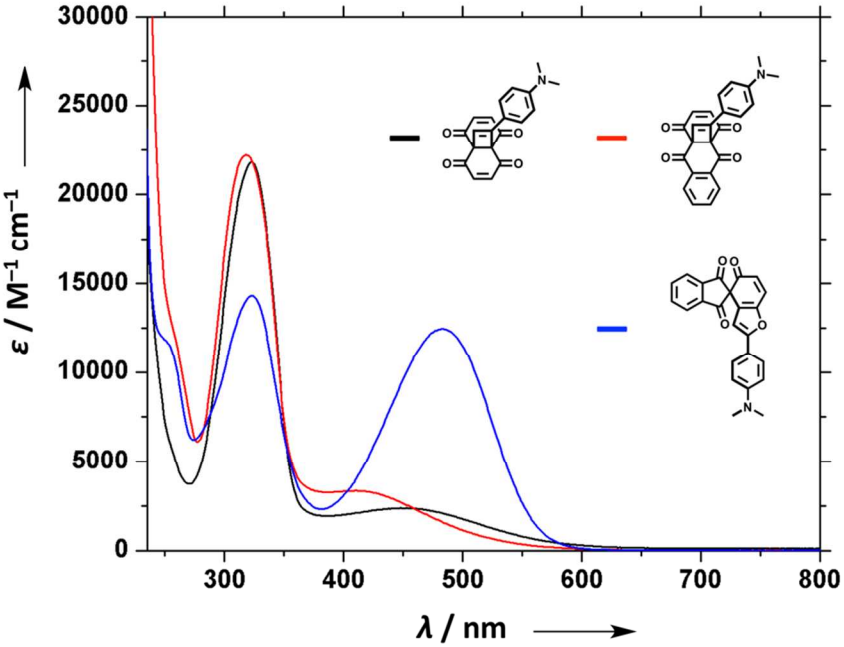


Figure 2. UV/Vis spectra of selected compounds **3a** (black line), **5a** (red line), and **6a** (blue line) in CH_2Cl_2 at 298 K.

The spiro compound **6a** displays positive solvatochromism which further support the intramolecular CT interactions (Figure S9). In addition to this observation, the selected compounds **3a**, **5a**, and **6a** were subjected to protonation experiments. Upon treatment with trifluoroacetic acid (TFA), the longest wavelength absorption band disappeared because of the quaternization of DAA moieties. The re-neutralization with trimethylamine (TEA) provided full recovery of the CT bands (Figures S10–S12 in the SI).

In summary, we have demonstrated the synthesis of three new push–pull chromophore types starting from cyano-free electron acceptors.[16] Despite the observed modest yields, the short synthetic method facilitates the formation of these interesting chromophores. The simplicity of the method will enable us to design new chromophores for desired optoelectronic applications.

Acknowledgment

We thank Dr. Peter Müller for collecting and solving X-ray crystal structure data, and Dr. Tristan A. Reekie for helpful discussions about the mechanism and reviewing the manuscript. C.D. acknowledges the receipt of an Early Postdoc Mobility fellowship from the Swiss National Science Foundation (SNF). We also appreciate the financial support of the Airforce Office of Scientific Research FA9550-14-1-0226.

Supporting Information for this article is available online at http://

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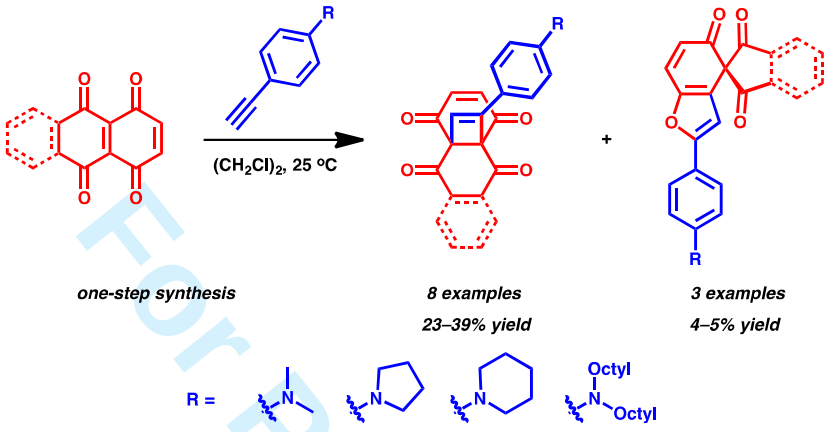
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[15] Frisch, M. J. et al. Gaussian 03, revision E.01, Gaussian, Inc., Wallingford CT, 2004. See the Supporting Information for the full list of the authors.
[16] **General procedure for the synthesis of homoconjugated and spiro push–pull systems:** Diquinone (1 equiv) was added under Ar to a solution of electron rich alkyne (1 equiv) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated and spirocyclic products.
3a: Naphthazarin **1** (100 mg, 0.532 mmol) was added under Ar to a solution of electron rich alkyne **2a** (77 mg, 0.532 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (FCC), (SiO_2, $CHCl_3$) to give homoconjugated chromophore **3a** (62 mg, 35%) as a dark-orange solid. R_f = 0.13 (SiO_2; $CHCl_3$); m.p. 215 – 218 °C ; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.99 (s, 6 H), 6.43 (s, 1 H), 6.65 (quasi d, J = 9.0 Hz, 2 H), 6.80 (s, 4 H), 7.63 ppm (quasi d, J = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 189.0, 187.6, 151.5, 150.7, 140.3, 139.7, 128.4, 123.7, 117.3, 111.6, 68.7, 64.6, 40.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 453 (2400), 323 nm (21800 M^{-1} cm^{-1}); HR-ESI-MS: found 334.1076 ($[M + H]^+$, calcd for $C_{20}H_{15}NO_4^+$: 334.1074).
5a and 6a: Quinizarin **4** (50 mg, 0.210 mmol) was added under Ar to a solution of electron rich alkyne **2a** (31 mg, 0.210 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **5a** (31mg, 39%) and **6a** (4 mg, 5%) as a dark-orange solids. **5a**: R_f = 0.13 (SiO_2; $CHCl_3$); m.p. 125 – 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.99 (s, 6 H), 6.53 (s, 1 H), 6.66 (quasi d, J = 8.9 Hz, 2 H), 6.83 (s, 2 H), 7.67 (quasi d, J = 8.9 Hz, 2 H), 7.73 – 7.80 (m, 2 H), 8.03 – 8.12 ppm (m, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 189.9, 188.5, 188.4, 187.3, 151.4, 150.9, 140.7, 139.9, 135.04, 134.96, 134.7, 134.2, 128.41, 128.39, 128.1, 124.2, 117.7, 111.6, 69.5, 65.5, 40.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 411 (3400), 318 nm (22200 M^{-1} cm^{-1}); HR-ESI-MS: found 384.1220 ($[M + H]^+$, calcd for $C_{24}H_{17}NO_4^+$: 384.1230). **6a**: R_f = 0.26 (SiO_2; $CHCl_3$); m.p. 144 – 147 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.00 (s, 6 H), 5.79 (d, J = 10.0 Hz, 1 H), 6.17 (s, 1 H), 6.68 (quasi d, J = 9.0 Hz, 2 H), 7.50 (quasi d, J = 9.0 Hz, 2 H), 7.53 (d, J = 10.0 Hz, 1 H), 7.93 (dd, J = 5.7, 3.1 Hz, 2 H), 8.13 (dd, J = 5.7, 3.1 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 193.3 (2 x C=O) 159.9, 150.8, 147.5, 144.4, 136.2, 134.7, 126.9, 126.0, 125.1, 118.6, 117.6, 112.2, 103.0, 73.2, 40.4 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 480 (12500), 323 nm (14300 M^{-1} cm^{-1}); HR-ESI-MS: found 384.1227 ($[M + H]^+$, calcd for $C_{24}H_{17}NO_4^+$: 384.1230).

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Graphical Abstract



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Supporting Information

Homoconjugated and Spiro Push–Pull Systems: Cycloadditions of Naphto- and Anthra-diquinones with Electron-Rich Alkynes

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S1. Experimental Section

General Methods and Materials:

Materials: All reactions were carried out under argon. All solvents were of ACS reagent grade or better. Silica gel (40 μm) was purchased from SiliCycle Inc. All reagent grade materials were purchased from Alfa Aesar, Strem and Sigma-Aldrich and used without further purification Compounds **1**[1], **2b–d**[2] and **4**[1] were prepared according to the procedures described in literature.

NMR Spectroscopy: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz, proton-decoupled) spectra were acquired in $CDCl_3$ on a Bruker Avance III HD Spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to residual NMR $CDCl_3$ peaks. ($CDCl_3$: δ 7.26 ppm for ^{1}H, 77.16 for ^{13}C).

Mass Spectrometry: High-resolution mass spectra (HR-MS) were obtained at the MIT Department of Chemistry Instrumentation Facility with electrospray ionization (ESI).

Absorption and Emission Spectroscopy: Ultraviolet-visible absorption spectra were measured with an Agilent Cary 4000 UV/Vis spectrophotometer and corrected for background signal with a solvent-filled cuvette.

Additional Characterizations: Thermogravimetric analyses (TGA) were performed with a TGA Q50 apparatus (TA Instruments). Experiments were carried out under nitrogen. Samples were heated 20 °C/min from 30 °C to 800 °C.

Experimental Data:

Compound 3a

Naphthazarin **1** (100 mg, 0.532 mmol) was added under Ar to a solution of electron rich alkyne **2a** (77 mg, 0.532 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (FCC), (SiO_2, $CHCl_3$) to give homoconjugated chromophore **3a** (62 mg, 35%) as a dark-orange solid. R_f = 0.13 (SiO_2; $CHCl_3$); m.p. 215 – 218 °C ; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.99 (s, 6 H), 6.43 (s, 1 H), 6.65 (quasi d, J = 9.0 Hz, 2 H), 6.80 (s, 4 H), 7.63 ppm (quasi d, J = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 189.0, 187.6, 151.5, 150.7, 140.3, 139.7, 128.4, 123.7, 117.3, 111.6, 68.7, 64.6, 40.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 453 (2400), 323 nm (21800 M^{-1} cm^{-1}); HR-ESI-MS: found 334.1076 ($[M + H]^+$, calcd for $C_{20}H_{15}NO_4^+$: 334.1074).

Compound 3b

Naphthazarin **1** (100 mg, 0.532 mmol) was added under Ar to a solution of electron rich alkyne **2b** (182 mg, 0.532 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3

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hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **3b** (65 mg, 23%) as a dark-orange viscous foam. R_f = 0.16 (SiO_2; $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.88 (t, J = 6.8 Hz, 6 H) 1.20 – 1.35 (m, 20 H), 1.49 – 1.63 (m, 4 H), 3.26 (quasi t, J = 7.7 Hz, 4 H), 6.38 (s, 1 H), 6.57 (quasi d, J = 9.0 Hz, 2 H), 6.79 (s, 4 H), 7.58 ppm (quasi d, J = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 189.1, 187.7, 150.7, 149.4, 140.3, 139.6, 128.6, 122.8, 116.2, 111.0, 68.7, 64.6, 51.1, 31.9, 29.6, 29.4, 27.3, 27.2, 22.8, 14.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 465 (1400), 331 nm (13700 M^{-1} cm^{-1}); HR-ESI-MS: found 530.3271 ($[M + H]^+$, calcd for $C_{34}H_{43}NO_4^+$: 530.3265).

Compound 3c

Naphthazarin **1** (100 mg, 0.532 mmol) was added under Ar to a solution of electron rich alkyne **2c** (91 mg, 0.532 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **3c** (56 mg, 29%) as a dark-orange solid. R_f = 0.08 (SiO_2; $CHCl_3$); m.p. 210 – 213 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.98 – 2.04 (m, 4 H), 3.28 – 3.34 (m, 4 H), 6.40 (s, 1 H), 6.50 (quasi d, J = 8.9 Hz, 2 H), 6.80 (s, 4 H), 7.61 ppm (quasi d, J = 8.9 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 189.1, 187.7, 150.9, 149.1, 140.3, 139.7, 128.5, 122.9, 116.6, 111.4, 68.7, 64.6, 47.6, 25.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 462 (2600), 329 nm (25200 M^{-1} cm^{-1}); HR-ESI-MS: found 360.1227 ($[M + H]^+$, calcd for $C_{22}H_{17}NO_4^+$: 360.1230).

Compound 3d

Naphthazarin **1** (100 mg, 0.532 mmol) was added under Ar to a solution of electron rich alkyne **2d** (99 mg, 0.532 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **3d** (54 mg, 27%) as a dark-orange solid. R_f = 0.08 (SiO_2; $CHCl_3$); m.p. 220 – 223 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.58 – 1.70 (m, 6 H), 3.20 – 3.30 (m, 4 H), 6.46 (s, 1 H), 6.80 (s, 4 H), 6.84 (quasi d, J = 9.0 Hz, 2 H), 7.61 ppm (quasi d, J = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 188.8, 187.5, 152.7, 150.4, 140.4, 139.6, 128.3, 124.6, 118.9, 114.6, 68.7, 64.7, 49.2, 25.5, 24.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 431 (2400), 322 nm (21600 M^{-1} cm^{-1}); HR-ESI-MS: found 374.1372 ($[M + H]^+$, calcd for $C_{23}H_{19}NO_4^+$: 374.1387).

Compounds 5a and 6a

Quinizarin **4** (50 mg, 0.210 mmol) was added under Ar to a solution of electron rich alkyne **2a** (31 mg, 0.210 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **5a** (31mg, 39%) and **6a** (4 mg, 5%) as a dark-orange solids. **5a**: R_f = 0.13 (SiO_2; $CHCl_3$); m.p. 125 – 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.99 (s, 6 H), 6.53 (s, 1 H), 6.66 (quasi d, J = 8.9 Hz, 2 H), 6.83 (s, 2 H), 7.67 (quasi d, J = 8.9 Hz, 2 H), 7.73 – 7.80 (m, 2 H), 8.03 – 8.12 ppm (m, 2 H); ^{13}C NMR (100 MHz, CDCl3,

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298 K): δ = 189.9, 188.5, 188.4, 187.3, 151.4, 150.9, 140.7, 139.9, 135.04, 134.96, 134.7, 134.2, 128.41, 128.39, 128.1, 124.2, 117.7, 111.6, 69.5, 65.5, 40.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 411 (3400), 318 nm (22200 M^{-1} cm^{-1}); HR-ESI-MS: found 384.1220 ([M + H]$^+$, calcd for $C_{24}H_{17}NO_4^+$: 384.1230).

