Supporting Information

Synthesis, Structures, and Optical Properties of Heteroarene-Fused Dispiro Compounds

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Data of X-ray crystallographic analysis:

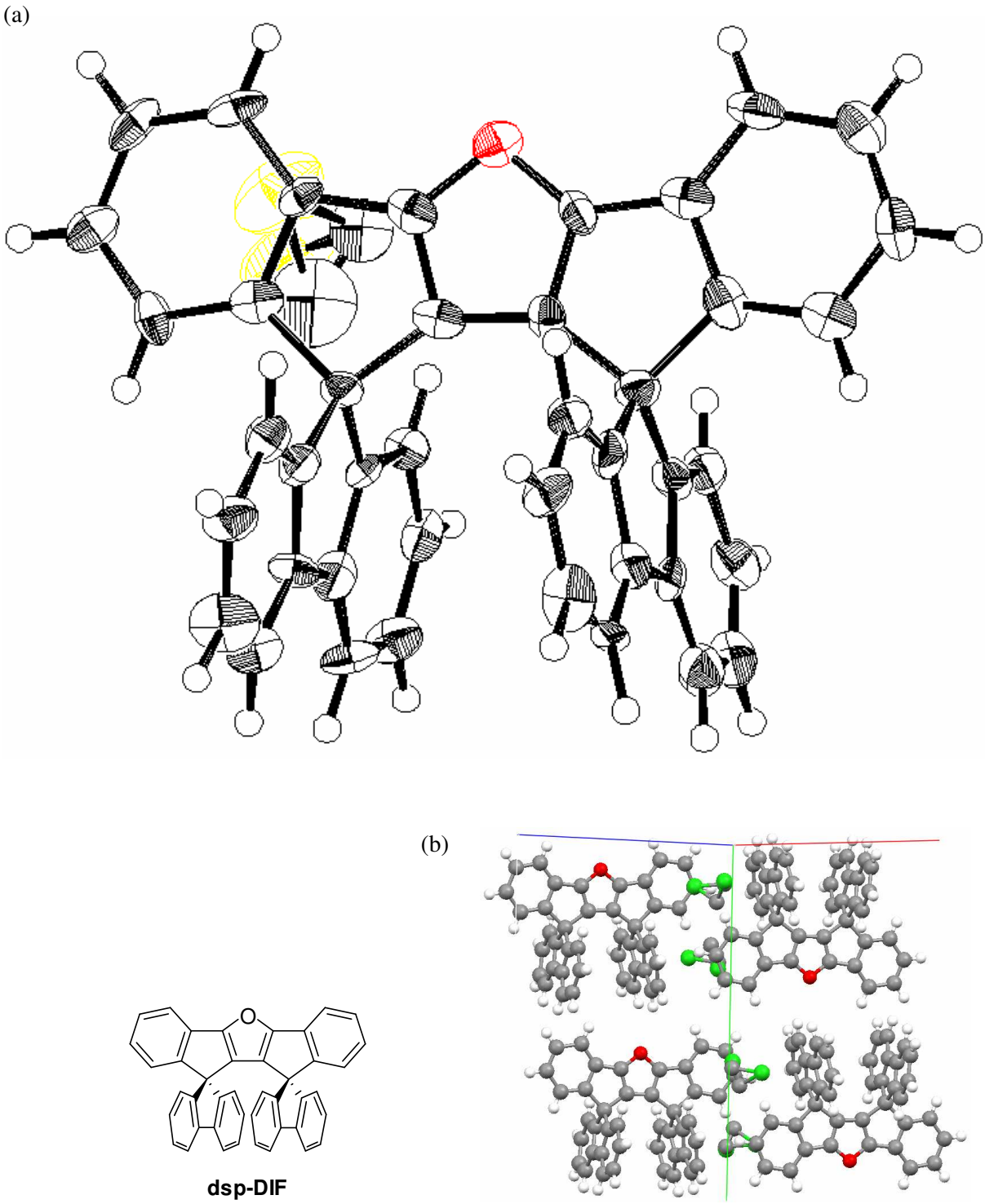


Figure S1. X-ray crystal structures of **dsp-DIF**: (a) ORTEP drawing (50% of thermal ellipsoid probability) and (b) packing structure. CH_2Cl_2 molecules were disordered.

Table S1. Crystal data and structure refinement for **dsp-DIF**

Empirical Formula	$C_{42}H_{24}O \cdot CH_2Cl_2$
Formula Weight	627.57
Temperature (°C)	−120
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.20 × 0.20 × 0.20 mm
Crystal System	monoclinic
Lattice Parameters	a = 13.182(7) Å
	b = 18.871(9) Å β = 112.214(3)°
	c = 13.862(8) Å
	V = 3193(3) Å^3
Space Group	*P*2$_1$/*n (#14)*
Z value	4
D_{calc}	1.306 g/cm^3
F(000)	1296.00
μ(MoKα)	2.375 cm^{-1}
Radiation	MoKα (λ = 0.71070 Å)
	graphite monochromated
2θ max	62.1°
No. of Reflections Measured	Total: 20328
	Unique: 7863 (R_{int} = 0.108)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
No. Observations (All reflections)	7863
No. Variables	436
Reflection/Parameter Ratio	18.03
Residuals: *R* (I>2.00σ(I))	0.1100
Residuals: R_w (All reflections)	0.1799
Goodness-of-fit on F^2	1.023
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.47 e$^-$/Å^3
Minimum peak in Final Diff. Map	−2.77 e$^-$/Å^3

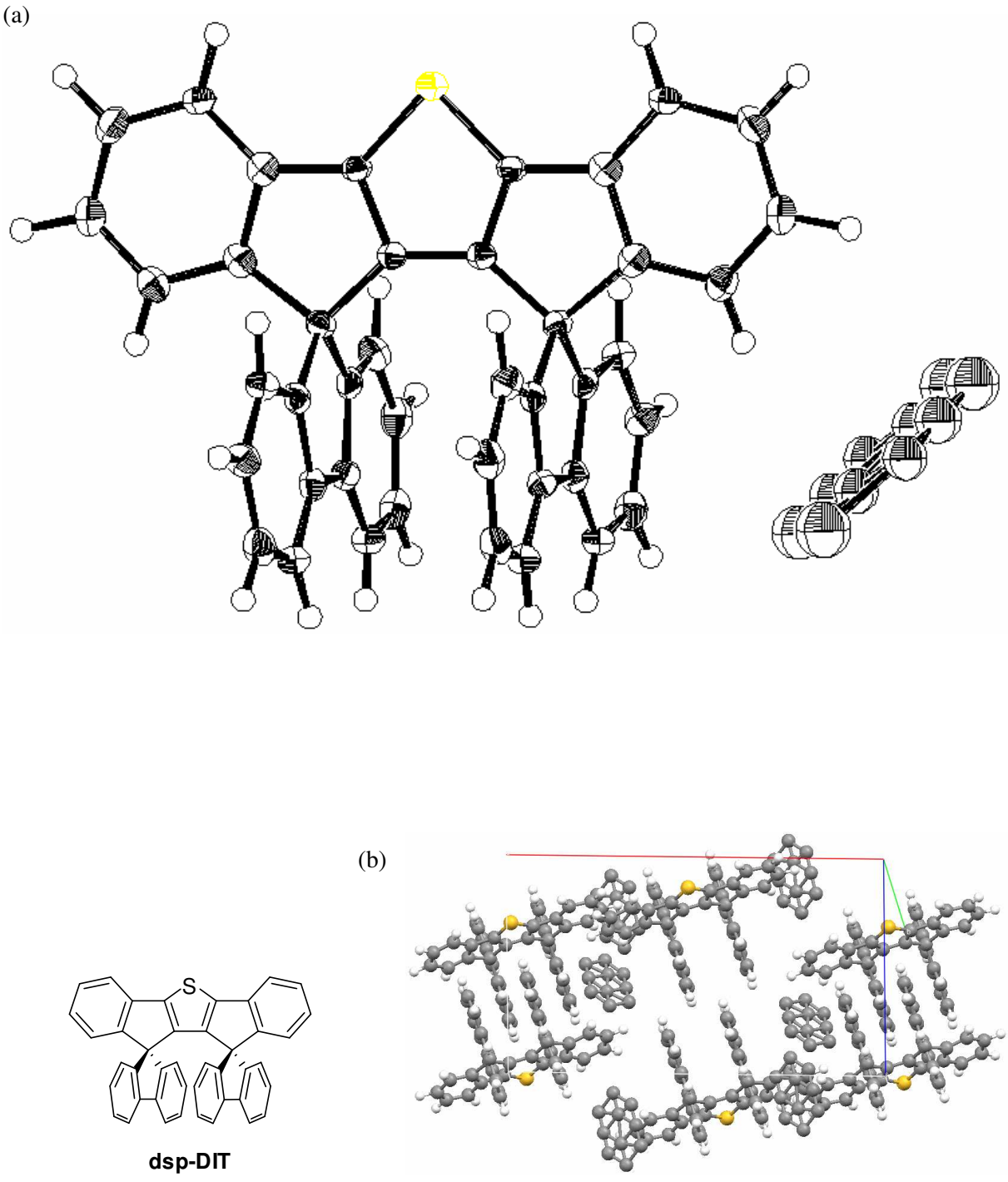


Figure S2. X-ray crystal structures of **dsp-DIT**: (a) ORTEP drawing (50% of thermal ellipsoid probability) and (b) packing structure. Toluene molecules were disordered.

