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ESI

An intermolecular C—H oxidizing strategy to access highly fused carbazole skeletons from simple naphthylamines

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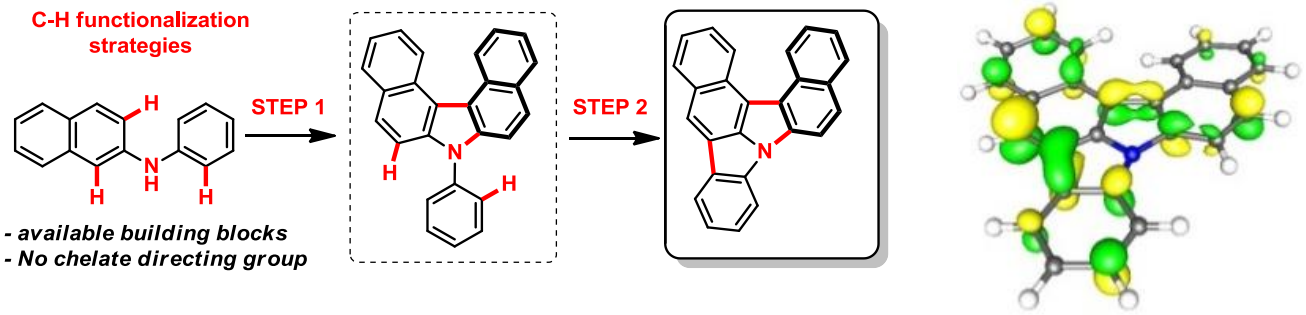
ABSTRACT: **Highly π-extended hetero-cyclic / aromatic skeletons are of great importance as they can be utilized in many organic material based technologies. Therefore, developing efficient, pre-activation-free, synthetic procedures for the rapid build-up of these complex structures remains a high priority objective. The herein presented approach delivers highly fused carbazole skeletons from simple naphthylamine derivatives.**



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1 General methods

All reactions were carried out in dried reaction vials containing a Teflon-coated stirring bar with sealed aluminous headspace caps containing a dry septum under air atmosphere, unless otherwise specified. NMR spectra were obtained on Bruker Avance 400 system using CD_2Cl_2 or $(CD_3)_2SO$ as solvents, with proton and carbon resonances at 400 MHz and 101 MHz, respectively. Coupling constants (J) are quoted in Hz. ^1H spectra were calibrated in relation to reference measurement of TMS (0.00 ppm). ^{13}C spectra were calibrated in relation to deuterated solvents, namely CD_2Cl_2 (54.00 ppm) or $(CD_3)SO$ (39.51 ppm). The following abbreviations were used for ^1H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet) and m (mulitplet) as well as combination of them. Only visible lines were reported in NMR. HR-MS spectra were notably recorded on a WATERS GCT-PremierTM or on a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer.

The absorption spectra were recorded with a Perkin-Elmer Lambda 900 double beam UV/VIS/NIR spectrophotometer and cylindrical quartz cuvettes with a path length of 1 cm. For detection of the emission a Horiba Jobin-Yvon Fluorolog 3-22 τ and 1 cm × 1 cm quartz cuvettes were used. All substances were measured in dichloromethane. The solvent was spectroscopy grade and purchased from Fluka. The used concentrations were in the range of 10^{-5} mol/L for all substances. All solutions were prepared and filled in the cuvettes with the common Schlenk technique. Argon 5.0 was used as inert gas and LUDOX® (TM-50 colloidal silica, 50 wt % suspension in water) was used as reference for lifetime measurements and purchased from Sigma-Aldrich.

Methods of Quantum Chemical Calculations:

Input structures for the compounds were generated by applying the universal force field (UFF)[S1] implemented in the Avogadro program.[S2] We performed structure optimization in Gaussian 09[S3] with the (TD)-DFT functional B3LYP as implemented in Turbomole 7.3[S4] by addition of Grimme's dispersion correction D3.[S5] The def2-TZVP basis set was used for all elements. Optimized structures were tested for minimum geometry by application of frequency calculations. No imaginary frequencies were found. The scaling factors 0.956 (CH stretching modes) and 0.97 (fingerprint) were used. To calculate the vertical electronic transitions, TD-DFT was used with the previously mentioned functional and basis set.

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[S3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, **2016**.

[S4] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2014**, *4*, 91.

[S5] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

1.1 Optimization

1.1.1 Variation of oxidants, amount of oxidant, vessel size, atmosphere, solvents, solvent amount, and temperature[a]

reaction vessel	catalyst [mmol]	oxidant	amount of oxidant [mmol]	solvent [mL]	temp. [°C]	atmosphere	yield [%]
85 mL reactor with Teflon screw cap	$[Ru(C_6Me_6)Cl_2]_2$ (0.05) + $Cu(OAc)_2 \cdot H_2O$ (1.10)	-	-	C_2Cl_4 (1.00) PhCl (0.25) AcOH (0.25)	150	O_2	4
	$[Ru(C_6Me_6)Cl_2]_2$ (0.05) + $Cu(OAc)_2$ (1.10)	-	-	"	150	O_2	14
	"	-	-	"	130	"	26
	"	-	-	"	110	"	32
	"	-	-	"	90	"	32
	$[Ru(p\text{-cymene})Cl_2]_2$ (0.05) + $Cu(OAc)_2$ (1.10)	-	-	"	110	"	22
	"	-	-	"	100	"	26
	"	-	-	"	90	"	28
	"	-	-	"	80	"	31
	"	-	-	"	70	"	37
	"	-	-	"	60	"	40
	"	-	-	"	50	"	35
	"	Ag_2O	0.50	"	60	N_2	35
	"	"	0.75	"	"	"	47
	"	"	"	"	"	air	46
	"	$(NH_4)_2S_2O_8$	0.50	"	"	N_2	17
	"	"	0.75	"		"	39
	"	DTBP	0.50	"	"	"	21
	"	"	0.75	"	"	"	33
	"	$NaIO_4$	0.50	"	"	"	32
	"	"	0.75	"	"	"	22
	"	DDQ	0.50	"	"	"	4
	"	"	0.75	"	"	"	2
50 mL crimp neck vial	"	Ag_2O	0.75	"	"	air	46
	"	"	1.00	"	"	"	48
	"	"	1.00	"	"	O_2	43
	"	"	1.25	"	"	air	48
	"	$(NH_4)_2S_2O_8$	1.00	"	"	N_2	37
	"	"	1.25	"	"	"	37
	"	MnO_2	0.50	"	"	air	34
	"	"	0.75	"	"	"	36
	"	CuO	0.50	"	"	"	24
	"	"	0.75	"	"	"	27
	"	Ag_2O	1.00	C_2Cl_4 (1.50) PhCl (0.375) AcOH (0.375)	"	"	49
	"	"	"	C_2Cl_4 (2.00) PhCl (0.50) AcOH (0.50)	"	"	50
	"	"	"	C_2Cl_4 (1.00) PhCl (0.25) AcOH (0.15)	"	"	45
	"	"	"	C_2Cl_4 (1.00) PhCl (0.25) AcOH (0.50)	"	"	50
	-	"	0.50	C_2Cl_4 (1.00)	"	"	42

				PhCl (0.25) AcOH (0.25)			
	-	"	0.75	"	"	"	44
	-	"	1.00	"	"	"	50
	-	"+ TEMPO (1 equiv.)	1.00	"	"	"	0
	-	Ag_2O	1.00	"	"	O_2	47
	-	"	1.00	"	"	N_2	50
	-	"	1.25	"	"	air	48
	-	MnO_2	0.50	"	"	"	24
	-	"	0.75	"	"	"	34
	-	CuO	0.50	"	"	"	2
	-	"	0.75	"	"	"	2
	-	$NaIO_4$	0.50	"	"	"	25
	-	"	0.75	"	"	"	28
	-	DTBP	0.50	"	"	"	1
	-	"	0.75	"	"	"	0
	-	$(NH_4)_2S_2O_8$	0.50	"	"	"	9
	-	"	0.75	"	"	"	11
	-	Ag_2O	1.00	PhMe (1.00) PhCl (0.25) AcOH (0.25)	"	"	50
	-	"	"	HFIP (1.00) PhCl (0.25) AcOH (0.25)	"	"	10
	-	"	"	DMSO (1.00) PhCl (0.25) AcOH (0.25)	"	"	42
	-	"	"	DMF (1.00) PhCl (0.25) AcOH (0.25)	"	"	46
	-	"	"	NMP (1.00) PhCl (0.25) AcOH (0.25)	"	"	24
	-	"	"	Dioxane (1.00) PhCl (0.25) AcOH (0.25)	"	"	50
	-	"	"	*n*-heptane (1.00) PhCl (0.25) AcOH (0.25)	"	"	43
	-	"	"	THF (1.00) PhCl (0.25) AcOH (0.25)	"	"	43
	-	"	"	PhMe (1.00) PhCl (0.25) PivOH (225 mg)	"	"	23
	-	"	"	PhMe (1.00) PhCl (0.25) K_2CO_3 (2.00 mmol)	"	"	5
	-	"	1.00	PhMe (1.00) PhCl (0.25) NaOAc (2.00 mmol)	"	"	4
	-	"	1.00	PhMe (1.00) PhCl (0.25) AcOH (0.25) NaOAc (1.00 mmol)	"	"	46
20 mL crimp neck vial	$[Ru(p\text{-cymene})Cl_2]_2$ (0.05) + $Cu(OAc)_2$ (1.10)	"	"	PhMe (1.00) PhCl (0.25) AcOH (0.25)	"	"	53

[a] All reactions were carried out with *N*-Phenyl-2-naphtylamine (1.00 mmol, 219.4 mg) as the substrate for 24 h. Yields were determined by ^{1}H-NMR using 1,2-DCE = 1,2-dichloroethane (40.0 µL, 0.50 mmol) as standard.

1.1.2 Variation of vessel size, solvents, and reaction time[a]

reaction vessel	oxidant (1 mmol)	solvent [mL]	temp. [°C]	time	atmosphere	yield [%]
50 mL crimp neck vial	Ag_2O	PhMe (1.00) PhCl (0.25) AcOH (0.25)	60	24	air	50
20 mL crimp neck vial	"	"	"	16	"	54
	"	PhMe (1.00) PhCl (0.25) CF_3CO_2H (0.25)	"		"	11

[a] All reactions were carried out with *N*-Phenyl-2-naphtylamine (1.00 mmol, 219.4 mg) as the substrate. Yields were determined by ^{1}H-NMR using 1,2-DCE = 1,2-dichloroethane (40.0 µL, 0.50 mmol) as standard.

1.1.3 Impact screening of different metals on the reaction[a]

reaction vessel	catalyst [10 mol%]	oxidant (1 mmol)	solvent [mL]	temp. [°C]	time [h]	yield [%][c]
20 mL crimp neck vial	-	Ag_2O	PhMe (1.00) PhCl (0.25) AcOH (0.25)	60	16	54
	$[(C_6H_5)_3P]_2NiCl_2$	"	"	"	"	58
	$NiCl_2$	"	"	"	"	49
	$Fe(OAc)_2$	"	"	"	"	57
	$FeCl_3$	"	"	"	"	54
	$Pd(OAc)_2$	"	"	"	"	19
	$(Cp^*)_2Co(II)$	"	"	"	"	55
	$Mn(CO)_5Br$	"	"	"	"	57
	Ferrocene	"	"	"	"	46
	$ZnCl_2$	"	"	"	"	53
	$AlCl_3$	"	"	"	"	56
	$Cu^{II}(phen)Cl_2$	"	"	"	"	52

[a] All reactions were carried out with *N*-Phenyl-2-naphtylamine (1.00 mmol, 219.4 mg) as the substrate for 16 h. Yields were determined by ^{1}H-NMR using 1,2-DCE = 1,2-dichloroethane (40.0 µL, 0.50 mmol) as standard.

1.1.4 Impact of drying agents on the reaction[a]

reaction vessel	oxidant (1 mmol)	solvent [mL] / additive	temp. [°C]	atmosphere	time [h]	yield [%]
20 mL crimp neck vial	Ag_2O	PhMe (1.00) PhCl (0.25) AcOH (0.25) Molecular Sieve (4Å) (50.0 mg)	60	air	16	52
	"	PhMe (1.00) PhCl (0.25) AcOH (0.25) $MgSO_4$ (50.0 mg)	"	"	"	52

[a] All reactions were carried out with *N*-Phenyl-2-naphtylamine (1.00 mmol, 219.4 mg) as the substrate for 16 h. Yields were determined by ^{1}H-NMR using 1,2-DCE = 1,2-dichloroethane (40.0 µL, 0.50 mmol) as standard.

1.1.5 Reaction time optimization

reaction vessel	oxidant (1 mmol)	solvent [mL]	temp. [°C]	atmosphere	time [h]	yield [%]
20 mL crimp neck vial	Ag_2O	PhMe (1.00) PhCl (0.25) AcOH (0.25)	60	air	40	41
	"	"	"	"	16	54
	"	"	"	"	4	54
	"	"	"	"	2	57
	"	"	"	"	1	55

[a] All reactions were carried out with *N*-Phenyl-2-naphtylamine (1.00 mmol, 219.4 mg) as the substrate. Yields were determined by ^{1}H-NMR using 1,2-DCE = 1,2-dichloroethane (40.0 µL, 0.50 mmol) as standard.

1.1.6 Second solvent screening[a]

reaction vessel	oxidant (1 mmol)	solvent [mL]/ additive	temp. [°C]	atmosphere	time [h]	yield [%]
20 mL crimp neck vial	Ag_2O	PhMe (1.00) PhCl (0.25) AcOH (0.25)	60	air	2	57
	"	PhMe (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	"	"	"	56
	"	PhMe (1.00) Ph^{i}Pr (0.50) AcOH (0.25)	"	"	"	53
	"	PhMe (1.00) Ph^{i}Pr (1.00) AcOH (0.25)	"	"	"	48
	"	PhMe (1.00) Ph^{i}Pr (1.25) AcOH (0.25)	"	"	"	44
	"	PhMe (1.00) Ph^{i}Pr (1.50) AcOH (0.25)	"	"	"	48
	"	CH_2Cl_2 (1.25) AcOH (0.25)	"	"	"	46
	"	$CHCl_3$ (1.25) AcOH (0.25)	"	"	"	51
	"	Ph^{i}Pr (1.25) AcOH (0.25)	"	O_2	"	-
	"	AcOH (1.50)	"	air	"	28
	"	CCl_3F (1.25) AcOH (0.25)	"	"	"	52
	"	PhMe (1.00) Ph^{i}Pr (0.25) AcOH (0.25) + $AgSbF_6$ (10 mol%)	"	"	"	9
	"	CH_3NO_2 (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	"	"	"	20
	"	PhMe (1.00) CH_3NO_2 (0.25) AcOH (0.25)	"	"	"	49
	"	$PhNO_2$ (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	"	"	"	25
	"	PhMe (1.00) $PhNO_2$ (0.25) AcOH (0.25)	"	"	"	49
	"	$CHCl_3$ (1.00)	"	"	"	54

		Ph^{i}Pr (0.25) AcOH (0.25)				
	"	PhMe (1.00) $CHCl_3$ (0.25) AcOH (0.25)	"	"	"	55
	"	Ph^{tert}But (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	"	"	"	49
	"	PhMe (1.00) Ph^{tert}But (0.25) AcOH (0.25)	"	"	"	54
	"	*o*-Cl-PhMe (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	"	"	"	52
	"	*p*-Xylene (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	"	"	"	54
	"	PhMe (1.00) *p*-Xylene (0.25) AcOH (0.25)	"	"	"	53
	"	CCl_4 (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	"	"	"	55
	"	PhMe (1.00) CCl_4 (0.25) AcOH (0.25)	"	"	"	55
	"	$(CH_3)_2(CO)$ (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	"	"	"	38
	"	PhMe (1.00) $(CH_3)_2(CO)$ (0.25) AcOH (0.25)	"	"	"	52
	"	C_6H_6 (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	"	"	"	53
	"	PhMe (1.00) C_6H_6 (0.25) AcOH (0.25)	"	"	"	56
	"	*o*-Cl-PhMe (1.25) AcOH (0.25)	"	"	"	52
	"	PhMe (1.00) *o*-Cl-PhMe (0.25) AcOH (0.25)	"	"	"	56
	"	*o*-Cl-PhMe (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	70	"	"	50
	"	*o*-Cl-PhMe (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	80	"	"	52
	"	*m*-Cl-PhMe (1.25) AcOH (0.25)	"	"	"	52
	"	PhMe (1.00) *m*-Cl-PhMe (0.25) AcOH (0.25)	"	"	"	55
	"	*p*-Cl-PhMe (1.25) AcOH (0.25)	"	"	"	54
	"	PhMe (1.00) *p*-Cl-PhMe (0.25) AcOH (0.25)	"	"	"	56
	"	PhMe (1.00) *p*-Cl-*o*-Xylene (0.25) AcOH (0.25)	"	"	"	52
	"	*p*-Cl-*o*-Xylene (1.00) PhMe (0.25)	"	"	"	49

		AcOH (0.25)				
	"	PhMe (1.00) *o*-Cl-*p*-Xylene (0.25) AcOH (0.25)	"	"	"	54
	"	*o*-Cl-*p*-Xylene (1.00) PhMe (0.25) AcOH (0.25)	"	"	"	53
	"	PhMe (1.00) 2,6-Dichloro-PhMe (0.25) AcOH (0.25)	"	"	"	51
	"	2,6-Dichloro-PhMe (1.00) PhMe (0.25) AcOH (0.25)	"	"	"	48
	"	PhMe (1.00) 2,4-Dichloro-PhMe (0.25) AcOH (0.25)	"	"	"	52
	"	2,4-Dichloro-PhMe (1.00) PhMe (0.25) AcOH (0.25)	"	"	"	47
	"	PhMe (1.00) 2,5-Dichloro-PhMe (0.25) AcOH (0.25)	"	"	"	50
	"	2,5-Dichloro-PhMe (1.00) PhMe (0.25) AcOH (0.25)	"	"	"	44
	"	PhMe (1.00) 2,3-Dichloro-PhMe (0.25) AcOH (0.25)	"	"	"	48
	"	2,3-Dichloro-PhMe (1.00) PhMe (0.25) AcOH (0.25)	"	"	"	44

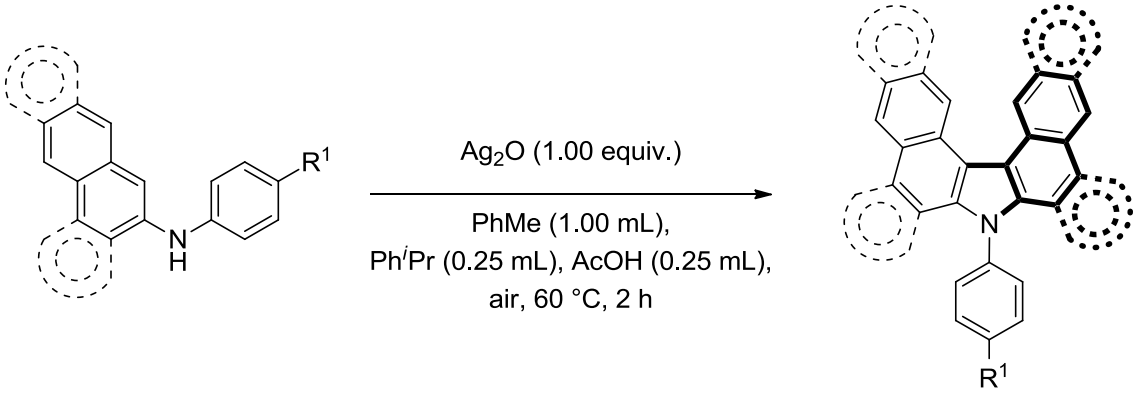
[a] All reactions were carried out with *N*-Phenyl-2-naphtylamine (1.00 mmol, 219.4 mg) as the substrate for 2 h. Yields were determined by ^{1}H-NMR using 1,2-DCE = 1,2-dichloroethane (40.0 µL, 0.50 mmol) as standard.

1.1.7 Silver source screening[a]

reaction vessel	oxidant (1 mmol)	solvent [mL]	temp. [°C]	atmosphere	time [h]	yield [%]
20 mL crimp neck vial	Ag_2O	PhMe (1.00) Ph^{i}Pr (0.25) AcOH (0.25)	60	air	2	56
	$AgCO_3$	"	"	"	"	52
	$Ag(CH_3COO)$	"	"	"	"	47
	AgF	"	"	"	"	2

[a] All reactions were carried out with *N*-Phenyl-2-naphtylamine (1.00 mmol, 219.4 mg) as the substrate for 2 h. Yields were determined by ^{1}H-NMR using 1,2-DCE = 1,2-dichloroethane (40.0 µL, 0.50 mmol) as standard.

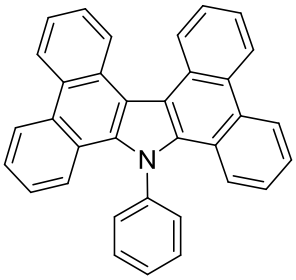
1.2 General Procedure A for the formation of the dibenzocarbazole motif



1 (1.00 mmol) **2**

Unless otherwise specified, the substrate **1** (1.00 mmol), Ag_2O (1.00 mmol, 231.74 mg), toluene (1.00 mL), cumene (0.25 mL) and AcOH (0.25 mL) were united under air in a 20 mL reaction vial equipped with an aluminous headspace cap. The reactor was sealed and exposed to 60 °C for 2 h. Magnetic stirring was set to approx. 550 turns/min. The reactor was then cooled to room temperature and the crude directly engaged (unless otherwise specified) on SiO_2 gel column chromatography for purification, which gave the desired product after concentration *in vacuo*.

Synthesis of compound 2a:



Predicted: Chemical Formula: $C_{34}H_{21}N$
Exact Mass: 443,1674
Molecular Weight: 443,5372
m/z: 443.1674 (100.0%), 444.1708 (36.8%), 445.1741 (6.6%)

Following general procedure **A**, using *N*-Phenyl-9-phenanthrenamine (1.00 mmol, 269.34 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 4:1. Isolated yield: 171 mg (77%) of a white solid.

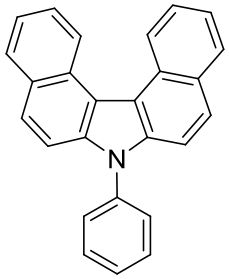
^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 8.92 (d, ^3J = 8.2 Hz, 2H), 8.87 (t, ^3J = 6.8 Hz, 4H), 7.94-7.83 (m, 5H), 7.71-7.63 (m, 4H), 7.56 (t, ^3J = 8.0 Hz, 2H), 7.28 (t, ^3J = 7.6 Hz, 2H), 7.15 (d, ^3J = 8.2 Hz, 2H).

^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$): δ (ppm) = 141.51 (s, $C_{quat.}$), 132.89 (s, $C_{quat.}$), 131.23 (s, CH), 130.69 (s, CH), 130.22 (s, $C_{quat.}$), 129.87 (s, CH), 127.69 (s, $C_{quat.}$), 127.49 (s, $C_{quat.}$), 126.50 (s, CH), 126.14 (s, CH), 125.60 (s, CH), 125.01 (s, CH), 124.91 (s, CH), 124.32 (s, CH), 123.09 (s, $C_{quat.}$), 121.30 (s, CH), 115.46 (s, $C_{quat.}$).

HRMS-TOF [EI$^+$]: *m/z* calc.: 443.1674 $[C_{34}H_{21}N]^{\bullet+}$, measured: 443.1671.

IR (neat, cm^{-1}): $\tilde{\nu}$ = 3079, 3053, 1607, 1595, 1574, 1514, 1496, 1437, 1392, 1294, 1238, 1155, 1049, 1035, 1023, 1002, 952, 942, 748, 726, 717, 705, 691.

Synthesis of compound 2b:



Predicted: Chemical Formula: $C_{26}H_{17}N$
Exact Mass: 343,1361
Molecular Weight: 343,4199
m/z: 343.1361 (100.0%), 344.1395 (28.1%), 345.1428 (3.8%)

Following general procedure **A**, using *N*-Phenyl-2-napthylamine (1.00 mmol, 219.3 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 4:1. Isolated yield: 92.7 mg (54%) of a white solid.

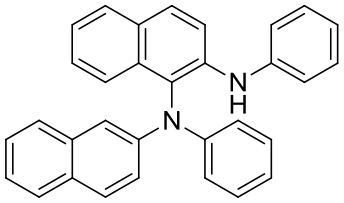
^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 9.13 (d, ^{3}J = 8.4 Hz, 2H), 8.12 (d, ^{3}J = 7.8 Hz, 2H), 7.95 (d, ^{3}J = 8.9 Hz, 2H), 7.77-7.73 (m, 4H), 7.67-7.65 (m, 3H), 7.58-7.52 (m, 4H).

^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$): δ (ppm) = 137.46 (s, $C_{quat.}$), 135.98 (s, $C_{quat.}$), 130.30 (s, CH), 129.84 (s, $C_{quat.}$), 129.32 (s, CH), 128.76 (s, CH), 128.32 (s, $C_{quat.}$), 128.01 (s, CH), 127.07 (s, CH), 125.83 (s, CH), 124.43 (s, CH), 123.59 (s, CH), 116.50 (s, $C_{quat.}$), 111.72 (s, CH).

HRMS-TOF [EI^{+}]: *m/z* calc.: 343.1361 $[C_{26}H_{17}N]^{\bullet+}$, measured: 343.1357.

IR (neat, cm^{-1}): $\tilde{\upsilon}$ = 3041, 1613, 1591, 1522, 1498, 1476, 1454, 1400, 1380, 1303, 1014, 796, 768, 741, 732, 694, 685, 670.

Byproduct 2b':



Predicted: Chemical Formula: $C_{32}H_{24}N_2$
Exact Mass: 436,1939
Molecular Weight: 436,5464
m/z: 436.1939 (100.0%), 437.1973 (34.6%), 438.2007 (5.8%)

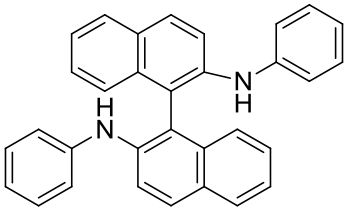
SiO_2 gel column chromatography hexane → hexane/toluene = 3:1. Isolated yield: 14.6 mg (7%) of a white solid. This compound was previously reported, notably in:

[S6] D. F. Bowman, B. S. Middleton and K. U. Ingold, *J. Org. Chem.* 1969, **34**, 3456.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.83-7.80 (m, 3H), 7.72 (t, ^3J = 8.7 Hz, 2H), 7.64 (d, ^3J = 9 Hz, 1H), 7.54 (d, ^3J = 8.2 Hz, 1H), 7.44-7.38 (m, 2H), 7.36 (dd, ^3J = 8 Hz, ^4J = 1.3 Hz, 1H), 7.34-7.28 (m, 3H), 7.27-7.19 (m, 7H), 7.02-6.99 (m, 2H), 6.97-6.95 (m, 1H), 6.29 (s, NH).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ (ppm) = 145.99 (s, $C_{quat.}$), 143.69 (s, $C_{quat.}$), 142.00 (s, $C_{quat.}$), 139.76 (s, $C_{quat.}$), 134.53 (s, C_{quat}), 133.25 (s, $C_{quat.}$), 129.96 (s, $C_{quat.}$), 129.48 (s, CH), 129.28 (s, CH), 129.20 (s, CH), 129.02 (s, C_{quat}), 128.62 (s, CH), 128.28 (s, CH), 127.53 (s, CH), 127.33 (s, CH), 126.79 (s, CH), 126.33 (s, CH), 125.31 (s, C_{quat}), 123.97 (s, CH), 123.44 (s, CH), 122.58 (s, CH), 122.27 (s, CH), 121.99 (s, CH), 120.92 (s, CH), 120.20 (s, CH), 119.94 (s, CH), 118.10 (s, CH), 115.49 (s, CH).

Byproduct 2b'':



Predicted: Chemical Formula: $C_{32}H_{24}N_2$
Exact Mass: 436,1939
Molecular Weight: 436,5464
m/z: 436.1939 (100.0%), 437.1973 (34.6%), 438.2007 (5.8%)

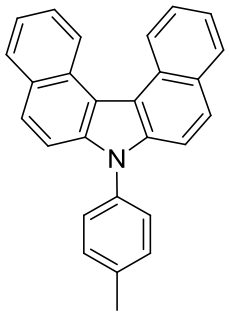
SiO_2 gel column chromatography hexane → hexane/toluene = 3:1. Isolated yield: 9.5 mg (4 %) of a white solid. This compound was previously reported, notably in:

[S7] X.-L. Li, J.-H. Huang, L.-M. Yang, *Org. Lett.* **2011**, *13*, 4950.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.89 (d, ^3J = 8.9 Hz, 2H), 7.85 (d, ^3J = 7.9 Hz, 2H), 7.69 (d, ^3J = 9.0 Hz, 2H), 7.32 (td, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 2H), 7.27-7.17 (m, 10H), 7.15 (s, 1H), 6.98-6.94 (m, 5H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ (ppm) = 142.44 (s, $C_{quat.}$), 140.31 (s, $C_{quat.}$), 133.93 (s, $C_{quat.}$), 129.38 (s, CH), 129.21 (s, CH), 128.18 (s, CH), 127.02 (s, CH), 124.42 (s, CH), 123.45 (s, CH), 122.15 (s, CH), 119.92 (s, CH), 117.81 (s, CH), 116.32 (s, $C_{quat.}$).

Synthesis of compound 2c:



Predicted: Chemical Formula: $C_{27}H_{19}N$
Exact Mass: 357,1517
Molecular Weight: 357,4465
m/z: 357.1517 (100.0%), 358.1551 (29.2%), 359.1585 (4.1%)

Following general procedure **A**, using *N*-(*p*-Tolyl)-2-napthylamine (1.00 mmol, 233.31 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 4:1. Isolated yield: 103 mg (58%) of a white solid.

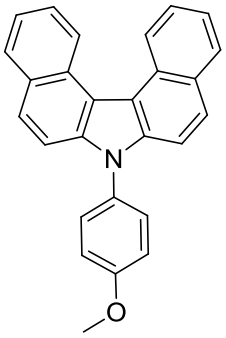
^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm) = 9.25 (d, ^{3}J = 8.6 Hz, 2H), 8.05 (d, ^{3}J = 8.0 Hz, 2H), 7.86 (d, ^{3}J = 8.8 Hz, 2H), 7.73-7.69 (m, 2H), 7.58- 7.46 (m, 8H), 2.54 (s, 3H).

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ (ppm) = 139.24 (s, $C_{quat.}$), 138.76 (s, $C_{quat.}$), 134.69 (s, $C_{quat.}$), 131.12 (s, CH), 130.74 (s, $C_{quat.}$), 129.67 (s, CH), 129.59 (s, $C_{quat.}$), 128.54 (s, CH), 127.20 (s, CH), 126.02 (s, CH), 125.74 (s, CH), 123.94 (s, CH), 117.84 (s, $C_{quat.}$), 112.49, (s, CH), 21.60 (s, CH_3).

HRMS-TOF [EI^{+}]: *m/z* calc.: 357.1517 $[C_{27}H_{19}N]^{\bullet+}$, measured: 357.1514.

