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Supplementary Information

Development of Type-I/Type-II hybrid dye sensitizer with both pyridyl group and catechol unit as anchoring group for Type-I/Type-II dye-sensitized solar cell

Yousuke Ooyama,* Kensuke Furue, Toshiaki Enoki, Masahiro Kanda, Yohei Adachi and Joji Ohshita*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, 739-8527, Japan.

Fax: +81 824 24 5494; Tel: +81 824 24 7689; E-mail:yooyama@hiroshima-u.ac.jp

Synthesis

5-(Pyridin-4-yl)-2-thienylboronic acid pinacol ester (1a): To a THF solution (20 mL) of 4-(thiophen-2-yl)pyridine[1] (1.0 g, 6.2 mmol) under an argon atmosphere was added 1.6 M hexane solution of *n*BuLi (4.0 ml, 6.2 mmol) at –78 °C. After stirring for 0.5 h, *i*PrOBPin (1.4 ml, 6.8 mmol) was added, and then the solution was stirred for 12 h at room temperature. The reaction was quenched with water, and then the solution was extracted with chloroform. The residue was dissolved in chloroform, and recycling gel permeation chromatography (GPC) was performed to give **1a** (0.9 g, yield 50 %) as a red solid; m.p. 161–164 °C; IR (ATR): $\tilde{\nu}$ = 1620, 1523, 1435 cm^{-1}; ^1H NMR (400 MHz, [D_6]acetone) δ = 1.35 (s, 12H), 7.61 (d, *J* = 3.6 Hz, 1H), 7.65 (dd, *J* = 1.6 and 4.5 Hz, 2H), 7.78 (d, *J* = 3.6 Hz, 1H), 8.60 (dd, *J* = 1.6 and 4.5 Hz, 2H) ppm; HRMS (ESI): *m*/*z* (%):[M+H^+] calcd for $C_{15}H_{19}O_2NBS$, 288.12241; found 288.12283.

2-(3,4-Bis(methoxymethoxy)phenyl)thiophene (2a): To a mixture of 4-bromo-1,2-bis(methoxymethoxy)benzene (1.0 g, 3.6 mmol), 2-thienylboronic acid (0.5 g, 3.9 mmol), and $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol) under an argon atmosphere was added aqueous Na_2CO_3 (0.8 g, 7.5 mmol) and DMF (18 ml) and stirred for 12 h at 90 ºC. After concentrating under reduced pressure, the resulting residue was dissolved in chloroform and washed with water. The chloroform extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (chloroform as eluent) to give **2a** (0.64 g, yield 64 %) as a yellow viscous solid; IR (ATR): $\tilde{\nu}$ = 1496, 1239, 1150, 1071 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ = 3.47 (s, 3H), 3.49 (s, 3H), 5.21 (s, 2H), 5.26 (s, 2H), 7.08 (dd, *J* = 3.6 and 5.1 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.25 (dd, *J* = 2.2 and 8.4 Hz, 1H), 7.33 (dd, *J* = 1.1 and 3.6 Hz, 1H), 7.38 (dd, *J* = 1.1 and 5.1 Hz, 1H), 7.42 (d, *J* = 2.2 Hz, 1H) ppm; HRMS (ESI): *m*/*z* (%):[M+Na^+] calcd for $C_{14}H_{16}O_4NaS$, 303.06615; found 303.06638.

(5-(3,4-Bis(methoxymethoxy)phenyl)thiophen-2-yl)boronic acid pinacol ester (3a): To a THF solution (12 mL) of **2a** (0.36 g, 1.3 mmol) under an argon atmosphere was added 1.6 M hexane solution of *n*BuLi (0.78 ml, 1.3 mmol) at –78 °C. After stirring for 0.5 h, *i*PrOBPin (0.26 ml, 1,4 mmol) was added, and then the solution was stirred for 12 h at room temperature. The reaction was quenched with water, and then the solution was extracted with chloroform. The chloroform extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (chloroform as eluent) to give **3a** (0.32 g, yield 61 %) as a blue solid; m.p. 71–73 °C; IR (ATR): $\tilde{\nu}$ = 1460, 1353, 1242, 1069 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ = 1.33 (s, 12H) , 3.47 (s, 3H), 3.50 (s, 3H), 5.23 (s, 2H), 5.27 (s, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.32 (dd, *J* = 2.2 and 8.4 Hz, 1H), 7.42 (d, *J* = 3.5 Hz, 1H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.52 (d, *J* = 3.5 Hz, 1H) ppm; HRMS (ESI): *m*/*z* (%):[M+Na^+] calcd for $C_{20}H_{27}O_6BNaS$, 429.15136; found 429.15155.

