Bisacenaphthopyrazinoquinoxaline Derivatives: Synthesis, Physical Properties and Applications as Semiconductors for n-Channel Field Effect Transistors

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1. Absorption spectrum of compound 1 in toluene at room temperature

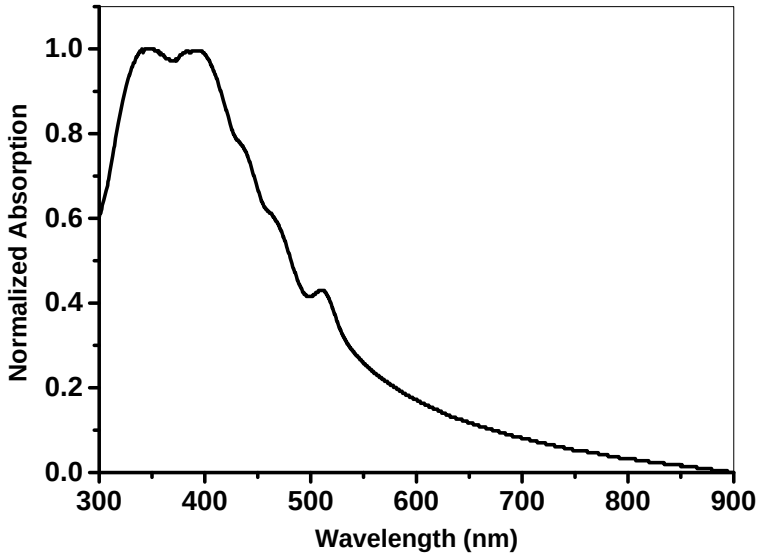
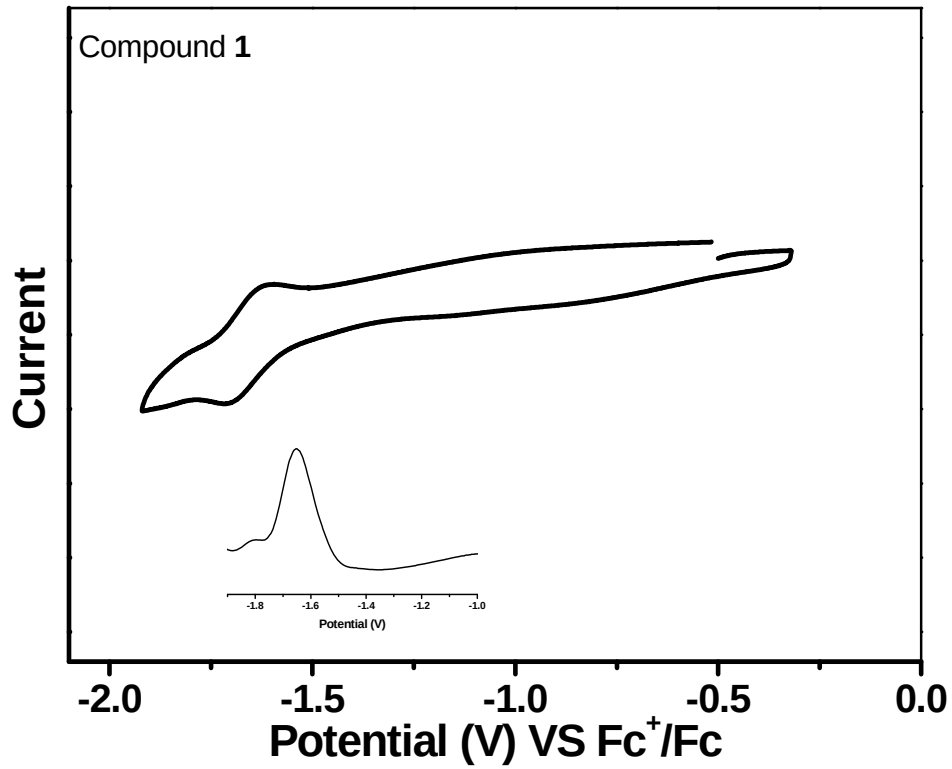


Fig. S1. The absorption spectrum of compound **1** in toluene at room temperature.

2. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of compounds 1-3



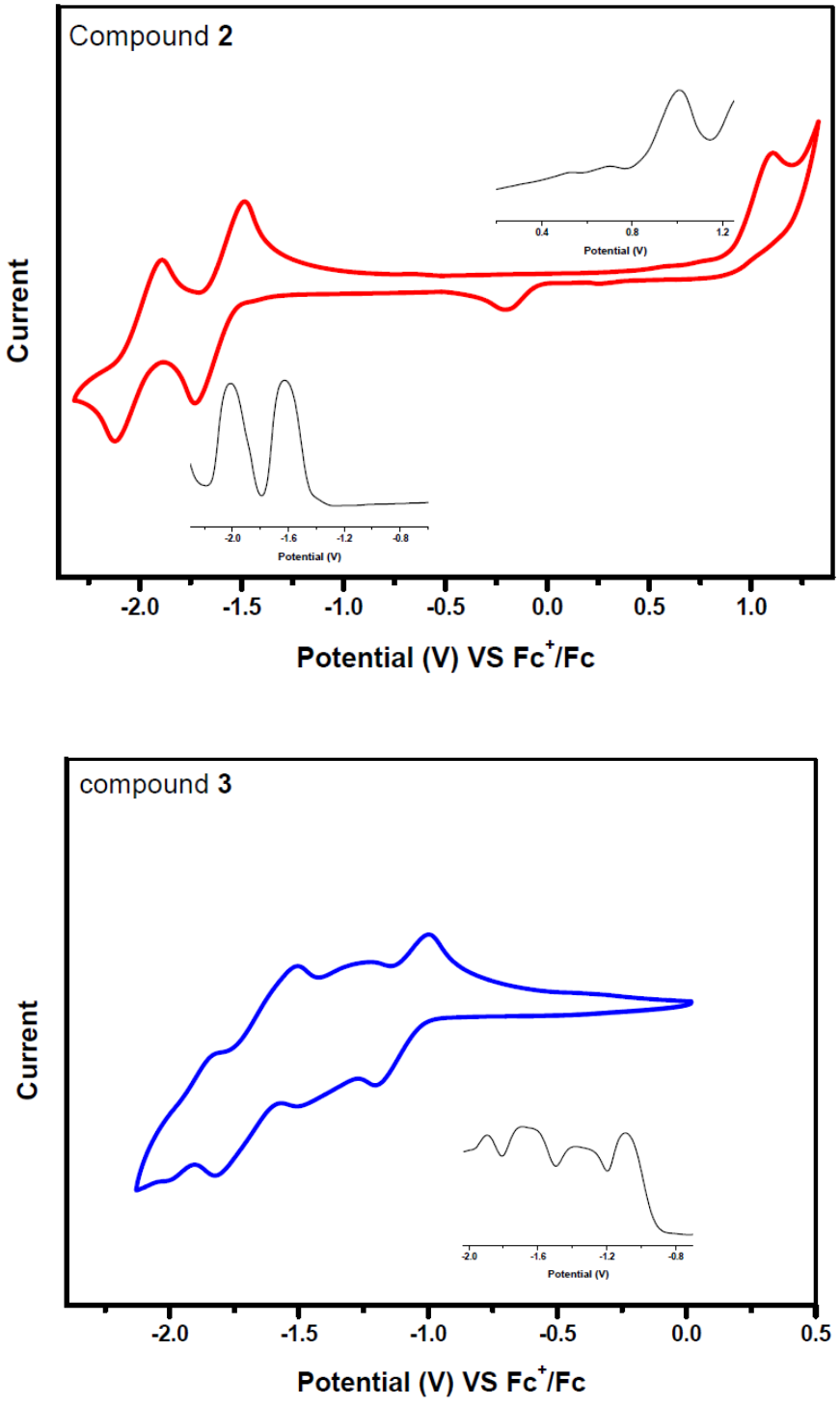


Fig. S2 Cyclic voltammograms of compounds **1-3** in chlorobenzene (inserted are the DPV curves of the corresponding redox waves).

3. TD-DFT calculations on compounds 1-3

The calculations were performed at the B3LYP/6-31G* level theory[1-5] by using Gaussian 09.[6] All the solubilizing aliphatic chains were displaced by ethyl groups to simplify the calculation. The geometries of **1-3** were fully optimized in gas phase using the default convergence criteria without any constraints and confirmed by frequency calculations. UV-vis-NIR absorption spectra were generated assuming an average UV-vis width of 4000 cm^{-1} at half-height using the SWizard program.[7]

	Hartree	eV
LUMO+4	-0.01375	-0.37
LUMO+3	-0.04197	-1.14
LUMO+2	-0.0623	-1.70
LUMO+1	-0.07526	-2.05
LUMO	-0.08615	-2.34
HOMO	-0.20086	-5.47
HOMO-1	-0.21968	-5.98
HOMO-2	-0.22047	-6.00
HOMO-3	-0.23693	-6.45
HOMO-4	-0.23706	-6.45
HOMO-5	-0.24158	-6.57
HOMO-6	-0.25033	-6.81
HOMO-7	-0.25183	-6.85
HOMO-8	-0.26168	-7.12
HOMO-9	-0.29784	-8.10
HOMO-10	-0.30431	-8.28

Table S1. Calculated energy levels of compound **1**.

	Hartree	**eV**
LUMO+4	-0.01649	-0.45
LUMO+3	-0.04399	-1.20
LUMO+2	-0.0659	-1.79
LUMO+1	-0.07942	-2.16
LUMO	-0.08942	-2.43
HOMO	-0.19473	-5.30
HOMO-1	-0.2232	-6.07
HOMO-2	-0.22573	-6.14
HOMO-3	-0.22588	-6.15
HOMO-4	-0.22695	-6.18
HOMO-5	-0.22951	-6.25
HOMO-6	-0.23343	-6.35

HOMO-7	-0.23994	-6.53
HOMO-8	-0.24344	-6.62
HOMO-9	-0.25321	-6.89
HOMO-10	-0.25327	-6.89

Table S2. Calculated energy levels of compound **2**.

	Hartree	**eV**
LUMO+4	-0.0539	-1.47
LUMO+3	-0.08287	-2.26
LUMO+2	-0.11569	-3.15
LUMO+1	-0.12462	-3.39
LUMO	-0.12671	-3.45
HOMO	-0.22272	-6.06
HOMO-1	-0.24616	-6.70
HOMO-2	-0.25129	-6.84
HOMO-3	-0.25365	-6.90
HOMO-4	-0.25445	-6.92
HOMO-5	-0.25883	-7.04
HOMO-6	-0.26222	-7.14
HOMO-7	-0.271	-7.37
HOMO-8	-0.27181	-7.40
HOMO-9	-0.28035	-7.63
HOMO-10	-0.29218	-7.95

Table S3. Calculated energy levels of compound **3**.

wavelength (nm)	*f*	composition (H = HOMO, L = LUMO)
366.4	3.1295	H-1->L+0(+66%) H-0->L+1(29%)
298.2	0.1389	H-5->L+1(+90%)
253.8	0.1334	H-0->L+4(+48%) H-6->L+2(20%) H-8->L+2(+19%)
242.4	0.1454	H-1->L+4(+37%) H-9->L+0(28%) H-0->L+6(+17%) H-6->L+3(13%)

Table S4. Calculated absorption data ($f > 0.1$) of compound **1**.

wavelength (nm)	*f*	composition (H = HOMO, L = LUMO)
461.6	0.1521	H-0->L+1(+88%) H-3->L+0(+6%)
364.6	1.0988	H-3->L+0(+38%) H-4->L+0(+29%) H-2->L+1(10%) H-0->L+1(9%)
343.8	1.1430	H-2->L+1(+76%) H-3->L+1(+8%) H-4->L+0(+7%)
275.6	0.5411	H-0->L+4(+45%) H-0->L+6(+30%) H-11->L+1(12%)

Table S5. Calculated absorption data ($f > 0.1$) of compound **2**.

wavelength (nm)	*f*	composition (H = HOMO, L = LUMO)
557.4	0.2800	H-0->L+0(+95%)
372.7	2.6300	H-5->L+1(+74%) H-3->L+0(+14%)

Table S6. Calculated absorption data ($f > 0.1$) of compound **3**.

