(Supporting Information)

Design of NIR-absorbing Simple Asymmetric Squaraine Dyes Carrying Indoline Moieties for Use in Dye-sensitized Solar Cells with Pt-free Electrodes

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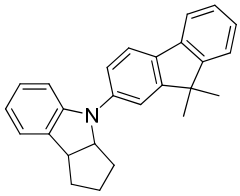
(Contents)

Measurement. Melting points were obtained on a Yanagimoto MP-S2 micro melting point apparatus and are uncorrected. IR was recorded on a Shimadzu FT-IR 8100A spectrometer. ^{1}H NMR spectra were measured with a JEOL α-400 (400 MHz) FT-NMR spectrometer in deuteriochloroform ($CDCl_3$), hexadeuterodimethyl sulfoxide (DMSO-d_6), tetradeuteromethanol (CD_3OD) solutions with tetramethylsilane (Me_4Si) as an internal standard. ^{13}C NMR spectra were obtained on a JEOL α-400 (100 MHz) FT-NMR spectrometer in $CDCl_3$, DMSO-d_6, and CD_3OD solution with Me_4Si as an internal standard. High resolution mass spectra (HRMS) were taken on a JEOL JMS-700 mass spectrometer operating at an ionization potential of 70 eV. UV-vis absorption and fluorescence spectra were taken on Hitachi U-3500 spectrophotometer and Horiba Fluoromax-4 spectrophotometers, respectively. Electrochemical measurement was carried out using an ALS CHI 800. The photoelectrochemical measurements of solar cells were performed on a Bunko-Keiki CEP-2000 system. The I–V curve measurements of solar cells were performed on an EKO Instruments I–V curve tracer MP-160 and Grating spectroradiometer LS-100.

The photoelectrochemical measurements of solar cells were performed on a Bunko-Keiki CEP-2000 system (AM 1.5).

Materials. Pure products were isolated by column chromatography using Wakogel C-200 (100-200 mesh, Wako Pure Chemical Ind., Ltd.) or Silica gel 60 (spherical, 40-50 μm, Kanto Chemical Co., Inc.). Analytical TLC was performed on Merck precoated (0.25 mm) silica gel 60 F_{254} plates. All chemicals were of reagent grade and, if necessary, purified in the usual manner prior to use. 3-Butylheptan-2-one (**1**) was prepared by reported method.[1] TiO_2 particles such as PST-18R (diameter: 18 nm) and PST-400C (diameter: 400 nm) were purchased from JGC C & C, Japan.

Synthesis of 4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (2a)



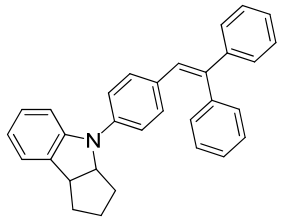
After a toluene (15 ml) solution of 2-bromo-9,9-dimethyl-9*H*-fluorene (1.395g, 5.11 mmol), 1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (1.150 g, 7.22 mmol), potassium *t*-butoxide (0.956 g, 8.52 mmol), palladium acetate (0.083 g, 0.41 mmol), and tri-*tert*-butylphosphine (0.070 g, 0.35 mmol) was heated at 80 °C for 3 days, the reaction mixture was cooled, filtered with Celite® 545RVS, and concentrated under vacuum to give a residue. The residue was purified by column chromatography under elution with hexane/dichloromethane (v/v = 10:1) to give 4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**2a**) in 76% yield (1.365 g).

Yield 76%; mp = 46.5–47.5 °C; *Rf* 0.19 (hexane: dichloromethane = 10:1); ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 6H), 1.52–1.55 (m, 1H), 1.63–1.70 (m, 1H), 1.87–1.91 (m, 2H), 1.95–2.02 (m, 1H), 2.03–2.10 (m, 1H), 3.86 (dt, *J* = 13.52, 2.42 Hz, 1H), 4.82 (dt, *J* = 7.55, 2.42 Hz, 1H), 6.74 (t, *J* = 7.24 Hz, 1H), 7.03–7.07 (m, 2H), 7.13 (d, *J* = 7.24 Hz, 1H), 7.22–7.27 (m, 2H), 7.31 (t, *J* = 7.24 Hz, 1H), 7.37–7.41 (m, 2H), 7.63–7.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.7, 27.4, 27.6, 34.2, 34.9, 45.7, 46.9,

[1] Funabiki, K.; Mase, H.; Hibino, A.; Tanaka, N.; Mizuhata, N.; Sakuragi, Y.; Nakashima, A.; Yoshida, T.; Kubota, Y.; Matsui, M. *Energy Environ. Sci.* **2011**, *4*, 2186.

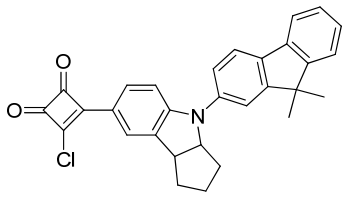
69.0, 108.4, 113.1, 118.1, 119.0, 119.3, 120.8, 122.6, 124.9, 126.3, 127.1, 127.3, 132.7, 135.1, 139.4, 143.0, 147.4, 153.3, 155.0; HRMS (EI): *m/z* calcd for $C_{26}H_{25}N$, 351.1987 (M); found, 351.1993.

4-(4-(2,2-Diphenylvinyl)phenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (2b)



Yield quant.; mp = 47.3–48.5 °C; *Rf* 0.21 (hexane: dichloromethane = 2:1); ^{1}H NMR ($CDCl_3$) δ 1.41–1.49 (m, 1H), 1.58–1.66 (m, 1H), 1.77–1.92 (m, 3H), 1.96–2.05 (m, 1H), 3.78–3.83 (m, 1H), 4.65 (dt, *J* = 7.70, 2.66 Hz, 1H), 6.71–6.74 (m, 1H), 6.92 (s, 1H), 6.96–6.98 (m, 2H), 7.01–7.05 (m, 4H), 7.09 (d, *J* = 7.24 Hz, 1H), 7.25–7.28 (m, 3H), 7.29–7.34 (m, 4H), 7.35–7.38 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 24.4, 34.1, 34.6, 45.4, 68.4, 108.9, 117.3, 119.1, 124.7, 127.1, 127.1, 127.3, 127.3, 127.8, 128.2, 128.8, 129.7, 130.4, 130.4, 135.2, 140.1, 140.9, 142.0, 143.7, 146.5; HRMS (EI): *m/z* calcd for $C_{31}H_{27}NO$, 413.2143 (M); found, 413.2144.

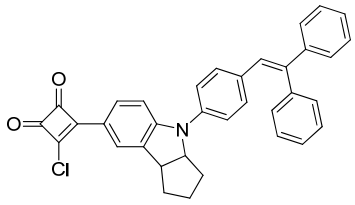
Synthesis of 3-chloro-4-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)cyclobut-3-ene-1,2-dione (4a)



After a toluene (8 ml) solution of 4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**2a**) (1.095 g, 3.12 mmol) and 3,4-dichlorocyclobut-3-ene-1,2-dione (0.570 g, 3.78 mmol) was heated at 80 °C for 3 h, the resultant reaction mixture was diluted with distilled water and toluene. The separated organic layer was dried over Na_2SO_4 and concentrated under vacuum to give a residue, which was purified by column chromatography under elution with dichloromethane to give 3-chloro-4-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)cyclobut-3-ene-1,2-dione (**4a**) in 50% yield (0.732 g).

