Electronic Supplementary Information

Room temperature columnar liquid crystalline phases of luminescent non-symmetric star-shaped molecules containing two 1,3,4-oxadiazole units

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Content:

(1) IR spectra for compound 3,4,5-ext-AMD-2

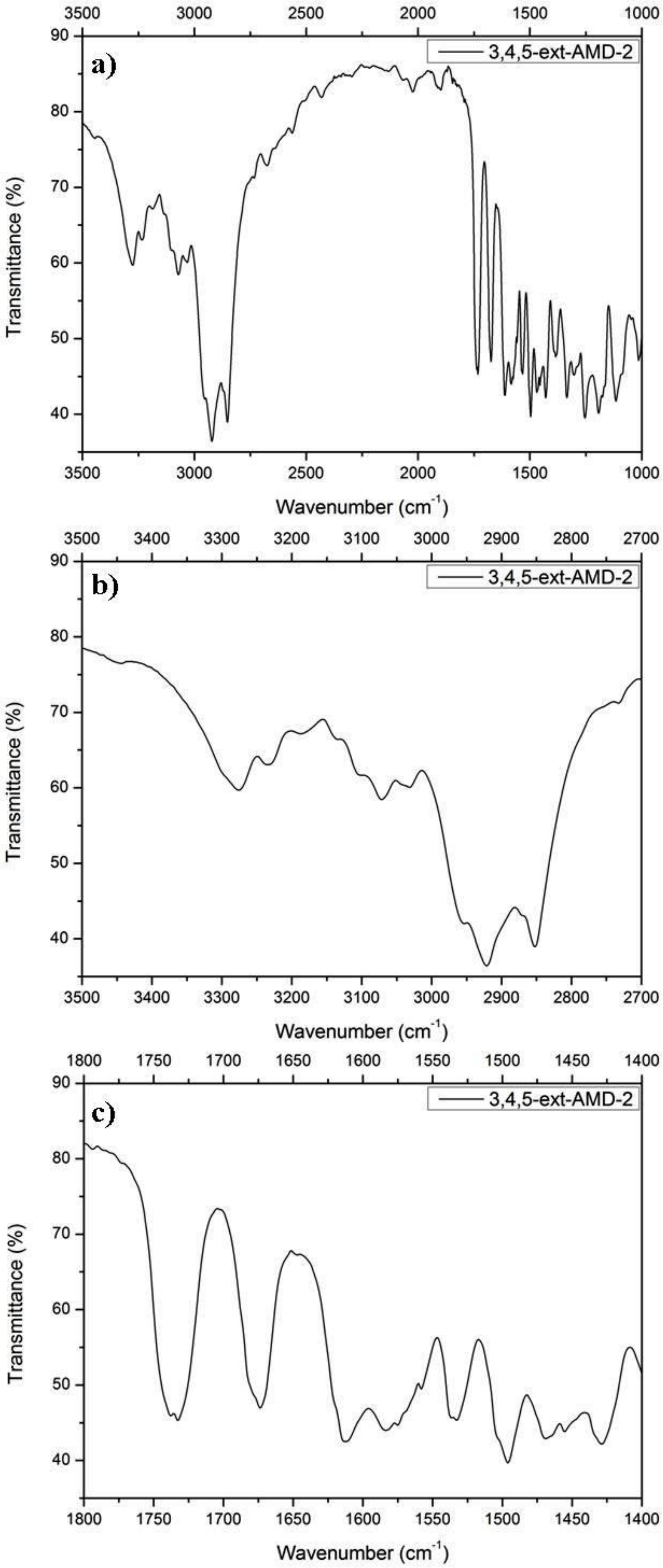


Fig. S1 IR spectra recorded for the neat compound **3,4,5-ext-AMD-2** at 25 °C.

(2) Calculation of the number of mesogens per unit cells

Table S1. Calculations of molecular volume (V_{mol}), volume of the (hypothetical) unit cells (V_{cell}) and number of molecules in these unit cells (n_{cell}).[a]

Compound	V_{cell} / nm^3	V_{mol} / nm^3	$n_{cell,cryst}$	$n_{cell,liq}$	n_{cell}
4-AMD-4	5.75	2.13	2.71	2.13	2.4
3,4-AMD-2	5.47	1.82	3.01	2.36	2.7
3,4-AMD-4	6.10	2.43	2.51	1.97	2.2
3,4,5-AMD-2	4.99	2.13	2.35	1.85	2.1
3,4,5-AMD-4	5.62	2.74	2.05	1.61	1.8
3,5-AMD-4	4.19	2.20	1.91	1.50	1.7
3,4,5-ext-AMD-2	6.73	2.26	2.97	2.33	2.7
3,4,5-ext-AMD-4	6.67	2.88	2.32	1.82	2.1

[a] V_{cell} = volume of the unit cell defined by the dimensions $a^2 \times sin(60^o) \times h$ (maximum of the diffuse wide angle scattering); V_{mol} = volume for a single molecule as calculated using the crystal volume increments;[1] $n_{cell,cryst}$ = number of molecules in the unit cell, calculated according to $n_{cell,cryst} = V_{cell}/V_{mol}$ (average packing coefficient in the crystal is $k = 0.7$;[2] $n_{cell,liq}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient $k = 0.55$, calculated according to $n_{cell,liq} = 0.55/0.7 \times n_{cell,cryst}$; n_{cell} = in the LC phase estimated as the average of that in the $n_{cell,cryst}$ and $n_{cell,liq}$.

(3) Crystallographic data

Table S2. Crystallographic data

Compound	T/°C	$2\theta_{\mathrm{obs}}$/°	d_{obs}/nm	*hk*	a_{hex}/nm
4-AMD-4	170	2.78	3.18	10	**3.67**
		17.98	0.49	diff	
3,4-AMD-2	170	2.85	3.10	10	**3.58**
		17.98	0.49	diff	
3,4-AMD-4	150	2.68	3.30	10	**3.81**
		4.63	1.91	11	
		18.30	0.48	diff	
	100	2.45	3.54	10	**4.08**
		4.31	2.05	11	
		18.63	0.48	diff	
3,4,5-AMD-2	135	2.98	2.97	10	**3.43**
		18.34	0.48	diff	
	100	2.94	3.01	109	**3.47**
		18.51	0.48	diff	
3,4,5-AMD-4	160	2.87	3.08	10	**3.55**
		18.45	0.48	diff	
	120	2.76	3.20	10	**3.70**
		18.710	0.47	diff	
3,4,5-IM-4	130	2.88	3.07	10	**3.55**
		18.55	0.48	diff	
3,5-AMD-4	70	3.16	2.79	10	**3.23**
		19.11	0.46	diff	
3,4,5-ext-AMD-2	170	2.63	3.36	10	**3.88**
		18.25	0.49	diff	
	140	2.55	3.47	10	**4.01**
		18.37	0.48	diff	
3,4,5-ext-AMD-4	150	2.56	3.46	10	**3.99**
		18.32	0.48	diff	

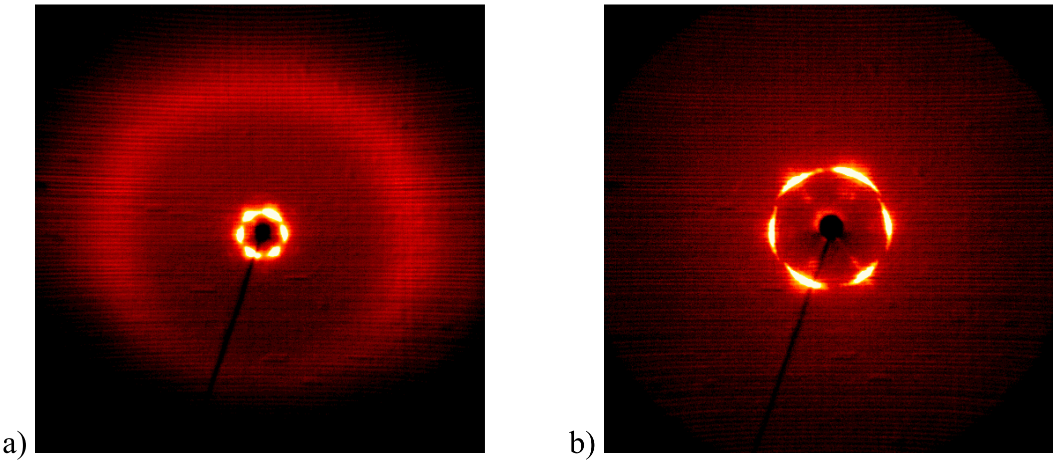


Fig. S2 XRD pattern of the Col$_{hex}$/*p6mm* phase of compound **4-AMD-4** at *T* = 170 °C, a) wide angle region and b) small angle region.

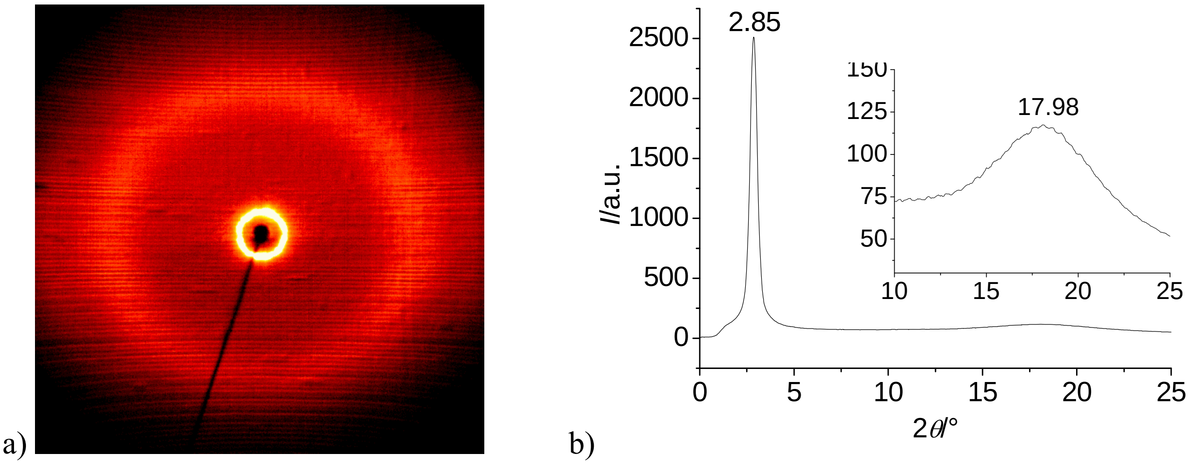
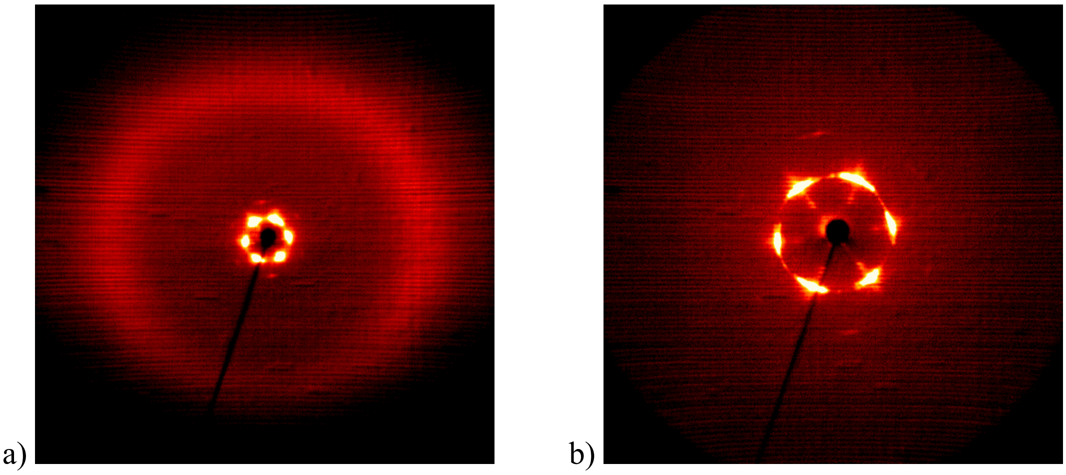


Fig. S3 XRD pattern of the Col$_{hex}$/*p6mm* phase of compound **3,4-AMD-2** at *T* = 170 °C, a) wide angle region and b) *θ* - scan of the diffraction pattern, the inset shows the diffuse scattering in the wide angle region.



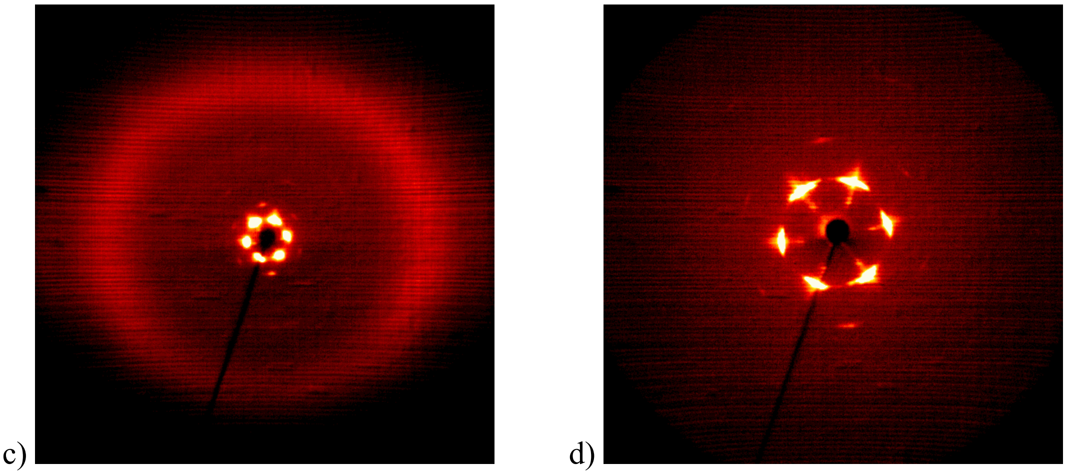


Fig. S4 XRD pattern of the $\mathrm{Col_{hex}}/p6mm$ phase of compound **3,4-AMD-4** at a,b) T = 150 °C wide and small angle region and c,d) T = 100 °C wide and small angle region.

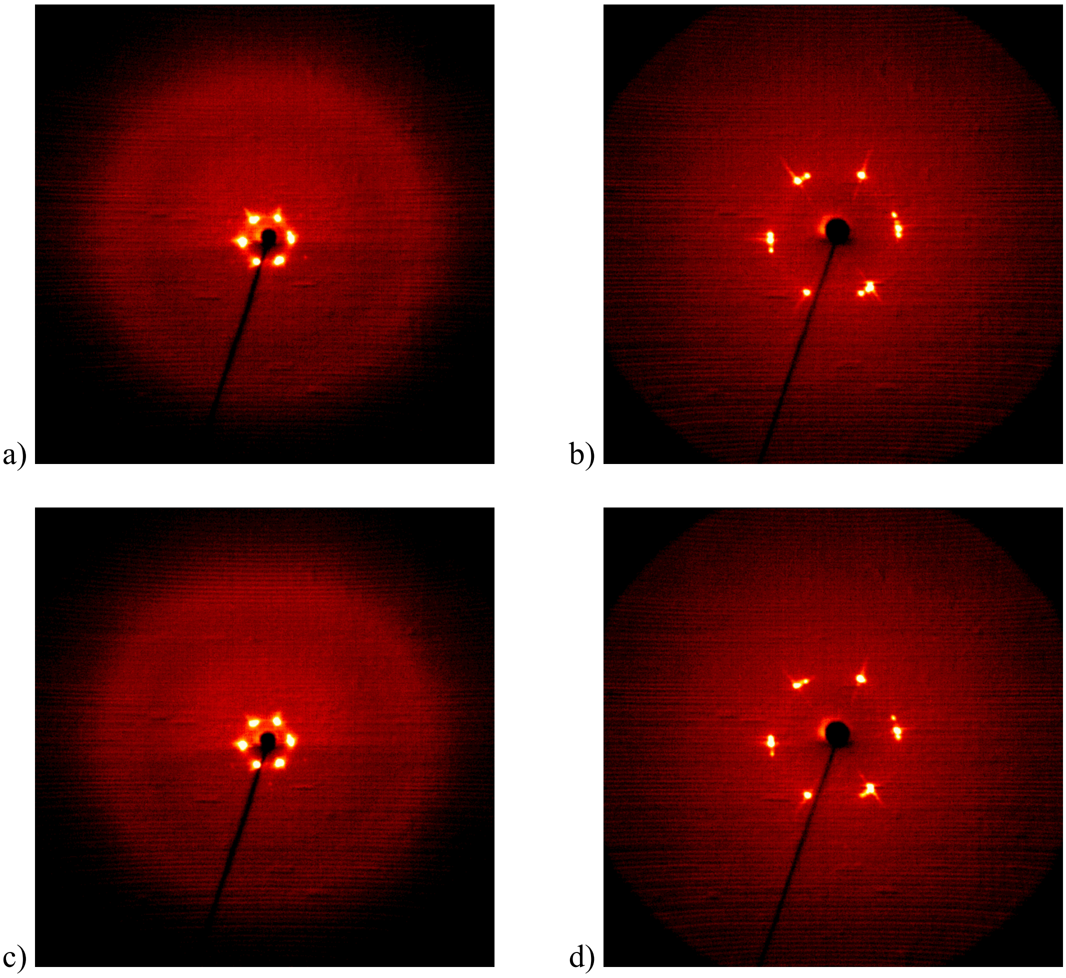


Fig. S5 XRD pattern of the $\mathrm{Col_{hex}}/p6mm$ phase of compound **3,4,5-AMD-2** at a,b) T = 135 °C wide and small angle region and c,d) T = 100 °C wide and small angle region.

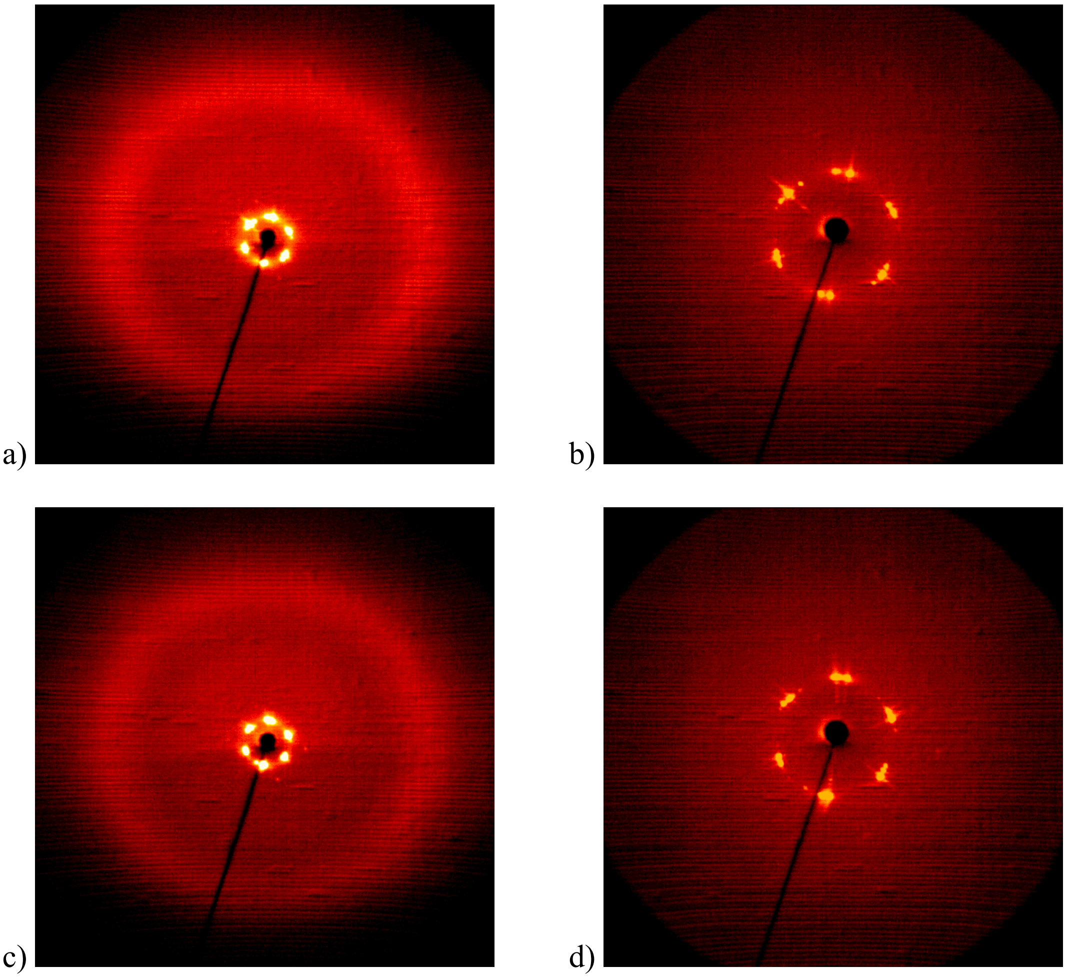


Fig. S6 XRD pattern of the Col$_{hex}$/*p*6*mm* phase of compound **3,4,5-AMD-4** at a,b) *T* = 160 °C wide and small angle region and c,d) *T* = 120 °C wide and small angle region.

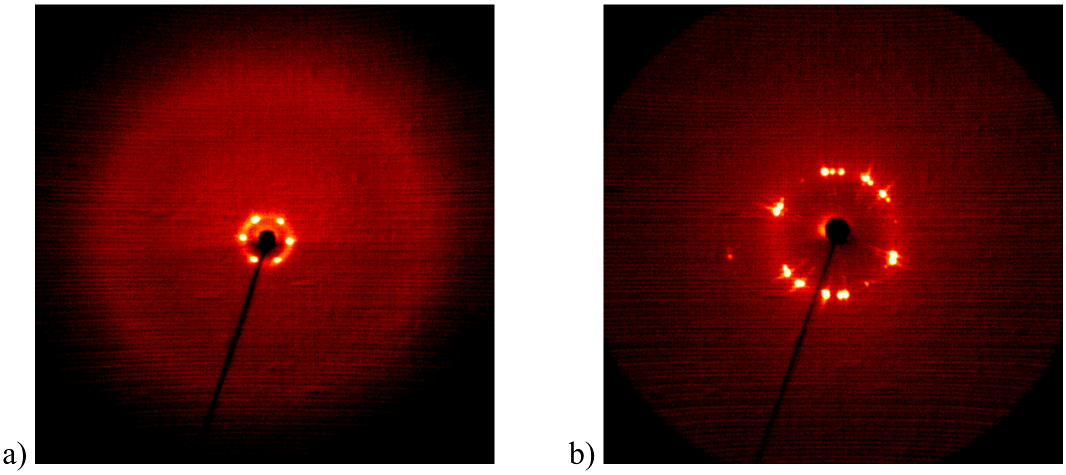


Fig. S7 XRD pattern of the Col$_{hex}$/*p*6*mm* phase of compound **3,4,5-IM-4** at *T* = 130 °C, a) wide angle region and b) small angle region.