6a: R_f = 0.26 (SiO_2; $CHCl_3$); m.p. 144 – 147 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.00 (s, 6 H), 5.79 (d, J = 10.0 Hz, 1 H), 6.17 (s, 1 H), 6.68 (quasi d, J = 9.0 Hz, 2 H), 7.50 (quasi d, J = 9.0 Hz, 2 H), 7.53 (d, J = 10.0 Hz, 1 H), 7.93 (dd, J = 5.7, 3.1 Hz, 2 H), 8.13 (dd, J = 5.7, 3.1 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 193.3 (2 x C=O) 159.9, 150.8, 147.5, 144.4, 136.2, 134.7, 126.9, 126.0, 125.1, 118.6, 117.6, 112.2, 103.0, 73.2, 40.4 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 480 (12500), 323 nm (14300 M^{-1} cm^{-1}); HR-ESI-MS: found 384.1227 ([M + H]$^+$, calcd for $C_{24}H_{17}NO_4^+$: 384.1230).

Compounds 5b and 6b

Quinizarin **4** (50 mg, 0.210 mmol) was added under Ar to a solution of electron rich alkyne **2b** (72 mg, 0.210 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **5b** (32 mg, 26%) and **6b** (5 mg, 4%) as a dark-orange viscous foams. **5b**: R_f = 0.21 (SiO_2; $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.88 (quasi t, J = 6.8 Hz, 6 H), 1.20 – 1.35 (m, 20 H), 1.50 – 1.63 (m, 4 H), 3.26 (quasi t, J = 7.7 Hz, 4 H), 6.46 (s, 1 H), 6.57 (quasi d, J = 8.8 Hz, 2 H), 6.82 (s, 2 H), 7.62 (quasi d, J = 8.8 Hz, 2 H), 7.71 – 7.78 (m, 2 H), 8.02 – 8.11 ppm (m, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 190.0, 188.6, 188.5, 187.3, 150.9, 149.3, 140.7, 139.9, 135.0, 134.9, 134.6, 134.2, 128.5, 128.4, 128.0, 123.3, 116.5, 111.0, 69.4, 65.4, 51.1, 31.9, 29.6, 29.4, 27.3, 27.2, 22.8, 14.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 411 (5900), 328 nm (19000 M^{-1} cm^{-1}); HR-ESI-MS: found 580.3420 ([M + H]$^+$, calcd for $C_{38}H_{45}NO_4^+$: 580.3421).

6b: R_f = 0.45 (SiO_2; $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.88 (quasi t, J = 6.7 Hz, 6 H), 1.20 – 1.37 (m, 20 H), 1.52 – 1.64 (m, 4 H), 3.27 (quasi t, J = 7.8 Hz, 4 H), 5.78 (d, J = 10.0 Hz, 1 H), 6.13 (s, 1 H), 6.58 (quasi d, J = 8.6 Hz, 2 H), 7.45 (quasi d, J = 8.6 Hz, 2 H), 7.52 (d, J = 10.0 Hz, 1 H), 7.93 (dd, J = 5.6, 3.1 Hz, 2 H), 8.13 (dd, J = 5.6, 3.1 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl3, 298 K): δ = 193.3 (2 x C=O) 160.1, 148.7, 147.2, 144.4, 136.2, 134.8, 127.1, 126.2, 125.1, 118.3, 116.4, 111.5, 102.6, 73.2, 51.1, 32.0, 29.6, 29.4, 27.4, 27.3, 22.8, 14.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 498 (16800), 330 nm (18600 M^{-1} cm^{-1}); HR-ESI-MS: found 580.3419 ([M + H]$^+$, calcd for $C_{38}H_{45}NO_4^+$: 580.3421).

Compounds 5c and 6c

Quinizarin **4** (50 mg, 0.210 mmol) was added under Ar to a solution of electron rich alkyne **2c** (36 mg, 0.210 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **5c** (29 mg, 34%) and **6c** (3 mg, 4%) as a dark-orange solids. **5c**: R_f = 0.13 (SiO_2; $CHCl_3$); m.p. 127 – 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.96 – 2.04 (m, 4 H), 3.26 – 3.34 (m, 4 H), 6.49 (s, 1 H), 6.50 (quasi d, J = 8.8 Hz, 2 H), 6.83 (s, 2 H), 7.65 (quasi d, J = 8.8 Hz, 2 H), 7.71 – 7.82 (m, 2 H), 8.04 – 8.12 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 190.0, 188.54, 188.53, 187.4, 151.1, 149.0, 140.7, 139.9,

135.0, 134.9, 134.7, 134.3, 128.5, 128.4, 128.1, 123.5, 117.0, 111.4, 69.5, 65.5, 47.6, 25.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 427 (3750), 327 nm (21000 M^{-1} cm^{-1}); HR-ESI-MS: found 410.1392 ($[M + H]^+$, calcd for $C_{26}H_{19}NO_4^+$: 410.1387).

6c: R_f = 0.24 (SiO_2; $CHCl_3$); m.p. 142 – 145 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.98 – 2.04 ppm (m, 4 H), 3.28 – 3.35 ppm (m, 4 H), 5.78 (d, J = 10.0 Hz, 1 H), 6.15 (s, 1 H), 6.52 (quasi d, J = 8.9 Hz, 2 H), 7.49 (quasi d, J = 8.9 Hz, 2 H), 7.52 (d, J = 10.0 Hz, 1 H), 7.93 (dd, J = 5.7, 3.1 Hz, 2 H), 8.13 (dd, J = 5.7, 3.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 193.3 (2 x C=O) 160.2, 151.3,148.3, 144.4, 136.2, 134.8, 127.6, 126.1, 125.1, 118.3, 116.7, 111.8, 102.7, 70.5, 47.7, 25.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 498 (16800), 328 nm (14350 M^{-1} cm^{-1}); HR-ESI-MS: found 410.1386 ($[M + H]^+$, calcd for $C_{26}H_{19}NO_4^+$: 410.1387).

Compounds 5d

Quinizarin **4** (50 mg, 0.210 mmol) was added under Ar to a solution of electron rich alkyne **2d** (39 mg, 0.210 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 25 °C for 3 hours and the solvent removed under reduced pressure. The residue was purified by FCC (SiO_2, $CHCl_3$) to give homoconjugated chromophore **5d** (30 mg, 34%). **5d**: R_f = 0.11 (SiO_2; $CHCl_3$); m.p. 115 – 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.54 – 1.71 (m, 6 H), 3.25 (t, J = 5.0 Hz, 4 H), 6.56 (s, 1 H), 6.83 (s, 2 H), 6.84 (quasi d, J = 8.4 Hz, 2 H), 7.66 (quasi d, J = 8.4 Hz, 2 H), 7.73 – 7.83 (m, 2 H), 8.02 – 8.14 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 189.7, 188.4, 188.3, 187.2, 152.7, 150.7, 140.8, 140.0, 135.1, 135.0, 134.7, 134.2, 128.5, 128.4, 128.1, 125.1, 119.3, 114.7, 69.5, 65.6, 49.2, 25.6, 24.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 408 (3300), 318 nm (19300 M^{-1} cm^{-1}); HR-ESI-MS: found 424.1553 ($[M + H]^+$, calcd for $C_{27}H_{21}NO_4^+$: 424.1543).

The R_f that was thought to correspond to compound **6d** was 0.21 (SiO_2; $CHCl_3$). However, isolation and characterization could not be achieved.

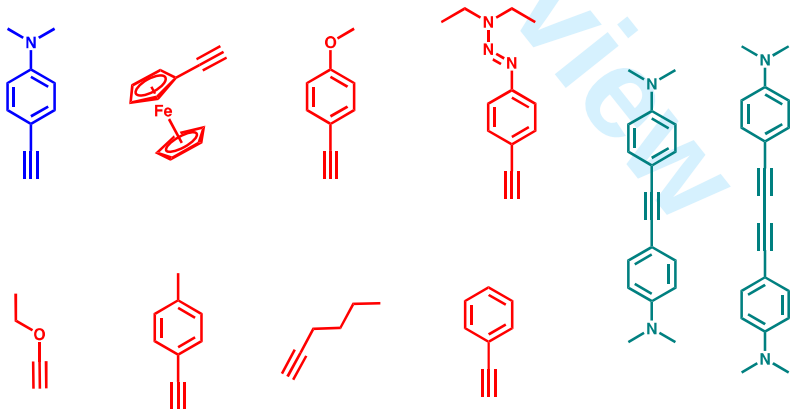


Figure S1. Alkynes screened for [2+2] cycloadditions. Compound with the blue color undergo [2+2] cycloadditions. Compounds with the red color show no reaction with electron-poor diquinones. Compounds with the green color show no reactivity towards [2+2] cycloadditions but they aromatize electron-poor diquinones through electron donation.[1]

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S2. X-ray analysis

The supplementary crystallographic data for this paper can be found using the following deposition numbers: CCDC 1525643 (**3a**), 1525645 (**5a**), and 1525644 (**6a**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk), or via www.ccdc.cam.ac.uk/data_request/cif.

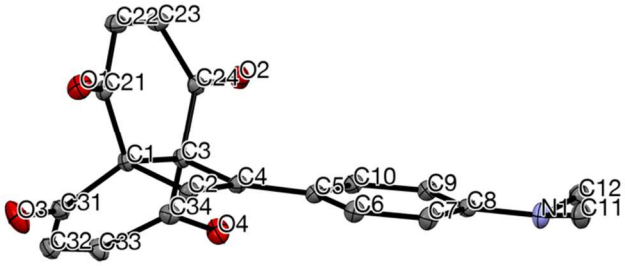


Figure S2. ORTEP plot of **3a**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters are drawn at 50% probability level. Selected bond length (Å) and torsional angles (°): C12–N1 1.4552(13), N1–C8 1.3822(13), C8–C9 1.4112(13), C9–C10 1.3910(14), C10–C5 1.4039(13), C5–C6 1.4085(13), C6–C7 1.3877(14), C7–C8 1.4185(14), C5–C4 1.4571(14), C4–C2 1.3515(13), C2–C1 1.5275(13), C1–C3 1.5795(13), C3–C4 1.5505(13), C3–C24 1.5317(13), C24–O2 1.2187(12), C24–C23 1.4783(14), C23–C22 1.3387(14), C22–C21 1.4695(14), C21–O1 1.2203(12), C21–C1 1.5278(13), C21-C1-C31 109.55(8), C2-C4-C5-C6 -4.2(2).

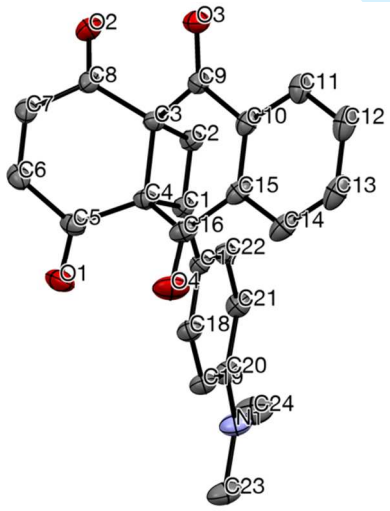


Figure S3. ORTEP plot of **5a**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters at are drawn at 50% probability level. Selected bond length (Å) and torsional angles (°): C24–N1 1.4399(17), N1–C20 1.3753(15), C20–C21 1.4146(16), C21–C22 1.3833(15), C22–C17 1.4033(14), C17–C18 1.4004(14), C18–C19 1.3869(15), C19–C20 1.4126(16), C17–C1 1.4548(14), C1–C2 1.3445(14), C2–C3 1.5251(14), C3–C4 1.5746(14), C4–C1 1.5449(14), C3–C8 1.5237(14), C8–O2 1.2157(14), C8–C7 1.4723(16), C7–C6 1.3382(16), C6–C5 1.4700(16), C5–O1 1.2118(14), C5–C4 1.5200(15), C3–C9 1.5290(15), C9–O3 1.2130(13), C9–C10 1.4866(15), C10–C15 1.4014(16), C15–C16 1.4836(17), C16–O4 1.2155(14), C16–C4 1.5310(15), C10–C11 1.3975(16), C11–C12 1.3884(17), C12–C13 1.390(2), C13–C14 1.383(2), C14–C15 1.4025(15), C5-C4-C16 110.42(9), C18-C17-C1-C4 -8.1(2).

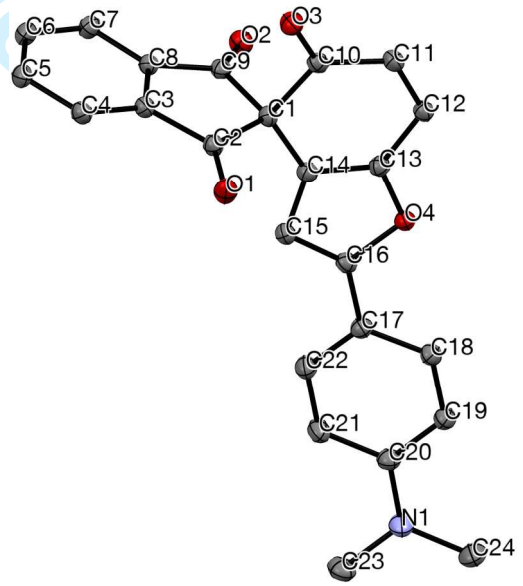


Figure S4. ORTEP plot of **6a**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters are drawn at 50% probability level. Selected bond length (Å) and torsional angles (°): C24–N1 1.4483(17), N1–C20 1.3786(15), C20–C21 1.4142(17), C21–C22 1.3812(17), C22–C17 1.3988(17), C17–C18 1.4005(16), C18–C19 1.3896(16), C19–C20 1.4075(17), C17–C16 1.4525(15), C16–C15 1.3788(16), C15–C14 1.4240(16), C14–C13 1.3651(16), C13–O4 1.3703(13), O4–C16 1.3802(14), C13–C12 1.4229(16), C12–C11 1.3565(15), C11–C10 1.4585(16), C10–O3 1.2250(14), C10–C1 1.5553(16), C1–C14 1.4906(15), C14–C13 1.3651(16), C1–C9 1.5634(15), C9–O2 1.2070(14), C9–C8 1.4791(16), C8–C3 1.3932(15), C3–C2 1.4811(15), C2–O1 1.2086(14), C2–C1 1.5469(16), C8–C7 1.3938(15), C7–C6 1.3904(17), C6–C5 1.4029(17), C5–C4 1.3934(16), C4–C3 1.3916(16), C9-C1-C10 105.33(8), C22-C17-C16-C15 16.7(2).

