Supporting Information

Rh(III)-catalyzed building up of fused heterocyclic cations: facile access to white-light-emitting materials

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I. General remarks

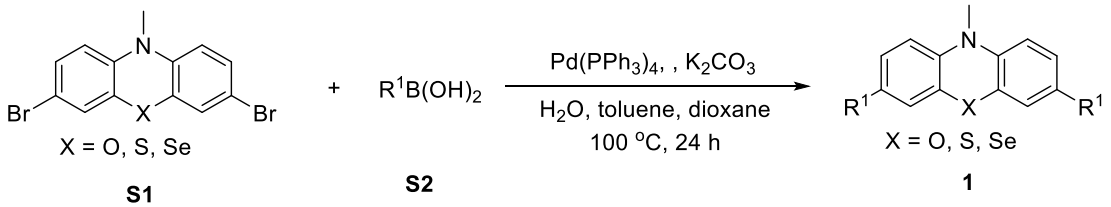
NMR spectra were obtained on Agilent 400MR DD2 (400 MHz) or 600MR DD2 (600 MHz) spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz or 125 MHz) chemical shifts were measured relative to $SiMe_4$, C_2D_6SO, CD_3CN, CD_3OD, or $CDCl_3$ using the chemical shift of residual solvent peaks as reference ($SiMe_4$: δ 0 ppm for ^{1}H NMR and ^{13}C NMR; C_2D_6SO: 2.50 ppm for ^{1}H NMR and 39.52 ppm for ^{13}C NMR; CD_3CN: 1.94 ppm for ^{1}H NMR and 1.32 ppm, 118.26 ppm for ^{13}C NMR; CD_3OD: 1.32 ppm for ^{1}H NMR and 49.00 ppm for ^{13}C NMR; $CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR). High-resolution mass spectra (HR-MS) were recorded using Agilent 6546 Q-TOF LC/MS system with Electrospray Ionization (ESI). Fluorescence spectra were collected on a HITACHI F-700003040428 Fluorescence Spectrometer. The CIE_{1931} chromaticity coordinates were calculated using a Color Coordinate.exe program. X-Ray single-crystal diffraction data were collected on an Agilent SuperNova Microfocal spot single-crystal diffractometer. EPR spectra were collected on a CIQTEK EPR200-Plus spectrometer. UV−vis spectra were recorded on Agilent Cary60 or HITACHI U-2910 spectrometer. Fluorescence spectra were collected on F-7000 or Agilent Technologies Cary Eclipse Fluorescence Spectrometer. The absolute quantum yields were taken using Edinburgh Instruments FLS1000 fluorescence spectrometer with a calibrated integrating sphere system. The excited-state lifetimes were performed using Edinburgh Instruments FLS1000. The

decomposition temperature corresponding to 5% weight loss was performed on NETZSCH TG 209F1 Iris.

Unless otherwise noted, all reagents were obtained from commercial sources and used directly. Thin-layer chromatography is performed on a plate bonded with sodium carboxymethyl cellulose (silica gel GF254) and visualized by fluorescence quenching under UV light. Column chromatography was performed through silica gel (200-300 mesh) using a proper solvent system. All syntheses and manipulations were carried out under an N_2 atmosphere using standard Schlenk. Diphenylacetylene[1], *N*-methyl-phenothiazin/phenoxazin/phenoselenazin[2,3] and its derivatives[4] was prepared according to the literature procedures. All calculations were performed using the Gaussian 09 program package[5]. The time-dependent density functional theory (TDDFT) calculations of the excitation energies were calculated at the optimized geometries of the ground states.

II. Synthesis of substrates 1

General procedure for the synthesis of substrates 1:



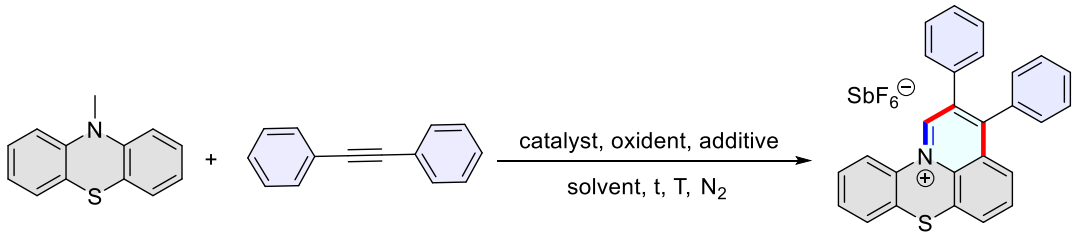
Scheme S1. Synthesis of substrates **1**.

A Schlenk test tube with a magnetic stir bar was charged with **S1** (264-312 mg, 0.75 mmol), **S2** (184-338 mg, 2.25 mmol), $Pd(PPh_3)_4$ (18 mg, 0.015 mmol), K_2CO_3 (315 mg, 2.2 mmol, 1.5 equiv), H_2O (0.1 μL, 0.005 mmol), toluene (7.5 mL), and dioxane (7.5 mL) under an N_2 atmosphere and the reaction mixture was allowed to stir at 100 ℃ for 24 h. The reaction mixture was cooled to ambient temperature, diluted with 10 mL of DCM, and evaporated under reduced pressure. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the corresponding substrates **1**.

III. Optimization of the rhodium-catalyzed nondirected C–H activation/annulation of 10-methyl-10*H*-phenothiazine

A schlenk tube with a magnetic stir bar was charged with Metal complex (0.005 mmol, 5.0 mmol%), oxidant (0.15 mmol, 1.5 equiv), additive 1 (0.04 mmol, 40.0 mmol%), additive 2 (0.15 mmol, 1.5 equiv), 10-methyl-10*H*-phenothiazine (**1a**, 0.1 mmol or 0.15 mmol), 1,2-diphenylethyne (**2a**, 0.1 mmol or 0.15 mmol), and solvent (1 mL) under an N_2 atmosphere, and then heated at indicated temperature for indicated time. The mixture was cooled to room temperature, diluted with 10 mL of dichloromethane, and evaporated under reduced pressure. The crude product was analyzed by ^1H NMR in $CDCl_3$. Yields are based on **1a**, determined by crude ^1H NMR using dibromomethane as the internal standard, and the residue was purified by flash column chromatography on silica gel to provide the desired product.

Table S1. Optimization of reaction conditions[a]



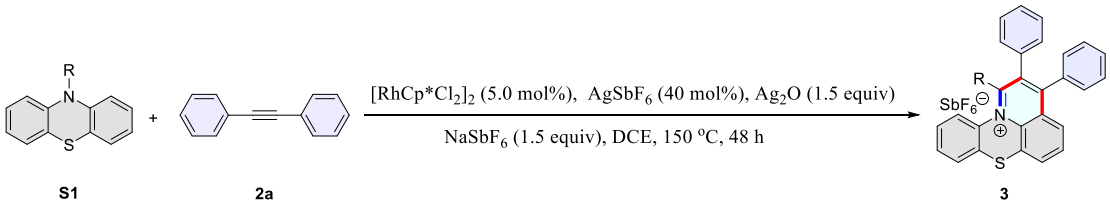
1a 2a 3a

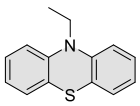
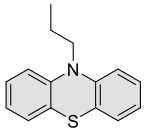
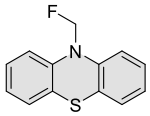
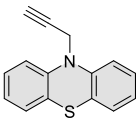
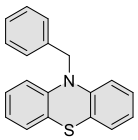
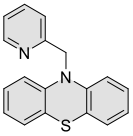
Entry	Metal complex	Oxidant	Additive 1	Additive 2	Solvent	T (h)	T (℃)	Yield (%)[b]
1	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	$NaSbF_6$	DCE	24	120	44
2[c]	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	$NaSbF_6$	DCE	24	120	22
3[d]	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	$NaSbF_6$	DCE	24	120	24
4	$[Cp^*RhCl_2]_2$	AgTFA	$AgSbF_6$	$NaSbF_6$	DCE	24	120	ND
5	$[Cp^*RhCl_2]_2$	AgOAc	$AgSbF_6$	$NaSbF_6$	DCE	24	120	ND
6	$[Cp^*RhCl_2]_2$	Ag_2CO_3	$AgSbF_6$	$NaSbF_6$	DCE	24	120	ND
7	$[Cp^*RhCl_2]_2$	AgOTf	$AgSbF_6$	$NaSbF_6$	DCE	24	120	ND
8	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	$AgSbF_6$	$NaSbF_6$ /PivOH	DCE	24	120	ND
9	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	PivOH	$NaSbF_6$	DCE	24	120	ND
10[e]	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	$NaSbF_6$	DCE	24	150	52
11	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	$NaSbF_6$	DCE	36	150	64
12[f]	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	$NaSbF_6$	DCE	48	150	75
13	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	-	DCE	48	150	50
14	$[Cp^*RhCl_2]_2$	Ag_2O	-	$NaSbF_6$	DCE	48	150	ND
15	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	$NaSbF_6$	DCE	60	150	70
16	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	$NaSbF_6$	DMF	48	150	ND
17	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	$NaSbF_6$	DMSO	48	150	ND
18	-	Ag_2O	$AgSbF_6$	$NaSbF_6$	DCE	48	150	ND
19[g]	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	$NaSbF_6$ /PivOH	DCE	48	150	50

20[h]	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	$NaSbF_6$/TEMPO	DCE	48	150	62

[a] **1a** (21 mg, 0.1 mmol), **2a** (28 mg, 0.15 mmol, 1.5 equiv), Metal complex (0.005 mmol, 5.0 mmol%), oxident (0.15 mmol, 1.5 equiv), additive 1 (0.04 mmol, 40 mmol%), additive 2 (0.15 mmol, 1.5 equiv), DCE (1 mL), 120-150 ℃, N_2, 24-60 h. [b] Yield is based on **1a**, determined by ^{1}H-NMR using dibromomethane as the internal standard. [c] **1a** (0.1 mmol), **2a** (0.1 mmol, 1 equiv). [d] **1a** (0.15 mmol, 1.5 equiv), **2a** (0.1 mmol). [e] $NaSbF_6$ (0.2 mmol). [f] Isolated yields. [g] $NaSbF_6$ (0.15 mmol)/PivOH (0.1 mmol). [h] $NaSbF_6$ (0.15 mmol)/TEMPO (1.0 mmol). N.D.: No detected.

Table S2. Replacing the Me group of **1a** with other substitutents [a]



Entry	1	2	3	4	5	6
S1	 **S1a**	 **S1b**	 **S1c**	 **S1d**	 **S1e**	 **S1f**
Yield (%)	ND	ND	ND	ND	Trace	ND

[a] **S1** (0.1 mmol), **2a** (0.15 mmol), $[Cp^*RhCl_2]_2$ (5.0 mmol%), Ag_2O (1.5 equiv), $AgSbF_6$ (40 mol%), $NaSbF_6$ (1.5 equiv), and DCE (1 mL) under an N_2 atmosphere and the reaction mixture was allowed to stir at 150 ℃ for 48 h. N.D.: No detected.

IV. General procedure for synthesizing the pyrido-phenothiazin/phenoxazin/phenoselenazin/phenazin-12-iums-hexafluorostibate (V)

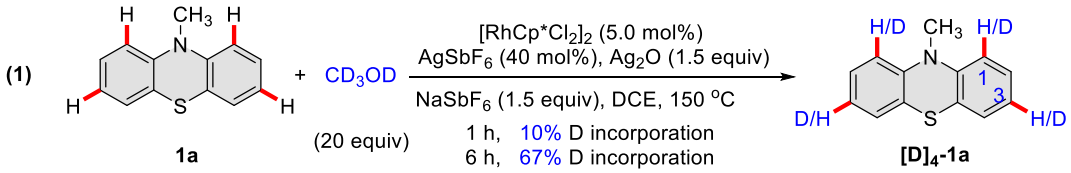
A Schlenk tube with a magnetic stir bar was charged with **1** (21-75 mg, 0.1 mmol), **2** (28-70 mg, 0.15 mmol), $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol, 5.0 mmol%), Ag_2O (34 mg, 0.15 mmol, 1.5 equiv), $AgSbF_6$ (14 mg, 0.04 mmol, 40 mol%), $NaSbF_6$ (40 mg, 0.15 mmol, 1.5 equiv), and DCE (1 mL) under an N_2 atmosphere and the reaction

mixture was allowed to stir at 150 ℃ for 48 h. The reaction mixture was cooled to ambient temperature, diluted with 10 mL of DCM, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:3, v/v, then dichloromethane/methanol = 50:1, v/v) and following stirred with $NaSbF_6$ (26.7 mg, 0.1 mmol) in CH_3CN (1 mL) at room temperature for 0.5 h, then filtered and removed solvent to provide the desired products **3-4**.

V. Mechanistic study

Control experiments:

Deuterium labelling experiments using CD_3OD as a co-solvent:



Scheme S2. Deuterium labelling experiments.

An oven-dried Schlenk tube with a magnetic stir bar was charged with **1a** (21 mg, 0.1 mmol) and $[Cp^*RhCl_2]_2$ (3.2 mg, 0.005 mmol, 5.0 mmol%), Ag_2O (34 mg, 0.15 mmol, 1.5 equiv), $AgSbF_6$ (14 mg, 0.04 mmol, 40 mmol%), $NaSbF_6$ (40 mg, 0.15 mmol, 1.5 equiv). The Schlenk tube was evacuated and filled with a nitrogen gas three times. Then, CD_3OD (81 μL, 20 equiv) and dry DCE (1.0 mL) were added under a nitrogen atmosphere and the reaction mixture was allowed to stir at 150 ℃ for

1 h or 6 h. The reaction mixture was cooled to ambient temperature, diluted with 10 mL of DCM, and evaporated under reduced pressure. Purification via column chromatography on silica gel (petroleum ether) afforded the 10% deuterated $[D]_4$-**1a** (1 h) or 67% deuterated $[D]_4$-**1a** (6 h). These results indicated that the C−H bond activation step might be reversible, and the C–H bond at the C_1 and C_3-positions of the 10-methyl-10*H*-phenothiazine (**1a**) has the same reaction activity, and the reaction might start from the metalation of C_1 and C_3-positions.

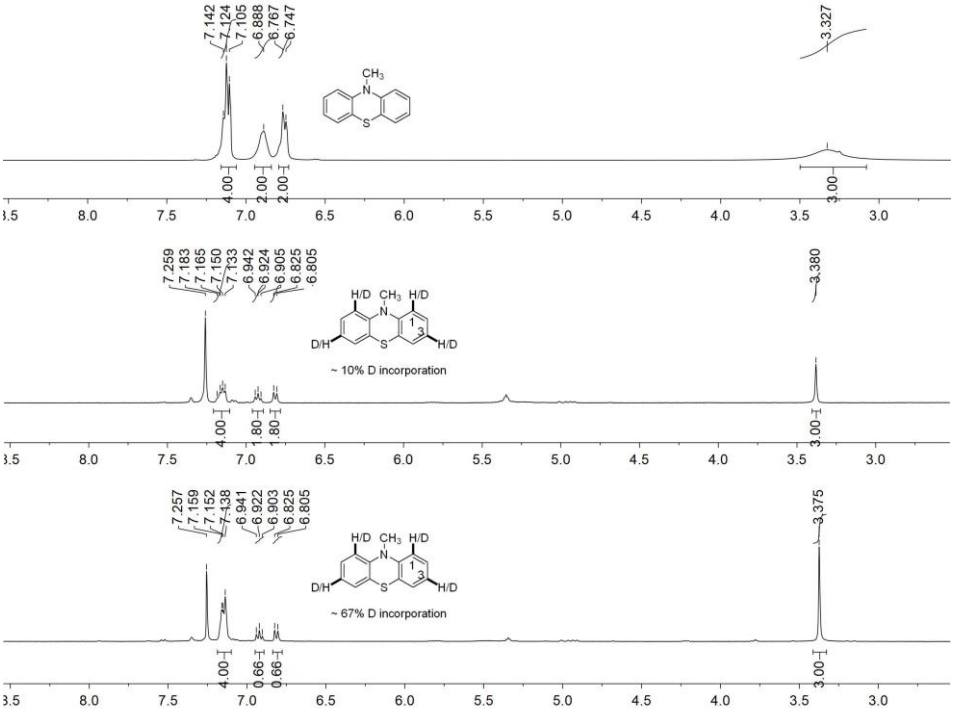
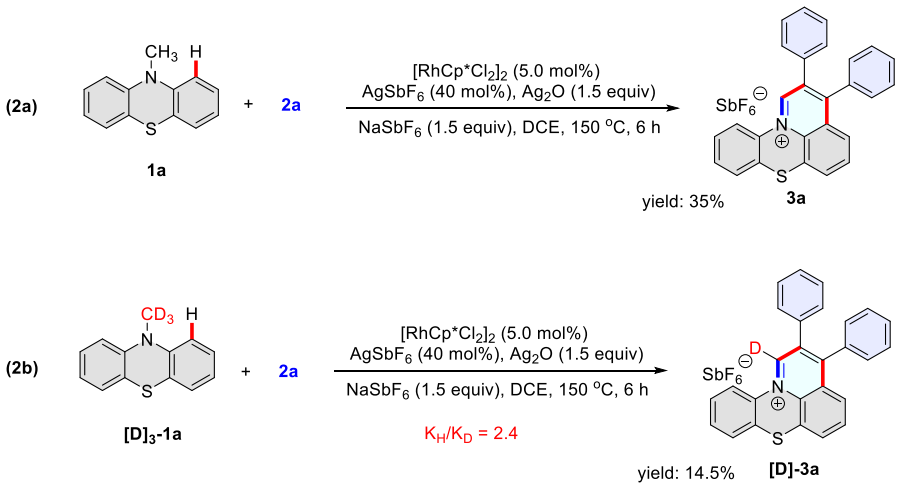


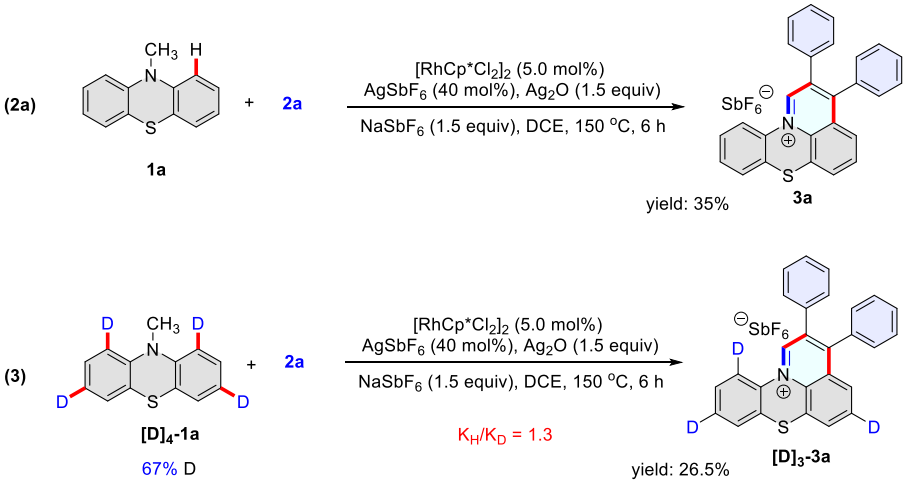
Fig. S1. Deuterium labelling experiments

Parallel KIE experiments:



Scheme S3. The first group of parallel KIE experiences.

An oven-dried Schlenk tube with a magnetic stir bar were charged separately with **1a** (21 mg, 0.1 mmol) or **[D]$_3$-1a** (0.2 mmol), diphenylacetylene **2a** (28 mg, 0.15 mmol), [Cp*RhCl$_2$]$_2$ (3.2 mg, 0.005 mmol, 5.0 mmol%), Ag_2O (34 mg, 0.15 mmol, 1.5 equiv), $AgSbF_6$ (14 mg, 0.04 mmol, 40 mmol%), $NaSbF_6$ (40 mg, 0.15 mmol, 1.5 equiv). The Schlenk tubes were evacuated and filled with a nitrogen gas three times. Then, dry DCE (1.0 mL) were added under a nitrogen atmosphere and the reaction mixture was allowed to stir at 150 ℃ for 6 h. The reaction mixture was cooled to ambient temperature, diluted with 10 mL of DCM and evaporated under reduced pressure. The crude product was analyzed by ^{1}H NMR in $CDCl_3$. Yields are determined by crude ^{1}H NMR using dibromomethane as the internal standard. A significant KIE value (k_H/k_D = 2.4) between **1a** and **[D]$_3$-1a** with **2a** was observed and revealed that the C(sp^3)–H bond of the methyl position of **1a** breaking might be involved in the rate-limiting step.



Scheme S4. The second group of parallel KIE experiences.

An oven-dried Schlenk tube with a magnetic stir bar were charged separately with **1a** (21 mg, 0.1 mmol) or **[D]$_4$-1a** (0.2 mmol), diphenylacetylene **2a** (28 mg, 0.15 mmol), [Cp*RhCl$_2$]$_2$ (3.2 mg, 0.005 mmol, 5.0 mmol%), Ag_2O (34 mg, 0.15 mmol, 1.5 equiv), $AgSbF_6$ (14 mg, 0.04 mmol, 40 mmol%), $NaSbF_6$ (40 mg, 0.15 mmol, 1.5 equiv). The Schlenk tubes were evacuated and filled with a nitrogen gas three times. Then, dry DCE (1.0 mL) were added under a nitrogen atmosphere and the reaction mixture was allowed to stir at 150 ℃ for 6 h. The reaction mixture was cooled to ambient temperature, diluted with 10 mL of DCM and evaporated under reduced pressure. The crude product was analyzed by ^{1}H NMR in $CDCl_3$. Yields are determined by crude ^{1}H NMR using dibromomethane as the internal standard. A significant KIE value (k_H/k_D = 1.3) between **1a** and **[D]$_4$-1a** with **2a** was observed.

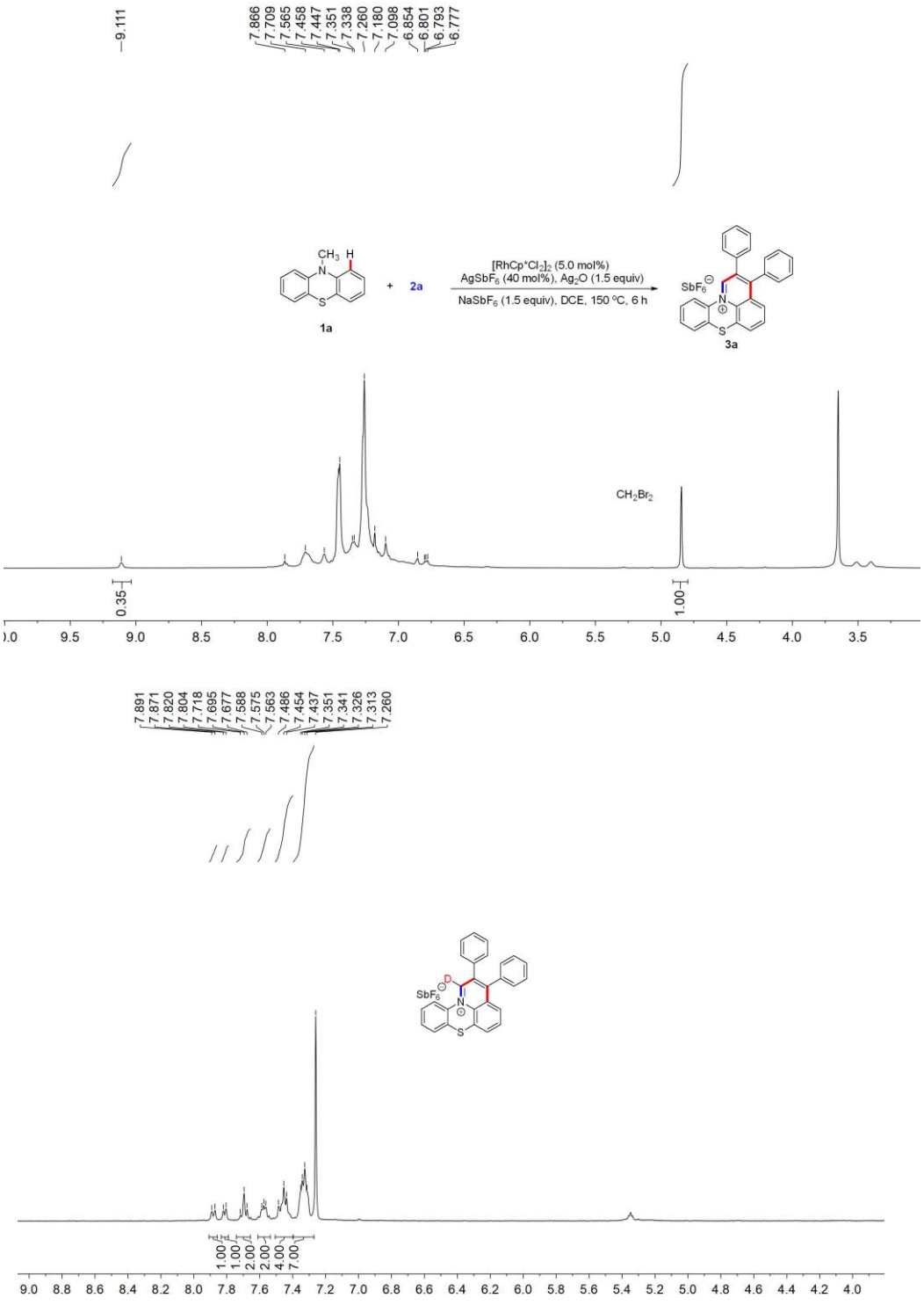


Fig. S2. Parallel KIE experiments.

MALDI-TOF-MS analysis for the reaction intermediate:

General procedure for the preparation of the sample: An oven-dried Schlenk tube with a magnetic stir bar was charged separately with **1a** (21 mg, 0.1 mmol),

diphenylacetylene **2a** (28 mg, 0.15 mmol), $[Cp^*RhCl_2]_2$ (6.4 mg, 0.01 mmol), Ag_2O (34 mg, 0.15 mmol, 1.5 equiv), $AgSbF_6$ (14 mg, 0.04 mmol, 40 mmol%), $NaSbF_6$ (40 mg, 0.15 mmol, 1.5 equiv). The Schlenk tubes were evacuated and filled with a nitrogen gas three times. Then, dry DCE (1.0 mL) was added under a nitrogen atmosphere and the reaction mixture was allowed to stir at 150 ℃ for 15 min. The reaction mixture was used as the sample for the Agilent 6546 Q-TOF LC/MS system detection.

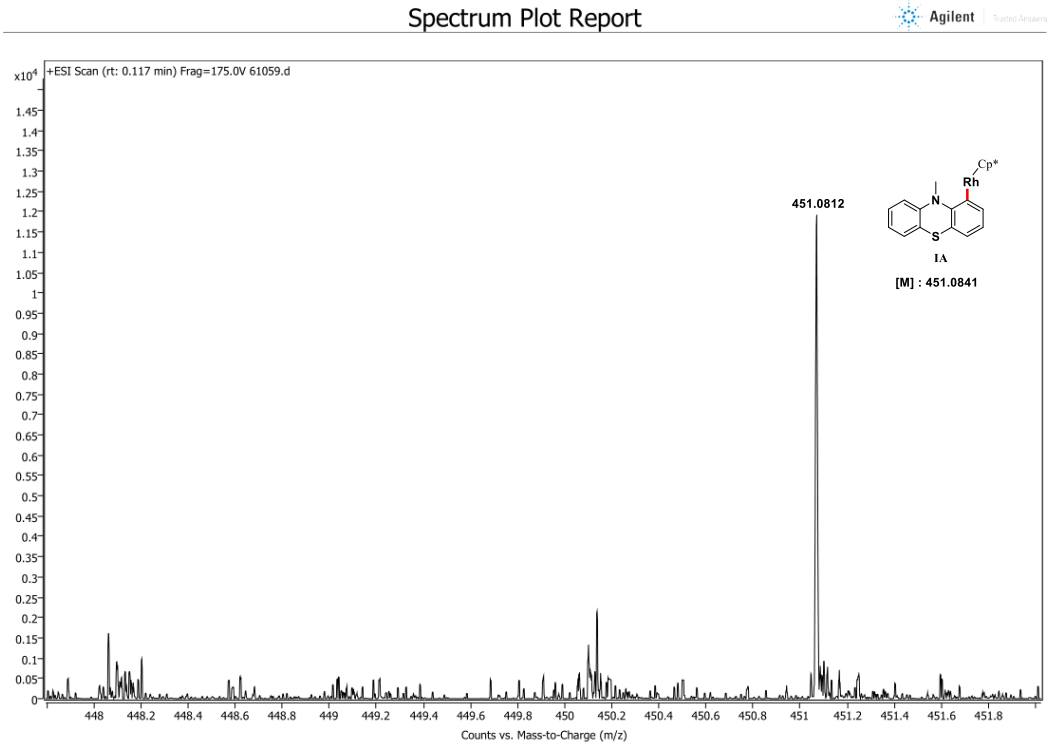
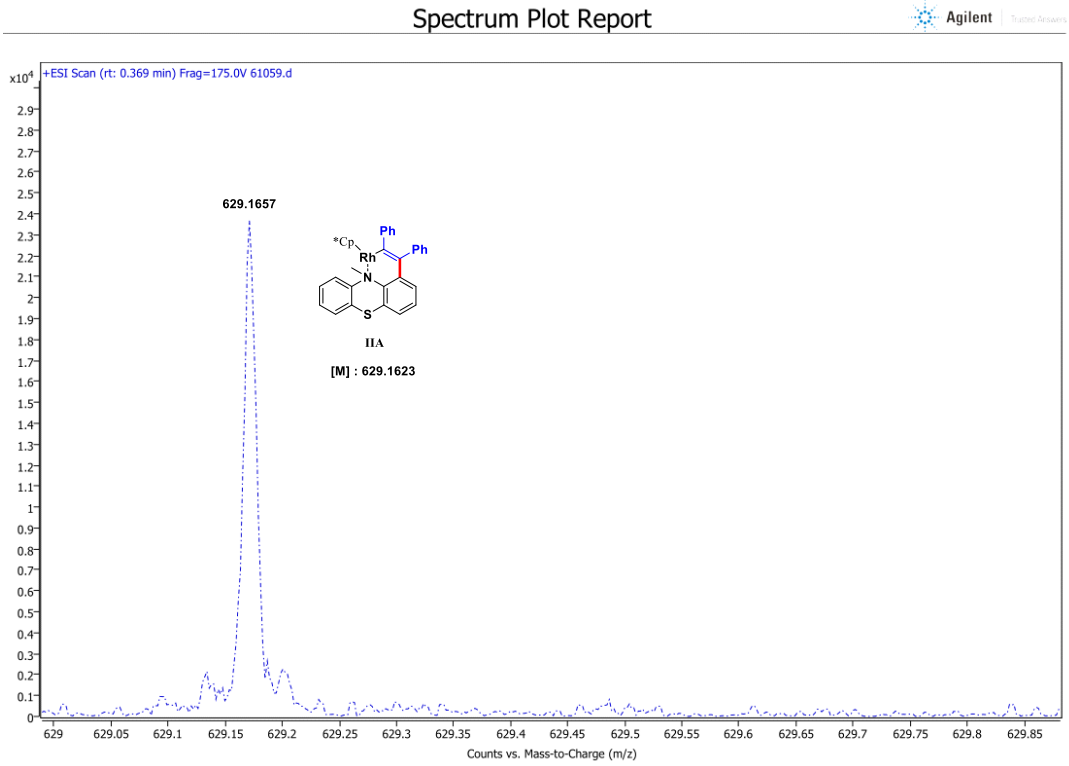


Fig. S3. MS spectrum of the intermediate **IA**.



F

Fig. S4. MS spectrum of the intermediate **IIA**.

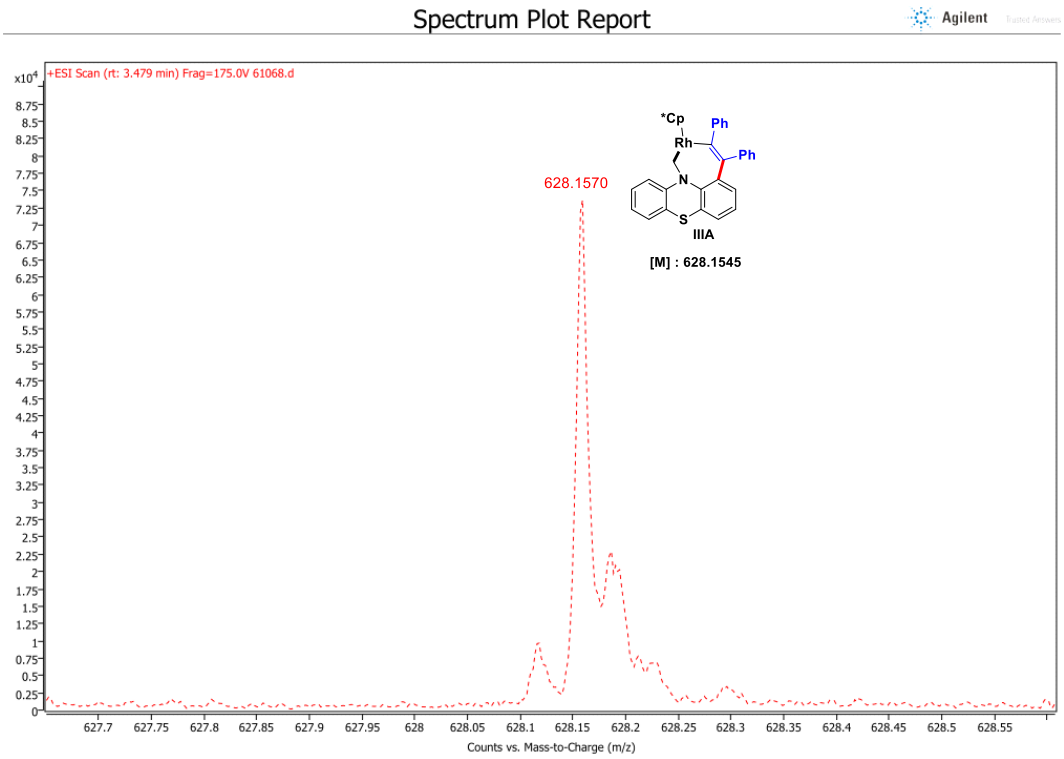


Fig. S5. MS spectrum of the intermediate **IIIA**.

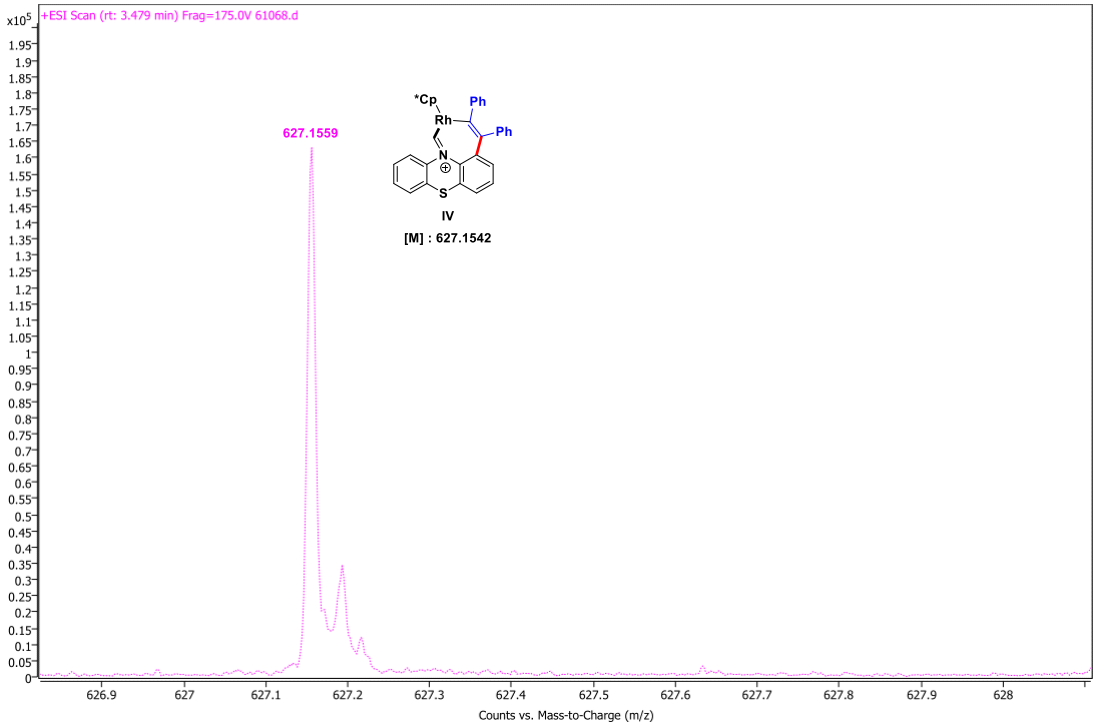


Fig. S6. MS spectrum of the intermediate **IV**.

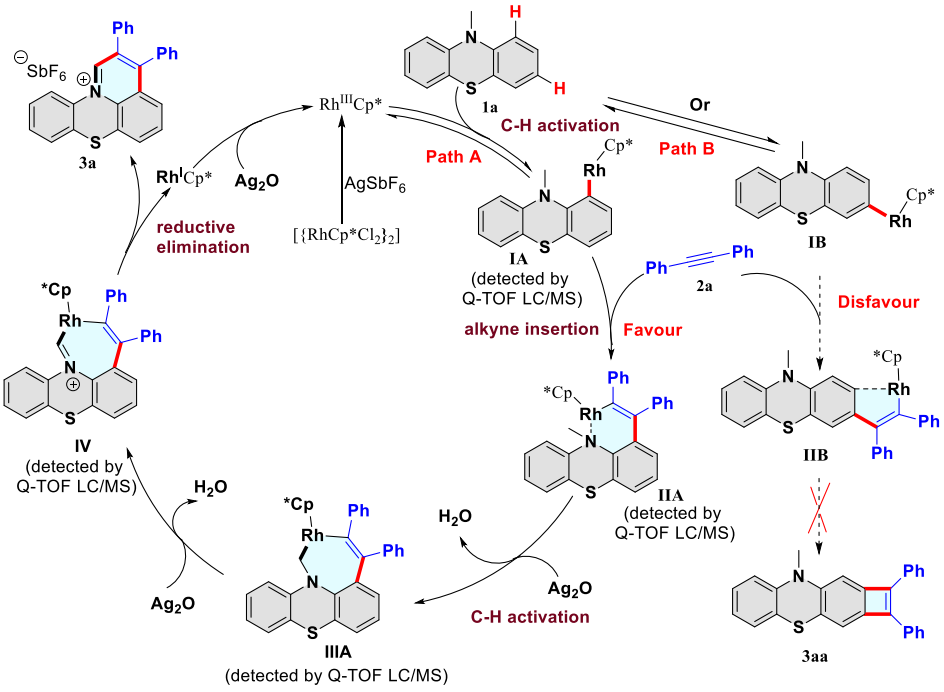


Fig. S7. Plausible catalytic cycle.

IV. The absorption and fluorescence properties of pyrido-phenothiazin/phenoxazin/phenoselenazin/phenazin-12-iums-hexafluorostibate (V)

Table S3. Absorption maxima, emission maxima, and CIE_{1931} of pyrido-phenothiazin/phenoxazin/phenoselenazin/phenazin-12-iums-hexafluorostibate (V)

Compounds	Absorb ($\lambda_{abs,}$ nm)[a]	Emission ($\lambda_{em,}$ nm)[b]	CIE_{1931}
3a	270, 508	428, 615	(0.49, 0.32)
3b	271, 331, 508	434, 614	(0.49, 0.26)
3c	272, 345, 409, 520	440, 615	(0.48, 0.28)
3d	271, 336, 400, 510	427, 610	(028, 0.20)
3e	269, 326, 505	487, 609	(0.30, 0.29)
3f	270, 319, 383, 515	431, 620	(0.45, 0.25)
3g	270, 301, 371, 522	434, 625	(0.34, 0.18)
3h	269, 303, 368, 519	445, 505, 620	(0.22, 0.29)
3i	279, 293, 303, 330, 521	441, 589	(0.24, 0.21)
3j	272, 330, 389, 522	437, 625	(0.46, 0.22)
3k	262, 300, 355, 534	453, 626	(0.36, 0.26)
3l	273, 291, 354, 517	435, 619	(0.20, 0.16)
3m	274, 289, 404	492, 605	(0.21, 0.32)
3n	273, 315, 382, 506	467, 587	(0.52, 0.43)
3o	271, 340, 500	437, 605	(0.55, 0.39)
3p	264, 297, 518	438, 606	(0.21, 0.24)
4a	256, 277, 301, 481	430, 540	(0.33, 0.57)
4b	273, 369, 557, 591	434, 567, 640	(0.26, 0.16)
4c	268, 324, 389, 520	449, 615	(0.62, 0.35)
4d	262, 327, 375, 485	446, 545	(0.29, 0.44)
4e	265, 316, 387, 517	444, 614	(0.60, 0.34)
4f[c]	272, 320, 394, 515	466, 611	(0.33 0.32)
4g	273, 328, 399, 515	477, 609	(0.32, 0.35)
4h	273, 412, 526	483, 612	(0.32, 0.32)
4i	275, 292, 514	499, 606	(0.22, 0.36)
4j	269, 320, 384, 515	498, 606	(0.23, 0.37)
4k	272, 390, 518	474, 611	(0.51, 0.35)
4l	270, 325, 378, 517	491, 609	(0.27, 0.37)
4m	275, 319, 385, 518	462, 608	(0.51, 0.31)
4n	267, 325, 438	464, 548	(0.32, 0.47)
4o	274, 403	469, 612	(0.58, 0.37)
4p	274, 311, 382, 518	435, 623	(0.25, 0.22)
4q	275, 318, 401, 515	460, 621	(0.40, 0.32)

4r[c]	271, 322, 394, 477	445, 623	(0.30, 0.27)

[a]Absorption maximum in CH_2Cl_2 (1×10^{-6} M). [b] Emission maximum in CH_2Cl_2 (5×10^{-5} M). [c] CH_2Cl_2 (1×10^{-5} M).

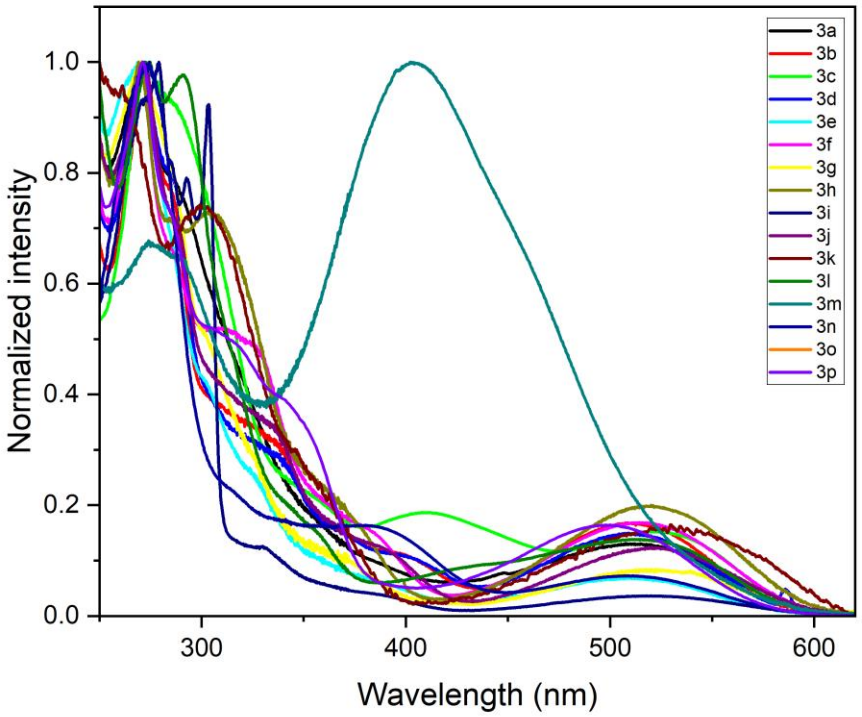


Fig. S8. Normalized UV-Vis absorption spectra of **3a-3n** in CH_2Cl_2 (1×10^{-6} M).

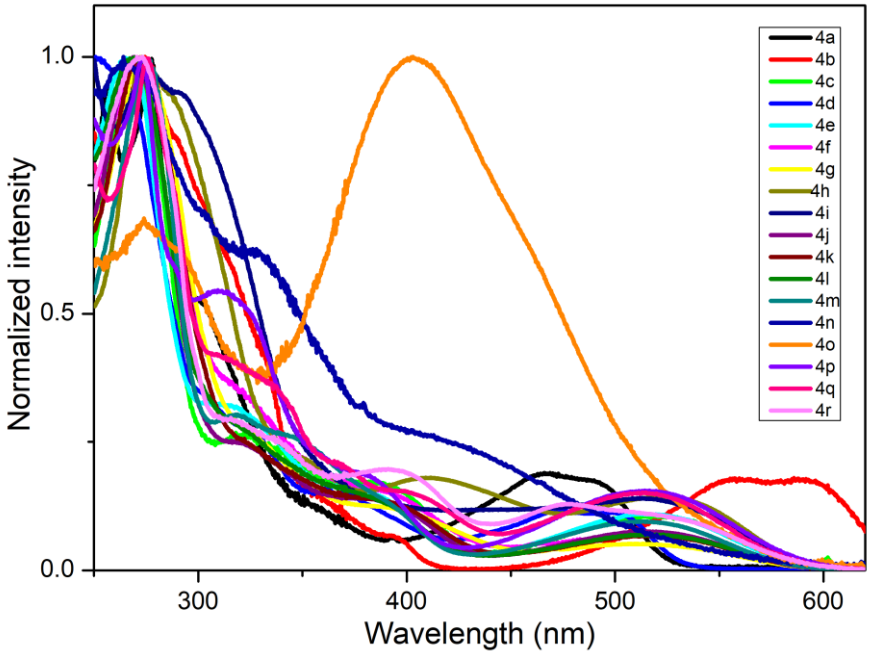


Fig. S9. Normalized UV-Vis absorption spectra of **4a-4r** in CH_2Cl_2 (1×10^{-6} M).

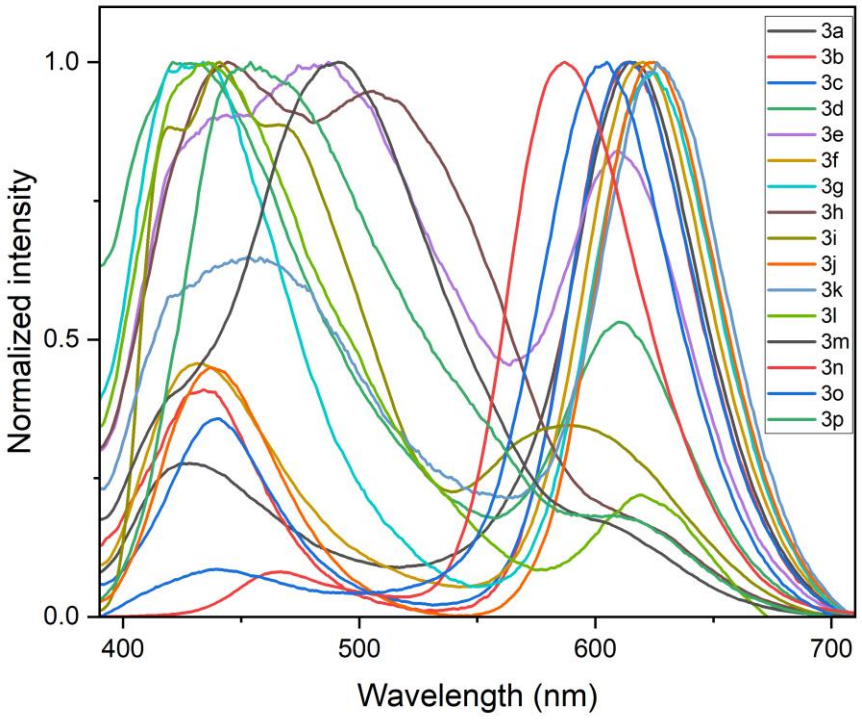


Fig. S10. Normalized emission spectra of **3a-3n** in CH_2Cl_2 (5×10^{-5} M).

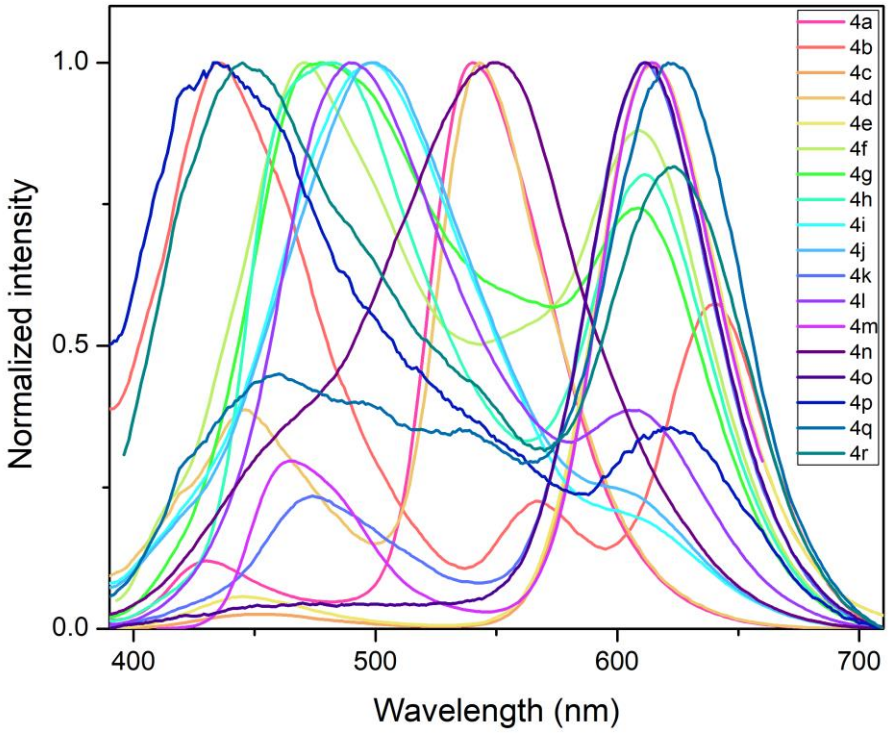


Fig. S11. Normalized emission spectra of **4a-4e**, **4g-4q** in CH_2Cl_2 (5×10^{-5} M), **4f**, **4r** in CH_2Cl_2 (1×10^{-5} M).