Table S2. Crystal data and structure refinement for **dsp-DIT**

Empirical Formula	$C_{42}H_{24}S \cdot C_7H_8$
Formula Weight	560.71
Temperature (°C)	−120
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.20 × 0.20 × 0.20 mm
Crystal System	monoclinic
Lattice Parameters	a = 23.110(15) Å
	b = 9.920(6) Å β = 95.349(3)°
	c = 14.678(10) Å
	V = 3350(4) Å^3
Space Group	*C*2/*c (#15)*
Z value	4
D_{calc}	1.112 g/cm^3
F(000)	1168.00
μ(MoKα)	1.229 cm^{-1}
Radiation	MoKα (λ = 0.71070 Å)
	graphite monochromated
2θ max	61.8°
No. of Reflections Measured	Total: 11967
	Unique: 4398 (R_{int} = 0.079)
Structure Solution	Direct Methods (SIR2004)
Refinement	Full-matrix least-squares on F^2
No. Observations (All reflections)	4398
No. Variables	263
Reflection/Parameter Ratio	16.72
Residuals: R_1 (I>2.00σ(I))	0.0622
Residuals: wR_2 (All reflections)	0.1191
Goodness-of-fit on F^2	1.063
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	2.13 e$^-$/Å^3
Minimum peak in Final Diff. Map	−0.80 e$^-$/Å^3

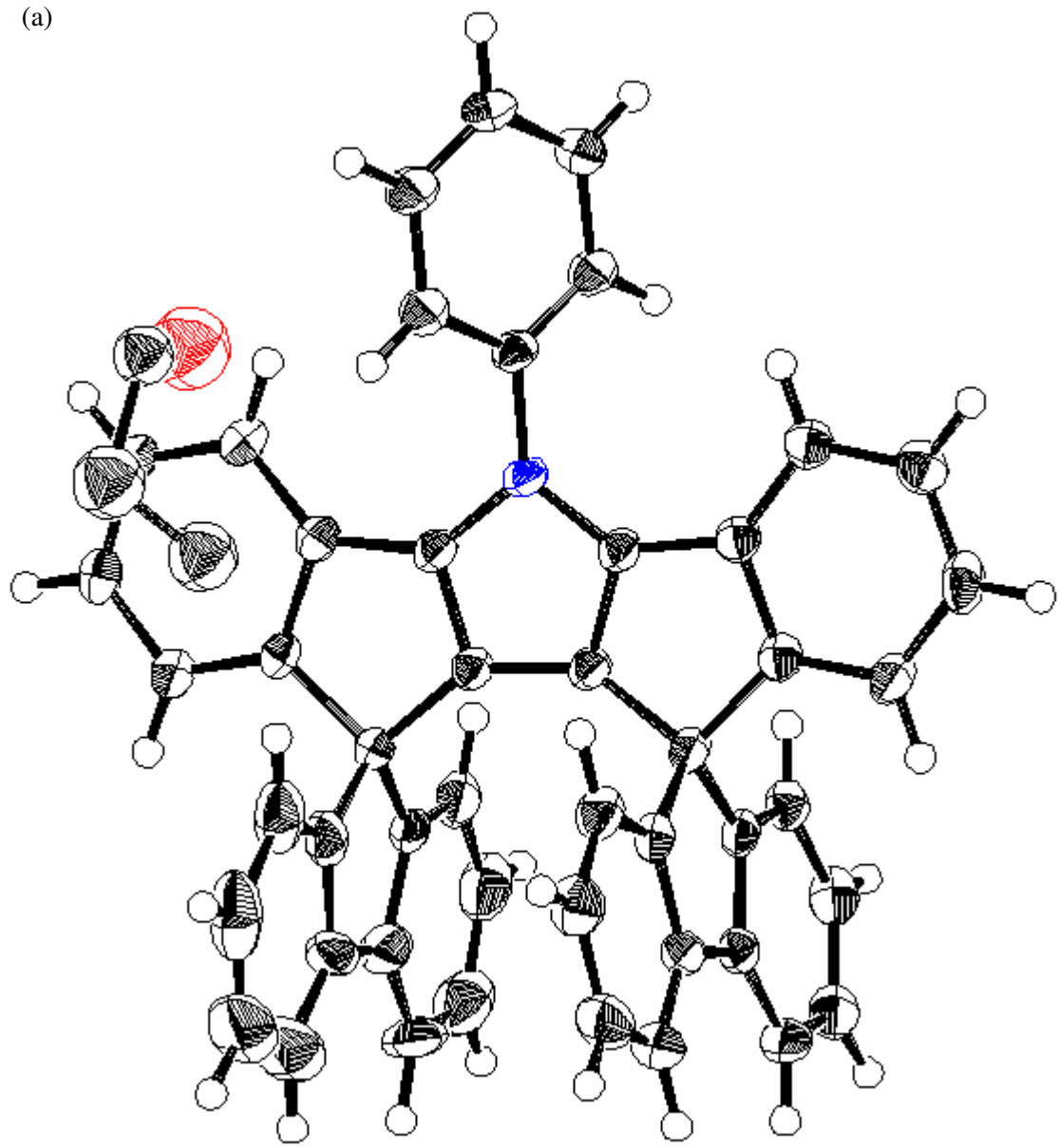
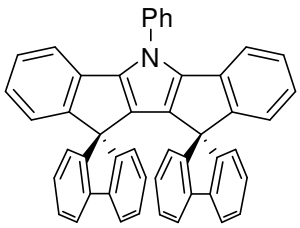


Figure S3. X-ray crystal structures of **dsp-DIF**: (a) ORTEP drawing (50% of thermal ellipsoid probability) and (b) packing structure. Ethyl acetate molecules were disordered.



dsp-DIP-Ph

(b)

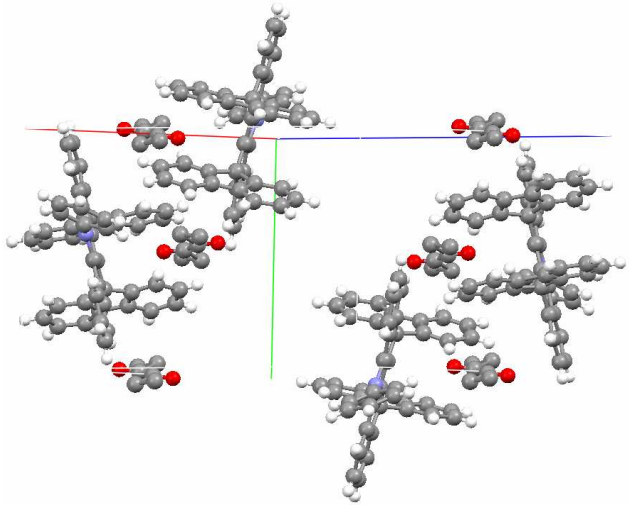


Figure S3. ‘(continued).

Table S3. Crystal data and structure refinement for **dsp-DIP-Ph**

Empirical Formula	$C_{48}H_{29}N \cdot C_4H_8O_2$
Formula Weight	671.80
Temperature (°C)	−120
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.20 × 0.20 × 0.20 mm
Crystal System	monoclinic
Lattice Parameters	a = 14.490(6) Å
	b = 11.893(4) Å β = 108.022(5)°
	c = 21.667(8) Å
	V = 3551(2) Å^3
Space Group	*P*2$_1$/*n (#14)*
Z value	4
D_{calc}	1.257 g/cm^3
F(000)	1400.00
μ(MoKα)	0.739 cm^{-1}
Radiation	MoKα (λ = 0.71070 Å)
	graphite monochromated
2θ max	62.3°
No. of Reflections Measured	Total: 29735
	Unique: 9914 (R_{int} = 0.048)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
No. Observations (All reflections)	9914
No. Variables	487
Reflection/Parameter Ratio	20.36
Residuals: *R* (I>2.00σ(I))	0.0695
Residuals: R_w (All reflections)	0.0860
Goodness-of-fit on F^2	1.028
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.10 e$^-$/Å^3
Minimum peak in Final Diff. Map	−0.67 e$^-$/Å^3

Theoretical calculation

Table S4. Cartesian atomic coordinates for the geometry optimized structure of **dsp-DIT** (B3LYP/6-31G(d)).