IR (neat, cm^{-1}): $\tilde{\nu}$ = 3053, 2920, 2857, 1610, 1596, 1515, 1496, 1455, 1438, 1380, 1311, 1296, 1252, 1205, 1174, 1121, 1104, 1047, 1016, 942, 796, 776, 747, 729, 691, 682, 671.

Synthesis of compound 2d:



Predicted: Chemical Formula: $C_{27}H_{19}NO$
Exact Mass: 373,1467
Molecular Weight: 373,4459
m/z: 373.1467 (100.0%), 374.1500 (29.2%), 375.1534 (4.1%)

Following general procedure **A**, using N-(4-methoxyphenyl)naphtylen-2-amine (1.00 mmol, 249.31 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 1:1. Isolated yield: 89 mg (48%) of a white solid.

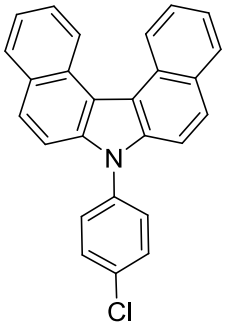
^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm) = 9.25 (d, ^3J = 8.5 Hz, 2H), 8.05 (dd, ^3J = 8.1 Hz, ^4J = 1.1 Hz, 2H), 7.86 (d,^3J = 8.9 Hz, 2H), 7.71 (td, ^3J = 7.7 Hz, J = 1.2 Hz, 2H), 7.56-7.52 (m, 4H), 7.50 (AA' part of an AA'BB' spin system, 7.5079, 7.5023, 7.4914, 7.4857, 7.4773, 2H), 7.19 (BB' part of an AA'BB' spin system 7.2059, 7.1978, 7.1921, 7.1809, 7.1756, 7.1672, 2H), 3.95 (s, 3H).

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ (ppm) = 160.30 (s, $C_{quat.}$), 139.05 (s, $C_{quat.}$), 130.74 (s, $C_{quat.}$), 130.03 (s, CH), 129.94 (s, $C_{quat.}$), 129.69 (s, CH), 129.61 (s, $C_{quat.}$), 127.21 (s, CH), 126.03 (s, CH), 125.74 (s, CH), 123.93 (s, CH), 117.75 (s, $C_{quat.}$), 115.69 (s, CH), 112.48 (s, CH), 56.24 (s, OCH_3).

EI-HRMS: *m/z* calc.: 373.14612 $[C_{27}H_{19}NO]^{\bullet+}$, measured: 373.14663.

IR (neat, cm^{-1}): $\tilde{\nu}$ = 3066, 3000, 2959, 2925, 2853, 2326, 2116, 2080, 1605, 1508, 1442, 1377, 1301, 1245, 1099, 1019, 851, 796, 735, 676.

Synthesis of compound 2e:



Predicted: Chemical Formula: $C_{26}H_{16}ClN$
Exact Mass: 377,0971
Molecular Weight: 377,8649
m/z: 377.0971 (100.0%), 379.0942 (32.0%), 378.1005 (28.1%), 380.0975 (9.0%), 379.1038 (3.8%), 381.1009 (1.2%)

Following general procedure **A**, using N-(4-chlorophenyl)naphtylen-2-amine (1.00 mmol, 253.73 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 3:1. Isolated yield: 104 mg (55%) of a white solid.

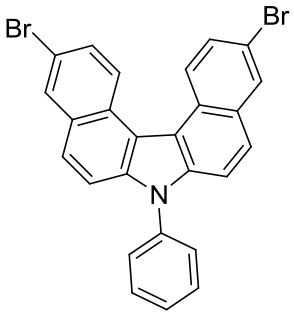
^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm) = 9.24 (d, ^3J = 8.5 Hz, 2H), 8.06 (dd, ^3J = 8.1 Hz, ^4J = 1.1 Hz, 2H), 7.88 (d, ^3J = 8.9 Hz 2H), 7.72 (td, ^3J = 7.6 Hz, J = 1.2 Hz, 2H), 7.67 (AA' part of an AA' BB' spin system 7.6909, 7.6838, 7.6785, 7.6672, 7.6619, 7.6550, 2H), 7.58-7.53 (m, 6H).

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ (ppm) = 138.50 (s, $C_{quat.}$), 136.08 (s, $C_{quat.}$), 134.74 (s, $C_{quat.}$), 130.86 (s, $C_{quat.}$), 130.81 (s, CH), 130.21 (s, CH), 129.71 (s, CH), 129.54 (s, $C_{quat.}$), 127.50 (s, CH), 126.18 (s, CH), 125.79 (s, CH), 124.16 (s, CH), 118.19 (s, $C_{quat.}$), 112.12 (s, CH).

EI-HRMS: *m/z* calc.: 377.09658 $[C_{26}H_{16}NCl]^{\bullet+}$, measured: 377.09685.

IR (neat, cm^{-1}): $\tilde{\nu}$ = 3054, 2117, 2082, 2024, 1987, 1612, 1586, 1522, 1490, 1398, 1377, 1307, 1204, 1172, 1084, 1045, 1011, 860, 796, 767, 738, 674.

Synthesis of compound 2f:



Predicted: Chemical Formula: $C_{26}H_{15}Br_2N$
Exact Mass: 498,9571
Molecular Weight: 501,2120
m/z: 500.9551 (100.0%), 498.9571 (51.4%), 502.9530 (48.6%), 501.9584 (28.1%), 499.9605 (14.5%), 503.9564 (13.7%), 502.9618 (3.8%), 500.9638 (2.0%), 504.9597 (1.8%)

Following general procedure **A**, using 6-bromo-N-phenylnaphthalen-2-amine (1.00 mmol, 298.18 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 3:1. Isolated yield: 102 mg (41%) of a white solid.

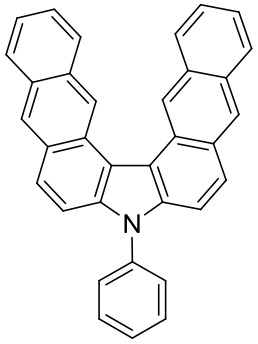
^{1}H-NMR (600 MHz, CD_2Cl_2): δ (ppm) = 9.03 (d, ^3J = 8.3 Hz, 2H), 8.20 (s, 2H), 7.78 (d, ^3J = 8.3 Hz, 4H), 7.70 (t, ^3J = 7.4 Hz, 2H), 7.63-7.57 (m, 5H).

^{13}C{^{1}H}-NMR (151 MHz, CD_2Cl_2): δ (ppm) = 138.88 (s, $C_{quat.}$), 136.96 (s, $C_{quat.}$), 132.15 (s, C_{quat}), 131.63 (s, CH), 130, 67 (s, CH), 129.35 (s, CH), 129.16 (s, CH), 128.72 (s, CH), 128.00 (s, $C_{quat.}$), 127.15 (s, CH), 126.60 (s, CH), 117.67 (s, $C_{quat.}$), 117.25 (s, $C_{quat.}$), 113.61 (s, CH).

ESI-HRMS: *m/z* calc.: 499.96440 $[C_{26}H_{15}NBr_2]H^+$, measured: 499.96439.

IR (neat, cm^{-1}): $\tilde{\upsilon}$ = 3058, 2329, 2110, 1586, 1555, 1498, 1453, 1401, 1365, 1296, 1182, 1071, 1029, 928, 875, 824, 795, 745, 699, 664.

Synthesis of compound 2g:



Predicted: Chemical Formula: $C_{34}H_{21}N$
Exact Mass: 443,1674
Molecular Weight: 443,5372
m/z: 443.1674 (100.0%), 444.1708 (36.8%), 445.1741 (6.6%)

Following general procedure **A**, using *N*-Phenyl-2-anthramine (1.00 mmol, 269.35 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 4:1. Isolated yield: 70.5 mg (32%) of a yellow solid.

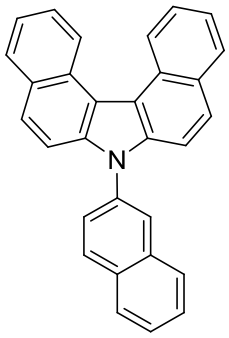
^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm) = 10.02 (s, 2H), 8.63 (s, 2H), 8.21 (d, ^3J = 8.3 Hz, 2H), 8.13 (d, ^3J = 8.2 Hz, 2H), 7.98 (d, ^3J = 9.2 Hz, 2H), 7.74-7.55 (m, 11H).

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ (ppm) = 137.24 (s, $C_{quat.}$), 137.13 (s, $C_{quat.}$), 131.86 (s, $C_{quat.}$), 130.73 (s, $C_{quat.}$), 130.54 (s, CH), 129.22 (s, CH), 128.84 (s, CH), 128.57 (s, CH), 128.40 (s, CH), 128.13 (s, $C_{quat.}$), 127.92 (s, CH), 127.39 (s, CH), 126.35 (s, CH), 125.45 (s, CH), 123.48 (s, CH), 117.42 (s, $C_{quat.}$), 113.93 (s, CH).

HRMS-TOF [EI$^+$]: *m/z* calc.: 443.1674 $[C_{34}H_{21}N]^{\bullet+}$, measured: 443.1690.

IR (neat, cm^{-1}): $\tilde{\upsilon}$ = 3045, 1608, 1596, 1576, 1499, 1489, 1456, 1439, 1396, 1356, 1326, 1285, 1255, 1205, 1076, 1033, 950, 891, 870, 798, 736, 730, 706.

Synthesis of compound 2h:



Predicted: Chemical Formula: $C_{30}H_{19}N$
Exact Mass: 393,1517
Molecular Weight: 393,4786
m/z: 393.1517 (100.0%), 394.1551 (32.4%), 395.1585 (5.1%)

Following general procedure **A**, using 2,2'-Dinapthylamine (1.00 mmol, 269.35 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 4:1. Isolated yield: 106 mg (54%) of a white solid.

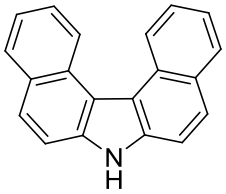
^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm) = 9.28 (d, ^{3}J = 8.5 Hz, 2H), 8.16 (d, ^{3}J = 8.6 Hz, 1H), 8.12-7.97 (m, 5H), 7.87 (d, ^{3}J = 8.9 Hz, 2H), 7.76-7.64 (m, 6H), 7.62 (s, 1H), 7.56 (t, ^{3}J = 7.4 Hz, 2H).

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ (ppm) = 138.80 (s, $C_{quat.}$), 134.85 (s, $C_{quat.}$), 134.48 (s, $C_{quat.}$), 133.50 (s, $C_{quat.}$), 130.84 (s, $C_{quat.}$), 130.55 (s, CH), 129.69 (s, CH), 129.59 (s, $C_{quat.}$), 128.59 (s, CH), 128.51 (s, CH), 127.61 (s, CH), 127.51 (s, CH), 127.39 (s, CH), 127.36 (s, CH), 126.54 (s, CH), 126.09 (s, CH), 125.79 (s, CH), 124.04 (s, CH), 118.08 (s, $C_{quat.}$), 112.47 (s, CH).

HRMS-TOF [EI^{+}]: *m/z* calc.: 393.1517 $[C_{30}H_{19}N]^{\bullet+}$, measured: 393.1511.

IR (neat, cm^{-1}): $\tilde{\upsilon}$ = 3053, 3030, 1613, 1594, 1520, 1506, 1475, 1438, 1401, 1380, 1339, 1306, 1271, 1252, 1203, 1186, 1170, 1151, 1126, 1045, 1015, 965, 945, 890, 865, 850, 795, 767, 754, 741, 731.

Scope limits: compound 2i:



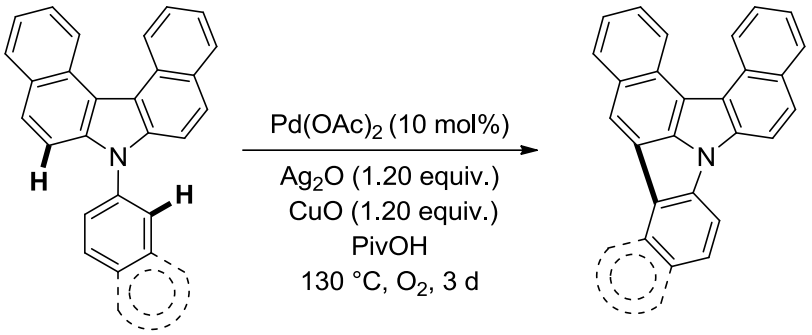
Predicted: Chemical Formula: $C_{20}H_{13}N$
Exact Mass: 267,1048
Molecular Weight: 267,3239
m/z: 267.1048 (100.0%), 268.1082 (21.6%), 269.1115 (2.2%)

Following general procedure **A**, using 2-Naphtylamine (1.00 mmol, 143.19 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 1:1. Isolated yield: 4.8 mg (< 5%) of a yellow solid.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm) = 9.21 (d, ^3J = 8.5 Hz, 2H), 8.98 (s, NH), 8.06 (d, ^3J = 8.1 Hz, 2H), 7.90 (d, ^3J = 8.8 Hz, 2H), 7.75 (d, ^3J = 8.8 Hz, 2H), 7.70 (td, ^3J = 7.7 Hz, J = 1.2 Hz, 2H), 7.53 (td, ^3J = 7.4 Hz, J = 0.9 Hz, 2H).

ESI-HRMS: *m/z* calc.: 268.11208 $[C_{20}H_{13}N]H^+$, measured: 268.11212.

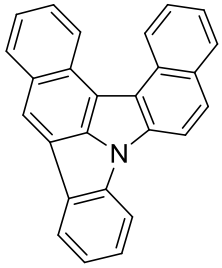
1.3 General Procedure B for the synthesis of Dibenzo-indolo-carbazoles



2 (0.50 mmol) **3**

Unless otherwise specified, the substrate **2** (0.50 mmol), $Pd(OAc)_2$ (10 mol%, 0.05 mmol, 11.2 mg), Ag_2O (0.60 mmol, 139 mg), CuO (0.60 mmol, 47.7 mg) and pivalic acid (1334 mg) were united under air in a 20 mL reaction vial equipped with an aluminous headspace cap. The vial was sealed, flushed with oxygen and exposed to 130 °C for 3 d. Magnetic stirring was set to approx. 450 turns/min. The reactor was then cooled to room temperature and the crude directly engaged (unless otherwise specified) on SiO2 gel column chromatography for purification, which gave the desired product after concentration in vacuo.

Synthesis of compound 3b:



Predicted: Chemical Formula: $C_{26}H_{15}N$
Exact Mass: 341,1204
Molecular Weight: 341,4040
m/z: 341.1204 (100.0%), 342.1238 (28.1%), 343.1272 (3.8%)

Following general procedure **B**, using compound **2a** (0.50 mmol, 178.73 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 4:1.
Isolated yield: 106 mg (62%) of a yellow solid.

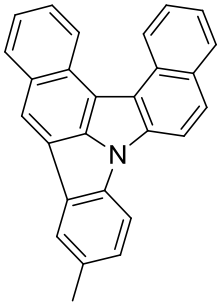
^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 9.28 (t, ^3J = 7.7 Hz, 2H), 8.83 (s, 1H), 8.64 (d, ^3J = 8.7 Hz, 1H), 8.48 (t, ^3J = 7.3 Hz, 2H), 8.41 (d, ^3J = 7.6 Hz, 1H), 8.24-8.19 (m, 2H), 7.97-7.88 (m, 2H), 7.72 (q, ^3J = 7.9 Hz, 2H), 7.64 (t, ^3J = 7.5 Hz, 1H), 7.51 (t, ^3J = 7.5 Hz, 1H).

^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$): δ (ppm) = 140.69 (s, $C_{quat.}$), 139.76 (s, $C_{quat.}$), 134.04 (s, $C_{quat.}$), 133.18 (s, $C_{quat.}$), 132.01 (s, CH), 130.23 (s, $C_{quat.}$), 129.70 (s, CH), 129.44 (s, $C_{quat.}$), 129.07 (s, $C_{quat.}$), 128.80 (s, CH), 128.53 (s, $C_{quat.}$), 127.79 (s, CH), 127.24 (s, CH), 127.03 (s, CH), 125.25 (s, CH), 125.22 (s, CH) 124.09 (s, CH), 123.73 (s, $C_{quat.}$), 123.45 (s, CH), 123.29 (s, CH), 121.78 (s, CH), 119.87 (s, $C_{quat.}$), 113.73 (s, CH), 113.11 (s, CH).

HRMS-TOF [EI$^+$]: *m/z* calc.: 341.1204 $[C_{26}H_{15}N]^{\bullet+}$, measured: 341.1200.

IR (neat, cm^{-1}): $\tilde{\upsilon}$ = 3043, 1598, 1584, 1522, 1454, 1435, 1416, 1370, 1309, 1287, 1206, 1186, 1164, 1137, 1104, 1062, 1033, 1022, 938, 869, 857, 856, 799, 772, 733, 717.

Synthesis of compound 3c:



Predicted: Chemical Formula: $C_{27}H_{17}N$
Exact Mass: 355,1361
Molecular Weight: 355,4306
m/z: 355.1361 (100.0%), 356.1395 (29.2%), 357.1428 (4.1%)

Following general procedure **B**, using compound **2c** (0.50 mmol, 178.73 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 4:1.

Isolated yield: 88.8 mg (50%) of a yellow solid.

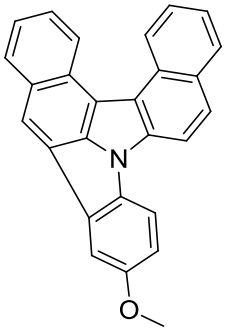
^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm) = 9.30 (d, ^3J = 8.5 Hz, 2H), 8.46 (s, 1H), 8.34 (d, ^3J = 8.0 Hz, 1H), 8.16 (d, ^3J = 8.6 Hz, 1H), 8.09 (d, ^3J = 8.0 Hz, 1H), 8.02 (d, ^3J = 6.9 Hz, 2H), 7.87-7.79 (m, 3H), 7.65-7.56 (m, 2H), 7.42 (d, ^3J = 8.0 Hz, 1H), 2.57 (s, 3H).

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ (ppm) = 142.22 (s, $C_{quat.}$), 139.05 (s, $C_{quat.}$), 133.94 (s, $C_{quat.}$), 133.10 (s, $C_{quat.}$), 132.23 (s, CH), 130.88 (s, $C_{quat.}$), 130.72 (s, $C_{quat.}$), 130.50 (s, $C_{quat.}$), 129.99 (s, CH), 129.71 (s, $C_{quat.}$), 129.46 (s, CH), 127.74 (s, CH), 127.01 (s, CH), 126.95 (s, CH), 126.32 (s, CH), 126.22 (s, CH), 124.65 (s, CH), 124.25 (s, CH), 123.57 (s, CH), 121.32 (s, CH), 113.56 (s, CH), 112.39 (s, CH), 21.76 (s, CH3).

HRMS-TOF [EI$^+$]: *m/z* calc.: 355.1361 $[C_{27}H_{17}N]^{\bullet+}$, measured: 355.1359.

IR (neat, cm^{-1}): $\tilde{\nu}$ = 3065, 3045, 2917, 2859, 1617, 1598, 1578, 1524, 1458, 1377, 1363, 1299, 1286, 1200, 1184, 1199, 1152, 1063, 1032, 1019, 951, 941, 883, 853, 848, 791, 770, 745, 730, 718.

Synthesis of compound 3d:



Predicted: Chemical Formula: $C_{27}H_{17}NO$
Exact Mass: 371,1310
Molecular Weight: 371,4300
m/z: 371.1310 (100.0%), 372.1344 (29.2%), 373.1377 (4.1%)

Following general procedure **A**, using compound **2f** (0.15 mmol, 56.0 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 3:1. Isolated yield: 9.7 mg (17%) of a yellow solid.

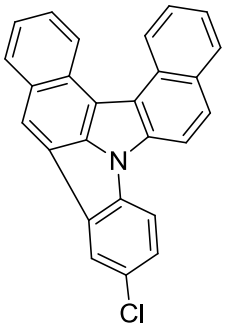
^{1}H-NMR (600 MHz, DMSO-d$_6$): δ (ppm) = 9.26 (d, ^3J = 9.2 Hz, 1H), 9.24 (d, ^3J = 8.2 Hz, 1H), 8.77 (s, 1H), 8.55 (d, ^3J = 9.2 Hz, 1H), 8.44 (d, ^3J = 8.3 Hz, 1H), 8.31 (d, ^3J = 9.2 Hz, 1H), 8.20 (d, ^3J = 8.2 Hz, 1H), 8.15 (d, ^3J = 9.2 Hz, 1H), 8.00 (d, ^4J = 2.8 Hz, 1H), 7.94 (t, ^3J = 7.8 Hz, 1H), 7.88 (t, ^3J = 6.9 Hz, 1H), 7.69 (t, ^3J = 7.4 Hz, 1H), 7.61 (t, ^3J = 7.4 Hz, 1H), 7.26 (dd,^3J = 8.3 Hz, ^4J = 2.8 Hz, 1H), 3.95 (s, 3H).

^{13}C{^{1}H}-NMR (151 MHz, DMSO-d$_6$): δ (ppm) = 155.92 (s, $C_{quat.}$), 140.97 (s, $C_{quat.}$), 134.08 (s, $C_{quat.}$), 133.88 (s, $C_{quat.}$), 132.89 (s, $C_{quat.}$), 131.96 (s, CH), 130.24 (s, $C_{quat.}$), 129.96 (s, $C_{quat.}$), 129.62 (s, CH), 129.46 (s, $C_{quat.}$), 128.58 (s, $C_{quat.}$), 127.58 (s, CH), 127.15 (s, CH), 126.88 (s, CH), 125.17 (s, CH), 125.08 (s, CH), 123.80 (s, CH), 123.29 (s, CH), 121.79 (s, CH), 120.06 (s, $C_{quat.}$), 114.91 (s, CH), 113.48 (s, CH), 113.39 (s, CH), 111.85 (s, $C_{quat.}$), 109.14 (s, CH), 55.78 (s, CH_3).

EI-HRMS: *m/z* calc.: 371.13047 $[C_{27}H_{17}NO]^{\bullet+}$, measured: 371.13043.

IR (neat, cm^{-1}): $\tilde{\nu}$ = 3058, 3005, 2921, 2851, 2111, 2075, 1994, 1600, 1578, 1523, 1460, 1381, 1302, 1263, 1209, 1186, 1117, 1056, 1021, 947, 864, 797, 739.

Synthesis of compound 3e:



Predicted: Chemical Formula: $C_{26}H_{14}ClN$
Exact Mass: 375,0815
Molecular Weight: 375,8491
m/z: 375.0815 (100.0%), 377.0785 (32.0%), 376.0848 (28.1%), 378.0819 (9.0%), 377.0882 (3.8%), 379.0852 (1.2%)

Following general procedure **A**, using compound **2g** (0.12 mmol, 45.4 mg). The mixture was engaged by SiO_2 gel column chromatography pentane/toluene = 3:1. Isolated yield: 18.5 mg (41%) of a yellow solid.

NMR was measured at 100.185°C:

^{1}H-NMR (600 MHz, DMSO-d$_6$): δ (ppm) = 9.23 (t, ^3J = 8.7 Hz, 2H), 8.74 (s, 1H), 8.45 (d, ^3J = 8.7 Hz, 1H), 8.41 (d, ^3J = 8.0 Hz, 1H), 8.39 (s, 1H), 8.31 (d, ^3J = 8.6 Hz, 1H), 8.18 (d, ^3J = 8.0 Hz, 1H), 8.13 (d, ^3J = 8.7 Hz, 1H), 7.92 (t, ^3J = 7.6 Hz, 1H), 7.87 (t, ^3J = 7.6 Hz, 1H), 7.68 (t, ^3J = 7.3 Hz, 2H), 7.62 (t, ^3J = 7.3 Hz, 1H).

^{13}C{^{1}H}-NMR (151 MHz, DMSO-d$_6$): δ (ppm) = 140.65 (s, $C_{quat.}$), 137.82 (s, $C_{quat.}$), 133.55 (s, $C_{quat.}$), 132.69 (s, $C_{quat.}$), 131.41 (s, CH), 130.33 (s, $C_{quat.}$), 129.87 (s, $C_{quat.}$), 129.00 (s, $C_{quat.}$), 128.38 (s, CH), 127.50 (s, CH), 127.22 (s, CH), 127.03 (s, $C_{quat.}$), 126.73 (s, CH), 126.27 (s, CH), 124.66 (s, CH), 123.48 (s, CH), 123.16 (s, CH), 122.85 (s, CH), 121.65 (s, CH), 118.36 (s, $C_{quat.}$), 113.35 (s, CH), 112.81 (s, CH), 111.84 (s, $C_{quat.}$).

ESI-HRMS: *m/z* calc.: 376.08875 $[C_{26}H_{14}NCl]H^+$, measured: 376.08902.

IR (neat, cm^{-1}): $\tilde{\upsilon}$ = 3071, 2922, 2854, 2327, 2108, 1595, 1523, 1443, 1371, 1293, 1211, 1184, 1056, 1020, 944, 902, 858, 789, 738.

1.4 NMR spectra of the products

^{1}H:

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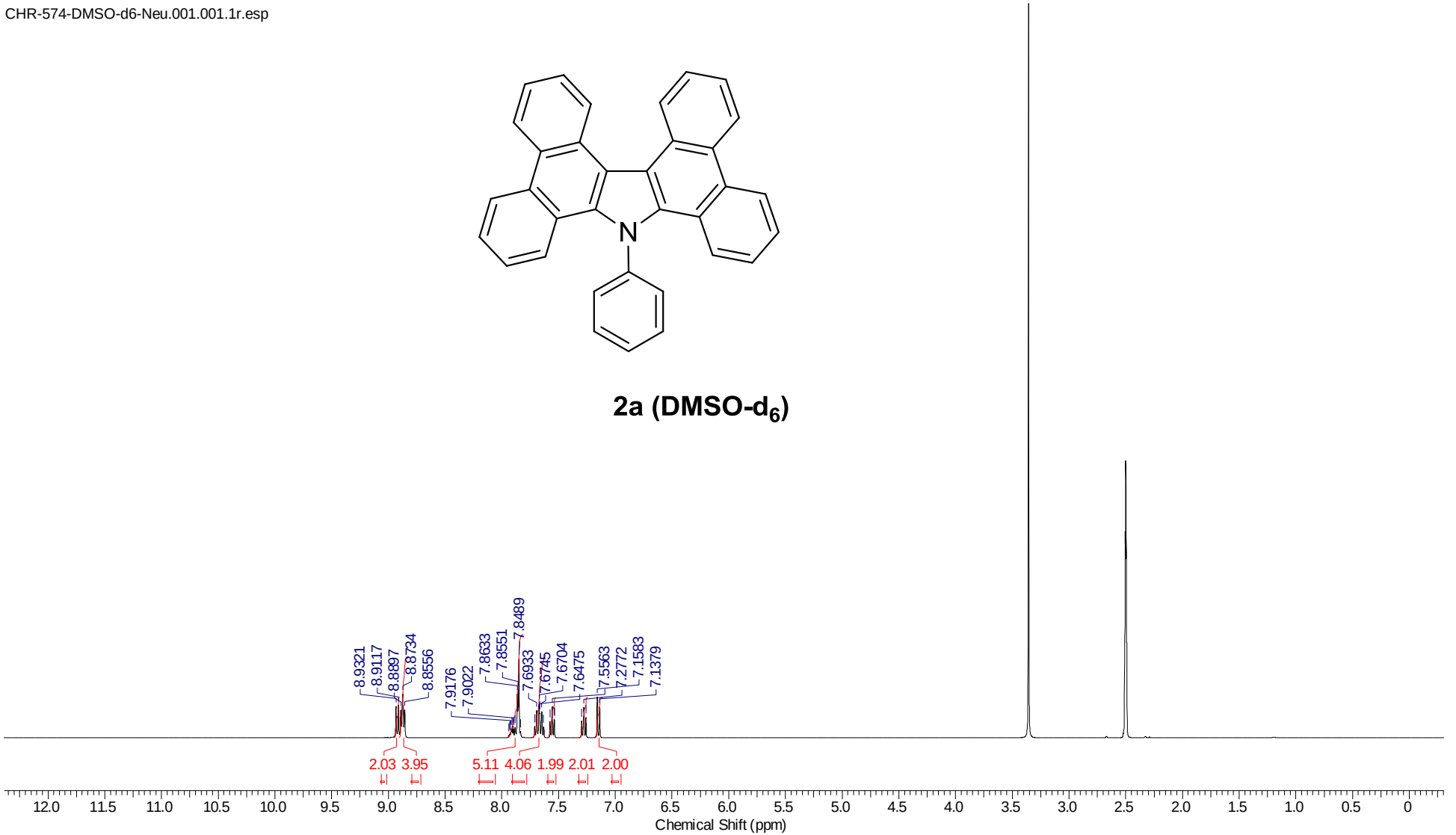

^{1}H Zoom:

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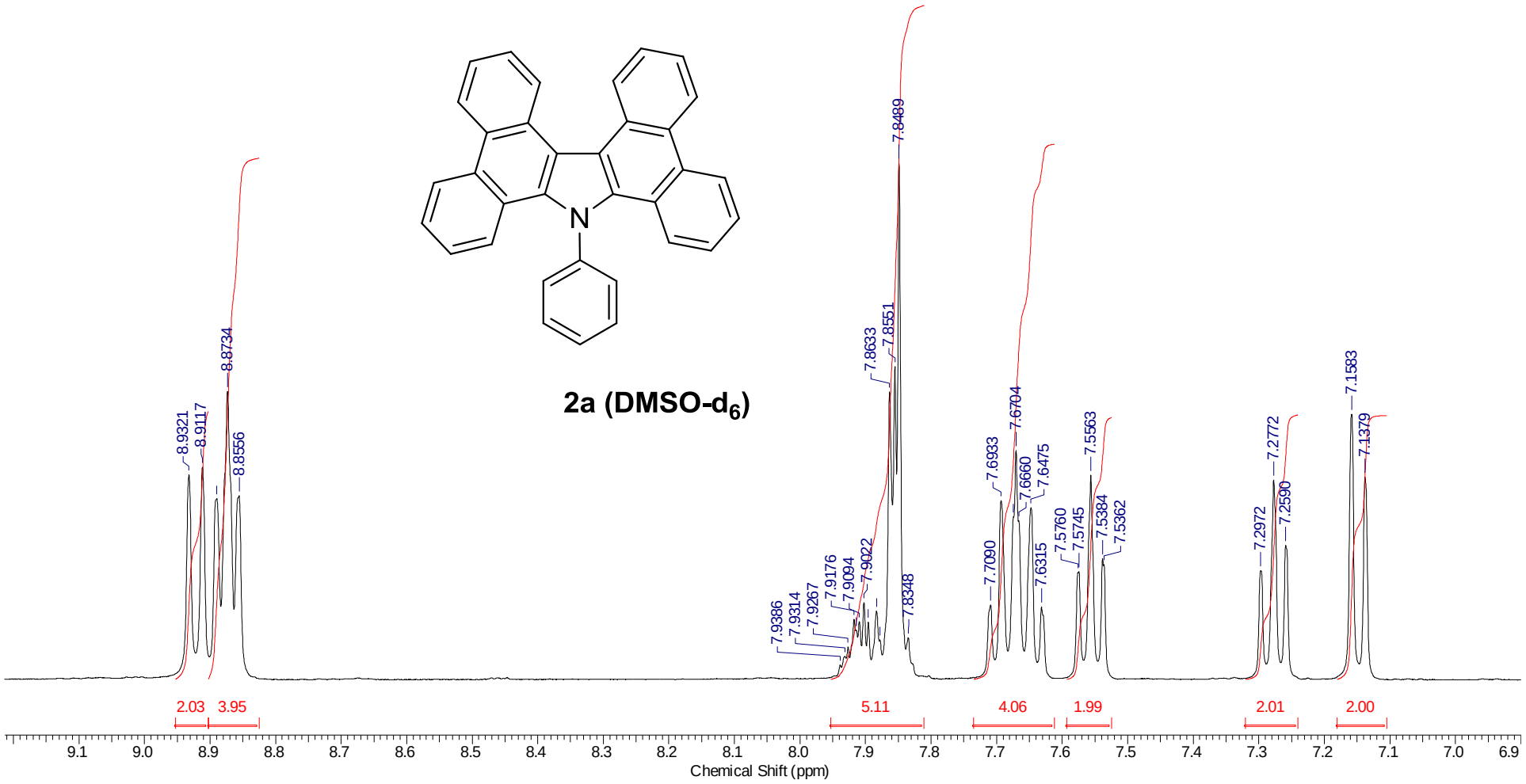
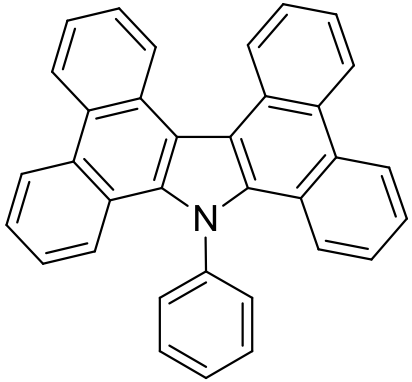


