Supplementary Material (ESI) for Chemical Communications
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Bowl-to-bowl inversion of sumanene derivatives

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Supplementary Information

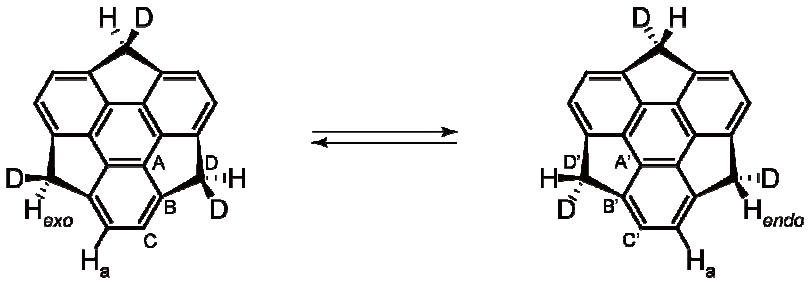
Experimental Section

General. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectra were measured on a Varian INOVA 600 spectrometer. $CDCl_3$, CD_2Cl_2, THF-d_8, 1,4-dioxane-d_8, benzene-d_6, toluene-d_8, *p*-xylene-d_{10}, and mesitylene-d_{12} were used as a solvent and the residual solvent peak (^{1}H, δ 7.26 for $CDCl_3$, 5.32 for CD_2Cl_2, 3.58 for THF-d_8, 3.53 for 1,4-dioxane-d_8, 7.15 for benzene-d_8, 2.36 for toluene-d_8, 2.11 for *p*-xylene-d_{10}, 2.11 for mesitylene-d_{12}; ^{13}C, 77.0 ppm for $CDCl_3$, 53.1 ppm for CD_2Cl_2) was used as a reference. Infrared spectra were recorded on JASCO FT/IR-480plus. Mass spectra were measured on a JEOL JMS-DX-303 spectrometer using either electron impact (EI) or fast atom bombardment (FAB) modes. Column chromatography was conducted on silica gel (Wakogel C-200). All reagents and solvents were purchased from commercial sources. Sumanene (**1**) was prepared according to the reported method.[1]

Trideuteriosumanene 3

All experiments about anion generation using *t*-BuLi and its trapping were carried out under dry nitrogen. Sumanene (10.0 mg, 0.038 mmol) was charged in an NMR tube attached with a resealable J-Young valve. Then, THF-d_8 (0.6 mL) was introduced via syringe. The tube was shaken for several minutes at room temperature. After the tube was chilled to approximately -100 °C using liq. nitrogen/silica gel bath. *t*-BuLi (79.0 μL, 0.114 mmol, 1.57 M in *n*-pentane) was added at below -80 °C, and the tube was shaken for a few minutes at the same temperature. The temperature was allowed to warm to room temperature. After the generation of the trianion was confirmed by NMR, CD_3OD (17.3 μL, 0.38 mmol) was added via syringe at below -80°C. The tube was shaken for a few minutes at the same temperature. The reaction mixture was poured into water. The aqueous layer was extracted with ether. The organic extract was washed with water and brine, dried over $MgSO_4$, and evaporated in *vacuo*. The residue was purified by chromatography on silica gel (pentane) to give **3** as a colorless solid (10.1 mg, 0.038 mmol, quant.): IR (KBr) cm^{-1}: 2957, 2917, 2888, 2848, 1684, 1653, 1559, 1457, 1255, 790, 759; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.40 (brs, 1.5H, H_{exo}), 4.70 (brs, 1.5H, H_{endo}), 7.10 (s, 6H, H_a); ^{13}C NMR (150 MHz, $CDCl_3$) 41.42 (t, J = 20.5 Hz, D), 41.44 (t, J = 19.9 Hz,

D'), 123.2 (C), 123.3 (C'), 148.78 (A or A'), 148.80 (A' or A), 148.87 (B'), 148.90 (B) ppm, determined by selecting decoupling ^{13}C NMR experiments (see page S11–14) and HMBC; HRMS (EI) calcd for $C_{21}H_9D_3$ [$M^{+\cdot}$]: 267.1127, found: 267.1113.



Preparation of 3b

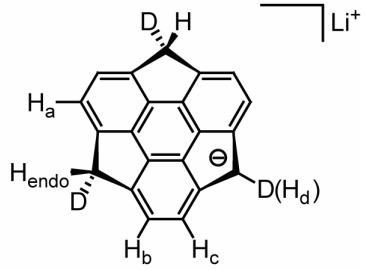
Anion generation and its trapping were carried out under dry nitrogen. Sumanene (**1**, 5.0 mg, 0.019 mmol) and magnetic stirring bar was charged in a small test tube (treated with *N*, *O*-bis(trimethylsilyl)acetamide (BSA), and dried completely before use). Then, THF (0.20 mL) was introduced via syringe and the mixture was stirred slowly. After the tube was chilled to ca. -100 °C with diethyl ether bath, *t*-BuLi (39 μL, 0.057 mmol, 1.57 M in pentane) was added at the same temperature. The mixture was stirred for several minutes at room temperature. After the tube was chilled to ca. -100 °C, THF (0.05 to 0.10 mL) was added to wash the inner wall of the tube. To generate the trianion completely, *t*-BuLi (39 μL, 0.057 mmol) was added again at the same temperature. The reaction mixture was stirred for 30 minutes at room temperature. After the tube was chilled to ca. -100 °C again, CH_3OD (120 μL, 0.295 mmol) was added via syringe (treated with CH_3OD and dried before use) and the mixture was stirred for one minute. Then, the cold methanol (1 mL, ca. -70 °C) was added. The reaction mixture was stirred for a few seconds, resulting in white precipitates. The precipitation was collected on membrane filter (polytetrafluoroethylene). The residue was washed with cold methanol and pentane for several times, dried in *vacuo* to give **3b** (5.0 mg, quant.) as a white solid. ^1H NMR and ^{13}C NMR sample for **3b** was prepared by using cold CD_2Cl_2 (ca. -60 °C).

^1H NMR (600 MHz, CD_2Cl_2, 213 K) δ 3.39 (brs, 3H, H_{endo}), 7.09 (s, 6H, H_a) ; ^{13}C NMR (150 MHz, CD_2Cl_2, 213 K) 44.4 (t, J = 19.4 Hz, D'), 122.5 (C'), 147.6 (A'), 148.1 (B') ppm.

Generation of 4b and 5b

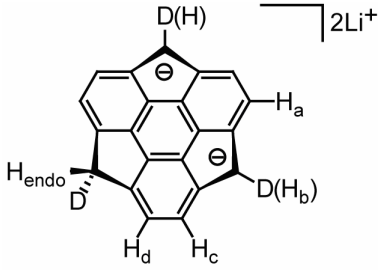
Anion generation was carried out under dry nitrogen. **3b** (2.7 mg, 0.010 mmol) was charged in an NMR-tube attached with a resealable J-Young valve. Then, the tube was chilled to -100 °C with diethyl ether bath. THF-d_8 (0.45 mL) was introduced via syringe. The tube was shaken for several minutes at the same temperature, consequentially *t*-BuLi (6.3 μL, 0.010 mmol, 1.57 M in

n-pentane) was added, and the mixture was shaken several times at ca. -45 °C to give **4b**: ^{1}H NMR (600 MHz, THF-d_8, 283 K) δ 2.98 (brs, 1H, H_{endo}), 5.88 (s, 0.5H, H_d), 6.74 (s, 2H, H_c) 6.75 (d, J = 8.4 Hz, 2H, H_b), 6.79 (d, J = 8.4 Hz, 2H, H_a).



4b

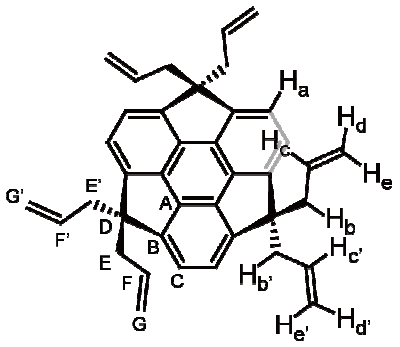
The same procedure was carried out to generate the di-anion **5b**. *t*-BuLi (12.6 μL, 0.200 mmol) was added to give **5b**: ^{1}H NMR (600 MHz, THF-d_8, 273 K) δ 2.28 (brs, 1H, H_{endo}), 5.36 (s, 1H, H_b), 6.34 (d, J = 7.8 Hz, 2H, H_c), 6.59 (d, J = 7.8 Hz, 2H, H_d), 6.77 (s, 2H, H_a).



5b

Hexaallylsumanene 6

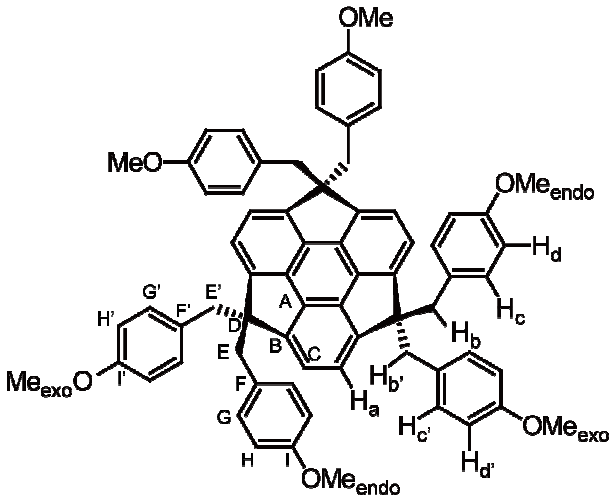
To vigorously stirred solution of sumanene (**1**, 6.2 mg, 0.023 mmol) and tetrabutylammonium bromide (22.7 mg, 0.070 mmol) in degassed THF (0.10 mL) were added the degassed 30 wt% aqueous NaOH (2.0 mL) and allyl bromide (0.22 ml, 0.234 mmol) at room temperature under argon. After 45 hours, the reaction mixture was poured into saturated aqueous NH_4Cl. The aqueous layer was extracted with ether. The organic extract was washed with water and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (1-10% chloroform in hexane) to give **6** as a white solid (11.6 mg, 0.023 mmol, quant.): IR (KBr) cm^{-1}: 3075, 2977, 2899, 1636, 1558, 1506, 1436, 1398, 995, 910, 808, 720; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.64 (d, J = 6.6 Hz, 6H, H_b), 3.09 (d, J = 7.2 Hz, 6H, $H_{b'}$), 3.51 (ddt, J = 17.4, 10.2, 6.6 Hz, 3H, $H_{c'}$), 3.96 (dd, J = 10.2, 1.2 Hz, 3H, H_d), 4.26 (dd, J =17.4, 1.2 Hz, 3H, H_e), 5.20 (dd, J = 10.2, 1.2 Hz, 3H, $H_{d'}$), 5.24 (dd, J = 17.4, 1.2 Hz, 3H, $H_{e'}$), 6.23 (ddt, J = 17.4, 10.2, 7.2 Hz, 3H, H_c), 6.98 (s, 6H, H_a); ^{13}C NMR (150 MHz, $CDCl_3$) δ 39.7 (E), 44.9 (E'), 63.0 (D), 116.0 (G), 117.9 (G'), 123.2 (C), 133.9 (F), 135.2 (F'), 146.8 (A), 153.5 (B) ppm determined by HMQC and HMBC experiments; HRMS (EI) calcd for $C_{39}H_{36}$ [$M^{+\cdot}$]: 504.2817, found: 504.2812.



6

Hexa-*p*-methoxybenzyl sumanene 7

To vigorously stirred solution of sumanene (**1**, 10.8 mg, 0.041 mmol) and tetrabutylammonium bromide (39.5 mg, 0.123 mmol) in degassed THF (0.15 mL) were added the degassed 30 wt% aqueous NaOH (2.0 mL), and then *p*-methoxybenzyl chloride (0.41 mL, 4.1 mmol) at room temperature under argon. After 24 hours, *p*-methoxybenzyl chloride (0.41 mL, 4.1 mmol) was again added to the mixture. After further 36 hours, the reaction mixture was poured into saturated aqueous NH_4Cl. The aqueous layer was extracted with ether. The organic extract was washed with water and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was chromatographed on silica gel twice (20-40% chloroform in toluene, then 5-20 % ethyl acetate in hexane) to give **7** (30.2 mg, 0.031 mmol, 75%) as a white solid: IR (KBr) cm^{-1}: 2994, 2908, 2834, 1611, 1511, 1301, 1249, 1178, 1110, 1036, 822; ^1H NMR (600 MHz, $CDCl_3$) δ 2.68 (s, 6H, H_b), 3.59 (s, 6H, $H_{b'}$), 3.63 (s, 9H, OMe_{endo}), 3.76 (s, 9H, OMe_{exo}), 6.10 (d, J = 9 Hz, 6H, H_c), 6.33 (d, J = 9 Hz, 3H, H_d), 6.66 (s, 6H, H_a), 6.75 (d, J = 9 Hz, 6H, $H_{d'}$), 7.18 (d, J = 9 Hz, 6H, $H_{c'}$): ^{13}C NMR (150 MHz, $CDCl_3$) 42.1 (E), 45.0 (E'), 54.9 (OMe_{exo}), 55.1 (OMe_{endo}), 65.2 (D), 112.5 (H), 112.8 (H'), 123.3 (A), 130.1 (F), 130.3 (F'), 131.2 (G), 131.7 (G'), 145.6 (C), 153.4 (B), 157.6 (I), 158.0 (I')ppm determined by HMBC and HMQC experiments; HRMS (FAB) calcd for $C_{69}H_{60}O_6$ [$M^{+\cdot}$]: 984.4390, found: 984.4379.



7

Bowl-to-bowl inversion rate measurement of 3, 6, and 7

The NMR experiments were conducted with 20 mM of sumanene derivatives. First, longitudinal relaxation time T_1 at the corresponding protons was measured for each spectrum using inversion recovery method with 180^o-τ-90^o the pulse sequence. 1D NOE experiments were carried out in various values of mixing time t_m. The optimum t_m was evaluated to be the t_m in which the value of [integration for chemical exchange at 1D NOE experiment] x [S/N ratio] reaches maximum. Relaxation decay d_1 was determined from the equation (eq 1). T_1 and t_m are summarized in Table S1.

$3T_1 = at + t_m + d_1$ (at: acquisition time) (1)

2D EXSY (2D NOESY) experiments were performed with a spectrum width of 8 ppm, with acquisition time of 0.213 s, using 1024 data points in the t_2 dimension and 512 in t_1, with subsequent weighting with the sinebell function with 16 scans for each t_1 increment. Exchange cross-peaks were integrated, which were then processed using the EXSYCalc distributed by Mestrelab research (http://www.mestrec.com/) to give the chemical exchange (k). The rate constant (k) was further substituted to the Eyring equation (eq 2) to derive activation energy ($\Delta G^{\ddagger}$) where T is temperature, k_B is the Boltzmann constant, and h is Planck's constant.

$k = (k_BT/h) \exp(-\Delta G^{\ddagger}/RT)$ (2)

Table S1

compound	solvent	T_1 / s	t_m / s
3	$CDCl_3$	3.7	4.0
	CD_2Cl_2	8.6	6.0
	THF-d_8	19.3	8.0
	1,4-dioxane-d_8	3.8	2.5
	benezene- d_6	8.0	4.0
	toluene-d_8	5.0	4.0
	p-xylene-d_{10}	6.0	4.0
	mesitylene-d_{12}	5.0	2.8
6	$CDCl_3$	1.2	2.5
7	$CDCl_3$	2.4	4

Bowl-to-bowl inversion rate measurement of 4 and 5

The progress of equilibration was monitored by ^{1}H NMR in THF-d_8 at 283 K for **4**, and 273 K (for **5** in THF-d_8) with a relaxation delay of 3.0 s. The region of benzylic protons (2 - 5 ppm) was carefully phase- and baseline-corrected before integration in each spectrum. The rate constant (k) for the reversible equilibration was determined by regression analysis using the equation $2kt = \ln[a/(a-2x)]$ where a is the initial concentration of **4b** (or **5b**) and x is the concentration of **4a** (or **5a**) at time t. Correlation coefficients of the linear regressions were 0.999 (for **4**) and 0.978 (for **5**). $\Delta G^{\ddagger}$s were calculated from the Eyling equation (eq 2, see page S5).