atom	x	y	z
C	1.2248012437	2.5318022384	0.0281689052
C	0.7113590938	1.2463436701	0.0095904098
C	-0.7113572505	1.2463445729	-0.0096048002
C	-1.2247975664	2.5318036592	-0.0281981807
S	0.0000027204	3.7698439796	-0.0000217903
C	2.6755770858	2.5360189160	0.0705089850
C	3.0815936659	1.1824577958	0.0590986698
C	1.8627161021	0.2409150400	-0.0299002205
C	-1.8627156956	0.2409180408	0.0298974512
C	-3.0815919158	1.1824615164	-0.0591123273
C	-2.6755733993	2.5360219230	-0.0705383067
C	3.6202178267	3.5624731675	0.1241540640
C	4.9751658489	3.2225585661	0.1689769288
C	5.3769843965	1.8835453320	0.1595185219
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C	-3.6202126686	3.5624769019	-0.1241952635
C	1.9252716328	-0.6067384156	-1.3090756127
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C	-1.9252724836	-0.6067205449	1.3090826259
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C	-1.9836838672	-2.1194271319	-0.4714983098
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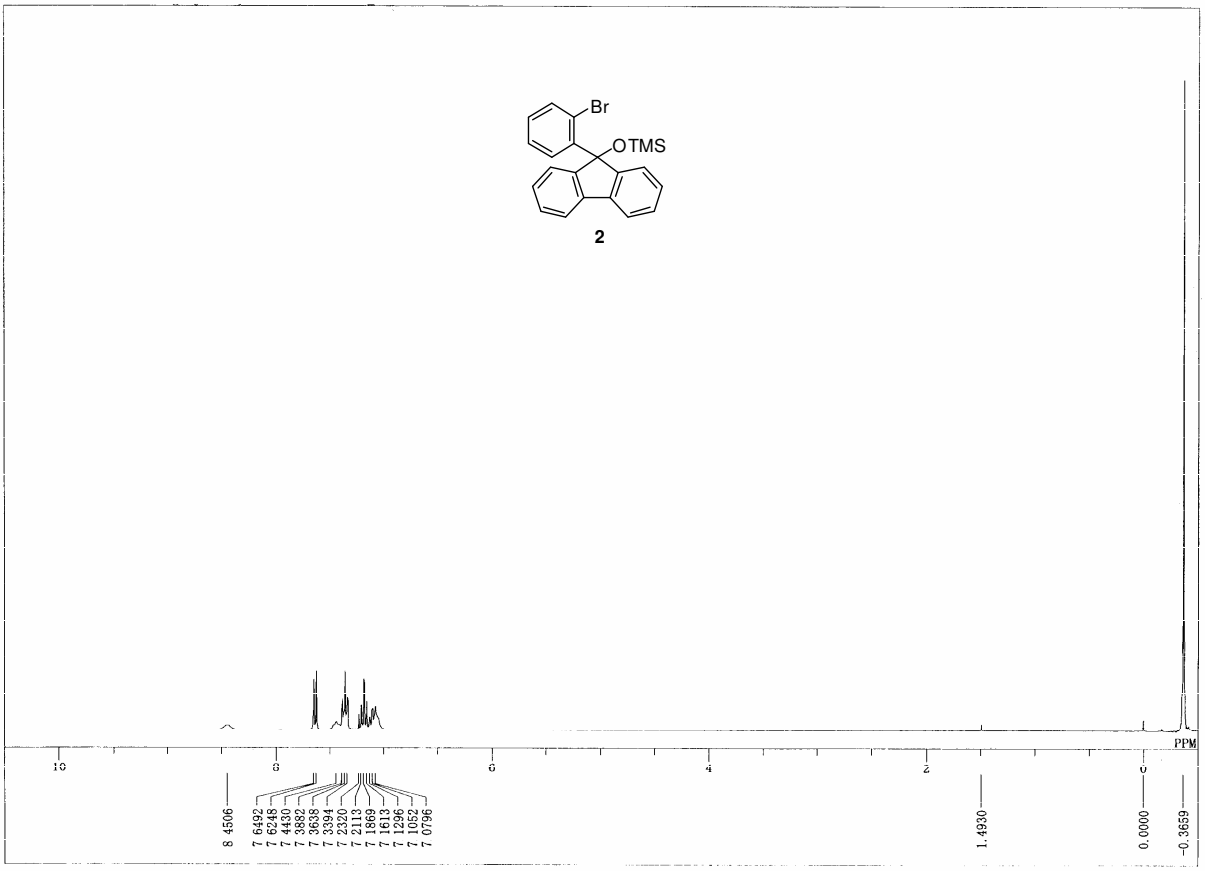
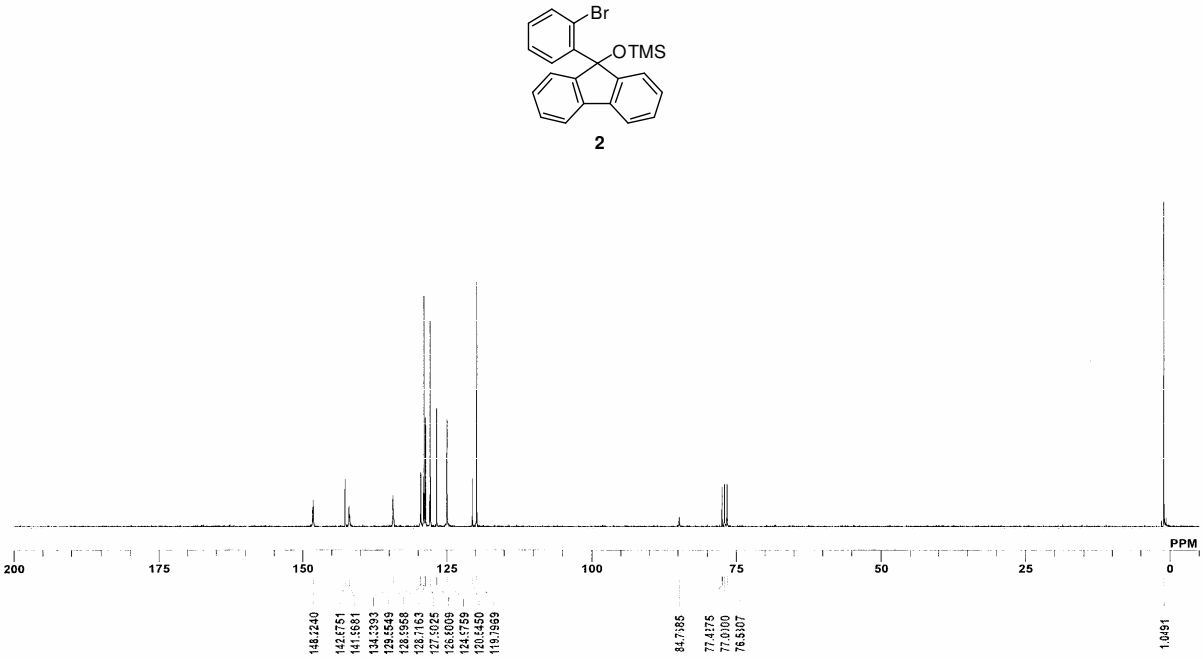
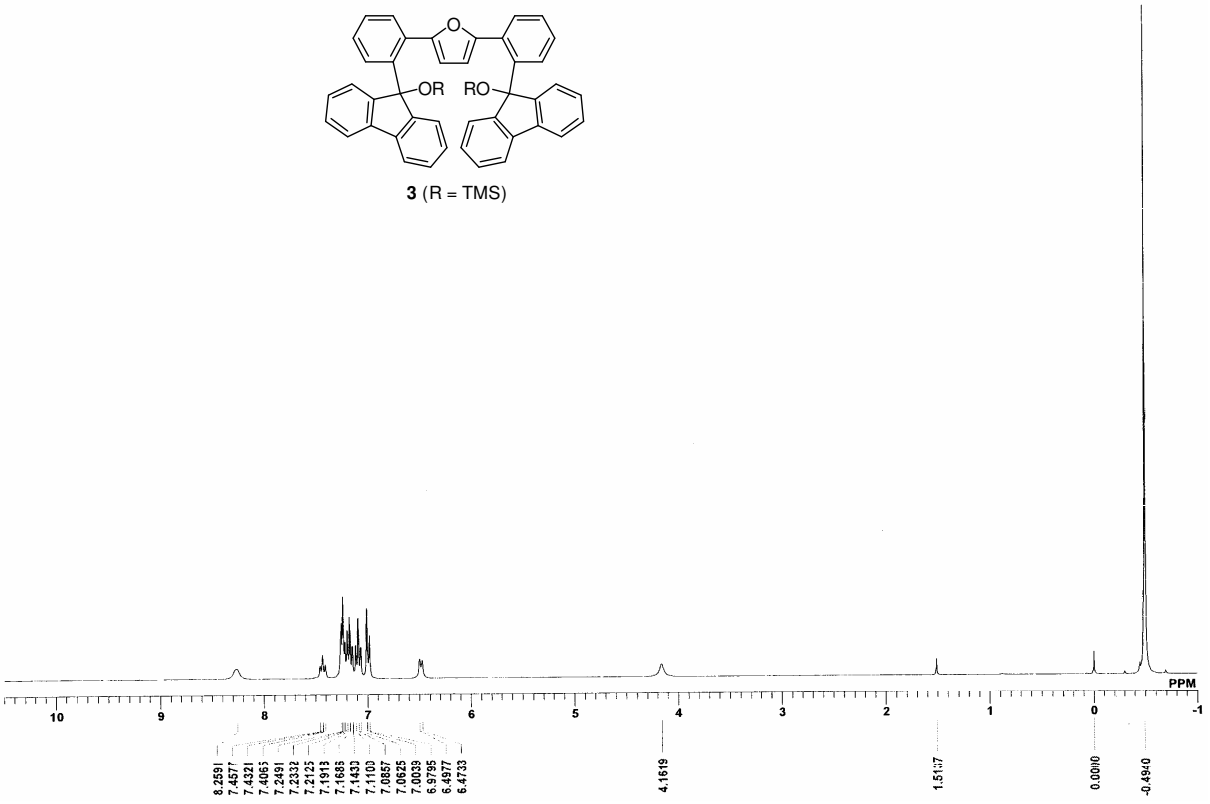
^{1}H and ^{13}C NMR Spectra



