

# Synthesis of poly(*para*-phenylene)(2-isocyano-2-tosylpropane-1,3-diyl) and Poly(*para*-phenylene)(2-oxopropane-1,3-diyl) via carbonylative coupling of $\alpha,\alpha'$ -dibromoxylene

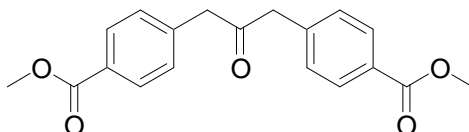
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## Supporting Information

### Experimental Details

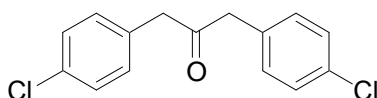
**General Details** NMR spectra were recorded on a Varian 500 MHz or Bruker ARX-500 instrument (at 500 and 125 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  respectively) at room temperature (303K  $\pm$  1K) in  $\text{CDCl}_3$  unless otherwise indicated. IR spectra were recorded on a Thermo Nicolet IR200, and were obtained neat at room temperature unless otherwise indicated; IR spectra of solids were obtained using an ATR probe. Low resolution CI-MS were recorded on a Finnigan MAT 4500 using a direct insertion probe, and MS of the macrocycle mixture was obtained on an Applied Biosystems/MDS Sciex Q 4000 Trap instrument using spray ionization. All starting materials and solvents were obtained from Aldrich, Acros or Strem and were used without further purification, unless otherwise noted. Chromatography was carried out using 40 $\mu\text{l}$  silica gel obtained from Fisher Scientific. GPC data was obtained using a 600mm/5mm mixed D PLgel column with THF as the eluent and a flow rate of 1.00 ml/min at 40  $^\circ\text{C}$ , and molecular weights were determined using a narrow standard.



### **1,3-Bis-(4-(methoxycarbonyl)phenyl)-propan-2-one (1a)<sup>1</sup>**

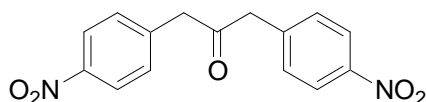
1.169 g (5.10 mmol) methyl-4-(bromomethyl) benzoate, 0.983 g (2.47 mmol) tosylmethylisocyanide, and 0.231g (0.6 mmol) tetrabutylammonium iodide were dissolved in 35 ml methylene chloride and stirred as rapidly as possible until completely homogenous. After 5 minutes, 20 ml 40% aqueous NaOH was added slowly to maintain the high stirring rate. The reaction was stirred vigorously for 4 hours prior to neutralization with HCl. The resulting

mixture was transferred to a separatory funnel and extracted with three portions of methylene chloride. Solvent was removed from the combined organic layers and dissolved in 8 ml of methylene chloride. 1.0 ml of 50% HCl was added and the resulting red solution was stirred for 30 minutes. The hydrolysis was quenched with aqueous sodium bicarbonate and partitioned between water and methylene chloride. The organic layer was removed and the aqueous layer was extracted with three portions of methylene chloride. Two column chromatographic purifications (column 1: methylene chloride on silica,  $R_f = 0.29$ ; column 2: 10% ethyl acetate in hexanes on silica,  $R_f = 0.14$ ) and subsequent recrystallization in 50:50 ethanol ethyl acetate (600mg crude in 65 ml) provided the desired ketone (0.518 g, 62%, m.p. = 139 °C)  $^1\text{H}$  NMR  $\delta$  7.99 (d,  $J = 8.6$  Hz, 4H), 7.21 (d,  $J = 8.6$  Hz, 4H), 3.91 (s, 6H), 3.80 (s, 4H);  $^{13}\text{C}$  NMR  $\delta$  203.67, 166.76, 138.73, 130.02, 129.55, 52.12, 49.20; FTIR (neat,  $\text{cm}^{-1}$ ) 2954.86, 1707.01, 1629.29, 1575.20, 1510.58, 1434.35, 1416.32, 1275.18, 1177.10, 1100.14, 1052.23, 1017.73, 964.64; PCIMS (m+1)/z calc'd.: 327.1154, found: 327.1



### 1,3-Bis-(4-chlorophenyl)-propan-2-one (1b)<sup>2</sup>

0.894 g of 4-chlorobenzyl chloride, 0.133 g of *tert*-butylammonium bromide and 0.538 g of tosylmethylisocyanide were dissolved in 50 ml methylene chloride and stirred vigorously until completely dissolved. After 5 minutes, 20 ml of 40% aqueous NaOH was added and the reaction mixture was stirred as rapidly as possible for 4 hours prior to neutralization with HCl. The resulting mixture was transferred to a separatory funnel and extracted with three portions of methylene chloride. Solvent was removed from the combined organic layers and dissolved in 8 ml methylene chloride. 1.0 ml of 50% HCl was added and the resulting red solution was stirred for 30 minutes. The hydrolysis was quenched with aqueous sodium bicarbonate and partitioned between water and methylene chloride. The organic layer was removed and the aqueous layer was extracted with three portions of methylene chloride. Column chromatography (hexanes on silica gel,  $R_f = 0.16$ ) followed by recrystallization from ethanol (500 mg crude in 45ml) gave the desired product (0.460 g, 59%, m.p. = 97 °C).  $^1\text{H}$  NMR  $\delta$  7.29 (d,  $J = 8.4$  Hz, 4H), 7.07 (d,  $J = 8.4$  Hz, 4H), 3.70 (s, 4H);  $^{13}\text{C}$  NMR  $\delta$  204.38, 133.00, 132.05, 130.74, 128.76, 48.25; FTIR (neat,  $\text{cm}^{-1}$ ) 2887.84, 1716.15, 1491.41, 1416.93, 1404.81, 1339.61, 1321.23, 1304.84, 1106.69, 1189.63, 1057.00, 1014.26, 942.90; PCIMS (m+1)/z calc'd.: 279.0265, found: 279.0



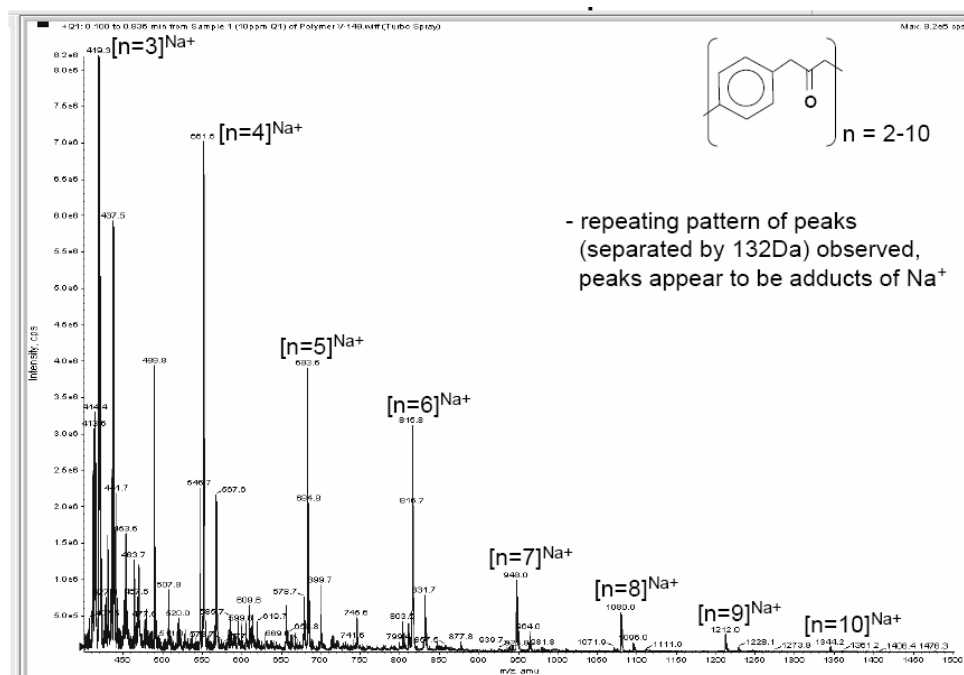
### 1,3-Bis-(4-nitrophenyl)-propan-2-one (1c)<sup>3</sup>

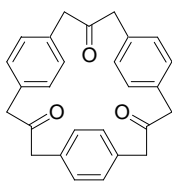
0.956 g of 4-nitrobenzyl bromide, 0.186 g tetrabutylammonium iodide and 0.432 g tosylmethylisocyanide were dissolved in 50 ml methylene chloride and stirred vigorously until completely dissolved. After 5 minutes, 20 ml of 40% aqueous NaOH was added and the reaction mixture stirred as rapidly as possible for 4 hours prior to neutralization with HCl. The resulting mixture was transferred to a separatory funnel and extracted with three portions of methylene chloride. Solvent was removed from the combined organic layers and dissolved in 8 ml of methylene chloride. 1.0 ml of 50% HCl was added and the resulting red solution was stirred for

30 minutes. The hydrolysis was quenched with aqueous sodium bicarbonate and partitioned between water and methylene chloride. The organic layer was removed and the aqueous layer was extracted with three portions of methylene chloride. Chromatography (methylene chloride on silica gel,  $R_f = 0.77$ ) followed by recrystallization from 50:50 ethanol/ethyl acetate (500 mg crude in 75ml) gave the desired product. (0.379 g, 57%, m.p. = 178-179 °C,  $R_f = 0.62$  in 10% EtOAc in hexanes)  $^1\text{H NMR}$   $\delta$  8.21 (d,  $J = 8.8$  Hz, 4H), 7.34 (d,  $J = 8.8$  Hz, 4H), 3.93 (s, 4H);  $^{13}\text{C NMR}$   $\delta$  201.86, 147.35, 140.42, 130.46, 123.93, 48.95; FTIR (neat,  $\text{cm}^{-1}$ ) 1719.94, 1598.68, 1507.55, 1407.68, 1342.06, 1214.37, 1177.94, 1108.83, 1051.83, 1017.22, 855.29, 826.77, 790.06, 736.43, 707.67, 656.61, 631.25; PCIMS (m+1)/z calc'd.: 300.0746, found: 300.2

## Macrocycles (2)<sup>4</sup>

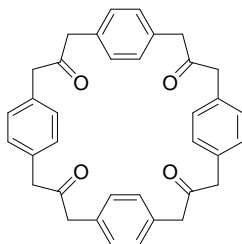
0.2301 g a,a'-dibromoxylene, 0.444 g tetrabutylammonium iodide and 1.726 g TOSMIC were dissolved in 450 ml methylene chloride and 300 ml of 40 wt% aqueous NaOH were added. The reaction was stirred for 18 hours at room temperature prior to heating to a mild reflux (note: prolonged heating and exposure to the coupling conditions led to decomposition of the isocyanide intermediates in the production of 1a, 1b and 1c). After refluxing for 60 hours, the reaction was brought to neutrality with HCl and extracted with 5 portions of methylene chloride. The organic layers were combined and solvent removed under reduced pressure. The crude mixture of tosylisocyanide macrocycles was then dissolved in 15 ml methylene chloride and 3 ml of 40% HCl were added. The reaction was stirred for 15 minutes prior to quenching with excess sodium bicarbonate, followed by dilution in 150 ml methylene chloride and 100 ml water. The aqueous layer was extracted with three portions of methylene chloride and the combined organic layers were concentrated under vacuum. A mass spectrum of the crude product from hydrolysis is provided below. Individual macrocycles were isolated in low yield from a series of flash column chromatographic separations (0 to 5% methanol in methylene chloride on silica gel). Below is an MS of the mixture of macrocycles, showing the creation of cyclic trimer through cyclic decamer.