(3,4-Bis(methoxymethoxy)phenyl)boronic acid pinacol ester (4a)[2]: To a THF solution (50 mL) of 4-bromo-1,2-bis(methoxymethoxy)benzene (1.0 g, 3.6 mmol) under an argon atmosphere was added 1.6 M

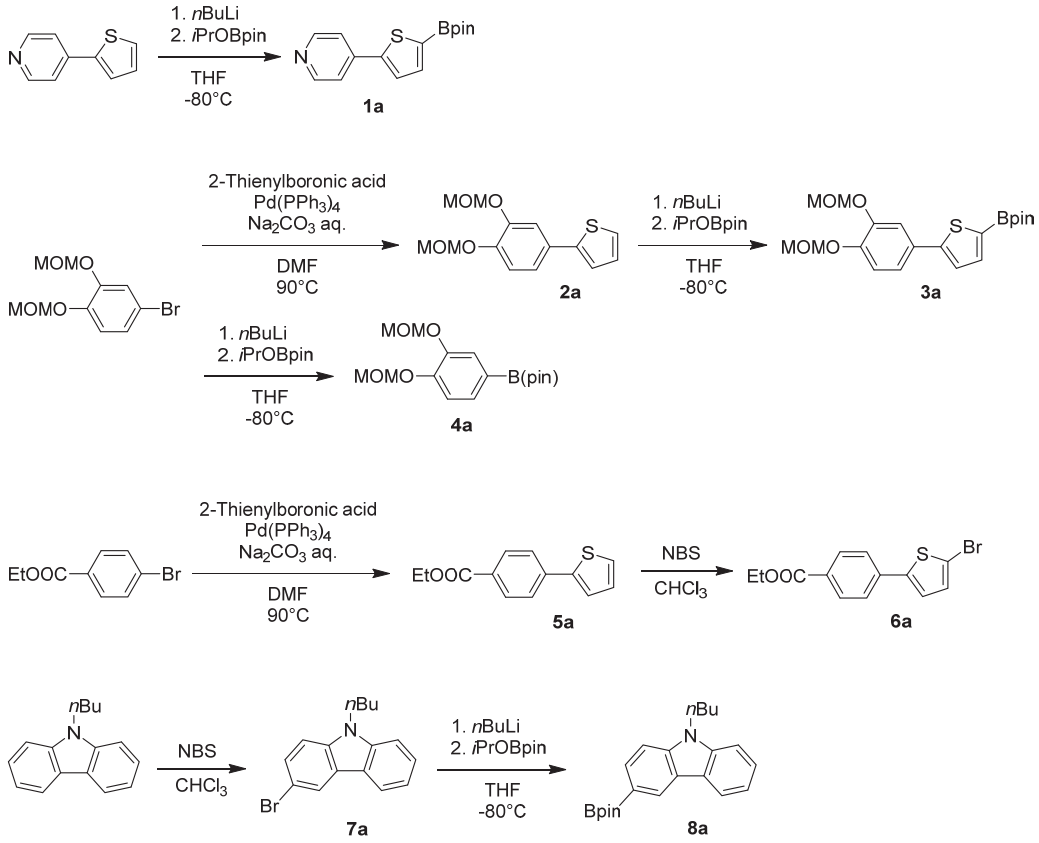
hexane solution of *n*BuLi (2.7 ml, 4.3 mmol) at –78 °C. After stirring for 0.5 h, *i*PrOBPin (0.9 ml, 4.3 mmol) was added, and then the solution was stirred for 12 h at room temperature. The reaction was quenched with water, and then the solution was extracted with dichloromethane. The dichloromethane extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate–hexane = 1 : 1 as eluent as eluent) to give **4a** (0.9 g, yield 79%) as a colorless solid; ^{1}H NMR (400 MHz, acetone-d_6) δ = 1.32 (s, 12H), 3.45 (s, 3H), 3.47 (s, 3H), 5.19 (s, 2H), 5.23 (s, 2H), 7.12 (d, *J* = 8.1 Hz, 1H), 7.37 (dd, *J* = 1.5 and 8.0 Hz, 1H), 7.46 (d, *J* = 1.5 Hz, 1H) ppm.