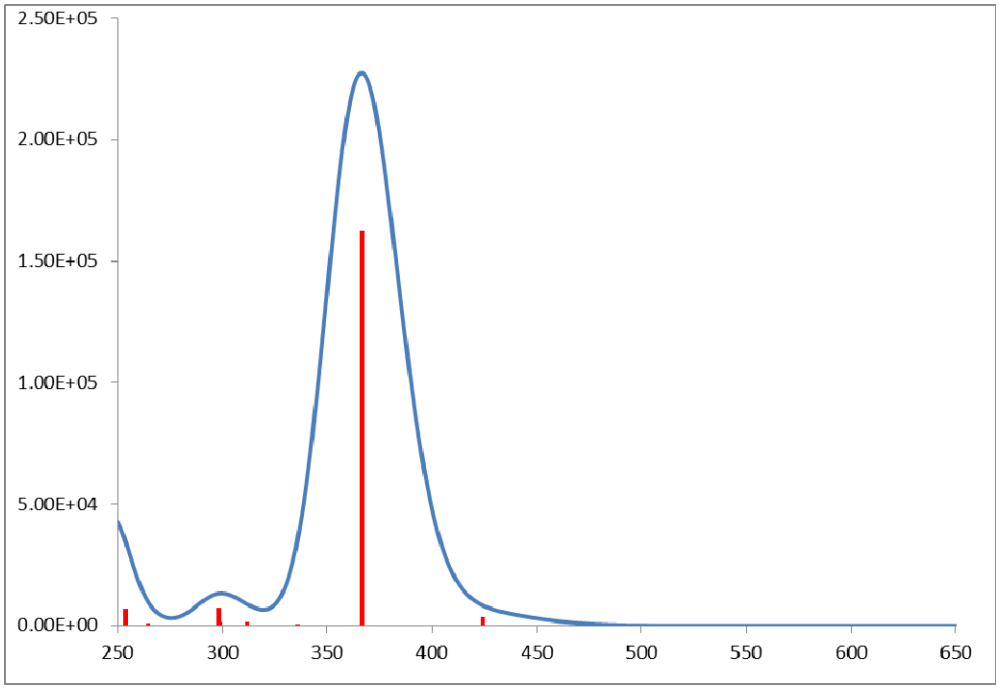


Fig. S3 Calculated absorption spectrum of compound **1**.

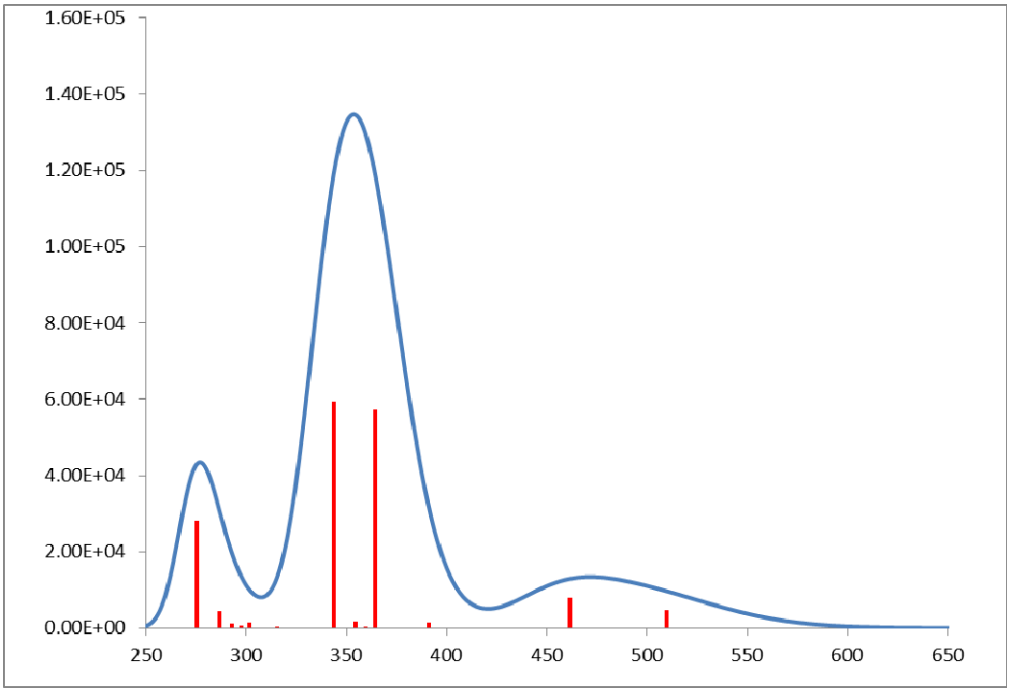


Fig. S4 Calculated absorption spectrum of compound **2**.

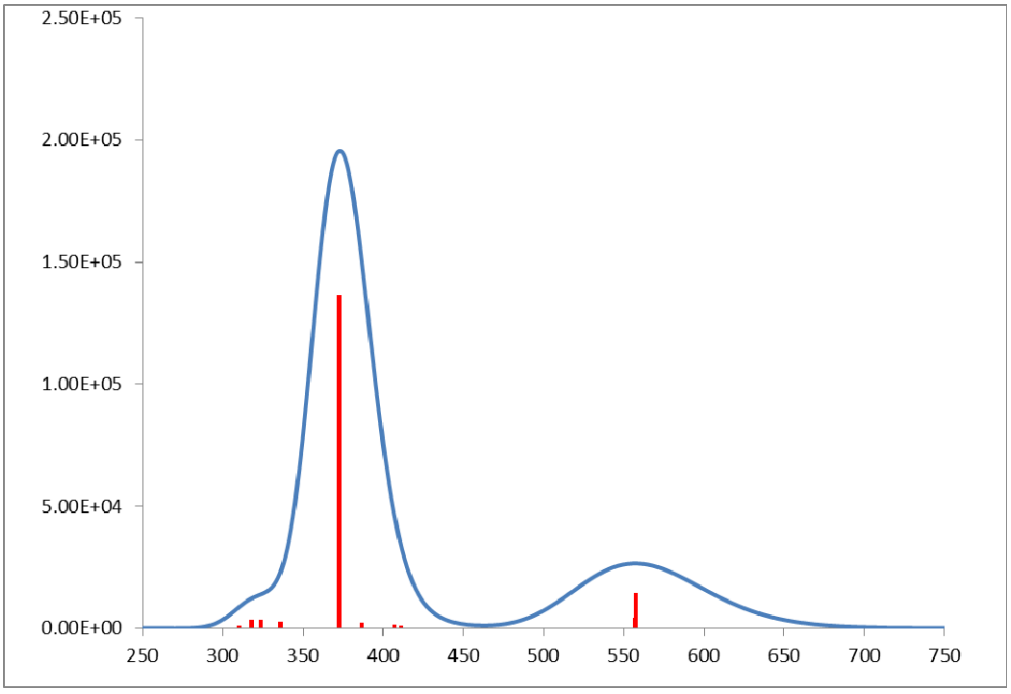


Fig. S5 Calculated absorption spectrum of compound **3**.

4. TGA curves of compounds 1-3

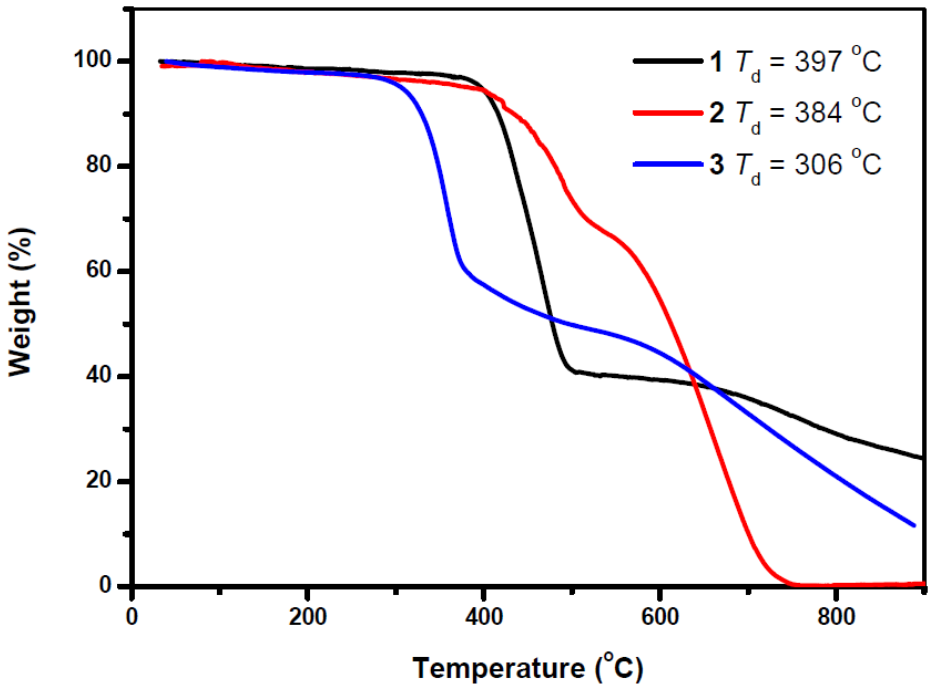


Fig. S6 TGA curves of compounds **1-3** at a heating rate of 10 °C/min.

5. XRD patterns in thin films

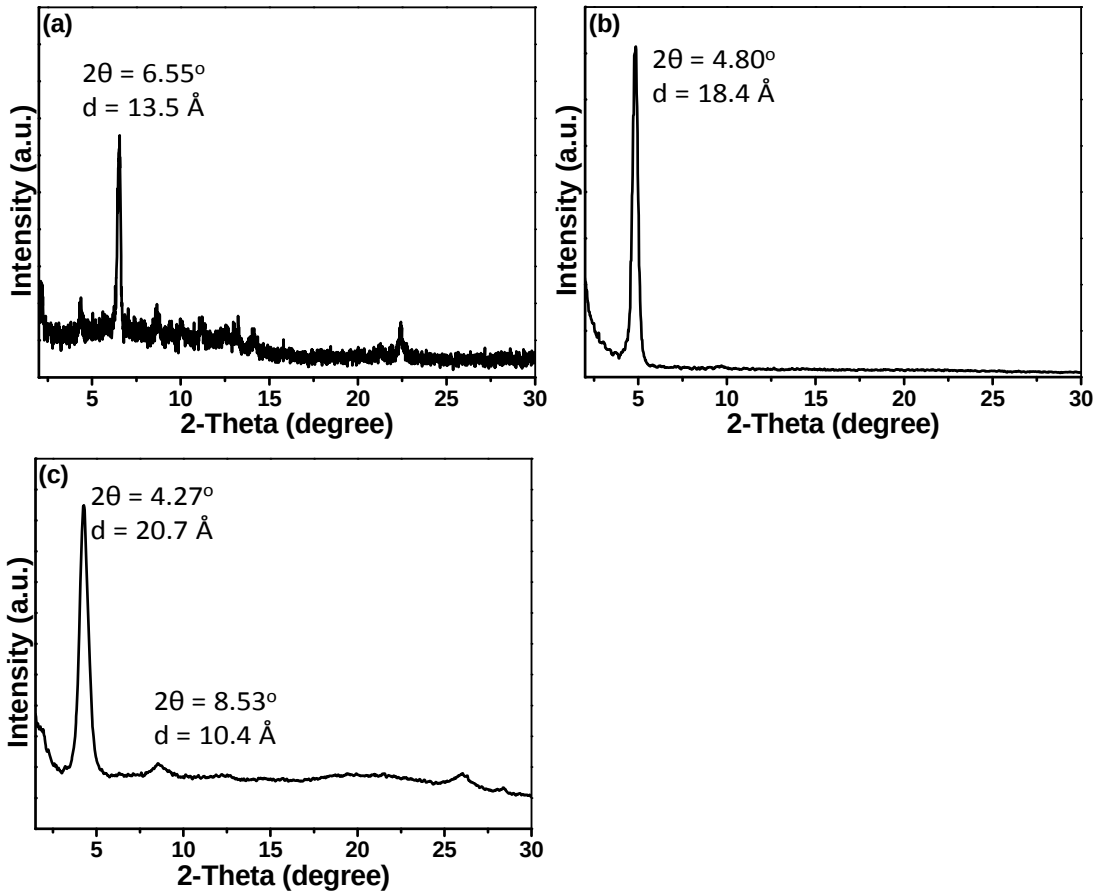


Fig. S7 XRD patterns of the thin films of (a) **1**, (b) **2**, and (c) **3** on an OTS modified SiO_2 substrate.