Fig. S1. Bowl-to-bowl inversion of monoanion **4**. Plot of $\ln[a/(a-2x)]$ vs t (s)

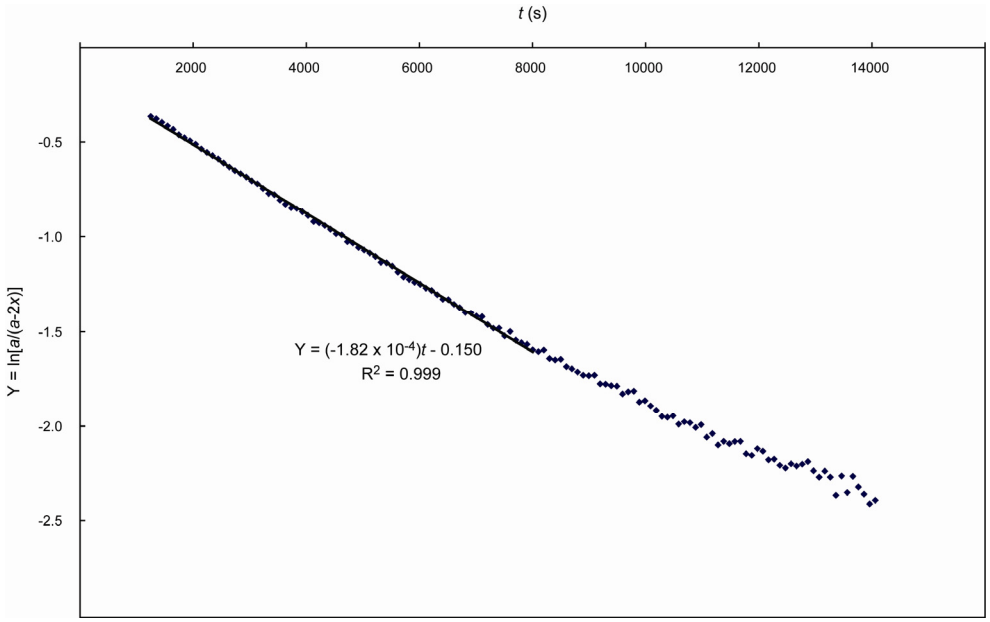
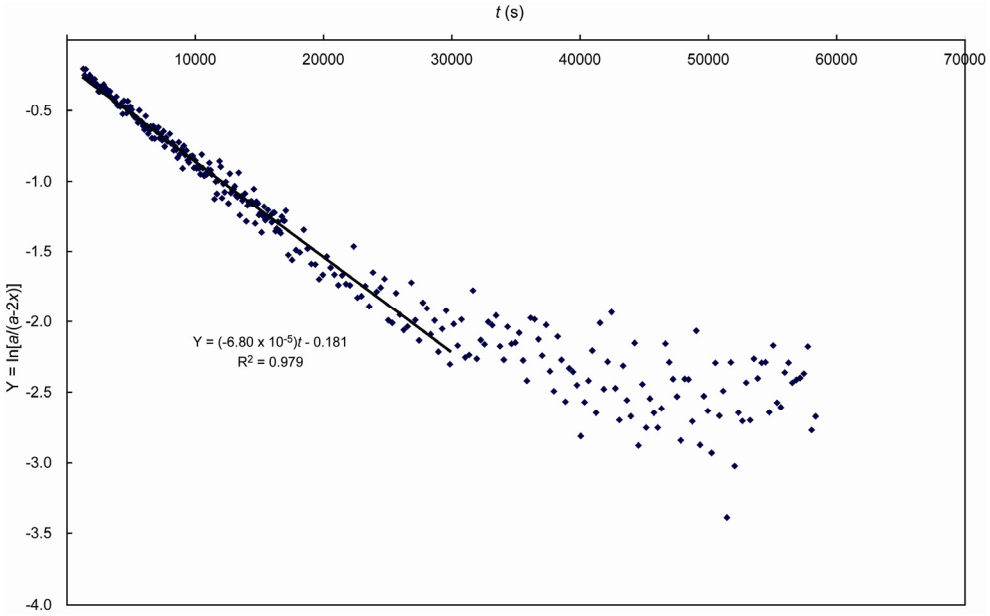


Fig. S2. Bowl-to-bowl inversion of dianion **5**. Plot of ln[*a*/(*a*-2*x*)] vs *t* (s)

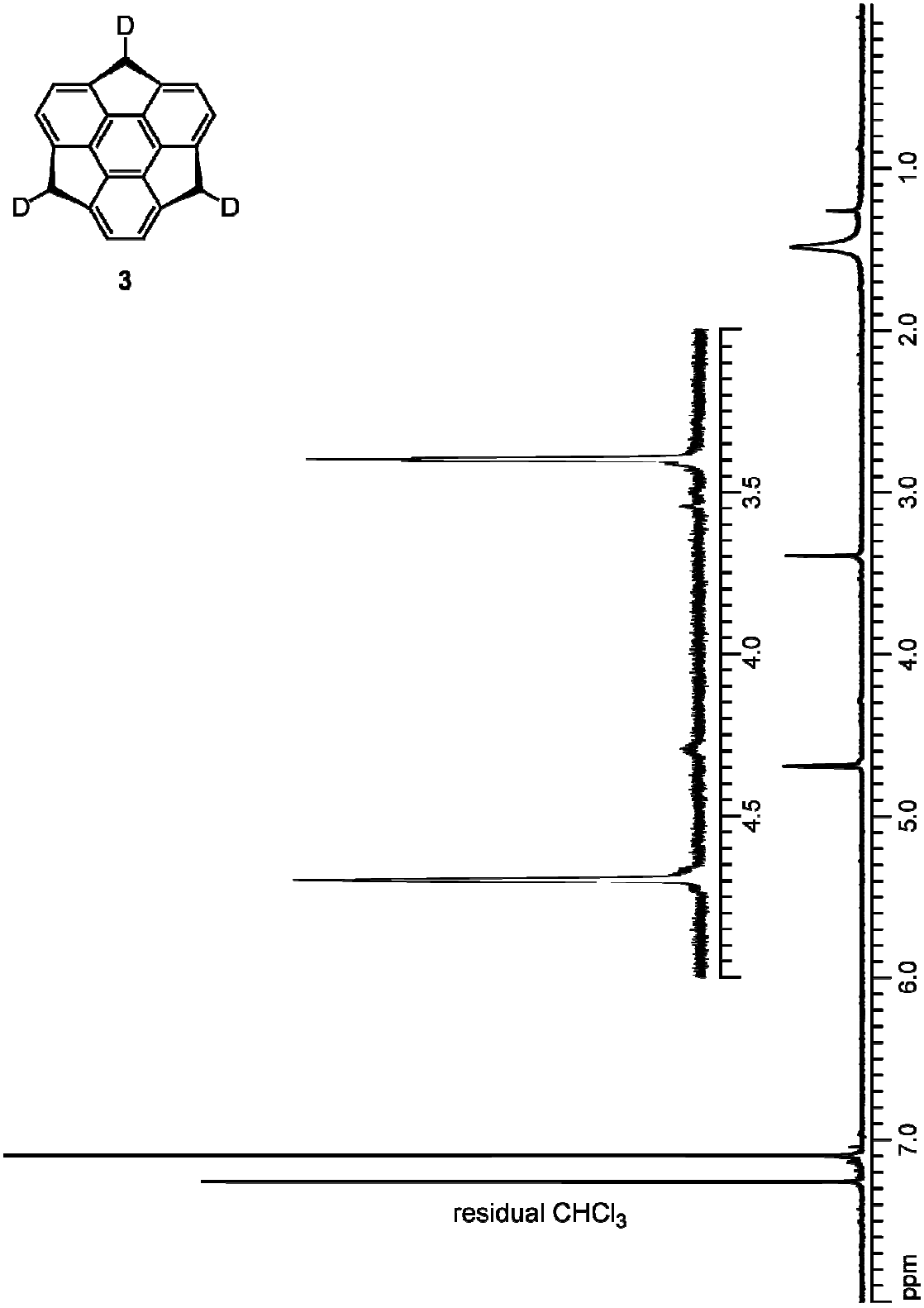


Reference

(1) (a) Sakurai, H.; Daiko, T.; Hirao, T. *Science*, **2003**, *301*, 1838. (b) Sakurai, H.; Daiko, T.; Sakane, H.; Amaya, T.; Hirao, T. *J. Am. Chem. Soc.*, **2005**, *127*, 11580.

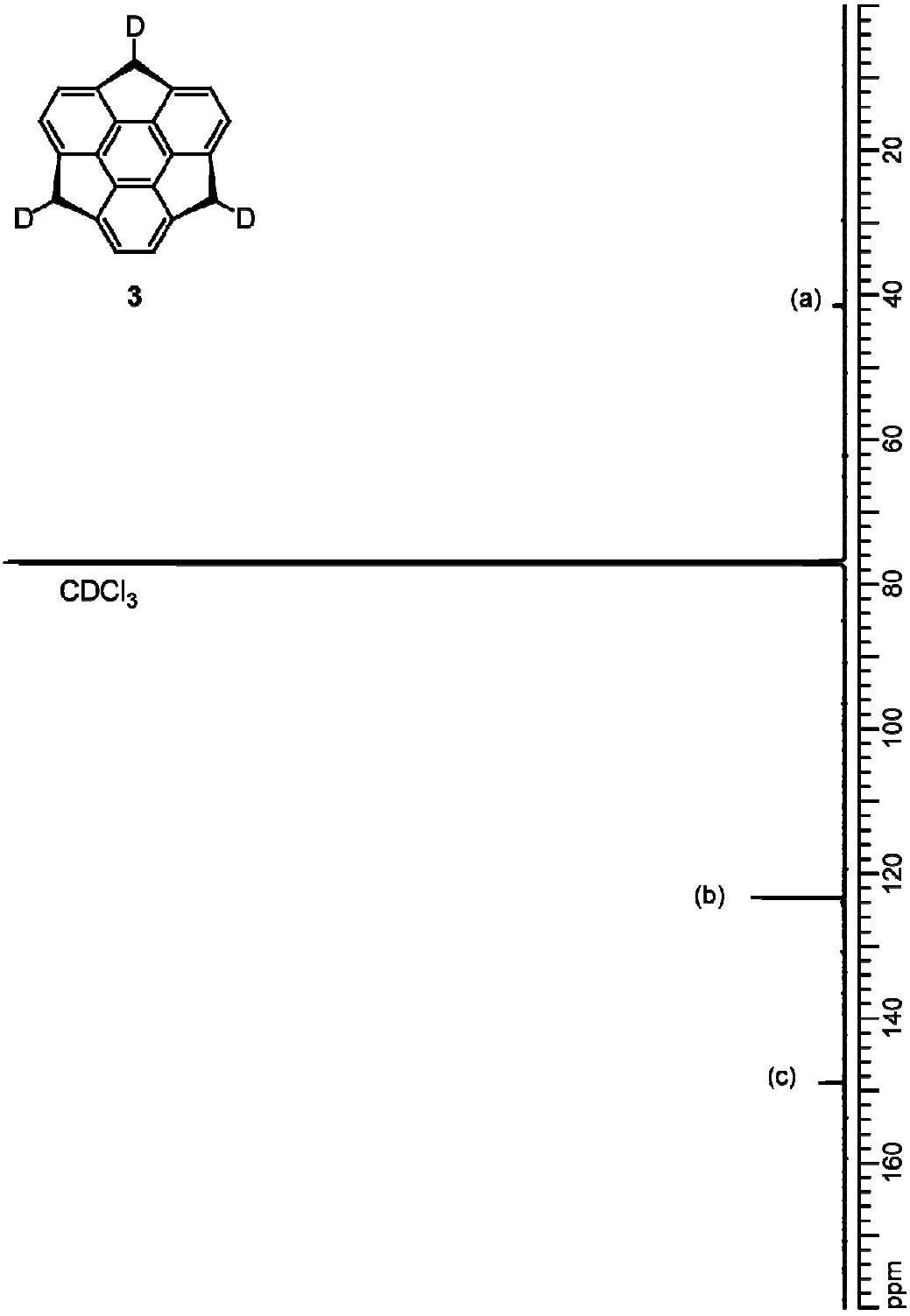
^{1}H NMR spectrum of trideuteriosumanene **3**

(600 MHz, $CDCl_3$)

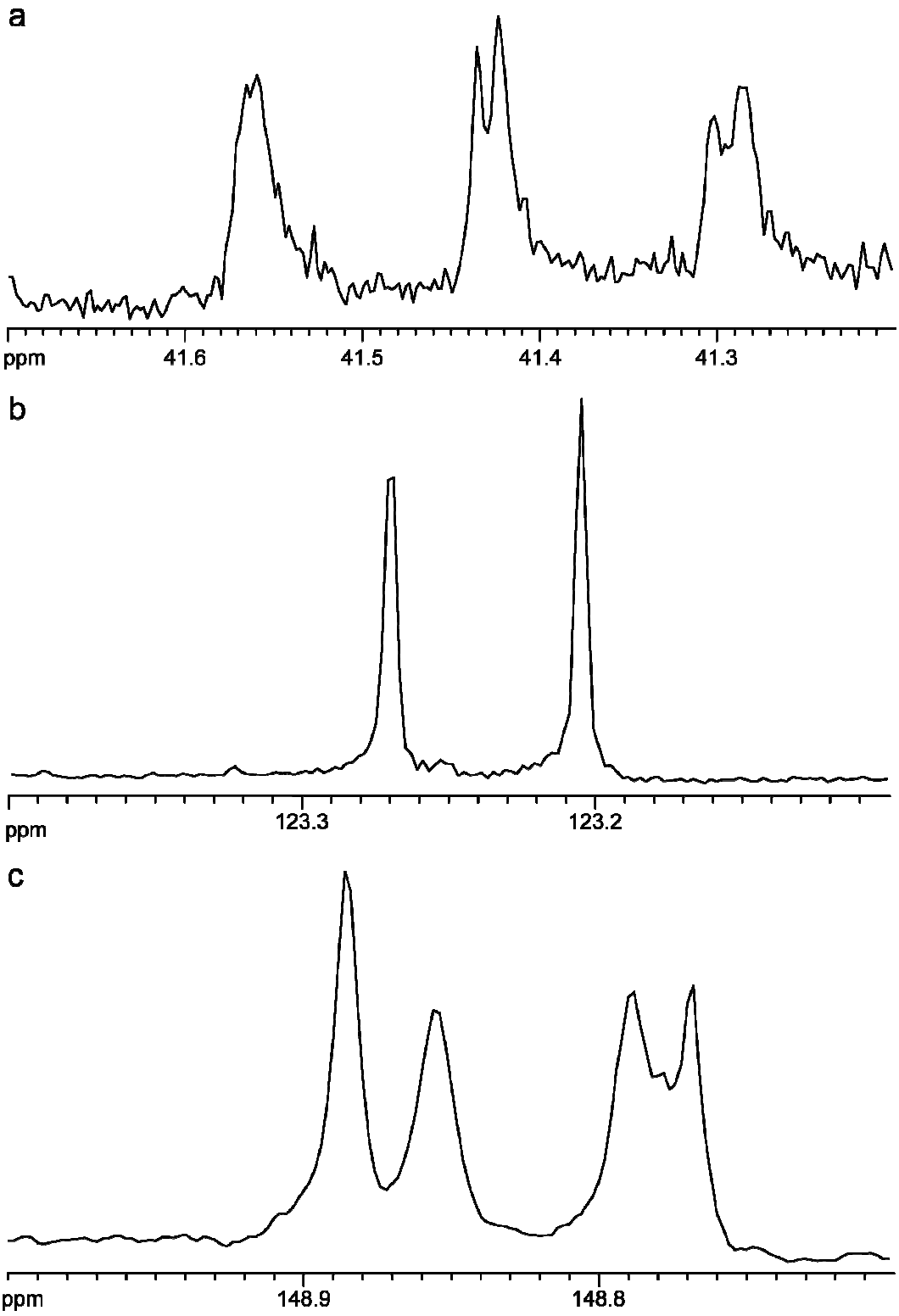


^{13}C NMR spectrum of trideuteriosumanene **3**

(150 MHz, $CDCl_3$)

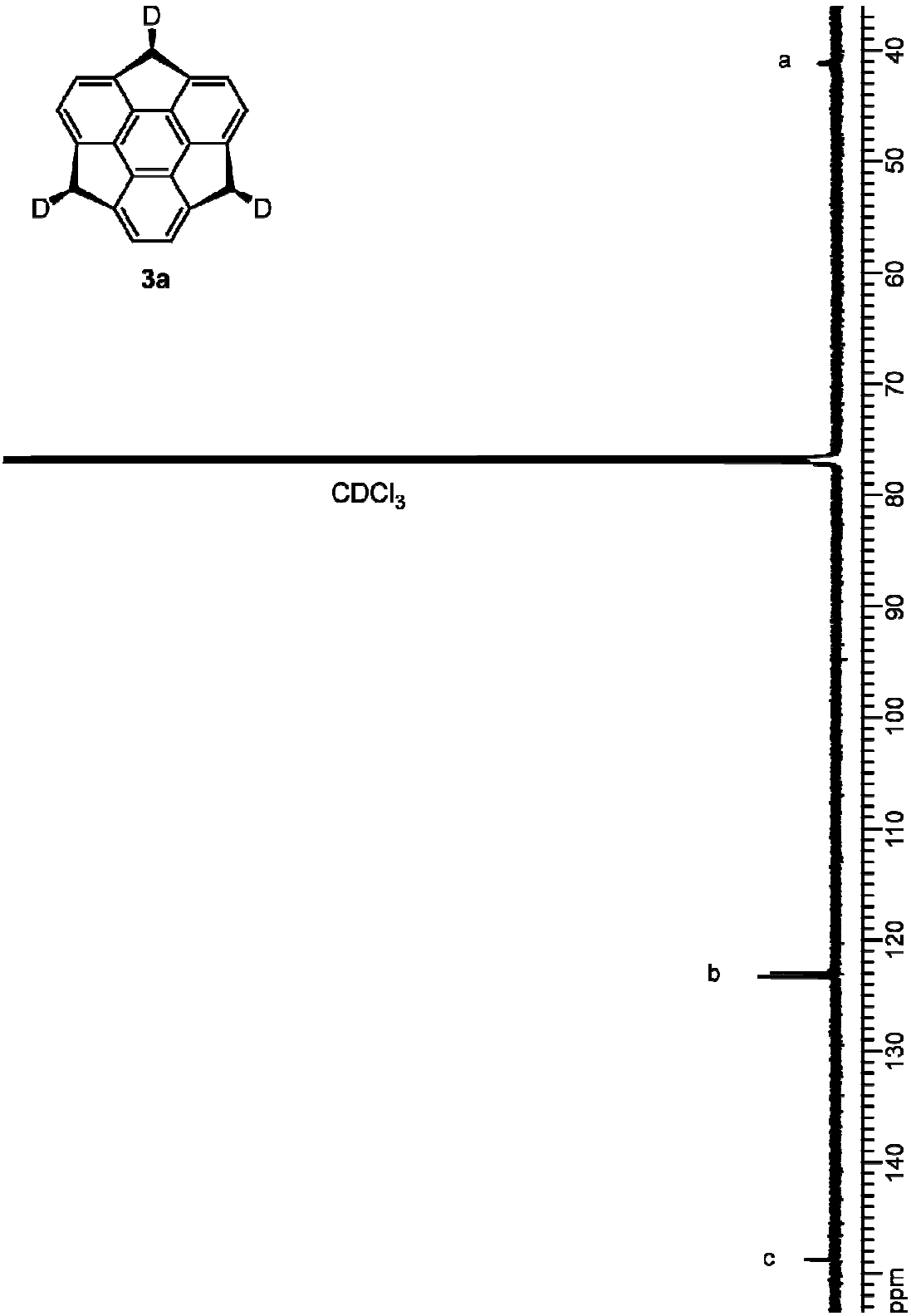


Enlarged view (a), (b), and (c) for ^{13}C NMR spectrum of trideuteriosumanene **3**

