Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Synthesis and application of 3,4,7,8-*tetrakis*-*exo*-methylenecycloocta-1,5-diene as a versatile Diels-Alder diene. Synthesis of V-shaped cyclooctatetraene fused acenes

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Supporting Information

Contents

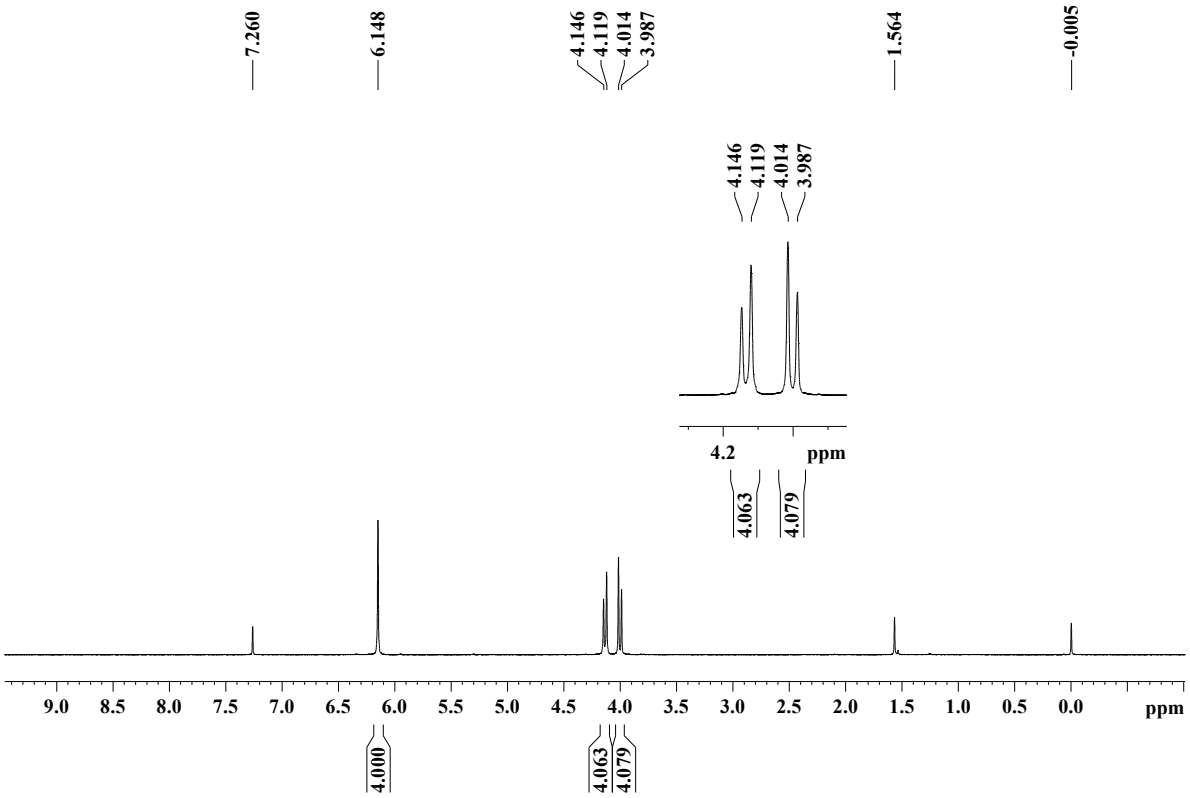


Figure 1 400 MHz ^{1}H NMR spectrum of **2** in $CDCl_3$

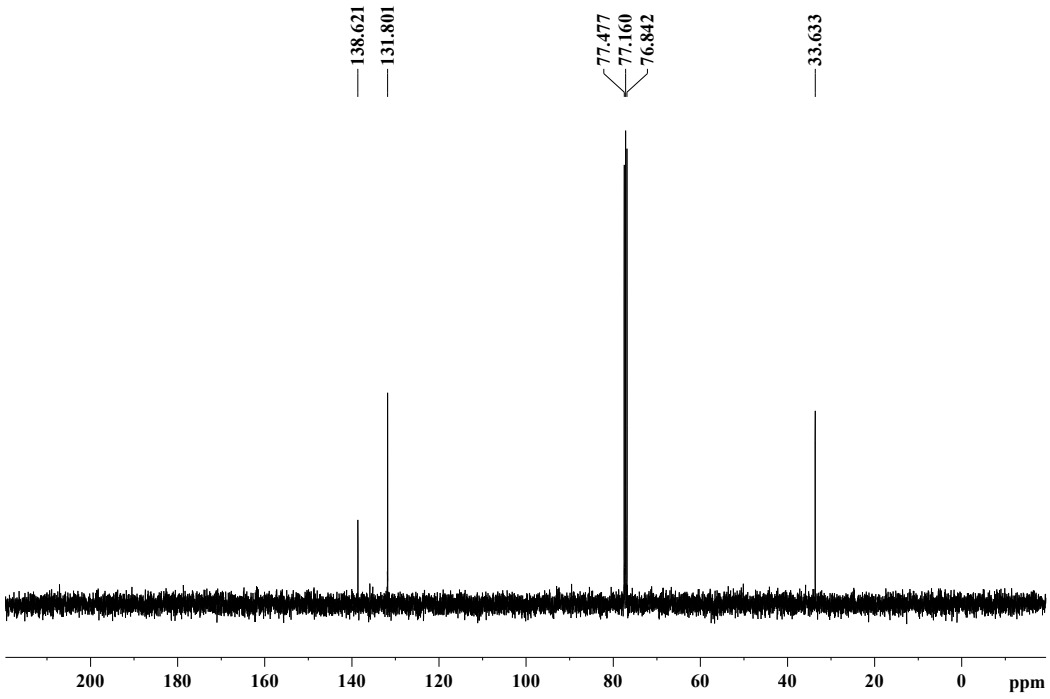
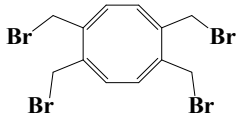


Figure 2 100 MHz ^{13}C NMR spectrum of **2** in $CDCl_3$



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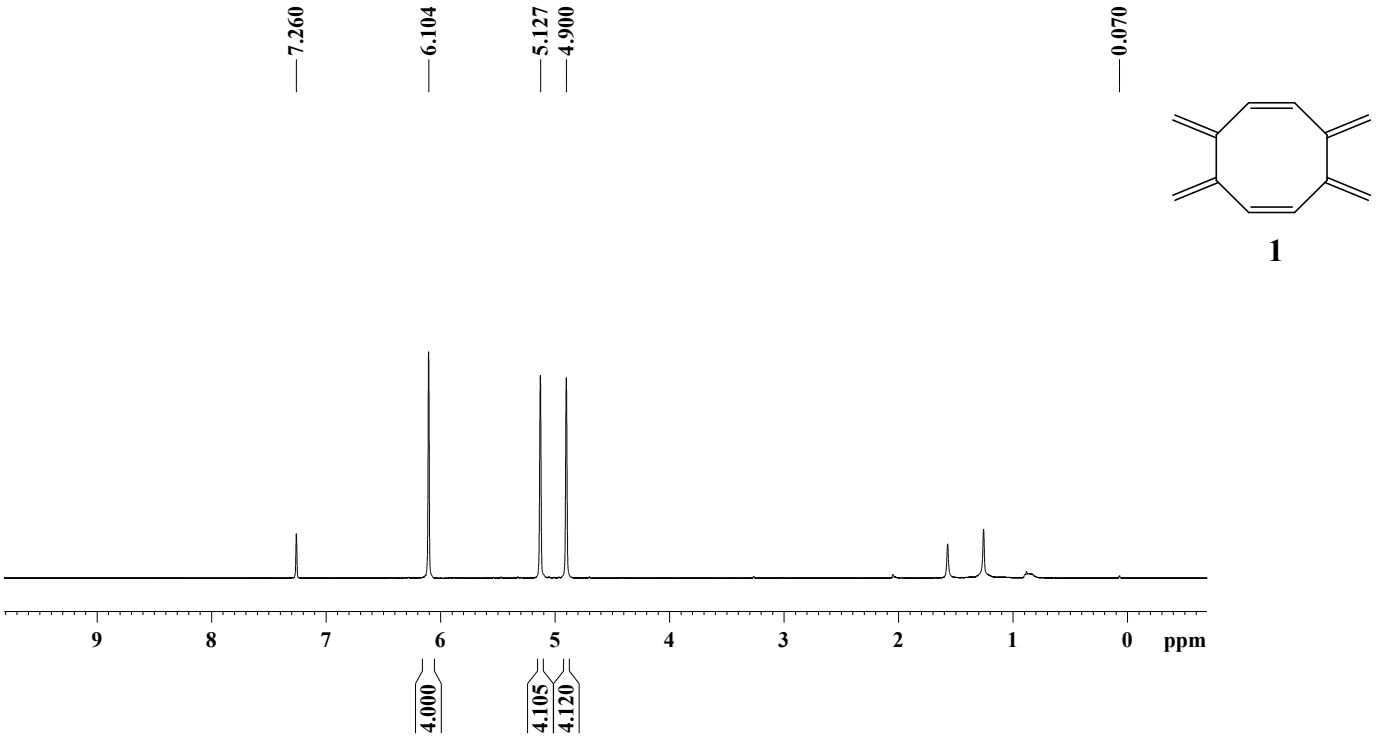