Yield 50%; mp = 49.0–50.2 °C; *Rf* 0.79 (dichloromethane); ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 3H), 1.50 (s, 3H), 1.66–1.77 (m, 2H), 1.83–1.92 (m, 2H), 2.03–2.10 (m, 2H), 3.81 (t, *J* = 7.24 Hz, 1H), 5.22 (t, *J* = 7.24 Hz, 1H), 6.74 (d, *J* = 8.45 Hz, 1H), 7.21–7.34 (m, 3H), 7.39–7.49 (m, 2H), 7.64–7.74 (m, 2H), 7.85–7.90 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.5, 27.3, 27.5, 33.1, 35.8, 44.7, 47.3, 71.0, 107.4, 116.8, 117.6, 120.1, 121.2, 122.1, 122.9, 125.8, 127.4, 127.5, 132.2, 136.5, 136.9, 138.7, 139.1, 153.8, 155.1, 155.6, 171.2, 185.5, 190.1, 196.2; HRMS (EI): *m/z* calcd for $C_{30}H_{24}ClNO_2$, 465.1496 (M); found, 465.1485.

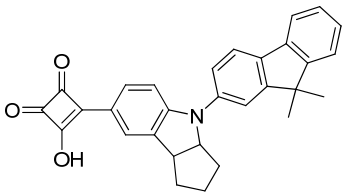
3-Chloro-4-(4-(4-(2,2-diphenylvinyl)phenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)cyclobut-3-ene-1,2-dione (4b)



Yield 84%; mp = 67.8–68.7 °C; *Rf* 0.69 (dichloromethane); ^{1}H NMR ($CDCl_3$) δ 1.38–1.50 (m, 1H), 1.62–1.75 (m, 2H), 1.81–1.83 (m, 2H), 1.99–2.09 (m, 2H), 3.75 (t, *J* = 7.24 Hz,1H), 4.87 (t, *J* = 7.24 Hz, 1H), 6.76 (d, *J* = 8.69 Hz, 1H), 6.93 (s, 1H), 7.04 (s, 4H), 7.21–7.35 (m, 10H), 7.85-7.89 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.1, 33.0, 35.4, 44.4, 70.0, 107.6, 116.8, 121.5,

125.4, 127.0, 127.4, 127.58, 127.63, 128.2, 128.9, 130.2, 130.7, 131.7, 134.0, 136.4, 138.2, 140.3, 142.4, 143.1, 153.9, 171.4, 185.3, 189.7, 195.8; HRMS (EI): *m/z* calcd for $C_{35}H_{26}{}^{35}ClNO_2$, 527.1652 (M); found, 527.1643.

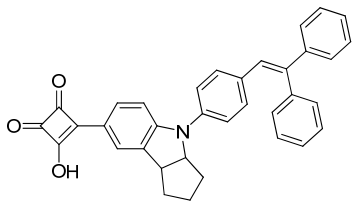
Synthesis of 3-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-4-hydroxy cyclobut-3-ene-1,2-dione (5a)



After a mixture of 3-chloro-4-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-he xahydrocyclopenta[*b*]indol-7-yl)cyclobut-3-ene-1,2-dione (**4a**) (0.467 g, 1.00 mmol), acetic acid (8 ml), and water (2 ml) was refluxed for 2 d, the resultant mixture was poured into water (50 ml) to form a precipitate. The precipitate was filtered and washed with $NaHCO_3$ aq. and brine to give 3-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-4-hydroxycyc lobut-3-ene-1,2-dione (**5a**) in 46% yield (0.206 g).

Yield 46%; mp = 83.5–84.5 °C; *Rf* 0.78 (dichloromethane/methanol = 5:1); ^{1}H NMR (DMSO-d_6) δ 1.43 (s, 6H), 1.46–1.58 (m, 2H), 1.76–1.85 (m, 3H), 2.00–2.10 (m, 1H), 3.82 (t, *J* = 7.24 Hz, 1H), 4.93 (t, *J* = 7.24 Hz, 1H), 7.01 (d, *J* = 8.45 Hz, 1H), 7.20–7.34 (m, 3H), 7.47–7.52 (m, 2H), 7.69–7.79 (m, 2H), 7.81–7.90 (m, 2H); ^{13}C NMR (DMSO-d_6) δ 24.5, 27.0, 27.2, 33.3, 34.9, 44.6, 46.7, 68.5, 107.5, 113.8, 116.5, 118.4, 119.5, 120.8, 121.0, 122.8, 124.0, 124.3, 126.9, 127.2, 132.6, 135.1, 135.4, 138.7, 141.6, 147.2, 153.2, 154.9, 176.8, 197.2; HRMS (FAB): *m/z* calcd for $C_{30}H_{25}NO_3$, 447.1834 (M); found, 447.1836.

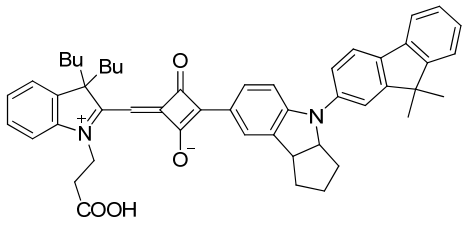
3-(4-(4-(2,2-Diphenylvinyl)phenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-4-hydroxyc yclobut-3-ene-1,2-dione (5b)



Yield 64%; mp = 97.2–98.8 °C; *Rf* 0.05 (dichloromethane/methanol = 5:1); ^{1}H NMR (DMSO-d_6) δ 1.26–1.38 (m, 1H), 1.58–1.66 (m, 2H), 1.71–1.85 (m, 2H), 2.00–2.09 (m, 1H), 3.82 (t, *J* = 7.24 Hz, 1H), 4.90 (t, *J* = 7.24 Hz, 1H), 6.98–7.03 (m, 3H), 7.07 (s, 1H), 7.13 (d, *J* = 7.24 Hz, 2H), 7.20 (d, *J* = 7.24 Hz, 2H), 7.29–7.36 (m, 5H), 7.39–7.48 (m, 3H), 7.74 (d, *J* = 7.24 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 24.8, 34.0, 35.5, 45.1, 68.8, 108.7, 119.0, 121.9, 123.9, 125.7, 127.6, 128.1, 128.4, 129.2, 130.0, 130.6, 130.9, 131.2, 136.1, 140.5, 141.1, 141.3, 143.5, 147.8, 197.1; HRMS (FAB): *m/z* calcd for $C_{35}H_{27}NO_3$, 509.1991 (M); found, 509.1997.

4-((3,3-Dibutyl-1-(2-carboxyethyl)-3*H*-indolium-2-yl)methylene)-2-(4-(9,9-dimethyl-9*H*-fluoren -2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-3-oxocyclobut-1-enolate (Sq 31)

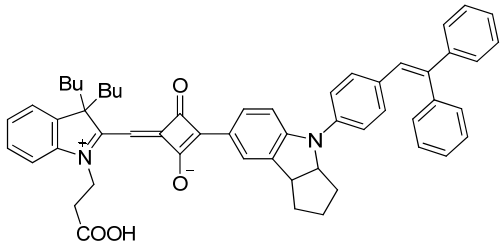
A mixture of 1-carboxyethyl-3,3-dibutyl-2-methylindolenium iodide (**3**) (0.227 g, 0.51 mmol), 3-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-4-hydroxycyc lobut-3-ene-1,2-dione **(5a)** (0.192 g, 0.43 mmol), toluene (4 ml), and 1-butanol (4 ml) was refluxed with a Dean-Stark apparatus for 5 h. The resultant mixture was cooled, diluted with



dichloromethane (20 ml), washed with brine (30 ml X 3), dried over Na_2SO_4, and concentrated under vacuum to give a residue, which was purified with dichloromethane/methanol (v/v = 20:1) to give 4-((3,3-dibutyl-1-(2-carboxyethyl)-3*H*-indolium-2-yl) methylene)-2-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3, 3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-3-oxocycl obut-1-enolate (**Sq 31**) in 29% yield (0.093 g).