Ethyl 4-(thiophen-2-yl)benzoate (5a)[3]: To a mixture of ethyl 4-bromobenzonate (5.0 g, 22.0 mmol), 2-thienylboronic acid (3.4 g, 26.4 mmol), and $Pd(PPh_3)_4$ (1.3 g, 1.1 mmol) under an argon atmosphere was added aqueous Na_2CO_3 (4.6 g, 44.0 mmol) and DMF (30 ml) and stirred for 12 h at 90 ºC. After concentrating under reduced pressure, the resulting residue was dissolved in chloroform and washed with water. The chloroform extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (dichloromethane as eluent) to give **5a** (5.0 g, yield 98 %) as a yellow solid; ^{1}H NMR (400 MHz, acetone-d_6) δ = 1.36 (t, *J* = 7.1 Hz, 3H), 4.25 (q, 2H), 7.17 (dd, *J* = 3.6 and 5.1 Hz, 1H), 7.57 (dd, *J* = 1.1 and 5.1 Hz, 1H), 7.62 (dd, *J* = 1.1 and 3.6 Hz, 1H), 7.80 (dd, *J* = 2.0 and 6.7 Hz, 2H), 8.03 (dd, *J* = 2.0 and 6.7 Hz, 2H) ppm.

Ethyl 4-(5-bromothiophen-2-yl)benzoate (6a)[3]: A solution of **5a** (1.0 g, 4.3 mmol) and *N*-bromosuccinimide (1.0 g, 5.6 mmol) in chloroform (30 ml) was stirred at 0 ºC. After 12 h, to a reaction mixture was added $Na_2S_2O_3$ aq. The organic extract was concentrated under reduced pressure. The residue was chromatographed on silica gel (dichloromethane as eluent) to give **6a** (1.2 g, yield 92 %) as a beige solid; ^{1}H NMR (400 MHz, acetone-d_6) δ = 1.36 (t, *J* = 7.2 Hz, 3H), 4.35 (q, 2H), 7.24 (d, *J* = 4.0 Hz, 1H), 7.45 (dd *J* = 4.0 Hz, 1H), 7.62 (dd, *J* = 1.1 and 3.6 Hz, 1H), 7.75 (dd, *J* = 2.0 and 6.7 Hz, 2H), 8.03 (dd, *J* = 2.0 and 6.7 Hz, 2H) ppm.

3-Bromo-9-butyl-9*H*-carbazole (7a)[4]: A solution of 9-butyl-9*H*-carbazole (10.0 g, 44.0 mmol) and *N*-bromosuccinimide (8.0 g, 44.0 mmol) in chloroform (400 ml) was stirred at 0 ºC under dark condition. After 12 h, to a reaction mixture was added $Na_2S_2O_3$ aq. The organic extract was concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane as eluent) to give **7a** (12.2 g, yield 94 %) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.94 (t, *J* = 6.0 Hz, 3H), 1.36-1.41 (m, 2H), 1.81-1.87 (m, 2H), 4.28 (t, *J* = 6.0 Hz, 2H), 7.22-7.25 (m, 1H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.40 (d, *J* = 6.6 Hz, 1H), 7.47-7.50 (m, 1H), 7.53 (dd, *J* = 1.5 and 6.8 Hz, 1H), 8.04 (d, *J* = 6.2 Hz, 1H), 8.20 (d, *J* = 1.5 Hz, 1H) ppm.

(9-Butyl-9*H*-carbazol-3-yl)boronic acid pinacol ester (8a)[5]**:** To a THF solution (15 mL) of **7a** (1.0 g, 3.3 mmol) under an argon atmosphere was added 1.6 M hexane solution of *n*BuLi (2.0 ml, 3.3 mmol) at –78 °C. After stirring for 0.5 h, *i*PrOBPin (4.0 ml, 23.6 mmol) was added, and then the solution was stirred for 12 h at room temperature. The reaction was quenched with water, and then the solution was extracted with chloroform. The residue was chromatographed on silica gel (chloroform as eluent) to give **8a** (0.95 g, yield 82 %) as a light yellow oil; ^{1}H NMR (400 MHz, acetone-d$_6$) δ = 0.92 (t, *J* = 7.6 Hz, 3H), 1.36 (s, 12H), 1.36-1.48 (m, 2H), 1.83-1.89 (m, 2H), 4.44 (t, *J* = 7.2 Hz, 2H), 7.21-7.25 (m, 1H), 7.44-7.48 (m, 1H), 7.55-7.59 (m, 2H), 7.84 (dd, *J* = 1.2 and 8.3 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 8.53 (s, 1H) ppm.