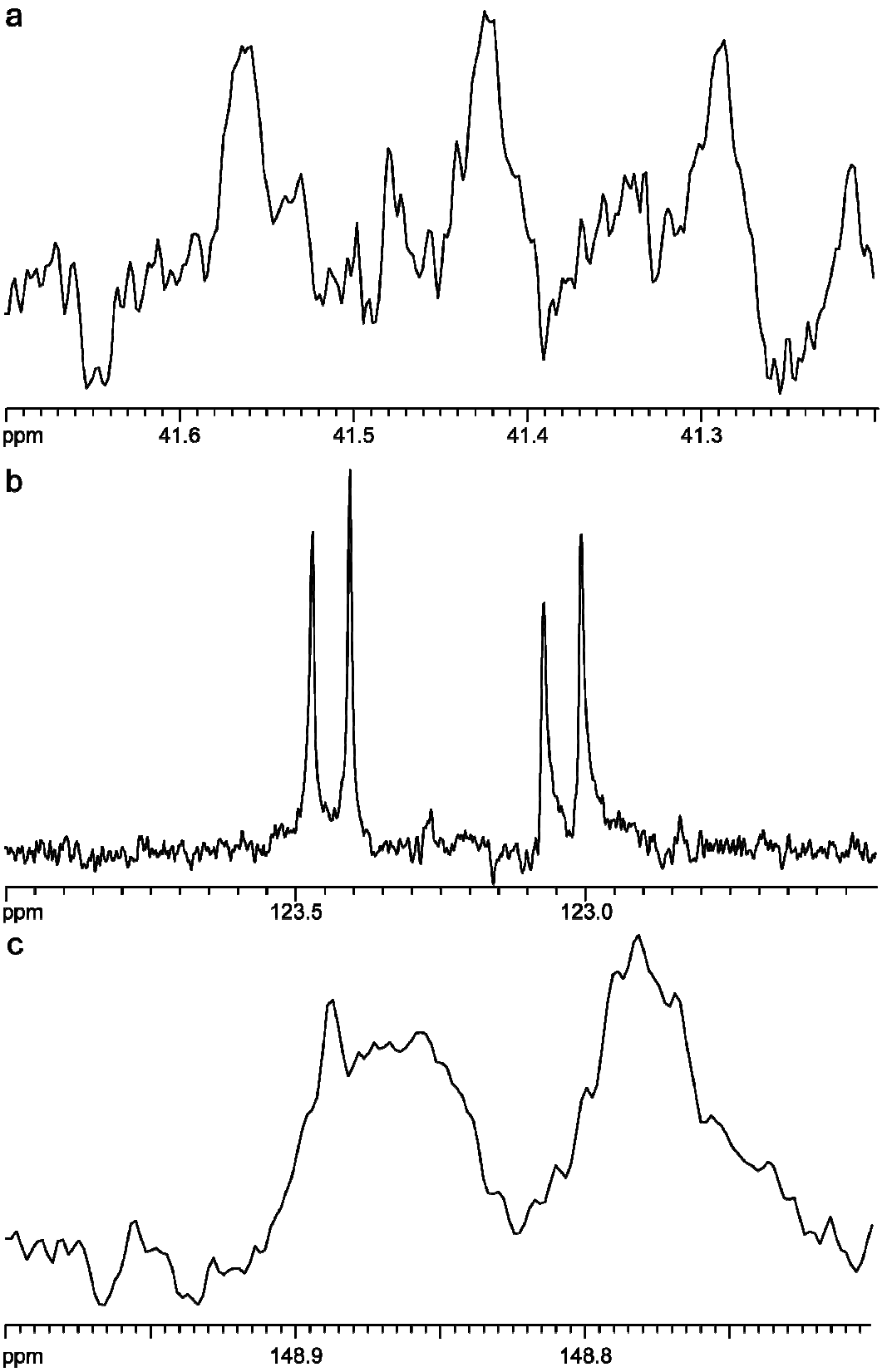


Selecting decouplilng ^{13}C NMR spectrum of trideuteriosumanene **3**

(600 MHz, $CDCl_3$, decoupling offset for *exo*-benzylic protons of **3a**: -185.1 Hz)

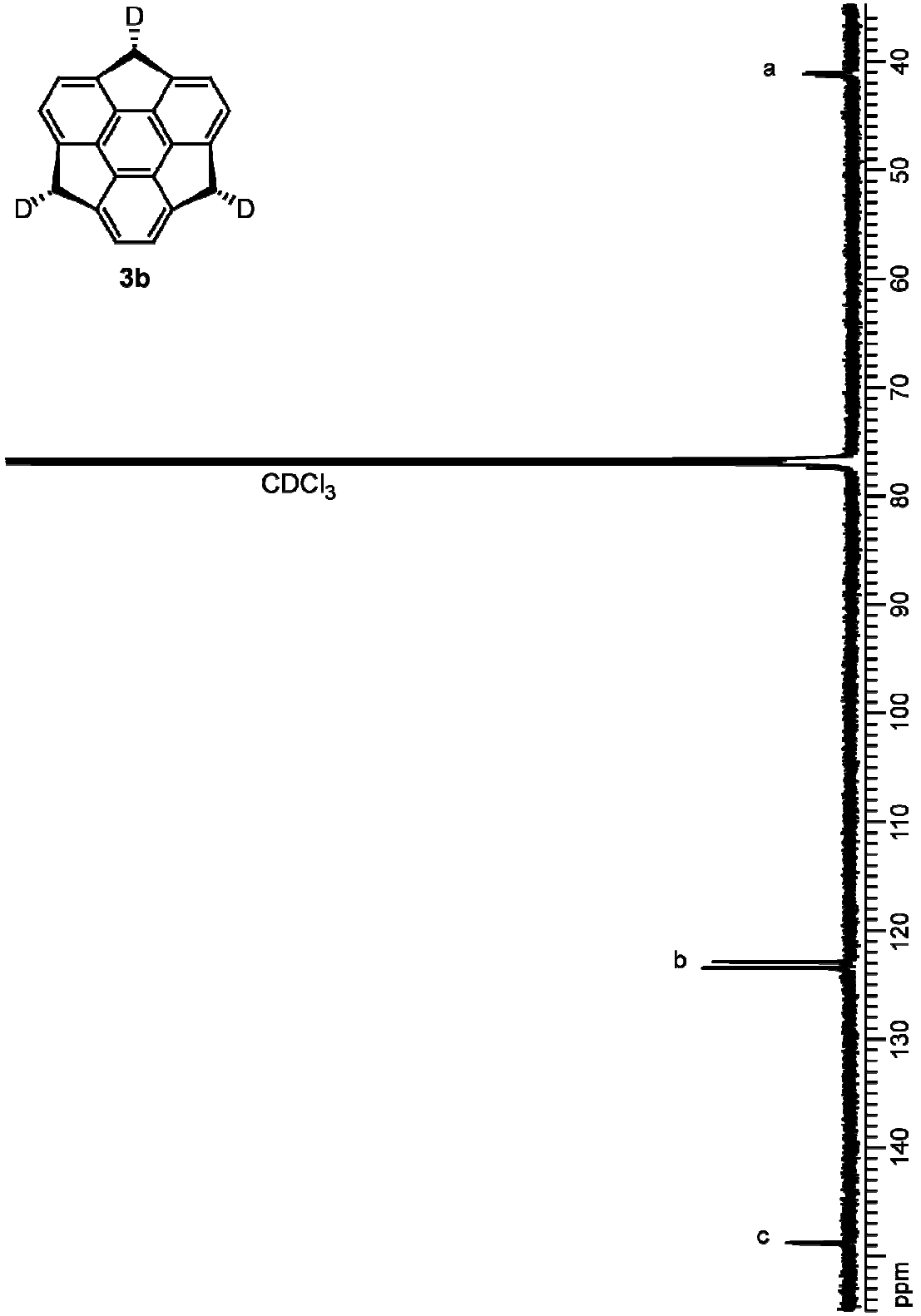


Enlarged view (a, b, and c) for ^{13}C NMR spectrum of trideuteriosumanene **3a**

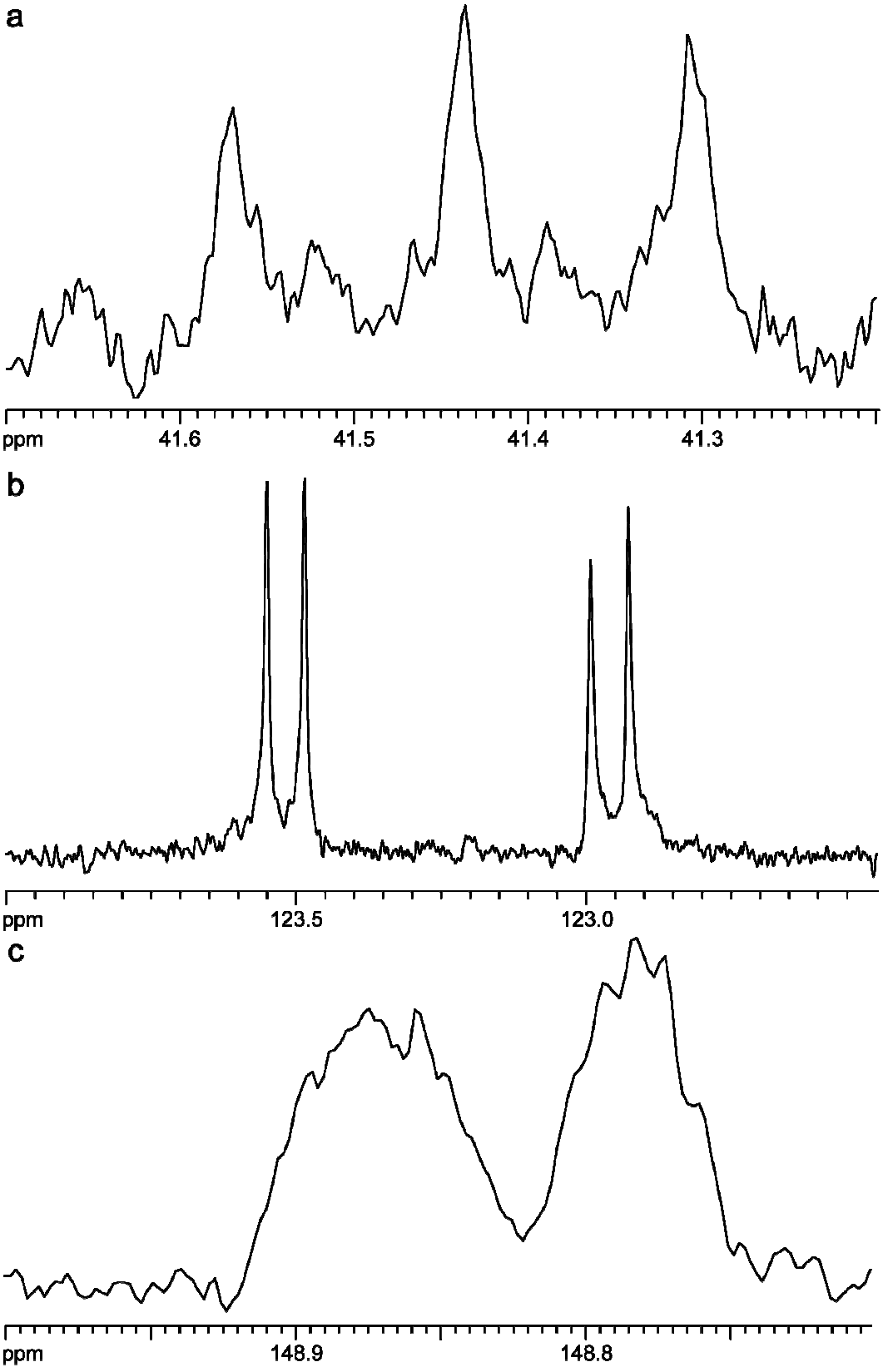


Selecting decouplilng ^{13}C NMR spectrum of trideuteriosumanene **3**

(600 MHz, $CDCl_3$, decoupling offset for *endo*-benzylic protons of **3b**: -960.1 Hz)

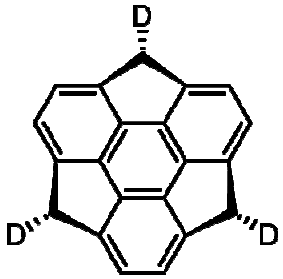


Enlarged view (a, b, and c) for ^{13}C NMR spectrum of trideuteriosumanene **3b**

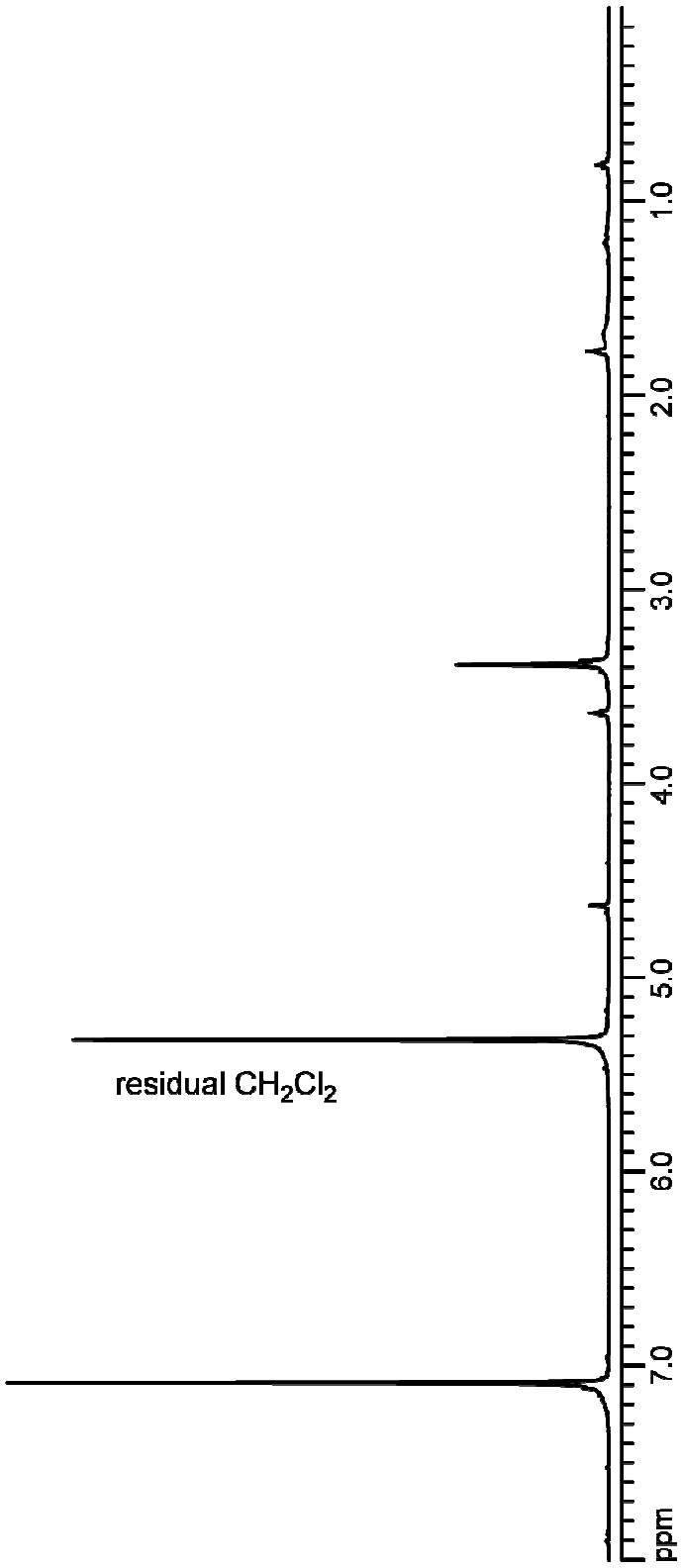


^{1}H NMR spectrum of **3b**

(600 MHz, CD_2Cl_2, 213 K)