Yield 29%; mp = 135.7–137.0 °C; *Rf* 0.71 (dichloromethane/methanol = 20:1); ^{1}H NMR ($CDCl_3$) δ 0.44–0.54 (m, 2H), 0.70 (s, *J* = 7.24 Hz, 6H), 0.82–0.93 (m, 2H), 1.09–1.15 (m, 4H), 1.24–1.30 (m, 4H), 1.50 (s, 3H), 1.51 (s, 3H), 1.67–1.85 (m, 2H), 1.93–2.02 (m, 2H), 2.05–2.12 (m, 2H), 3.08 (t, *J* = 11.59 Hz, 2H), 3.88 (t, *J* = 7.00 Hz, 1H), 4.61 (t, *J* = 11.59 Hz, 2H), 5.01 (t, *J* = 7.00 Hz, 1H), 6.64 (s, 1H), 6.94 (d, *J* = 8.45 Hz, 1H), 7.25–7.28 (m, 3H), 7.30–7.35 (m, 3H), 7.39–7.44 (m, 3H), 7.68–7.74 (m, 2H), 8.17–8.22 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.2, 13.4, 18.6, 22.3, 23.9, 25.8, 26.7, 26.8, 29.3, 30.1, 31.3, 32.8, 34.8, 39.1, 40.0, 44.3, 46.5, 59.7, 69.8, 90.7, 107.5, 110.1, 115.8, 119.3, 120.4, 121.5, 122.2, 122.3, 125.0, 125.6, 126.6, 126.7, 128.0, 130.8, 135.2, 135.7, 138.2, 139.5, 142.2, 151.8, 153.1, 154.7, 170.7, 172.2, 174.0, 179.9, 184.7, 186.2; HRMS (FAB): *m/z* calcd for $C_{50}H_{52}N_2O_4$, 744.3927 (M); found, 744.3931.

4-((3,3-dibutyl-1-(2-carboxyethyl)-3*H*-indolium-2-yl)methylene)-2-(4-(4-(2,2-diphenylvinyl)phe nyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-3-oxocyclobut-1-enolate (Sq 33)



Yield 9%; mp = 160.5–162.0 °C; *Rf* 0.56 (dichloromethane/methanol = 10:1); ^{1}H NMR (CD_3OD) δ 0.46–0.55 (m, 2H), 0.69 (t, *J* = 7.24 Hz, 6H), 0.84–0.94 (m, 6H), 1.08–1.13 (m, 4H), 1.39–1.45 (m, 2H), 1.78–1.81 (m, 2H), 2.06–2.15 (m, 2H), 2.88 (t, *J* = 7.00 Hz, 2H), 3.85 (t, *J* = 7.24 Hz, 1H), 4.63 (t, *J* = 7.00 Hz, 2H), 4.95 (t, *J* = 7.24 Hz, 1H), 6.40 (s, 1H), 6.89 (d, *J* = 8.93 Hz, 1H), 7.01 (s, 1H), 7.06–7.13 (m, 5H), 7.19–7.21 (m, 2H), 7.29–7.31 (m, 4H), 7.36–7.41 (m, 4H), 7.49–7.53 (m, 3H), 7.98–8.01 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.6, 13.7, 19.0, 22.6, 24.2, 26.2, 29.7, 30.4, 33.3, 36.1, 39.4, 40.5, 44.6, 60.1, 69.6, 91.2, 108.3, 110.6, 120.5, 122.2, 122.7, 125.3, 126.1, 127.3, 127.4, 127.5, 128.2, 128.4, 128.8, 129.8, 130.3, 130.5, 130.8, 132.9, 136.2, 139.3, 139.9, 140.4, 141.9, 142.6, 143.3, 151.3, 171.3, 172.6, 174.7, 180.3, 185.5, 186.6; HRMS (FAB): *m/z* calcd for $C_{55}H_{54}N_2O_4$, 806.4084 (M); found, 806.4095.

Electrochemical measurements of Sq 31 and Sq 33

Electrochemical measurement of **Sq 31** and **Sq 33** was performed in acetonitrile. The oxidation potential (E_{ox}) was measured with the use of three small electrodes. A Ag quasi reference electrode (QRE) was used as a reference. Platinum wire was used for the working and counter electrodes. All electrode potentials were calibrated with respect to a ferrocene (Fc)/ferrocenium (Fc+) redox

couple. An acetonitrile solution of dye (concentration: 5 μM) containing tetrabutylammonium perchlorate (0.1 M) and ferrocene (ca. 1 mM) was prepared. The electrochemical measurement was performed at a scan rate of 50 mV s^{-1}.

Device fabrication

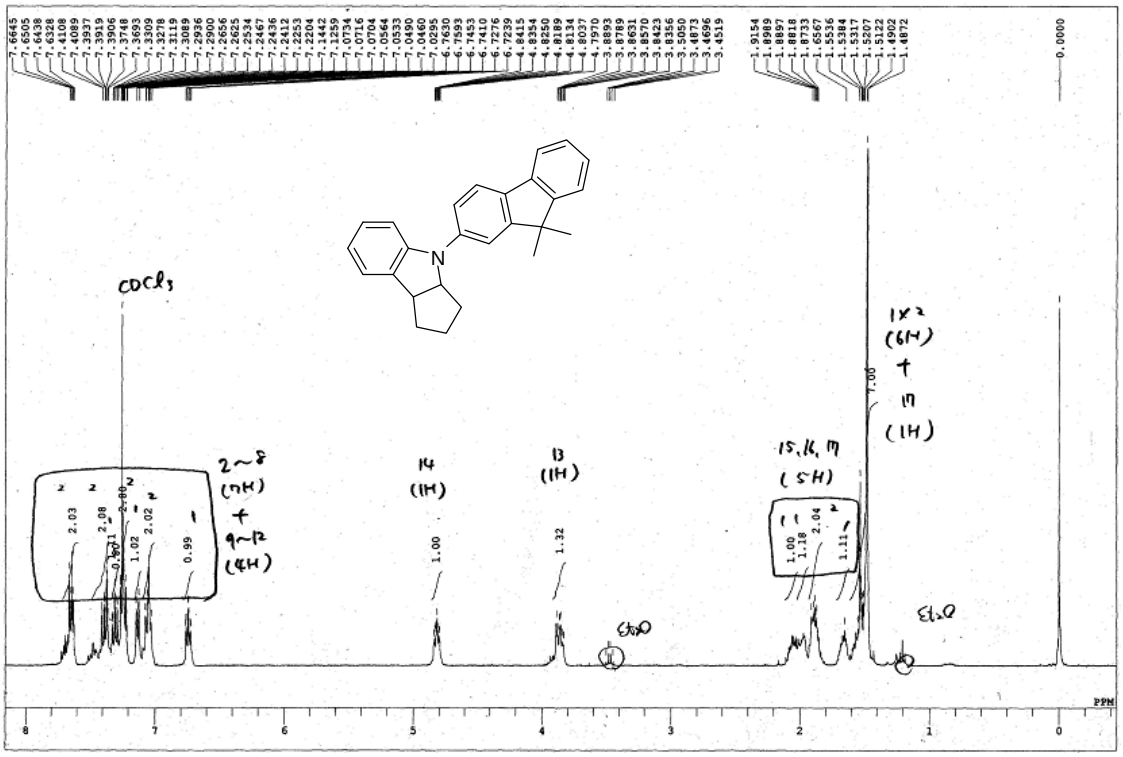
Screen-printed double-layers of TiO_2 particles were used as photoelectrodes in this study. A film of 18 nm TiO_2 particles (PST-18R, JGC C & C, Japan) of up to 9 μm thick was first printed on a F-doped SnO_2 (FTO) conducting glass electrode and coated with a second layer (up to 5 μm thick) comprised of 400 nm light-scattering anatase particles (PST-400C, JGC C & C, Japan). After the TiO_2 layers were sintered at 500 °C, the film was cooled to room temperature and immersed in 10 mM aqueous $TiCl_4$. The TiO_2 electrodes were immersed in an acetonitrile and *t*-BuOH (v/v = 1/1) solution of dye (100 μM) containing deoxycholic acid (DCA) (0.5 mM) at room temperature for 1 h. The dye-coated thin film was then washed with the solution. The film was used as a working electrode. A PEDOT-PTS coated film on FTO glass [2] was used as counter-electrode. Sandwich-type cells (two electrodes) consisting of the dye-coated TiO_2 electrode and PEDOT-PTS coated FTO glass counter electrode were attached in a face-to-face configuration using a 25 μm hot melt polymer (HIMILAN®) film spacer (Du Pont-Mitsui Polychemicals. Co., Ltd.). 3-Methoxypropionitrile (3-MPN) containing 0.1 M iodine (I_2), 0.1 M lithium iodide (LiI) and 1.0 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI) was used as an electrolyte.