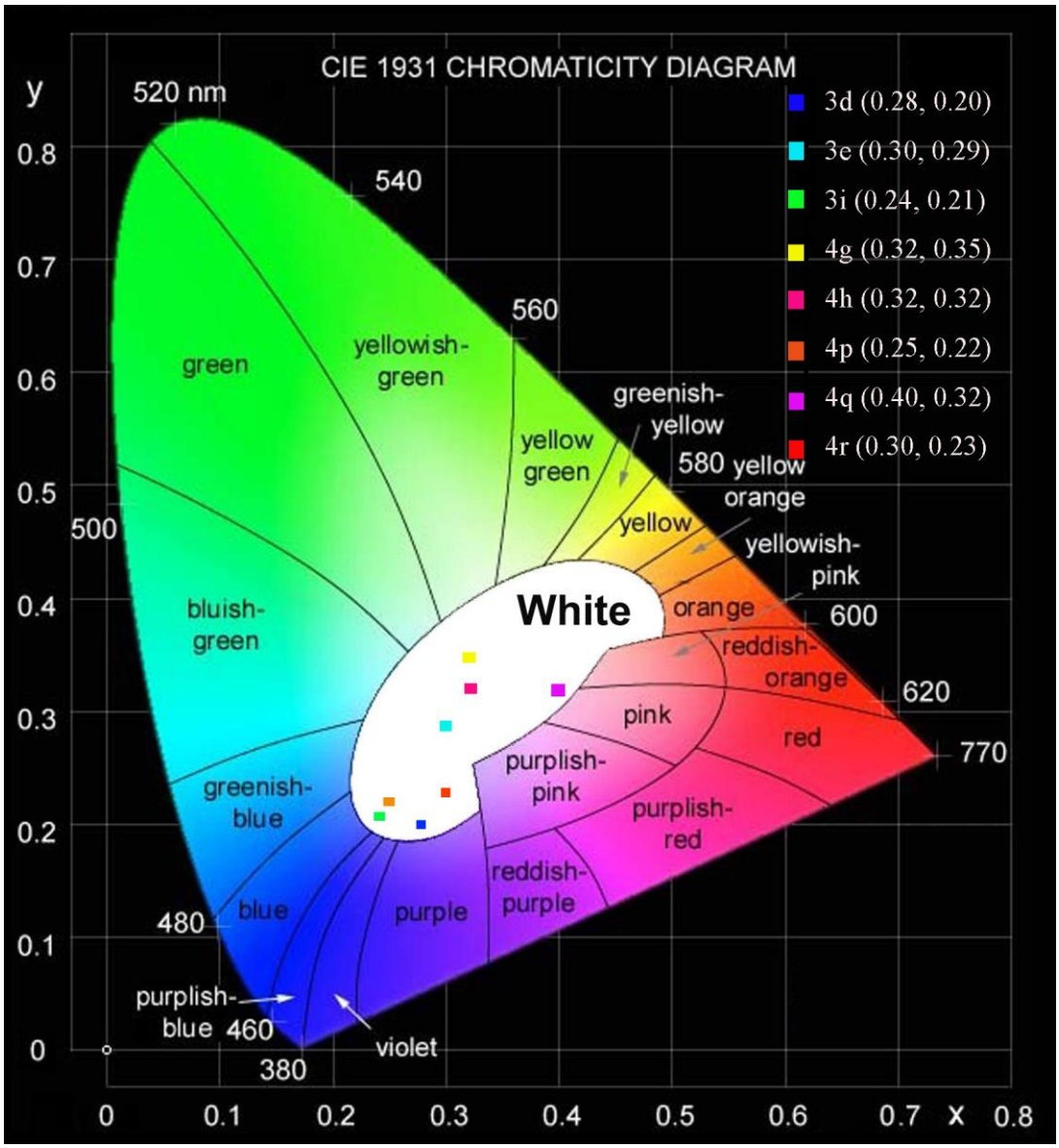


Fig. S12. Commission Internationale de l'Eclairage (CIE) coordinates of **3d** (0.28, 0.20), **3e** (0.30, 0.29), **3i** (0.24, 0.21), **4g** (0.32, 0.35), **4h** (0.32, 0.32), **4p** (0.25, 0.22), **4q** (0.40, 0.32), and **4r** (0.30, 0.23) in CH_2Cl_2, respectively.

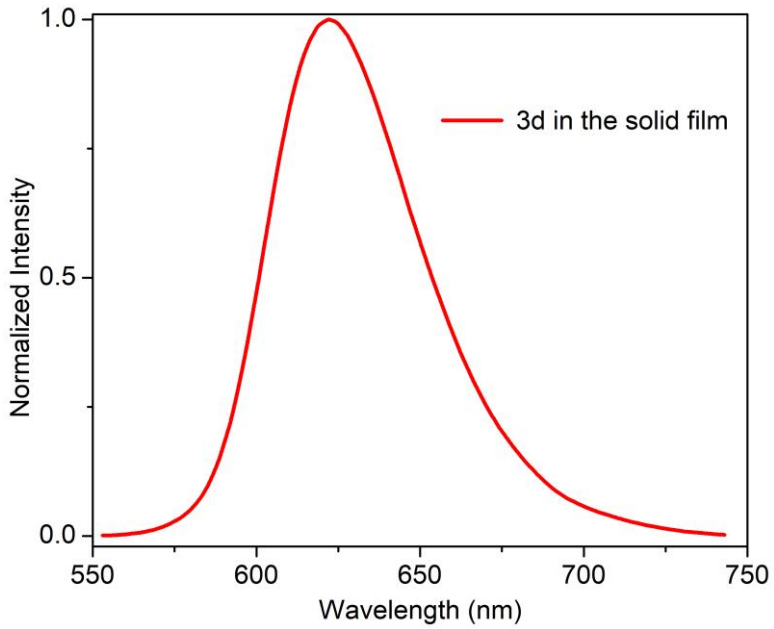


Fig. S13. Emission spectrum of **3d** in the solid film.

VII. The excited state lifetimes of 4f in DCM and film

Table S4 The excited state lifetimes of **4f**.[a]

Compd.	λ_{em} [nm] in DCM	Lifetime in DCM	λ_{em} [nm] in PMMA	Lifetime in PMMA
4f	470	τ_1 = 1.2888 ns, (35.1%) τ_2 = 5.5733 ns, (64.9%) χ^2 = 0.9660	470	τ_1 = 1.8404 ns, (54.02%) τ_2 = 9.9557 ns, (45.98%) χ^2 = 1.0162
	610	τ_1 = 2.9719 ns, (9.09%) τ_2 = 6.7643 ns, (90.91%) χ^2 = 1.0023	580	τ_1 = 2.1829 ns, (1.69%) τ_2 = 14.1718 ns, (98.31%) χ^2 = 1,0135

[a]The excited state lifetimes were determined on an Edinburgh FLS1000 Steady transient fluorescence spectrometer.

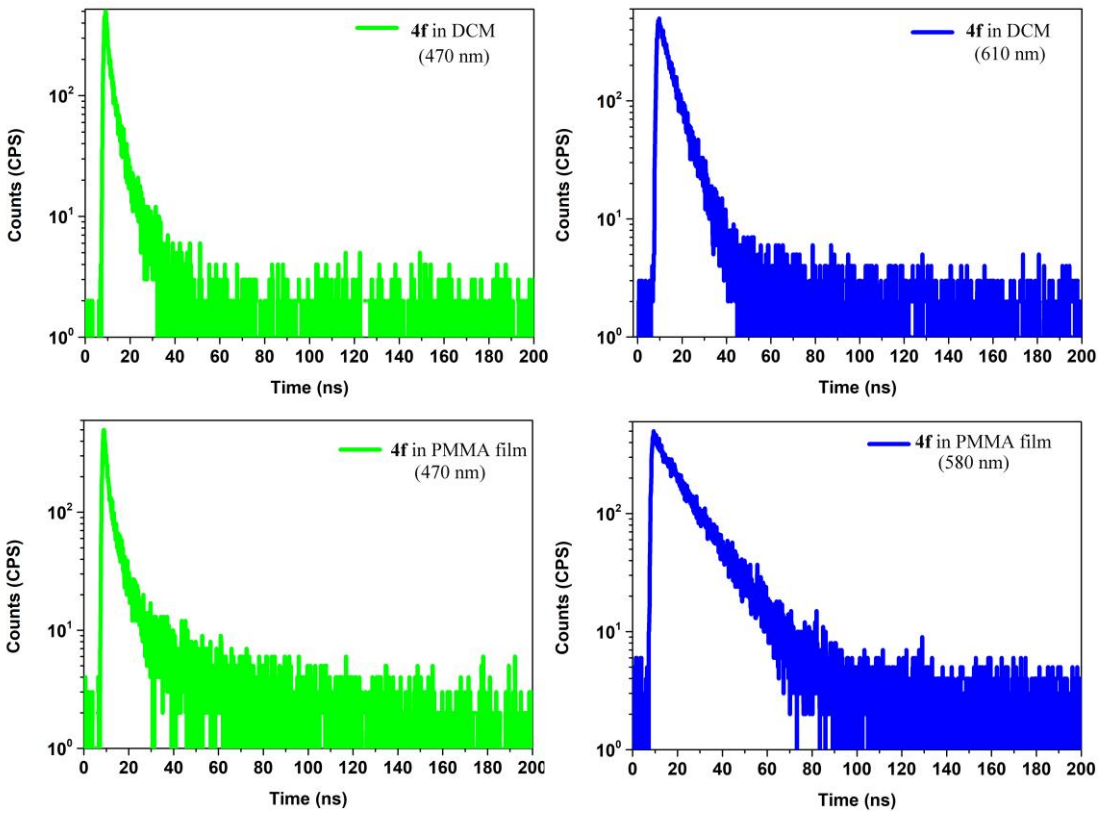


Fig. S14. Transient emission spectra of **4f** in DCM and PMMA film at room temperature.

VIII. The thermal properties of 4f and 4h

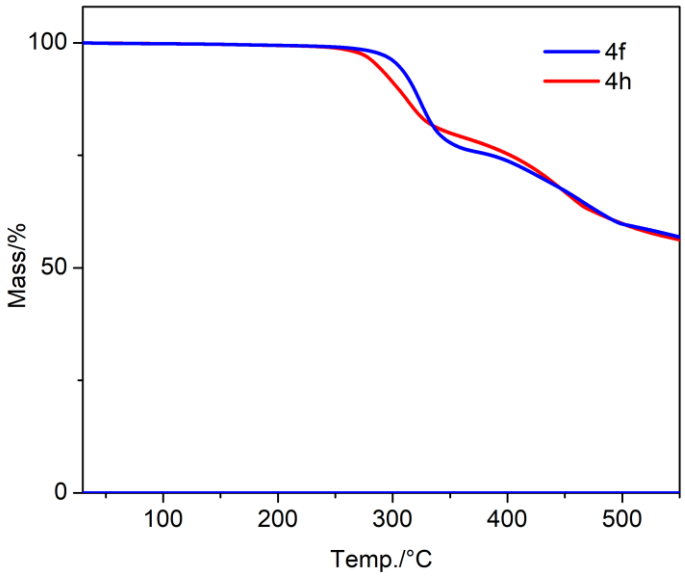
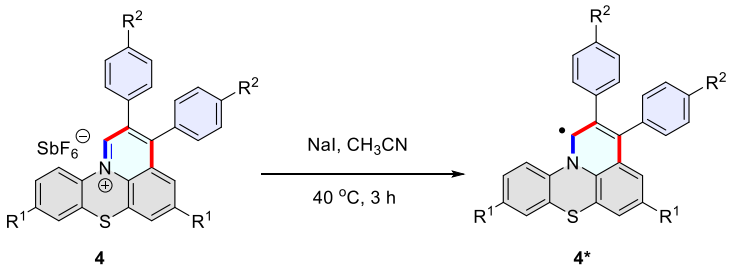


Fig. S15. The TGA curves of **4f** and **4h**.

IX. Radical detection

1. General procedure for the preparation of radicals



Following the literature report, an oven-dried Schlenk tube with a magnetic stir bar was charged with the cation (0.015 mmol), Nal (32.0 mg, 0.21 mmol), freshly distilled CH_3CN (3.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at room temperature for 10 min and then at 40 ℃ for 3 h. Then, the solvent was removed to get a solid.

Electron paramagnetic resonance (EPR) measurements

The EPR spectra of reduced **4c** and **4h** were recorded in the solid state at room temperature under air on a CIQTEK EPR200-Plus spectrometer. Experimental conditions: modulation frequency, 100.00 kHz; modulation amplitude, 1.00 G; sweep width, 400.00 G; time constant, 300 ms; conversion time, 100 ms; sweep time, 163.84 ms; receiver gain, 303; The microwave frequency, 9.500000 GHz; power, 2.00 mW. The corresponding reduced products are EPR active and offer g values of 2.0025 (**4c**) and 2.0023 (**4h**), respectively.

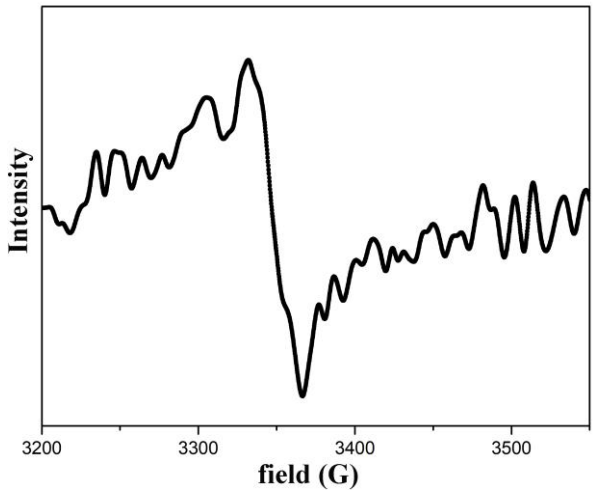


Fig. S16. EPR spectrum of reduced **4c** in solid state at room temperature.

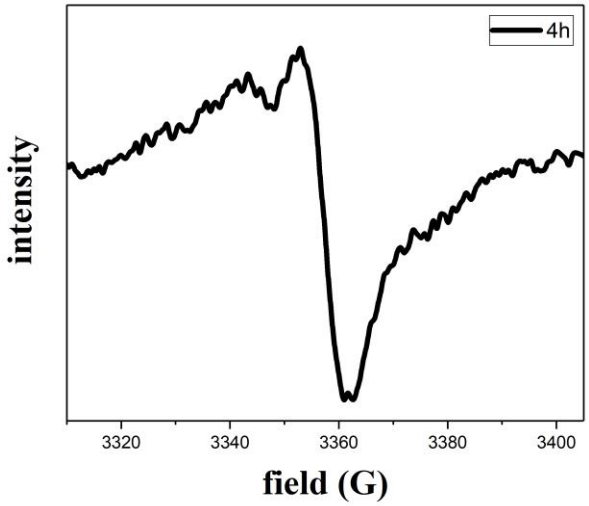


Fig. S17. EPR spectrum of reduced **4h** in solid state at room temperature.

X. Single crystal X-ray structure of 4d

The single crystal was obtained in a chloroform solution. CCDC-2298889 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data request/cif.

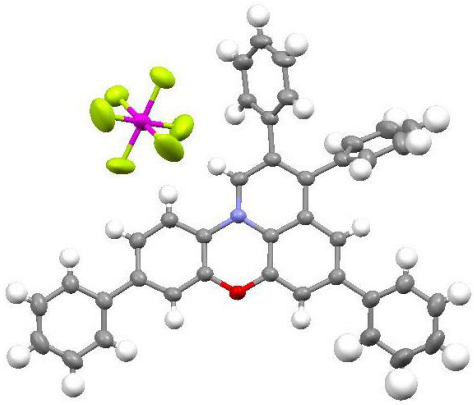


Fig. S18. The single crystal (CCDC-2298889) structure of **4d**.

Bond precision: C-C = 0.0053 A Wavelength=1.54184

Cell: a=15.2592(2) b=12.0316(1) c=18.0659(2)
alpha=90 beta=103.902(1) gamma=90
Temperature: 250 K

	Calculated	Reported
Volume	3219.61(6)	3219.61(6)
Space group	P 2/c	P 1 2/c 1
Hall group	-P 2yc	-P 2yc
Moiety formula	C39 H26 N O, F6 Sb	2(F3 Sb0.5), C39 H26 N O
Sum formula	C39 H26 F6 N O Sb	C39 H26 F6 N O Sb
Mr	760.37	760.36
Dx,g cm-3	1.569	1.569
Z	4	4
Mu (mm-1)	7.391	7.391
F000	1520.0	1520.0
F000'	1524.72	
h,k,lmax	18,14,22	18,14,22
Nref	6181	6179
Tmin,Tmax	0.189,0.183	0.589,1.000
Tmin'	0.084	

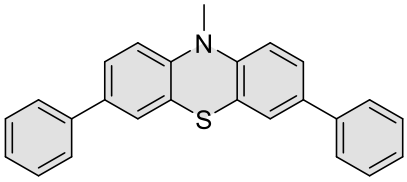
Correction method= # Reported T Limits: Tmin=0.589 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 70.569

R(reflections)= 0.0445(5595) wR2(reflections)= 0.1190(6179)

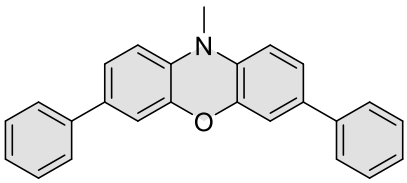
Fig. S19. Selected crystallographic data.

XI. Experimental data for the substrates 1



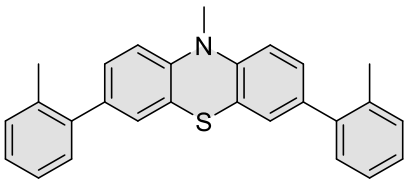
10-Methyl-3,7-diphenyl-10*H*-phenothiazine (1c)

Yellow solid 233 mg, yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57-7.55 (m, 4H), 7.46-7.42 (m, 8H), 7.36-7.32 (m, 2H), 6.88 (d, J = 8.4 Hz, 2H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.0, 140.1, 135.8, 128.9, 127.1, 126.6, 126.3, 125.8, 123.7, 114.4, 35.5. HRMS (ESI^+): calcd for $C_{25}H_{20}NS$ $[M+H]^+$ 366.1311, found 366.1307.



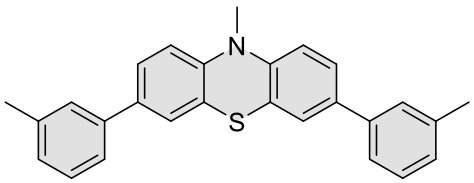
10-Methyl-3,7-diphenyl-10*H*-phenoxazine (1d)

Yellow solid 156 mg, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56-7.55 (m, 4H), 7.44-7.41 (m, 4H), 7.33-7.32 (m, 2H), 7.14-7.12 (m, 2H), 7.02 (s, 2H), 6.60-6.59 (m, 2H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.7, 140.1, 134.2, 128.9, 126.9, 126.4, 122.3, 114.0, 111.8, 29.8. HRMS (ESI^+): calcd for $C_{25}H_{20}NO$ $[M+H]^+$ 350.1540, found 350.1531.



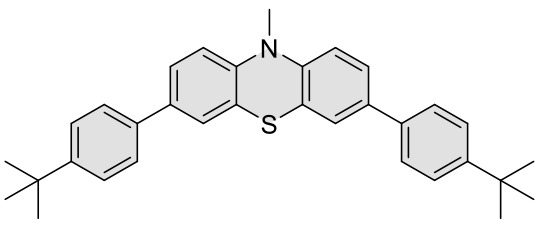
10-Methyl-3,7-di-o-tolyl-10*H*-phenothiazine (1e)

Yellow solid 242 mg, yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.23 (d, J = 3.2 Hz, 4H), 7.21-7.19 (m, 4H), 7.13 (s, 4H), 6.86 (s, 2H), 3.45 (s, 3H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.9, 135.5, 130.5, 129.8, 128.5, 127.4, 125.9, 113.8, 20.7. HRMS (ESI^+): calcd for $C_{27}H_{24}NS$ $[M+H]^+$ 394.1624, found 364.1613.



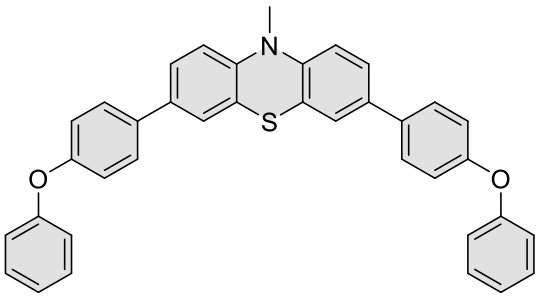
10-Methyl-3,7-di-m-tolyl-10*H*-phenothiazine (1f)

Yellow solid 243 mg, yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.41-9.40 (m, 4H), 7.36-7.29 (m, 6H), 7.13 (d, J = 6.8 Hz, 2H), 6.89-6.87 (m, 2H), 3.45 (s, 3H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.9, 140.1, 138.5, 135.8, 128.8, 127.9, 127.4, 126.3, 125.8, 123.8, 123.6, 114.3, 35.5, 21.7. HRMS (ESI^+): calcd for $C_{27}H_{24}NS$ $[M+H]^+$ 394.1624, found 394.1625.



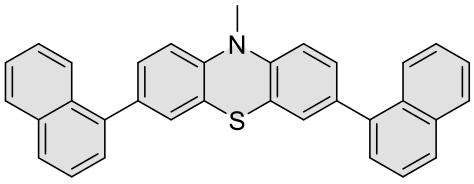
3,7-Bis(4-(tert-butyl)phenyl)-10-methyl-10*H*-phenothiazine (1g)

Yellow solid 306 mg, yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52-7.46 (m, 8H), 7.43-7.41 (m, 4H), 6.89-6.87 (m, 2H), 3.41 (s, 3H), 1.39 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.1, 137.2, 126.3, 126.1, 125.9, 114.4, 34.6, 31.5. HRMS (ESI^+): calcd for $C_{33}H_{36}NS$ $[M+H]^+$ 478.2563, found 478.2574.



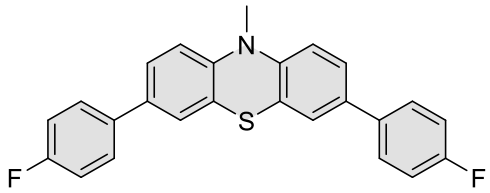
10-Methyl-3,7-bis(4-phenoxyphenyl)-10*H*-phenothiazine (1h)

Yellow solid 216 mg, yield: 52%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.51 (d, J = 8.4 Hz, 4H), 7.40-7.36 (m, 8H), 7.15 (t, J = 7.6 Hz, 2H), 7.09-7.07 (m, 8H), 6.87 (d, J = 8.4 Hz, 2H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 157.3, 156.7, 144.7, 135.2, 129.9, 127.9, 126.0, 125.5, 123.5, 119.3, 119.1, 114.4, 35.5. HRMS (ESI^+): calcd for $C_{37}H_{28}NO_2S$ $[M+H]^+$ 550.1836, found 550.1836.



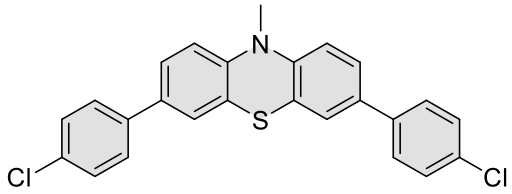
10-Methyl-3,7-di(naphthalen-1-yl)-10*H*-phenothiazine (1i)

Yellow solid 233 mg, yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.54-7.44 (m, 6H), 7.42-7.41 (m, 2H), 7.36-7.35 (m, 4H), 6.99 (d, J = 8.4 Hz, 2H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.1, 139.3, 135.4, 134.0, 131.8, 129.4, 128.8, 128.4, 127.7, 126.9, 126.2, 126.1, 125.9, 125.5, 123.4, 114.0, 35.6. HRMS (ESI$^+$): calcd for $C_{33}H_{24}NS$ $[M+H]^+$ 466.1624, found 466.1621.



3,7-Bis(4-fluorophenyl)-10-methyl-10*H*-phenothiazine (1j)

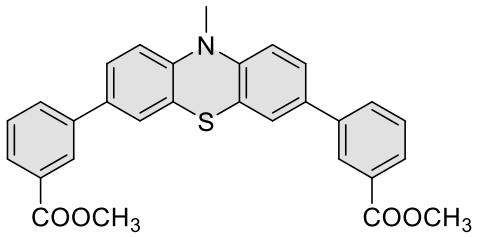
Yellow solid 252 mg, yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50-7.47 (m, 4H), 7.36-7.34 (m, 4H), 7.10 (t, J = 8.4 Hz, 4H), 6.88 (d, J = 8.8 Hz, 2H), 3.44 (s, 3H). The ^{13}C NMR data could not be recorded due to its poor solubility. HRMS (ESI$^+$): calcd for $C_{25}H_{18}F_2NS$ $[M+H]^+$ 402.1123, found 402.1126.



3,7-Bis(4-chlorophenyl)-10-methyl-10*H*-phenothiazine (1k)

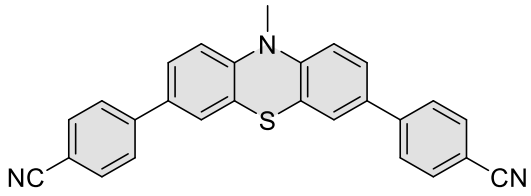
Yellow solid 227 mg, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.47-7.45 (m, 4H), 7.39-7.35 (m, 8H), 6.88 (d, J = 8.0 Hz, 2H), 3.44 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ (ppm) 145.2, 138.5, 134.6, 133.2, 129.1, 127.9, 126.2, 125.6, 123.8, 114.5, 35.6. HRMS (ESI^+): calcd for $C_{25}H_{18}Cl_2NS$ $[M+H]^+$ 434.0532, found 434.0527.



Dimethyl 3,3'-(10-methyl-10*H*-phenothiazine-3,7-diyl)dibenzoate (1l)

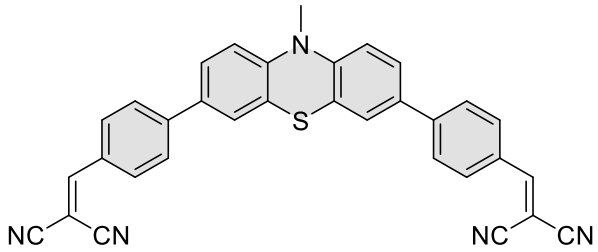
Yellow solid 234 mg, yield: 65%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.22 (s, 2H), 7.98 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.44-7.42 (m, 4H), 6.88 (d, J = 8.4 Hz, 2H), 3.95 (s, 6H), 3.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.2, 145.3, 140.3, 134.7, 131.0, 130.9, 129.0, 128.2, 127.7, 126.4, 125.7, 123.8, 114.5, 52.3, 35.6. HRMS (ESI^+): calcd for $C_{29}H_{23}NO_4S$ $[M+H]^+$ 366.1305, found 366.1307. HRMS (ESI^+): calcd for $C_{29}H_{24}NO_4S$ $[M+H]^+$ 482.1421, found 482.1421.



4,4'-(10-Methyl-10*H*-phenothiazine-3,7-diyl)dibenzonitrile (1m)

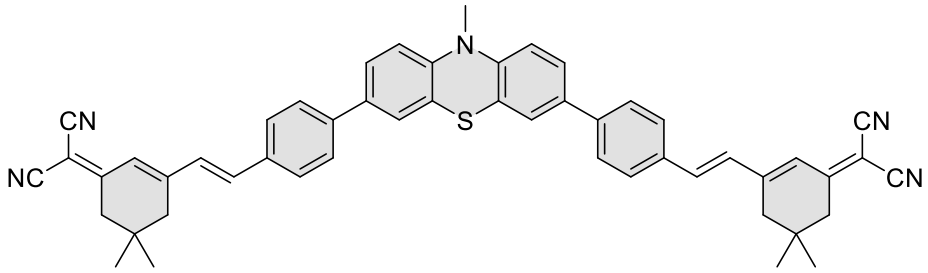
Yellow solid 260 mg, yield: 84%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69-7.63 (m, 8H), 7.39 (s, 4H), 6.91 (s, 2H), 3.46 (s, 3H). The ^{13}C NMR data could not be recorded

due to its poor solubility. HRMS (ESI^+): calcd for $C_{27}H_{18}N_3S$ $[M+H]^+$ 416.1216, found 416.1214.



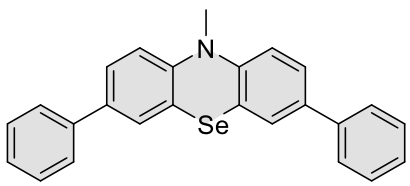
2,2'-(((10-Methyl-10*H*-phenothiazine-3,7-diyl)bis(4,1-phenylene))bis(methanylylidene))dimalononitrile (1n)

To a solution of malononitrile (48 mg, 0.75 mmol) and 4,4'-(10-methyl-10H-phenothiazine-3,7-diyl)dibenzaldehyde (105 mg, 0.25 mmol) in dry ethanol (4 mL) was added piperidine (20 μL, 0.23 μmol). The solution was stirred at 60 ℃ for 12 h. After cooling to room temperature, the black solution was removed by the evaporation under reduced pressure. Purification on silica gel petroleum ether/ ethyl acetate = 3:1, v/v) afforded compound. Black solid 225 mg, yield: 58%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97 (d, J = 7.6 Hz, 4H), 7.76 (s, 2H), 7.71 (d, J = 7.2 Hz, 4H), 7.50 (d, J = 8.4 Hz, 2H), 7.45 (s, 2H), 6.94 (d, J = 8.0 Hz, 2H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, C_2D_6SO): δ (ppm) 160.6, 131.4, 129.93, 128.89, 126.7, 125.1, 122.5, 115.3, 114.5, 113.6, 80.0, 22.2. HRMS (ESI^+): calcd for $C_{33}H_{20}N_5S$ $[M+H]^+$ 518.1434, found 518.1430.



2,2'-(((1*E*,1'*E*)-((10-Methyl-10*H*-phenothiazine-3,7-diyl)bis(4,1-phenylene))bis(ethene-2,1-diyl))bis(5,5-dimethylcyclohex-2-en-3-yl-1-ylidene))dimalononitrile (1o)

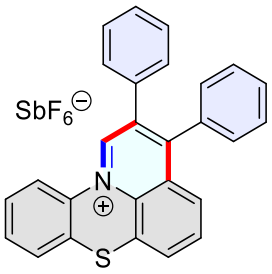
To a solution of 2-(3,5,5-trimethylcyclohex-2-en-1-ylidene)malononitrile (279 mg, 1.5 mmol) and 4,4'-(10-methyl-10*H*-phenothiazine-3,7-diyl)dibenzaldehyde (210 mg, 0.5 mmol) in dry CH_3CN (2.5 mL) was added piperidine (40 μL, 0.46 μmol). The solution was stirred at 82 ℃ for 1 h. After cooling to room temperature, the black solution was removed by the evaporation under reduced pressure. Purification on silica gel (petroleum ether/ ethyl acetate = 3:1, v/v) afforded compound **1o**. Black solid 262 mg, yield: 46%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57 (q, J_1 = 8.4 Hz, J_2 = 12.4 Hz, 8H), 7.46-7.43 (m, 4H), 7.11-6.99 (m, 4H), 6.90 (d, J = 8.8 Hz, 2H), 6.86 (s, 2H), 3.46 (s,3H), 2.61 (s, 4H), 2.49 (s, 4H), 1.09 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.3, 154.0, 136.7, 129.1, 128.3, 127.0, 126.3, 125.6, 123.7, 114.6, 113.7, 43.2, 39.4, 35.7, 32.2, 28.2. HRMS (ESI^+): calcd for $C_{51}H_{44}N_5S$ $[M+H]^+$ 758.3312, found 758.3305.



10-Methyl-3,7-diphenyl-10*H*-phenoselenazine (1r)

Yellow solid 201 mg, yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60-7.55 (m, 6H), 7.48-7.41 (m, 6H), 7.34-7.31 (m, 2H), 6.99 (d, J = 8.4 Hz, 2H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.2, 140.1, 136.3, 128.9, 128.3, 127.2, 126.8, 126.6, 120.1, 115.6, 37.1. HRMS (ESI^+): calcd for $C_{25}H_{20}NSe$ $[M+H]^+$ 414.0756, found 414.0747.

XII. Experimental data for the pyrido-phenothiazin/phenoxazin/phenoslenazin/phenazin-12-iums-hexafluorostibate (V)



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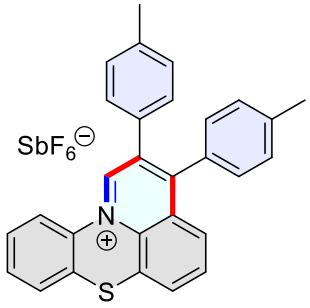
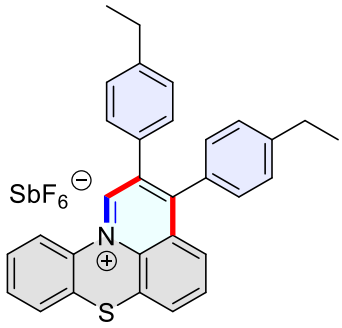
2,3-Diphenylpyrido[3, 2, 1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3a)

Red solid 47 mg, yield: 75%. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.26 (s, 1H), 7.90 (d, J = 5.2 Hz, 1H), 7.81 (d, J = 4.8 Hz, 1H), 7.71-7.66 (m, 2H), 7.60-7.55 (m, 2H), 7.48-7.44 (m, 4H), 7.35-7.32 (m, 7H); ^{13}C NMR (100 MHz, C_2D_6SO): δ (ppm) 157.3, 145.1, 136.0, 135.2, 134.0, 133.5, 133.2, 131.5, 130.9, 130.5, 130.2, 129.7, 129.6, 129.33, 129.28, 128.8, 128.6, 128.24, 128.15, 125.8, 125.3, 125.2, 123.6. HRMS [ESI^+]: calcd for $C_{27}H_{18}N^+S$, 388.1155, found 388.1157.



2,3-Di-p-tolylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3b)

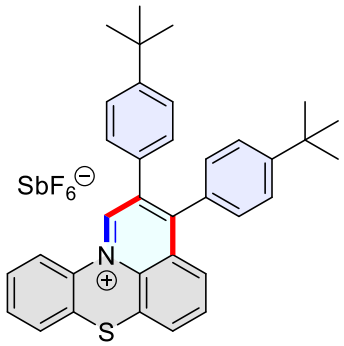
Red solid 47 mg, yield: 72%. ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 9.70 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 8.00 (dd, J_1 = 1.2 Hz, J_2 = 7.2 Hz, 1H), 7.80-7.72 (m, 2H), 7.65-7.59 (m, 3H), 7.33-7.31 (m, 2H) , 7.25-7.18 (m, 6H), 2.42 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 147.2, 145.3, 141.7, 140.4, 138.3, 132.7, 131.9, 131.4, 131.2, 131.1, 130.9, 130.8, 130.6, 130.4, 129.4, 127.0, 125.3, 123.7, 122.2, 21.4, 21.2. HRMS [ESI$^+$]: calcd for $C_{29}H_{22}N^+S$, 416.1468, found 416.1471.



2,3-Bis(4-ethylphenyl)pyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3c)

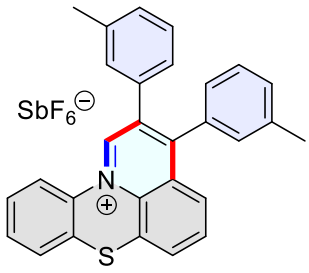
Red solid 43 mg, yield: 63%. ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 9.70 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 8.01-7.99 (m, 1H), 7.80-7.72 (m, 2H), 7.65-7.59 (m, 3H), 7.35-7.33 (m, 2H), 7.27-7.20 (m, 6H), 2.72 (q, J = 7.6 Hz, 2H), 2.65 (q, J = 7.6 Hz,

2H), 1.27 (t, J = 7.6 Hz, 3H), 1.21 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 160.3, 148.1, 146.8, 145.5, 141.8, 138.3, 137.6, 135.5, 133.1, 133.0, 132.7, 132.2, 131.5, 131.4, 131.1, 131.0, 130.8, 129.5, 129.3, 128.3, 127.1, 125.8, 125.4, 29.7, 29.6, 15.93, 15.85. HRMS [ESI$^+$]: calcd for $C_{31}H_{26}N^+S$, 444.1781, found 444.1787.



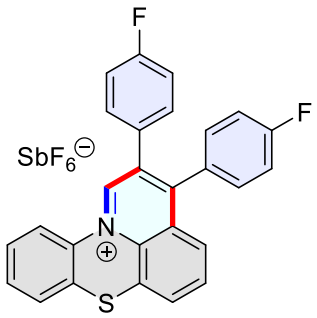
2,3-Bis(4-(tert-butyl)phenyl)pyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3d)

Red solid 52 mg, yield: 71%. ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 9.72 (s, 1H), 8.02 (dd, J_1 = 8.0 Hz, J_2 = 16.8 Hz, 2H), 7.80-7.74 (m, 2H), 7.64-7.60 (m, 3H), 7.55-7.53 (m, 2H), 7.41-7.39 (m, 2H), 7.28-7.26 (m, 4H), 1.35 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 160.2, 154.8, 153.4, 145.4, 140.9, 135.5, 132.9, 132.6, 132.0, 131.4, 131.1, 130.8, 129.4, 128.2, 127.1, 126.9, 126.6, 125.7, 125.4, 31.6. HRMS [ESI$^+$]: calcd for $C_{35}H_{34}N^+S$, 500.2407, found 500.2405.



2,3-Di-m-tolylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3e)

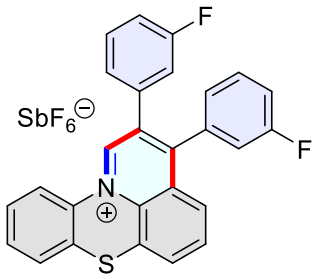
Red solid 39 mg, yield: 60%. ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 9.72 (s, 1H), 8.02 (dd, J_1 = 8.0 Hz, J_2 = 18.4 Hz, 2H), 7.77 (t, J = 8.0 Hz, 1H), 7.72-7.69 (m, 1H), 7.63-7.59 (m, 3H), 7.38-7.32 (m, 2H), 7.20-7.11 (m, 6H), 2.33 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 160.2, 145.3, 140.1, 139.7, 138.3, 137.5, 135.4, 134.8, 132.9, 132.6, 131.9, 131.6, 131.4, 131.2, 131.1, 130.8, 130.7, 129.8, 129.5, 129.4, 128.4, 128.2, 127.9, 127.0, 125.7, 125.4, 21.33, 21.31. HRMS [ESI$^+$]: calcd for $C_{29}H_{22}N^+S$, 416.1468, found 416.1470.



2,3-Bis(4-fluorophenyl)pyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3f)

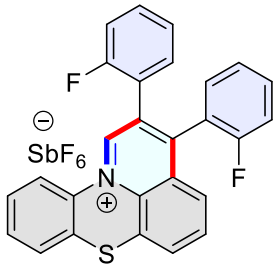
Red solid 40 mg, yield: 60%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.43 (s,1H), 7.99 (d, J = 7.2 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.78 (t, J = 8.4 Hz, 1H), 7.68-7.63 (m, 3H), 7.61-7.57 (m, 1H), 7.33-7.23 (m, 6H), 7.15 (t, J = 8.8 Hz, 2H); ^{13}C NMR (100

MHz, CD_3CN): δ (ppm) 158.7, 153.6, 144.9, 134.7, 133.4, 133.3, 132.9, 132.8, 132.7, 131.6, 131.0, 130.8, 129.4, 127.8, 126.6, 125.3, 117.1, 116.9, 116.6, 116.4. HRMS [ESI^+]: calcd for $C_{27}H_{16}N^+S$, 424.0966, found 424.0966.



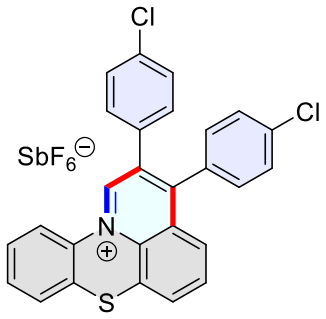
2,3-Bis(3-fluorophenyl)pyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3g)

Red solid 34 mg, yield: 53%. ^1H NMR (400 MHz, CD_3OD): δ (ppm) 9.83 (s, 1H), 8.07 (t, J = 9.2 Hz, 2H), 7.83 (t, J = 8.0 Hz, 1H), 7.70-7.62 (m, 4H), 7.57-7.51 (m, 1H), 7.44-7.38 (m, 1H), 7.28 (t, J = 8.8 Hz, 1H), 7.18-7.14 (m, 5H); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 144.8, 132.8, 132.7, 132.5, 132.2, 132.1, 131.8, 131.6, 131.5, 131.2, 130.9, 130.6, 130.0, 129.4, 128.9, 128.4, 128.2, 127.9, 127.3, 126.6, 126.53, 126.49, 125.3, 124.8. HRMS [ESI^+]: calcd for $C_{27}H_{16}F_2N^+S$, 424.0966, found 424.0967.



(R)-2,3-Bis(2-fluorophenyl)pyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibat e (V) (3h)

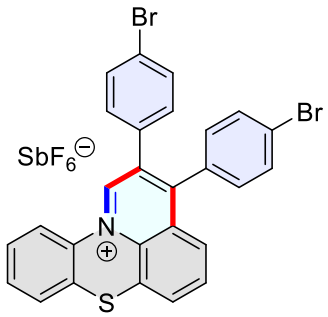
Red solid 36 mg, yield: 55%. ^{1}H NMR (400 MHz, C_2D_6SO): δ (ppm) 9.99 (s, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 7.6 Hz, 1H), 7.89 (t, J = 8.0 Hz, 1H), 7.81-7.79 (m, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.66-7.56 (m, 3H), 7.46-7.37 (m, 2H), 7.33-7.26 (m, 3H), 7.17-7.15 (m, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 145.0, 134.0, 133.9, 133.3, 133.2, 132.9, 131.9, 131.8, 131.4, 130.9, 130.1, 129.4, 129.0, 128.4, 128.1, 126.2, 125.87, 125.84, 125.7, 125.6, 125.3, 117.2, 117.0, 116.7, 116.5. HRMS [ESI^{+}]: calcd for $C_{27}H_{16}F_2N^{+}S$, 424.0966, found 424.0964.



2,3-Bis(4-chlorophenyl)pyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3i)

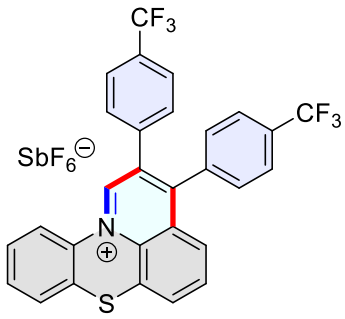
Red solid 40 mg, yield: 58%. ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) 9.18 (s, 1H), 7.88-7.82 (m, 2H), 7.70 (t, J = 8.0 Hz, 1H), 7.65-7.63 (m, 1H), 7.58-7.56 (m, 2H), 7.49-7.44 (m, 3H), 7.37-7.35 (m, 3H), 7.28 (s. 3H); ^{13}C NMR (100 MHz, CD_3Cl): δ (ppm) 158.3, 144.8, 137.0, 136.7, 135.8, 134.6, 133.4, 132.8, 132.6, 132.5, 132.1,

131.7, 131.1, 130.8, 130.1, 129.7, 129.4, 128.9, 128.3, 128.2, 127.8, 126.5, 125.3. HRMS [ESI$^+$]: calcd for $C_{27}H_{16}Cl_2N^+S$, 456.0375, found 456.0373.



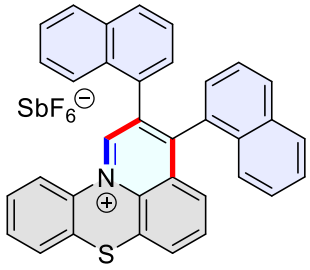
2,3-Bis(4-bromophenyl)pyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3j)

Red solid 56 mg, yield: 72%. ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 9.80 (s, 1H), 8.06 (dd, J_1 = 8.4 Hz, J_2 = 10.8 Hz, 2H), 7.82 (t, J = 8.0 Hz, 1H), 7.71-7.61 (m, 6H), 7.58-7.56 (m, 2H), 7.28 (dd, J_1 = 5.2 Hz, J_2 = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 158.3, 144.8, 136.7, 134.7, 133.9, 133.1, 132.9, 132.8, 132.5, 132.3, 131.8, 131.2, 130.9, 130.1, 129.5, 128.4, 128.3, 127.9, 126.6, 125.4, 125.3, 125.0, 124.2. HRMS [ESI$^+$]: calcd for $C_{27}H_{16}Br_2N^+S$, 545.9344, found 545.9341.



2,3-Bis(4-(trifluoromethyl)phenyl)pyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3k)

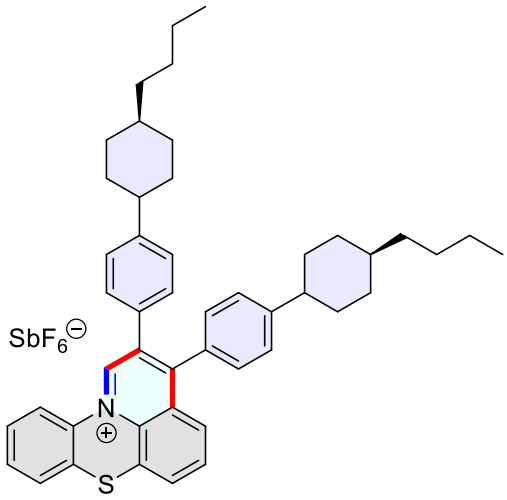
Red solid 46 mg, yield: 61%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.48 (s, 1H), 8.04-8.02 (m, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.82-7.78 (m, 3H), 7.71 (d, J = 8.4 Hz, 2H), 7.67-7.64 (m, 2H), 7.62-7.57 (m, 2H), 7.50 (t, J = 6.8 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 158.0, 144.9, 138.5, 137.9, 137.2, 136.5, 134.7, 133.0, 132.6, 132.4, 132.0, 131.9, 131.4, 131.3, 131.0, 129.5, 128.0, 127.0, 126.94, 126.91, 126.87, 126.54, 126.49, 126.45, 126.4, 125.6, 125.4. HRMS [ESI^+]: calcd for: $C_{29}H_{16}F_6N^+S$, 524.0902, found 524.0900.



(R)-2,3-Di(naphthalen-1-yl)pyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3l)

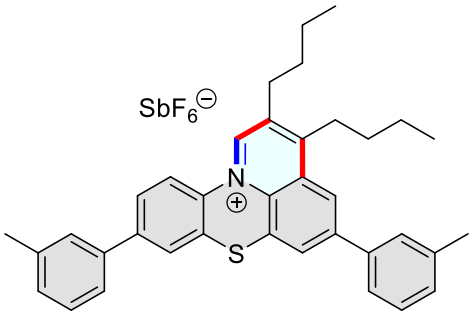
Red solid 48 mg, yield: 66%. ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 9.98 (s, 1H), 8.06 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.94-7.91 (m, 1H), 7.89-7.83 (m, 2H), 7.80-7.73 (m, 2H), 7.72-7.64 (m, 3H), 7.61-7.45 (m, 5H), 7.43-7.18 (m, 5H), 7.13 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 160.6, 145.4, 145.3, 132.7, 131.6, 131.5, 131.0, 130.8, 130.7, 130.6, 129.8, 129.5, 129.4, 128.9, 128.3,

128.1, 127.8, 127.6, 127.5, 127.3, 127.2, 126.8, 126.6, 126.5, 126.3, 126.2, 125.8, 125.7, 125.3. HRMS [ESI$^+$]: calcd for $C_{35}H_{22}F_6N^+S$, 488.1468, found 488.1469.



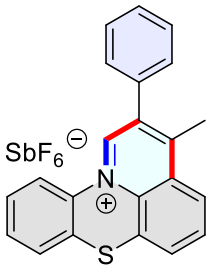
2,3-Bis(4-(4-butylcyclohexyl)phenyl)pyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3m)

Red solid 47 mg, yield: 52%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.38 (s, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 8.4 Hz, 1H), 7.64-7.62 (m, 3H), 7.59-7.56 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.23-7.16 (m, 6H), 2.59-2.47 (m, 2H), 1.87-1.80 (m, 8H), 1.53-1.38 (m, 4H), 1.33-1.25 (m, 14H), 1.13-1.01 (m, 4H), 0.93-0.91 (m, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 159.7, 151.1, 149.9, 144.9, 137.7, 136.9, 134.7, 132.7, 132.6, 132.5, 131.7, 131.3, 131.0, 130.74, 130.69, 130.4, 129.3, 128.1, 127.9, 127.7, 126.7, 125.3, 125.0, 45.1, 44.9, 37.9, 37.8, 34.88, 34.85, 34.2, 29.9, 23.7, 14.4. HRMS [ESI$^+$]: calcd for $C_{47}H_{54}N^+S$, 664.3972, found 664.3972.



2,3-Dibutyl-5,9-di-*m*-tolylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3n)

Orange solid 38 mg, yield: 52%. ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) 9.28 (s, 1H), 8.06-8.03 (m, 1H), 7.96-7.94 (m, 1H), 7.89-7.82 (m, 1H), 7.58-7.52 (m, 2H), 7.46-7.31 (m, 7H), 7.23-7.21 (m, 1H), 3.29-3.26 (m, 1H), 3.14-3.11 (m, 2H), 2.49 (s, 3H), 2.46-2.44 (m, 2H), 2.41 (s, 3H), 1.83-1.61 (m, 7H), 1.46-1.43 (m, 2H), 1.09-1.01 (m, 4H); ^{13}C NMR (125 MHz, CD_3Cl): δ (ppm) 161.5, 144.4, 143.5, 141.8, 139.6, 139.1, 138.4, 137.5, 137.0, 133.7, 132.2, 131.2, 130.5, 130.1, 129.6, 129.2, 128.3, 128.1, 127.8, 126.2, 125.8, 125.5, 124.7, 124.3, 123.9, 119.9, 33.3, 32.2, 30.9, 29.6, 23.5, 22.9, 21.7, 21.6, 13.9, 13.8. HRMS [ESI$^+$]: calcd for $C_{37}H_{38}N^+S$, 528.2720, found 528.2719.



