Supporting Information for

Nonpolar selective emission (NPSE) of carbonyl-bridged rhodols

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1. Instrumentation and Materials

Instruments

^{1}H- and ^{13}C-NMR spectra were recorded on JEOL ECZ 400S spectrometer (400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR) and JEOL ECA 500 spectrometer (500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR). ^{1}H- and ^{13}C- spectra were referenced to $CHCl_3$ (δ: 7.26 and 77.16 ppm for ^{1}H- and ^{13}C-NMR, respectively) as an internal standard. The following abbreviations are used: s = singlet, d = doublet, m = multiplet. HRMS (ESI) spectra were recorded on Agilent 6230 Accurate-Mass TOF LC/MS system using electrospray ionization. UV/Vis spectra were recorded at room temperature on a HITACHI U-2900 spectrophotometer and fluorescence spectra on a HITACHI F-7100 spectrophotometer. The relative emission quantum yield Φ_{em} were measured by excitation at using reference material of Oxazine 170 (Φ_{em} = 58% in ethanol[1]) Crystal structures were determined by the single-crystal X-ray diffraction method at T = 103 K. These diffraction data were collected using Rigaku XtaLAB Synergy-i diffractometer (Cu-Kα radiation).

Materials

Reagents were purchased from Wako Pure Chemical Industries, Kanto Chemical Co., Inc., and Tokyo Chemical Industry Co., Ltd. All solvents were used without further purification.

Computational Details

All calculations were carried out with the Gaussian 09[2] and Gaussian 16[3] program package. The molecular structures optimizations were conducted at the B3LYP or CAM-B3LYP level using 6-31+G** or cc-pVDZ basis set for all the atoms. Excitation wavelengths and oscillator strengths were obtained at the density functional level using time-dependent perturbation theory (TDDFT) approach. Solvation was evaluated by the self-consistent reaction field (SCRF) method using the polarizable continuum model (PCM).[4] The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum or a transition state and to evaluate its zero-point vibrational energy and thermal corrections at 298 K.

Reference

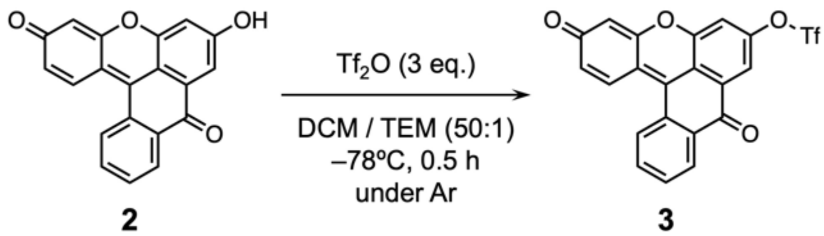
[1] Rurack, K.; Spieles, M. *Anal. Chem.* **2011**, *83*, 1232–1242.

[2]. Gaussian 09, Revision E. 01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; 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.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2013**.

[3]. Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

[4]. Miertuš, S.; Scrocco, E.; Tomasi, *J. Chem. Phys.* **1981**, *55*, 117-129.

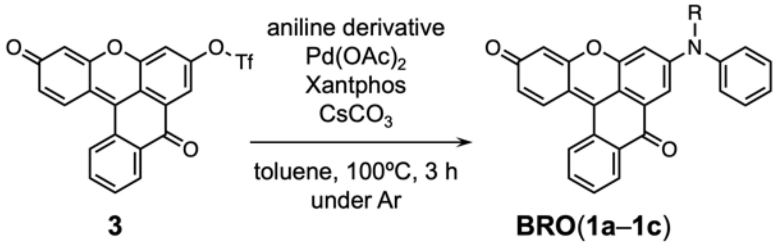
2. Experimental Procedure



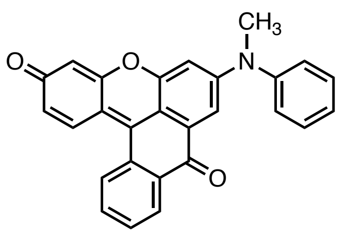
Synthesis of 3: **2** (100 mg, 0.301 mmol) was suspended in CH_2Cl_2 (100 ml) and triethylamine (2 ml), and the mixture was stirred at room temperature for 10 minutes. After cooling the mixture to –78ºC, trifluoromethanesulfonic anhydride was slowly added and stirred for 0.5 h. It was subsequently diluted with water and extracted with CH_2Cl_2 (2×). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Flash chromatography on silica gel ($CHCl_3$) afforded 114 mg (79%) of **3** as a dark red solid.

Compound **3**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, J = 7.2 Hz, 2.0 Hz, 1H), 8.22-8.14 (m, 2H), 8.11 (d, J = 2.0 Hz, 1H), 7.94-7.85 (m, 2H), 7.65 (d, J = 2.8 Hz, 1H), 7.00 (dd, J = 10.0 Hz, 2.0 Hz, 1H), 6.68 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.9, 180.3, 159.0, 151.9, 151.6, 133.9, 133.4, 133.0, 132.0, 131.6, 131.1, 130.8, 129.8, 122.8, 119.4, 116.9, 114.5, 107.7; HRMS (ESI, positive) m/z calcd. for $C_{21}H_{10}F_3O_6S$ $(M+H)^+$: 447.0150, found: 447.0155.

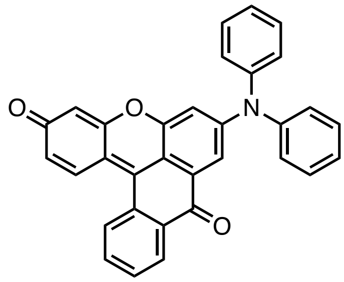
General procedure for synthesis of BRO (1a–1c)



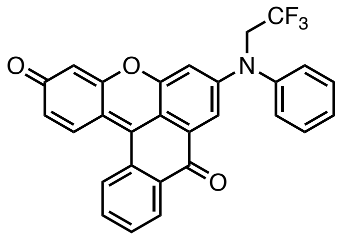
1a~**1c** were synthesized from **3** according to the reported procedure[1]. A Schlenk flask was charged with **2** (100 mg), $Pd(OAc)_2$ (10 mg, 0.2 eq), BINAP (45 mg, 0.3 eq), and Cs_2CO_3 (119 mg, 2.8 eq). The Schlenk flask was sealed and evacuated/backfilled with argon (3×). Toluene (1 mL) was added, and the reaction was flushed again with nitrogen (3×). aniline derivatives (2.4 eq) were then added. The reaction was stirred at 100°C for 3 h. It was subsequently cooled to room temperature and purified by silica gel chromatography (CH_2Cl_2/MeOH, 100:0~50:1).



Compound **1a** (black powder): ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, J = 7.0 Hz, 1H), 8.11 (d, J = 7.5 Hz, 1H), 8.01 (d, J = 10 Hz, 1H), 7.80-7.68 (m, 2H), 7.58-7.47 (m, 3H), 7.38 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 9.5 Hz, 1H), 6.78 (d, J = 2.5 Hz, 1H), 6.60 (s, 1H), 3.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.0, 159.5, 153.4, 153.2, 145.7, 133.5, 133.2, 132.3, 131.4, 130.6, 130.4, 129.5, 129.2, 127.6, 126.7, 117.0, 111.3, 110.5, 106.4, 103.2, 41.1; HRMS (ESI, positive) m/z calcd. for $C_{27}H_{18}NO_3$ $(M+H)^+$: 404.1287, found: 404.1282.



Compound **1b** (black powder): ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (dd, *J* = 7.5 Hz, 1.0 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 9.5 Hz, 1H), 7.83-7.71 (m, 3H), 7.41 (t, *J* = 7.5 Hz, 4H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 4H), 7.05 (d, *J* = 3.0 Hz, 1H), 6.85 (d, *J* = 10 Hz, 1H), 6.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.0, 159.5, 153.0, 152.6, 145.2, 133.6, 133.2, 132.4, 131.5, 131.5, 130.5, 130.3, 130.2, 129.8, 129.3, 126.7, 126.5, 118.5, 115.5, 112.3, 108.8, 106.8; HRMS (ESI, positive) m/z calcd. for $C_{32}H_{20}NO_3$ $(M+H)^+$: 464.1443, found: 466.1448.



Compound **1c** (black powder): ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (d, *J* = 7.0 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.82-7.67 (m, 2H), 7.63-7.50 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 2H), 6.83-6.73 (m, 2H), 6.45 (s, 1H), 4.47 (q, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.8, 159.3, 152.7, 152.3 144.3, 133.4, 133.1, 132.2, 131.3, 131.0, 130.6, 130.3, 129.7, 129.2, 128.5, 127.8, 125.8, 123.6, 118.8, 111.6, 110.3, 106.9, 105.2, 54.2, 53.9; HRMS (ESI, positive) m/z calcd. for $C_{28}H_{17}F_3NO_3$ $(M+H)^+$: 472.1160, found: 472.1156.

Reference

[1] Grimm, J. B.; Lavis, L. D. *Org. Lett.* **2011**, *13*, 6354–6357.

3. Single X-ray Structure Analysis

Single crystals of **1a**, **1b**, and **1c** were obtained by slow diffusion of Et_2O into a $CHCl_3$ solution of **1a**, **1b**, and **1c** at 10ºC. These crystal structures were determined by the single-crystal X-ray diffraction method at T = 103 K. The diffraction data were collected using Rigaku XtaLAB Synergy-i diffractometer (Cu-Kα radiation). The structure was solved using the SHELXT[1] and refined with SHELXL-2018/3[2] via OLEX2[3]. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were put on calculated geometrically, and were refined by applying riding models. Crystal data, structure refinement and included solvents are summarized in **Table S1-S3**. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition code CCDC 2332061 (**1a**); 2332062 (**1b**); and 2332063 (**1c**).

Table S1 Crystal data and structure refinement for **1a**.

	1a
Chemical formula	$C_{27}H_{17}NO_3$
Recrystallization solvent	$CHCl_3$ / Et_2O
Included solvent	–
Crystal system	Orthorhombic
Space group [No.]	*P b c a* [61]
Crystal color, habit	Metallic black, plate
Crystal size, mm	0.309 × 0.050 × 0.020
a, Å	7.3843(2)
b, Å	20.0427(5)
c, Å	24.5666(6)
α, °	90
β, °	90
γ, °	90
Volume, Å^3	3635.89(16)
Z	8
D_{calcd}, g/cm^3	1.474
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	0.775
$2\theta_{max}$ °	67.6560
F(000)	1680
Reflns collected	3292
Unique reflns	2655
No. of parameters	281
R1 ($I > 2.00\sigma$(i))	0.0527
R (all reflection)	0.0663
GOF	1.026

Table S2 Crystal data and structure refinement for **1b**.

	1b
Chemical formula	$C_{32}H_{19}NO_3$
Recrystallization solvent	$CHCl_3$ / Et_2O
Included solvent	–
Crystal system	Orthorhombic
Space group [No.]	*P b c a* [61]
Crystal color, habit	Metallic black, plate
Crystal size, mm	0.939 × 0.314 × 0.061
a, Å	7.75825(12)
b, Å	18.8157(4)
c, Å	31.7145(6)
α, °	90
β, °	90
γ, °	90
Volume, Å^3	4629.59(14)
Z	8
D_{calcd}, g/cm^3	1.336
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	0.687
$2\theta_{max}$ °	68.1400
F(000)	1936
Reflns collected	4249
Unique reflns	3827
No. of parameters	326
R1 ($I > 2.00\sigma$(i))	0.0387
R (all reflection)	0.0426
GOF	1.027

Table S3 Crystal data and structure refinement for **1c**.

