Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium-catalysed dual ring-opening [3 + 4] annulation of isatoic anhydrides with cyclic iodoniums to build tribenzo*[b,d,f]*azepines and mechanistic DFT study

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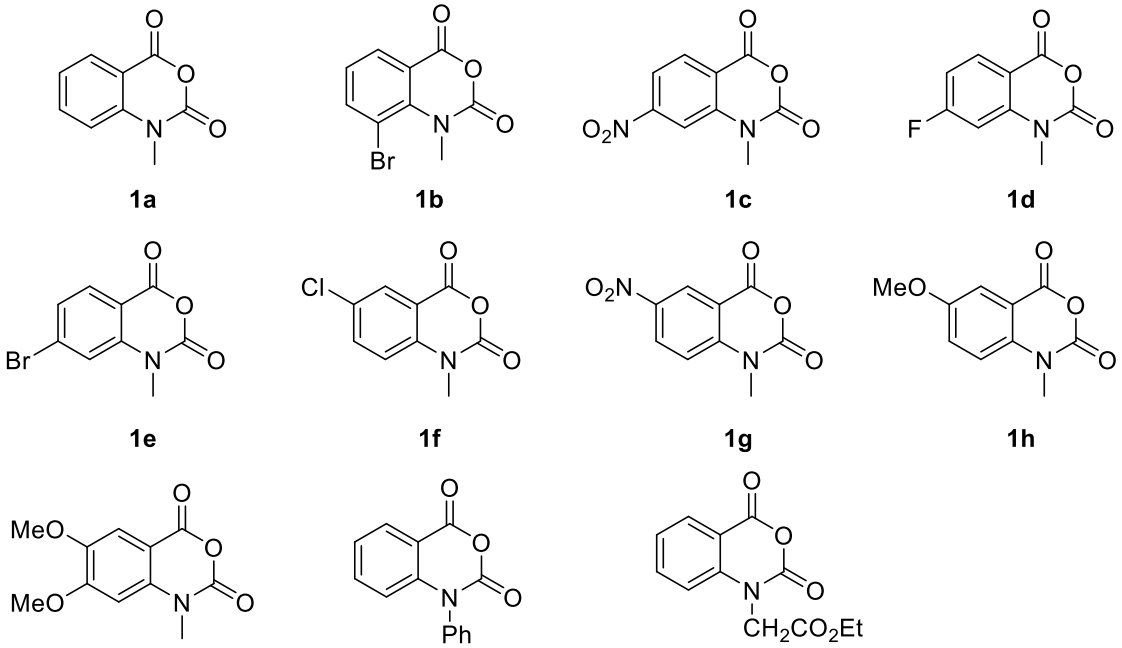
I. General remarks

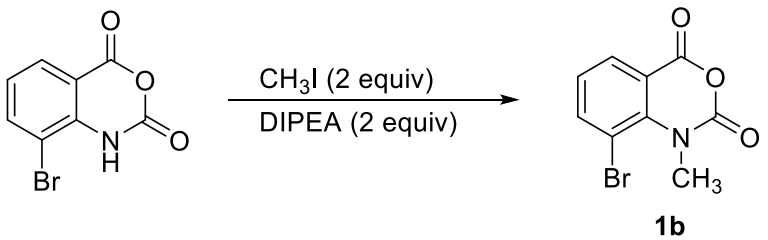
NMR spectra were obtained on a BRUKER Ascend500. The ^{1}H NMR (500 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (125 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HR-MS) were obtained with a BRUKER solanX 70 FT-MS (ESI^+). Melting points were determined with SGW® X-4 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Isatoic anhydride and palladium were purchased from Beijing InnoChem Science & Technology (China) Co., Ltd. TfOH and *m*-CPBA (purity of 75%) were purchased from Adamas-Beta Co., Ltd.

II. General procedure for the synthesis of substrate 1

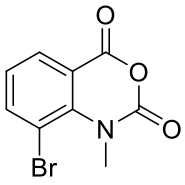


Compound **1a** was purchased from Beijing InnoChem Science & Technology (China) Co., Ltd. Compounds **1c** and **1h**;[1] **1d, 1f** and **1i**;[2] **1e**;[2] **1g**;[4] **1j**;[5] **1k**[5] were prepared according to the modified literature procedures. Compounds **1b** was prepared as follows:



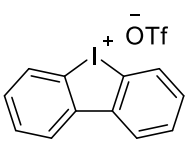
Compound **1b**: To a solution of 3-bromoisatoic anhydride (242 mg, 1 mmol) in *N*,*N*-dimethylacetamide (DMAc, 2 mL), diisopropylethylamine (DIPEA, 0.34 mL, 2 equiv) was added to stirred at room temperature for 10 min. Then methyl iodide (0.12 mL, 2 equiv) was added to react at 40 ℃ overnight. The solution was cooled to room temperature before pouring into ice water (5 mL). The resulting suspension was vigorously stirred for 1 h. The precipitated solid was collected by filtration, washing with ice water (5 mL) and *n*-hexane (5 mL), and dried to give **1b** as a yellow solid (138 mg, 54% yield).

8-bromo-1-methyl-2*H*-benzo[*d*][1,3]oxazine-2,4(1*H*)-dione (1b)

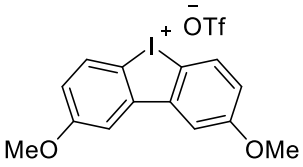


A yellow solid (138 mg, 54% yield). M.p.: 66.7–68.7 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.13 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.97 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 3.86 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 157.75, 148.71, 143.89, 141.76, 130.38, 125.82, 116.09, 108.45, 39.37 ppm. **HRMS (ESI) *m/z*:** calcd for $C_9H_7BrNO_3$ (M+H) 255.9609, found 255.9606.

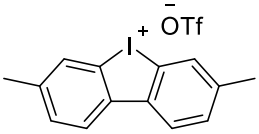
III. General procedure for the synthesis of the cyclic diaryliodonium salts



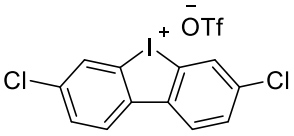
2a



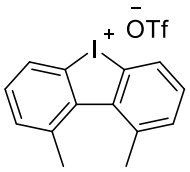
2b



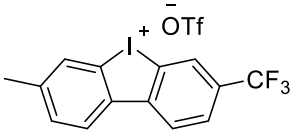
2c



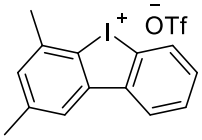
2d



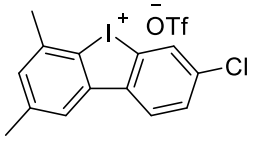
2e



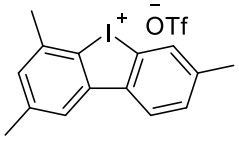
2f



2g



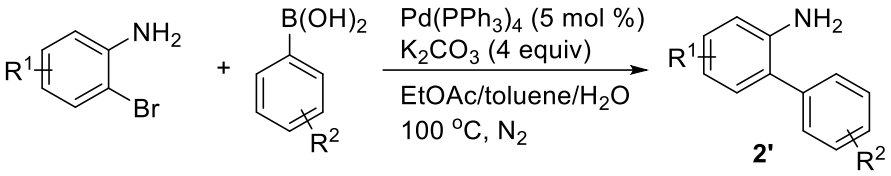
2h



2i

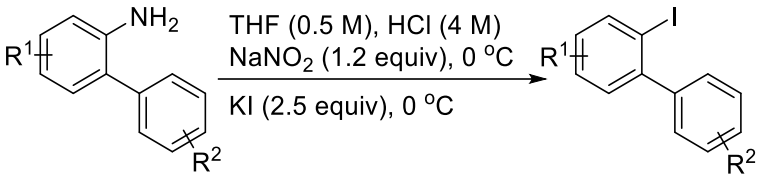
Compounds **2a-d** and **2q**;[7] **2d**;[7] **2g**[8] and **2h**[10]were prepared according to modified literature procedures. Compounds **2f** and **2i** are prepared as follows:

General procedure for the preparation of 2-aminobiaryl derivatives (2')



2-Bromonaniline derivatives (5 mmol, 1 equiv), arylboronic acids (7.5 mmol, 1.5 equiv), K_2CO_3 (2.76 g, 20 mmol, 4 equiv), $Pd(PPh_3)_4$ (288.9 mg, 5 mol %), EtOH (10 mL), toluene (20 mL) and H_2O (8 mL) were added to a round-bottom flask. The mixture was stirred at 100 ℃ for 16 h under nitrogen atmosphere. After being cooled down to room temperature, the mixture was extracted with EtOAc (3 × 30 mL). The combined organic phase was dried by Na_2SO_4, and filtered. After removal of volatile components from the filtrate, the resulting crude products was purified by column chromatography on a silica gel to afford the desired 2-aminobiaryl derivatives (**2'**).

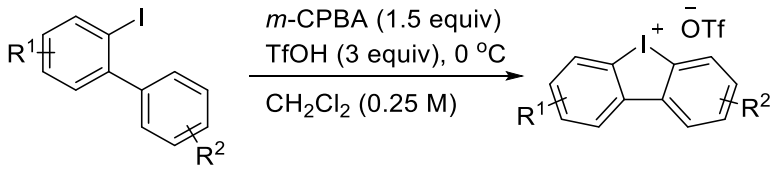
General procedure for the preparation of 2-iodobiaryl (2'') from 2-aminobiaryl



2' **2''**

To a solution of **2'** (5 mmol, 1 equiv) in THF (10 mL) was added 4 M aqueous HCl (10 mL). After cooled down to 0 ℃ in an ice water bath, an aqueous solution of $NaNO_2$ (414 mg, 6 mmol, 1.2 equiv) in water (6 mL) was added dropwise. After 20 min stirring under the same temperature, a solution of KI (2.08 g, 12.5 mmol, 2.5 equiv) in H_2O (10 mL) was added. The reaction mixture was stirred at 0 ℃ for 10 min, then removed the ice water bath. The reaction was stirred overnight at room temperature before 1 M aqueous $Na_2S_2O_3$ was added until the color of the mixture didn't change. The phases were separated, and the aqueous phase was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with H_2O (3 × 10 mL), dried over anhydrous Na_2SO_4, concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to afford the desired 2-iodobiaryl derivatives (**2''**).

General procedure of the preparation of cyclic diaryliodonium salts (2)

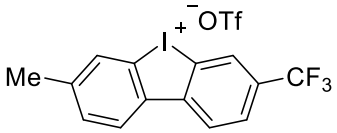


2'' **2**

To a stirred solution of **2''** (5 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was added *m*-CPBA (1.73 g, 75%, 7.5 mmol, 1.5 equiv), and TfOH (3 equiv) at ice-bath. The solution was stirred for 3 h at room temperature before CH_2Cl_2 was removed by rotary evaporation. To the residue was added Et_2O (20 mL), and the resulting mixture was stirred for 20 min. The solid precipitate was collected by vacuum

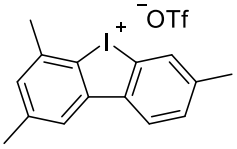
filtration, washed with Et_2O for three times, and dried under vacuum to afford cyclic diaryliodonium salt derivatives (**2**).

3-methyl-7-(trifluoromethyl)dibenzo[*b,d*]iodol-5-ium triflate (2f)



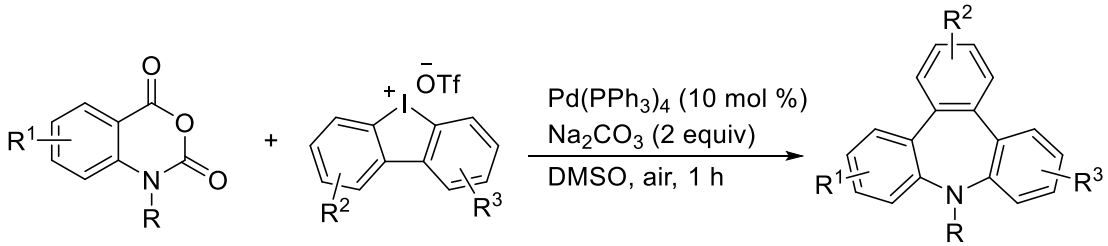
A white solid (1100 mg, 43% yield). M.p.: > 240 ℃. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 8.62 (d, *J* = 8.0 Hz, 1H), 8.50–8.48 (m, 2H), 8.20 (d, *J* = 7.5 Hz, 2H), 8.01 (s, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 2.52 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 145.65, 143.01, 137.71, 131.91, 130.34, 129.61 (q, $J_{C\text{-}F}$ = 32.6 Hz), 127.65, 127.49 (q, $J_{C\text{-}F}$ = 4.0 Hz), 127.26, 123.36 (q, $J_{C\text{-}F}$ = 270.9 Hz), 123.02, 121.74, 119.40, 21.33 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{14}H_9F_3I^+$ ([M−OTf$^-$]$^+$) 360.9696, found 360.9697.

2,4,7-trimethyldibenzo[b,d]iodol-5-ium triflate (2i)



A white solid (1505 mg, 64% yield). M.p.: > 240 ℃. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 8.25–8.21 (m, 1H), 8.06–7.98 (m, 2H), 7.64 (s, 1H), 7.34–7.32 (m, 1H), 2.61–2.59 (m, 3H), 2.48 (s, 3H), 2.44 (d, *J* = 3.5 Hz) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 142.05, 141.62, 141.20, 139.87, 138.81, 131.92, 131.85, 130.81, 127.17, 124.71, 122.12, 121.86, 24.70, 21.28, 20.60 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{15}H_{14}I^+$ ([M−OTf$^-$]$^+$) 321.0135, found 321.0137.

IV. General procedure for the synthesis of tribenzo[*b,d,f*]azepines



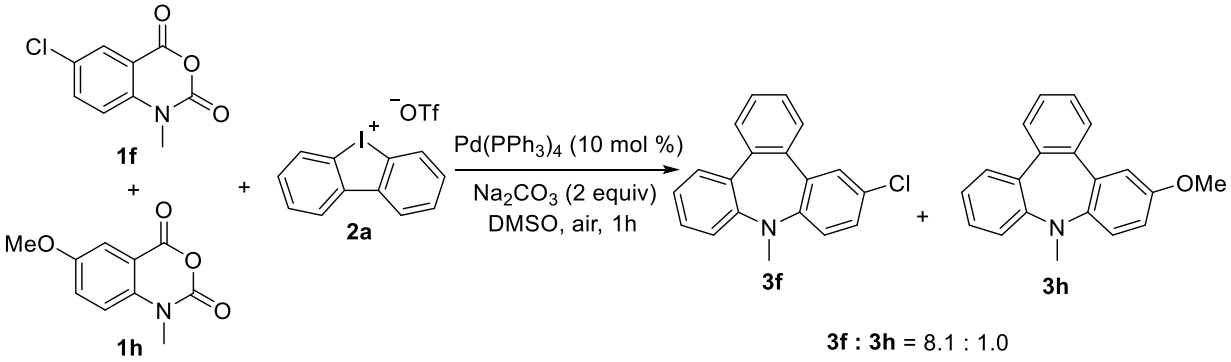
1 **2** **3** and **4**

To a dry Schlenk tube containing a magnetic stir bar was added **1** (0.3 mmol), cyclic diaryliodonium salts **2** (0.2 mmol), Na_2CO_3 (42.4 mg, 0.4 mmol, 2 equiv), $Pd(PPh_3)_4$ (23.1 mg, 10 mol %) and DMSO (2 mL). The reaction mixture was stirred at 140 ℃ for 1 h under air before it was cooled to room temperature. The mixture was purified by a silica gel column (200-300 mesh), eluting with petroleum ether/EtOAc (100/1→50/1, v/v) to afford products **3** and **4**.

Scale-up reaction: To a dry Schlenk tube containing a magnetic stir bar was added **1a** (1.5 mmol), cyclic diaryliodonium salts **2a** (1 mmol), Na_2CO_3 (212.0 mg, 2 mmol, 2 equiv), $Pd(PPh_3)_4$ (115.6 mg, 10 mol %) and DMSO (10 mL). The reaction mixture was stirred at 140 ℃ for 3 h under air before it

was cooled to room temperature. The mixture was purified by a silica gel column (200-300 mesh), eluting with petroleum ether/EtOAc (100/1, v/v) to afford products **3a** (224 mg, 87%).

V. Mechanistic studies



To a dry Schlenk tube with a magnetic stir bar was charged with **1h** (0.15 mmol, 1.5 equiv), **1f** (0.15 mmol, 1.5 equiv), **2a** (43 mg, 0.1 mmol, 1 equiv), Na_2CO_3 (21.2 mg,0.2 mmol, 2 equiv), $Pd(PPh_3)_4$ (11.6 mg, 10 mol %) and DMSO (1 mL). The reaction mixture was stirred at 140 ℃ for 1 h under air before it was cooled to room temperature. And the mixture was purified by a silica gel column (200-300 mesh), eluting with petroleum ether/EtOAc (80/1, v/v) to afford a mixture of **3f** and **3h**. The ratio of **3f**/**3h** was determined to be 8.1/1.0 by ^{1}H NMR (see below).

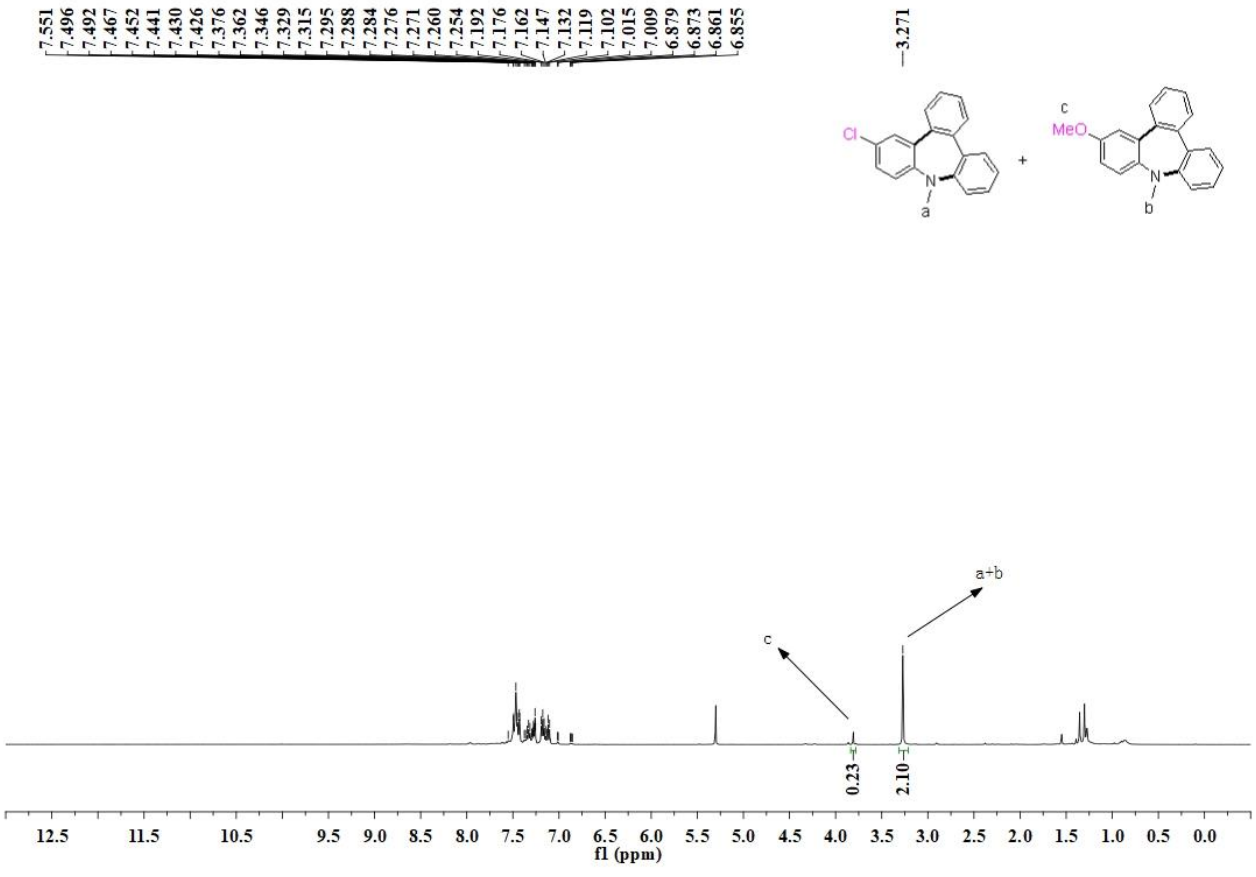
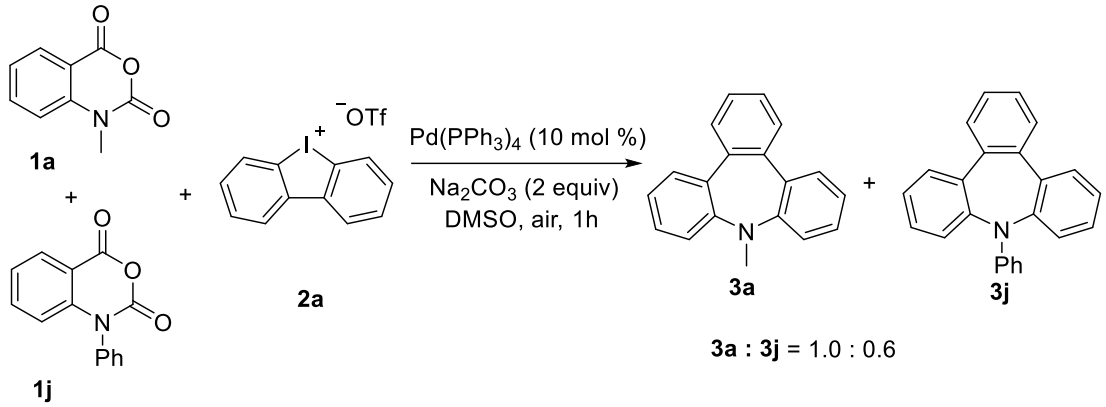


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) of the mixture of **3h** and **3f**



To a dry Schlenk tube with a magnetic stir bar was charged with **1a** (0.15 mmol, 1.5 equiv), **1j** (0.15 mmol, 1.5 equiv), **2a** (43 mg, 0.1 mmol, 1 equiv), Na_2CO_3 (21.2 mg, 0.2 mmol, 2 equiv), $Pd(PPh_3)_4$ (11.6 mg, 10 mol %) and DMSO (1 mL). The reaction mixture was stirred at 140 ℃ for 1 h under air before it was cooled to room temperature. And the mixture was purified by a silica gel column (200-300 mesh), eluting with petroleum ether/EtOAc (60/1, v/v) to afford a mixture of **3a** and **3j**. The ratio of **3a**/**3j** was determined to be 1.0/0.6 by ^{1}H NMR (see below).

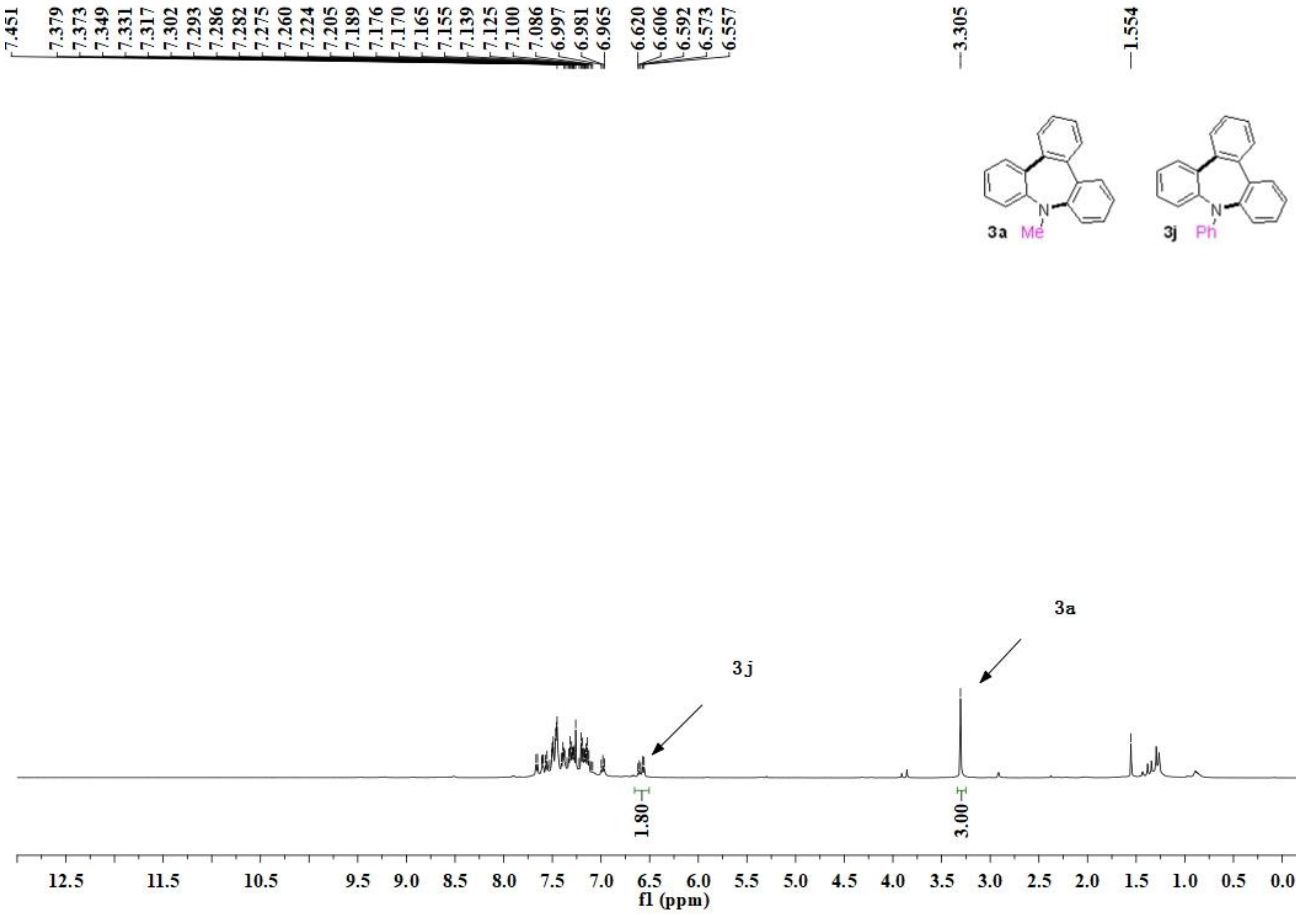


Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) of the mixture of **3a** and **3j**

VI. X-ray Crystallographic Analysis

General Crystal Growing Conditions of **4j**: X-ray quality single crystals of **4j** was grown from the co-solvent of DCM, MeOH, EA and petroleum ether (5:1:1:1, v/v) at room temperature by slow evaporation for three days.

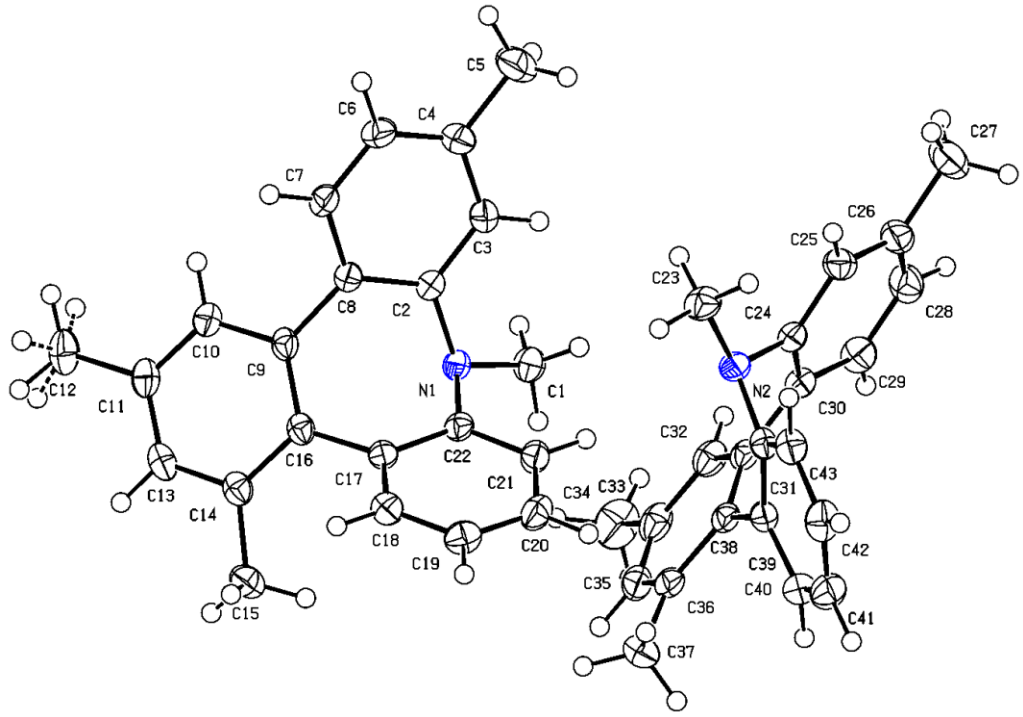


Figure S3 The molecular structure of **4j** (CCDC 2190754). Thermal ellipsoids are shown at the 50% probability level.

