Electronic supplementary information

Complexation of 2,7-diazapyrene with boron for structural and electronic tuning

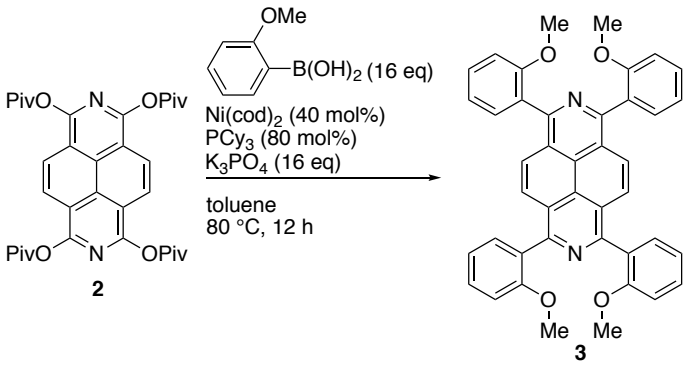
Takumi Nakazato, Hiroshi Shinokubo, and Yoshihiro Miyake*

Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Nagoya, 464-8603, Japan.

Instrumentation and Materials

^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{11}B NMR (160 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CDCl_3$ (δ = 7.260 ppm) and DMSO-d_6 (δ = 2.500 ppm) for ^{1}H NMR, $CDCl_3$ (δ = 77.16 ppm) and DMSO-d_6 (δ = 39.52 ppm) for ^{13}C NMR and BF_3•OEt_2 (δ = 0.00 ppm) for ^{11}B NMR respectively. UV/vis absorption spectra were recorded on a JASCO V670 spectrometer. Emission spectra were recorded using a JASCO FP-6500 spectrometer, and absolute fluorescence quantum yields were measured by the photon-counting method using an integration sphere. Mass spectra were recorded on a Bruker microTOF using positive mode for acetonitrile solutions with APCI-TOF methods for **3** and **4**, ESI-TOF method for **anti-1** and **syn-1** respectively. Melting points were measured by a SRS MPA100 OptiMelt Automated Melting Point System. Redox potentials were measured by cyclic voltammetry method on an ALS electrochemical analyzer model 612C. The DSC measurement was recorded using NETZSCH DSC3500 Sirius at a heating rate of 10 K min^{-1}. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. All of reactions were conducted under argon atmosphere. 2,7-Diazapyrene **2** was prepared according to the reported procedure.[S1]

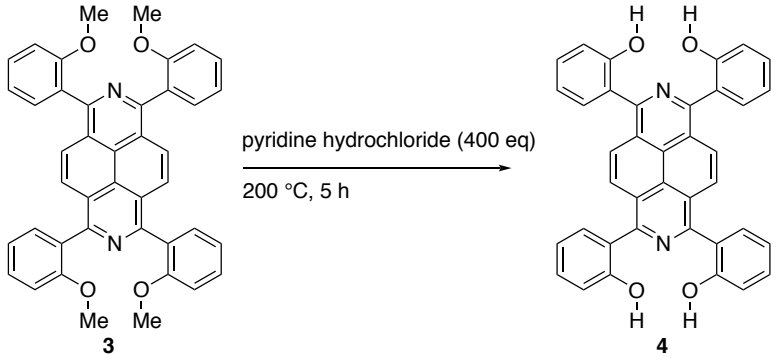
Preparation of 1,3,6,8-tetrakis(2-methoxyphenyl)-2,7-diazapyrene (3)



In a 50 mL J-Young tube was placed K_3PO_4 (340 mg, 1.6 mmol) and then heated under the reduced pressure (120 °C, 1.0 Torr) for 1 h. After drying, **2** (60.4 mg, 0.10 mmol) and 2-methoxyphenylboronic acid (284.5 mg, 1.6 mmol) were added to the tube. In the glove box, $Ni(cod)_2$ (11.1 mg, 0.040 mmol), tricyclohexylphosphine (22.3 mg, 0.080 mmol), and toluene (3 mL) were added to the tube. The reaction mixture was stirred for 12 h at 80 °C. The resulting solution was filtrated thorough celite. After the filtrate was concentrated in *vacuo*, the residue was purified by column chromatography (amino-SiO_2) with CH_2Cl_2/hexane (1/1) to give **3** (18.8 mg, 0.030 mmol, 30% yield).

3: A pale yellow solid, m.p. 225.8 °C (decomp.). ^{1}H NMR ($CDCl_3$ at 50 °C): δ 7.83 (s, 4H), 7.61 (br, 4H), 7.46 (dt, J = 1.8 and 8.0 Hz, 4H), 7.15 (t, J = 7.4 Hz, 4H), 7.08 (d, J = 8.1 Hz, 4H), 3.71 (s, 12H). ^{13}C NMR ($CDCl_3$): δ157.8, 151.7, 132.6, 130.0, 129.7, 127.9, 126.4, 124.3, 121.2, 111.7, 55.9. HRMS(APCI) Calcd. For $C_{42}H_{33}N_2O_4$ [M+H]: 629.2435. Found: 629.2439.

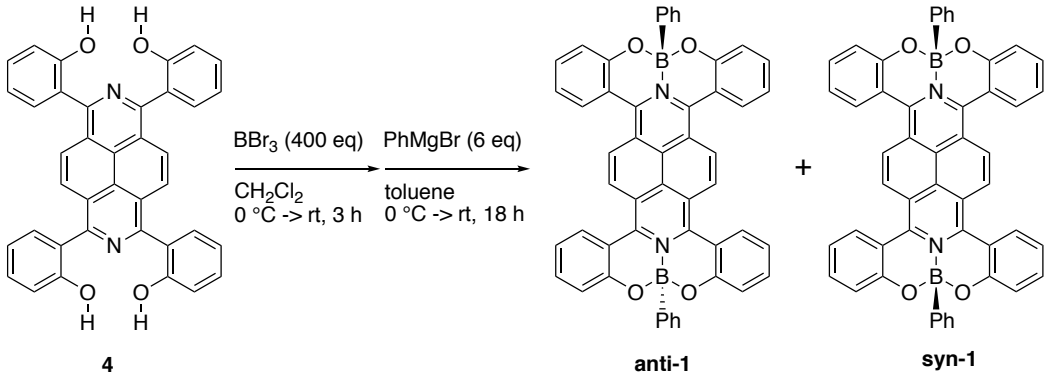
Demethylation of 3 to 4.



In a test tube were placed **3** (62.9 mg, 0.10 mmol) and pyridine hydrochloride (1.85 g, 16 mmol). The mixture was stirred for 5 h at 200 °C. Aqueous solution of $NaHCO_3$ (50 mL) was added to the reaction mixture, and the resulting solution was extracted with EtOAc (50 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by column chromatography (SiO_2) with CH_2Cl_2/EtOAc (10/1) to give **4** (48.1 mg, 0.084 mmol, 84% yield)

4: A pale yellow solid, m.p. 250.8 °C (decomp.). ^{1}H NMR (DMSO-d_6 containing 0.05% of TMS): δ 9.99 (s, 4H), 8.04 (s, 4H), 7.56 (dd, J = 1.7 and 7.6 Hz, 4H), 7.40 (dt, J = 1.7 and 7.8 Hz, 4H), 7.09 (dd, J = 0.9 and 8.2 Hz, 4H), 7.05 (dt, J = 1.0 and 7.5 Hz, 4H). ^{13}C NMR (DMSO-d_6 containing 0.05% of TMS): δ155.3, 151.0, 132.0, 130.1, 127.5, 126.2, 125.7, 122.8, 119.2, 116.2. HRMS(APCI) Calcd. For $C_{38}H_{24}N_2O_4$ [M]: 572.1731. Found: 572.1737.

Complexation of 4 with BBr_3 and Grignard reagent (method A).

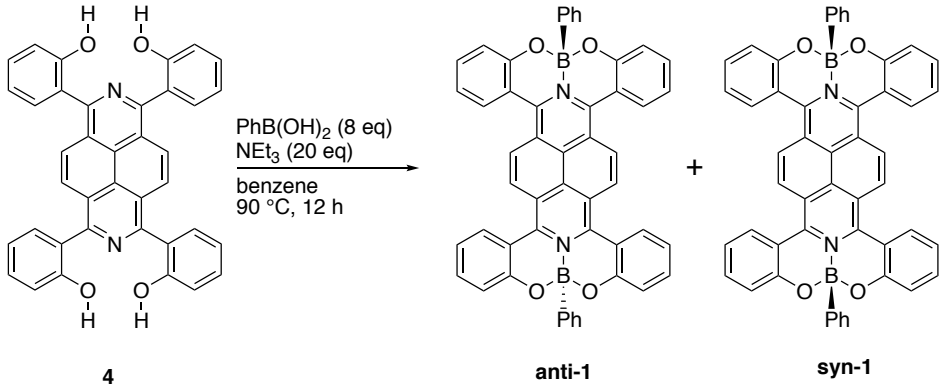


A 20 mL Schlenk tube containing **4** (28.6 mg, 0.050 mmol) was evacuated and then refilled with N_2. To the tube, BBr_3 (10.8 mmol, 12 mL, 17% CH_2Cl_2 solution) was added at 0 °C. The mixture was stirred at r.t. for 5 h. The volatiles were removed in *vacuo* and the tube was refilled with N_2. To the tube, dry and degassed toluene (2 mL) was added. To the solution, phenylmagnesium bromide (0.30 mmol, 0.33 mL, 0.89 M THF solution) was added at 0 °C. After stirring at room temperature for 18 h, 20 mL of 1 M aq. HCl was added to the solution. The aqueous layer was separated and extracted with dichloromethane (20 mL × 3). The combined organic layer was concentrated in *vacuo*. The residue was purified by column chromatography (SiO2) with CH_2Cl_2 to give **anti-1** (21.6 mg, 0.029 mmol, 58% yield) and **syn-1** (2.60 mg, 0.0035 mmol, 7% yield)

anti-1: A pale yellow solid. ^{1}H NMR ($CDCl_3$): δ 9.03 (s, 4H), 7.99 (dd, J = 1.4 and 7.9 Hz, 4H), 7.44 (td, J = 1.5 and 7.8 Hz, 4H), 7.23 (dd, J = 1.1 and 8.2 Hz, 4H), 7.15 (dd, J = 1.6 and 7.5 Hz, 4H), 7.05 (td, J = 1.1 and 8.1 Hz, 4H), 6.97-6.93 (m, 6H). The ^{13}C NMR spectrum of **anti-1** was not measured because **anti-1** was not soluble enough to show detectable signals.^{11}B NMR ($CDCl_3$): δ6.65. HRMS(ESI) Calcd. For $C_{50}H_{31}N_2O_4B_2$ [M+H]: 745.2480. Found: 745.2479.

