Which isomer is it, 1,2,5,6- or 1,4,5,8-tetrasubstituted cycloocta-1,3,5,7-tetraene? Synthesis of symmetrically tetrasubstituted cycloocta-1,3,5,7-tetraene derivatives

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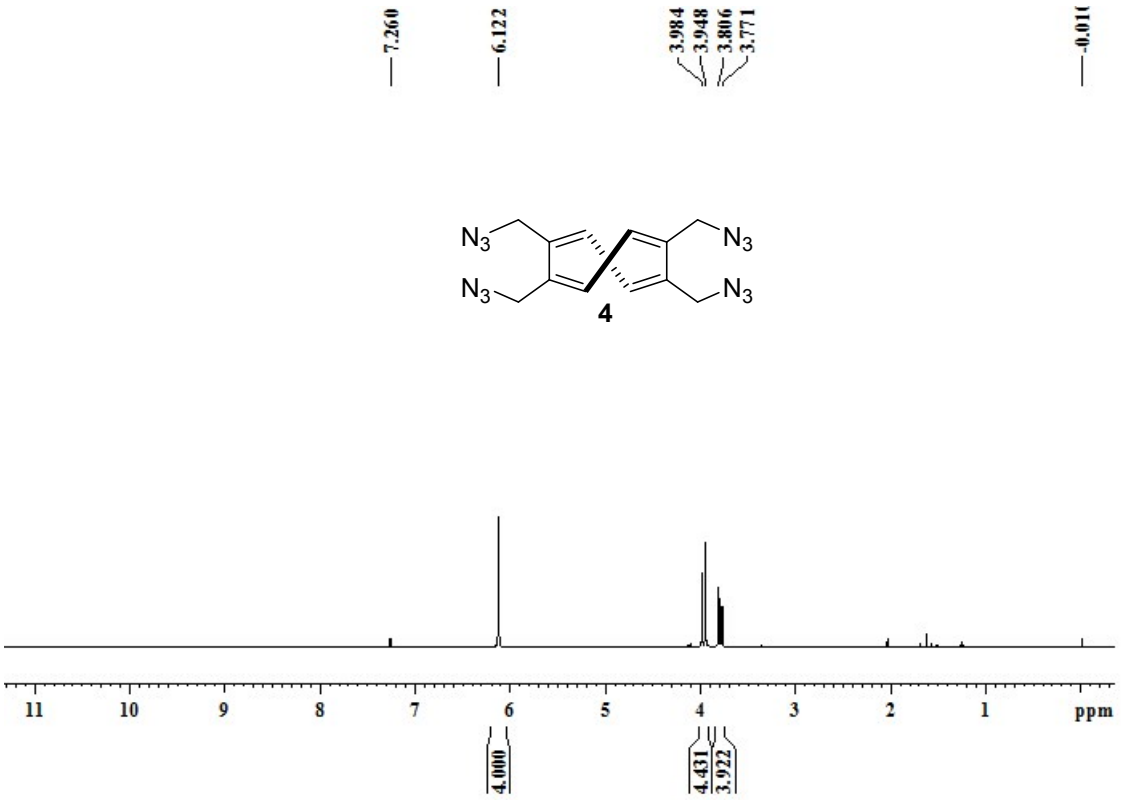


Figure 1 400 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$

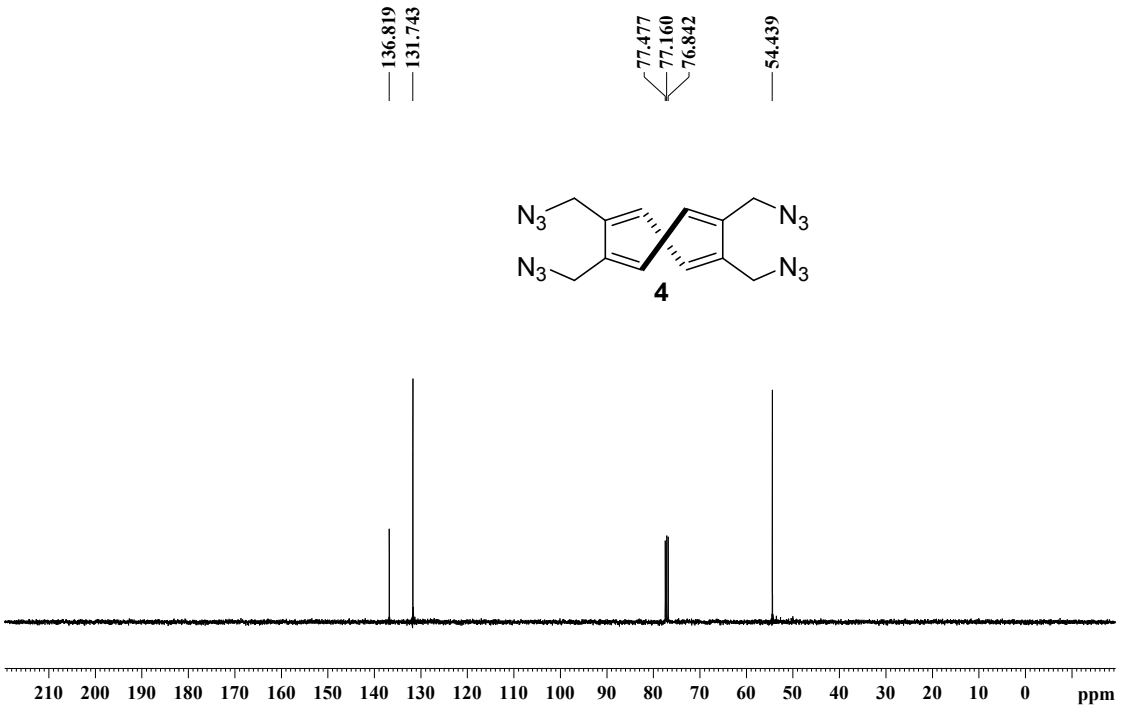


Figure 2 100 MHz ^{13}C NMR spectrum of **4** in $CDCl_3$

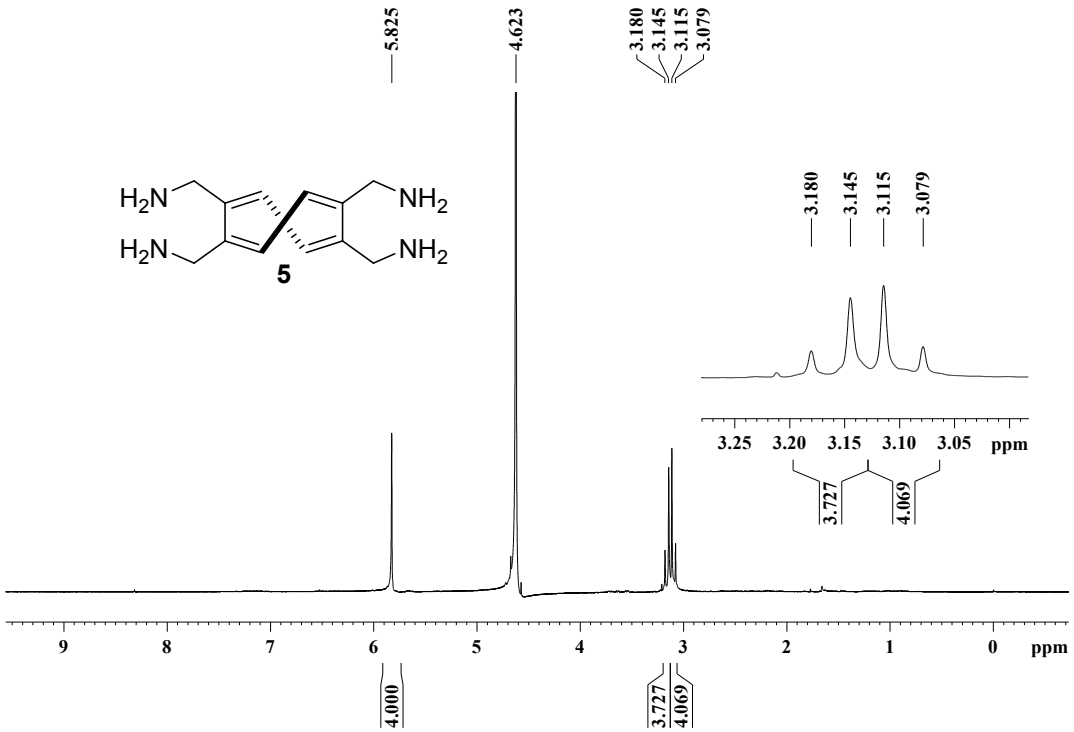


Figure 3 400 MHz ^{1}H NMR spectrum of **4** in D_2O.

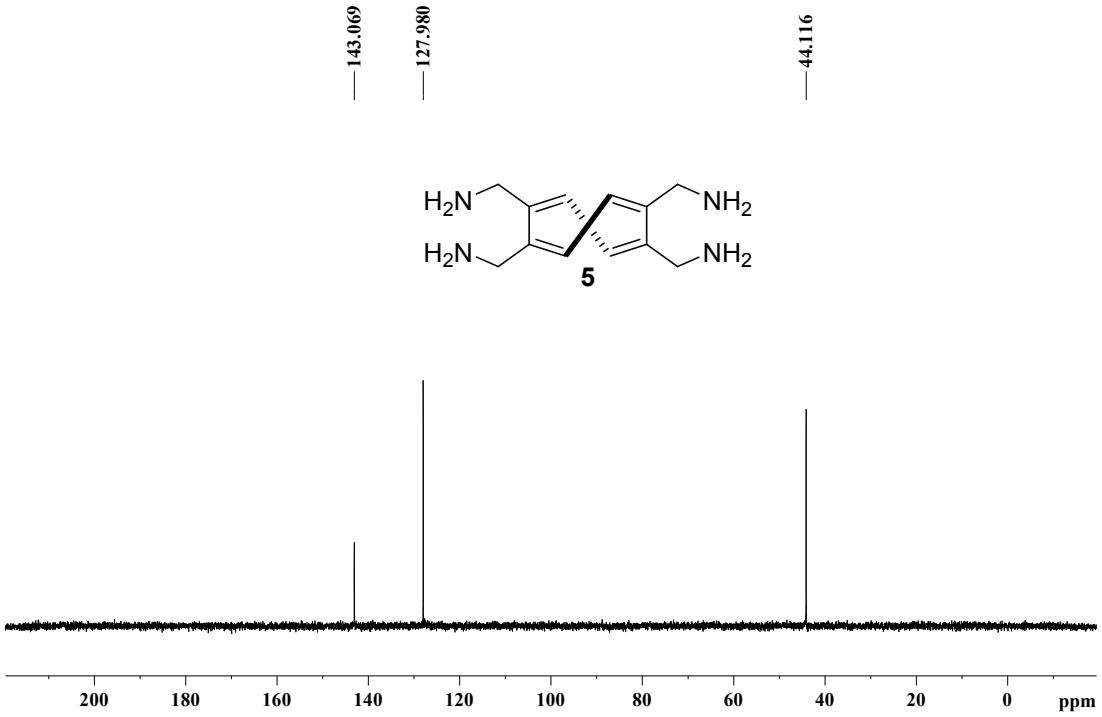


Figure 3 100 MHz ^{13}C NMR spectrum of **5** in D_2O.

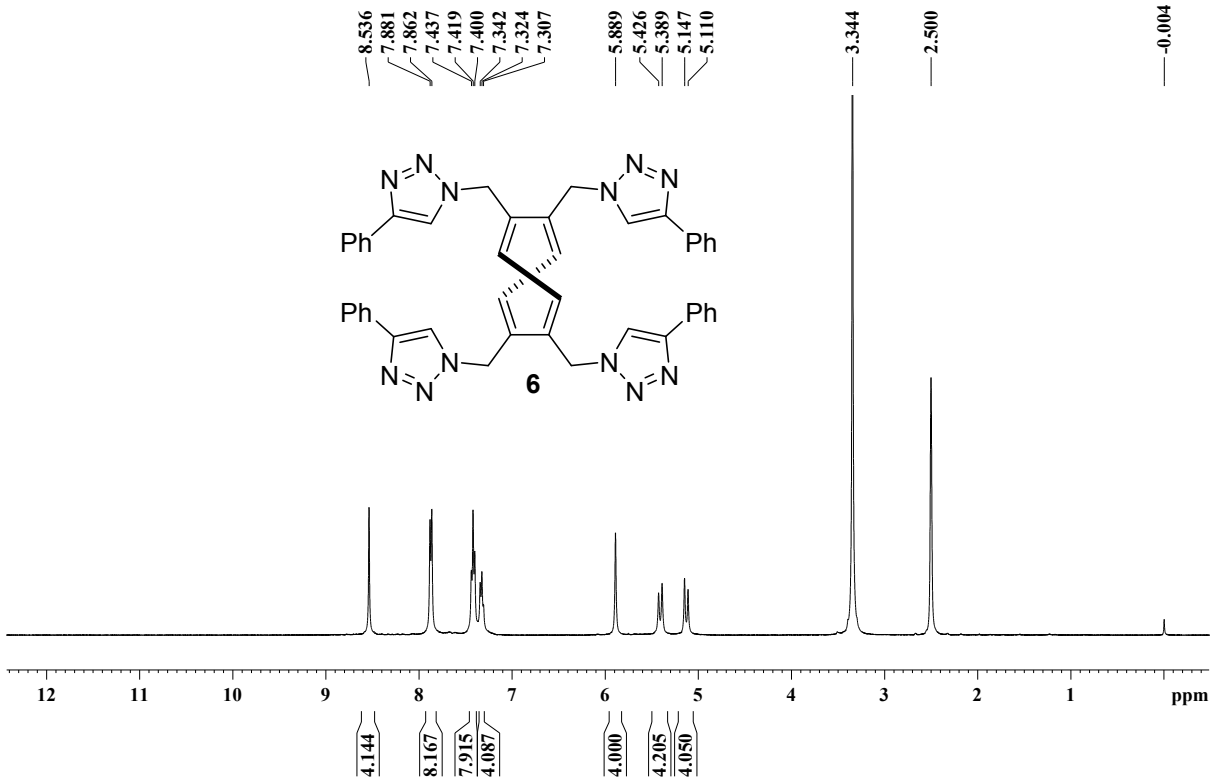


Figure 4 400 MHz ^{1}H NMR spectrum of **6** in $CDCl_3$.

