Supporting Information for

Design strategy for tautomerization-based small panchromatic molecules

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1. General Experimental Procedure

General methods

Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (Merck Kieselgel 60F_{254}). Column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 63-210 μm) and flash column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 40-50 μm). Infrared spectra were obtained on a JASCO FT/IR-460Plus spectrometer. Only the strongest and/or structurally important absorption are reported as the IR data afforded in cm^{-1}. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a JEOL ECA 500II spectrometer (500 MHz for ^{1}H NMR and 125 MHz for $^{13}C\{^{1}H\}$ NMR). Coupling constant (*J*) is reported in hertz. Multiplicities are reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. ^{1}H and $^{13}C\{^{1}H\}$ spectra were referenced to $CHCl_3$ (δ: 7.26 and 77.16 ppm for ^{1}H and $^{13}C\{^{1}H\}$ NMR, respectively), trifluoroacetic acid (δ: 11.50 and 164.20 ppm for ^{1}H and $^{13}C\{^{1}H\}$ NMR, respectively) as an internal standard. The following abbreviations are used: s = singlet, d = doublet, m = multiplet. HRMS (ESI) spectra were recorded on Thermo Scientific LTQ Orbitrap XL ETD. Absorption spectra were recorded using a JASCO V-730BIO.

Single X-ray Structure Analysis

Single crystals of **1** and **2** were obtained by slow diffusion of Et_2O into a $CHCl_3$ solution of **1** at 10 ºC. Single crystals of **2** was obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of **2** at 10 ºC. 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. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition code CCDC 2423887 (**1**) and CCDC 2423533 (**2**)

Photoreactions

Photoreactions were performed in a Schlenck tube or two-neck round-bottom flask using a LED light (Techno Sigma PER-AMP series for 405 nm, 521 nm, 631 nm, ASAHI SPECTRA CL series for 730 nm, 830 nm and 940 nm, Kessil KSPR160L-740-C for 740 nm).

Materials

Reagents were purchased from FUJIFILM 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[4] and Gaussian 16[5] program package. The molecular structures optimizations were conducted at the B3LYP, CAM-B3LYP and M06-2X level using 6-31+G(d,p) 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, solvent = DMSO).[6] 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. Intrinsic reaction coordinates (IRC) were calculated to confirm the connection between the transition states and the reactants/products. In this study, the Gibbs free energy was adopted as the basis for discussion.

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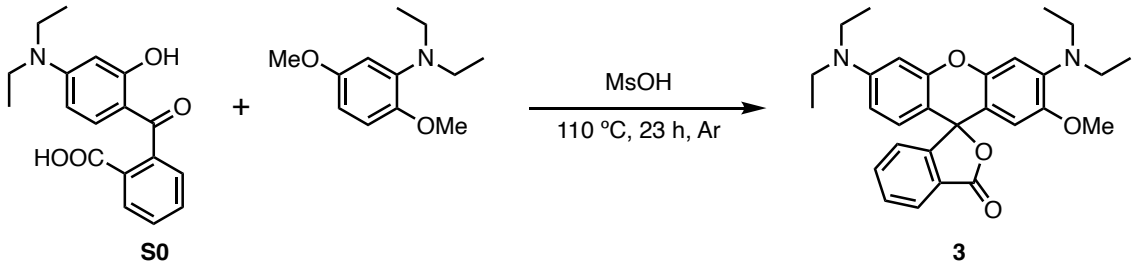
2. Experimental Procedure

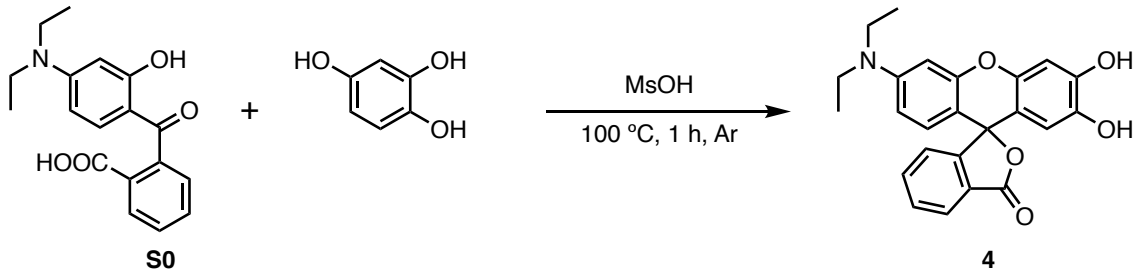
Synthesis of 3



2-(4-Diethylamino-2-hydroxybenzoyl)benzoic acid **S0** (153.4 mg, 0.490 mmol, 1 eq.) and *N,N*-diethyl-2,5-dimethyoxyaniline (106.4 mg, 0.508 mmol, 1.04 eq.) were dissolved in methanesulfonic acid (5 mL, 97.9 mM). The resulting mixture was stirred for 23 h at 110 °C in an oil bath. The reaction mixture was allowed to cool and was slowly poured into water (50 mL). 5 M NaOH aq. solution was added to the reaction mixture to neutralize it, and the solution was transferred to a separating funnel. The target compound was extracted from the aqueous solution with CH_2Cl_2 (50 mL ×3), and the organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash silica gel column chromatography (CH_2Cl_2/MeOH = 10/1–2/1) to afford rhodamine **3** (182.2 mg, 0.386 mmol, 76%) as a purple solid.

^{1}H NMR (500 MHz, DMSO-d6): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.81-7.75 (m, 1H), 7.74-7.68 (m, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 6.73 (s, 1H), 6.45-6.40 (s, 3H), 6.00 (s, 1H), 3.44 (s, 3H), 3.34 (q, *J* = 7.0 Hz, 4H), 3.18 (q, *J* = 7.0 Hz, 4H), 1.08 (t, *J* = 7.0 Hz, 6H), 1.00 (t, *J* = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d6): δ 168.8, 152.5, 152.2, 149.1, 148.4, 145.9, 142.4, 135.4, 130.0, 128.6, 126.6, 124.6, 124.1, 109.4, 109.2, 108.4, 106.6, 104.5, 96.8, 55.7, 44.8, 43.8, 12.3, 12.2; IR (KBr) 3490, 2969, 2930, 1760, 1631, 1612, 1504, 1414, 1233, 1217, 1103 cm^{-1}; HRMS (ESI, positive) *m/z* calcd. for $C_{29}H_{33}N_2O_4$ ($M+H^+$): 473.2435, found: 473.2437.

Synthesis of 4



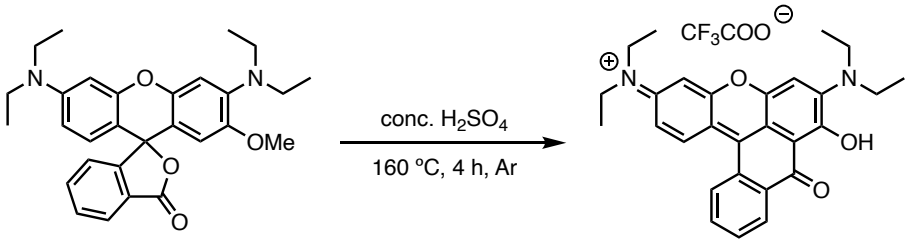
S0 **4**

S0 (204 mg, 0.651 mmol, 1 eq.) and 1,2,4-trihydroxybenzene (106.4 mg, 0.768 mmol, 1.18 eq.) were dissolved in methanesulfonic acid (10 mL, 65.1 mM). The resulting mixture was stirred for 1 h at 100 °C in an oil bath. The reaction mixture was allowed to cool and was slowly poured into water (50 mL). 5 M NaOH aq. solution was added to the reaction mixture to neutralize it, and the solution was transferred to a separating funnel. The target compound was extracted from the aqueous solution with CH_2Cl_2 (50 mL ×3), and the organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated in *vacuo*. Rhodol **4** was obtained as a red solid (260.0 mg, 0.644 mmol, 99%).

^{1}H NMR (500 MHz, DMSO-d6): δ 9.15 (bs, 1H), 8.11 (d, J = 7.0 Hz, 1H), 7.82-7.73 (m, 1H), 7.73-7.63 (m, 1H), 7.32 (d, J = 7.5 Hz, 1H), 6.80-6.40 (m, 4H) 6.03 (s, 1H), 3.50-3.25 (m, 4H), 1.08 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d6): δ 167.5, 153.6, 150.5, 133.5, 129.7, 128.6, 110.0, 102.5, 96.3, 44.3, 12.5; ^{1}H NMR* (500 MHz, TFA-d6): δ 8.53-8.37 (m, 1H), 7.93-7.75 (m, 2H), 7.62-6.87 (m, 5H), 6.86-6.76 (m, 1H), 3.82-3.62 (m, 4H), 1.35-1.18 (m, 6H); ^{13}C{^{1}H} NMR* (125 MHz, trifluoroacetic acid-d): δ 173.05, 172.96, 165.8, 159.8, 157.9, 154.6, 148.0, 137.2, 135.3, 134.5, 134.1, 132.6, 130.3, 121.8, 121.3, 121.0, 113.3, 105.6, 99.0, 52.7, 49.4, 13.5, 12.8; IR (KBr) 3239, 2972, 2508, 1696, 1606, 1526, 1482, 1398, 1340, 1222, 1176 cm^{-1}; HRMS (ESI, positive) *m*/*z* calcd. for $C_{24}H_{22}NO_5$ ($M+H^+$): 404.1492, found: 404.1496.

NOTE*: Because the ^{13}C{^{1}H} NMR signals originating from the xanthene skeleton of **4 could not be detected in neutral deuterated solvents (such as DMSO-d6), we also measured the ^{1}H and ^{13}C{^{1}H} NMR spectra of protonated **4** using deuterated trifluoroacetic acid (TFA-d).

Synthesis of 1

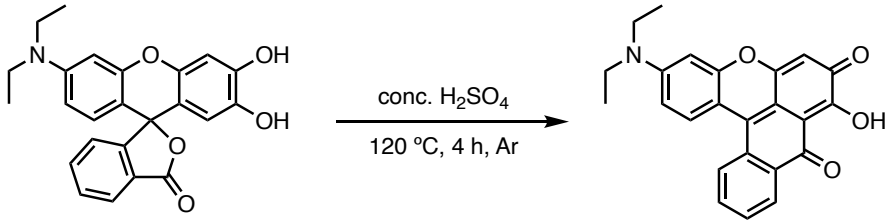


3 **1**

3 (104.9 mg, 0.222 mmol, 1 eq.) was dissolved in concentrated H_2SO_4 (10 mL, 22.2 mM). The resulting mixture was stirred for 4 h at 160 °C in an oil bath. The reaction mixture was allowed to cool to room temperature and was slowly added to the crash ice (100 g). MeOH (50 ml) was then added to the aqueous solution, and the mixed solution was extracted with CH_2Cl_2 (50 mL ×3). The combined organic phases were dried over Na_2SO_4 and concentrated in *vacuo*. **1** was isolated by silica gel column chromatography using CH_2Cl_2/MeOH (50/1) containing 0.5% trifluoroacetic acid (TFA). The fractions containing **1** were washed with water to remove excess TFA. The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo* to obtain **1** as a dark green solid. (33.3 mg, 60.0 μmol, 27%).

1: 27%, Dark green solid, ^{1}H NMR (500 MHz, trifluoroacetic acid-d): δ 8.97 (d, J = 9.0 Hz, 1H), 8.70-8.90 (m, 2H), 8.18-8.04 (m, 2H), 8.04-7.94 (m, 2H), 7.84 (d, J = 8.0 Hz, 1H), 6.86 (s, 1H), 3.96-3.66 (m, 8H), 1.59-1.17 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, trifluoroacetic acid-d): δ 179.1, 175.0, 166.9, 157.5, 154.5, 141.3, 137.8, 135.6, 134.9, 133.3, 131.9, 131.8, 131.5, 130.5, 122.8, 121.8, 119.8, 118.4, 106.2, 98.7, 58.0, 42.4, 13.9, 11.6; IR (KBr) 3406, 3209, 2976, 2933, 1691, 1627, 1592, 1554, 1522, 1330, 1185, 1120 cm^{-1}; HRMS (ESI, positive) *m/z* calcd. for $C_{28}H_{29}N_2O_3$ (M^+): 441.2173, found: 441.2183.

Synthesis of 2

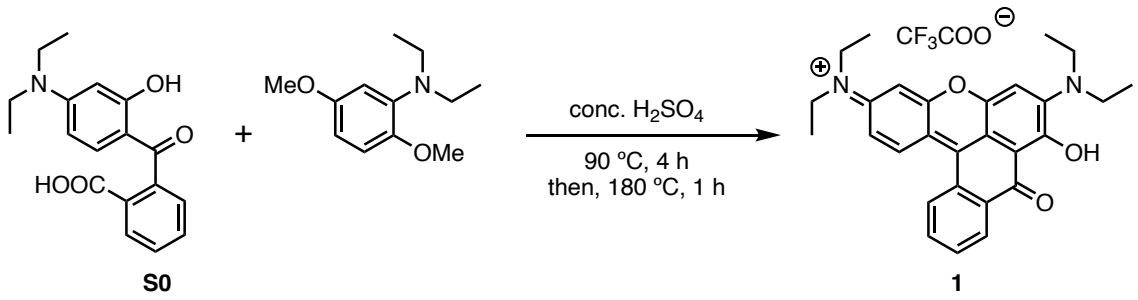


4 **2**

4 (100.3 mg, 0.249 mmol, 1 eq.) was dissolved in concentrated H_2SO_4 (5 mL, 49.7 mM). The resulting mixture was stirred for 4 h at 120 °C in an oil bath. The reaction mixture was allowed to cool to room temperature and was slowly added to the crash ice (200 g). 10% NaOH aq. solution was added to the reaction mixture to neutralize it, and the solution was then left at room temperature for over 1 h until **2** had fully precipitated. The precipitated solid was collected by filtration using a Kiriyama funnel and washed with water (10 mL ×2). The obtained solid was vacuum-dried, **2** was obtained as a green solid (95.7 mg, 0.248 mmol, 100%).

2: 100%, Green solid, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, J = 5.5 Hz, 1H), 8.06 (d, J = 6.0 Hz, 1H), 7.75-7.45 (m, 3H), 6.48 (d, J = 8.0 Hz, 1H), 6.27 (s, 1H), 6.08 (s, 1H), 3.65-3.20 (m, 4H), 1.45-1.08 (m, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 177.12, 176.04, 174.95, 159.61, 154.02, 150.00, 132.97, 132.73, 130.00, 128.86, 128.09, 127.65, 126.85, 112.60, 110.00, 106.65, 106.50, 97.20, 44.89, 12.73; IR (KBr) 3434, 2971, 2869, 1626, 1558, 1405, 1241, 1066 cm^{-1}; HRMS (ESI, positive) *m*/*z* calcd. for $C_{24}H_{19}NO_4$ ($M+H^+$): 386.1387, found: 386.1400.

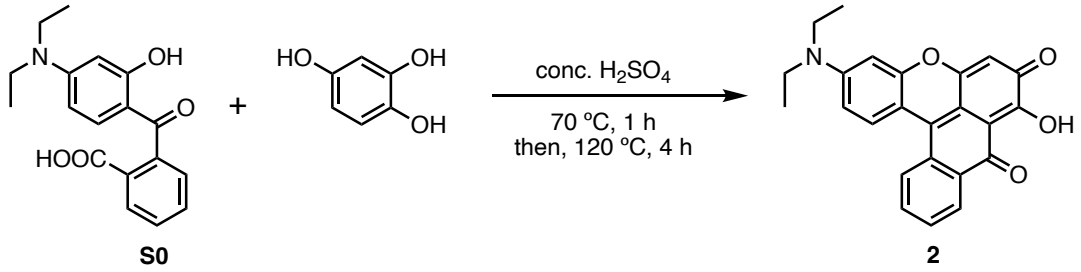
One–pot synthesis of 1



S0 **1**

S0 (232 mg, 0.741 mmol, 1 eq.) and dimethoxy *N,N*-diethylaniline (155 mg, 0.741 mmol, 1 eq.) was dissolved in concentrated H_2SO_4 (10 mL, 0.74 M). The resulting mixture was stirred at 90 °C for 4 h, heated to 180 °C, and stirred for an additional hour. The reaction mixture was allowed to cool to room temperature and was slowly added to the crash ice (100 g). MeOH (50 ml) was then added to the aqueous solution, and the mixed solution was extracted three times CH_2Cl_2 (50 mL ×3). The combined organic phases were dried over Na_2SO_4 and concentrated in *vacuo*. **1** was isolated by silica gel column chromatography using CH_2Cl_2/MeOH (50/1) containing 0.5% trifluoroacetic acid (TFA). The fractions containing **1** were washed with water to remove excess TFA. The combined organic phase was dried over Na_2SO_4 and concentrated in *vacuo* to obtain **1** as a dark green solid. (91.6 mg, 0.208 mmol, 22%).

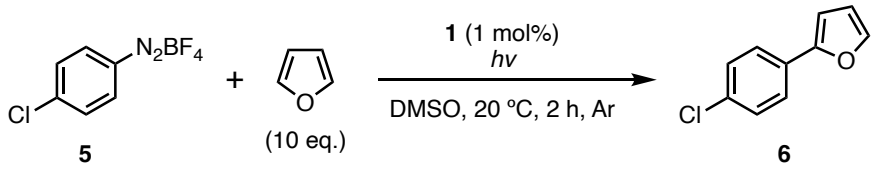
One–pot synthesis of 2



S0 **2**

S0 (100 mg, 0.319 mmol, 1 eq.) and 1,2,4-trihydroxy benzene (48.3 mg, 0.383 mmol, 1.2 eq.) were dissolved in concentrated H_2SO_4 (5 ml, 0.64 M). After stirring the mixture at 70 ºC in an oil bath for 1 h, the temperature was then further increased to 120 ºC in an oil bath, and the mixture was stirred for another 4 h. The reaction mixture was allowed to cool and was slowly poured onto crushed ice (200 g). 10% NaOH aq. solution was added to the reaction mixture to neutralize it, and the solution was then left at room temperature for over 1 h until the **2** had fully precipitated. The precipitated solid was collected by filtration using a Kiriyama funnel and washed with water (10 mL ×3). The obtained solid was vacuum-dried, **2** was obtained as a green solid (122 mg, 0.317mmol, 99%).

Procedure for the reaction of aryl diazonium tetrafluoroborates with furan[1]

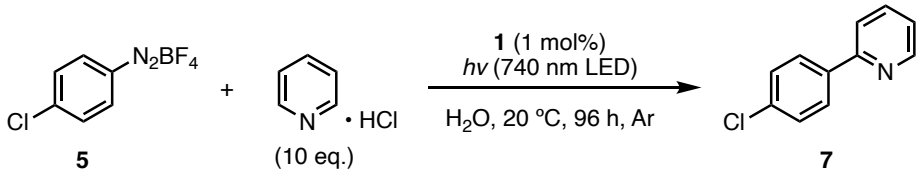


The photoreactions were performed with reference to the condition of ref [1]. In a 10 mL dried round bottom flask equipped with magnetic stirring bar, the **1** (5.5 mg, 10.0 μmol, 0.01 eq.), 4-chlorobenzenediazonium tetrafluoroborate **5** (226.4 mg, 1.00 mmol, 1 eq.) and furan (0.727 ml, 10.0 mmol, 10 eq.) were dissolved in dehydrated DMSO (4 mL, 0.25 mM). Then, LED (λ = 405 nm) was attached to the flask. After 2 h of irradiation the reaction mixture was transferred to separating funnel, diluted with diethyl ether (100 mL) and washed with water (100 mL ×2). The organic layers were dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash silica gel column chromatography (Hexane/AcOEt = 100/0–10/1) to afford **6** (102.6 mg, 0.574 mmol, 57%) as a colorless powder. ^1H and $^{13}C\{^1H\}$ NMR of **6** were in agreement with the literature[1].

2-(4-Chloro-phenyl)-furan (6)

6: 57%, Colorless powder, ^1H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 1.5 Hz, 1H), 7.37 (d, J = 9.0 Hz, 2H), 6.65 (d, J = 3.5 Hz, 1H), 6.49 (dd, J = 3.5 Hz, 2.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 153.0, 142.5, 142.3, 133.0, 129.4, 129.1, 128.8, 125.2, 124.9, 111.9, 105.5.

Procedure for the reaction of aryl diazonium tetrafluoroborates with pyridine hydrochloride[2]



In a 10 mL dried round bottom flask equipped with magnetic stirring bar, the **1** (5.5 mg, 10 μmol, 0.01 eq.), **5** (226.2 mg, 1.00 mmol, 1 eq.) and pyridine hydrochloride (1.15 g, 9.99 mmol, 10 eq.) were dissolved in H_2O (4.0 mL, 0.25 mM). Then, 740 nm LED was attached to the flask. After 96 h of irradiation the reaction mixture was transferred to separating funnel, diluted with diethyl ether (100 mL) and washed with water (100mL ×2). The organic layers were dried over Na_2SO_4, filtered and concentrated in *vacuo*. Purification of the crude product was achieved by flash column chromatography using hexane/AcOEt (100/0–10/1) as eluent. **7** was obtained as a colorless powder (94.2 mg, 0.526 mmol, 53%). ^1H and $^{13}C\{^1H\}$ NMR of **7** were in agreement with the literature[3].

7: 53%, Colorless powder, ^1H NMR (500 MHz, $CDCl_3$): δ 8.70-8.66 (m, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.77-7.71 (m, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.23 (ddd, J = 7.5 Hz, 4.5 Hz, 1.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 156.3, 149.9, 137.9, 138.0,135.2, 129.0, 128.3, 122.5, 120.4.

Reference

[1] Hari, D. P.; Schroll, P.; König, B. *J. Am. Chem. Soc.* **2012**, *134*, 2958−2961.

[2] Xue, D.; Jia, Z.-H.; Zhao, C.-J.; Zhang, Y.-Y.; Wang, C.; Xiao, J. *Chem.-Eur. J.* **2014**, *20*, 2960–2965.

[3] Tanioka, M. Oyama, M.; Nakajima, K.; Mori, M.; Harada, M.; Matsuya, Y.; Kamino, S. *Phys. Chem. Chem. Phys.*, **2024**, *26*, 4474–4479.

3. Figure and Tables

In this paper, the atomic numberings of compounds **1** and **2** follows Fig. S1. The crystal structure of compound **1** contained six different molecular structures, A–F, while the crystal structure of compound **2** contained two different molecular structures, A and B. In the labels of each atom in the crystal structures of **1** and **2**, suffixes A–F are added after each atomic numbering to distinguish each molecular structure.