Photochemical measurements

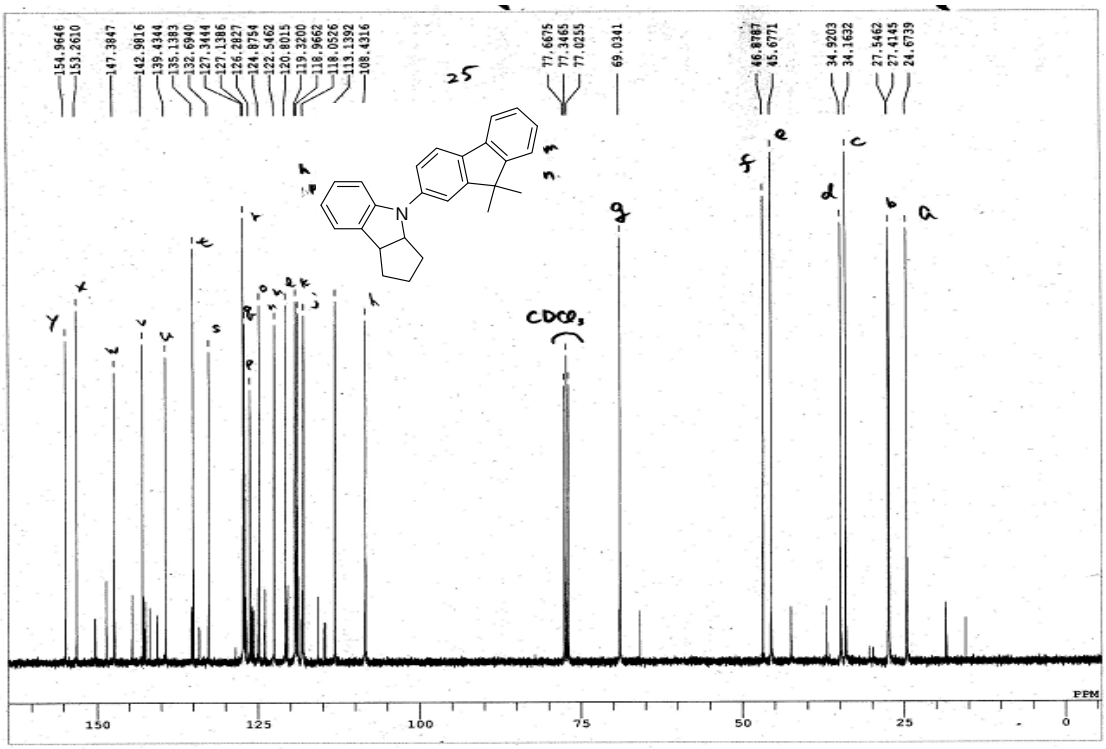
An action spectrum was measured under monochromatic light with a constant photon number under illumination with AM 1.5 simulated sunlight (100 mW cm^{-2}) through a shading mask (5.0 mm x 4.0 mm) using a Bunko-Keiki CEP-2000 system.

[2] Saito, Y.; Kitamura, T.; Wada, Y.; Yanagida, S. *Chem. Lett.* **2002**, 1060.