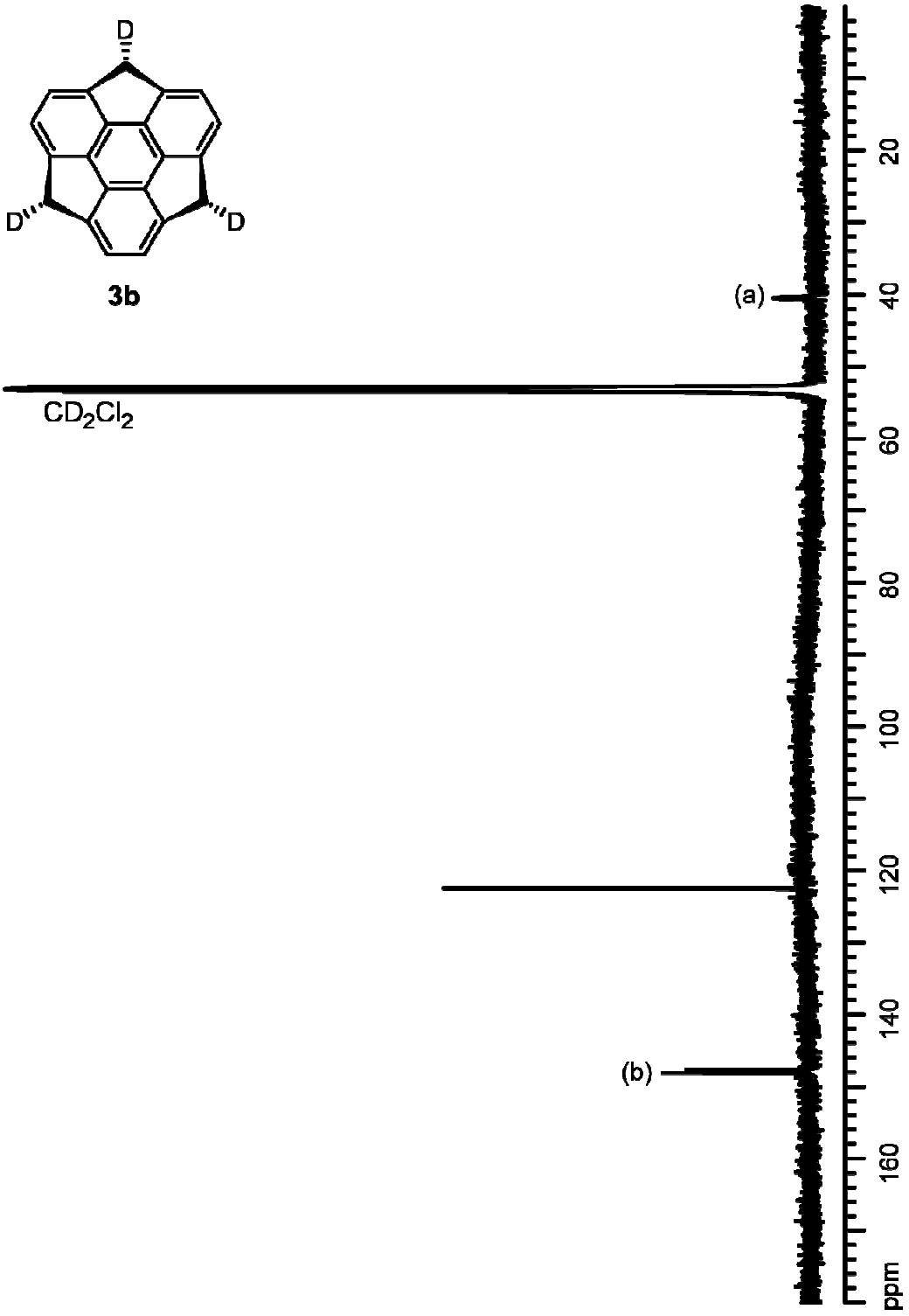


3b

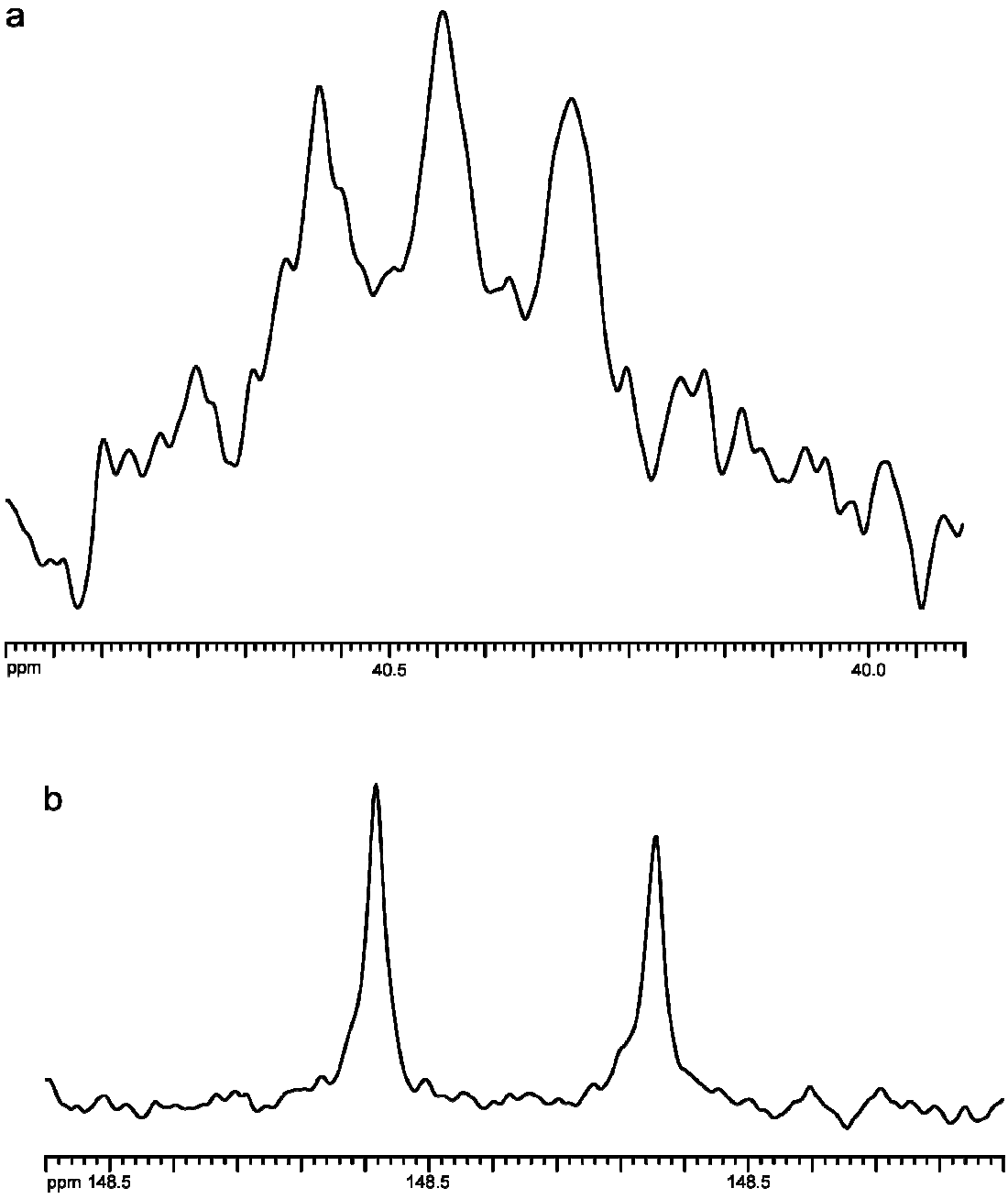


^{13}C NMR spectrum of **3b**

(600 MHz, CD_2Cl_2, 213 K)

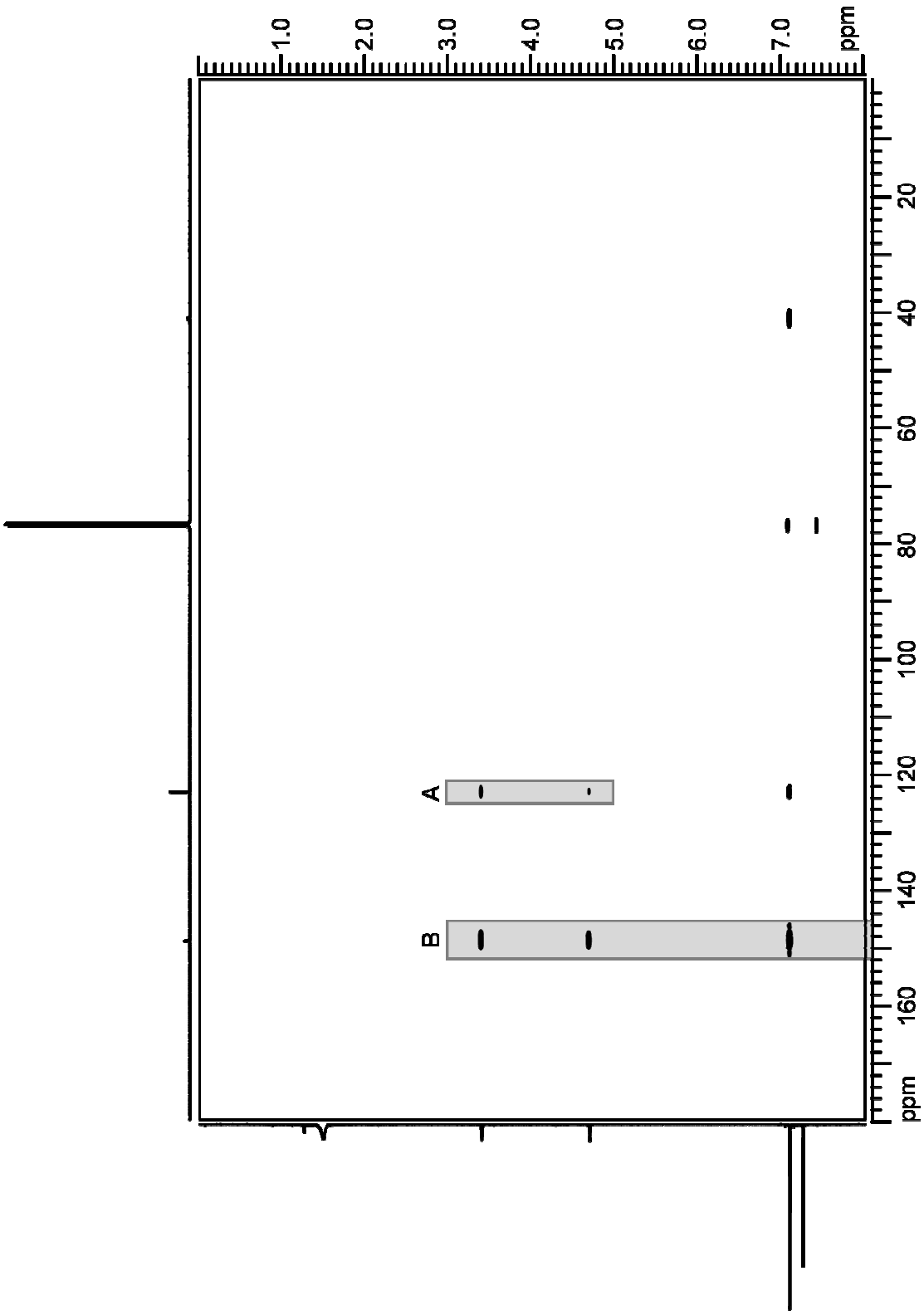


Enlarged view (a), (b), and (c) for ^{13}C NMR spectrum of trideuteriosumanene **3b**

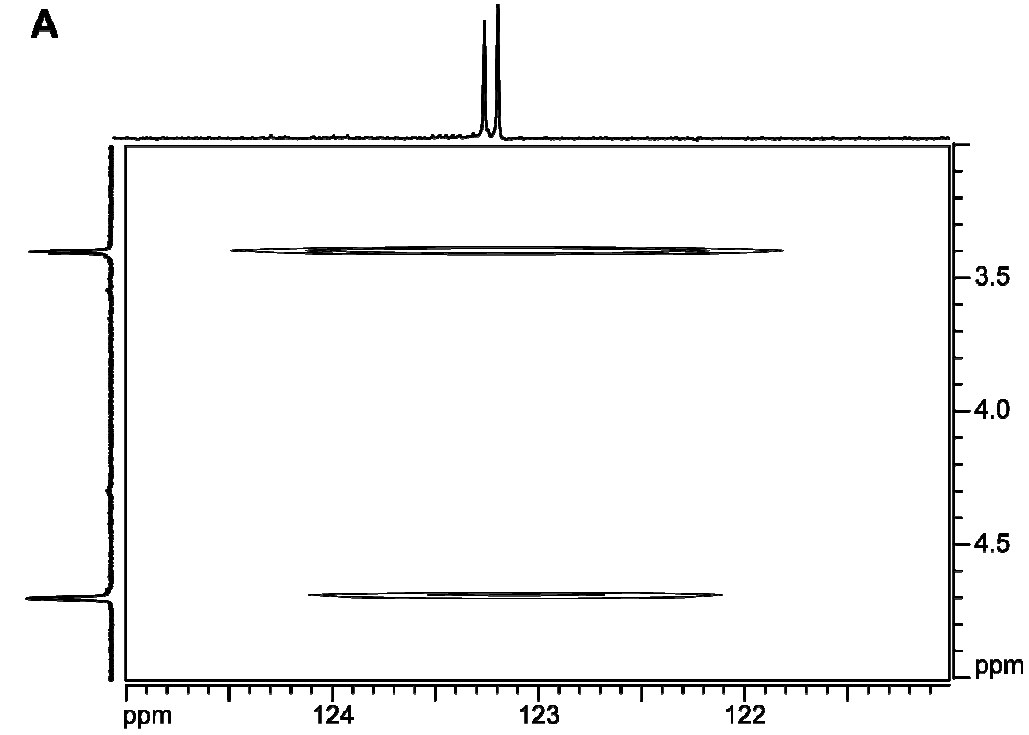


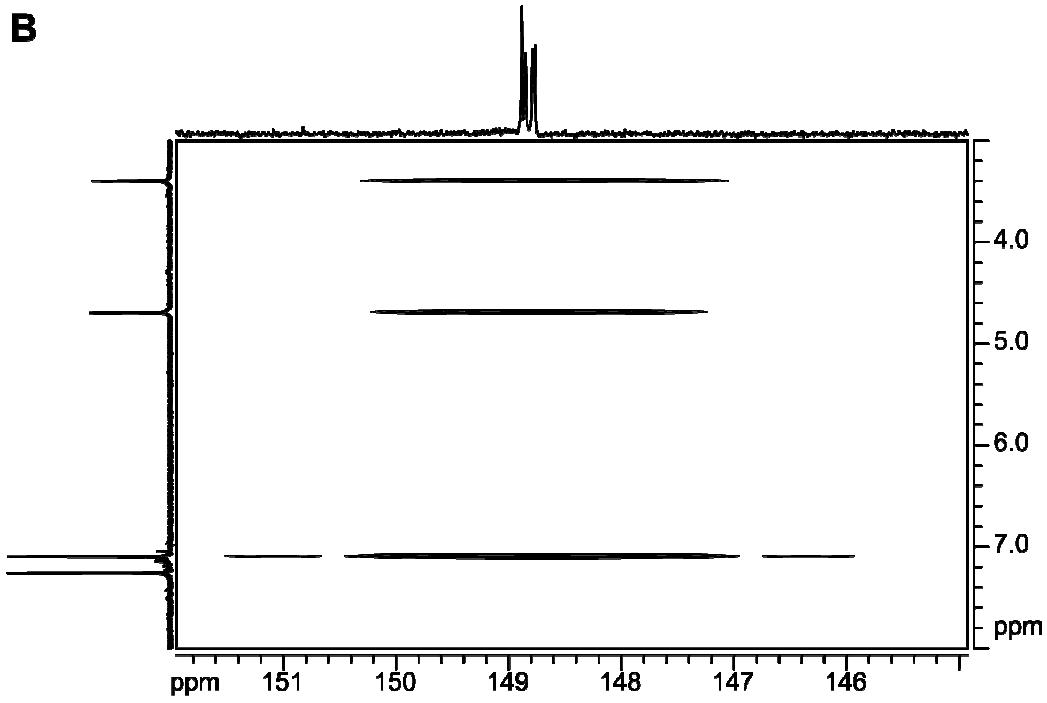
HMBC experiment of trideuteriosumanene **3**

(600 MHz, $CDCl_3$)



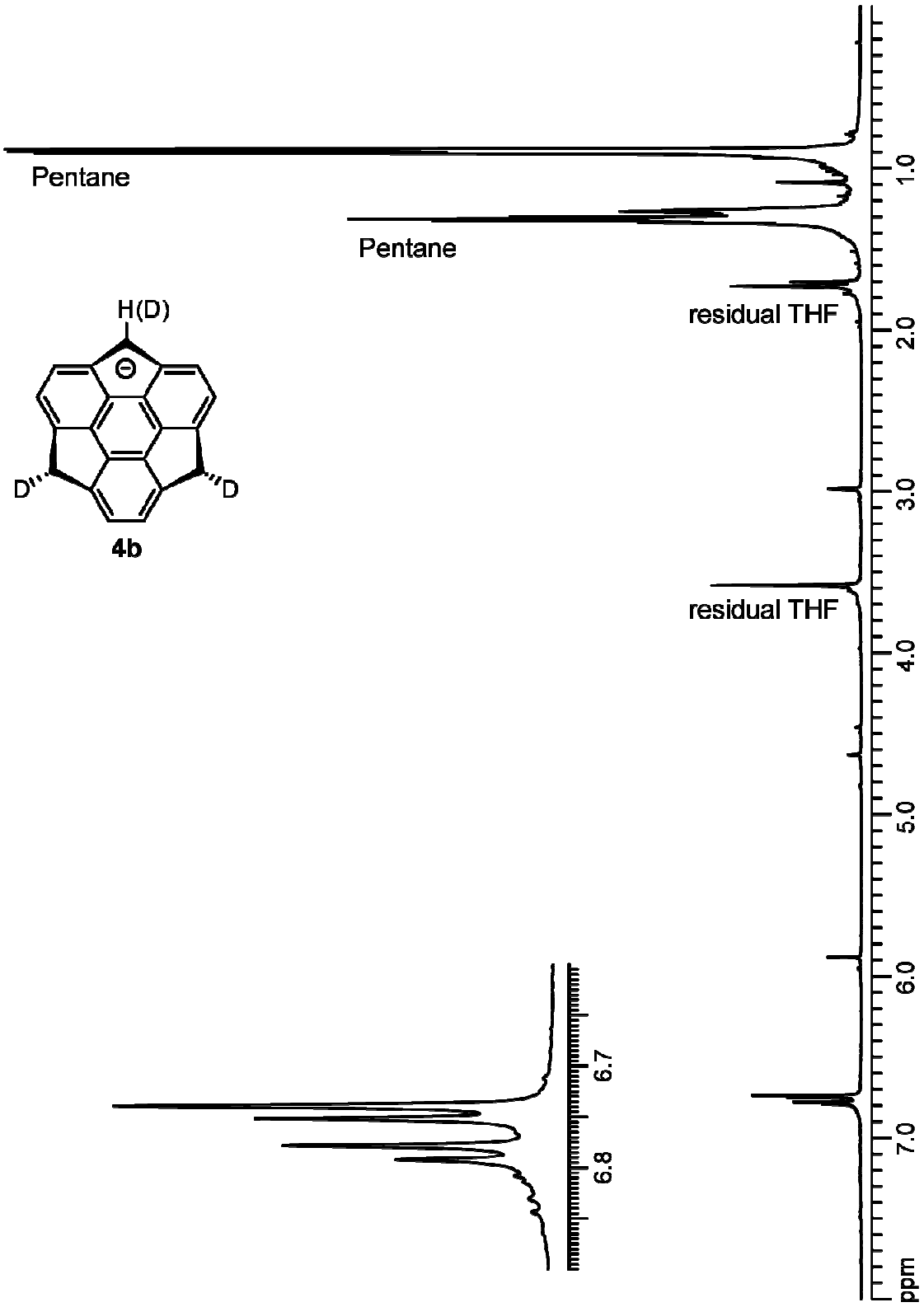
Enlarged view A and B for HMBC experiment of trideuteriosumanene **3**