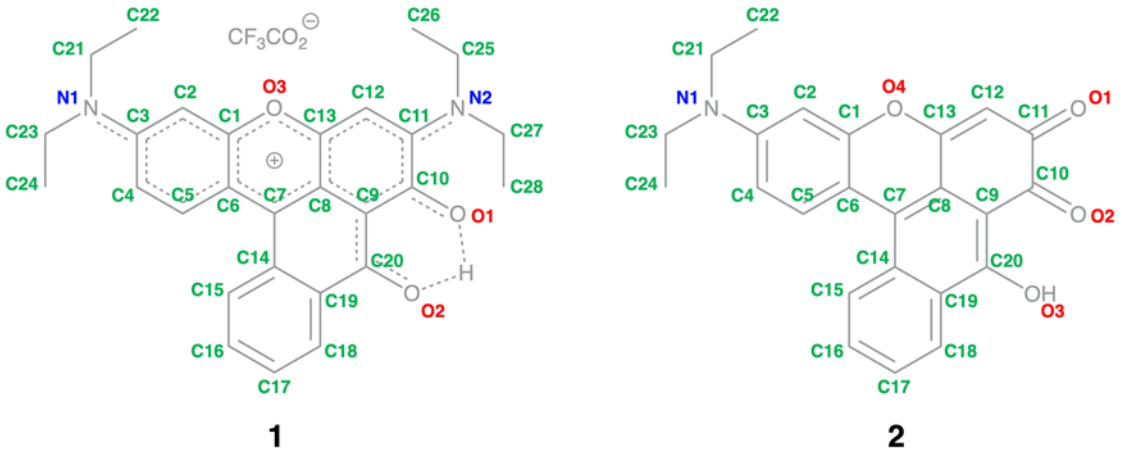
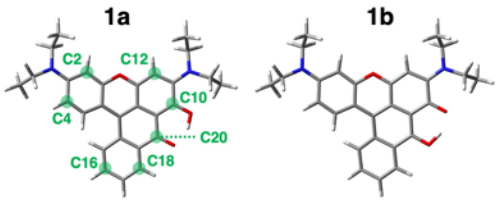
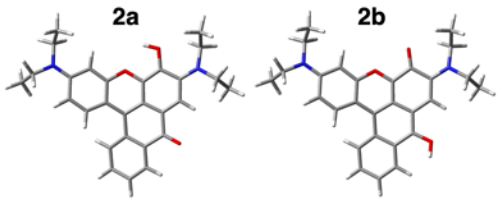


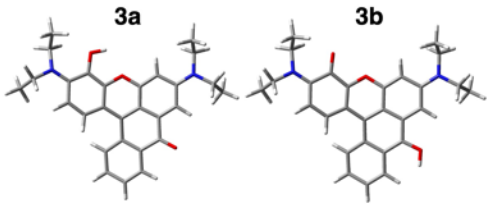
Fig. S1. The atomic numbering scheme employed in the present work



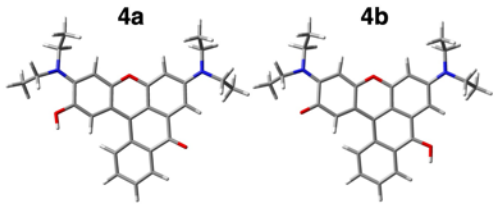
	1a	1b
Energy difference (kJ/mol)		
B3LYP/6-31+G**	+1.43	0
CAM-B3LYP/6-31+G**	+0.46	0
M062X/6-31+G**	+0.28	0
Ratio		
B3LYP/6-31+G**	36	64



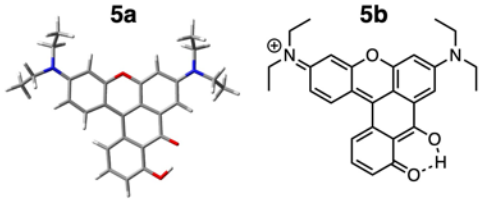
	2a	2b
Energy difference (kJ/mol)		
B3LYP/6-31+G**	0	+61.97
CAM-B3LYP/6-31+G**	0	+73.20
M062X/6-31+G**	0	+72.63
Ratio		
B3LYP/6-31+G**	100	0



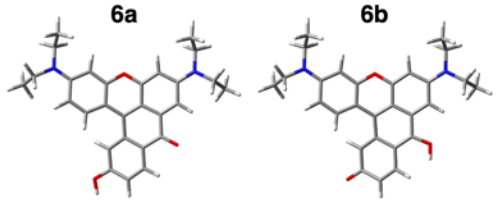
	3a	3b
Energy difference (kJ/mol)		
B3LYP/6-31+G**	0	+117.16
CAM-B3LYP/6-31+G**	0	+145.91
M062X/6-31+G**	0	+141.97
Ratio		
B3LYP/6-31+G**	100	0



	4a	4b
Energy difference (kJ/mol)		
B3LYP/6-31+G**	0	+68.45
CAM-B3LYP/6-31+G**	0	+88.27
M062X/6-31+G**	0	+86.69
Ratio		
B3LYP/6-31+G**	100	0



	5a	5b
Energy difference (kJ/mol)		
B3LYP/6-31+G**	0	–
CAM-B3LYP/6-31+G**	0	–
M062X/6-31+G**	0	–
Ratio		
B3LYP/6-31+G**	100	0



	6a	6b
Energy difference (kJ/mol)		
B3LYP/6-31+G**	0	+77.92
CAM-B3LYP/6-31+G**	0	+87.53
M062X/6-31+G**	0	+86.85
Ratio		
B3LYP/6-31+G**	100	0

Fig. S2. Relationship between the introduction site of the hydroxyl group and the energies of the C20-carbonyl (**a**) and C20-hydroxy (**b**) forms. Calculations were performed in gas phase. The energy value of **5b** could not be obtained because it changed to **5a** during the structural optimization.

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

Chemical formula	$C_{32}H_{30}F_6N_2O_7$ ($C_{28}H_{29}N_2O_3^+ + CF_3COO^- + CF_3COOH$)
Chemical formula weight	668.58
Recrystallization solvent	CH_2Cl_2 / Et_2O
Included solvent	CF_3COOH, CF_3COO^-
Crystal system	Monoclinic
Space group [No.]	*P 1 c* 1 [7]
Crystal color, habit	Metallic greenish black
Crystal size, mm	0.596 × 0.173 × 0.128
a, Å	10.37180(10)
b, Å	56.7017(7)
c, Å	16.5454(2)
α, °	90
β, °	105.4720(10)
γ, °	90
Volume, Å^3	9377.71(19)
Z	12
D_{calcd}, g/cm^3	1.421
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	1.070
$2\theta_{max}$ °	68.2510
F(000)	4152
Reflns collected	24581
Unique reflns	22512
No. of parameters	2732
R1 ($I > 2.00\sigma(I)$)	0.0706
R (all reflection)	0.0745
GOF	1.039

Table S2. Crystal data and structure refinement for **2**.

Chemical formula	$C_{26}H_{21}Cl_6NO_4$ ($C_{24}H_{19}NO_4 + 2(CHCl_3)$)
Chemical formula weight	624.14
Recrystallization solvent	$CHCl_3$ / Et_2O
Included solvent	$CHCl_3$
Crystal system	Orthorhombic
Space group [No.]	$P\,n\,a\,2_1$ [33]
Crystal color, habit	Clear light green
Crystal size, mm	0.149 × 0.123 × 0.051
a, Å	24.0040(6)
b, Å	7.00530(10)
c, Å	31.8407(7)
α, °	90
β, °	90
γ, °	90
Volume, Å^3	5354.18(19)
Z	8
D_{calcd}, g/cm^3	1.549
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	6.153
$2\theta_{max}$ °	67.9070
F(000)	2544
Reflns collected	7655
Unique reflns	6875
No. of parameters	746
R1 ($I > 2.00\sigma(i)$)	0.0863
R (all reflection)	0.0916
GOF	1.076

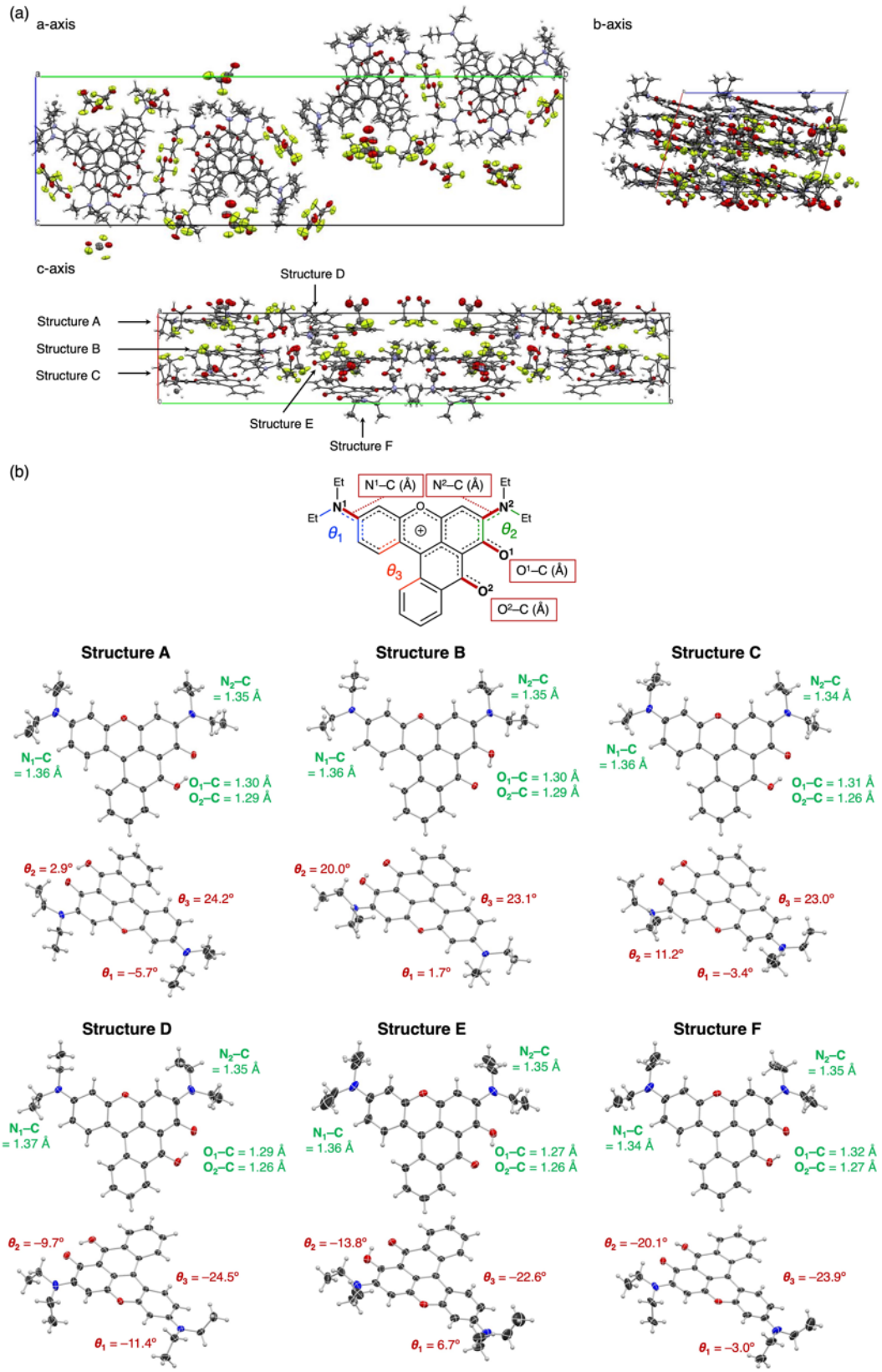


Fig. S3. (a) X-ray crystal structure for **1**. The thermal ellipsoids are scaled to the 30% probability level. (b) Six distinct structural motifs in the crystal structure of compound **1**

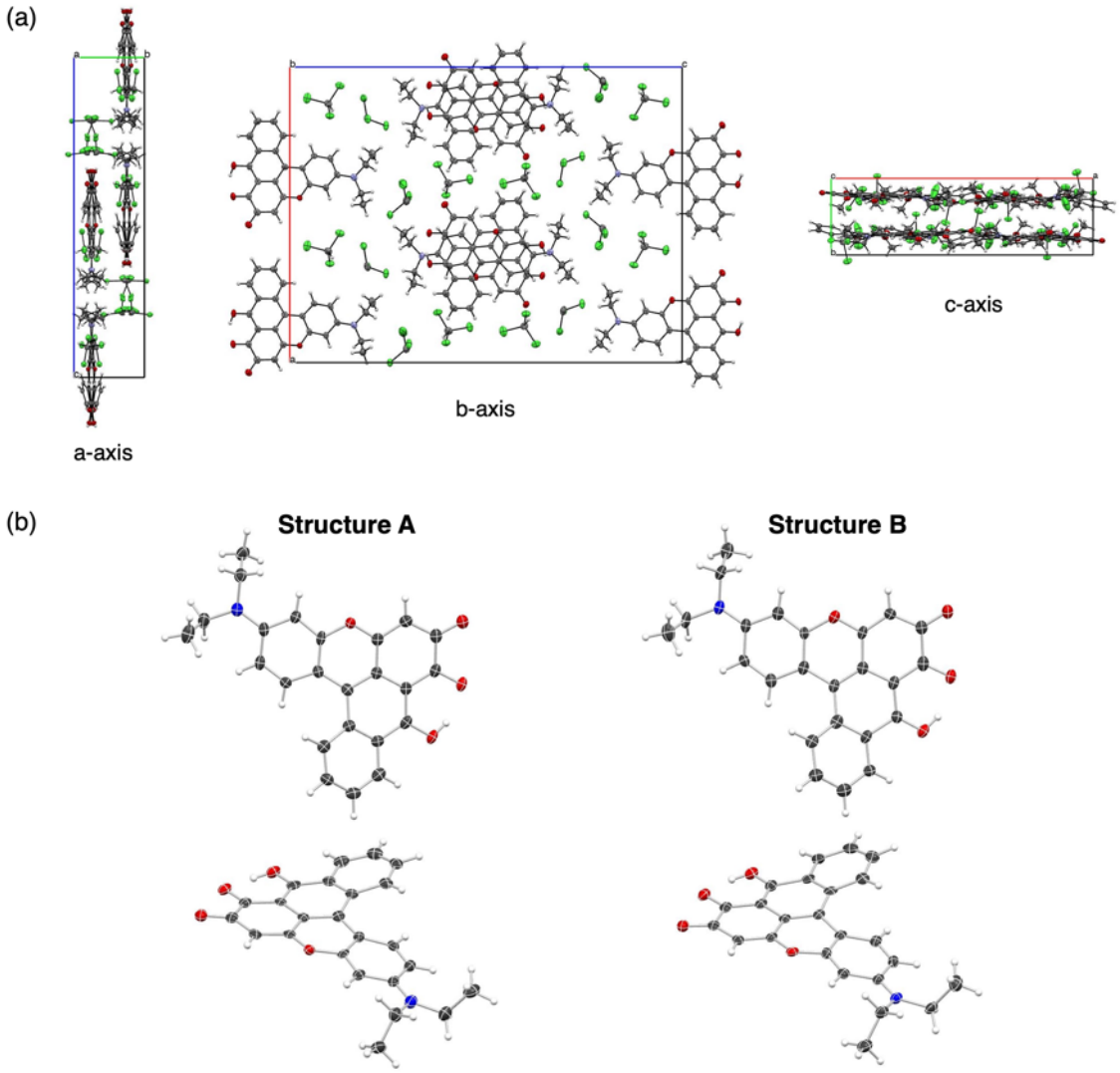


Fig. S4. (a) X-ray crystal structure for **2**. The thermal ellipsoids are scaled to the 30% probability level. (b) Six distinct structural motifs in the crystal structure of compound **1**

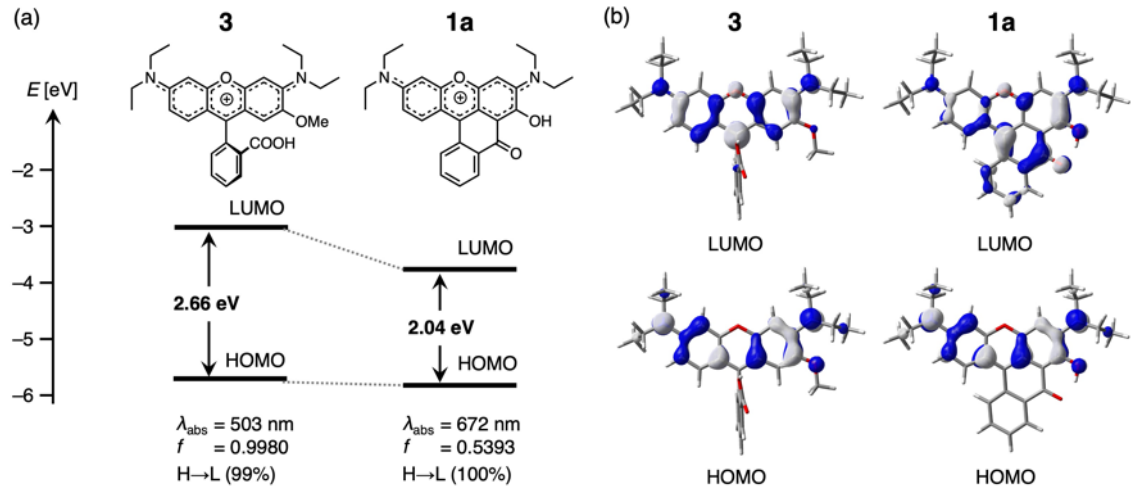


Fig. S5. Energy diagrams and frontier molecular orbitals of **3** and **1a**. Calculations were performed at B3LYP/6-31+G** level in PCM (DMSO).

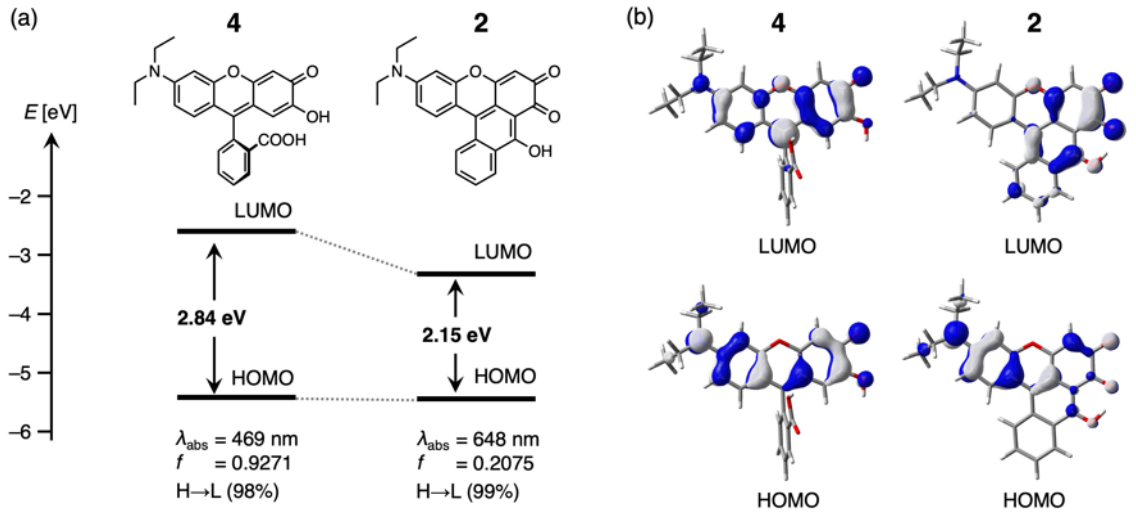


Fig. S6. Energy diagrams and frontier molecular orbitals of **4** and **2**. Calculations were performed at B3LYP/6-31+G** level in PCM (DMSO).

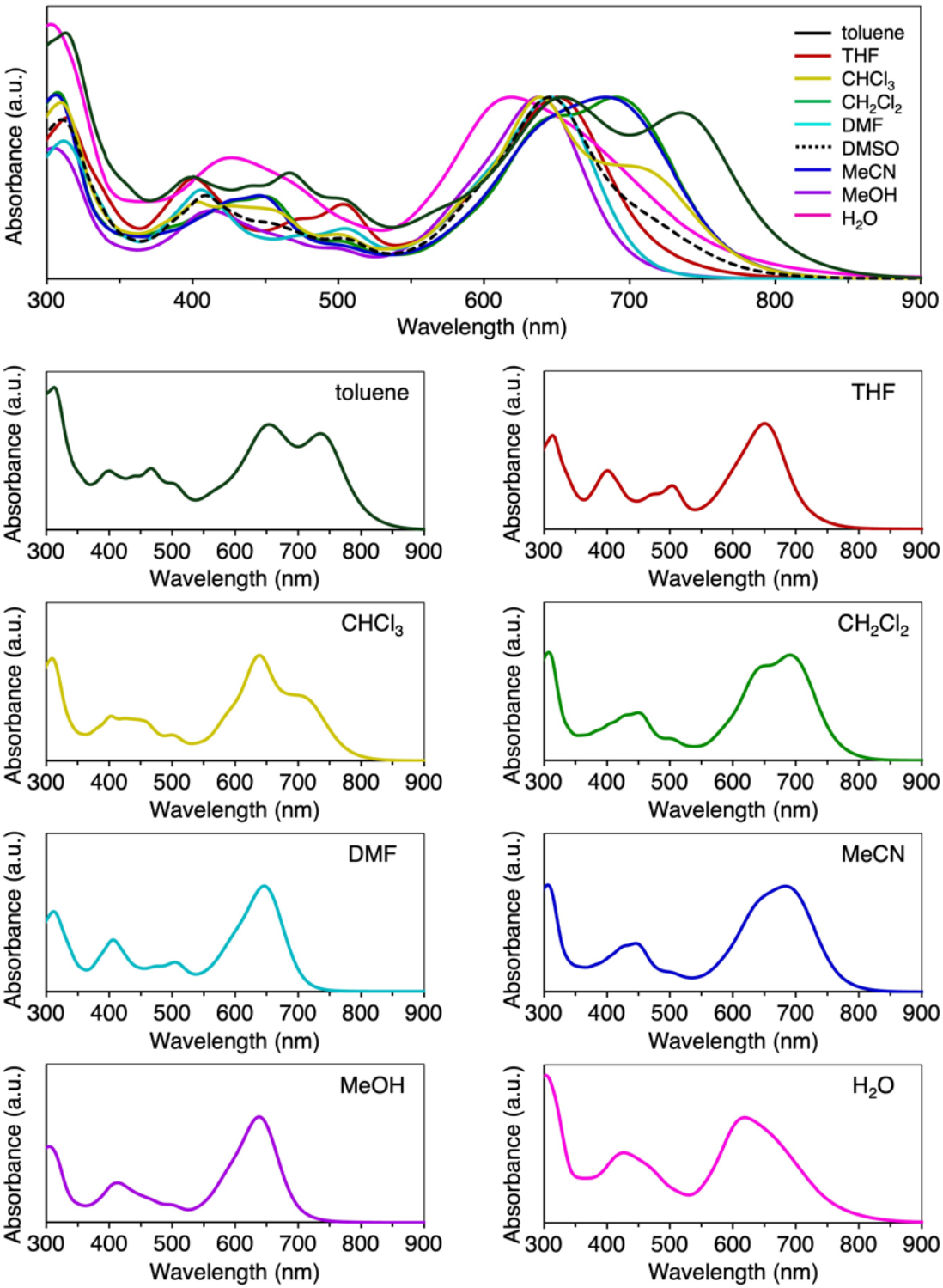


Fig. S7. Absorption spectra of **1** in various organic solvent.

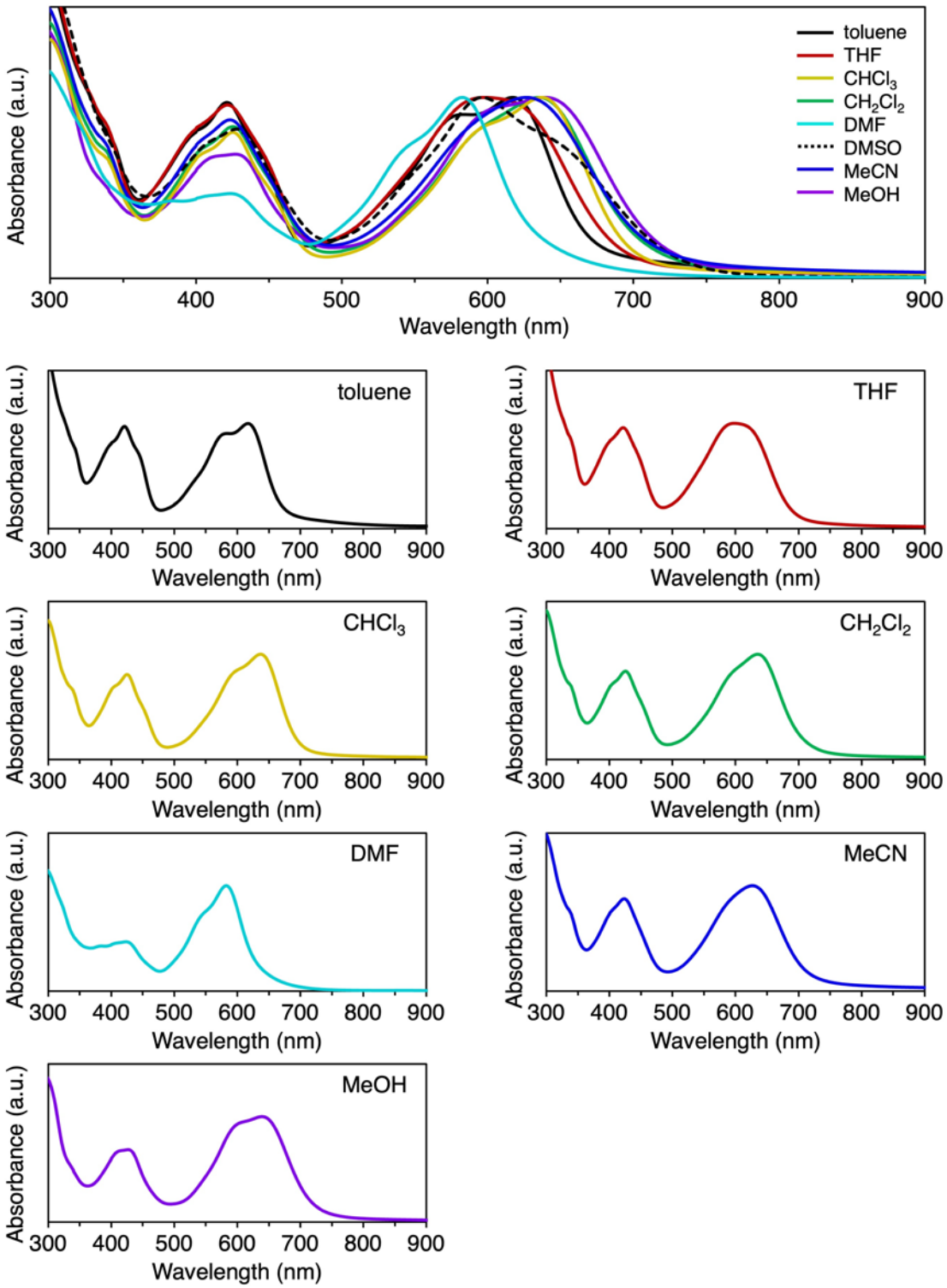


Fig. S8. Absorption spectra of **2** in various organic solvent.

Table S3. Optical properties of **1** and **2** in organic solvents.