6. Reference

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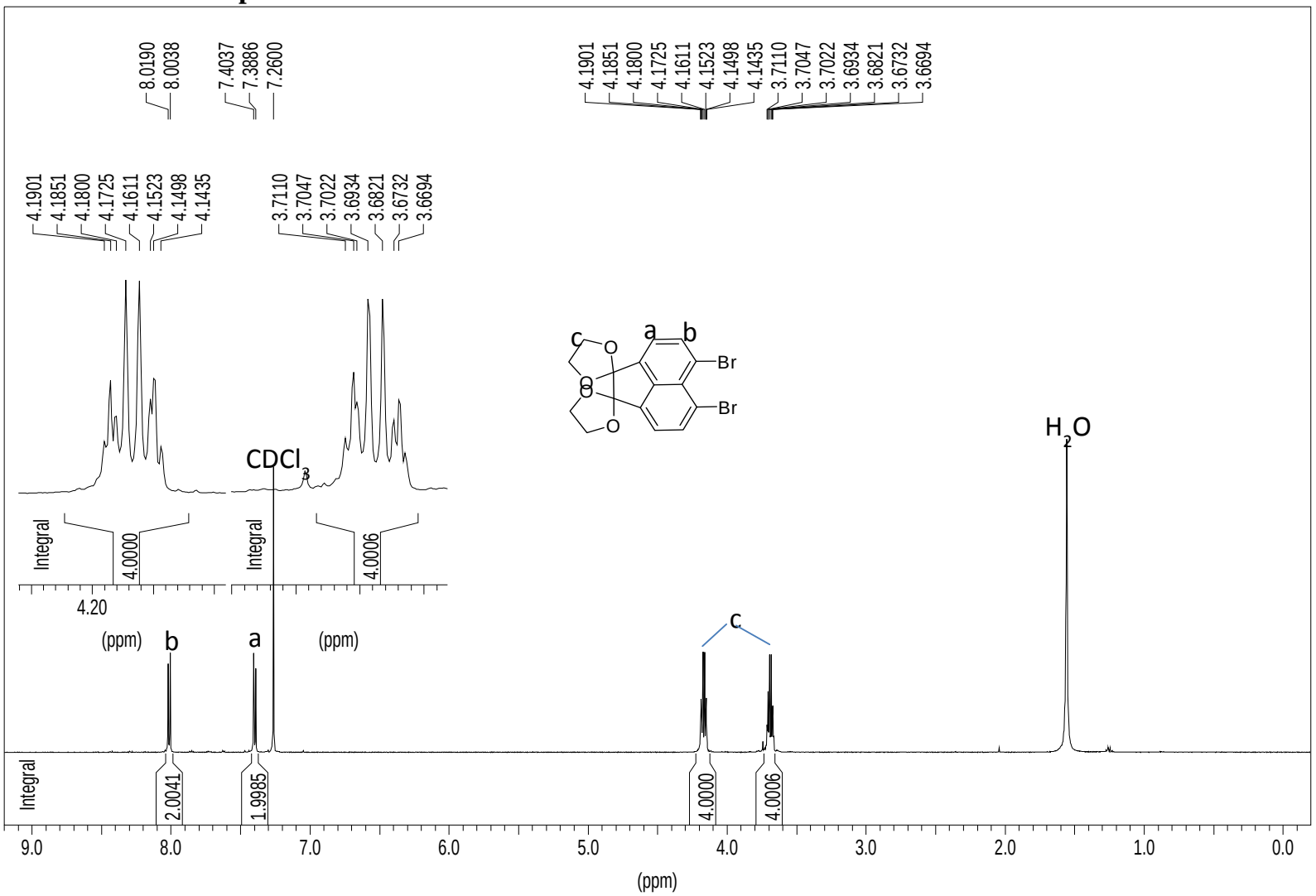
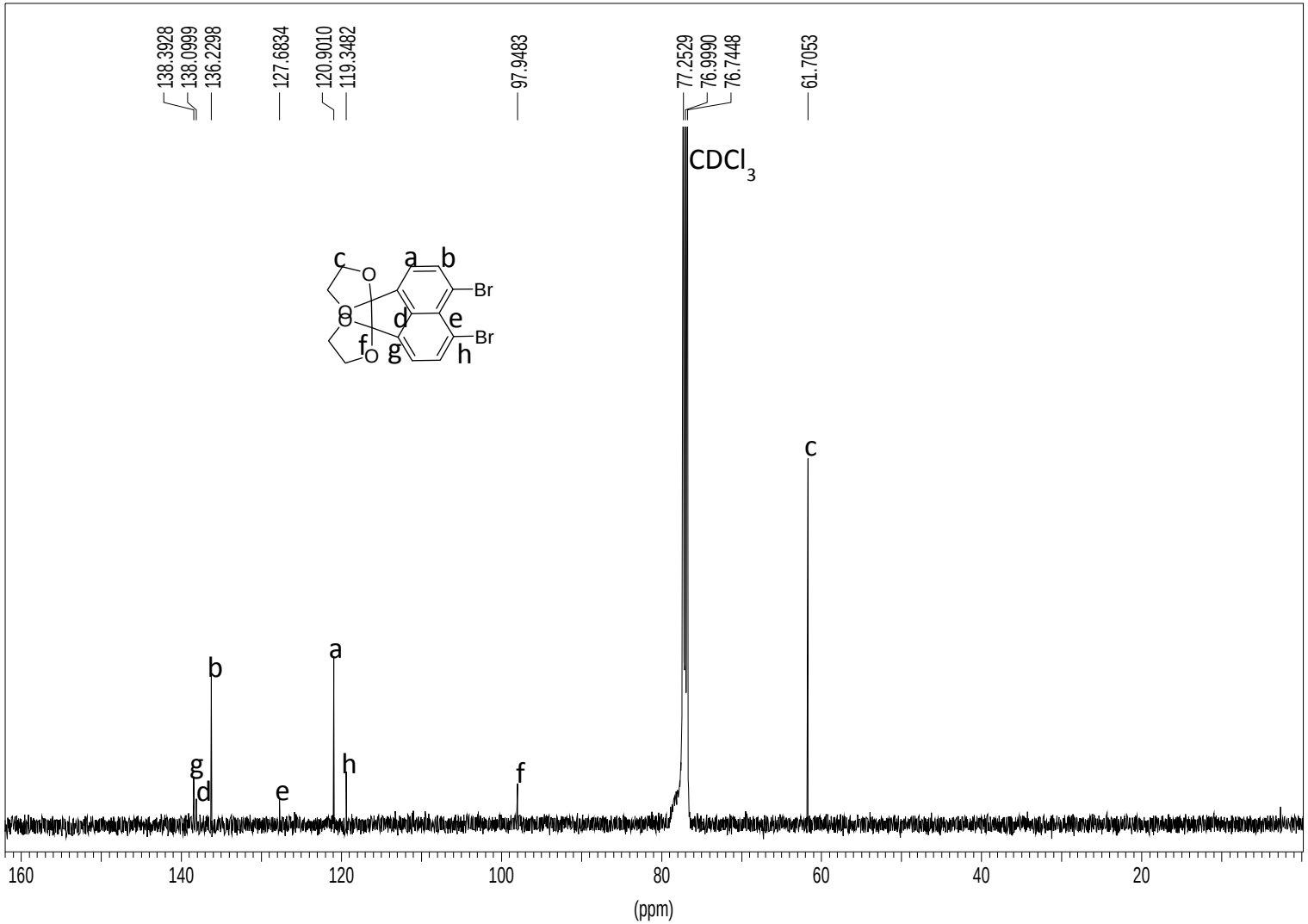
(6) Gaussian 09; Revision A.2; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT, 2009.

(7) Gorelsky, S. I., *SWizard program*, http://www.sg-chem.net/, University of Ottawa, Ottawa, Canada, **2010**.

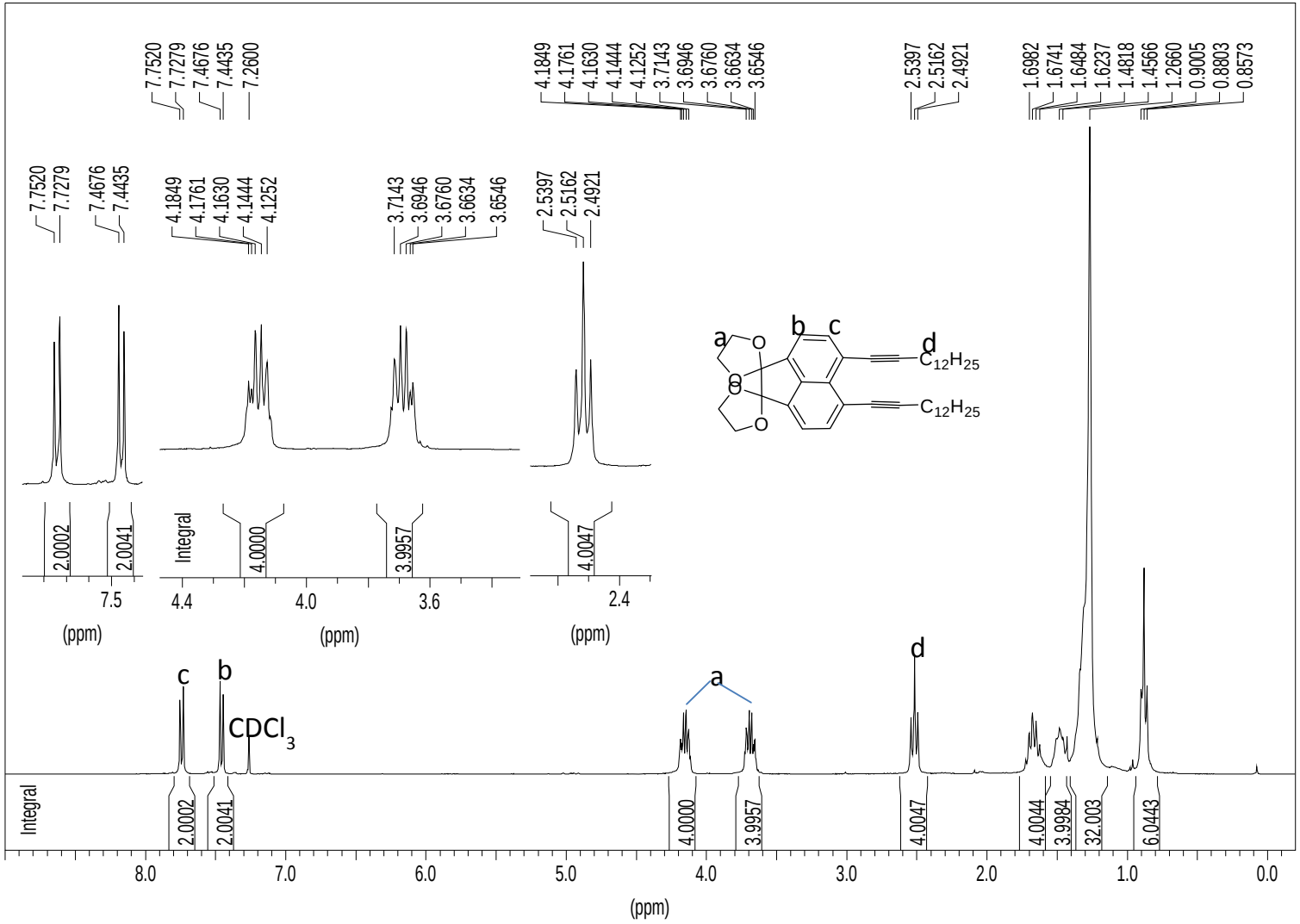
7. Appendix: NMR and mass spectra



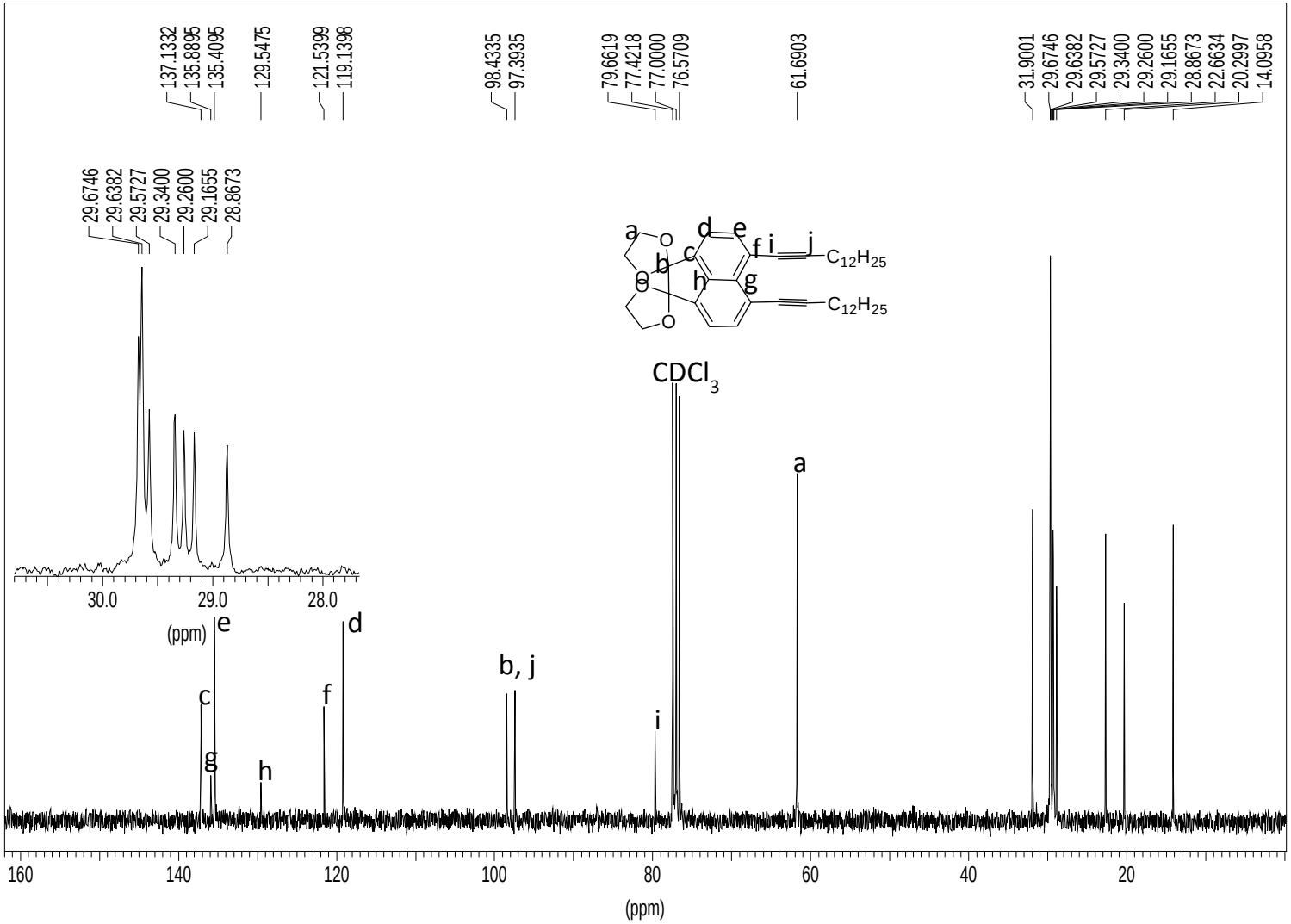
^{1}H NMR spectrum of compound **5** in $CDCl_3$