Figure 3 400 MHz ^{1}H NMR spectrum of **1** in $CDCl_3$

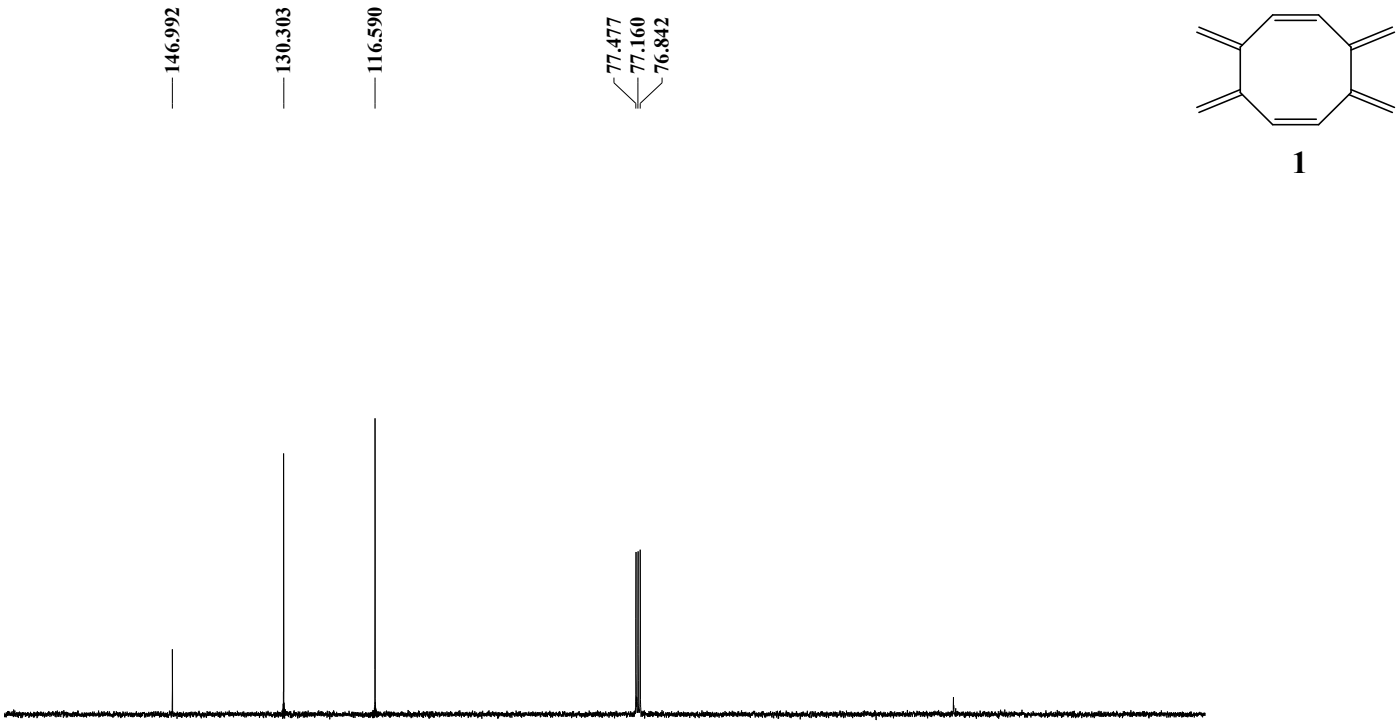


Figure 4 100 MHz ^{13}C NMR spectrum of **1** in $CDCl_3$

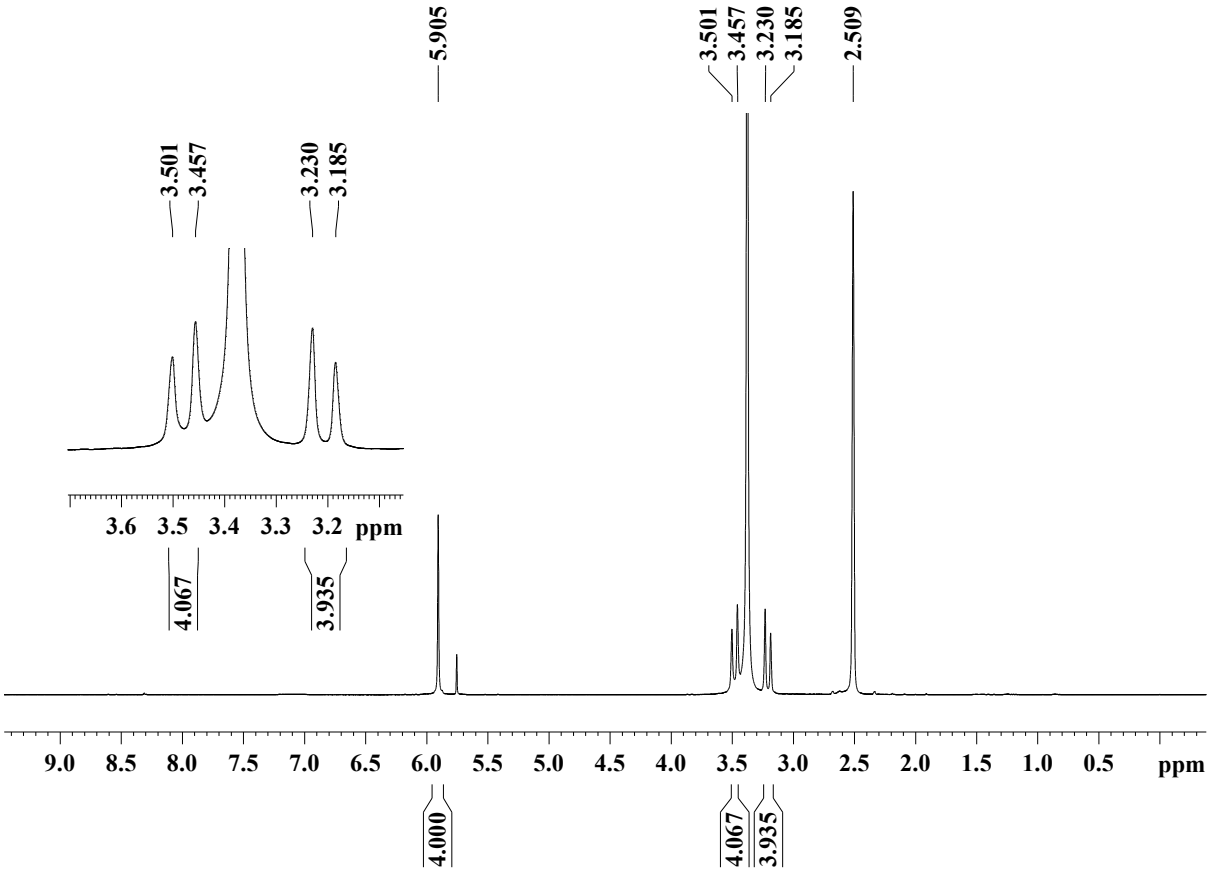
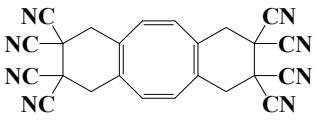


Figure 5 400 MHz ^{1}H NMR spectrum of **3** in DMSO-d_6



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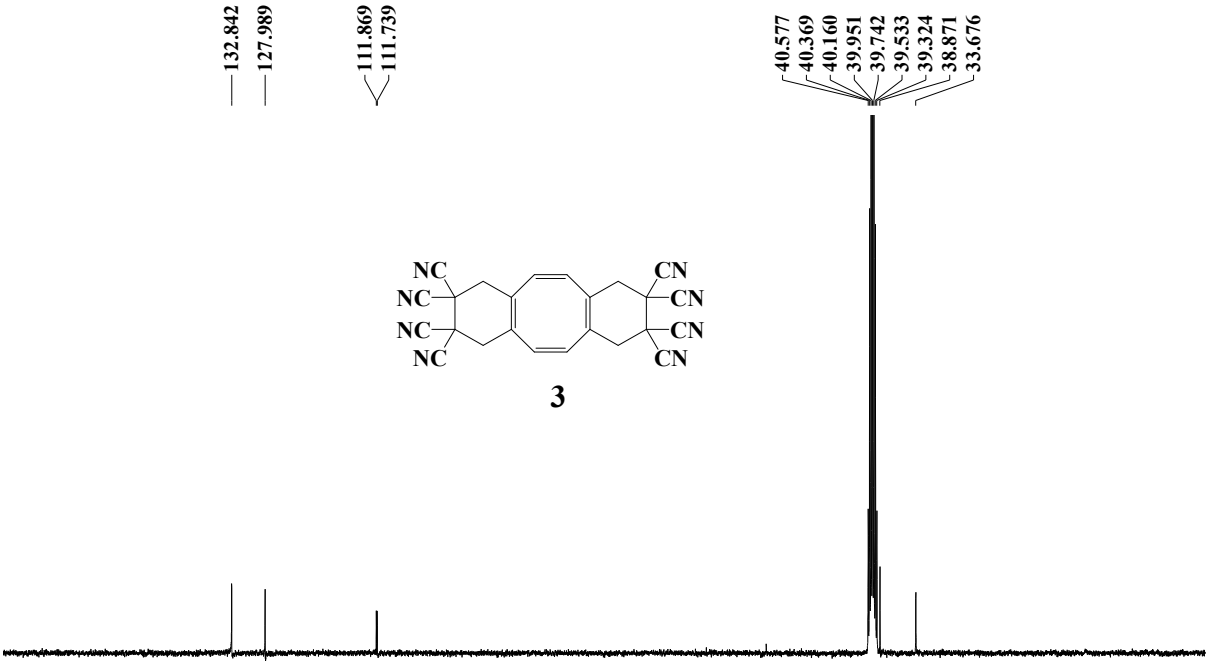