syn-1: A pale yellow solid. ^{1}H NMR ($CDCl_3$): δ 8.30 (s, 4H), 7.60 (d, J = 7.3 Hz, 4H), 7.24 (td, J = 1.4 Hz, 7.8 Hz, 4H), 7.00 (td, J = 1.1 Hz, 7.6 Hz, 4H), , 6.88-6.80 (m, 14H). ^{13}C NMR ($CDCl_3$): δ156.6, 144.5, 135.0, 132.3, 131.6, 130.2, 129.3, 129.0, 127.3, 126.9, 122.6, 121.3, 120.9, 120.1. ^{11}B NMR ($CDCl_3$): δ6.07. HRMS(ESI) Calcd. For $C_{50}H_{31}N_2O_4B_2$ [M+H]: 745.2480. Found: 745.2466.

Complexation of 4 with phenylboronic acid (method B).



In a 20 mL Schlenk tube, **4** (28.2 mg, 0.050 mmol) and phenylboronic acid (48.7 mg, 0.40 mmol) were dissolved in benzene (2 mL). Triethylamine (0.18 mL, 2.0 mmol) was added and the reaction mixture was stirred at 90 °C for 12 h. The resulting solution was evaporated to remove solvents. The residue was purified by column chromatography (SiO_2) with CH_2Cl_2 to give **anti-1** (3.75 mg, 0.0050 mmol, 10% yield) and **syn-1** (23.1 mg, 0.031 mmol, 68% yield).

X-Ray Diffraction Analysis

Crystals suitable for X-ray analysis of **anti-1** and **syn-1** were obtained by recrystallization from chlorform and toluene/octane, respectively. X-ray diffraction data for **anti-1** and **syn-1** were taken on a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics using graphite monochromated Mo-Kα radiation (λ = 0.71075 Å). All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. Crystallographic data for the structures of **anti-1** and **syn-1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 2045674 (**anti-1**) and CCDC 2045675 (**syn-1**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystallographic Data for **anti-1** and **syn-1.**

Compound	**anti-1**	**syn-1**
Formula	$C_{50}H_{30}B_2N_2O_4$	$C_{50}H_{30}B_2N_2O_4$
Formula weight (M_w)	744.42	744.42
Crystal system	triclinic	orthorhombic
Space group	*P*–1	$P2_12_12$
Crystal color	Orange	Pale yellow
Crystal description	Prism	Prism
a [Å]	9.5439 (2)	17.5029 (4)
b [Å]	10.6657 (2)	11.0272 (3)
c [Å]	14.8023 (3)	6.7696 (2)
α [°]	86.851 (2)	90
β [°]	73.687 (2)	90
γ [°]	74.975 (2)	90
V [Å^3]	1396.40 (5)	1306.59 (12)
Z	2	4
d_{calcd} [g cm^{-3}]	1.595	1.323
*R*1 ($I > 2\sigma(I)$)	0.0634	0.0943
*R*w (all data)	0.1579	0.3216
GOF	1.097	1.088
Temperature [K]	93	93
Structure solution	SHELXT-2014/7 (Sheldrick, 2014)	SHELXT-2014/7 (Sheldrick, 2014)
Structure refinement	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2

Variable-Concentration and Variable-Temperature ^{1}H NMR measutrements

^{1}H NMR (500 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CDCl_3$ (δ = 7.260 ppm).

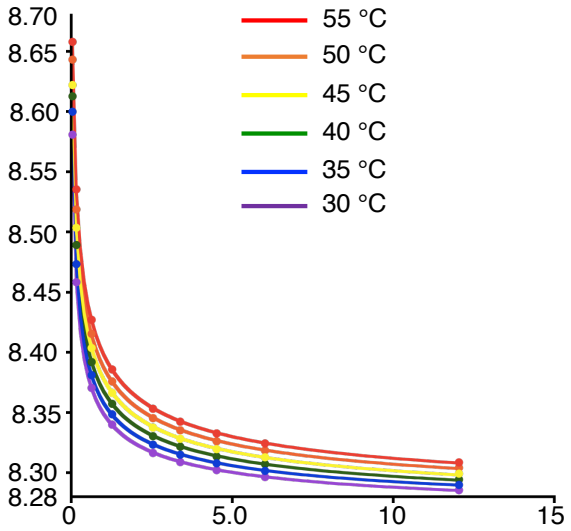


Fig. S1. Curve fitting of **syn-1** in $CDCl_3$ at different temperatures.

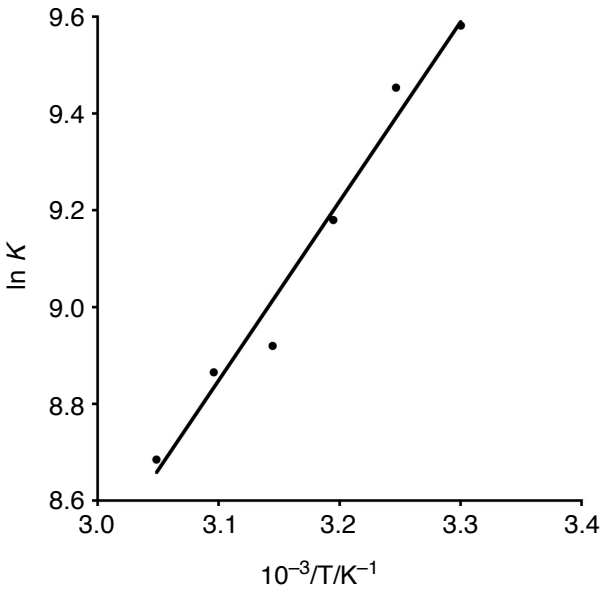


Fig. S2. van't Hoff plots of **syn-1** in $CDCl_3$.

Table S2. Summary of chemical shifts of H_a of **syn-1** in $CDCl_3$, calculated association constants (K_2), and calculated chemical shifts of H_a proton for oligomer (δ_o) and monomer (δ_m).

Conc. (mM)	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C
12	8.2857	8.2900	8.2944	8.2993	8.3042	8.3087
6.0	8.2965	8.3017	8.3073	8.3129	8.3185	8.3245
4.5	8.3022	8.3079	8.3135	8.3197	8.3262	8.3328
3.4	8.3090	8.3151	8.3218	8.3282	8.3353	8.3425
2.5	8.3165	8.3234	8.3304	8.3376	8.3454	8.3532
1.3	8.3400	8.3486	8.3573	8.3664	8.3759	8.3859
0.6	8.3706	8.3812	8.3920	8.4037	8.4154	8.4271
0.2	8.4583	8.4734	8.4892	8.5036	8.5187	8.5354
δ_d	8.2569 ± 0.0003	8.2590 ± 0.0004	8.2601 ± 0.0003	8.2613 ± 0.0006	8.2644 ± 0.0007	8.2655 ± 0.0004
δ_m	8.8022 ± 0.004	8.8121 ± 0.004	8.7926 ± 0.003	8.7705 ± 0.003	8.7949 ± 0.004	8.7945 ± 0.002
K_2	14497 ± 351	12750 ± 350	9700 ± 169	7311 ± 184	7080 ± 189	5912 ± 94

Absorption and Fluorescence Spectra.

UV/vis absorption and fluorescence spectra were recorded on a JASCO V670 spectrometer and a JASCO FP-6500 spectrometer, respectively. Absolute fluorescence quantum yields were measured by the photon-counting method using an integration sphere. Dilute solutions in distilled solvent in a 1 cm square quartz cuvette were used for the absorption and fluorescence measurements.