	1		**2**	
	λ_{abs} ($S_0 \rightarrow S_1$) [nm]	ε [cm^{-1} M^{-1}]	λ_{abs} ($S_0 \rightarrow S_1$) [nm]	ε [cm^{-1} M^{-1}]
Toluene	654	–[a)]	617	16000
THF	652	31000	598	15000
$CHCl_3$	639	35000	637	18000
CH_2Cl_2	691	34000	635	19000
DMF	646	38000	583	22000
DMSO	646	41000	596	16000
MeCN	684	26000	627	17000
MeOH	638	41000	640	20000
H_2O	619	16000	–[b)]	–[b)]

a) Accurate numerical values could not be determined because of the low solubility of the **1**.

b) Compound **2** is insoluble in water.

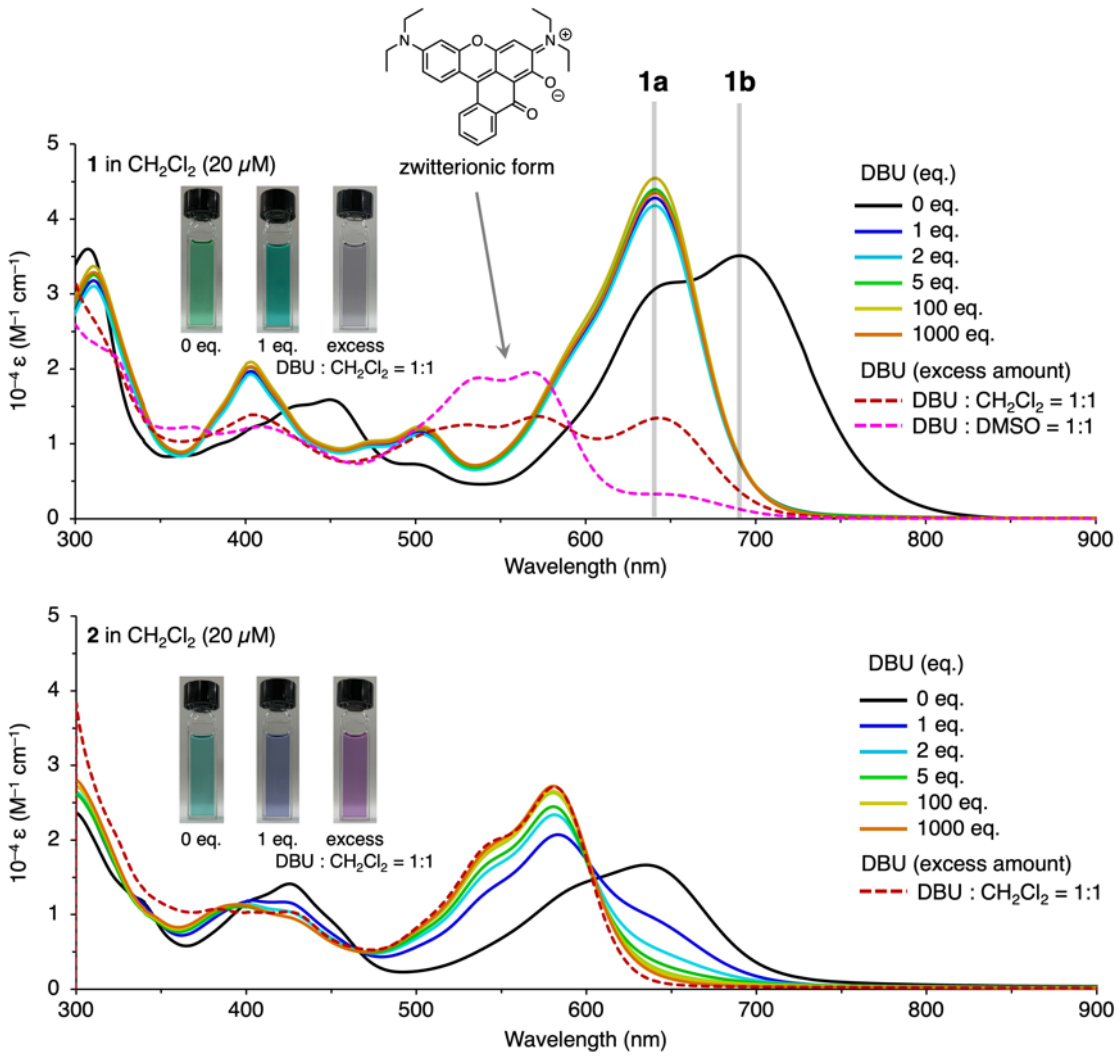


Fig. S9. Absorption spectra of **1** (top panel) and **2** (bottom panel) in CH_2Cl_2 containing DBU. These dyes concentration were 20 μM. The inset photographs show the color change upon addition of DBU.

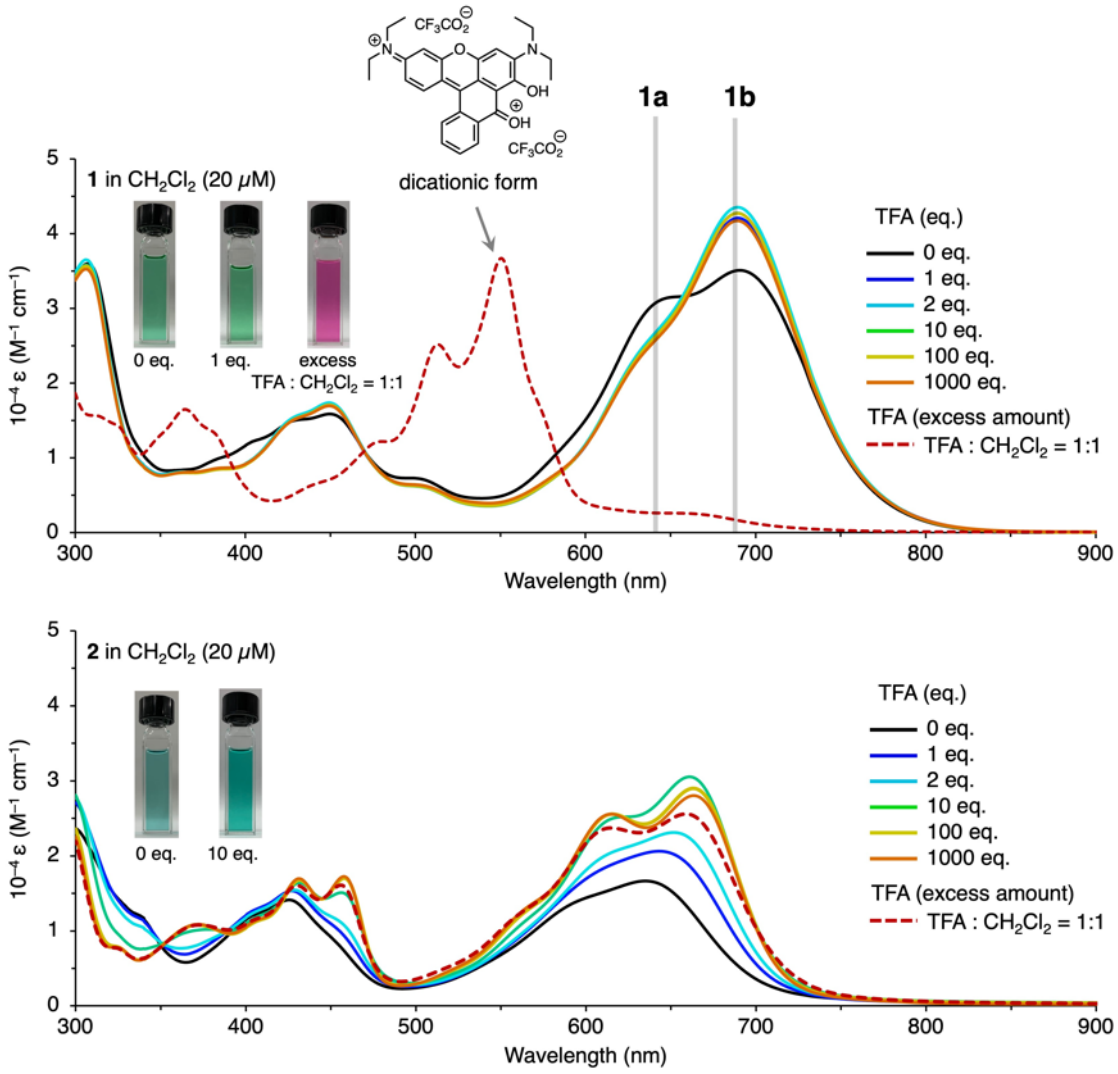


Fig. S10. Absorption spectra of **1** (top panel) and **2** (bottom panel) in CH_2Cl_2 containing trifluoroacetic acid (TFA). These dyes concentration were 20 μM. The inset photographs show the color change upon addition of TFA.

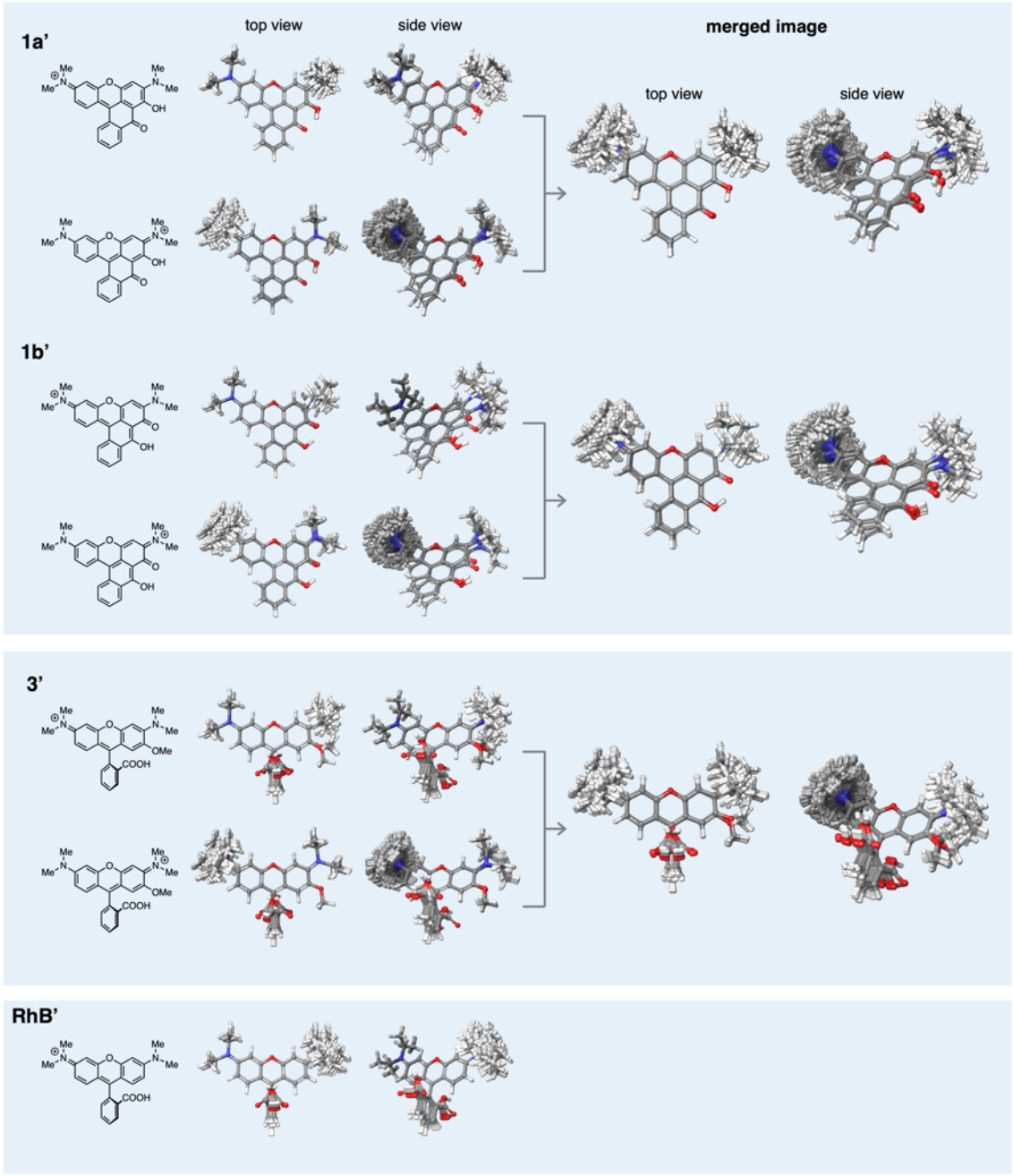


Fig. S11. Overlays of stable conformations of **1a'**, **1b', 3'** and **RhB'.** The conformations were obtained by MacroModel-based Monte Carlo simulation. Model **1a'**, **1b', 3'** and **RhB'** are analogues of **1a, 1b**, **3**, **RhB** respectively, with ethyl groups shortened to methyl groups. Conditions: OPLS4, Mixed torsional/Low-mode sampling, 3000 conformers, under vacuum. Energy window for obtained structures: 3 kJ/mol

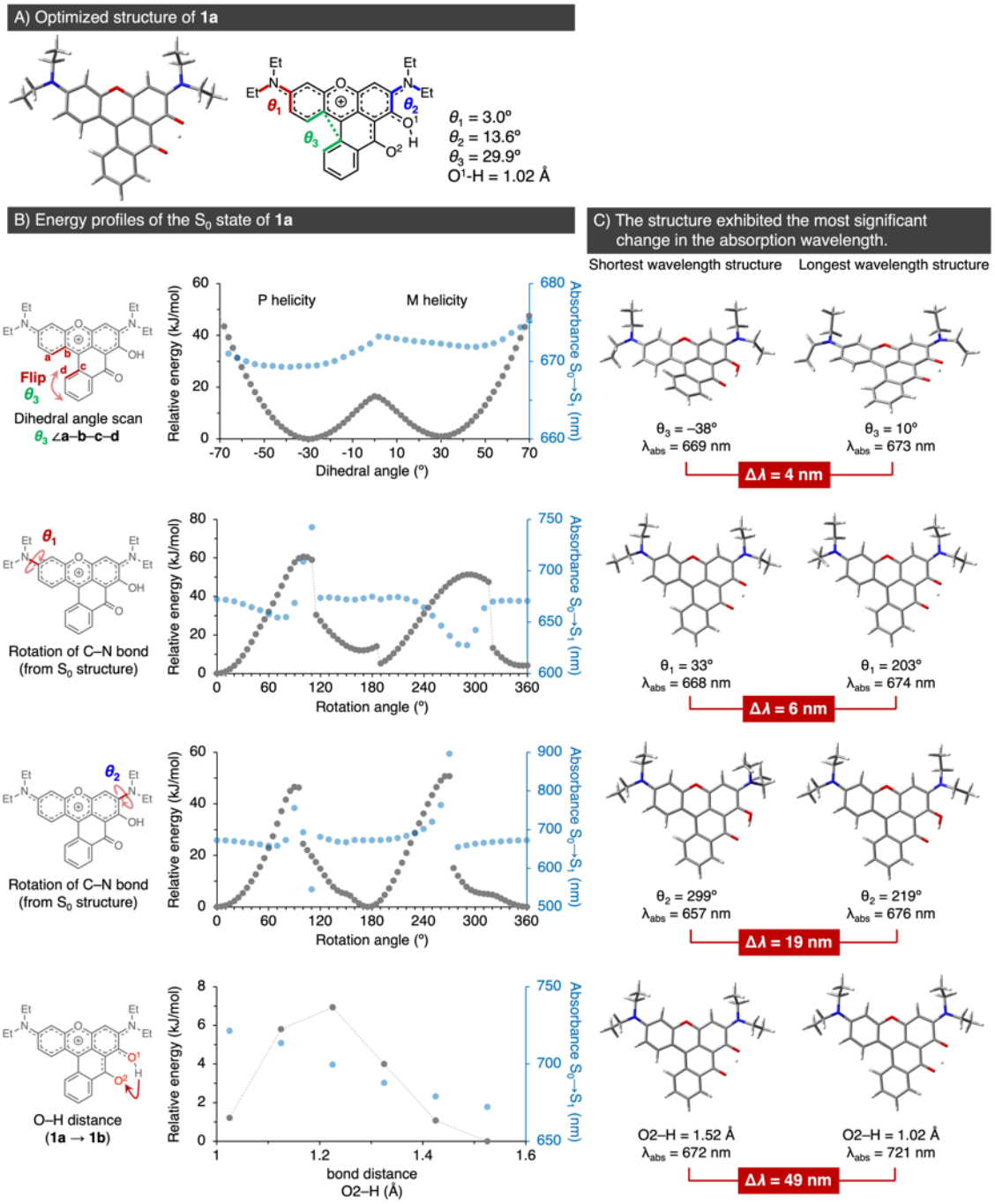


Fig. S12. Energy profiles of the S_0 state of **1a** as a function of dihedral angles (θ_1–θ_3) and O–H distance (O1–H). The geometries were optimized at the B3LYP/6-31+G** level in PCM (DMSO). The absorption spectrum of each structure was calculated at the TD-B3LYP/6-31+G** level in PCM (DMSO).

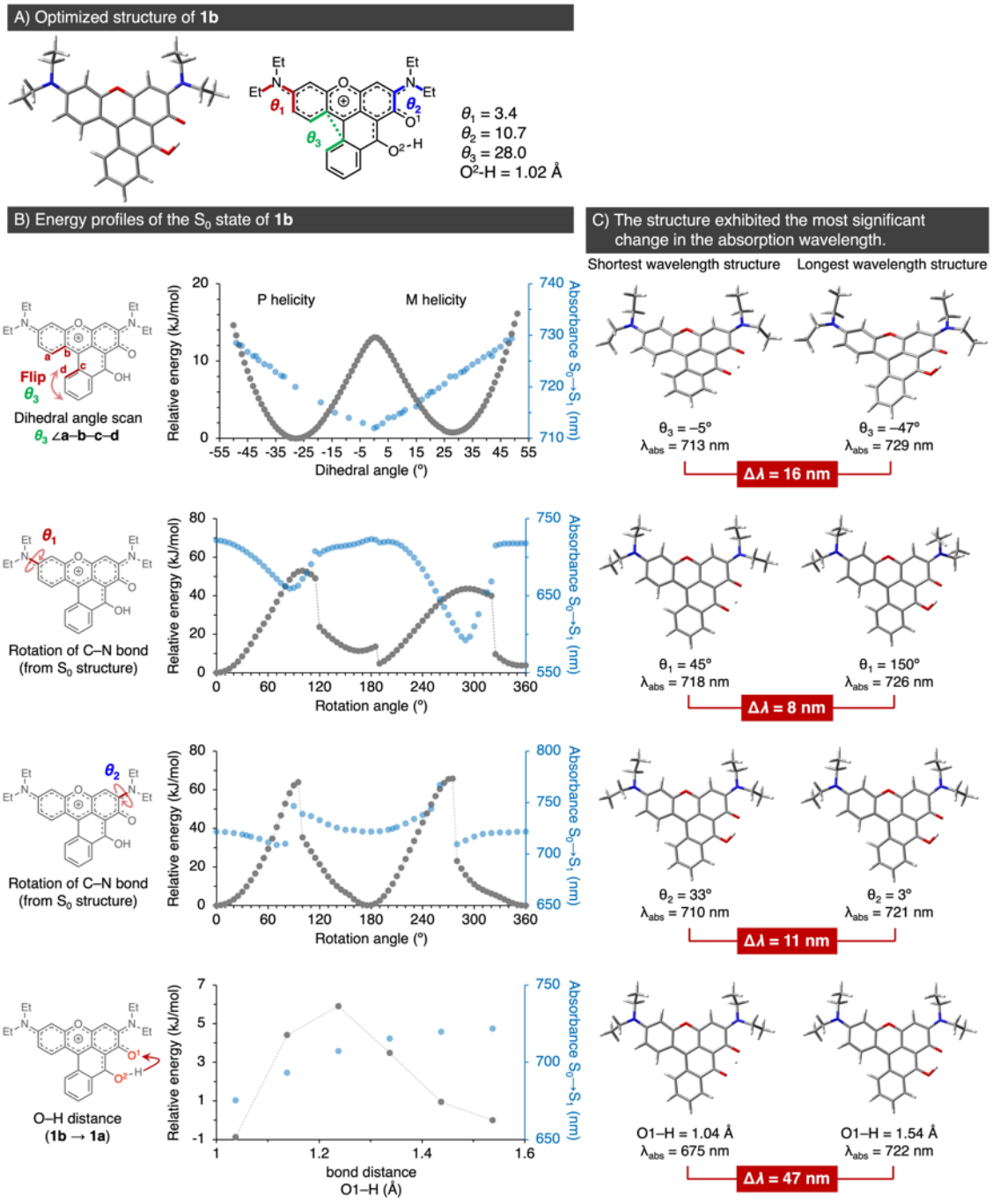


Fig. S13. Energy profiles of the S_0 state of **1b** as a function of dihedral angles (θ_1–θ_3) and O–H distance (O2–H). The geometries were optimized at the B3LYP/6-31+G** level in PCM (DMSO).

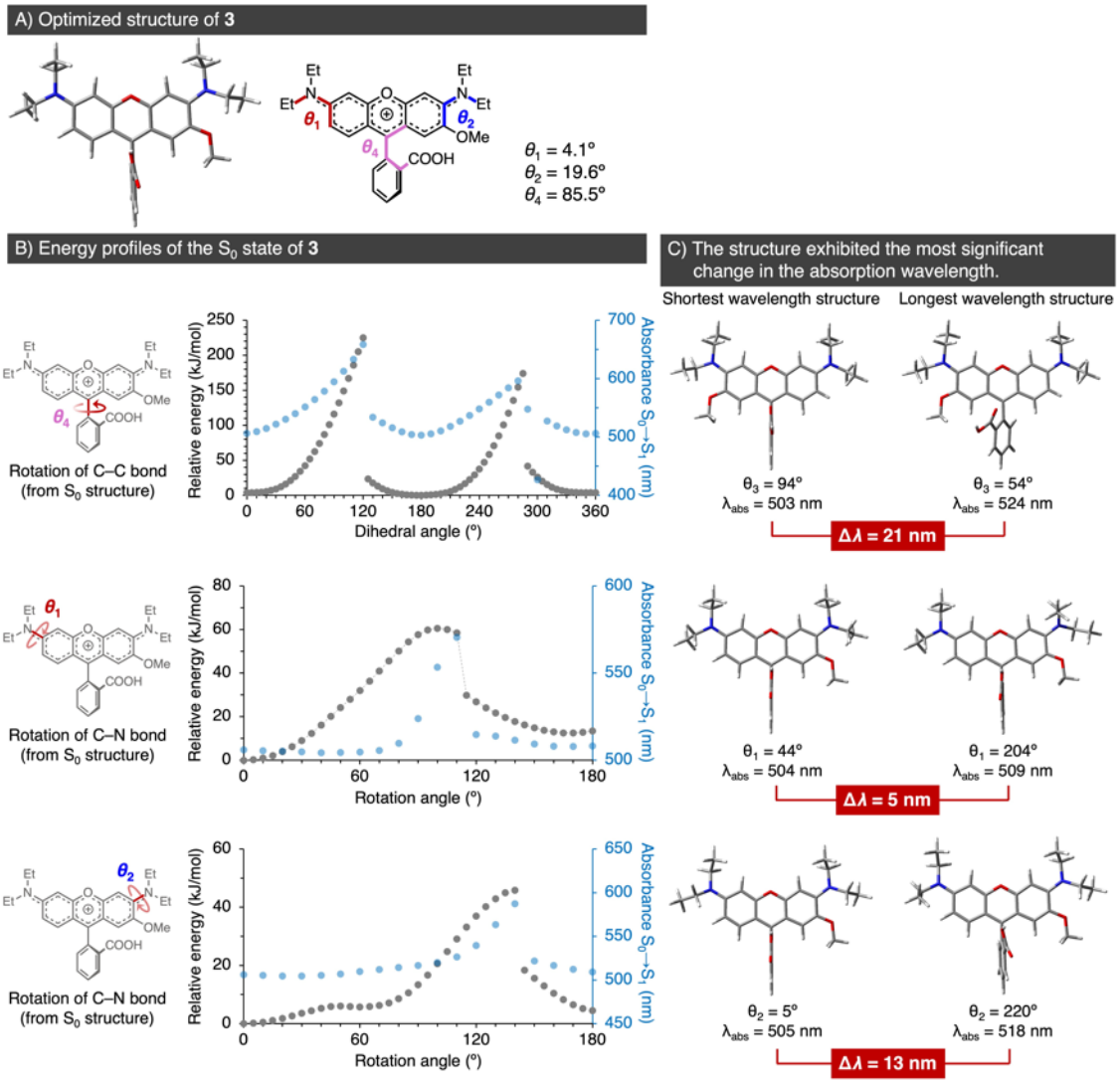


Fig. S14. Energy profiles of the S_0 state of **S1** as a function of dihedral angles (θ_1–θ_3). The geometries were optimized at the B3LYP/6-31+G** level in PCM (DMSO).