Table S1 **Crystal data and structure refinement for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq.**

Identification code	mo_20220424LWX_201321_HLY_674_ZCS_0m_sq
Empirical formula	$C_{88}H_{84}N_4$
Formula weight	1197.59
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	8.4028(5)
b/Å	11.9177(8)

c/Å	18.7199(11)
α/°	78.497(3)
β/°	86.338(2)
γ/°	74.483(2)
Volume/Å^3	1769.93(19)
Z	1
ρ_{calc}g/cm^3	1.124
μ/mm^{-1}	0.065
F(000)	640.0
Crystal size/mm^3	0.2 × 0.1 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.864 to 54.932
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 15, -24 ≤ l ≤ 24
Reflections collected	38325
Independent reflections	8076 [R_{int} = 0.0665, R_{sigma} = 0.0473]
Data/restraints/parameters	8076/3/436
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0491, wR_2 = 0.1269
Final R indexes [all data]	R_1 = 0.0685, wR_2 = 0.1402
Largest diff. peak/hole / e Å^{-3}	0.27/-0.25

Table S2 **Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
N2	94.7(15)	5725.8(10)	2682.1(7)	24.5(3)
N1	4519.4(15)	7413.4(10)	2352.0(6)	22.9(3)
C22	4007.2(17)	7499.0(12)	1620.2(8)	22.2(3)
C17	4619.5(17)	8236.3(12)	1043.9(8)	22.9(3)
C38	2665.3(17)	3846.6(12)	2242.0(8)	24.4(3)

Table S2 **Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
C39	1008.5(17)	4251.5(13)	1898.4(8)	24.4(3)
C14	7344.5(18)	8760.7(12)	719.5(8)	26.1(3)
C16	5917.7(17)	8817.7(12)	1171.4(8)	22.8(3)
C9	5736.7(17)	9440.1(12)	1748.4(8)	23.9(3)
C2	3809.7(17)	8499.1(12)	2607.6(7)	22.6(3)
C44	-203.2(17)	5220.3(12)	2083.8(8)	23.9(3)
C24	70.6(18)	4925.2(13)	3360.9(8)	24.4(3)
C31	2814.1(18)	3650.7(12)	3004.5(8)	24.3(3)
C8	4311.4(17)	9516.6(12)	2269.0(8)	23.5(3)
C30	1357.9(18)	3875.5(13)	3500.5(8)	25.4(3)
C10	6945.4(18)	9998.0(13)	1862.8(8)	27.0(3)
C18	3991.3(18)	8388.2(13)	347.3(8)	27.3(3)
C11	8361.7(18)	9929.9(13)	1428.9(9)	28.7(3)
C43	-1675.8(19)	5667.7(14)	1695.9(8)	29.7(3)
C3	2668.4(19)	8567.0(13)	3183.8(8)	28.1(3)
C21	2897.3(18)	6887.3(13)	1480.7(8)	27.3(3)
C25	-1177.9(18)	5160.1(14)	3884.4(8)	29.1(3)
C7	3553.1(19)	10588.5(13)	2490.7(9)	28.8(3)
C32	4379.5(19)	3232.6(13)	3318.6(9)	31.1(3)
C20	2345.5(19)	7026.0(14)	777.6(9)	31.6(3)
C36	4122.4(19)	3640.3(13)	1807.2(9)	29.2(3)
C1	4446(2)	6318.2(13)	2861.9(8)	29.9(3)
C13	8531.9(18)	9305.3(13)	864.0(8)	28.5(3)
C40	631(2)	3698.6(15)	1362.4(9)	31.9(3)
C35	5646.3(19)	3229.5(14)	2148.7(10)	34.1(4)
C4	1958(2)	9637.5(14)	3416.6(9)	31.8(3)
C6	2379(2)	10649.7(14)	3049.5(9)	32.6(4)
C29	1293(2)	3086.5(14)	4156.6(8)	32.6(4)

Table S2 **Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
C33	5812.2(19)	3015.3(14)	2895.4(10)	34.9(4)
C42	-1975(2)	5132.7(15)	1142.6(9)	35.5(4)
C23	-804(2)	6970.0(13)	2668.0(9)	32.9(4)
C26	-1218(2)	4367.8(16)	4536.7(9)	34.4(4)
C19	2869.0(19)	7790.2(14)	213.7(9)	31.2(3)
C41	-839(2)	4136.4(16)	985.7(9)	36.4(4)
C15	7676(2)	8124.1(15)	80.9(9)	34.0(4)
C28	33(2)	3322.1(16)	4662.8(9)	37.1(4)
C37	4131(2)	3868.2(17)	982.6(9)	40.0(4)
C12	9699(2)	10478.1(17)	1579.2(11)	40.2(4)
C27	-2594(2)	4631(2)	5087.7(10)	48.7(5)
C5	773(3)	9672.8(18)	4057.3(11)	50.8(5)
C34	7500(2)	2598.0(19)	3242.6(13)	53.8(5)

Table S3 **Anisotropic Displacement Parameters (Å^2×10^3) for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	25.5(6)	19.5(6)	27.2(6)	-5.2(5)	0.7(5)	-3.5(5)
N1	26.6(6)	18.3(6)	23.8(6)	-2.3(5)	0.8(5)	-7.3(5)
C22	22.1(7)	16.4(6)	26.9(7)	-4.5(5)	0.1(5)	-2.7(5)
C17	21.7(7)	18.8(6)	26.9(7)	-4.8(5)	2.3(5)	-3.4(5)
C38	24.4(7)	17.4(6)	32.6(8)	-7.3(6)	2.3(6)	-6.2(5)
C39	24.6(7)	23.9(7)	25.3(7)	-3.7(6)	2.8(6)	-8.6(6)
C14	25.9(7)	21.4(7)	27.0(7)	1.5(6)	1.1(6)	-4.3(6)
C16	22.2(7)	18.5(6)	24.9(7)	0.7(5)	0.6(5)	-4.4(5)
C9	23.8(7)	18.5(7)	28.0(7)	0.0(6)	1.8(6)	-6.5(5)
C2	23.7(7)	20.8(7)	24.1(7)	-4.5(6)	-1.7(5)	-6.7(5)

Table S3 **Anisotropic Displacement Parameters ($Å^2×10^3$) for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C44	24.2(7)	23.0(7)	24.6(7)	-1.4(6)	1.8(6)	-8.8(6)
C24	25.1(7)	25.4(7)	25.6(7)	-7.6(6)	-0.8(6)	-9.3(6)
C31	25.4(7)	16.5(6)	31.3(8)	-5.4(6)	-0.4(6)	-5.3(5)
C8	23.2(7)	22.9(7)	25.8(7)	-5.8(6)	1.0(5)	-7.9(5)
C30	26.9(7)	25.1(7)	26.2(7)	-7.0(6)	-1.3(6)	-8.3(6)
C10	28.3(7)	23.5(7)	30.3(8)	-3.5(6)	-0.5(6)	-9.6(6)
C18	27.2(7)	24.5(7)	27.6(8)	-2.1(6)	-0.5(6)	-4.3(6)
C11	25.2(7)	24.9(7)	34.2(8)	3.1(6)	-3.4(6)	-9.0(6)
C43	26.1(8)	27.8(8)	33.4(8)	-1.7(6)	0.3(6)	-6.8(6)
C3	29.4(8)	26.4(7)	29.5(8)	-4.1(6)	3.4(6)	-10.9(6)
C21	25.9(7)	23.1(7)	34.1(8)	-5.8(6)	2.3(6)	-8.6(6)
C25	24.7(7)	35.1(8)	29.5(8)	-10.6(6)	0.3(6)	-7.8(6)
C7	30.2(8)	22.3(7)	36.5(8)	-8.8(6)	3.6(6)	-9.8(6)
C32	29.8(8)	22.7(7)	40.0(9)	-5.4(6)	-6.1(7)	-4.7(6)
C20	29.7(8)	29.3(8)	40.0(9)	-10.3(7)	-3.3(7)	-11.3(6)
C36	29.9(8)	20.5(7)	39.8(9)	-12.0(6)	6.9(6)	-8.1(6)
C1	36.2(8)	20.7(7)	30.3(8)	0.2(6)	0.2(6)	-7.0(6)
C13	21.6(7)	27.9(8)	31.6(8)	2.8(6)	3.3(6)	-6.0(6)
C40	35.0(8)	32.1(8)	32.3(8)	-11.9(7)	4.8(7)	-11.8(7)
C35	24.0(8)	25.4(8)	55.5(11)	-14.7(7)	9.5(7)	-8.1(6)
C4	29.7(8)	35.4(9)	31.6(8)	-11.7(7)	6.3(6)	-8.5(7)
C6	32.8(8)	27.8(8)	39.3(9)	-15.1(7)	4.8(7)	-6.6(6)
C29	37.1(9)	30.0(8)	29.5(8)	-2.2(6)	-4.4(7)	-8.1(7)
C33	26.0(8)	22.7(7)	56.7(11)	-9.7(7)	-4.2(7)	-4.9(6)
C42	33.6(9)	40.2(9)	33.2(9)	0.4(7)	-8.4(7)	-13.7(7)
C23	33.5(8)	22.7(7)	39.7(9)	-7.5(7)	-0.5(7)	-1.4(6)
C26	33.7(8)	48.7(10)	28.1(8)	-13.5(7)	3.6(6)	-19.5(7)
C19	30.2(8)	32.3(8)	30.7(8)	-8.2(6)	-5.8(6)	-4.8(6)

Table S3 **Anisotropic Displacement Parameters ($Å^2×10^3$) for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C41	40.4(9)	42.7(10)	32.3(8)	-11.1(7)	-3.5(7)	-17.7(8)
C15	31.4(8)	37.2(9)	33.0(8)	-8.7(7)	8.6(7)	-8.6(7)
C28	45.8(10)	42.6(10)	25.2(8)	-0.7(7)	-0.4(7)	-19.8(8)
C37	37.9(9)	47.6(10)	40.0(9)	-18.8(8)	13.8(7)	-16.0(8)
C12	32.2(9)	45.9(10)	46.5(11)	-2.1(8)	-2.7(8)	-21.3(8)
C27	43.9(11)	72.1(14)	35.9(10)	-14.9(9)	13.0(8)	-24.5(10)
C5	53.1(12)	46.0(11)	52.8(12)	-17.6(9)	26.4(9)	-12.2(9)
C34	28.4(9)	50.2(11)	81.5(15)	-15.4(11)	-12.4(9)	-3.1(8)

Table S4 **Bond Lengths for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N2	C44	1.4372(18)	C31	C30	1.487(2)
N2	C24	1.4315(19)	C31	C32	1.398(2)
N2	C23	1.4687(18)	C8	C7	1.397(2)
N1	C22	1.4383(18)	C30	C29	1.398(2)
N1	C2	1.4339(17)	C10	C11	1.391(2)
N1	C1	1.4687(18)	C18	C19	1.386(2)
C22	C17	1.412(2)	C11	C13	1.389(2)
C22	C21	1.393(2)	C11	C12	1.509(2)
C17	C16	1.494(2)	C43	C42	1.387(2)
C17	C18	1.398(2)	C3	C4	1.398(2)
C38	C39	1.489(2)	C21	C20	1.387(2)
C38	C31	1.408(2)	C25	C26	1.391(2)
C38	C36	1.419(2)	C7	C6	1.390(2)
C39	C44	1.406(2)	C32	C33	1.392(2)
C39	C40	1.399(2)	C20	C19	1.382(2)
C14	C16	1.417(2)	C36	C35	1.390(2)

Table S4 **Bond Lengths for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C14	C13	1.393(2)	C36	C37	1.513(2)
C14	C15	1.513(2)	C40	C41	1.384(2)
C16	C9	1.406(2)	C35	C33	1.379(2)
C9	C8	1.4901(19)	C4	C6	1.386(2)
C9	C10	1.402(2)	C4	C5	1.509(2)
C2	C8	1.408(2)	C29	C28	1.384(2)
C2	C3	1.397(2)	C33	C34	1.514(2)
C44	C43	1.396(2)	C42	C41	1.380(2)
C24	C30	1.409(2)	C26	C28	1.388(2)
C24	C25	1.400(2)	C26	C27	1.511(2)

Table S5 **Bond Angles for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C44	N2	C23	116.02(12)	C2	C8	C9	121.35(12)
C24	N2	C44	110.92(11)	C7	C8	C9	120.08(13)
C24	N2	C23	116.21(12)	C7	C8	C2	118.23(13)
C22	N1	C1	115.53(11)	C24	C30	C31	121.78(13)
C2	N1	C22	110.94(11)	C29	C30	C24	117.60(14)
C2	N1	C1	116.05(11)	C29	C30	C31	120.41(13)
C17	C22	N1	118.91(12)	C11	C10	C9	121.65(14)
C21	C22	N1	120.80(13)	C19	C18	C17	121.53(14)
C21	C22	C17	120.28(13)	C10	C11	C12	121.38(15)
C22	C17	C16	121.12(13)	C13	C11	C10	117.74(14)
C18	C17	C22	117.82(13)	C13	C11	C12	120.85(15)
C18	C17	C16	121.05(13)	C42	C43	C44	120.18(14)
C31	C38	C39	120.59(13)	C2	C3	C4	121.47(14)
C31	C38	C36	118.81(13)	C20	C21	C22	120.25(14)

Table S5 **Bond Angles for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C36	C38	C39	120.59(13)	C26	C25	C24	121.91(15)
C44	C39	C38	121.27(13)	C6	C7	C8	121.33(14)
C40	C39	C38	120.71(13)	C33	C32	C31	121.68(15)
C40	C39	C44	117.99(14)	C19	C20	C21	120.16(14)
C16	C14	C15	123.59(14)	C38	C36	C37	123.90(14)
C13	C14	C16	119.33(14)	C35	C36	C38	118.96(15)
C13	C14	C15	117.07(14)	C35	C36	C37	117.12(14)
C14	C16	C17	121.33(13)	C11	C13	C14	122.58(14)
C9	C16	C17	120.04(12)	C41	C40	C39	121.46(15)
C9	C16	C14	118.62(13)	C33	C35	C36	122.93(15)
C16	C9	C8	122.72(13)	C3	C4	C5	120.15(15)
C10	C9	C16	120.05(13)	C6	C4	C3	118.42(14)
C10	C9	C8	117.22(13)	C6	C4	C5	121.42(14)
C8	C2	N1	118.26(12)	C4	C6	C7	120.69(14)
C3	C2	N1	122.07(13)	C28	C29	C30	121.99(15)
C3	C2	C8	119.66(13)	C32	C33	C34	121.02(17)
C39	C44	N2	118.86(12)	C35	C33	C32	117.85(15)
C43	C44	N2	121.00(13)	C35	C33	C34	121.09(16)
C43	C44	C39	120.13(13)	C41	C42	C43	120.18(15)
C30	C24	N2	118.27(13)	C25	C26	C27	120.96(16)
C25	C24	N2	122.06(13)	C28	C26	C25	118.08(15)
C25	C24	C30	119.67(14)	C28	C26	C27	120.96(16)
C38	C31	C30	122.49(13)	C20	C19	C18	119.83(14)
C32	C31	C38	119.75(14)	C42	C41	C40	119.81(15)
C32	C31	C30	117.77(13)	C29	C28	C26	120.71(15)

Table S6 **Torsion Angles for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N2	C44	C43	C42	-176.92(14)	C24	C25	C26	C27	-178.91(15)
N2	C24	C30	C31	7.0(2)	C31	C38	C39	C44	49.5(2)
N2	C24	C30	C29	-178.22(13)	C31	C38	C39	C40	-132.57(15)
N2	C24	C25	C26	178.54(14)	C31	C38	C36	C35	1.3(2)
N1	C22	C17	C16	6.68(19)	C31	C38	C36	C37	-177.23(14)
N1	C22	C17	C18	-174.39(12)	C31	C30	C29	C28	173.81(14)
N1	C22	C21	C20	176.59(13)	C31	C32	C33	C35	0.2(2)
N1	C2	C8	C9	-10.2(2)	C31	C32	C33	C34	178.14(15)
N1	C2	C8	C7	176.52(13)	C8	C9	C10	C11	176.87(13)
N1	C2	C3	C4	-178.52(14)	C8	C2	C3	C4	2.5(2)
C22	N1	C2	C8	-66.61(16)	C8	C7	C6	C4	1.7(2)
C22	N1	C2	C3	114.41(15)	C30	C24	C25	C26	-1.9(2)
C22	C17	C16	C14	131.05(14)	C30	C31	C32	C33	-179.01(14)
C22	C17	C16	C9	-49.10(18)	C30	C29	C28	C26	-0.5(3)
C22	C17	C18	C19	-3.3(2)	C10	C9	C8	C2	-130.11(15)
C22	C21	C20	C19	-1.3(2)	C10	C9	C8	C7	43.0(2)
C17	C22	C21	C20	-2.0(2)	C10	C11	C13	C14	0.3(2)
C17	C16	C9	C8	2.3(2)	C18	C17	C16	C14	-47.85(19)
C17	C16	C9	C10	-179.23(12)	C18	C17	C16	C9	132.00(14)
C17	C18	C19	C20	0.2(2)	C43	C42	C41	C40	-2.6(3)
C38	C39	C44	N2	-8.1(2)	C3	C2	C8	C9	168.80(13)
C38	C39	C44	C43	172.70(14)	C3	C2	C8	C7	-4.5(2)
C38	C39	C40	C41	-173.45(14)	C3	C4	C6	C7	-3.7(2)
C38	C31	C30	C24	-46.2(2)	C21	C22	C17	C16	-174.72(12)
C38	C31	C30	C29	139.14(15)	C21	C22	C17	C18	4.21(19)
C38	C31	C32	C33	0.8(2)	C21	C20	C19	C18	2.2(2)
C38	C36	C35	C33	-0.2(2)	C25	C24	C30	C31	-172.62(13)
C39	C38	C31	C30	-2.3(2)	C25	C24	C30	C29	2.2(2)
C39	C38	C31	C32	177.88(13)	C25	C26	C28	C29	0.8(2)

Table S6 **Torsion Angles for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C39	C38	C36	C35	-178.14(13)	C32	C31	C30	C24	133.59(15)
C39	C38	C36	C37	3.4(2)	C32	C31	C30	C29	-41.1(2)
C39	C44	C43	C42	2.3(2)	C36	C38	C39	C44	-131.13(15)
C39	C40	C41	C42	-0.7(3)	C36	C38	C39	C40	46.8(2)
C14	C16	C9	C8	-177.86(13)	C36	C38	C31	C30	178.27(13)
C14	C16	C9	C10	0.6(2)	C36	C38	C31	C32	-1.5(2)
C16	C17	C18	C19	175.59(13)	C36	C35	C33	C32	-0.5(2)
C16	C14	C13	C11	-1.4(2)	C36	C35	C33	C34	-178.41(15)
C16	C9	C8	C2	48.4(2)	C1	N1	C22	C17	-155.17(12)
C16	C9	C8	C7	-138.44(15)	C1	N1	C22	C21	26.24(18)
C16	C9	C10	C11	-1.7(2)	C1	N1	C2	C8	158.91(13)
C9	C8	C7	C6	-170.90(14)	C1	N1	C2	C3	-20.07(19)
C9	C10	C11	C13	1.2(2)	C13	C14	C16	C17	-179.29(13)
C9	C10	C11	C12	-176.76(15)	C13	C14	C16	C9	0.9(2)
C2	N1	C22	C17	70.09(16)	C40	C39	C44	N2	173.88(13)
C2	N1	C22	C21	-108.50(14)	C40	C39	C44	C43	-5.3(2)
C2	C8	C7	C6	2.5(2)	C23	N2	C44	C39	155.52(14)
C2	C3	C4	C6	1.6(2)	C23	N2	C44	C43	-25.3(2)
C2	C3	C4	C5	-177.91(15)	C23	N2	C24	C30	-156.07(14)
C44	N2	C24	C30	68.57(16)	C23	N2	C24	C25	23.5(2)
C44	N2	C24	C25	-111.84(15)	C15	C14	C16	C17	0.1(2)
C44	C39	C40	C41	4.6(2)	C15	C14	C16	C9	-179.72(13)
C44	C43	C42	C41	1.8(2)	C15	C14	C13	C11	179.16(14)
C24	N2	C44	C39	-69.01(16)	C37	C36	C35	C33	178.34(15)
C24	N2	C44	C43	110.17(15)	C12	C11	C13	C14	178.32(14)
C24	C30	C29	C28	-1.1(2)	C27	C26	C28	C29	-179.92(16)
C24	C25	C26	C28	0.3(2)	C5	C4	C6	C7	175.82(16)

Table S7 **Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq.**

Atom	*x*	*y*	*z*	U(eq)
H10	6793.14	10433.51	2246.3	32
H18	4341.89	8913.61	-43.49	33
H43	-2475.12	6340.16	1811.27	36
H3	2368.41	7870.37	3422.91	34
H21	2516.62	6373.2	1868.48	33
H25	-2022.29	5881.43	3791.55	35
H7	3845.59	11289.64	2254.78	35
H32	4467.31	3093.43	3834	37
H20	1606.08	6594.45	683.65	38
H1A	3292.11	6290.56	2941.84	45
H1B	4932.23	6302.32	3327.14	45
H1C	5065.18	5631.05	2656.94	45
H13	9495.83	9247.31	564.6	34
H40	1401.17	3007.34	1254.61	38
H35	6616.91	3090.15	1854.58	41
H6	1861.01	11393.25	3181.07	39
H29	2137.92	2366.9	4258.07	39
H42	-2964.53	5453.14	870.98	43
H23A	-600.35	7453.48	2200.21	49
H23B	-421.12	7253.6	3065.46	49
H23C	-1989.73	7033	2728.84	49
H19	2460.66	7905.48	-264.38	37
H41	-1065.32	3752.18	620.1	44
H15A	7226.38	7429.17	189.54	51
H15B	8869.7	7868.94	-5.26	51
H15C	7146.43	8661.84	-355.22	51
H28	25.26	2762.17	5101.37	45
H37A	4176.95	3131.1	815.78	60

Table S7 **Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq.**

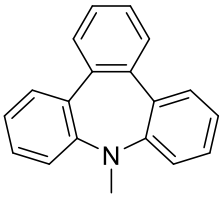
Atom	*x*	*y*	*z*	U(eq)
H37B	5098.65	4151.21	795.68	60
H37C	3123.45	4469.95	802.07	60
H12A	10234.54	10741.35	1119.24	60
H12B	10520.51	9889.41	1902.88	60
H12C	9211.72	11159.76	1813.14	60
H27A	-3237.42	4043.36	5137.92	73
H27B	-3315.65	5425.6	4922.47	73
H27C	-2122.78	4593.57	5559.95	73
H5A	414.86	10482.35	4153.22	76
H5B	1324.97	9134.47	4488.51	76
H5C	-190.72	9424.58	3946.39	76
H34A	8114.84	1858.17	3092.18	81
H34B	7372.52	2461.01	3774.48	81
H34C	8104.78	3204.83	3085.82	81
H12D	9520(50)	11290(20)	1300(20)	38(12)
H12E	10800(30)	10090(40)	1390(20)	33(11)
H12F	9810(60)	10370(40)	2099(11)	41(13)

Table S8 **Atomic Occupancy for mo_20220424LWX_201321_HLY_674_ZCS_0m_sq.**

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H12A	0.53(3)	H12B	0.53(3)	H12C	0.53(3)
H12D	0.47(3)	H12E	0.47(3)	H12F	0.47(3)

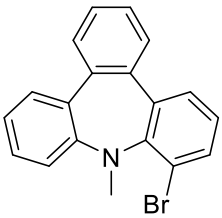
VII. Experimental data for the described substances

9-methyl-9*H*-tribenzo[*b,d,f*]azepine (3a)[11]



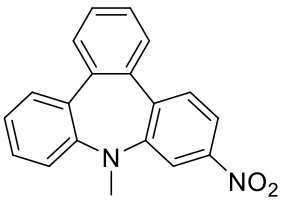
A white solid (50 mg, 97% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.50–7.46 (m, 6H), 7.32 (t, J = 7.5 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 7.0 Hz, 2H), 3.31(s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 154.47, 139.79, 134.85, 129.91, 129.68, 128.32, 127.70, 124.11, 117.41, 37.99 ppm.

8-bromo-9-methyl-9*H*-tribenzo[*b,d,f*]azepine (3b)



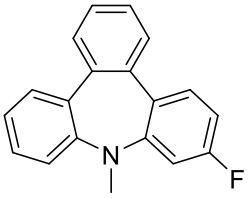
A white solid (40 mg, 60% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). M.p.: 55.5–57.5 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.60–7.57 (m, 3H), 7.54 (d, J = 7.5 Hz, 2H), 7.50–7.46 (m, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.26–7.23 (m, 1H), 7.08 (t, J = 7.8 Hz, 1H), 3.16 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 152.60, 149.34, 141.86, 138.98, 138.54, 137.70, 133.00, 130.06, 129.91, 129.61, 129.58, 128.78, 128.05, 127.55, 127.00, 126.25, 125.98, 123.00, 40.30 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{15}Br$ (M+H) 336.0388, found 336.0340.

9-methyl-7-nitro-9*H*-tribenzo[*b,d,f*]azepine (3c)



A yellow solid (57 mg, 95% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v).. M.p.: 79.4–81.4 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8..02–7.98 (m, 2H), 7.57 (d, J = 8.5 Hz, 1H), 7.54–7.52 (m, 2H), 7.50–7.45 (m, 3H), 7.38–7.34 (m, 1H), 7.24–7.18 (m, 2H), 3.36 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 155.13, 153.23, 148.08, 141.78, 140.09, 137.83, 134.31, 130.30, 130.10, 130.04, 129.91, 129.21, 128.88, 128.01, 124.96, 119.07, 117.93, 112.53, 38.20 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{15}N_2O_2$ (M+H) 303.1134, found 303.1132.

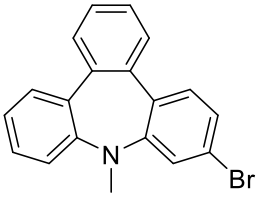
7-fluoro-9-methyl-9*H*-tribenzo[*b,d,f*]azepine (3d)



A white solid (42 mg, 76% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v).. M.p.: 154.6–156.6 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.49–7.38 (m, 6H), 7.32 (t, J = 7.8 Hz, 1H), 7.19–7.15 (m, 2H), 6.90 (d, J = 10.5 Hz, 1H), 6.85 (t, J = 8.0 Hz, 1H), 3.27 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 163.55 (d, J_{C-F} = 245.8 Hz), 155.96 (d, J_{C-F} = 8.13 Hz), 153.83, 139.50, 138.99, 134.85, 130.79, 130.75 (d, J_{C-F} =9.6 Hz), 130.01, 129.70, 129.60, 128.42, 127.8 (d, J_{C-F} = 5.6

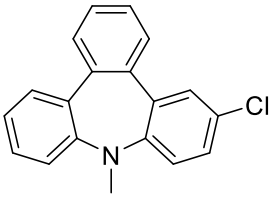
Hz), 124.49, 117.57, 110.86 (d, $J_{C\text{-}F}$ = 21.1 Hz), 105.15 (d, $J_{C\text{-}F}$ = 22.9 Hz), 38.04 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{15}FN$ (M+H) 276.1189, found 276.1188.

7-bromo-9-methyl-9*H*-tribenzo[*b,d,f*]azepine (3e)



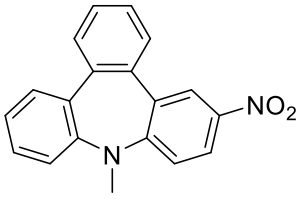
A white solid (62 mg, 92% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v).. M.p.: 141.2–143.2 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.50–7.43 (m, 5H), 7.35–7.27 (m, 4H), 7.20–7.15 (m, 2H), 3.28 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 155.48, 153.81, 139.66, 138.79, 134.72, 133.87, 130.94, 130.00, 129.75, 129.50, 128.51, 128.06, 127.84, 127.16, 124.53, 122.65, 121.01, 117.68, 38.07 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{15}BrN$ (M+H) 336.0388, found 336.0385.

6-chloro-9-methyl-9*H*-tribenzo[*b,d,f*]azepine (3f)



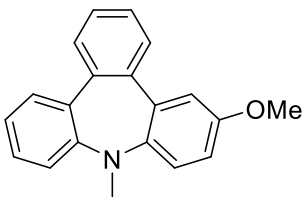
A white solid (38 mg, 65% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v).. M.p.: 133.8–135.8 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.49–7.44 (m, 5H), 7.42 (d, J = 2.5 Hz, 1H), 7.34–7.31 (m, 1H),7.27–7.25 (m, 1H), 7.19–7.14 (m, 2H), 7.11 (d, J = 8.5 Hz, 1H), 3.27 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 154.08, 153.01, 139.84, 138.52, 136.49, 134.62, 130.00, 129.77, 129.60, 129.53, 129.22, 128.51, 128.25, 127.99, 127.85, 124.41, 118.65, 117.48, 38.07 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{18}NO$ (M+H) 288.1388, found 288.1385.

9-methyl-6-nitro-9*H*-tribenzo[*b,d,f*]azepine (3g)



A white solid (52 mg, 86% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v).. M.p.: 68.8–70.8 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.34 (d, J = 2.5 Hz, 1H), 8.18 (dd, J = 9.0 Hz, 2.5 Hz, 1H), 7.52–7.46 (m, 5H), 7.37–7.34 (m, 1H), 7.24–7.19 (m, 3H), 3.36 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 160.54, 152.66, 144.04, 139.69, 137.89, 135.49, 134.45, 130.22, 130.19, 129.71, 128.91, 128.77, 128.20, 125.25, 125.17, 123.73, 118.35, 117.60, 38.48 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{15}N_2O_2$ (M+H) 303.1134, found 303.1133.

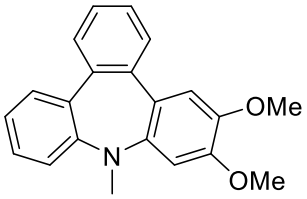
6-methoxy-9-methyl-9*H*-tribenzo[*b,d,f*]azepine (3h)



A white solid (30 mg, 52% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v). M.p.: 128.4–130.4 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.54–7.44 (m, 5H), 7.31 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.14–7.11 (m, 2H), 7.00 (d, J = 2.0 Hz), 6.86 (dd, J = 8.8 Hz, 1.8 Hz, 1H), 3.80 (s, 3H), 3.26 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 156.22, 154.88, 147.83,

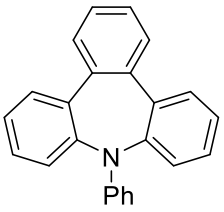
139.93, 139.58, 135.90, 134.74, 129.93, 129.83, 129.39, 128.36, 127.83, 127.70, 123.96, 118.14, 117.03, 115.14, 113.51, 55.73, 38.08 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{18}NO$ (M+H) 288.1388, found 288.1385.

6,7-dimethoxy-9-methyl-9*H*-tribenzo[*b,d,f*]azepine(3i)



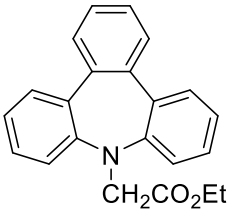
A white solid (33 mg, 54% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 139.1–141.1 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.49–7.41 (m, 5H), 7.31 (t, *J* = 7.25 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.96 (s, 1H), 6.77 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.28 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 155.06, 149.42, 147.58, 145.58, 139.74, 139.61, 134.99, 129.97, 129.85, 129.00, 128.25, 127.68, 127.25, 126.70, 124.10, 117.10, 112.83, 101.97, 56.43, 56.21, 38.03 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{20}NO_2$ (M+H) 318.3960, found 318.3961.