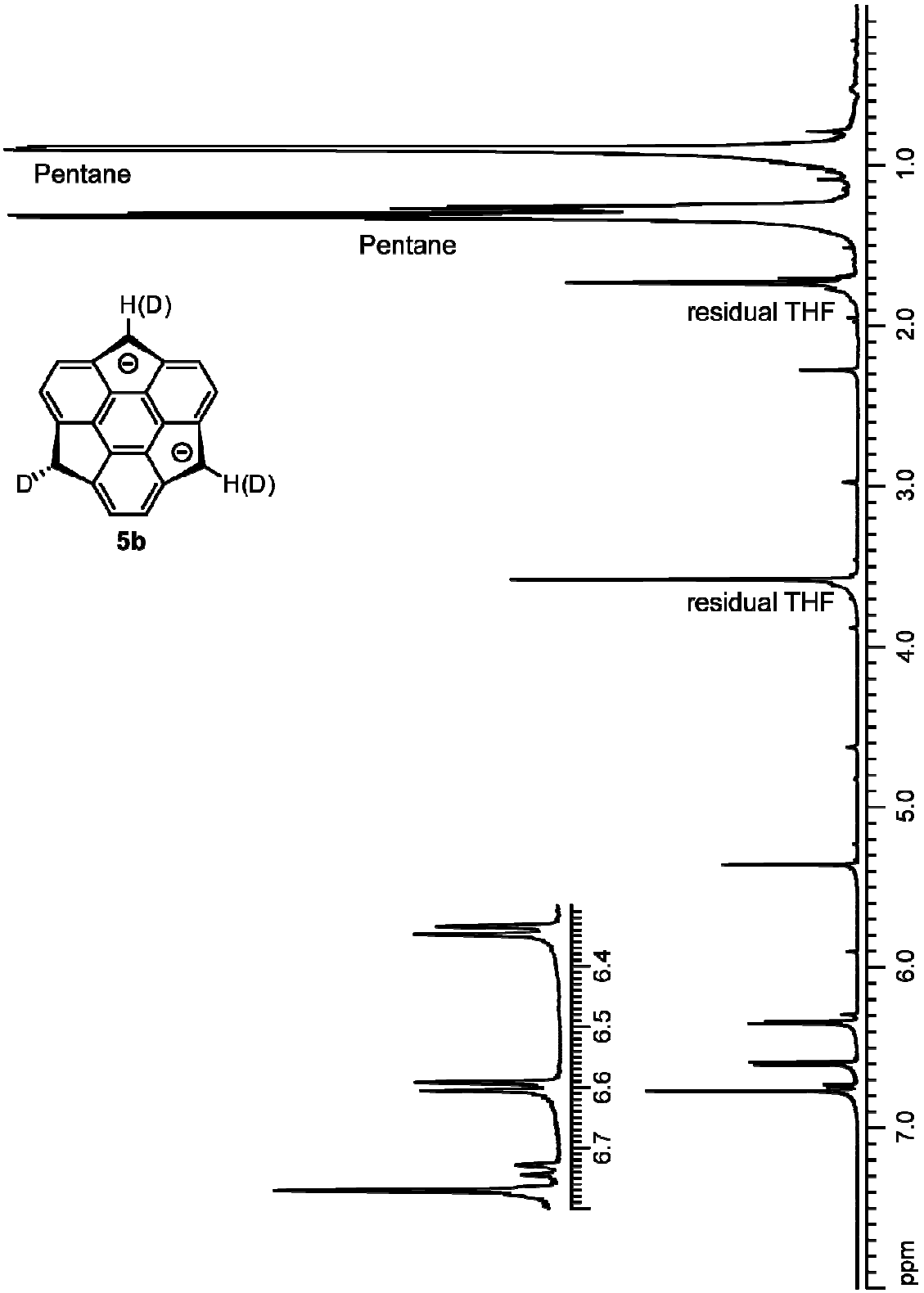
^{1}H NMR spectrum of monoanion **4b**

(600 MHz, THF-d_8, 283 K)

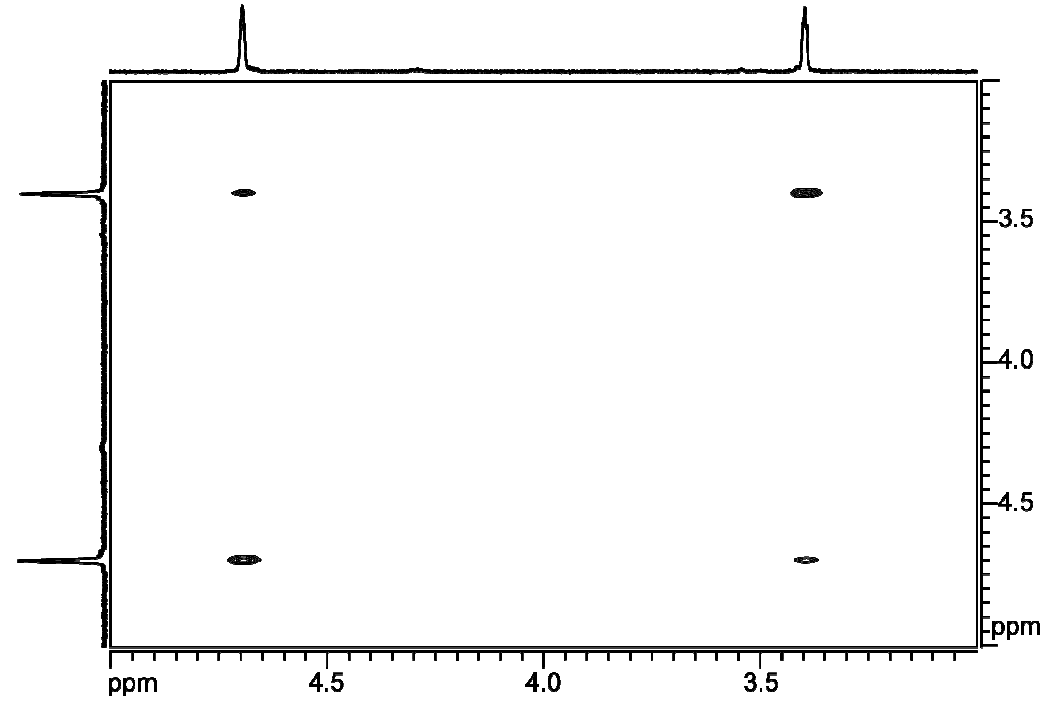


^{1}H NMR spectrum of dianion **5b**

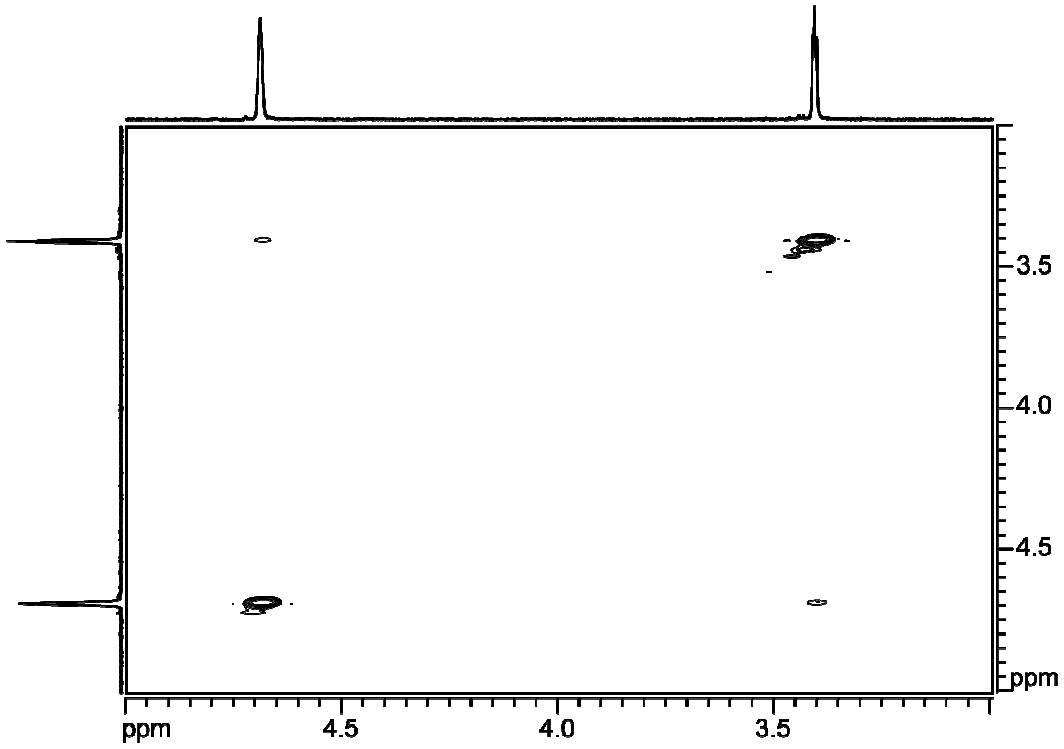
(600 MHz, THF-d_8, 273 K)



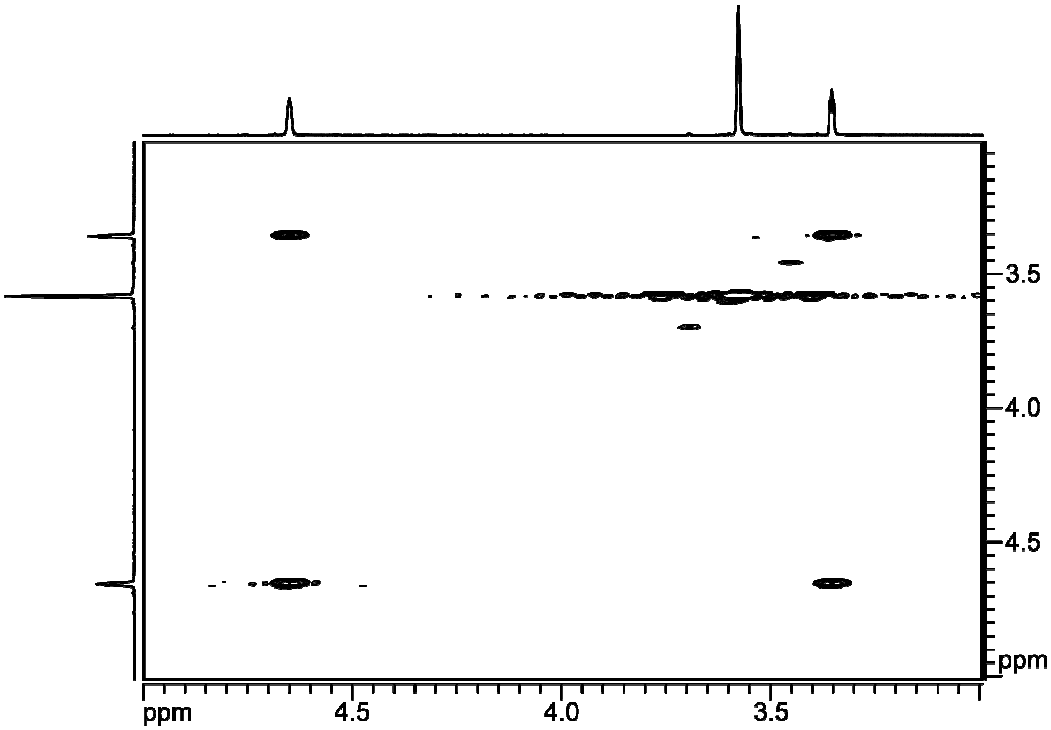
Selected region of 2D EXSY NMR spectrum of **3** (600 MHz, $CDCl_3$, 318 K)



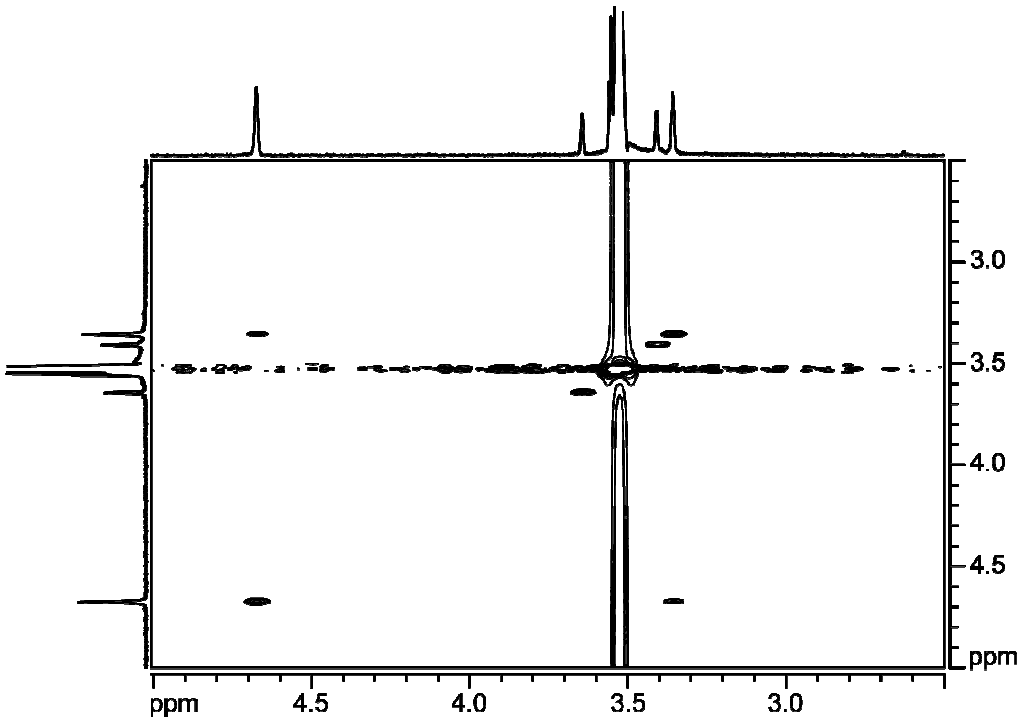
Selected region of 2D EXSY NMR spectrum of **3** (600 MHz, CD_2Cl_2, 303 K)



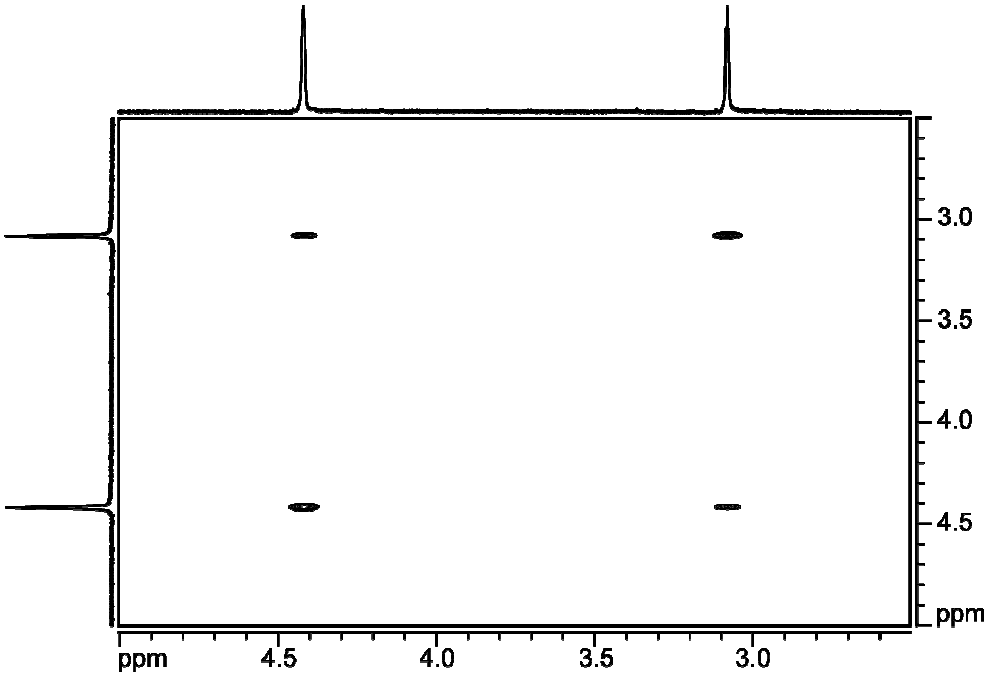
Selected region of 2D EXSY NMR spectrum of **3** (600 MHz, THF-d_8, 318 K)



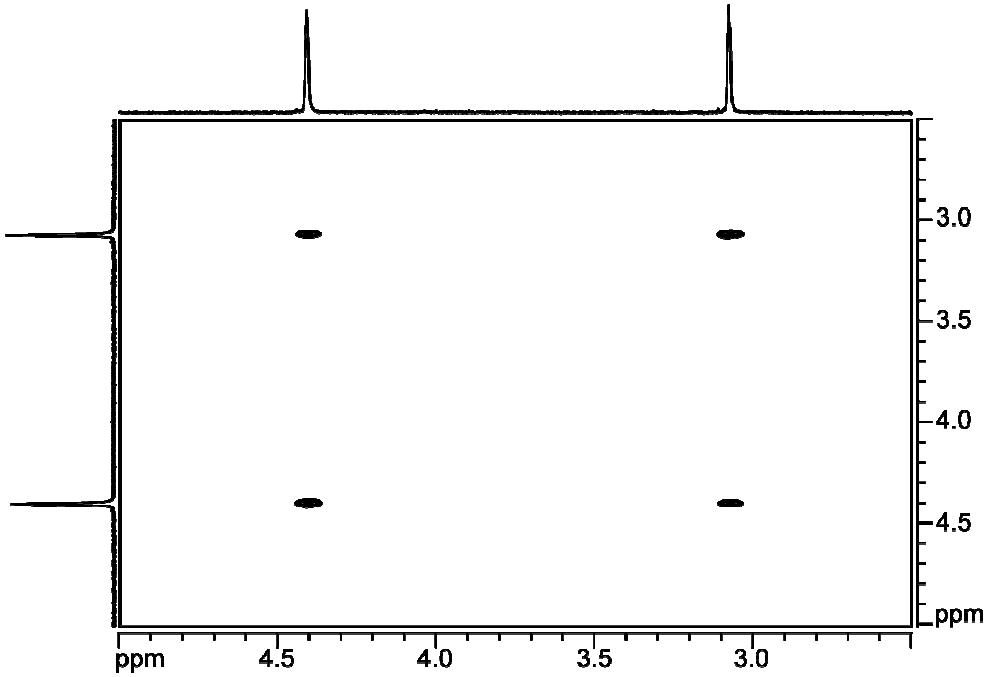
Selected region of 2D EXSY NMR spectrum of **3** (600 MHz, 1,4-dioxane-d_8, 318 K)