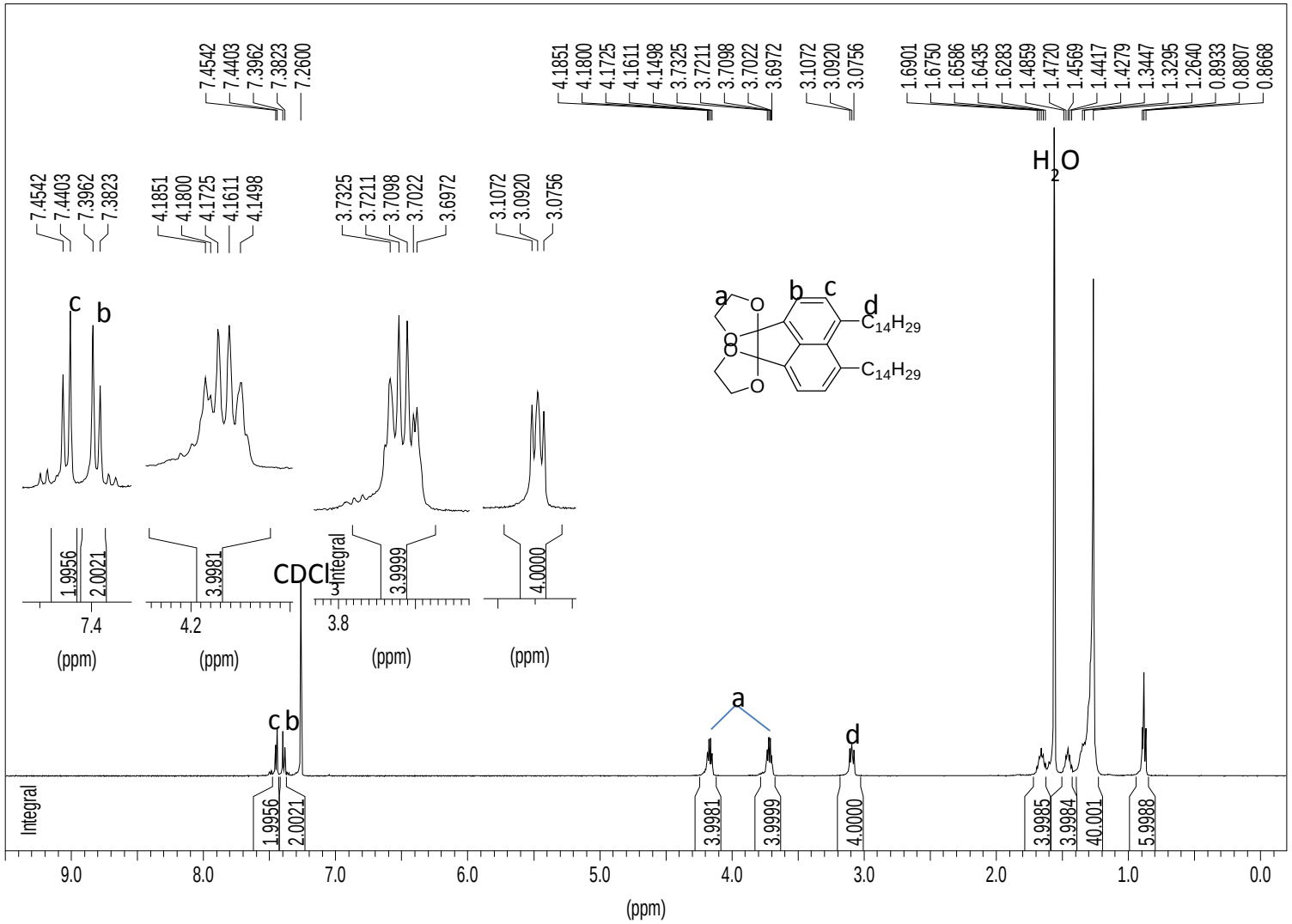
^{13}C NMR spectrum of compound **5** in $CDCl_3$



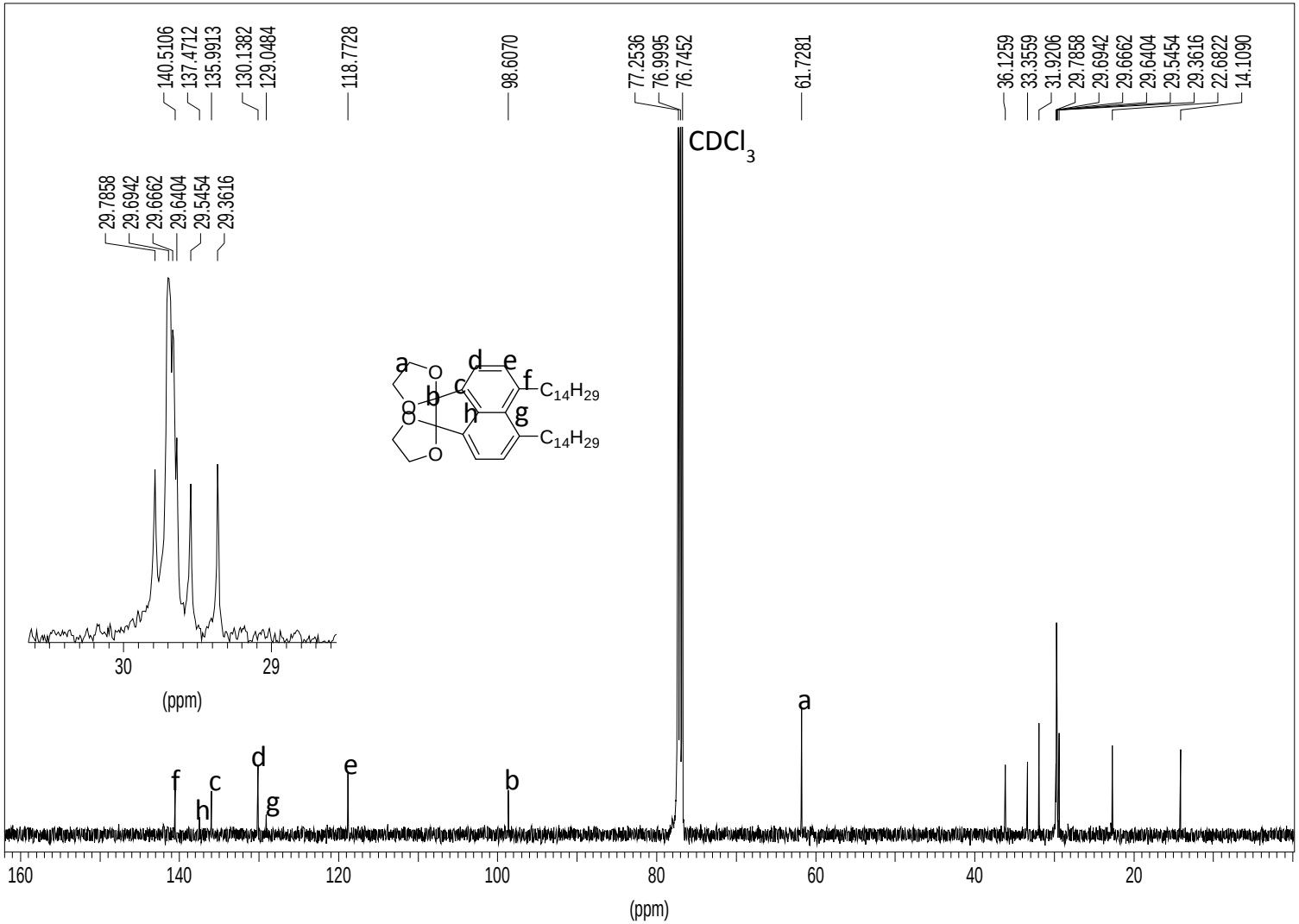
^{1}H NMR spectrum of compound **6** in $CDCl_3$



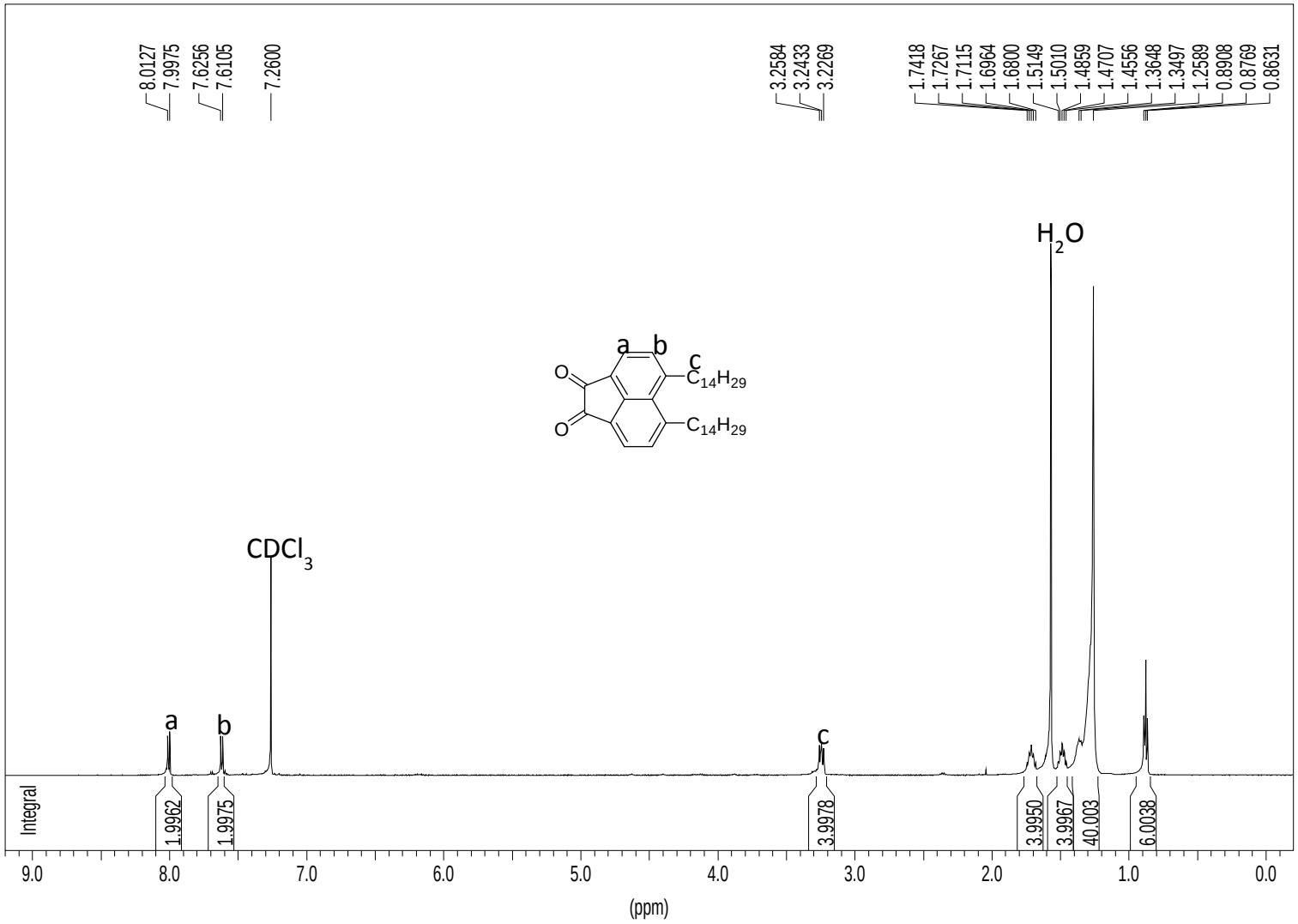
^{13}C NMR spectrum of compound **6** in $CDCl_3$



