Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Synthesis and photovoltaic properties of acceptor materials based on the dimerization of fullerene C_{60} for efficient polymer solar cells

Yuta Morinaka,[a] *Masahiro Nobori,*[a] *Michihisa Murata,*[a] *Atsushi Wakamiya,*[a] *Takashi Sagawa,*[b] *Susumu Yoshikawa,*[b] and *Yasujiro Murata**[a]

[a] *Institute for Chemical Research, Kyoto University, Uji, 611-0011, Japan*
[b] *Institute of Advanced Energy, Kyoto University, Uji, 611-0011, Japan*

Contents

1. General

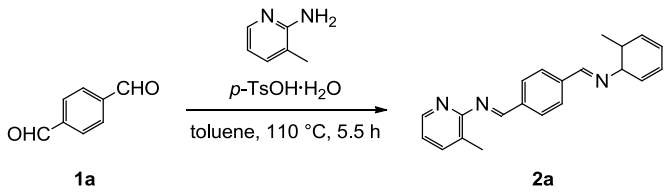
The ^{1}H and ^{13}C NMR measurements were carried out with a Varian Mercury 300 instrument and a Bruker AVANCE III 600 instrument. The NMR chemical shifts are reported in ppm with reference to residual protons and carbons of $CDCl_3$ (δ 7.26 ppm in ^{1}H NMR, δ 77.0 ppm in ^{13}C NMR), and *o*-dichlorobenzene-d_4 (ODCB-d_4) (δ 7.20 ppm in ^{1}H NMR, δ 132.35 ppm in ^{13}C NMR). High-resolution (HR) mass spectra were recorded on a JEOL MStation JMS-700 and a Bruker micrOTOF-QII. The high-pressure liquid chromatography (HPLC) was performed with the use of Cosmosil Buckyprep columns (two directly connected columns; 250 mm length, 20 mm inner diameter) for preparative purpose. Preparative GPC was performed on JAI LC-9130 system equipped with RI-700 next detector, JAIGEL-1H-40 columns (two directly connected columns; 600 mm length, 40 mm inner diameter), and FC-3310 fraction collector using chloroform as eluent (flow rate: 14.0 mL/min).

Photocurrent-voltage characteristics were measured by using a SMO-250III (BUNKOUKEIKI Co., Ltd.). The light intensity of the illumination source was adjusted by using standard silicon photodiodes: BS520 (BUNKOUKEIKI Co., Ltd.) for *J-V* characteristics and SiPD S1337-1010BQ (BUNKOUKEIKI Co., Ltd.) for EQE measurement. The thicknesses of the films were determined with an Alpha-Step IQ Surface Profiler (KLA-Tencor Co.).

Terephthalaldehyde, 2-amino-3-picoline, and $RhCl(PPh_3)_3$ were purchased from Tokyo Chemical Industry Co., Ltd. Isophthalaldehyde, ^{n}BuOH, *p*-toluenesulfonylhydrazide, *p*-TsOH·H_2O, and titanium tetraisopropoxide were purchased from Wako Pure Chemical Industries, Ltd. Methyl 3-butenoate, ODCB-d_4, and poly(3-hexylthiophene) (P3HT) were purchased from Sigma-Aldrich Co. [6,6]-Phenyl C_{61}-butyric acid methyl ester (PCBM) was purchased from Nano-C, Inc. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) (Denatron PT-100) was purchased from Nagase ChemteX Co. The glass substrates covered with indium tin oxide (ITO) (5 Ω sq^{-1}) were purchased from GEOMATEC Co., Ltd. The ITO/glass substrate was cleaned with a UV/ozone cleaner (UV-253) (Filgen, Inc.). Pentafluorophenylammonium triflate (PFPAT)[1] and PTB7[2] were prepared by following the literature.

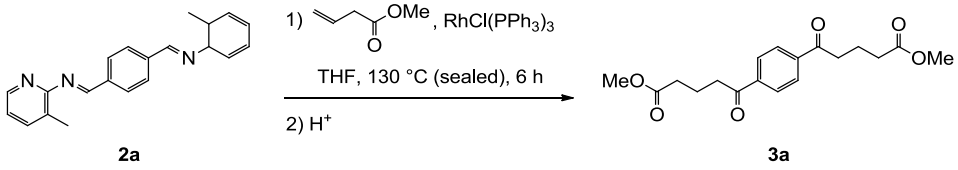
2. Synthesis of PDB

2-1. Synthesis of **2a**



A solution of terephthalaldehyde **1a** (7.38 g, 55.0 mmol), 2-amino-3-picoline (12.5 g, 116 mmol), and *p*-toluenesulfonic acid monohydrate (523 mg, 2.75 mmol) in toluene (100 mL) was refluxed for 5.5 h in a Dean-Stark apparatus. The resulting yellow solution was washed with aqueous solution of $NaHCO_3$ (saturated, 100 mL) and distilled water (100 mL × 3) to remove excess amine. The organic layer was evaporated under vacuum. The residue was purified by recrystallization ($CHCl_3$-hexane) to give **2a** (14.1 g, 44.9 mmol, 82%) as yellow needles. Compound **2a** was characterized with reference to the reported data.[3]

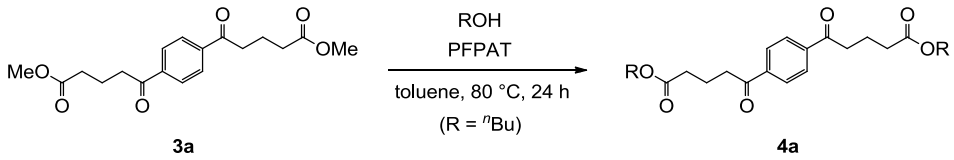
2-2. Synthesis of **3a**



To an orange solution containing **2a** (523.3 mg, 1.67 mmol) and $RhCl(PPh_3)_3$ (306.2 mg, 0.33 mmol) in THF (5.0 mL) was added methyl 3-butenoate (1.1 mL, 10.03 mmol) at room temperature, and the solution was heated at 130 ºC in a Young-valve flask. After 6 h the resulting red solution was diluted with EtOAc (ca. 20 mL) and treated with 1 M aqueous HCl. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine. After dried with Na_2SO_4 the organic layer was concentrated under reduced pressure and the residue was subjected to silica gel column chromatography (eluent: CH_2Cl_2) to give **3a** (367.5 mg, 66%, TLC; R_f = 0.35) as a colorless solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (s, 4H), 3.69 (s, 6H), 3.08 (t, J = 7.2 Hz, 4H), 2.46 (t, J = 7.2 Hz, 4H), 2.08 (quintet, J = 6.9 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.03, 173.84, 140.07, 128.46, 51.87, 38.04, 33.17, 19.34; HRMS (EI): m/z calcd for $C_{18}H_{22}O_6$ (M^+), 334.1416; found, 334.1416.

2-3. Synthesis of **4a**

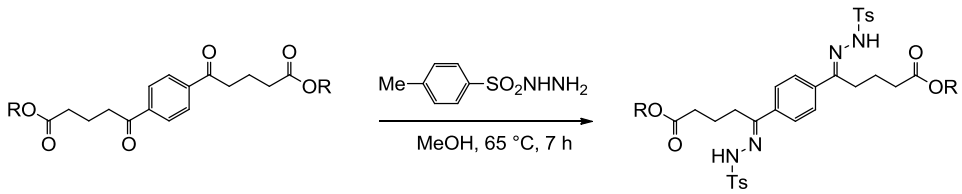


3a **4a**

A solution containing **3a** (503.2 mg, 1.50 mmol), ^{n}BuOH (1.35 mL, 14.75 mmol), and PFPAT[1] (50.1 mg, 0.15 mmol) in toluene (3.0 mL) was heated at 80 ºC. After 24 h the solution was directly subjected to silica gel column chromatography (eluent: CH_2Cl_2-EtOAc (10:1)) to give **4a** (581.3 mg, 92%, TLC; R_f = 0.52) as a colorless solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 4H), 4.07 (t, J = 6.6 Hz, 4H), 3.07 (t, J = 7.2 Hz, 4H), 2.43 (t, J = 7.2 Hz, 4H), 2.06 (quintet, J = 7.2 Hz, 4H), 1.60 (quintet , J = 6.6 Hz, 4H), 1.35 (sextet, J = 7.2 Hz, 4H), 0.91 (t, J = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.06, 173.46, 140.06, 128.42, 64.55, 38.05, 33.42, 30.82, 19.40, 19.32, 13.89; HRMS (EI): m/z calcd for $C_{24}H_{34}O_6$ (M^+), 418.2355; found, 418.2357.

2-4. Synthesis of **5a**

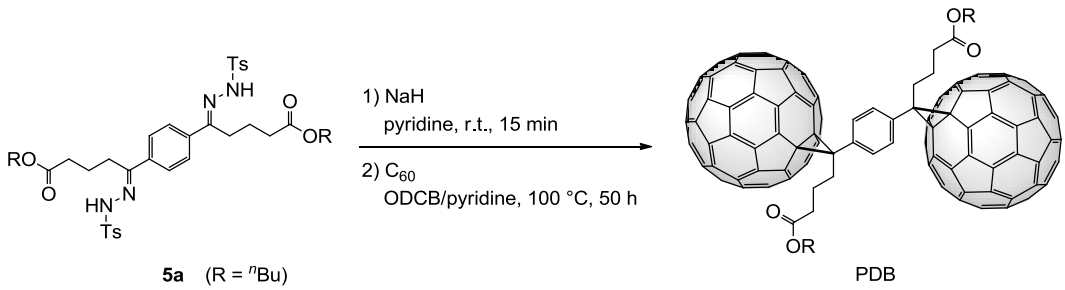


4a (R = ^{n}Bu) **5a**

A solution containing **4a** (418.3 mg, 1.00 mmol) and *p*-toluenesulfonylhydrazide (447.0 mg, 2.40 mmol) in methanol (10.0 mL) was refluxed for 7 h. The solution was cooled in refrigerator for 13 h to form pale yellow precipitates. The solid was collected by filtration and washed with cold methanol to give **5a** (714.6 mg, 95%) as pale yellow powder.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.39 (s, 2H), 7.90 (d, J = 7.8 Hz, 4H), 7.62 (s, 4H), 7.30 (d, J = 7.8 Hz, 2H), 4.21 (t, J = 6.6 Hz, 4H), 2.61 (t, J = 8.4 Hz, 4H), 2.41 (s, 6H), 2.30 (t, J = 6.6 Hz, 4H), 1.70–1.60 (m, 8H), 1.40 (sextet, J = 7.5 Hz, 4H), 0.96 (t, J = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.84, 152.89, 143.99, 137.22, 136.20, 129.72, 128.11, 126.43, 65.57, 32.43, 30.80, 25.94, 21.81, 21.14, 19.31, 13.94; HRMS (FAB): m/z calcd for $C_{38}H_{51}N_4O_8S_2$ ([M+H]$^+$), 755.3148; found, 755.3152.

2-5. Synthesis of PDB



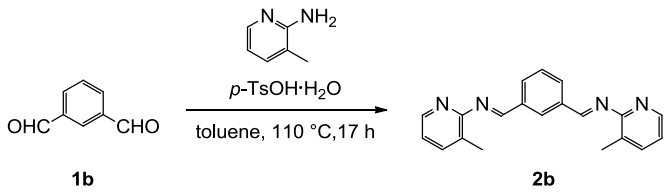
5a (R = ^{n}Bu) PDB

To a solution of **5a** (92.1 mg, 0.13 mmol) in pyridine (1.3 mL) was added NaH (9.47 mg, 0.39 mmol) and the resulting suspension was stirred at room temperature for 15 min. Small bubbles and white precipitates were formed. To the solution was added a solution of C_{60} (378.3 mg, 0.53 mmol) in ODCB (38.0 mL) and the mixture was heated at 100 ºC for 50 h. The color of the solution changed from purple to brown. The resulting solution was concentrated and subjected to silica gel column chromatography (eluent: toluene-EtOAc (10:1)). The resulting solid was further purified with preparative HPLC (BuckyPrep, eluent: toluene) to give PDB (56.0 mg, 23%) as a brown solid.