Additional Characterization:

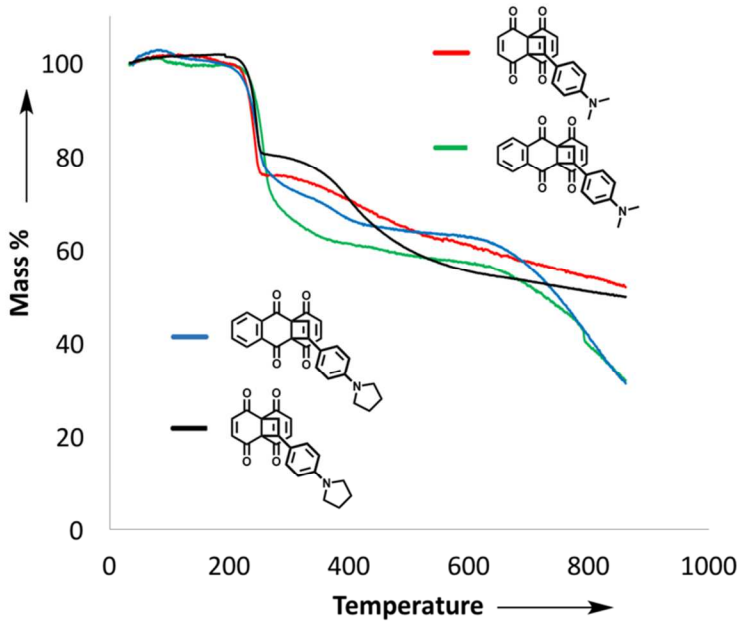


Figure S5. Thermal stability of a selection of the synthesized compounds as demonstrated by thermogravimetric analysis (TGA) of compounds **3a** (red line), **5a** (green line) **3c** (black line), and **5c** (blue line).

In Review

S3. UV/Vis Spectra

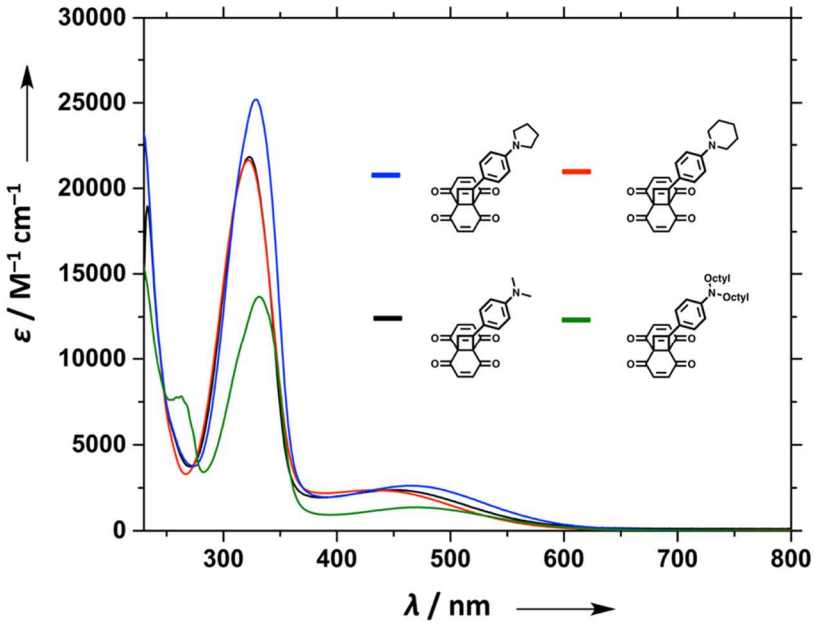


Figure S6. UV/Vis spectra of compounds **3a** (black line), **3b** (green line), **3c** (blue line), and **3d** (red line) in CH_2Cl_2 at 298 K.

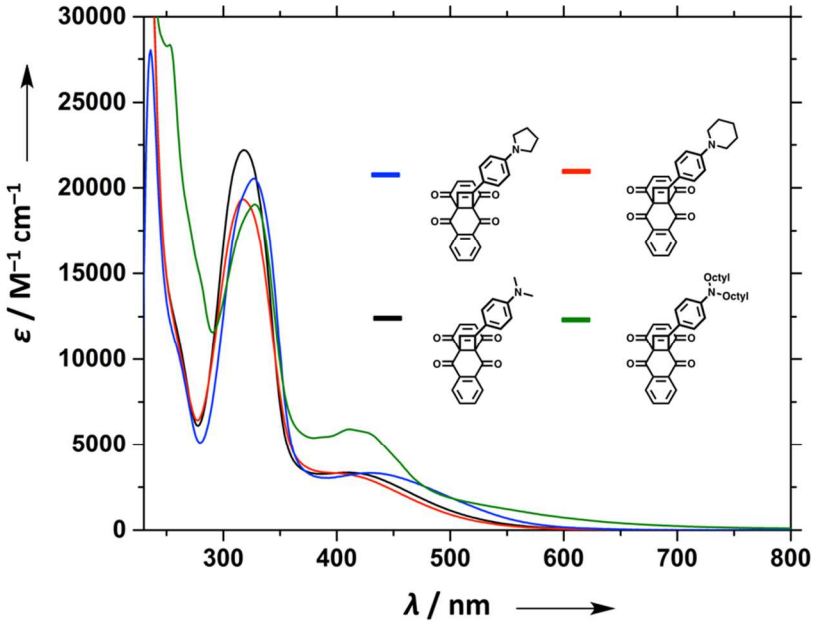


Figure S7. UV/Vis spectra of compounds **5a** (black line), **5b** (green line), **5c** (blue line), and **5d** (red line) in CH_2Cl_2 at 298 K.

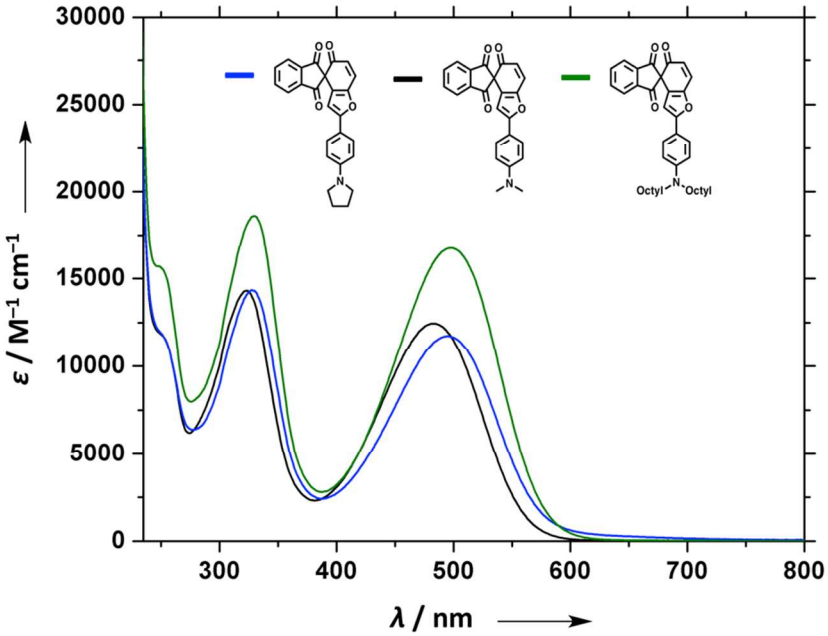


Figure S8. UV/Vis spectra of compounds **5a** (black line), **5b** (green line), and **5c** (blue line) in CH_2Cl_2 at 298 K.

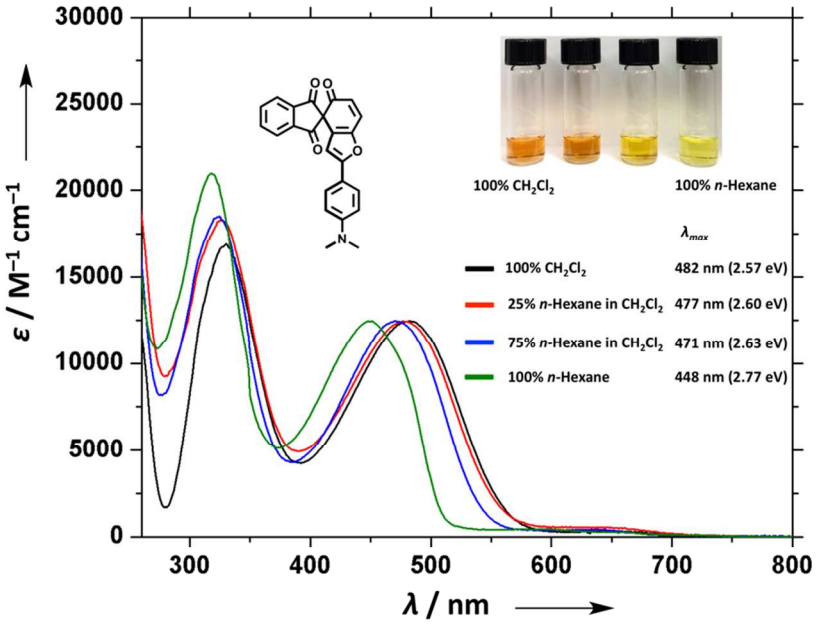


Figure S9. UV/Vis spectra of chromophore **6a** in CH_2Cl_2/*n*-hexane mixtures at 298 K.

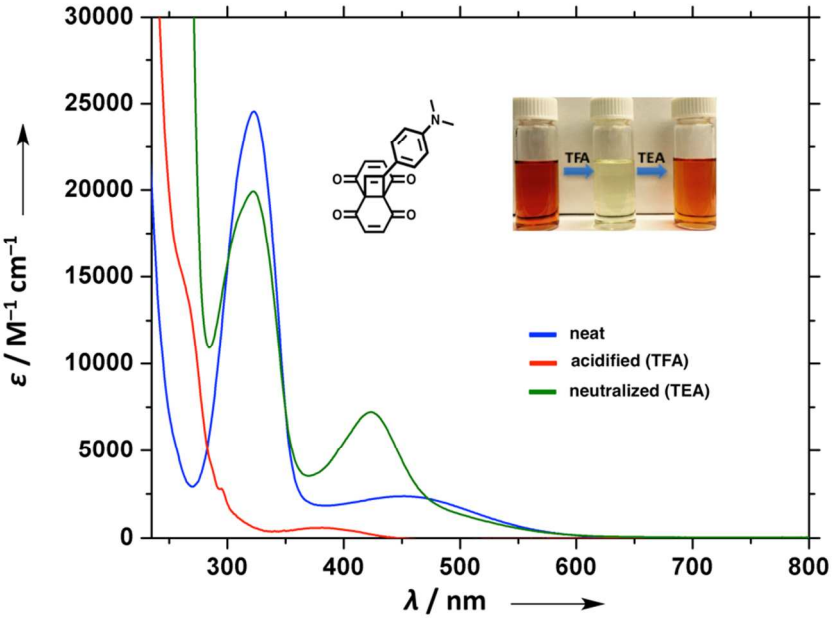


Figure S10. UV/Vis spectra of compounds **3a** in CH_2Cl_2 at 298 K recorded neat, after acidification with TFA, and after neutralization with TEA.

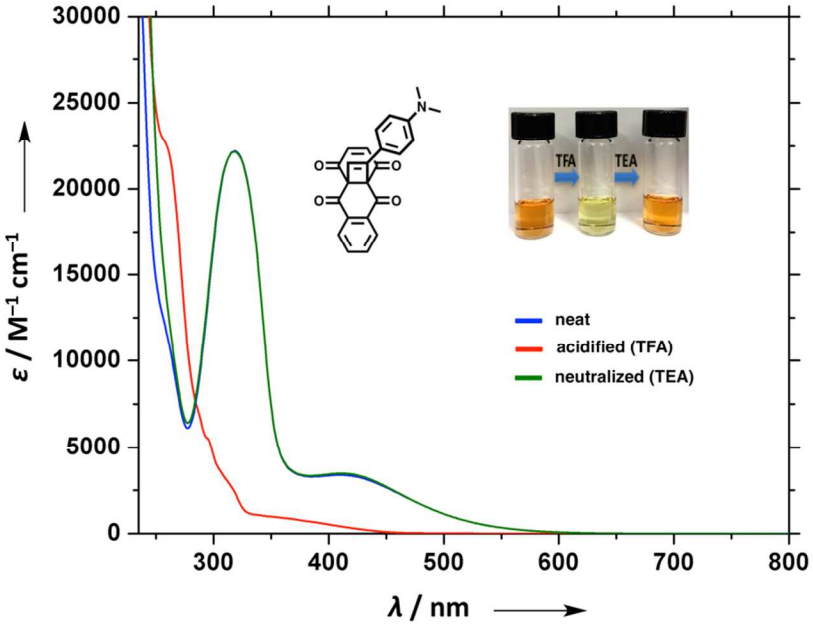


Figure S11. UV/Vis spectra of compounds **5a** in CH_2Cl_2 at 298 K recorded neat, after acidification with TFA, and after neutralization with TEA.