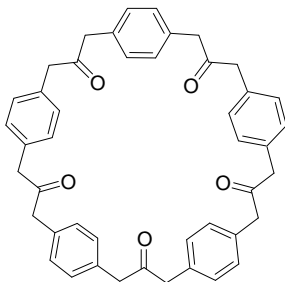
**3,7,11-trioxo-1,5,9(1,4)-tribenzenacyclooctaphane (2b)**

(0.463 g, 22.5%)  $^1\text{H}$  NMR  $d$  6.77 (s, 12H), 3.66 (s, 12H);  $^{13}\text{C}$  NMR  $d$  205.13, 132.81, 129.67, 49.29; FTIR (neat,  $\text{cm}^{-1}$ ) 2926.10, 1705.81, 1508.93, 1422.47, 1318.54, 1264.47, 1178.66, 1114.82, 1055.52, 1022.70, 809.18; ESMS ( $m+23$ )/ $z$  calc'd.: 419.1623, found: 419.3;  $R_f$  = 0.8, 3% MeOH in  $\text{CH}_2\text{Cl}_2$



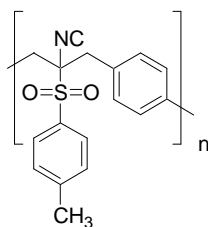
**3,7,11,15-tetraoxo-1,5,9,13(1,4)-tetrabenzenacyclooctaphane (2c)**

(0.236 g 13.4%)  $^1\text{H}$  NMR  $d$  6.91 (s, 16H), 3.63 (s, 16H);  $^{13}\text{C}$  NMR  $d$  205.24, 132.83, 129.79, 48.93; FTIR (neat,  $\text{cm}^{-1}$ ) 2924.45, 1706.43, 1510.78, 1421.69, 1310.89, 1144.12, 1114.64, 1084.19, 1063.01, 814.05, 720.22, 648.23, 541.62; ESMS ( $m+23$ )/ $z$ : calc'd.: 551.2198, found: 551.5;  $R_f$  = 0.67, 3% MeOH in  $\text{CH}_2\text{Cl}_2$



**3,7,11,15,19-pentaoxo-1,5,9,13,17(1,4)-pentabenzenacyclooctaphane (2d)**

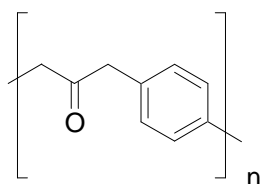
(0.121 g, 7.1%)  $^1\text{H}$  NMR  $d$  7.03 (s, 20H), 3.67 (s, 20H);  $^{13}\text{C}$  NMR  $d$  205.14, 132.87, 129.85, 48.80; FTIR (neat,  $\text{cm}^{-1}$ ) 2924.77, 1703.61, 1512.28, 1422.14, 1304.05, 1145.70, 1059.50, 1021.83, 814.69, 663.90, 615.46, 583.03, 554.20; ESMS ( $m+23$ )/ $z$ : calc'd.: 683.2773, found: 683.6;  $R_f$  = 0.51, 3% MeOH in  $\text{CH}_2\text{Cl}_2$



**Poly(*para*-phenylene)(2-isocyano-2-tosylpropane-1,3-diyl) (3)**

1.909 g (7.2 mmol) *a,a'*-dibromoxylene, 1.41 g tosylmethylisocyanide (7.2 mmol), and 0.130 g (0.4 mmol) tetrabutylammonium iodide were dissolved in 40 ml of methylene chloride. 40 ml 40% (wt/wt) aqueous NaOH was added while the reaction mixture was stirred as rapidly as possible. The reaction was stirred for eight hours prior to quenching to neutral pH with cold 40% (vol/vol) aqueous HCl. The aqueous layer was extracted with three portions of methylene chloride and the combined organic layers were concentrated under vacuum. Two consecutive columns (0 to 20% methanol in methylene chloride on silica gel) gave the desired polymer (1.745 g, 81.4% conversion of tosylmethylisocyanide). <sup>1</sup>H NMR  $\delta$  7.85-7.78 (m, 2H), 7.39-7.33 (m, 2H), 7.03-6.96 (m, 4H), 3.23-3.14 (m 2H), 3.07 (d  $J$  = 14.0 Hz, 2H), 2.44 (br. s, 3H); <sup>13</sup>C NMR  $\delta$  167.44, 146.4, 132.30, 131.24, 130.95, 130.65, 129.97, 129.89, 81.70, 39.20, 21.66; FTIR (neat, cm<sup>-1</sup>) 210.23, 1595.4, 1514.84, 1440.00, 1323.29, 1147.13, 1083.91, 813.51, 707.84, 652.71, 579.21; GPC (trace shown below):

Peak #	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1 (11.12 mins)	9802	7525	10072	13324	16667	9614	1.33847
2 (14.30 mins)	1031	889	1056	1262	1488	1026	1.18785

**Poly(*para*-phenylene)(2-oxopropane-1,3-diyl) (4)****Method A**

0.111 g of **3** was dissolved in 10 ml THF, and 3 ml 50% vol/vol aqueous HCl was added. The reaction was brought to reflux for 3 hours prior to cooling to room temperature and quenching with sodium bicarbonate. The reaction was then diluted in 100 ml methylene chloride and 100 ml water and extracted with 3 portions of methylene chloride. The combined organic layers were concentrated under vacuum and three column chromatographic purifications (methylene chloride and methanol on silica gel) gave the desired polymer. (0.017 g, 35% conversion). <sup>1</sup>H NMR  $\delta$  7.07 (br. s 4H), 3.66 (br. s 4H); <sup>13</sup>C NMR  $\delta$  132.78, 129.77, 48.68; FTIR (neat, cm<sup>-1</sup>) 2922.03, 1704.28, 1509.89, 1422.40, 1317.07, 1264.87, 1178.61, 1148.29, 1115.51, 1054.32, 1022.12, 802.28; GPC (trace shown below):

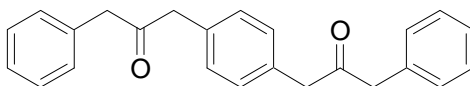
Peak #	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1(16.47 mins)	367	628	1217	4106	8921	1025	1.9379
2 (16.92 mins)	242	220	227	235	239	225	1.03182

**Method B**

0.950 g of **3** was dissolved in 15 ml THF, and 3 ml 50% vol/vol aqueous HCl was added. The reaction was stirred at room temperature for 8 hrs before quenching with sodium bicarbonate. The reaction was then diluted in 100 ml methylene chloride and 100 ml water and extracted with 3 portions of methylene chloride. The combined organic layers were concentrated under vacuum and column chromatography (methylene chloride and methanol on silica gel) gave the desired polymer (88% conversion). Optimization of the hydrolysis and purification is still under study.  $^1\text{H}$  NMR  $\delta$  7.07 (br. s 4H), 3.66 (br. s 4H); FTIR (neat,  $\text{cm}^{-1}$ ) 2922.03, 1704.28, 1509.89, 1422.40, 1317.07, 1264.87, 1178.61, 1148.29, 1115.51, 1054.32, 1022.12, 802.28.

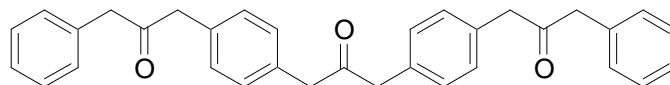
#### Method C

0.280 g of **3** was dissolved in 20 ml THF:toluene (both solvents distilled over sodium prior to rxn), and .475g  $\text{Pb}(\text{OAc})_4$  (1.1mmol) was added. The reaction was stirred vigorously for 1 ½ hrs. The reaction was then poured over water and stirred for 5 minutes. The aqueous layer was extracted with two portions methylene chloride (footnote: FTIR and  $^{13}\text{C}$  NMR analysis of the crude indicated complete disappearance of the isocyanide and almost full conversion to the isocyanate, but this intermediate hydrolyzes under standard chromatographic methods and was used without further purification). The combined organic layers were concentrated under vacuum and stirred over 2 grams alumina in 15 ml  $\text{CH}_2\text{Cl}_2$ . The alumina slurry was filtered and washed with methylene chloride and column chromatography (methylene chloride and methanol on silica gel) gave the desired polymer (27% conversion).  $^1\text{H}$  NMR  $\delta$  7.07 (br. s 4H), 3.66 (br. s 4H); FTIR (neat,  $\text{cm}^{-1}$ ) 2922.03, 1704.28, 1509.89, 1422.40, 1317.07, 1264.87, 1178.61, 1148.29, 1115.51, 1054.32, 1022.12, 802.28.



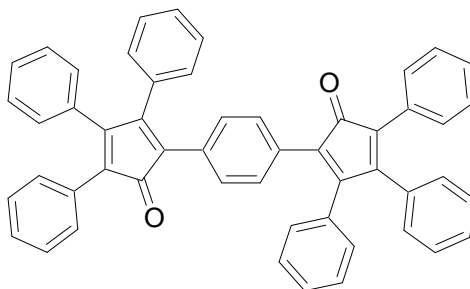
#### 1-[4-(2-Oxo-3-phenylpropyl)-phenyl]-3-phenylpropan-2-one (**5a**)

2.106 g (7.8 mmol) *a,a'*-dibromoxylene, 2.73 g (16.0 mmol) benzyl bromide, 0.740 g (2.0 mmol) tetrabutylammonium iodide and 3.123 g (16.0 mmol) tosylmethylisocyanide were dissolved in 75 ml of methylene chloride and stirred vigorously until completely dissolved. After 5 minutes, 20 ml 40% (wt/wt) aqueous NaOH was added and the reaction was stirred as rapidly as possible for 4 hours prior to neutralization with HCl. The resulting mixture was transferred to a separatory funnel and extracted with three portions of methylene chloride. Solvent was removed from the combined organic layers and dissolved in 8 ml methylene chloride. 1 ml of 50% HCl was added and the resulting red solution was stirred for 30 minutes. The hydrolysis was quenched with aqueous sodium bicarbonate and partitioned between water and methylene chloride. The organic layer was removed and the aqueous layer was extracted with three portions methylene chloride. Column chromatography (10% ethyl acetate in hexanes on silica,  $R_f$  = 0.46 in 1:5 ethyl acetate:hexanes) followed by recrystallization from ethanol/ethyl acetate gave the desired product (0.493 g, 18%, m.p. = 74 °C).  $^1\text{H}$  NMR  $\delta$  7.32 (t,  $J$  = 7.0 Hz, 4H), 7.27 (t,  $J$  = 7.3 Hz, 2H), 7.15 (d,  $J$  = 6.9 Hz, 4H), 7.10 (s, 4H), 3.72 (s, 4H), 3.70 (s, 4H);  $^{13}\text{C}$  NMR  $\delta$  205.47, 133.91, 132.77, 129.82, 129.47, 128.72, 127.07, 49.20, 48.59; FTIR (neat,  $\text{cm}^{-1}$ ) 3028.79, 1713.65, 1603.35, 1514.77, 1496.28, 1453.23, 1403.94, 1338.69, 1052.92, 828.13, 761.70, 724.51, 696.60, 675.23; HRMS ( $m+1/z$ ) calc'd.: 343.1693, found: 343.1703



### 1,3-Bis-[4-(2-oxo-3-phenylpropyl)-phenyl]-propan-2-one (5b)

The product was isolated in same manner as **5a** as a minor product of the same reaction;  $R_f = 0.213$  in 1:5 ethyl acetate:hexanes solution; (0.256 g 10% m.p. = 102 °C)  $^1\text{H}$  NMR  $\delta$  7.32 (t,  $J = 7.0$  Hz, 4H), 7.26 (t  $J = 7.3$  Hz 2H), 7.15 (d,  $J = 7.3$  Hz) 7.10 (s, 8H), 3.72 (s, 4H), 3.70 (s, 8H);  $^{13}\text{C}$  NMR  $\delta$  205.45, 205.35, 133.90, 132.80, 132.69, 129.85, 129.80, 129.47, 128.73, 127.08, 49.22, 48.70, 48.57; FTIR (neat,  $\text{cm}^{-1}$ ) 3061.47, 3034.43, 2929.09, 2880.04, 1714.54, 1601.16, 1520.01, 1497.68, 1453.64, 1410.54, 1314.39, 1056.76, 946.63, 821.95, 768.44, 719.53, 696.73, 670.20; HRMS ( $m+1$ )/ $z$  calc'd.: 475.2268, found: 475.2249