2-Phenyl-3-methylpyrido[3, 2, 1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3o)

Orange solid 32 mg, yield: 60%. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.96 (s, 1H), 8.25-8.23 (m, 1H), 8.05 (d, J = 7.2 Hz, 1H), 7.79-7.68 (m, 7H), 7.44 (d, J = 6.8 Hz, 2H), 7.36 (d, J = 8.4 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 158.2, 145.7, 134.7, 133.5, 133.4, 132.6, 131.4, 130.8, 130.2, 129.9, 129.6, 129.4, 128.9, 128.3, 128.2, 125.8, 124.7, 124.4, 123.3, 17.6. HRMS [ESI^{+}]: calcd for $C_{22}H_{16}N^{+}S$ 326.0998, found 326.1003.

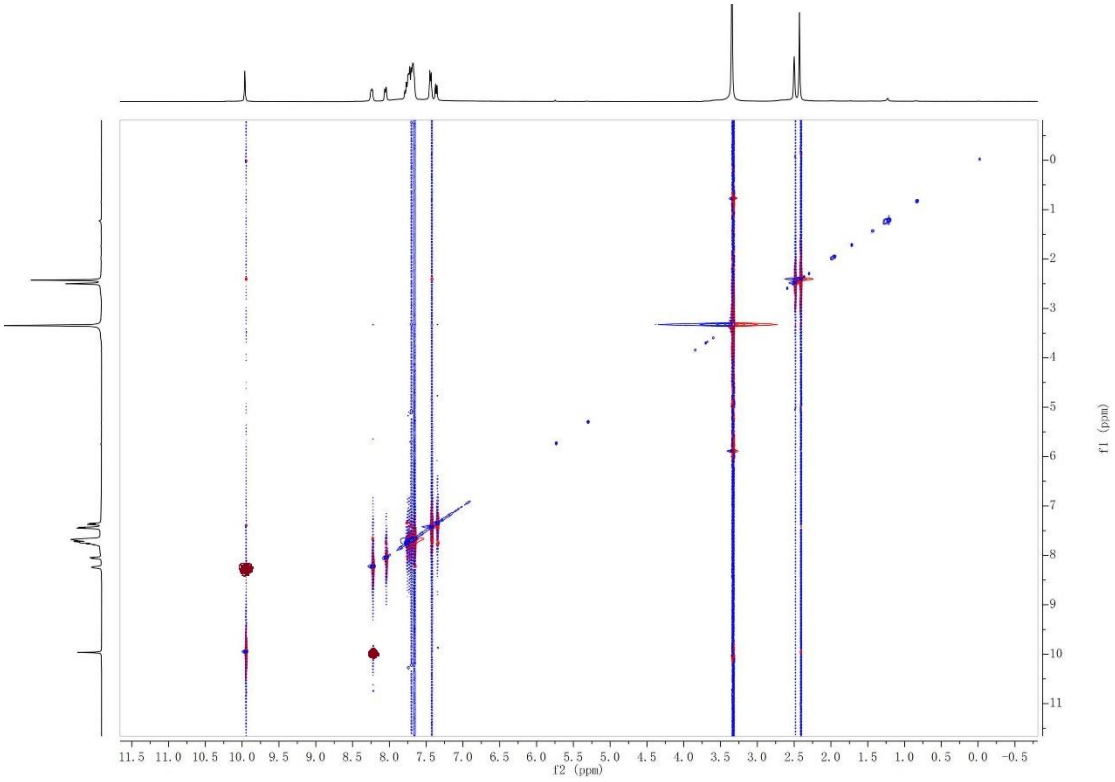
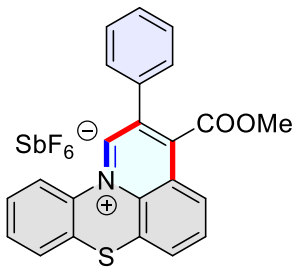


Fig. S20. ^{1}H-^{1}H nuclear overhauser effect spectroscopy of **3o**.



3-(Methoxycarbonyl)-2-phenylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3p)

Orange solid 29 mg, yield: 48%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 10.04 (s, 1H), 8.22 (t, J = 8.4 Hz, 1H), 8.01 (d, J = 8 Hz, 1H), 7.88 (q, J = 8 Hz, 2H), 7.79-7.77 (m, 1H), 7.68 (s, 4H), 7.56 (d, J = 8.4 Hz, 1H), 7.44 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ (ppm) 163.0, 144.4, 143.1, 135.3, 132.2, 131.7, 131.2, 130.8, 130.3, 129.9, 128.9, 128.2, 126.2, 124.7, 123.6, 117.5, 102.9, 53.3. HRMS [ESI$^+$]: calcd for $C_{23}H_{16}N^+S$ 370.0897, found 370.0895.

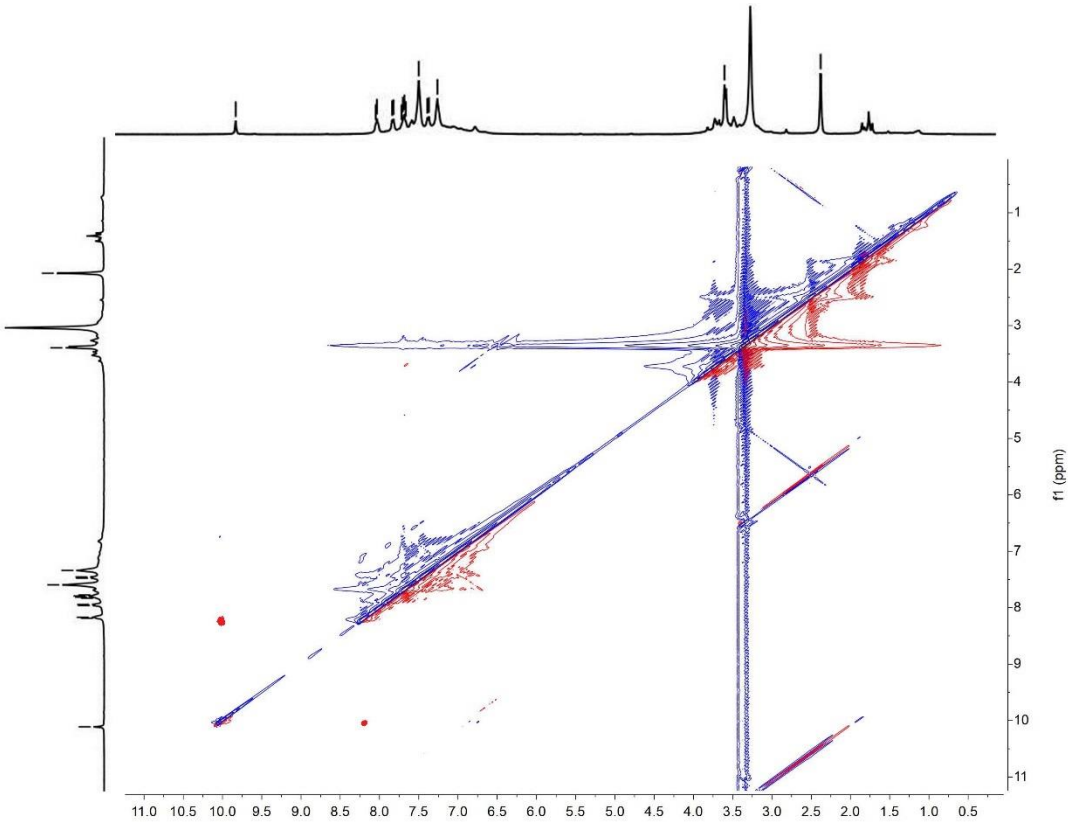
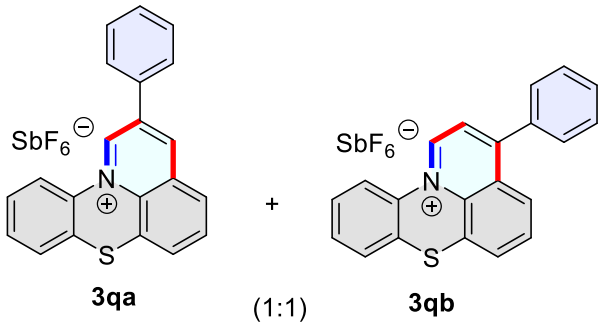
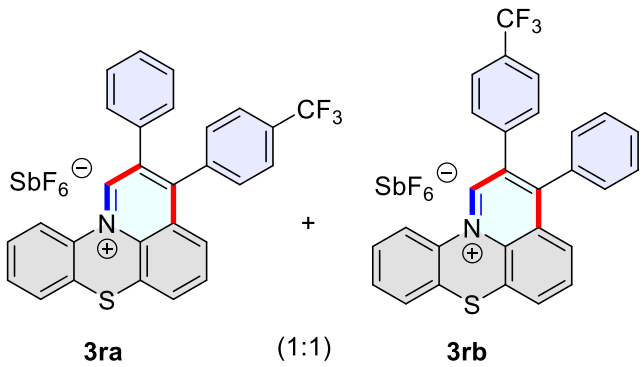


Fig. S21. ^{1}H-^{1}H nuclear overhauser effect spectroscopy of **3p**.



2-Phenylpyrido[3, 2, 1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (3q)

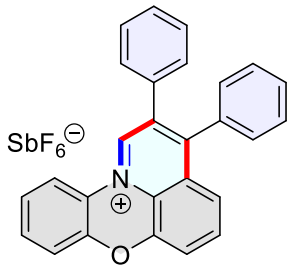
Red solid 22 mg, yield: 41%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 9.96 (s, 1H), 9.94 (s, 1H), 8.19 (d, J = 6.4 Hz, 2H), 8.16 (d, J = 6.8 Hz, 2H), 8.07 (s, 1H), 8.05 (s, 1H), 7.92-7.90 (m, 2H), 7.89-7.86 (m, 2H), 7.74 (s, 12H), 7.69-7.67 (m, 2H), 7.66-7.65 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ (ppm) 159.6, 144.4, 136.4, 134.4, 133.9, 131.3, 130.3, 130.0, 129.7, 129.5, 129.4, 128.2, 125.8, 125.2, 124.3, 123.9, 123.7. HRMS [ESI$^+$]: calcd for $C_{21}H_{14}N^+S$ 312.0842, found 312.0846.



2-Phenyl-3-(4-(trifluoromethyl)phenyl)pyrido[3,2,1-*kl*]phenothiazin-12-ium-hexa fluorostibate (V) (3r)

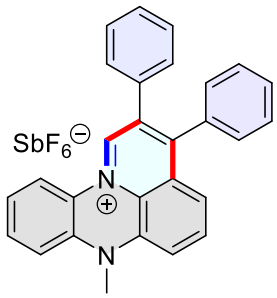
Red solid 43 mg, yield: 62%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 9.99 (s, 1H), 9.98 (s, 1H), 8.29-8.26 (m, 2H), 8.22-8.19 (m, 2H), 7.91-7.86 (m, 2H), 7.78 (s, 6H),

7.72-7.67 (m, 2H), 7.64-7.54 (m, 14H), 7.33 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 157.5, 145.2, 138.3, 135.4, 134.7, 133.5, 132.8, 131.6, 131.2, 130.9, 130.7, 130.1, 130.0, 129.7, 129.3, 128.9, 128.3, 125.9, 125.5, 125.1, 123.7. HRMS [ESI$^+$]: calcd for $C_{28}H_{17}F_3N^+S$ 456.1029, found 456.1032.



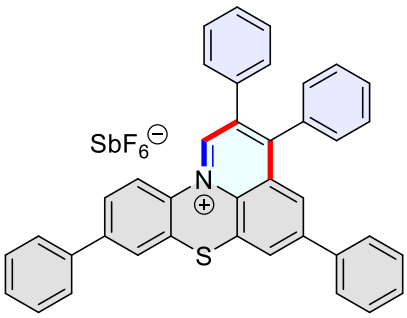
2,3-Diphenylpyrido[3,2,1-*kl*]phenoxazin-12-ium-hexafluorostibate (V) (4a)

Yellow solid 37 mg, yield: 61%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.38 (s, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.82 (t, J = 8.0 Hz, 1H), 7.70-7.66 (m, 2H), 7.50-7.43 (m, 6H), 7.41-7.35 (m, 3H), 7.33-7.27 (m, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 157.4, 147.2, 145.6, 141.4, 138.3, 137.2, 135.2, 135.0, 134.4, 132.9, 132.0, 131.2, 130.8, 130.4, 130.0, 129.8, 129.5, 126.9, 123.9, 122.5, 120.1, 119.5, 118.5. HRMS [ESI$^+$]: calcd for $C_{27}H_{18}N^+O$, 372.1383, found 372.1385.



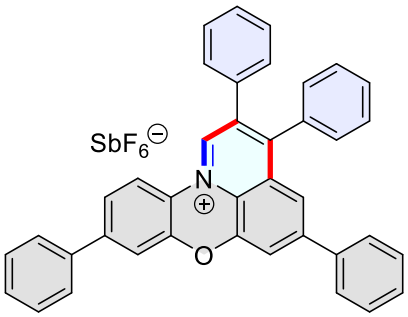
7-Methyl-2,3-diphenyl-7*H*-pyrido[3,2,1-*de*]phenazin-12-ium-hexafluorostibate (V) (4b)

Purple solid 32 mg, yield: 52%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.09 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.69-7.60 (m, 2H), 7.46-7.44 (m, 3H), 7.39-7.34 (m, 4H), 7.30-7.28 (m, 2H), 7.25-7.18 (m, 4H), 7.06 (d, J = 8.4 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 154.2, 137.9, 137.1, 136.8, 135.7, 135.6, 135.0, 134.3, 132.9, 132.6, 131.8, 131.0, 130.3, 130.2, 129.9, 129.7, 129.4, 125.5, 124.4, 120.4, 117.44, 117.37, 112.6, 34.7. HRMS [ESI$^+$]: calcd for $C_{28}H_{21}N_2^+$, 385.1700, found 385.1701.



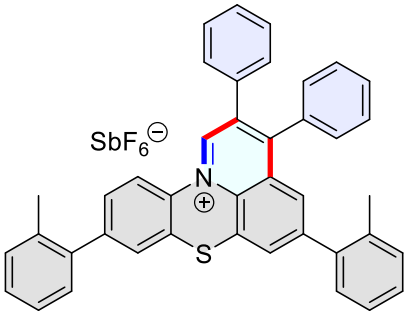
2,3,5,9-Tetraphenylpyrido[3,2,1-*kl*]phenothiazin-12-ium hexafluorostibate (V) (4c)

Red solid 55 mg, yield: 71%.^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.40 (s, 1H), 8.24 (d, J = 1.6Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.86 (d, J = 1.6 Hz, 1H), 7.83-7.80 (m, 1H), 7.75-7.74 (m, 3H), 7.61-7.59 (m, 2H), 7.52-7.45 (m, 9H), 7.42-7.38 (m, 3H), 7.36-7.33 (m, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 159.1, 144.9, 143.8, 143.6, 138.1, 137.99, 137.95, 135.8, 135.0, 134.2, 133.5, 133.1, 131.1, 131.0, 130.54, 130.46, 130.3, 130.2, 130.0, 129.9, 129.7, 129.5, 128.9, 128.4, 128.2, 128.1, 127.2, 126.0, 125.4, 123.6. HRMS [ESI$^+$]: calcd for $C_{39}H_{26}N_2^+$, 540.1781, found 540.1782.



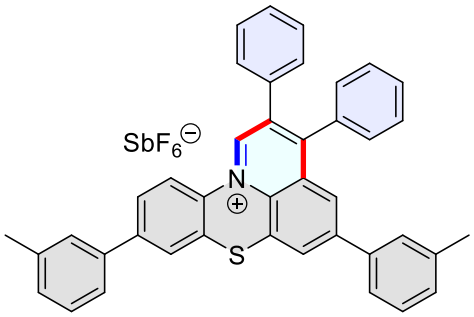
2,3,5,9-Tetraphenylpyrido[3, 2, 1-*kl*]phenoxazin-12-ium-hexafluorostibate (V) (4d)

Yellow solid 55 mg, yield: 72%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.24 (s, 1H), 8.14 (d, J = 9.2 Hz, 1H), 7.79 (s, 1H), 7.70-7.64 (m, 3H), 7.57-7.55 (m, 3H), 7.51-7.49 (m, 4H), 7.43-7.41 (m, 7H), 7.38-7.33 (m, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 156.8, 147.1, 146.8, 145.6, 145.1, 138.1, 137.7, 137.5, 137.3, 135.0, 134.1, 132.1, 131.2, 131.0, 130.5, 130.4, 130.3 130.1, 129.9, 129.6, 128.3, 127.8, 126.3, 125.0, 122.6, 119.9, 119.5, 117.3, 117.2. HRMS [ESI$^+$]: calcd for $C_{39}H_{26}N^+O$, 524.2009, found 524.2009.



2,3-Diphenyl-5,9-di-o-tolylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (4e)

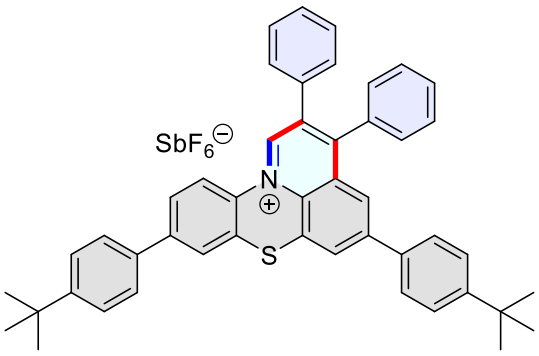
Red solid 60 mg, yield: 75%.^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.48 (s, 1H), 8.02 (s, 1H), 8.00-7.99 (m, 1H), 7.60 (d, J = 1.6 Hz, 1H), 7.57-7.55 (m, 1H), 7.47-7.46 (m, 4H), 7.41-7.40 (m, 3H), 7.37-7.36 (m, 4H), 7.32-7.31 (m, 6H), 7.26-7.24 (m, 2H), 2.33 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 159.2, 146.4, 144.8, 144.2, 139.4, 139.0, 138.1, 136.4, 136.3, 135.8, 135.0, 134.3, 133.4, 132.7, 131.8, 131.7, 131.6, 131.1, 130.9, 130.5, 130.42, 130.38, 130.04, 129.95, 129.6, 129.5, 127.6, 127.3, 127.2, 126.4, 125.3, 124.9, 20.5. HRMS [ESI$^+$]: calcd for $C_{41}H_{30}N^+S$, 568.2094, found 568.2098.



2,3-Diphenyl-5,9-di-m-tolylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (4f)

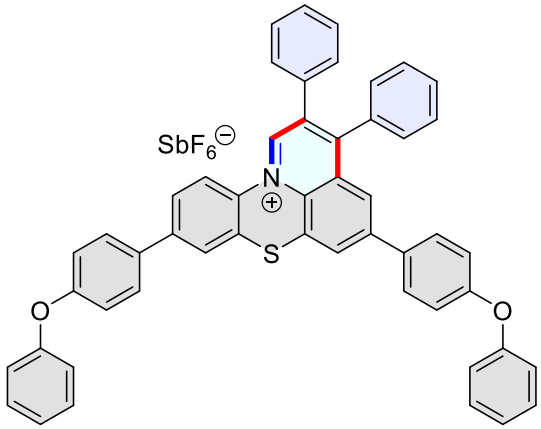
Red solid 58 mg, yield: 72%.^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.40 (s, 1H), 8.24 (s, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.86-7.80 (m, 2H), 7.73 (s, 1H) 7.59 (s, 1H), 7.55-7.50 (m, 4H), 7.45-7.27 (m, 13H), 2.42 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 159.1, 145.1, 143.7, 140.3, 140.2, 138.1, 138.0, 135.8, 135.1, 134.3, 133.4, 133.1, 131.1, 131.0, 130.6, 130.2, 130.1, 130.0, 129.9, 129.8, 129.6,

129.0, 128.9, 128.8, 128.2, 127.1, 125.9, 125.5, 125.4, 125.2, 123.6, 21.5, 21.4. HRMS [ESI$^+$]: calcd for $C_{41}H_{30}N^+S$, 568.2094, found 568. 2093.



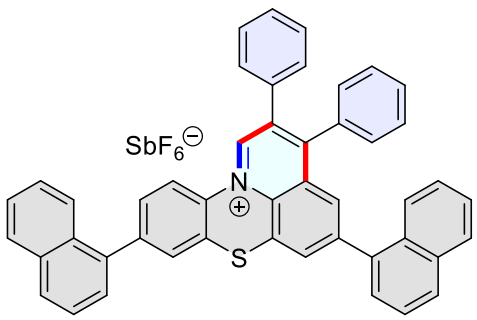
5,9-Bis(4-(tert-butyl)phenyl)-2,3-diphenylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (4g)

Red solid 62 mg, yield: 70%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.39 (s, 1H), 8.21 (s, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.82 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.65 (s, 2H), 7.63 (s, 1H), 7.54-7.50 (m, 9H), 7.43-7.38 (m, 3H), 7.36-7.31 (m, 4H), 1.33 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 158.9, 154.0, 153.7, 144.6, 143.5, 143.4, 138.1, 135.5, 135.01, 134.95, 134.92, 134.3, 133.2, 133.1, 131.2, 131.0, 130.6, 130.0, 129.9, 129.6, 129.5, 128.6, 128.1, 128.0, 127.7, 127.3, 127.2, 126.8, 125.8, 125.3, 123.3, 35.4, 31.40, 31.35. HRMS [ESI$^+$]: calcd for $C_{47}H_{42}N^+S$, 652.3033, found 568.652.3035.



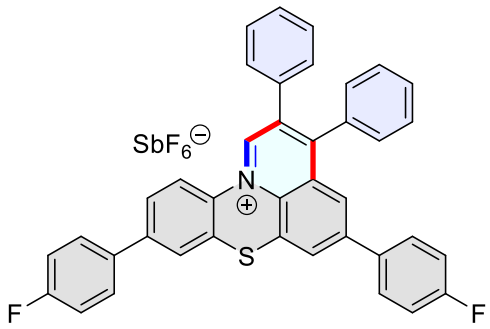
5,9-Bis(4-phenoxyphenyl)-2,3-diphenylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexa fluorostibate (V) (4h)

Red solid 75 mg, yield: 78%.^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.36 (s, 1H), 8.16 (d, J = 1.6 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.77-7.74 (m, 2H), 7.70-7.66 (m, 3H), 7.55-7.48 (m, 5H), 7.43-7.38 (m, 7H), 7.35-7.31 (m, 4H), 7.22-7.17 (m, 2H), 7.06-7.00 (m, 8H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 159.9, 159.8, 158.9, 157.3, 157.2, 144.1, 143.4, 142.8, 138.2, 135.5, 135.0, 134.2, 133.1, 132.5, 131.1, 131.0, 130.6, 130.1, 129.9, 129.7, 129.6, 129.3, 128.5, 128.2, 126.6, 125.9, 125.4, 125.2, 123.0, 120.44, 120.42, 119.8, 119.6. HRMS [ESI$^+$]: calcd for $C_{51}H_{34}N^+O_2S$, 724.2305, found 724.2303.



5,9-Di(naphthalen-1-yl)-2,3-diphenylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate (V) (4i)

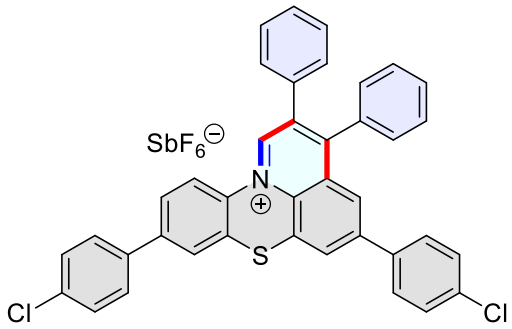
Red solid 65 mg, yield: 74%.^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.44 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.98-7.96 (m, 3H), 7.92-7.86 (m, 3H), 7.78-7.75 (m, 1H), 7.67 (dd, J_1 = 1.6 Hz, J_2 = 8.8 Hz, 1H), 7.64-7.60 (m, 2H), 7.58-7.49 (m, 7H), 7.43-7.36 (m, 9H), 7.31-7.28 (m, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 159.2, 145.2, 144.1, 143.6, 138.2, 137.4, 136.9, 135.9, 134.9, 134.84, 134.75, 134.2, 133.5, 132.8, 132.28, 132.25, 131.7, 131.5, 131.2, 130.9, 130.5, 130.4, 130.3, 130.2, 130.1, 129.8, 129.6, 128.9, 128.4, 128.2, 128.0, 127.9, 127.44, 127.38, 127.2, 126.6, 126.5, 125.8, 125.6, 125.4, 125.0. HRMS [ESI$^+$]: calcd for $C_{47}H_{30}N^+S$, 640.2094, found 640.2091.



5,9-Bis(4-fluorophenyl)-2,3-diphenylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate(V) (4j)

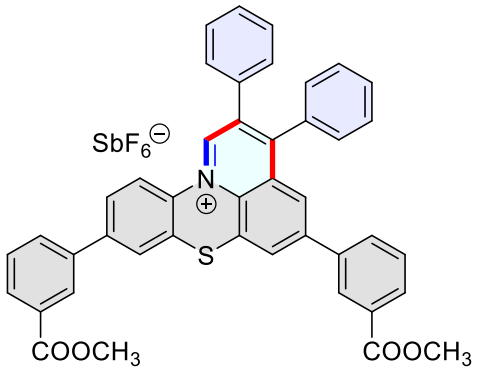
Red solid 60 mg, yield: 74%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.43 (s, 1H), 8.24 (d, J = 1.2 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.87-7.86 (m, 1H), 7.81-7.77 (m, 3H), 7.72 (d, J = 1.6 Hz, 1H), 7.65-7.62 (m, 2H), 7.54-7.50 (m, 2H), 7.42-7.37 (m, 3H), 7.35-7.33 (m, 4H), 7.30-7.20 (m, 5H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm)

159.2, 144.0, 143.9, 142.6, 138.2, 135.9, 135.0, 134.4, 134.2, 133.5, 133.1, 131.1, 131.0, 130.7, 130.6, 130.5, 130.4, 130.3, 130.0, 129.9, 129.6, 129.5, 128.8, 128.3, 127.2, 126.0, 125.5, 123.6, 117.3, 117.13, 117.06, 116.9. HRMS [ESI$^+$]: calcd for $C_{39}H_{24}F_2N^+S$, 576.1593, found 576.1593.



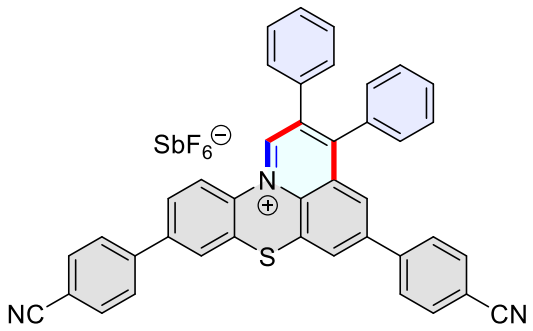
5,9-Bis(4-chlorophenyl)-2,3-diphenylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate(V) (4k)

Red solid 54 mg, yield: 64%.^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.40 (s, 1H), 8.18 (d, J = 1.6 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.81-7.77 (m, 2H), 7.72 (s, 2H), 7.70 (s, 1H), 7.57-7.55 (m, 3H), 7.52-7.45 (m, 7H), 7.43-7.38 (m, 2H), 7.35-7.32 (m, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 159.3, 144.0, 143.6, 142.4, 138.3, 136.7, 136.2, 136.0, 135.0, 134.2, 133.7, 133.0, 131.2, 131.1, 130.6, 130.4, 130.2, 130.1, 130.0, 129.9, 129.8, 129.6, 129.5, 128.9, 128.3, 127.2, 126.1, 125.5, 123.7. HRMS [ESI$^+$]: calcd for $C_{39}H_{24}Cl_2N^+S$, 608.1002, found 608.0997.



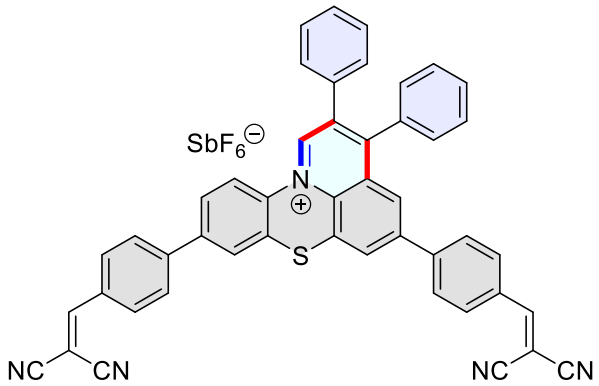
5,9-Bis(3-(methoxycarbonyl)phenyl)-2,3-diphenylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate(V) (4l)

Red solid 56 mg, yield: 63%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.35 (s, 1H), 8.26 (s, 1H), 8.13-8.10 (m, 2H), 7.99-7.95 (m, 3H), 7.88 (d, J = 8.0 Hz, 1H), 7.80-7.77 (m, 1H), 7.74-7.72 (m, 3H), 7.56-7.50 (m, 5H), 7.44-7.38 (m, 3H), 7.35-7.33 (m, 4H), 3.86 (s, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 167.1, 167.0, 159.3, 143.9, 143.6, 142.4, 138.24, 138.16, 135.7, 134.8, 134.1, 133.5, 132.9, 132.7, 132.4, 132.2, 132.1, 131.1, 131.0, 130.8, 130.6, 130.5, 130.1, 129.9, 129.6, 129.4, 129.0, 128.9, 128.7, 128.2, 127.2, 126.1, 125.4, 123.9, 53.0. HRMS [ESI$^+$]: calcd for $C_{43}H_{30}N^+O_4S$, 656.1891, found 656.1886.



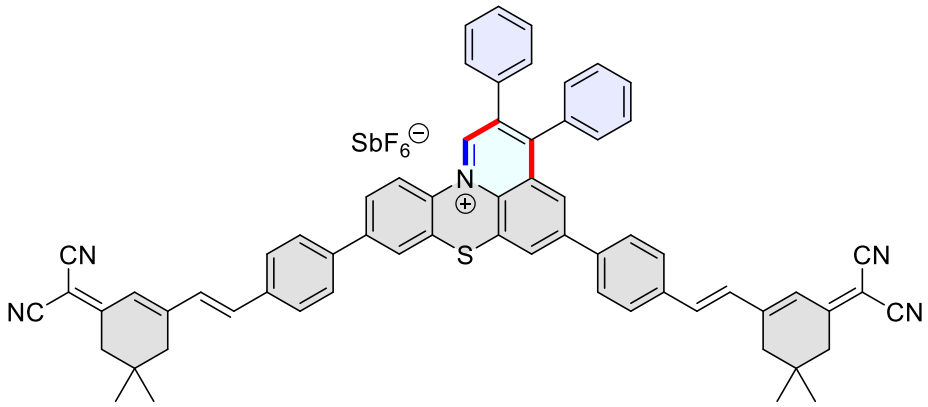
5,9-Bis(4-cyanophenyl)-2,3-diphenylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate(V) (4m)

Red solid 53 mg, yield: 64%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.47 (s, 1H), 8.25 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.91-7.73 (m, 11H), 7.53-7.51 (m, 3H), 7.42-7.34 (m, 7H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 159.8, 144.7, 143.0, 142.4, 142.3, 141.8, 138.5, 136.4, 134.9, 134.4, 134.1, 134.0, 133.0, 131.1, 130.6, 130.1, 129.9, 129.7, 129.6, 129.30, 129.27, 129.0, 128.5, 127.8, 126.3, 125.7, 124.6, 119.3, 119.2, 113.7, 113.5. HRMS [ESI$^+$]: calcd for $C_{41}H_{24}N_3{}^+S$, 590.1686, found 590.1682.



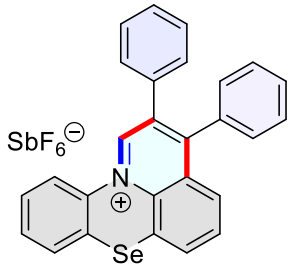
5,9-Bis(4-(2,2-dicyanovinyl)phenyl)-2,3-diphenylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate(V) (4n)

Dark red solid 42 mg, yield: 45%. ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) 9.31 (s, 1H), 8.03-7.98 (m, 7H), 7.87 (s, 1H), 7.82-7.75 (m, 5H), 7.69-7.67 (m, 3H), 7.49-7.47 (m, 3H), 7.37-7.35 (m, 6H); ^{13}C NMR (100 MHz, C_2D_6SO): δ (ppm) 160.5, 160.4, 141.7, 140.8, 139.8, 136.6, 134.8, 133.2, 131.3, 131.2, 130.2, 129.6, 128.9, 128.3, 128.2, 128.0, 127.0, 126.8, 126.3, 125.6, 125.1, 124.0, 122.6, 114.2, 113.4, 113.1, 82.0. HRMS [ESI$^+$]: calcd for $C_{47}H_{26}N_5{}^+S$, 692.1904, found 692.1896.



5,9-Bis(4-((*E*)-2-(3-(dicyanomethylene)-5,5-dimethylcyclohex-1-en-1-yl)vinyl)phenyl)-2,3-diphenylpyrido[3,2,1-*kl*]phenothiazin-12-ium-hexafluorostibate(V) (4o)

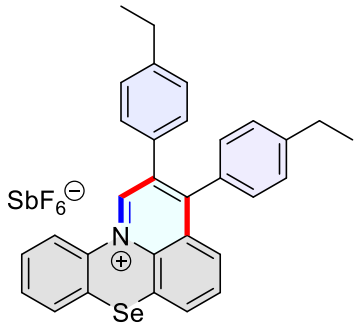
Dark red solid 49 mg, yield: 42%. ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) 9.21 (s, 1H), 7.98-7.94 (m, 2H), 7.79 (s, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.63-7.46 (m, 12H), 7.37-7.34 (m, 6H), 7.06-6.94 (m, 5H), 6.85-6.81 (m, 2H), 2.60-2.59 (m, 4H), 2.46-2.44 (m, 4H), 1.08 (s, 12H); ^{13}C NMR (100 MHz, CD_3Cl): δ (ppm) 169.3, 153.4, 150.4, 137.8, 135.5, 135.0, 130.7, 130.1, 129.8, 129.3, 129.2, 128.6, 128.4, 128.1, 127.7, 127.3, 125.4, 124.5, 124.3, 43.1, 39.3, 32.2, 28.1. HRMS [ESI$^+$]: calcd for $C_{65}H_{50}N_5^+S$, 932.3782, found 932.3775.



2,3-Diphenylpyrido[3,2,1-*kl*]phenoselenazin-12-ium-hexafluorostibate(V) (4p)

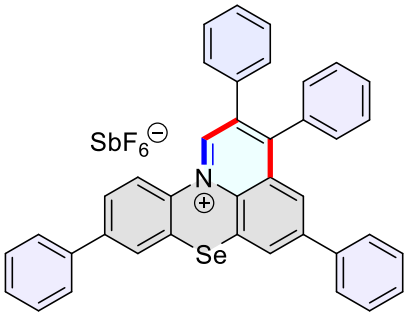
Red solid 42 mg, yield: 63%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.45 (s, 1H), 8.20 (d, J = 6.4 Hz, 1H), 7.83-7.71 (m, 4H), 7.65-7.58 (m, 2H), 7.53-7.47 (m, 3H),

7.41-7.36 (m, 3H), 7.33-7.29 (m, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 160.4, 147.1, 135.0, 134.7, 134.4, 132.8, 132.6, 132.1, 131.22, 131.17, 130.9, 130.5, 130.0, 129.7, 129.5, 127.7, 124.5. HRMS [ESI$^+$]: calcd for $C_{27}H_{18}N^+Se$, 436.0599, found 436.0599.



2,3-Bis(4-ethylphenyl)pyrido[3,2,1-*kl*]phenoselenazin-12-ium-hexafluorostibate(V) (4q)

Red solid 45 mg, yield: 62%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.41 (s, 1H), 8.18 (d, J =4.0 Hz, 1H), 7.82 (d, J =4.8 Hz, 1H), 7.78-7.72 (m, 3H), 7.64-7.59 (m, 2H), 7.35 (d, J = 5.2 Hz, 2H), 7.23 (s, 4H), 7.22-7.21 (m, 2H), 2.72 (q, J = 5.2 Hz, 2H), 2.65 (q, J = 5.2 Hz, 2H), 1.25 (t, J = 5.2 Hz, 3H), 1.21 (t, J = 4.8 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 147.6, 147.1, 146.3, 137.7, 136.6, 134.5, 132.8, 132.4, 132.0, 131.7, 131.5, 131.1, 130.6, 129.1, 129.0, 127.63, 127.60, 29.2, 29.0, 15.7, 15.6. HRMS [ESI$^+$]: calcd for $C_{31}H_{26}N^+Se$, 492.1225, found 492.1227.



2,3,5,9-Tetraphenylpyrido[3,2,1-*kl*]phenoselenazin-12-ium-hexafluorostibate(V)

(4r)

Deep red solid 48 mg, yield: 58%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.36 (s, 1H), 8.38 (s, 1H), 7.97 (s, 1H), 7.84-7.82 (m, 1H), 7.79-7.77 (m, 2H), 7.68 (d, J = 5.2 Hz, 2H), 7.56-7.49 (m, 5H), 7.48-7.39 (m, 9H), 7.35-7.33 (m, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 159.8, 145.9, 144.5, 143.5, 138.1, 138.0, 137.8, 137.3, 135.3, 134.9, 134.2, 132.9, 131.2, 131.0, 130.6, 130.4, 130.3, 130.2, 130.0, 129.8, 129.7, 129.5, 129.2, 128.3, 128.0, 127.6, 124.9, 124.3, 121.9. HRMS [ESI$^+$]: calcd for $C_{39}H_{26}N^+Se$, 588.1225, found 588.1225.

XIII. Molecular orbitals of 4p and 4f

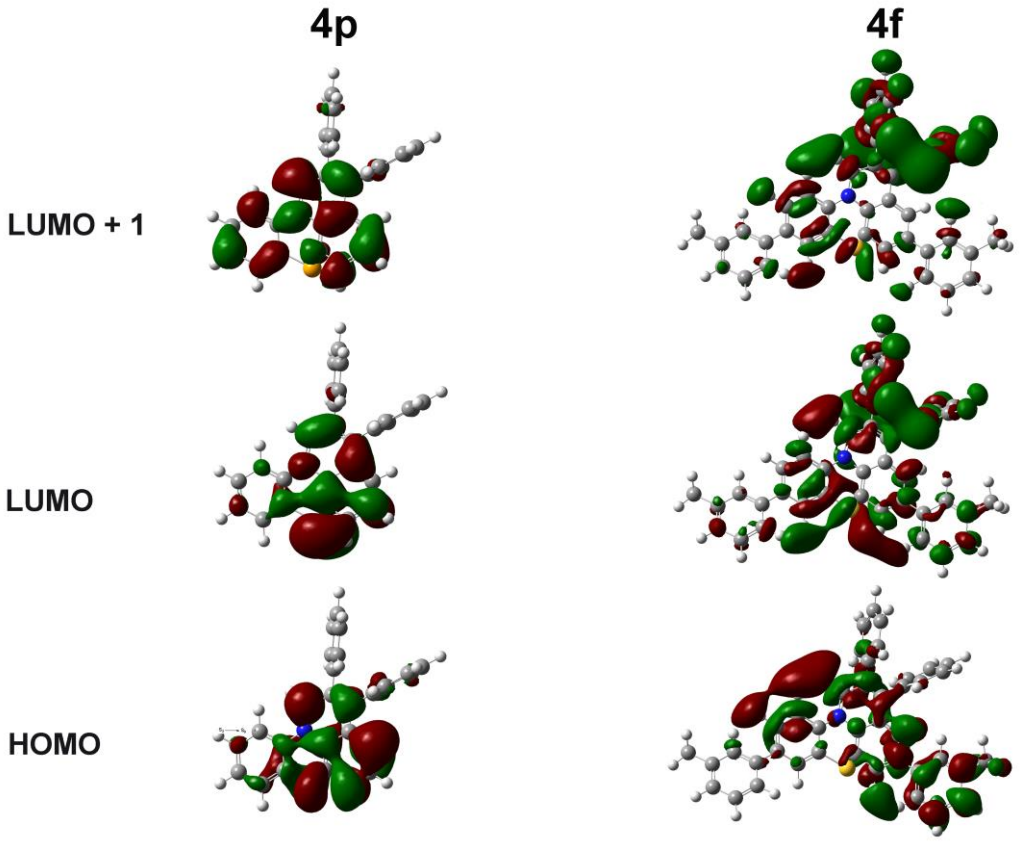


Fig. S22. Molecular orbitals of **4p** and **4f**.

XIV. References

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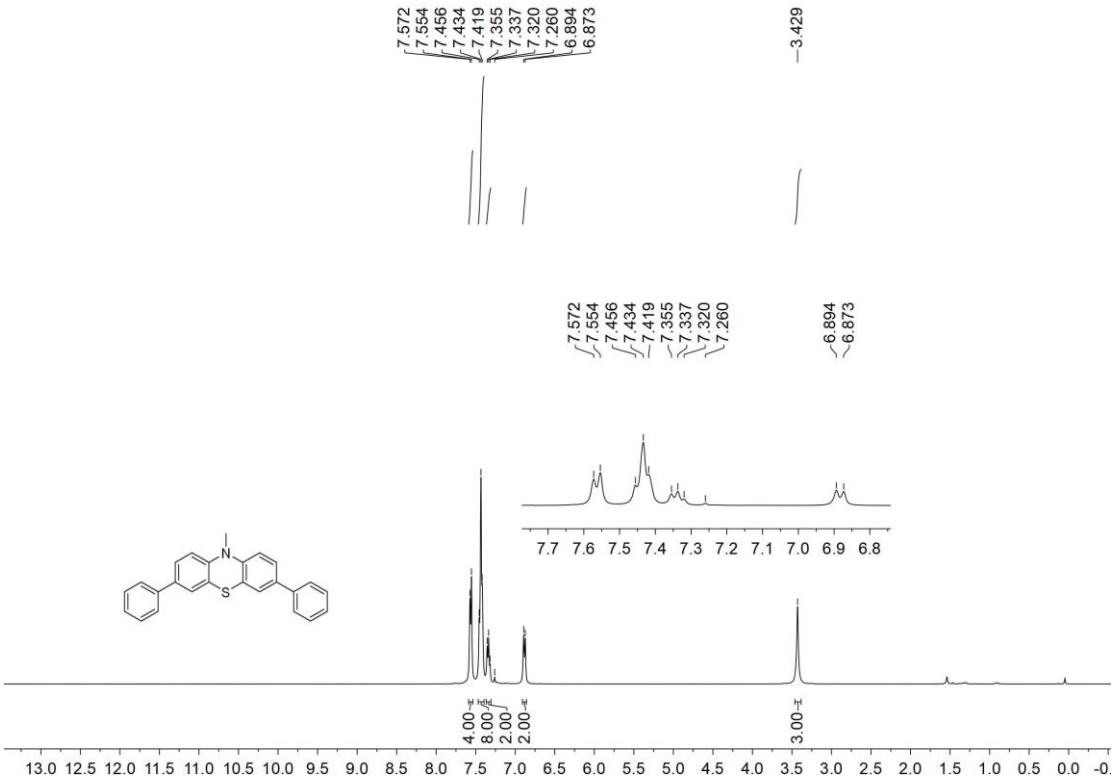
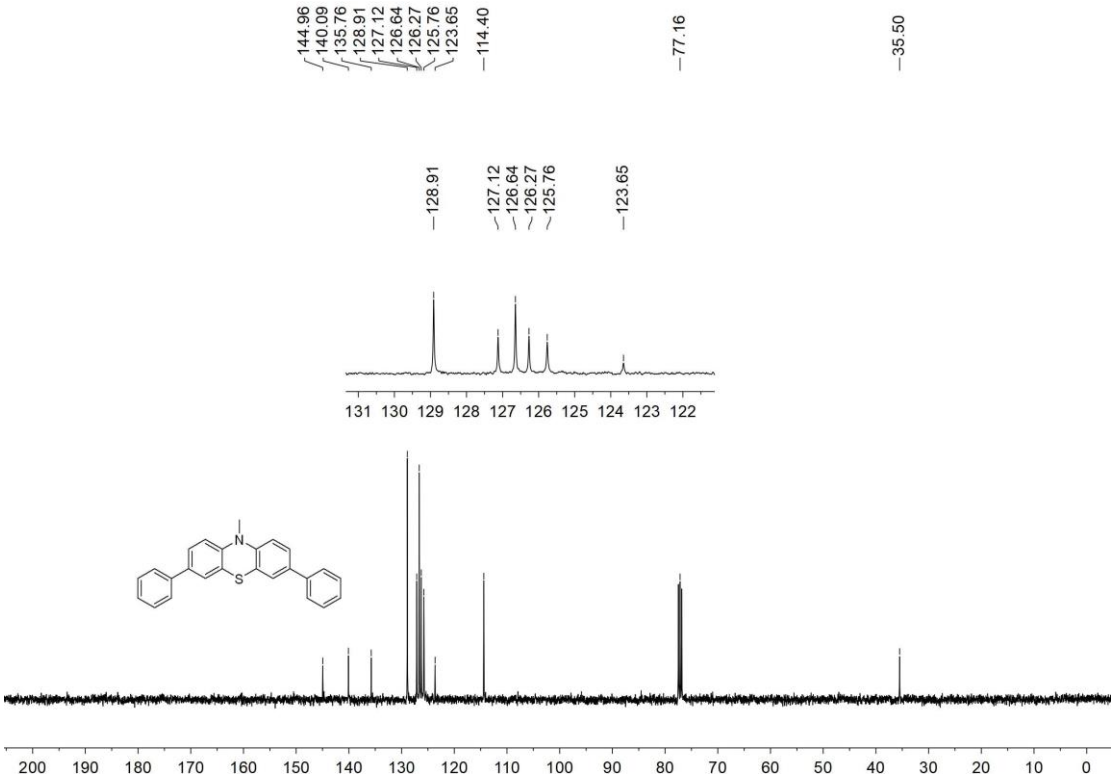
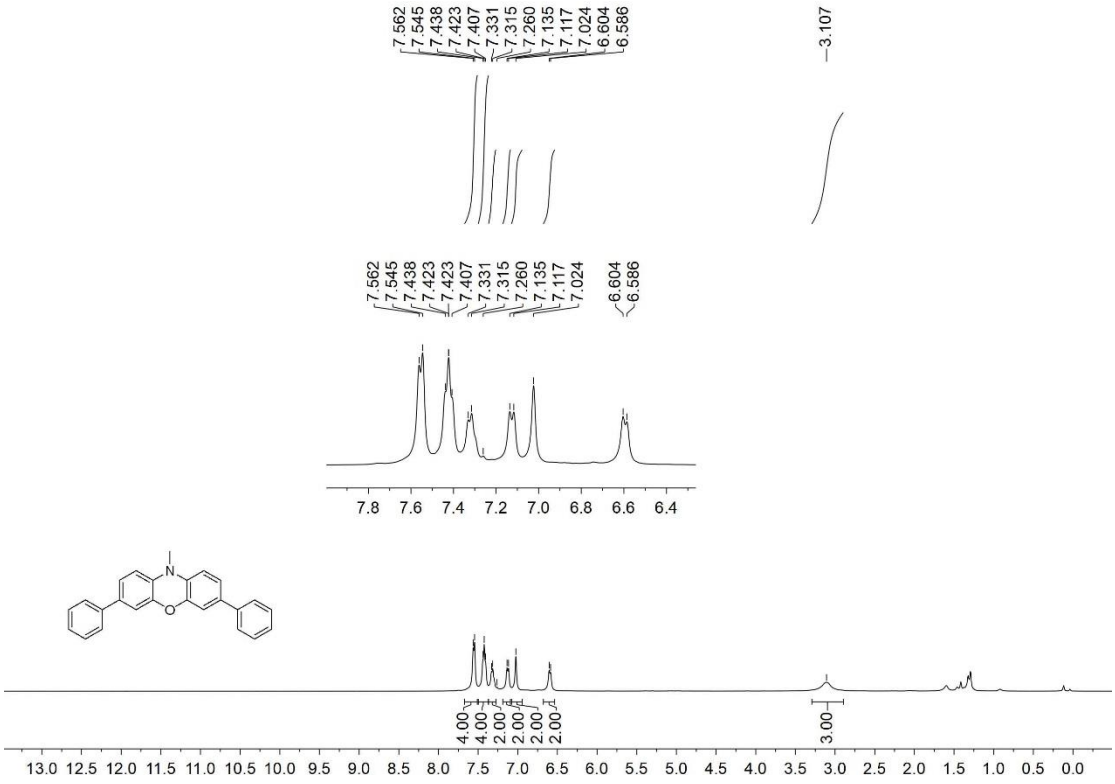
XV. Copies of ^{1}H and ^{13}C NMR spectra.