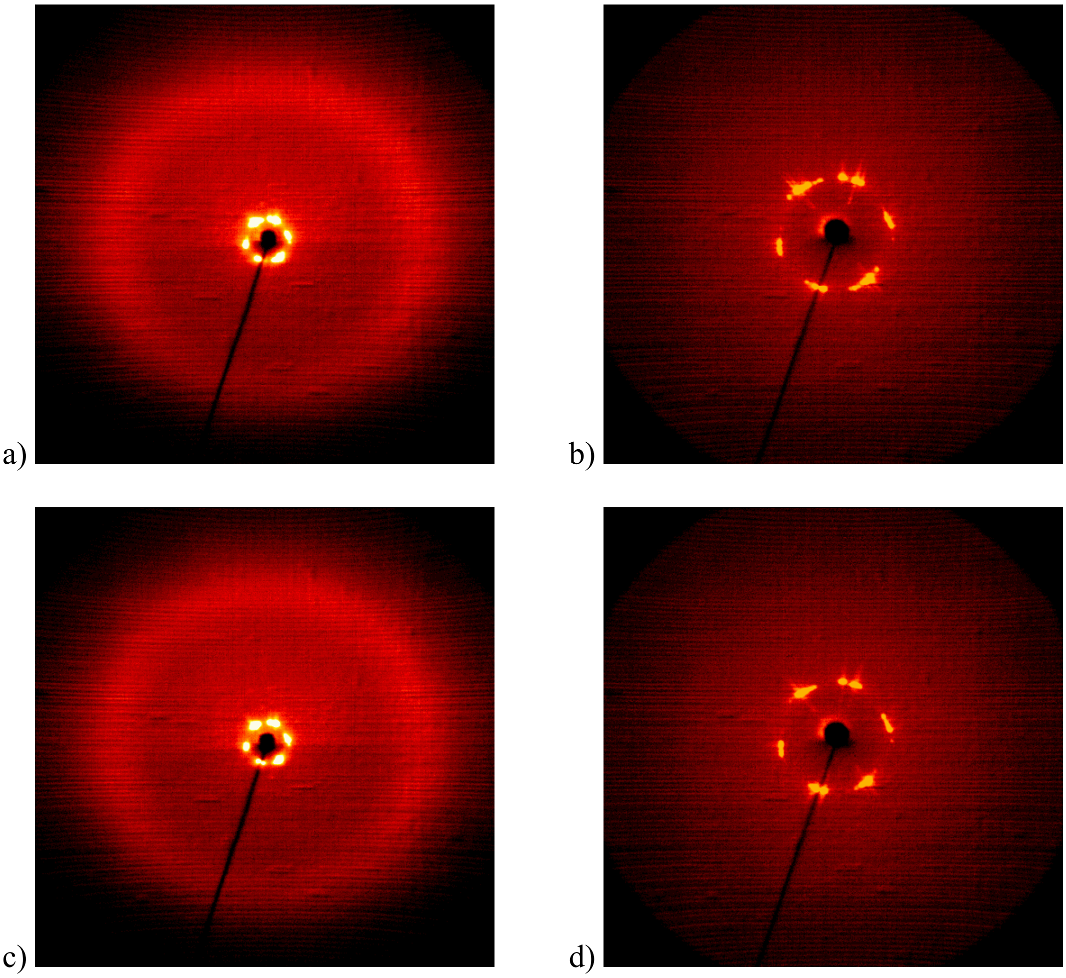


Fig. S8 XRD pattern of the Col$_{hex}$/*p*6*mm* phase of compound **3,4,5-ext-AMD-2** at a,b) *T* = 170 °C wide and small angle region and c,d) *T* = 140 °C wide and small angle region.

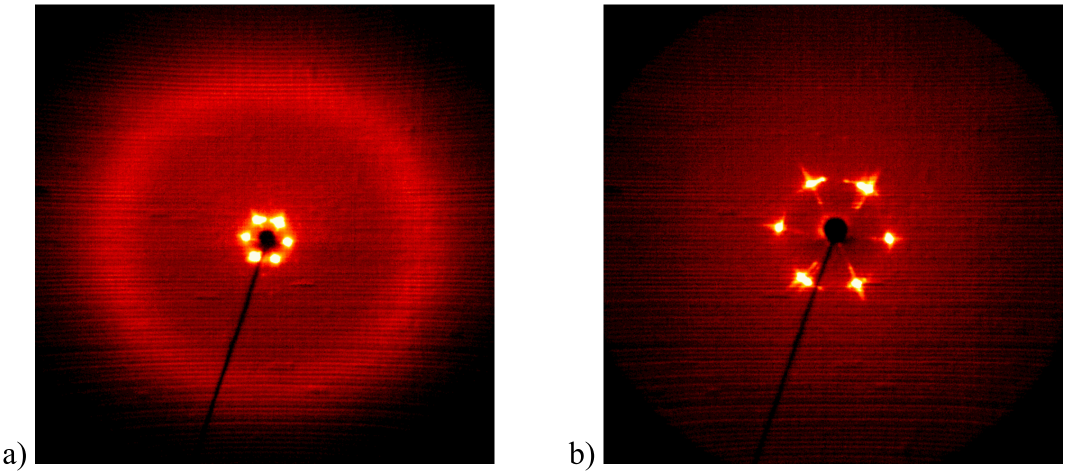


Fig. S9 XRD pattern of the Col$_{hex}$/*p*6*mm* phase of compound **3,4,5-ext-AMD-4** at *T* = 150 °C, a) wide angle region and b) small angle region.

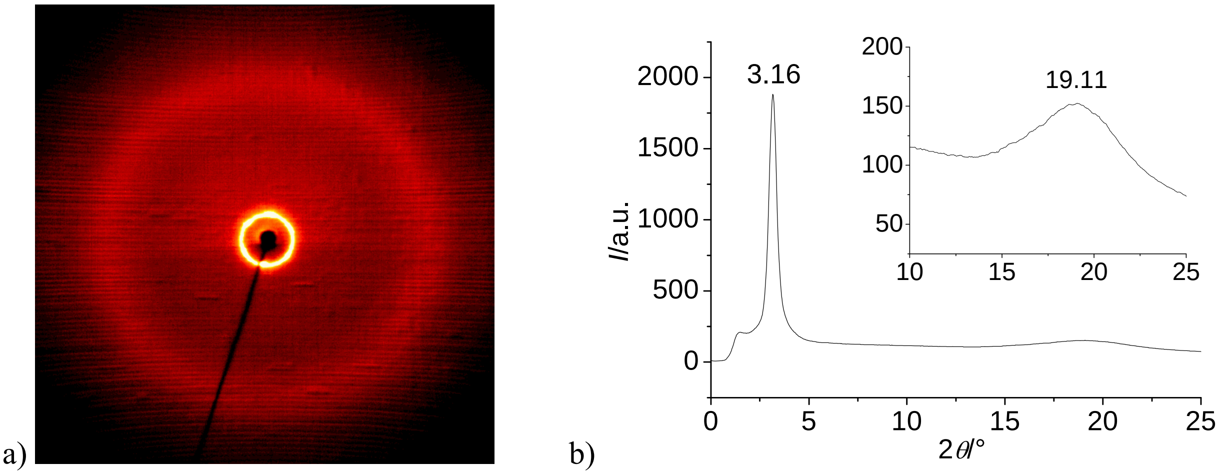


Fig. S10 XRD pattern of the $\mathrm{Col_{hex}}/p6mm$ phase of compound **3,5-AMD-4** at $T = 170$ °C, a) wide angle region and b) θ- scan of the diffraction pattern, the inset shows the diffuse scattering in the wide angle region.

(4) Additional photophysical data

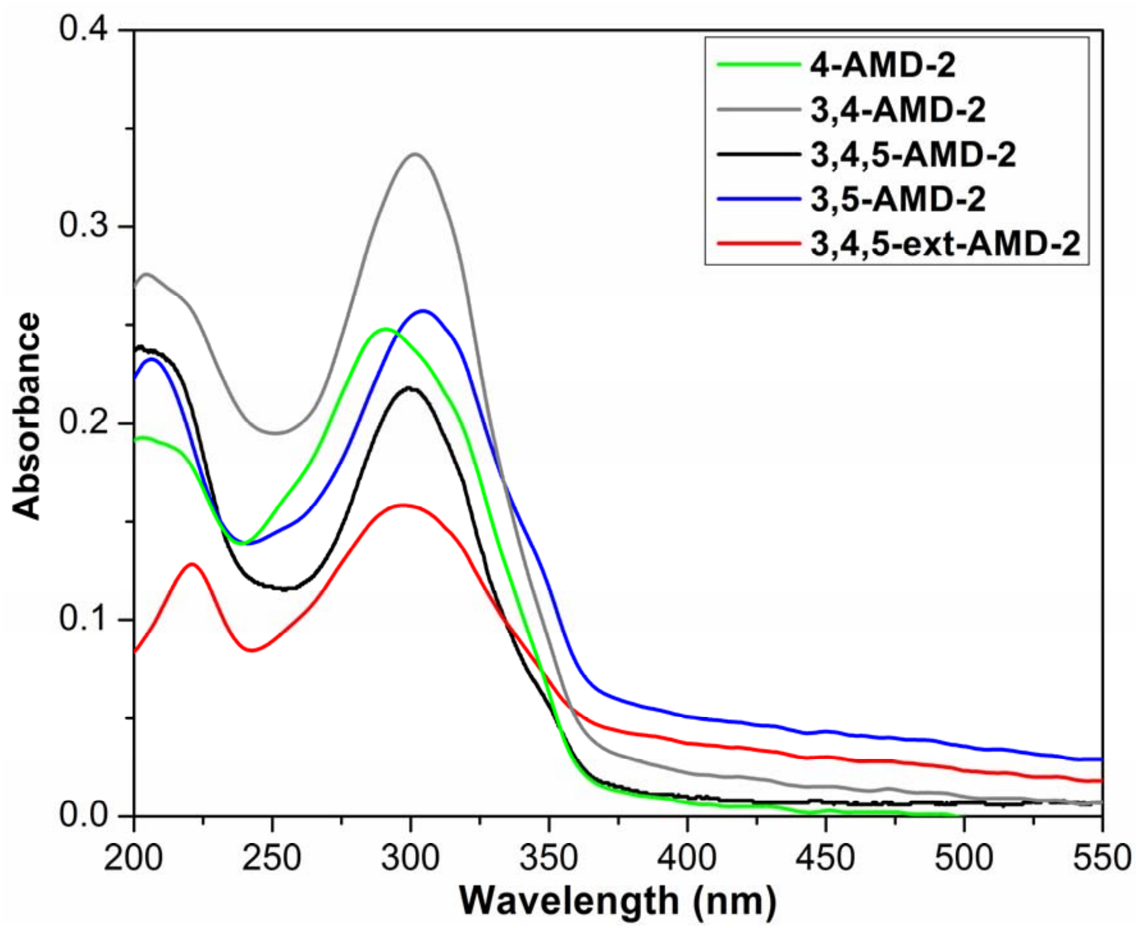


Fig. S11 Absorption spectrum for thin solid film of compounds from **AMD-2** group.

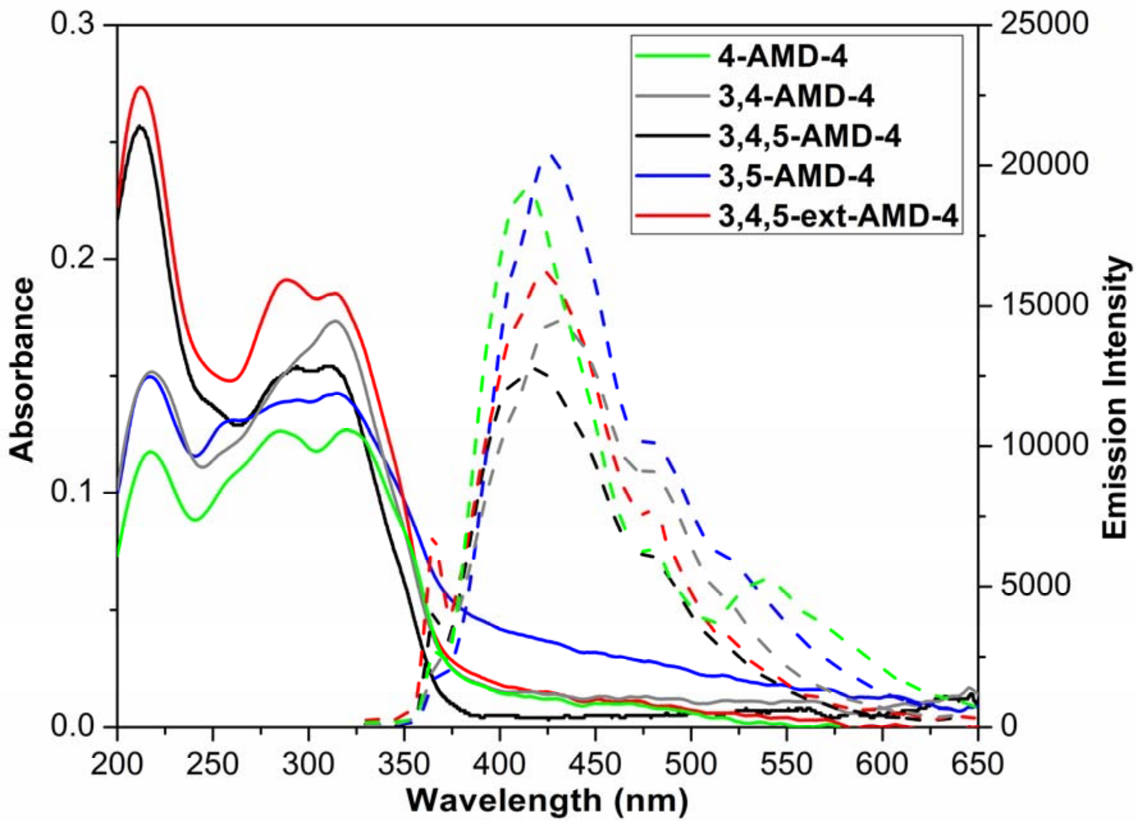


Fig. S12 Absorption spectrum (continuous line) and emission spectrum (dashed line) for thin solid film of compounds from **AMD-4** group.

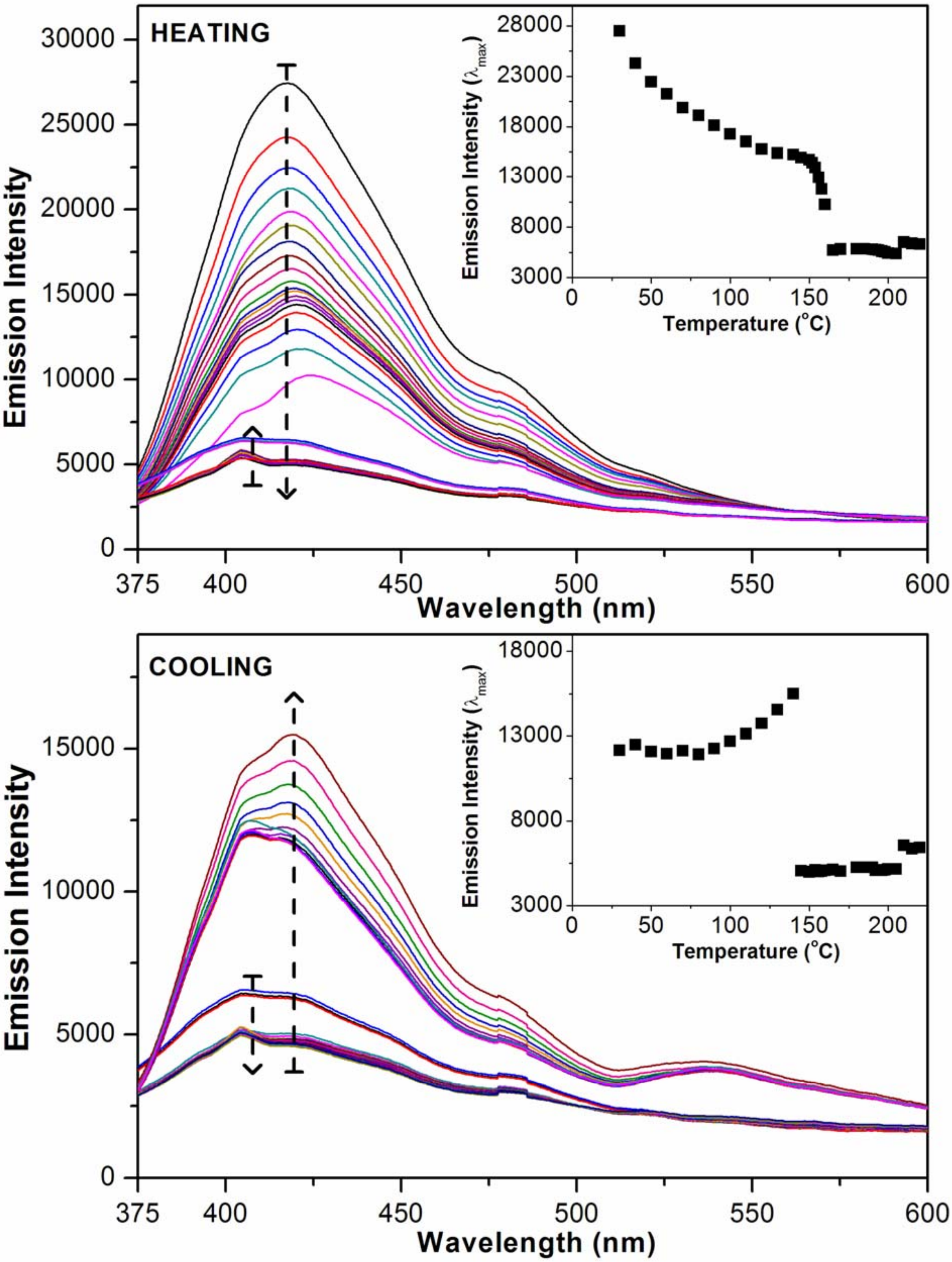


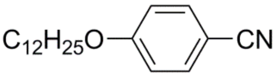
Fig. S13 Figure 10 of the paper (bigger and with more curves). Variation of the emission spectra of compound **4-AMD-4** during heating (left) and cooling (right) process. The insets show the variation of the intensity at the wavelength of maximum emission as a function of the temperature.

(5) Synthesis

The main chemicals used in this study were: gallic acid (97%, Sigma-Aldrich), 3,5-dihydroxybenzoic acid (97%, Sigma-Aldrich), 4-hydroxybenzonitrile (95%, Sigma-Aldrich), 3,4-dihydroxybenzonitrile (97%, Sigma-Aldrich), 1-bromododecane (97%, Sigma-Aldrich), 5-nitroisophthalic acid (98%, Acros Organics). All other inorganic, organic and solvents were of the highest purity, purchased from commercial sources (Merck, Sigma-Aldrich, Fluka, Vetec and Acros Organics), and used as received. Purifications were carried out by recrystallization using commercial grade solvents and by column chromatography on silica-gel 60–200 mesh 60A (Sigma-Aldrich and Acros). ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR spectrometer operating at 400 and 100.6 MHz, respectively. Melting points were determined with a Nikon Optishot 2 microscope equipped with a Mettler FP-82 Hot Stage. Elemental analysis was carried out using a Leco CHNS-932 instrument. High Resolution Mass Spectra were recorded on Bruker micrOTOF-Q II APPI mass spectrometer

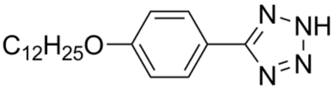
The 4-dodecyloxybenzoic acid and the 3,4-bis(dodecyloxy)benzoic acid were prepared according to the respective literature procedures.[3-5]

4-(dodecyloxy)benzonitrile



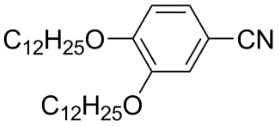
A mixture of 4-hydroxybenzonitrile (10.00 g; 84.0 mmol), 1-bromododecane (20.0 mL; 84.0 mmol), K_2CO_3 (23.18 g; 168 mmol) and 200 mL butanone were added to a round-bottomed flask and stirred under reflux for 22 hours. After this period, the suspension was filtered and washed with hot butanone. The solvent was removed and the solid obtained dissolved in ether. The organic phase was washed with NaOH 5% (1x50 mL), HCl 5% (1x50 mL) and H_2O (1x50 mL) and dried over anhydrous Na_2SO_4. The removal of the solvent afforded 21,46 g (89 %) of a white solid. **m.p.:** 42.8 – 43.9 °C (lit. 42 – 43 °C)[6]. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.87 (t, *J* = 6.7 Hz, 3H, CH_3), 1.22 – 1.33 (m, 16H, $-CH_2-$), 1.44 (m, 2H, $-CH_2-$), 1.78 (m, 2H, $-CH_2CH_2O-$), 3.98 (t, *J* = 6.6 Hz, 2H, $-CH_2O-$), 6.92 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.55 (d, *J* = 8.9 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.35, 22.93, 26.16, 29.21, 29.55, 29.58, 29.77, 29.81, 29.86, 29.88, 32.15, 68.64, 103.83, 115.40, 119.54, 134.15, 162.69.

5-(4-dodecyloxyphenyl)tetrazole (TET-2)



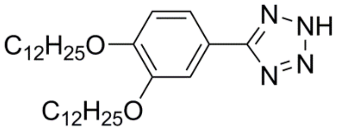
To a 100 mL round-bottomed flask were added 4-(dodecyloxy)benzonitrile (19.90 g; 69.3 mmol), NaN_3 (13.51 g; 207.9 mmol), NH_4Cl (11.12 g; 207.9 mmol) and 100 mL DMF. The mixture was refluxed under strong stirring for 20 hours, cooled to room temperature and poured into 400 mL water/ice. The pH of the suspension was adjusted to ≈ 3 with HCl (10 %), the crude product collected by filtration and washed with plenty of water. The product was recrystallized over acetone, affording 19.70 g (86 %) of an off-white solid. **m.p.:** 148.4 – 150.7 °C (lit. 152 - 155 °C)[7]. **^{1}H NMR** ($CDCl_3$ + DMSO-d_6) δ ppm: 0,88 (t, *J* = 6,7 Hz, 3H, CH_3), 1,21 – 1,39 (m, 16H, -CH_2-), 1,47 (m, 2H, -CH_2-), 1,81 (m, 2H, -C$\underline{H}_2$$CH_2$O-), 4,03 (t, *J* = 6,6 Hz, 2H, -CH_2O-), 7,02 (d, *J* = 9,0 Hz, 2H, Ar-H), 8,01 (d, *J* = 9,0 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$ + DMSO-d_6) δ ppm: 13.63, 22.07, 25.39, 28.53, 28.70, 28.76, 28.94, 29.01, 29.05, 31.28, 67.63, 114.51, 115.92, 128.28, 128.90, 160.80.