9-phenyl-9*H*-tribenzo[*b,d,f*]azepine (3j)[11]



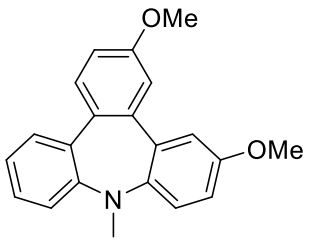
A white solid (40 mg, 63% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.66 (d, *J* = 7.5 Hz, 2H), 7.61–7.55 (m, 4H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.40–7.38 (m, 4H), 6.98 (t, *J* = 8.0 Hz, 2H), 6.62–6.55 (m, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 147.48, 146.11, 139.22, 137.78, 131.07, 129.51, 129.09, 128.86, 128.74, 127.86, 127.49, 117.56, 111.87 ppm.

ethyl 2-(9*H*-tribenzo[*b,d,f*]azepin-9-yl)acetate (3k)



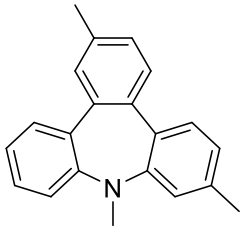
A white solid (54 mg, 82% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 70.3–72.3 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.54–7.52 (m, 2H), 7.49–7.44 (m, 4H), 7.29 (td, *J* = 8.0 Hz, 1.3 Hz, 2H), 7.17–7.11 (m, 4H), 4.54 (s, 2H), 3.98 (q, *J* = 7.17 Hz, 2H), 0.98 (t, *J* = 7.25 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 169.44, 152.54, 139.53, 135.85, 130.15, 129.53, 128.38, 127.66, 124.75, 118.19, 60.89, 52.39, 13.96 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{22}H_{20}NO_2$ (M+H) 330.1494, found 330.1495.

2,12-dimethoxy-9-methyl-9*H*-tribenzo[*b,d,f*]azepine (4a)



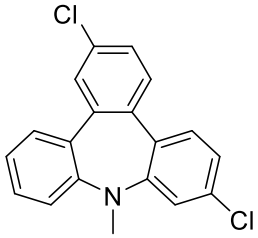
A white solid (26 mg, 41% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 56.3–58.3 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.43–7.40 (m, 2H), 7.29–7.27 (m, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.13–7.09 (m, 2H), 7.05 (d, J = 2.5 Hz, 1H), 7.03–7.00 (m, 2H), 6.86 (dd, J = 9.0 Hz, 3.0 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 3.26 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.10, 156.18, 154.24, 147.63, 140.64, 135.91, 134.48, 132.63, 131.11, 129.52, 127.82, 123.92, 118.25, 116.96, 115.17, 114.26, 114.02, 113.59, 55.76, 55.61, 38.16 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{20}NO_2$ (M+H) 318.1494, found 318.1492.

2,7,9-trimethyl-9*H*-tribenzo[*b,d,f*]azepine (4b)



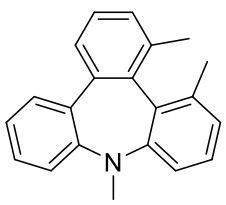
A white solid (47 mg, 87% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 133.3–135.3 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.44 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.31–7.24 (m, 3H, cover the solvent), 7.20–7.17 (m, 1H), 7.12 (td, J = 7.5 Hz, 1.0 Hz, 1H), 6.99 (s, 1H), 6.94 (d, J = 8.0 Hz, 1H), 3.23 (s, 3H), 2.45 (s, 3H), 2.36 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 154.41, 154.11, 139.45, 138.02, 137.13, 136.97, 135.04, 131.95, 130.29, 129.87, 129.44, 129.41, 128.60, 128.21, 124.85, 123.99, 118.17, 117.34, 38.04, 21.41, 21.37 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{20}$ (M+H) 286.1596, found 286.1599.

2,7-dichloro-9-methyl-9*H*-tribenzo[*b,d,f*]azepine (4c)



A white solid (45 mg, 69% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). M.p.: 50.5–52.5 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.47 (d, J = 2.0 Hz, 1H), 7.41 (t, J = 8.3 Hz, 2H), 7.36–7.34 (m, 2H), 7.31 (d, J = 8.0 Hz, 1H), 7.20–7.15 (m, 3H), 7.11 (dd, J = 8.3 Hz, 1.8Hz, 1H), 3.27 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 155.16, 153.74, 141.20, 137.24, 134.82, 133.80, 133.56, 132.37, 130.86, 130.46, 129.90, 129.44, 129.09, 127.80, 124.71, 124.36, 118.28, 117.86, 38.00 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{14}Cl_2N$ (M+H) 326.0503, found 326.0500.

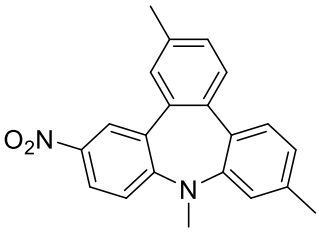
1,9,13-trimethyl-9*H*-tribenzo[*b,d,f*]azepine (4d)



A white solid (24 mg, 42% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 92.3–94.3 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.58 (d, J = 7.5 Hz, 1H), 7.34–7.31 (m, 1H), 7.28–7.23 (m, 3H, cover the solvent), 7.16–7.06 (m, 4H), 6.95 (d, J = 7.5 Hz, 1H), 3.23 (s, 3H), 2.20 (s, 3H), 2.10 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 156.75, 154.69, 140.56, 138.50, 138.43,

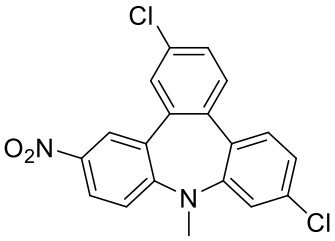
136.32, 135.29, 131.85, 128.96, 128.78, 127.84, 127.29, 127.27, 126.98, 125.97, 123.64, 116.52, 113.93, 37.37, 20.18, 20.14 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{20}N$ (M+H) 286.1596, found 286.1599.

2,7,9-trimethyl-12-nitro-9*H*-tribenzo[*b,d,f*]azepine (4e)



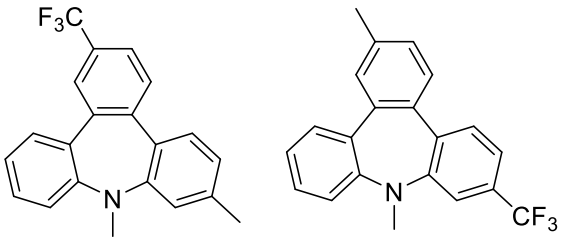
A yellow solid (45 mg, 68% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 121.1–123.1 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.32 (d, J = 2.5 Hz, 1H), 8.16 (dd, J = 8.8 Hz, 2.8 Hz, 1H), 7.40–7.38 (m, 1H), 7.34–7.31 (m, 2H), 7.22 (d, J = 9.0 Hz, 1H), 7.01–6.99 (m, 2H), 3.34 (s, 3H), 2.47 (s, 3H), 2.37 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 160.51, 152.27, 143.94, 138.60, 137.84, 137.50, 136.82, 135.71, 131.48, 130.75, 129.80, 129.73, 129.44, 125.92, 125.20, 123.63, 119.06, 117.54, 38.54, 21.37, 21.31 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{19}N_2O_2$ (M+H) 331.1447, found 331.1445.

7-chloro-1,3,9-trimethyl-9*H*-tribenzo[*b,d,f*]azepine (4f)



A yellow solid (24 mg, 32% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 71.7–73.7 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.30 (d, J = 2.5 Hz, 1H), 8.22 (dd, J = 8.5 Hz, 2.3 Hz, 1H), 7.48–7.46 (m, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.5 Hz, 1H), 7.26–7.25 (m, 1H, cover the solvent), 7.19–7.17 (m, 2H), 3.33 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.67, 153.32, 144.40, 139.17, 137.12, 135.31, 134.42, 134.27, 131.93, 130.94, 130.75, 129.91, 129.06, 125.45, 125.22, 124.35, 119.17, 118.24, 38.49 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{13}Cl_2N_2O_2$ (M+H) 371.0354, found 371.0355.

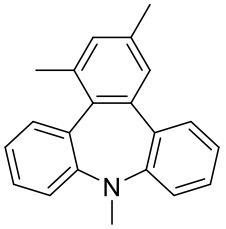
7,9-dimethyl-2-(trifluoromethyl)-9*H*-tribenzo[*b,d,f*]azepine and 2,9-dimethyl-7-(trifluoromethyl)-9*H*-tribenzo[*b,d,f*]azepine (4g and 4g')



An yellow oil (36 mg, with a ratio of 1/2) purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.74 (s, 1.5H), 7.68 (d, J = 8.5 Hz, 1.5H), 7.60–7.55(m, 2.5H), 7.48 (t, J = 8.0 Hz, 2.2H), 7.41-7.35(m, 5.7H), 7.31 (d, J = 8.0 Hz, 1.2H), 7.25-7.22 (m, 2H), 7.20-7.17 (m, 1.7H), 7.04 (s, 1.2H), 7.00 (d, J = 8.0 Hz, 1H) 3.35 (s, 1.5H), 3.32 (s, 3H), 2.50 (s, 1.5H), 2.40 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 154.67, 154.42, 153.65, 143.32, 140.27, 139.70, 139.36, 138.46, 135.72, 134.60, 133.78, 130.62 (q, $J_{C\text{-}F}$ = 35.0 Hz), 130.00, 129.94, 129.89, 129.83, 129.78, 129.49, 129.24, 128.82, 128.58, 126.48 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.53, 125.19, 124.56, 124.41, 124.09 (q, $J_{C\text{-}F}$ = 3.5 Hz), 123.37, 120.73 (d, $J_{C\text{-}F}$ = 3.8 Hz), 118.52,

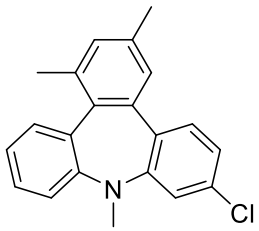
117.72, 117.61, 114.27 (q, J_{C-F} = 3.8 Hz), 114.25, 38.10, 37.89, 21.46, 21.44 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{17}F_3N$ (M+H) 340.1313, found 340.1312.

1,3,9-trimethyl-9*H*-tribenzo[*b,d,f*]azepine (4h)



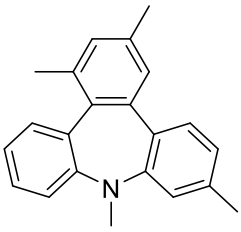
A white solid (50 mg, 84% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). M.p.: 164.3–166.3 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.52 (d, J = 7.5 Hz, 1H), 7.29 (d, J = 8.0 Hz,1H), 7.26–7.23 (m, 3H, cover the solvent), 7.16–7.05 (m , 5H), 3.27 (s, 3H), 2.42 (s, 3H), 2.38 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 155.22, 154.69, 140.49, 136.83, 136.02, 135.58, 134.95, 132.52, 132.20, 131.34, 129.64, 128.53, 127.99, 127.64, 123.71, 122.98, 117.26, 116.25, 37.34, 21.93, 21.31 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{20}N$ (M+H) 286.1596, found 286.1595.

7-chloro-1,3,9-trimethyl-9*H*-tribenzo[*b,d,f*]azepine (4i)



A white solid (20 mg, 31% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). M.p.: 173.1–175.1 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.42 (dd, J = 8.0 Hz, J = 2.5 Hz, 1H), 7.29–7.23 (m, 3H, cover the solvent), 7.17 (s, 1H), 7.17–7.07 (m, 4H), 3.24 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 155.54, 154.50, 139.46, 137.02, 135.86, 135.76, 134.01, 133.46, 132.41, 132.24, 131.63, 130.43, 128.34, 127.82, 123.80, 123.41, 117.48, 116.96, 37.38, 21.87, 21.30 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{19}ClN$ (M+H) 320.1206, found 320.1201.

1,3,7,9-tetramethyl-9*H*-tribenzo[*b,d,f*]azepine (4j)



A white solid (30 mg, 50% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). M.p.: 173.8–175.8 ℃. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.40 (d, J = 8.0 Hz, 1H), 7.29–7.24 (m, 3H, cover the solvent), 7.15 (s, 1H), 7.12 (s, 1H), 7.01–7.05 (m, 1H), 6.95 (s, 1H), 6.92 (d, J = 7.5 Hz), 3.26 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 155.20, 154.52, 140.41, 137.94, 136.80, 135.87, 135.56, 132.57, 132.20, 132.02, 131.11, 129.40, 128.28, 127.58, 124.50, 122.93, 117.17, 117.06, 37.33, 21.96, 21.47, 21.32 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{22}H_{22}N$ (M+H) 300.1752, found 300.1750.

VIII. References

[1] G. Beutner, J. Kuethe and N. Yasuda, A Practical Method for Preparation of 4-Hydroxyquinolinone Esters, *J. Org. Chem.* 2007, **72**, 7058–7061.

[2] A. D′Souza, N. Spiccia, J. Basutto, P, Jokisz, L. Wong, A. Meyer, A. Holmes, J. White and J. Ryan, 1,3-Dipolar Cycloaddition−Decarboxylation Reactions of an Azomethine Ylide with Isatoic Anhydrides: Formation of Novel Benzodiazepinones, *Org. Lett.* 2011, **13**, 486–489.

[3] A. Lee, J. Zhu, T. Feoktistova, A. Brueckner, P. Cheong and K. Scheidt, Carbene-Catalyzed Enantioselective Decarboxylative Annulations to Access Dihydrobenzoxazinones and Quinolones, *Angew. Chem., Int. Ed.,* 2019, **58**, 5941–5945.

[4] S. Ursuegui, N. Chivot, S. Moutin, A. Burr, C. Fossey, T. Cailly, A. Laayoun, F. Fabis and A. Laurent, Biotin-conjugated N-methylisatoic anhydride: a chemical tool for nucleic acid separation by selective 2′ -hydroxyl acylation of RNA, *Chem. Commun.,* 2014, **50**, 5748–5751.

[5] G. M. Coppola, N-Arylation of Isatins. A Direct Route to N-arylisatoic Anhydrides, *J. Heterocycl. Chem.,* 1987, **24**, 1249–1251.

[6] R. Clark, C. Clements, M. Barrett, S. Mackay, R. Rathnam, G. Owusu-Dapaah, J. Spencer and J. Huggan, Identification and development of the 1,4-benzodiazepin-2-one and quinazoline-2,4-dione scaffolds as submicromolar inhibitors of HAT, *Bioorg. Med. Chem.*, 2012, **20**, 6019–6033.

[7] R. Xie, H. Lv, X. Ye, X. Kong and S. Li, Cu-Catalyzed Tandem N-arylation of Phthalhydrazides with Cyclic Iodoniums to Yield Dihydrobenzo[*c*]cinnolines, *Org. Biomol. Chem.,* 2020, **18**, 4824–4830.

[8] S. Yang, F. Wang, Y. Wu, W. Hua and F. Zhang, Synthesis of Functionalized Triphenylenes via a Traceless Directing Group Strategy, *Org. Lett.*, 2018, **20**, 1491–1495.

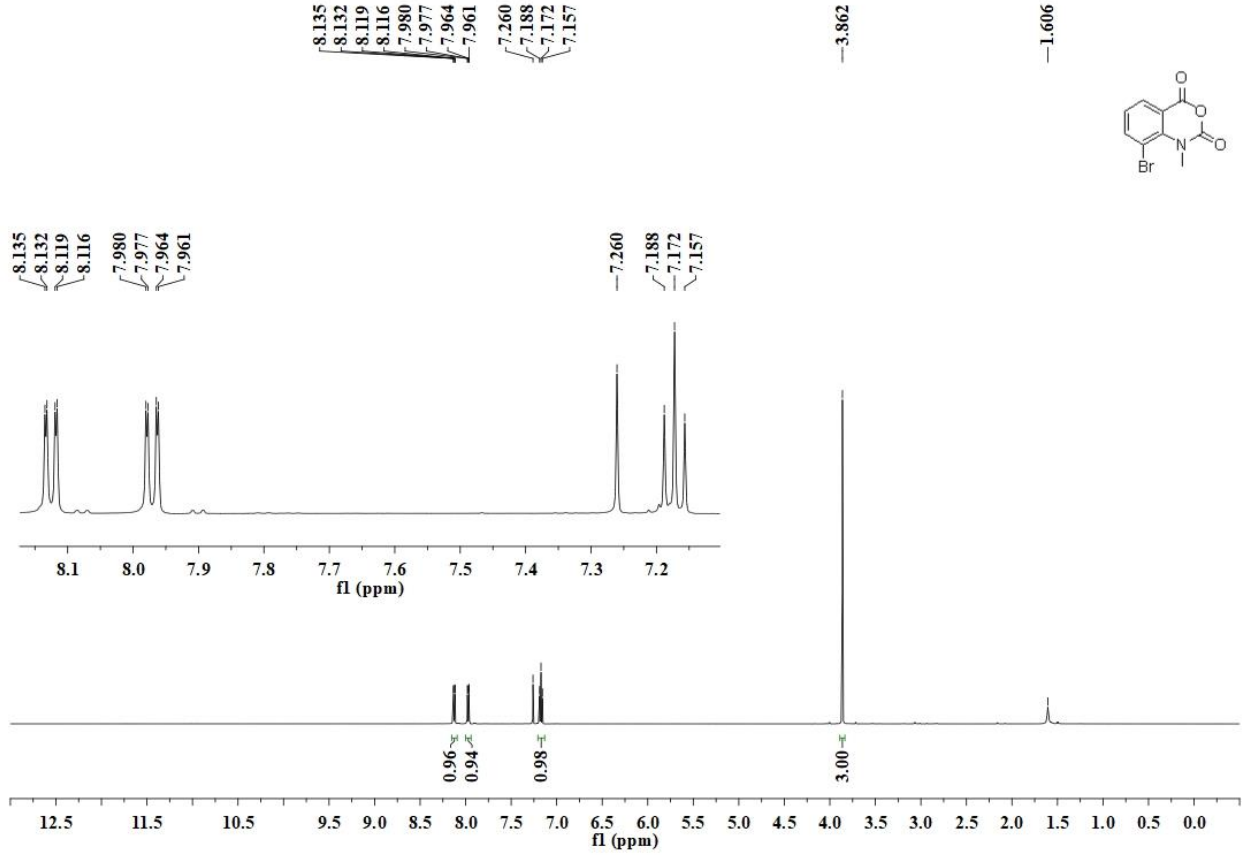
[9] B. Wu and Yoshikai, N. Conversion of 2-Iodobiaryls into 2,2′-Diiodobiaryls via Oxidation-Iodination Sequences: A Versatile Route to Ladder-Type Heterofluorenes, *Angew. Chem.,* 2015, **127**, 8860–8863.

[10] M. Ding, W. Hua, M. Liu and F.Zhang, Pd-Catalyzed C(sp^3)–H Biarylation via Transient Directing Group Strategy, *Org. Lett*., 2020, **22**, 7419–7423.

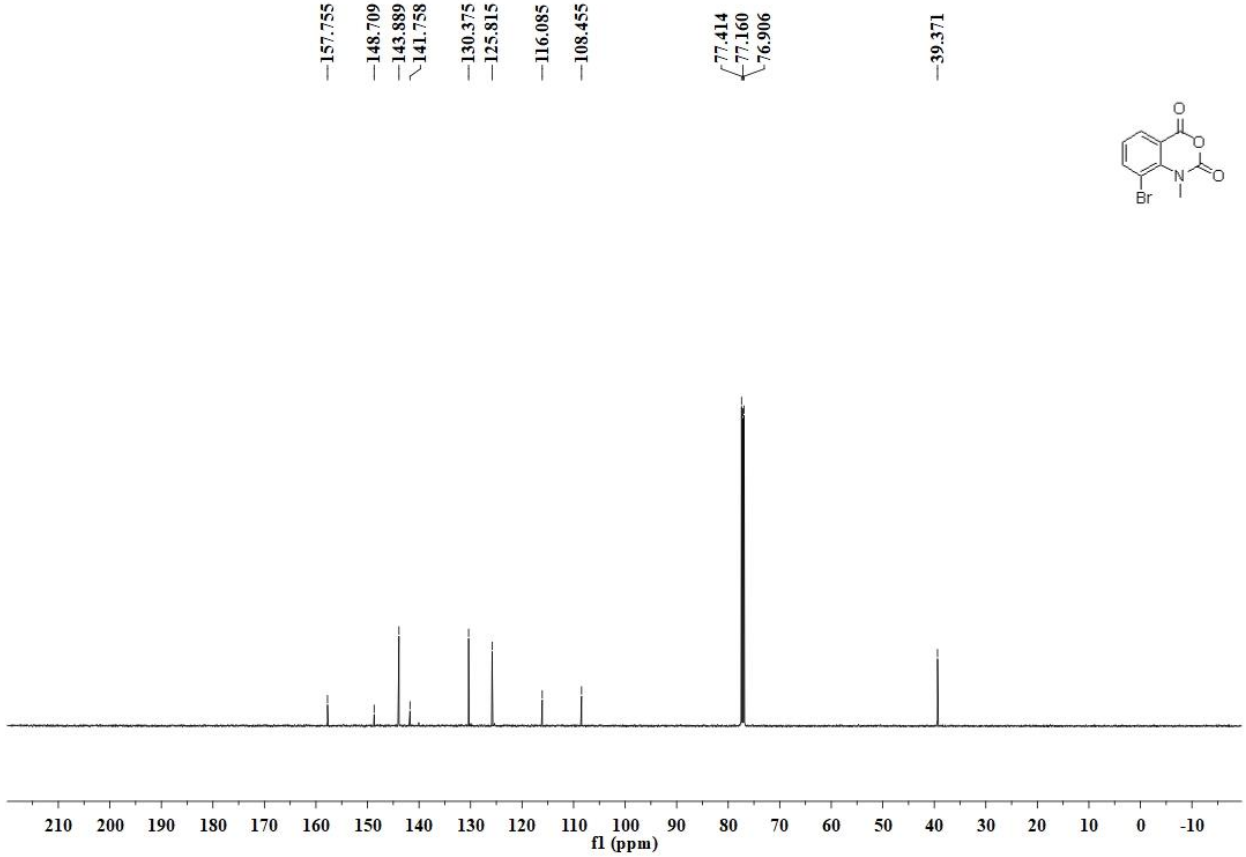
[11] C. Cheng, D. Tu, X. Zuo, Z. Wu, B. Wan and Y. Zhang, Palladium-Catalyzed Dual Coupling Reaction of 2-Iodobiphenyls with o-Bromoanilines through C–H Activation: An Approach for the Synthesis of Tribenzo[*b,d,f*]azepines, *Org. Lett*., 2021, **23**, 1239–1242.

IX. Copies of ^{1}H and ^{13}C NMR spectra

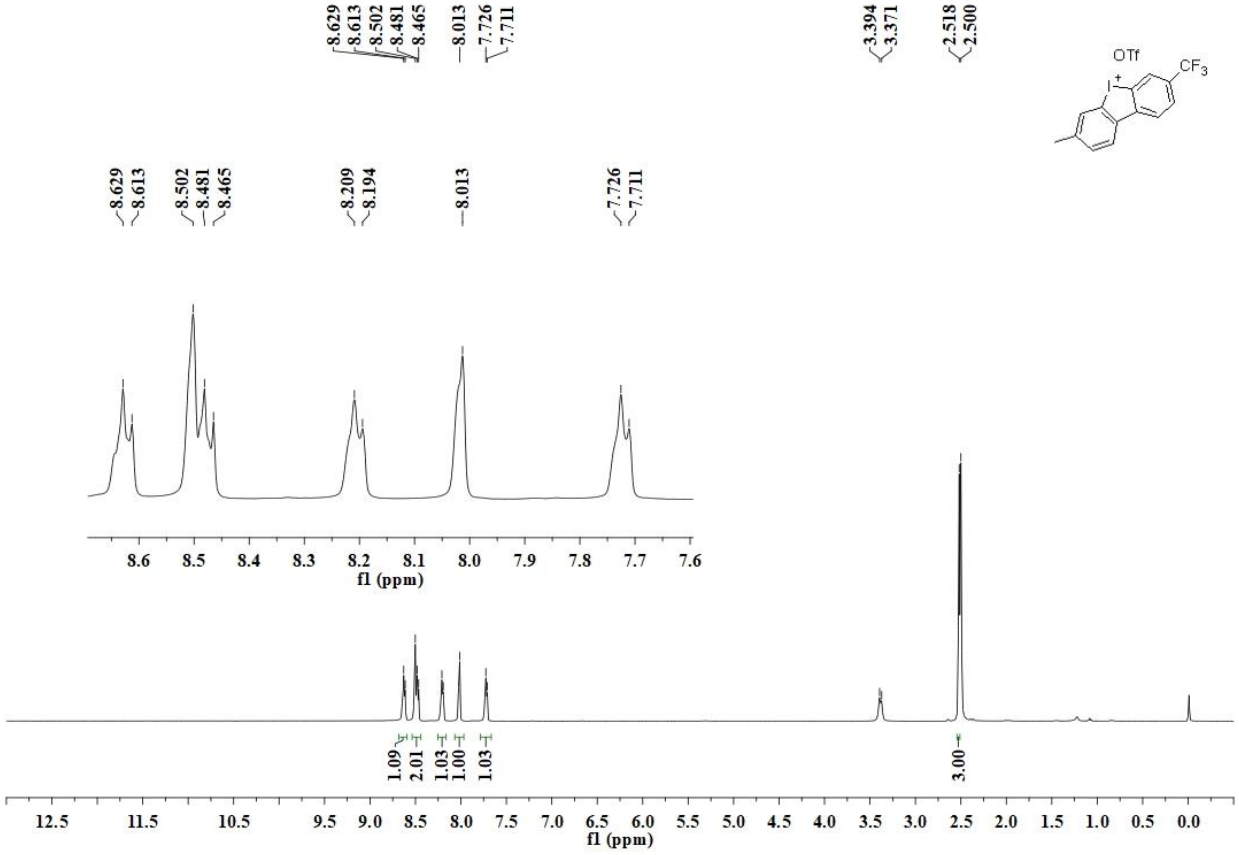
^{1}H NMR (500 MHz, $CDCl_3$) of **1b**



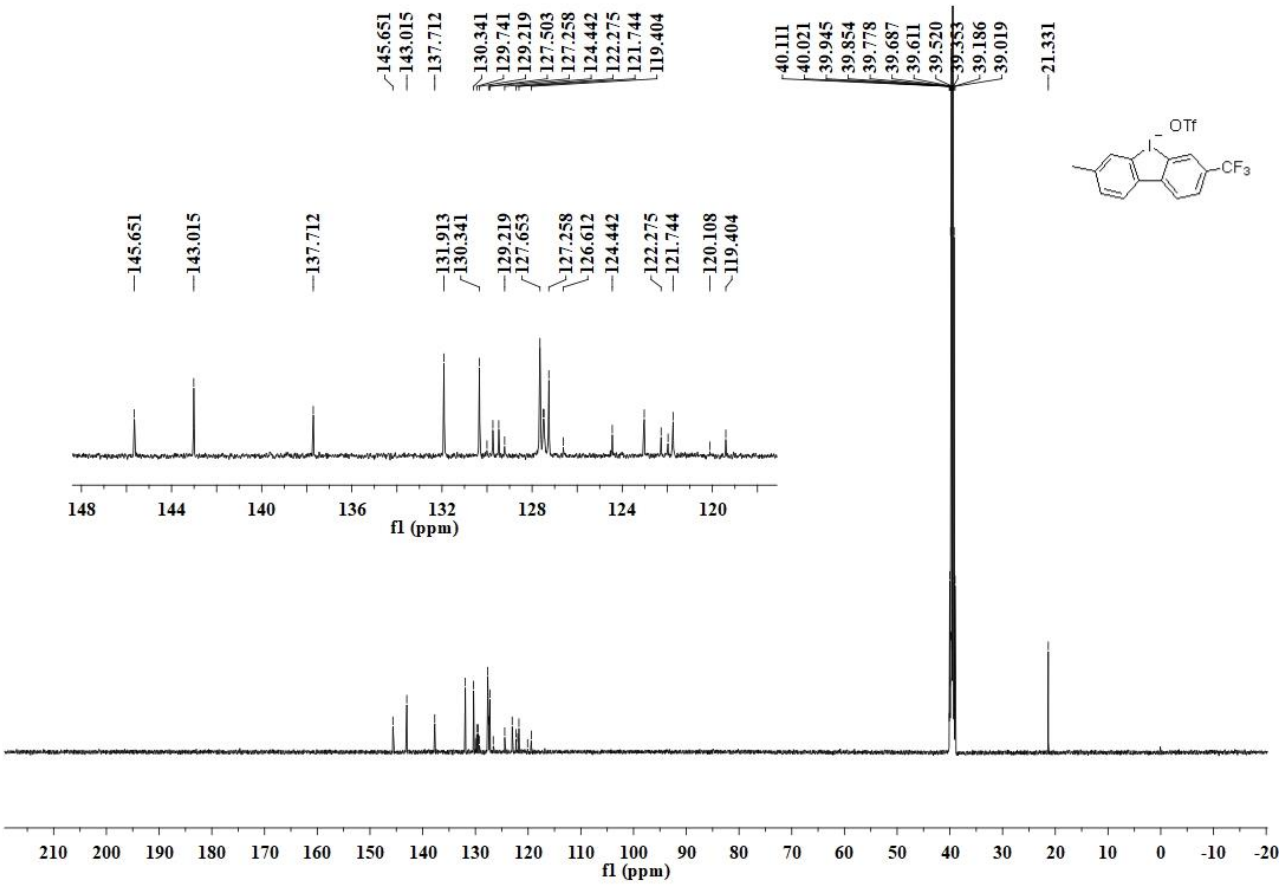
^{13}C NMR (125 MHz, $CDCl_3$) of **1b**



