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Electronic supplementary information for

Synthesis of Helically π-Stacked Poly(quinolylene-2,3-methylene)s with Anthracene Derivatives at the Chain-End: Intramolecular Energy Transfer Based on the π-Stacked Architecture

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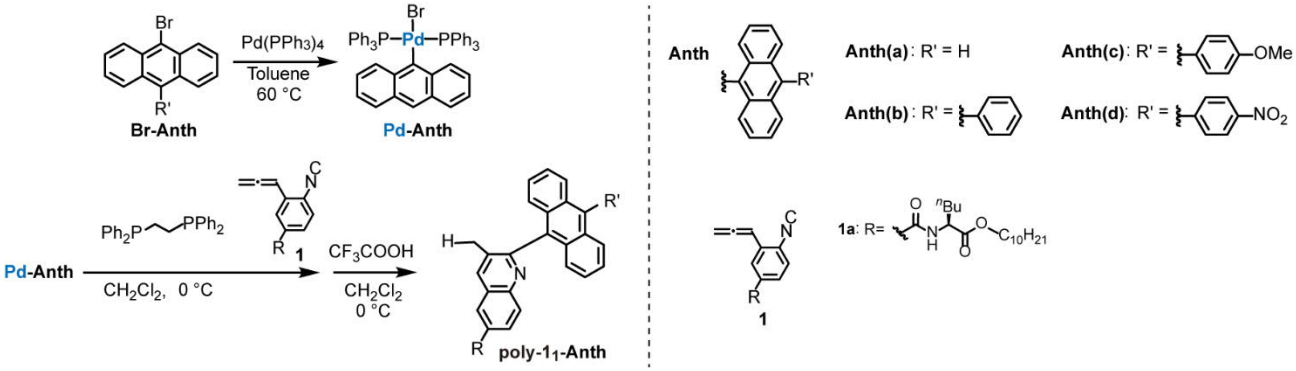
1. Experimental Section

General.

All reactions were carried out under an Ar atmosphere whereas the work-up was performed in air. NMR spectra were recorded on JEOL JNM-ECS400 and JEOL JNM-ECA500 spectrometers. In ^{1}H and ^{13}C NMR, $SiMe_4$ was used as an internal standard, and an external 85% H_3PO_4 reference was used for ^{31}P NMR. The number-average molar mass (M_n) and the molar mass dispersity (M_w/M_n) of the polymers were determined at 40 °C by size exclusion chromatography (SEC) using a SHIMADZU LC-10AS, SPD-10AD UV-vis detector, and CTO-10A column oven equipped with three SEC columns SHODEX GPC KF-805L using THF as an eluent, and calibrated against standard PS samples. CD spectra were obtained by JASCO J-720WO. UV-vis spectra were obtained by SHIMADZU UV 3100PC. Fluorescence spectra were measured by HORIBA FluoroMax-4. Absolute quantum yield was measured by HAMAMATSU C9920-02. ESI-HRMS measurements were carried out on Thermo Fisher Scientific LTQ-Orbitrap XL.

Materials

All solvents used for reactions were passed through purification columns just before use. Other chemicals reagents which are commercially available were used without further purification. Monomer **1** was prepared as reported previously.[1-2]



<u>Standard Method of model compound (poly-1a$_1$-Anth(a-d)).</u>

A solution of $Pd(PPh_3)_4$ (0.3 mmol, 1.0 eq.) and **Br-Anth** (0.3 mmol, 1.0 eq.) in toluene (3.0 mL) was stirred at 60 °C for overnight. The reaction mixture was concentrated under reduced pressure. The residue and 1,3-bis(diphenylphosphino)etane (0.6 mmol, 2.0 eq.) were dissolved with CH_2Cl_2 (15.0 mL) stirred for 5 min at 0 °C. After then, the mixture was added **1a** (0.2 mmol, 0.7 eq.) in CH_2Cl_2 (2.0 mL) at 0 °C. The mixture was stirred at 0 °C. After stirring for 30 min, the reaction mixture was concentrated under reduced pressure. $NaBH_4$ (3.0 mmol, 10.0 eq.) was added, dissolved with THF (8.0 mL) and stirred at 0 °C for 30 min. The reaction mixture was neutralized with sat $NaHCO_3$ aq, and extracted with AcOEt. The organic layer was dried over with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/AcOEt = 10/1).

Synthesis of **poly-1a$_1$-Anth(a)**

This compound was prepared from **Br-Anth(a)** (24.8 mg, 0.10 mmol) to give a yellow solid (31.8 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.59 (s, 1H, Ar), 8.46 (d, 1H, *J* = 1.7 Hz, Ar), 8.28 (s, 1H, Ar), 8.22 (d, 1H, *J* = 8.8 Hz, Ar), 8.09 (d, 3H, *J* = 8.7 Hz, Ar), 7.50-7.45 (m, 2H, Ar), 7.34-7.31 (m, 4H, Ar), 6.90 (d, 1H, *J* = 7.7 Hz, N*H*), 4.92 (q, 1H, *J* = 6.1 Hz, C*H*CH_2), 4.25-4.20 (m, 2H, OC*H*$_2$), 2.07 (s, 3H, Ar-C*H*$_3$), 2.05 (m, 1H, CHC*H*$_2$$(CH_2)_2CH_3$), 1.90 (m, 1H, CHC*H*$_2$$(CH_2)_2CH_3$), 1.70 (m, 2H, OCH_2C*H*$_2$$(CH_2)_7CH_3$), 1.42-1.20 (m, 18H, OCH_2CH_2(C*H*$_2$$)_7CH_3$, $CHCH_2$(C*H*$_2$$)_2CH_3$), 0.94 (t, 3H, *J* = 7.1 Hz, $CH(CH_2)_3$C*H*$_3$), 0.88 (t, 3H, *J* = 7.0 Hz, $O(CH_2)_9$C*H*$_3$). HRMS (ESI): Calcd for $C_{41}H_{48}N_2O_3$ ($[M+Na]^+$): m/z 639.3557, Found: m/z 639.3555.

Synthesis of **poly-1a$_1$-Anth(b)**

This compound was prepared from **Br-Anth(b)** (102.3 mg, 0.30 mmol) to give a yellow solid (57.7 mg, 28%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.48 (d, 1H, *J* = 2.0 Hz, Ar), 8.31 (s, 1H, Ar), 8.24 (d, 1H, *J* = 8.7 Hz, Ar), 8.10 (dd, 1H, *J* = 8.9, 1.8 Hz, Ar), 7.74-7.71 (m, 2H, Ar), 7.65-7.53 (m, 4H, Ar), 7.43-7.31 (m, 7H, Ar), 6.91 (d, 1H, *J* = 7.4 Hz, N*H*), 4.93 (q, 1H, *J* = 6.1 Hz, C*H*CH_2), 4.25-4.20 (m, 2H, OC*H*$_2$), 2.18 (s, 3H, Ar-C*H*$_3$), 2.05 (m, 1H, CHC*H*$_2$$(CH_2)_2CH_3$), 1.90 (m, 1H, CHC*H*$_2$$(CH_2)_2CH_3$), 1.71 (m, 2H, OCH_2C*H*$_2$$(CH_2)_7CH_3$), 1.44-1.20 (m, 18H, OCH_2CH_2(C*H*$_2$$)_7CH_3$, $CHCH_2$(C*H*$_2$$)_2CH_3$), 0.95 (t, 3H, *J* = 7.1 Hz, $O(CH_2)_9$C*H*$_3$), 0.89 (t, 3H, *J* = 7.0 Hz, $CH(CH_2)_3$C*H*$_3$). HRMS (ESI): Calcd for $C_{47}H_{52}N_2O_3$ ($[M+Na]^+$): m/z 715.3870, Found: m/z 715.3868.

Synthesis of **poly-1a$_1$-Anth(c)**

This compound was prepared from **Br-Anth(c)** (113.1 mg, 0.30 mmol) to give a yellow solid (79.3 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.48 (s, 1H, Ar), 8.31 (s, 1H, Ar), 8.24 (d, 1H, *J* = 8.5 Hz, Ar), 8.10 (d, 1H, *J* = 8.6, Ar), 7.80 (m, 2H, Ar), 7.47 (m, 2H, Ar), 7.35-7.31 (m, 7H, Ar), 7.16 (m, 2H, Ar), 7.04 (m, 1H, Ar), 6.91 (d, 1H, *J* = 7.8 Hz, N*H*), 4.92 (q, 1H, *J* = 6.1 Hz, C*H*CH_2), 4.24-4.22 (m, 2H, OC*H*$_2$), 3.98 (s, 3H, OC*H*$_3$), 2.17 (s, 3H, Ar-C*H*$_3$), 2.07 (m, 1H, CHC*H*$_2$$(CH_2)_2CH_3$), 1.90 (m, 1H, CHC*H*$_2$$(CH_2)_2CH_3$), 1.71 (m, 2H, OCH_2C*H*$_2$$(CH_2)_7CH_3$), 1.41-1.25 (m, 18H, OCH_2CH_2(C*H*$_2$$)_7CH_3$, $CHCH_2$(C*H*$_2$$)_2CH_3$), 0.95 (t, 3H, *J* = 7.1 Hz, $O(CH_2)_9$C*H*$_3$), 0.89 (t, 3H, *J* = 7.0 Hz, $CH(CH_2)_3$C*H*$_3$). HRMS (ESI): Calcd for $C_{48}H_{54}N_2O_4$ ($[M+Na]^+$): m/z 745.3976, Found: m/z 745.3973.

Synthesis of **poly-1a$_1$-Anth(d)**

This compound was prepared from **Br-Anth(d)** (75.6 mg, 0.20 mmol) to give an orange solid (36.3 mg, 26%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.53-8.49 (m, 3H, Ar), 8.33 (s, 1H, Ar), 8.24 (d, 1H, *J* = 8.1 Hz, Ar), 8.11 (d, 1H, *J* = 8.6 Hz, Ar), 7.77 (d, 1H, *J* = 8.0 Hz, Ar), 7.64-7.58 (m, 3H, Ar), 7.39-7.37 (m, 5H, Ar), 6.92 (d, 1H, *J* = 7.6 Hz, N*H*), 4.93 (q, 1H, *J* = 6.1 Hz, C*H*CH_2), 4.32-4.20 (m, 2H, OC*H*$_2$), 2.18 (s, 3H, Ar-C*H*$_3$), 2.04 (m, 1H, CHC*H*$_2$$(CH_2)_2CH_3$), 1.90 (m, 1H, CHC*H*$_2$$(CH_2)_2CH_3$), 1.71 (m, 2H, OCH_2C*H*$_2$$(CH_2)_7CH_3$), 1.45-1.28 (m, 18H, OCH_2CH_2(C*H*$_2$$)_7CH_3$, $CHCH_2$(C*H*$_2$$)_2CH_3$), 0.95 (t, 3H, *J* = 7.1 Hz, $O(CH_2)_9$C*H*$_3$), 0.91 (t, 3H, *J* = 7.0 Hz, $CH(CH_2)_3$C*H*$_3$). HRMS (ESI): Calcd for $C_{47}H_{51}N_3O_5$ ($[M+Na]^+$): m/z 760.3721, Found: m/z 760.3719.

2. CD, UV, and emission spectra

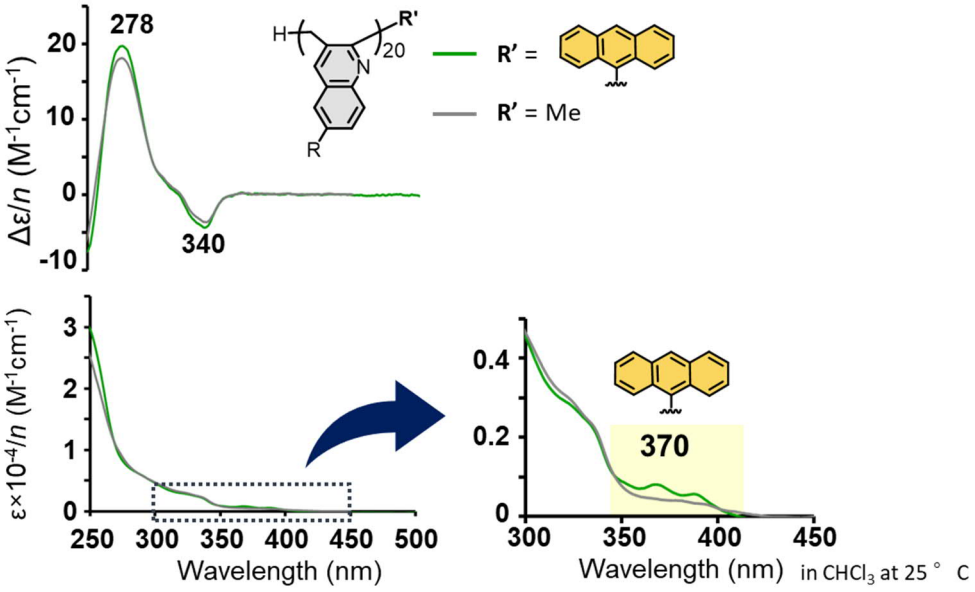


Fig S1. CD and UV spectra of **poly-1a$_{20}$-Anth(a)** (green line) and **poly-1a$_{20}$-Me** (gray line).

