Electronic Supplementary Information

Aromatic hydrocarbon macrocycles for highly efficient organic light-emitting devices with single-layer architectures

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Supplementary Data

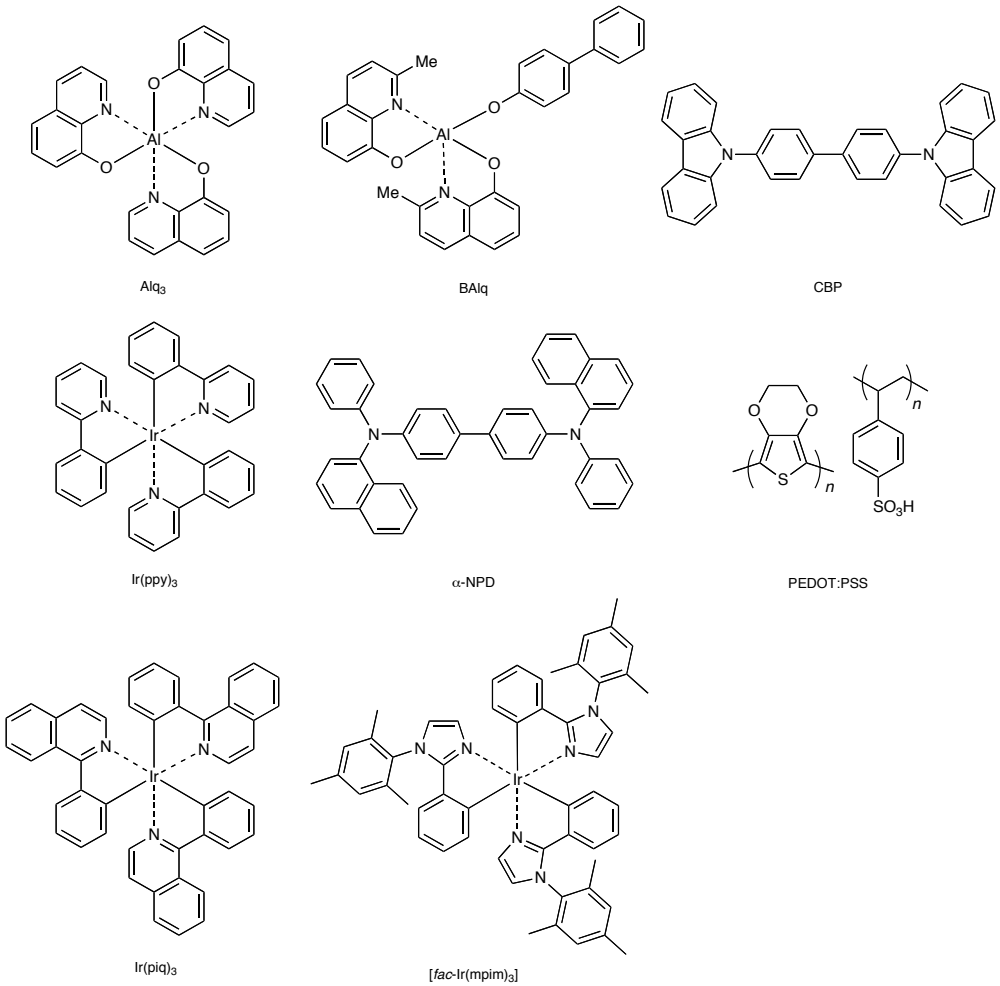


Fig. S1 Chemical structures of molecular materials.

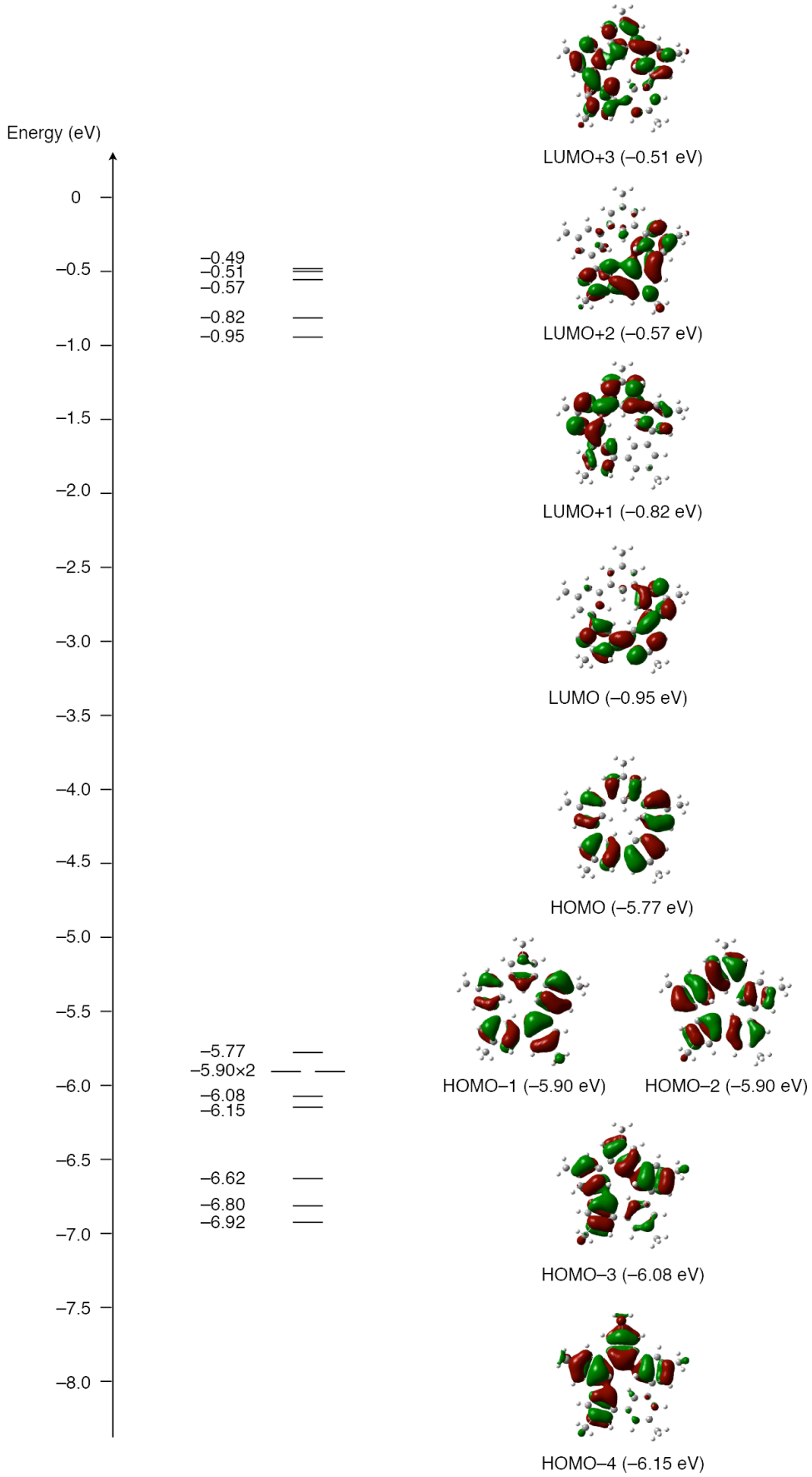


Fig. S2 MO diagram of 5Me-[5]CMP from DFT calculations at B3LYP/6-31G(d,p) level. See Table S1 for the theoretical analysis of the excitations with TD DFT calculations.

Table S1 Adiabatic transitions of 5Me-[5]CMP for 30 states. The cyclic structure resulted in a negligible oscillator strength of the excitation at the narrowest gap between HOMO and LUMO. Note that DFT methods tend to underestimate the excitation energy to afford slightly red-shifted excitations.

entry	wavelength (nm)	oscillator strength	assignment (major component)
1	291.19	0.0340	HOMO–1 → LUMO+1
2	285.99	0.0003	HOMO–2 → LUMO
3	283.59	0.0140	HOMO → LUMO+1
4	276.71	0.0156	HOMO–4 → LUMO+1
5	275.75	0.0201	HOMO → LUMO
6	273.68	0.0517	HOMO → LUMO
7	271.24	0.0527	HOMO–1 → LUMO+1
8	270.69	0.0103	HOMO → LUMO+2
9	267.56	0.0162	HOMO → LUMO+1
10	263.61	0.0019	HOMO–4 → LUMO
11	262.37	0.0628	HOMO–2 → LUMO+1
12	261.18	0.1005	HOMO–2 → LUMO+2
13	256.81	0.1612	HOMO–4 → LUMO
14	256.21	0.0884	HOMO → LUMO+4
15	255.31	0.0431	HOMO → LUMO+3
16	254.19	0.1015	HOMO–2 → LUMO+2
17	253.01	0.1957	HOMO–1 → LUMO+2
18	250.23	0.4762	HOMO–4 → LUMO+1
19	248.59	0.1646	HOMO–3 → LUMO+2
20	247.39	0.0602	HOMO–1 → LUMO+4
21	246.42	0.0295	HOMO–4 → LUMO+2
22	243.39	0.0071	HOMO–3 → LUMO+3
23	243.09	0.0010	HOMO–2 → LUMO+4
24	240.97	0.0306	HOMO–4 → LUMO+4
25	240.39	0.0092	HOMO–5 → LUMO
26	238.76	0.1130	HOMO–4 → LUMO+3
27	236.50	0.0359	HOMO–5 → LUMO+1
28	232.84	0.0359	HOMO–6 → LUMO
29	228.82	0.0078	HOMO–7 → LUMO
30	227.32	0.0383	HOMO–6 → LUMO+1

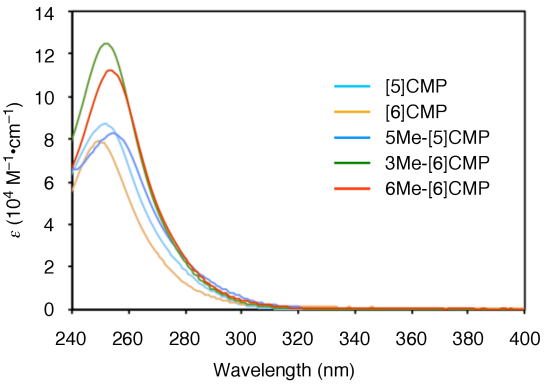


Fig. S3 UV-vis absorption spectra of CMP. Spectra were recorded in $CHCl_3$ at ambient temperature using a Jasco V-670 spectrometer. The concentrations of compounds were as follows: [5]CMP = 2.96×10^{-6} M, [6]CMP = 1.65×10^{-6} M, 5Me-[5]CMP = 3.60×10^{-6} M, 3Me-[6]CMP = 3.85×10^{-6} M and 6Me-[6]CMP = 5.34×10^{-6} M. The concentrations were carefully determined using combustion elemental analysis data.

