Supporting information for

Modulating the Singlet Oxygen Generation Property of *Meso*–β Directly Linked BODIPY Dimers

Weidong Pang,[a] Xian-Fu Zhang,[b] Jinyuan Zhou,[a] Changjiang Yu,[a] Erhong Hao[a] and Lijuan Jiao*[a]*

[a]Laboratory of Functional Molecular Solids, Ministry of Education; Anhui Laboratory of Molecule-Based Materials; School of Chemistry and Materials Science, Anhui Normal University, Wuhu, China 241000.

Fax: (+) (+86) 553-388-3517; E-mail: jiao421@mail.ahnu.edu.cn

[b]Chemistry Department, Hebei Normal University of Science & Technology, Qinhuangdao, Hebei, China 066004.

Fax: (+86) 1062770304, E-mail: zhangxianfu@tsinghua.org.cn

Contents:

1. Experimental Section

1.1 General

Reagents and solvents were used as received from commercial suppliers unless noted otherwise. All reactions were performed in oven-dried or flame-dried glassware unless otherwise stated, and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). ^{1}H and ^{13}C NMR are obtained on a 300 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ (7.26 ppm for ^{1}H and 77 ppm for ^{13}C) or to internal TMS (0 ppm for ^{1}H). High-resolution mass spectra were obtained using APCI-TOF in positive mode.

UV-visible absorption spectra were recorded on a Hitachi U-3010 Spectrophotometer (190-1100 nm scan range). Fluorescence emission spectra were recorded on a Hitachi F-4600 FL Spectrophotometer. The slit width was 2.5 nm and 5.0 nm for excitation and emission, respectively. Relative quantum efficiencies of fluorescence of BODIPY derivatives were obtained by comparing the areas under the corrected emission spectrum of the test sample in various solvent with fluorescein (0.95 in 0.1 M NaOH aqueous solution)[1]. Non-degassed, spectroscopic grade solvents and a 10 mm quartz cuvette were used. Dilute solutions ($0.01<A<0.05$) were used to minimize the reabsorption effects. Quantum yields were determined using the following equation[2]:

$$\Phi_X = \Phi_S (I_X/I_S) (A_S/A_X) (\eta_X/\eta_S)^2$$

Where Φ_S stands for the reported quantum yield of the standard, I stands for the integrated emission spectra, A stands for the absorbance at the excitation wavelength and η stands for the refractive index of the solvent being used (η = 1 when the same solvent was used for both the test sample and the standard). X subscript stands for the test sample, and S subscript stands for the standard.

1.2 Single Crystal X-ray Structure of BODIPYs

Crystals of BODIPYs **2a**, **2b**, **2c** and **2d** suitable for X-ray analysis were obtained by slow evaporation of their dichloromethane solutions. The vial containing this solution was placed, loosely capped, to promote the crystallization. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were collected using a diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. Cell parameters were retrieved using SMART[3] software and refined using SAINT on all observed reflections. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ) at 0.71073 Å. Data reduction was performed using the SAINT software,[4] which corrects for Lp and decay. The structure was solved by the direct method using the SHELXS-974 program and refined by least squares method on F^2, SHELXL-97,[5] incorporated in SHELXTL V5.10.[6]

Table S1. Details of structure determination, refinement, and experimental parameters for BODIPY dimers **2a-d.**

	2a	**2b**	**2c**	**2d**
Formula	$C_{25}H_{18}B_2F_4N_4O$	$C_{29}H_{26}B_2F_4N_4O$	$C_{24}H_{14}B_2Cl_2F_4N_4$	$C_{28}H_{22}B_2Cl_2F_4N_4$
Formula wt	488.05	544.16	526.91	583.02
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/n$	$P2_1/c$	$P2_1/n$
Crystal size/mm	0.23 x 0.21 x 0.18	0.34 × 0.30 × 0.26	0.22 x 0.21 x 0.19	0.16 x 0.15 x 0.13
a/Å	21.151(11)	13.7354(3)	10.6288(9)	19.4958(14)
b/Å	7.492(4)	14.3655(3)	11.0950(9)	14.4053(11)
c/Å	28.471(15)	13.8591(3)	19.9094(17)	20.2393(15)
α/□	90.00	90.00	90.00	90.000(5)
β/□	99.012(6)	100.259(2)	103.688(10)	91.3190(10)
γ/◦	90.00	90.00	90.00	90.00
V/Å^3	4456(4)	2690.90(10)	2281.2(3)	5682.6(7)
Z	8	4	4	8
Dc/mg m^{-3}	1.455	1.343	1.534	1.363
μ/mm^{-1}	0.113	0.847	0.340	0.280
F(000)	2000.0	1128.0	1064.0	2384
θ range/◦	1.45-27.68	4.18-67.54	1.97–27.60	1.47–27.56
Reflns. collected	18201	10429	19393	48743
Reflns. unique	5186	4752	5248	13059
Parameters	326	366	325	730
Goodness-of-fit on F^2	1.088	1.019	1.040	1.025
*R*1, w*R*2 [$I > 2s(I)$]	0.0903, 0.2566	0.0424, 0.1094	0.0527, 0.1456	0.0674, 0.1787
*R*1, w*R*2 [all data]	0.1969, 0.3084	0.0556, 0.1218	0.0742, 0.1635	0.1816, 0.2348
Max, min $\Delta\rho$/e Å^{-3}	0.317, -0.276	0.138, -0.200	0.783, -0.586	0.736, -0.683

1.3 Syntheses and Characterizations of Compounds

BODIPYs **1a** and **1b** were synthesized according to literature.[7]

Synthesis of BODIPY 2a: To a mixture of **1a** (52 mg, 0.16 mmol) and pyrrole (2 ml, 28 mmol) was added trifluoroacetic acid (0.021 mL, 0.27 mmol) under argon. The reaction mixture was stirred at room temperature for 30 min, quenched by adding 30 mL aqueous solution of NaOH (0.2 M), extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. Organic layers were combined and evaporated under vacuum. The residue was purified through column chromatography (silica, CH_2Cl_2) afforded dipyrromethane intermediate, which was dissolved in 20 ml CH_2Cl_2 and directly used for the subsequent oxidation with DDQ (66 mg, 0.29 mmol) (1 h at room temperature). The resultant mixture was further treated with triethylamine (1 ml, 7.2 mmol) for 20 min, and complexed with boron trifluoride etherate (3 ml, 23.9 mmol) for 2 hrs at room temperature. Solvent was removed under vacuum and the reside was purified through column chromatograph (silica, hexane/ethyl acetate = 3/1, v/v) to afford **2a** as a red solid in 31% yield (24 mg): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 2H), 7.90 (s, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.23-7.09 (m, 6H), 6.73 (d, J = 3 Hz, 1H), 6.56 (s, 2H), 3.93 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 148.6, 147.7, 143.5, 141.7, 139.5, 136.4, 134.8, 134.4, 134.0, 132.6, 130.4, 130.1, 125.5, 125.1, 120.1, 118.4, 114.6, 55.7. HRMS (APCI) Calcd. for $C_{25}H_{19}B_2F_4N_4O$ $[M + H]^+$ 489.1676, found 489.1668; HRMS (APCI) Calcd. for $C_{25}H_{18}B_2F_3N_4O$ $[M - F]^+$ 469.1613, found 469.1611.