^{1}H NMR (600 MHz, 80 ºC, ODCB-d_4) δ 8.39 (s, 4H), 4.35 (t, J = 6.8 Hz, 4H), 3.36–3.33 (m, 4H), 2.80 (t, J = 7.2 Hz, 4H), 2.69–2.64 (m, 4H), 1.84 (quintet, J = 7.1 Hz, 4H), 1.60 (sextet, J = 7.4 Hz, 4H), 1.15 (t, J = 7.4 Hz, 6H); ^{13}C NMR (150 MHz, 80 ºC, ODCB-d_4) δ 171.89, 148.81, 147.47, 145.58, 144.89, 144.82, 144.75, 144.53, 144.46, 144.34, 144.22, 144.19, 143.81, 143.49, 143.48, 142.80, 142.69, 142.67, 142.63, 142.62, 142.58, 142.06, 142.04, 141.85, 141.81, 140.80, 140.52, 138.04, 137.43, 137.13, 132.37 (overlapped with the signal of ODCB-d_4 as confirmed by DEPT-135), 79.86, 64.01, 51.88, 33.90, 33.19, 30.85, 22.66, 19.19, 13.50; HRMS (FAB): m/z calcd for $C_{144}H_{34}O_4$ (M^+), 1826.2457; found, 1826.2461.

3. Synthesis of MDB

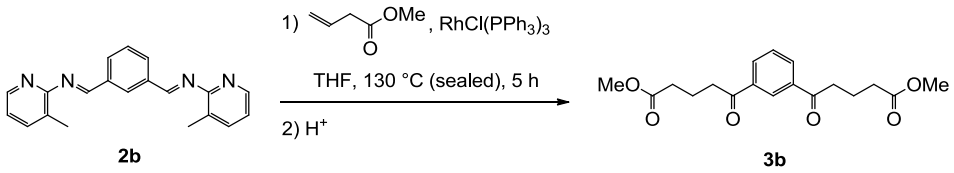
3-1. Synthesis of **2b**



A solution of isophthalaldehyde **1b** (2.37 g, 17.7 mmol), 2-amino-3-picoline (5.13 g, 47.5 mmol), and *p*-toluenesulfonic acid monohydrate (8.8 mg, 0.05 mmol) in toluene (30.0 mL) was refluxed for 17 h in a Dean-Stark apparatus. The resulting yellow solution was washed with distilled water (50 mL × 4 times) to remove excess amine. The organic layer was evaporated under vacuum. The residue was subjected to preparative GPC (eluent: $CHCl_3$) to give **2b** (19.9 g, quant.) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.17 (s, 2H), 8.59 (t, J = 1.5 Hz, 1H), 8.32 (dd, J = 1.5 Hz, 4.8 Hz, 2H), 8.17 (dd, J = 1.8 Hz, 7.8 Hz, 2H), 7.62–7.57 (m, 3H), 7.11 (dd, J =4.8 Hz, 7.5 Hz, 2H), 2.49 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.06, 159.38, 146.39, 139.18, 137.06, 132.23, 131.04, 129.35, 129.25, 122.29, 17.63; HRMS (EI): m/z calcd for $C_{20}H_{18}N_4$ (M^+), 314.1531; found, 314.1530.

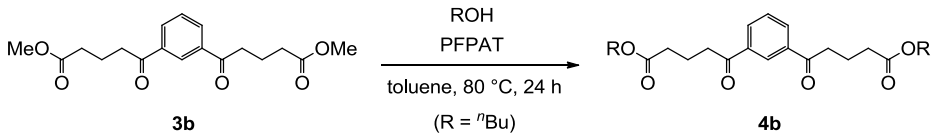
3-2. Synthesis of **3b**



To an orange solution containing **2b** (947.2 mg, 3.01 mmol) and $RhCl(PPh_3)_3$ (552.6 mg, 0.60 mmol) in THF (10.0 mL) was added methyl 3-butenoate (1.9 mL, 17.82 mmol) and the mixture was heated at 130 ºC in a Young-valve flask. After 5 h the resulting red solution was diluted with EtOAc (ca. 40 mL) and treated with 1 M aqueous HCl. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine. After dried with Na_2SO_4 the organic layer was concentrated under reduced pressure and subjected to silica gel column chromatography (eluent: CH_2Cl_2-EtOAc (10:1)) to give **3b** (420.4 mg, 42%, TLC; R_f = 0.53) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (t, J = 1.5 Hz, 1H), 8.14 (dd, J = 1.5 Hz, 7.8 Hz, 2H), 7.57 (t, J = 7.8 Hz, 1H), 3.68 (s, 6H), 3.10 (t, J = 7.2 Hz, 4H), 2.46 (t, J = 6.9 Hz, 4H), 2.08 (quintet, J = 6.9 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.87, 173.82, 137.30, 132.45, 129.30, 127.70, 51.83, 37.84, 33.18, 19.39; HRMS (EI): m/z calcd for $C_{18}H_{22}O_6$ (M^+), 334.1416; found, 334.1416.

3-3. Synthesis of **4b**

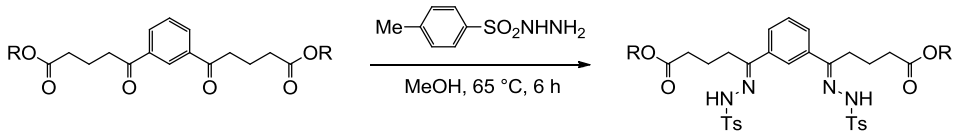


3b **4b**

A solution containing **3b** (335.6 mg, 1.00 mmol), ^{n}BuOH (0.9 mL, 9.84 mmol), and PFPAT[1] (33.2 mg, 0.10 mmol) in toluene (2.0 mL) was heated at 80 ºC. After 24 h the solution was subjected to silica gel column chromatography (eluent: CH_2Cl_2-EtOAc (10:1)) to give **4b** (380.9 mg, 91%, TLC; R_f = 0.51) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (t, J = 1.8 Hz, 1H), 8.15 (dd, J = 1.8 Hz, 7.8 Hz, 2H), 7.57 (t, J = 7.8 Hz, 1H), 4.08 (t, J = 6.6 Hz, 4H), 3.10 (t, J = 6.6 Hz, 4H), 2.44 (t, J = 7.2 Hz, 4H), 2.08 (quintet, J = 7.2 Hz, 4H), 1.60 (quintet, J = 7.2 Hz, 4H), 1.36 (sextet, J = 7.2 Hz, 4H), 0.94 (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.93, 173.49, 137.34, 132.45, 129.30, 127.70, 64.58, 37.88, 33.46, 30.85, 19.47, 19.34, 13.91; HRMS (EI): m/z calcd for $C_{24}H_{34}O_6$ (M^+), 418.2355; found, 418.2357.

3-4. Synthesis of **5b**

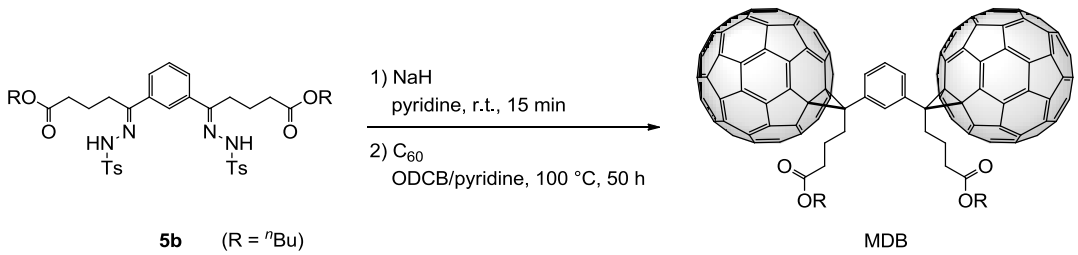


4b (R = ^{n}Bu) **5b**

A solution containing **4b** (333.5 mg, 0.80 mmol) and *p*-toluenesulfonylhydrazide (358.5 mg, 1.93 mmol) in methanol (10.0 mL) was refluxed for 6 h. The solution was cooled in refrigerator for 13 h to form pale yellow co-crystals (needle) with methanol. The crystals were collected by filtration and washed with cold methanol. The crystals were dissolved in $CHCl_3$ and the solvent was evaporated under vacuum to give **5b** (600.1 mg, 99.7%) as pale yellow powder.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.40 (s, 2H), 8.01 (s, 1H), 7.90 (dd, J = 2.1 Hz, 6.6 Hz, 4H), 7.60 (dd, J = 1.8 Hz, 7.8 Hz, 2H), 7.33–7.27 (m, 5H), 4.22 (t, J = 6.6 Hz, 4H), 2.63 (t, J = 8.4 Hz, 4H), 2.39 (s, 6H), 2.31 (t, J = 6.6 Hz, 4H), 1.70–1.61 (m, 8H), 1.40 (sextet, J = 7.5 Hz, 4H), 0.96 (t, J = 7.5 Hz, 6H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.86, 153.22, 144.00, 136.62, 136.20, 129.76, 128.77, 128.07, 127.35, 124.06, 65.55, 32.35, 30.79, 26.02, 21.79, 21.13, 19.31, 13.93; HRMS (FAB): m/z calcd for $C_{38}H_{51}N_4O_8S_2$ ([M+H]$^+$), 755.3147; found, 755.3152.