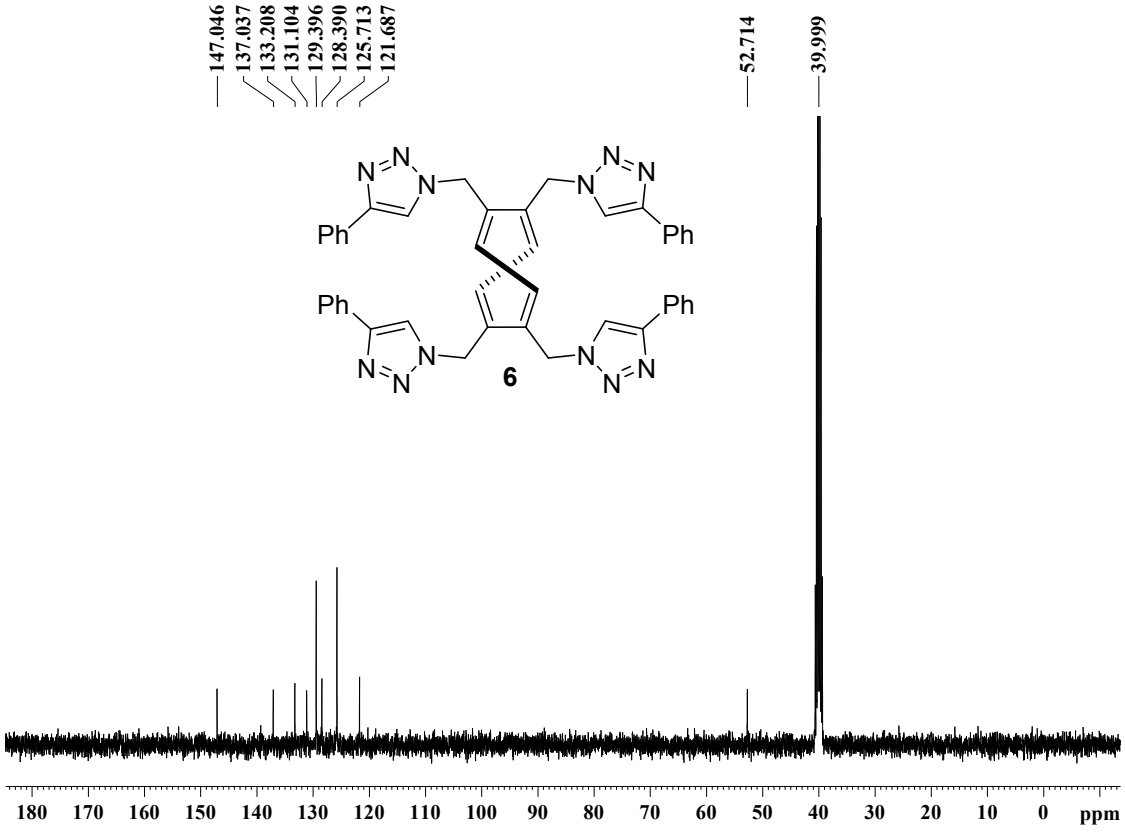


Figure 5 100 MHz ^{13}C NMR spectrum of **6** in $CDCl_3$

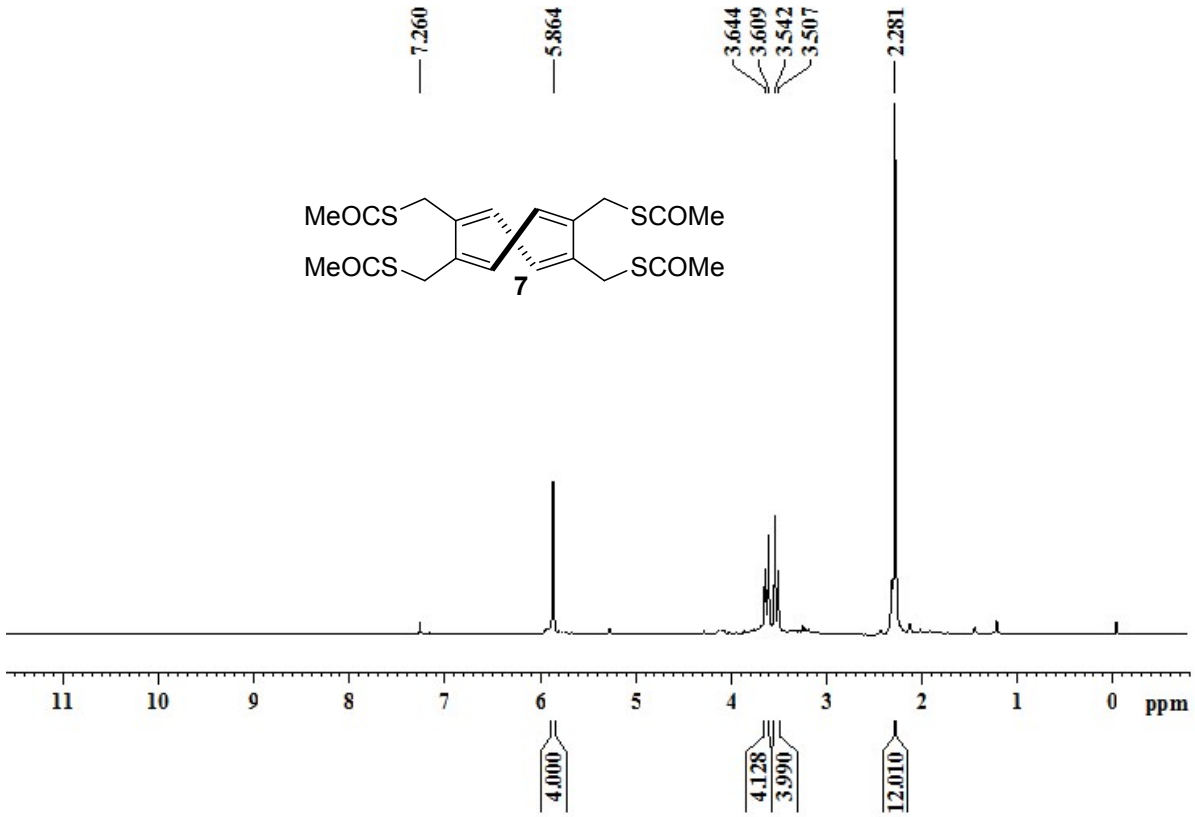


Figure 6 400 MHz ^{1}H NMR spectrum of **7** in $CDCl_3$.

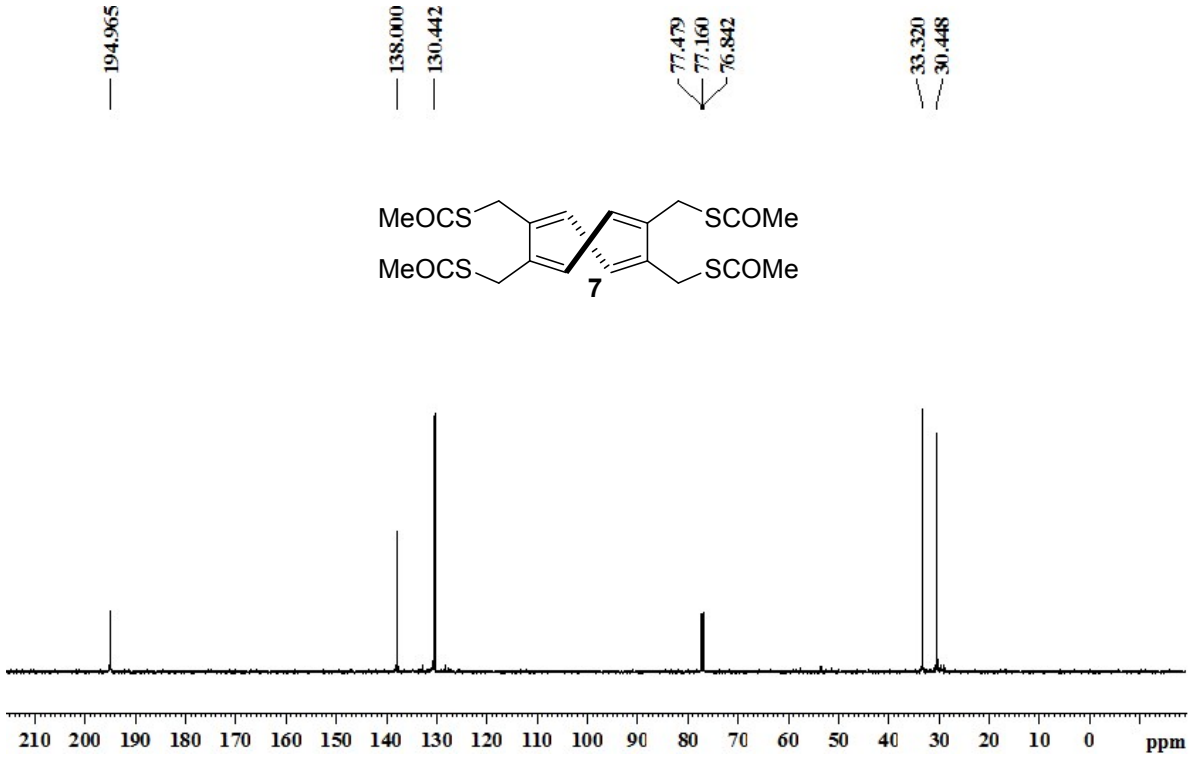


Figure 7 100 MHz ^{13}C NMR spectrum of **7** in $CDCl_3$

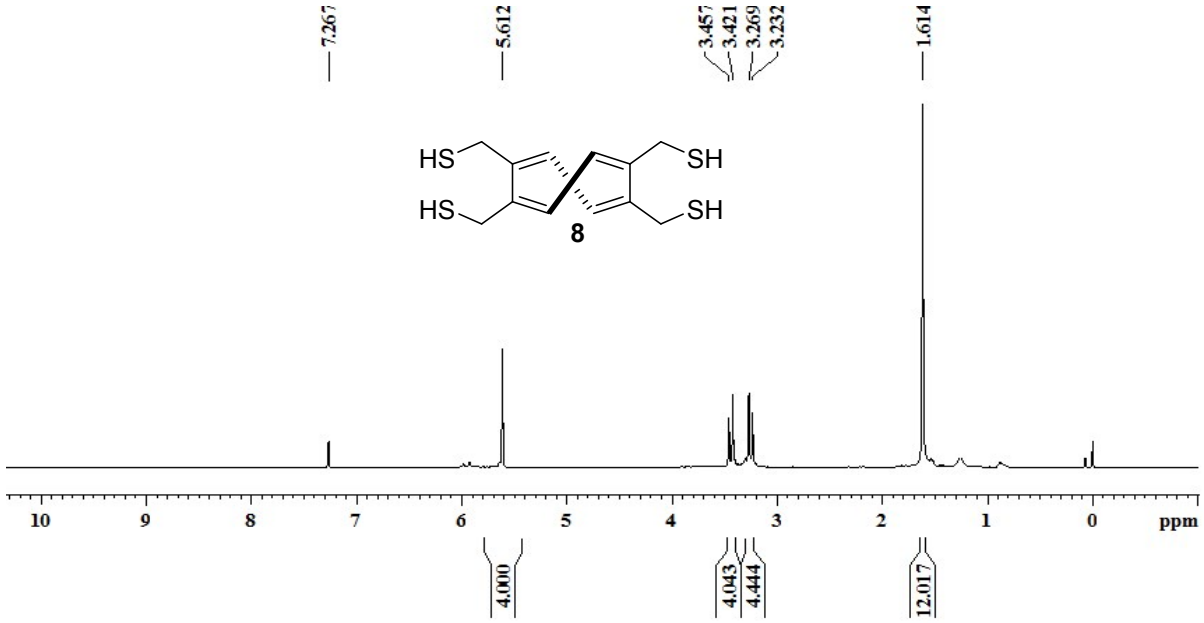


Figure 8 400 MHz ^{1}H NMR spectrum of **8** in $CDCl_3$.

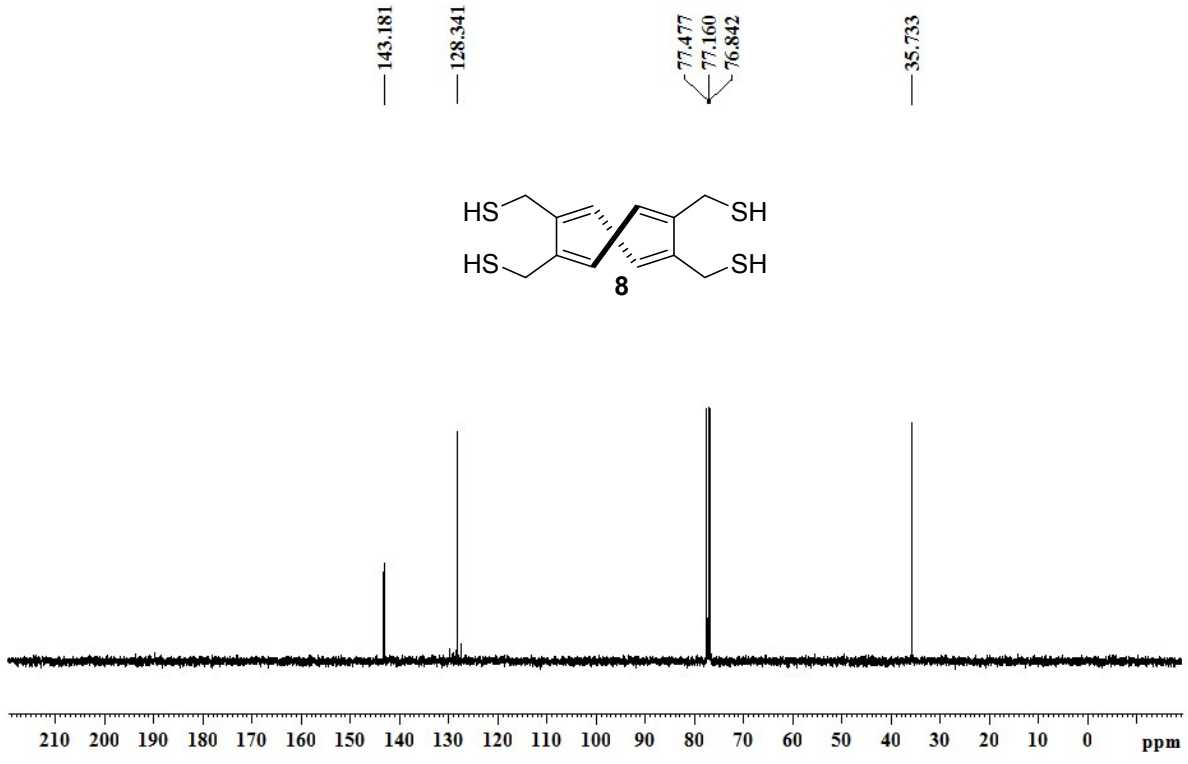


Figure 9 100 MHz ^{13}C NMR spectrum of **8** in $CDCl_3$

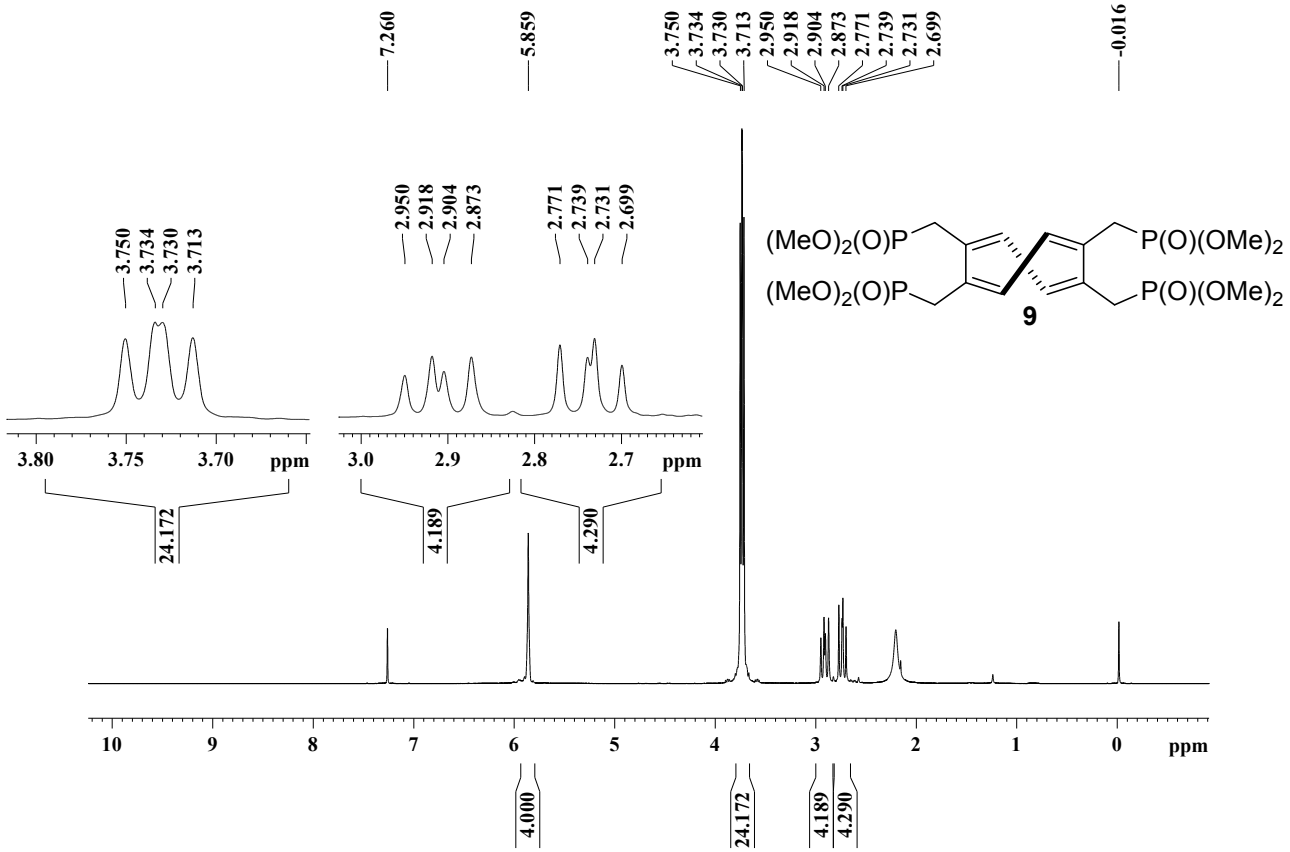


Figure 10 400 MHz ^{1}H NMR spectrum of **9** in $CDCl_3$.