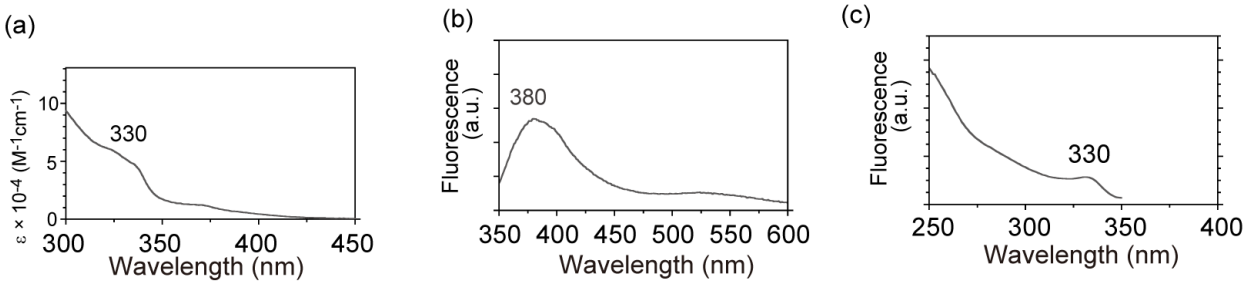


Fig S2. (a) UV, (b) emission excited at 330 nm, and (c) excitation at 380 nm spectra in $CHCl_3$ of **poly-1a$_{20}$-Me**.

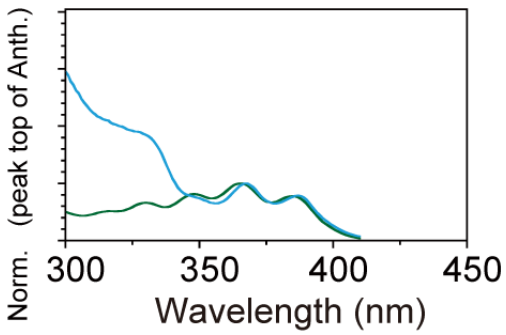


Fig S3. Excitation spectra of **poly-1a$_{20}$-Anth(a)** (blue line) and **poly-1a$_1$-Anth(a)** (green line) at 430 nm in $CHCl_3$. The spectra were normalized by the peak top of anthracenyl group.

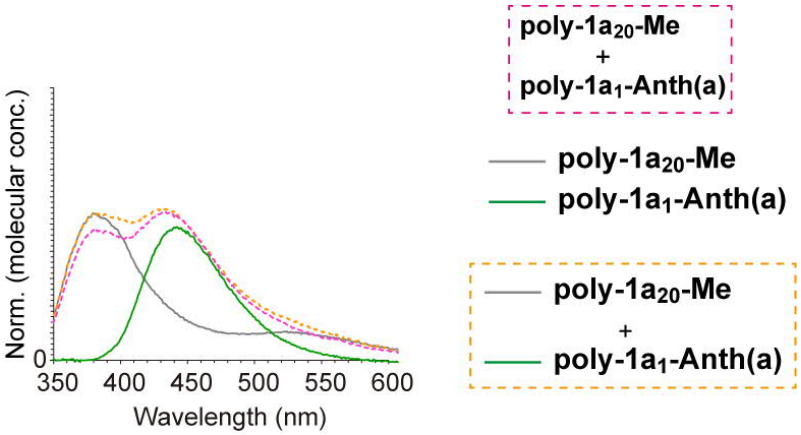


Fig S4. Emission spectra of **poly-1a$_{20}$-Me** (grey line), **poly-1a$_1$-Anth(a)** (green line), and a mixture of **poly-1a$_{20}$-Me** and **poly-1a$_1$-Anth(a)** (dashed pink line) in $CHCl_3$ at excited 330 nm. The sum of the spectra of **poly-1a$_{20}$-Me** and **poly-1a$_1$-Anth(a)** (dashed orange line). The spectra were normalized by molecular concentration.

In our previous study,[3] when the π-stacking structure was collapsed, the absorption band at 315 and 329 nm was appeared. Compared with the UV spectra **poly-1a$_{20}$-Anth(a)** (green line) and **poly-1c$_{20}$-Anth(a)** (purple line), the UV spectrum of **poly-1b$_{20}$-Anth(a)** (pink line) shows a weaker absorption band at 316 and 330 nm originated from aromatic chromophores without π-stacking conformation, which is in agreement with previous results of **poly-1$_{20}$-Me** bearing methyl group at α-chain end. These results suggested that **poly-1b$_{20}$-Anth(a)** forms an incomplete π-stacked structure.

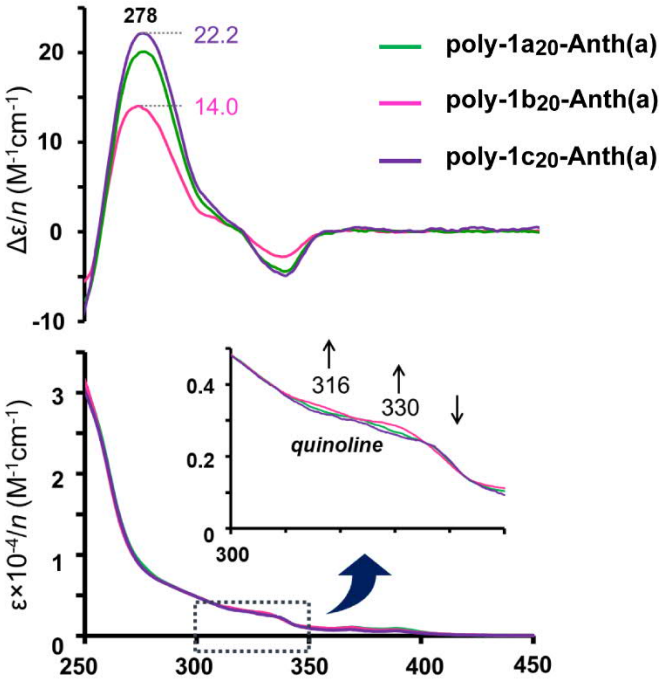


Fig S5. CD and UV spectra of poly **poly-1a$_{20}$-Anth(a)** (green line), **poly-1b$_{20}$-Anth(a)** (pink line) and **poly-1c$_{20}$-Anth(a)** (purple line).

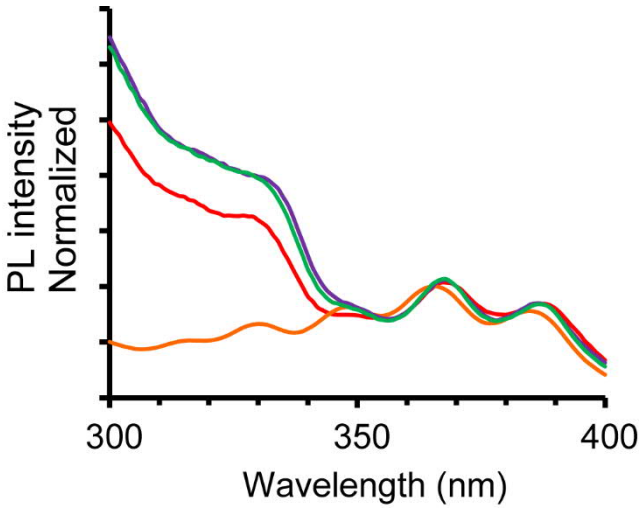


Fig S6. Excitation spectra of poly **poly-1a$_{20}$-Anth(a)** (green line), **poly-1b$_{20}$-Anth(a)** (red line), **poly-1c$_{20}$-Anth(a)** (purple line) and **poly-1a$_1$-Anth(a)** (orange line) excited at 430 nm in $CHCl_3$.

2-2 Determination of Energy Transfer Efficiency

The energy transfer efficiency (*E*) was determined using photoluminescent quantum yield (Φ_{PL}) and molar absorption coefficients (ε) of **poly-1$_n$-Anth**, **poly-1$_n$-Me**, and **poly-1$_1$-Anth** (model), according to the reported formula,[3] as described below. The calculation method of energy transfer efficiency of **poly-1a$_{20}$-Anth(a)** using the Φ_{PL} and ε derived form **poly-1a$_{20}$-Anth(a)**, **poly-1a$_{20}$-Me** and **poly-1a$_1$-Anth(a)** is shown below.

$$\Phi_{poly\text{-}Anth} = \{(1-E)\times(\varepsilon_{poly\text{-}Me}/\varepsilon_{poly\text{-}Anth})\times\Phi_{poly\text{-}Me}\}+\{E\times(\varepsilon_{poly\text{-}Me}/\varepsilon_{poly\text{-}Anth})\times\Phi_{model}\}$$
$$+\{(\varepsilon_{model}/\varepsilon_{poly\text{-}Anth})\times\Phi_{model}\}$$

poly-1a$_{20}$-Anth(a): $\Phi_{poly\text{-}anth}$ = 5.5%, $\Phi_{poly\text{-}Me}$ = 2.3%, Φ_{model} = 10.1%, $\varepsilon_{poly\text{-}Me}/\varepsilon_{poly\text{-}anth}$ = 0.88, $\varepsilon_{model}/\varepsilon_{poly\text{-}anth}$ =0.12

5.5 = {(1-***E***)×(0.88)×2.3}+{***E*** × (0.88) × 10.1}+{(0.12) × 10.1}

E = 34%

3. MS Spectrum

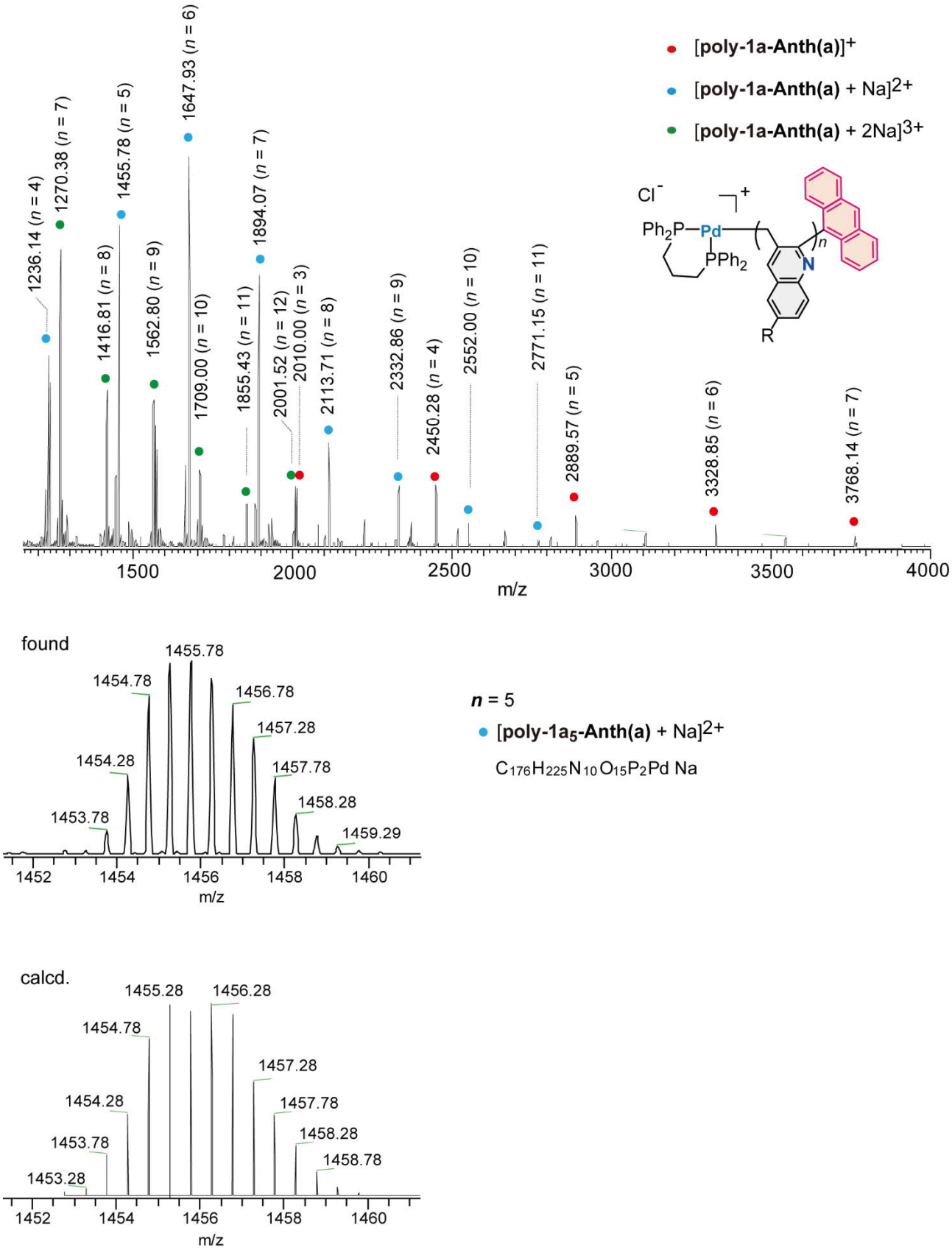


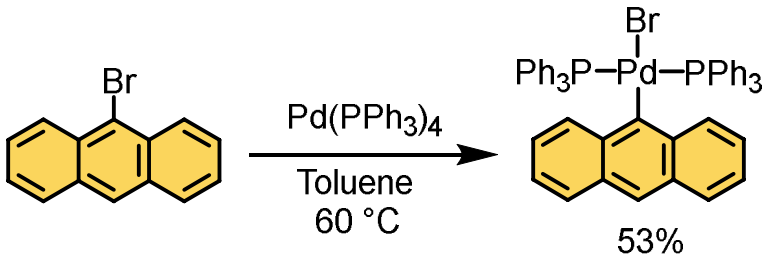
Fig S7. ESI-Orbitrap MS spectrum of **poly-1a$_7$-Anth(a)** ($M_{n(SEC)}$ = 2100, M_w/M_n = 1.12; [**1a**]/[**Pd-Anth(a)**] = 7) in MeOH/CH_2Cl_2 (= 1/1). The Expand spectra of **poly-1a$_5$-Anth(a)** (z = 2).