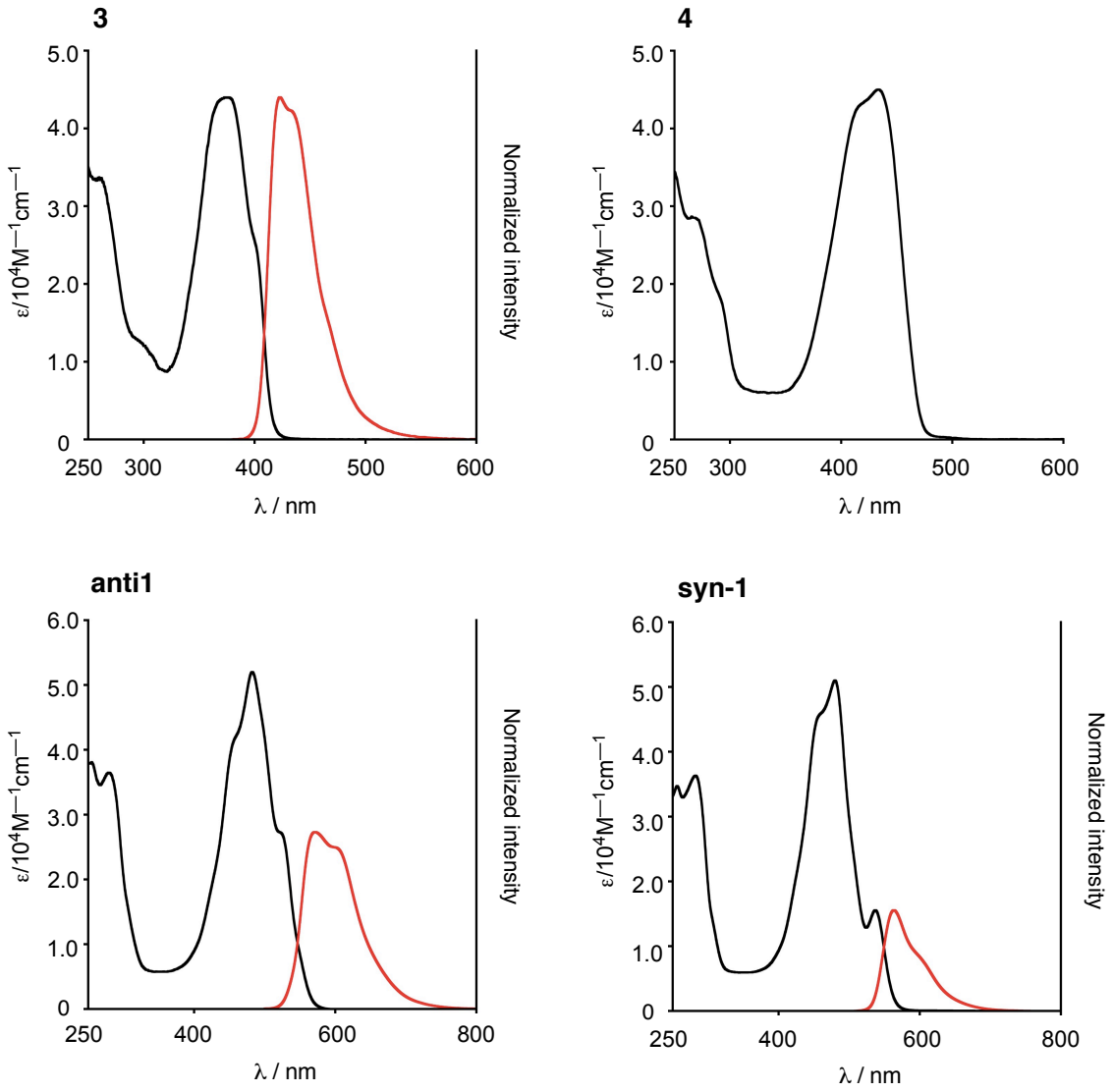


Fig. S3. Absorption spectra in CH_2Cl_2 (black line) and fluorescence spectra in CH_2Cl_2 (red line) of **3**, **4**, **anti-1** and **syn-1**. **4** exhibited no fluorescence in CH_2Cl_2.

Table S3. Excited Wavelength and Fluorescence Quantum Yields of **3**, **4**, **anti-1** and **syn-1** in CH_2Cl_2.

Compound	λ_{ex} (nm)	Φ (in CH_2Cl_2)
3	350	0.46
4	400	—[a]
anti-1	450	0.25
syn-1	450	0.41

[a]No emission was observed in CH_2Cl_2.

Electrochemical Measurement

Electrochemical measurements were recorded on ALS electrochemical analyser 612C. Measurements were performed in dehydrated THF with tetrabutylammonium hexafluorophosphate as an electrolyte (0.1 M). A glassy carbon electrode, a platinum wire and $Ag/AgClO_4$ were used as working, counter, and reference electrodes, respectively. The scan rate was 100 mVs^{-1}. The measurements were performed under nitrogen atmosphere. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.

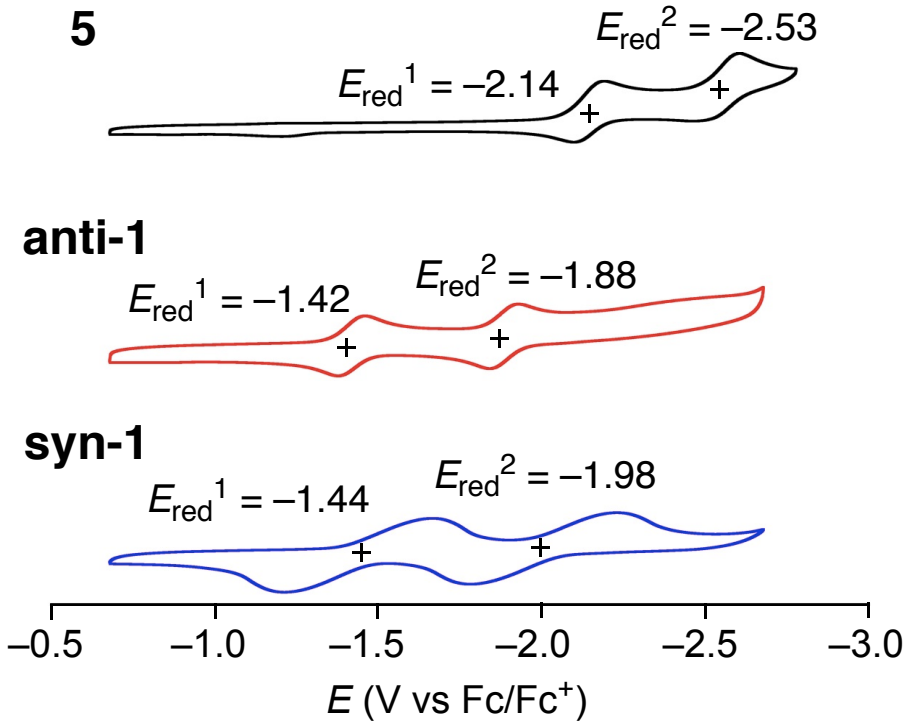


Fig. S4. Cyclic voltammogram of **5**, **anti-1 and syn-1** in THF.

Table S4. Redox potentials of **anti-1** and **syn-1** in THF (V vs Fc/Fc^{+}).

Compound	E_{red}^{1}	E_{red}^{2}
5	–2.14	–2.53
anti-1	–1.42	–1.88
syn-1	–1.44	–1.98

DSC measurement

The DSC measurement was recorded using NETZSCH DSC3500 sirius at a heating rate of 10 K min^{-1}.

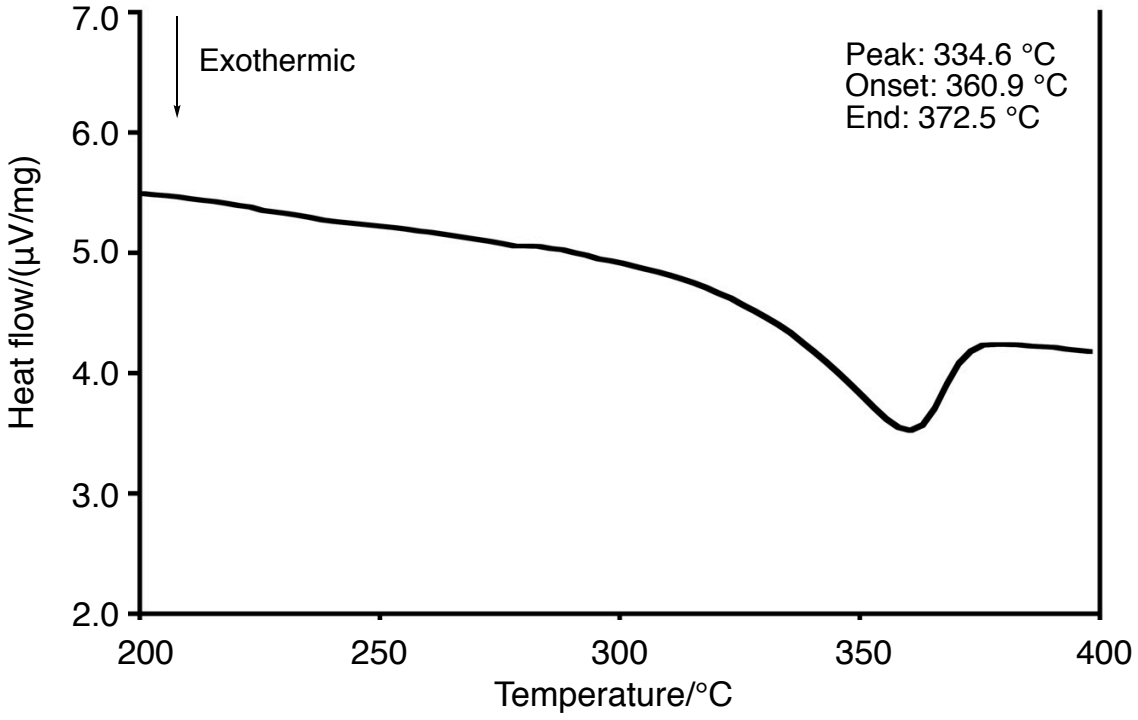


Fig. S5. The DSC curve of **anti-1**.

Theoretical calculations

All calculations were performed using the Gaussian 09 program.[S2] Initial geometries were obtained from the X-ray structure. Full optimization was performed without any symmetric restriction with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP)[S3] and the 6-31G(d) basis set for C, H, N, B and O atoms. The electrostatic potential map of **syn-1** was calculated from X-ray structure without optimization. The vibrational frequencies were calculated at the same level to check whether each optimized structure is an energy minimum (no imaginary frequency) or a transition state (one imaginary frequency) and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298.15 K. The intrinsic reaction coordinates (IRC) were calculated using the global reaction route mapping (GRRM17) program[S4] to track minimum energy paths from transition structures to the corresponding local minima.