^{13}C:

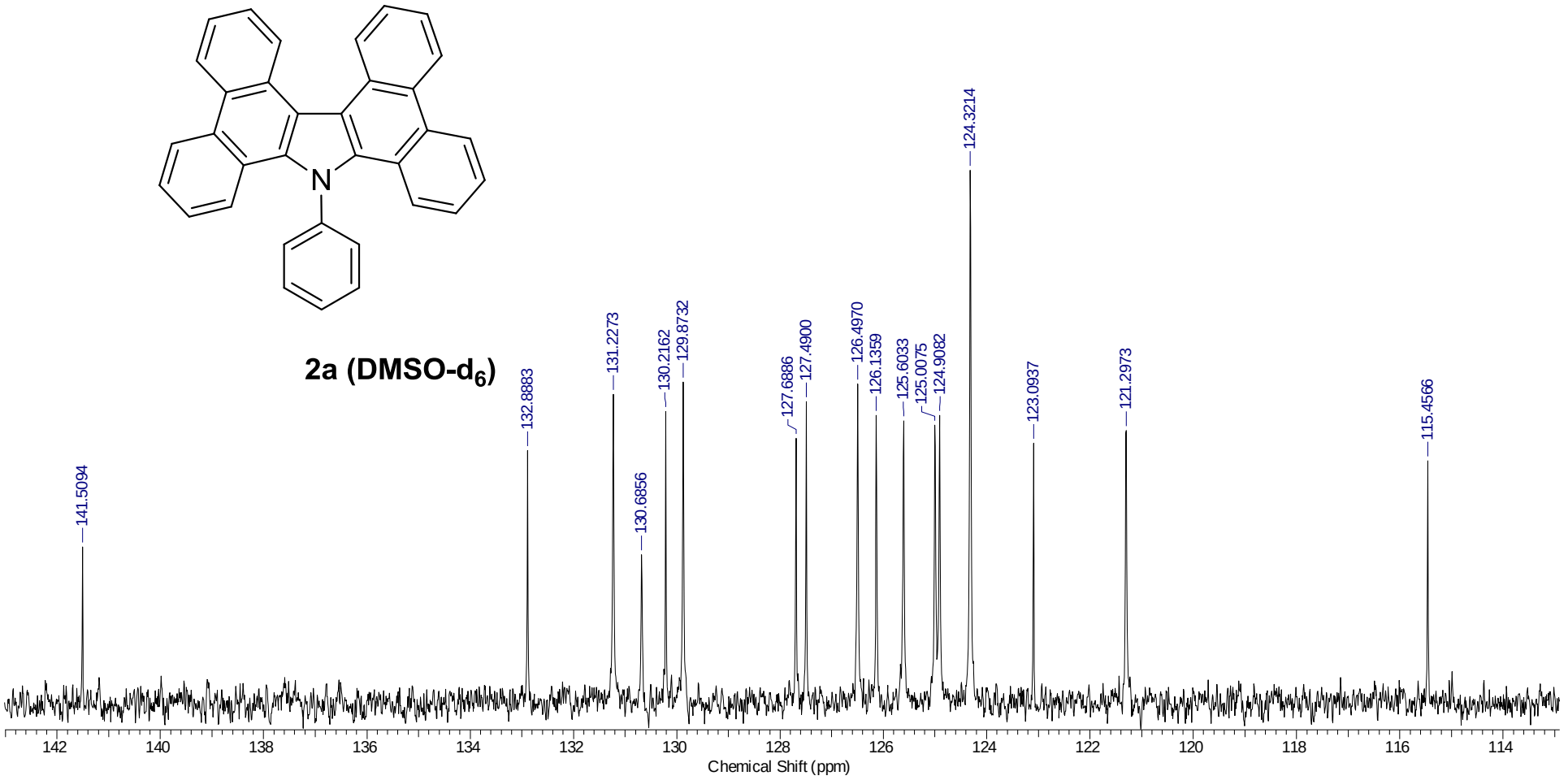
CHR-574-DMSO-d6-Neu.002.001.1r.esp



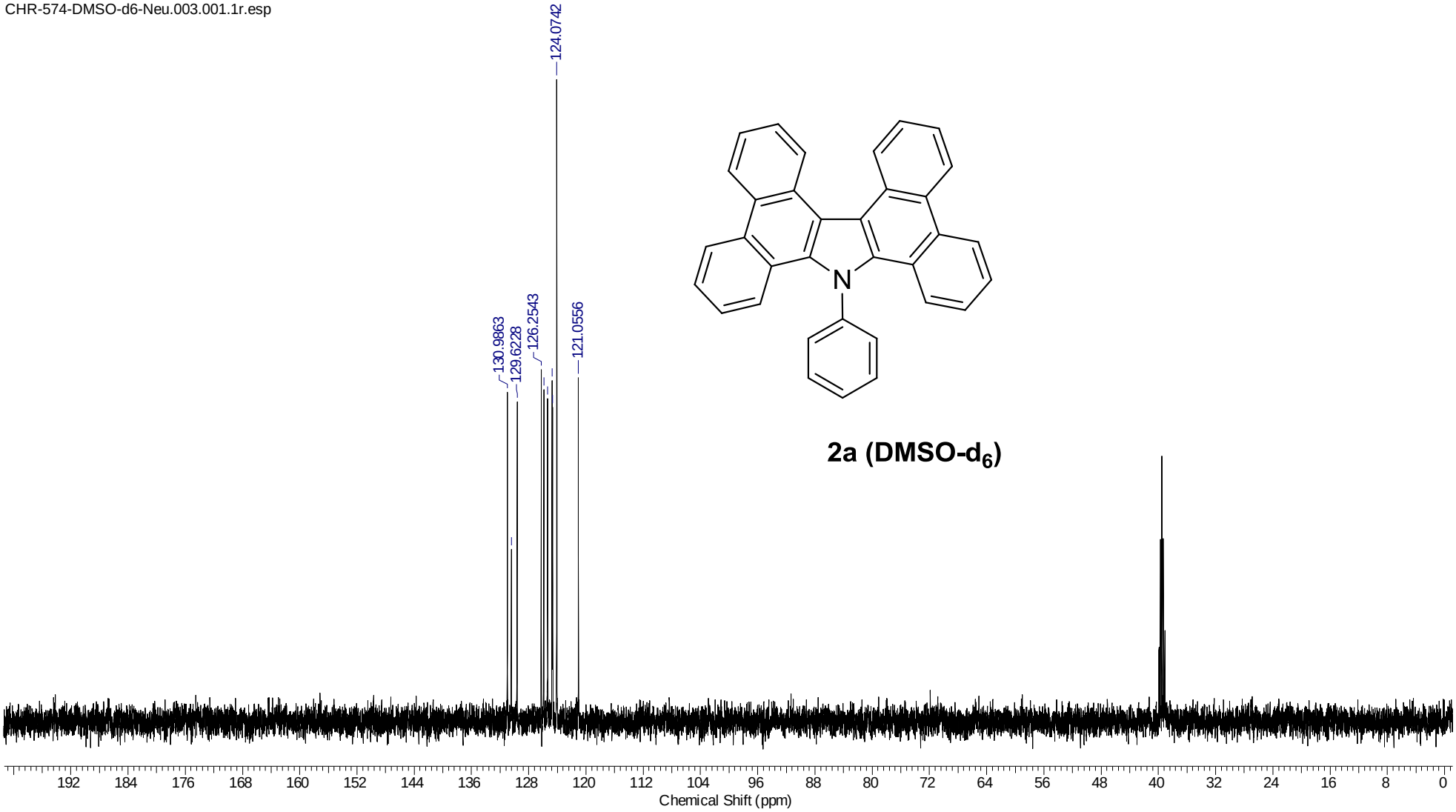
2a (DMSO-d_6)

^{13}C Zoom:

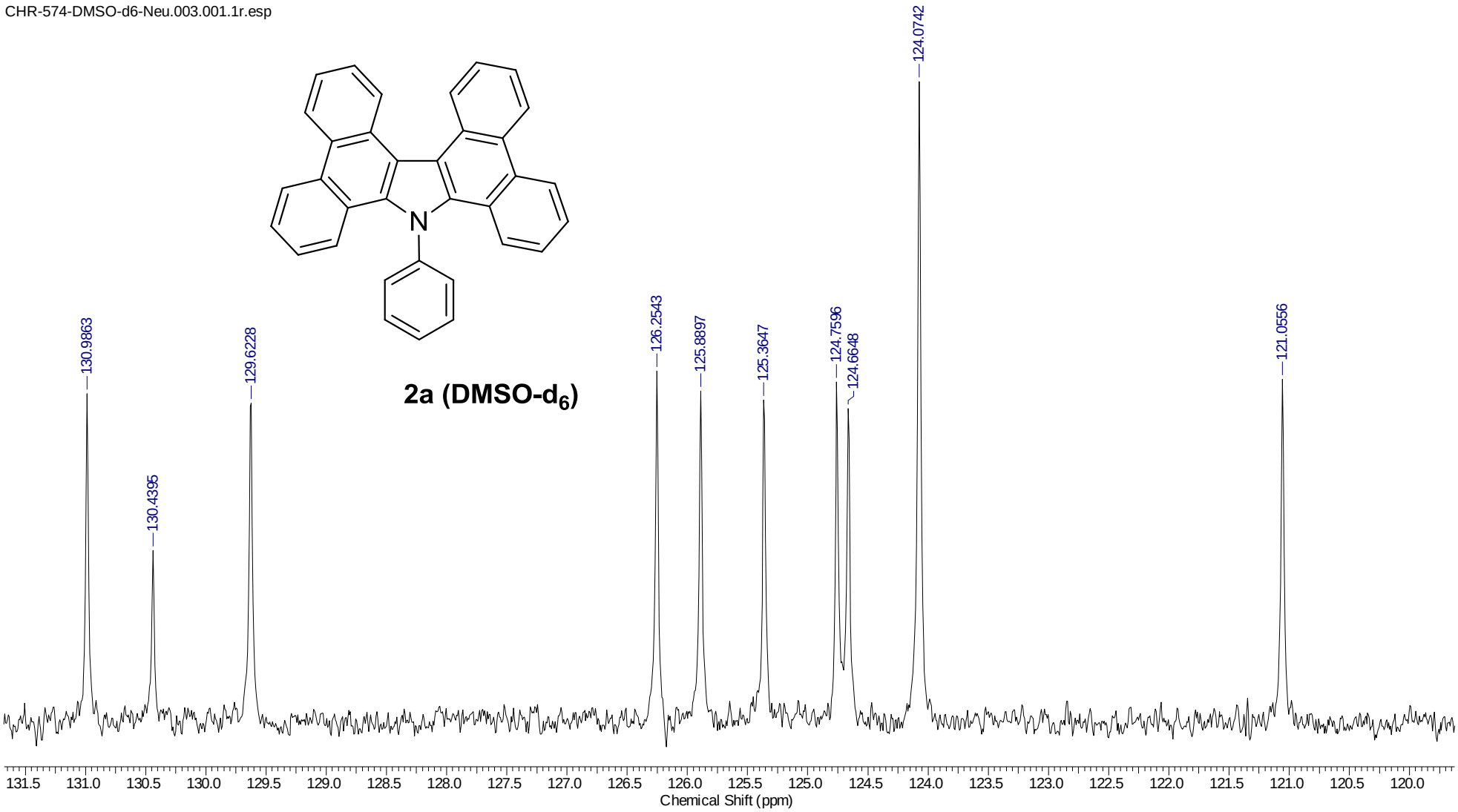
CHR-574-DMSO-d6-Neu.002.001.1r.esp



Dept:

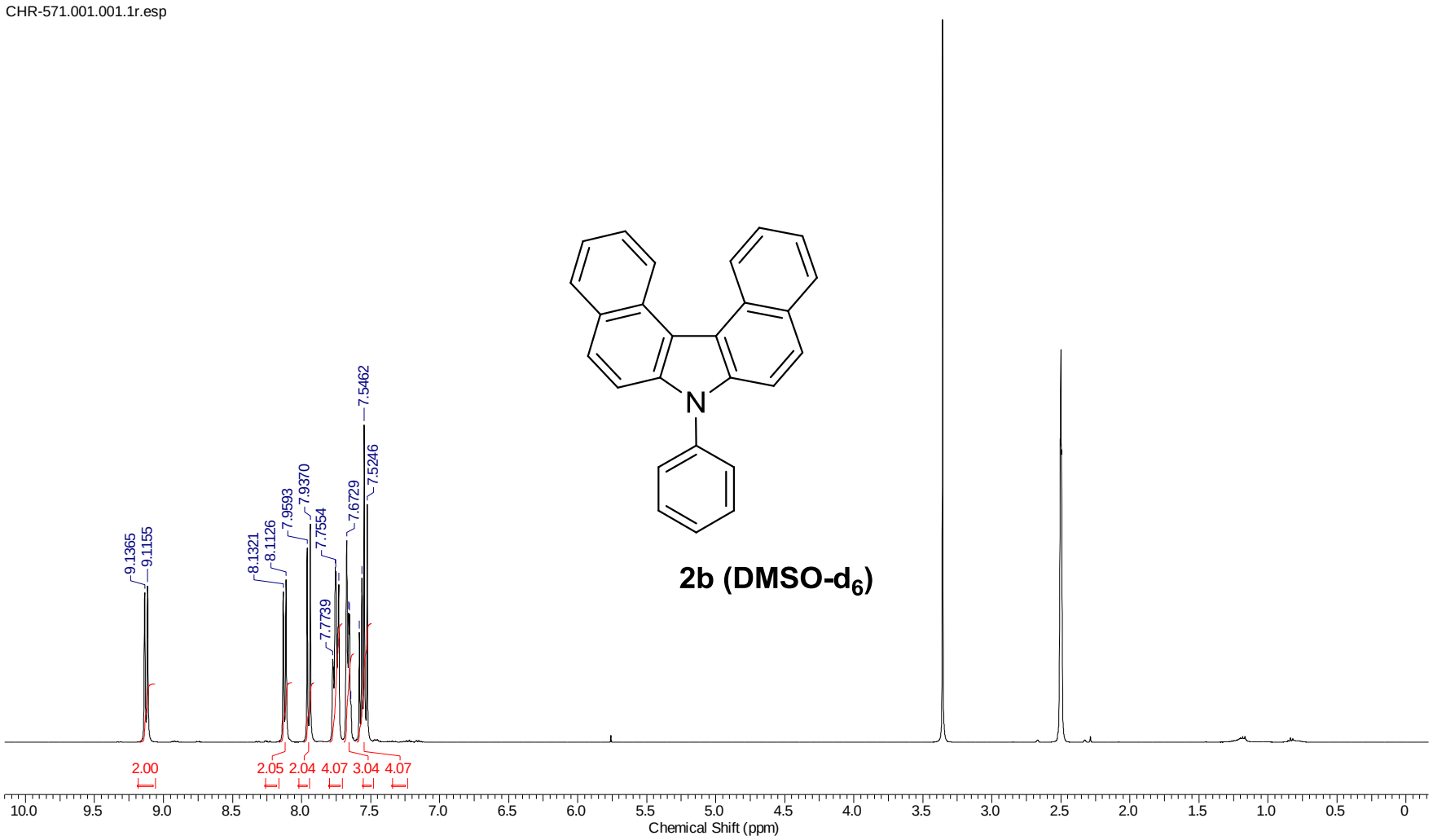

CHR-574-DMSO-d6-Neu.003.001.1r.esp
124.0742
130.9863
129.6228
126.2543
121.0556
N
2a (DMSO-d6)
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

Dept Zoom:


CHR-574-DMSO-d6-Neu.003.001.1r.esp
N
2a (DMSO-d6)
130.9863
130.4395
129.6228
126.2543
125.8897
125.3647
124.7596
124.6648
124.0742
121.0556
131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 123.5 123.0 122.5 122.0 121.5 121.0 120.5 120.0
Chemical Shift (ppm)

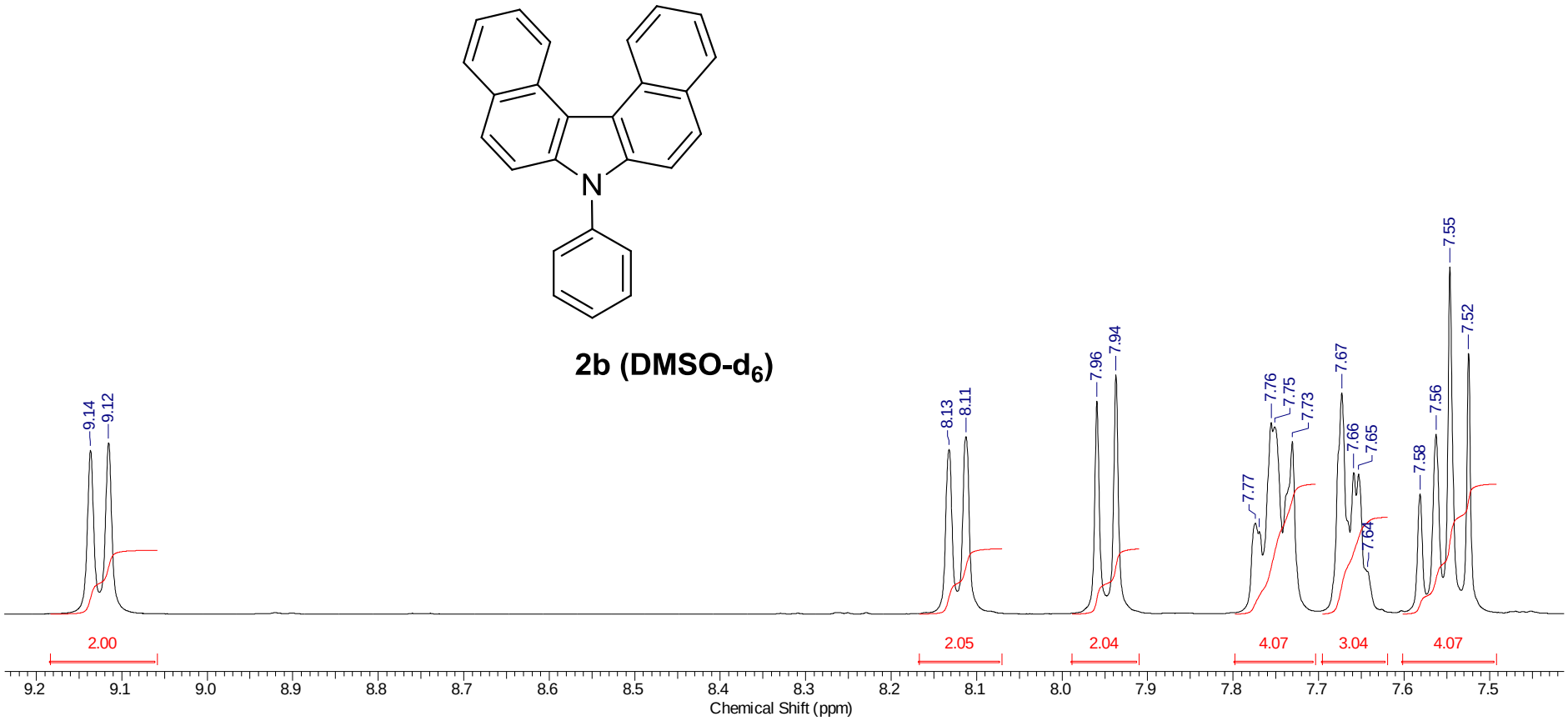
^{1}H:

^{1}H:


CHR-571.001.001.1r.esp
9.1365
9.1155
8.1321
8.1126
7.9593
7.9370
7.7554
7.7739
7.6729
7.5462
7.5246
2.00
2.05
2.04
4.07
3.04
4.07
N
2b (DMSO-d6)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

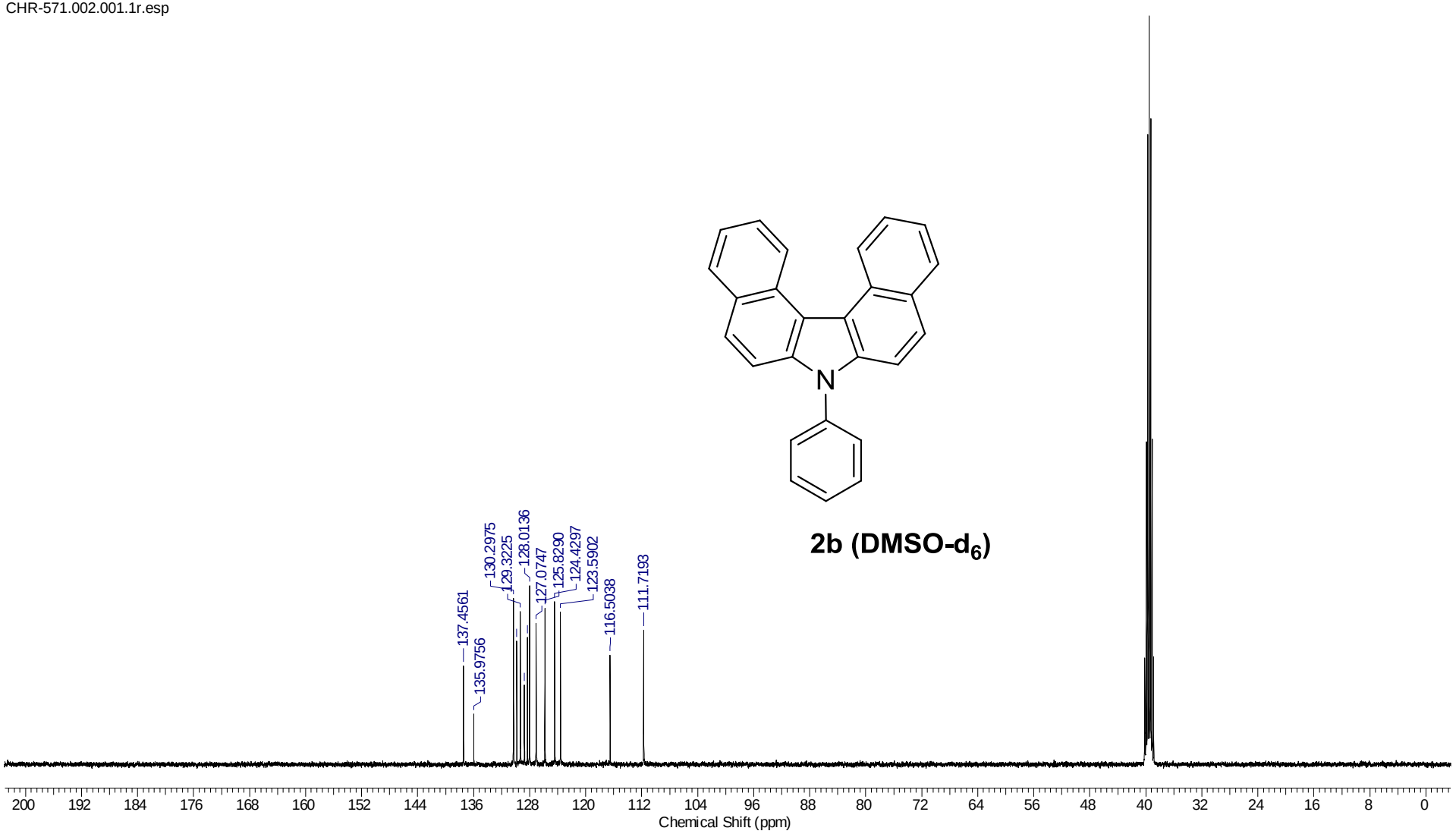
^{1}H Zoom:

CHR-571.001.001.1r.esp



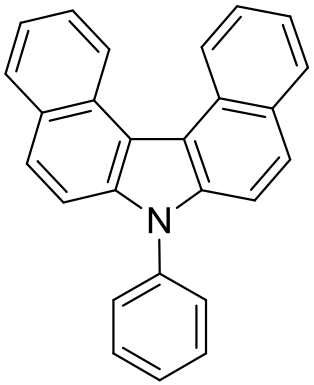
^{13}C:

CHR-571.002.001.1r.esp

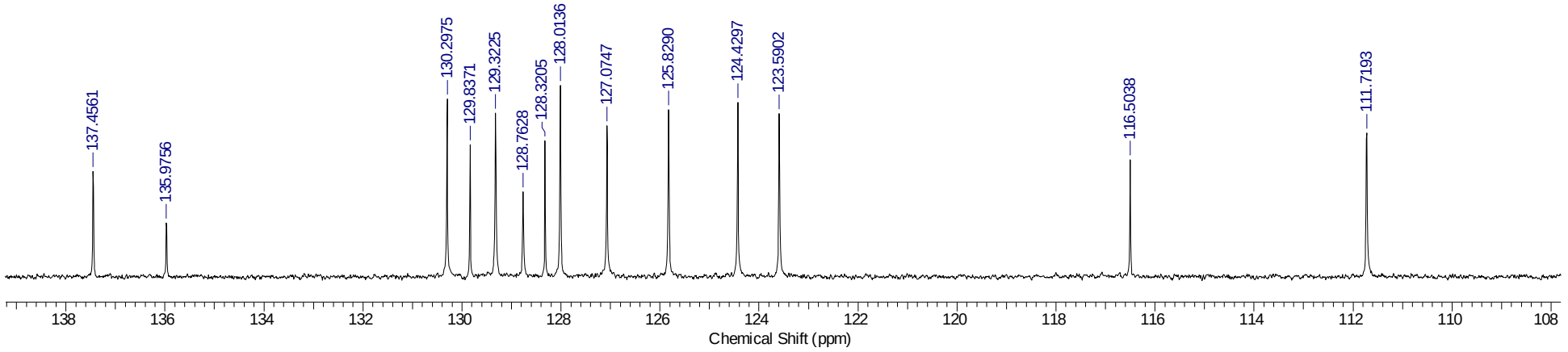


^{13}C Zoom:

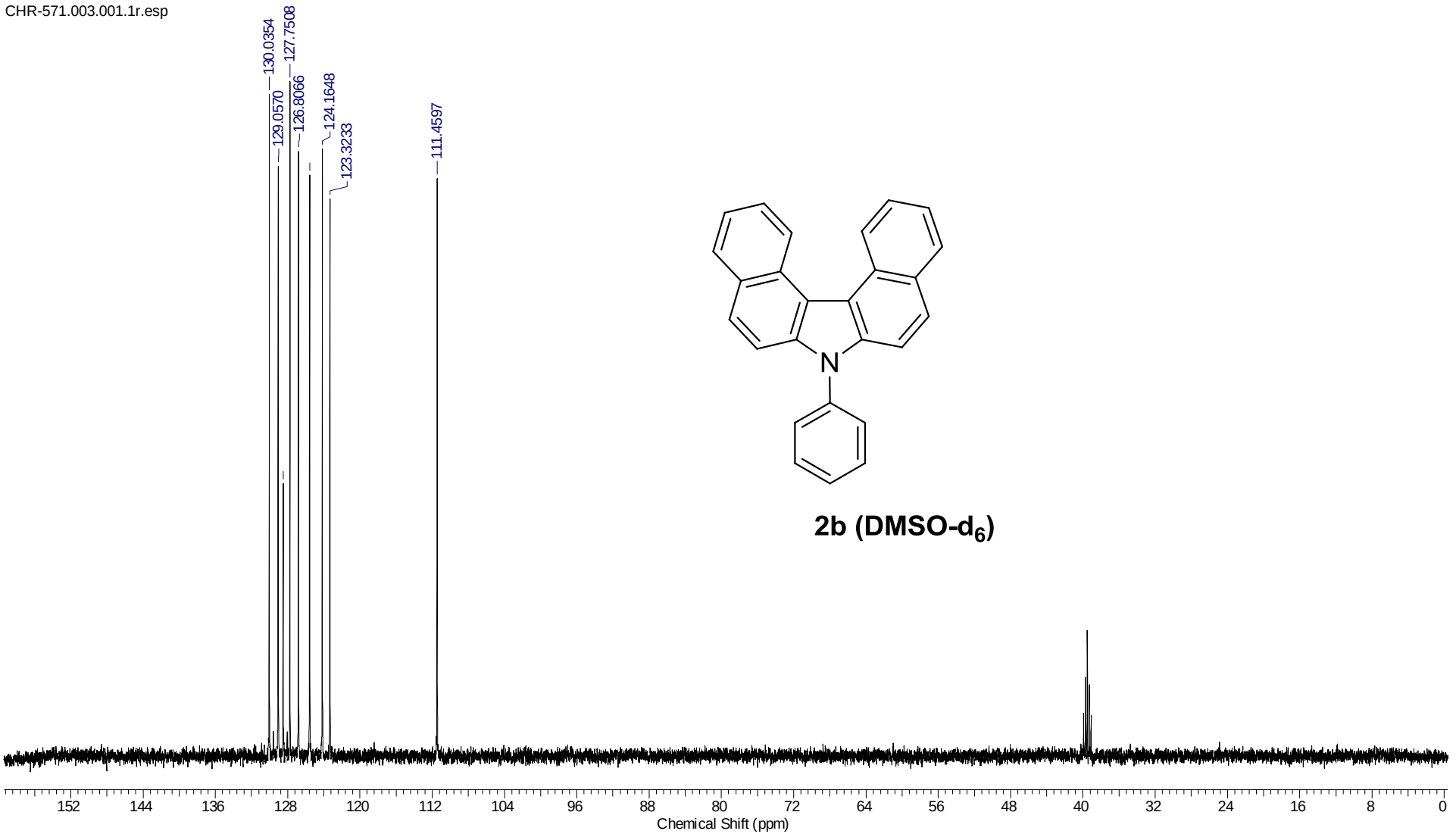
CHR-571.002.001.1r.esp



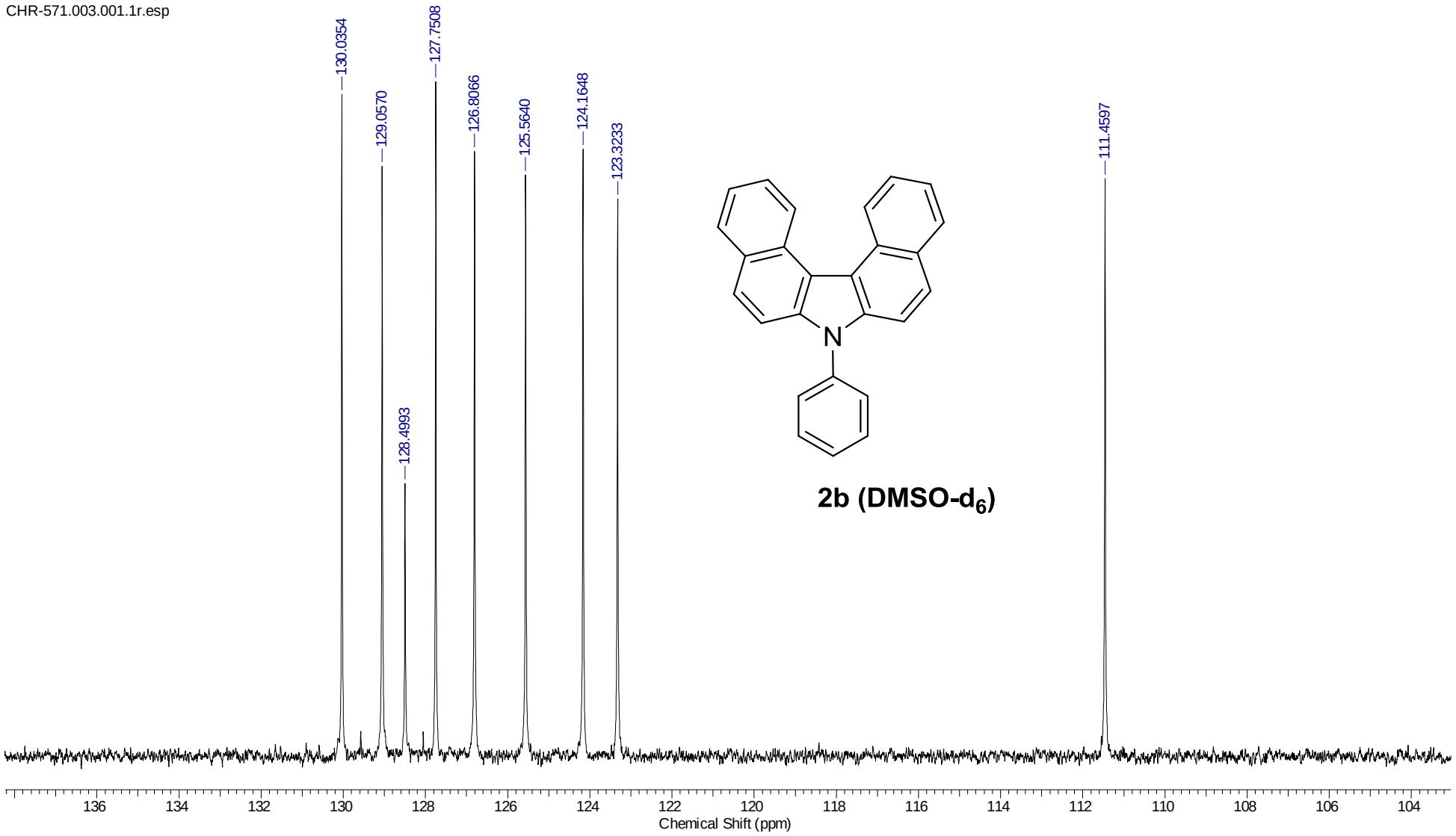
2b (DMSO-d_6)



