Electronic Supplementary Material (ESI) for Chemical Communications

Manipulating the nanostructure of organogels generated from molecules with a 3-dimensional truxene core

Kuo-Pi Tseng,[a] Min-Tzu Kao,[a] Tim W.T. Tsai,[a] Chia-Huei Hsu,[a] Jerry C.C. Chan,[a] Jing-Jong Shyue,[b] Shih-Sheng Sun[c] and Ken-Tsung Wong*[a]

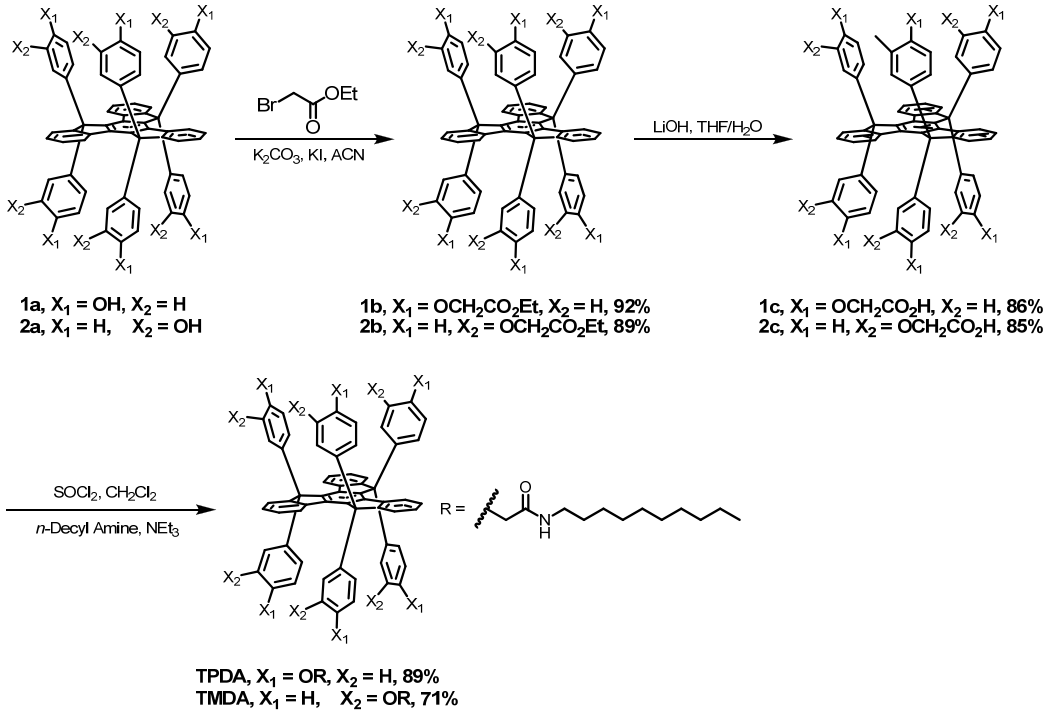
[a] *Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan, E-mail: kenwong@ntu.edu.tw*
[b] *Research Center for Applied Sciences, Acamedia Sinica 128 Academia Road, Nankang, Taipei 115, Taiwan.*
[c] *Institute of Chemistry, Acamedia Sinica 128 Academia Road, Nankang, Taipei 115,Taiwan.*

Supplementary Information[1]

Materials and methods:

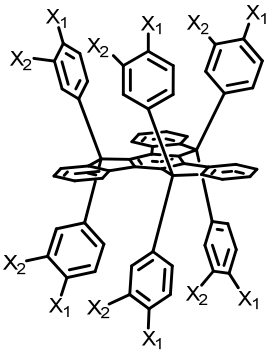
All the starting materials were purchased from commercial sources and used without further purification. Solvents for chemical synthesis were purified by distillation. All chemical reactions were carried out under an argon or nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra of compounds were collected on a 400 MHz spectrometer at room temperature. IR data was obtained from a Perkin Elmer Spectrum 2000 FT-IR spectrometer.

Synthesis:



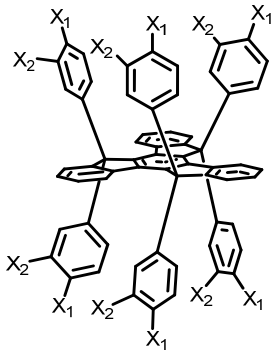
Scheme S1

[1] We thank Dr. Tsung-Han Lin for the Powder X-ray diffraction experiments and technical assistant of Technology Commons, College of Life Science and Precision Instrumentation Center, NTU with CLSM and TEM analysis.



1b, X_1 = OCH_2CO_2Et, X_2 = H

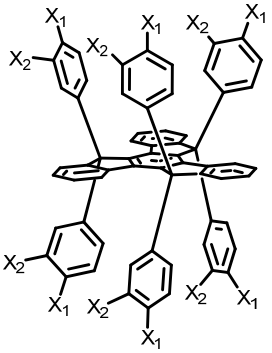
Synthesis of 1b. A mixture of **1a**[1] (2.31g, 2.58 mmol), ethyl bromoacetate (5mL, 41.88 mmol), potassium carbonate (10g, 72.36 mmol) and potassium iodide (4g, 24 mmol) was added to a solution of acetonitrile (120 mL). After refluxing for 24 hours, the reaction mixture was cooled down to room temp, extracted with EtOAc and dried over MgSO4. After removal of solvent under vacuum, the crude product was filtered off and washed with *n*-hexane, compound **1b** as a white powder was obtained. (3.3g, 91.6%). mp:183-184^{o}C; IR (KBr) ν 3044, 2982, 2908, 1887, 1758, 1582, 1507, 1441, 1377, 1299, 1210, 1081, 1011, 835, 737, 628, 593, 519 cm^{-1}; ^{1}H NMR (Acetone-d_6, 400 MHz) δ 7.52 (d, J = 8.8 Hz, 12H), 7.36 (d, J = 7.6Hz, 3H), 7.20 (d, J = 7.6 Hz, 3H), 7.00 (t, J = 8 Hz, 3H), 6.82-6.77 (m, 15H), 4.61 (s, 12H), 4.13 (q, J = 7.2 Hz, 12H), 1.17 (t, J = 7.2 Hz, 18H); ^{13}C NMR (DMSO-d_6, 500 MHz) δ 168.552, 156.178, 155.795,146.791, 139.143, 135.539, 132.634, 129.439, 127.515, 126.235, 125.279, 124.531, 114.143, 64.554, 63.216, 60.503, 13.909; HRMS (m/z, FAB^{+}) Calcd. for $C_{87}H_{79}O_{18}$ 1411.54, found 1411.5273.



2b, X_1 = H, X_2 = OCH_2CO_2Et

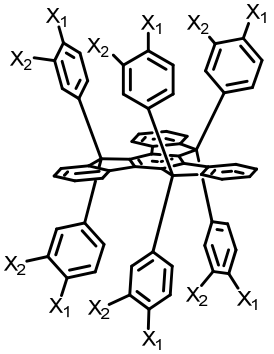
Synthesis of 2b. A mixture of **2a** (2.31g, 2.58 mmol), ethyl bromoacetate (5mL, 41.88 mmol), potassium carbonate (10g, 72.36 mmol) and potassium iodide (4g, 24 mmol) was added to a solution of acetonitrile (120 mL). After refluxing for 24 hours, the reaction mixture was cooled down to room temp, extracted with EtOAc and dried over MgSO4. After removal of solvent under vacuum, the crude product was filtered

off and washed with *n*-hexane, compound **2b** as a white powder was obtained. (3.2g, 88.8%) mp:109-111°C; IR (KBr) ν 3067, 2981, 2934, 1757, 1596, 1486, 1439, 1377, 1205, 1081, 1026, 940, 855, 782, 751, 701, 632 cm^{-1}; ^1H NMR (Acetone-d_6, 400 MHz) δ 7.41 (d, J = 7.8 Hz, 3H), 7.29 (s, 6H), 7.24 (d, J = 7.8, 3H), 7.19-7.13 (m, 12H), 7.06 (t, J = 7.2 Hz, 3H), 6.88 (t, J = 7.2 Hz, 3H), 6.50 (dt, J = 7.2, 2.2, 12H), 4.51 (s, 12H), 4.12-4.06 (m, 12H), 1.14 (t, J = 7.6 Hz, 18H); ^{13}C NMR (DMSO-d_6, 500 MHz) δ 168.44, 127.28, 154.78, 146.22, 141.50, 139.48, 135.67, 129.31, 127.72, 126.09, 125.65, 124.70, 121.26, 115.23, 112.89, 64.66, 64.33, 60.54, 13.87; HRMS (m/z, FAB^+) Calcd. for $C_{87}H_{79}O_{18}$ 1411.54, found 1411.5259. 146.9, 139.1, 136.0, 132.5., 129.4, 126.8, 126.6, 125.0, 123.9, 113.0, 63.9, 55.3; MS (m/z, FAB^+) 978 (43); HRMS (m/z, FAB^+) Calcd. for $C_{69}H_{54}O_6$ 978.3943, found 978.3932.



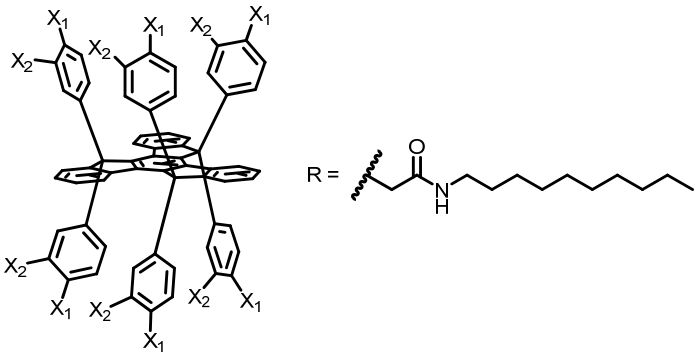
1c, X_1 = OCH_2CO_2H, X_2 = H

Synthesis of 1c. To a stirred mixture of **1b** (3.6g, 2.58 mmol) in THF (100mL) was added lithium hydroxide monohydrate (2g, 0.25mol) then slowed added distilled water (100mL). After refluxing for 24 hours, the reaction mixture was cooled down to room temp, extracted with EtOAc and dried over $MgSO_4$. After removal of solvent under vacuum, the crude product was purified through re-precipitation from EtOAc and hexane. The product **1c** was obtained as a white solid (2.5g, 86%). mp:182-183°C; IR (KBr) ν 3531, 3066, 2918, 2756, 2542, 2088, 1915, 1736, 1605, 1506, 1469, 1373, 1294, 1220, 1183, 1076, 1010, 832, 813, 755, 687, 629, 592, 565 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.43 (d, J = 7.6 Hz, 12H), 7.37 (d, J = 7.6 Hz, 3H), 7.08 (d, J = 7.6 Hz, 3H), 7.00 (t, J = 7.6 Hz, 3H), 6.82-6.77 (m, J = 8.4 Hz, 15H), 4.670 (s, 12H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ 170.92, 156.31, 156.00, 146.80, 139.25, 135.62, 132.54, 129.53, 127.59, 126.35, 125.39, 124.64, 114.15, 64.43, 63.26 ; HRMS (m/z, ESI^+) Calcd. for $C_{75}H_{54}O_{18}$ 1242.33, found 1242.32.



2c, X_1 = H, X_2 = OCH_2CO_2H

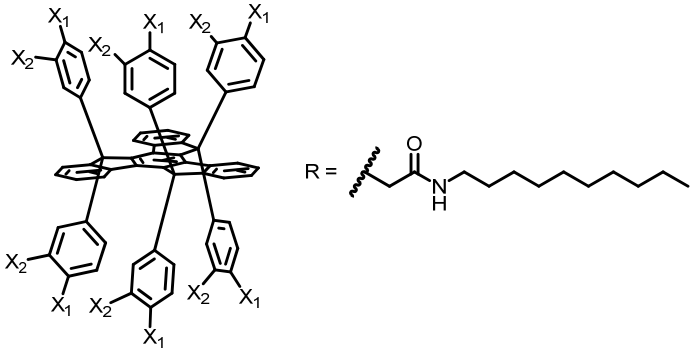
Synthesis of 2c. To a stirred mixture of **2b** (3.6g, 2.58 mmol) in THF (100mL) was added lithium hydroxide monohydrate (2g, 0.25mol) then slowed added distilled water (100mL). After refluxing for 24 hours, the reaction mixture was cooled down to room temp, extracted with EtOAc and dried over $MgSO_4$. After removal of solvent under vacuum, the crude product was purified through re-precipitation from EtOAc and hexane. The product **2c** was obtained as a white solid (2.7g, 85.3%). mp: $>200^oC$; IR (KBr) ν 3521, 3068, 2921, 2548, 1941, 1733, 1585, 1485, 1438, 1221, 1082, 881, 808, 755, 702, 579 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.40 (d, J = 8 Hz, 3H), 7.22 (s, 6H), 7.140 (t, J = 8 Hz, 6H), 7.08 (d, J = 8 Hz, 3H), 7.05-6.99 (m, 9H), 6.834 (t, J = 8 Hz, 3H), 6.72 (dd, J = 8 Hz, 6H), 4.52 (s, 12H); ^{13}C NMR ((DMSO-d_6, 500 MHz) δ 169.94, 157.40, 154.90, 146.24, 141.4, 139.503, 135.65, 129.34, 127.74, 126.10, 125.67, 124.62, 121.05, 115.49, 112.60, 64.58, 64.25, 21.01; HRMS (m/z, ESI^+) Calcd. for $C_{75}H_{54}O_{18}$ 1242.33, found 1242.32.