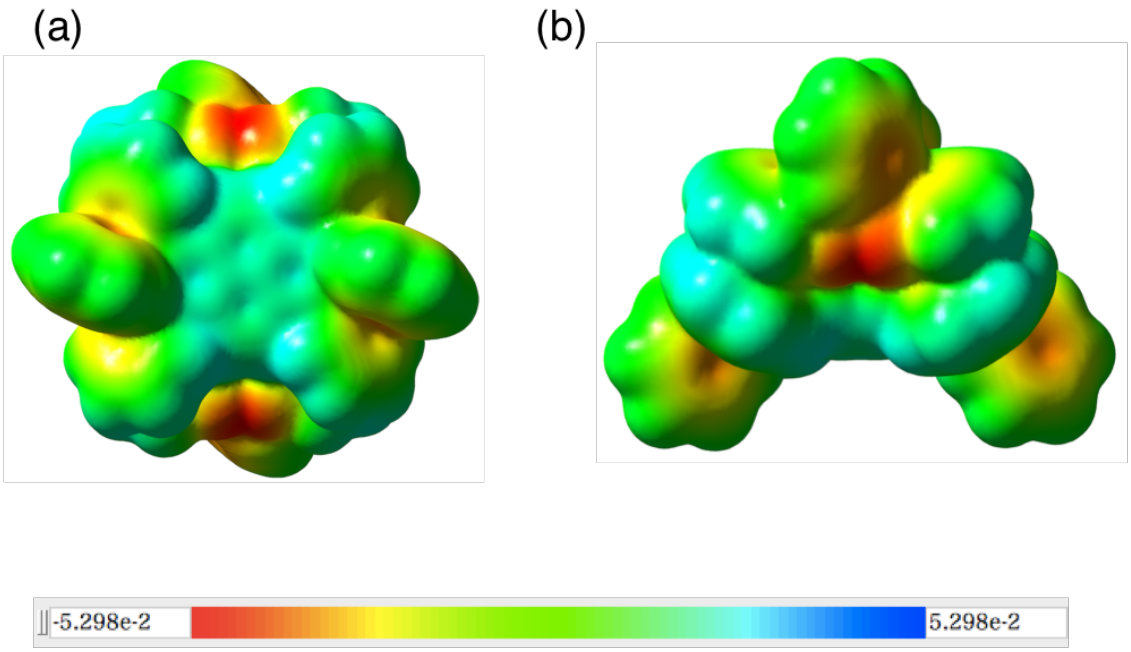


Fig. S6. Electrostatic potential map of **syn-1** dimer. (a) top view and (b) side view of **syn-1** dimer calculated at B3LYP/6-31G(d) level of theory.

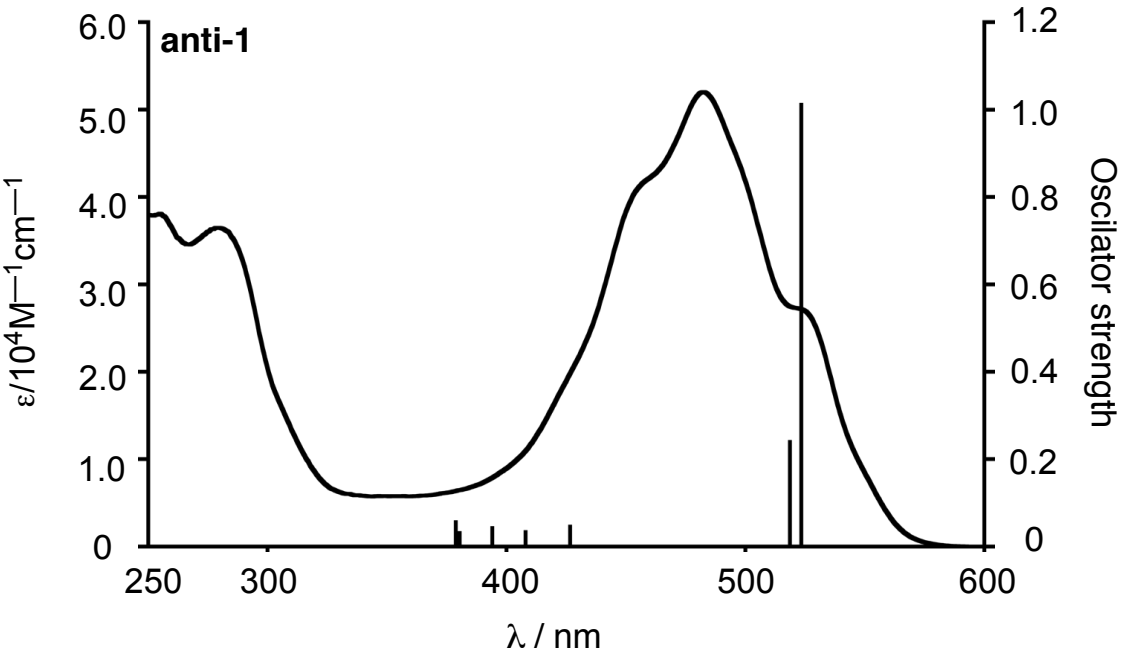


Fig. S7. Absorption spectrum of **anti-1** in CH_2Cl_2 and oscillator strengths calculated at the B3LYP/6-31G(d) level of theory.

Table S5. Calculated exited wavelengths (λ) and oscillator strengths (f) of selected transitions of **anti-1**.

Total energy = −2383.71732843 [Hartree]

Excited State 1:	Singlet-A	2.3689 eV	523.38 nm	f=1.0111	<S**2>=0.000
HOMO ->LUMO	0.70182				
Excited State 2:	Singlet-A	2.3907 eV	518.61 nm	f=0.2396	<S**2>=0.000
HOMO ->LUMO+1	0.70097				
Excited State 3:	Singlet-A	2.8838 eV	429.93 nm	f=0.0000	<S**2>=0.000
HOMO–1 ->LUMO	0.70194				
Excited State 4:	Singlet-A	2.8994 eV	427.62 nm	f=0.0000	<S**2>=0.000
HOMO–2 ->LUMO	0.69026				
HOMO–1 ->LUMO+1	-0.13576				
Excited State 5:	Singlet-A	2.9063 eV	426.60 nm	f=0.0455	<S**2>=0.000
HOMO–3 ->LUMO	0.70310				
Excited State 6:	Singlet-A	2.9412 eV	421.55 nm	f=0.0000	<S**2>=0.000
HOMO–2 ->LUMO	0.13738				
HOMO–1 ->LUMO+1	0.68443				
Excited State 7:	Singlet-A	3.0387 eV	408.02 nm	f=0.0333	<S**2>=0.000
HOMO–3 ->LUMO+1	0.70113				
Excited State 8:	Singlet-A	3.0409 eV	407.73 nm	f=0.0000	<S**2>=0.000
HOMO–2 ->LUMO+1	0.70015				
Excited State 9:	Singlet-A	3.1461 eV	394.09 nm	f=0.0421	<S**2>=0.000
HOMO–4 ->LUMO	0.69865				
Excited State 10:	Singlet-A	3.2097 eV	386.28 nm	f=0.0000	<S**2>=0.000
HOMO–5 ->LUMO	0.70204				
Excited State 11:	Singlet-A	3.2595 eV	380.38 nm	f=0.0311	<S**2>=0.000
HOMO–4 ->LUMO+1	0.69046				
Excited State 12:	Singlet-A	3.2730 eV	378.81 nm	f=0.0557	<S**2>=0.000
HOMO–6 ->LUMO	0.70100				
Excited State 13:	Singlet-A	3.3263 eV	372.74 nm	f=0.0000	<S**2>=0.000
HOMO–8 ->LUMO	0.70269				
Excited State 14:	Singlet-A	3.3268 eV	372.68 nm	f=0.0061	<S**2>=0.000
HOMO–7 ->LUMO	0.70281				
Excited State 15:	Singlet-A	3.3295 eV	372.39 nm	f=0.0000	<S**2>=0.000
HOMO–5 ->LUMO+1	0.69740				
Excited State 16:	Singlet-A	3.3875 eV	366.00 nm	f=0.0088	<S**2>=0.000
HOMO–6 ->LUMO+1	0.69256				
Excited State 17:	Singlet-A	3.4314 eV	361.32 nm	f=0.0000	<S**2>=0.000
HOMO ->LUMO+2	0.68688				
Excited State 18:	Singlet-A	3.4580 eV	358.54 nm	f=0.0004	<S**2>=0.000
HOMO–7 ->LUMO+1	0.69872				
Excited State 19:	Singlet-A	3.4583 eV	358.51 nm	f=0.0000	<S**2>=0.000
HOMO–8 ->LUMO+1	0.69560				
Excited State 20:	Singlet-A	3.6706 eV	337.77 nm	f=0.0000	<S**2>=0.000
HOMO–9 ->LUMO	0.57777				
HOMO ->LUMO+3	0.40015				

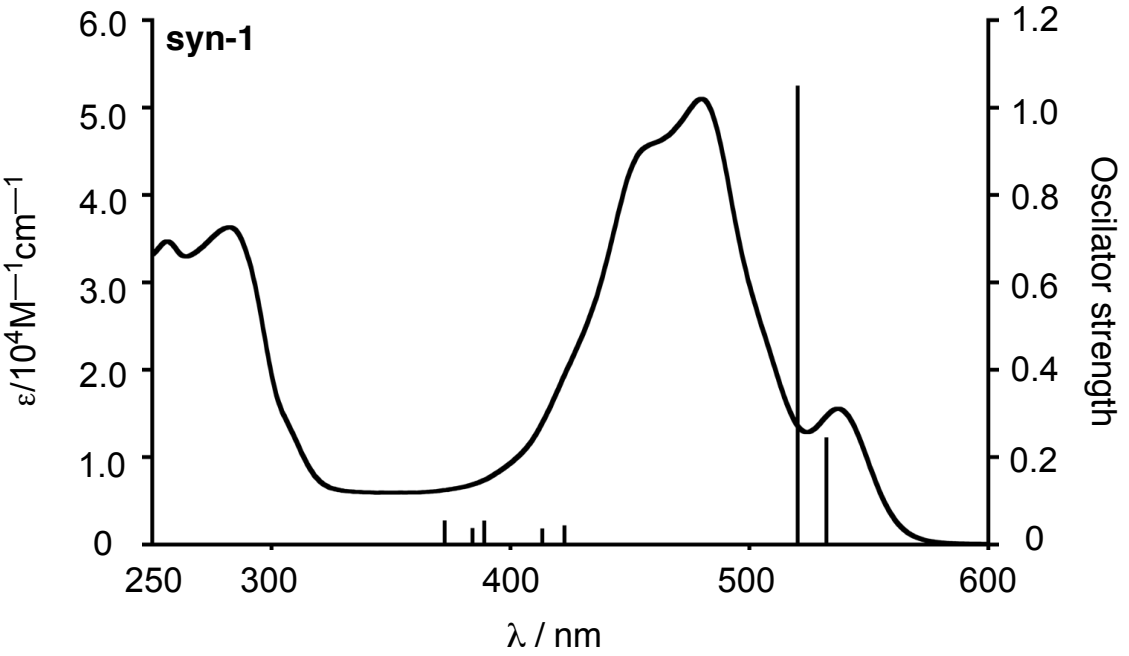


Fig. S8. Absorption spectrum of **syn-1** in CH_2Cl_2 and oscillator strengths calculated at the B3LYP/6-31G(d) level of theory.