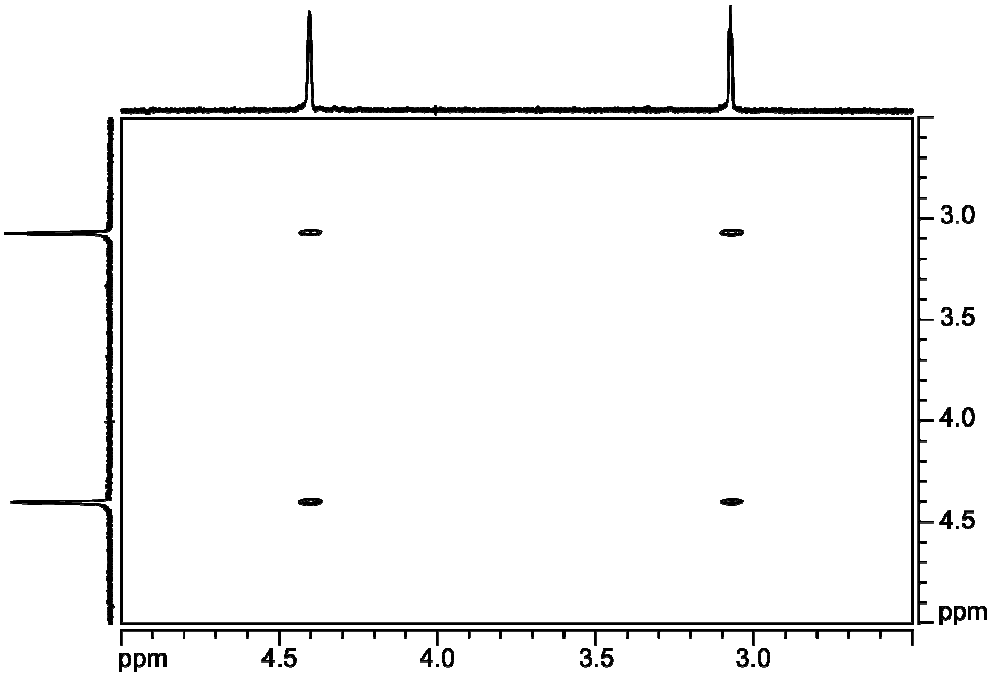
Selected region of 2D EXSY NMR spectrum of **3** (600 MHz, benzene-d_6, 318 K)



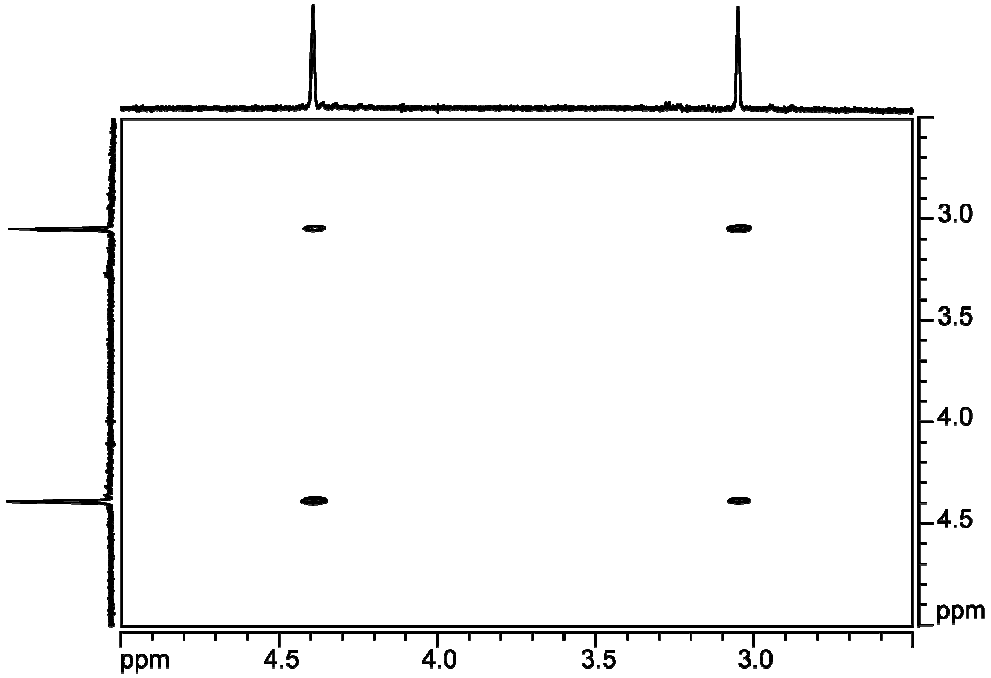
Selected region of 2D EXSY NMR spectrum of **3** (600 MHz, toluene-d_8, 318 K)



Selected region of 2D EXSY NMR spectrum of **3** (600 MHz, xylene-d_{10}, 318 K)

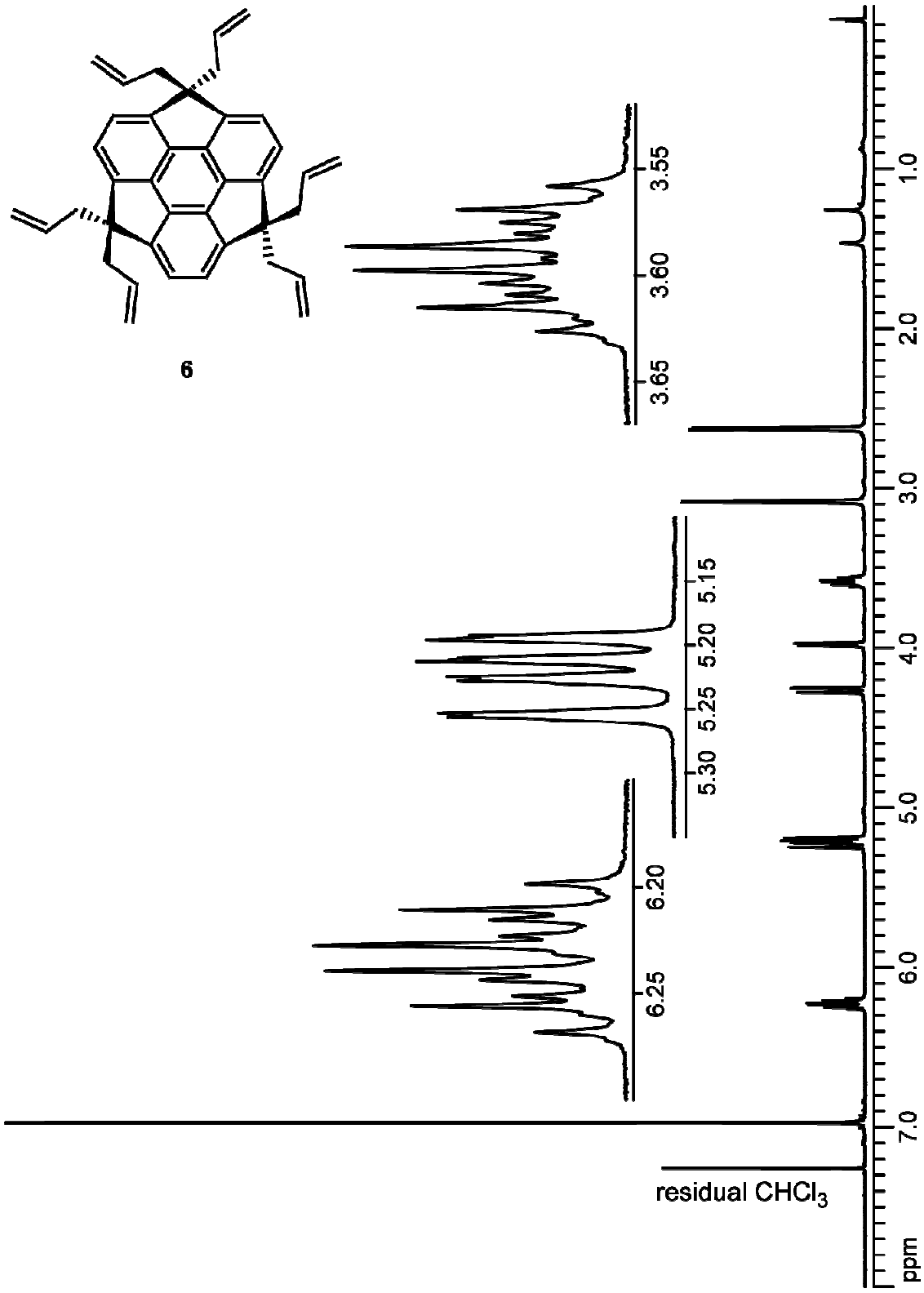


Selected region of 2D EXSY NMR spectrum of **3** (600 MHz, mesitylene-d_{12}, 318 K)



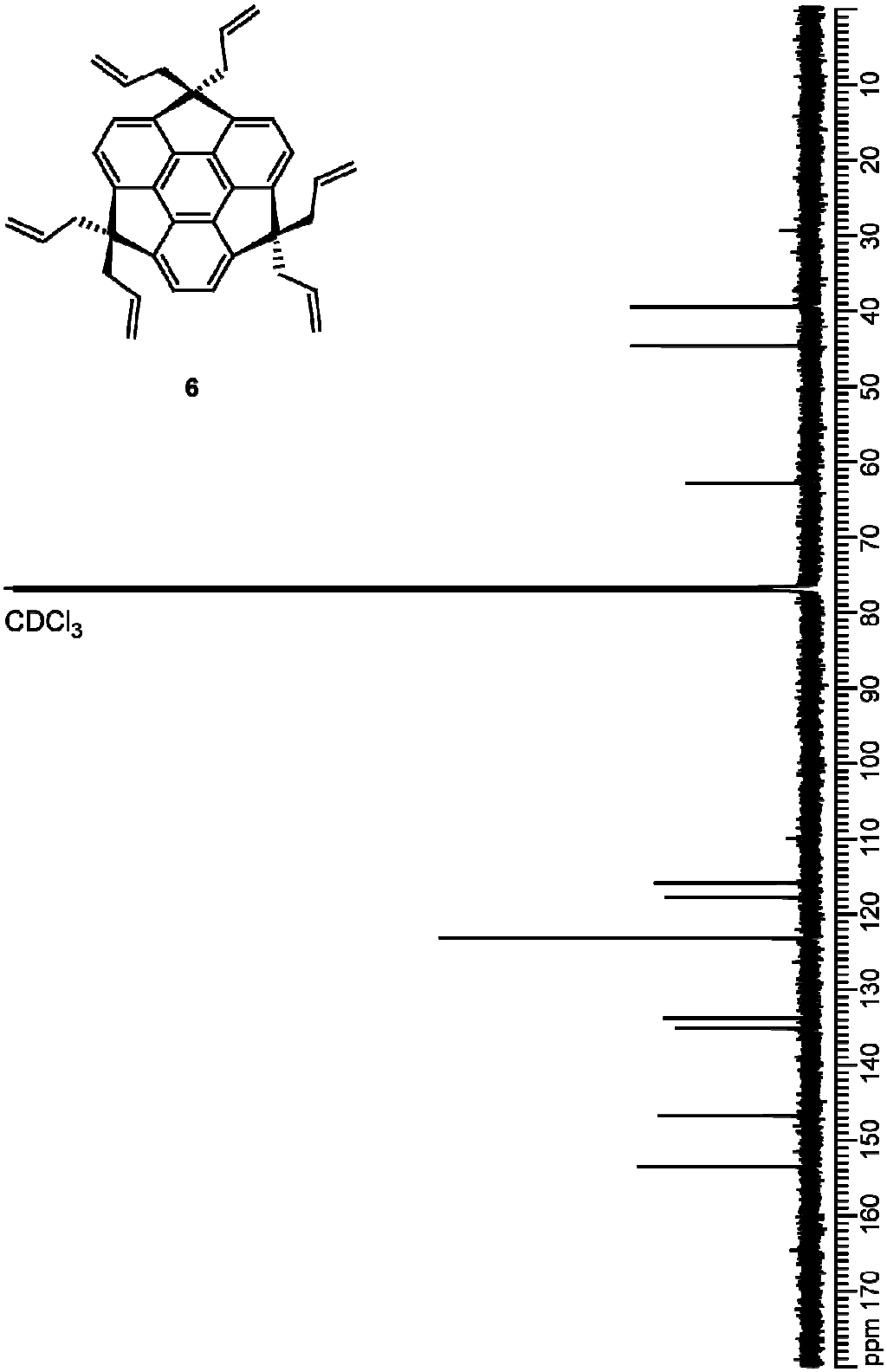
^{1}H NMR spectrum of hexaallylsumanene **6**

(600 MHz, $CDCl_3$)



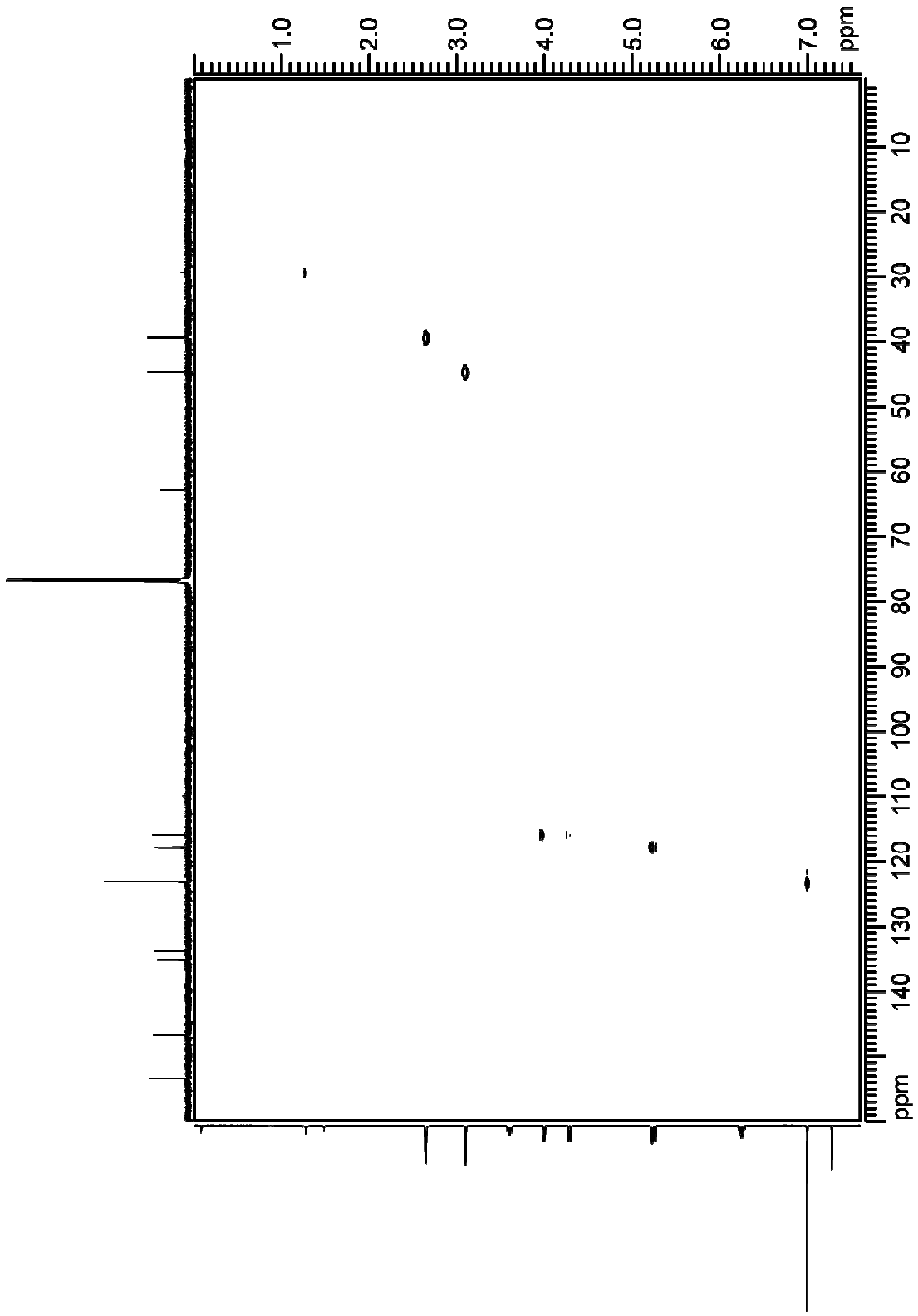
^{13}C NMR spectrum of hexaallylsumanene **6**

(150 MHz, $CDCl_3$)