TPDA, X_1 = OR, X_2 = H

Synthesis of TPDA. (500 mg, 0.407 mmol) was stirred in thionyl chloride (25 ml) reflux for 2 hr. After concentraction in vacuo, the residue was rediluted in CH_2Cl_2 and concentrated again. This was redissolved in dry CH_2Cl_2 (30 mL), cooled to 0 $^\circ$C, and NEt_3 (10 mL, excess) and *n*-decyl amine (0.82 mL, 4.07 mmol) were added. The reaction mixture was stirred for 16 h then extracted with EtOAc and dried over $MgSO_4$. After removal of solvent under vacuum, the crude product was purified

through re-precipitation from EtOAc and hexane. The product **TPDA** was obtained as a white solid (750 mg, 88.6%). mp:110-111°C; IR (KBr) ν 3302, 3069, 2924, 2853, 1663, 1606, 1540, 1506, 1467, 1245, 1182, 1060, 812, 738, 593, 521. ^{1}H NMR (Acetone-d_6, 400 MHz) δ 7.54 (d, J = 9.2 Hz, 12H), 7.42 (t, J = 6 Hz, 6H), 7.36 (d, J = 7.8 Hz, 3H), 7.21 (d, J = 7.8 Hz, 3H), 7.01 (t, J = 7 Hz, 3H), 6.84-6.78 (m, 15H), 4.37 (s, 12H), 3.2 (q, J = 7.2 Hz, 12H), 1.47-1.45 (m, 12H), 1.27 (s, 84H), 0.87 (t, J = 6.8 Hz, 18H). ^{13}C NMR (DMSO-d_6, 500 MHz) δ 167.135, 156.307, 155.830, 146.821, 139.148, 135.574, 132.623, 129.389, 127.411, 126.235, 125.272, 124.498, 114.312, 66.929, 63.245, 52.007, 31.245, 28.916, 28.642, 26.257, 22.033, 13.858, 7.135; HRMS (m/z, FAB$^+$) Calcd. for $C_{135}H_{180}O_{12}N_6$ 2077.3659, found 2077.3657.



TMDA, X_1 = H, X_2 = OR

Synthesis of TMDA. 2c (500 mg, 0.407 mmol) was stirred in thionyl chloride (25 ml) reflux for 2 hr. After concentration in vacuo, the residue was rediluted in CH_2Cl_2 and concentrated again. This was redissolved in dry CH_2Cl_2 (30 mL), cooled to 0 °C, and NEt_3 (10 mL, excess) and *n*-decyl amine (0.82 mL, 4.07 mmol) were added. The reaction mixture was stirred for 16 h then extracted with EtOAc and dried over $MgSO_4$. After removal of solvent under vacuum, the crude product was purified through re-precipitation from EtOAc and hexane. The product **TMDA** was obtained as a brown solid (600 mg, 71%). mp:112-113°C; IR (KBr) ν 3313, 3072, 2924, 2853, 1663, 1595, 1538, 1486, 1437, 1374, 1226, 1166, 1068, 851, 748, 702, 580. ^{1}H NMR (Acetone-d_6, 400 MHz) δ 7.50 (t, J = 5.8 Hz, 6H), 7.39 (d, J = 7.6 Hz, 3H), 7.31 (s, 6H), 7.25-7.19 (m, 12H), 7.04 (t, J = 7.5 Hz, 3H), 6.87 (d, J = 7.5 Hz, 3H), 6.79-6.76 (m, 6H), 4.28-4.19 (m, 12H), 3.20-3.12 (m, 12H), 1.45-1.43 (m, 12H), 1.27 (s, 78H), 0.87 (t, J = 6.8 Hz, 18H); ^{13}C NMR (DMSO-d_6, 500 MHz) δ 167.149, 157.343, 154.902, 146.289, 141.476, 139.429, 135.669, 129.279, 127.615, 126.131, 125.593, 124.570, 121.057, 115.382, 113.152, 66.984, 64.343, 31.232, 29.013, 28.943, 28.915, 28.686, 28.639, 26.324, 22.025, 13.847; HRMS (m/z, FAB$^+$) Calcd. for $C_{135}H_{180}O_{12}N_6$ 2077.3659, found 2077.3635.

Instruments and Experimental Techniques

Optical Measurements:

UV-visible absorption spectra were recorded on a spectrophotometer (HITACHI U2800A). PL spectra were measured with a fluorescence spectrophotometer (HITACHI F9500).

Field Emission-Scanning Electron Microscope (FE-SEM):

Samples were prepared by dropcasting a cyclohexane solution of **TPDA** or **TMDA** onto a flat SiO_2/Si substrate as described above. The samples were imaged using a FEI Nova NanoSEM 200 in low-vacuum mode with no conductive overcoat. The chamber pressure was maintained at 0.45 Torr water using a differential pumping system. An immersion lens was employed and the secondary electrons amplified by gas vapor and collected by an electrode mounted on the pole piece.

Transmission Electron Microscope (TEM):

Samples were dropcast onto a 200 mesh copper grid coated with formvar film stabilized with vacuum-evaporated carbon and dried under air. The samples were examined in electron microscopes operating at 75 kv (Hitachi H-7650).

Confocal Laser Scanning Microscope (CLSM):

Confocal laser scanning microscope (CLSM) images were taken with Leica laser scanning confocal microscope (Leica TCS SP5 Spectral Confocal) equipped with 50 mW diode Laser / 100 mW Ar blue Laser / 10 mW Green DPSS Laser / 10 mW He-Ne Red Laser. The sample was air-dried on a glass slide and the excitation wavelength for images is 405 nm using 50 mW diode Laser.

Power X-ray diffraction:

Powder X-ray diffraction (XRD) patterns were recorded using a PANalytical X'pert Pro diffractometer with Cu Kα radiation operated at 40 mA and 45 kV.

Solid-State NMR:

All NMR experiments were carried out at ^{13}C and ^{1}H frequencies of 100.6 and 400.0 MHz, respectively, on a Bruker Avance III NMR spectrometer equipped with a commercial 3.2-mm probe. The measurements were carried out at ambient temperature. The sample was confined to the middle one-third of the rotor volume using Teflon spacers. Chemical shifts were externally referenced to tetramethylsilane (TMS) for ^{13}C and ^{1}H. Unless stated otherwise, the $^{13}C\{^{1}H\}$ cross-polarization magic-angle spinning (CPMAS) spectra were measured at a spin rate of 17 kHz with a

variation limited to ±3 Hz using a commercial pneumatic control unit (Bruker, MAS II). During the CP period, the ^{1}H rf field was set to 50 kHz and that of ^{31}P was linearly ramped through the zero-quantum Hartmann–Hahn matching condition.[2] The rf field of TPPM proton decoupling[3] was set to 90 kHz during the acquisition period. Recycle delay was set to 4 s. For the variable contact-time experiments, the CP period was varied from 0.3 to 10 ms.

Table S1 Organic solvents tested for gelation for two isomeric organogelators.[a]

Solvent	**TPDA**	**TMDA**
Cyclohexane	G(5.0)	G(5.0)
Methyl cyclohexane	G(4.8)	G(5.2)
Toluene	PG	PG
Benzene	PG	PG
Ethyl acetate	S	S
CH_2Cl_2	S	S
$CHCl_3$	S	S
THF	S	S
Acetone	S	S
Hexane	P	P
Dodecane	PG	PG
MeOH	P	P
EtOH	P	P
DMF	S	S
DMSO	S	S

[a] G = gel, PG = partial gel, P = precipitation, S = solution. The values in parentheses are the critical gelation concentration (CGC) wt %.

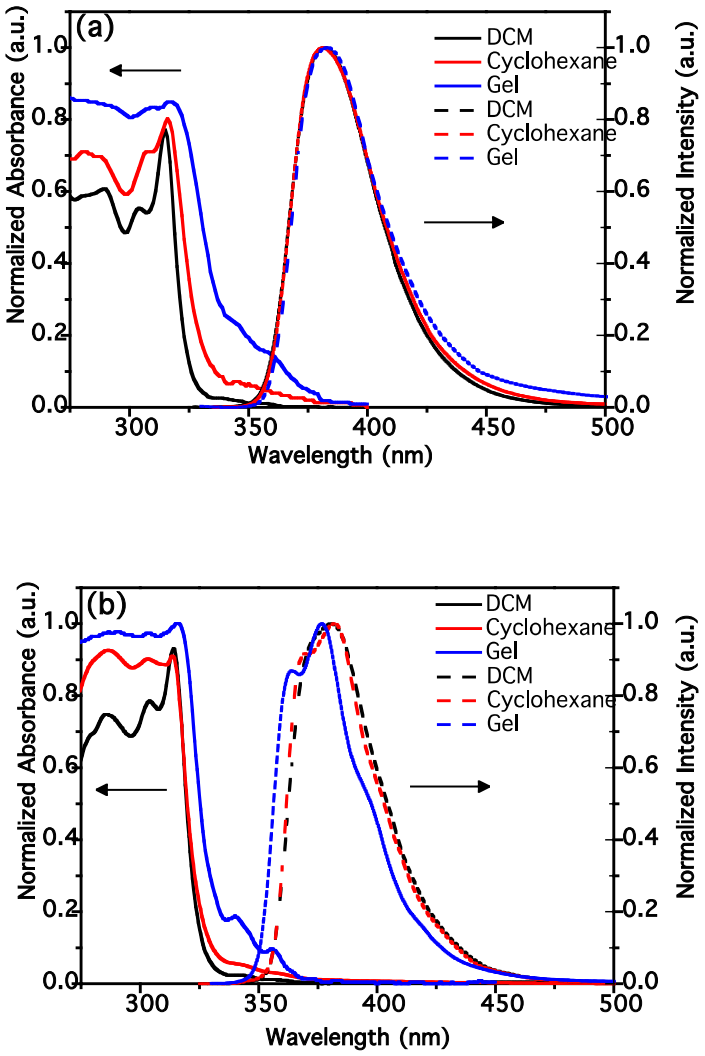


Fig. S1 Normalized absorption/emission spectra of **TPDA** (a) and **TMDA** (b).

Table S2 Optical Properties of **TPDA** and **TMDA** in different phases.

	TPDA		**TMDA**	
	λ_{abs}/nm	λ_{PL}/nm	λ_{abs}/nm	λ_{PL}/nm
DCM	315 (3.6)[a]	382	314 (1.5)	381
Cyclohexane	316 (1.6)	382	314 (2.7)	382
Gel	318	383	316	377

[a] The values in parentheses are the extinction coefficients (ε= number × 10^4 / $M^{-1}cm^{-1}$).

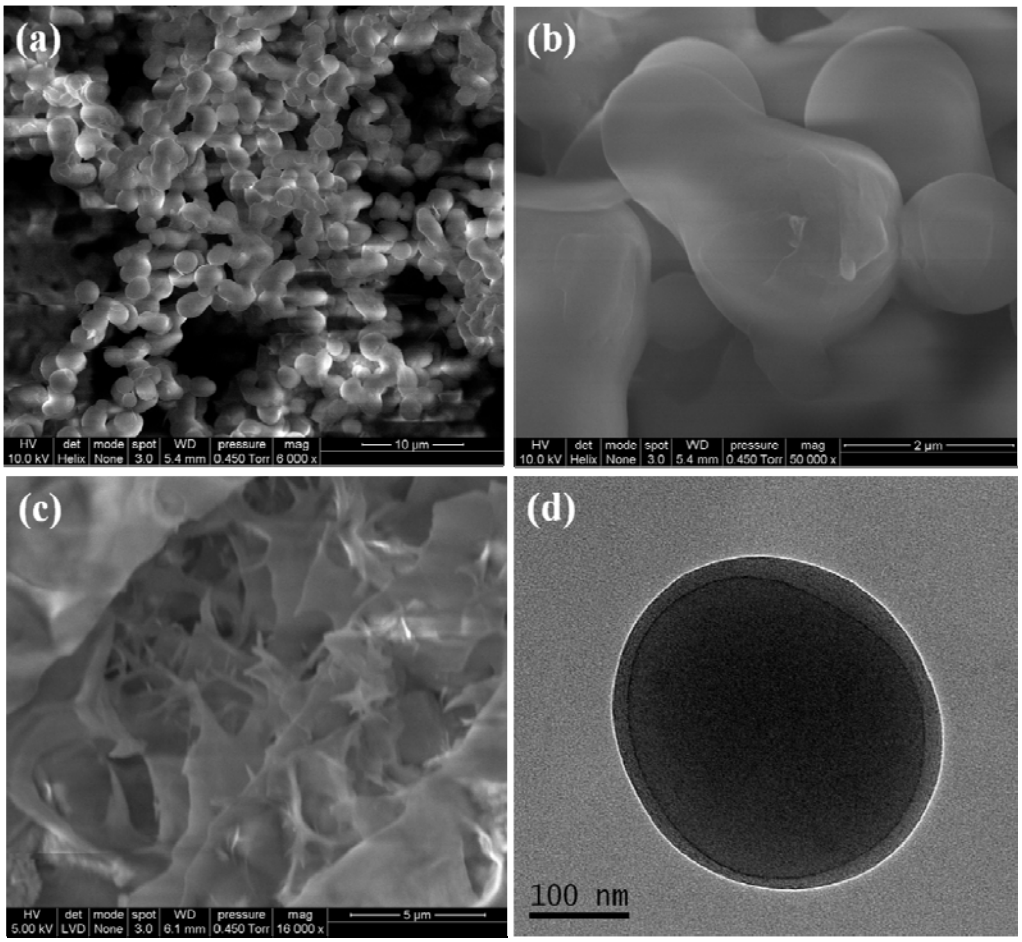


Fig. S2 SEM images of gels (5 wt% in cyclohexane) of **TPDA** (a, b) and **TMDA** (c). The hollow sphere was characterized by TEM (d).