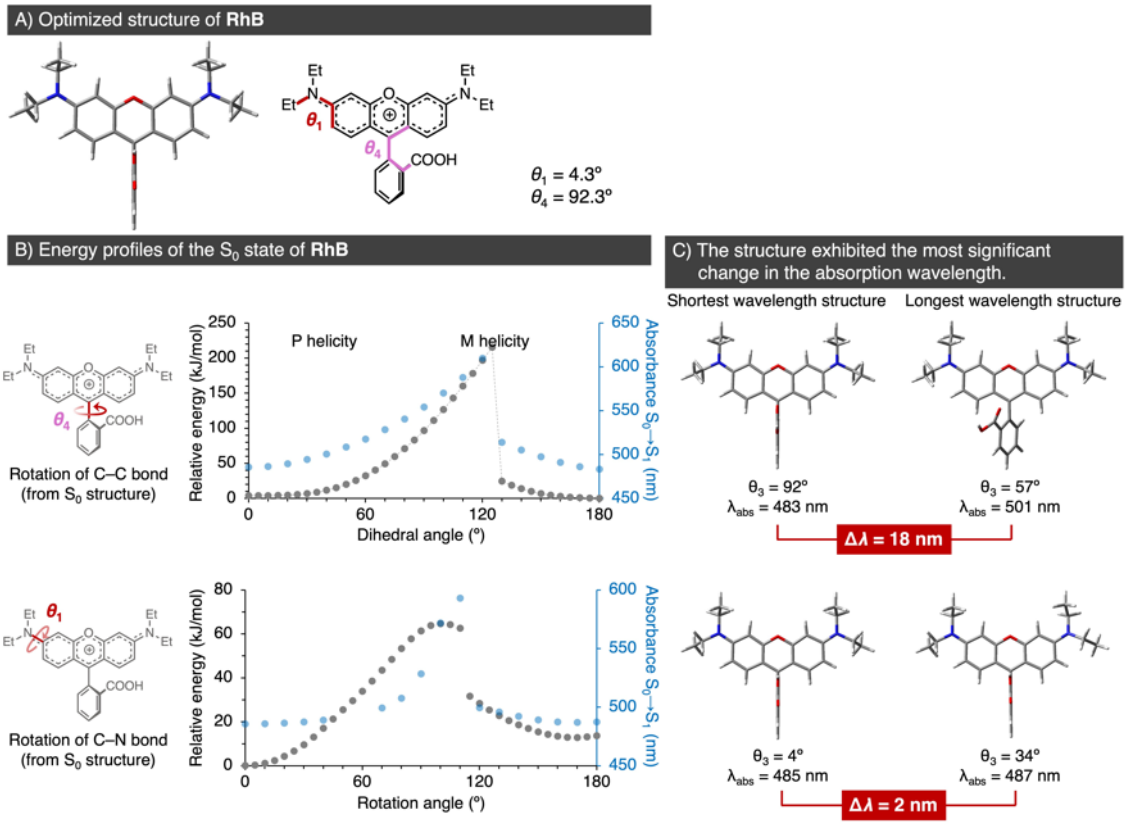


Fig. S15. Energy profiles of the S_0 state of **S1** as a function of dihedral angles (θ_1–θ_3). The geometries were optimized at the B3LYP/6-31+G** level in PCM (DMSO).

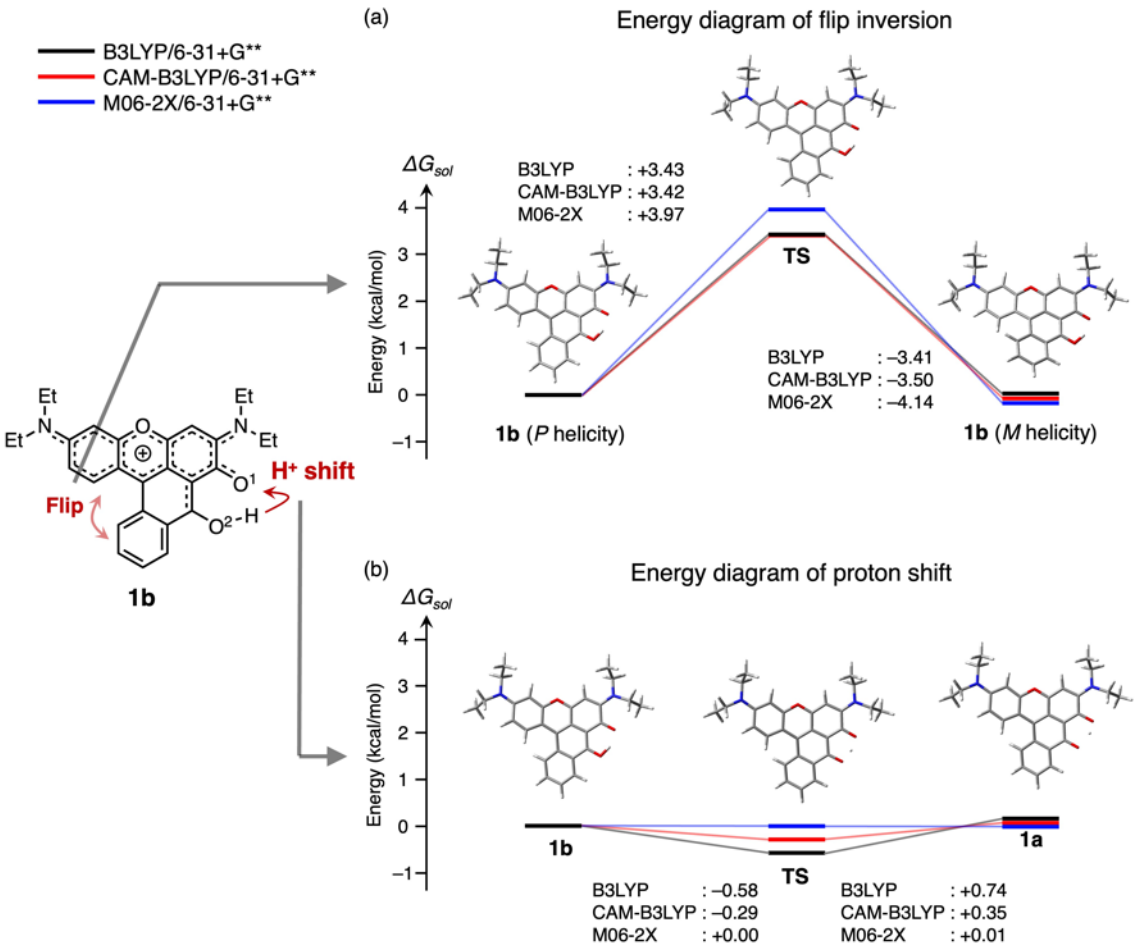


Fig. S16. Energy diagram of (a) flip inversion and (b) proton shift of **1b**. The calculations were performed at the B3LYP/6-31G** level in PCM (DMSO). Regarding the calculation of (b), the electronic energy value was highest for the TS state under all calculation conditions. On the other hand, the value of the zero-point vibrational energy was the smallest in the TS state. As a result, the Gibbs free energy of the TS state was lower than that of **1a** and **1b**. These results suggest that the proton shift proceeds with almost no barrier.

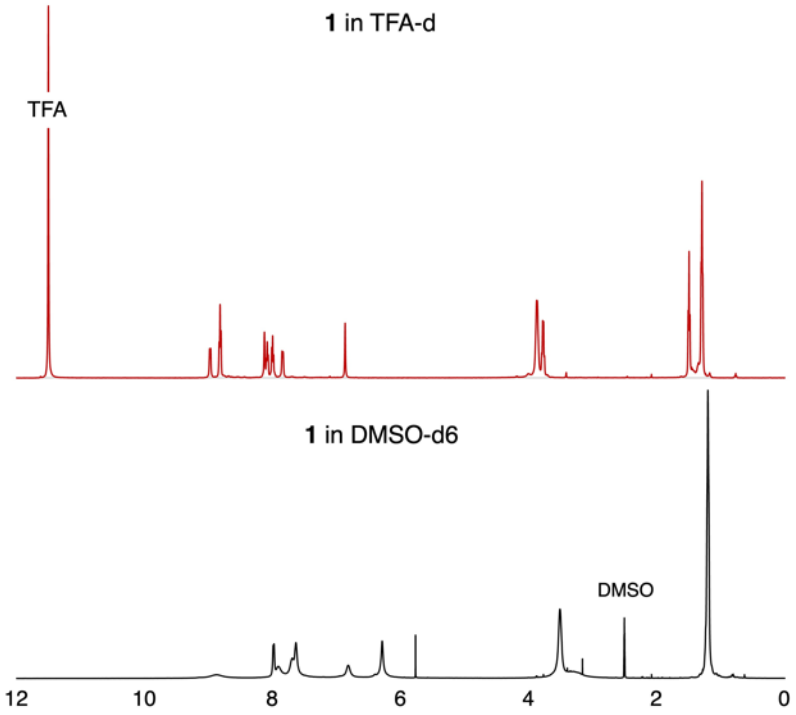


Fig. S17. Comparison of the ^{1}H NMR spectra of **1** in TFA-d and DMSO-d6.

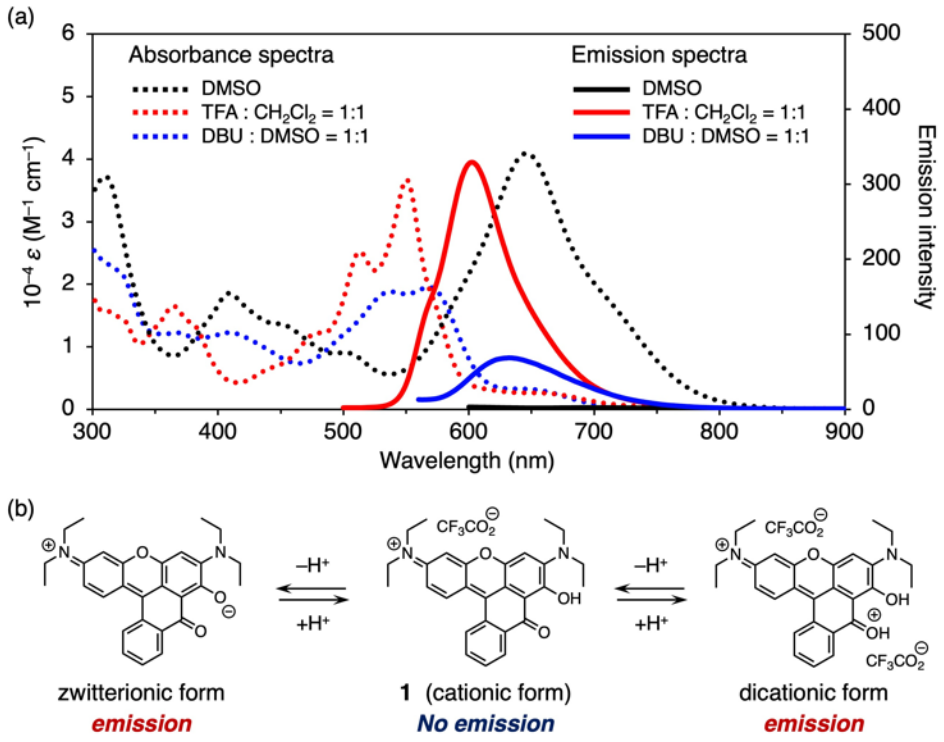


Fig. S18. Absorption and emission spectra of 1 in cationic (DMSO), dicationic (TFA in CH_2Cl_2), and zwitterionic (DBU in DMSO) forms. The dye concentration was 20 μM.

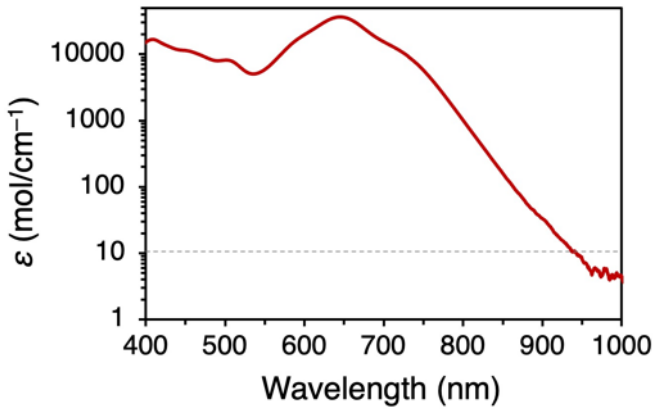


Fig. S19. Absorption Spectra of **1** in DMSO. The dye concentration was 20 µM.

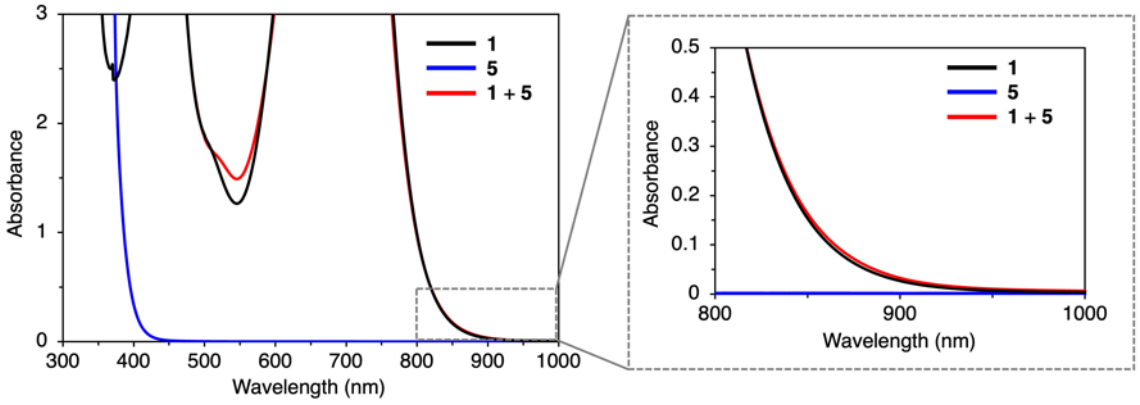
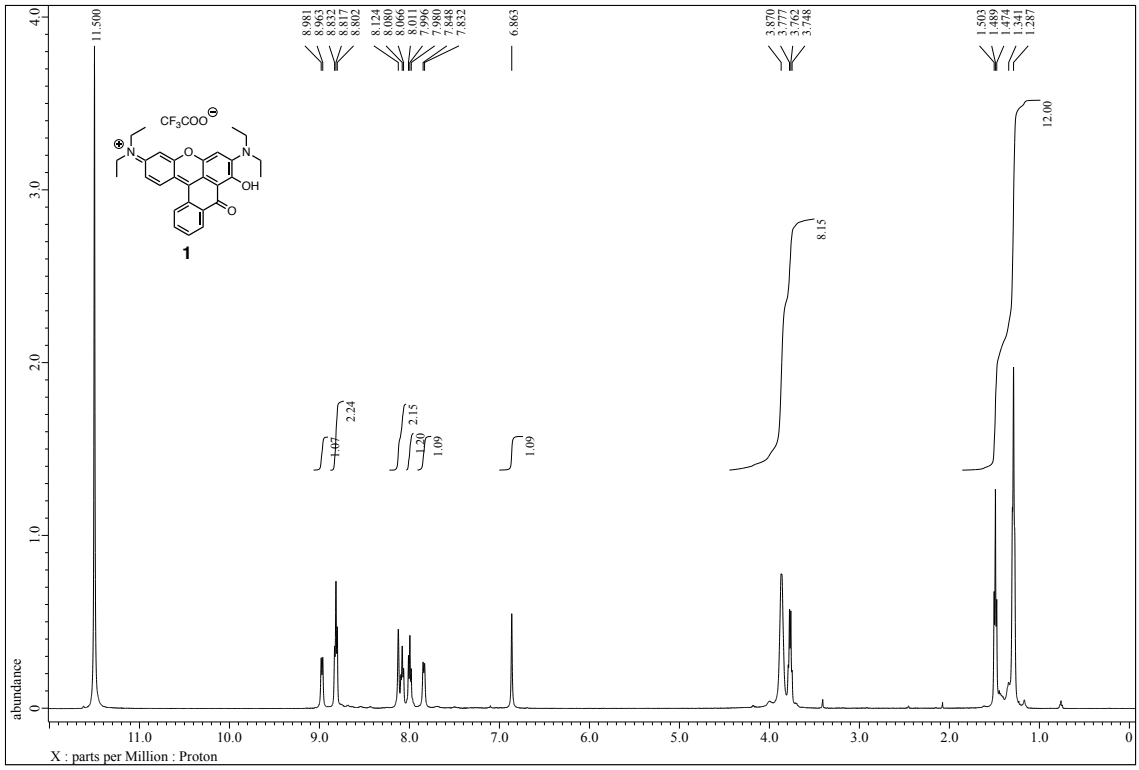
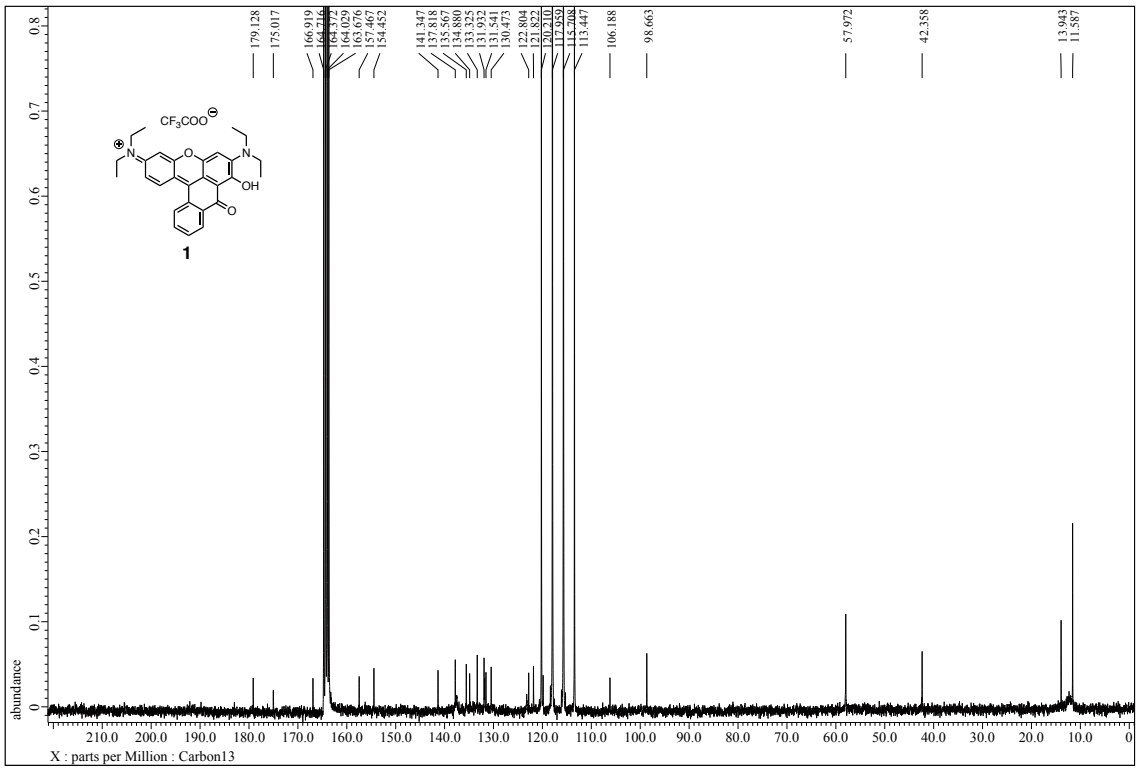


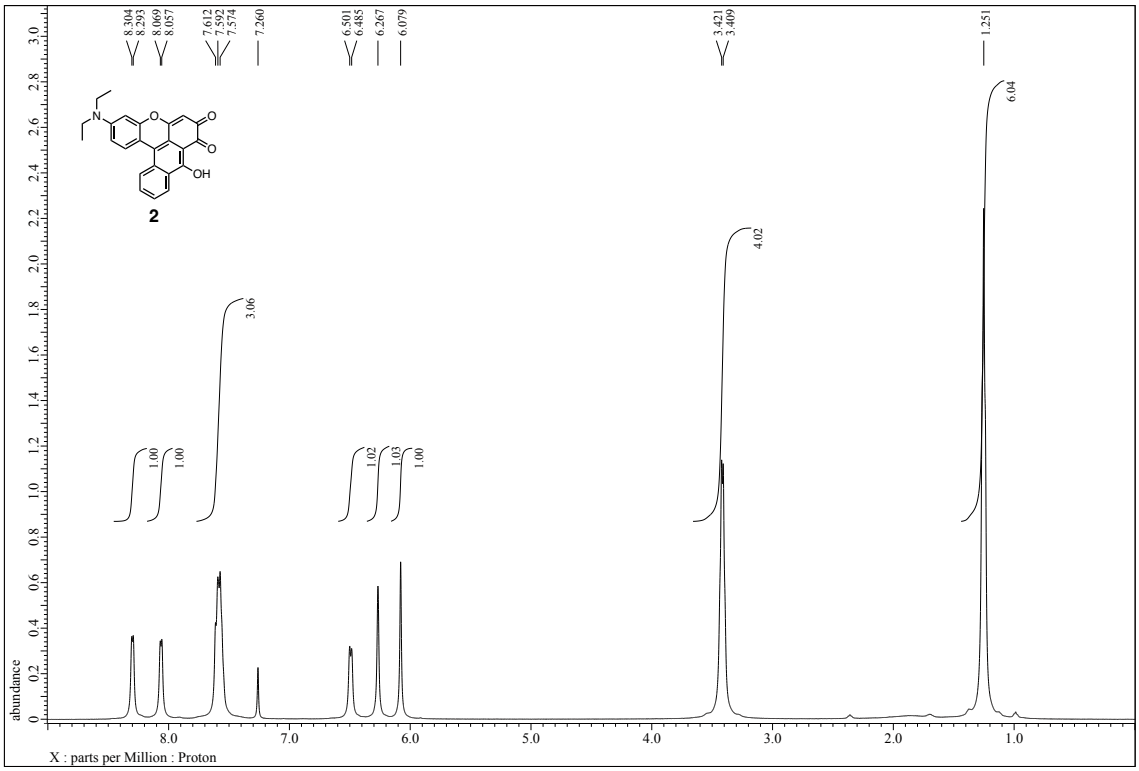
Fig. S20. Absorption spectra of **1**, aryldiazonium salt **5**, and a mixture of **1** and **5**. DMSO was used as the solvent, and 1 and 5 were prepared at concentrations corresponding to the photoreaction in Fig. 6a (**1**: 2.5 mM, **5**: 250 mM).