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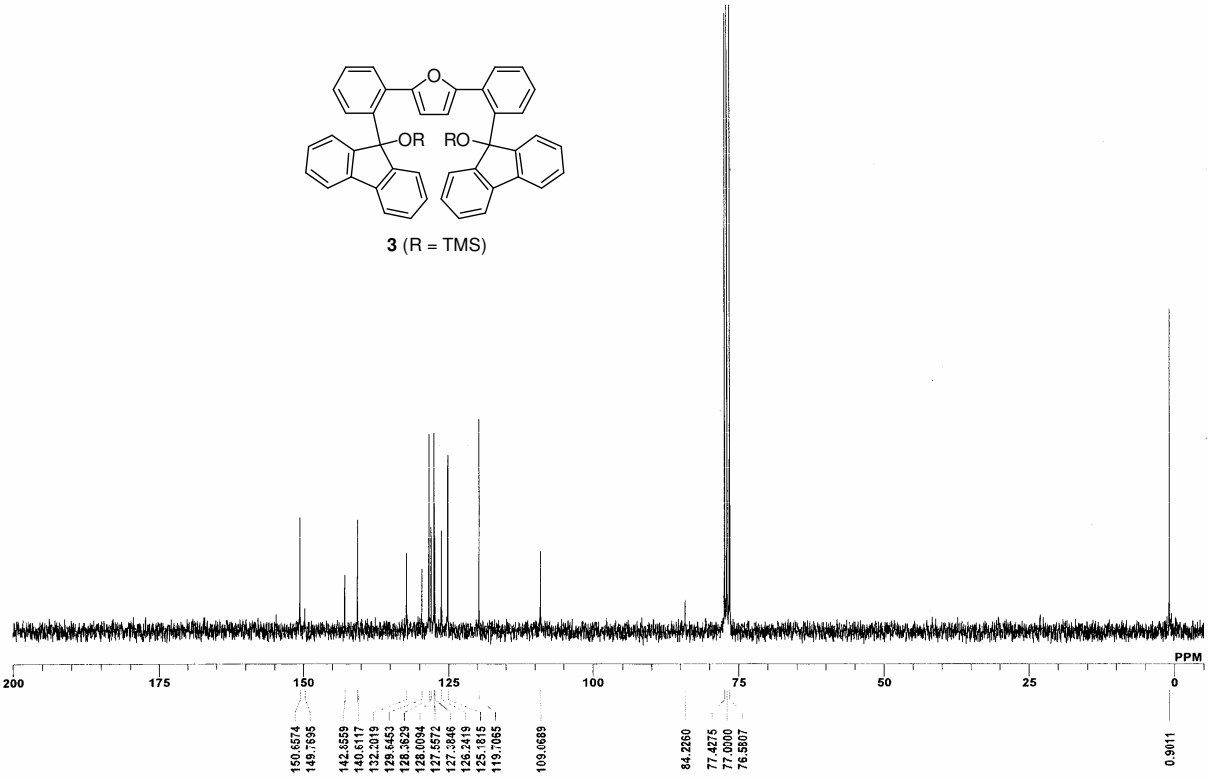
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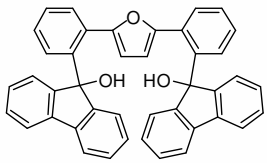
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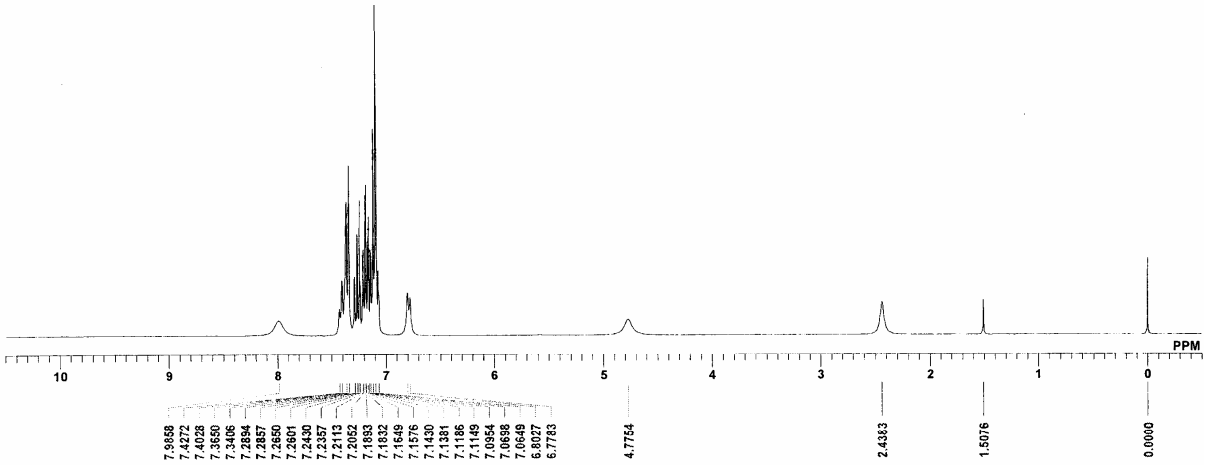
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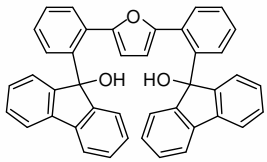
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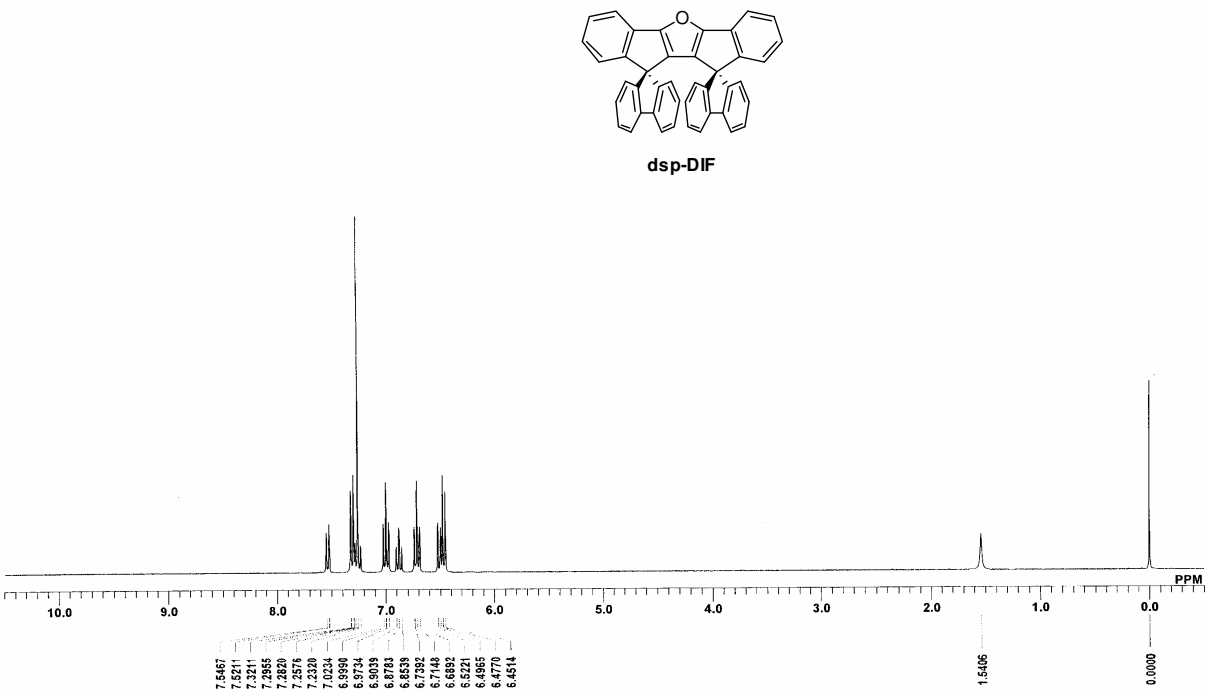
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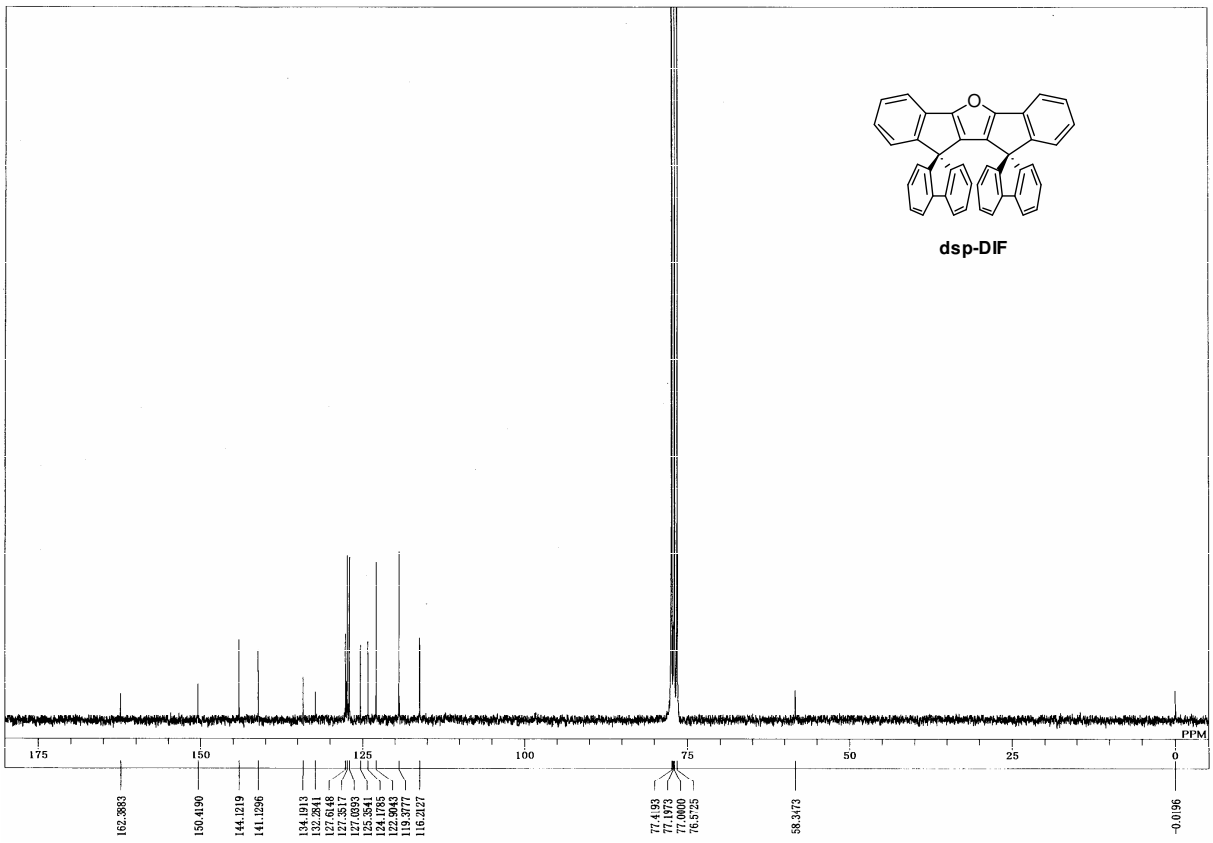