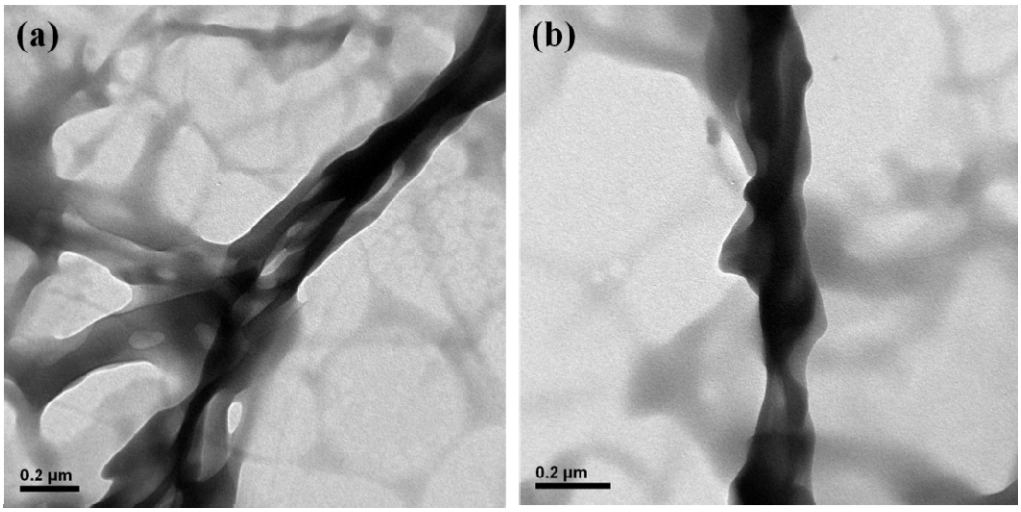


Fig. S3 TEM images of **TMDA** fibers (a, b) indicate the twisting and interlacing features.

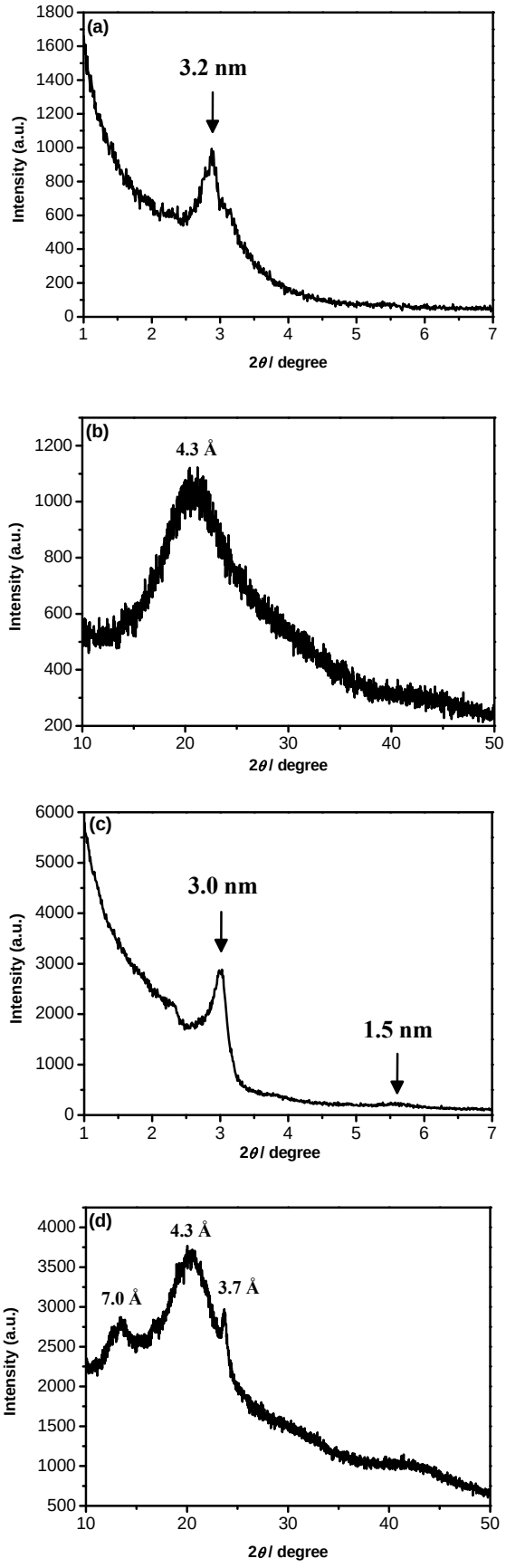


Fig. S4 SXRD and WXRD measurements of **TPDA** (a, b) and **TMDA** (c, d).

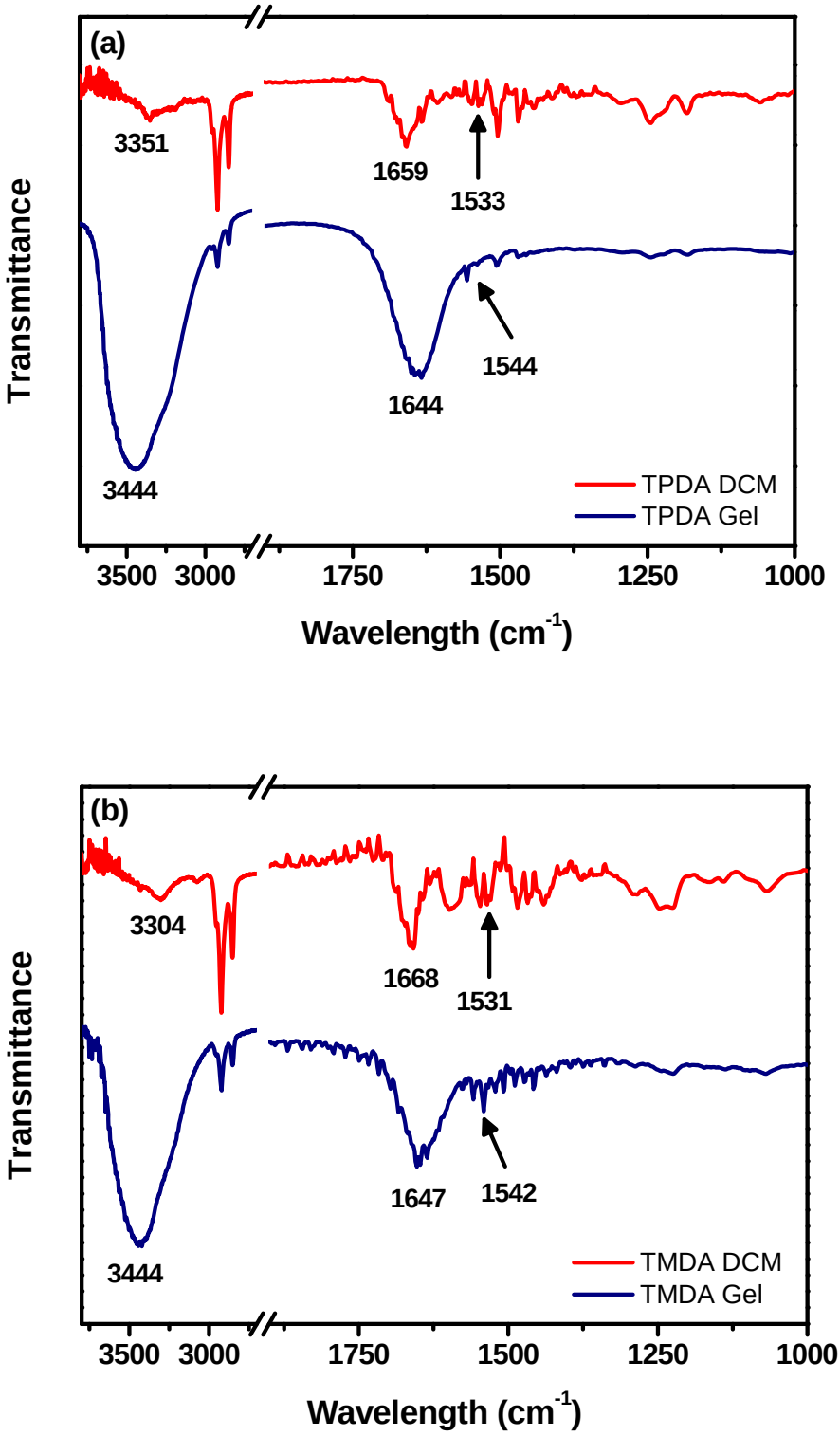
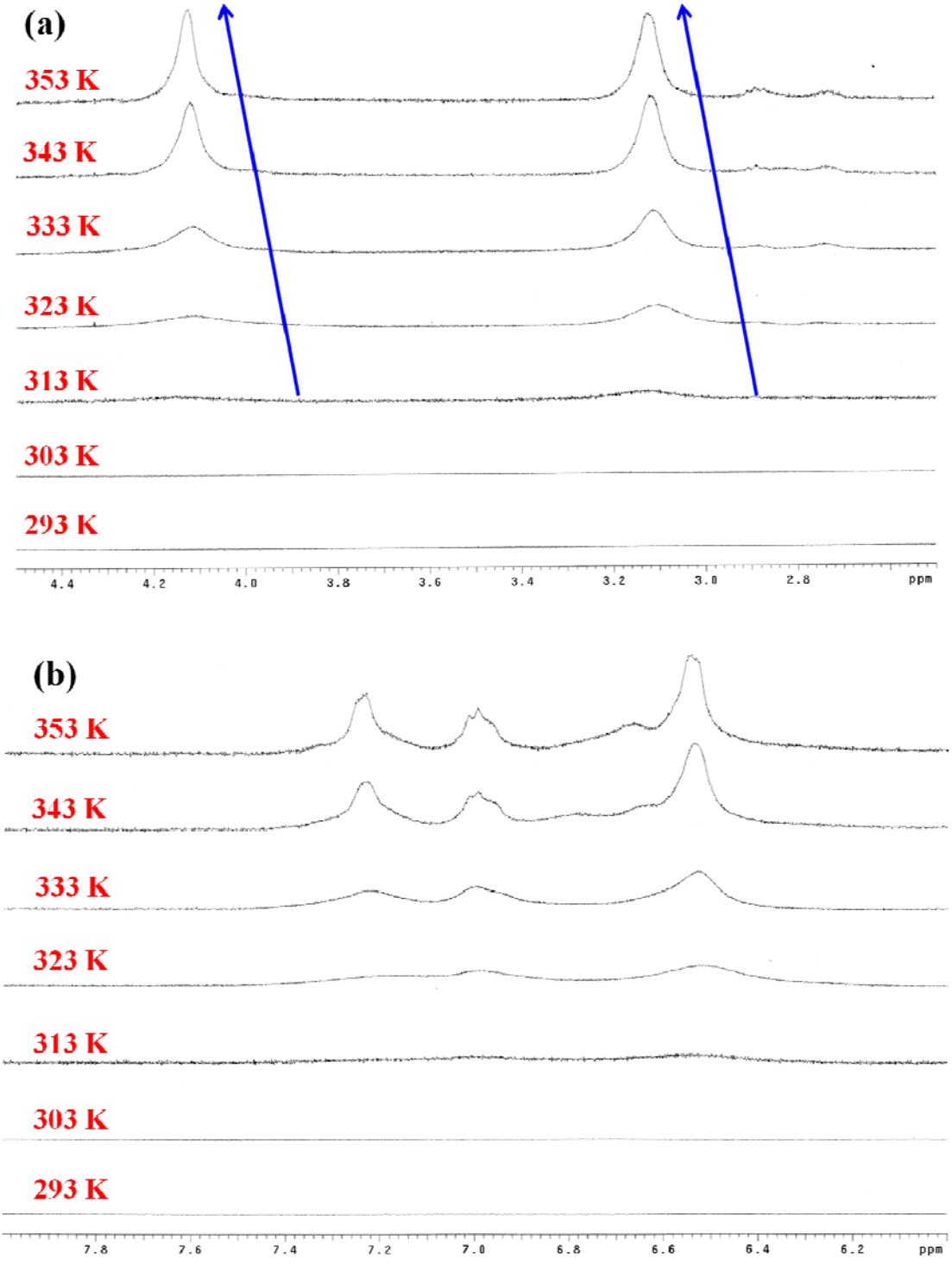


Fig. S5 FT-IR spectra of (a) **TPDA** in CH_2Cl_2 and in gel phase, (b) **TMDA** in CH_2Cl_2 and in gel phase.

Temperature-dependent ^{1}H NMR analysis of TPDA and TMDA.