3-5. Synthesis of MDB



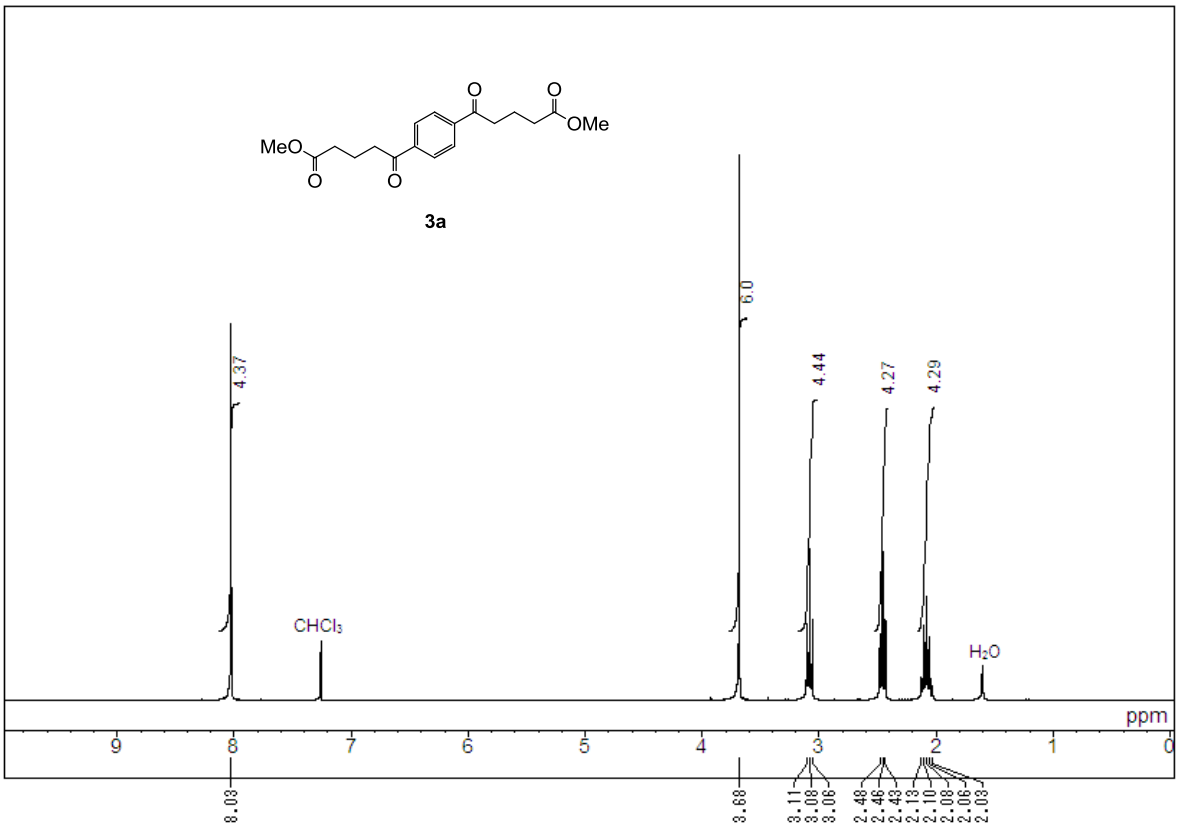
5b (R = ^{n}Bu) MDB

To a solution of **5b** (113.8 mg, 0.15 mmol) in pyridine (1.5 mL) was added NaH (10.91 mg, 0.45 mmol) and the resulting suspension was stirred at room temperature for 15 min. Small bubbles and white precipitates were formed. To the solution was added a solution of C_{60} (438.0 mg, 0.61 mmol) in ODCB (44.0 mL) and the mixture was heated at 100 ºC for 50 h. The color of the solution changed from purple to brown. The resulting solution was concentrated and subjected to silica gel column chromatography (eluent: ODCB-EtOAc (10:1)). The resulting solid was further purified with preparative HPLC (BuckyPrep, eluent: toluene) to give MDB (102.3 mg, 37%) as a brown solid.

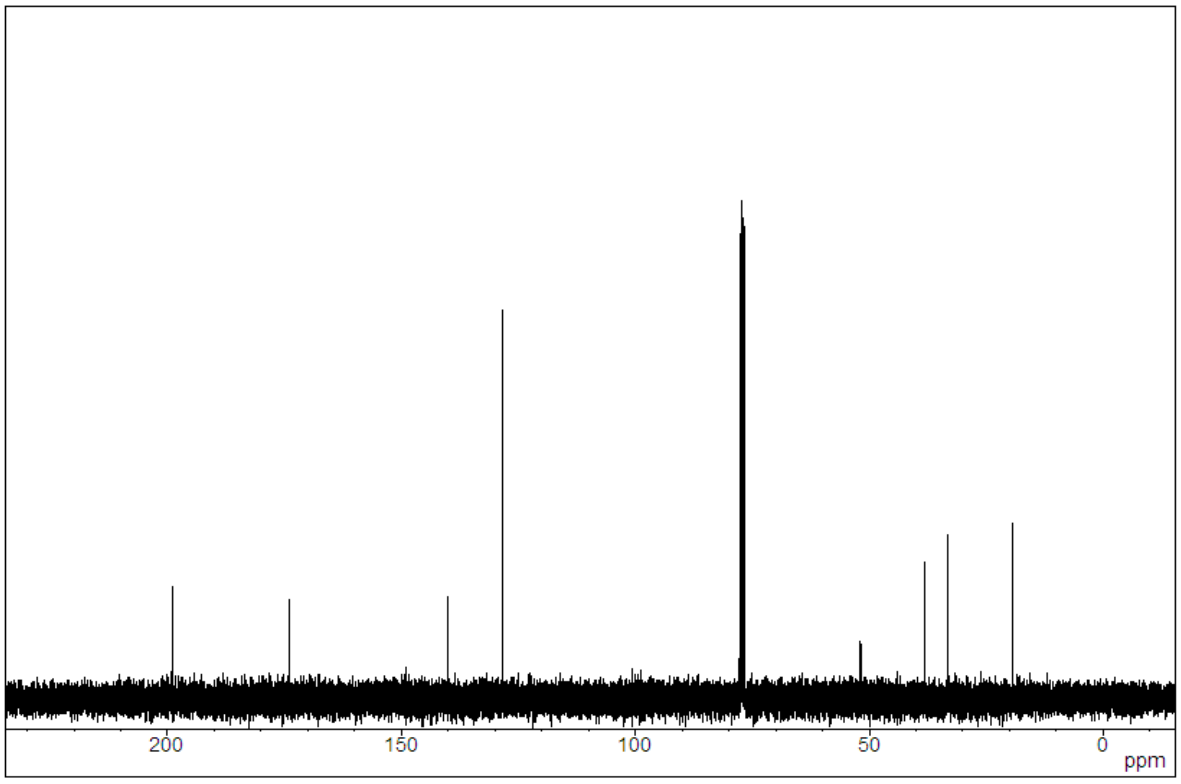
^{1}H NMR (600 MHz, 100 ºC, ODCB-d_4) δ 8.87 (t, J = 1.8 Hz, 1H), 8.32 (dd, J = 1.8 Hz, 7.7 Hz, 2H), 7.87 (t, J = 7.7 Hz, 1H), 4.37 (t, J = 6.7 Hz, 4H), 3.40–3.37 (m, 4H), 2.86 (t, J = 7.1 Hz, 4H), 2.67–2.62 (m, 4H), 1.85 (quintet, J = 7.1 Hz, 4H), 1.61 (sextet, 7.4 Hz, 4H), 1.15 (t, J = 7.4 Hz, 6H); ^{13}C NMR (150 MHz, 100 ºC, ODCB-d_4) δ 171.88, 148.46, 147.41, 145.56, 144.86, 144.85, 144.83, 144.79, 144.75, 144.48, 144.44, 144.34, 144.32, 144.14, 144.13, 143.90, 143.42, 143.36, 142.78, 142.70, 142.63, 142.60, 141.99, 141.95, 141.81, 141.79, 140.73, 140.66, 137.95, 137.46, 137.42, 135.85, 131.64, 128.45, 80.07, 63.98, 51.75, 33.82, 33.78, 30.83, 22.58, 19.10, 13.35; APCI-HRMS (–): m/z calcd for $C_{144}H_{34}O_4$ (M^-), 1826.2463; found, 1826.2539.

4. ^{1}H and ^{13}C NMR spectra

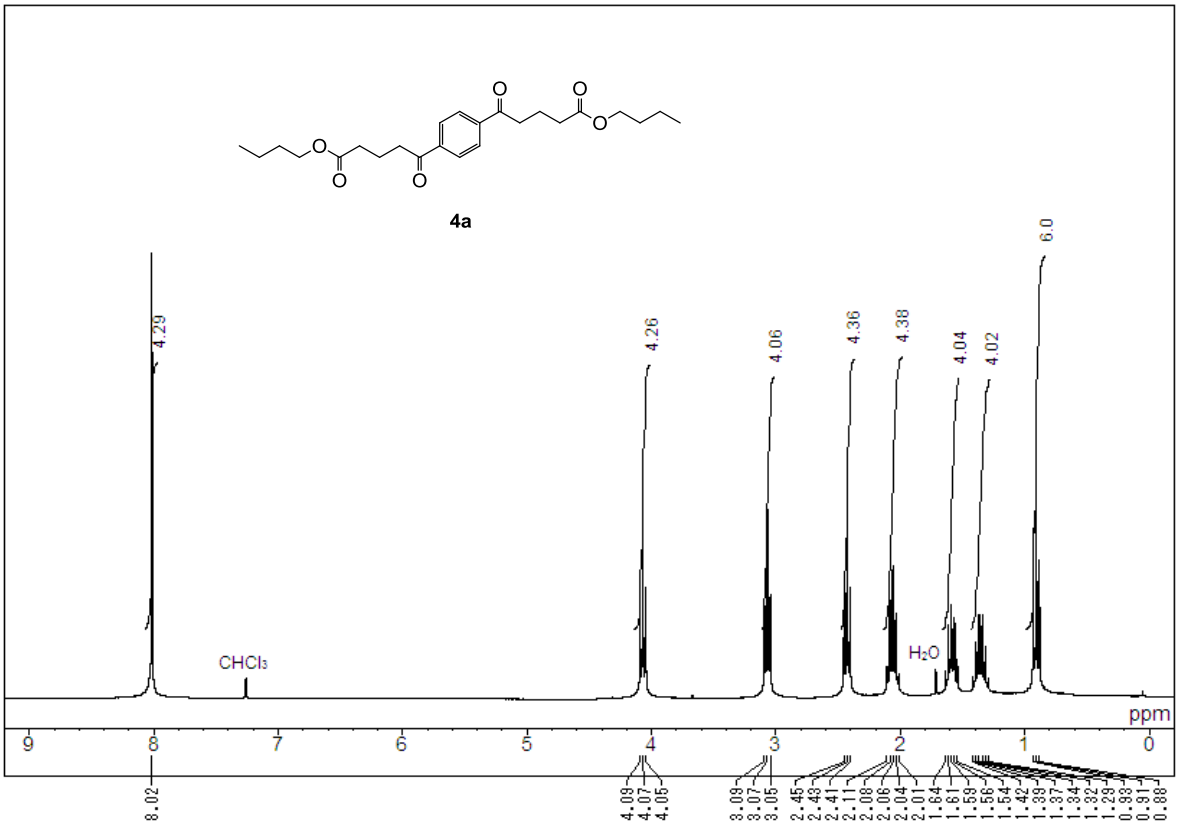
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3a**



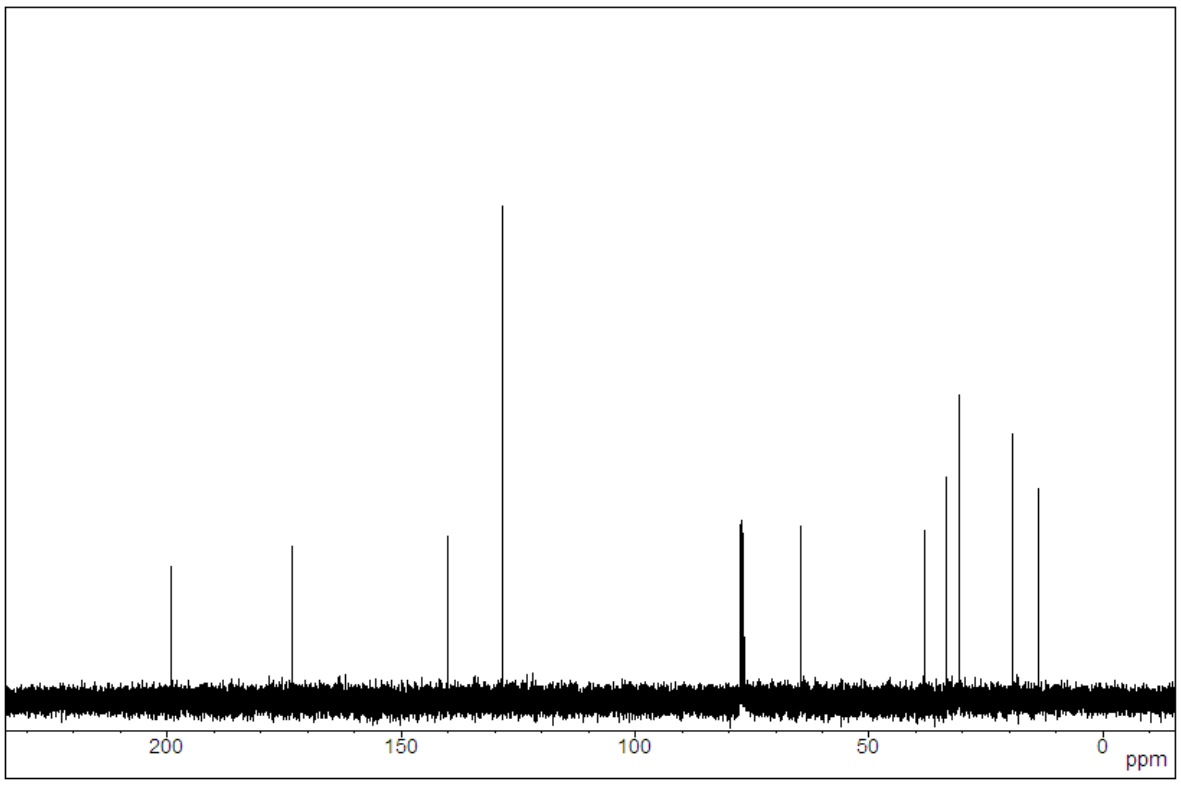
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **3a**