	1c
Chemical formula	$C_{28}H_{16}F_3NO_3$
Recrystallization solvent	$CHCl_3$ / Et_2O
Included solvent	–
Crystal system	Triclinic
Space group [No.]	*P*-1 [2]
Crystal color, habit	Metallic black, plate
Crystal size, mm	0.313 × 0.247 × 0.216
a, Å	10.9940(3)
b, Å	11.0404(3)
c, Å	17.6631(4)
α, °	83.512(2)
β, °	80.770(2)
γ, °	72.972(3)
Volume, Å^3	2018.43(10)
Z	2
D_{calcd}, g/cm^3	1.551
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	1.012
$2\theta_{max}$ °	67.9470
F(000)	452
Reflns collected	7344
Unique reflns	6165
No. of parameters	631
R1 ($I > 2.00\sigma$(i))	0.0527
R (all reflection)	0.0600
GOF	1.022

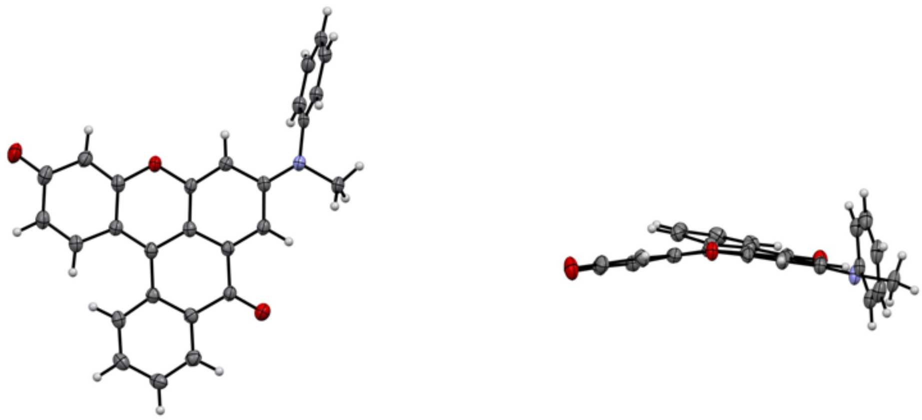


Fig. S1 Top and side views of the X-ray crystal structure for **1a**. The thermal ellipsoids are scaled to the 50% probability level.

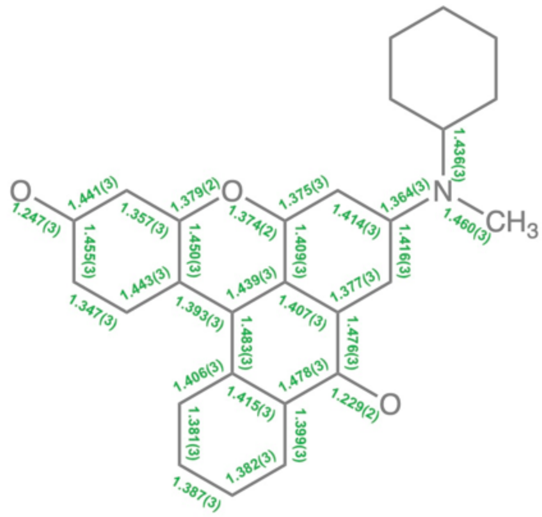


Fig. S2 Bond length (Å) obtained from X-ray crystallographic analysis of **1a**.

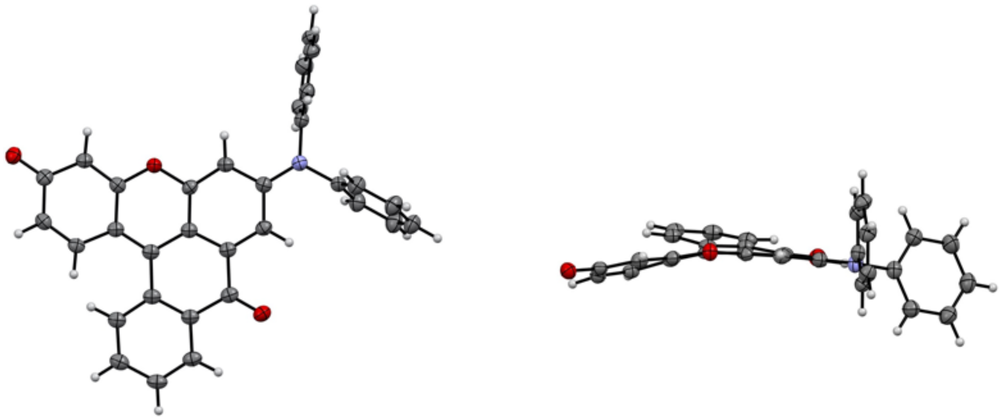


Fig. S3 Top and side views of the X-ray crystal structure for **1b**. The thermal ellipsoids are scaled to the 50% probability level.

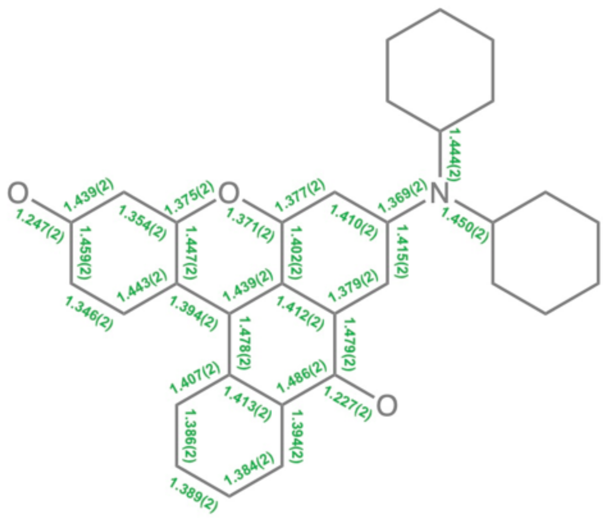


Fig. S4 Bond length (Å) obtained from X-ray crystallographic analysis of **1b**.

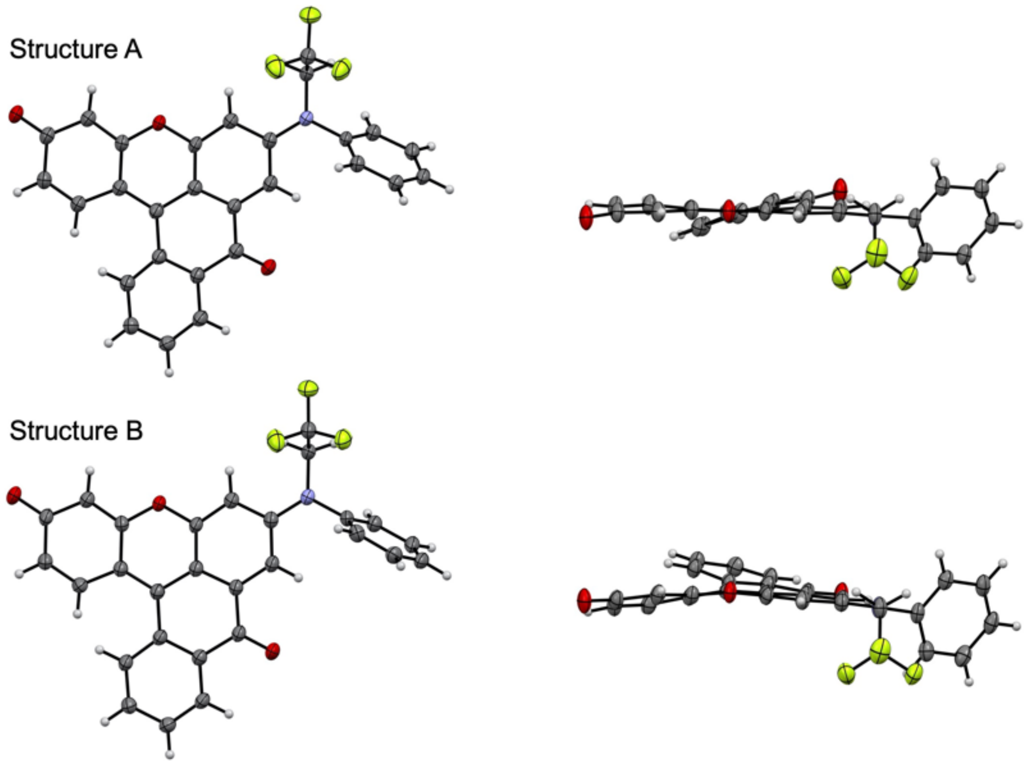


Fig. S5 Top and side views of the X-ray crystal structure for **1c**. The thermal ellipsoids are scaled to the 50% probability level.

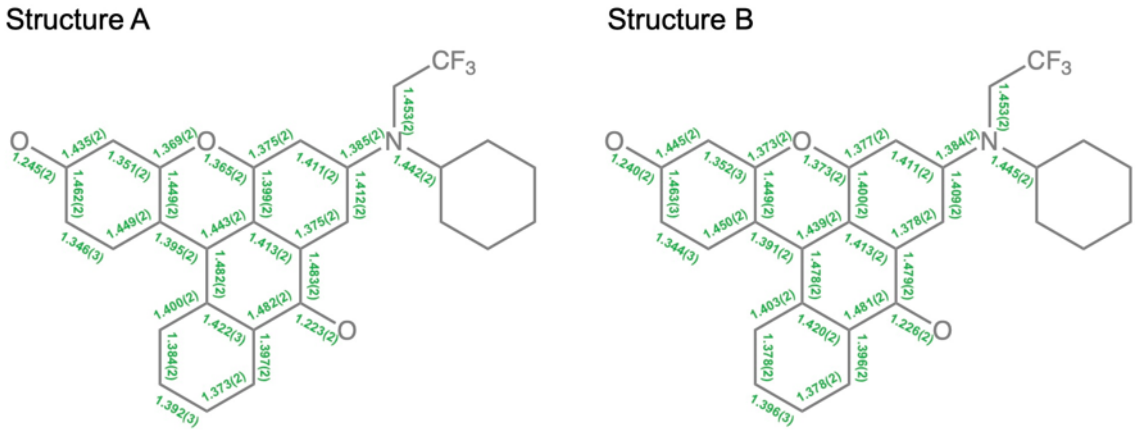


Fig. S6 Bond length (Å) obtained from X-ray crystallographic analysis of **1c**.

Reference

[1] Sheldrick, G. M. *Acta Cryst*. **2015**, *A71*, 3–8.

[2] Sheldrick, G. M. *Acta Cryst*. **2015**, *C71*, 3–8.

[3] Dolomanov O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann. H. *J. Appl. Cryst.* **2009**, *42*, 339–341.