Dept:


CHR-571.003.001.1r.esp
130.0354
127.7508
129.0570
126.8066
124.1648
123.3233
111.4597
N
2b (DMSO-d6)
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

Dept-Zoom:


CHR-571.003.001.1r.esp
130.0354
129.0570
128.4993
127.7508
126.8066
125.5640
124.1648
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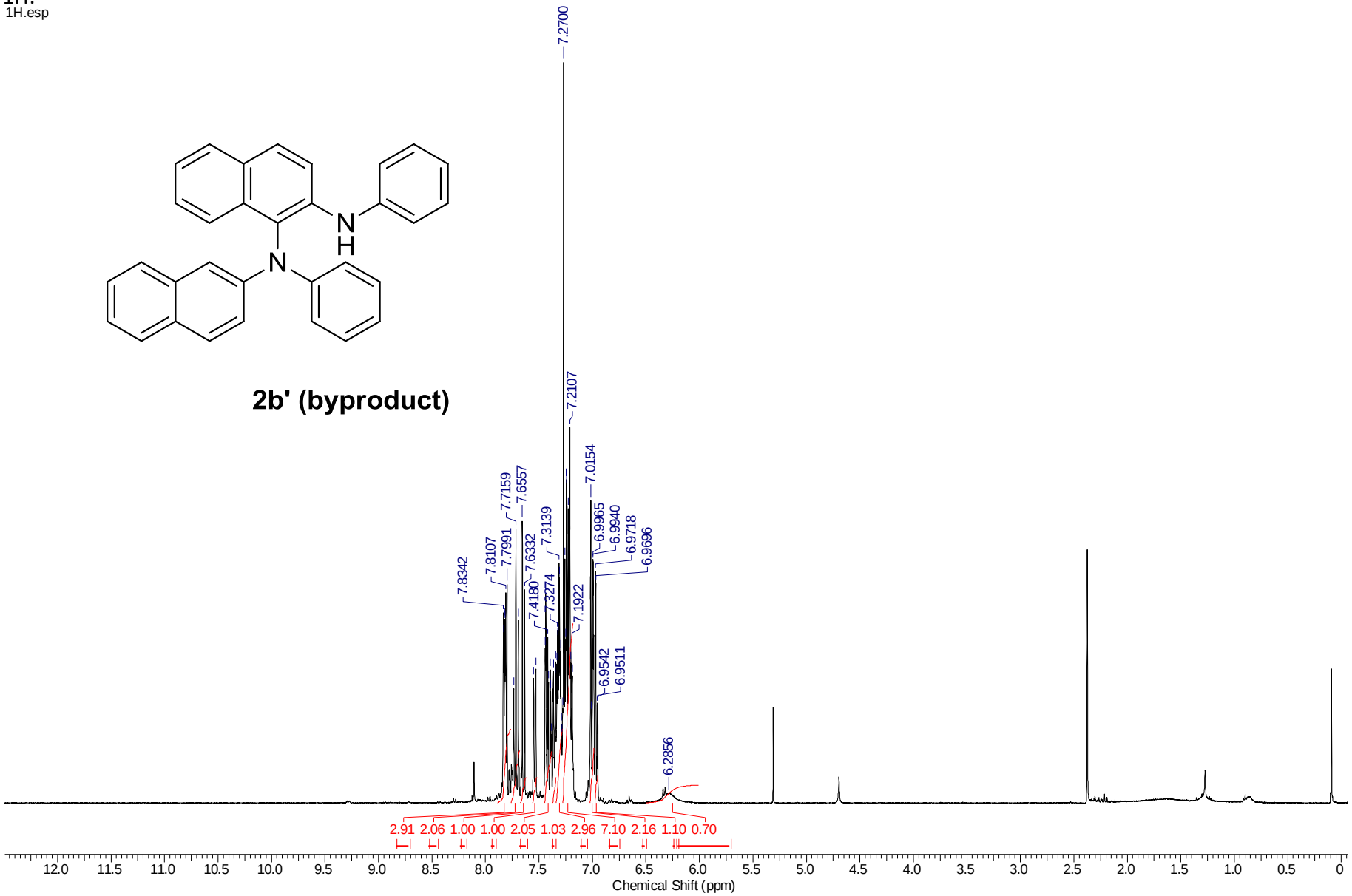
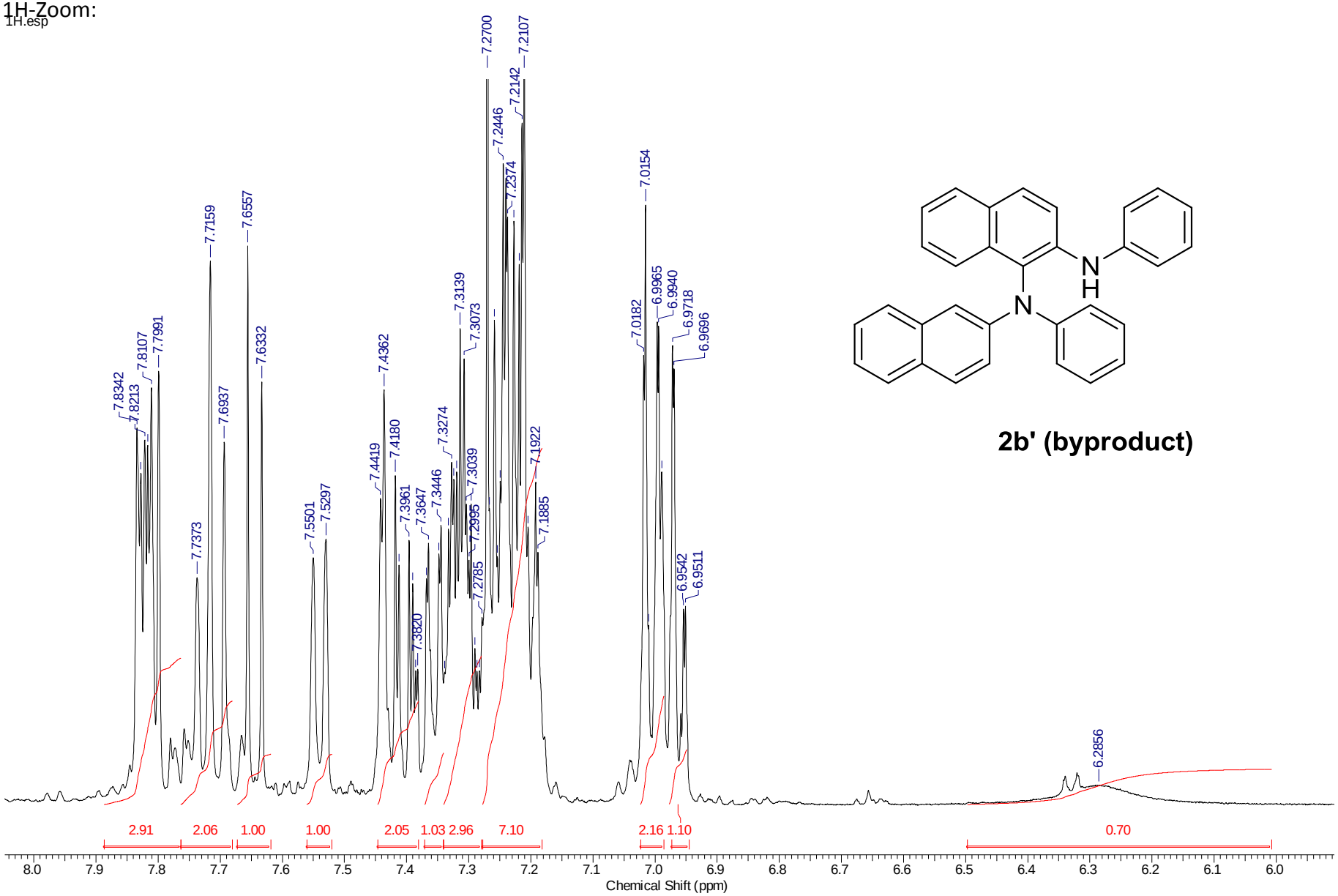
111.4597
N
2b (DMSO-d6)
136
134
132
130
128
126
124
122
120
118
116
114
112
110
108
106
104
Chemical Shift (ppm)

1H:

1H.esp

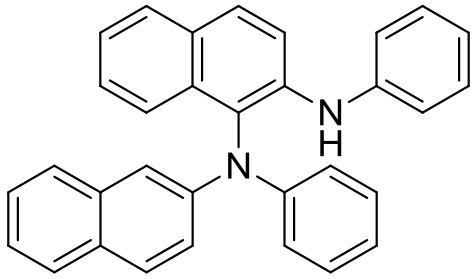

N
H
N
2b' (byproduct)
7.2700
7.2107
7.0154
7.7159
7.6557
7.8107
7.7991
7.6332
7.3139
6.9965
6.9940
6.9718
6.9696
7.8342
7.4180
7.3274
7.1922
6.9542
6.9511
6.2856
2.91 2.06 1.00 1.00 2.05 1.03 2.96 7.10 2.16 1.10 0.70
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

1H-Zoom:



2b' (byproduct)

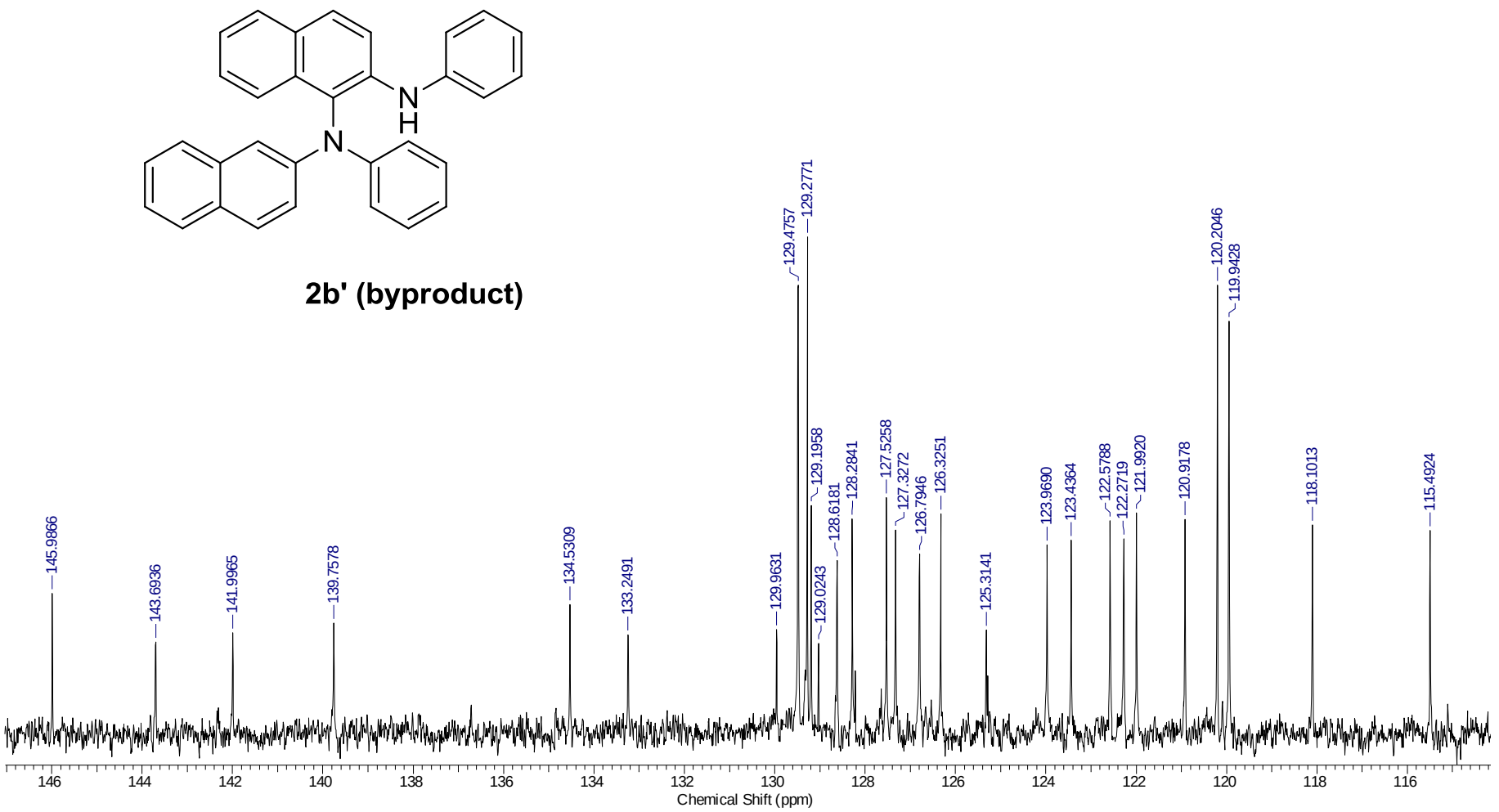
13C:
13C.esp



2b' (byproduct)

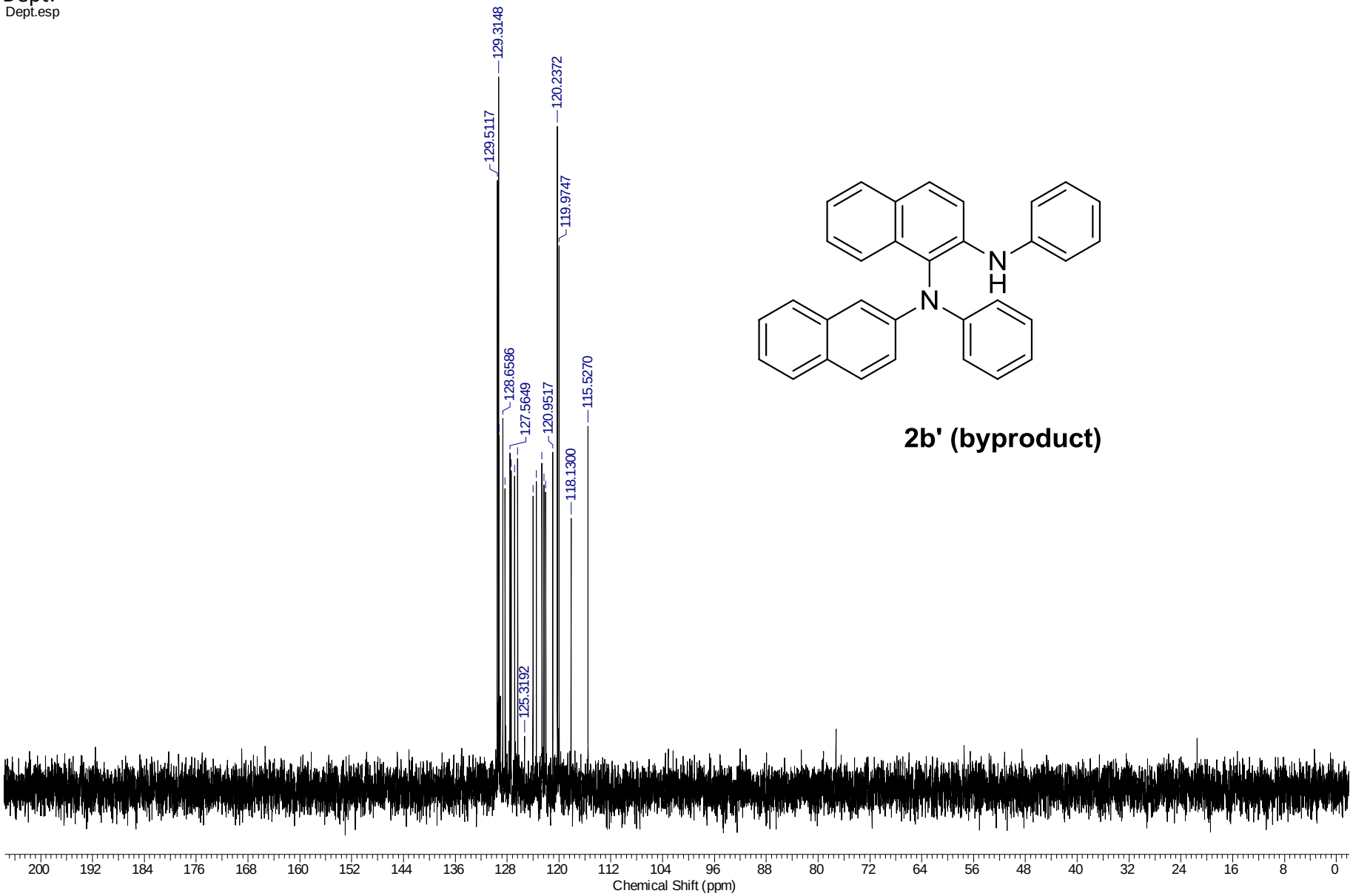
13C-Zoom:

13C.esp



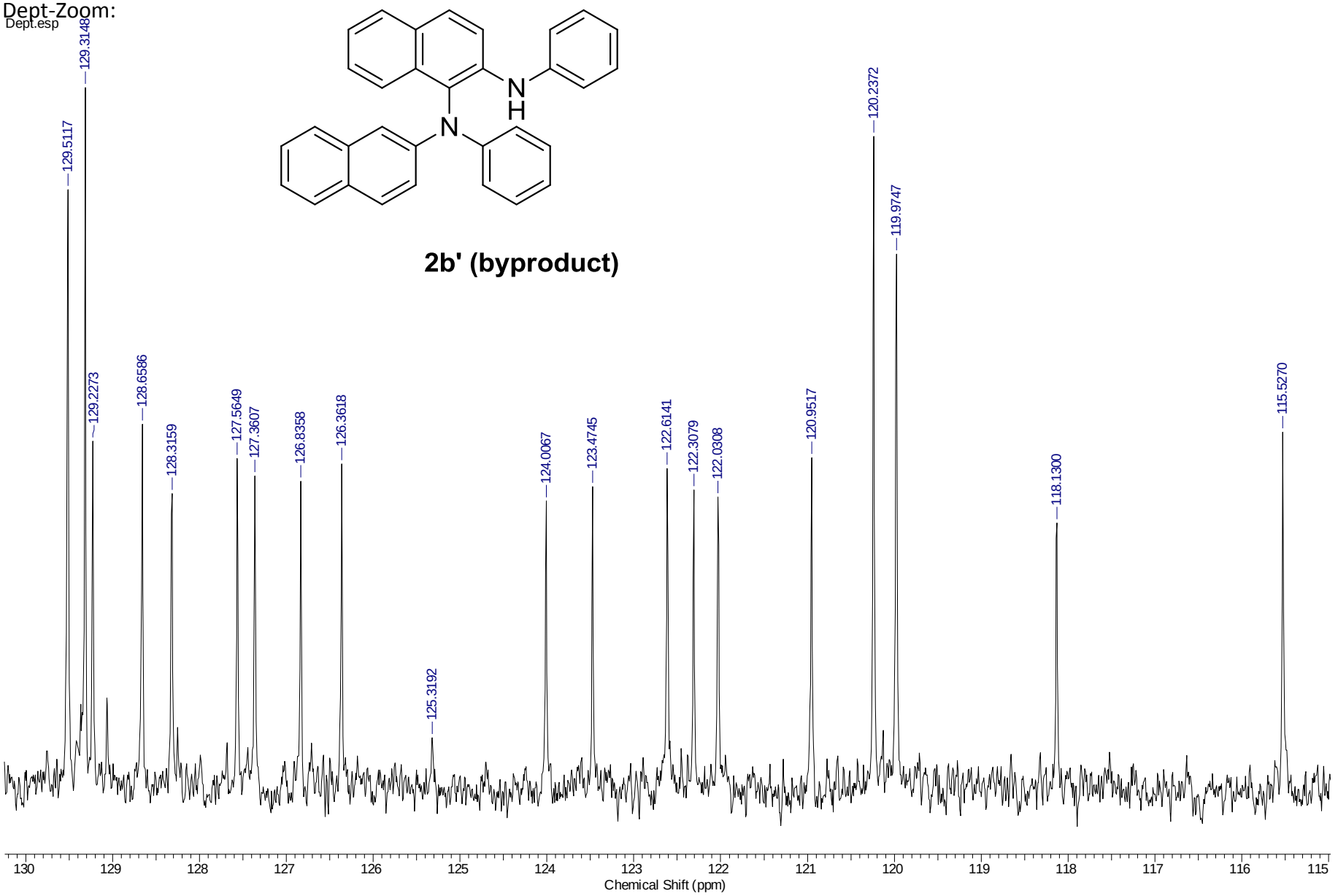
Dept:

Dept.esp

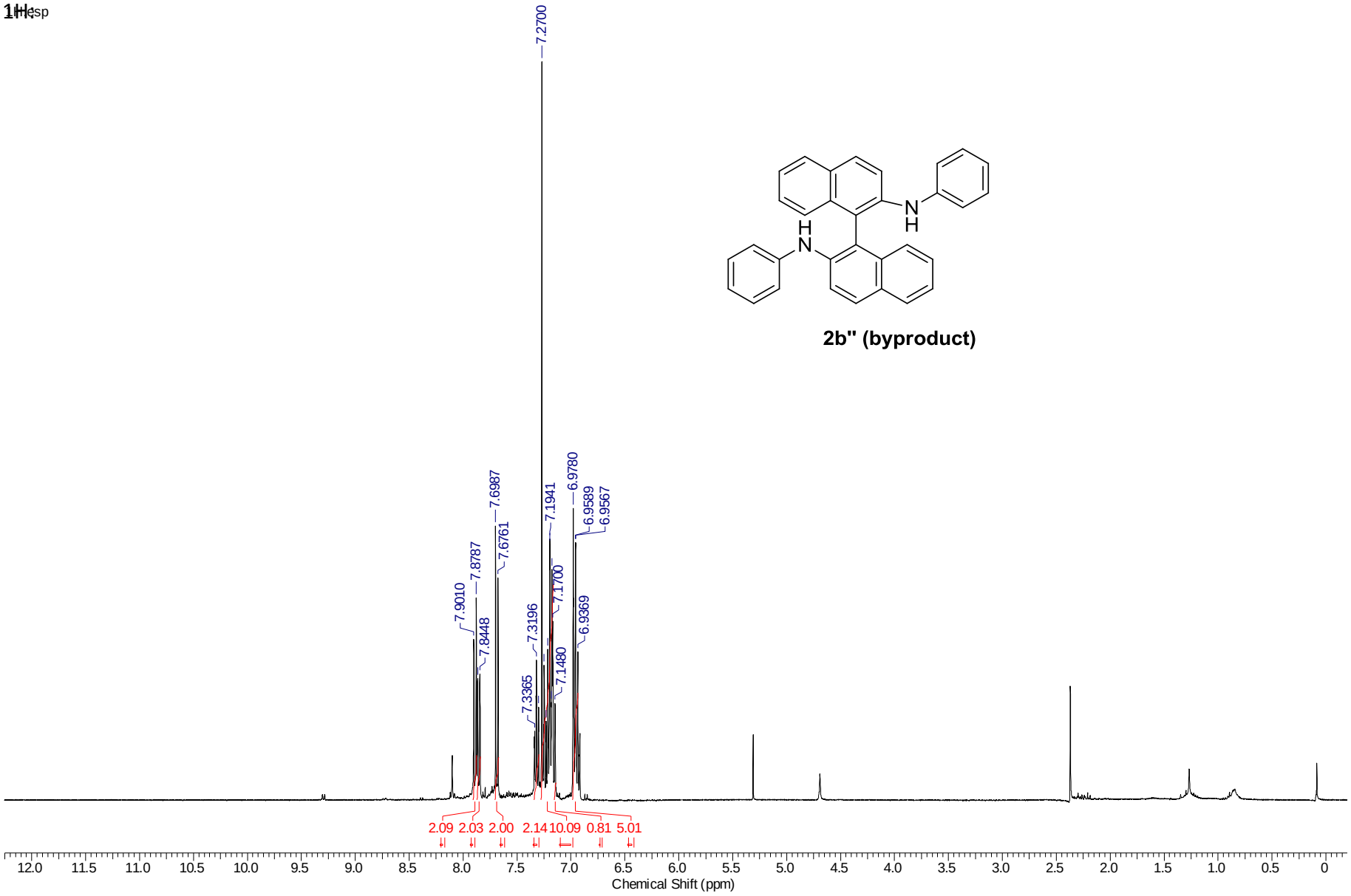


2b' (byproduct)

Dept-Zoom:



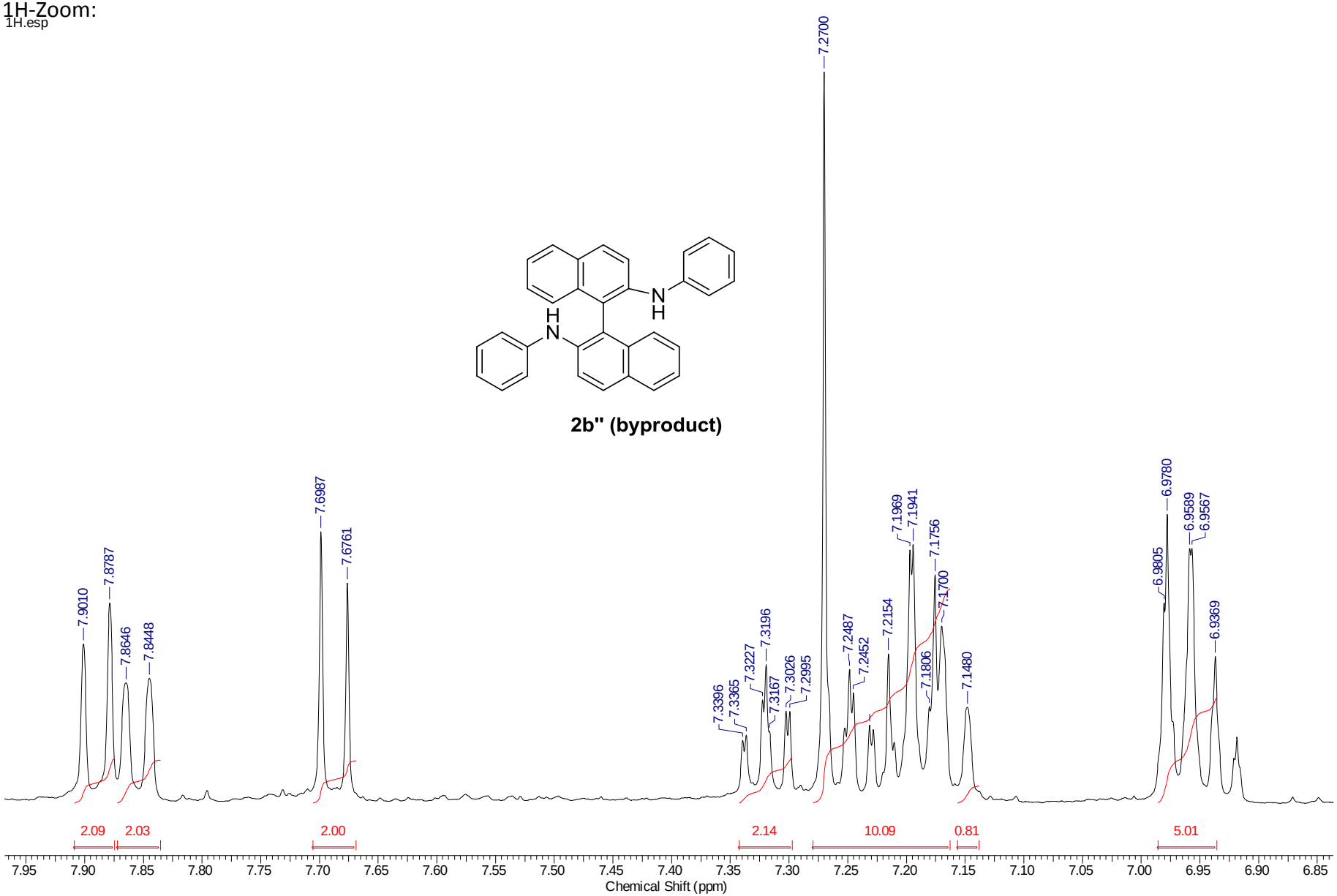
2b' (byproduct)