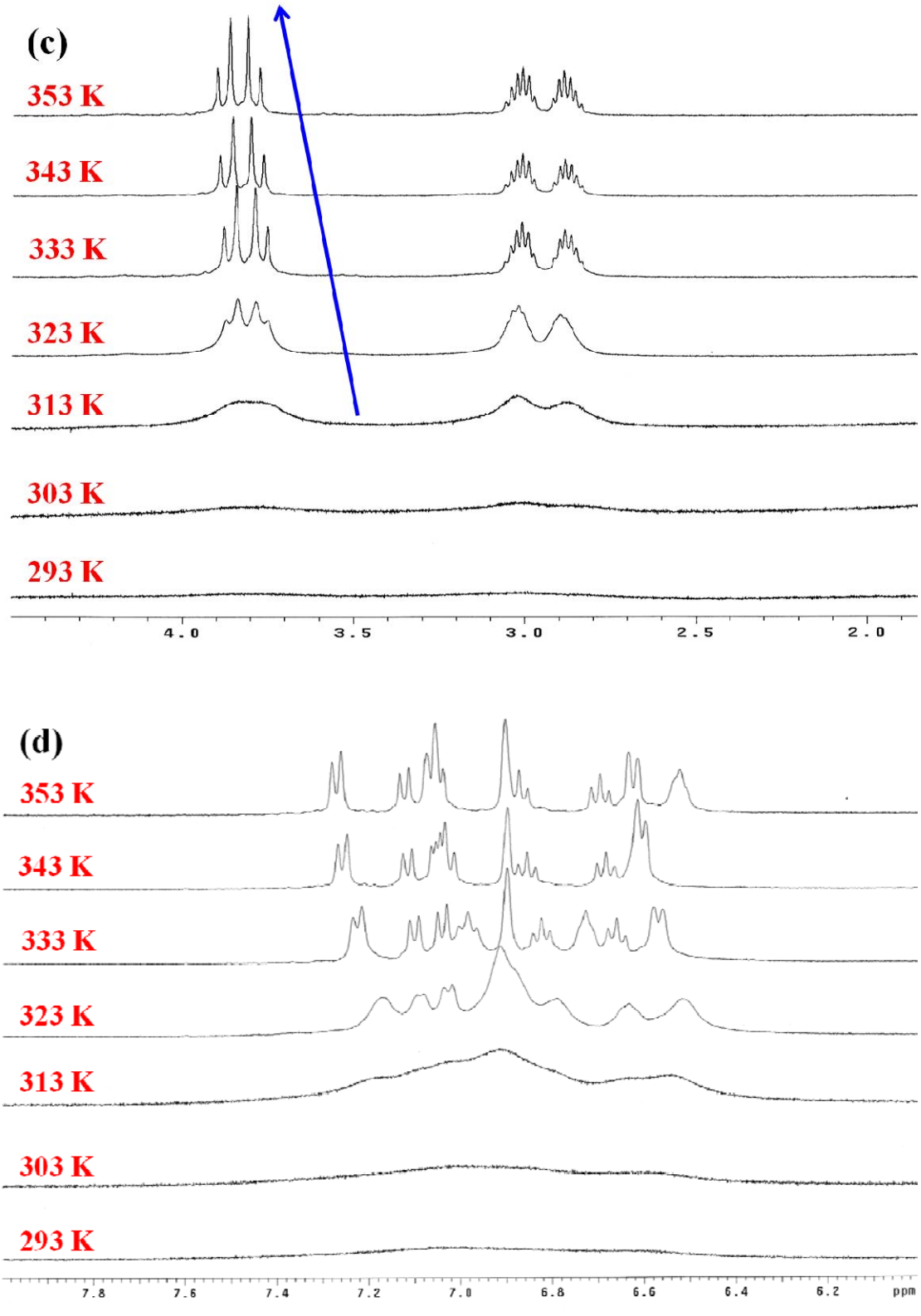


Fig. S6 Temperature-dependent ^{1}H NMR spectra of aliphatic and aromatic signals for **TPDA** (a, b) verse aliphatic and aromatic signals for **TMDA** (c, d) in cyclohexane-d_{12}, respectively.

Solid-state NMR results.

Fig. S7 shows the $^{13}C\{^{1}H\}$ CPMAS spectra obtained for the model compounds **1c** and **2c**. It is intriguing to find that the spectral features of these two isomers are quite different. In particular, the linewidths of **2c** are so narrow that some spectral fine structures are observed in the carbonyl (170–180 ppm), peripheral arene (150–160 ppm, 110–120 ppm), and truxene core (120–150 ppm) regions. Additional measurements of the variable contact-time experiments show that **1c** and **2c** have somewhat different CP dynamics for the peaks in the truxene core region (Table S3). Therefore, the observation of these fine structures indicates that **2c** has a higher degree of molecular ordering than **1c**. One may also infer that the motional dynamics of the peripheral arene and truxene core of **1c** have a correlation time comparable to the NMR time scale, leading to a broadening of the corresponding ^{13}C NMR peaks. Because alkyl chains usually have considerable motional dynamics. As such, the relatively narrow linewidths of the aliphatic carbons are due to the effects of motional narrowing. The main difference between the ^{13}C spectra of **TMDA** and **TPDA** are in the linewidths of the aromatic signals (Fig. S8). Accordingly, **TMDA** shows a higher structural order than **TPDA**.

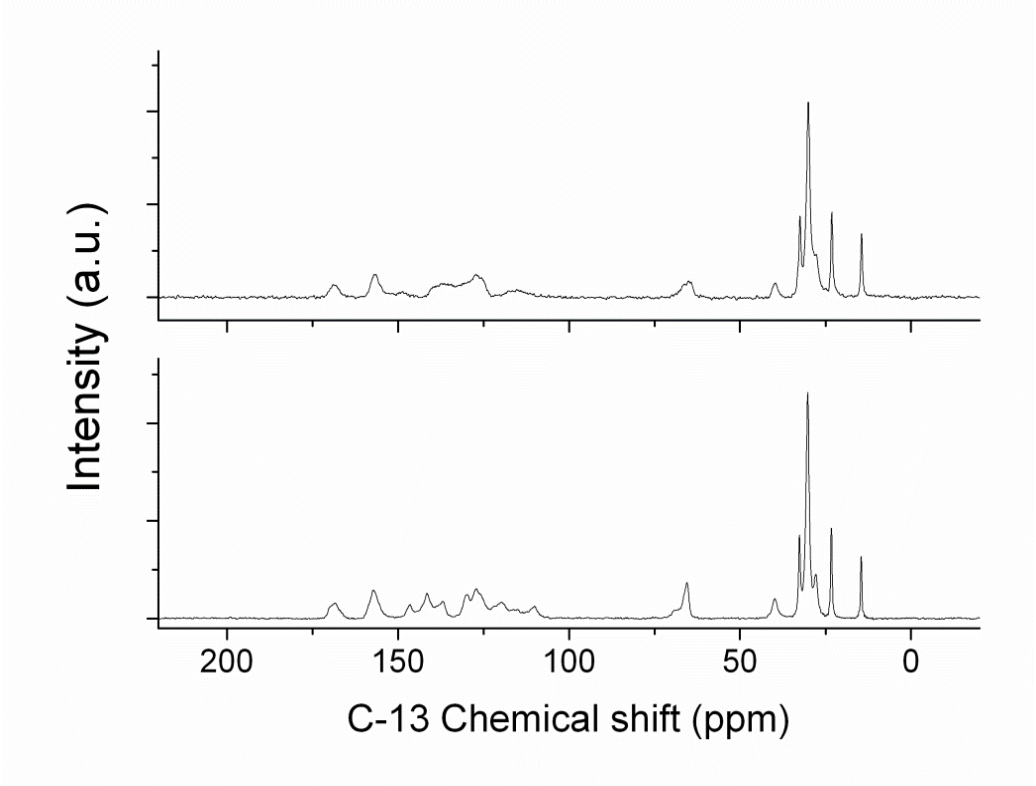


Fig. S7 $^{13}C\{^{1}H\}$CPMAS spectrum measured for **1c** (top) and **2c** (bottom). The contact time was set to 3 ms.

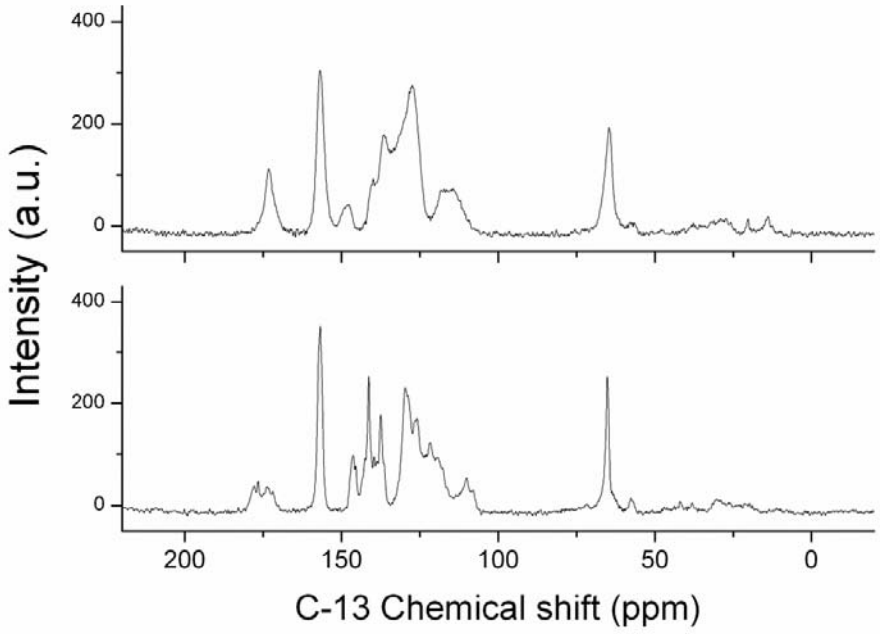


Fig. S8 $^{13}C\{^{1}H\}$CPMAS spectrum measured for **TPDA** (top) and **TMDA** (bottom). The contact time was set to 3 ms.

The $^{13}C\{^{1}H\}$ CPMAS spectra of **1c** and **2c** measured at 10 kHz, where the signals of the sp^2 carbons exhibit sizable spinning sidebands are shown in Fig. S9. The sideband intensities can provide a sensitive measurement of the chemical shift anisotropy (CSA), which in turn depends on the electronic environment of the resonating nuclei. Although the spectral resolution and the limited number of sidebands do not allow us to quantify the CSA accurately, we can infer from the sideband intensities that there is no significant variation in the electronic environment of the aromatic carbons for **1c** and **2c**. From the $^{13}C\{^{1}H\}$ CPMAS spectra of **TMDA** and **TPDA** in Fig. S10, we find that the sideband intensities of the aromatic carbons are again very similar. Consequently, we conclude that the molecular geometry of the truxene region is not significantly perturbed by the alkylation when **1c** or **2c** is transformed to **TPDA** or **TMDA**. Apparently, the fibrillar structure of **TMDA** has a higher structural order, whereas the globular structure of **TPDA** has considerable motional dynamics in the truxene region.

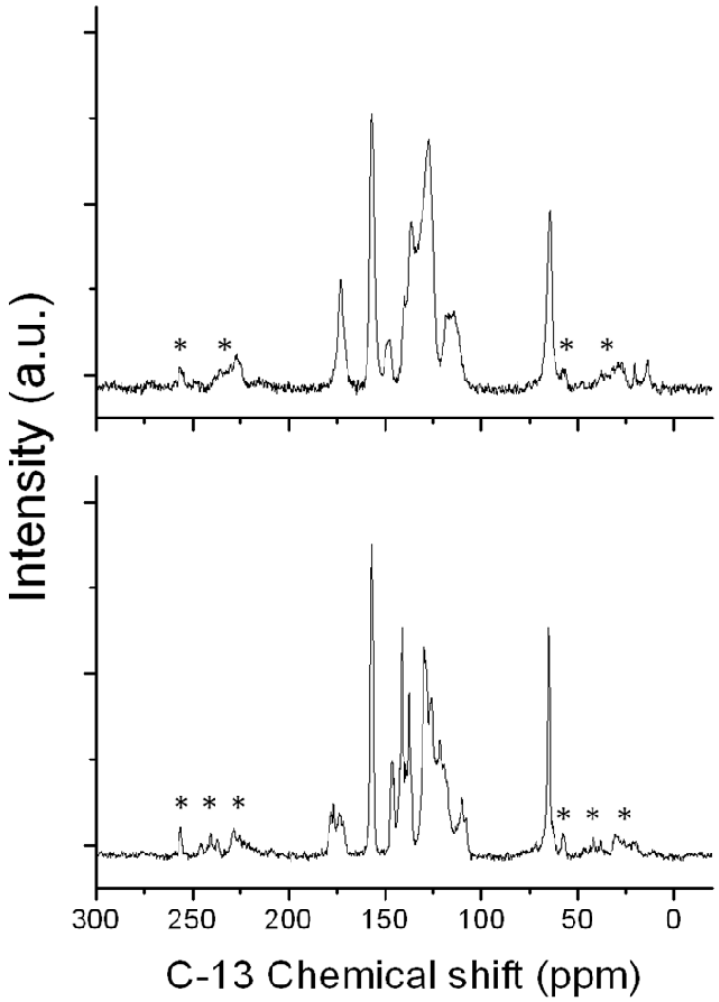


Fig. S9 $^{13}C\{^{1}H\}$CPMAS spectra measured for **1c** (top) and **2c** (bottom) at a MAS frequency of 10 kHz. The contact time was set to 1.5 ms. The asterisks represent the spinning sidebands.