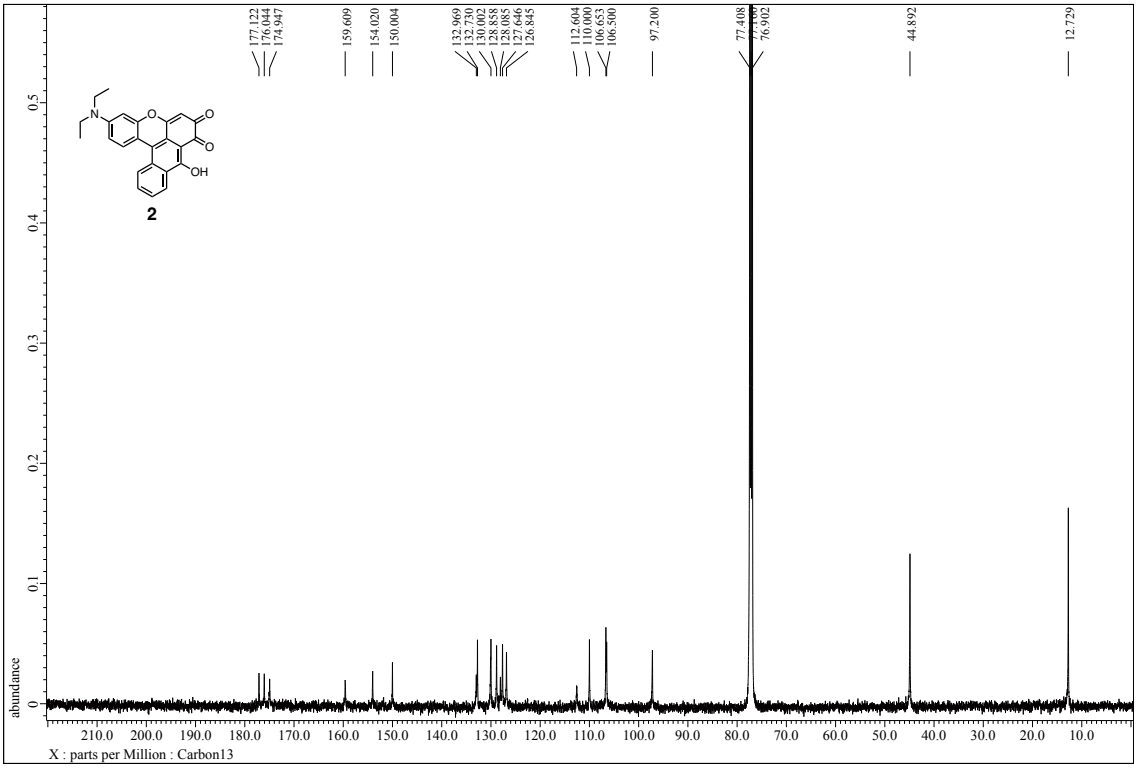
4. NMR Spectra of Compounds



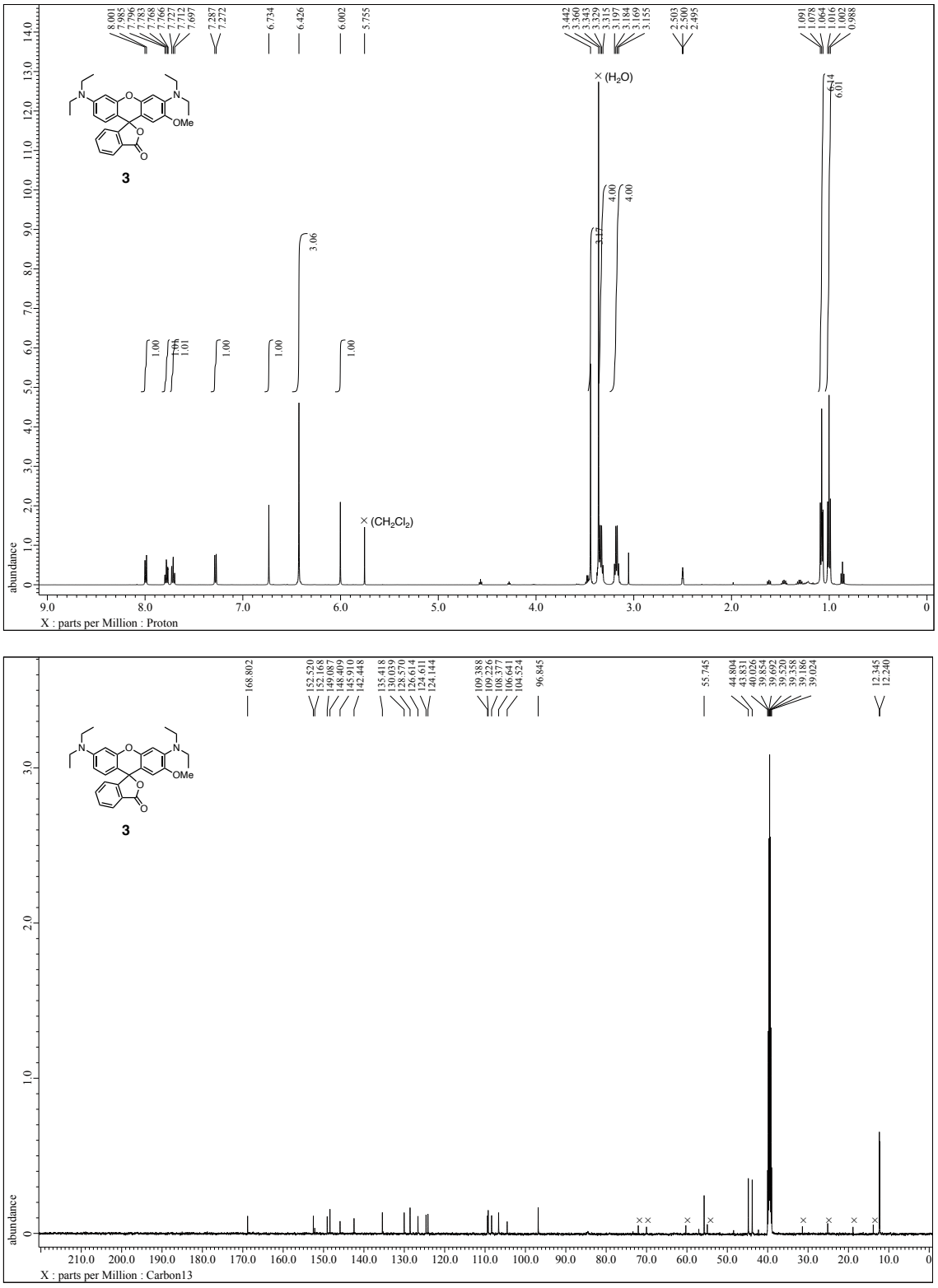


^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **1** at 25°C in TFA-d.

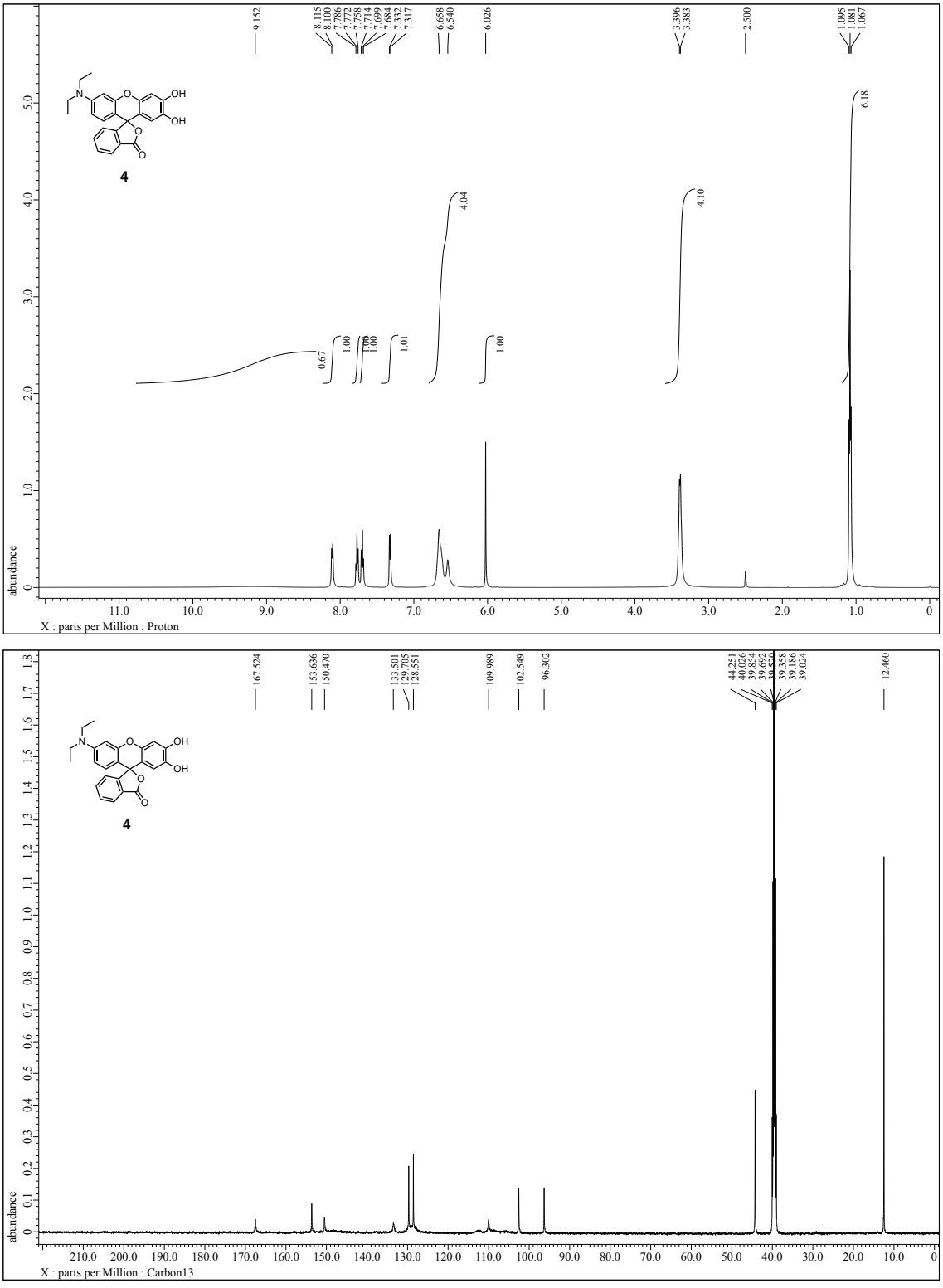




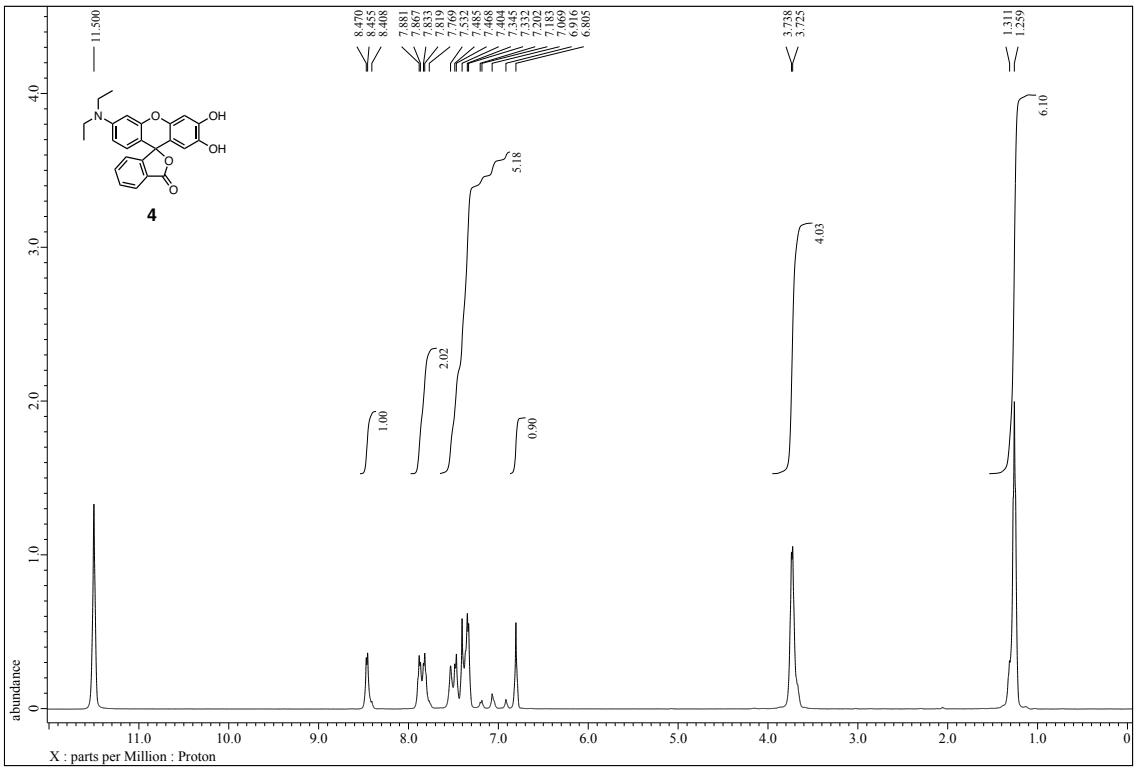
^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **2** at 25°C in $CDCl_3$.

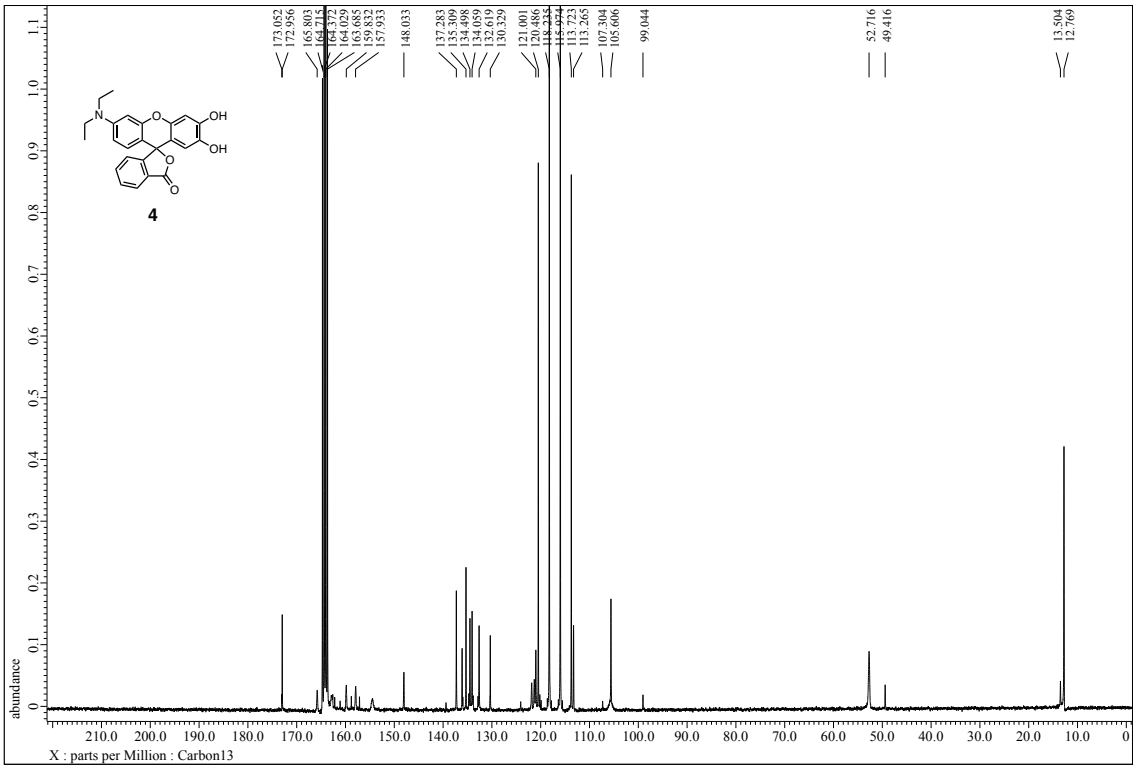


^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR spectra of **3** at 25°C in DMSO-d6. ×: Solvent and impurities.

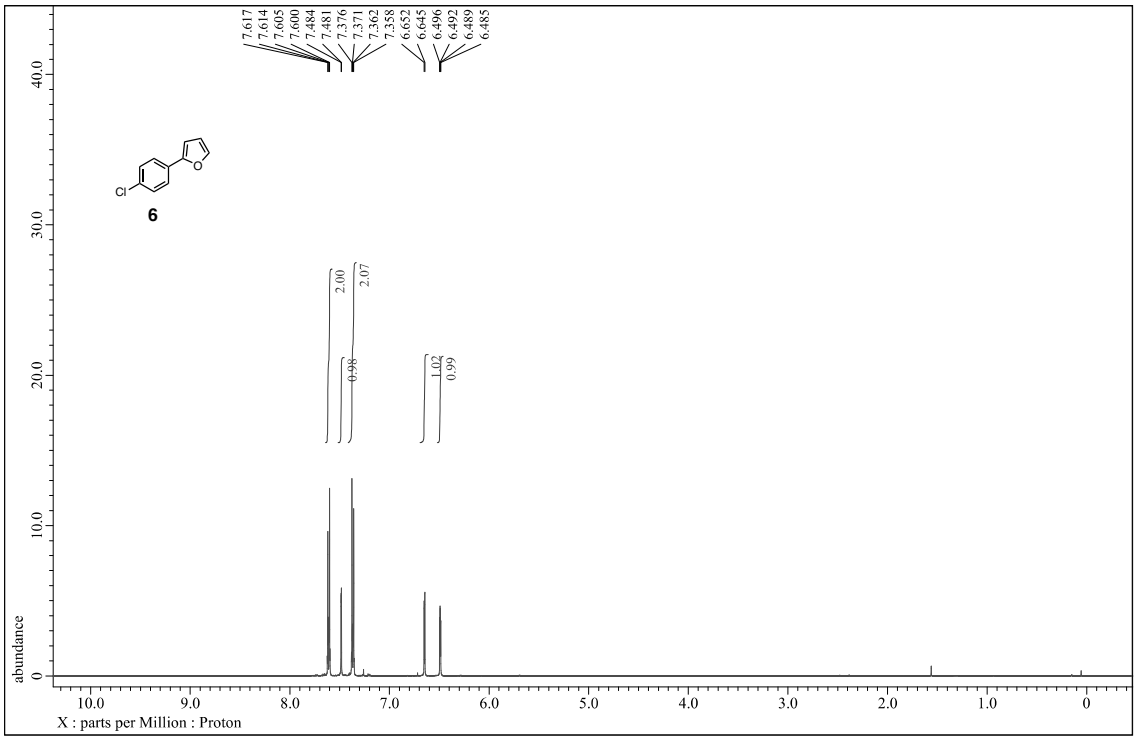


^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **4** at 25°C in DMSO-d6.

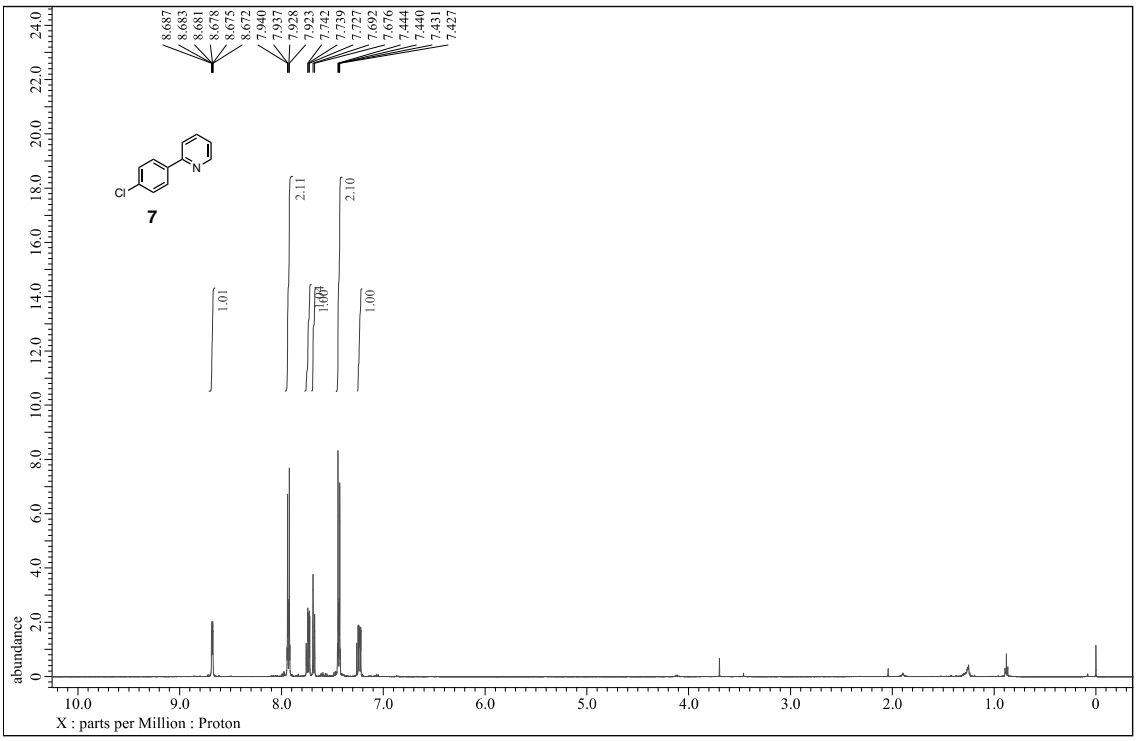




^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **4** at 25°C in TFA-d.



^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **6** at 25°C in $CDCl_3$.



^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **7** at 25°C in $CDCl_3$.

5. Cartesian Coordinates (in Å) and Energies

1a (Fig. 1a)

B3LYP/6-31+G** (DMSO)

G = –1419.137432 A. U.

O	4.525019	0.464003	-0.384816
H	4.432267	1.467376	-0.535751
O	3.616165	2.752106	-0.630379
O	-0.543536	-1.451531	0.373127
N	4.109451	-2.317946	0.129269
C	-1.653710	-0.684442	0.163772
C	-2.762105	1.367468	-0.404158
H	-2.750312	2.401701	-0.717555
N	-5.271177	-1.314279	-0.040346
C	0.696051	-0.930983	0.205155
C	2.212789	0.904269	-0.166580
C	1.329585	3.250516	-0.203867
C	3.294994	0.009366	-0.178727
C	-1.537605	0.722255	-0.056300
C	0.017503	2.769461	0.067256
C	2.460156	2.321488	-0.376412
C	-0.245835	1.324007	0.012084
C	0.870270	0.455741	0.022717
C	1.597536	4.627121	-0.201741
H	2.605631	4.957780	-0.424286
C	3.090956	-1.422182	0.062696
C	-2.856054	-1.364969	0.185787
H	-2.822114	-2.429948	0.367910
C	-0.667916	5.077192	0.479212
H	-1.437552	5.776151	0.790614
C	1.752045	-1.829331	0.249139
H	1.499688	-2.869049	0.394658
C	-3.964574	0.709455	-0.420305
H	-4.845350	1.268012	-0.705641
C	-4.069762	-0.682724	-0.077340
C	-7.183607	0.102510	0.759579
H	-8.129594	0.545103	0.431265
H	-6.540536	0.905313	1.132454
H	-7.396199	-0.578824	1.589411
C	-0.952470	3.713512	0.461001
H	-1.924751	3.386917	0.801578
C	-6.529156	-0.642944	-0.408502
H	-7.203020	-1.419699	-0.779222
H	-6.351736	0.028728	-1.251438
C	0.600057	5.543522	0.115560
H	0.815821	6.606895	0.118032
C	3.853348	-3.700563	0.578690
H	3.094703	-3.687042	1.364520
H	4.776092	-4.048057	1.049845
C	3.462770	-4.656587	-0.555043
H	2.532643	-4.355011	-1.044592
H	3.324496	-5.663175	-0.148227
H	4.247435	-4.704274	-1.316097
C	-5.396622	-2.717967	0.382244
H	-6.382750	-2.824661	0.842520
H	-4.668333	-2.920904	1.171228
C	5.510916	-2.088913	-0.294483
H	5.536933	-1.341115	-1.081158
H	5.845115	-3.032584	-0.735231
C	-5.248510	-3.716431	-0.771372
H	-6.006182	-3.540457	-1.541373
H	-5.376766	-4.736327	-0.394757

H	-4.262582	-3.645373	-1.240067
C	6.436297	-1.698901	0.860815
H	6.145725	-0.735068	1.285093
H	7.463246	-1.617782	0.489335
H	6.424785	-2.451356	1.655765

1a (Fig. 1a)

CAM-B3LYP/6-31+G** (DMSO)

G = –1418.371387 A. U.

O	4.507847	0.456181	-0.383629
H	4.429335	1.452240	-0.539684
O	3.594676	2.741147	-0.639436
O	-0.541451	-1.446142	0.362263
N	4.091493	-2.304475	0.133988
C	-1.646409	-0.684432	0.159991
C	-2.752895	1.361313	-0.399640
H	-2.740338	2.395376	-0.711336
N	-5.247710	-1.309483	-0.039763
C	0.690580	-0.930136	0.202719
C	2.206711	0.896553	-0.166495
C	1.318349	3.237378	-0.209352
C	3.278945	0.011440	-0.178230
C	-1.531220	0.714514	-0.056716
C	0.016920	2.757495	0.064833
C	2.450833	2.310711	-0.382789
C	-0.244809	1.310529	0.009627
C	0.865146	0.449179	0.022820
C	1.586987	4.606041	-0.204057
H	2.594117	4.936407	-0.428742
C	3.074980	-1.419669	0.065253
C	-2.845059	-1.364019	0.182749
H	-2.810299	-2.428919	0.361311
C	-0.666736	5.050594	0.485948
H	-1.435210	5.747361	0.802462
C	1.745098	-1.827058	0.250283
H	1.491980	-2.866057	0.394605
C	-3.948548	0.707089	-0.415334
H	-4.830557	1.264128	-0.697185
C	-4.051799	-0.682908	-0.076157
C	-7.140373	0.109173	0.757857
H	-8.085822	0.555818	0.438111
H	-6.490918	0.908290	1.124568
H	-7.348373	-0.569303	1.589820
C	-0.949042	3.691239	0.465000
H	-1.918563	3.362229	0.808904
C	-6.498623	-0.639812	-0.405974
H	-7.176078	-1.415277	-0.770094
H	-6.324208	0.025895	-1.253092
C	0.593101	5.517140	0.119680
H	0.807820	6.579964	0.125456
C	3.837947	-3.680637	0.580574
H	3.083096	-3.668923	1.368821
H	4.760890	-4.030134	1.047672
C	3.444621	-4.625365	-0.552282
H	2.517503	-4.315798	-1.040223
H	3.301369	-5.633578	-0.154982
H	4.228499	-4.670246	-1.312824
C	-5.371485	-2.706390	0.380091
H	-6.359312	-2.817003	0.833549
H	-4.649323	-2.908138	1.173837
C	5.486495	-2.076985	-0.289137
H	5.514151	-1.338199	-1.082949
H	5.822816	-3.023073	-0.720487
C	-5.212304	-3.696003	-0.770543

H	-5.964995	-3.518209	-1.543538
H	-5.337461	-4.718102	-0.402894
H	-4.225098	-3.616850	-1.232858
C	6.401170	-1.676165	0.861471
H	6.105953	-0.708964	1.271985
H	7.430409	-1.598454	0.499707
H	6.382068	-2.419127	1.663779

1a (Fig. 1a)

M06-2X/6-31+G** (DMSO)

G = –1418.512462 A. U.

