Supporting Information

Crafting 1,4-Diaryl Spirobifluorene Hosts in OLEDs via Interannular C−H Arylation: Synergistic Effects of Molecular Linearity and Orthogonality

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I. General remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $Pd(OAc)_2$ was purchased from J&K Chemicals. The amino acids, iodobenzene, biphenyl-2-formaldehyde, silver trifluoroacetate, zinc carbonate and 2,2,2-trifluoroethanol were purchased from Shanghai Energy Chemical Co., Ltd and used without further purification. NMR spectra were recorded on an Agilent 400-MR DD2 spectrometer. The ^1H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard (δ = 77.16 ppm). ^{19}F NMR (376 MHz) was recorded on Bruker AV II-400 MHz. High resolution mass spectra (HRMS) were collected on Shimadzu LCMS-ITTOF (ESI). X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single-crystal diffractometer. UV-visible absorption spectra experiments were conducted on a HITACHI U-2910 spectrometer. Fluorescence spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. Phosphorescence spectra were collected on a HITACHI F-7100 fluorescence spectrophotometer. Thermogravimetric analysis (TGA) curves were carried out using DTG-60(H) at a rate of 10 ºC/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) thermograms were recorded on DSC 200PC equipment under nitrogen atmosphere at a rate of 10 ºC/min. Cyclic voltammograms were performed on LK2005A with a solution of tetrabutylammonium hexafluorophosphate (NBu_4PF_6, 0.1 M) in DMF and in DCM as electrolyte and ferrocene/ferrocenium (Fc/Fc^+) as standard, the sweep rate is 100 mV^{-1}. Three-electrode system (Ag/Ag^+, platinum wire and glassy carbon electrode as reference, counter and work electrode respectively) was used in the CV measurement.

II. OLED fabrication and characterization

ITO (indium tin oxide) glass substrates with a sheet resistance of 15 Ω per square were cleaned with alkaline detergent, boiled deionized water, and deionized water thoroughly

in ultrasonic bath and then treated with O_2 plasma for 10 min. Organic layers, LiF and Al were deposited on ITO substrates by thermal evaporation in a high vacuum chamber below 6×10^{-6} mbar in an inert gas glovebox. The quartz crystal oscillators controlled the thicknesses of deposited films. The as-fabricated OLEDs were measured in the inert gas glovebox without any encapsulation. Current density of OLEDs was measured by Keithley B1500A. The luminance and EL spectra were collected with model DLM-100Z photometer and OPT2000 spectrophotometer, respectively.

III. Synthesis of biphenyl-2-formaldehydes

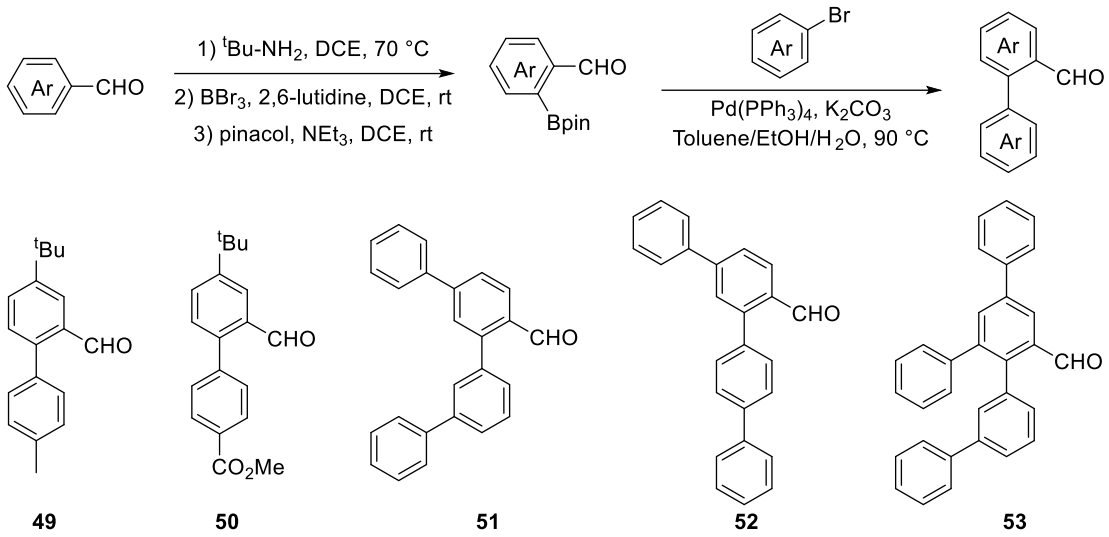
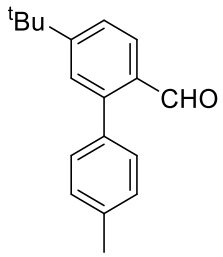


Fig. S1 Synthesis of biphenyl-2-formaldehydes

A Schlenk tube with a magnetic stir bar was charged with benzaldehyde derivative (2.0 mmol, 1 equiv), *tert*-butyl amine (8.0 mmol, 4 equiv), and DCE (1 mL) under a nitrogen atmosphere and the vial was placed in an oil bath at 70 °C for 4 h. The solvent and excess of *tert*-butyl amine were removed under vacuum and 2,6-lutidine (4.0 mmol, 2 equiv) and DCE (5 mL) were added. BBr_3 (4.0 mmol, 2 equiv; present as a 1 mol/L solution in CH_2Cl_2) was added dropwise to the reaction mixture while stirring and the reaction was continued for 4 h at room temperature. The reaction was quenched with pinacol (4.0 mmol, 2 equiv) and triethylamine (20.0 mmol, 10 equiv) and stirred for another 2 h at room temperature. After the reaction reached completion, the volatiles were removed under vacuum and the crude mixture was dissolved in ethyl acetate (20 mL) and H_2O (20 mL). The aqueous layer was washed with ethyl acetate (3 x 20 mL)

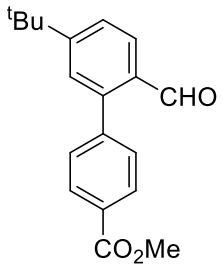
and the organic layers were collected and dried over $MgSO_4$ and filtered. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ CH_2Cl_2 = 1/1 to 100% CH_2Cl_2) to provide the desired product.[1]

A Schlenk tube with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (72.5 mg, 5mol%), K_2CO_3 (496.8 mg, 3.6 mmol, 2.0 equiv), pinacol phenylboronate (493.1 mg, 1.6 mmol, 1.1 equiv), bromobenzene (0.17 mL, 1.8 mmol, 1.1 equiv), toluene (3 mL), H_2O (1 mL) and EtOH (1 mL) under a nitrogen atmosphere. The resulting mixture was heated to 90 °C and stirred for 24 h. After cooling to room temperature, the organic layer was extracted with ethyl acetate and washed with brine. The combined organic extracts were dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate = 30/1, v/v) to provide the desired product.[2]



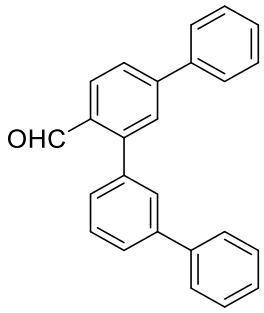
5-(*tert*-Butyl)-4'-methyl-[1,1'-biphenyl]-2-carbaldehyde (49)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 30/1, v/v) afforded the desired product **49** as colorless oil (379.2 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (s, 1H), 7.96 (d, J = 8.0, 1H), 7.51 (dd, J_1 = 8.4, J_2 = 1.2, 1H), 7.42 (d, J = 1.2, 1H), 7.29 (s, 4H), 2.44 (s, 3H), 1.37 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.50, 157.57, 146.06, 138.06, 135.58, 131.57, 130.22, 129.24, 127.88, 127.63, 125.02, 35.49, 31.23, 21.34 ppm. HRMS (ESI^+): calcd for $C_{18}H_{20}NaO$ $[M+Na]^+$ 275.1406, found: 275.1404.



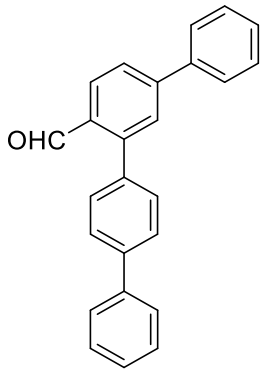
Methyl 5'-(*tert*-butyl)-2'-formyl-[1,1'-biphenyl]-4-carboxylate (50)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded the desired product **50** as colorless oil (371.2 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.91 (s, 1H), 8.14 (d, J = 8.4, 2H), 7.99 (d, J = 8.0, 1H), 7.58 (dd, J_1 = 8.4, J_2 = 2.8, 1H), 7.47 (d, J = 8.4, 2H), 7.41 (d, J = 2.0, 1H), 3.97 (s, 3H), 1.38 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.68, 166.86, 157.84, 144.74, 143.21, 131.40, 130.28, 129.82, 129.72, 128.03, 127.65, 125.85, 52.47, 35.54, 31.19 ppm. HRMS (ESI^+): calcd for $C_{19}H_{20}NaO_3$ $[M+Na]^+$ 319.1305, found: 319.1303.



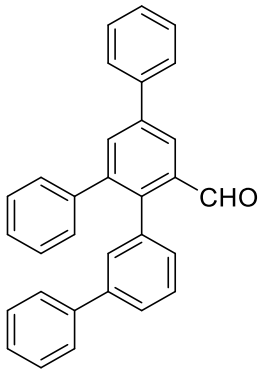
[1,1':3',1'':3'',1'''-Quaterphenyl]-4'-carbaldehyde (51)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 30/1, v/v) afforded the desired product **51** as a white solid (507.9 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.10 (s, 1H), 8.15 (d, J = 8.4, 1H), 7.77-7.64 (m, 8H),7.58 (t, J = 7.6, 1H), 7.51-7.37 (m, 7H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.15, 146.56, 146.48, 141.75, 140.57, 139.74, 138.51, 132.70, 129.60, 129.17, 129.14, 129.06, 128.98, 128.67, 128.47, 127.86, 127.55, 127.40, 127.14, 126.72 ppm. HRMS (ESI^+): calcd for $C_{25}H_{18}NaO$ $[M+Na]^+$ 357.1250, found: 357.1246.



[1,1':3',1'':4'',1'''-Quaterphenyl]-4'-carbaldehyde (52)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 30/1, v/v) afforded the desired product **52** as a white solid (491.9 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.10 (s, 1H), 8.14 (d, J = 8.4, 1H), 7.76-7.67 (m, 8H), 7.54-7.48 (m, 6H), 7.43-7.38 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.20, 146.47, 146.24, 141.31, 140.44, 139.77, 136.88, 132.68, 130.71, 129.56, 129.17, 129.08, 128.66, 128.54, 127.84, 127.54, 127.34, 127.30, 126.66 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{18}NaO$ $[M+Na]^+$ 357.1250, found: 357.1248.



5'-Phenyl-[1,1':2',1'':3'',1'''-quaterphenyl]-3'-carbaldehyde (53)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 30/1, v/v) afforded the desired product **53** as a white solid (610.8 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 8.32 (d, J = 1.6, 1H), 7.94 (d, J = 2.0, 1H), 7.74 (d, J = 7.6, 2H), 7.50 (t, J =7.6, 3H), 7.44-7.32 (m, 8H), 7.25-7.23 (m, 3H), 7.19-7.15 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.92, 143.40, 142.96, 140.97, 140.92, 140.61, 140.34, 139.55, 136.21, 135.22, 134.09, 130.46, 130.39, 130.00, 129.16, 128.89, 128.45, 128.21, 128.12, 127.65,

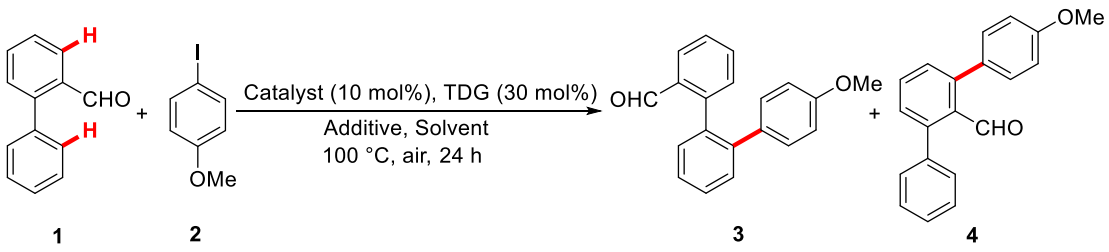
127.30, 127.25, 127.15, 126.57, 124.92 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{22}NaO$ $[M+Na]^+$ 433.1563, found: 433.1558.

IV. Palladium-catalyzed interannular selective C−H arylation

i) Condition optimization

A Schlenk tube with a magnetic stir bar was charged with biphenyl-2-formaldehyde derivative (**1**, 0.2 mmol, 1.0 equiv), 4-iodoanisole (**2**, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (0.02 mmol, 10.0 mol%), L-*tert*-leucine (0.06 mmol, 30 mol%), AgTFA (0.3 mmol, 1.5 equiv), $ZnCO_3$ (0.2 mmol, 1.0 equiv) and TFE (1.0 mL) under an air atmosphere. The reaction mixture was heated at 100 °C for 24 hours. The reaction mixture was cooled to room temperature, diluted with 5 mL CH_2Cl_2, filtered through a celite pad, and washed with 20-30 mL CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 20/1, v/v) to provide the desired product.

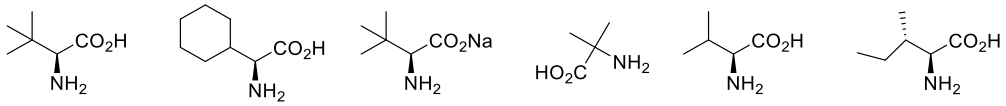
Table S1. Optimization of the interannular C−H arylation of biphenyl-2-formaldehyde[a]



1 **2** **3** **4**

Entry	Catalyst	TDG	Additive I	Additive II	Solvent	Yiled of **3** (%)	Yiled of **4** (%)
1	$Pd(OAc)_2$	T1	Ag_2CO_3	$ZnCO_3$	TFE	42	0
2	$Pd(OAc)_2$	T1	AgOAc	$ZnCO_3$	TFE	44	0
3	$Pd(OAc)_2$	T1	AgTFA	$ZnCO_3$	TFE	72	0
4	$Pd(OAc)_2$	T1	none	$ZnCO_3$	TFE	0	0
5	$Pd(OAc)_2$	T1	AgTFA	K_2CO_3	TFE	53	0
6	$Pd(OAc)_2$	T1	AgTFA	PivOH	TFE	0	37

7	$Pd(OAc)_2$	T1	AgTFA	none	TFE	25	0
8	$Pd(TFA)_2$	T1	AgTFA	$ZnCO_3$	TFE	65	0
9	$Pd(dba)_2$	T1	AgTFA	$ZnCO_3$	TFE	trace	0
10	$Pd(acac)_2$	T1	AgTFA	$ZnCO_3$	TFE	60	0
11	nono	T1	AgTFA	$ZnCO_3$	TFE	0	0
12	$Pd(OAc)_2$	T2	AgTFA	$ZnCO_3$	TFE	60	0
13	$Pd(OAc)_2$	T3	AgTFA	$ZnCO_3$	TFE	65	0
14	$Pd(OAc)_2$	T4	AgTFA	$ZnCO_3$	TFE	0	48
15	$Pd(OAc)_2$	T5	AgTFA	$ZnCO_3$	TFE	0	trace
16	$Pd(OAc)_2$	T6	AgTFA	$ZnCO_3$	TFE	0	35
17	$Pd(OAc)_2$	none	AgTFA	$ZnCO_3$	TFE	0	0
18	$Pd(OAc)_2$	T1	AgTFA	$ZnCO_3$	HFIP/AcOH (9:1)	12	38
19	$Pd(OAc)_2$	T1	AgTFA	$ZnCO_3$	TFE/TFA (9:1)	trace	47
20	$Pd(OAc)_2$	T1	AgTFA	$ZnCO_3$	TFE/AcOH (9:1)	0	35

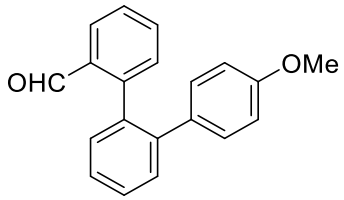


[a]Reaction conditions: biphenyl-2-formaldehyde **1** (0.20 mmol), 4-iodoanisole **2** (0.30 mmol), catalyst (10 mol %), TDG (30 mol %), additive I (0.30 mmol), additive II (0.20 mmol) and solvent (1mL) at 100 °C for 24 h under air. AcOH = glacial acetic acid.

ii) General procedure for the interannular C–H arylation of bi(hetero)aryl aldehyde

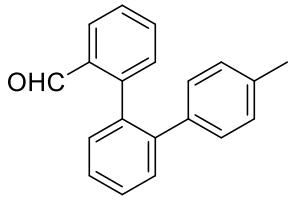
A Schlenk tube with a magnetic stir bar was charged with bi(hetero)aryl aldehyde (0.2 mmol, 1.0 equiv), iodobenzene (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), L-*tert*-leucine (0.06 mmol, 30 mol%), AgTFA (0.3 mmol, 1.5 equiv), $ZnCO_3$ (0.2 mmol, 1.0 equiv) and TFE (1.0 mL) under an air atmosphere. The reaction mixture was heated at 100 °C for 24 hours. The reaction mixture was cooled to room temperature, diluted with 5 mL CH_2Cl_2, filtered through a celite pad, and washed with 20-30 mL CH_2Cl_2.

The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 20/1, v/v) to provide the desired product.



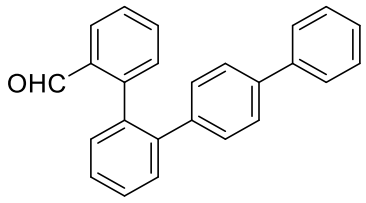
4''-Methoxy-[1,1':2',1''-terphenyl]-2-carbaldehyde (3)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product **3** as light yellow oil (41.5 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1H), 7.82 (d, J = 7.6, 1H), 7.55-7.36 (m, 6H), 7.30 (d, J = 7.6, 1H), 6.95 (d, J = 8.4, 2H), 6.69 (d, J = 8.8, 2H), 3.73 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.76, 158.66, 145.69, 141.70, 136.41, 133.63, 133.53, 132.71, 131.83, 131.44, 131.09, 130.21, 128.79, 127.68, 127.21, 127.17, 113.74, 55.25 ppm. HRMS (ESI^+): calcd for $C_{20}H_{16}NaO_2$ $[M+Na]^+$ 311.1043, found: 311.1037.



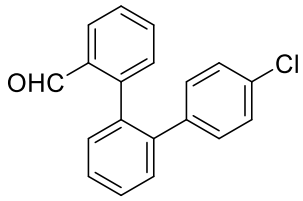
4''-Methyl-[1,1':2',1''-terphenyl]-2-carbaldehyde (5)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **5** as colorless oil (29.9 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (s, 1H), 7.81 (d, J = 8.0, 1H), 7.55-7.42 (m, 4H), 7.38 (t, J = 7.2, 2H), 7.30 (d, J = 7.6, 1H), 6.98-6.91 (m, 4H), 2.25 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.89, 145.69, 142.00, 137.37, 136.73, 136.36, 133.56, 133.52, 131.85, 131.46, 130.28, 129.82, 129.00, 128.78, 127.67, 127.30, 127.12, 21.22 ppm. HRMS (ESI^+): calcd for $C_{20}H_{16}NaO$ $[M+Na]^+$ 295.1093, found: 295.1088.



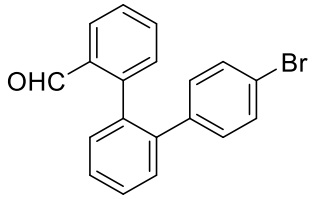
[1,1':2',1'':4'',1'''-Quaterphenyl]-2-aldehyde (6)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **6** as a colorless solid (40.1 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.82 (s, 1H), 7.84 (dd, J_1 = 7.6, J_2 = 1.2, 1H), 7.55-7.51 (m, 5H), 7.49-7.45 (m, 1H), 7.42-7.38 (m, 6H), 7.33-7.30 (m, 2H), 7.12 (d, J = 8.4, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.84, 145.50, 141.57, 140.47, 139.62, 139.36, 136.44, 133.66, 133.57, 131.90, 131.60, 130.34, 130.29, 128.86, 127.79, 127.56, 127.48, 127.35, 127.10, 126.88 ppm. HRMS (ESI^+): calcd for $C_{25}H_{18}NaO$ $[M+Na]^+$ 357.1250, found: 357.1245.



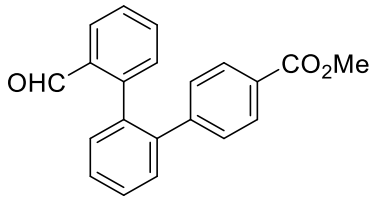
4''-Chloro-[1,1':2',1''-terphenyl]-2-carbaldehyde (7)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **7** as colorless oil (29.2 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (s, 1H), 7.83 (d, J = 9.2, 1H), 7.56-7.47 (m, 3H), 7.45-7.38 (m, 3H), 7.27 (d, J = 7.6, 1H), 7.13 (d, J = 8.4, 2H), 6.96 (d, J = 8.4, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.57, 144.98, 140.76, 139.45, 136.45, 133.73, 133.59, 131.82, 131.57, 131.47, 131.42, 130.11, 128.91, 127.97, 127.87, 127.63, 121.46 ppm. HRMS (ESI^+): calcd for $C_{19}H_{13}ClNaO$ $[M+Na]^+$ 315.0547, 317.0518, found: 315.0542, 317.0520.



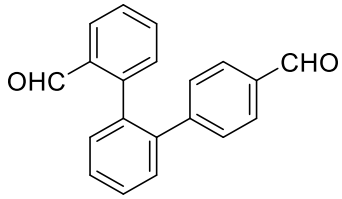
4''-Bromo-[1,1':2',1''-terphenyl]-2-carbaldehyde (8)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **8** as colorless oil (35.6 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (s, 1H), 7.84 (d, J = 8.0, 1H), 7.55-7.47 (m, 3H), 7.45-7.37 (m, 3H), 7.30-7.25 (m, 3H), 6.91 (d, J = 8.4, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.57, 144.98, 140.76, 139.45, 136.45, 133.73, 133.59, 131.82, 131.57, 131.47, 131.42, 130.11, 128.91, 127.97, 127.87, 127.63, 121.46 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{13}BrNaO$ $[M+Na]^+$ 359.0042, 361.0022, found: 359.0042, 361.0020.



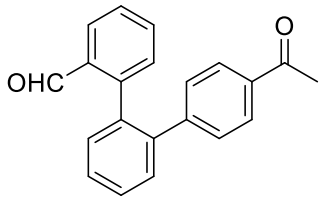
Methyl 2''-formyl-[1,1':2',1''-terphenyl]-4-carboxylate (9)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product **9** as a colorless solid (37.9 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (s, 1H), 7.83 (t, J = 8.4, 3H), 7.57-7.49 (m, 4H), 7.42-7.38 (m, 2H), 7.27 (d, J = 2.8, 1H), 7.12 (d, J = 8.0, 2H), 3.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.51, 166.91, 145.25, 144.85, 140.99, 136.58, 133.77, 133.56, 131.84, 131.59, 130.15, 129.91, 129.51, 128.89, 128.70, 128.15, 128.01, 127.63, 52.20 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{16}NaO_3$ $[M+Na]^+$ 339.0992, found: 339.0992.



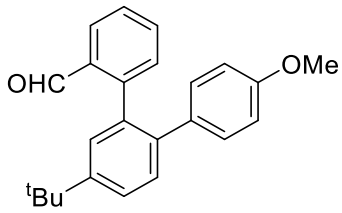
[1,1':2',1''-Terphenyl]-2,4''-dicarbaldehyde (10)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product **10** as colorless oil (31.5 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.92 (s, 1H), 9.78 (s, 1H), 7.81 (dd, J_1 = 7.6, J_2 = 1.2, 1H), 7.68 (d, J = 8.0, 2H), 7.58-7.48 (m, 4H), 7.4-7.38 (m, 2H), 7.28 (d, J = 7.6, 1H), 7.21 (d, J = 8.4, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.02, 191.50, 146.85, 144.65, 140.70, 136.58, 134.77, 133.70, 133.68, 131.83, 131.64, 130.56, 130.11, 129.63, 128.98, 128.43, 128.13, 127.73 ppm. HRMS (ESI^+): calcd for $C_{20}H_{14}NaO_2$ $[M+Na]^+$ 309.0886, found: 309.0885.



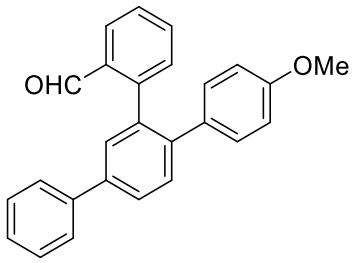
4''-Acetyl-[1,1':2',1''-terphenyl]-2-carbaldehyde (11)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product **11** as a colorless solid (34.8 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.77 (s, 1H), 7.81 (dd, J_1 = 7.6, J_2 = 1.2, 1H), 7.75 (d, J = 8.4, 2H), 7.57-7.47 (m, 4H), 7.42-7.38 (m, 2H), 7.28 (d, J = 7.6, 1H), 7.14 (d, J = 8.4, 2H), 2.54 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.85, 191.57, 145.40, 144.83, 140.85, 136.51, 135.45, 133.66, 131.82, 131.61, 130.13, 130.10, 128.93, 128.29, 128.23, 128.05, 127.61, 26.74 ppm. HRMS (ESI^+): calcd for $C_{21}H_{16}NaO_2$ $[M+Na]^+$ 323.1043, found: 323.1042.



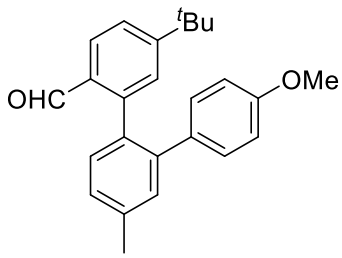
5'-(*tert*-Butyl)-4''-methoxy-[1,1':2',1''-terphenyl]-2-carbaldehyde (12)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product **12** as a colorless oil (48.2 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (s, 1H), 7.84 (dd, J_1 = 7.6, J_2 = 1.2, 1H), 7.56-7.51 (m, 2H), 7.40-7.36 (m, 3H), 7.32 (d, J = 8.4, 1H), 6.94 (d, J = 8.8, 2H), 6.69 (d, J = 8.8, 2H), 3.73 (s, 3H), 1.39 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.02, 158.45, 150.19, 146.32, 138.78, 135.78, 133.64, 133.53, 132.60, 131.91, 131.07, 129.88, 128.59, 127.56, 127.04, 125.82, 113.67, 55.23, 34.73, 31.50 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{24}NaO_2$ $[M+Na]^+$ 367.1669, found: 367.1667.



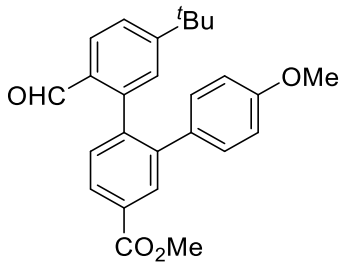
4''-Methoxy-5'-phenyl-[1,1':2',1''-terphenyl]-2-carbaldehyde (13)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product **13** as light yellow oil (47.3 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.82 (s, 1H), 7.84 (d, J = 8.0, 1H), 7.74 (dd, J_1 = 8.0, J_2 = 2.0, 1H), 7.67 (d, J = 7.2, 2H), 7.62 (d, J = 2.0, 1H), 7.59-7.53 (m, 2H), 7.47 (t, J = 7.2, 2H), 7.43-7.36 (m, 3H), 6.99 (d, J = 8.8, 2H), 6.72 (d, J = 8.8, 2H), 3.75 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.75, 158.68, 145.61, 140.62, 140.19, 140.06, 136.76, 133.68, 133.59, 132.23, 131.84, 131.09, 130.68, 130.13, 129.05, 127.82, 127.78, 127.39, 127.25, 127.23, 113.78, 55.26 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{20}NaO_2$ $[M+Na]^+$ 387.1356, found: 387.1351.



5-(*tert*-Butyl)-4''-methoxy-4'-methyl-[1,1':2',1''-terphenyl]-2-carbaldehyde (14)

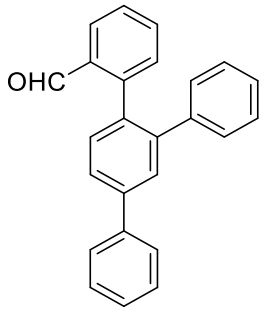
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product **14** as light yellow oil (47.3 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.81 (s, 1H), 7.78 (d, J = 8.4, 1H), 7.37 (dd, J = 8.4, J_2 = 1.2, 1H), 7.28-7.23 (m, 3H), 7.16 (d, J = 1.6, 1H), 6.93 (d, J = 8.8, 2H), 6.69 (d, J = 8.8, 2H), 3.73 (s, 3H), 2.47 (s, 3H), 1.21 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.95, 158.53, 157.04, 145.34, 141.56, 138.47, 133.93, 133.13, 131.69, 131.50, 131.03, 130.97, 129.68, 127.75, 127.16, 124.42, 113.60, 55.33, 35.21, 31.02, 21.37 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{26}NaO_2$ $[M+Na]^+$ 381.1825, found: 381.1820.



Methy 5-(*tert*-butyl)-2-formyl-4''-methoxy-[1,1':2',1''-terphenyl]-4'-carboxylate (15)

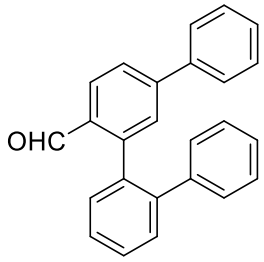
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product **15** as a light yellow solid (33.0 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1H), 8.15 (d, J = 1.6, 1H), 8.01 (dd, J_1 = 8.0, J_2 = 2.0, 1H), 7.79 (d, J = 8.4, 1H), 7.46 (d, J = 8.0, 1H), 7.42-7.40 (m, 1H), 7.17 (d, J = 1.6, 1H), 6.94 (d, J = 8.8, 2H), 6.70 (d, J = 8.8, 2H), 3.97 (s, 3H), 3.73 (s, 3H), 1.23 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =

191.12, 166.89, 158.87, 157.37, 144.10, 141.97, 141.66, 132.03, 131.72, 131.35, 131.25, 130.97, 130.33, 129.15, 127.96, 127.75, 125.12, 113.76, 55.35, 52.45, 35.29, 31.01 ppm. HRMS (ESI^+): calcd for $C_{26}H_{26}NaO_4$ $[M+Na]^+$ 425.1723, found: 415.1718.



4'-Phenyl-[1,1':2',1''-terphenyl]-2-carbaldehyde (16)

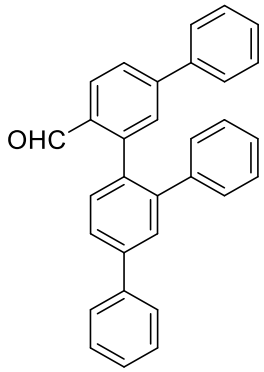
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **16** as light yellow oil (37.4 mg, 56% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.85 (s, 1H), 7.84 (dd, J = 7.6, 1H), 7.73-7.69 (m, 4H), 7.56-7.47 (m, 4H), 7.42-7.38 (m, 2H), 7.34 (d, J = 8.4, 1H), 7.20-7.19 (m, 3H), 7.12-7.09 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.73, 145.13, 142.49, 141.69, 140.33, 135.40, 133.72, 133.53, 132.02, 131.92, 130.00, 129.06, 128.30, 127.88, 127.80, 127.32, 127.28, 127.18, 126.14 ppm. HRMS (ESI^+): calcd for $C_{25}H_{19}O$ $[M+H]^+$ 335.1430, found: 335.1428.



[1,1':2',1'':3'',1'''-Quaterphenyl]-6''-carbaldehyde (17)

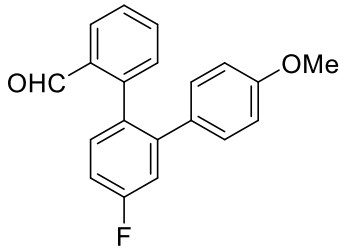
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **17** as a light yellow solid (36.8 mg, 55% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.81 (s, 1H), 7.89 (d, J = 8.0, 1H), 7.61 (dd, J_1 = 8.0, J_2 = 1.2, 1H), 7.54-7.39 (m, 10H), 7.21-7.17 (m,

3H), 7.11-7.09 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.42, 145.93, 145.87, 142.10, 140.41, 139.64, 136.43, 132.45, 131.51, 130.60, 130.33, 130.01, 129.06, 128.89, 128.54, 128.30, 127.85, 127.57, 127.40, 127.11, 126.36 ppm. HRMS (ESI^+): calcd for $C_{25}H_{19}O$ $[M+H]^+$ 335.1430, found: 335.1431.



5'-Phenyl-[1,1':2',1'':3'',1'''-quaterphenyl]-6''-carbaldehyde (18)

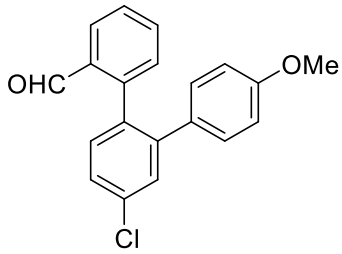
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **18** as a light yellow solid (45.1 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.90 (s, 1H), 7.92 (d, J = 8.0, 1H), 7.76-7.71 (m, 4H), 7.62 (d, J = 8.0, 1H), 7.55-7.39 (m, 10H), 7.23-7.16 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.31, 145.99, 145.56, 142.61, 141.81, 140.50, 140.38, 139.71, 135.48, 132.67, 132.08, 130.68, 130.06, 129.13, 129.08, 128.55, 128.38, 128.01, 127.91, 127.42, 127.35, 127.26, 126.42, 126.17 ppm. HRMS (ESI^+): calcd for $C_{31}H_{22}NaO$ $[M+Na]^+$ 433.1563, found: 433.1559.



4'-Fluoro-4''-methoxy-[1,1':2',1''-terphenyl]-2-carbaldehyde (19)

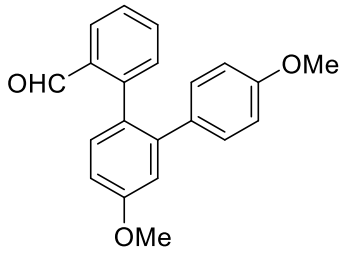
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product **19** as light yellow oil (37.3 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.72 (s, 1H), 7.81

(dd, J_1 = 8.0, J_2 = 1.6, 1H), 7.56-7.52 (m, 1H), 7.39 (t, J = 8.0, 1H), 7.36-7.32 (m, 1H), 7.28 (d, J = 8.4, 1H), 7.18-7.10 (m, 2H), 6.93 (d, J = 8.4, 2H), 6.79 (d, J = 8.4, 2H), 3.73 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.38, 162.72 (d, J = 247.0 Hz), 158.80, 144.44, 143.60 (d, J = 8.0 Hz), 133.56, 133.50, 132.81 (d, J = 8.0 Hz), 132.20 (d, J = 3.0 Hz), 131.80, 131.45 (d, J = 2.0 Hz), 130.83, 127.75, 127.33, 116.73 (d, J = 21.0 Hz), 113.96 (d, J = 21.0 Hz), 113.69, 55.14 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{15}FNaO_2$ $[M+Na]^+$ 329.0948, found: 329.0943.



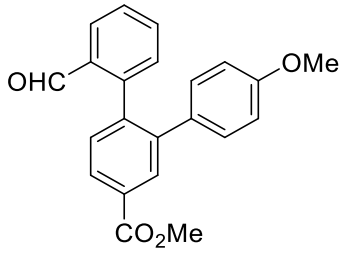
4'-Chloro-4''-methoxy-[1,1':2',1''-terphenyl]-2-carbaldehyde (20)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product **20** as light yellow oil (43.8 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.72 (s, 1H), 7.81 (d, J = 8.4, 1H), 7.54 (t, J = 8.4, 1H), 7.45 (d, J = 2.0, 1H), 7.40 (t, J = 8.0, 2H), 7.31-7.26 (m, 2H), 6.92 (d, J = 8.4, 2H), 6.69 (d, J = 8.8, 2H), 3.73 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.30, 159.00, 144.31, 143.28, 134.92, 134.63, 133.69, 133.56, 132.55, 131.75, 131.38, 130.97, 130.07, 128.02, 127.60, 127.22, 113.86, 55.28 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{15}ClNaO_2$ $[M+Na]^+$ 345.0653, 347.0623, found: 345.0650, 347.0620.



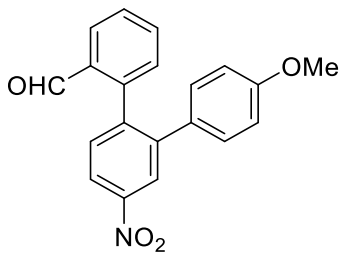
4',4''-Dimethoxy-[1,1':2',1''-terphenyl]-2-carbaldehyde (21)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded the desired product **21** as light yellow oil (42.6 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1H), 7.79 (dd, J_1 = 8.0, J_2 = 2.0, 1H), 7.53-7.49 (m, 1H), 7.35 (t, J = 7.6,1H), 7.30-7.26 (m, 2H), 6.98-6.94 (m, 4H), 6.69 (d, J = 8.8, 2H), 3.90 (s, 3H), 3.74 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.00, 159.86, 158.71, 145.49, 142.99, 133.81, 133.52, 132.66, 132.10, 131.04, 128.76, 127.40, 127.16, 115.51, 113.72, 112.73, 55.58, 55.26 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{18}NaO_3$ $[M+Na]^+$ 341.1148, found: 341.1146.



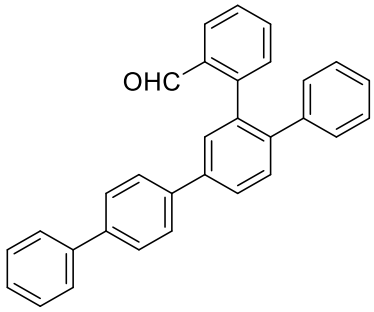
Methyl 2-formyl-4''-methoxy-[1,1':2',1''-terphenyl]-4'-carboxylate (22)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded the desired product **22** as light yellow oil (31.2 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.70 (s, 1H), 8.13 (s, 1H), 8.08 (dd, J_1 = 8.0, J_2 = 8.0, 1H), 7.82 (d, J = 7.6, 1H), 7.59-7.55 (m, 1H), 7.47-7.40 (m, 2H), 7.30 (d, J = 6.8, 1H), 6.96 (d, J = 8.8, 2H), 6.70 (d, J = 8.8, 2H), 3.97 (s, 3H), 3.74 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.15, 166.87, 158.90, 144.46, 141.94, 141.13, 133.74, 133.34, 131.65, 131.54, 131.50, 131.29, 131.09, 130.53, 128.23, 128.14, 127.68, 113.84, 55.29, 52.49 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{18}NaO_4$ $[M+Na]^+$ 369.1097, found: 369.1095.



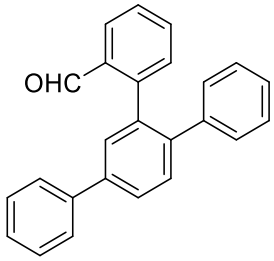
4''-Methoxy-4'-nitro-[1,1':2',1''-terphenyl]-2-carbaldehyde (23)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded the desired product **23** as a yellow solid (26.6 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.69 (s, 1H), 8.32-8.25 (m, 2H), 7.83 (d, J = 7.6, 1H), 7.60 (t, J = 7.6, 1H), 7.54 (d, J = 8.4, 1H), 7.48 (t, J = 8.0, 1H), 7.29 (d, J = 7.6, 1H), 6.96 (d, J = 8.8, 2H), 6.72 (d, J = 7.6, 2H), 3.75 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.58, 159.35, 148.05, 143.50, 143.12, 142.76, 133.91, 133.30, 132.12, 131.37, 130.99, 130.42, 128.80, 128.74, 124.89, 121.86, 114.05, 55.32 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{15}NNaO_4$ $[M+Na]^+$ 356.0893, found: 356.0889.



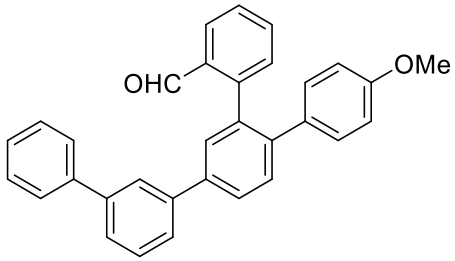
6'-Phenyl-[1,1':3',1'':4'',1'''-quaterphenyl]-2-carbaldehyde (24)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) afforded the desired product **24** as a light yellow solid (52.5 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.85 (s, 1H), 7.85-7.80 (m, 2H), 7.77-7.65 (m, 7H), 7.60-7.55 (m, 2H), 7.48 (t, J = 7.2, 2H), 7.43-7.38 (m, 3H), 7.20-7.18 (m, 3H), 7.10-7.08 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.72, 145.35, 141.03, 140.69, 140.63, 139.93, 139.89, 138.96, 136.95, 133.66, 133.63, 131.90, 130.84, 130.00, 129.95, 128.99, 128.31, 127.91, 127.78, 127.61, 127.27, 127.19, 127.14 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{22}NaO$ $[M+Na]^+$ 433.1563, found: 433.1563.



5'-Phenyl-[1,1':2',1''-terphenyl]-2-carbaldehyde (25)

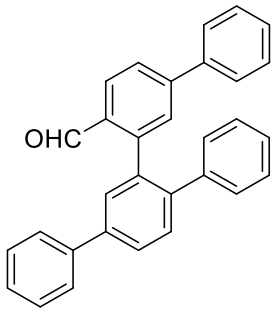
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **25** as light yellow oil (41.4 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.84 (s, 1H), 7.83 (d, J = 8.0, 1H), 7.76 (dd, J_1 =8.4, J_2 = 2.0, 1H), 7.67 (d, J = 7.2, 2H), 7.63 (s, 1H), 7.58-7.53 (m, 2H), 7.47 (t, J = 7.6, 2H), 7.42-7.36 (m, 3H), 7.19-7.17 (m, 3H), 7.09-7.07 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.70, 145.39, 140.99, 140.45, 140.15, 140.00, 136.93, 133.74, 133.57, 131.92, 130.79, 130.16, 129.96, 129.07, 128.30, 127.88, 127.86, 127.41, 127.28, 127.12 ppm. HRMS (ESI^+): calcd for $C_{25}H_{18}NaO$ $[M+Na]^+$ 357.1250, found: 357.1249.



6'-(4-Methoxyphenyl)-[1,1':3',1'':3'',1'''-quaterphenyl]-2-carbaldehyde (26)

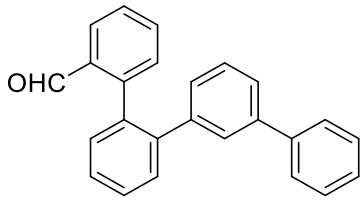
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product **26** as a light yellow solid (59.9 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.82 (s, 1H), 7.87-7.83 (m, 2H), 7.79 (dd, J_1 = 8.0, J_2 = 2.0, 1H), 7.67-7.64 (m, 4H), 7.62-7.52 (m, 4H), 7.49-7.36 (m, 5H), 7.00 (d, J = 8.4, 2H), 6.72 (d, J = 8.4, 2H), 3.75 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.70, 158.74, 145.56, 142.16, 141.19, 140.81, 140.77, 140.03, 136.88, 133.70, 133.61, 132.22, 131.85, 131.11, 130.71, 130.17, 129.49,

128.97, 127.87, 127.63, 127.50, 127.42, 127.30, 126.66, 126.19, 113.81, 55.28 ppm. HRMS (ESI^+): calcd for $C_{32}H_{24}NaO_2$ $[M+Na]^+$ 463.1669, found: 463.1669.



4'-Phenyl-[1,1':2',1'':3'',1'''-quaterphenyl]-6''-carbaldehyde (27)

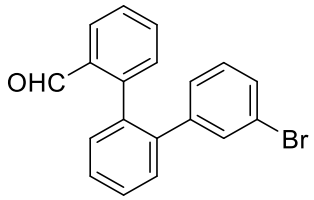
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **27** as a light yellow solid (45.9 mg, 56% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.89 (s, 1H), 7.78 (dd, J_1 = 2.0, J_2 = 2.0, 1H), 7.70-7.68 (m, 3H), 7.64 (d, J = 9.2, 1H), 7.61-7.59 (m, 2H), 7.56-7.54 (m, 2H), 7.50-7.37 (m, 6H), 7.22-7.19 (m, 3H), 7.16-7.13 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.27, 146.08, 145.82, 141.08, 140.55, 140.17, 140.11, 139.68, 136.99, 132.62, 130.84, 130.63, 130.19, 130.01, 129.09, 128.58, 128.37, 127.98, 127.89, 127.48, 127.44, 127.30, 127.20, 126.49 ppm. HRMS (ESI^+): calcd for $C_{31}H_{22}NaO$ $[M+Na]^+$ 433.1563, found: 433.1566.



[1,1':2',1'':3'',1'''-Quaterphenyl]-2-carbaldehyde (28)

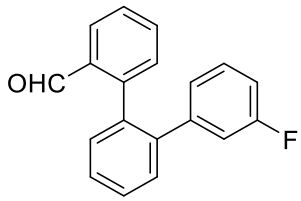
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **28** as light yellow oil (37.4 mg, 56% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.81 (s, 1H), 7.85 (d, J = 7.2, 1H), 7.59-7.52 (m, 3H), 7.50-7.46 (m, 1H), 7.42 (d, J = 8.8, 2H), 7.38-7.34 (m, 4H), 7.31-7.26 (m, 4H), 7.24-7.22 (m, 1H), 7.08 (d, J = 7.6, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.66, 145.54, 141.92, 141.13, 140.96, 140.74, 136.61, 133.81,

133.52, 131.99, 131.47, 130.22, 129.12, 128.88, 128.77, 128.75, 127.82, 127.67, 127.41, 127.40, 127.22, 125.91 ppm. HRMS (ESI^+): calcd for $C_{25}H_{18}NaO$ $[M+Na]^+$ 357.1250, found: 357.1245.



3''-Bromo-[1,1':2',1''-terphenyl]-2-carbaldehyde (29)

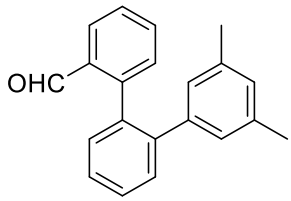
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **29** as light yellow oil (30.9 mg, 46% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.77 (s, 1H), 7.84 (d, J = 7.6, 1H), 7.56-7.45 (m, 4H), 7.43-7.38 (m, 2H), 7.29-7.26 (m, 2H), 7.22 (s, 1H), 7.01 (t, J = 8.0, 1H), 6.93 (d, J = 6.4, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.55, 144.82, 142.55, 140.44, 136.59, 133.78, 133.56, 132.84, 131.87, 131.53, 130.15, 130.12, 129.67, 128.91, 128.54, 128.04, 128.02, 127.61, 122.26 ppm. HRMS (ESI^+): calcd for $C_{19}H_{13}BrNaO$ $[M+Na]^+$ 359.0042, 361.0022, found: 359.0042, 361.0017.



3''-Fluoro-[1,1':2',1''-terphenyl]-2-carbaldehyde (30)

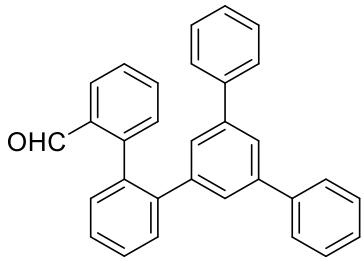
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **30** as light yellow oil (28.7 mg, 52% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.77 (s, 1H), 7.83 (d, J = 8.0, 1H), 7.55-7.46 (m, 4H), 7.40 (t, J = 7.6, 2H), 7.28 (d, J = 7.6, 1H), 7.15-7.10 (m, 1H), 6.88-6.81 (m, 2H), 6.74 (d, J = 10.0, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.45, 144.79, 140.59, 139.33, 134.96 (d, J = 279.0 Hz), 133.45, 131.65, 131.39, 130.00, 129.58 (d, J = 8.0 Hz), 128.73, 127.83, 127.35, 125.54 (d, J = 3.0 Hz),

116.77, 116.55, 113.98, 113.77 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{13}FNaO$ $[M+Na]^+$ 299.0843, found: 299.0843.



3'',5''-Dimethyl-[1,1':2',1''-terphenyl]-2-carbaldehyde (31)

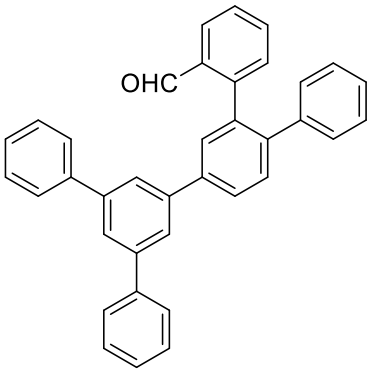
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded the desired product **31** as colorless oil (33.2 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1H), 7.82 (dd, J_1 = 7.6, J_2 = 1.2, 1H), 7.54-7.46 (m, 3H), 7.46-7.41 (m, 1H), 7.39-7.35 (m, 2H), 7.30 (d, J = 7.2, 1H), 2.13 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.83, 145.76, 142.27, 140.20, 137.59, 136.48, 133.71, 133.32, 131.87, 131.31, 130.15, 128.68, 128.63, 127.88, 127.59, 127.29, 127.02, 21.27 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{18}NaO$ $[M+Na]^+$ 309.1250, found: 309.1250.



5''-Phenyl-[1,1':2',1'':3'',1'''-quaterphenyl]-2-carbaldehyde (32)

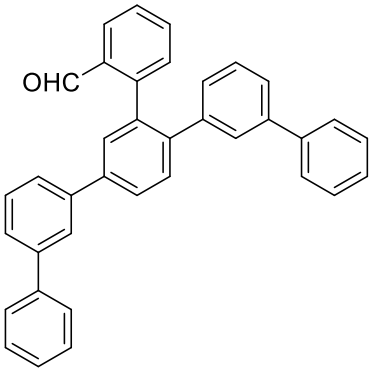
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) afforded the desired product **32** as light yellow oil (50.0 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.85 (s, 1H), 7.89 (d, J = 8.0, 1H), 7.64-7.60 (m, 2H), 7.58-7.49 (m, 3H), 7.47-7.30 (m, 14H), 7.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.69, 145.58, 141.74, 141.72, 141.07, 140.90, 136.62, 133.76, 133.63, 132.04, 131.47, 130.16, 128.96, 128.83, 127.91, 127.87, 127.80, 127.56, 127.50, 127.32, 124.95 ppm. HRMS (ESI$^+$): calcd for

$C_{31}H_{22}NaO$ $[M+Na]^+$ 433.1563, found: 433.1561.



