SUPPORTING INFORMATION

Design and synthesis of a new chromophore, 2-(4-nitrophenyl)benzofuran, for two-photon uncaging using near-IR light

Naomitsu Komori,[a] Satish Jakkampudi,[a,b] Ryusei Motoishi,[a] Manabu Abe*[a,b,c], Kenji Kamada,*[d] Ko Furukawa,[e] Claudine Katan*[f], Wakako Sawada,[g] Noriko Takahashi,[g] Haruo Kasai,[b,g] Bing Xue,[b,h] and Takayoshi Kobayashi[b,h]

[a]*Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan.*

[b]*JST-CREST, K's Gobancho, 7, Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan.*

[c]*Research Centre for Smart Materials, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan.*

[d]*IFMRI, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan.*

[e]*Centre for Instrumental Analysis, Niigata University, 8050 Ikarashi 2-no-cho, Nishi-ku, Niigata, 950-2181, Japan.*

[f]*Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Universite Rennes 1, 35042 Rennes, France.*

[g]*Laboratory of Structural Physiology, CDBIM, Graduate School of Medicine, The University of Tokyo, Bunkyo-ku, Tokyo, 113-0033, Japan*

[h]*Advanced Ultrafast Laser Research Center, The University of Electro-Communications, Chofugaoka 1-5-1,Chofu,Tokyo 182-8585 Japan*

Contents **Page**

Computational details:

We used density functional theory (DFT) and time-dependent (TD) DFT approaches, as implemented in the Gaussian 03 and 09 packages [1,2], to model chromophores **NPBF** and **NDBF**. Calculations have been performed in vacuum and were limited to properties related to the ground state geometry: geometry optimization, one and two-photon absorption related to the electronically excited states (ES). Optical spectra were obtained employing the density matrix formalism for non-linear optical responses as proposed by S. Tretiak and V. Chernyak [3,4]. Figure 2 shows one-photon absorption (OPA) and two-photon absorption (TPA) spectra obtained at the TD-B3LYP/6-31G*//HF/6-31G* level of theory in conventional quantum chemical notation “single point//optimization level” including up to 20 singlet ES. This level of theory has been shown to provide good predictions for structure-TPA relationships [4]. The damping factor introduced to simulate the finite linewidth in the resonant spectra has been fixed to Γ=0.10 eV. The ES structure was further checked for related chromophores at different levels of theory using different basis sets and exchange correlation DFT functionals.

Both chromophores lead to sizable TPA cross sections in the vicinity of twice the wavelength of the first OPA band, which is related to the dipolar nature of the chromophores of interest. This can be further interpreted by considering the two-level approximation, which is a standard approach for push-pull chromophores. The TPA cross section at the maximum ($\hbar\omega = \hbar\omega_{0i}/2$) reads [4]:

$$\sigma_2 = 2{,}0757\ 10^{-3}\ \frac{\mu_{0i}^2(\mu_{ii} - \mu_{00})^2}{\Gamma}\ (GM) ,$$

where 0 and *i* label the ground and excited state of interest, respectively, and units of the input parameters are eV for Γ and Debye for dipole moments. This expression highlights that σ_2 is inversely proportional to the average linewidth broadening parameter Γ. Calculated state and transition dipole moments as well as the values of σ_2 deduced from the two-state model are reported in Table S1 for **NPBF** and **NDBF**. When using the same exchange correlation functional, namely B3LYP, the two-state approximation (Table S1) leads to almost quantitative agreement with the calculated spectra based on an extended sum over states shown Figure 2. **The three-fold increase of the TPA amplitude when going from NDBF to NPBF can be traced back to both larger excited state dipole moments and transition dipole moments, whereas ground state dipole moments remain similar for both chromophores.**

The nature of the electronic redistribution upon photo-excitation related to the transition dipole moments is illustrated by the corresponding natural transition orbitals [5] shown Figure S1. Besides, the use of other model chemistry, as implemented for **NDBF**, illustrates the great sensitivity of TPA amplitude to dipole moment matrix elements in addition to other limitations [4].

Table S1. Calculated state and transition dipole moments using the 6-31G* basis set and for geometries optimized at the HF/6-31G* level of theory. The TPA cross section at the maximum is derived from the two-state model.

	TD-DFT functional	i	μ_{ii} (D)			μ_{00} (D)			μ_{01} (D)			σ_2 (GM)
			x	y	z	x	y	z	x	y	z	
NPBF	B3LYP	1	-17,6	1,0	0,0	-5,2	0,9	0,0	-6,6	0,4	0,0	140
NDBF	B3LYP	3	13,0	3,9	0,0	5,0	2,3	0,0	5,1	1,1	0,0	41
	CAM-B3LYP	3	10,5	1,1	0,0	5,2	1,5	0,0	5,4	0,2	0,0	17
	ωB97XD	3	10,2	1,6	0,0	5,3	1,5	0,0	5,4	0,0	0,0	15

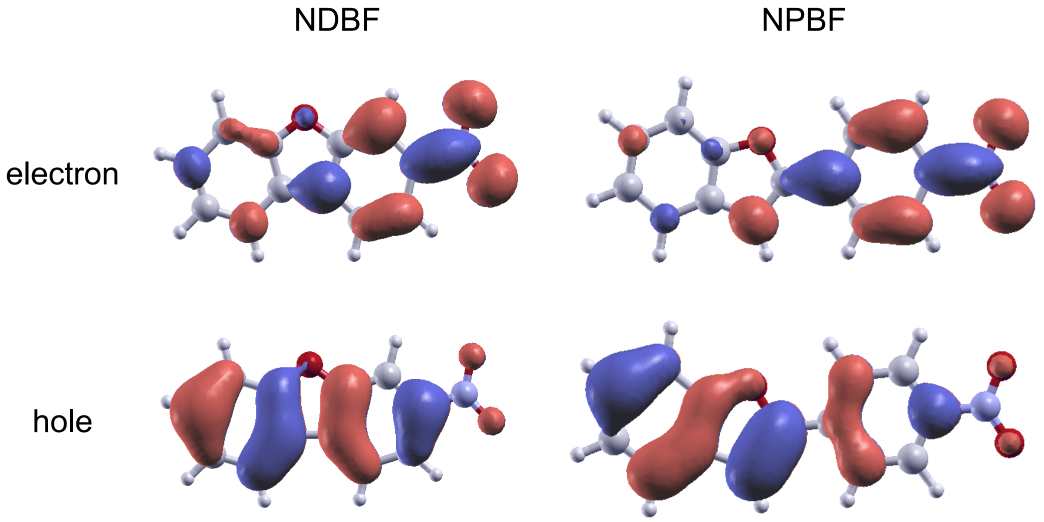

Figure S1. Natural transition orbitals[5] of the excited state that dominates OPA and TPA bands of NDBF and NPBF.

Experimental Procedures and Product Characterization

(*1-(5-bromo-2-nitrophenyl)ethane-1-one* (*2*): A flask was charged with KNO_3 (205.23 mg, 2.03 mmol) and was cooled to 0 °C, to which conc. H_2SO_4 (5 mL) was added slowly and mixture was allowed to stir for 10 min. 3-bromoacetophenone **1** (0.27 mL, 0.23 mmol) was added at 0°C. Temperature was raised to room temperature and stirred for 2 h. Subsequently the reaction mixture was poured into crushed ice. Aqueous layer was extracted with CH_2Cl_2. Organic layer was washed with brine, dried over Na_2SO_4, and purified through silica gel column chromatography to give required product (336.9 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.7 Hz, 1 H), 7.73 (dd, J = 8.7 and 2.1 Hz, 1H), 7.54 (d, J = 2.1 Hz, 1 H), 2.55 (s, 3H); HRMS-APCI: calcd for $C_8H_7O_3NBr$: 243.96038, found 243.96010 $[M + H]^+$.