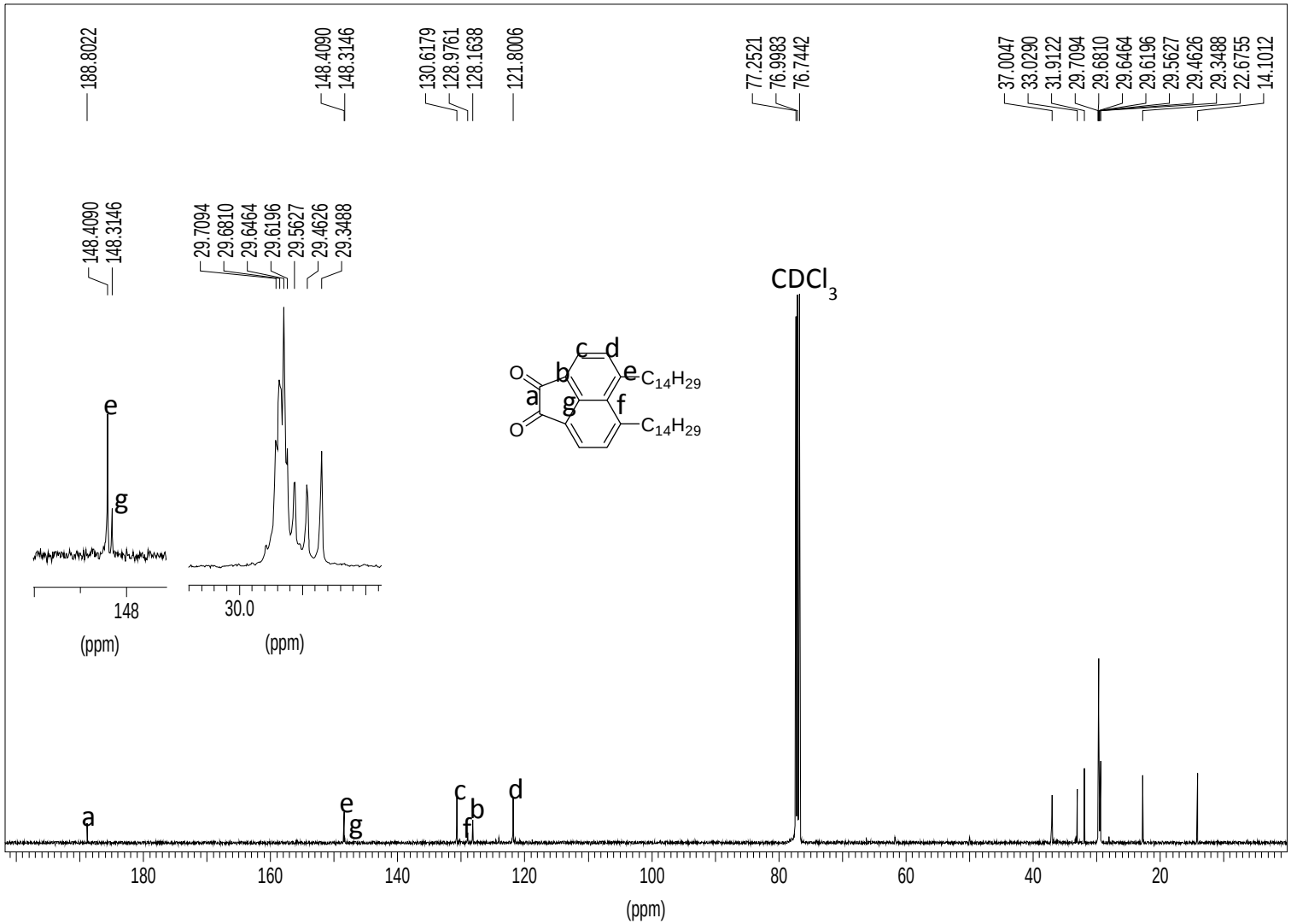
^{1}H NMR spectrum of compound **7** in $CDCl_3$



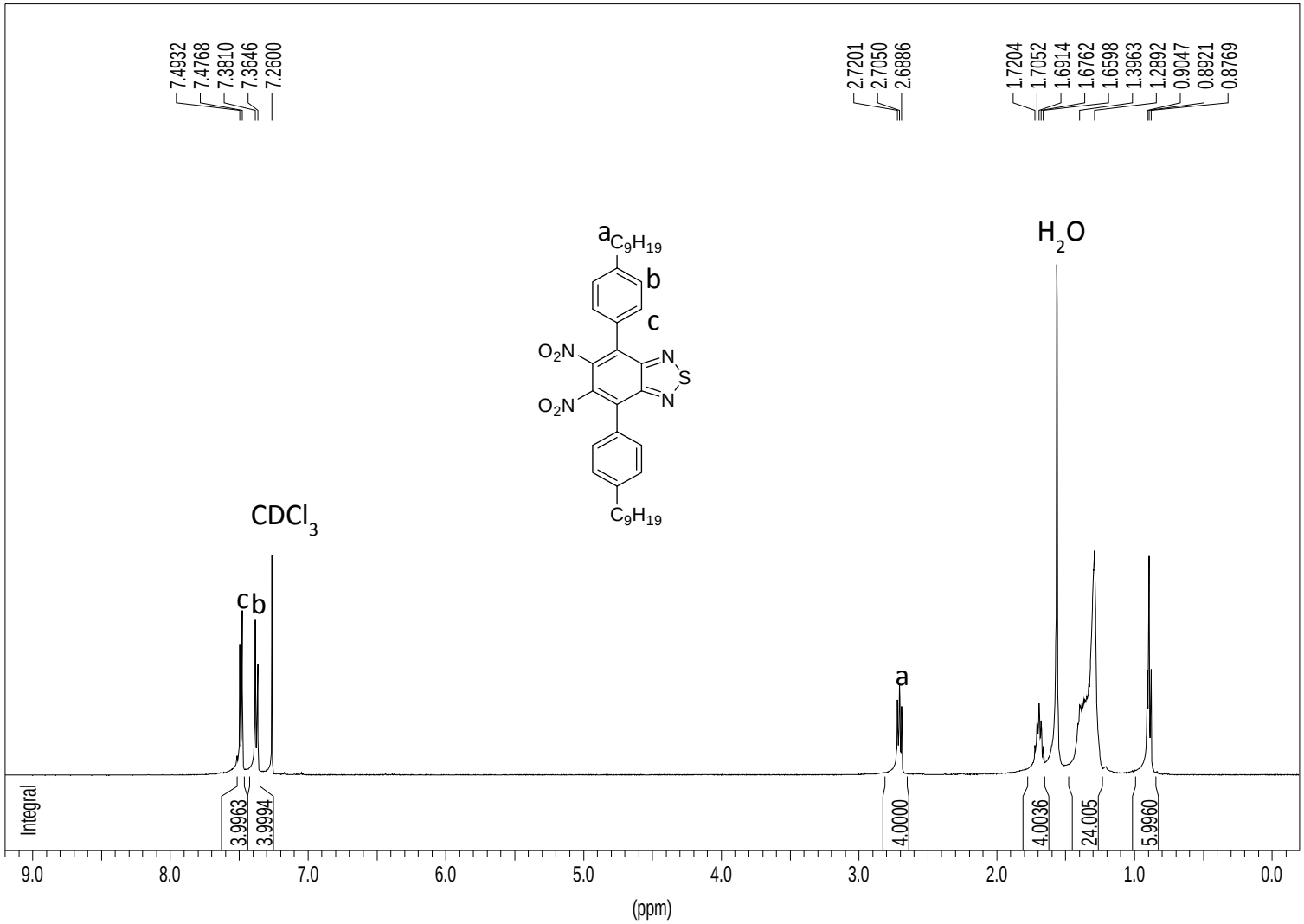
^{13}C NMR spectrum of compound **7** in $CDCl_3$



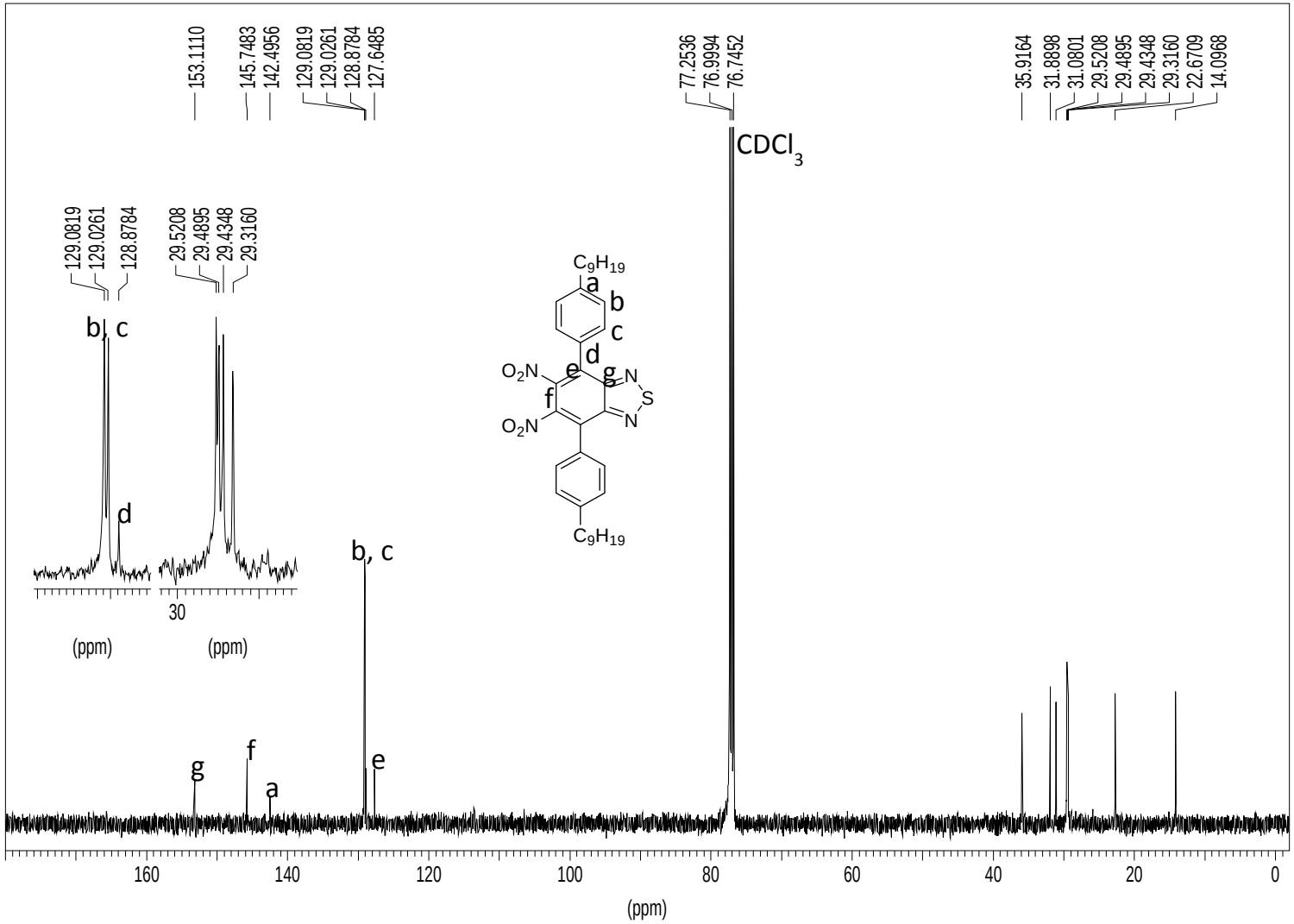
^{1}H NMR spectrum of compound **8a** in $CDCl_3$