5'',6'-Diphenyl-[1,1':3',1'':3'',1'''-quaterphenyl]-2-carbaldehyde (33)

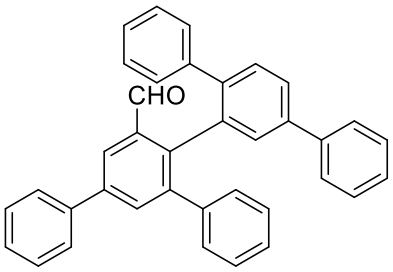
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) afforded the desired product **33** as a light yellow solid (58.3 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1H), 7.89-7.83 (m, 5H), 7.76-7.72 (m, 5H), 7.62 (d, J = 8.0, 1H), 7.57 (dd, J_1 = 7.6, J_2 = 1.2, 1H), 7.50 (t, J = 7.2, 4H), 7.44-7.39 (m, 4H), 7.21-7.19 (m, 3H), 7.12-7.10 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.53, 145.15, 142.60, 141.17, 141.15, 140.98, 140.24, 139.79, 136.95, 133.56, 133.52, 131.79, 130.73, 130.11, 129.86, 128.91, 128.22, 127.85, 127.68, 127.50, 127.40, 127.19, 127.07, 125.66, 125.11 ppm. HRMS (ESI^+): calcd for $C_{37}H_{26}NaO$ $[M+Na]^+$ 509.1876, found: 509.1874.



2-[2,5-Bis(3-phenylphenyl)phenyl]benzene-1-carbaldehyde (34)

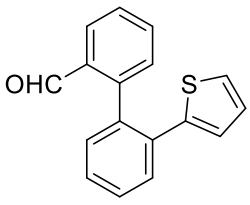
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) afforded the desired product **34** as a light yellow solid (59.3 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.90 (s, 1H), 7.90-

7.83 (m, 3H), 7.73 (s, 1H), 7.69-7.54 (m, 7H), 7.50-7.44 (m, 4H), 7.41-7.28 (m, 9H), 7.14 (d, J = 7.6, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.45, 145.26, 142.04, 141.03, 141.00, 140.82, 140.75, 140.54, 140.39, 140.14, 136.95, 133.61, 133.55, 131.86, 130.60, 130.04, 129.39, 128.95, 128.84, 128.72, 128.65, 128.59, 127.84, 127.52, 127.44, 127.33, 127.30, 127.28, 127.07, 126.62, 126.09, 125.88 ppm. HRMS (ESI^+): calcd for $C_{37}H_{27}O$ $[M+H]^+$ 487.2056, found: 487.2051.



5',5''-Diphenyl-[1,1':2',1'':2'',1'''-quaterphenyl]-3'-carbaldehyde (35)

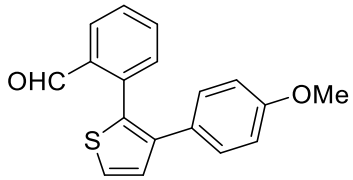
Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) afforded the desired product **35** as a colorless solid (52.5 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.10 (s, 1H), 8.26 (d, J = 2.0, 1H), 7.74 (d, J = 2.0, 1H), 7.71 (d, J = 7.2, 2H), 7.67 (dd, J_1 = 8.0, J_2 = 2.0, 1H), 7.59-7.55 (m, 3H), 7.49-7.43 (m, 4H), 7.41-7.35 (m, 3H), 7.20-7.06 (m, 6H), 6.79-6.74 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =192.69, 143.25, 142.35, 141.17, 140.81, 140.07, 139.98, 139.86, 139.66, 139.42, 135.57, 134.48, 134.19, 131.97, 130.91, 129.67, 129.39, 129.11, 129.03, 128.17, 128.01, 127.84, 127.81, 127.38, 127.19, 127.17, 126.89, 126.85, 124.81 ppm. HRMS (ESI^+): calcd for $C_{37}H_{26}NaO$ $[M+Na]^+$ 509.1876, found: 509.1872.



2'-(Thiophen-2-yl)-[1,1'-biphenyl]-2-carbaldehyde (36)

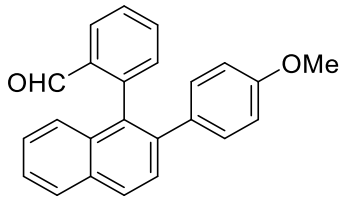
Following the general procedure, purification via silica gel column chromatography

(petroleum ether/ethyl acetate = 30/1, v/v) afforded the desired product **36** as colorless oil (19.5 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.77 (s, 1H), 7.91 (d, J = 7.6, 1H), 7.64-7.58 (m, 2H), 7.47 (t, J = 7.2, 2H), 7.42 (t, J = 7.6, 1H), 7.35 (d, J = 7.6, 2H), 7.16 (d, J = 4.8, 1H), 6.83 (t, J = 3.6, 1H), 6.63 (d, J = 3.6, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.68, 133.78, 131.71, 131.52, 130.07, 128.86, 128.27, 127.75, 127.35, 127.25, 126.58 ppm. HRMS (ESI^+): calcd for $C_{17}H_{12}NaOS$ $[M+Na]^+$ 287.0501, found: 287.0500.



2-(3-(4-Methoxyphenyl)thiophen-2-yl)benzaldehyde (37)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 30/1, v/v) afforded the desired product **37** as colorless oil (25.3mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.82 (s, 1H), 7.88 (d, J = 7.6, 1H), 7.63-7.59 (m, 1H), 7.52-7.45 (m, 3H), 7.23 (d, J = 5.2, 1H), 7.04 (d, J = 8.4, 2H), 6.74 (d, J = 8.8, 2H), 3.75 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.41, 158.83, 141.42, 138.08, 134.15, 133.88, 132.46, 132.25, 130.19, 129.45, 128.68, 127.74, 127.53, 126.09, 114.22, 55.29 ppm. HRMS (ESI^+): calcd for $C_{18}H_{14}NaO_2S$ $[M+Na]^+$ 317.0607, found: 317.0605.



2-(2-(4-Methoxyphenyl)naphthalen-1-yl)benzaldehyde (38)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 30/1, v/v) afforded the desired product **38** as colorless oil (52.7 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.57 (s, 1H), 7.99 (d, J = 8.8, 1H), 7.93 (t, J = 7.6, 2H), 7.61-7.57 (m, 2H), 7.52-7.40 (m, 4H), 7.35 (d, J = 7.6,

1H), 7.00 (d, J = 8.8, 2H), 6.70 (d, J = 8.8, 2H), 3.74 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.91, 158.47, 143.36, 139.51, 134.96, 133.54, 133.51, 133.30, 133.13, 132.81, 132.63, 131.06, 128.79, 128.25, 128.06, 127.31, 127.01, 126.49, 126.05, 113.62, 55.27 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{18}NaO_2$ $[M+Na]^+$ 361.1199, found: 361.1195.

iii) Scale-up synthesis

A 120 mL Schlenk tube with a magnetic stir bar was charged with bi(hetero)aryl aldehyde (4.0 mmol, 1.0 equiv), iodobenzene (6.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (90.6 mg, 10 mol%), L-*tert*-leucine (135.8 mg, 30 mol%), AgTFA (1.3 g, 1.5 equiv), $ZnCO_3$ 501.6 mg, 1.0 equiv) and TFE (10 mL) under an air atmosphere. The reaction mixture was heated at 100 °C for 24 hours. The reaction mixture was cooled to room temperature, diluted with 20 mL CH_2Cl_2, filtered through a celite pad, and washed with 40-50 mL CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to provide the desired product.

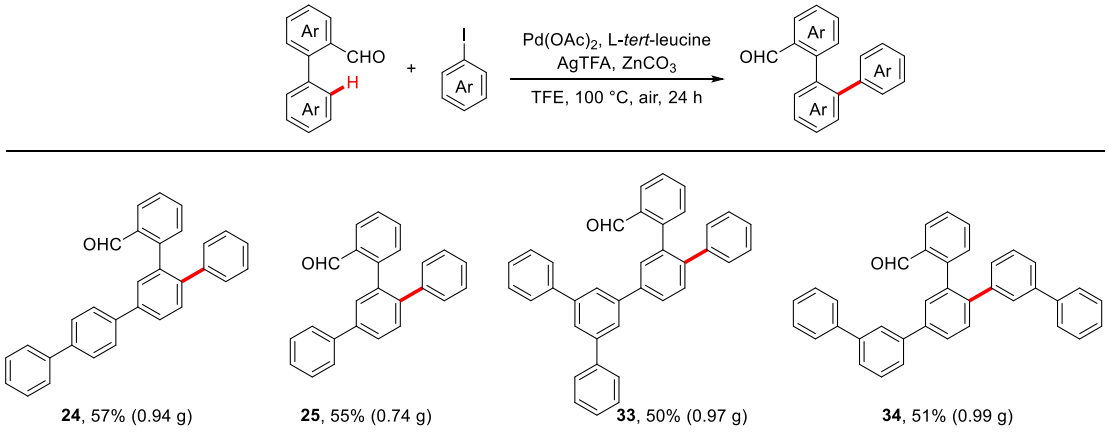
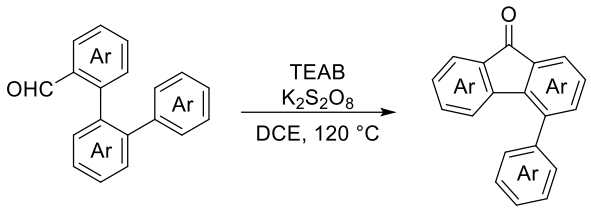
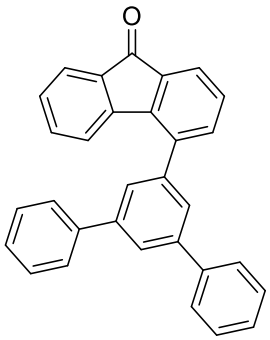


Fig. S2 Scale-up synthesis

V. Synthesis of multi-aryl fluorenones

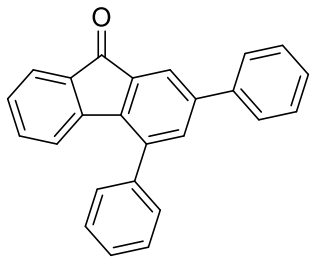


To a 100 mL Schlenk tube was added TEAB (42 mg, 10 mol %), $K_2S_2O_8$ (1.08 g, 2.0 equiv) and the tube was purged with Ar for three times, followed by addition of biphenyl-2-formaldehyde (364 mg, 2.0 mmol) and DCE (10 mL). The formed mixture was stirred at 120 ºC under N_2 for 36 h. The solution was then cooled to rt, and DCE was removed under vaccum directly. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 3/1, v/v) to provide the desired product.[3]



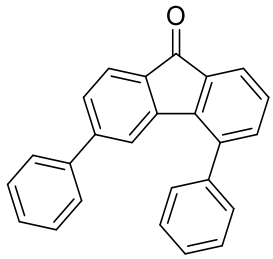
4-(3,5-Diphenyl)phenyl-9*H*-fluoren-9-one (39)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 3/1, v/v) afforded the desired product **39** as a yellow solid (538.8 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 1H), 7.74-7.66 (m, 8H), 7.50-7.45 (m, 5H), 7.42-7.35 (m, 3H), 7.23-7.19 (m, 2H), 7.00-6.97 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.97, 144.67, 142.33, 141.27, 140.62, 140.55, 138.10, 136.87, 134.91, 134.71, 134.59, 129.09, 128.98, 128.95, 127.93, 127.36, 126.60, 125.87, 124.43, 123.62, 123.27 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{21}O$, $[M+H]^+$ 409.1587, found: 409.1582.



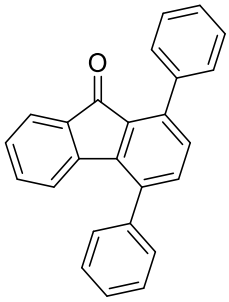
2,4-Diphenyl-9*H*-fluoren-9-one (40)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 3/1, v/v) afforded the desired product **40** as a yellow solid (431.8 g, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 7.6, 1H), 7.69-7.65 (m, 3H), 7.59 (d, J = 1.6, 1H), 7.52 (s, 5H), 7.46 (t, J = 8.0, 2H), 7.39 (d, J = 7.6, 1H), 7.22-7.19 (m, 2H), 6.80-6.78 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.96, 144.53, 141.93, 139.99, 139.57, 139.55, 138.67, 135.66, 135.25, 134.88, 134.67, 129.09, 128.97, 128.93, 128.77, 128.39, 128.18, 126.95, 124.39, 123.21, 121.96 ppm. HRMS (ESI^+): calcd for $C_{25}H_{17}O$, $[M+H]^+$ 333.1274, found: 333.1275.



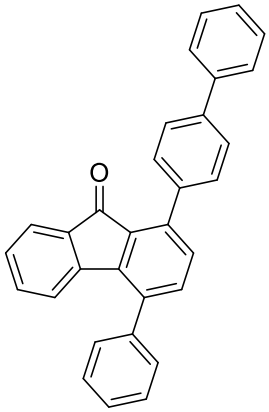
3,5-Diphenyl-9*H*-fluoren-9-one (41)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 3/1, v/v) afforded the desired product **41** as a yellow solid (395.6 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.70 (m, 2H), 7.55-7.49 (m, 5H), 7.45 (dd, J_1 = 7.6, J_2 = 1.2, 1H), 7.38-7.32 (m, 7H), 6.98 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.62, 147.10, 145.41, 140.95, 140.02, 139.58, 138.39, 136.58, 135.36, 133.39, 129.01, 128.98, 128.87, 128.39, 127.38, 126.98, 124.72, 123.37, 122.15 ppm. HRMS (ESI^+): calcd for $C_{25}H_{17}O$, $[M+H]^+$ 333.1274, found: 333.1273.



1,4-Diphenyl-9*H*-fluoren-9-one (42)

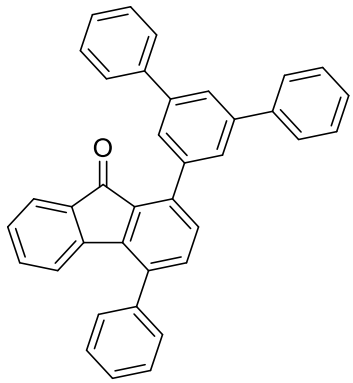
Following the general procedure, purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 3/1, v/v) afforded the desired product **42** as a yellow solid (411.8 g, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.44 (m, 11H), 7.35 (d, J = 8.0, 1H), 7.24-7.14 (m, 3H), 6.71-6.69 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.09, 143.69, 142.14, 141.35, 139.67, 137.66, 137.34, 136.30, 134.68, 134.24, 131.42, 131.40, 130.23, 129.29, 129.01, 128.94, 128.88, 128.30, 128.01, 124.05, 123.20 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{17}O$, $[M+H]^+$ 333.1274, found: 333.1273.



1-([1,1'-Biphenyl]-4-yl)-4-phenyl-9*H*-fluoren-9-one (43)

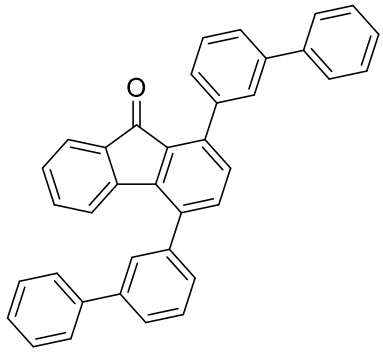
Following the general procedure, purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 3/1, v/v) afforded the desired product **43** as a yellow solid (522.4 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (t, J = 8.0, 4H), 7.56 (d, J = 8.4, 2H), 7.60 (d, J = 8.0, 1H), 7.53-7.46 (m, 7H), 7.40-7.36 (m, 2H), 7.28 (d, J = 8.0, 1H), 7.22-7.16 (m, 2H), 6.71 (d, J = 6.4, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.20, 143.69, 142.26, 141.12, 141.01, 140.96, 139.64, 137.40, 136.59, 136.40, 134.68, 134.30, 131.41, 130.23, 129.81, 129.01, 128.96, 128.91, 128.33 ppm. HRMS

(ESI$^+$): calcd for $C_{31}H_{21}NaO$, $[M+Na]^+$ 431.1406, found: 431.1404.



1-(3,5-Diphenyl)phenyl-4-phenyl-9*H*-fluoren-9-one (44)

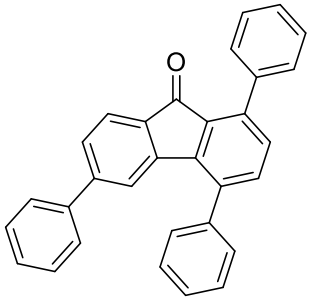
Following the general procedure, purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 3/1, v/v) afforded the desired product **44** as a yellow solid (581.0 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.88 (m, 1H), 7.80-7.74 (m, 6H), 7.63 (d, J = 6.0, 1H), 7.53-7.47 (m, 9H), 7.40-7.35 (m, 4H), 7.23-7.16 (m, 2H), 6.71 (d, J = 7.6, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.08, 143.67, 142.33, 141.50, 141.33, 141.07, 139.66, 138.39, 137.57, 136.41, 134.72, 134.28, 131.50, 130.36, 129.02, 128.97, 128.92, 128.36, 127.60, 127.53, 127.39, 126.14, 124.17, 123.25 ppm. HRMS (ESI$^+$): calcd for $C_{37}H_{25}O$, $[M+H]^+$ 485.1900, found: 485.1901.



1,4-Di([1,1'-biphenyl]-3-yl)-9*H*-fluoren-9-one (45)

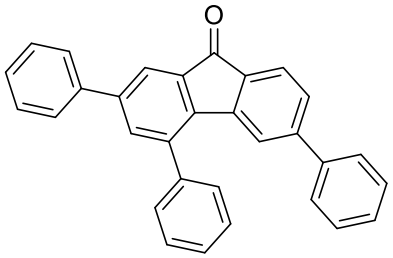
Following the general procedure, purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 2/1, v/v) afforded the desired product **45** as a yellow solid (590.7 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.77-7.75 (m, 2H), 7.71-7.67 (m, 5H), 7.64-7.60 (m, 2H), 7.57-7.56 (m, 2H), 7.50-7.42 (m, 6H), 7.41-

7.35 (m, 2H), 7.32 (d, J = 7.6, 1H), 7.23-7.17 (m, 2H), 6.84-6.82 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.05, 143.68, 142.29, 141.77, 141.32, 141.30, 140.99, 140.62, 140.13, 137.99, 137.31, 136.37, 134.71, 134.36, 131.52, 130.33, 129.46, 129.05, 128.97, 128.88, 128.42, 128.34, 128.28, 127.85, 127.79, 127.77, 127.49, 127.40, 127.27, 127.15, 127.02, 124.17, 123.22 ppm. HRMS (ESI^+): calcd for $C_{37}H_{25}O$, $[M+H]^+$ 485.1900, found: 485.1900.



1,4,7-Triphenyl-9*H*-fluoren-9-one (46)

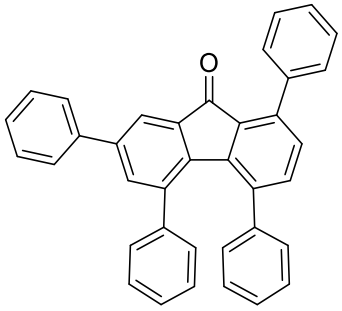
Following the general procedure, purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 3/1, v/v) afforded the desired product **46** as a yellow solid (489.8 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 7.6, 1H), 7.59-7.53 (m, 7H), 7.51-7.31 (m, 11H), 7.27-7.25 (m, 1H), 6.93 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.66, 146.79, 144.45, 141.98, 141.37, 140.13, 139.74, 137.71, 137.40, 136.00, 133.60, 131.56, 130.82, 129.35, 129.12, 128.96, 128.40, 128.31, 128.03, 127.44, 126.99, 124.47, 122.13 ppm. HRMS (ESI^+): calcd for $C_{31}H_{20}NaO$, $[M+Na]^+$ 431.1406, found: 431.1404.



2,4,7-Triphenyl-9*H*-fluoren-9-one (47)

Following the general procedure, purification via silica gel column chromatography

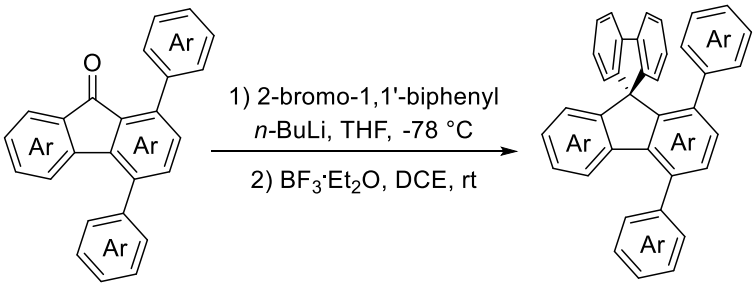
(petroleum ether/CH_2Cl_2 = 3/1, v/v) afforded the desired product **47** as a yellow solid (514.3 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1H), 7.74-7.76 (m, 5H), 7.56-7.36 (m, 13H), 7.03 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =193.45, 147.26, 145.30, 142.13, 140.07, 139.79, 139.64, 139.62, 138.72, 136.26, 134.96, 133.77, 129.11, 129.07, 129.00, 128.92, 128.50, 128.42, 128.20, 127.33, 127.01, 124.79, 122.07, 121.92 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{21}O$, $[M+H]^+$ 409.1587, found: 409.1585



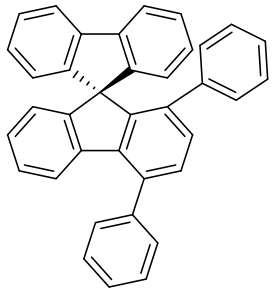
2,4,7-Tetraphenyl-9*H*-fluoren-9-one (48)

Following the general procedure, purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 3/1, v/v) afforded the desired product **48** as a yellow solid (590.7 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 1.6, 1H), 7.64-7.60 (m, 4H), 7.53-7.42 (m, 6H), 7.38-7.34 (m, 1H), 7.25-7.20 (m, 2H), 7.07-6.90 (m, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.07, 143.88, 141.87, 141.08, 141.03, 140.88, 140.79, 139.60, 139.42, 138.29, 138.18, 137.75, 137.52, 136.12, 133.18, 131.11, 129.48, 129.05, 128.58, 128.53, 128.40, 128.36, 128.32, 128.10, 127.01, 126.93, 121.17 ppm. HRMS (ESI$^+$): calcd for $C_{37}H_{25}O$, $[M+H]^+$ 485.1900, found: 485.1900.

VI. Synthesis of 1,4-diaryl 9,9'-spirobifluorenes



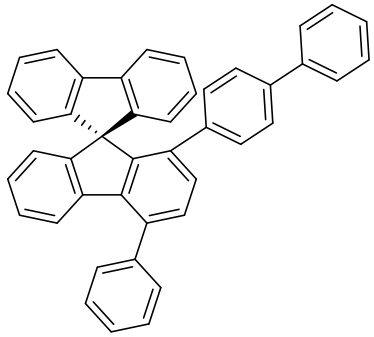
2-Bromobiphenyl (1.1 equiv) was dissolved in dry THF (40 mL) and cooled down to -78 °C. A 2.5 M pentane solution of *n*-BuLi (1.0 equiv) was then added dropwise to the solution at -78 °C. The resulting mixture was stirred at the same temperature for one hour and the fluorenone (1.0 equiv) dissolved in dry THF (20 mL) was added dropwise. The reaction mixture was allowed to warm up to 75 °C and stirred for 24 h. After cooling to room temperature, a saturated solution of ammonium chloride was added. The organic layer was extracted with ethyl acetate. The combined organic extracts were dried over sodium sulfate, and concentrated under reduced pressure. The residue was dissolved in DCE (50-100 mL) before trifluoroboron etherate (5.0 equiv) was added slowly and the solution was stirred for 3 h at room temperature. The reaction was quenched with methanol and evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/CH_2Cl_2 = 6/1, v/v) to give the desired product.



1,4-Diphenyl-9,9'-spirobifluorene (1,4-dp-SBF)

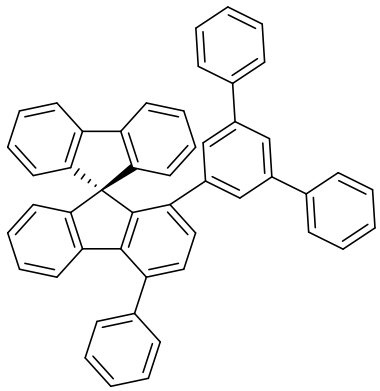
Prepared according to general procedure from 1,4-diphenyl-9*H*-fluoren-9-one (**42**, 996.4 mg, 3 mmol), purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 6/1, v/v) afforded the desired product 1,4-dp-SBF as a white solid (1.12 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 7.6, 2H), 7.62-7.52 (m, 3H), 7.38 (d, J = 7.6, 2H), 7.29 (d, J = 7.6, 1H), 7.22 (t, J = 7.2, 2H), 7.08 (t, J = 7.6, 2H), 7.00-6.96 (m, 4H), 6.90 (t, J = 7.2, 1H), 6.84 (d, J = 7.6, 2H), 6.68 (t, J = 7.6, 2H), 6.56 (d, J = 7.2, 1H), 6.17 (d, J = 8.0, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.63, 148.51, 145.83, 142.10, 141.03, 139.68, 139.24, 138.60, 136.84, 129.73, 129.37, 128.84, 128.63, 128.44, 127.69, 127.52, 127.25, 127.21, 126.94, 126.42,

125.61, 123.80, 123.61, 123.00, 119.85, 65.49 ppm. HRMS (ESI$^+$): calcd for $C_{37}H_{25}$ $[M+H]^+$ 469.1951, found: 469.1953.



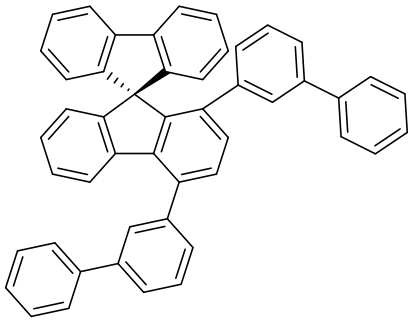
1-([1,1'-Biphenyl]-4-yl)-4-phenyl-9,9'-spirobifluorene (1-pbp-4-p-SBF)

Prepared according to general procedure from 1-([1,1'-biphenyl]-4-yl)-4-phenyl-9*H*-fluoren-9-one (**43**, 1.22 g, 3 mmol), purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 6/1, v/v) afforded the desired product 1-pbp-4-p-SBF as a white solid (1.32 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.68 (m, 2H), 7.62-7.54 (m, 3H), 7.64 (d, *J* = 4.4, 4H), 7.39-7.29 (m, 4H), 7.22 (t, *J* = 7.6, 2H), 7.10 (t, *J* = 7.2, 2H), 7.05-6.95 (m, 4H), 6.86 (t, *J* = 8.4, 4H), 6.56 (d, *J* = 7.2, 1H), 6.21 (d, *J* = 8.0, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.64, 148.61, 146.43, 142.31, 141.67, 141.20, 141.12, 139.40, 139.35, 138.54, 137.78, 137.06, 129.89, 129.48, 128.93, 128.80, 128.76, 128.71, 127.82, 127.67, 127.41, 127.37, 127.16, 127.10, 125.32, 123.97, 123.77, 123.14, 119.93, 65.62 ppm. HRMS (ESI$^+$): calcd for $C_{43}H_{28}Na$, $[M+Na]^+$ 567.2083, found: 567.2080.



1-(3,5-Diphenyl) phenyl-4-phenyl-9,9'-spirobifluorene (1-mtp-4-p-SBF)

Prepared according to general procedure from 1-(3,5-diphenyl) phenyl-4-phenyl-9*H*-fluoren-9-one (**44**, 1.45 g, 3 mmol), purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 5/1, v/v) afforded the desired product 1-mtp-4-p-SBF as a white solid (1.45 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 6.8, 2H), 7.61-7.55 (m, 3H), 7.42-7.28 (m, 12H), 7.22-7.20 (m, 2H), 7.09 (d, J = 7.6, 1H), 7.04-7.00 (m, 4H), 6.97-6.93 (m, 1H), 6.91-6.87 (m, 4H), 6.52 (d, J = 7.2, 1H), 6.44 (d, J = 2.0, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.77, 148.23, 145.92, 141.95, 140.98, 140.96, 140.06, 139.49, 139.35, 139.32, 137.07, 129.85, 129.36, 128.76, 128.66, 128.38, 127.74, 127.57, 127.45, 127.26, 127.16, 127.01, 126.97, 126.81, 123.70, 123.58, 123.57, 123.04, 119.71, 65.60 ppm. HRMS (ESI$^+$): calcd for $C_{49}H_{33}$, $[M+H]^+$ 621.2577, found: 621.2579.

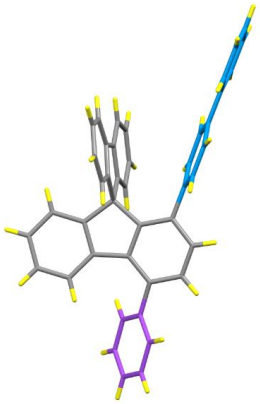


1,4-Di([1,1'-biphenyl]-3-yl)-9,9'-spirobifluorene (1,4-d(mbp)-SBF)

Prepared according to general procedure from 1,4-di([1,1'-biphenyl]-3-yl)-9*H*-fluoren-9-one (**45**, 1.45 g, 3 mmol), purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 5/1, v/v) afforded the desired product 1,4-d(mbp)-SBF as a white solid (1.43 g, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (s, 1H), 7.79-7.74 (m, 3H), 7.67 (d, J = 4.8, 2H), 7.50 (t, J = 7.6, 2H), 7.42-7.29 (m, 7H), 7.23-7.12 (m, 4H), 7.07-7.01 (m, 6H), 6.96 (t, J = 7.6, 1H), 6.89 (s, 2H), 6.76 (t, J = 7.6, 1H), 6.54 (d, J = 8.4, 1H), 6.47 (s, 1H), 6.16 (d, J = 7.6, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.75, 148.37, 145.96, 142.05, 141.47, 141.03, 140.99, 140.97, 139.64, 139.51, 139.34, 139.03, 136.82, 129.81, 129.10, 128.86, 128.29, 128.24, 128.18, 127.59, 127.57, 127.49, 127.34, 127.27, 127.21, 127.17, 127.03, 126.87, 126.82, 126.44, 124.51, 123.76, 123.63, 123.02, 119.79, 65.59 ppm. HRMS (ESI$^+$): calcd for $C_{49}H_{32}Na$, $[M+Na]^+$ 643.2396, found: 643.2397.

VII. Crystallographic data

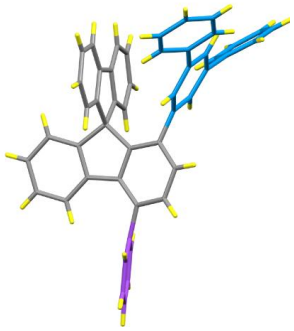
Table S2 Crystal data and structure refinement for **1-pbp-4-p-SBF**



Identification code	1-pbp-4-p-SBF
Empirical formula	$C_{43}H_{28}$
Formula weight	544.65
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	10.0916(4)
b/Å	10.7661(4)
c/Å	13.9350(5)
α/°	74.8680(10)
β/°	84.9120(10)
γ/°	78.065(2)
Volume/Å^3	1428.94(9)
Z	2
ρ_{calc}g/cm^3	1.266
μ/mm^{-1}	0.072
F(000)	572.0
Crystal size/mm^3	0.4 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.992 to 55.034
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -18 ≤ l ≤ 16

Reflections collected	22766
Independent reflections	6535 [R_{int} = 0.0449, R_{sigma} = 0.0422]
Data/restraints/parameters	6535/0/388
Goodness-of-fit on F_2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.1029
Final R indexes [all data]	R_1 = 0.0632, wR_2 = 0.1174
Largest diff. peak/hole / e Å^{-3}	0.22/-0.24

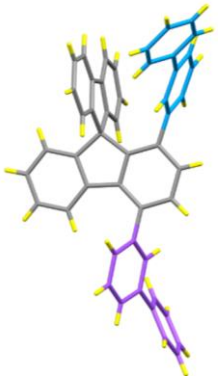
Table S3 Crystal data and structure refinement for **1-mtp-4-p-SBF**



Identification code	1-mtp-4-p-SBF
Empirical formula	$C_{49}H_{32}$
Formula weight	620.74
Temperature/K	302.0
Crystal system	triclinic
Space group	P-1
a/Å	10.5749(4)
b/Å	12.4865(5)
c/Å	12.8313(5)
α/°	90.4010(10)
β/°	90.1470(10)
γ/°	99.5750(10)
Volume/Å^3	1670.63(11)
Z	2
ρ_{calc}g/cm^3	1.234
μ/mm^{-1}	0.070

F(000)	652.0
Crystal size/mm^3	0.42 × 0.3 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.906 to 55.032
Index ranges	-11 ≤ h ≤ 13, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16
Reflections collected	28738
Independent reflections	7628 [R_{int} = 0.0912, R_{sigma} = 0.0818]
Data/restraints/parameters	7628/0/442
Goodness-of-fit on F_2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0582, wR_2 = 0.1395
Final R indexes [all data]	R_1 = 0.1014, wR_2 = 0.1653
Largest diff. peak/hole / e Å^{-3}	0.19/-0.21

Table S4 Crystal data and structure refinement for **1,4-d(mbp)-SBF**



Identification code	1,4-d(mbp)-SBF
Empirical formula	$C_{49}H_{32}$
Formula weight	620.74
Temperature/K	280.0
Crystal system	triclinic
Space group	P-1
a/Å	9.9178(5)
b/Å	13.3016(8)
c/Å	14.7232(9)
α/°	68.269(2)

β/°	83.486(2)
γ/°	69.787(2)
Volume/Å^3	1692.94(17)
Z	2
ρ_{calc}g/cm^3	1.218
μ/mm^{-1}	0.069
F(000)	652.0
Crystal size/mm^3	0.4 × 0.34 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.614 to 55.052
Index ranges	-12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	40814
Independent reflections	7781 [R_{int} = 0.0995, R_{sigma} = 0.0732]
Data/restraints/parameters	7781/0/442
Goodness-of-fit on F_2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0603, wR_2 = 0.1433
Final R indexes [all data]	R_1 = 0.1127, wR_2 = 0.1720
Largest diff. peak/hole / e Å^{-3}	0.31/-0.28

VIII. Photophysical properties

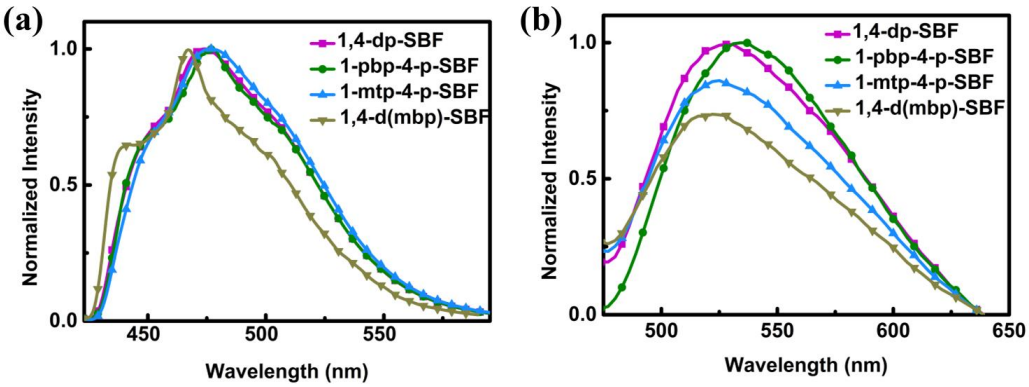


Fig. S3 (a) Phosphorescence spectra at 77 K in toluene, and (b) in thin film of **1,4-dp-SBF**, **1-pbp-4-p-SBF**, **1-mtp-4-p-SBF**, and **1,4-d(mbp)-SBF**

IX. Thermal properties

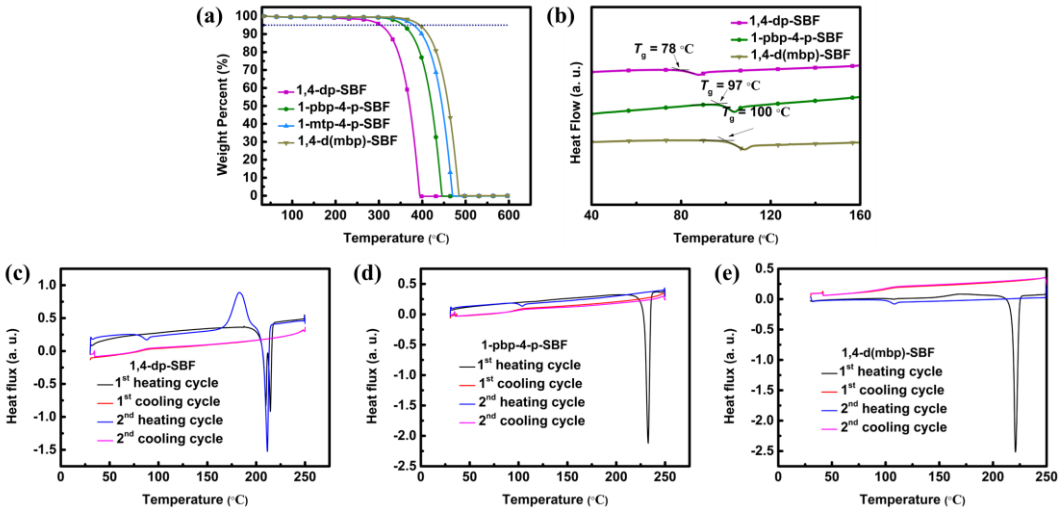


Fig. S4 TGA curves and DSC curves. (a) TGA curves of **1,4-dp-SBF**, **1-pbp-4-p-SBF**, **1-mtp-4-p-SBF** and **1,4-d(mbp)-SBF**. (b) DSC curves of **1,4-dp-SBF**, **1-pbp-4-p-SBF** and **1,4-d(mbp)-SBF**. (c) DSC curves with two heating cycles and two cooling cycles of **1,4-dp-SBF** (d) DSC curves with two heating cycles and two cooling cycles of **1-pbp-4-p-SBF**, (e) DSC curves with two heating cycles and two cooling cycles of **1,4-d(mbp)-SBF**

X. Charge transport properties

Space-charged limited current (SCLC) diodes

The hole-only device (HOD) has a configuration of ITO/HAT-CN (10 nm)/host (60 nm)/HAT-CN (10 nm)/ Al (100 nm), and the electron-only device (EOD) is ITO/LiF (0.8 nm)/host (60 nm)/LiF (0.8 nm)/Al (100 nm).

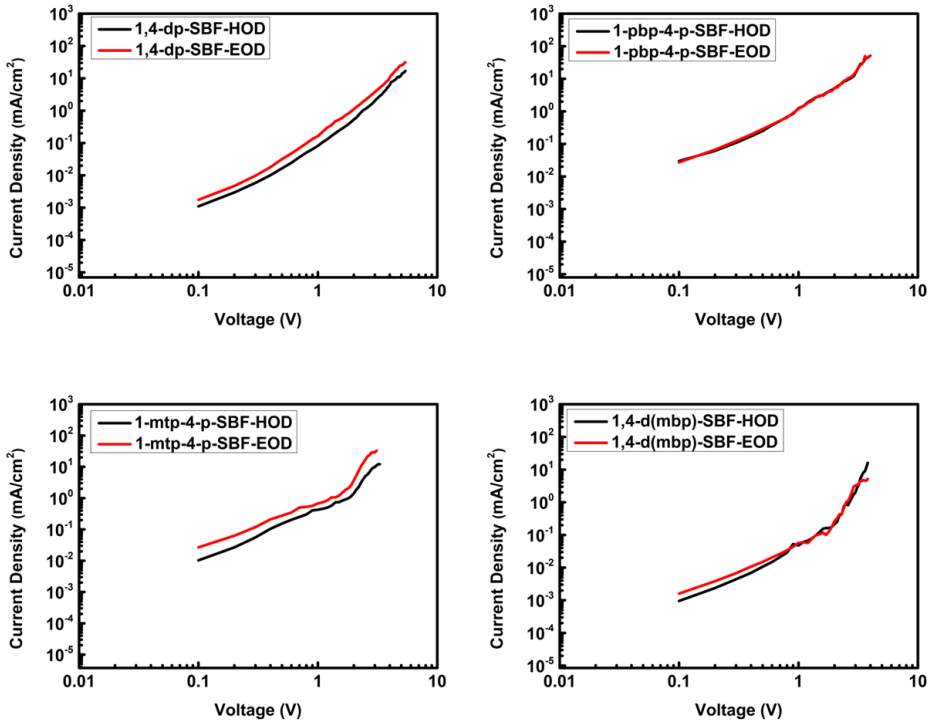


Fig. S5 The *J-V* curves of hole-only (HOD) and electron-only (EOD) devices using **1,4-dp-SBF**, **1-pbp-4-p-SBF**, **1-mtp-4-p-SBF**, and **1,4-d(mbp)-SBF**

The *J-V* curves of charge-only devices show the charge transport ability of the compounds. Based on the Schottky thermionic region and space-charge-limited current (SCLC) model, the curves can be divided into two parts under low bias. We assign the second region of the *J-V* curve as assigned as the SCLC region, which then can be described by an equation:

$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu_0 exp(\beta\sqrt{\frac{V}{L}})\frac{V^2}{L^3}$$

in which V is the driving voltage, L is the thickness of the thin layer, ε_0 the permittivity of the free space, ε is the relative dielectric constant (estimated to be 3.0 here), μ_0 is the zero-field mobility and β is Poole-Frenkel factor. The thickness L equals to 60 nm, and the zero-field mobility of the compounds was calculated and summarized in Table 2.

XI. Phosphorescent OLED characteristics

The device configuration of blue PhOLEDs is ITO/**HAT-CN** (10 nm)/**TAPC** (30 nm for **1,4-dp-SBF**, **1-pbp-4-p-SBF**, **1-mtp-4-p-SBF** and 35 nm for **1,4-d(mbp)-SBF**) /**TCTA** (8 nm)/**mCP** (10 nm)/host: 15 wt% **Flrpic** (20 nm)/**TmPyPB** (40 nm)/LiF (0.8 nm)/Al (100 nm). In the PhOLED devices, LiF and 1,4,5,8,9,12-hexaazatriphenylene hexacarbonitrile (**HAT-CN**) act as the electron- and hole-injecting materials, respectively. 1,3,5-Tri(*m*-pyrid-3-ylphenyl)benzene (**TmPyPB**) and 1,1-bis(2-(*N*,*N*-di-4-tolylamino)phenyl)cyclohexane (**TAPC**) serve as the electron- and hole-transporting materials, respectively. 4,4',4''-Tris(9*H*-carbazol-9-yl)triphenylamine (**TCTA**) and *m*-di(9*H*-carbazol-9-yl)benzene (**mCP**) constitute exciton-blocking layers together. The device configuration of green PhOLEDs is ITO/ **HAT-CN** (10 nm)/**TAPC** (45 nm for **1,4-dp-SBF**, 35 nm for **1-pbp-4-p-SBF** and 40 nm for **1-mtp-4-p-SBF**, **1,4-d(mbp)-SBF**)/**TCTA** (10 nm)/host: 14 wt% **Ir(ppy)$_2$acac** (20 nm)/**TmPyPB** (45 nm for **1,4-dp-SBF**, 40 nm for **1-pbp-4-p-SBF**, **1-mtp-4-p-SBF**, **1,4-d(mbp)-SBF**)/LiF (0.8 nm)/Al (100 nm). The device configuration of red PhOLEDs is ITO/**HAT-CN** (10 nm)/**TAPC** (40 nm for **1,4-dp-SBF**, **1-mtp-4-p-SBF**, **1,4-d(mbp)-SBF**, 30 nm for **1-pbp-4-p-SBF**)/**TCTA** (10 nm)/**mCP** (10 nm)/host: 3 wt% **Ir(mphmq)$_2$tmd** (20 nm)/**TmPyPB** (50 nm for **1,4-dp-SBF**, **1-pbp-4-p-SBF**, **1,4-d(mbp)-SBF**, 40 nm for **1-mtp-4-p-SBF**)/LiF (0.8 nm)/Al (100 nm).

i) Device structure and energy-level diagram of OLED devices

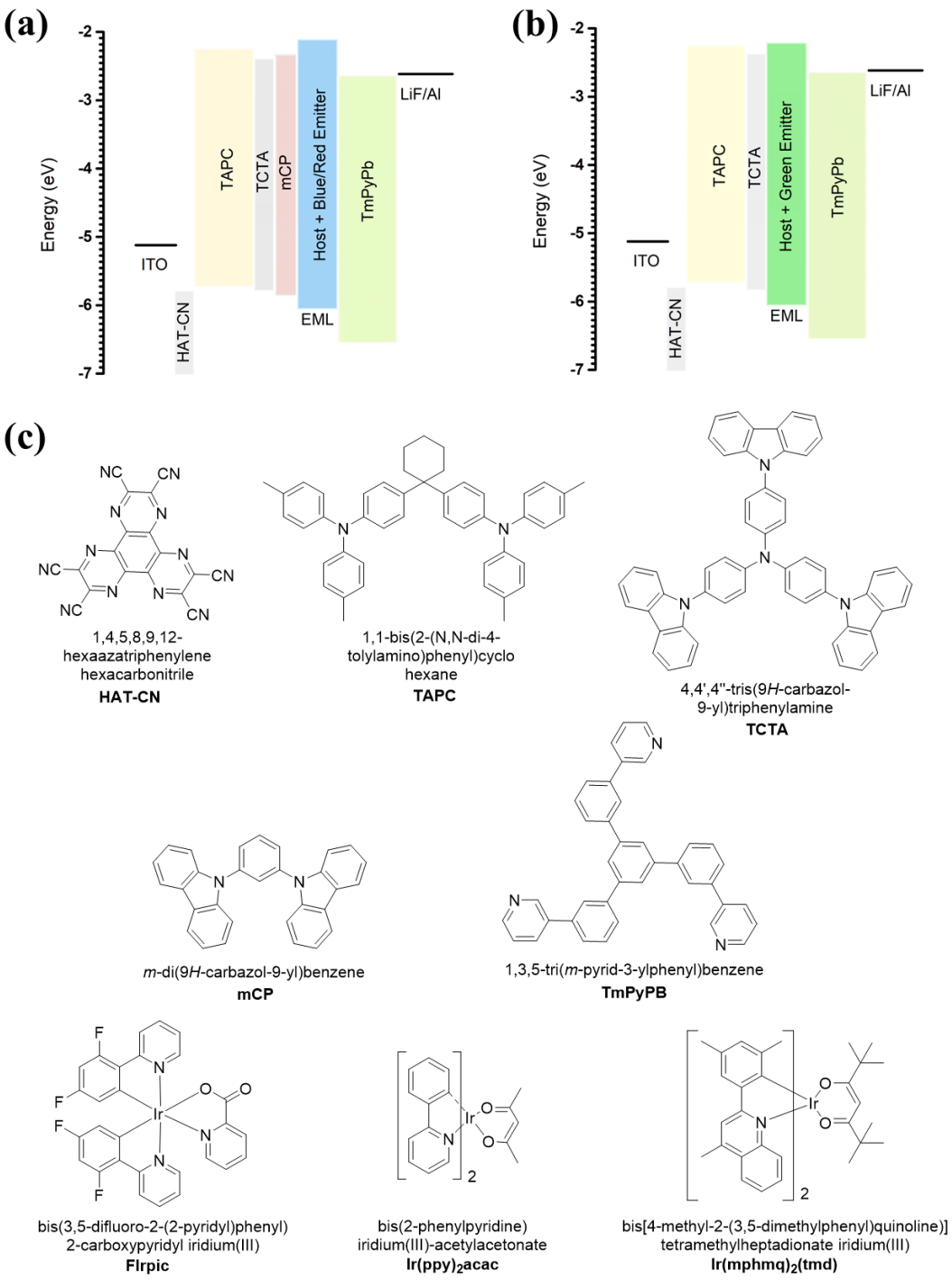


Fig. S6 Device structure and energy-level diagram of OLED devices. (a) Red and blue OLED devices structure with corresponding energy levels. (b) green OLED devices structure with corresponding energy levels. (c) Molecular structures of the materials used in OLEDs

ii) Optimized device structures

Red:

ITO/**HAT-CN** (10 nm)/**TAPC** (40 nm)/**TCTA** (10 nm)/**mCP** (10 nm)/ **1,4-dp-SBF**: 3 wt% **Ir(mphmq)$_2$tmd** (20 nm)/**TmPyPB** (50 nm)/LiF (0.8 nm)/Al (100 nm).

ITO/**HAT-CN** (10 nm)/**TAPC** (30 nm)/**TCTA** (10 nm)/**mCP** (10 nm)/**1-pbp-4-p-SBF**: 3 wt% **Ir(mphmq)$_2$tmd** (20 nm)/**TmPyPB** (50 nm)/LiF (0.8 nm)/Al (100 nm).

ITO/**HAT-CN** (10 nm)/**TAPC** (40 nm)/**TCTA** (10 nm)/**mCP** (10 nm)/**1-mtp-4-p-SBF**: 3 wt% **Ir(mphmq)$_2$tmd** (20 nm)/**TmPyPB** (40 nm)/LiF (0.8 nm)/Al (100 nm).

ITO/**HAT-CN** (10 nm)/**TAPC** (40 nm)/**TCTA** (10 nm)/**mCP** (10 nm)/**1,4-d(mbp)-SBF**: 3 wt% **Ir(mphmq)$_2$tmd** (20 nm)/**TmPyPB** (50 nm)/LiF (0.8 nm)/Al (100 nm).

Green:

ITO/**HAT-CN** (10 nm)/**TAPC** (45 nm)/**TCTA** (10 nm)/ **1,4-dp-SBF**: 14 wt% **Ir(ppy)$_2$acac** (20 nm)/**TmPyPB** (45 nm)/LiF (0.8 nm)/Al (100 nm).