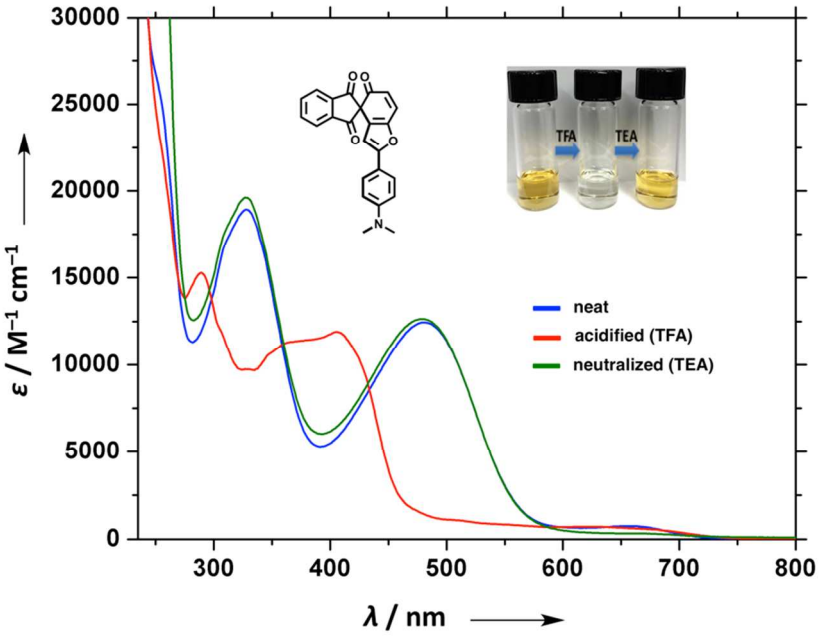


Figure S12. UV/Vis spectra of compounds **6a** in CH_2Cl_2 at 298 K recorded neat, after acidification with TFA, and after neutralization with TEA.

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S4. Theoretical Calculations

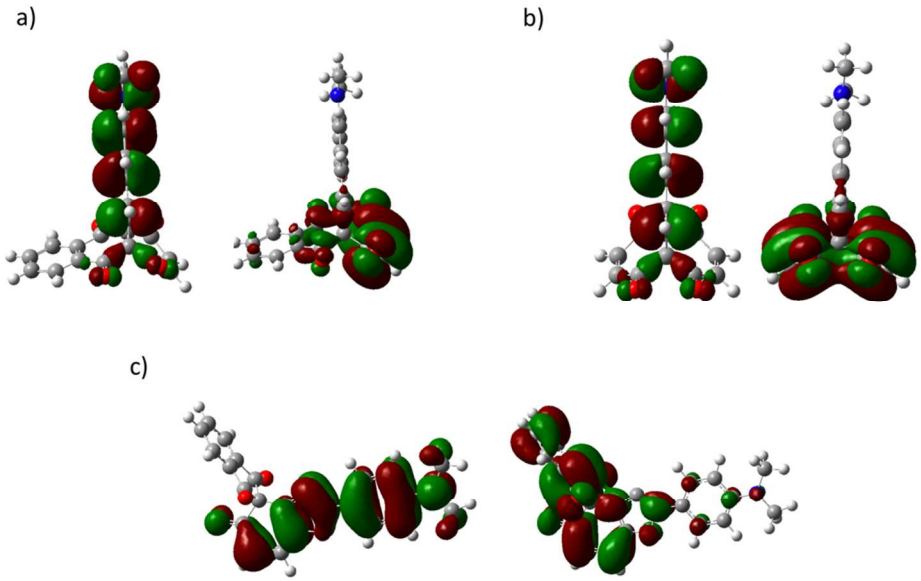
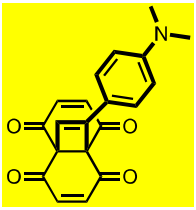


Figure S13. Molecular orbital plots of (a) **5a**, (b) **3a**, and (c) **6a** calculated by B3LYP/6-31G(d). The plots on the left represent the HOMOs, and the plots on the right represents LUMOs.

Calculated Optical and Electronic Properties of 3a, 5a, and 6a

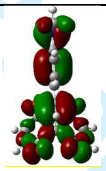
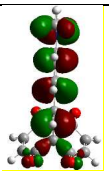
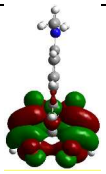
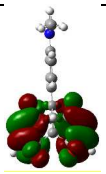
On the optimized molecular structures of **3a**, **5a**, and **6a** at the B3LYP/6-31G(d) level of theory with the CPCM solvation model in CH_2Cl_2, the vertical optical transitions were calculated by time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G(d) level of theory, again with the CPCM solvation model in CH_2Cl_2 using the software package Gaussian 03.

Table S1. Depiction of calculated HOMOs and LUMOs over optimized groundstate geometries, transition energies (*E*), and oscillator strengths (*f*) for **3a**.



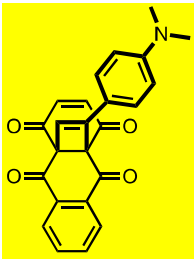
Exptl.: λ = 453 nm (in CH_2Cl_2)

Excited state	Δ*E* (eV)	*λ* (nm)	*f*	assignments
1	1.84	674	0.0245	H➔L+1
2	3.89	319	0.5601	H➔L+3, H–6➔L

Orbital		*E* (eV)
HOMO–1		–6.60
HOMO		–5.10
LUMO		–2.85
LUMO+1		–2.65

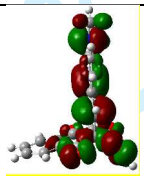
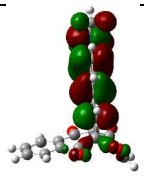
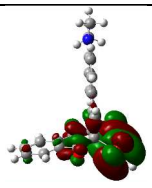
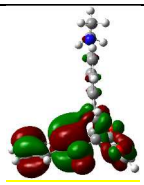
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Table S2. Depiction of calculated HOMOs and LUMOs over optimized groundstate geometries, transition energies (*E*), and oscillator strengths (*f*) for **5a**.



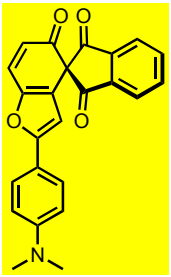
Exptl.: λ = 411 nm (in CH_2Cl_2)

Excited state	Δ*E* (eV)	λ (nm)	*f*	assignments
1	2.13	581	0.0527	H➔L+1
2	3.88	320	0.5036	H➔L+3, H➔L+4

Orbital		*E* (eV)
HOMO–1		–6.69
HOMO		–5.11
LUMO		–2.64
LUMO+1		–2.47

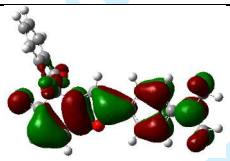
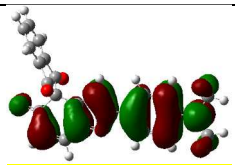
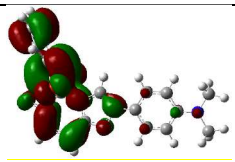
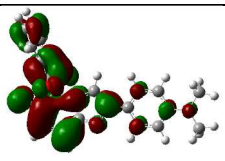
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Table S3. Depiction of calculated HOMOs and LUMOs over optimized groundstate geometries, transition energies (*E*), and oscillator strengths (*f*) for **6a**.



Exptl.: λ = 480 nm (in CH_2Cl_2)

Excited state	Δ*E* (eV)	*λ* (nm)	*f*	assignments
1	2.42	514	0.6149	H➔L, H➔L+1
2	3.97	312	0.6074	H➔L+3, H–4➔L+1

Orbital		*E* (eV)
HOMO–1		–6.18
HOMO		–4.94
LUMO		–2.35
LUMO+1		–2.21

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Cartesian Coordinates and Structural Parameters of the Push–Pull Chromophores

DFT calculations were performed with the Gaussian 03 program using the B3LYP functional with basis set 6-31G**.[1] Cartesian coordinates of the selected compounds **3a**, **5a** and **6a** are listed below: Atom type, (x,y,z) coordinates

Compound 3a

C	1.46183300	0.56192900	0.00420900
C	2.46855800	-0.66590700	0.00042200
C	1.22194200	-1.53523100	-0.01193100
H	1.15025800	-2.61669200	-0.02042700
C	0.33760900	-0.51346200	-0.00950400
C	-1.11133600	-0.41091100	-0.01726700
C	-1.79129500	0.82108700	-0.01661500
C	-1.89373200	-1.58309200	-0.02224600
C	-3.17775000	0.87777800	-0.02487900
H	-1.22491600	1.74442200	-0.00624400
C	-3.27706600	-1.53808600	-0.03049500
H	-1.40489500	-2.55417600	-0.01609100
C	-3.96471800	-0.29775200	-0.04022000
H	-3.65070300	1.85234000	-0.01825600
H	-3.82841800	-2.47069800	-0.02812400
C	3.34101300	-0.86906800	-1.24899300
O	3.97097500	-1.89524700	-1.42527300
C	1.47814900	1.47080600	-1.23815200
O	0.64938900	2.34791600	-1.40543700
C	3.33075200	-0.88412800	1.25394200
O	3.95076000	-1.91666800	1.42821800
C	1.46657700	1.45174500	1.25998500
O	0.62741500	2.31629400	1.44004900
C	2.53196100	1.25746700	-2.25681400
H	2.53651100	1.99565600	-3.05492300
C	3.36996600	0.20851000	-2.26415800
H	4.08340600	0.05509800	-3.07015400
C	2.52361000	1.23608100	2.27504500
H	2.52682700	1.96837100	3.07858700
C	3.36306100	0.18815400	2.27473700
H	4.07669400	0.02950500	3.07955500
N	-5.34488200	-0.24274800	-0.06797400
C	-6.12304500	-1.46483300	0.04100800
H	-7.18454100	-1.22018300	-0.02492600
H	-5.89023900	-2.15962800	-0.77602300
H	-5.95124200	-1.99028500	0.99295800
C	-6.01974200	1.03949800	0.04432200
H	-5.80076200	1.54751800	0.99573900
H	-5.73215800	1.71311000	-0.77275400
H	-7.09804100	0.88301200	-0.01794200

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Compound 5a

C	0.97133600	-0.70340000	0.57752600
C	1.94158200	-1.08609100	-0.61865300
C	0.70410200	-0.99002200	-1.49668300
H	0.61266300	-1.15187800	-2.56463100
C	-0.14899100	-0.66590100	-0.49980400
C	-1.56622800	-0.35809100	-0.41923800
C	-2.22002900	-0.08773000	0.79707200
C	-2.34349300	-0.32510100	-1.59418100
C	-3.57710800	0.19978200	0.83672700
H	-1.65996600	-0.12142800	1.72400100
C	-3.69782100	-0.04068100	-1.56626500
H	-1.87410100	-0.52937200	-2.55331100
C	-4.35805300	0.23785300	-0.34236300
H	-4.03270500	0.39061800	1.80088600
H	-4.24749200	-0.03393600	-2.49990800
C	3.01069300	-0.06074900	-1.04237200
O	3.85745000	-0.35112500	-1.86777300
C	1.16954800	0.67553000	1.24032400
O	0.55271400	0.97555200	2.24736100
C	2.56206400	-2.48568600	-0.58658300
O	2.96033300	-3.03302300	-1.59747600
C	0.81431400	-1.76925200	1.66956100
O	-0.11210300	-1.76162600	2.46043100
C	2.08212500	1.65829200	0.58805600
C	2.93673400	1.31769700	-0.47578400
C	1.84252100	-2.83543900	1.75479500
H	1.82113000	-3.41391600	2.67511400
C	2.64146800	-3.16760600	0.72691800
H	3.30084500	-4.03121000	0.76767300
N	-5.70659900	0.53756000	-0.30690000
C	-6.50572900	0.42584200	-1.51534300
H	-7.53718900	0.70121600	-1.28895500
H	-6.14372400	1.10550100	-2.29745800
H	-6.50596000	-0.59532100	-1.92617200
C	-6.37733700	0.69643500	0.97262000
H	-6.34115300	-0.21870000	1.58303400
H	-5.92995000	1.51052500	1.55643300
H	-7.42472100	0.94927000	0.79870000
C	2.08456500	2.97016500	1.08530800
H	1.42136200	3.20629500	1.91042200
C	2.92092200	3.93190000	0.52978700
H	2.91452000	4.94580000	0.92005700
C	3.78086600	2.29336200	-1.02517800
H	4.43650300	2.00283600	-1.83906600
C	3.77207500	3.59230400	-0.52900200
H	4.42821900	4.34207100	-0.96233400

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Compound 6a

C	-5.53226400	-2.84465900	0.71141100
C	-4.70799900	-1.97761600	1.42723400
C	-3.89739700	-1.10370200	0.70228100
C	-3.90295200	-1.10184400	-0.69454100
C	-4.71929600	-1.97386100	-1.41528800
C	-5.53785800	-2.84279500	-0.69520300
H	-6.18067700	-3.53493100	1.24397500
H	-4.68970700	-1.96991400	2.51259300
H	-4.70963600	-1.96332900	-2.50073300
H	-6.19050000	-3.53167000	-1.22439600
C	-2.92576200	-0.11070400	1.22343300
C	-2.93540600	-0.10743900	-1.22070400
C	-2.37927600	0.69782000	0.00010400
O	-2.60290600	0.05230500	2.37820200
O	-2.62155800	0.05838000	-2.37755700
C	-3.13886900	2.07485900	0.00583300
C	-0.89616100	0.83429600	-0.00483000
C	-0.29631000	2.07652300	-0.00011300
C	-2.35650800	3.30836800	0.01011600
H	-2.93154000	4.22798300	0.01511900
C	-0.99360500	3.31335900	0.00724600
O	-4.36465500	2.06447300	0.00715300
H	-0.42848900	4.24182300	0.01010000
C	0.18536700	-0.06227500	-0.01309000
C	1.37414000	0.62596500	-0.01275600
O	1.06837300	1.97354100	-0.00473900
C	2.76459100	0.23392900	-0.01874100
C	3.11832600	-1.12745400	-0.03259400
C	3.80545900	1.17854300	-0.00664800
C	4.44321800	-1.53089100	-0.03729000
H	2.33530400	-1.88144900	-0.03726300
C	5.13536600	0.78657200	-0.01086100
H	3.56480500	2.23670900	0.00954400
C	5.49673000	-0.58267200	-0.03334100
H	4.66175000	-2.59181400	-0.04354700
H	5.90022800	1.55360000	0.00462100
N	6.82057400	-0.97812700	-0.05472700
C	7.15781300	-2.38845400	0.03539500
H	8.24224900	-2.50075000	-0.01089800
H	6.80592500	-2.84497000	0.97301900
H	6.72771300	-2.95589800	-0.80004700
C	7.87463900	0.01475200	0.06295300
H	8.84389400	-0.48349400	0.00803800
H	7.82815000	0.74480900	-0.75539600
H	7.82657800	0.56687300	1.01386000