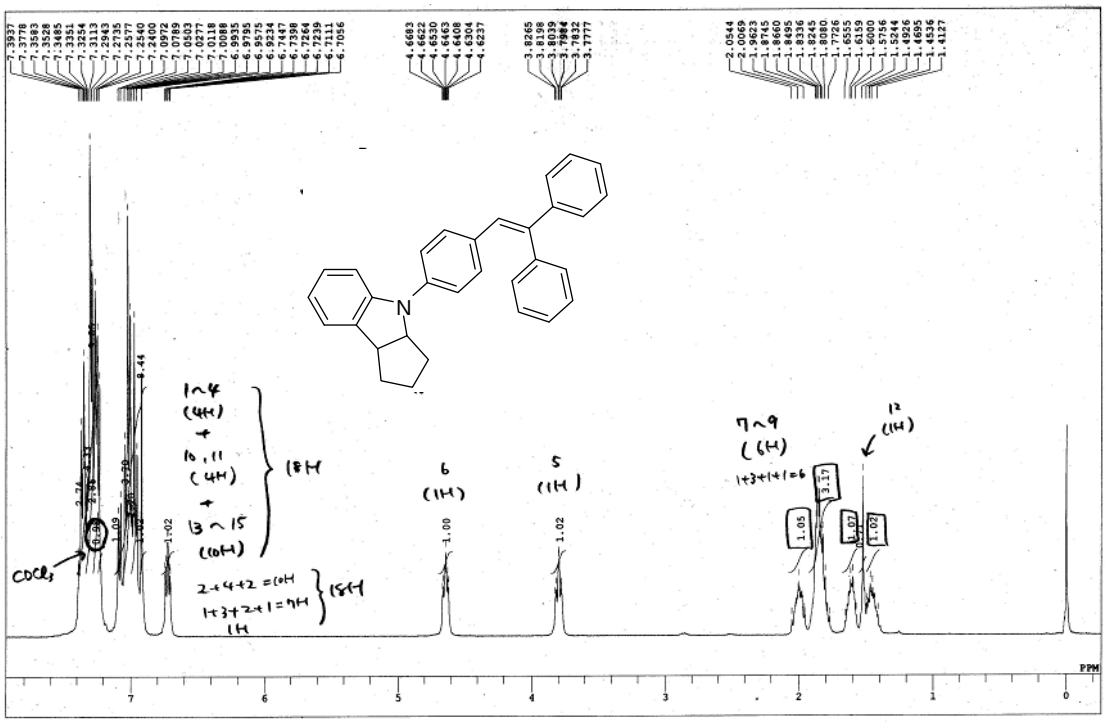
^{1}H NMR of **2a**



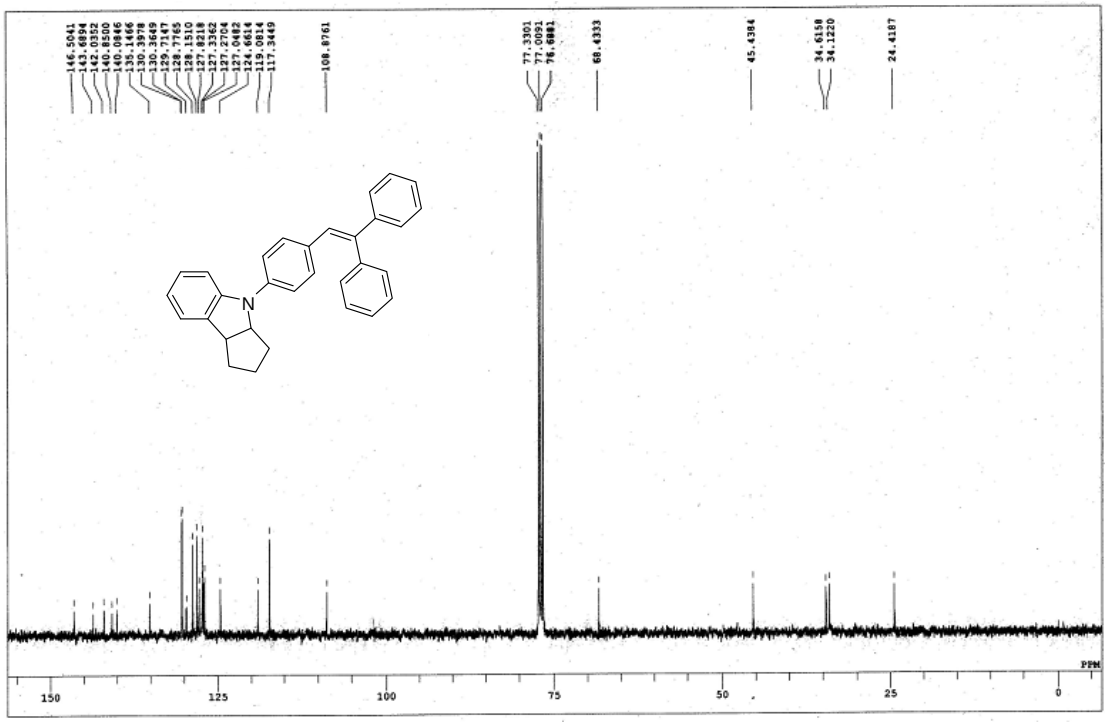
^{13}C NMR of **2a**



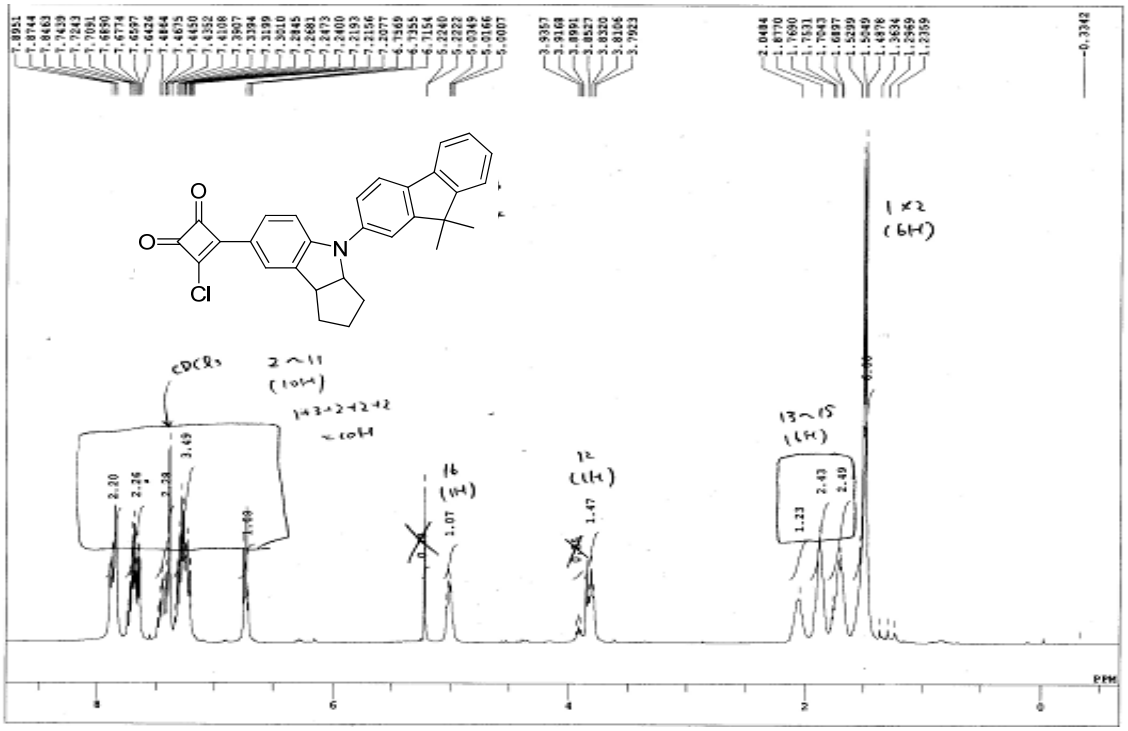
^{1}H NMR of **2b**



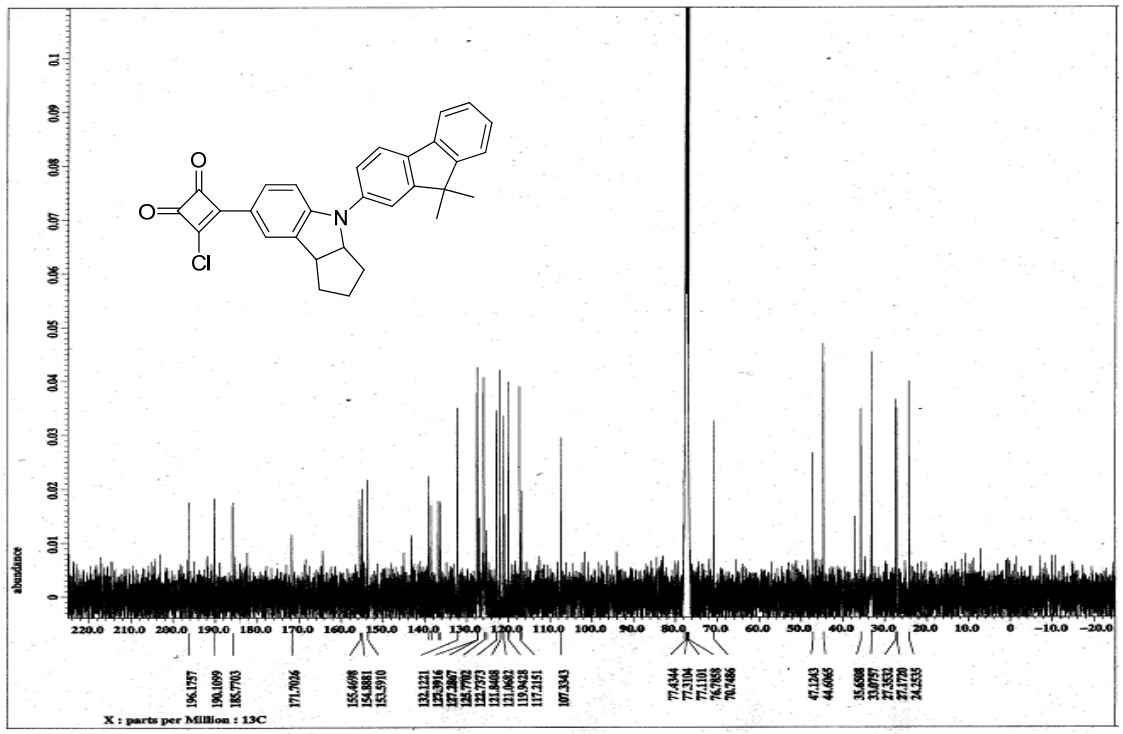