ITO/**HAT-CN** (10 nm)/**TAPC** (35 nm)/**TCTA** (10 nm)/**1-pbp-4-p-SBF**: 14 wt% **Ir(ppy)$_2$acac** (20 nm)/**TmPyPB** (40 nm)/LiF (0.8 nm)/Al (100 nm).

ITO/**HAT-CN** (10 nm)/**TAPC** (40 nm)/**TCTA** (10 nm)/**1-mtp-4-p-SBF**: 14 wt% **Ir(ppy)$_2$acac** (20 nm)/**TmPyPB** (40 nm)/LiF (0.8 nm)/Al (100 nm).

ITO/**HAT-CN** (10 nm)/**TAPC** (40 nm)/**TCTA** (10 nm)/**1,4-d(mbp)-SBF**: 14 wt% **Ir(ppy)$_2$acac** (20 nm)/**TmPyPB** (40 nm)/LiF (0.8 nm)/Al (100 nm).

Blue:

ITO/**HAT-CN** (10 nm)/**TAPC** (30 nm)/**TCTA** (8 nm)/**mCP** (10 nm)/**1,4-dp-SBF**: 15 wt% **Flrpic** (20 nm)/**TmPyPB** (40 nm)/LiF (0.8 nm)/Al (100 nm).

ITO/**HAT-CN** (10 nm)/**TAPC** (30 nm)/**TCTA** (8 nm)/**mCP** (10 nm)/**1-pbp-4-p-SBF**: 15 wt% **Flrpic** (20 nm)/**TmPyPB** (40 nm)/LiF (0.8 nm)/Al (100 nm).

ITO/**HAT-CN** (10 nm)/**TAPC** (30 nm)/**TCTA** (8 nm)/**mCP** (10 nm)/**1-mtp-4-p-SBF**: 15 wt% **Flrpic** (20 nm)/**TmPyPB** (40 nm)/LiF (0.8 nm)/Al (100 nm).

ITO/**HAT-CN** (10 nm)/**TAPC** (35 nm)/**TCTA** (8 nm)/**mCP** (10 nm)/**1,4-d(mbp)-SBF**: 15 wt% **Flrpic** (20 nm)/**TmPyPB** (40 nm)/LiF (0.8 nm)/Al (100 nm).

Table S5 EQE and power efficiency for green PhOLED devices at the luminance of 5000 cd m^{-2}

Emitter	Host	EQE [%]	PE [lm W^{-1}]
$Ir(ppy)_2acac$	**1,4-dp-SBF**	17.9	41.5
	1-pbp-4-p-SBF	23.0	56.8
	1-mtp-4-p-SBF	20.4	52.2
	1,4-d(mbp)-SBF	17.0	34.1

XII. References

1. S. Rej and N. Chatani, *J. Am. Chem. Soc.* 2021, **143**, 2920-2929.
2. J. Zhao, D. Yue, M. A. Campo and R. C. Larock, *J. Am. Chem. Soc.* 2007, **129**, 5288-5295.
3. Z. Shi and F. Glorius, *Chem. Sci.* 2013, **4**, 829-833.

XIII. Copies of ^{1}H, ^{13}C NMR and ^{19}F NMR spectra

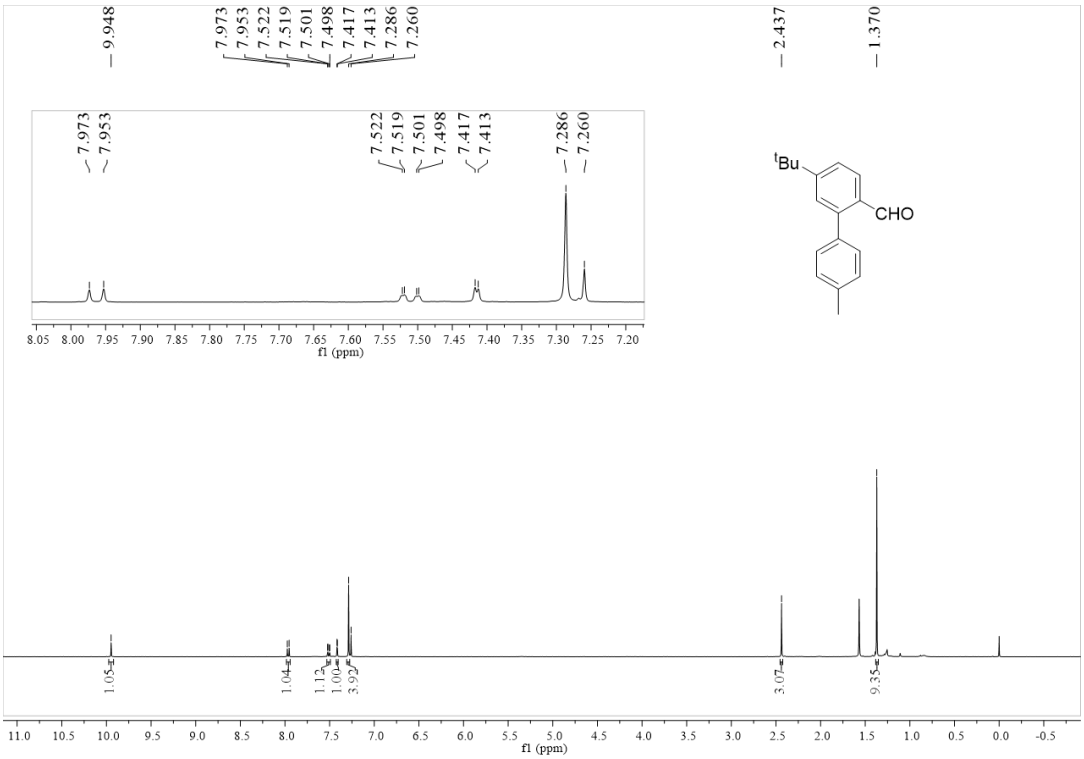


Fig. S7 ^{1}H NMR spectrum of **49** in $CDCl_3$.

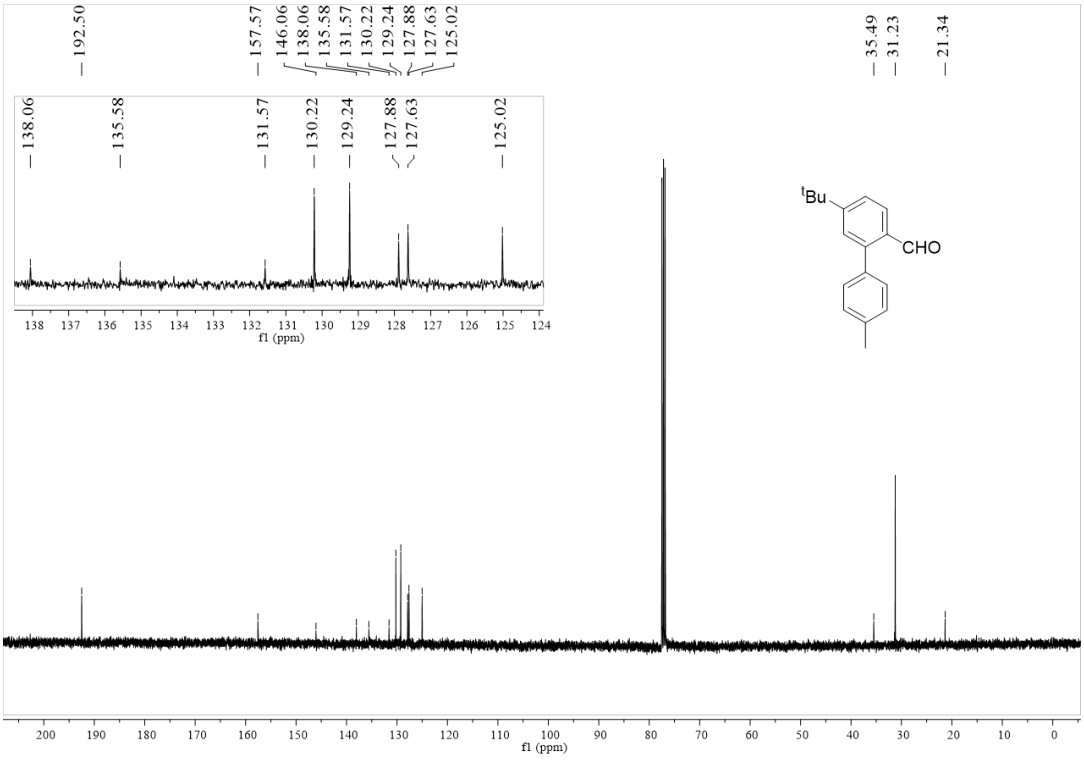


Fig. S8 ^{13}C NMR spectrum of **49** in $CDCl_3$.