3. References

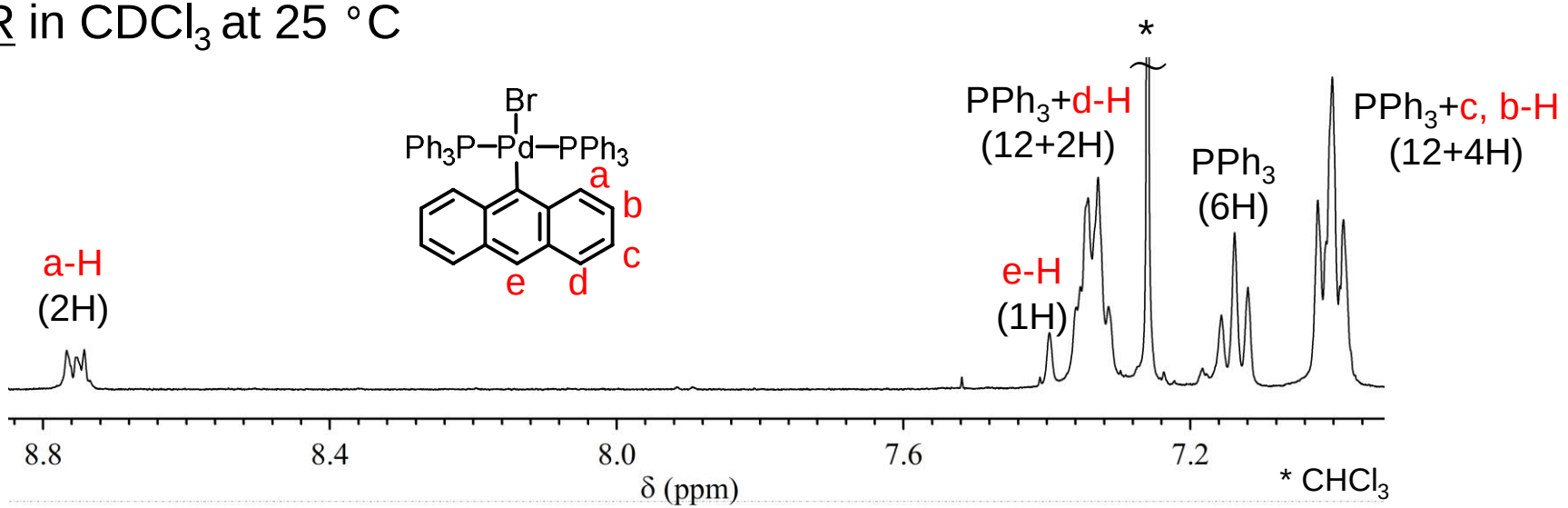
1.Kanbayashi, N.; Kataoka, Y.; Okamura, T.; Onitsuka, K., Stability Enhancement of a π-Stacked Helical Structure Using Substituents of an Amino Acid Side Chain: Helix Formation via a Nucleation–Elongation Mechanism. *J. Am. Chem. Soc.* **2022,** *144* (13), 6080-6090.

2.Kataoka, Y.; Kanbayashi, N.; Fujii, N.; Okamura, T.; Haino, T.; Onitsuka, K., Construction of Helically Stacked π-Electron Systems in Poly(quinolylene-2,3-methylene) Stabilized by Intramolecular Hydrogen Bonds. *Angew. Chem. Int. Ed.* **2020,** *59* (26), 10286-10291.

3. T. Nishikawa, Y. Nagata and M. Suginome, Poly(quinoxaline-2,3-diyl) as a Multifunctional Chiral Scaffold for Circularly Polarized Luminescent Materials: Color Tuning, Energy Transfer, and Switching of the CPL Handedness. *ACS Macro Lett.*, **2017,** *6*, 431-435.



^{1}H NMR in $CDCl_3$ at 25 °C



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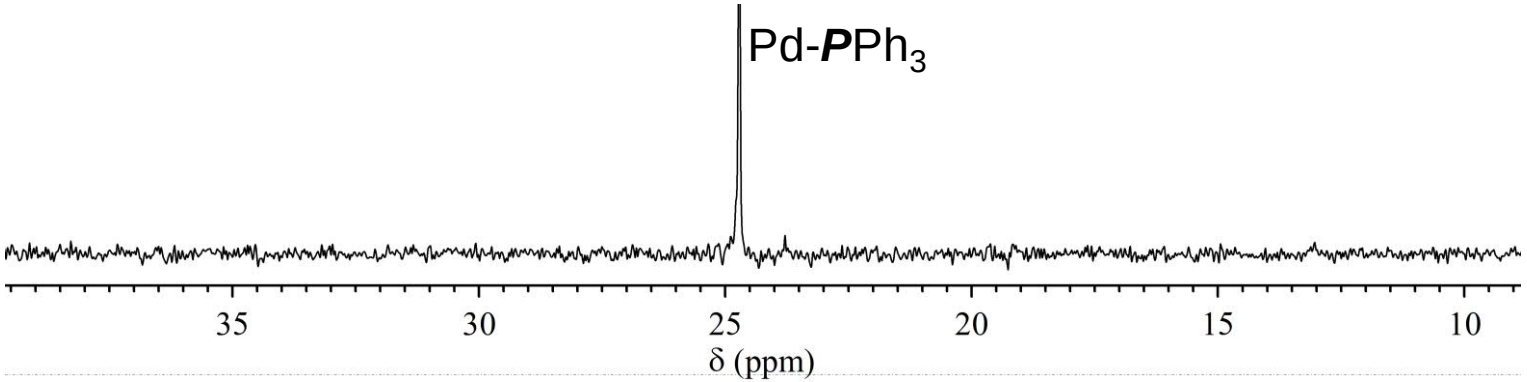

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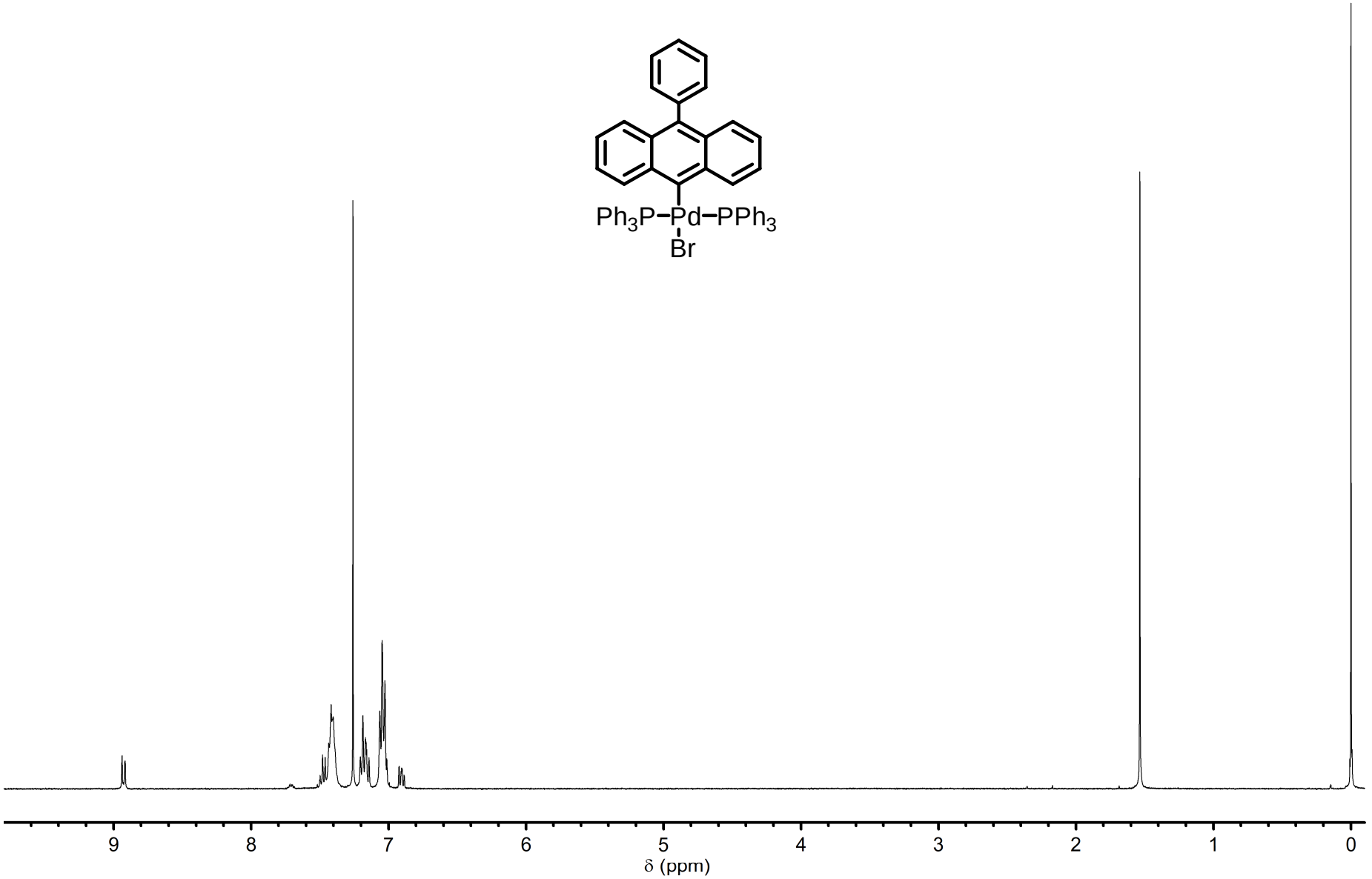
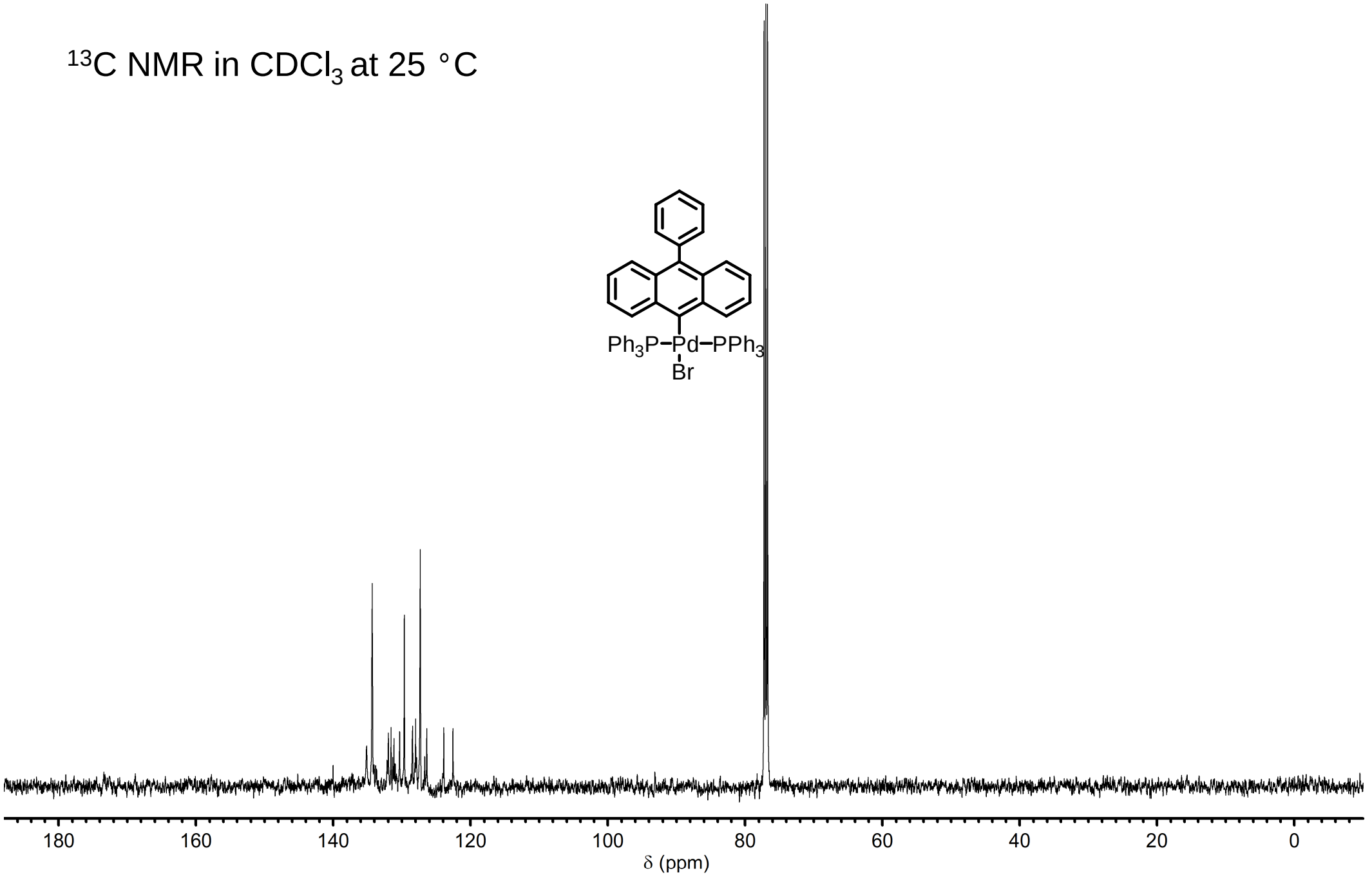
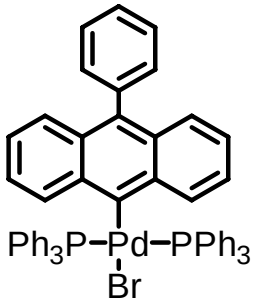
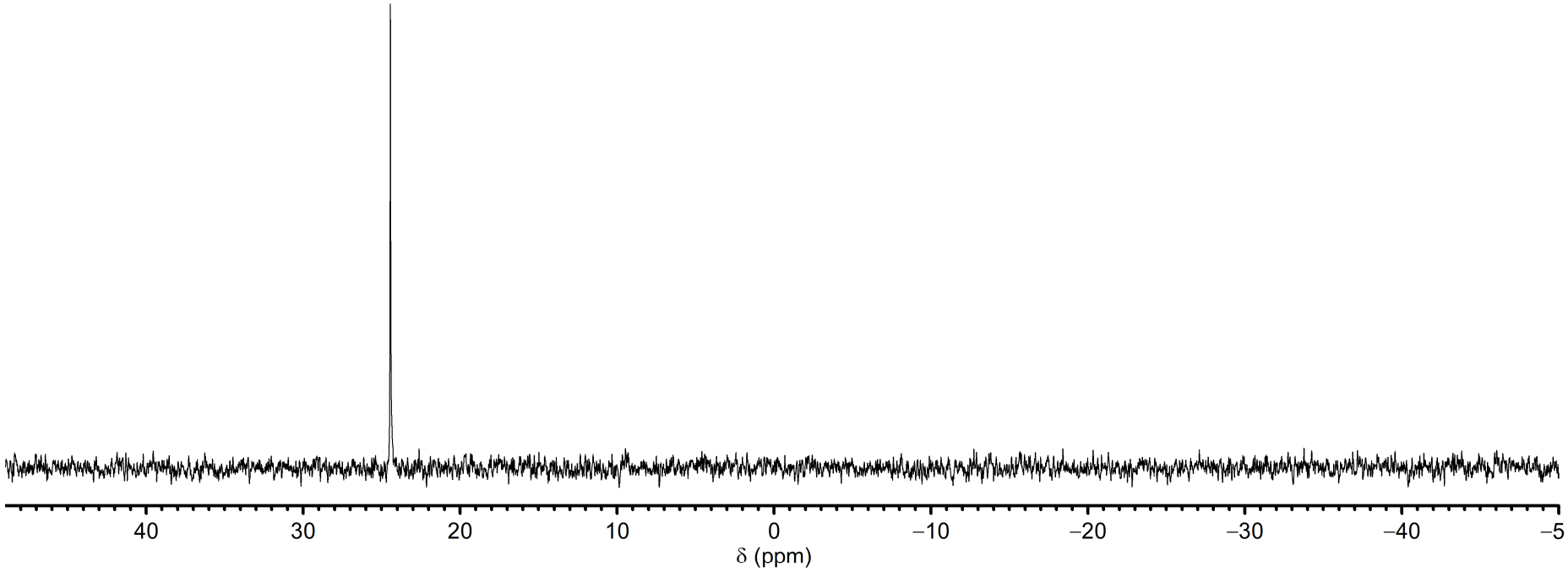