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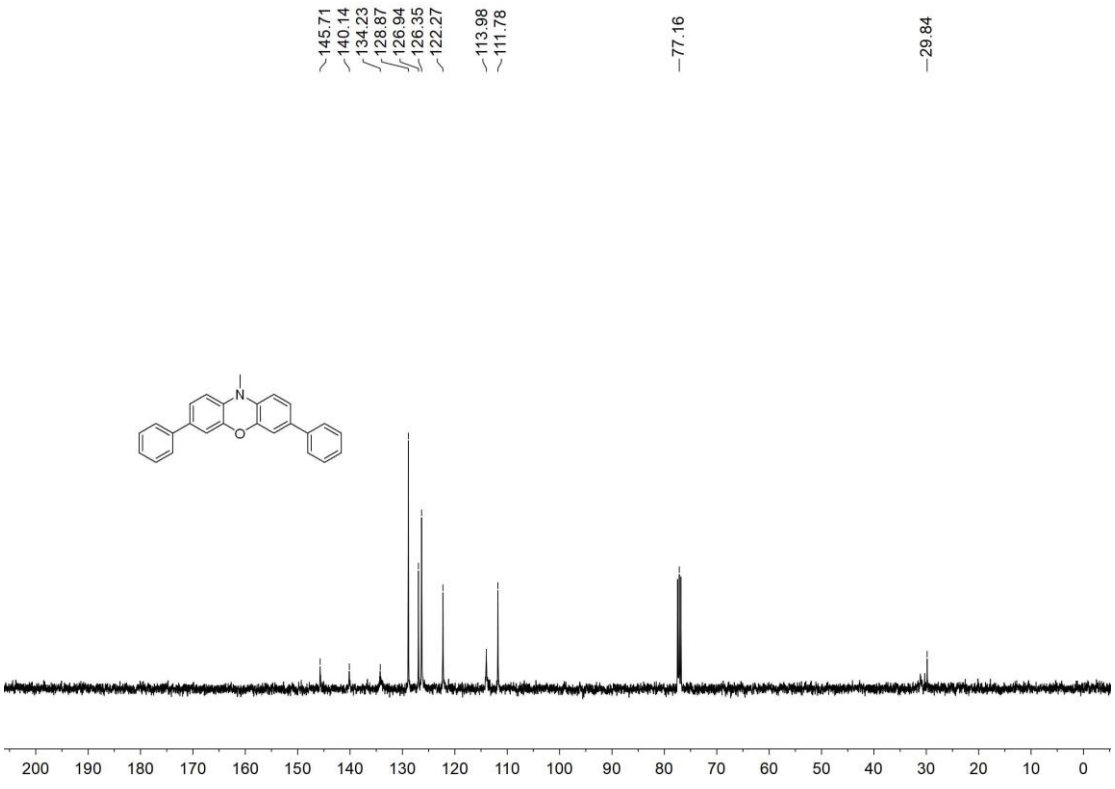
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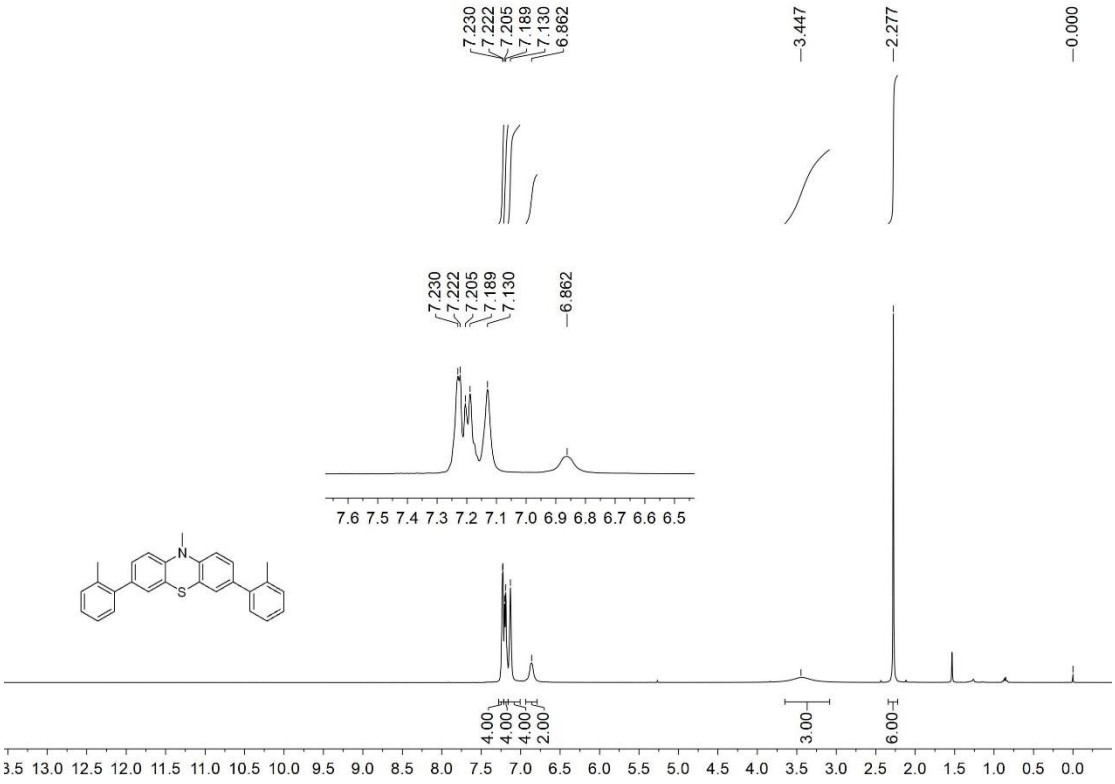
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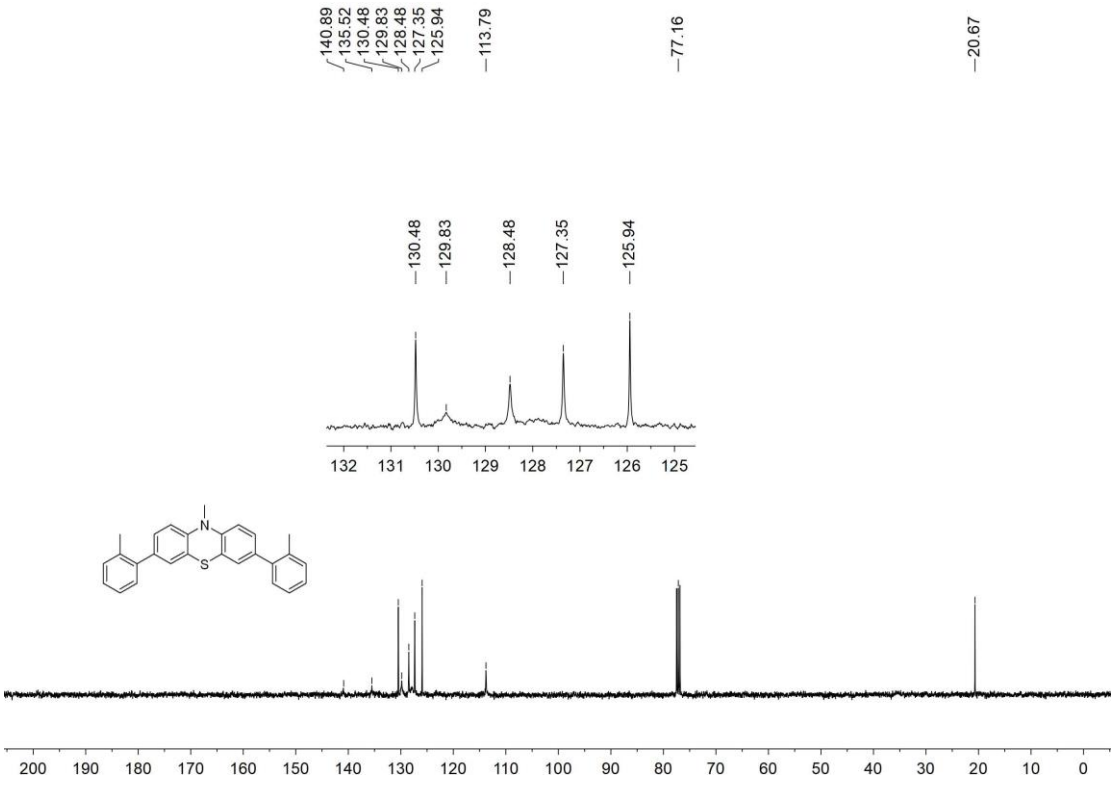
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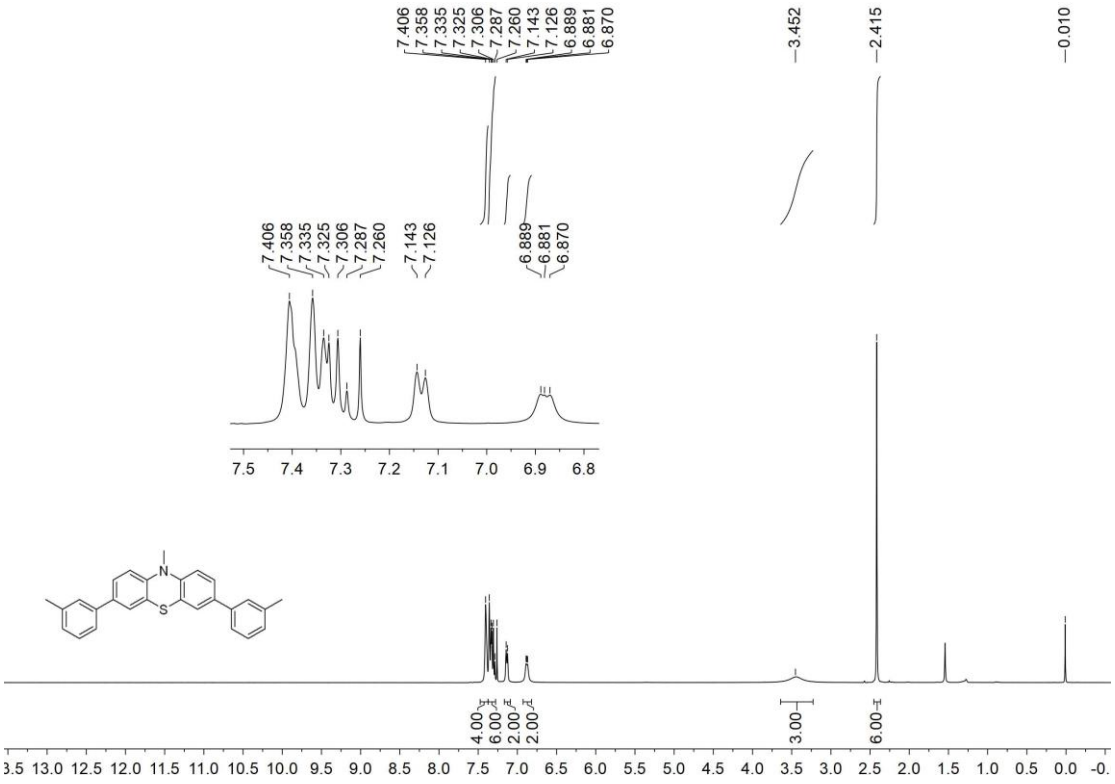
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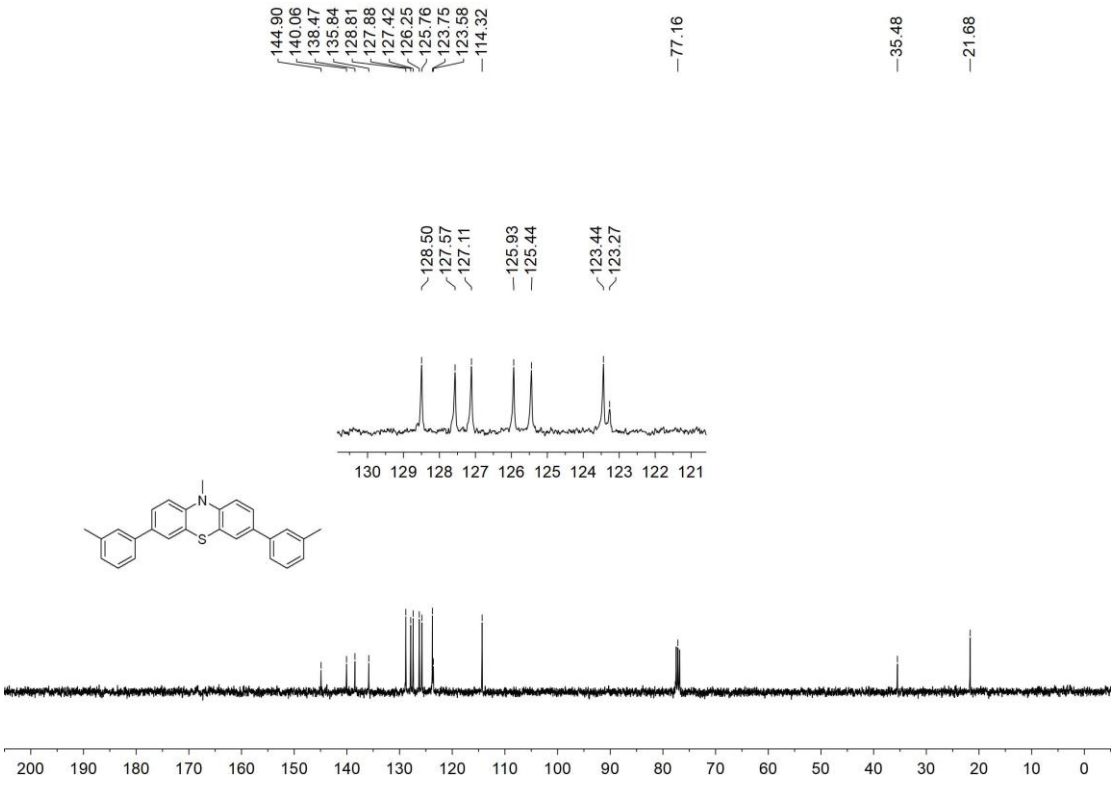
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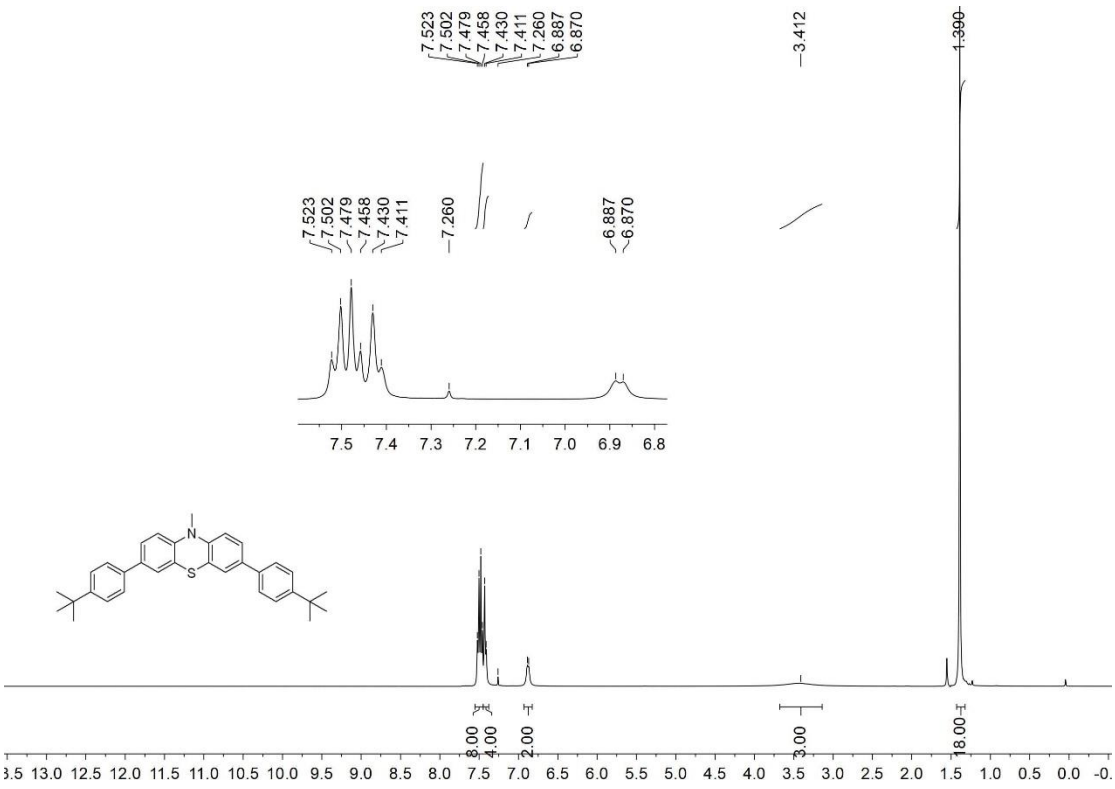
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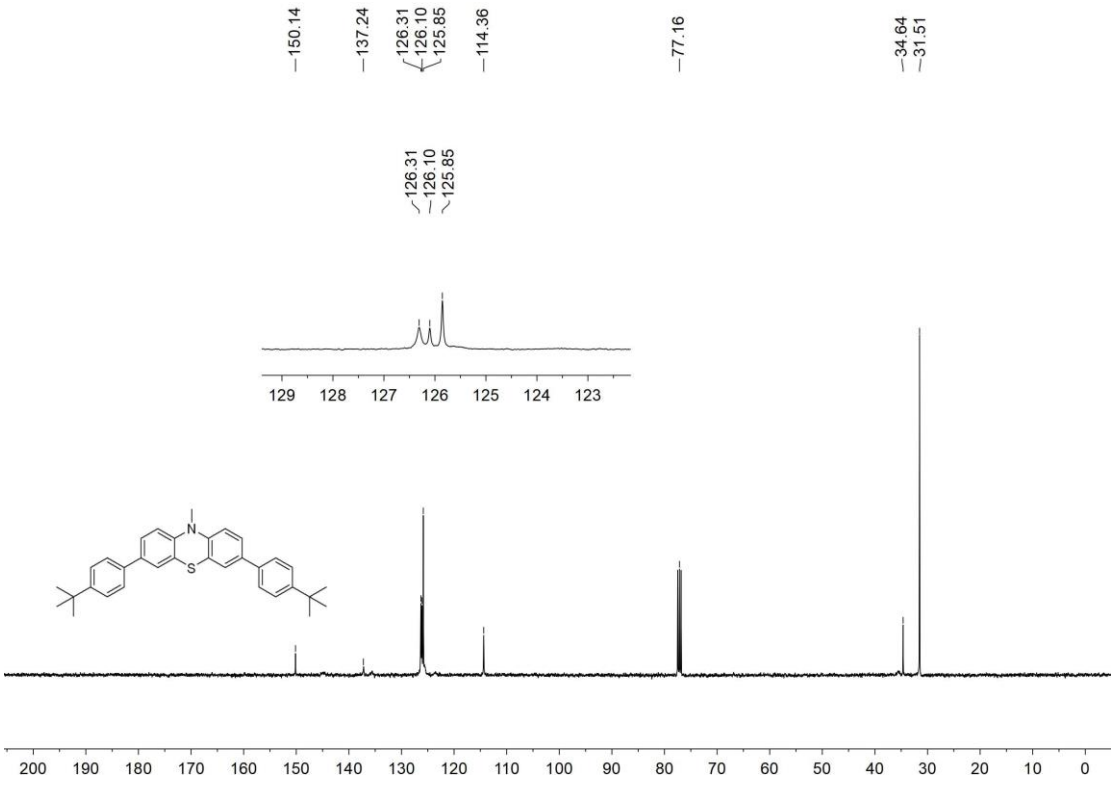
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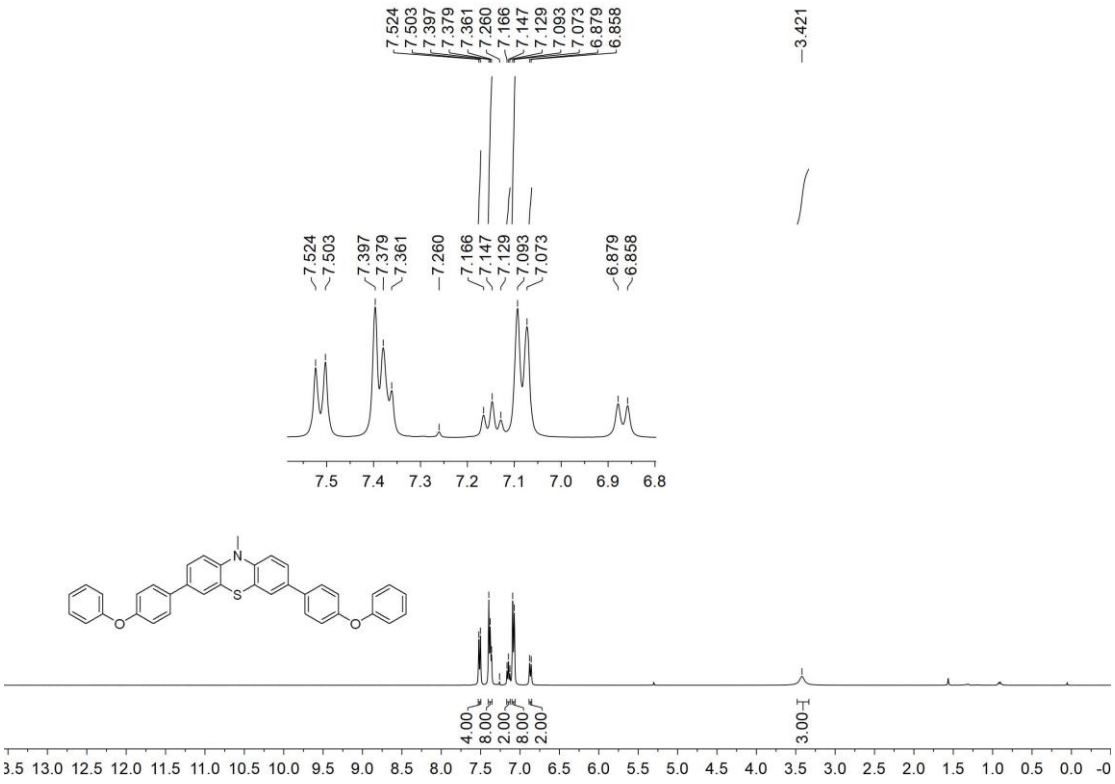
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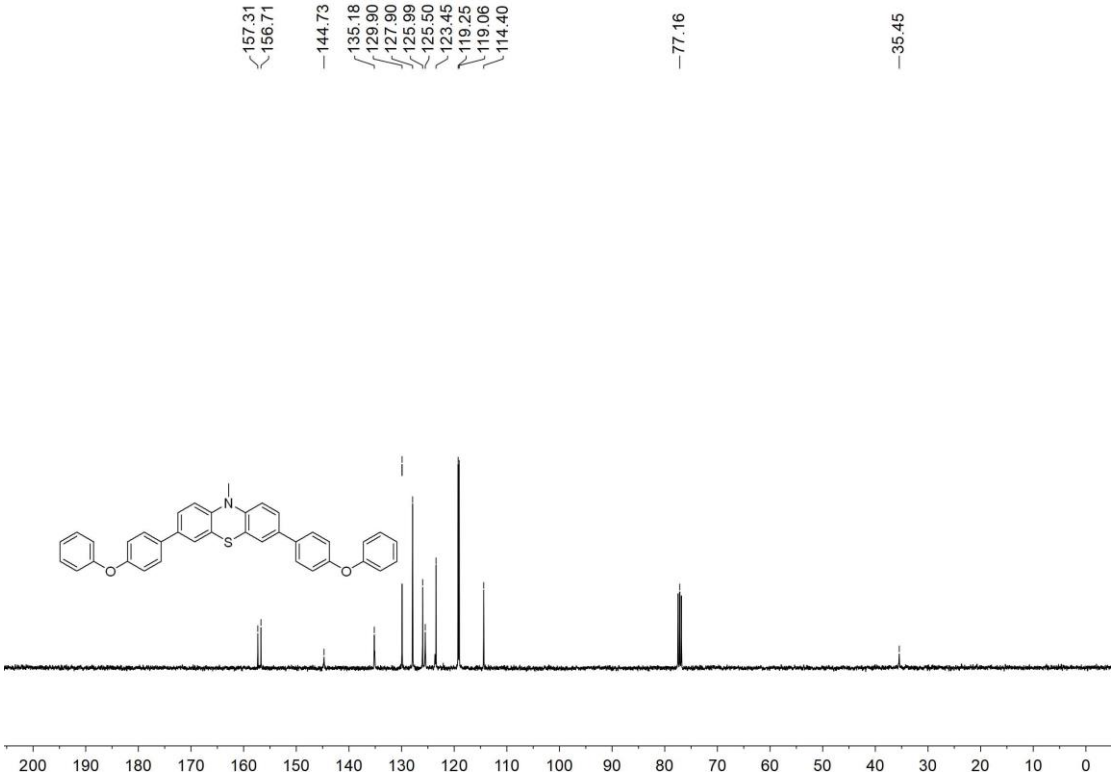
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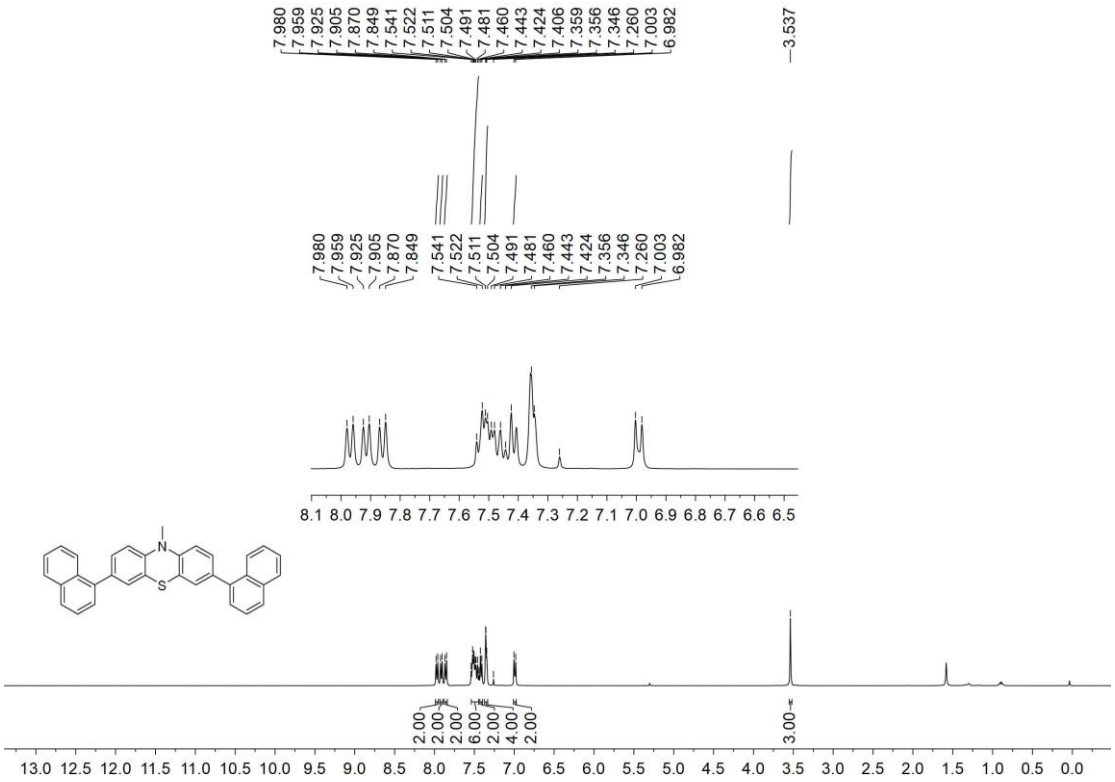
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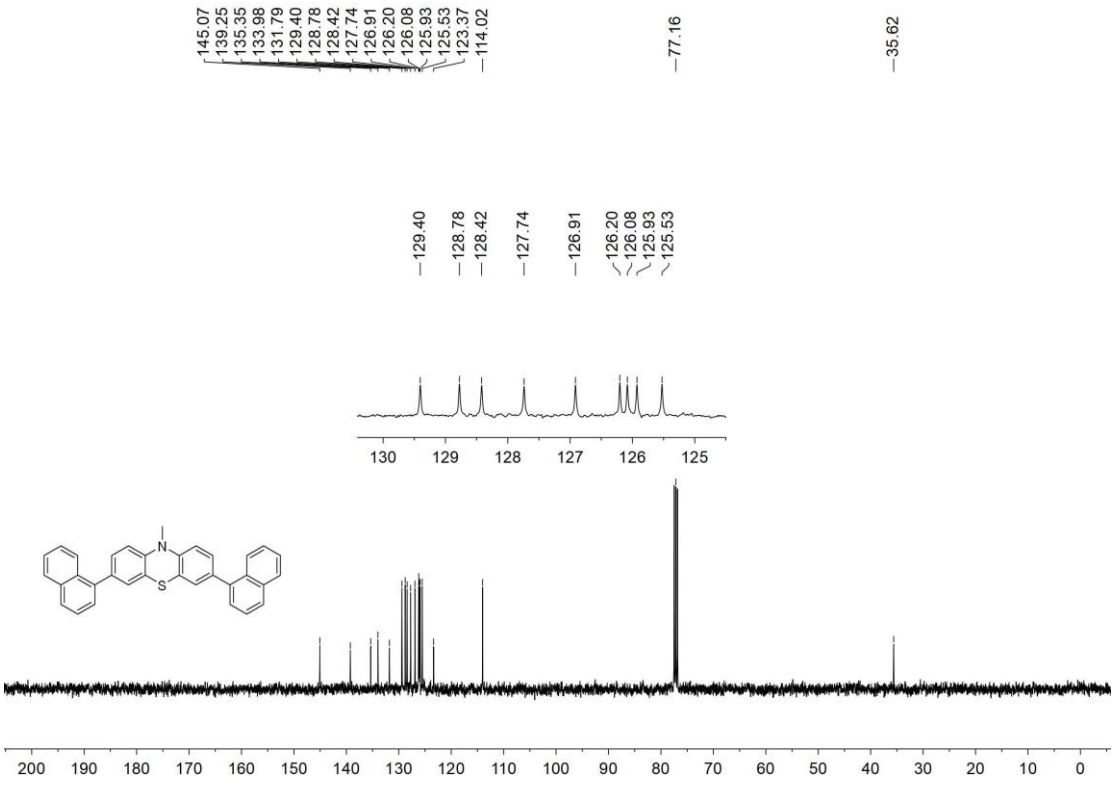
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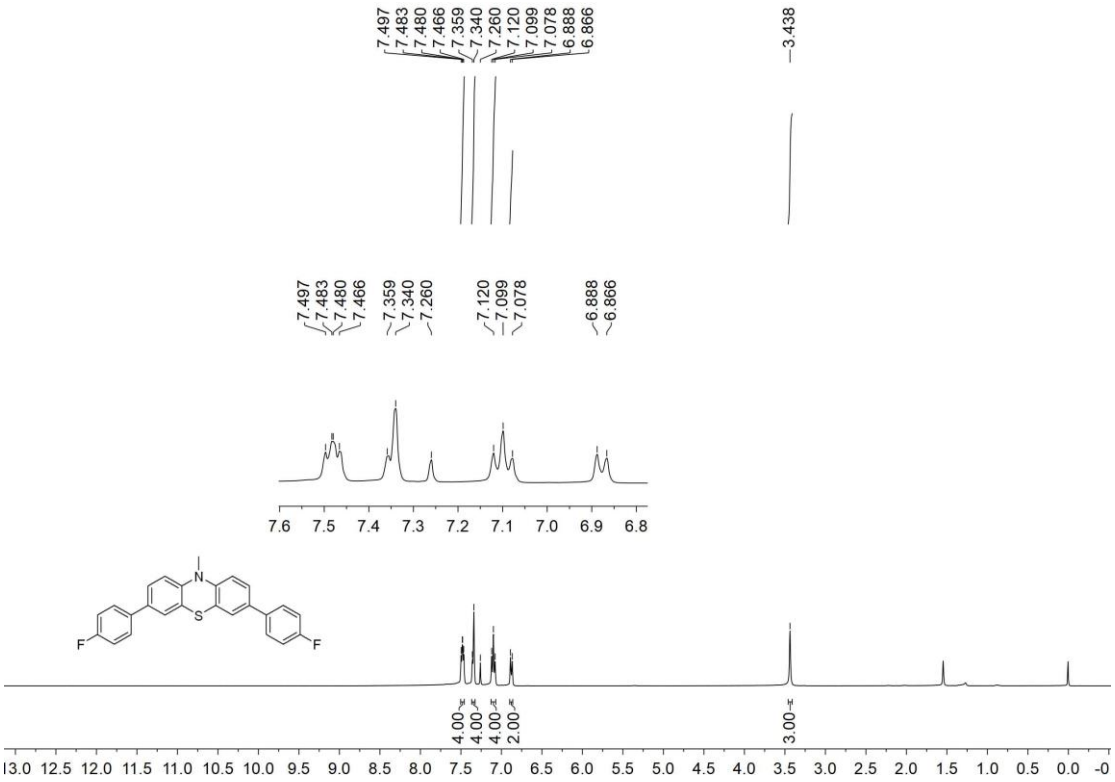
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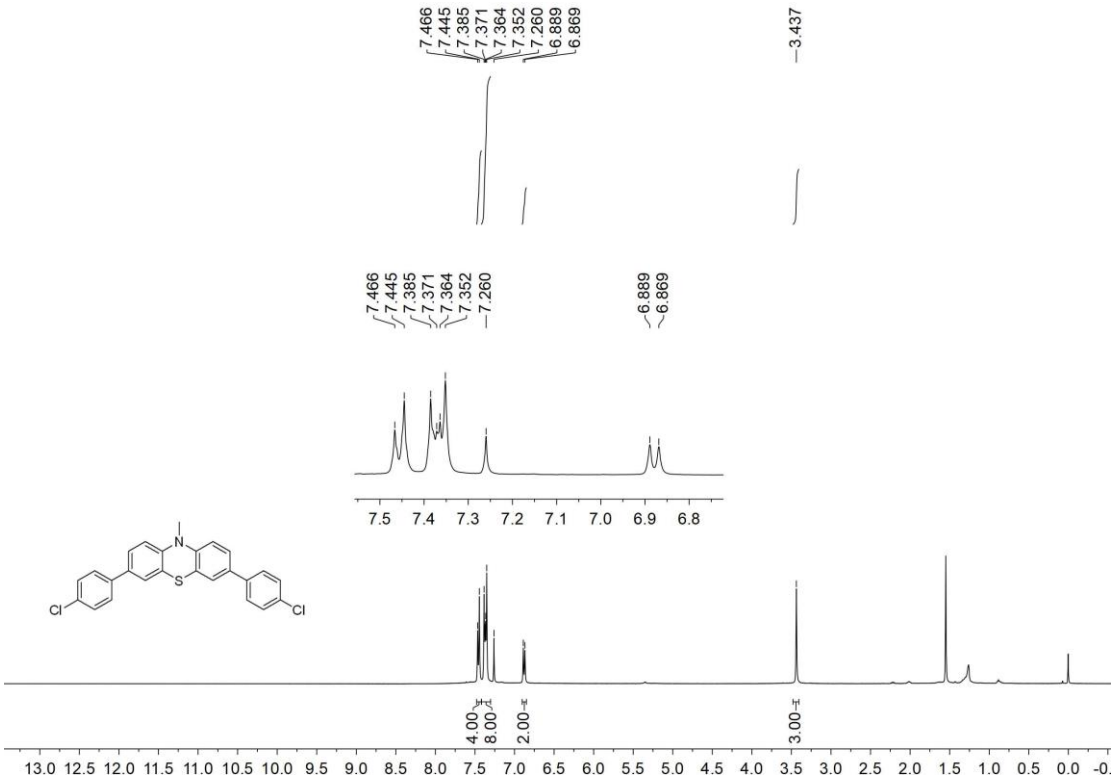
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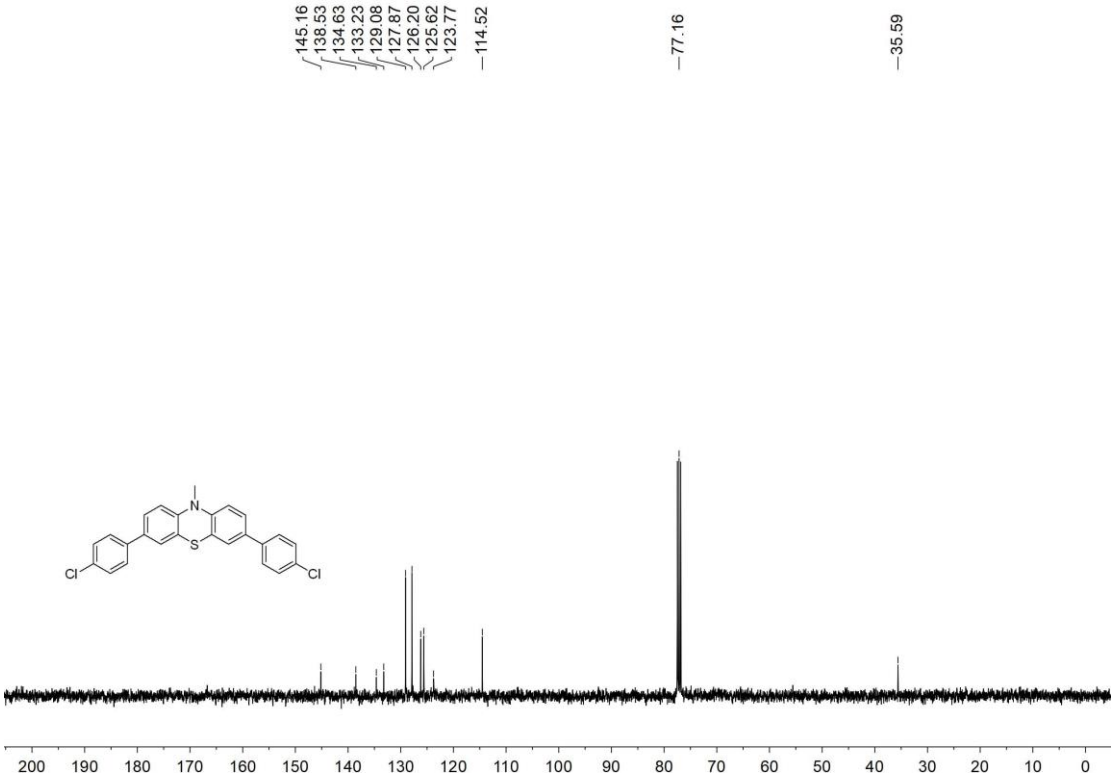
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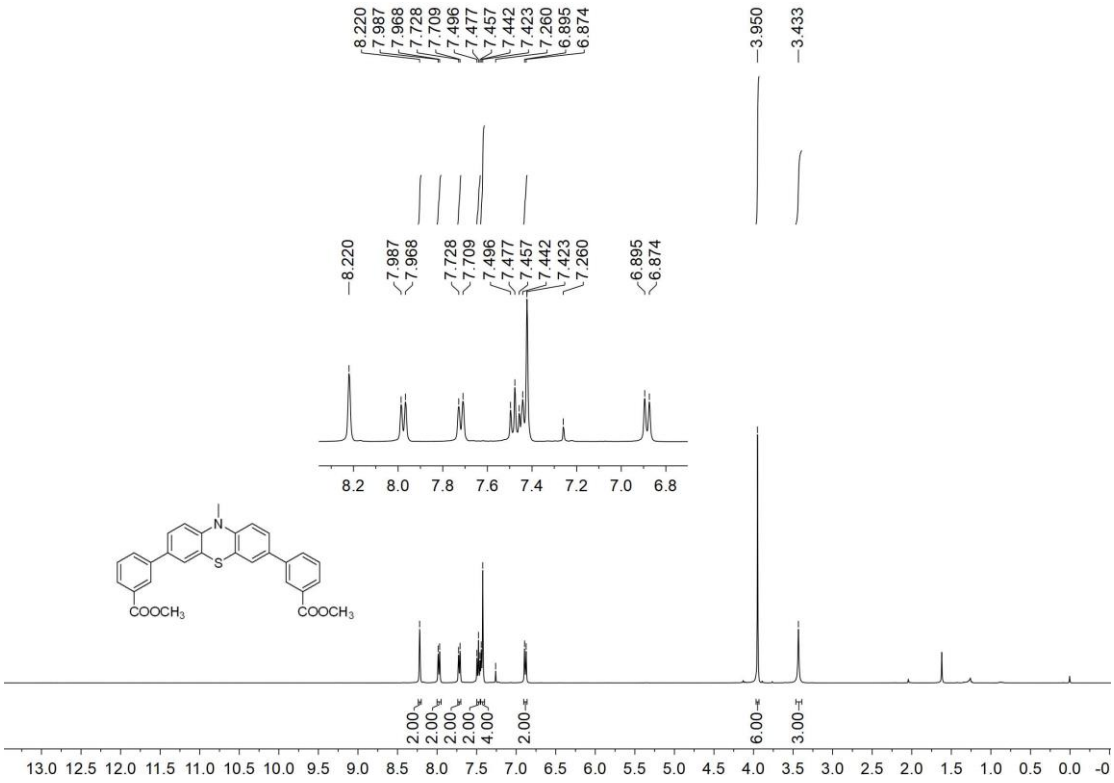
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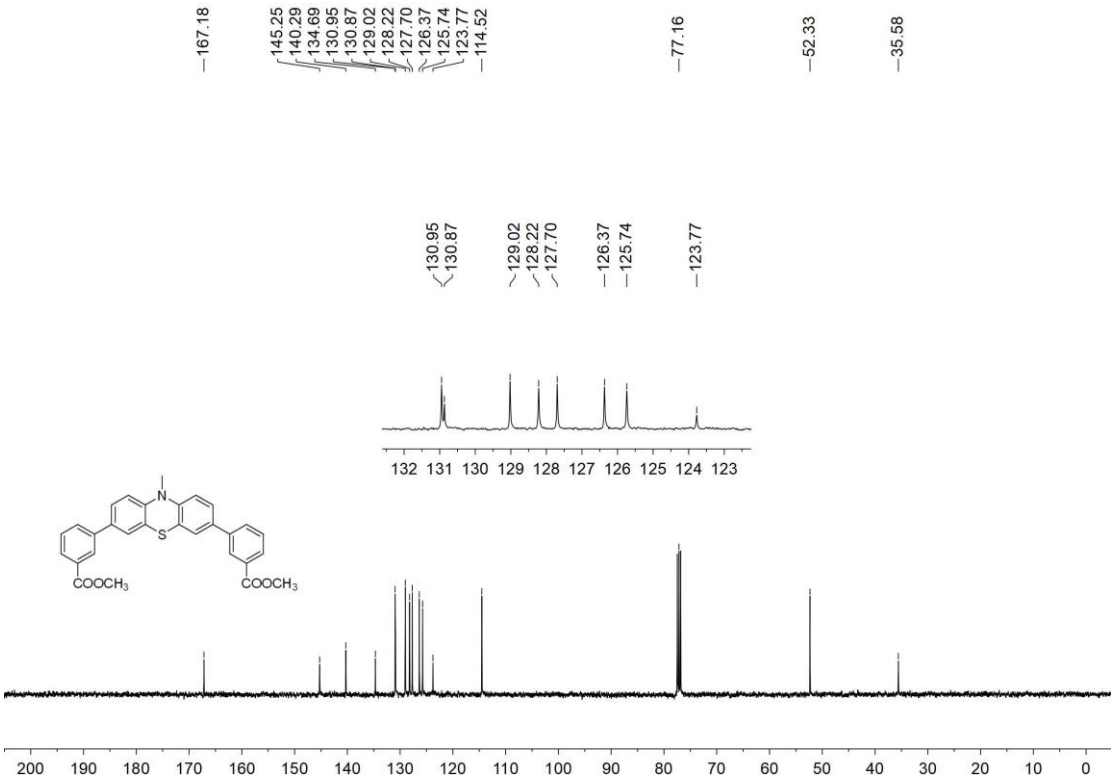
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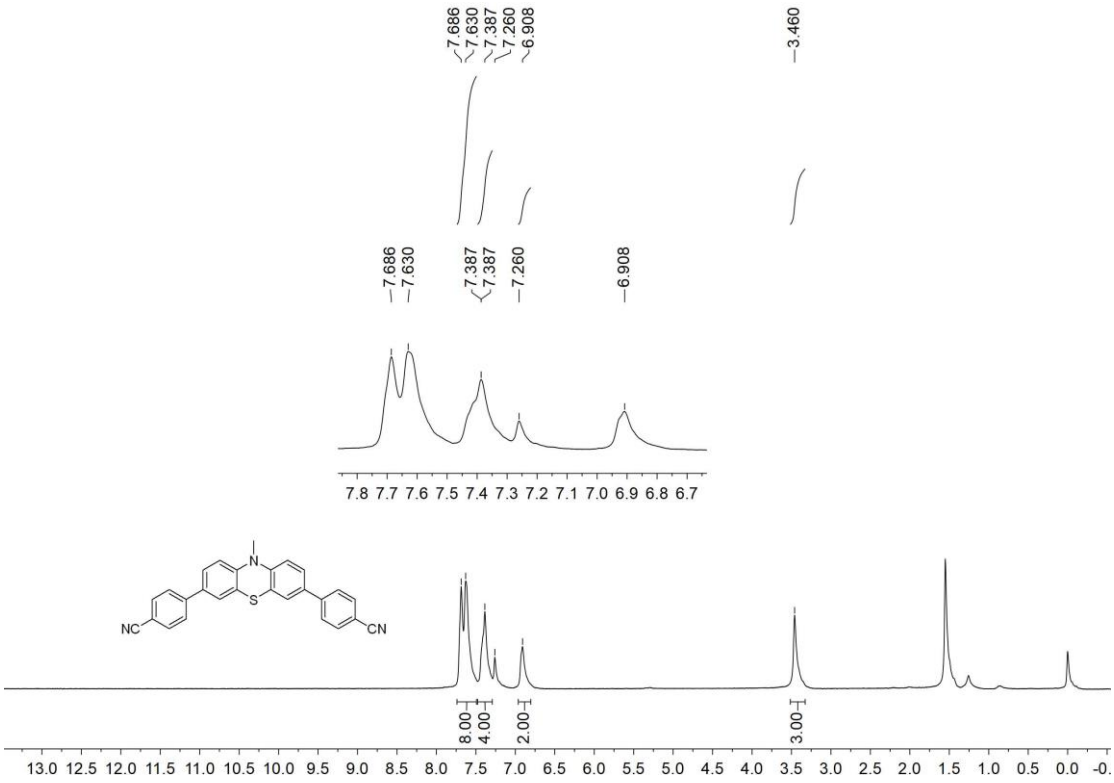
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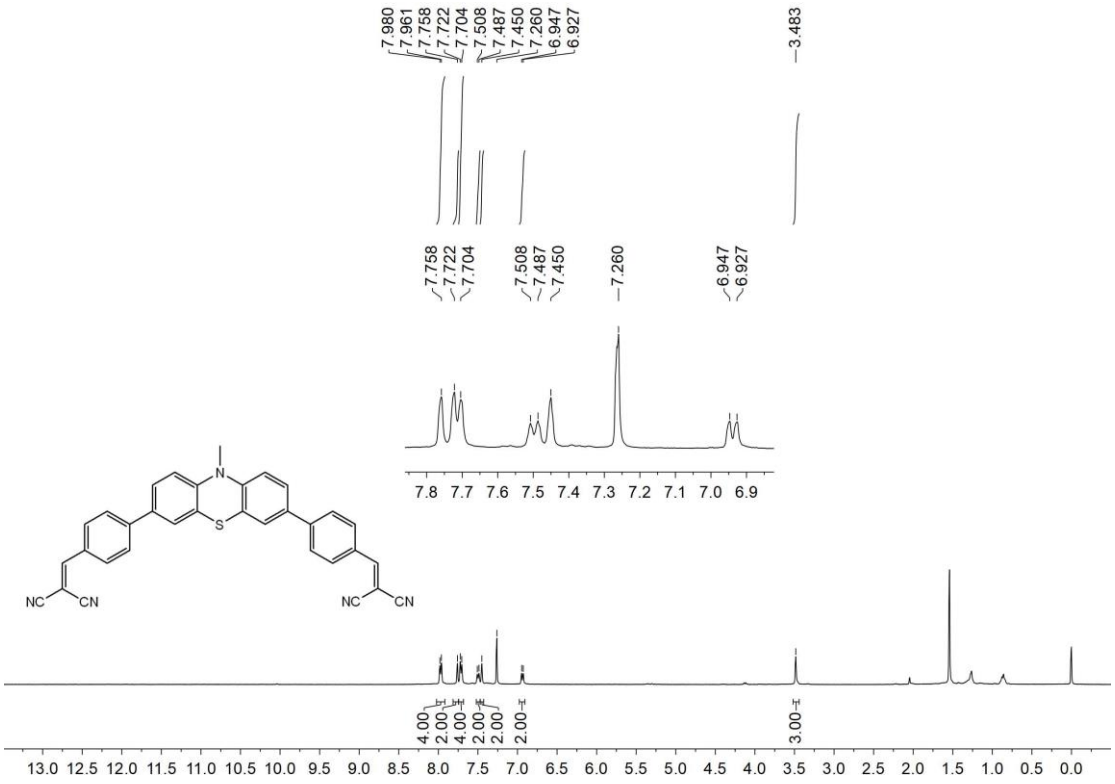