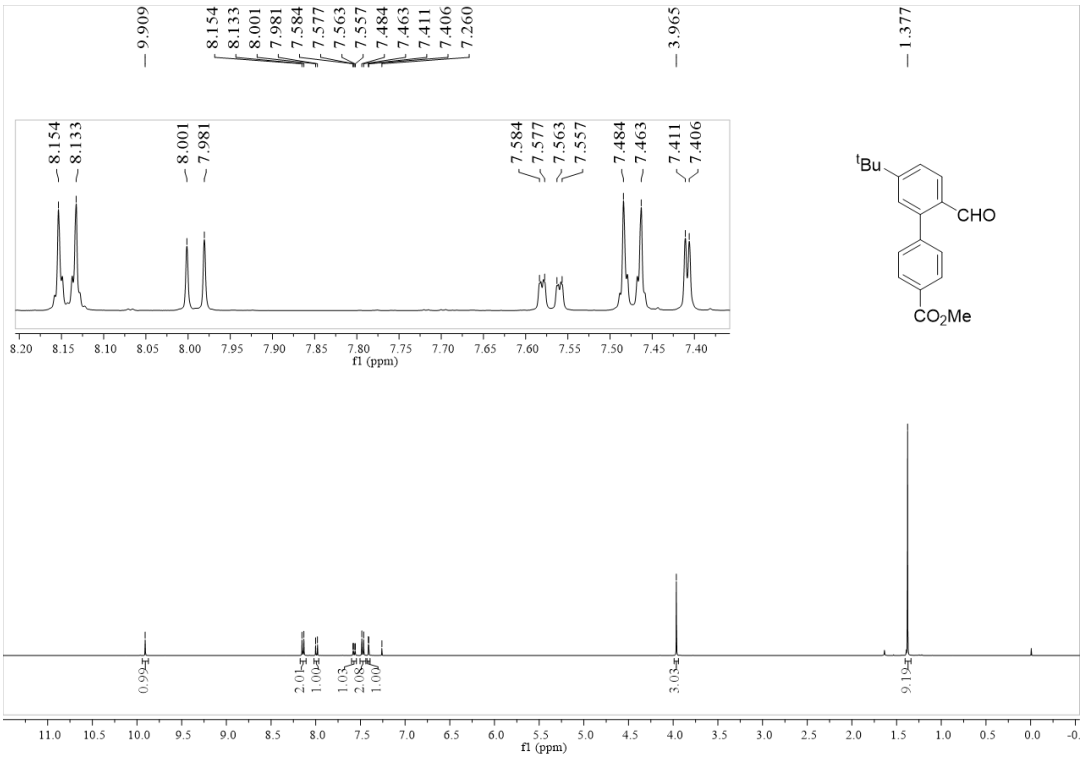


Fig. S9 ^{1}H NMR spectrum of **50** in $CDCl_3$

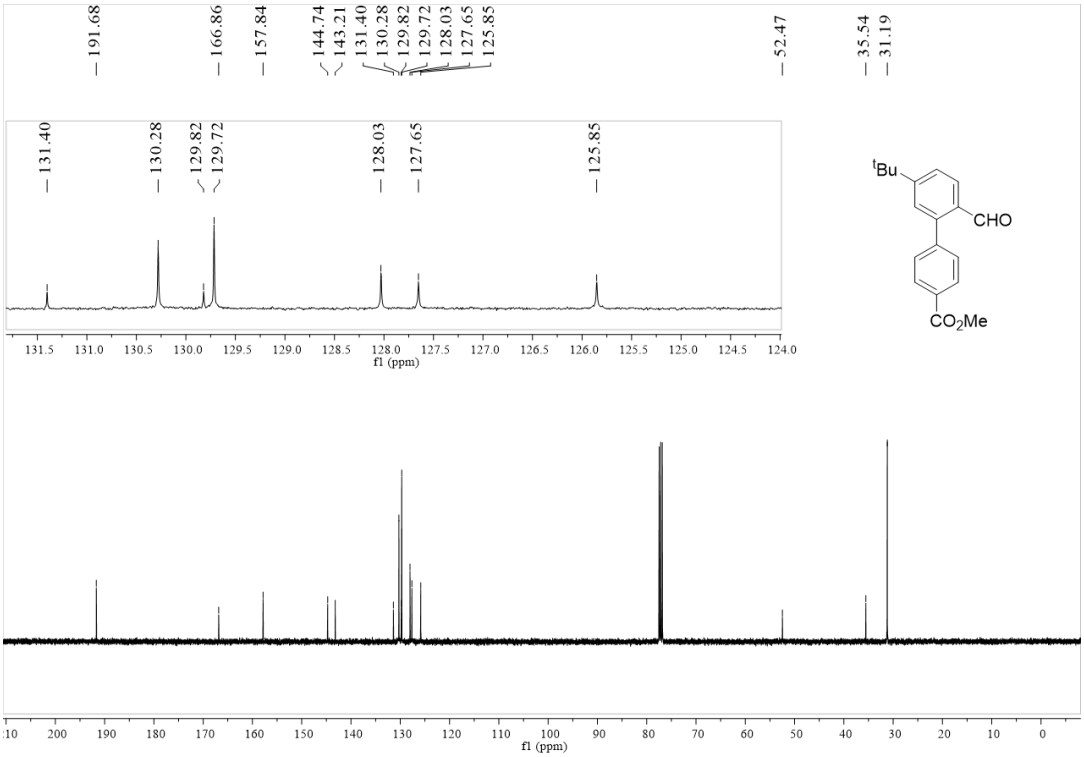


Fig. S10 ^{13}C NMR spectrum of **50** in $CDCl_3$

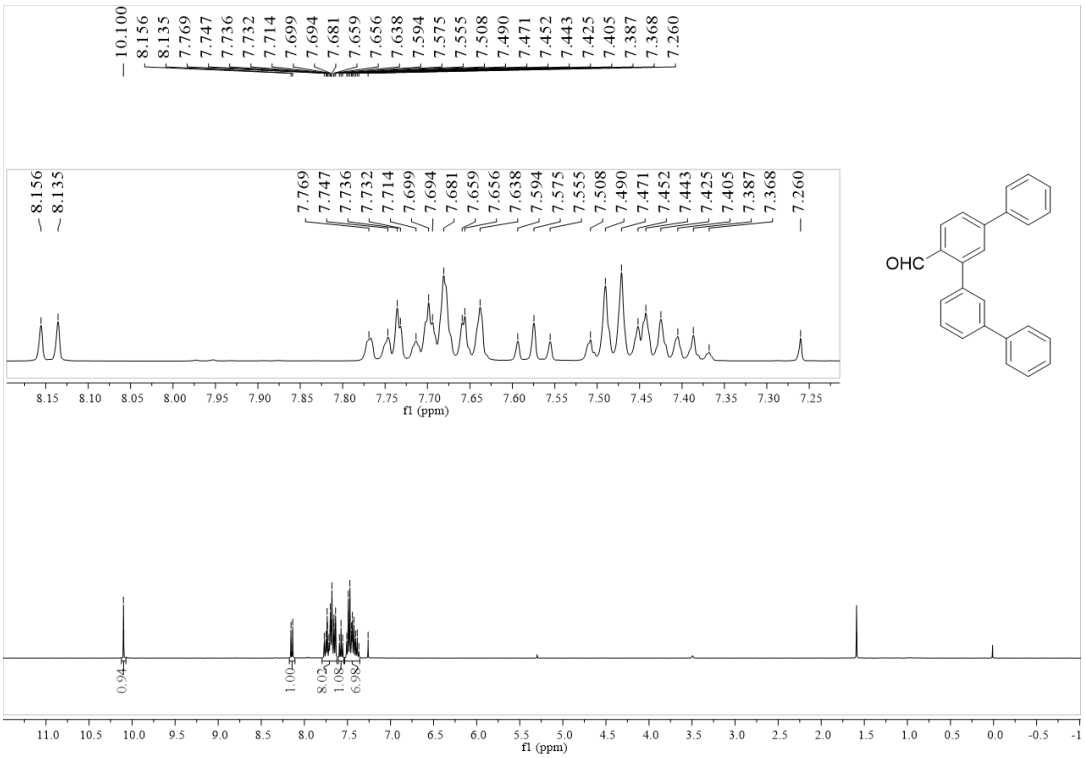


Fig. S11 ^{1}H NMR spectrum of **51** in $CDCl_3$

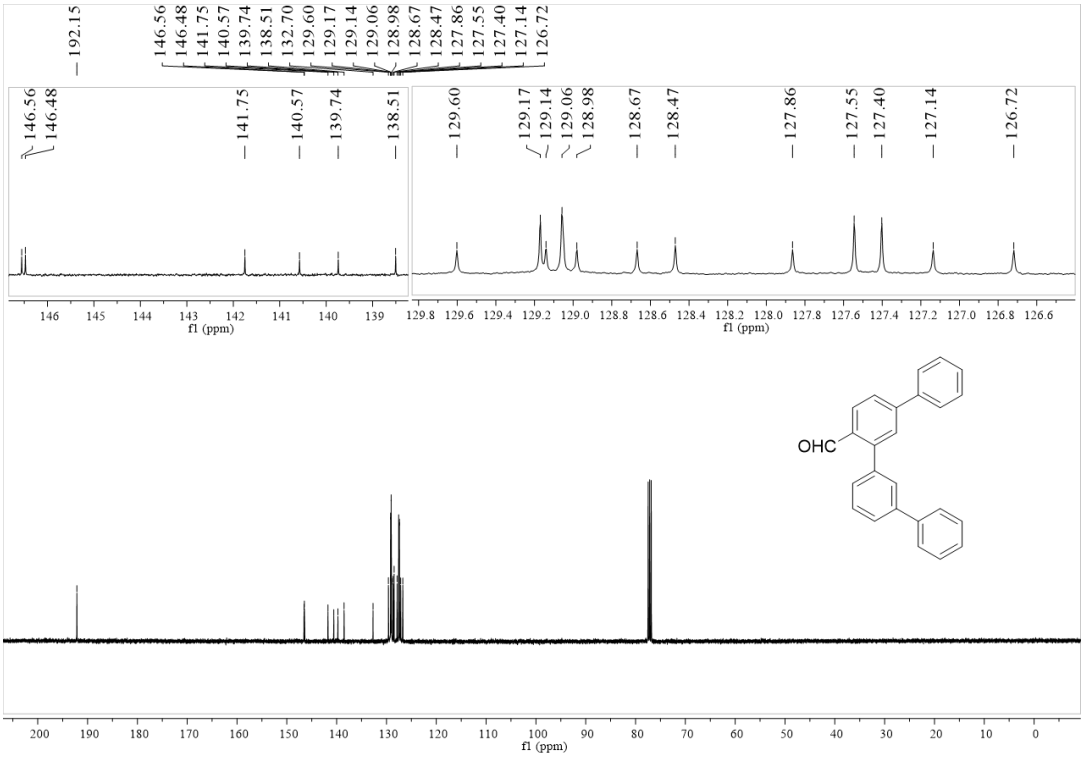


Fig. S12 ^{13}C NMR spectrum of **51** in $CDCl_3$

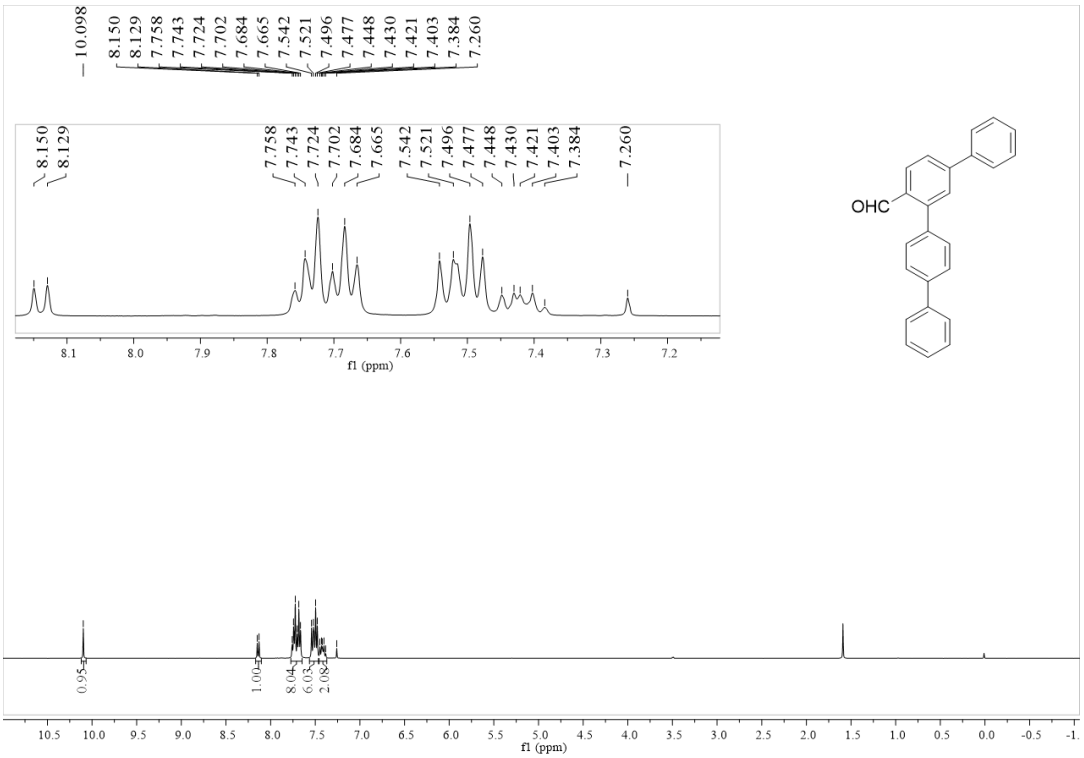


Fig. S13 ^{1}H NMR spectrum of **52** in $CDCl_3$

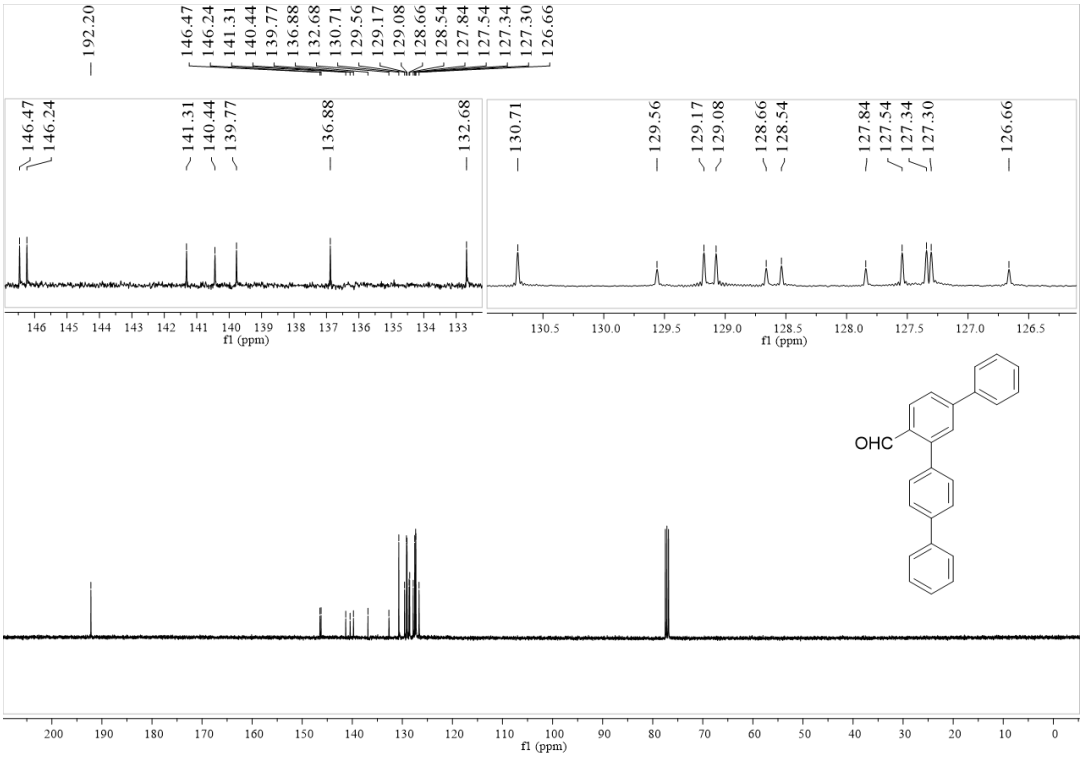


Fig. S14 ^{13}C NMR spectrum of **52** in $CDCl_3$

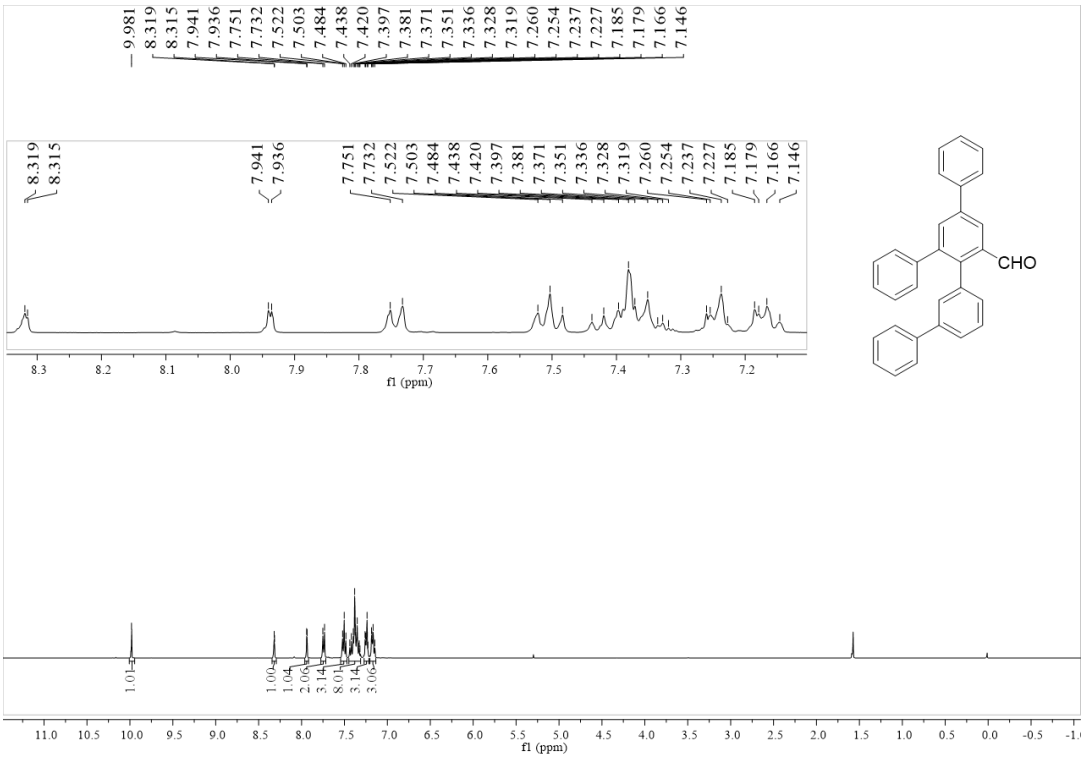


Fig. S15 ^{1}H NMR spectrum of **53** in $CDCl_3$

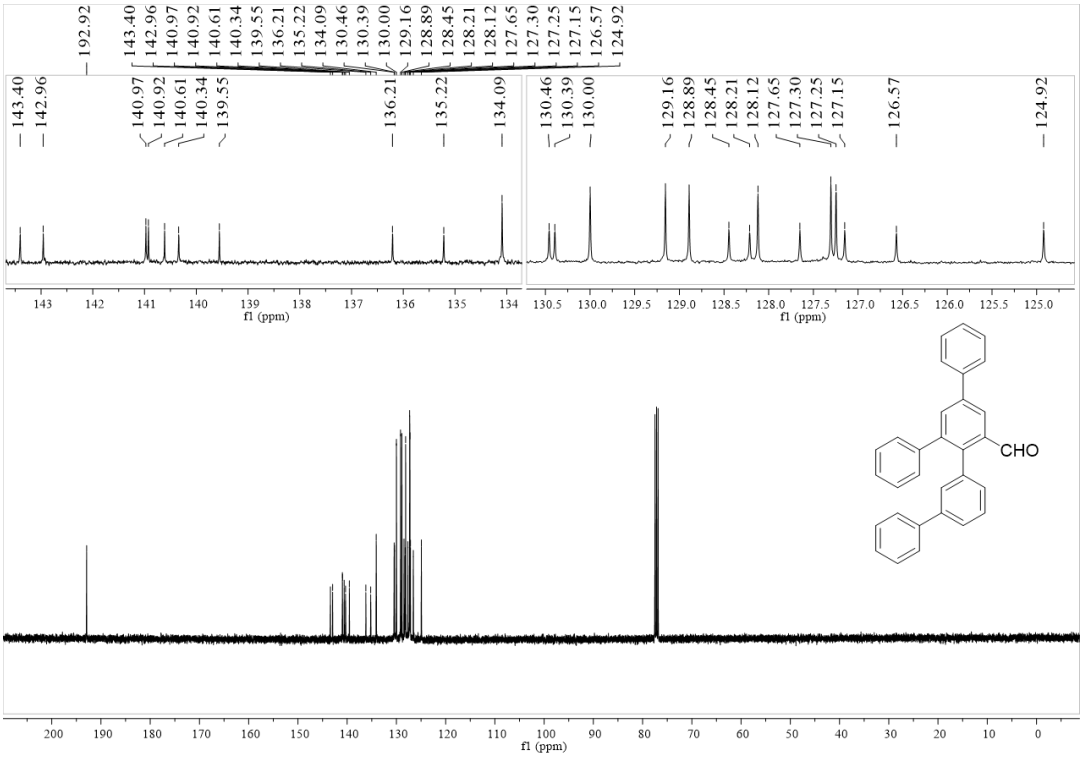


Fig. S16 ^{13}C NMR spectrum of **53** in $CDCl_3$

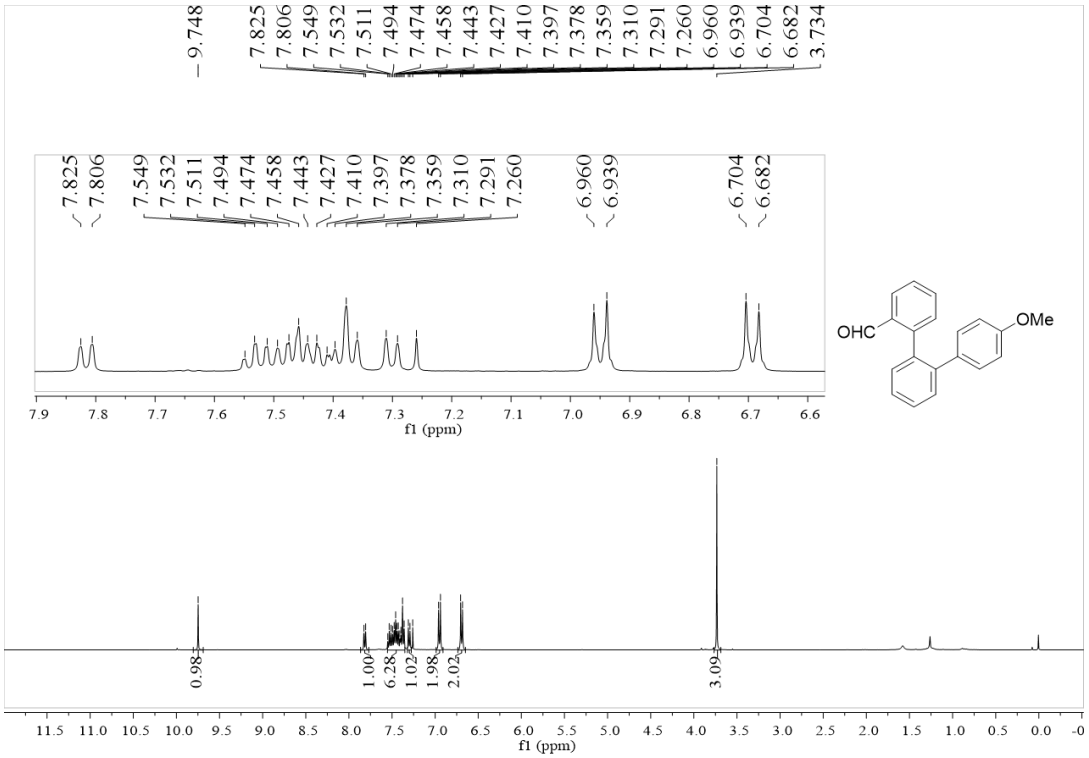


Fig. S17 ^{1}H NMR spectrum of **3** in $CDCl_3$

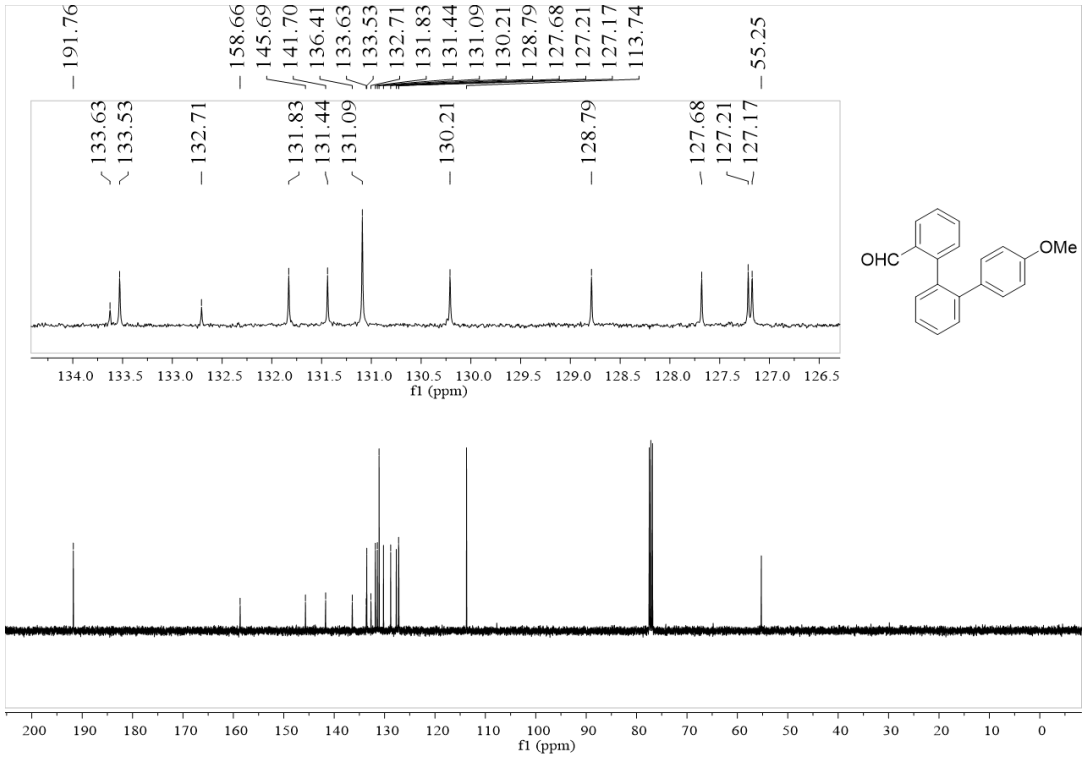


Fig. S18 ^{13}C NMR spectrum of **3** in $CDCl_3$

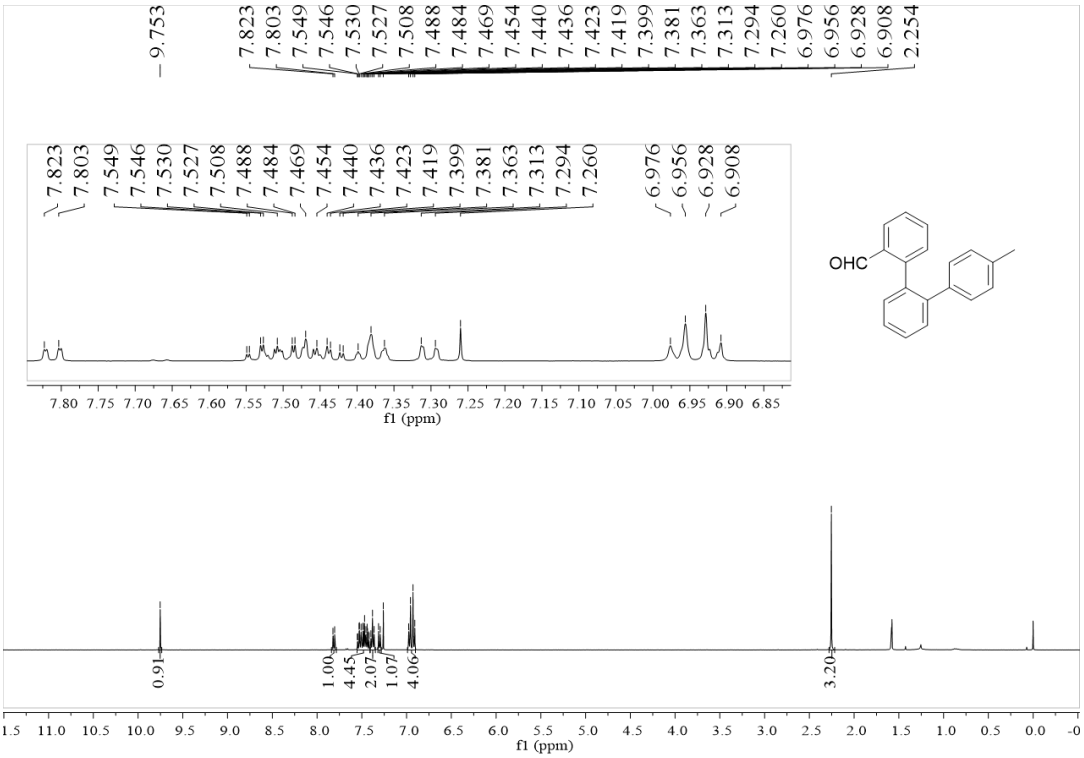


Fig. S19 ^{1}H NMR spectrum of **5** in $CDCl_3$

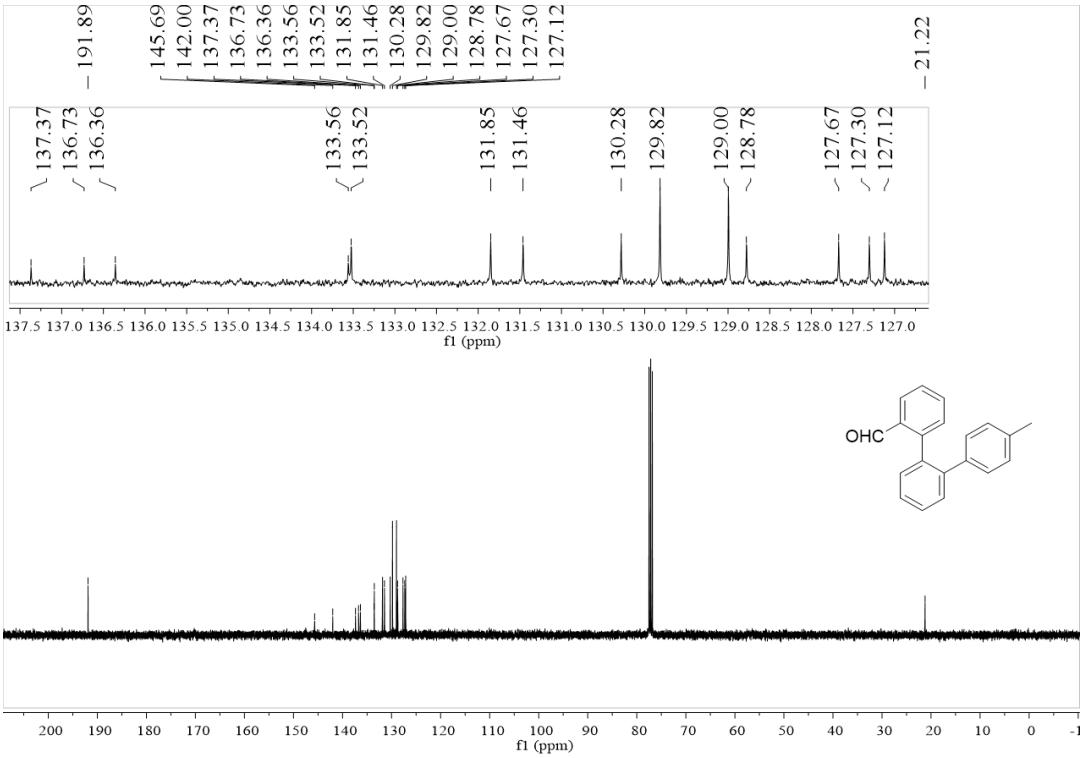


Fig. S20 ^{13}C NMR spectrum of **5** in $CDCl_3$

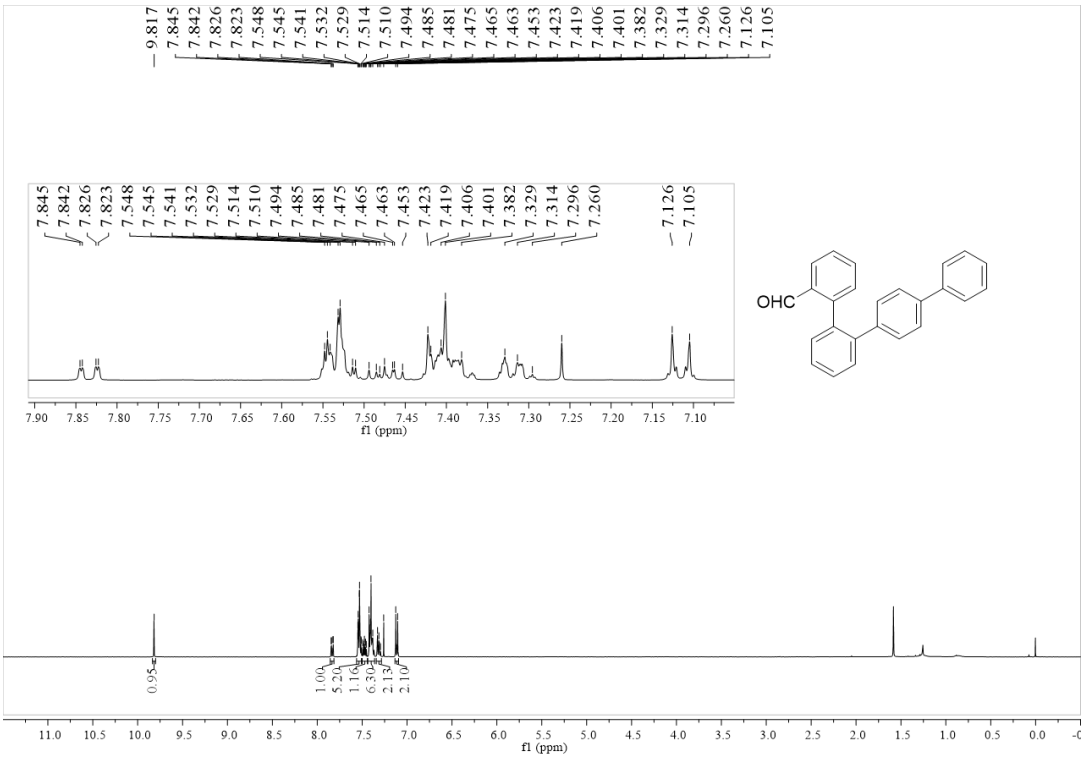


Fig. S21 ^{1}H NMR spectrum of **6** in $CDCl_3$

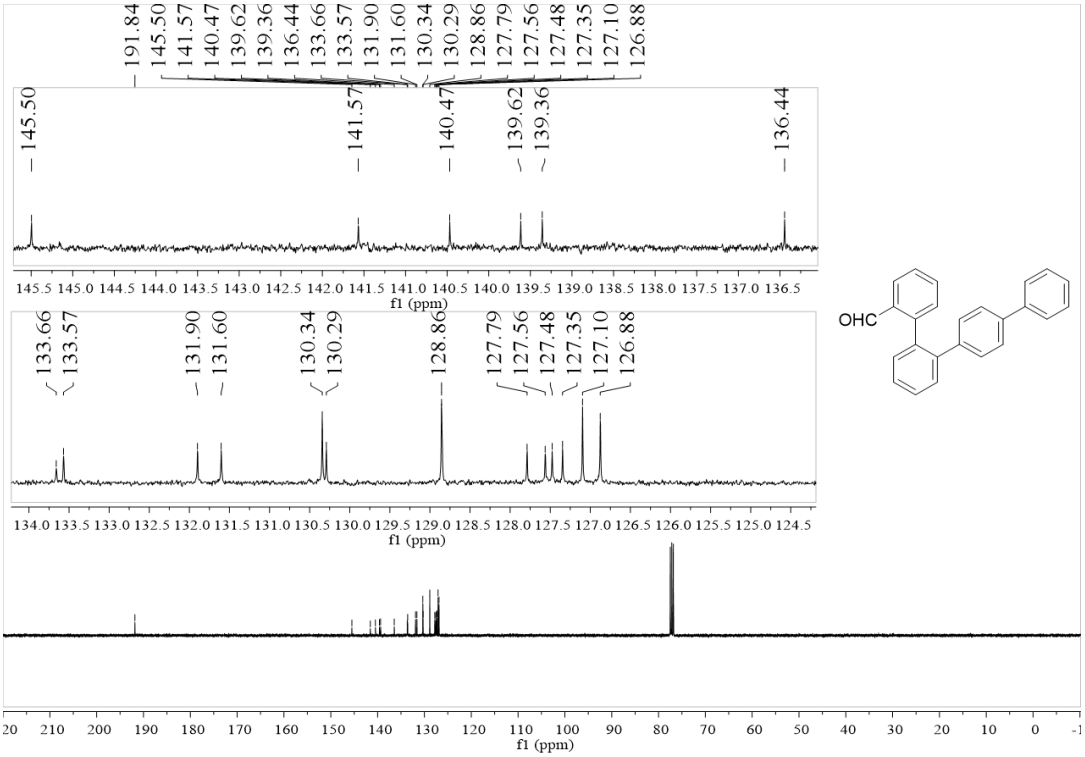


Fig. S22 ^{13}C NMR spectrum of **6** in $CDCl_3$

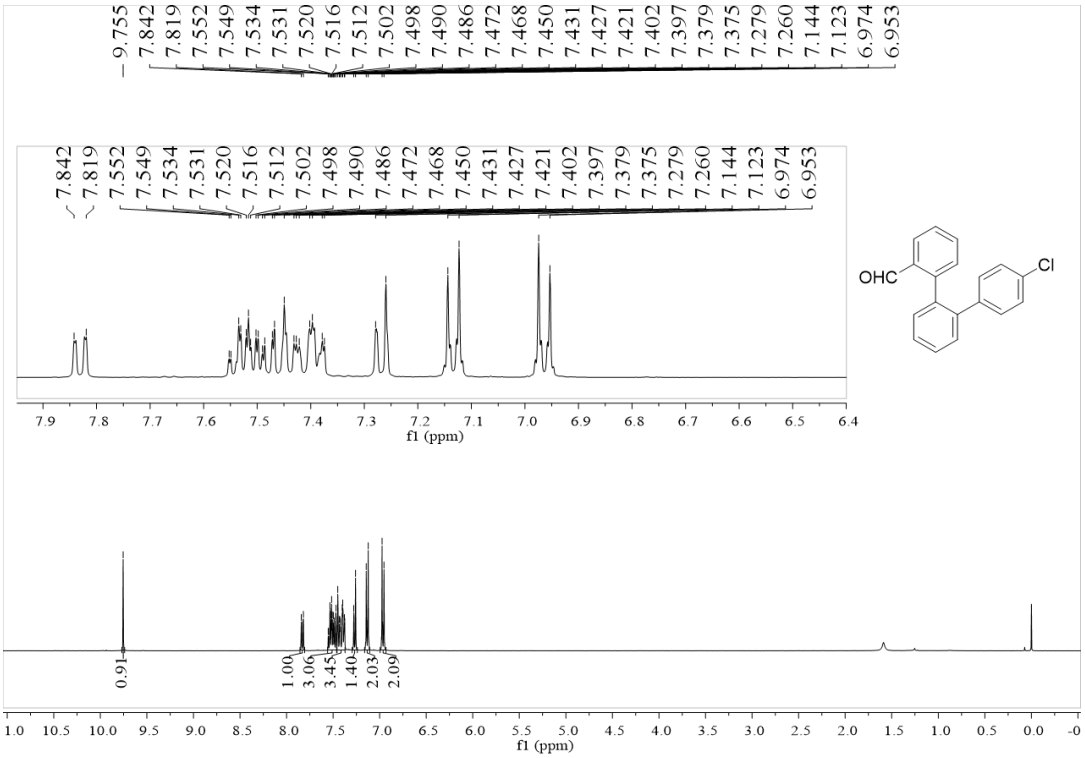


Fig. S23 ^{1}H NMR spectrum of **7** in $CDCl_3$

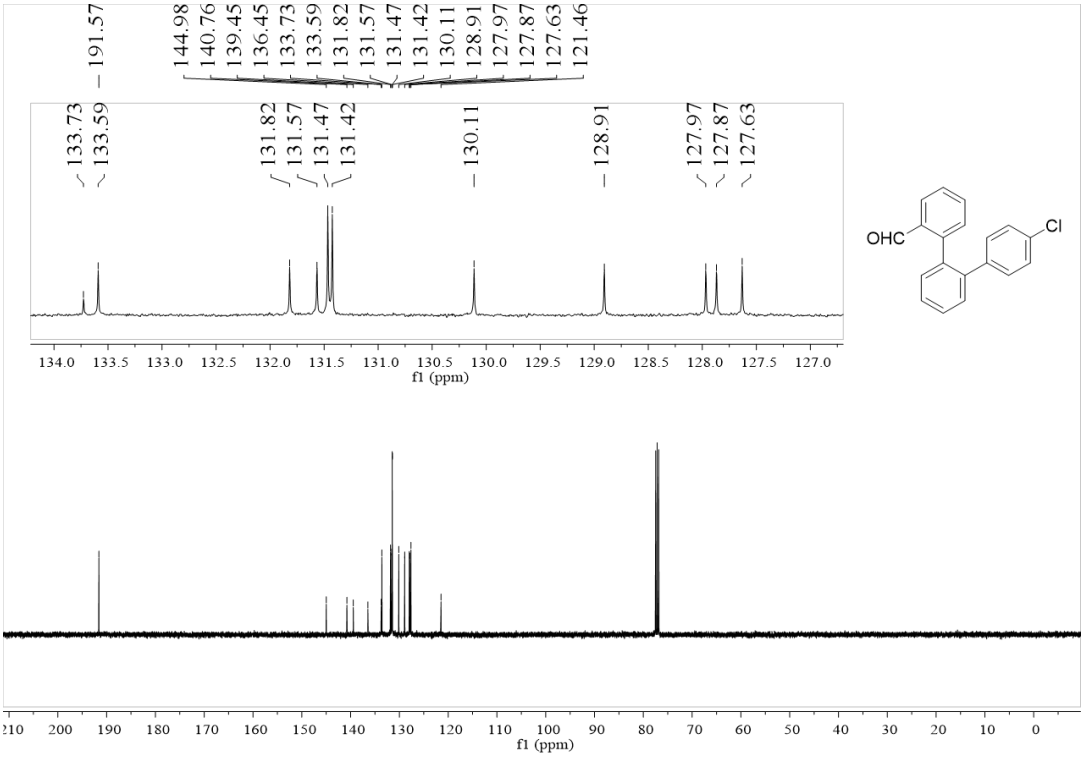


Fig. S24 ^{13}C NMR spectrum of **7** in $CDCl_3$

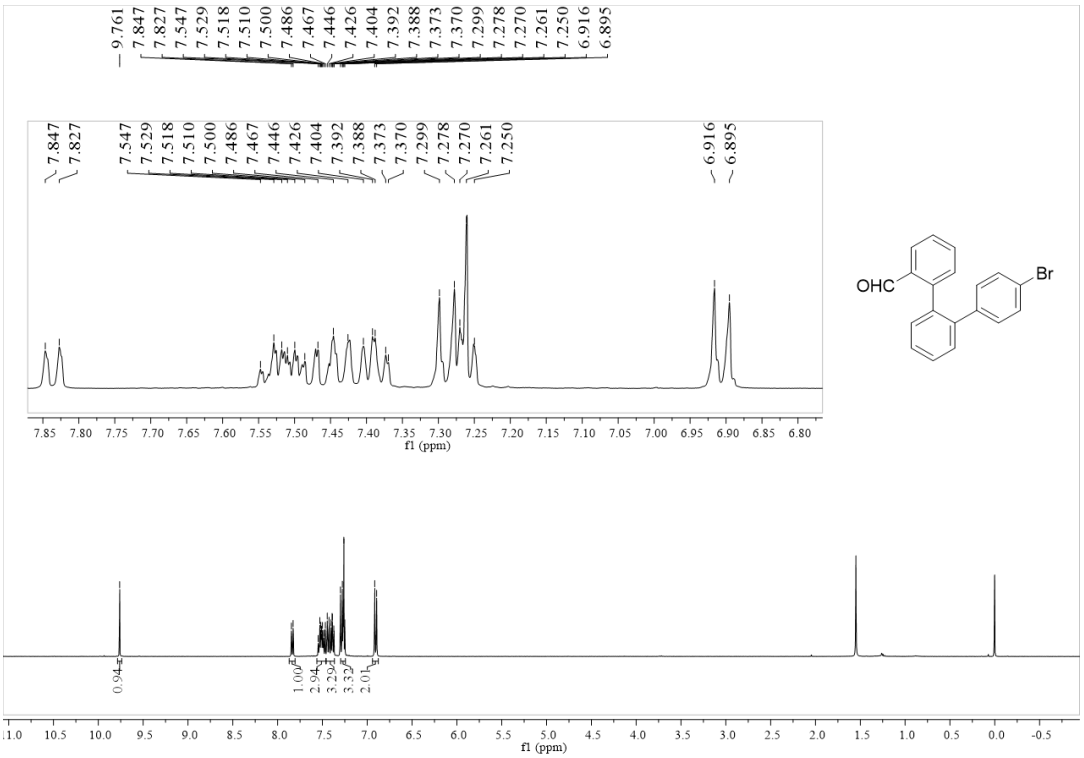


Fig. S25 ^{1}H NMR spectrum of **8** in $CDCl_3$

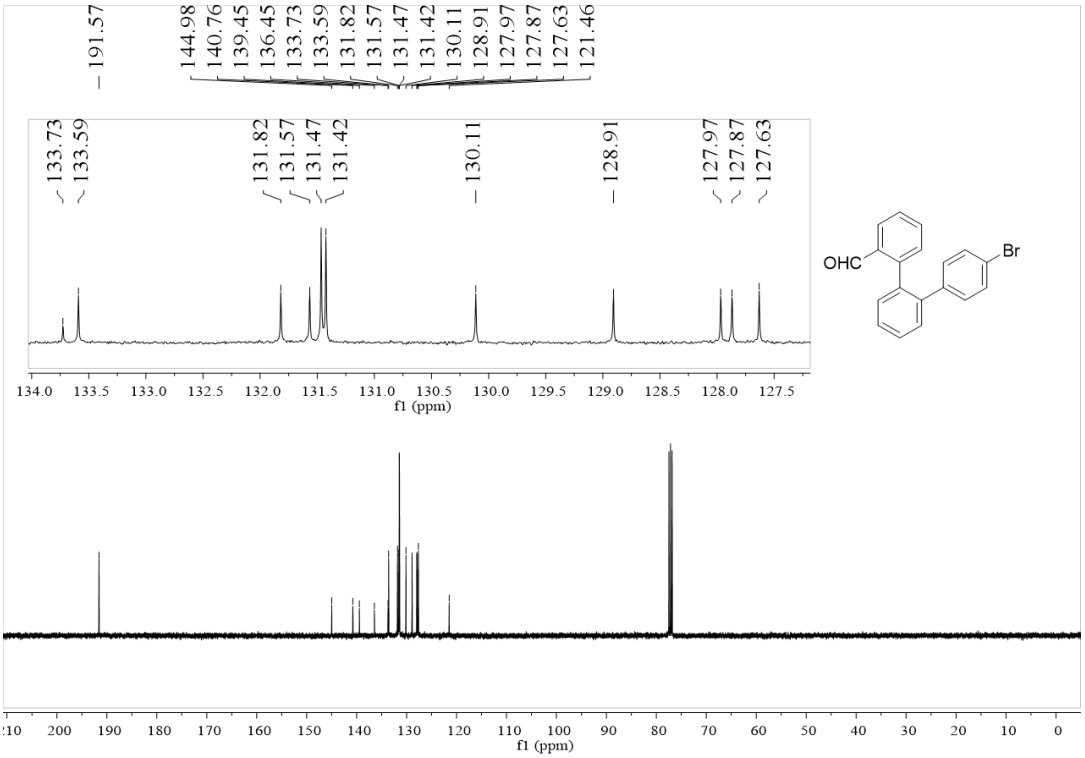


Fig. S26 ^{13}C NMR spectrum of **8** in $CDCl_3$

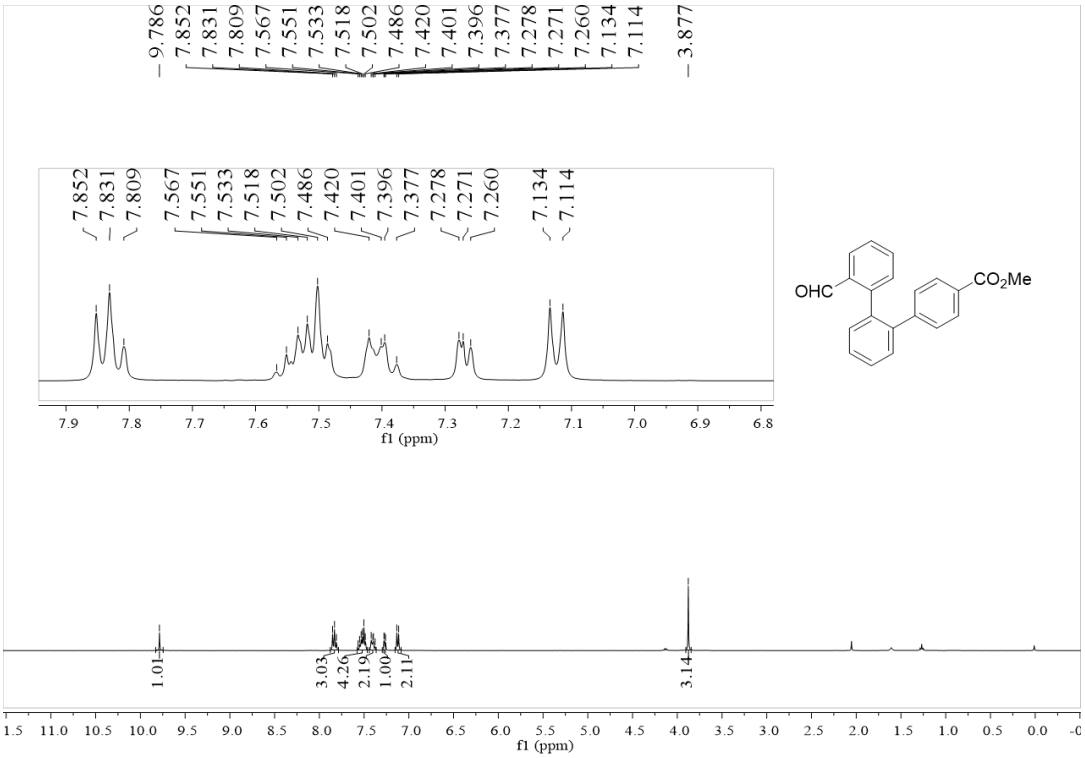


Fig. S27 ^{1}H NMR spectrum of **9** in $CDCl_3$

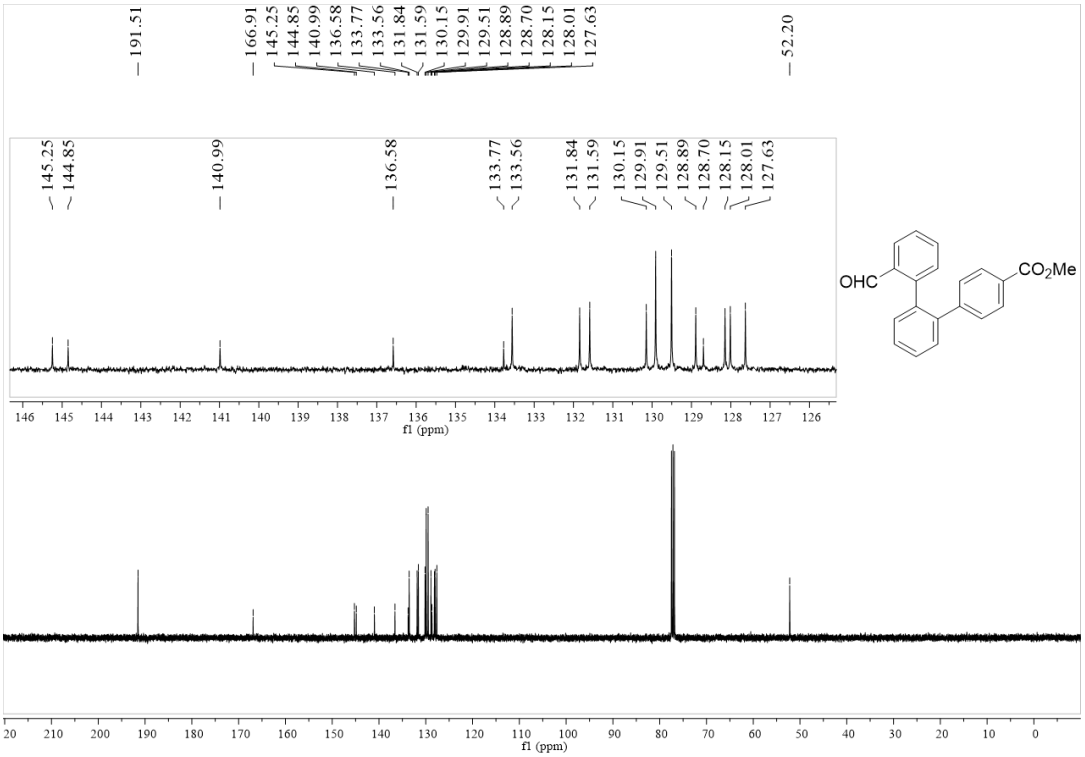


Fig. S28 ^{13}C NMR spectrum of **9** in $CDCl_3$

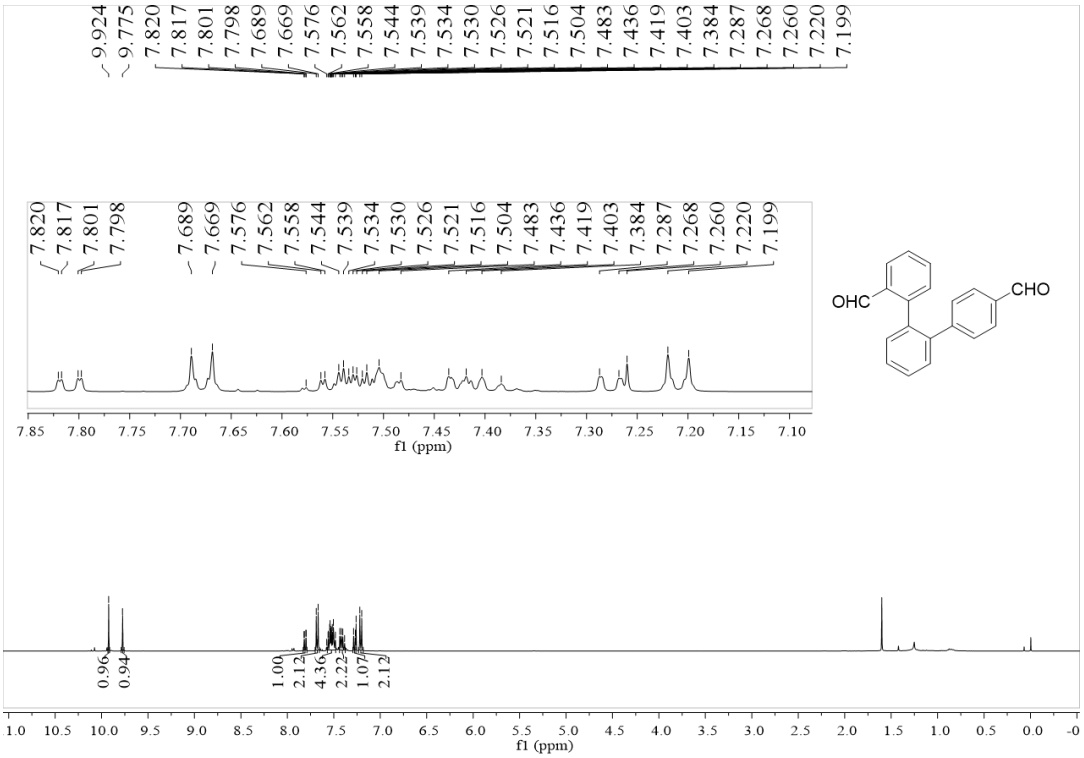


Fig. S29 ^{1}H NMR spectrum of **10** in $CDCl_3$.