Supplementary Methods

1. Synthesis general

All the solvents and the chemicals were reagent grade and used without further purification. 3,5-Dibromotoluene was purchased from Tokyo Chemical Industry, tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct was purchased from Sigma-Aldrich and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl and cesium carbonate were purchased from Wako Pure Chemical Industries. DMF was purchased from Kanto Chemical and purified by a Glass Contour solvent purification system equipped with columns of activated alumina and supported copper catalyst (Q-5). Thin-layer chromatography was performed on MERCK TLC Silica gel 60 F254 plates, and the R_f values were reported. Gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-9104 with JAIGEL 1H, 2H and 2.5H polystyrene columns (40 ϕ × 600 mm for each column) with the eluent of chloroform. The analysis of product purity was performed on a HPLC system equipped with a Cosmosil Buckyprep column (4.6 ϕ × 250 mm) at the flow rate of 1.0 mL/min and at 40 °C in a column oven (JASCO CO-2060PLUS) under the detection at 250 nm wavelength with UV-vis detector (JASCO MD2018PLUS). The product purity was further quantified by combustion elemental analysis on a J-Science Lab JM-11 for CHN and Yanaco YHS-11 for Cl. NMR spectra were obtained on JEOL RESONANCE JNM-ECS 400 or JNM-ECA 600 spectrometers, and the chemical shift values (δ) were given in ppm relative to internal $CHCl_3$ for ^{1}H NMR (δ 7.26) and $CDCl_3$ for ^{13}C NMR (δ 77.16). Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer equipped with an attenuated total reflection (ATR) accessory and reported as wavenumbers (ν) in cm^{-1}. Matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI TOF MS) was performed on a Bruker Daltonics microflex instrument with tetracyanoquinodimethane (TCNQ) as the matrix. High-resolution mass spectrometry (HRMS) by MALDI method was performed on a Bruker Daltonics

solariX 9.4T FT-ICR spectrometer with TCNQ as the matrix.

2. Physical data

5Me-[5]CMP: 15% yield (567 mg, 1.26 mmol). R_f = 0.30 (chloroform:hexane, 20:80 v/v); ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.27 (s, 5H), 7.50 (s, 10H), 2.53 (s, 15H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 141.3, 138.6, 132.4, 124.8, 22.2; IR (powder) ν 2915, 1582, 1473, 1392, 1315, 1039, 944, 919, 858, 843, 767, 696, 682, 639; HRMS (*m*/*z*): $[M]^+$ calcd for $C_{35}H_{30}$, 450.2342; found 450.2342; analysis (% calcd, % found for $C_{35}H_{30}$): C (93.29, 92.98), H (6.71, 6.63). A single crystal suitable for X-ray diffraction studies was obtained by slow diffusion of acetonitrile into the sample solution of chloroform.

6Me-[6]CMP: 24% yield (1.05 g, 1.61 mmol). R_f = 0.30 (chloroform:hexane, 25:75 v/v); ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.14 (t, J = 0.8 Hz, 6H), 7.53 (d, J = 0.8 Hz, 12H), 2.54 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 141.3, 139.0, 126.3, 124.6, 21.9; IR (powder) ν 2917, 1589, 1474, 1386, 1213, 1107, 1040, 954, 886, 843, 818, 768, 757, 696, 664; HRMS (*m*/*z*): $[M]^+$ calcd for $C_{42}H_{36}$, 540.2812; found 540.2812; analysis (% calcd, % found for $C_{42}H_{36}$•0.85$CHCl_3$•0.5H_2O): C (79.03, 78.91), H (5.86, 5.77), Cl (13.88, 13.55). A single crystal suitable for X-ray diffraction studies was obtained by slow diffusion of acetonitrile into the sample solution of chloroform.

7Me-[7]CMP: 10% yield (362 mg, 0.570 mmol). R_f = 0.17 (chloroform:hexane, 20:80 v/v); ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.81 (s, 7H), 7.44 (s, 14H), 2.50 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 141.8, 138.8, 127.4, 123.1, 21.8; IR (powder) ν 2914, 1590, 1469, 1384, 1039, 844, 734, 709, 698, 657, 646; HRMS (*m*/*z*): $[M]^+$ calcd for $C_{49}H_{42}$, 630.3281; found 630.3283; analysis (% calcd, % found for $C_{49}H_{42}$•0.03$CHCl_3$): C (92.98, 92.84), H (6.69, 6.59), Cl (0.34, 0.56). A single crystal suitable for X-ray diffraction studies was obtained by slow diffusion of acetonitrile into the sample solution of chloroform.

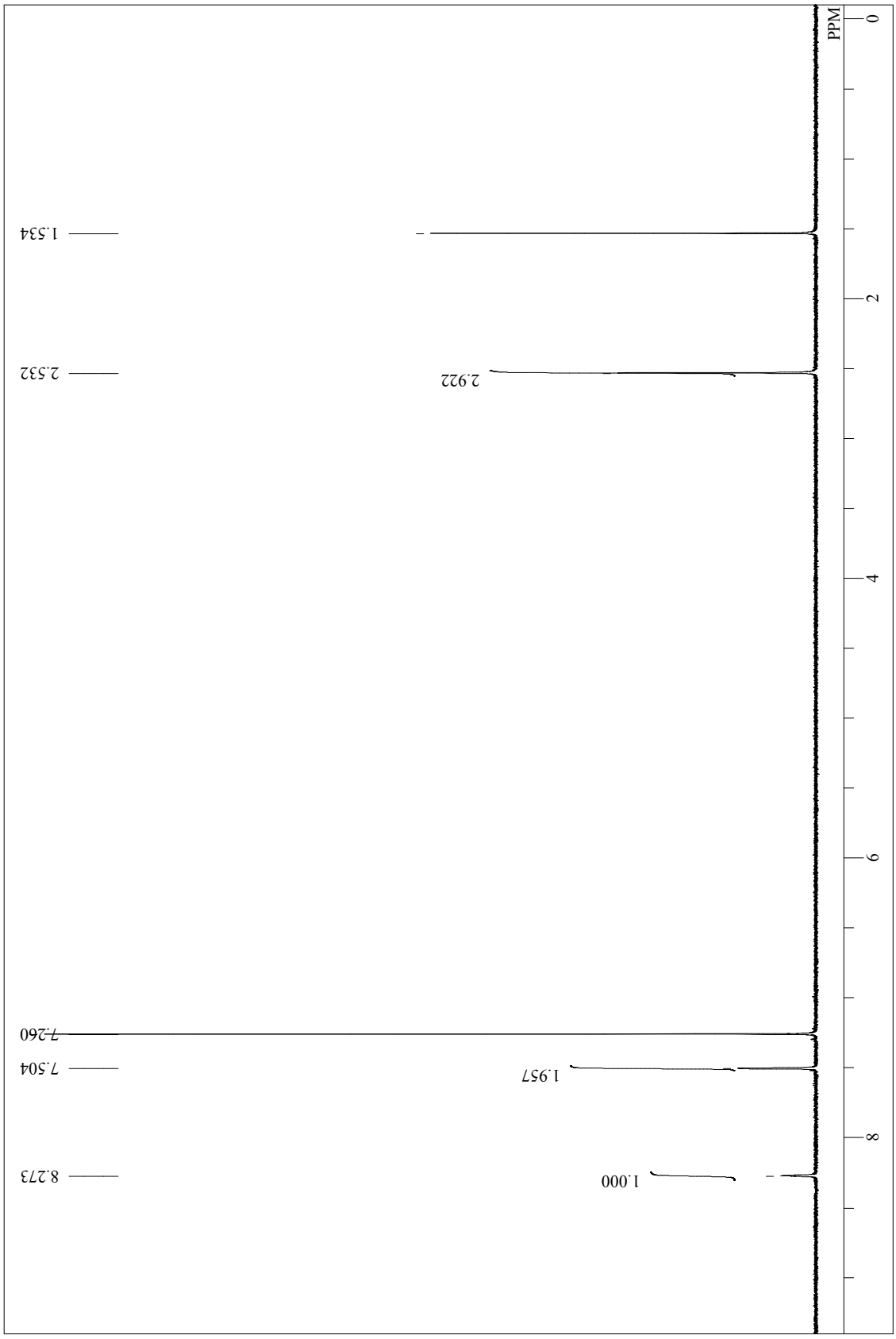
8Me-[8]CMP: 5% yield (205 mg, 0.239 mmol). R_f = 0.17 (chloroform:hexane, 20:80 v/v); ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.57 (s, 8H), 7.34 (s, 16H), 2.47 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 142.5, 138.6, 127.4, 124.5, 21.7; IR (powder) ν 2919, 1588, 1466, 1388, 1213, 1103, 1038, 886, 849, 753, 707, 700, 666, 645; HRMS (*m*/*z*): $[M]^+$ calcd for $C_{56}H_{48}$, 720.3751; found 720.3752; analysis (% calcd, % found for $C_{56}H_{48}$•0.9$CHCl_3$•0.9CH_3OH): C (80.98, 80.61), H (6.17, 5.88), Cl (11.17, 11.28). A single crystal suitable for X-ray diffraction studies was obtained by slow diffusion of hexane into the sample solution of chloroform.

9Me-[9]CMP: 3% yield (100 mg, 0.123 mmol). R_f = 0.17 (chloroform:hexane, 20:80 v/v); ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.53 (s, 9H), 7.36 (s, 18H), 2.46 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 142.2, 138.8, 127.2, 124.3, 21.7; IR (powder) ν 2916, 1589, 1456, 1386, 1038, 882, 844, 811, 761, 701, 645; HRMS (*m*/*z*): $[M]^+$ calcd for $C_{63}H_{54}$, 810.4220; found 810.4222; analysis (% calcd, % found for $C_{63}H_{54}$): C (93.29, 92.94), H (6.71, 6.83). A single crystal suitable for X-ray diffraction studies was obtained by slow diffusion of acetonitrile into the sample solution of chloroform.

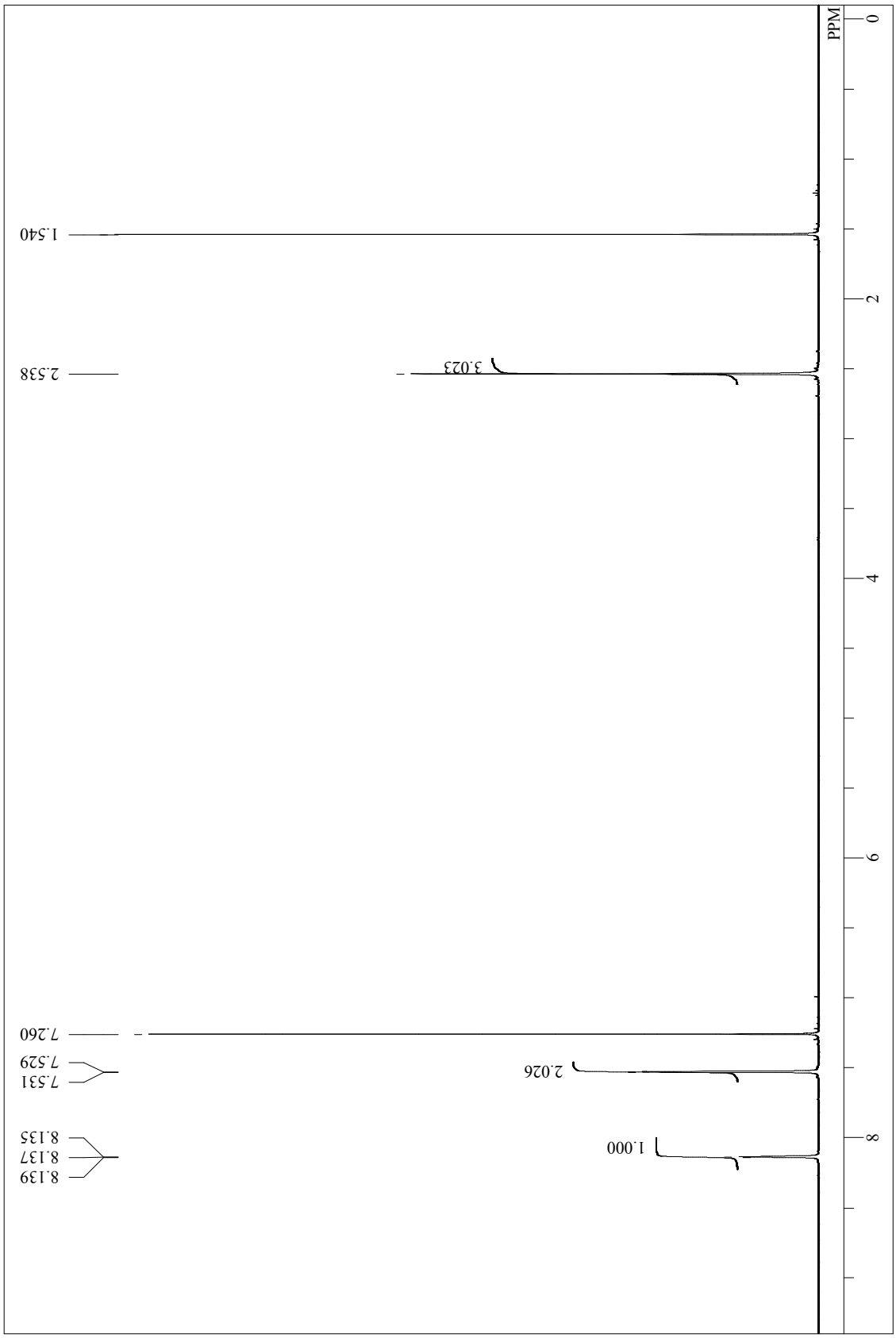
3Me-[6]CMP: R_f = 0.28 (chloroform:hexane, 25:75 v/v); ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.35 (s, 3H),