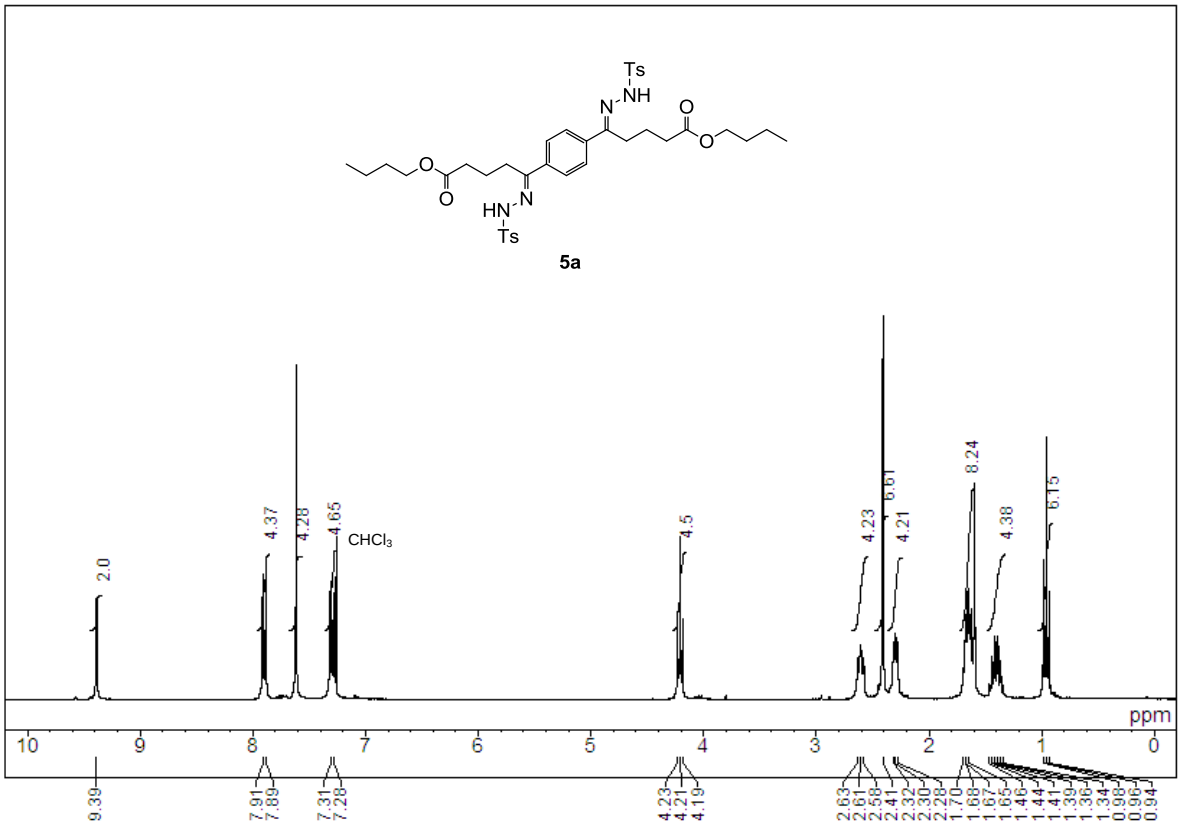
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4a**



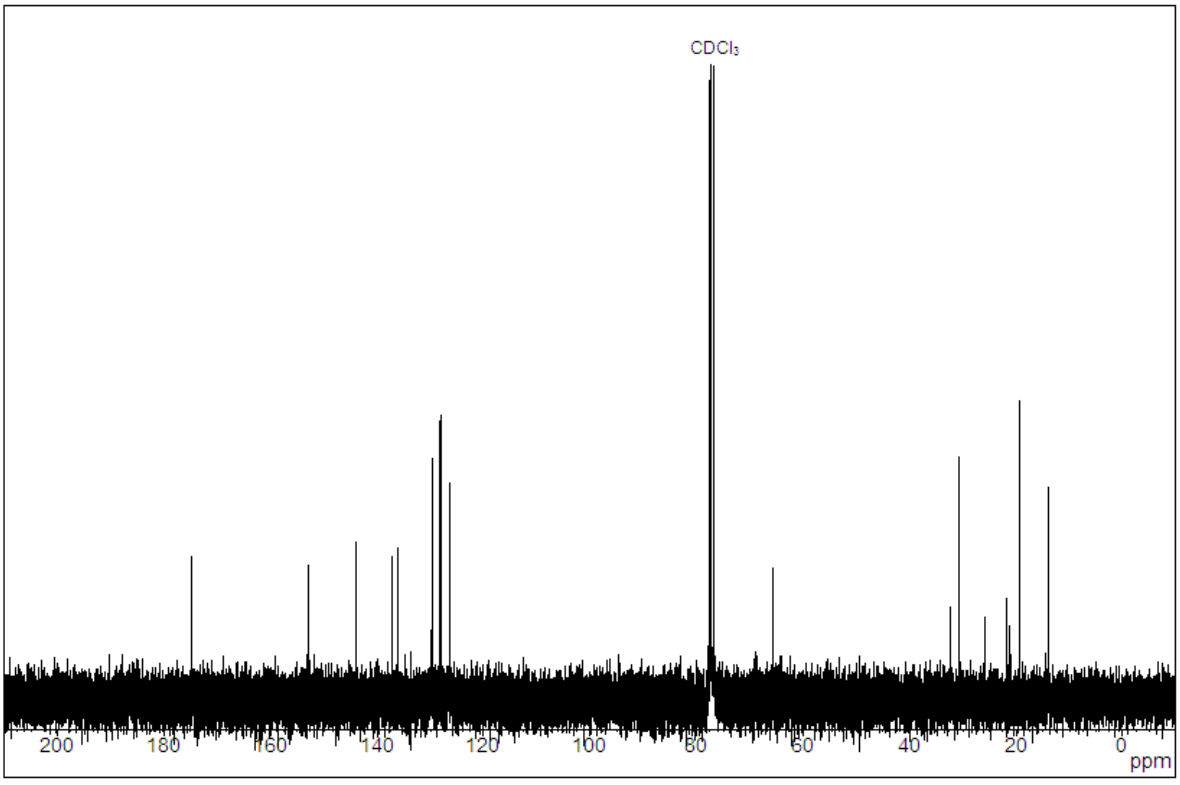
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **4a**



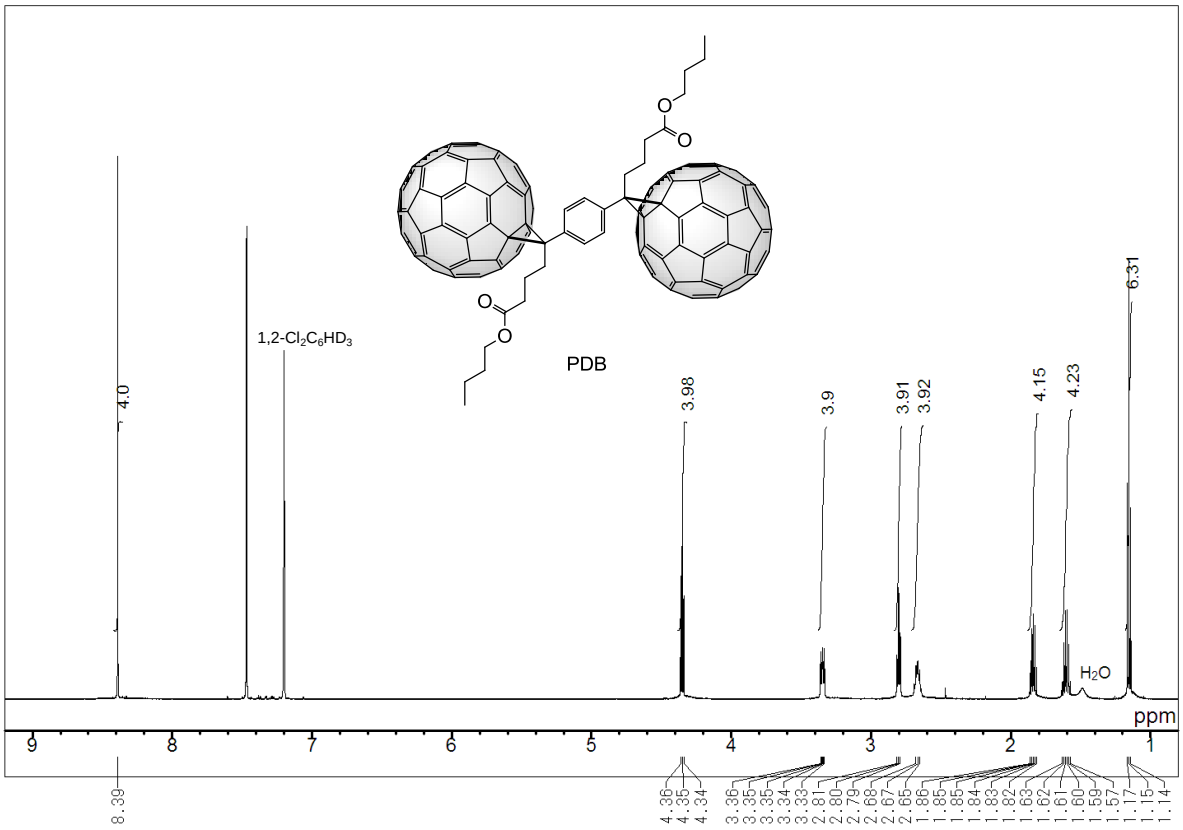
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **5a**