Synthesis of BODIPY 2b: To a mixture of **1a** (56.3 mg, 0.17 mmol) and 2,4-dimethylpyrrole (0.2 ml, 1.61 mmol) in 2 mL CH_2Cl_2 was added trifluoroacetic acid (0.021 mL, 0.27 mmol) under argon. The reaction mixture was stirred at room temperature for 30 min, quenched by adding 30 mL aqueous solution of NaOH (0.2 mol/L), extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. Organic layers were combined and evaporated under vacuum. The residue was purified through column chromatography (silica, CH_2Cl_2) to

afford dipyrromethane intermediate, which was dissolved in 20 mL CH_2Cl_2 and treated with DDQ (56.8 mg, 0.25 mmol) for 1 h at room temperature. The resultant mixture was further treated with triethylamine (1 ml, 7.2 mmol) for 20 min, and complexed with boron trifluoride etherate (3 ml, 23.9 mmol) for 2 hrs at room temperature. Solvent was removed under vacuum and the residue was purified through column chromatograph (silica, hexane/ethyl acetate = 3/1, v/v) to afford **2b** as a red solid in 23% yield (22 mg): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.77 (s, 1H), 7.55 (d, J = 7.8 Hz, 2H), 7.11 (s, 1H), 7.06 (d, J = 8.1 Hz, 2H), 6.89 (s, 1H), 6.66 (s, 1H), 6.00 (s, 2H), 3.91 (s, 3H), 2.54 (s, 6H), 1.76 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6, 155.8, 148.0, 145.9, 142.7, 140.3, 135.5, 134.7, 133.7, 133.2, 132.6, 131.8, 129.1, 125.8, 125.5, 121.5, 119.7, 114.4, 55.6, 15.2, 14.6. HRMS (APCI) Calcd. for $C_{29}H_{27}B_2F_4N_4O$ $[M + H]^+$ 545.2302, found 545.2297. HRMS (APCI) Calcd. for $C_{29}H_{26}B_2F_3N_4O$ $[M - F]^+$ 525.2239, found 525.2234.

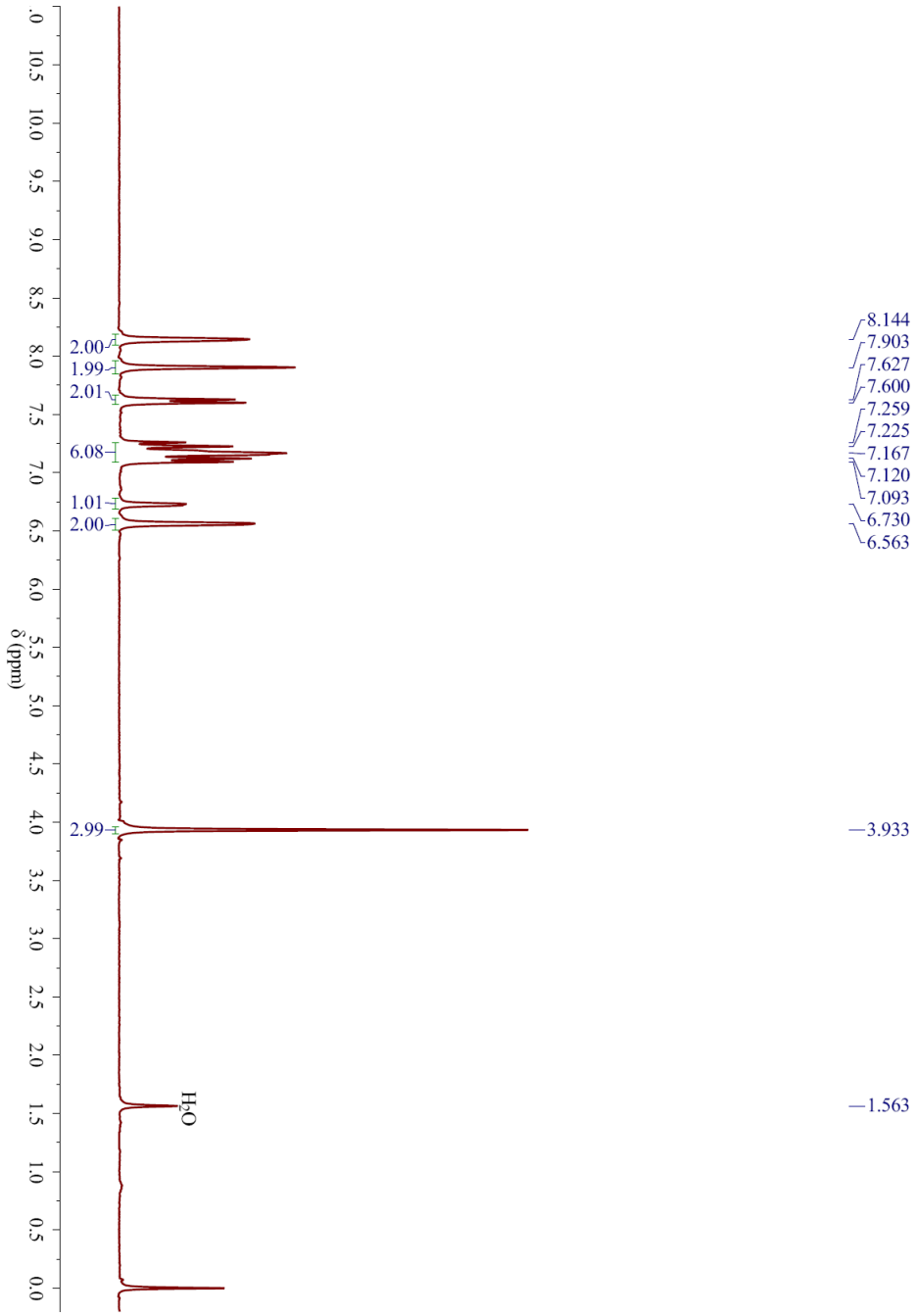
Synthesis of BODIPY 2c: To a mixture of **1b** (60 mg, 0.16 mmol) and pyrrole (2 ml, 28 mmol) was added trifluoroacetic acid (0.021 mL, 0.27 mmol) under argon. The reaction mixture was stirred at room temperature for 30 min, quenched by adding 30 mL aqueous solution of NaOH (0.2 mol/L), extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. Organic layers were combined and evaporated under vacuum. The residue was purified through column chromatography (silica, CH_2Cl_2) to afford dipyrromethane intermediate, which was dissolved in 20 mL CH_2Cl_2 and treated with DDQ (60 mg, 0.26 mmol) for 1 h at room temperature. The resultant mixture was further treated with triethylamine (1 ml, 7.2 mmol) for 20 min, and complexed with boron trifluoride etherate (3 ml, 23.9 mmol) for 2 hrs at room temperature. Solvent was removed under vacuum and the residue was purified through column chromatograph (silica, hexane/ethyl acetate = 4/1, v/v) to afforded **2c** as a red solid in 33% yield (29 mg): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.16 (s, 1H), 7.90 (s, 2H), 7.53-7.46 (m, 3H), 7.15 (s, 2H), 6.93 (s, 2H), 6.71 (s, 1H), 6.57 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 143.7, 143.1, 141.9, 138.8, 137.1, 135.0, 134.2, 134.0, 133.1, 132.0, 130.4,

130.1, 128.9, 128.6, 125.5, 122.0, 118.4. HRMS (APCI) Calcd. for $C_{24}H_{15}B_2Cl_2F_4N_4$ $[M + H]^+$ 527.0791, found 527.0795; HRMS (APCI) Calcd. for $C_{24}H_{14}B_2Cl_2F_3N_4$ $[M - F]^+$ 507.0728, found 507.0723.