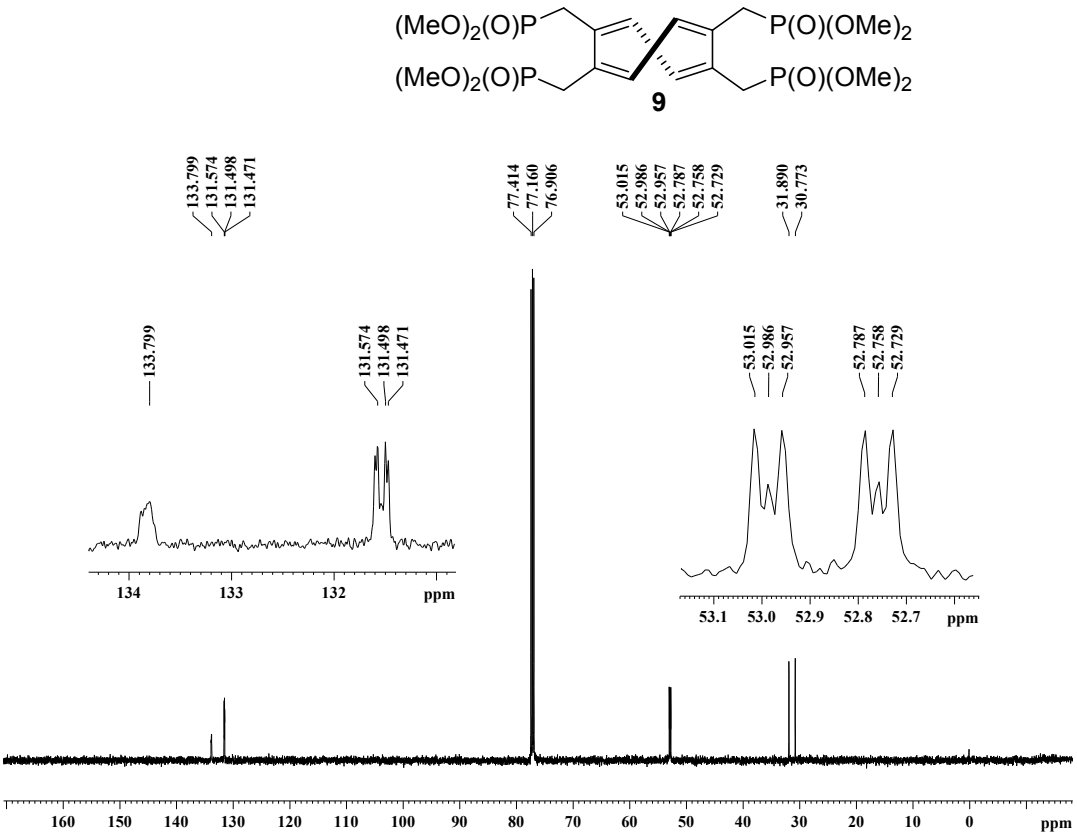


Figure 11 100 MHz ^{13}C NMR spectrum of **9** in $CDCl_3$

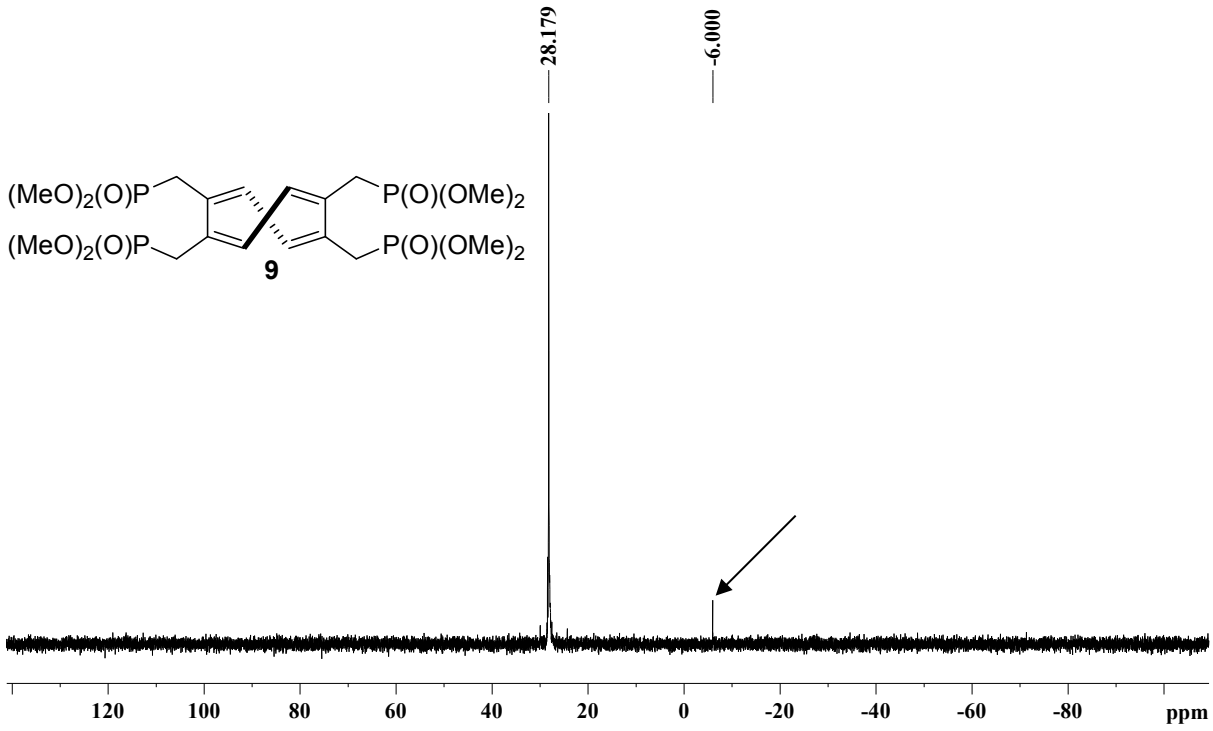


Figure 12 202 MHz ^{31}P NMR of **9** in $CDCl_3$ with PPh_3 as internal standard (pointed by the arrow)

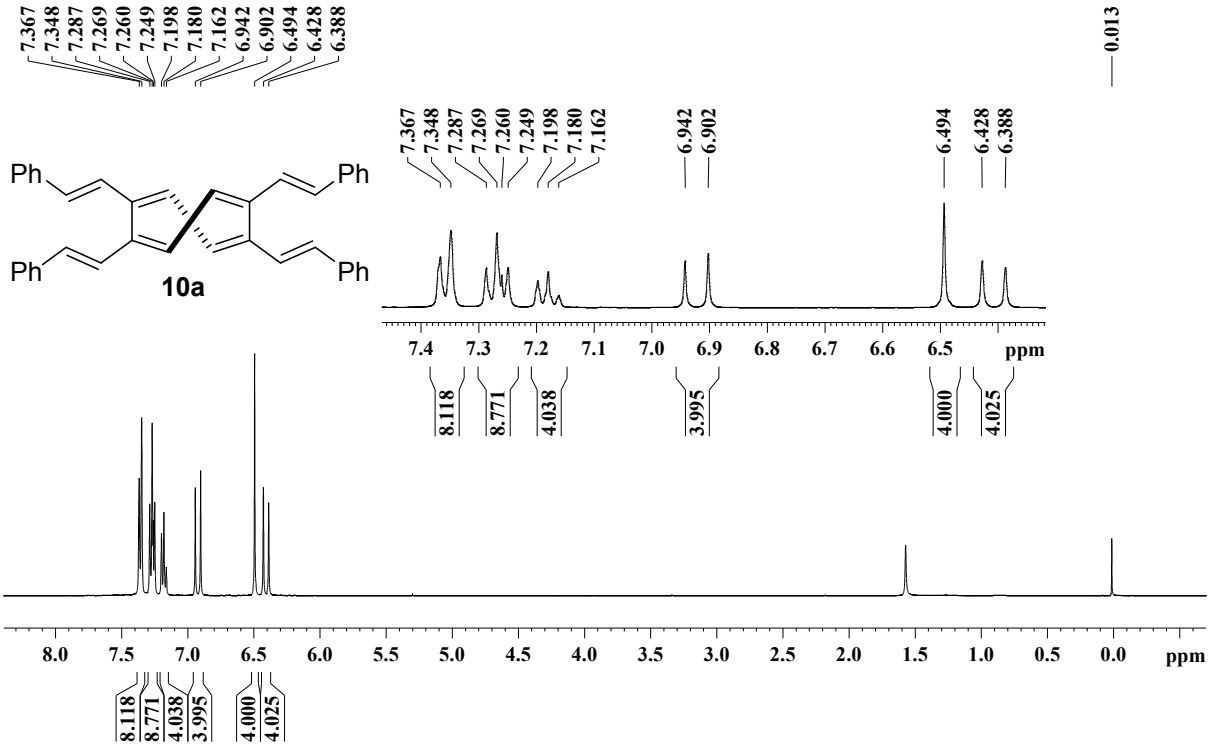


Figure 13 400 MHz ^{1}H NMR spectrum of **10a** in $CDCl_3$.

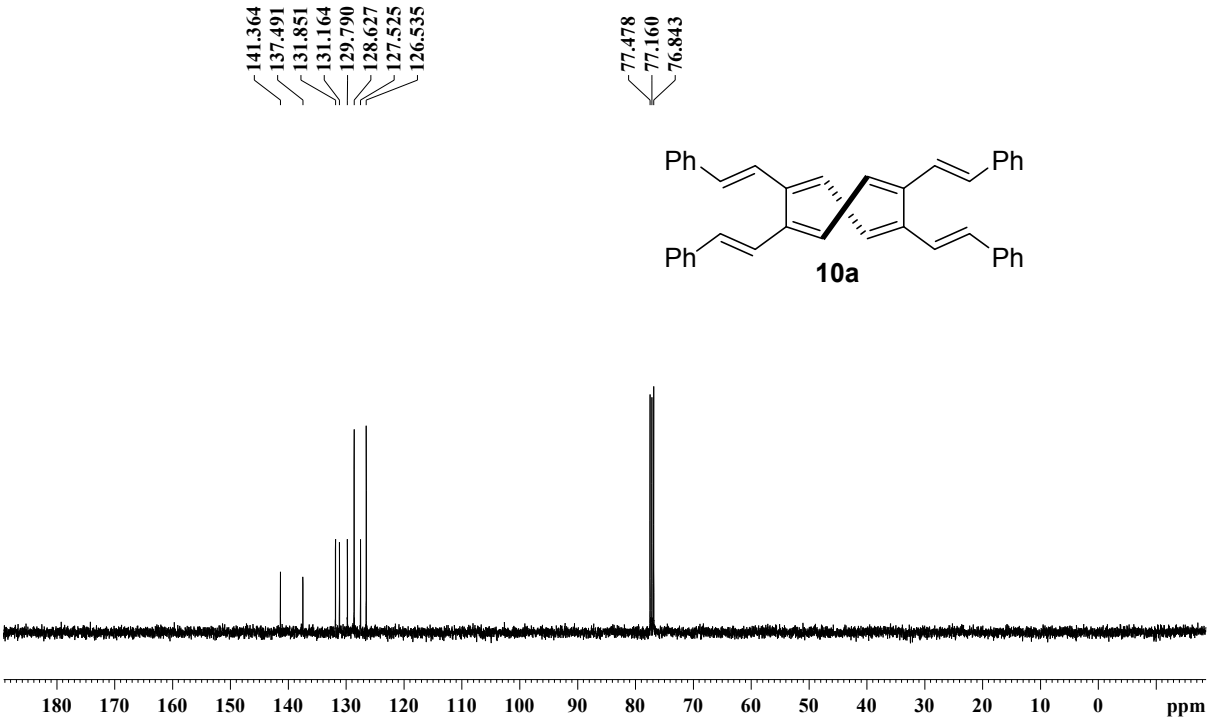


Figure 14 100 MHz ^{13}C NMR spectrum of **10a** in $CDCl_3$

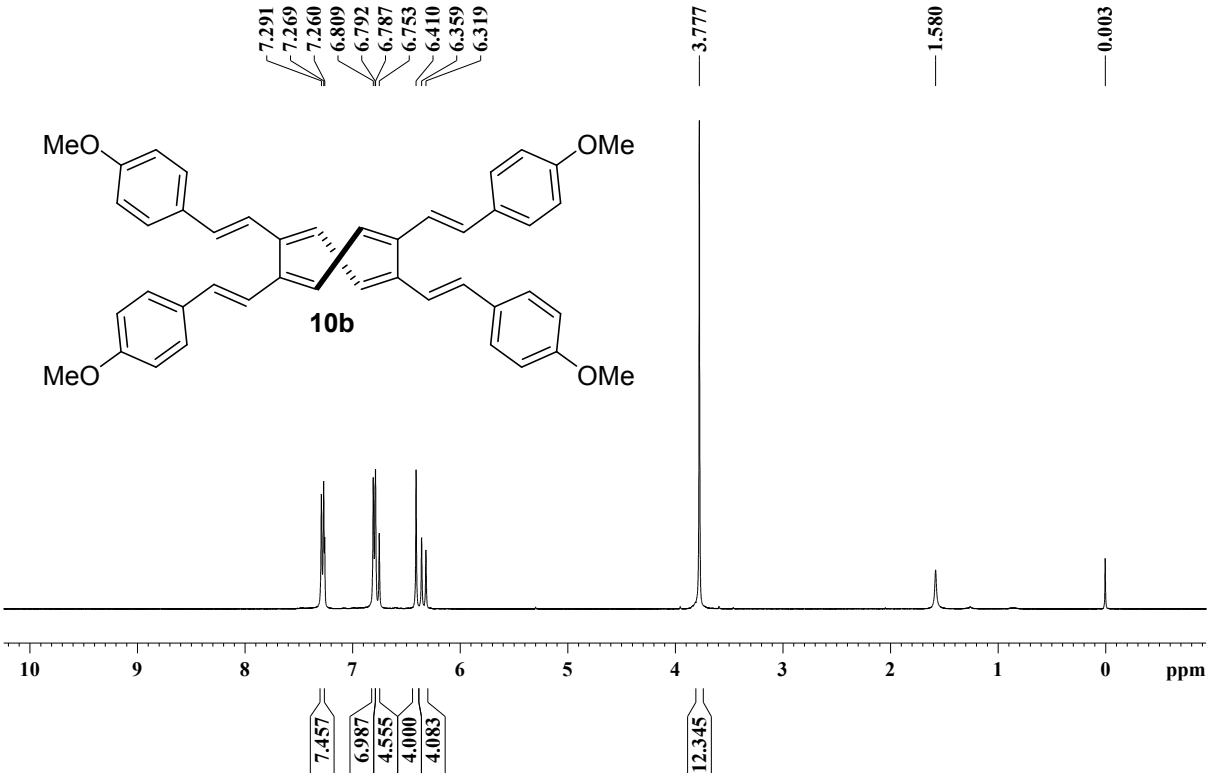


Figure 15 400 MHz ^{1}H NMR spectrum of **10b** in $CDCl_3$.