Table S6. Calculated exited wavelengths (λ) and oscillator strengths (f) of selected transitions of **syn-1**.

Total energy = –2383.72367349 [Hartree]

Excited State 1:	Singlet-A	2.3295 eV	532.24 nm	f=0.2412	<S**2>=0.000
HOMO ->LUMO+1	0.70161				
Excited State 2:	Singlet-A	2.3834 eV	520.20 nm	f=1.0460	<S**2>=0.000
HOMO ->LUMO	0.70195				
Excited State 3:	Singlet-A	2.9014 eV	427.33 nm	f=0.0000	<S**2>=0.000
HOMO–3 ->LUMO	0.13780				
HOMO–1 ->LUMO+1	0.68447				
Excited State 4:	Singlet-A	2.9150 eV	425.34 nm	f=0.0003	<S**2>=0.000
HOMO–1 ->LUMO	0.69829				
Excited State 5:	Singlet-A	2.9338 eV	422.60 nm	f=0.0396	<S**2>=0.000
HOMO–2 ->LUMO	0.70268				
Excited State 6:	Singlet-A	2.9351 eV	422.41 nm	f=0.0000	<S**2>=0.000
HOMO–3 ->LUMO	0.68986				
HOMO–1 ->LUMO+1	-0.13699				
Excited State 7:	Singlet-A	2.9997 eV	413.33 nm	f=0.0326	<S**2>=0.000
HOMO–2 ->LUMO+1	0.70158				
Excited State 8:	Singlet-A	3.0085 eV	412.12 nm	f=0.0025	<S**2>=0.000
HOMO–3 ->LUMO+1	0.69728				
Excited State 9:	Singlet-A	3.1867 eV	389.07 nm	f=0.0508	<S**2>=0.000
HOMO–4 ->LUMO	0.69997				
Excited State 10:	Singlet-A	3.2277 eV	384.13 nm	f=0.0335	<S**2>=0.000
HOMO–4 ->LUMO+1	0.69314				
Excited State 11:	Singlet-A	3.2656 eV	379.67 nm	f=0.0008	<S**2>=0.000
HOMO–5 ->LUMO	0.70142				
Excited State 12:	Singlet-A	3.3161 eV	373.89 nm	f=0.0000	<S**2>=0.000
HOMO–5 ->LUMO+1	0.69753				
Excited State 13:	Singlet-A	3.3283 eV	372.51 nm	f=0.0511	<S**2>=0.000
HOMO–6 ->LUMO	0.70182				
Excited State 14:	Singlet-A	3.3744 eV	367.42 nm	f=0.0061	<S**2>=0.000
HOMO–6 ->LUMO+1	0.69718				
Excited State 15:	Singlet-A	3.3785 eV	366.98 nm	f=0.0003	<S**2>=0.000
HOMO–7 ->LUMO	0.70286				
Excited State 16:	Singlet-A	3.3787 eV	366.96 nm	f=0.0011	<S**2>=0.000
HOMO–8 ->LUMO	0.70283				
Excited State 17:	Singlet-A	3.3898 eV	365.76 nm	f=0.0000	<S**2>=0.000
HOMO ->LUMO+2	0.69048				
Excited State 18:	Singlet-A	3.4411 eV	360.30 nm	f=0.0000	<S**2>=0.000
HOMO–7 ->LUMO+1	0.69788				
Excited State 19:	Singlet-A	3.4412 eV	360.29 nm	f=0.0007	<S**2>=0.000
HOMO–8 ->LUMO+1	0.70025				
Excited State 20:	Singlet-A	3.6384 eV	340.77 nm	f=0.0007	<S**2>=0.000
HOMO–9 ->LUMO	-0.43818				
HOMO ->LUMO+3	0.54696				

Table S7. Calculated coordinates of **anti-1**

Total energy = –2383.78535441 [Hartree]

C	-2.8452588	1.2006284	0.244491	C	2.845251	-1.2006118	-0.2445068
C	-1.4311282	1.2347351	0.1043435	C	1.4311239	-1.2347144	-0.1043473
C	-0.677664	2.4503711	0.0643854	C	0.6776631	-2.450352	-0.0643851
H	-1.1902074	3.3966887	0.1498816	H	1.19021	-3.3966685	-0.1498792
C	0.6775649	2.4503946	-0.0645976	C	-0.6775648	-2.4503752	0.0646037
H	1.1900949	3.3967244	-0.1502143	H	-1.1900987	-3.3967036	0.1502179
C	-1.4310887	-1.2347639	0.1043925	C	1.4310923	1.2347849	-0.1043825
C	-2.8452504	-1.2006742	0.2444379	C	2.8452572	1.2006906	-0.2444187
C	-0.7183067	-0.0000044	0.04981	C	0.7183066	0.0000268	-0.0498067
C	-3.7087823	2.3897424	0.3204308	C	3.7087582	-2.3897342	-0.3204728
C	-4.8279457	2.330228	1.1902272	C	4.8279264	-2.3302144	-1.1902626
C	-5.5765666	3.4853001	1.4517525	C	5.5765317	-3.4852912	-1.4518106
H	-6.4017458	3.411718	2.1525503	H	6.4017163	-3.4117044	-2.1526013
C	-5.2932796	4.6648211	0.7753034	C	5.2932205	-4.6648258	-0.7753945
H	-5.8964067	5.5490933	0.9629678	H	5.8963349	-5.5491027	-0.963078
C	-4.2722987	4.7052226	-0.1842944	C	4.2722253	-4.7052394	0.1841878
H	-4.097754	5.6071309	-0.7628153	H	4.0976561	-5.6071628	0.7626776
C	-3.488958	3.5797045	-0.4031961	C	3.4889001	-3.579715	0.403112
H	-2.7276126	3.6066817	-1.1753281	H	2.7275365	-3.6067032	1.1752262
C	-3.7086869	-2.3898327	0.3202961	C	3.7087108	2.3898409	-0.3202516
C	-4.8278412	-2.3304897	1.1901117	C	4.827858	2.3305024	-1.1900768
C	-5.5761532	-3.4857613	1.4517383	C	5.5761866	3.4857685	-1.4516809
H	-6.4012673	-3.412419	2.1526406	H	6.4012943	3.41243	-2.1525911
C	-5.292678	-4.6651919	0.775227	C	5.2927392	4.6651855	-0.7751351
H	-5.8955843	-5.5496026	0.9629481	H	5.895659	5.5495909	-0.9628377
C	-4.2717795	-4.7053955	-0.1844851	C	4.2718564	4.7053777	0.184594
H	-4.0971909	-5.6072558	-0.7630662	H	4.097294	5.6072227	0.7632069
C	-3.4886646	-3.5797395	-0.4033944	C	3.4887251	3.579729	0.4034816
H	-2.727287	-3.6064831	-1.1755146	H	2.7273674	3.6064621	1.1756214
C	-6.0514246	-0.0000942	-0.3630035	C	6.0514244	0.0000832	0.3630013
C	-7.4311118	-0.0001615	-0.0834814	C	7.4311111	0.0001543	0.0834775
H	-7.7596607	-0.0003791	0.9539338	H	7.7596587	0.0003878	-0.9539381
C	-8.3864069	0.00001	-1.099158	C	8.3864077	-0.000033	1.0991528
H	-9.445243	-0.0000061	-0.8501577	H	9.4452434	-0.0000135	0.8501509
C	-7.9831837	0.0002082	-2.437049	C	7.9831861	-0.0002522	2.4370442
H	-8.7240092	0.0003537	-3.2329873	H	8.7240125	-0.0004108	3.2329818
C	-6.6226118	0.0002172	-2.7426144	C	6.6226146	-0.0002661	2.7426113
H	-6.2972032	0.0003164	-3.7805165	H	6.2972077	-0.0003813	3.7805138
C	-5.6754649	0.000069	-1.7145979	C	5.6754663	-0.000101	1.7145961
H	-4.6203114	0.0000656	-1.9821854	H	4.6203133	-0.0001016	1.9821853
N	-3.4691661	-0.0000254	0.383947	N	3.4691654	0.0000395	-0.3839464
O	-5.1687234	-1.1681174	1.7607128	O	5.1687251	1.168137	-1.7607003
O	-5.1685352	1.1677691	1.7609007	O	5.1685277	-1.1677493	-1.7609164
B	-5.035529	-0.0001041	0.8905057	B	5.035527	0.000114	-0.8905072

Table S8. Calculated coordinates of **syn-1**

Total energy = –2383.79059878 [Hartree]