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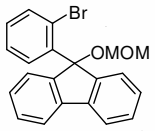
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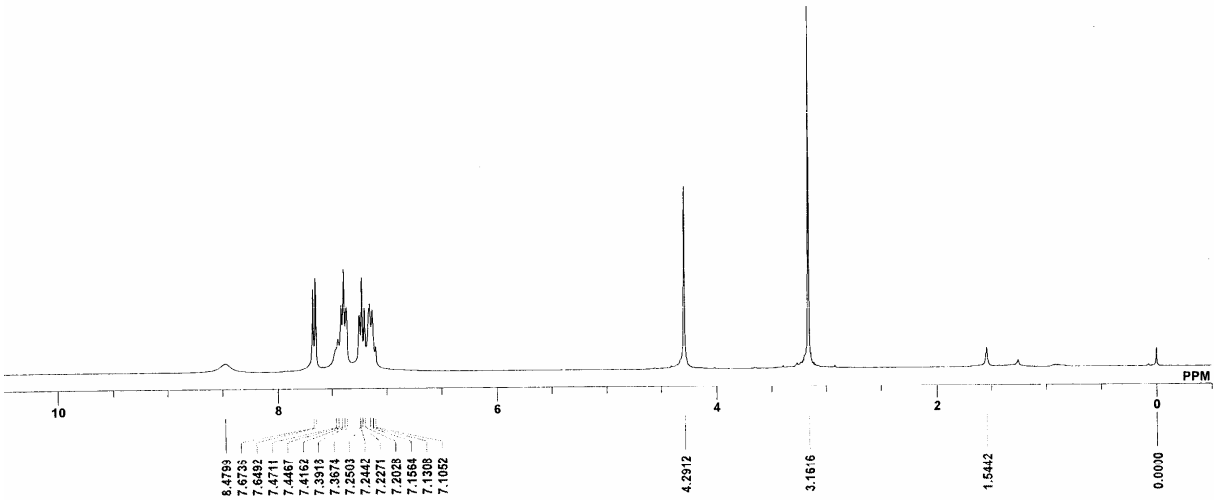
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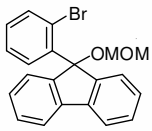
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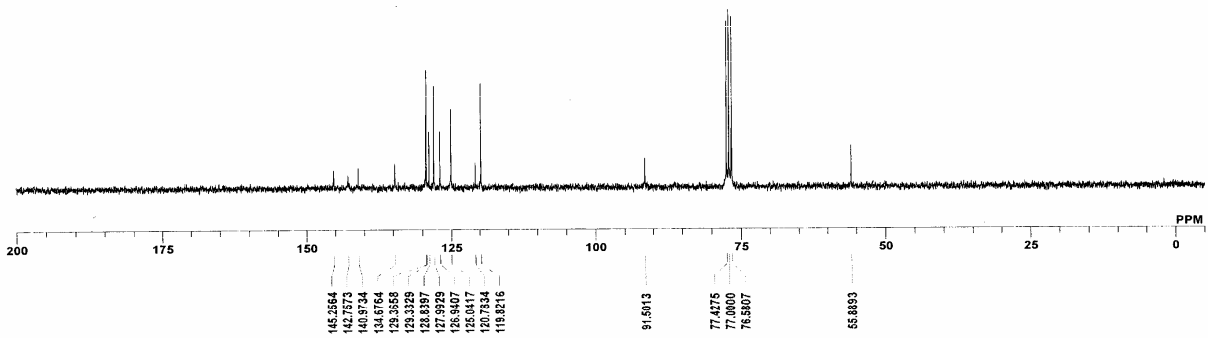
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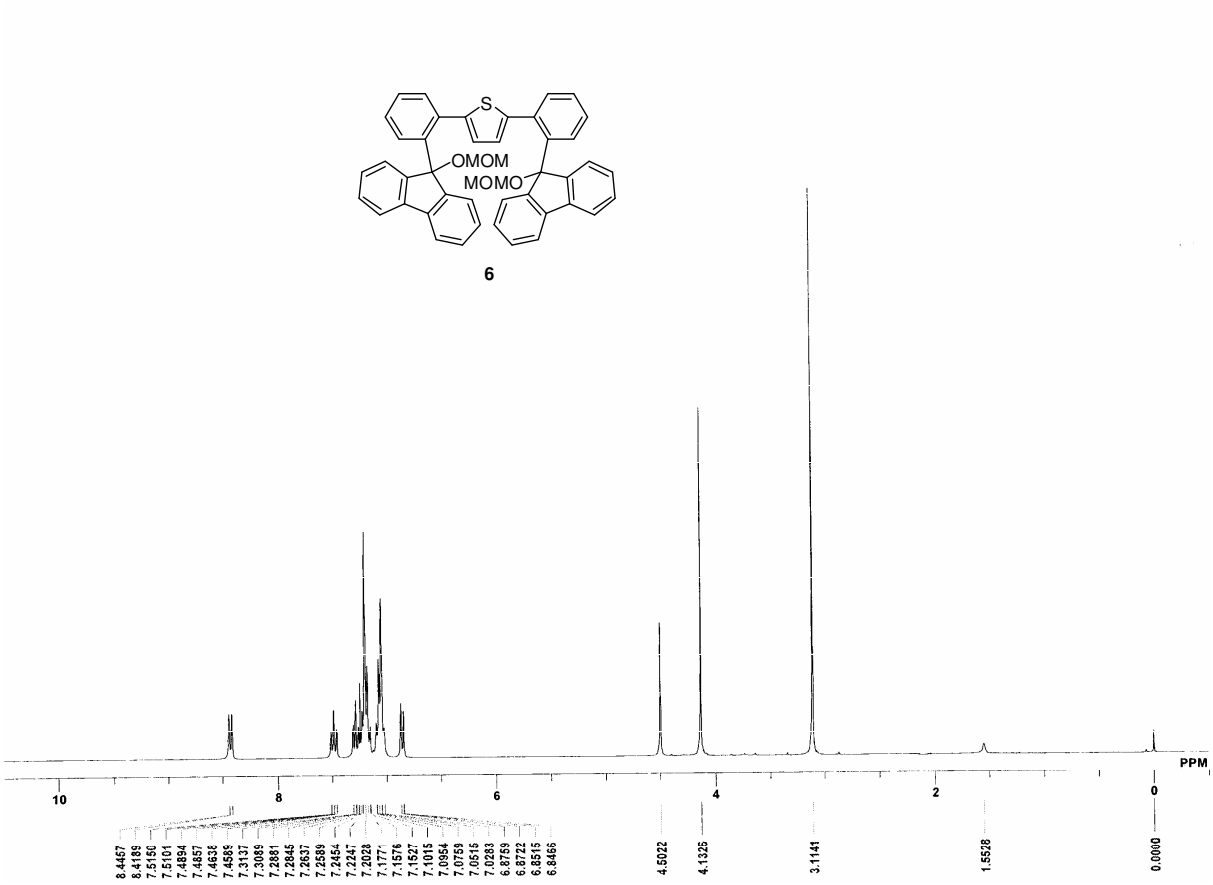