Scheme S1 Synthesis of **1a**-**8a**.

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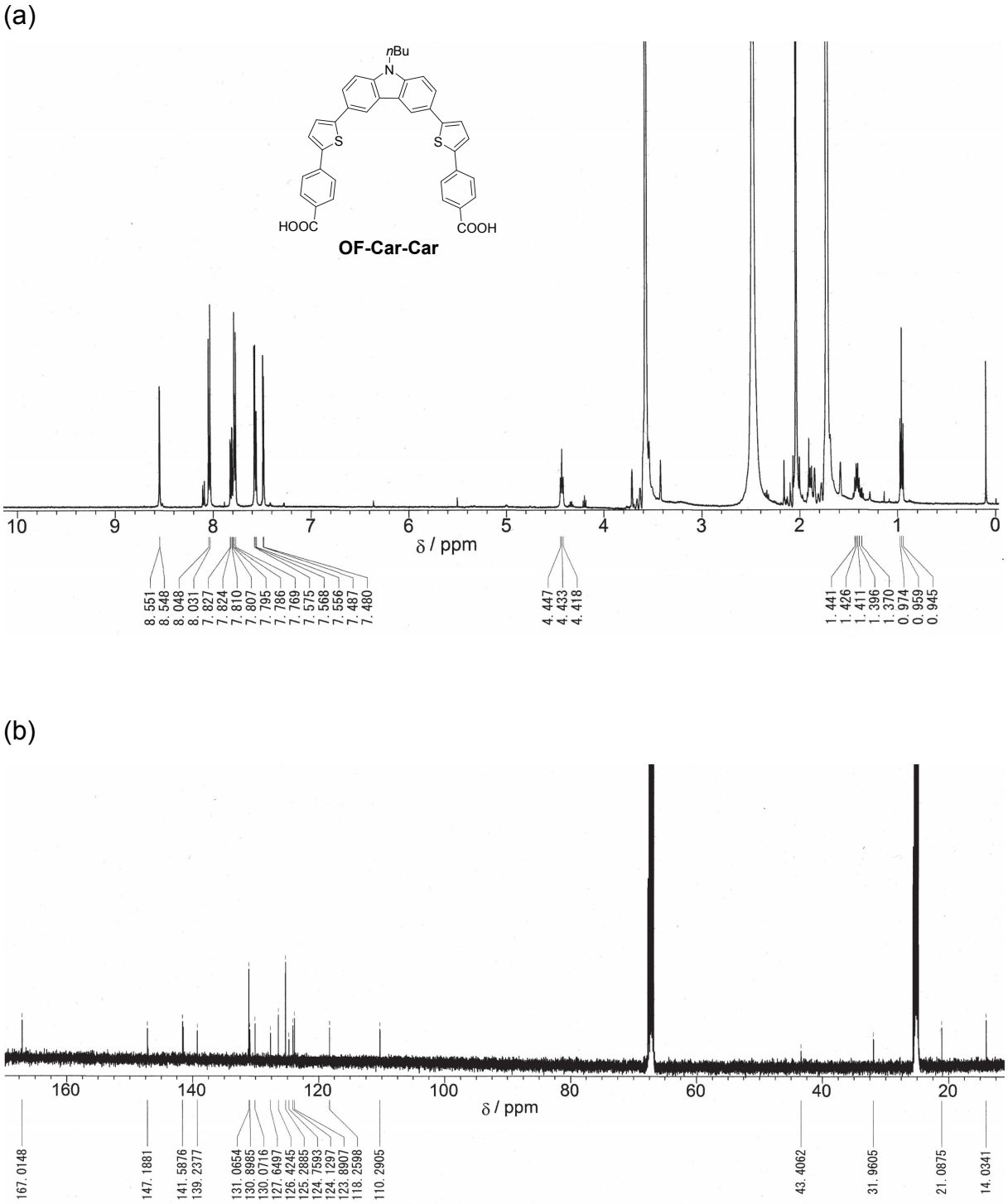

Fig. S1 (a) ^{1}H HMR (500 MHz) and (b) ^{13}C NMR (125 MHz) of **OF-Car-Car** in tetrahydrofuran-d_8.