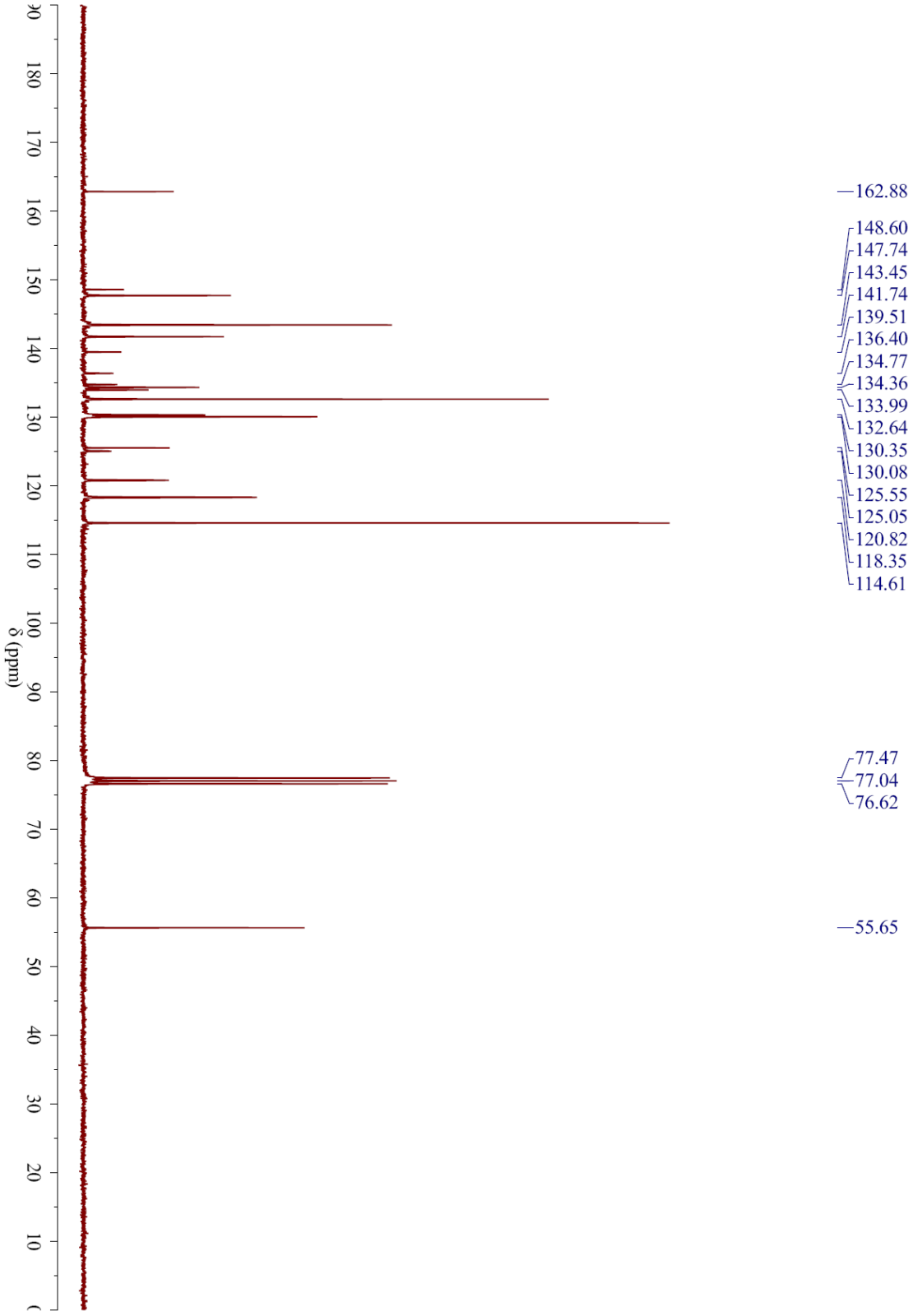
Synthesis of BODIPY 2d: To a mixture of **1b** (61 mg, 0.17 mmol) and 2,4-dimethylpyrrole (0.2 ml, 1.61 mmol) in CH_2Cl_2 (2 ml) was added trifluoroacetic acid (0.021 mL, 0.27 mmol) under argon. The reaction mixture was stirred at room temperature for 30 min, quenched by adding 30 mL aqueous solution of NaOH (0.2 mol/L), extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. Organic layers were combined and evaporated under vacuum. The residue was purified through column chromatography (silica, CH_2Cl_2) to afford dipyrromethane intermediate, which was dissolved in 20 mL CH_2Cl_2 and treated with DDQ (58 mg, 0.26 mmol) for 1 h at room temperature. The resultant mixture was further treated with triethylamine (1 ml, 7.2 mmol) for 20 min, and complexed with boron trifluoride etherate (3 ml, 23.9 mmol) for 2 hrs at room temperature. Solvent was removed under vacuum and the residue was purified through column chromatograph (silica, hexane/ethyl acetate = 4/1, v/v) to afford **2d** as a red solid in 25% yield (24 mg): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.79 (s, 1H), 7.47 (br, 3H), 6.84 (s, 1H), 6.61 (d, J = 9.3 Hz, 2H), 5.99 (s, 2H), 2.52 (s, 6H), 1.76 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 148.5, 142.8, 141.9, 141.2, 135.8, 134.9, 134.5, 133.0, 131.9, 131.7, 131.6, 130.7, 128.4, 127.8, 126.1, 121.5, 120.8, 15.2, 14.6. HRMS (APCI) Calcd. for $C_{28}H_{23}B_2Cl_2F_4N_4$ $[M + H]^+$ 583.1417, found 583.1411; HRMS (APCI) Calcd. for $C_{28}H_{22}B_2Cl_2F_3N_4$ $[M - F]^+$ 563.1354, found 563.1359.

