Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION FOR:

Synthesis of B_{12}-BODIPY Dyad for B_{12}-inspired Photochemical Transformations of Trichloromethylated Organic Compound

Yuki Anai,[a] Keita Shichijo,[a] Mamoru Fujitsuka,[b] Yoshio Hisaeda*[a] and Hisashi Shimakoshi*[a]

[a]Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan

[b]The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Osaka 567-0047, Japan

Chemicals

All solvents and chemicals used in this study were obtained from commercial sources of reagent grade and used as received unless otherwise noted. Amino-BODIPY (**Chart S1**) was purchased from PorphyChem. The cobalamin derivative, $[(CN)(H_2O)Cob(III)6C_1ester]ClO_4$ (**Chart S1**), was synthesized by a previously reported method.[S1] The BODIPY dye (**P1**) was synthesized by a reported method.[S2] Authentic samples of the products from the catalytic reactions were purchased from Aldrich or Tokyo Kasei Kogyo (TCI). Products **1**~**10** were isolated by chromatography (Silica Gel 60N, spherical, neutral) using dichloromethane/*n*-hexane (1:1) as the eluent and identified by IR, NMR, and GC-MS. Data were compared to those of reported compounds except for the new compounds **3** and **5**.[S3-S5] The analytical data of **3** and **5** are shown in **Figures S9**-**14**.

Measurements

The ^{1}H NMR and ^{13}C NMR spectra were recorded by a Bruker Avance 500 spectrometer at the Centre of Advanced Instrumental Analysis, Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual solvent peak of $CDCl_3$ at 7.27 ppm. The gas chromatography-mass spectra (GC-MS) were obtained using a Shimadzu GCMS-QP5050A equipped with a J&W Scientific DB-1 column (length: 30m; ID: 0.25 mm, film: 0.25 mm) and helium as the carrier gas. For the measurement, the injector and detector temperatures were 250 ^{o}C, the oven temperature was initially held at 100 ^{o}C for 2 min, then increased to 240 ^{o}C at the rate of 10 ^{o}C/min. The UV-vis absorption spectra were obtained by a Hitachi U-3300 spectrophotometer at room temperature. The light emitting diode (LED PER-AMP, λ=521 nm) purchased from TechnoSigma was used as the light source for the light irradiation experiments. The MALDI-TOF mass spectra were obtained by a Bruker autoflex II using 6-aza-2-thiothymine as the matrix. The high resolution-mass spectrum of **C1** was obtained by a JEOL JMS-700 using *m*-nitrobenzylalcohol as the matrix. The IR spectra were recorded by a JASCO FT-IR 460 plus KH spectrophotometer using KBr disks. The PL spectra were measured by a Hitachi F-4500. The high resolution-mass spectra of new compounds (**3** and **5**) were obtained on a JEOL JMS-700 using *m*-nitrobenzylalcohol as a matrix.

Photophysical measurements

The photoluminescence quantum yield (Φ_{PL}) value of **C1** and **P1** were measured using an absolute photoluminescence quantum efficiency measurement system (Hamamatsu

C9920-02) incorporating an integrating sphere. To measure Φ_{PL}, a degassed solution of **C1** in CH_3OH was prepared and the concentration was adjusted so that the absorbance of the solution at 500 nm would be less than 0.1. The excitation was performed at 500 nm. For the absolute photoluminescence quantum efficiency measurement, the values less than 1 % are not correct values from the viewpoint of sensitivity of the instruments.

Time-resolved absorption spectroscopic measurements

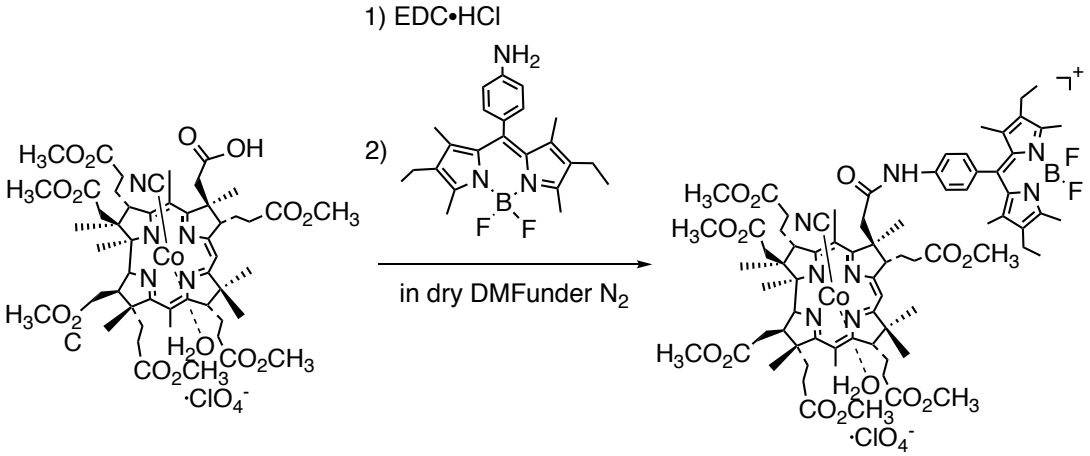
The femtosecond time-resolved absorption spectra were measured by the pump and probe method using a regeneratively amplified titanium sapphire laser (Spectra-Physics, Spitfire Pro F, 1 kHz) pumped by a Nd:YLF laser (Spectra-Physics, Empower 15). The seed pulse was generated by a titanium sapphire laser (Spectra-Physics, Mai Tai VFSJW; fwhm 80 fs). The output of an optical parametric amplifier (520 nm, 3 μJ $pulse^{-1}$, Spectra-Physics, OPA-800CF-1) was used as the excitation pulse. A white light continuum pulse, which was generated by focusing the residual of the fundamental light on a sapphire crystal after the computer controlled optical delay, was divided into two parts and used as the probe and reference lights of which the latter was used to compensate the laser fluctuation. Both the probe and reference lights were directed to a quartz sample cell with a 1.0- mm optical path and detected by a CCD detector equipped with a polychromator (Solar, MS3504). For the transient absorption measurements, the concentration was adjusted so that the absorbance of the solution at 520 nm would be 0.9 in a cell with 1.0-mm optical path length.

Cyclic voltammetry study

Cyclic voltammogram (CV) of **C1** was obtained using a BAS CV 50 W electrochemical analyzer as shown in **Figure S16**. A three-electrode cell equipped with a 3.0-mm diameter glassy carbon rod and 1.6-mm diameter platinum wire as the working and counter electrodes were used, respectively. An Ag/AgCl (3.0 M NaCl) electrode served as a reference. Nonaqueous CH_3CN solutions containing **C1** ($1.0x10^{-3}$ M) and *n*-Bu_4NClO_4 ($1.0x10^{-1}$ M) were deaerated prior to measurement, and the inside of the cell was maintained under a nitrogen atmosphere throughout measurement. The $E_{1/2}$ value of ferrocene/ferrocenium (Fc/Fc^+) was +0.44 V *vs*. Ag/AgCl with this setup.