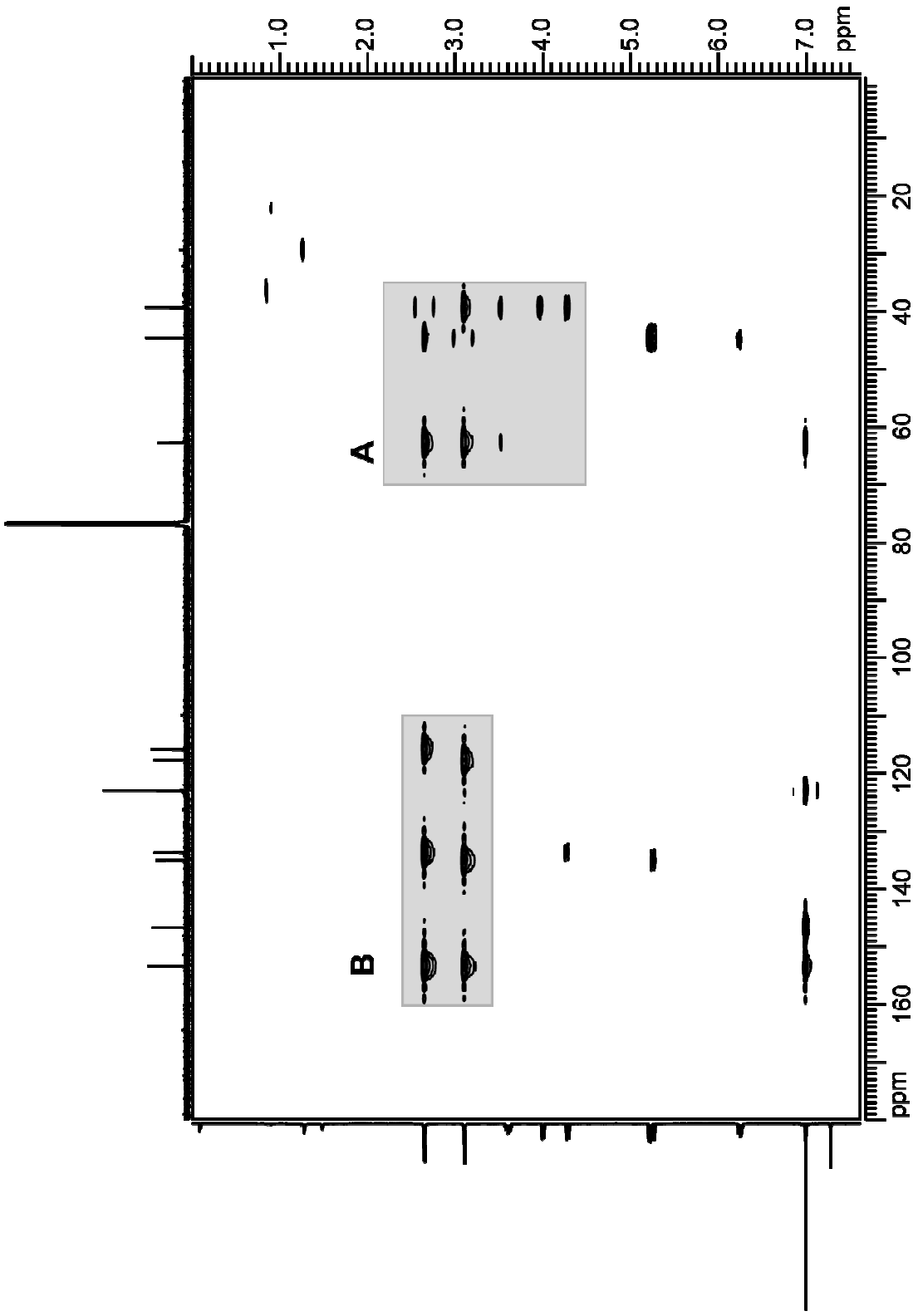
HMQC experiment of hexaallylsumanene **6**

(600 MHz, $CDCl_3$)

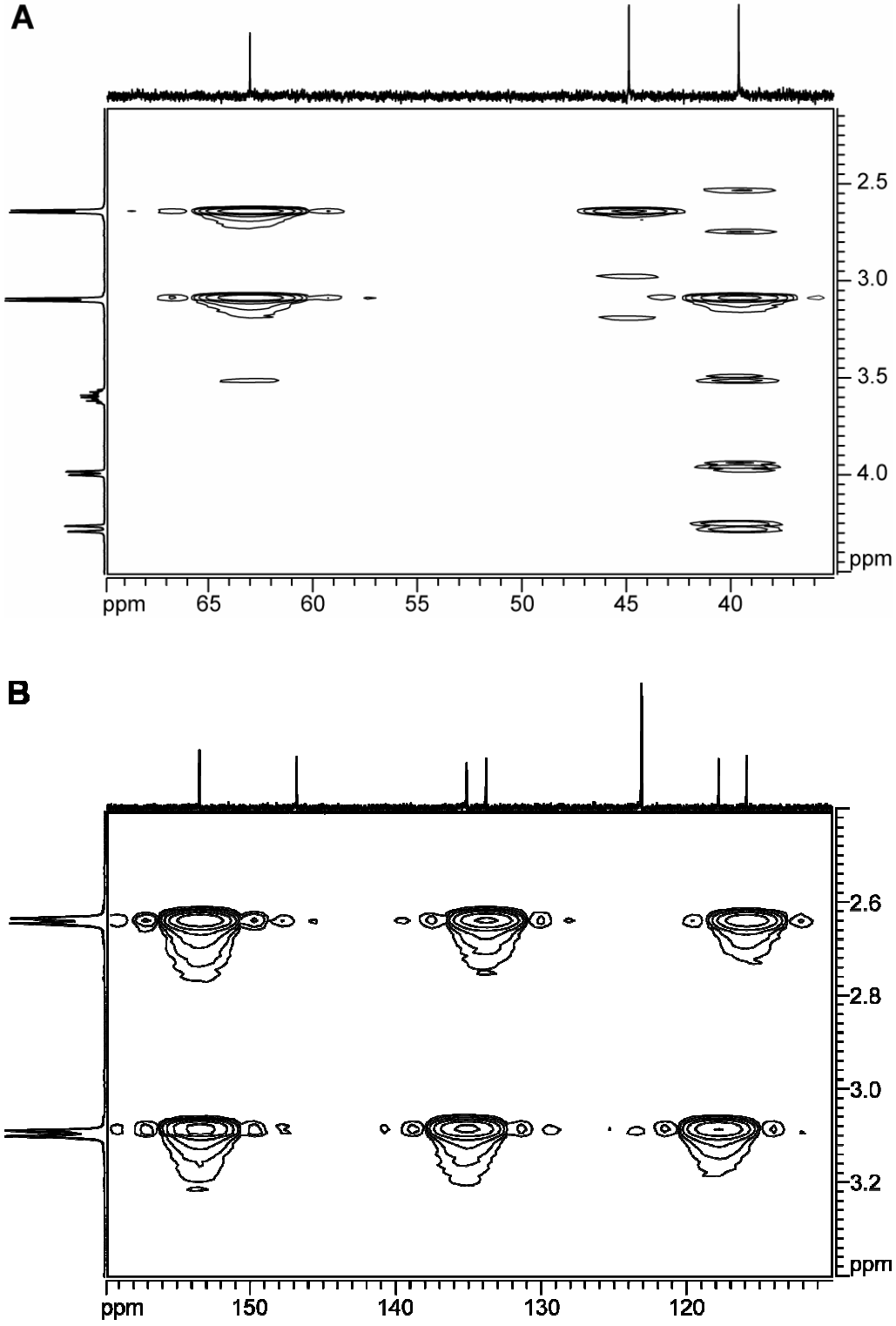


HMBC experiment of hexaallylsumanene **6**

(600 MHz, $CDCl_3$)

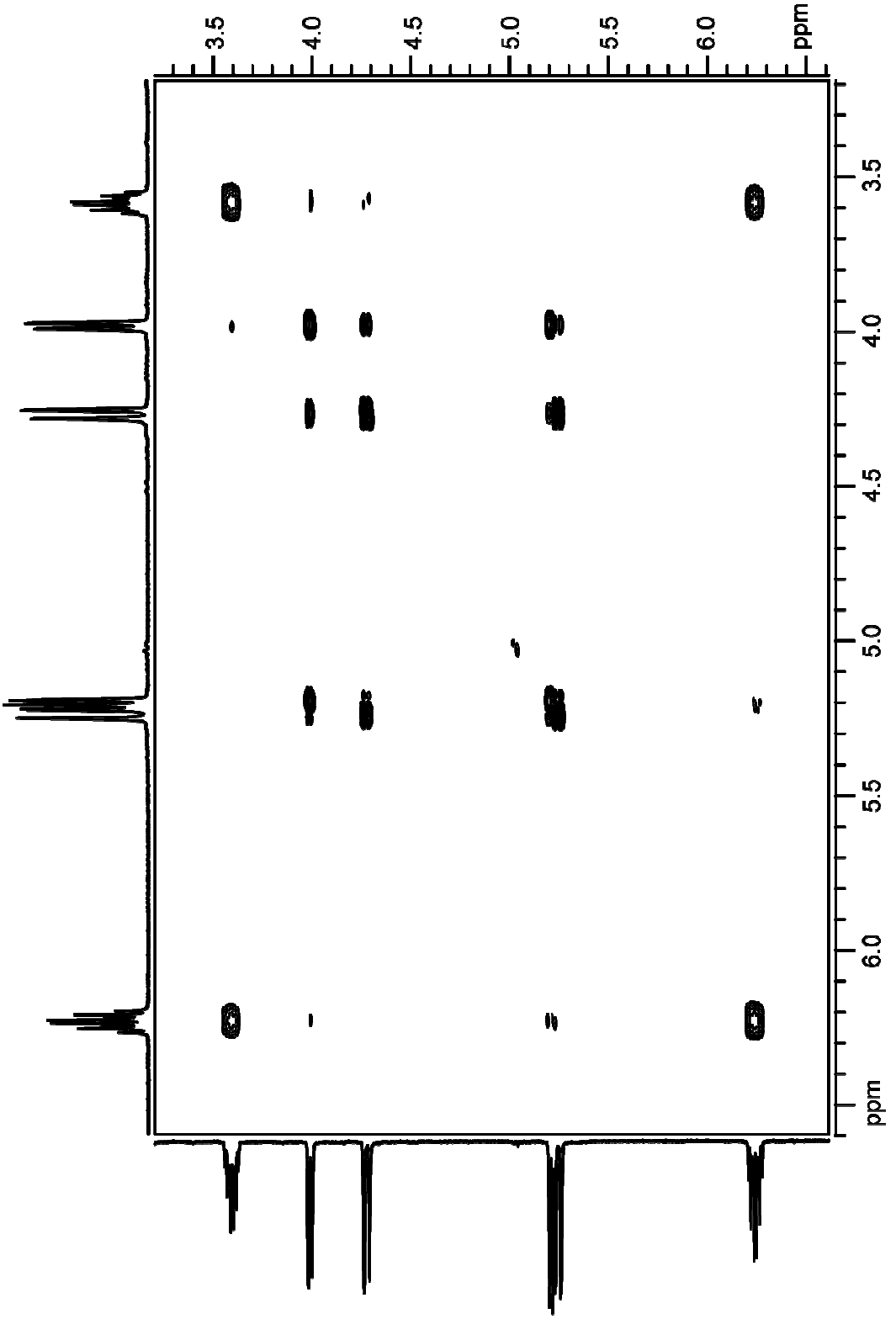


Enlarged view A and B for HMBC experiment of hexaallylsumanene **6**



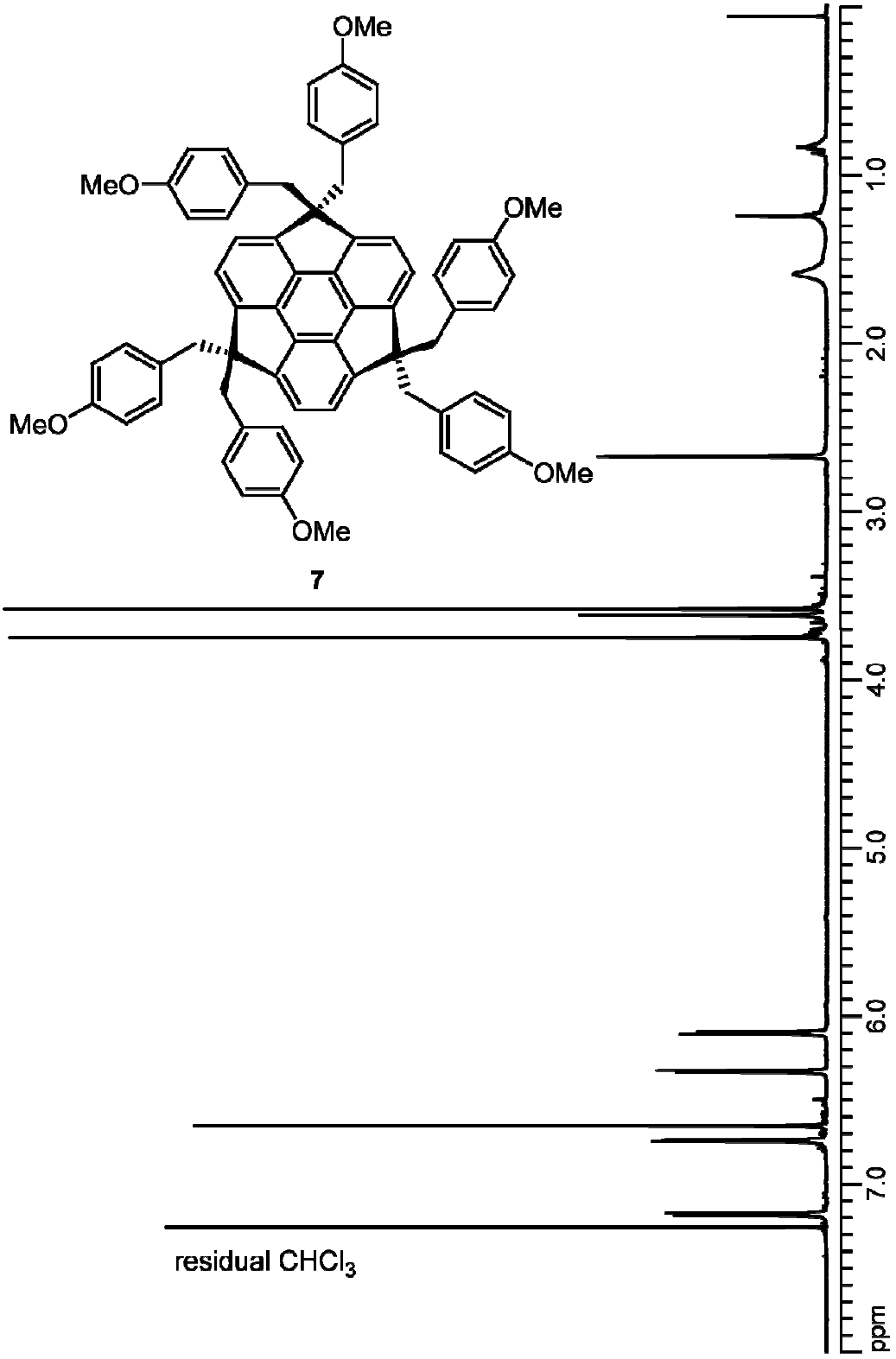
Selected region of 2D EXSY NMR spectrum of **6**

(600 MHz, $CDCl_3$, 318 K)



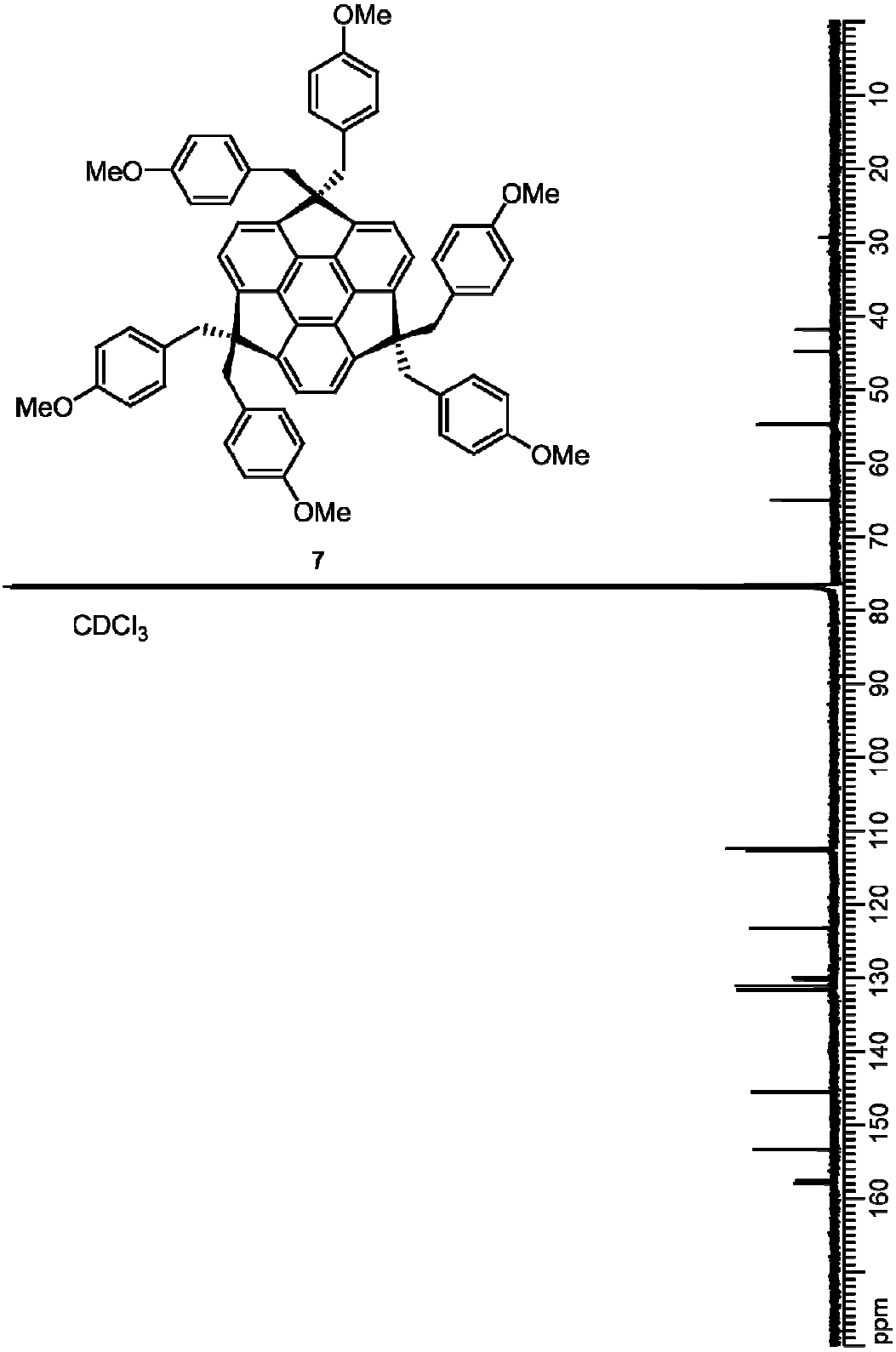
^{1}H NMR spectrum of hexaanisylsumanene **7**