4. Optical Properties and DFT calculation

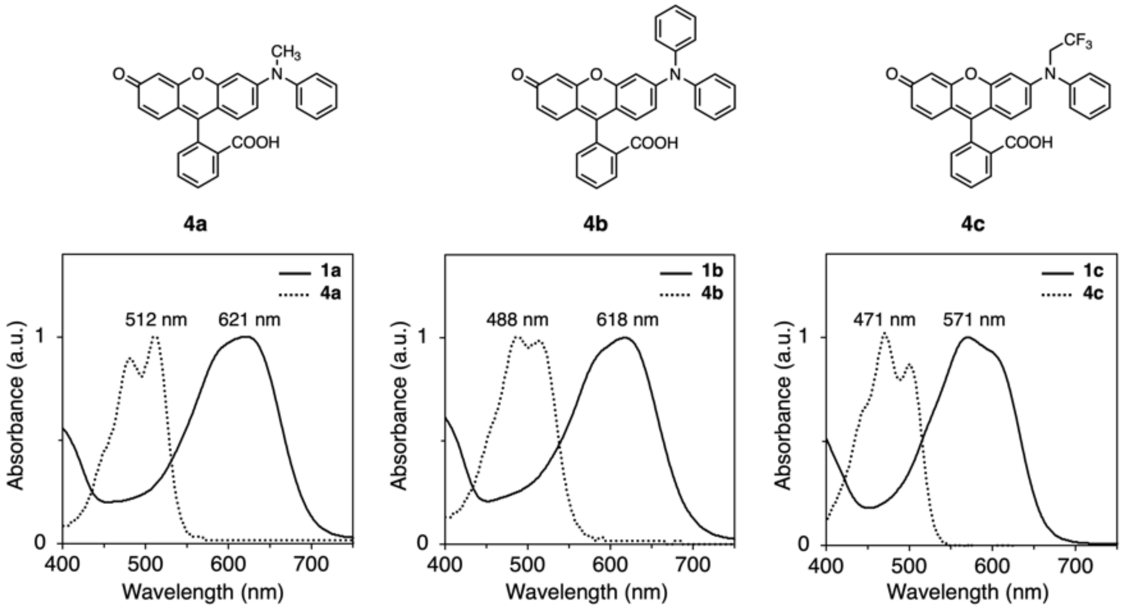


Fig. S7 Comparison of absorption spectra of **Rhodol** (**4a**–**4c**) and **BRO** (**1a**–**1c**) in DMSO.

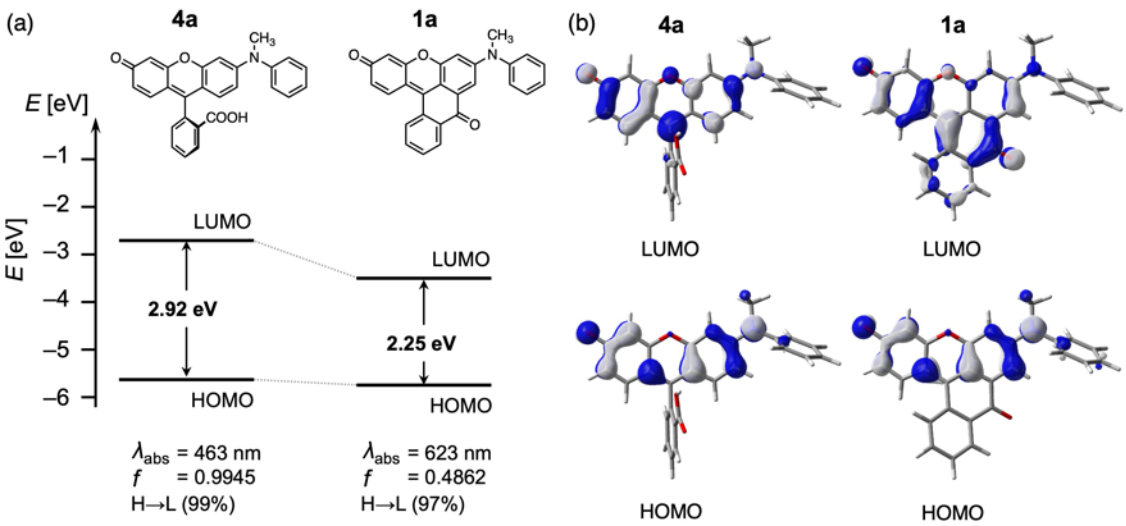


Fig. S8 Energy diagrams and frontier molecular orbitals of **4a** and **1a**. Calculations were performed at B3LYP/6-31+G** level in the gas phase.

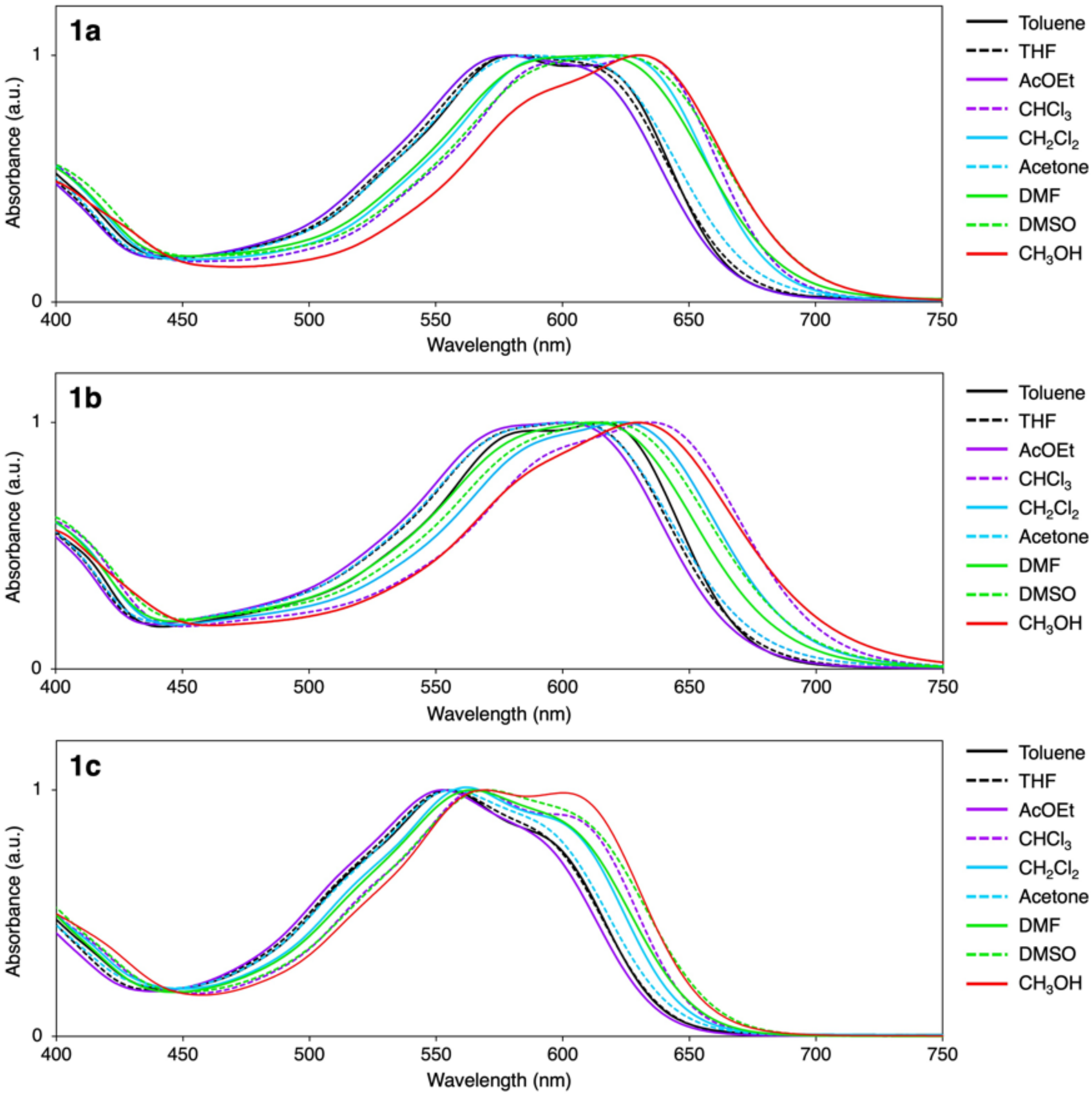


Fig. S9 Absorption spectra of **1a**–**1c** in various organic solvents.

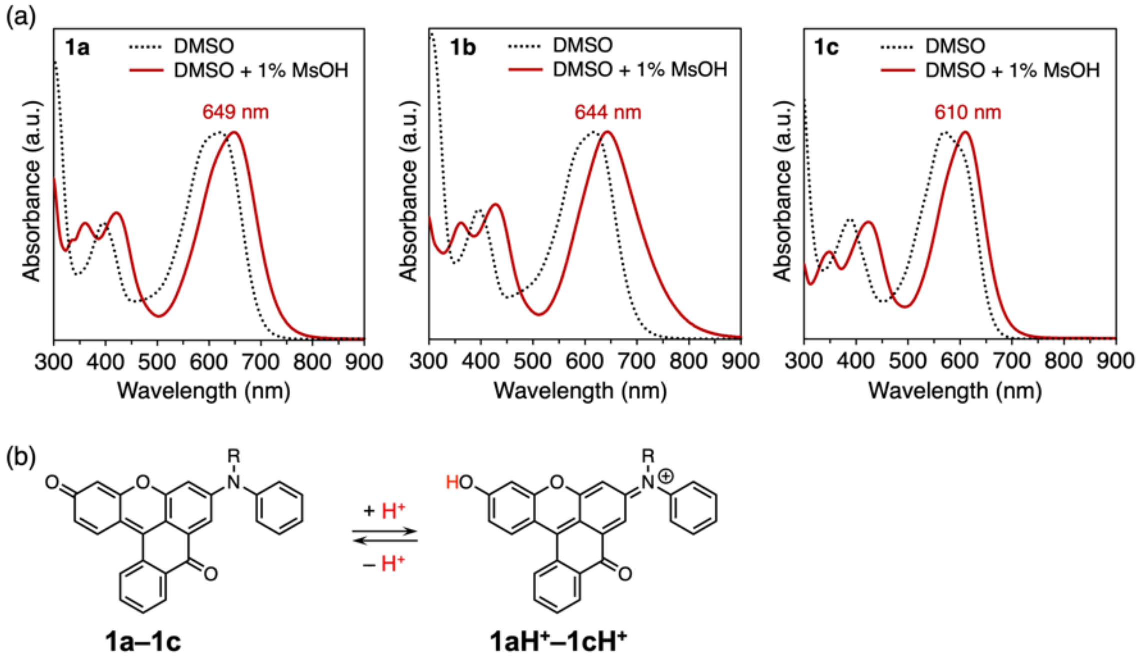


Fig. S10 Absorption spectra of **1a**–**1c** in DMSO containing 1% MsOH.

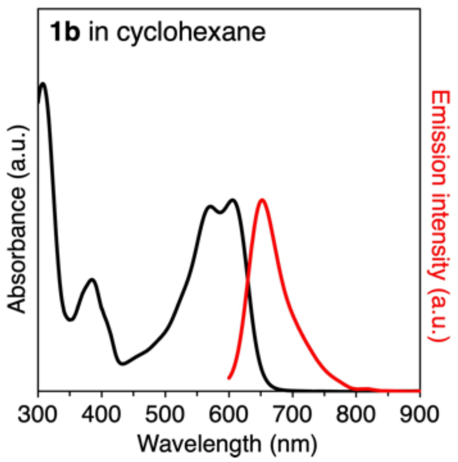


Fig. S11 Absorption and emission spectra of **1b** in cyclohexane. λ_{ex} = 400 nm.

Table S4 Optical properties of **1a** in organic solvents.