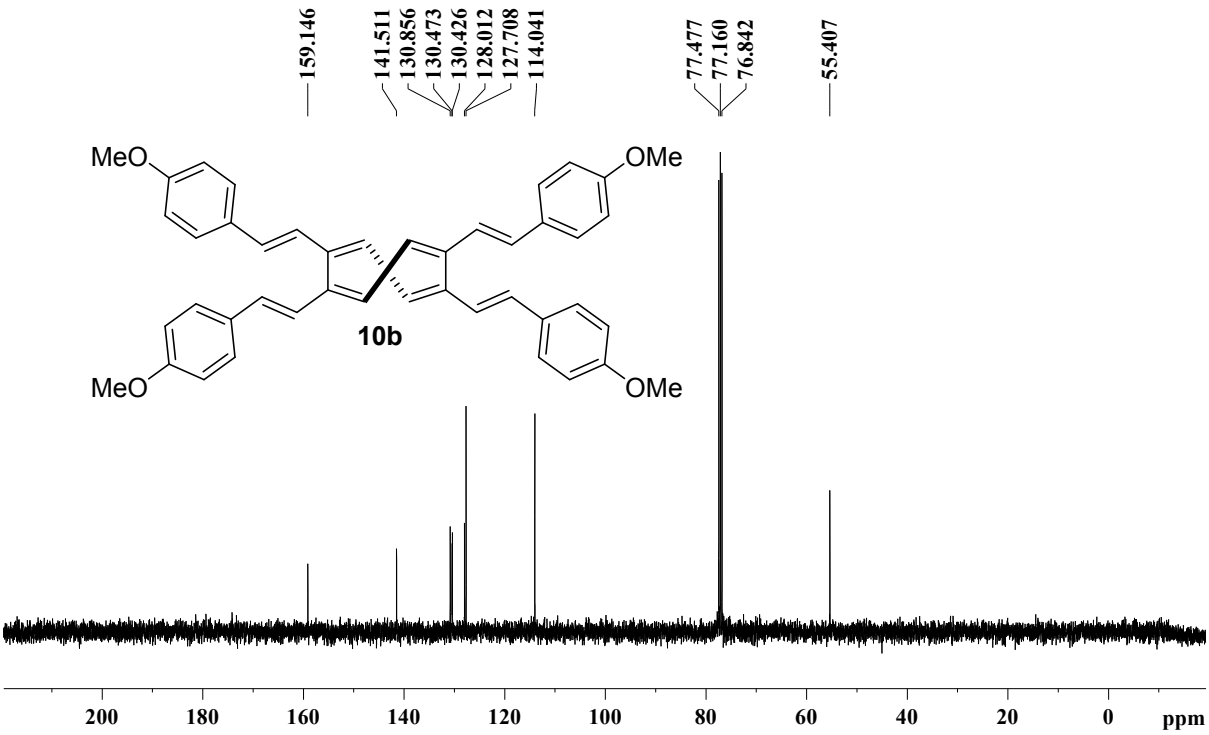


Figure 16 100 MHz ^{13}C NMR spectrum of **10b** in $CDCl_3$

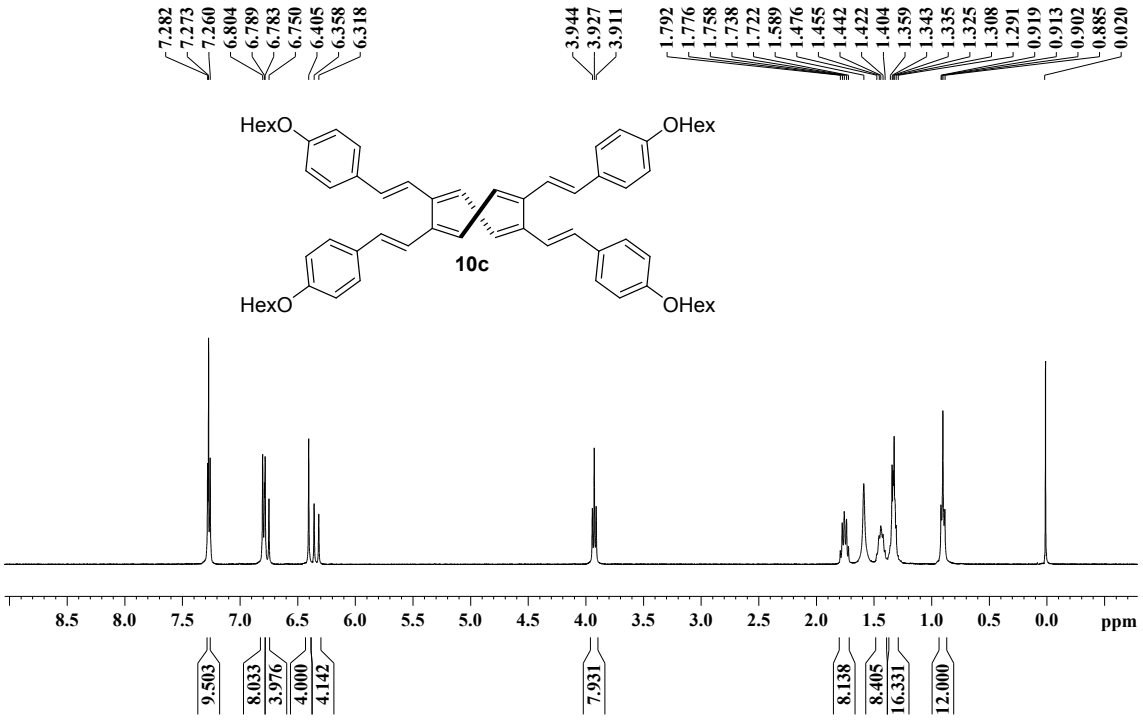


Figure 17 400 MHz ^{1}H NMR spectrum of **10c** in $CDCl_3$.

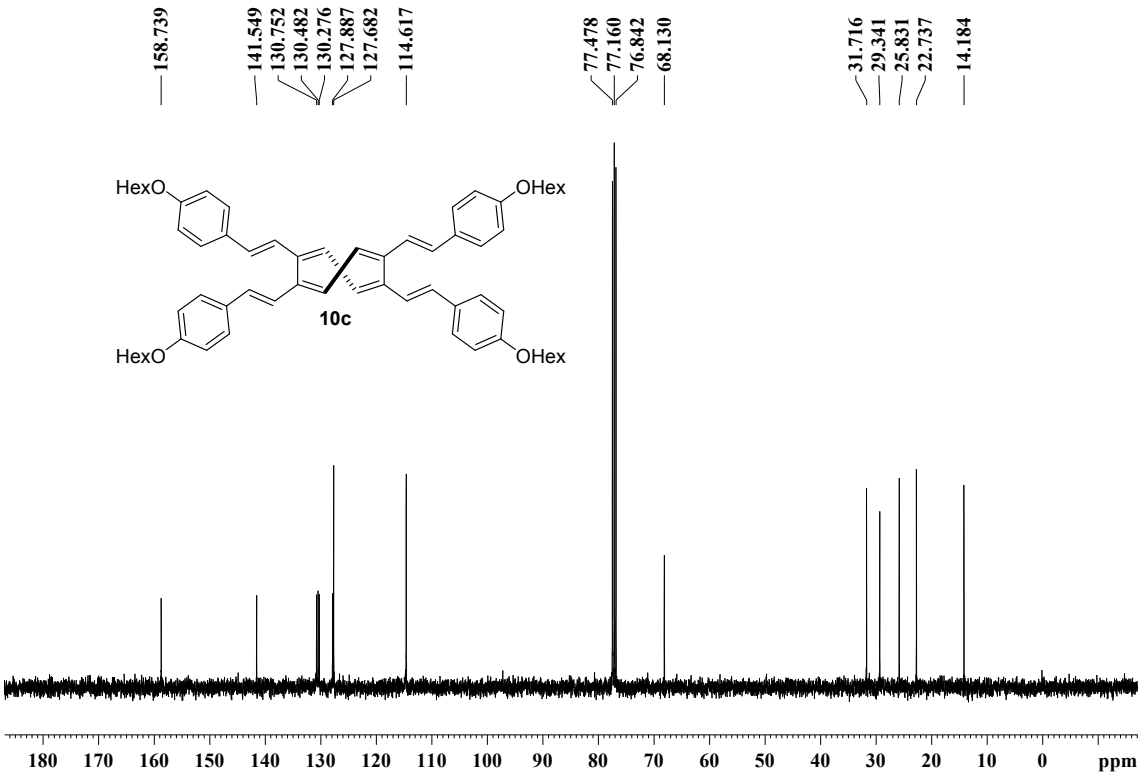


Figure 18 100 MHz ^{13}C NMR spectrum of **10c** in $CDCl_3$

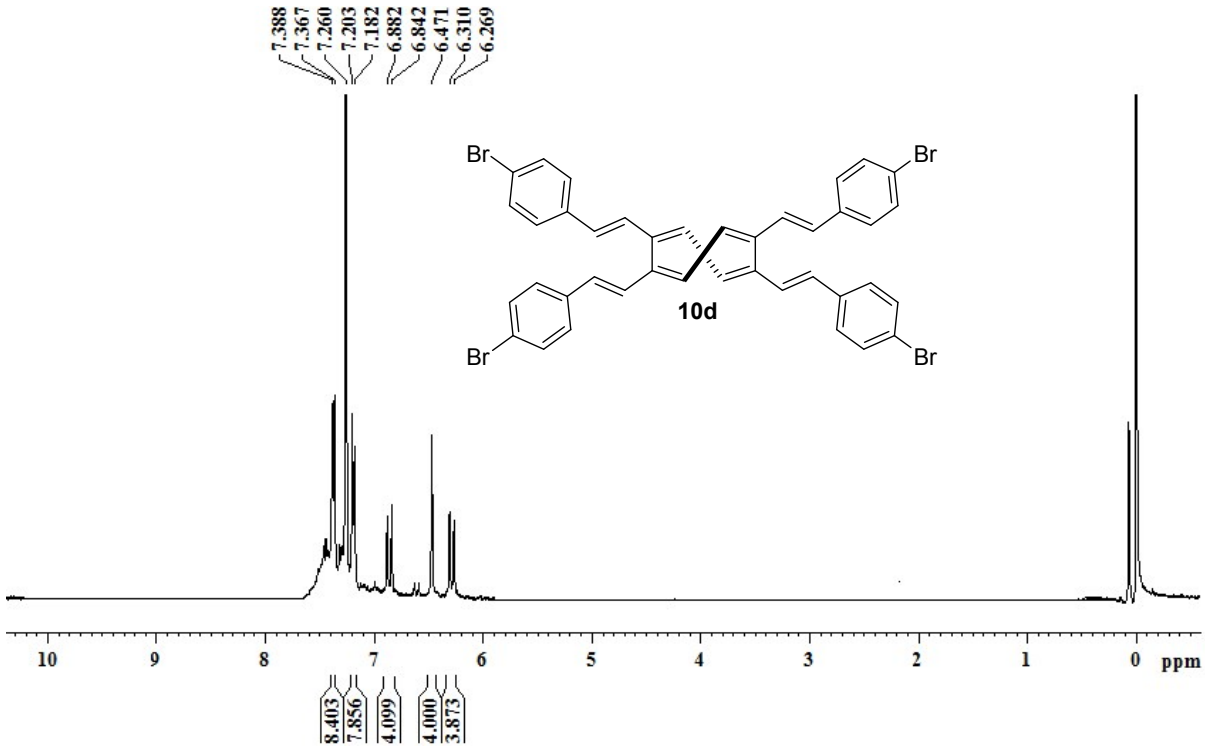


Figure 19 400 MHz ^{1}H NMR spectrum of **10d** in $CDCl_3$.

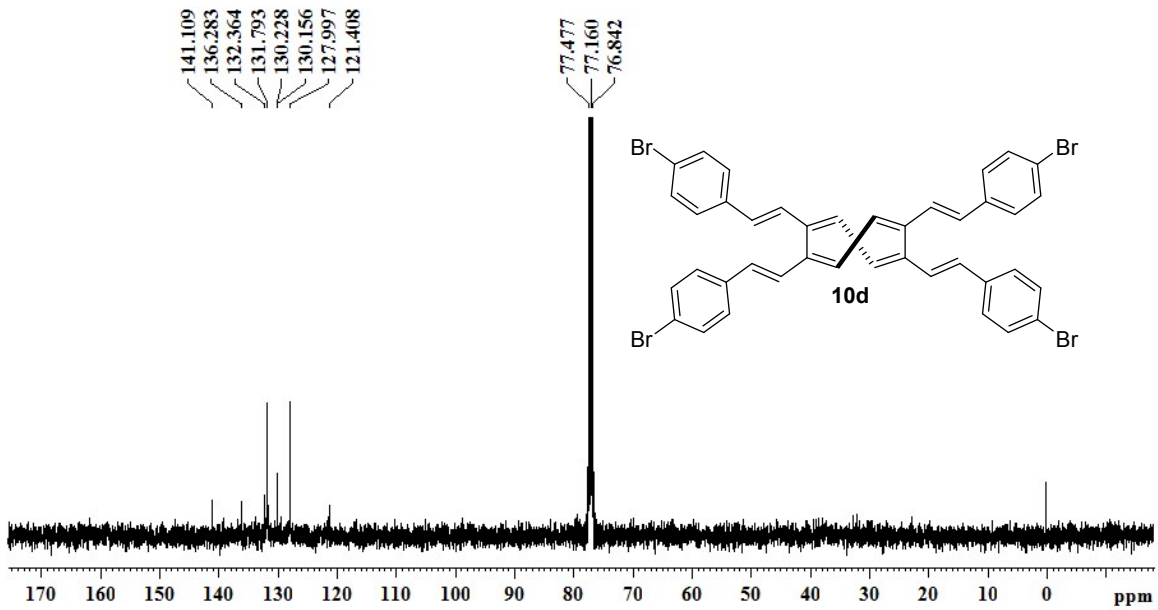


Figure 20 100 MHz ^{13}C NMR spectrum of **10d** in $CDCl_3$

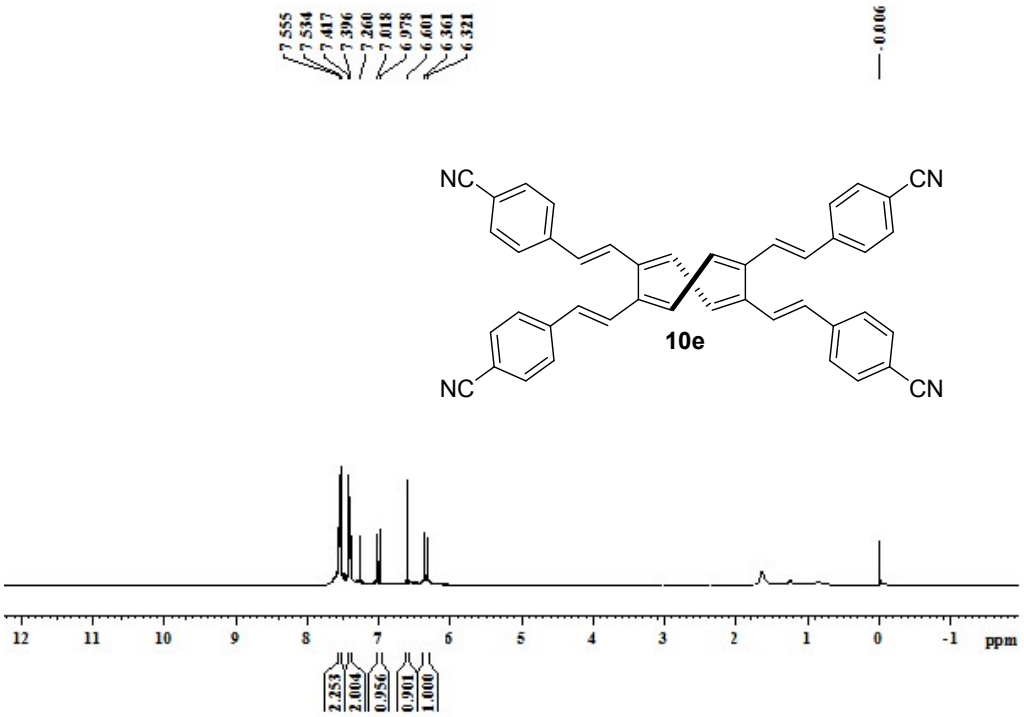


Figure 21 400 MHz ^{1}H NMR spectrum of **10e** in $CDCl_3$.