C	2.8502966	1.2017175	-0.4191466	C	-2.850294	-1.2017146	-0.4191804
C	1.4315589	1.2336047	-0.4918454	C	-1.4315561	-1.2336011	-0.4918705
C	0.6808717	2.4336348	-0.713338	C	-0.6808676	-2.4336285	-0.7133732
H	1.2079018	3.3485891	-0.9471504	H	-1.207896	-3.3485797	-0.9472011
C	-0.68082	2.4336477	-0.7133366	C	0.6808241	-2.4336416	-0.7133621
H	-1.2078327	3.3486123	-0.9471441	H	1.2078385	-3.3486033	-0.9471776
C	1.4315325	-1.2336276	-0.4918514	C	-1.4315296	1.233631	-0.4918464
C	2.8502712	-1.2017755	-0.4191433	C	-2.8502687	1.2017778	-0.4191489
C	0.7189544	-0.000005	-0.4712857	C	-0.7189517	0.0000082	-0.4712908
C	3.6986616	2.3988444	-0.3677124	C	-3.6986592	-2.3988419	-0.3677641
C	4.9778256	2.3334562	-0.9785612	C	-4.9778199	-2.3334469	-0.9786187
C	5.748255	3.4957315	-1.1188374	C	-5.7482493	-3.4957202	-1.1189103
H	6.7050039	3.4163523	-1.6245366	H	-6.7049958	-3.4163352	-1.6246134
C	5.3075291	4.6926682	-0.5696921	C	-5.3075269	-4.6926627	-0.5697749
H	5.9241131	5.5829735	-0.6600963	H	-5.9241108	-5.5829667	-0.660191
C	4.0996305	4.7477778	0.140344	C	-4.0996318	-4.7477799	0.1402667
H	3.7879611	5.6688494	0.6230951	H	-3.7879653	-5.6688566	0.6230102
C	3.3060642	3.6128346	0.2342138	C	-3.3060656	-3.612838	0.2341523
H	2.3891919	3.6514961	0.8124814	H	-2.3891966	-3.6515057	0.8124245
C	3.6986092	-2.3989157	-0.3676902	C	-3.6986068	2.3989174	-0.3676883
C	4.9777942	-2.3335527	-0.978501	C	-4.9777866	2.3335616	-0.9785103
C	5.7481982	-3.4958517	-1.1187644	C	-5.7481888	3.4958624	-1.1187674
H	6.7049637	-3.4164841	-1.6244355	H	-6.70495	3.4165009	-1.6244475
C	5.3074287	-4.69278	-0.5696446	C	-5.3074235	4.6927845	-0.5696307
H	5.9239913	-5.5831013	-0.6600372	H	-5.923985	5.5831071	-0.6600186
C	4.099505	-4.7478663	0.1403569	C	-4.0995058	4.7478623	0.1403815
H	3.7877983	-5.6689353	0.6230883	H	-3.7878026	5.6689258	0.6231258
C	3.3059659	-3.6129059	0.2342126	C	-3.305968	3.6129005	0.2342313
H	2.3890768	-3.6515502	0.8124546	H	-2.3890835	3.6515384	0.8124811
C	5.8520356	0.0000093	0.8357512	C	-5.8520409	-0.0000154	0.8357115
C	7.2597269	0.0002252	0.8558855	C	-7.2597322	-0.0002007	0.8558368
H	7.8013935	0.0004005	-0.0879236	H	-7.8013929	-0.0003429	-0.0879757
C	7.9771814	0.000226	2.0514339	C	-7.9771946	-0.0002115	2.0513805
H	9.0647379	0.0003948	2.0332627	H	-9.0647508	-0.0003557	2.0332024
C	7.2987762	0.0000113	3.2731587	C	-7.2987971	-0.0000382	3.2731097
H	7.8536478	0.0000044	4.2082935	H	-7.8536747	-0.0000393	4.2082409
C	5.9044915	-0.0001985	3.282667	C	-5.9045125	0.0001403	3.2826267
H	5.3659453	-0.00036	4.2277206	H	-5.3659722	0.0002696	4.2276838
C	5.1975397	-0.0001977	2.0767729	C	-5.197553	0.0001501	2.0767372
H	4.1097265	-0.000359	2.1143994	H	-4.1097402	0.0002863	2.1143707
N	3.4906571	-0.0000358	-0.4335657	N	-3.4906544	0.0000387	-0.4335896
B	5.1230432	-0.0000305	-0.6044457	B	-5.1230393	0.0000361	-0.6044803
O	5.4458116	1.1648841	-1.4285378	O	-5.4458034	-1.16487	-1.4285852
O	5.4458312	-1.1650036	-1.4284588	O	-5.4458205	1.1650175	-1.4284844

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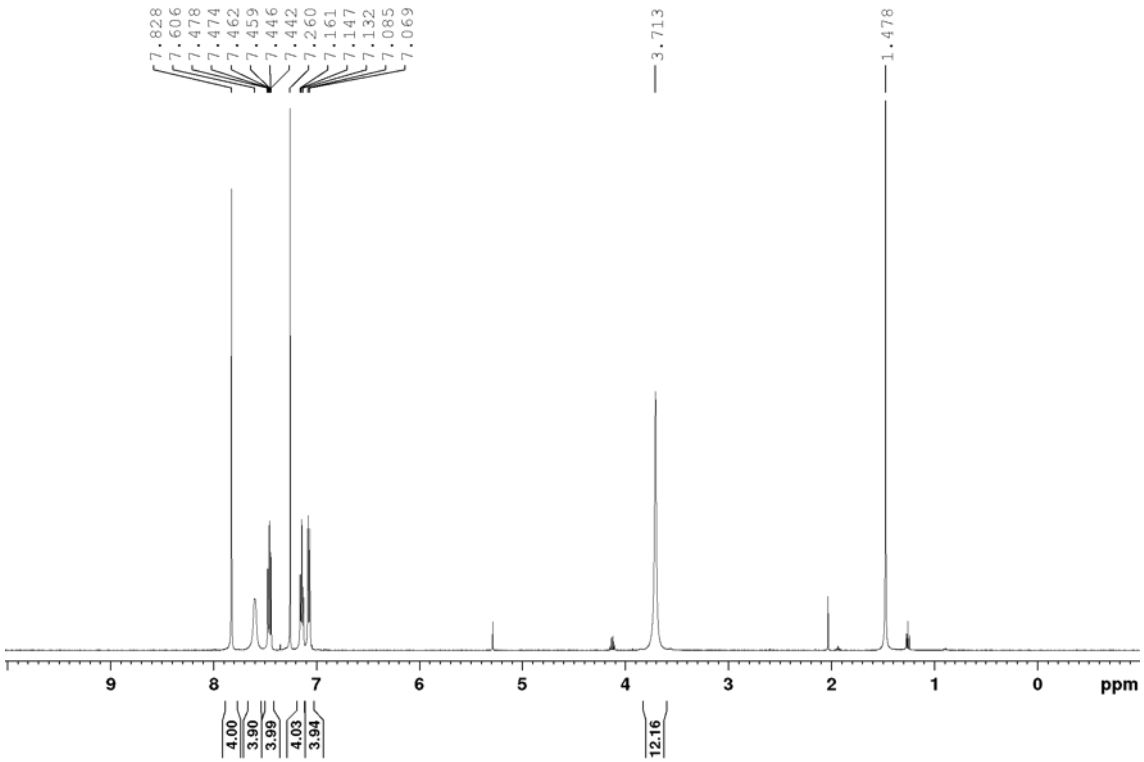

Fig. S9. ^{1}H NMR spectrum of **3** in $CDCl_3$ at 50 ℃.

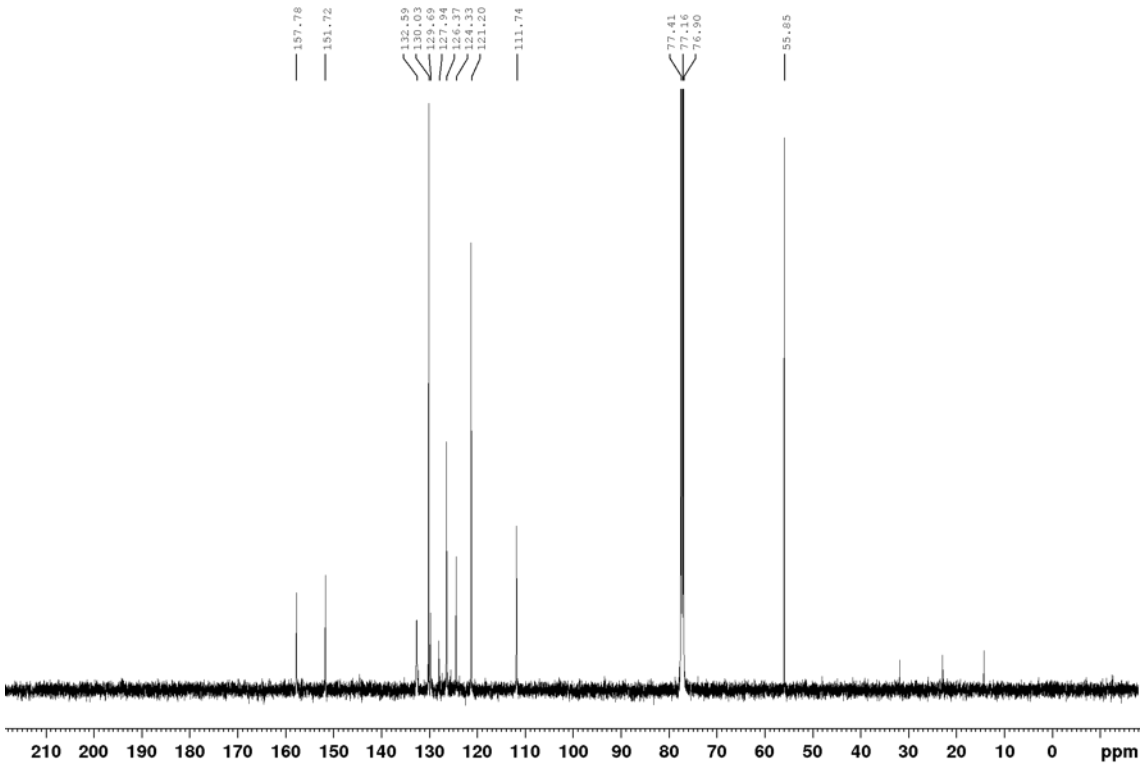

Fig. S10. ^{13}C NMR spectrum of **3** in $CDCl_3$ at 50 ℃.