Solvent	Solvent polarity parameters		λ_{abs} [nm]	λ_{fl} [nm]	ε [cm^{-1} M^{-1}]	Φ_{em}^{*2} [%]
	$E_T(30)$	ε_r^{*1}				
Toluene	33.9	2.4	580	671	14000	2.9
Benzene	34.3	2.3	623	674	14000	1.4
THF	37.9	7.6	580	674	20000	< 0.1
AcOEt	38.1	6.0	579	669	14000	< 0.1
$CHCl_3$	39.1	4.8	630	689	23000	< 0.1
CH_2Cl_2	40.7	9.1	622	687	23000	< 0.1
Acetone	42.2	20.6	590	590	13000	< 0.1
DMF	43.2	36.7	613	n.d.	23000	n.d.
DMSO	45.1	46.5	622	n.d.	22000	n.d.
CH_3OH	55.4	32.7	630	n.d.	19000	n.d.

*1 The dielectric constant (ε_r) was measured at 25ºC. *2 The relative emission quantum yield Φ_{em} was measured by excitation at using reference material of Oxazine 170 (Φ_{em} = 58% in ethanol[1]). λ_{ex} = 400 nm.

Table S5 Optical properties of **1b** in organic solvents.

Solvent	Solvent polarity parameters		λ_{abs} [nm]	λ_{fl} [nm]	ε [cm^{-1} M^{-1}]	Φ_{em}^{*2} [%]
	$E_T(30)$	ε_r^{*1}				
Cyclohexane	30.9	2.0	606	652	–^{*3}	1.8
Toluene	33.9	2.4	615	681	20000	5.3
Benzene	34.3	2.3	617	690	21000	3.9
THF	37.9	7.6	606	668	23000	< 0.1
AcOEt	38.1	6.0	602	679	21000	< 0.1
$CHCl_3$	39.1	4.8	633	716	25000	< 0.1
CH_2Cl_2	40.7	9.1	623	713	23000	< 0.1
Acetone	42.2	20.6	605	n.d.	20000	n.d.
DMF	43.2	36.7	610	n.d.	22000	n.d.
DMSO	45.1	46.5	617	n.d.	21000	n.d.
CH_3OH	55.4	32.7	630	n.d.	23000	n.d.

*1 The dielectric constant (ε_r) was measured at 25ºC. *2 The relative emission quantum yield Φ_{em} was measured by excitation at using reference material of Oxazine 170 (Φ_{em} = 58% in ethanol[1]). λ_{ex} = 400 nm. *3 An accurate value could not be determined due to low solubility

Table S6 Optical properties of **1c** in organic solvents.

Solvent	Solvent polarity parameters		λ_{abs} [nm]	λ_{fl} [nm]	ε [cm^{-1} M^{-1}]	Φ_{em}*2 [%]
	$E_T(30)$	ε_r*1				
Toluene	33.9	2.4	555	645	14000	1.3
Benzene	34.3	2.3	557	645	13000	1.9
THF	37.9	7.6	555	652	17000	1.4
AcOEt	38.1	6.0	552	647	19000	1.6
$CHCl_3$	39.1	4.8	566	656	24000	3.2
CH_2Cl_2	40.7	9.1	562	654	25000	2.5
Acetone	42.2	20.6	560	653	21000	0.4
DMF	43.2	36.7	564	668	22000	0.3
DMSO	45.1	46.5	570	675	23000	0.4
CH_3OH	55.4	32.7	569	663	18000	0.1

*1 The dielectric constant (ε_r) was measured at 25ºC. *2 The relative emission quantum yield Φ_{em} was measured by excitation at using reference material of Oxazine 170 (Φ_{em} = 58% in ethanol[1]). λ_{ex} = 400 nm.

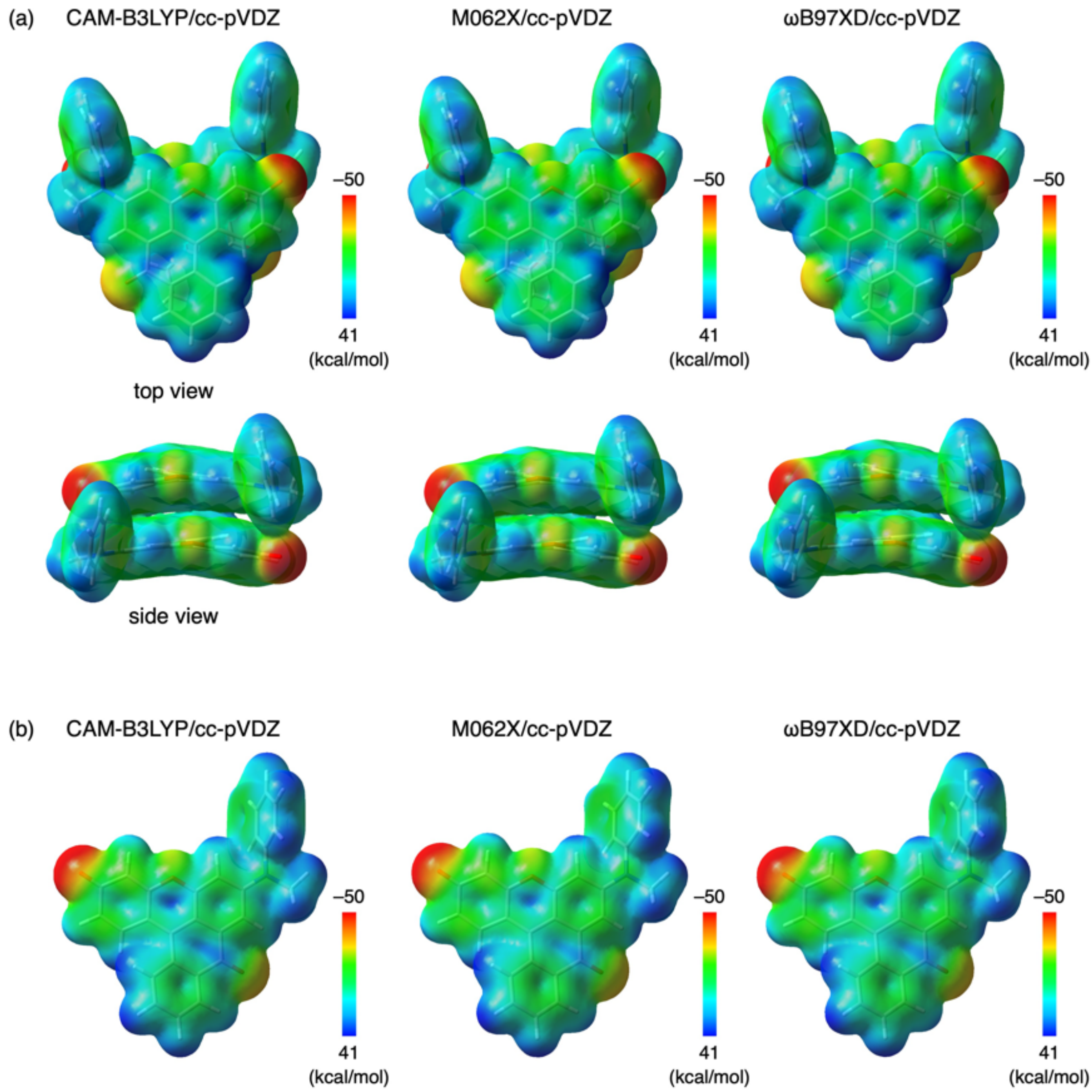


Fig. S12 Comparison of functionals in the calculation of Electrostatic potential (ESP) distribution. All ESP surfaces were generated at an isodensity value of 5×10^{-3} electron per $Bohr^3$. (a) ESP distribution of dimeric structure of **1a** in the crystal packing structure. (b) ESP distribution of the optimized structure of **1a**.

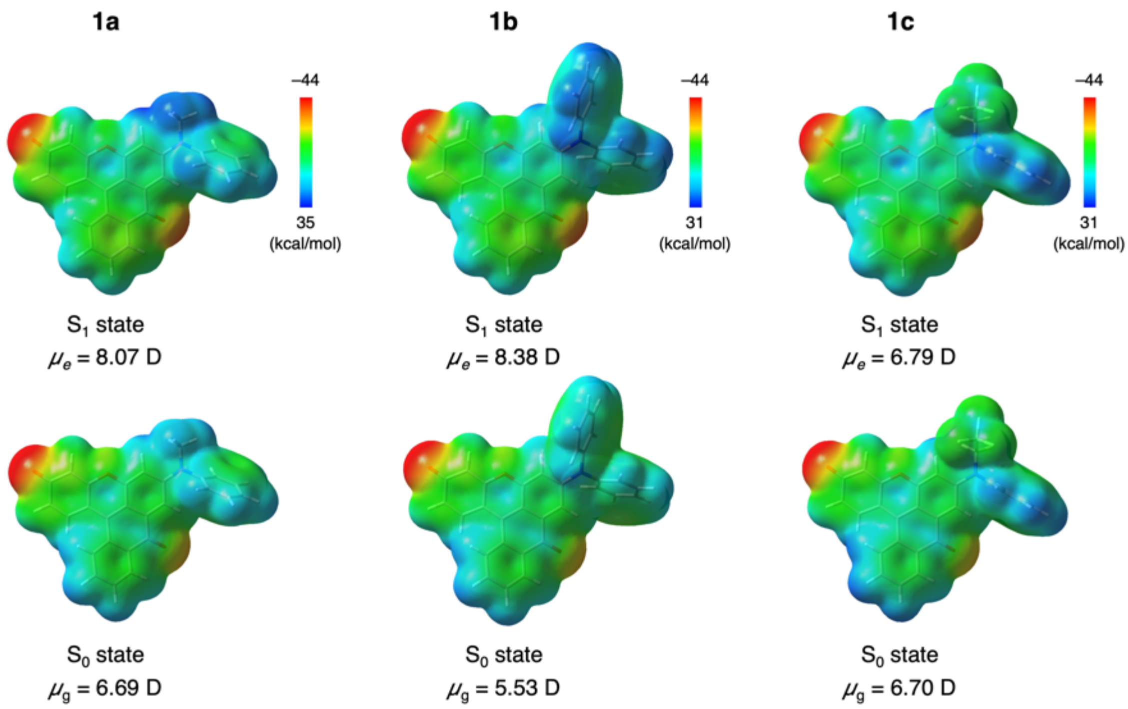


Fig. S13 Electrostatic potential (ESP) distribution of **1a**–**1c** in the S_0 and S_1 states. ESP surfaces were generated at an isodensity value of 1.5×10^{-3} electron per Bohr^3. μ_g and μ_e are the calculated dipole moments in the S_0 and S_1 states. All calculations were performed at (TD) CAM-B3LYP/cc-pVDZ level in the gas phase.