8.16 (s, 3H), 7.71 (dd, J = 1.8, 7.8 Hz, 6H), 7.56 (t, J = 7.8 Hz, 3H), 7.55 (s, 6H), 2.55 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$, rt): δ 141.4, 141.3, 139.2, 129.5, 127.2, 126.5, 125.5, 124.4, 22.0; IR (powder) ν 3054, 2997, 2918, 1592, 1576, 1495, 1383, 1226, 1211, 1090, 852, 780, 752, 696; HRMS (m/z): $[M]^+$ calcd for $C_{39}H_{30}$, 498.2342; found 498.2343; analysis (% calcd, % found for $C_{39}H_{30}$): C (93.94, 93.83), H (6.06, 6.14). A single crystal suitable for X-ray diffraction studies was obtained by slow diffusion of methanol into the sample solution of chloroform.

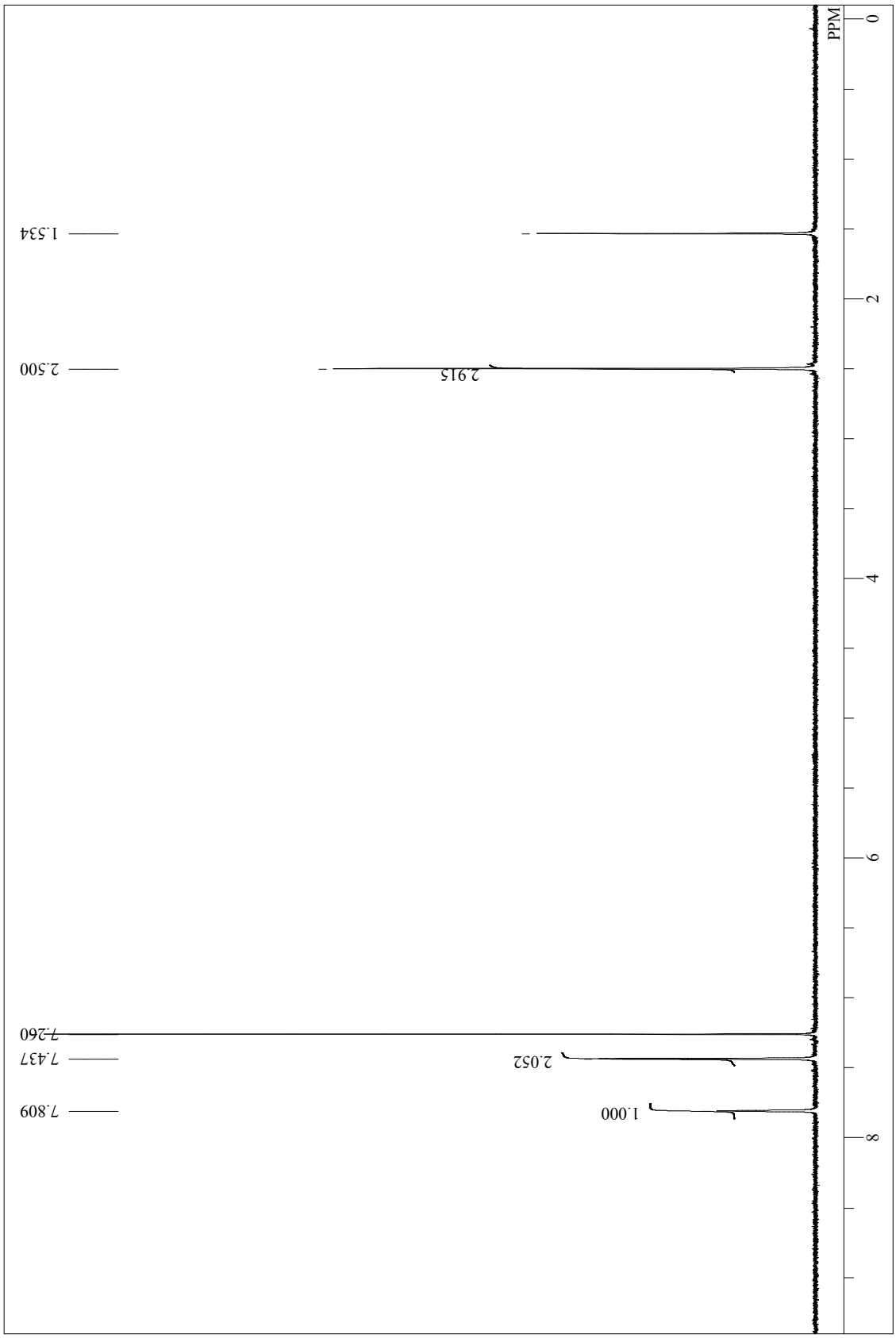
3. Spectra



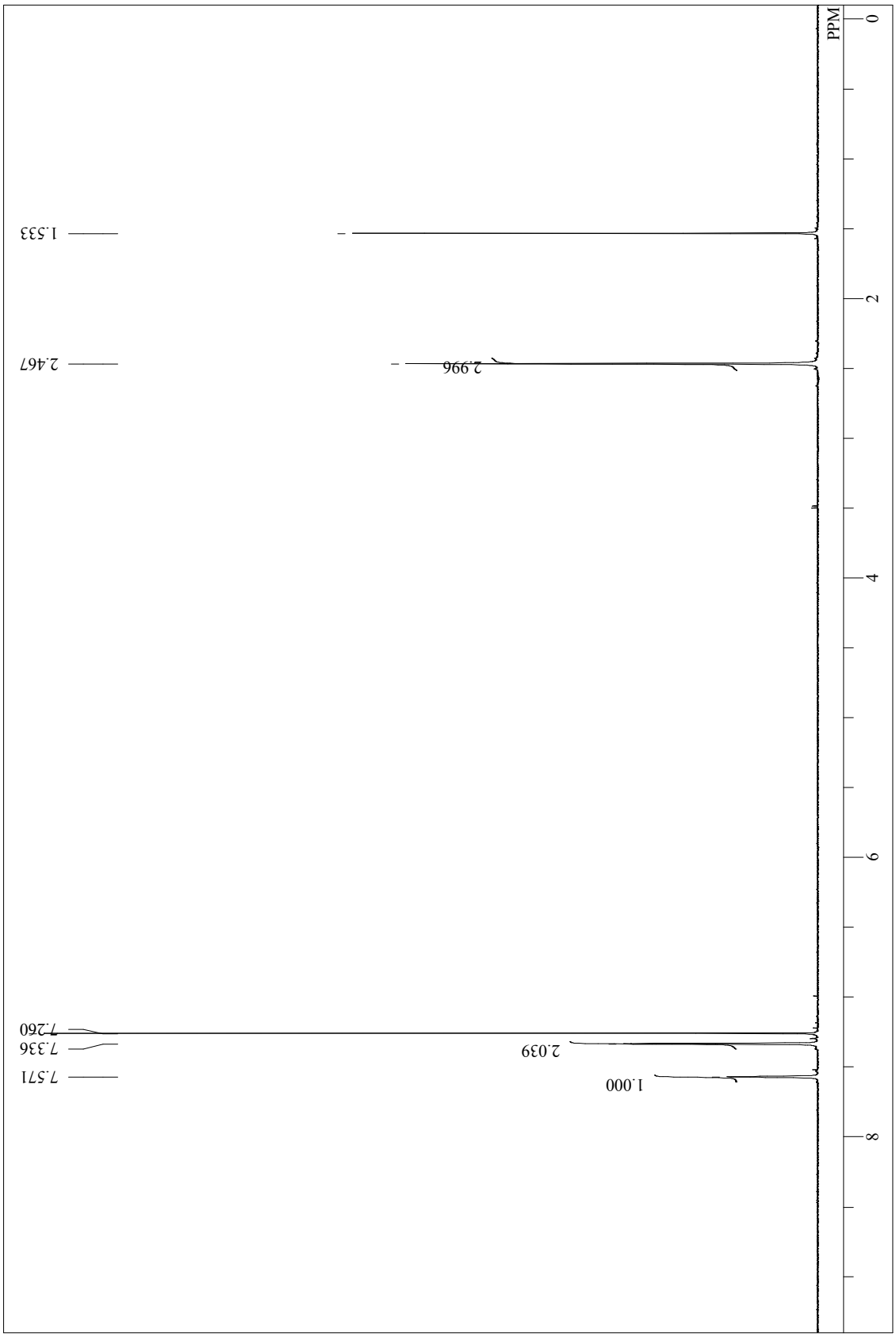
Spectrum S1 ^{1}H NMR spectrum of 5Me-[5]CMP in $CDCl_3$.