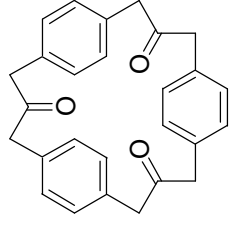


### 1,4-Bis(2-oxo-3,4,5-triphenylcyclopentadienon-2-yl)benzene (6)

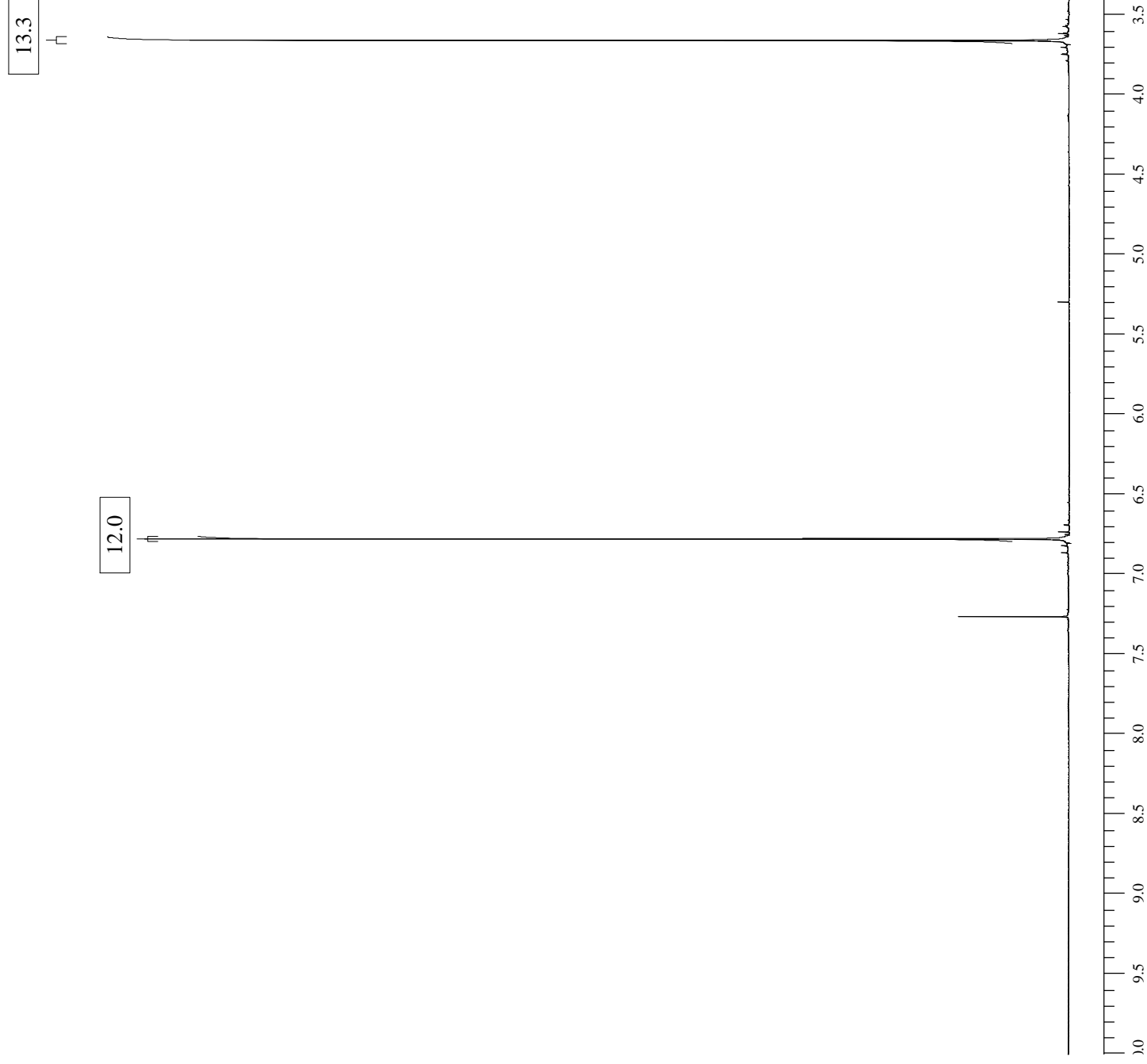
0.207 g (0.6 mmol) **5a** and 0.471 g benzil (2.2 mmol) dissolved in 6 ml distilled THF and deoxygenated with three freeze-pump-thaw cycles. The solution was stirred at 50 °C in the dark as 3 ml of KHMDS (0.5 M in toluene, 1.5 mmol) was added over 90 minutes. The reaction was quenched by cooling in an ice bath, diluting to 200 ml with THF and filtering through celite. Due to the limited solubility of the product mixture, column chromatography was laborious. An initial column (5% ethyl acetate in hexanes on silica) removed the excess benzil and two red-purple byproducts. Flushing this column with methylene chloride gave the desired product in 90% purity. Two successive column chromatographic separations were carried out on the combined purple fractions (column 1: toluene on silica; column 2: 10% ethyl acetate in hexanes to 10% hexanes in methylene chloride on silica) The blue-violet band of this last column was isolated as a violet solid (0.415 g, 89%, m.p.(dec.) = 276 °C,  $R_f = 0.6$  in 2% EtOAc in hexanes)  $^1\text{H}$  NMR (47 °C)  $\delta$  7.25-7.20 (m 14H), 7.17-7.13 (m 12 H), 6.92-6.90 (m 8H);  $^{13}\text{C}$  NMR  $\delta$  154.67, 133.09, 133.06, 130.72, 130.13, 129.86, 129.71, 129.29, 127.99, 127.98, 127.96, 127.88, 127.48, 127.43, 125.38, 124.88 (5 carbons were not observed); FTIR (neat,  $\text{cm}^{-1}$ ) 3058.23, 1703.85, 1448.80, 1441.01, 1355.53, 1303.93, 1086.87, 1025.62, 852.64, 770.40, 736.56, 712.79, 693.03; MALDI-MS ( $m+1$ )/ $z$ : calc'd.: 690.2559, found: 690.2555

#### References Cited:

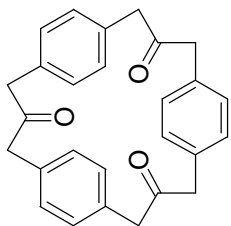
- 1 S.-i. Inaba, R. Rieke, D. Reuben, *J. Org. Chem.*, 1985, **50**, 1373
- 2 O. Possel, A. M. van Leusen, *Tet. Lett.*, 1977, **48**, 4232
- 3 E. Campaigne, B. E. Edwards, *J. Org. Chem.*, 1962, **27**, 3760
- 4 K. Kurosawa, M. Suenaga, T. Inazu, T. Yoshino, *Tet. Lett.*, 1982, **23**, 5335