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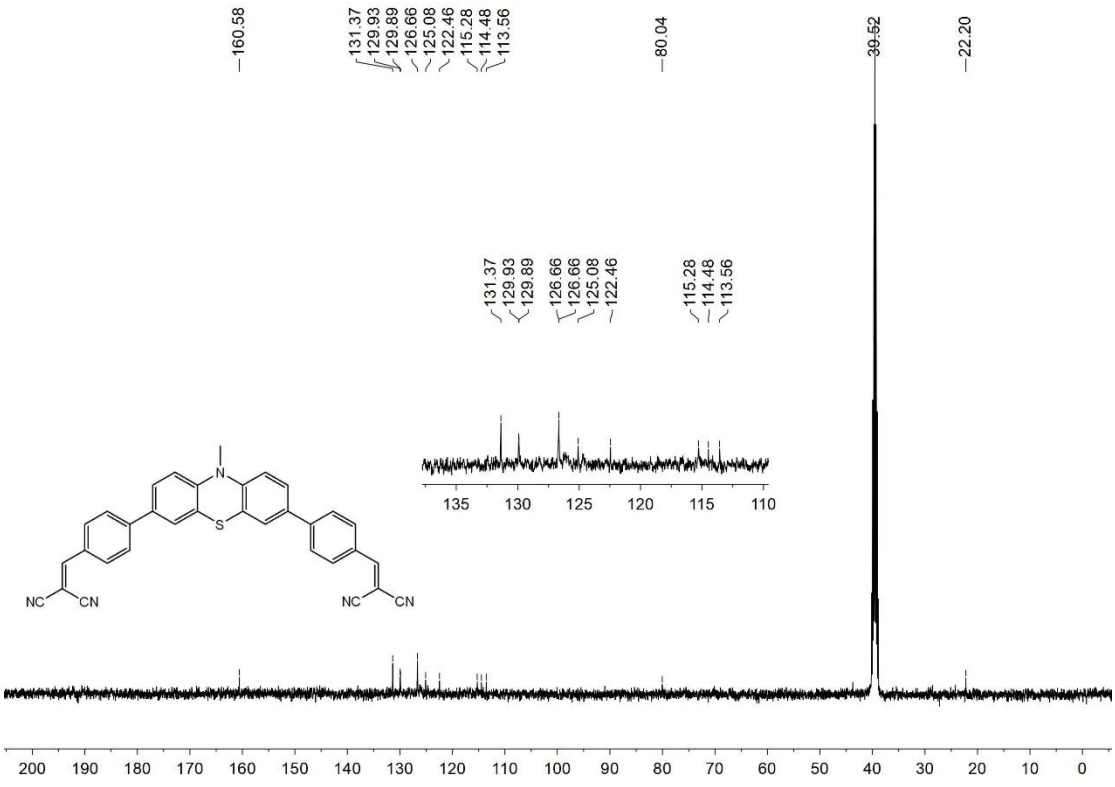
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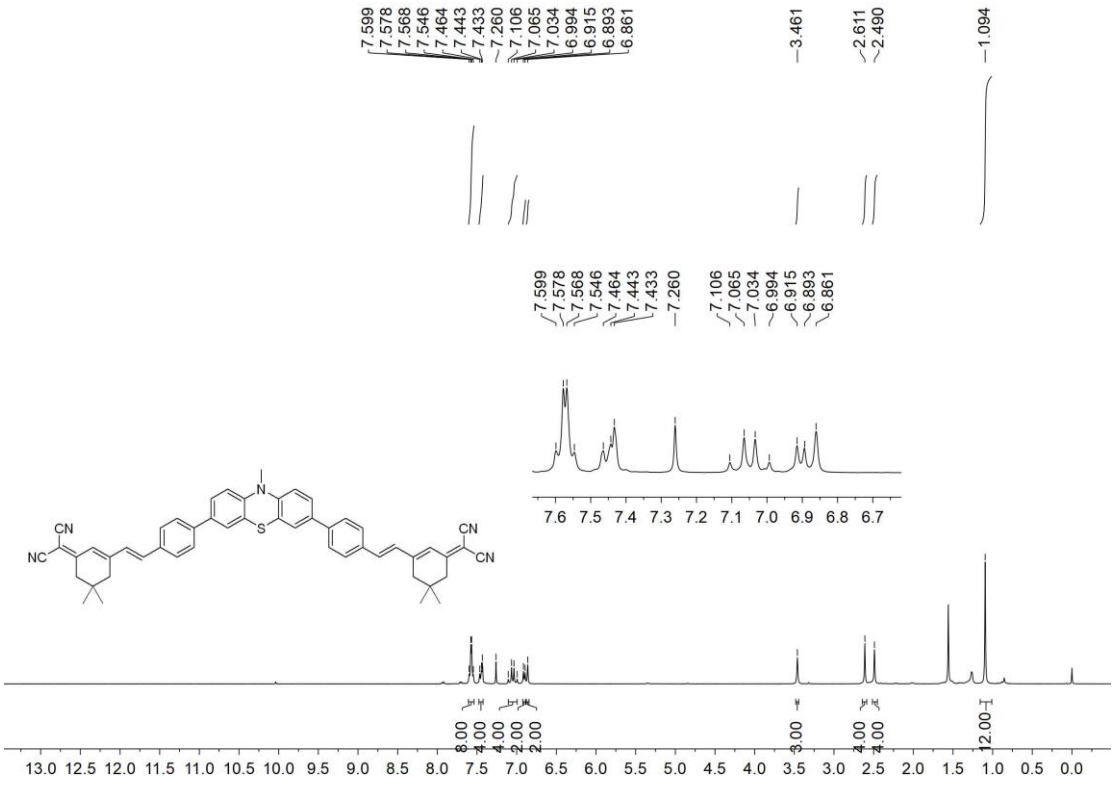
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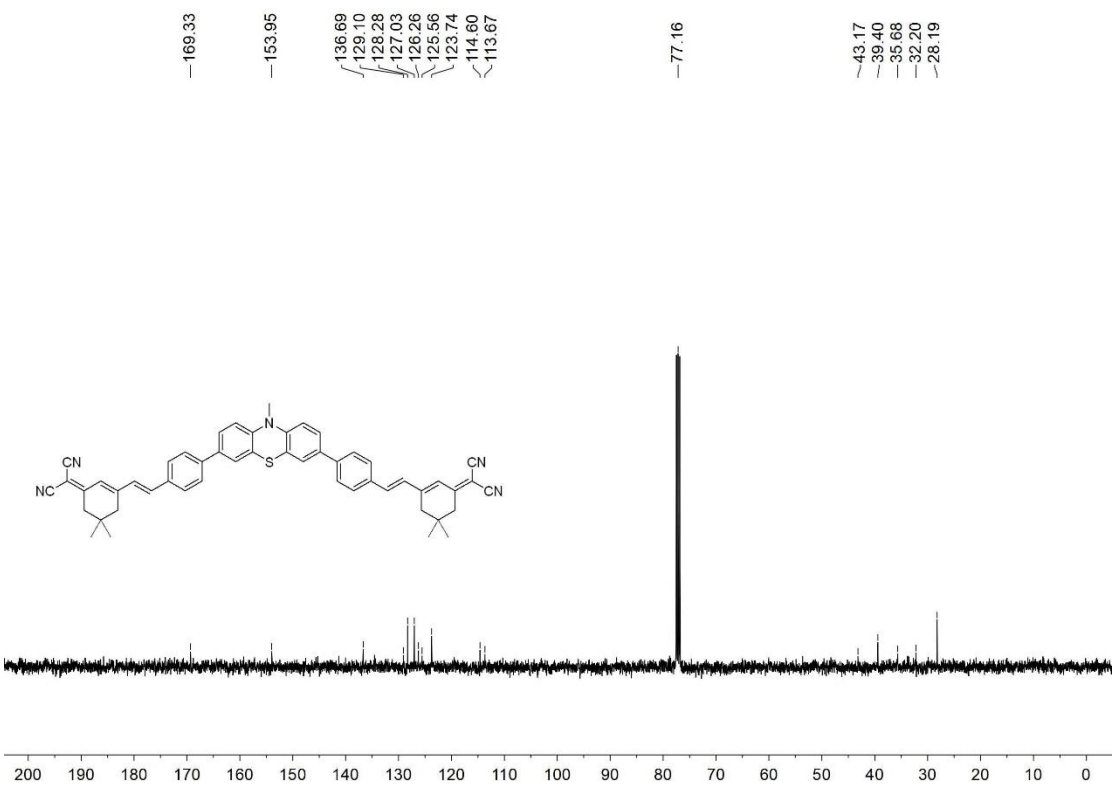
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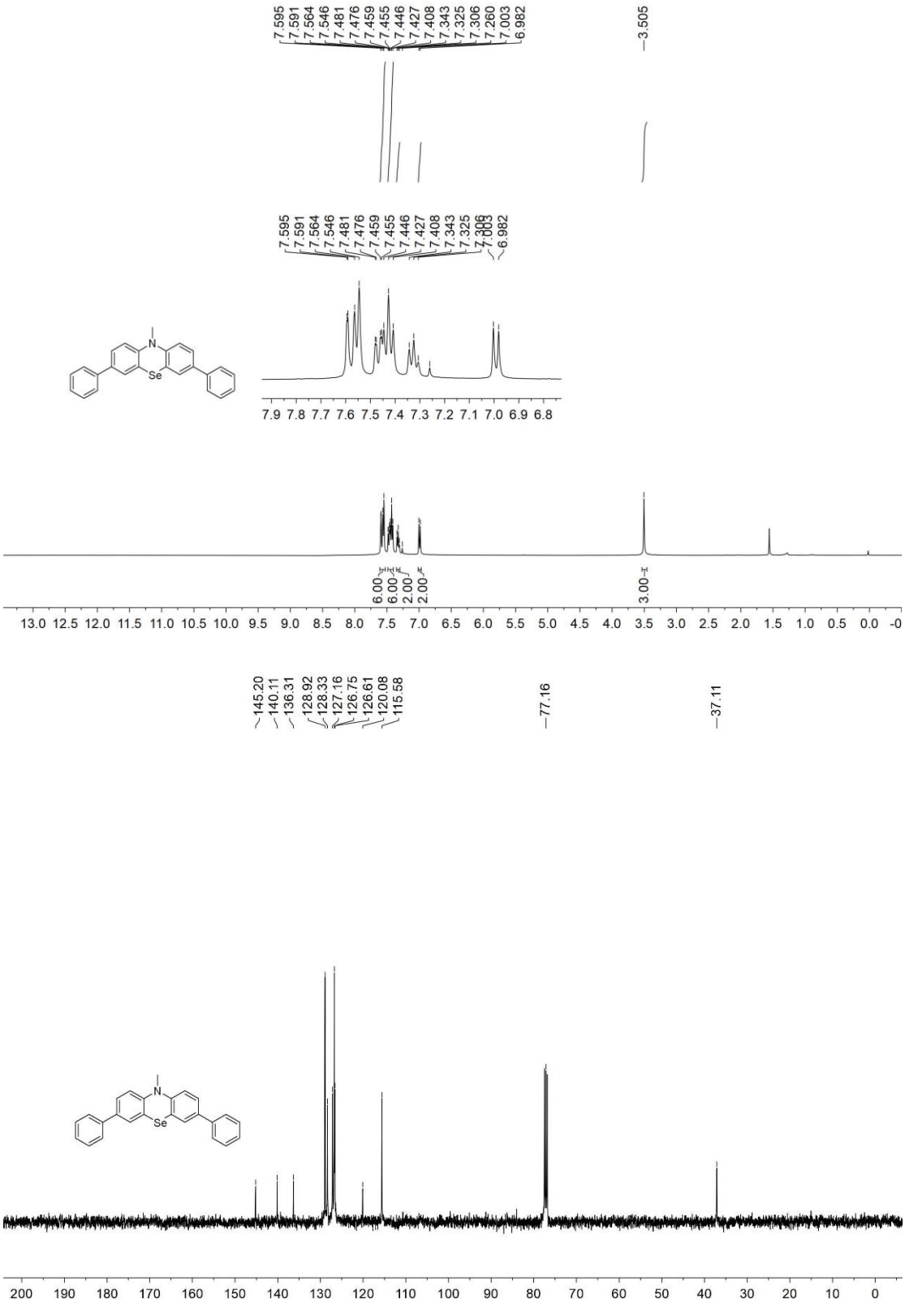
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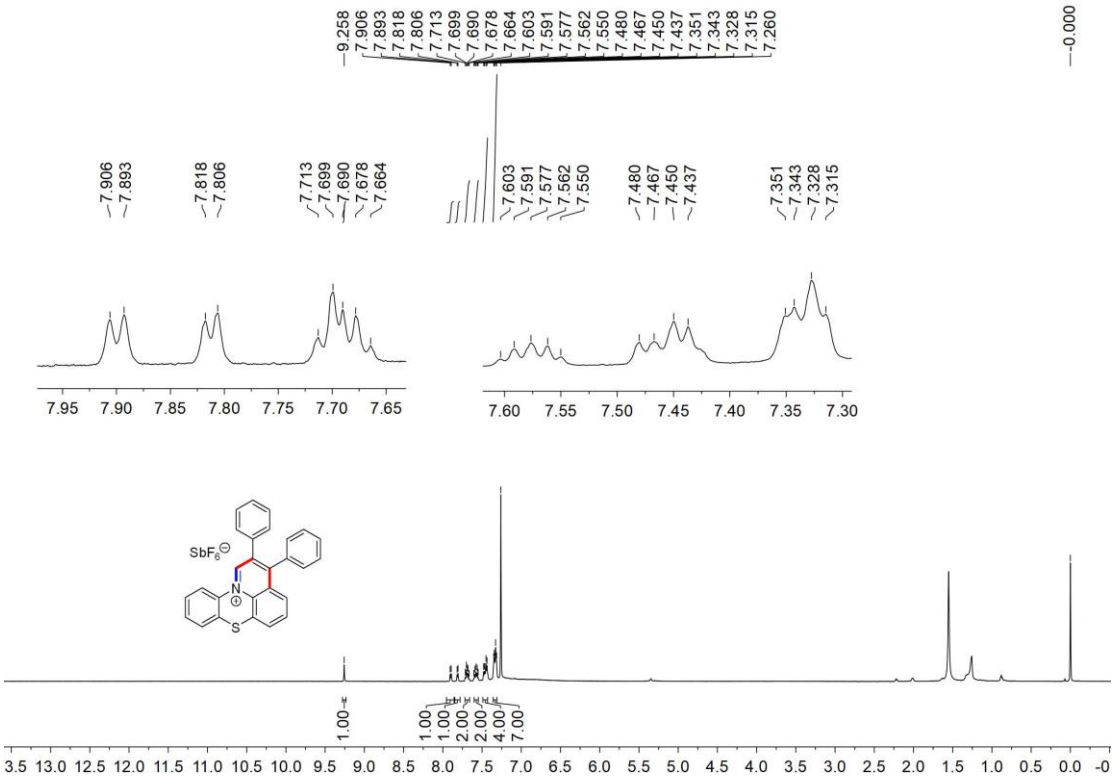
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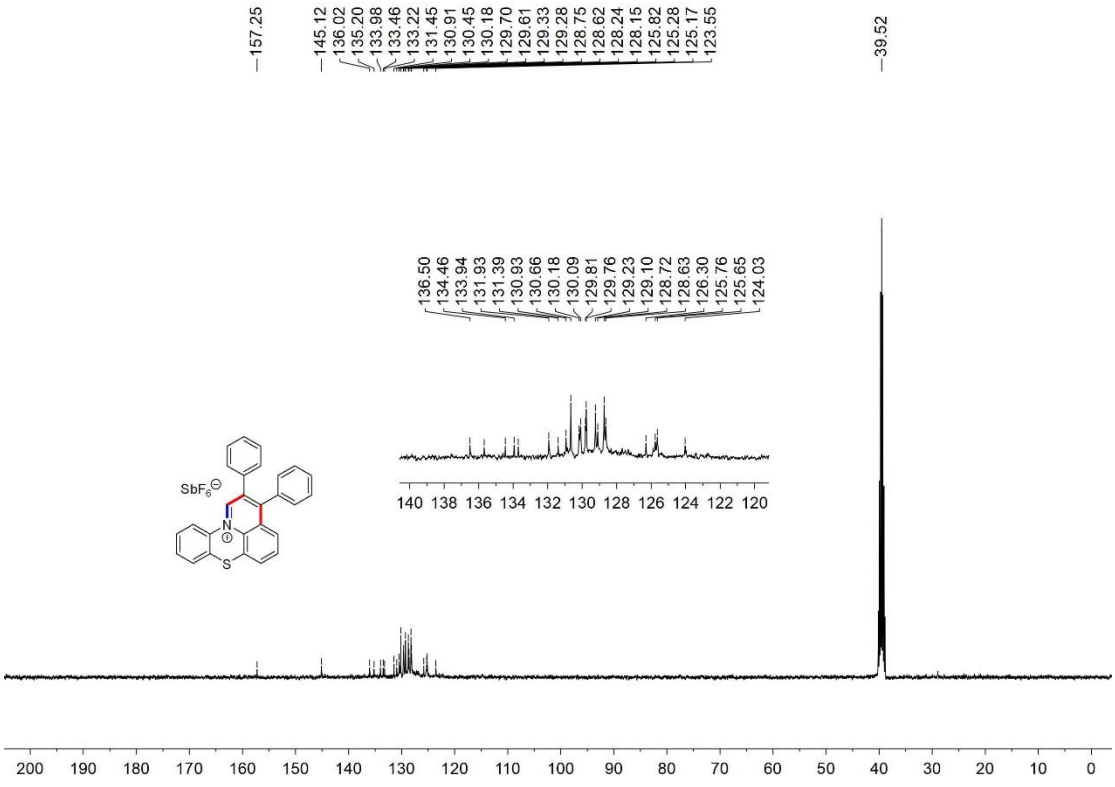
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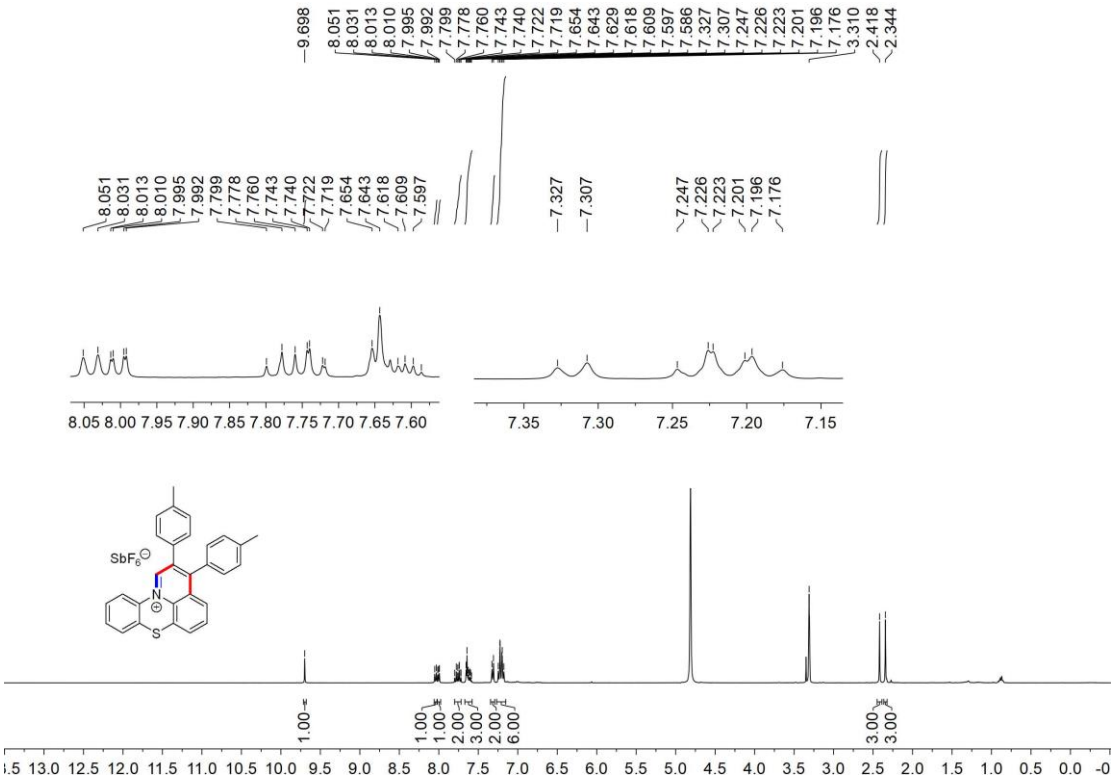
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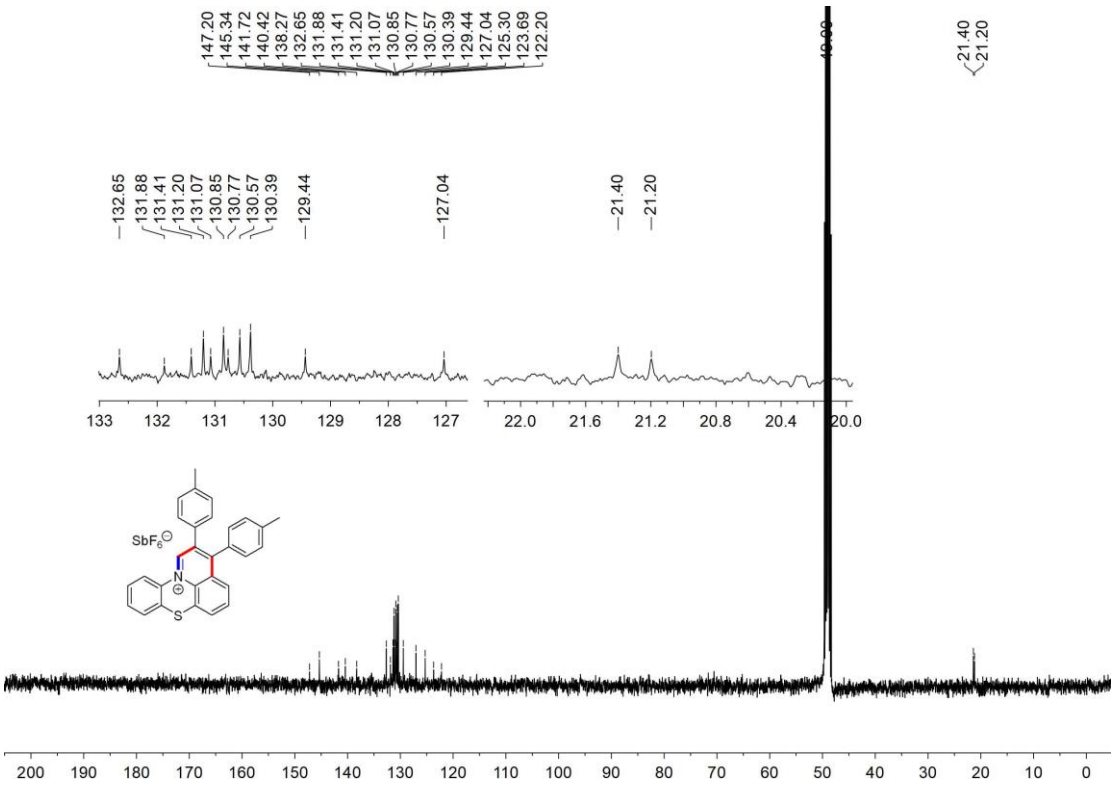
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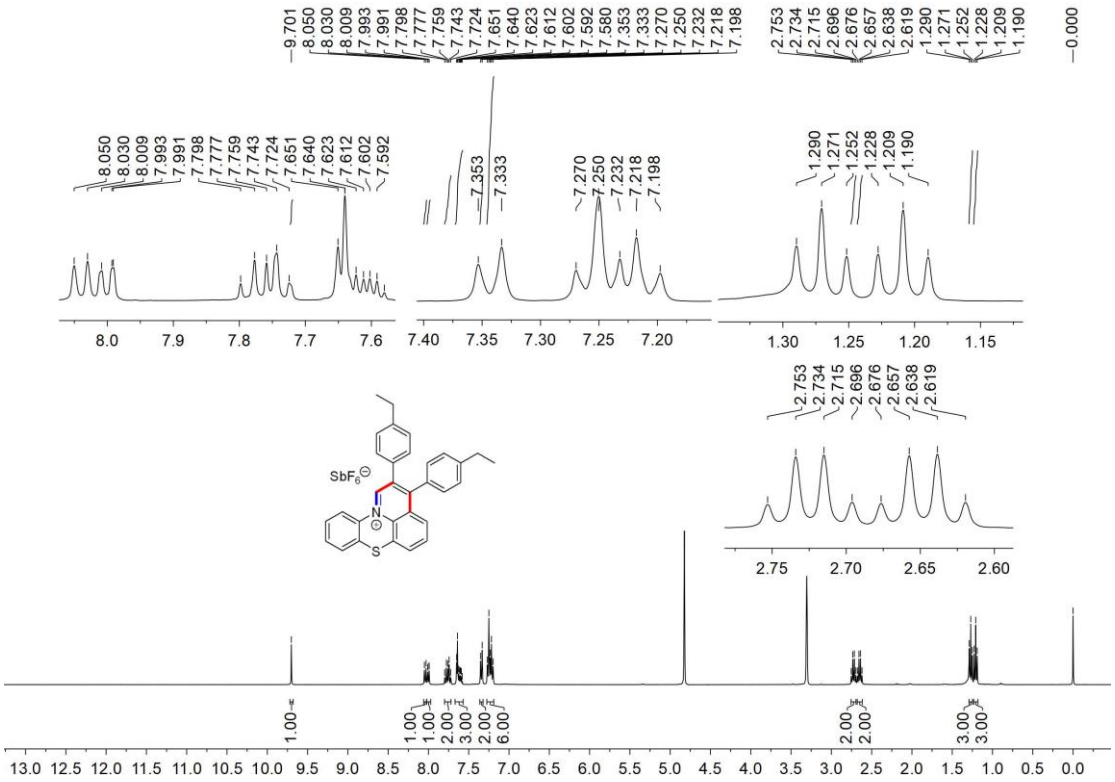
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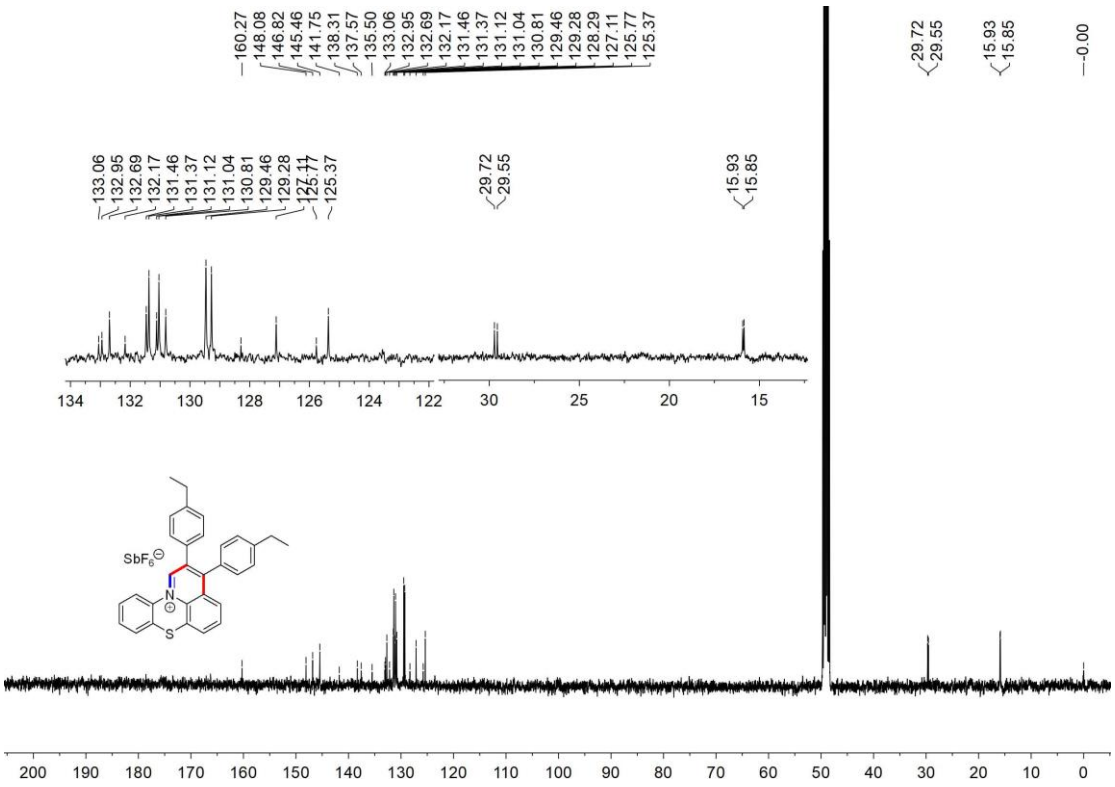
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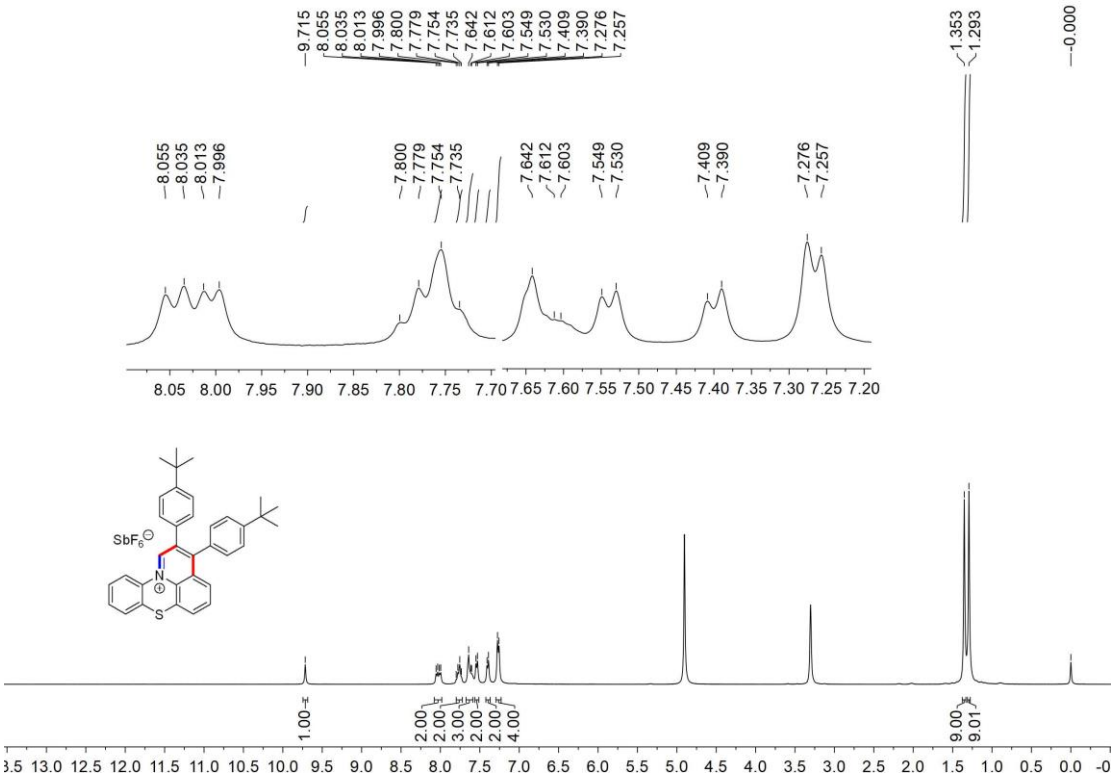
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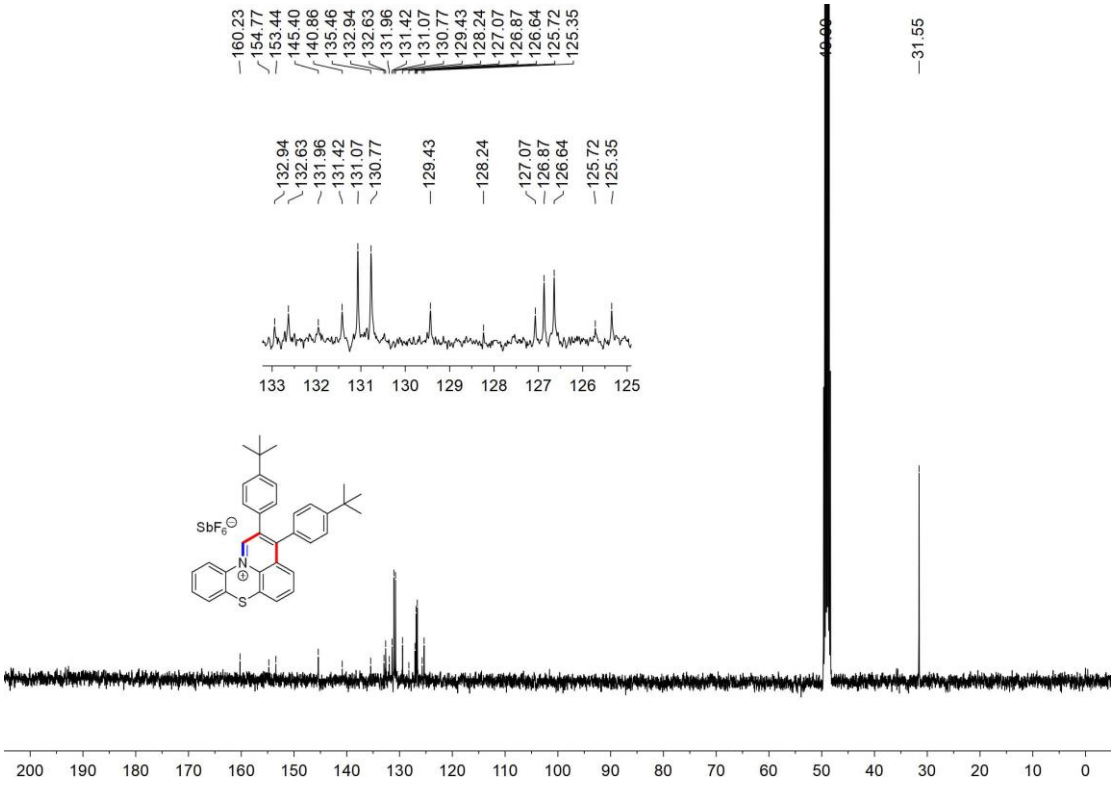
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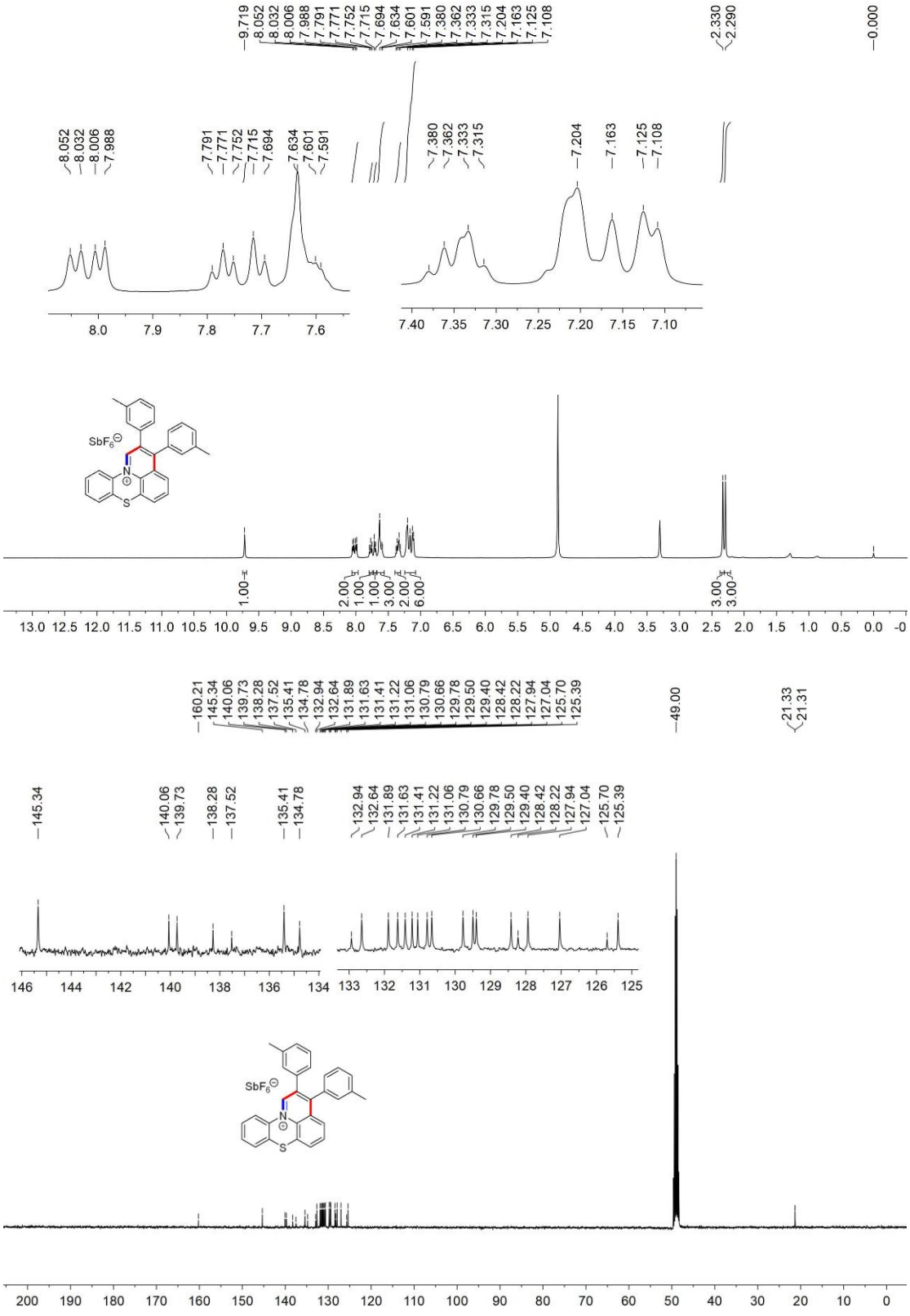
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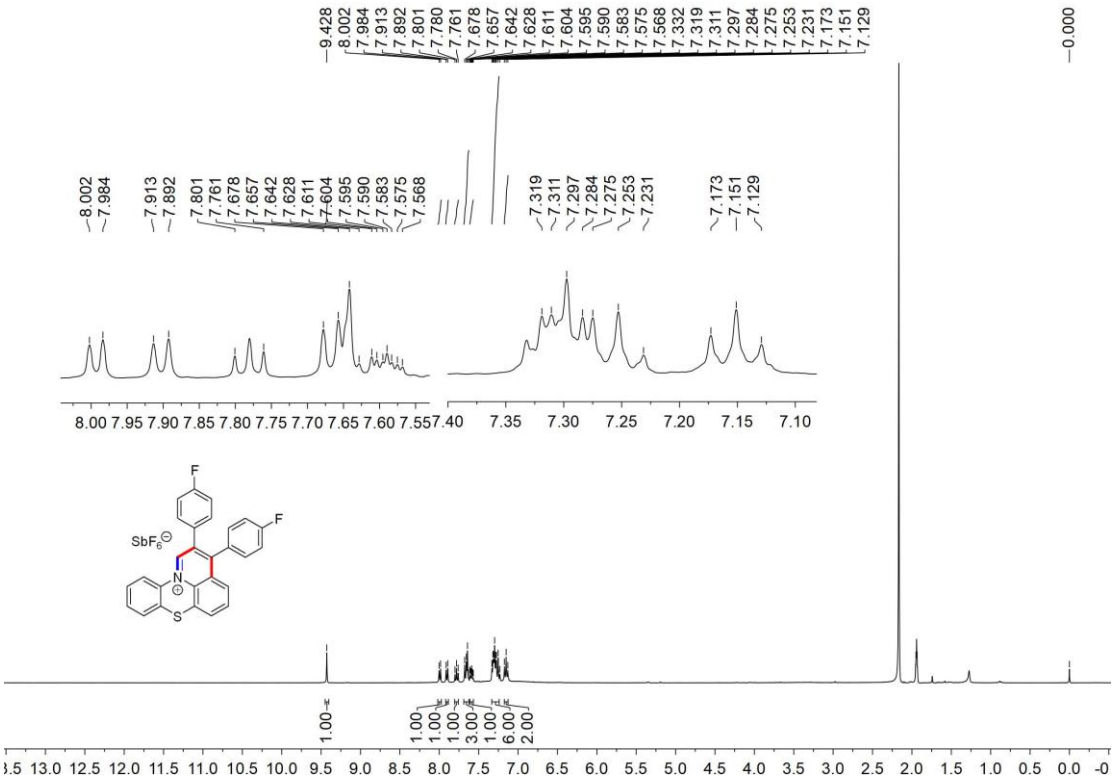
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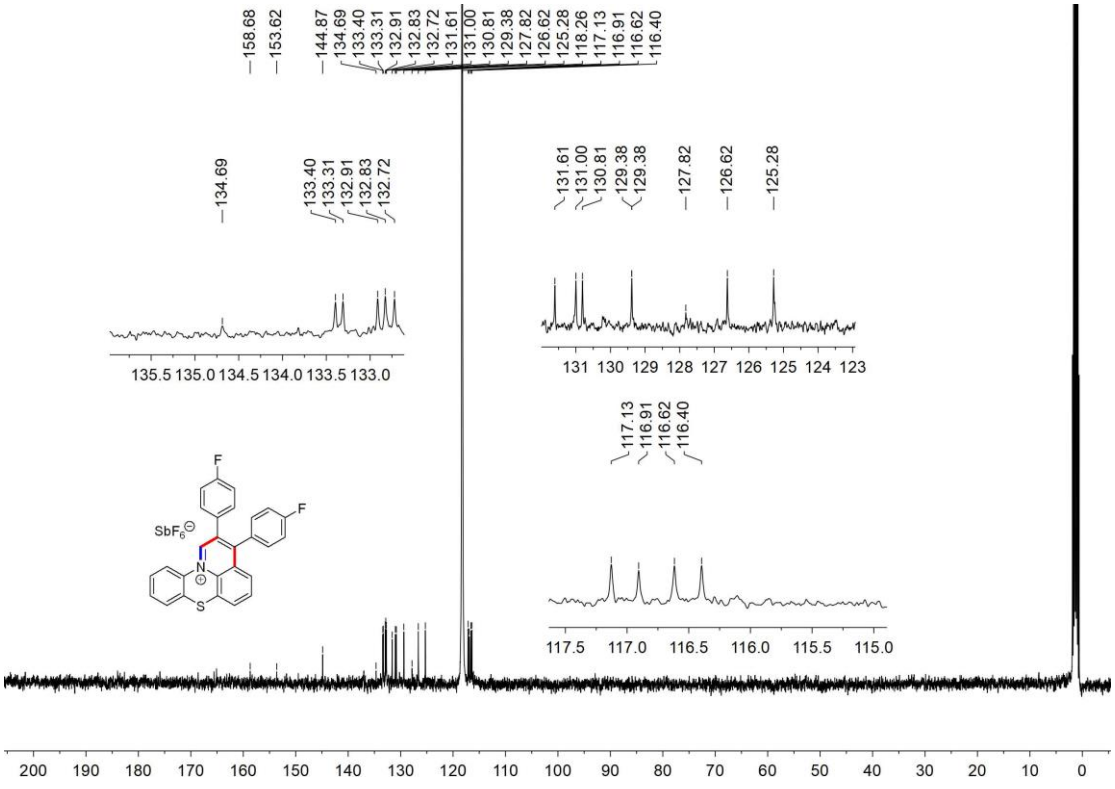
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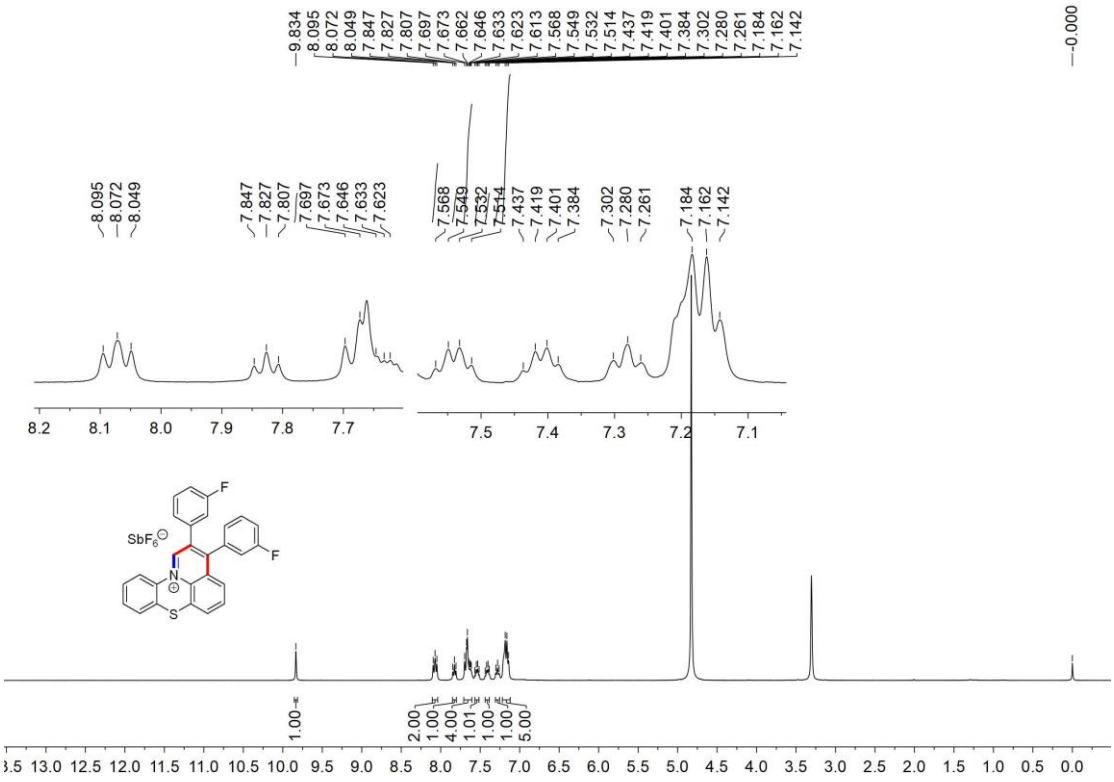
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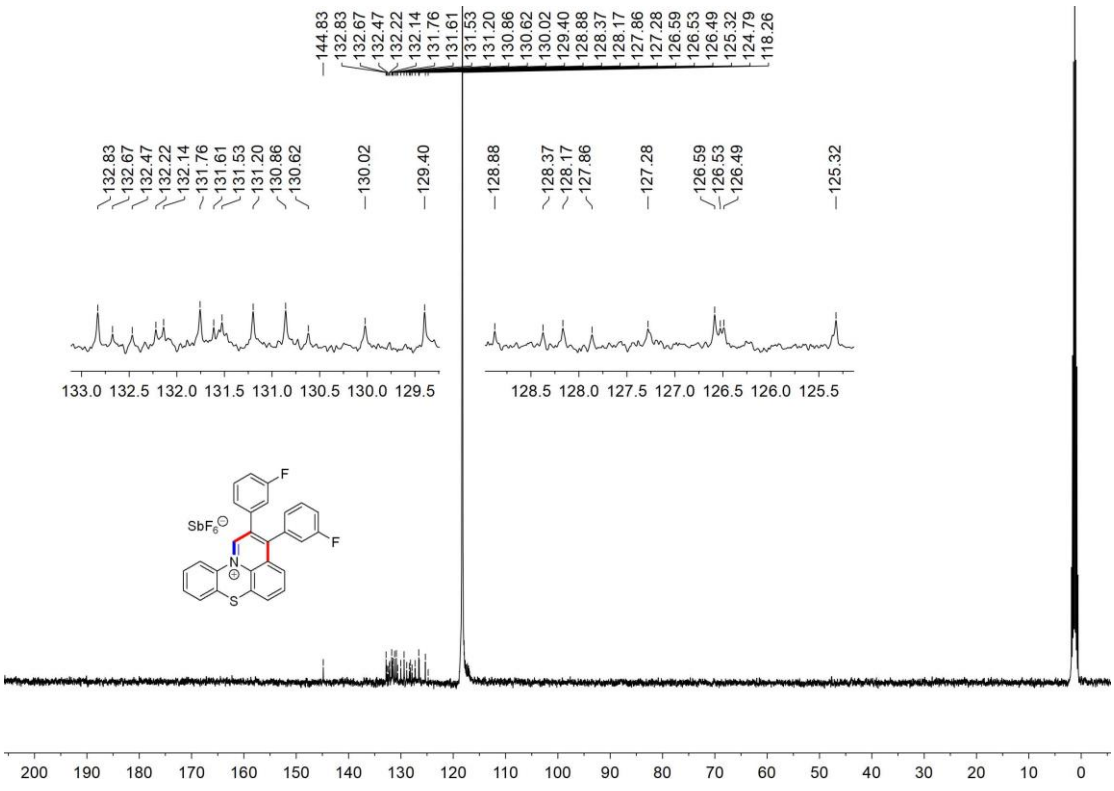
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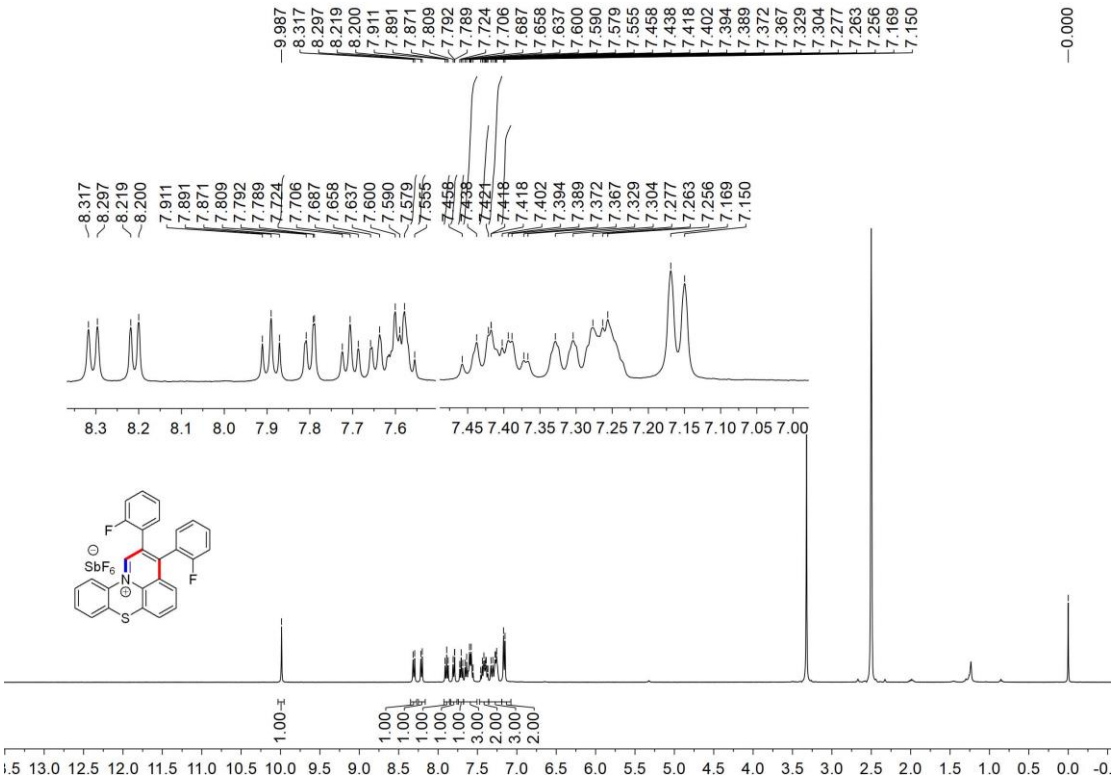