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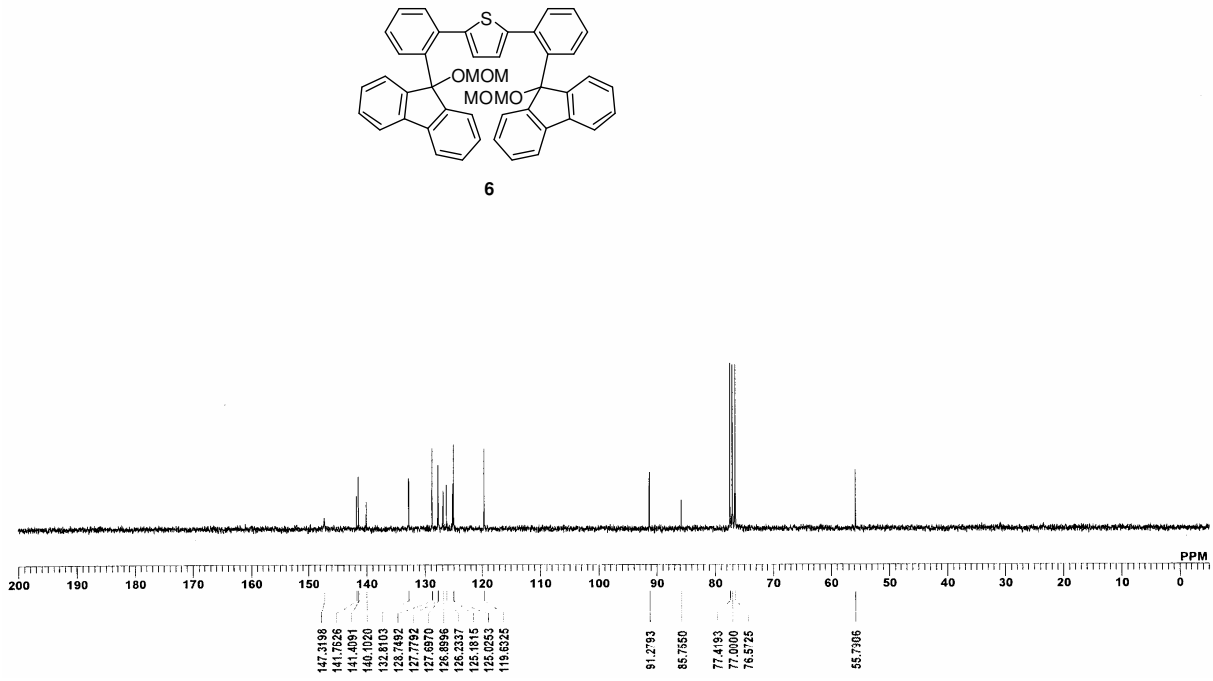
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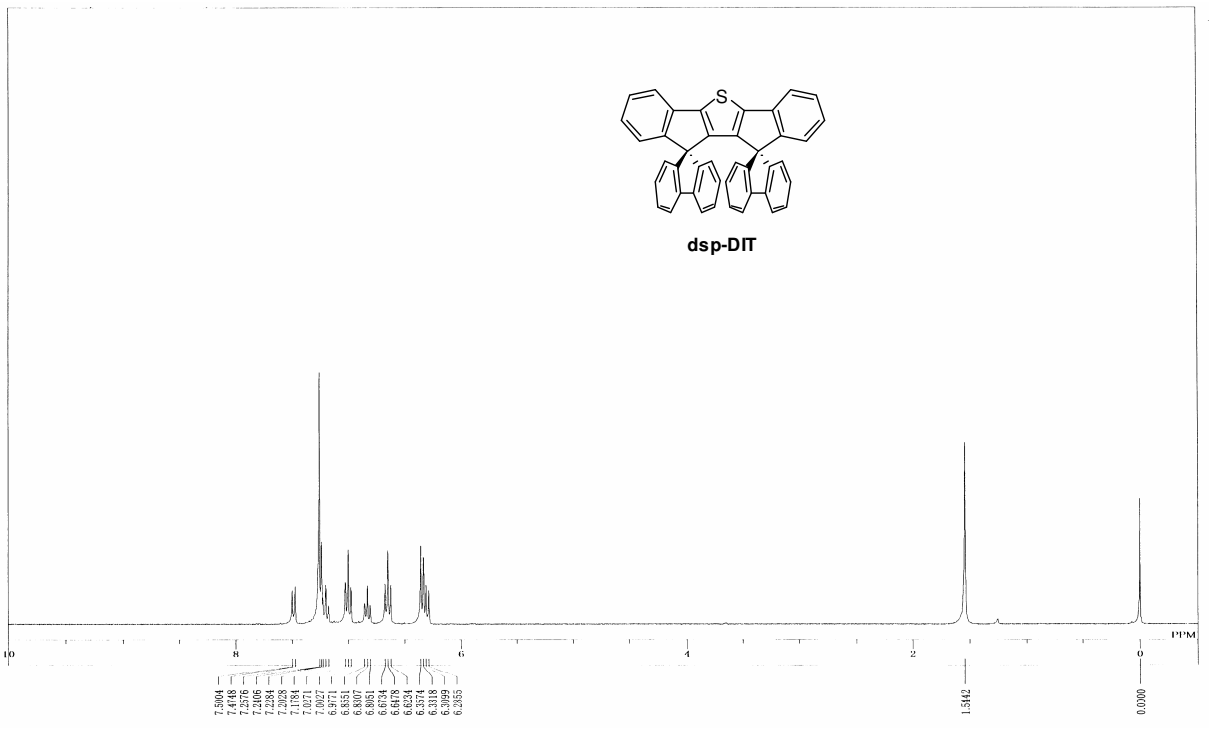
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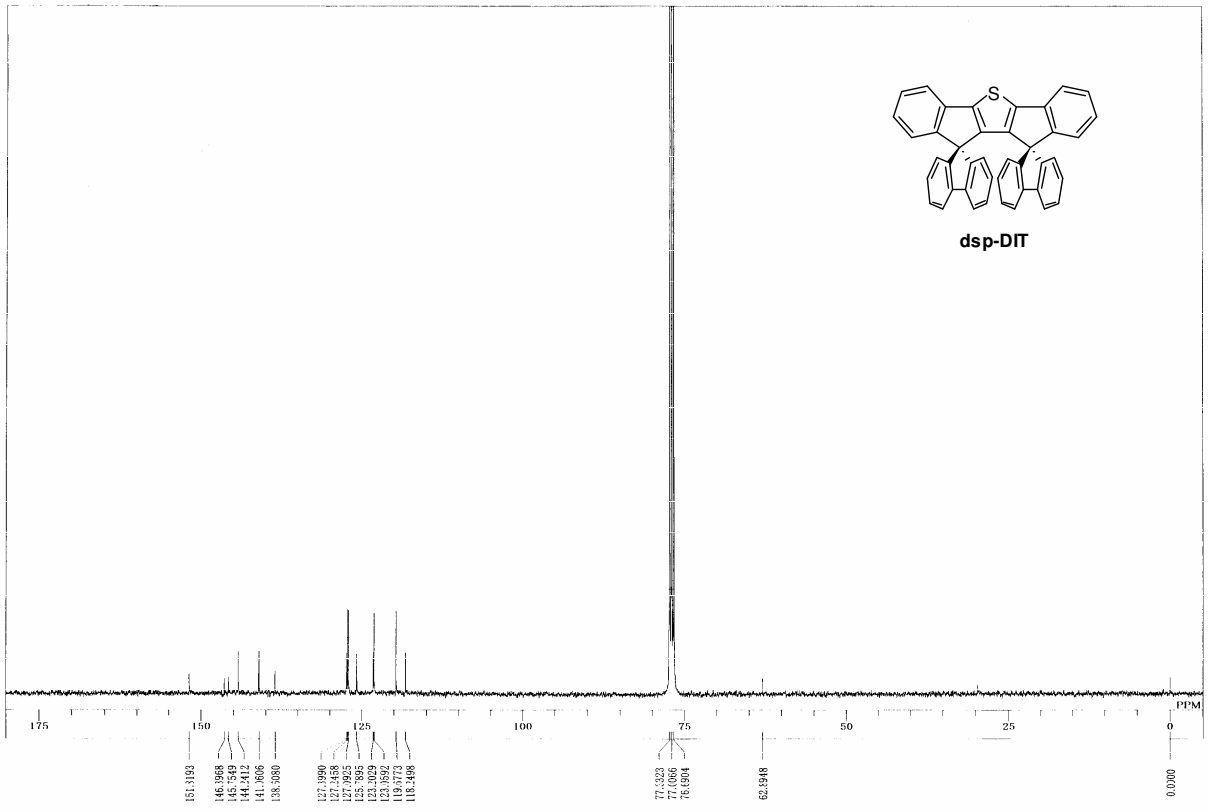
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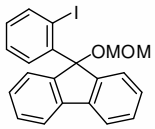
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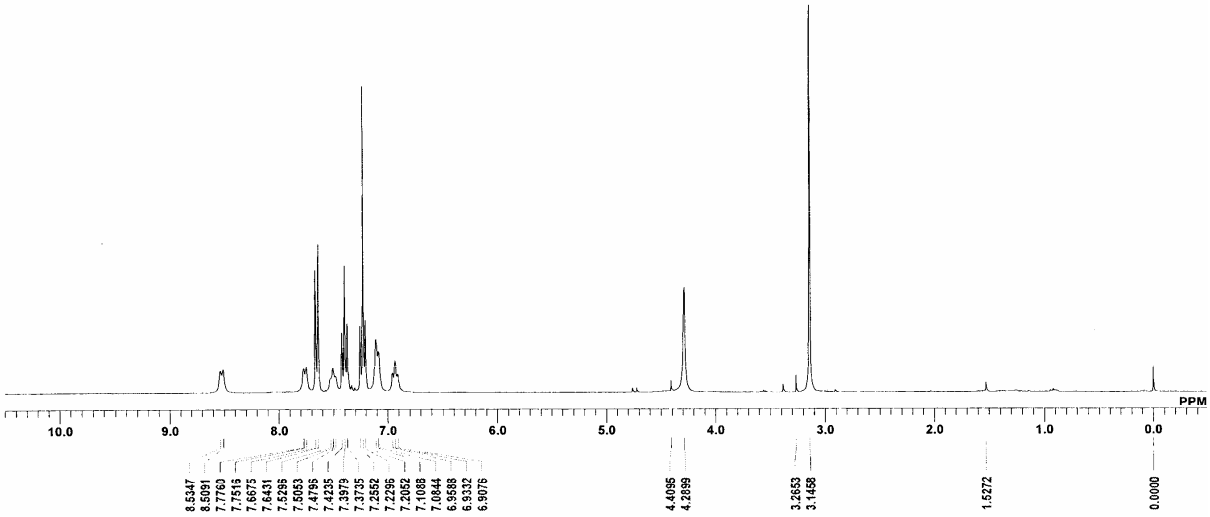
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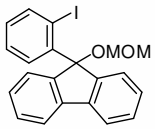