1-(5-bromo-2-nitrophenyl)ethane-1-ol **(*3*):** To a stirred solution of 1-(5-bromo-2-nitrophenyl)ethane-1-one **2** (301.3 mg, 1.23 mmol) in methanol (10 mL) was added $NaBH_4$ (60.2 mg, 1.48 mmol) in portion at 0 °C. Temperature was slowly raised to room temperature. Stirring was continued for additional 1 h. After completion of the reaction, methanol was removed under reduced pressure. Reaction mixture was partitioned between the ethyl acetate and water, organic layer was combined, washed with brine, dried over Na_2SO_4, filtered and evaporated under reduced pressure to give the required compound which requires no further purification (287.5 mg, 95%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 2.1 Hz, 1 H), 7.82 (d, J = 8.7 Hz, 1 H), 7.55 (dd, J = 8.7 and 2.1 Hz, 1 H), 5.47 (m, 1 H), 2.24 (d, J = 3.9, 1 H), 1.57 (d, J = 1.3, 3 H); HRMS-APCI: calcd for $C_8H_7O_3NBr$: 243.96038, found 243.95999 $[M - H]^+$.

1-(5-(benzofuran-2-yl)-2-nitrophenyl)ethane-1-ol **(*4*):** To a mixture 2-benzofuranboronic acid (100.3 mg, 0.62 mmol), 1-(5-bromo-2-nitrophenyl)ethane-1-ol **3** (152.7 mg, 0.62 mmol), and K_2CO_3 (120.2 mg, 0.87 mmol) in THF/H_2O (1:1) (5 mL) was added $Pd(PPh_3)_4$ (37.1 mg, 0.032 mmol) under N_2 and the mixture was heated under reflux for 15 h. The reaction mixture was quenched with saturated NH_4Cl solution (6 mL) and extracted with ethyl acetate. The combined extracts were washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. Flash chromatography on silica gel using hexane/ethyl acetate (5:1) afforded compound **4** (167.6 mg, 95%). mp 112-114 °C. IR (KBr): v 3306, 2993, 2929, 1608, 1584, 1511,1334, 1324, 1298, 1105, 861 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ 8.40 (d, J = 2.0 Hz, 1 H), 8.03 (d, J = 8.6, 1 H), 7.96 (dd, J = 8.6 and 2.0 Hz, 1 H), 7.67 (m, 1 H), 7.58 (dd, J = 8.2 and 0.7 Hz, 1 H), 7.45 (d, J = 0.9 Hz, 1 H), 7.37 (m, 1 H), 7.28 (dt, J = 7.7 and 0.9 Hz, 1 H), 5.43 (q, J = 6.3 Hz, 1 H), 1.55 (d, J = 6.3 Hz); ^{13}C NMR (100 MHz, CD_3OD): δ 156.79, 154.94, 148.08, 144.49, 136.40, 130.24, 126.75, 126.22, 124.79, 124.58, 124.50, 122.75, 112.25, 105.87, 66.15, 25.20; HRMS-ESI: calcd for $C_{16}H_{13}O_4NNa$: 306.07368, found 306.07364 $[M + Na]^+$.

1-(5-(benzofuran-2-yl)-2-nitrophenyl)ethyl benzoate **(*5*):** Benzoic acid (15.3 mg, 0.13 mmol), DMAP (1.5 mg, 0.012 mmol) and 1-(5-(benzofuran-2-yl)-2-nitrophenyl)ethane-1-ol **4** (35.0 mg, 0.12 mmol) in anhydrous dichloromethane (5 mL) was stirred for 10 min. To the reaction mixture DCC (25.7 mg, 0.13 mmol) was added and stirred for 16 h at room temperature. Subsequently water was added into reaction mixture and compound was extracted with dichloromethane. The organic layer was washed with sodium bicarbonate solution and then with water and dried with anhydrous sodium sulfate and evaporated under reduced pressure. Flash chromatography on silica gel (hexane/EtOAc = 5/1, v/v) afforded compound **5** (30.5 mg, 64%). mp 192-194 °C. IR (KBr): v 2931, 2854, 1706, 1513, 1347, 1321, 1111, 821 cm^{-1}; ^1H NMR(400 MHz, DMSO-d_6): δ 8.30 (d, J = 1.8 Hz, 1 H), 8.16 (d, J = 8.6 Hz, 1 H), 8.10 (dd, J = 8.6 and 1.8 Hz, 1 H), 8.03 (m, 2 H), 7.82 (d, J = 0.8 Hz, 1 H), 7.73 (d, J = 7.6 Hz, 1 H), 7.68 (m, 2 H), 7.56 (t, J = 7.5 Hz, 2 H), 7.40 (dt, J = 7.6 and 1.3 Hz, 1H), 7.31 (dt, J = 7.6 and 0.8 Hz, 1 H), 6.44 (q, J = 6.5 Hz 1 H), 1.82 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.66, 155.51, 153.28, 146.84, 139.47, 135.69, 133.44, 130.03, 129.84, 128.75, 128.67, 125.87, 125.75, 124.50, 123.65, 123.24, 121.72, 111.64, 105.04, 69.02, 22.26; HRMS-ESI: calcd for $C_{23}H_{17}O_5NNa$: 410.09989, found 410.10001 $[M + Na]^+$.

***1-(3-nitrodibenzo[b,d]furan-2-yl)ethan-1-ol* (*7*):** 1-(3-nitrodibenzo[b,d]furan-2-yl)ethan-1-one **6** (56.2 mg, 0.22 mmol) was dissolved in CH_2Cl_2/MeOH (5/1 mL) and $NaBH_4$ (15.7 mg, 0.41 mmol) was added and stirred at room temperature for 1 h. After completion of the reaction, solvent was removed under reduced pressure. Reaction mixture was partitioned between CH_2Cl_2 and water, organic layer was combined, washed with brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 5/2, v/v) to give **7** as a yellow solid (43.2 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1 H), 8.17 (s, 1 H), 8.05 (d, J = 7.7 Hz, 1 H), 7.64 (d, J = 8.2 Hz, 1 H), 7.59 (t, J = 8.2 Hz, 1 H), 7.44 (t, J = 7.7 Hz, 1 H), 5.64-5.56 (m, 1 H), 2.39 (d, J = 3.7 Hz, 1 H), 1.68 (d, J = 6.3 Hz, 1 H).

***1-(3-nitrodibenzo[b,d]furan-2-yl)ethyl benzoate* (*8*):** 1-(3-nitrodibenzo[b,d]furan-2-yl)ethan-1-ol **7** (30.9 mg, 0.12 mmol) and benzoic acid (14.7 mg, 0.12 mmol), DMAP (1.5 mg, 0.012 mmol) in anhydrous dichloromethane (5 mL) was stirred for 10 min. To the reaction mixture DCC (24.6 mg, 0.12 mmol) was added and stirred for 23 h at room temperature. Subsequently water was added into reaction mixture and compound was extracted with dichloromethane. The organic layer was washed with sodium bicarbonate solution and then with water and dried with anhydrous sodium sulphate and evaporated under reduced pressure. Flash chromatography on silica gel (hexane/EtOAc = 5/1, v/v) afforded compound **8** (24.4 mg, 56%). mp 182-184 °C. IR (KBr): ν 3003, 2937, 1717, 1522, 1453, 1340, 1320, 1278, 1202, 713cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 2.0 Hz, 2 H), 8.10 (dd, J = 8.5 Hz and 1.3 Hz, 2 H), 8.01 (d, J = 7.7 Hz, 1 H), 7.64-7.55 (m, 3 H), 7.47 (t, J = 7.7 Hz, 2 H), 7.41 (dt, J = 7.5 and 1.1 Hz, 1 H), 6.70 (q, J = 6.4 Hz, 1 H), 1.89 (d, J = 6.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.64, 158.49, 154.19, 146.63, 133.62, 133.38, 130.14, 129.82, 129.66, 129.36, 128.64, 123.84, 122.56, 121.88, 118.84, 112.42, 108.76, 69.30, 22.77; HRMS-APCI: calcd for $C_{21}H_{15}O_5NNa$: 384.08424, found 384.08417 [M + Na]$^+$.