^{13}C NMR in $CDCl_3$ at 25 °C



^{31}P NMR in $CDCl_3$ at 25 °C





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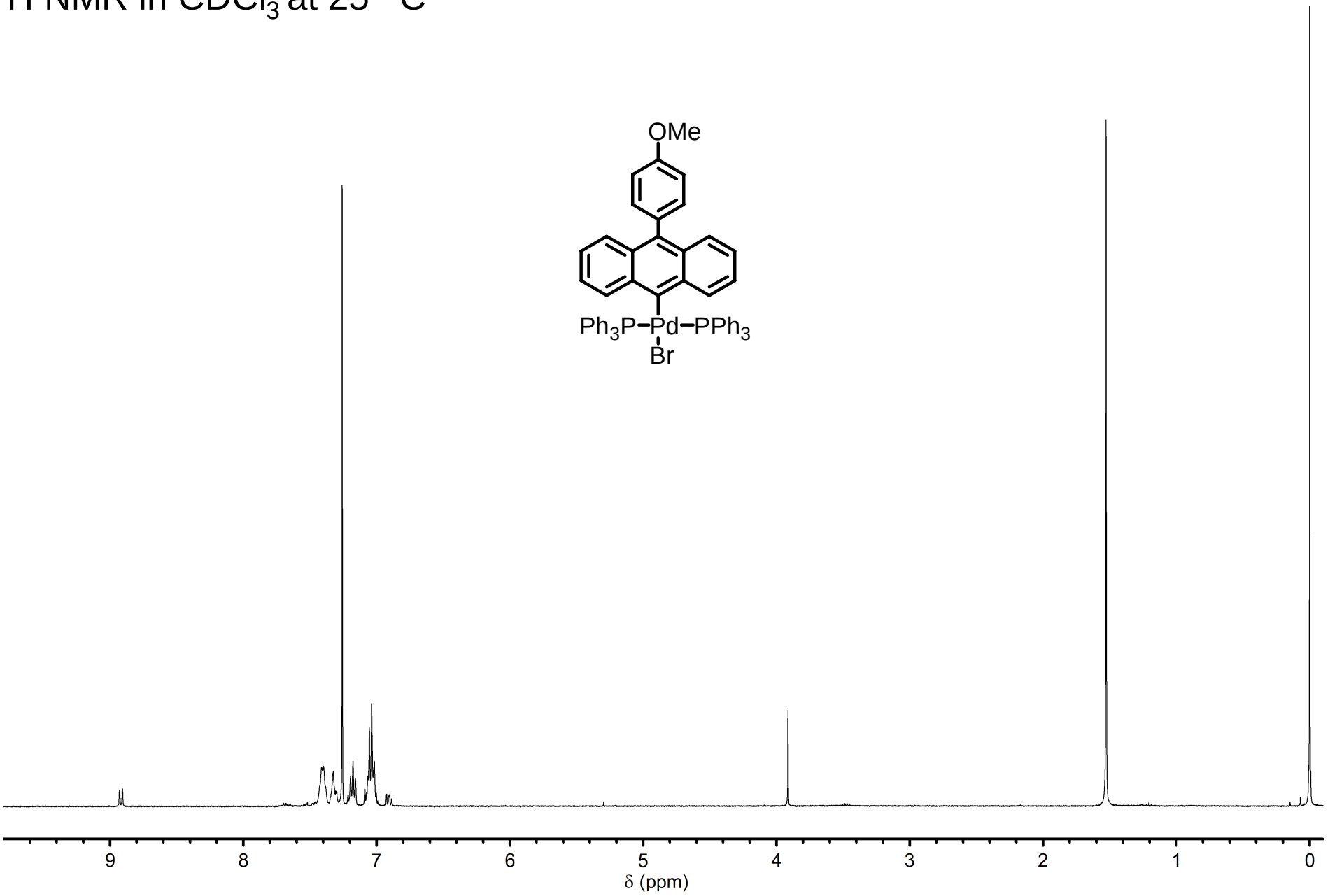

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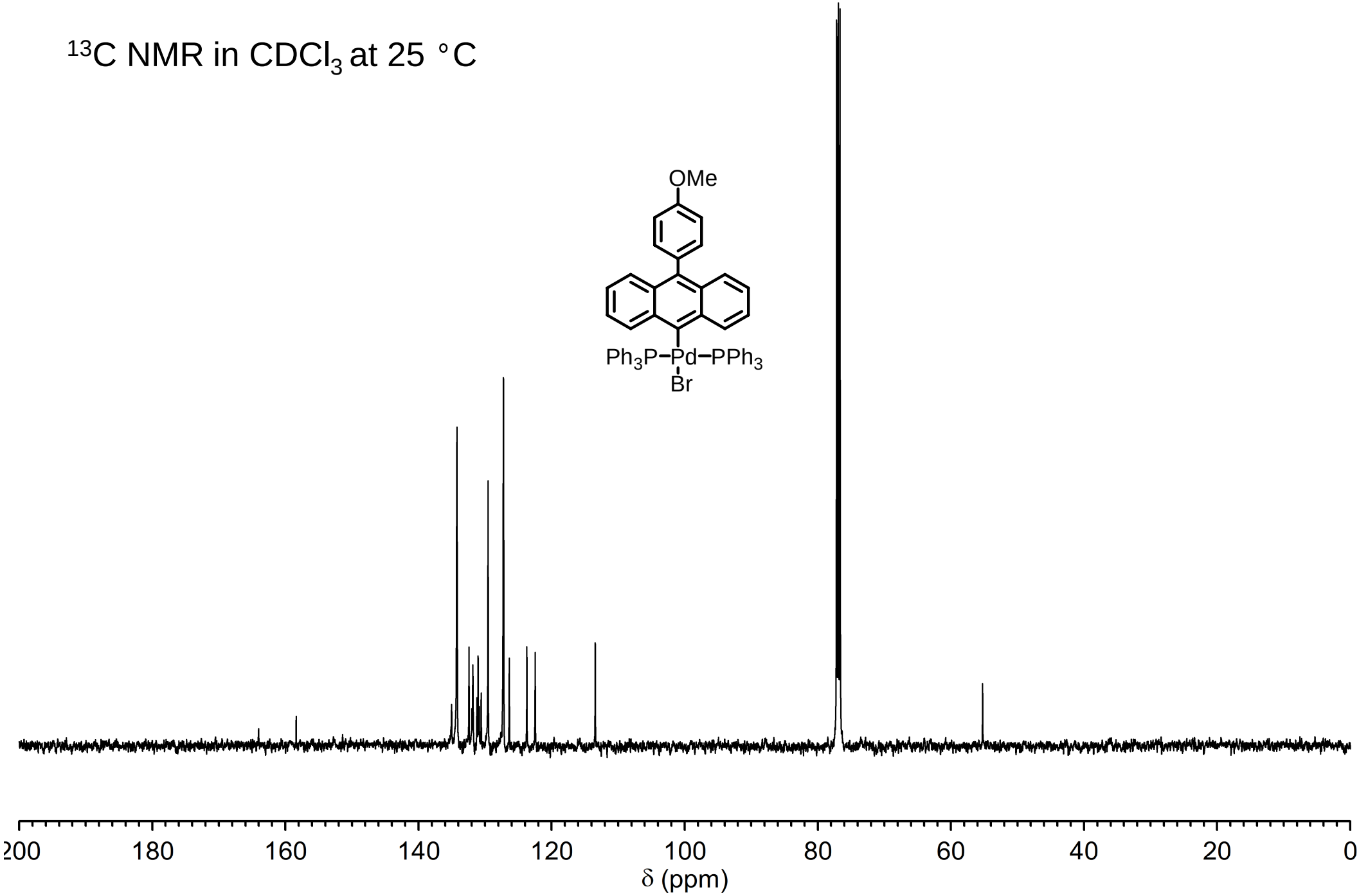
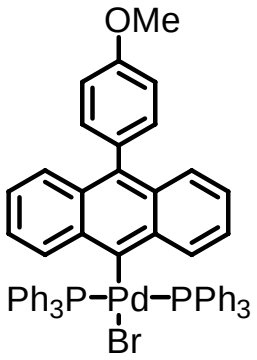
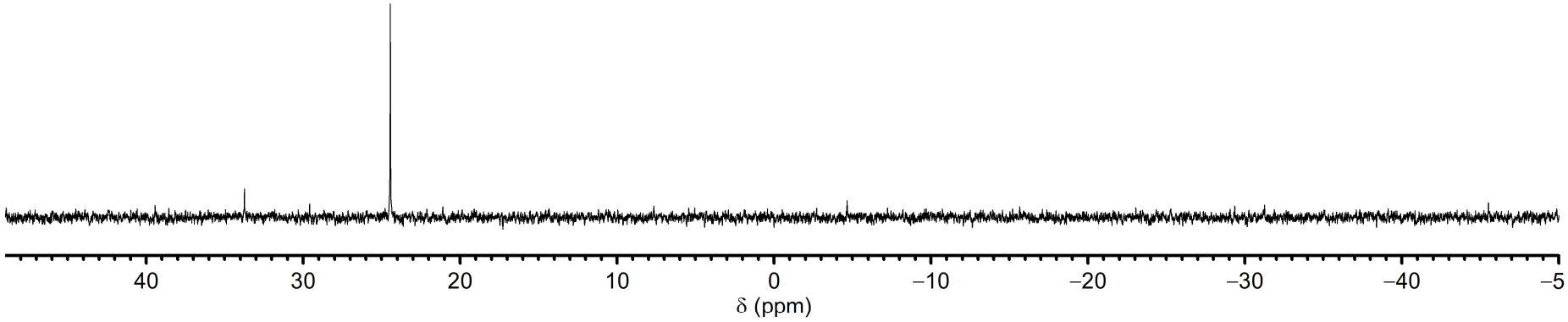
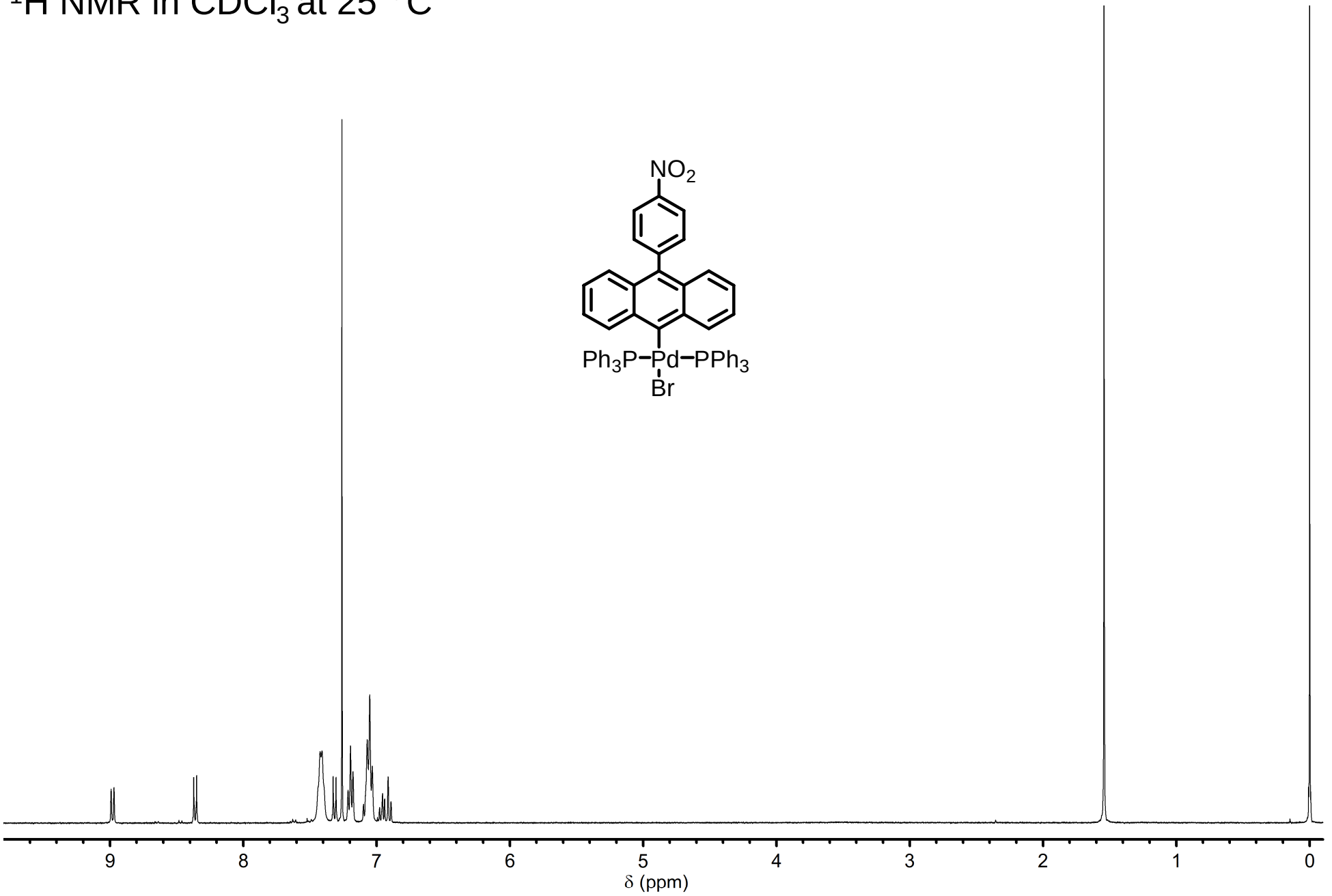