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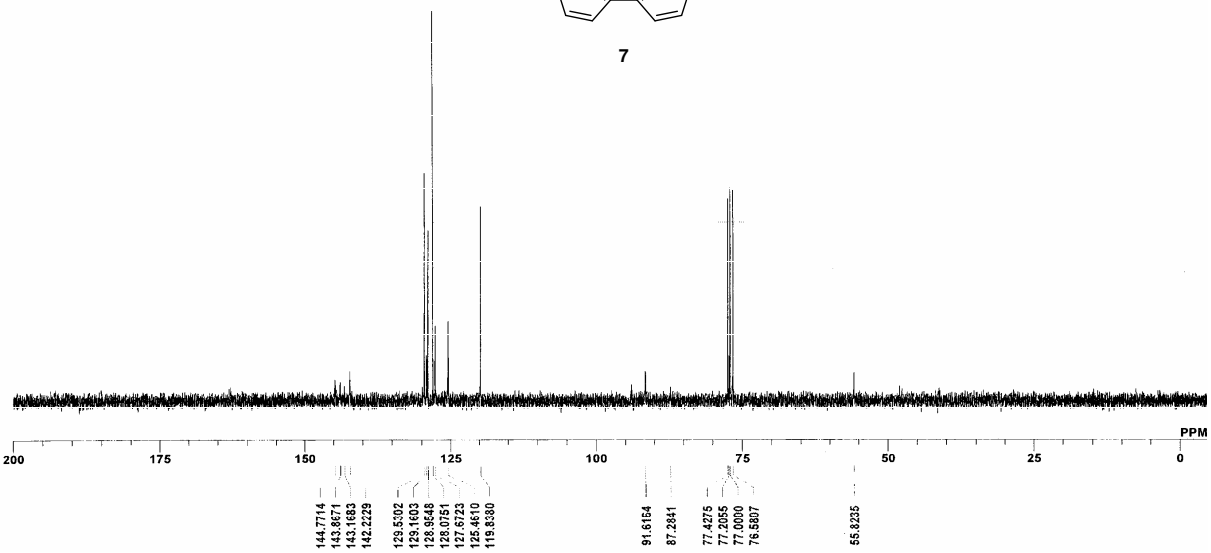
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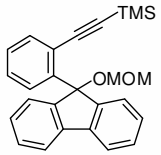
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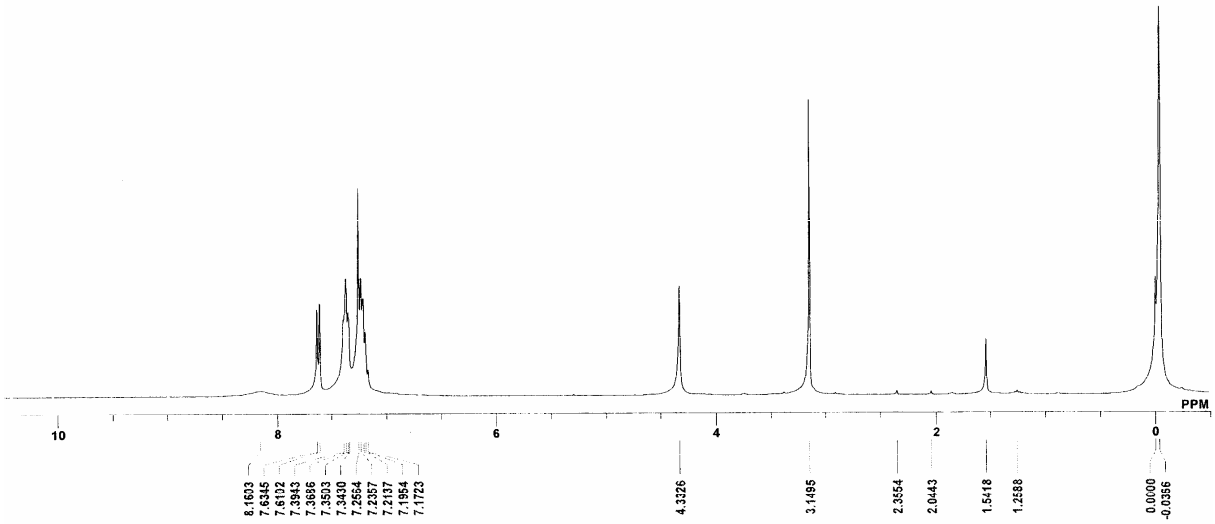
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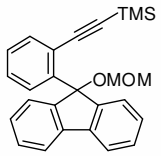
TMS
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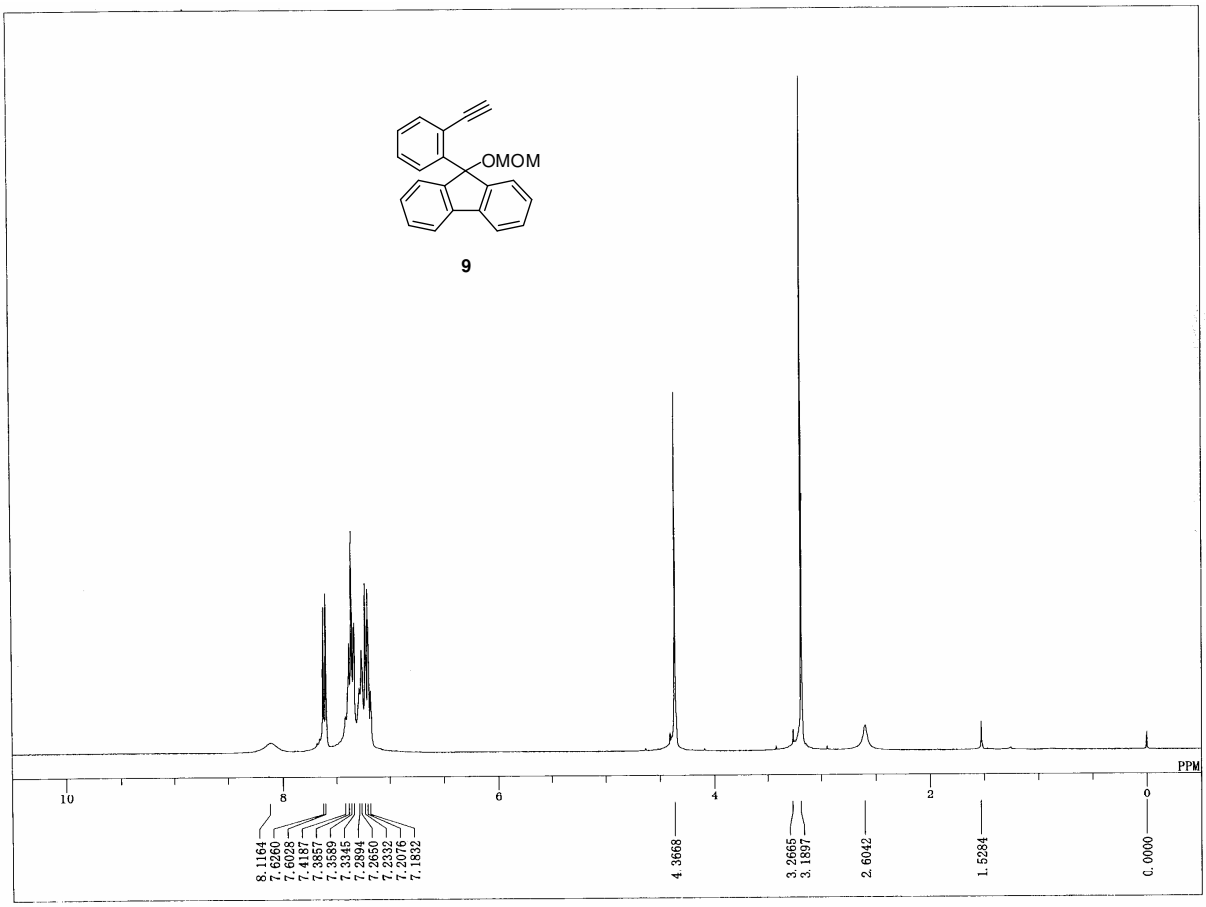