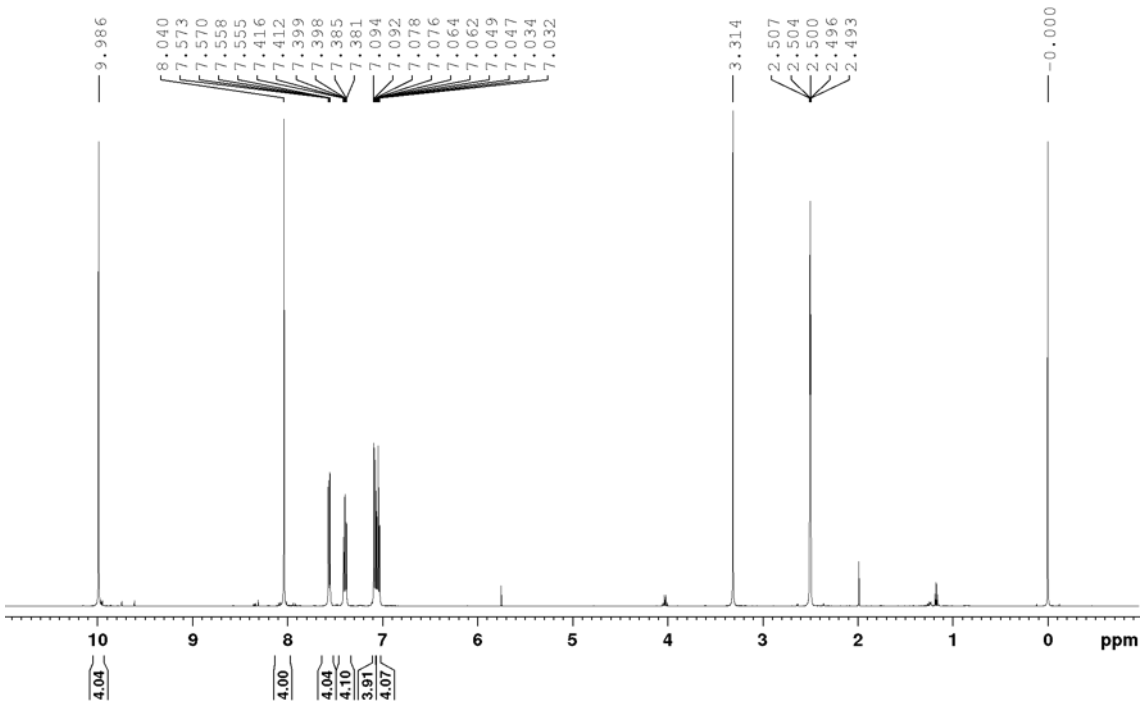

Fig. S11. ^{1}H NMR spectrum of **4** in DMSO-d_6.

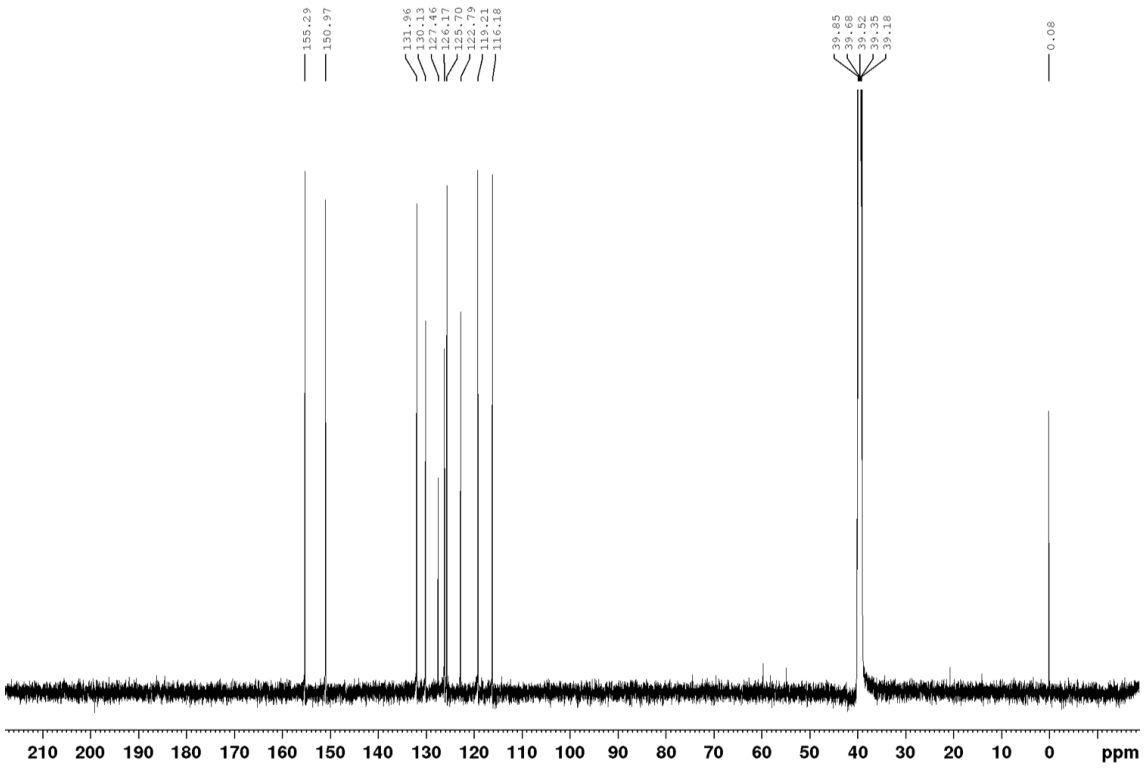

Fig. S12. ^{13}C NMR spectrum of **4** in DMSO-d_6.

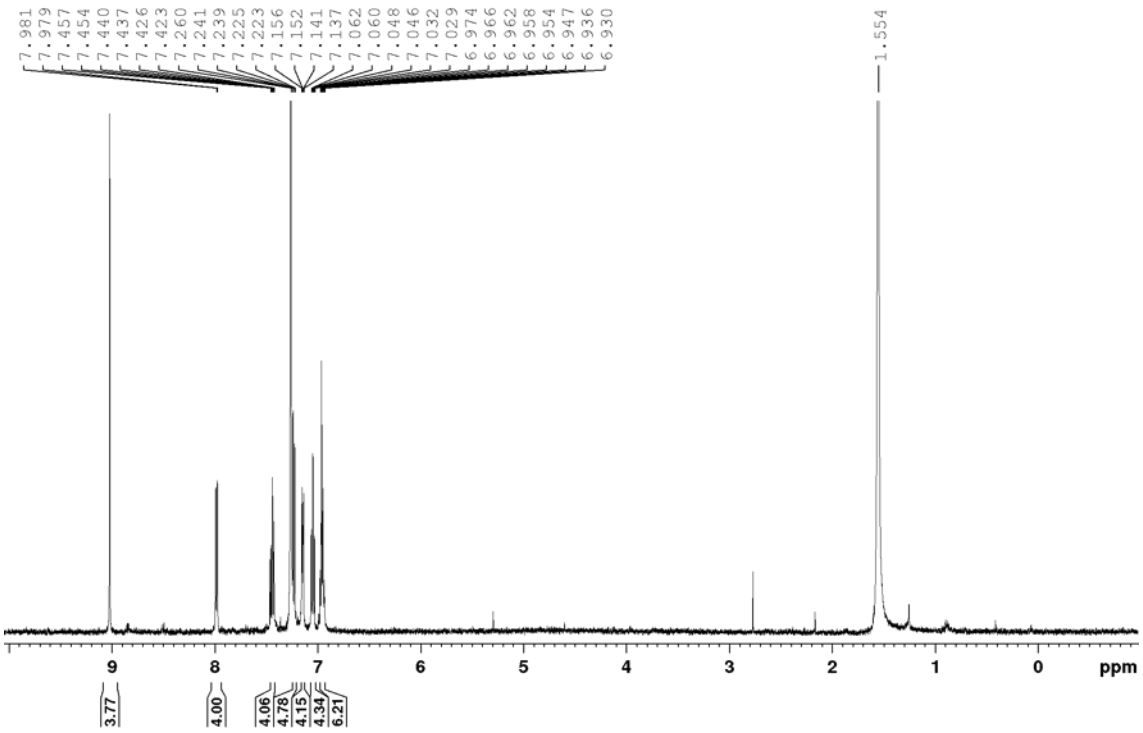

Fig. S13. ^{1}H NMR spectrum of **anti-1** in $CDCl_3$.

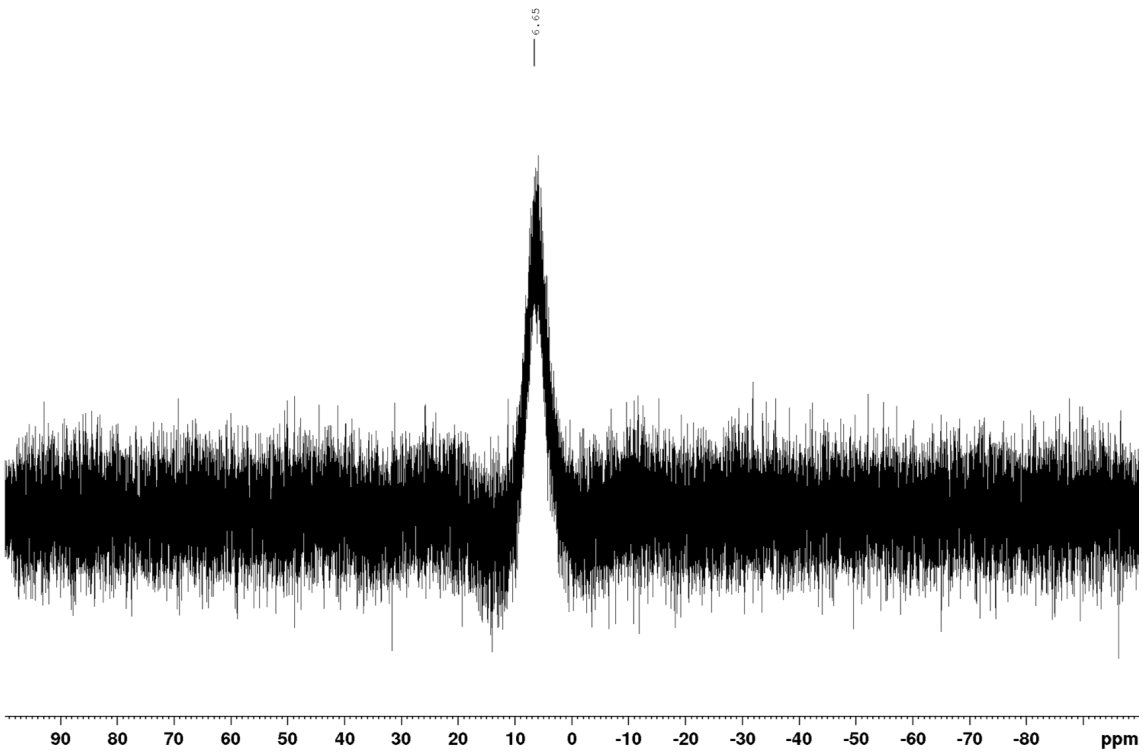

Fig. S14. ^{11}B NMR spectrum of **anti-1** in $CDCl_3$.