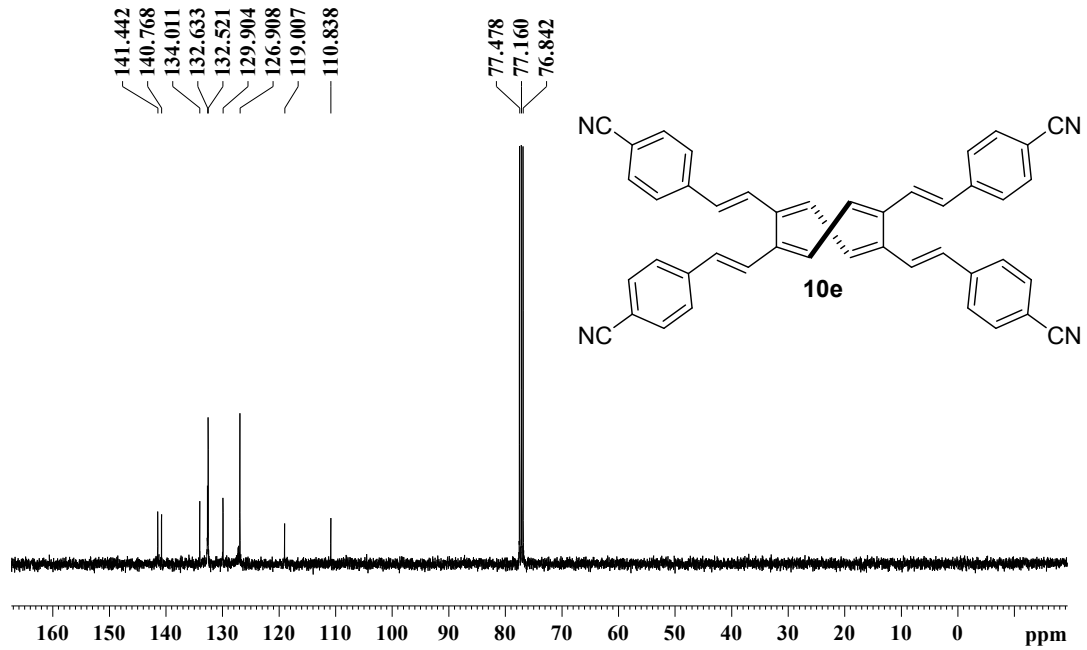


Figure 22 100 MHz ^{13}C NMR spectrum of **10e** in $CDCl_3$

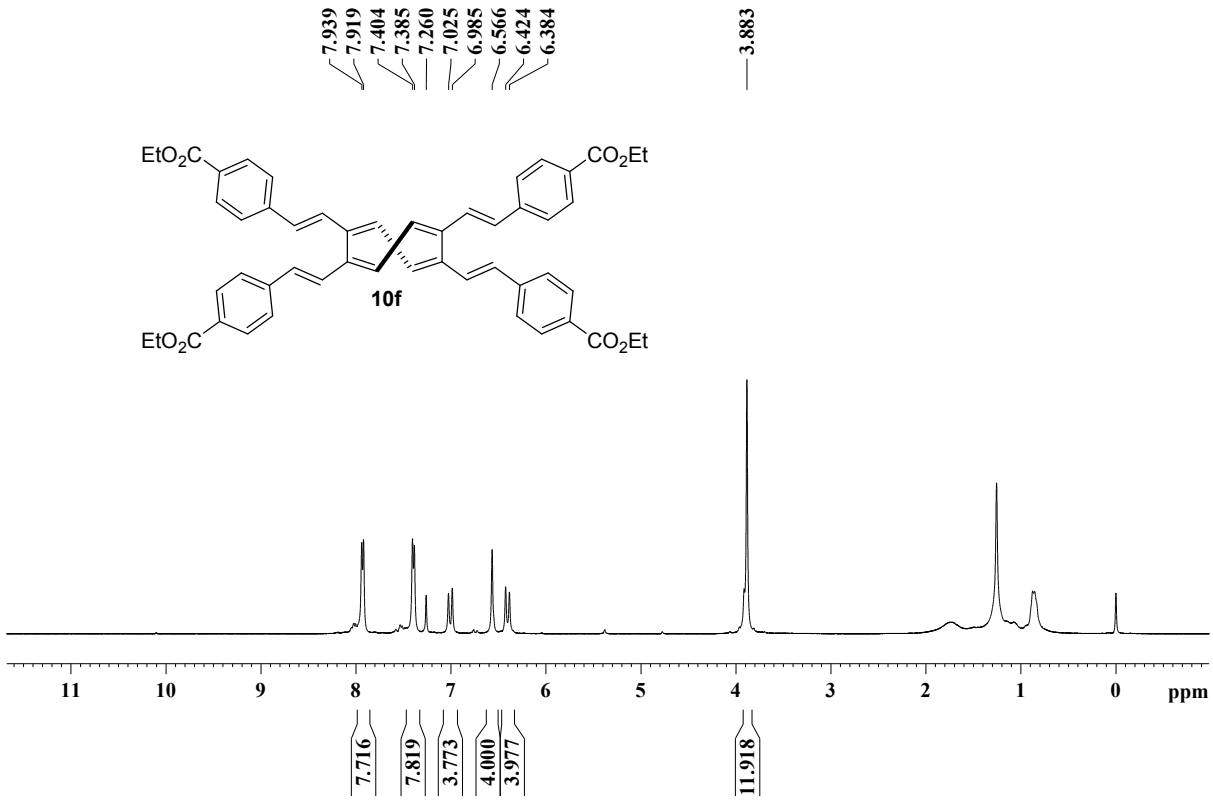


Figure 23 400 MHz ^{1}H NMR spectrum of **10f** in $CDCl_3$.

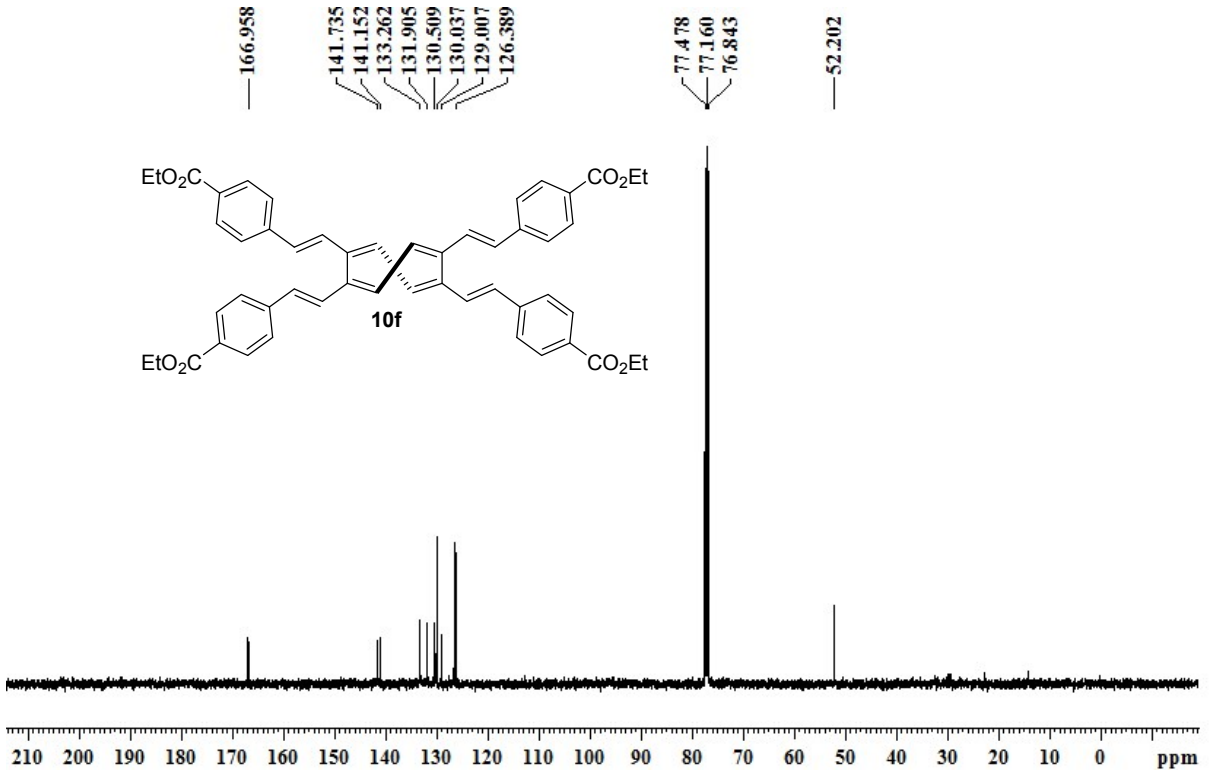


Figure 24 100 MHz ^{13}C NMR spectrum of **10f** in $CDCl_3$

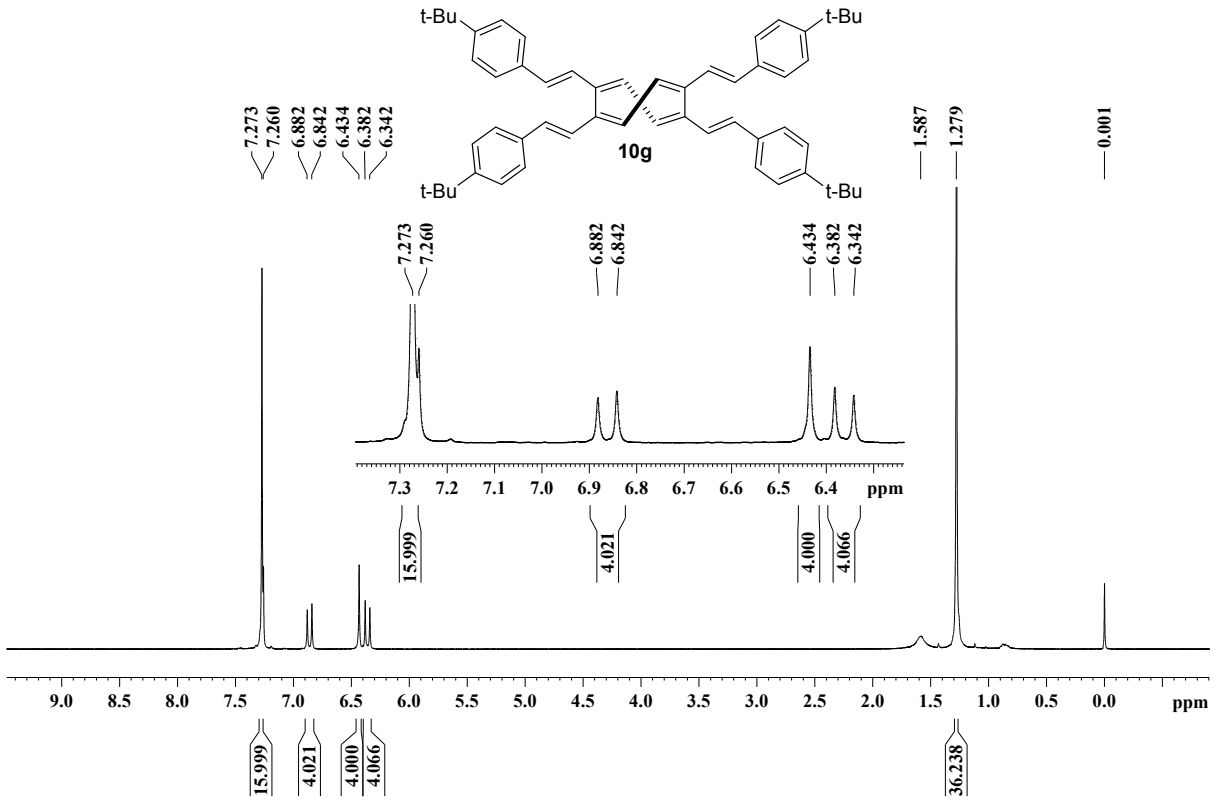


Figure 25 400 MHz ^{1}H NMR spectrum of **10g** in $CDCl_3$.

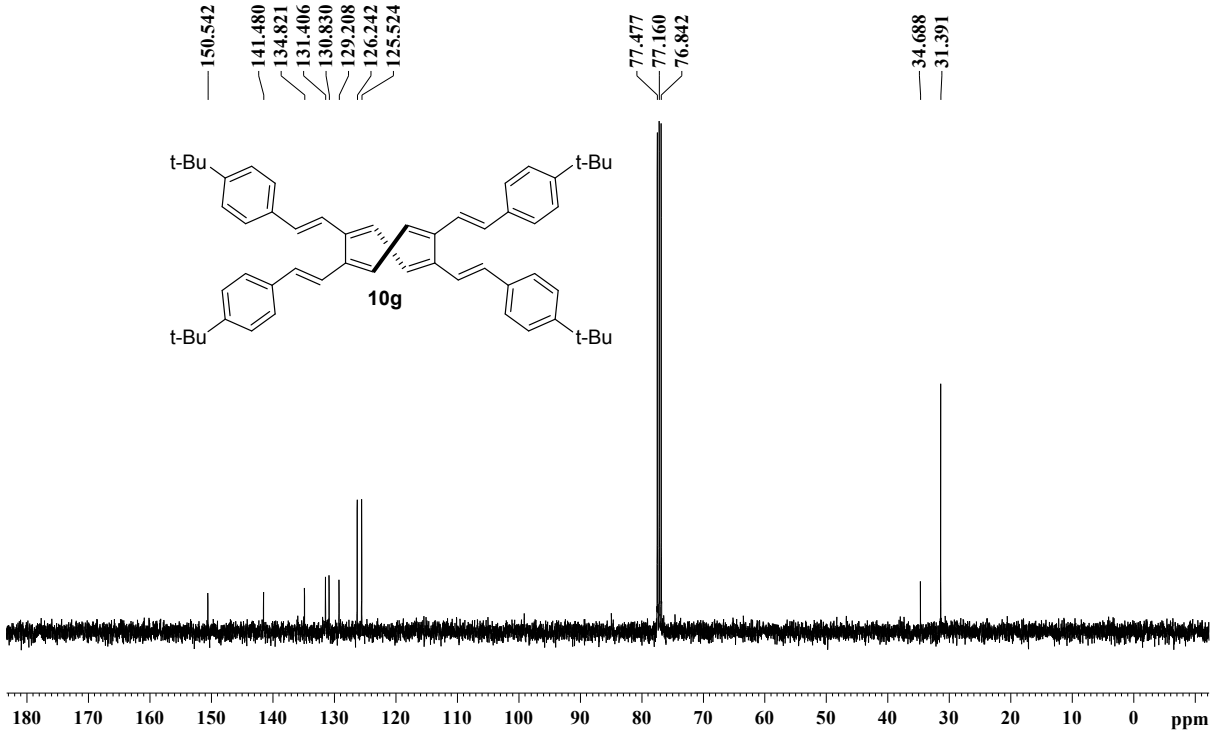


Figure 26 100 MHz ^{13}C NMR spectrum of **10g** in $CDCl_3$

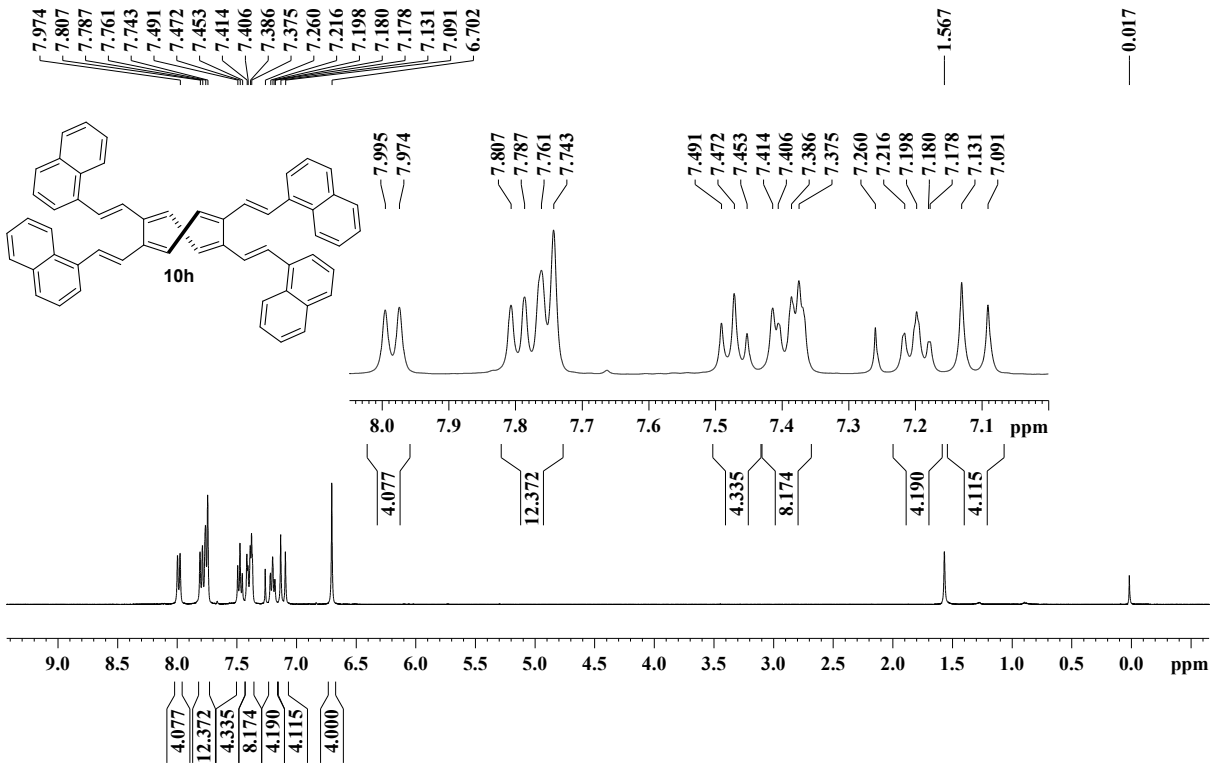


Figure 27 400 MHz ^{1}H NMR spectrum of **10h** in $CDCl_3$.