O	4.510946	0.459676	-0.367350
H	4.433771	1.454221	-0.524521
O	3.585071	2.746431	-0.635608
O	-0.541486	-1.455406	0.381406
N	4.100273	-2.293396	0.136973
C	-1.646580	-0.697668	0.168325
C	-2.752753	1.350284	-0.419740
H	-2.732488	2.381346	-0.746359
N	-5.246581	-1.317795	-0.040320
C	0.690352	-0.940534	0.215556
C	2.204243	0.894022	-0.162552
C	1.304597	3.236571	-0.213233
C	3.281246	0.014683	-0.171578
C	-1.534529	0.703036	-0.058464
C	0.005548	2.748883	0.063467
C	2.446161	2.313299	-0.383429
C	-0.248723	1.300194	0.009237
C	0.864201	0.441632	0.026674
C	1.568833	4.607536	-0.204036
H	2.575145	4.943470	-0.428926
C	3.078514	-1.418876	0.072664
C	-2.846426	-1.378504	0.193113
H	-2.813368	-2.443226	0.380475
C	-0.690634	5.037480	0.496991
H	-1.460398	5.729735	0.820800
C	1.748228	-1.835549	0.267861
H	1.499692	-2.876030	0.419946
C	-3.950061	0.695026	-0.437215
H	-4.831927	1.246885	-0.733810
C	-4.052296	-0.693946	-0.079359
C	-7.107777	0.137900	0.728473
H	-8.047461	0.597086	0.411391
H	-6.432688	0.928358	1.067982
H	-7.314485	-0.522584	1.575289
C	-0.966973	3.674376	0.473792
H	-1.931624	3.334187	0.825905
C	-6.492928	-0.650692	-0.424658
H	-7.179376	-1.433962	-0.756056
H	-6.314771	-0.014044	-1.294049
C	0.567295	5.512860	0.124873
H	0.775310	6.577159	0.133313
C	3.855440	-3.670107	0.585335
H	3.114387	-3.658448	1.387487
H	4.789822	-4.022293	1.029388
C	3.439251	-4.595878	-0.556352
H	2.514280	-4.260298	-1.031781
H	3.283983	-5.607144	-0.172975
H	4.218992	-4.636386	-1.321593
C	-5.369934	-2.708430	0.397975
H	-6.367673	-2.818557	0.831245
H	-4.659029	-2.893043	1.207008
C	5.486449	-2.063564	-0.314166
H	5.496250	-1.340265	-1.123725

H	5.821360	-3.018787	-0.728756
C	-5.179035	-3.698421	-0.748617
H	-5.925217	-3.527164	-1.529532
H	-5.291243	-4.722372	-0.383595
H	-4.186706	-3.596365	-1.196278
C	6.404331	-1.637574	0.825788
H	6.093449	-0.670665	1.225474
H	7.430267	-1.551427	0.458030
H	6.393422	-2.374896	1.633717

1b (Fig. 1a)

B3LYP/6-31+G** (DMSO)

G = –1419.137662 A. U.

O	4.511583	0.431840	-0.350790
H	4.285932	1.941449	-0.532515
O	3.672262	2.752595	-0.546522
O	-0.547207	-1.429255	0.370889
N	4.076296	-2.367810	0.111706
C	-1.661641	-0.654910	0.174364
C	-2.764190	1.386317	-0.392179
H	-2.757931	2.420230	-0.706315
N	-5.281683	-1.297892	-0.025999
C	0.689508	-0.921840	0.201935
C	2.221099	0.910693	-0.149999
C	1.377761	3.236151	-0.192832
C	3.342706	-0.004056	-0.167851
C	-1.542187	0.744575	-0.047241
C	0.046624	2.776809	0.050932
C	2.458289	2.283910	-0.324664
C	-0.234806	1.341082	0.010441
C	0.870905	0.468195	0.021201
C	1.667893	4.614927	-0.210241
H	2.683283	4.933680	-0.413658
C	3.075617	-1.463889	0.062667
C	-2.863128	-1.341220	0.196964
H	-2.824760	-2.406965	0.374513
C	-0.609690	5.104536	0.401918
H	-1.374560	5.821905	0.681576
C	1.733641	-1.841251	0.246217
H	1.454758	-2.874777	0.389776
C	-3.970833	0.727025	-0.402632
H	-4.851718	1.288984	-0.681642
C	-4.077278	-0.661931	-0.063049
C	-7.197711	0.122441	0.761761
H	-8.141166	0.566608	0.427683
H	-6.555202	0.924784	1.136831
H	-7.416297	-0.556354	1.592304
C	-0.916644	3.749071	0.399575
H	-1.903087	3.445993	0.718779
C	-6.536836	-0.628402	-0.399736
H	-7.211209	-1.404852	-0.771141
H	-6.356873	0.041158	-1.244484
C	0.677842	5.546568	0.063500
H	0.908373	6.606703	0.052776
C	3.799196	-3.765486	0.503739
H	3.033625	-3.773251	1.282405
H	4.714127	-4.143144	0.965975
C	3.405103	-4.661562	-0.676153
H	2.484927	-4.321250	-1.158805
H	3.246035	-5.682482	-0.315878
H	4.197193	-4.687505	-1.430353
C	-5.402980	-2.699436	0.398742
H	-6.389237	-2.810414	0.858503
H	-4.675290	-2.898877	1.189849

C	5.492804	-2.132812	-0.261487
H	5.543478	-1.360553	-1.022414
H	5.836294	-3.068430	-0.711676
C	-5.249458	-3.703162	-0.750124
H	-6.007117	-3.533167	-1.521690
H	-5.373456	-4.722757	-0.370710
H	-4.263604	-3.629609	-1.218850
C	6.375024	-1.773723	0.936511
H	6.071172	-0.818569	1.370766
H	7.414530	-1.687175	0.603663
H	6.332620	-2.544610	1.712479

1b (Fig. 1a)

CAM-B3LYP/6-31+G** (DMSO)

G = –1418.371485 A. U.

O	4.493638	0.412438	-0.336002
H	4.286340	1.940040	-0.523657
O	3.667179	2.737464	-0.537455
O	-0.546322	-1.417590	0.367511
N	4.048215	-2.365294	0.109078
C	-1.657100	-0.645212	0.177914
C	-2.753208	1.384484	-0.384996
H	-2.746733	2.417935	-0.698304
N	-5.261897	-1.288137	-0.023717
C	0.681371	-0.920789	0.201382
C	2.217292	0.906086	-0.147895
C	1.379530	3.220055	-0.195730
C	3.329799	-0.008292	-0.162676
C	-1.537064	0.742428	-0.042238
C	0.056818	2.767122	0.045113
C	2.459017	2.266734	-0.321940
C	-0.227219	1.332762	0.008836
C	0.866207	0.466846	0.019109
C	1.674485	4.591559	-0.213737
H	2.691155	4.905408	-0.415533
C	3.055151	-1.471159	0.065206
C	-2.854895	-1.332105	0.199996
H	-2.815313	-2.397610	0.375421
C	-0.594376	5.084442	0.391226
H	-1.357240	5.803826	0.668405
C	1.718733	-1.842418	0.250339
H	1.434444	-2.873638	0.393366
C	-3.955418	0.729049	-0.394781
H	-4.836672	1.290905	-0.670429
C	-4.061159	-0.655065	-0.058684
C	-7.160544	0.136659	0.751880
H	-8.101535	0.585491	0.421448
H	-6.512083	0.935123	1.122018
H	-7.378947	-0.537314	1.585039
C	-0.903199	3.736018	0.389563
H	-1.889959	3.435097	0.707027
C	-6.507961	-0.621169	-0.400954
H	-7.185525	-1.396492	-0.766463
H	-6.327866	0.040792	-1.250673
C	0.690377	5.521485	0.056238
H	0.923019	6.580464	0.045843
C	3.769390	-3.759751	0.487755
H	3.009073	-3.772848	1.269913
H	4.684351	-4.145443	0.940537
C	3.367567	-4.630306	-0.699190
H	2.450209	-4.274154	-1.173276
H	3.201432	-5.655234	-0.358417
H	4.156939	-4.648017	-1.454936
C	-5.381296	-2.681224	0.401662

H	-6.369956	-2.796261	0.853231
H	-4.661043	-2.877183	1.199426
C	5.461942	-2.132356	-0.254008
H	5.520564	-1.367490	-1.020467
H	5.807393	-3.070338	-0.694615
C	-5.213803	-3.679969	-0.740662
H	-5.965314	-3.511259	-1.517055
H	-5.334203	-4.700821	-0.367317
H	-4.226039	-3.598549	-1.201696
C	6.324754	-1.767581	0.946980
H	6.017246	-0.808730	1.367582
H	7.368621	-1.687277	0.631533
H	6.266307	-2.530896	1.727856

1b (Fig. 1a)

M06-2X/6-31+G** (DMSO)

G = –1418.512494 A. U.

O	4.496332	0.411588	-0.318105
H	4.287120	1.965802	-0.518317
O	3.658662	2.749453	-0.536133
O	-0.545858	-1.423528	0.389454
N	4.054068	-2.358696	0.107406
C	-1.657219	-0.655291	0.189251
C	-2.752671	1.374054	-0.405600
H	-2.738622	2.403917	-0.735824
N	-5.260544	-1.296586	-0.023667
C	0.681667	-0.929248	0.215078
C	2.215392	0.906911	-0.145733
C	1.367880	3.218651	-0.199197
C	3.335499	-0.005913	-0.156522
C	-1.540447	0.733011	-0.042481
C	0.046660	2.759083	0.044955
C	2.454057	2.268758	-0.322990
C	-0.230541	1.324399	0.009153
C	0.866214	0.461908	0.021848
C	1.658578	4.593320	-0.214901
H	2.674244	4.912335	-0.418574
C	3.057616	-1.473483	0.070645
C	-2.855964	-1.344422	0.212705
H	-2.817356	-2.409652	0.397630
C	-0.615827	5.072551	0.404623
H	-1.379027	5.788203	0.691144
C	1.720328	-1.851202	0.269188
H	1.438225	-2.883347	0.419889
C	-3.956699	0.717084	-0.416947
H	-4.837846	1.273217	-0.708616
C	-4.061384	-0.665154	-0.060874
C	-7.129791	0.165195	0.717896
H	-8.064312	0.626237	0.387642
H	-6.456313	0.955219	1.061871
H	-7.348786	-0.489793	1.566093
C	-0.919715	3.720859	0.400843
H	-1.901679	3.409166	0.728627
C	-6.501392	-0.633426	-0.421693
H	-7.187318	-1.417048	-0.754804
H	-6.316489	-0.001581	-1.294131
C	0.667589	5.517658	0.061347
H	0.893995	6.578170	0.052951
C	3.782872	-3.753225	0.491336
H	3.037184	-3.764528	1.288298
H	4.709465	-4.140739	0.920532
C	3.355690	-4.604648	-0.701939
H	2.439087	-4.223911	-1.158929
H	3.179440	-5.631440	-0.373837

H	4.138802	-4.617339	-1.464438
C	-5.378450	-2.683317	0.419747
H	-6.377251	-2.799302	0.850166
H	-4.670383	-2.861431	1.233635
C	5.461270	-2.123252	-0.280819
H	5.505294	-1.374015	-1.064613
H	5.805083	-3.071043	-0.703656
C	-5.176931	-3.682607	-0.717630
H	-5.921699	-3.522020	-1.502396
H	-5.282725	-4.705409	-0.346745
H	-4.184180	-3.576626	-1.163773
C	6.324184	-1.732846	0.913156
H	5.999584	-0.774430	1.322002
H	7.365686	-1.642831	0.594246
H	6.272221	-2.491378	1.699342

RhB (Fig. 5c)

B3LYP/6-31+G** (DMSO)

G = –1420.336838 A. U.

O	-0.000078	-1.694274	-0.119091
N	-4.748674	-1.929653	-0.127032
C	1.188068	-1.027228	-0.165670
C	2.509426	0.992757	-0.283101
H	2.586337	2.072004	-0.352271
N	4.748493	-1.929971	-0.127154
C	-1.188180	-1.027167	-0.165658
C	-2.509436	0.992906	-0.283087
C	0.000277	3.530618	0.631591
C	-3.655019	0.245011	-0.242051
C	1.214725	0.395950	-0.247250
C	0.000031	2.598266	-0.433118
C	-0.000005	1.108725	-0.275095
C	-1.214755	0.396020	-0.247265
C	0.000352	4.905808	0.340973
H	0.000543	5.603542	1.170477
C	-3.610342	-1.193325	-0.160122
C	2.327679	-1.803788	-0.121775
H	2.203637	-2.874425	-0.040767
C	-0.000090	4.448632	-2.023211
H	-0.000238	4.790717	-3.053358
C	-2.327837	-1.803661	-0.121716
H	-2.203848	-2.874299	-0.040679
C	3.654975	0.244804	-0.242092
H	4.605870	0.756875	-0.290406
C	3.610219	-1.193539	-0.160196
C	6.670771	-1.024938	-1.465886
H	7.676894	-0.606259	-1.361473
H	6.055749	-0.306721	-2.016235
H	6.743552	-1.940014	-2.062000
C	-0.000162	3.079712	-1.751206
H	-0.000350	2.368446	-2.571177
C	6.087362	-1.316915	-0.079509
H	6.733984	-2.016204	0.457170
H	6.050874	-0.411385	0.529508
C	0.000171	5.367590	-0.971676
H	0.000223	6.433972	-1.172123
C	-4.725628	-3.401701	-0.137552
H	-3.909997	-3.744130	-0.778762
H	-5.650190	-3.729259	-0.620223
C	-4.621155	-4.017886	1.261952
H	-3.694396	-3.723101	1.762826
H	-4.637184	-5.109801	1.185271
H	-5.462614	-3.708661	1.889839
C	4.725288	-3.402008	-0.137718

H	5.649806	-3.729658	-0.620412
H	3.909609	-3.744321	-0.778929
C	-6.087484	-1.316471	-0.079412
H	-6.050879	-0.410836	0.529444
H	-6.734140	-2.015602	0.457435
C	4.620753	-4.018226	1.261772
H	5.462261	-3.709125	1.889653
H	4.636637	-5.110140	1.185056
H	3.694037	-3.723331	1.762662
C	-6.670908	-1.024668	-1.465811
H	-6.055835	-0.306570	-2.016263
H	-7.677002	-0.605905	-1.361465
H	-6.743744	-1.939819	-2.061802
H	-2.586271	2.072157	-0.352250
C	0.000427	3.176694	2.083001
O	0.000944	4.002522	2.983015
O	-0.000048	1.853907	2.334295
H	0.000145	1.733029	3.300459
H	-4.605887	0.757139	-0.290328

3 (Fig. S5)

B3LYP/6-31+G** (DMSO)

G = –1534.828402 A. U.

O	-4.595309	0.420534	-0.422024
O	0.463736	-1.736597	-0.151556
N	-4.234343	-2.359738	-0.123037
C	1.604232	-0.990926	-0.176375
C	2.782336	1.115036	-0.242461
H	2.786042	2.198279	-0.287857
N	5.219970	-1.649770	-0.113316
C	-0.762894	-1.147356	-0.193095
C	-2.223619	0.772175	-0.309842
C	-0.034432	3.442549	0.690467
C	-3.327046	-0.047158	-0.288066
C	1.531836	0.430645	-0.234585
C	0.169099	2.547854	-0.387180
C	0.269405	1.059650	-0.260030
C	-0.892746	0.264872	-0.253098
C	-0.145027	4.819354	0.430763
H	-0.301474	5.487562	1.269828
C	-3.182492	-1.497879	-0.171537
C	2.795285	-1.689281	-0.131790
H	2.743877	-2.767068	-0.068478
C	0.152419	4.439297	-1.928611
H	0.227330	4.812506	-2.945153
C	-1.854187	-1.992426	-0.154283
H	-1.653863	-3.050103	-0.071995
C	3.976612	0.445814	-0.202393
H	4.890200	1.023320	-0.228496
C	4.031594	-0.992708	-0.146620
C	7.083465	-0.583467	-1.416617
H	8.056734	-0.096988	-1.295194
H	6.423071	0.100826	-1.957581
H	7.224910	-1.478484	-2.030720
C	0.259418	3.068757	-1.687213
H	0.410329	2.386275	-2.517742
C	6.511432	-0.945732	-0.041893
H	7.202678	-1.608599	0.485559
H	6.407795	-0.057721	0.585401
C	-0.051587	5.320190	-0.864314
H	-0.135967	6.387434	-1.041059
C	-4.015591	-3.814204	-0.249010
H	-3.221824	-3.994352	-0.977274
H	-4.928414	-4.227123	-0.686139

C	-3.720251	-4.523122	1.079077
H	-2.803318	-4.154487	1.546965
H	-3.604681	-5.596645	0.899027
H	-4.541267	-4.388038	1.789675
C	5.297139	-3.118860	-0.146008
H	6.247786	-3.376532	-0.620513
H	4.514905	-3.506195	-0.803580
C	-5.631165	-2.010847	0.226630
H	-5.642324	-1.084200	0.792853
H	-5.978404	-2.801913	0.899209
C	5.216029	-3.763679	1.242339
H	6.026046	-3.407990	1.886855
H	5.307075	-4.850768	1.149998
H	4.264869	-3.540170	1.734385
C	-6.562494	-1.919368	-0.984321
H	-6.262404	-1.101846	-1.643509
H	-7.585724	-1.732341	-0.641187
H	-6.568994	-2.850733	-1.559635
H	-2.353971	1.841292	-0.402951
C	-0.140196	3.044848	2.126560
O	-0.461633	3.812185	3.021003
O	0.163294	1.756185	2.371833
H	0.058470	1.601394	3.327455
C	-4.807074	1.826118	-0.590627
H	-4.451746	2.383717	0.282275
H	-4.309541	2.190234	-1.495869
H	-5.885294	1.946685	-0.689337

4 (Fig. S6)

B3LYP/6-31+G** (DMSO)

G = –1357.845579 A. U.

O	5.113756	2.270244	-0.377534
H	5.511028	1.388692	-0.433630
O	-0.406902	2.188738	-0.115889
C	-1.142532	1.039205	-0.147438
C	-1.360643	-1.351621	-0.262260
H	-0.924003	-2.341328	-0.341230
N	-4.721488	0.168603	-0.020307
C	0.958259	2.164068	-0.187250
C	3.088346	0.973669	-0.354611
C	2.112067	-2.400476	0.565074
C	3.753908	2.164337	-0.322903
C	-0.501887	-0.221139	-0.245360
C	1.605011	-1.595435	-0.482893
C	0.919890	-0.274923	-0.304814
C	1.654639	0.909373	-0.288206
C	2.755615	-3.611859	0.255250
H	3.139684	-4.211063	1.072834
C	3.042178	3.456313	-0.227897
C	-2.517372	1.189277	-0.069534
H	-2.907419	2.193342	0.023953
C	2.395081	-3.248719	-2.097277
H	2.497688	-3.565445	-3.130563
C	1.608516	3.372332	-0.159834
H	1.041898	4.294426	-0.086919
C	-2.728597	-1.232121	-0.190121
H	-3.324992	-2.133473	-0.226342
C	-3.362679	0.051734	-0.089664
C	-6.019593	-1.548090	-1.317323
H	-6.703782	-2.393837	-1.191143
H	-5.151631	-1.891791	-1.888073
H	-6.532564	-0.780920	-1.906257
C	1.759154	-2.041450	-1.804978
H	1.375873	-1.425997	-2.612986

C	-5.607987	-1.001419	0.054611
H	-6.497433	-0.691580	0.610798
H	-5.133808	-1.780227	0.657019
C	2.897161	-4.039588	-1.061093
H	3.394273	-4.979878	-1.276330
C	-5.387702	1.477702	-0.013206
H	-6.372901	1.338300	-0.467453
H	-4.846178	2.162407	-0.671526
C	-5.544221	2.079228	1.388760
H	-6.127686	1.415965	2.035455
H	-6.067745	3.038970	1.325372
H	-4.573168	2.249822	1.863098
H	3.646212	0.045122	-0.430634
C	2.029206	-2.070864	2.019827
O	2.590009	-2.715776	2.893751
O	1.269290	-0.998542	2.310675
H	1.289757	-0.873695	3.276108
O	3.669147	4.545931	-0.211073

2 (Fig. S6)

B3LYP/6-31+G** (DMSO)

G = –1281.432599 A. U.

O	-4.971180	-1.940707	0.278979
H	-5.265102	-0.989103	0.452252
O	-4.936183	0.556108	0.573784
O	0.458114	-1.915091	-0.456098
C	1.223864	-0.807722	-0.209749
C	1.533319	1.476634	0.418558
H	1.156678	2.436884	0.742350
N	4.839265	-0.150053	0.088240
C	-0.890222	-1.884181	-0.287193
C	-2.974434	-0.664902	0.079190
C	-2.960840	1.831813	0.175511
C	-3.665960	-1.877807	0.060472
C	0.621862	0.456331	0.030877
C	-1.561008	1.830371	-0.084768
C	-3.701037	0.566466	0.320667
C	-0.812654	0.561147	-0.047767
C	-1.547540	-0.630542	-0.089669
C	-3.684150	3.034075	0.186805
H	-4.746270	2.994134	0.401082
C	-2.975105	-3.171703	-0.203585
C	2.591864	-1.026362	-0.208267
H	2.933814	-2.033135	-0.404954
C	-1.705508	4.241156	-0.460669
H	-1.218360	5.165840	-0.753960
C	-1.557494	-3.087944	-0.367870
H	-1.000794	-4.001104	-0.547583
C	2.895391	1.282440	0.454837
H	3.517900	2.111113	0.764082
C	3.485844	0.026874	0.099165
C	6.161723	1.867859	-0.611919
H	6.880359	2.604925	-0.238347
H	5.289919	2.404567	-0.998095
H	6.627605	1.330129	-1.443976
C	-0.971520	3.057048	-0.453459
H	0.057840	3.088704	-0.781058
C	5.772071	0.903013	0.513946
H	6.665055	0.400813	0.896674
H	5.347565	1.446581	1.361811
C	-3.059989	4.241255	-0.108050
H	-3.626434	5.166857	-0.101388
C	5.451122	-1.408880	-0.356651
H	6.423618	-1.157688	-0.790232

H	4.855825	-1.829294	-1.171622
C	5.634570	-2.433947	0.769032
H	6.269423	-2.031247	1.564819
H	6.114267	-3.336340	0.375690
H	4.675560	-2.720739	1.210741
O	-3.633041	-4.237370	-0.255743

1b (*P* helicity) (Fig. S16a)

B3LYP/6-31+G** (DMSO)

G = –1419.137670 A. U.