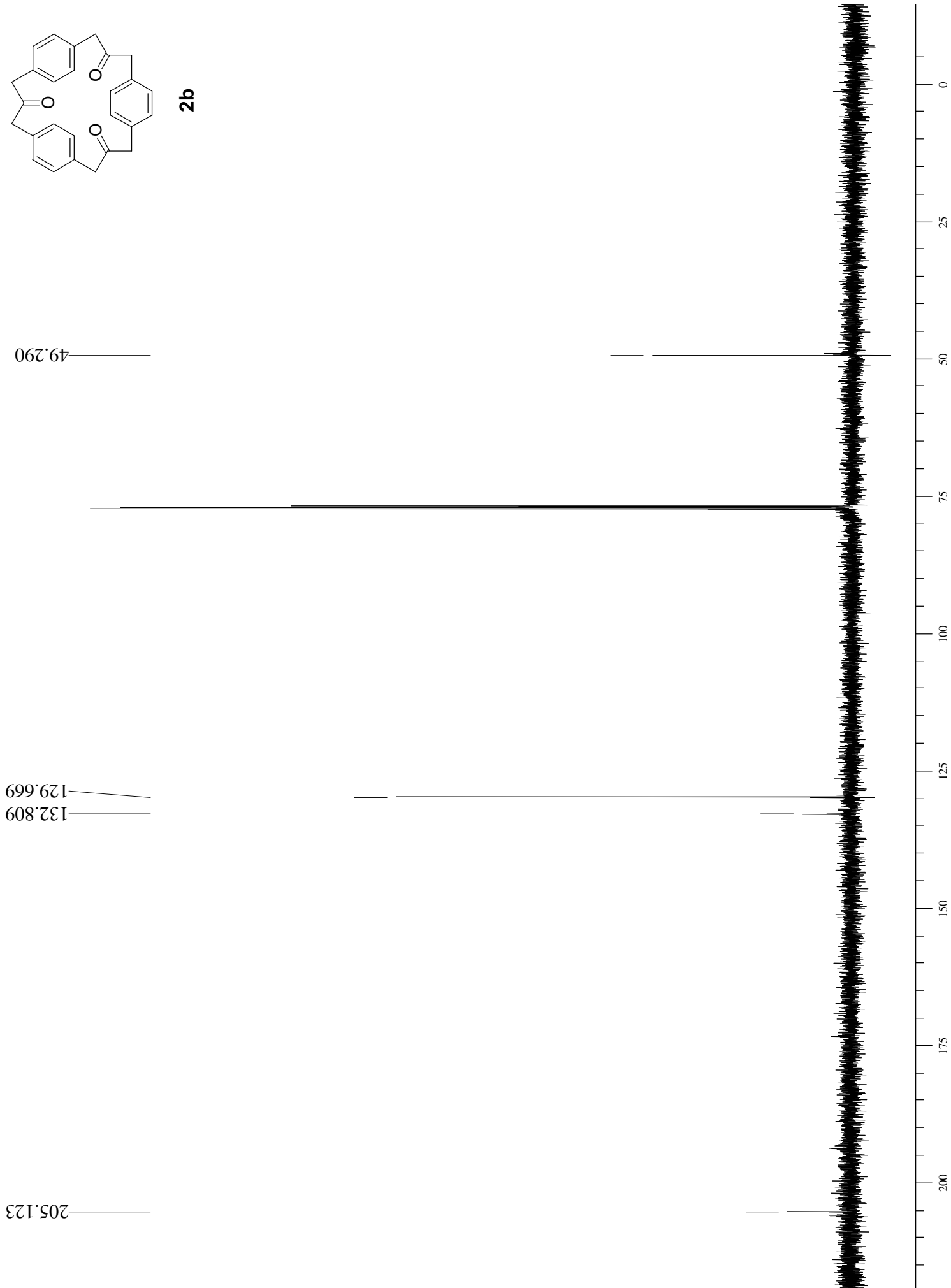
**2b**

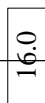
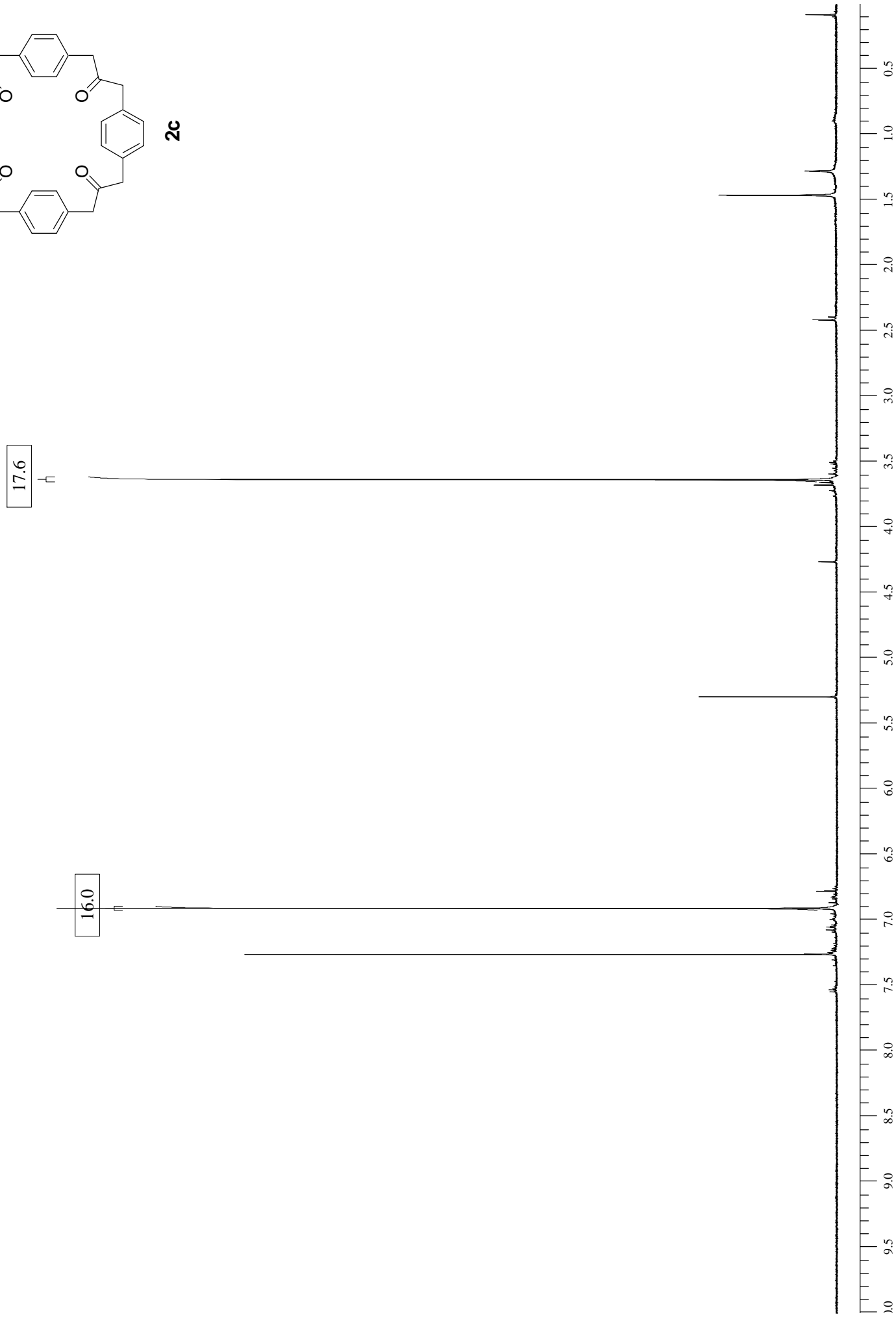
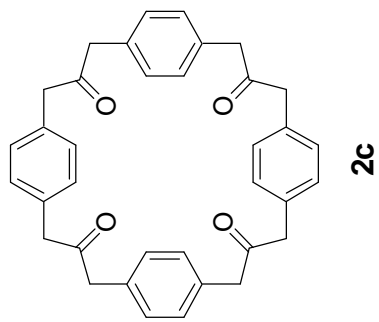