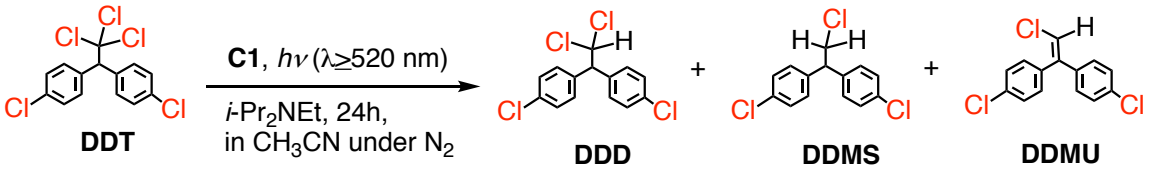
The $E_{(BODIPY+/BODIPY^*)}$ of BODIPY unit in **C1** was calculated by equation: $E_{(BODIPY+/BODIPY^*)}=E_{(BODIPY/BODIPY+)}-E^{00}$= -1.11 V *vs*. Ag/AgCl.

Synthesis of C1



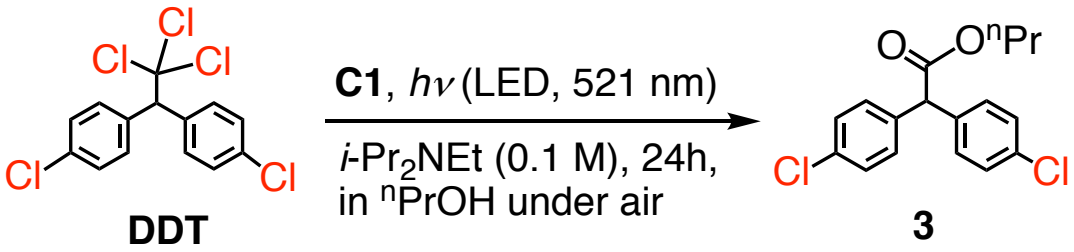
In 2 mL of dry DMF, 15 mg (1.4×10^{-2} mmol) of [(CN)(H_2O)Cob(III)6C_1ester]ClO_4, 6 mg (1.4×10^{-2} mmol) of BODIPY-NH_2, and 7 mg (5.7×10^{-2} mmol) of DMAP, 7 mg (3.7×10^{-2} mmol) of EDC/HCl were dissolved and the solution was cooled to 0 °C using an ice-bath under a nitrogen atmosphere. After stirring for 6 h at 0 °C, then for 15 h at room temperature under a nitrogen atmosphere. To the resulting red purple solution was added 50 mL of water and washed with dichloromethane (50 mL x 6). After concentrated to dryness, the product was isolated by chromatography (Sephadex column, spherical, neutral) using methanol as the eluent. Yield 51 %; **C1** was characterized by IR, ν/cm^{-1}: 3398 (N-H, str.) 1732 (ester C=O, str.), 1648 (amide C=O, str.) (**Figure S1**). TOF MS (MALDI, *m*/*z*): [M-CN-H_2O], 1399.9 (**Figure S2**). HR-MS: [M-H_2O], 1425.6567. UV-VIS (in CH_3OH, nm), 353, 405(sh), 494(sh), 521.

General procedure for catalytic reaction by the B_{12} under N_2



A 10 mL methanol solution of the B_{12}-BODIPY (**C1**) (1.0×10^{-5} M) (1 mol%), *i*-Pr_2NEt (0.1 M), and **DDT** (3.0×10^{-3} M) was degassed by N_2 gas, then irradiated using a tungsten lamp (λ≥520 nm), a LED lamp (λ=521 nm) or a solar simulator as the light source with stirring. After a 24-hour irradiation, the resulting solution was dried and 1,4-dioxane was added as the internal standard then analyzed by ^{1}H NMR. The yields of the products were calculated by comparison to the peak area ratio of the internal standard. All the products were isolated by silica gel column chromatography (Kanto Chemicals, 60N) using the CH_2Cl_2/hexane eluent and identified by GC-MS, and ^{1}H and ^{13}C NMR.

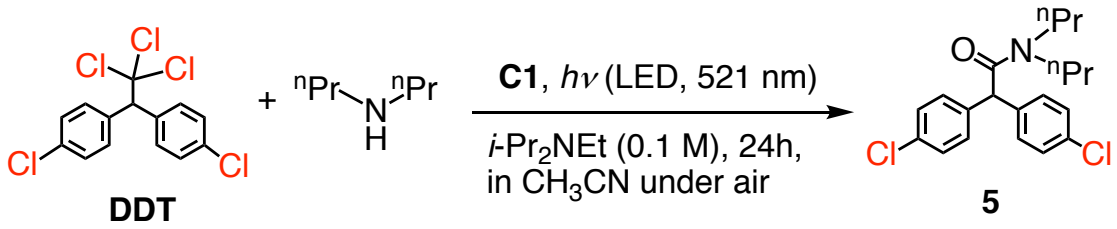
General procedure for catalytic reaction by the B_{12} under air for esterification



A 10 mL $CH_3CH_2CH_2OH$ solution of the B_{12}-BODIPY (**C1**) (1.0×10^{-5} M) (1 mol%), *i*-Pr_2NEt (0.1 M), and **DDT** (3.0×10^{-3} M) was irradiated in air using a LED lamp (λ=521 nm) as the light source with stirring. After a 24-hour irradiation, the resulting solution was dried and 1,4-dioxane was added as the internal standard then analyzed by ^{1}H NMR. The yield of the product was calculated by comparison to the peak area ratio of the internal standard. The product was isolated by silica gel column chromatography (Kanto Chemicals, 60N) using the CH_2Cl_2/hexane eluent and identified by GC-MS, IR, and ^{1}H and ^{13}C NMR (**Figures S9-S11**).

Colorless solid, yield (40%). GC-MS: M^+=322; HR-MS (EI, *m*/*z*): 322.0525; ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.30-7.29 (d, 2H), 7.23-7.21 (d, 2H), 4.94 (s, 1H), 4.12-4.09 (t, 2H), 1.66-1.62 (q, 2H), 0.89-0.86 (t, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=172.20, 137.26, 133.84, 130.26, 129.22, 67.46, 56.25, 22.28, 10.65; IR, ν/cm^{-1}: 3031 (aromatic C-H, weak.), 2967 (^{n}Pr C-H, str.), 1732 (ester C=O, str.), 1491 (C-H, m.), 1090 (ester C-O, str.) .

General procedure for catalytic: reaction by the B_{12} under air for amidation



A 10 mL CH_3CN solution of the B_{12}-BODIPY (**C1**) (1.0×10^{-5} M) (1 mol%), *i*-Pr_2NEt (0.1 M), **DDT** (3.0×10^{-3} M), di-*n*-propylamine (3.0×10^{-1} M), and diphenyl as the internal standard was irradiated in air using a LED lamp (λ=521 nm) as the light source with stirring. After a 24-hour irradiation, the resulting solution was passed through a short silica-gel column to remove the B_{12} complex then analyzed by GC-MS. The yield of the product was calculated by comparison to the peak area ratio of the internal standard. The product was isolated by silica gel column chromatography (Kanto Chemicals, 60N) using the CH_2Cl_2/hexane eluent and identified by GC-MS, IR, and ^{1}H and ^{13}C NMR (**Figures S12-14**).

Yellow oil, yield (61%). GC-MS M^+=363; HR-MS (EI, *m*/*z*): 364.1211; ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.29-7.27 (d, 2H), 7.18-7.16 (d, 2H), 5.10 (s, 1H), 3.33-3.30 (t, 2H), 3.19-3.16 (t, 2H), 1.63-1.53 (m, 2H), 0.93-0.90 (t, 3H), 0.89-0.86 (t, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=170.85, 138.42, 133.53, 130.59, 129.14, 53.54, 50.25, 21.19, 11.71; IR, ν/cm^{-1}: 3051 (aromatic C-H, weak.), 2966, 2926 (^{n}Pr C-H, str.), 1649 (amide C=O, str.), 1489 (C-H, m.) .