Figure 6 100 MHz ^{13}C NMR spectrum of **3** in DMSO-d_6

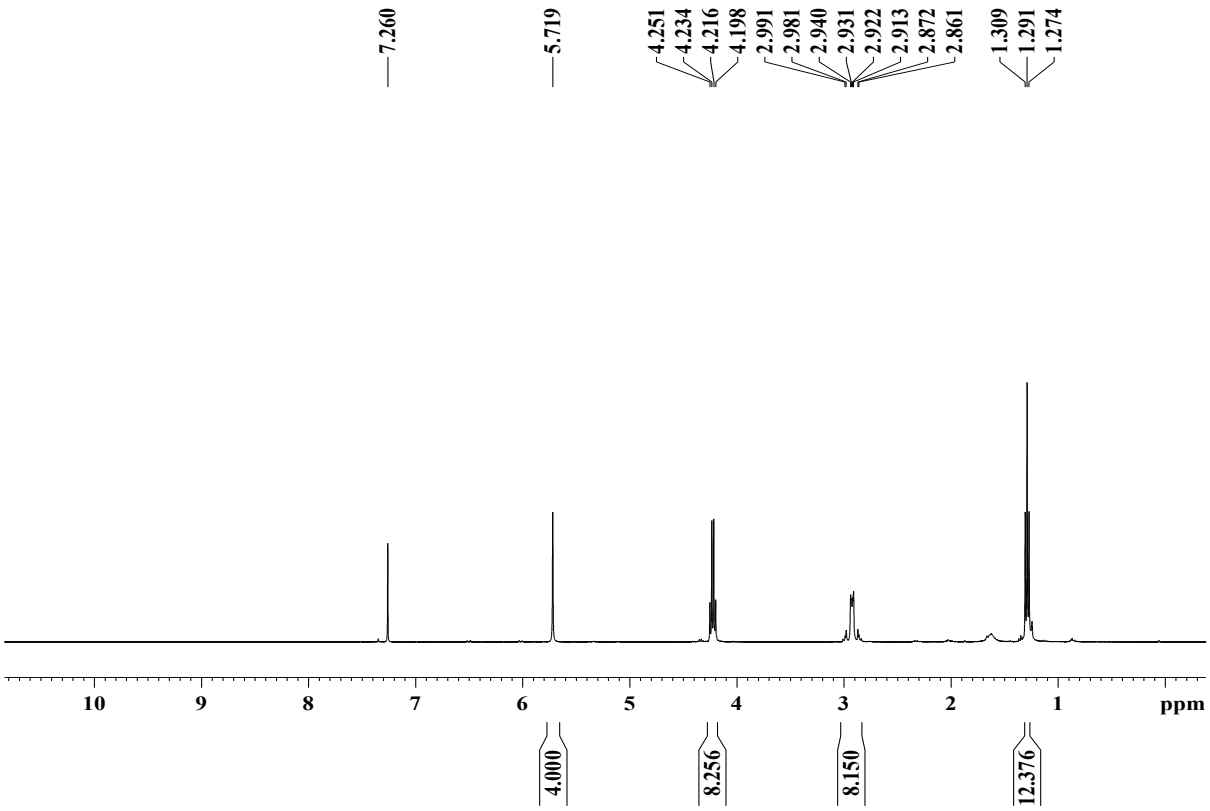


Figure 7 400 MHz ^{1}H NMR spectrum of **4a** in $CDCl_3$

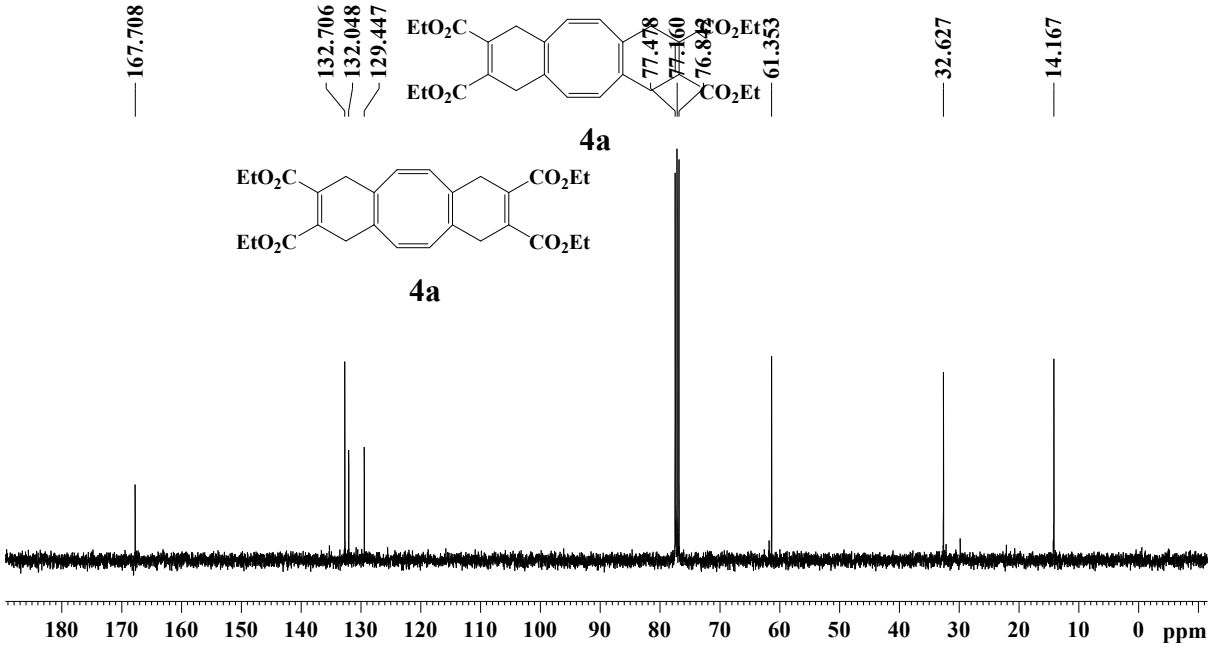


Figure 8 100 MHz ^{13}C NMR spectrum of **4a** in $CDCl_3$

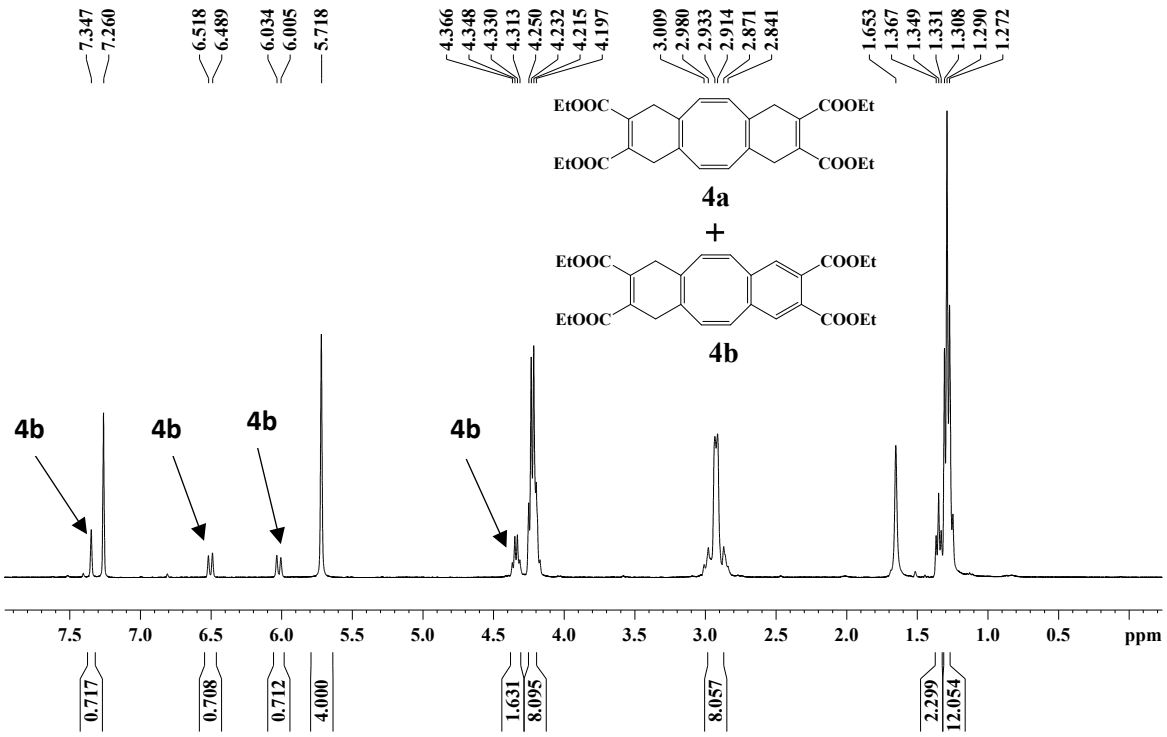


Figure 9 400 MHz ^{1}H NMR spectrum of a mixture of **4a** and **4b** in $CDCl_3$

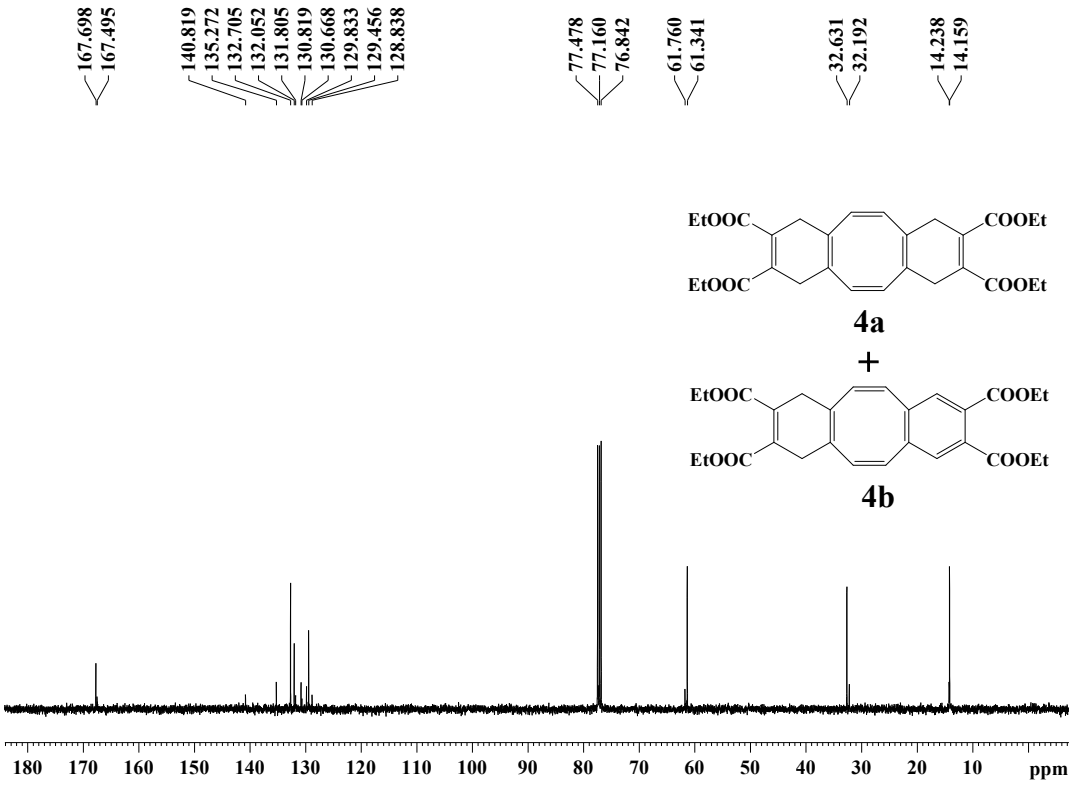


Figure 10 100 MHz ^{13}C NMR spectrum of a mixture of **4a** and **4b** in $CDCl_3$

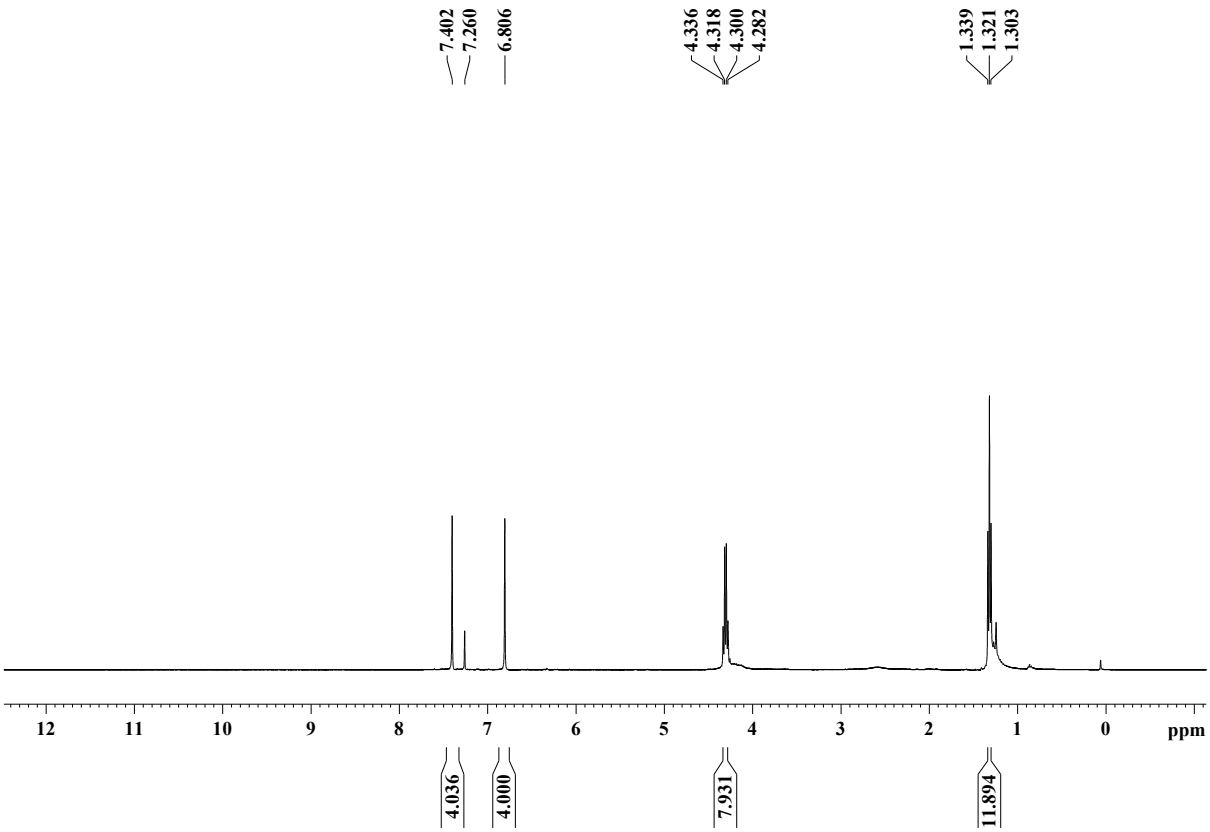


Figure 11 400 MHz ^{1}H NMR spectrum of **5** in $CDCl_3$

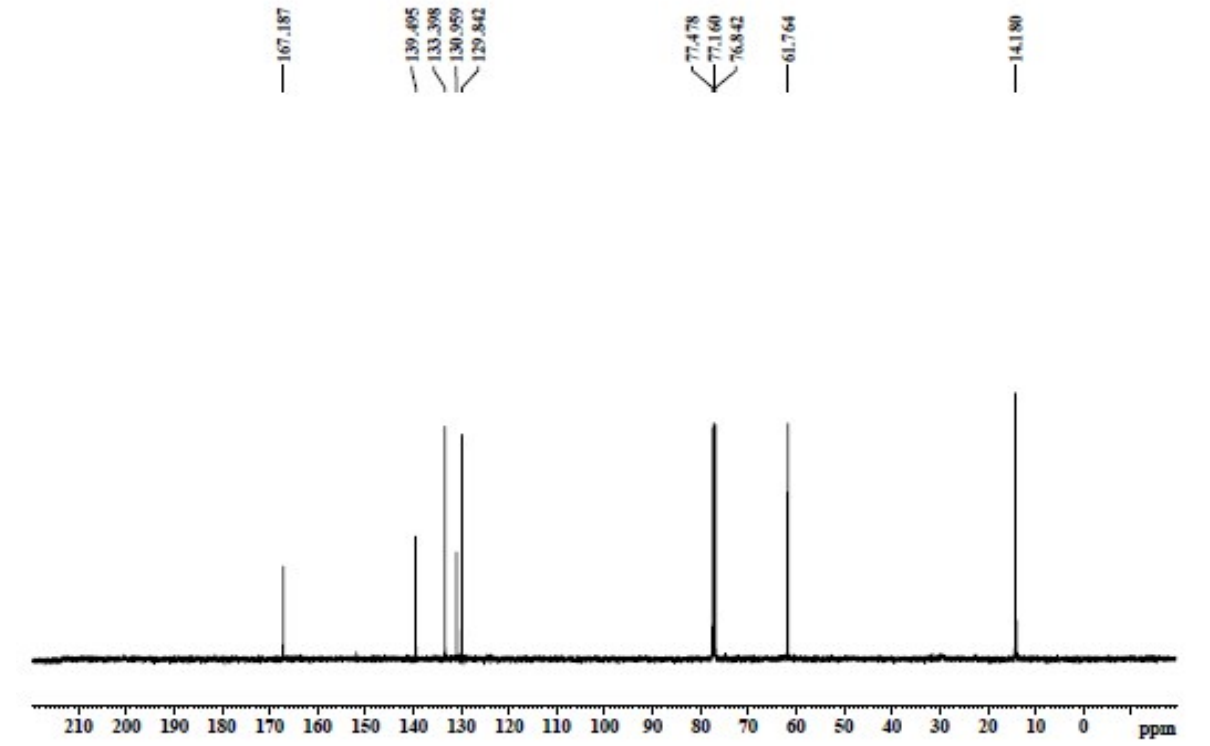
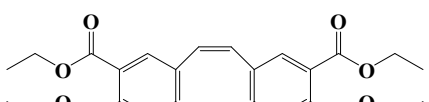
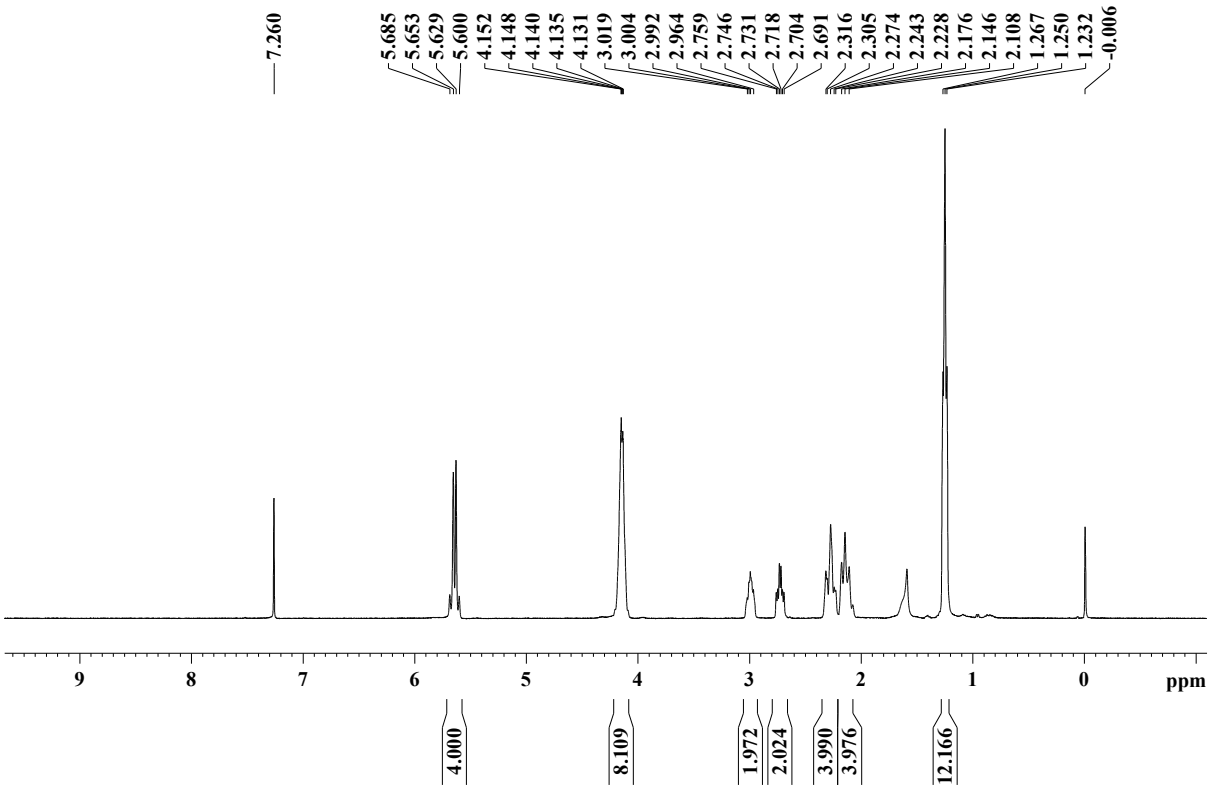