^{31}P NMR in $CDCl_3$ at 25 °C

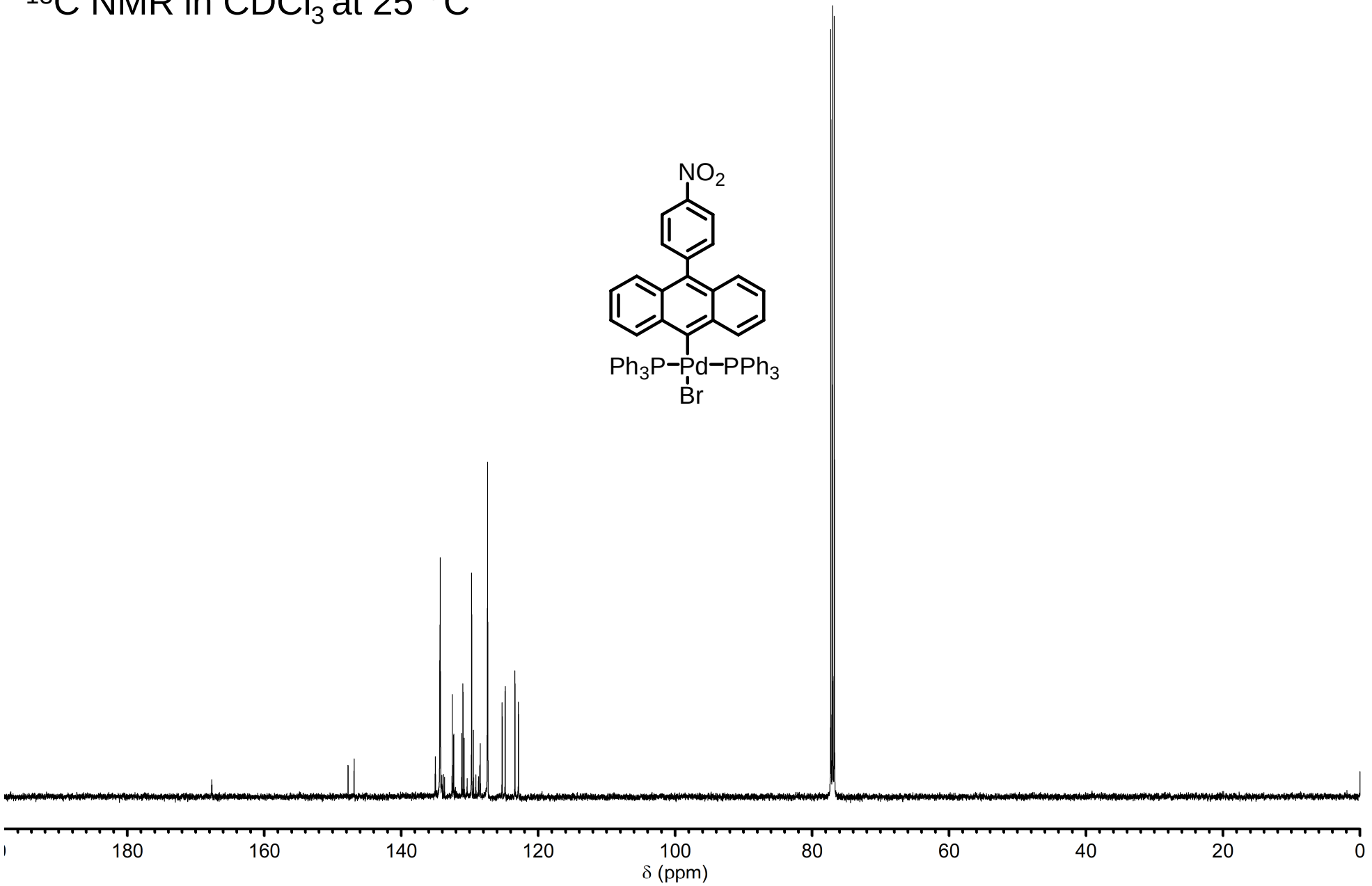




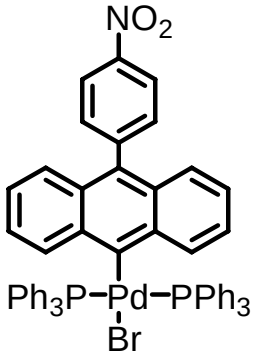
^{1}H NMR in $CDCl_3$ at 25 °C

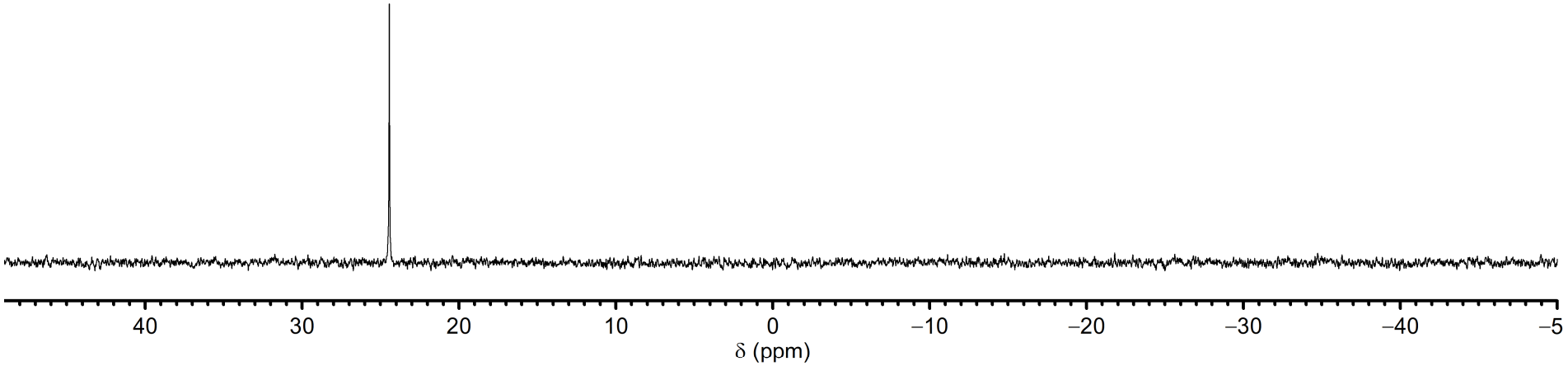


^{13}C NMR in $CDCl_3$ at 25 °C



^{31}P NMR in $CDCl_3$ at 25 °C