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S5. ^{1}H and ^{13}C NMR spectra

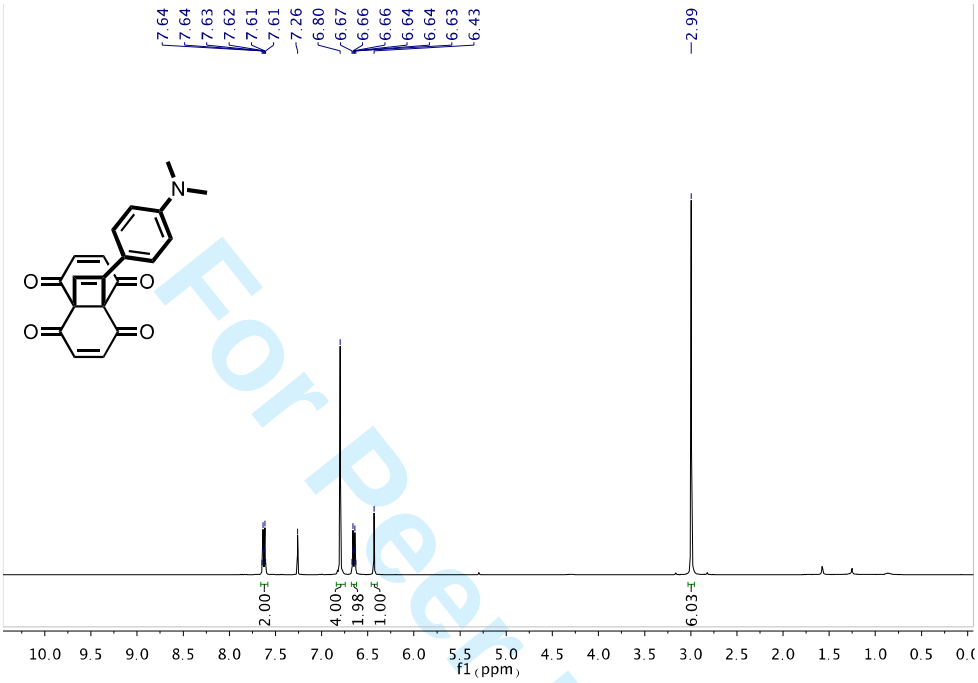


Figure S14. ^{1}H NMR spectrum of **3a** in $CDCl_3$ solution (400 MHz).

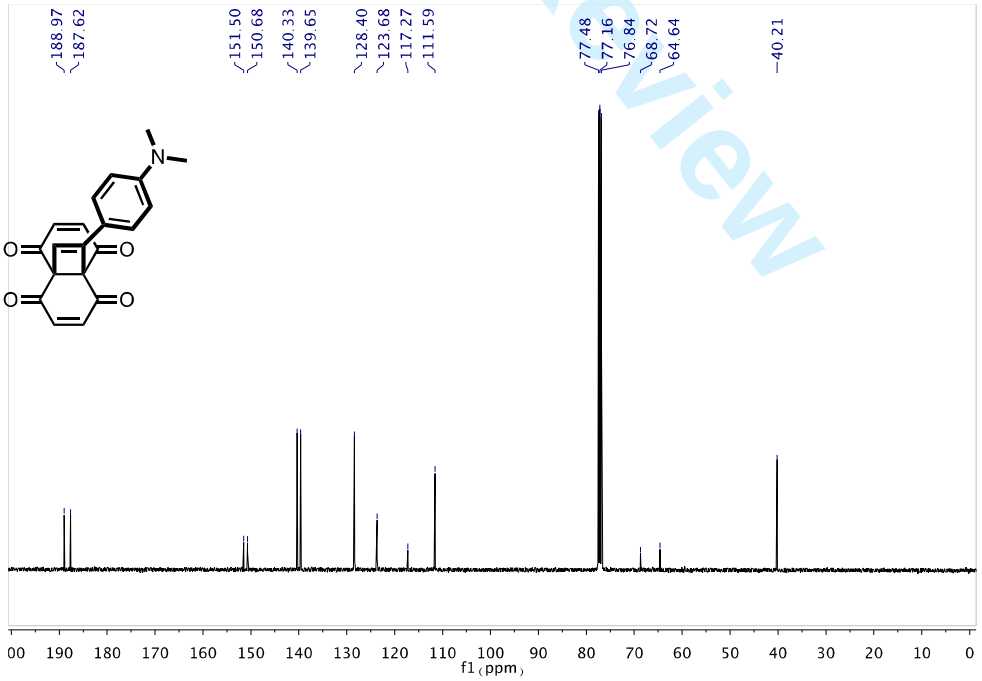


Figure S15. ^{13}C NMR spectrum of **3a** in $CDCl_3$ solution (100 MHz).

For Peer Review

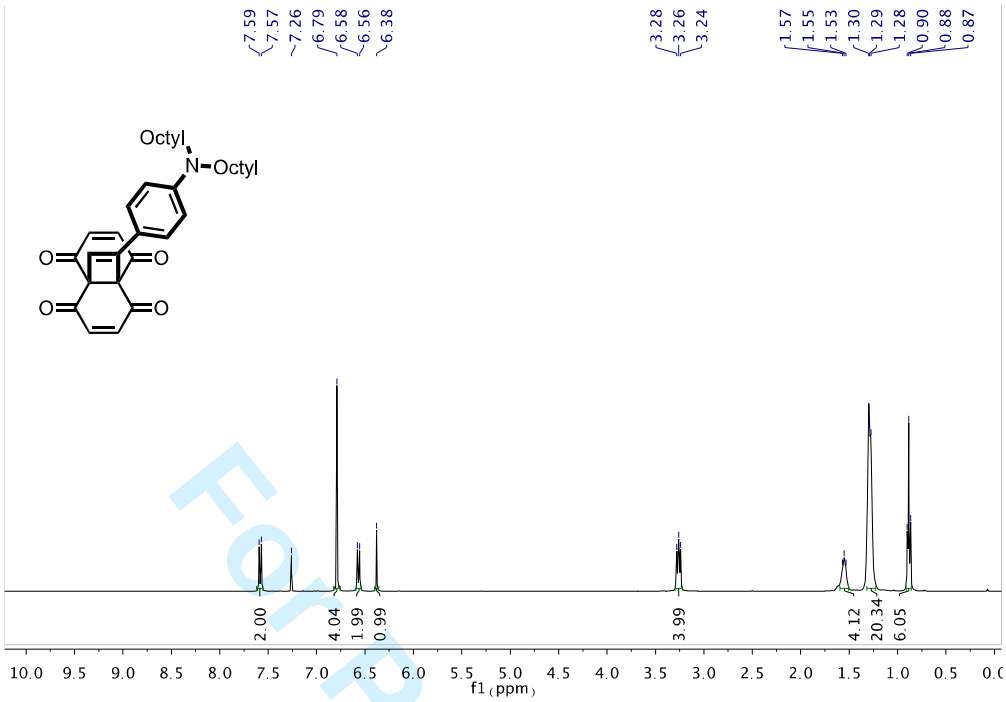


Figure S16. ^{1}H NMR spectrum of **3b** in $CDCl_3$ solution (400 MHz).

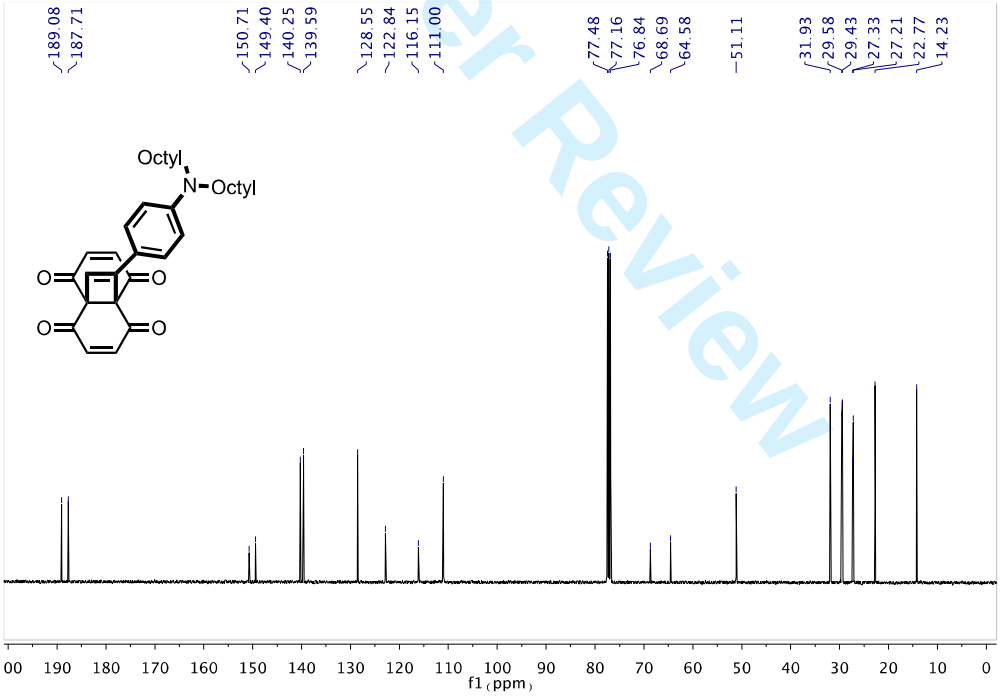


Figure S17. ^{13}C NMR spectrum of **3b** in $CDCl_3$ solution (100 MHz).

For Peer Review

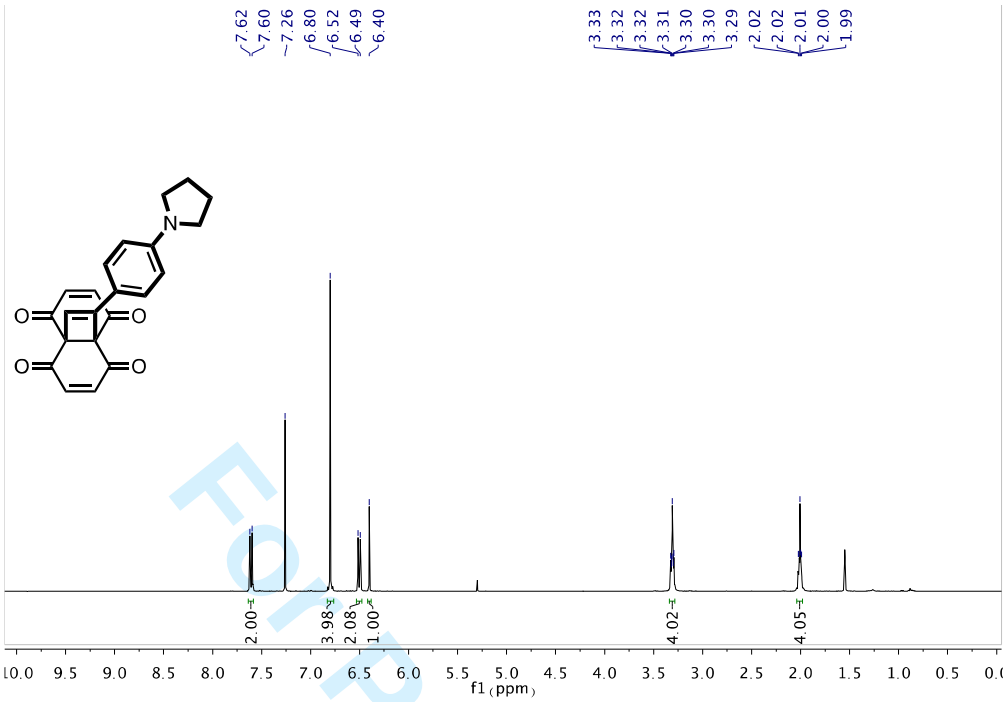


Figure S18. ^{1}H NMR spectrum of **3c** in $CDCl_3$ solution (400 MHz).

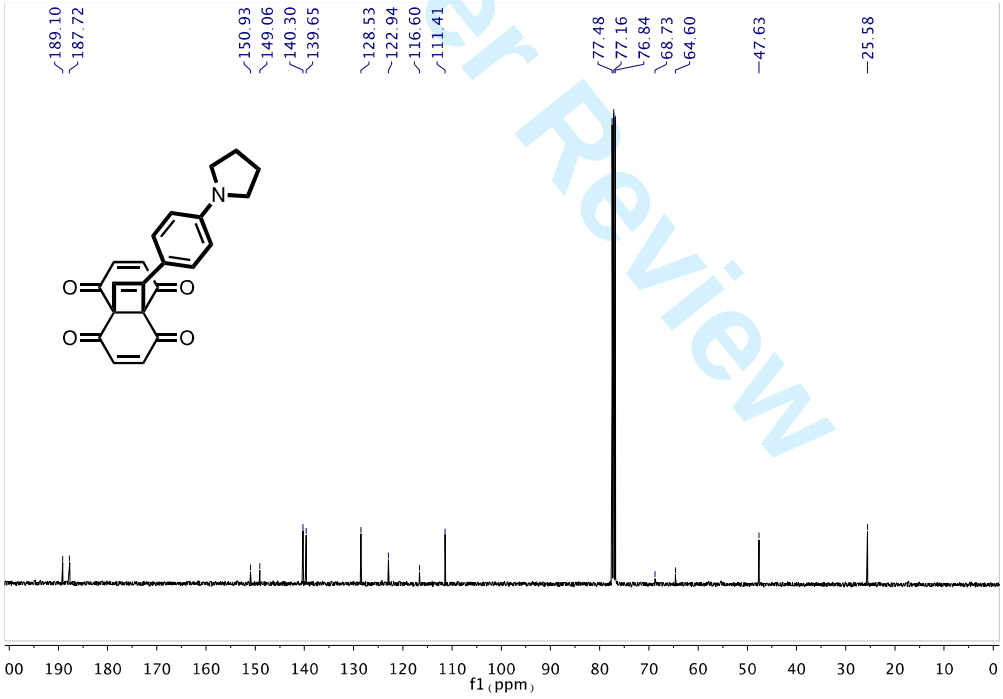


Figure S19. ^{13}C NMR spectrum of **3c** in $CDCl_3$ solution (100 MHz).