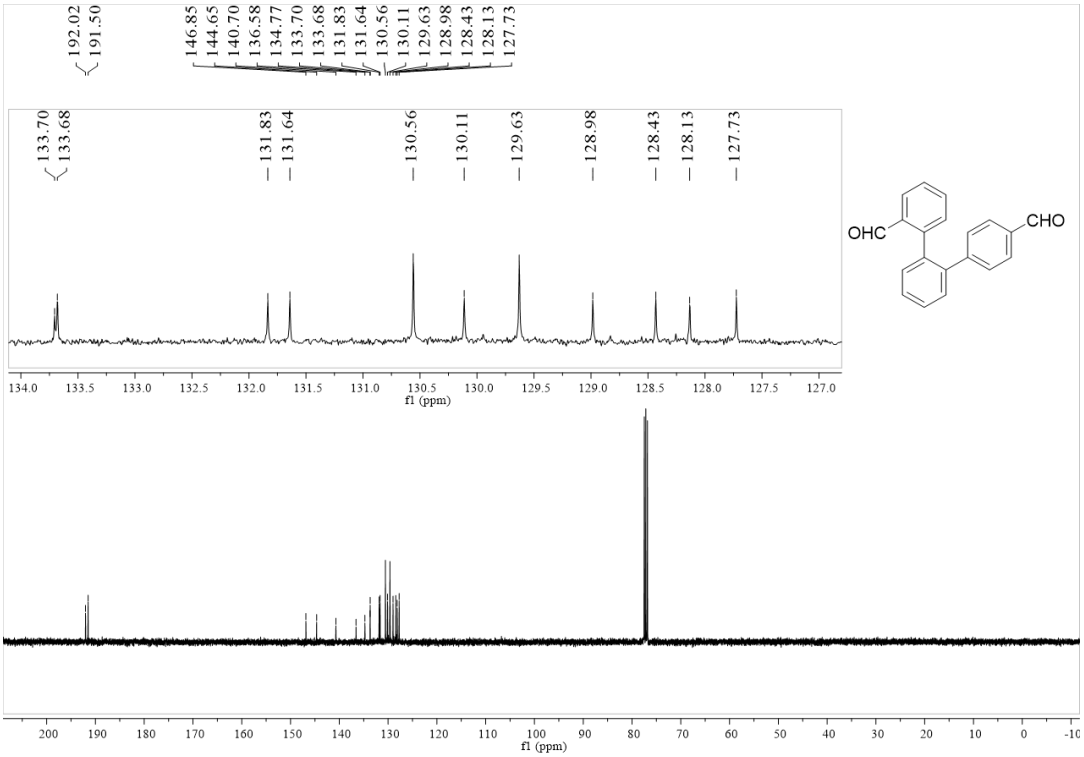


Fig. S30 ^{13}C NMR spectrum of **10** in $CDCl_3$

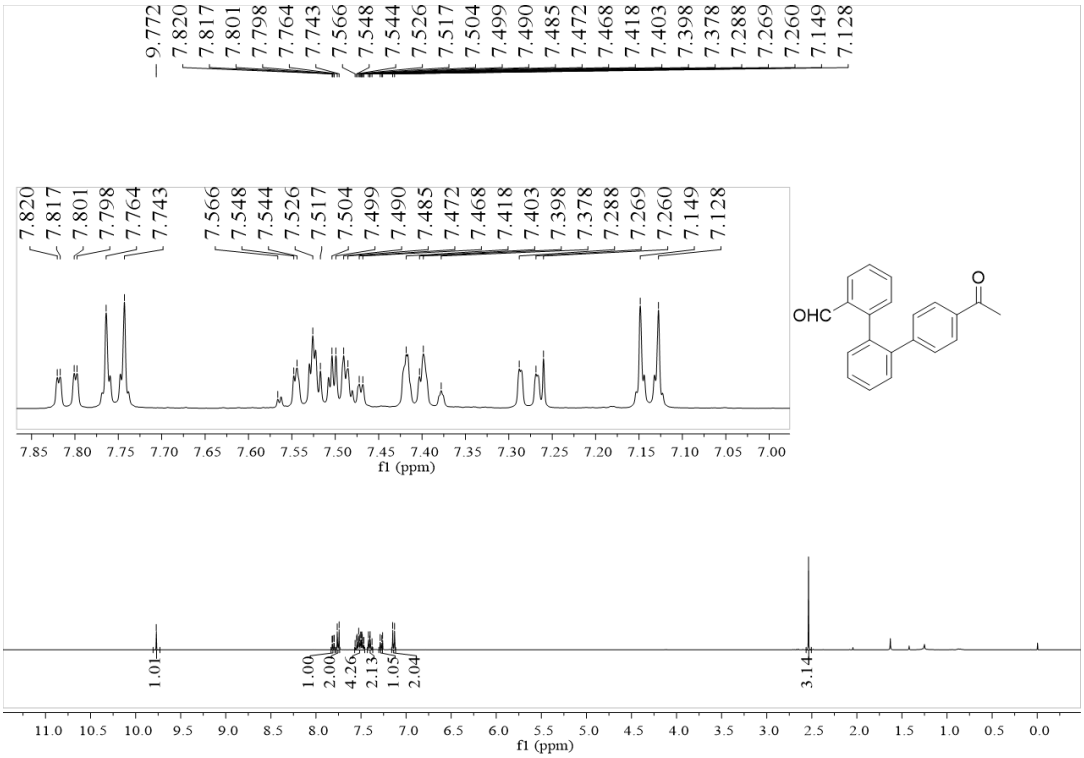


Fig. S31 ^{1}H NMR spectrum of **11** in $CDCl_3$

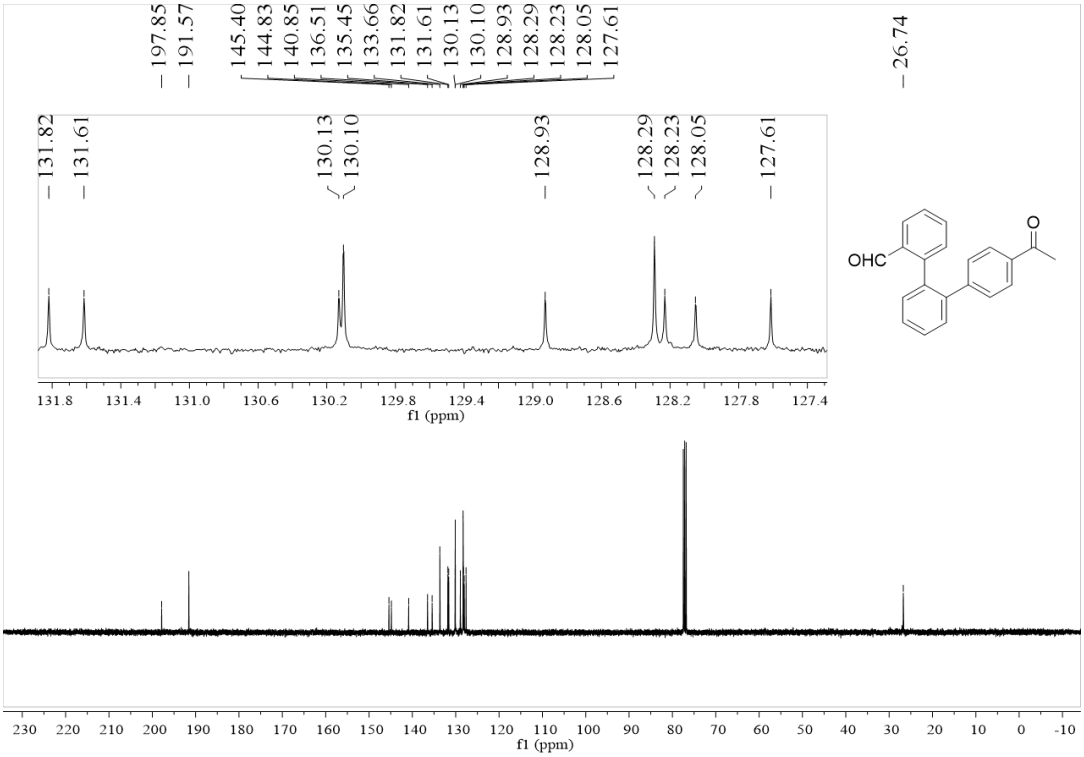


Fig. S32 ^{13}C NMR spectrum of **11** in $CDCl_3$

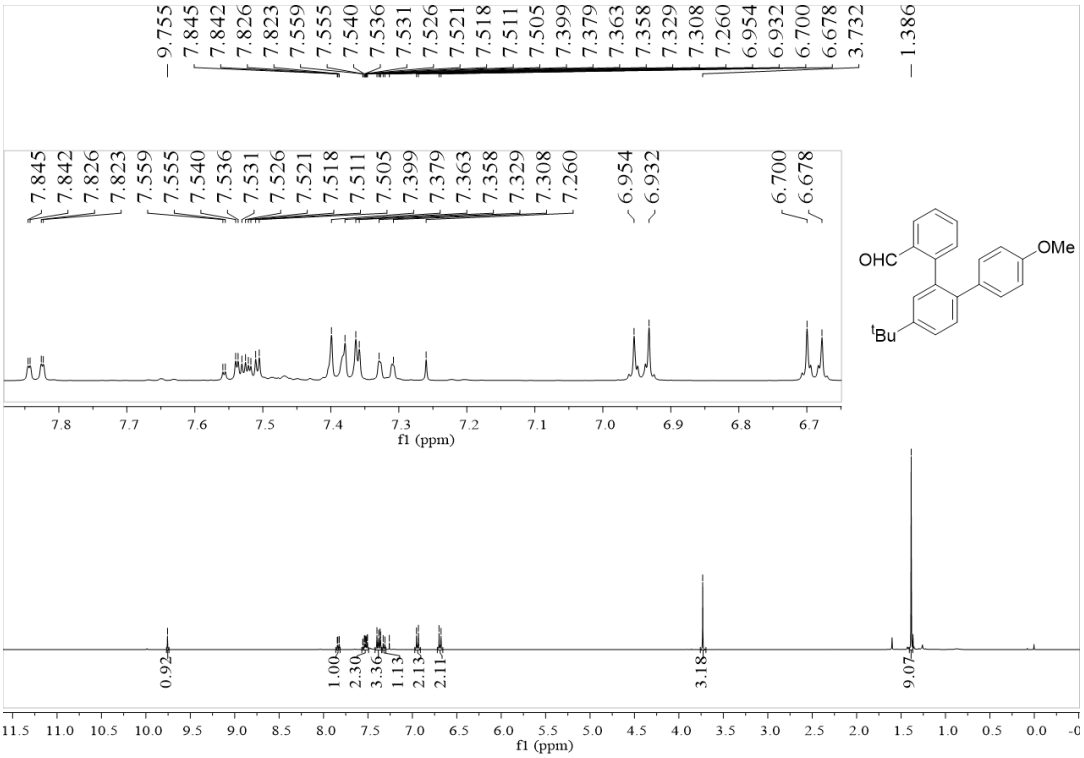


Fig. S33 ^{1}H NMR spectrum of **12** in $CDCl_3$

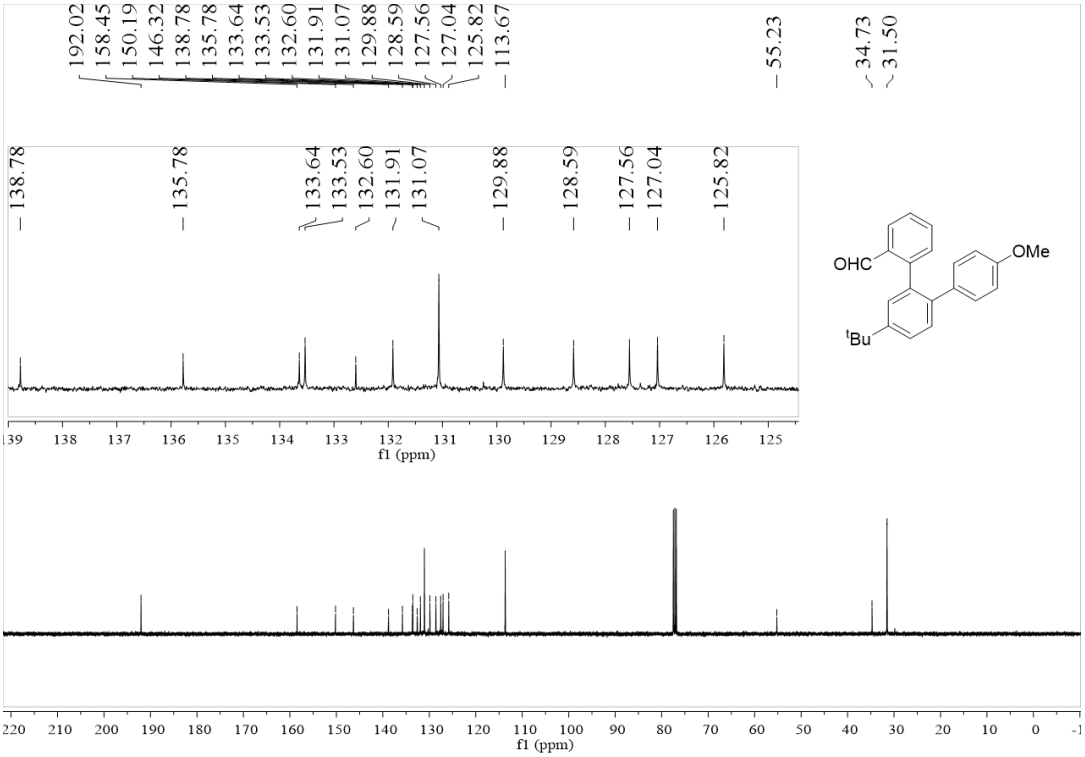


Fig. S34 ^{13}C NMR spectrum of **12** in $CDCl_3$

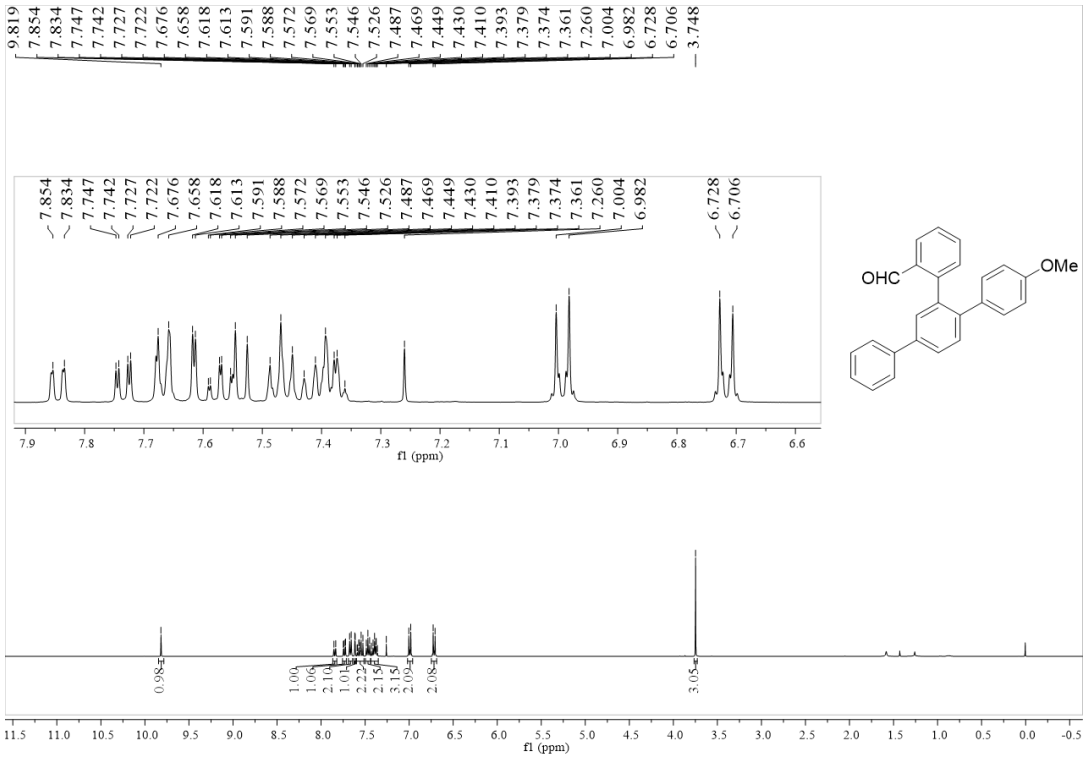


Fig. S35 ^{1}H NMR spectrum of **13** in $CDCl_3$

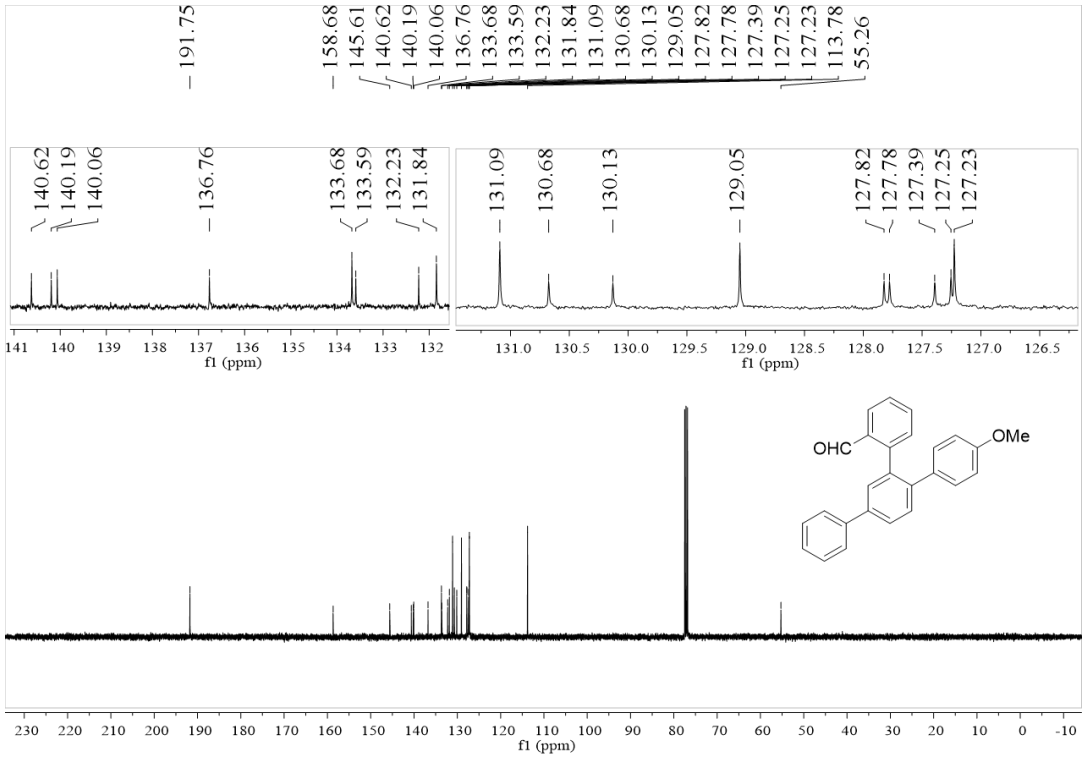


Fig. S36 ^{13}C NMR spectrum of **13** in $CDCl_3$

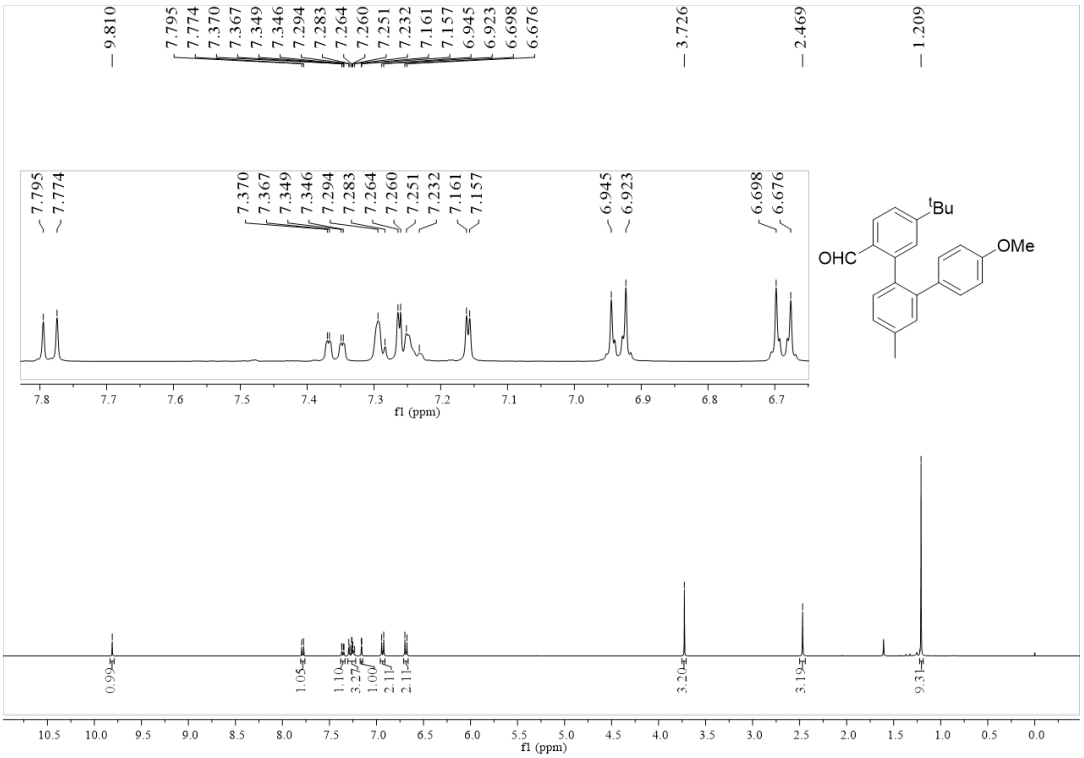


Fig. S37 ^{1}H NMR spectrum of **14** in $CDCl_3$

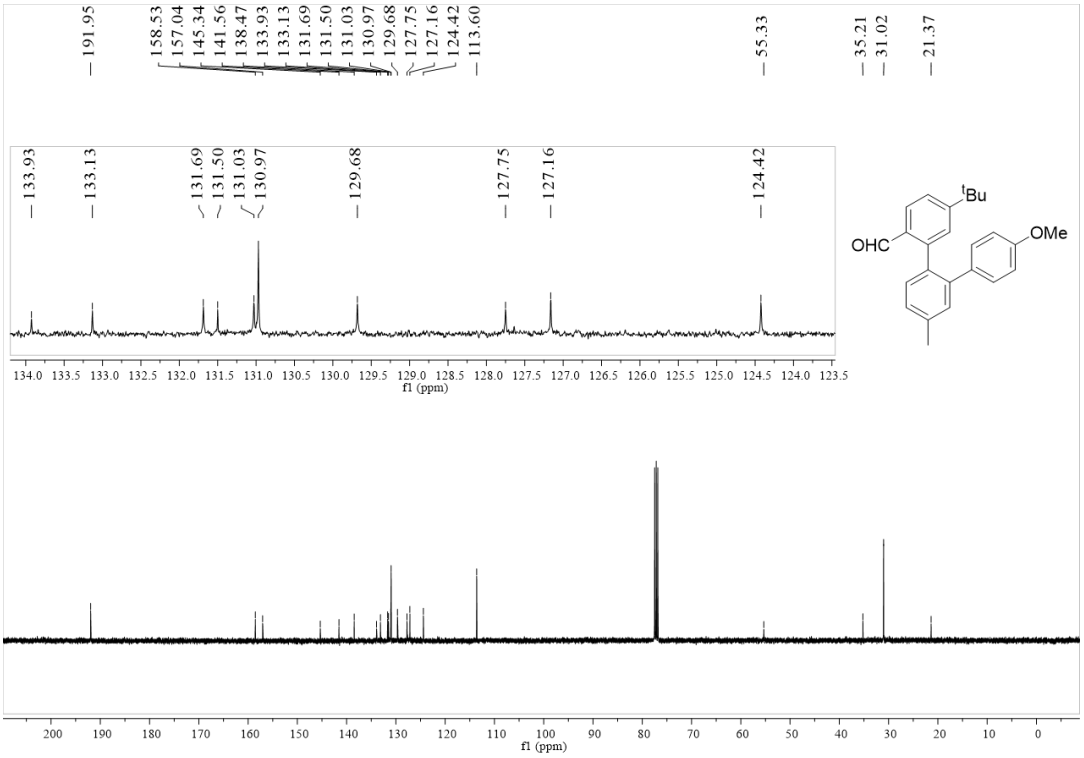


Fig. S38 ^{13}C NMR spectrum of **14** in $CDCl_3$

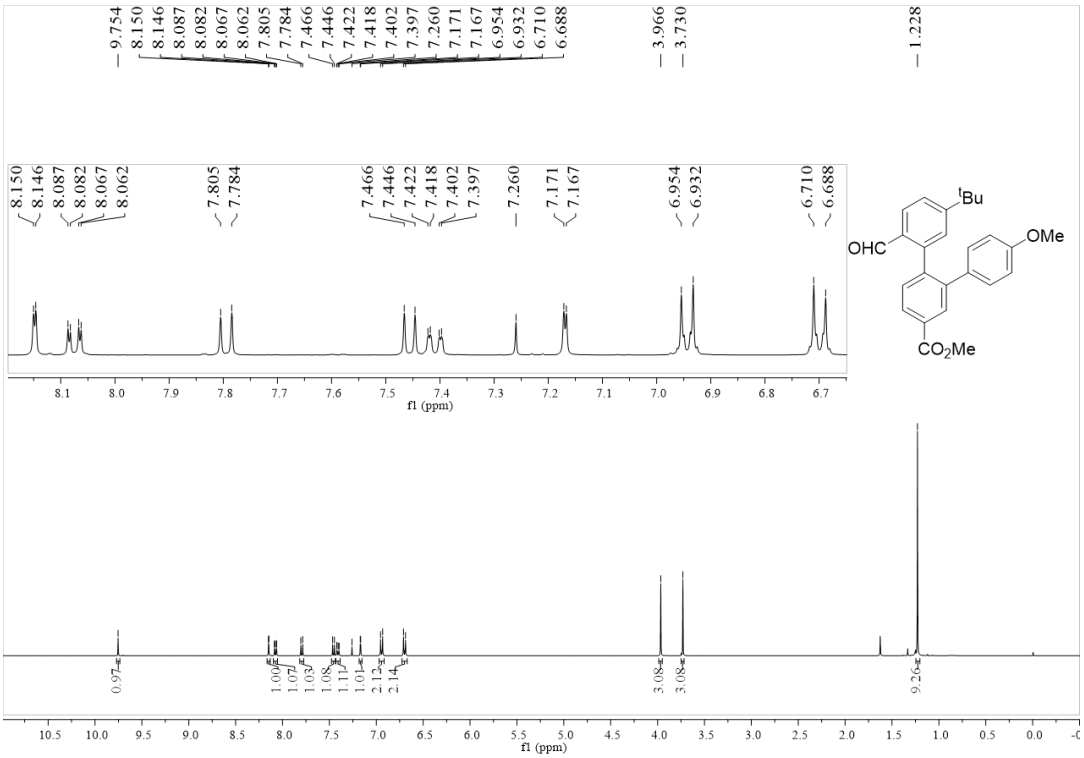


Fig. S39 ^{1}H NMR spectrum of **15** in $CDCl_3$

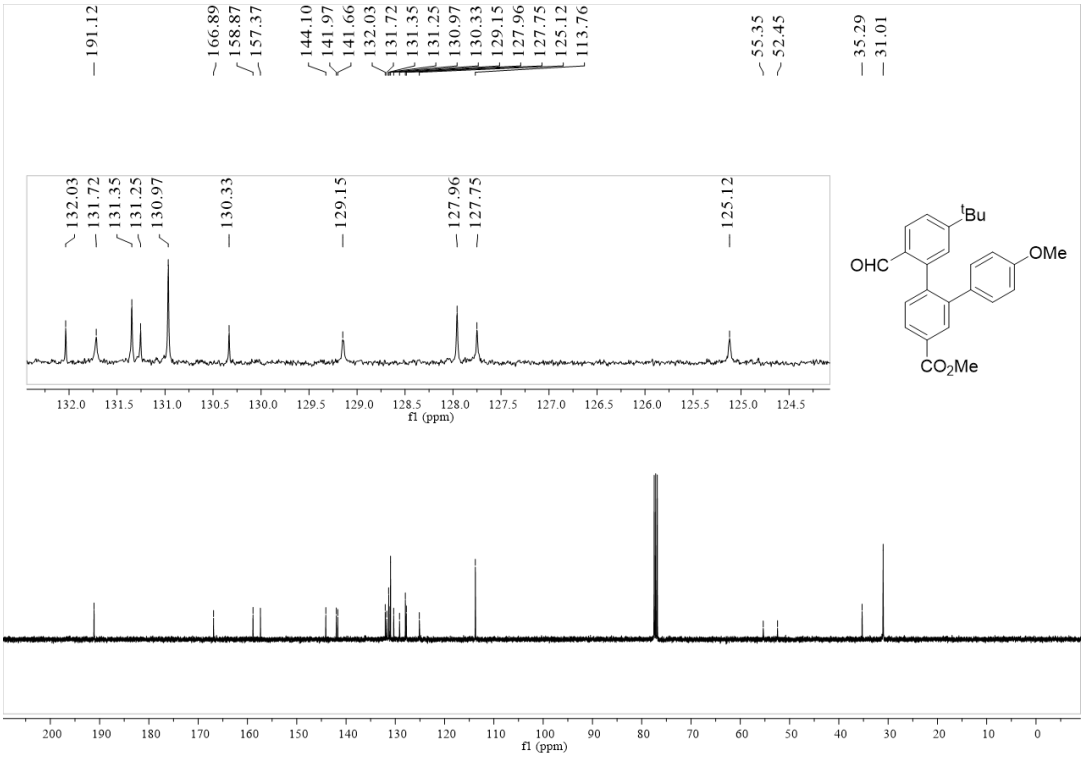


Fig. S40 ^{13}C NMR spectrum of **15** in $CDCl_3$

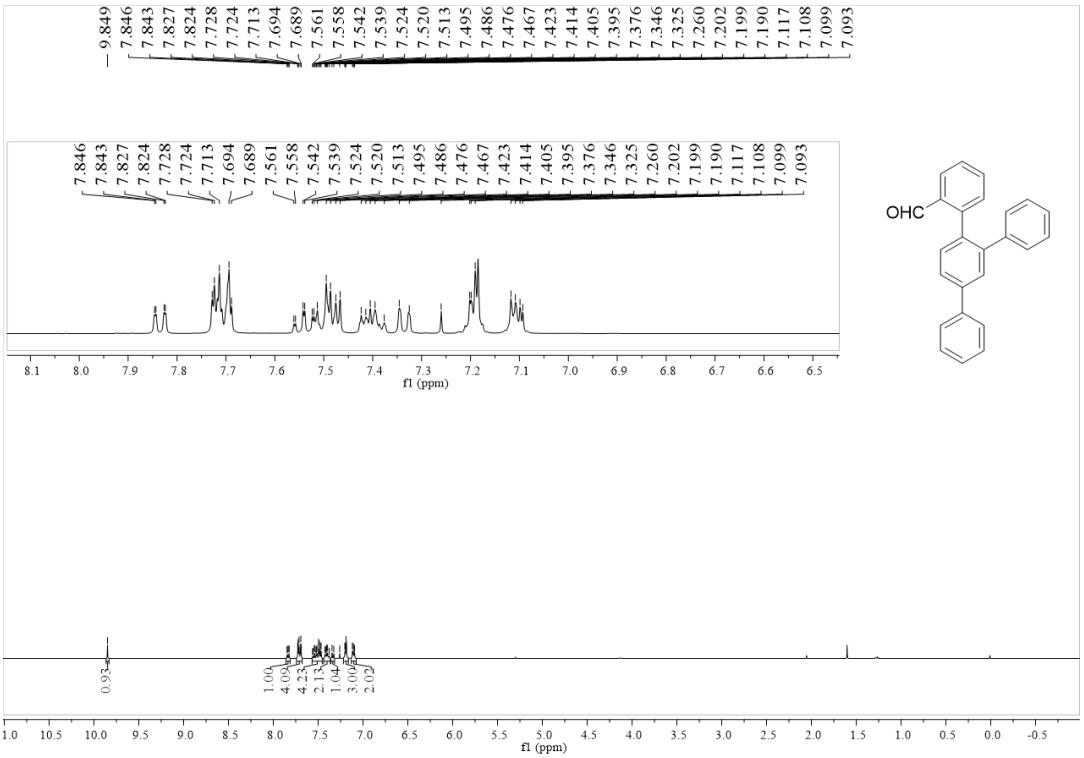


Fig. S41 ^{1}H NMR spectrum of **16** in $CDCl_3$

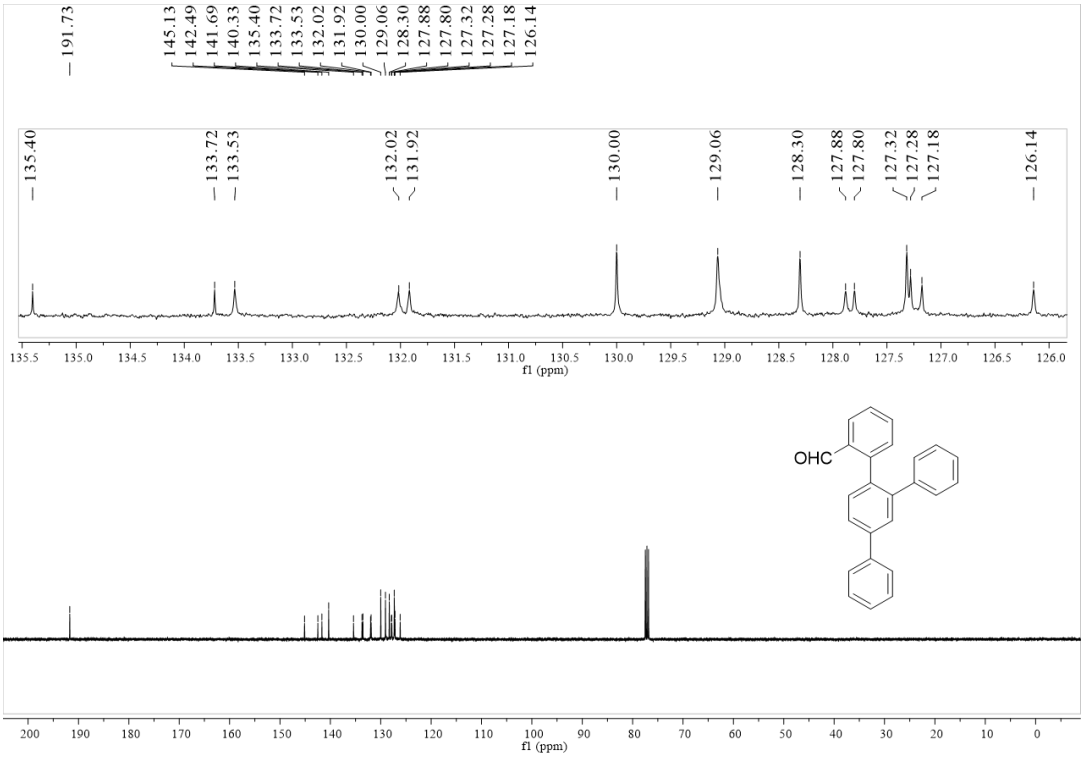


Fig. S42 ^{13}C NMR spectrum of **16** in $CDCl_3$

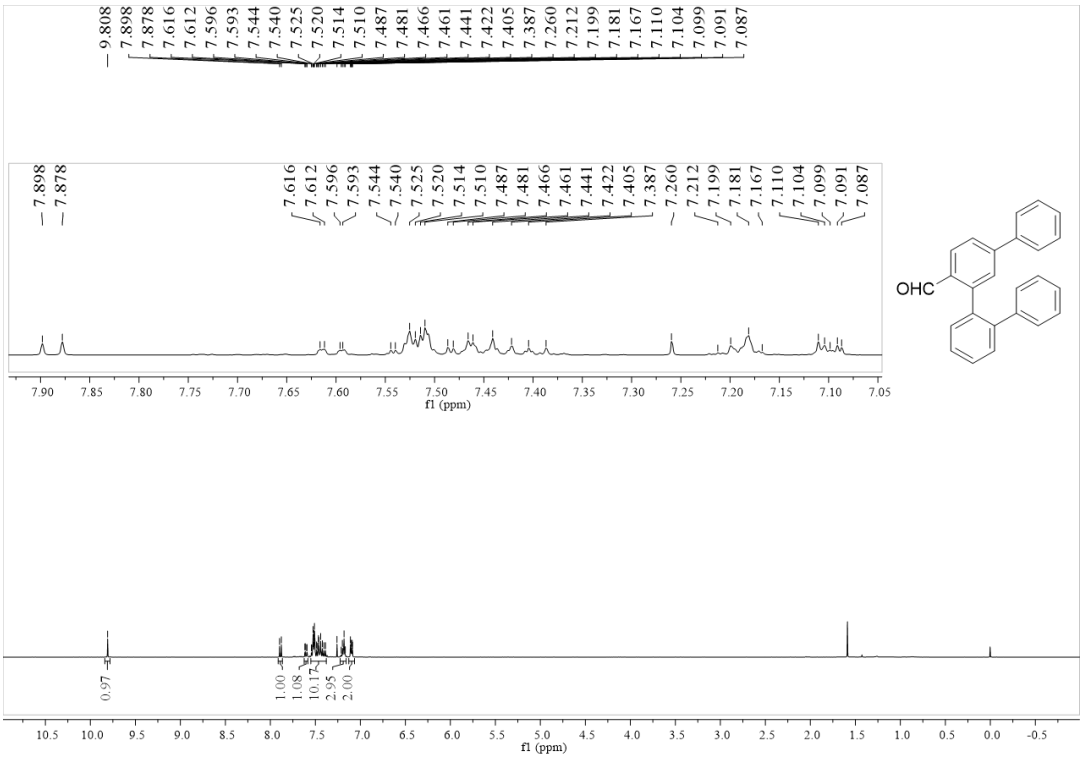


Fig. S43 ^{1}H NMR spectrum of **17** in $CDCl_3$

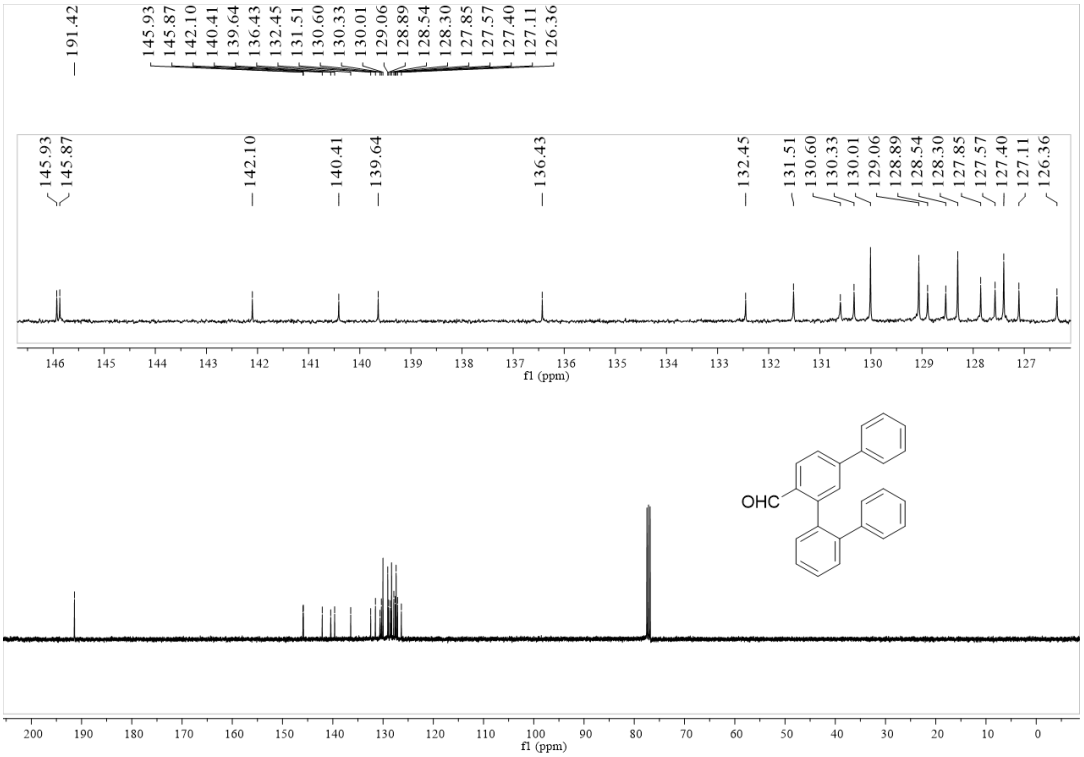


Fig. S44 ^{13}C NMR spectrum of **17** in $CDCl_3$

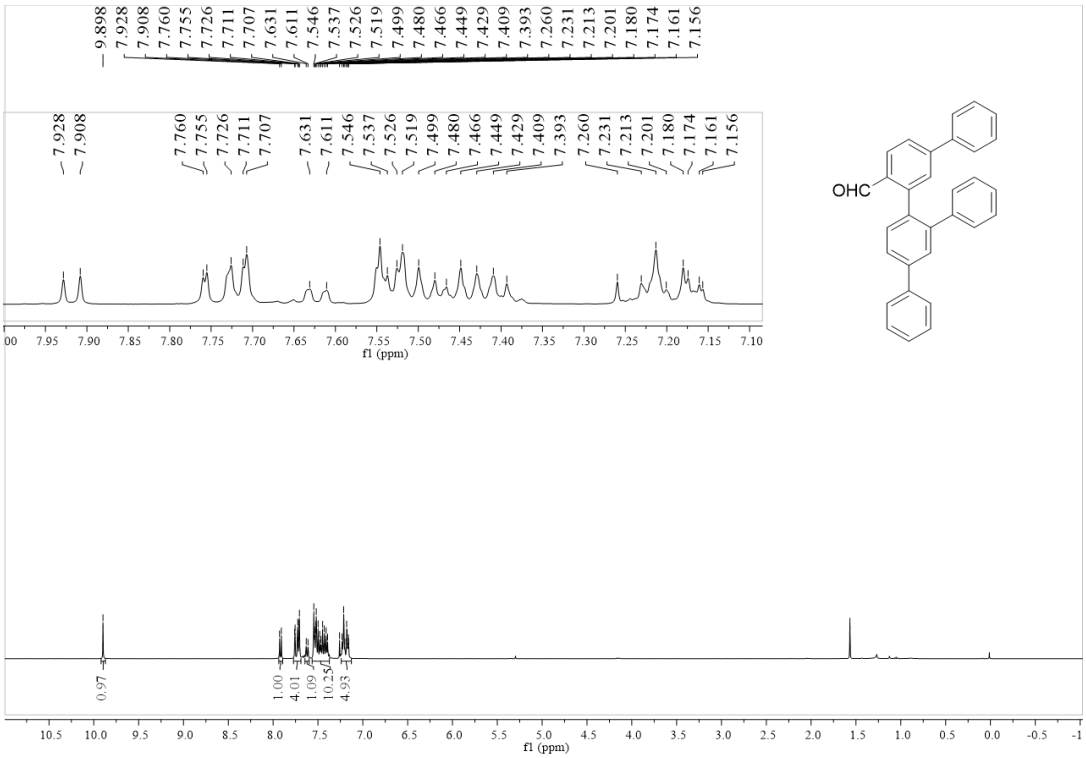


Fig. S45 ^{1}H NMR spectrum of **18** in $CDCl_3$

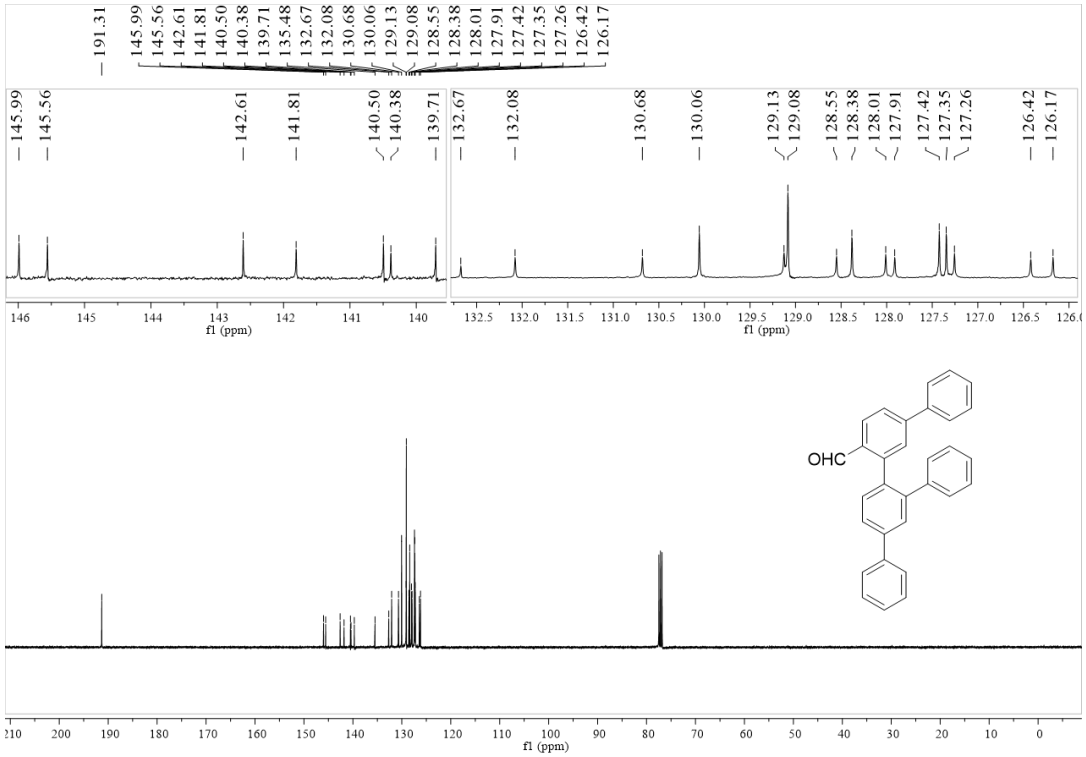


Fig. S46 ^{13}C NMR spectrum of **18** in $CDCl_3$

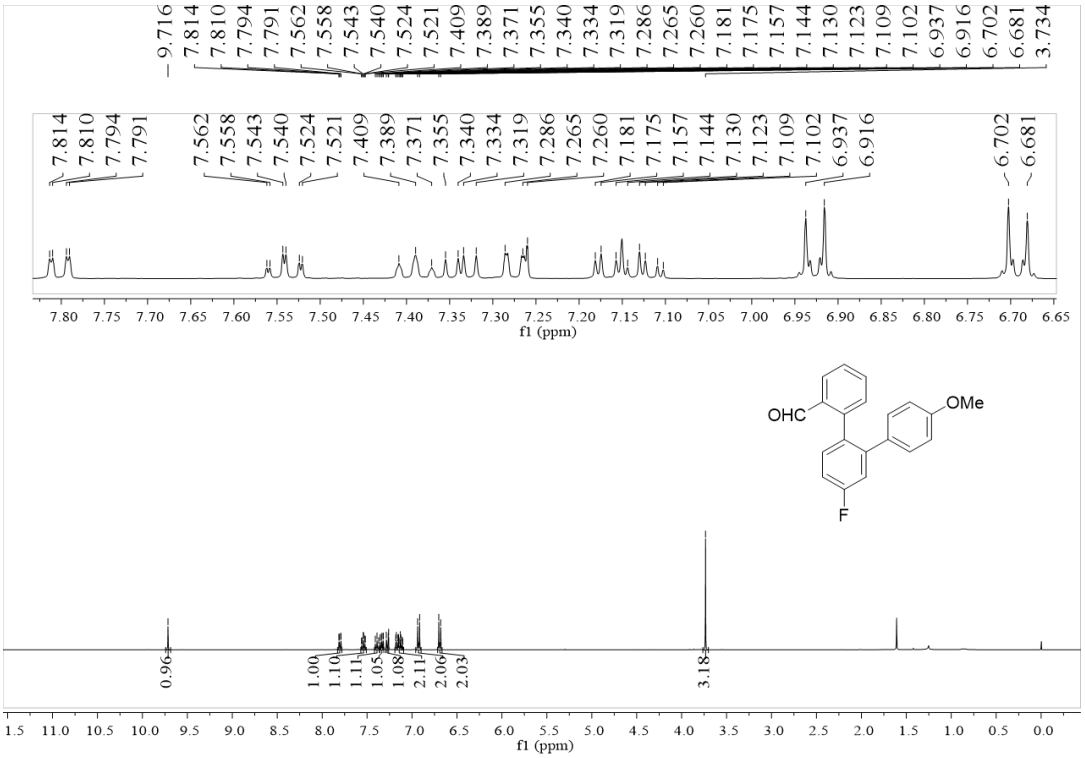


Fig. S47 ^{1}H NMR spectrum of **19** in $CDCl_3$

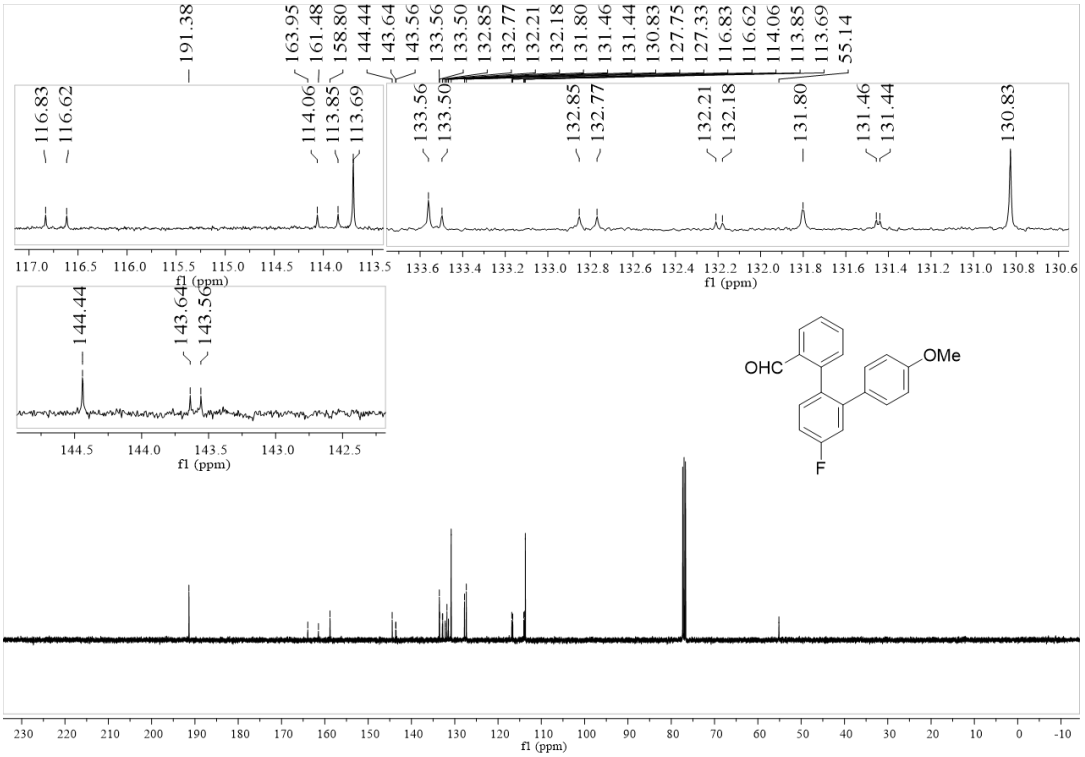


Fig. S48 ^{13}C NMR spectrum of **19** in $CDCl_3$

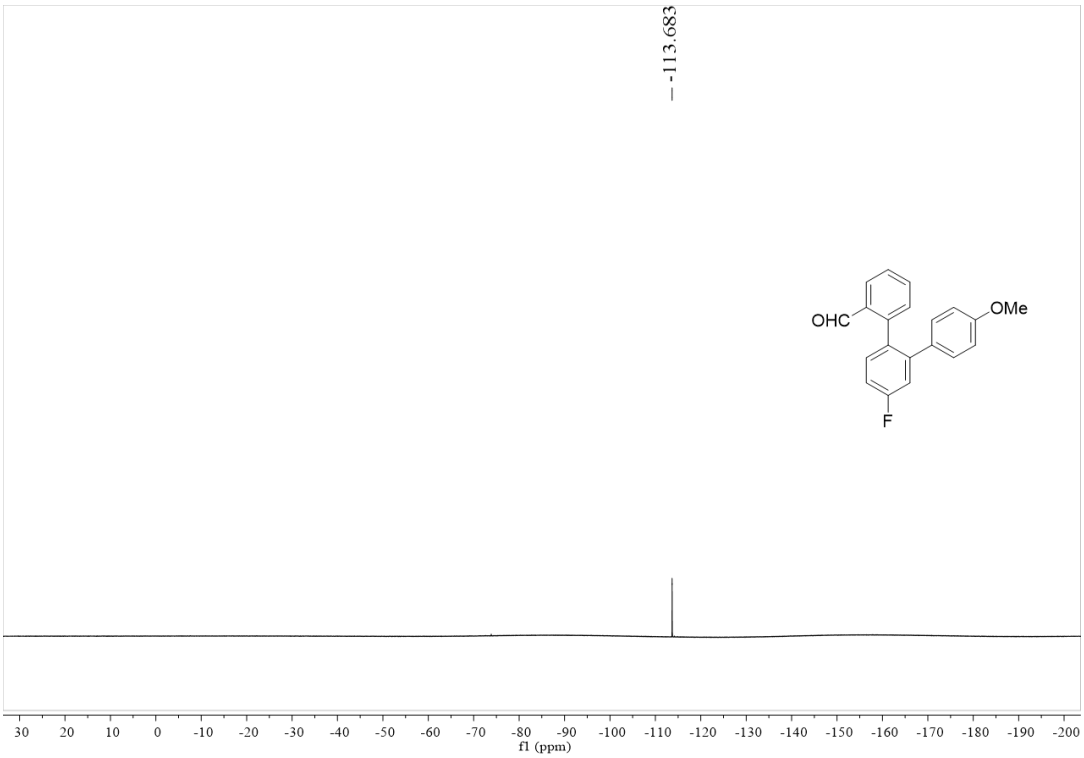


Fig. S49 ^{19}F NMR spectrum of **19** in $CDCl_3$

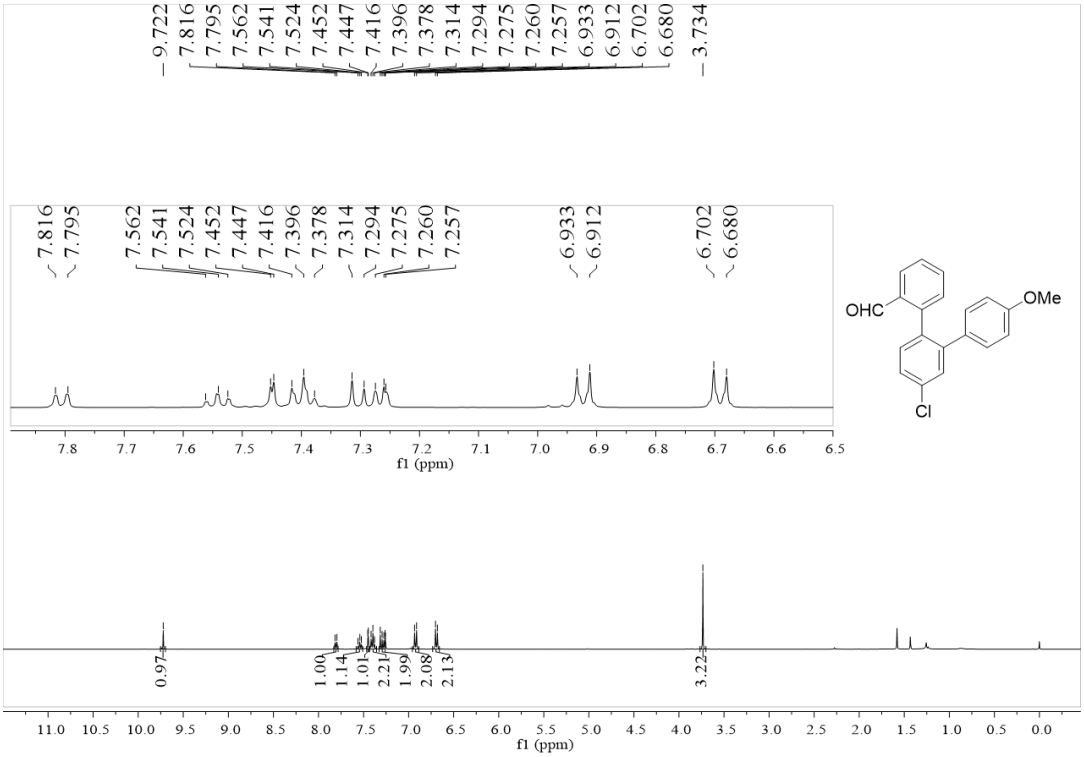


Fig. S50 ^{1}H NMR spectrum of **20** in $CDCl_3$

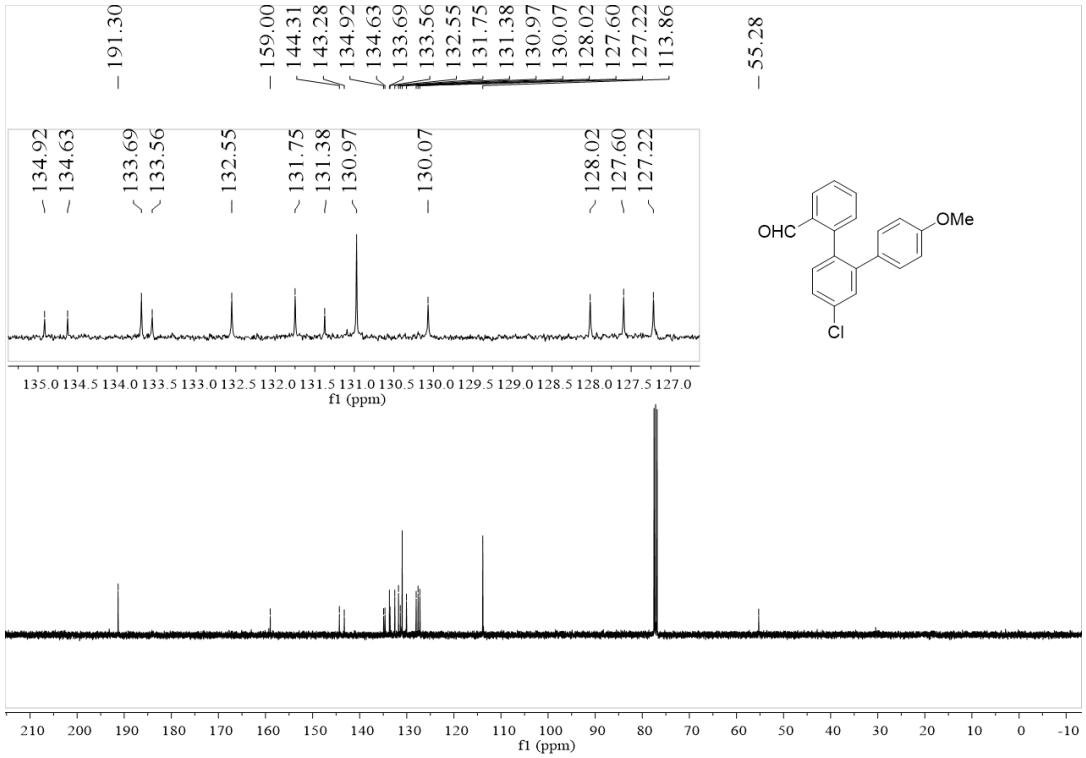


Fig. S51 ^{13}C NMR spectrum of **20** in $CDCl_3$.

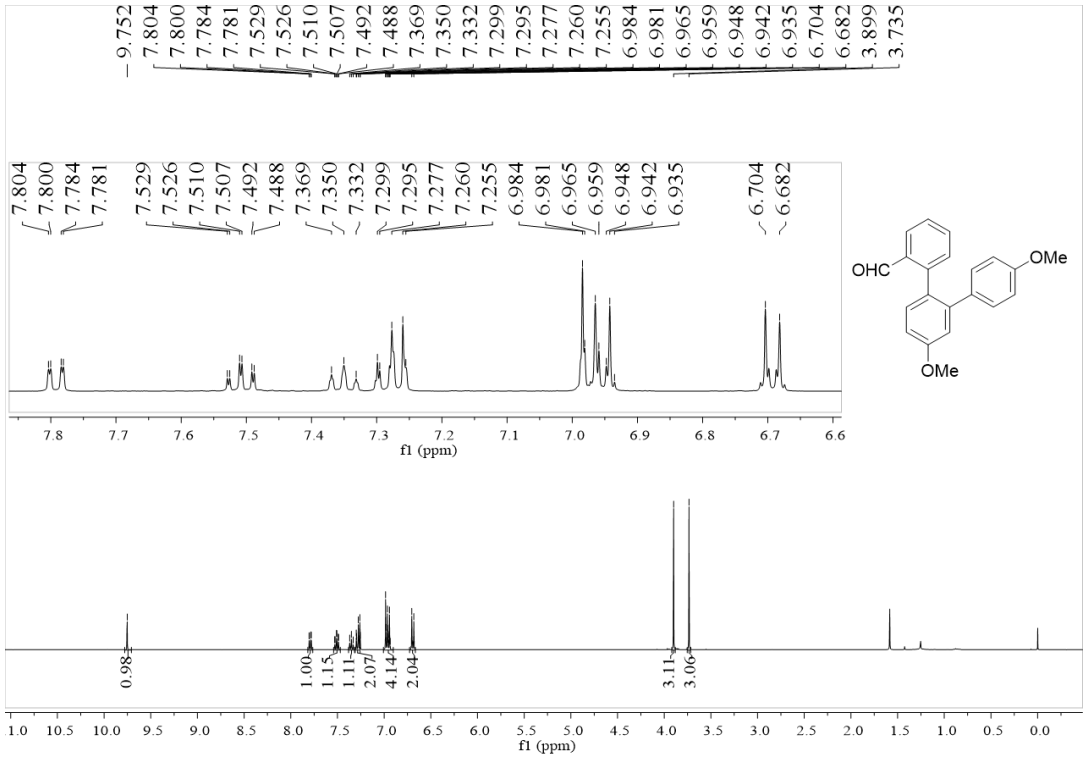


Fig. S52 ^{1}H NMR spectrum of **21** in $CDCl_3$

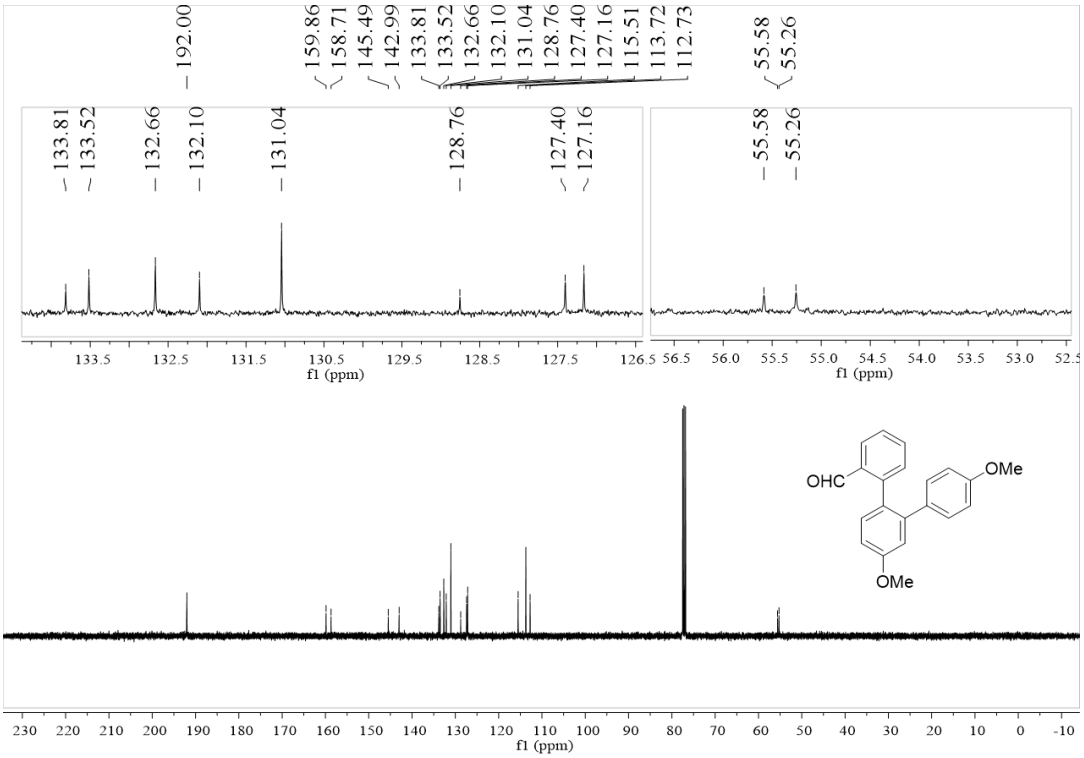


Fig. S53 ^{13}C NMR spectrum of **21** in $CDCl_3$

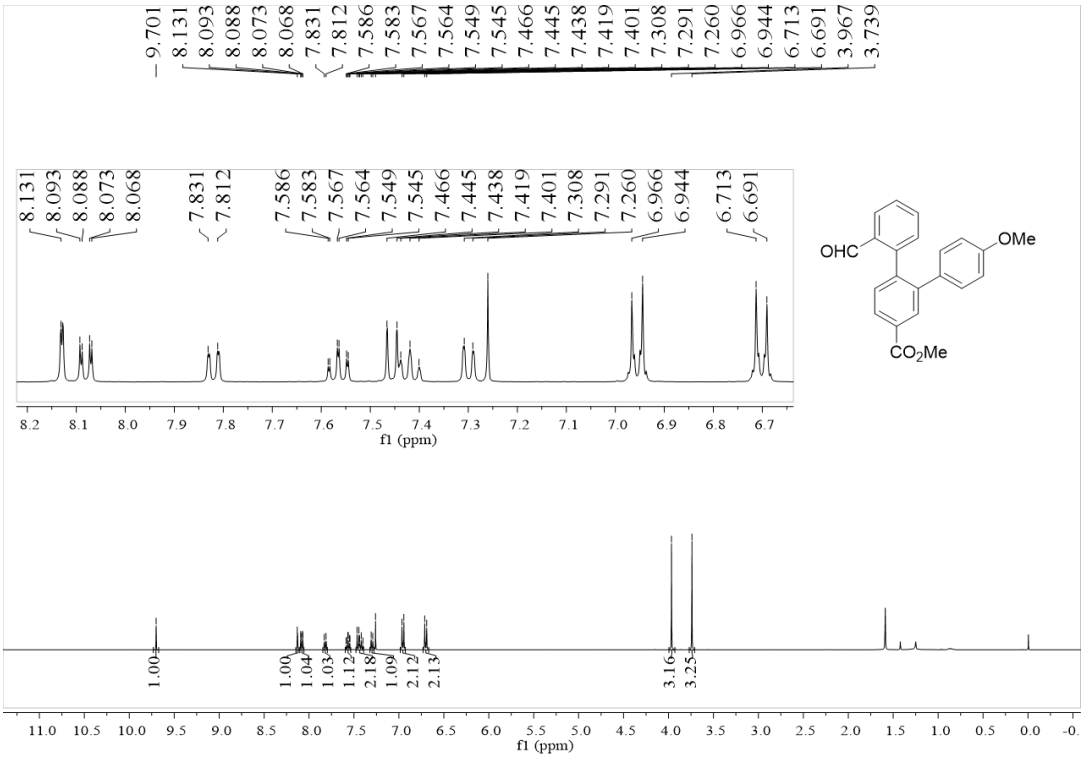


Fig. S54 ^{1}H NMR spectrum of **22** in $CDCl_3$

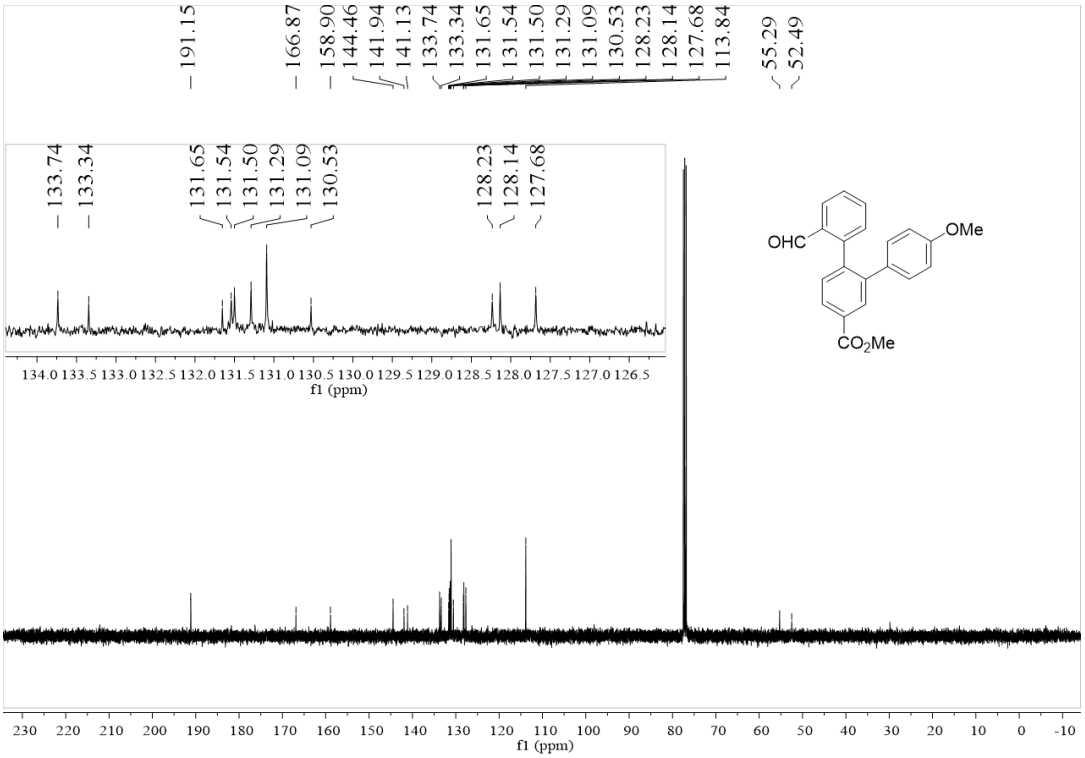


Fig. S55 ^{13}C NMR spectrum of **22** in $CDCl_3$

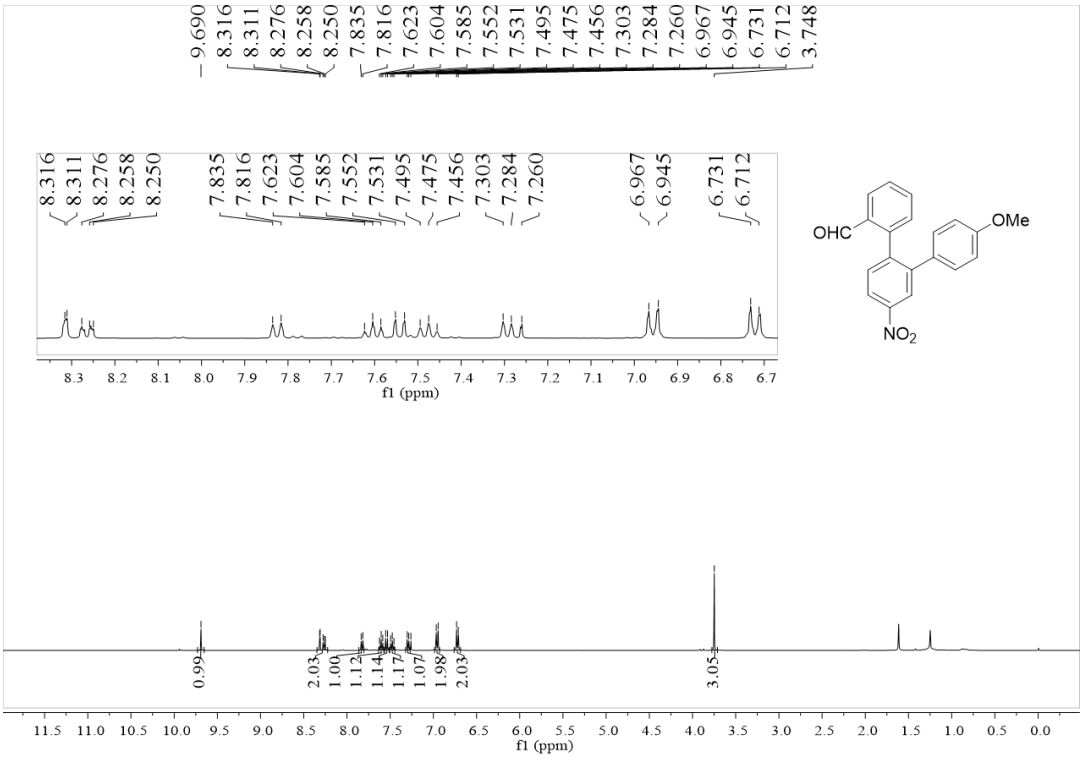


Fig. S56 ^{1}H NMR spectrum of **23** in $CDCl_3$

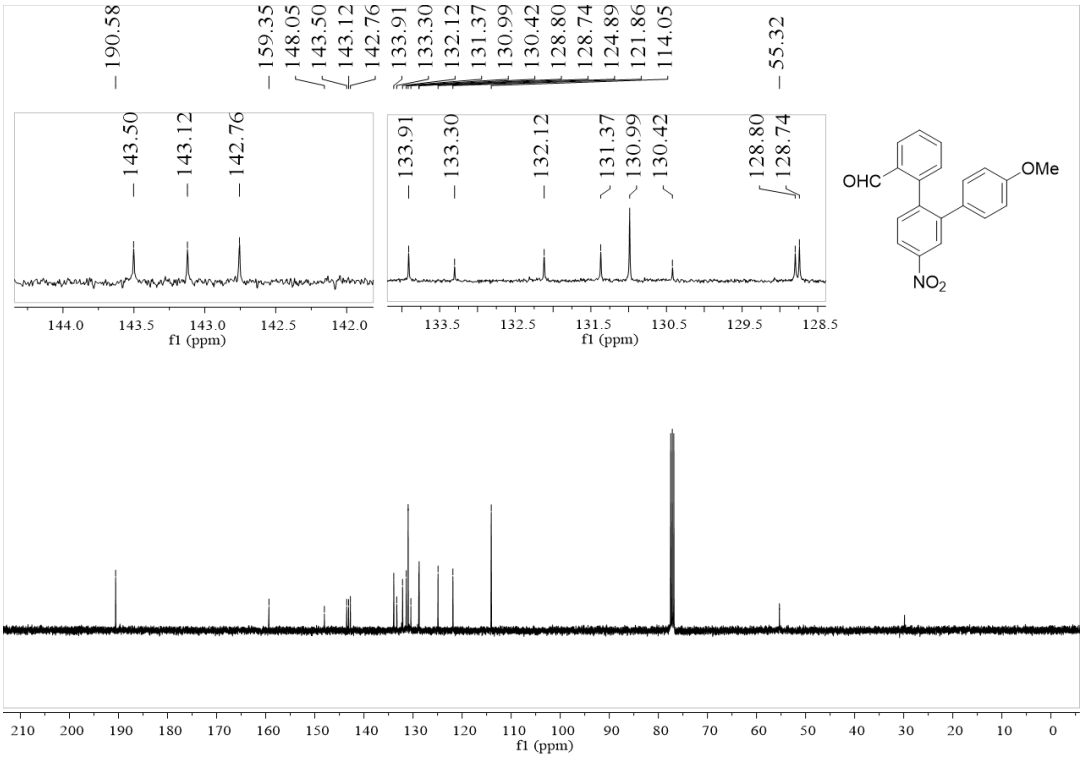


Fig. S57 ^{13}C NMR spectrum of **23** in $CDCl_3$

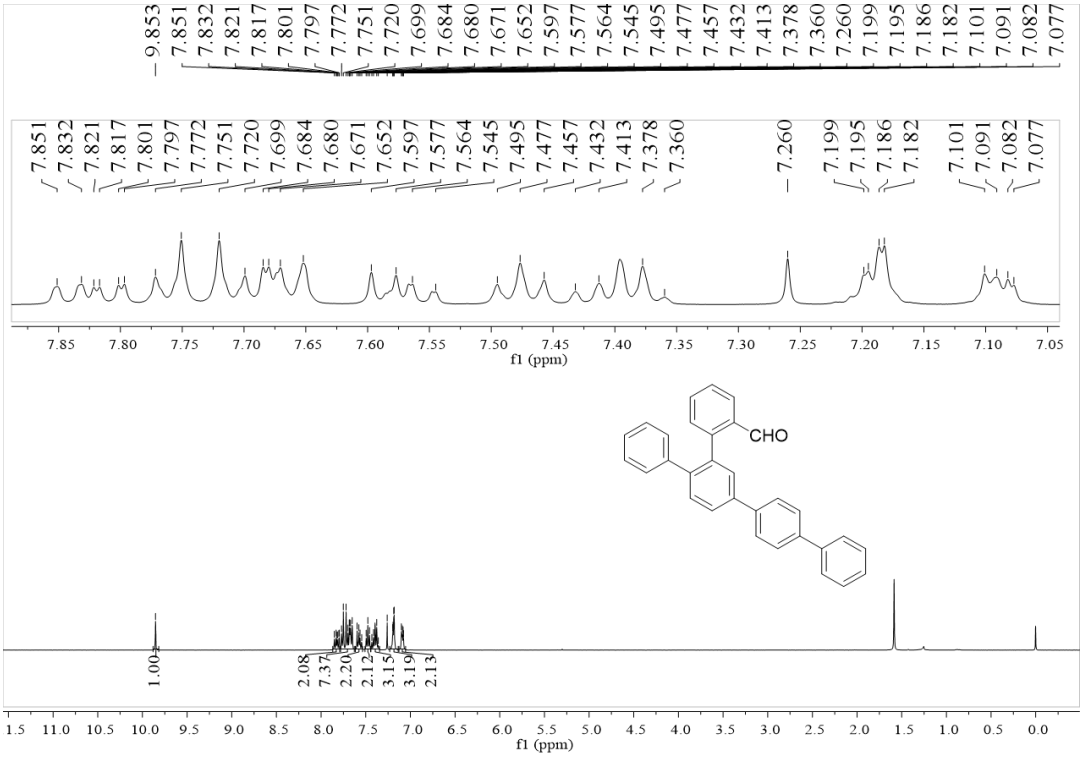


Fig. S58 ^{1}H NMR spectrum of **24** in $CDCl_3$

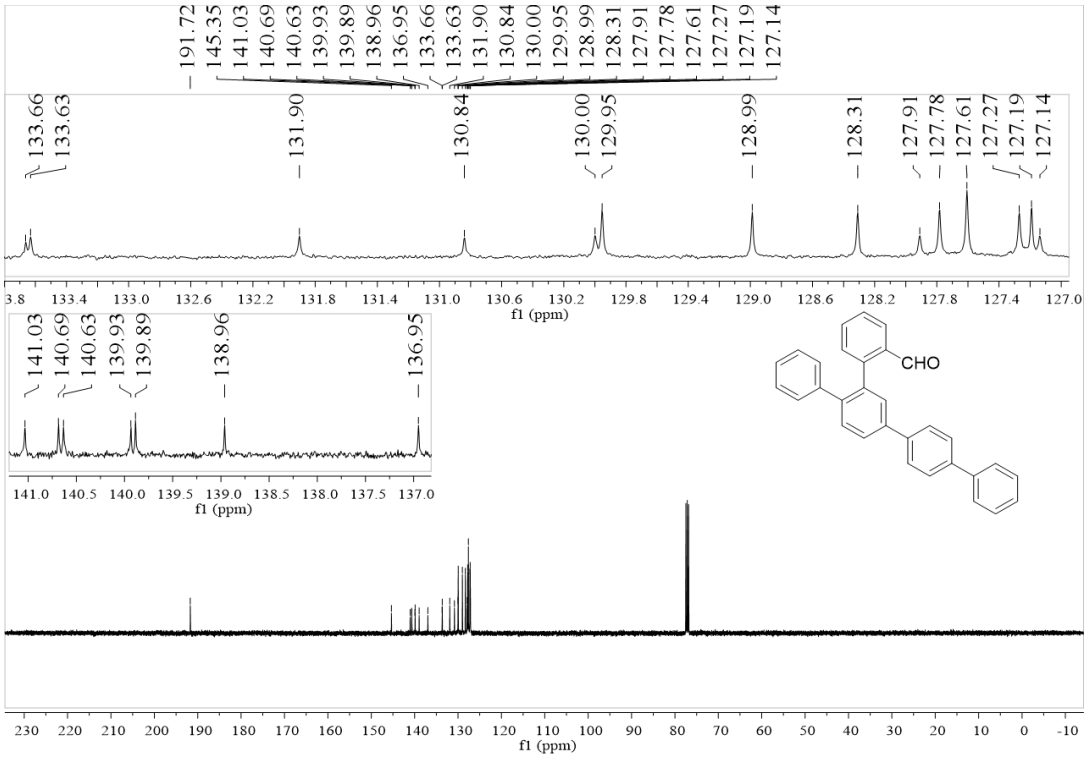


Fig. S59 ^{13}C NMR spectrum of **24** in $CDCl_3$

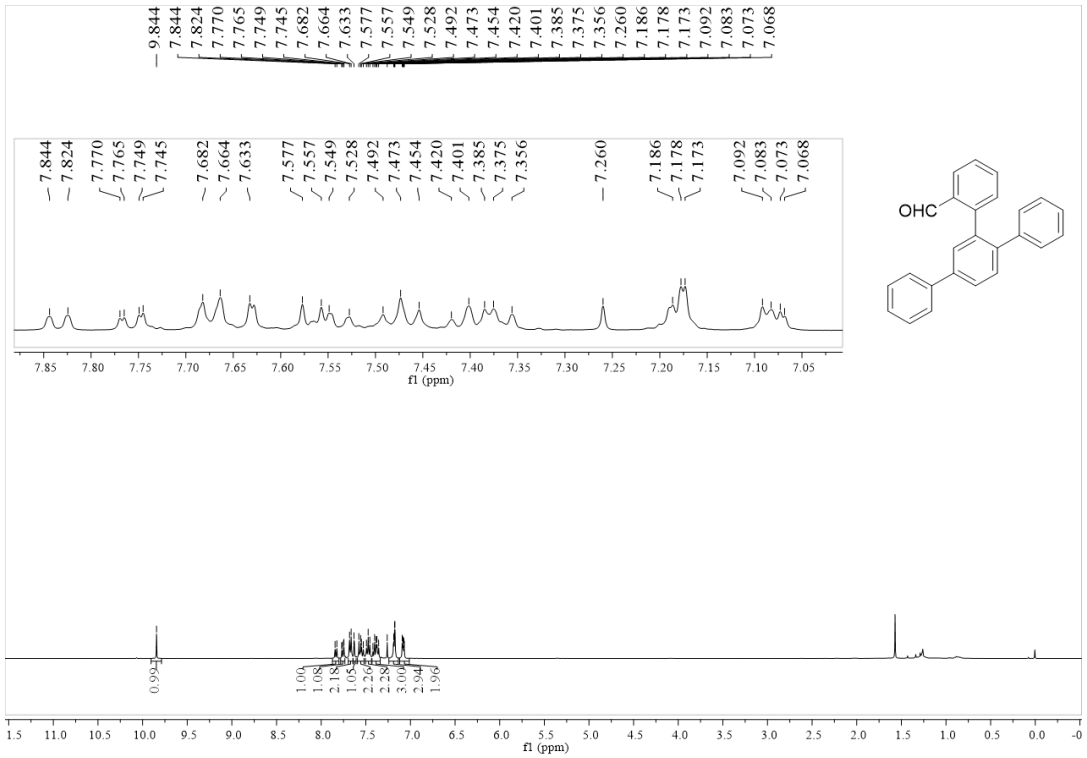


Fig. S60 ^{1}H NMR spectrum of **25** in $CDCl_3$

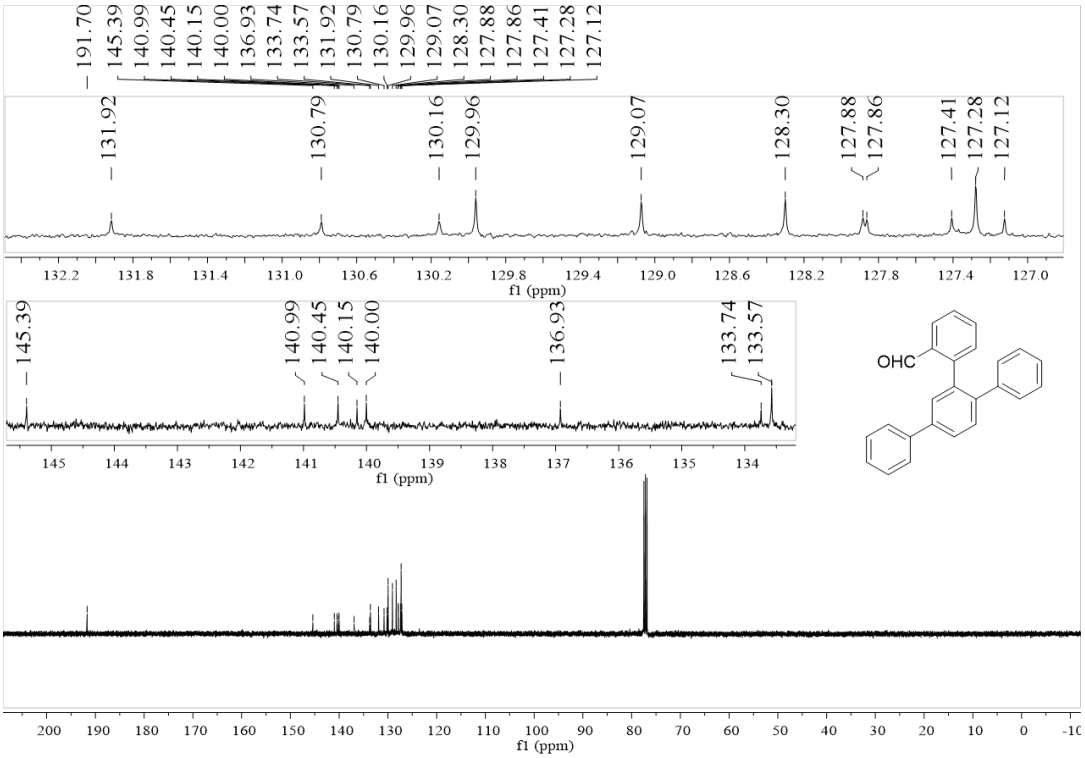


Fig. S61 ^{13}C NMR spectrum of **25** in $CDCl_3$

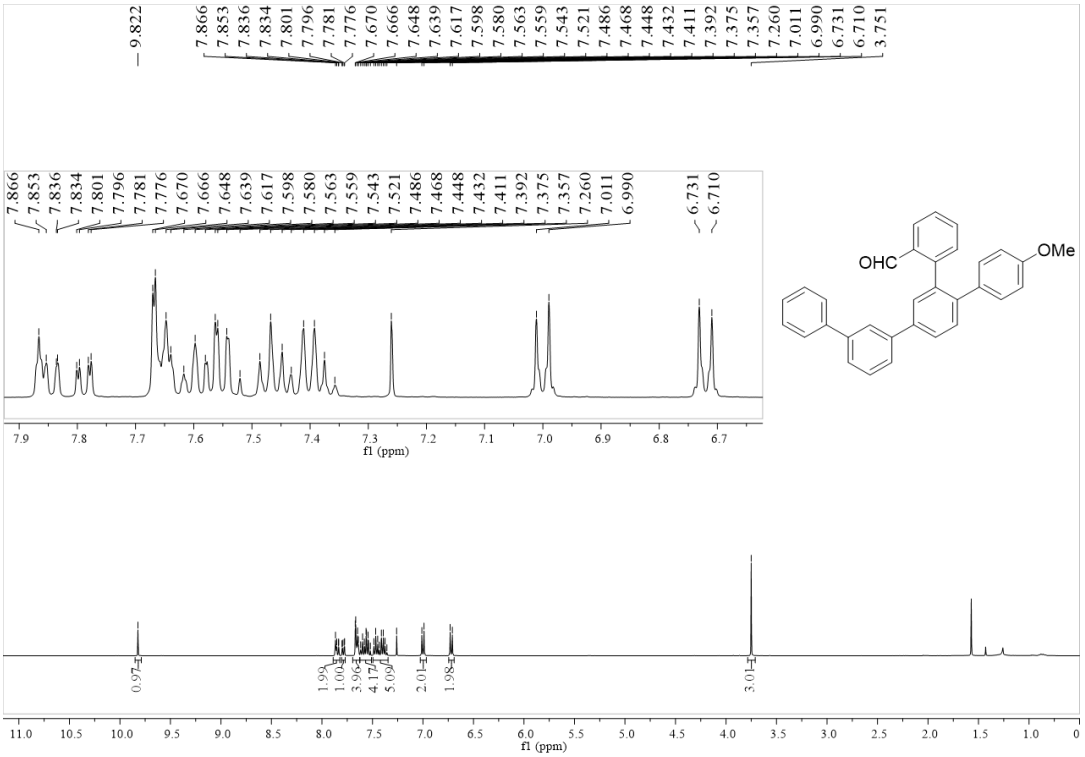


Fig. S62 ^{1}H NMR spectrum of **26** in $CDCl_3$

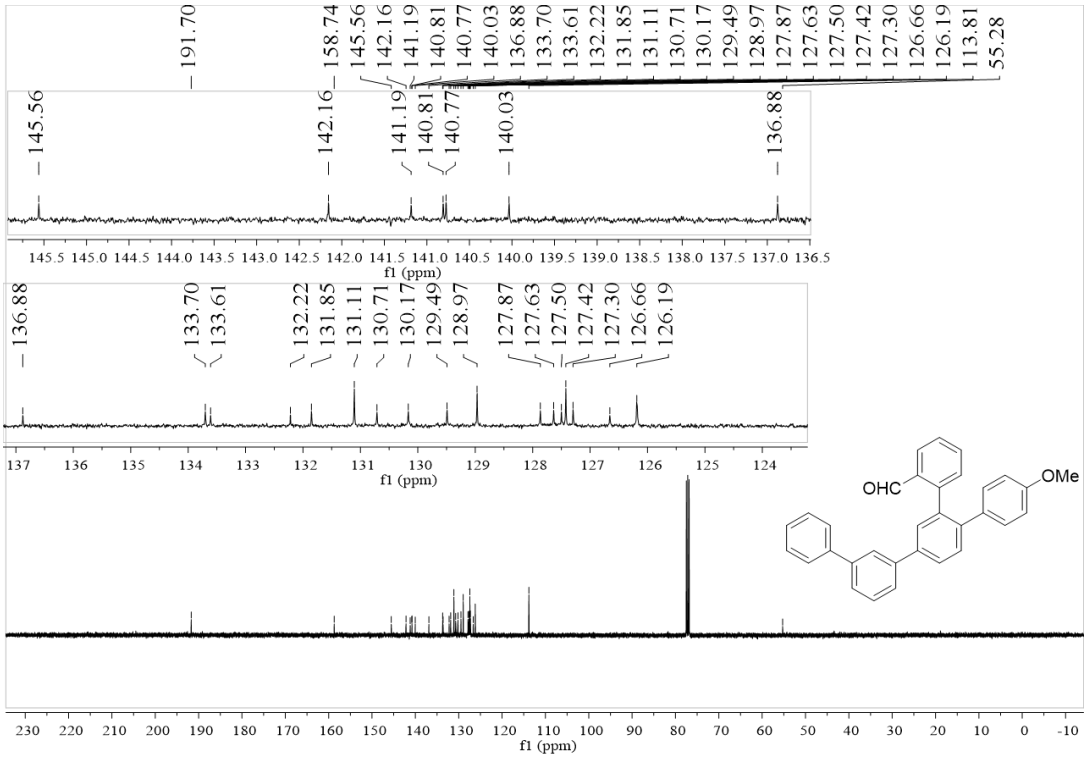


Fig. S63 ^{13}C NMR spectrum of **26** in $CDCl_3$.