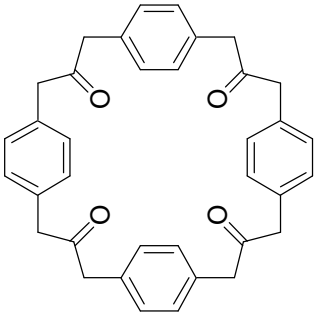




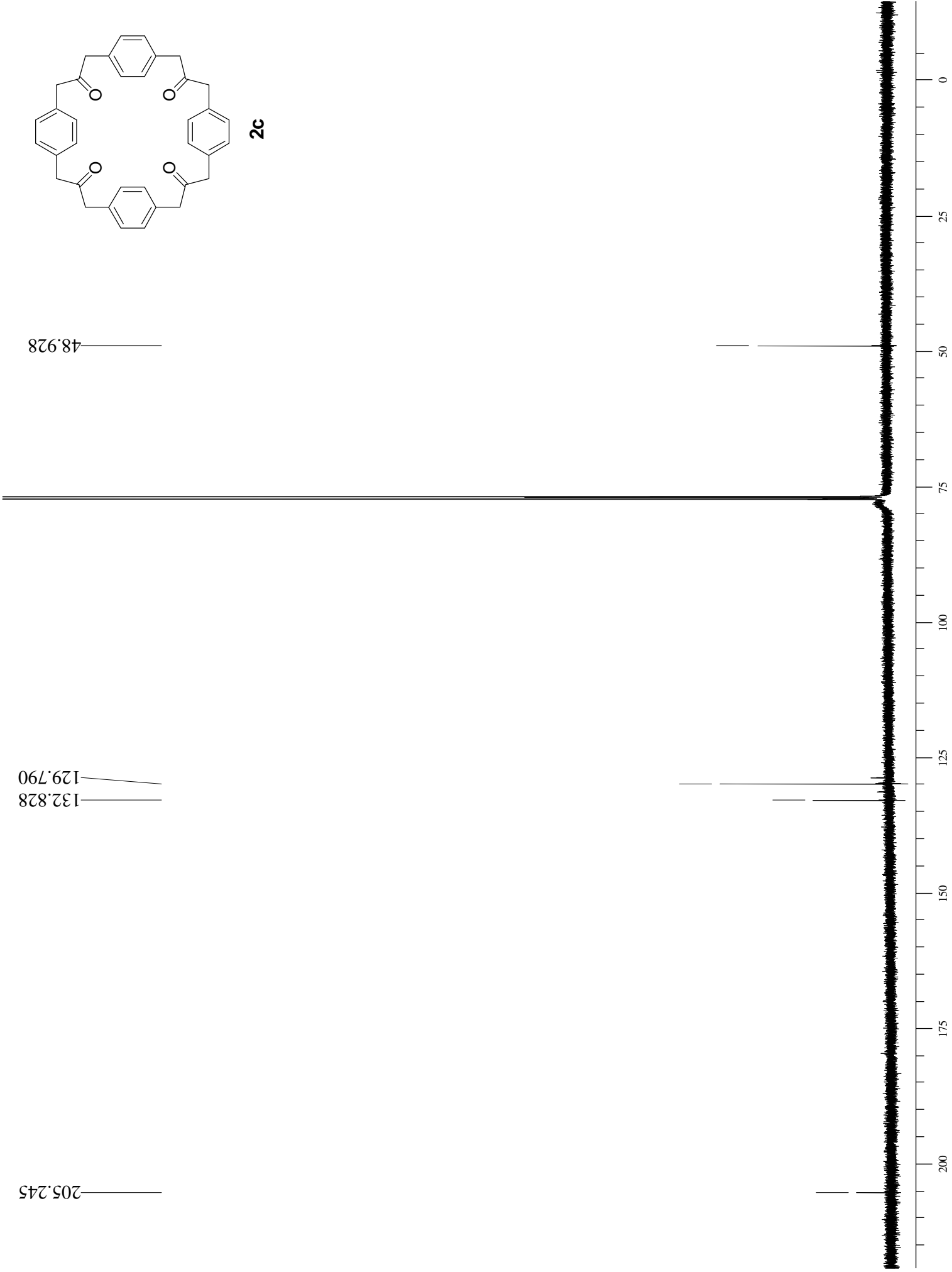
**2b**

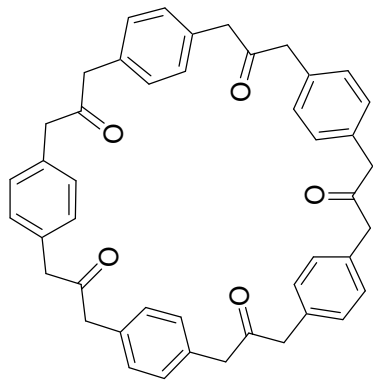




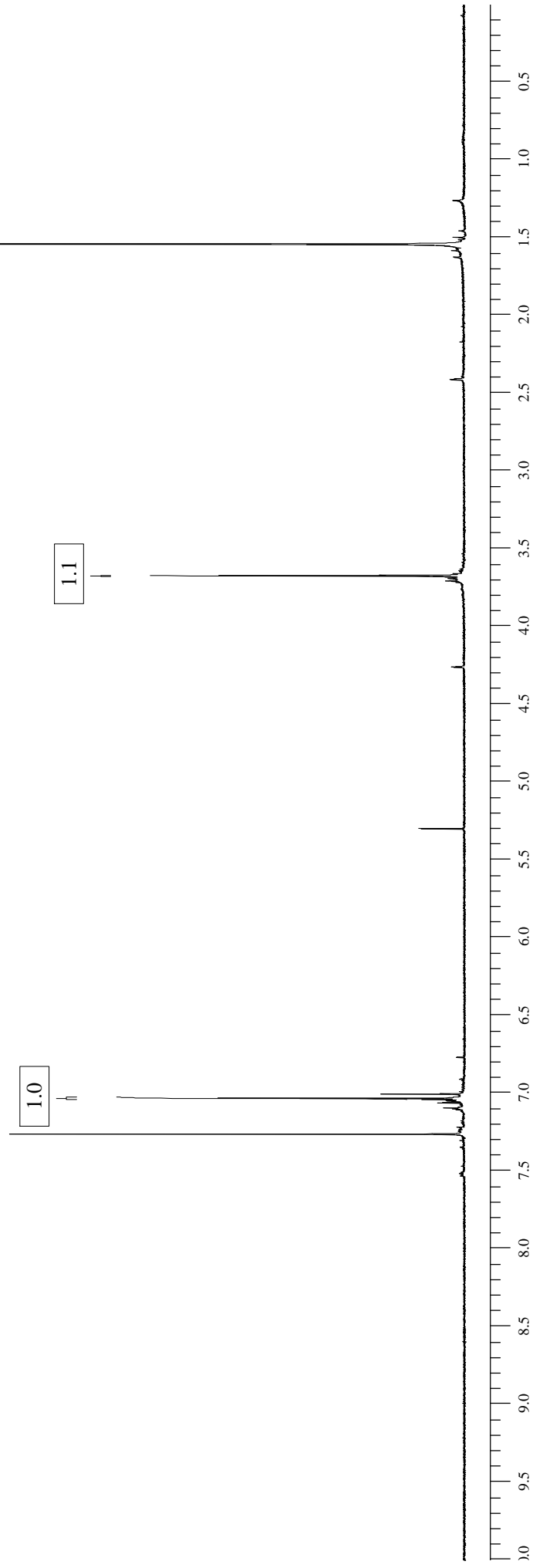


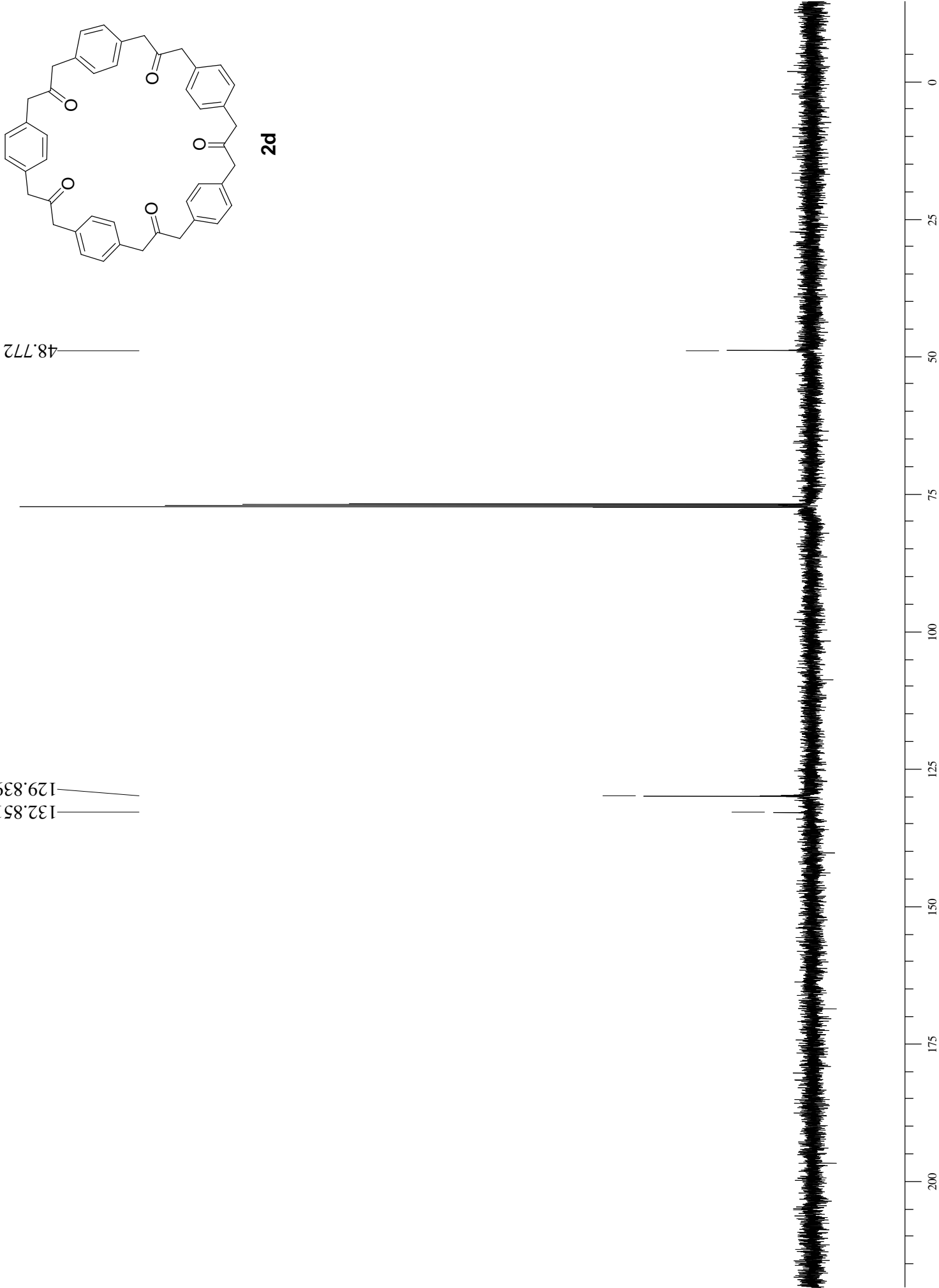
2c

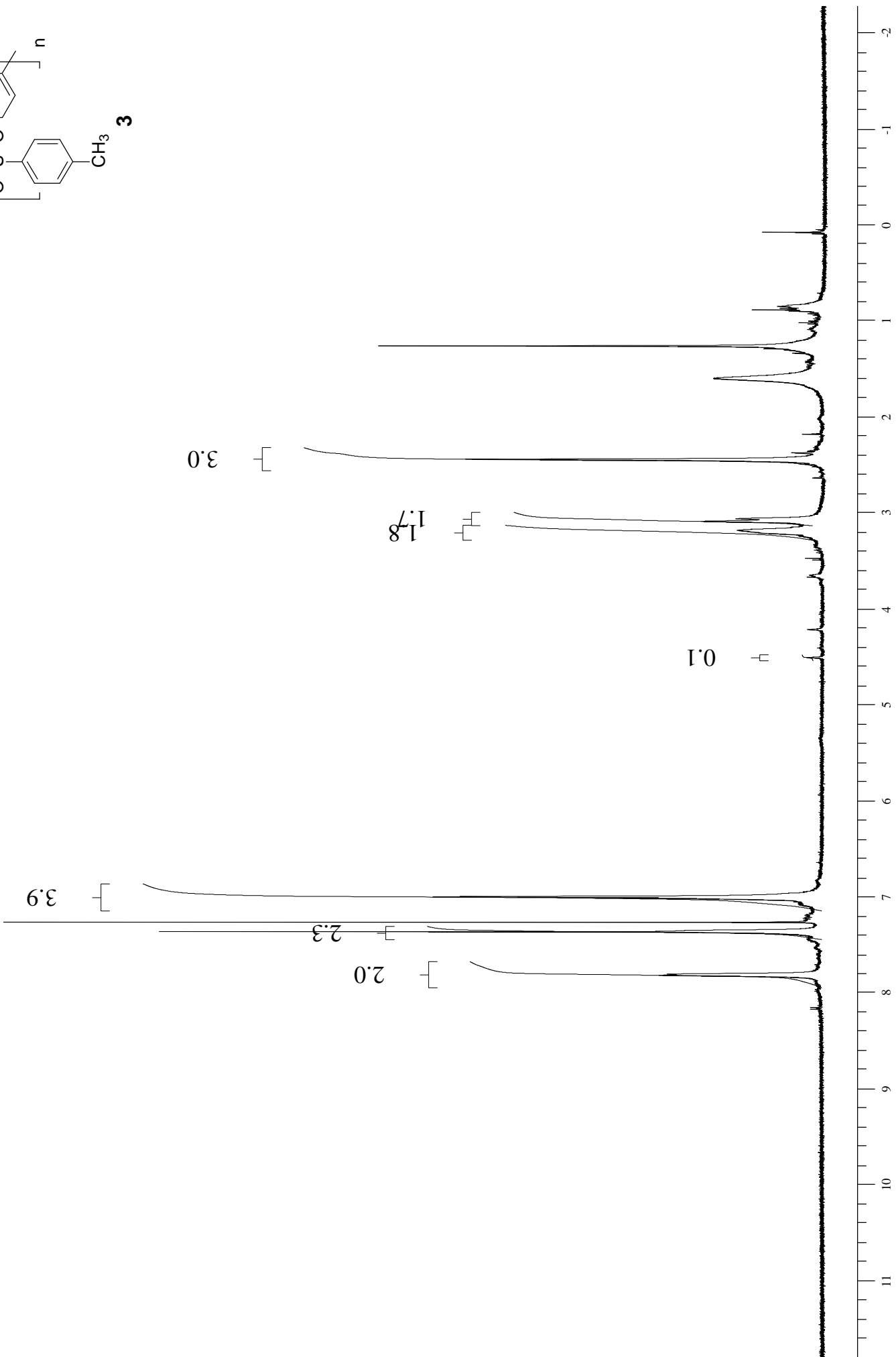
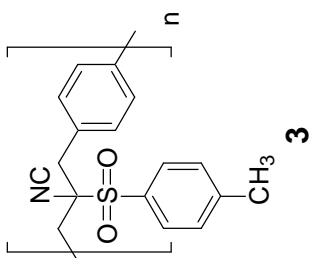