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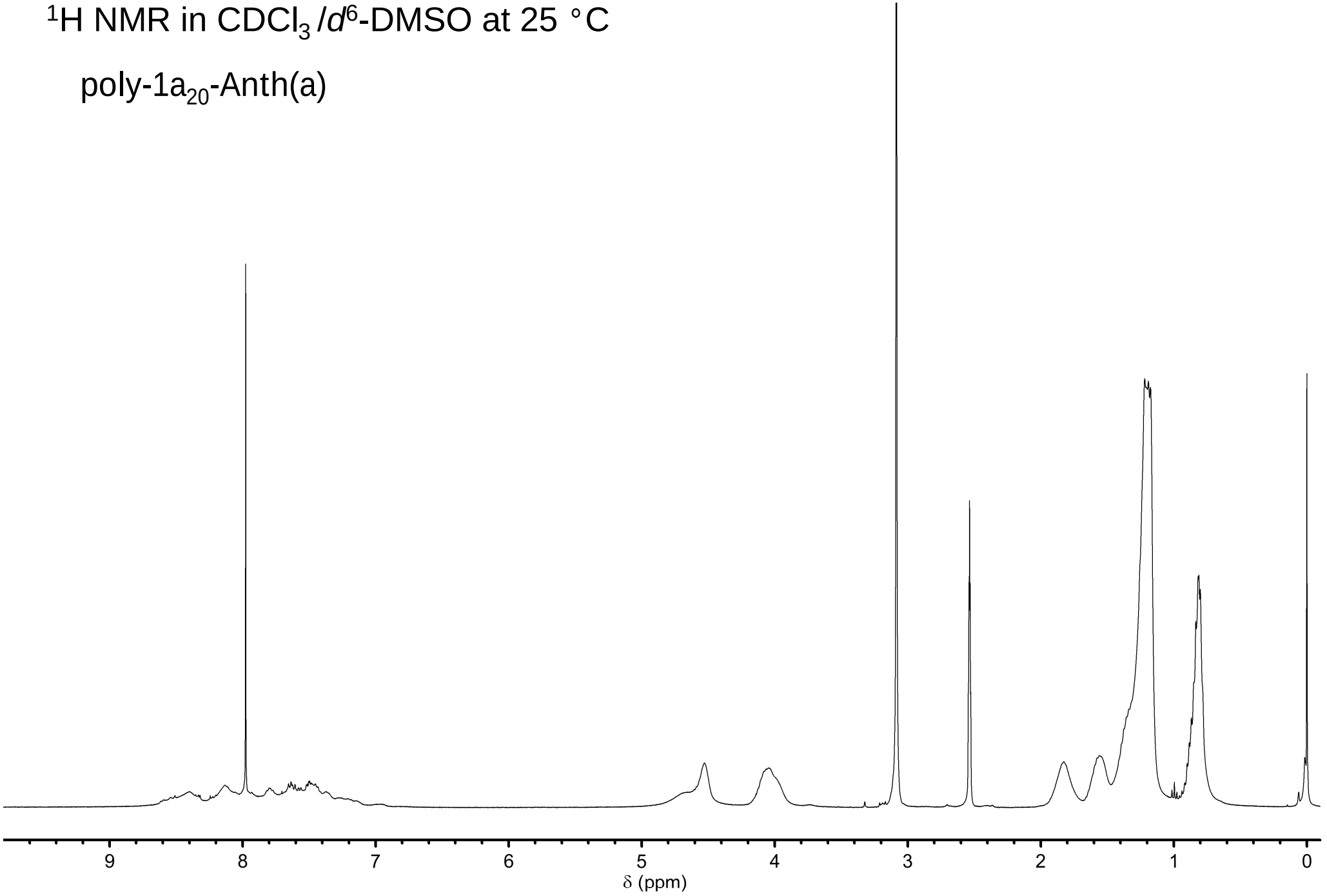
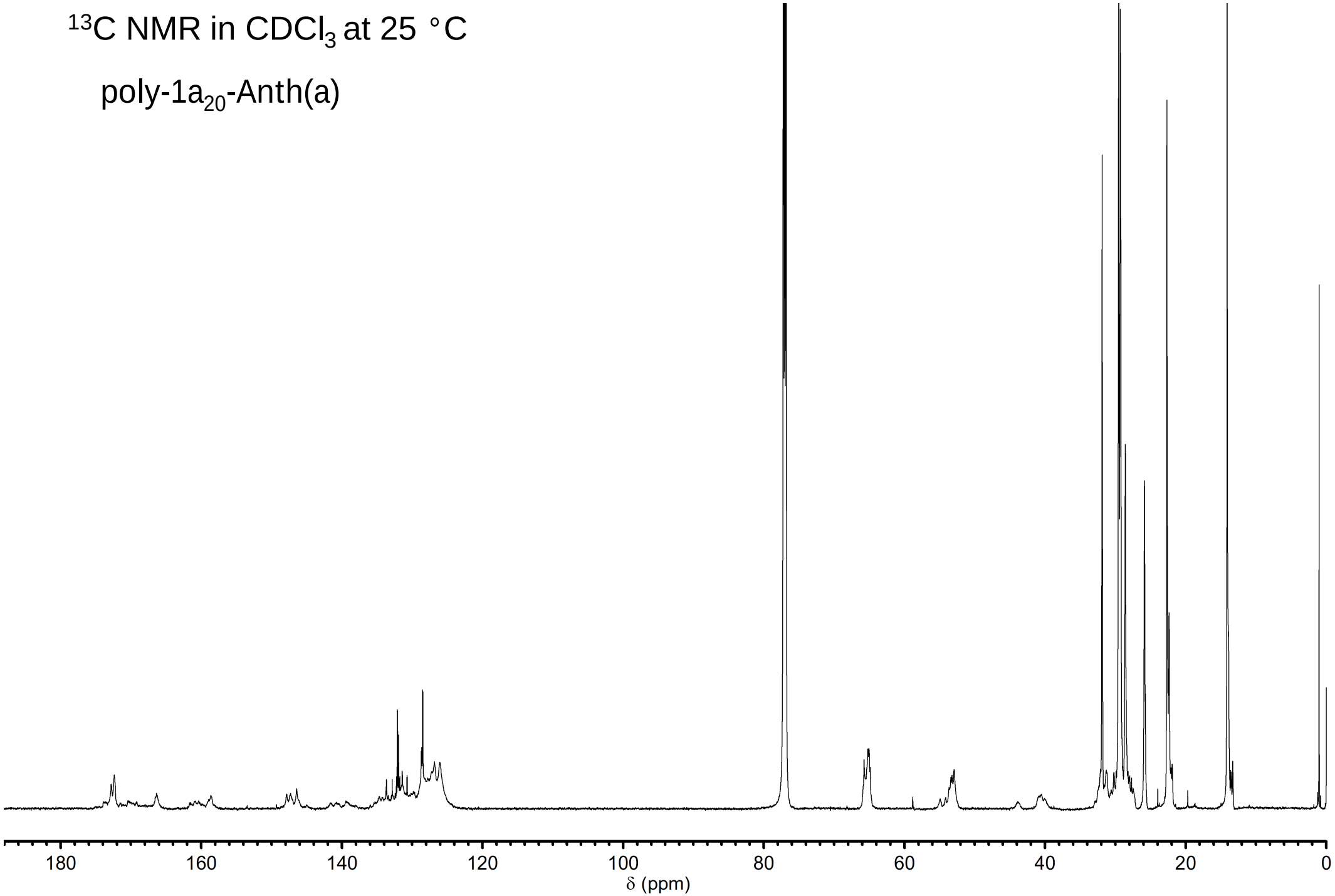
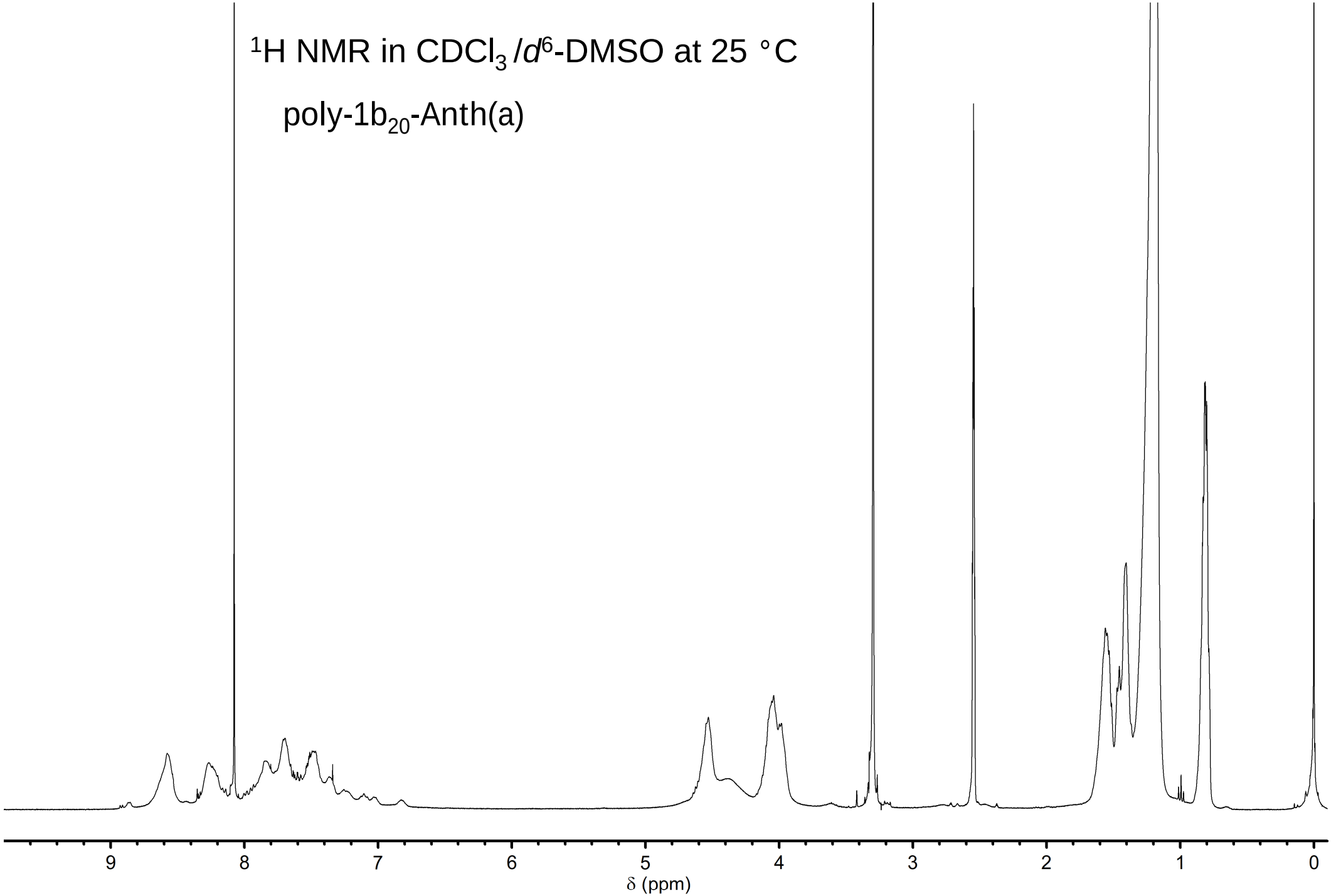
poly-1a$_{20}$-Anth(a)



^{13}C NMR in $CDCl_3$ at 25 °C

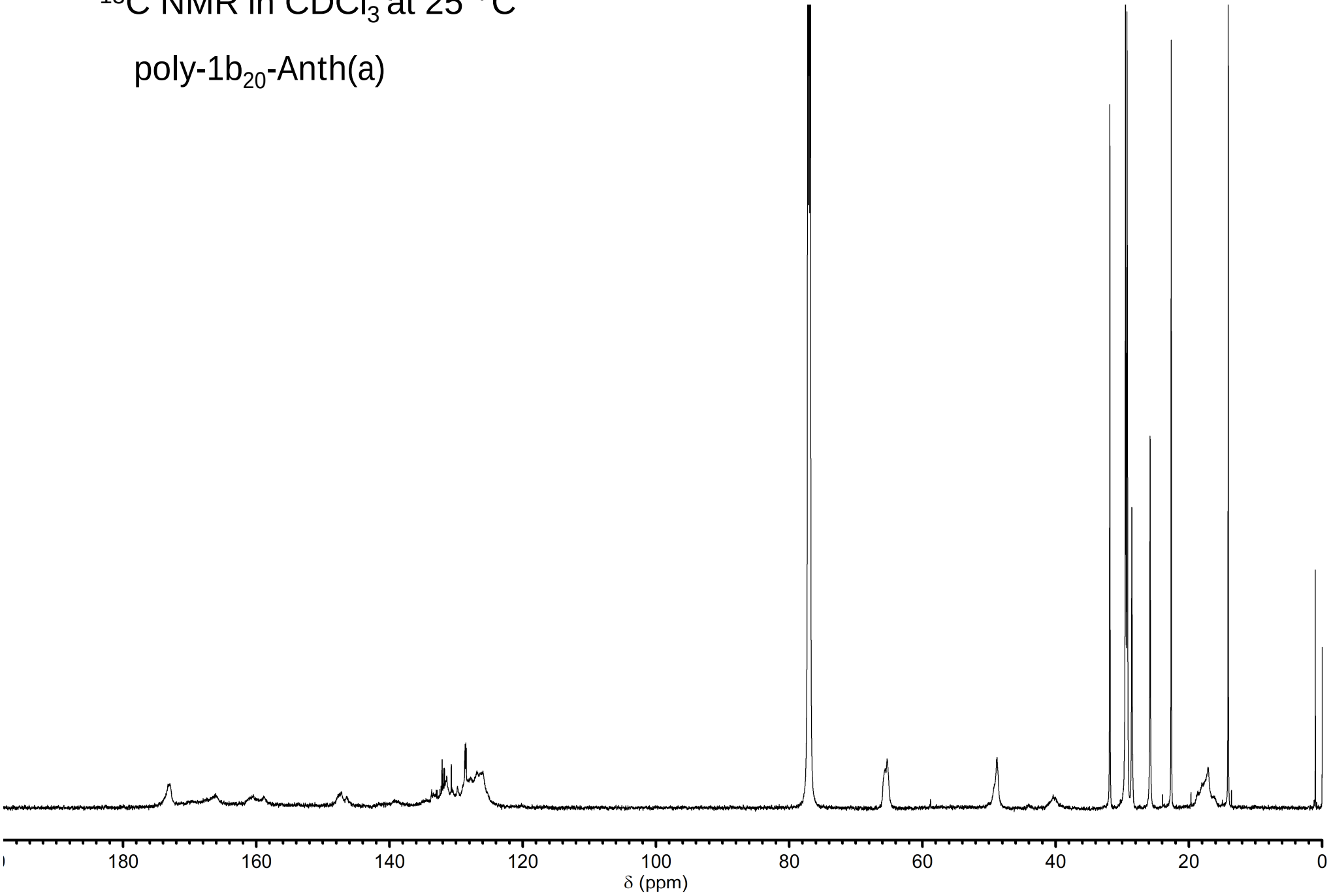
poly-$1a_{20}$-Anth(a)