^{13}C NMR of **2b**



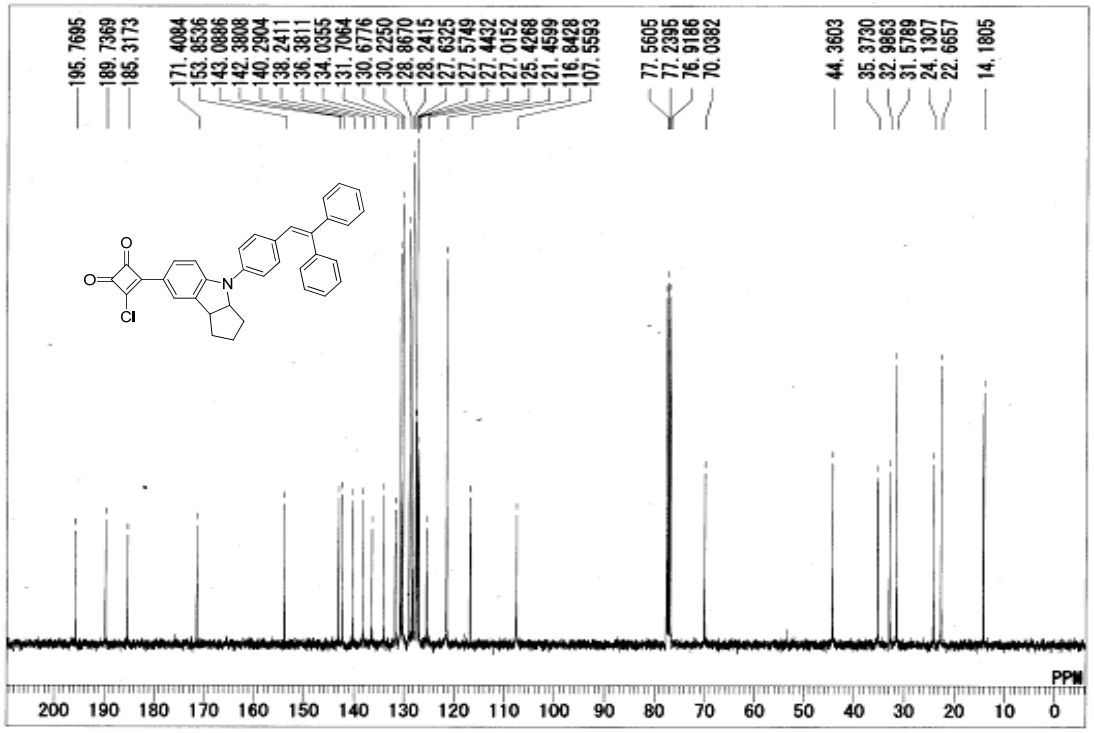
^{1}H NMR of **4a**



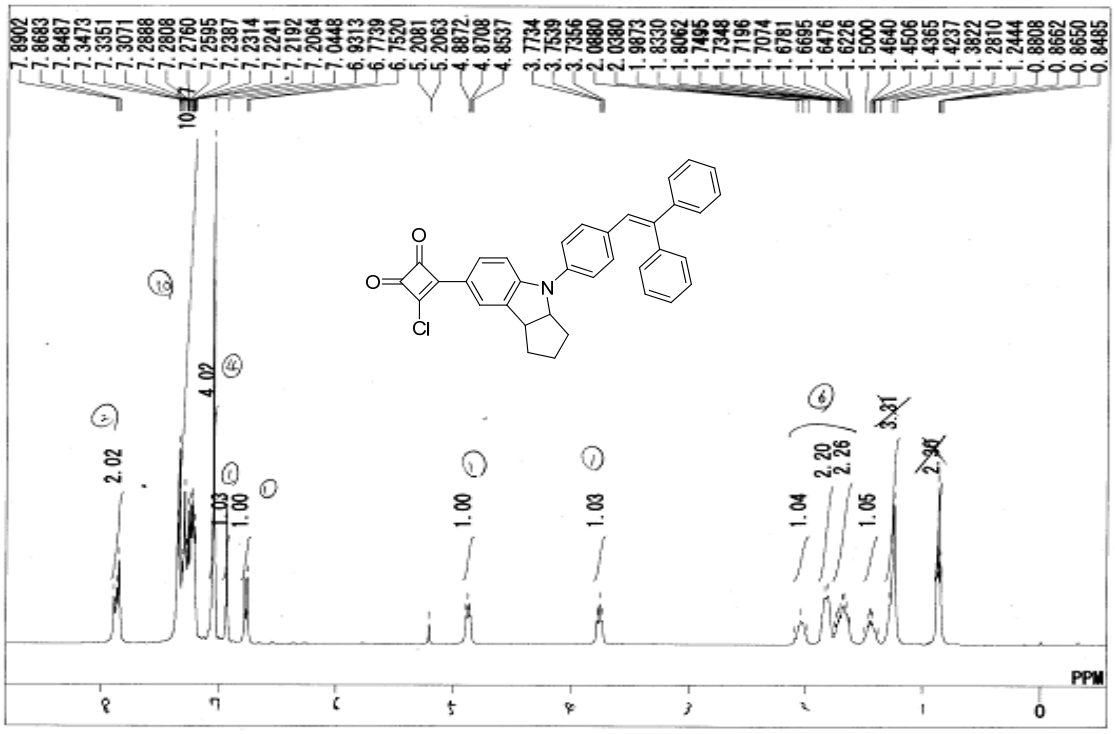
^{13}C NMR of **4a**



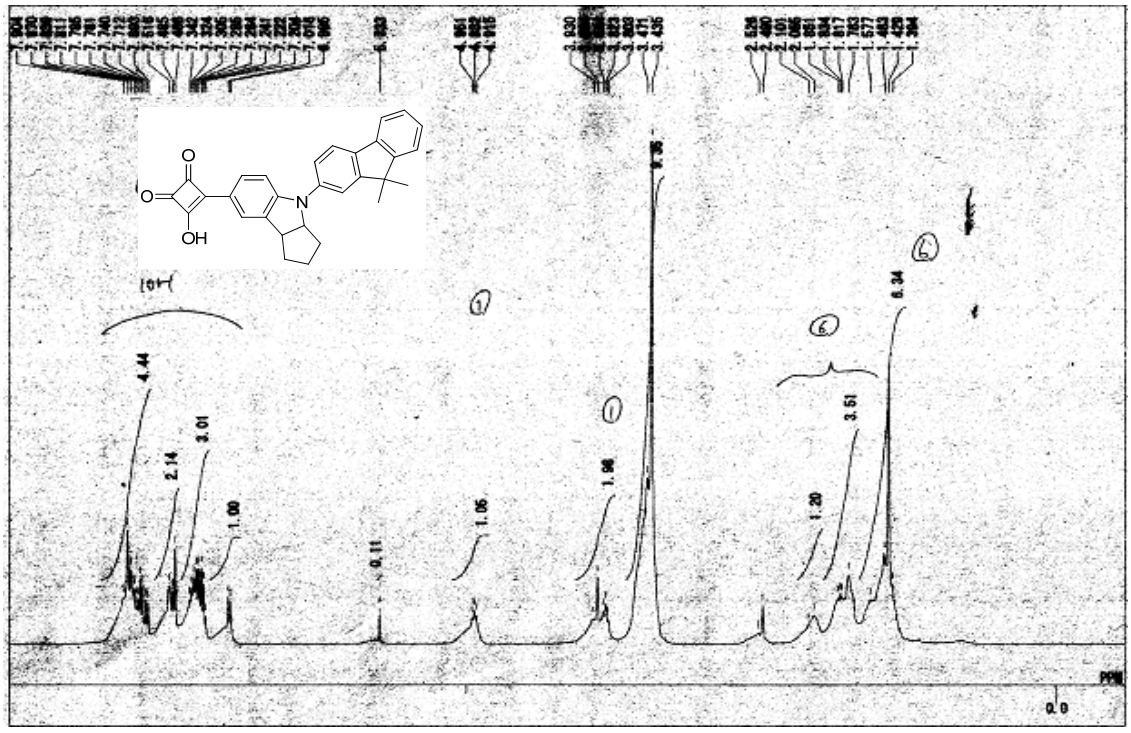
^{1}H NMR of **4b**