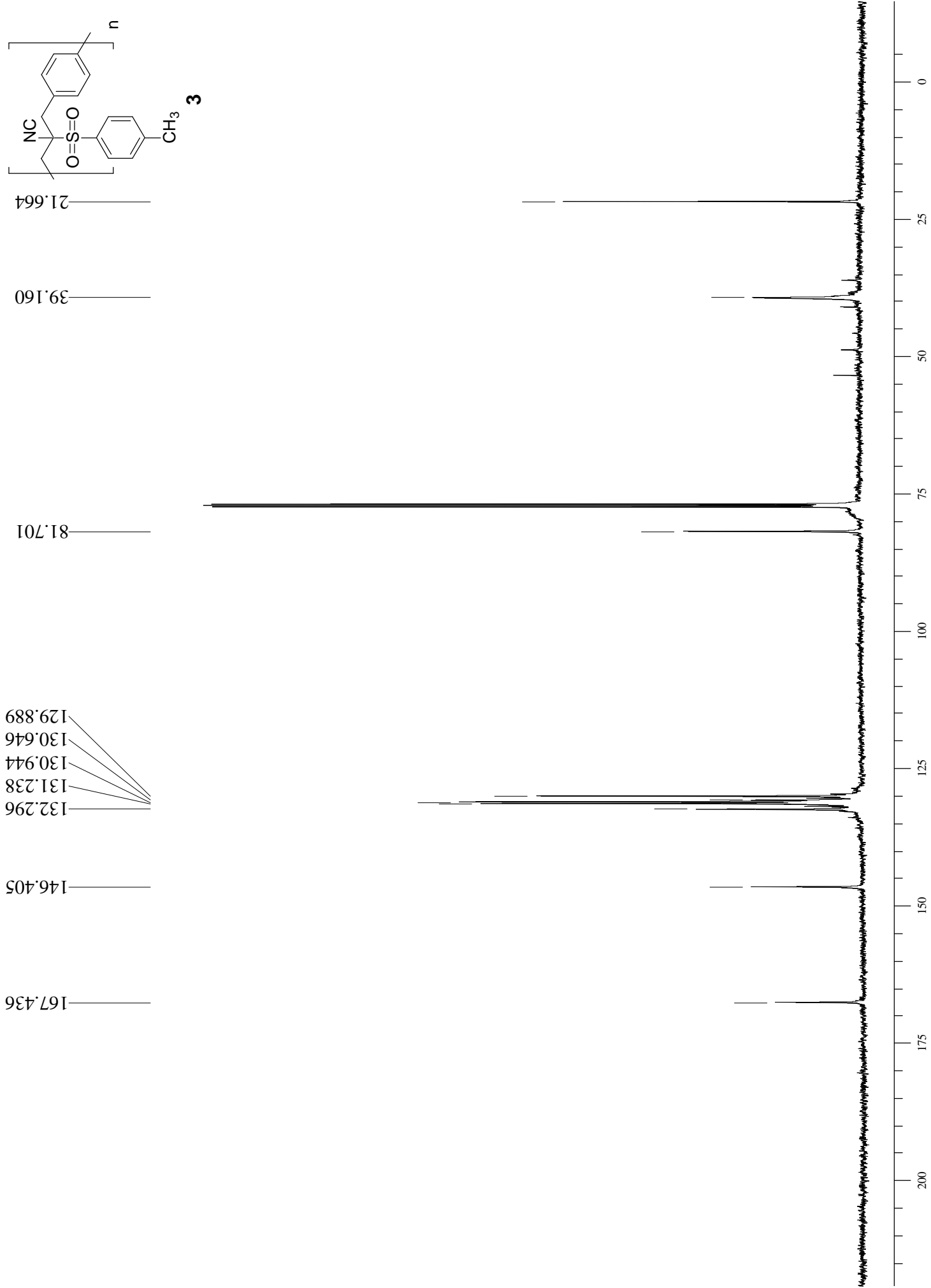


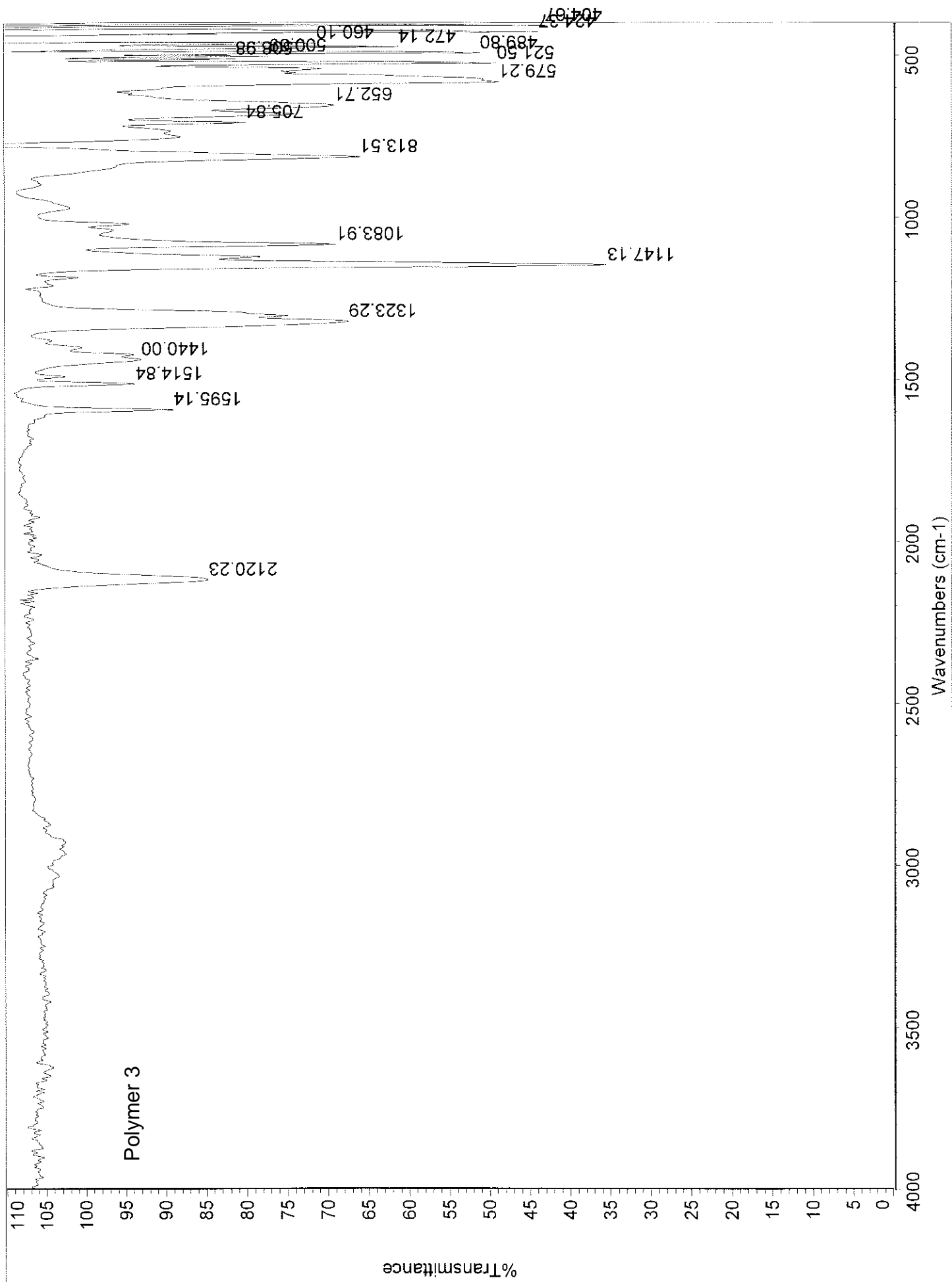
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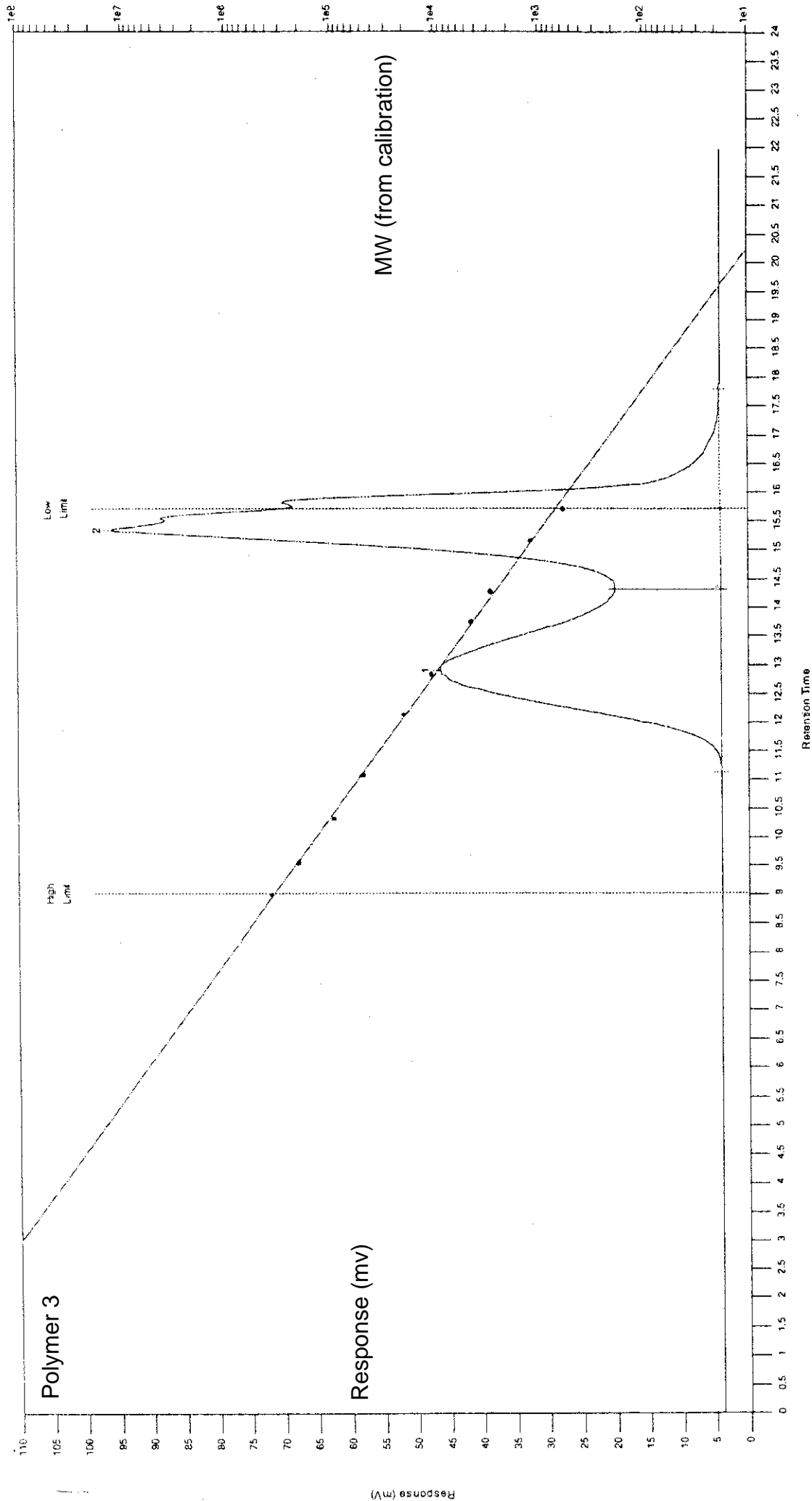


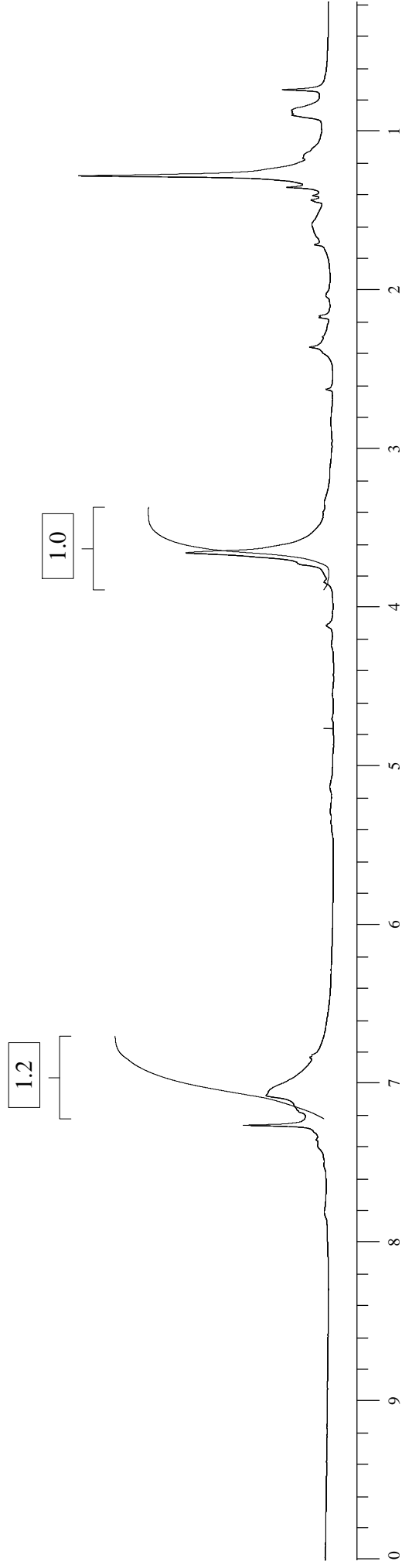
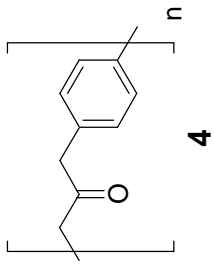