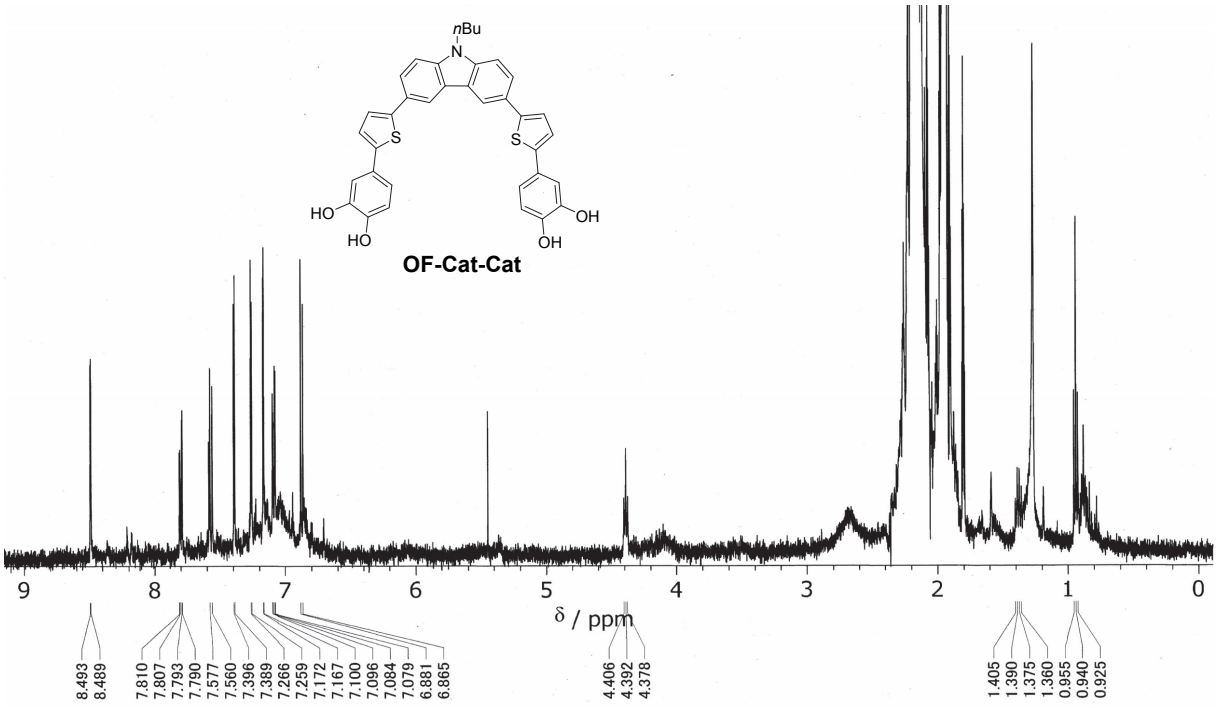

Fig. S2 [1]H HMR (500 MHz) of **OF-Cat-Cat** in acetonitrile-d_3.