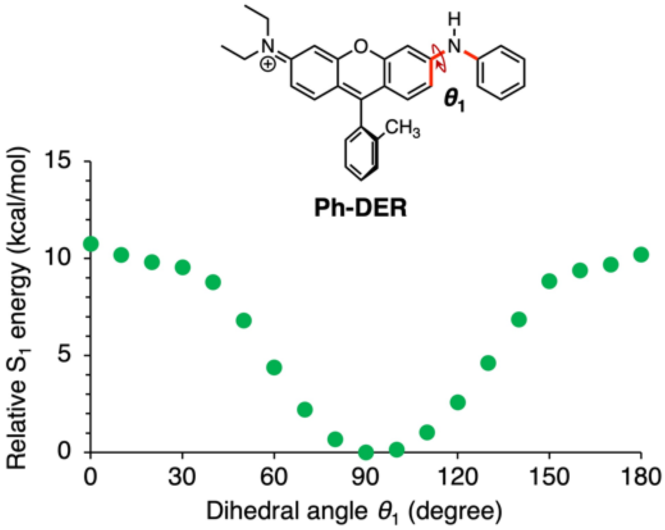


Fig. S14 The energy profile of the S_1 state of **Ph-DER** as a function of dihedral angle θ_1. Geometries were optimized at the TD-CAM-B3LYP/cc-pVDZ level in the gas phase.

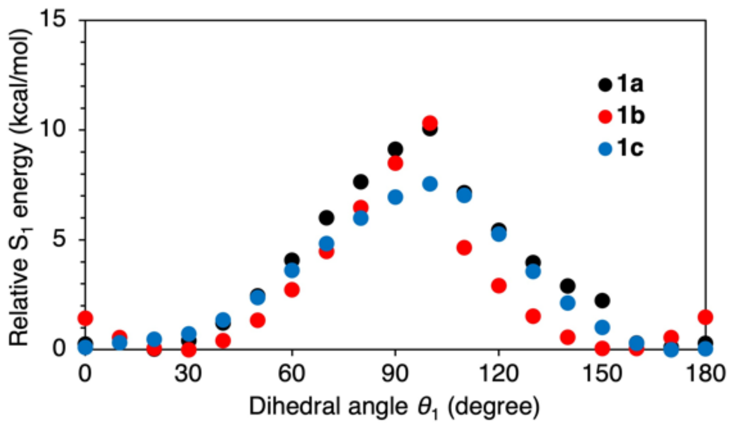


Fig. S15 The energy profile of the S_1 state of **1a**–**1c** in MeOH as a function of dihedral angle θ_1. Geometries were optimized at the TD-CAM-B3LYP/cc-pVDZ level PCM (MeOH).

Reference

[1] Rurack, K.; Spieles, M. *Anal. Chem.* **2011**, *83*, 1232–1242.

5. Gas Sensor and Time-dependent Security Ink by utilizing the NPSE

Preparation method for gas sensing film (Fig 4)

Polystyrene (500 mg) was dissolved in a **BRO**-containing (1 mg/ 10 mL) toluene solution (2 mL). After coating this solution to a glass plate, the toluene solvent was removed by vacuum drying at room temperature.

Preparation method for time-dependent security ink (Fig. 5 and Fig S16)

Polystyrene (500 mg) and additive (emission quencher, 0.2 mL) were dissolved in a **1b**-containing (1 mg/ 10 mL) CH_2Cl_2 solution (2 mL). These solutions were applied to a glass plate. It should be noted that the polystyrene solution and quencher (2-hexanone and cyclohexanone) were somewhat difficult to mix. After mixing, the solution was allowed to stand in the dark for two days to ensure that it was a completely homogeneous solution before it was used in the experiment.

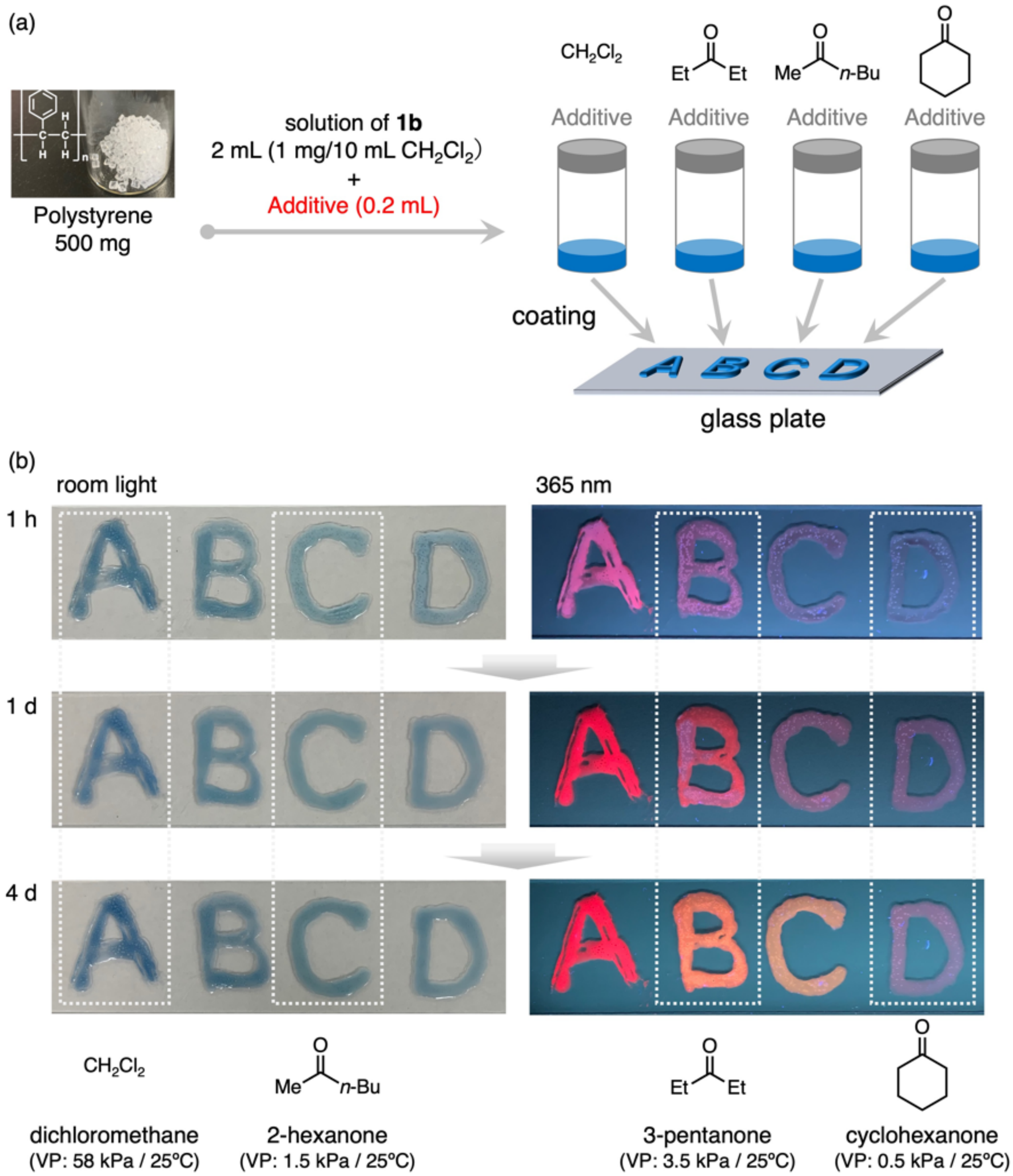
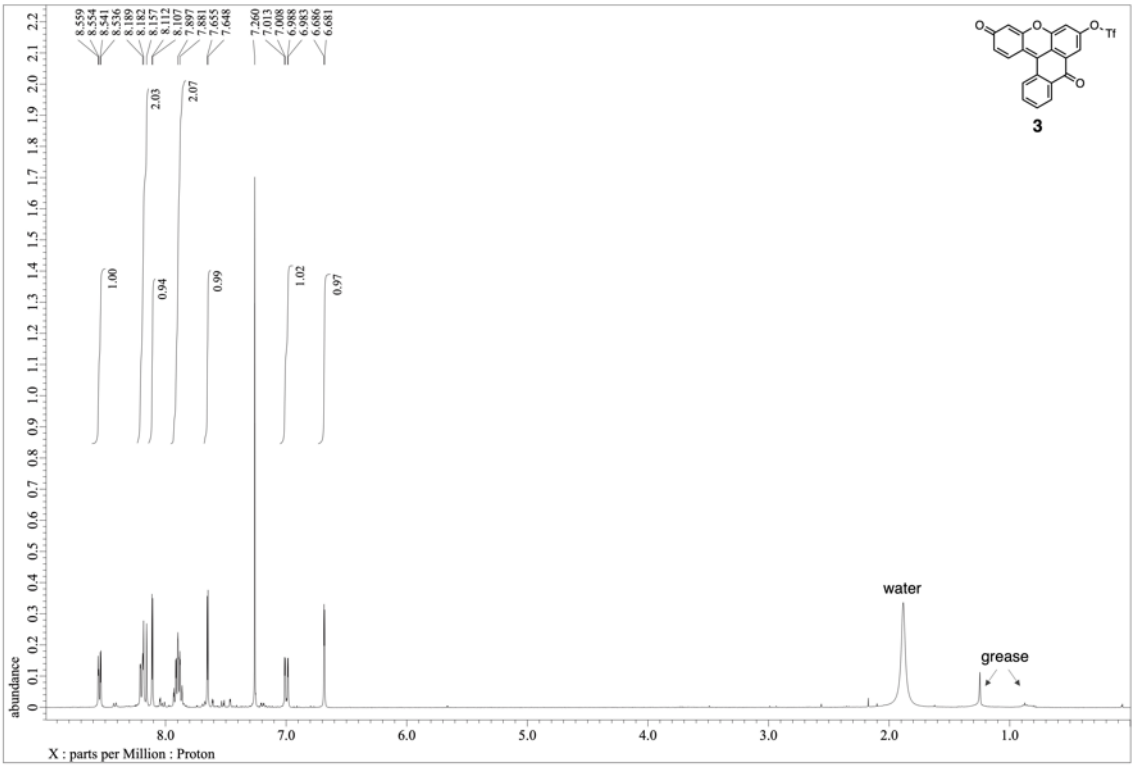
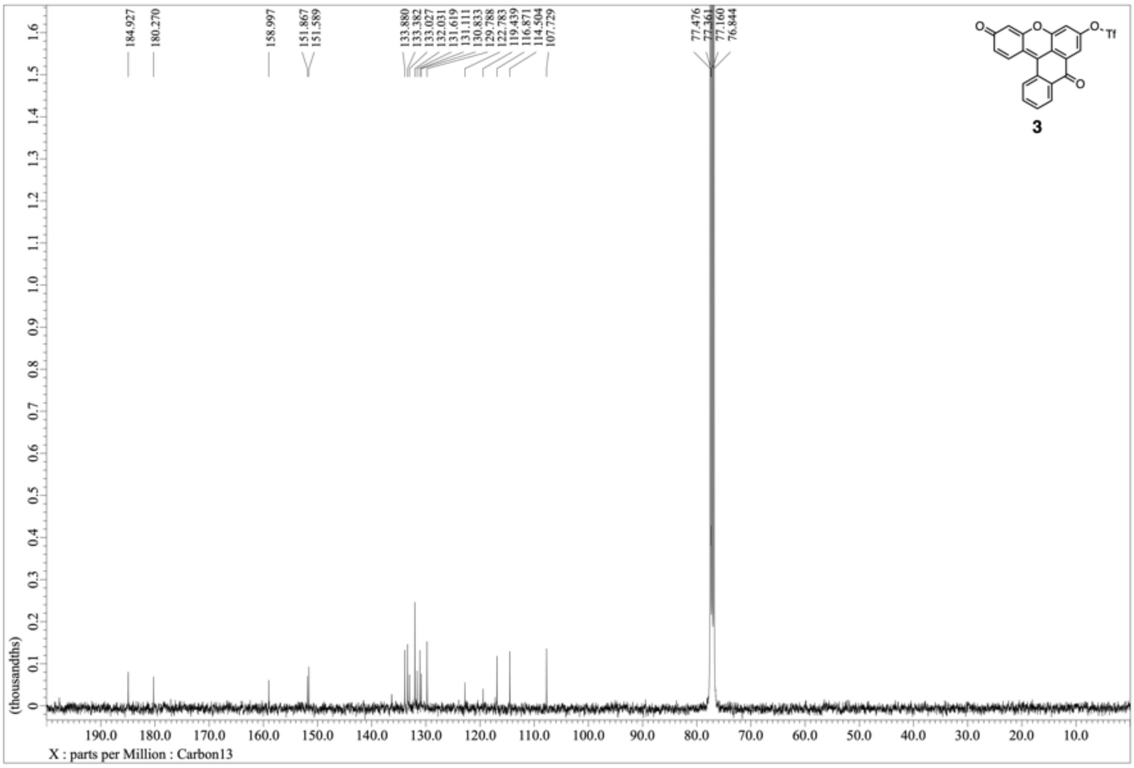


Fig. S16 (a) Method for preparing a **1b** doped polymer films. (b) Relationship between emission of **1b** doped films and additives. VP = vapor pressure. These experiments were performed in the dark at 20°C.