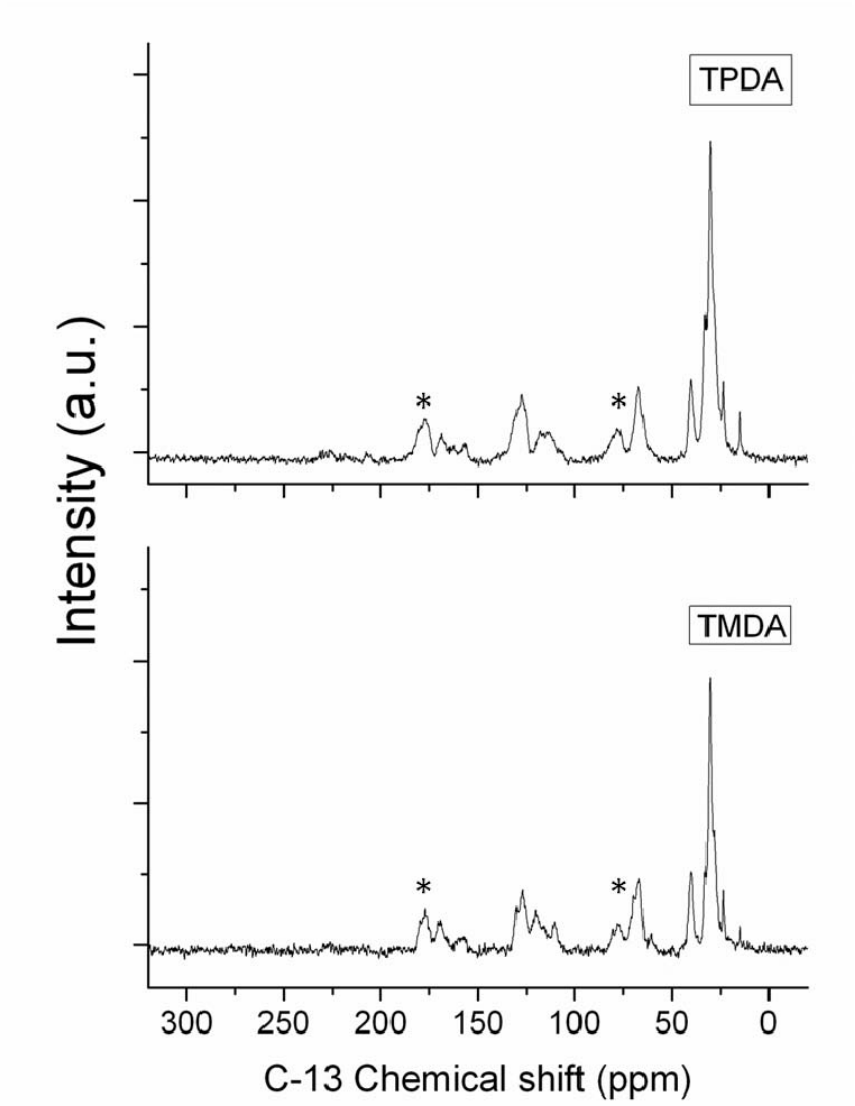


Fig. S10 $^{13}C\{^{1}H\}$CPMAS spectra measured for **TPDA** and **TMDA** under 5 kHz spinning. The contact time was set to 1.5 ms. The asterisks represent the spinning sidebands.

Summary of the variable contact-time data

The data of the variable contact-time experiments were analyzed by the following equation:

$$M(t) = M_0\{1-\exp(-t/\tau_{CP})\}\exp(-t/T_{1\rho}^{H})$$

where the parameters of τ_{CP} and $T_{1\rho}^{H}$ can characterize the rate of polarization transfer from ^{1}H to ^{13}C and the dipolar coupling among the proton spins, respectively. The results are summarized in Tables 1 and 2.

Table S3 Summary of the chemical shift data and the parameters characterizing the $^{13}C\{^{1}H\}$ CP dynamics of **1c** and **2c**.

Sample	Assignment[a]	δ_{iso} (ppm)	τ_{CP} (ms)	$T_{1\rho}^{H}$ (ms)
1c	C	179–171	0.30 ± 0.01	6.0 ± 0.1
	P	156	0.39 ± 0.05	10.4 ± 1.4
	T	146	1.3 ± 0.4	11.3 ± 3.5
	T	141–136	0.72 ± 0.15	12.9 ± 3.2
	T	129	< 0.1	10.6 ± 0.2
	T	125.9–121.5	< 0.1	11.0 ± 0.5
	P	110.0–107	< 0.1	9.7 ± 0.7
	B	65.0	0.43 ± 0.08	11.3 ± 2.4
2c	C	172.9	0.56 ± 0.10	6.0 ± 0.9
	P	156.7	0.38 ± 0.05	6.7 ± 0.7
	T	148.7	2.1 ± 0.8	5.3 ± 1.1
	T	136.4	0.36 ± 0.05	8.1 ± 1.0
	T	130.7	< 0.1	4.6 ± 0.4
	T	126.0	< 0.1	6.2 ± 0.3
	P	114.7	< 0.1	2.7 ± 0.4
	B	64.8	0.15 ± 0.03	7.2 ± 0.6

[a] C = carbonyl, P = peripheral arene, T = truxene core, TC = Truxene sp^3 carbon, B = peripheral benzylic carbon, A = alkyl chain.

Table S4 Summary of the NMR data and the parameters characterizing the $^{13}C\{^{1}H\}$ CP dynamics of **TMDA** and **TPDA**.

Sample	Assignment[a]	δ_{iso} (ppm)	τ_{CP} (ms)	$T_{1\rho}^{H}$ (ms)	T_1 (s)
TMDA	C	168.7	0.25 ± 0.02	8.4 ± 0.4	47.4 ± 6.6
	P	157.2	0.38± 0.05	11.8 ± 1.8	175 ± 19
	T	146.8	1.12 ± 0.25	13.0 ± 3.6	n.d.
	T	141.6	0.79 ± 0.17	13.8 ± 3.9	28.6 ± 2.5
	T	137.2	0.64 ± 0.12	12.5 ± 2.9	n.d.
	T	130.2	< 0.1	13.7 ± 0.8	20.0 ± 0.7
	T	127.2	< 0.1	12.1 ± 0.6	
	T	119.9	< 0.1	13.6 ± 0.4	n.d.
	P	115.5	< 0.1	8.4 ± 0.4	7.3 ± 0.5
	P	110.3	< 0.1	12.8 ± 0.9	
	TC	69.6	< 0.1	7.3 ± 1.6	n.d.
	B	65.9	0.45 ± 0.09	12.6 ± 2.9	n.d.
	A	40.0	< 0.1	5.0 ± 0.4	0.64 ± 0.05
	A	32.6	0.55 ± 0.12	21.2 ± 8.1	0.45 ± 0.02
	A	30.2	0.23 ± 0.03	11.6 ± 1.2	0.34 ± 0.01
	A	27.9	0.14 ± 0.02	7.1 ± 0.4	n.d.
	A	23.3	0.78 ± 0.14	38.4 ± 20	0.63 ± 0.04
	A	14.6	1.77 ± 0.12	>50	0.89 ± 0.05
TPDA	C	168.6	0.26 ± 0.02	4.9 ± 0.3	n.d.
	P	157.0	0.35 ± 0.03	6.3 ± 0.4	n.d.
	T	136.6	0.33 ± 0.08	8.3 ± 1.8	22.2 ± 1.9
	T	127.0	<0.1	5.1 ± 0.2	13.2 ± 0.1
	P	114.3	<0.1	2.8 ± 0.5	n.d.
	TC	67.2	<0.1	4.1 ± 0.4	n.d.
	B	64.1	0.62 ± 0.12	6.8 ± 1.1	n.d.
	A	39.9	<0.1	3.2 ± 0.3	0.42 ± 0.03
	A	32.5	0.37 ± 0.05	14.5 ± 2.5	0.87 ± 0.05
	A	30.1	0.20 ± 0.02	7.4 ± 0.4	0.41 ± 0.01
	A	27.6	<0.1	6.0 ± 0.4	n.d.
	A	23.1	0.59 ± 0.12	20.1 ± 6.7	1.07 ± 0.06
	A	14.4	1.21 ± 0.14	> 50	1.21 ± 0.06

[a] C = carbonyl, P = peripheral arene, T = truxene core, TC = Truxene sp^3 carbon, B = peripheral benzylic carbon, A = alkyl chain.

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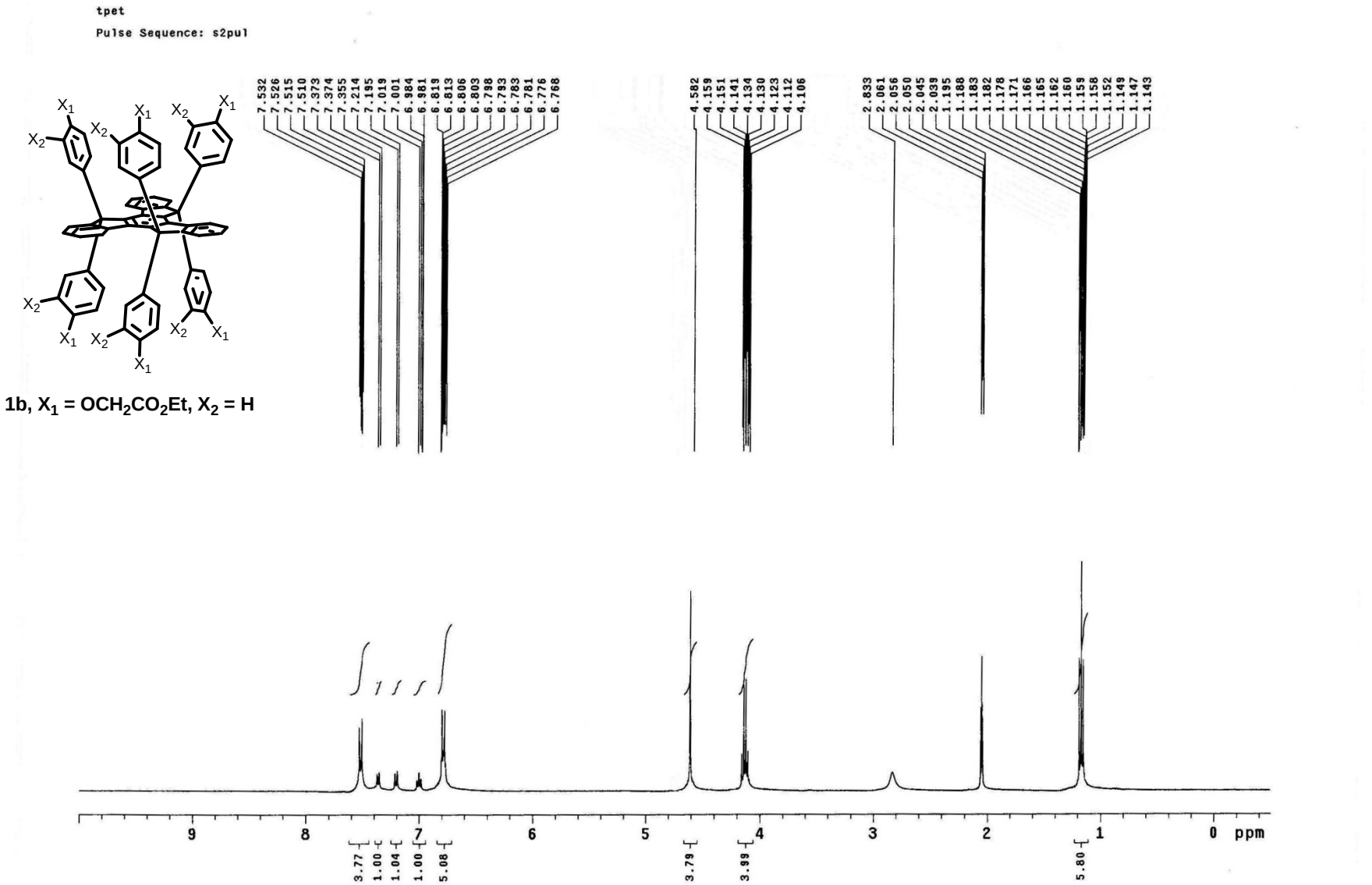
(1) M.-T. Kao, J.-H. Chen, Y.-Y. Chu, K.-P. Tseng, C.-H. Hsu, K.-T. Wong, C.-W. Chang, C.-P. Hsu and Y.-H. Liu, *Org. Lett.*, 2011, **13**, 1714.

(2) G. Metz, X. L. Wu and S. O. Smith, *J. Magn. Reson. Ser. A*, **1994**, *110*, 219-227.

(3) A. E. Bennett, C. M. Rienstra, M. Auger, K. V. Lakshmi and R. G. Griffin, *J. Chem. Phys.*, **1995**, *103*, 6951-6958.