Diethyl 5-(5-(benzofuran-2-yl)-2-nitrophenyl)-3,12-bis(2-ethoxy-2-oxoethyl)-6,9-dioxa-3,12-diazatetradecanedioate (9): NPBF-EGTA ethyl ester was obtained in 9 synthetic steps as a yellow liquid which was used for uncaging reaction. IR: ν 2974, 2903, 2859, 1730, 1610, 1515, 1445, 1346, 1255, 1178, 1024, 746. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1 H), 8.1 (d, J = 8.6 Hz, 1 H), 7.9 (dd, J = 2.0 and 8.6 Hz, 1 H), 7.68 (d, J = 7.7 Hz, 1 H), 7.6 (d, J = 8.1 Hz, 1 H), 7.4-7.29 (m, 3H), 5.34-5.3 (m, 1 H), 4.22-4.07(m, 8 H), 3.8 (s, 4 H), 3.65-3.5(m, 10 H), 3.17-2.9(m, 4 H), 1.31-1.3(m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.82, 171.34, 170.19, 155.42, 147.24, 128.74, 125.68, 124.77, 124.04, 123.45, 121.65, 111.53, 105.18, 78.16, 77.35, 77.24, 77.03, 76.72, 70.29, 69.06, 61.30, 60.42, 55.87, 55.75, 53.71, 21.08, 14.28, 14.22. HRMS-ESI calcd for $C_{36}H_{47}N_3O_{13}Na$ 752.30011 found 752.30011 [M + Na]$^+$.

General Procedure of TP uncaging: TP photolysis measurements were carried out in air at room temperature. Concentration of samples was adjusted to an optical density of 0.5 at 360 nm. The excitation source for TP photolysis was a Ti:sapphire laser, Mai Tai, Spectra Physics, pulse width 100 fs, 80 MHz. The measurements were performed at a power of 700 mW at 700, 710, 720, 730, 740, 750 and 760 nm. After irradiated at 700-760 nm, each sample in 1.0 cm quartz cell is analyzed by HPLC to determine the percentage of unreacted caged benzoate. The TPA spectra over a wavelength range of 700-760 nm were extrapolated based on the obtained TP uncaging rate constant at 700-760 nm and the TPA cross-section values at 720 nm of the two species.

^{1}H and ^{13}C Spectra of Compounds

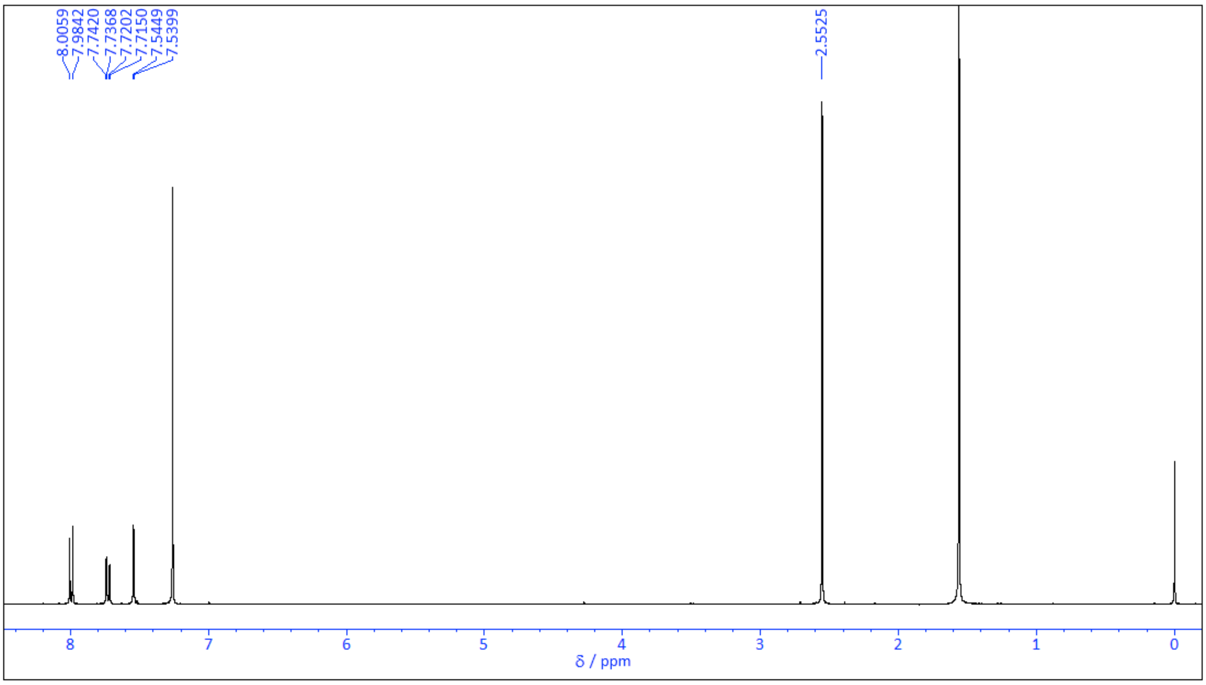

Figure S2. ^{1}H NMR spectrum of compound **2** (400 MHz, $CDCl_3$)

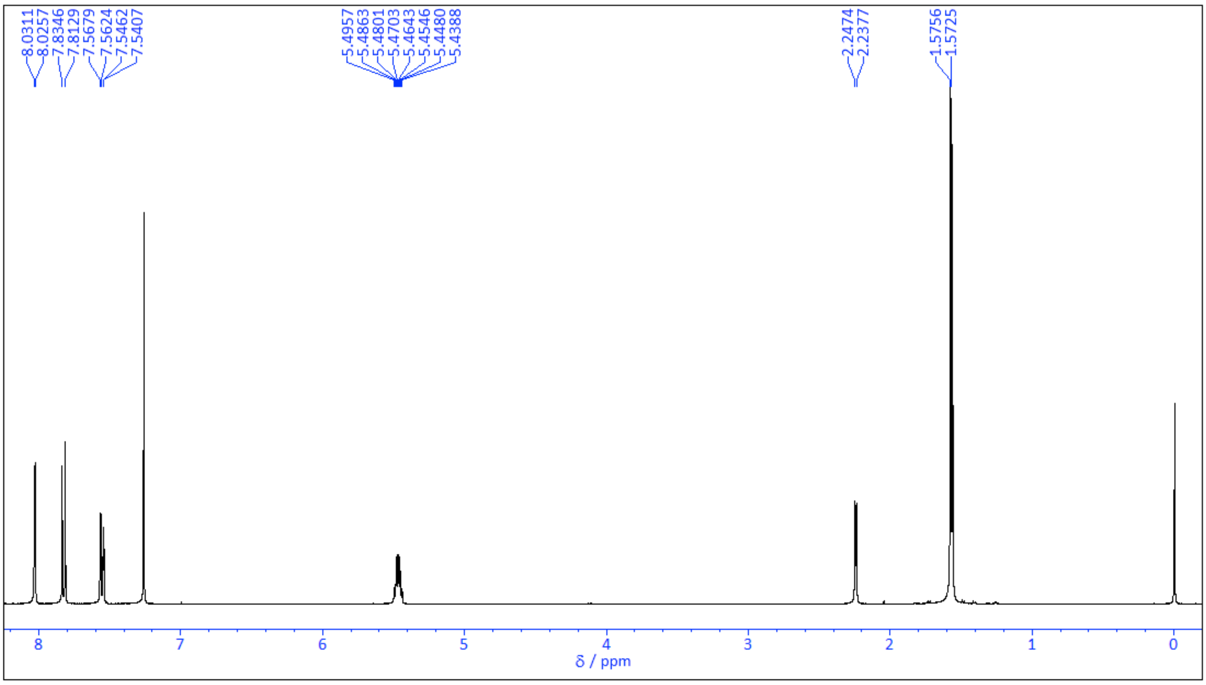

Figure S3. ^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$)