Figure 1 100 MHz ^{13}C NMR spectrum of **5** in $CDCl_3$





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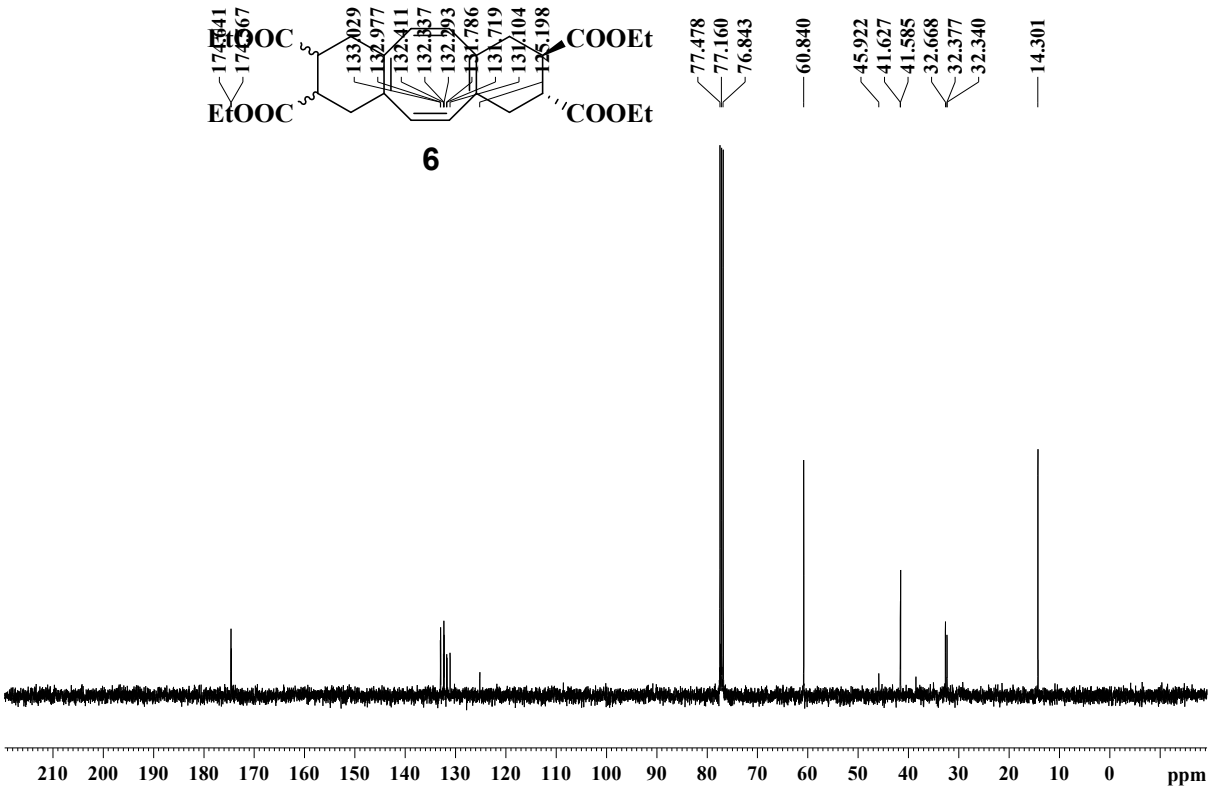

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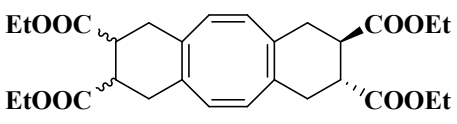
Figure 3 100 MHz ^{13}C NMR spectrum of **6** in $CDCl_3$



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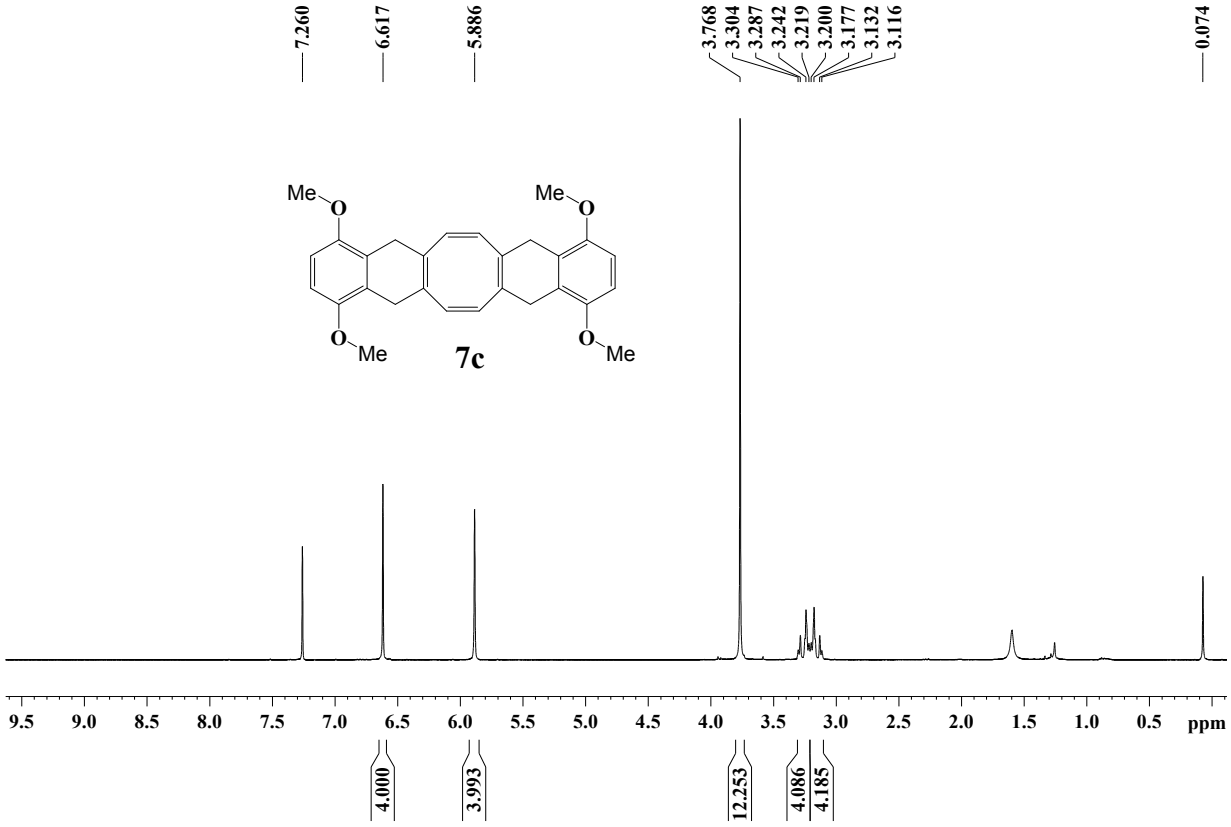