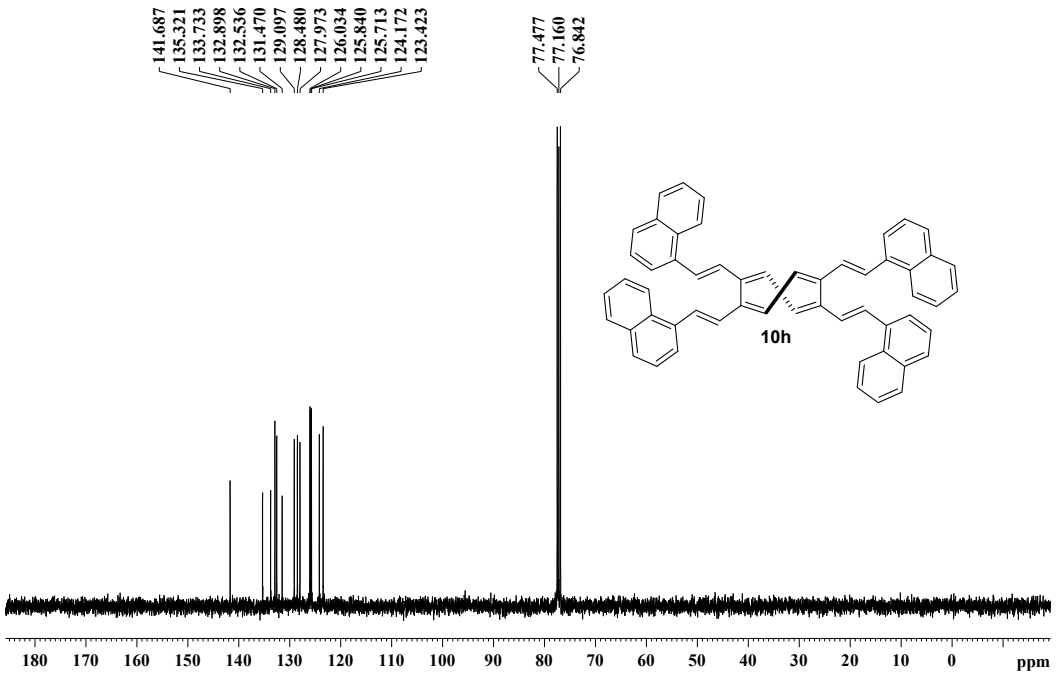


Figure 28 100 MHz ^{13}C NMR spectrum of **10h** in $CDCl_3$

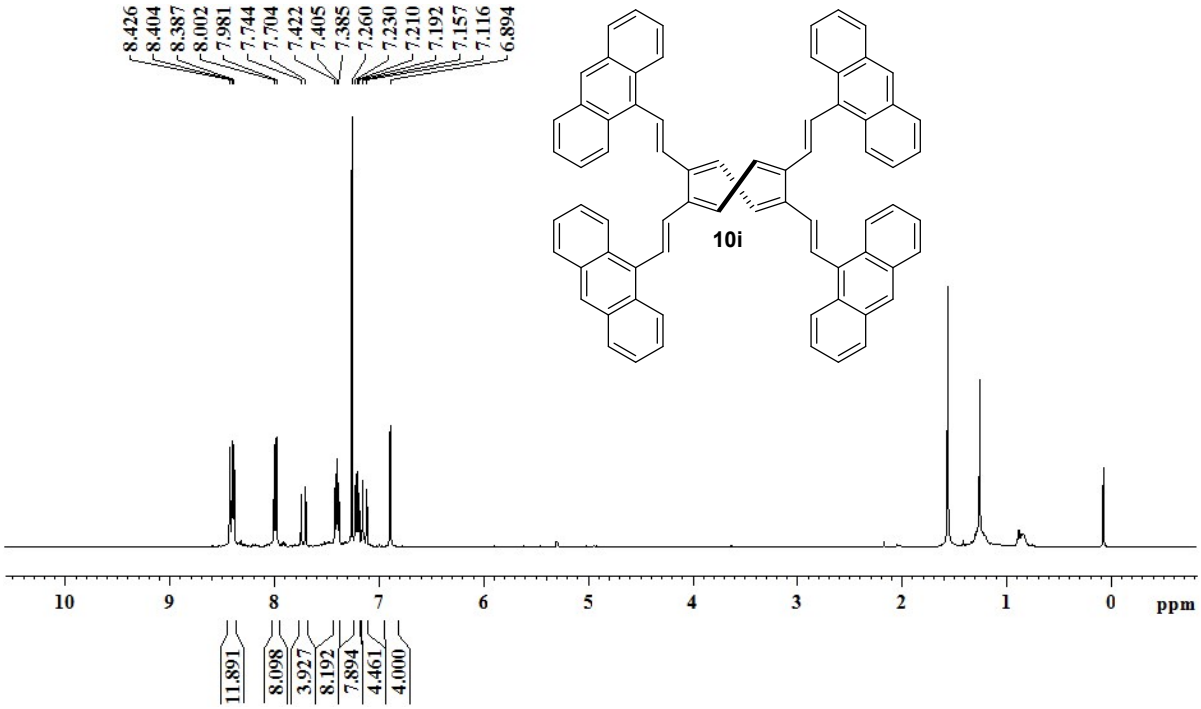


Figure 29 400 MHz ^{1}H NMR spectrum of **10i** in $CDCl_3$.

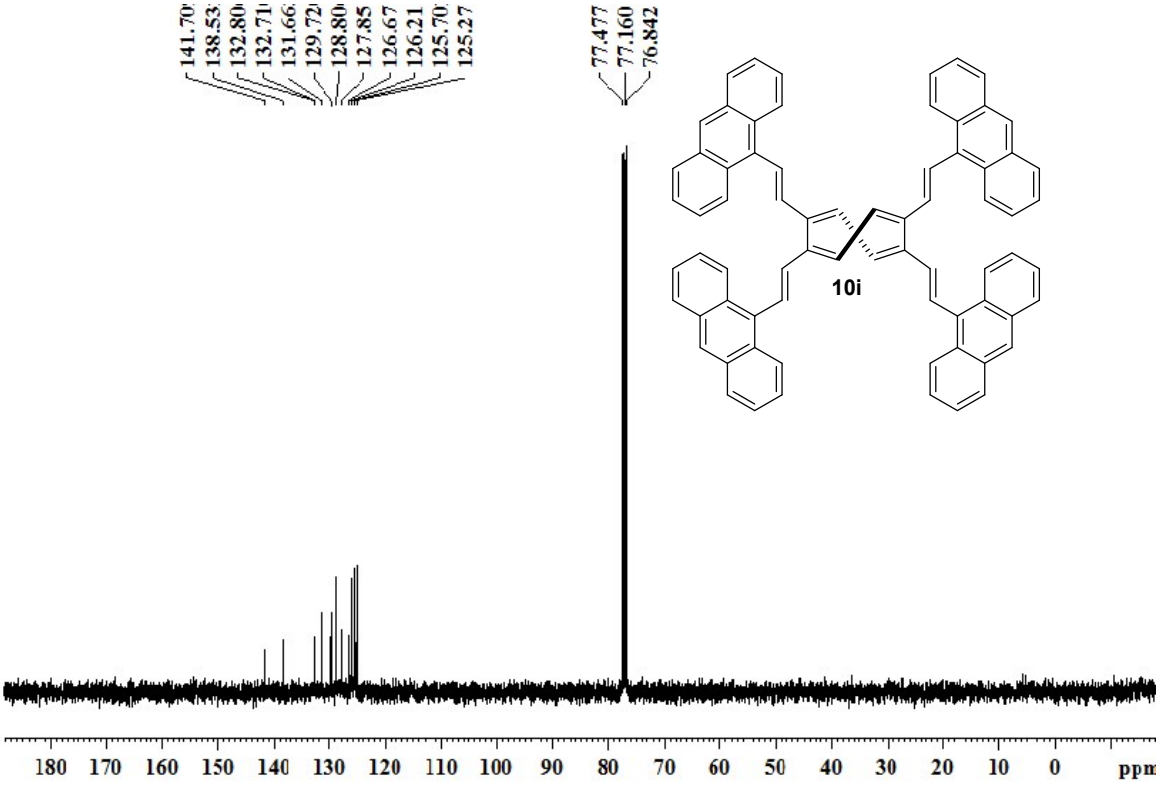


Figure 30 100 MHz ^{13}C NMR spectrum of **10i** in $CDCl_3$

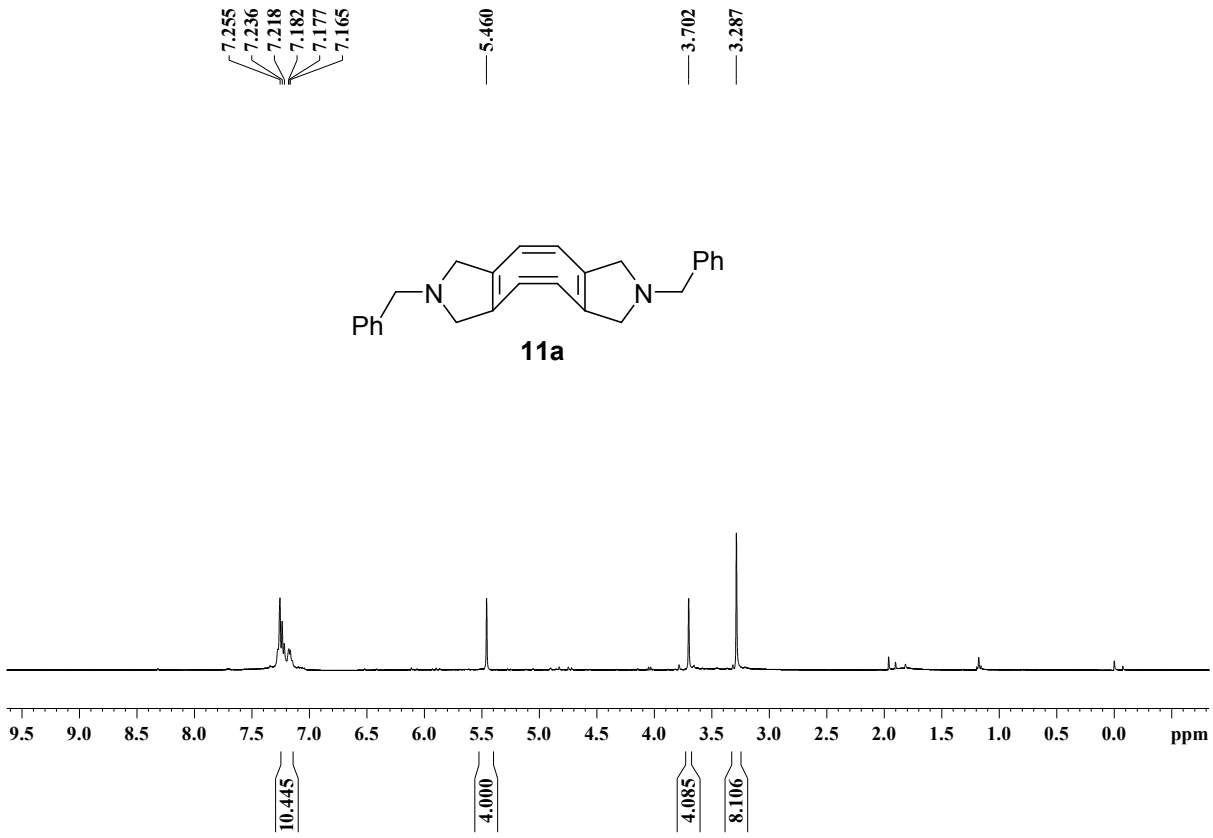


Figure 31 400 MHz ^{1}H NMR spectrum of **11a** in $CDCl_3$.

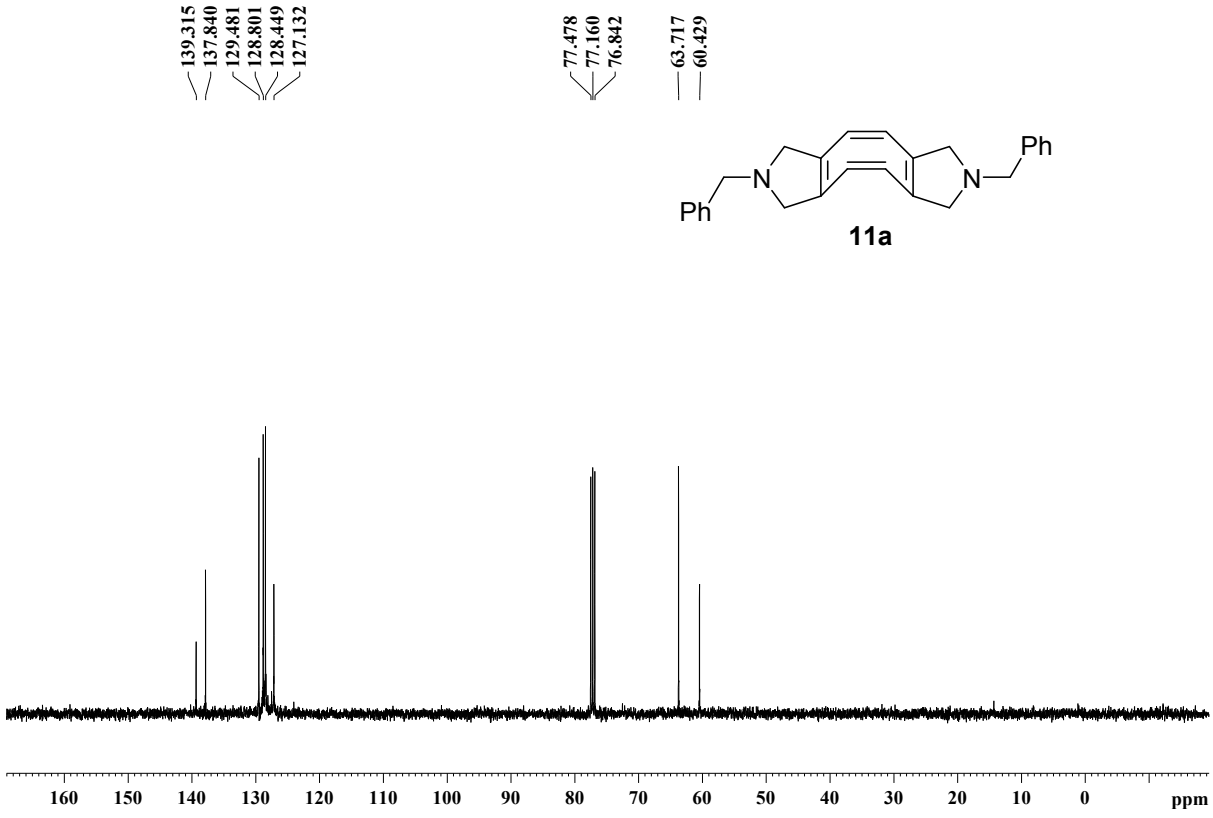


Figure 32 100 MHz ^{13}C NMR spectrum of **11a** in $CDCl_3$

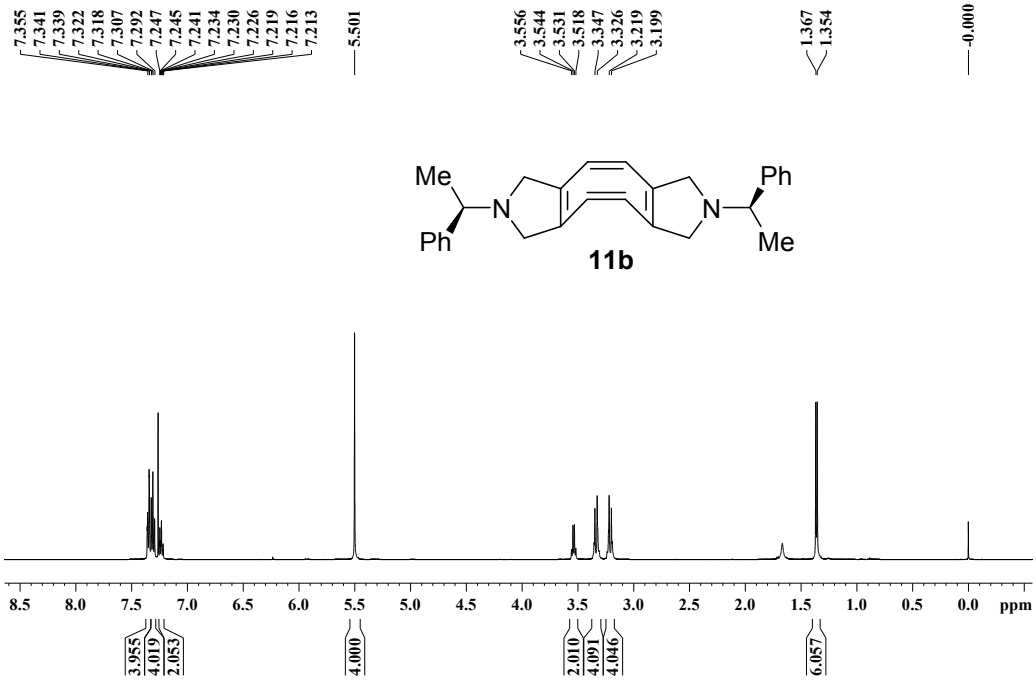


Figure 33 400 MHz ^{1}H NMR spectrum of **11b** in $CDCl_3$.