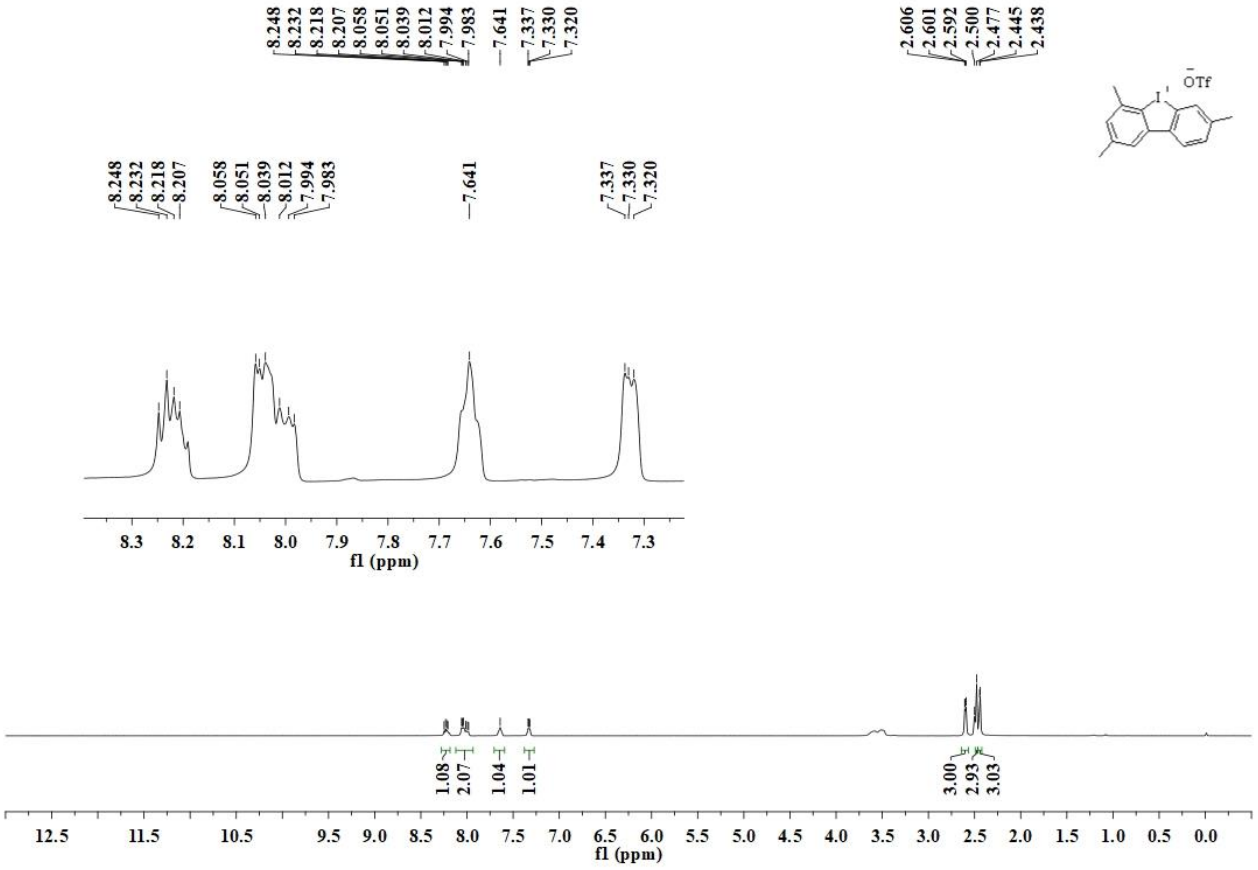
^{1}H NMR (500 MHz, DMSO-*d6*) of **2f**



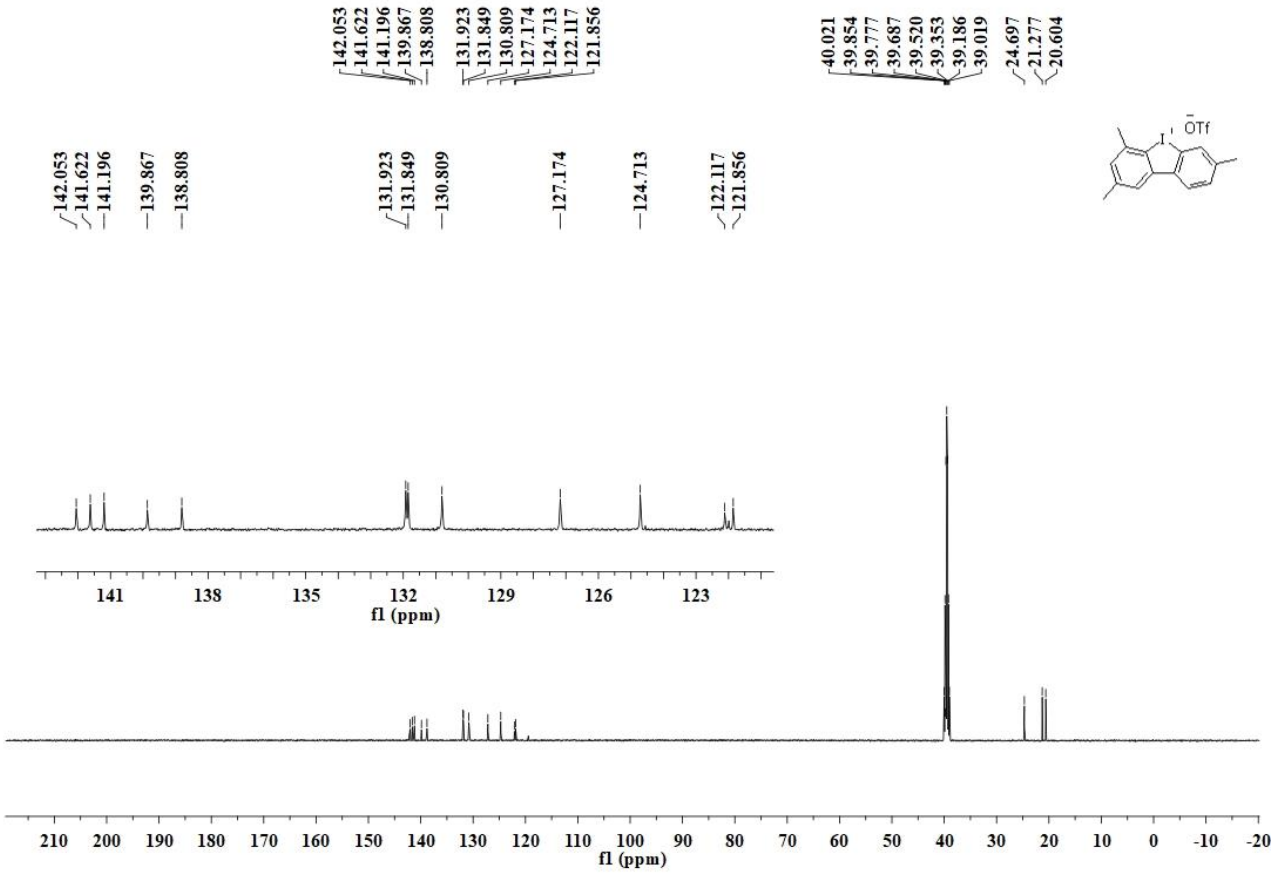
^{13}C NMR (125 MHz, DMSO-*d6*) of **2f**



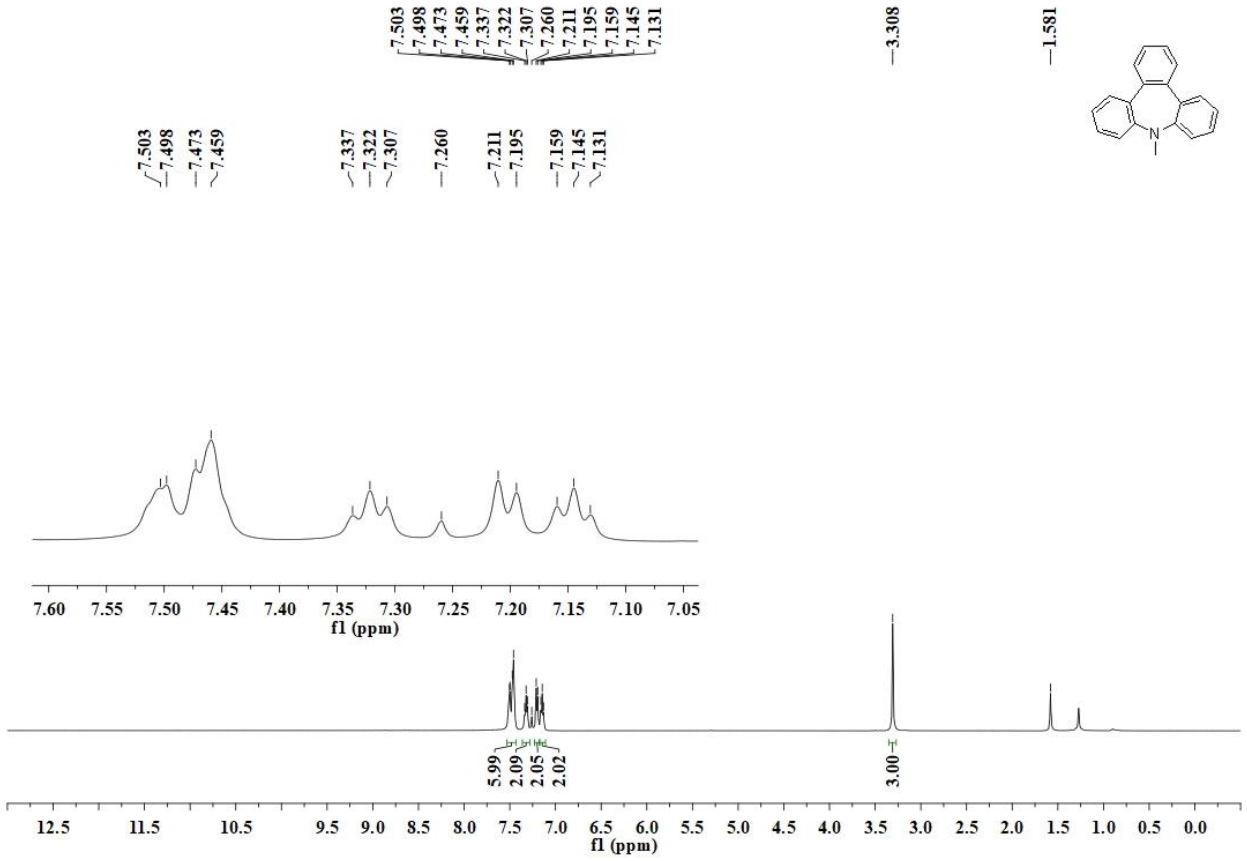
^{1}H NMR (500 MHz, DMSO-*d6*) of **2i**



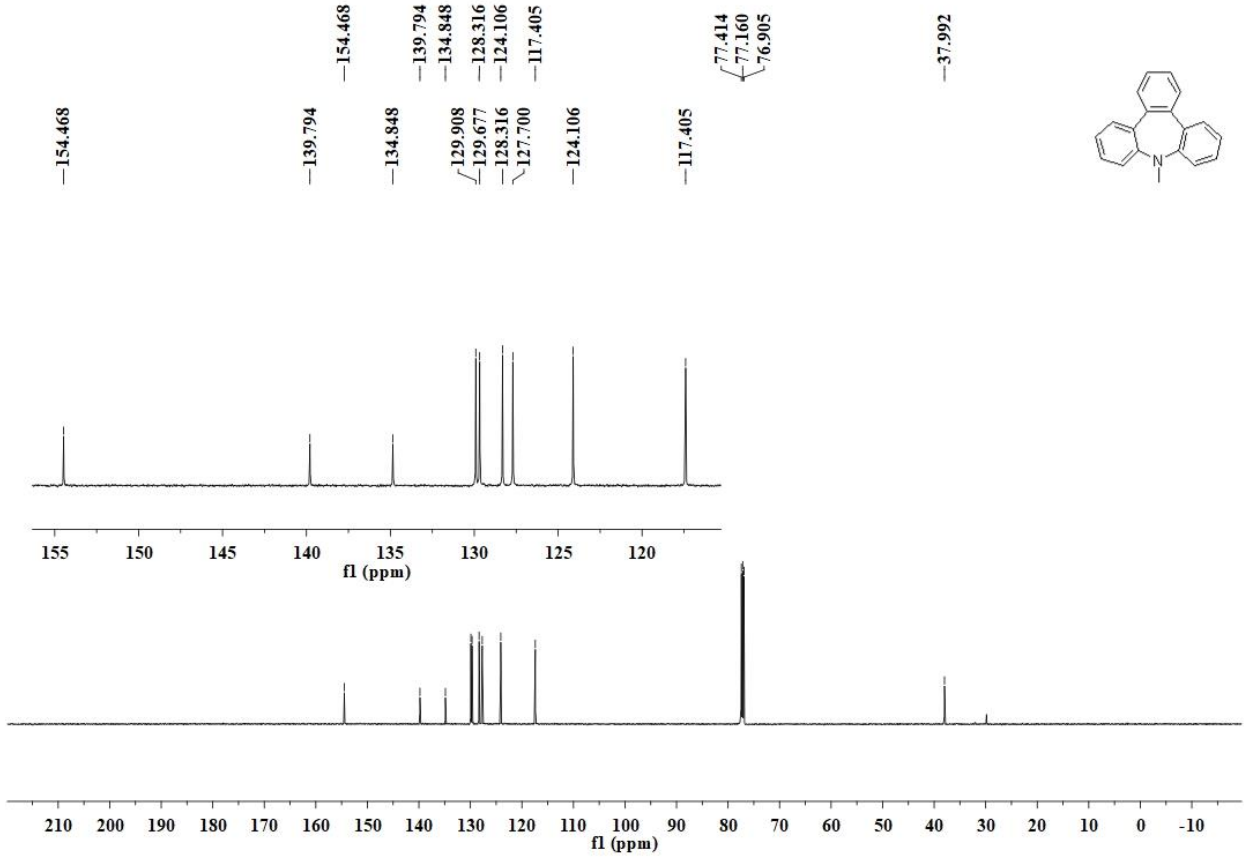
^{13}C NMR (125 MHz, DMSO-*d6*) of **2i**



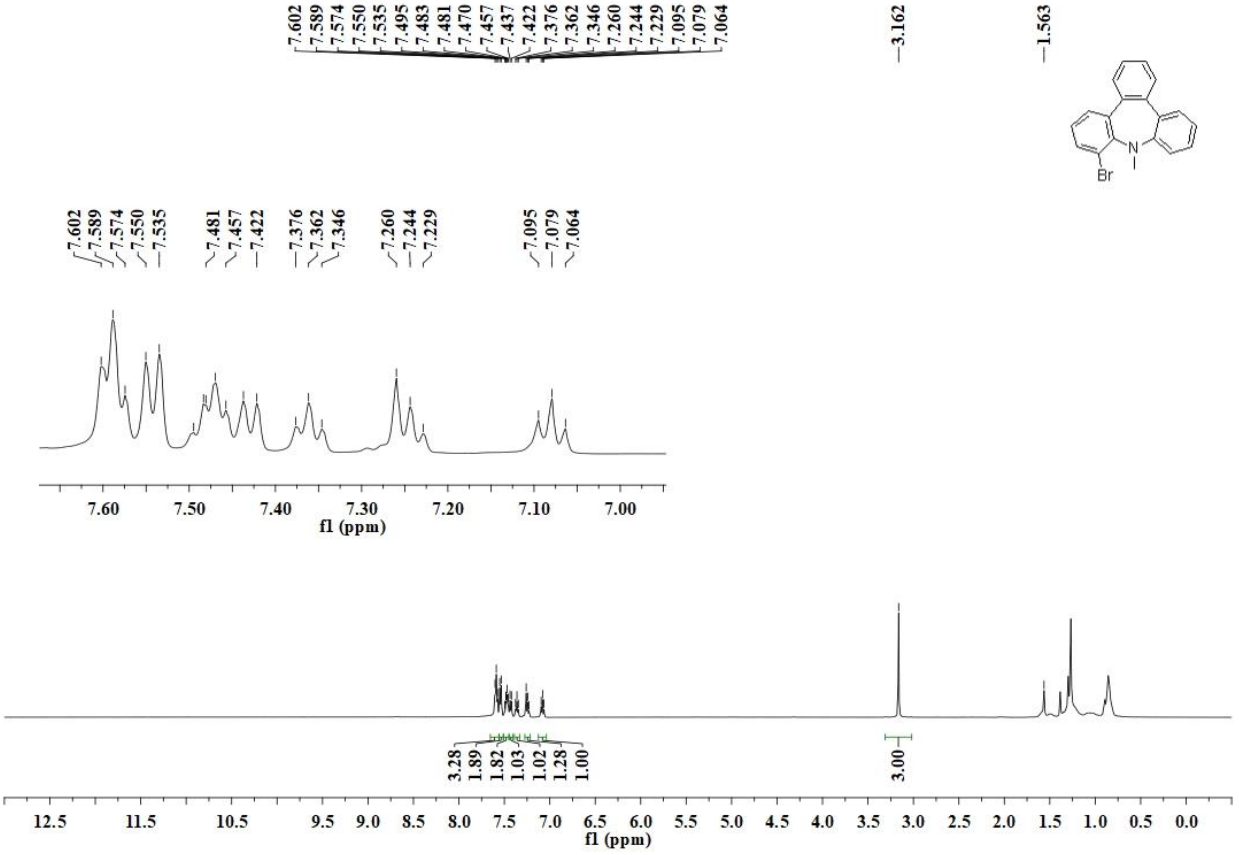
^{1}H NMR (500 MHz, $CDCl_3$) of **3a**



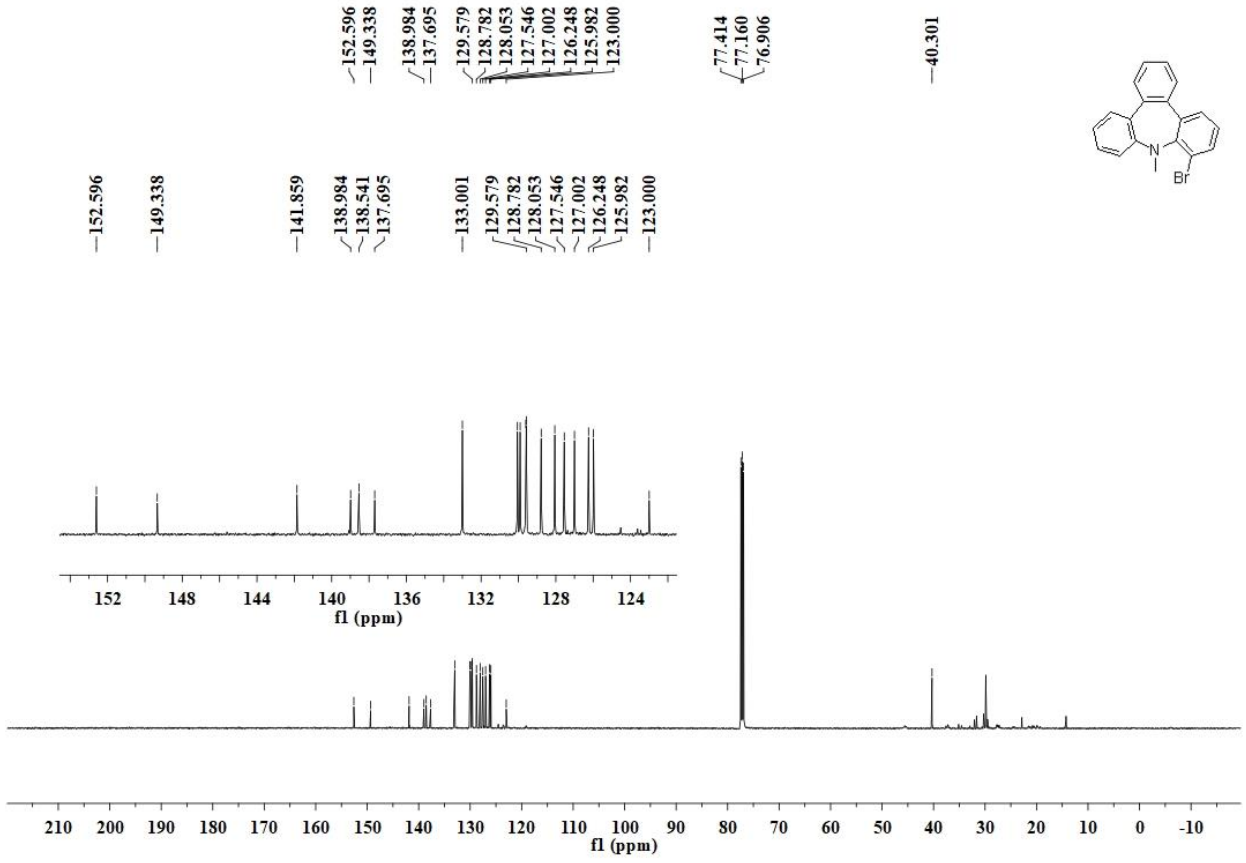
^{13}C NMR (125 MHz, $CDCl_3$) of **3a**



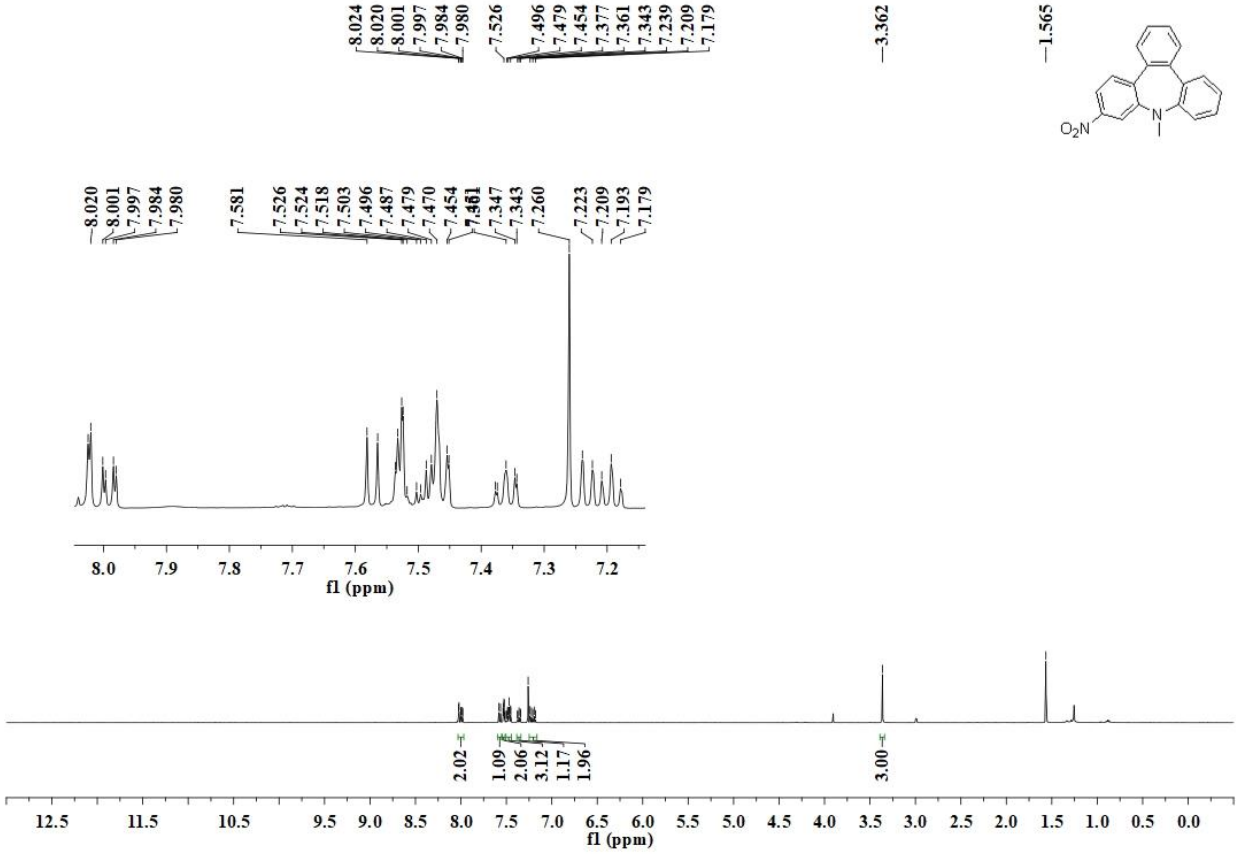
^{1}H NMR (500 MHz, $CDCl_3$) of **3b**



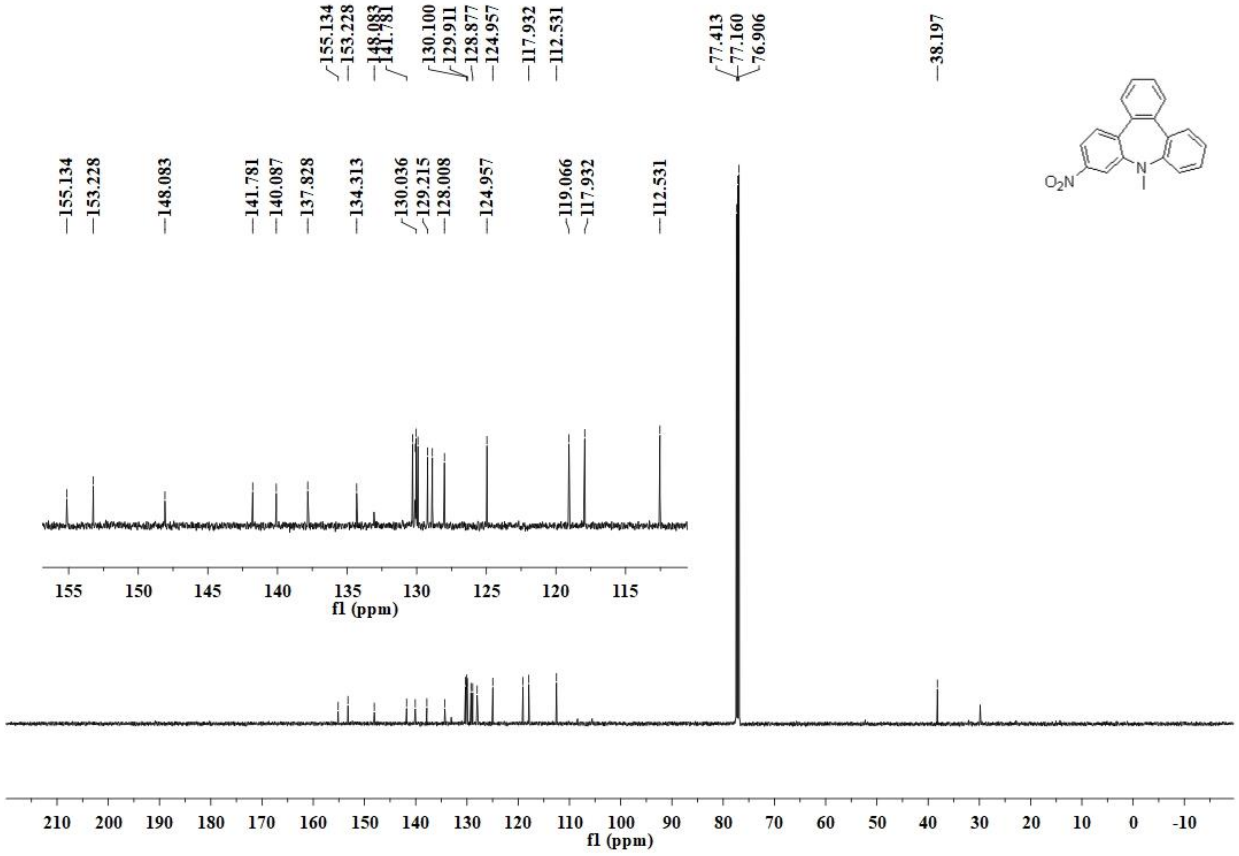
^{13}C NMR (125 MHz, $CDCl_3$) of **3b**



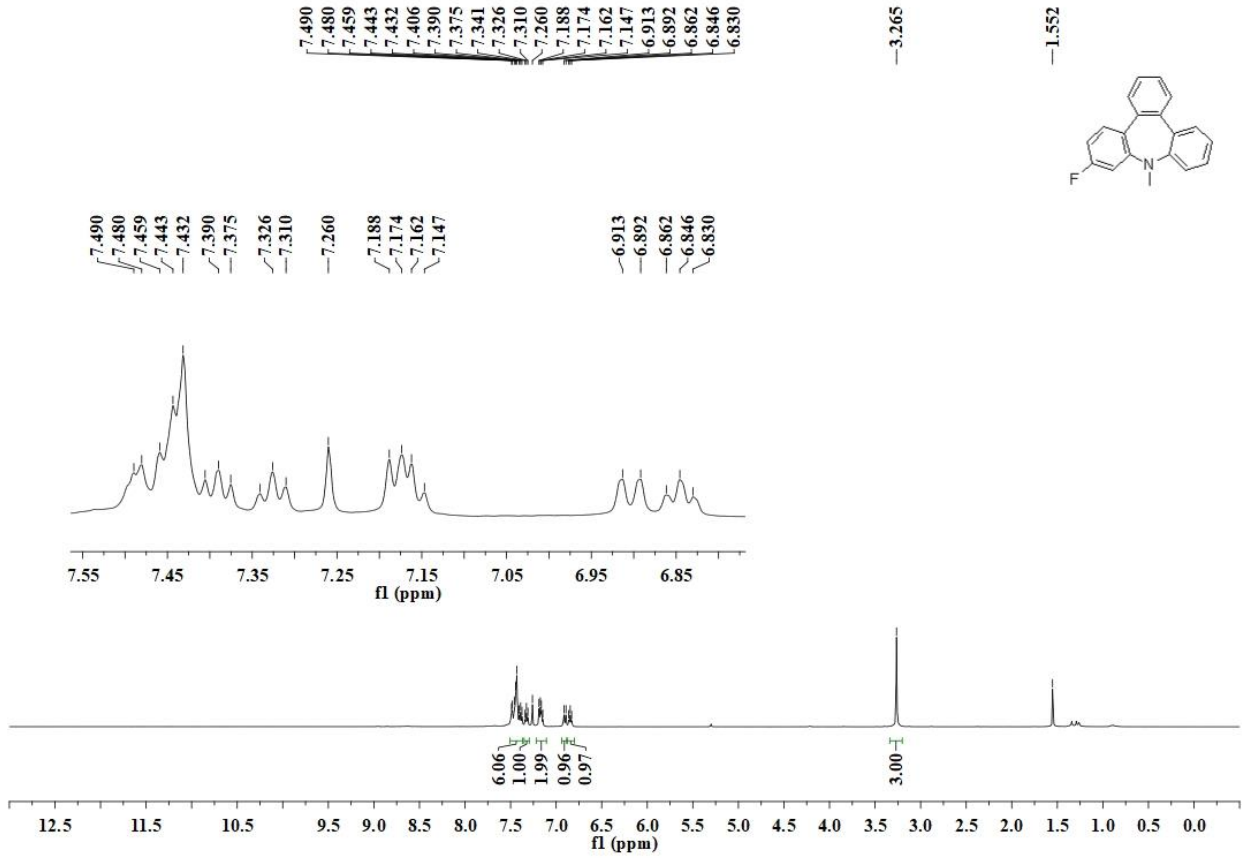
^{1}H NMR (500 MHz, $CDCl_3$) of **3c**



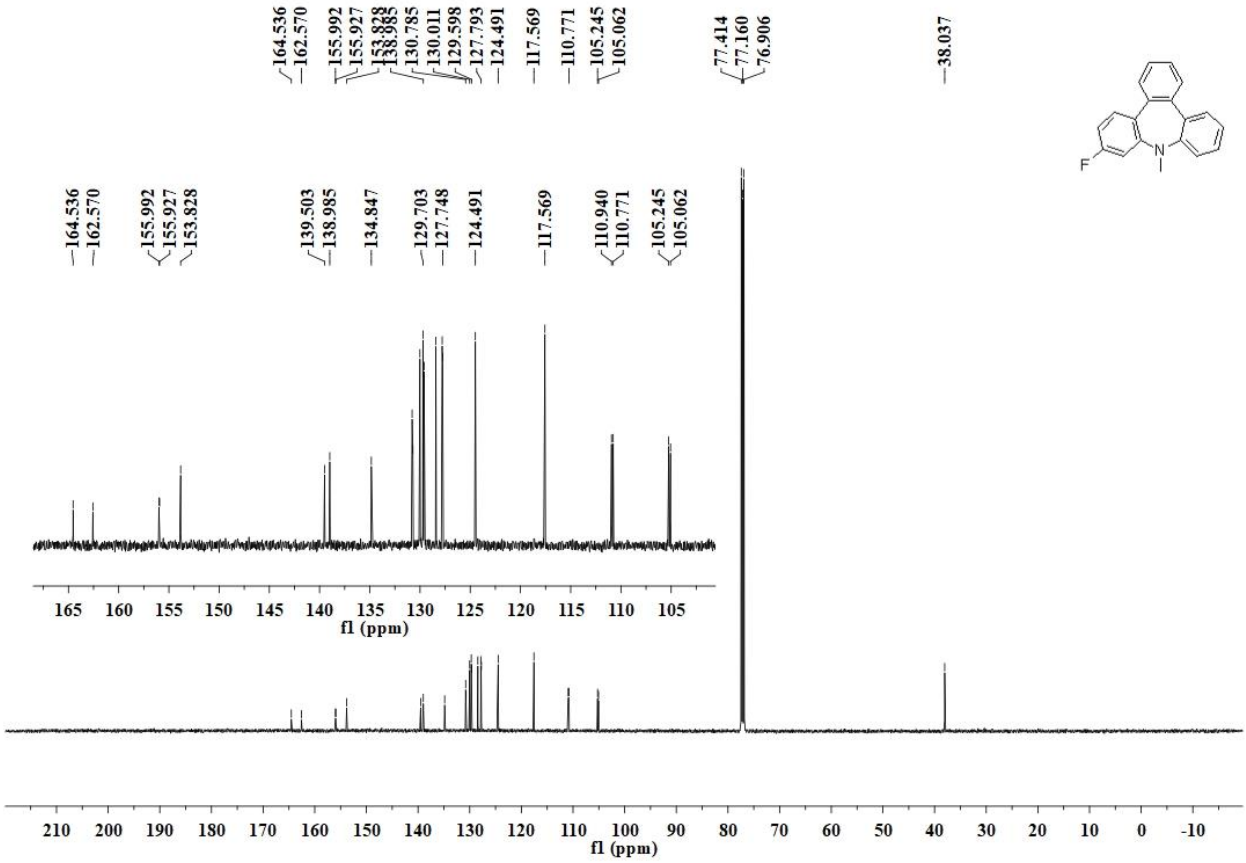
^{13}C NMR (125 MHz, $CDCl_3$) of **3c**