(600 MHz, $CDCl_3$)



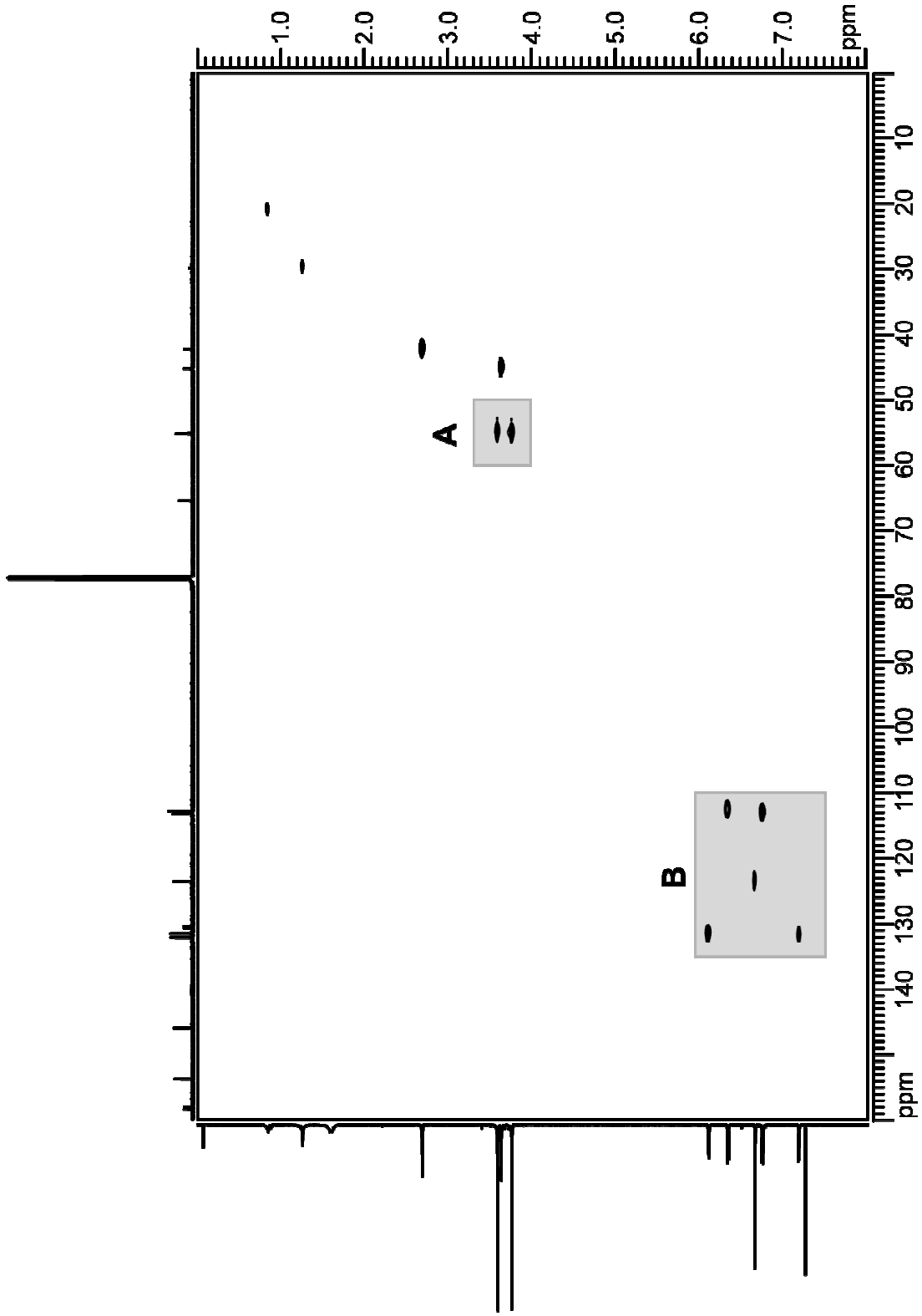
^{13}C NMR spectrum of hexaanisylsumanene **7**

(150 MHz, $CDCl_3$)

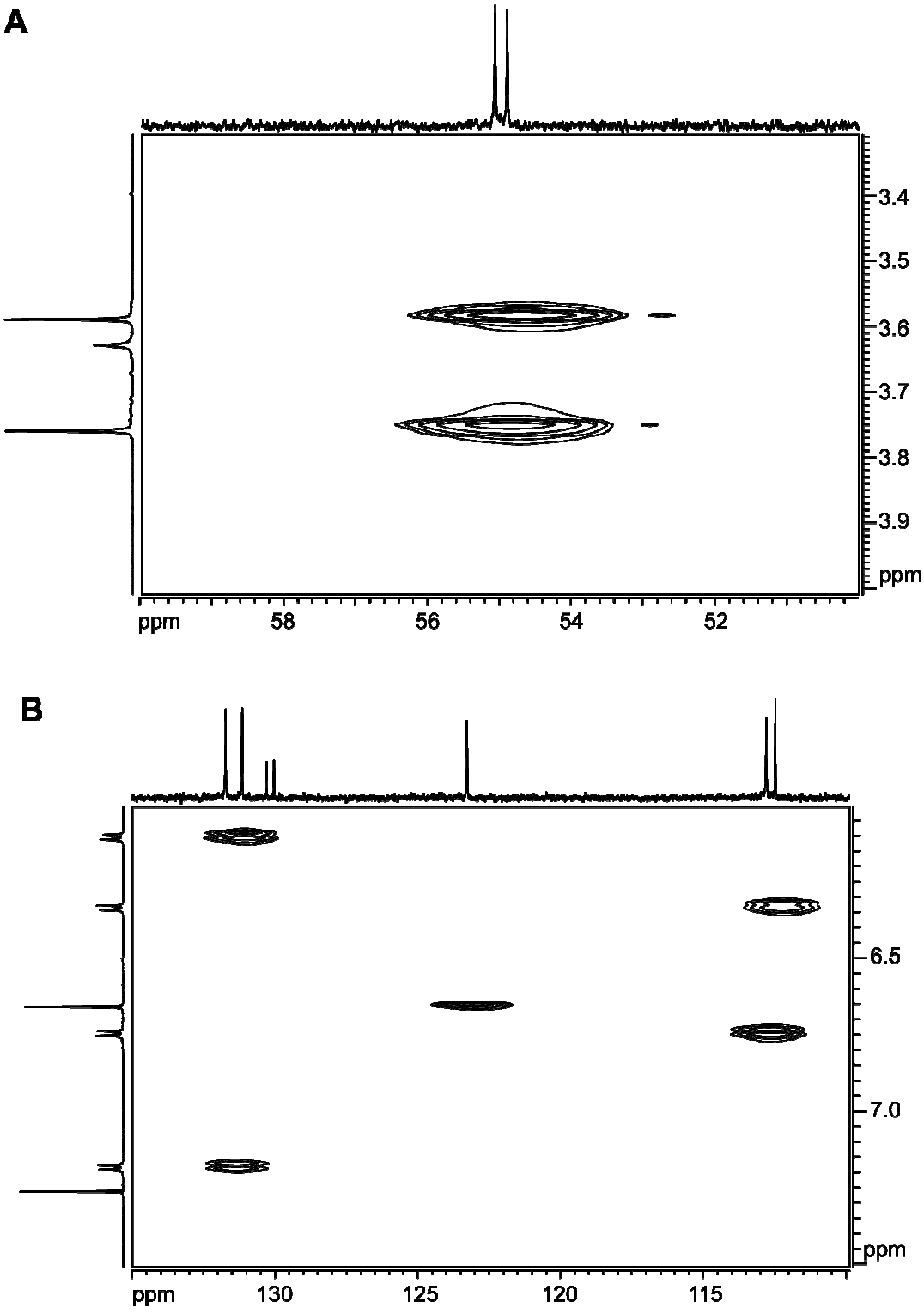


HMQC experiment of hexaanisylsumanene **7**

(600 MHz, $CDCl_3$)

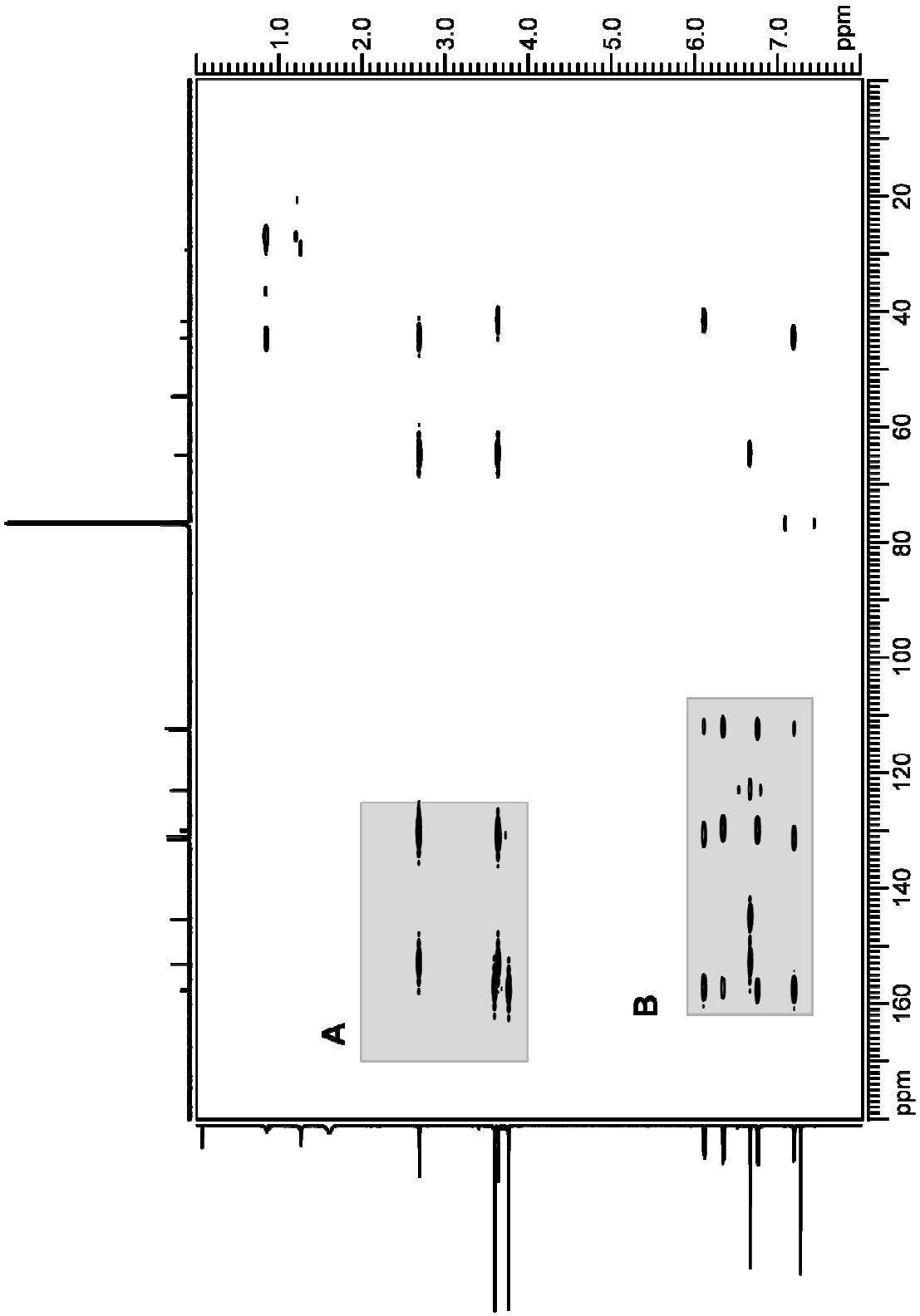


Enlarged view A and B for HMQC experiment of hexaanisylsumanene **7**

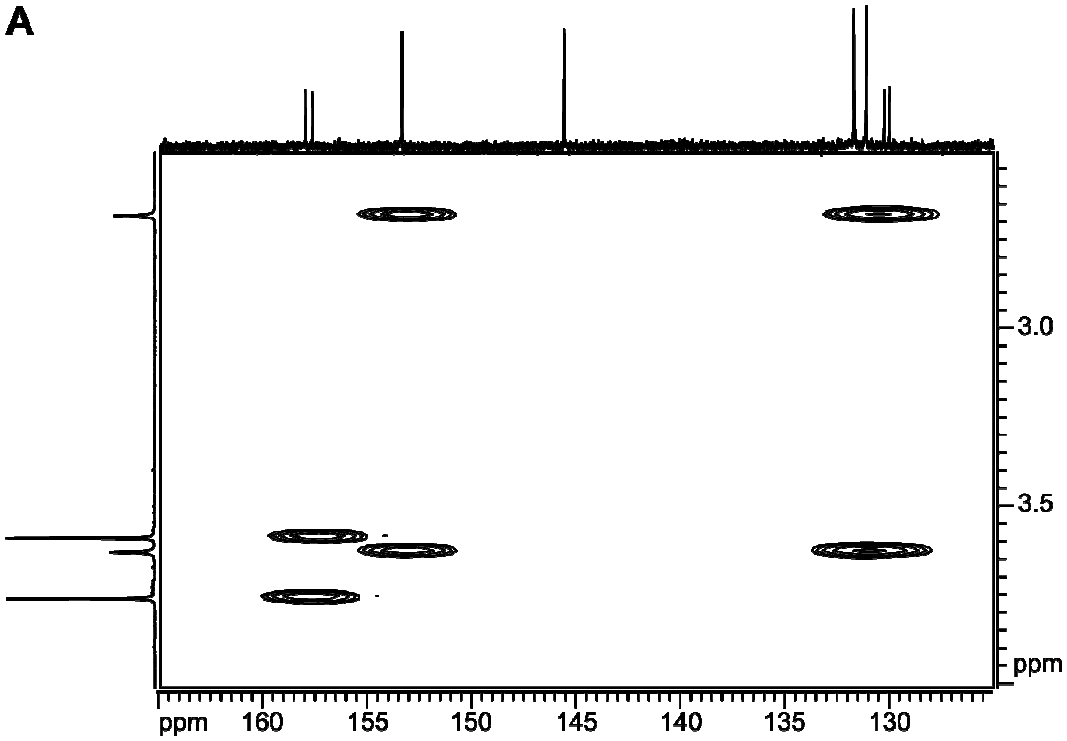


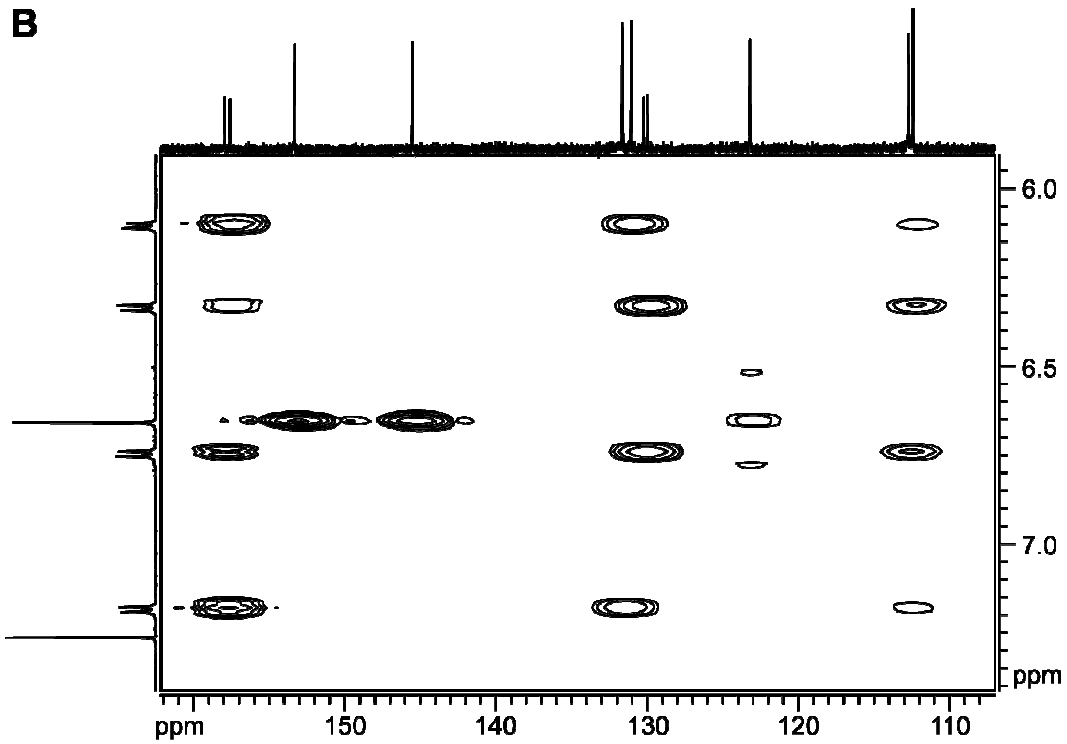
HMBC experiment of hexaanisylsumanene **7**

(600 MHz, $CDCl_3$)



Enlarged view A and B for HMBC experiment of hexaanisylsumanene **7**





Selected region of 2D EXSY NMR spectrum of **7**

(600 MHz, $CDCl_3$, 318 K)