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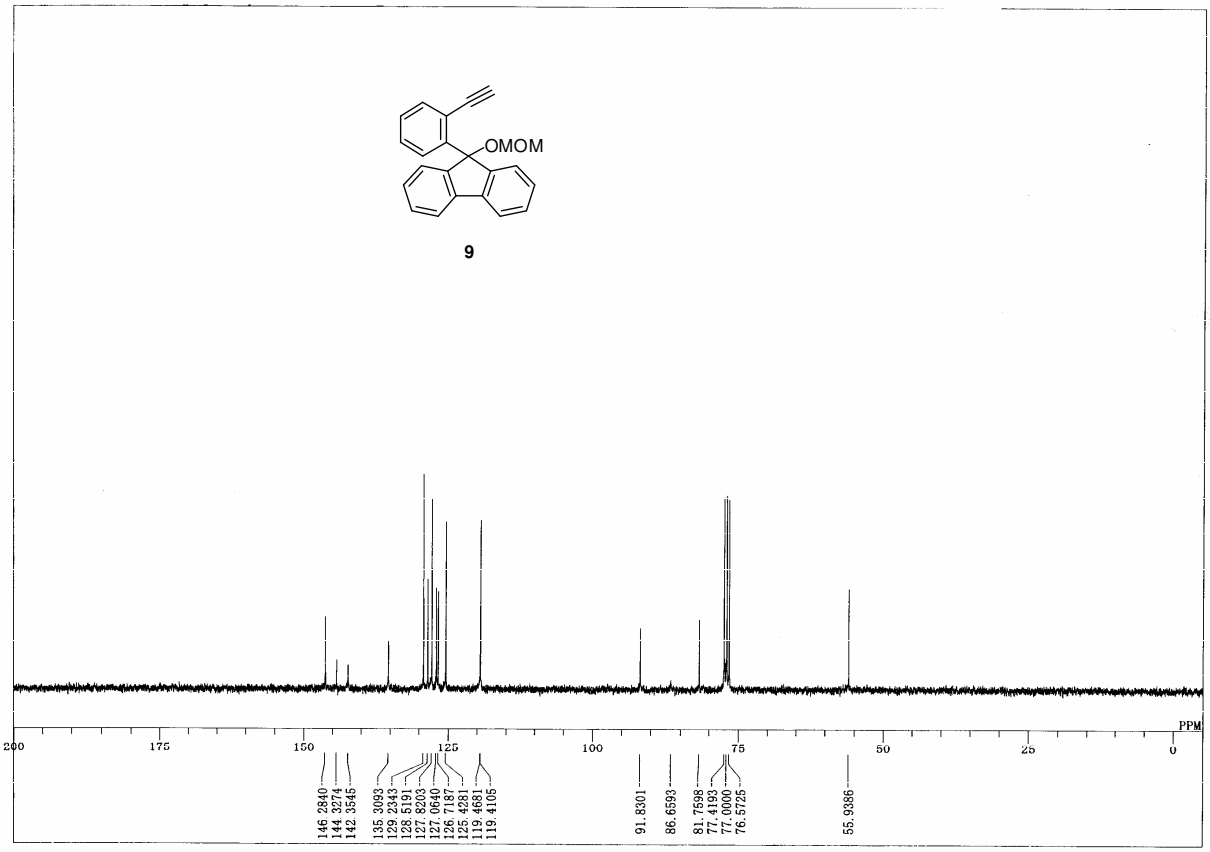
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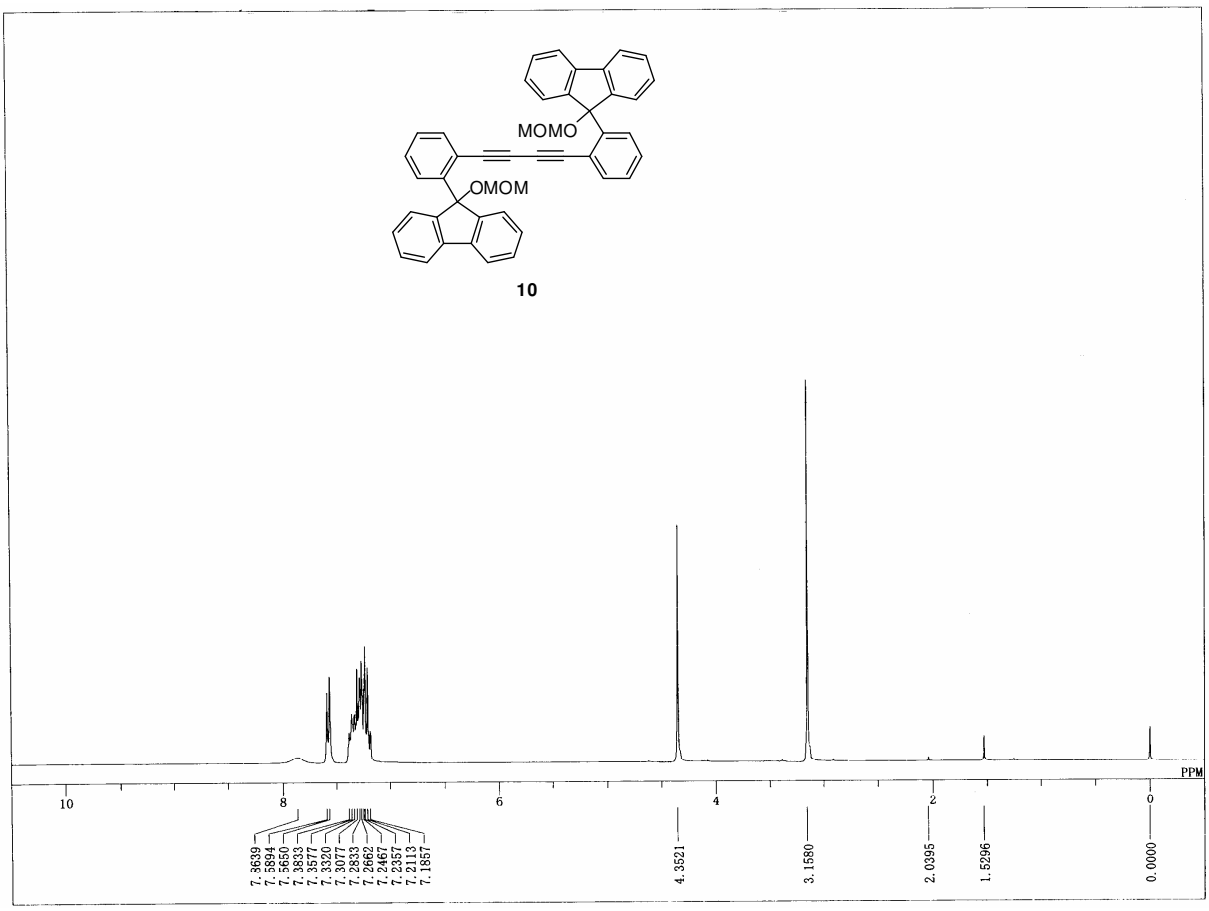
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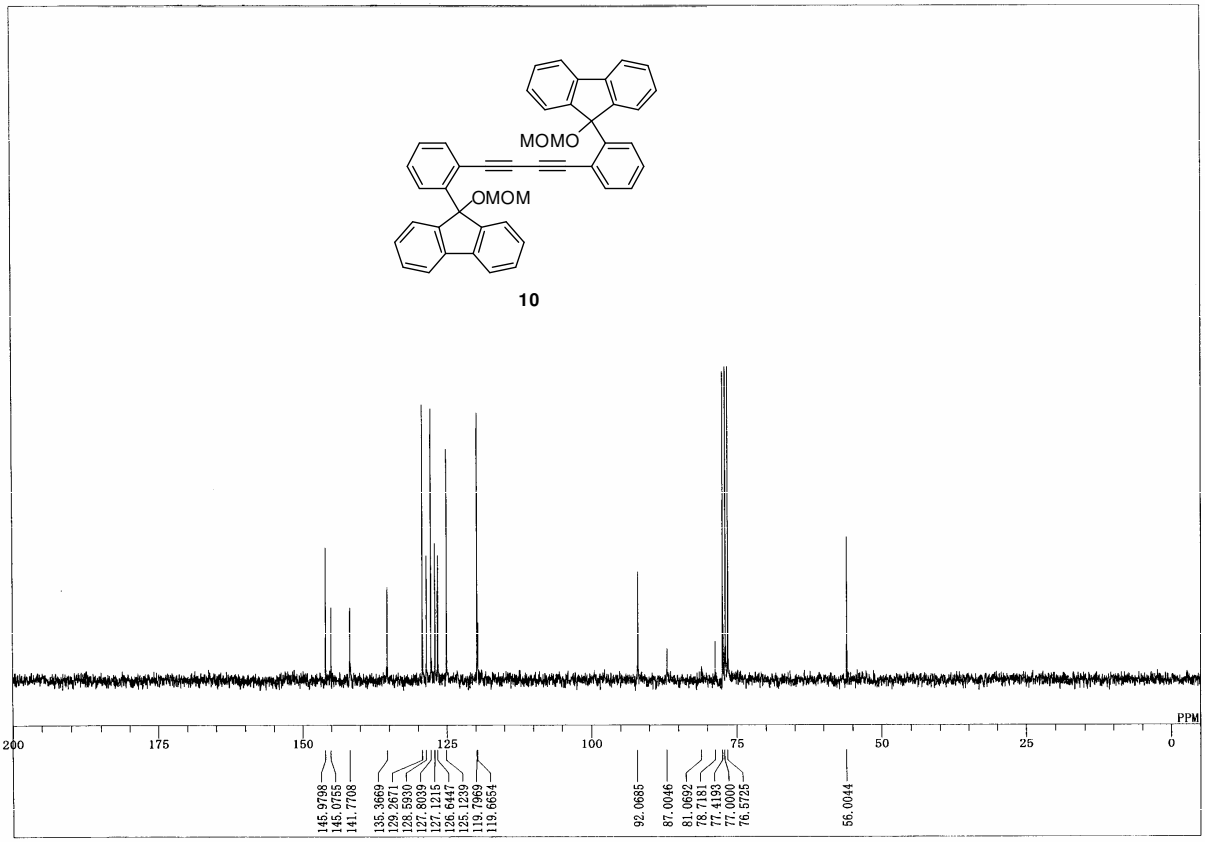
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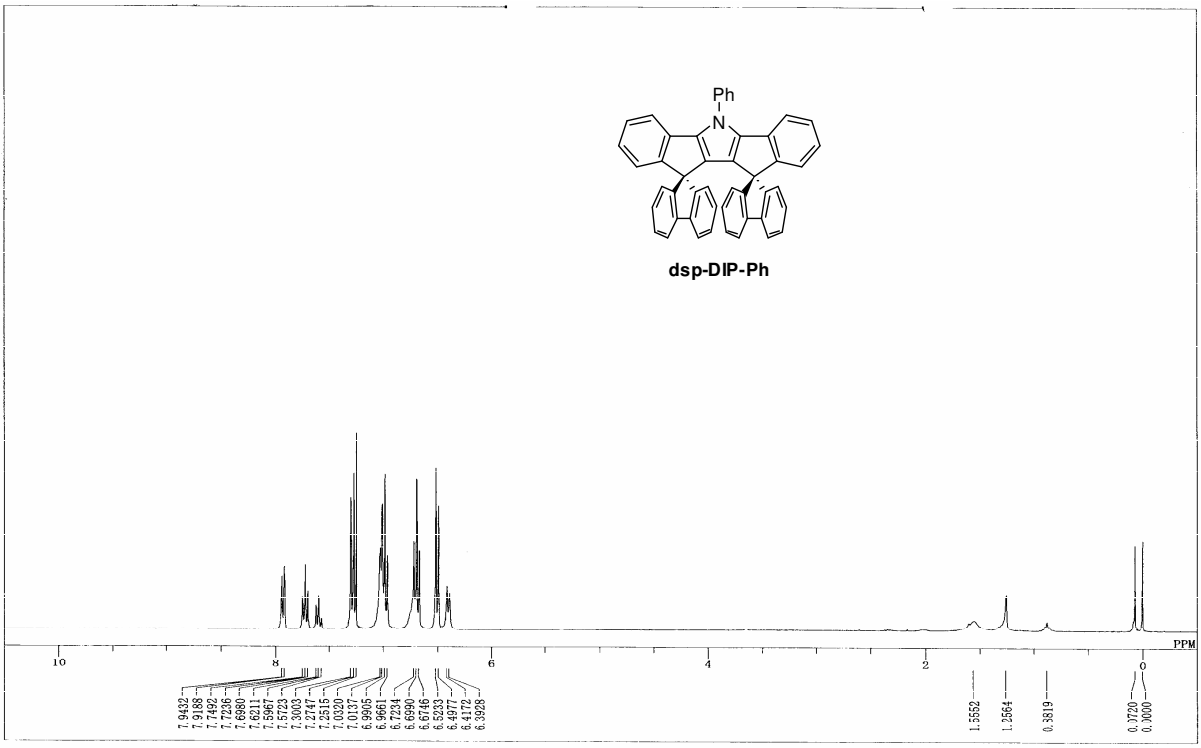
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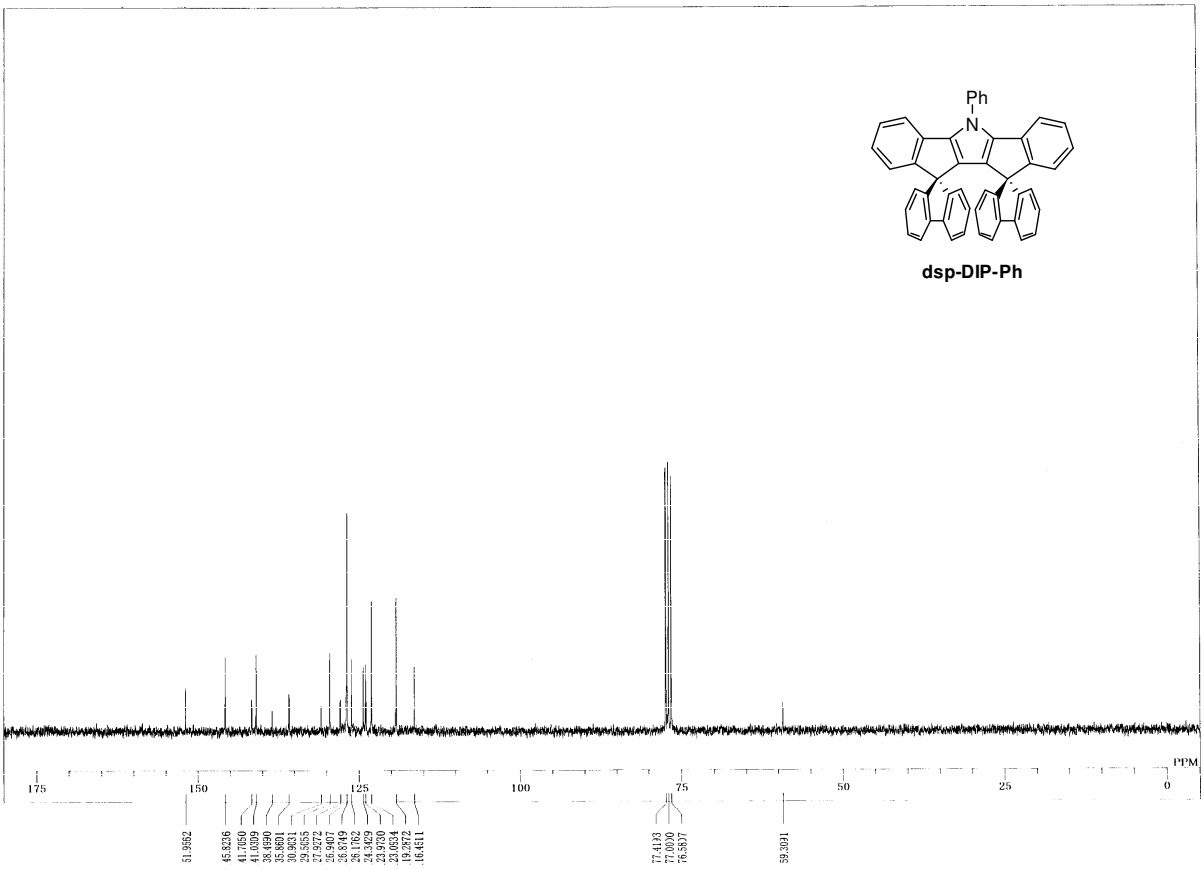
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