3,4-(didodecyloxy)benzonitrile



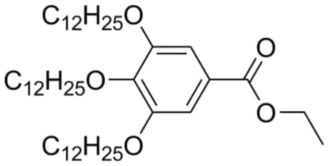
A mixture of 3,4-dihydroxybenzonitrile (5.00 g; 37.0 mmol), 1-bromododecane (22.0 mL; 92.5 mmol), K_2CO_3 (25.00 g; 181.2 mmol), TBAB (0.50 g; 1.55 mmol) and 150 mL butanone were added to a round-bottomed flask and stirred under reflux for 31 hours. After this period, the suspension was filtered and washed with hot butanone. The solvent was removed and the solid obtained dissolved in CH_2Cl_2. The organic phase was washed with NaOH 5% (1x30 mL), HCl 5% (1x30 mL) and H_2O (1x30 mL) and dried over anhydrous Na_2SO_4. The product was recrystallized over acetonitrile, affording 15.87 g (91 %) of a pure white solid. **m.p.:** 79.8 – 82.8 °C (lit. 81 - 83 °C)[6]. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 6.7 Hz, 6H, CH_3), 1.25 – 1.36 (m, 32H, -CH_2-), 1.46 (m, 4H, -CH_2-), 1.83 (m, 4H, -C$\underline{H}_2$$CH_2$O-), 3.98 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 4.02 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 6.86 (d, *J* = 8,4 Hz, 1H, Ar-H), 7.07 (d, *J* = 1.9 Hz, 1H, Ar-H), 7.23 (dd, *J* = 8.4 Hz e 1.9 Hz, 1H, Ar-H). **^{13}C NMR** (DMSO-d_6 – 90 ^{o}C) δ ppm: 12.31, 20.59, 24.07, 27.23, 27.27, 27.51, 27.56, 27.61, 29.87, 67.61, 68.05, 107.97, 112.88, 115.84, 117.59, 125.13, 147.72, 151.81.

5-(3,4-didodecyloxyphenyl)tetrazole (TET-4)



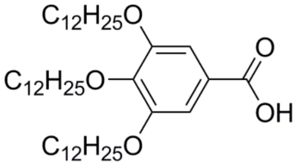
To a 100 mL round-bottomed flask were added 3,4-(didodecyloxy)benzonitrile (5.00 g, 10.6 mmol), NaN_3 (2.07 g, 31.8 mmol), NH_4Cl (1.70 g; 31.8 mmol) and 30 mL DMF. The mixture was refluxed under strong stirring for 24 hours, cooled to room temperature and poured into 200 mL water/ice. The pH of the suspension was adjusted to ≈ 2 with HCl (10 %), the crude product collected by filtration and washed with plenty of water. The product was recrystallized over acetone, affording 5.06 g (93 %) of a white solid. **m.p.:** 157.8 – 159.0 °C (lit. 159.3 – 159.5 °C)[8]. **^{1}H NMR** ($CDCl_3$ + 2 drops DMSO-d_6) δ ppm: 0.88 (t, *J* = 6.8 Hz, 6H, CH_3), 1.22 – 1.40 (m, 32H, -C$\underline{H}_2$-), 1.49 (m, 4H, -CH_2-), 1.84 (m, 4H, -C$\underline{H}_2$$CH_2$O-), 4.06 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 4.09 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 6.97 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.62 (dd, *J* = 8.4 Hz e *J* = 1.9 Hz, 1H, Ar-H), 7.68 (d, *J* = 1.9 Hz, 1H, Ar-H). **^{13}C NMR** ($CDCl_3$ + 2 drops DMSO-d_6) δ ppm: 14.05, 22.57, 25.88, 25.92, 29.02, 29.09, 29.22, 29.28, 29.45, 29.46, 29.49, 29.52, 31.78, 69.02, 69.22, 112.16, 113.16, 114.48, 116.86, 120.26, 149.25, 151.35.

Ethyl 3,4,5-tris(dodecyloxy)benzoate



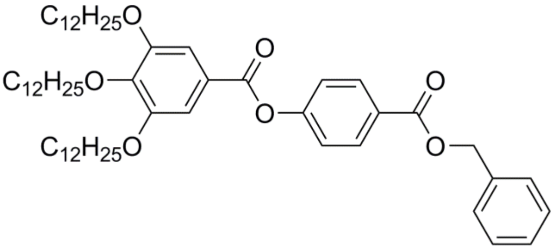
A mixture of ethyl 3,4,5-trihydroxybenzoate (8.00 g; 40.4 mmol), 1-bromododecane (31.0 mL; 129 mmol), K_2CO_3 (33.45 g; 242.4 mmol), TBAB (0.65 g; 2.02 mmol) and 200 mL butanone were added to a round-bottomed flask and stirred under reflux for 18 hours. After this period, the suspension was filtered, washed with hot butanone and the solvent removed. The remaining oil was poured into 500 mL of hot methanol and slowly cooled under strong stirring. The white precipitate formed was filtered, affording 27.28 g (96 %) of a pure white solid. **m.p.:** 41.3 – 42.9 °C (lit. 42.5 °C)[9]. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, J = 6.7 Hz, 9H, CH_3), 1.21 – 1.35 (m, 48H, -CH_2-), 1.38 (t, J = 7.1 Hz, 3H, -$OCH_2C\underline{H}_3$), 1.47 (m, 6H, -CH_2-), 1.70 – 1.85 (m, 6H, -$C\underline{H}_2CH_2O$-), 4.01 (t, J = 6.5 Hz, 6H, -CH_2O-), 4.35 (qua, J = 7.1 Hz, 2H, -$OC\underline{H}_2CH_3$), 7.25 (s, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.10, 14.39, 22.68, 26.04, 26.07, 29.21, 29.29, 29.35, 29.39, 29.56, 29.62, 29.64, 29.68, 29.72, 29.74, 30.30, 31.92, 60.95, 69.13, 73.46. 107.91, 125.00, 142.24, 152.76. 166.46.

3,4,5-tris(dodecyloxy)benzoic acid



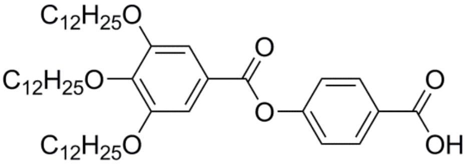
In a round-bottomed flask were added 24.00 g (34.1 mmol) of ethyl 3,4,5-tris(dodecyloxy)benzoate and 80 mL of 50 °C ethanol. After complete dissolution, 1.54 g (38.5 mmol) of NaOH in pellets were slowly added and the mixture refluxed until complete hydrolysis (observed by TLC). The solution was then cooled to room temperature, acidified to pH 1 with concentrated HCl, filtered and the solid washed with plenty of water. The product was dissolved in CH_2Cl_2 and filtered to remove insoluble impurities, affording 21.66 g (94 %) of the pure compound. **m.p.:** 57.3 – 59.8 °C (lit. 60.0 °C)[9]. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, J = 6.7 Hz, 9H, CH_3), 1.18 – 1.38 (m, 48H, -CH_2-), 1.47 (m, 6H, -CH_2-), 1.71 – 1.86 (m, 6H, -$C\underline{H}_2CH_2O$-), 4.03 (m, 6H, -CH_2O-), 7.33 (s, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.11, 22.69, 26.04, 26.08, 29.27, 29.37, 29.39, 29.56, 29.64, 29.66, 29.70, 29.72, 29.74, 29.75, 30.32, 31.92, 69.15, 73.54. 108.51, 123.80, 143.06, 152.82. 171.84.

Benzyl 4-[3,4,5-tris(dodecyloxy)benzoyloxy]benzoate



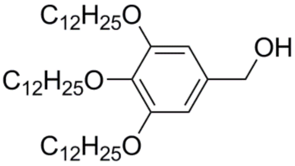
Under Argon atmosphere, 3.72 g (5.52 mmol) of 3,4,5-tris(dodecyloxy)benzoic acid, 1.26 g (5.52 mmol) of benzyl 4-hydroxybenzoate, catalytic amount of DMAP and 50 mL of dry CH_2Cl_2 were added to a Schlenk flask. After 10 minutes, 1.25 g (6.06 mmol) of DCC were added and the mixture stirred for further 12 hours under Argon atmosphere. The resulting precipitate was filtered off and washed with 40 mL of CH_2Cl_2. The solvent was removed and the crude product purified by silica column chromatography in $CHCl_3$, affording 3.91 g (80%) of a white solid. **m.p.:** 46.8 – 47.3 °C. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (m, 9H, CH_3), 1.19 – 1.38 (m, 48H, -CH_2-), 1.49 (m, 6H, -CH_2-), 1.73 – 1.87 (m, 6H, -C$\underline{H}_2$CH$_2$O-), 4.05 (m, 6H, -CH_2O-), 5.38 (s, 2H, -OC$\underline{H}_2$Ar), 7.28 (d, J = 8.8 Hz, 2H, Ar-H), 7.32 – 7.48 (m, 7H, Ar-H), 8.16 (d, J = 8.8 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.11, 22.69, 26.05, 26.07, 29.27, 29.35, 29.38, 29.39, 29.56, 29.62, 29.65, 29.69, 29.72, 29.74, 29.75, 30.34, 31.92, 66.82, 69.26, 73.59. 108.57, 121.87, 123.34, 127.66. 128.20, 128.29, 128.61, 131.32, 135.93, 143.21, 152.98, 154.82, 164.49, 165.67.

4-[3,4,5-tris(dodecyloxy)benzoyloxy]benzoic acid



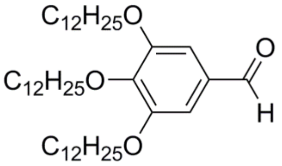
A mixture of benzyl 4-[3,4,5-tris(dodecyloxy)benzoyloxy]benzoate (3.57 g; 4.03 mmol), 50 ml of THF and approximately 0.40 g of Pd/C (10%) catalyst were added to an appropriate flask and submitted to catalytic hydrogenation for 16 hours. The suspension was filtered in celite, washed with THF and the solvent removed. The crude product was recrystallized under ethanol, affording 3.01 g (94%) of a white solid. **m.p.:** 83.5 – 84.8 °C (lit. 87 °C)[10]. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (m, 9H, CH_3), 1.23 – 1.40 (m, 48H, -CH_2-), 1.49 (m, 6H, -CH_2-), 1.73 – 1.88 (m, 6H, -C$\underline{H}_2$CH$_2$O-), 4.06 (m, 6H, -CH_2O-), 7.33 (d, J = 8.8 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 8.21 (d, J = 8.8 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.10, 22.69, 26.06, 26.09, 29.30, 29.36, 29.39, 29.57, 29.63, 29.66, 29.70, 29.73, 29.75, 30.35, 31.94, 69.33, 73.62. 108.70, 122.03, 123.29, 126.71, 131.90, 143.37, 153.02, 155.48, 164.44, 170.59.

3,4,5-tris(dodecyloxy)benzyl alcohol



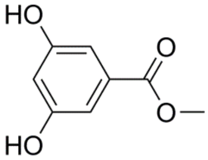
Under Argon atmosphere, 1.07 g (28.2 mmol) of $LiAlH_4$ and 100 mL of dry THF were added to a Schlenk flask equipped with a dropping funnel. The suspension was cooled to -5 °C with a ice/NaCl bath and 13.20 g (18.8 mmol) of ethyl 3,4,5-tris(dodecyloxy)benzoate (dissolved in 75 mL of dry THF) were added dropwise during approximately 1 hour. After the addition was completed, the reaction mixture was stirred at -5 °C for 30 minutes and at room temperature for further 3 hours. The reaction mixture was quenched by dropwise addition of methanol (30 mL) and water (30 mL). The solvent was removed, the product dissolved in 300 mL of ethyl acetate and filtered to remove insoluble impurities, affording 11.66 g (94%) of a pure off-white solid. **m.p.:** 52.2 – 52.9 °C (lit. 51.6 °C)[11]. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, J = 6.7 Hz, 9H, CH_3), 1.23 – 1.37 (m, 48H, -CH_2-), 1.46 (m, 6H, -CH_2-), 1.59 (broad, 1H, -OH), 1.70 – 1.82 (m, 6H, -C$\underline{H}_2$CH$_2$O-), 3.93 (t, J = 6.6 Hz, 2H, -CH_2O-), 3.97 (t, J = 6.6 Hz, 4H, -CH_2O-), 4.59 (broad, 2H, -C$\underline{H}_2$OH), 7.56 (s, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.11, 22.69, 26.11, 26.14, 29.37, 29.40, 29.42, 29.43, 29.63, 29.66, 29.70, 29.74, 29.76, 30.34, 31.93, 31.95, 65.71, 69.14, 73.43. 105.41, 135.99, 137.68, 153.30.

3,4,5-tris(dodecyloxy)benzaldehyde



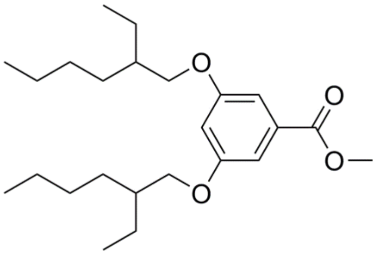
In a round-bottomed flask, 4.00 g (6.05 mmol) of 3,4,5-tris(dodecyloxy)benzyl alcohol were dissolved in 80 mL of CH_2Cl_2 and cooled to 0 °C with a ice/NaCl bath. To this solution, 1.30 g (6.05 mmol) of PCC were added in small portions (≈ 10 minutes). The solution was stirred at 0 °C for 15 minutes and at room temperature for further 3 hours. The solvent was removed and the black crude product purified by silica column chromatography, using $CHCl_3$ as eluent. The obtained product was recrystallized over acetone, affording 3.58 g (90 %) of the pure desired compound. **m.p.:** 50,6 – 51,3 °C (lit. 48,4 °C)[11]. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 6.7 Hz, 9H, CH_3), 1.23 – 1.38 (m, 48H, $-CH_2-$), 1.48 (m, 6H, $-CH_2-$), 1.71 – 1.87 (m, 6H, $-C\underline{H_2}CH_2O-$), 4.04 (m, 6H, $-CH_2O-$), 7.08 (s, 2H, Ar-H), 9.83 (s, 1H, $Ar-C\underline{H}O$). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.10, 22.69, 26.03, 26.07, 29.27, 29.36, 29.38, 29.54, 29.62, 29.65, 29.69, 29.71, 29.74, 30.35, 31.93, 31.94, 69.27, 73.64. 107.90, 131.45, 143.90, 153.53. 191.25.

Methyl 3,5-dihydroxybenzoate



In a round-bottomed flask were added 10.00 g (64.9 mmol) of 3,5-dihydroxybenzoic acid, 150 mL of methanol and 1 mL of sulfuric acid. The mixture was refluxed for 18 hours, the solvent removed under reduced pressure and the solid dissolved in 150 mL of ethyl acetate. The organic phase was washed with H_2O (3 x 50 mL), dried over anhydrous Na_2SO_4 and the solvent removed, affording 10.11 g (93 %) of a white and pure compound. **m.p.:** 164.3 – 165.8 °C (lit. 163 – 165.0 °C)[12]. **^{1}H NMR** (DMSO-d_6) δ ppm: 3.78 (s, 3H, $-OC\underline{H_3}$), 6.44 (t, *J* = 2.2 Hz, 1H, Ar-H), 6.82 (d, *J* = 2.2 Hz, 2H, Ar-H), 9.65 (broad, 2H, Ar-OH). **^{13}C NMR** (DMSO-d_6) δ ppm: 52.03, 107.15, 131.36, 158.60, 166.33.

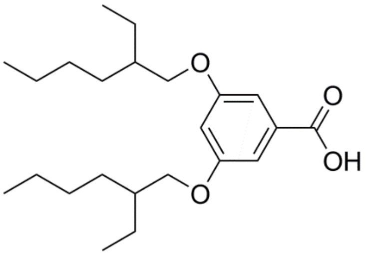
Methyl 3,5-bis(2-ethylhexyloxy)benzoate



A mixture of methyl 3,5-dihydroxybenzoate (4.00 g; 23.8 mmol), 2-ethylhexylbromide (10.2 mL; 57.1 mmol), K_2CO_3 (13.10 g; 95.2 mmol), 18-crown-6 (0.39 g) and 100 mL acetonitrile were added to a round-bottomed flask and stirred under reflux for 20 hours. After this period, the suspension was filtered, washed with hot acetonitrile and the solvent removed under reduced pressure. The resultant oil was purified by silica chromatography, using a mixture of hexane/chloroform (gradient from 100:0 to 50:50) as eluent, affording 8.58 g (92%) of a colorless oil. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.92 (m, 12H, CH_3), 1.29 – 1.55 (m, 16H, $-CH_2-$), 1.72 (m, 2H, -

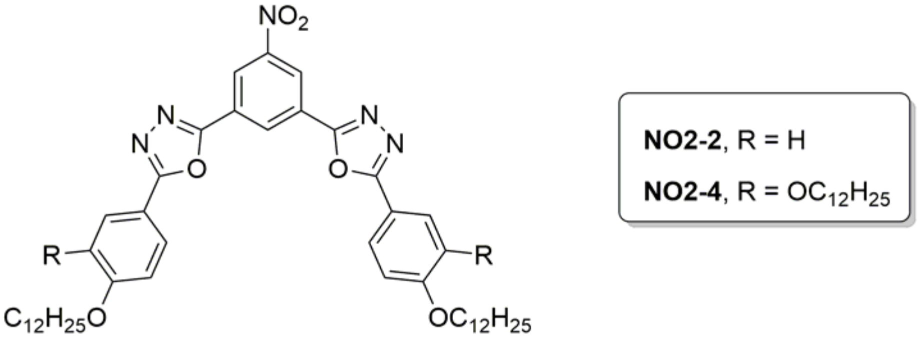
C<u>H</u>(Et)-), 3.86 (dd, *J* = 5.6 Hz e *J* = 1.6 Hz, 4H, $-CH_2O-$), 3.90 (s, 3H, $-OCH_3$), 6.65 (t, *J* = 2.3 Hz, 1H, Ar-H), 7.17 (d, *J* = 2.3 Hz, 2H, Ar-H). ^{13}**C NMR** ($CDCl_3$) δ ppm: 11.03, 14.01, 22.99, 23.81, 29.02, 30.46, 39.31, 52.03, 70.57, 106.40, 107.45, 131.67, 160.33, 166.94.

3,5-bis(2-ethylhexyloxy)benzoic acid



In a round-bottomed flask were added 8.30 g (21.2 mmol) of methyl 3,5-bis(2-ethylhexyloxy)benzoate, 1.01 g (25.4 mmol) of NaOH in pellets and 50 mL methanol and the mixture was refluxed for 20 hours. The solution was cooled to room temperature, 100 mL of water was added to the flask and the pH was adjusted to ≈ 1 with HCl (conc.). The product was extracted with 150 mL of ethyl acetate, the organic phase washed with H_2O (3 x 50 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded 7.84 g (98 %) of a pure oil. ^{1}**H NMR** ($CDCl_3$) δ ppm: 0.92 (m, 12H, CH_3), 1.29 – 1.55 (m, 16H, $-CH_2-$), 1.73 (m, 2H, -C<u>H</u>(Et)-), 3.87 (dd, *J* = 5.6 Hz e *J* = 1.6 Hz, 4H, $-CH_2O-$), 6.70 (t, *J* = 2.3 Hz, 1H, Ar-H), 7.22 (d, *J* = 2.3 Hz, 2H, Ar-H). ^{13}**C NMR** ($CDCl_3$) δ ppm: 11.11, 14.07, 23.04, 23.87, 29.07, 30.52, 39.37, 70.80, 107.40, 108.08, 130.72, 160.46, 170.80.

General method for NO2-2 and NO2-4

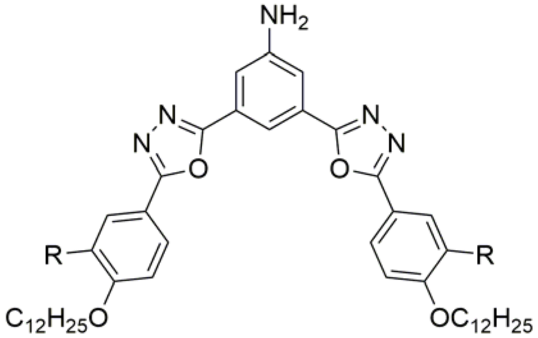


In a round-bottomed flask equipped with a condenser and a $CaCl_2$ drying tube were added 3.20 g (15,1 mmol) of 5-nitroisophthalic acid (**1**), 15 mL of $SOCl_2$ and 3 drops of DMF. The mixture was refluxed for 7 hours and the remaining $SOCl_2$ was removed by vacuum distillation. To the freshly prepared acid chloride were added 30.8 mmol of the respective tetrazole (**TET-2** or **TET-4**) and 40 mL of dry pyridine and the mixture refluxed for further 22 hours. The solution was then cooled to room temperature, poured into 500 mL of water/ice and basified to pH ≈ 10 with a NaOH aqueous solution (10%). The product was filtered and washed with plenty of water.

NO2-2: Recrystallized over acetonitrile/toluene, affording 9.90 g (84 %) of an off-white solid. **m.p.:** (cooling) I – 135 °C – SmA – 109 °C – Cr. ^{1}**H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 6.8 Hz, 6H, CH_3), 1.22 - 1.39 (m, 32H, -C<u>H$_2$</u>-), 1.49 (m, 4H, $-CH_2-$), 1.84 (m, 4H, -C<u>H$_2$</u>CH$_2$O-), 4.06 (t, *J* = 6.5 Hz, 4H, $-OCH_2-$), 7.07 (d, *J* = 8.9 Hz, 4H, Ar-H), 8.13 (d, *J* = 8.9 Hz, 4H, Ar-H), 9.08 (d, *J* = 1.6 Hz, 2H, Ar-H), 9.18 (t, *J* = 1.6 Hz, 1H, Ar-H). ^{13}**C NMR** ($CDCl_3$) δ ppm: 14.13, 22.69, 25.99, 29.10, 29.35, 29.37, 29.56, 29.59, 29.63, 29.66, 31.91, 68.41, 115.03, 115.20, 123.49, 126.93, 129.14, 129.52, 149.20, 161.44, 162.66, 165.82.