References

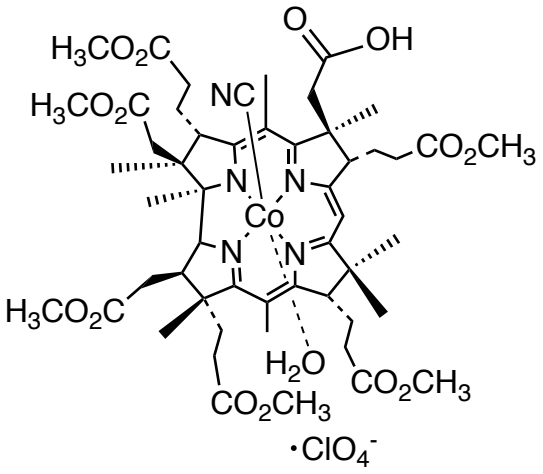
S1. Y. Murakami, Y. Hisaeda, T. Ohno, H. Kohno, T. Nishioka, *J. Chem. Soc. Perkin Trans. 2* **1995**, 1175-1183.

S2. S. Thakare, P. Stachelek, S. Mula, A. B. More, S. Chattopadhyay, A. K. Ray, N. Sekar, R. Ziessel, A. Harriman, *Chem. Eur. J.* 2016, **22**, 14356-14366.

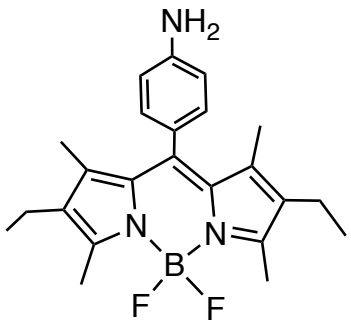
S3. H. Shimakoshi, Y. Hisaeda, *Angew. Chem. Int. Ed.* 2015, **54**, 15439-15443.

S4. H. Tian, H. Shimakoshi, T. Ono, Y. Hisaeda, *ChemPlusChem* 2019, **84**, 237-240.

S5. H. Shimakoshi, Z. Luo, T. Inaba, Y. Hisaeda, *Dalton Trans.* 2016, **45**, 10173-10180.



[(CN)(H_2O)Cob(III)6C_1ester]ClO_4



BODIPY-NH_2

Chart S1. Structure of [(CN)(H_2O)Cob(III)6C_1ester]ClO_4 and BODIPY-NH_2.

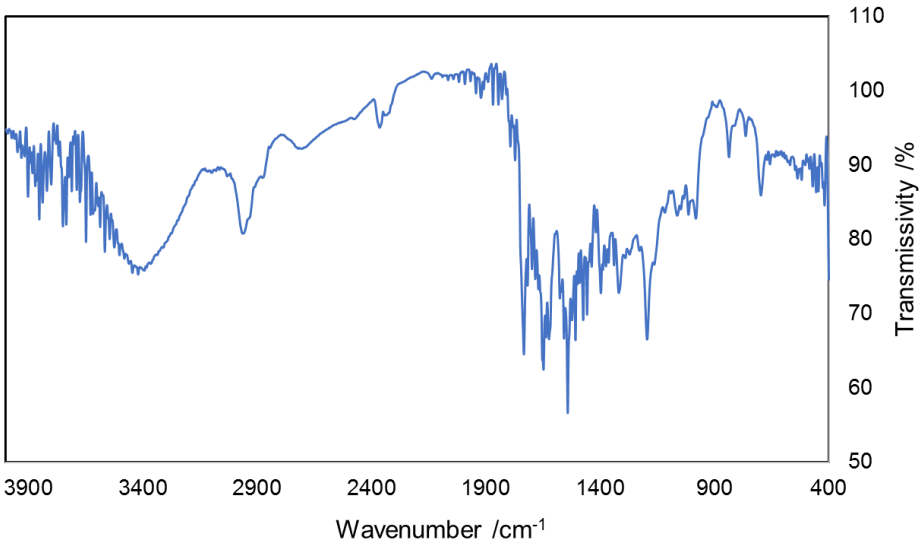


Figure S1. IR spectrum of **C1** (KBr disk).

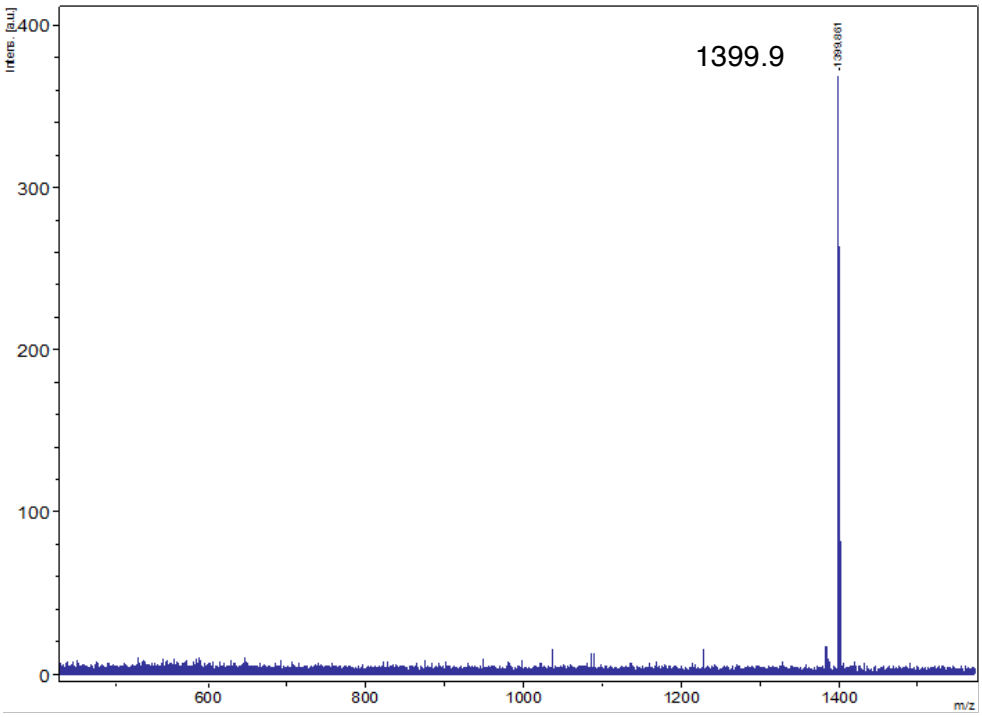
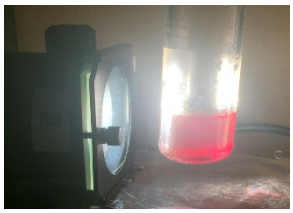


Figure S2. MALDI-MS of **C1**.