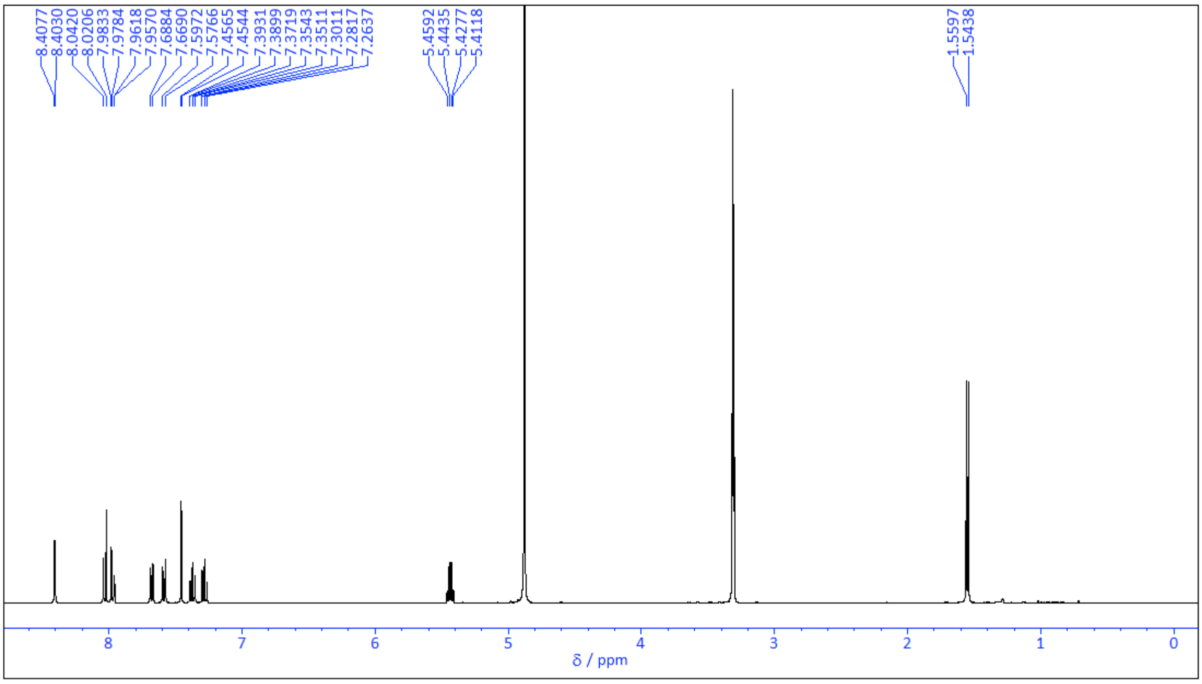

Figure S4. ^{1}H NMR spectrum of compound **4** (400 MHz, CD_3OD)

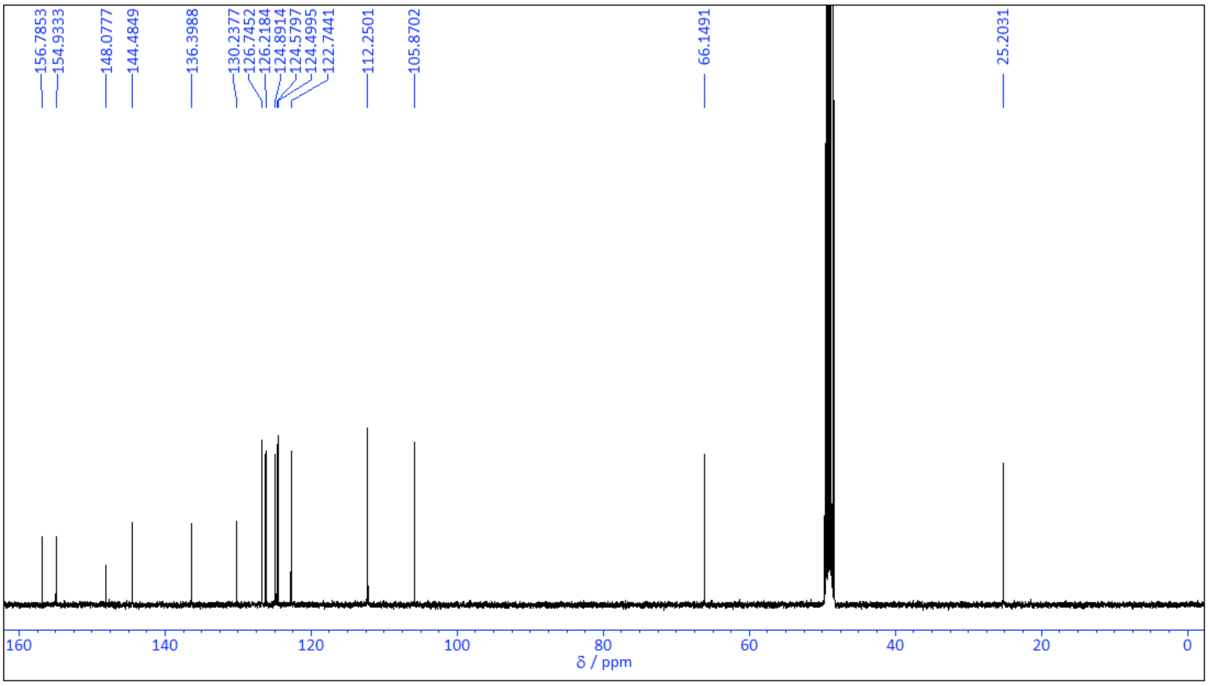

Figure S5. ^{13}C NMR spectrum of compound **4** (100 MHz, CD_3OD)

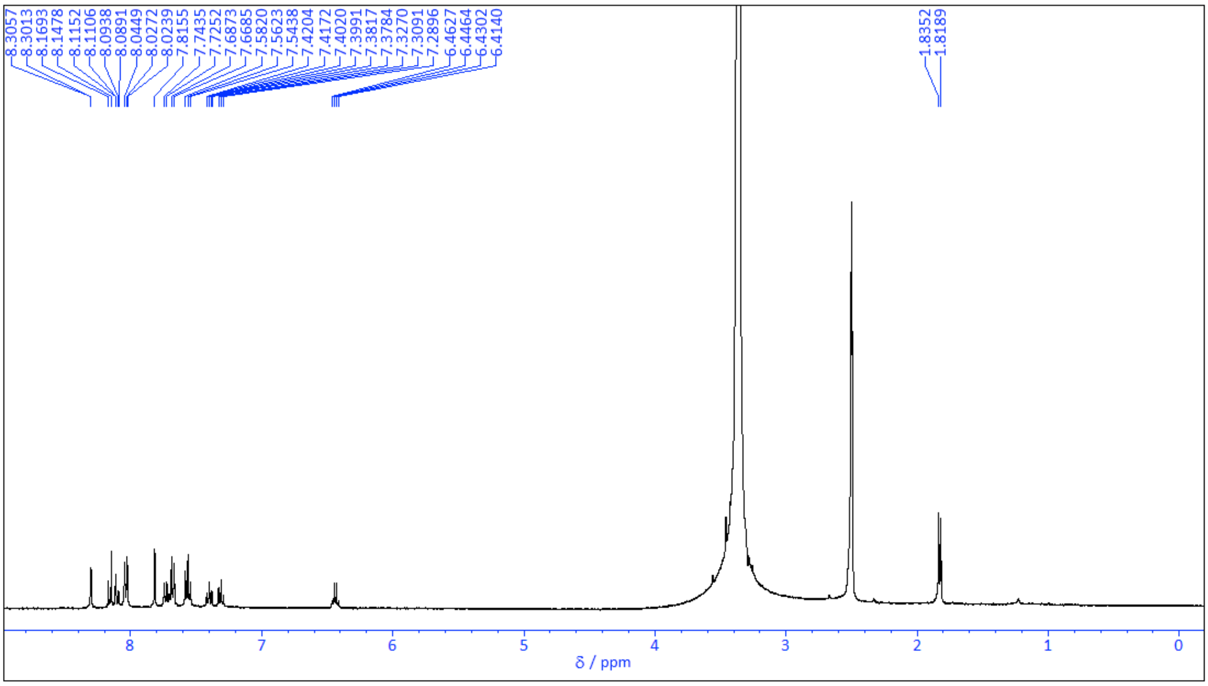

Figure S6. ^{1}H NMR spectrum of compound **5** (400 MHz, DMSO-d_6)