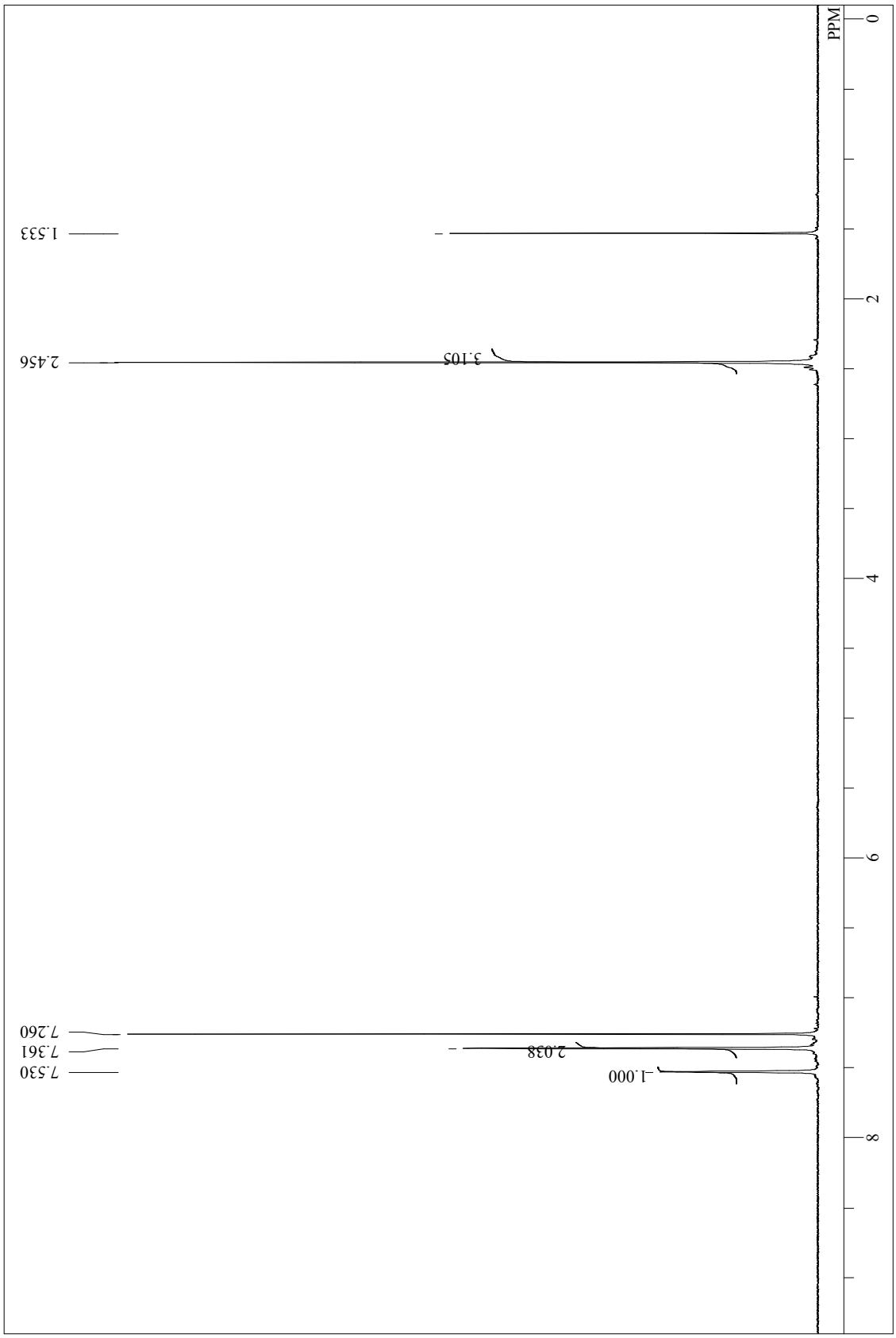
Spectrum S2 ^{1}H NMR spectrum of 6Me-[6]CMP in $CDCl_3$.



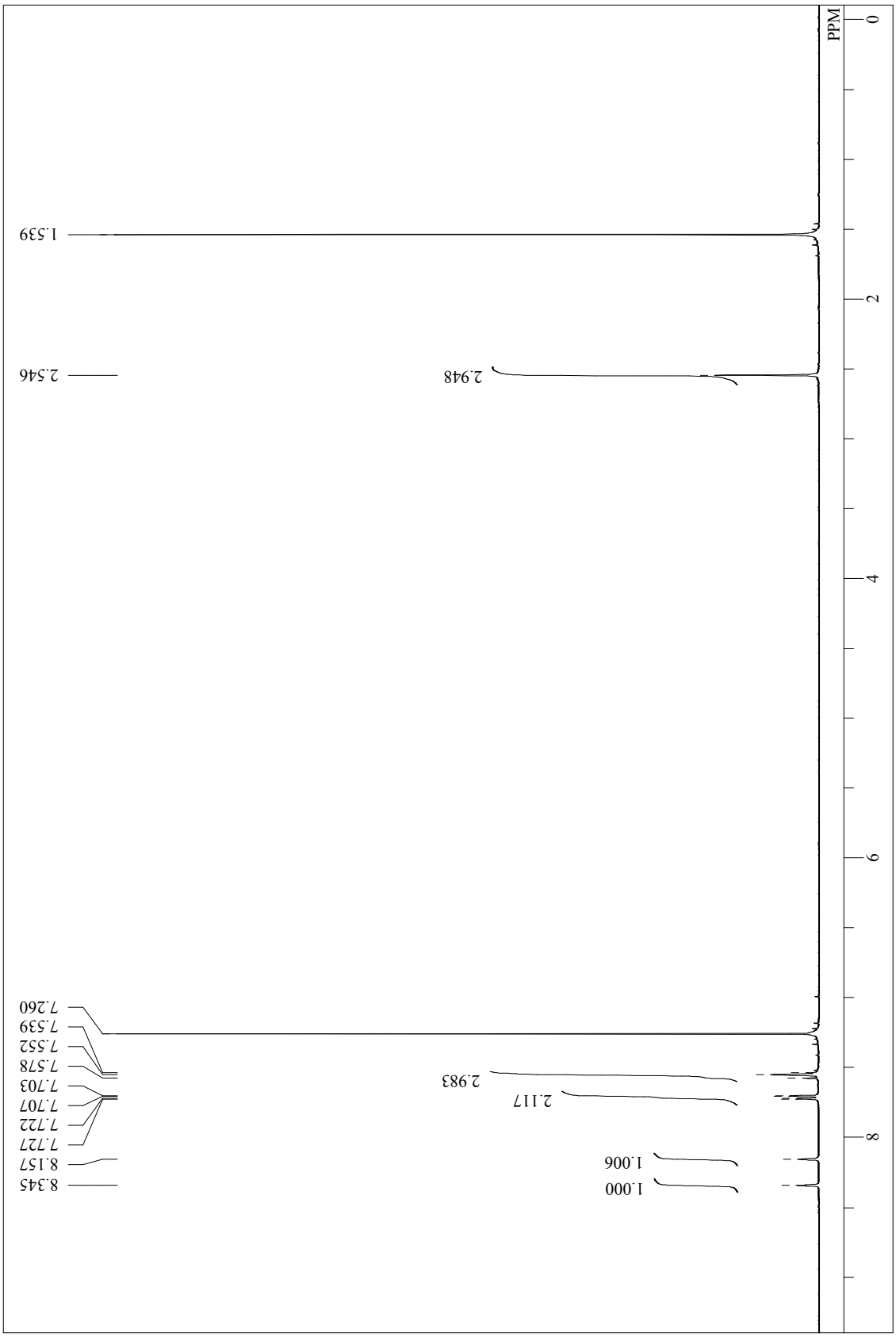
Spectrum S3 ^{1}H NMR spectrum of 7Me-[7]CMP in $CDCl_3$.



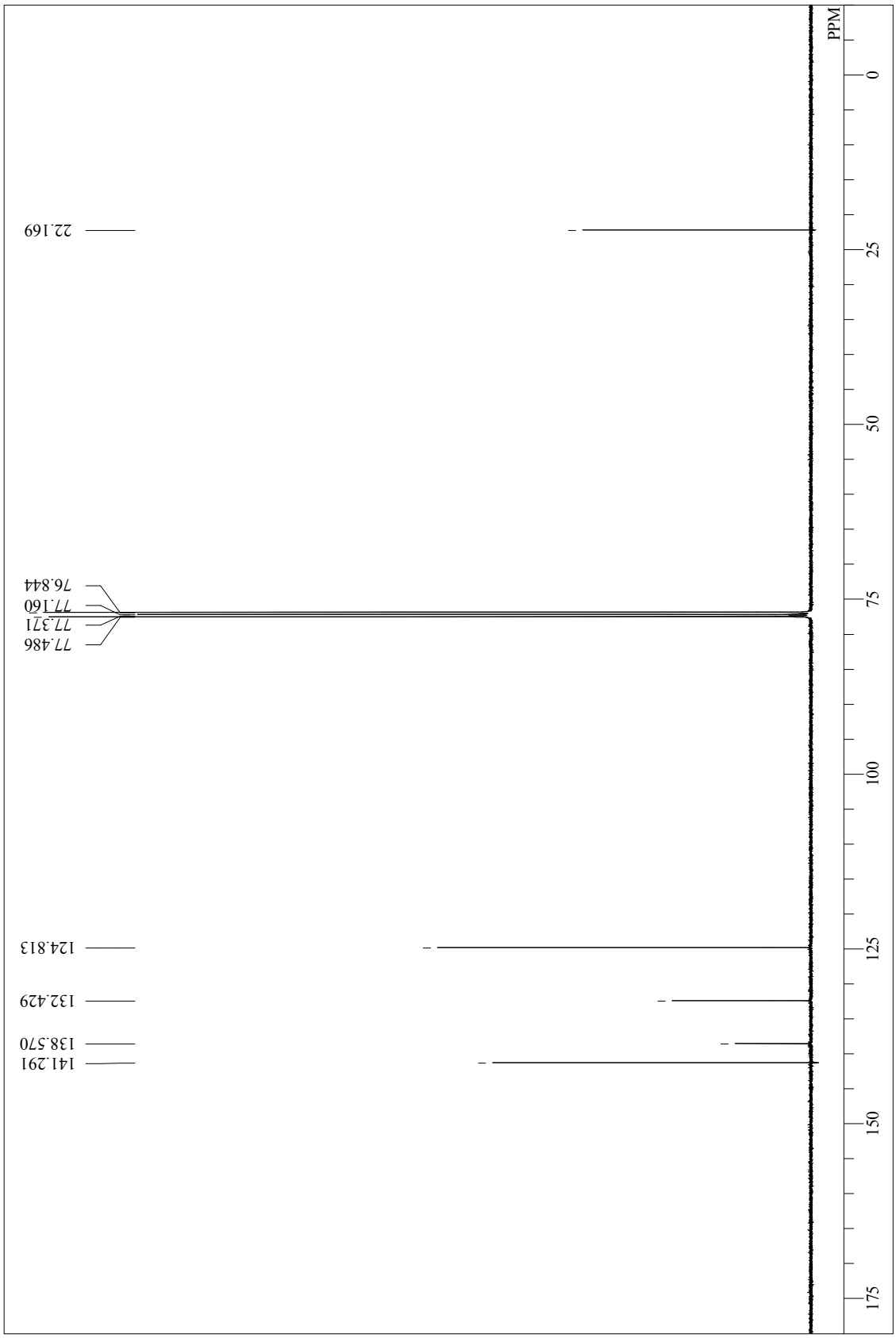
Spectrum S4 ^{1}H NMR spectrum of 8Me-[8]CMP in $CDCl_3$.



