Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

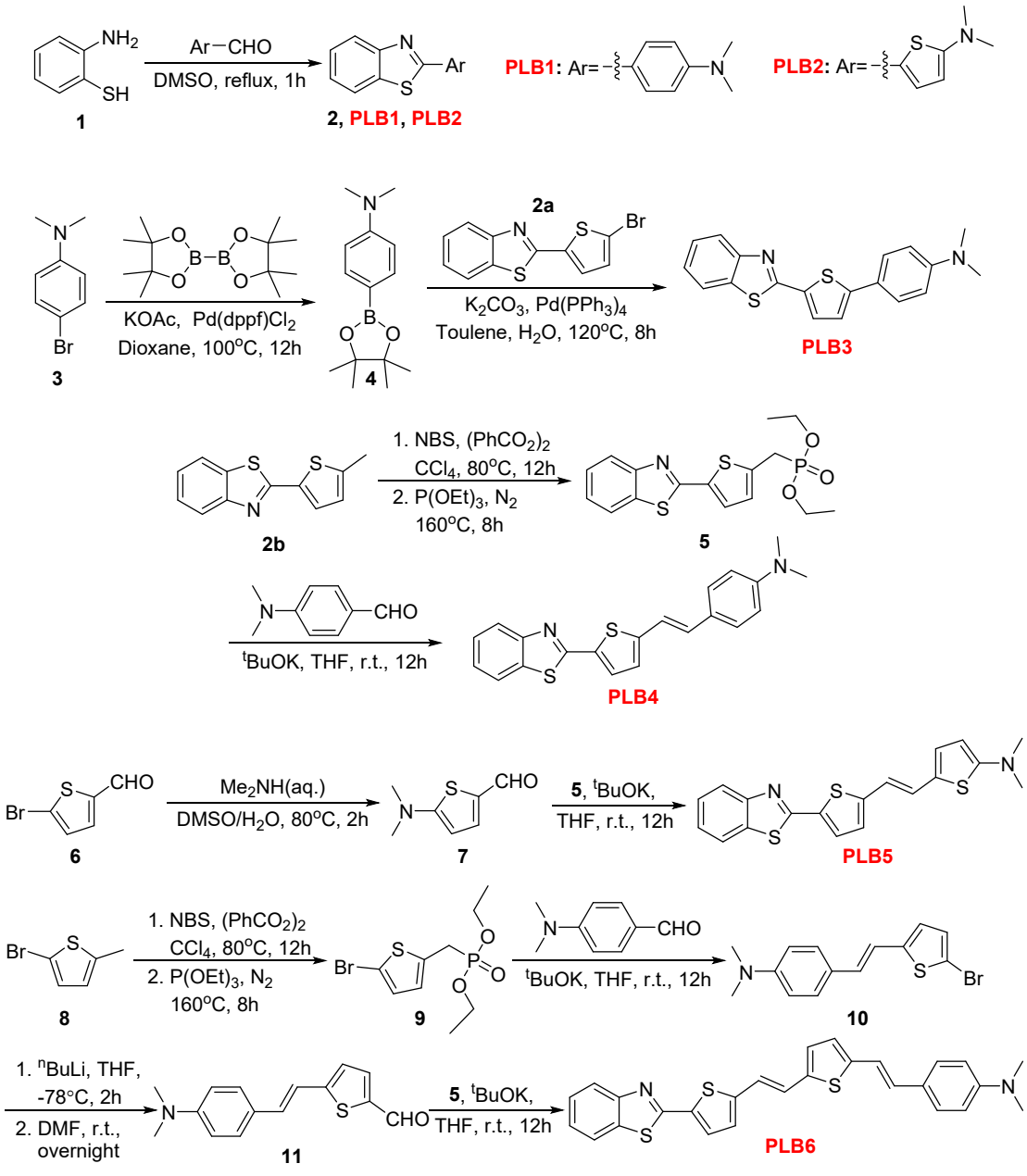
Modulation of π-bridges to obtain a series of D-π-A benzothiazoles with efficient panchromatic luminescence and application to WLEDs

Yuwei Song, Zhiyuan Chen, Lai Hu, Qian Cheng, Yue He, Rui Liu, Senqiang Zhu* and Hongjun Zhu*

Department of Applied Chemistry, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China. E-mail: rui.liu@njtech.edu.cn

Experimental section

Materials and methods. ^{1}H NMR spectra were recorded on a BrukerAV-400 spectrometer at 400 MHz and ^{13}C NMR were recorded on a BrukerAV-400 spectrometer at 101 MHz. $CDCl_3$ with internal standard tetramethylsilane (TMS) was used as the solvent. Mass analyses were performed on a Thermo Scientific LTQ Orbitrap XL mass spectrometer and the ion source is Electron Spray Ionization (ESI).



Scheme S1 Synthetic procedure of **PLB1**~**PLB6**.

Synthesis of compound PLB1.[1] 2-Aminobenzenethiol (1.38 g, 11.0 mmol), 4-dimethylaminobenzaldehyde (1.49 g, 10.0 mmol), and dimethyl sulfoxide (10 mL) were added to a 100 mL two-necked round bottom flask. The reaction was stirred at 195 °C for 1 h. The reaction solution was cooled and recrystallized by adding n-hexane

(20 mL) to obtain **PLB1** as a pale-yellow solid. The yield was 91.13%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, J=8.0, 1H), 7.93 (dd, J=12.0, 4.0, 2H), 7.80 (d, J=8.0, 1H), 7.41 (t, J=8.0, 1H), 7.27 (t, J=8.0, 1H), 6.68 (dd, J=12.0, 4.0, 2H), 2.97 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.76, 153.35, 151.06, 133.47, 127.77, 124.90, 123.10, 121.17, 120.28, 120.22, 110.57, 39.02. **HRMS** (ESI) m/z calcd for $C_{15}H_{15}N_2S^+$ $(M+H)^+$ 255.09505, found 255.09396.

Synthesis of compound PLB2. 2-Aminobenzenethiol (1.38 g, 11.0 mmol), 5-dimethylaminothiene-2-formaldehyde (1.55 g, 10.0 mmol), and dimethyl sulfoxide (10 mL) were added to a 100 mL two-necked round bottom flask. The reaction was stirred at 195 °C for 1 h. The reaction solution was cooled and recrystallized by adding n-hexane (20 mL) to obtain **PLB2** as a yellow solid. The yield was 47.31%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 6.1 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 5.89 (d, *J* = 4.1 Hz, 1H), 3.07 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.81, 162.31, 153.92, 133.95, 130.60, 126.02, 123.90, 121.70, 121.09, 119.69, 102.34, 42.23. **HRMS** (ESI) m/z calcd for $C_{13}H_{13}N_2S_2^+$ $(M+H)^+$ 261.05147, found 261.04987.

Synthesis of intermediate 2a. 2-Aminobenzenethiol (1.38 g, 11.0 mmol), 5-bromothiophen-2-formaldehyde (1.91 g, 10.0 mmol), and dimethyl sulfoxide (10 mL) were added to a 100 mL two-necked round bottom flask. The reaction was stirred at 195 °C for 1 h. The reaction solution was cooled and recrystallized by adding n-hexane (20 mL) to obtain **2a** as a white solid. The yield is 97.46%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04–7.99 (m, 1H), 7.87–7.82 (m, 1H), 7.48 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.41–7.35 (m, 2H), 7.10 (d, *J* = 4.0 Hz, 1H).

Synthesis of intermediate 4.[2] 4-Dimethylaminobromobenzene (2 g, 10 mmol), potassium acetate (2.94 g, 30 mmol), biboronic acid pinacol ester (5.08 g, 20 mmol) and 1,1-[bis(diphenylphosphino)]ferrocene palladium II) dichloride (0.82 g, 0.1 mmol) and 1,4-dioxane (50 mL) were added to a 100 mL two-necked round-bottom flask. . The reaction was charged with nitrogen and stirred at 80°C for 6 hours. After the reaction was completed, the reaction was filtered while it was still hot. The reaction was washed with water (3×20 mL), saturated salt water (20 mL), and extracted with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by thin-layer chromatography using silica gel (eluent: petroleum ether:dichloromethane=5:1) to obtain intermediate 4. It was a white solid with an 83.13% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 3.02 (s, 6H), 1.37 (s, 12H).

Synthesis of compound PLB3.[3] Intermediate 2a (0.86 g, 2.9 mmol), Intermediate 4 (0.65 g, 2.6 mmol), K_2CO_3 (1.82 g, 13.2 mmol), $Pd(PPh_3)_4$ (0.31 g, 0.26 mmol), toluene (21 mL) and water (7 mL) were added to a 100 mL two-necked round-bottom flask. The reaction was charged with nitrogen and stirred at 125°C for 12 hours. After the reaction was completed, the reaction was filtered while it was still hot. The reaction was washed with water (3×20 mL), saturated salt water (20 mL), and extracted with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by thin-layer chromatography using silica gel (eluent: petroleum ether:dichloromethane=2:1) to obtain **PLB3**. It is a yellow

solid with a yield of 83.75%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.53 (m, 3H), 7.49–7.42 (m, 1H), 7.38–7.30 (m, 1H), 7.18 (d, *J* = 3.9 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 2H), 3.02 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.63, 153.81, 148.33, 136.81, 134.53, 129.78, 129.68, 126.98, 126.32, 124.87, 122.66, 121.51, 121.35, 119.33, 112.43, 40.40. **HRMS** (ESI) m/z calcd for $C_{19}H_{17}N_2S_2^+$ $(M+H)^+$ 337.08227, found 337.08157.

Synthesis of intermediate 2b. 2-Aminobenzenethiol (1.38 g, 11.0 mmol), 5-methylthiophen-2-formaldehyde (1.26 g, 10.0 mmol), and dimethyl sulfoxide (10 mL) were added to a 100 mL two-necked round bottom flask. The reaction was stirred at 195 °C for 1 h. The reaction solution was cooled and recrystallized by adding n-hexane (20 mL) to obtain **2b** as a white solid. The yield is 98.28%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (ddd, *J* = 8.2, 1.0, 0.6 Hz, 1H), 7.82 (ddd, *J* = 8.0, 1.2, 0.6 Hz, 1H), 7.45 (ddd, *J* = 8.3, 6.2, 1.3 Hz, 2H), 7.34 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 6.81–6.77 (m, 1H), 2.55 (d, *J* = 0.8 Hz, 3H).

Synthesis of intermediate 5.[4] Intermediate **2b** (2.31 g, 10.0 mmol), NBS (2.67 g, 15.0 mmol), benzoyl peroxide (72.6 mg, 0.3 mmol), and carbon tetrachloride (20 mL) were added to a 100 mL two-necked round-bottom flask. The reaction was stirred at 85 °C for 12 h. The reaction solution was cooled to room temperature and filtered through diatomaceous earth. Wash with dichloromethane and collect 200 mL of filtrate. Concentrate under reduced pressure to obtain a yellow solid without any purification. Transfer the above yellow solid to a 50 mL two-necked round bottom flask. Triethyl phosphite (10 mL) was added and stirred at 160 °C for 8 h. The excess triethyl phosphite was then removed by distillation under reduced pressure. The residue was purified by thin-layer chromatography using silica gel (eluent: petroleum ether/ethyl acetate = 1:1) to obtain Intermediate **5**. It was a yellow oily liquid with a yield of 73.30%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 3.6 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 3.3 Hz, 1H), 4.14–4.09 (m, 4H), 3.39 (d, *J* = 21.2 Hz, 2H), 1.31 (dd, *J* = 6.9, 2.9 Hz, 6H).

Synthesis of compound PLB4.[5] A solution of 4-dimethylaminobenzaldehyde (298.0 mg, 2.0 mmol), Intermediate **5** (880.8 mg, 2.4 mmol), and THF (20 mL) were added to a 100 mL two-necked round bottom flask. After stirring for 30 min under a nitrogen atmosphere, potassium tert-butoxide (672.0 mg, 6.0 mmol) was added. Stirring was continued for 12 h at room temperature. Filter the reaction solution. The filtrate was washed with water (3×20 mL), saturated salt water (20 mL), and extracted with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by thin-layer chromatography using silica gel (eluent: petroleum ether:dichloromethane=2:1) to obtain **PLB4**. It is a red solid with a yield of 58.94%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 3.3 Hz, 1H), 7.49–7.43 (m, 1H), 7.42–7.32 (m, 3H), 7.04–6.96 (m, 3H), 6.71 (d, *J* = 8.4 Hz, 2H), 3.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.67, 161.29, 153.81, 148.04, 134.62, 130.97, 130.65, 129.30, 127.91, 126.38, 125.45, 124.99, 122.77, 122.01, 121.37, 116.97, 112.66, 40.64. **HRMS** (ESI) m/z calcd for $C_{21}H_{19}N_2S_2^+$ $(M+H)^+$ 363.09842, found 363.09711.

Synthesis of compound PLB5. A solution of 5-dimethylaminothiene-2-

formaldehyde (310.0 mg, 2.0 mmol), Intermediate **5** (880.8 mg, 2.4 mmol), and THF (20 mL) were added to a 100 mL two-necked round bottom flask. After stirring for 30 min under a nitrogen atmosphere, potassium tert-butoxide (672.0 mg, 6.0 mmol) was added. Stirring was continued for 12 h at room temperature. Filter the reaction solution. The filtrate was washed with water (3×20 mL), saturated salt water (20 mL), and extracted with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by thin-layer chromatography using silica gel (eluent: petroleum ether:dichloromethane=2:1) to obtain **PLB5**. It is a red solid with a yield of 61.30%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 3.9 Hz, 1H), 7.39 (dd, *J* = 11.3, 4.2 Hz, 1H), 7.28 (t, *J* = 7.1 Hz, 1H), 6.99 (d, *J* = 15.6 Hz, 1H), 6.85 (d, *J* = 3.9 Hz, 1H), 6.75 (d, *J* = 3.9 Hz, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 5.70 (d, *J* = 4.0 Hz, 1H), 2.93 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.34, 159.45, 154.66, 153.67, 148.10, 134.50, 133.18, 129.58, 129.49, 126.40, 125.17, 124.95, 124.74, 122.65, 121.36, 114.73, 102.25, 42.45. **HRMS** (ESI) m/z calcd for $C_{19}H_{17}N_2S_3^+$ $(M+H)^+$ 369.05484, found 369.05292.

Synthesis of intermediate 7. 5-Bromothiophene-2-carboxaldehyde (1.9 g, 10.0 mmol), dimethyl sulfoxide (20 mL), and purified water (5 mL) were added to a 100 mL two-necked round bottom flask. Then add dimethylamine aqueous solution (33%, 5.5 g, 40 mmol). Stir for 2 h at 80 °C. Subsequently, it was washed with water (3×20 mL), saturated saline (20 mL), and extracted with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by thin-layer chromatography using silica gel (eluent: petroleum ether: ethyl acetate=2:1) to obtain Intermediate **7**. It is a brown solid with a 32.26% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.49 (d, *J* = 4.3 Hz, 1H), 5.94 (d, *J* = 4.4 Hz, 1H), 3.10 (s, 6H).