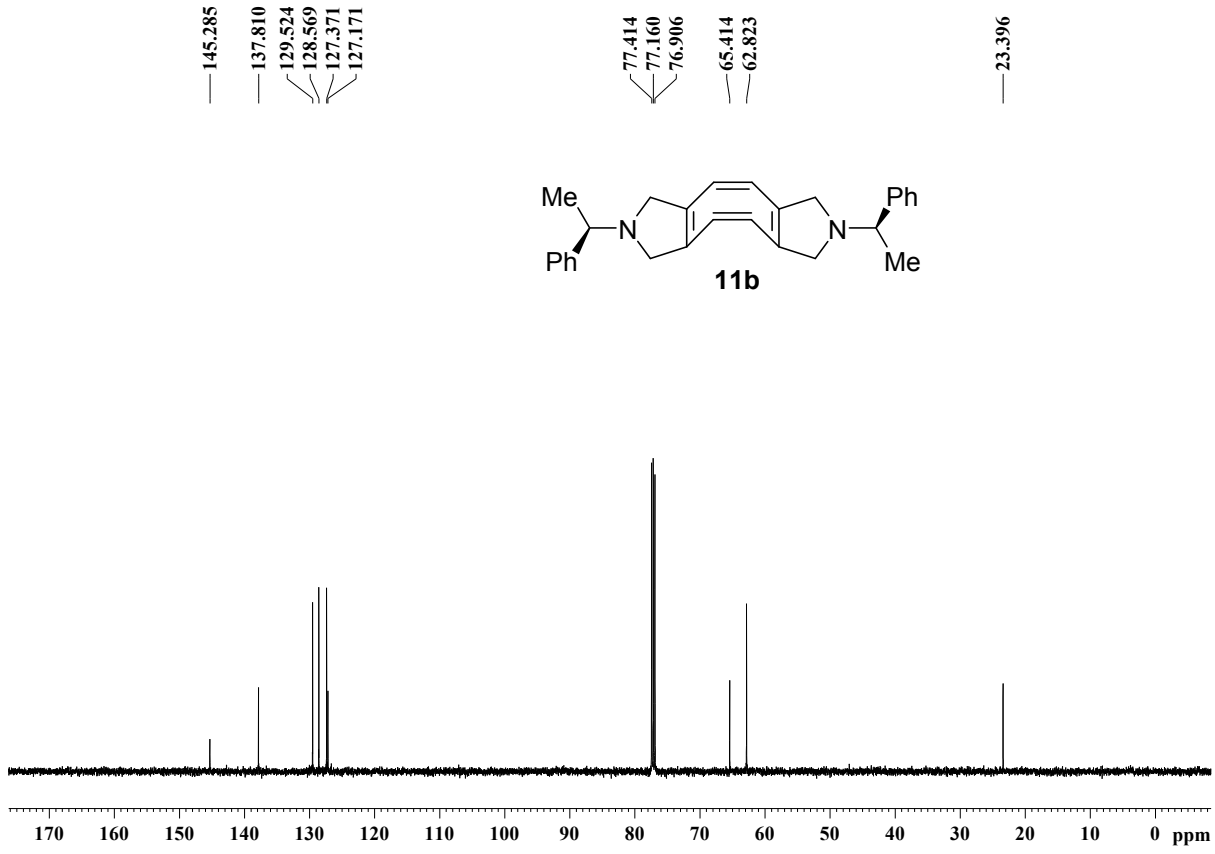


Figure 34 100 MHz ^{13}C NMR spectrum of **11b** in $CDCl_3$

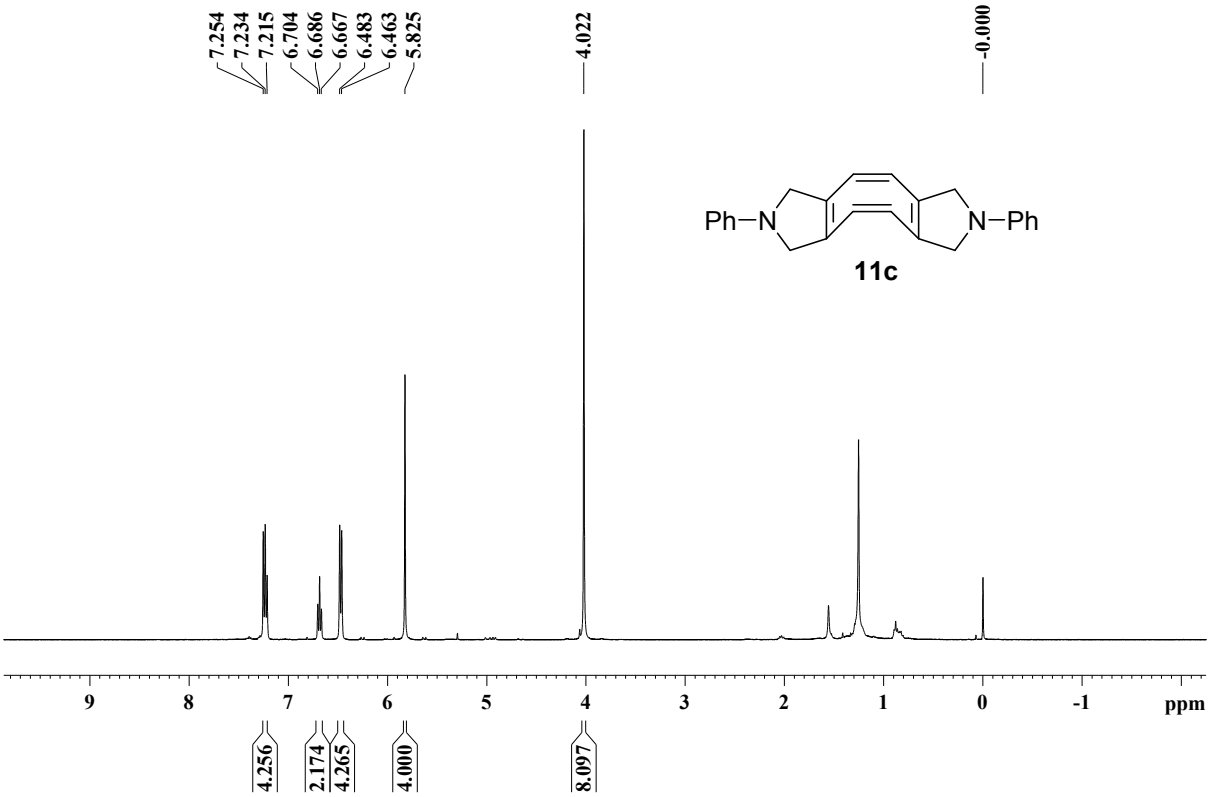


Figure 35 400 MHz ^{1}H NMR spectrum of **11c** in $CDCl_3$.

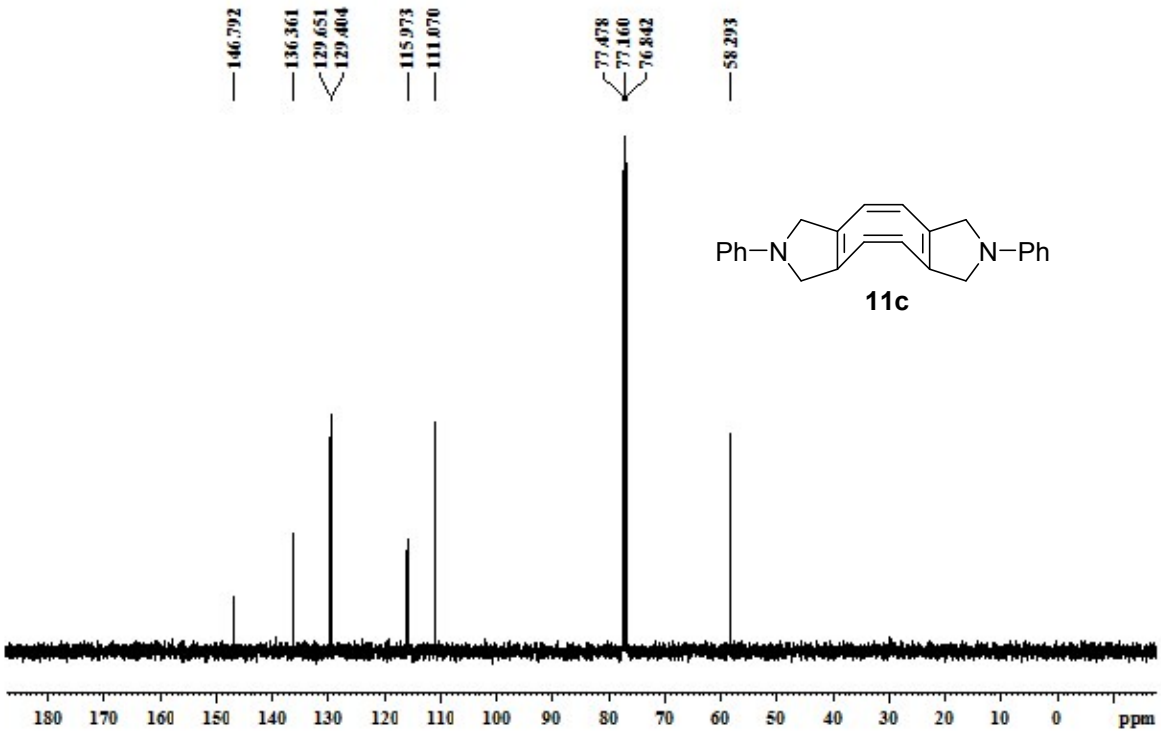


Figure 36 100 MHz ^{13}C NMR spectrum of **11c** in $CDCl_3$

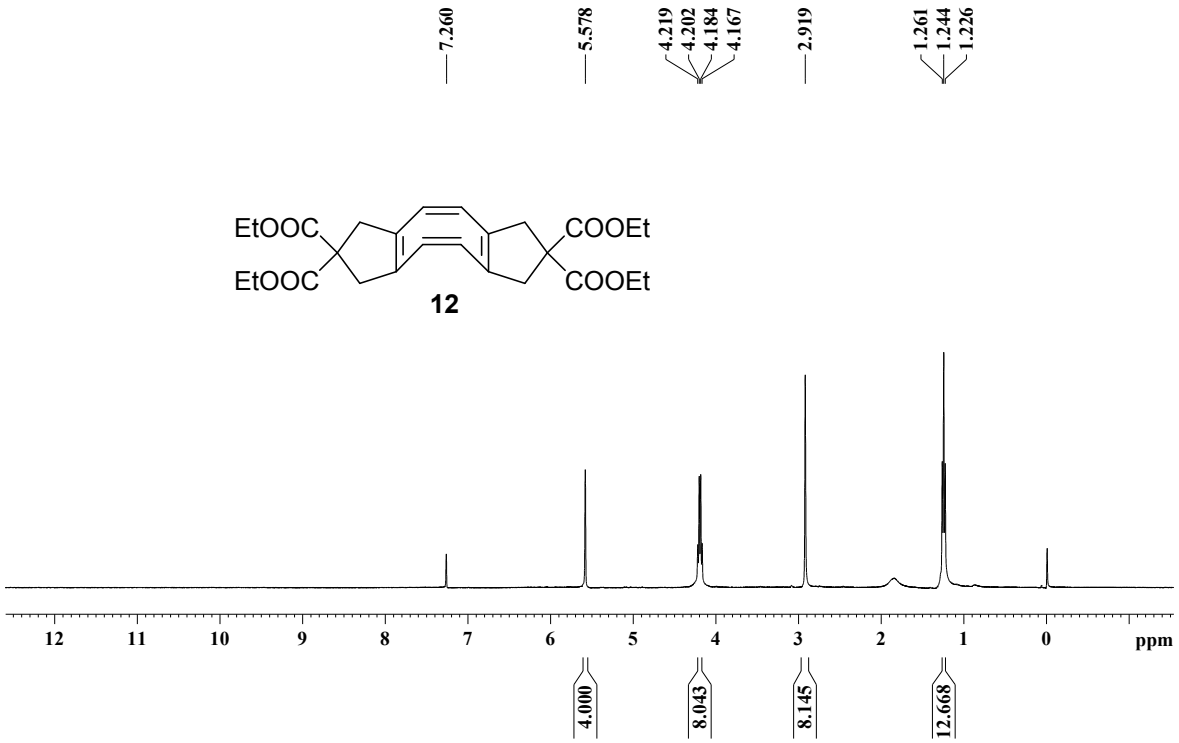


Figure 37 400 MHz ^{1}H NMR spectrum of **12** in $CDCl_3$.

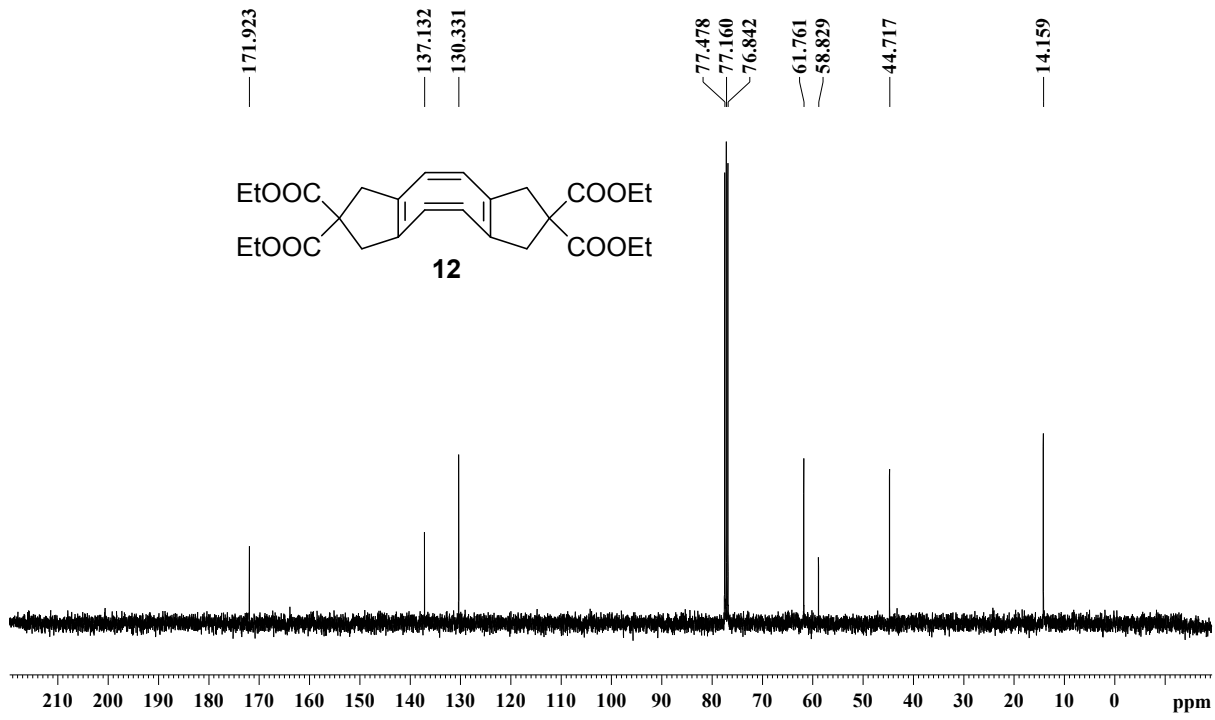


Figure 38 100 MHz ^{13}C NMR spectrum of **12** in $CDCl_3$

Single crystal X-ray crystallographic data:

Single crystals of Compounds **1, 2, 3, 6, 9, 10a, 11b** suitable for XRD studies have been taken from the synthesized compounds. The crystals of compounds **1, 2, 3, 6, 9, 10a, 11b** were grown by slow evaporation of solvents- methanol, chloroform, chloroform/hexane(1:1), chloroform/acetone(1:1), dichloromethane, ethylacetate/hexane (1:1), chloroform respectively at room temperature over a period of 1-4 days.