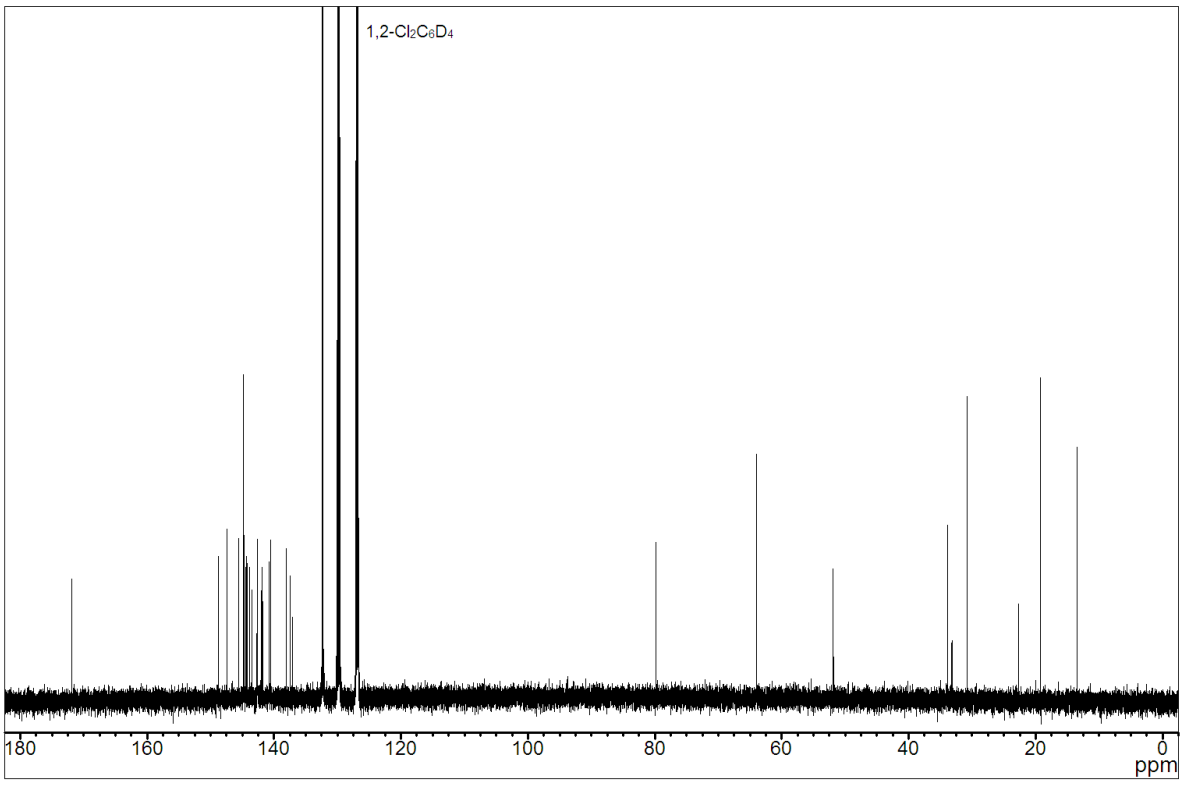
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **5a**



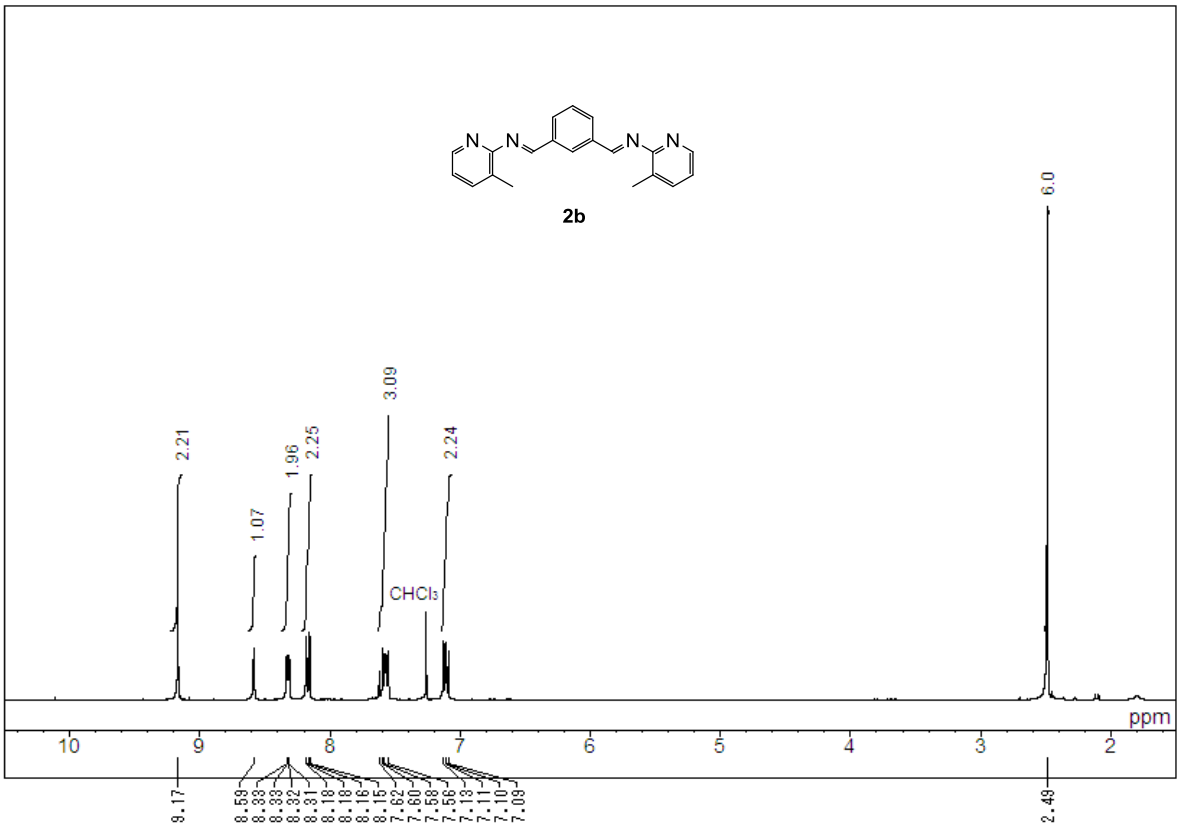
^{1}H NMR spectrum (600 MHz, 80 ºC, ODCB-d_4) of PDB



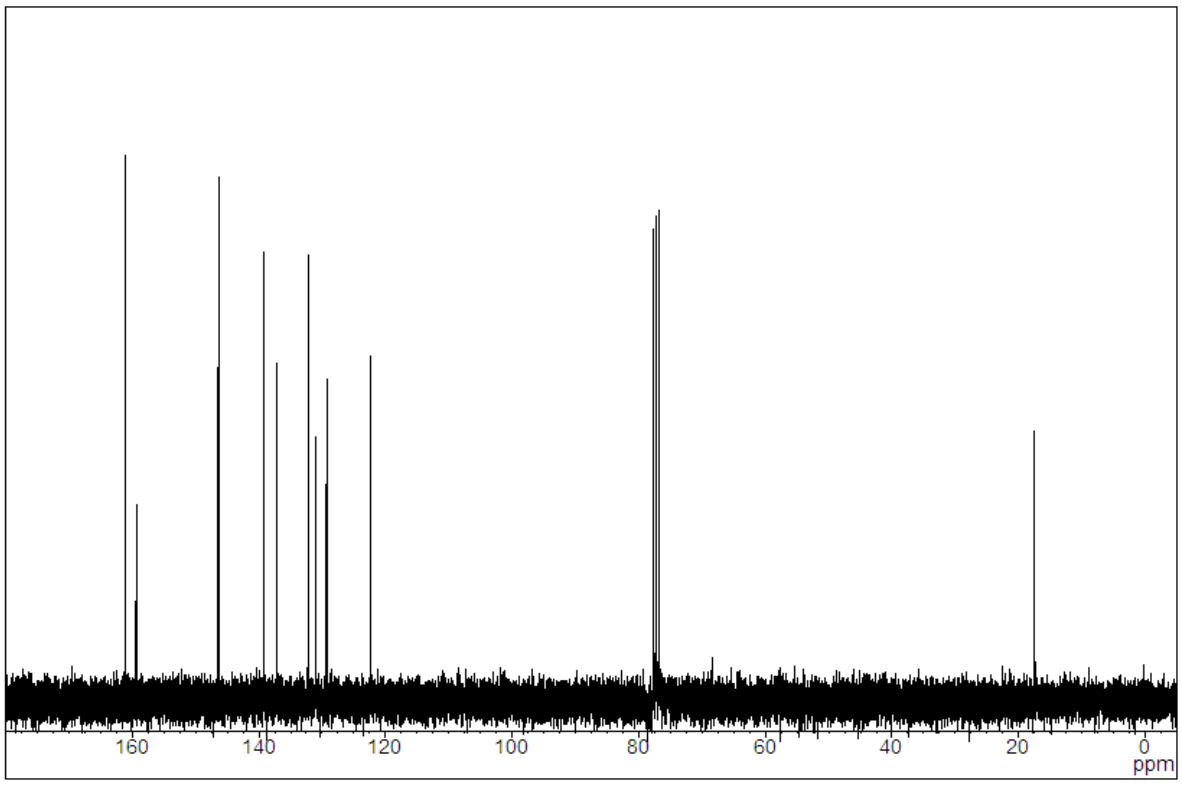
^{13}C NMR spectrum (150 MHz, 80 ºC, ODCB-d_4) of PDB



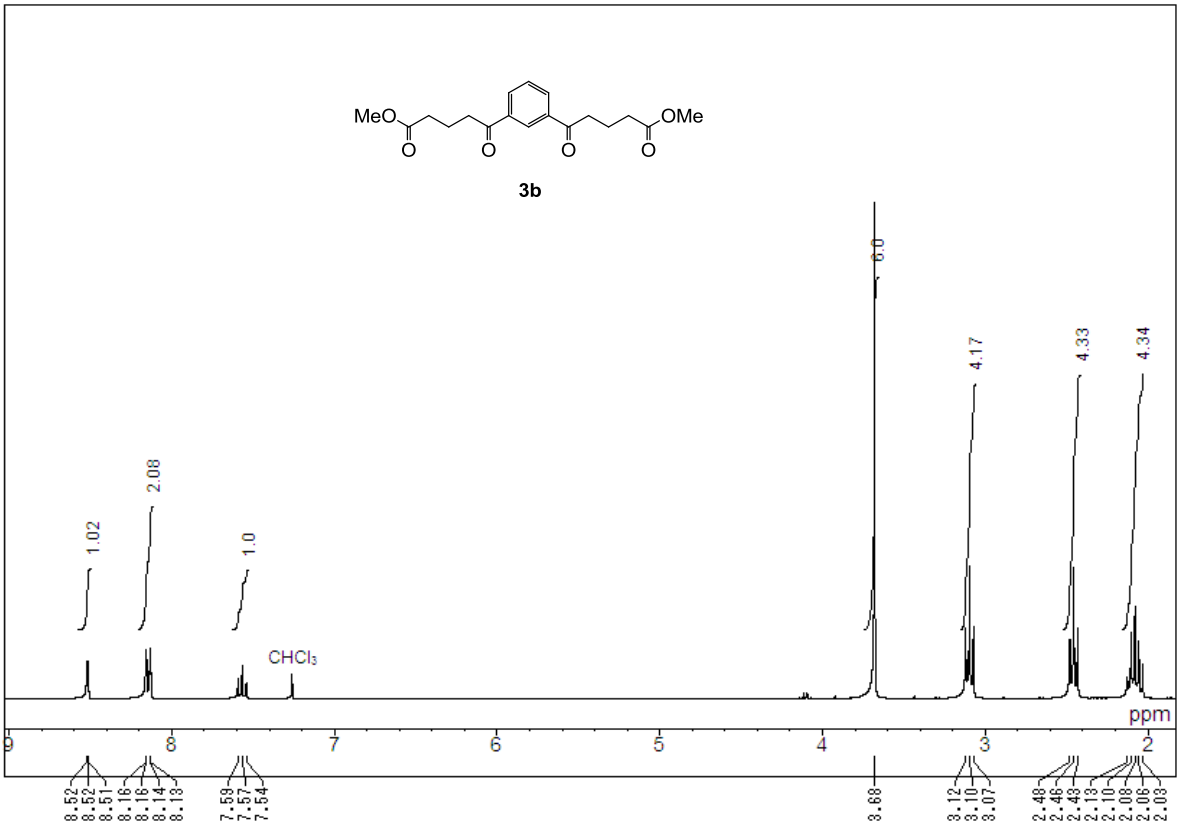
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2b**