NO2-4: Recrystallized over methyl isobutyl ketone, affording 16.0 g (92 %) of an off-white solid. **m.p.:** Cr – 121 °C – Col$_{hex}$ – 147 °C – I. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (m, 12H, CH_3), 1.20 – 1.41 (m, 64H, -C$\underline{H}_2$-), 1.50 (m, 8H, -CH_2-), 1.88 (m, 8H, -C$\underline{H}_2$$CH_2$O-), 4.10 (t, *J* = 6.8 Hz, 4H, -CH_2O-), 4.13 (t, *J* = 6.8 Hz, 4H, -CH_2O-), 7.01 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.68 (d, *J* = 1.9 Hz, 2H, Ar-H), 7.75 (dd, *J* = 8.6 Hz e *J* = 1.9 Hz, 2H, Ar-H), 9.09 (d, *J* = 1.5 Hz, 2H, Ar-H), 9.20 (t, *J* = 1.5 Hz, 1H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.12, 22.69, 25.98, 26.02, 29.05, 29.17, 29.36, 29.39, 29.43, 29.61, 29.63, 29.66, 29.71, 31,92, 69.12, 69.50, 111,55, 112.74, 115.16, 120.96, 123.48, 126.95, 129.61, 149.16, 149.42, 152.88, 161.52, 165.93.

General method for NH2-2 and NH2-4



NH2-2, R = H

NH2-4, R = $OC_{12}H_{25}$

The nitro compound (**NO2-2** or **NO2-4**) (10.2 mmol), $SnCl_2.2H_2O$ (51.0 mmol), 100 mL ethanol and 200 mL THF were added to a round-bottomed flask and stirred under reflux for 16 hours. The suspension was then cooled to room temperature, 50 mL of a NaOH aqueous solution (10%) were added to the flask and the suspension stirred for further 2 hours. The solvent was removed under reduced pressure, the product dissolved in 400 mL of CH_2Cl_2 and the insoluble fraction was removed by vacuum filtration and later by filtration in celite. The organic fraction was then washed with NaOH 5% (1 x 100 mL) and H_2O (2 x 100 mL), dried over anhydrous Na_2SO_4 and the solvent removed.

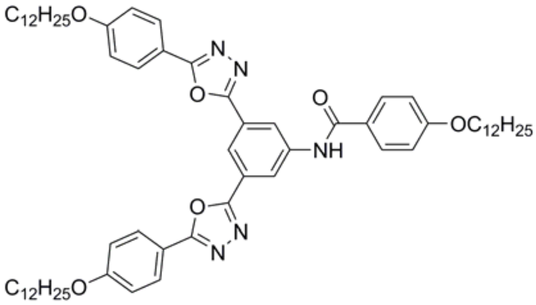
NH2-2: The product was recrystallized over acetonitrile/butanone, affording 6.93 g (90 %) of a yellowish solid. **m.p.:** 168.3 – 169.9 ºC. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 6.8 Hz, 6H, CH_3), 1.24 - 1.40 (m, 32H, -C$\underline{H}_2$-), 1.48 (m, 4H, -CH_2-), 1.83 (m, 4H, -C$\underline{H}_2$$CH_2$O-), 4.06 (t, *J* = 6.6 Hz, 4H, -OCH_2-), 4.13 (broad, 2H, -NH_2), 7.03 (d, *J* = 9.0 Hz, 4H, Ar-H), 7.60 (d, *J* = 1.4 Hz, 2H, Ar-H), 8.09 (d, *J* = 9.0 Hz, 4H, Ar-H), 8.16 (t, *J* = 1.4 Hz, 1H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.10, 22.68, 25.99, 29.14, 29.34, 29.37, 29.56, 29.59, 29.63, 29.65, 31.91, 68.32, 114.76, 115.02, 115.32, 115.94, 125.94, 128.79, 147.64, 162.13, 163.47, 164.89.

NH2-4: The product was recrystallized over acetonitrile/butanone, affording 10.0 g (88 %) of a yellowish solid. **m.p.:** Cr – 132 °C – Col$_{hex}$ – 160 °C – I. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (m, 12H, CH_3), 1.22 – 1.41 (m, 64H, -C$\underline{H}_2$-), 1.50 (m, 8H, -CH_2-), 1.87 (m, 8H, -C$\underline{H}_2$$CH_2$O-), 4.08 (t, *J* = 6.6 Hz, 4H, -CH_2O-), 4.12 (t, *J* = 6.6 Hz, 4H, -CH_2O-), 6.98 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.60 (d, *J* = 1.4 Hz, 2H, Ar-H), 7.66 (d, *J* = 1.9 Hz, 2H, Ar-H), 7.69 (dd, *J* = 8.4 Hz e *J* = 1.9 Hz, 2H, Ar-H), 8.18 (t, *J* = 1.4 Hz, 1H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.10, 22.68, 26.00, 26.04, 29.13, 29.23, 29.36, 29.41, 29.44, 29.62, 29.64, 29.66, 29.70, 31.92, 69.16, 69.51, 111,74, 112.91, 114.88, 115.36, 116.05, 120.59, 125.93, 147.61, 149.40, 152.44, 163.55, 165.02.

General method for the amide derivatives final compound (4-AMD-n, 3,4-AMD-n, 3,4,5-AMD-n, 3,5-AMD-n or 3,4,5-ext-AMD-n)

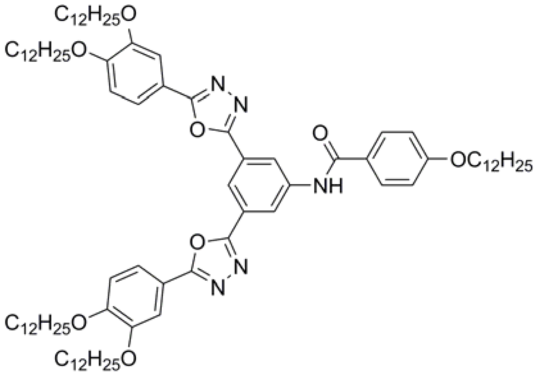
Under argon atmosphere, 0.50 mmol of the respective carboxylic acid, 10 mL of dry CH_2Cl_2 and 1 drop of dry DMF were added to a Schlenk flask. To this solution, 0.30 mL (0.60 mmol) of a 2M oxalyl chloride solution (in CH_2Cl_2) was carefully added and the mixture stirred for 5 hours at room temperature and under Argon atmosphere. The solvent and remaining oxalyl chloride were removed by vacuum distillation and, to the freshly prepared acid chloride, 0.50 mmol of the amino compound (**NH2-2** or **NH2-4**) and 15 mL of dry pyridine were added. The mixture was heated to 80 ^{o}C, stirred at this temperature for further 20 hours, cooled down to room temperature, poured into 100 mL of water and filtered. The crude product was purified by silica flash chromatography, using a mixture of chloroform/hexane/ethyl acetate (75:15:10) as eluent. Some products were subsequently recrystallized.

4-AMD-2



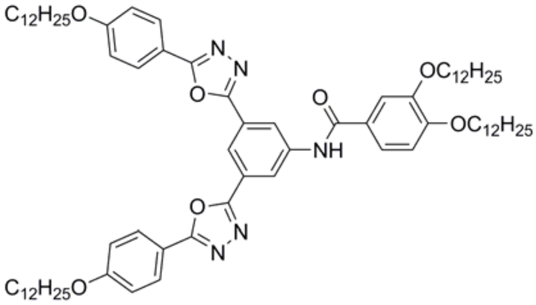
A subsequent recrystallization over ethyl acetate afforded 0.42 g (82 %) of the pure product. **m.p.:** 167 – 168 ºC. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.89 (t, *J* = 6.8 Hz, 9H, CH_3), 1.24 – 1.41 (m, 48H, -C$\underline{H}_2$-), 1.48 (m, 6H, -CH_2-), 1.82 (m, 6H, -C$\underline{H}_2$$CH_2$O-), 3.99 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 4.04 (t, *J* = 6.6 Hz, 4H, -CH_2O-), 6.96 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.00 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.93 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.06 (d, *J* = 8.8 Hz, 4H, Ar-H), 8.52 (broad, 1H, -CON$\underline{H}$-), 8.60 (t, *J* = 1.5 Hz, 1H, Ar-H), 8.75 (d, *J* = 1.5 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.11, 22.69, 25.99, 26.02, 29.13, 29.16, 29.35, 29.39, 29.57, 29.60, 29.63, 29.66, 31.92, 68.32, 68.34, 114.61, 114.99, 115.68, 120.18, 120.50, 125.83, 126.02, 128.93, 129.18, 140.15, 162.21, 162.59, 163.10, 165.19, 165.81. **Elemental Analysis** – Calculated for $C_{65}H_{91}N_5O_6$: C 75.18 %; H 8.83 %; N 6.74 %. Found: C 75.40 %; H 8.90 %; N 6.76 %. Q-TOF/MS for $C_{65}H_{92}N_5O_6$ $[M+H]^+$: Calculated: 1038.7042; Found: 1038.7038.

4-AMD-4



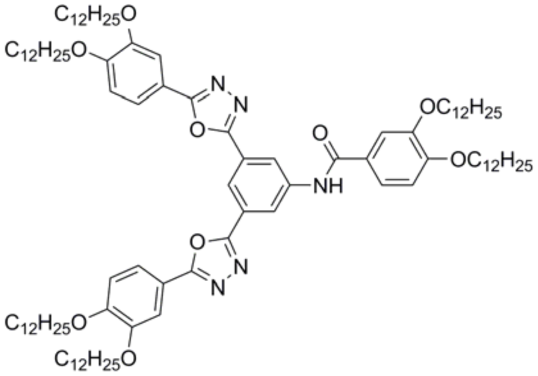
A subsequent recrystallization over ethyl acetate afforded 0.44 g (65 %) of the pure product. **m.p.:** Cr – 154 °C – Col$_{hex}$ – 195 °C – I. ^{1}**H NMR** (CDCl$_3$) δ ppm: 0.86 – 0.90 (m, 15H, CH$_3$), 1.23 – 1.42 (m, 80H, -C$\underline{H}_2$-), 1.50 (m, 10H, -CH$_2$-), 1.80 (m, 2H, -C$\underline{H}_2$CH$_2$O-), 1.87 (m, 8H, -C$\underline{H}_2$CH$_2$O-), 3.99 (t, *J* = 6.6 Hz, 2H, -CH$_2$O-), 4.07 (t, *J* = 6.6 Hz, 4H, -CH$_2$O-), 4.09 (t, *J* = 6.6 Hz, 4H, -CH$_2$O-), 6.95 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.96 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.64 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.67 (dd, *J* = 8.4 Hz e *J* = 2.0 Hz, 2H, Ar-H), 7.93 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.48 (broad, 1H, -CON$\underline{H}$-), 8.61 (t, *J* = 1.5 Hz, 1H, Ar-H), 8.72 (d, *J* = 1.5 Hz, 2H, Ar-H). ^{13}**C NMR** (CDCl$_3$) δ ppm: 14.10, 22.68, 26.00, 26.02, 29.06, 29.14, 29.24, 29.35, 29.37, 29.40, 29.43, 29.47, 29.57, 29.61, 29.63, 29.66, 29.67, 29.71, 29.72, 31.92, 68.35, 69.13, 69.49, 111.69, 112.84, 114.61, 115.78, 120.29, 120.67, 120.80, 125.83, 125.89, 129.15, 140.07, 149.38, 152.54, 162.59, 163.19, 165.33, 165.66. **Elemental Analysis** – Calculated for $C_{89}H_{139}N_5O_8$: C 75.97 %; H 9.96 %; N 4.98 %. Found: C 75.86 %; H 10.02 %; N 4.94 %. Q-TOF/MS for $C_{89}H_{140}N_5O_8$ $[M+H]^+$: Calculated: 1407.0696; Found: 1407.0687.

3,4-AMD-2



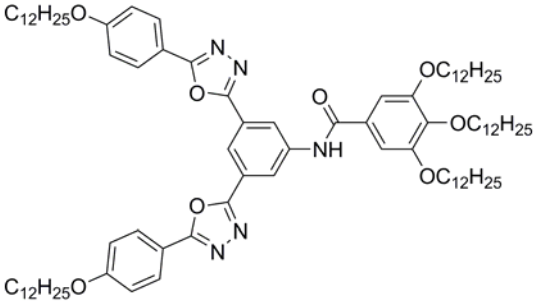
A subsequent recrystallization over ethyl acetate afforded 0.52 g (84 %) of the pure product. **m.p.:** Cr – 88 °C – Col$_{hex}$ – 178 °C – I. ^{1}**H NMR** (CDCl$_3$) δ ppm: 0.86 – 0.91 (m, 12H, CH$_3$), 1.23 – 1.42 (m, 64H, -C$\underline{H}_2$-), 1.49 (m, 8H, -CH$_2$-), 1.85 (m, 8H, -C$\underline{H}_2$CH$_2$O-), 4.03 – 4.12 (m, 8H, -CH$_2$O-), 6.93 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.03 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.47 (dd, *J* = 8.4 Hz e *J* = 2.2 Hz, 1H, Ar-H), 7.53 (d, *J* = 2.2 Hz, 1H, Ar-H), 8.10 (d, *J* = 8.8 Hz, 4H, Ar-H), 8.25 (broad, 1H, -CON$\underline{H}$-), 8.63 (t, *J* = 1.4 Hz, 1H, Ar-H), 8.70 (d, *J* = 1.4 Hz, 2H, Ar-H). ^{13}**C NMR** (CDCl$_3$) δ ppm: 14.11, 22.69, 26.00, 26.03, 26.04, 29.11, 29.17, 29.26, 29.36, 29.38, 29.41, 29.43, 29.45, 29.58, 29.61, 29.64, 29.67, 29.72, 31.92, 31.93, 68.32, 69.14, 69.44, 112.23, 112.77, 114.99, 115.65, 120.12, 120.22, 120.50, 125.80, 126.44, 128.93, 140.26, 149.24, 152.82, 162.22, 163.13, 165.21, 166.05. **Elemental Analysis** – Calculated for $C_{77}H_{115}N_5O_7$: C 75.63 %; H 9.48 %; N 5.73 %. Found: C 75.44 %; H 9.60 %; N 5.68 %. Q-TOF/MS for $C_{77}H_{116}N_5O_7$ $[M+H]^+$: Calculated: 1222.8869; Found: 1222.8872.

3,4-AMD-4



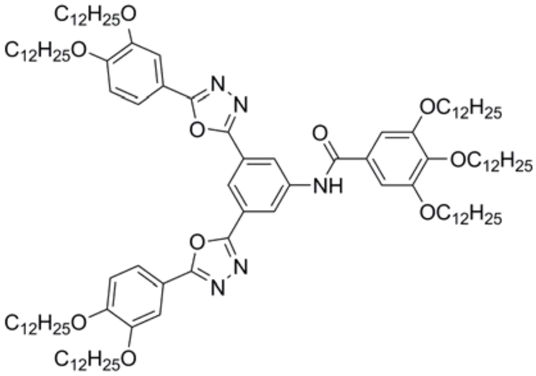
A subsequent maceration over a mixture of ethyl acetate and ethanol afforded 0.42 g (53 %) of the pure product. **m.p.:** Cr – 132 °C – Col$_{hex}$ – 193 °C – I. **^{1}H NMR** (CDCl$_3$) δ ppm: 0.86 – 0.91 (m, 18H, CH$_3$), 1.23 – 1.42 (m, 96H, -C$\underline{H}_2$-), 1.51 (m, 12H, -CH$_2$-), 1.87 (m, 12H, -C$\underline{H}_2$CH$_2$O-), 4.06 – 4.15 (m, 12H, -CH$_2$O-), 6.95 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.98 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.46 (dd, *J* = 8.4 Hz e *J* = 2.2 Hz, 1H, Ar-H), 7.52 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.69 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.72 (dd, *J* = 8.4 Hz e *J* = 2.0 Hz, 2H, Ar-H), 8.12 (broad, 1H, -CON$\underline{H}$-), 8.64 (t, *J* = 1.4 Hz, 1H, Ar-H), 8.66 (d, *J* = 1.4 Hz, 2H, Ar-H). **^{13}C NMR** (CDCl$_3$) δ ppm: 14.09, 22.69, 26.00, 26.02, 26.06, 29.11, 29.14, 29.24, 29.36, 29.42, 29.46, 29.63, 29.64, 29.67, 29.70, 29.72, 31.93, 69.14, 69.17, 69.45, 69.51, 111.73, 112.27, 112.71, 112.86, 115.78, 120.08, 120.30, 120.56, 120.81, 125.86, 126.25, 140.06, 149.28, 149.41, 152.57, 152.86, 163.20, 165.36, 165.75. **Elemental Analysis** – Calculated for $C_{101}H_{163}N_5O_9$: C 76.23 %; H 10.32 %; N 4.40 %. Found: C 76.11 %; H 10.41 %; N 4.38 %. Q-TOF/MS for $C_{101}H_{164}N_5O_9$ [M+H]$^+$: Calculated: 1591.2524; Found: 1591.2550.

3,4,5-AMD-2



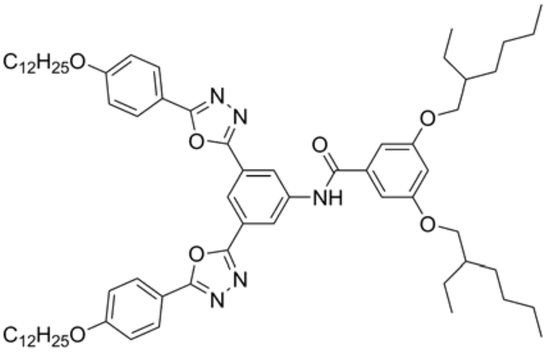
A subsequent recrystallization over acetone afforded 0.55 g (79 %) of the pure product. **m.p.:** Cr – 73 °C – Col$_{hex}$ – 143 °C – I. **^{1}H NMR** (CDCl$_3$) δ ppm: 0.85 – 0.91 (m, 15H, CH$_3$), 1.22 – 1.42 (m, 80H, -C$\underline{H}_2$-), 1.49 (m, 10H, -CH$_2$-), 1.72 – 1.89 (m, 10H, -C$\underline{H}_2$CH$_2$O-), 4.05 (m, 10H, -CH$_2$O-), 7.03 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.14 (s, 2H, Ar-H), 8.09 (d, *J* = 8.8 Hz, 4H, Ar-H), 8.29 (broad, 1H, -CON$\underline{H}$-), 8.64 (t, *J* = 1.5 Hz, 1H, Ar-H), 8.72 (d, *J* = 1.5 Hz, 2H, Ar-H). **^{13}C NMR** (CDCl$_3$) δ ppm: 14.11, 22.68, 26.03, 26.10, 29.17, 29.35, 29.37, 29.40, 29.59, 29.61, 29.64, 29.66, 29.67, 29.72, 29.76, 29.77, 30.37, 31.92, 31.95, 68.33, 69.46, 73.57, 105.95, 115.02, 115.58, 120.23, 120.51, 125.83, 128.91, 129.03, 140.16, 141.97, 153.38, 162.26, 163.11, 165.26, 166.23. **Elemental Analysis** – Calculated for $C_{89}H_{139}N_5O_8$: C 75.97 %; H 9.96 %; N 4.98 %. Found: C 76.03 %; H 9.78 %; N 4.97 %. Q-TOF/MS for $C_{89}H_{140}N_5O_8$ [M+H]$^+$: Calculated: 1407.0696; Found: 1407.0684.

3,4,5-AMD-4



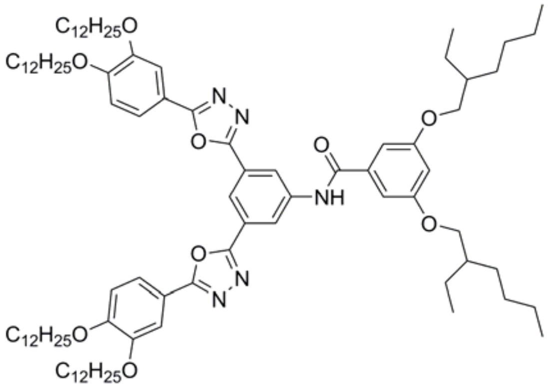
A subsequent recrystallization over ethyl acetate afforded 0.51 g (59 %) of the pure product. **m.p.:** Cr – 88 °C – Col$_{hex}$ – 173 °C – I. **^{1}H NMR** (CDCl$_3$) δ ppm: 0.85 – 0.90 (m, 21H, CH$_3$), 1.21 – 1.43 (m, 112H, -C$\underline{H}_2$-), 1.50 (m, 14H, -CH$_2$-), 1.72 – 1.91 (m, 14H, -C$\underline{H}_2$CH$_2$O-), 4.01 – 4.13 (m, 14H, -CH$_2$O-), 6.96 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.16 (s, 2H, Ar-H), 7.66 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.69 (dd, *J* = 8.4 Hz e *J* = 2.0 Hz, 2H, Ar-H), 8.34 (broad, 1H, -CON$\underline{H}$-), 8.63 (t, *J* = 1.4 Hz, 1H, Ar-H), 8.71 (d, *J* = 1.4 Hz, 2H, Ar-H). **^{13}C NMR** (CDCl$_3$) δ ppm: 14.10, 22.68, 26.01, 26.06, 29.09, 29.14, 29.24, 29.37, 29.40, 29.42, 29.46, 29.56, 29.63, 29.65, 29.66, 29.71, 29.74, 29.76, 30.36, 31.92, 31.94, 69.13, 69.51, 73.60, 105.83, 111.71, 112.84, 115.74, 120.42, 120.53, 120.81, 125.90, 128.80, 139.90, 142.03, 149.42, 152.60, 153.41, 163.17, 165.40, 165.91. **Elemental Analysis** – Calculated for $C_{113}H_{187}N_5O_{10}$: C 76.43 %; H 10.61 %; N 3.94 %. Found: C 76.31 %; H 10.47 %; N 3.95 %. Q-TOF/MS for $C_{113}H_{188}N_5O_{10}$ $[M+H]^+$: Calculated: 1775.4351; Found: 1775.4343.