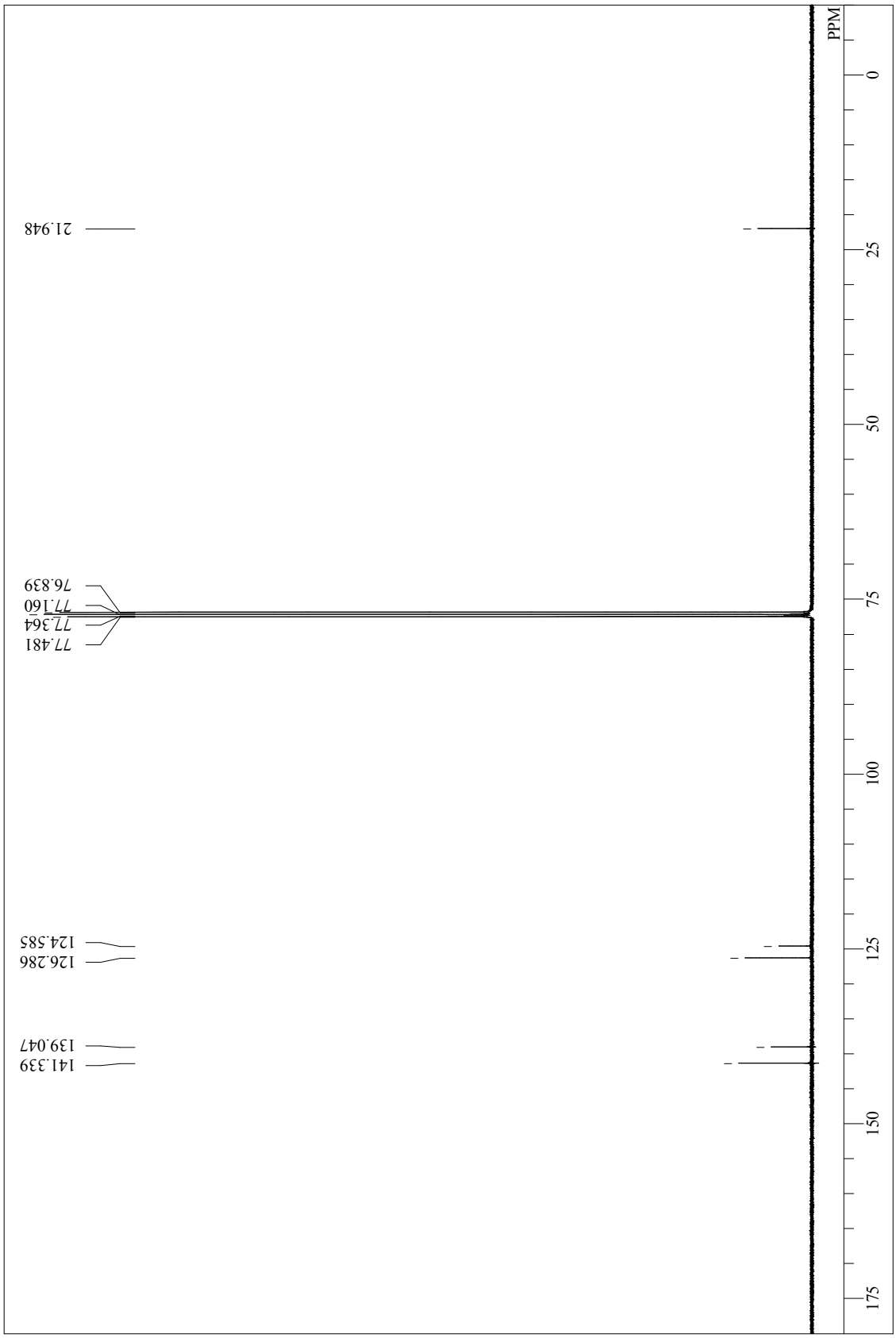
Spectrum S5 ^{1}H NMR spectrum of 9Me-[9]CMP in $CDCl_3$.



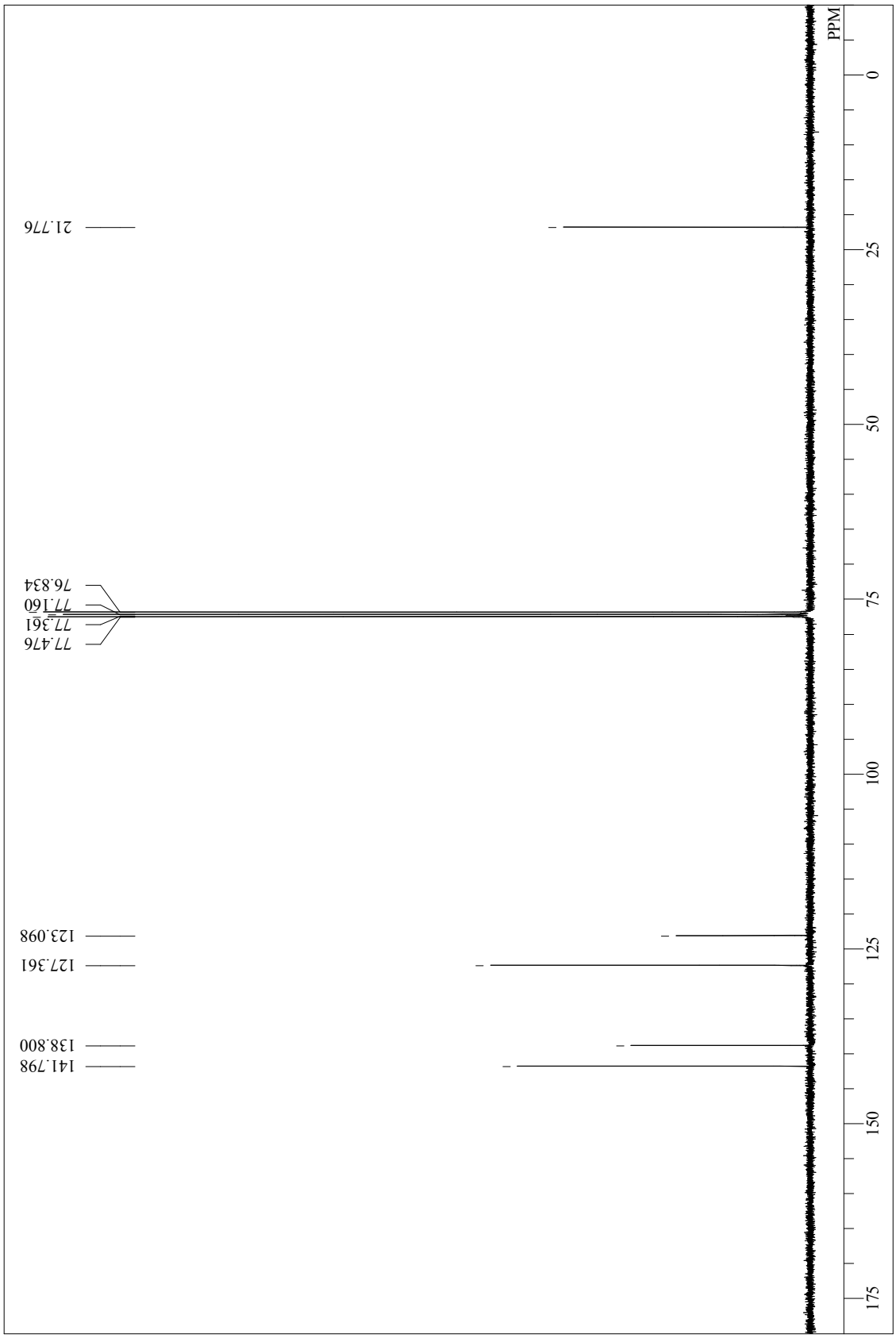
Spectrum S6 ^{1}H NMR spectrum of 3Me-[6]CMP in $CDCl_3$.



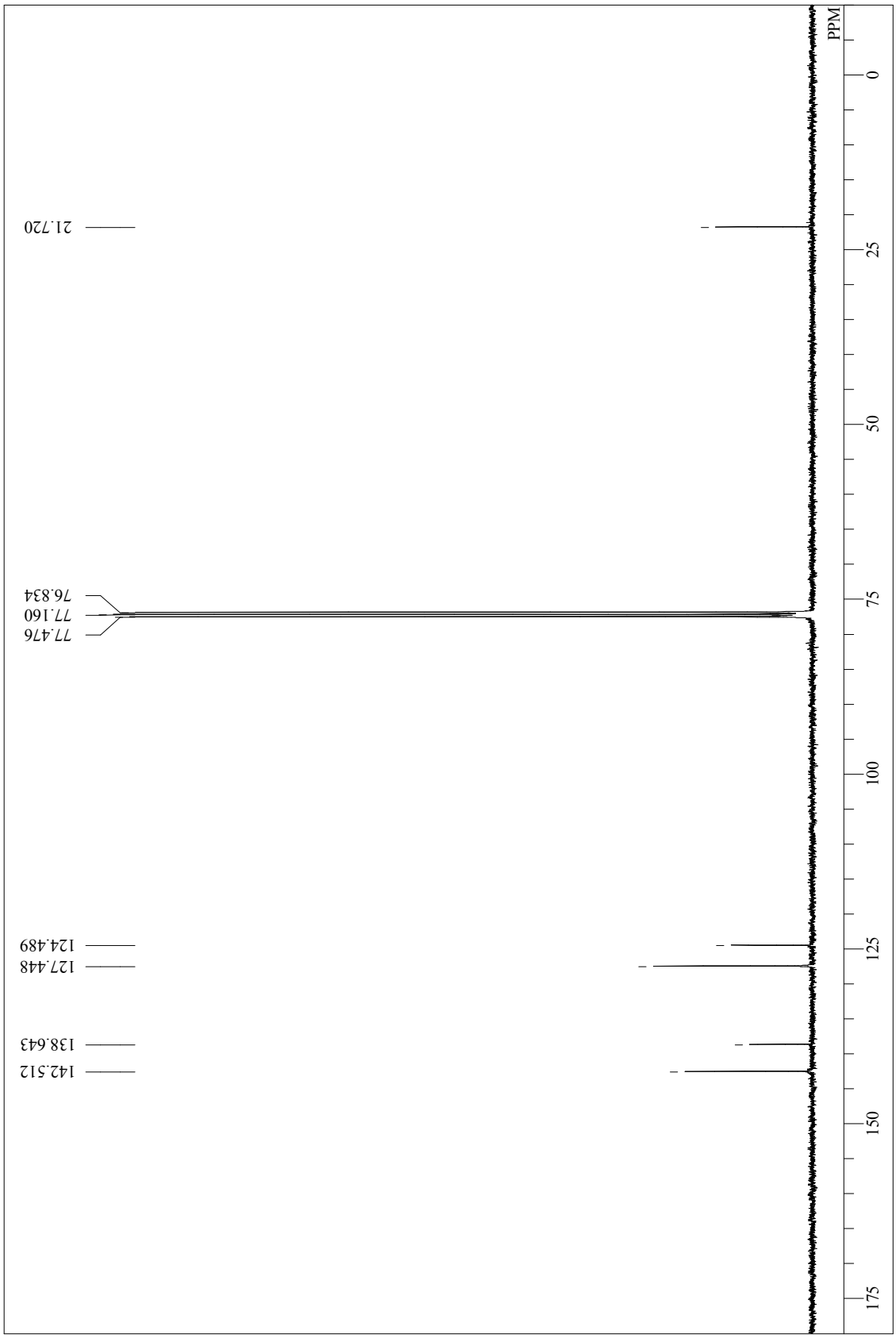
Spectrum S7 ^{13}C NMR spectrum of 5Me-[5]CMP in $CDCl_3$.