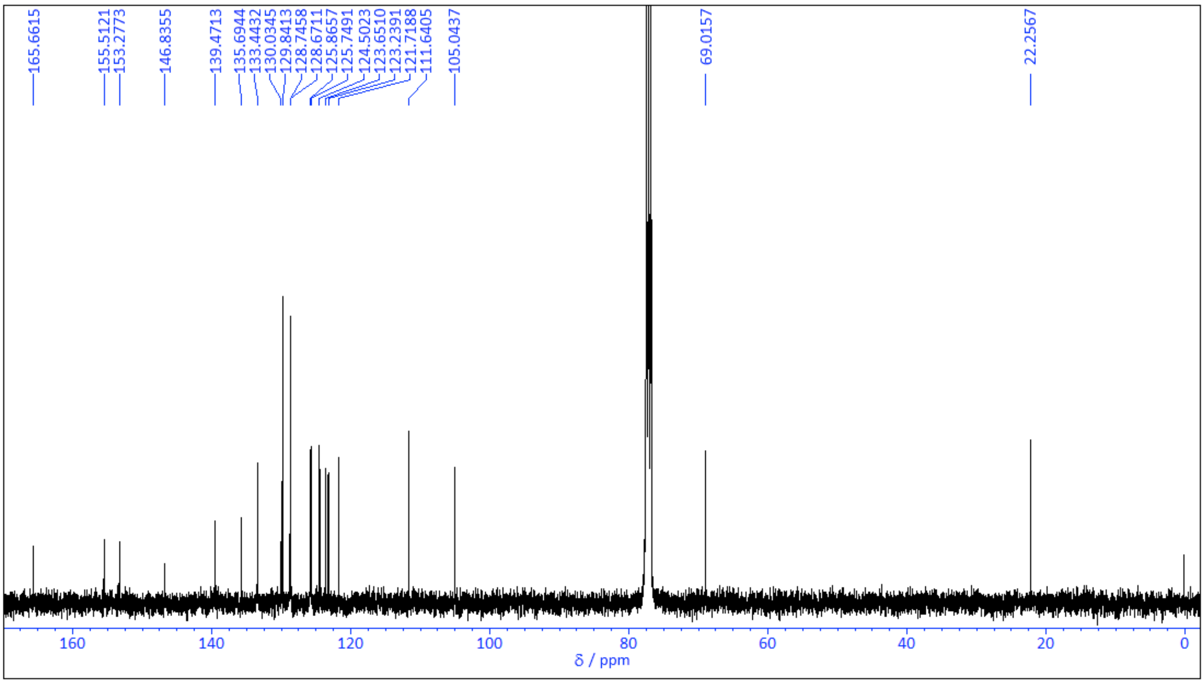

Figure S7. ^{13}C NMR spectrum of compound **5** (100 MHz, CDCl$_3$)

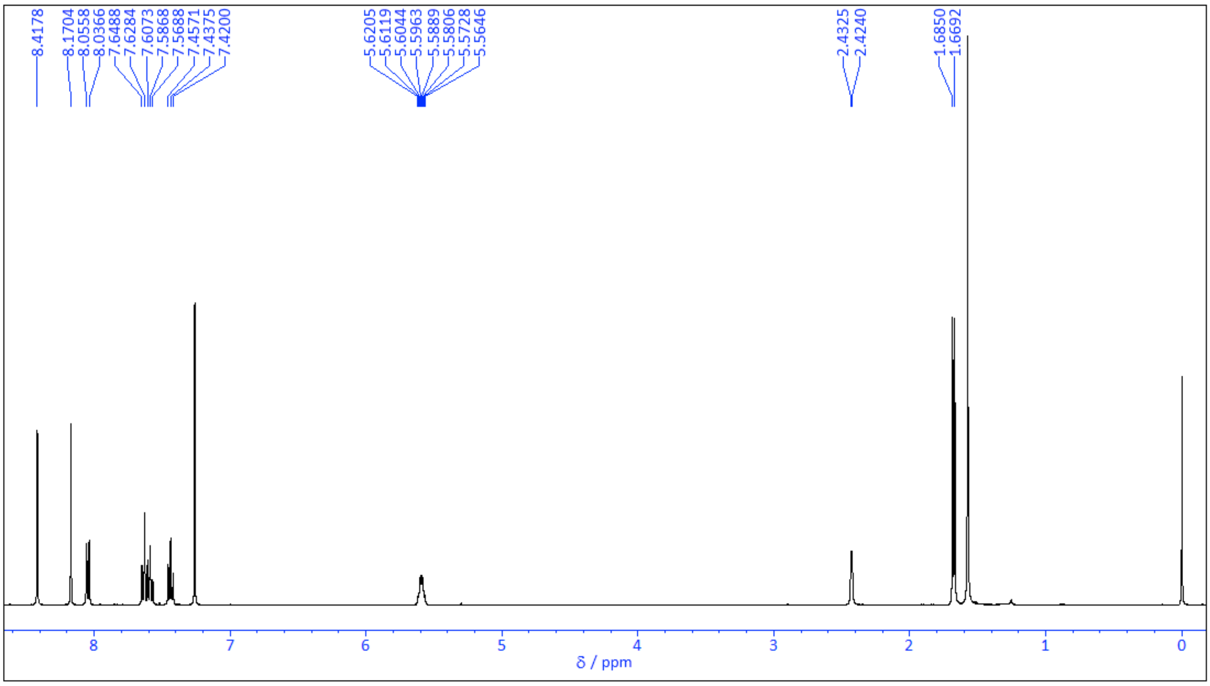

Figure S8. ^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$)

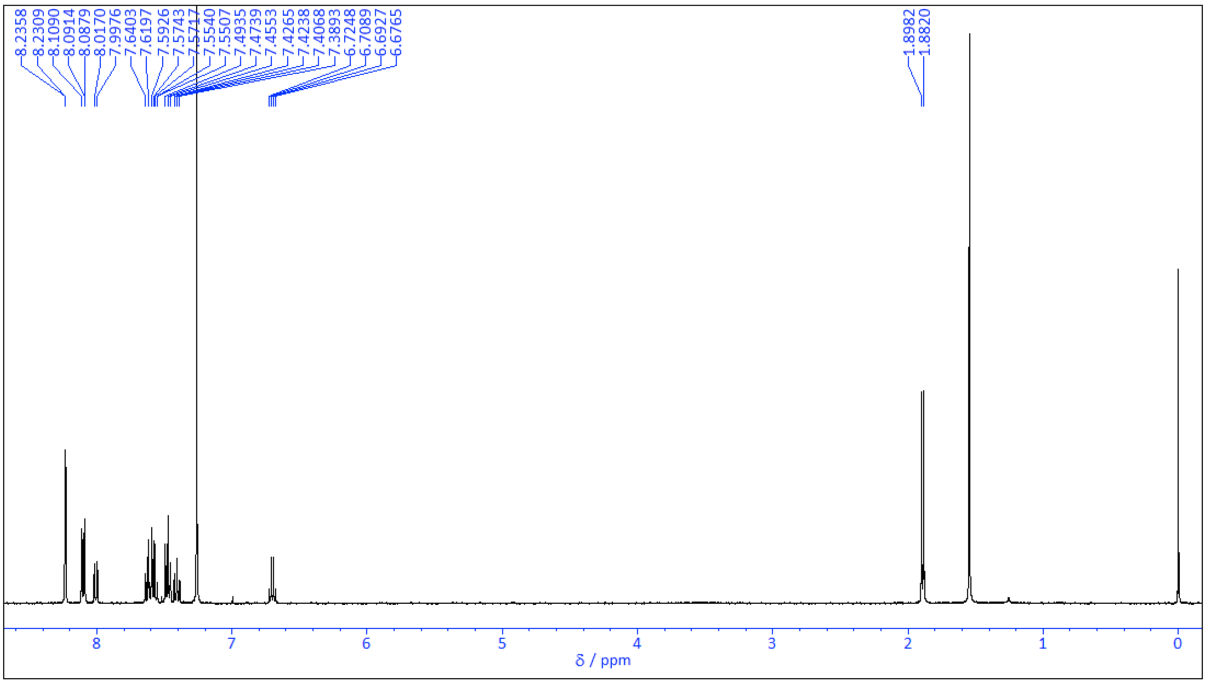

Figure S9. ^{1}H NMR spectrum of compound **8** (400 MHz, $CDCl_3$)