3,5-AMD-2



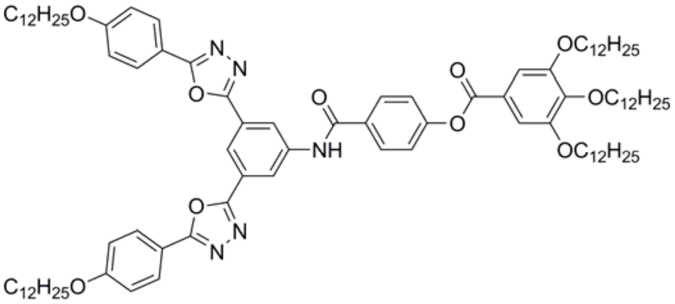
A subsequent recrystallization over acetone afforded 0.52 g (94 %) of the pure product. **m.p.:** 129 – 130 ºC. **^{1}H NMR** (CDCl$_3$) δ ppm: 0.86 – 0.96 (m, 18H, CH$_3$), 1.24 – 1.54 (m, 52H, -C$\underline{H}_2$-), 1.73 (m, 2H, -C$\underline{H}$(Et)-), 1.83 (m, 4H, -C$\underline{H}_2$CH$_2$O-), 3.89 (dd, *J* = 5.6 Hz e *J* = 1.6 Hz, 4H, -CH$_2$O-), 4.04 (t, *J* = 6.5 Hz, 4H, -OCH$_2$-), 6.64 (t, *J* = 2.0 Hz, 1H, Ar-H), 7.01 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.07 (d, *J* = 2.0 Hz, 2H, Ar-H), 8.06 (d, *J* = 8.8 Hz, 4H, Ar-H), 8.59 (broad, 1H, -CON$\underline{H}$-), 8.64 (t, *J* = 1.4 Hz, 1H, Ar-H), 8.79 (d, *J* = 1.4 Hz, 2H, Ar-H). **^{13}C NMR** (CDCl$_3$) δ ppm: 11.12, 14.09, 22.69, 23.04, 23.87, 26.02, 29.08, 29.16, 29.35, 29.39, 29.58, 29.60, 29.64, 29.67, 30.52, 31.92, 39.41, 68.33, 70.89, 105.40, 105.46, 115.03, 115.66, 120.38, 120.44, 125.91, 128.94, 136.15, 139.97, 160.96, 162.24, 163.07, 165.24, 166.25. **Elemental Analysis** – Calculated for $C_{69}H_{99}N_5O_7$: C 74.62 %; H 8.99 %; N 6.31 %. Found: C 74.44 %; H 8.94 %; N 6.19 %. Q-TOF/MS for $C_{69}H_{100}N_5O_7$ $[M+H]^+$: Calculated: 1110.7617; Found: 1110.7610.

3,5-AMD-4



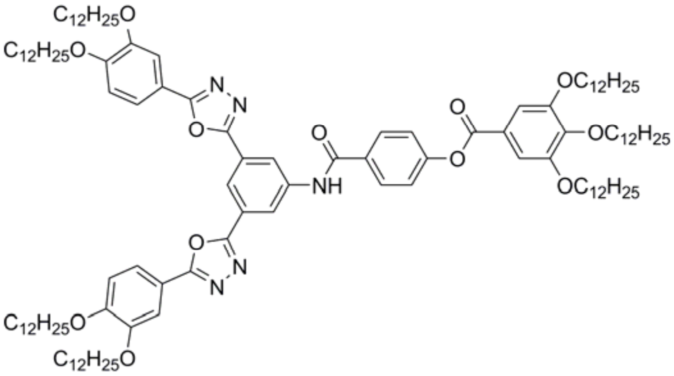
A subsequent recrystallization over acetone afforded 0.45 g (62 %) of the pure product. **m.p.:** Cr – 57 °C – Col_{hex} – 77 °C – I. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.85 – 0.98 (m, 24H, CH_3), 1.22 – 1.55 (m, 88H, -C$\underline{H}_2$-), 1.71 (m, 2H, -C$\underline{H}$(Et)-), 1.86 (m, 8H, -C$\underline{H}_2CH_2O$-), 3.85 (dd, *J* = 5.6 Hz e *J* = 1.6 Hz, 4H, -CH_2O-), 4.06 (t, *J* = 6.5 Hz, 8H, -OCH_2-), 6.62 (t, *J* = 2.0 Hz, 1H, Ar-H), 6.93 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.12 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.62 (d, *J* = 1.8 Hz, 2H, Ar-H), 7.65 (dd, *J* = 8.6 Hz e *J* = 1.8 Hz, 2H, Ar-H), 8.62 (t, *J* = 1.4 Hz, 1H, Ar-H), 8.82 (d, *J* = 1.4 Hz, 2H, Ar-H), 8.88 (broad, 1H, -CON$\underline{H}$-). **^{13}C NMR** ($CDCl_3$) δ ppm: 11.07, 14.06, 14.09, 22.67, 23.02, 23.83, 26.01, 26.06, 29.04, 29.13, 29.23, 29.36, 29.42, 29.45, 29.62, 29.64, 29.70, 30.47, 31.91, 39.36, 69.11, 69.44, 70.86, 105.42, 105.52, 111.63, 112.80, 115.69, 120.39, 120.78, 120.85, 125.78, 135.99, 140.01, 149.39, 152.54, 160.89, 163.17, 165.35, 166.18. **Elemental Analysis** – Calculated for $C_{93}H_{147}N_5O_9$: C 75.51 %; H 10.02 %; N 4.73 %. Found: C 75.34 %; H 10.07 %; N 4.74 %. Q-TOF/MS for $C_{93}H_{148}N_5O_9$ $[M+H]^+$: Calculated: 1479.1272; Found: 1479.1277.

3,4,5-ext-AMD-2



Afforded 0.60 g (79 %) of the pure product. **m.p.:** Cr – -24 °C – Col_{hex} – 173 °C – I. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (m, 15H, CH_3), 1.22 – 1.41 (m, 80H, -C$\underline{H}_2$-), 1.49 (m, 10H, -CH_2-), 1.73 – 1.88 (m, 10H, -C$\underline{H}_2CH_2O$-), 4.05 (m, 10H, -CH_2O-), 7.01 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.37 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 8.07 (m, 6H, Ar-H), 8.56 (broad, 1H, -CON$\underline{H}$-), 8.63 (t, *J* = 1.5 Hz, 1H, Ar-H), 8.73 (d, *J* = 1.5 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.11, 22.68, 26.01, 26.07, 26.11, 29.14, 29.33, 29.36, 29.40, 29.41, 29.57, 29.60, 29.64, 29.66, 29.70, 29.73, 29.76, 30.37, 31.92, 31.94, 68.33, 69.34, 73.63, 108.69, 115.04, 115.65, 120.66, 122.44, 123.24, 125.94, 128.83, 128.93, 131.63, 139.75, 143.41, 153.05, 154.29, 162.25, 162.99, 164.55, 165.24, 165.34. **Elemental Analysis** – Calculated for $C_{96}H_{143}N_5O_{10}$: C 75.50 %; H 9.44 %; N 4.59 %. Found: C 75.66 %; H 9.26 %; N 4.58 %. Q-TOF/MS for $C_{96}H_{144}N_5O_{10}$ $[M+H]^+$: Calculated: 1527.0908; Found: 1527.0874.

3,4,5-ext-AMD-4

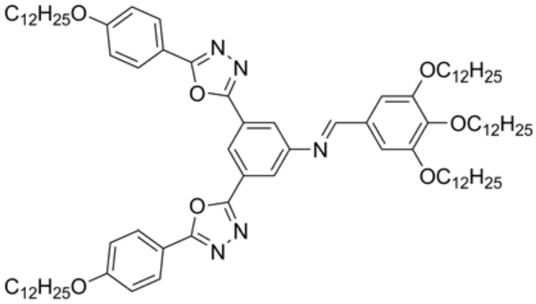


Afforded 0.37 g (38 %) of the pure product. **m.p.:** Cr – 133 °C – Col$_{hex}$ – 178 °C – I. **^{1}H NMR** (CDCl$_3$) δ ppm: 0.88 (m, 21H, CH$_3$), 1.22 – 1.42 (m, 112H, -C$\underline{H}_2$-), 1.50 (m, 14H, -CH$_2$-), 1.74 – 1.90 (m, 14H, -C$\underline{H}_2$CH$_2$O-), 4.03 – 4.13 (m, 14H, -CH$_2$O-), 6.97 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.38 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 7.67 (d, *J* = 1.9 Hz, 2H, Ar-H), 7.70 (dd, *J* = 8.4 Hz e *J* = 1.9 Hz, 2H, Ar-H), 8.06 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.43 (broad, 1H, -CON$\underline{H}$-), 8.65 (t, *J* = 1.5 Hz, 1H, Ar-H), 8.69 (d, *J* = 1.5 Hz, 2H, Ar-H). **^{13}C NMR** (CDCl$_3$) δ ppm: 14.10, 22.68, 26.01, 26.06, 26.11, 29.14, 29.24, 29.32, 29.36, 29.39, 29.40, 29.43, 29.46, 29.57, 29.63, 29.65, 29.67, 29.69, 29.72, 29.74, 29.76, 30.37, 31.92, 31.94, 69.14, 69.34, 69.51, 73.63, 108.70, 111.72, 112.87, 115.78, 120.71, 120.80, 122.49, 123.21, 125.99, 128.77, 131.57, 139.65, 143.43, 149.41, 152.58, 153.05, 154.31, 163.07, 164.56, 165.21, 165.38. **Elemental Analysis** – Calculated for $C_{120}H_{191}N_5O_{12}$: C 76.02 %; H 10.15 %; N 3.69 %. Found: C 75.90 %; H 10.37 %; N 3.66 %. Q-TOF/MS for $C_{120}H_{192}N_5O_{12}$ [M+H]$^+$: Calculated: 1895.4562; Found: 1895.4531.

General method for the imine derivatives final compound (3,4,5-IM-n)

In a round-bottomed flask were added 0.29 g (0,45 mmol) of 3,4,5-tris(dodecyloxy)benzaldehyde, 0.45 mmol of the amino compound (**NH2-2** or **NH2-4**), 15 mL of dry toluene, 1 drop of acetic acid and molecular sieves (3Å). The mixture was heated to 90 °C and stirred for 24 hours under Argon atmosphere. After this period, the mixture was cooled down to room temperature, poured into 50 mL CH$_2$Cl$_2$, filtered and the solvent removed. The crude product was purified by neutral alumina (50-200 microns) column chromatography, using a mixture of CH$_2$Cl$_2$/TEA (99:1) as eluent.

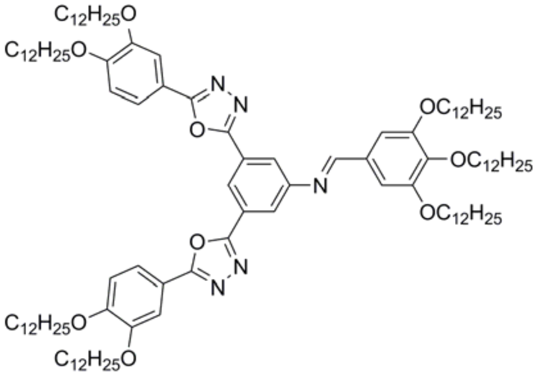
3,4,5-IM-2



Two subsequent recrystallization over acetone afforded 0.21 g (34 %) of the pure product. **m.p.:** 38 – 42 ºC. **^{1}H NMR** (CDCl$_3$) δ ppm: 0.88 (m, 15H, CH$_3$), 1.22 – 1.42 (m, 80H, -C$\underline{H}_2$-), 1.50 (m, 10H, -CH$_2$-), 1.74 – 1.90 (m, 10H, -C$\underline{H}_2$CH$_2$O-), 4.07 (m, 10H, -CH$_2$O-), 7.05 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.19 (s, 2H, Ar-H), 8.11 (d, *J* = 1.5 Hz, 2H, Ar-H), 8.12 (d, *J* = 8.8 Hz, 4H, Ar-H), 8.50

(s, 1H, -C$\underline{H}$=N-), 8.69 (t, *J* = 1.5 Hz, 1H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.11, 22.68, 26.00, 26.10, 26.13, 29.14, 29.34, 29.36, 29.38, 29.39, 29.43, 29.56, 29.59, 29.63, 29.66, 29.71, 29.74, 29.76, 30.38, 30.91, 31.95, 68.34, 69.27, 73.62, 107.51, 115.07, 115.83, 121.60, 121.86, 126.07, 128.89, 130.53, 141.99, 153.51, 153.71, 162.23, 162.55, 163.14, 165.12. **Elemental Analysis** – Calculated for $C_{89}H_{139}N_5O_7$: C 76.84 %; H 10.07 %; N 5.03 %. Found: C 76.65 %; H 10.06 %; N 4.98 %.

3,4,5-IM-4



A subsequent recrystallization over ethyl acetate afforded 0.29 g (37 %) of the pure product. **m.p.:** Cr – 56 °C – Col$_{hex}$ – 136 °C – I. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (m, 21H, CH_3), 1.22 – 1.43 (m, 112H, -C$\underline{H}_2$-), 1.51 (m, 14H, -CH_2-), 1.74 – 1.92 (m, 14H, -C$\underline{H}_2$$CH_2$O-), 4.05 – 4.16 (m, 14H, -CH_2O-), 6.99 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.19 (s, 2H, Ar-H), 7.68 (d, *J* = 1.9 Hz, 2H, Ar-H), 7.72 (dd, *J* = 8.4 Hz e *J* = 1.9 Hz, 2H, Ar-H), 8.11 (d, *J* = 1.5 Hz, 2H, Ar-H), 8.51 (s, 1H, -C$\underline{H}$=N-), 8.70 (t, *J* = 1.5 Hz, 1H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.10, 22.69, 26.00, 26.05, 26.10, 26.12, 29.13, 29.23, 29.36, 29.39, 29.41, 29.42, 29.44, 29.60, 29.62, 29.64, 29.66, 29.70, 29.71, 29.73, 29.76, 30.38, 30.90, 31.92, 31.94, 69.17, 69.28, 69.54, 73.63, 107.51, 111.76, 112.93, 115.93, 120.69, 121.89, 126.08, 130.50, 142.02, 149.44, 152.55, 153.53, 153.72, 162.65, 163.23, 165.26. **Elemental Analysis** – Calculated for $C_{113}H_{187}N_5O_9$: C 77.13 %; H 10.71 %; N 3.98 %. Found: C 76.91 %; H 10.85 %; N 4.03 %.

(6) ^{1}H and ^{13}C NMR spectra of final compounds

4-AMD-2

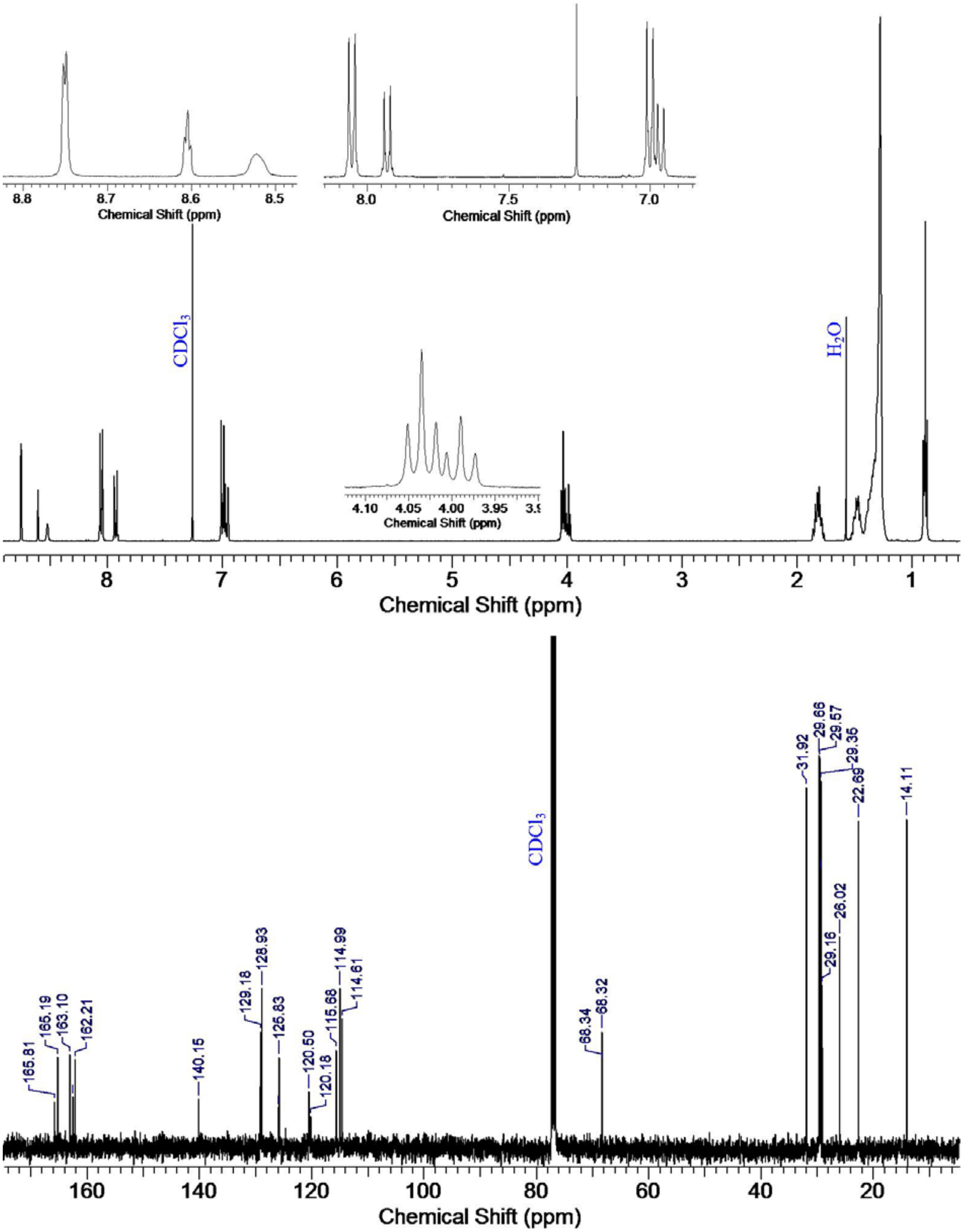


Fig. S14 ^{1}H and ^{13}C NMR spectra of compound **4-AMD-2** in $CDCl_3$.

4-AMD-4

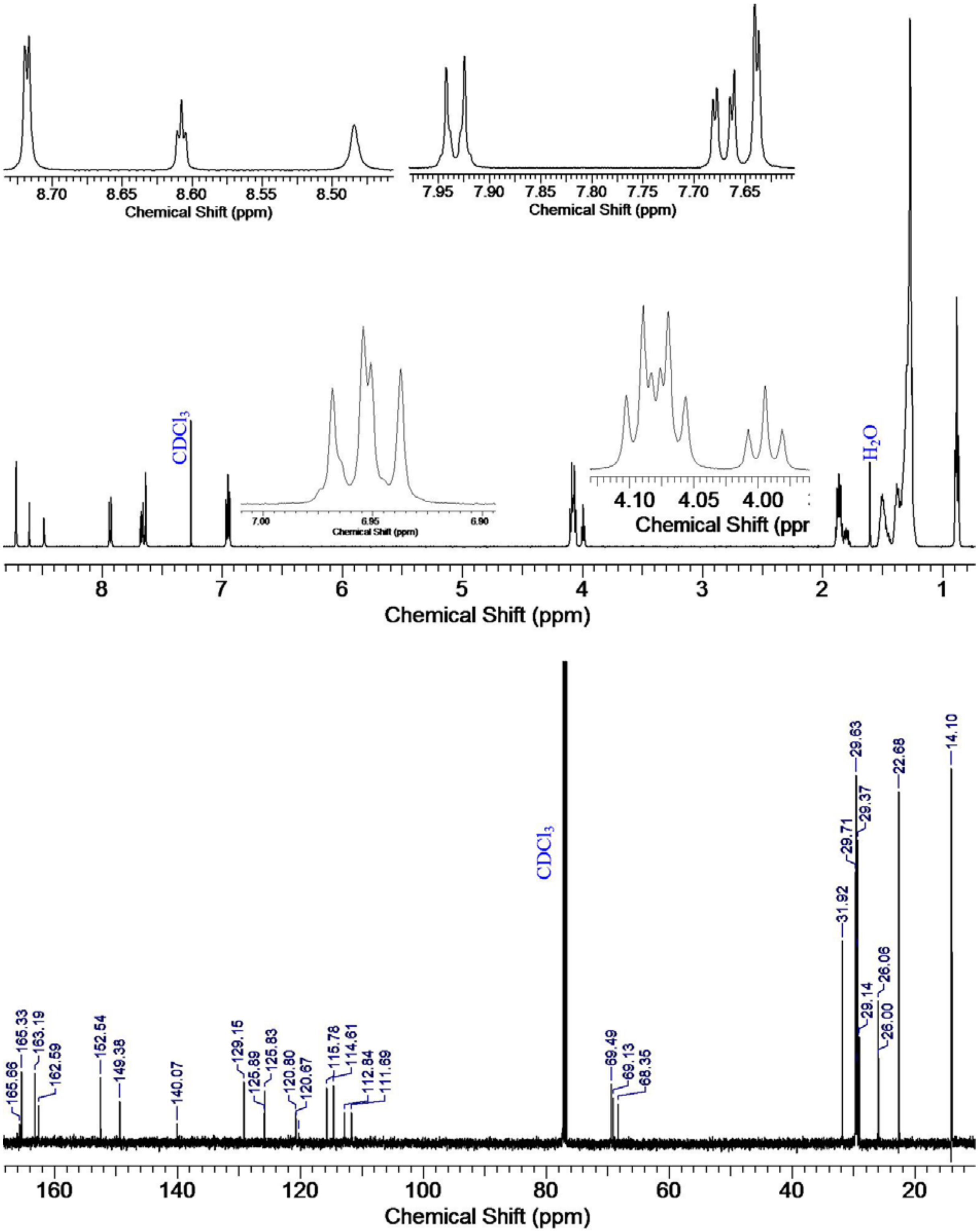


Fig. S15 ^{1}H and ^{13}C NMR spectra of compound **4-AMD-4** in $CDCl_3$.