For Peer Review

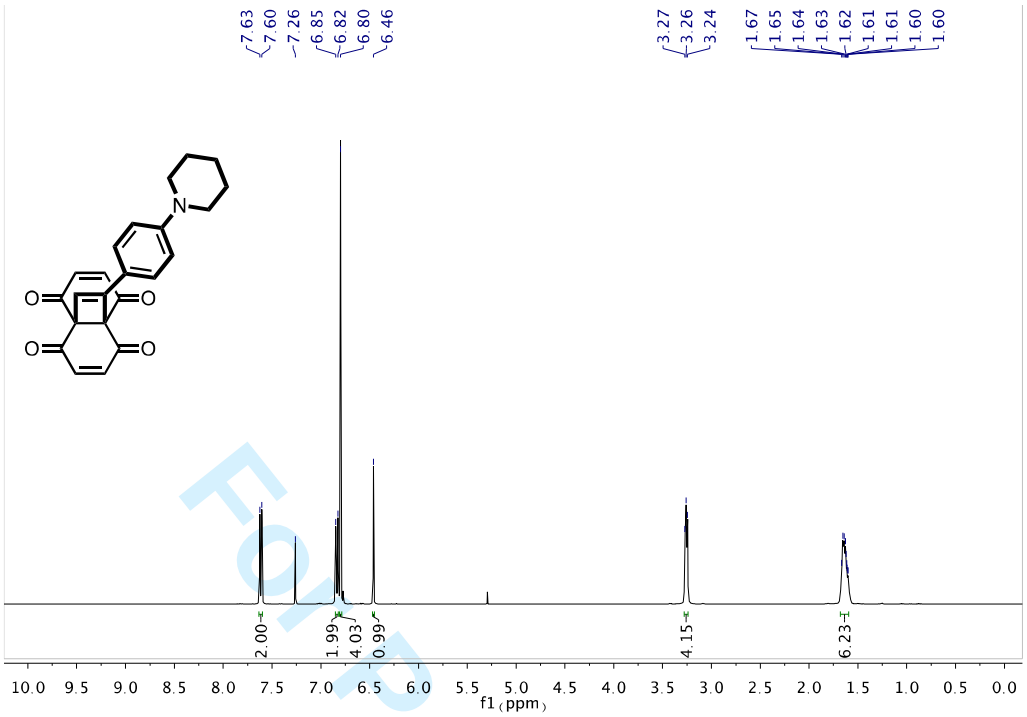


Figure S20. ^{1}H NMR spectrum of **3d** in $CDCl_3$ solution (400 MHz).

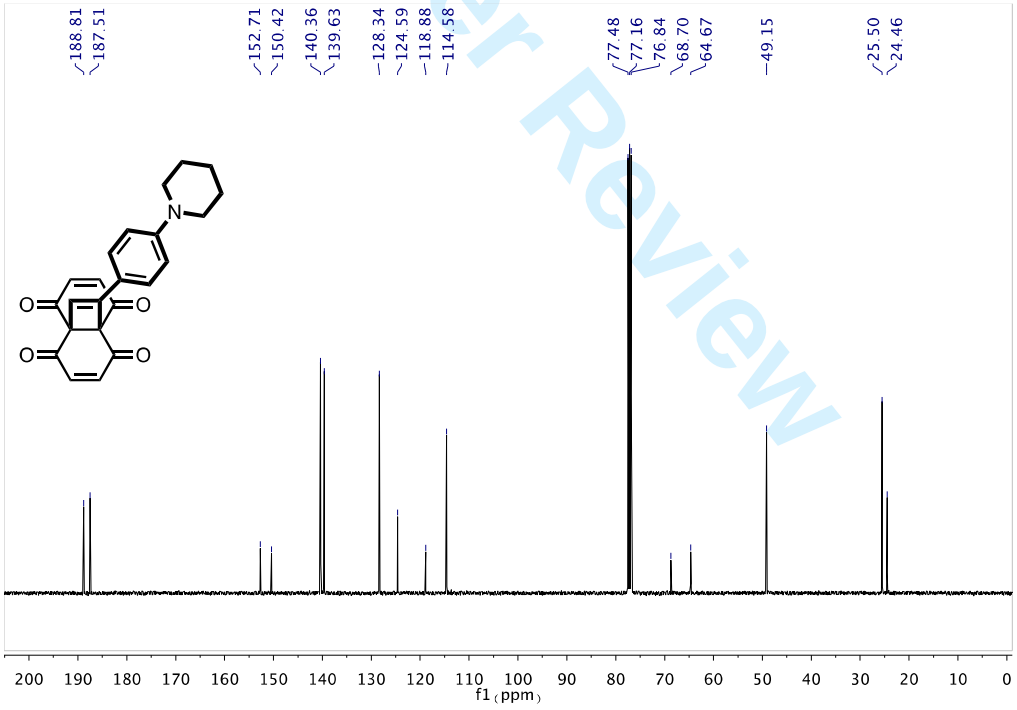


Figure S21. ^{13}C NMR spectrum of **3d** in $CDCl_3$ solution (100 MHz).

For Peer Review

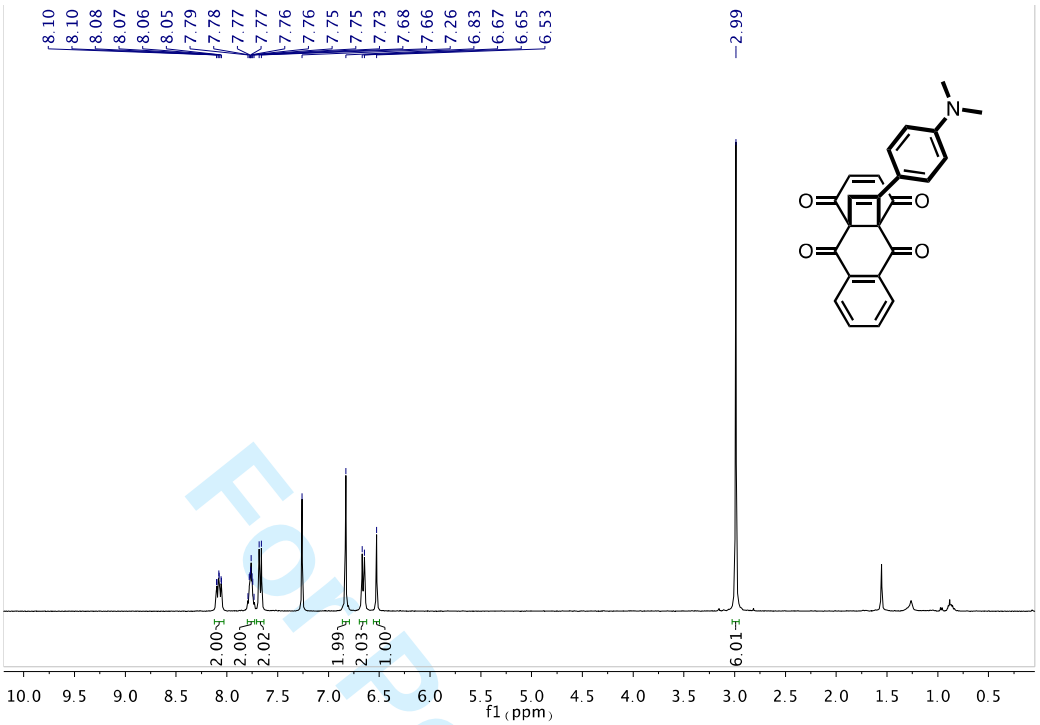


Figure S22. ^{1}H NMR spectrum of **5a** in $CDCl_3$ solution (400 MHz).

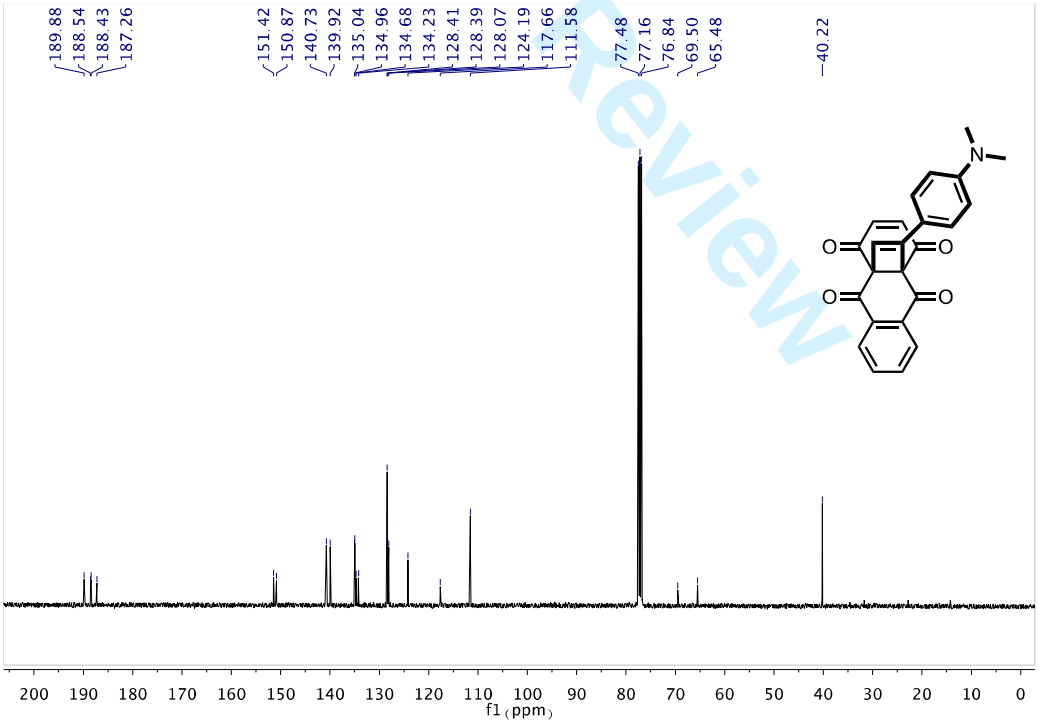


Figure S23. ^{13}C NMR spectrum of **5a** in $CDCl_3$ solution (100 MHz).

For Peer Review

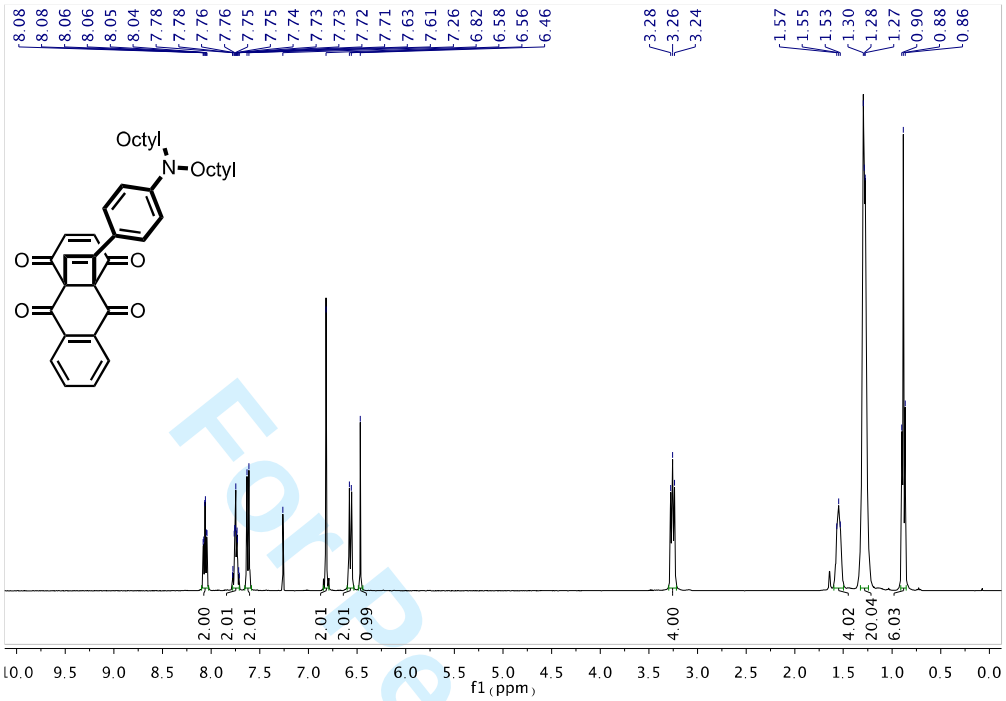


Figure S24. ^{1}H NMR spectrum of **5b** in $CDCl_3$ solution (400 MHz).

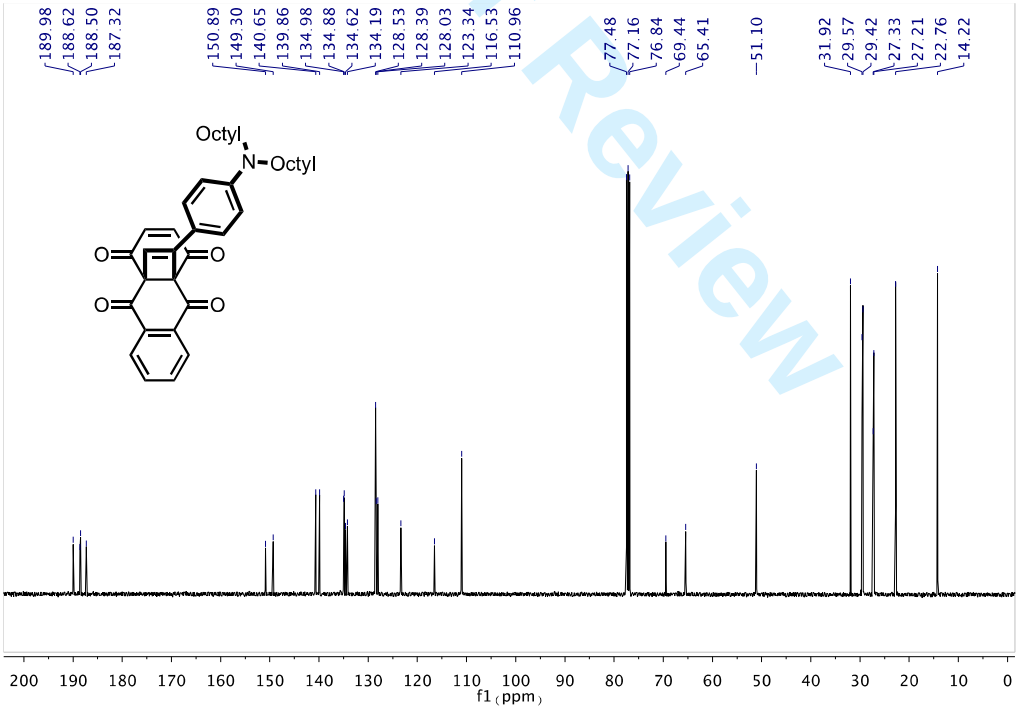


Figure S25. ^{13}C NMR spectrum of **5b** in $CDCl_3$ solution (100 MHz).