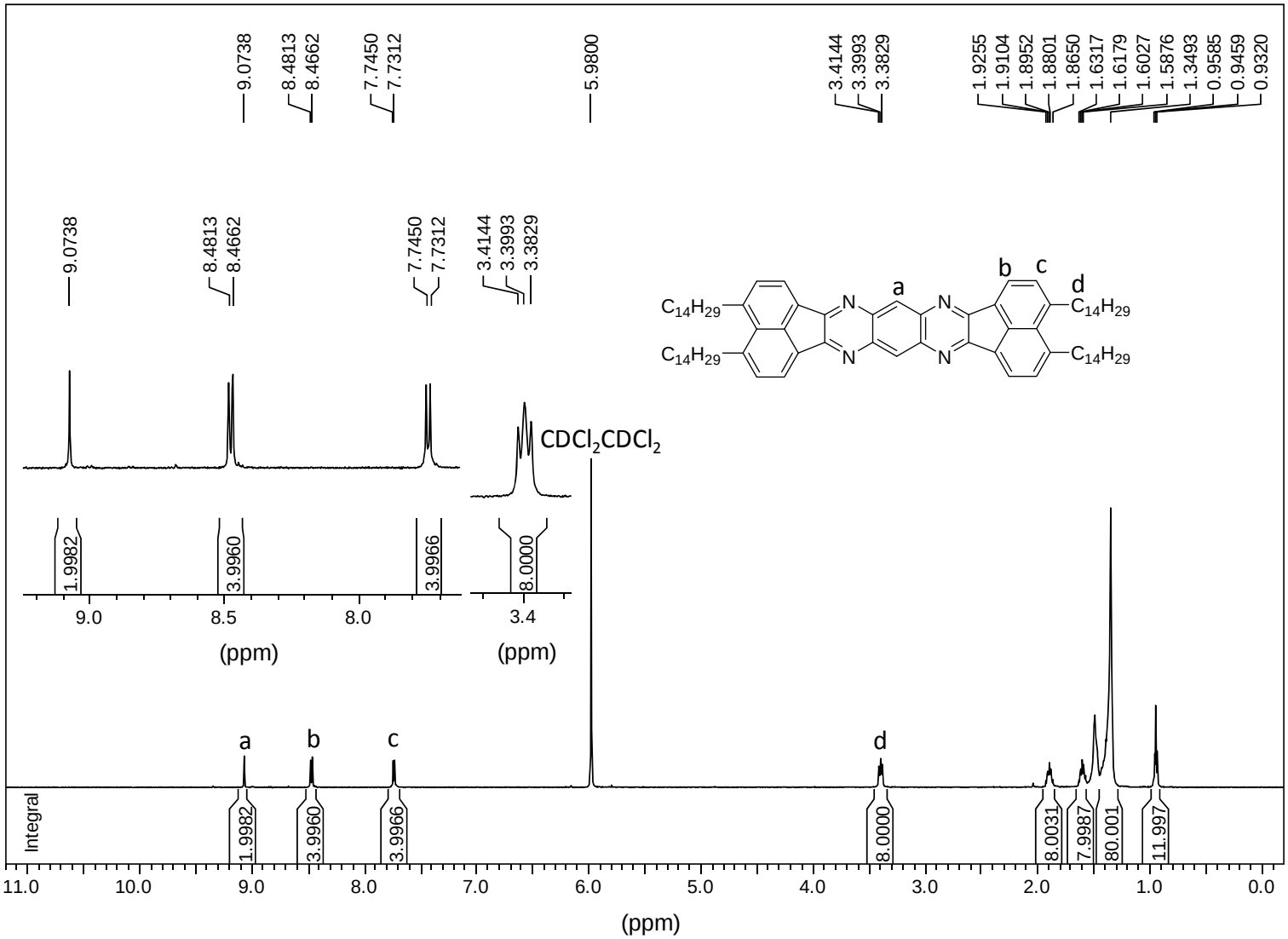
^{13}C NMR spectrum of compound **8a** in $CDCl_3$



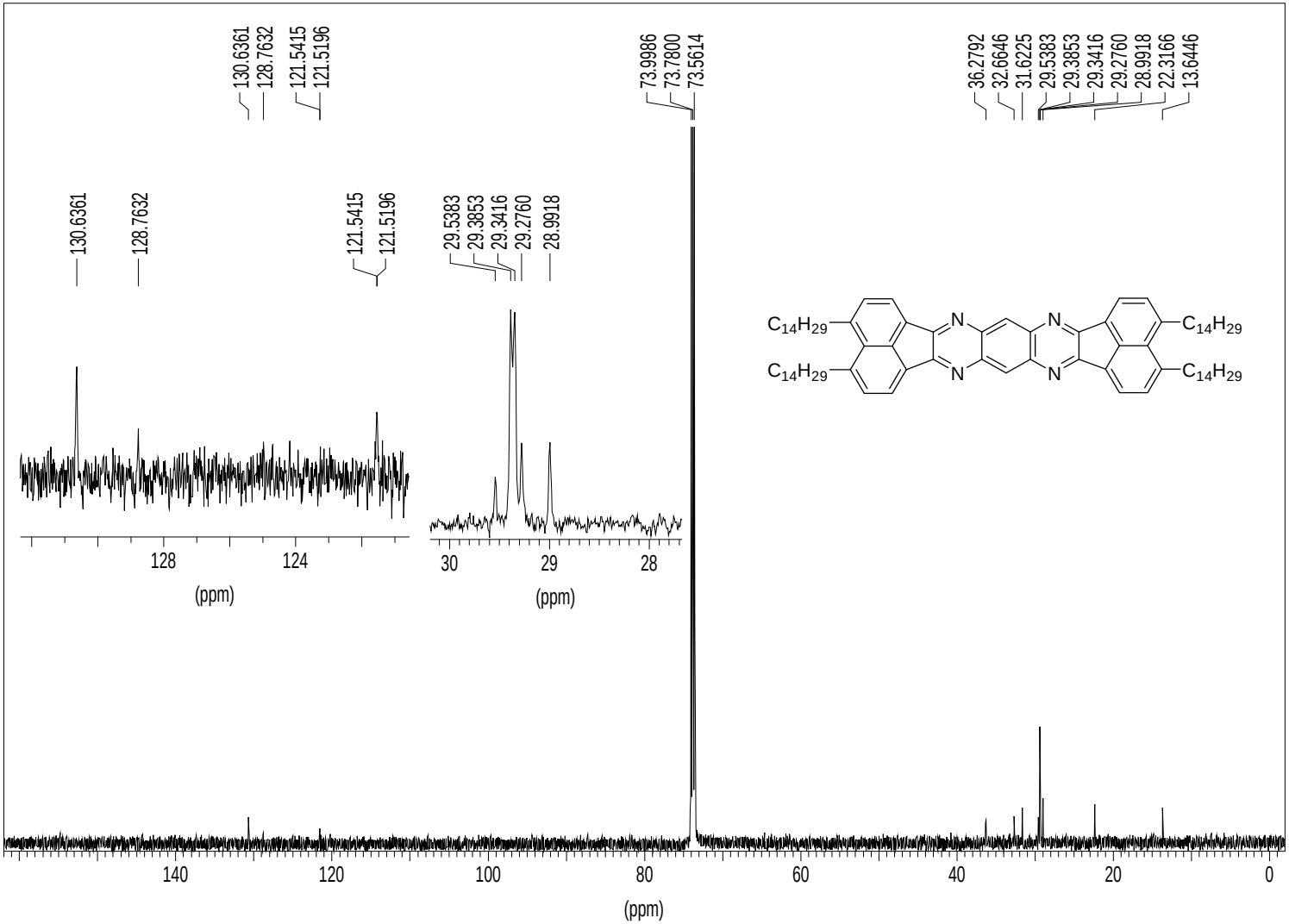
^{1}H NMR spectrum of compound **12** in $CDCl_3$



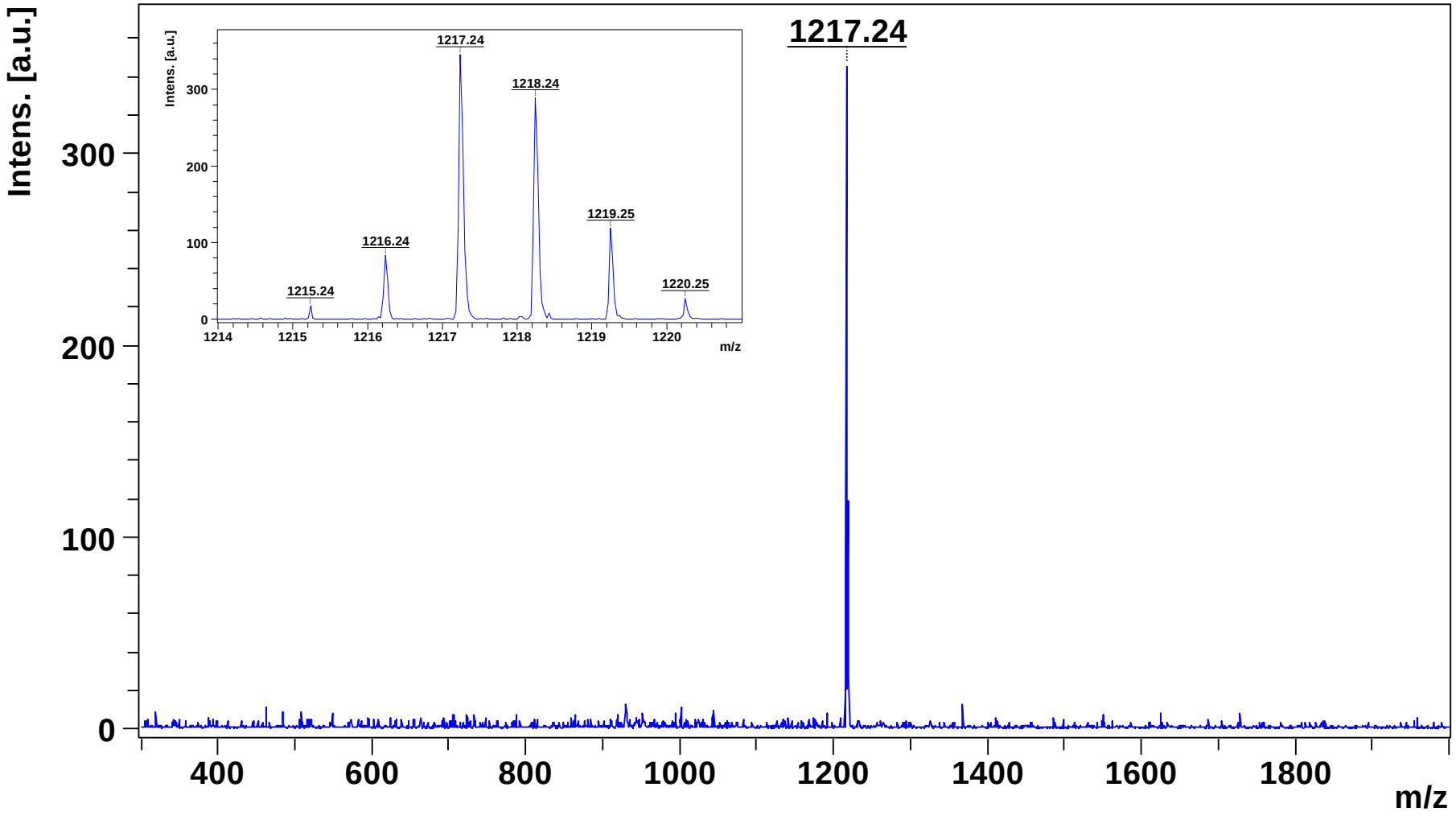
^{13}C NMR spectrum of compound **12** in $CDCl_3$