$\lambda \geq 520nm$

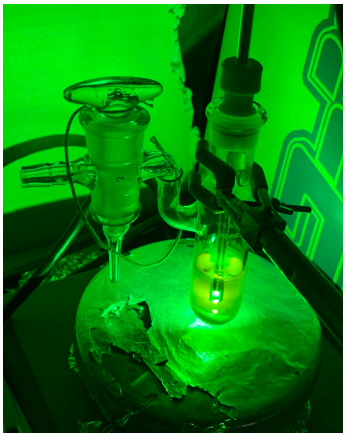
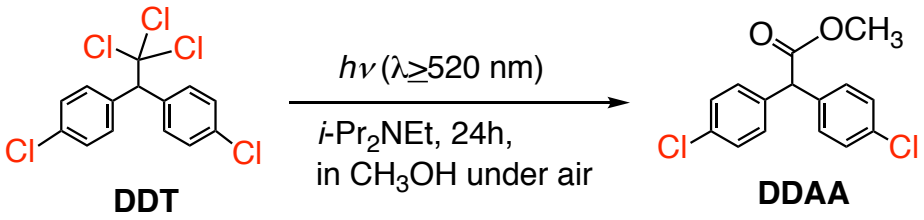


Figure S3. Experiment set-up image of photo-driven the dyad (**C1**) catalyzed the reaction using halogen lump ($\lambda \geq 520$ nm) or LED (λ_{max}=521 nm).

Table S1 Optimization of reaction conditions



Entry	Catalyst	*i*-Pr_2NEt/M	Yield of **DDAA**/%	TON	TON_{C1}/TON_{C2+P1}
1[a]	**C1**	0.1	52	118	1.5
2[b]	**C2** + **P1**	0.1	34	77	
3[a]	**C1**	0	0	0	
4[a,c]	**C1**	0.1	0	0	
5[a,d]	**C1**	0.1	72	163	
6[a]	**C1**	0.05	51	116	4.2
7[b]	**C2** + **P1**	0.05	12	27	
8[a]	**C1**	0.03	39	89	4.4
9[b]	**C2** + **P1**	0.03	9	20	

[a]Conditions: [**C1**]=1.0x10^{-5} M, [**DDT**]=1.0x10^{-3} M, solvent: CH_3OH under air at room temperature. Reaction time: 24 h. The product yields were based on the initial concentration of the substrate. The TONs were based on the concentration of the B_{12} complex.

[b][**C2**]=1x10^{-5} M, [**P1**]= 1x10^{-5} M.

[c]No light irradiation

[d]Light source is LED (λ_{max}=521 nm). Data from Scheme 2 (1).

Table S2 Data analysis of **P1** and **C1** by transient absorption spectroscopy.

Entry	1	2	3	4	5
Sample	**P1**	**P1** + **C2**	**P1**+*i*-Pr_2NEt	**C1**	**P1**
A_1(long time)	0.0461	0.0372	0.0316	0.0109	0.0141
A_2(short time)	0.0141	0.0142	0.00712	0.0191	0.0162
A_1/A_2	3.27	2.23	4.44	0.618	0.870
long time k_1 / s^{-1}	2.08×10^8	3.67×10^8	8.19×10^8	6.14×10^9	8.08×10^9
short time k_2 / s^{-1}	8.22×10^9	8.64×10^9	3.37×10^{10}	4.42×10^{10}	7.89×10^{10}
long time τ_1 / ps	4808	2724	1221	163	124
short time τ_2 / ps	122	116	30	23	13
τ_{ave} / ps	3710	2003	1002	74	65
k_{ave} / s^{-1}	2.70×10^8(k_0)	4.99×10^8	9.98×10^8	1.35×10^{10}	1.54×10^{10}
k_{ET} (=k-k_0)	-	2.29×10^8	7.28×10^8	1.32×10^{10}	1.51×10^{10}

$\tau_{ave} = (A_1\tau_1+A_2\tau_2)/(A_1+A_2)$

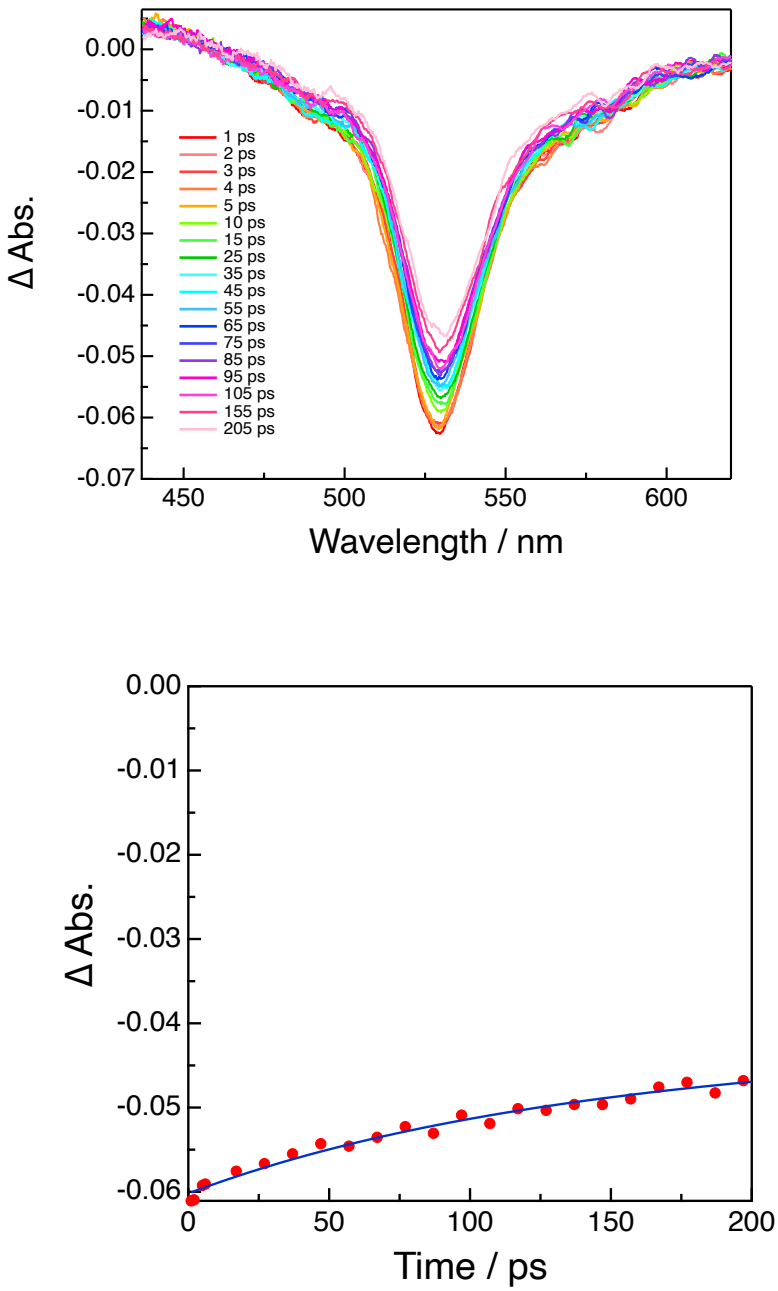


Figure S4 Transient absorption spectra of the BODIPY (**P1**) in CH_3OH during the laser flash photolysis using 520 nm femtosecond pulse for excitation. Spectra were obtained from 1 to 205 ps after the laser excitation. Lower panel is kinetic trace of ΔO.D. at 529 nm during the laser flash photolysis. Blue curve is a fitted curve.