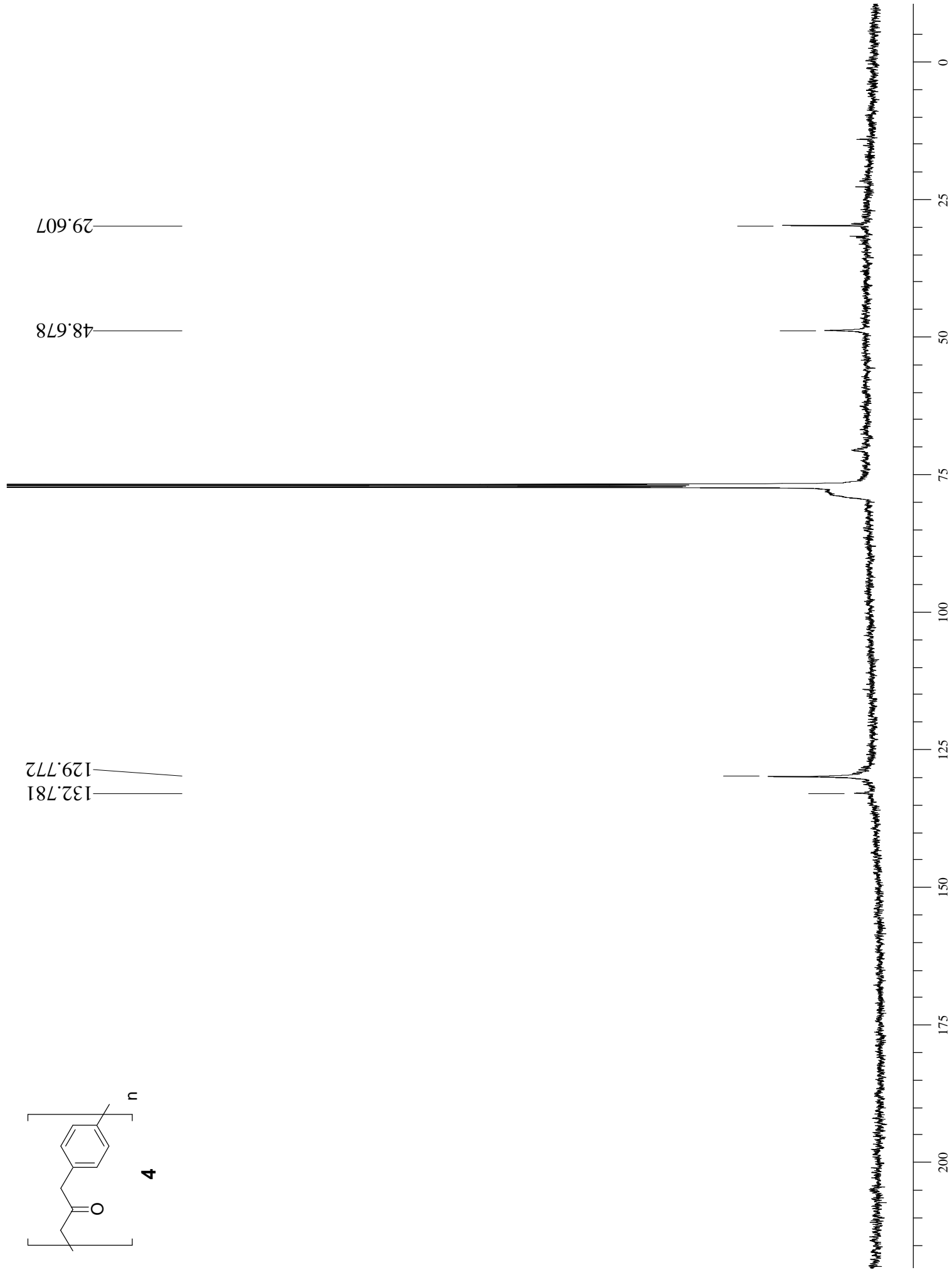


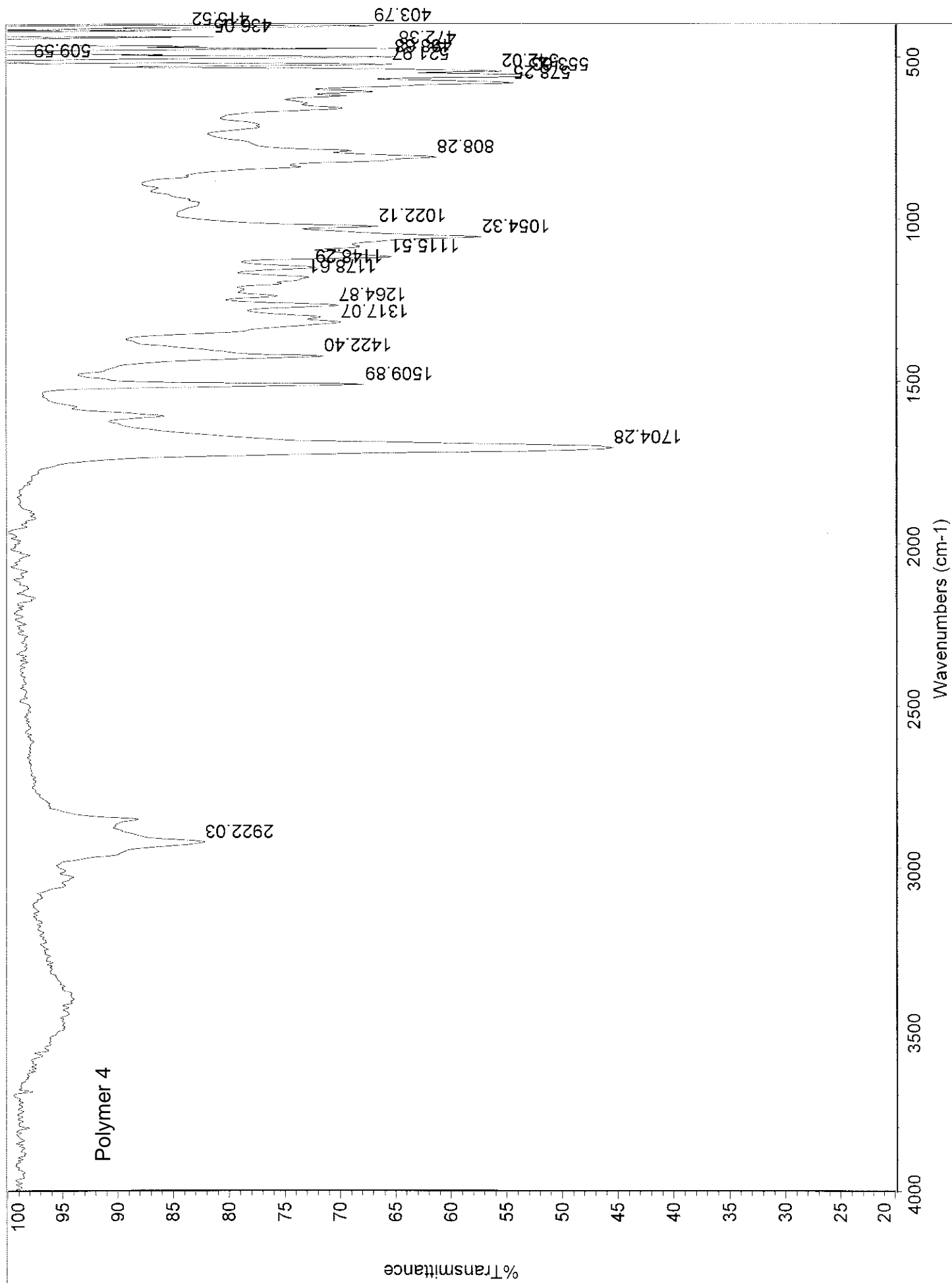


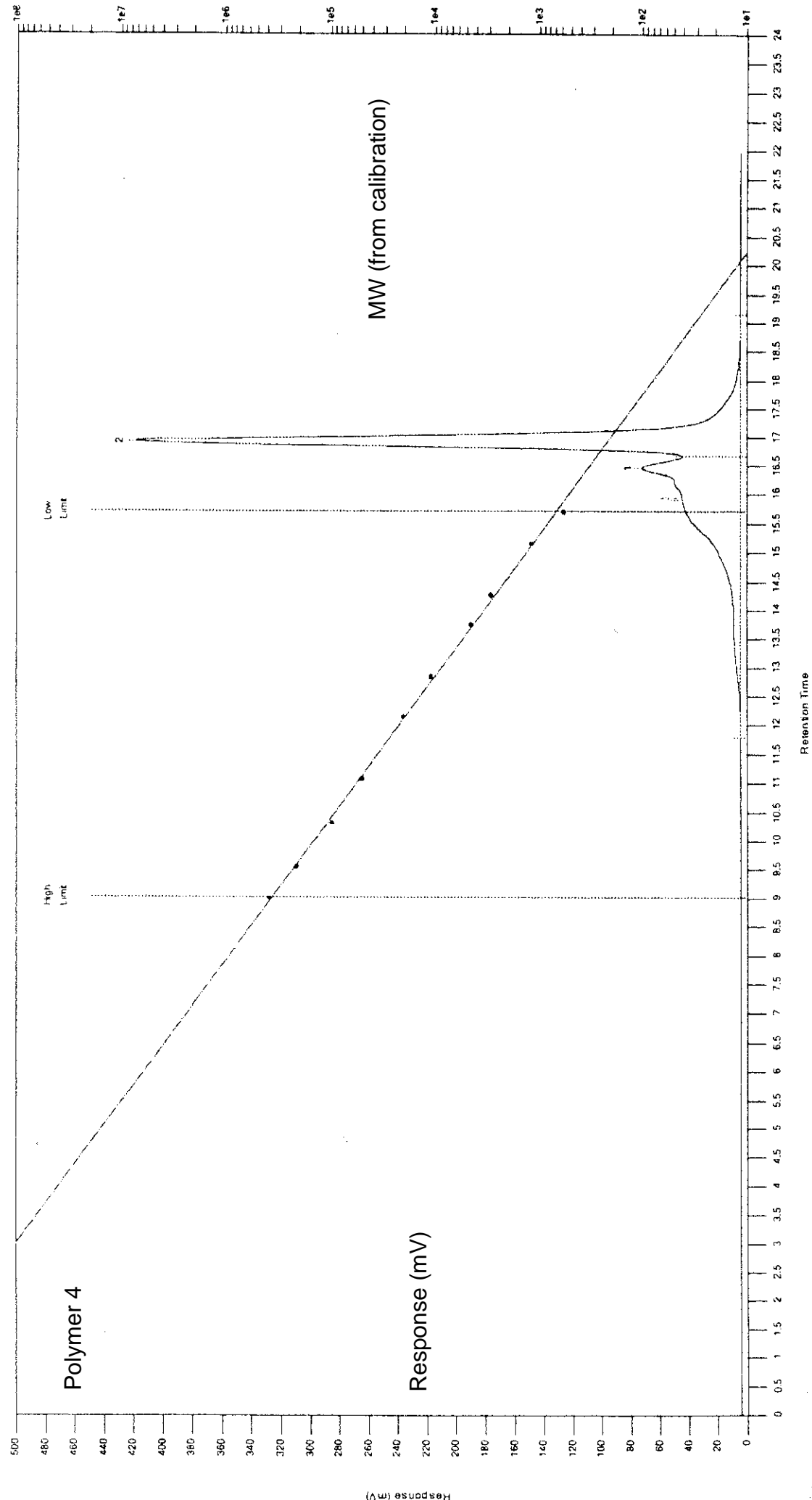


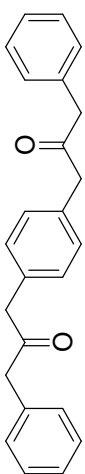




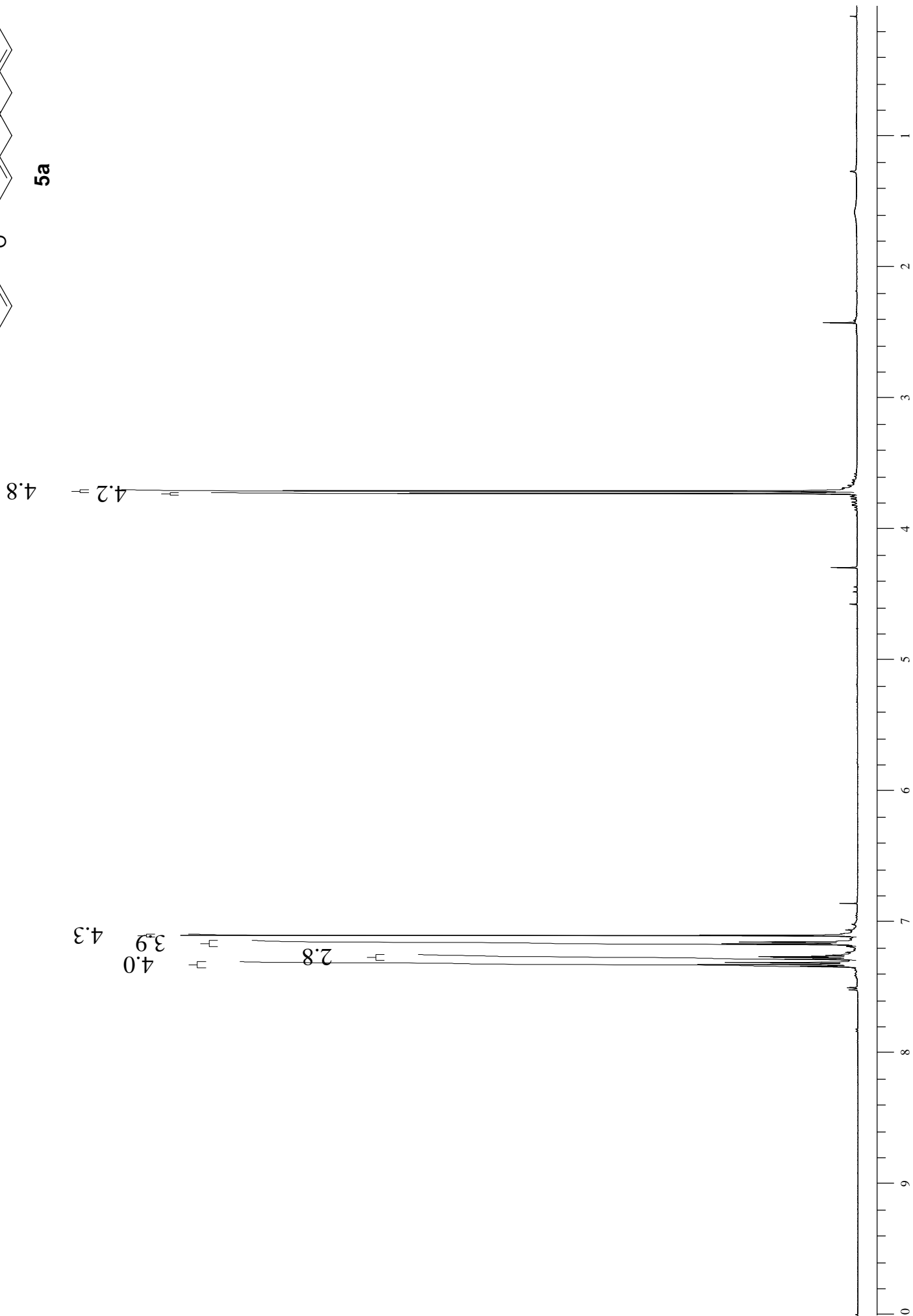


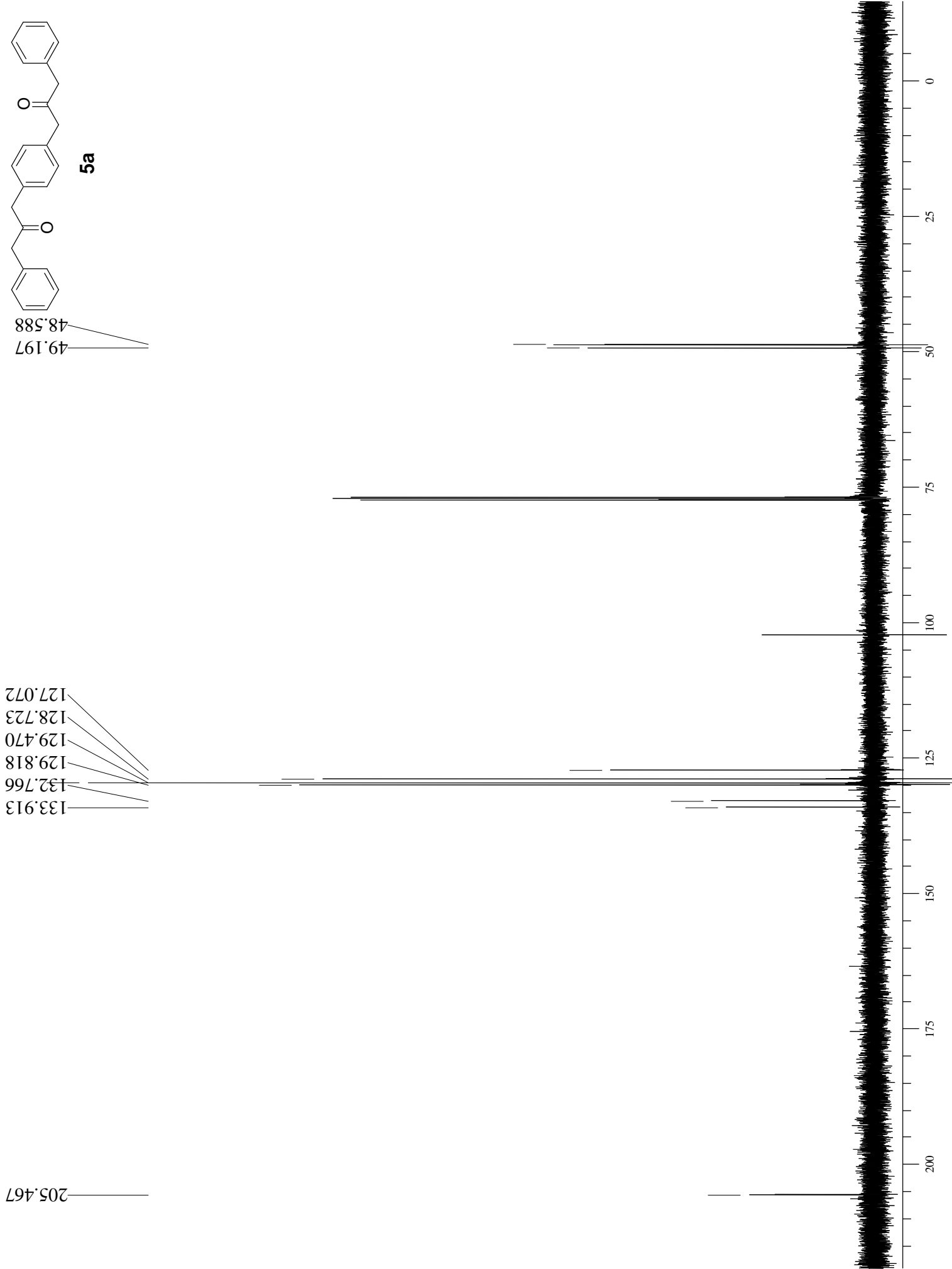