2. Copies of ^{1}H and ^{13}C NMR

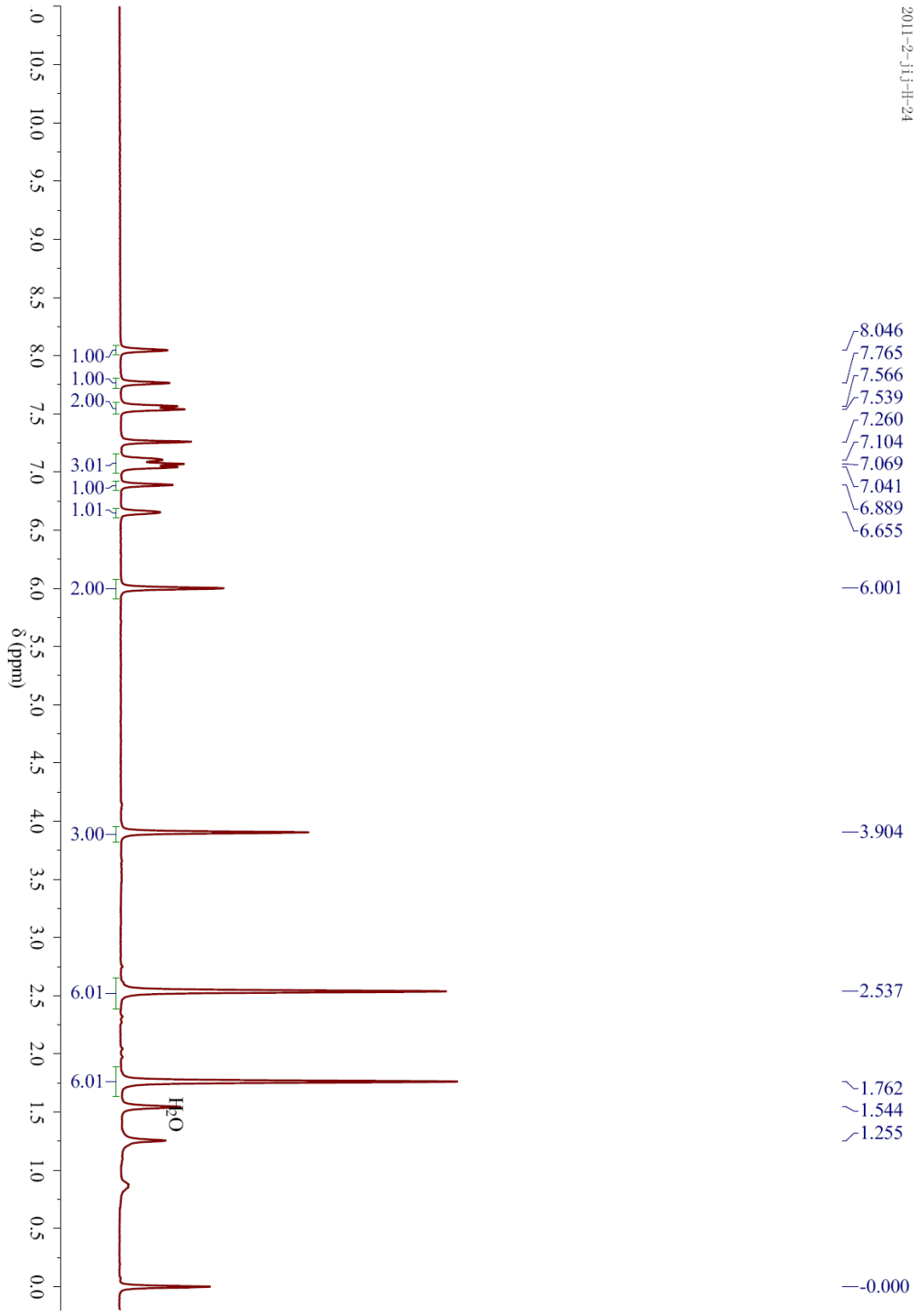
^{1}H NMR compound **2a** in $CDCl_3$



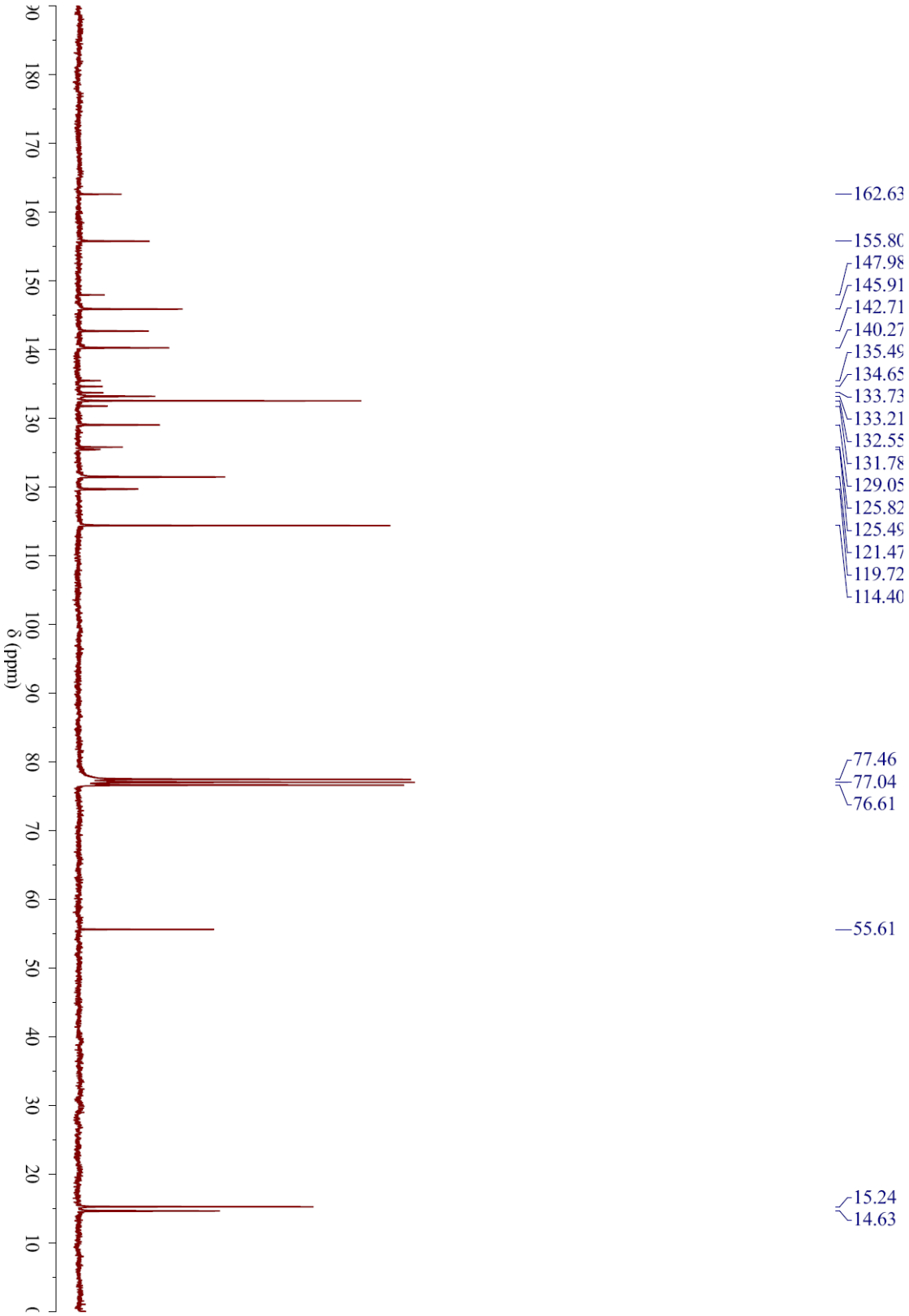
^{13}C NMR compound **2a** in CDCl$_3$



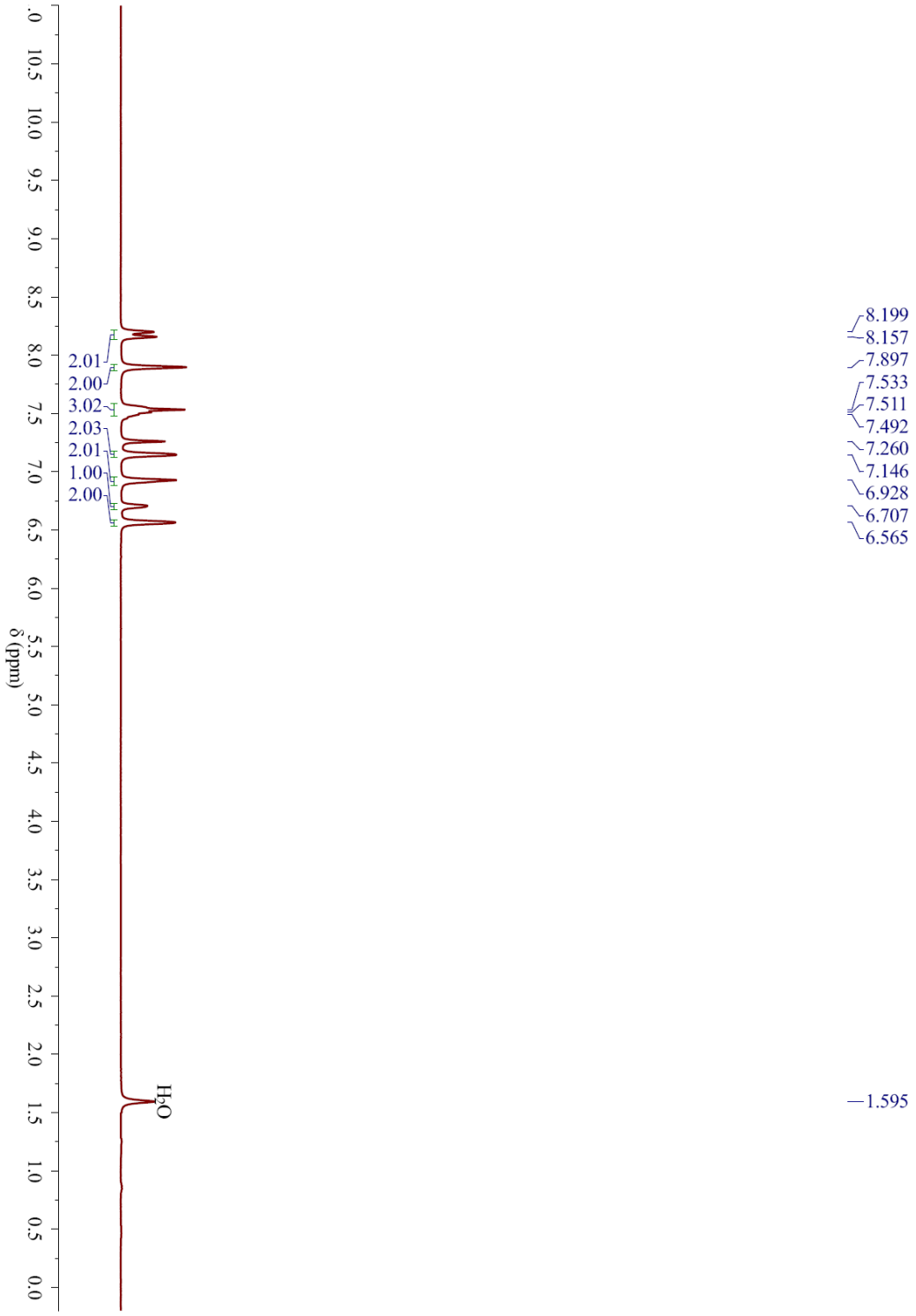
^{1}H NMR compound **2b** in $CDCl_3$



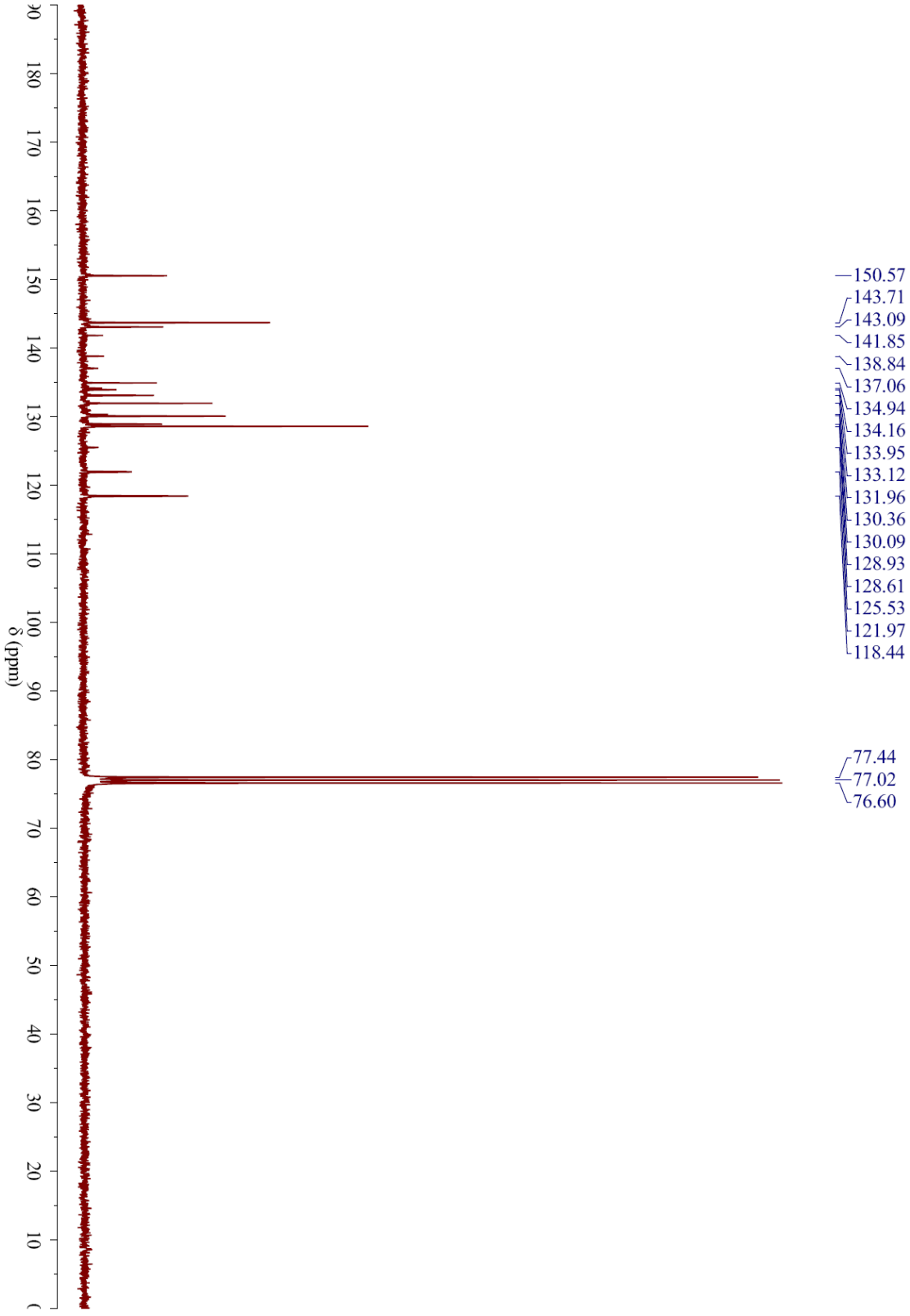
^{13}C NMR compound **2b** in $CDCl_3$



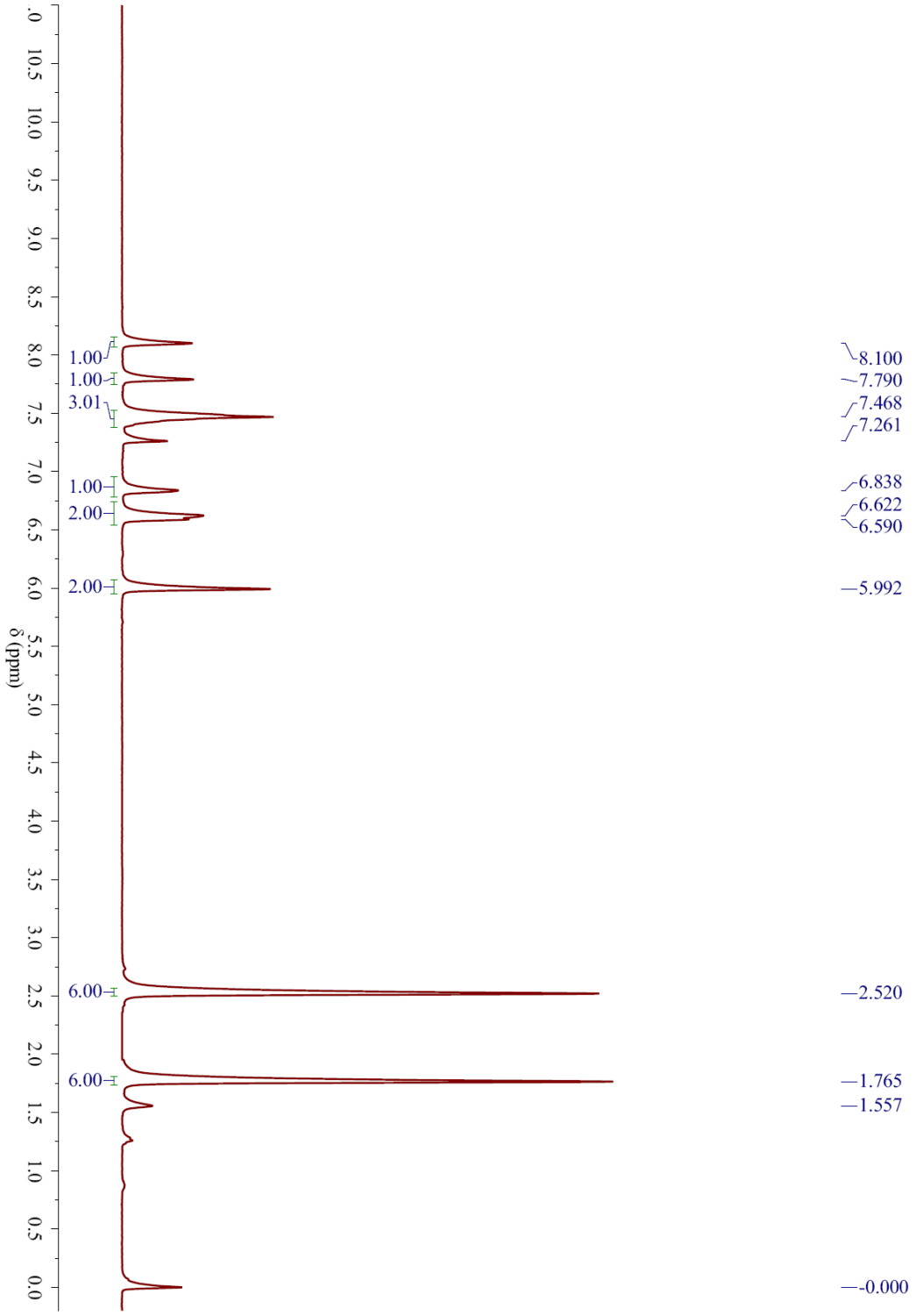
^{1}H NMR compound **2c** in $CDCl_3$



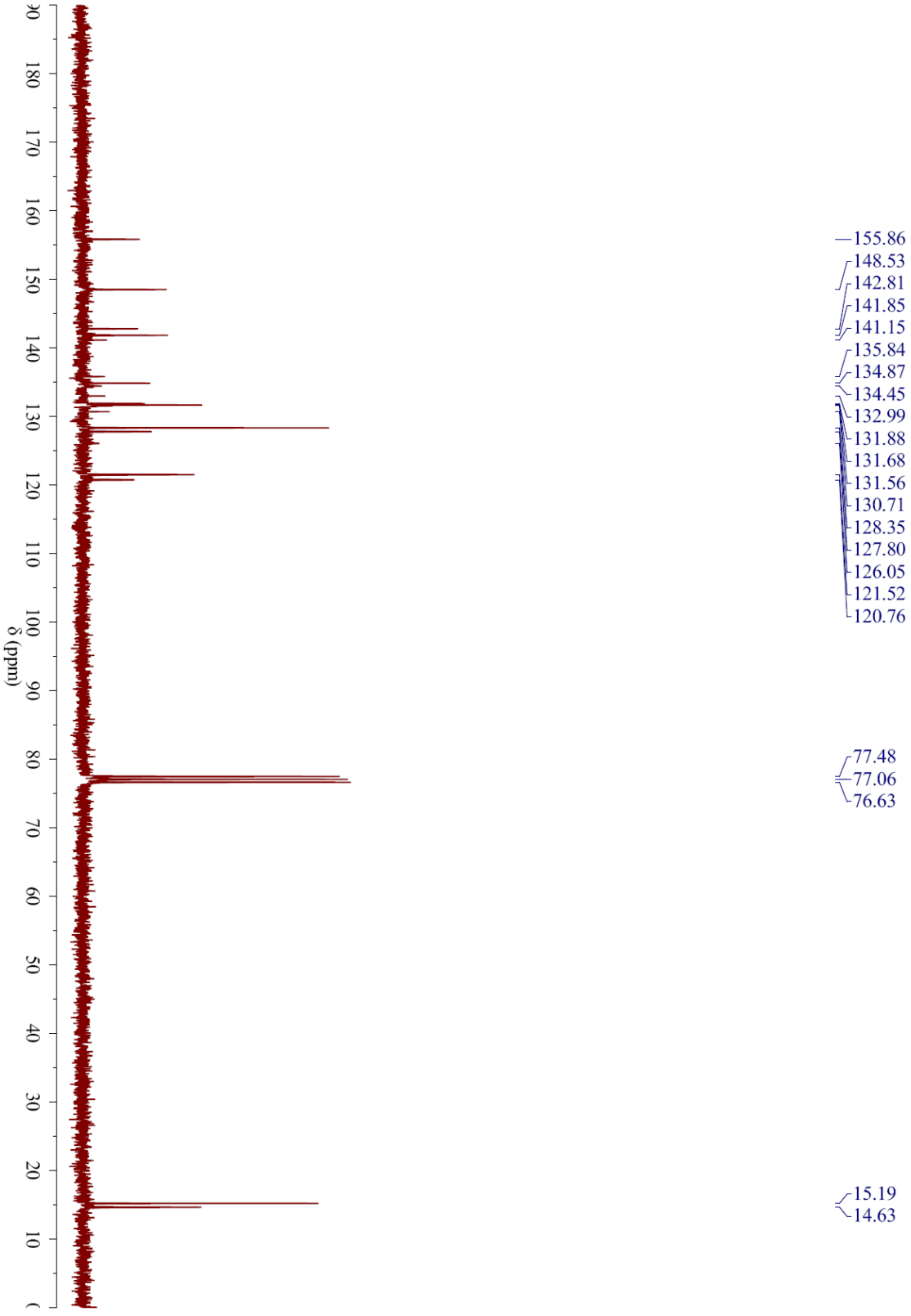