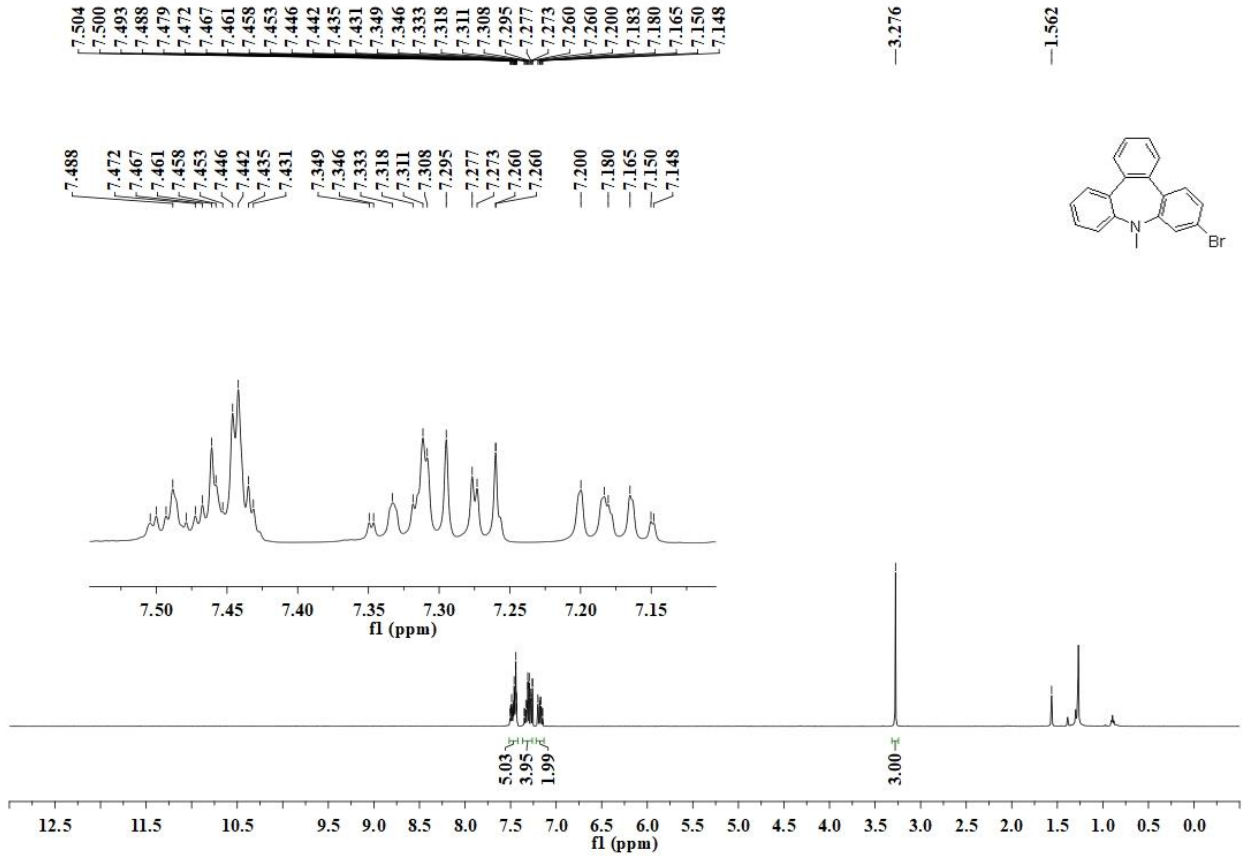
^{1}H NMR (500 MHz, $CDCl_3$) of **3d**



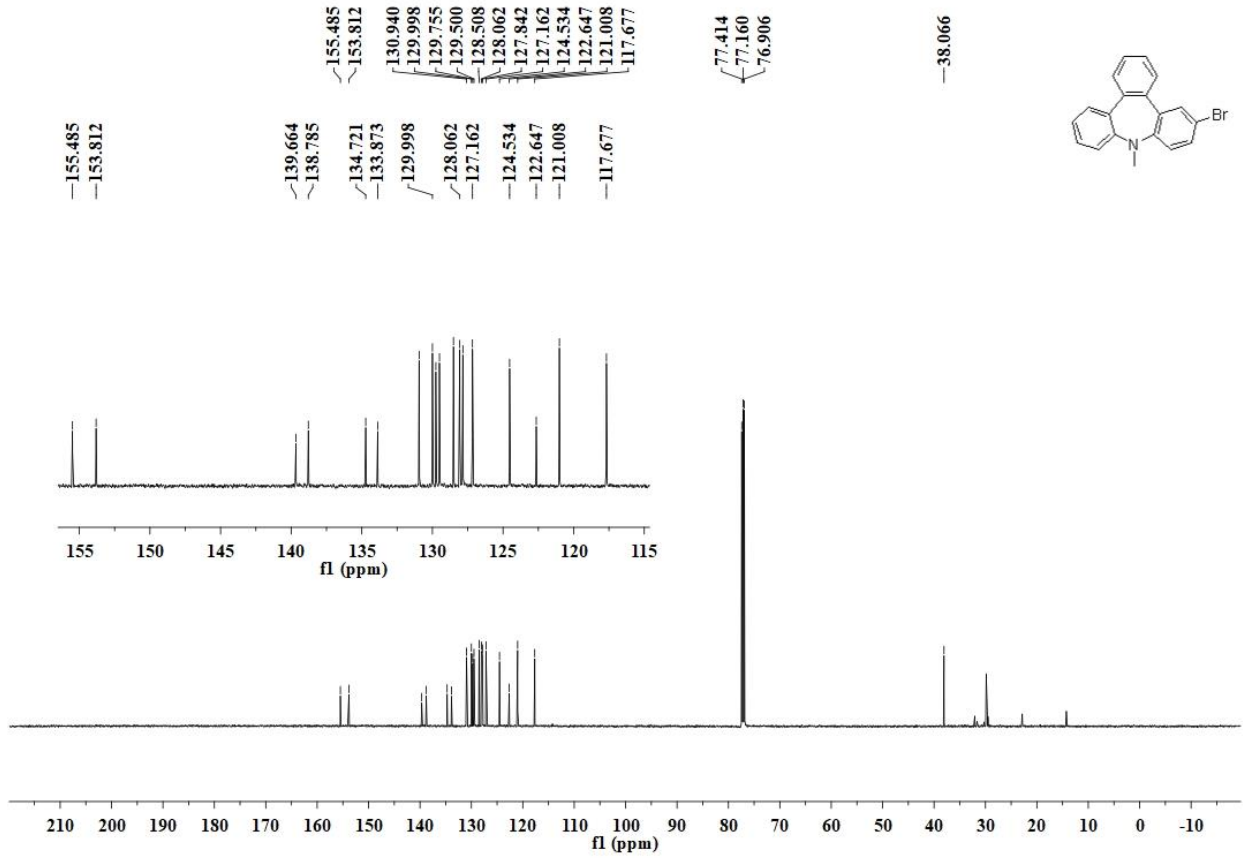
^{13}C NMR (125 MHz, $CDCl_3$) of **3d**



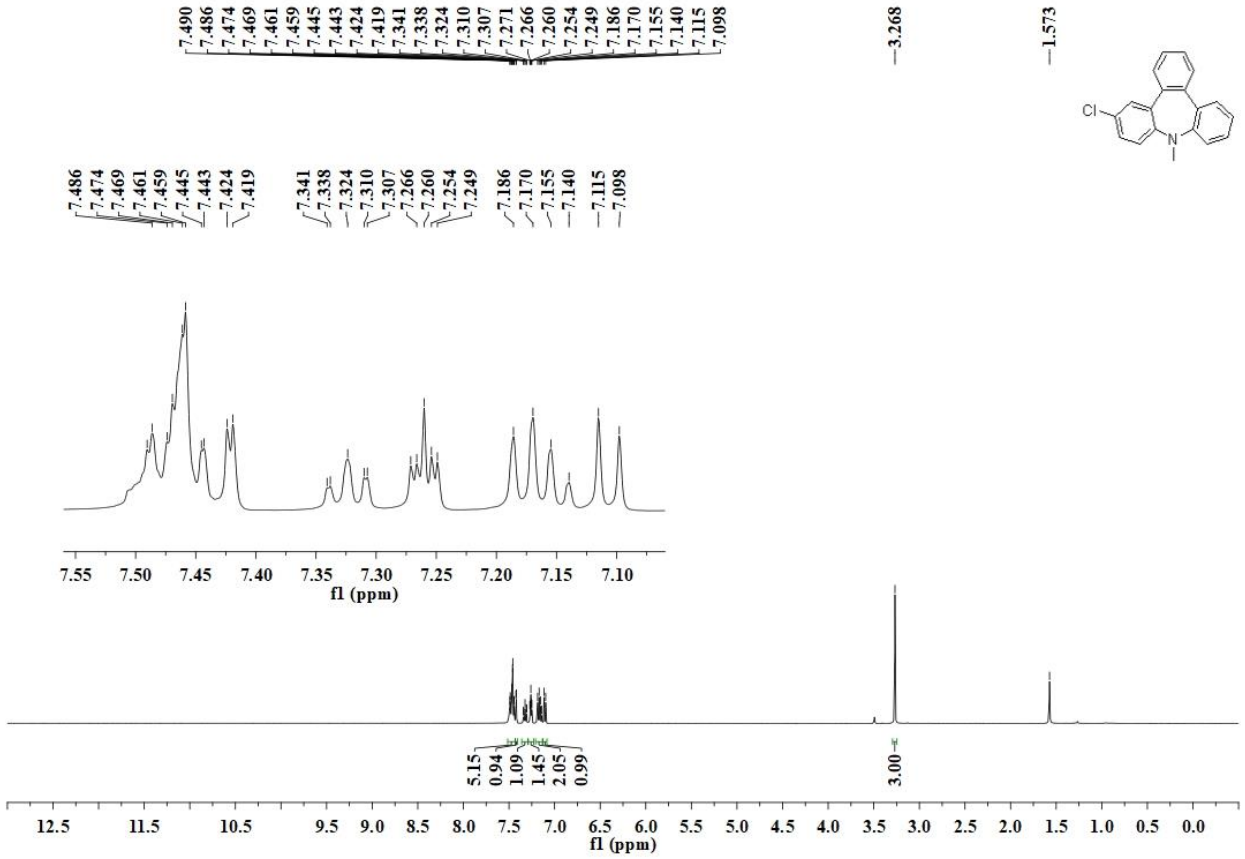
^{1}H NMR (500 MHz, $CDCl_3$) of **3e**



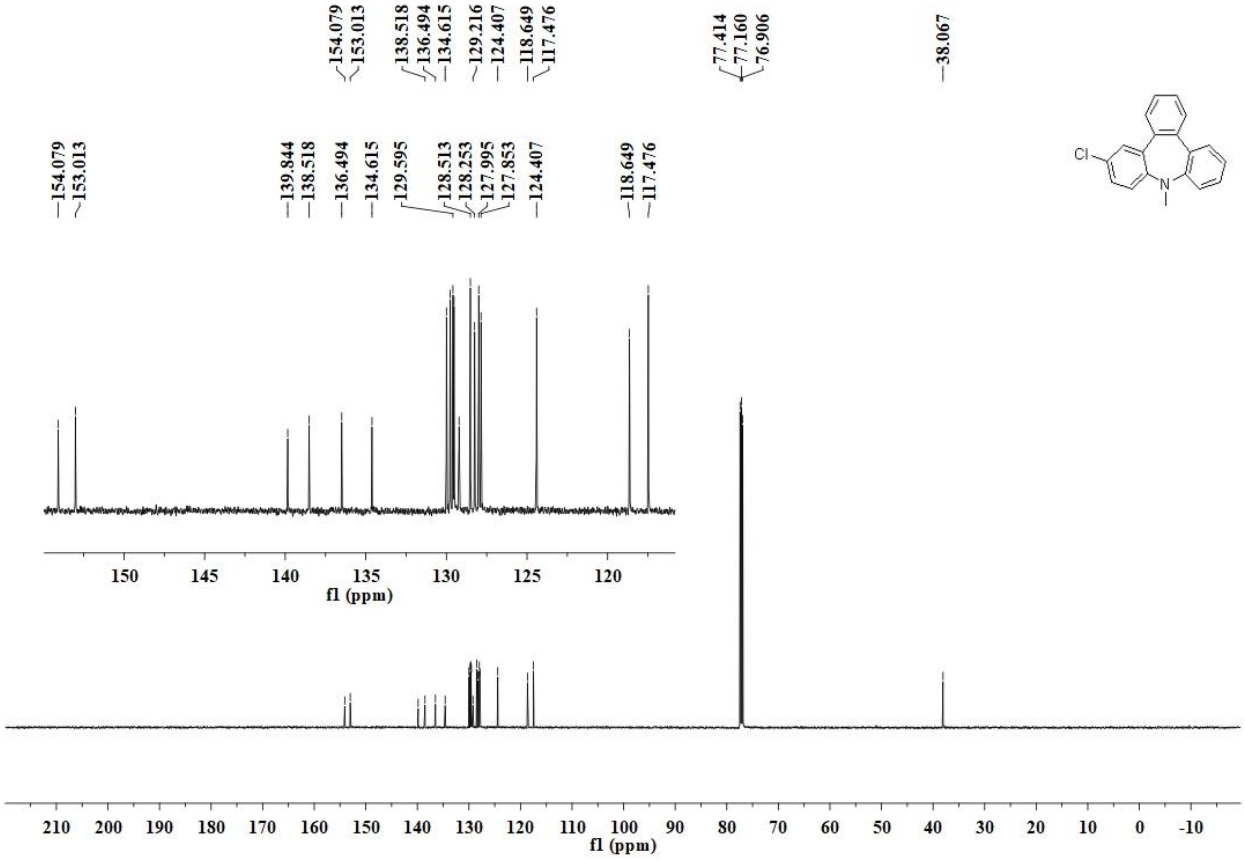
^{13}C NMR (125 MHz, $CDCl_3$) of **3e**



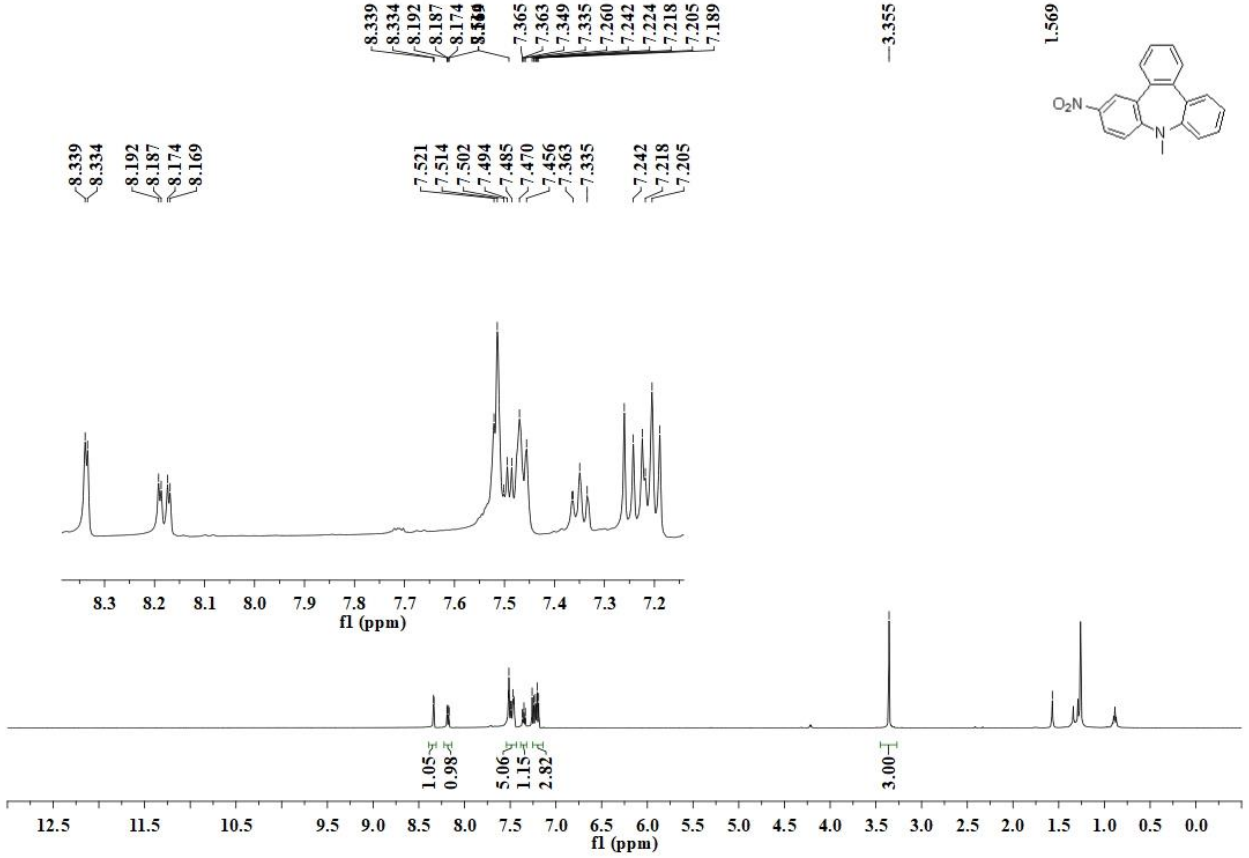
^{1}H NMR (500 MHz, $CDCl_3$) of **3f**



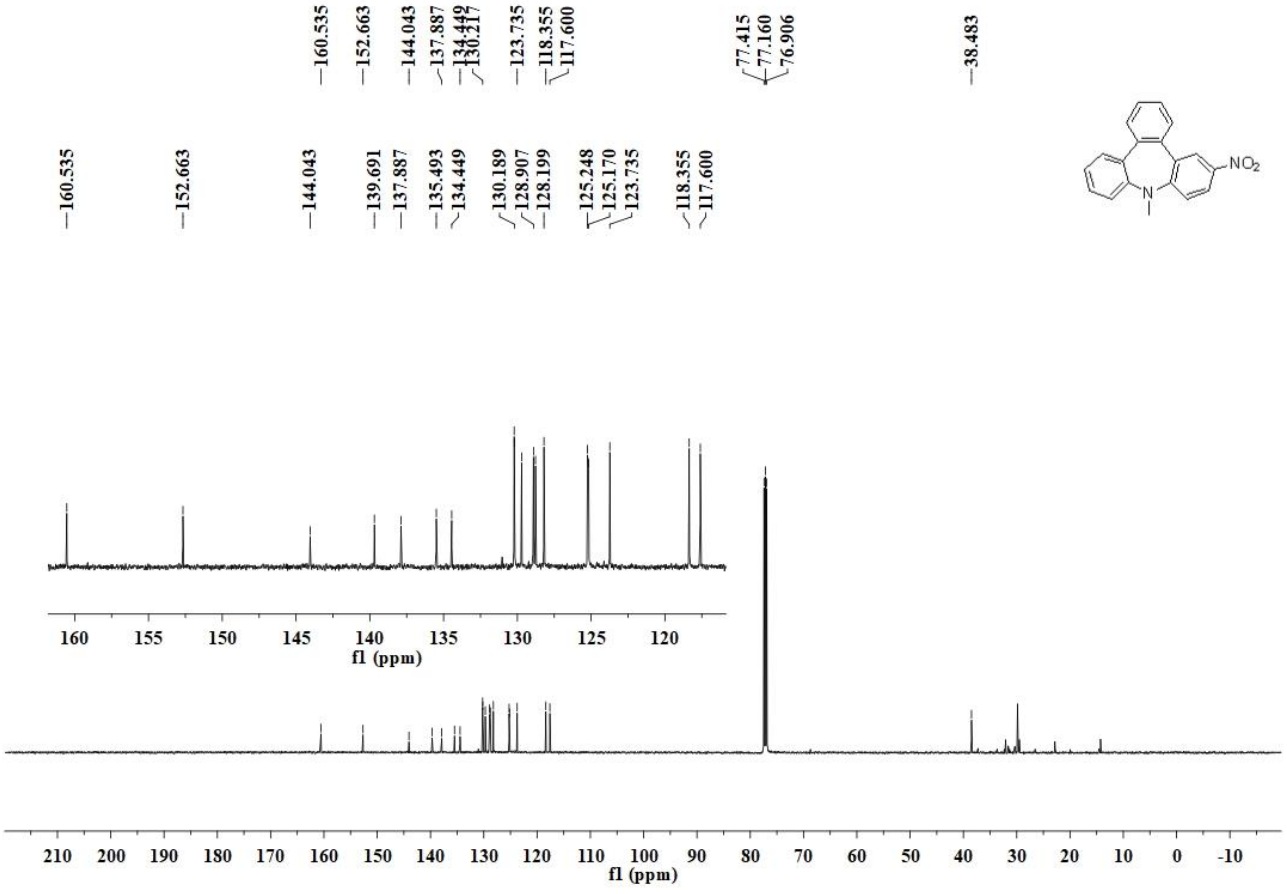
^{13}C NMR (125 MHz, $CDCl_3$) of **3f**



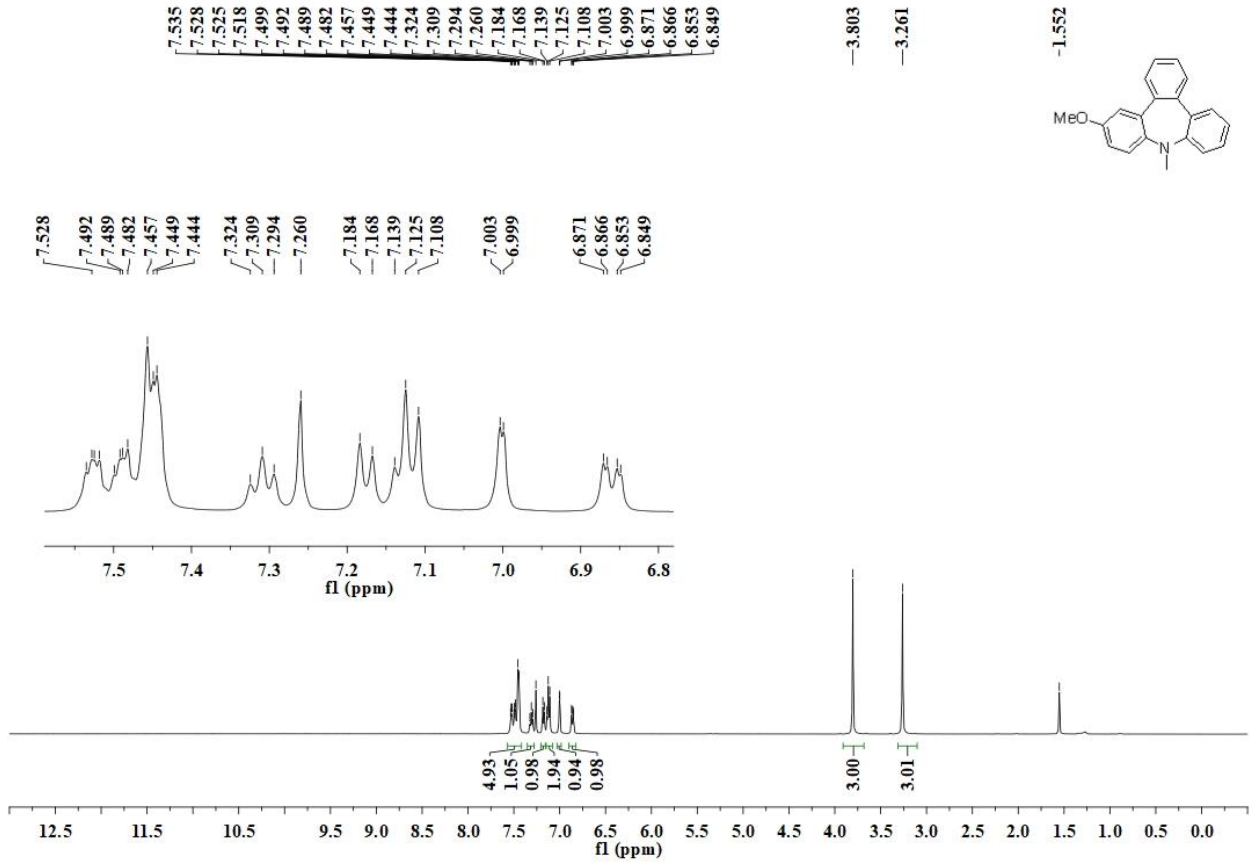
^{1}H NMR (500 MHz, $CDCl_3$) of **3g**



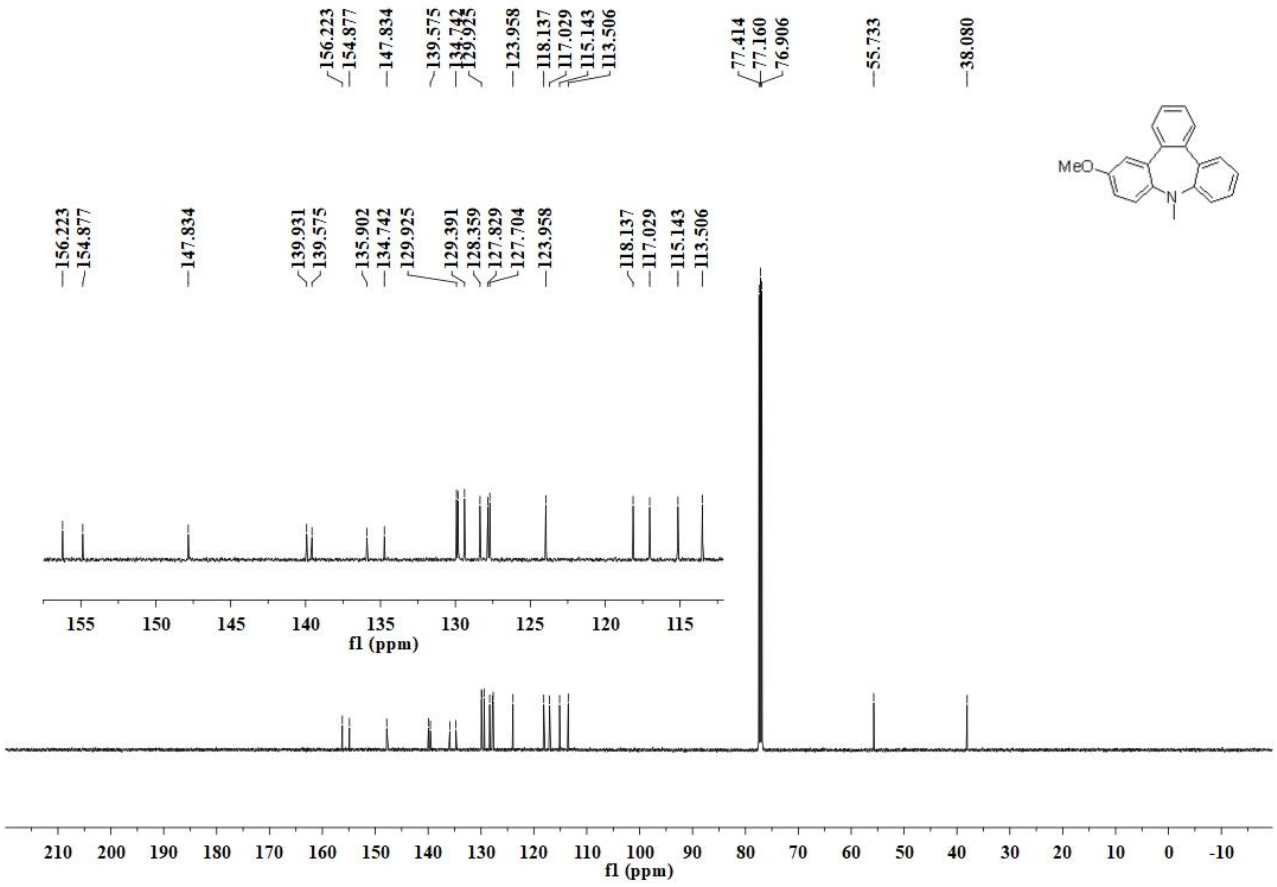
^{13}C NMR (125 MHz, $CDCl_3$) of **3g**