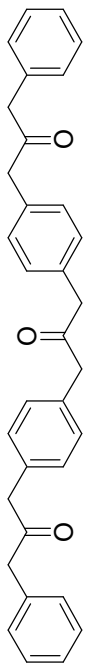




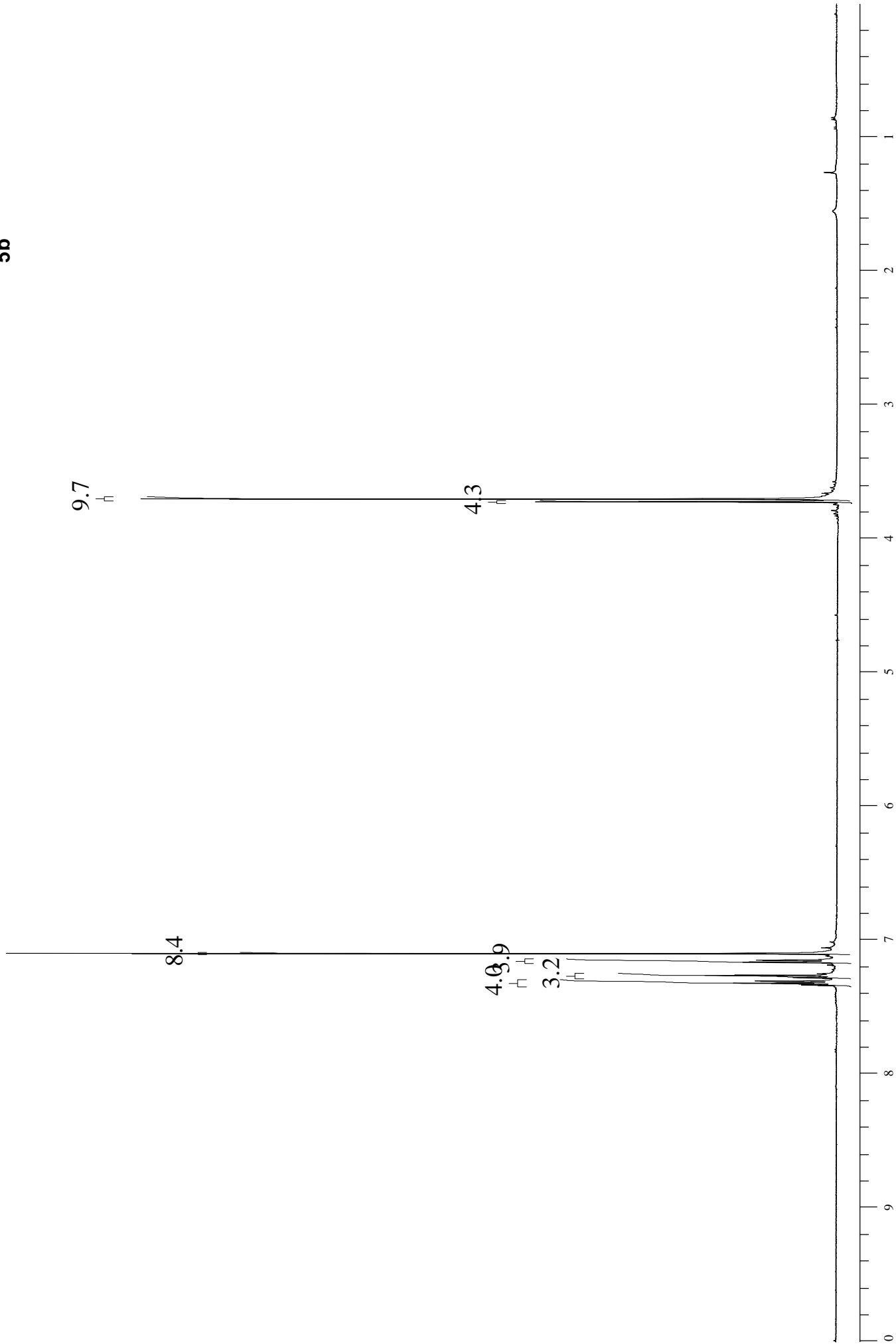
**5a**



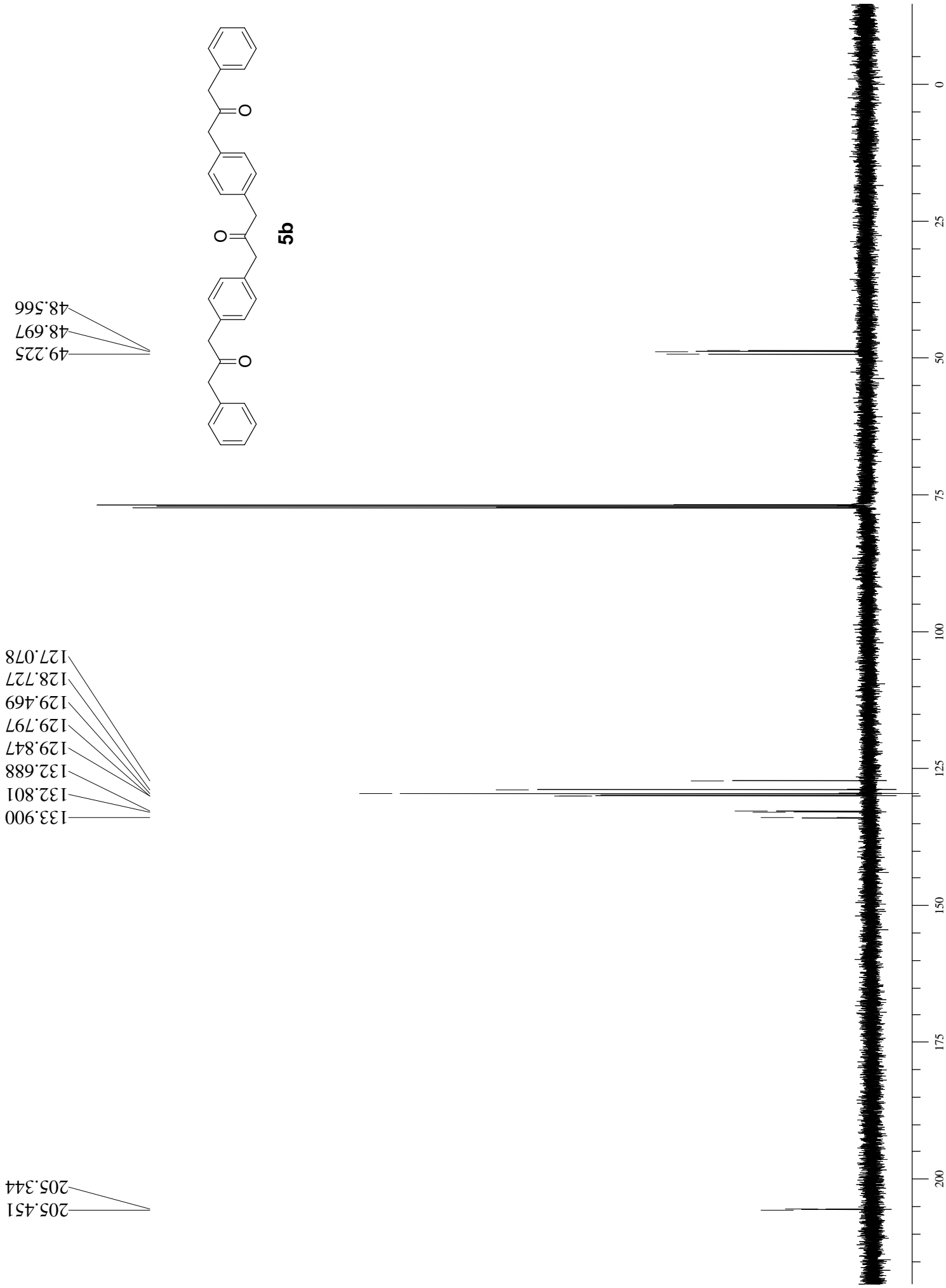


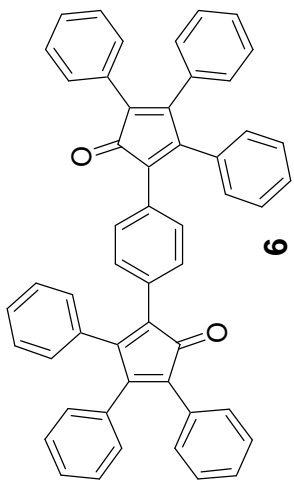


**5b**









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