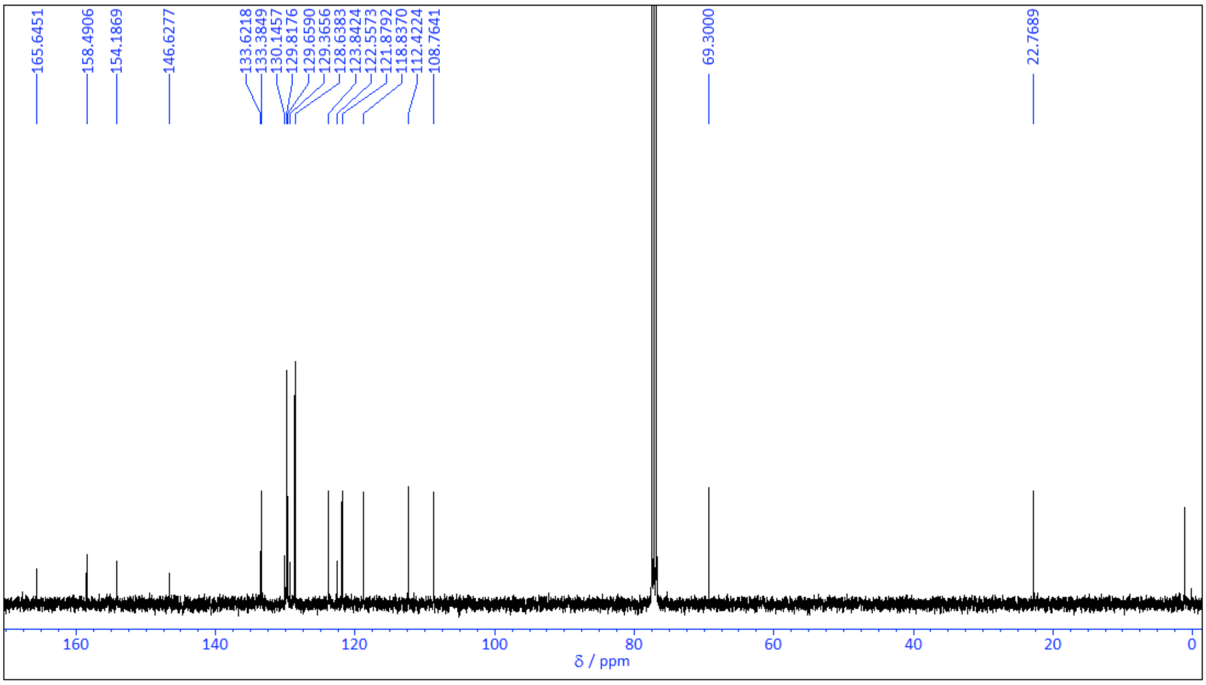

Figure S10. ^{13}C NMR spectrum of compound **8** (100 MHz, $CDCl_3$)

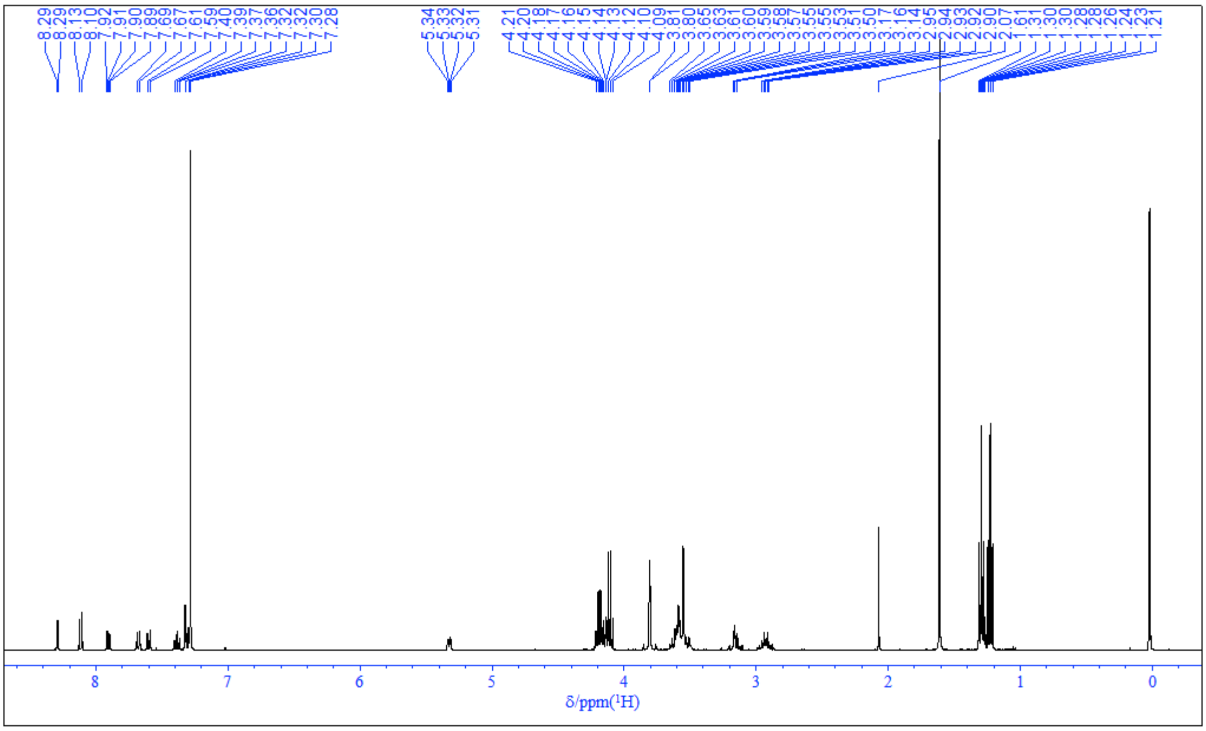

Figure S11. ^{1}H NMR spectrum of compound **9** (400 MHz, $CDCl_3$)

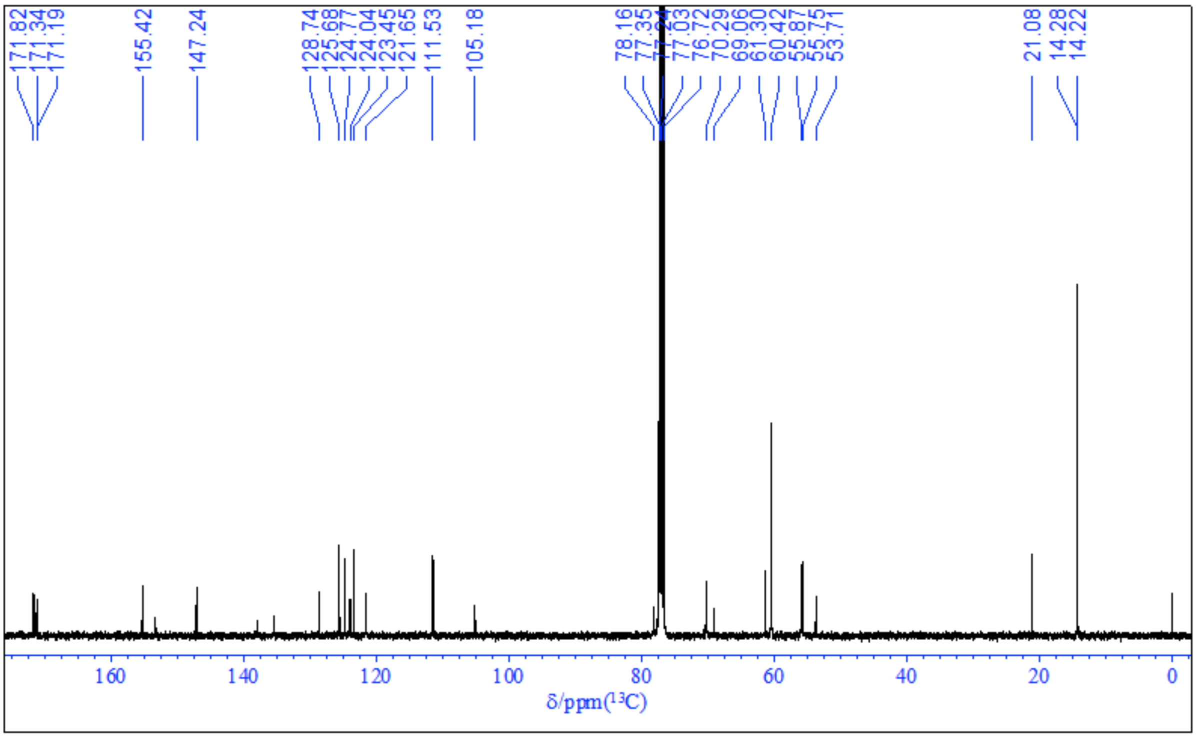

Figure S12. ^{13}C NMR spectrum of compound **9** (100 MHz, CDCl$_3$)