^{1}H NMR (500 MHz, $CDCl_3$) of **3h**



^{13}C NMR (125 MHz, $CDCl_3$) of **3h**



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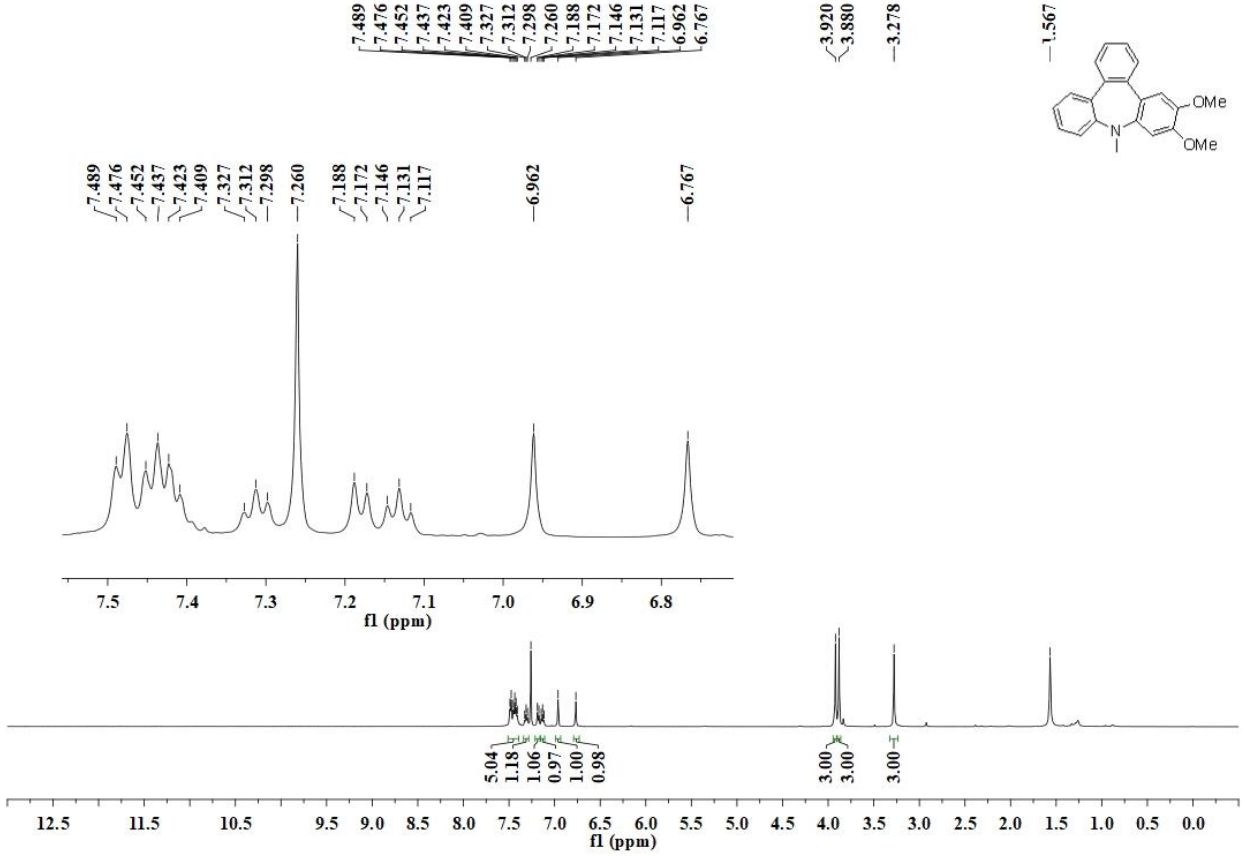
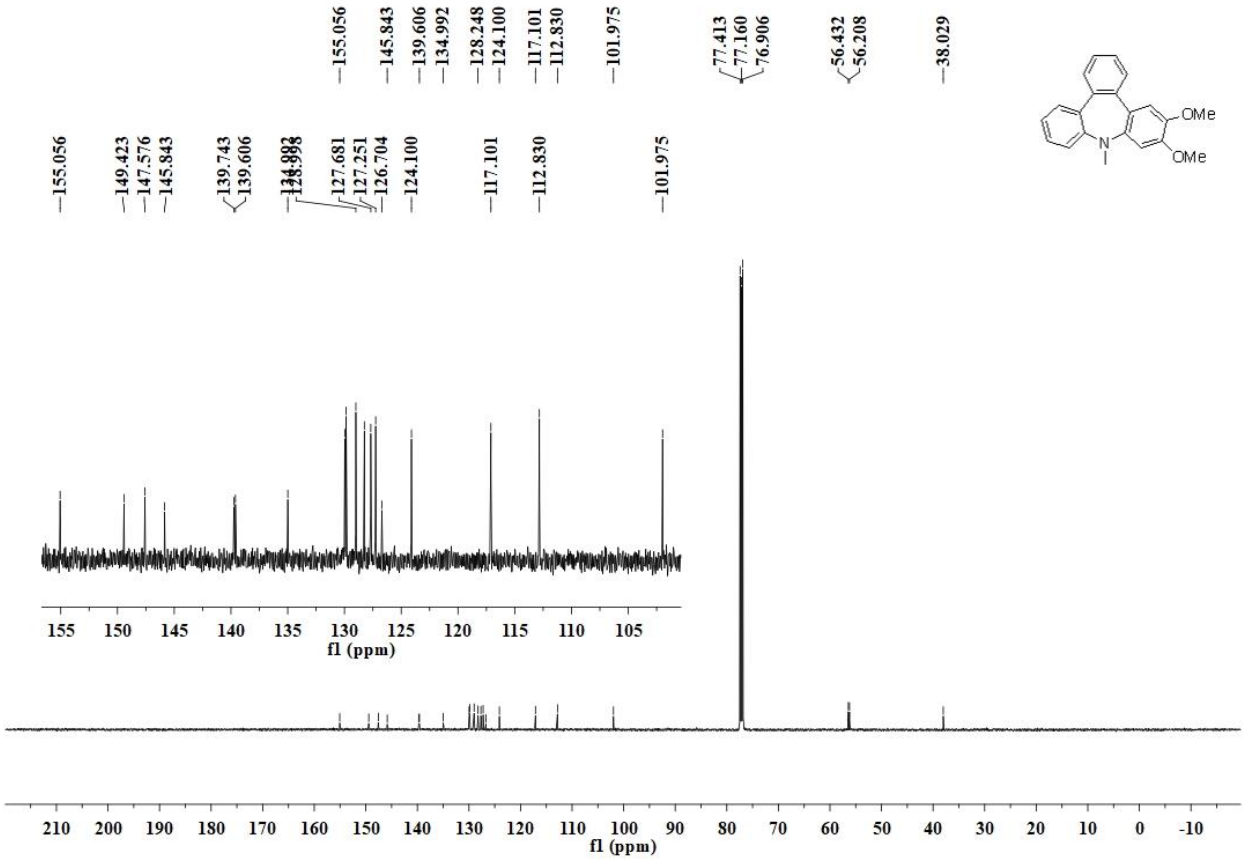
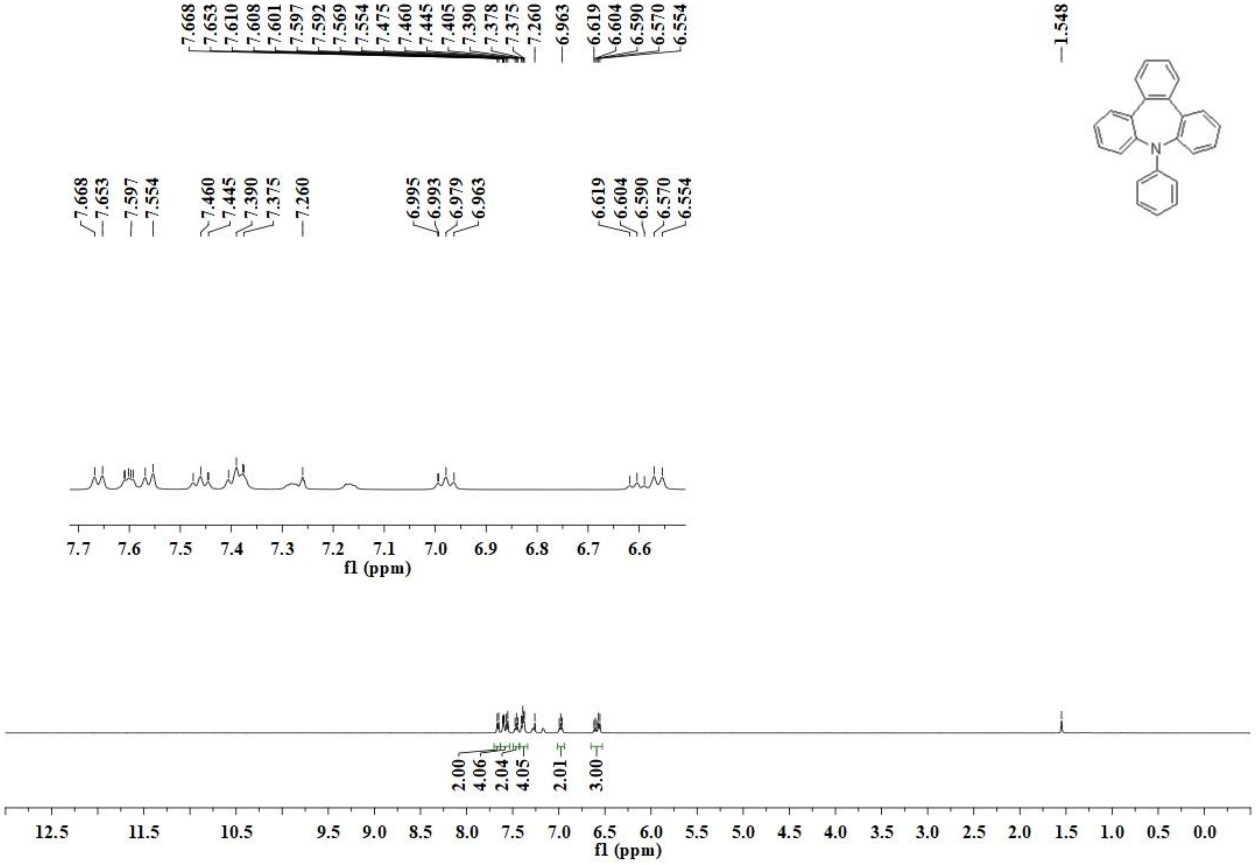


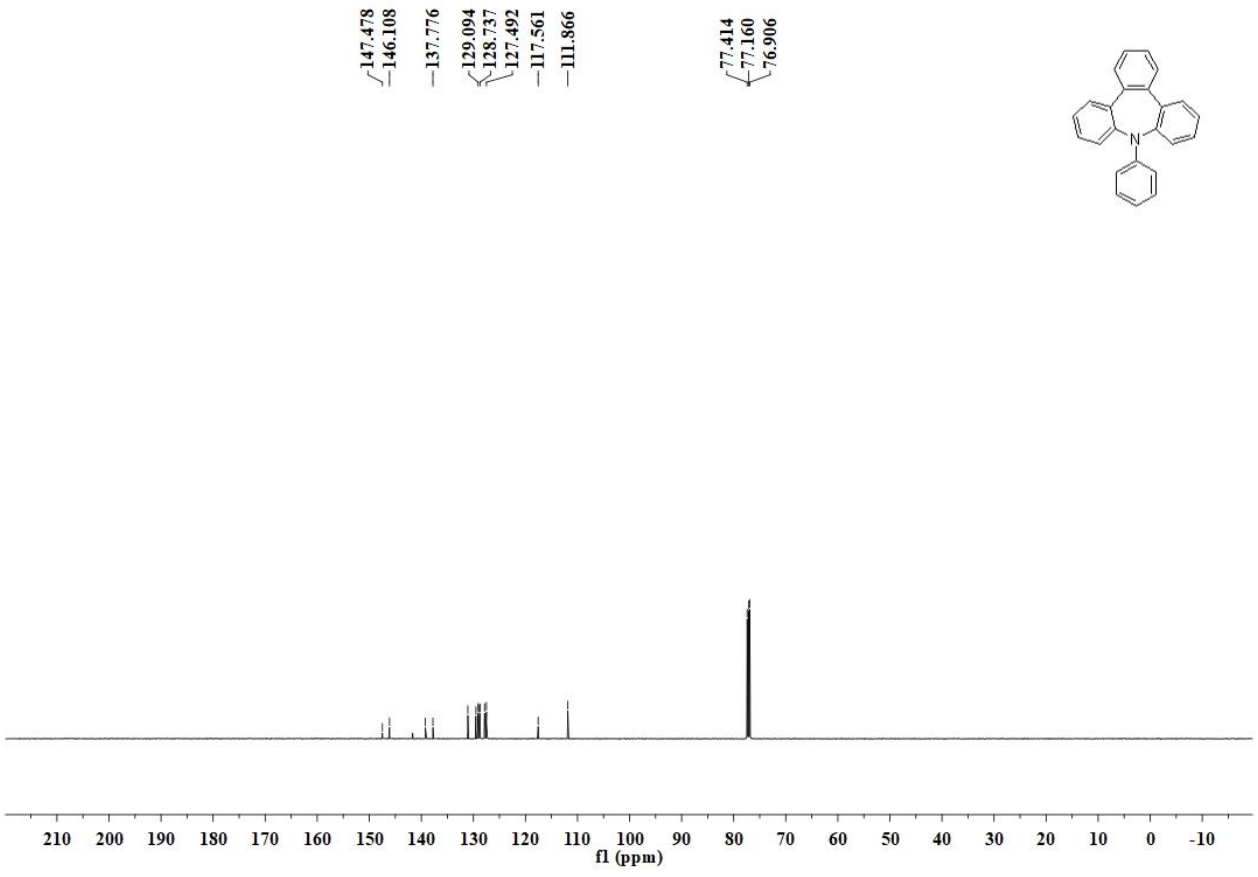
^{13}C NMR (125 MHz, $CDCl_3$) of **3i**



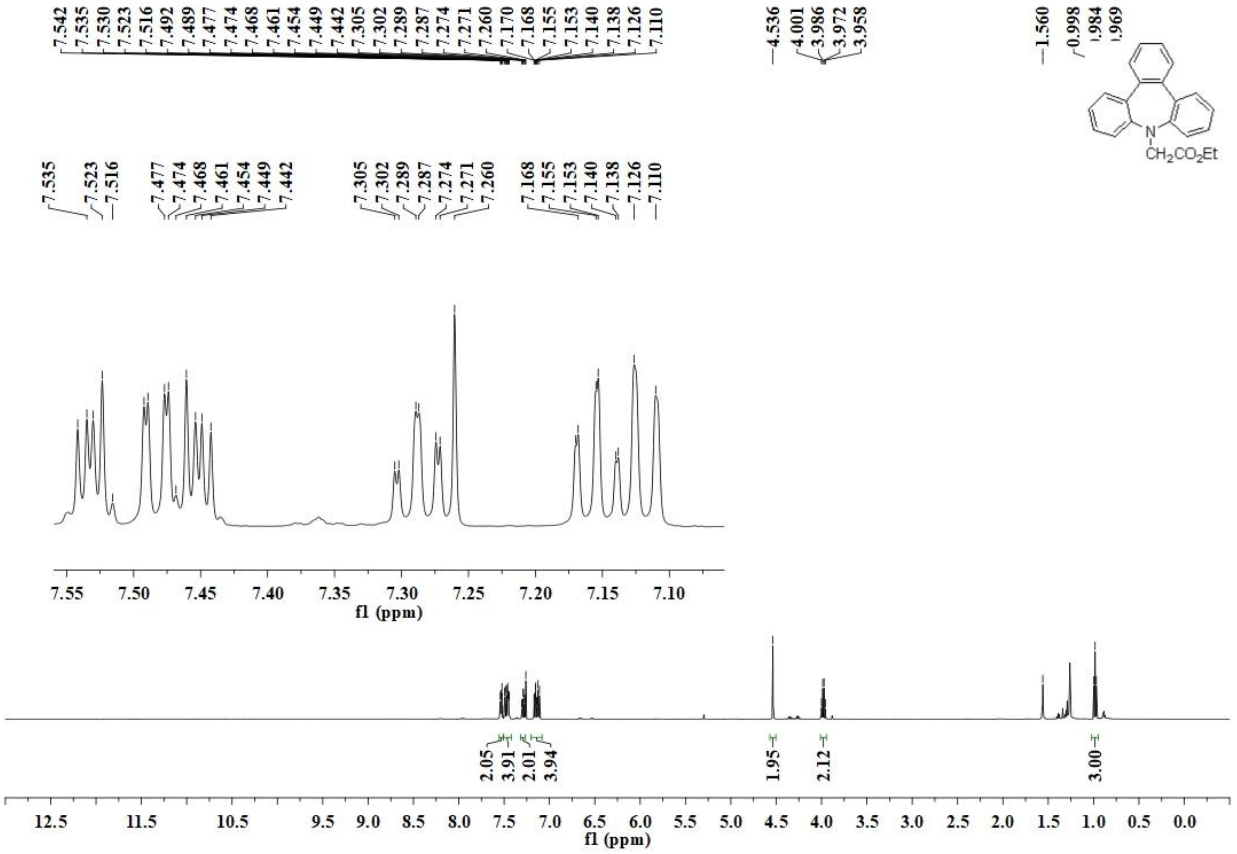
^{1}H NMR (500 MHz, $CDCl_3$) of **3j**



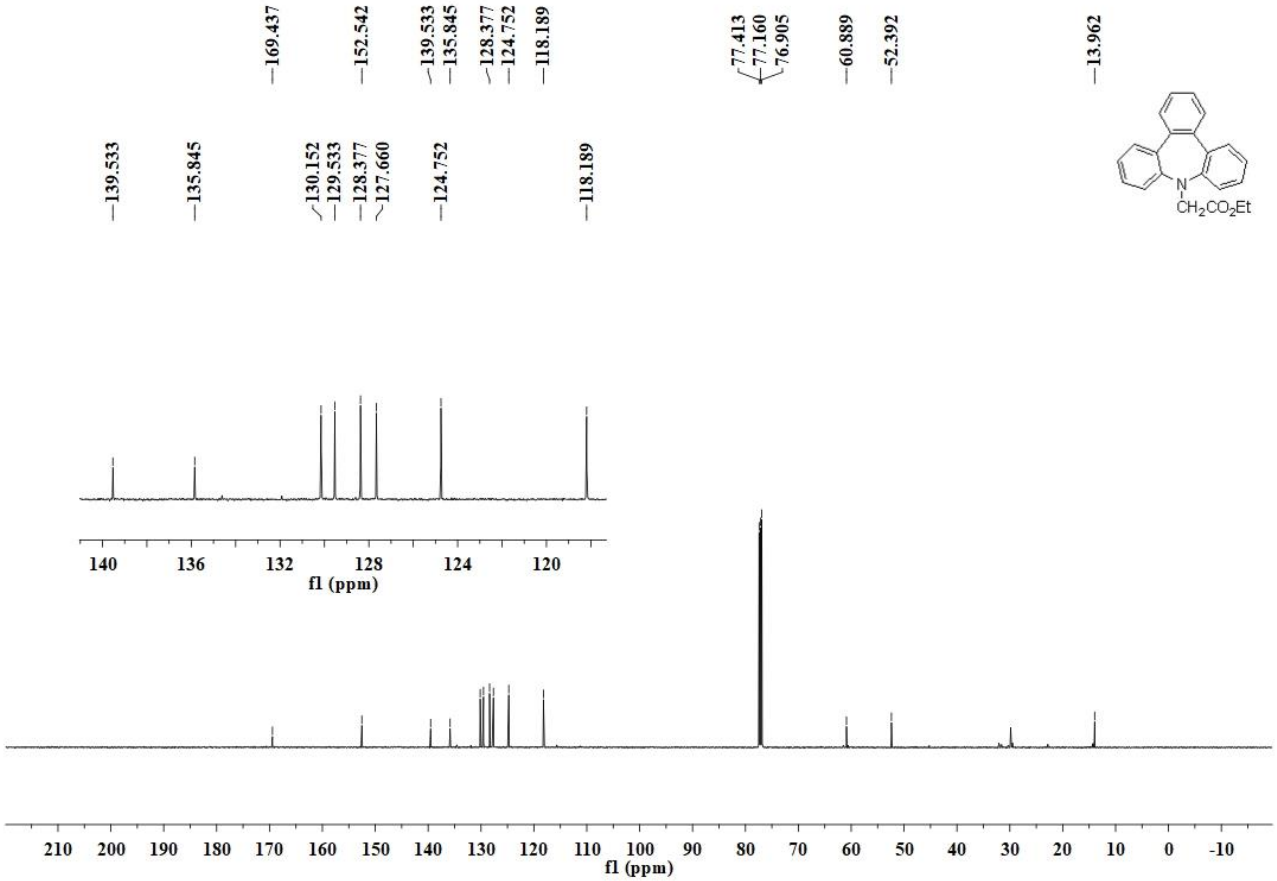
^{13}C NMR (125 MHz, $CDCl_3$) of **3j**



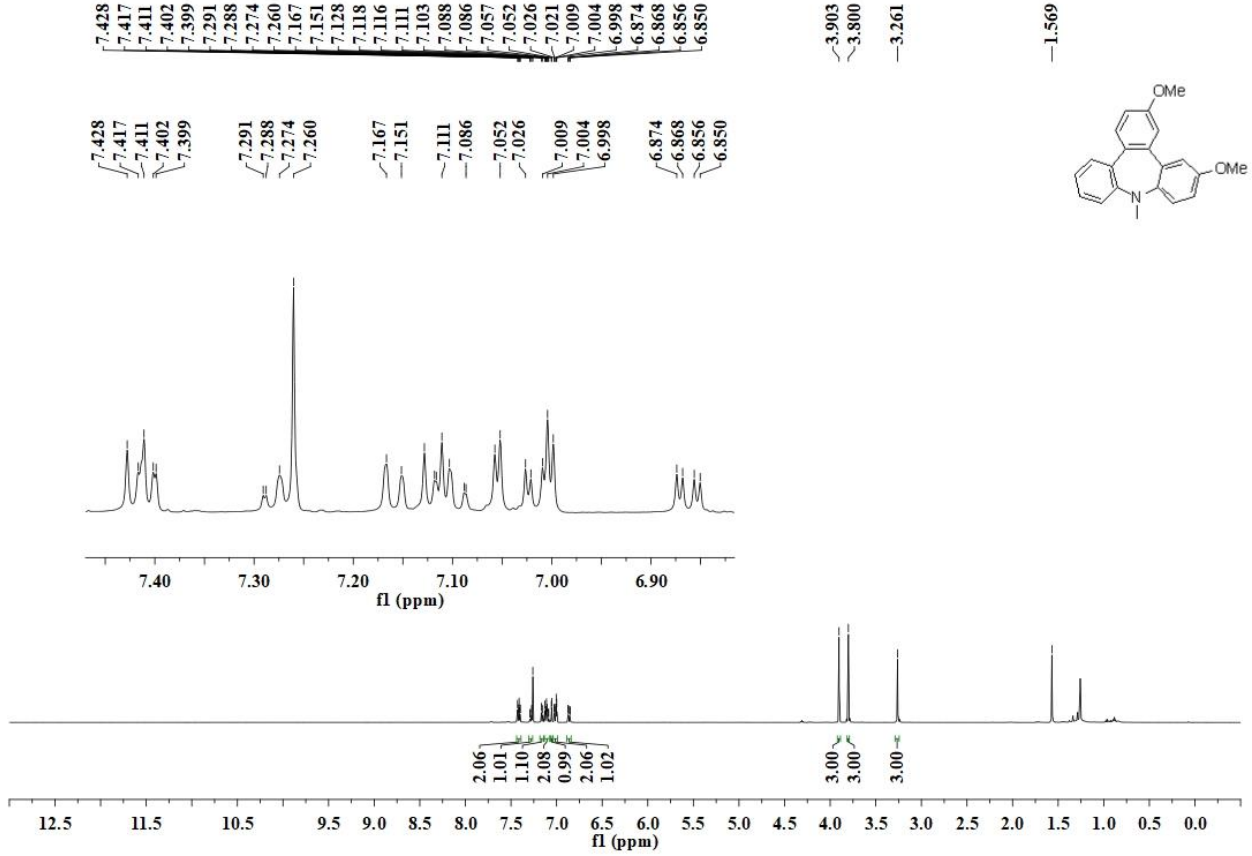
^{1}H NMR (500 MHz, $CDCl_3$) of **3k**



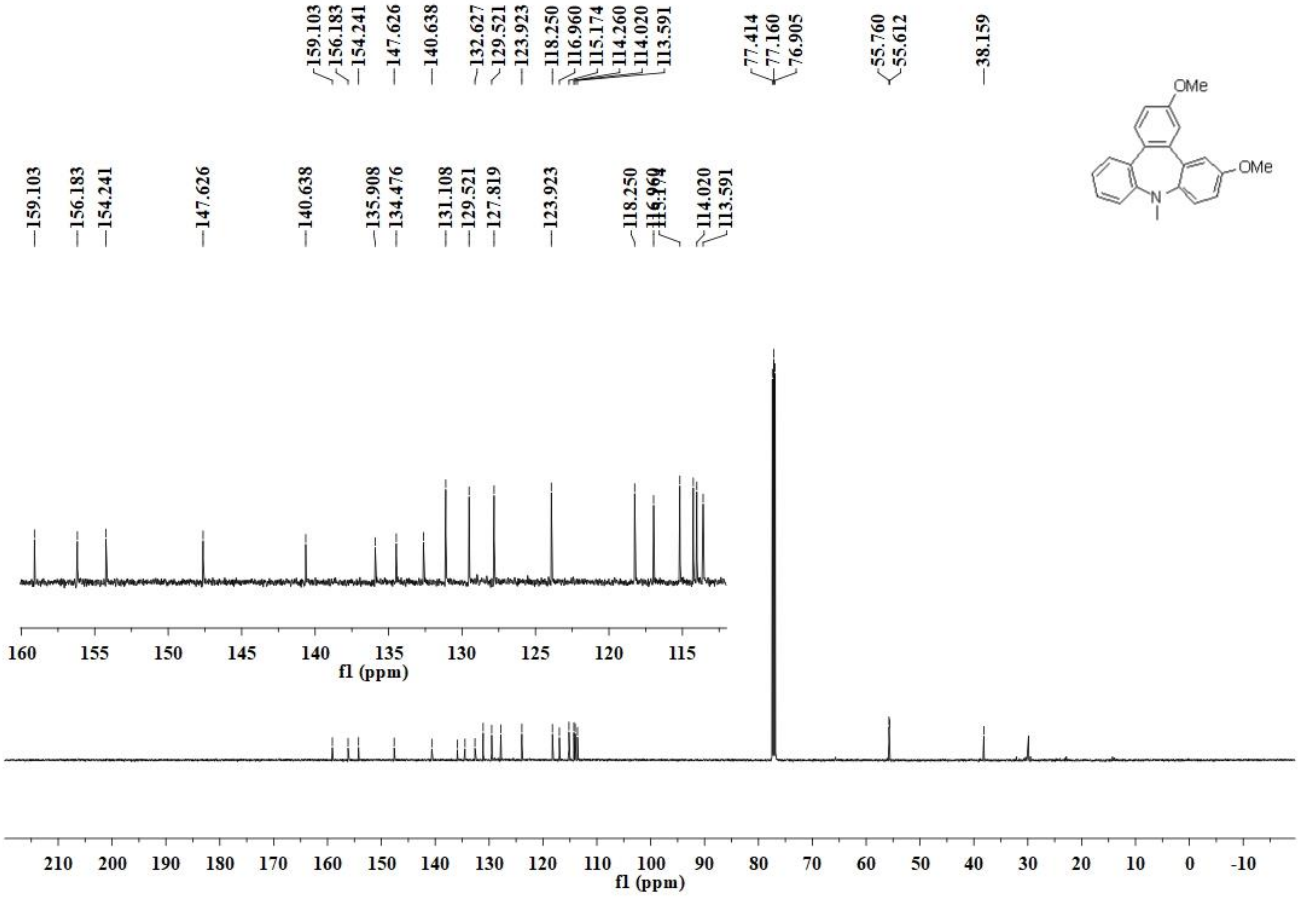
^{13}C NMR (125 MHz, $CDCl_3$) of **3k**