2b" (byproduct)

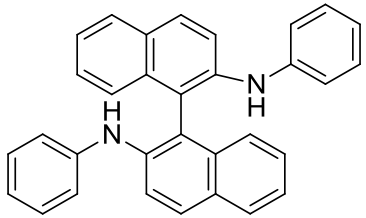
1H-Zoom:

1H.esp



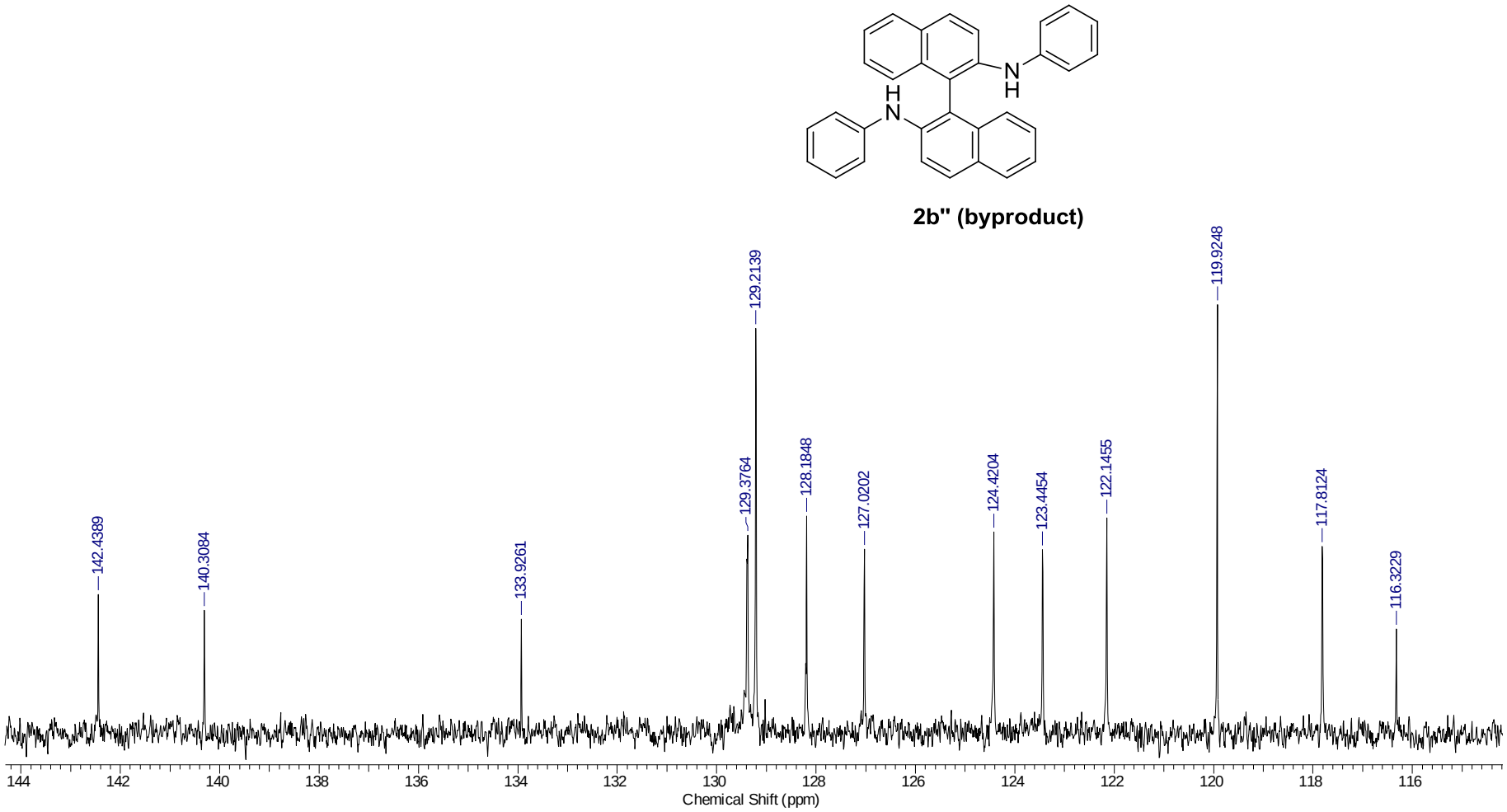
2b" (byproduct)

13C:
13C.esp

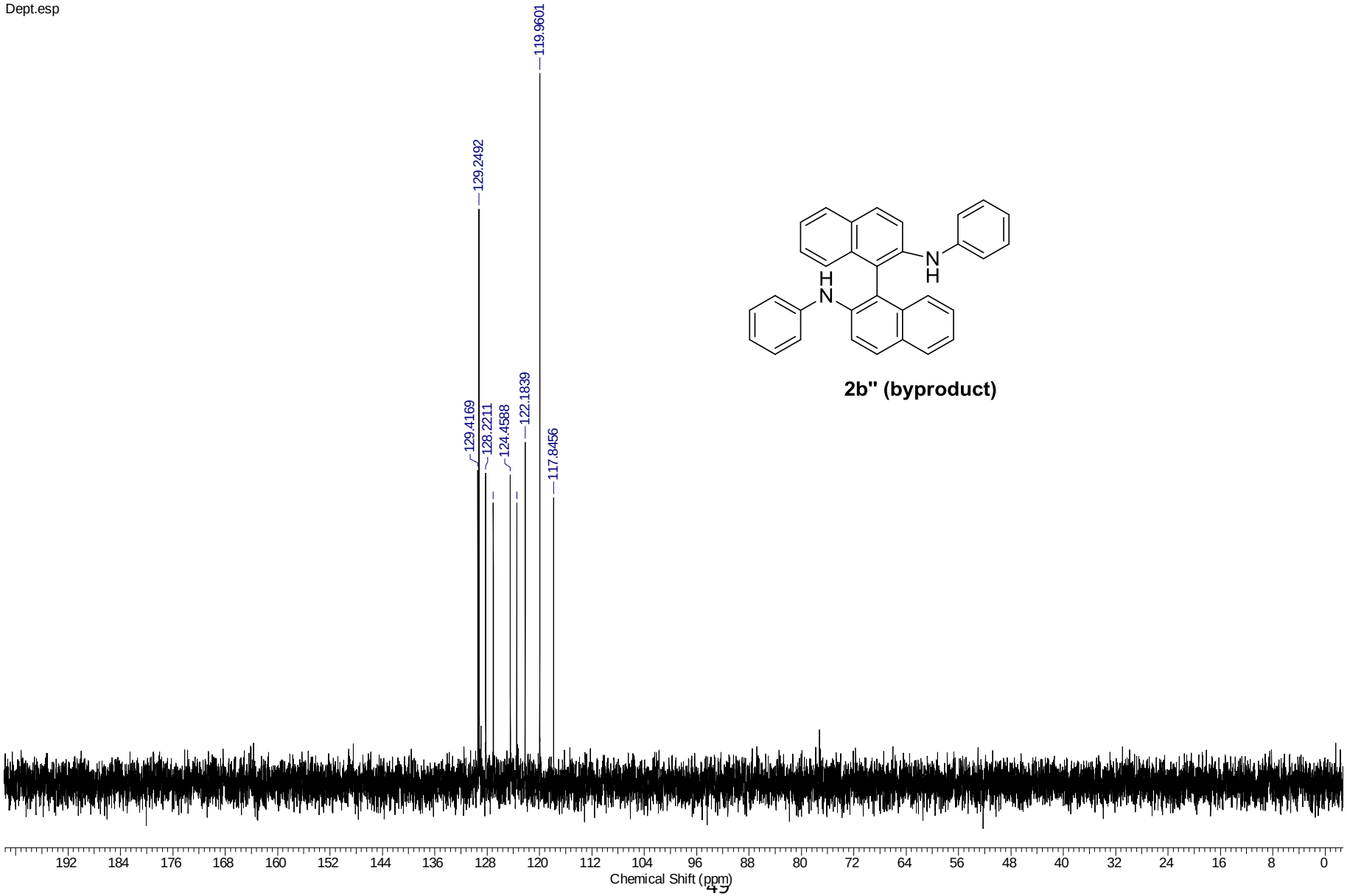


2b'' (byproduct)

13C-Zoom:
13C.esp



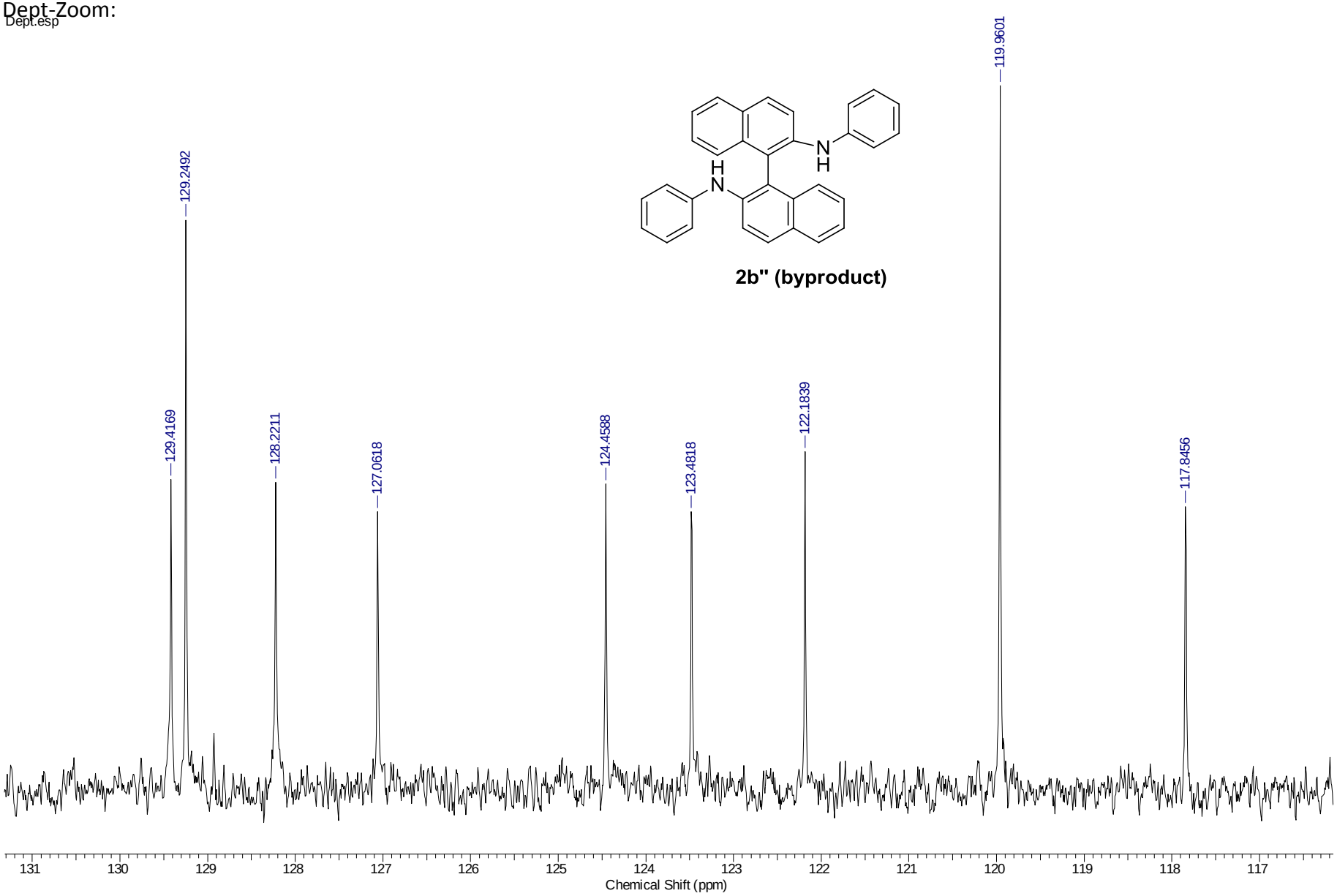
Dept:



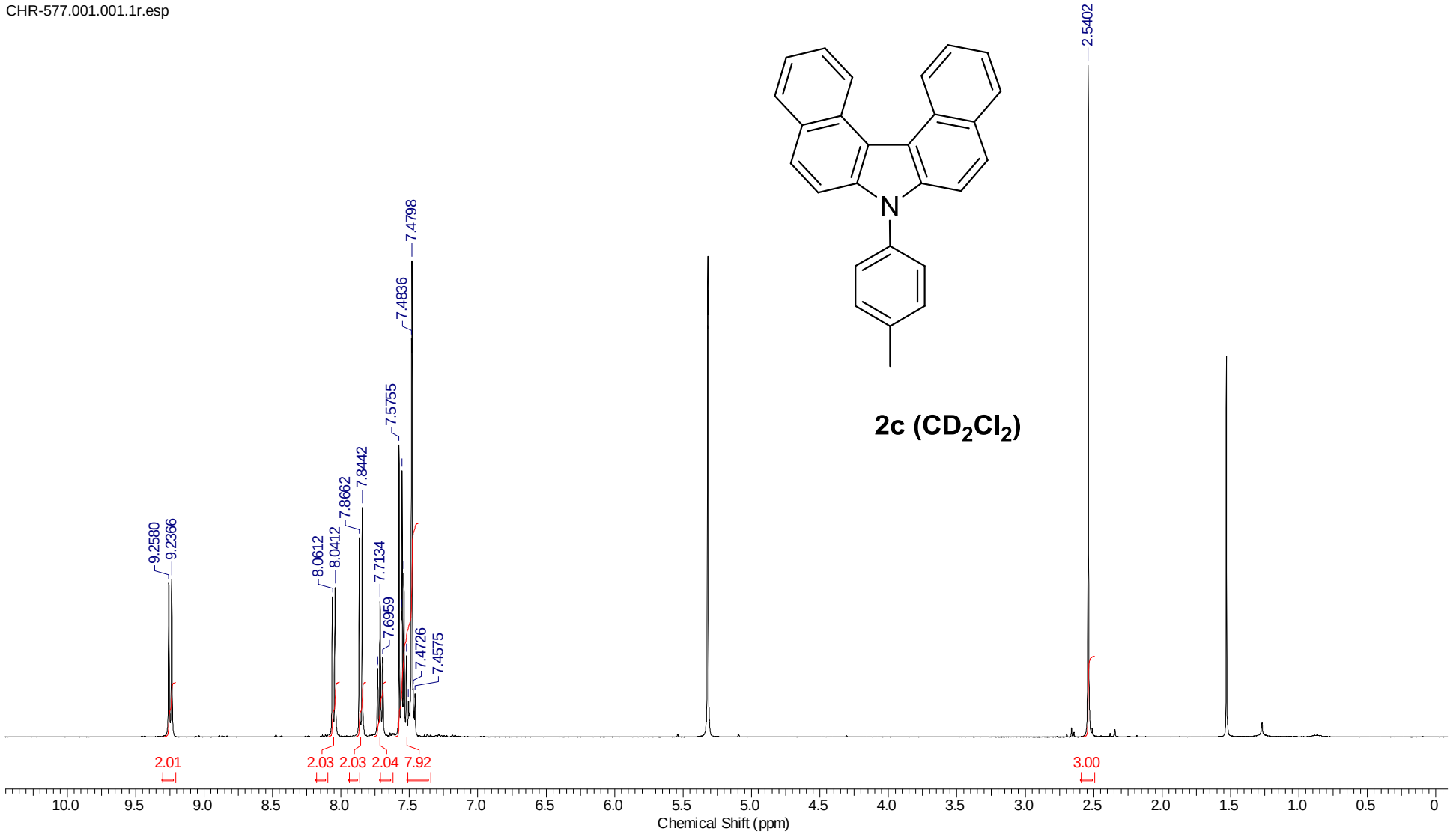
2b'' (byproduct)

Dept-Zoom:

Dept.esp

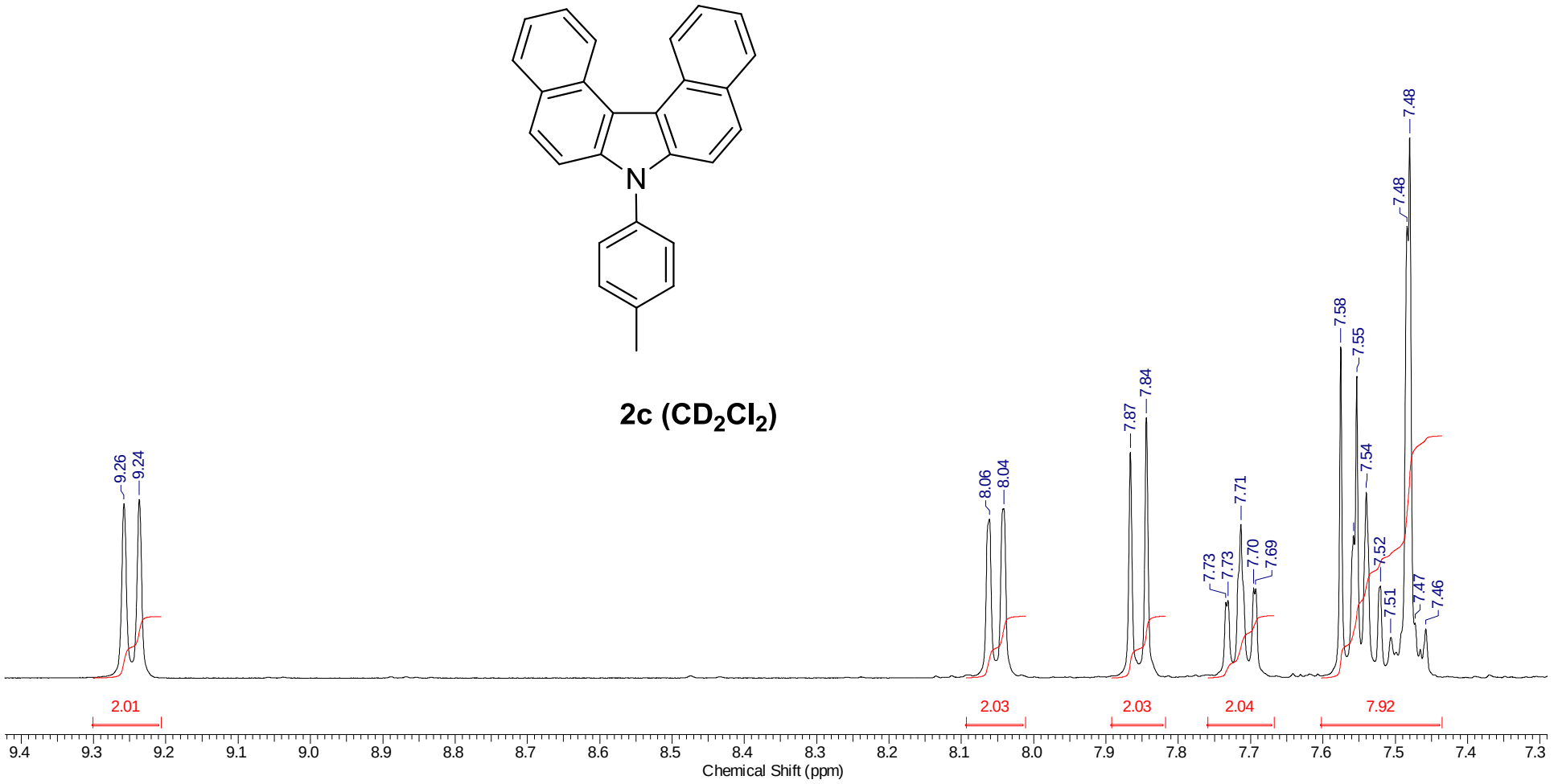


2b'' (byproduct)


CHR-577.001.001.1r.esp
2.5402
7.4798
7.4836
7.5755
7.8442
7.8662
8.0412
8.0612
7.7134
7.6959
7.4726
7.4575
9.2366
9.2580
2.01
2.03
2.03
2.04
7.92
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
N
2c (CD2Cl2)

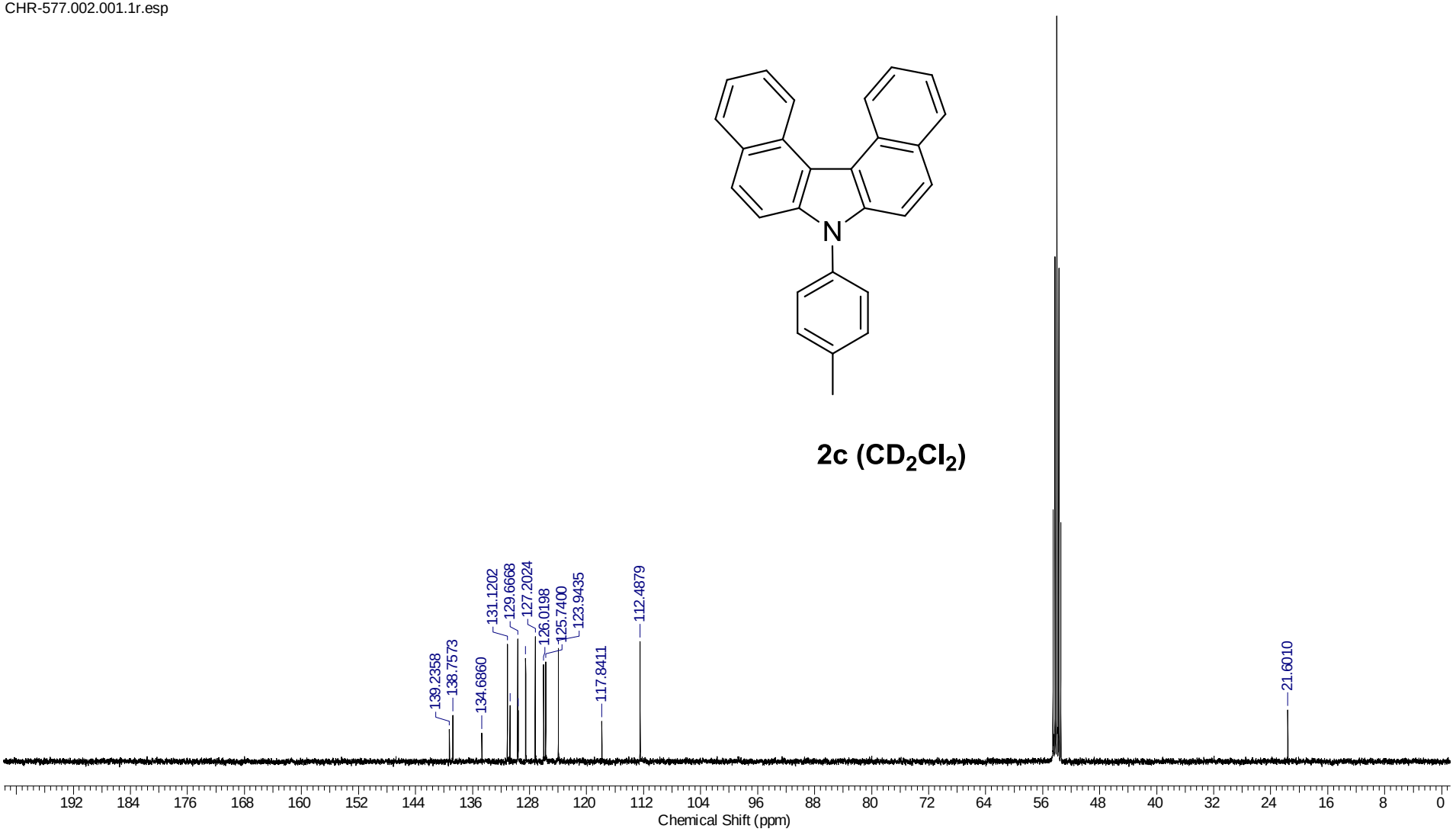
^{1}H Zoom:

CHR-577.001.001.1r.esp



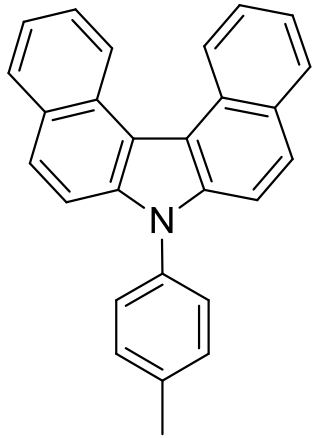
^{13}C:

CHR-577.002.001.1r.esp

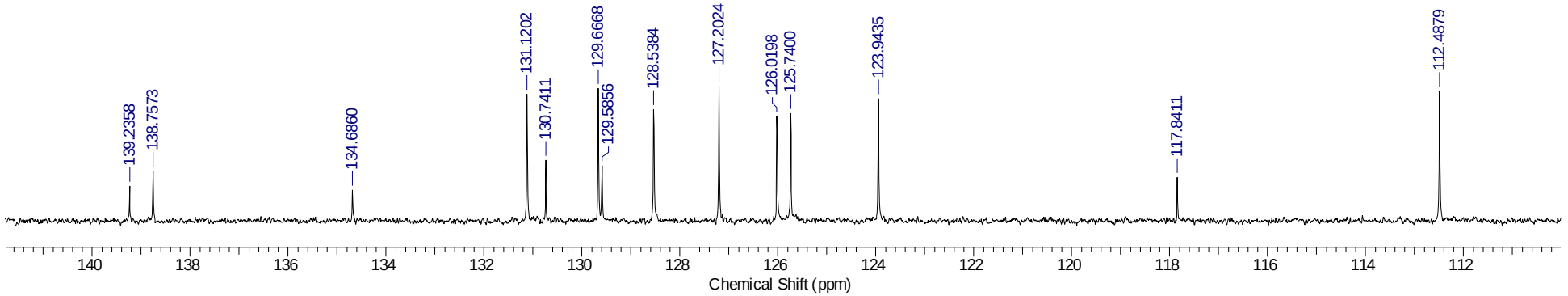


^{13}C Zoom:

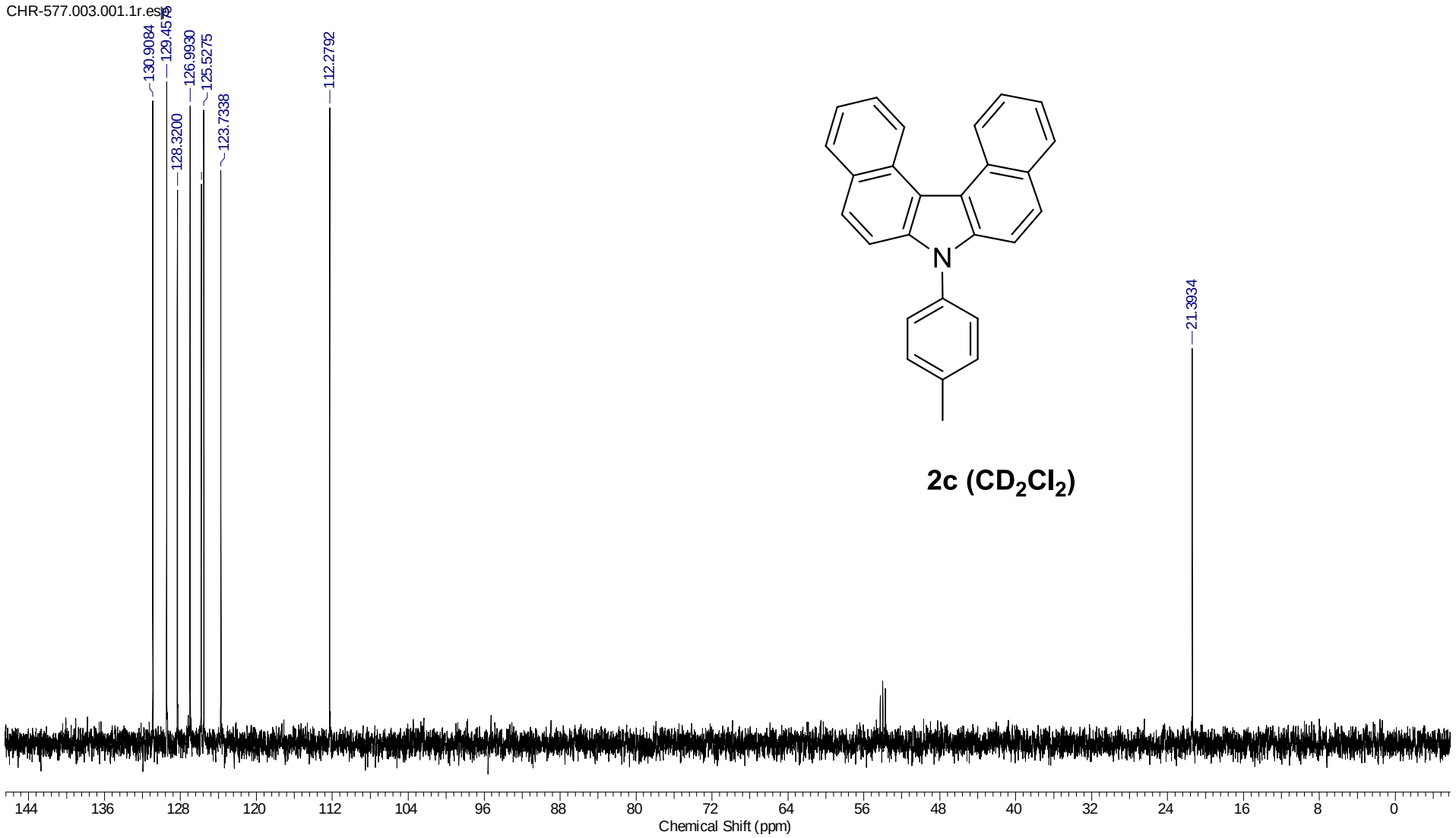
CHR-577.002.001.1r.esp



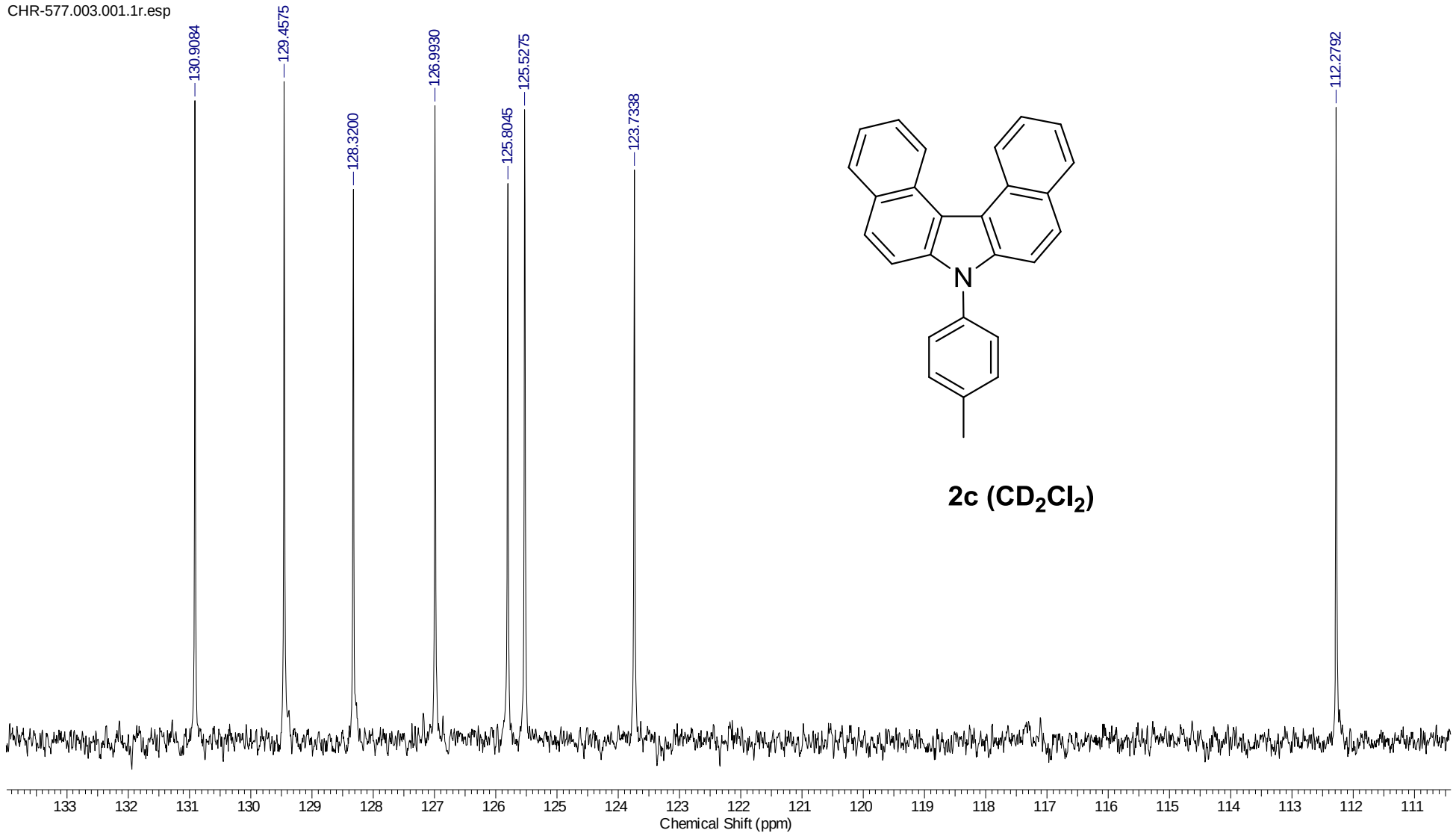
2c (CD_2Cl_2)