3,4-AMD-2

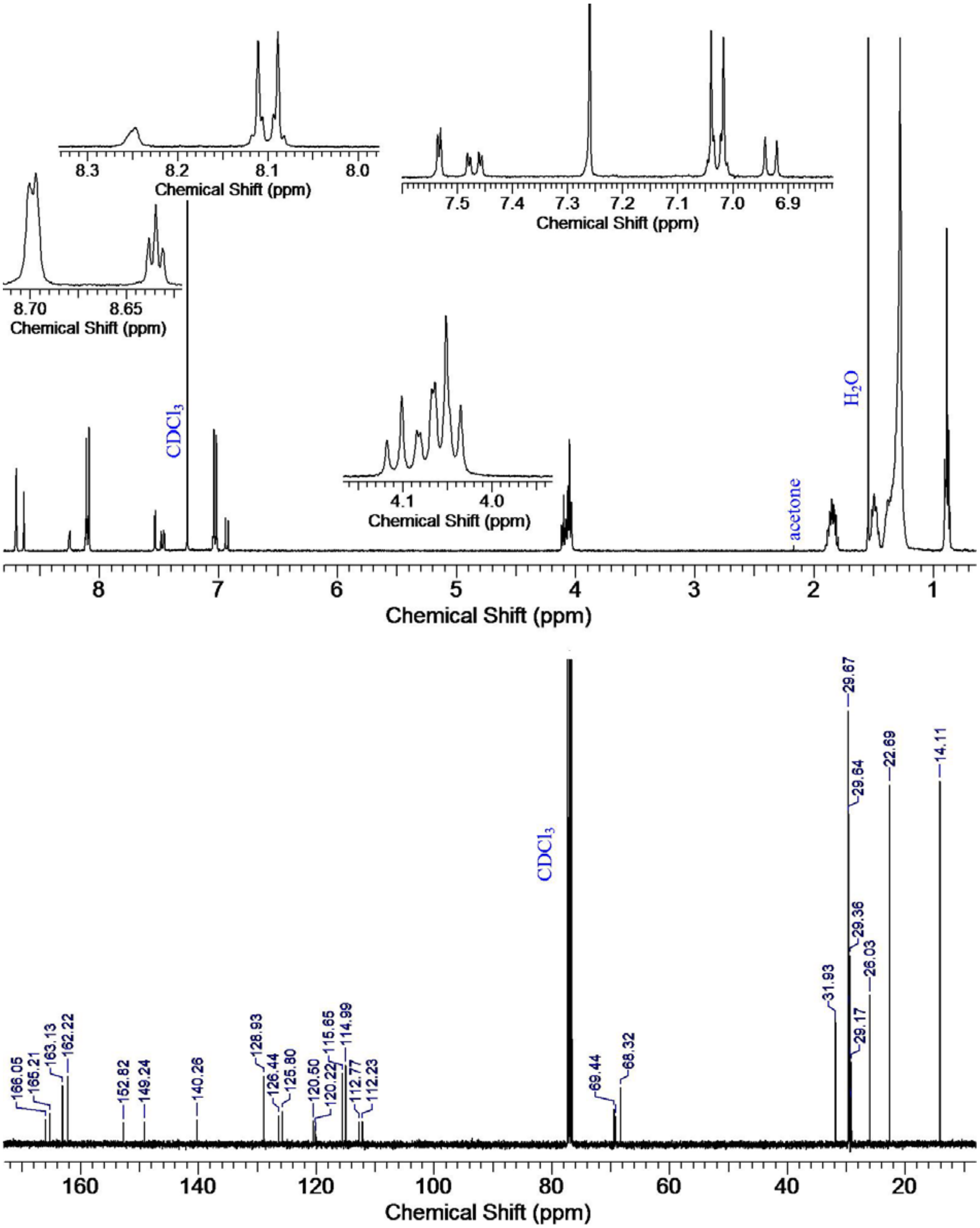


Fig. S16 ^{1}H and ^{13}C NMR spectra of compound **3,4-AMD-2** in $CDCl_3$.

3,4-AMD-4

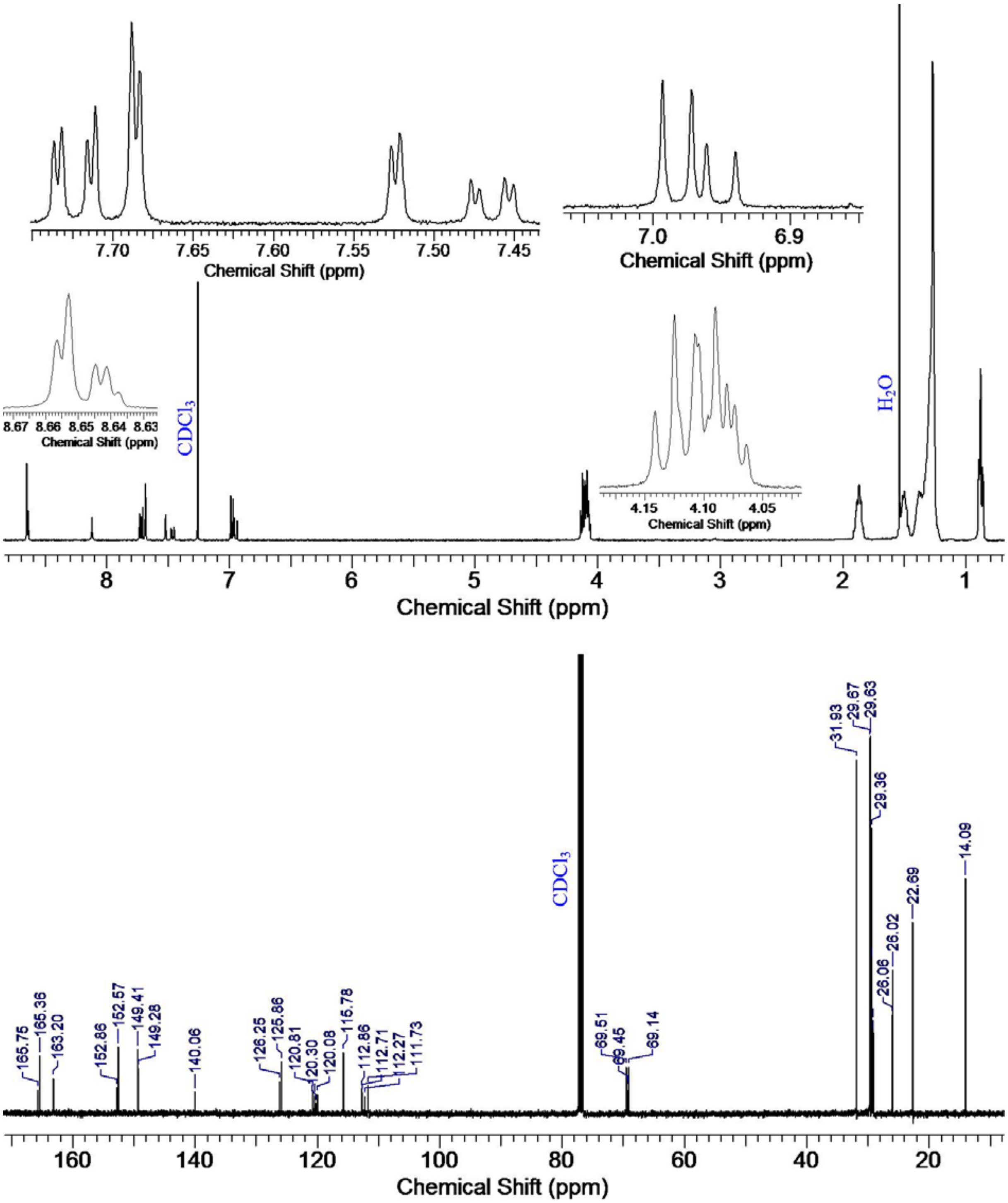


Fig. S17 ^{1}H and ^{13}C NMR spectra of compound **3,4-AMD-4** in CDCl$_3$.

3,4,5-AMD-2

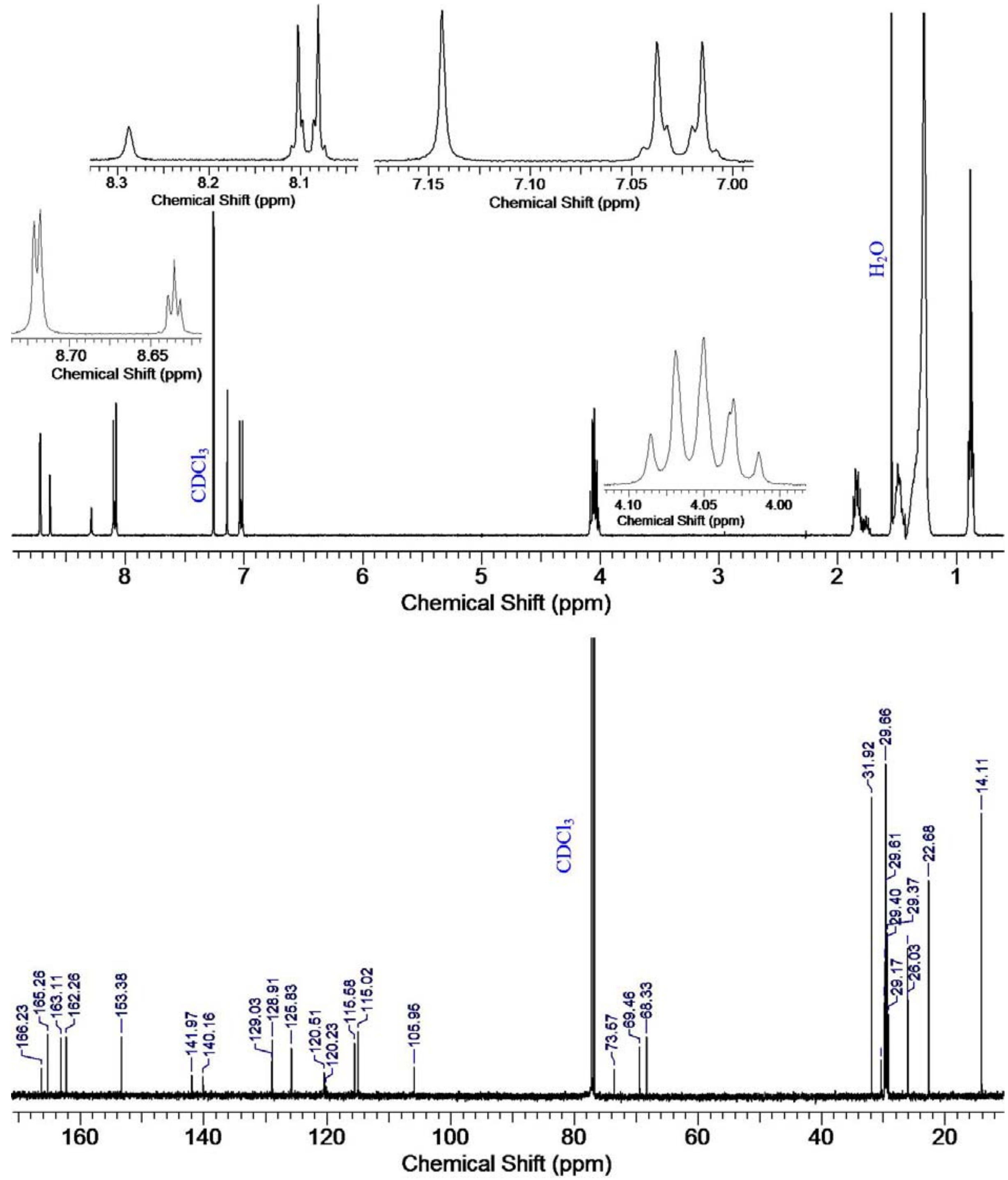


Fig. S18 ^{1}H and ^{13}C NMR spectra of compound **3,4,5-AMD-2** in CDCl$_3$.

3,4,5-AMD-4

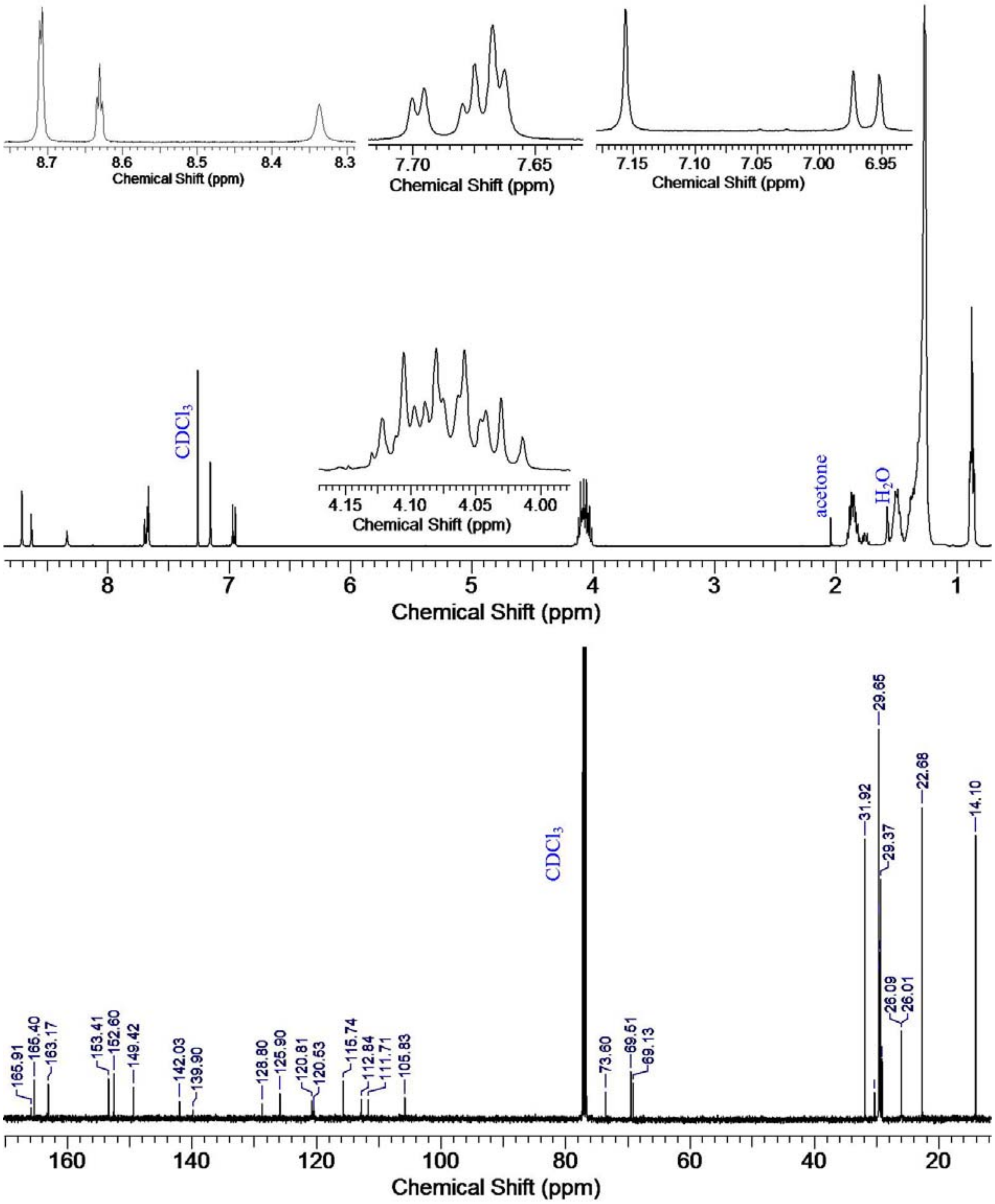
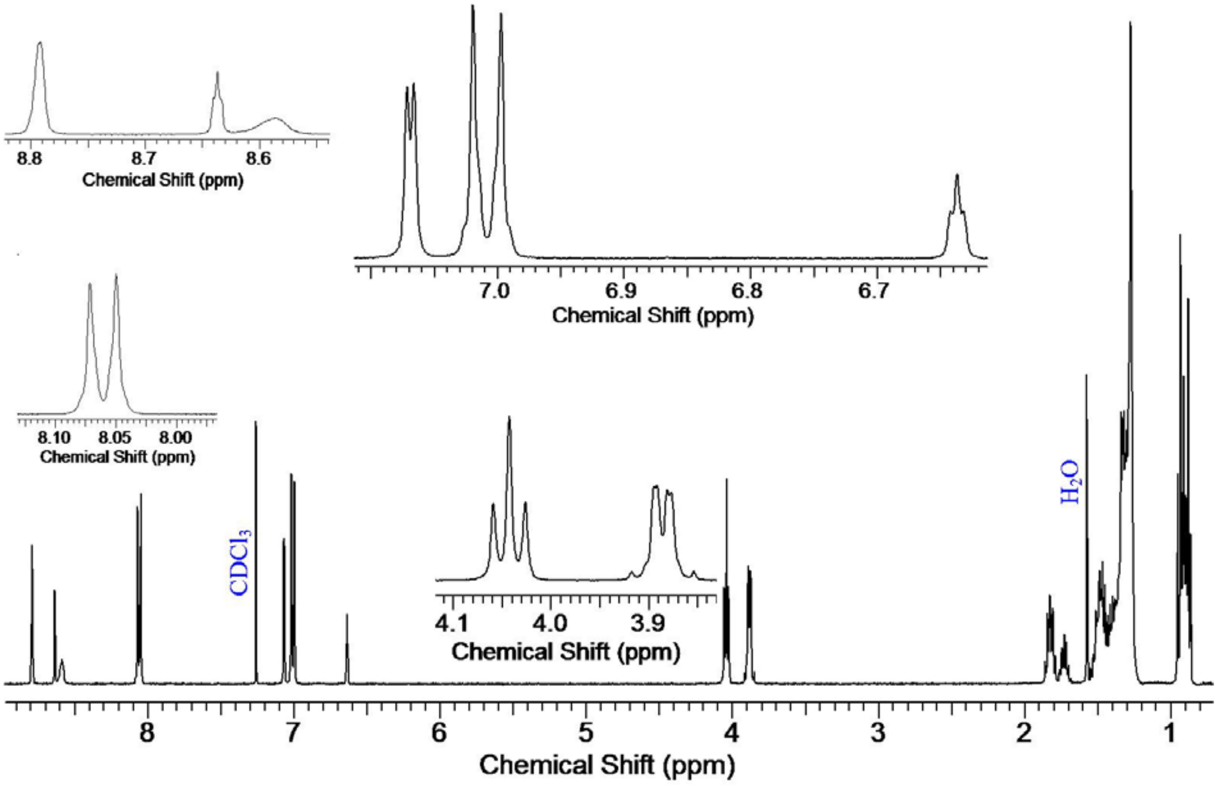


Fig. S19 ^{1}H and ^{13}C NMR spectra of compound **3,4,5-AMD-4** in $CDCl_3$.

3,5-AMD-2



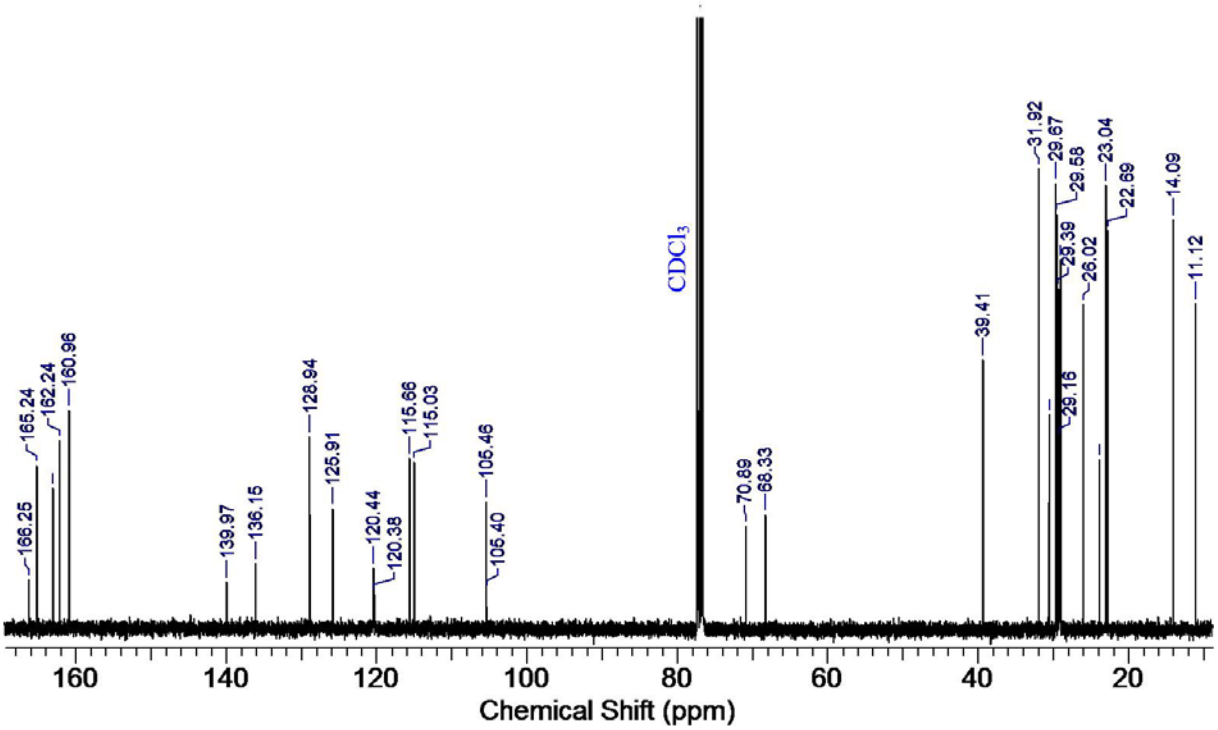


Fig. S20 ^{1}H and ^{13}C NMR spectra of compound **3,5-AMD-2** in $CDCl_3$.

3,5-AMD-4

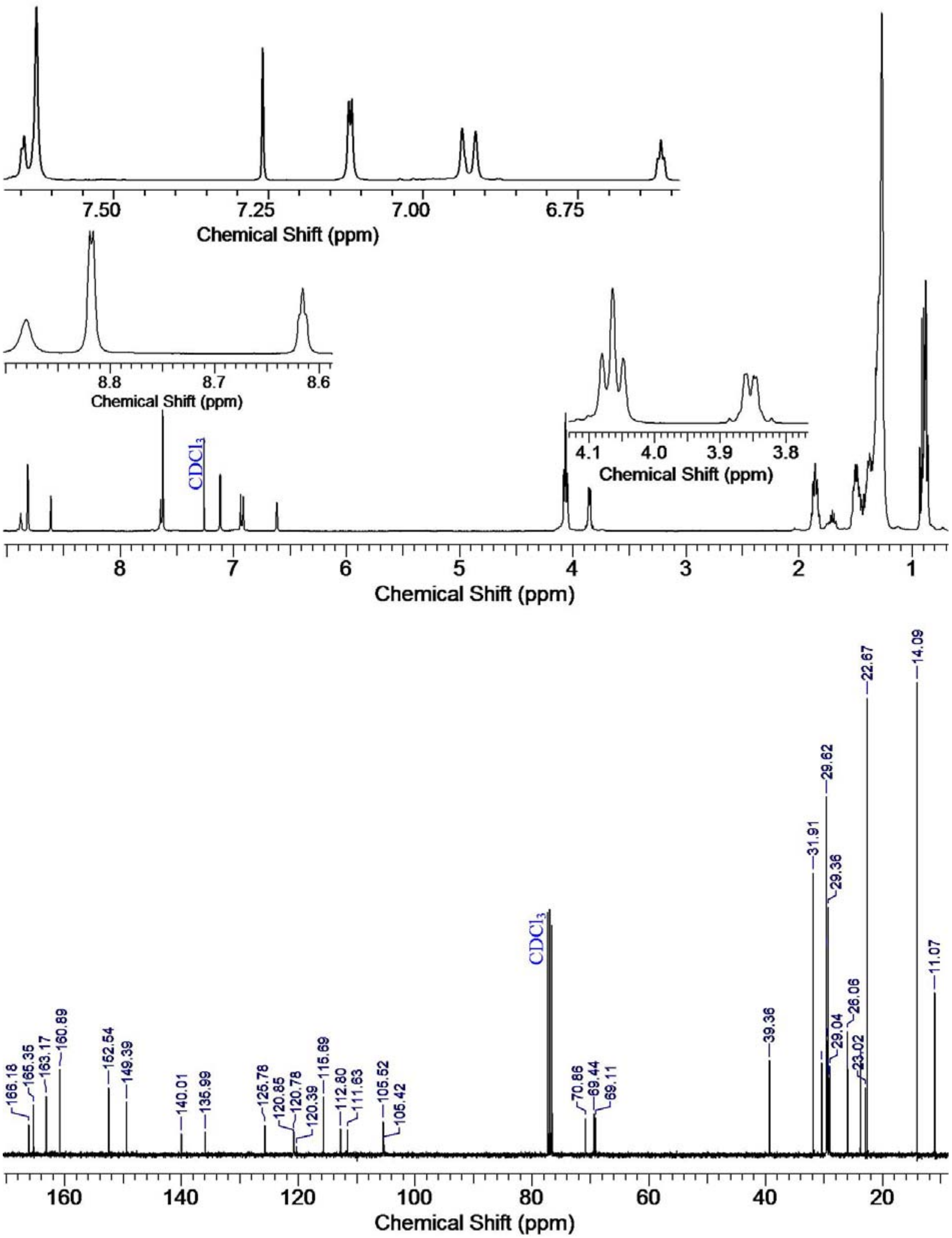


Fig. S21 ^{1}H and ^{13}C NMR spectra of compound **3,5-AMD-4** in $CDCl_3$.