^{13}C NMR compound **2c** in $CDCl_3$



^{1}H NMR compound **2d** in $CDCl_3$



^{13}C NMR compound **2d** in $CDCl_3$



3. Photophysical data

3.1 Absorption and fluorescence spectra

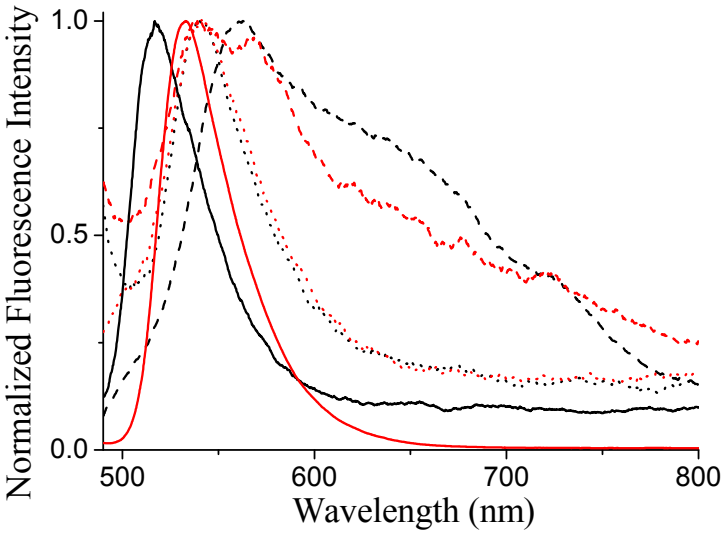


Figure S1. Overlapped Normalized fluorescence spectra of BODIPYs **1a** (black, solid line), **1b** (red, solid line), BODIPY dimers **2a** (balck, dashed line), **2b** (balck, dotted line), **2c** (red, dashed line) and **2d** (red, dotted line) in dichloromethane.