Dept:


CHR-577.003.001.1r.esp
130.9084
129.4574
128.3200
126.9930
125.5275
123.7338
112.2792
21.3934
N
2c (CD_2Cl_2)
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

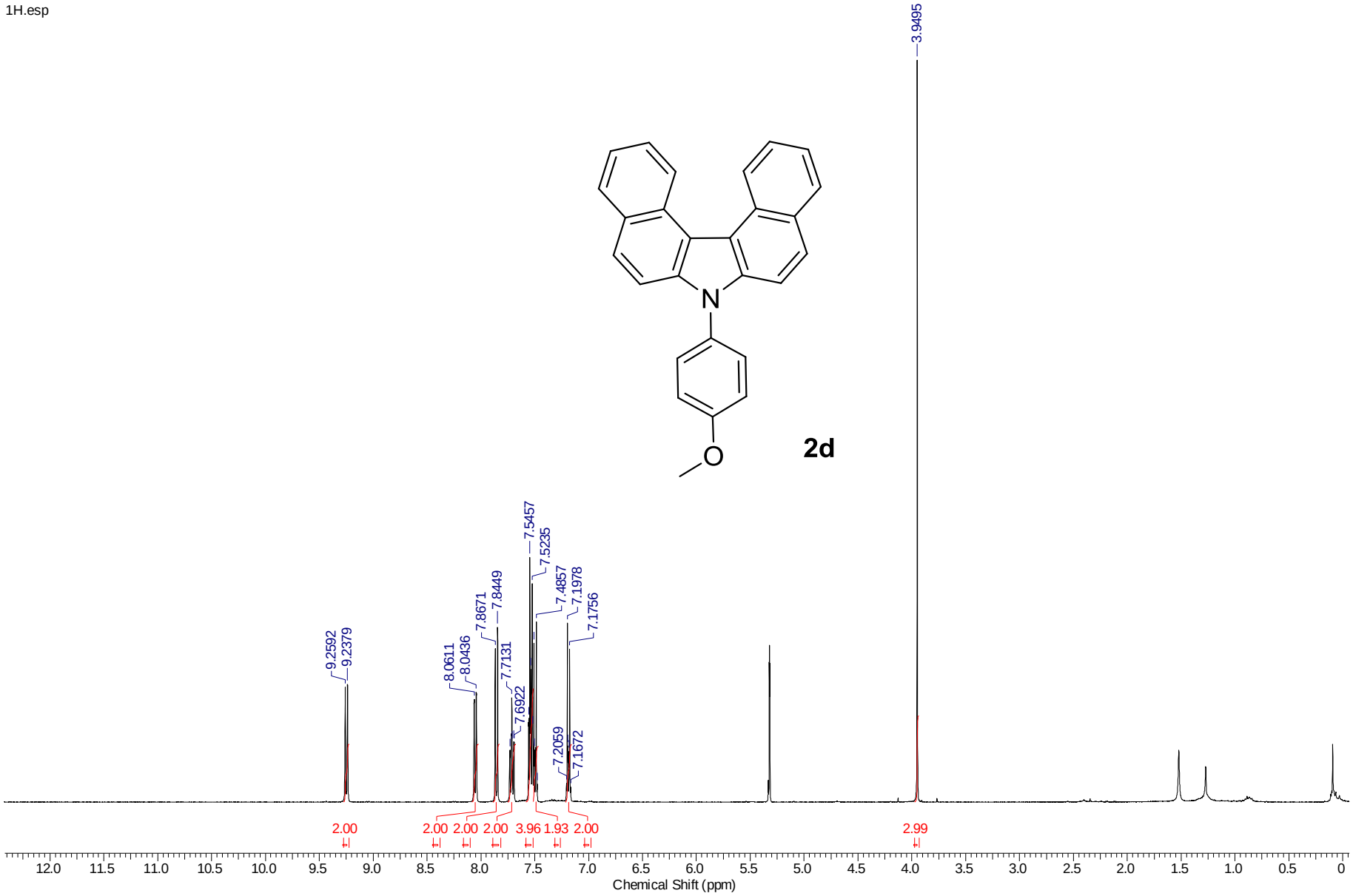
Dept Zoom:


CHR-577.003.001.1r.esp
130.9084
129.4575
128.3200
126.9930
125.8045
125.5275
123.7338
112.2792
N
2c (CD_2Cl_2)
133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111
Chemical Shift (ppm)

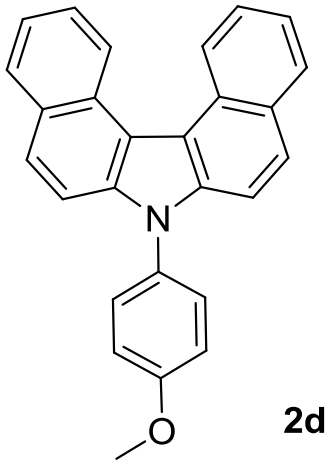
^1H:

1H:

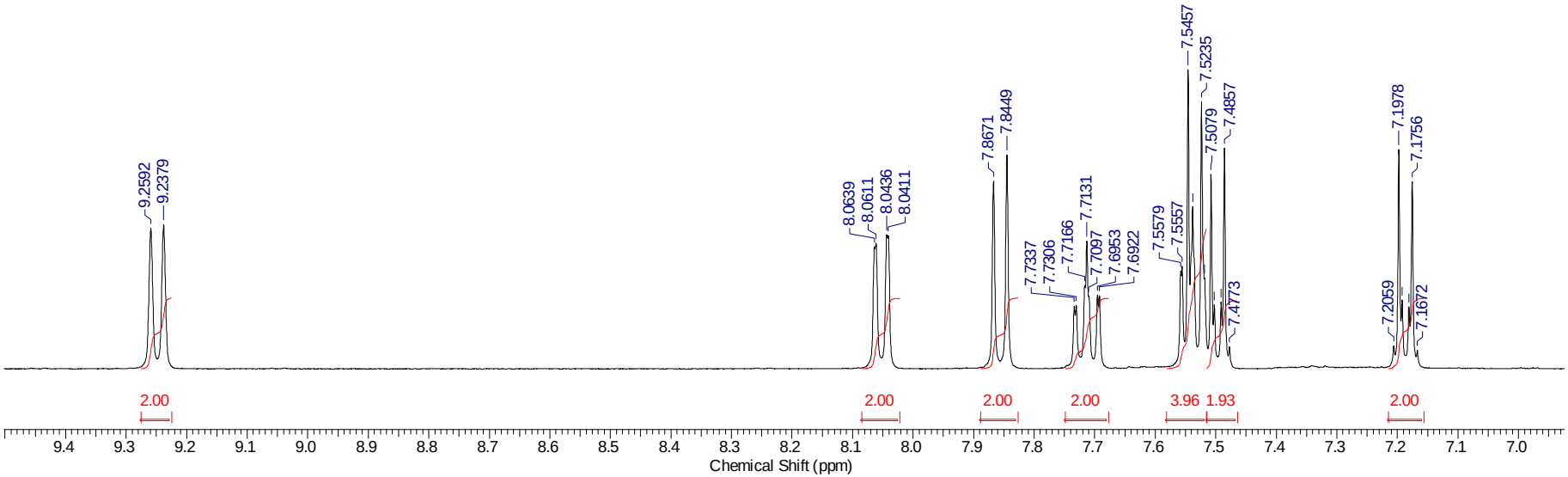
1H.esp


3.9495
N
O
2d
9.2592
9.2379
8.0611
8.0436
7.8671
7.8449
7.7131
7.6922
7.5457
7.5235
7.4857
7.1978
7.1756
7.2059
7.1672
2.00
2.00
2.00
2.00
3.96
1.93
2.00
2.99
Chemical Shift (ppm)

1H-Zoom:
1H.esp

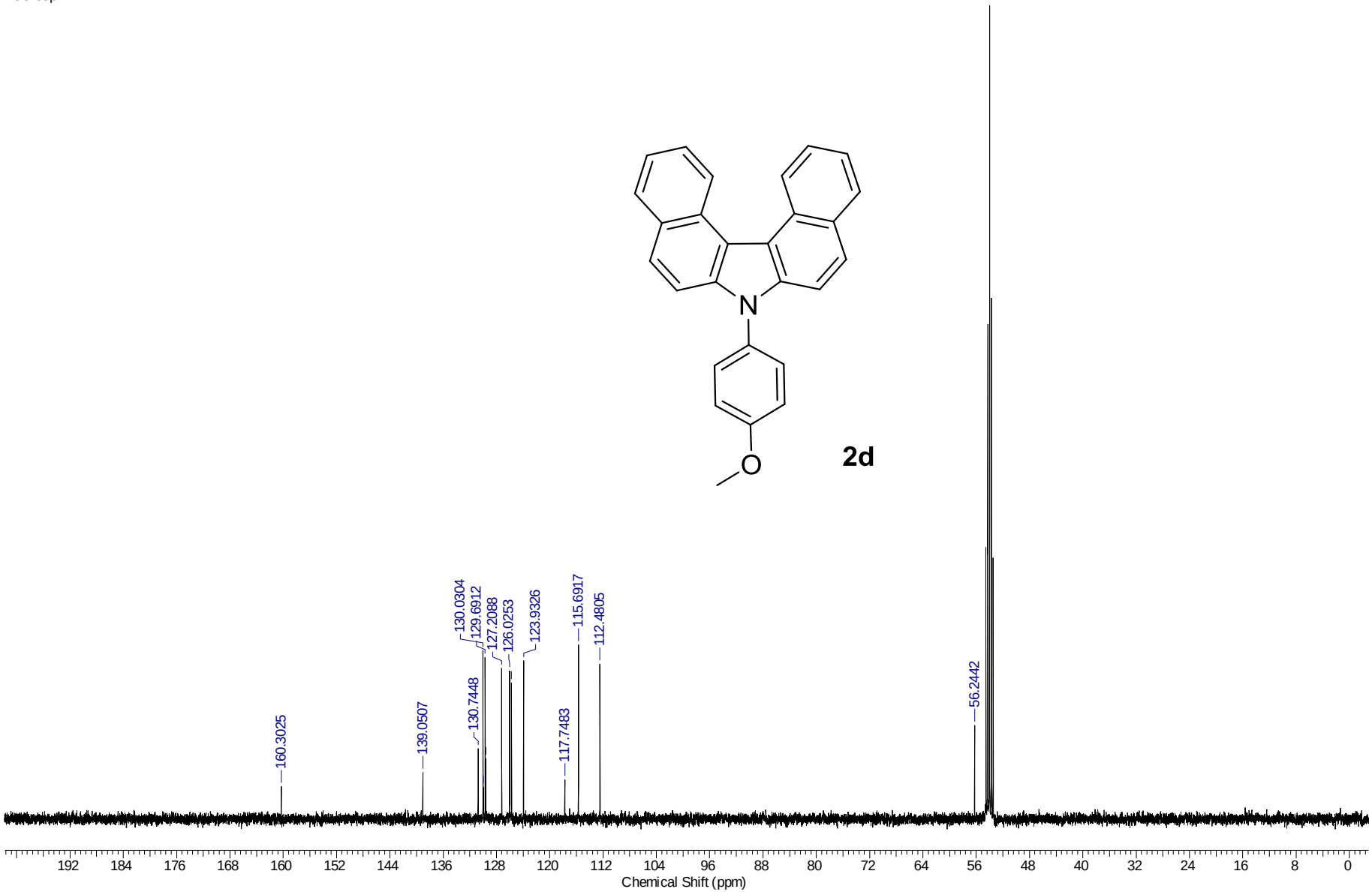


2d

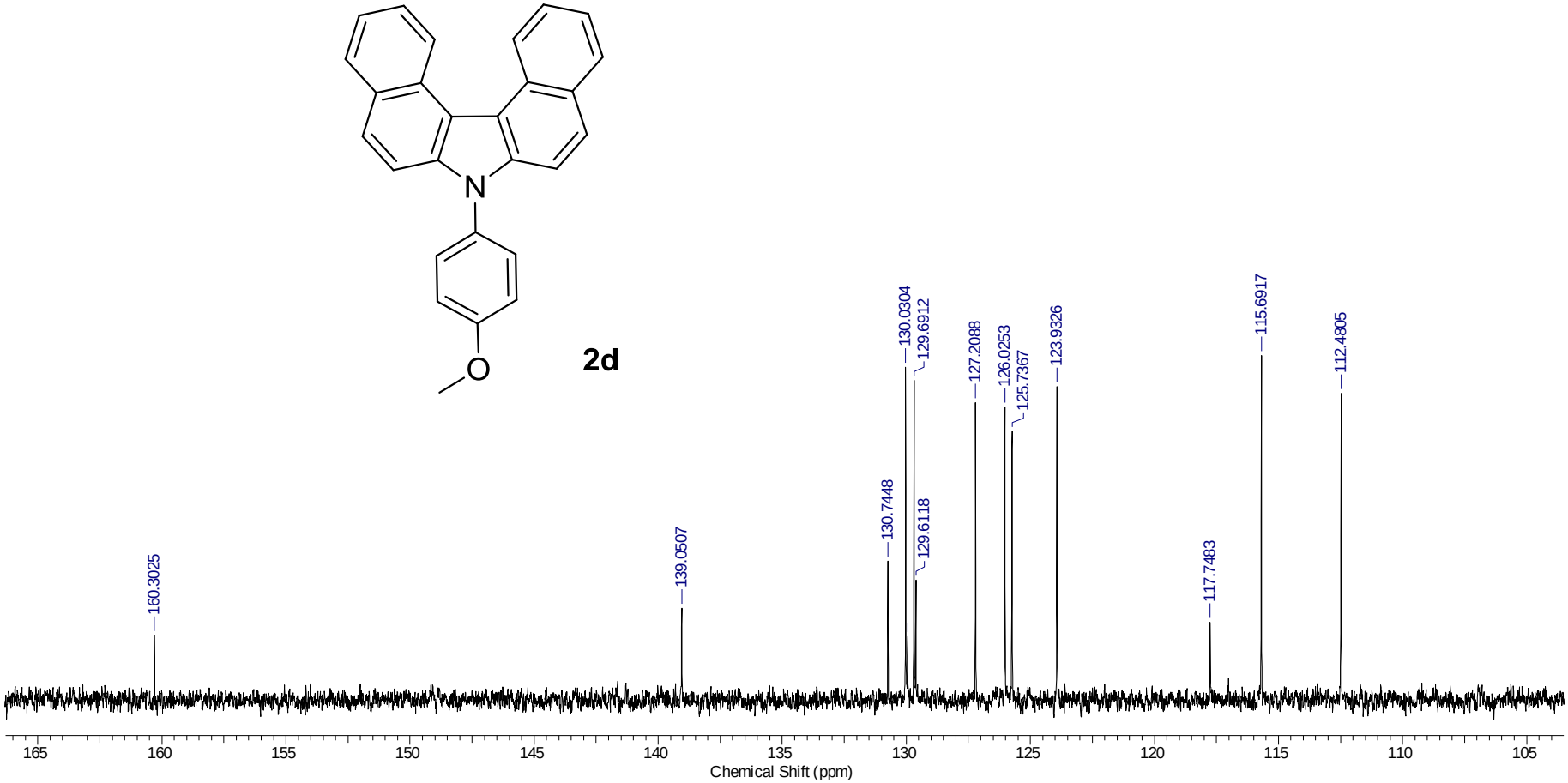


13C:

13C.esp

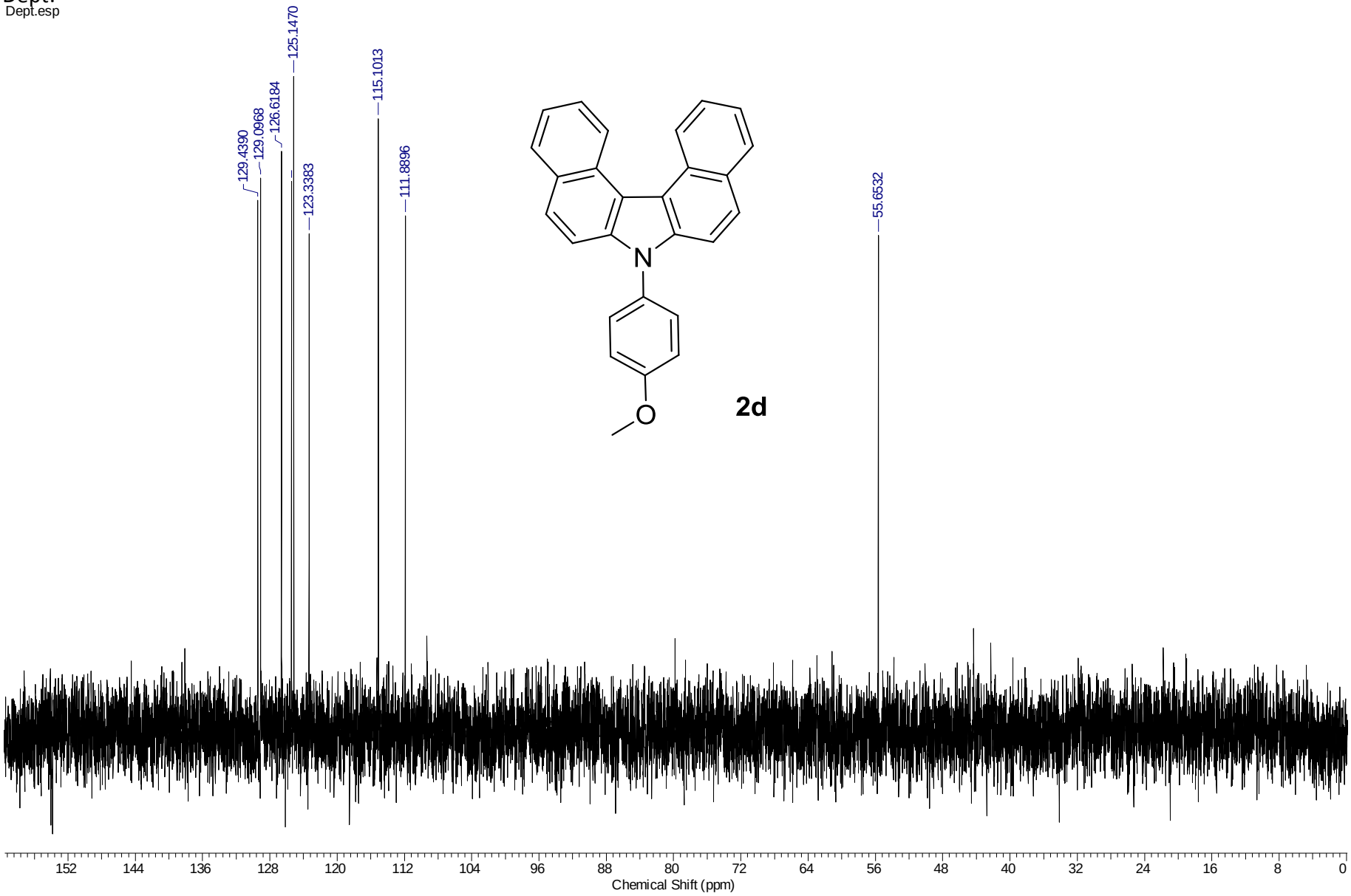

N
O
2d
160.3025
139.0507
130.7448
130.0304
129.6912
127.2088
126.0253
123.9326
117.7483
115.6917
112.4805
56.2442
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

13C-Zoom:
13C.esp

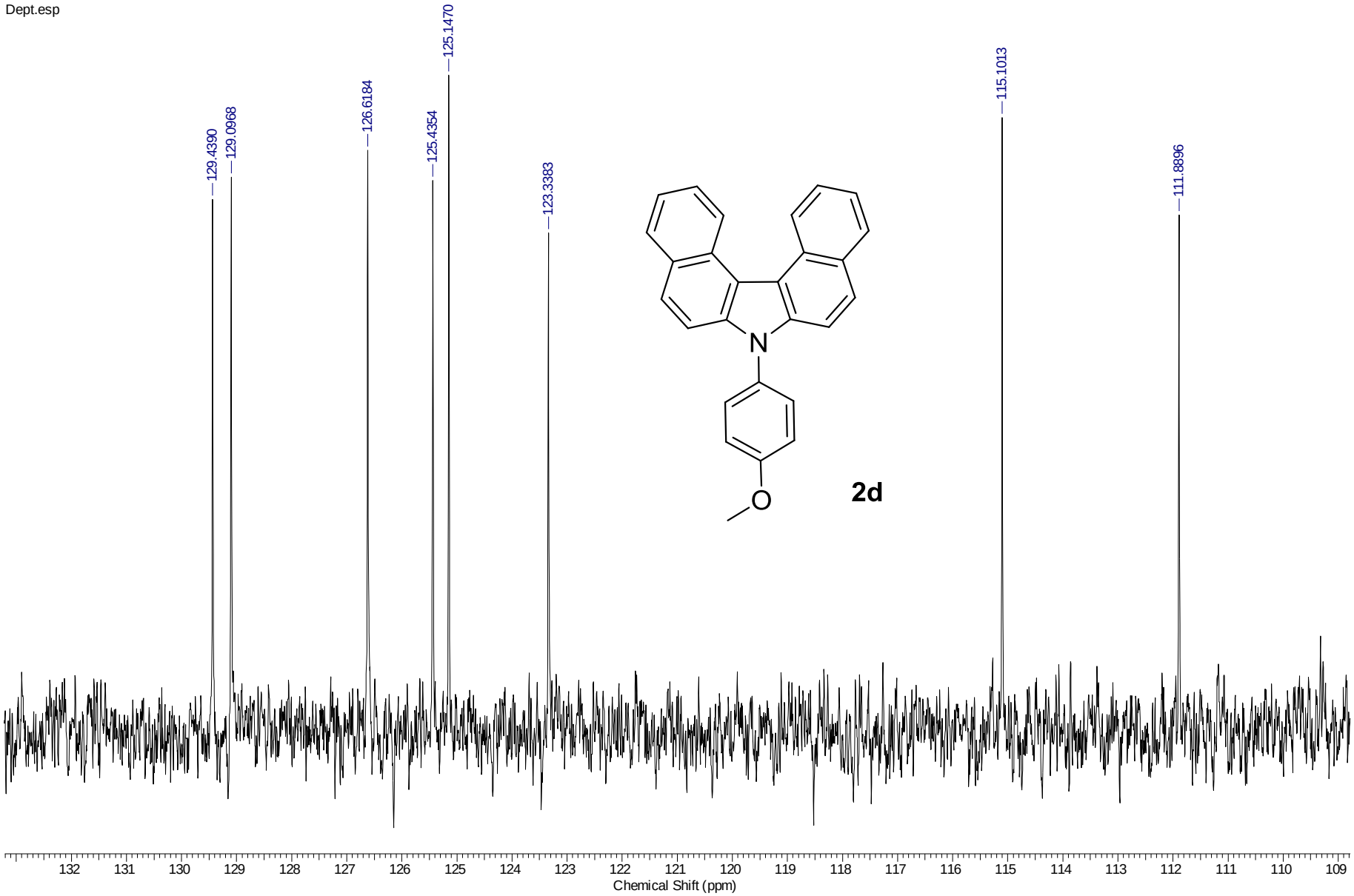


Dept:

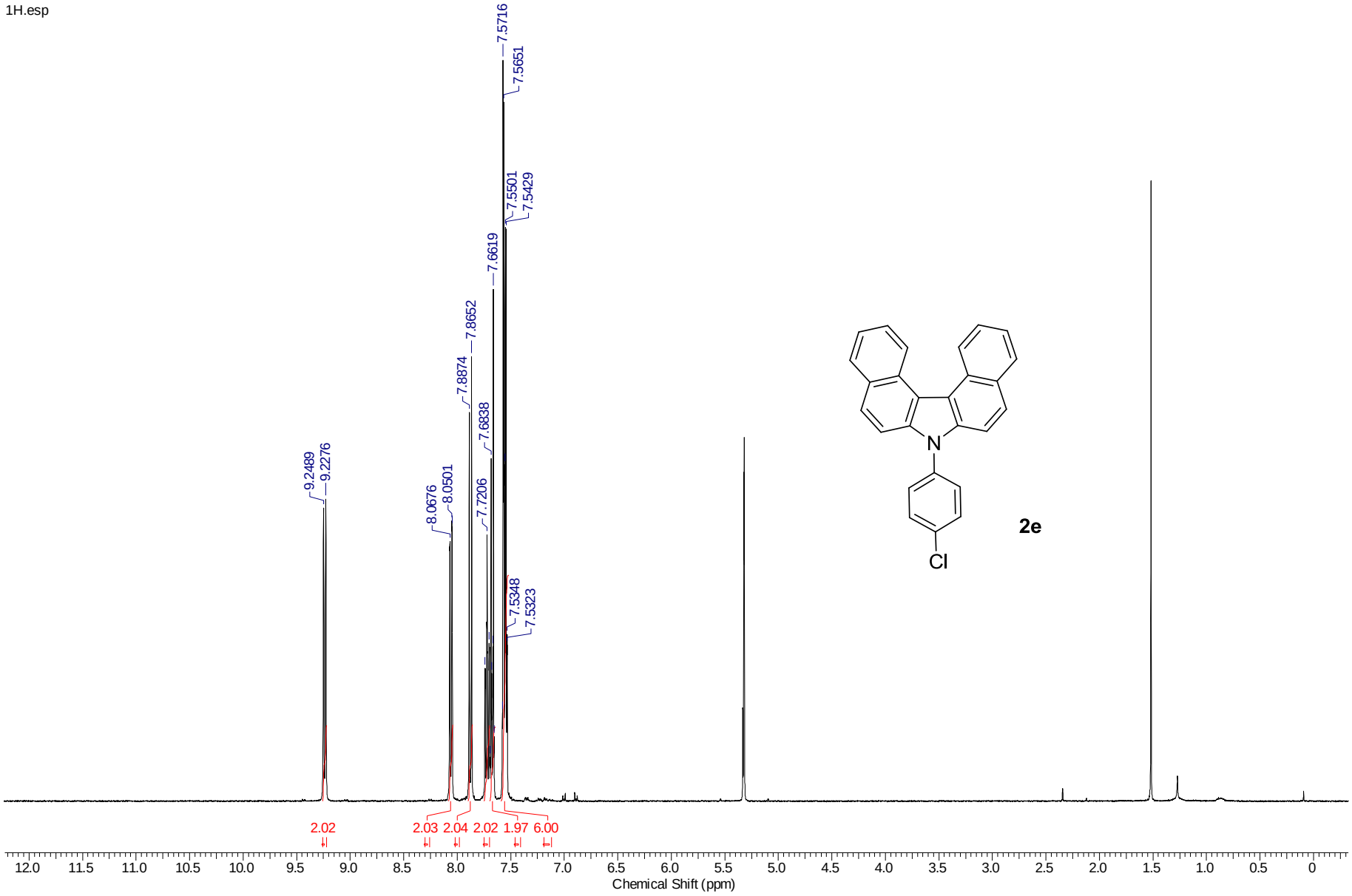
Dept.esp



Dept-Zoom:

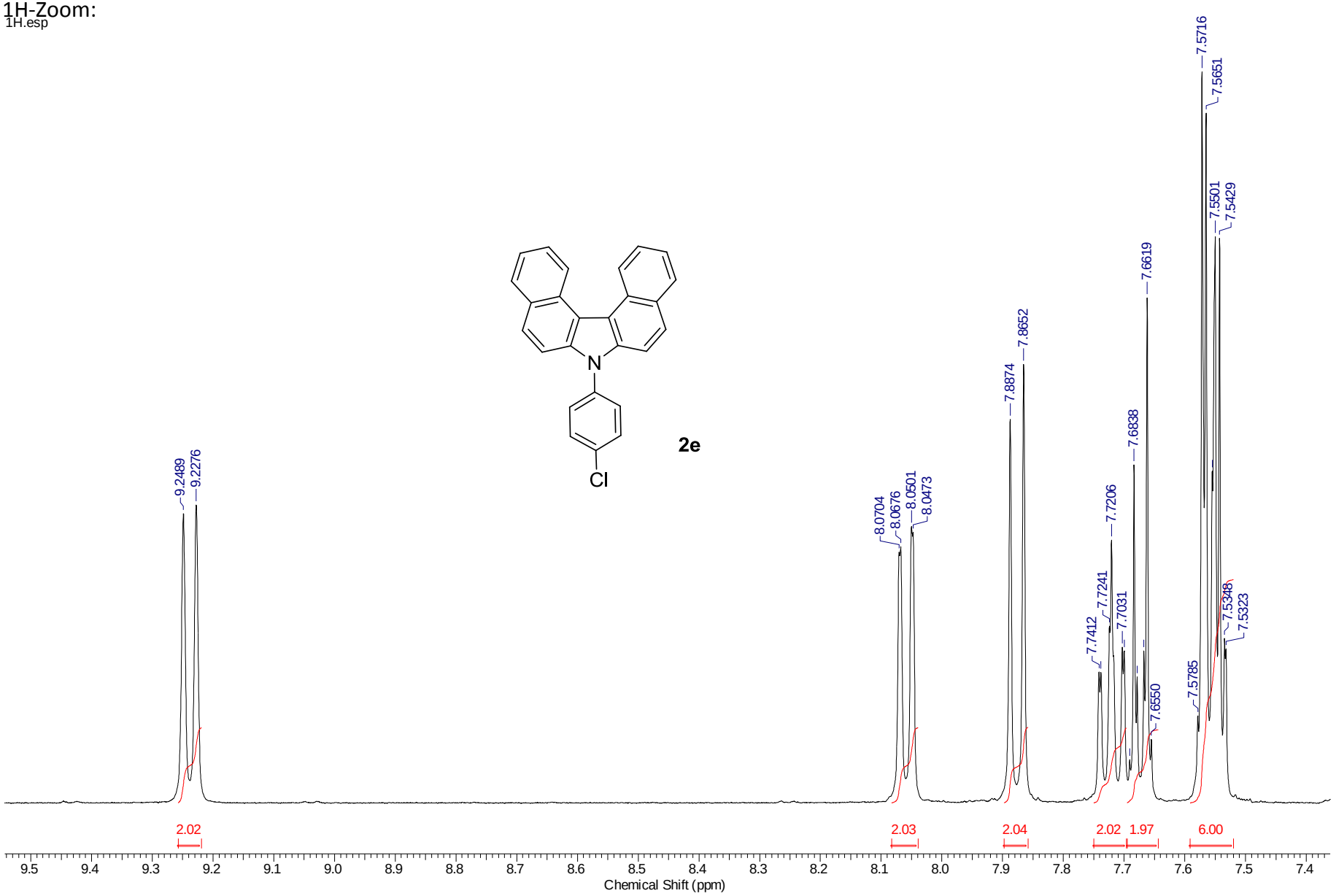

Dept.esp
129.4390
129.0968
126.6184
125.4354
125.1470
123.3383
115.1013
111.8896
N
O
2d
132
131
130
129
128
127
126
125
124
123
122
121
120
119
118
117
116
115
114
113
112
111
110
109
Chemical Shift (ppm)