O	4.511661	0.431617	-0.350999
H	4.286036	1.941291	-0.532545
O	3.672330	2.752470	-0.546813
O	-0.547238	-1.429278	0.370794
N	4.076257	-2.368055	0.111528
C	-1.661605	-0.654932	0.174293
C	-2.764132	1.386388	-0.392204
H	-2.757792	2.420293	-0.706360
N	-5.281708	-1.297688	-0.025875
C	0.689541	-0.921898	0.201682
C	2.221117	0.910540	-0.150342
C	1.377854	3.236019	-0.193003
C	3.342744	-0.004264	-0.168303
C	-1.542145	0.744579	-0.047292
C	0.046742	2.776756	0.050891
C	2.458366	2.283743	-0.324977
C	-0.234769	1.341026	0.010343
C	0.870933	0.468114	0.021030
C	1.668057	4.614769	-0.210298
H	2.683432	4.933502	-0.413841
C	3.075614	-1.464088	0.062415
C	-2.863152	-1.341151	0.196931
H	-2.824869	-2.406904	0.374449
C	-0.609395	5.104461	0.402286
H	-1.374161	5.821850	0.682173
C	1.733603	-1.841354	0.245876
H	1.454686	-2.874879	0.389373
C	-3.970798	0.727167	-0.402601
H	-4.851687	1.289140	-0.681569
C	-4.077278	-0.661795	-0.062997
C	-7.197632	0.122727	0.761989
H	-8.141088	0.566937	0.427971
H	-6.555061	0.925044	1.137008
H	-7.416198	-0.556047	1.592554
C	-0.916423	3.749001	0.399821
H	-1.902824	3.445907	0.719136
C	-6.536869	-0.628151	-0.399544
H	-7.211281	-1.404590	-0.770897
H	-6.356927	0.041389	-1.244310
C	0.678106	5.546442	0.063715
H	0.908727	6.606562	0.053102
C	3.799108	-3.765771	0.503385
H	3.033543	-3.773670	1.282052
H	4.714037	-4.143529	0.965531
C	3.404989	-4.661604	-0.676684
H	2.484774	-4.321197	-1.159194
H	3.245979	-5.682616	-0.316641
H	4.197040	-4.687325	-1.430937
C	-5.403088	-2.699197	0.398998
H	-6.389302	-2.810038	0.858884
H	-4.675320	-2.898636	1.190031
C	5.492944	-2.132966	-0.260892
H	5.543967	-1.361113	-1.022203
H	5.836920	-3.068760	-0.710329

C	-5.249782	-3.703016	-0.749808
H	-6.007508	-3.533019	-1.521307
H	-5.373823	-4.722575	-0.370309
H	-4.263970	-3.629579	-1.218641
C	6.374261	-1.772949	0.937494
H	6.070016	-0.817475	1.370784
H	7.414004	-1.686583	0.605349
H	6.331318	-2.543221	1.714043

TS (Fig. S16a)

B3LYP/6-31+G** (DMSO)

G = –1419.132202 A. U.

imaginary frequency = –122.37 cm–1

O	4.531663	0.333490	0.097839
H	4.382802	1.839599	0.032184
O	3.805693	2.677157	-0.027189
O	-0.593164	-1.401831	0.098449
N	3.984546	-2.473512	0.077863
C	-1.689616	-0.589595	0.043938
C	-2.824109	1.481284	-0.108357
H	-2.901308	2.548808	-0.181944
N	-5.316625	-1.250128	0.066346
C	0.650379	-0.903787	0.069450
C	2.245983	0.882585	-0.008705
C	1.507894	3.233318	-0.118027
C	3.338346	-0.070091	0.046105
C	-1.556383	0.828336	-0.046776
C	0.128725	2.841005	-0.130137
C	2.557801	2.247177	-0.048489
C	-0.222039	1.405676	-0.063351
C	0.863981	0.495137	-0.005556
C	1.889584	4.589540	-0.172572
H	2.945522	4.829608	-0.159575
C	3.018713	-1.532540	0.064427
C	-2.886896	-1.286066	0.078337
H	-2.823865	-2.364061	0.130230
C	-0.411968	5.239014	-0.256812
H	-1.178616	6.005257	-0.310936
C	1.657647	-1.864905	0.103231
H	1.326476	-2.892747	0.126281
C	-4.030403	0.821377	-0.074775
H	-4.927991	1.423662	-0.112471
C	-4.119369	-0.602726	0.024563
C	-7.152324	-0.023488	1.263957
H	-8.119570	0.462802	1.099682
H	-6.476707	0.704279	1.723515
H	-7.300652	-0.845356	1.971667
C	-0.799974	3.905954	-0.201700
H	-1.856427	3.727410	-0.216395
C	-6.597626	-0.540403	-0.068191
H	-7.304710	-1.243714	-0.516981
H	-6.488024	0.275443	-0.786862
C	0.941268	5.594850	-0.242607
H	1.242737	6.636072	-0.285438
C	3.630590	-3.898522	0.245814
H	2.811410	-3.981437	0.963228
H	4.495499	-4.379273	0.708099
C	3.290017	-4.599047	-1.074751
H	2.419245	-4.152023	-1.561939
H	3.069085	-5.652426	-0.877371
H	4.132593	-4.553724	-1.771144
C	-5.400126	-2.705340	0.253340
H	-6.349337	-2.909816	0.756461
H	-4.615666	-3.025340	0.944566

C	5.433780	-2.248680	-0.144654
H	5.572688	-1.374974	-0.773722
H	5.783860	-3.121241	-0.703538
C	-5.326232	-3.495410	-1.058724
H	-6.139597	-3.209701	-1.733329
H	-5.416250	-4.566891	-0.851944
H	-4.377690	-3.325340	-1.576760
C	6.223827	-2.110486	1.158789
H	5.912843	-1.219356	1.708613
H	7.289500	-2.019153	0.924656
H	6.094351	-2.986426	1.802299

1b (*M* helicity) (Fig. S16a)

B3LYP/6-31+G** (DMSO)

G = –1419.137636 A. U.

O	4.495142	0.441550	0.448613
H	4.272892	1.969788	0.488892
O	3.664947	2.779432	0.401738
O	-0.552351	-1.460552	-0.183657
N	4.080461	-2.367220	0.055512
C	-1.665082	-0.667144	-0.072959
C	-2.767148	1.424682	0.263724
H	-2.758913	2.483282	0.481005
N	-5.290255	-1.276094	0.148391
C	0.685590	-0.941645	-0.068096
C	2.220063	0.914479	0.102137
C	1.381203	3.234691	-0.053316
C	3.338130	0.002403	0.208801
C	-1.543224	0.747549	0.002421
C	0.053008	2.756759	-0.277239
C	2.456052	2.296126	0.181561
C	-0.233741	1.331775	-0.105094
C	0.869616	0.459402	-0.030067
C	1.673912	4.609346	-0.152935
H	2.686218	4.944525	0.039336
C	3.075275	-1.467737	0.052267
C	-2.869247	-1.348757	-0.044809
H	-2.835353	-2.424127	-0.151357
C	-0.591479	5.043640	-0.847777
H	-1.349388	5.733722	-1.204428
C	1.729862	-1.862231	-0.049976
H	1.453339	-2.902043	-0.145581
C	-3.975910	0.772754	0.327623
H	-4.853462	1.356629	0.569529
C	-4.083609	-0.643731	0.129113
C	-7.025303	-0.316289	1.692414
H	-7.988656	0.204241	1.694665
H	-6.307708	0.288445	2.255166
H	-7.152852	-1.268844	2.216501
C	-0.902056	3.694186	-0.728153
H	-1.883803	3.363573	-1.034650
C	-6.560336	-0.541611	0.249258
H	-7.308784	-1.125562	-0.294266
H	-6.473207	0.407583	-0.284726
C	0.690978	5.513149	-0.527544
H	0.923959	6.569704	-0.608591
C	3.785563	-3.815180	0.055614
H	2.921505	-4.003967	0.696211
H	4.637041	-4.303643	0.534396
C	3.577227	-4.393694	-1.348924
H	2.723333	-3.937327	-1.856787
H	3.395253	-5.469940	-1.271809
H	4.465138	-4.243429	-1.970143
C	-5.400033	-2.738361	0.050423

H	-6.318896	-3.025248	0.569130
H	-4.581624	-3.201084	0.608471
C	5.528766	-2.061422	-0.037186
H	5.666693	-1.115269	-0.551402
H	5.955679	-2.848050	-0.666241
C	-5.435866	-3.252211	-1.393718
H	-6.285309	-2.827439	-1.938030
H	-5.540110	-4.342175	-1.397216
H	-4.520412	-2.994008	-1.934292
C	6.225993	-2.043952	1.324964
H	5.836603	-1.236269	1.948575
H	7.298668	-1.881878	1.176721
H	6.099596	-2.993308	1.854877

1b (*P* helicity) (Fig. S16a)

CAM-B3LYP/6-31+G** (DMSO)

G = –1418.371482 A. U.

O	4.493635	0.412408	-0.336199
H	4.286392	1.939894	-0.523504
O	3.667250	2.737369	-0.537434
O	-0.546335	-1.417602	0.367328
N	4.048193	-2.365376	0.109073
C	-1.657098	-0.645182	0.177834
C	-2.753210	1.384539	-0.384973
H	-2.746749	2.417989	-0.698264
N	-5.261931	-1.288068	-0.023657
C	0.681367	-0.920822	0.201284
C	2.217301	0.906039	-0.147896
C	1.379589	3.220026	-0.195777
C	3.329800	-0.008321	-0.162699
C	-1.537057	0.742464	-0.042281
C	0.056880	2.767123	0.045073
C	2.459079	2.266691	-0.321974
C	-0.227190	1.332756	0.008796
C	0.866216	0.466832	0.019063
C	1.674600	4.591515	-0.213778
H	2.691273	4.905342	-0.415578
C	3.055142	-1.471211	0.065164
C	-2.854902	-1.332077	0.199962
H	-2.815297	-2.397584	0.375361
C	-0.594236	5.084455	0.391214
H	-1.357080	5.803855	0.668404
C	1.718720	-1.842451	0.250233
H	1.434385	-2.873666	0.393238
C	-3.955420	0.729109	-0.394699
H	-4.836694	1.290957	-0.670288
C	-4.061156	-0.655019	-0.058647
C	-7.160552	0.136722	0.752055
H	-8.101553	0.585567	0.421652
H	-6.512079	0.935173	1.122207
H	-7.378939	-0.537277	1.585202
C	-0.903099	3.736033	0.389556
H	-1.889861	3.435157	0.707045
C	-6.508005	-0.621069	-0.400821
H	-7.185581	-1.396390	-0.766318
H	-6.327937	0.040910	-1.250534
C	0.690513	5.521469	0.056210
H	0.923178	6.580442	0.045830
C	3.769262	-3.759860	0.487649
H	3.008862	-3.772965	1.269726
H	4.684171	-4.145607	0.940491
C	3.367522	-4.630301	-0.699398
H	2.450246	-4.274035	-1.173564
H	3.201264	-5.655238	-0.358698

H	4.156981	-4.648027	-1.455058
C	-5.381332	-2.681160	0.401715
H	-6.369980	-2.796175	0.853322
H	-4.661046	-2.877134	1.199447
C	5.461995	-2.132472	-0.253781
H	5.520737	-1.367732	-1.020355
H	5.807549	-3.070529	-0.694157
C	-5.213910	-3.679907	-0.740615
H	-5.965451	-3.511188	-1.516981
H	-5.334314	-4.700757	-0.367254
H	-4.226161	-3.598503	-1.201692
C	6.324537	-1.767476	0.947322
H	6.016953	-0.808536	1.367674
H	7.368479	-1.687260	0.632086
H	6.265892	-2.530638	1.728337

TS (Fig. S16a)

CAM-B3LYP/6-31+G** (DMSO)

G = –1418.366032 A. U.

imaginary frequency = –123.20 cm–1

O	4.509956	0.315373	0.120520
H	4.379903	1.839433	0.051221
O	3.797032	2.662824	-0.014266
O	-0.591930	-1.389896	0.111103
N	3.958429	-2.467107	0.071308
C	-1.684726	-0.580872	0.050925
C	-2.813101	1.476668	-0.114173
H	-2.891127	2.542587	-0.194544
N	-5.296670	-1.242146	0.067308
C	0.642571	-0.902748	0.080259
C	2.240651	0.878557	-0.001309
C	1.507796	3.217164	-0.116851
C	3.323956	-0.072974	0.058012
C	-1.551352	0.824197	-0.046103
C	0.138243	2.829777	-0.131853
C	2.555887	2.230666	-0.040651
C	-0.214994	1.396240	-0.062112
C	0.858664	0.494090	-0.000523
C	1.893120	4.565987	-0.174099
H	2.949367	4.801991	-0.158537
C	2.998282	-1.537898	0.069647
C	-2.878102	-1.278232	0.086464
H	-2.813445	-2.355363	0.143152
C	-0.398337	5.215847	-0.265875
H	-1.162609	5.983166	-0.323906
C	1.643206	-1.865699	0.117648
H	1.307578	-2.891225	0.141337
C	-4.014552	0.820139	-0.079918
H	-4.912274	1.420855	-0.122384
C	-4.102921	-0.597975	0.026144
C	-7.120093	0.001853	1.235073
H	-8.084292	0.490084	1.067486
H	-6.440650	0.731367	1.683729
H	-7.269685	-0.809209	1.953319
C	-0.787111	3.889843	-0.208071
H	-1.842599	3.713041	-0.224096
C	-6.568483	-0.535488	-0.082510
H	-7.276732	-1.242681	-0.521216
H	-6.456528	0.267379	-0.814227
C	0.950779	5.568135	-0.249571
H	1.253478	6.608181	-0.294810
C	3.607105	-3.887375	0.229407
H	2.797214	-3.976807	0.954800
H	4.475884	-4.373181	0.676335

C	3.253114	-4.563304	-1.092028
H	2.381927	-4.103508	-1.563953
H	3.028275	-5.617466	-0.912009
H	4.089311	-4.510161	-1.793834
C	-5.378621	-2.687700	0.266211
H	-6.331574	-2.891216	0.760835
H	-4.602218	-3.000610	0.968500
C	5.401222	-2.243268	-0.156900
H	5.540097	-1.372297	-0.788207
H	5.746762	-3.115794	-0.716332
C	-5.288482	-3.482850	-1.033862
H	-6.095502	-3.202724	-1.716709
H	-5.374927	-4.553091	-0.826132
H	-4.337089	-3.309186	-1.543316
C	6.187261	-2.106378	1.140412
H	5.878263	-1.213865	1.686906
H	7.252726	-2.020040	0.910319
H	6.051789	-2.979730	1.784346

1b (*M* helicity) (Fig. S16a)

CAM-B3LYP/6-31+G** (DMSO)

G = –1418.371602 A. U.

O	4.472847	0.422194	0.464539
H	4.268275	1.969554	0.503966
O	3.655566	2.765145	0.408840
O	-0.551151	-1.450193	-0.172519
N	4.054928	-2.360469	0.050194
C	-1.660604	-0.659316	-0.073494
C	-2.757287	1.422205	0.248253
H	-2.749451	2.481521	0.458615
N	-5.270633	-1.267768	0.149668
C	0.677460	-0.941269	-0.059911
C	2.214882	0.910430	0.106227
C	1.380968	3.218677	-0.050652
C	3.323526	-0.000947	0.217758
C	-1.538754	0.743859	-0.005639
C	0.062508	2.746048	-0.277291
C	2.454045	2.279605	0.187094
C	-0.226851	1.322471	-0.106258
C	0.864355	0.457812	-0.026407
C	1.678265	4.585991	-0.151426
H	2.690680	4.917288	0.043970
C	3.055356	-1.473351	0.055641
C	-2.860884	-1.341852	-0.041995
H	-2.825449	-2.417201	-0.142550
C	-0.575392	5.020928	-0.851664
H	-1.329962	5.711810	-1.211664
C	1.715297	-1.863941	-0.039566
H	1.434510	-2.901698	-0.135317
C	-3.961303	0.773809	0.313851
H	-4.839735	1.357811	0.549642
C	-4.067604	-0.638570	0.126050
C	-6.994359	-0.282957	1.666730
H	-7.955447	0.238988	1.665679
H	-6.273812	0.327635	2.217302
H	-7.120807	-1.226271	2.205458
C	-0.887763	3.678632	-0.730866
H	-1.868289	3.348839	-1.039391
C	-6.532932	-0.533764	0.233787
H	-7.282047	-1.125068	-0.299112
H	-6.445378	0.404592	-0.317534
C	0.702537	5.486771	-0.529589
H	0.937399	6.542046	-0.612669
C	3.763044	-3.802668	0.040407

H	2.906281	-3.998553	0.686697
H	4.618562	-4.294266	0.506064
C	3.544330	-4.357235	-1.364268
H	2.687931	-3.892015	-1.857384
H	3.362665	-5.433225	-1.305501
H	4.426715	-4.196130	-1.988752
C	-5.377166	-2.723327	0.071202
H	-6.299689	-3.005856	0.584124
H	-4.565039	-3.178277	0.643230
C	5.497932	-2.056037	-0.040102
H	5.639878	-1.112595	-0.556197
H	5.923791	-2.843346	-0.666874
C	-5.397245	-3.251143	-1.361064
H	-6.241651	-2.833013	-1.916190
H	-5.497610	-4.340151	-1.358571
H	-4.478752	-2.993476	-1.894686
C	6.182702	-2.039192	1.320128
H	5.791614	-1.229385	1.937990
H	7.256154	-1.883012	1.182434
H	6.046129	-2.986076	1.849687

1b (*P* helicity) (Fig. S16a)

M06-2X/6-31+G** (DMSO)

G = –1418.512487 A. U.

O	4.496296	0.411776	-0.318078
H	4.287191	1.965947	-0.518117
O	3.658722	2.749526	-0.535971
O	-0.545849	-1.423444	0.389552
N	4.054012	-2.358803	0.107327
C	-1.657194	-0.655218	0.189315
C	-2.752668	1.374133	-0.405621
H	-2.738616	2.403989	-0.735837
N	-5.260484	-1.296576	-0.023816
C	0.681675	-0.929170	0.215200
C	2.215382	0.906998	-0.145599
C	1.367930	3.218734	-0.199095
C	3.335513	-0.005815	-0.156393
C	-1.540446	0.733108	-0.042417
C	0.046702	2.759196	0.045059
C	2.454100	2.268815	-0.322879
C	-0.230539	1.324492	0.009266
C	0.866215	0.461990	0.021987
C	1.658692	4.593383	-0.214797
H	2.674361	4.912377	-0.418487
C	3.057594	-1.473475	0.070629
C	-2.855927	-1.344363	0.212700
H	-2.817341	-2.409604	0.397593
C	-0.615689	5.072683	0.404810
H	-1.378845	5.788361	0.691387
C	1.720328	-1.851146	0.269229
H	1.438182	-2.883293	0.419854
C	-3.956668	0.717123	-0.417025
H	-4.837839	1.273199	-0.708744
C	-4.061330	-0.665121	-0.060950
C	-7.129950	0.165155	0.717215
H	-8.064466	0.626055	0.386749
H	-6.456593	0.955298	1.061180
H	-7.349017	-0.489729	1.565484
C	-0.919628	3.720994	0.401016
H	-1.901578	3.409319	0.728835
C	-6.501303	-0.633553	-0.422178
H	-7.187082	-1.417286	-0.755339
H	-6.316254	-0.001799	-1.294646
C	0.667732	5.517752	0.061497

H	0.894178	6.578257	0.053121
C	3.782688	-3.753270	0.491372
H	3.037202	-3.764440	1.288526
H	4.709356	-4.140857	0.920347
C	3.355118	-4.604689	-0.701774
H	2.438483	-4.223822	-1.158609
H	3.178767	-5.631425	-0.373548
H	4.138080	-4.617573	-1.464438
C	-5.378469	-2.683195	0.419947
H	-6.377318	-2.799014	0.850308
H	-4.670471	-2.861115	1.233934
C	5.461179	-2.123694	-0.281195
H	5.505231	-1.374535	-1.065063
H	5.804634	-3.071617	-0.704032
C	-5.176859	-3.682749	-0.717185
H	-5.921505	-3.522303	-1.502109
H	-5.282775	-4.705459	-0.346078
H	-4.184030	-3.576928	-1.163211
C	6.324419	-1.733500	0.912615
H	6.000133	-0.775019	1.321568
H	7.365880	-1.643739	0.593487
H	6.272420	-2.492054	1.698788

TS (Fig. S16a)

M06-2X/6-31+G** (DMSO)

G = –1418.506154 A. U.

imaginary frequency = –139.75 cm–1

O	4.507313	0.300134	0.170232
H	4.384170	1.841798	0.097017
O	3.799717	2.659240	0.020530
O	-0.598230	-1.391595	0.137924
N	3.955190	-2.469084	0.063964
C	-1.689086	-0.582217	0.064731
C	-2.819691	1.476658	-0.132231
H	-2.903639	2.541392	-0.227471
N	-5.300300	-1.244608	0.068299
C	0.637244	-0.909084	0.101857
C	2.238869	0.874377	0.015970
C	1.511158	3.214289	-0.110276
C	3.325221	-0.079808	0.083524
C	-1.556369	0.824963	-0.048219
C	0.139487	2.827693	-0.137583
C	2.559819	2.226167	-0.019567
C	-0.217359	1.395066	-0.061772
C	0.856372	0.491686	0.010865
C	1.903194	4.563343	-0.169487
H	2.960873	4.796118	-0.143479
C	2.993096	-1.547206	0.079068
C	-2.882915	-1.282894	0.103378
H	-2.816298	-2.360493	0.172444
C	-0.390220	5.217488	-0.290235
H	-1.152397	5.986082	-0.361248
C	1.635205	-1.877273	0.143080
H	1.296475	-2.903127	0.171392
C	-4.022909	0.818220	-0.097572
H	-4.922565	1.417256	-0.152428
C	-4.108883	-0.601104	0.026526
C	-7.106355	0.034409	1.200719
H	-8.064123	0.533308	1.031161
H	-6.407961	0.760332	1.626690
H	-7.257875	-0.763401	1.933471
C	-0.784355	3.890781	-0.229989
H	-1.841125	3.720207	-0.257995
C	-6.568798	-0.539587	-0.107918

H	-7.278828	-1.260077	-0.523531
H	-6.449833	0.241050	-0.863459
C	0.961941	5.568447	-0.260300
H	1.266692	6.607954	-0.307347
C	3.607799	-3.890657	0.217108
H	2.816462	-3.984894	0.963048
H	4.491073	-4.382238	0.630370
C	3.217796	-4.532745	-1.112266
H	2.345405	-4.044503	-1.553303
H	2.981413	-5.587153	-0.952978
H	4.043411	-4.470157	-1.825898
C	-5.378172	-2.686126	0.290768
H	-6.344213	-2.887048	0.762239
H	-4.615063	-2.980258	1.016737
C	5.390879	-2.240488	-0.203442
H	5.510788	-1.370821	-0.842039
H	5.721956	-3.117204	-0.767049
C	-5.247169	-3.486532	-1.003419
H	-6.045468	-3.216745	-1.700691
H	-5.318415	-4.557333	-0.795665
H	-4.288053	-3.291335	-1.491115
C	6.197091	-2.102747	1.082330
H	5.886757	-1.213523	1.633449
H	7.258161	-2.011375	0.836726
H	6.070246	-2.980913	1.721729

1b (*M* helicity) (Fig. S16a)

M06-2X/6-31+G** (DMSO)

G = –1418.512754 A. U.

O	4.467205	0.413845	0.509003
H	4.262713	1.998003	0.545703
O	3.641718	2.777470	0.437575
O	-0.552008	-1.460571	-0.170508
N	4.062133	-2.352055	0.048366
C	-1.662013	-0.670867	-0.073488
C	-2.758861	1.417890	0.253385
H	-2.744234	2.477363	0.471122
N	-5.272121	-1.272074	0.150787
C	0.676415	-0.952946	-0.051351
C	2.211726	0.910054	0.119661
C	1.369787	3.215466	-0.046335
C	3.326273	-0.001195	0.240354
C	-1.542931	0.734892	-0.007750
C	0.054680	2.735272	-0.284440
C	2.446591	2.280388	0.205062
C	-0.229964	1.312580	-0.107048
C	0.863685	0.451071	-0.018612
C	1.664163	4.585136	-0.153638
H	2.673820	4.922542	0.050491
C	3.057111	-1.476880	0.061856
C	-2.863764	-1.354914	-0.041507
H	-2.829333	-2.431604	-0.141600
C	-0.588499	5.002317	-0.888648
H	-1.339954	5.687004	-1.267048
C	1.715043	-1.876935	-0.028396
H	1.436177	-2.916476	-0.125712
C	-3.965434	0.769596	0.320205
H	-4.844599	1.351735	0.563251
C	-4.070262	-0.645248	0.127376
C	-6.964037	-0.272164	1.675698
H	-7.918286	0.260789	1.693900
H	-6.220604	0.329357	2.206282
H	-7.086296	-1.215541	2.215595
C	-0.897536	3.657680	-0.761189

H	-1.870718	3.314985	-1.084769
C	-6.531379	-0.534367	0.235076
H	-7.286733	-1.133669	-0.281461
H	-6.444129	0.397692	-0.328523
C	0.685328	5.478119	-0.550736
H	0.915052	6.534247	-0.639307
C	3.778932	-3.795855	0.031890
H	2.934507	-4.000040	0.692777
H	4.649669	-4.286447	0.471903
C	3.536318	-4.318421	-1.382201
H	2.676438	-3.831682	-1.848653
H	3.348803	-5.393870	-1.346526
H	4.412753	-4.143601	-2.011608
C	-5.375687	-2.727249	0.073852
H	-6.311830	-3.008639	0.563890
H	-4.573913	-3.179204	0.664298
C	5.501581	-2.035801	-0.063484
H	5.629842	-1.095279	-0.590305
H	5.923155	-2.828964	-0.687432
C	-5.360415	-3.239917	-1.364785
H	-6.198520	-2.818841	-1.927455
H	-5.447888	-4.329406	-1.379775
H	-4.433268	-2.959767	-1.872473
C	6.189346	-2.009614	1.296043
H	5.785682	-1.203565	1.910860
H	7.260564	-1.843199	1.156807
H	6.058560	-2.959502	1.822033

1b (Fig. S16b)

B3LYP/6-31+G** (DMSO)

G = –1419.137683 A. U.