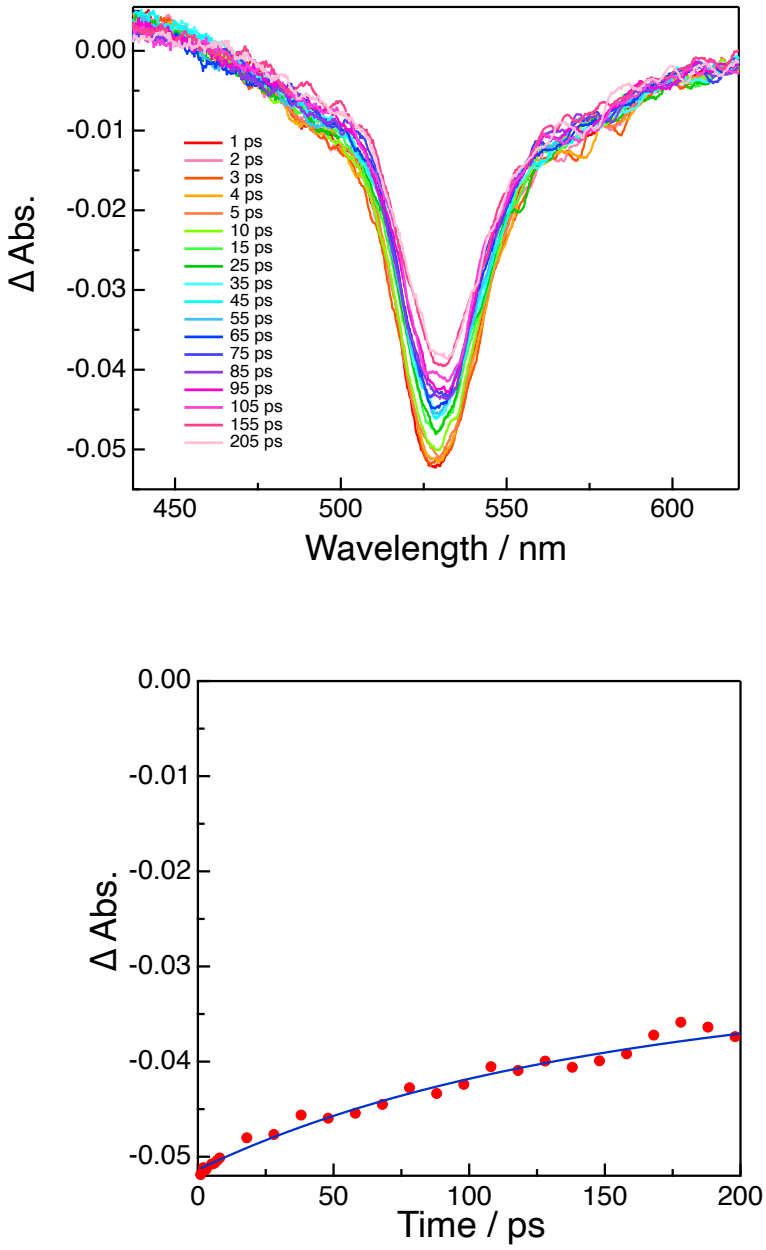


Figure S5 Transient absorption spectra of the BODIPY (**P1**) + **C2** in CH_3OH during the laser flash photolysis using 520 nm femtosecond pulse for excitation. Spectra were obtained from 1 to 205 ps after the laser excitation. Lower panel is kinetic trace of ΔO.D. at 529 nm during the laser flash photolysis. Blue curve is a fitted curve.

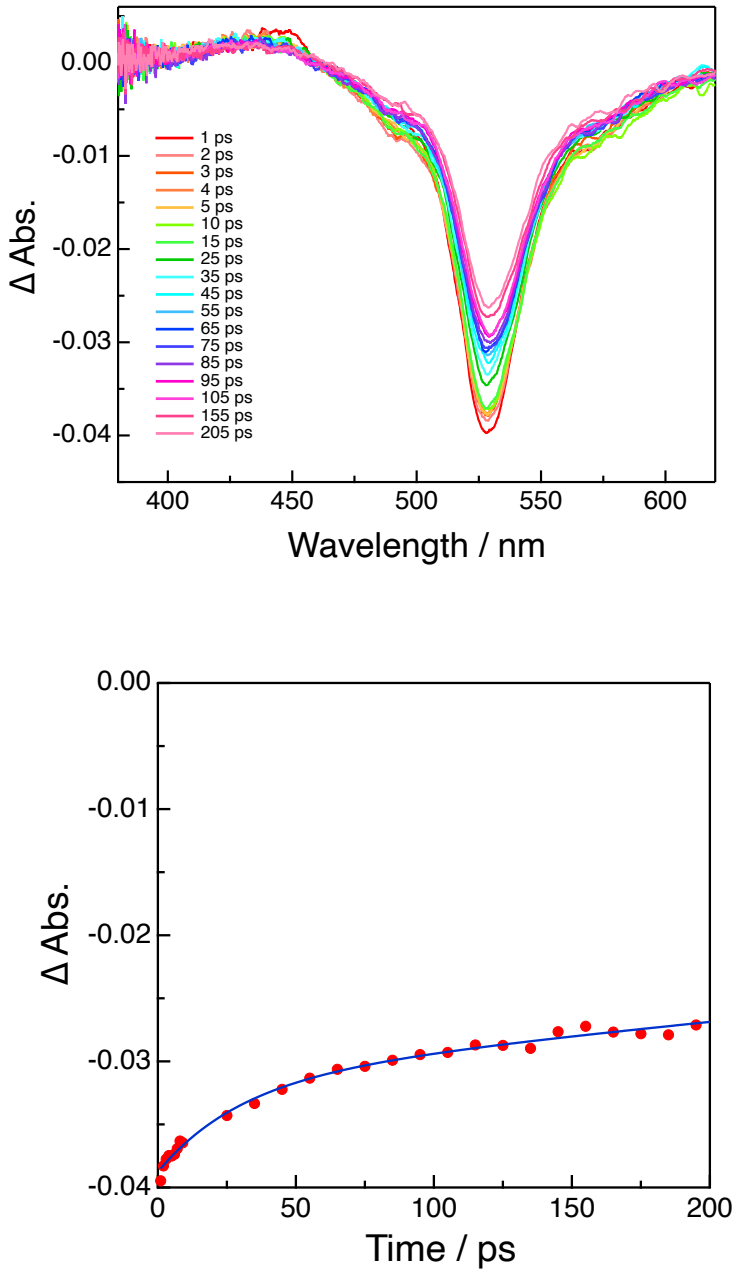


Figure S6 Transient absorption spectra of the BODIPY (**P1**) + *i*-Pr_2NEt in CH_3OH during the laser flash photolysis using 520 nm femtosecond pulse for excitation. Spectra were obtained from 1 to 205 ps after the laser excitation. Lower panel is kinetic trace of ΔO.D. at 529 nm during the laser flash photolysis. Blue curve is a fitted curve.