1H:

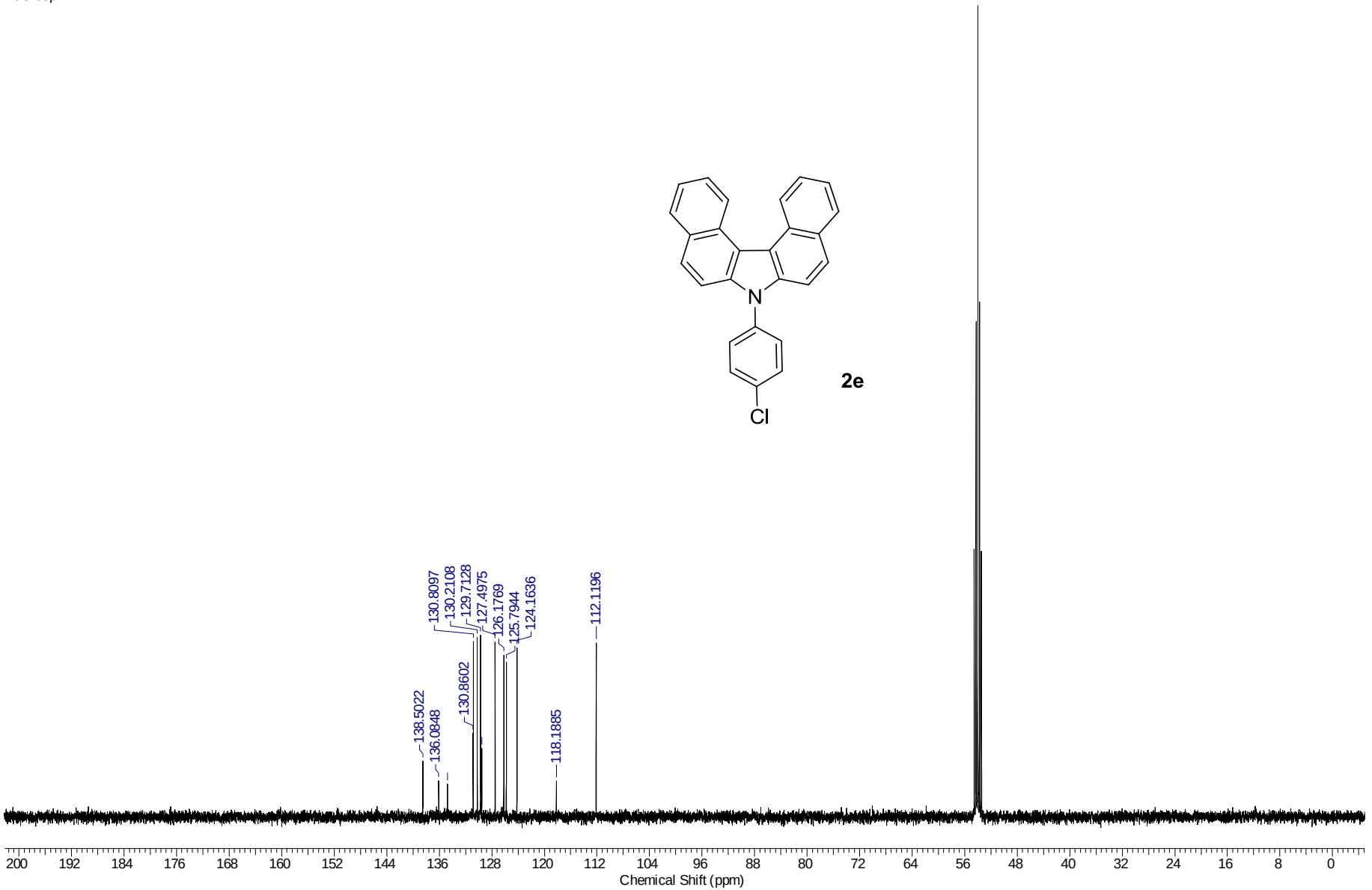

1H.esp
7.5716
7.5651
7.5501
7.5429
7.6619
7.8652
7.8874
7.6838
9.2489
9.2276
8.0676
8.0501
7.7206
7.5348
7.5323
N
Cl
2e
2.02
2.03
2.04
2.02
1.97
6.00
Chemical Shift (ppm)

1H-Zoom:

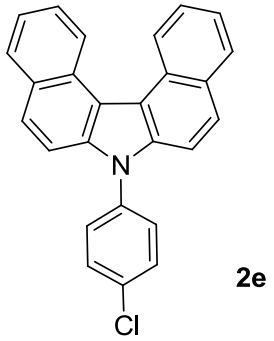
1H.esp



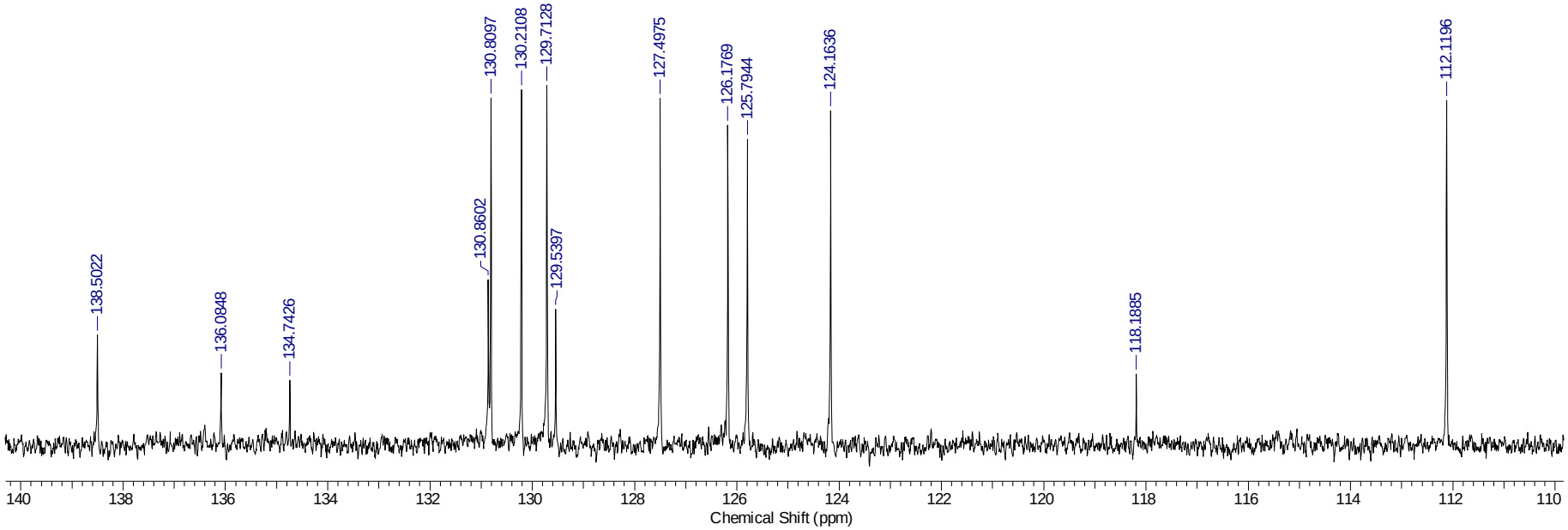
13C:
13C.esp


N
Cl
2e
138.5022
136.0848
130.8602
130.8097
130.2108
129.7128
127.4975
126.1769
125.7944
124.1636
118.1885
112.1196
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

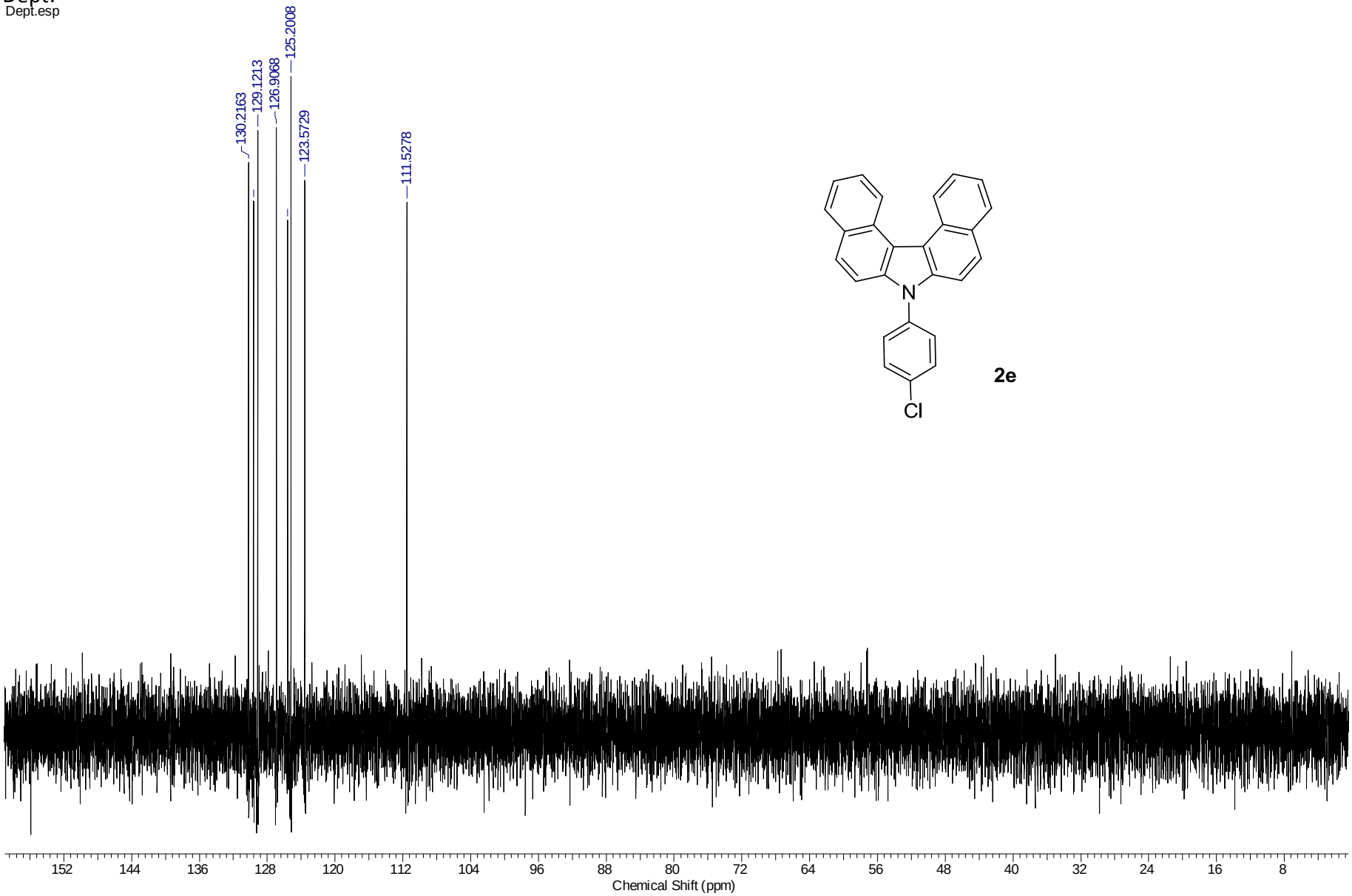
13C-Zoom:
13C.esp



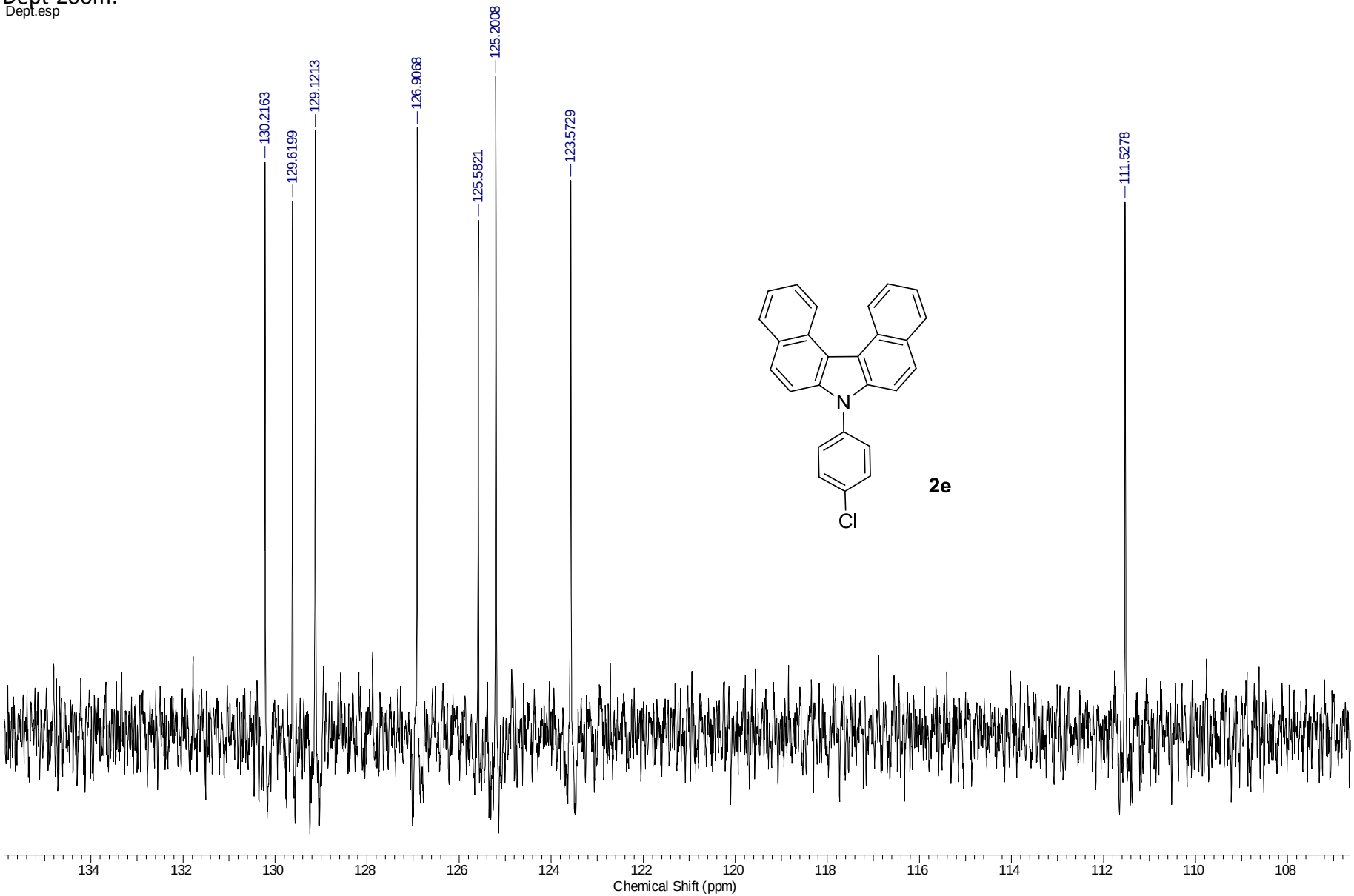
2e



Dept:

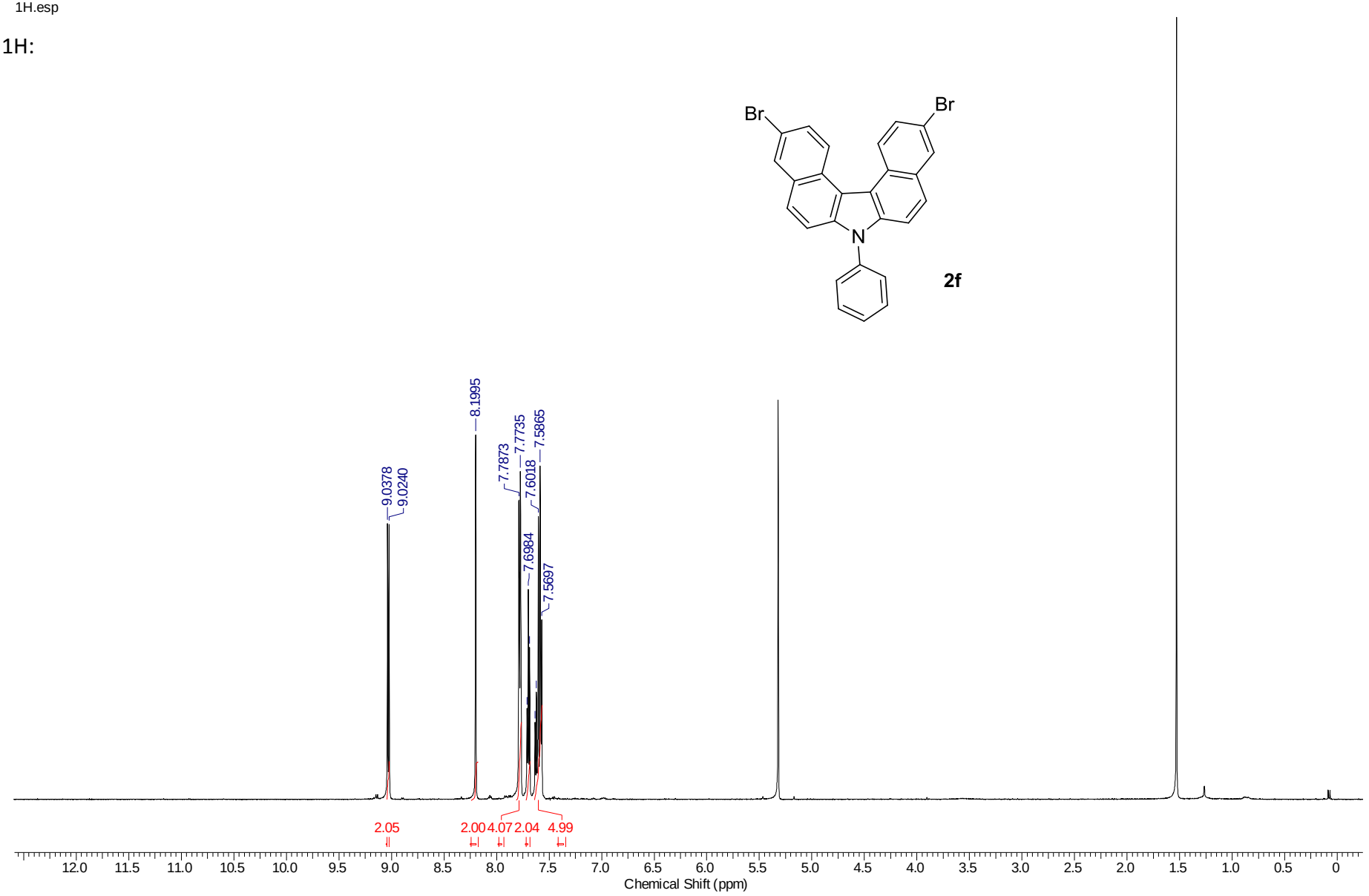

Dept.esp
130.2163
129.1213
126.9068
125.2008
123.5729
111.5278
N
Cl
2e
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

Dept-Zoom:

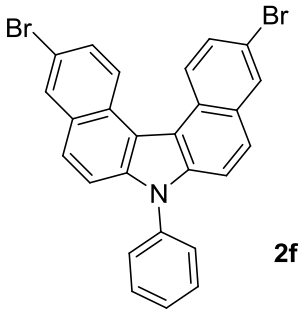

Dept.esp
130.2163
129.6199
129.1213
126.9068
125.5821
125.2008
123.5729
111.5278
N
Cl
2e
134
132
130
128
126
124
122
120
118
116
114
112
110
108
Chemical Shift (ppm)

1H.esp

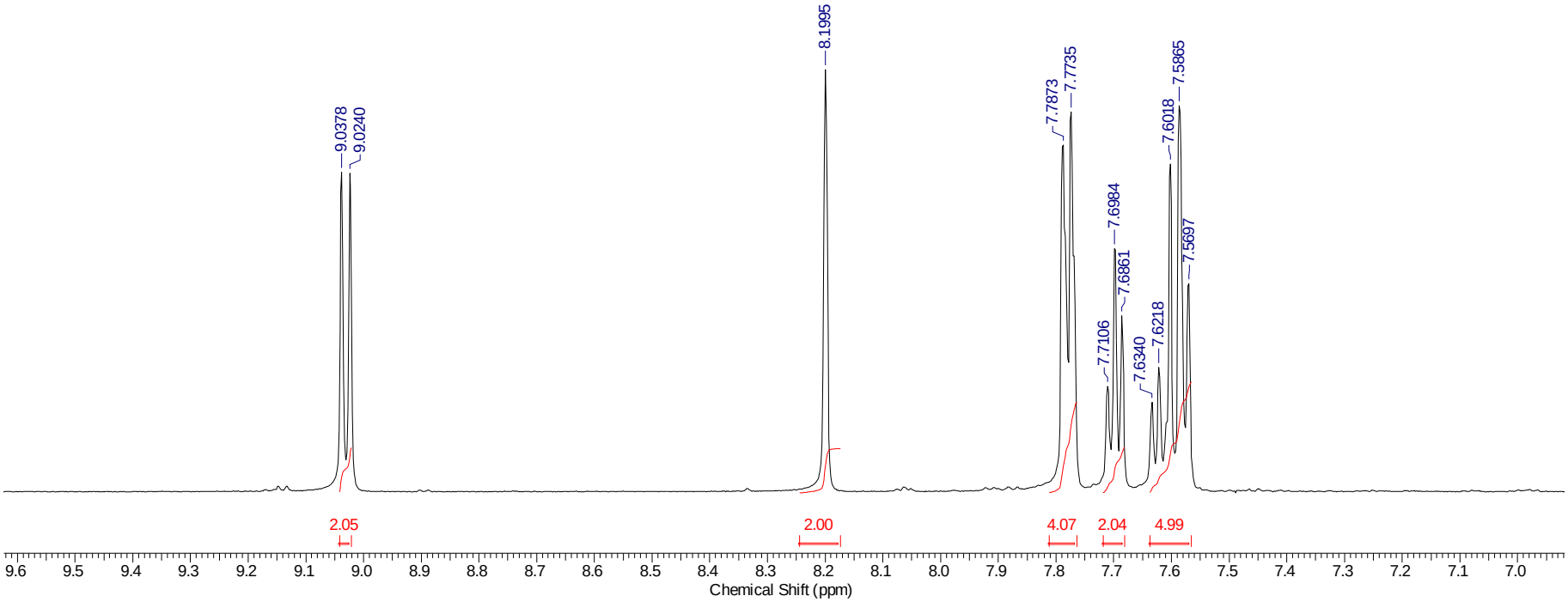
1H:


Br
Br
N
2f
9.0378
9.0240
8.1995
7.7873
7.7735
7.6018
7.5865
7.6984
7.5697
2.05
2.00
4.07
2.04
4.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

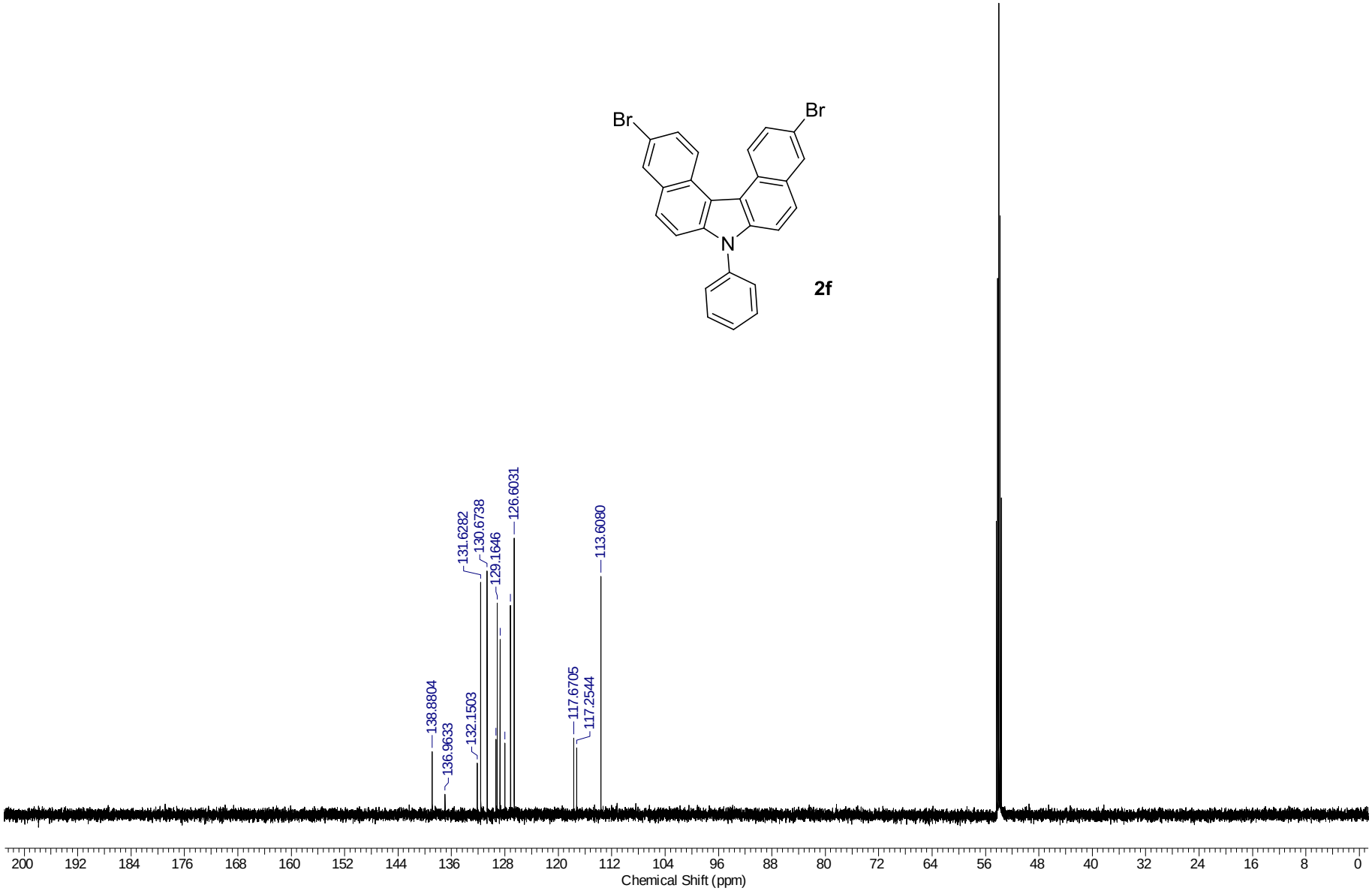
1H-Zoom:
1H.esp



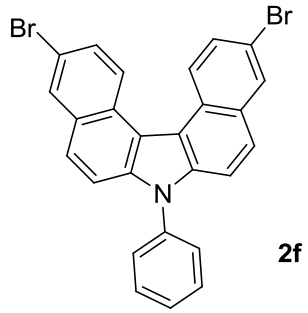
2f



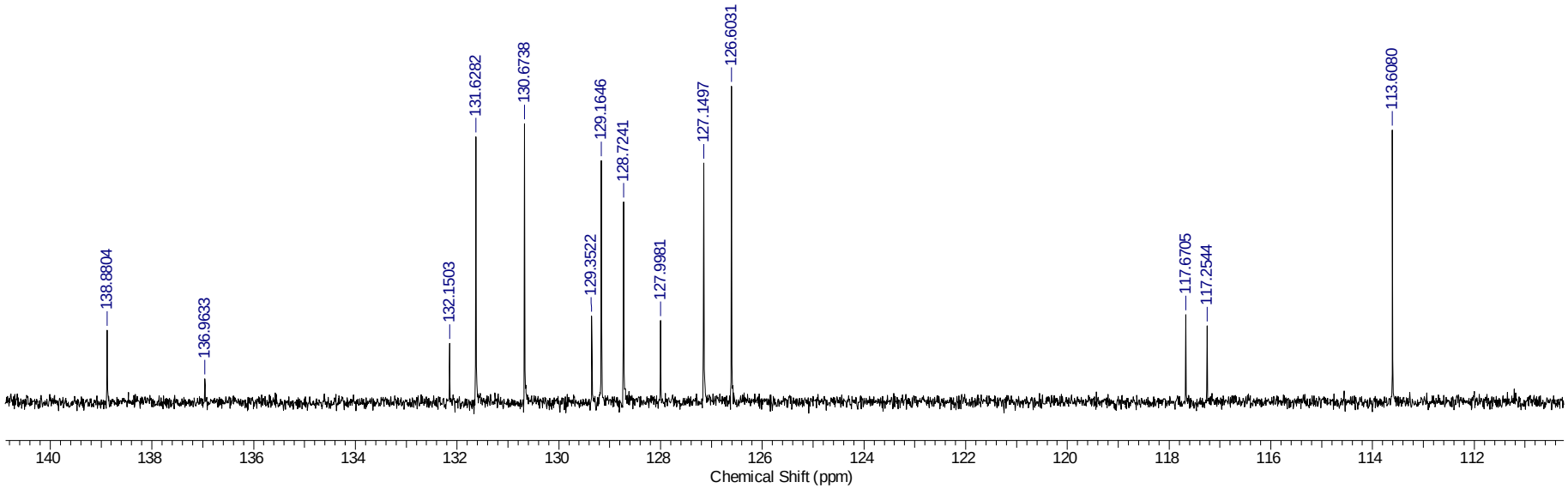
13C:
13C.esp


Br
Br
N
2f
138.8804
136.9633
132.1503
131.6282
130.6738
129.1646
126.6031
117.6705
117.2544
113.6080
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