Synthesis of intermediate 9. 5-bromo-2-methylthiophene (1.77 g, 10.0 mmol), NBS (2.67 g, 15.0 mmol), benzoyl peroxide (72.6 mg, 0.3 mmol), and carbon tetrachloride (20 mL) were added to a 100 mL two-necked round-bottom flask. The reaction was stirred at 85 °C for 12 h. The reaction solution was cooled to room temperature and filtered through diatomaceous earth. Wash with dichloromethane and collect 200 mL of filtrate. Concentrate under reduced pressure to obtain a yellow solid without any purification. Transfer the above yellow solid to a 50 mL two-necked round bottom flask. Triethyl phosphite (10 mL) was added and stirred at 160 °C for 8 h. The excess triethyl phosphite was then removed by distillation under reduced pressure. The residue was purified by thin layer chromatography using silica gel (eluent: petroleum ether/ethyl acetate = 1:1) to obtain Intermediate **9**. It was a yellow oily liquid with a yield of 51.24%. **^{1}H NMR** (400 MHz, Acetone) δ 7.02 (dd, *J* = 3.7, 0.6 Hz, 1H), 6.85 (dd, *J* = 4.1, 3.3 Hz, 1H), 4.10–4.04 (m, 4H), 3.41 (dd, *J* = 20.8, 0.9 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 7H).

Synthesis of intermediate 10. A solution of 5-dimethylaminothiene-2-formaldehyde (465.0 mg, 3.0 mmol), intermediates **7** (1.1 g, 3.6 mmol), and THF (20 mL) was added to a 100 mL two-necked round bottom flask. After stirring for 30 min under a nitrogen atmosphere, potassium tert-butoxide (1.0 g, 9.0 mmol) was added.

Stirring was continued for 12 h at room temperature. Filter the reaction solution. The filtrate was washed with water (3×20 mL), saturated salt water (20 mL), and extracted with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by thin-layer chromatography using silica gel (eluent: petroleum ether:dichloromethane=3:1) to obtain intermediate **10**. It is a yellow solid with a yield of 38.52%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.7 Hz, 2H), 6.91 (dd, *J* = 9.9, 6.1 Hz, 2H), 6.78–6.66 (m, 4H), 2.98 (s, 6H).

Synthesis of intermediate 11. Intermediate **8** (616.0 mg, 2.0 mmol) and anhydrous THF (10 mL) were added to a 100 mL two-necked round bottom flask. Stir and cool down to -78 °C under a nitrogen atmosphere. The reaction was continued for 2 h. Anhydrous DMF (0.3 mL) was added to the reaction solution and warmed to room temperature and stirred overnight. Subsequently, it was washed with water (3×20 mL), saturated saline (20 mL), and extracted with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by thin layer chromatography using silica gel (eluent: petroleum ether:dichloromethane=2:1) to obtain Intermediate **11**. It is a yellow solid with a 47.16% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.62 (s, 1H), 7.40 (s, 2H), 7.18–6.88 (m, 3H), 6.69 (s, 2H), 3.00 (s, 6H).

Synthesis of compound PLB6. A solution of intermediate **5** (440.4 mg, 1.2 mmol), intermediate **9** (257.0 mg, 1 mmol), and THF (20 mL) was added to a 100 mL two-necked round bottom flask. After stirring for 30 min under a nitrogen atmosphere, potassium tert-butoxide (336.0 mg, 3.0 mmol) was added. Stirring was continued for 12 h at room temperature. Filter the reaction solution. The filtrate was washed with water (3×20 mL), saturated salt water (20 mL), and extracted with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by thin-layer chromatography using silica gel (eluent: petroleum ether:dichloromethane=2:1) to obtain **PLB6**. It is a red solid with a yield of 81.47%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 3.9 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 3H), 7.12 (d, *J* = 15.7 Hz, 1H), 7.04 (d, *J* = 3.8 Hz, 1H), 7.02 – 6.92 (m, 3H), 6.86 (d, *J* = 15.8 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 3.00 (s, 6H). **HRMS** (ESI) m/z calcd for $C_{27}H_{23}N_2S_3^+$ $(M+H)^+$ 471.10179, found 471.09946.

Spectroscopy. UV-vis absorption spectra were recorded on a TU-1900 UV-vis spectrophotometer. Photoluminescence was spectra recorded on a Hitachi-F4600 fluorescence Spectrophotometer. Fluorescence quantum yields were recorded on an Edinburgh FS-5 fluorescence Spectrophotometer and referenced by integrating spheres. Fluorescence lifetimes were recorded on an Edinburgh FS-5 fluorescence Spectrophotometer and the light emitter was an Edinburgh EPLED-360.

Electrochemical. Cyclic voltammetric curves were recorded on a CHI 660E electrochemical workstation. The cyclic voltammograms of **PLB1~PLB6** (1×10^{-5} $mol\cdot L^{-1}$) were measured in THF at 298 K, $^nBu_4NPF_6$ (0.1 $mol\cdot L^{-1}$), scan rate=100 $mV\cdot s^{-1}$. The reference electrode is Ag/AgCl, the working electrode is glassy carbon, the auxiliary electrode is platinum wire, reference is ferrocenium/ferrocene (Fc^+/Fc)

redox couple.[6]

Single crystal and XRD characterization. The single crystals were obtained by slow evaporation of the solution samples (Ethanol / Dichloromethane = 2:1, v/v). The X-ray data were collected using a Bruker Smart APEX II area-detector diffractometer with graphite-monochromator Mo Kα radiation.[7] CCDC 2232818 (for **PLB1**), 2232819 (for **PLB2**), 2232820 (for **PLB3**), and 2232821 (for **PLB4**).

Fabrication of LEDs Devices. The solid material is ground and the fine powder is sieved out using a 200-mesh sieve. Then mix the powder with A/B glue (polydimethylsiloxane, purchased from Guangdong Evergrande New Material Technology Co., Ltd., the brand is kafuter, the product model is K-8810W.) and stir well. Wait for 5 min in a vacuum atmosphere to remove the gas. Apply the mixed glue to the surface of the LED chip and dry naturally. The mixed glue is deposited on commercial LEDs and dried naturally. The commercial LEDs used were all fully encapsulated hair removal chips (purchased from Hangzhou Yongdian Lighting Co., Ltd.) with 3 W power, 3.2-3.4 V voltage, and 700 mA current. The loading ratio of these compounds in the gel solution is A:B:C=100:10:x/mg (C: our compounds). The value of x for each device is shown in **Fig. S5**. Spectral parameters of LEDs recorded on Keithley 2400 source measure unit.[8,9]

Additional characterization and analysis

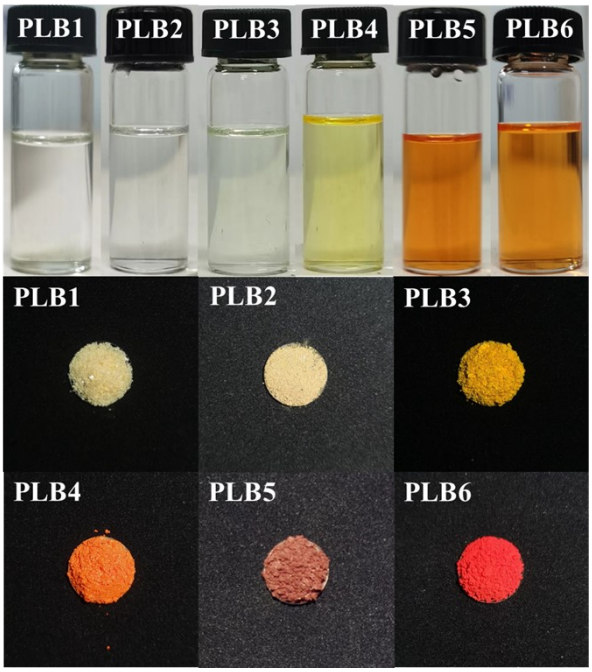


Fig. S1. Images of the six compounds in CH_2Cl_2 solution (1×10^{-5} mol L^{-1}) and solid powder state under natural lighting.

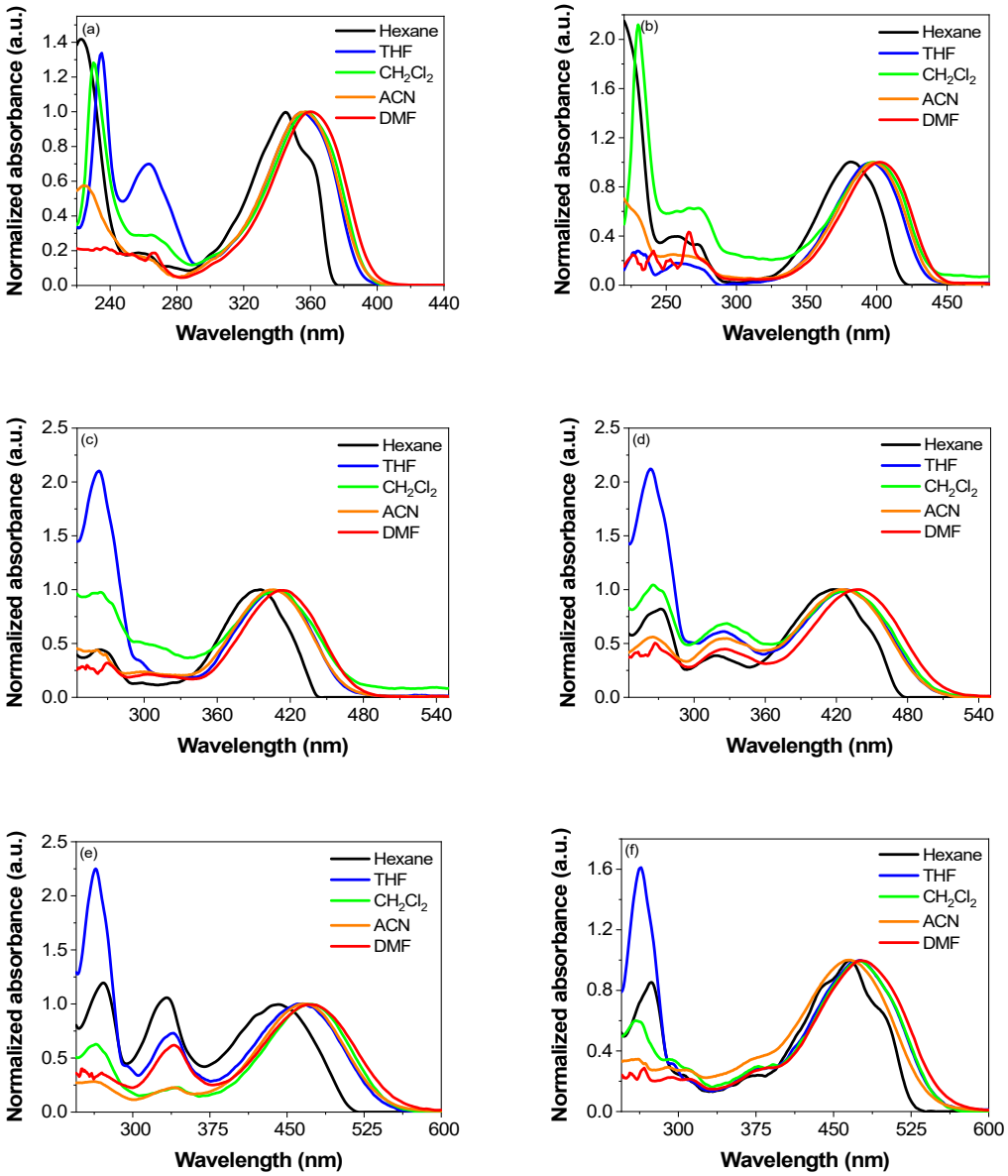
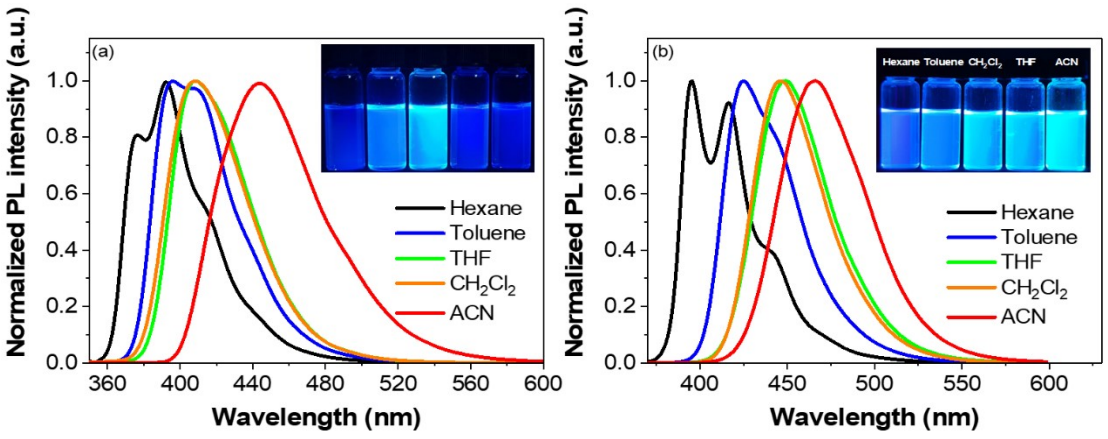


Fig. S2. (a-f) The UV-vis absorbance spectra of **PLB1~PLB6** in different polar solvents (1×10^{-5} mol L^{-1}).



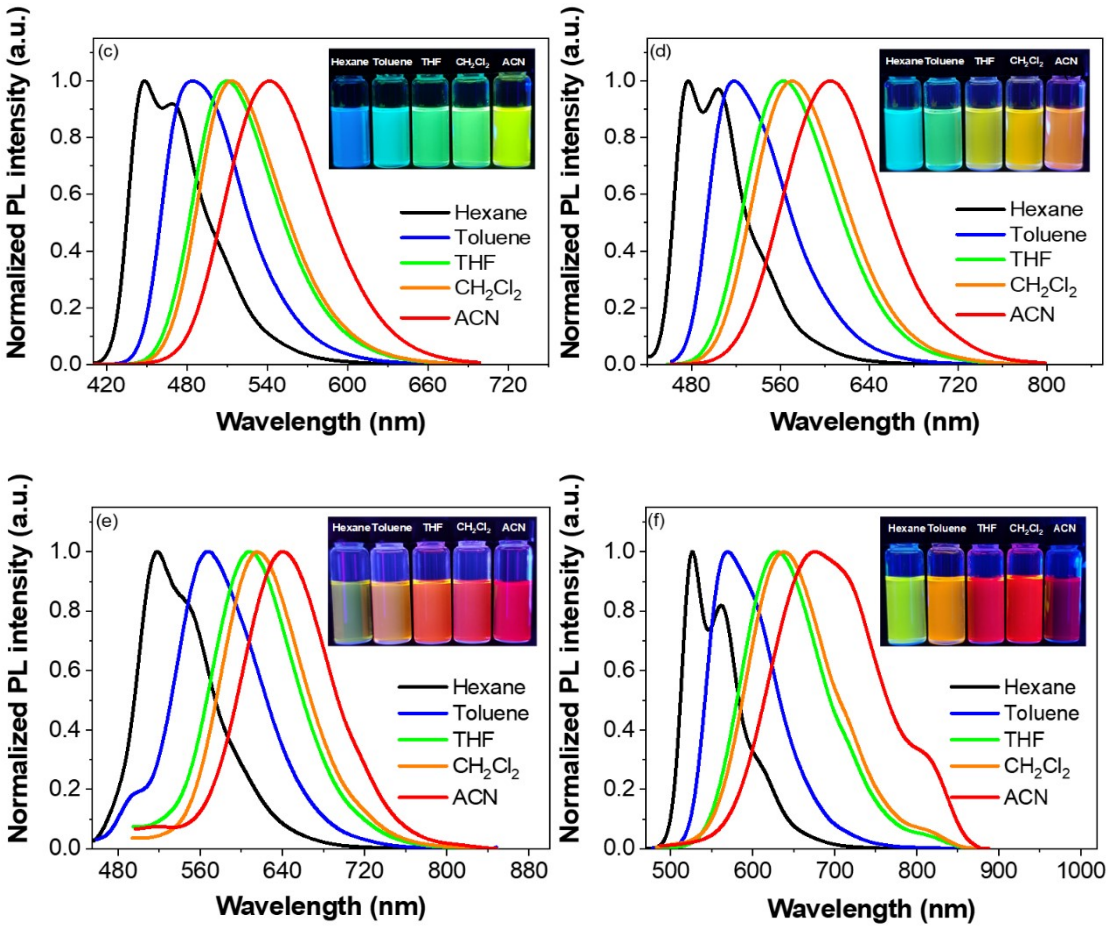


Fig. S3. (a-f) Photoluminescence spectra of **PLB1~PLB6** in different polar solvents (1×10^{-5} mol L^{-1}) and luminescence images of the six compounds under the excitation of ultraviolet light at 365 nm.