1b, X_1 = OCH_2CO_2Et, X_2 = H

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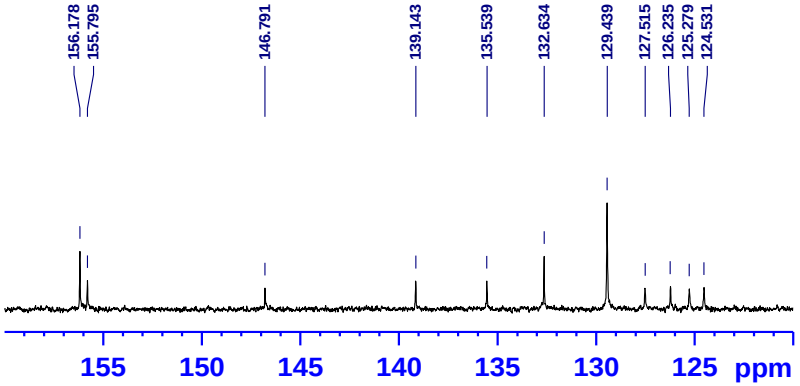

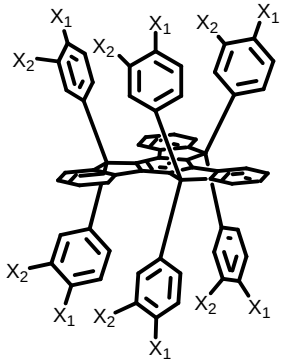

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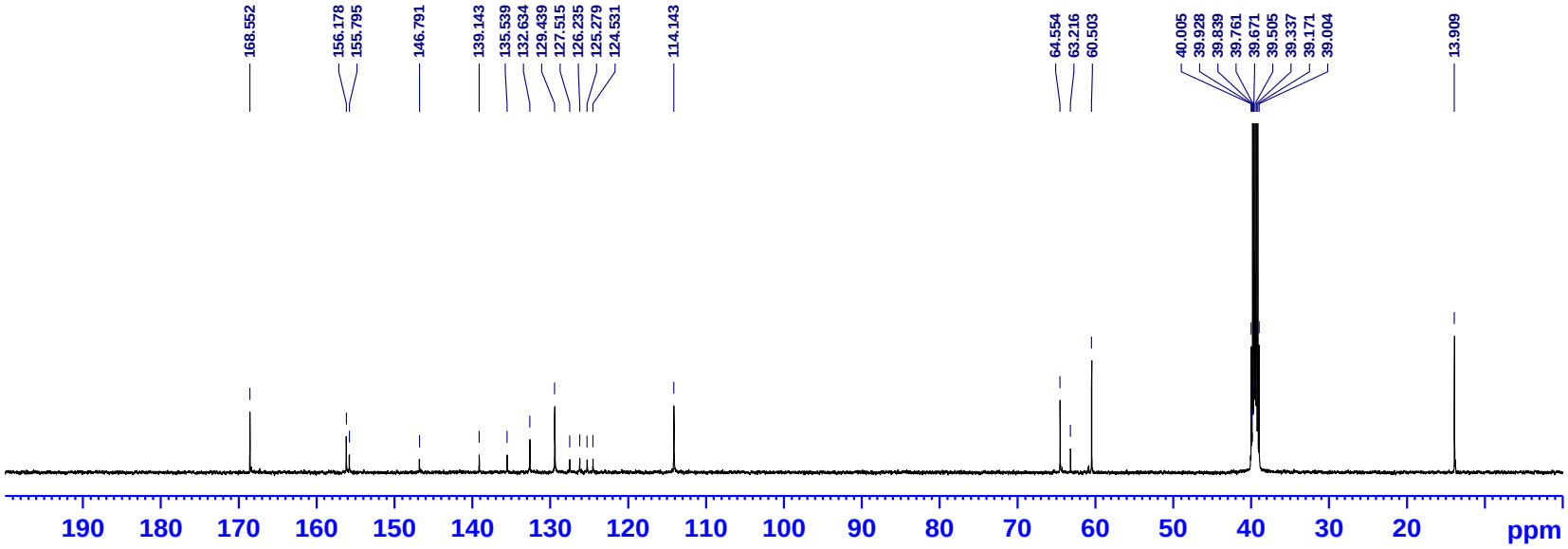

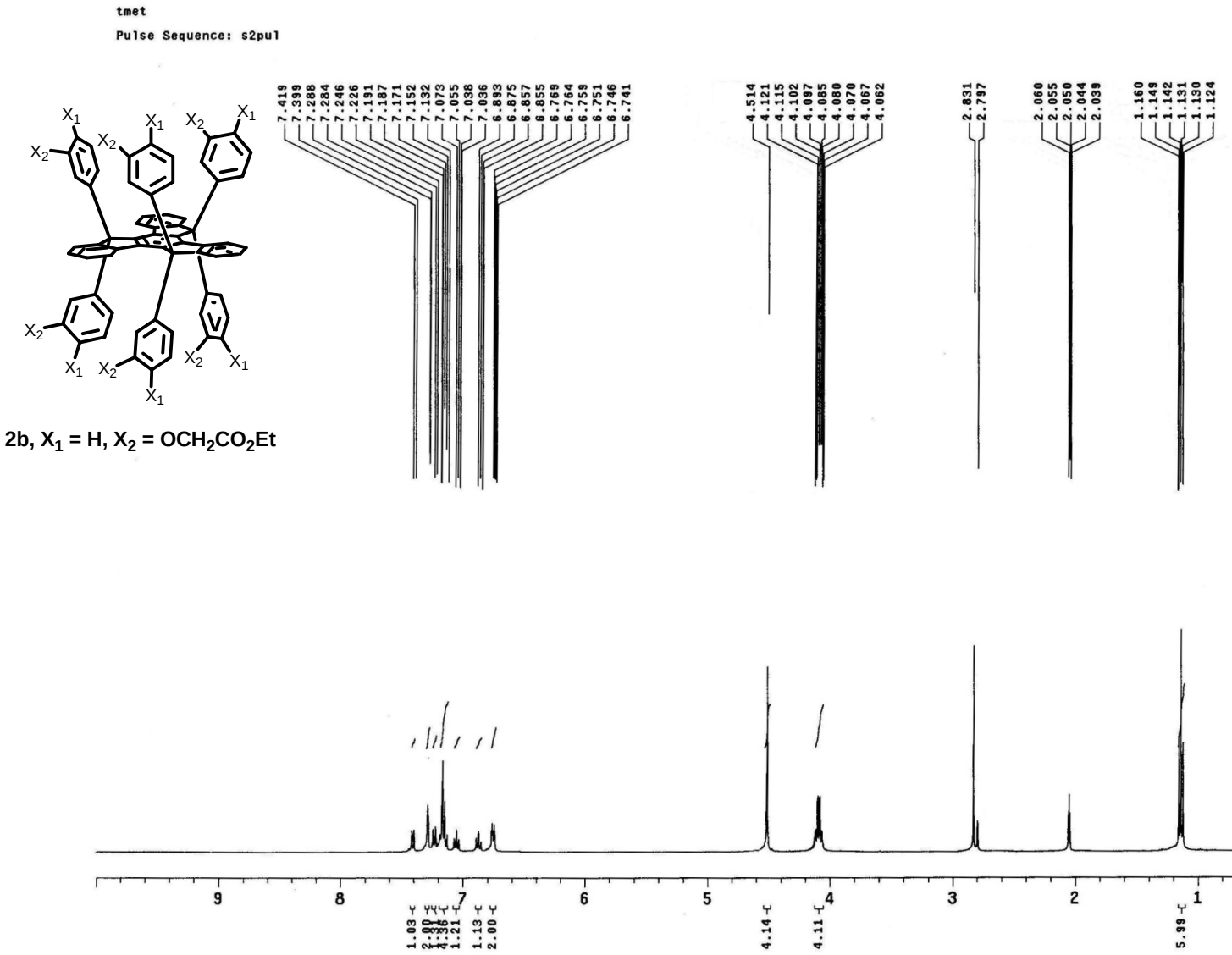

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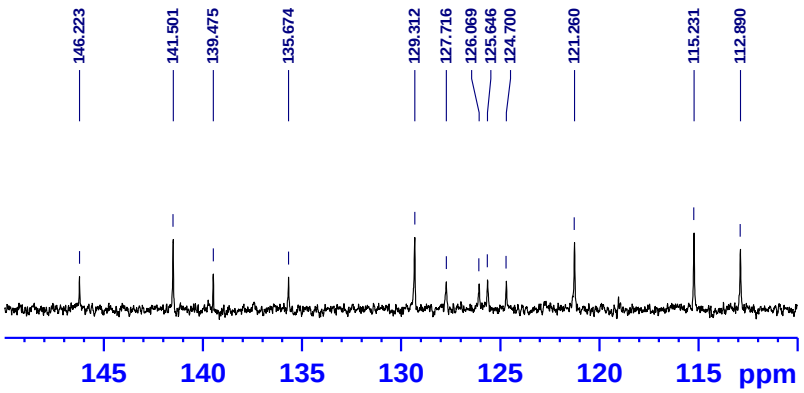

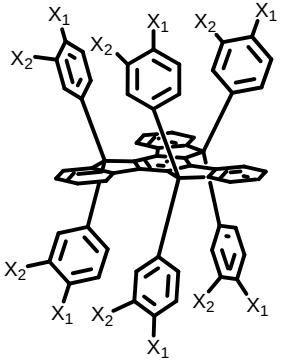

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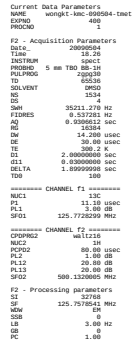

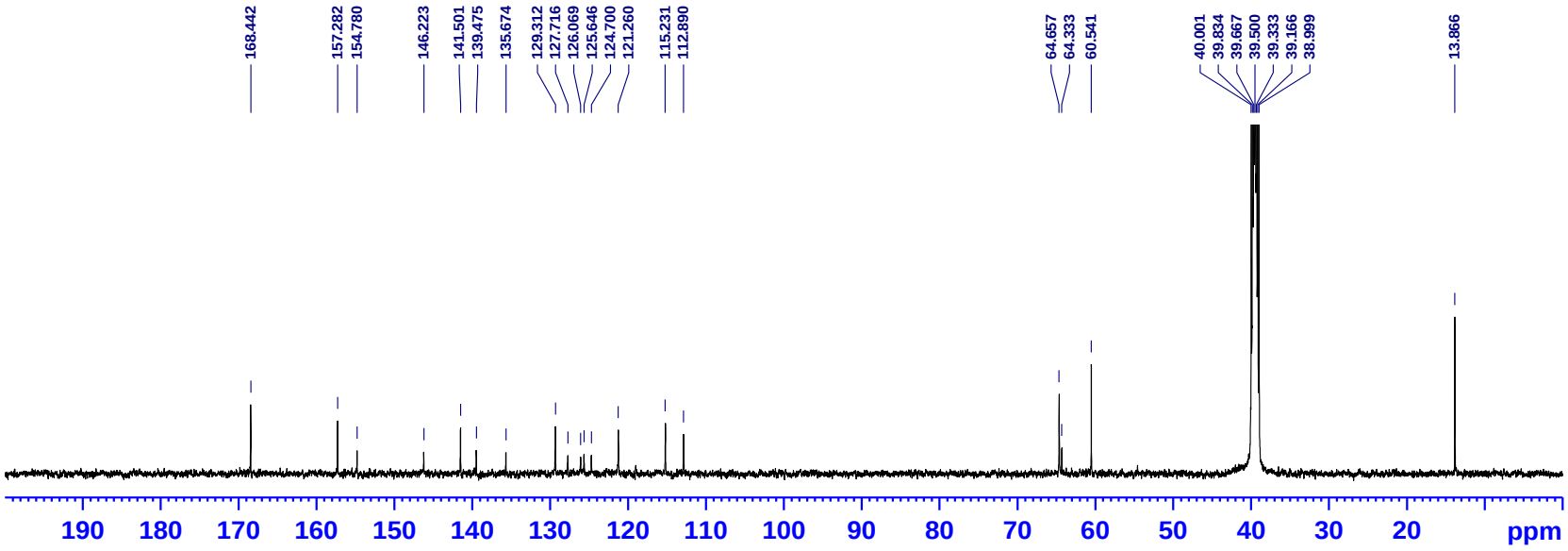

tpac

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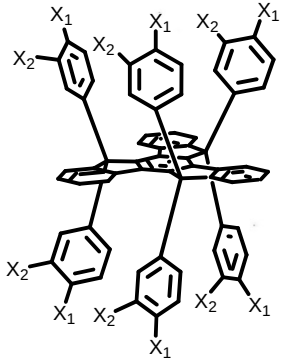

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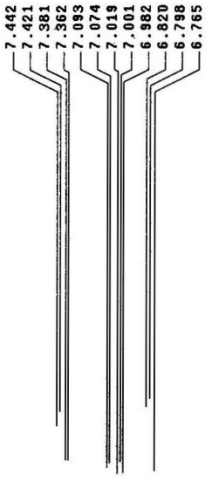