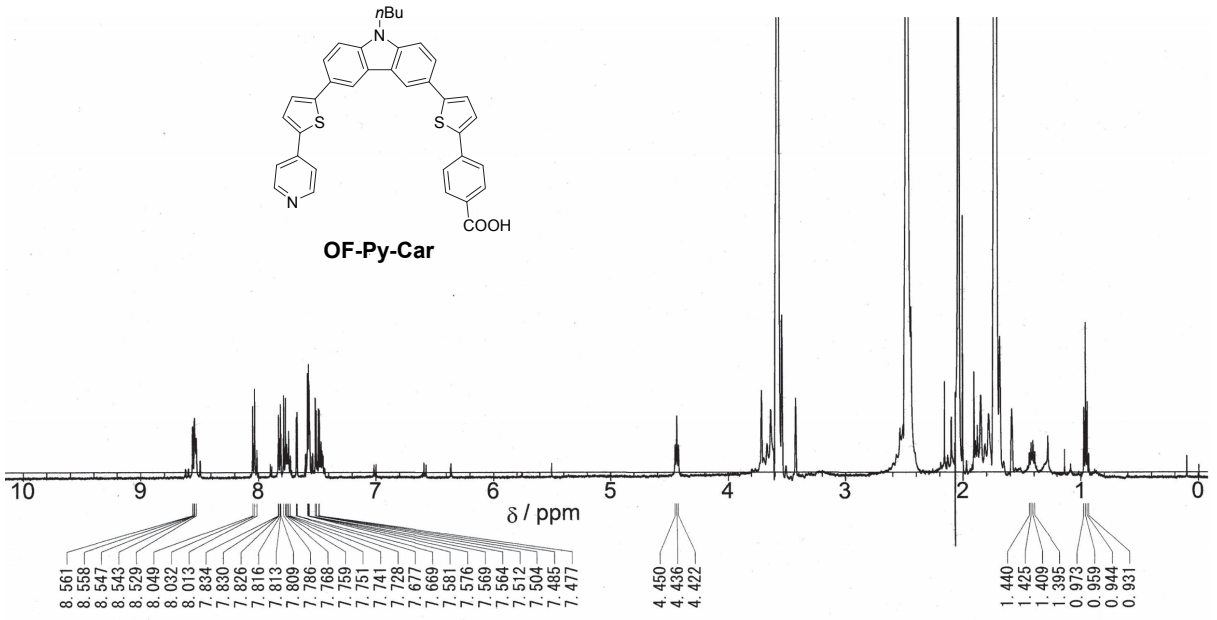

Fig. S3 [1]H HMR (500 MHz) of **OF-Py-Car** in tetrahydrofuran-d_8.

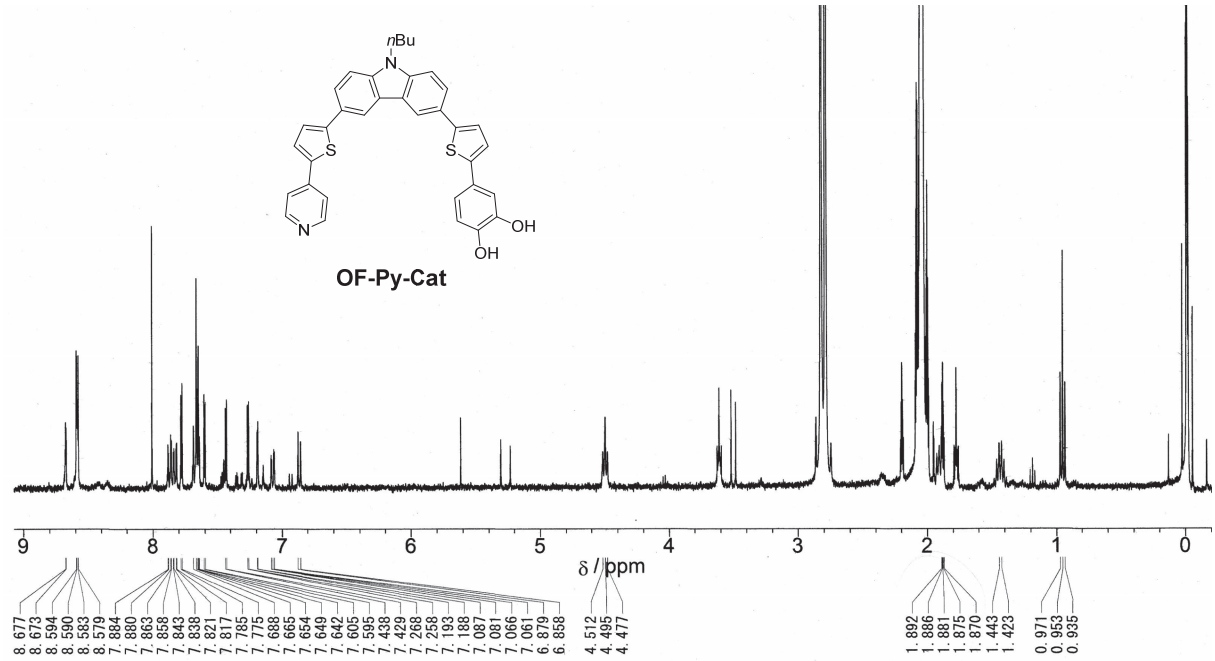

Fig. S4 ^{1}H HMR (400 MHz) of **OF-Py-Cat** in acetone-d_6.