Table S1. Fluorescence quantum yield of **PLB1~PLB6** in different polar solvents

	Hexane	Toluene	CH_2Cl_2	THF	ACN
PLB1	0.499	0.984	0.965	0.698	0.631
PLB2	0.960	0.980	0.990	0.940	0.910
PLB3	0.980	0.996	0.998	0.997	0.997
PLB4	0.588	0.542	0.635	0.535	0.583
PLB5	0.023	0.045	0.114	0.097	0.140
PLB6	0.582	0.503	0.280	0.283	0.114

Table S2. Electrochemical properties of **PLB1~PLB6**.

Entry	E_{onset}^{ox} (V) [a]	E_{onset}^{red} (V) [a]	HOMO (eV) [b]	LUMO (eV) [c]	E_{gap} (eV) [d]

PLB1	1.70	-1.59	-6.10	-2.94	3.16
PLB2	1.43	-1.41	-5.83	-2.65	2.93
PLB3	1.20	-1.38	-5.60	-2.94	2.66
PLB4	1.15	-1.36	-5.55	-3.07	2.48
PLB5	0.68	-1.33	-5.08	-2.80	2.28
PLB6	-0.21	-1.27	-4.19	-1.94	2.25

[a] Oxidation and reduction potentials measured by cyclic voltammetry.

[b] $E_{HOMO} = -(E_{onset}^{ox} + 4.4)$ eV.

[c] $E_{LUMO} = E_{HOMO} + \Delta E_{gap}$.

[d] $\Delta E_{gap} = 1240/\lambda_{edge}$, estimated from the UV-vis absorption spectra.

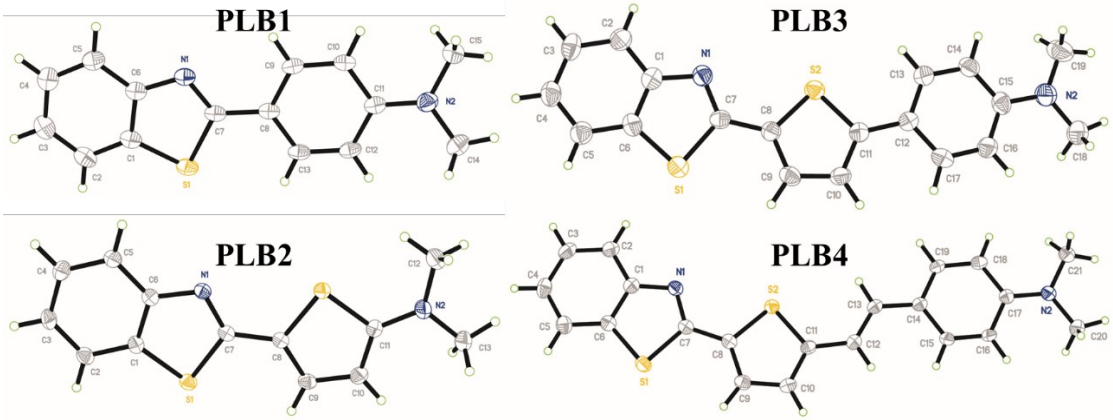


Fig. S4 Crystal structure of **PLB1**~**PLB4**.

Table S3. Crystallographic data of **PLB1**~**PLB4**

	PLB1	**PLB2**	**PLB3**	**PLB4**
formula	$C_{15}H_{14}N_2S$	$C_{13}H_{12}N_2S_2$	$C_{19}H_{17}N_2S_2$	$C_{21}H_{18}N_2S_2$
Formula weight	254.34	260.37	337.46	362.49
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	Pbca	$Pna2_1$	$Pna2_1$	$P2_12_12_1$
a, Å	10.9301(7)	19.7351(8)	25.7622(18)	5.95260(10)
b, Å	7.7862(4)	10.4230(4)	10.7438(7)	7.5011(2)
c, Å	29.5973(15)	5.9647(2)	5.8585(4)	40.2359(9)
α, deg	90	90	90	90
β, deg	90	90	90	90
γ, deg	90	90	90	90
V, Å^3	2518.8(2)	1226.93(8)	1621.54(19)	1796.58(7)
Z	8	4	4	4

ρ_{calcd}, g cm^{-3}	1.341	1.410	1.382	1.340
T / K	296(2)	193.00	193.00	193.00
μ, mm^{-1}	0.239	3.737	2.961	2.713
θ	5.506-50.01	8.962-136.156	6.862-136.548	8.79-136.46
F (000)	1072.0	544.0	708.0	760.0
Index ranges	-13 ⩽ h ⩽ 10 -9 ⩽ k ⩽ 8 -35 ⩽ l ⩽ 35	-22 ⩽ h ⩽ 23 -12 ⩽ k ⩽ 12 -6 ⩽ l ⩽ 7	-24 ⩽ h ⩽ 31 -12 ⩽ k ⩽ 8 -7 ⩽ l ⩽ 6	-4 ⩽ h ⩽ 7 -9 ⩽ k ⩽ 9 -48 ⩽ l ⩽ 48
Data / restraints / parameters	2204/0/165	2086/1/156	2662/1/211	3198/0/228
GOF (F^2)	1.015	1.066	1.021	1.051
$R_1{}^a$,$wR_2{}^b$ (I>2σ(I))	0.0345, 0.1013	0.0313, 0.0825	0.0632, 0.1502	0.0349, 0.0824
$R_1{}^a$, $wR_2{}^b$	0.0400, 0.1083	0.0331, 0.0839	0.1004, 0.1763	0.0398, 0.0849

$R_1{}^a = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2{}^b = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^1$

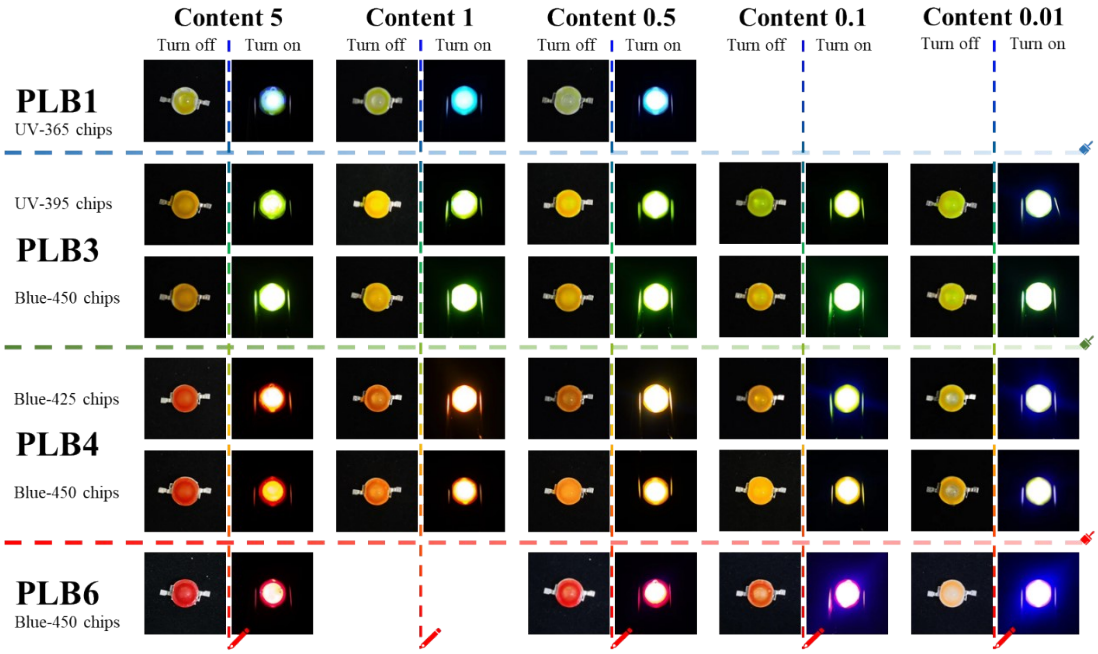


Fig. S5. Turn on and turn off photos of the LEDs prepared by **PLB1**、**PLB3**、**PLB4** and **PLB6** on different doping amounts and different excitation chips. The content is the doping mass (mg) of each compound in 110 mg (100 mg A glue +10 mg B glue) AB glue.

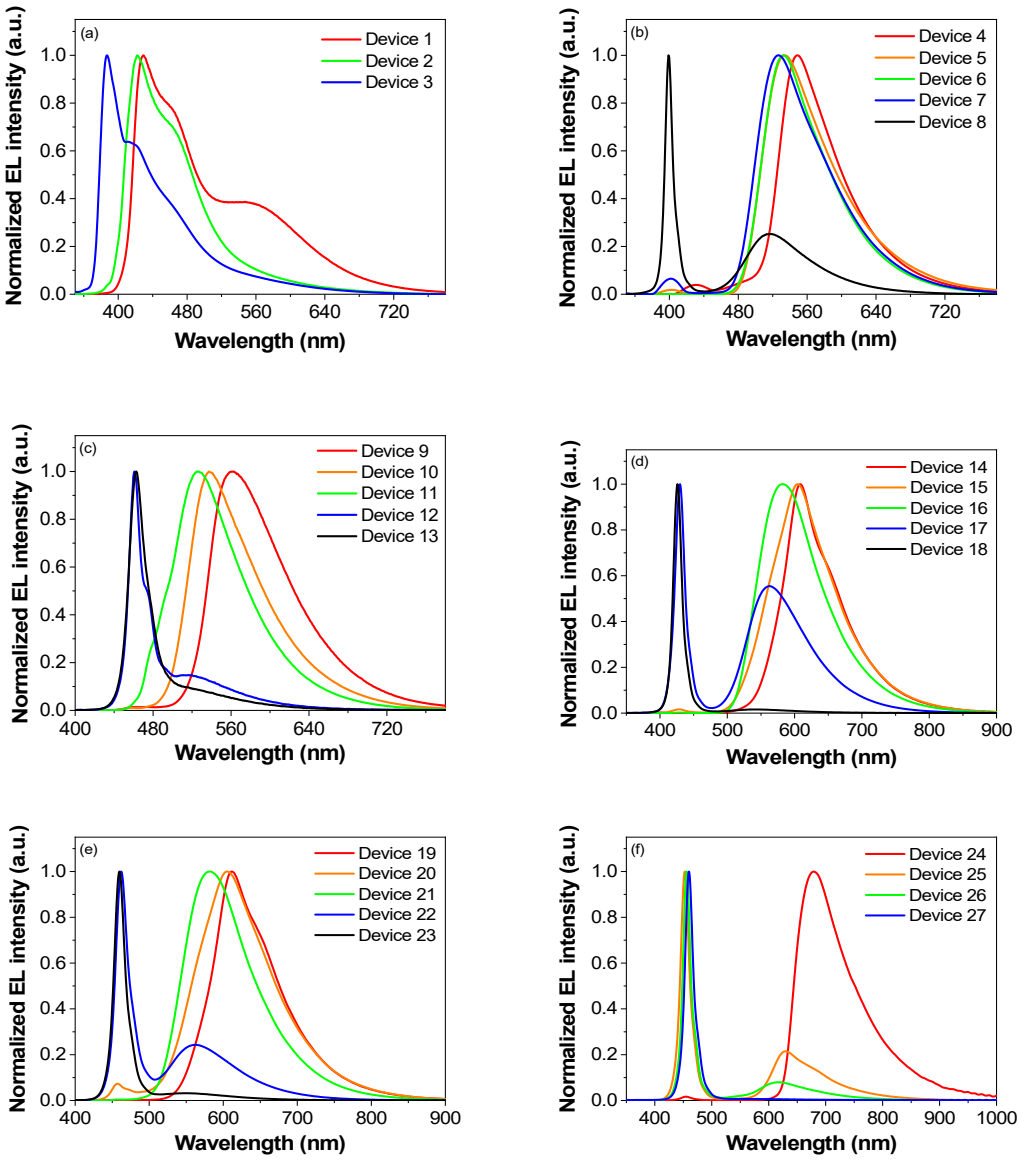


Fig. S6. (a) Spectra of devices made from **PLB1** and UV-365 chips. (b) Spectra of devices made from **PLB3** and UV-395 chips. (c) Spectra of devices made from **PLB3** and Blue-450 chips. (d) Spectra of devices made from **PLB4** and Blue-425 chips. (e) Spectra of devices made from **PLB4** and Blue-450 chips. (f) Spectra of devices made from **PLB6** and Blue-450 chips.

Table S4. The spectral parameters of LEDs device.