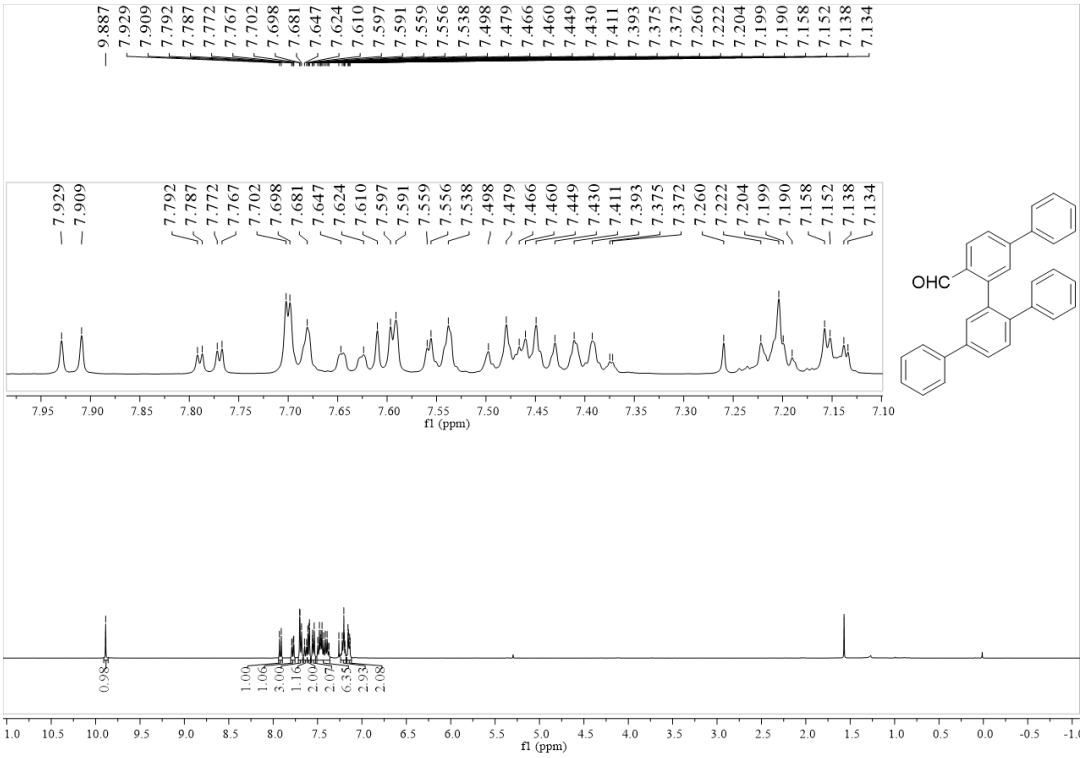


Fig. S64 ^{1}H NMR spectrum of **27** in $CDCl_3$

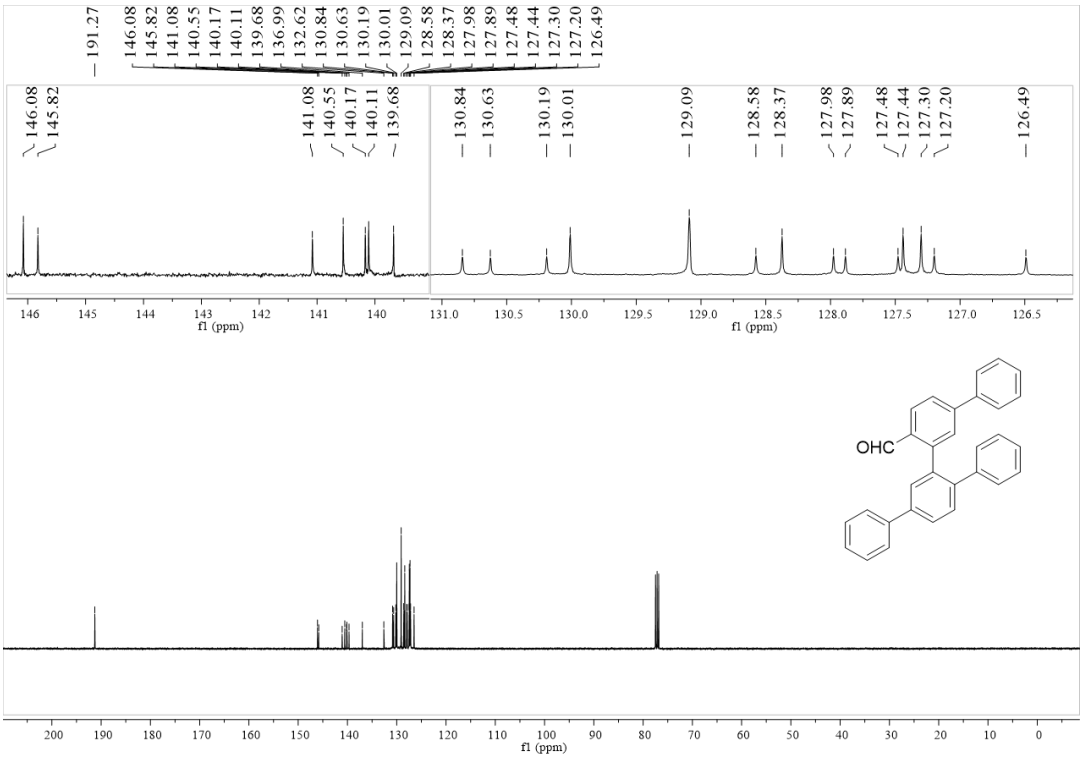


Fig. S65 ^{13}C NMR spectrum of **27** in $CDCl_3$

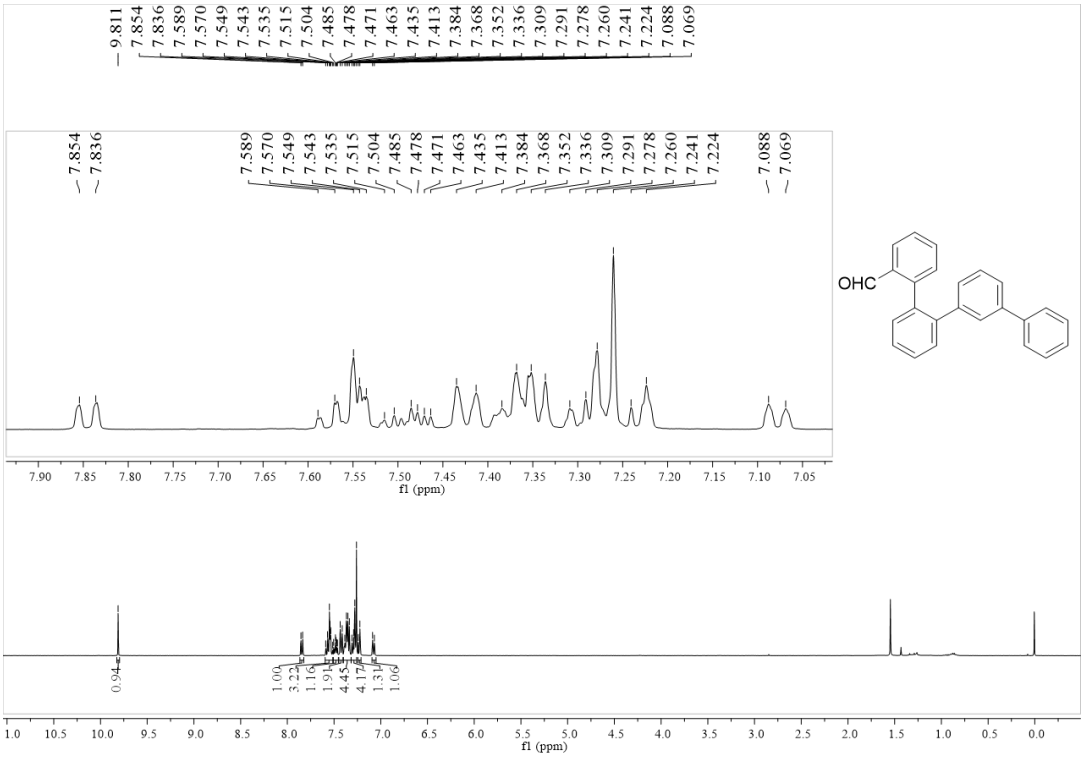


Fig. S66 ^{1}H NMR spectrum of **28** in $CDCl_3$

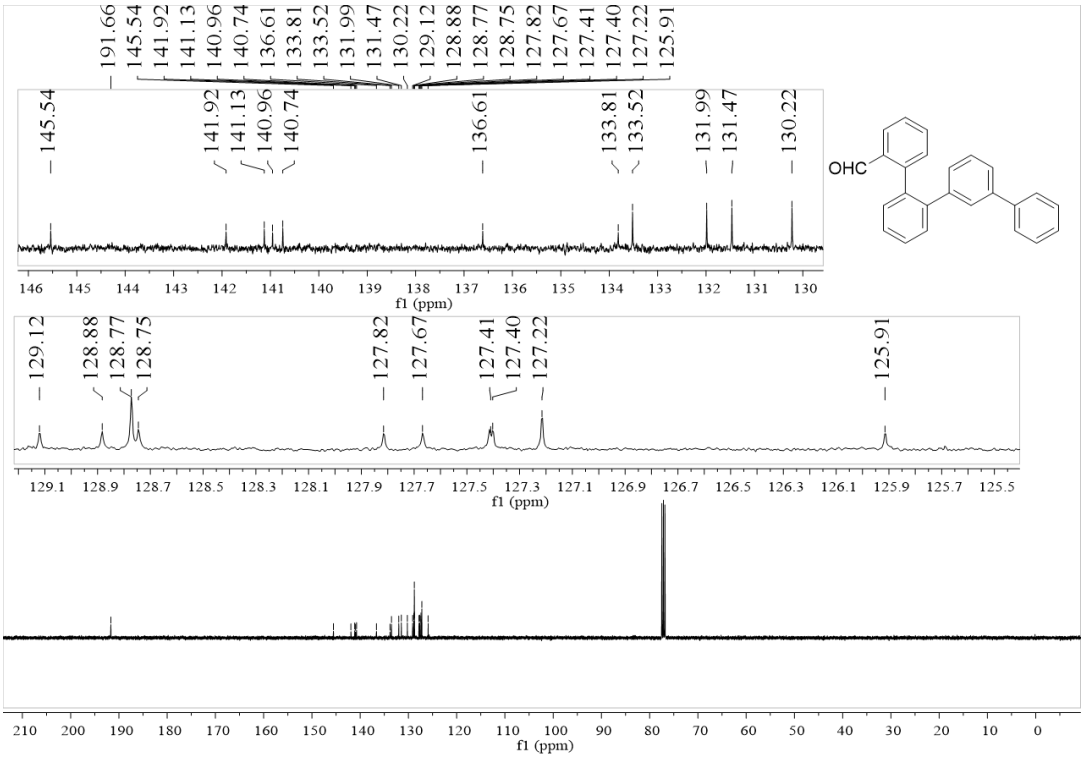


Fig. S67 ^{13}C NMR spectrum of **28** in $CDCl_3$

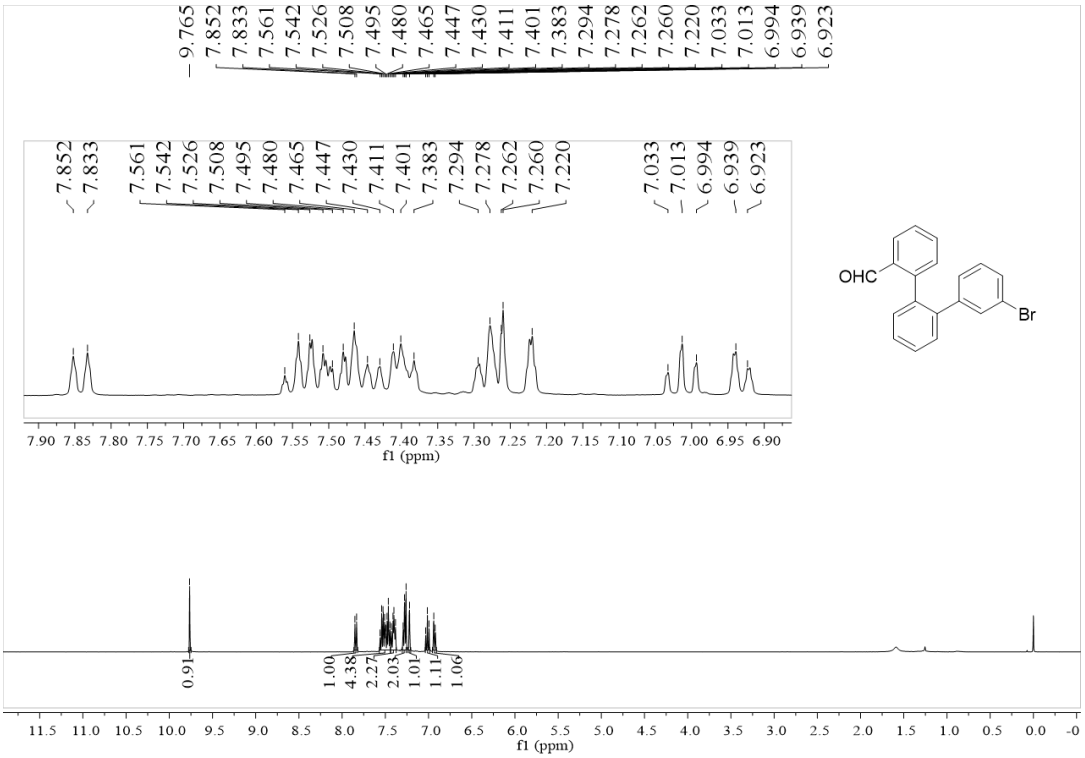


Fig. S68 ^{1}H NMR spectrum of **29** in $CDCl_3$

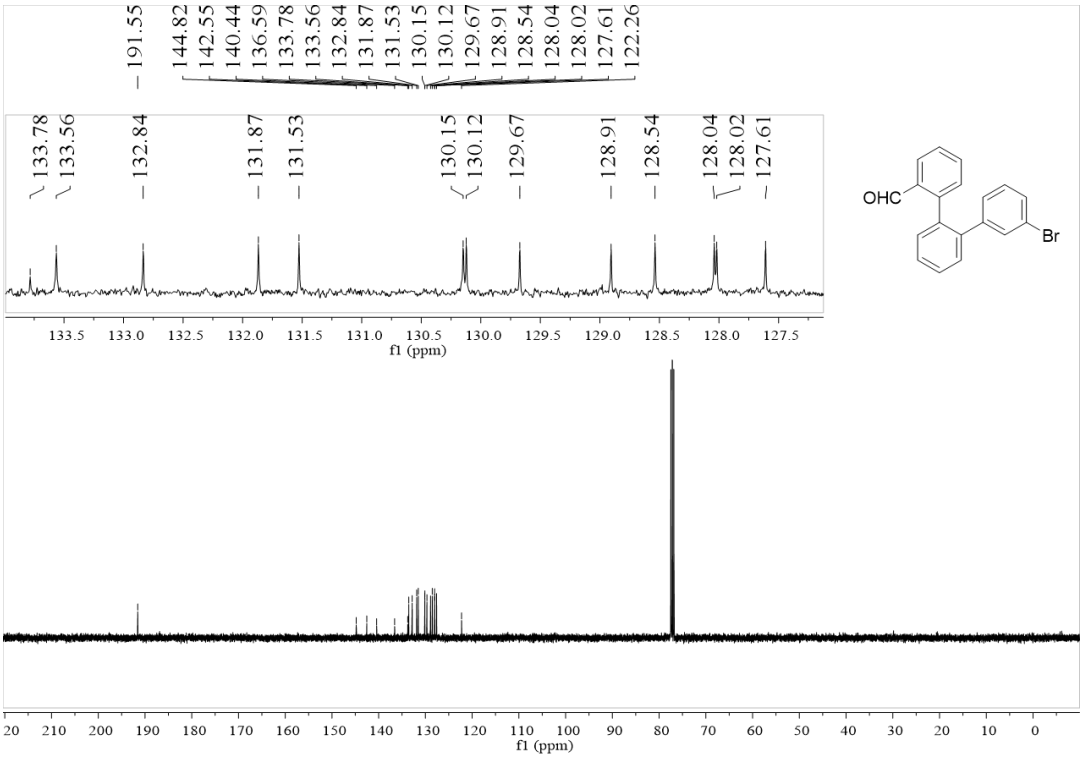


Fig. S69 ^{13}C NMR spectrum of **29** in $CDCl_3$

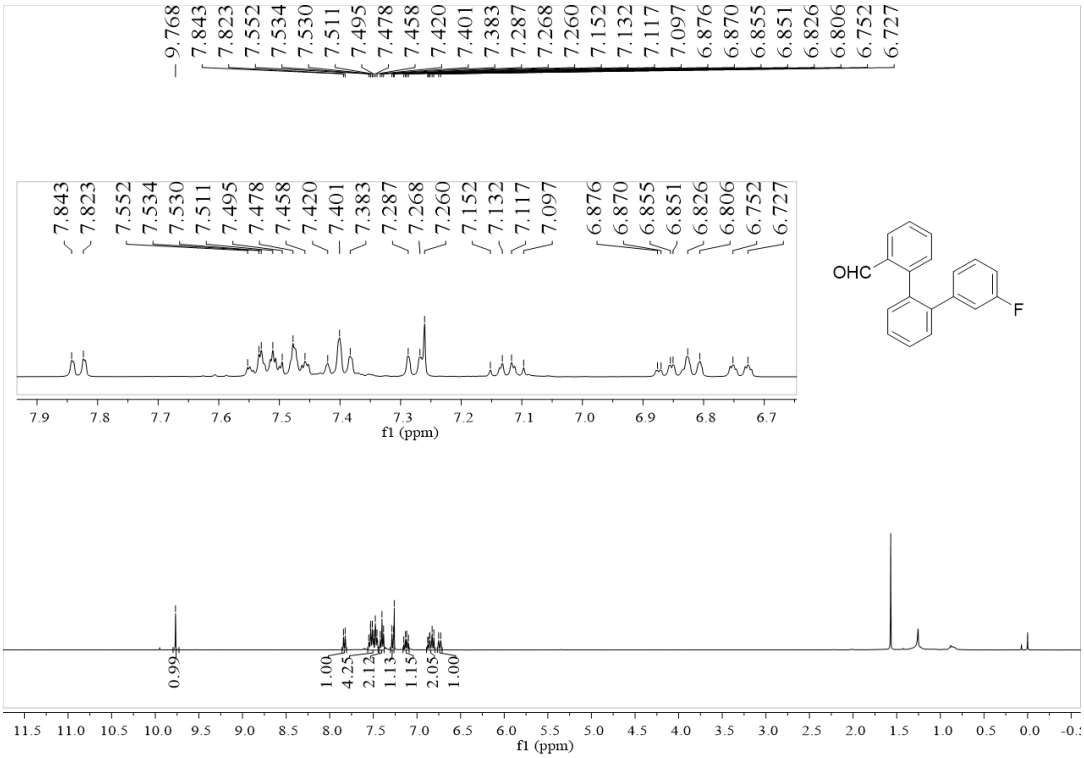


Fig. S70 ^{1}H NMR spectrum of **30** in $CDCl_3$

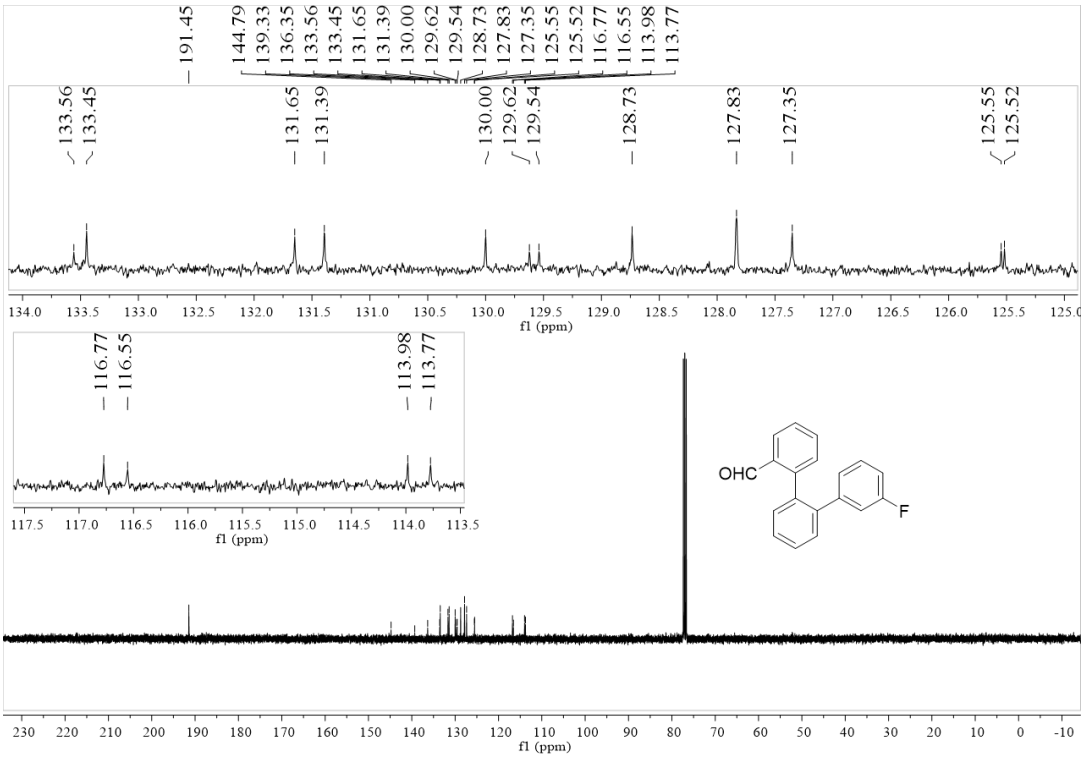


Fig. S71 ^{13}C NMR spectrum of **30** in $CDCl_3$

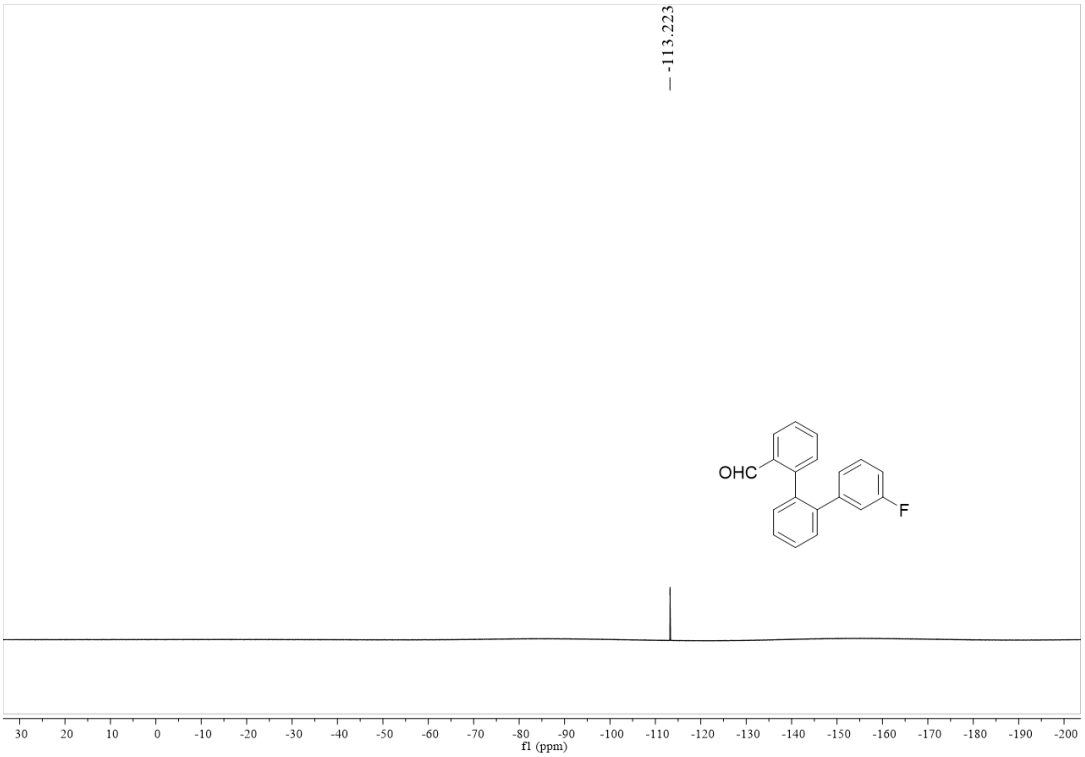


Fig. S72 ^{19}F NMR spectrum of **30** in $CDCl_3$

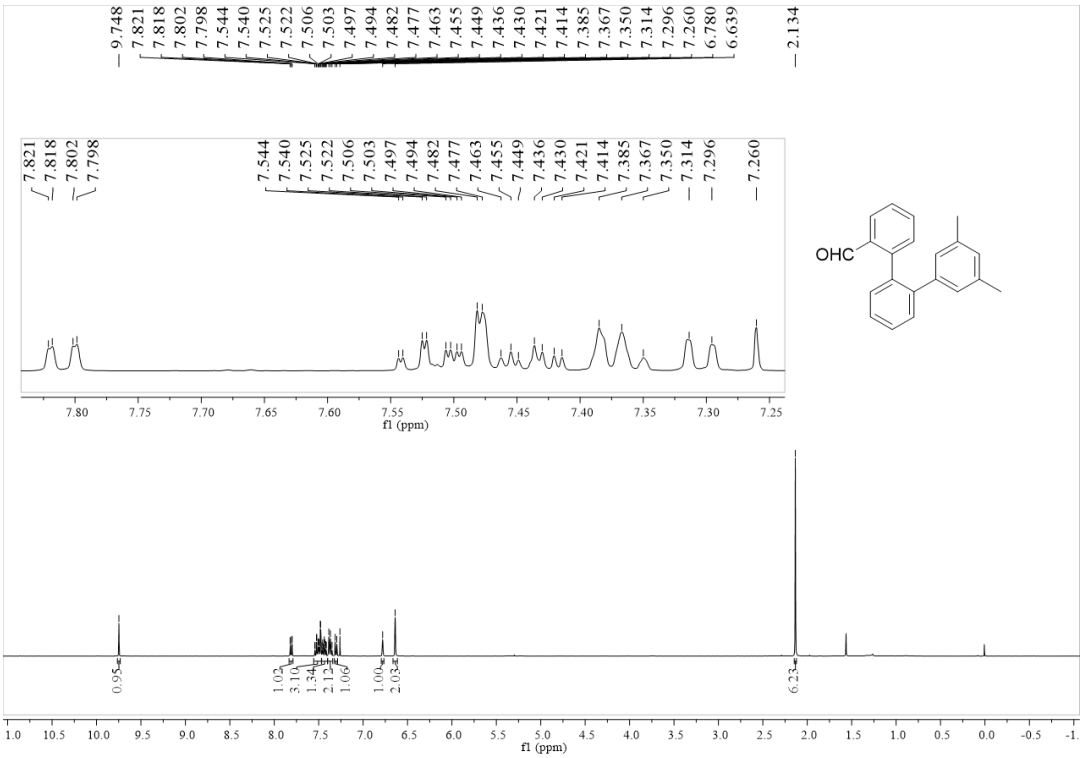


Fig. S73 ^{1}H NMR spectrum of **31** in $CDCl_3$

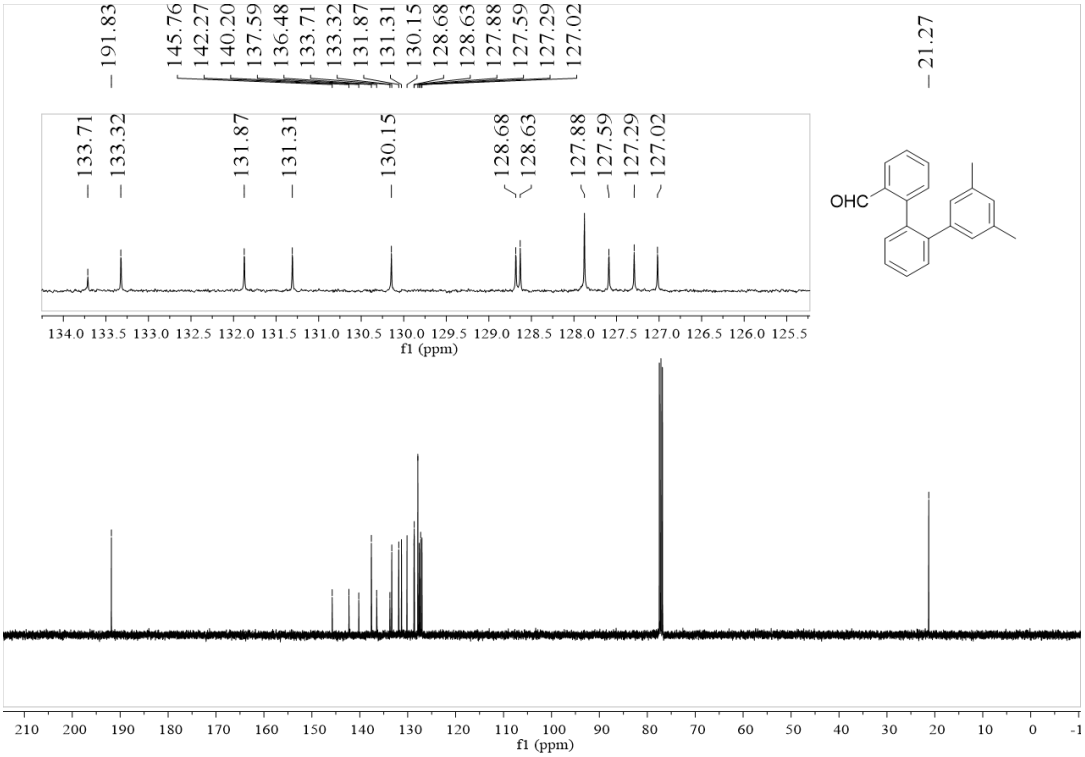


Fig. S74 ^{13}C NMR spectrum of **31** in $CDCl_3$

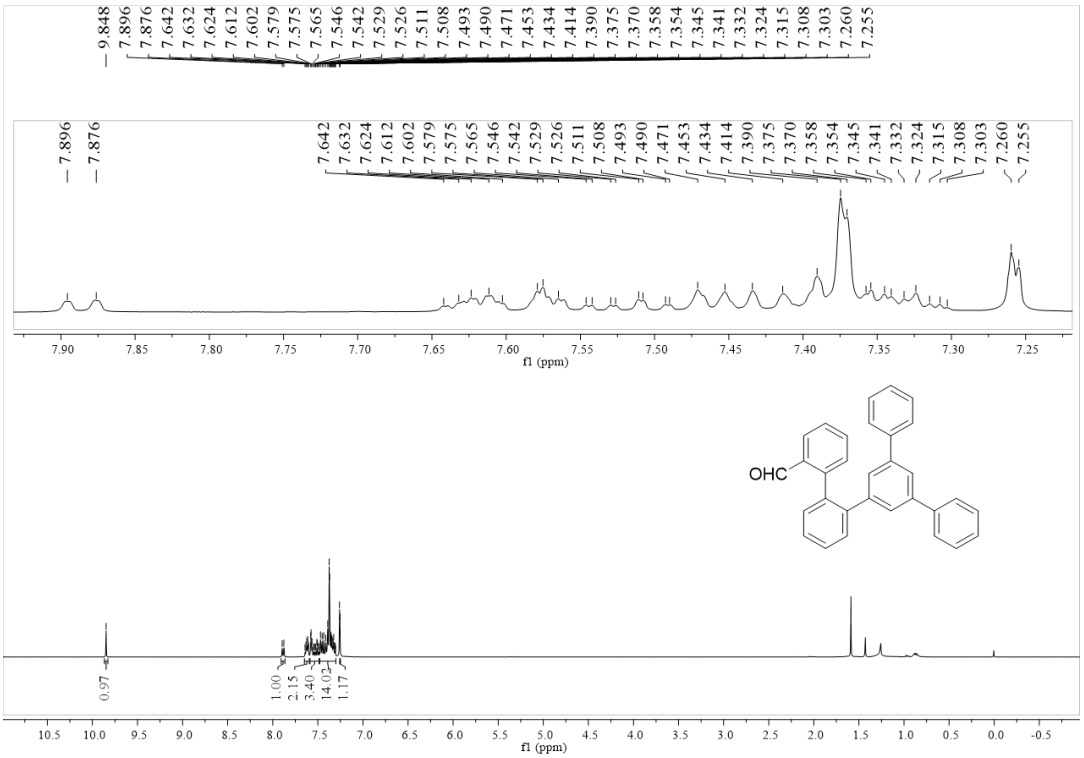


Fig. S75 ^{1}H NMR spectrum of **32** in $CDCl_3$

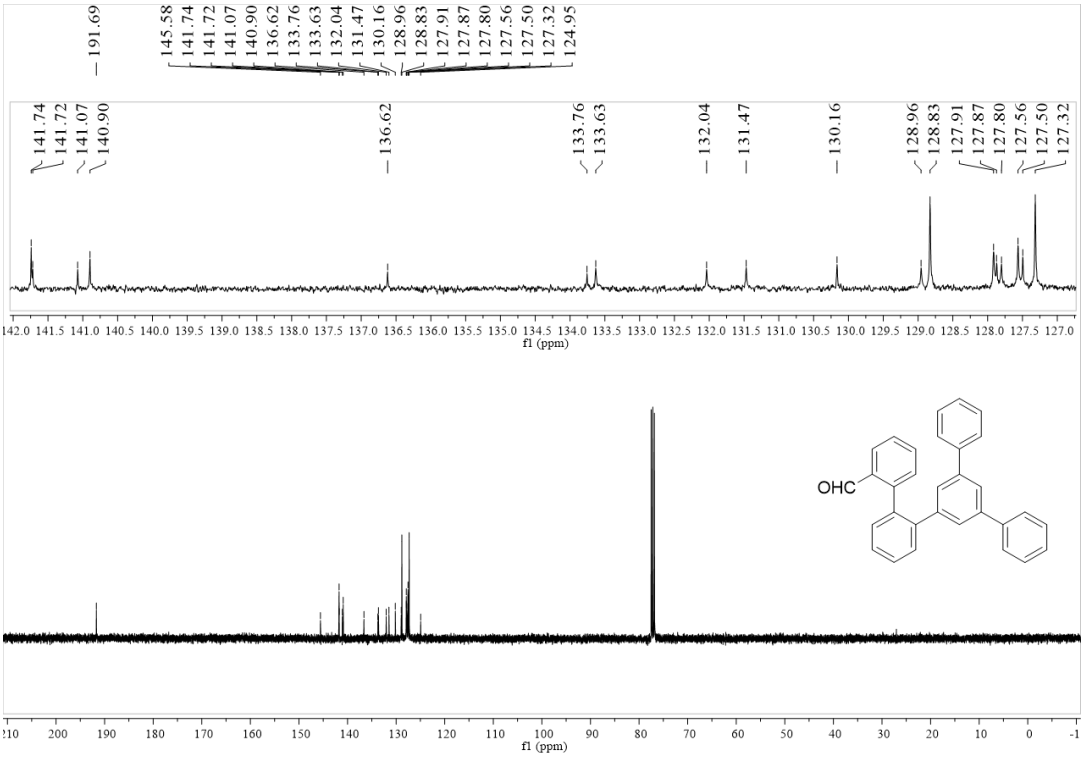


Fig. S76 ^{13}C NMR spectrum of **32** in $CDCl_3$

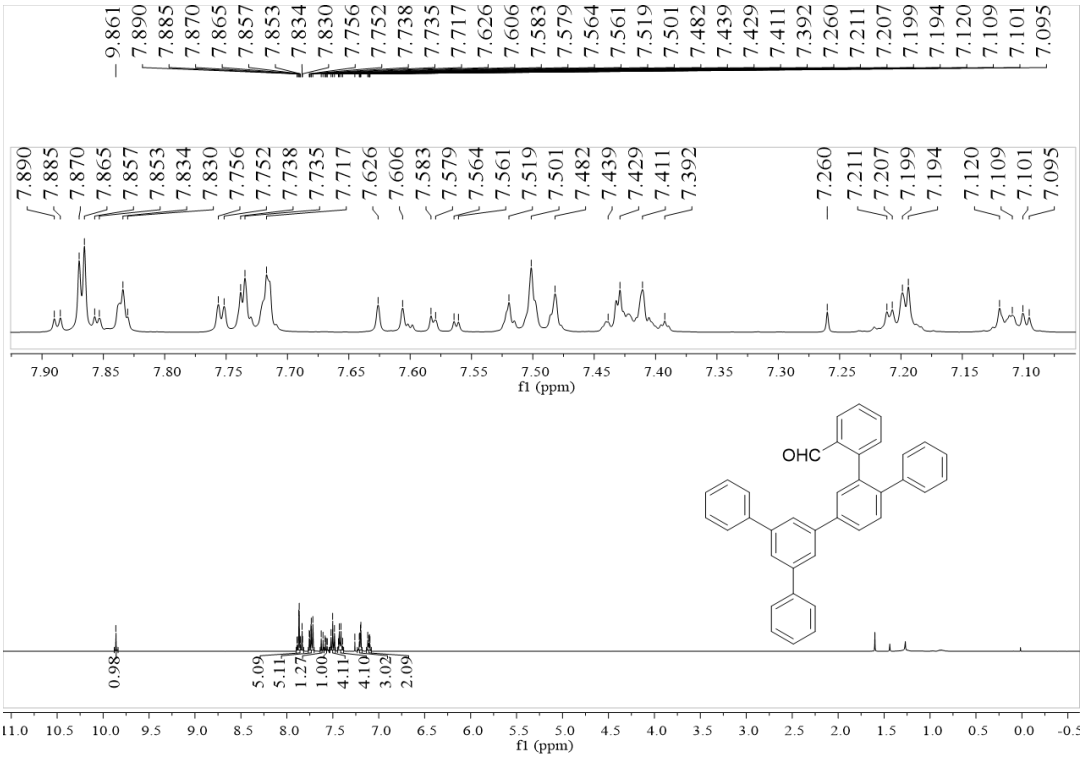


Fig. S77 ^{1}H NMR spectrum of **33** in $CDCl_3$

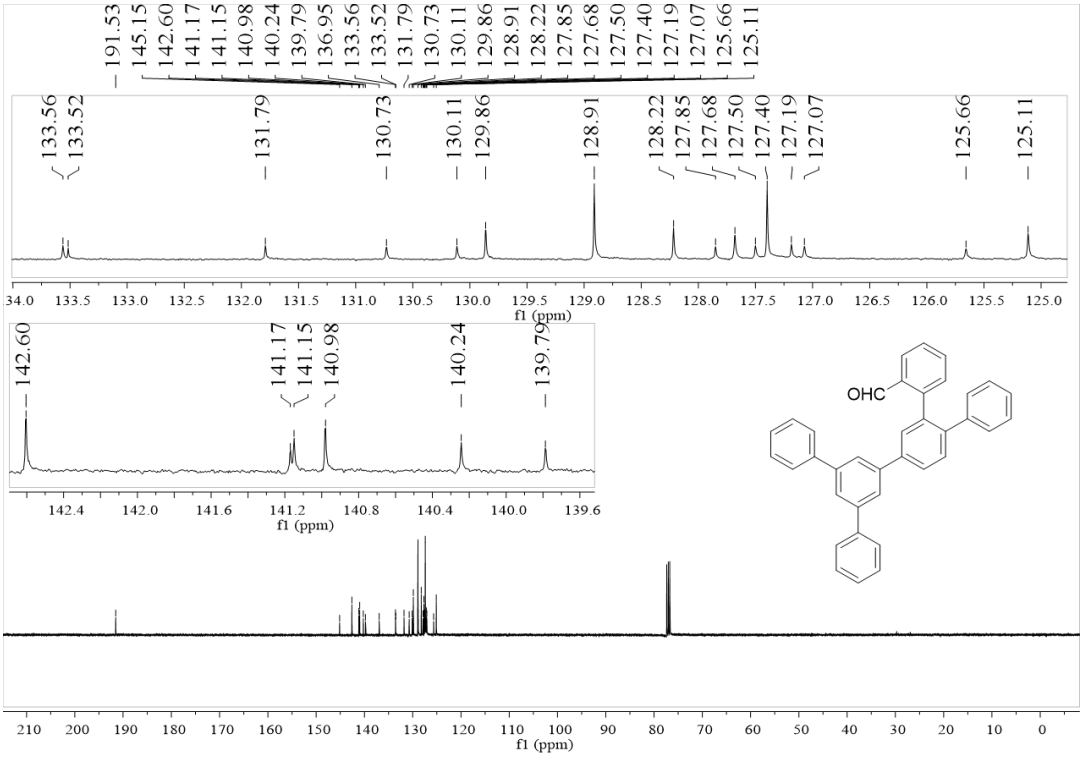


Fig. S78 ^{13}C NMR spectrum of **33** in $CDCl_3$

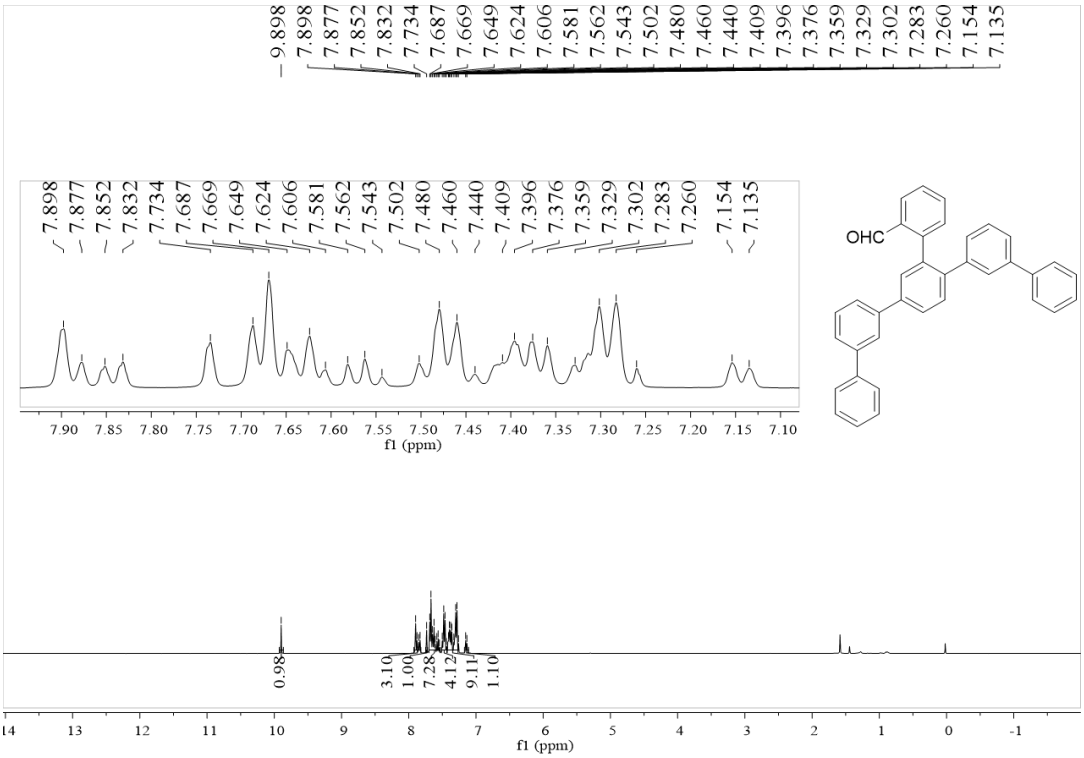


Fig. S79 ^{1}H NMR spectrum of **34** in $CDCl_3$

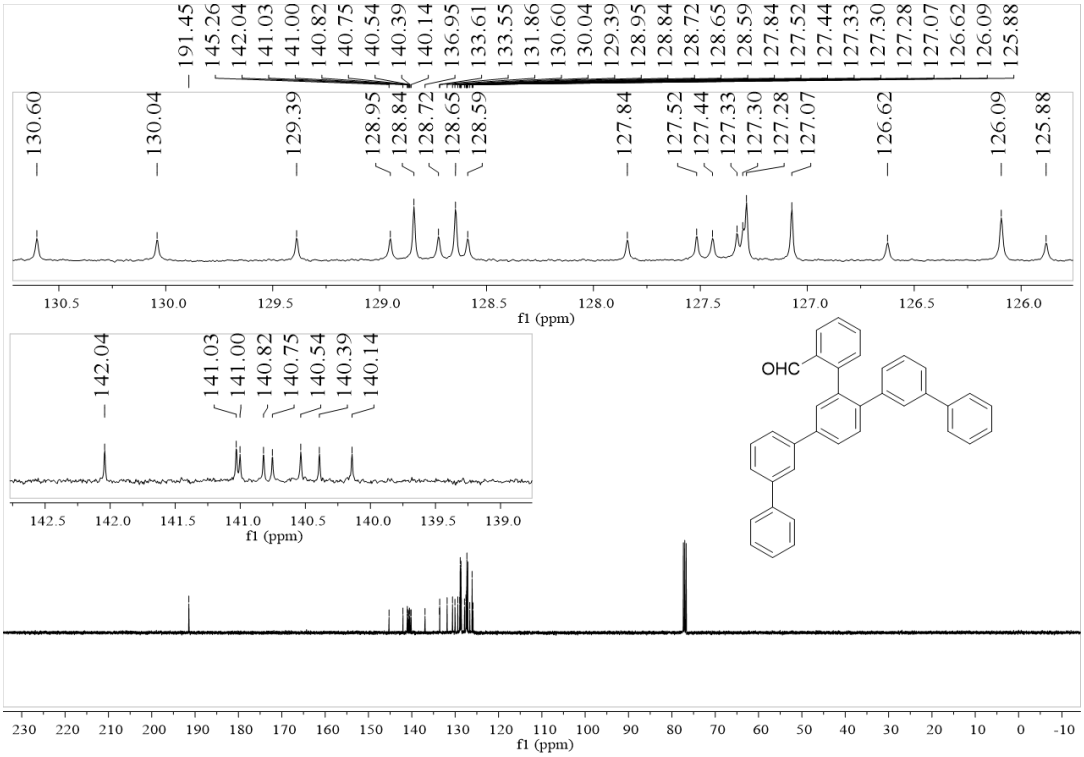


Fig. S80 ^{13}C NMR spectrum of **34** in $CDCl_3$

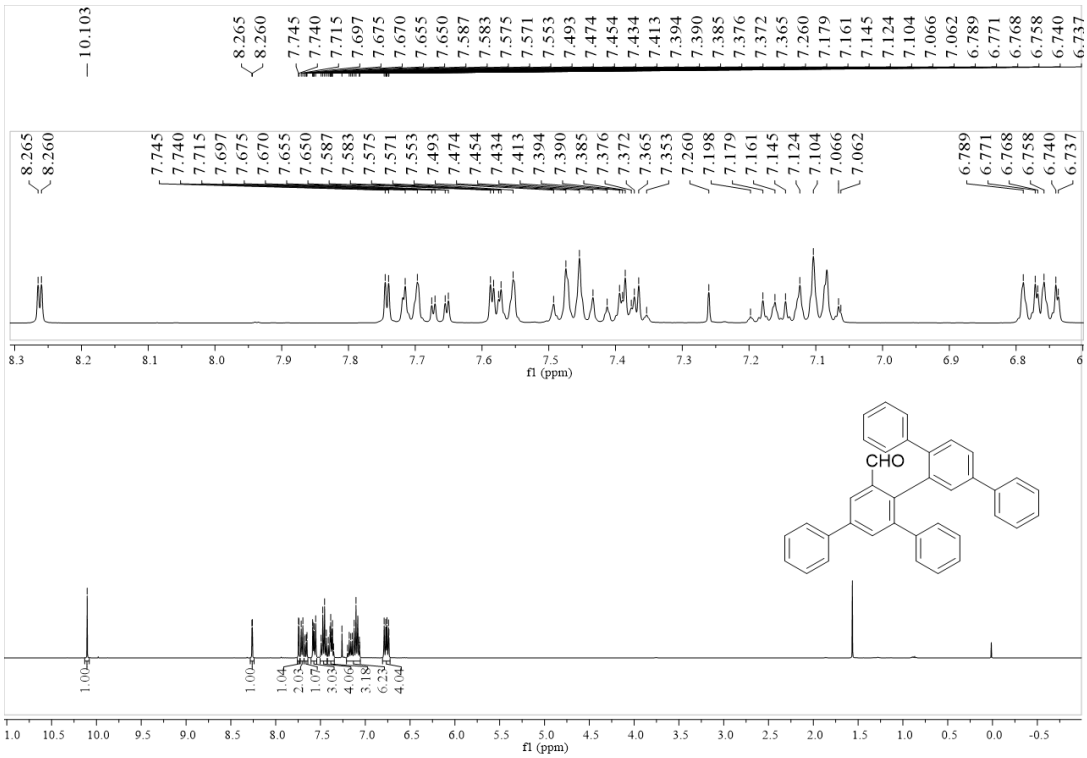


Fig. S81 ^{1}H NMR spectrum of **35** in $CDCl_3$