Figure 4 400 MHz ^{1}H NMR spectrum of **7c** in $CDCl_3$

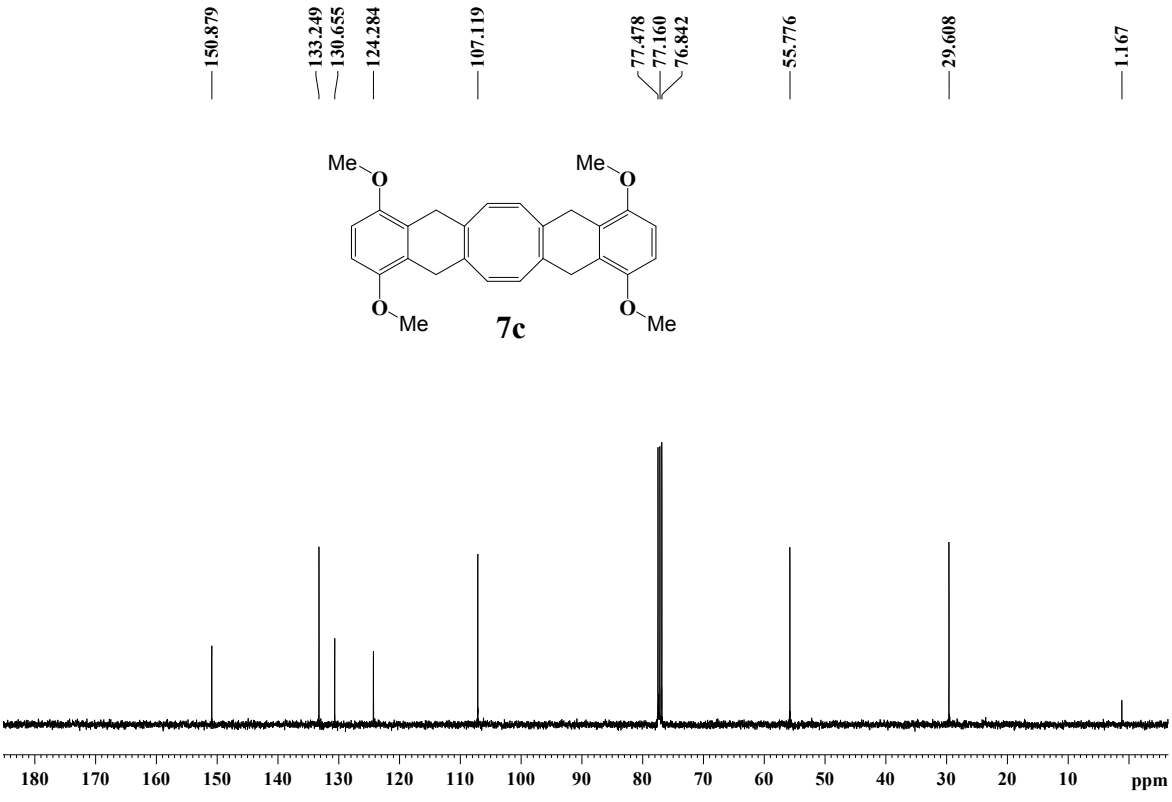


Figure 5 100 MHz ^{13}C NMR spectrum of **7c** in $CDCl_3$

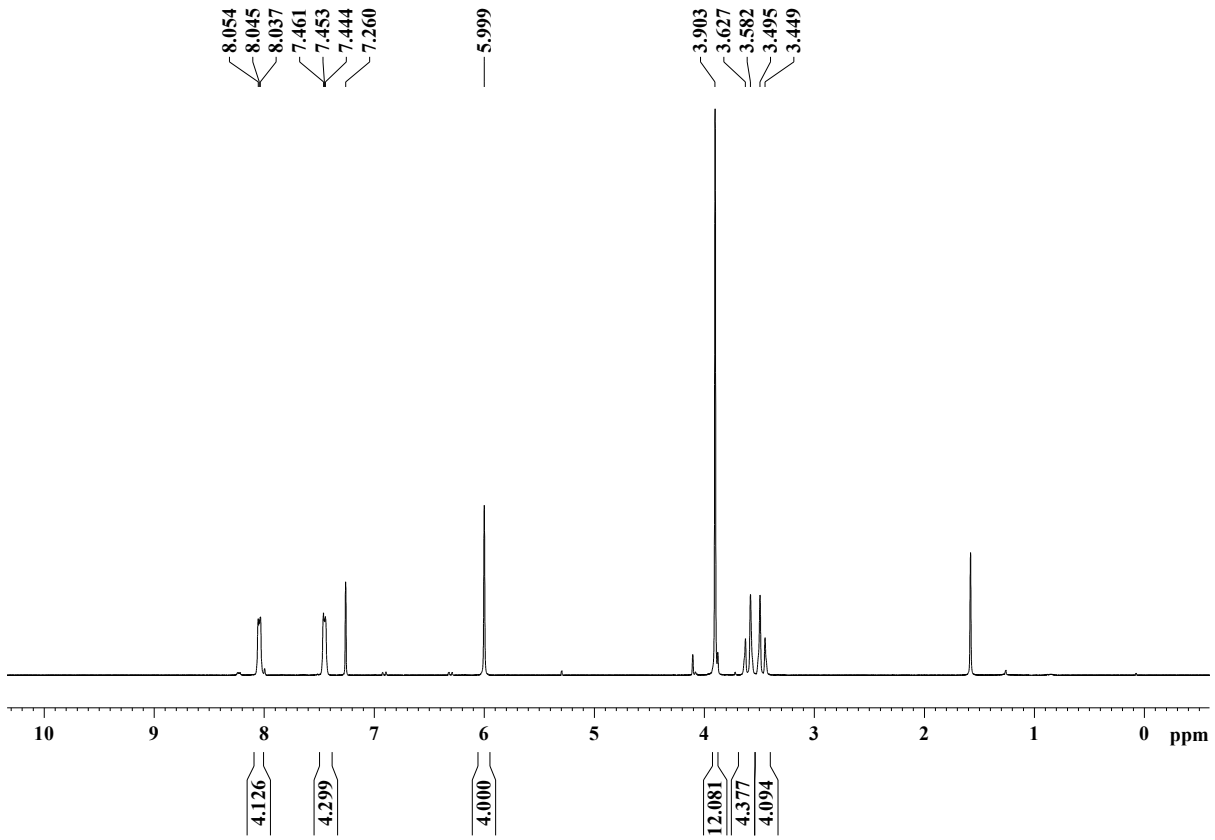


Figure 17 400 MHz ^{1}H NMR spectrum of **8c** in $CDCl_3$

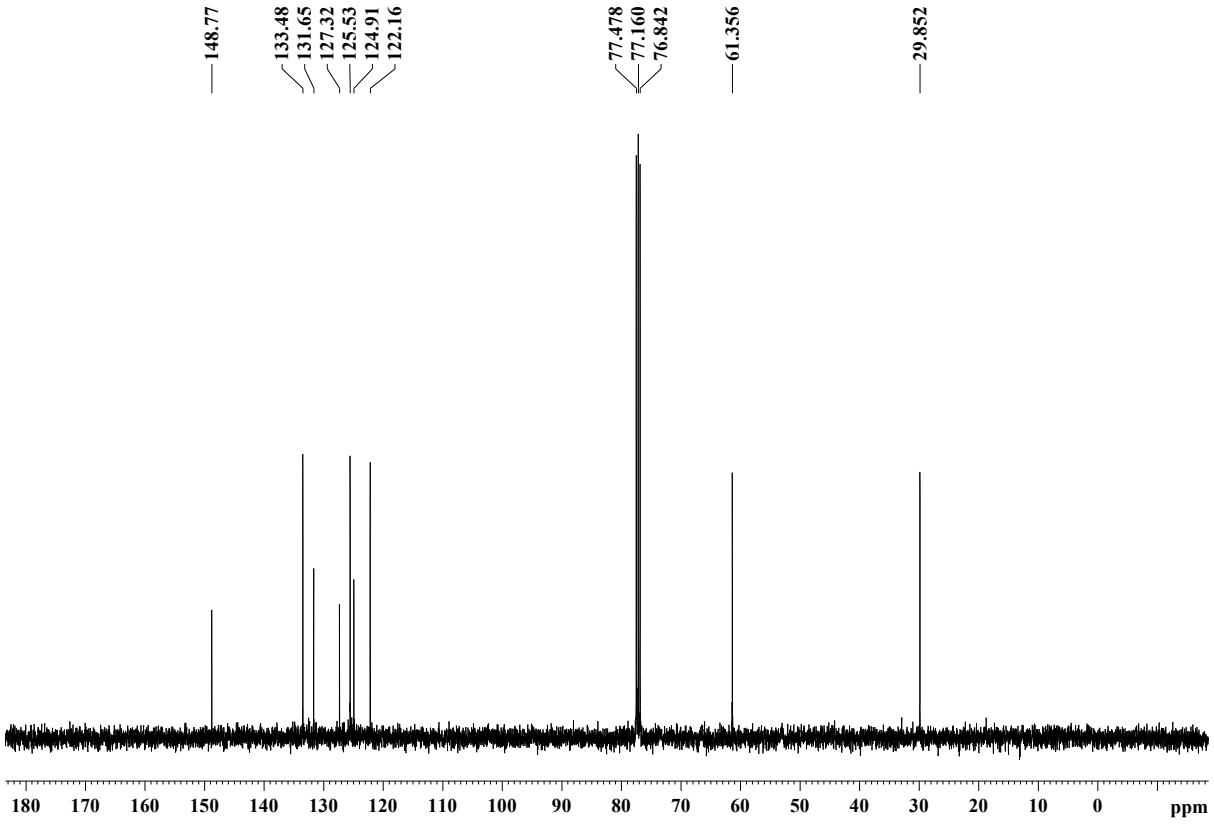
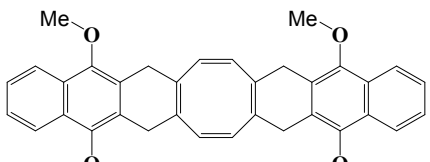


Figure 18 100 MHz ^{13}C NMR spectrum of **8c** in $CDCl_3$



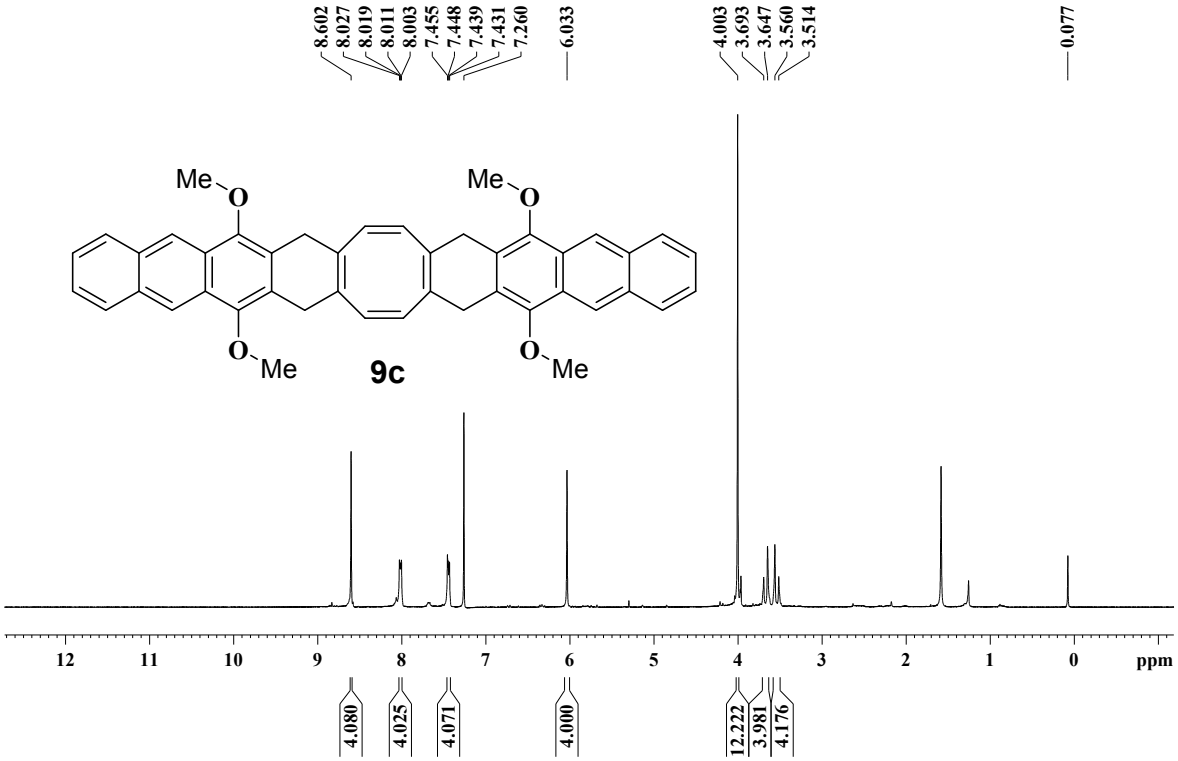
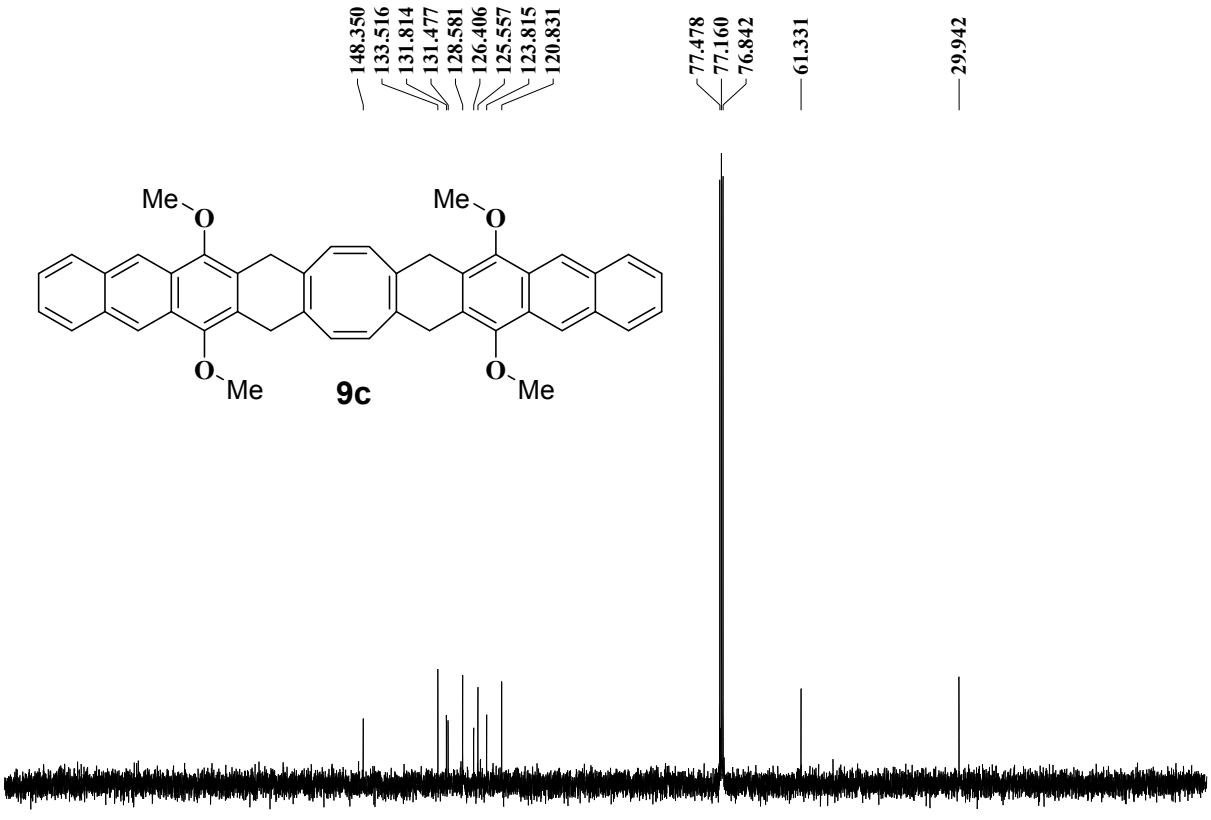