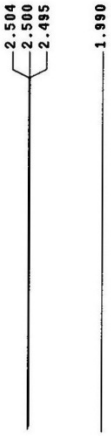

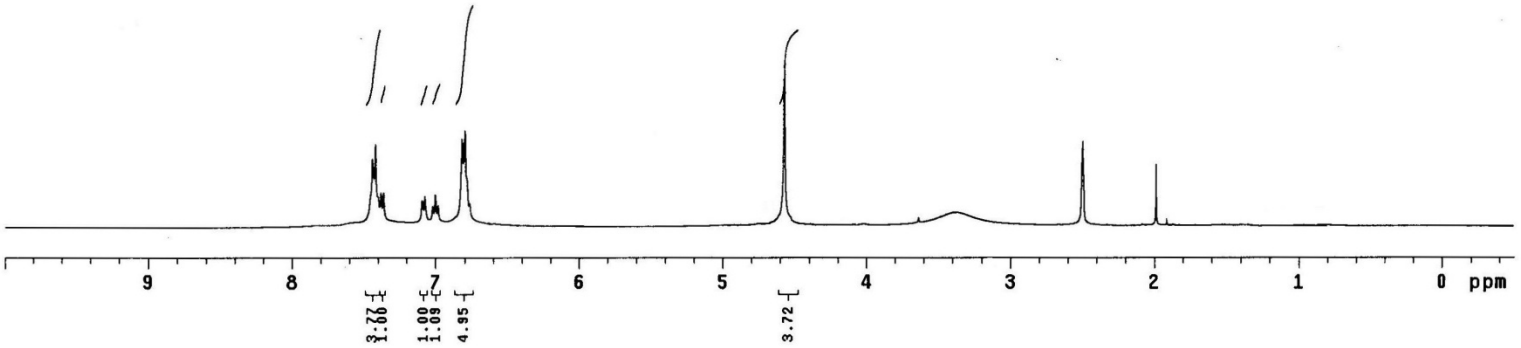

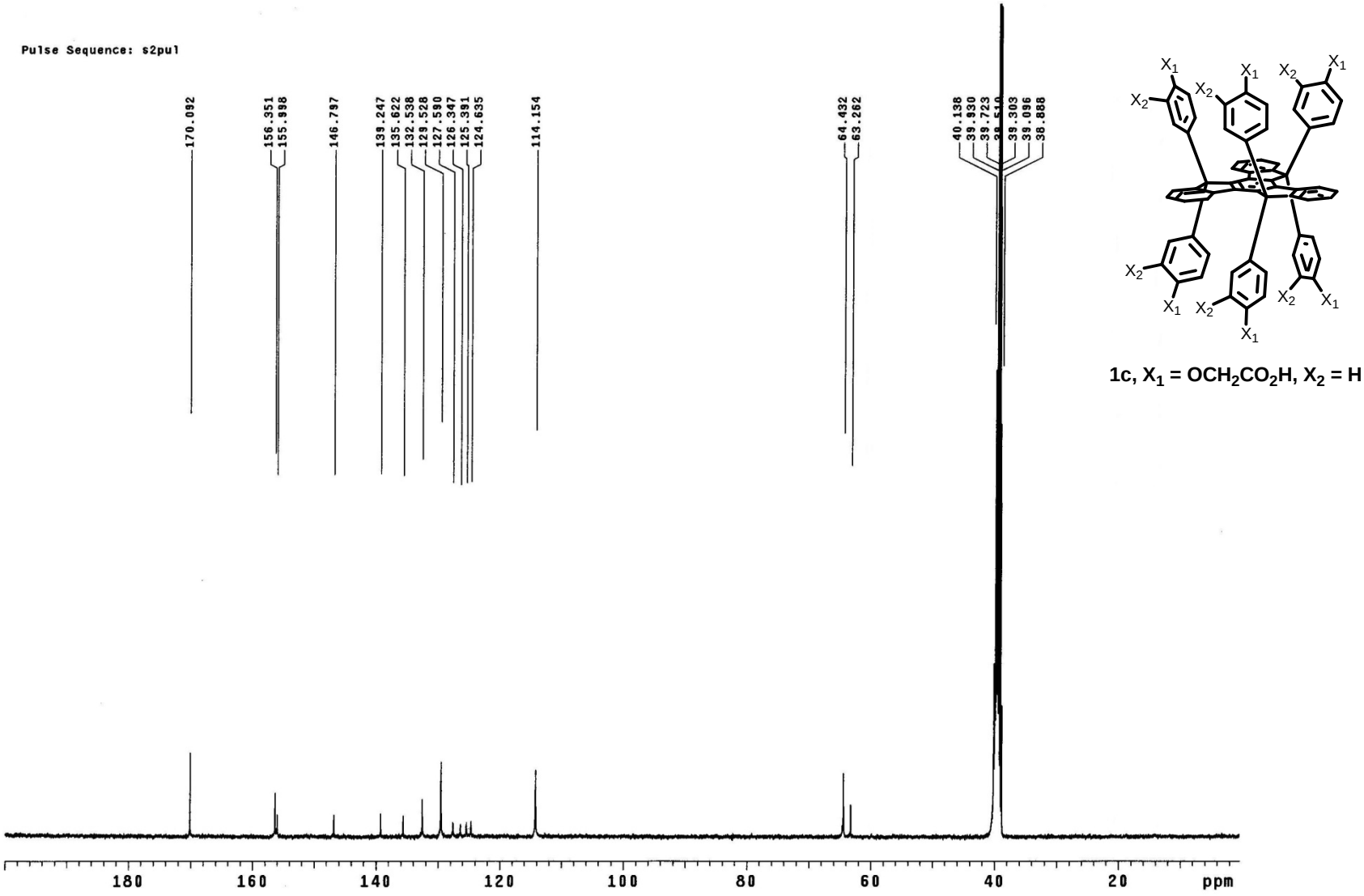

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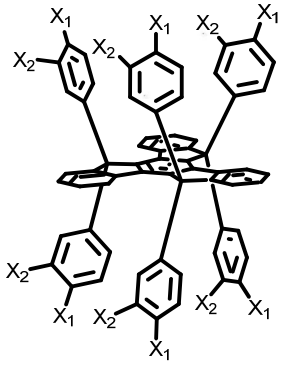
tmac

Pulse Sequence: s2pul



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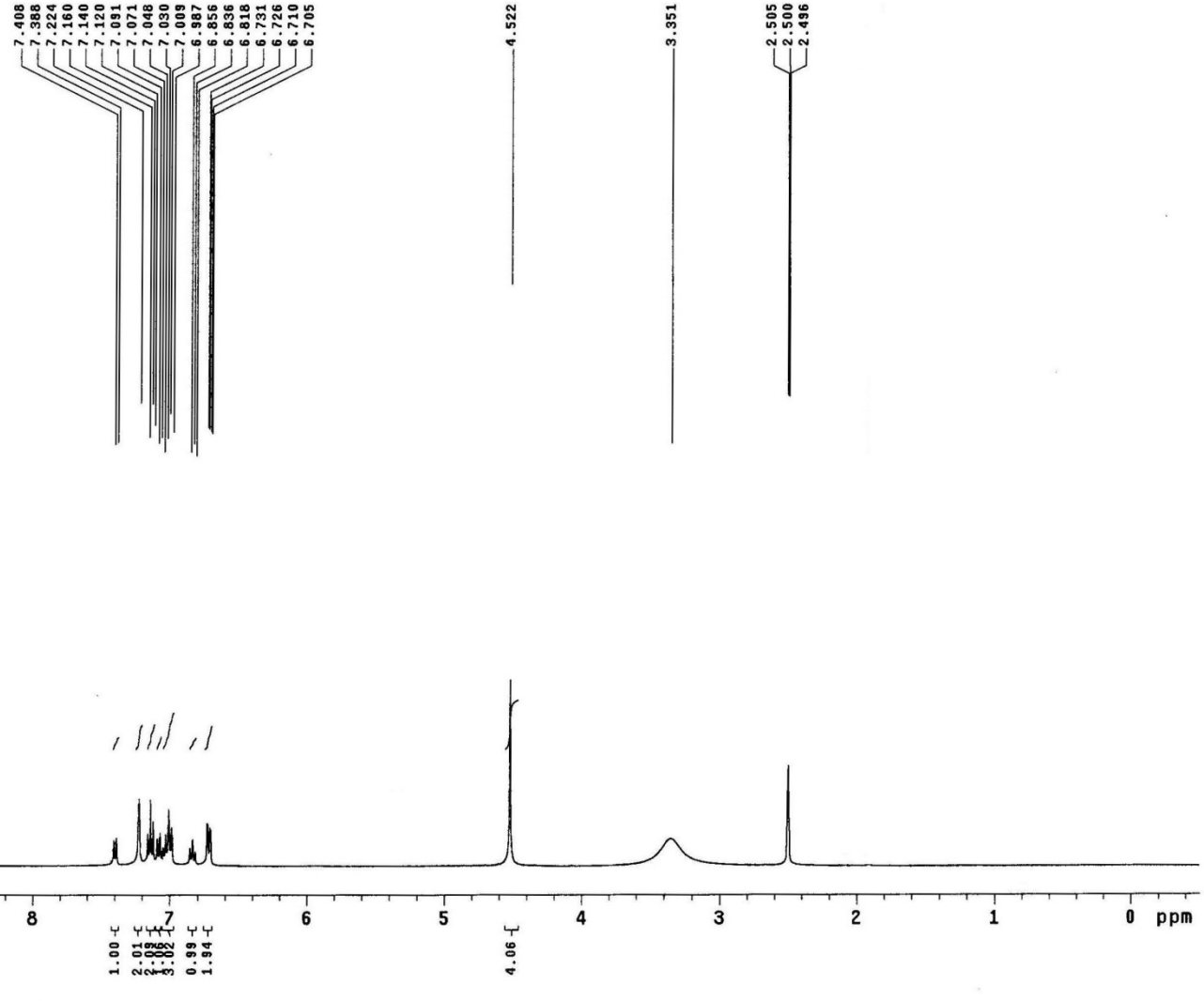

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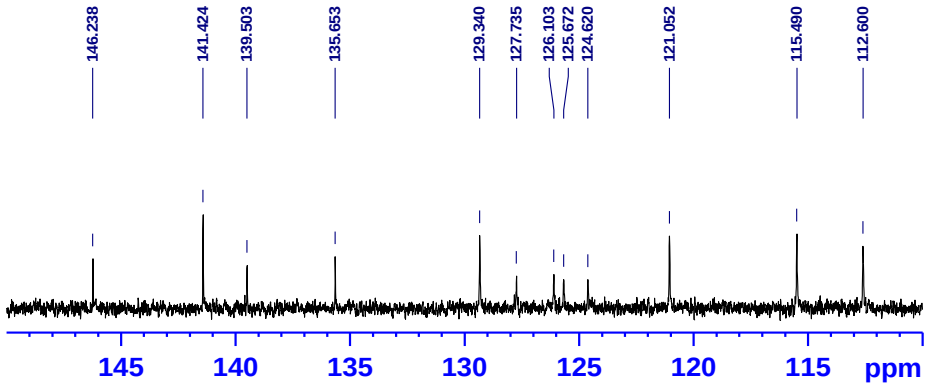

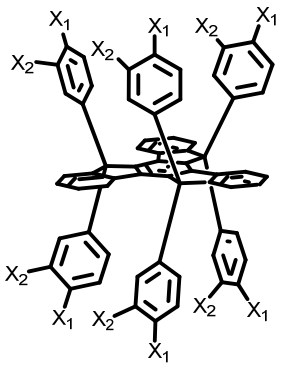

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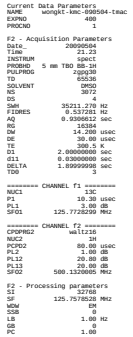