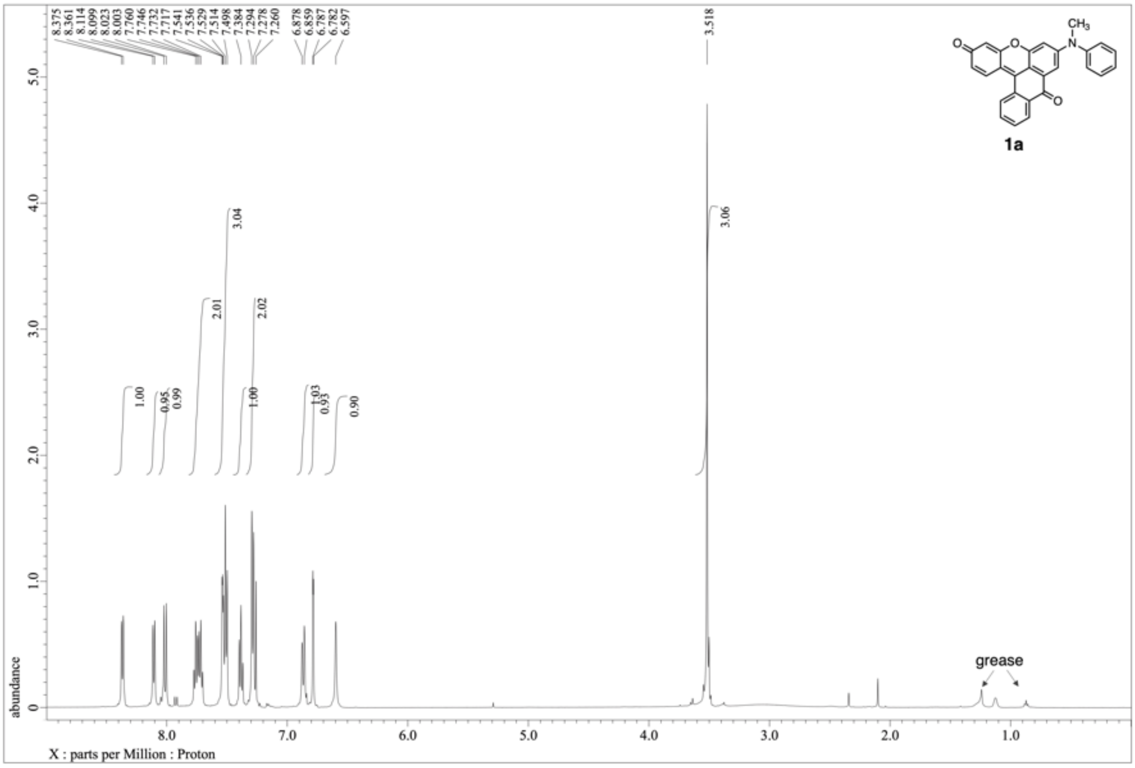
6. NMR Spectra of Compounds

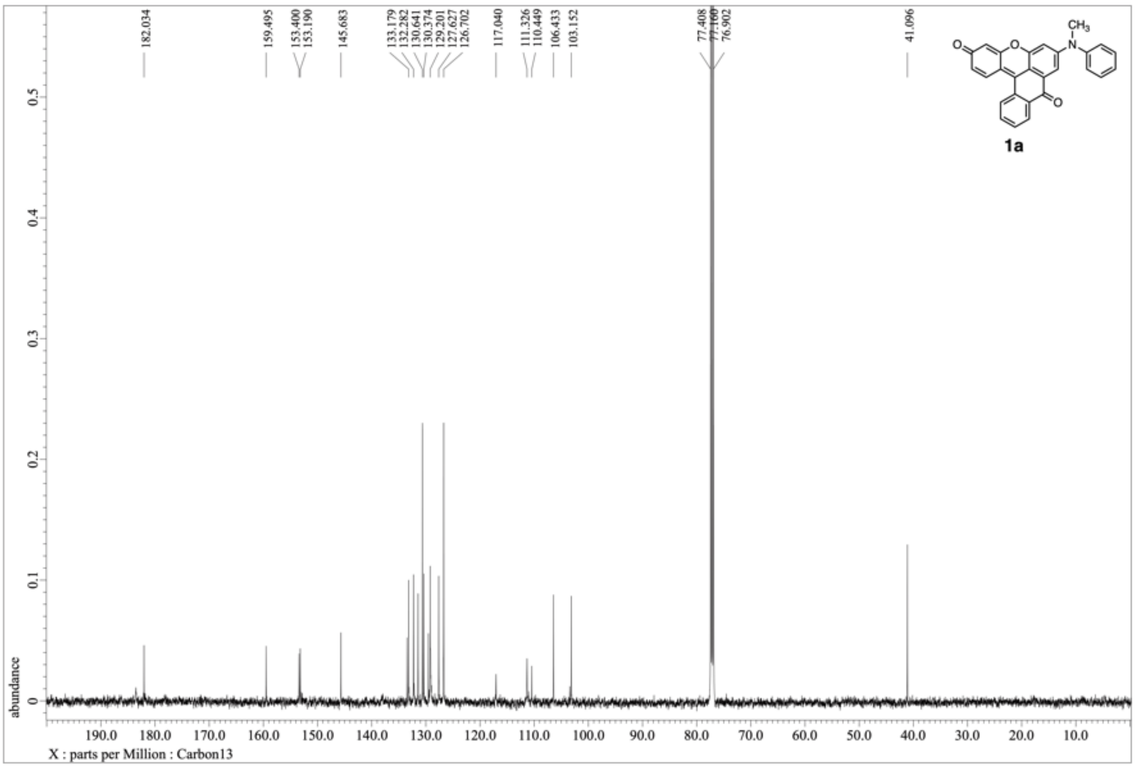
^{1}H- and ^{13}C-NMR spectra were recorded on JEOL ECZ 400S spectrometer (400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR) and JEOL ECA 500 spectrometer (500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR). ^{1}H- and ^{13}C- spectra were referenced to $CHCl_3$ (δ: 7.26 and 77.16 ppm for ^{1}H- and ^{13}C-NMR, respectively) as an internal standard. The NMR spectra of compounds **3** and **1a**-**1c** were measured after purification by silica gel column chromatography and recrystallization. It should be noted that a certain amount of impurities (grease and solvent) contained in **1a**-**1c** remained even when purification methods such as preparative TLC, size exclusion chromatography, extraction, and recrystallization were used.