Entry	Cpd.	Content (%)	Chips	wavelength （nm）	CIE	CCT (K)	CRI	Efficiency (lm/W)
1	PLB1	5	UV365	429	(0.25, 0.24)	27431	42	79.47
2	PLB1	1	UV365	412	(0.18, 0.18)	6596	40	52.42
3	PLB1	0.5	UV365	384	(0.19, 0.15)	7325	51	31.73
4	PLB3	5	UV395	552	(0.49, 0.51)	3491	27	156.32
5	PLB3	1	UV395	533	(0.38, 0.58)	4678	22	165.55
6	PLB3	0.5	UV395	533	(0.37, 0.59)	4902	18	172.88
7	PLB3	0.1	UV395	525	(0.36, 0.58)	5081	29	162.55

8	PLB3	0.01	UV395	396	(0.29, 0.50)	6569	47	99.39
9	PLB3	5	Blue450	561	(0.48, 0.51)	3108	17	158.31
10	PLB3	1	Blue450	538	(0.33, 0.56)	5514	31	161.28
11	PLB3	0.5	Blue450	513	(0.26, 0.35)	9595	64	106.48
12	PLB3	0.1	Blue450	459	(0.18, 0.20)	6614	49	74.63
13	PLB3	0.01	Blue450	458	(0.16, 0.15)	7821	25	155.92
14	PLB4	5	Blue425	609	(0.60, 0.40)	1719	-	90.14
15	PLB4	1	Blue425	605	(0.55, 0.44)	1930	-	110.65
16	PLB4	0.5	Blue425	580	(0.51, 0.48)	2551	1	135.27
17	PLB4	0.1	Blue425	429	(0.37, 0.36)	4290	60	115.81
18	PLB4	0.01	Blue425	426	(0.19, 0.06)	1731	-	18.70
19	PLB4	5	Blue450	613	(0.61, 0.39)	1751	-	82.42
20	PLB4	1	Blue450	605	(0.54, 0.43)	2001	-	104.98
21	PLB4	0.5	Blue450	581	(0.51, 0.48)	2554	-	135.74
22	PLB4	0.1	Blue450	456	(0.28, 0.27)	11580	80	95.31
23	PLB4	0.01	Blue450	452	(0.17, 0.11)	2659	-	44.04
24	PLB6	5	Blue450	678	(0.69, 0.27)	7855	-	7.65
25	PLB6	0.5	Blue450	450	(0.26, 0.10)	2020	-	81.83
26	PLB6	0.1	Blue450	450	(0.22, 0.10)	1733	-	39.74
27	PLB6	0.01	Blue450	452	(0.15, 0.05)	1766	-	23.69
28	-	-	Blue425	426	(0.17, 0.01)	1858	-	5.36
29	-	-	Blue450	449	(0.14, 0.05)	1760	-	20.74
30	-	-	Green	523	(0.23, 0.72)	6948	-	206.21
31	-	-	Yellow	594	(0.54, 0.45)	2080	-	128.97
32	-	-	Red	622	(0.68, 0.32)	4207	-	98.28
33	-	-	White1	443	(0.28, 0.27)	8397	78	109.52
34	-	-	White2	447	(0.37, 0.37)	4160	63	122.79
35	-	-	UV395	398	(0.19, 0.07)	-	-	3.03
36	-	-	UV365	369	-	-	-	-

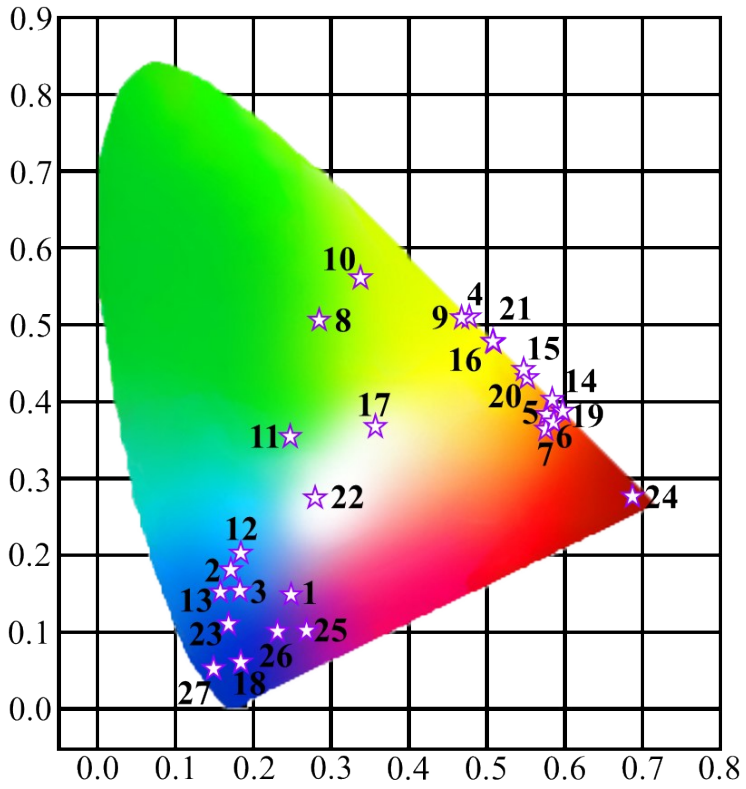


Fig. S7. The chromaticity coordinate chart of LED Devices.

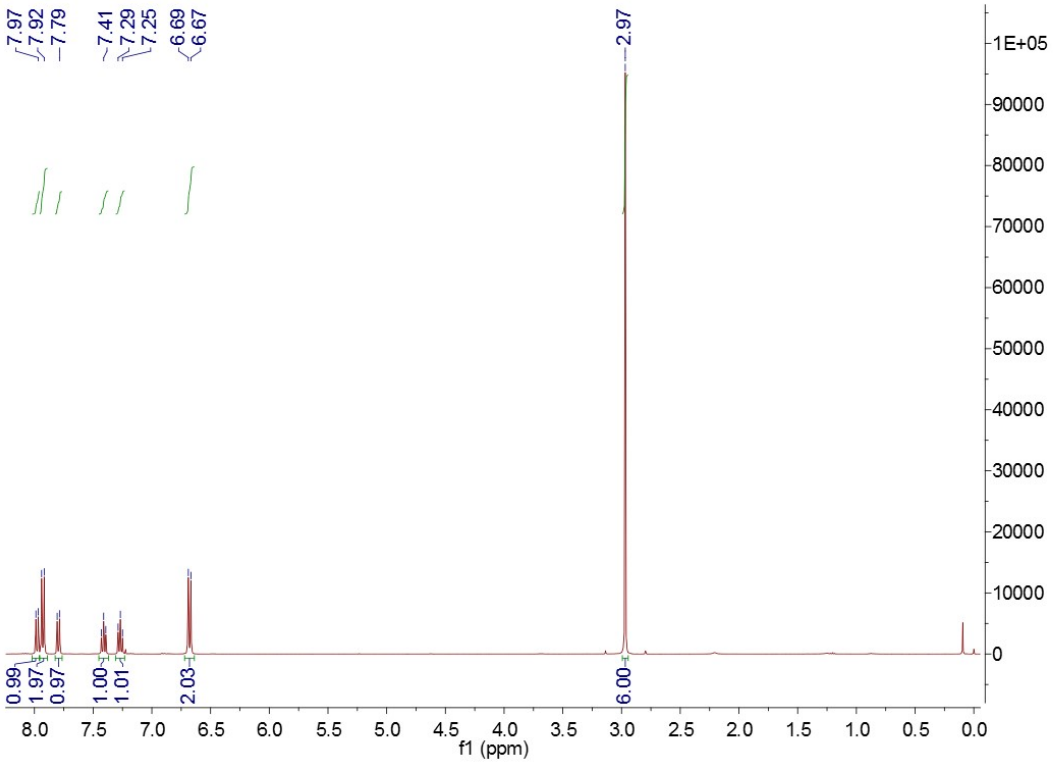


Fig. S8. ^{1}H NMR spectrum of **PLB1** (400 MHz, $CDCl_3$)

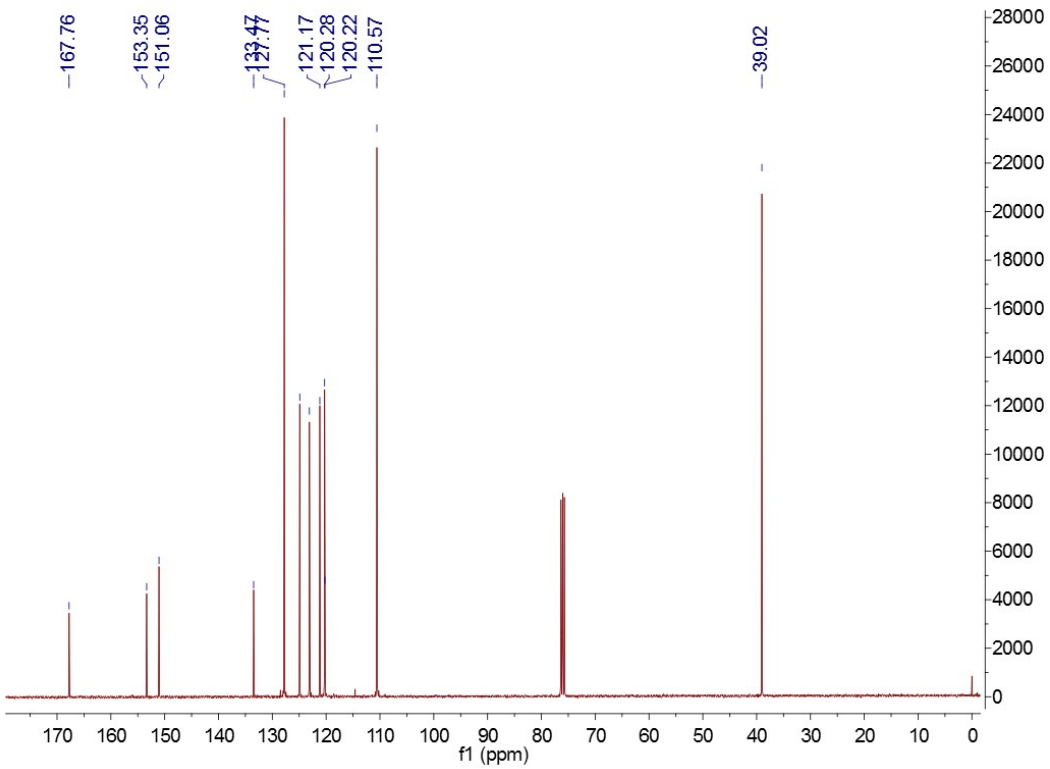


Fig. S9. ^{13}C NMR spectrum of **PLB1** (400 MHz, $CDCl_3$)

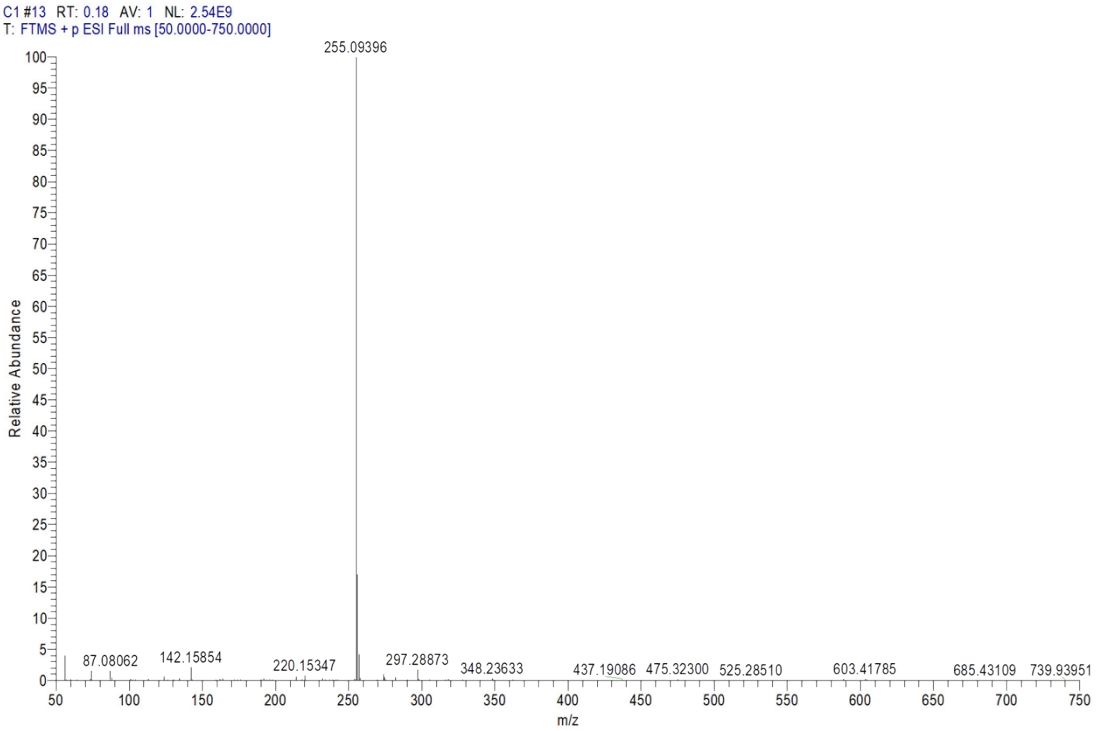


Fig. S10. Mass spectrum of **PLB1**

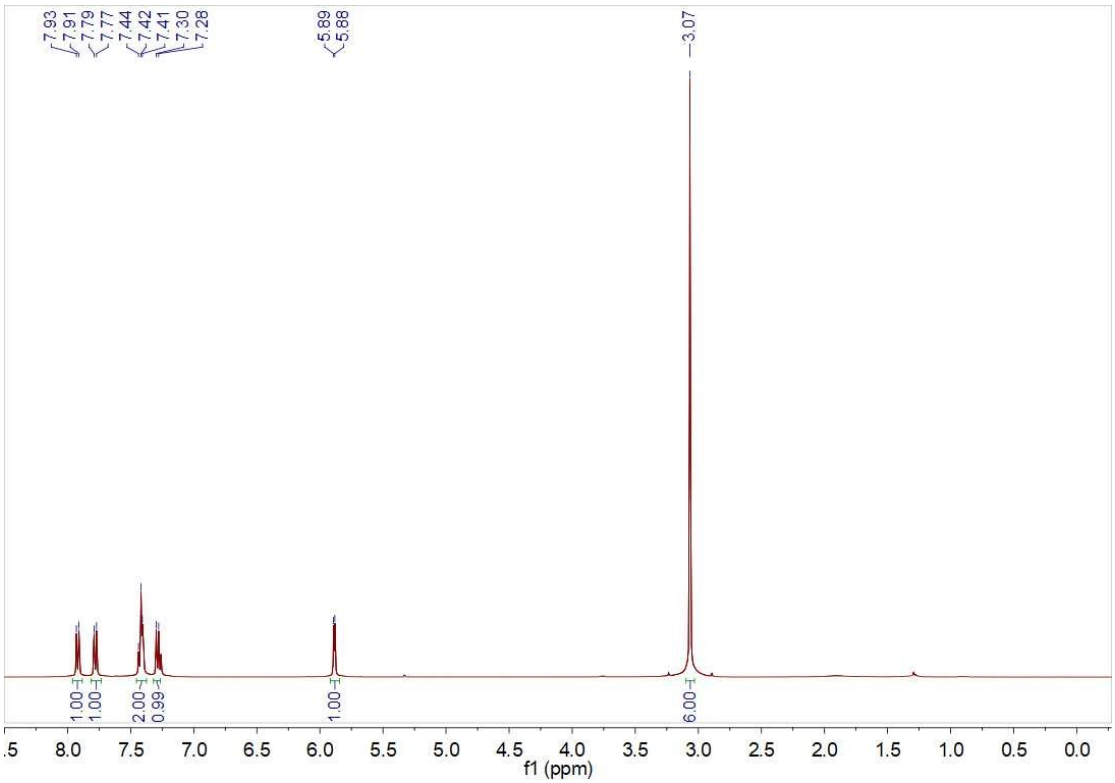


Fig. S11. ^{1}H NMR spectrum of **PLB2** (400 MHz, $CDCl_3$)