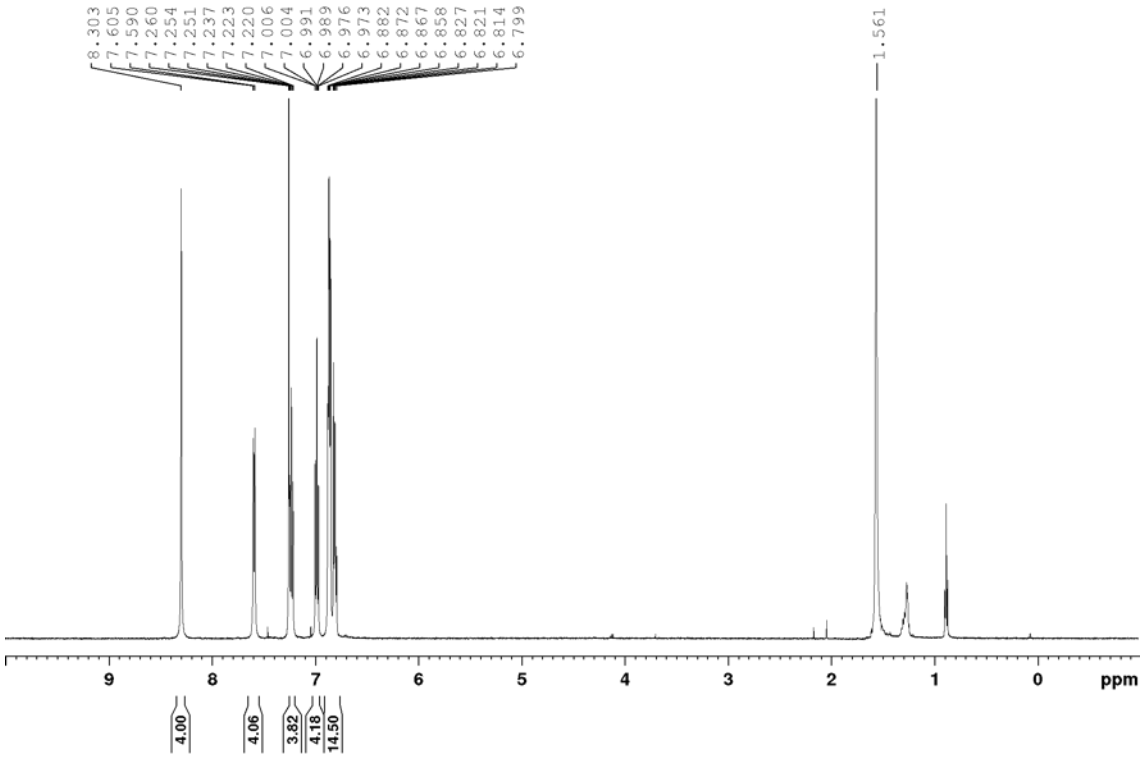

Fig. S15. ^{1}H NMR spectrum of **syn-1** in $CDCl_3$.

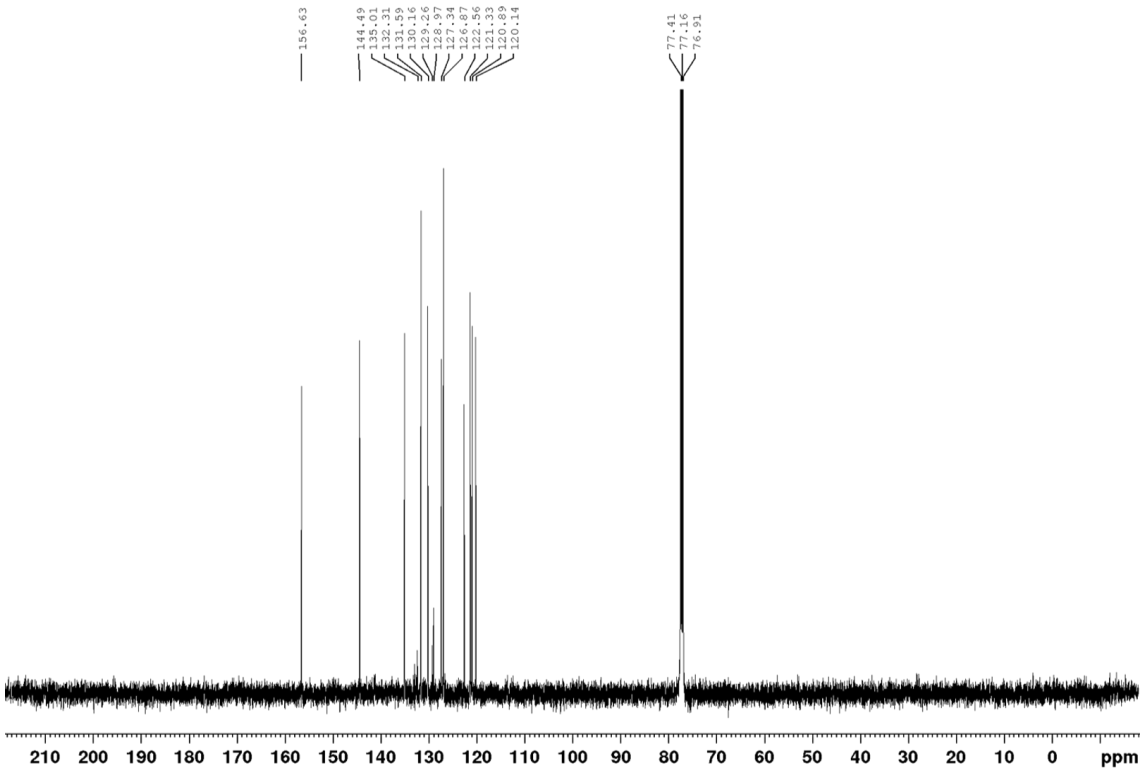

Fig. S16. ^{13}C NMR spectrum of **syn-1** in $CDCl_3$.

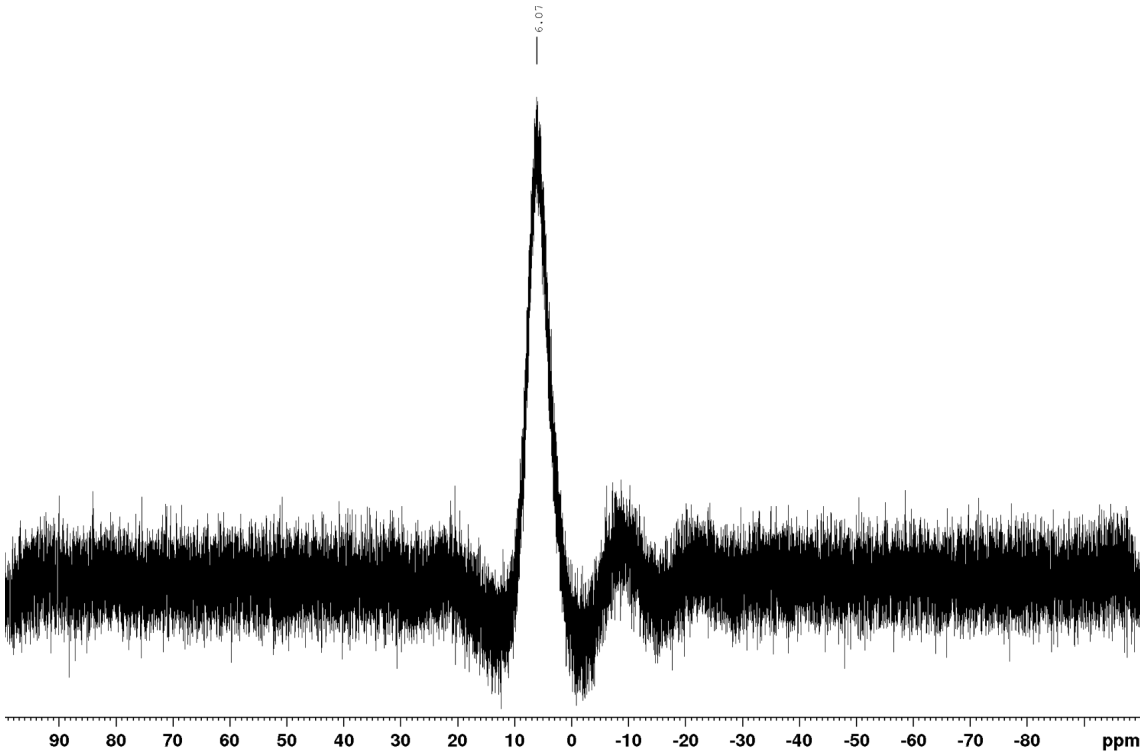

Fig. S17. ^{11}B NMR spectrum of **syn-1** in $CDCl_3$.