3,4,5-ext-AMD-2

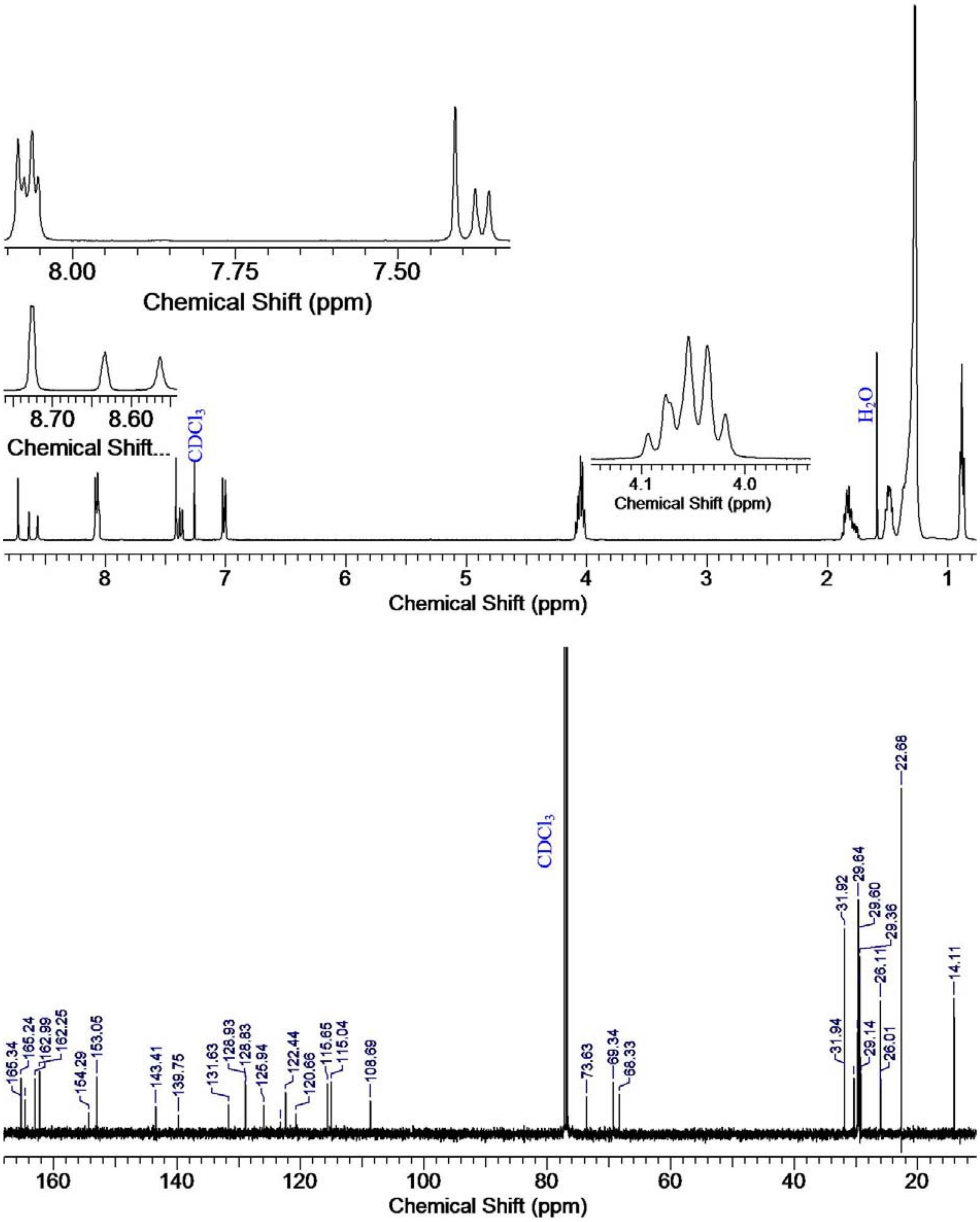


Fig. S22 ^{1}H and ^{13}C NMR spectra of compound **3,4,5-ext-AMD-2** in CDCl$_3$.

3,4,5-ext-AMD-4

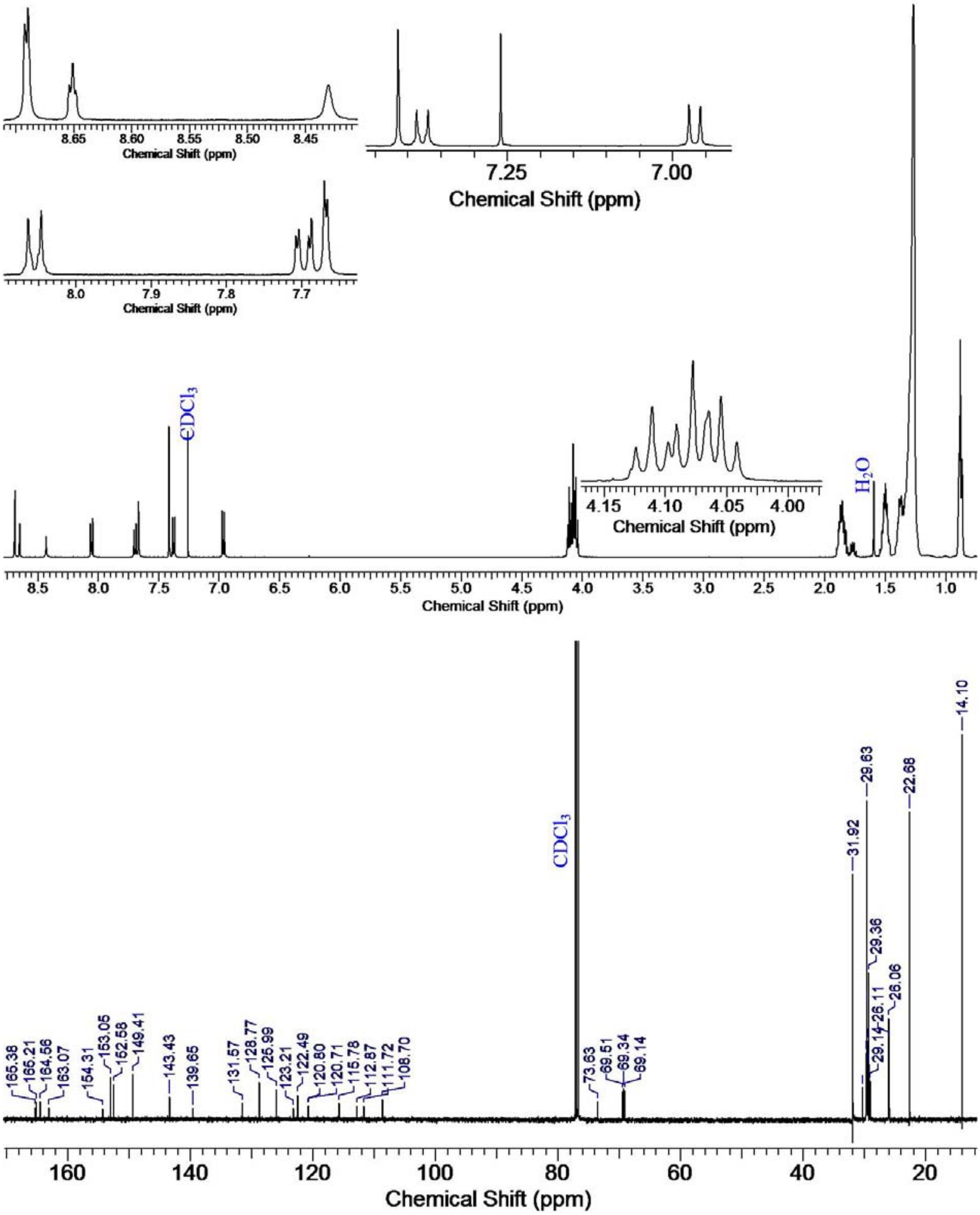


Fig. S23 ^{1}H and ^{13}C NMR spectra of compound **3,4,5-ext-AMD-4** in $CDCl_3$.

3,4,5-IM-2

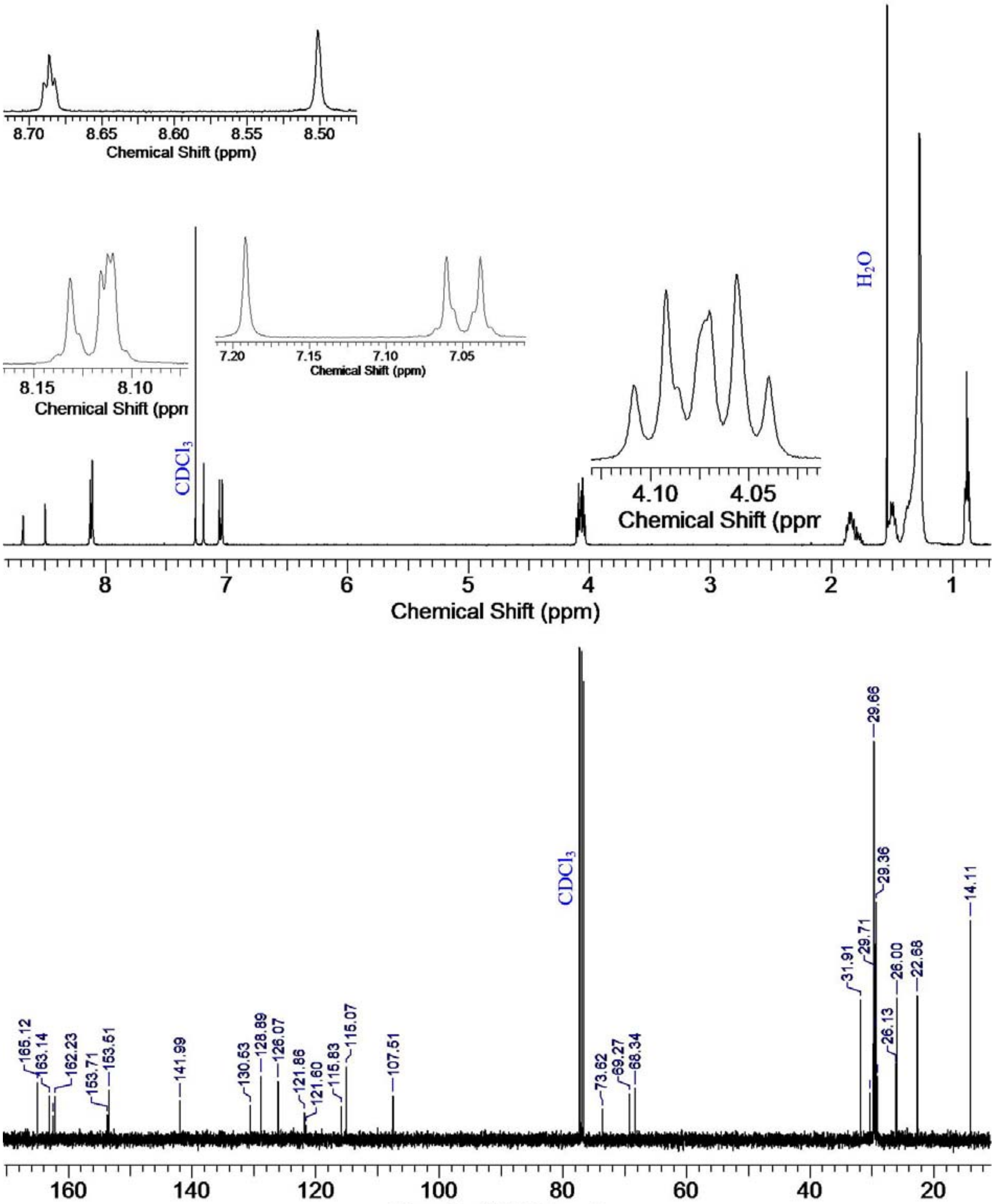


Fig. S24 ^{1}H and ^{13}C NMR spectra of compound **3,4,5-IM-2** in CDCl$_3$.

3,4,5-IM-4

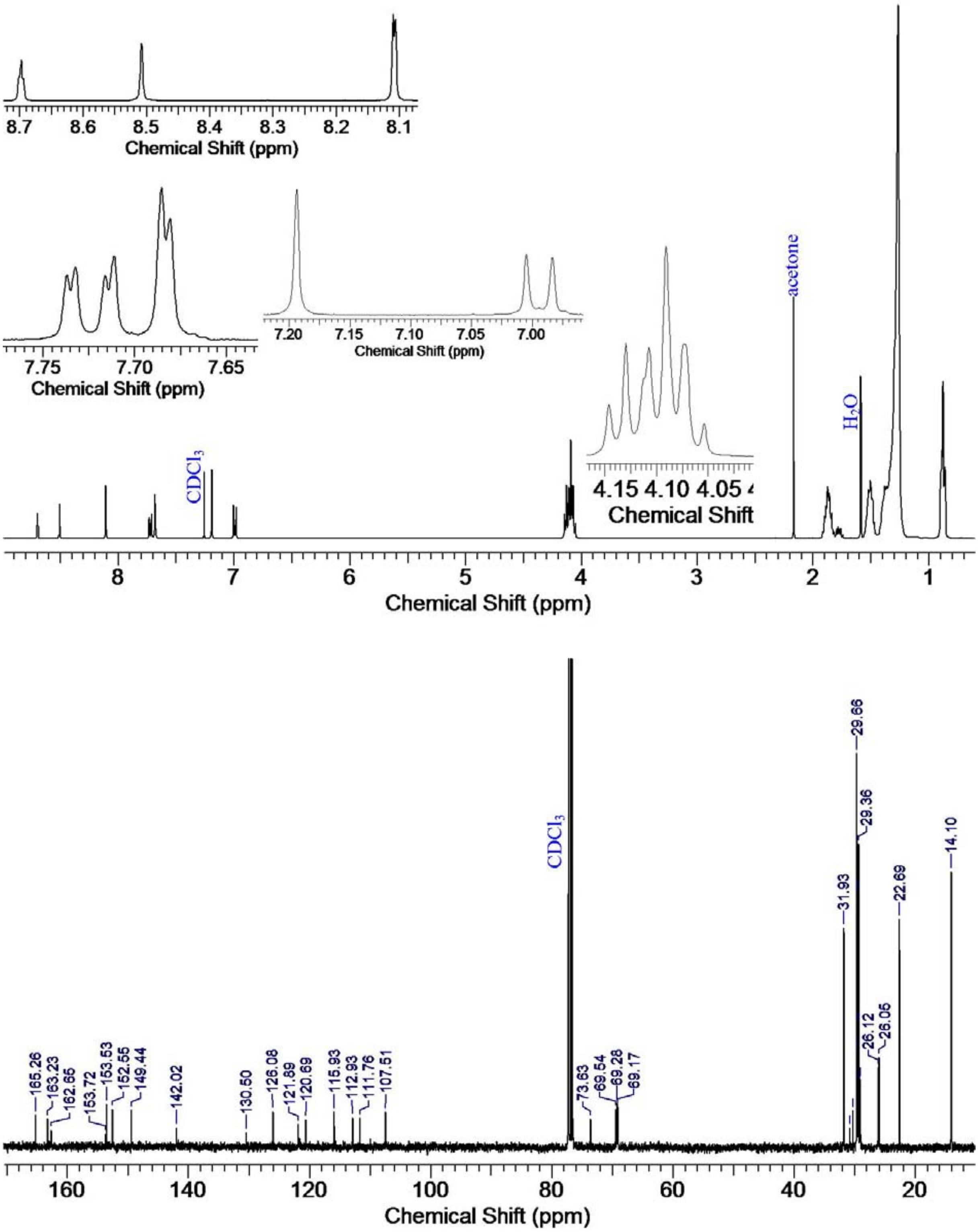


Fig. S25 ^{1}H and ^{13}C NMR spectra of compound **3,4,5-IM-4** in CDCl$_3$.

(7) HR-MS for final compounds (Q-TOF/MS)

4-AMD-2

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	1000 V	Set Dry Heater	200 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	5000 m/z	Set Collision Cell RF	2000.0 Vpp	Set Divert Valve	Source

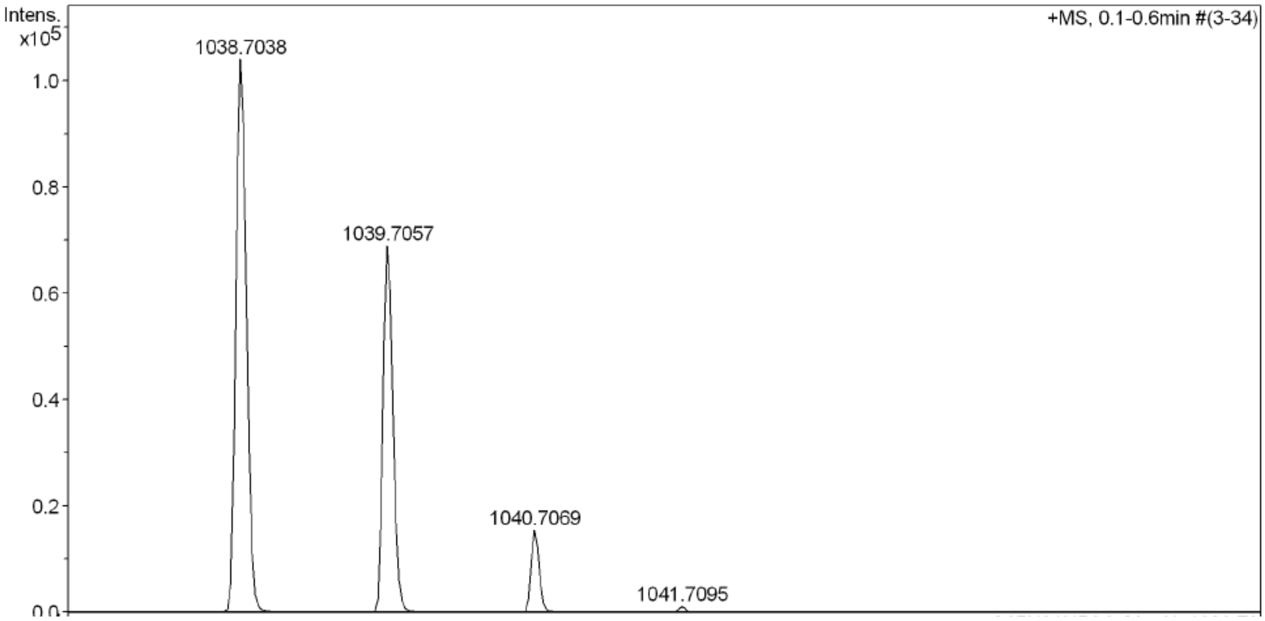


Fig. S26 Q-TOF/MS spectra for compound **4-AMD-2**.

4-AMD-4

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	1000 V	Set Dry Heater	200 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	5000 m/z	Set Collision Cell RF	2000.0 Vpp	Set Divert Valve	Source

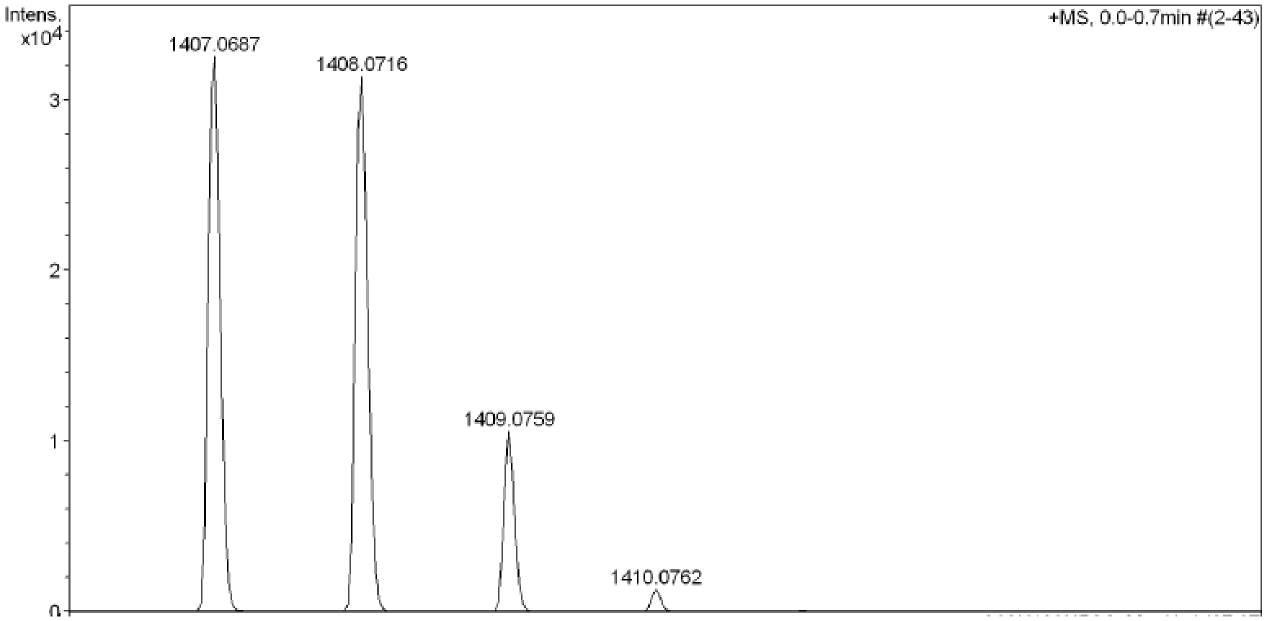


Fig. S27 Q-TOF/MS spectra for compound **4-AMD-4**.