For Peer Review

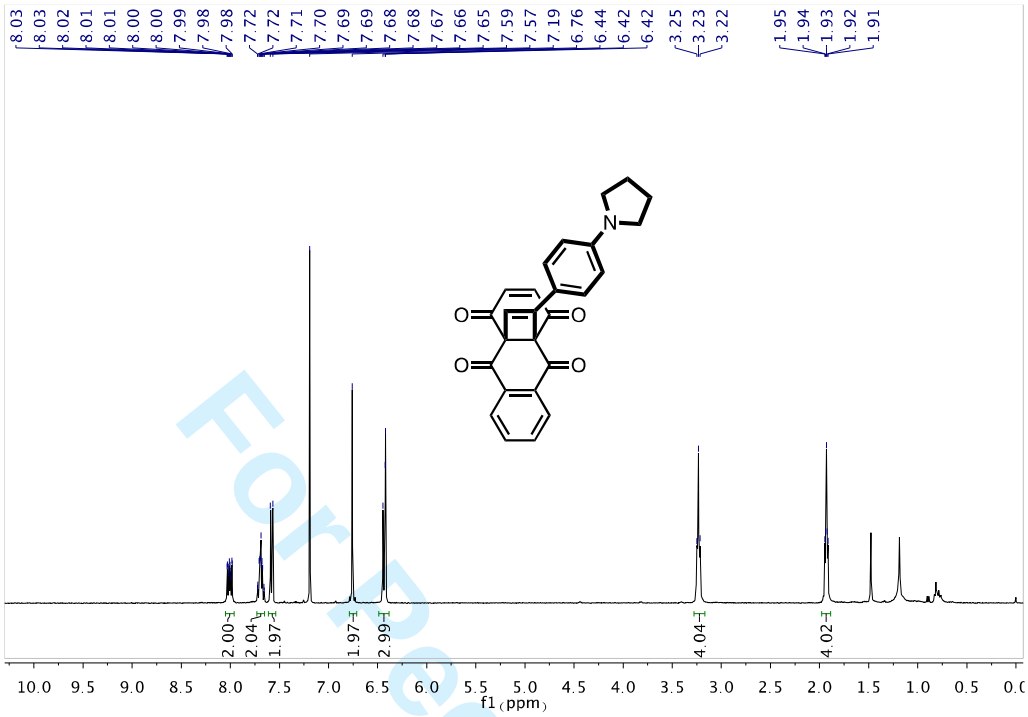


Figure S26. ^{1}H NMR spectrum of **5c** in $CDCl_3$ solution (400 MHz).

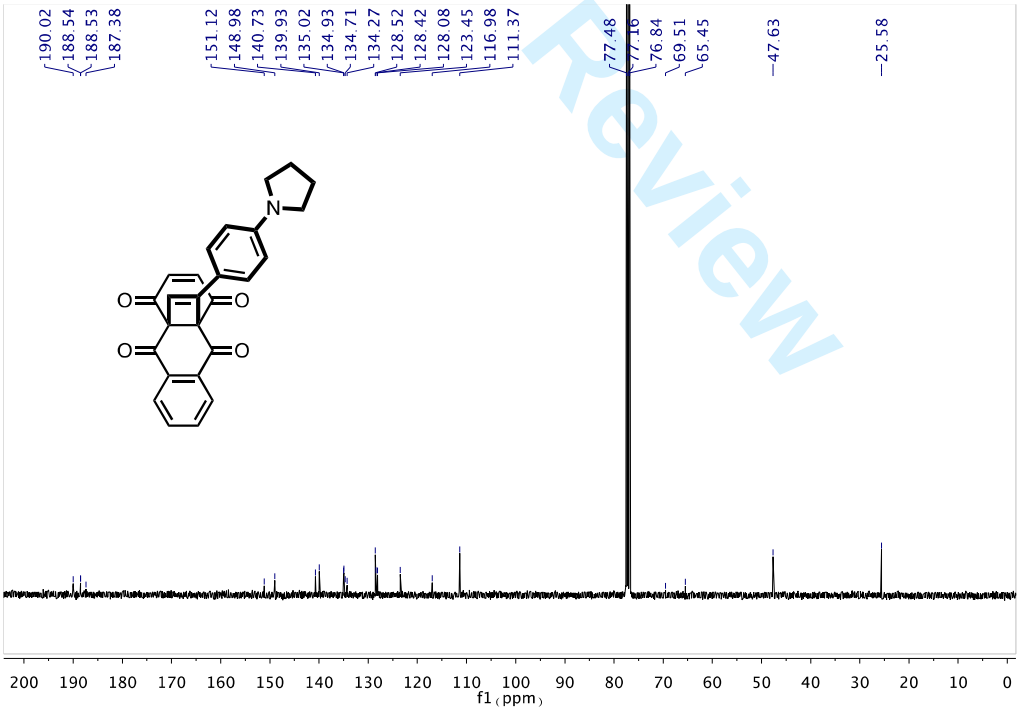


Figure S27. ^{13}C NMR spectrum of **5c** in $CDCl_3$ solution (100 MHz).

For Peer Review

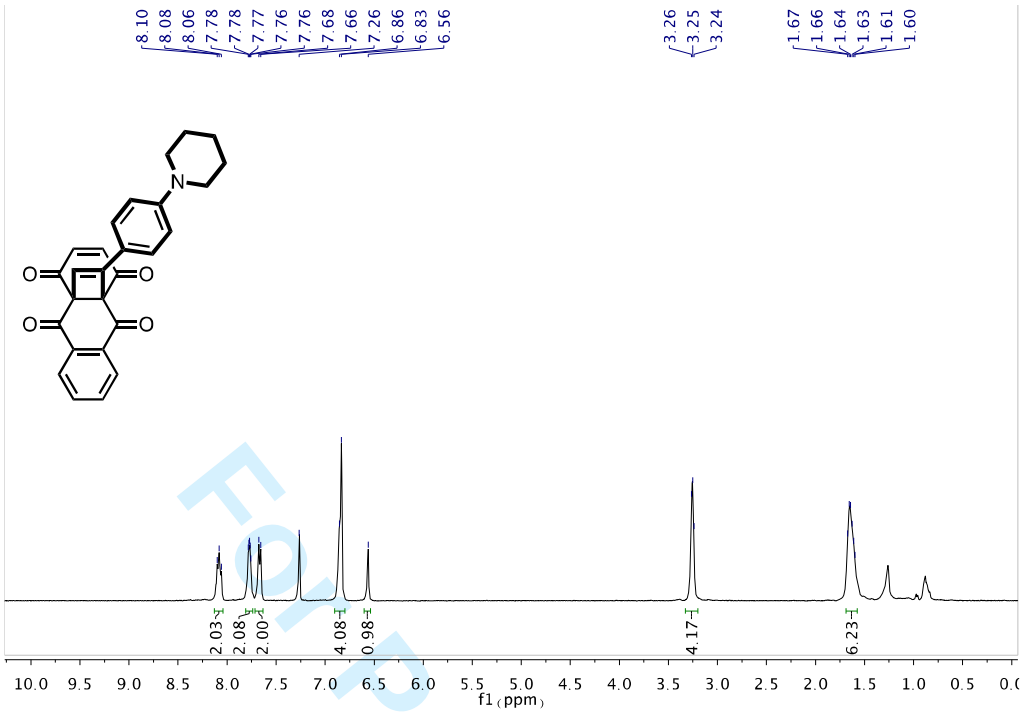


Figure S28. ^{1}H NMR spectrum of **5d** in $CDCl_3$ solution (400 MHz).

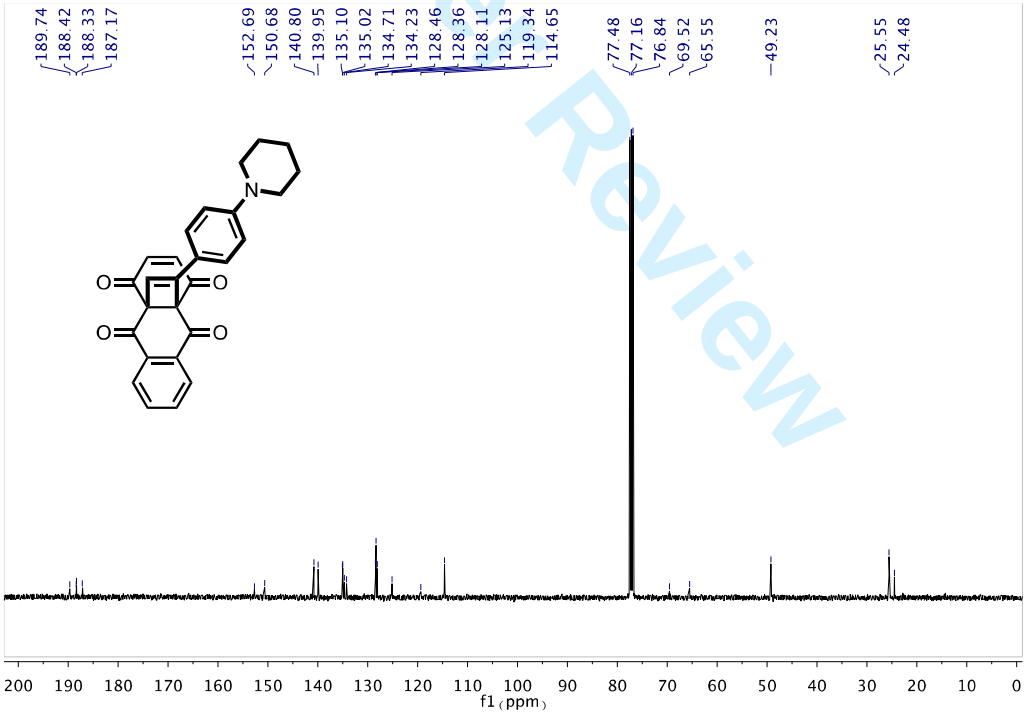


Figure S29. ^{13}C NMR spectrum of **5d** in $CDCl_3$ solution (100 MHz).

For Peer Review

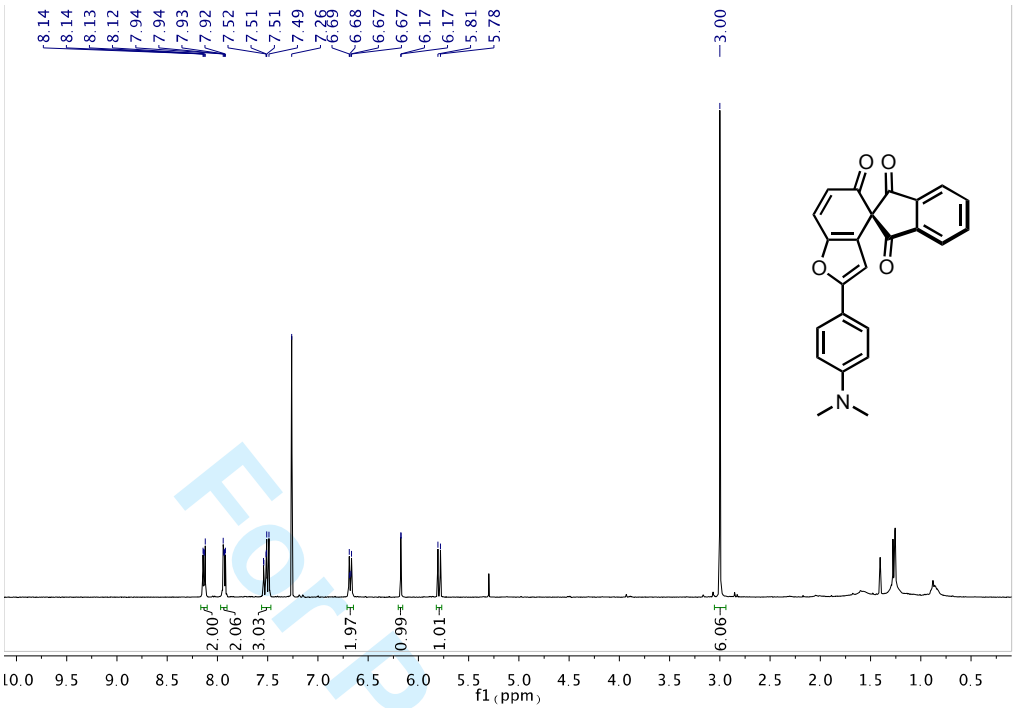


Figure S30. ^{1}H NMR spectrum of **6a** in $CDCl_3$ solution (400 MHz).