3.2 Fluorescence lifetime spectra

Fluorescence lifetime was measured in distilled toluene by time-correlated single photon counting method (Edinburgh FL-900 spectrophotometer) with excitation at 380 nm by a CdS portable diode laser (100 ps).

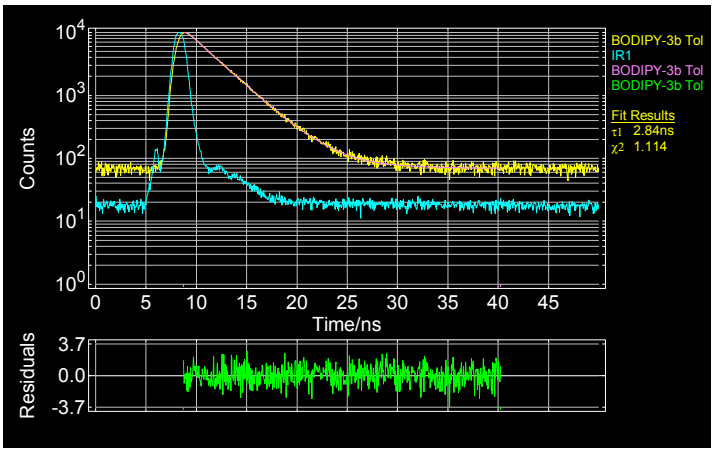


Figure S2. The fluorescence decay of dimer **2a** in distilled toluene measured by single photon counting method with emission was monitored at 625 nm.