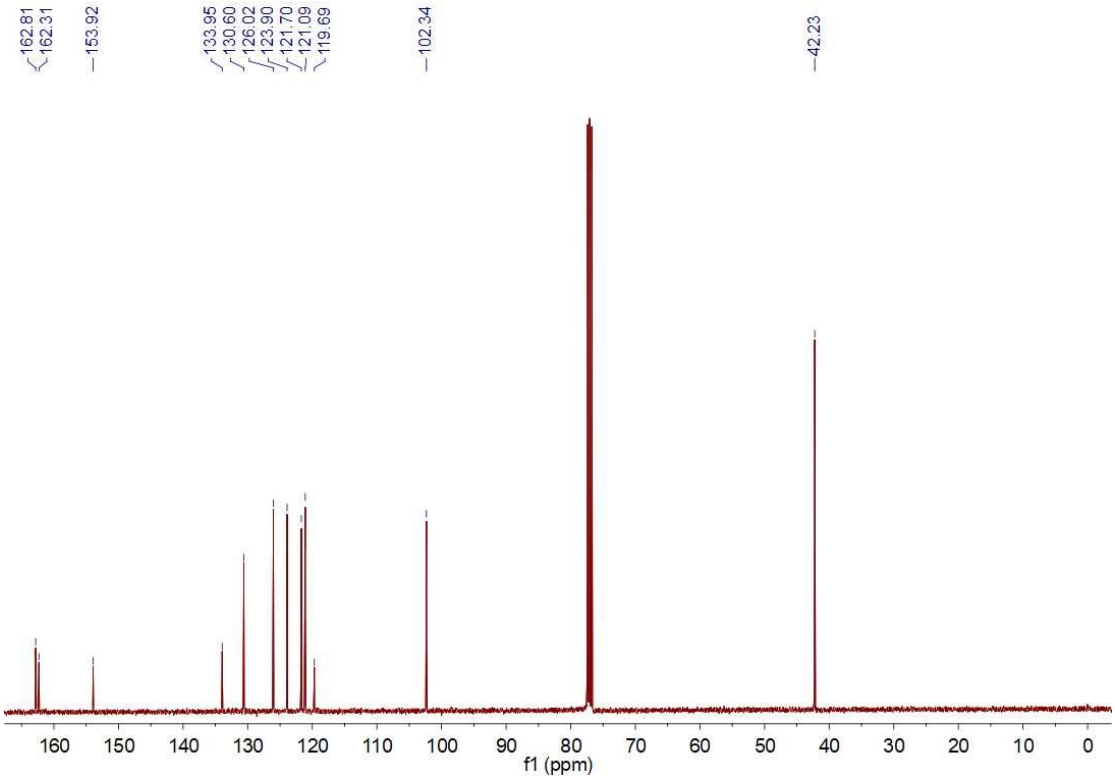


Fig. S12. ^{13}C NMR spectrum of **PLB2** (400 MHz, $CDCl_3$)

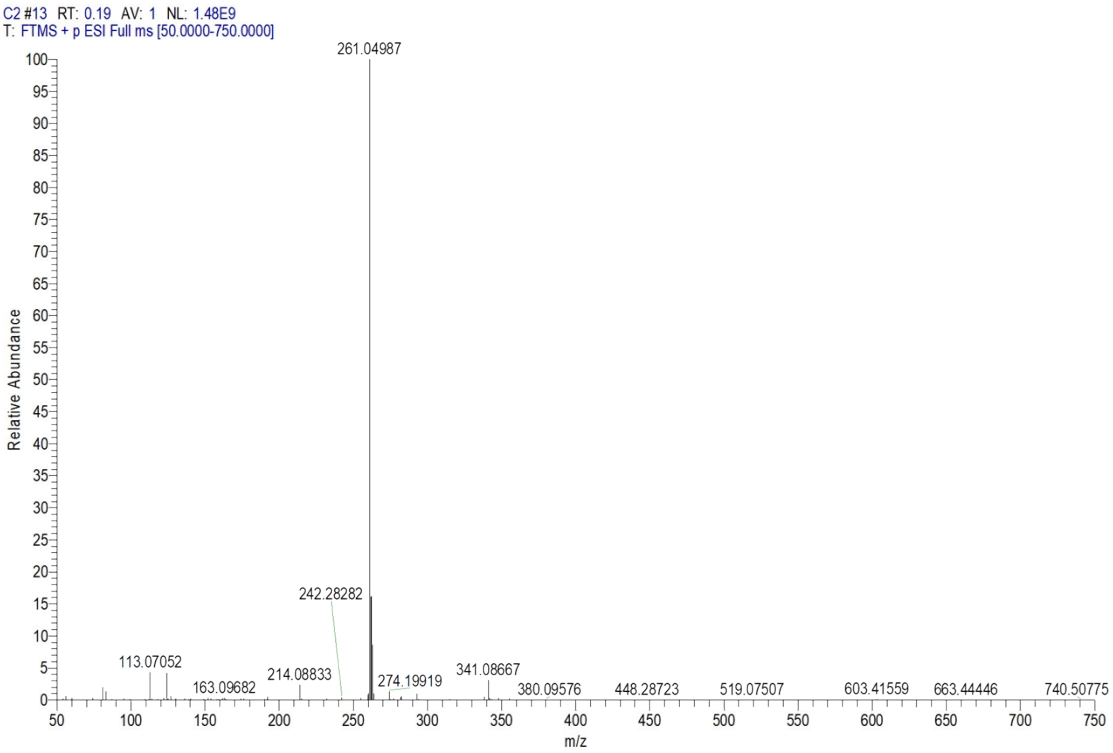


Fig. S6. Mass spectrum of **PLB2**

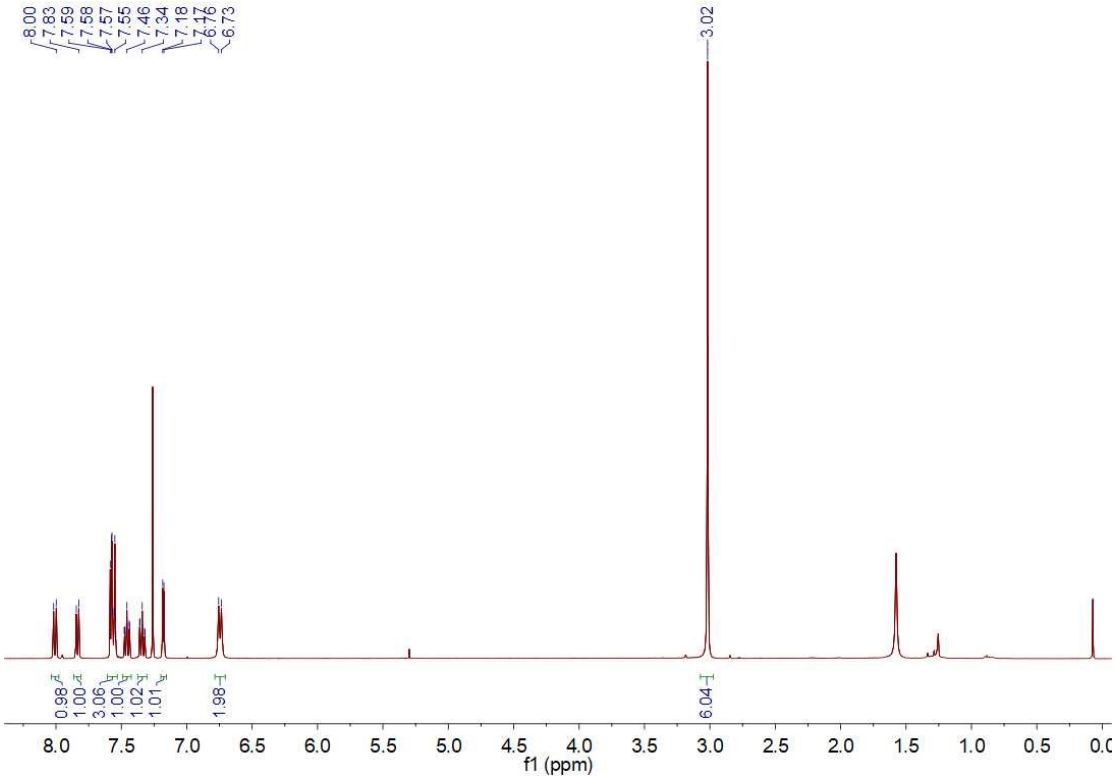


Fig. S13. ^{1}H NMR spectrum of **PLB3** (400 MHz, $CDCl_3$)

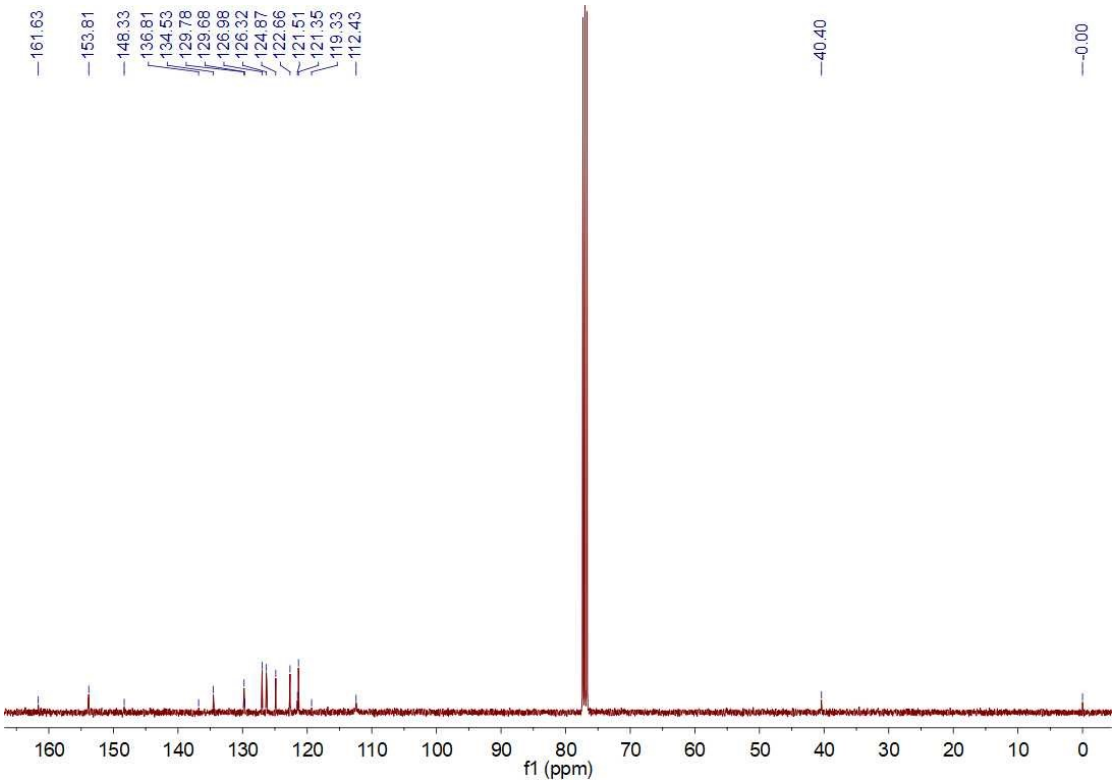


Fig. S14. ^{13}C NMR spectrum of **PLB3** (400 MHz, $CDCl_3$)

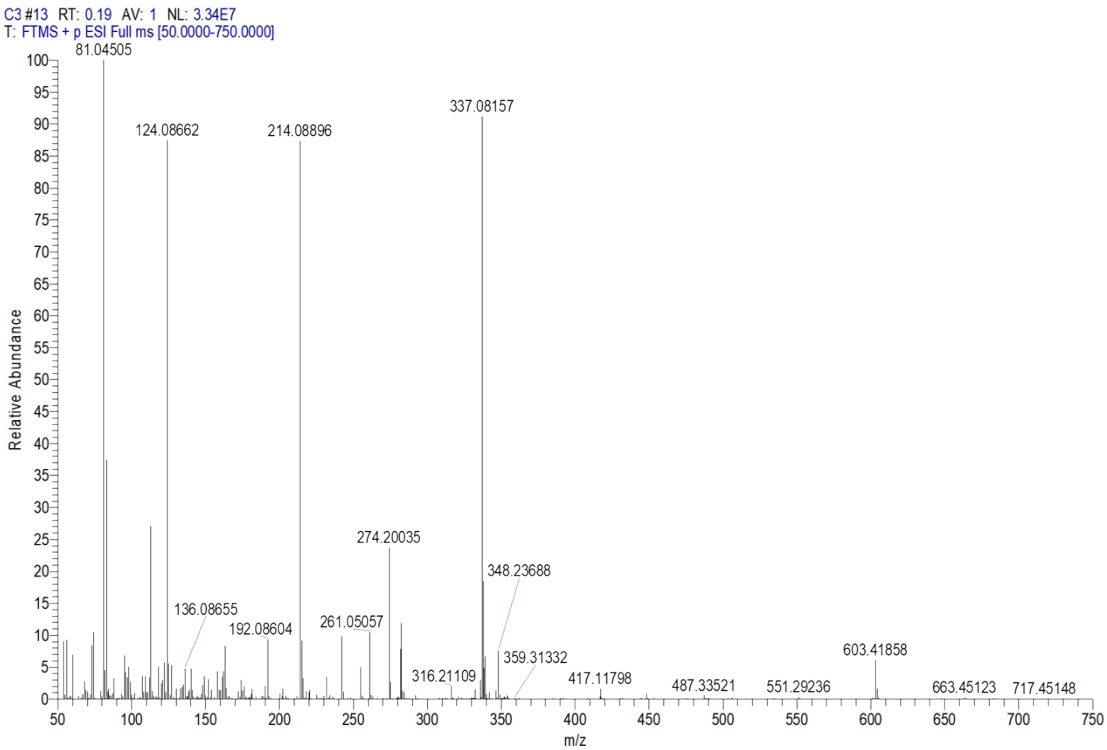


Fig. S15. Mass spectrum of **PLB3**

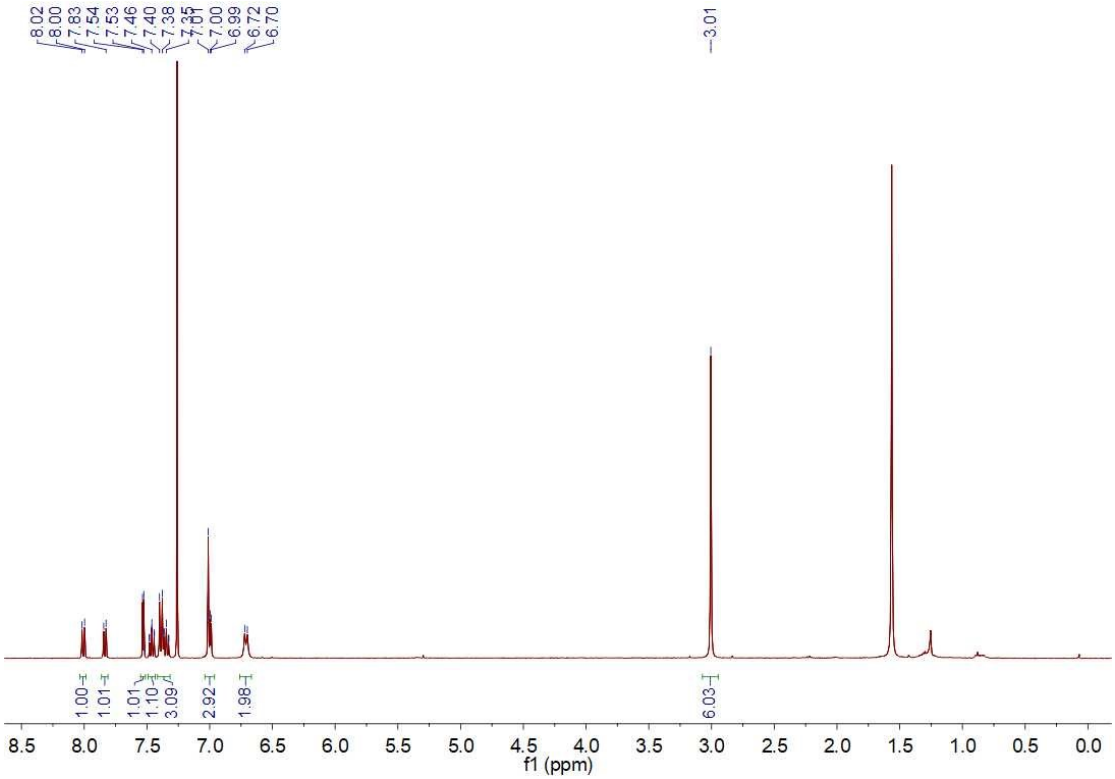


Fig. S16. ^{1}H NMR spectrum of **PLB4** (400 MHz, $CDCl_3$)