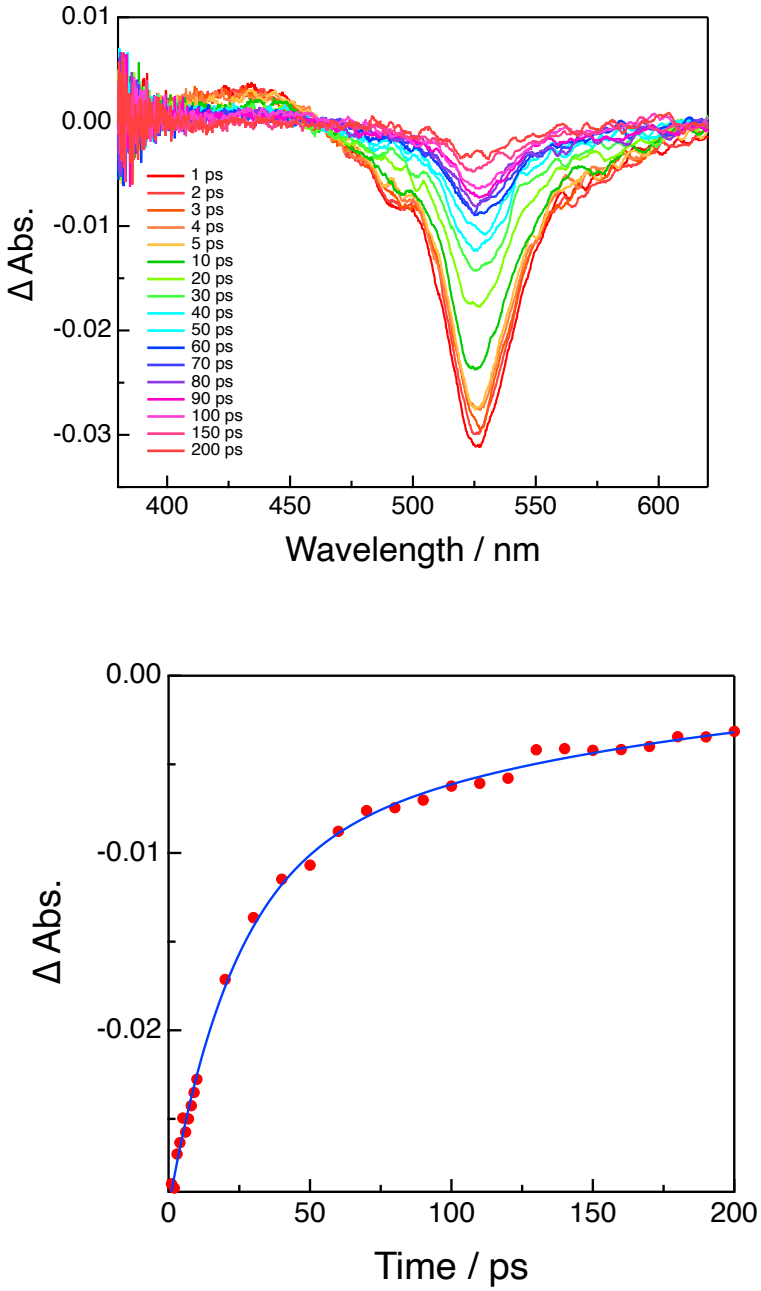


Figure S7 Transient absorption spectra of the **C1** in CH_3OH during the laser flash photolysis using 520 nm femtosecond pulse for excitation (Same to **Fig. 3**). Spectra were obtained from 1 to 200 ps after the laser excitation. Lower panel is kinetic trace of ΔO.D. at 529 nm during the laser flash photolysis. Blue curve is a fitted curve.

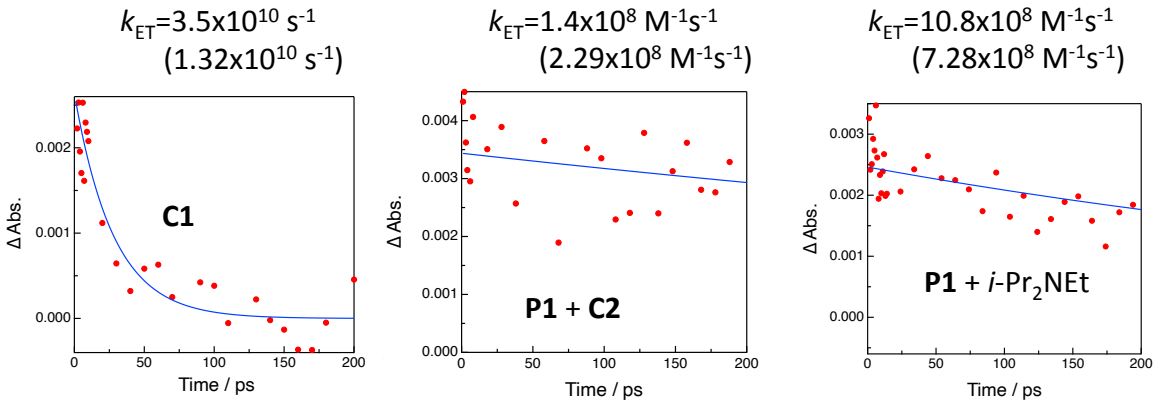


Figure S8 Kinetic trace of ΔO.D. at 437 nm during the laser flash photolysis of the **C1** (a), **P1**+**C2** (b), **P1**+*i*-Pr_2NEt (c) from 1 to 200 ps after the laser excitation. Blue curve is a fitted curve. Values shown in parentheses are determined by kinetic trace of ΔO.D. at 529 nm shown **Table 1**.

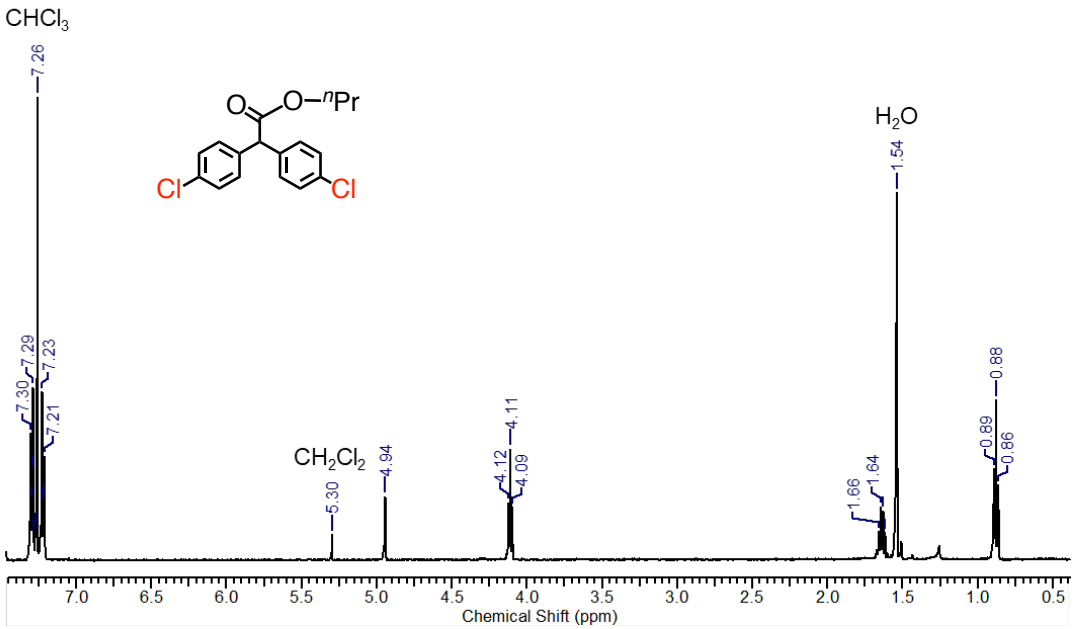


Figure S9 ^{1}H NMR spectrum of **3** in $CDCl_3$.