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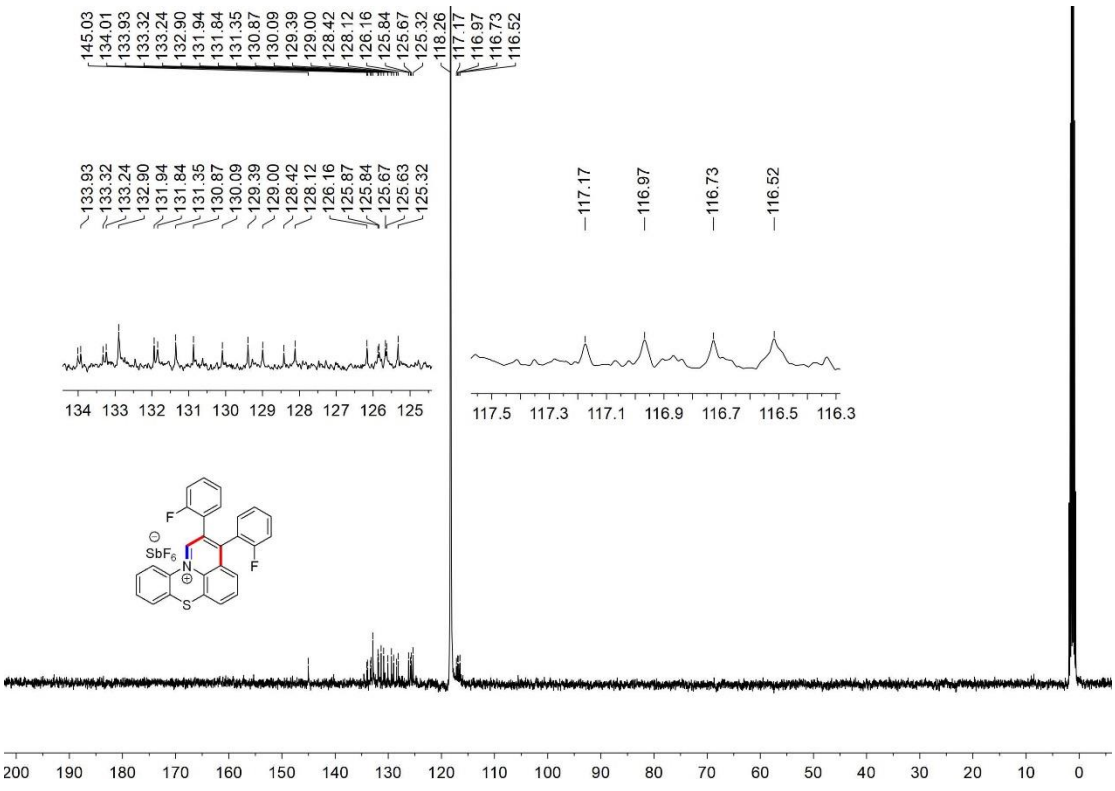
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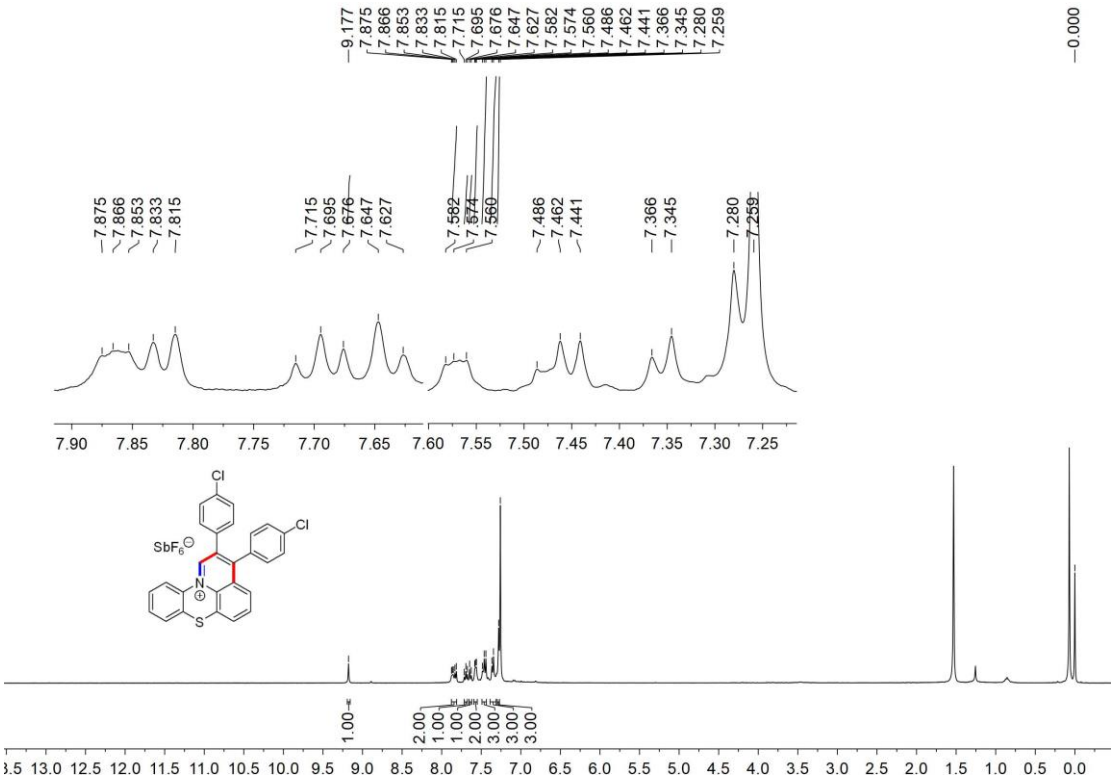
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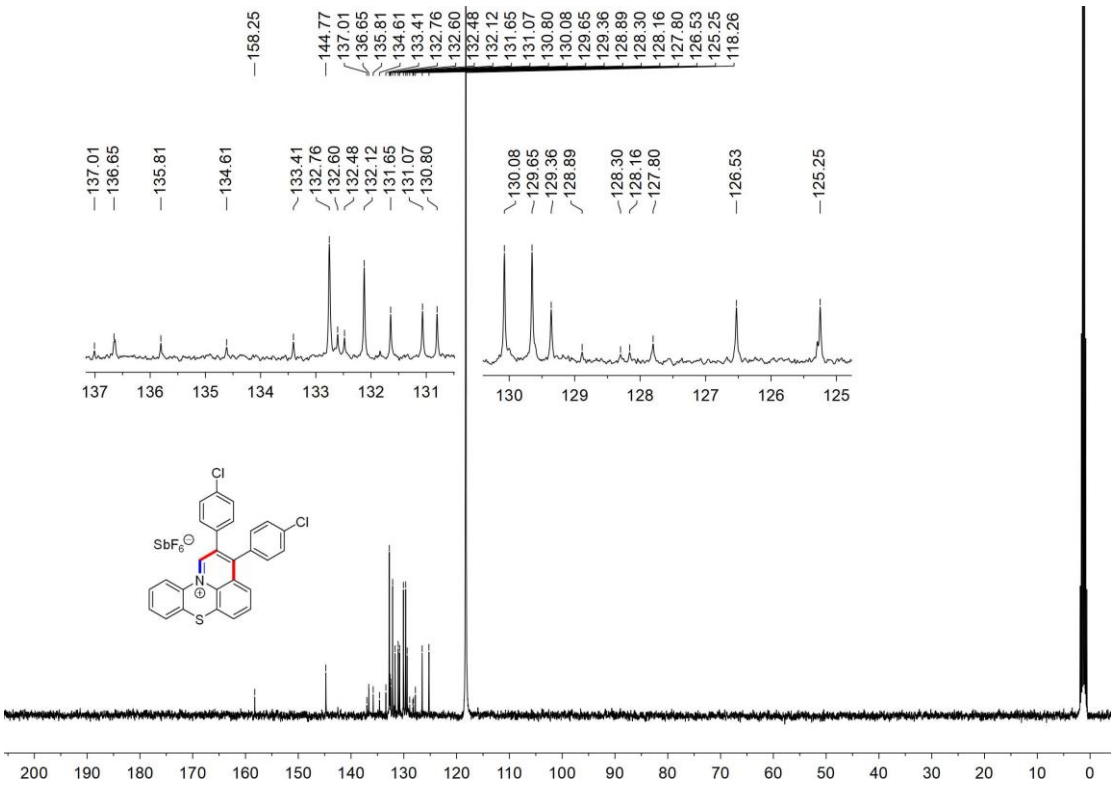
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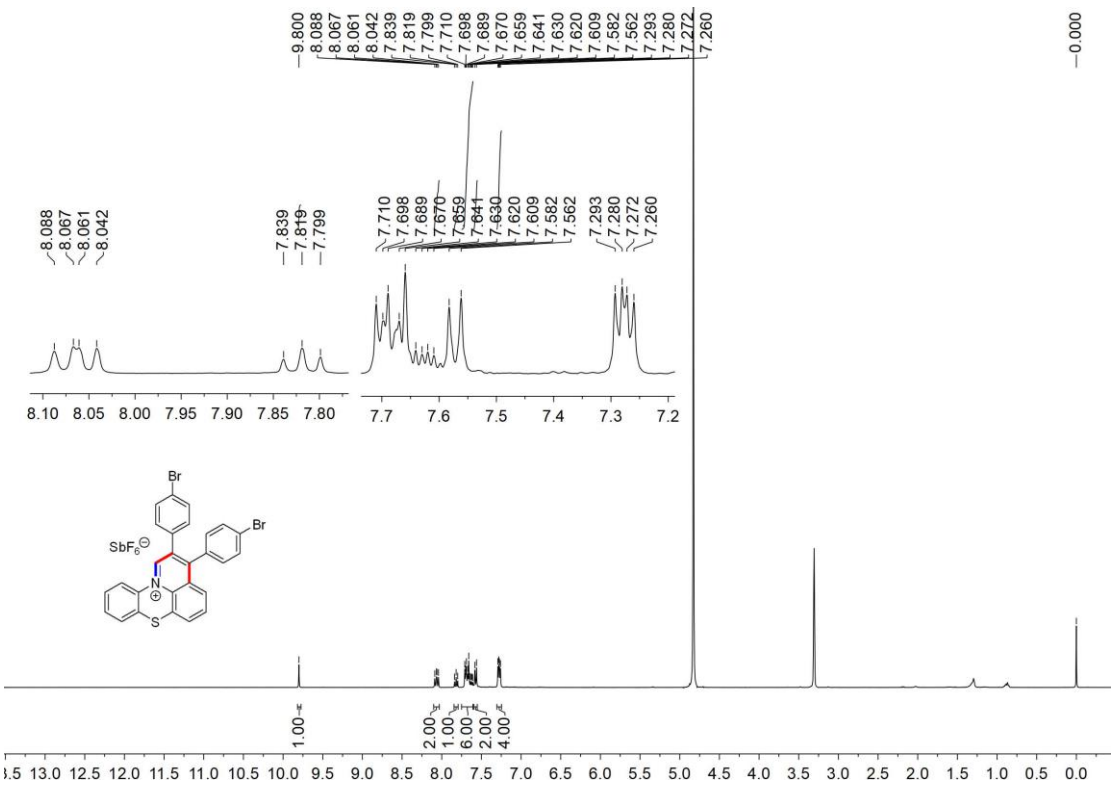
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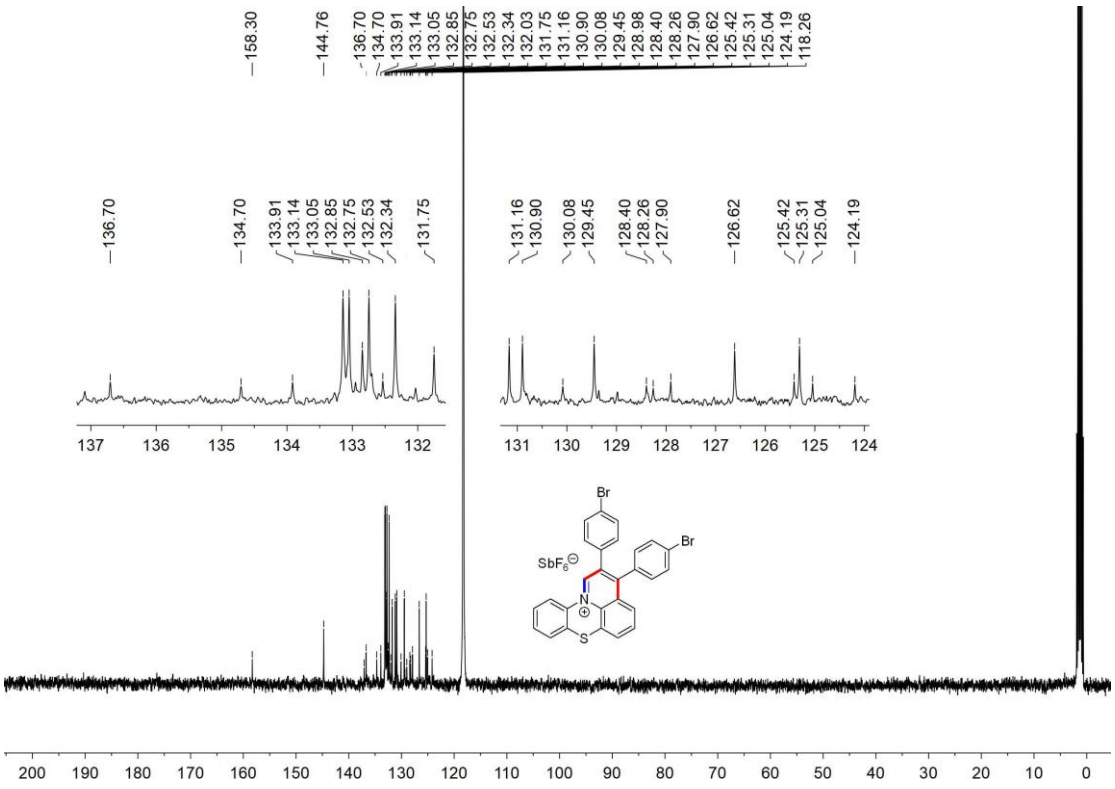
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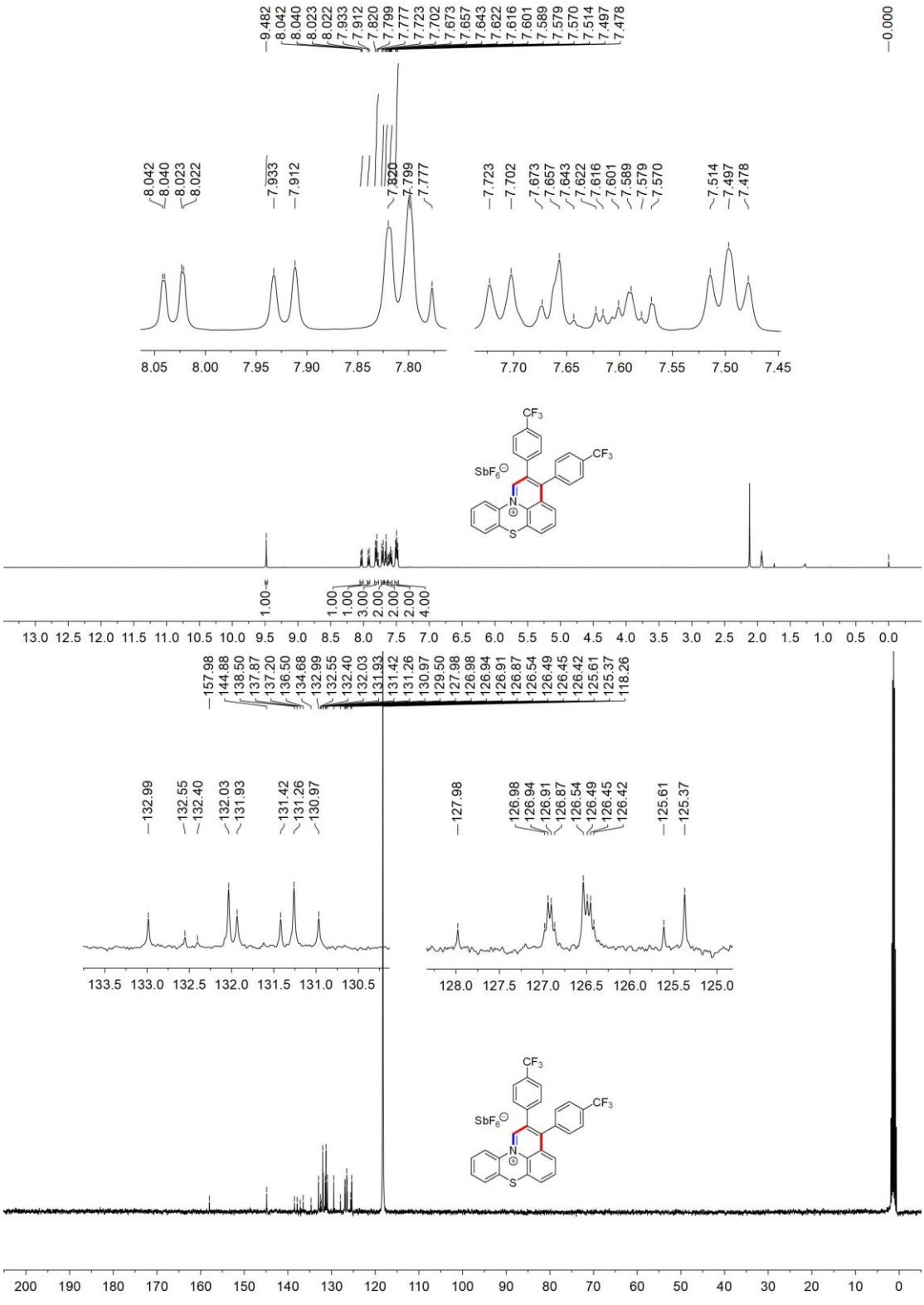
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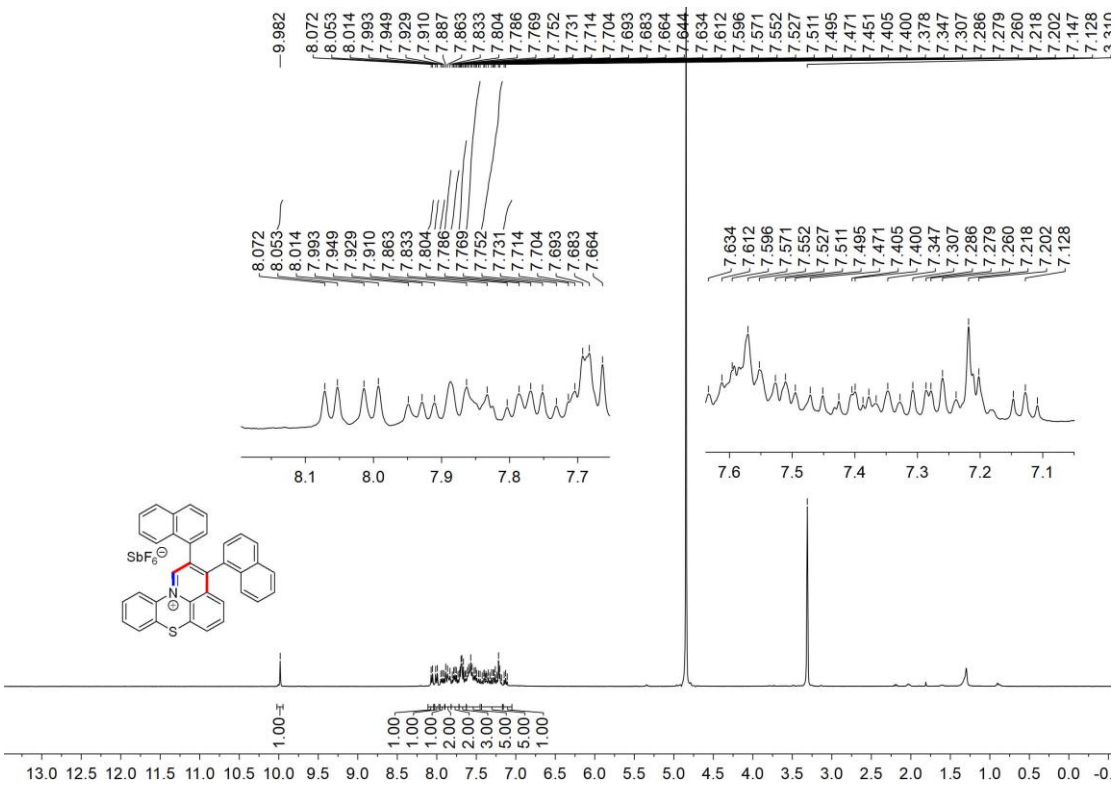
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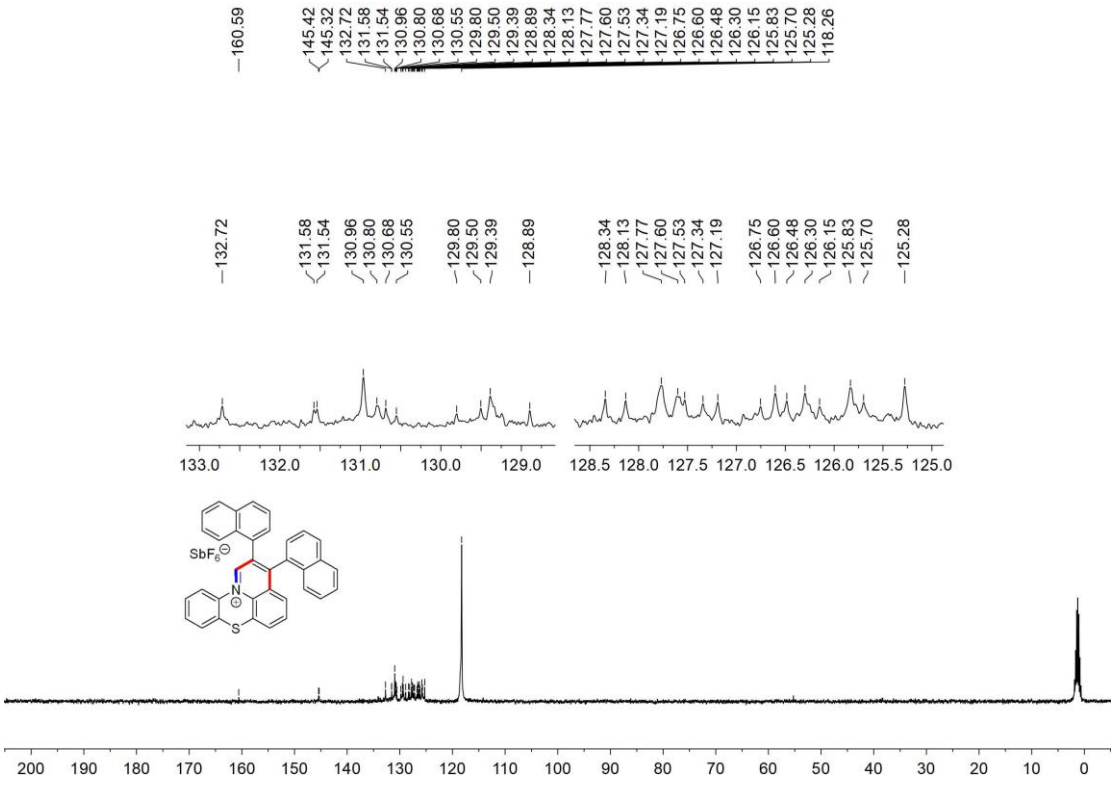
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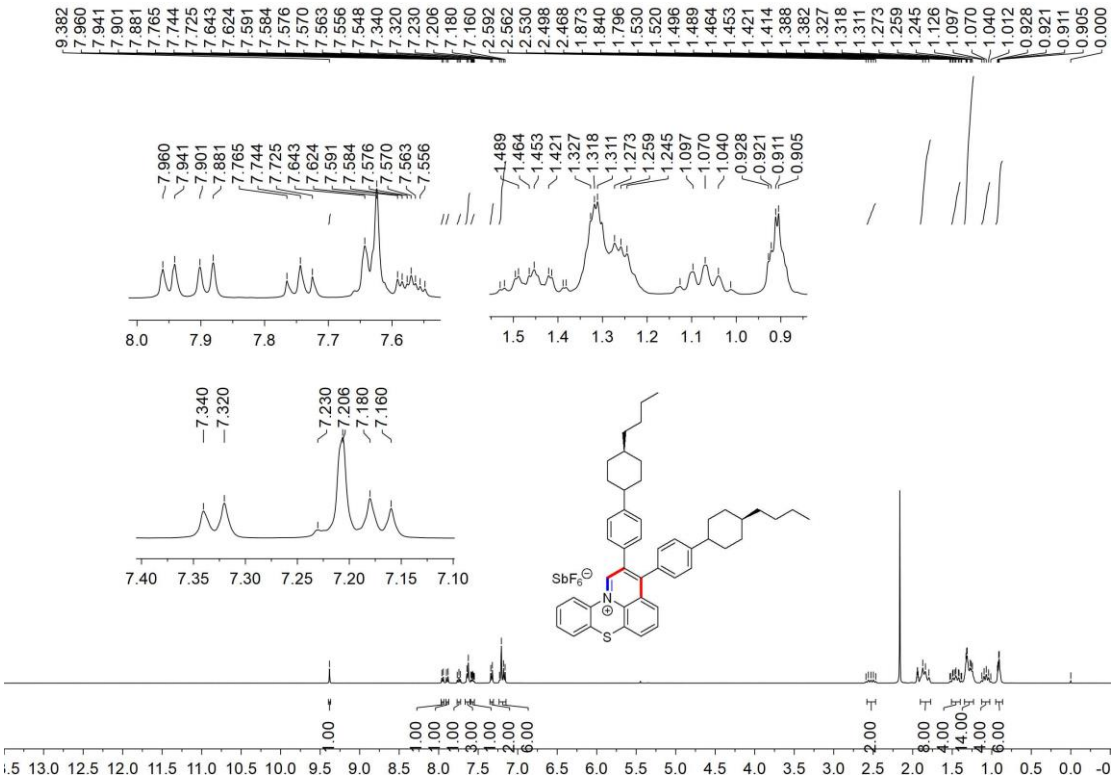
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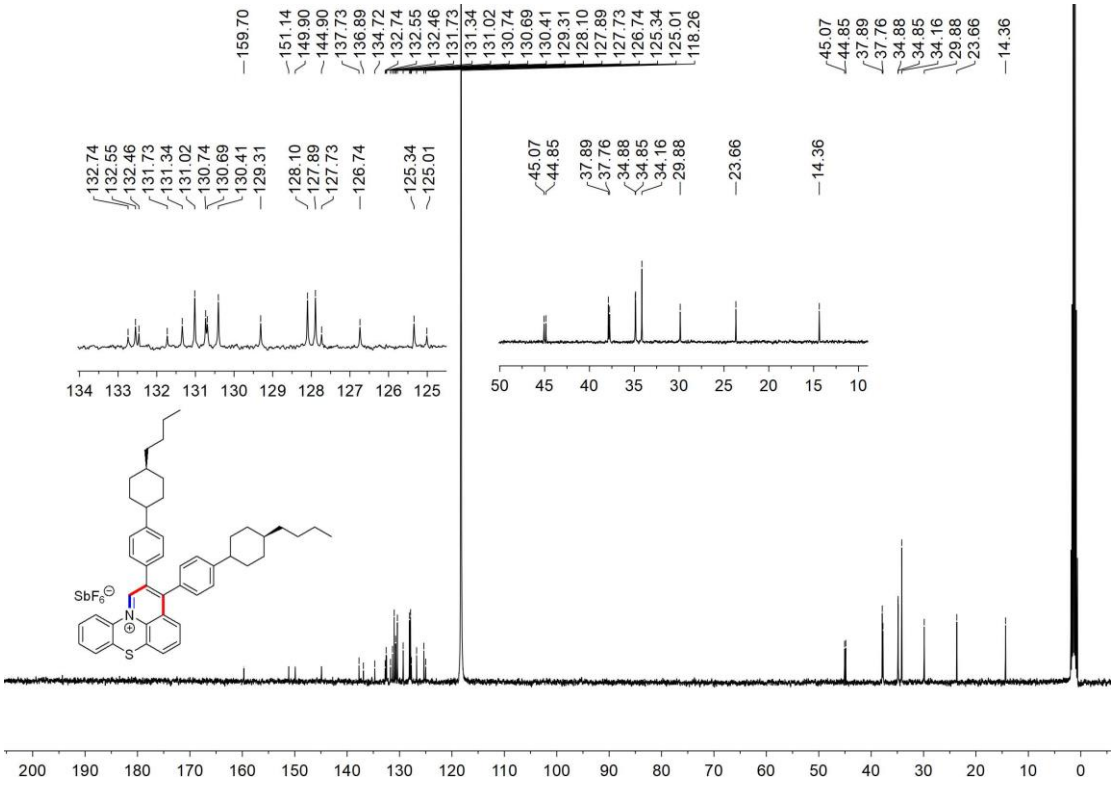
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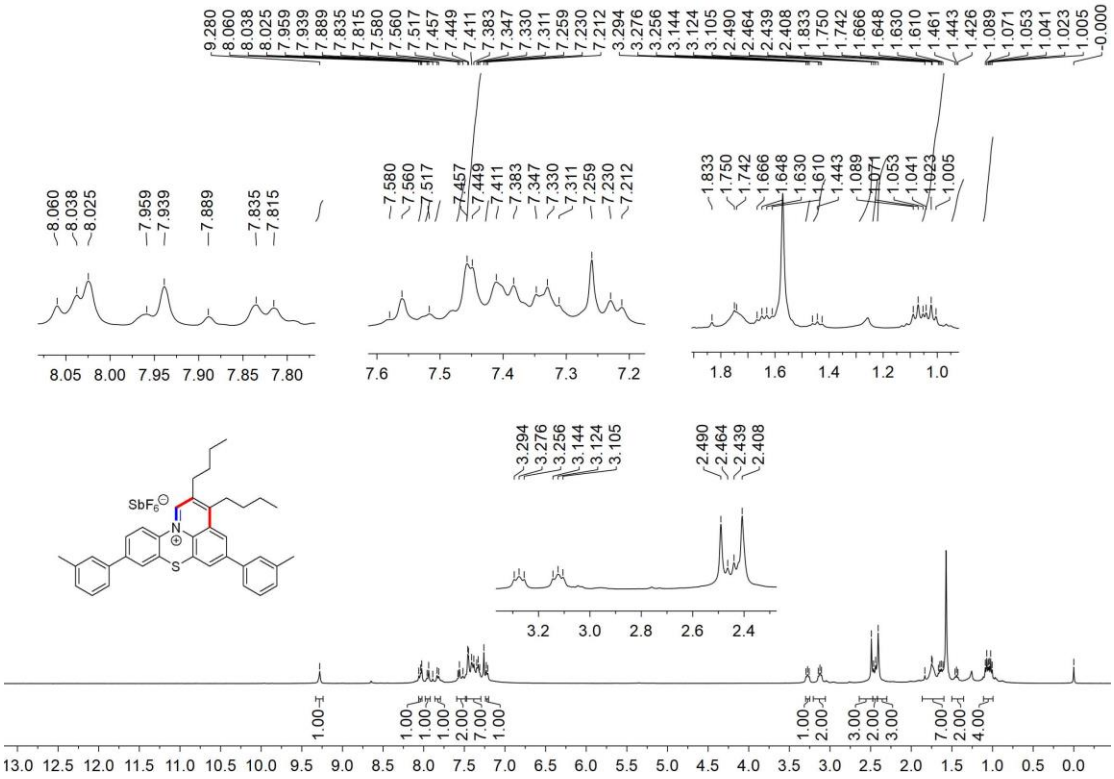
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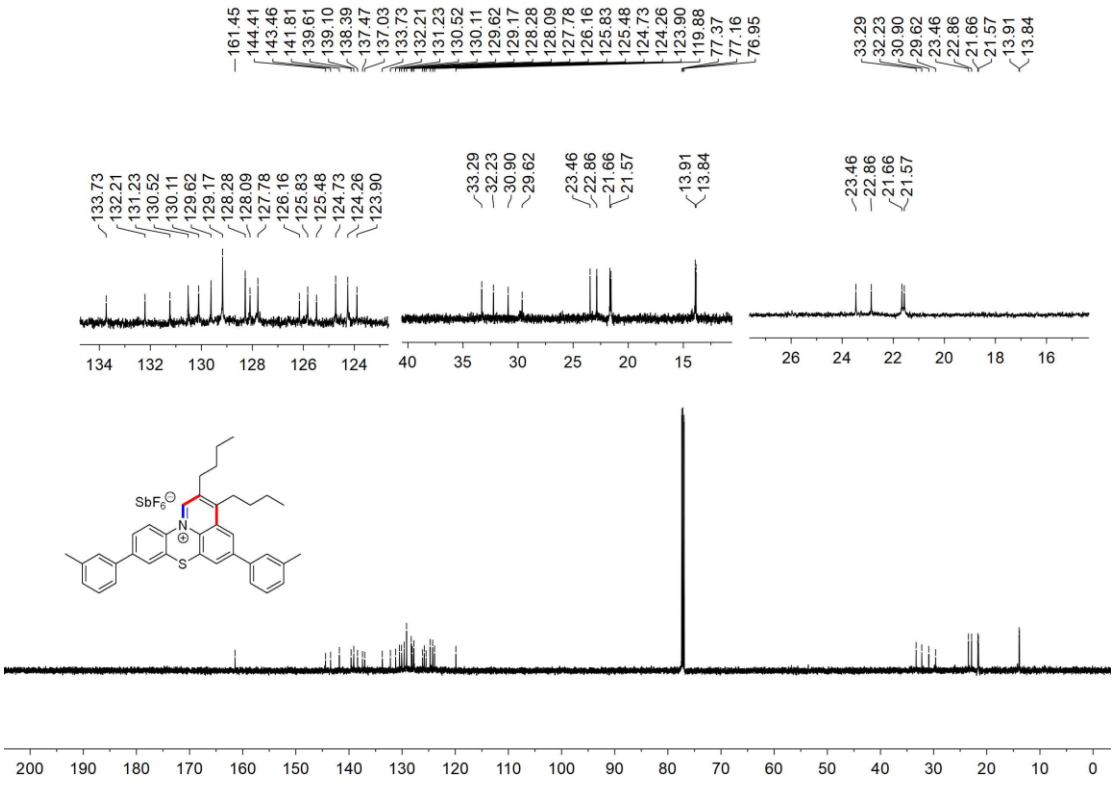
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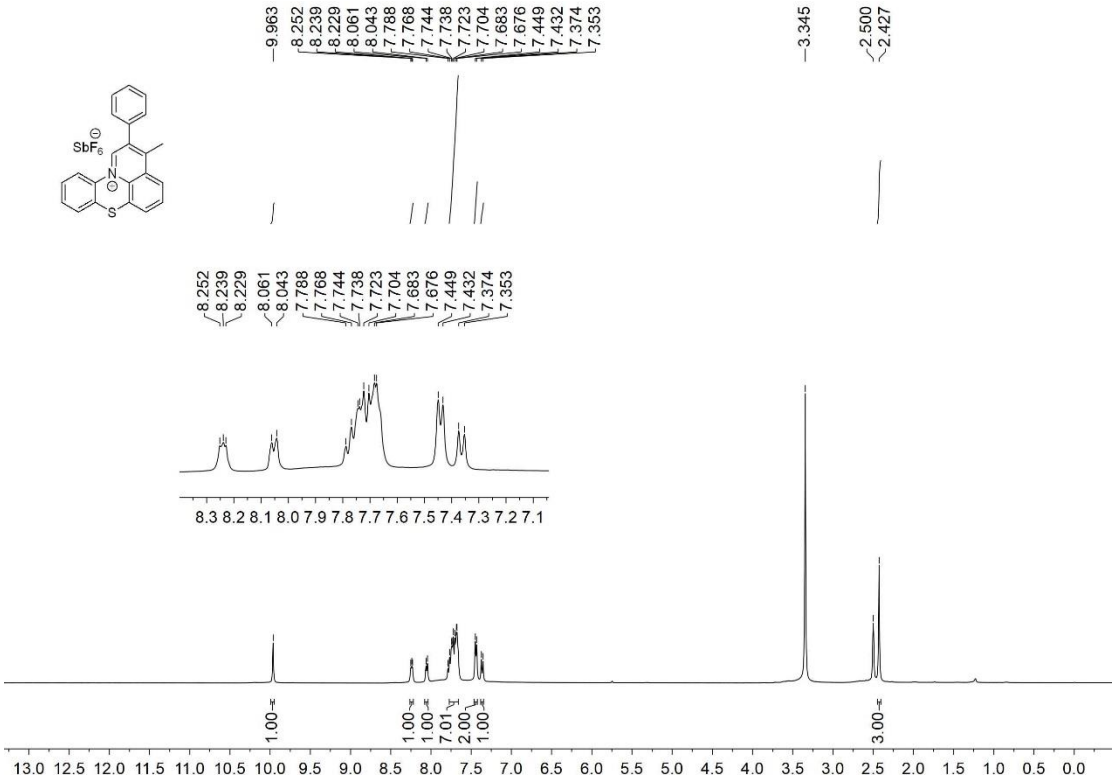
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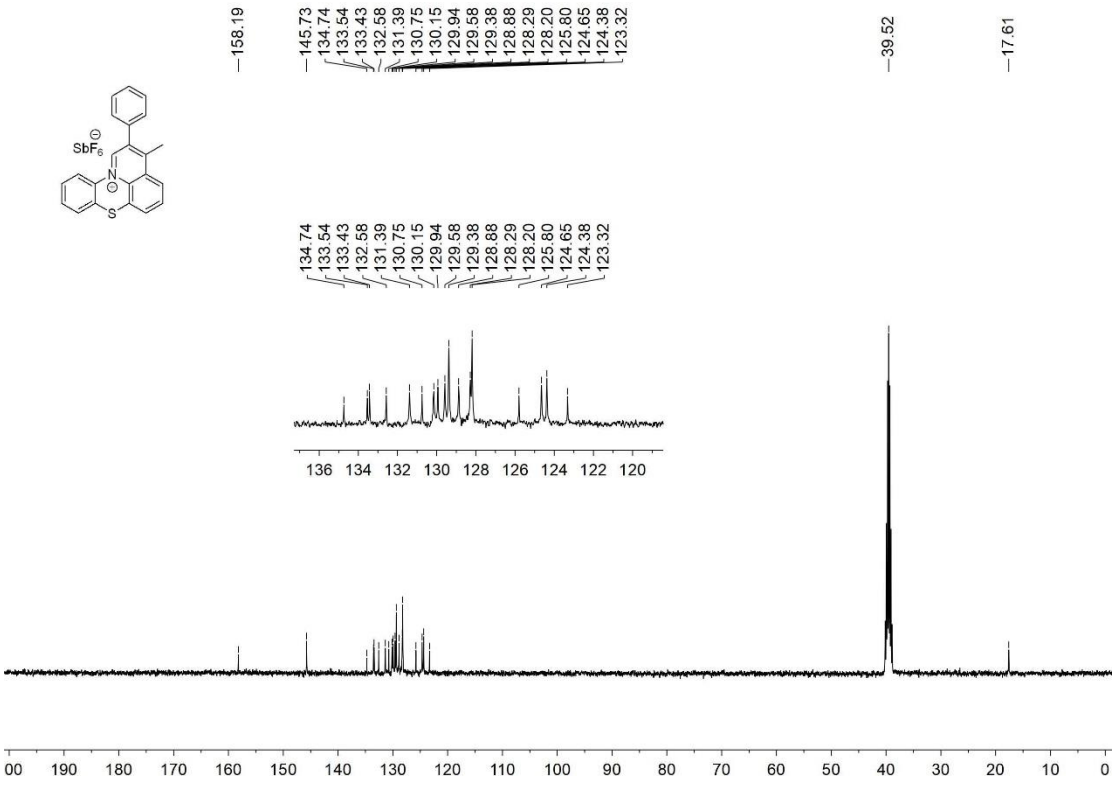
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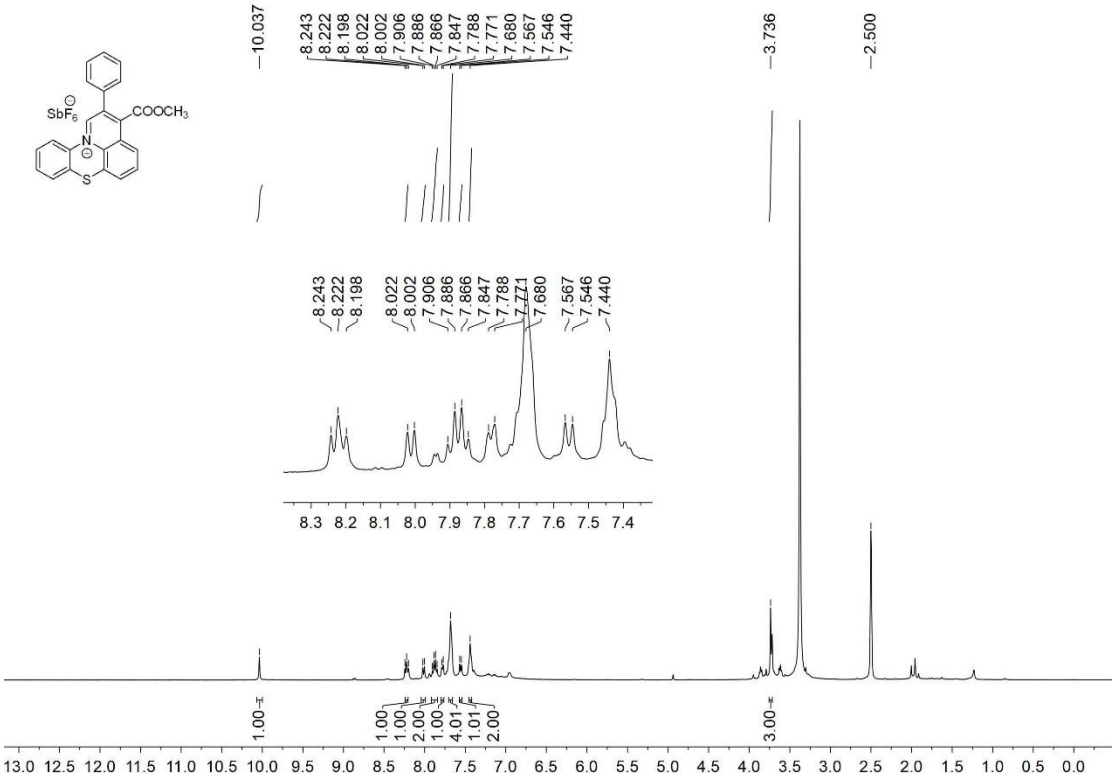
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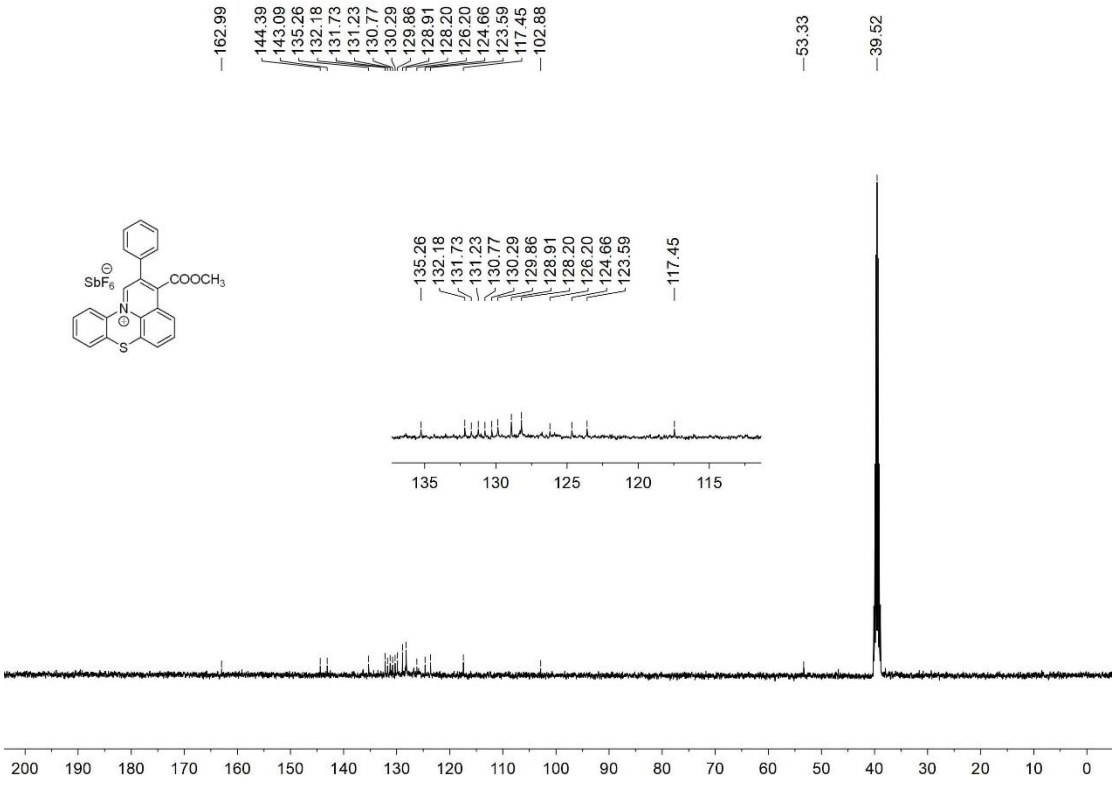
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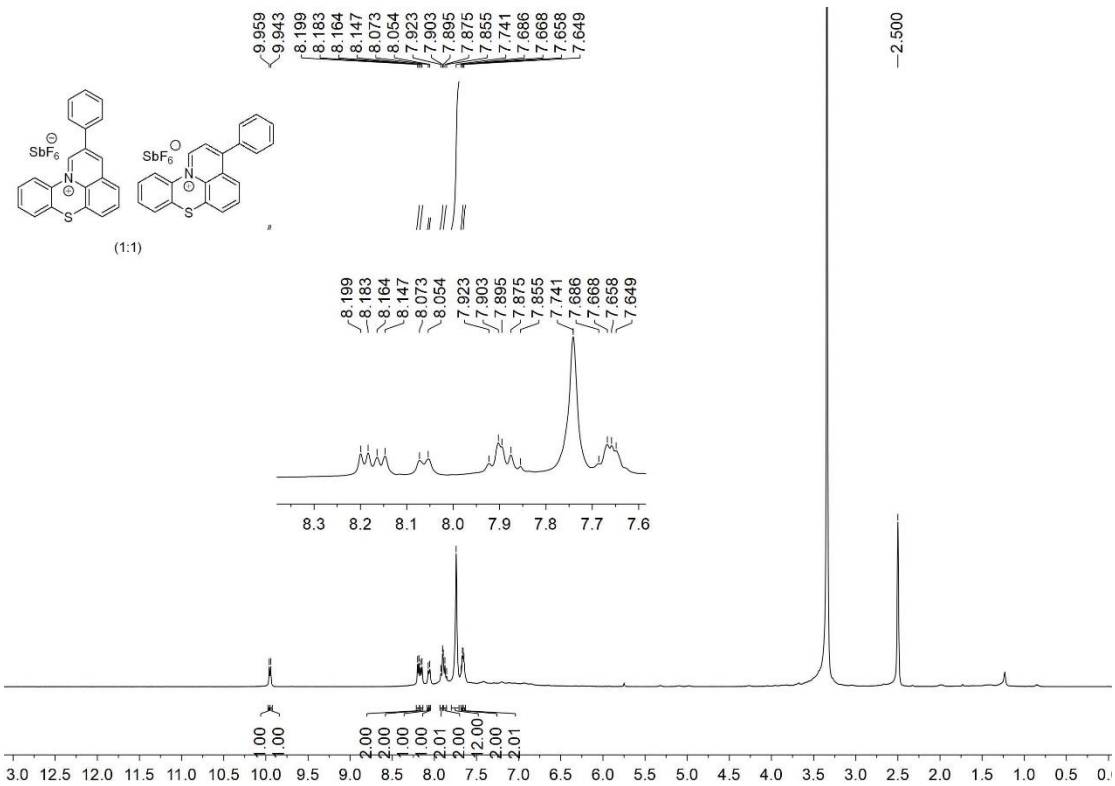
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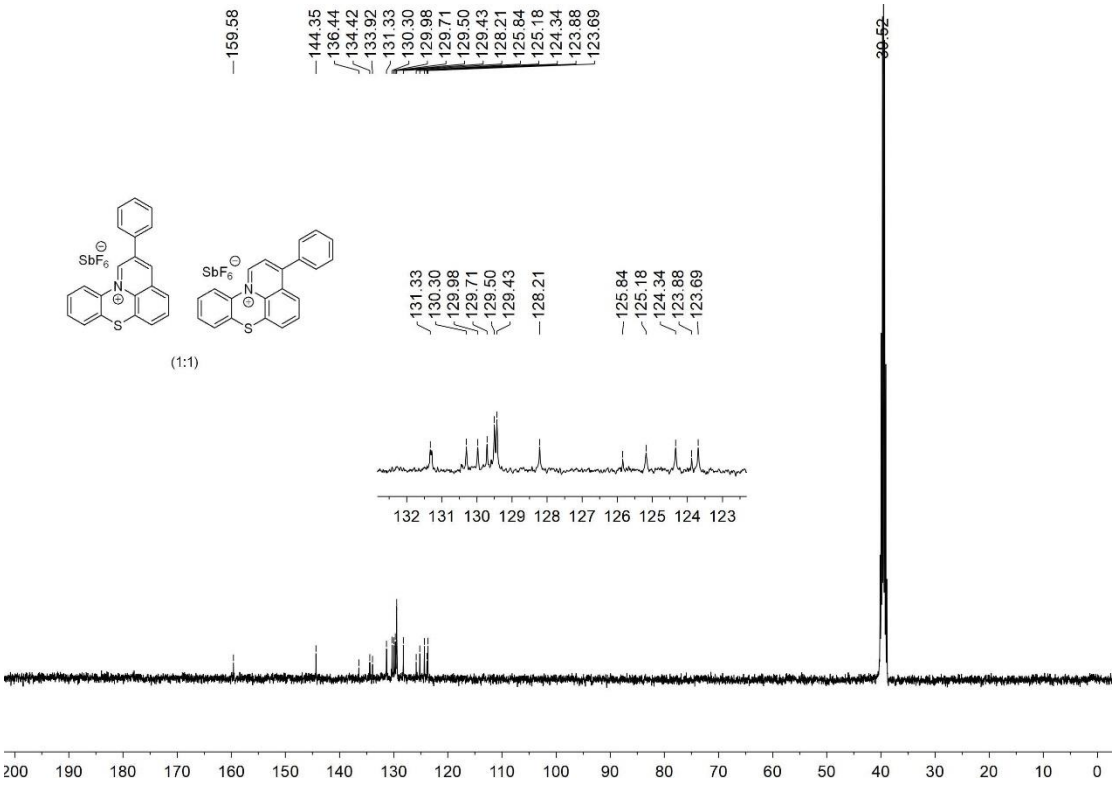