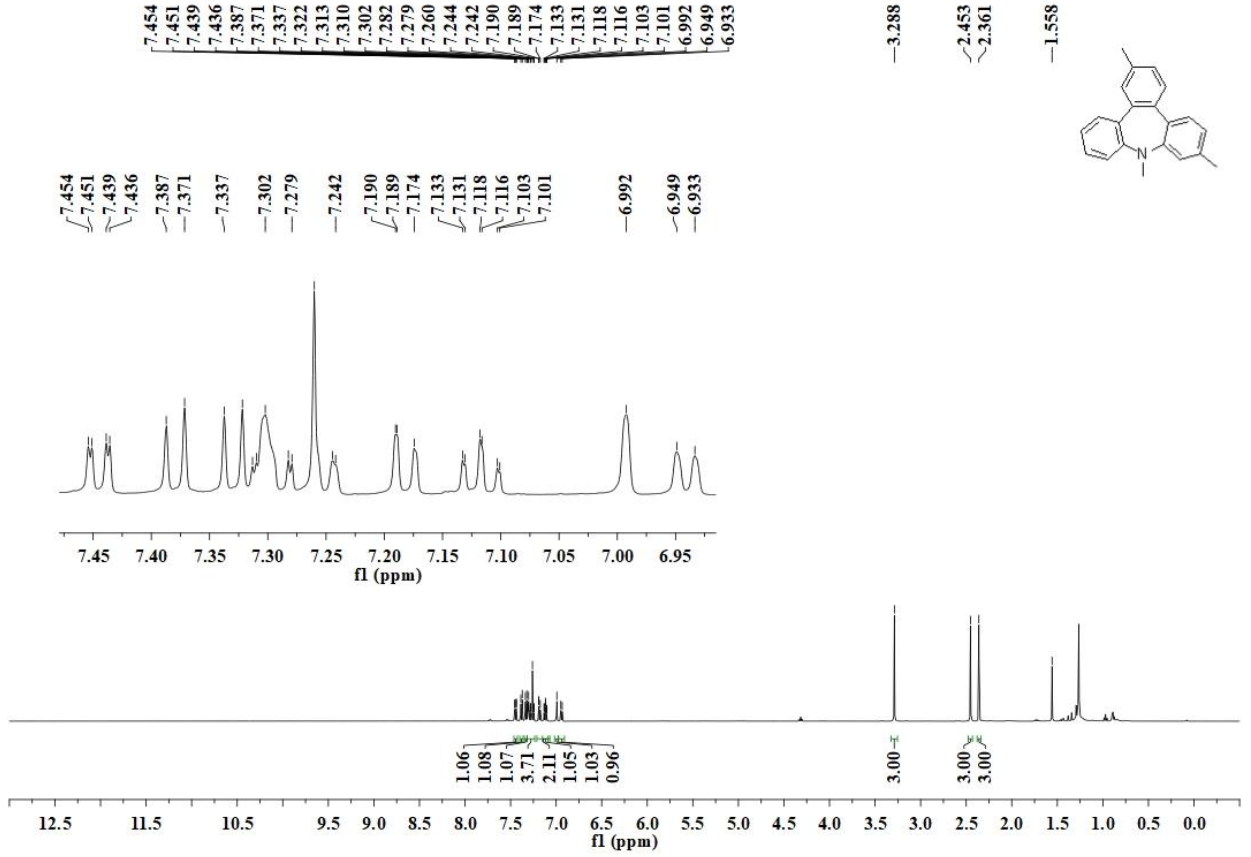
^{1}H NMR (500 MHz, $CDCl_3$) of **4a**



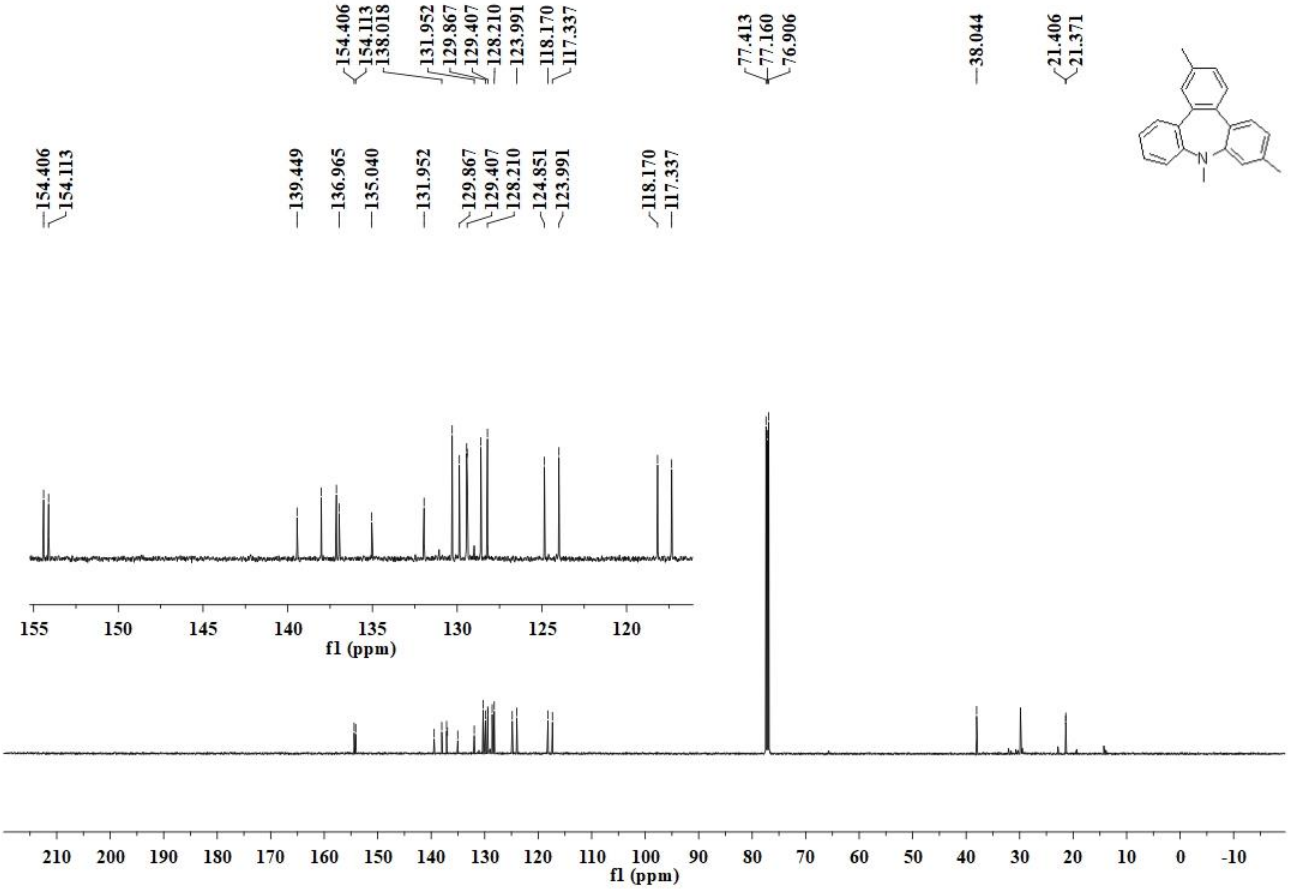
^{13}C NMR (125 MHz, $CDCl_3$) of **4a**



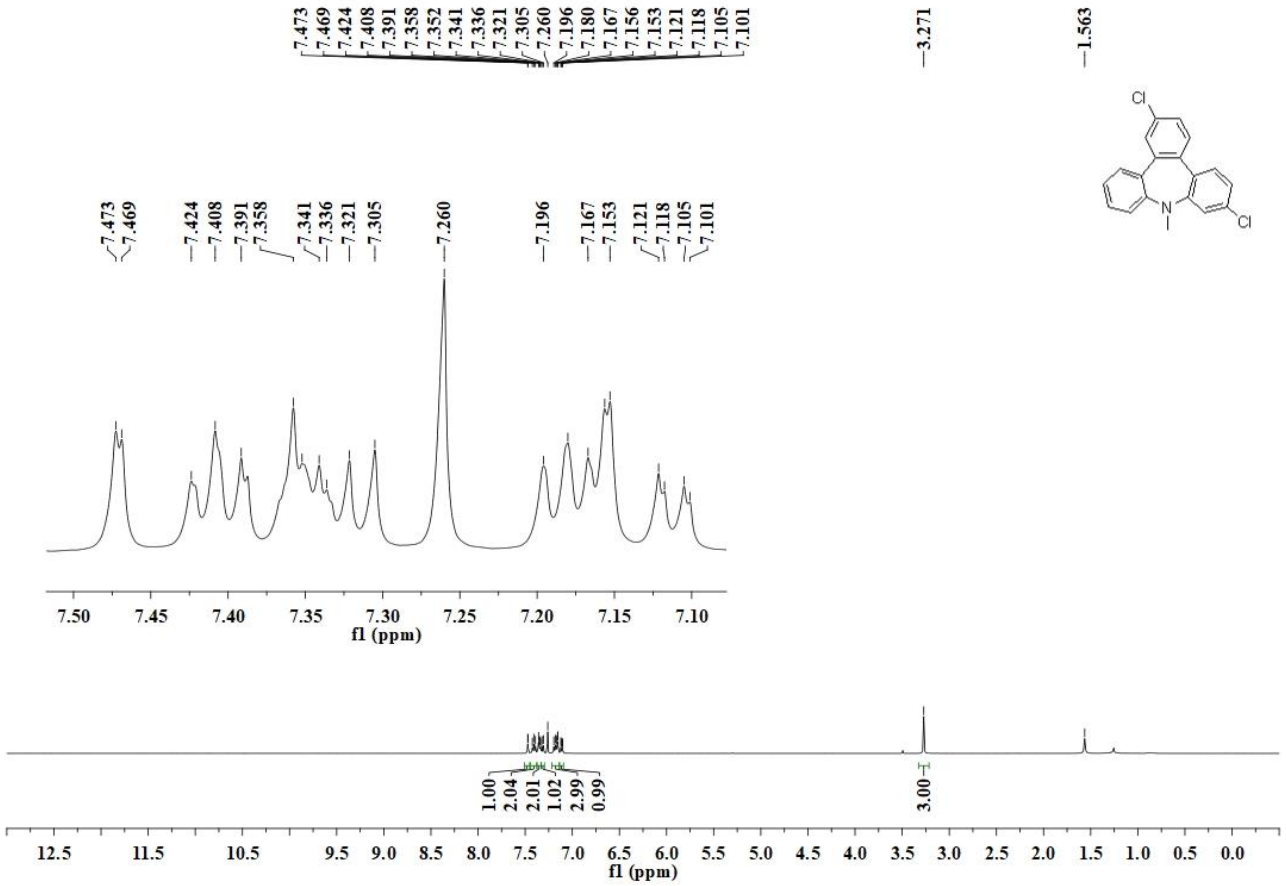
^{1}H NMR (500 MHz, $CDCl_3$) of **4b**



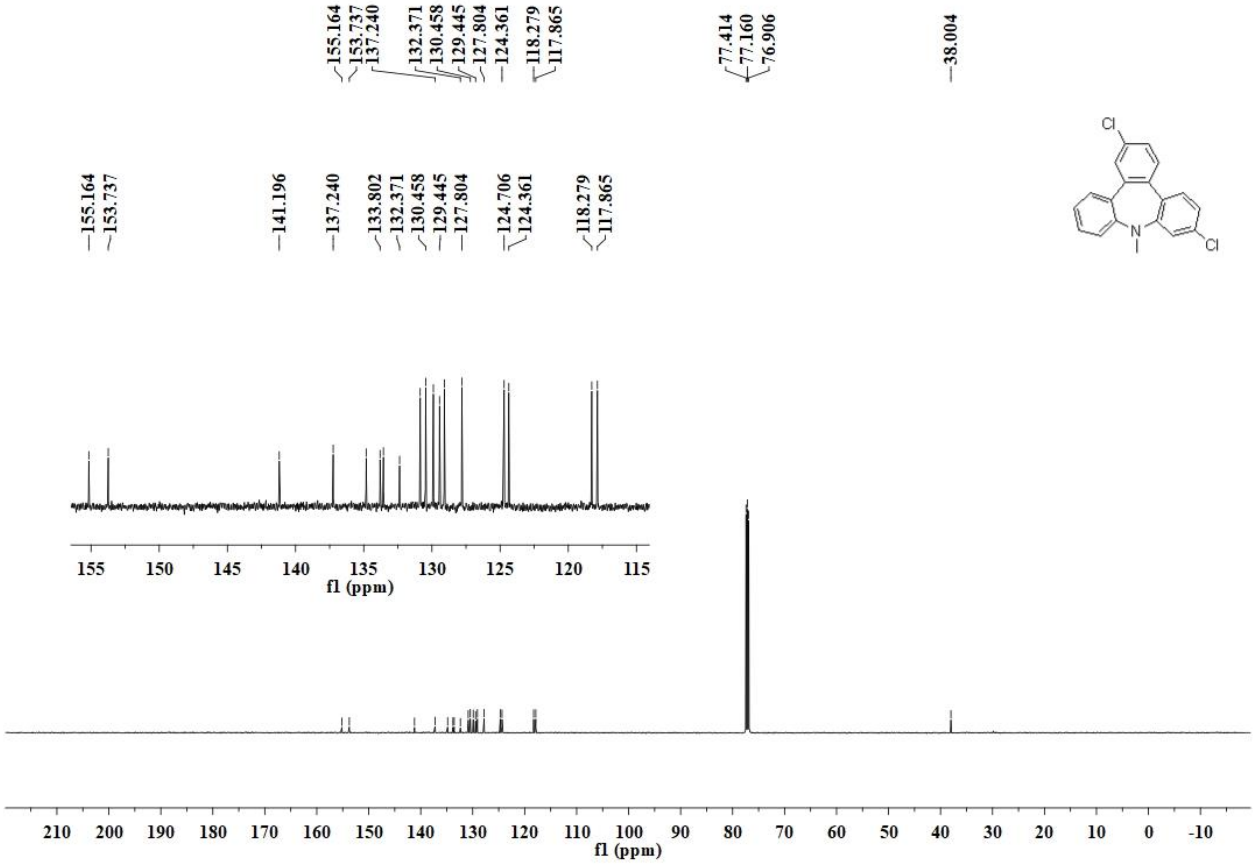
^{13}C NMR (125 MHz, $CDCl_3$) of **4b**



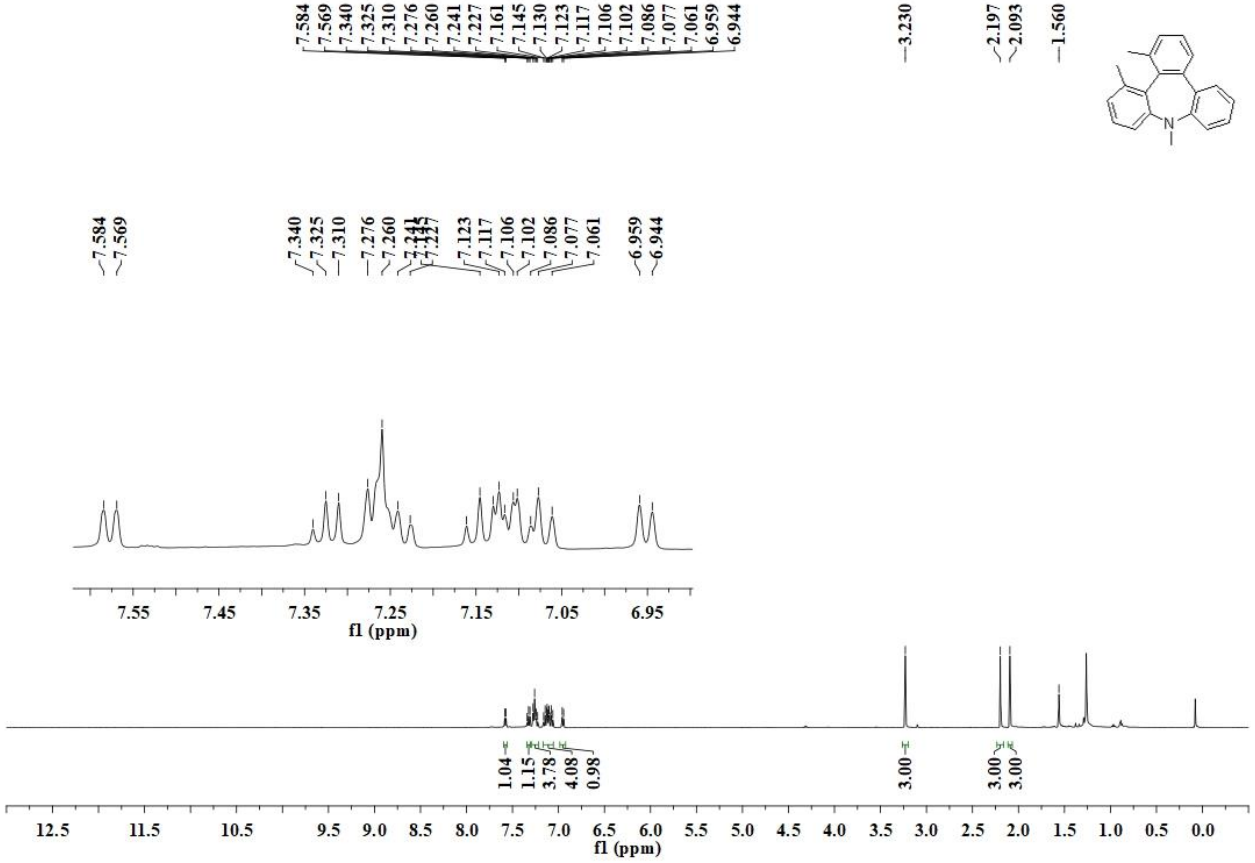
^{1}H NMR (500 MHz, $CDCl_3$) of **4c**



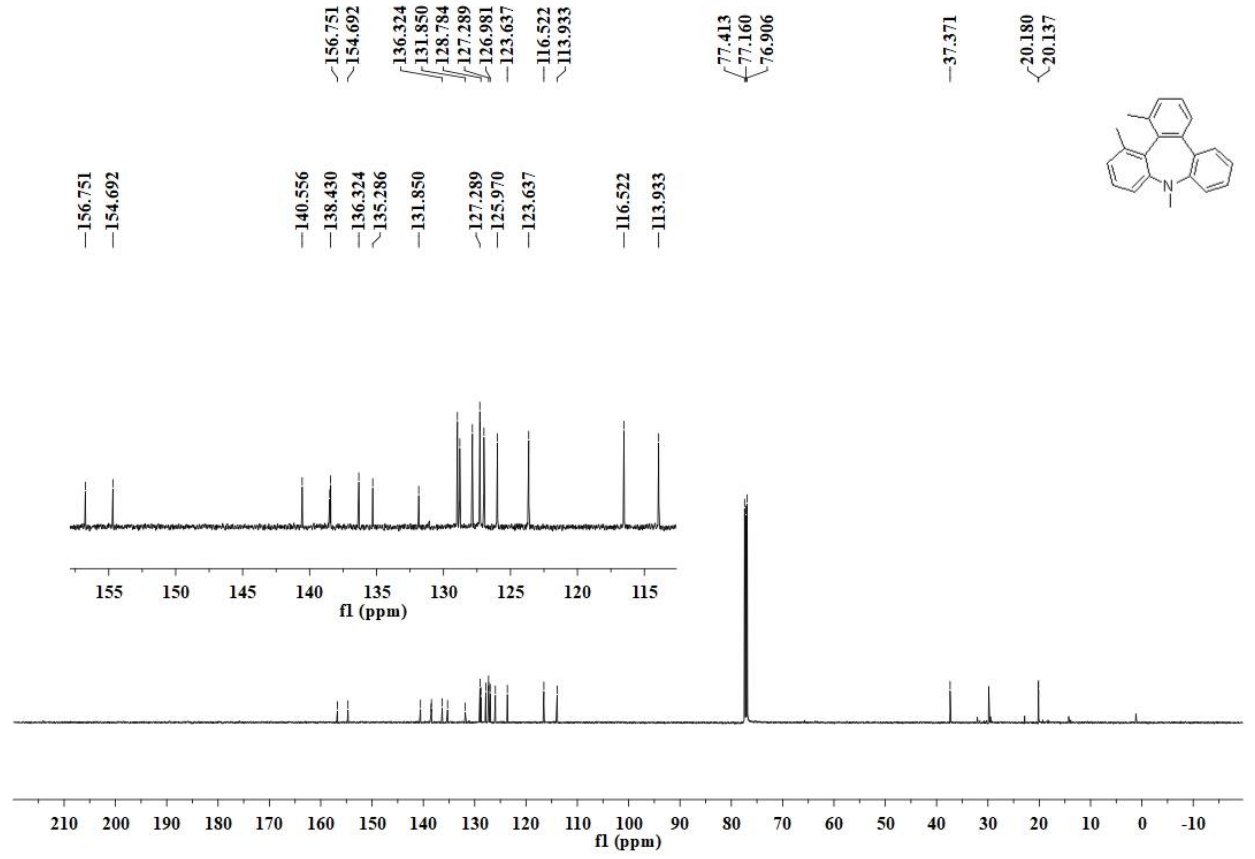
^{13}C NMR (125 MHz, $CDCl_3$) of **4c**



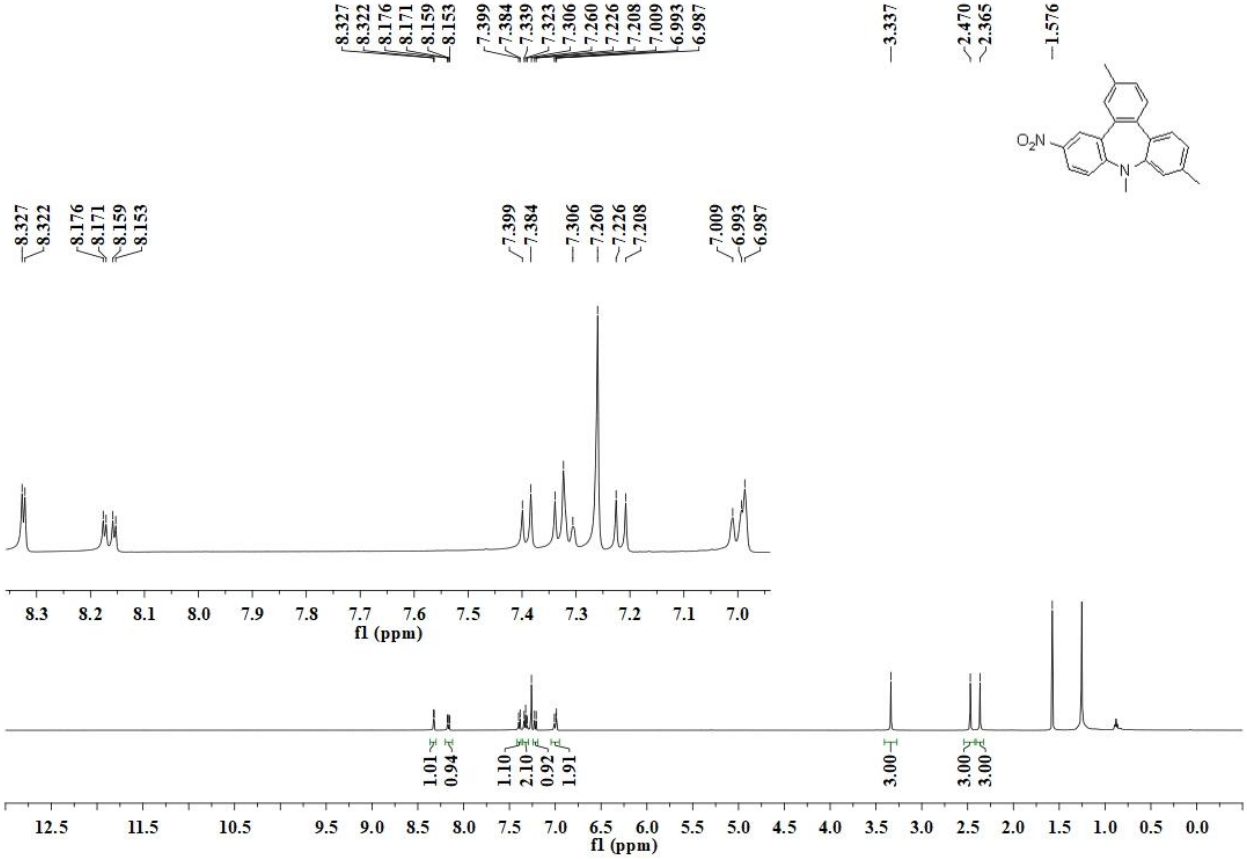
^{1}H NMR (500 MHz, $CDCl_3$) of **4d**



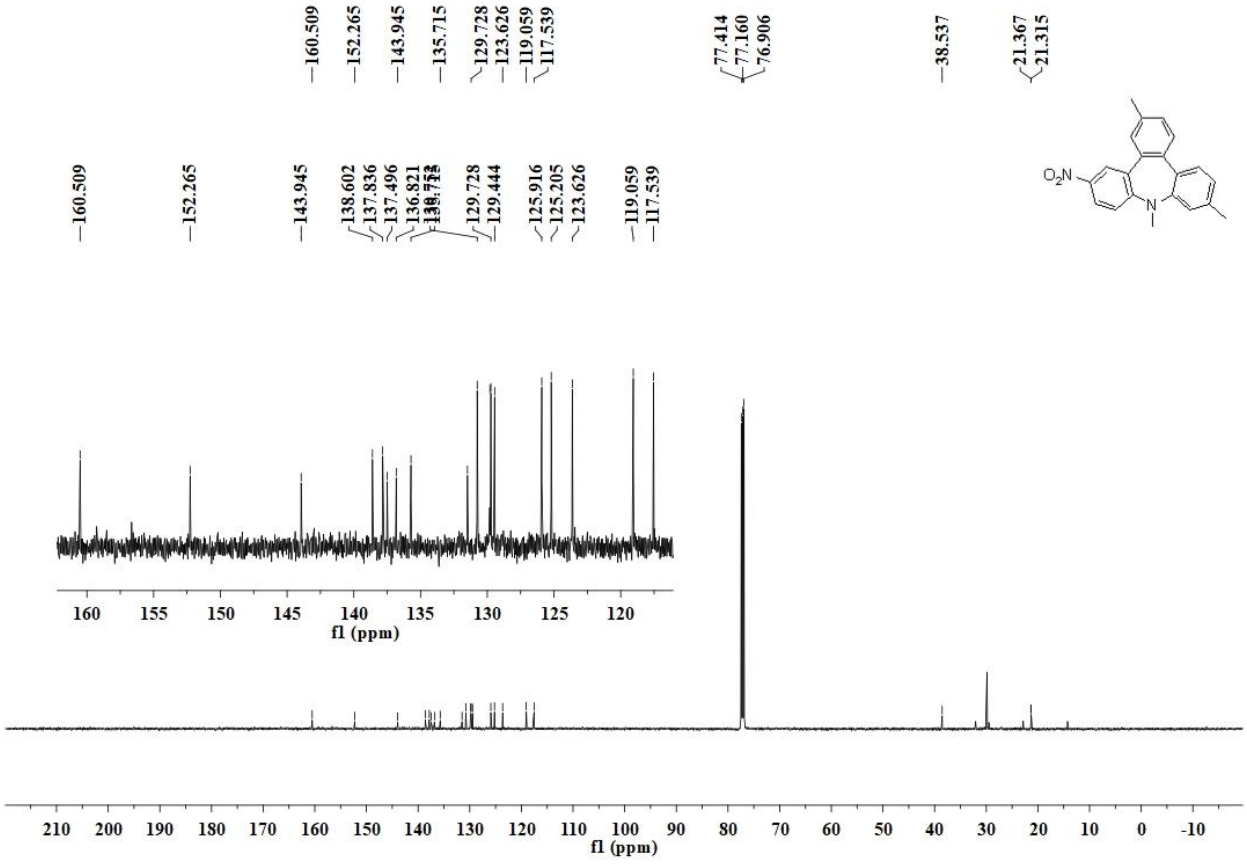
^{13}C NMR (125 MHz, $CDCl_3$) of **4d**



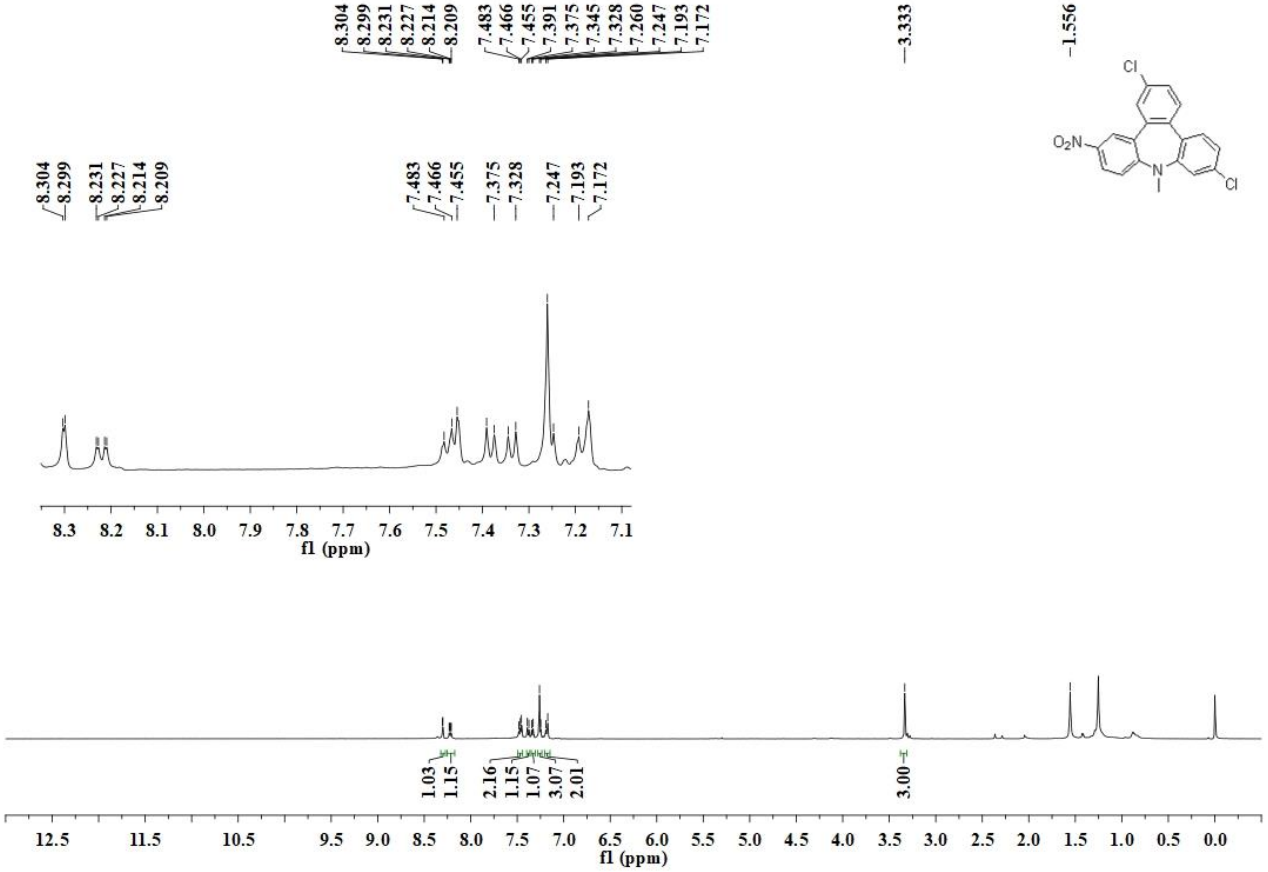
^{1}H NMR (500 MHz, $CDCl_3$) of **4e**



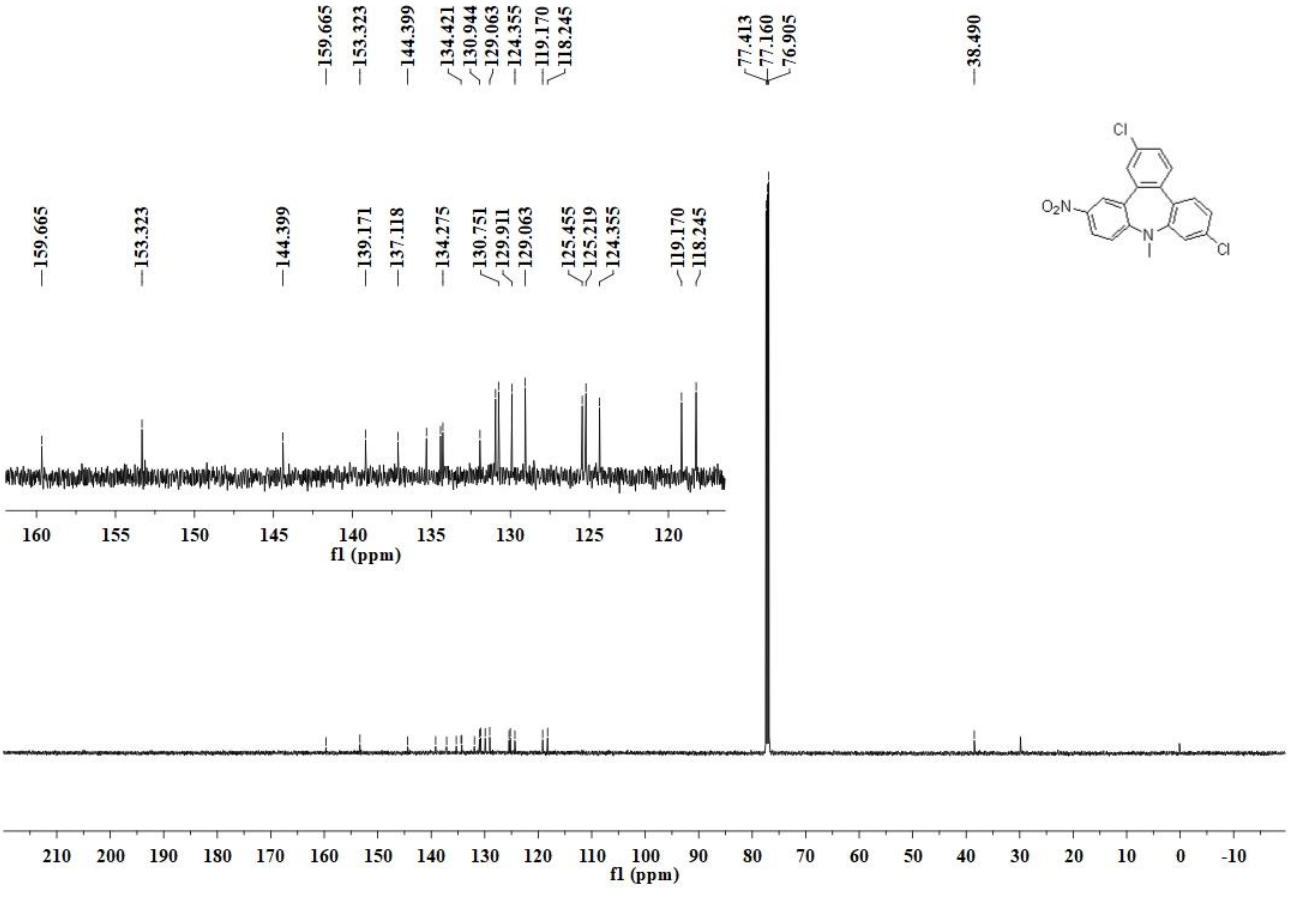
^{13}C NMR (125 MHz, $CDCl_3$) of **4e**