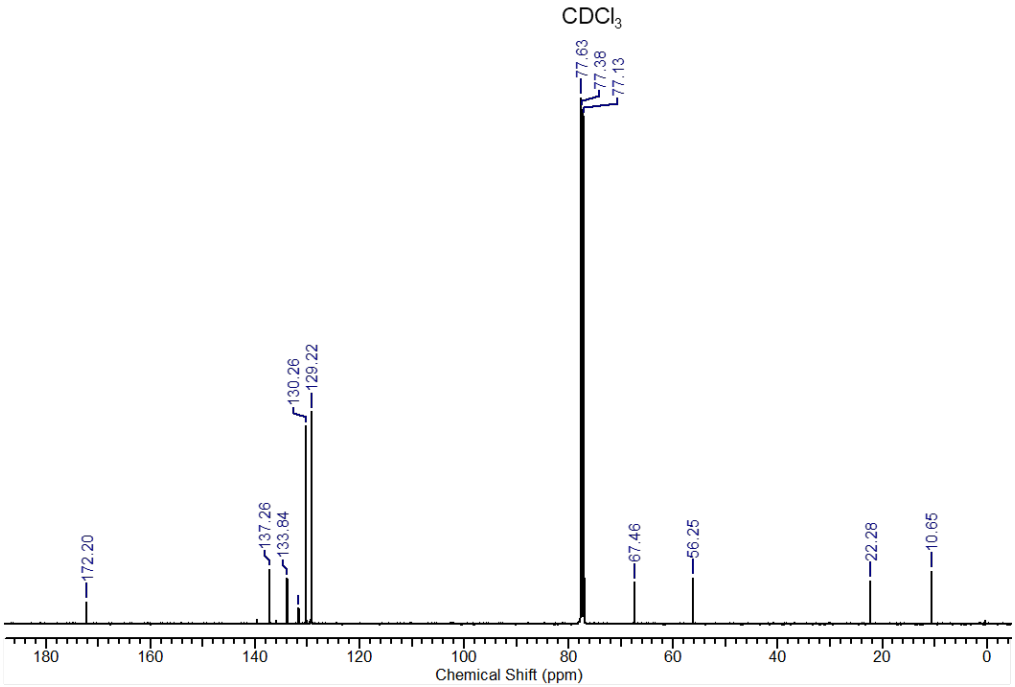


Figure S10 ^{13}C NMR spectrum of **3** in $CDCl_3$.

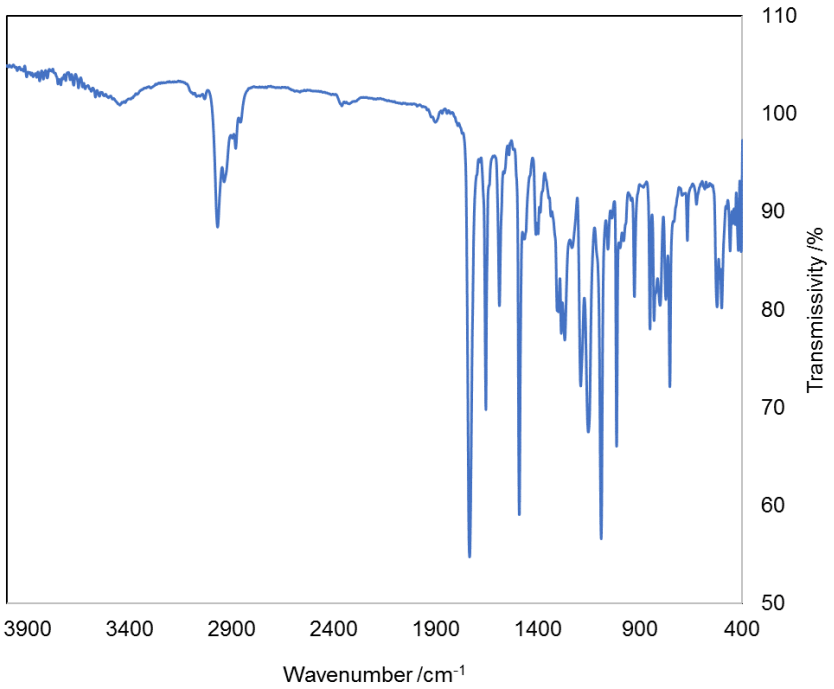


Figure S11 IR spectra of **3** (KBr disk).

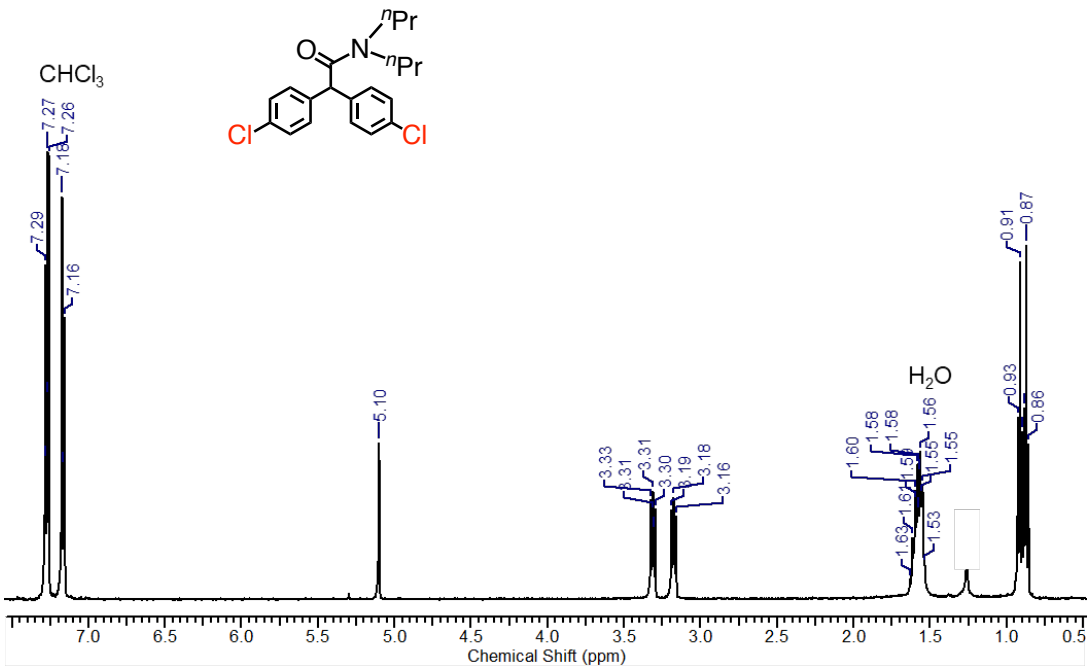


Figure S12 ^{1}H NMR spectrum of **4** in $CDCl_3$.