Figure 19 400 MHz ^{1}H NMR spectrum of **9c** in $CDCl_3$



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

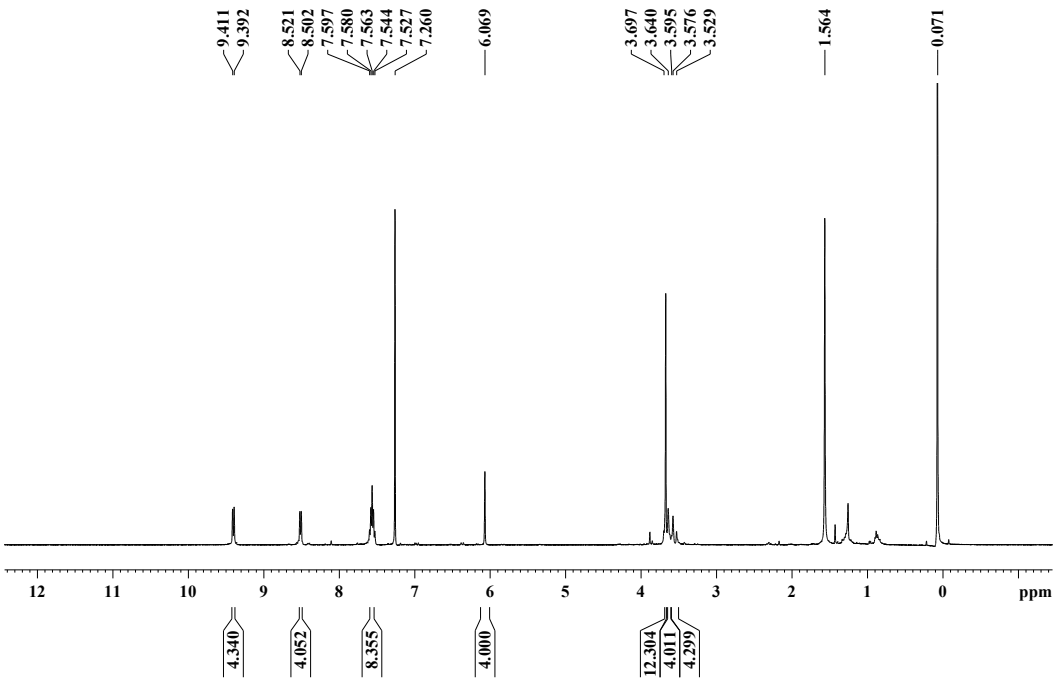
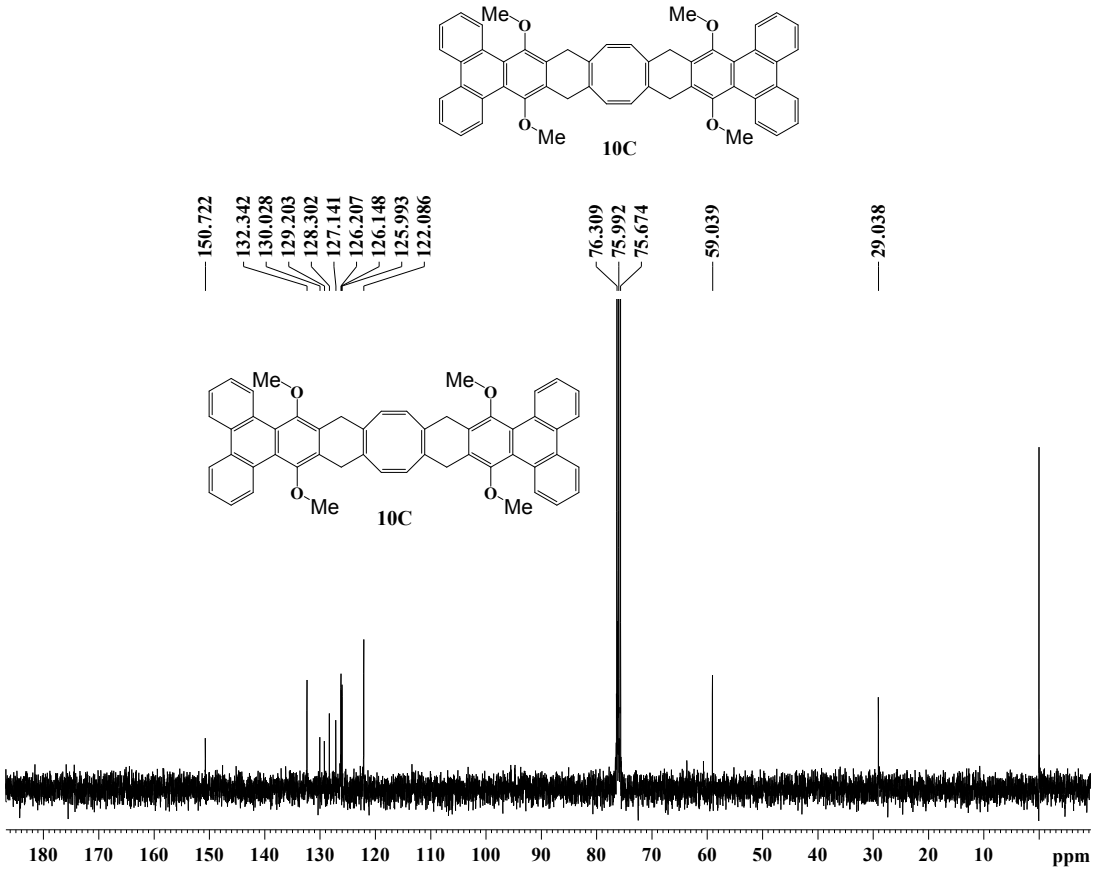


Figure 21 400 MHz ^{1}H NMR spectrum of **10c** in $CDCl_3$



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

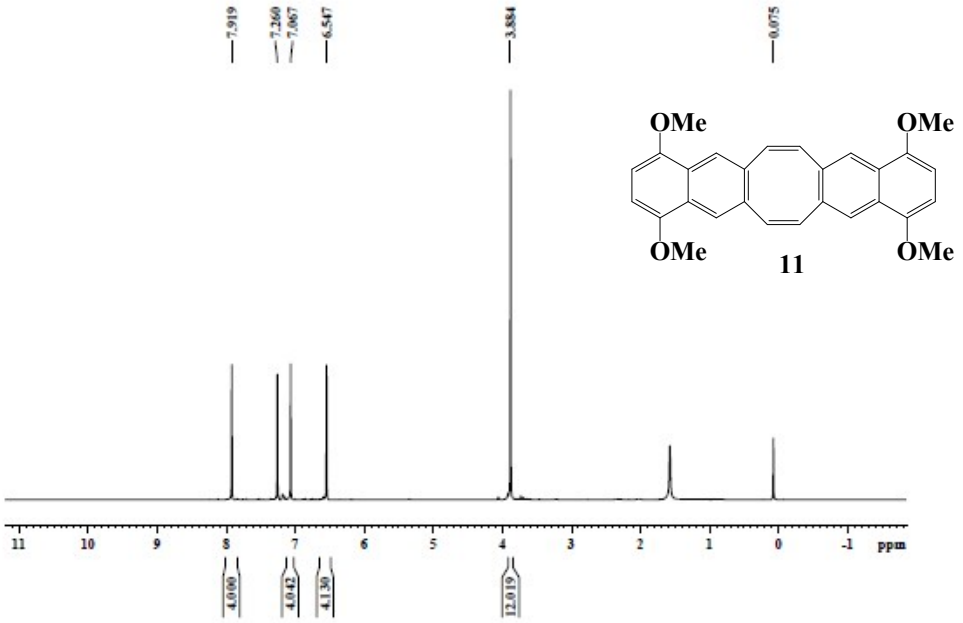


Figure 23 400 MHz ^{1}H NMR spectrum of **11** in $CDCl_3$

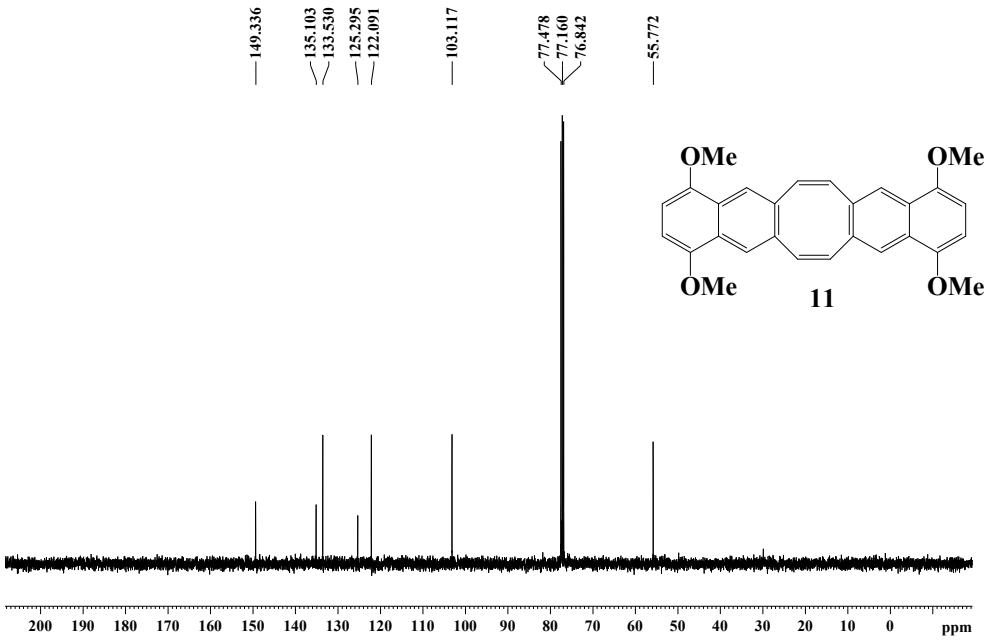


Figure 24 100 MHz ^{13}C NMR spectrum of **11** in $CDCl_3$

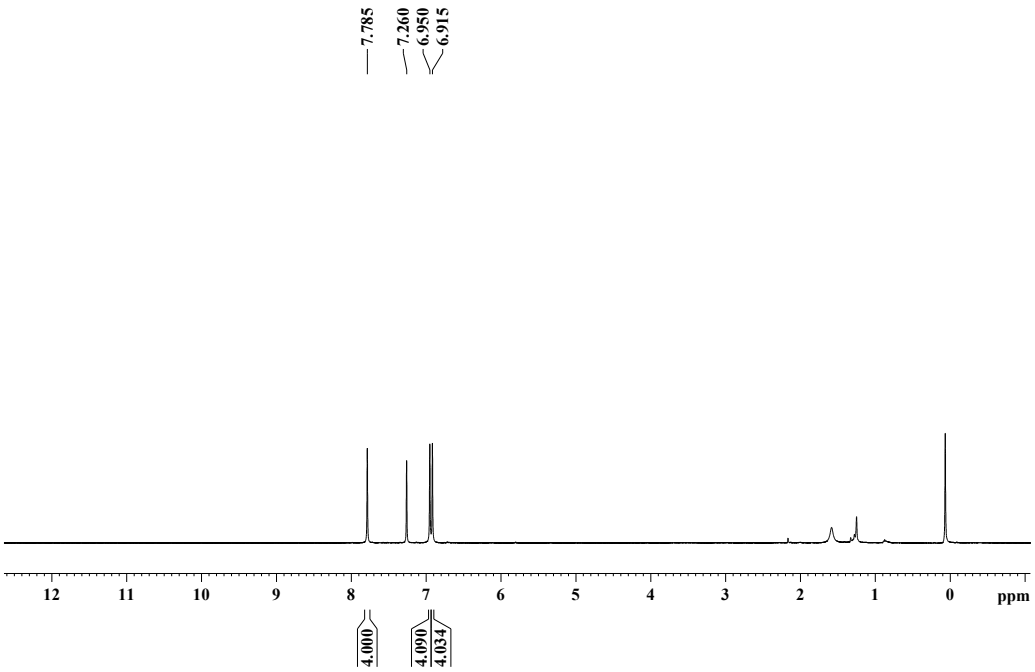
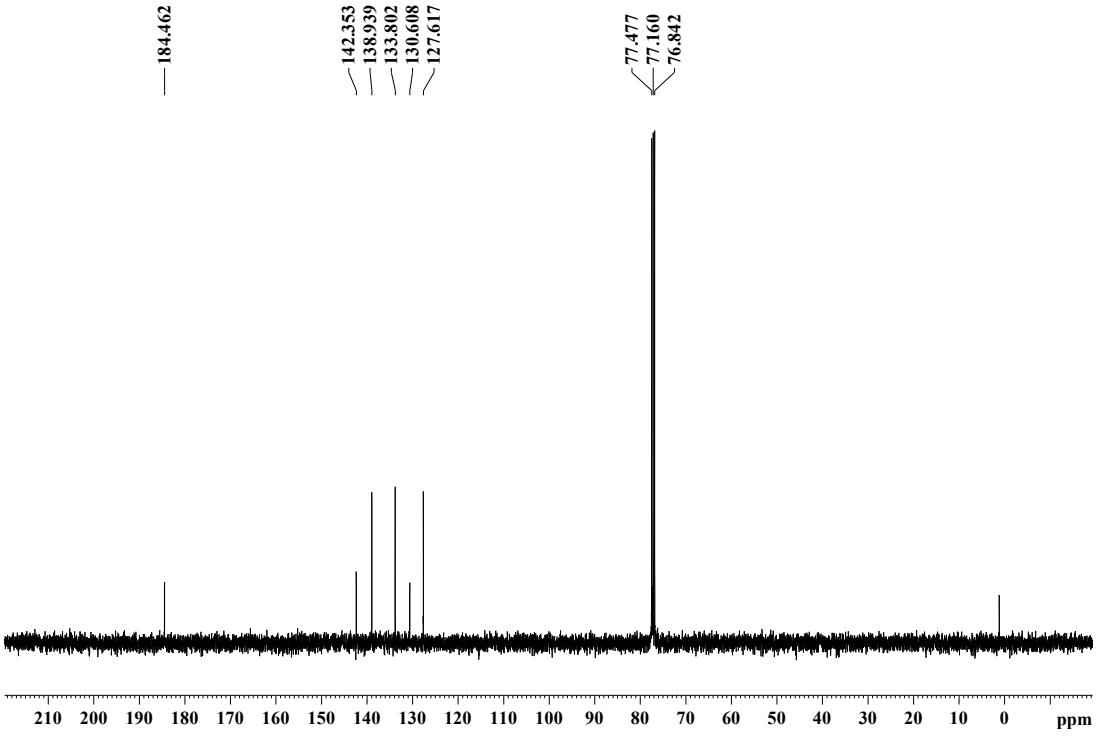