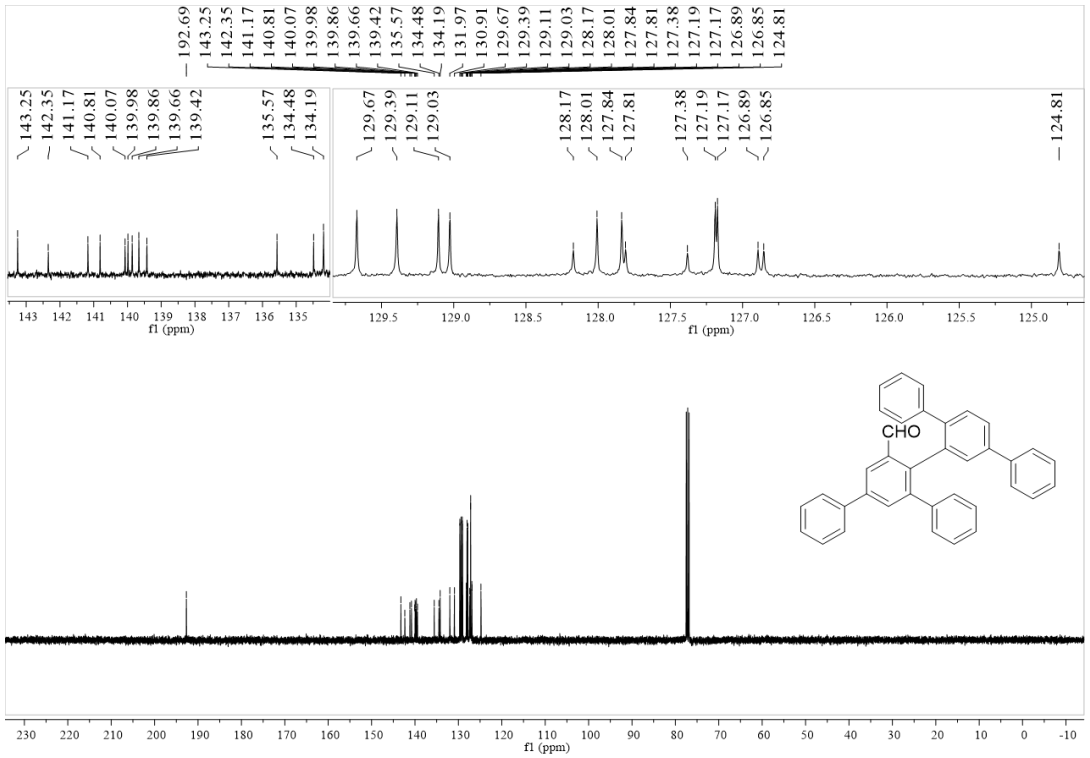


Fig. S82 ^{13}C NMR spectrum of **35** in $CDCl_3$

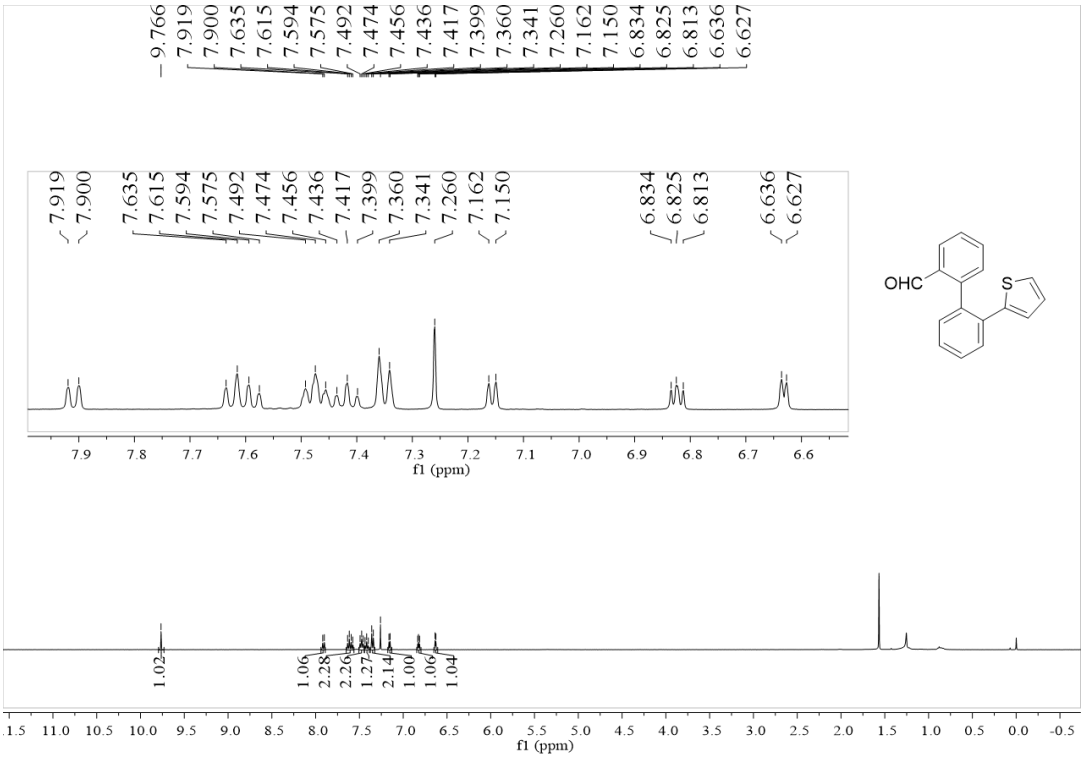


Fig. S83 ^{1}H NMR spectrum of **36** in $CDCl_3$

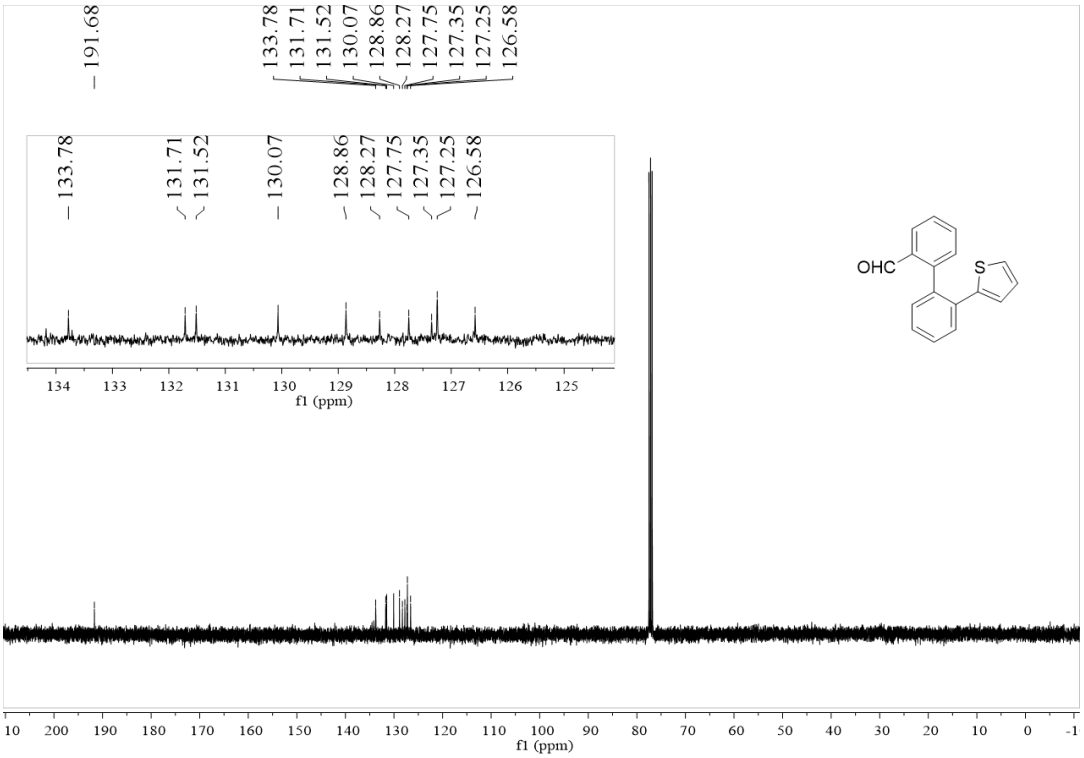


Fig. S84 ^{13}C NMR spectrum of **36** in $CDCl_3$

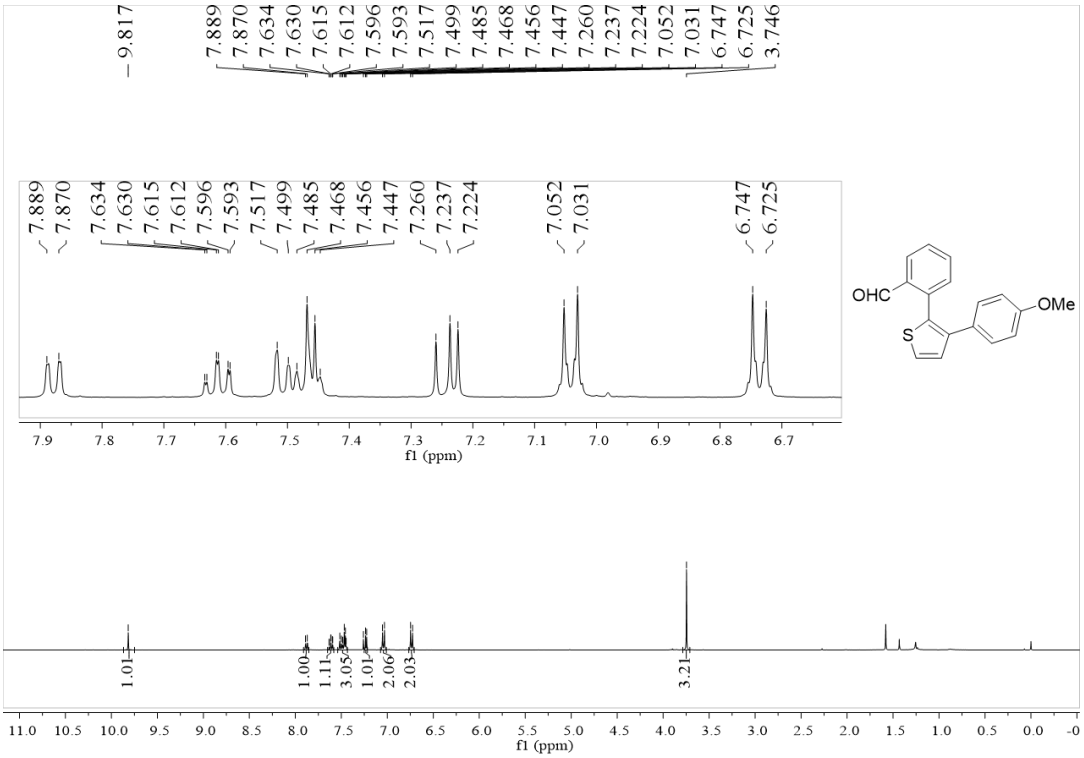


Fig. S85 ^{1}H NMR spectrum of **37** in $CDCl_3$

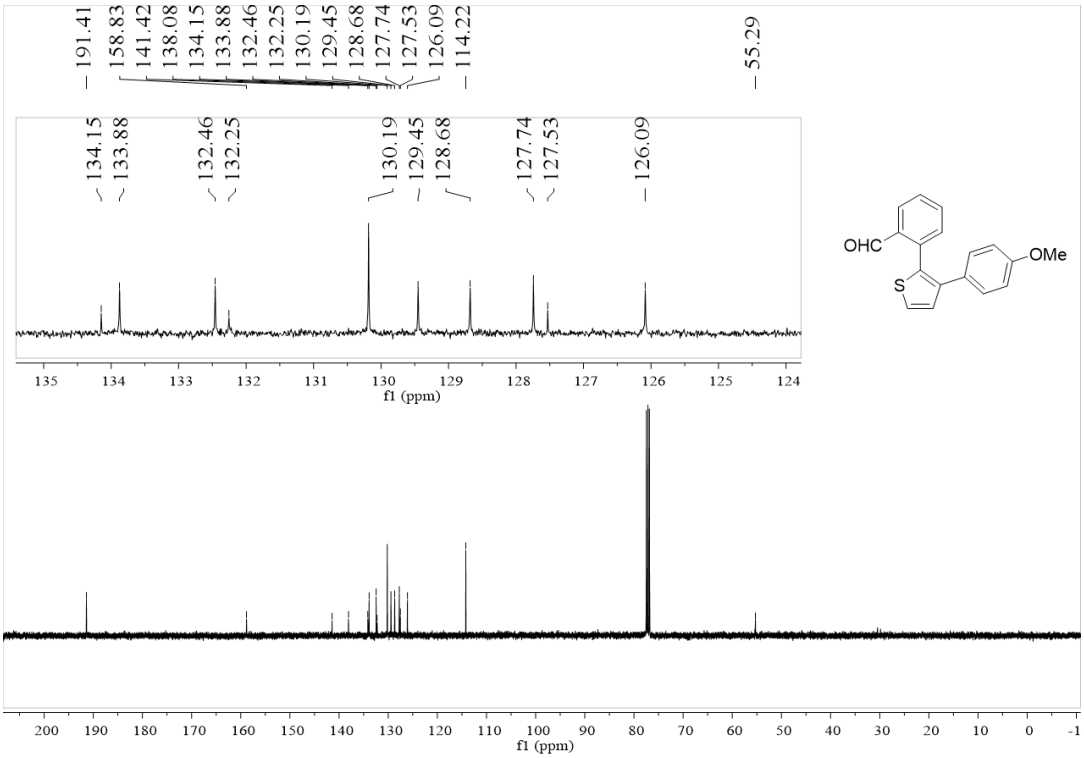


Fig. S86 ^{13}C NMR spectrum of **37** in $CDCl_3$

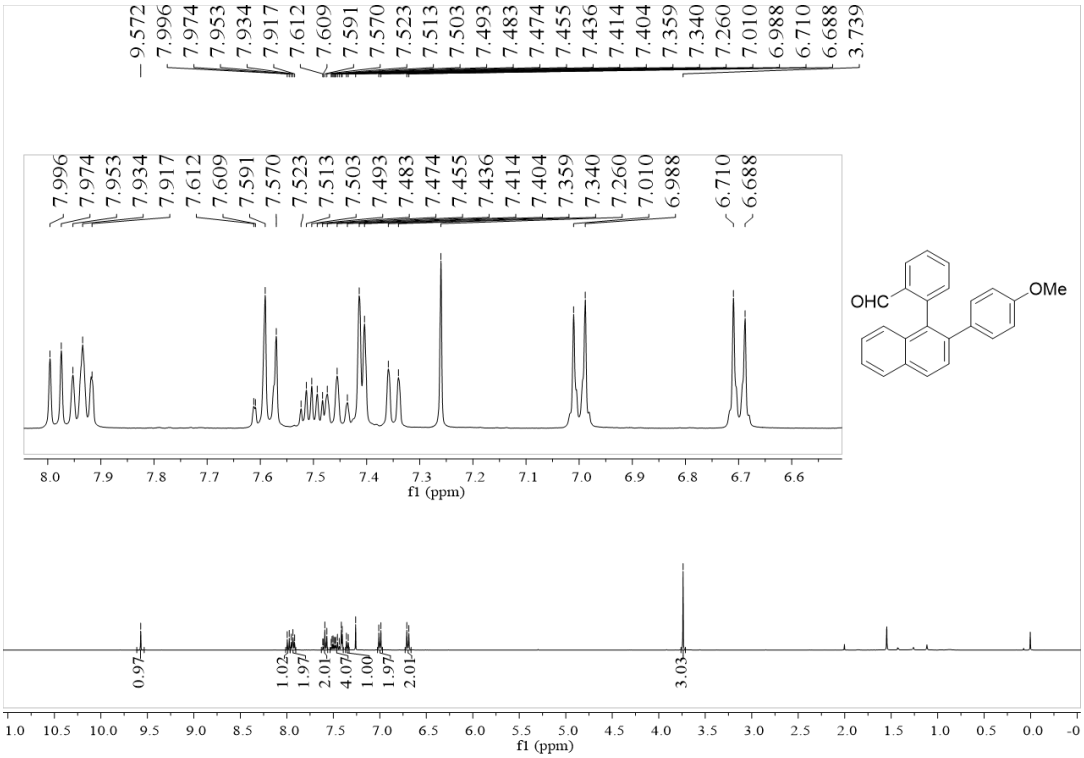


Fig. S87 ^{1}H NMR spectrum of **38** in $CDCl_3$

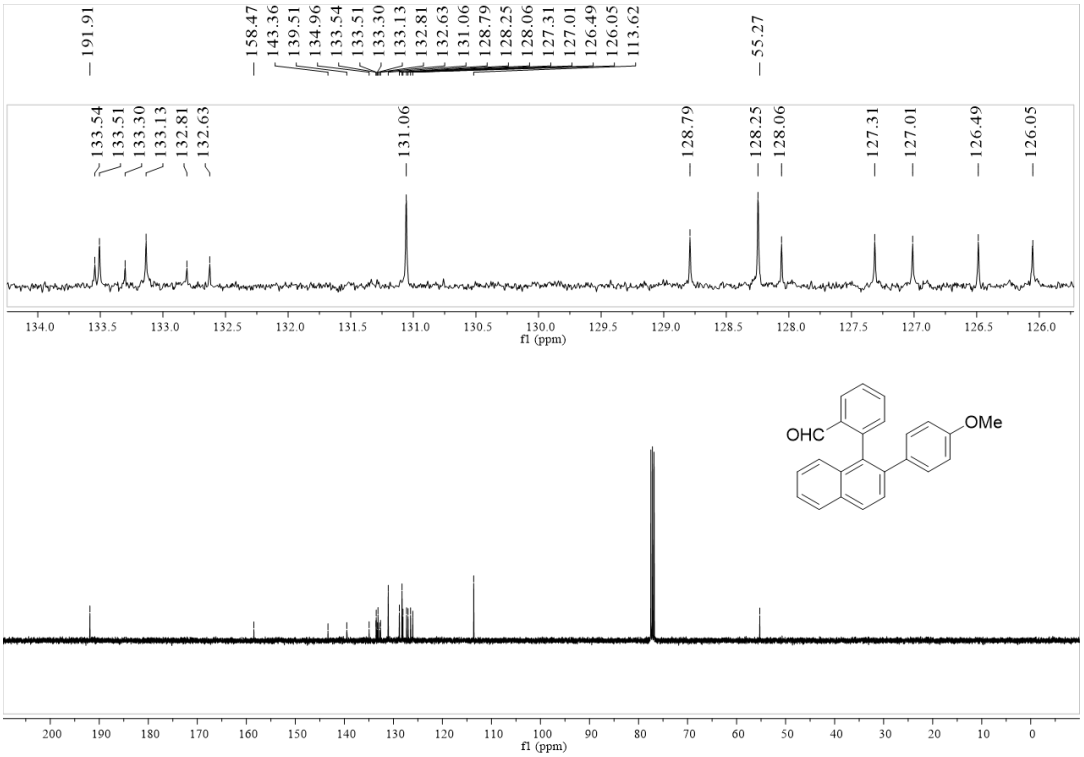


Fig. S88 ^{13}C NMR spectrum of **38** in $CDCl_3$

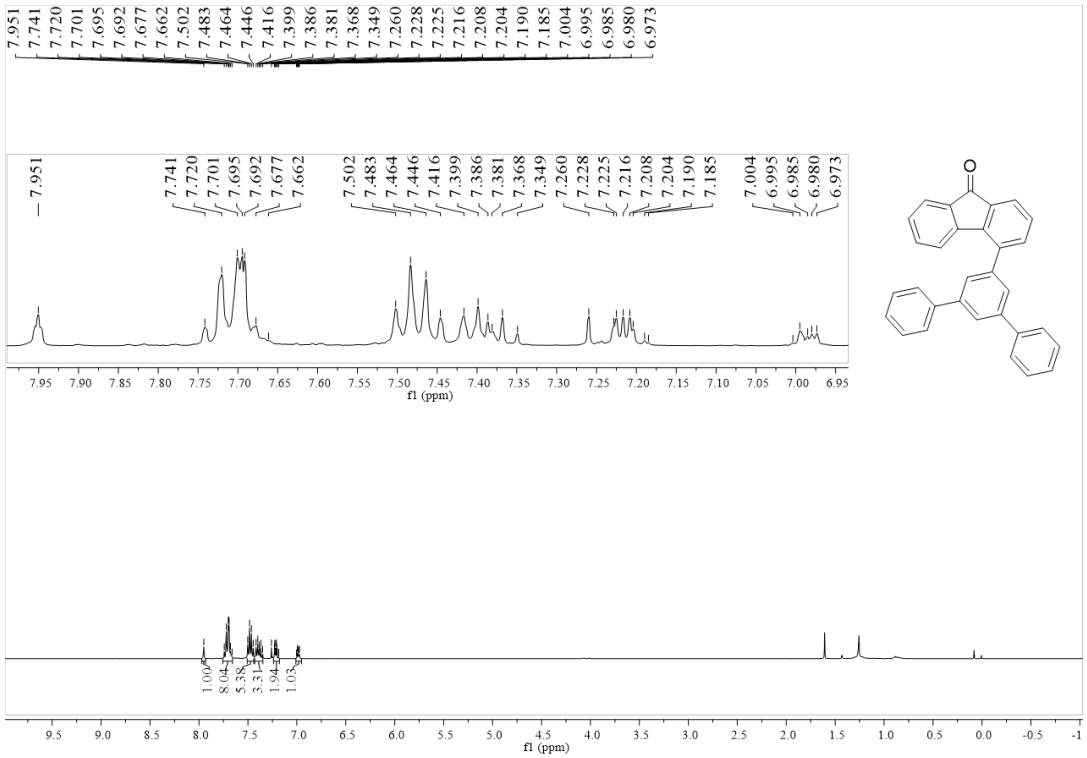


Fig. S89 ^{1}H NMR spectrum of **39** in $CDCl_3$

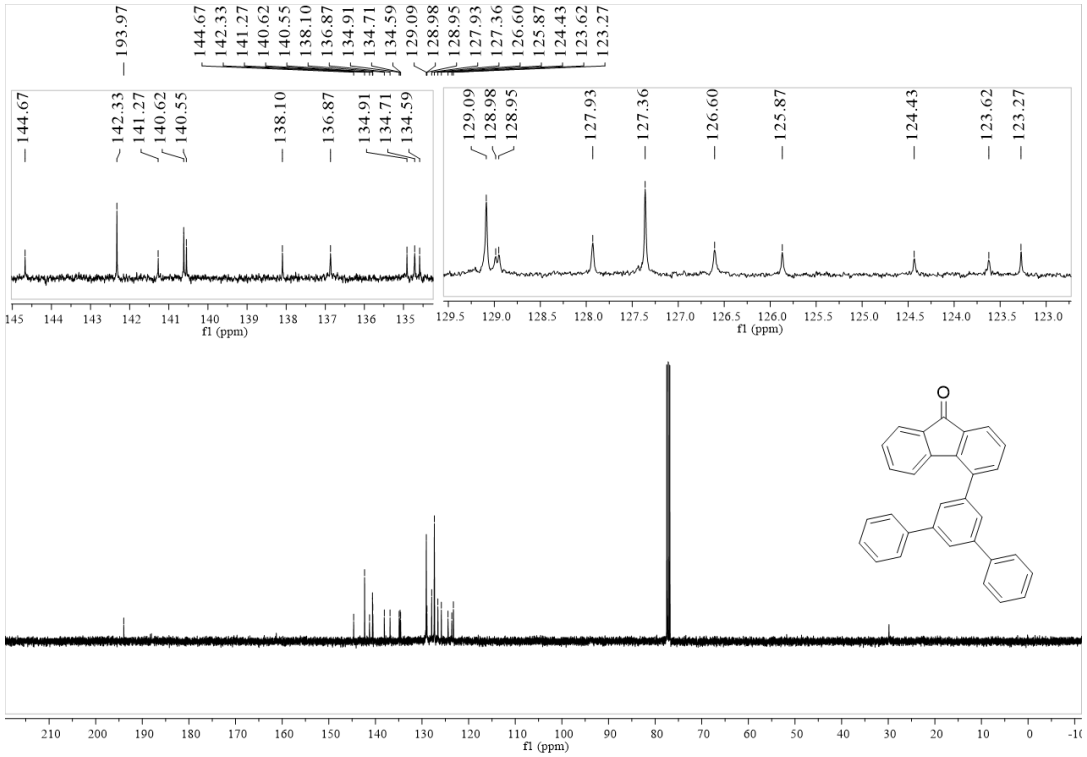


Fig. S90 ^{13}C NMR spectrum of **39** in $CDCl_3$

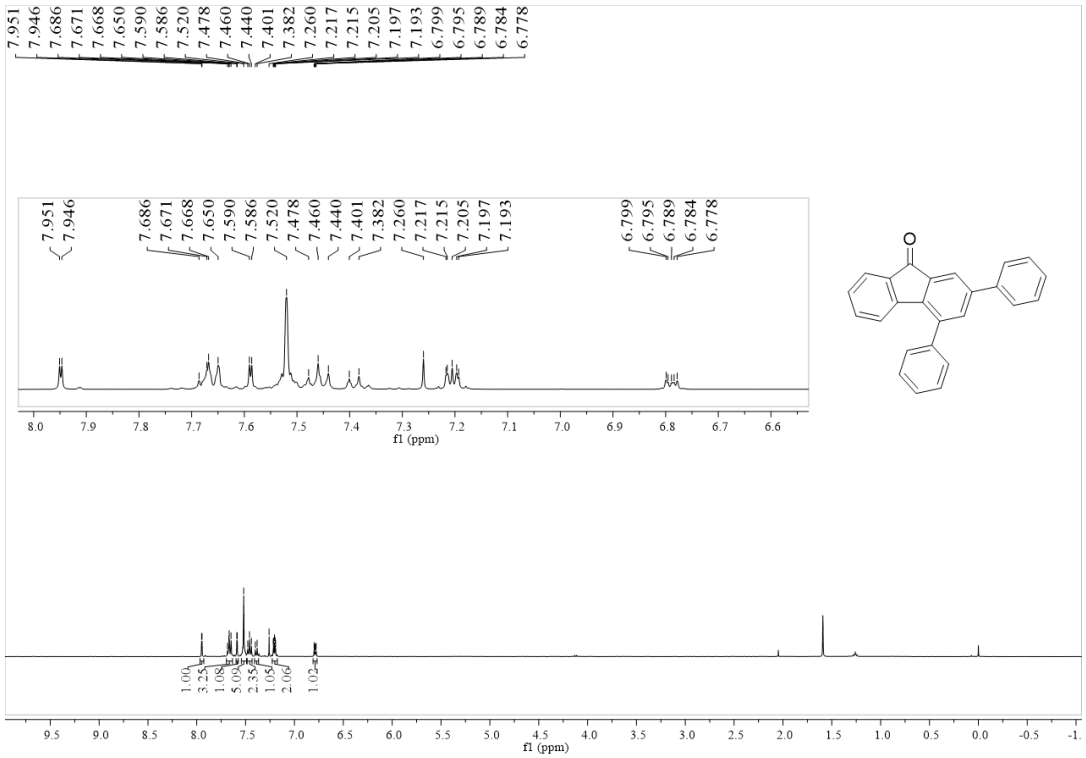


Fig. S91 ^{1}H NMR spectrum of **40** in $CDCl_3$

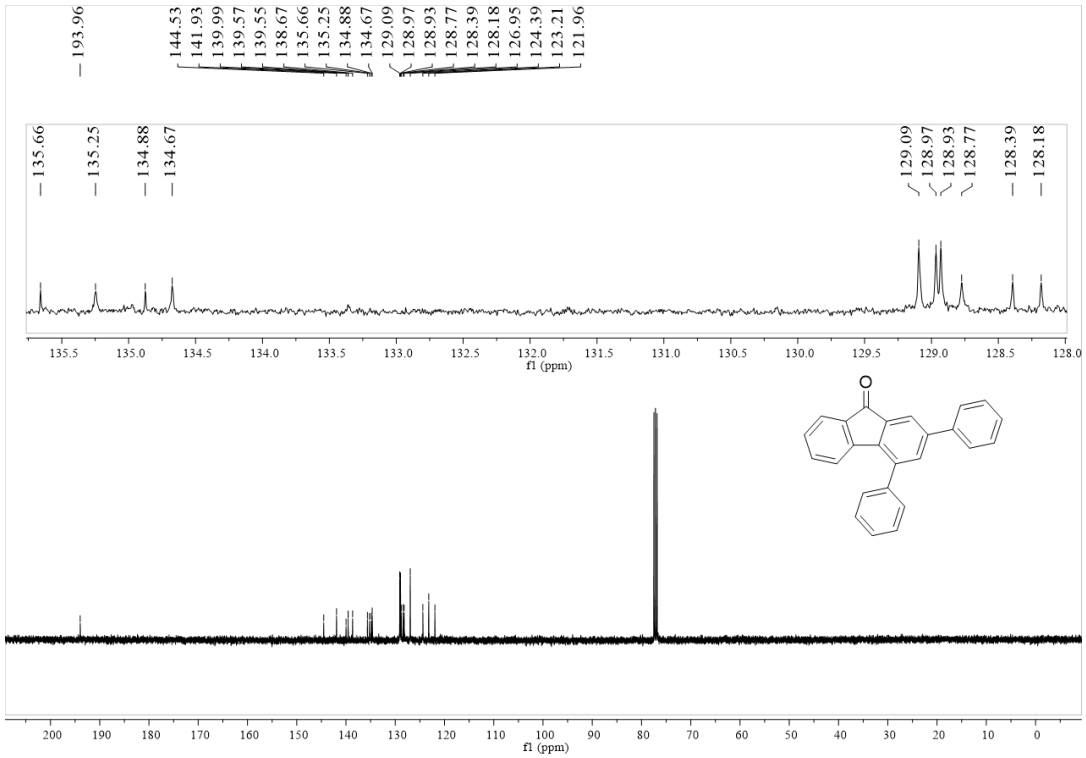


Fig. S92 ^{13}C NMR spectrum of **40** in $CDCl_3$

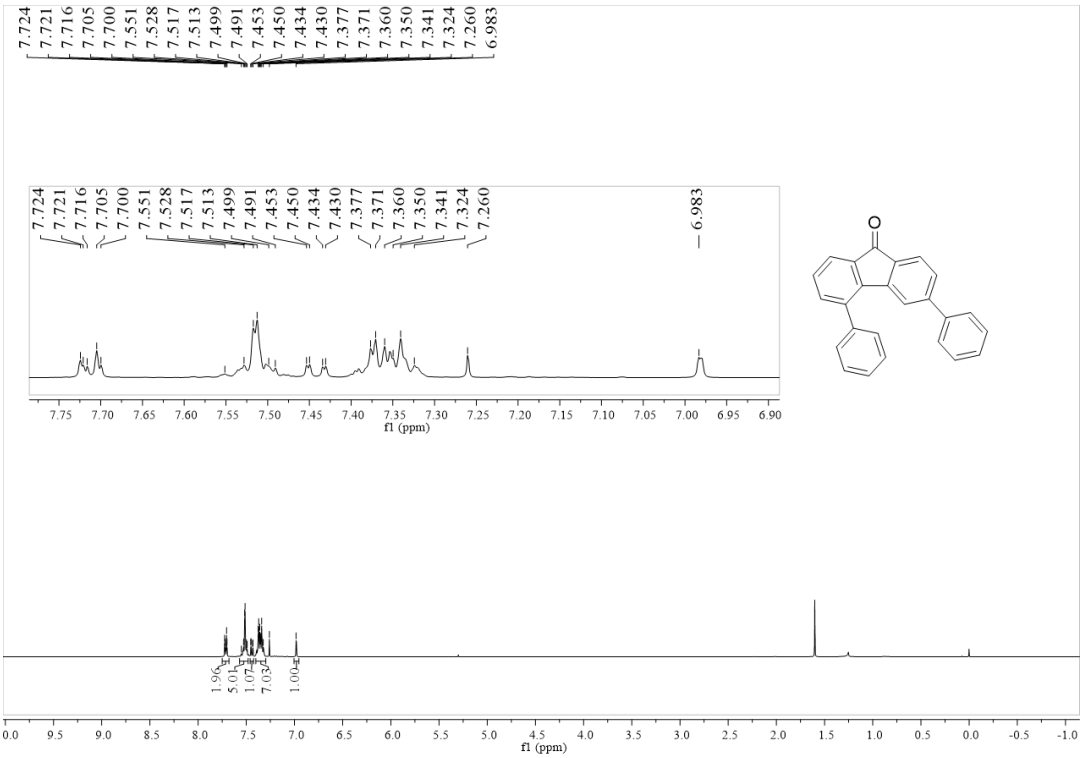


Fig. S93 ^{1}H NMR spectrum of **41** in $CDCl_3$

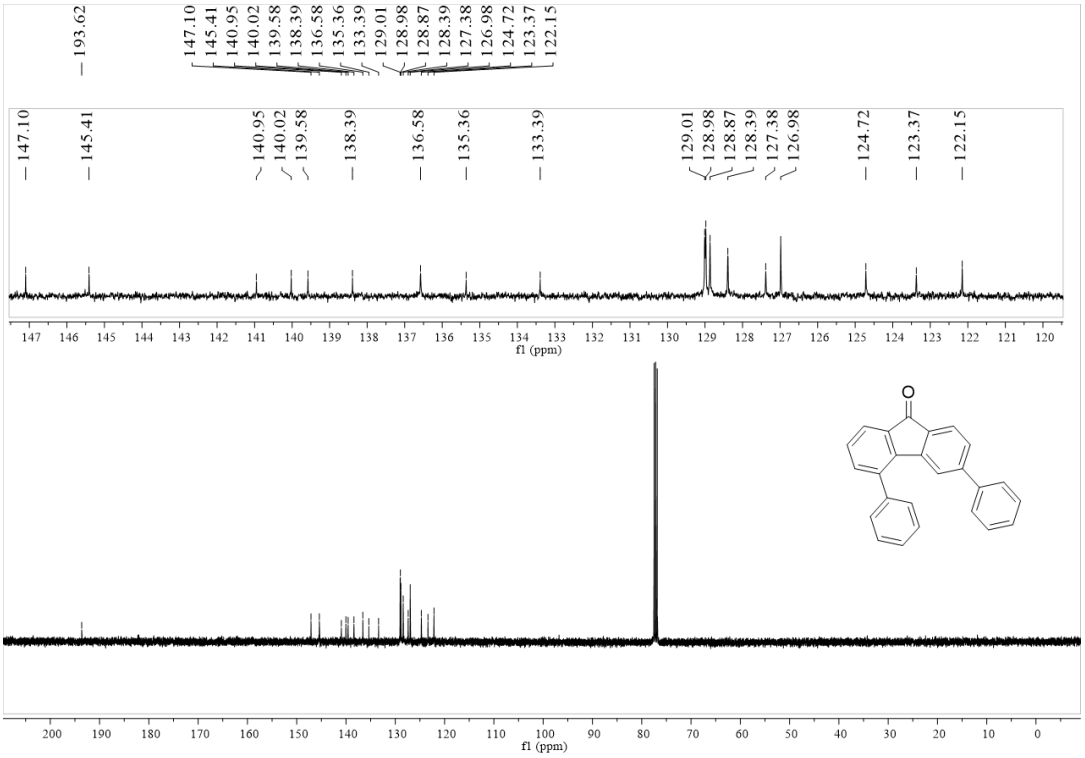


Fig. S94 ^{13}C NMR spectrum of **41** in $CDCl_3$

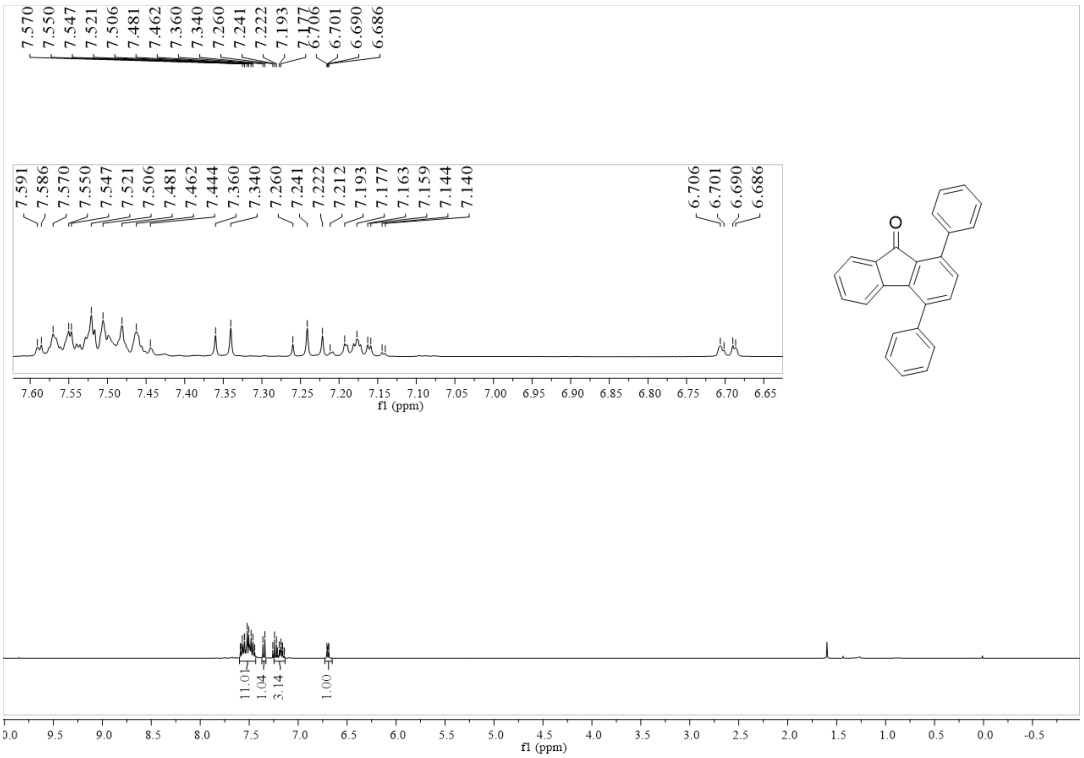


Fig. S95 ^{1}H NMR spectrum of **42** in $CDCl_3$

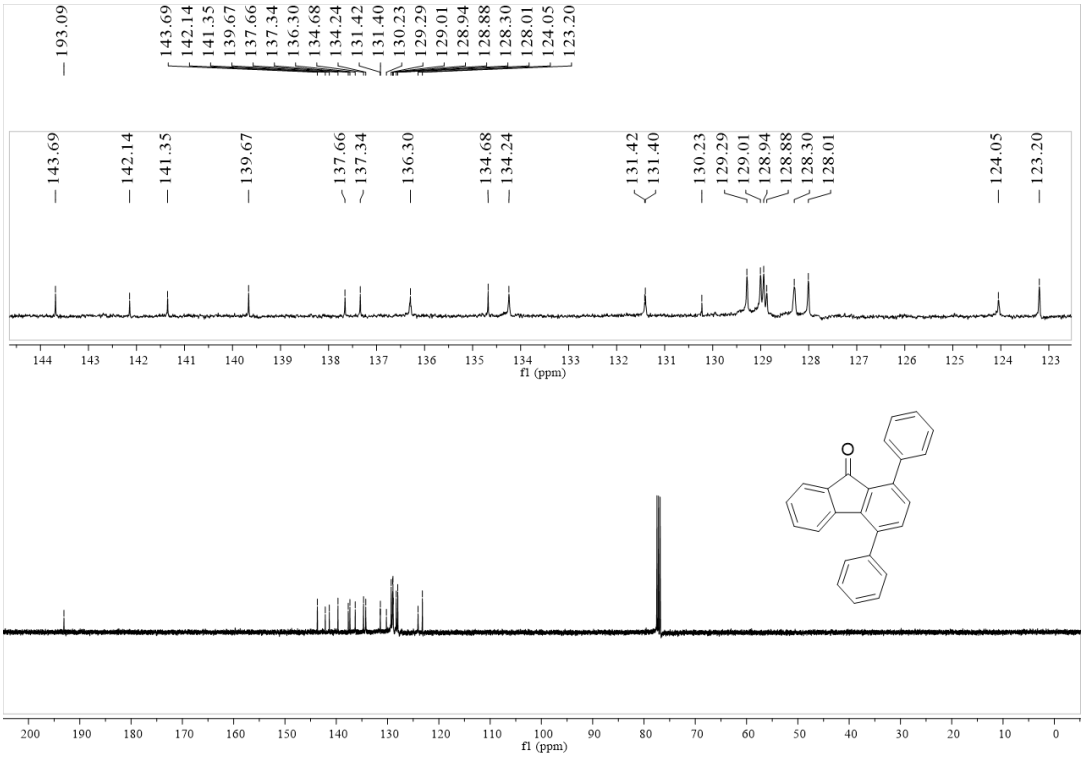


Fig. S96 ^{13}C NMR spectrum of **42** in $CDCl_3$

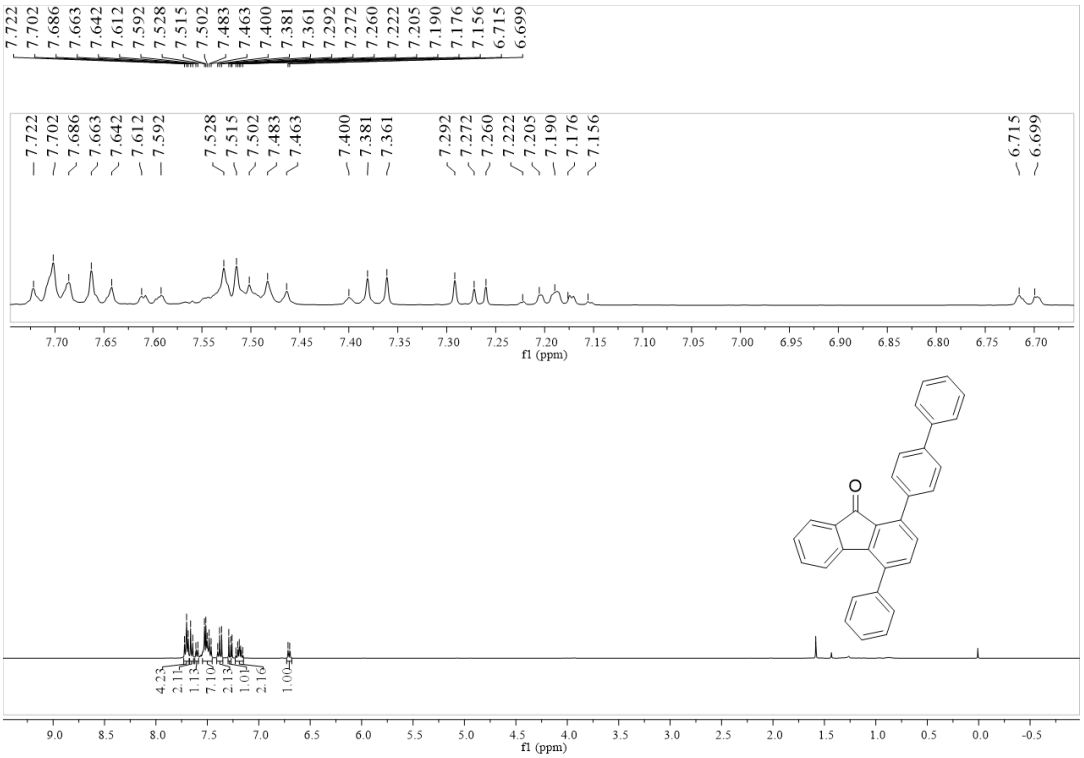


Fig. S97 ^{1}H NMR spectrum of **43** in $CDCl_3$

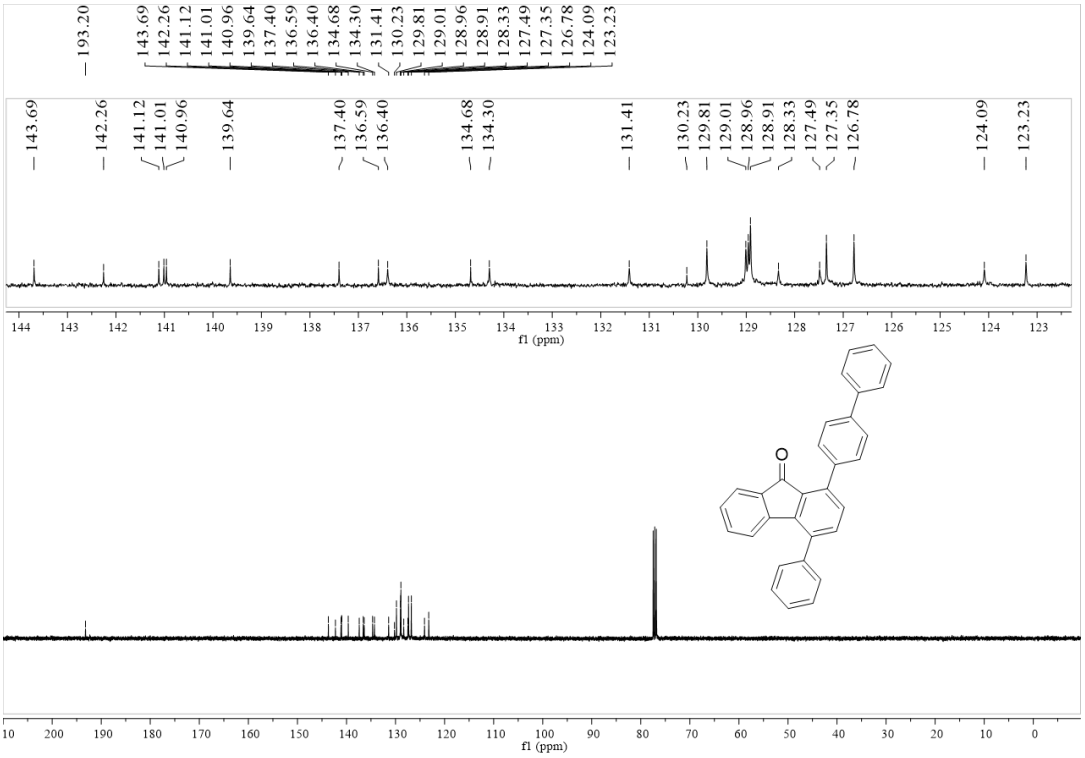


Fig. S98 ^{13}C NMR spectrum of **43** in $CDCl_3$

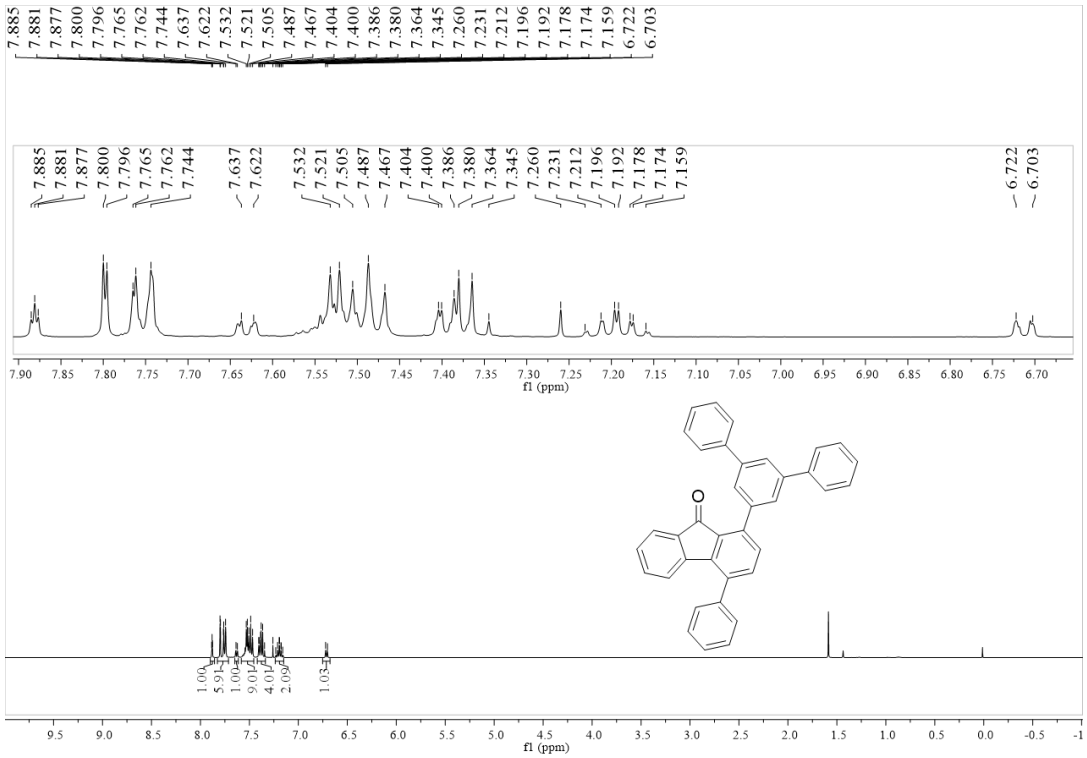


Fig. S99 ^{1}H NMR spectrum of **44** in $CDCl_3$