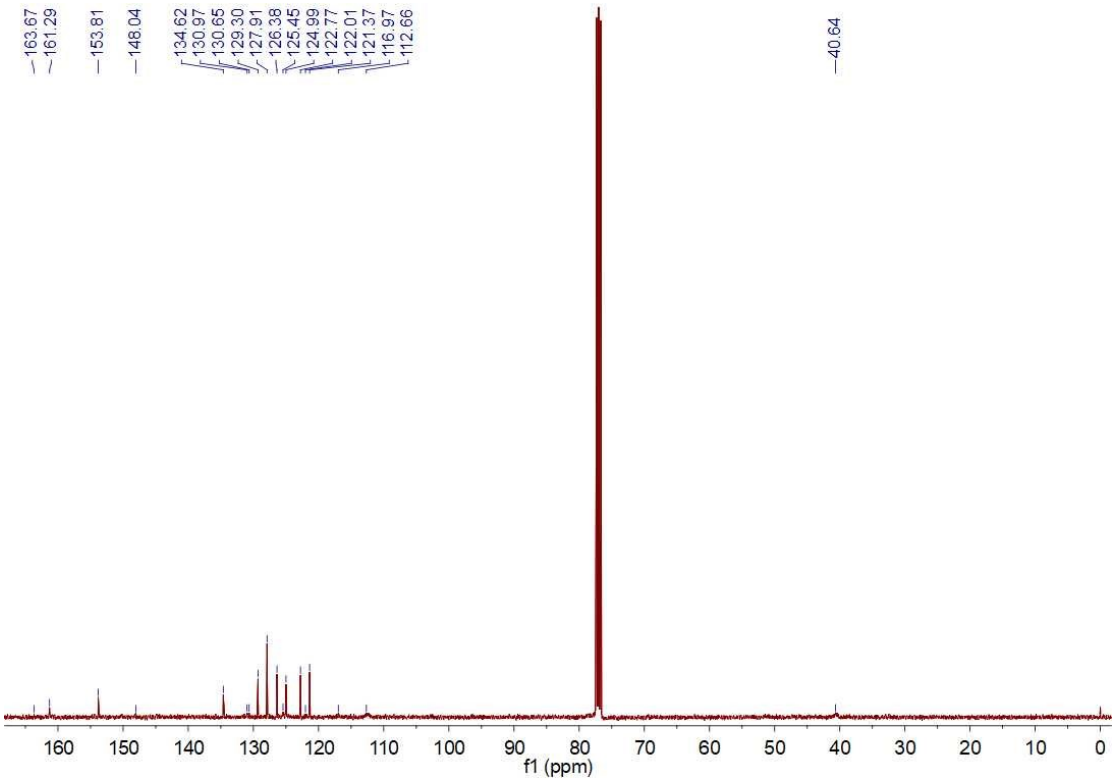


Fig. S17. ^{13}C NMR spectrum of **PLB4** (400 MHz, $CDCl_3$)

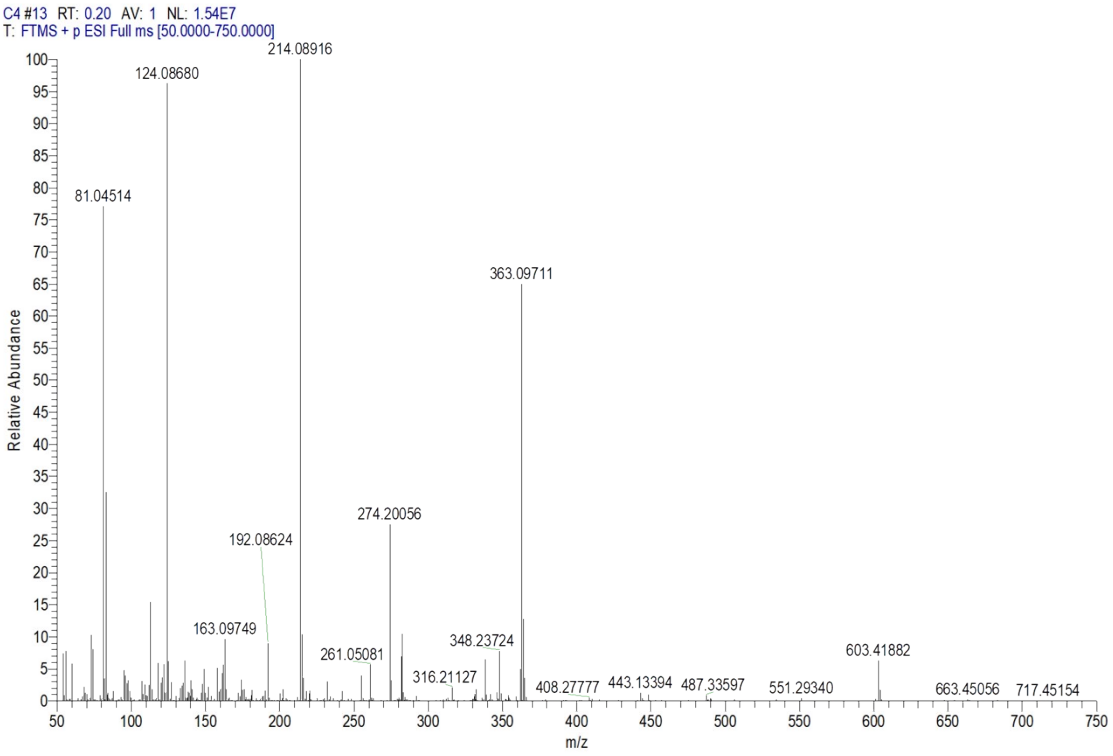


Fig. S18. Mass spectrum of **PLB4**

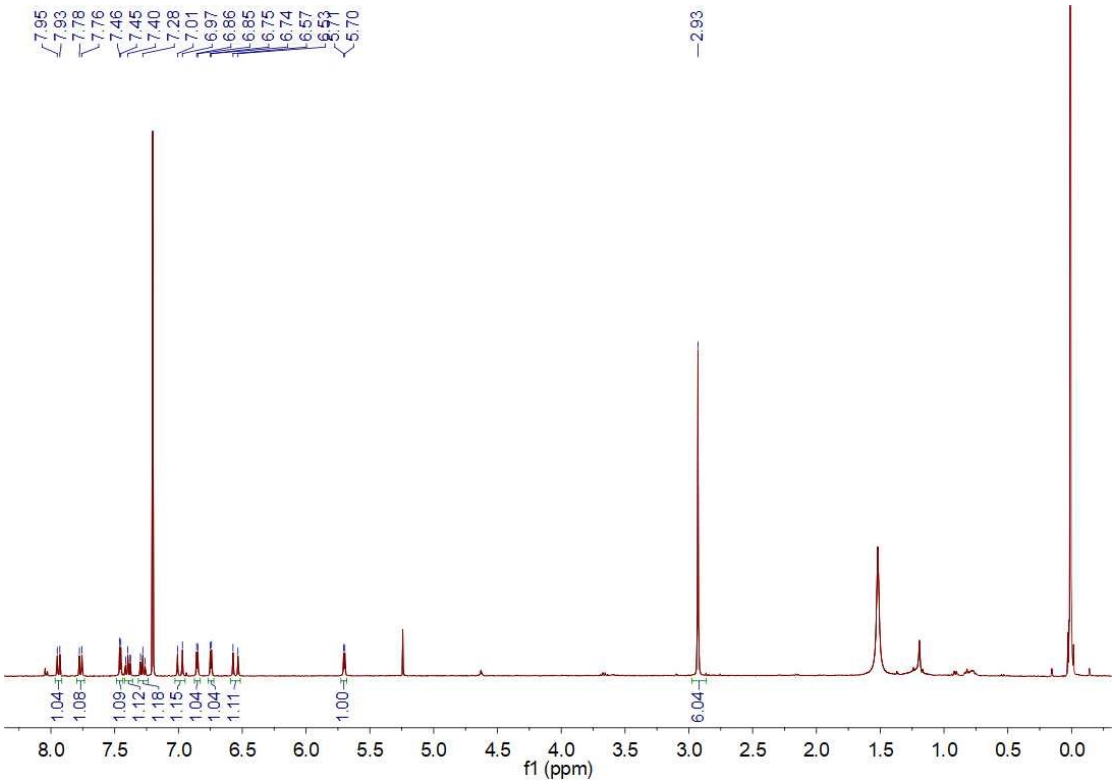


Fig. S19. ^{1}H NMR spectrum of **PLB5** (400 MHz, $CDCl_3$)

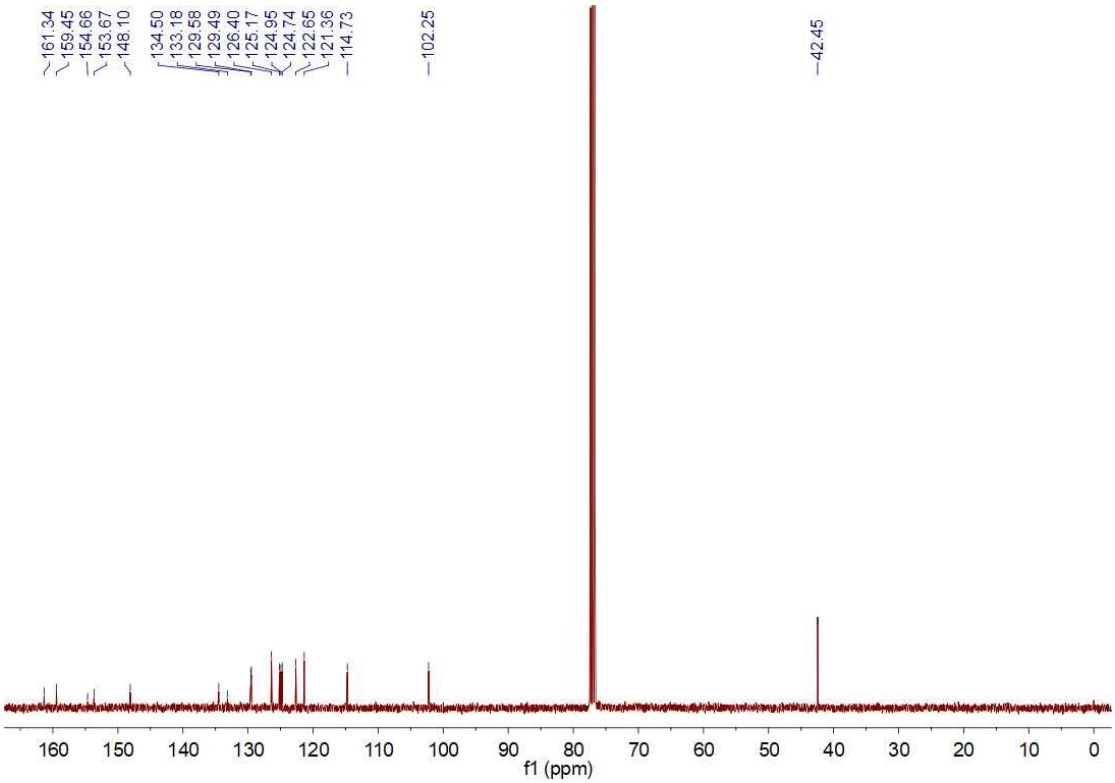


Fig. S20. ^{13}C NMR spectrum of **PLB5** (400 MHz, $CDCl_3$)