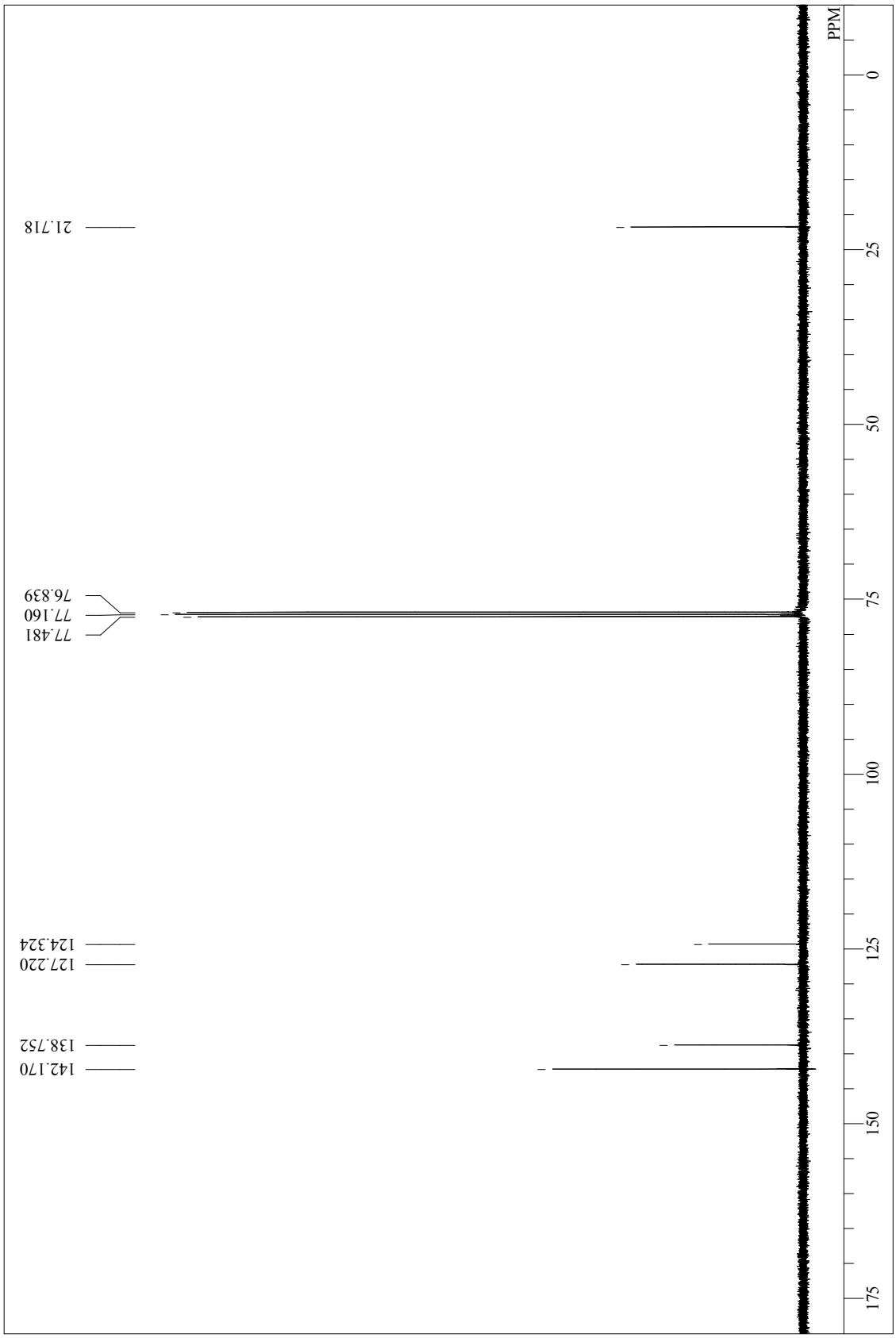
Spectrum S8 ^{13}C NMR spectrum of 6Me-[6]CMP in $CDCl_3$.



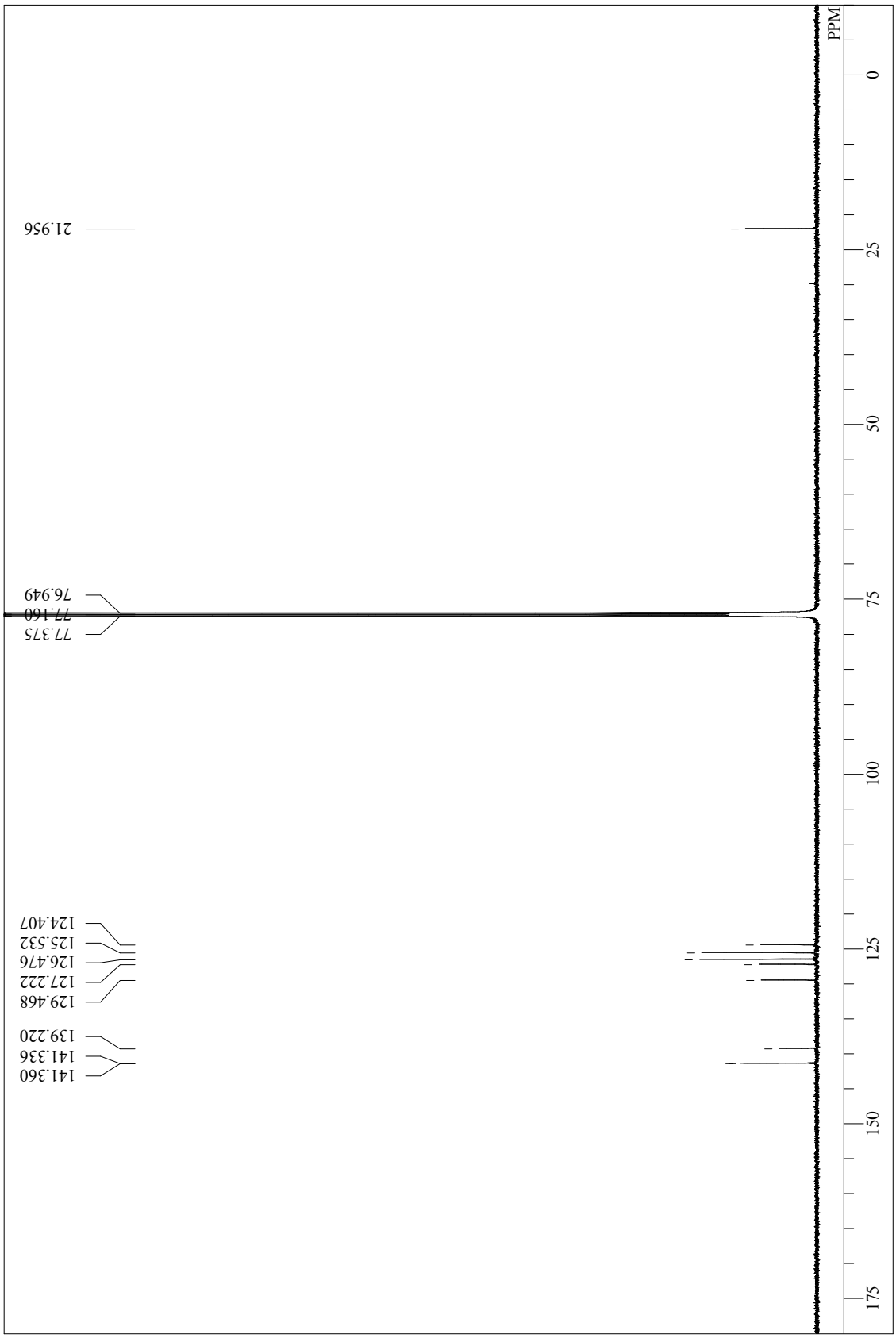
Spectrum S9 ^{13}C NMR spectrum of 7Me-[7]CMP in $CDCl_3$.



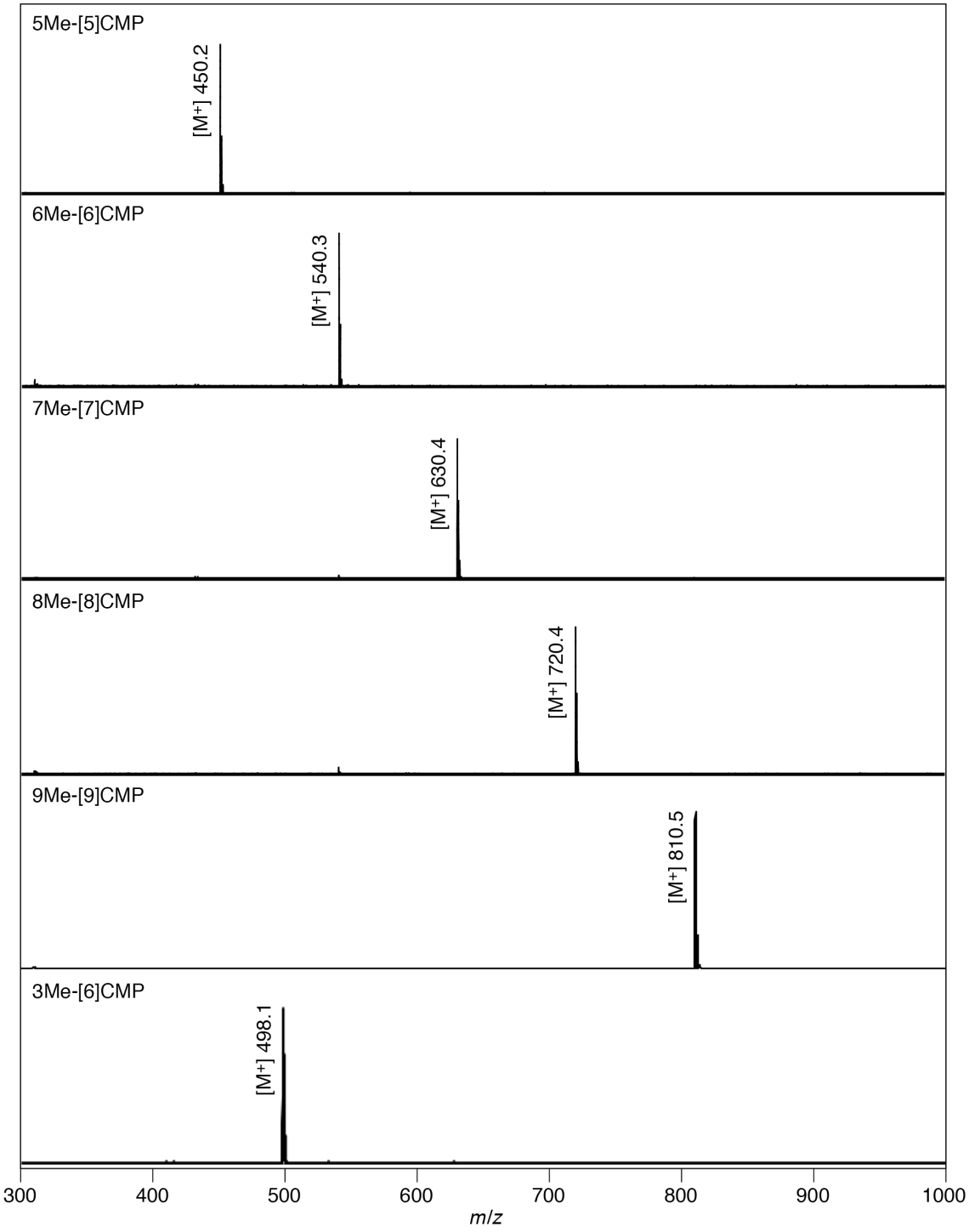
Spectrum S10 ^{13}C NMR spectrum of 8Me-[8]CMP in $CDCl_3$.