UV/vis absorption spectra of compounds

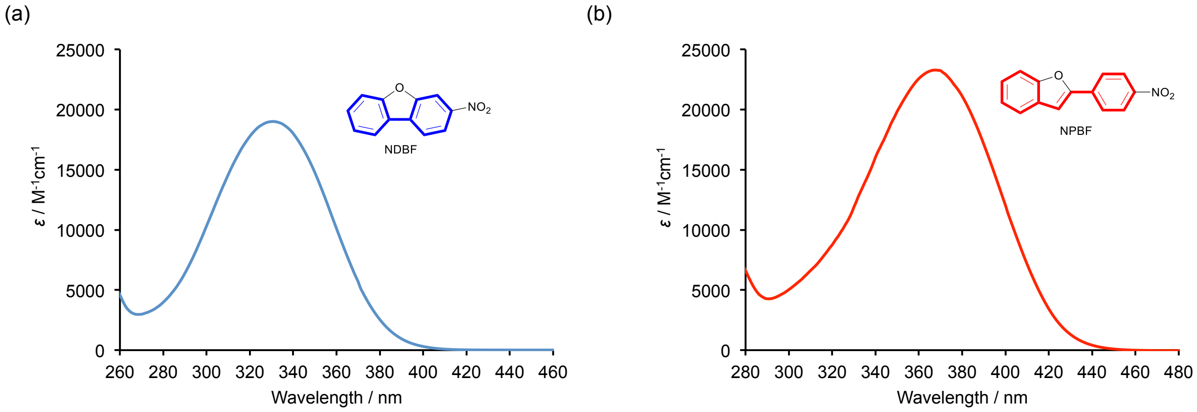

Figure S13. UV/vis absorption spectra in DMSO of (a) NDBF and (b) NPBF.

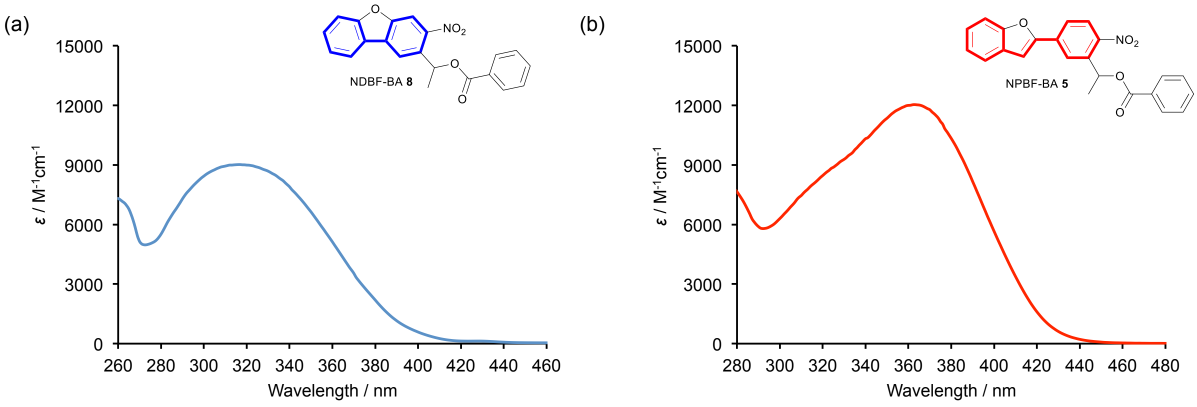

Figure S14. UV/vis absorption spectra in DMSO of (a) NDBF-BA **8** and (b) NPBF-BA **5.**

TPA cross-section of NPBF and NDBF at 720 nm

TPA cross-sections of NPBF and NDBF were measured at room temperature in solution of spectroscopic grade demithylsilfoxide (DMSO) with a concentration of 10 mM for both chromophores. The open-aperture Z-scan method has been used [6,7] based on the setup and analytical procedure described elsewhere [8,9]. For the measurements, femtosecond pulses (pulse width 130 fs , repetition rate 1 kHz) centered at 720 nm from an optical parametric amplifier were used. The Rayleigh range of the setup at the wavelength was 4.3 mm, longer enough to satisfy the thin sample condition compared to the optical pathlength of the cuvette (2 mm). The average irradiation power was varied for different scans in the range of 0.05–0.50 mW. This range corresponds to that of the on-axis optical peak intensity at the focal point of 23–230 $\mathrm{GW/cm^2}$, which is smaller than the optical intensity at which unwanted other nonlinear optical effects, such as stimulated Raman effect, become significant (~1 $\mathrm{TW/cm^2}$ or over). Examples of the open-aperture Z-scan traces for **NDBF** and **NPBF** are shown in Fig. S15 at the average irradiation power of 0.48 W. **NPBF** gave deeper dip centerd at the focal point (z=0), meaning more intense signal, than **NDBF**. The traces at different powers have the similar shape but differ in magnitude of the dip. For each open-aperture Z-scan traces, the on-axis two-photon absorbance q_0 were obtained by curve fitting with the theoretical equation assuming spatial and temporal Gaussian pulses [9]. The obtained q_0's showed linear behavior with the average power, thus the optical intensity (Figure S16), showing that the observed nonlinear absorption is dominated by TPA processes. From the slope of the plots, the TPA coefficient β was determined and then the TPA cross section σ_2, using the convention $\sigma_2 = h\nu\beta/N$, where $h\nu$ is the photon energy at the wavelength of interest and N is the number density calculated from the concentrations. We also measured in-house standard sample (MPPBT/DMSO, 2.3 mM) [9] at the same time under the same condition. The values of σ_2 were corrected based on that of the standard (481±52 GM at 720 nm) . The final results are summerized in Table S2.

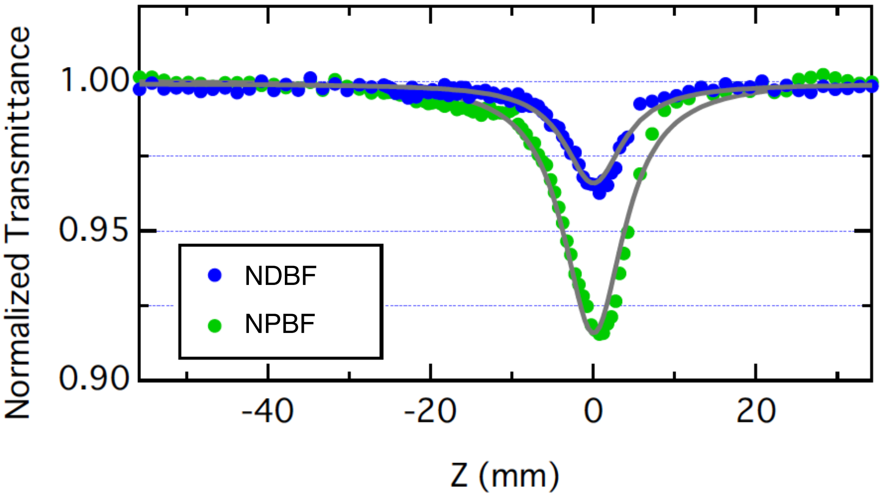

Figure S15. Open-aperture Z-scan traces of (a) NPBF and (b) NDBF in DMSO at the average irradiation power of 0.48 mW (filled circles) overlapped with their best fits of the theoretical curve (gray lines).