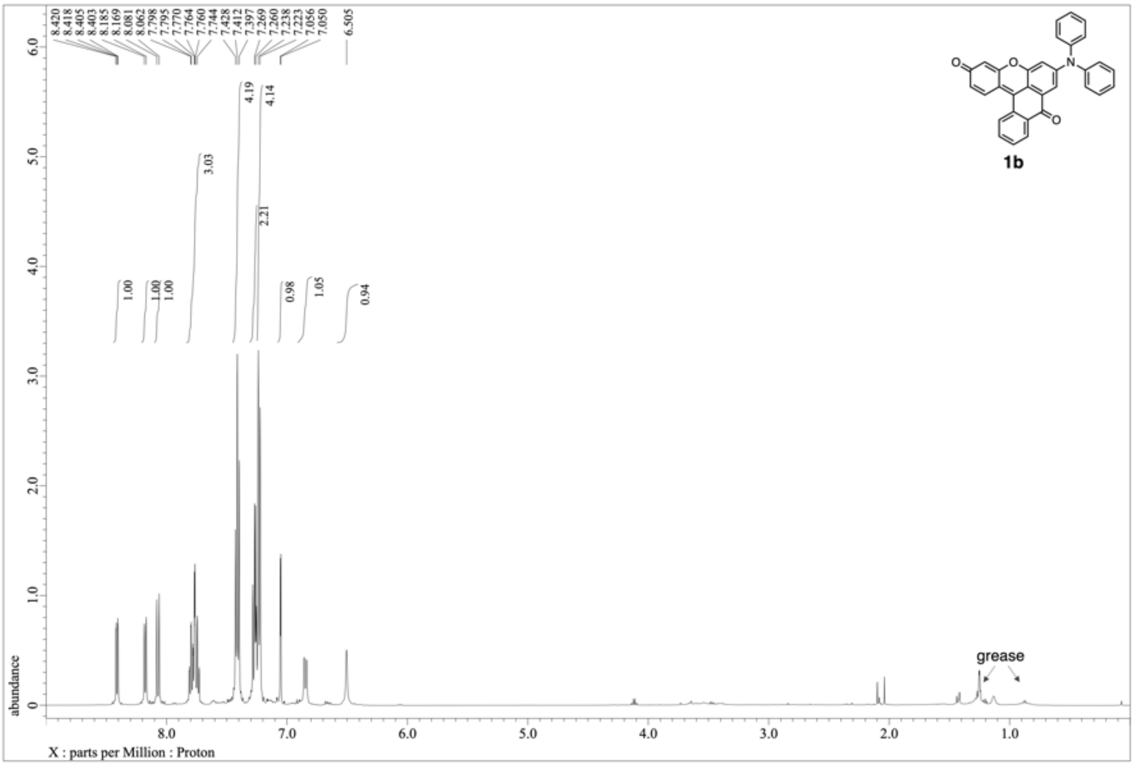


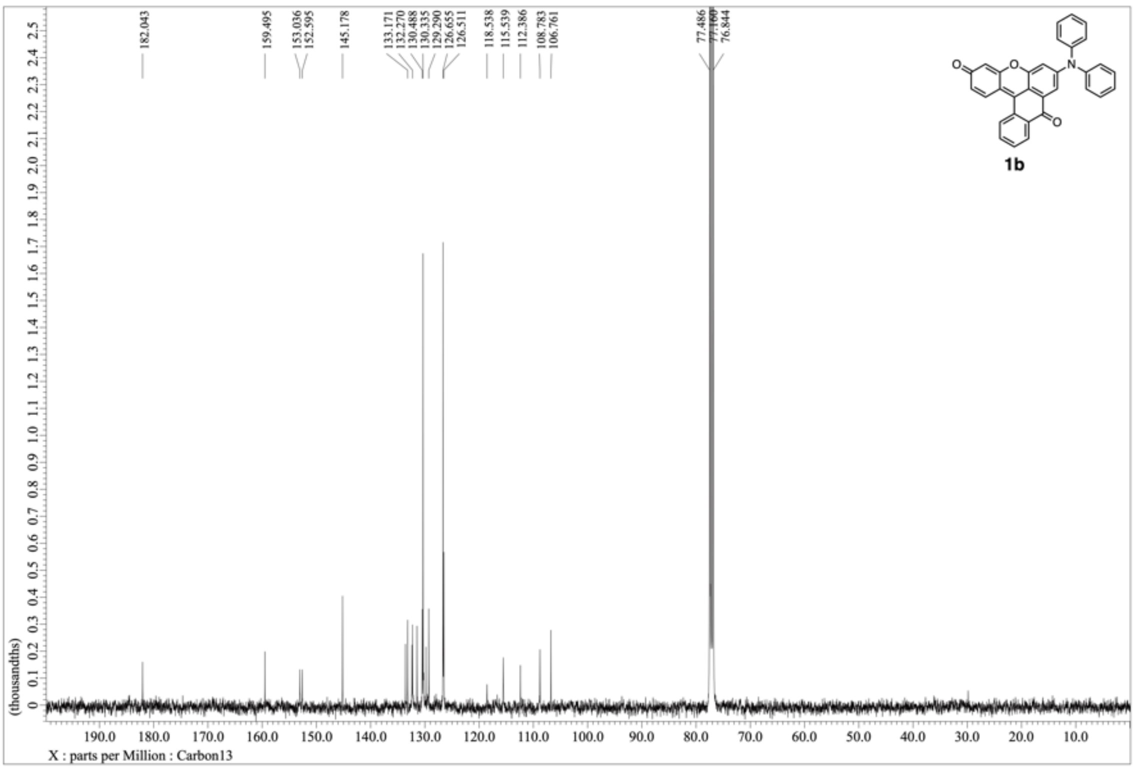
[1]H (top) and [13]C (bottom) NMR spectra of **3** at 25°C in $CDCl_3$.



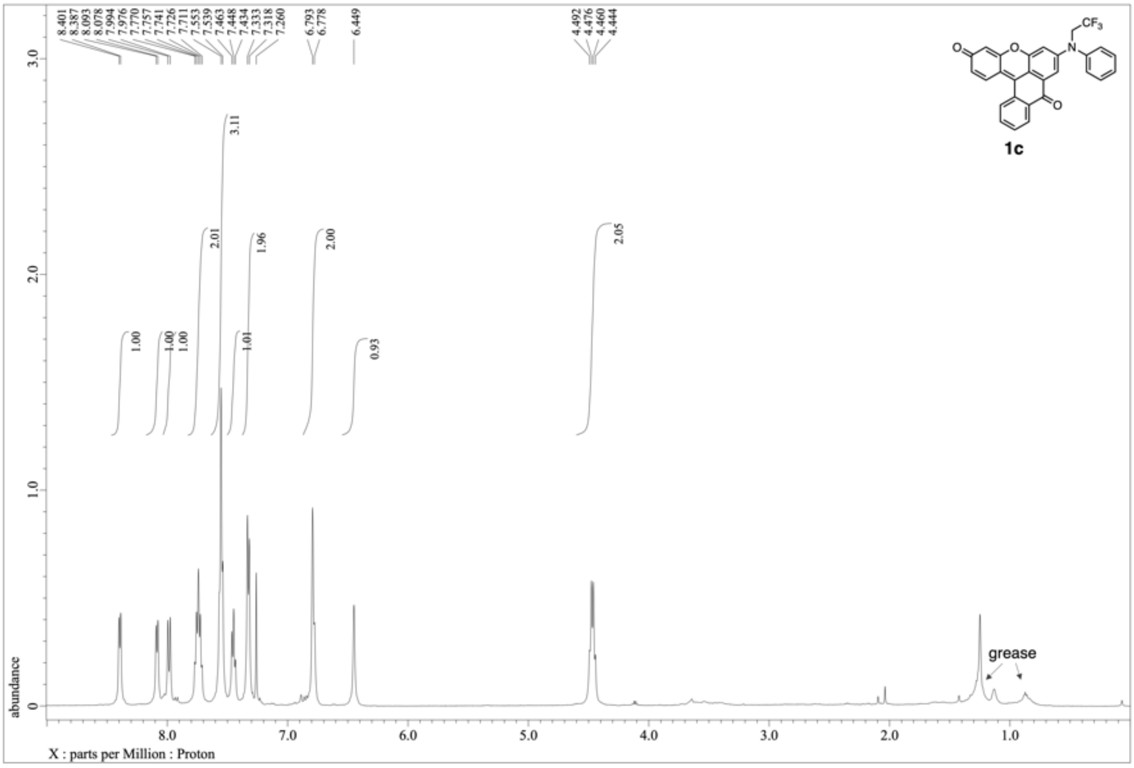


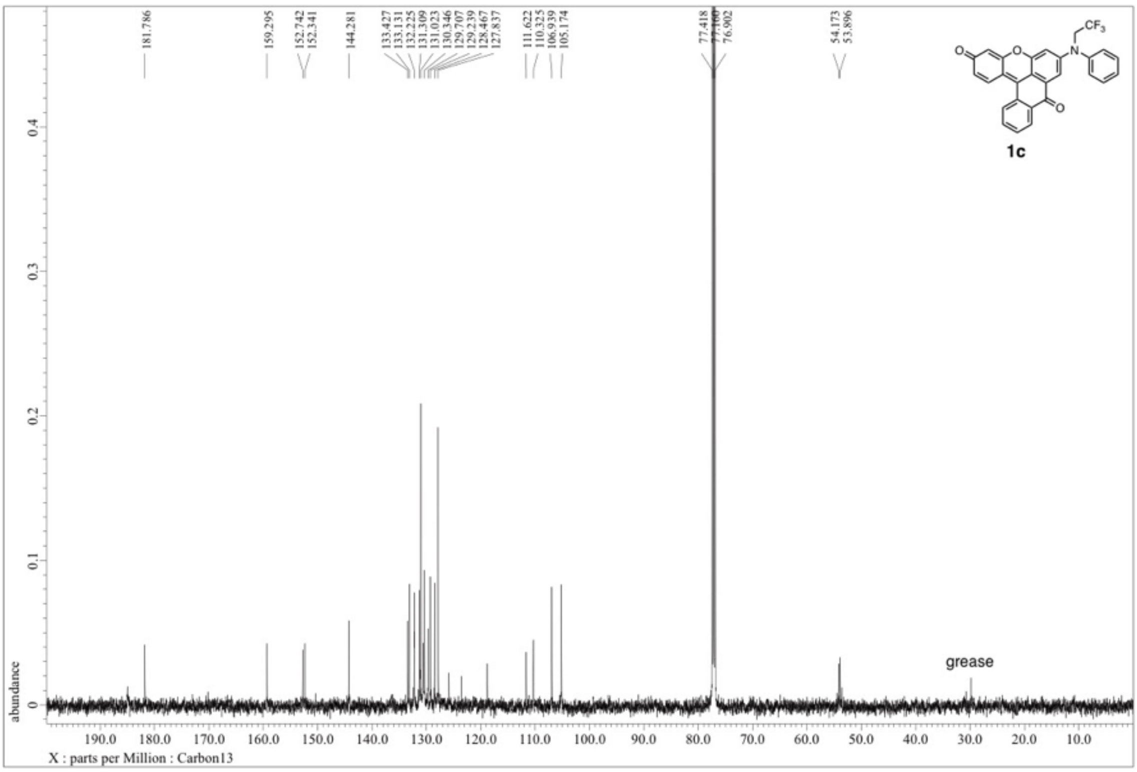
^{1}H (top) and ^{13}C (bottom) NMR spectra of **1a** at 25°C in $CDCl_3$.





[1]H (top) and [13]C (bottom) NMR spectra of **1b** at 25°C in $CDCl_3$.





[1]H (top) and [13]C (bottom) NMR spectra of **1c** at 25°C in $CDCl_3$.

7. Cartesian Coordinates (in Å) and Energies

1a (Fig. S8)

B3LYP/6-31+G**

G = -1319.313053 A. U.

C	-4.443547	-0.245337	0.168598
C	-3.486631	-1.306002	-0.112445
C	-2.148778	-1.061887	-0.113089
C	-1.574850	0.263592	0.085765
C	-2.524646	1.295519	0.455660
C	-3.859535	1.066325	0.504104
C	-0.198571	0.437042	-0.039409
C	0.623747	-0.756103	-0.064144
C	0.020589	-2.014798	-0.228922
C	0.762382	-3.193342	-0.270859
H	0.245887	-4.136435	-0.422401
C	2.147866	-3.128314	-0.096745
C	2.779380	-1.897271	0.125049
C	2.025522	-0.728516	0.133155
H	-3.864063	-2.302793	-0.310641
H	-2.139496	2.258204	0.766015
H	-4.553233	1.839200	0.820316
H	3.848584	-1.850638	0.295497
C	0.499653	1.731630	-0.132409
C	1.888592	1.798962	0.154506
C	-0.132576	2.910678	-0.579014
C	2.563104	3.026805	0.118581
C	0.553864	4.121348	-0.631734
H	-1.154889	2.875895	-0.931589
C	1.898809	4.191434	-0.252290
H	3.620472	3.031504	0.361203
H	0.039268	5.010119	-0.984606
H	2.429529	5.137939	-0.283746
C	2.698056	0.572064	0.393900
O	2.937727	-4.236439	-0.116888
H	2.408779	-5.031112	-0.269810
O	-5.669464	-0.428082	0.167562
O	-1.324897	-2.132100	-0.377233
O	3.877208	0.629765	0.732835

4a (Fig. S8)

B3LYP/6-31+G**

G = -1395.739330 A. U.

C	4.554493	-3.028945	0.116704
C	3.129397	-3.258069	0.155003
C	2.248629	-2.219765	0.002491
C	2.667660	-0.856138	-0.205631
C	4.088282	-0.626610	-0.238468
C	4.981397	-1.643156	-0.088322
C	1.707354	0.143064	-0.337392
C	0.324421	-0.202038	-0.294680
C	-0.039344	-1.556255	-0.093511
C	-1.357554	-1.984305	-0.031833
H	-1.544639	-3.036507	0.134556
C	-2.407429	-1.049652	-0.173069
C	-2.061564	0.322955	-0.385055
H	2.760798	-4.267041	0.307170
H	4.440897	0.388849	-0.386043
H	6.050426	-1.453506	-0.114812
H	-2.845564	1.057590	-0.516045
C	2.108325	1.558432	-0.621773
C	2.231513	2.581281	0.348816

C	2.349797	1.877211	-1.967153
C	2.588548	3.878734	-0.058413
C	2.706117	3.169278	-2.356092
H	2.252118	1.097711	-2.716327
C	2.826098	4.177082	-1.396556
H	2.678671	4.646717	0.701215
H	2.887817	3.383408	-3.404701
H	3.103018	5.185153	-1.687490
O	0.913282	-2.520493	0.055235
O	2.030336	3.324648	2.619910
N	-3.718326	-1.452013	-0.143738
C	-4.057413	-2.875700	-0.048119
H	-3.567147	-3.446566	-0.842723
H	-3.763973	-3.293056	0.923619
H	-5.135347	-2.983487	-0.157557
O	5.394124	-3.960180	0.251532
C	-4.797090	-0.508982	-0.041829
C	-5.717097	-0.392239	-1.091046
C	-4.959307	0.257976	1.119443
C	-6.794409	0.491103	-0.978562
H	-5.584045	-0.988176	-1.988965
C	-6.031579	1.147899	1.222298
H	-4.248839	0.154420	1.933850
C	-6.952297	1.264940	0.175649
H	-7.504293	0.578576	-1.795589
H	-6.151939	1.741077	2.123895
H	-7.787690	1.953380	0.259884
C	-0.747062	0.719574	-0.442679
H	-0.520402	1.766010	-0.615255
C	2.016682	2.403842	1.816474
O	1.810846	1.130924	2.203225
H	1.680292	1.131230	3.168113

Rh-DER (Fig. S14)

CAM-B3LYP/cc-pVDZ

G = -1344.066413 A. U.