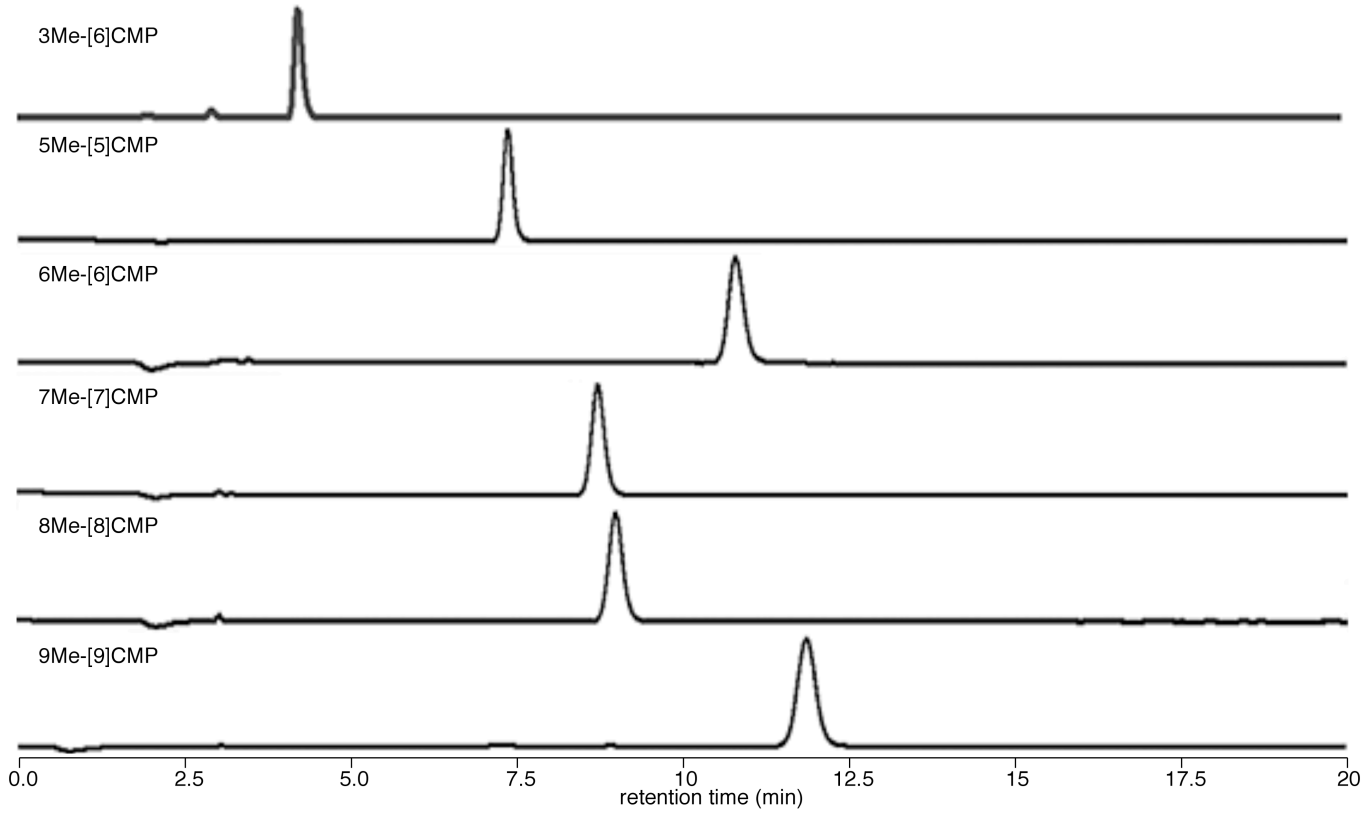
Spectrum S11 ^{13}C NMR spectrum of 9Me-[9]CMP in $CDCl_3$.



Spectrum S12 ^{13}C NMR spectrum of 3Me-[6]CMP in $CDCl_3$.

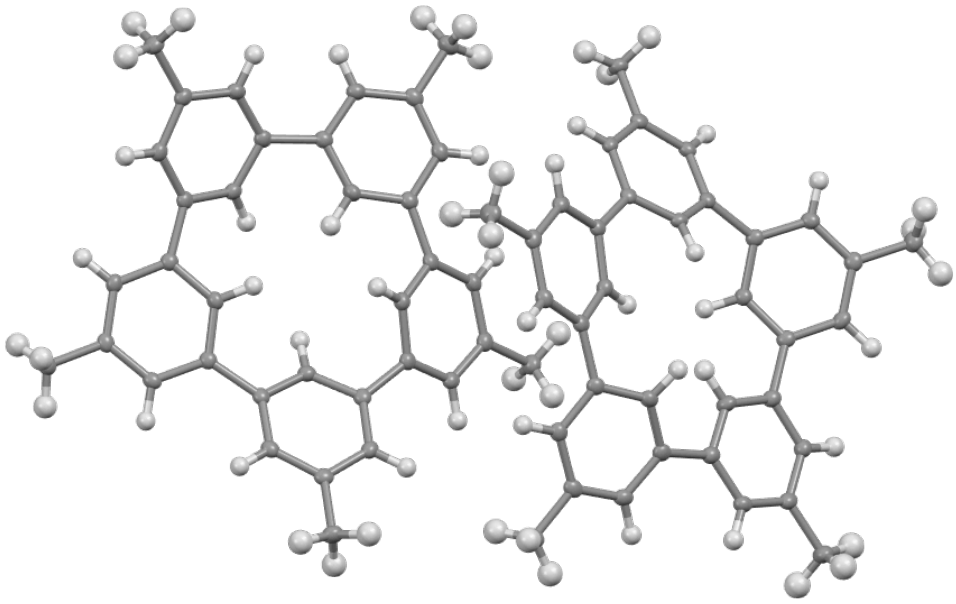


Spectrum S13 MALDI MS spectra of CMP.

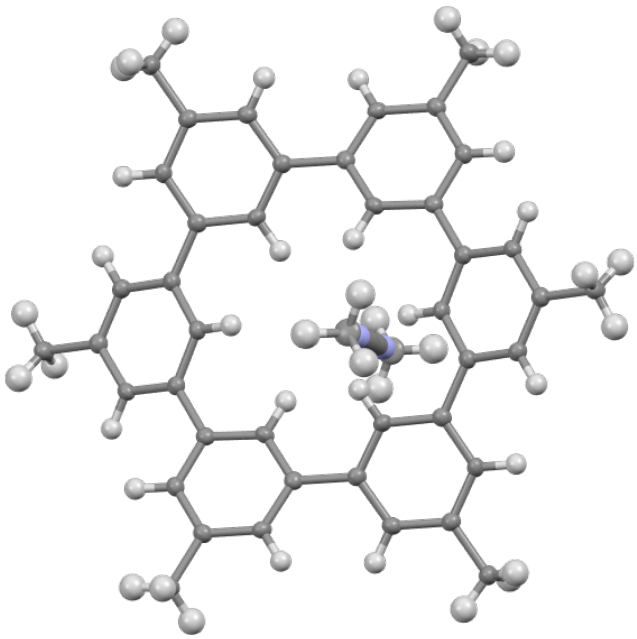


HPLC chart S1 HPLC charts of CMP. Eluent = 40% methanol/chloroform for *n*Me-[*n*]CMP (*n* = 5-9) and 35% methanol/chloroform for 3Me-[6]CMP.

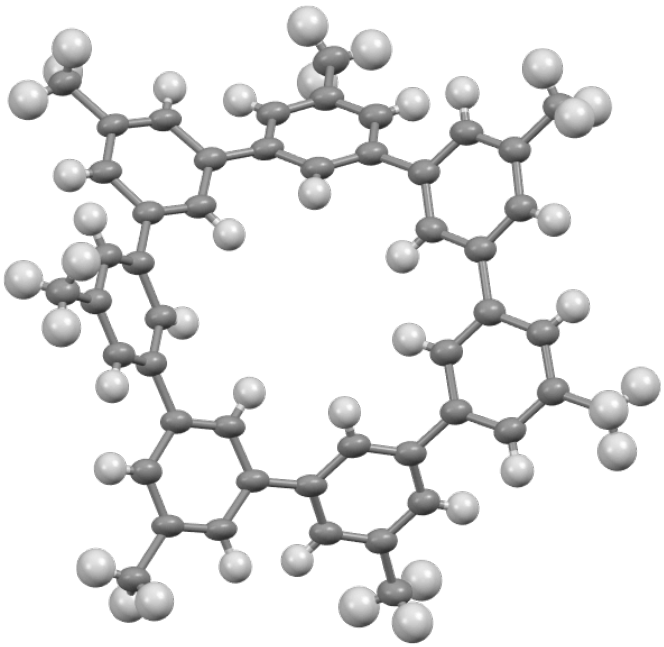
4. X-ray data



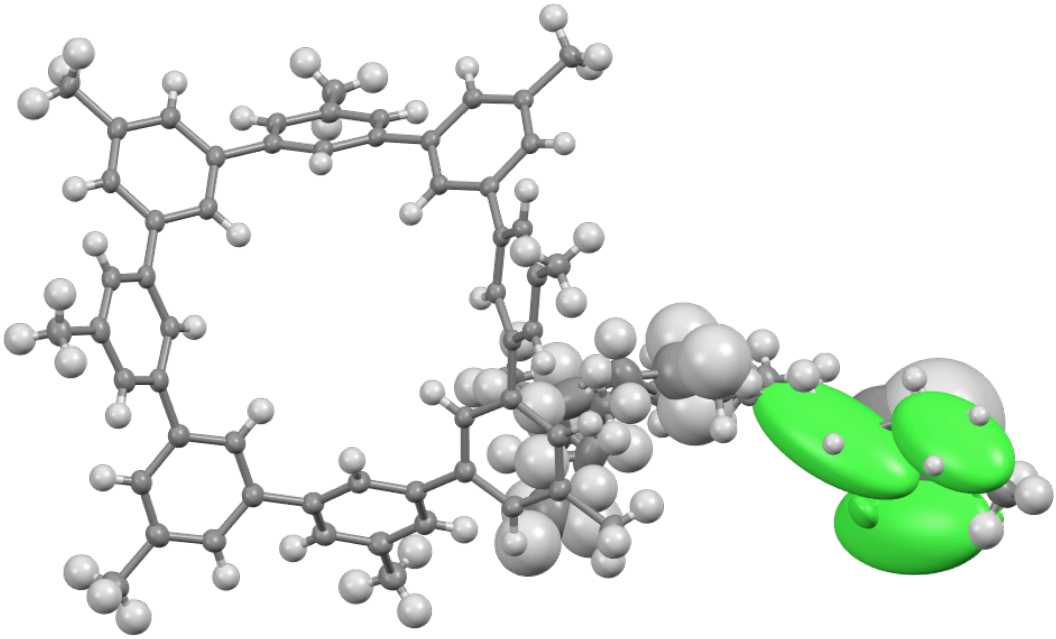
ORTEP Diagram S1 5Me-[5]CMP. Thermal ellipsoids are drawn at 50% probability. CCDC 1054912.



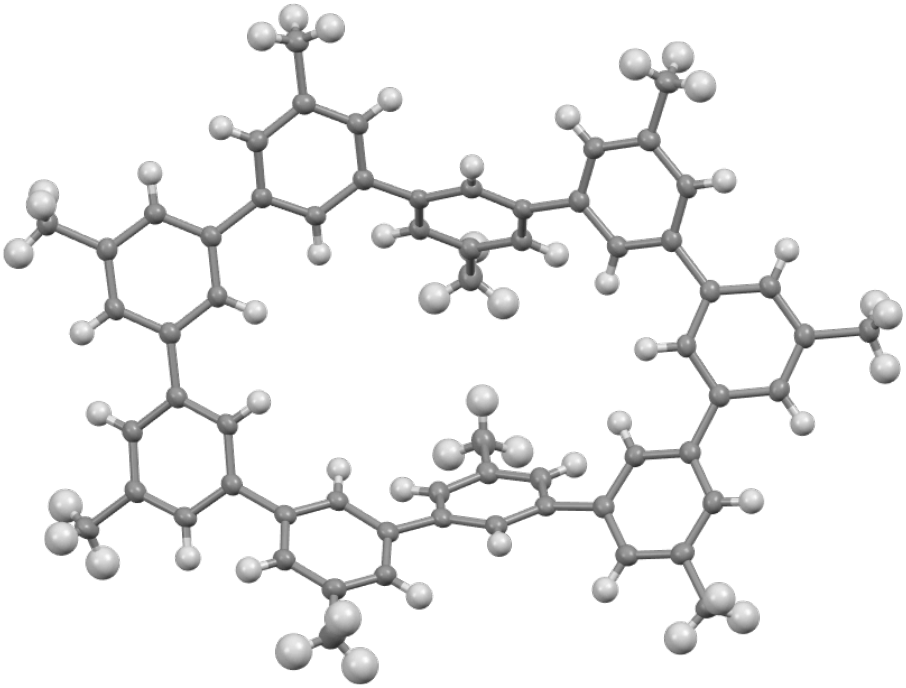
ORTEP Diagram S2 6Me-[6]CMP. Thermal ellipsoids are drawn at 50% probability. CCDC 1054913.