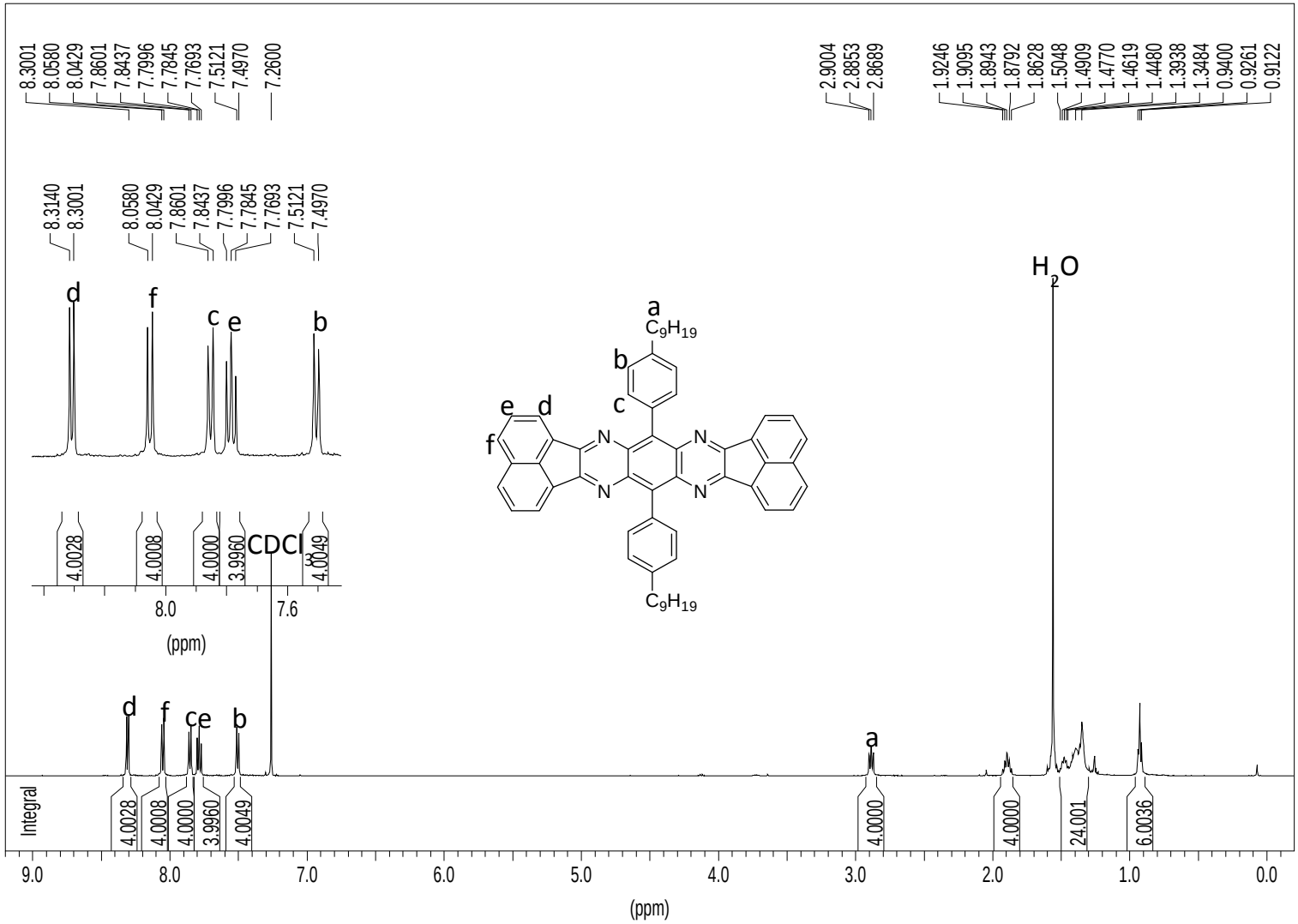
^{1}H NMR spectrum of compound **1** in $CDCl_2CDCl_2$ at 100 ^{o}C



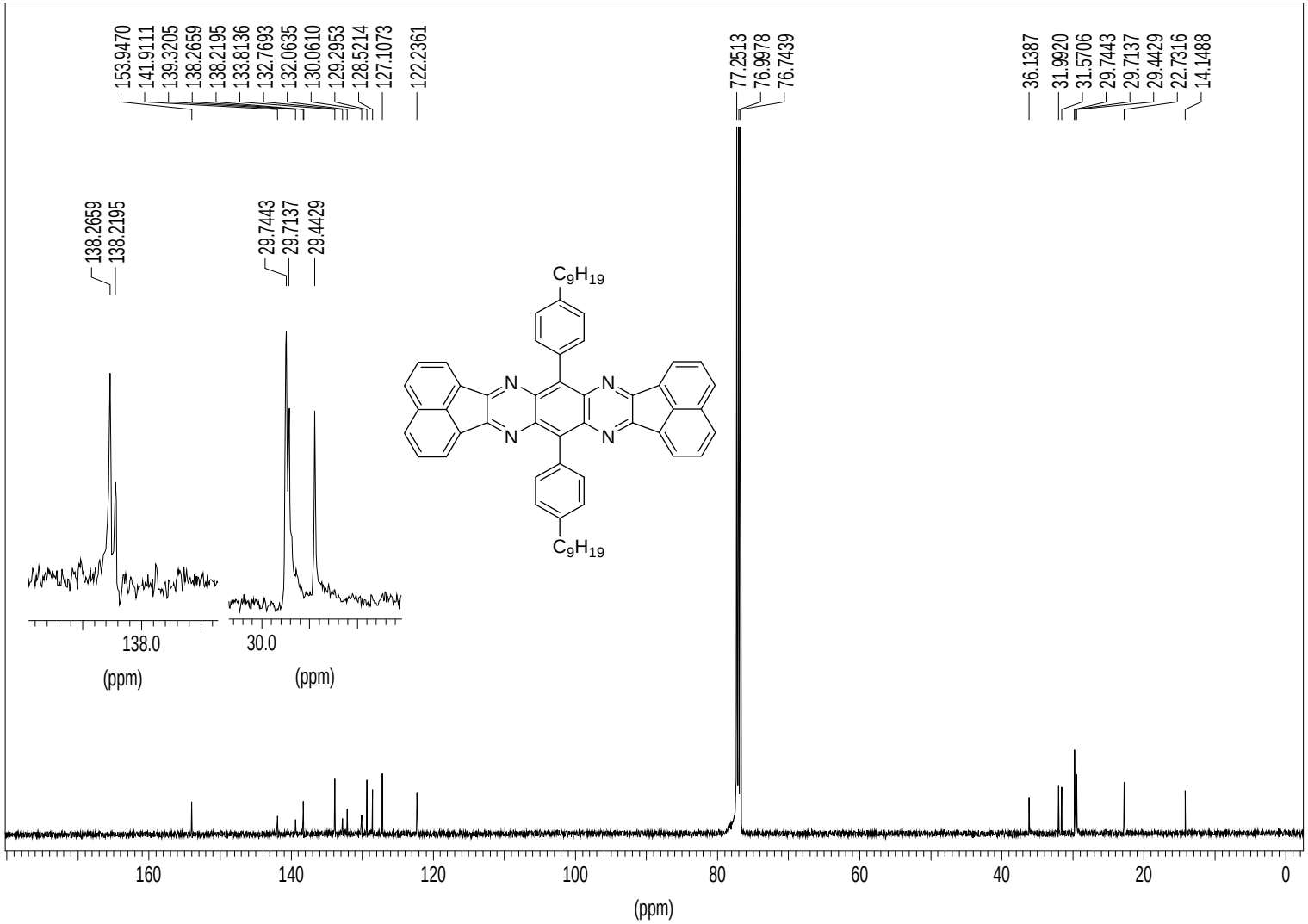
^{13}C NMR spectrum of compound **1** in $CDCl_2CDCl_2$ at 100 ^oC



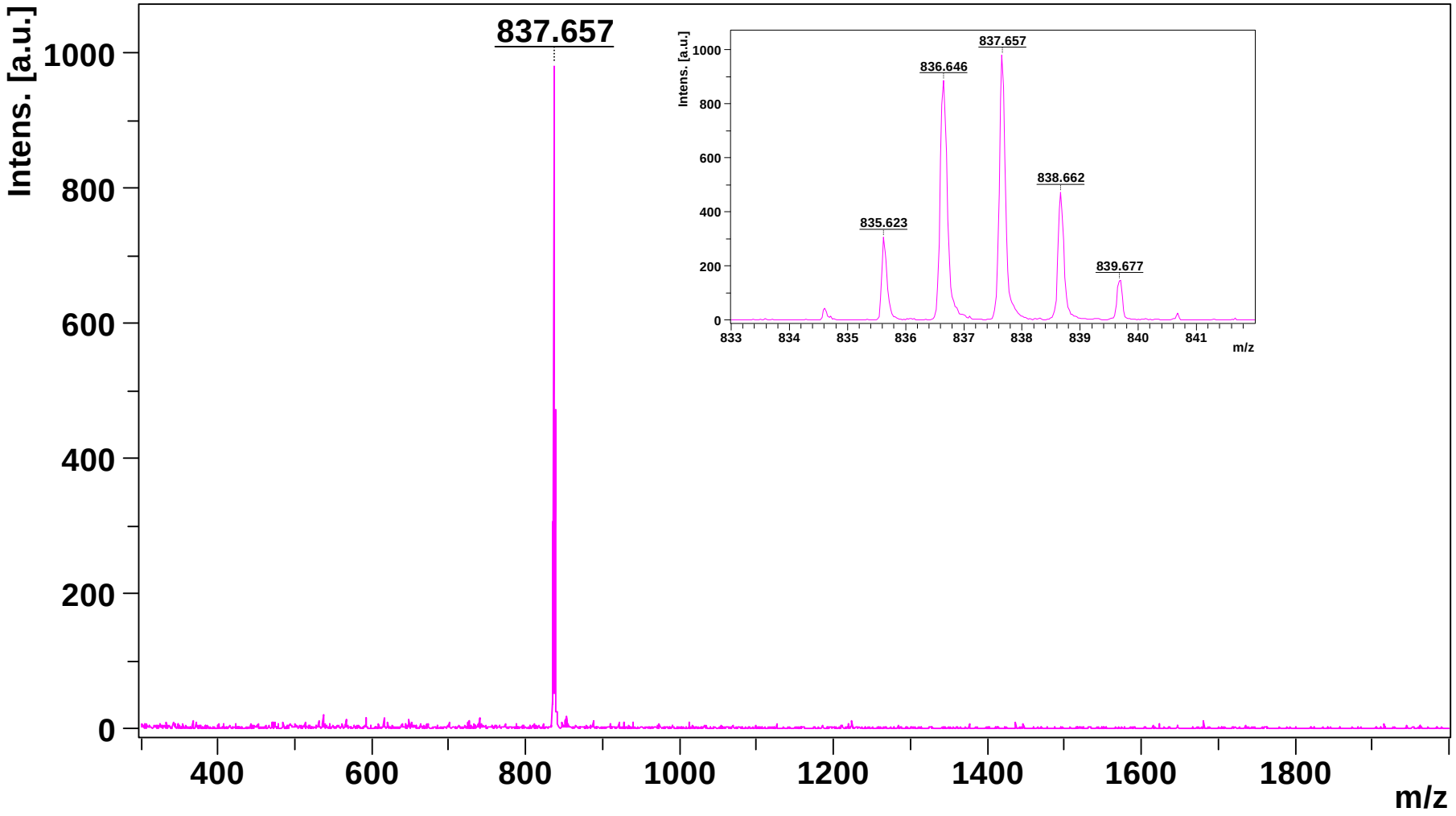
MALDI-TOF spectrum of compound **1**



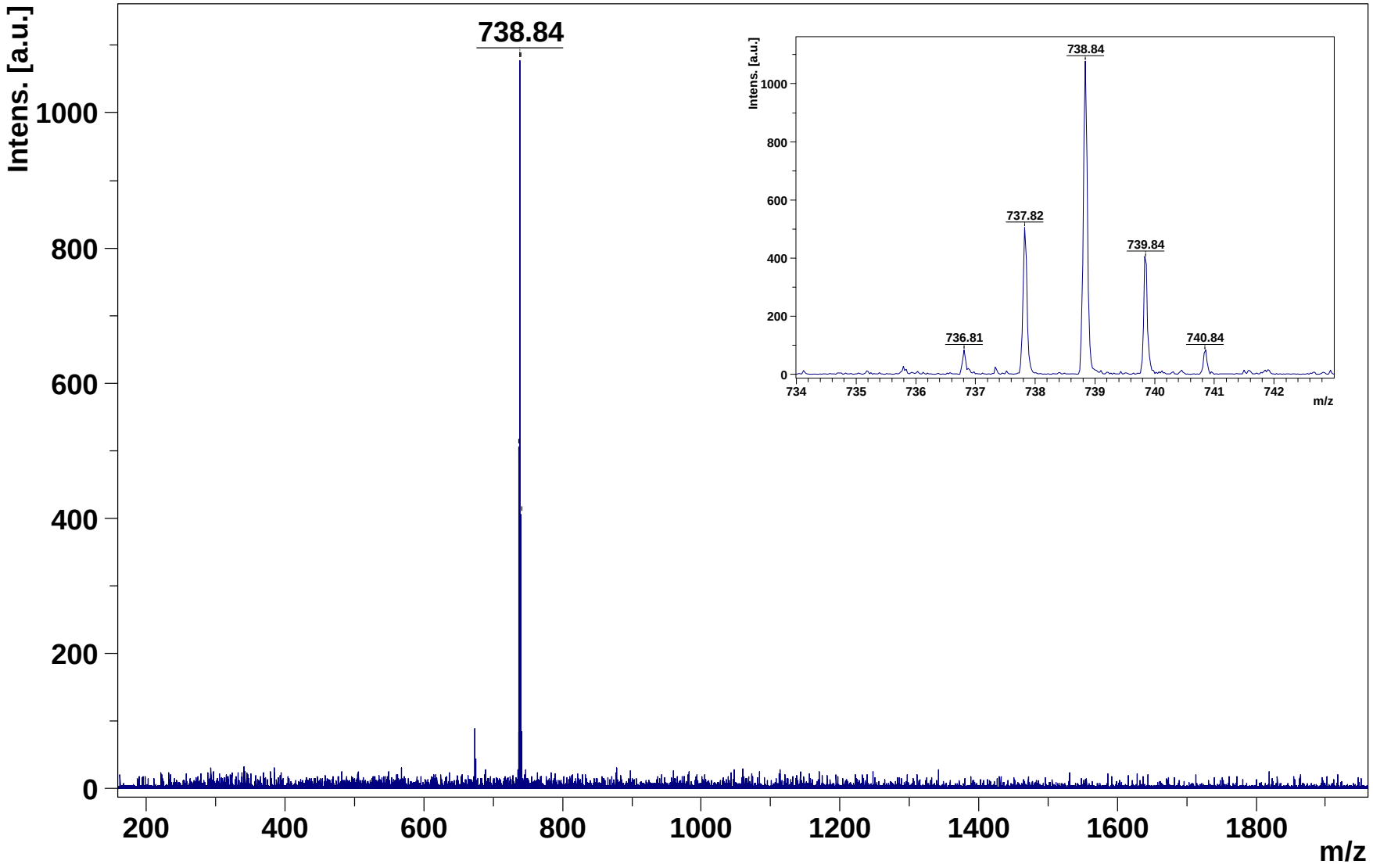
^{1}H NMR spectrum of compound **2** in $CDCl_3$