Figure 25 400 MHz ^{1}H NMR spectrum of **12** in $CDCl_3$



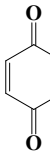


Figure 26 100 MHz ^{13}C NMR spectrum of **12** in $CDCl_3$

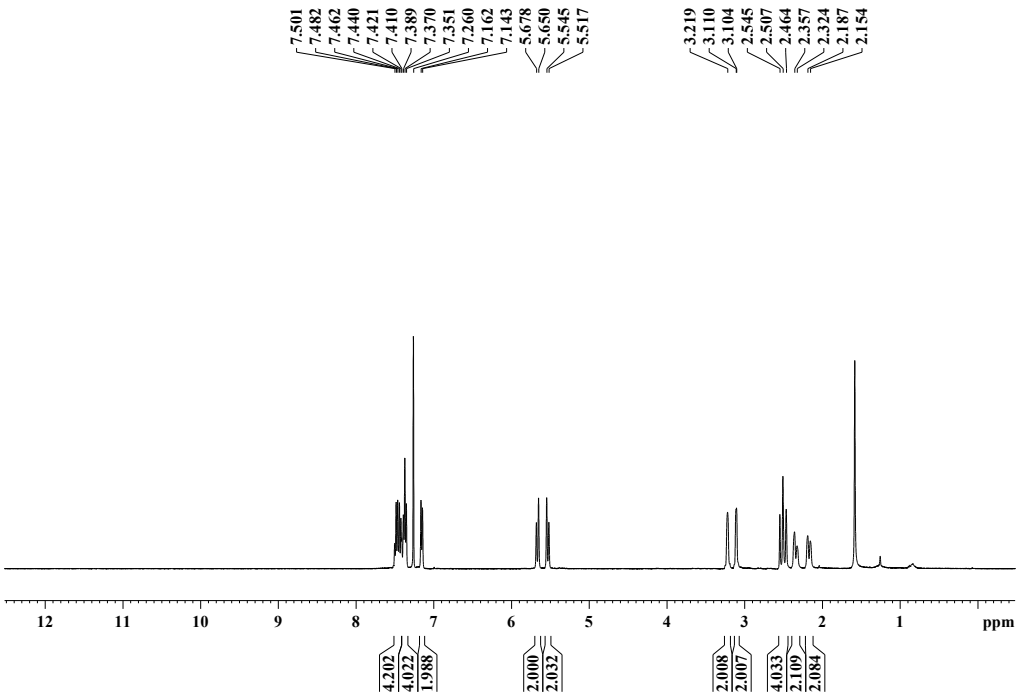


Figure 27 400 MHz ^{1}H NMR spectrum of **13b** in $CDCl_3$

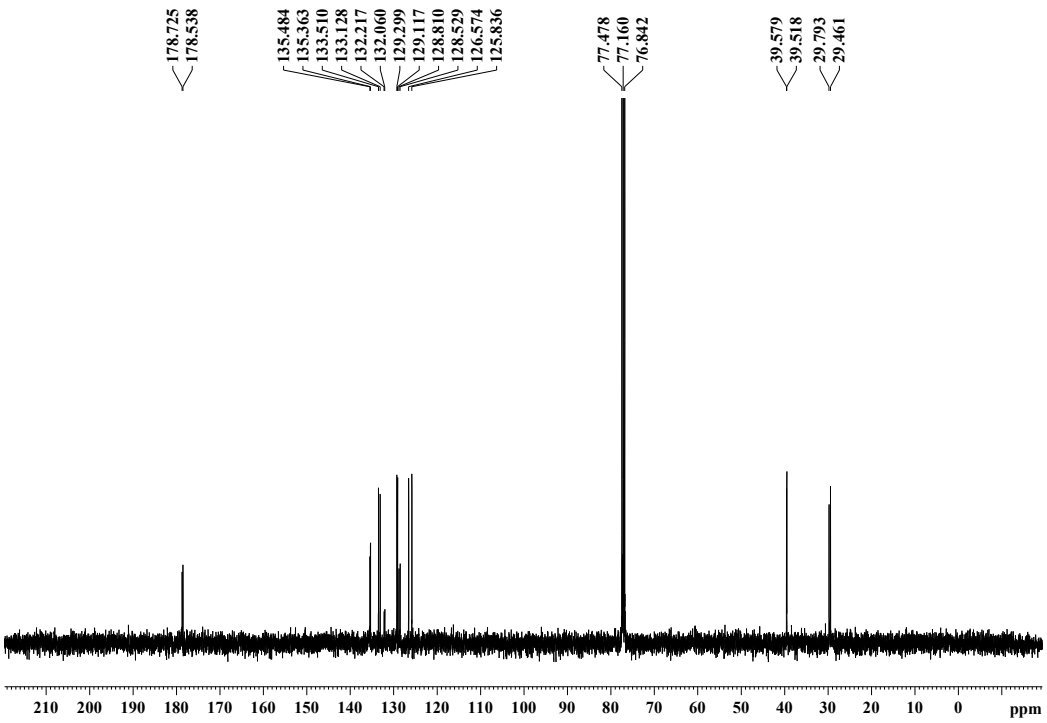
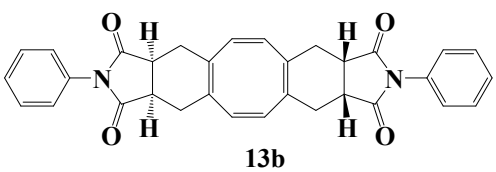
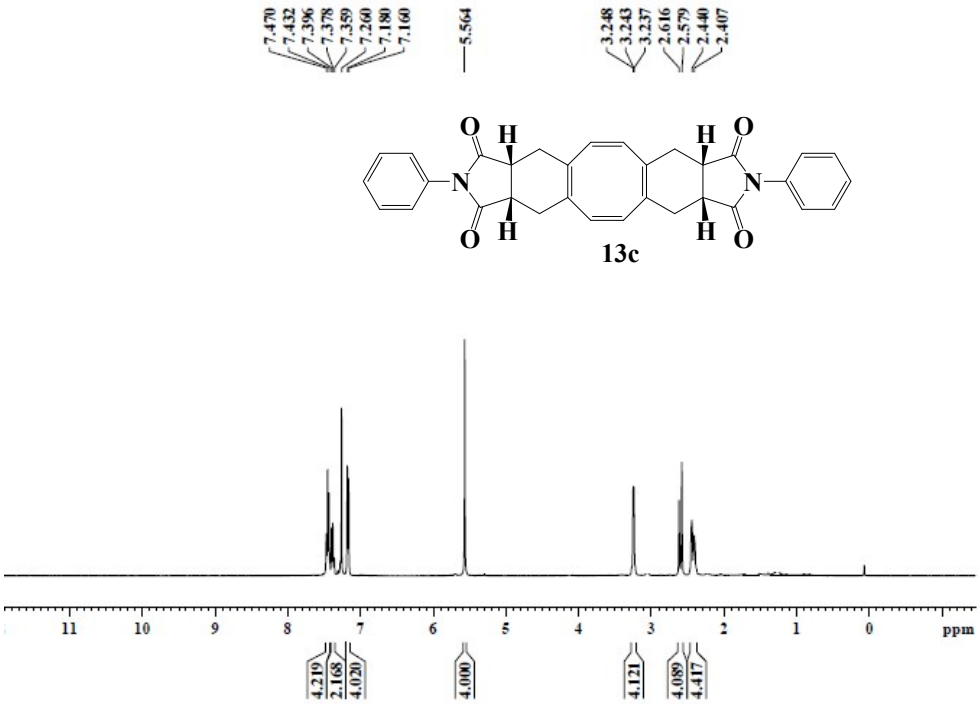


Figure 28 100 MHz ^{13}C NMR spectrum of **13b** in $CDCl_3$



13b



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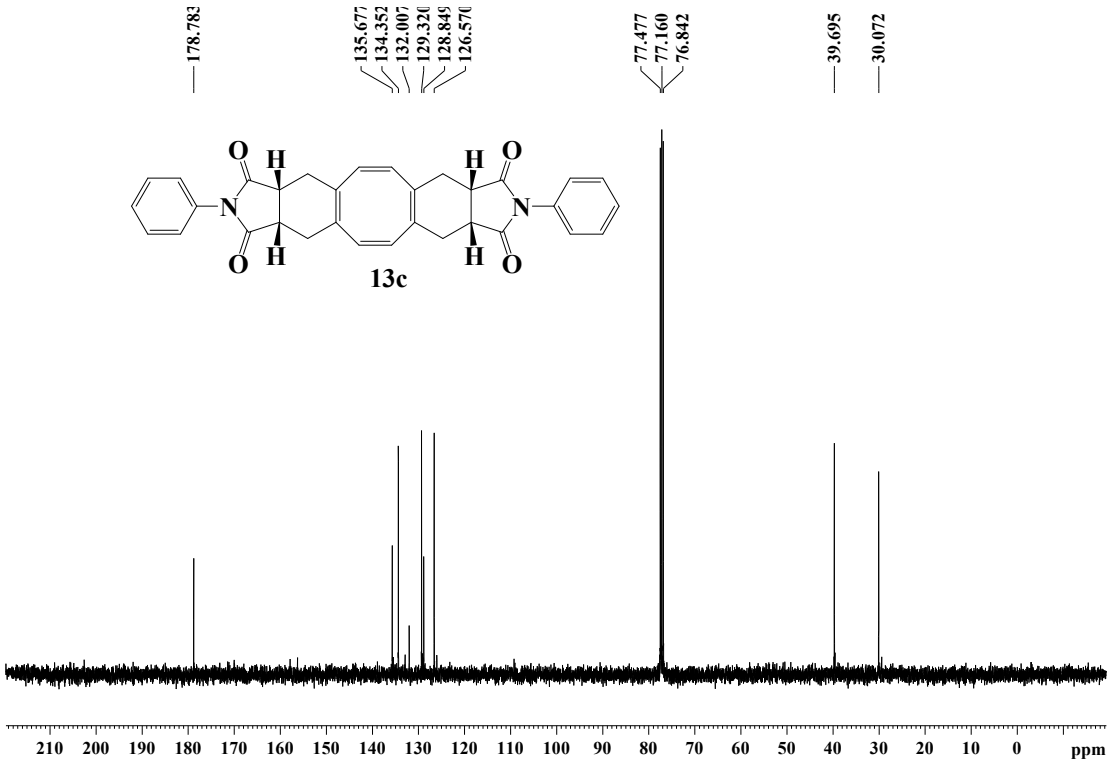