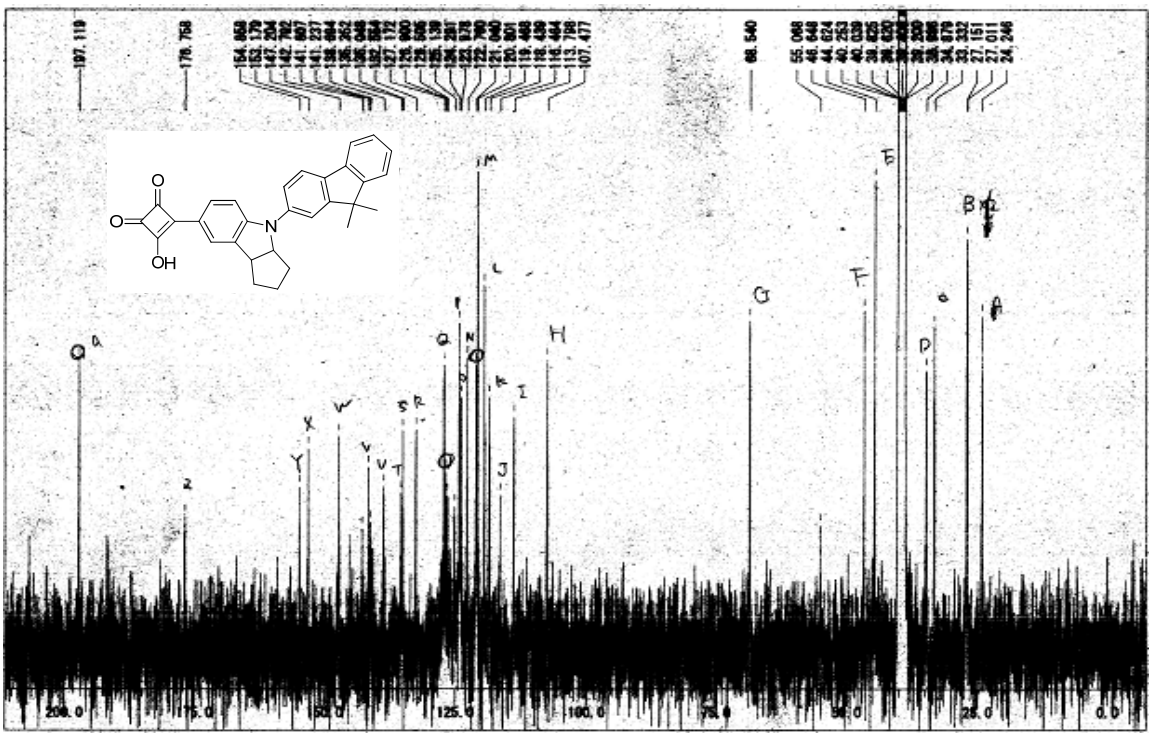
^{13}C NMR of **4b**



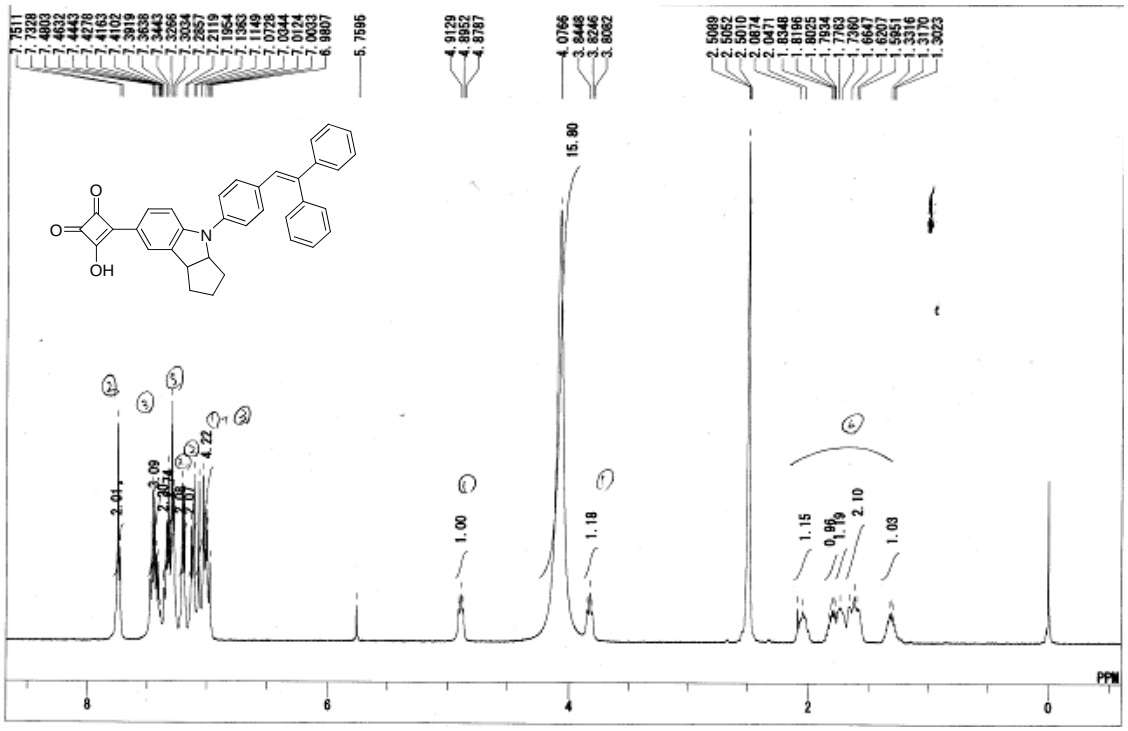
^{1}H NMR of **5a**



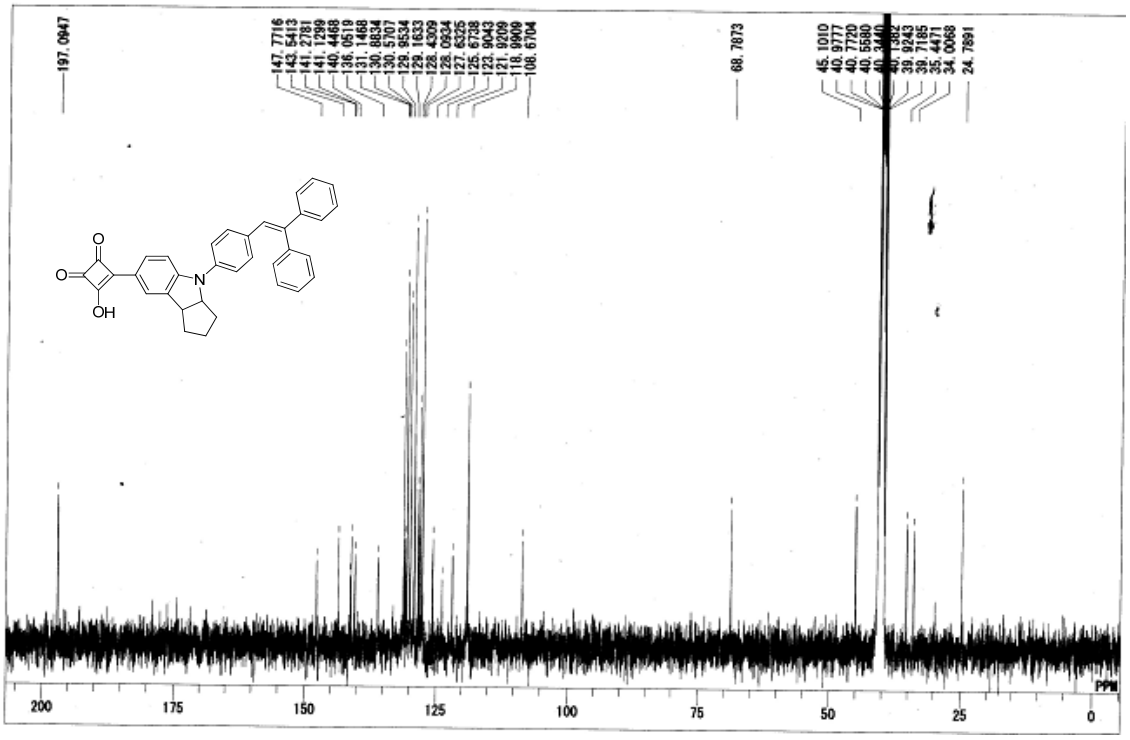
^{13}C NMR of **5a**



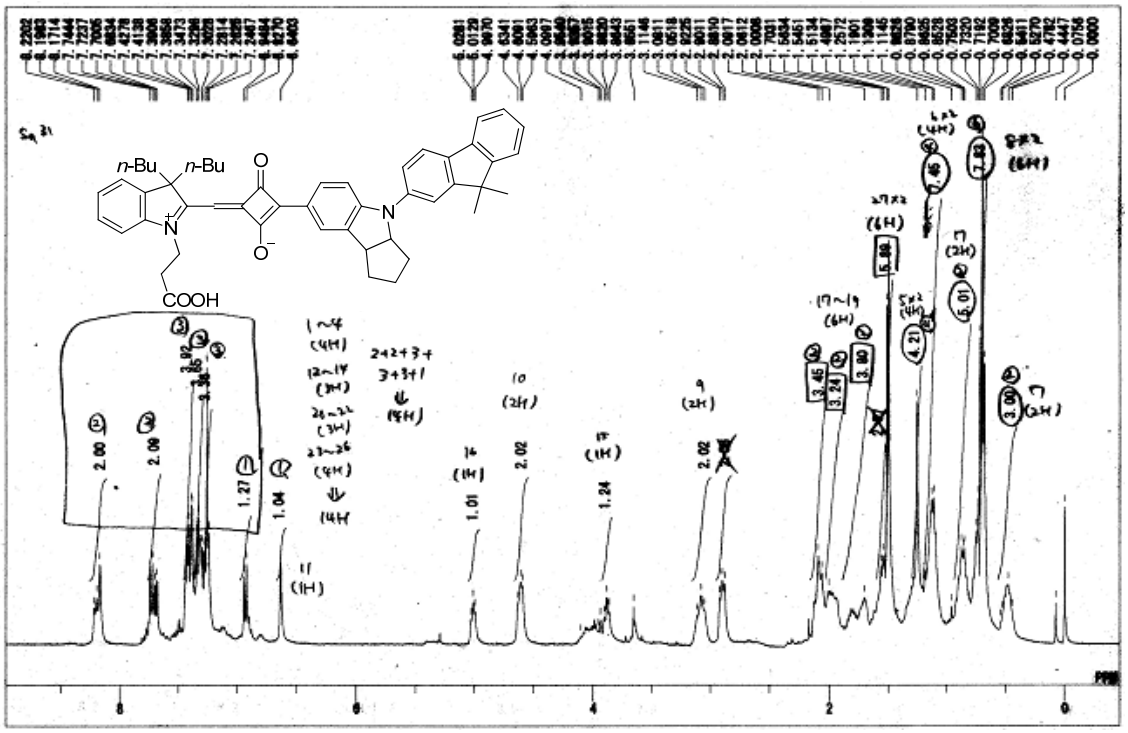