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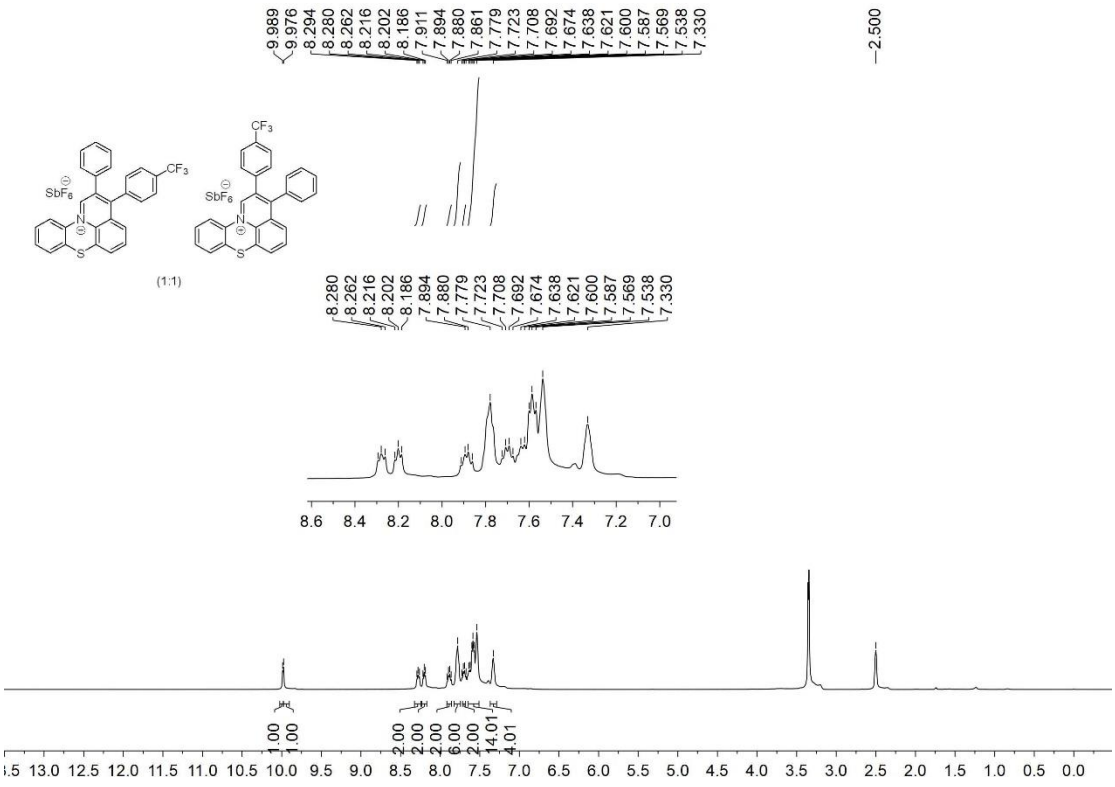
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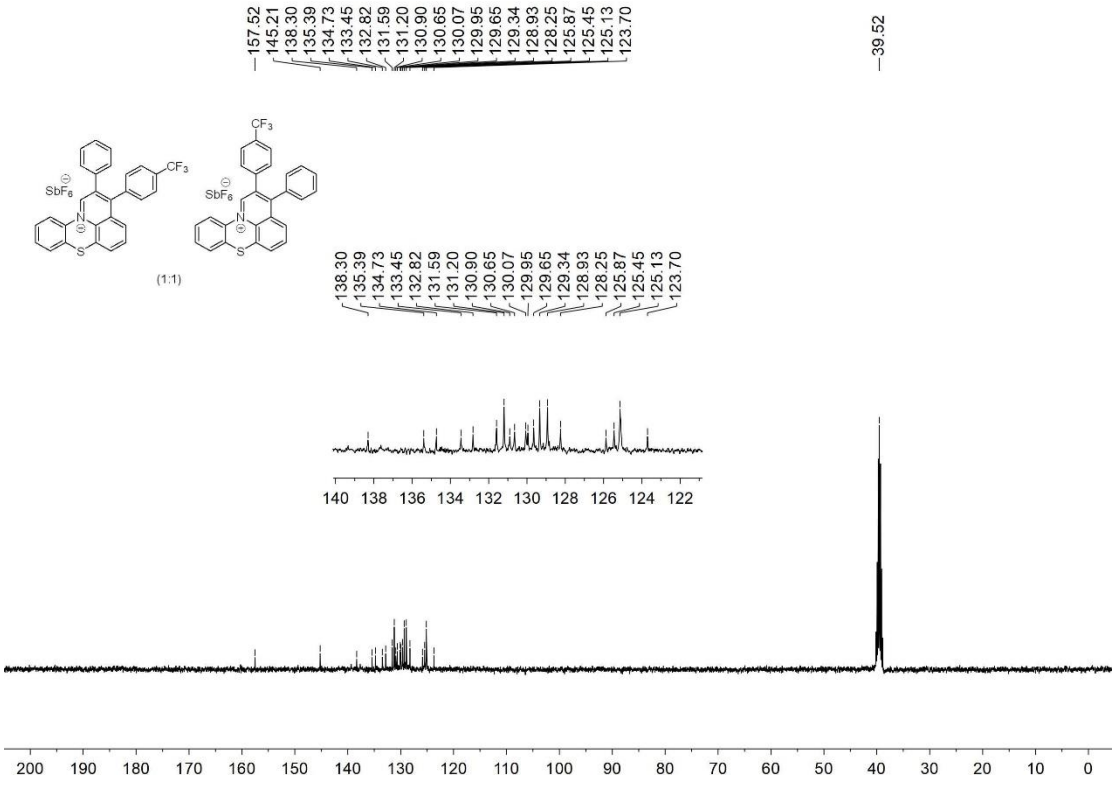
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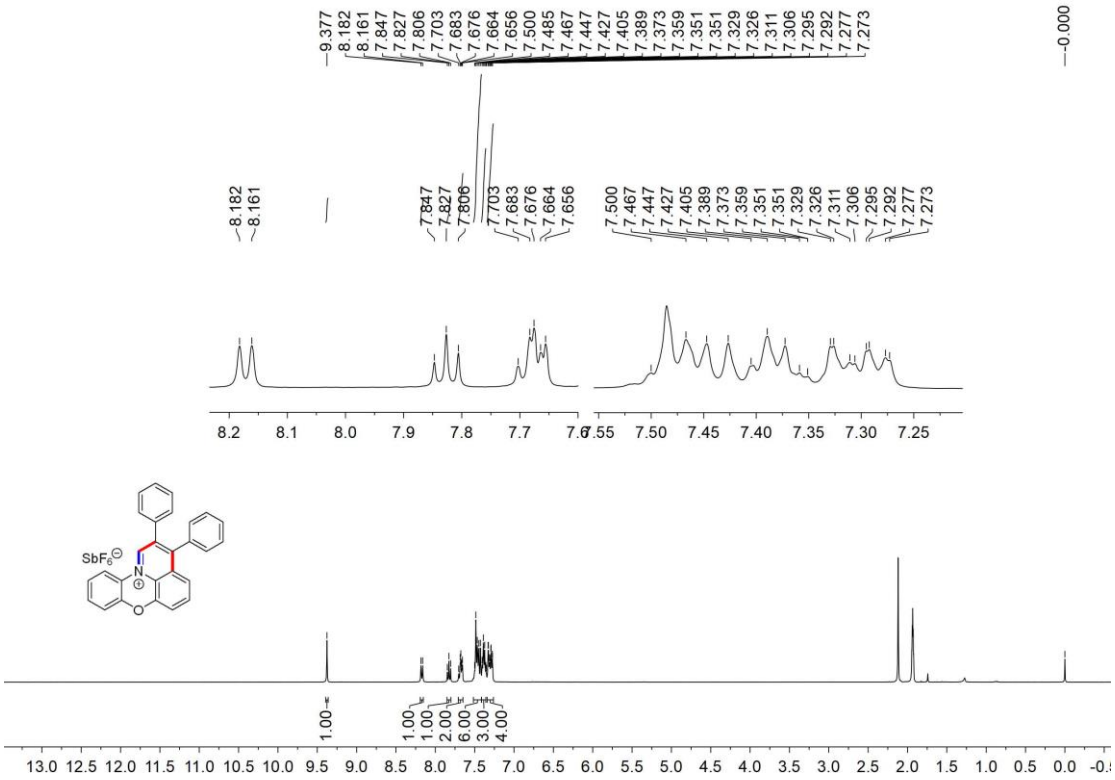
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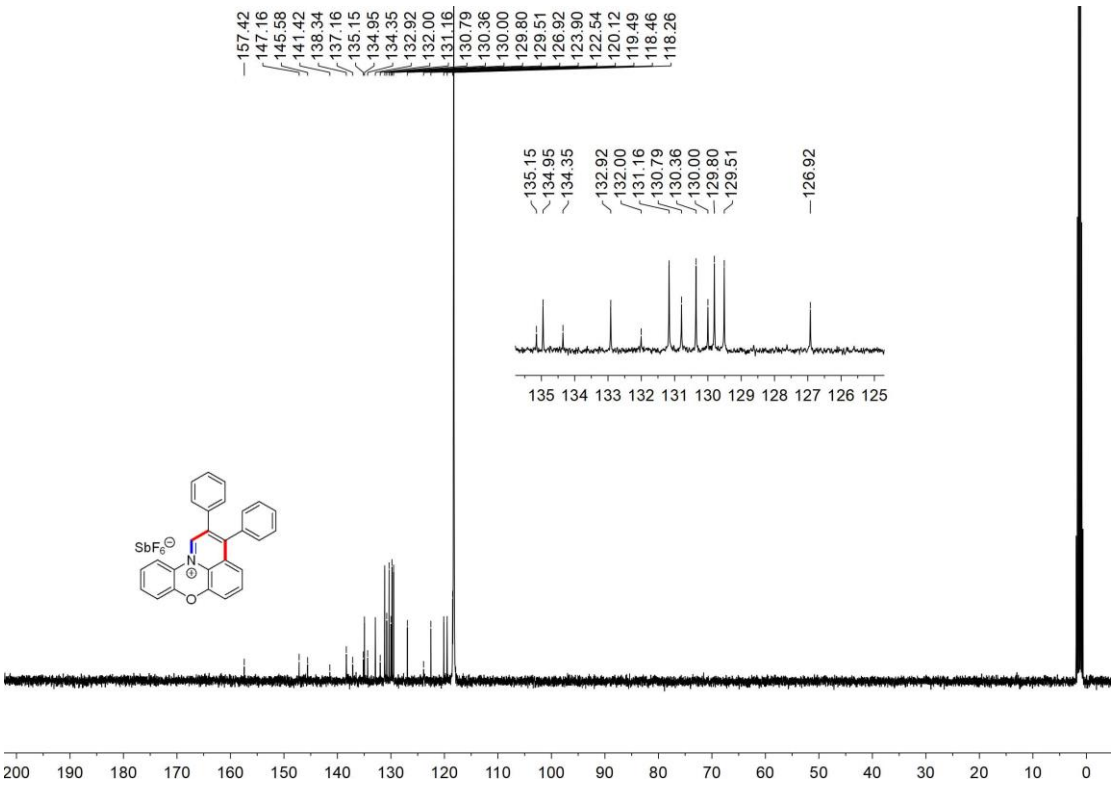
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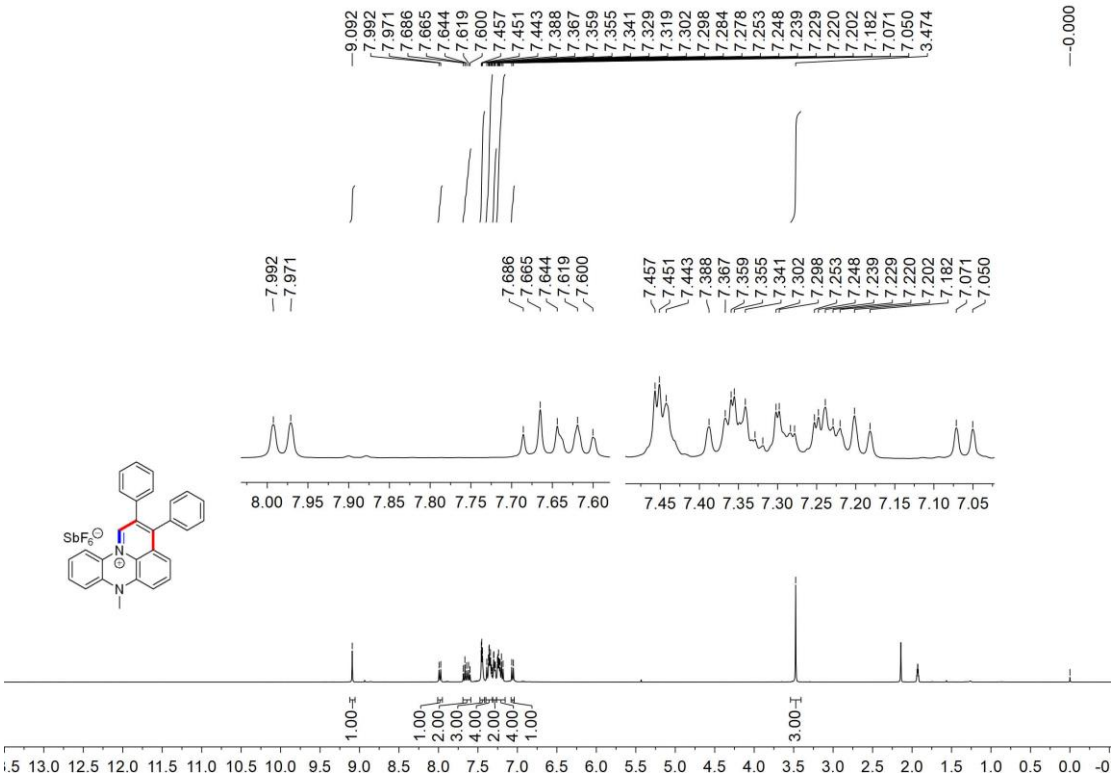
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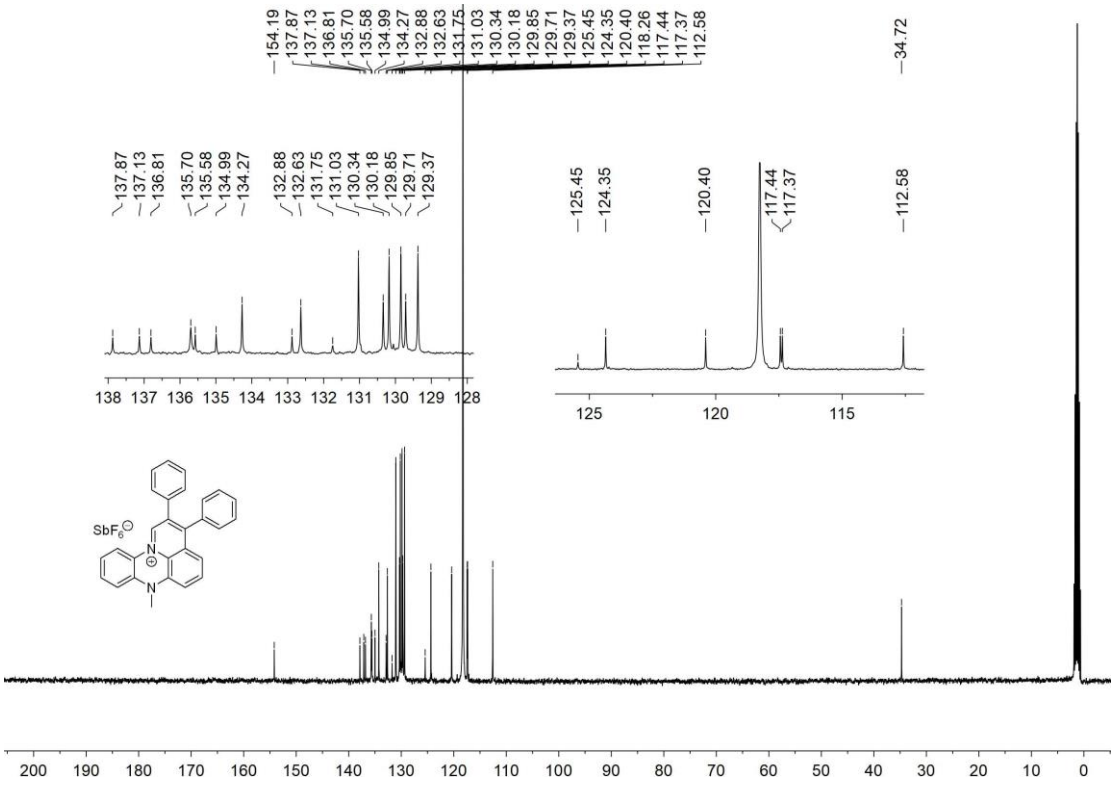
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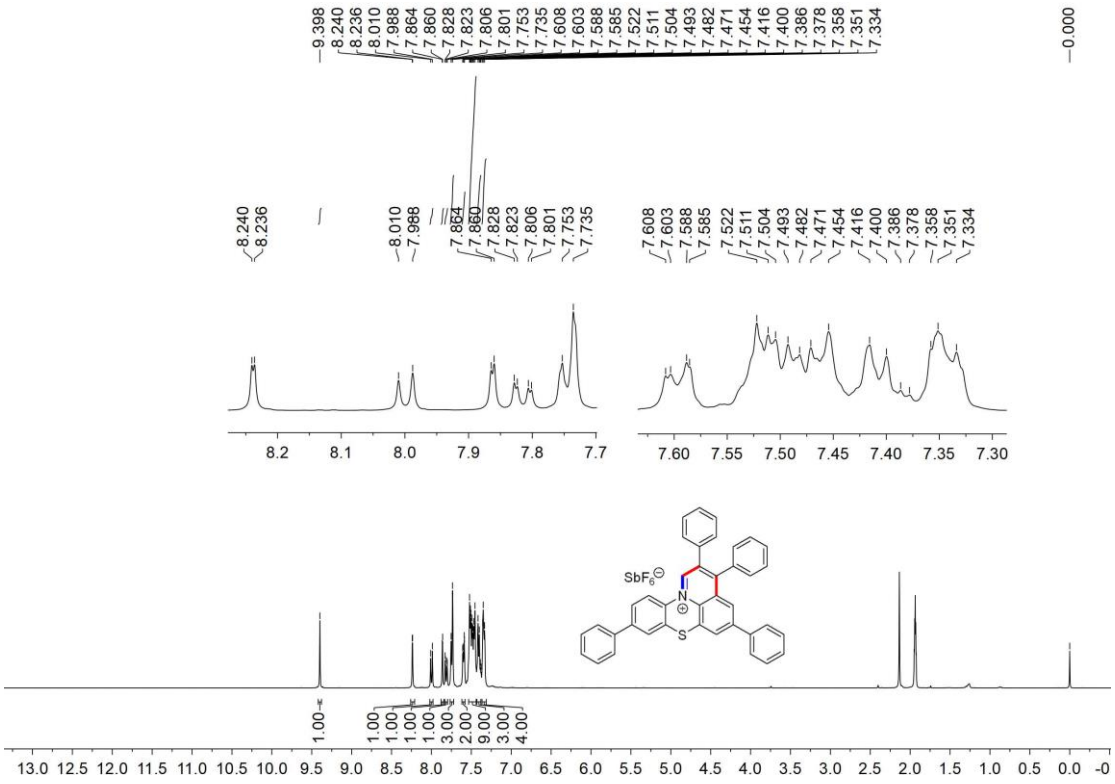
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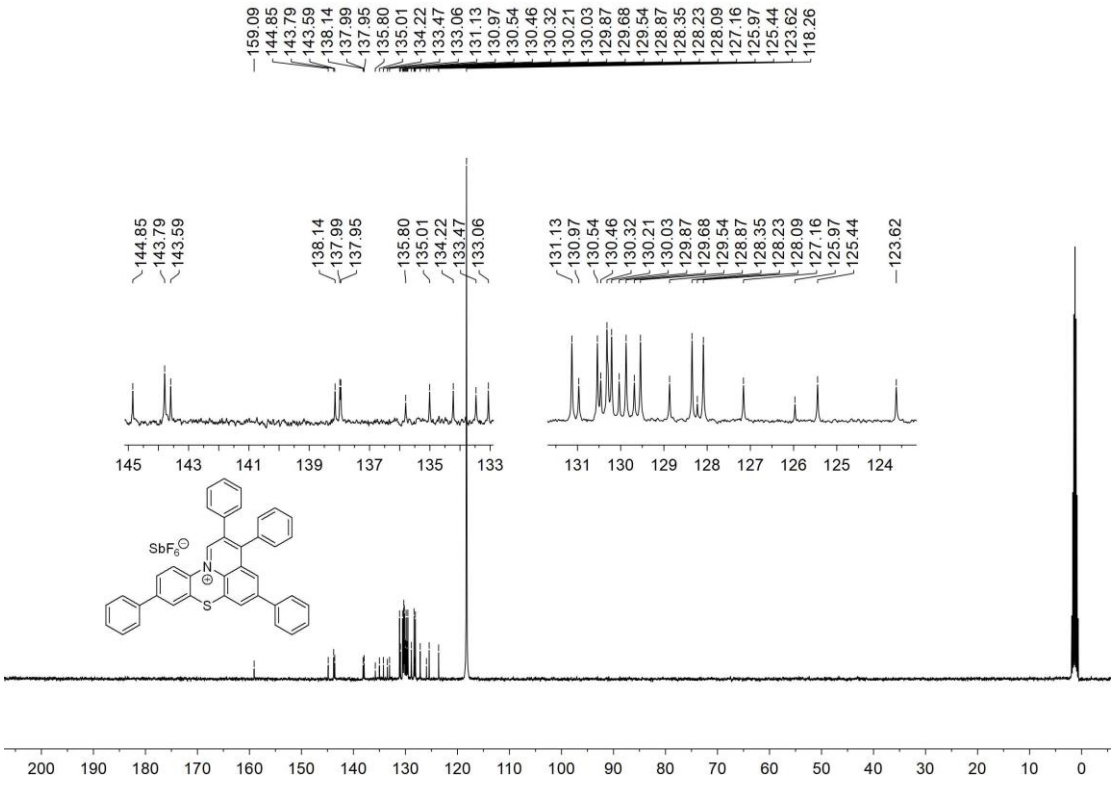
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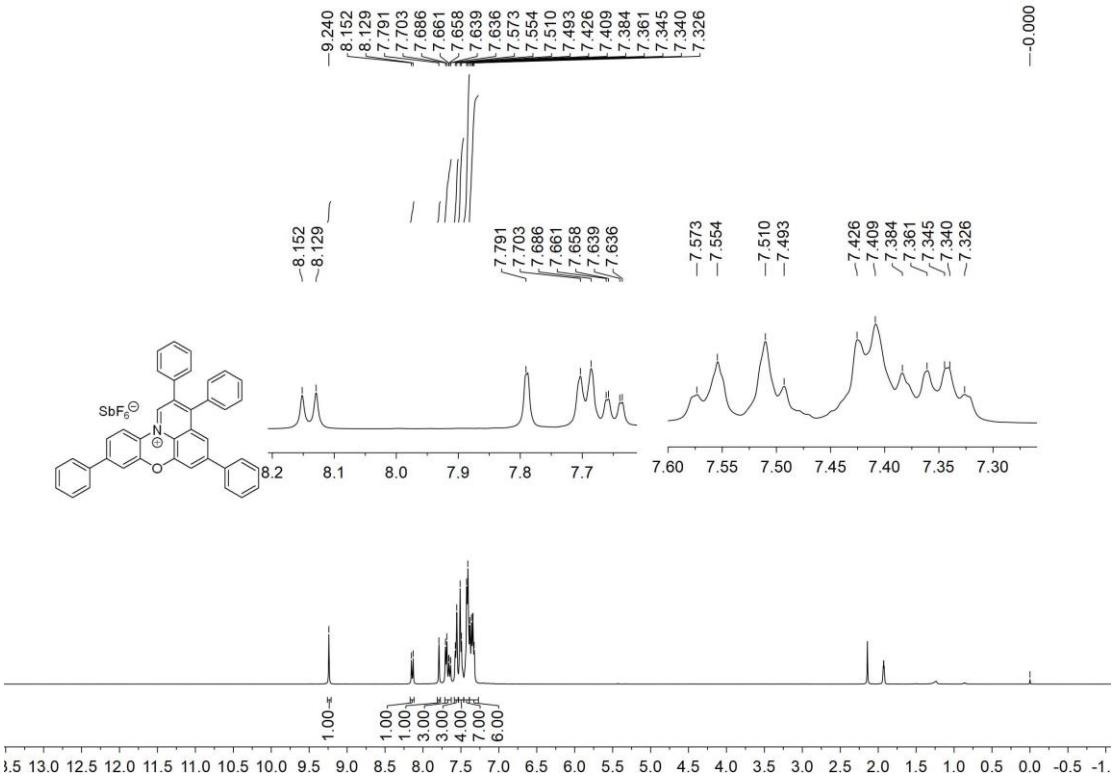
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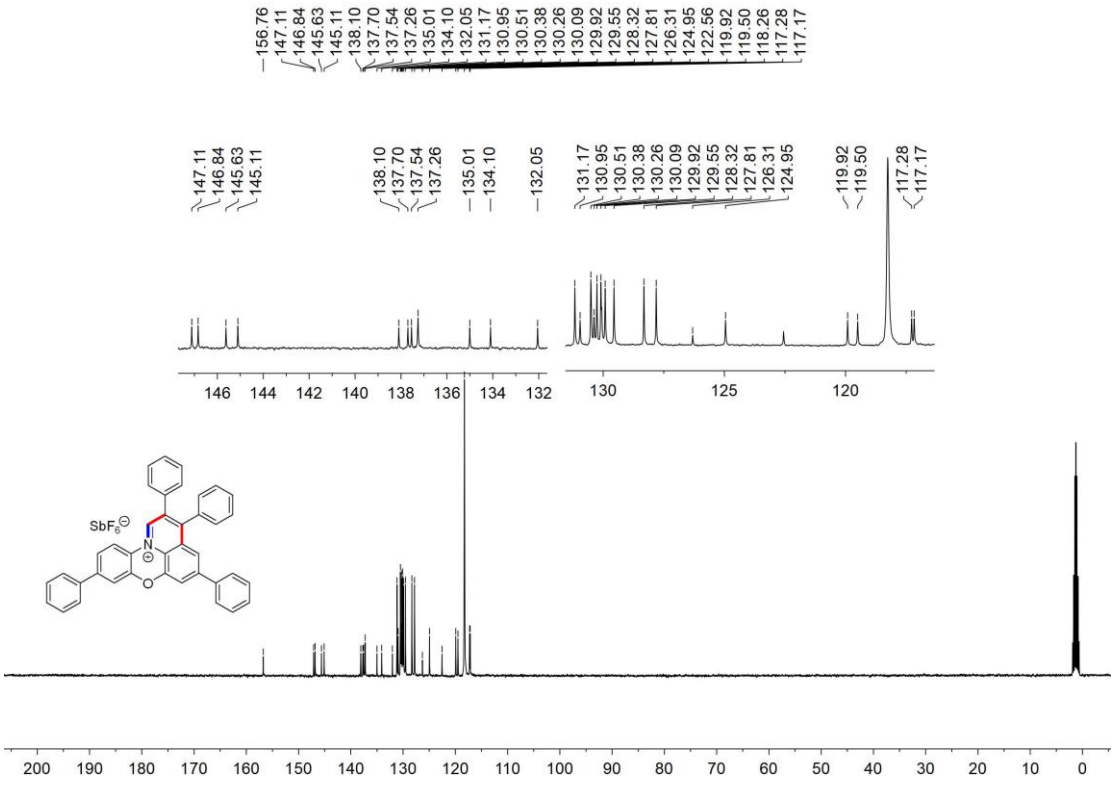
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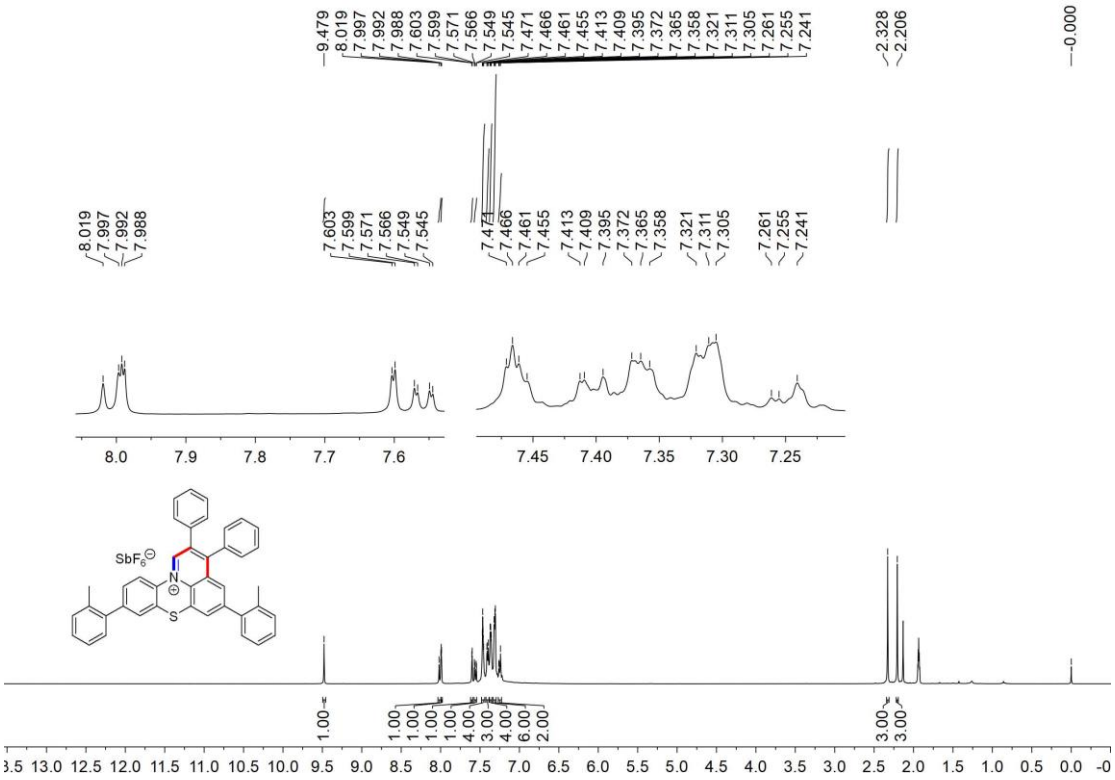
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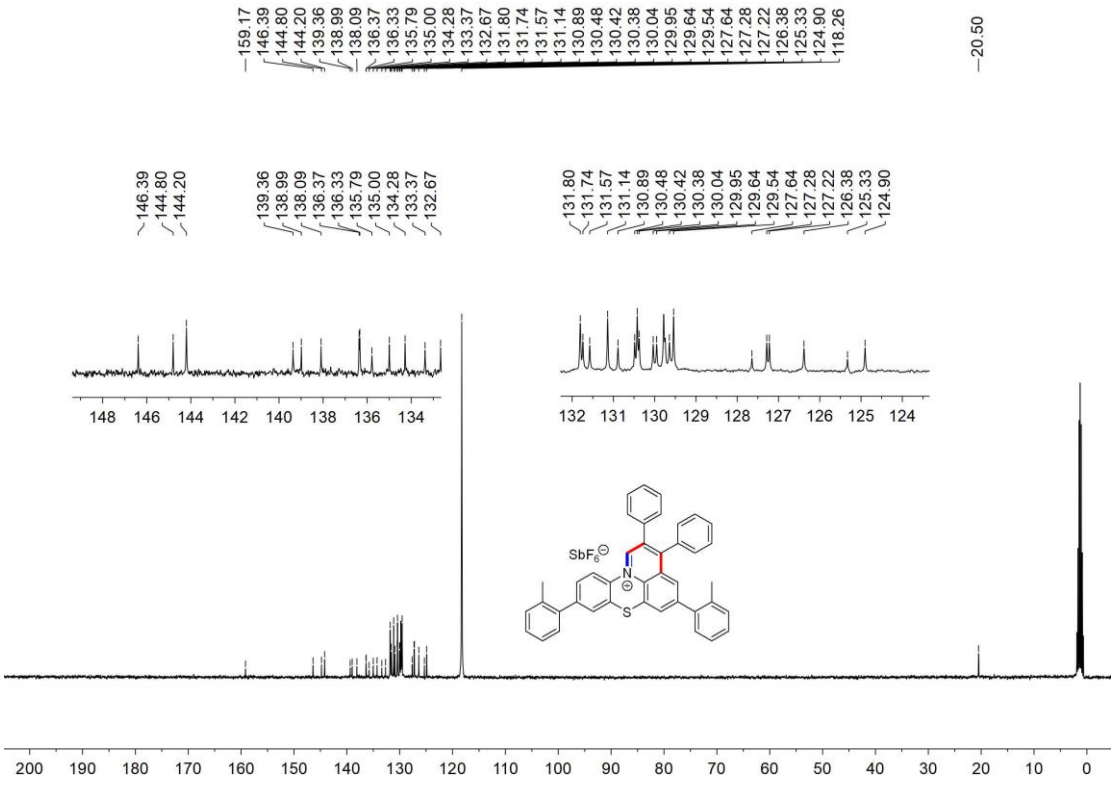
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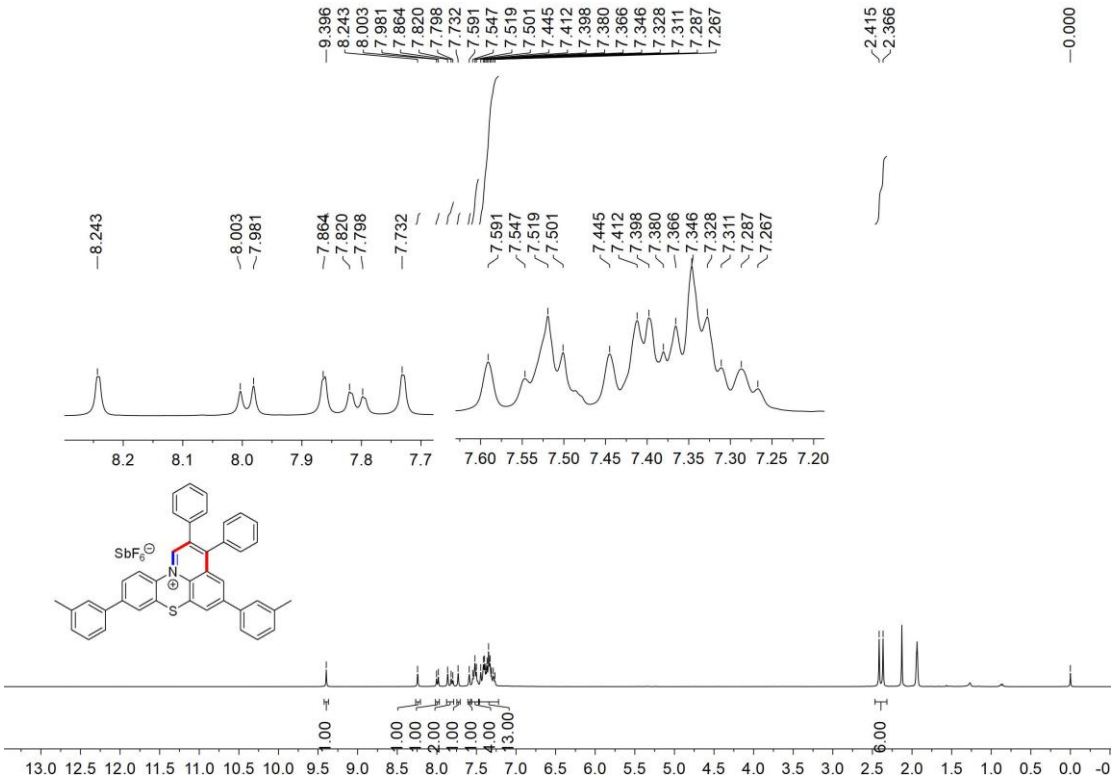
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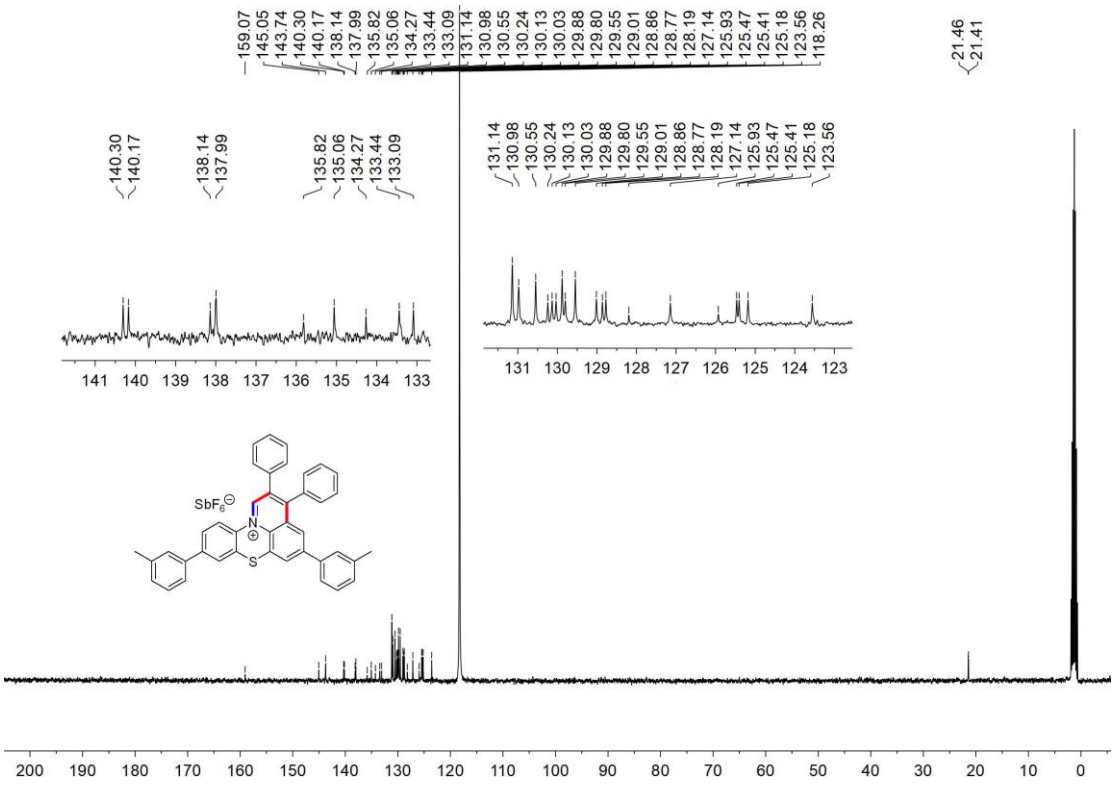
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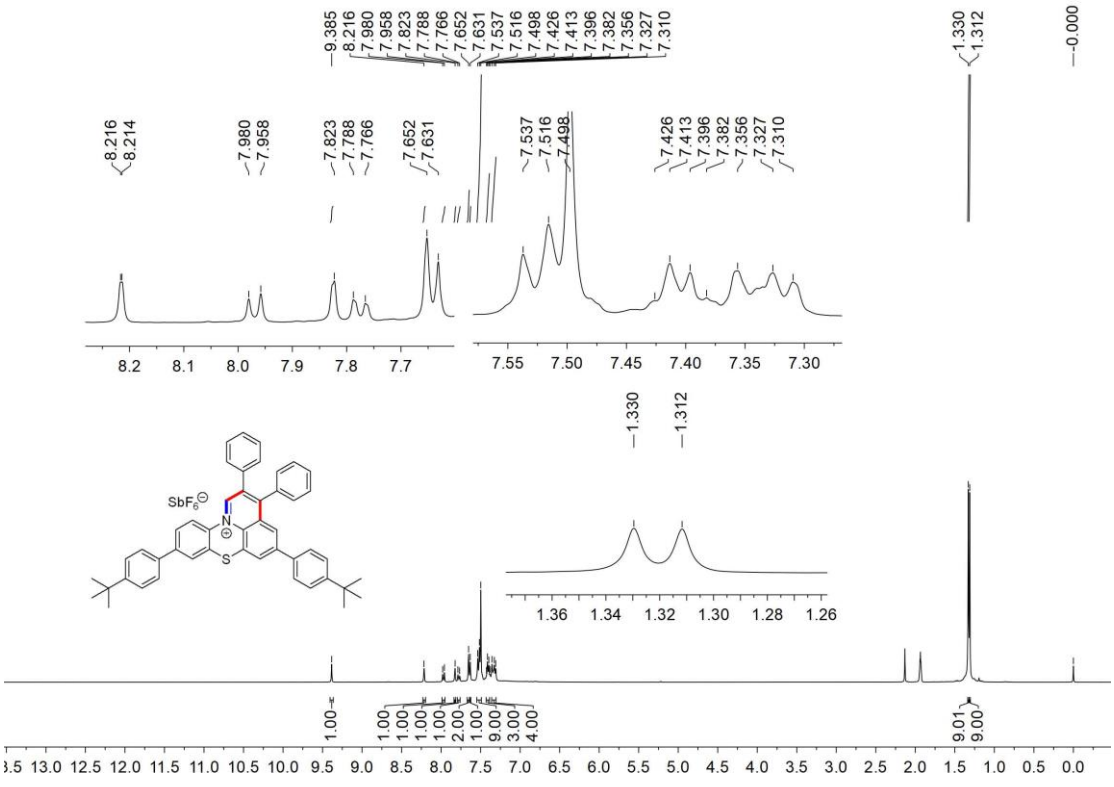
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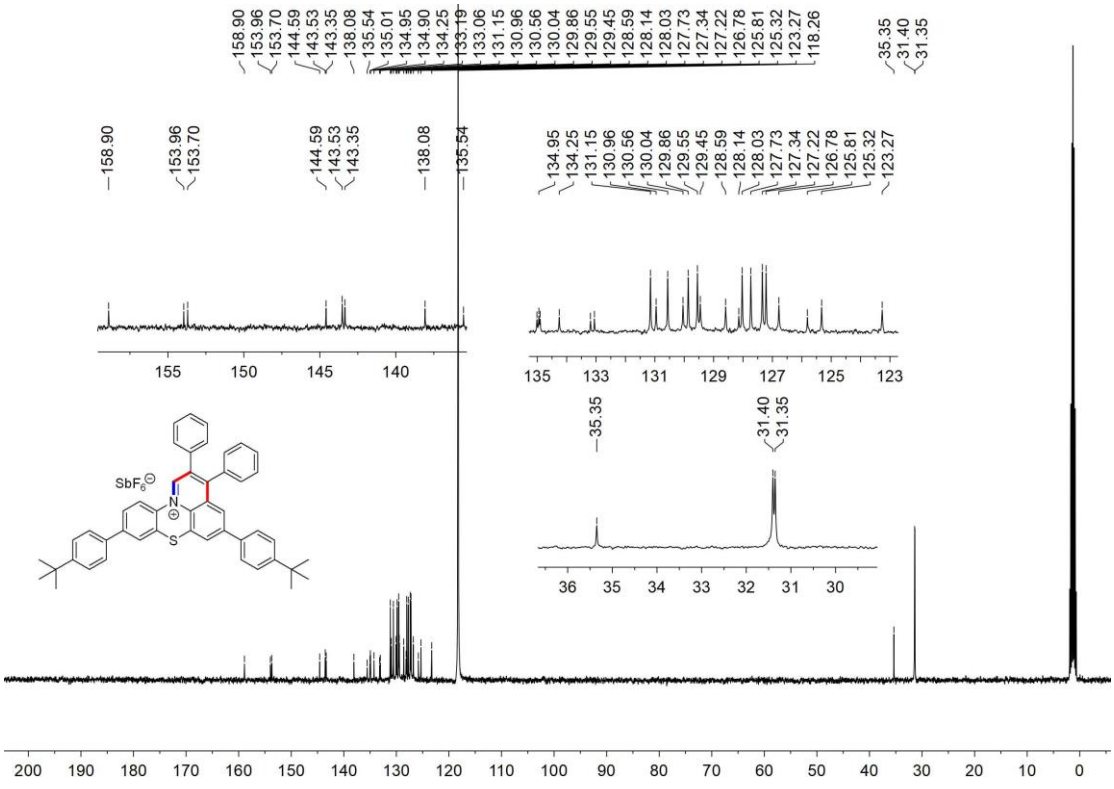
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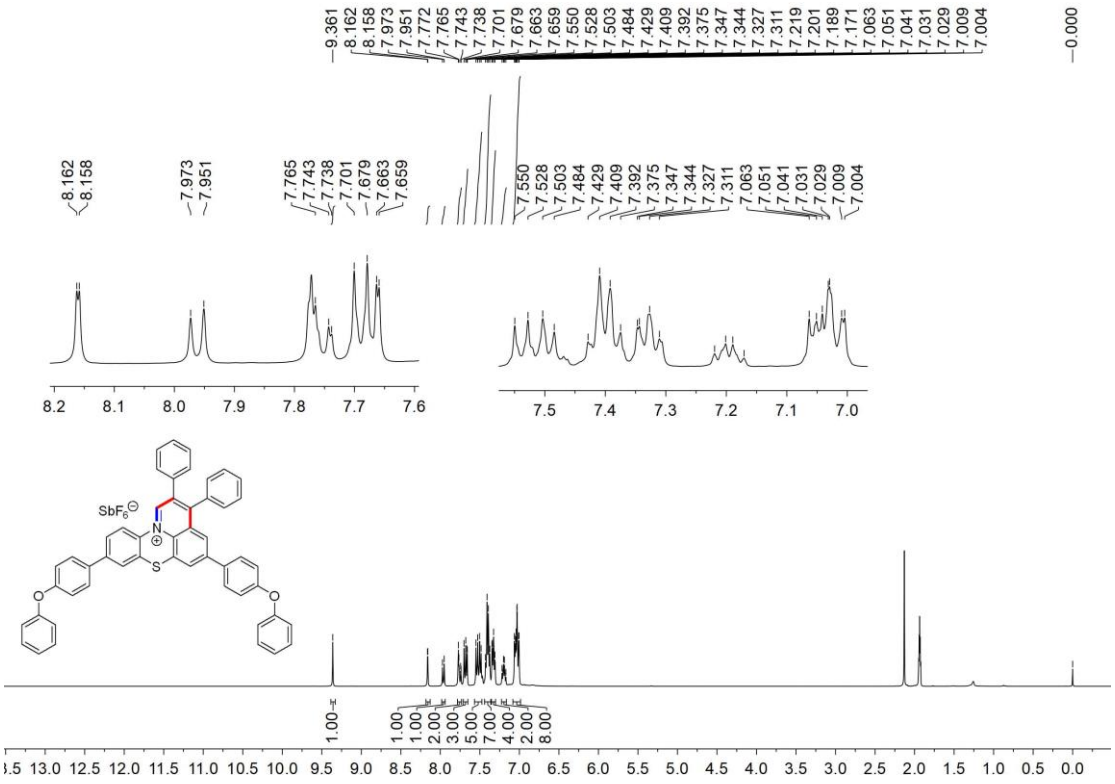
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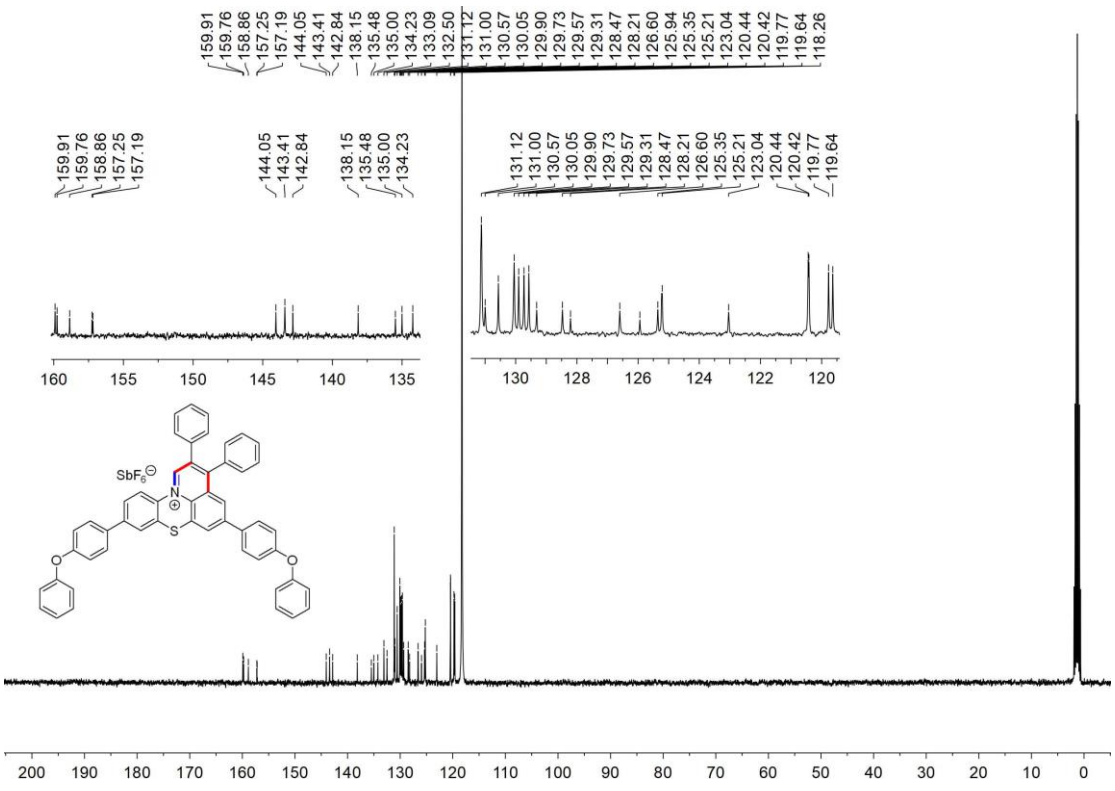