Figure 30 100 MHz ^{13}C NMR spectrum of **13c** in $CDCl_3$

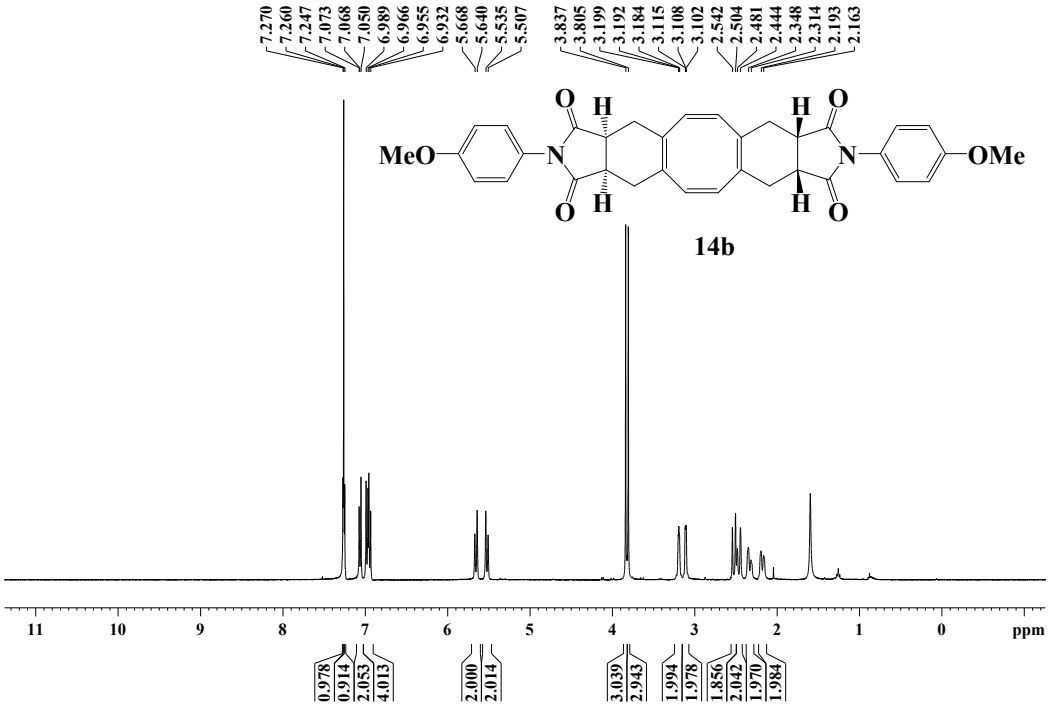


Figure 31 400 MHz ^{1}H NMR spectrum of **14b** in $CDCl_3$

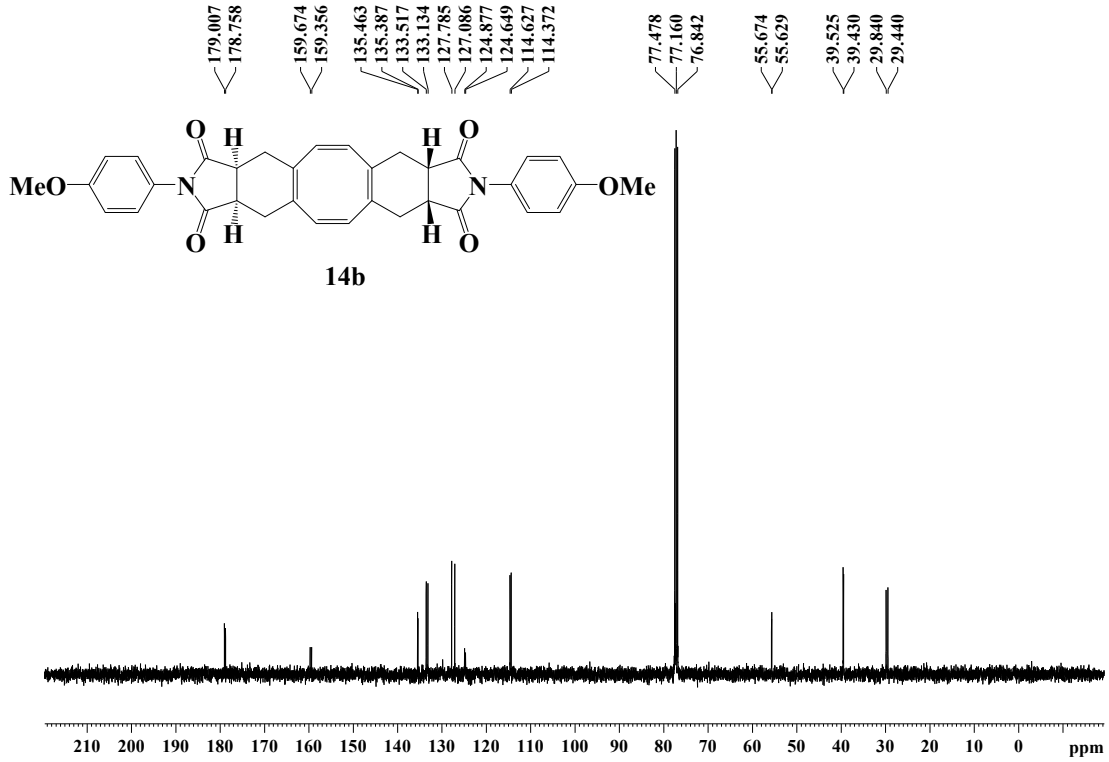


Figure 32 100 MHz ^{13}C NMR spectrum of **14b** in $CDCl_3$

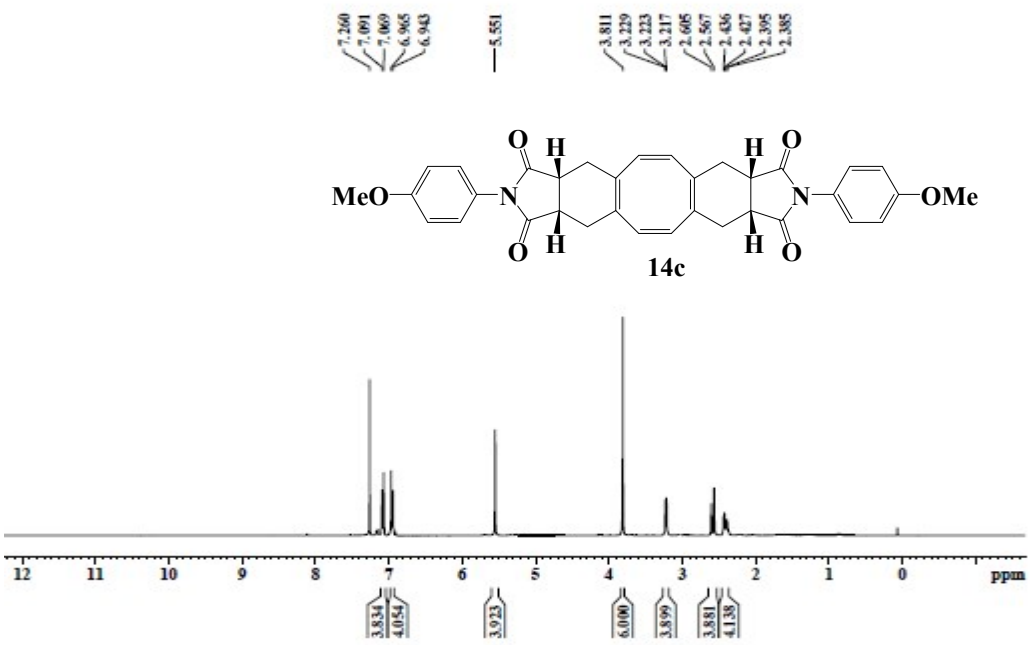


Figure 33 400 MHz ^{1}H NMR spectrum of **14c** in $CDCl_3$

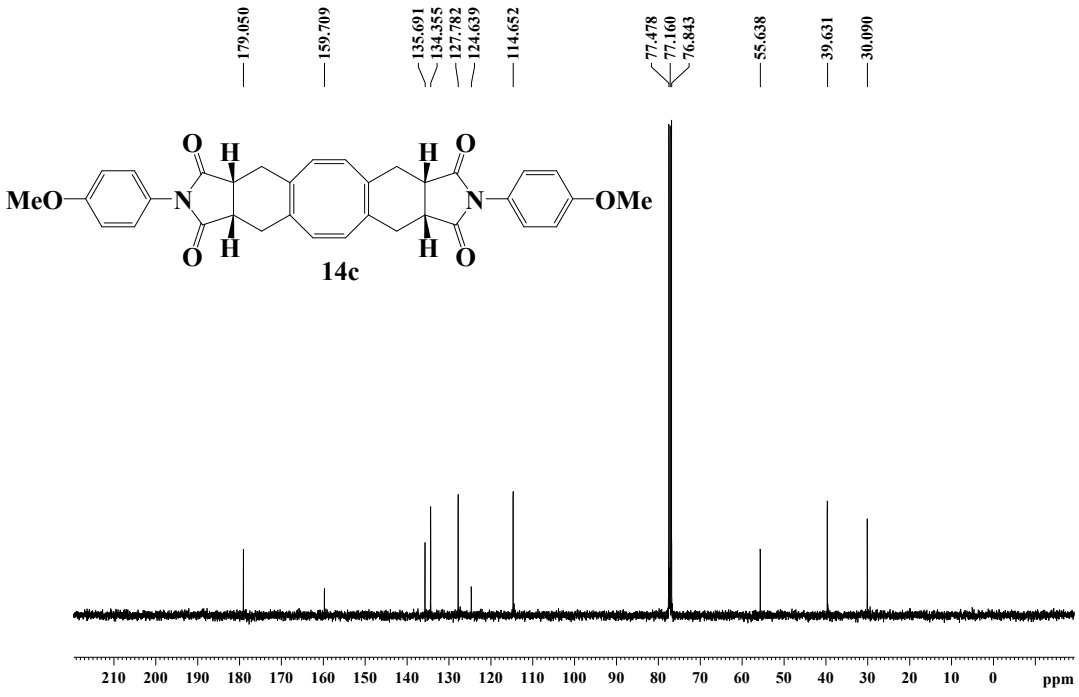
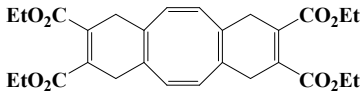


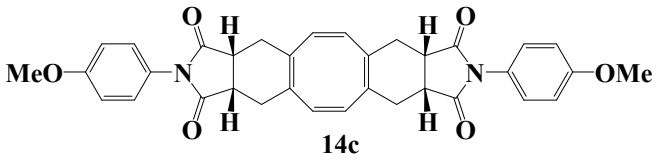
Figure 34 100 MHz ^{13}C NMR spectrum of **14c** in $CDCl_3$



4a

Table 1 Crystallographic data for **4a**

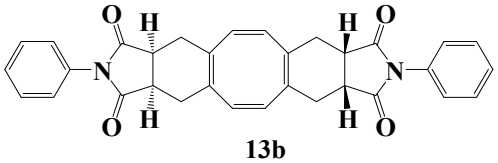
Parameter	Data
CCDC Number	2017969
Empirical Formula	$C_{28}H_{32}O_8$
Formula weight	496.53
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Tetragonal, I-4
Unit cell dimensions	a =31.5358(10) Å, alpha = 90˚ b = 31.5358 (10) Å, beta = 90˚ c = 5.2684 (2)Å, gamma = 90˚
Volume	5239.5(4) A^3
Z, Calculated density	8, 1.259 Mg/m^3
Absorption coefficient	0.092 mm^{-1}
F(000)	2112
Crystal size	0.250 × 0.220 × 0.100 mm
Theta range for data collection	0.913 to 24.785 deg
Limiting indices	-36<=h<=37, -37<=k<=37, -5<=l=<6
Reflections collected / unique	14835 / 4221 [R (int) = 0.0424]
Completeness to theta = 24.990	94.2%
Absorption correction	None
Refinement method	Full – matrix least – squares on F^2
Data/ restraints / parameters	4221 / 1 / 320
Goodness-of-fit on F^2	0.939
Final R indices [I>2sigma(I)]	R1 = 0.0514, wR2 = 0.1360
R indices (all data)	R1 = 0.0977, wR2 = 0.1715
Extinction coefficient	0.0013 (6)



14c

Table 2 Crystallographic data for **14c**

Parameter	Data
CCDC Number	2017970
Empirical Formula	$C_{34}H_{30}N_2O_4$
Formula weight	562.62
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1) / c
Unit cell dimensions	a =13.8398(4) A°, alpha = 90° b = 21.1600 (3) A°, beta = 122.381° c = 12.9507 (6)A°, gamma = 90°
Volume	3156.79 (14) A^3
Z, Calculated density	4, 1.248 Mg/ m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	1056
Crystal size	0.250 × 0.220 × 0.160 mm
Theta range for data collection	2.095 to 24.989 deg
Limiting indices	-16<=h<=16, -11<=k<=11, -23<=l=<23
Reflections collected / unique	15204 / 4008 [R (int) = 0.0432]
Completeness to theta = 24.990	85.2%
Absorption correction	None
Refinement method	Full – matrix least – squares on F^2
Data/ restraints / parameters	4008 / 0 / 344
Goodness-of-fit on F^2	0.889
Final R indices [l>2sigma(I)]	R1 = 0.0493, wR2 = 0.1128
R indices (all data)	R1 = 0.0903, wR2 = 0.1295
Extinction coefficient	0.0117 (12)



13b

Table 3 Crystallographic data for **13b**

Parameter	Data
CCDC Number	2017972
Empirical Formula	$C_{32}H_{26}N_2O_4$
Formula weight	502.55
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1) / c
Unit cell dimensions	a =13.8872(4) A°, alpha = 90° b = 9.9072 (3) A°, beta = 90° c = 19.4383 (6)A°, gamma = 90°
Volume	2674.38(14) A^3
Z, Calculated density	4, 1.248 Mg/ m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	1056
Crystal size	0.250 × 0.220 × 0.160 mm
Theta range for data collection	2.095 to 24.989 deg
Limiting indices	-16<=h<=16, -11<=k<=11, -23<=l=<23
Reflections collected / unique	15204 / 4008 [R (int) = 0.0432]
Completeness to theta = 24.990	85.2%
Absorption correction	None
Refinement method	Full – matrix least – squares on F^2
Data/ restraints / parameters	4008 / 0 / 344
Goodness-of-fit on F^2	0.889
Final R indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.1128
R indices (all data)	R1 = 0.0903, wR2 = 0.1295
Extinction coefficient	0.0117 (12)