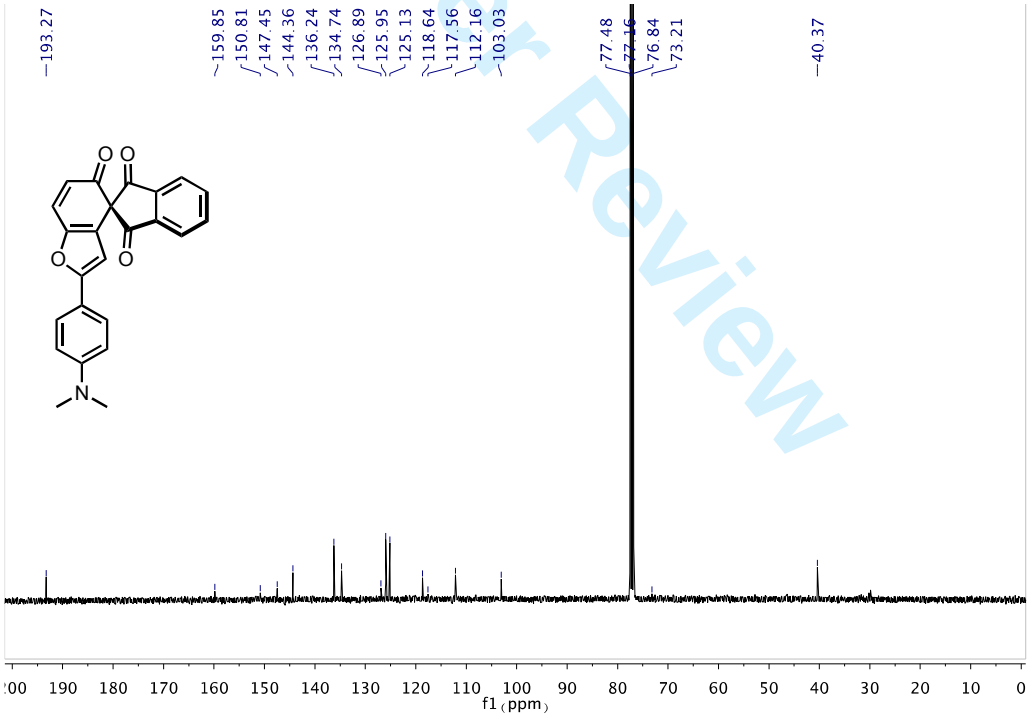


Figure S31. ^{13}C NMR spectrum of **6a** in $CDCl_3$ solution (100 MHz).

For Peer Review

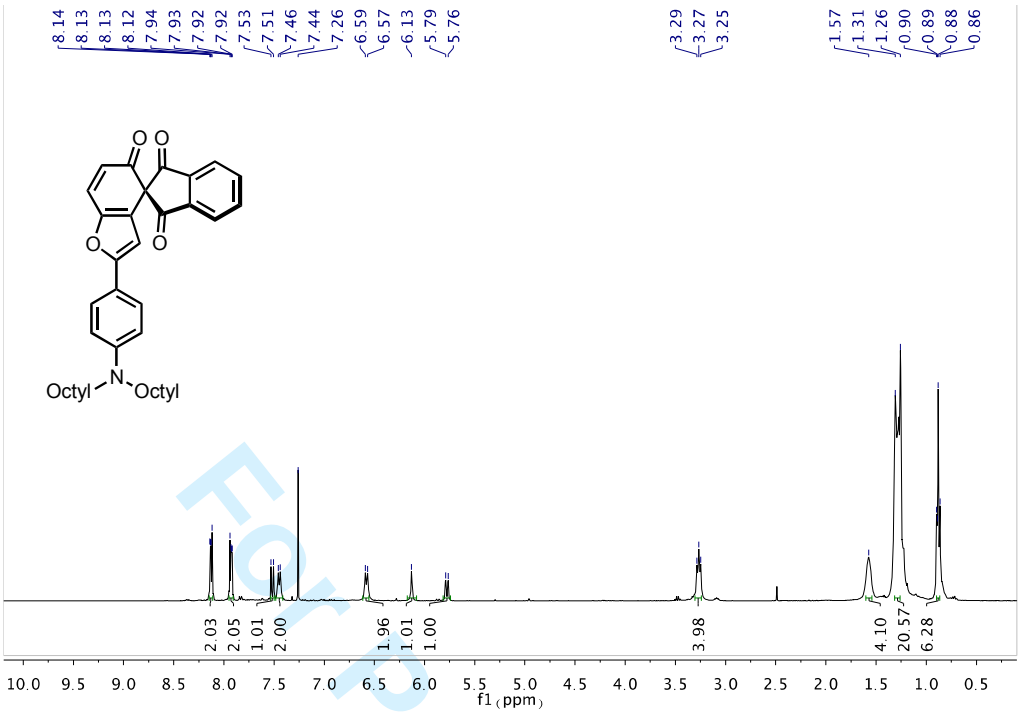


Figure S32. ^{1}H NMR spectrum of **6b** in $CDCl_3$ solution (400 MHz).

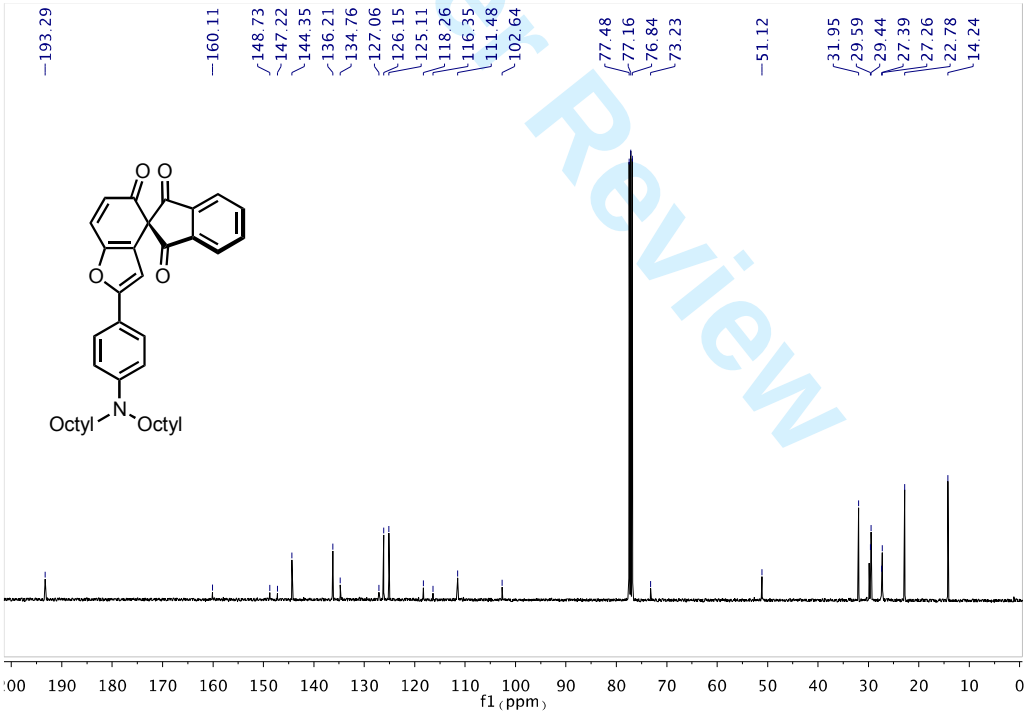


Figure S33. ^{13}C NMR spectrum of **6b** in $CDCl_3$ solution (100 MHz).

For Peer Review

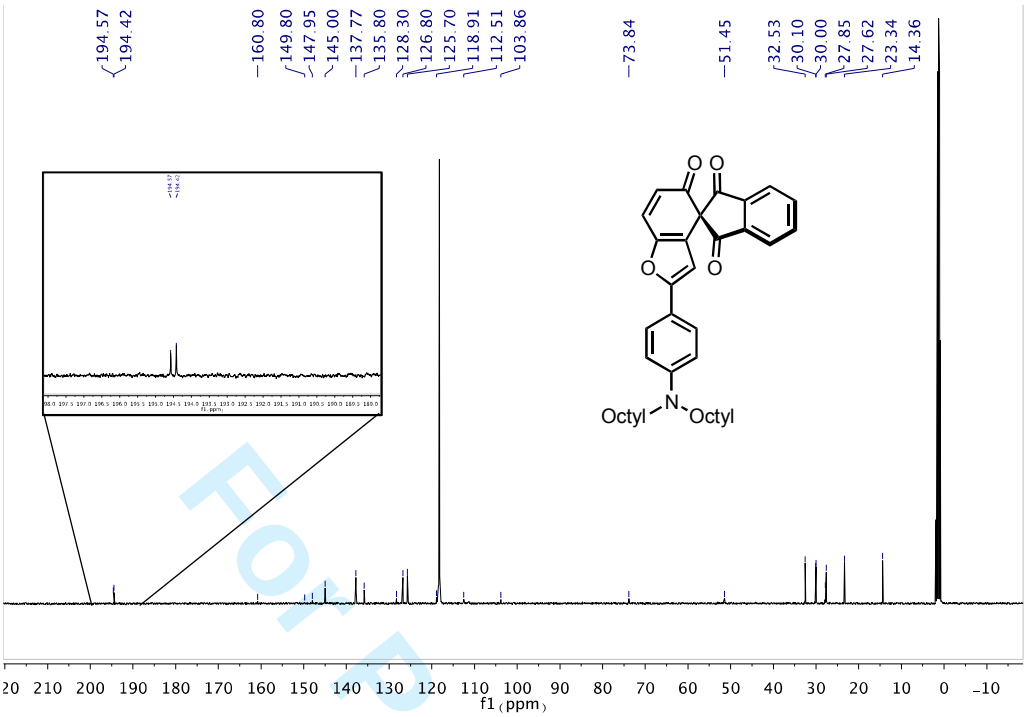


Figure S34. ^{13}C NMR spectrum of **6b** in CD_3CN solution (100 MHz).

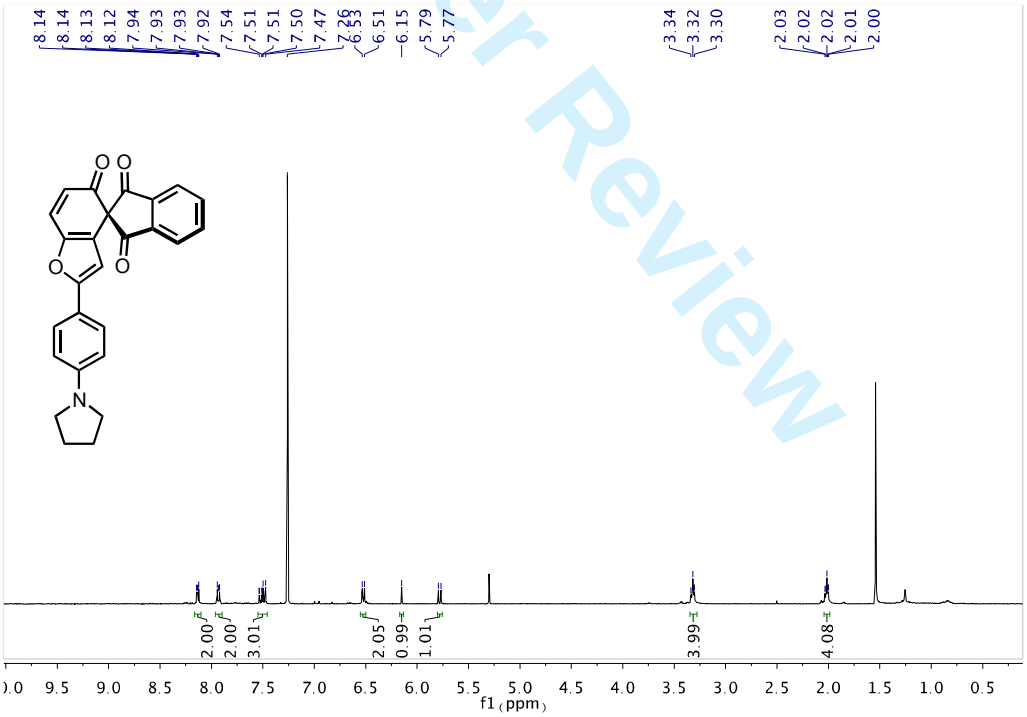


Figure S35. ^{1}H NMR spectrum of **6c** in $CDCl_3$ solution (400 MHz).

For Peer Review

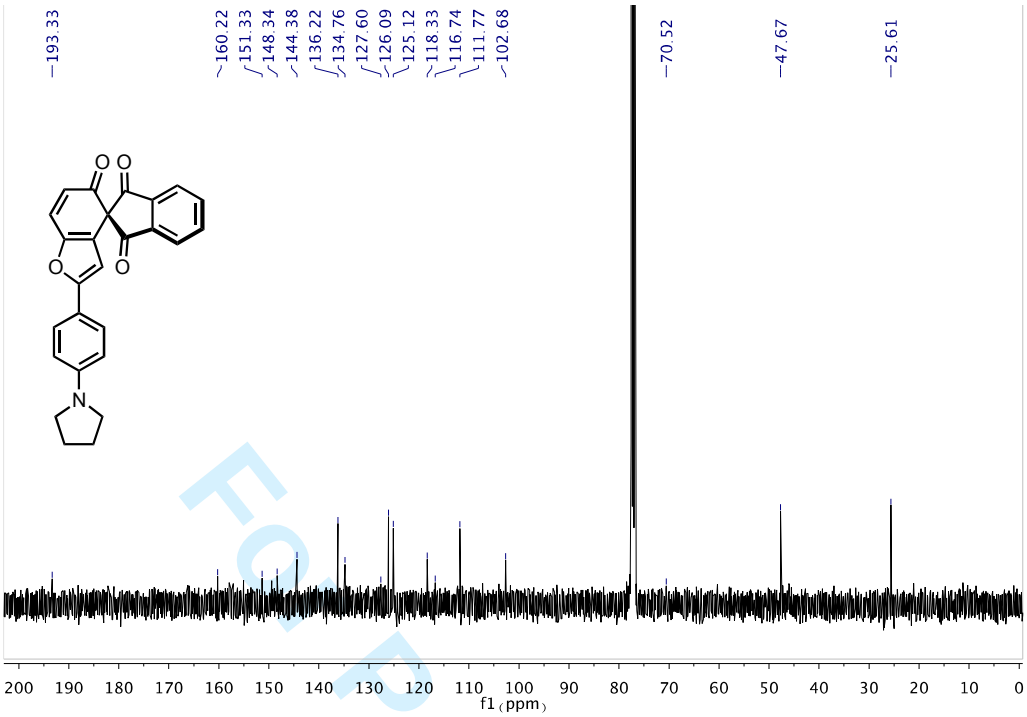


Figure S36. ^{13}C NMR spectrum of **6c** in $CDCl_3$ solution (100 MHz).

S6. References

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