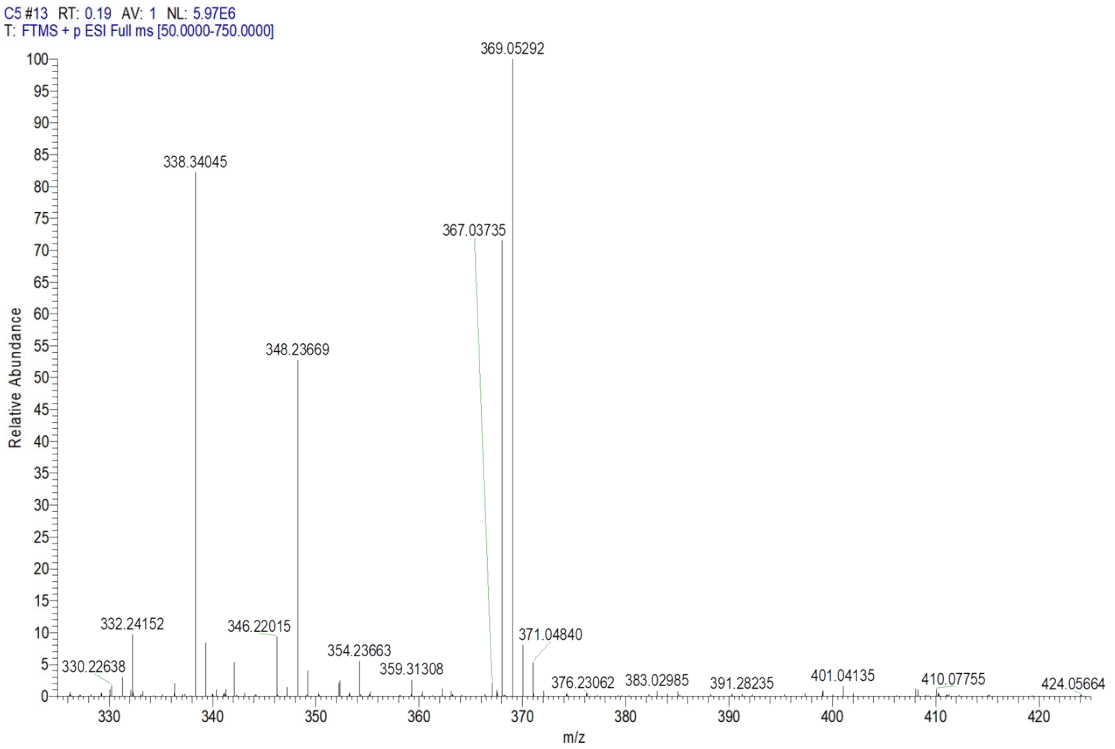


Fig. S21. Mass spectrum of **PLB5**

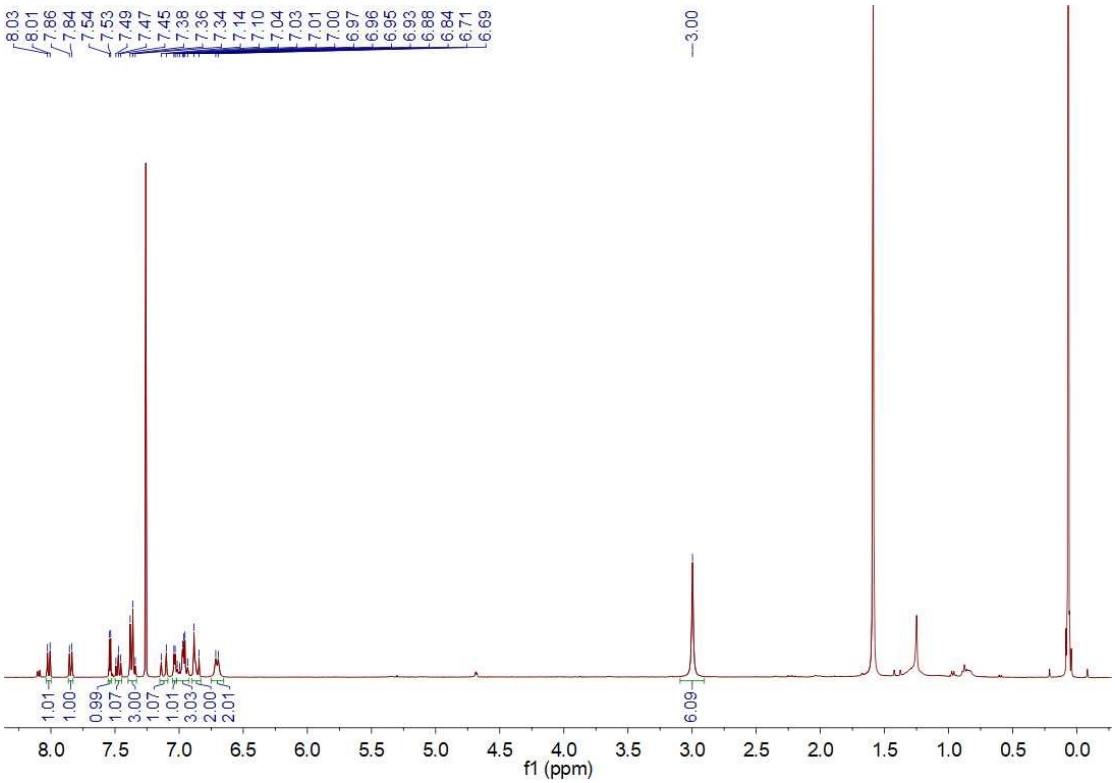


Fig. S22. ^{1}H NMR spectrum of **PLB6** (400 MHz, $CDCl_3$)

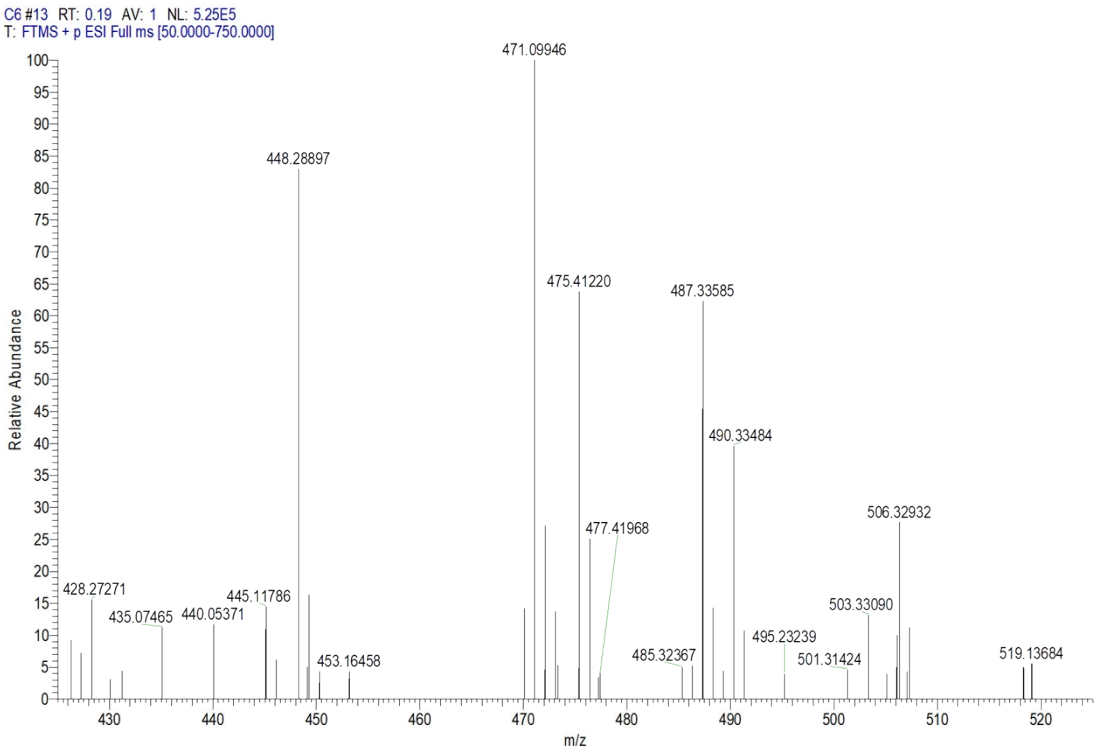


Fig. S23. Mass spectrum of **PLB6**

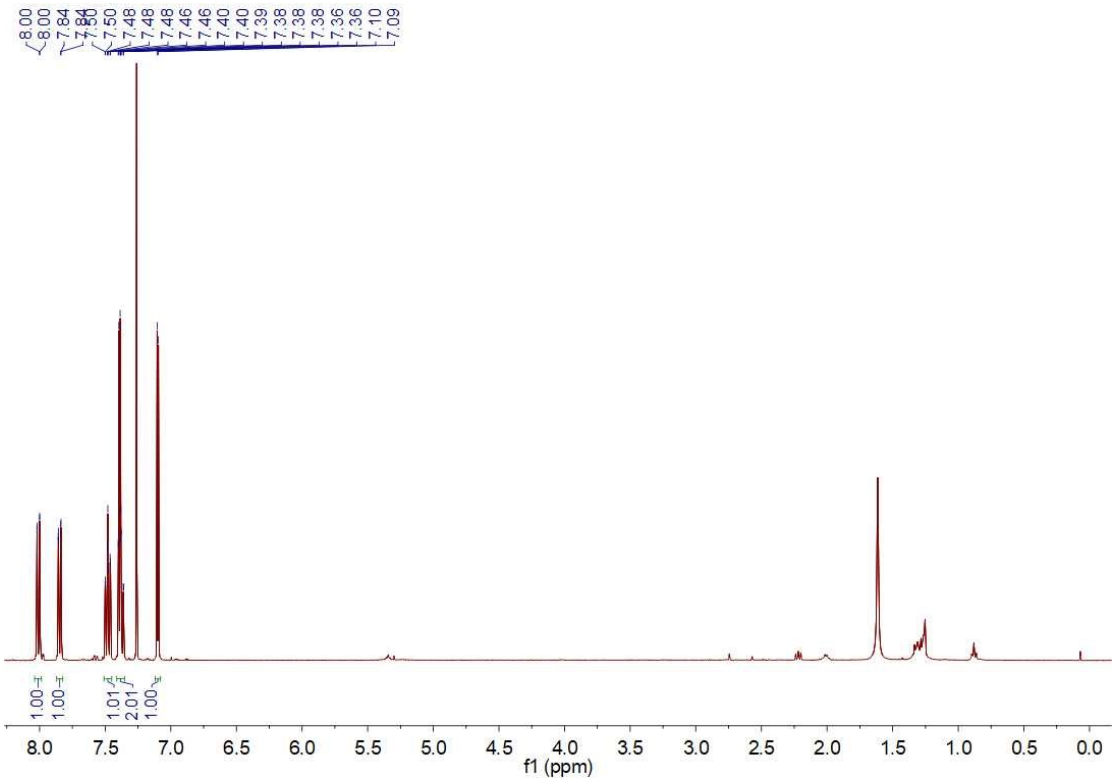


Fig. S24. ^{1}H NMR spectrum of intermediate **2a** (400 MHz, $CDCl_3$)

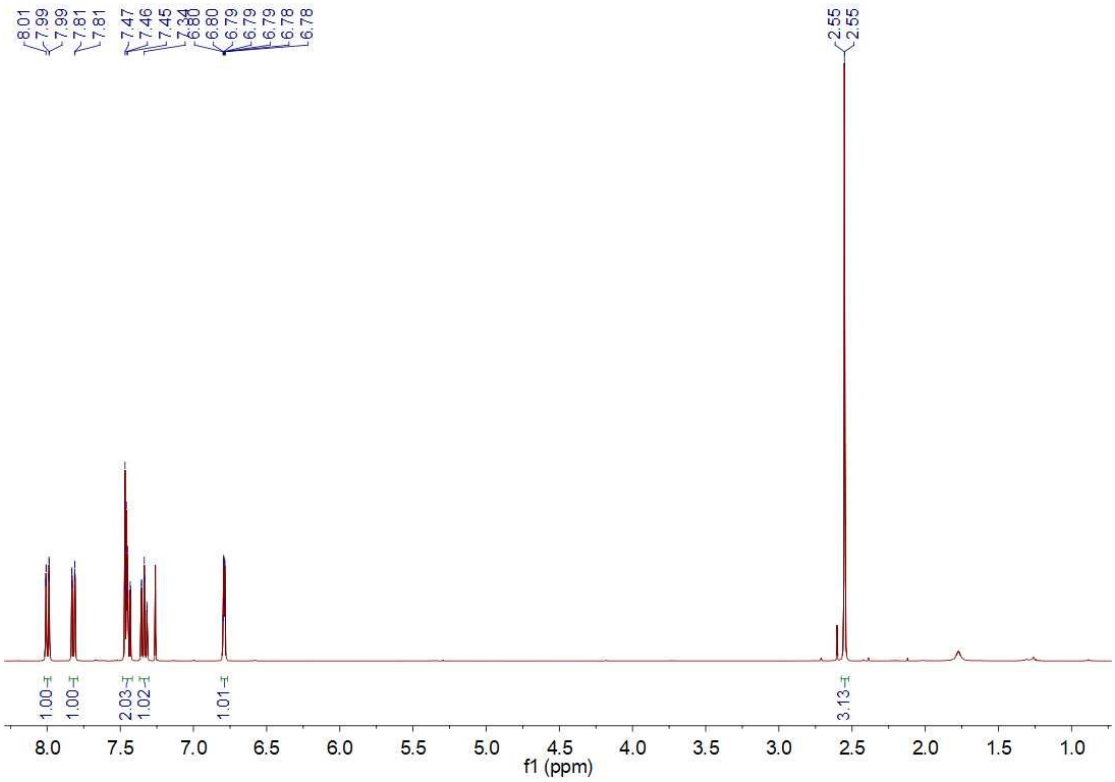


Fig. S25. ^{1}H NMR spectrum of intermediate **2b** (400 MHz, $CDCl_3$)

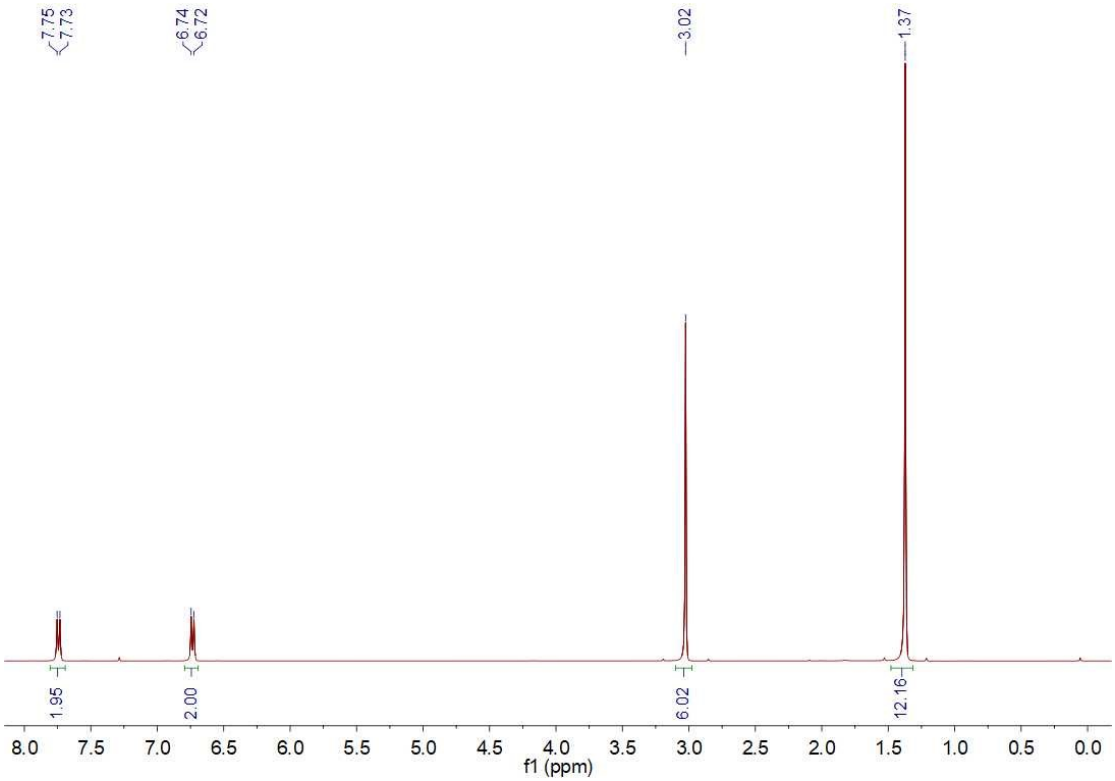


Fig. S26. ^{1}H NMR spectrum of intermediate **4** (400 MHz, $CDCl_3$)