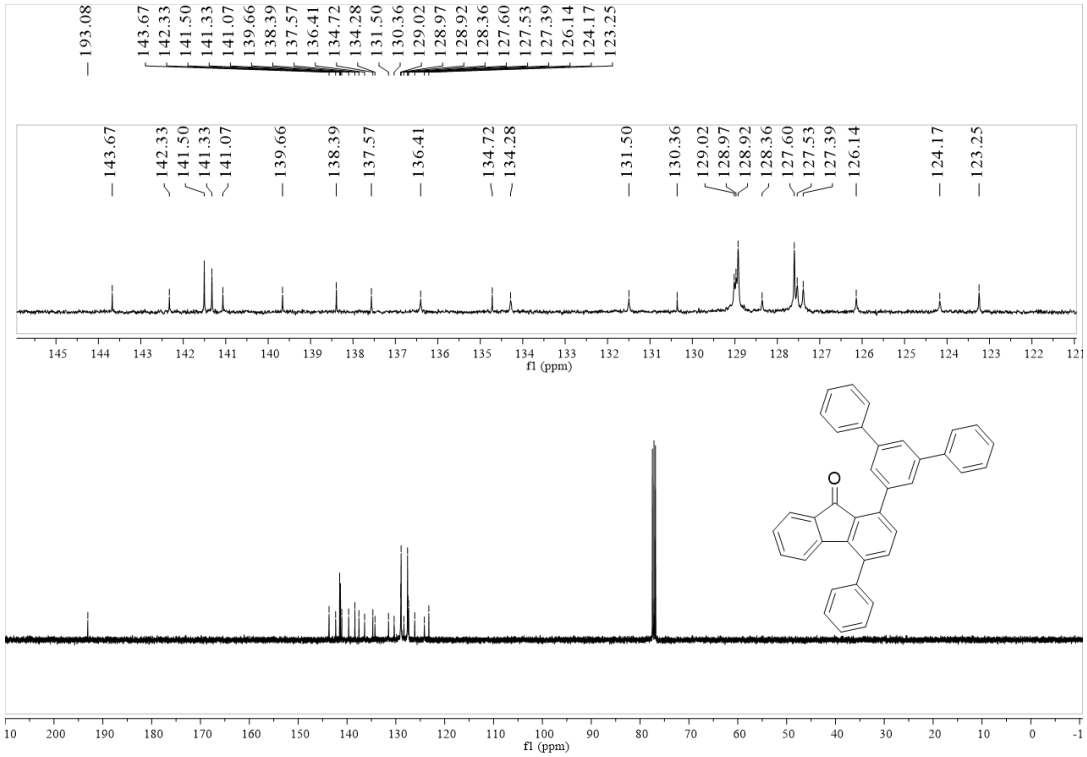


Fig. S100. ^{13}C NMR spectrum of **44** in $CDCl_3$

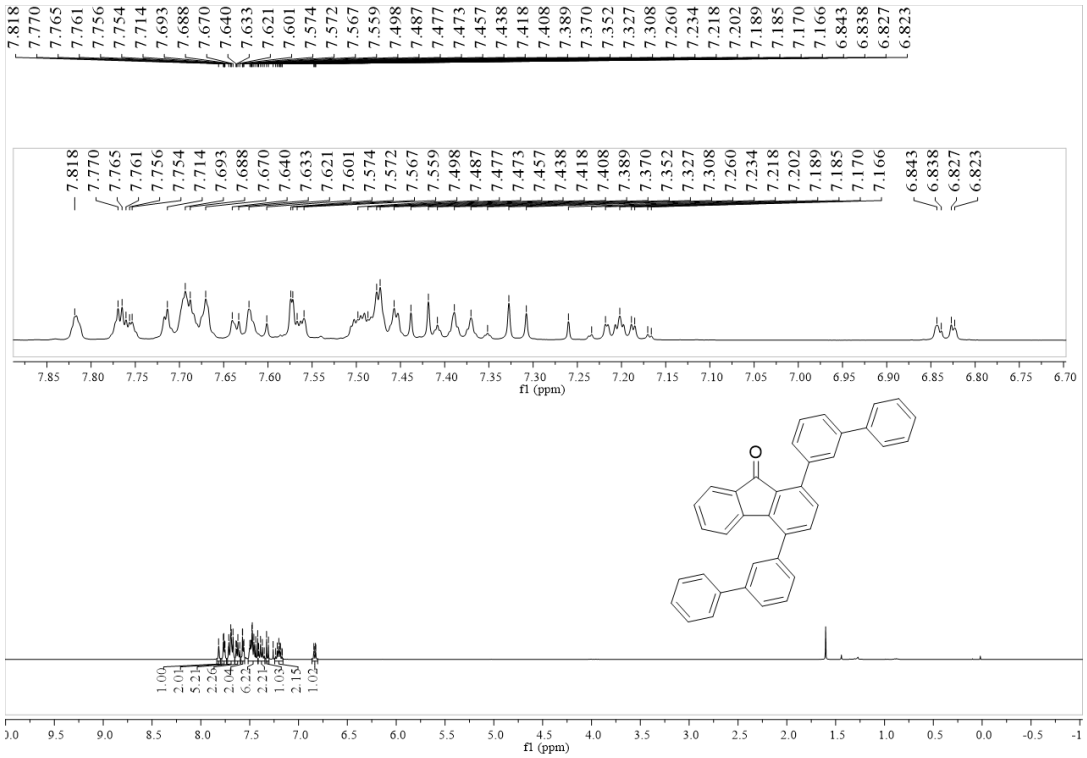


Fig. S101 ^{1}H NMR spectrum of **45** in $CDCl_3$

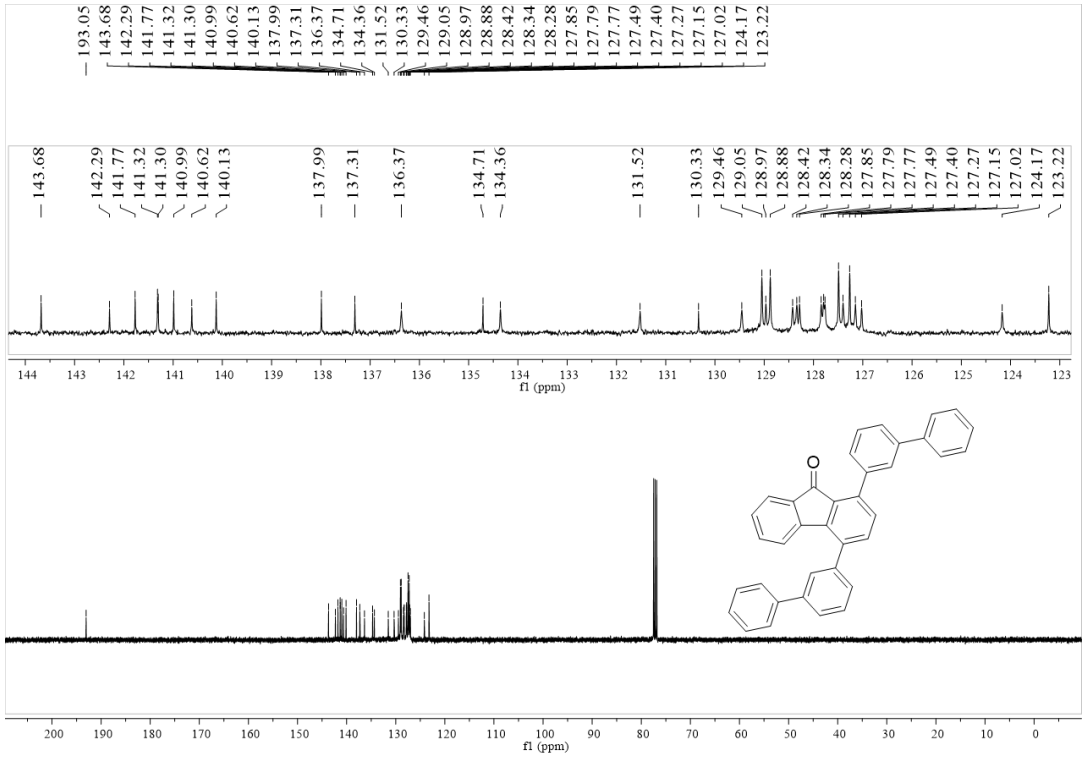


Fig. S102 ^{13}C NMR spectrum of **45** in $CDCl_3$

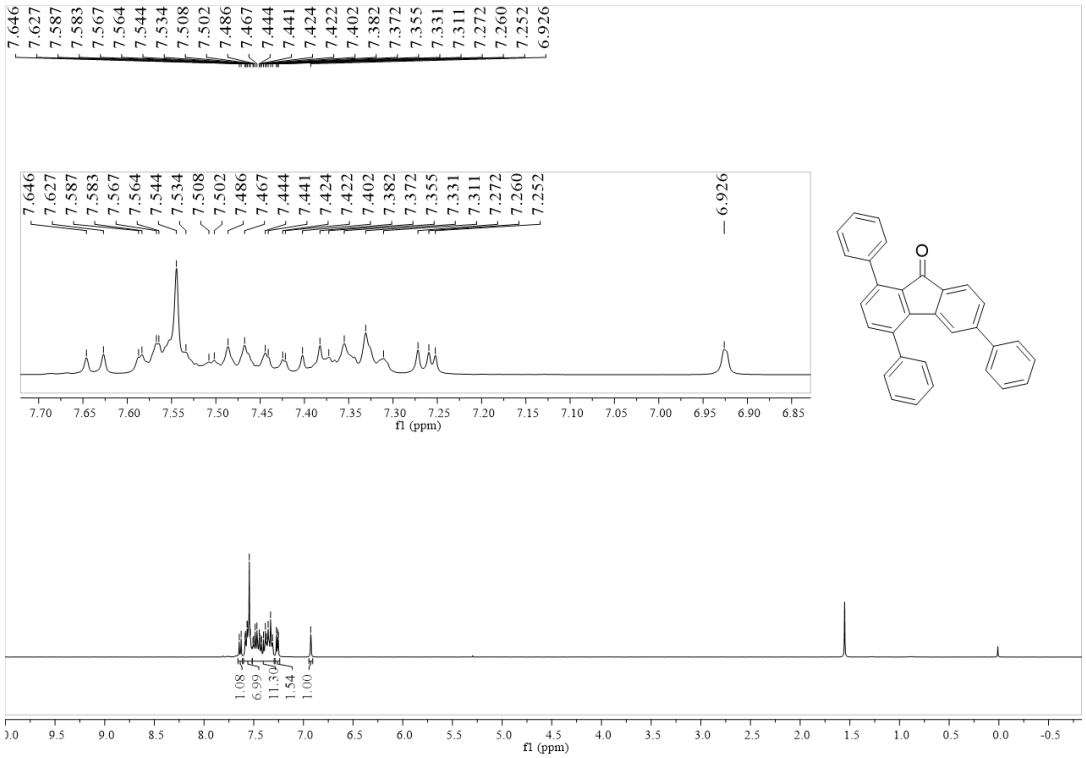


Fig. S103 ^{1}H NMR spectrum of **46** in $CDCl_3$

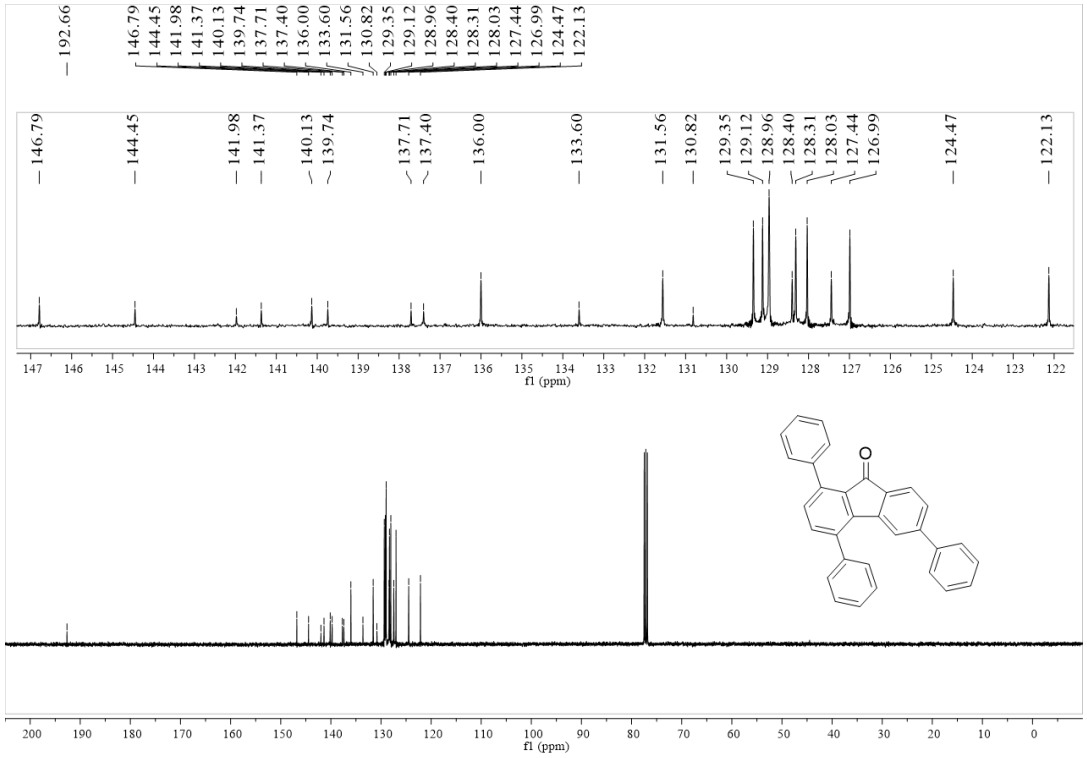


Fig. S104 ^{13}C NMR spectrum of **46** in $CDCl_3$

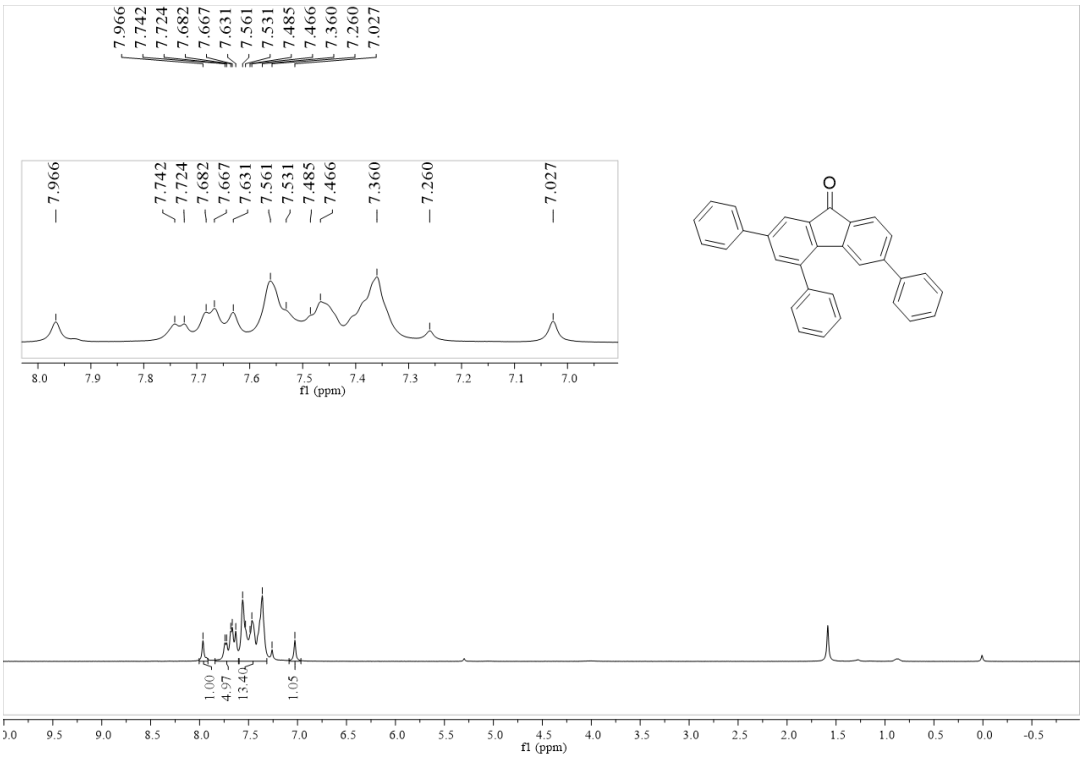


Fig. S105 ^{1}H NMR spectrum of **47** in $CDCl_3$

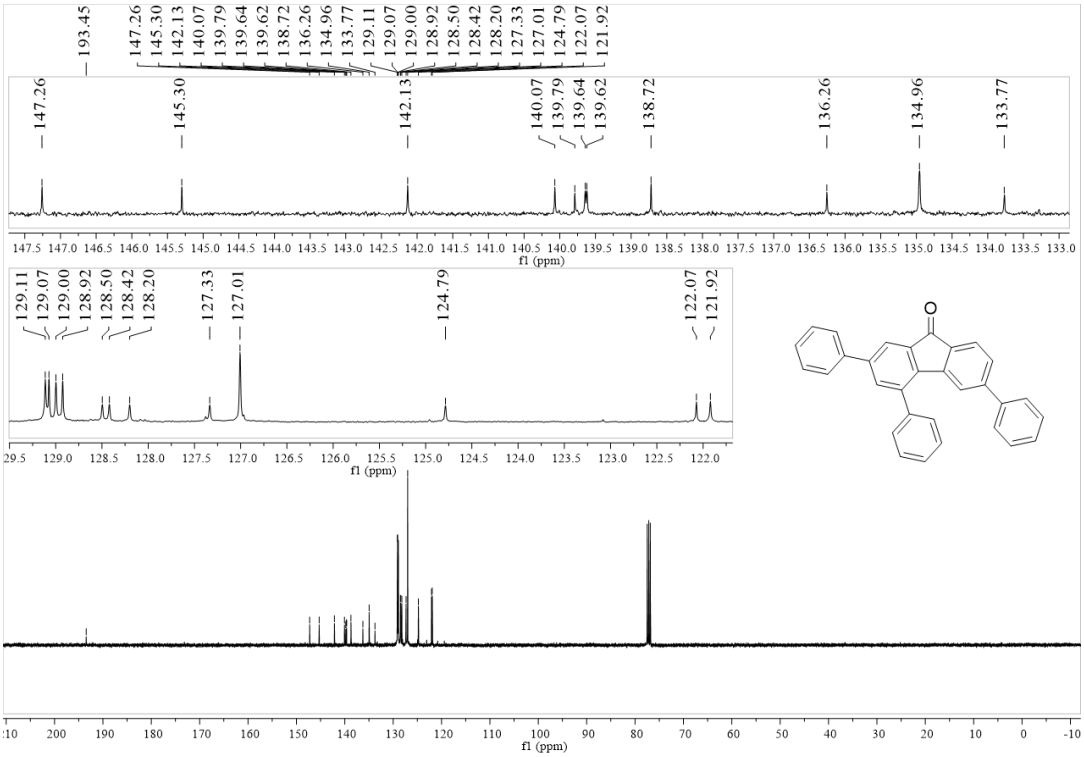


Fig. S106 ^{13}C NMR spectrum of **47** in $CDCl_3$

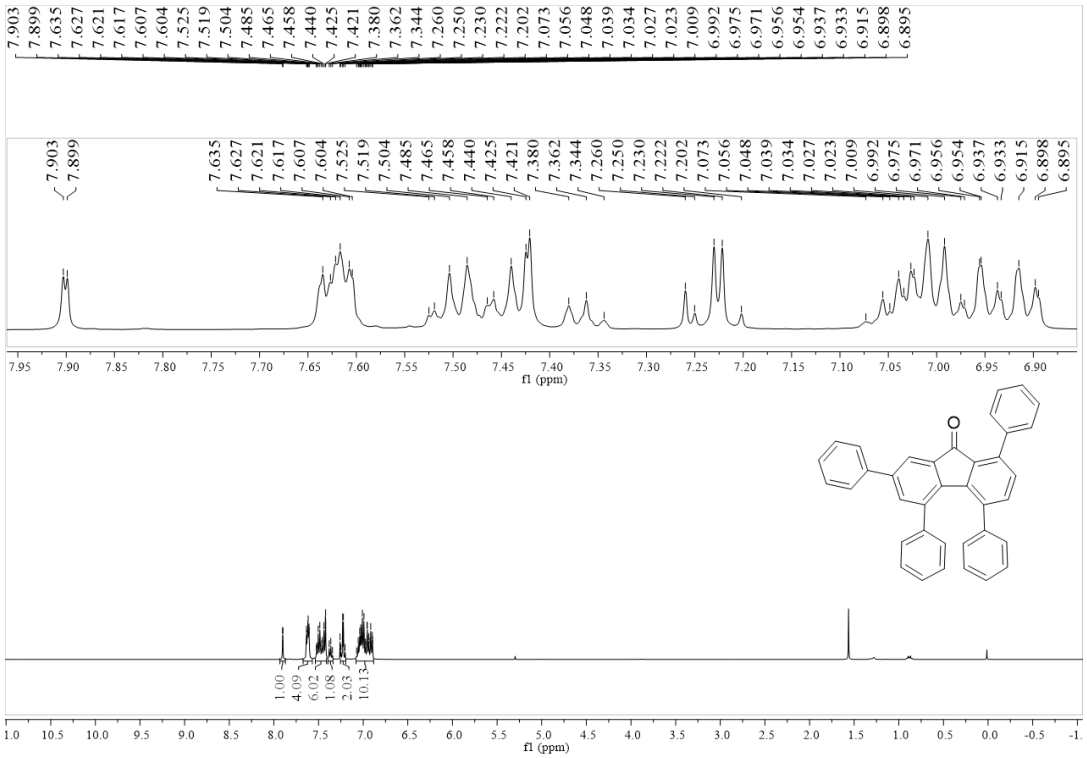


Fig. S107 ^{1}H NMR spectrum of **48** in $CDCl_3$

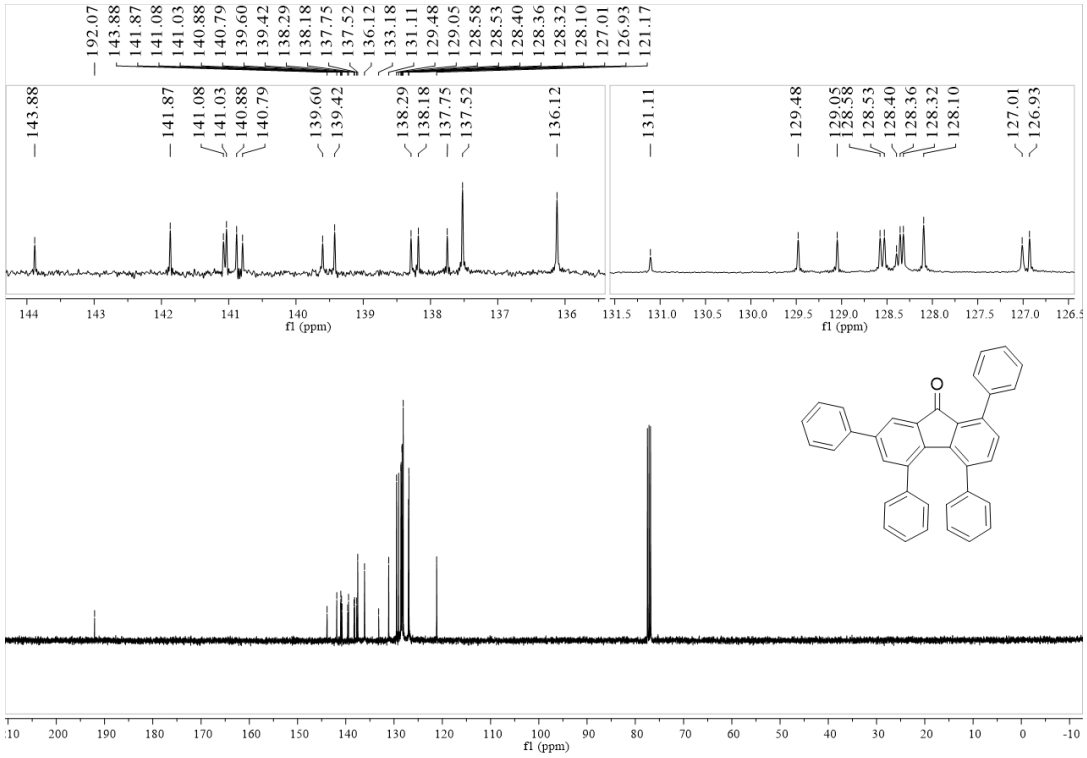


Fig. S108 ^{13}C NMR spectrum of **48** in $CDCl_3$

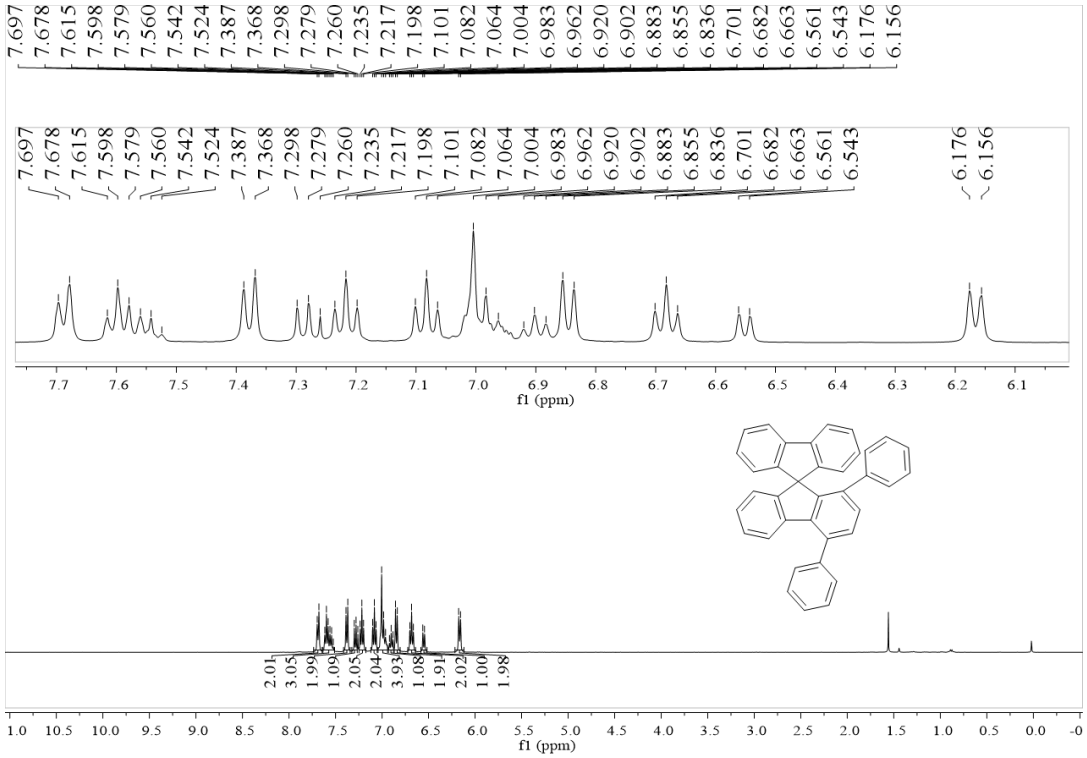


Fig. S109 ^{1}H NMR spectrum of 1,4-dp-SBF in $CDCl_3$

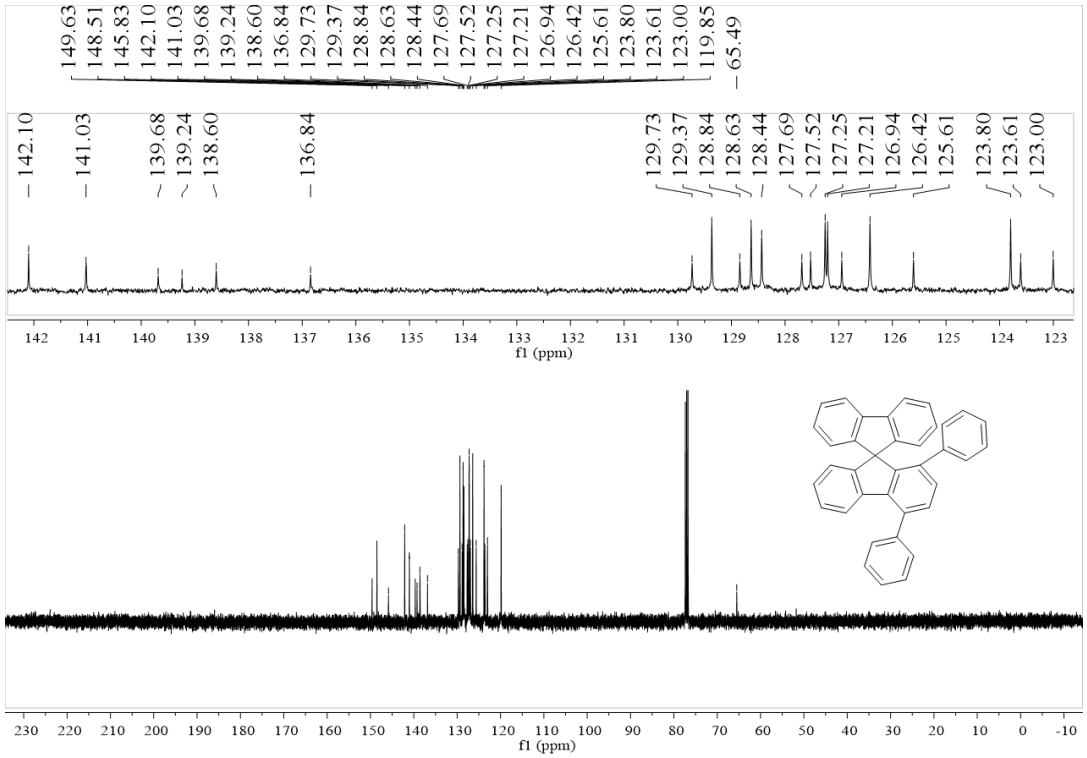


Fig. S110 ^{13}C NMR spectrum of 1,4-dp-SBF in $CDCl_3$

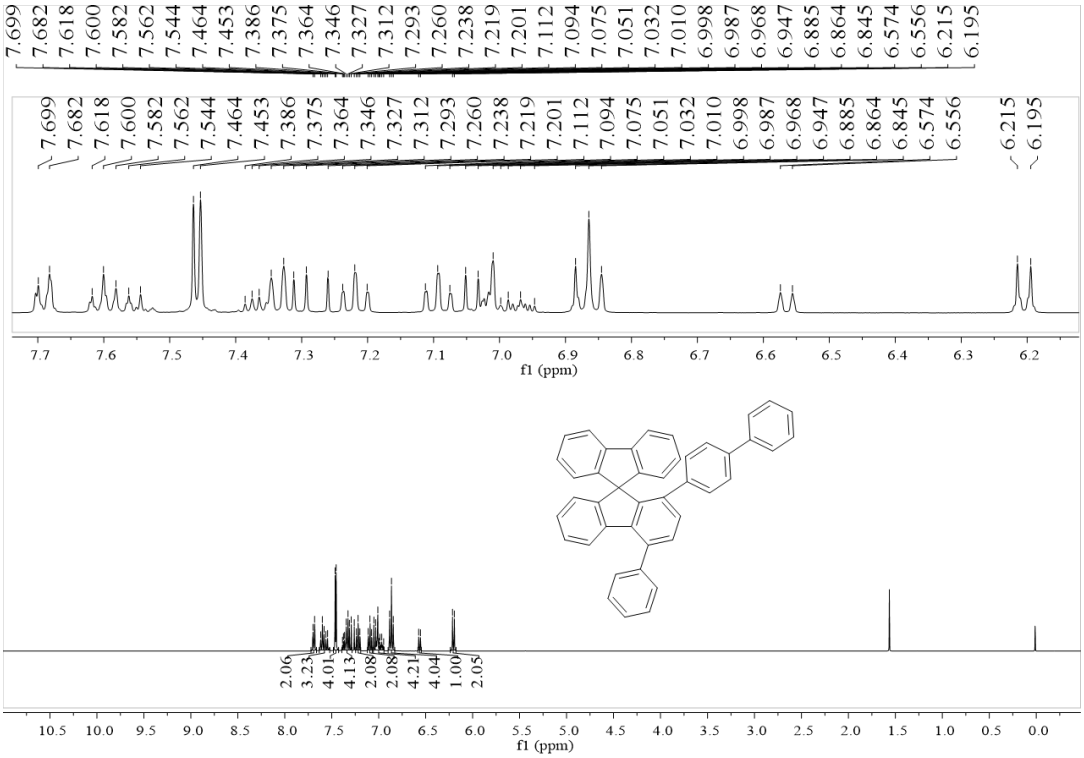


Fig. S111 ^{1}H NMR spectrum of 1-pbp-4-p-SBF in $CDCl_3$

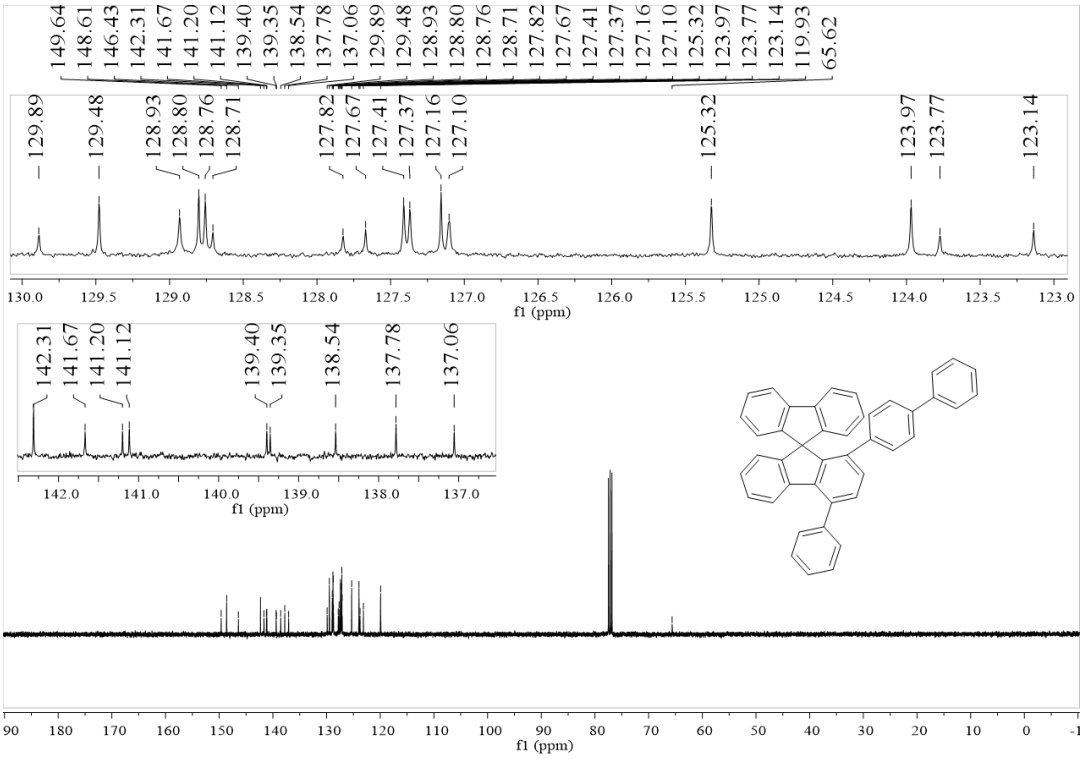


Fig. S112 ^{13}C NMR spectrum of 1-pbp-4-p-SBF in $CDCl_3$

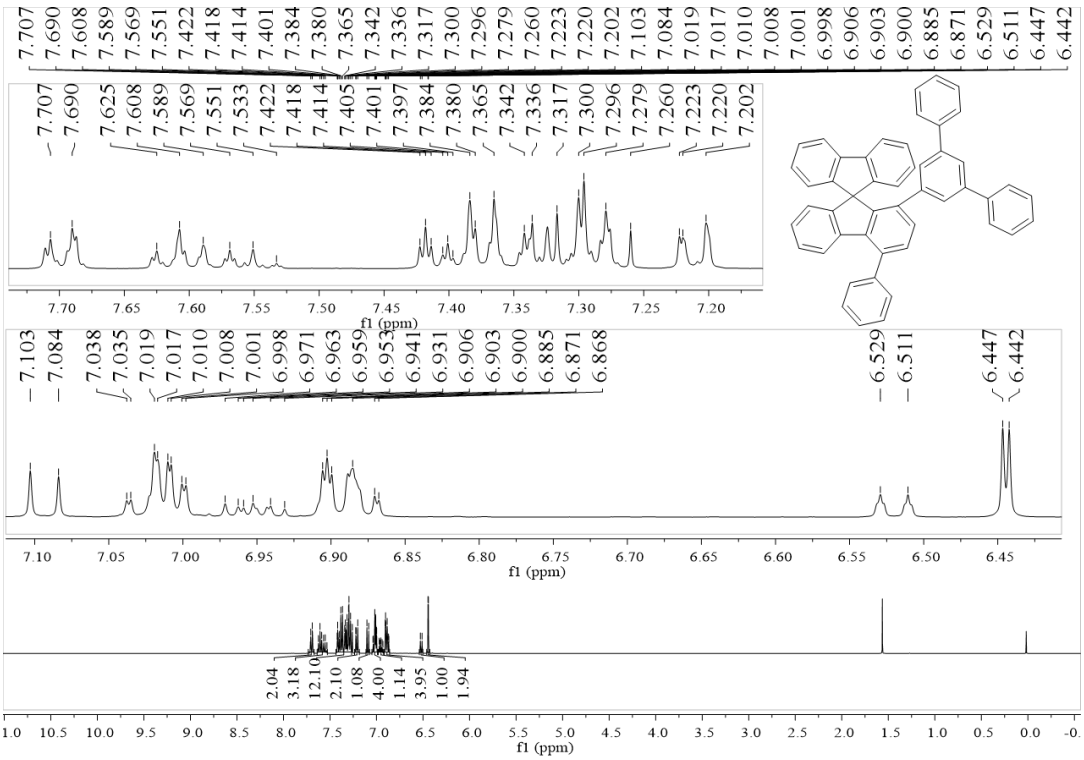


Fig. S113 ^{1}H NMR spectrum of 1-mtp-4-p-SBF in $CDCl_3$

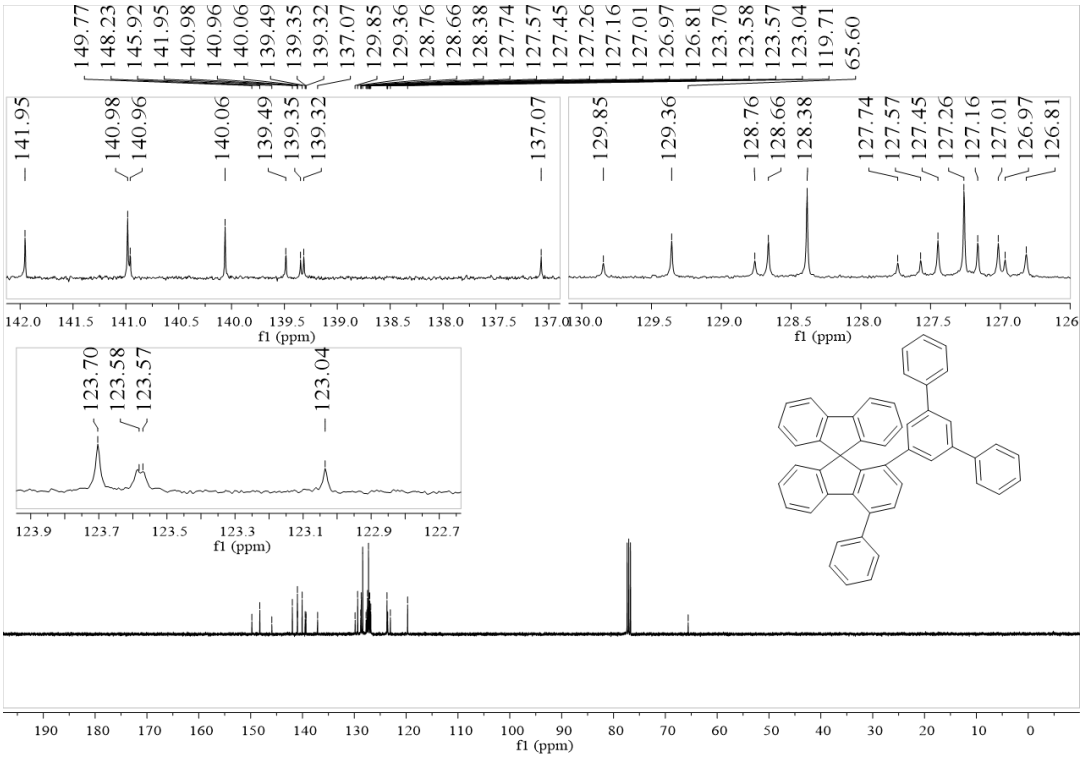


Fig. S114 ^{13}C NMR spectrum of 1-mtp-4-p-SBF in $CDCl_3$

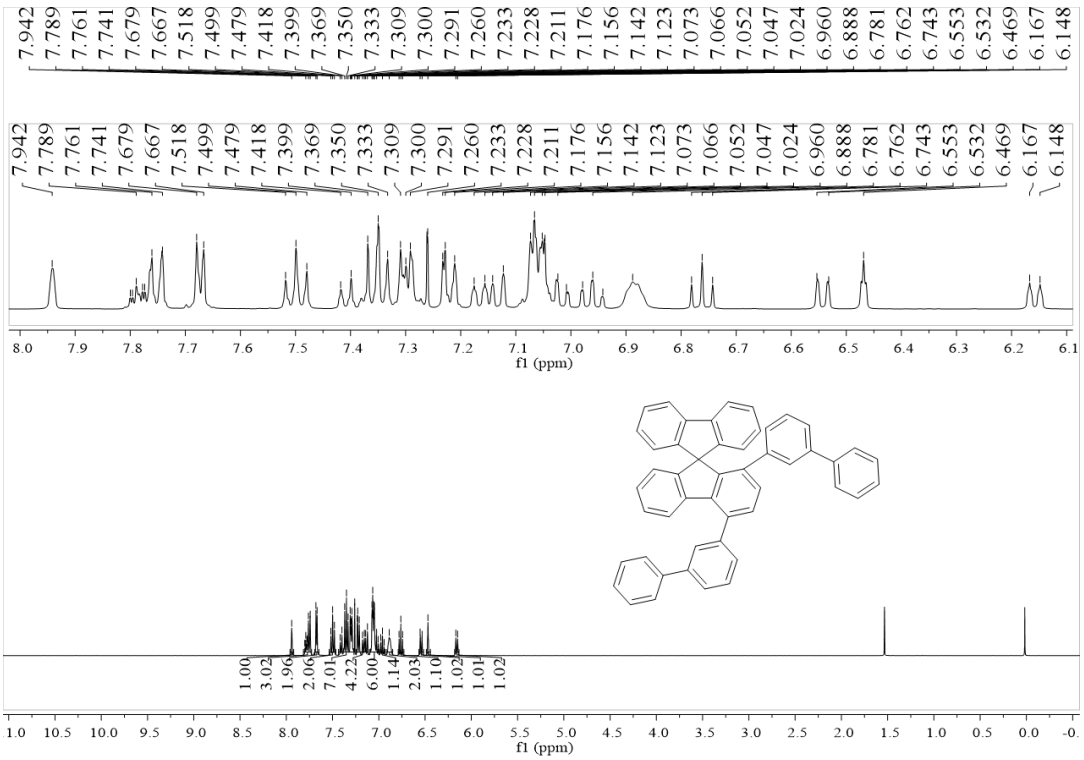


Fig. S115 ^{1}H NMR spectrum of 1,4-d(mbp)-SBF in $CDCl_3$

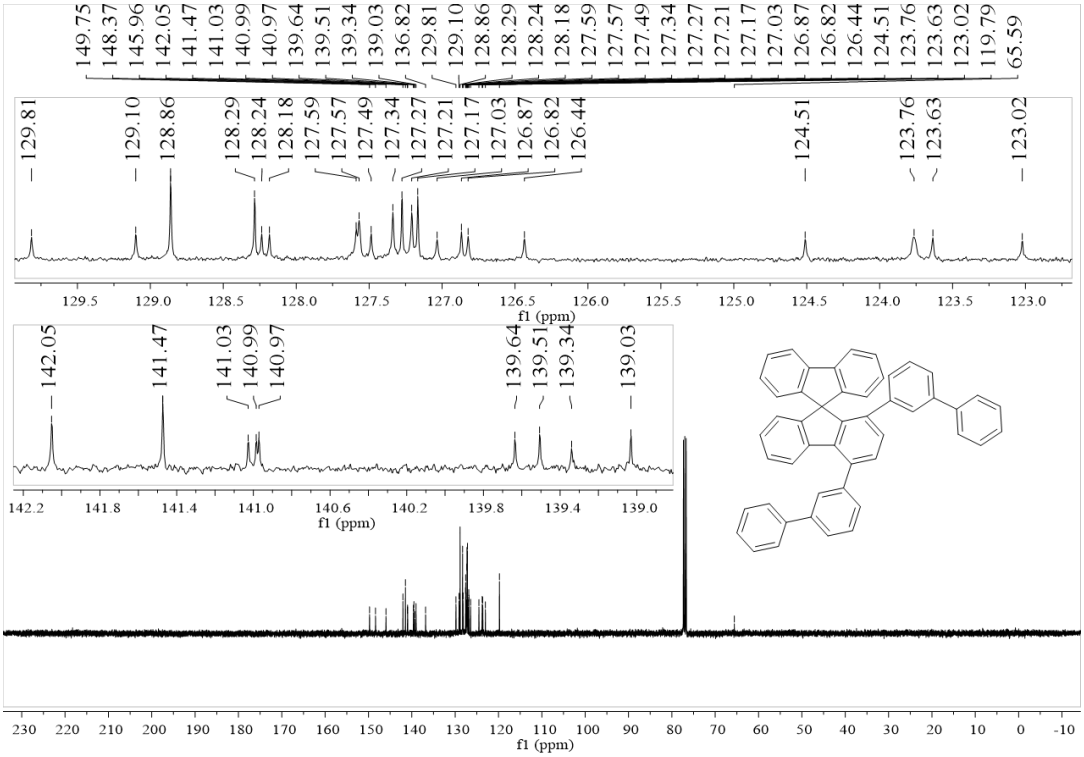


Fig. S116 ^{13}C NMR spectrum of 1,4-d(mbp)-SBF in $CDCl_3$