3,4-AMD-2

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	1000 V	Set Dry Heater	200 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	5000 m/z	Set Collision Cell RF	2000.0 Vpp	Set Divert Valve	Source

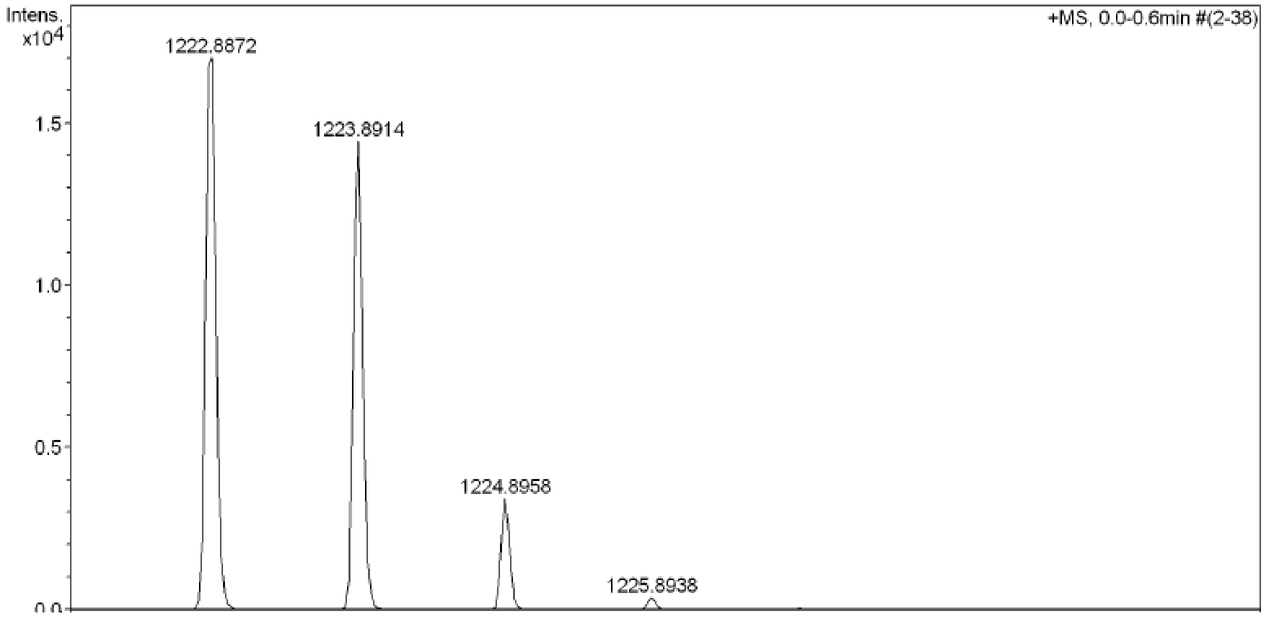


Fig. S28 Q-TOF/MS spectra for compound **3,4-AMD-2**.

3,4-AMD-4

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.5 Bar
Focus	Not active	Set Capillary	1000 V	Set Dry Heater	200 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	5000 m/z	Set Collision Cell RF	2500.0 Vpp	Set Divert Valve	Source

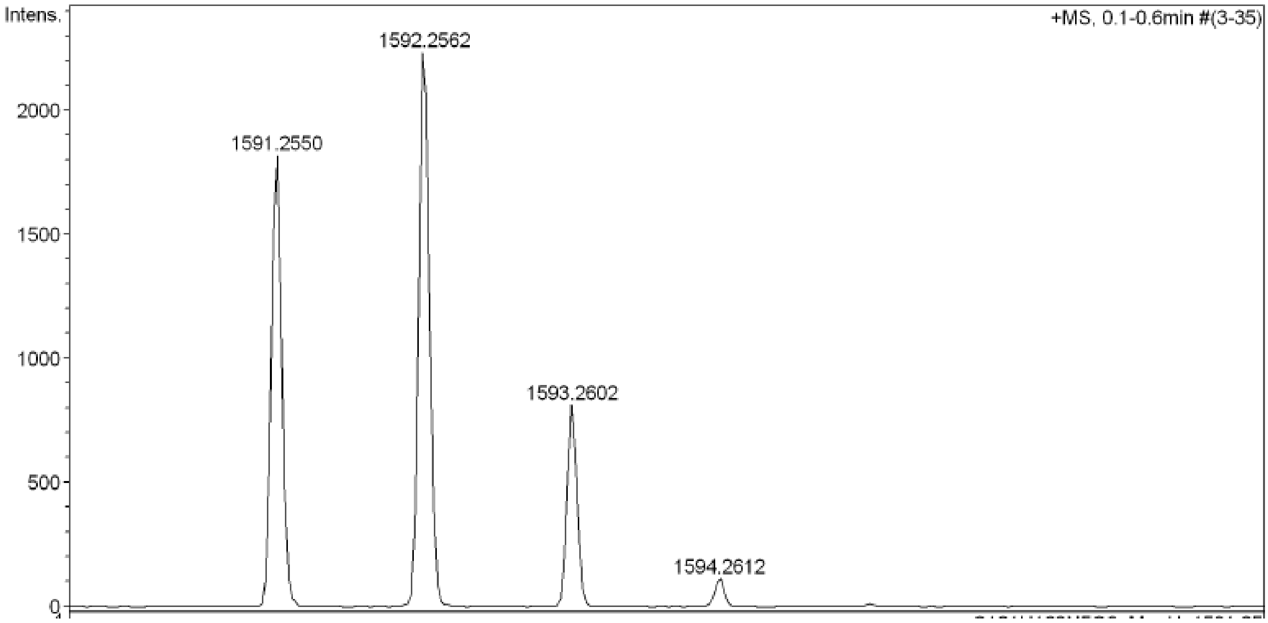


Fig. S29 Q-TOF/MS spectra for compound **3,4-AMD-4**.

3,4,5-AMD-2

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	1000 V	Set Dry Heater	200 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	5000 m/z	Set Collision Cell RF	2000.0 Vpp	Set Divert Valve	Source

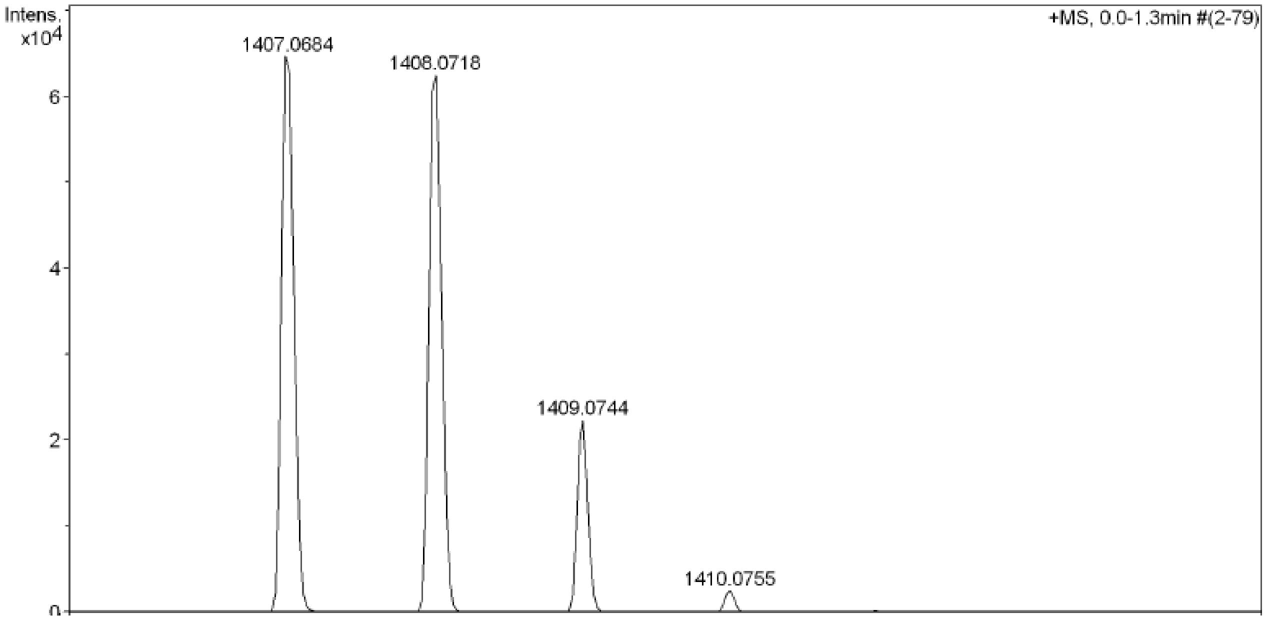


Fig. S30 Q-TOF/MS spectra for compound **3,4,5-AMD-2**.

3,4,5-AMD-4

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.5 Bar
Focus	Not active	Set Capillary	1000 V	Set Dry Heater	200 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	5000 m/z	Set Collision Cell RF	1200.0 Vpp	Set Divert Valve	Source

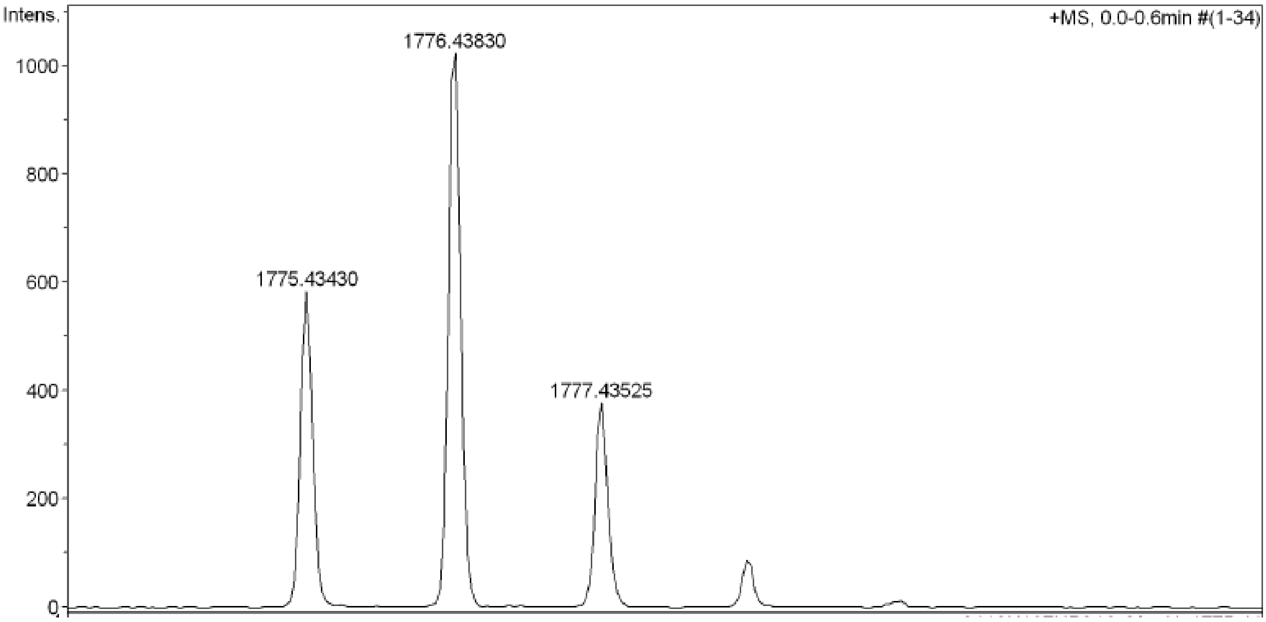


Fig. S31 Q-TOF/MS spectra for compound **3,4,5-AMD-4**.

3,5-AMD-2

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	1000 V	Set Dry Heater	200 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	5000 m/z	Set Collision Cell RF	2000.0 Vpp	Set Divert Valve	Source

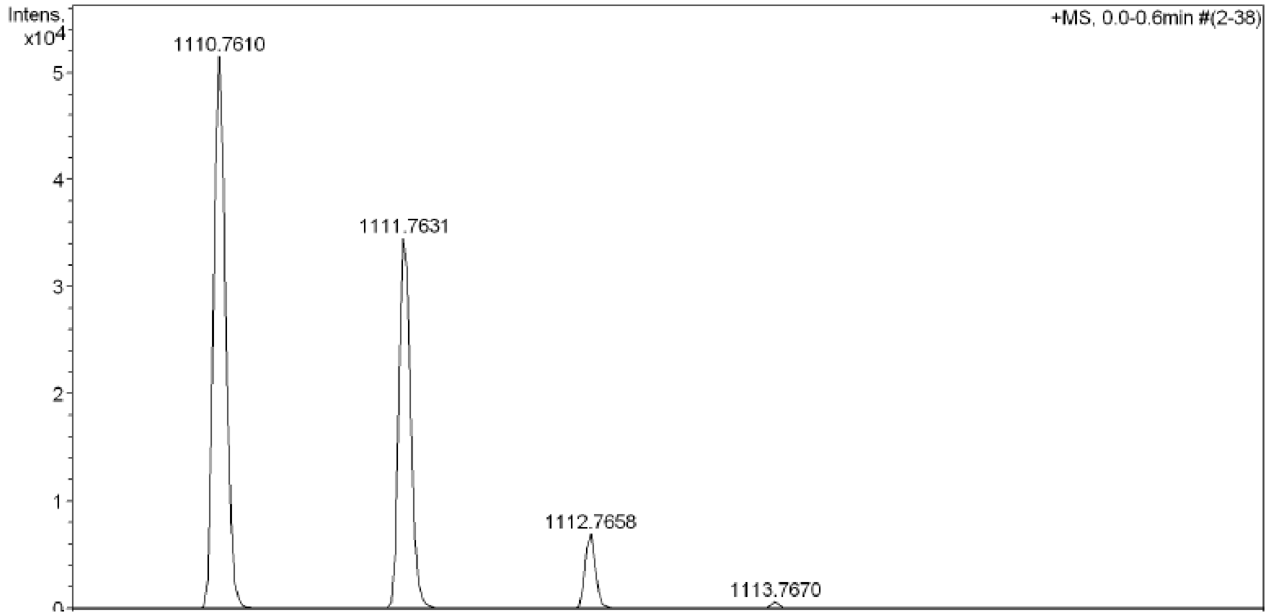


Fig. S32 Q-TOF/MS spectra for compound **3,5-AMD-2**.

3,5-AMD-4

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	1000 V	Set Dry Heater	200 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	5000 m/z	Set Collision Cell RF	2000.0 Vpp	Set Divert Valve	Source

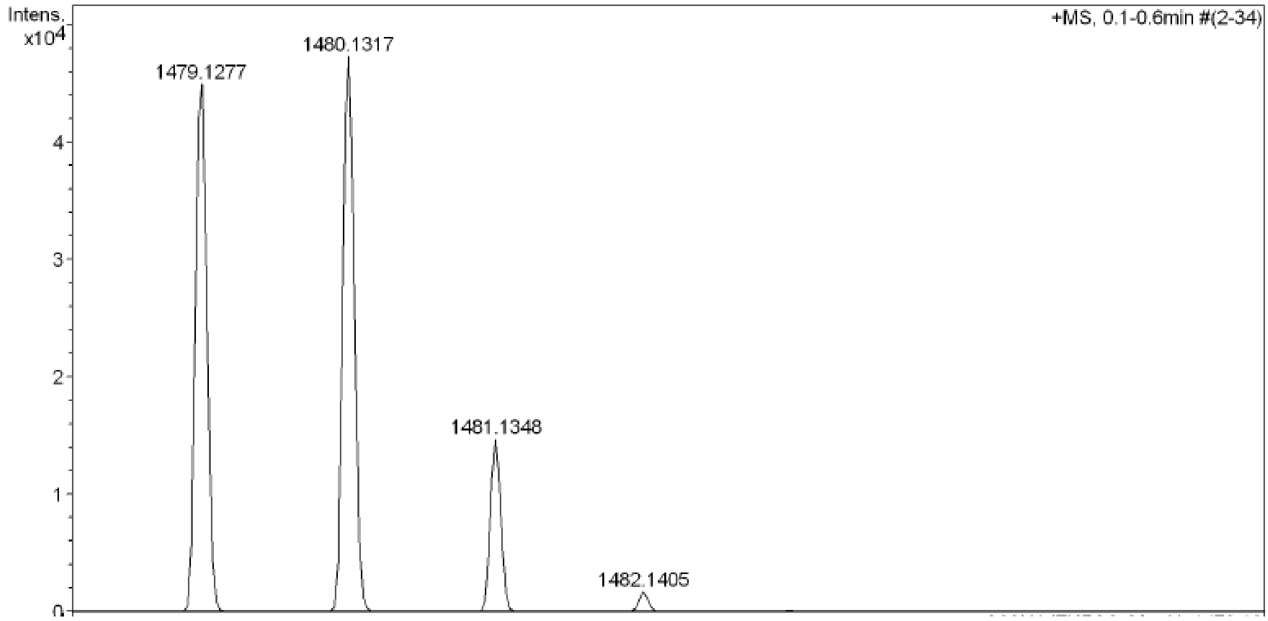


Fig. S33 Q-TOF/MS spectra for compound **3,5-AMD-4**.

3,4,5-ext-AMD-2

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.5 Bar
Focus	Not active	Set Capillary	1000 V	Set Dry Heater	200 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	5000 m/z	Set Collision Cell RF	1600.0 Vpp	Set Divert Valve	Source

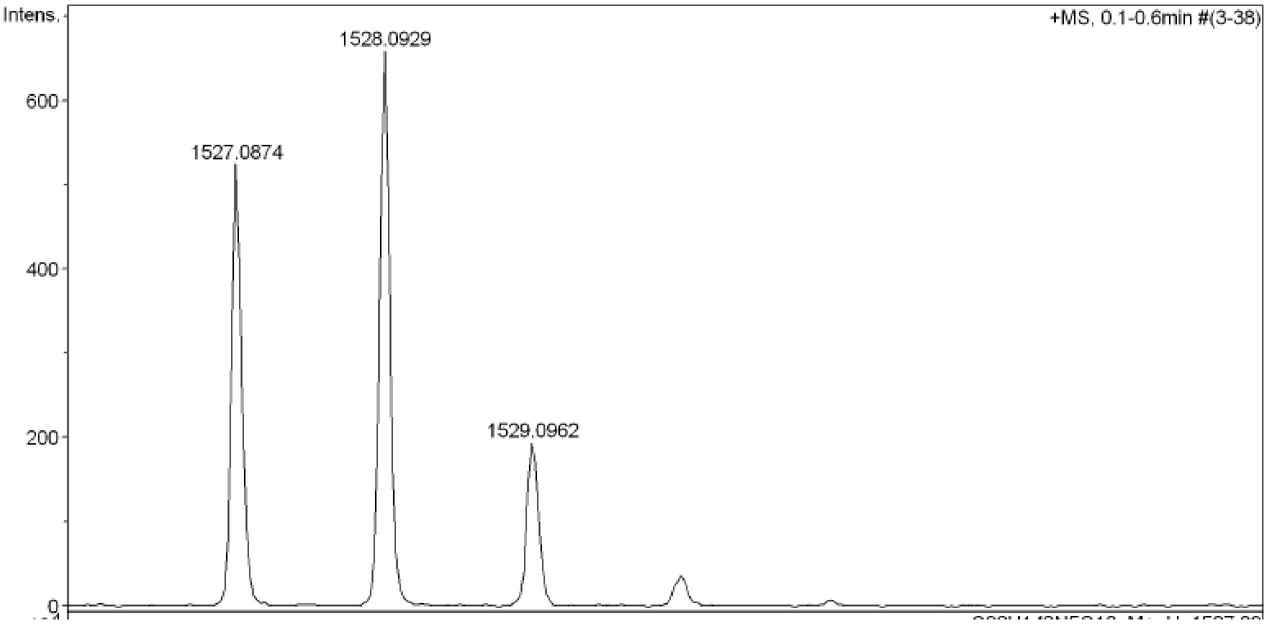


Fig. S34 Q-TOF/MS spectra for compound **3,4,5-ext-AMD-2**.

3,4,5-ext-AMD-4

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	1000 V	Set Dry Heater	200 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	5000 m/z	Set Collision Cell RF	1600.0 Vpp	Set Divert Valve	Source

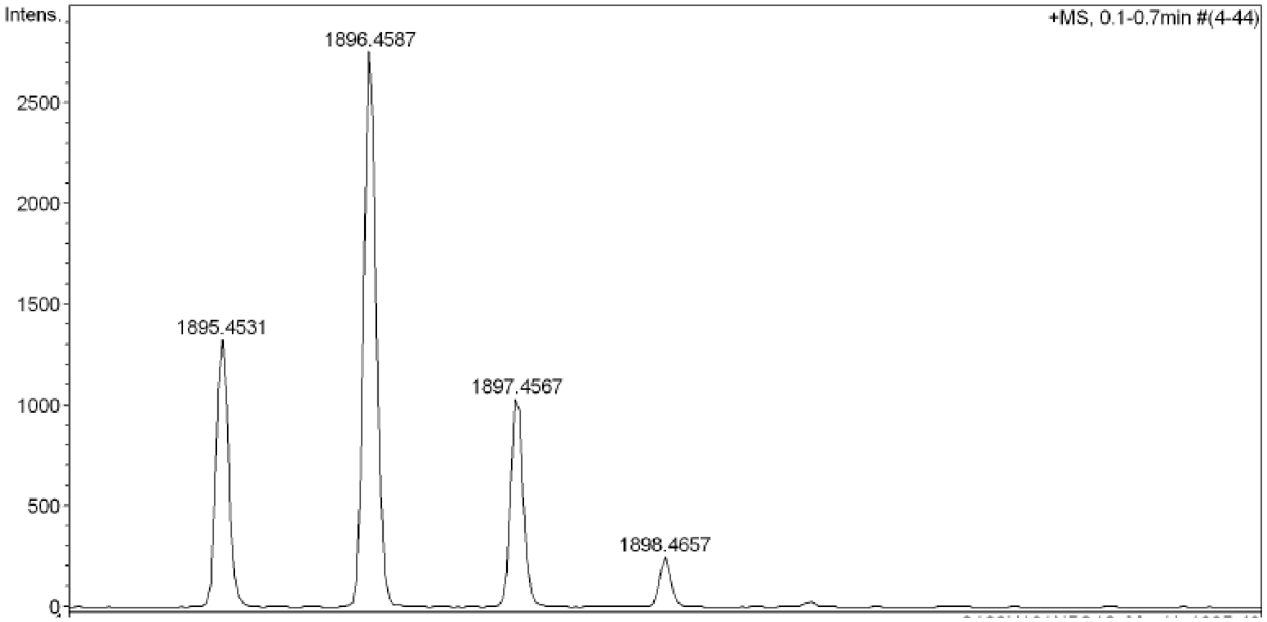


Fig. S35 Q-TOF/MS spectra for compound **3,4,5-ext-AMD-4**.

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