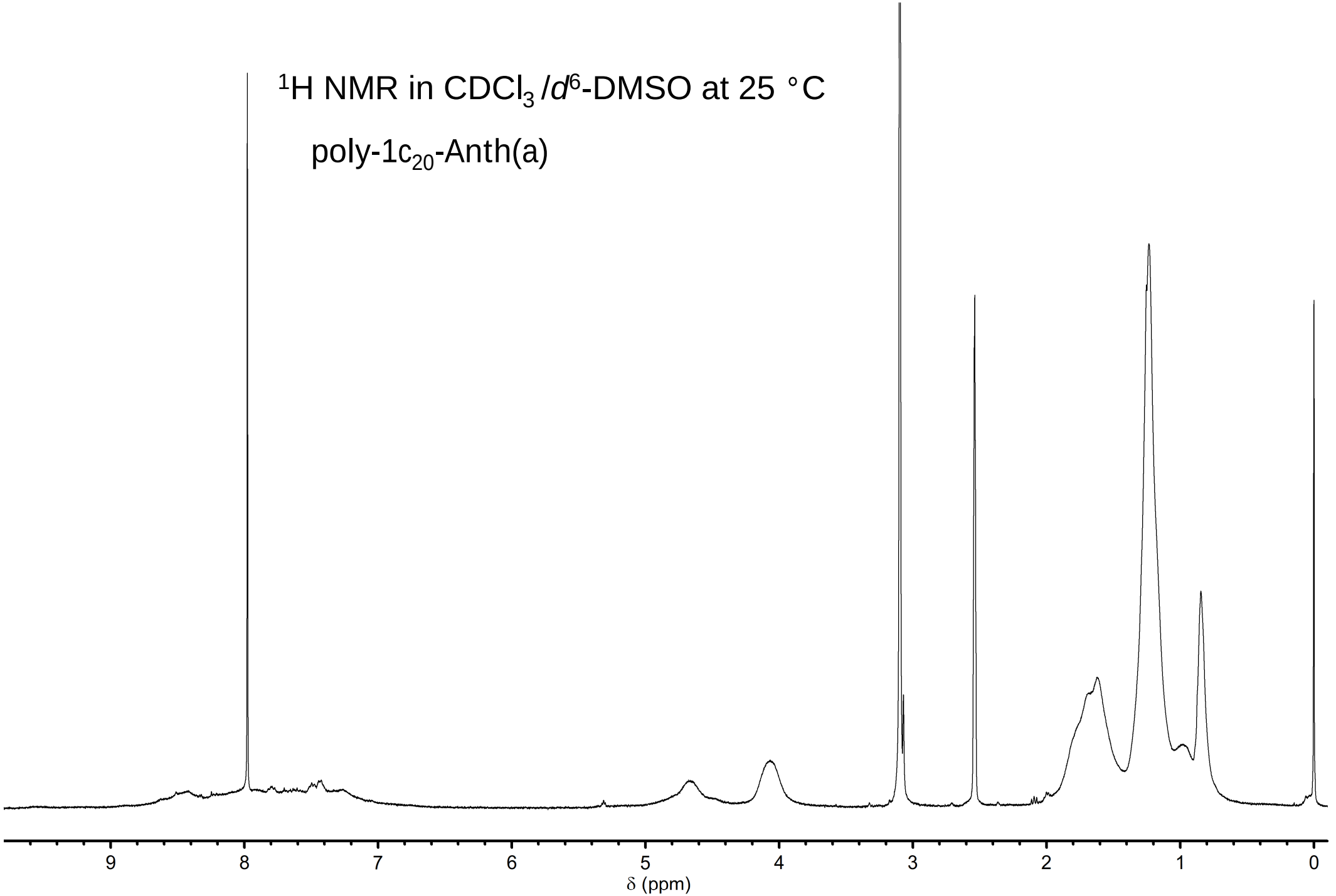



^{1}H NMR in $CDCl_3$ /d^6-DMSO at 25 °C
poly-1b$_{20}$-Anth(a)
9
8
7
6
5
4
3
2
1
0
δ (ppm)

^{13}C NMR in $CDCl_3$ at 25 °C

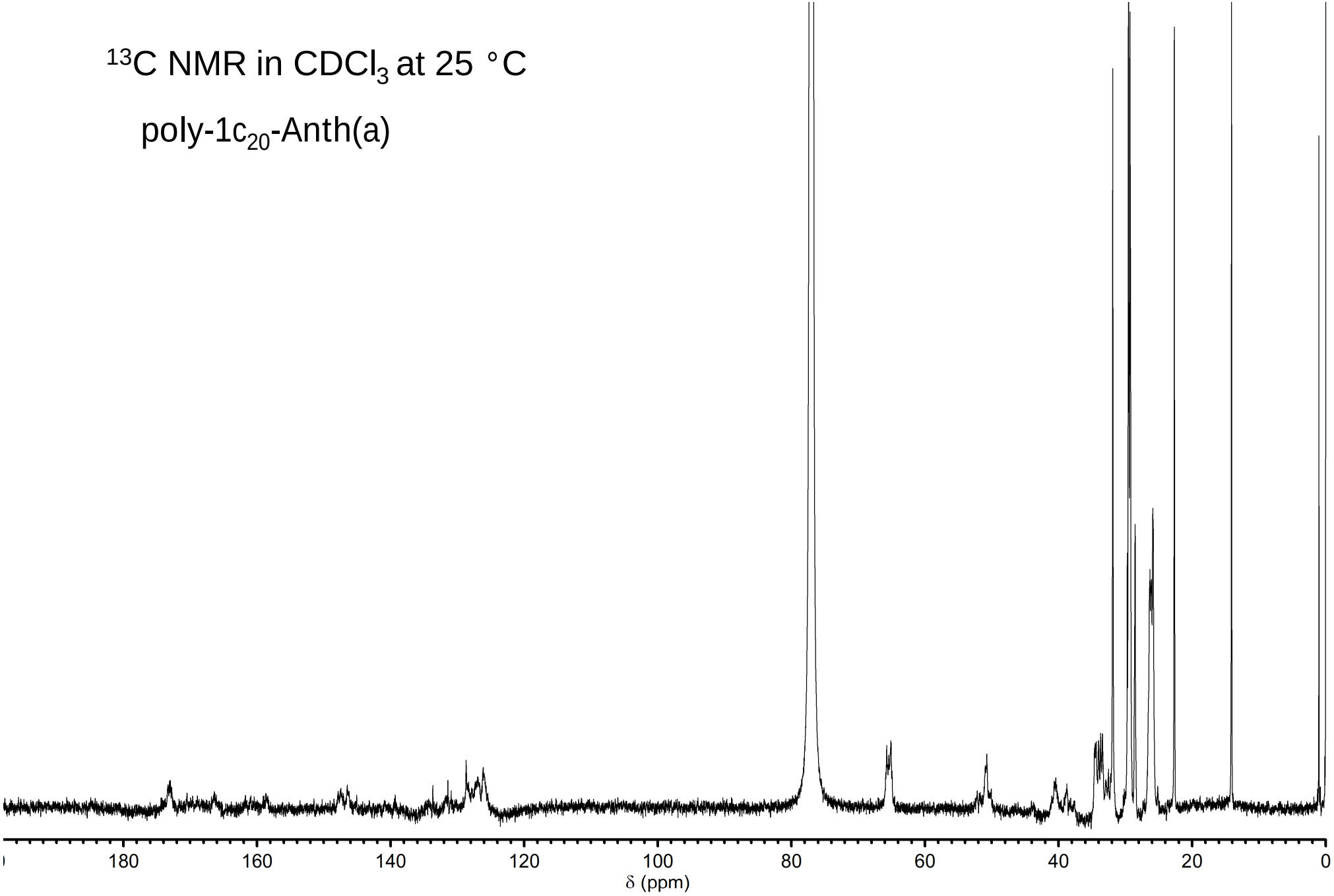
poly-$1b_{20}$-Anth(a)




^{1}H NMR in $CDCl_3$ /d^6-DMSO at 25 °C
poly-1c$_{20}$-Anth(a)
9
8
7
6
5
4
3
2
1
0
δ (ppm)

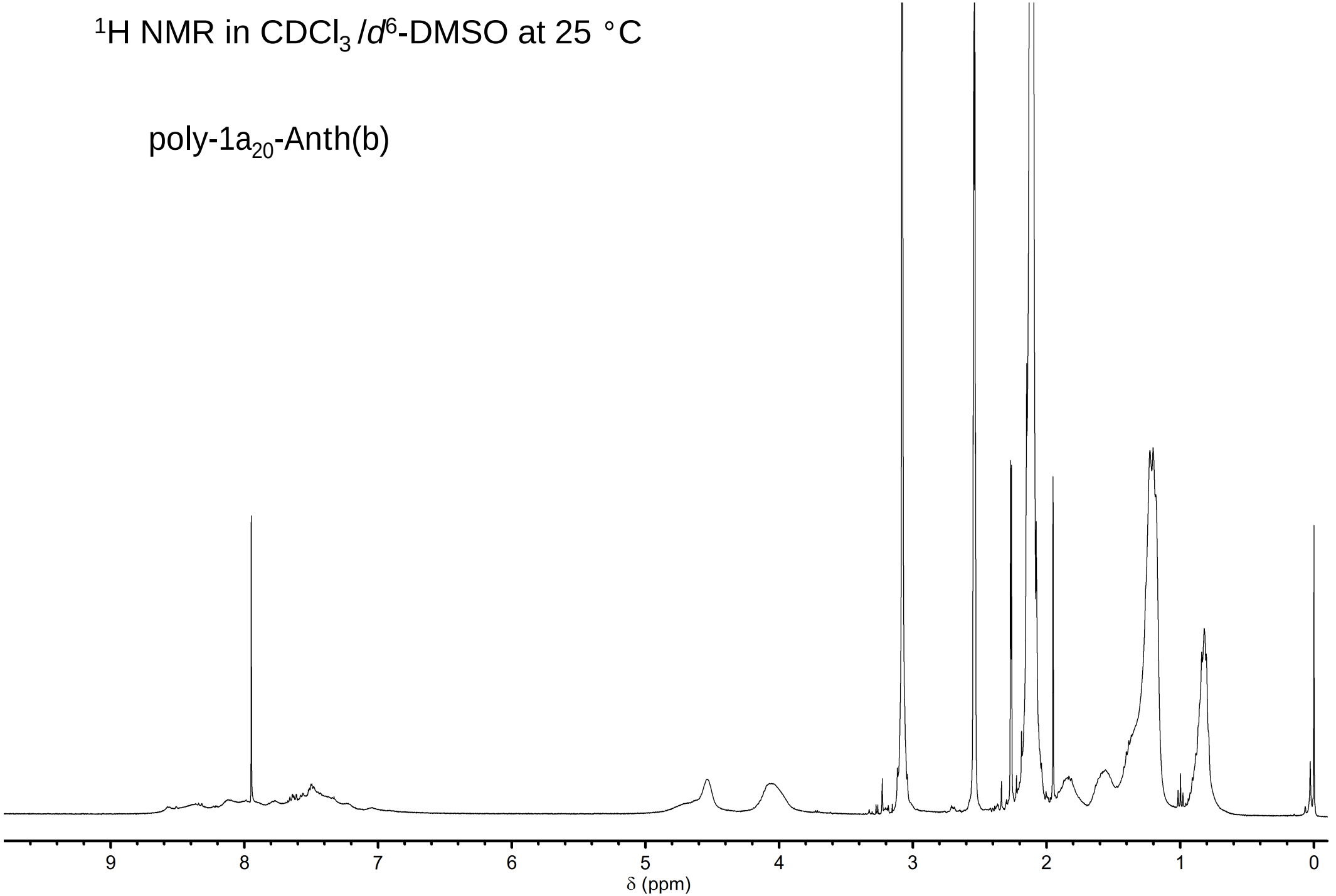
^{13}C NMR in $CDCl_3$ at 25 °C

poly-$1c_{20}$-Anth(a)



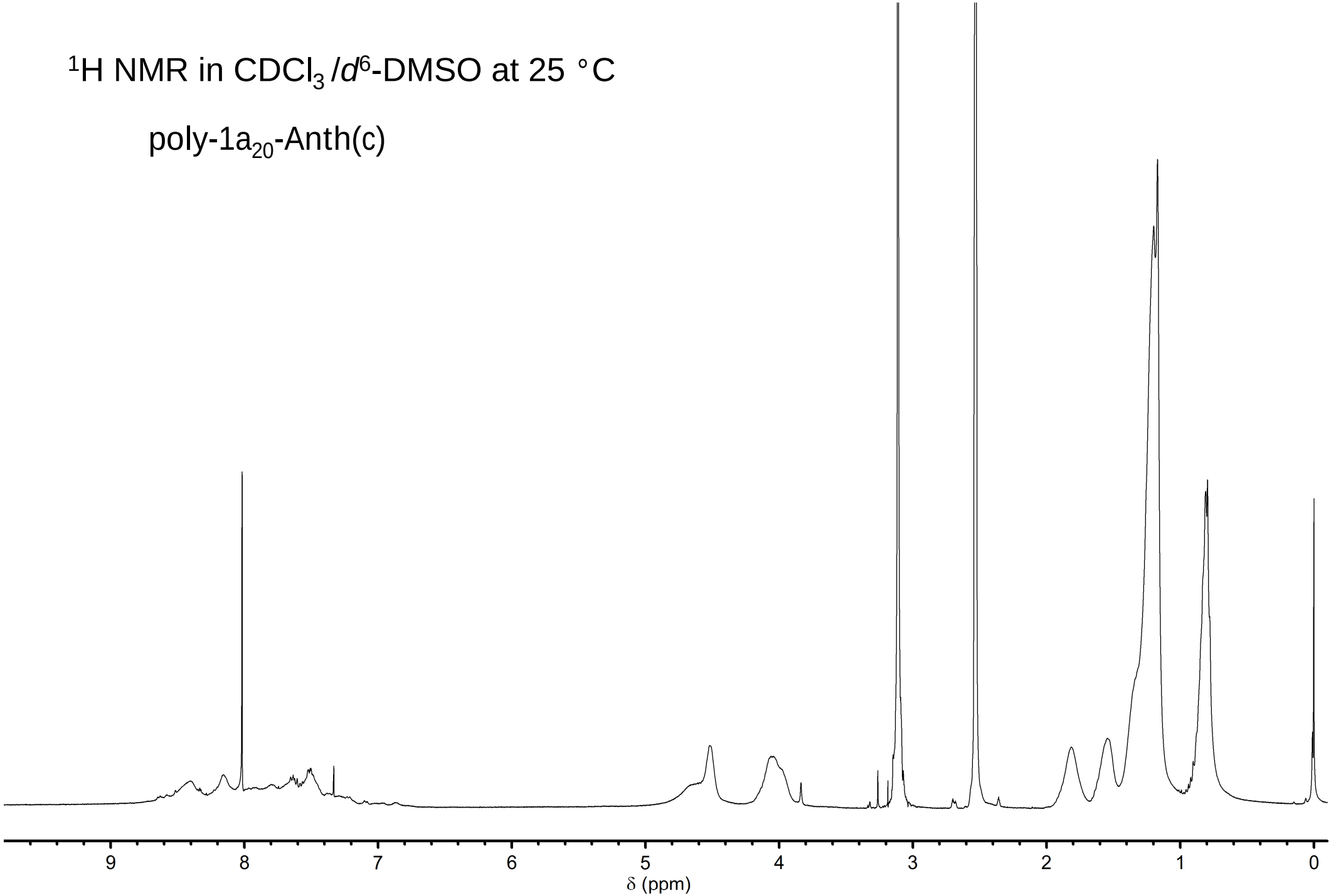
^{1}H NMR in $CDCl_3$ /d^6-DMSO at 25 °C

poly-1a$_{20}$-Anth(b)