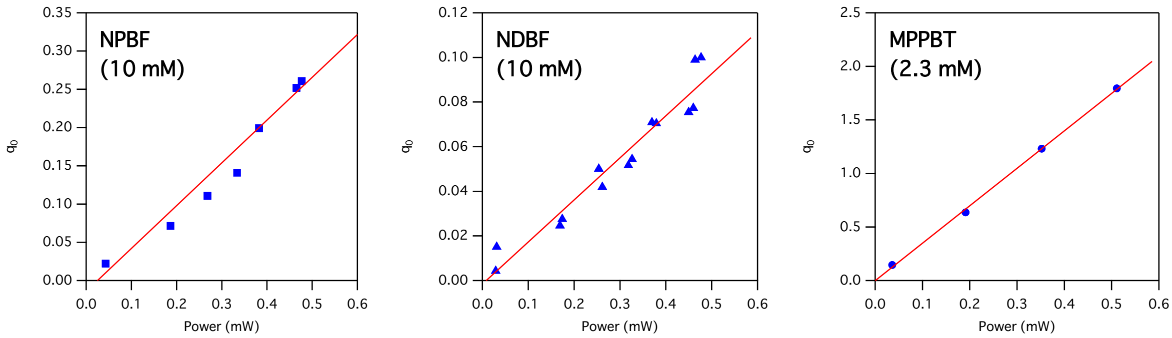

Figure S16. Plot of two-photon absorbance q_0 against the average input power of NPBF (left), NDBF (center), and MPPBT (the reference, see the SI text, right) in DMSO.

Table S2. TPA cross sections σ_2 at 720 nm.

Compounds	σ_2/GM	Note
NPBF	18±3	
NDBF	6±1	
MPPBT	481±52	reference

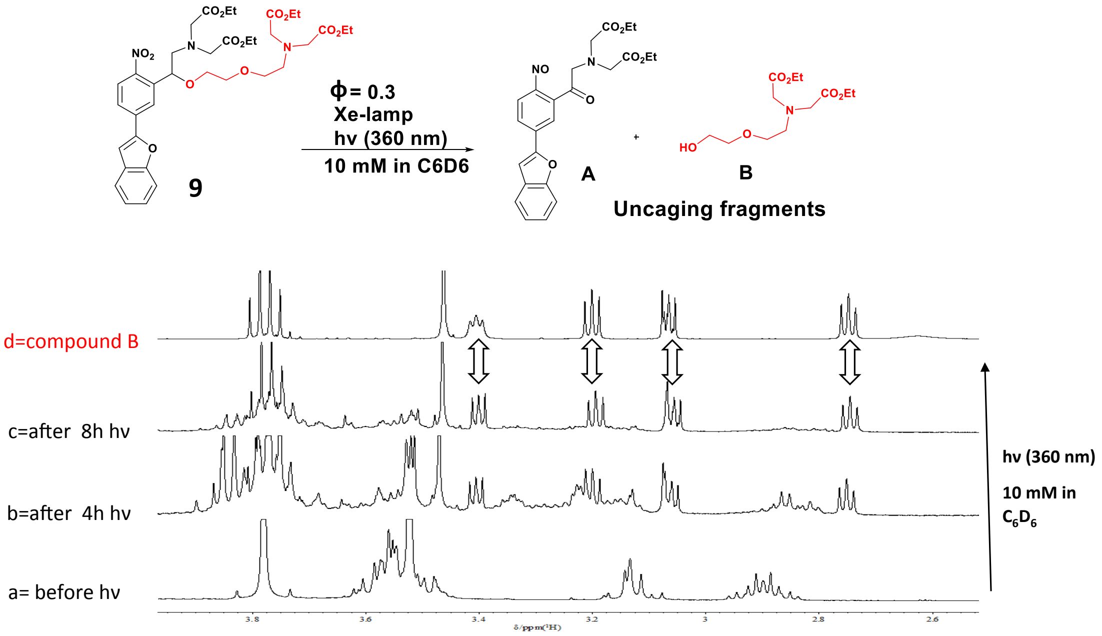

Figure S17. (a) ^{1}H NMR (400 MHz) of EGTA ethyl ester in C_6D_6; (b) ^{1}H NMR spectrum (δ 2.6-3.7 ppm) after four hour irradiation by using Xenon lamp (360 nm) in C_6D_6. (c) ^{1}H NMR spectrum after 8 h irradiation in C_6D_6. (d) ^{1}H NMR spectrum for fragment-B in C_6D_6.

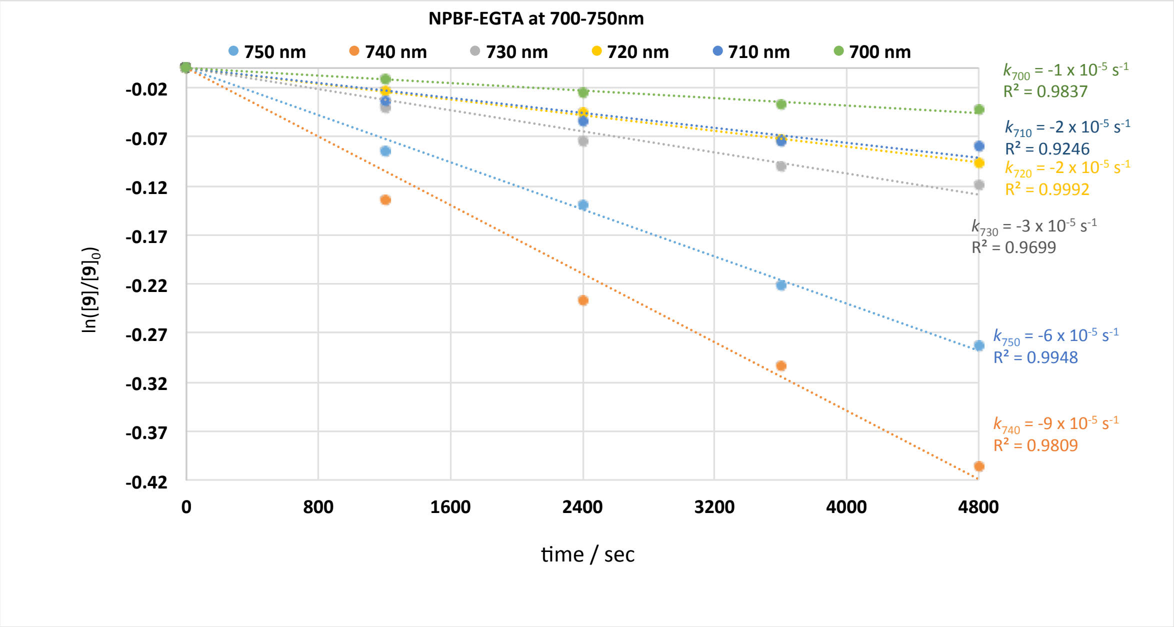

Figure S18 Time profile of TP uncaging of **9**, ln([**9**]/[**9**]$_0$) versus irradiation time at 700-750 nm.

References

[1] Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[2] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M.

Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

[3] S. Tretiak, V. Chernyak, *J. Chem. Phys.* **2003**, *119*, 8809.

[4] F. Terenziani, C. Katan, E. Badaeva, S. Tretiak, M. Blanchard-Desce, *Advanced Materials* **2008**, *20*, 4641.

[5] R. L. Martin, *J. Chem. Phys.* **2003**, *118*, 4775-4777.

[6] M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W. Van Stryland, *IEEE J. Quant. Electron.*, **1990**, *26*, 760-769.

[7] R. L. Sutherland, "Handbook of Nonlinear Optics", 2nd Ed., (Mercel Dekker Inc., 2003, New York)

[8] K. Kamada, K. Matsunaga, A. Yoshino, K. Ohta, *J. Opt. Soc. Am. B*, **2003**, *20*, 529–537.

[9] K. Kamada, Y. Iwase, K. Sakai, K. Kondo, K. Ohta, *J. Phys. Chem. C*, **2009**, *113*, 11469-11474.