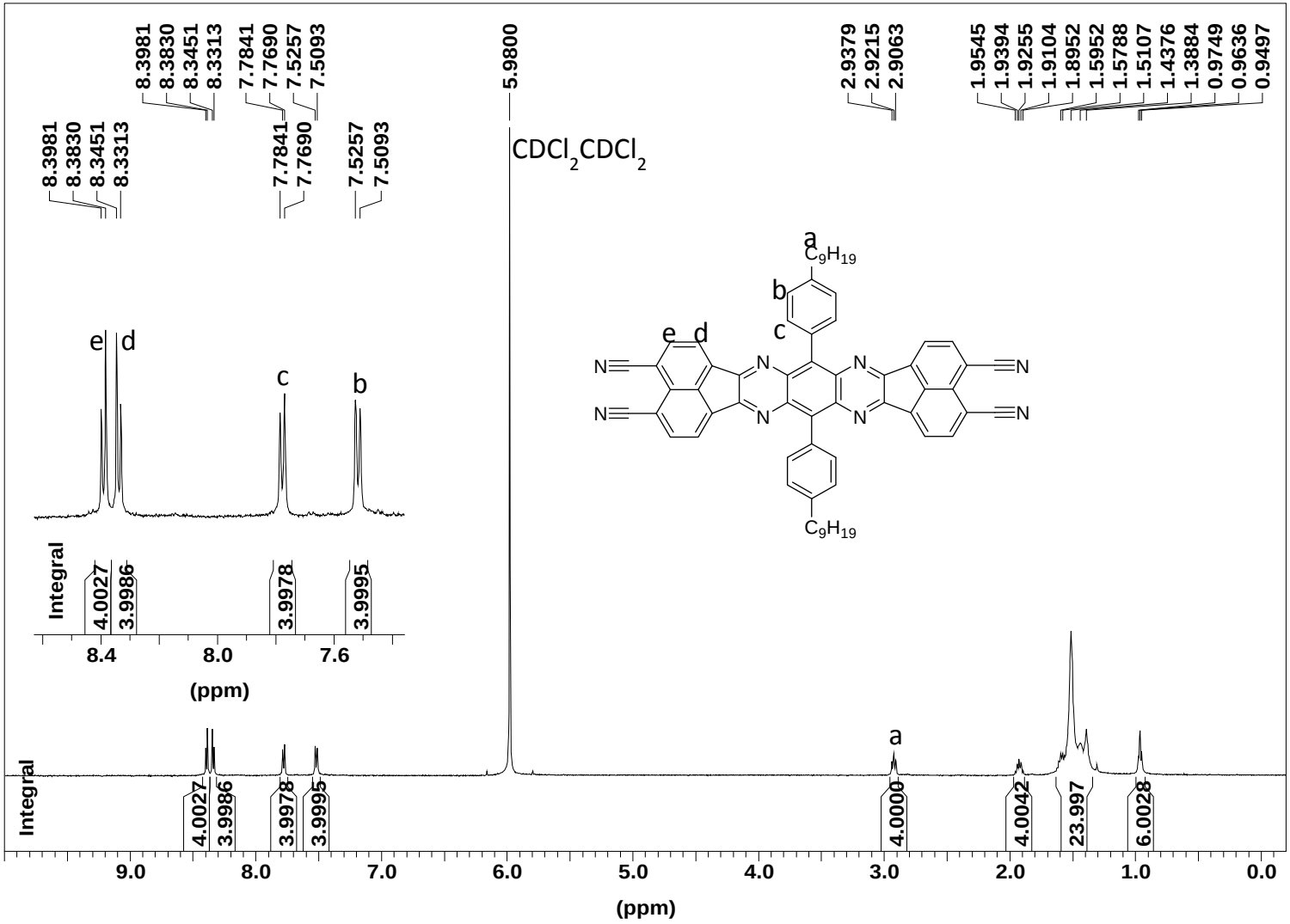
^{13}C NMR spectrum of compound **2** in $CDCl_3$



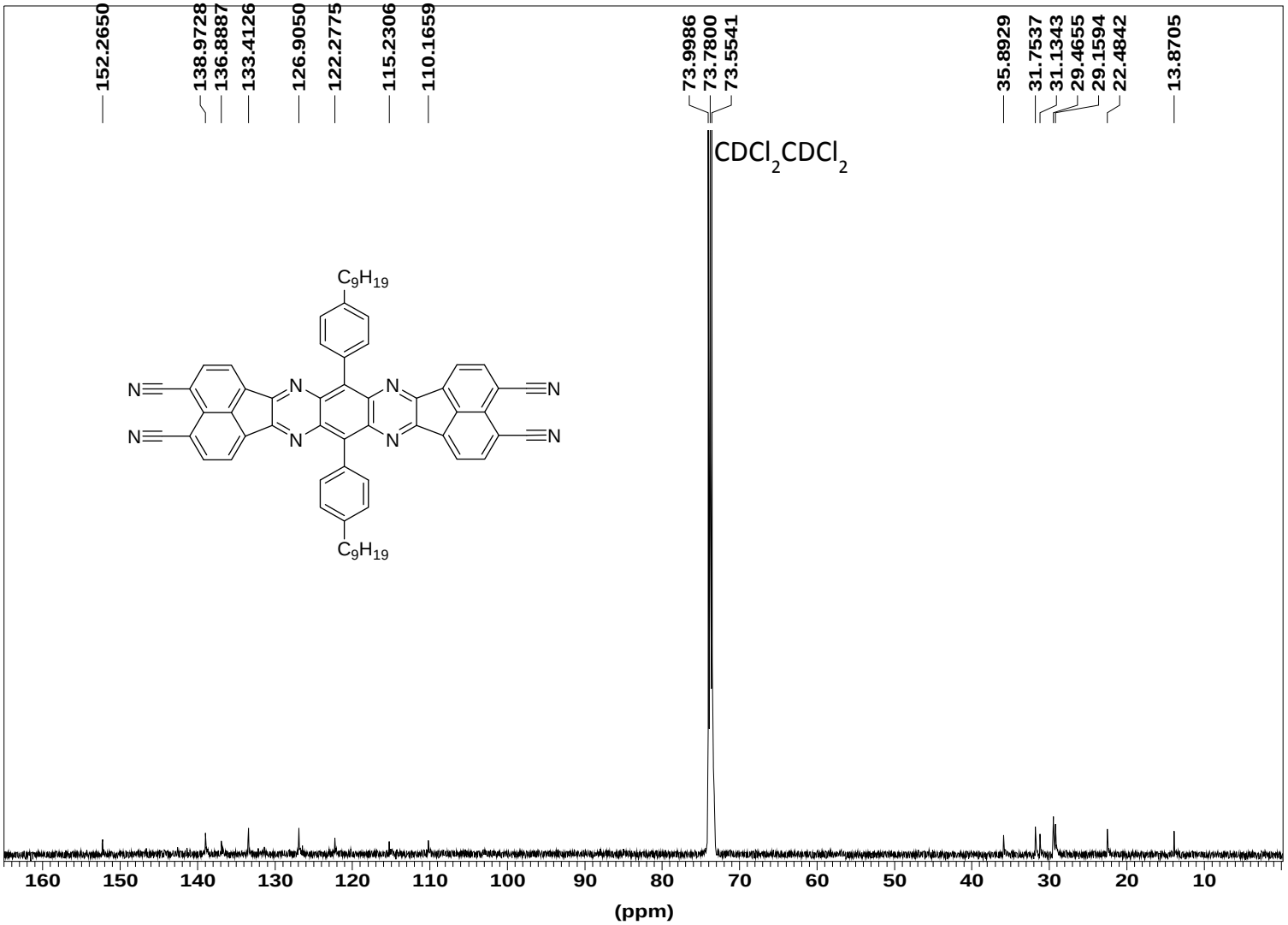
MALDI-TOF spectrum of compound **2**



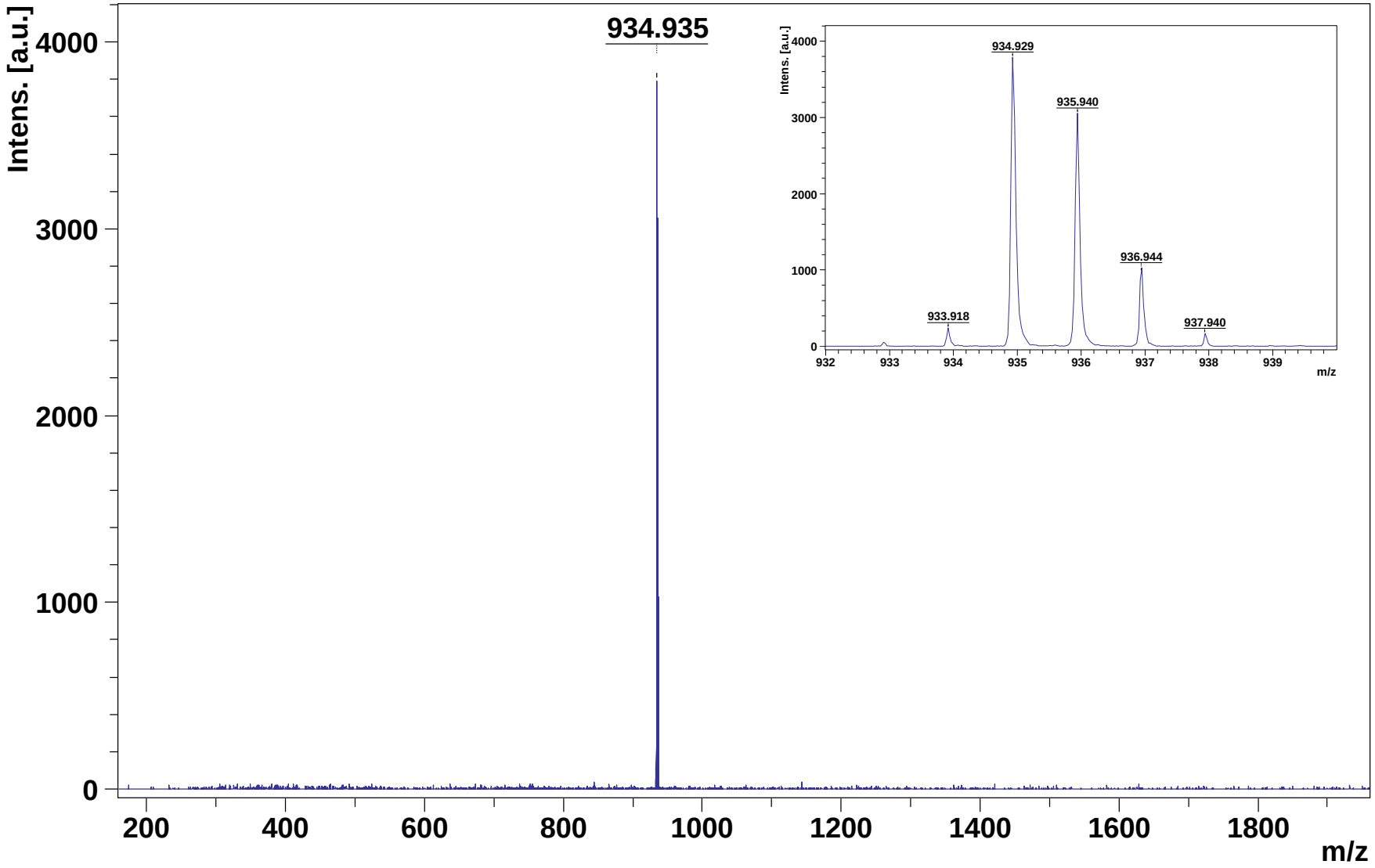
MALDI-TOF spectrum of intermediate **16**



^{1}H NMR spectrum of compound **3** in $CDCl_2CDCl_2$ at 75 ^{o}C



^{13}C NMR spectrum of compound **3** in $CDCl_2CDCl_2$ at 75 ^{o}C



MALDI-TOF spectrum of compound **3**