C	-4.159571	-1.031381	-0.025700
C	-2.903990	-1.684547	-0.031119
C	-1.741032	-0.948374	-0.065075
C	-1.722401	0.472566	-0.095524
C	-2.994704	1.115518	-0.088484
C	-4.157406	0.408419	-0.054330
C	-0.493832	1.148573	-0.125358
C	0.694102	0.392423	-0.126271
C	0.614951	-1.024939	-0.092643
C	1.733581	-1.830342	-0.087921
H	1.605031	-2.912390	-0.056093
C	3.013530	-1.246777	-0.117337
C	3.121285	0.178431	-0.162561
C	2.000879	0.956677	-0.168473
H	-2.811390	-2.765716	0.010335
H	-3.024480	2.204449	-0.119185
H	-5.098407	0.951342	-0.068242
H	4.106825	0.636675	-0.211659
C	-0.446102	2.638183	-0.171578
C	-0.352160	3.391074	1.012119
C	-0.496686	3.271199	-1.416369
C	-0.311124	4.782626	0.898483
C	-0.452001	4.658640	-1.503826
H	-0.569441	2.668668	-2.323861
C	-0.358965	5.414791	-0.340277
H	-0.240191	5.382571	1.807878
H	-0.490186	5.144626	-2.479481
H	-0.323966	6.503878	-0.394779
O	-0.584163	-1.650787	-0.060710

N	4.107594	-2.043807	-0.121756
C	5.473455	-1.634404	-0.075119
C	6.336515	-2.037859	-1.093158
C	5.955201	-0.885526	0.999281
C	7.681849	-1.687350	-1.037364
H	5.949448	-2.622583	-1.929554
C	7.297700	-0.522191	1.037687
H	5.281013	-0.602210	1.808920
C	8.163015	-0.923588	0.022815
H	8.355981	-2.007243	-1.833032
H	7.673097	0.064773	1.877105
H	9.216916	-0.645161	0.061585
H	2.094346	2.041491	-0.217143
C	-0.299516	2.729074	2.364238
H	-1.183129	2.096671	2.541249
H	0.585304	2.081566	2.464725
H	-0.257943	3.477953	3.165359
H	3.942221	-3.039666	-0.211177
N	-5.316195	-1.723490	0.000922
C	-5.342533	-3.186160	-0.061092
H	-6.289799	-3.467850	-0.541703
H	-4.548830	-3.532438	-0.736903
C	-5.229868	-3.850174	1.305803
H	-5.286980	-4.943415	1.200697
H	-4.278655	-3.602119	1.798832
H	-6.047319	-3.532046	1.969790
C	-6.624258	-1.069015	0.094786
H	-6.545673	-0.188955	0.746445
H	-7.290283	-1.768286	0.619417
C	-7.213134	-0.700396	-1.260918
H	-8.209192	-0.252491	-1.131536
H	-6.578518	0.022782	-1.793882
H	-7.322972	-1.588530	-1.900883

1a (Fig. 2a, Fig. 3a, Fig. S13)

CAM-B3LYP/cc-pVDZ

G = -1318.602458 A. U.

C	5.065698	-2.592286	-0.073842
C	3.659842	-2.899448	0.151892
C	2.711597	-1.935167	0.120250
C	3.016048	-0.520777	-0.074201
C	4.404217	-0.229990	-0.391425
C	5.355604	-1.182475	-0.399488
C	1.997821	0.406124	0.012949
C	0.639856	-0.093920	0.016153
C	0.399074	-1.460967	0.170804
C	-0.880755	-1.998667	0.183861
H	-0.969432	-3.070698	0.339420
C	-1.997014	-1.168797	-0.011395
C	-1.767152	0.208544	-0.232935
C	-0.486511	0.723656	-0.206946
H	3.380699	-3.935316	0.341392
H	4.659354	0.782294	-0.695424
H	6.386915	-0.956681	-0.675561
H	-2.586355	0.892516	-0.443995
C	2.166755	1.873005	0.087252
C	1.077020	2.712892	-0.226753
C	3.347416	2.484364	0.538993
C	1.219931	4.101007	-0.211687
C	3.474210	3.867249	0.570805
H	4.167253	1.874765	0.909930
C	2.420213	4.683959	0.165482
H	0.349104	4.699914	-0.478441
H	4.404967	4.310302	0.928923

H	2.525444	5.769723	0.180475
C	-0.288769	2.171496	-0.475636
O	1.422221	-2.332761	0.338145
O	-1.207932	2.892312	-0.819655
N	-3.271924	-1.692581	-0.035151
C	-3.470235	-3.126070	0.079265
H	-2.906528	-3.669937	-0.694882
H	-3.158280	-3.510653	1.066903
H	-4.535449	-3.345453	-0.050544
O	5.951016	-3.438530	-0.036528
C	-4.424861	-0.852689	0.038829
C	-5.340039	-0.839308	-1.014278
C	-4.663191	-0.070651	1.170652
C	-6.488035	-0.056522	-0.932369
H	-5.140560	-1.442864	-1.901293
C	-5.803658	0.722829	1.241924
H	-3.945705	-0.086354	1.992454
C	-6.720671	0.728798	0.193481
H	-7.198952	-0.051660	-1.760262
H	-5.981095	1.334540	2.128025
H	-7.616811	1.348341	0.253429

1b (Fig. S13)

CAM-B3LYP/cc-pVDZ

G = -1510.196956 A. U.

O	1.322472	2.219474	0.129347
O	5.289619	4.484838	1.128360
O	0.395326	-3.671107	-0.027596
N	-2.970647	0.156831	-0.027226
C	1.251721	-0.166464	-0.072976
C	0.609268	1.071104	0.030945
C	2.665245	2.177952	0.376909
C	3.383542	0.908356	0.295653
C	0.429557	-1.307808	-0.106226
C	2.699728	-0.232272	-0.067725
C	3.275282	3.357630	0.631837
H	2.698235	4.281641	0.638943
C	1.055638	-2.654290	-0.140460
C	3.308470	-1.527729	-0.435705
C	-1.578419	0.048367	-0.027844
C	4.703750	3.431893	0.909027
C	4.789534	0.972470	0.660774
H	5.334836	0.037496	0.764119
C	2.522842	-2.699234	-0.394740
C	-3.612996	1.340186	-0.495978
C	-0.951057	-1.210209	-0.082765
H	-1.528805	-2.132041	-0.106995
C	-0.771924	1.192644	0.040093
H	-1.202549	2.189152	0.117363
C	4.624481	-1.645485	-0.911447
H	5.224054	-0.754228	-1.077856
C	5.404734	2.133436	0.952075
H	6.450643	2.163571	1.261815
C	3.081265	-3.942528	-0.694417
H	2.431331	-4.815320	-0.631058
C	-3.788881	-0.897392	0.475217
C	5.166276	-2.884879	-1.227116
H	6.191624	-2.941365	-1.596295
C	-4.577063	1.971216	0.293399
H	-4.821285	1.557373	1.272430
C	-3.301636	1.865276	-1.753372
H	-2.556619	1.365770	-2.374096
C	4.406060	-4.044997	-1.090893
H	4.836762	-5.018617	-1.329023

C	-5.221525	3.112818	-0.172138
H	-5.974263	3.597078	0.452313
C	-4.901727	3.643592	-1.419093
H	-5.403982	4.542746	-1.778960
C	-4.870513	-1.357040	-0.279545
H	-5.068393	-0.913486	-1.256043
C	-3.937494	3.016691	-2.205073
H	-3.685062	3.419562	-3.187444
C	-3.534426	-1.461144	1.728189
H	-2.695578	-1.095944	2.322052
C	-4.344690	-2.483915	2.209770
H	-4.133943	-2.920493	3.187468
C	-5.425766	-2.939024	1.459047
H	-6.063420	-3.737021	1.842224
C	-5.687294	-2.367643	0.216258
H	-6.530271	-2.718800	-0.381360

1c (Fig. S13)

CAM-B3LYP/cc-pVDZ

G = -1655.587784 A. U.

O	-1.474420	-2.210155	0.001050
F	4.773679	-1.914707	-1.395443
F	2.843160	-2.884171	-1.402840
F	4.483953	-3.755881	-0.288019
O	-0.059652	3.560571	0.491288
O	-5.671251	-4.212305	0.497883
N	2.968648	-0.513643	0.350494
C	1.598940	-0.301642	0.242409
C	-1.200244	0.167123	0.050411
C	-0.284436	1.228027	0.169734
C	-2.634716	0.358690	-0.023651
C	0.696456	-1.369553	0.131389
H	1.017804	-2.404728	0.061787
C	-0.667951	-1.124048	0.070420
C	-2.233718	2.820440	-0.085039
C	-2.824849	-2.077258	0.163830
C	-3.109282	1.732711	-0.290232
C	1.077067	1.007648	0.272597
H	1.722929	1.874569	0.390470
C	-3.431563	-0.748405	0.176059
C	3.877011	0.597709	0.381065
C	5.253911	2.202156	-0.775335
H	5.637446	2.616596	-1.708952
C	4.368930	1.128458	-0.809550
H	4.058819	0.686563	-1.756352
C	5.653685	2.741230	0.444851
H	6.348982	3.581846	0.469048
C	-0.793651	2.621874	0.240551
C	-2.667736	4.131750	-0.284170
H	-1.953312	4.933113	-0.095553
C	4.273264	1.138980	1.603904
H	3.871684	0.723172	2.529824
C	3.522197	-1.818785	0.615030
H	2.826757	-2.441509	1.195734
H	4.441388	-1.709016	1.206084
C	-4.377768	2.012970	-0.823508
H	-5.036791	1.199225	-1.114851
C	-4.989389	-3.197233	0.429954
C	-3.543501	-3.219394	0.250500
H	-3.044291	-4.185990	0.193022
C	5.164757	2.207256	1.634577
H	5.471938	2.629602	2.592573
C	-4.794413	3.320513	-1.038015
H	-5.785874	3.503590	-1.455487

C	-4.860034	-0.727310	0.446452
H	-5.334603	0.235836	0.617691
C	-3.951611	4.389707	-0.740025
H	-4.284526	5.416341	-0.899152
C	-5.585204	-1.854115	0.571553
H	-6.649216	-1.824815	0.811912
C	3.904815	-2.594655	-0.631814