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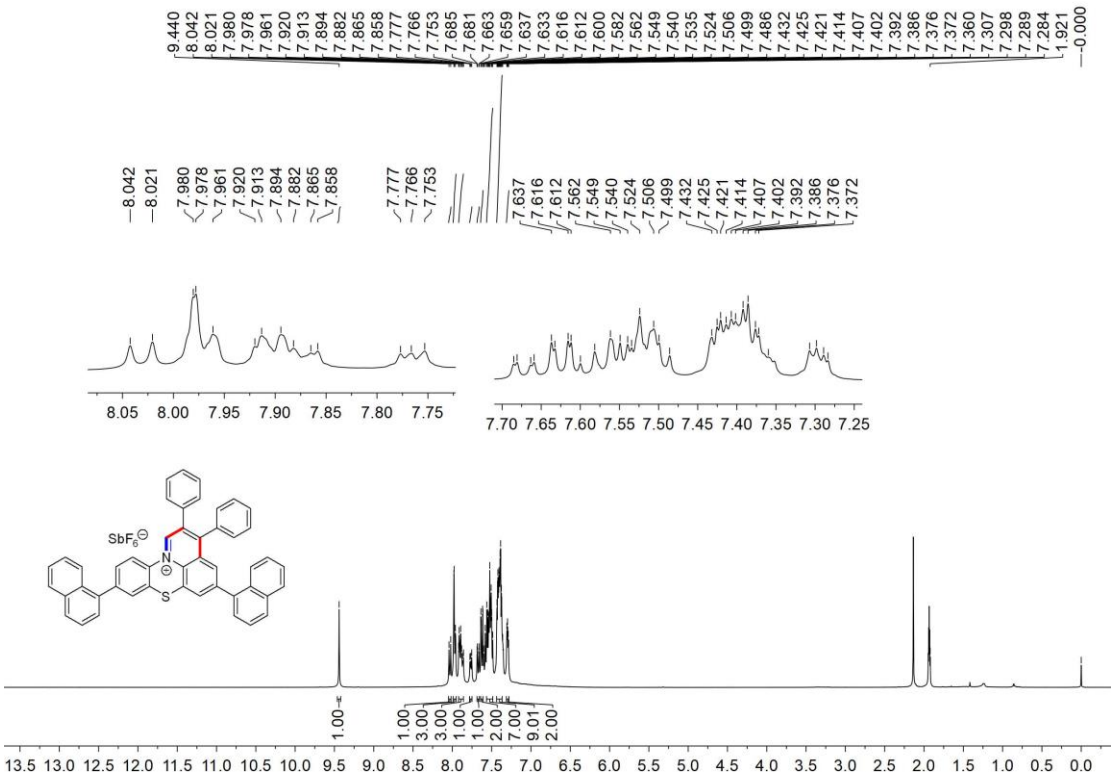
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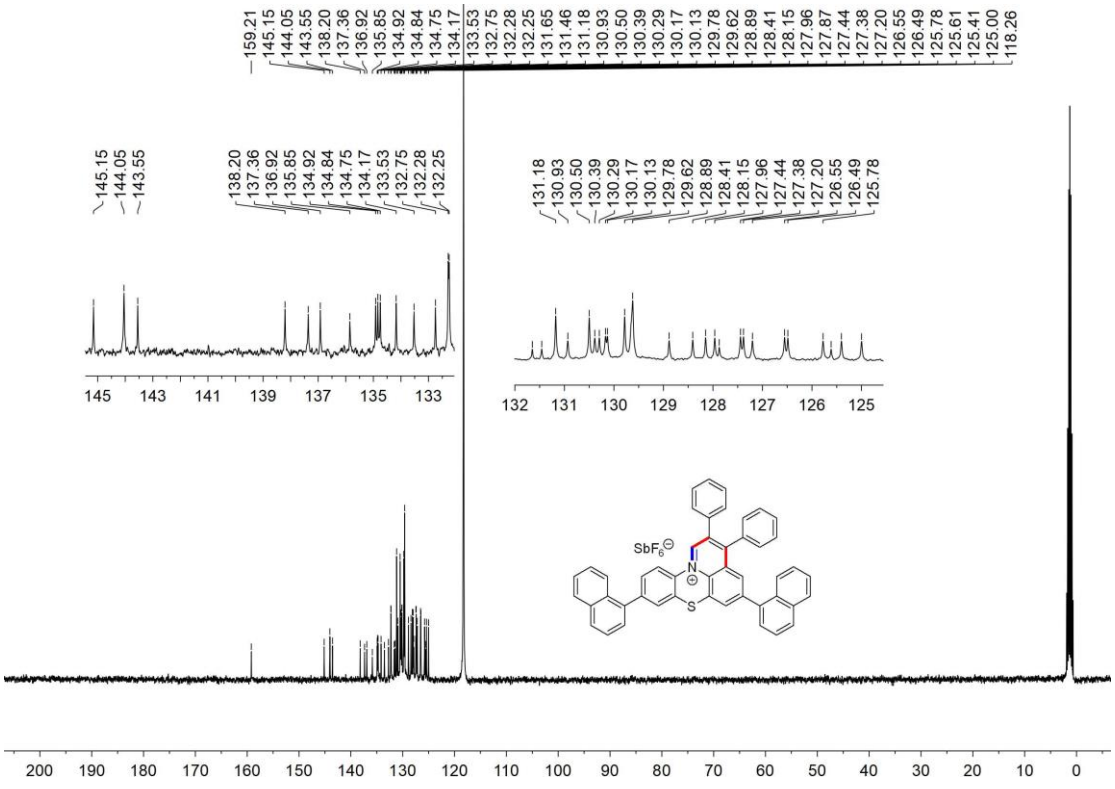
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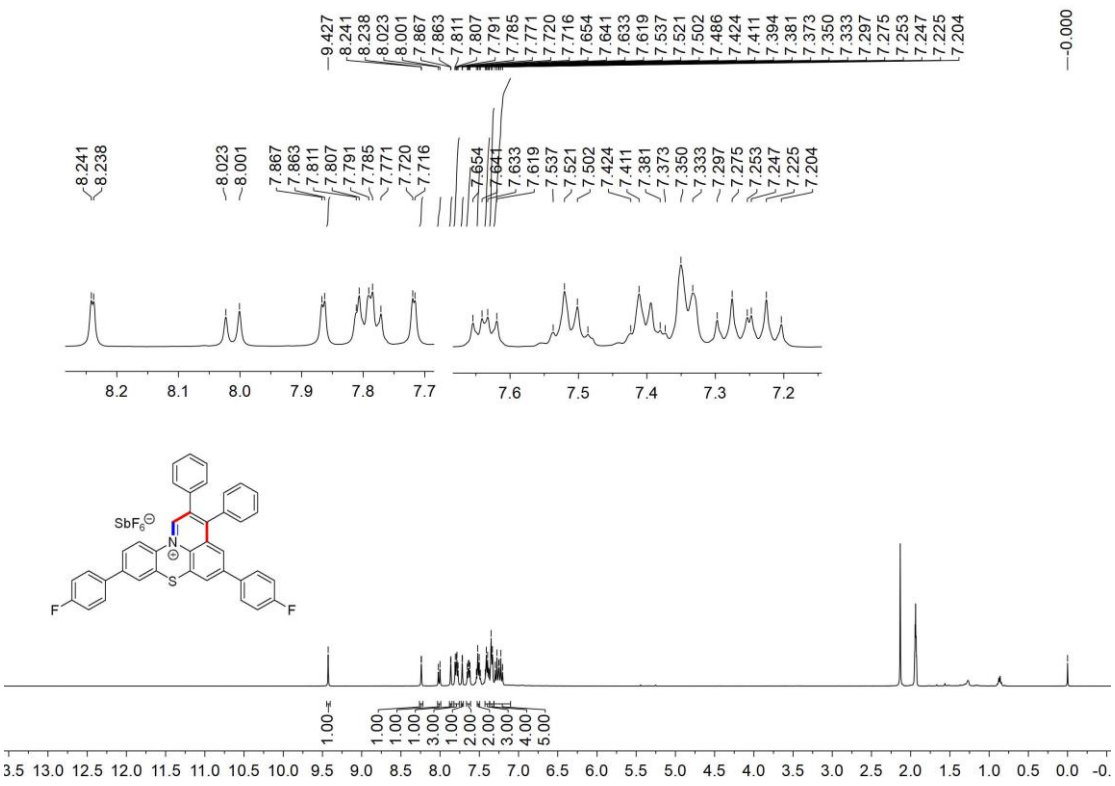
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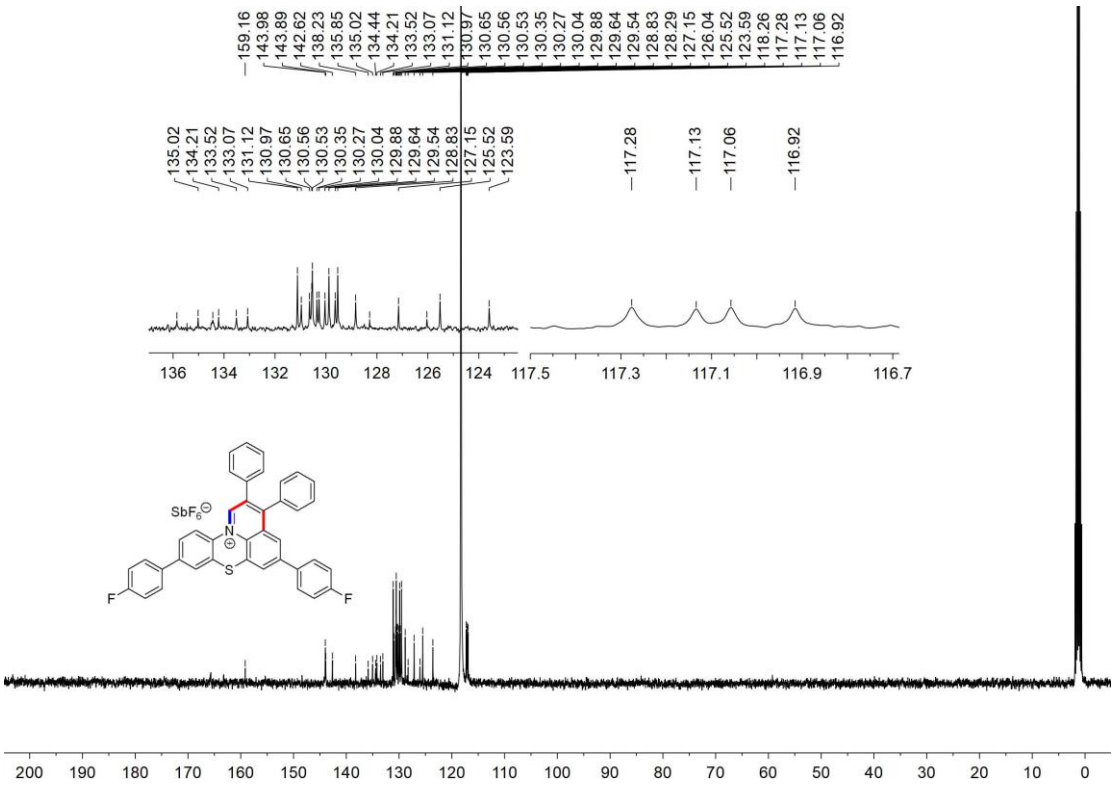
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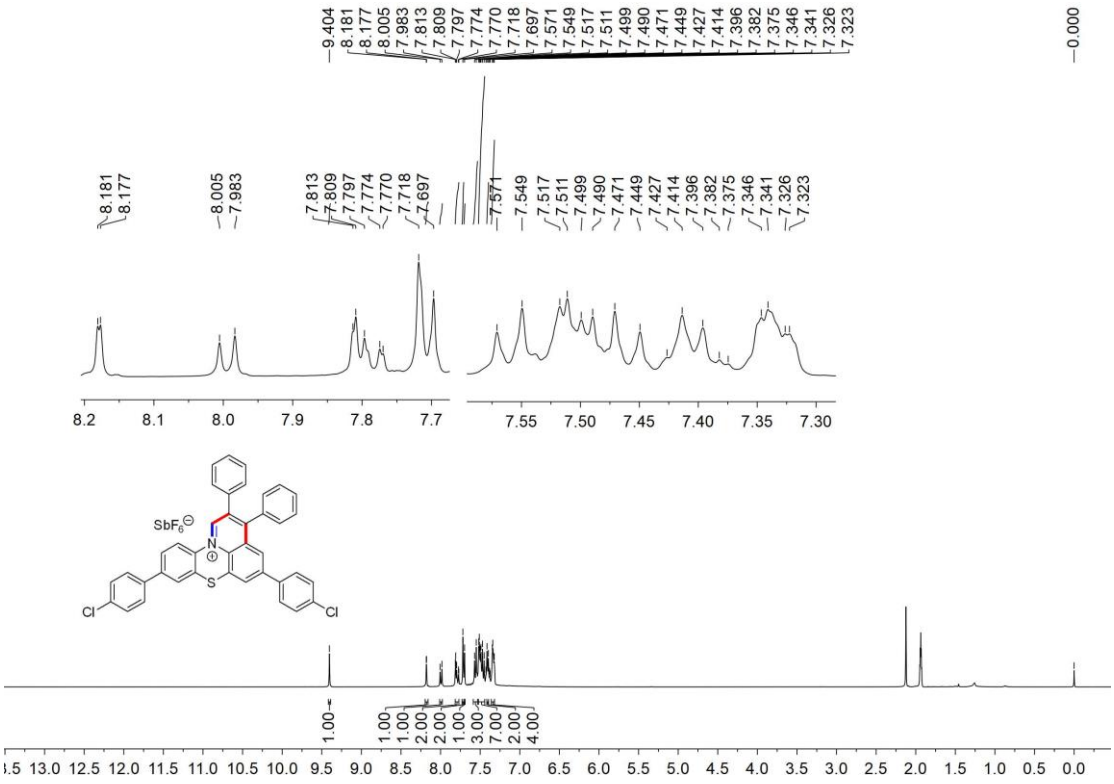
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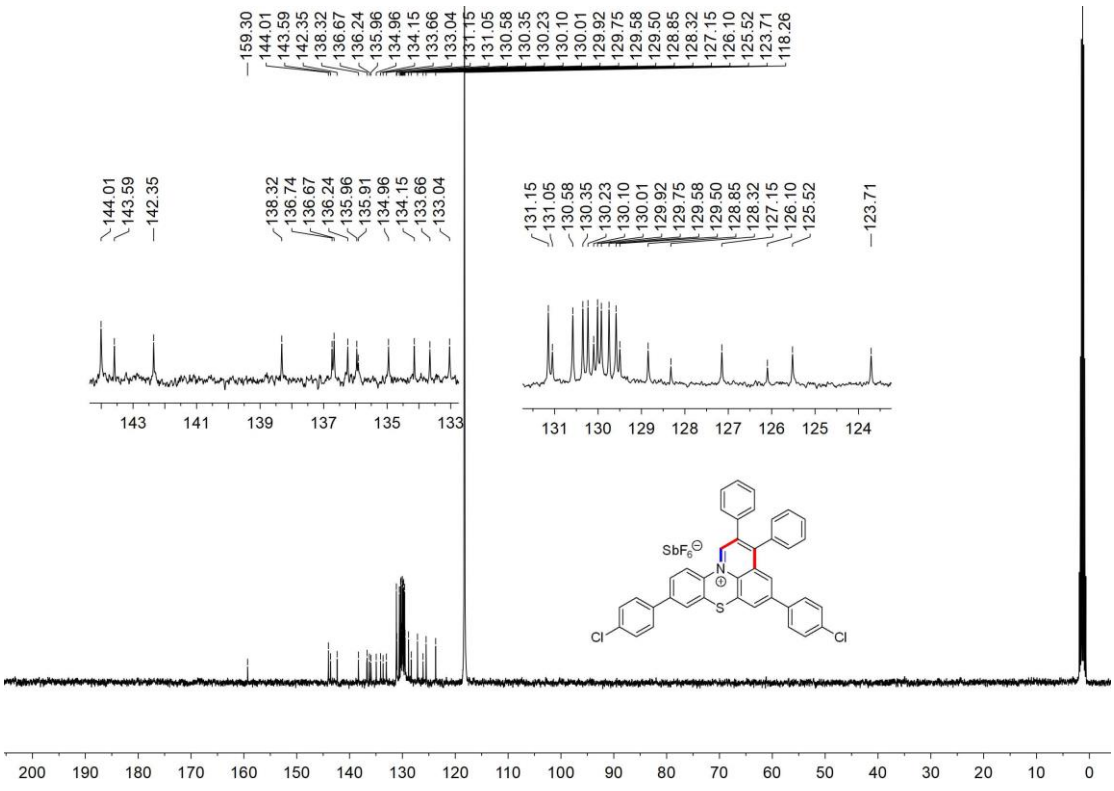
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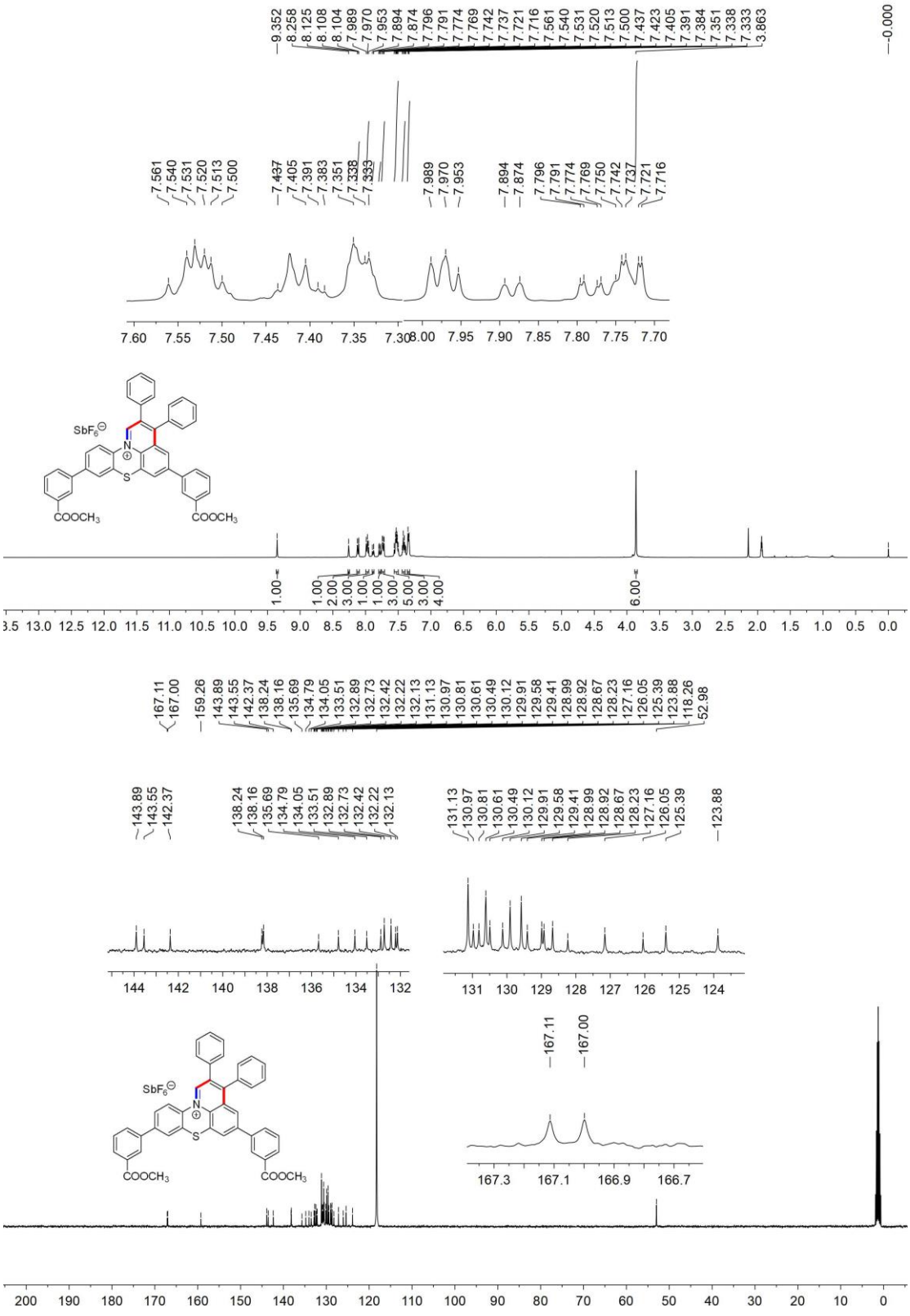
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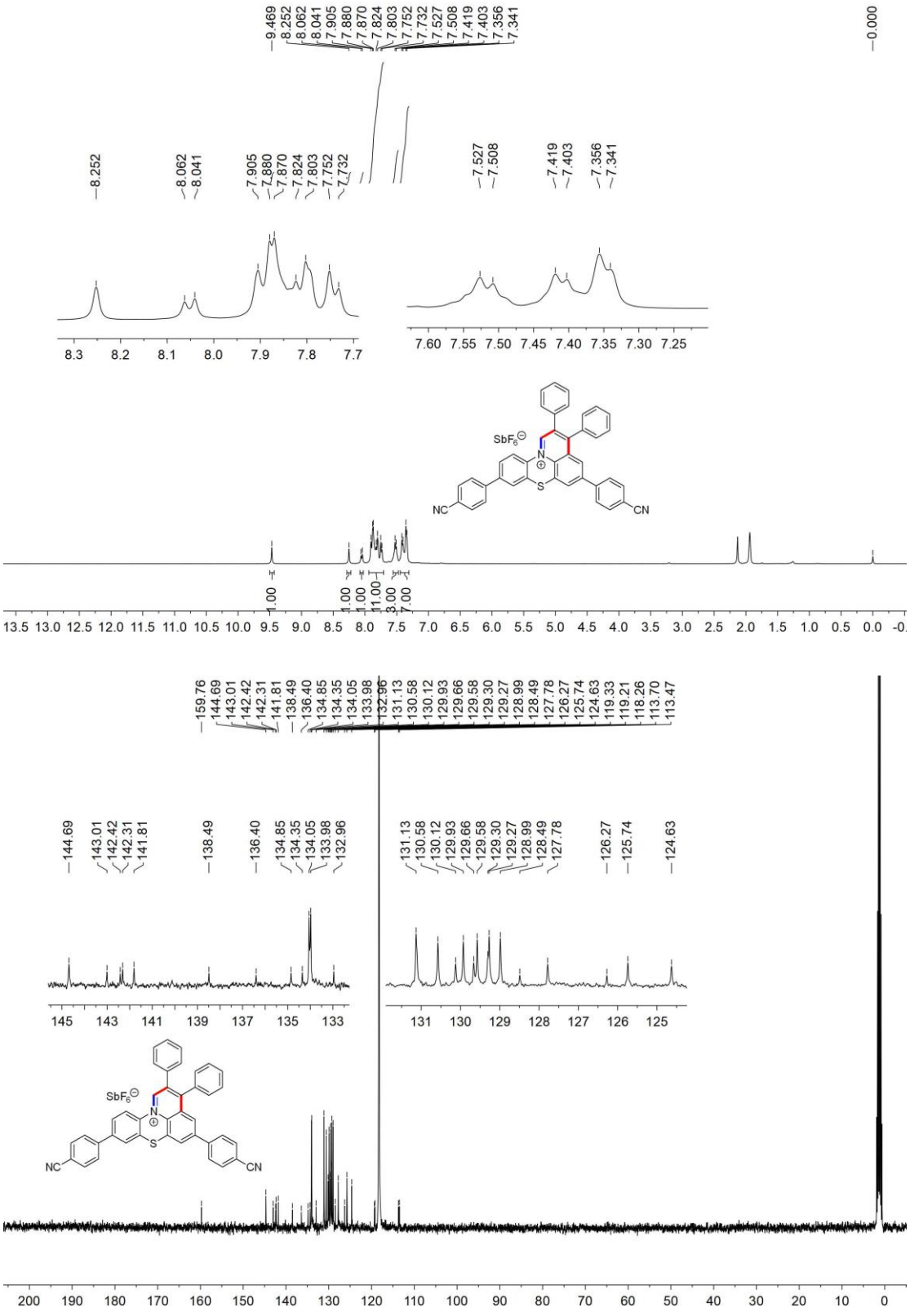
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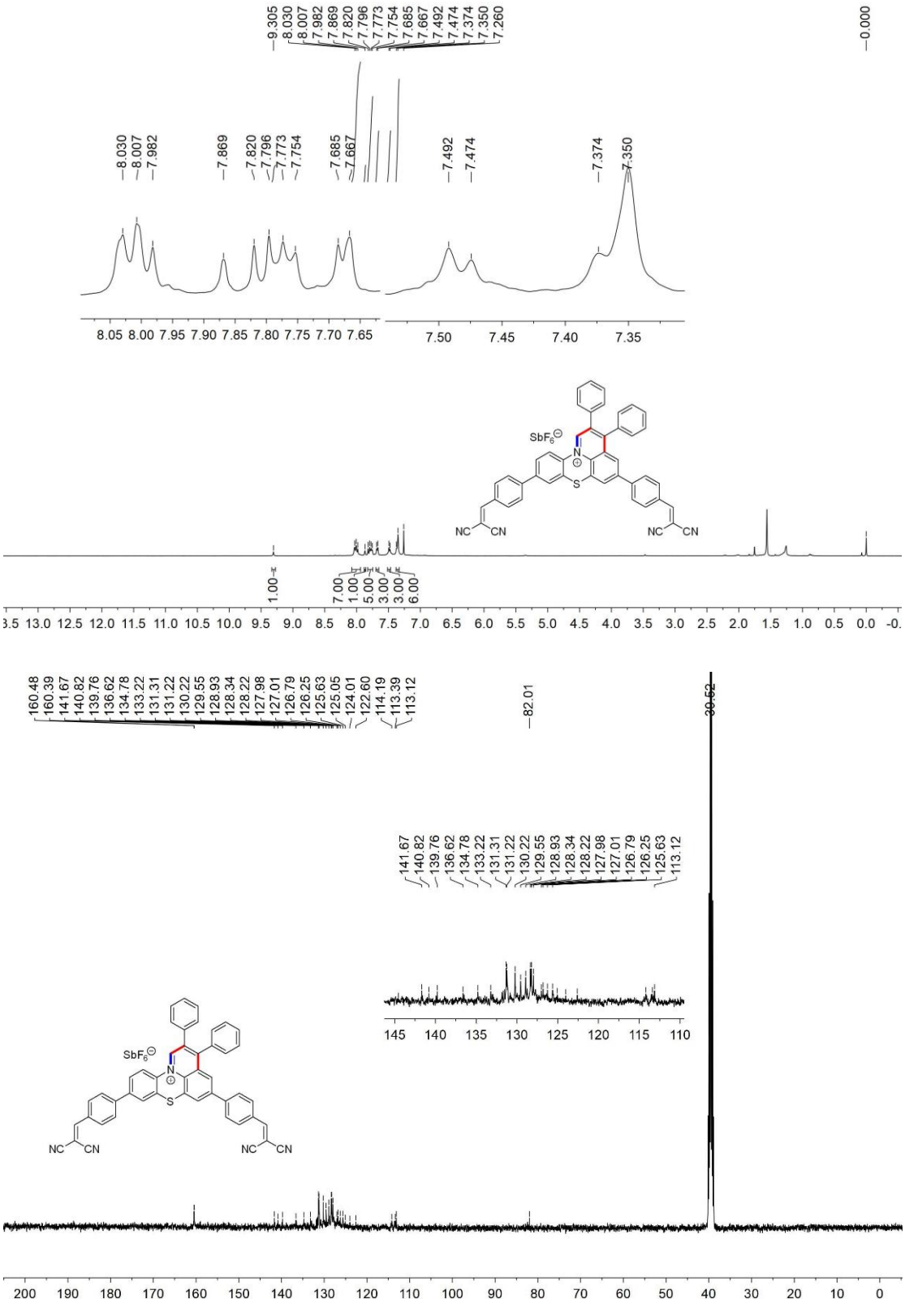
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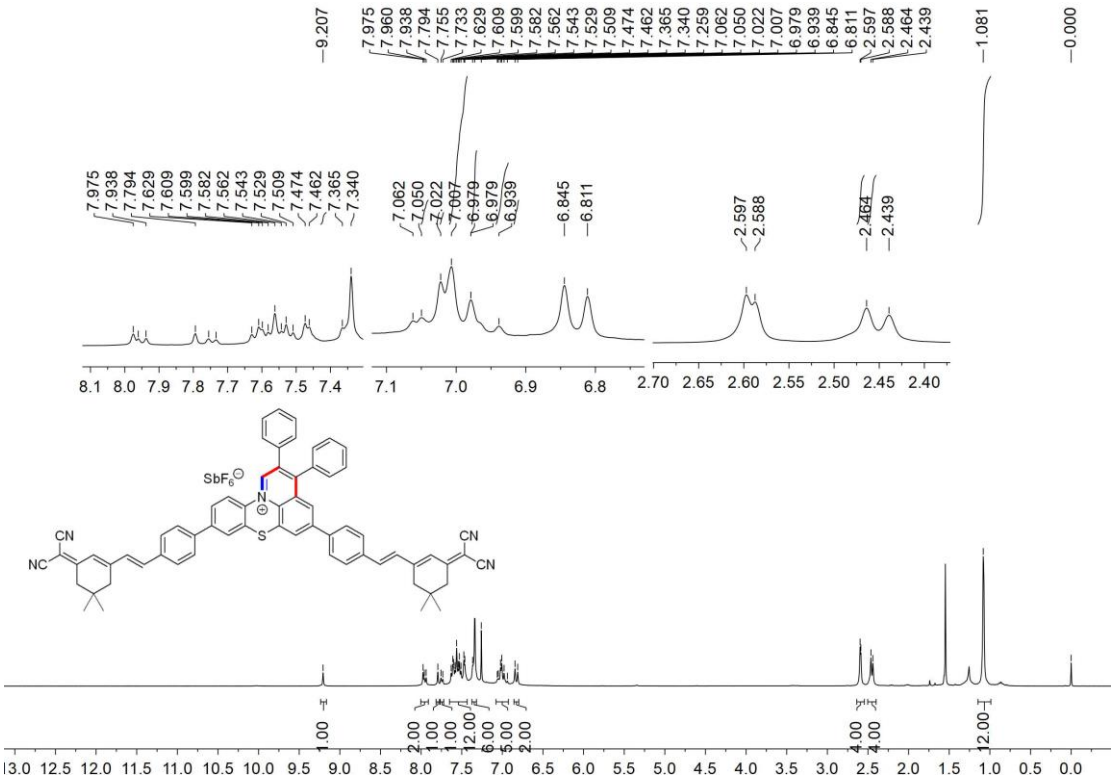
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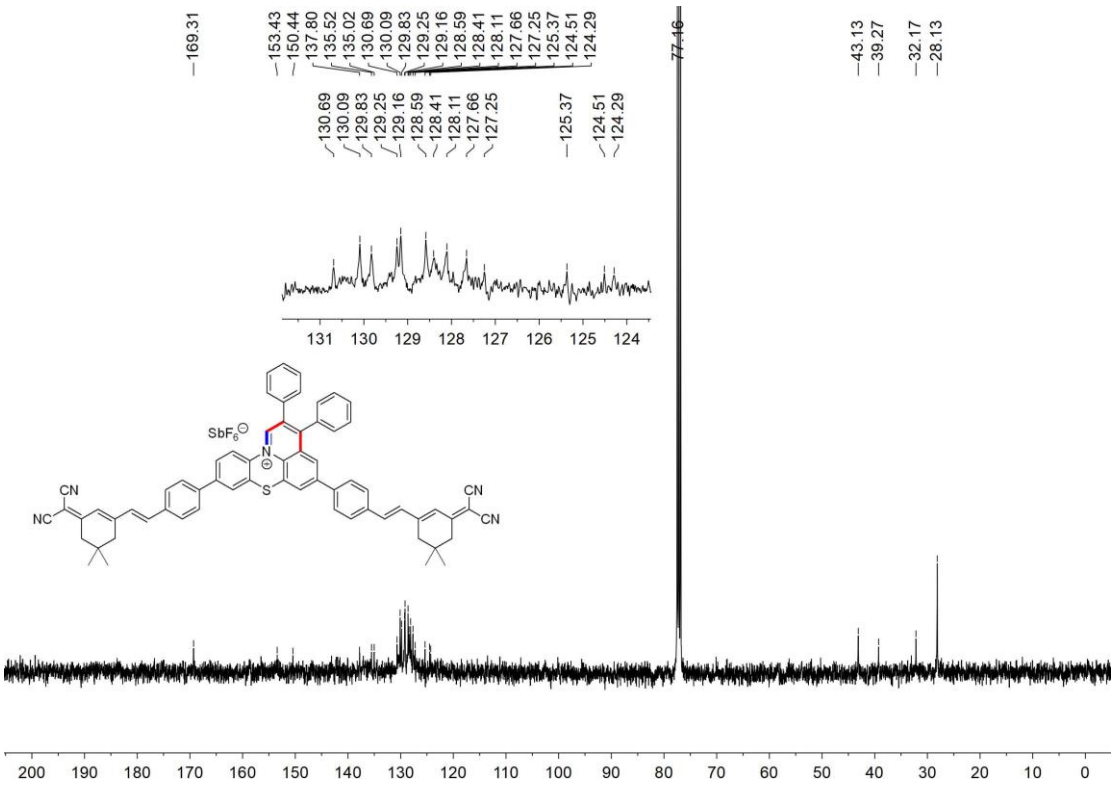
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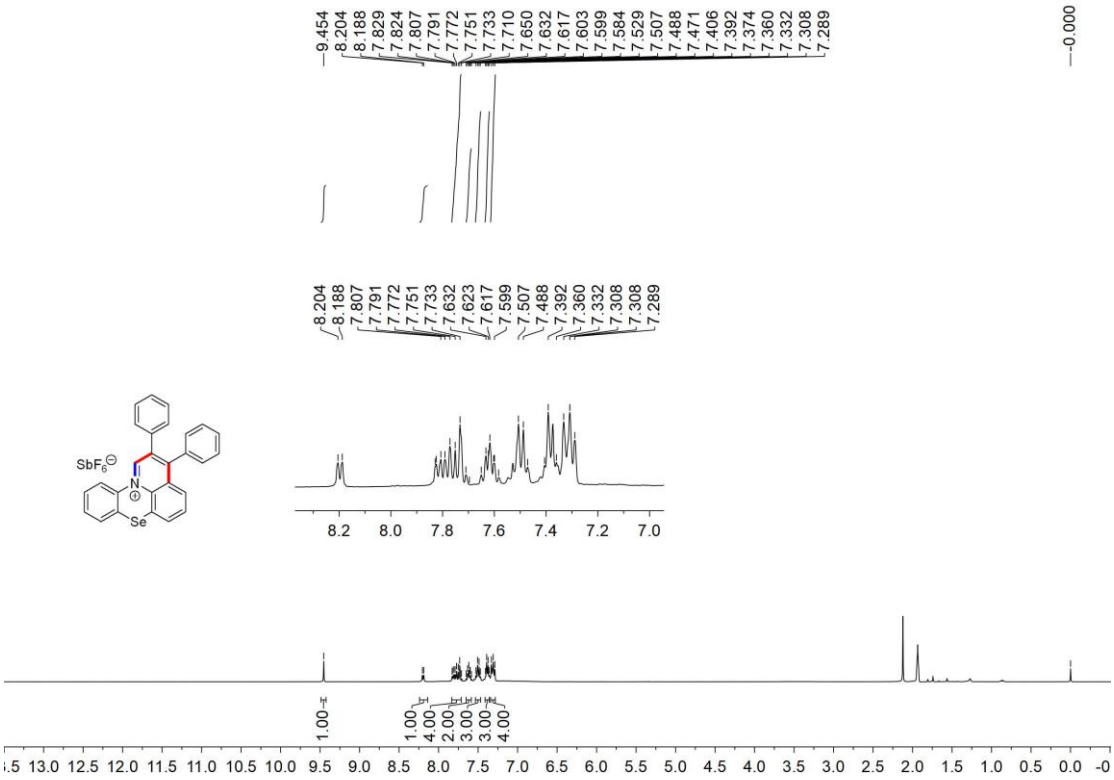
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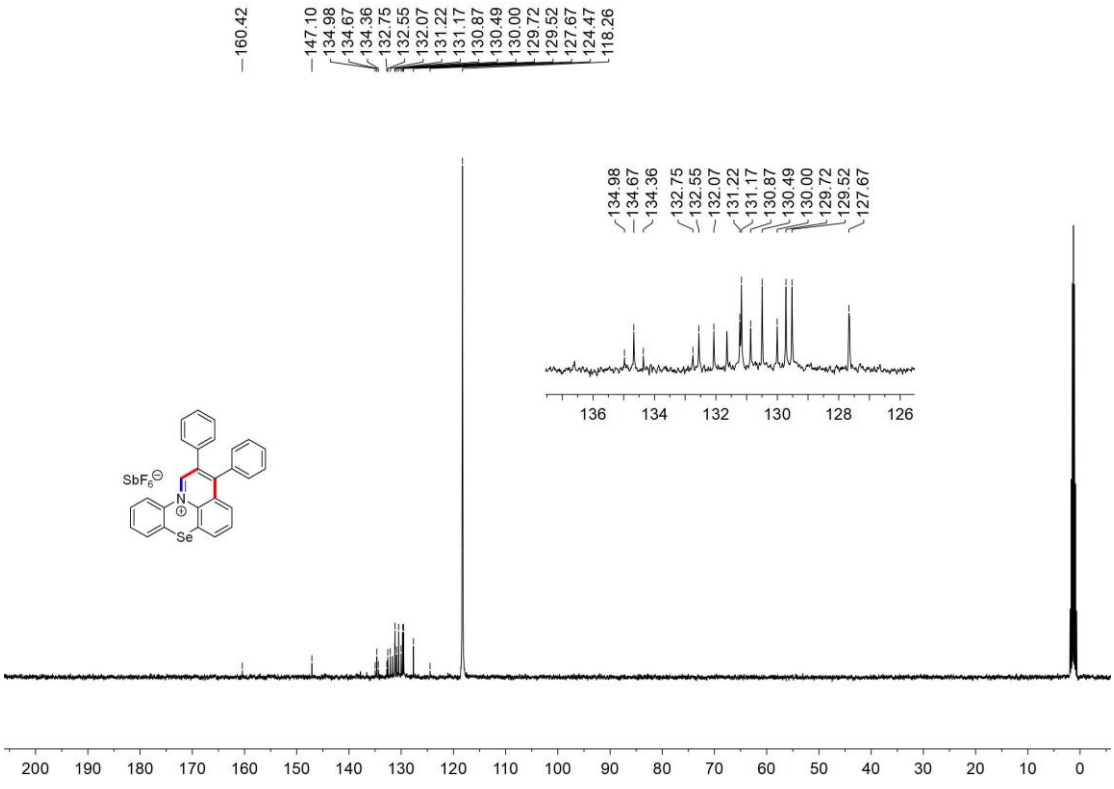
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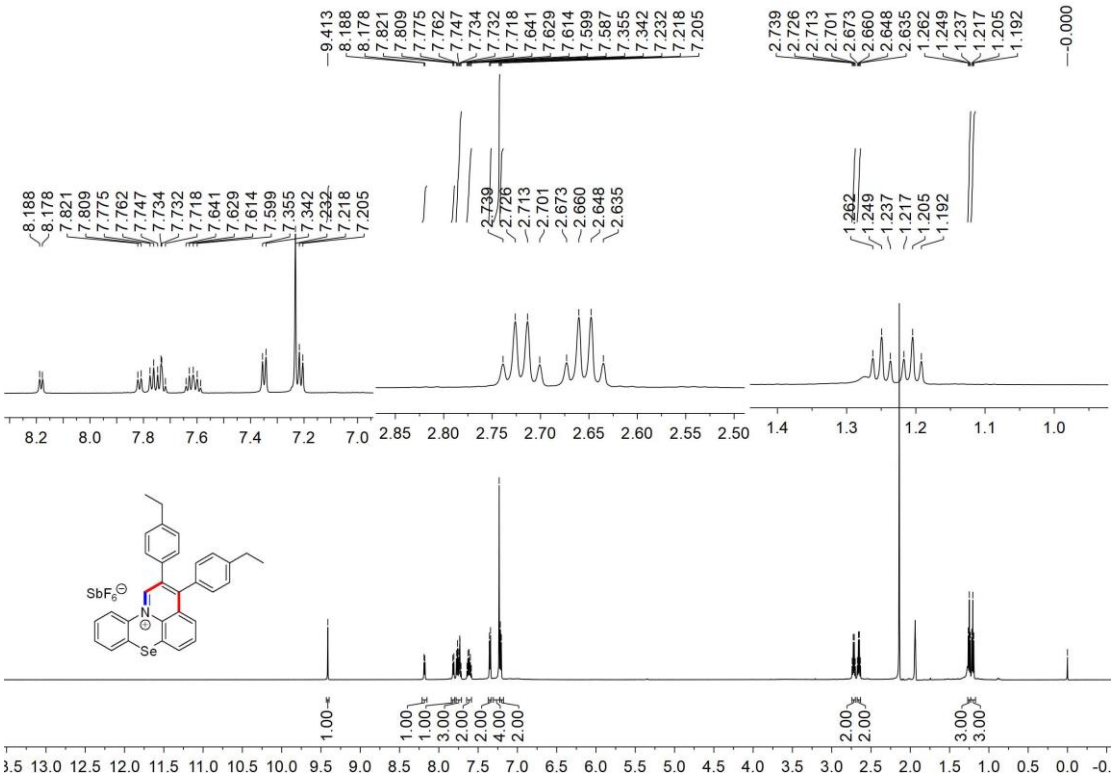
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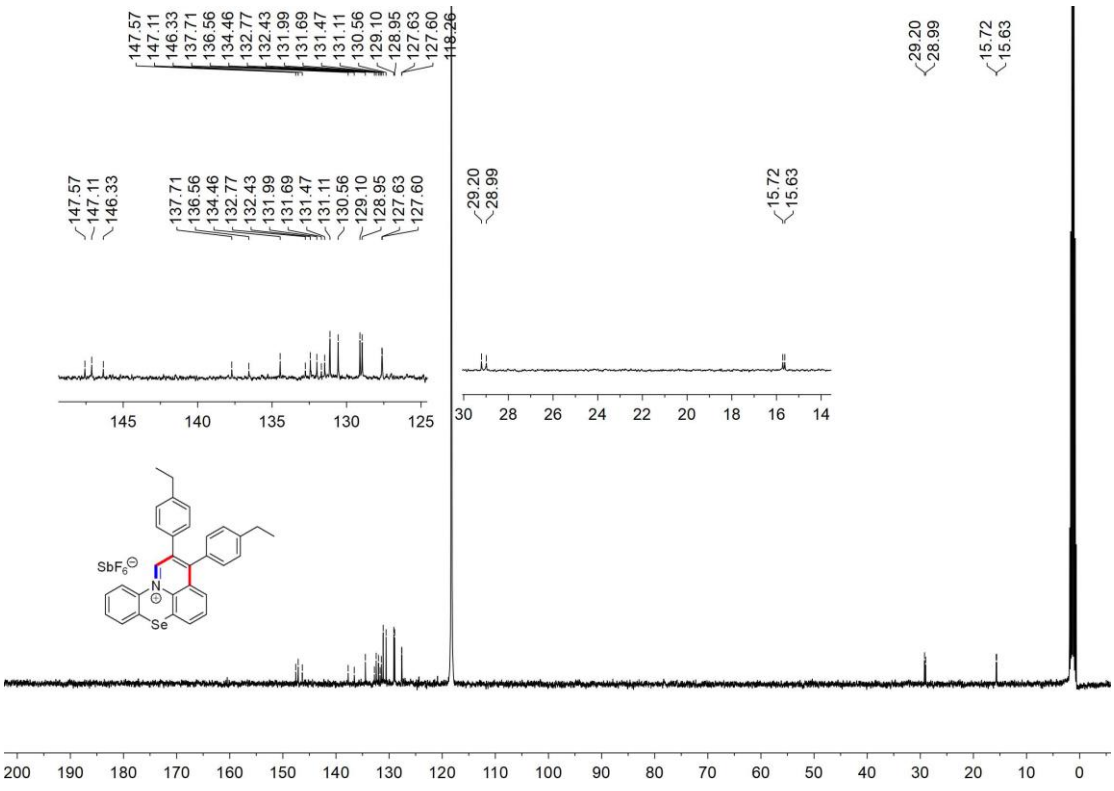
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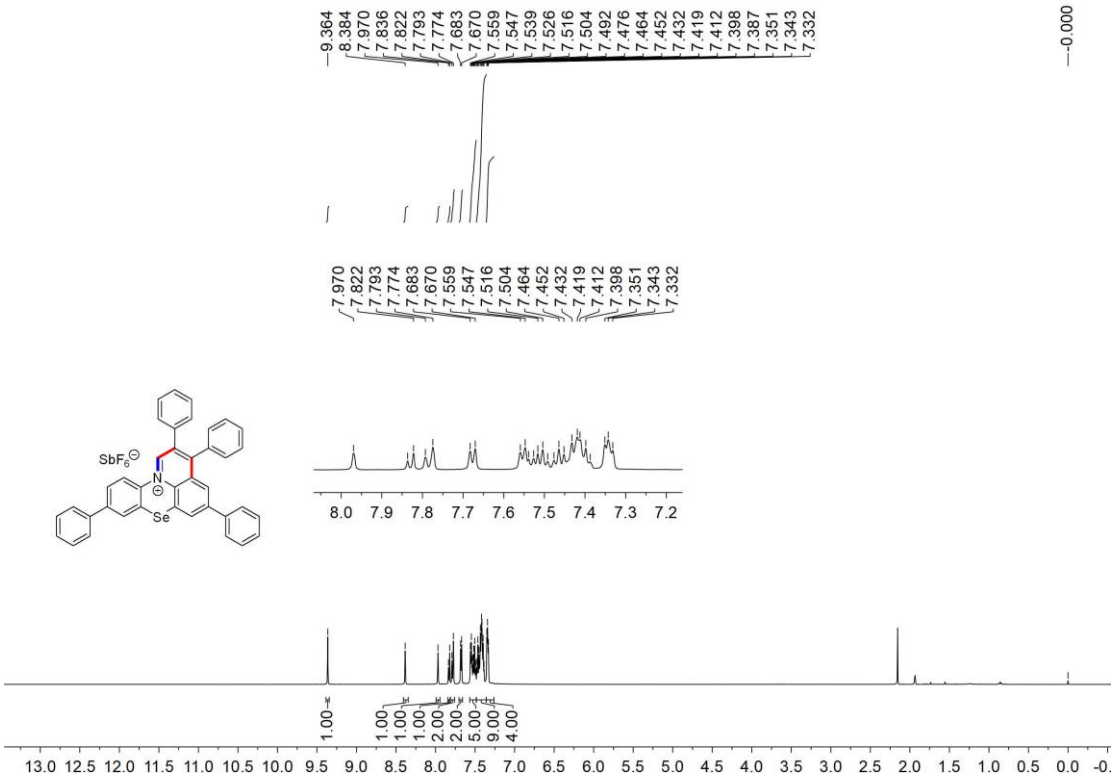
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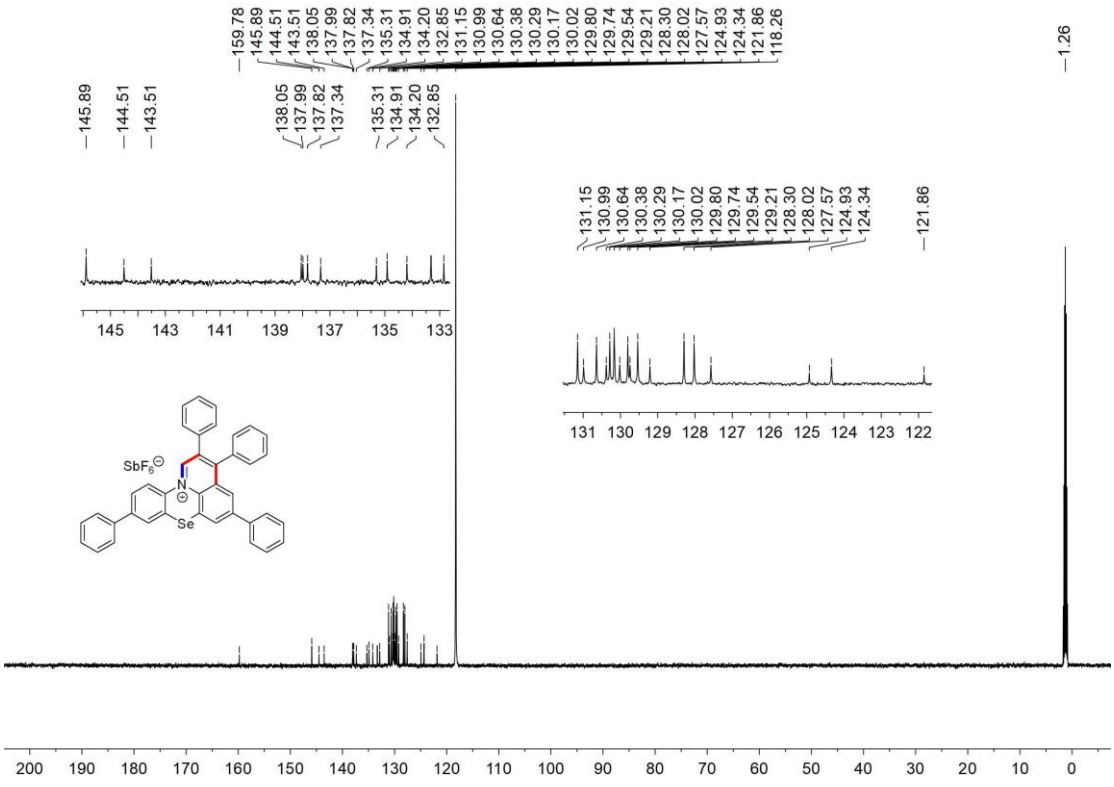
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