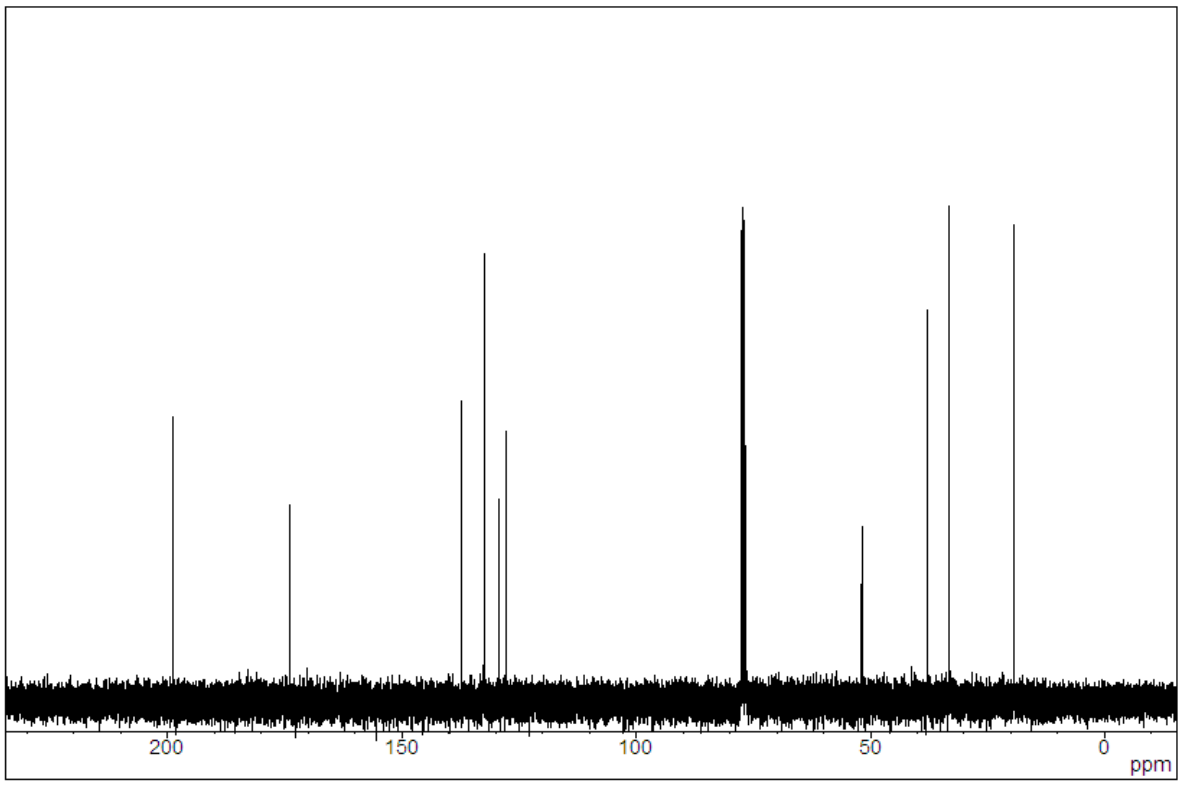
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **2b**



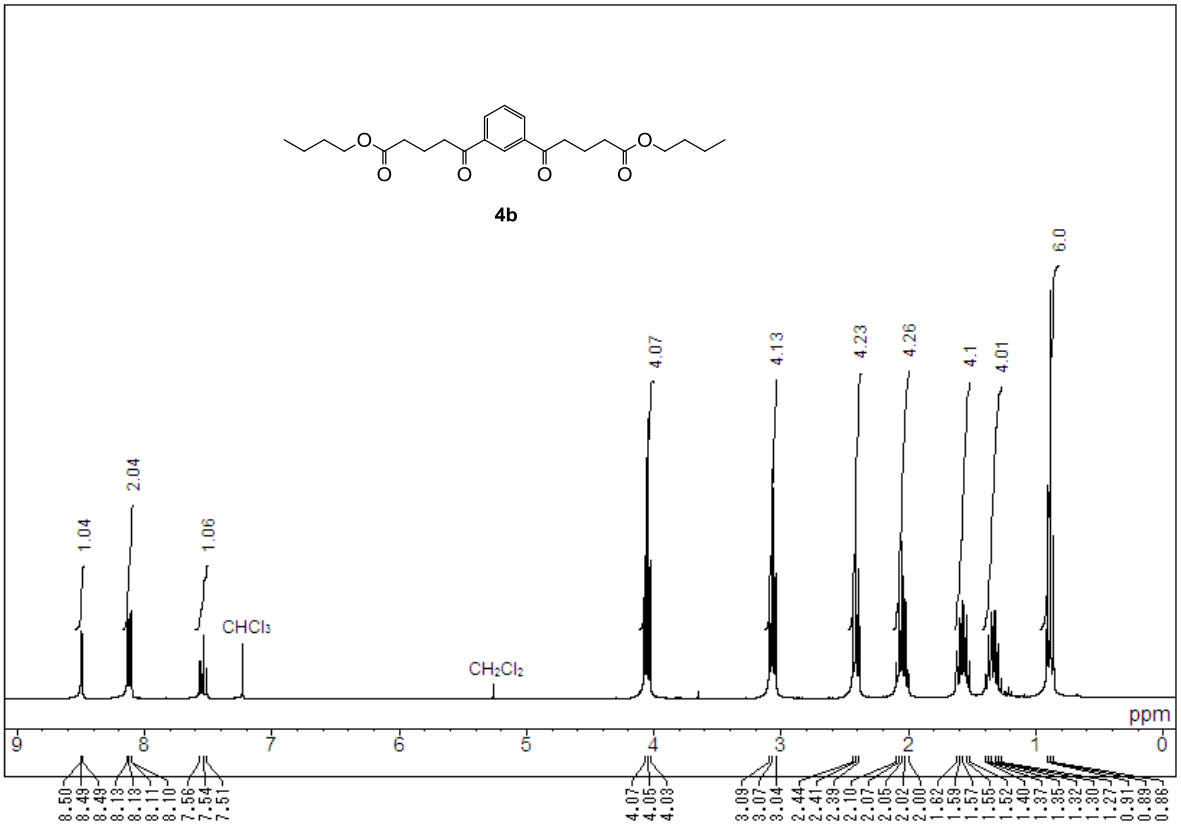
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3b**



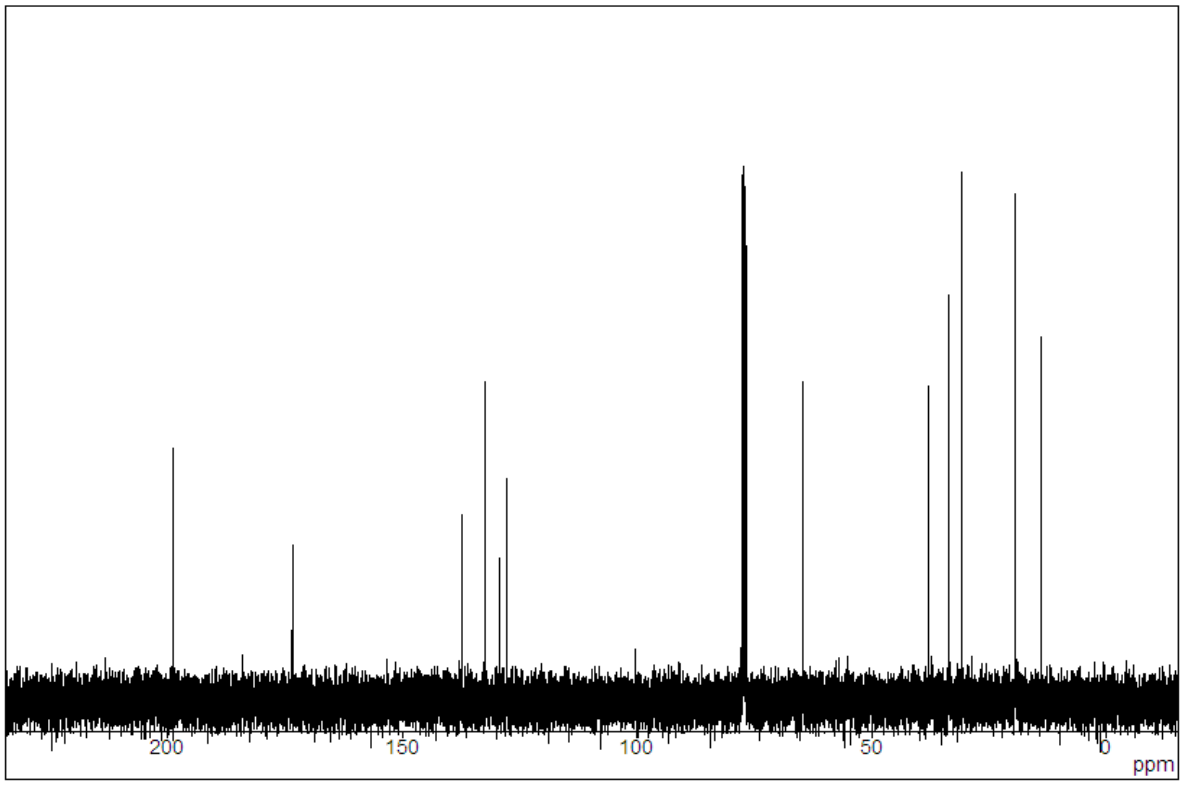
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **3b**



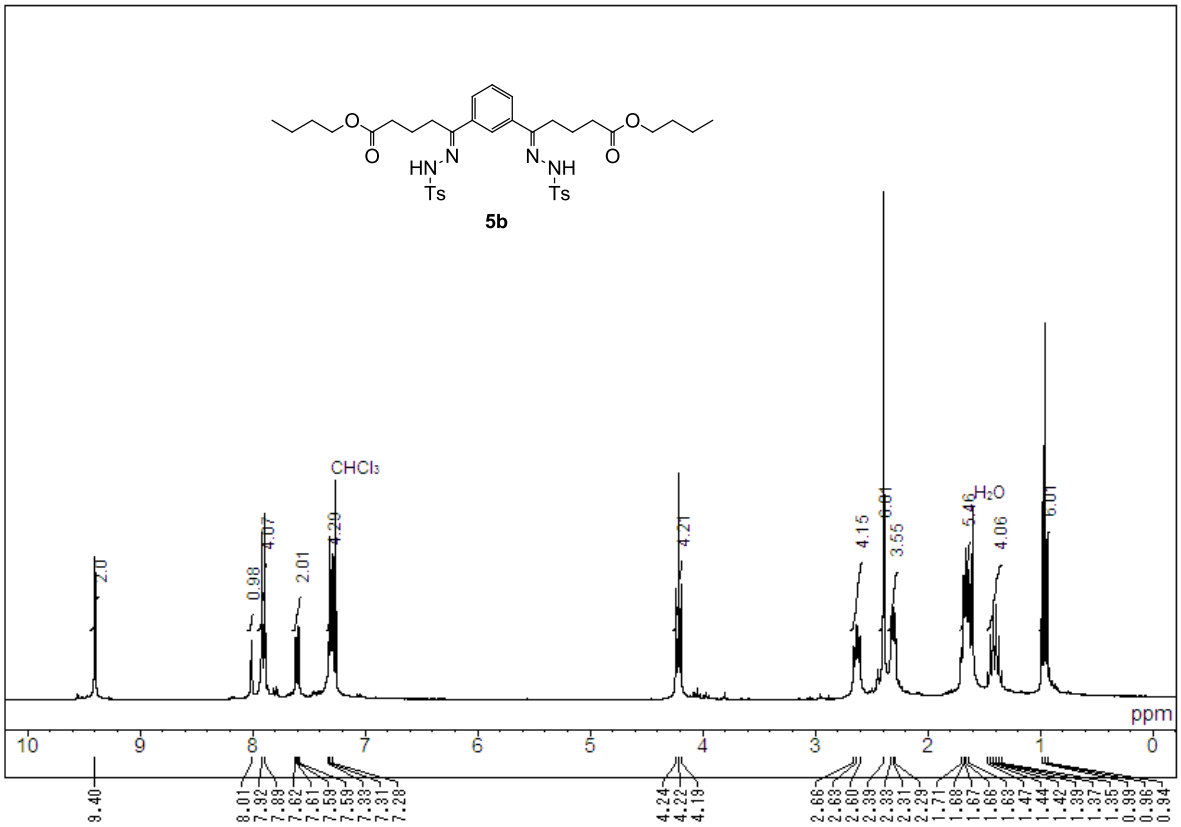
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4b**