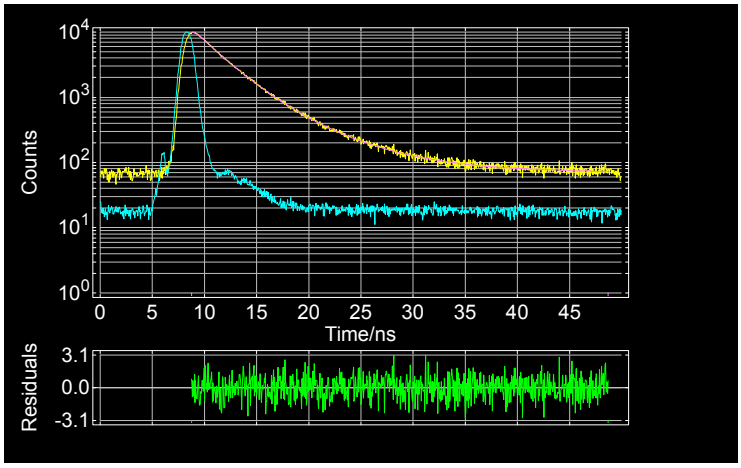


Figure S3. The fluorescence decay of dimer **2b** in distilled toluene measured by single photon counting method with emission was monitored at 705 nm.

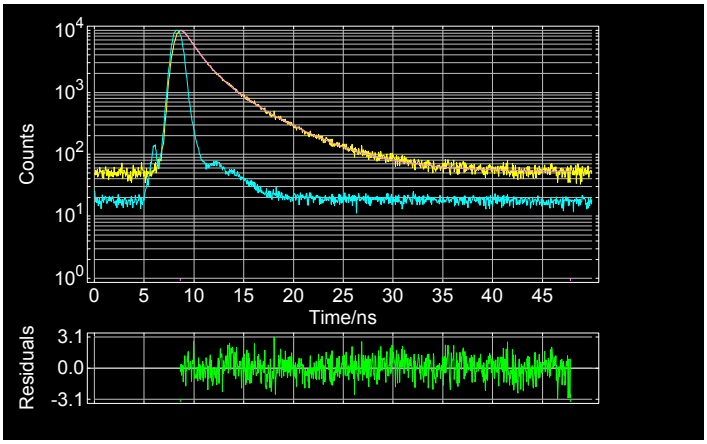


Figure S4. The fluorescence decay of dimer **2c** in distilled toluene measured by single photon counting method with emission was monitored at 650 nm.

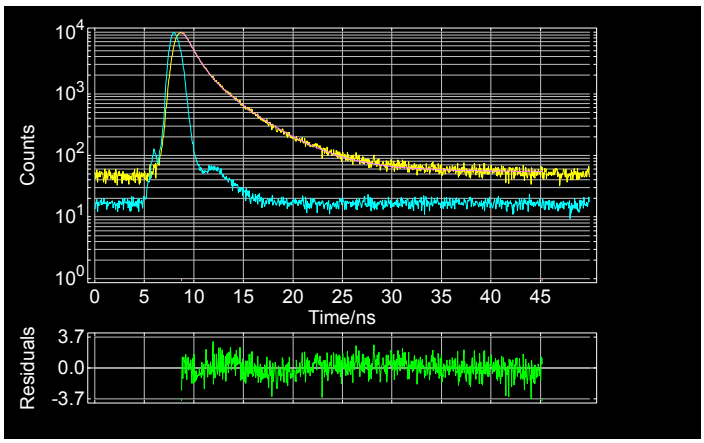


Figure S5. The fluorescence decay of dimer **2d** in distilled toluene measured by single photon counting method with emission was monitored at 745 nm.

3.3 Singlet oxygen phosphorescence

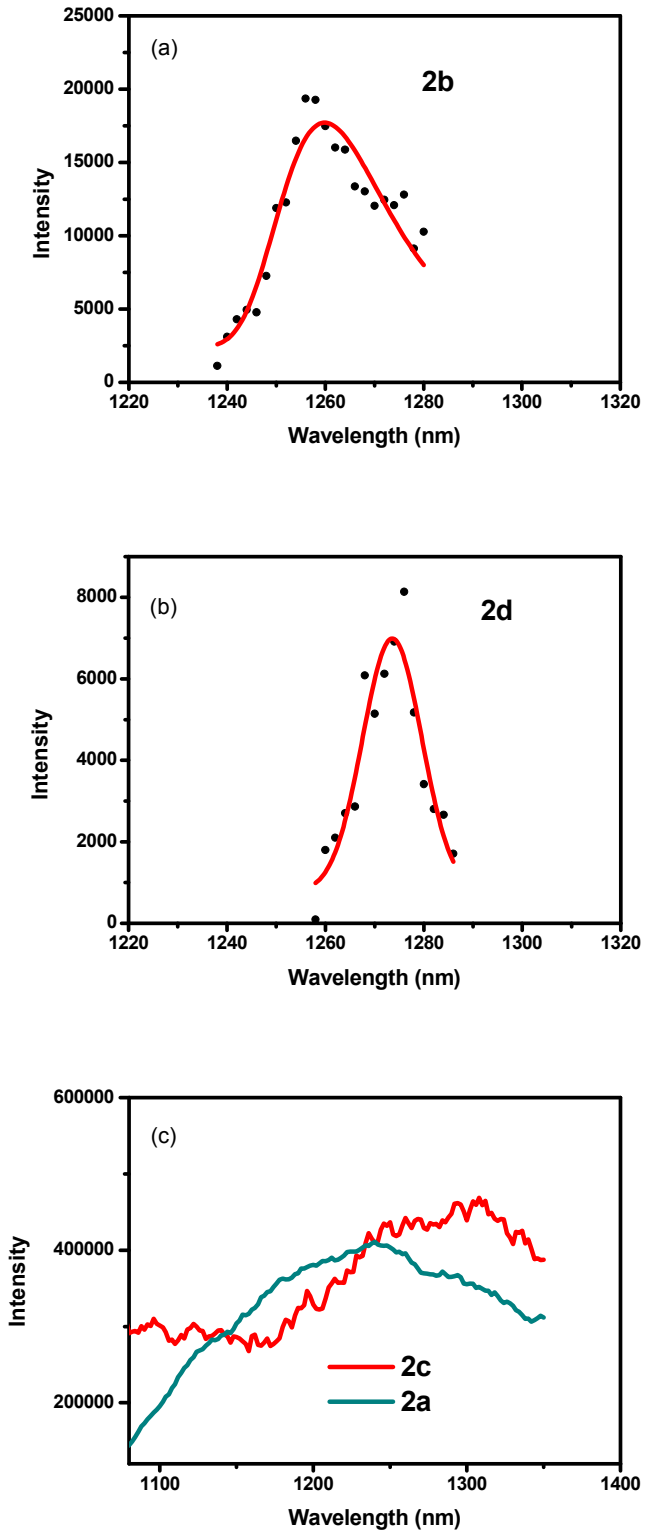


Figure S6. Singlet oxygen phosphorescence with sensitization from dimeric BODIPYs **2b** (a), **2d** (b), **2a**(c), and **2c** (c) in toluene at equal absorbances at the wavelength of 509 nm with InGaAs as detector. Plots were based on the average of 10 times collection.