^{1}H NMR of **5b**



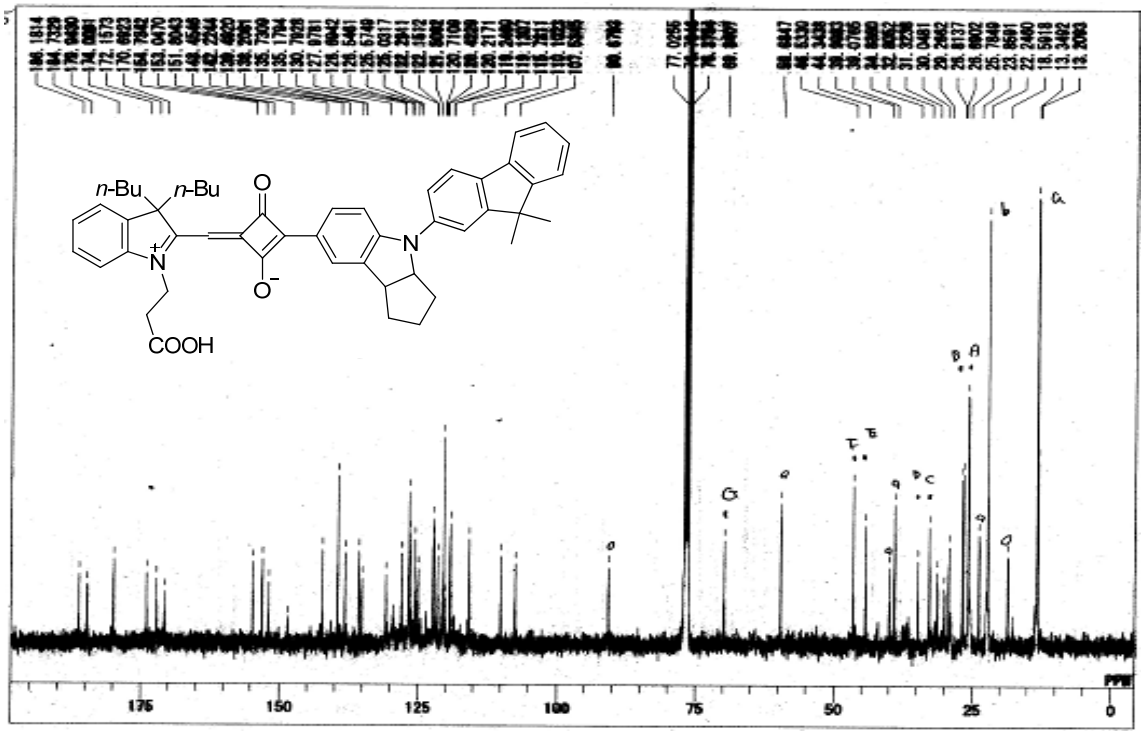
^{13}C NMR of **5b**



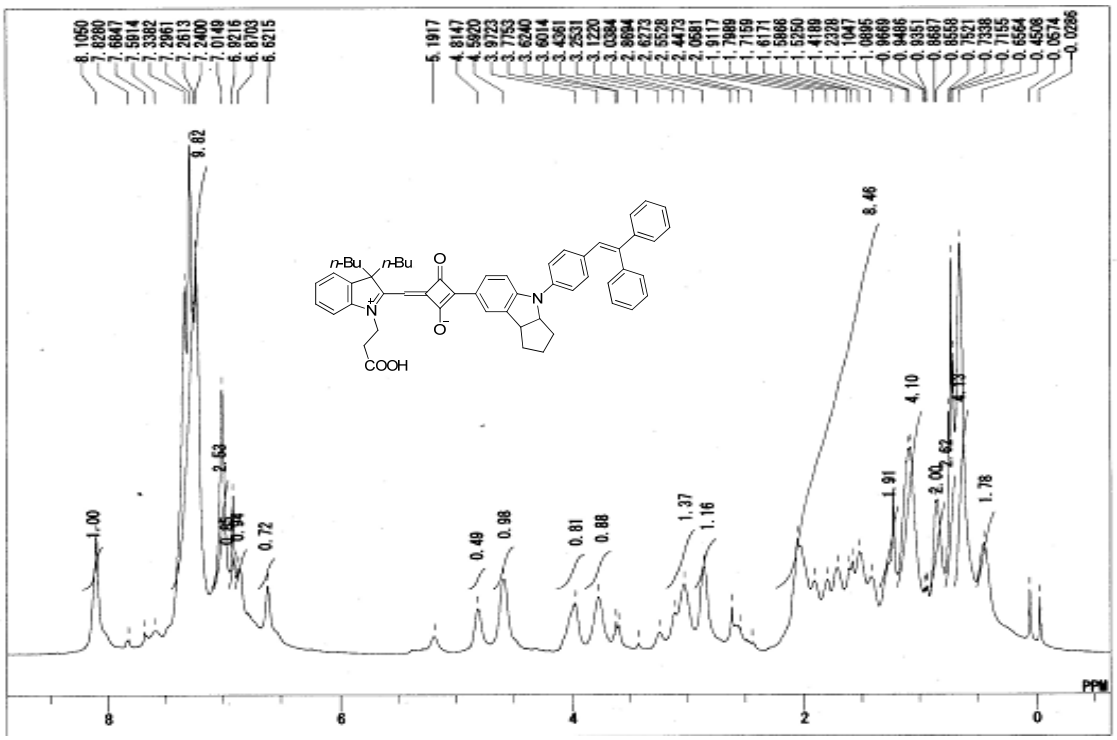
^{1}H NMR of **Sq 31**



^{13}C NMR of **Sq 31**



^{1}H NMR of **Sq 33**



^{13}C NMR of **Sq 33**