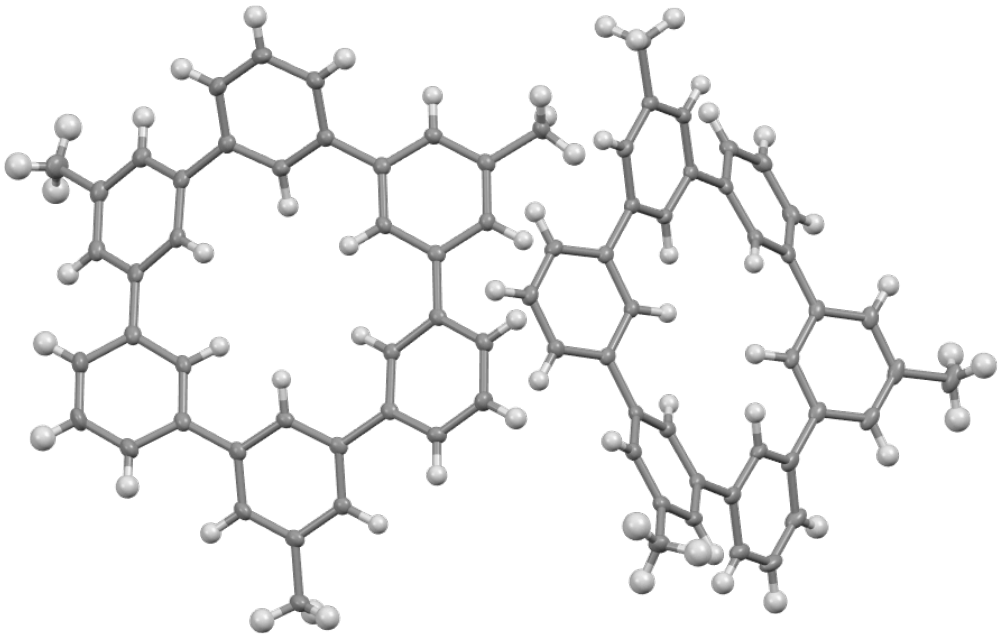
ORTEP Diagram S3 7Me-[7]CMP. Thermal ellipsoids are drawn at 50% probability. CCDC 1054914.



ORTEP Diagram S4 8Me-[8]CMP. Thermal ellipsoids are drawn at 50% probability. CCDC 1054915.



ORTEP Diagram S5 9Me-[9]CMP. Thermal ellipsoids are drawn at 50% probability. CCDC 1054916.



ORTEP Diagram S6 3Me-[6]CMP. Thermal ellipsoids are drawn at 50% probability. CCDC 1054917.

Table S2 Crystal data and structure refinement for 5Me-[5]CMP (CCDC 1054912).

Empirical formula	$C_{35}H_{30}$
Formula weight	450.62
Temperature	93 K
Wavelength	1.54187 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 7.3879(4) Å α = 90º
	b = 15.8520(10) Å β = 90.675(3)º
	c = 41.261(3) Å γ = 90º
Volume	4831.9(5) Å^3
Z	8
Density (calculated)	1.239 Mg/m^3
Absorption coefficient	0.524 mm^{-1}
F(000)	1920.00
Crystal size	0.60 x 0.50 x 0.40 mm^3
Crystal color	Colorless
Theta range for data collection	4.26º to 68.90º
Index ranges	–8<=h<=8, –19<=k<=19, –48<=l<=33
Reflections collected	65777
Independent reflections	8824 [R(int) = 0.0621]

Completeness to theta = 68.90º	98.6%
Absorption correction	Empirical
Max. and min. transmission	0.811 and 0.561
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8824 / 0 / 641
Goodness-of-fit on F^2	1.097
Final R indices [I > 2sigma(I)]	R_1 = 0.0494, wR_2 = 0.1236
R indices (all data)	R_1 = 0.0539, wR_2 = 0.1274
Largest diff. peak and hole	0.40 and –0.58 e.Å^{-3}

Table S3 Crystal data and structure refinement for 6Me-[6]CMP (CCDC 1054913).

Empirical formula	$C_{44}H_{39}N$	
Formula weight	581.80	
Temperature	93 K	
Wavelength	1.54187 Å	
Crystal system	Trigonal	
Space group	*R*$\bar{3}$:H	
Unit cell dimensions	a = 18.861(11) Å	α = 90º
	b = 18.861(11) Å	β = 90º
	c = 7.446(5) Å	γ = 120º
Volume	2294(2) Å^3	
Z	3	
Density (calculated)	1.263 Mg/m^3	
Absorption coefficient	0.544 mm^{-1}	
F(000)	930.00	
Crystal size	0.08 x 0.04 x 0.03 mm^3	
Crystal color	Colorless	
Theta range for data collection	4.69º to 68.44º	
Index ranges	–20<=h<=22, –22<=k<=22, –8<=l<=8	
Reflections collected	10140	
Independent reflections	940 [R(int) = 0.0550]	
Completeness to theta = 68.44º	99.8%	
Absorption correction	Empirical	
Max. and min. transmission	0.984 and 0.767	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	940 / 14 / 75	

Goodness-of-fit on F^2	1.078
Final R indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0517$, $wR_2 = 0.1287$
R indices (all data)	$R_1 = 0.0725$, $wR_2 = 0.1494$
Largest diff. peak and hole	0.38 and –0.64 e.Å^{-3}

Table S4 Crystal data and structure refinement for 7Me-[7]CMP (CCDC 1054914).

Empirical formula	$C_{49}H_{42}$	
Formula weight	630.83	
Temperature	93 K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	$a = 29.026(6)$ Å	$\alpha = 90^\circ$
	$b = 7.5010(15)$ Å	$\beta = 104.96(3)^\circ$
	$c = 33.242(7)$ Å	$\gamma = 120^\circ$
Volume	6992(2) Å^3	
Z	8	
Density (calculated)	1.199 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	2688	
Crystal size	0.10 x 0.01 x 0.01 mm^3	
Crystal color	Colorless	
Theta range for data collection	2.68º to 24.64º	
Index ranges	$-30 \le h \le 31$, $-7 \le k \le 7$, $-36 \le l \le 36$	
Reflections collected	16620	
Independent reflections	4846 [R(int) = 0.0997]	
Completeness to theta = 24.64º	95.8%	
Absorption correction	Empirical	
Max. and min. transmission	0.999 and 0.993	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4846 / 0 / 449	
Goodness-of-fit on F^2	0.988	
Final R indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0720$, $wR_2 = 0.1942$	
R indices (all data)	$R_1 = 0.0919$, $wR_2 = 0.2118$	
Largest diff. peak and hole	0.41 and –0.33 e.Å^{-3}	

Table S5 Crystal data and structure refinement for 8Me-[8]CMP (CCDC 1054915).

Empirical formula	$C_{62.9}H_{62.9}Cl_{2.71}$
Formula weight	914.97
Temperature	93 K
Wavelength	1.54187 Å
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	a = 14.3269(11) Å α = 90º
	b = 17.0916(12) Å β = 90º
	c = 42.481(3) Å γ = 90º
Volume	10402.3(13) Å^3
Z	8
Density (calculated)	1.168 Mg/m^3
Absorption coefficient	1.739 mm^{-1}
F(000)	3890.96
Crystal size	0.01 x 0.01 x 0.01 mm^3
Crystal color	Colorless
Theta range for data collection	3.72º to 68.36º
Index ranges	–17<=h<=14, –20<=k<=20, –51<=l<=48
Reflections collected	65483
Independent reflections	9529 [R(int) = 0.0300]
Completeness to theta = 68.36º	99.9%
Absorption correction	Empirical
Max. and min. transmission	0.706 and 0.631
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9529 / 189 / 758
Goodness-of-fit on F^2	1.028
Final R indices [I > 2sigma(I)]	R_1 = 0.0618, wR_2 = 0.1835
R indices (all data)	R_1 = 0.0675, wR_2 = 0.1884
Largest diff. peak and hole	0.67 and –0.47 e.Å^{-3}

Table S6 Crystal data and structure refinement for 9Me-[9]CMP (CCDC 1054916).

Empirical formula	$C_{63}H_{54}$
Formula weight	811.12
Temperature	93 K
Wavelength	1.54187 Å

Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 22.263(2) Å	α = 90º
	b = 7.4477(8) Å	β = 109.502(3)º
	c = 28.978(3) Å	γ = 120º
Volume	4529.1(8) Å^3	
Z	4	
Density (calculated)	1.189 Mg/m^3	
Absorption coefficient	0.504 mm^{-1}	
F(000)	1728.00	
Crystal size	0.30 x 0.12 x 0.03 mm^3	
Crystal color	Colorless	
Theta range for data collection	4.21º to 74.65º	
Index ranges	–27<=h<=27, –9<=k<=8, –35<=l<=35	
Reflections collected	89912	
Independent reflections	8924 [R(int) = 0.0518]	
Completeness to theta = 74.65º	96.0%	
Absorption correction	Empirical	
Max. and min. transmission	0.985 and 0.836	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8924 / 0 / 577	
Goodness-of-fit on F^2	1.033	
Final R indices [I > 2sigma(I)]	R_1 = 0.0534, wR_2 = 0.1502	
R indices (all data)	R_1 = 0.0604, wR_2 = 0.1562	
Largest diff. peak and hole	0.42 and –0.25 e.Å^{-3}	

Table S7 Crystal data and structure refinement for 3Me-[6]CMP (CCDC 1054917).

Empirical formula	$C_{39}H_{30}$	
Formula weight	498.67	
Temperature	93 K	
Wavelength	1.54187 Å	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	a = 16.2912(16) Å	α = 90º
	b = 15.2859(17) Å	β = 90º
	c = 43.960(4)Å	γ = 90º

Volume	10947.2(19) $Å^3$
Z	16
Density (calculated)	1.210 Mg/m^3
Absorption coefficient	0.516 mm^{-1}
F(000)	4224.00
Crystal size	0.60 x 0.30 x 0.03 mm^3
Crystal color	Colorless
Theta range for data collection	3.38º to 68.33º
Index ranges	–19<=*h*<=19, –18<=*k*<=15, –52<=*l*<=52
Reflections collected	60215
Independent reflections	9831 [*R*(int) = 0.0311]
Completeness to theta = 68.33º	97.8%
Absorption correction	Empirical
Max. and min. transmission	0.985 and 0.880
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9831 / 0 / 720
Goodness-of-fit on F^2	1.050
Final *R* indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0343$, $wR_2 = 0.0904$
R indices (all data)	$R_1 = 0.0370$, $wR_2 = 0.0926$
Largest diff. peak and hole	0.23 and –0.25 $e.Å^{-3}$