3.4 Photooxidation of 1,3-diphenylisobenzofuran (DPBF) with BODIPY dimers 2a-d

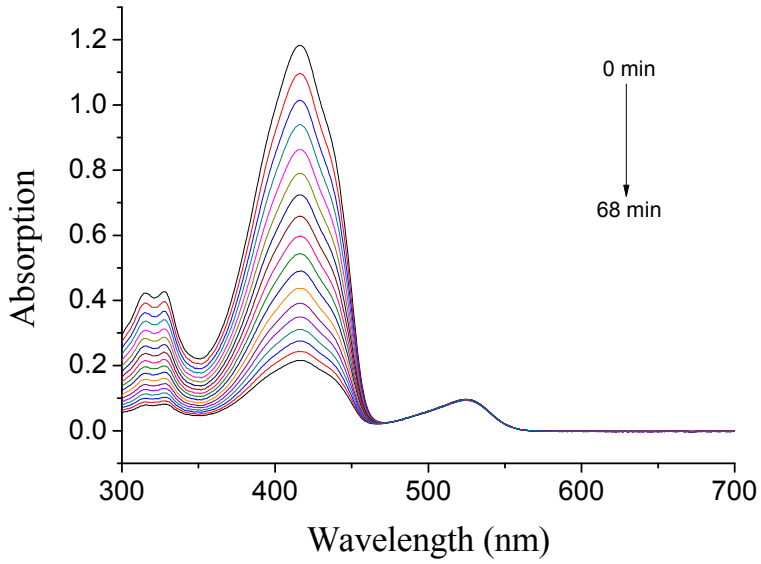


Figure S7. DPBF (initial concentration at 5×10^{-5} M) degradation profile in toluene by BODIPY dimer **2a** (1×10^{-6} M). Filtered light > 455 nm used.

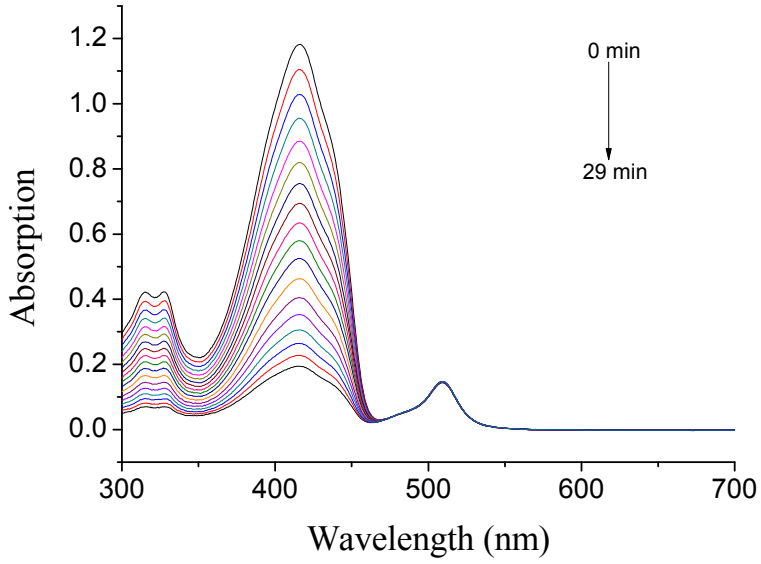


Figure S8. DPBF (initial concentration at 5×10^{-5} M) degradation profile in toluene by BODIPY dimer **2b** (1×10^{-6} M). Filtered light > 455 nm used.

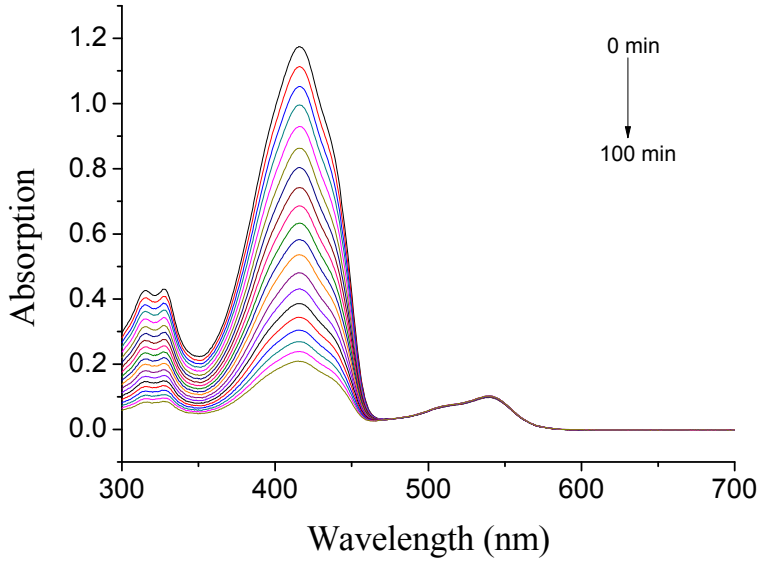


Figure S9. DPBF (initial concentration at 5×10^{-5} M) degradation profile in toluene by BODIPY dimer **2c** (1×10^{-6} M). Filtered light > 455 nm used.

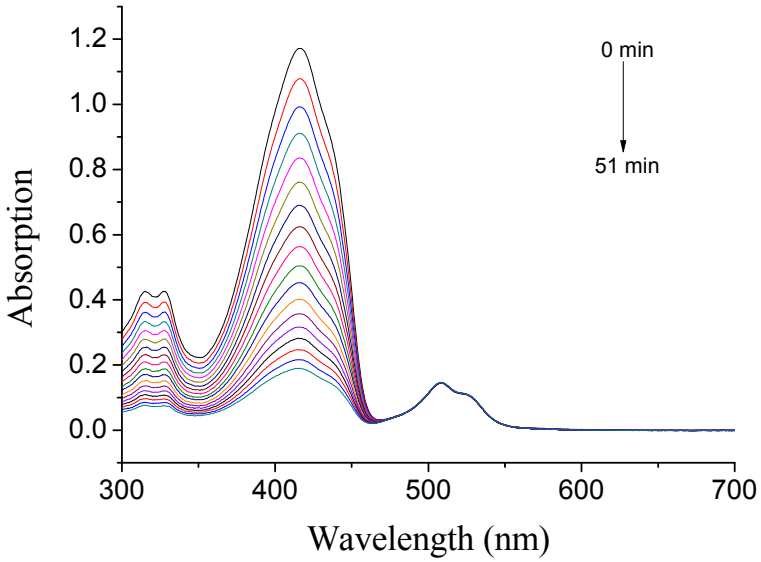


Figure S10. DPBF (initial concentration at 5×10^{-5} M) degradation profile in toluene by BODIPY dimer **2d** (1×10^{-6} M). Filtered light > 455 nm used.

Reference:

(1) K. G. Casey, E. L. Quitevis, *J. Phys. Chem.* **1988**, *92*, 6590.

(2) S. Fery-Forgues, D. Lavabre, *J. Chem. Educ.* **1999**, *76*, 1260.

(3) SAINT V 6.01 (NT) *Software for the CCD Detector System,* Bruker Analytical X-ray Systems, Madison, WI (**1999**).

(4) G. M. Sheldrick, SHELXS-90, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1990**.

(5) SHELXL-97, *Program for the Refinement of Crystal Structure*, University of G¨ ottingen, Germany, **1997**.

(6) SHELXTL 5.10 (PC/NT-Version), *Program Library for Structure Solution and Molecular Graphics*, Bruker Analytical X-ray Systems,Madison, WI (**1998**).

(7) a) L. Jiao, C. Yu, J. Li, Z. Wang, M. Wu, E. Hao, *J. Org. Chem.* **2009**, *74*, 7525 – 7528; b) C. Yu, L. Jiao, H. Yin, Z. Zhou, W. Pang, Y. Wu, Z. Wang, Y. Gao, E. Hao, *Eur. J. Org. Chem.* **2011**, 5460 – 5468.