O	4.511652	0.431646	-0.351076
H	4.286012	1.941105	-0.532613
O	3.672414	2.752338	-0.546827
O	-0.547238	-1.429254	0.370707
N	4.076229	-2.368137	0.111504
C	-1.661604	-0.654893	0.174232
C	-2.764153	1.386471	-0.392032
H	-2.757873	2.420449	-0.705945
N	-5.281712	-1.297664	-0.025819
C	0.689539	-0.921897	0.201588
C	2.221150	0.910528	-0.150223
C	1.377927	3.236003	-0.193113
C	3.342775	-0.004260	-0.168110
C	-1.542134	0.744629	-0.047293
C	0.046796	2.776774	0.050749
C	2.458428	2.283705	-0.324968
C	-0.234743	1.341049	0.010292
C	0.870946	0.468123	0.021031
C	1.668146	4.614747	-0.210503
H	2.683542	4.933451	-0.413986
C	3.075641	-1.464103	0.062433
C	-2.863163	-1.341091	0.196963
H	-2.824876	-2.406834	0.374542
C	-0.609348	5.104519	0.401861
H	-1.374132	5.821942	0.681610
C	1.733594	-1.841372	0.245690
H	1.454627	-2.874906	0.389009
C	-3.970826	0.727266	-0.402374
H	-4.851746	1.289313	-0.681086
C	-4.077294	-0.661739	-0.062941
C	-7.197820	0.122521	0.762029
H	-8.141291	0.566666	0.427968
H	-6.555354	0.924871	1.137160

H	-7.416391	-0.556334	1.592526
C	-0.916389	3.749059	0.399498
H	-1.902813	3.445999	0.718775
C	-6.536900	-0.628198	-0.399513
H	-7.211224	-1.404655	-0.771001
H	-6.356943	0.041440	-1.244195
C	0.678185	5.546455	0.063359
H	0.908817	6.606572	0.052673
C	3.798850	-3.766014	0.502621
H	3.032939	-3.774273	1.280945
H	4.713560	-4.144013	0.964999
C	3.405244	-4.661243	-0.678074
H	2.485263	-4.320548	-1.160827
H	3.246029	-5.682436	-0.318631
H	4.197642	-4.686594	-1.431976
C	-5.403009	-2.699187	0.399036
H	-6.389265	-2.810113	0.858807
H	-4.675307	-2.898548	1.190157
C	5.493185	-2.132871	-0.259794
H	5.544777	-1.360827	-1.020873
H	5.837535	-3.068546	-0.709178
C	-5.249531	-3.702996	-0.749755
H	-6.007246	-3.533078	-1.521283
H	-5.373484	-4.722562	-0.370247
H	-4.263714	-3.629474	-1.218561
C	6.373543	-1.773170	0.939394
H	6.069029	-0.817757	1.372629
H	7.413577	-1.686824	0.608146
H	6.329861	-2.543599	1.715751

TS (Fig. S16b)

B3LYP/6-31+G** (DMSO)

G = –1419.138614 A. U.

imaginary frequency = –1051.32 cm–1

O	4.496098	0.474774	-0.360572
H	4.295162	1.661541	-0.497146
O	3.676055	2.678774	-0.547873
O	-0.557793	-1.448202	0.359889
N	4.090759	-2.347926	0.115802
C	-1.666199	-0.668637	0.164640
C	-2.766392	1.384273	-0.392733
H	-2.755224	2.418998	-0.703871
N	-5.288832	-1.289722	-0.026041
C	0.682235	-0.937859	0.196864
C	2.205619	0.888444	-0.148953
C	1.377089	3.229332	-0.200186
C	3.310237	-0.005573	-0.167184
C	-1.543991	0.736104	-0.052462
C	0.047396	2.770301	0.048604
C	2.469413	2.275358	-0.333680
C	-0.241819	1.329991	0.008543
C	0.860189	0.450337	0.023248
C	1.671007	4.603424	-0.212783
H	2.688791	4.915343	-0.417373
C	3.078893	-1.451406	0.059667
C	-2.871307	-1.346651	0.188863
H	-2.838742	-2.412820	0.364659
C	-0.601565	5.098884	0.407958
H	-1.365231	5.816199	0.691043
C	1.735943	-1.845089	0.236562
H	1.472594	-2.883419	0.374642
C	-3.973527	0.730441	-0.403290
H	-4.853215	1.295134	-0.680158
C	-4.083521	-0.660662	-0.065820

C	-7.194690	0.134269	0.778279
H	-8.138781	0.582281	0.451542
H	-6.547430	0.933290	1.152151
H	-7.410114	-0.547126	1.607422
C	-0.911394	3.741705	0.404277
H	-1.897364	3.440976	0.727557
C	-6.544059	-0.613398	-0.390777
H	-7.222519	-1.386384	-0.761474
H	-6.365707	0.058682	-1.233528
C	0.683524	5.539433	0.066995
H	0.916545	6.599032	0.058598
C	3.828795	-3.744503	0.516966
H	3.060334	-3.755942	1.293076
H	4.745946	-4.108424	0.986204
C	3.449883	-4.656552	-0.655906
H	2.527927	-4.331541	-1.145810
H	3.301105	-5.676200	-0.287441
H	4.245245	-4.680032	-1.406824
C	-5.416251	-2.692767	0.394922
H	-6.400919	-2.798548	0.858905
H	-4.685720	-2.898732	1.181374
C	5.502237	-2.094871	-0.259442
H	5.541908	-1.322585	-1.021414
H	5.858655	-3.023966	-0.713315
C	-5.274512	-3.691899	-0.759182
H	-6.034842	-3.514168	-1.526254
H	-5.403143	-4.711951	-0.382837
H	-4.290392	-3.622586	-1.232050
C	6.383883	-1.724556	0.935752
H	6.068374	-0.774010	1.372182
H	7.421281	-1.623239	0.600310
H	6.354420	-2.496269	1.711494

1a (Fig. S16b)

B3LYP/6-31+G** (DMSO)

G = –1419.137431 A. U.

O	4.524929	0.463942	-0.385646
H	4.432250	1.467246	-0.536602
O	3.615930	2.752160	-0.631059
O	-0.543517	-1.451588	0.372981
N	4.109533	-2.317807	0.129477
C	-1.653705	-0.684508	0.163684
C	-2.762155	1.367480	-0.403843
H	-2.750432	2.401750	-0.717109
N	-5.271171	-1.314345	-0.040452
C	0.696069	-0.931008	0.204994
C	2.212736	0.904258	-0.166843
C	1.329429	3.250504	-0.203853
C	3.294938	0.009362	-0.179146
C	-1.537612	0.722227	-0.056210
C	0.017412	2.769407	0.067457
C	2.460027	2.321516	-0.376716
C	-0.245888	1.323973	0.012188
C	0.870247	0.455737	0.022661
C	1.597325	4.627130	-0.201691
H	2.605376	4.957818	-0.424364
C	3.090976	-1.422127	0.062522
C	-2.856051	-1.365038	0.185668
H	-2.822089	-2.430040	0.367647
C	-0.668032	5.077078	0.479646
H	-1.437685	5.775967	0.791162
C	1.752059	-1.829351	0.248733
H	1.499725	-2.869114	0.393938
C	-3.964611	0.709482	-0.420002
H	-4.845405	1.268133	-0.705088

C	-4.069781	-0.682767	-0.077297
C	-7.183662	0.102157	0.759861
H	-8.129655	0.544824	0.431663
H	-6.540619	0.904864	1.132985
H	-7.396255	-0.579416	1.589494
C	-0.952532	3.713399	0.461391
H	-1.924739	3.386804	0.802169
C	-6.529166	-0.642929	-0.408431
H	-7.202985	-1.419599	-0.779405
H	-6.351740	0.029001	-1.251161
C	0.599862	5.543486	0.115815
H	0.815586	6.606867	0.118307
C	3.853529	-3.700281	0.579367
H	3.094597	-3.686573	1.364920
H	4.776172	-4.047393	1.051003
C	3.463473	-4.656913	-0.554036
H	2.533285	-4.355905	-1.043822
H	3.325542	-5.663391	-0.146825
H	4.248241	-4.704616	-1.314989
C	-5.396577	-2.718133	0.381822
H	-6.382749	-2.824974	0.841963
H	-4.668360	-2.921189	1.170848
C	5.510980	-2.088786	-0.294324
H	5.536944	-1.341308	-1.081309
H	5.845366	-3.032586	-0.734653
C	-5.248288	-3.716332	-0.771995
H	-6.005908	-3.540239	-1.542020
H	-5.376502	-4.736318	-0.395612
H	-4.262328	-3.645102	-1.240592
C	6.436252	-1.698178	0.860877
H	6.145490	-0.734296	1.284887
H	7.463175	-1.616940	0.489373
H	6.424898	-2.450408	1.656023

1b (Fig. S16b)

CAM-B3LYP/6-31+G** (DMSO)

G = –1418.371477 A. U.

O	4.493604	0.412093	-0.336903
H	4.286442	1.939557	-0.523939
O	3.667358	2.737102	-0.537772
O	-0.546423	-1.417616	0.367056
N	4.048140	-2.365590	0.109179
C	-1.657149	-0.645130	0.177649
C	-2.753217	1.384740	-0.384681
H	-2.746823	2.418272	-0.697679
N	-5.262047	-1.287824	-0.023741
C	0.681299	-0.920908	0.200974
C	2.217335	0.905859	-0.148102
C	1.379784	3.219904	-0.195831
C	3.329769	-0.008585	-0.163151
C	-1.537040	0.742559	-0.042266
C	0.057061	2.767103	0.045105
C	2.459200	2.266501	-0.322197
C	-0.227142	1.332753	0.008773
C	0.866215	0.466755	0.018909
C	1.674923	4.591361	-0.213742
H	2.691612	4.905110	-0.415579
C	3.055093	-1.471410	0.064994
C	-2.855010	-1.331953	0.199817
H	-2.815432	-2.397466	0.375204
C	-0.593811	5.084484	0.391443
H	-1.356582	5.803929	0.668717
C	1.718628	-1.842595	0.249865
H	1.434199	-2.873801	0.392762

C	-3.955457	0.729394	-0.394352
H	-4.836740	1.291417	-0.669544
C	-4.061246	-0.654814	-0.058639
C	-7.160832	0.136536	0.752347
H	-8.101844	0.585427	0.422039
H	-6.512439	0.934902	1.122828
H	-7.379233	-0.537767	1.585243
C	-0.902790	3.736084	0.389718
H	-1.889544	3.435305	0.707296
C	-6.508123	-0.620757	-0.400763
H	-7.185609	-1.395962	-0.766695
H	-6.327991	0.041599	-1.250156
C	0.690948	5.521400	0.056394
H	0.923730	6.580348	0.046107
C	3.769180	-3.759990	0.487989
H	3.008775	-3.772964	1.270060
H	4.684078	-4.145694	0.940894
C	3.367433	-4.630605	-0.698924
H	2.450196	-4.274355	-1.173181
H	3.201100	-5.655475	-0.358059
H	4.156921	-4.648495	-1.454550
C	-5.381445	-2.680976	0.401439
H	-6.370194	-2.796117	0.852787
H	-4.661320	-2.876983	1.199318
C	5.462032	-2.132651	-0.253268
H	5.520959	-1.368368	-1.020284
H	5.807962	-3.070915	-0.692914
C	-5.213782	-3.679581	-0.740977
H	-5.965253	-3.510813	-1.517402
H	-5.334180	-4.700471	-0.367722
H	-4.225995	-3.598096	-1.201951
C	6.323982	-1.766717	0.947983
H	6.016103	-0.807497	1.367512
H	7.368075	-1.686612	0.633202
H	6.265020	-2.529325	1.729525

TS (Fig. S16b)

CAM-B3LYP/6-31+G** (DMSO)

G = –1418.371934 A. U.

imaginary frequency = –1104.39 cm–1

O	4.476272	0.461410	-0.357150
H	4.285330	1.648382	-0.495635
O	3.666453	2.657675	-0.546697
O	-0.557966	-1.439971	0.350439
N	4.066636	-2.341317	0.117249
C	-1.661461	-0.663032	0.164079
C	-2.756672	1.381957	-0.384114
H	-2.744956	2.416724	-0.692702
N	-5.269050	-1.279976	-0.023813
C	0.673695	-0.937845	0.193866
C	2.200239	0.879807	-0.148124
C	1.375942	3.212940	-0.205642
C	3.294840	-0.007904	-0.166314
C	-1.538683	0.731822	-0.049444
C	0.055064	2.759318	0.043665
C	2.467149	2.257579	-0.335479
C	-0.237243	1.318637	0.006492
C	0.854066	0.445109	0.022145
C	1.674777	4.578651	-0.217447
H	2.693338	4.886190	-0.422125
C	3.059428	-1.455739	0.061151
C	-2.863392	-1.340464	0.188290
H	-2.830115	-2.406673	0.360028
C	-0.586863	5.076740	0.403844

H	-1.348143	5.795170	0.687725
C	1.723821	-1.846015	0.237178
H	1.457206	-2.882937	0.373737
C	-3.958512	0.732499	-0.393998
H	-4.838881	1.297283	-0.665950
C	-4.067833	-0.655423	-0.061995
C	-7.154838	0.147896	0.775575
H	-8.097172	0.601394	0.455875
H	-6.500581	0.942204	1.144337
H	-7.368007	-0.530290	1.606575
C	-0.898582	3.725397	0.399814
H	-1.883969	3.426501	0.723920
C	-6.515865	-0.604511	-0.387992
H	-7.198556	-1.375404	-0.752719
H	-6.339048	0.061422	-1.234897
C	0.693219	5.512997	0.063282
H	0.928329	6.571410	0.056320
C	3.805369	-3.732815	0.511539
H	3.041323	-3.747091	1.290570
H	4.722784	-4.101197	0.974351
C	3.421190	-4.627541	-0.663622
H	2.502435	-4.290651	-1.149156
H	3.265804	-5.649506	-0.308726
H	4.215124	-4.646750	-1.414643
C	-5.395071	-2.675892	0.394123
H	-6.381863	-2.786031	0.850479
H	-4.671367	-2.880852	1.186086
C	5.473890	-2.088670	-0.250485
H	5.518715	-1.325359	-1.019856
H	5.834307	-3.020425	-0.692857
C	-5.241078	-3.666761	-0.756550
H	-5.995860	-3.487520	-1.527289
H	-5.366641	-4.689020	-0.389128
H	-4.255321	-3.589149	-1.222373
C	6.337515	-1.707092	0.944962
H	6.016786	-0.751863	1.364408
H	7.378924	-1.611166	0.625361
H	6.294248	-2.468529	1.728706

1a (Fig. S16b)

CAM-B3LYP/6-31+G** (DMSO)

G = –1418.371383 A. U.

O	4.507789	0.456123	-0.384379
H	4.429276	1.452129	-0.540425
O	3.594424	2.741185	-0.640205
O	-0.541454	-1.446252	0.362026
N	4.091587	-2.304404	0.134039
C	-1.646409	-0.684556	0.159833
C	-2.752921	1.361318	-0.399453
H	-2.740402	2.395438	-0.710983
N	-5.247708	-1.309515	-0.039851
C	0.690582	-0.930220	0.202458
C	2.206683	0.896505	-0.166778
C	1.318206	3.237348	-0.209425
C	3.278910	0.011401	-0.178649
C	-1.531213	0.714447	-0.056712
C	0.016848	2.757415	0.064995
C	2.450712	2.310697	-0.383204
C	-0.244850	1.310451	0.009665
C	0.865132	0.449113	0.022720
C	1.586813	4.606021	-0.204059
H	2.593903	4.936409	-0.428912
C	3.075029	-1.419665	0.065085
C	-2.845074	-1.364112	0.182563

H	-2.810336	-2.429037	0.361026
C	-0.666786	5.050451	0.486484
H	-1.435230	5.747154	0.803215
C	1.745118	-1.827134	0.249872
H	1.492015	-2.866173	0.393939
C	-3.948575	0.707115	-0.415195
H	-4.830582	1.264260	-0.696854
C	-4.051832	-0.682959	-0.076232
C	-7.140171	0.109154	0.758129
H	-8.085626	0.555908	0.438567
H	-6.490595	0.908191	1.124816
H	-7.348114	-0.569359	1.590078
C	-0.949061	3.691084	0.465463
H	-1.918500	3.362018	0.809569
C	-6.498636	-0.639767	-0.405860
H	-7.176169	-1.415152	-0.770019
H	-6.324279	0.026030	-1.252916
C	0.592971	5.517072	0.119978
H	0.807662	6.579902	0.125784
C	3.838181	-3.680474	0.580905
H	3.083218	-3.668721	1.369050
H	4.761100	-4.029733	1.048239
C	3.445117	-4.625530	-0.551770
H	2.517873	-4.316346	-1.039726
H	3.302197	-5.633721	-0.154301
H	4.228965	-4.670299	-1.312356
C	-5.371473	-2.706439	0.379933
H	-6.359294	-2.817104	0.833394
H	-4.649306	-2.908223	1.173675
C	5.486669	-2.076726	-0.288663
H	5.514456	-1.338151	-1.082681
H	5.823327	-3.022855	-0.719652
C	-5.212269	-3.695963	-0.770773
H	-5.964968	-3.518133	-1.543755
H	-5.337400	-4.718093	-0.403210
H	-4.225069	-3.616766	-1.233098
C	6.400873	-1.675460	0.862176
H	6.105309	-0.708253	1.272432
H	7.430209	-1.597556	0.500737
H	6.381692	-2.418292	1.664607

1b (Fig. S16b)

M06-2X/6-31+G** (DMSO)

G = –1418.512487 A. U.

O	4.496267	0.412081	-0.317893
H	4.287010	1.965754	-0.518224
O	3.658600	2.749473	-0.536020
O	-0.545813	-1.423570	0.389554
N	4.054214	-2.358613	0.107247
C	-1.657182	-0.655380	0.189241
C	-2.752662	1.374036	-0.405592
H	-2.738640	2.403880	-0.735841
N	-5.260510	-1.296595	-0.023767
C	0.681710	-0.929261	0.215119
C	2.215304	0.907001	-0.145614
C	1.367773	3.218713	-0.199149
C	3.335489	-0.005696	-0.156372
C	-1.540450	0.732975	-0.042457
C	0.046582	2.759115	0.045059
C	2.453995	2.268825	-0.322884
C	-0.230602	1.324390	0.009251
C	0.866170	0.461922	0.021951
C	1.658466	4.593372	-0.214937
H	2.674111	4.912412	-0.418659

C	3.057709	-1.473369	0.070590
C	-2.855950	-1.344491	0.212668
H	-2.817393	-2.409737	0.397613
C	-0.615921	5.072596	0.404679
H	-1.379135	5.788235	0.691199
C	1.720458	-1.851158	0.269158
H	1.438379	-2.883323	0.419869
C	-3.956662	0.717063	-0.416937
H	-4.837818	1.273216	-0.708541
C	-4.061343	-0.665184	-0.060874
C	-7.130163	0.164903	0.717237
H	-8.064752	0.625652	0.386772
H	-6.456939	0.955149	1.061233
H	-7.349137	-0.490031	1.565492
C	-0.919785	3.720885	0.400971
H	-1.901717	3.409215	0.728841
C	-6.501339	-0.633625	-0.422185
H	-7.186996	-1.417381	-0.755554
H	-6.316248	-0.001733	-1.294534
C	0.667463	5.517716	0.061313
H	0.893865	6.578230	0.052863
C	3.782968	-3.753132	0.491077
H	3.037389	-3.764483	1.288142
H	4.709609	-4.140725	0.920107
C	3.355636	-4.604419	-0.702246
H	2.439029	-4.223556	-1.159145
H	3.179329	-5.631219	-0.374196
H	4.138714	-4.617108	-1.464792
C	-5.378521	-2.683159	0.420146
H	-6.377424	-2.798994	0.850387
H	-4.670603	-2.860957	1.234224
C	5.461423	-2.123300	-0.280974
H	5.505584	-1.373955	-1.064664
H	5.804993	-3.071104	-0.703992
C	-5.176730	-3.682811	-0.716862
H	-5.921316	-3.522488	-1.501868
H	-5.282622	-4.705490	-0.345659
H	-4.183859	-3.576973	-1.162801
C	6.324467	-1.733390	0.913086
H	6.000132	-0.774992	1.322198
H	7.365995	-1.643602	0.594182
H	6.272275	-2.492128	1.699080

TS (Fig. S16b)

M06-2X/6-31+G** (DMSO)

G = –1418.512486 A. U.

imaginary frequency = –1201.43 cm–1

O	4.476588	0.463903	-0.349612
H	4.283525	1.647737	-0.490286
O	3.659670	2.657249	-0.546683
O	-0.559592	-1.449617	0.367928
N	4.073888	-2.333241	0.118684
C	-1.662727	-0.675258	0.172348
C	-2.756208	1.372655	-0.403510
H	-2.735949	2.404359	-0.727373
N	-5.269718	-1.285046	-0.024335
C	0.672255	-0.949725	0.204506
C	2.196686	0.875133	-0.147386
C	1.365791	3.209567	-0.210438
C	3.297242	-0.007028	-0.164470
C	-1.542281	0.721305	-0.050376
C	0.046654	2.749742	0.043434
C	2.463781	2.256161	-0.338800
C	-0.240861	1.308107	0.006274

C	0.852338	0.436277	0.024018
C	1.662495	4.577352	-0.217747
H	2.680665	4.888402	-0.424381
C	3.062009	-1.457790	0.065516
C	-2.866500	-1.353111	0.198272
H	-2.835576	-2.419384	0.377872
C	-0.603276	5.063800	0.420196
H	-1.364142	5.778824	0.714382
C	1.725365	-1.856497	0.251833
H	1.463046	-2.895004	0.395614
C	-3.960333	0.723059	-0.415159
H	-4.840288	1.283437	-0.701817
C	-4.069590	-0.663780	-0.064984
C	-7.123380	0.180559	0.746065
H	-8.059345	0.647452	0.428783
H	-6.443105	0.965415	1.088372
H	-7.336106	-0.479835	1.591570
C	-0.911546	3.709088	0.413095
H	-1.892168	3.400242	0.748068
C	-6.511374	-0.611291	-0.406725
H	-7.203432	-1.389415	-0.739354
H	-6.330391	0.025872	-1.275651
C	0.675195	5.507339	0.071102
H	0.905220	6.567038	0.067379
C	3.821756	-3.723888	0.520514
H	3.070494	-3.735689	1.312820
H	4.750635	-4.091717	0.962699
C	3.416131	-4.603686	-0.660061
H	2.497858	-4.245150	-1.131653
H	3.252302	-5.627459	-0.315970
H	4.205257	-4.617988	-1.416430
C	-5.395932	-2.674780	0.411338
H	-6.392537	-2.783988	0.848027
H	-4.683189	-2.863476	1.218277
C	5.474127	-2.076070	-0.273058
H	5.503154	-1.331963	-1.062923
H	5.836678	-3.018540	-0.692766
C	-5.211398	-3.665963	-0.735642
H	-5.960049	-3.492668	-1.513870
H	-5.324320	-4.690177	-0.371179
H	-4.220657	-3.565873	-1.187438
C	6.334437	-1.660304	0.914407
H	5.992632	-0.704741	1.316435
H	7.373555	-1.552937	0.592635
H	6.298586	-2.412890	1.707271

1a (Fig. S16b)

M06-2X/6-31+G** (DMSO)

G = –1418.512464 A. U.

O	4.510986	0.459792	-0.367055
H	4.433999	1.454290	-0.524199
O	3.584866	2.746710	-0.635389
O	-0.541435	-1.455445	0.381322
N	4.100473	-2.293151	0.137047
C	-1.646547	-0.697783	0.168244
C	-2.752828	1.350155	-0.419791
H	-2.732616	2.381233	-0.746362
N	-5.246516	-1.318007	-0.040416
C	0.690386	-0.940493	0.215550
C	2.204193	0.894142	-0.162368
C	1.304328	3.236657	-0.213101
C	3.281228	0.014833	-0.171411
C	-1.534561	0.702954	-0.058525
C	0.005316	2.748875	0.063530

C	2.446052	2.313483	-0.383076
C	-0.248832	1.300168	0.009297
C	0.864174	0.441681	0.026804
C	1.568438	4.607642	-0.204007
H	2.574743	4.943639	-0.428834
C	3.078552	-1.418754	0.072699
C	-2.846360	-1.378659	0.193016
H	-2.813261	-2.443380	0.380391
C	-0.691102	5.037432	0.496865
H	-1.460954	5.729628	0.820590
C	1.748289	-1.835494	0.267766
H	1.499737	-2.875994	0.419666
C	-3.950086	0.694839	-0.437306
H	-4.831994	1.246669	-0.733846
C	-4.052255	-0.694164	-0.079500
C	-7.107686	0.137752	0.728188
H	-8.047410	0.596841	0.411089
H	-6.432586	0.928296	1.067490
H	-7.314307	-0.522579	1.575147
C	-0.967309	3.674296	0.473760
H	-1.931944	3.334051	0.825861
C	-6.492877	-0.650985	-0.424851
H	-7.179284	-1.434324	-0.756182
H	-6.314701	-0.014424	-1.294290
C	0.566793	5.512905	0.124761
H	0.774701	6.577224	0.133104
C	3.855942	-3.669926	0.585336
H	3.114924	-3.658491	1.387521
H	4.790427	-4.021898	1.029347
C	3.439971	-4.595801	-0.556351
H	2.514882	-4.260492	-1.031743
H	3.285019	-5.607112	-0.172963
H	4.219684	-4.636086	-1.321639
C	-5.369932	-2.708528	0.398249
H	-6.367672	-2.818466	0.831567
H	-4.659004	-2.892976	1.207297
C	5.486484	-2.063152	-0.314483
H	5.495988	-1.339600	-1.123827
H	5.821286	-3.018237	-0.729482
C	-5.179143	-3.698789	-0.748125
H	-5.925331	-3.527654	-1.529067
H	-5.291431	-4.722644	-0.382863
H	-4.186816	-3.596916	-1.195838
C	6.404746	-1.637561	0.825317
H	6.093967	-0.670836	1.225524
H	7.430555	-1.551234	0.457241
H	6.394128	-2.375231	1.632937