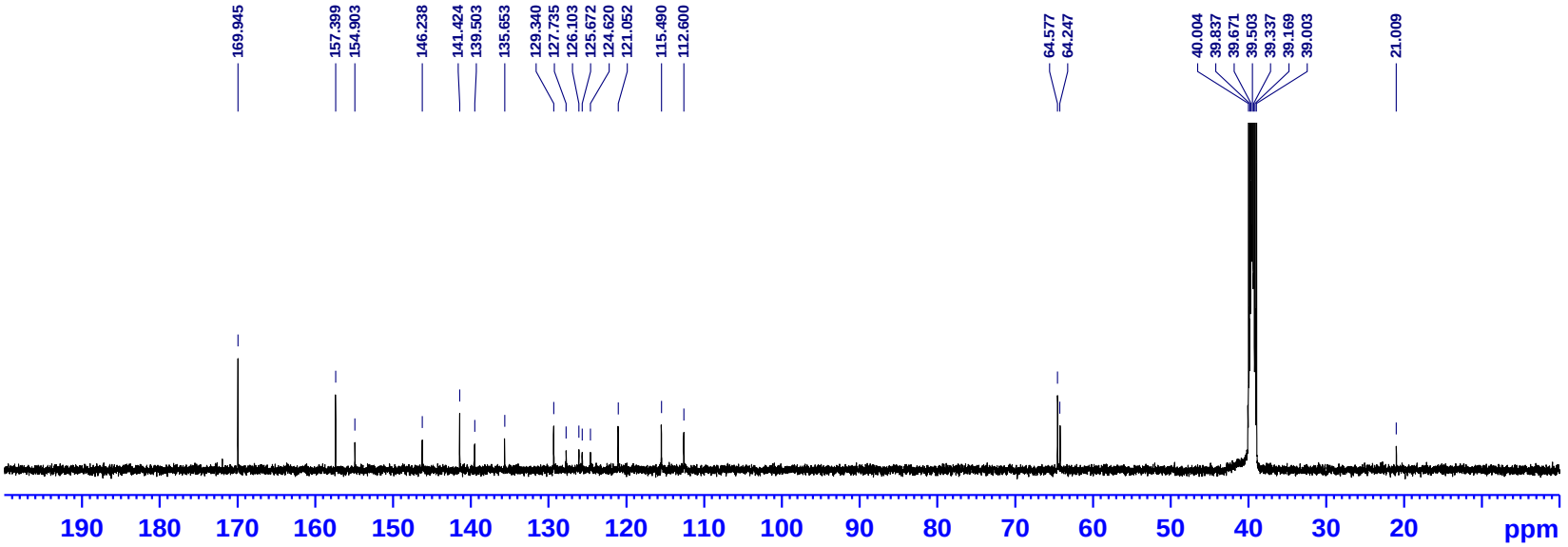

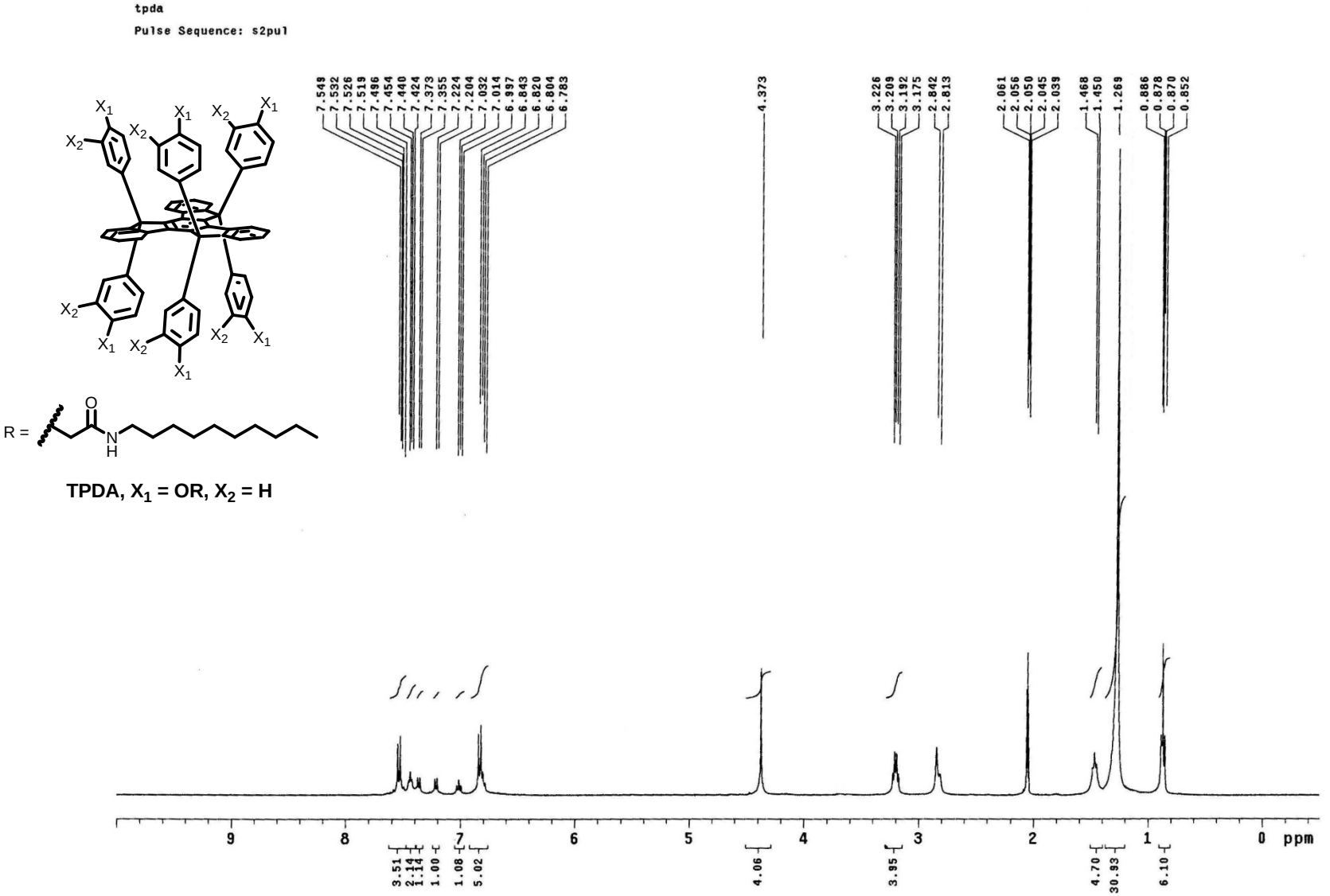

TPDA, X_1 = OR, X_2 = H

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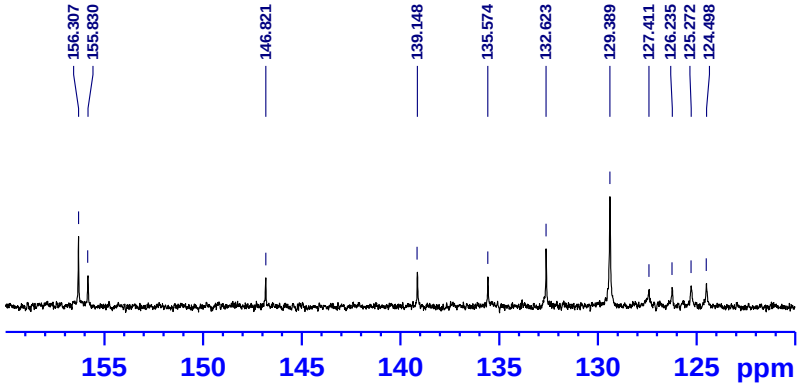

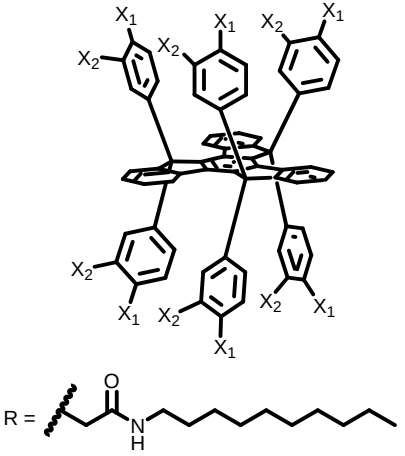

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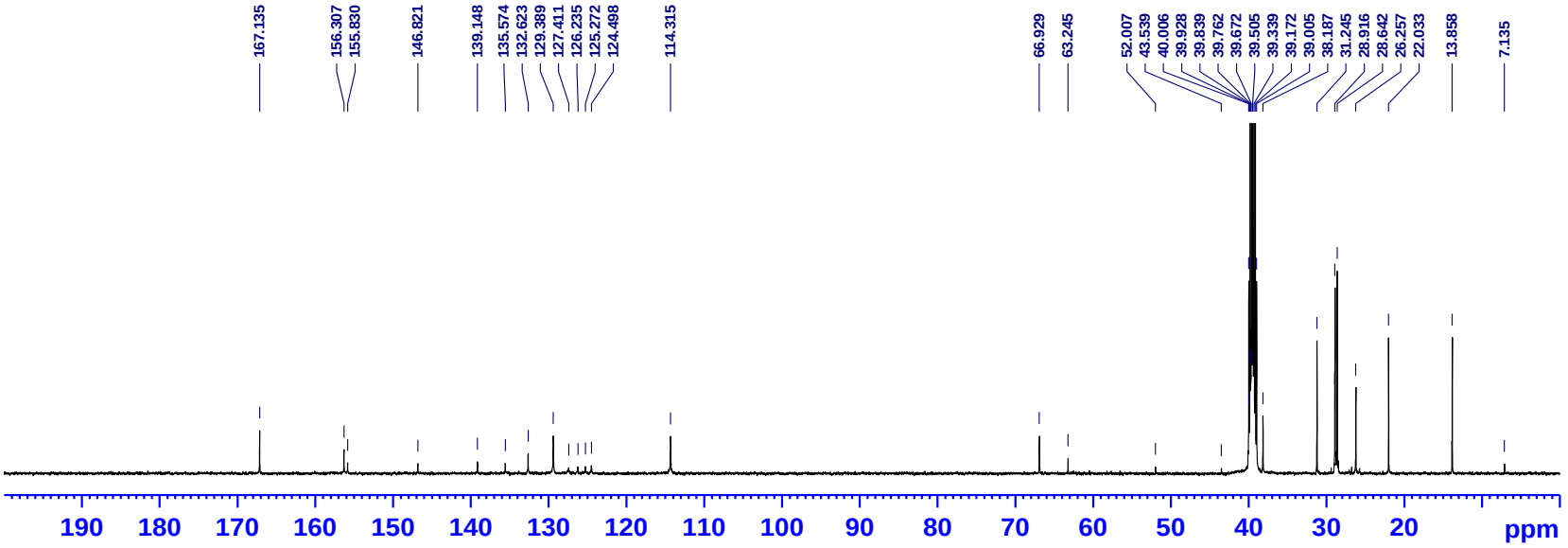
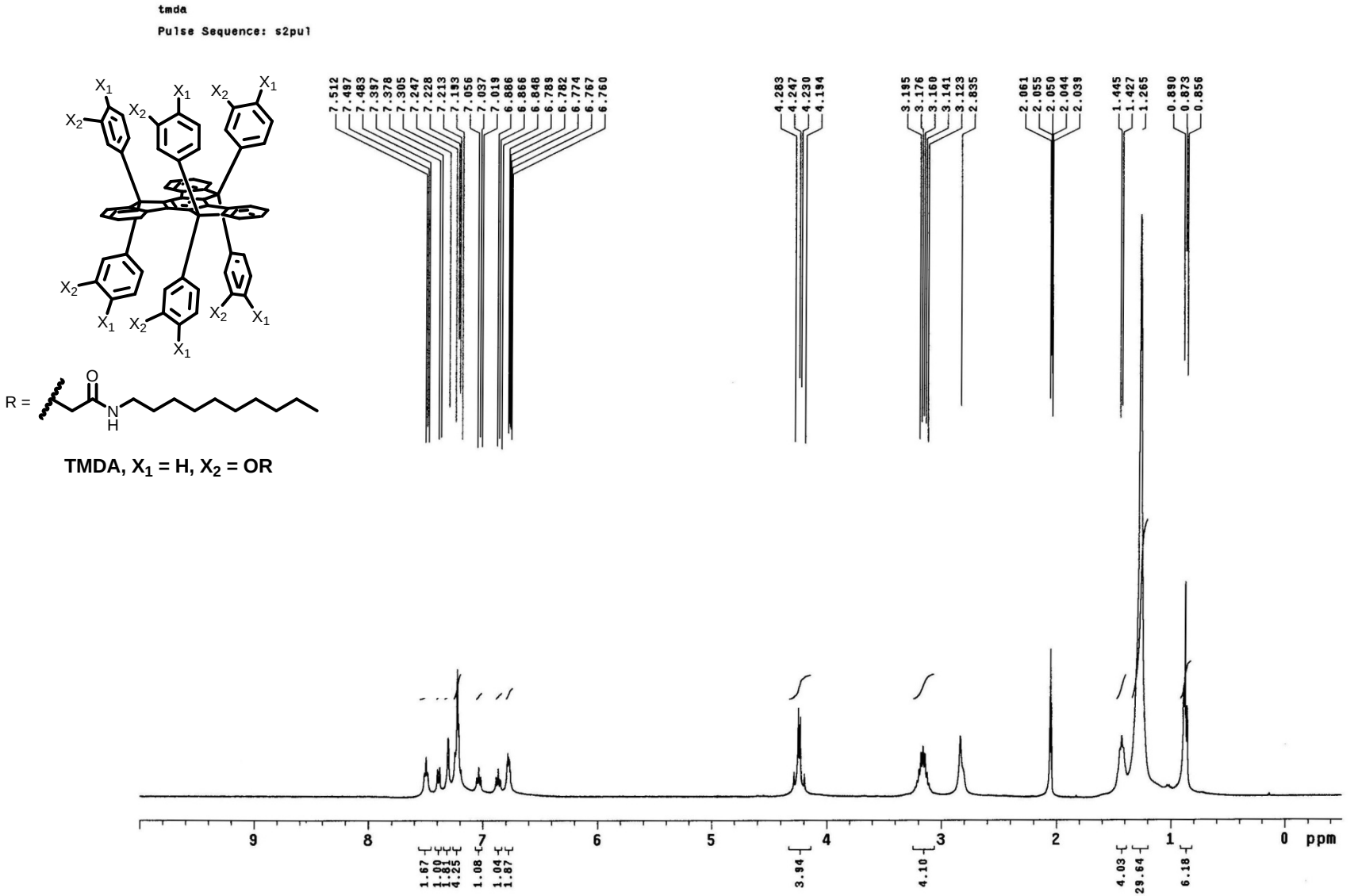
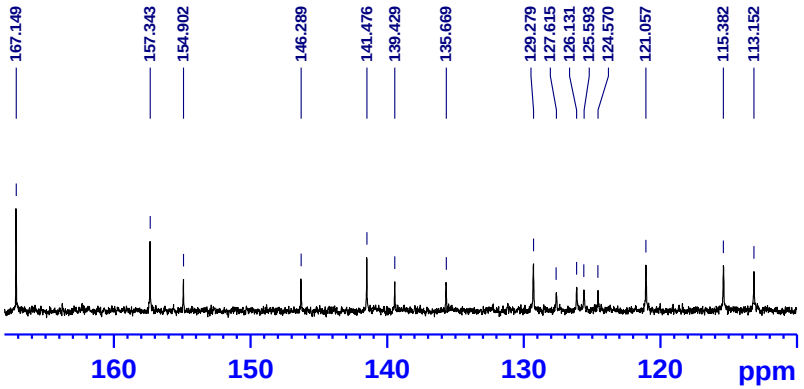
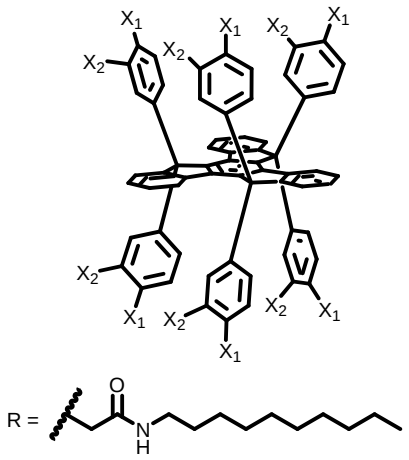




TMDA, X_1 = H, X_2 = OR

500MHz 13C DMSO TMDA





TMDA, X_1 = H, X_2 = OR