X-ray data of **1, 2, 3, 6, 9, 10a, 11b** were collected by Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with graphite monochromatic Mo (Kα) (λ = 0.7107 A) radiation source. The crystals were solved by direct methods using Bruker SHELXS (Sheldrick, 1997). The Structure was refined using the Bruker SHELXTL (Version 6.12) software package.

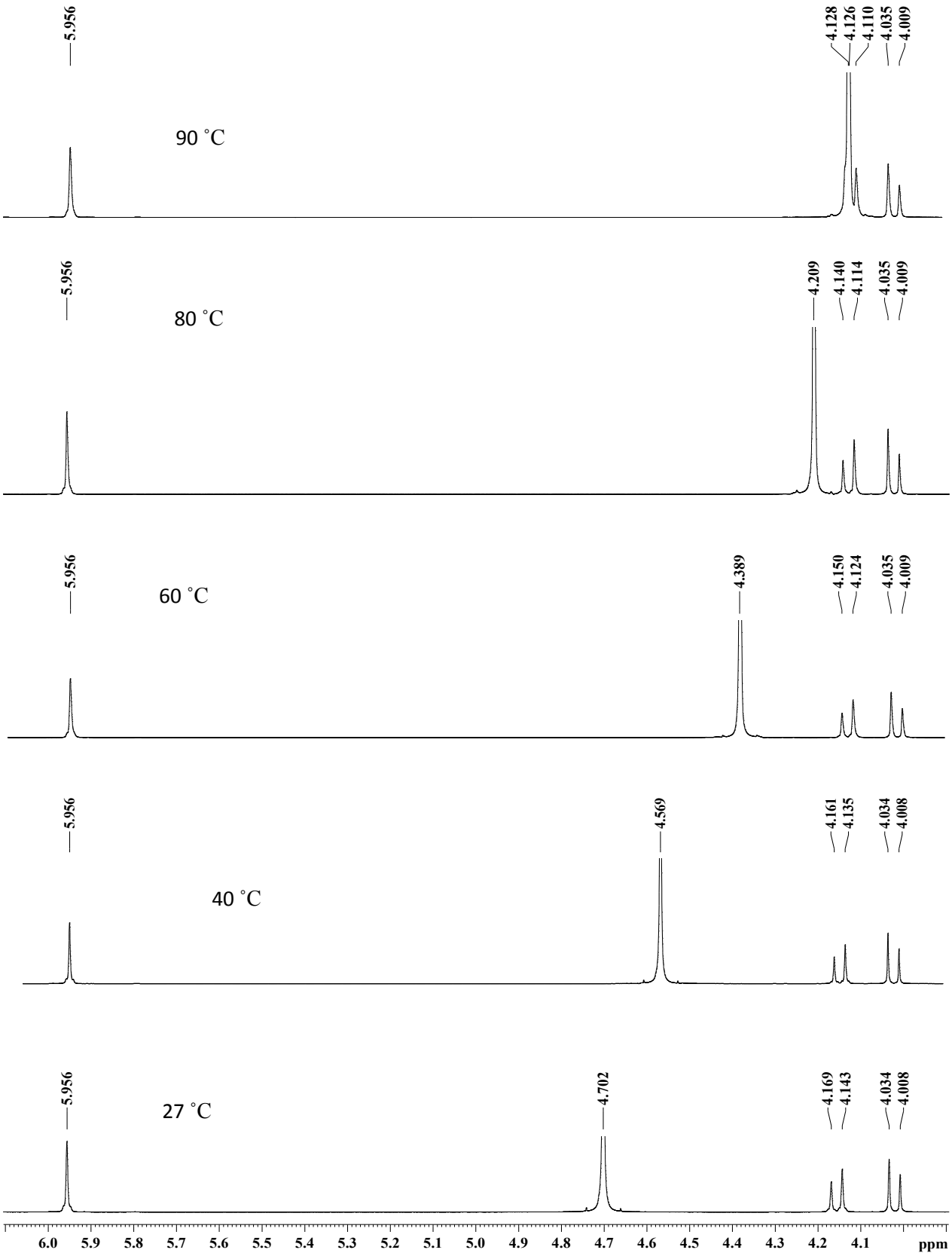
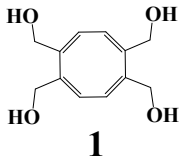


Figure 39 VT-NMR (^{1}H NMR, 400 MHz, in D_2O) of tetra alcohol **1**

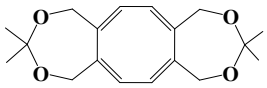
Table S1: X- Ray Analysis data for compound 1 (CCDC number: 2026059)



1

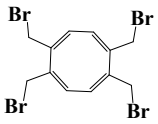
Empirical formula	$C_{12}H_{16}O_4$
Formula weight	224.25
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 11.6744(7) Å, α = 90 °. b = 9.2737(6) Å, β = 114.210(2) °. c = 11.2747(5) Å, γ = 90 °.
Volume	1113.29(11) $Å^3$
Z, Calculated density	4, 1.338 Mg/m^3
Absorption coefficient	0.100 mm^{-1}
F (000)	480
Crystal size	0.100 x 0.200 x 0.120 mm
Theta range for data collection	2.913 to 24.990 deg.
Limiting indices	-13<=h<=13, -10<=k<=10, -13<=l<=12
Reflections collected / unique	4305 / 981 [R(int) = 0.0348]
Completeness to theta = 24.990	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	981 / 0 / 82
Goodness-of-fit on F^2	1.042
Final R indices [I> 2σ (I)]	R1 = 0.0431, wR2 = 0.0979
R indices (all data)	R1 = 0.0604, wR2 = 0.1096
Extinction coefficient	0.0088(19)
Largest diff. peak and hole	0.303 and -0.154 e. $Å^{-3}$

Table S2: X- Ray Analysis data for compound 2 (CCDC number: 2026058)



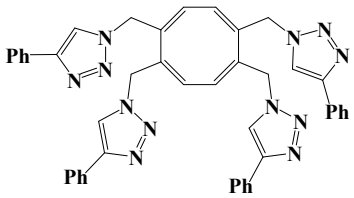
Empirical formula	$C_{18}H_{24}O_4$
Formula weight	304.37
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.9814(6) Å α = 62.708(4) °. b = 11.3970(10) Å β = 82.487(5) °. c = 11.8876(11) Å γ = 73.520(5) °.
Volume	806.03(13) $Å^3$
Z, Calculated density	2, 1.254 Mg/m^3
Absorption coefficient	0.087 mm^{-1}
F(000)	328
Crystal size	0.250 x 0.220 x 0.100 mm
Theta range for data collection	1.928 to 24.991 deg.
Limiting indices	-8<=h<=8, -13<=k<=10, -14<=l<=13
Reflections collected / unique	11837 / 2841 [R(int) = 0.0558]
Completeness to theta = 24.991	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2841 / 0 / 204
Goodness-of-fit on F^2	1.032
Final R indices [I>2 σ (I)]	R1 = 0.0652, wR2 = 0.1980
R indices (all data)	R1 = 0.0953, wR2 = 0.2217
Extinction coefficient	0.027(8)
Largest diff. peak and hole	0.381 and -0.237 e. $Å^{-3}$

Table S3: X- Ray Analysis data for compound 3 (CCDC number: 2026057)



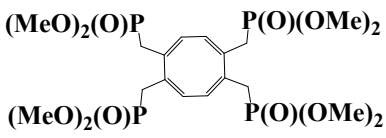
Empirical formula	C_{72} H_{72} Br_{24}
Formula weight	2855.13
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 13.2408(7) Å, α = 90.016(3) °. b = 14.8169(9) Å, β = 90.019(3) °. c = 23.1350(15) Å, γ = 94.823(3) °.
Volume	4522.7(5) $Å^3$
Z, Calculated density	2, 2.097 Mg/m^3
Absorption coefficient	10.652 mm^{-1}
F(000)	2688
Crystal size	0.250 x 0.220 x 0.100 mm
Theta range for data collection	0.880 to 24.999 deg.
Limiting indices	-15<=h<=14, -17<=k<=17, -27<=l<=27
Reflections collected / unique	43850 / 15423 [R(int) = 0.1486]
Completeness to theta = 24.999	96.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15423 / 12 / 865
Goodness-of-fit on F^2	1.171
Final R indices [I>2 σ (I)]	R1 = 0.0801, wR2 = 0.1433
R indices (all data)	R1 = 0.2562, wR2 = 0.1869
Extinction coefficient	n/a
Largest diff. peak and hole	1.564 and -1.142 e. $Å^{-3}$

Table S4: X- Ray Analysis data for compound 6 (CCDC number: 2023452)



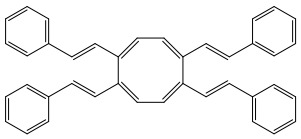
Empirical formula	$C_{44}H_{36}N_{12}$	
Formula weight	732.85	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.8429(11) Å	α= 90°.
	b = 14.4588(7) Å	β= 116.4550(10) °.
	c = 12.0020(5) Å	γ = 90°.
Volume	3704.3(3) $Å^3$	
Z	4	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	1536	
Crystal size	0.300 x 0.250 x 0.200 mm^3	
Theta range for data collection	3.191 to 25.997°.	
Index ranges	-29<=h<=29, -17<=k<=17, -12<=l<=14	
Reflections collected	36006	
Independent reflections	3632 [R(int) = 0.0415]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.7022	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3632 / 0 / 254	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1170	
R indices (all data)	R1 = 0.0810, wR2 = 0.1456	
Extinction coefficient	0.0114(11)	
Largest diff. peak and hole	0.162 and -0.195 e.$Å^{-3}$	

Table S5: X- Ray Analysis data for compound 9 (CCDC number: 2023451)



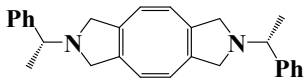
Empirical formula	$C_{20}H_{38}O_{13}P_4$	
Formula weight	610.38	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 15.6392(6) Å	α= 90°.
	b = 18.8539(9) Å	β= 127.7290(10)°.
	c = 12.4008(7) Å	γ = 90°.
Volume	2892.0(2) $Å^3$	
Z	4	
Density (calculated)	1.402 Mg/m^3	
Absorption coefficient	0.320 mm^{-1}	
F(000)	1288	
Crystal size	0.200 x 0.200 x 0.150 mm^3	
Theta range for data collection	2.160 to 24.996°.	
Index ranges	-18<=h<=18, -22<=k<=22, -14<=l<=14	
Reflections collected	26490	
Independent reflections	2557 [R(int) = 0.0371]	
Completeness to theta = 24.996°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6985	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2557 / 62 / 191	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.0992	
R indices (all data)	R1 = 0.0613, wR2 = 0.1168	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.336 and -0.292 $e.Å^{-3}$	

Table S6: X- Ray Analysis data for compound 10a (CCDC number: 2023450)



Empirical formula	$C_{40}H_{32}$
Formula weight	12.65
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.4475(5) Å α = 100.338(2) °. b = 12.2806(5) Å β = 99.001(3) ° c = 12.3903(7) Å, γ= 104.084(2) °.
Volume	1483.14(13) $Å^3$
Z, Calculated density	2, 1.148 Mg/m^3
Absorption coefficient	0.065 mm^{-1}
F(000)	544
Crystal size	0.250 x 0.220 x 0.100 mm
Theta range for data collection	1.755 to 24.888 deg.
Limiting indices	-12<=h<=12, -14<=k<=13, -14<=l<=14
Reflections collected / unique	19603 / 5144 [R(int) = 0.0456]
Completeness to theta = 24.888	99.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5144 / 0 / 362
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1054
R indices (all data)	R1 = 0.1036, wR2 = 0.1347
Extinction coefficient	0.0080(14)
Largest diff. peak and hole	0.136 and -0.143 e $Å^{-3}$

Table S7: X- Ray Analysis data for compound 11b (CCDC number: 2023453)



Empirical formula	C_{28} H_{30} N_2
Formula weight	394.54
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2 (1)2(1)2(1)
Unit cell dimensions	a = 6.8590(5) Å α = 90 ° b = 17.0662(11) Å β= 90 ° c = 19.6709(10) Å γ= 90 °
Volume	2302.6(3) $Å^3$
Z, Calculated density	4, 1.138 Mg/m^3
Absorption coefficient	0.066 mm^{-1}
F(000)	848
Crystal size	0.250 x 0.220 x 0.100 mm
Theta range for data collection	1.580 to 24.994 deg.
Limiting indices	-8<=h<=4, -20<=k<=15, -23<=l<=21
Reflections collected / unique	9856 / 4034 [R(int) = 0.0384]
Completeness to theta = 24.994	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4034 / 0 / 274
Goodness-of-fit on F^2	0.979
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.0917
R indices (all data)	R1 = 0.0893, wR2 = 0.1133
Absolute structure parameter	-0.8(10)
Extinction coefficient	0.017(2)
Largest diff. peak and hole	0.115 and -0.153 e. $Å^{-3}$

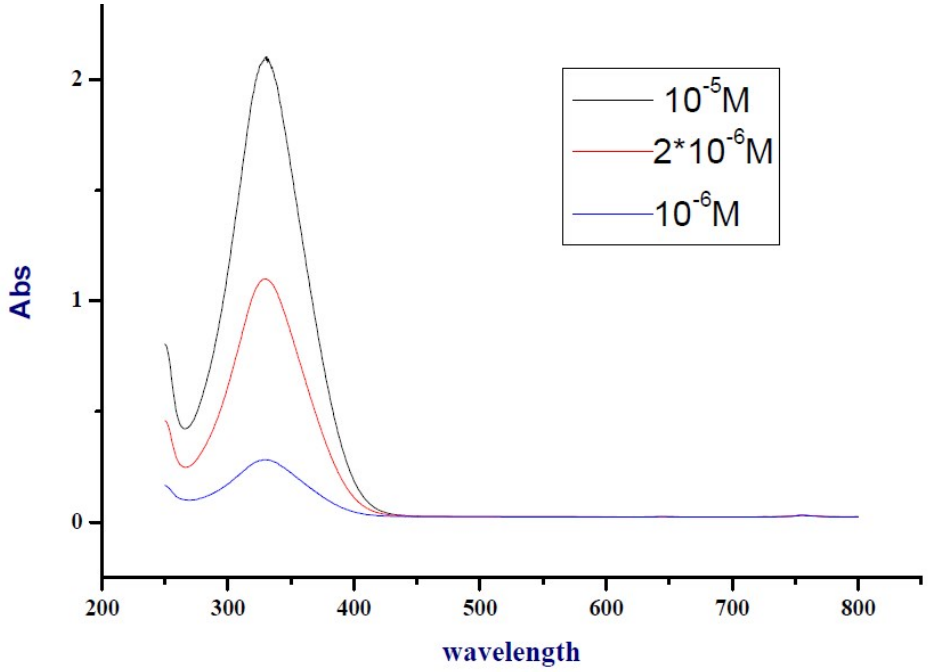


Figure 40 UV-Vis spectrum of compound **10a** in THF (concentration shown in the inset)