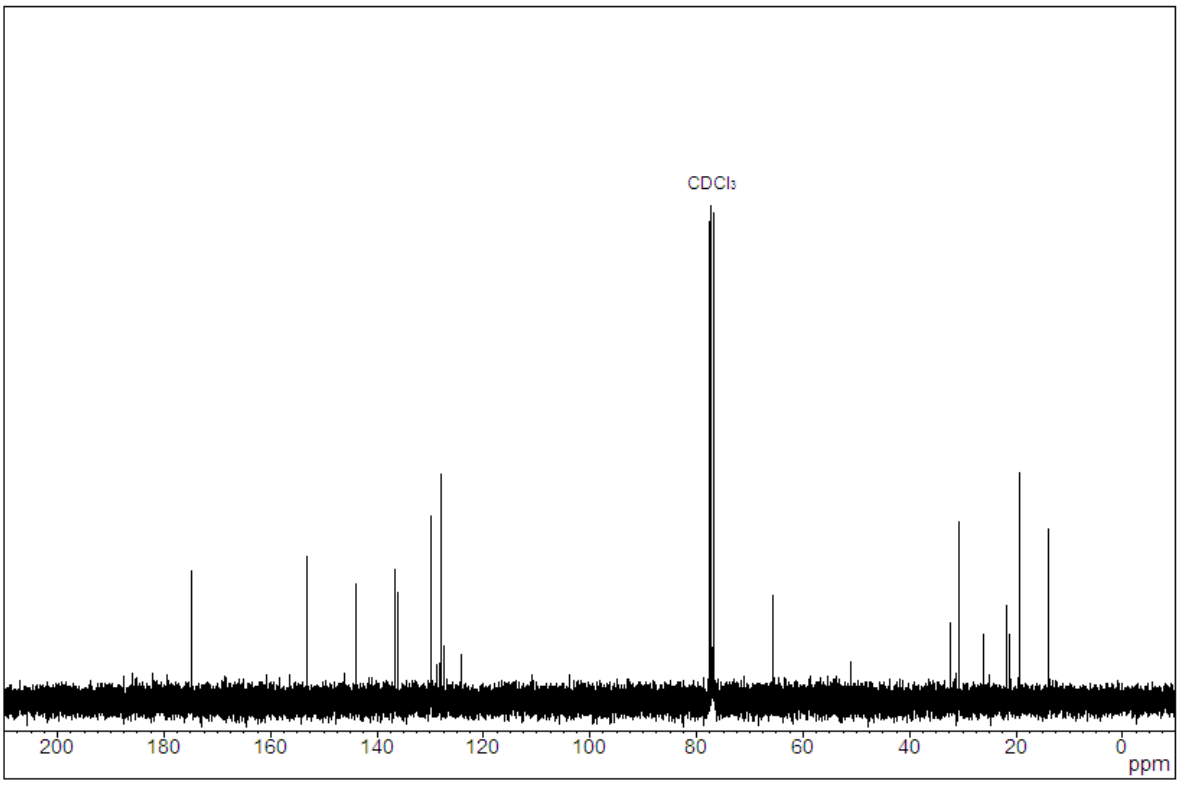
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **4b**



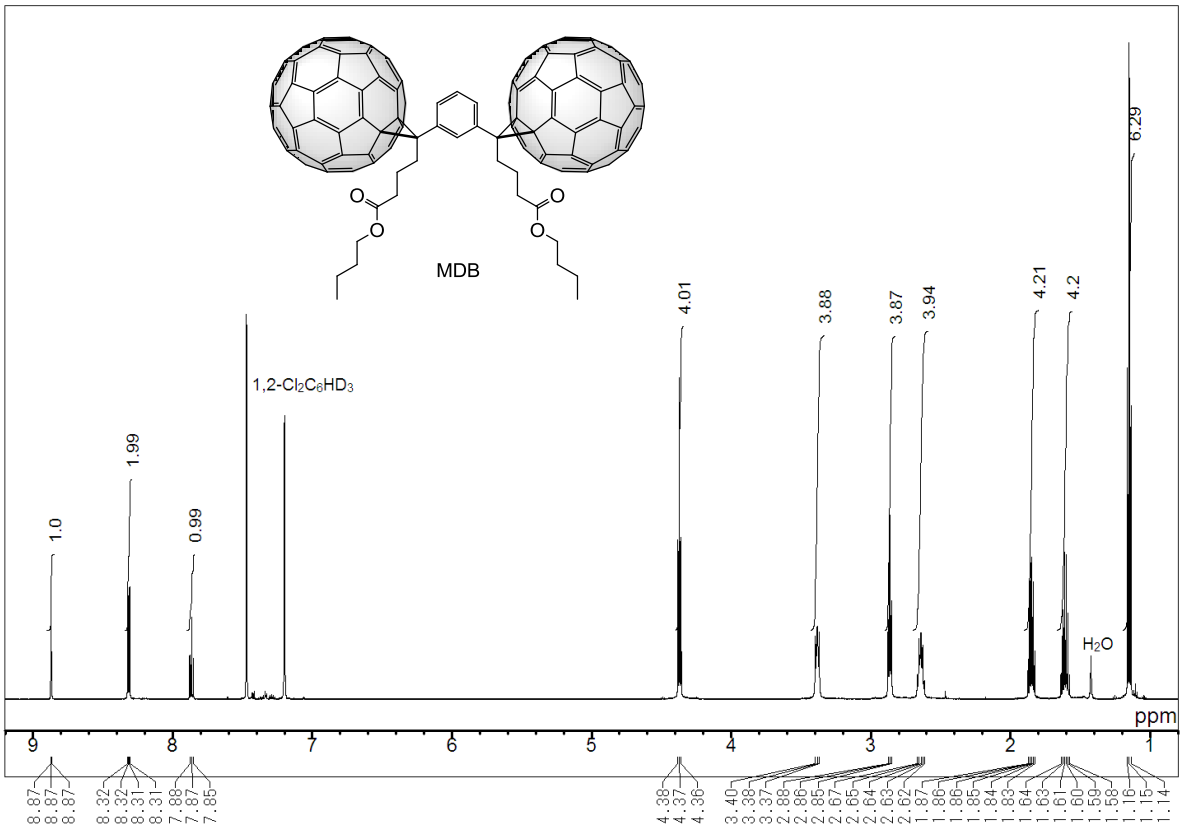
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **5b**



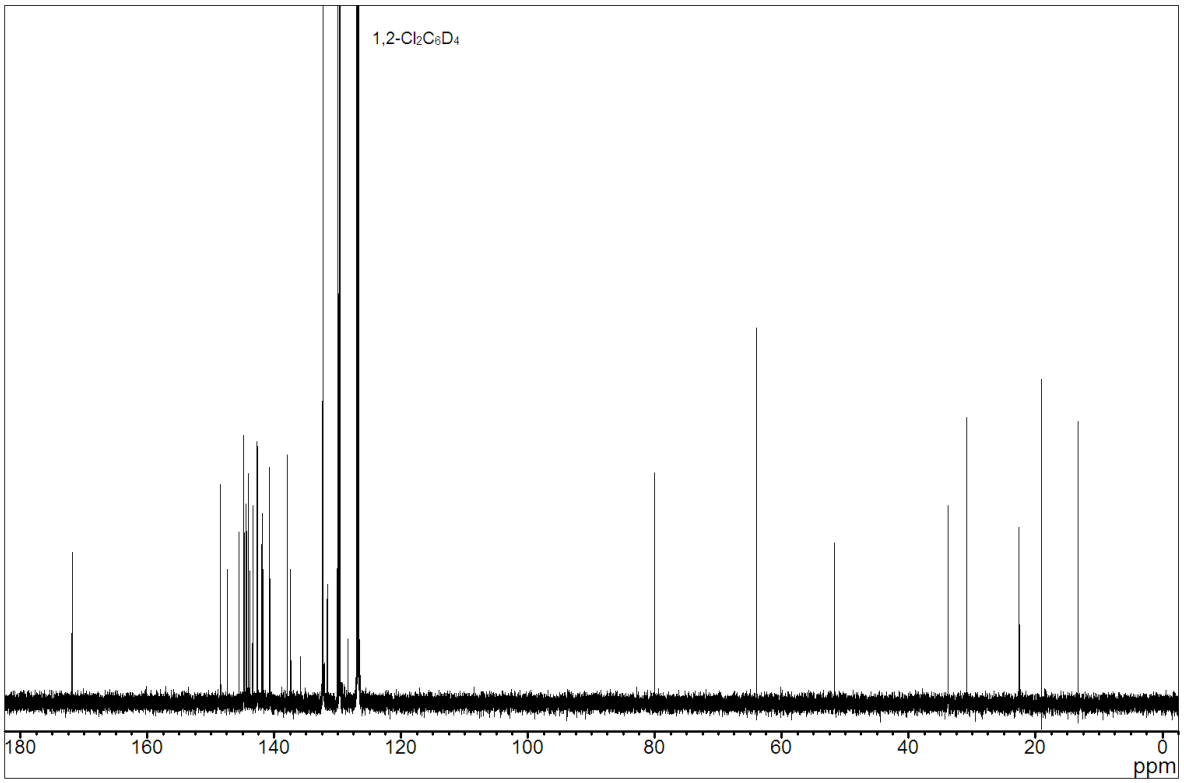
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **5b**



^{1}H NMR spectrum (600 MHz, 100 ºC, ODCB-d_4) of MDB



^{13}C NMR spectrum (150 MHz, 100 ºC, ODCB-d_4) of MDB



5. UV-vis absorption spectra of PDB and MDB

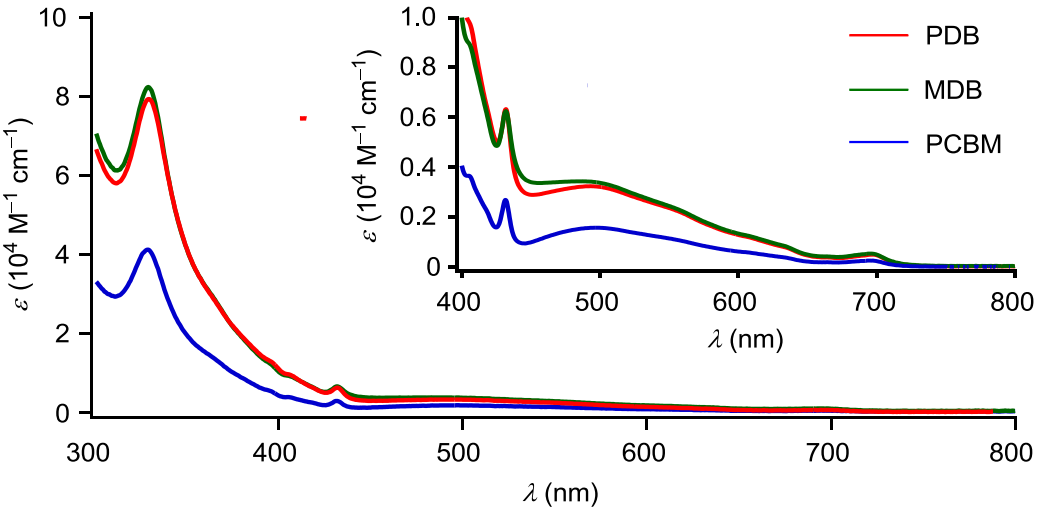


Fig. S1 UV-vis absorption spectra of PDB, MDB, and PCBM in cyclohexane.