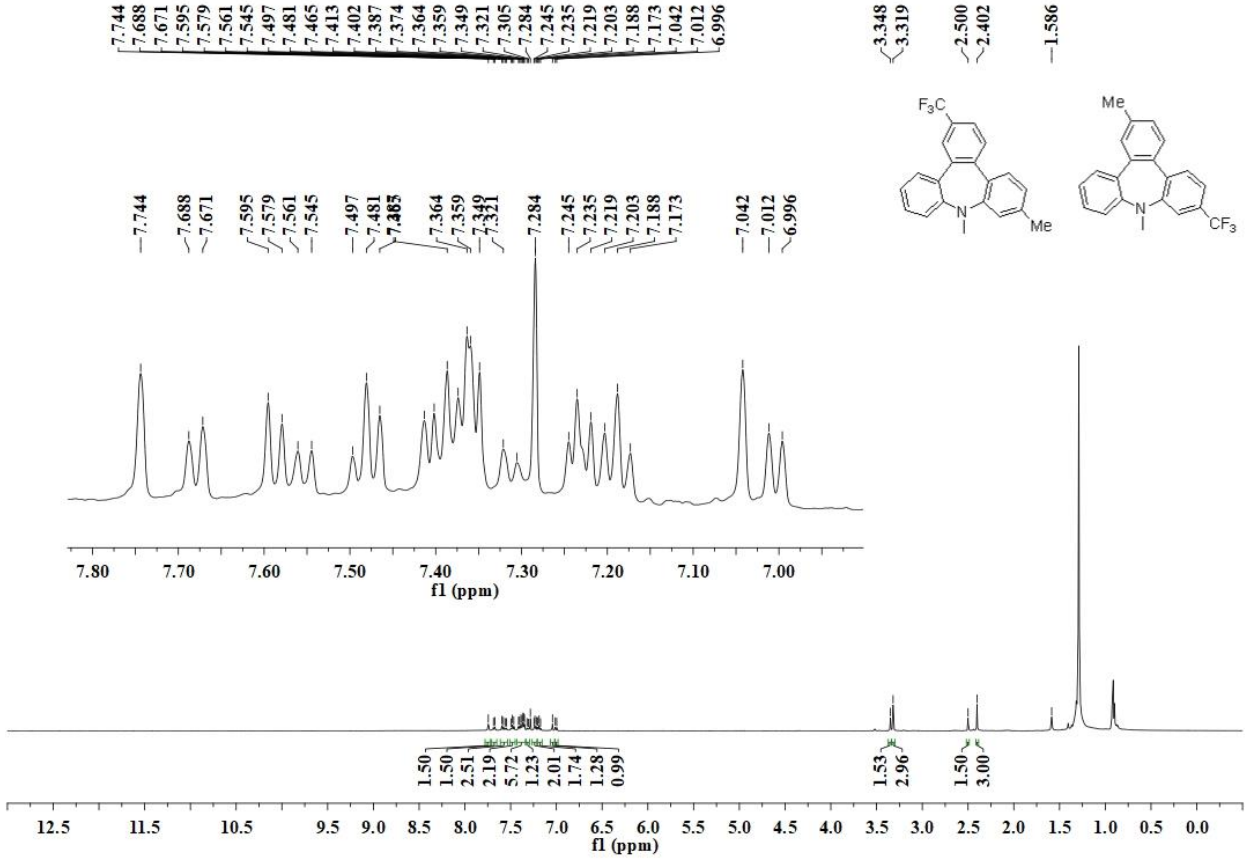
^{1}H NMR (500 MHz, $CDCl_3$) of **4f**



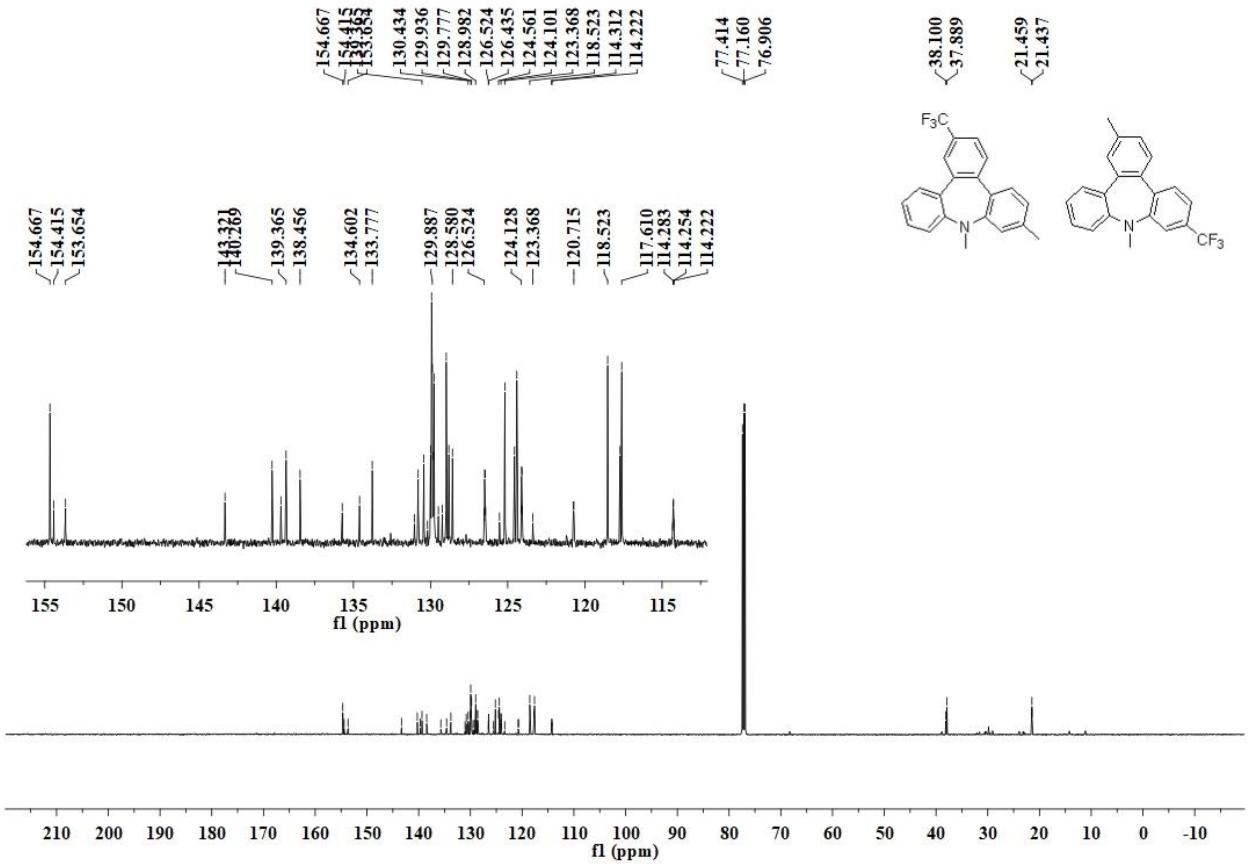
^{13}C NMR (125 MHz, $CDCl_3$) of **4f**



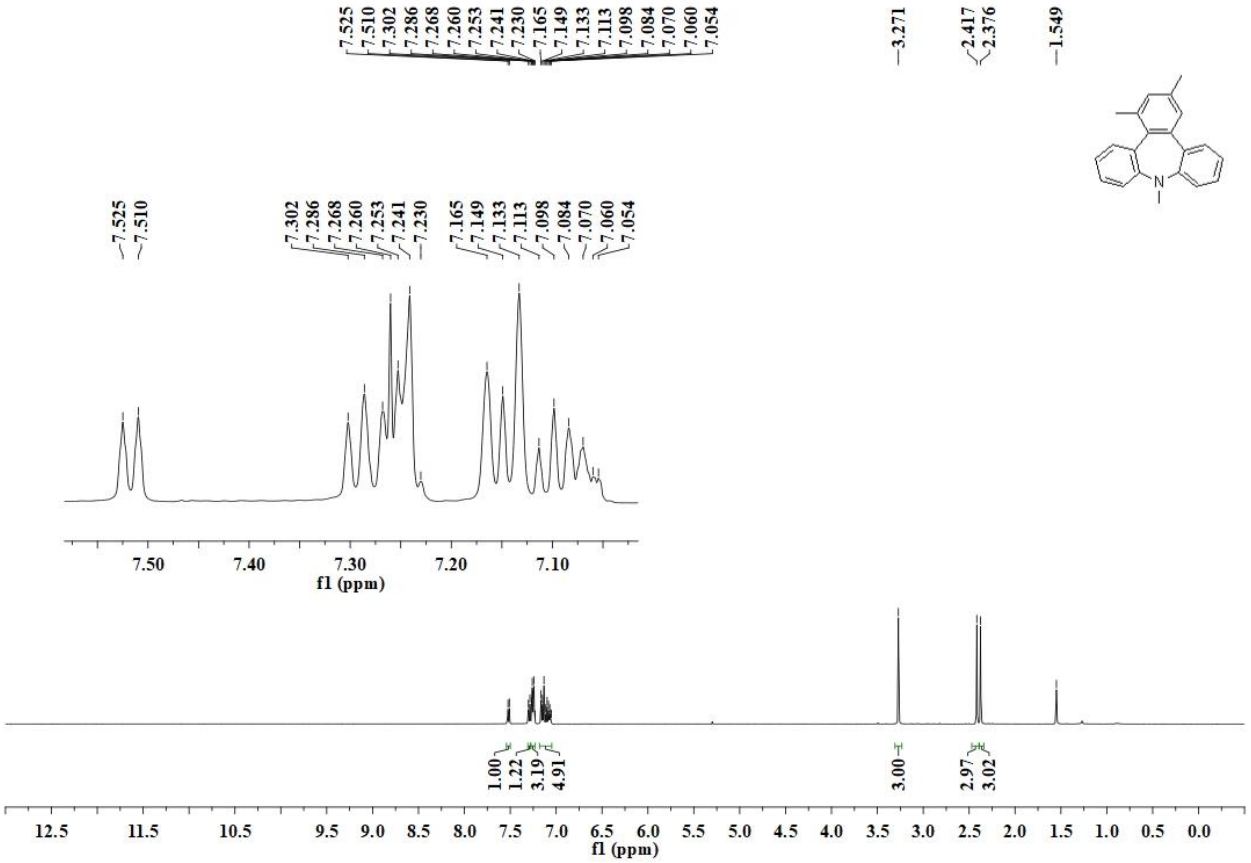
^{1}H NMR (500 MHz, $CDCl_3$) of **4g** and **4g′**



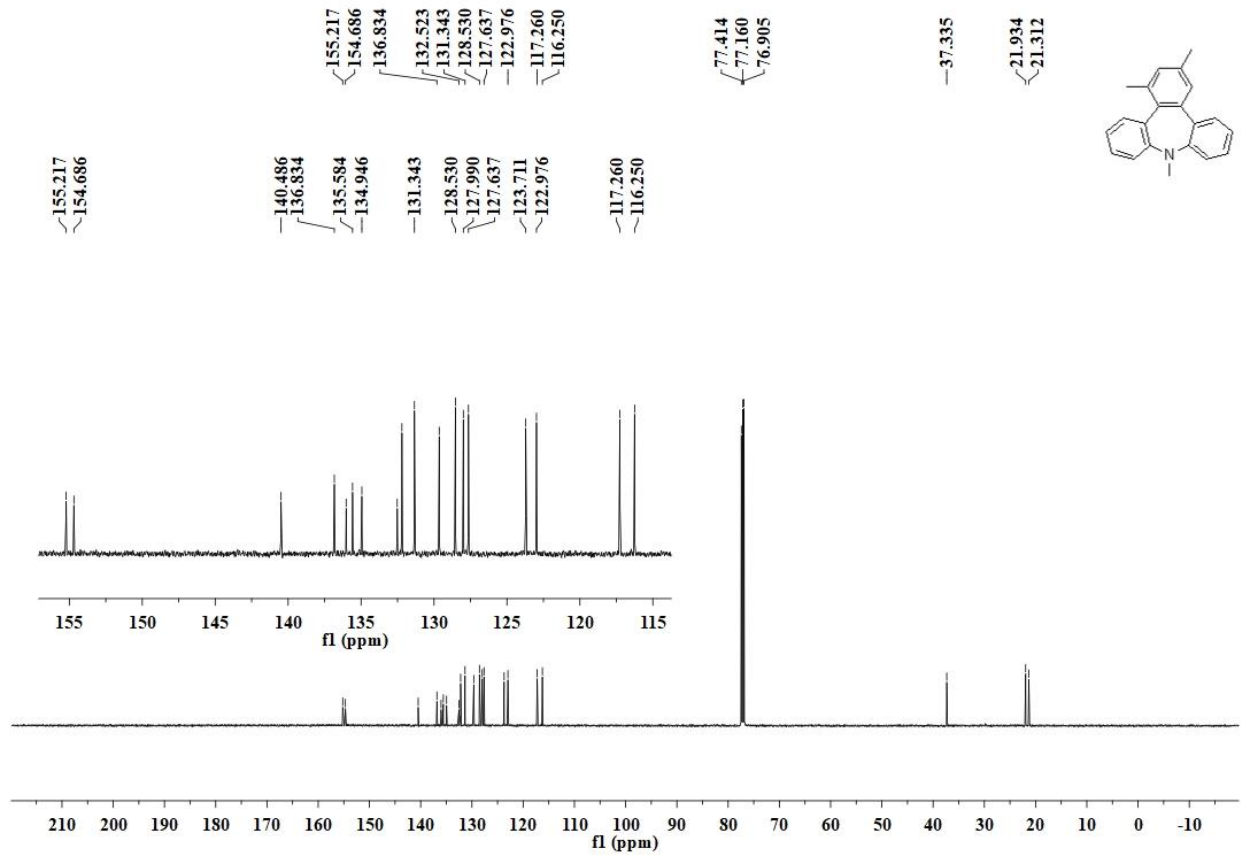
^{13}C NMR (125 MHz, $CDCl_3$) of **4g** and **4g′**



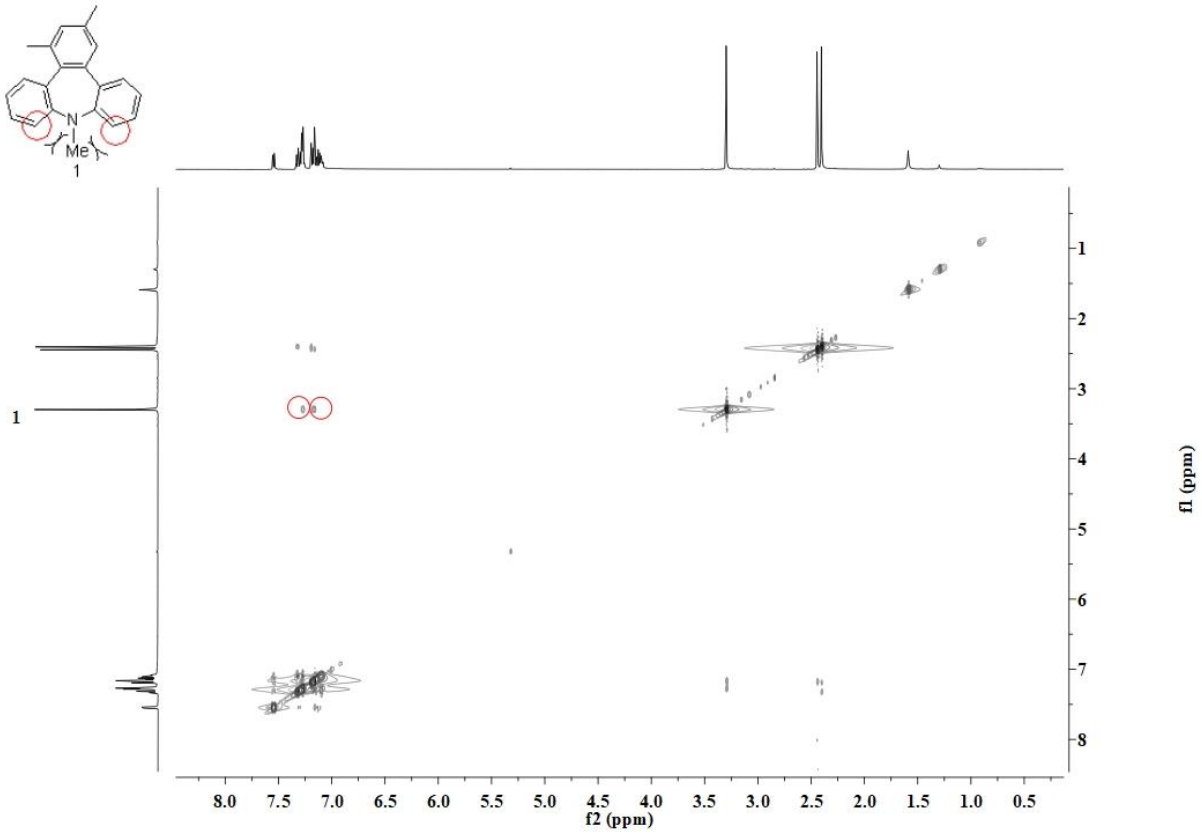
^{1}H NMR (500 MHz, $CDCl_3$) of **4h**



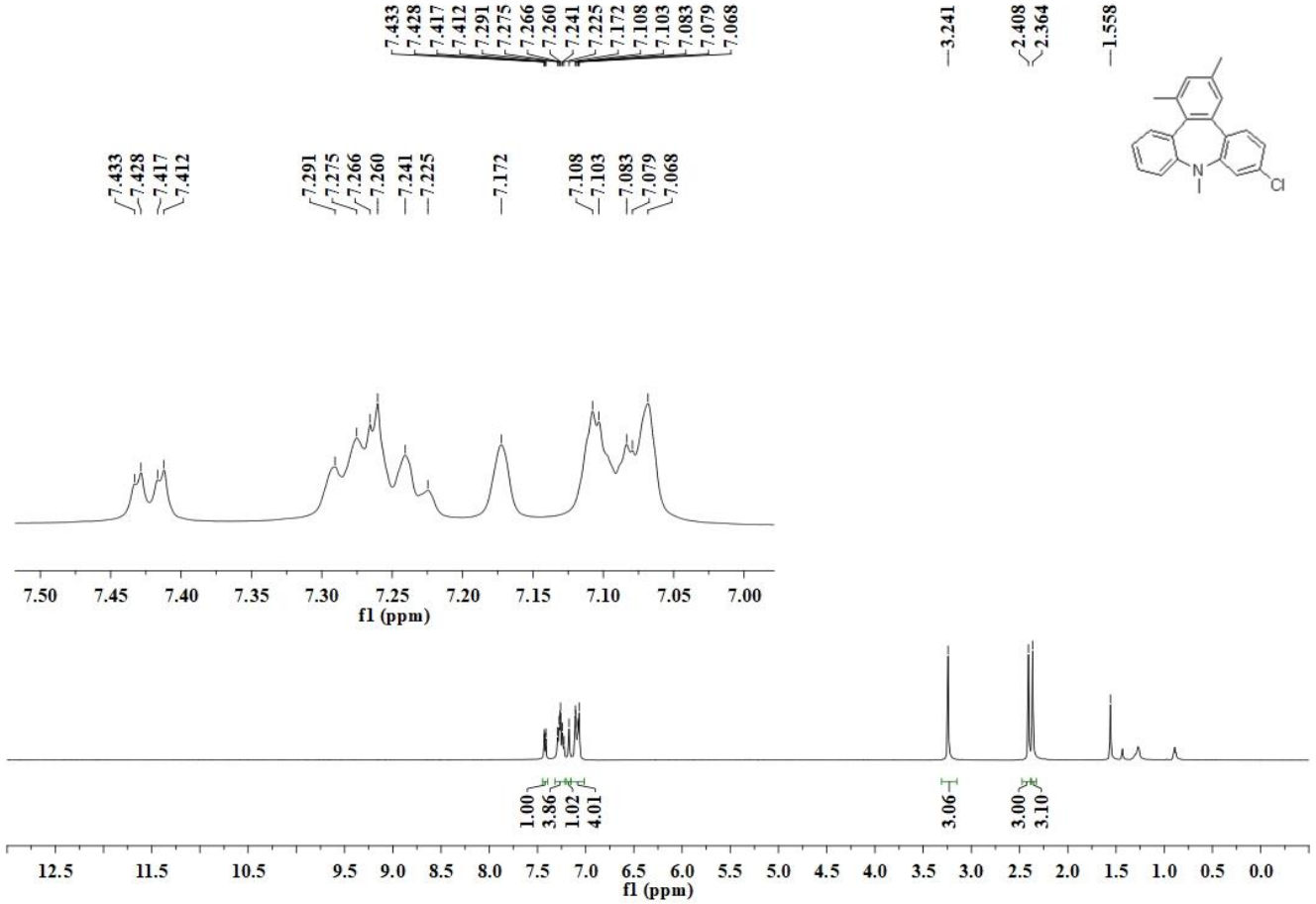
^{13}C NMR (125 MHz, $CDCl_3$) of **4h**



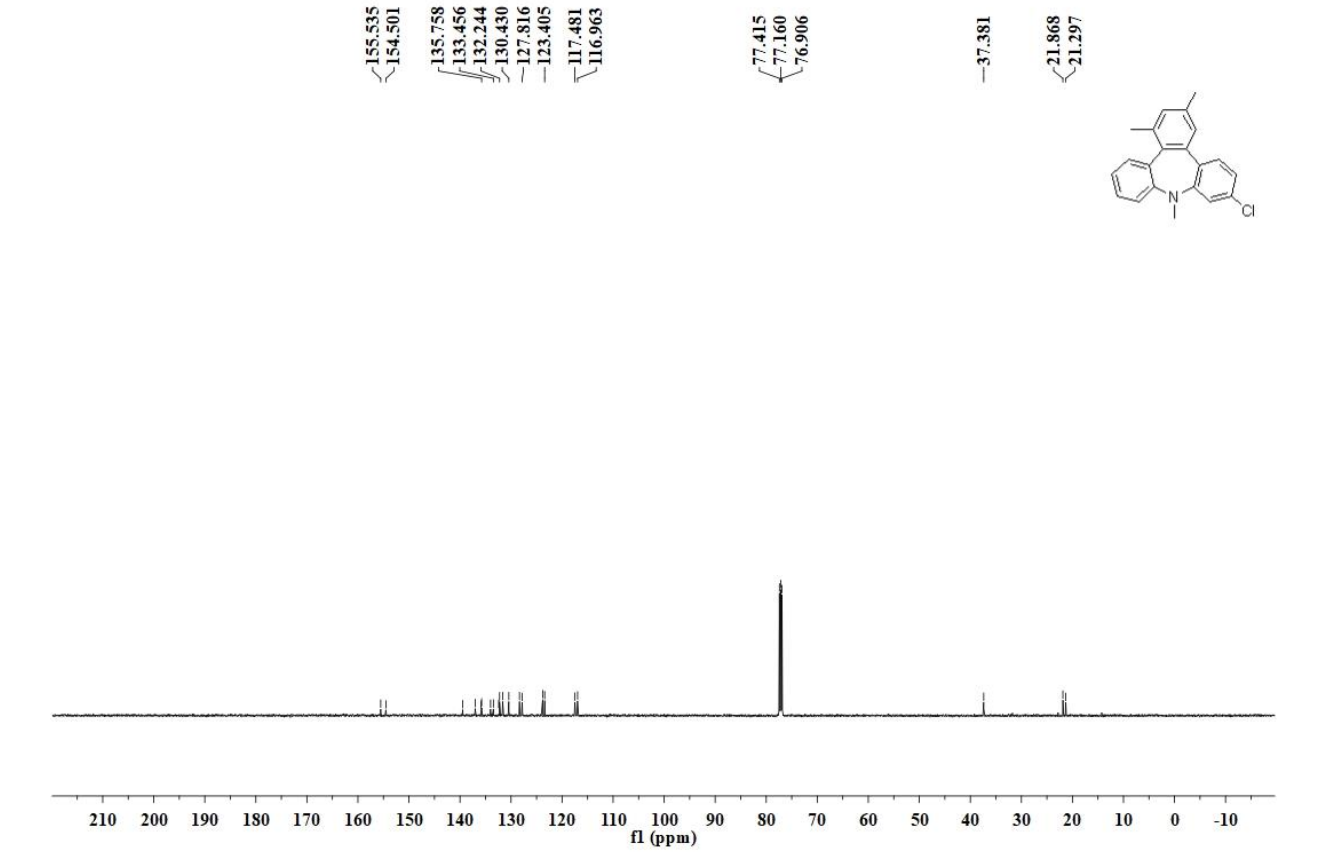
H-H NOESY (500 MHz, $CDCl_3$) of **4h**



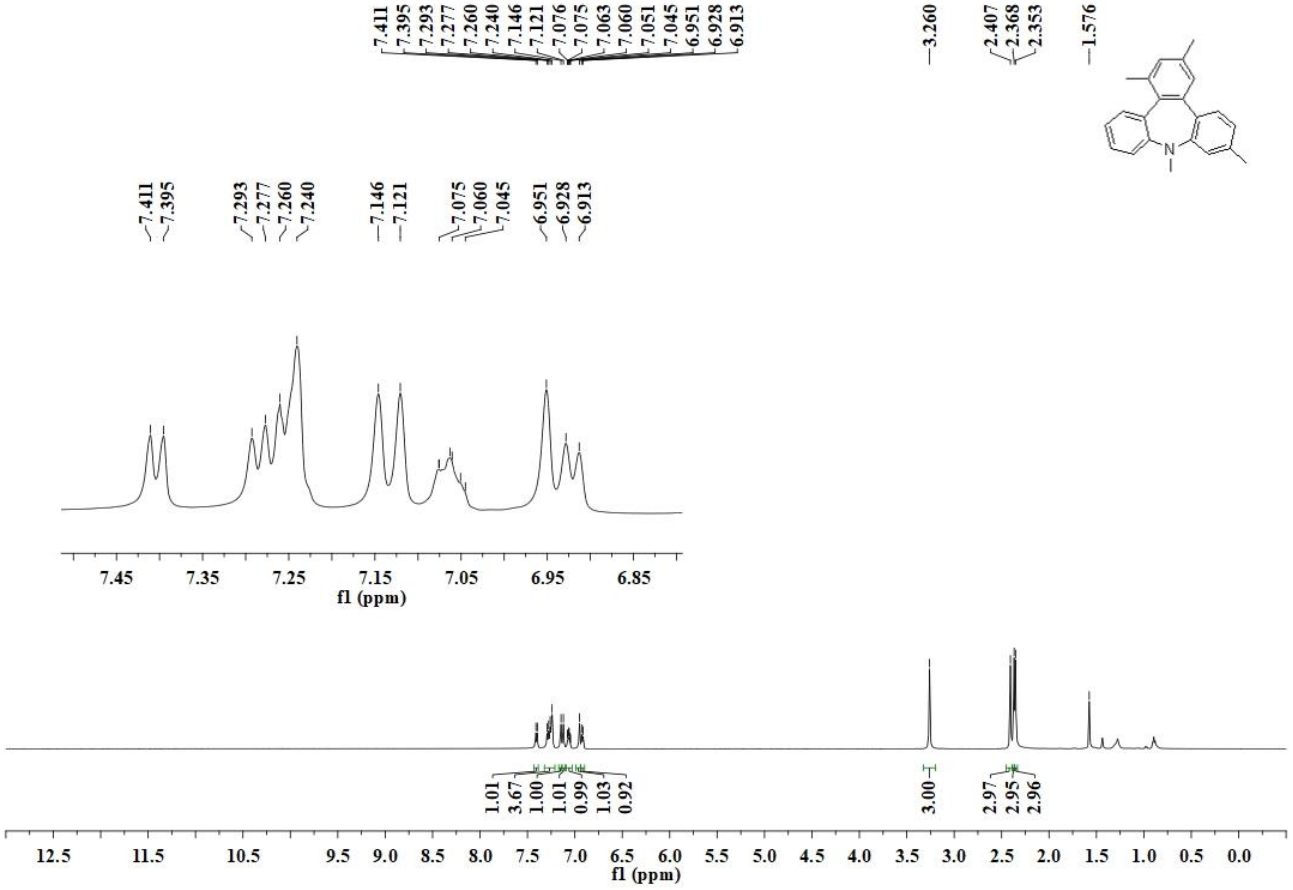
^{1}H NMR (500 MHz, $CDCl_3$) of **4i**



^{13}C NMR (125 MHz, $CDCl_3$) of **4i**



^{1}H NMR (500 MHz, $CDCl_3$) of **4j**



^{13}C NMR (125 MHz, $CDCl_3$) of **4j**