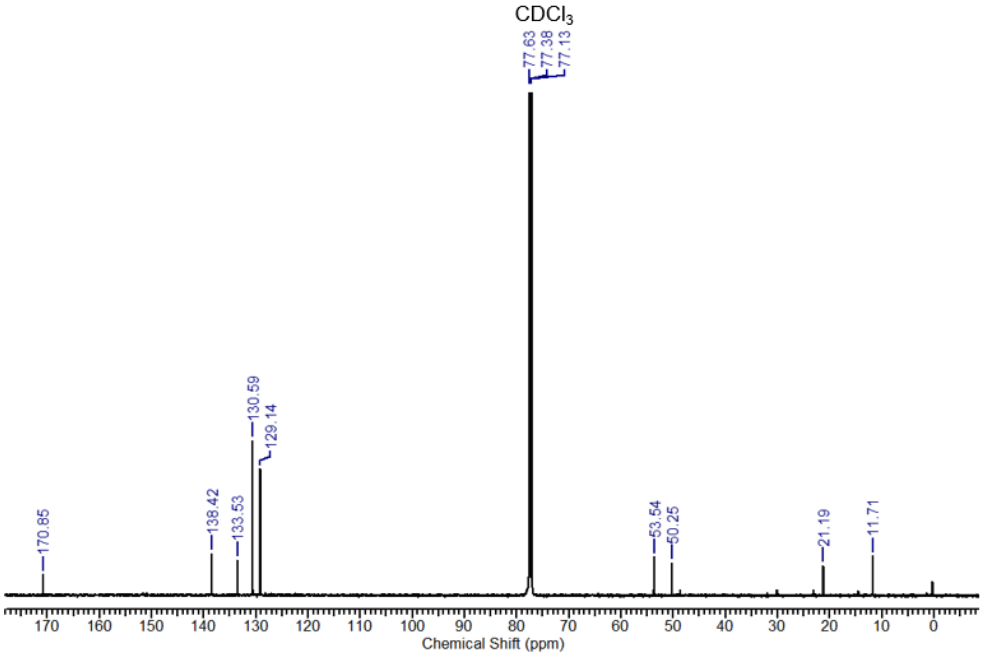


Figure S13 ^{13}C NMR spectrum of **4** in $CDCl_3$.

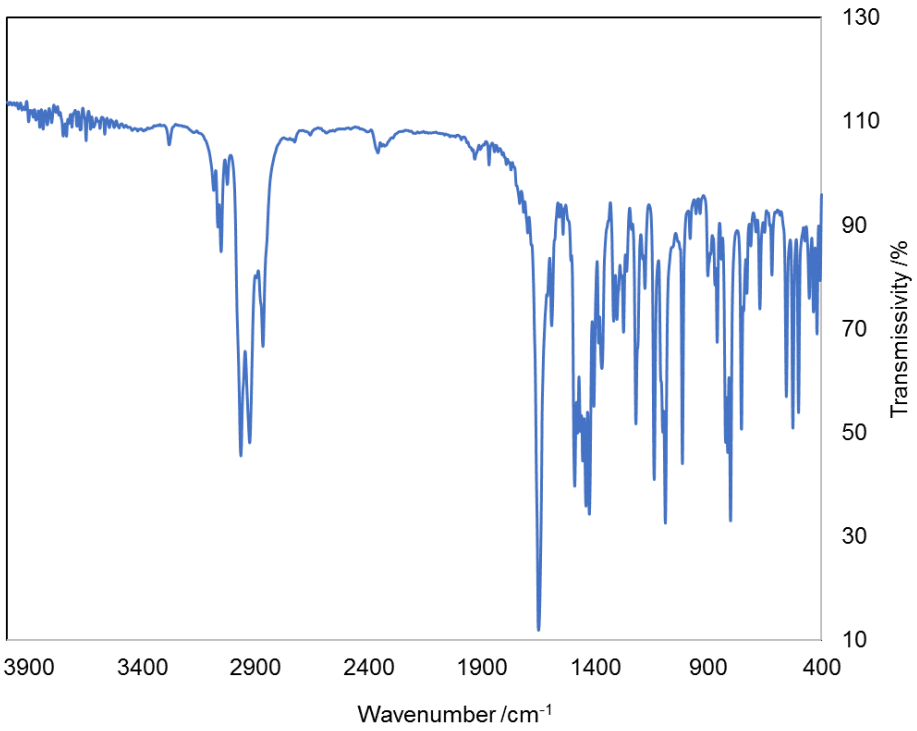


Figure S14 IR spectrum of **4** (KBr disk).

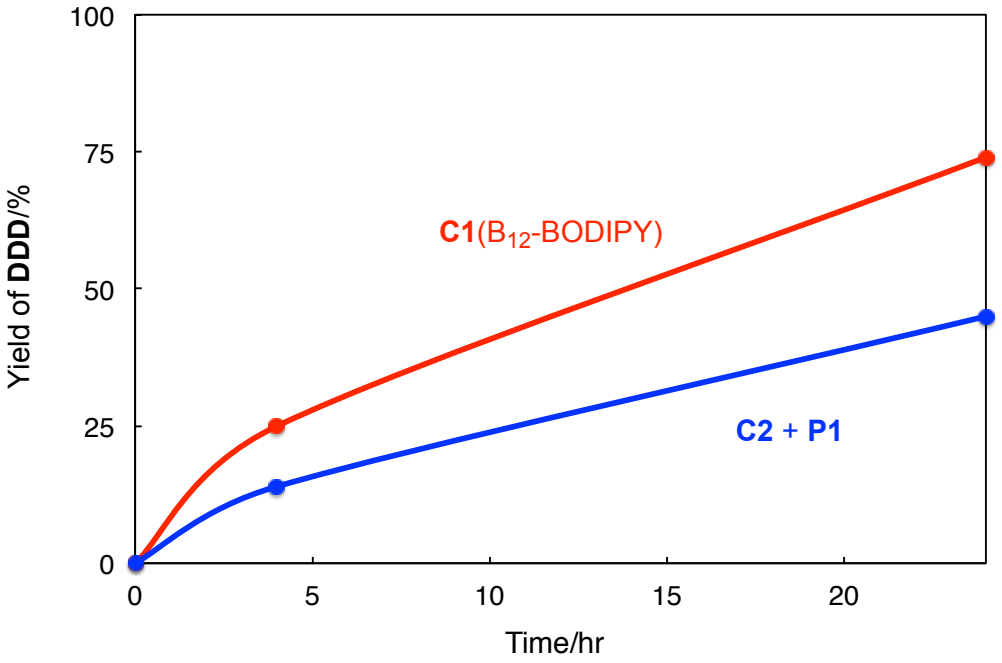


Figure S15 Time course of dechlorination reactions of **DDT** catalyzed by **C1** and **C2**+**P1** under N_2 at room temperature (24 hr data from **Table 2**).

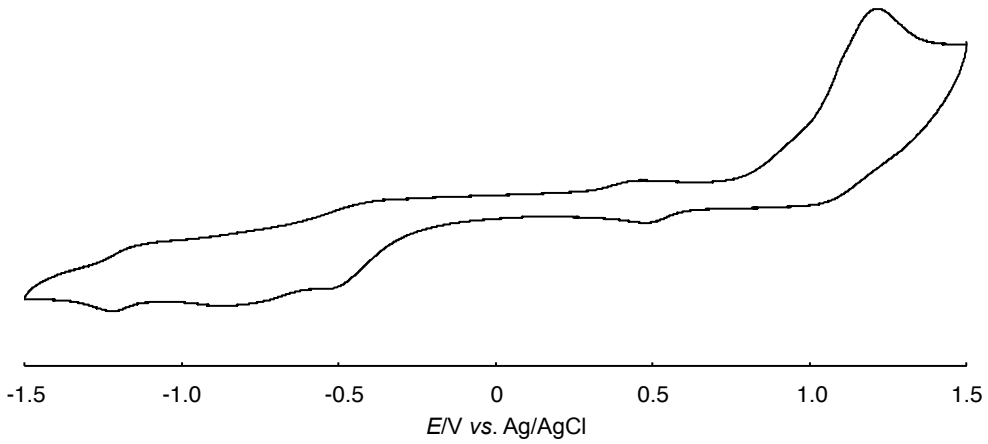


Figure S16 CV of **C1** ($1x10^{-3}$ M) in CH_3CN containing $1.0x10^{-1}$ M *n*-Bu_4NClO_4 at room temperature; sweep rate: 100 mVs^{-1}.