6. Cyclic voltammetry

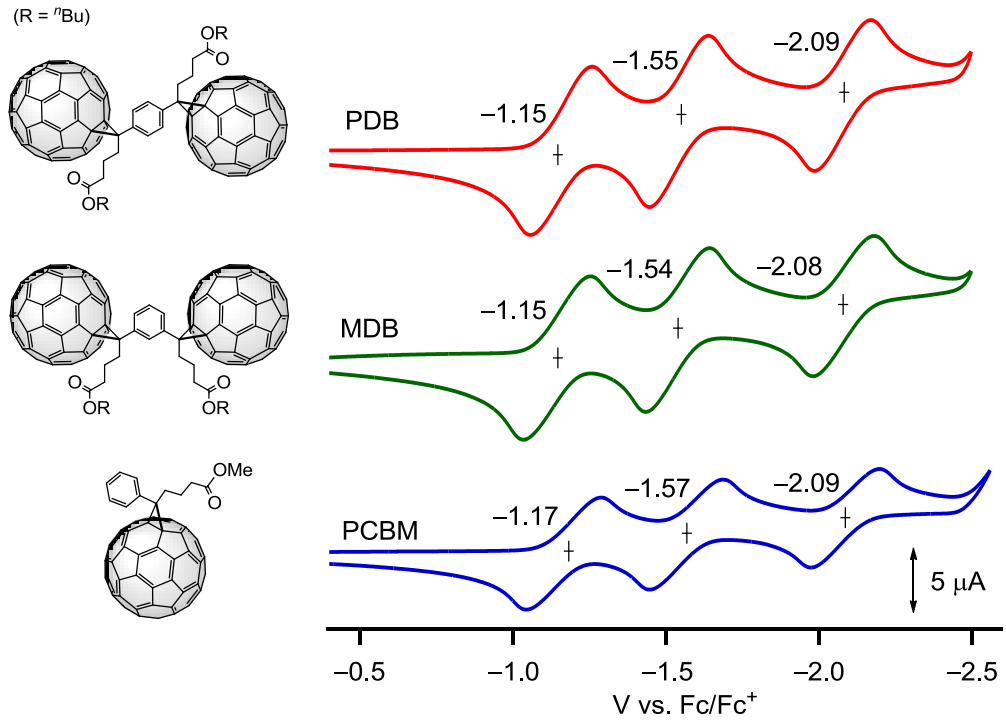


Fig. S2 Cyclic voltammograms: 1 mM samples in ODCB with 0.1 M Bu_4NBF_4, scan rate of 20 mV s^{-1}, Pt wire as a counter electrode and glassy carbon as a working electrode.

7. Procedure for fabrication of the BHJ solar cells

The ITO-coated glass substrate (GEOMATEC, 5 Ω/sq, 2.5 cm × 2.5 cm) was washed carefully under ultrasonic irradiation using acetone (15 min), and ethanol (15 min). The substrate was further cleaned with a Filgen UV230 UV/ozone cleaner. A thin layer of PEDOT:PSS (Nagase ChemteX, Denatron PT-100) was prepared onto the ITO surface by the spin-coating method at 5000 rpm for 1 min. The resulting substrate was heated at 200 ºC for 10 min under ambient conditions.

7-1. P3HT-based solar cells

A solution for the active layer was prepared by dissolving P3HT and fullerene derivative at a 1.6 : 1 weight ratio in chlorobenzene (24 mg mL^{-1}) followed by heating at 100 ºC for 2 h under ambient conditions. The resulting solution was spin-coated onto the PEDOT:PSS layer at 1000 rpm for 40 s. Then, the substrate was annealed at 150 ºC for 6 min in an argon-filled glove box. After cooling to room temperature the substrate was transferred into another glove box where the humidity was controlled around 15% by flowing nitrogen gas. Then, a thin layer (ca. 5 nm) of TiO_x was prepared on the active layer by spin-coating a dehydrated ethanol solution of titanium tetraisopropoxide at 4000 rpm for ca. 20 s followed by being hydrolyzed for 20 min under ambient conditions. Finally, aluminum (Nilaco) was thermally deposited under vacuum (1.1×10^{-4} Torr).

7-2. PTB7-based solar cells

The solution for the active layer was prepared by dissolving PTB7 and fullerene derivative at a 1 : 1 weight ratio in *o*-dichlorobenzene solution (24 mg mL^{-1}) followed by heating at 165 ºC for 3 h in an argon-filled glove box. The resulting solution was spin-coated onto the PEDOT:PSS layer at 800 rpm for 1 min. Then, the substrate was transferred into another glove box where the humidity was controlled around 15% by flowing nitrogen gas. Then, a thin layer (ca. 5 nm) of TiO_x was prepared on the active layer by spin-coating a dehydrated ethanol solution of titanium tetraisopropoxide at 4000 rpm for ca. 20 s followed by being hydrolyzed for 20 min under ambient conditions. Finally, aluminum (Nilaco) was thermally deposited under vacuum (6.8×10^{-5} Torr).

8. UV-vis absorption spectra of blend films

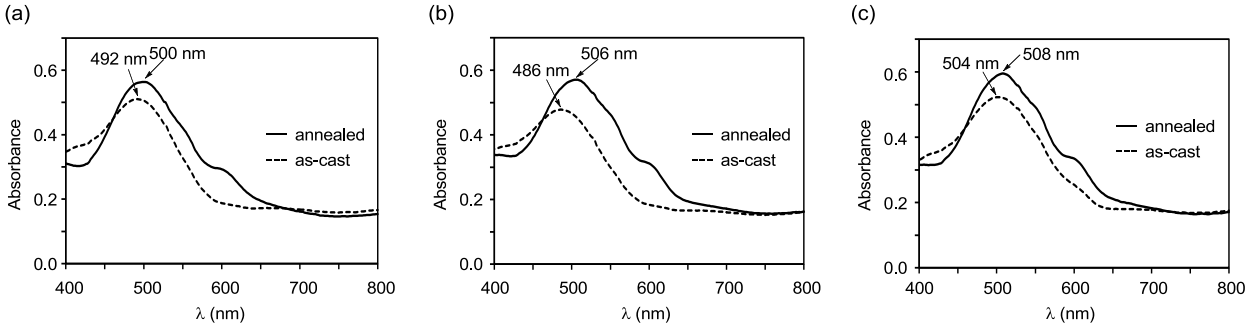


Fig. S3 UV-vis absorption spectra of (a) P3HT:PDB, (b) P3HT:MDB, and (c) P3HT:PCBM blend films (1.6 : 1 weight ratio) cast from chlorobenzene solution on a quartz glass.

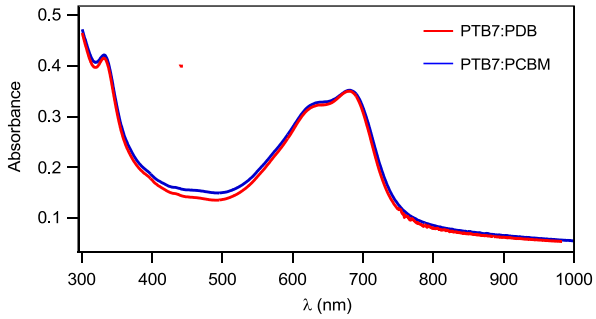


Fig. S4 UV-vis absorption spectra of PTB7-based blend films (1 : 1 weight ratio) cast from *o*-dichlorobenzene solution on a quartz glass.

9. AFM images (plane view) of blend films

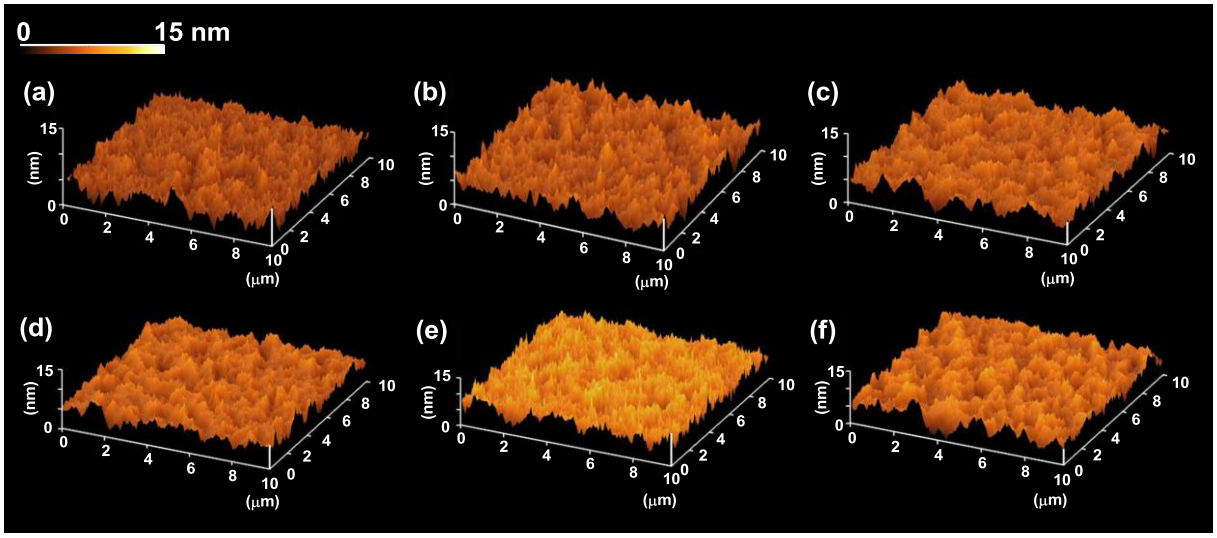


Fig. S5 AFM height images of blend films showing a 10 μm × 10 μm surface area (tapping mode). The compositions of blend films are (a) P3HT:PDB, (b) P3HT:MDB, (c) P3HT:PCBM, (d) PTB7:PDB, (e) PTB7:MDB, and (f) PTB7:PCBM. P3HT-based blend films were annealed at 150 ºC for 6 min.

10. References

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2 a) Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, *Adv*. *Mater*. 2010, **22**, E135; b) Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray, L. Yu, *J*. *Am*. *Chem*. *Soc*., 2009, **131**, 7792.

3 M. C. Willis, S. Sapmaz, *Chem*. *Commun*. 2001, 2558-2559.