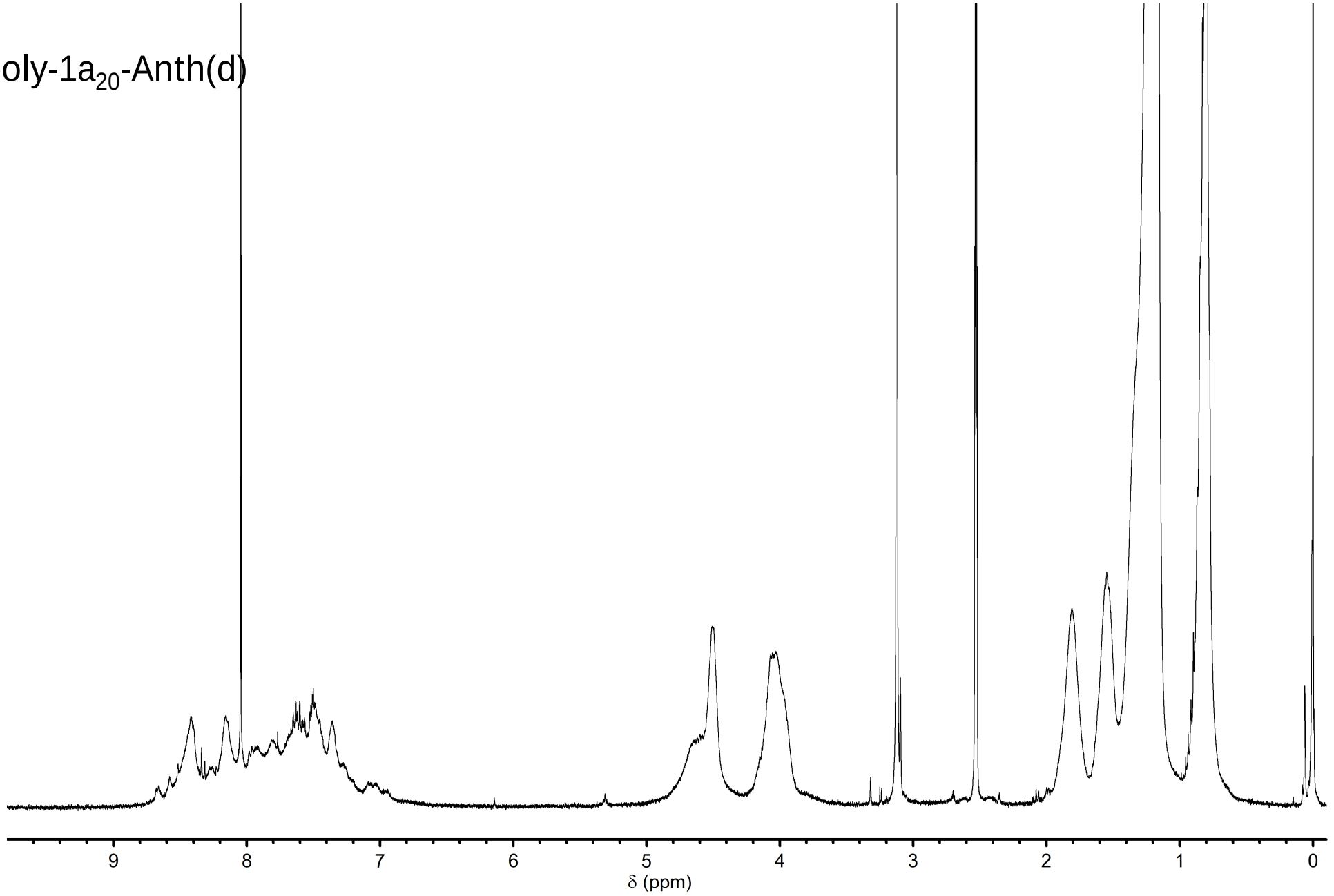
^{1}H NMR in $CDCl_3$ /d^6-DMSO at 25 °C

poly-1a$_{20}$-Anth(c)

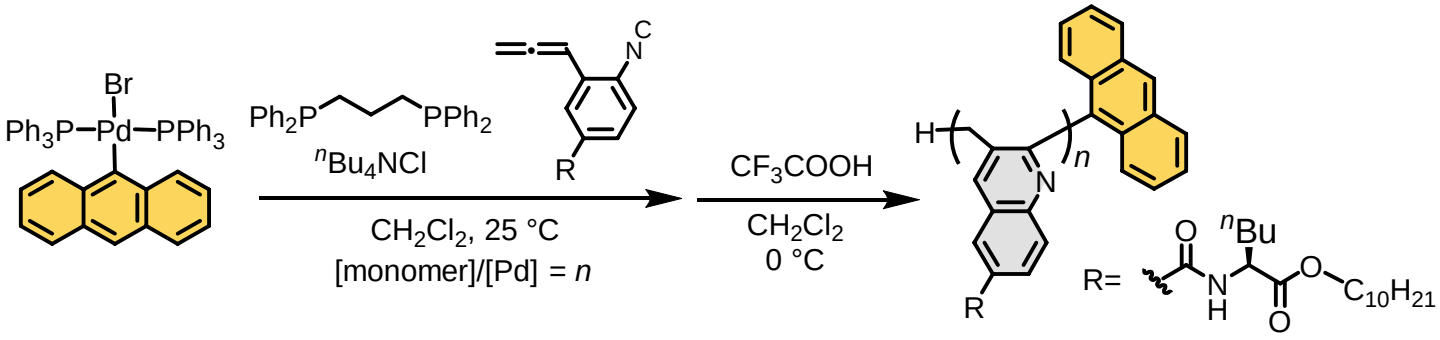


^{1}H NMR in $CDCl_3$ /d^6-DMSO at 25 °C

poly-1a$_{20}$-Anth(d)

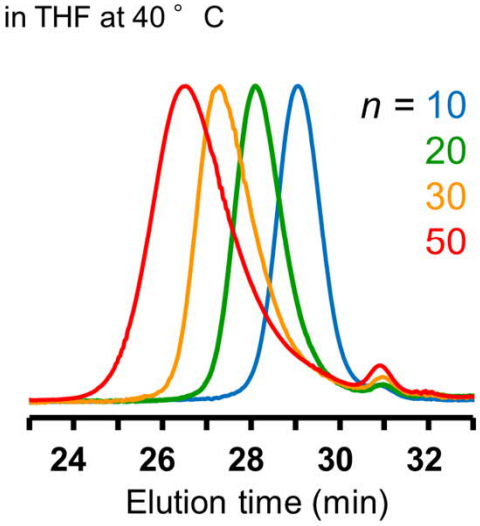


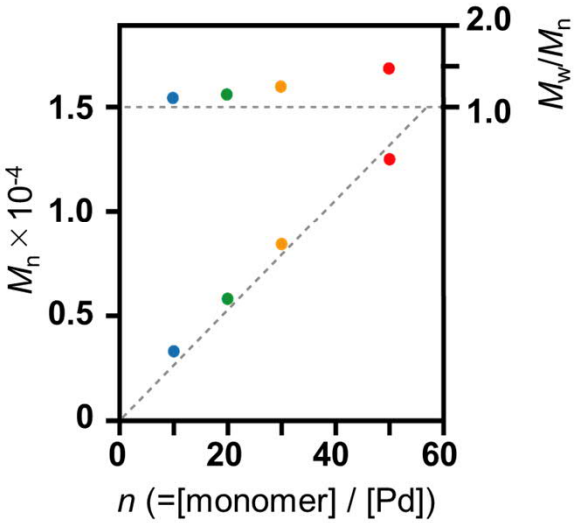
6. SEC Analysis



Entry	*n* (= [**1a**]/[Pd])	Yield	M_n (g mol^{-1})	M_w/M_n
1	10	82	3300	1.11
2	20	90	5800	1.15
3	30	91	7300	1.32
4	50	93	12 500	1.47

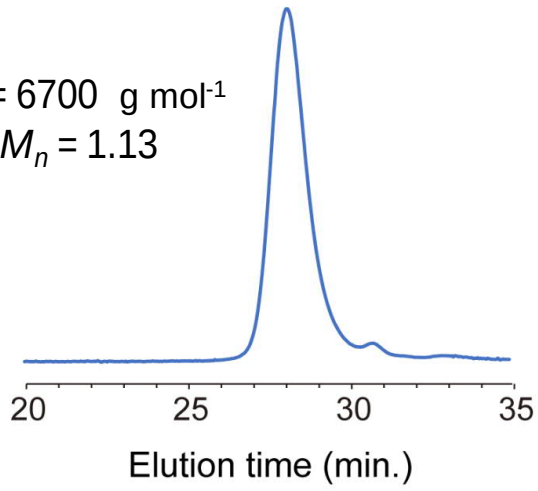
SEC curves





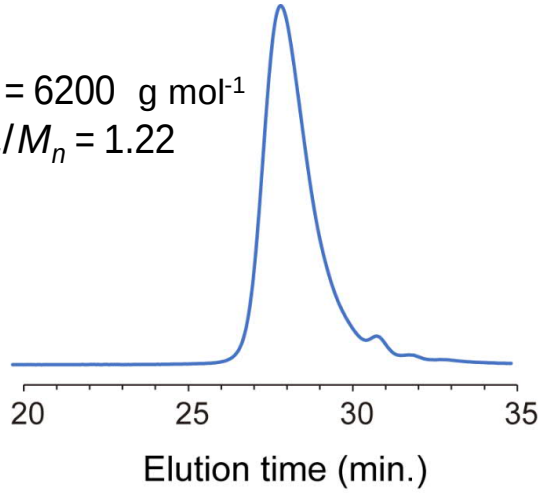
poly-1a$_{20}$-Anth(b)

M_n = 6700 g mol^{-1}
M_w/M_n = 1.13



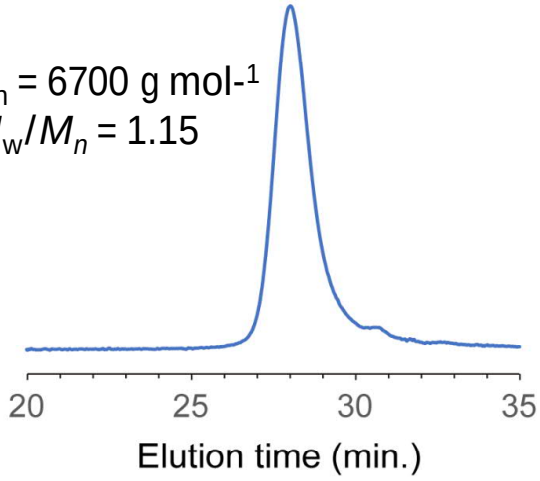
poly-1a$_{20}$-Anth(c)

M_n = 6200 g mol^{-1}
M_w/M_n = 1.22



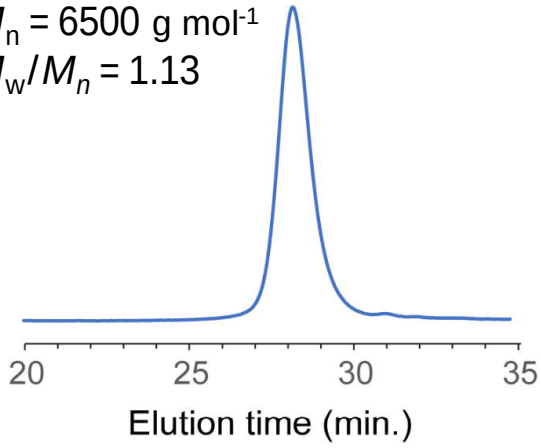
poly-1a$_{20}$-Anth(d)

M_n = 6700 g mol^{-1}
M_w/M_n = 1.15



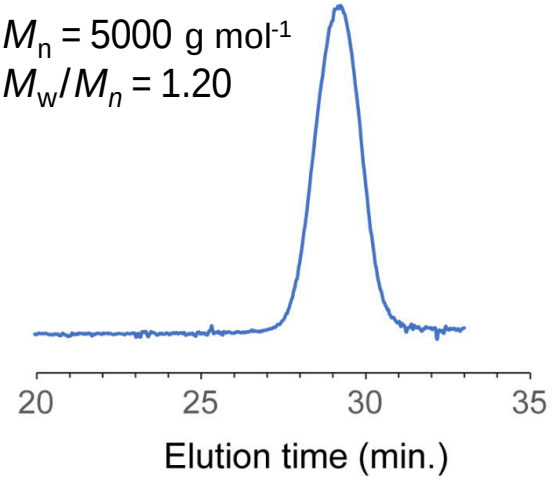
poly-1b$_{20}$-Anth(a)

M_n = 6500 g mol^{-1}
M_w/M_n = 1.13



poly-1c$_{20}$-Anth(a)

M_n = 5000 g mol^{-1}
M_w/M_n = 1.20



in THF 40 ºC

Molar mass and molecular weight distribution are determined by SEC using polystyrene standards.