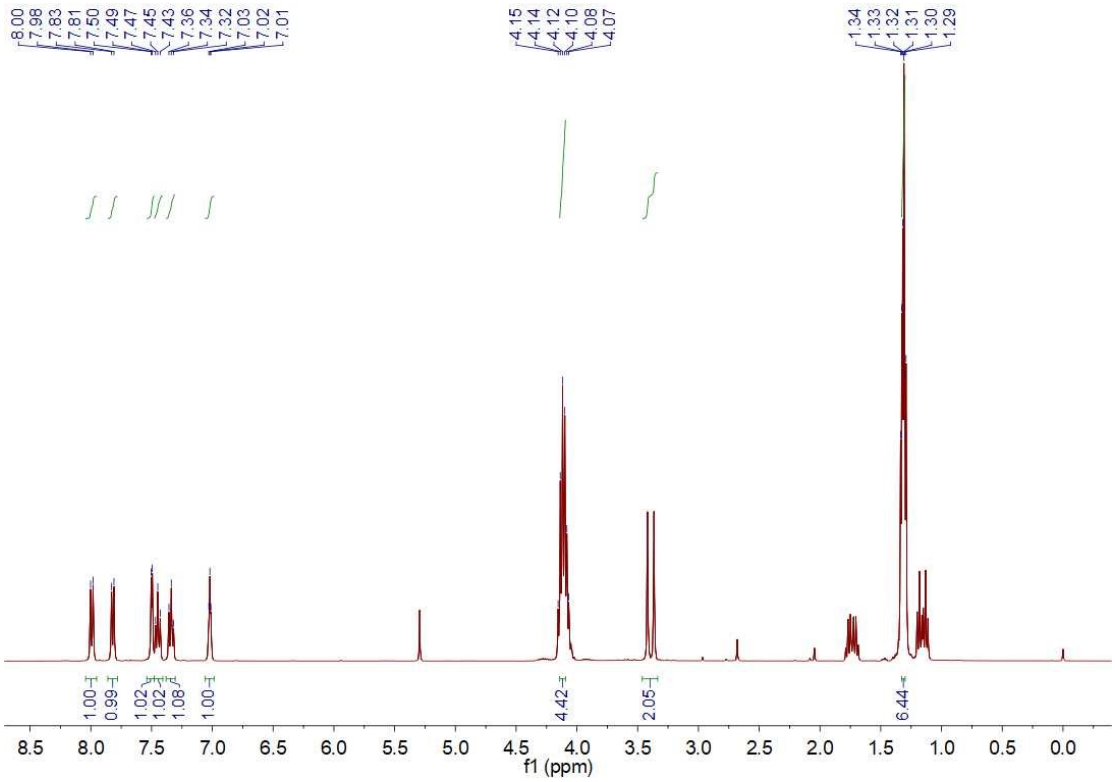


Fig. S27. ^{1}H NMR spectrum of intermediate **5** (400 MHz, $CDCl_3$)

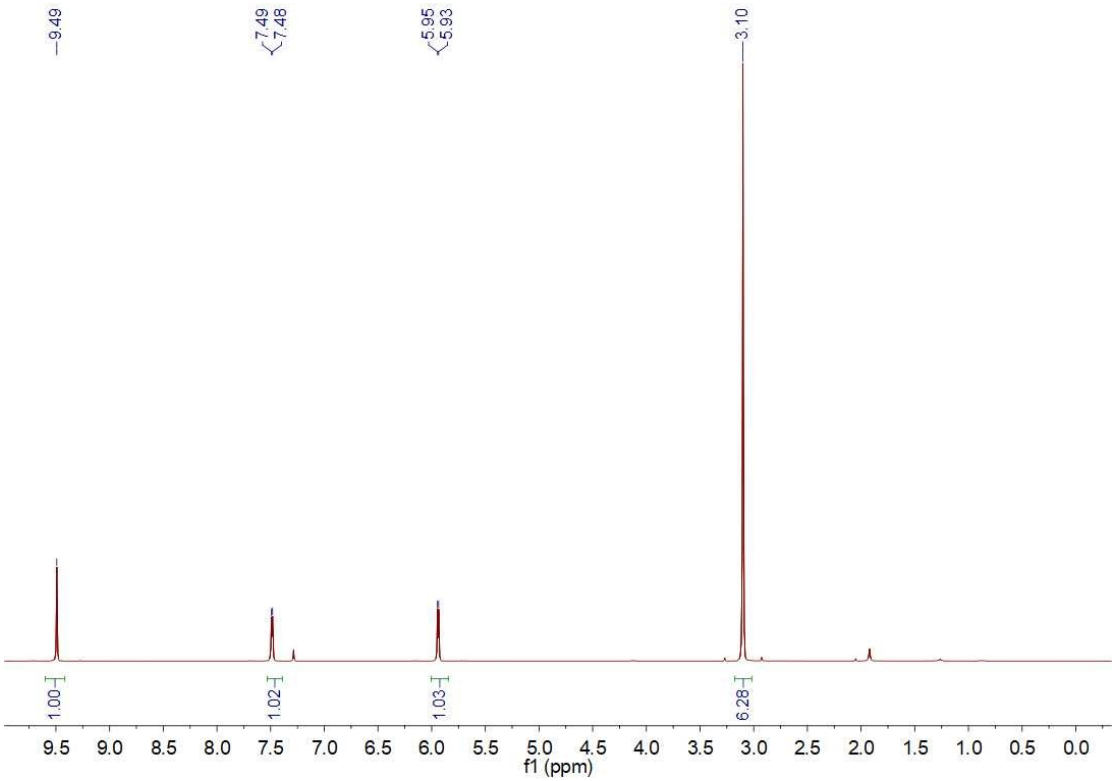


Fig. S28. ^{1}H NMR spectrum of intermediate **7** (400 MHz, $CDCl_3$)

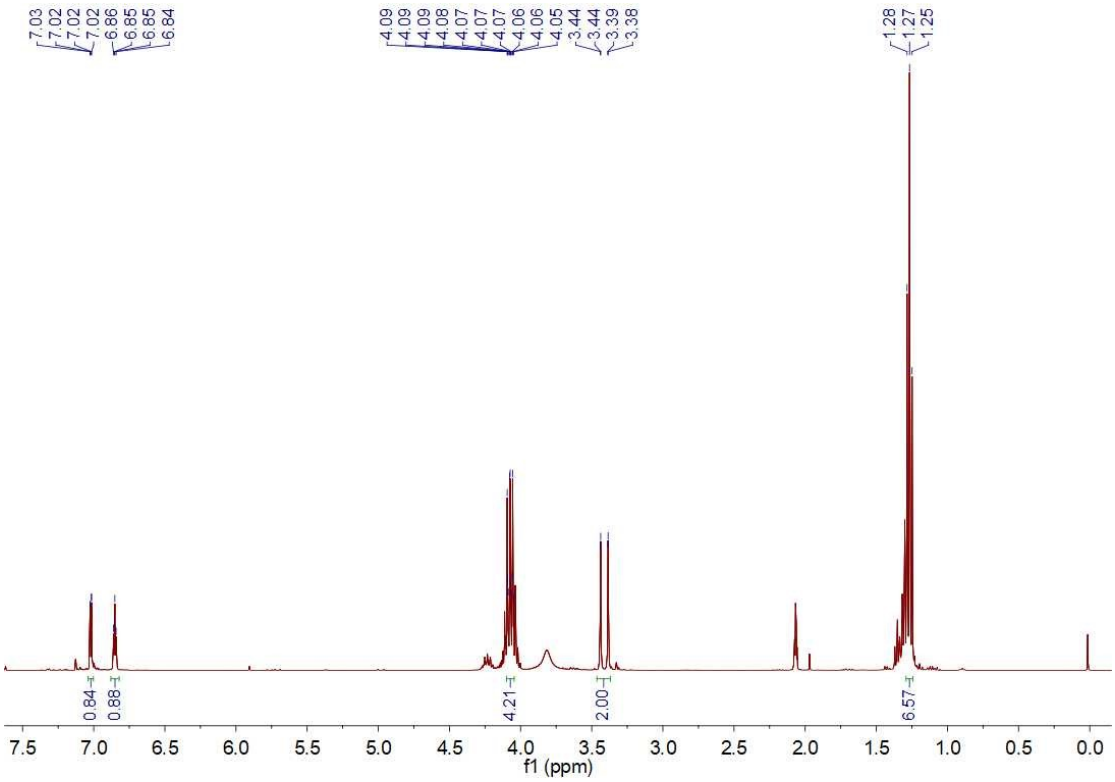


Fig. S29. ^{1}H NMR spectrum of intermediate **9** (400 MHz, $CDCl_3$)

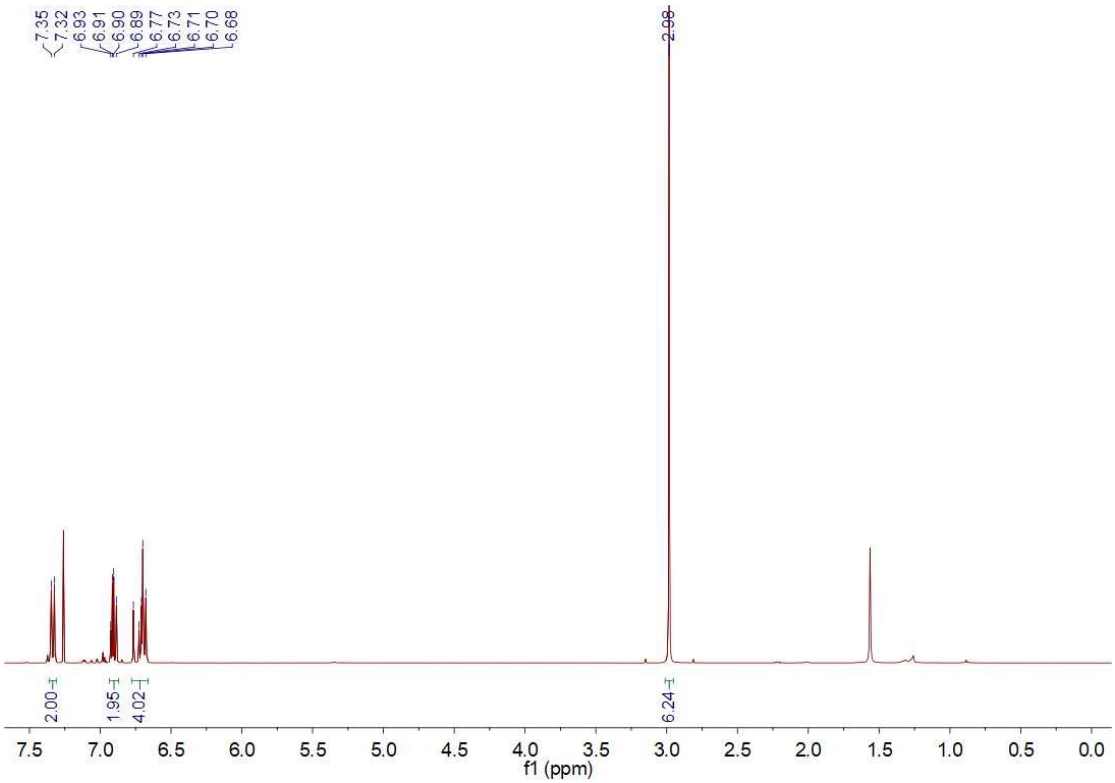


Fig. S30. ^{1}H NMR spectrum of intermediate **10** (400 MHz, $CDCl_3$)

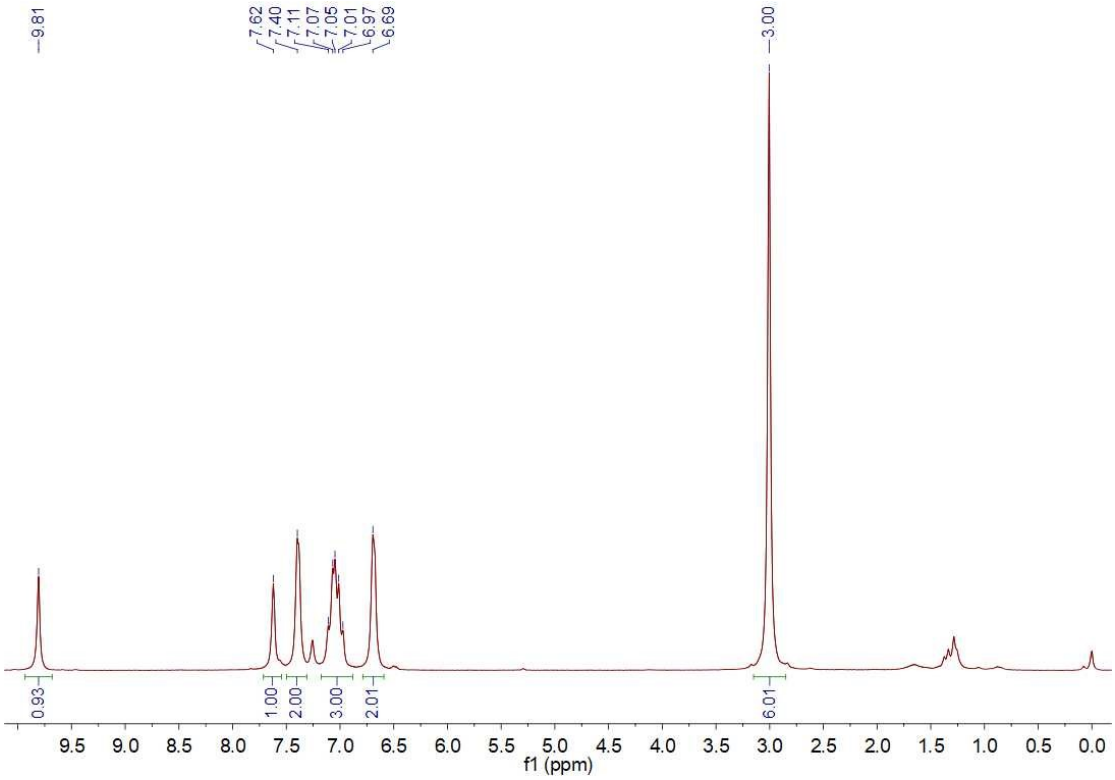


Fig. S31. ^{1}H NMR spectrum of intermediate **11** (400 MHz, $CDCl_3$)

References

1. L. Wang, H. Yin, M.A. Jabed, et al. π-Expansive Heteroleptic Ruthenium(II) Complexes as Reverse Saturable Absorbers and Photosensitizers for Photodynamic Therapy. *Inorg. Chem.* **2017**, 56 (6), 3245–3259.
2. Y. Liu, X. Li, Q. Liu, X. Li, H. Liu. Electromagnetic Mill Promoted Mechanochemical Solvent-Free Palladium-Catalyzed Borylation of Aryl Bromides. *Org. Lett.* **2022**, 24 (36), 6604–6608.
3. H. Su, R. Liu, M. Shu, et al. Fluorenone-based organogel and self-assembled fibrous film: Synthesis, optical properties and reversible detection of aniline vapor. *Dyes and Pigments* **2019**, 162, 52–58.
4. L. Duan, J. Chen, B. Liu, et al. The A-D-A type small molecules with isomeric benzodithiophene cores: Synthesis and influence of isomers on photoelectronic properties. *Tetrahedron* **2017**, 73 (5), 550–557.
5. R.D.A. Hudson, A.R. Manning, J.F. Gallagher, et al. Chiral organometallic chromophores for nonlinear optics derived from [Fe2(h5-C5H5)2(CO)2(m-CO)(m-C-/CH3)]+[BF4]-. *Journal of Organometallic Chemistry* **2002**, 655, 70–88.
6. J. Lu, S. Zhu, H. Su, et al. Synthesis, luminescence and excited state absorption properties of conjugated D-π-A and D-π-D phenothiazine compounds. *Journal of Luminescence* **2019**, 205, 158–166.
7. Y. Li, M. Tang, J. Wang, et al. Synthesis, crystal structure and luminescent properties of p-diphenylsulphone compounds with different substituents. *Optical Materials* **2018**, 86, 449–454.
8. Y. Song, L. Hu, Q. Cheng, et al. Benzothiazole derivatives with varied π-conjugation: synthesis, tunable solid-state emission, and application in single-component LEDs. *J. Mater. Chem. C* **2022**, 10 (16), 6392–6401.
9. X. Zheng, Y. Huang, D. Xiao, et al. Space conjugation induced white light and room-temperature phosphorescence from simple organic small molecules: single-component WLED driven by both UV and blue chips. *Mater. Chem. Front.* **2021**, 5 (18), 6960–6968.