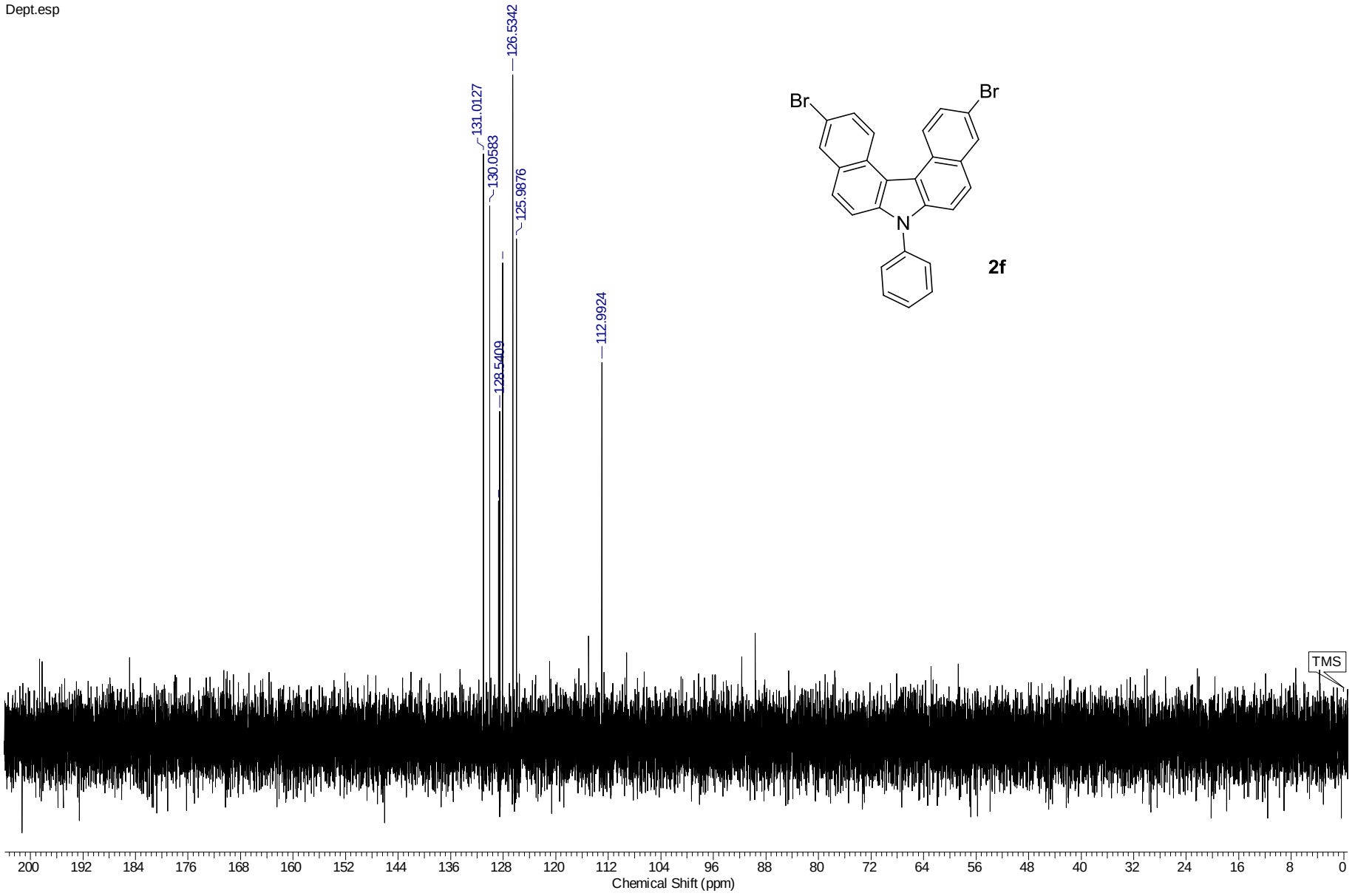
13C-Zoom:
13C.esp



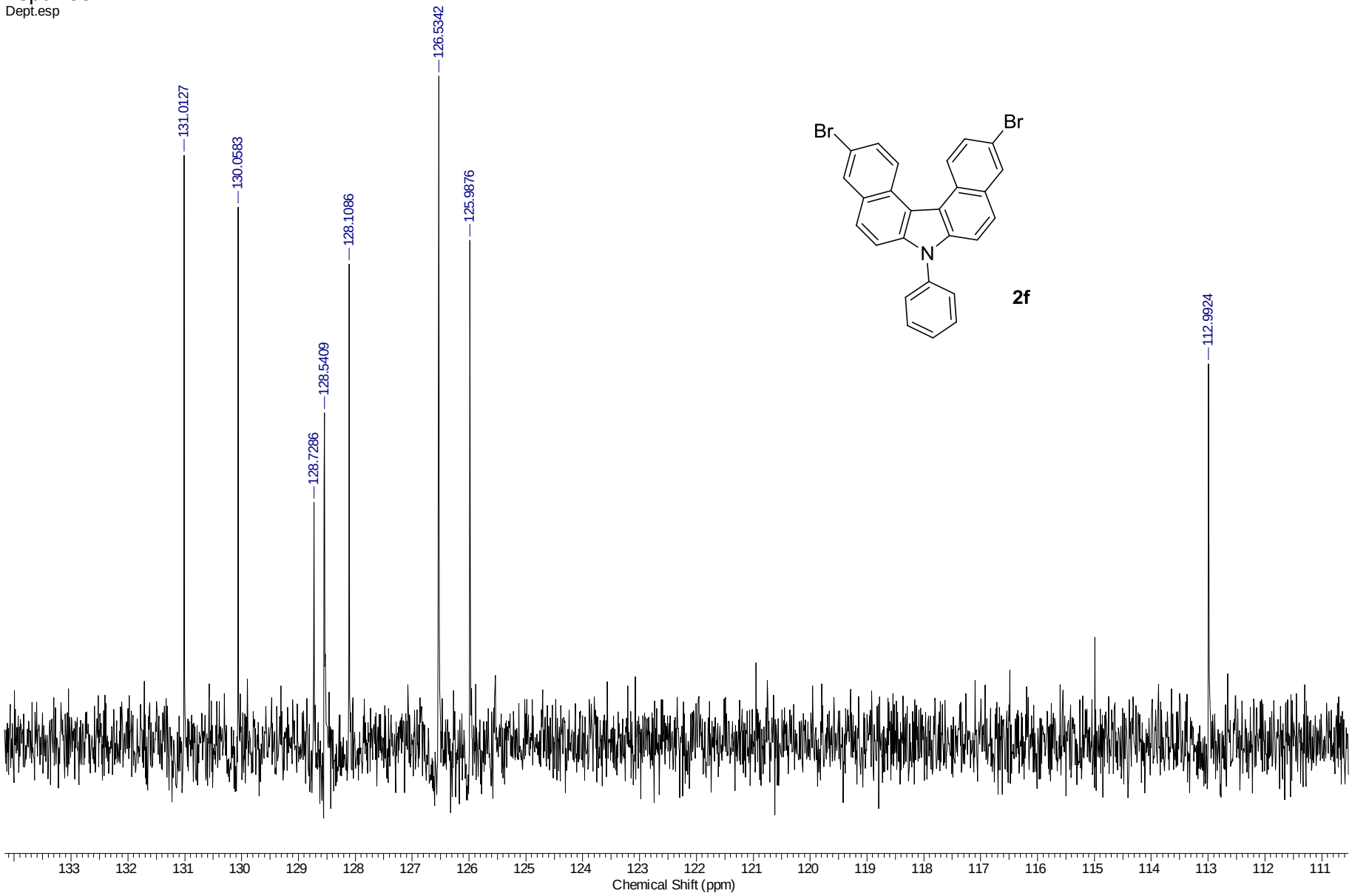
2f



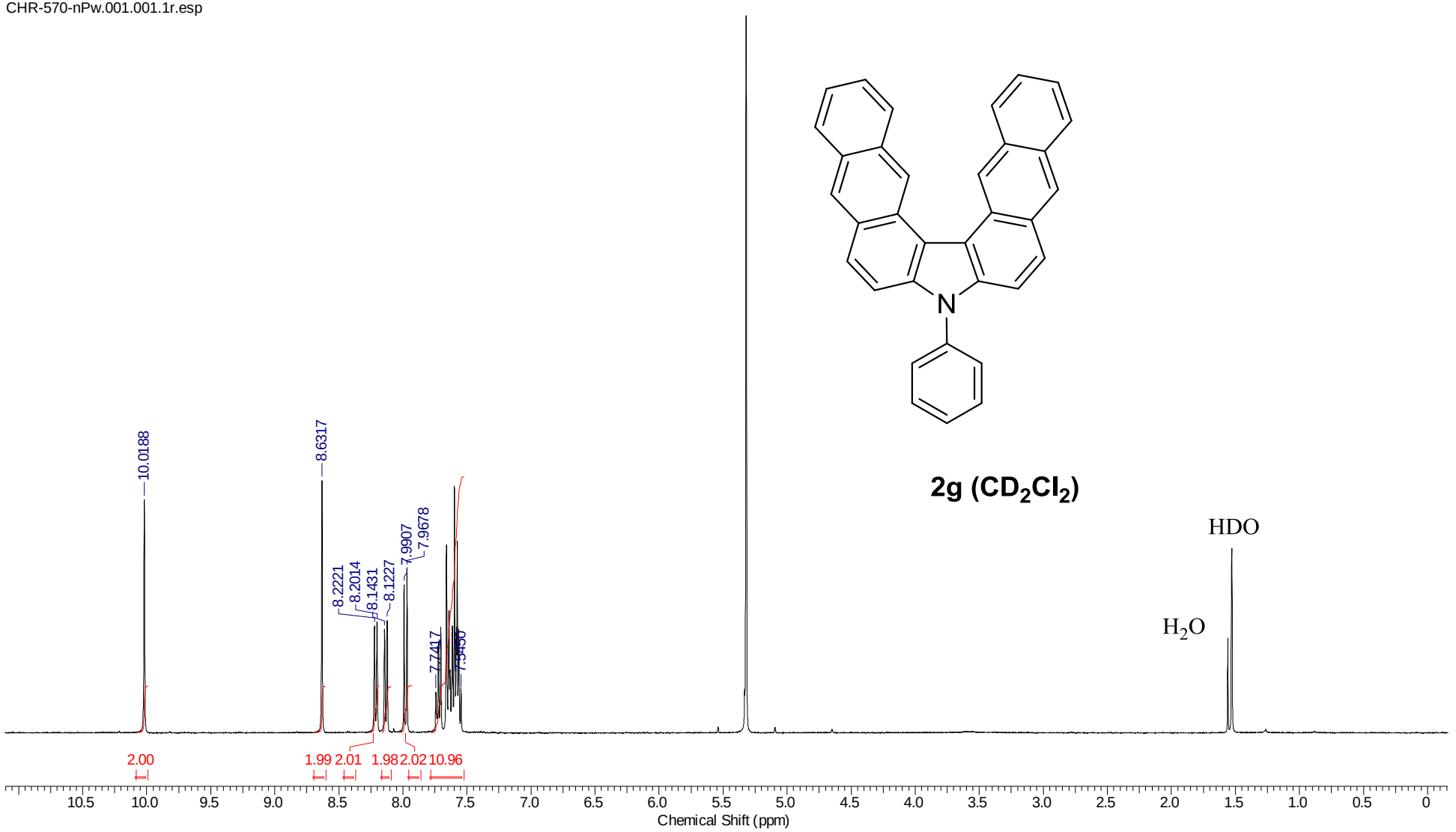
Dept:


Dept.esp
131.0127
130.0583
126.5342
125.9876
128.5409
112.9924
Br
Br
N
2f
TMS
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

Dept-Zoom:


Dept.esp
131.0127
130.0583
128.7286
128.5409
128.1086
126.5342
125.9876
112.9924
Br
Br
N
2f
133
132
131
130
129
128
127
126
125
124
123
122
121
120
119
118
117
116
115
114
113
112
111
Chemical Shift (ppm)

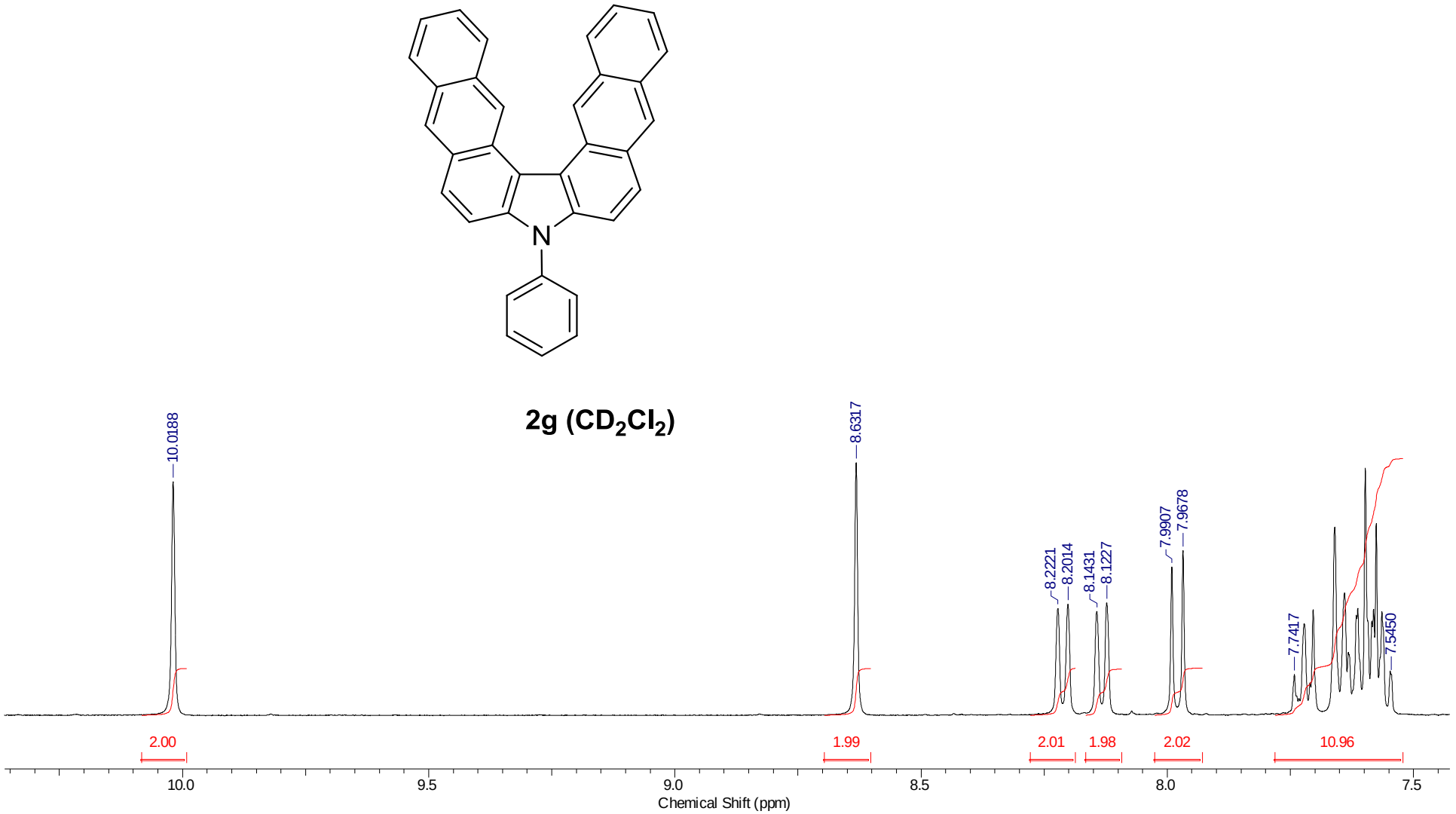
CHR-570-nPw.001.001.1r.esp



2g (CD_2Cl_2)

^{1}H Zoom:

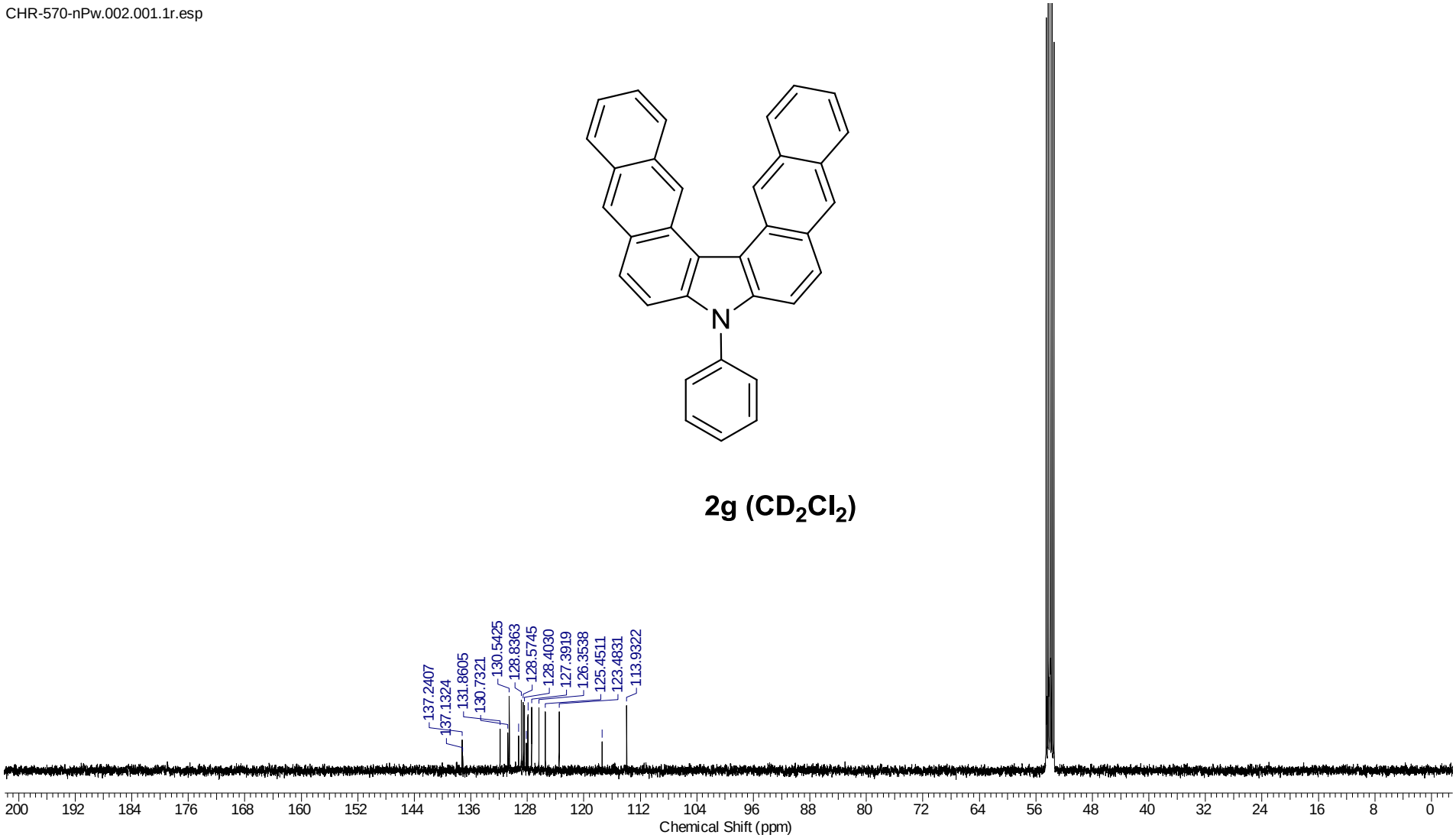
CHR-570-nPw.001.001.1r.esp



^{1}H: *Mixture of H_2O and HDO in CD_2Cl_2*

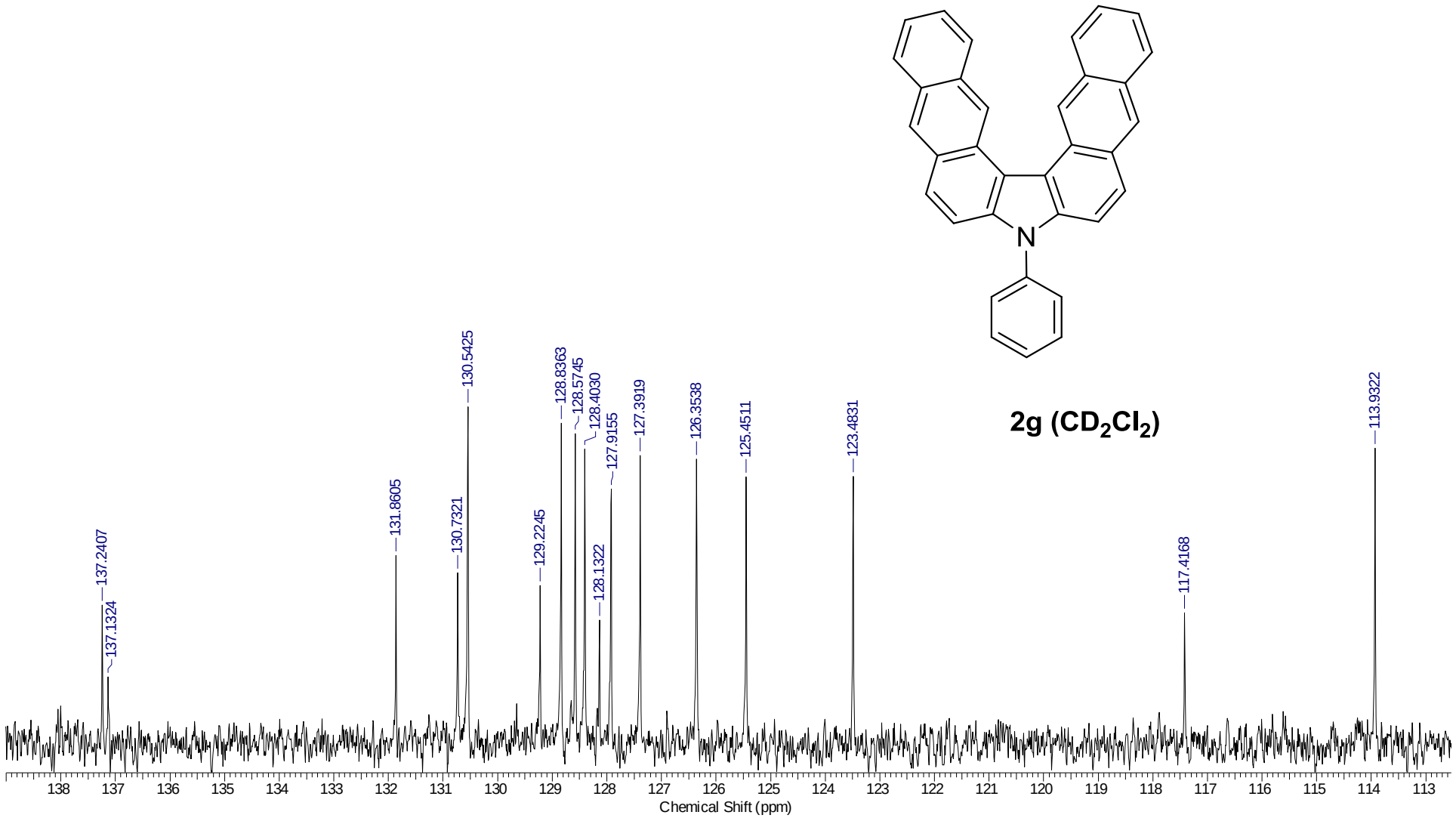
^{13}C:

CHR-570-nPw.002.001.1r.esp

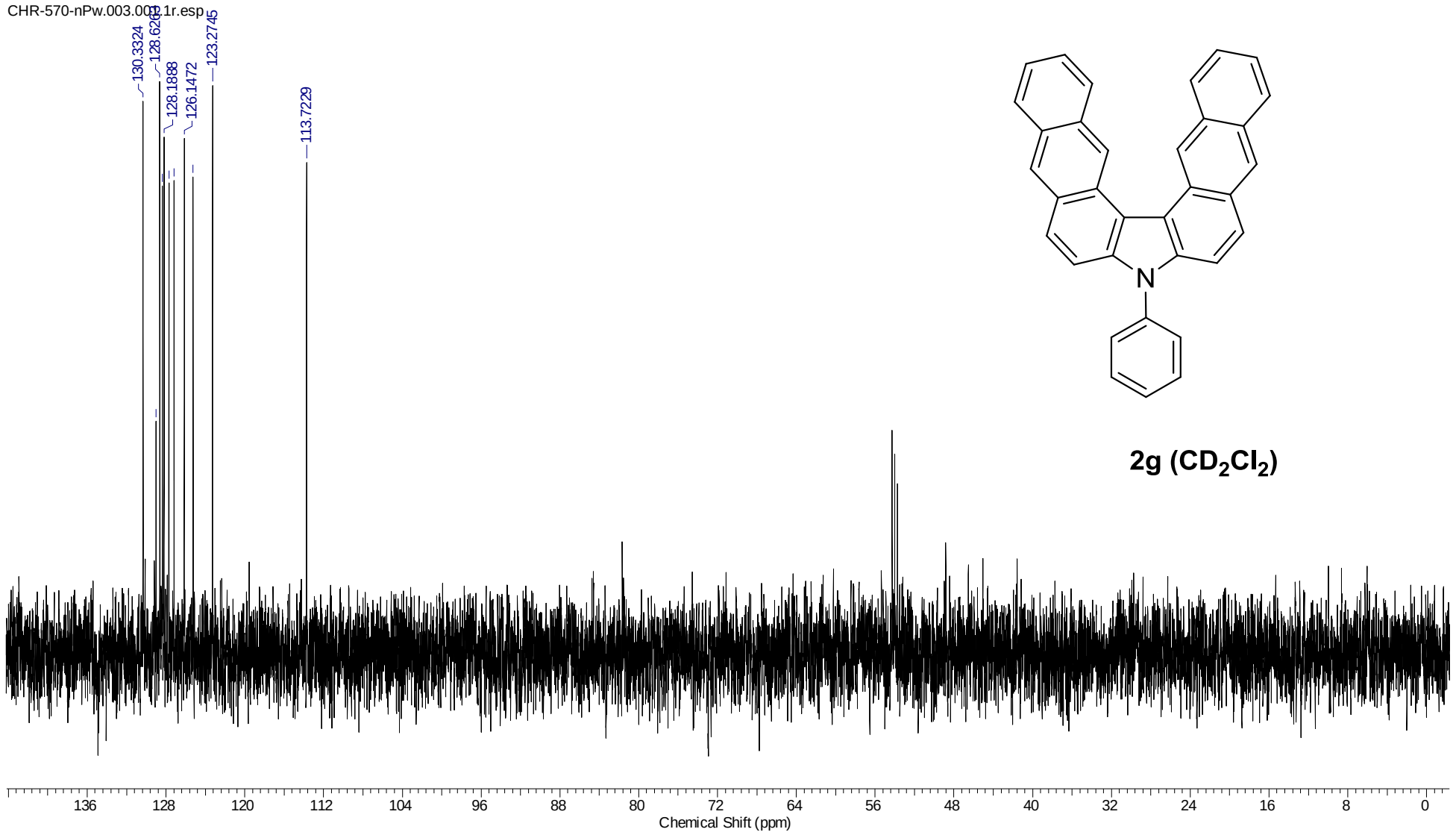


^{13}C Zoom:

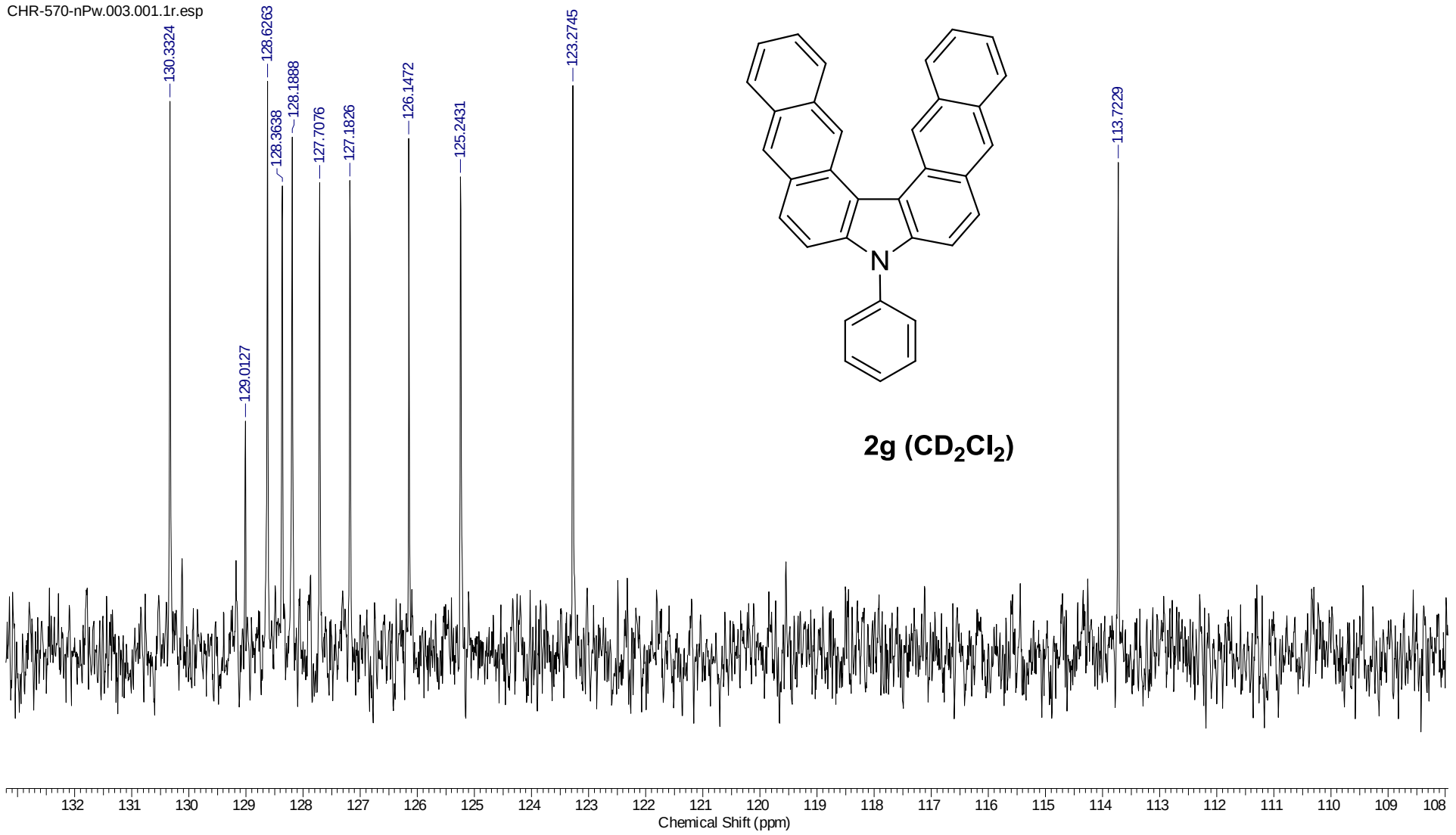
CHR-570-nPw.002.001.1r.esp



Dept:

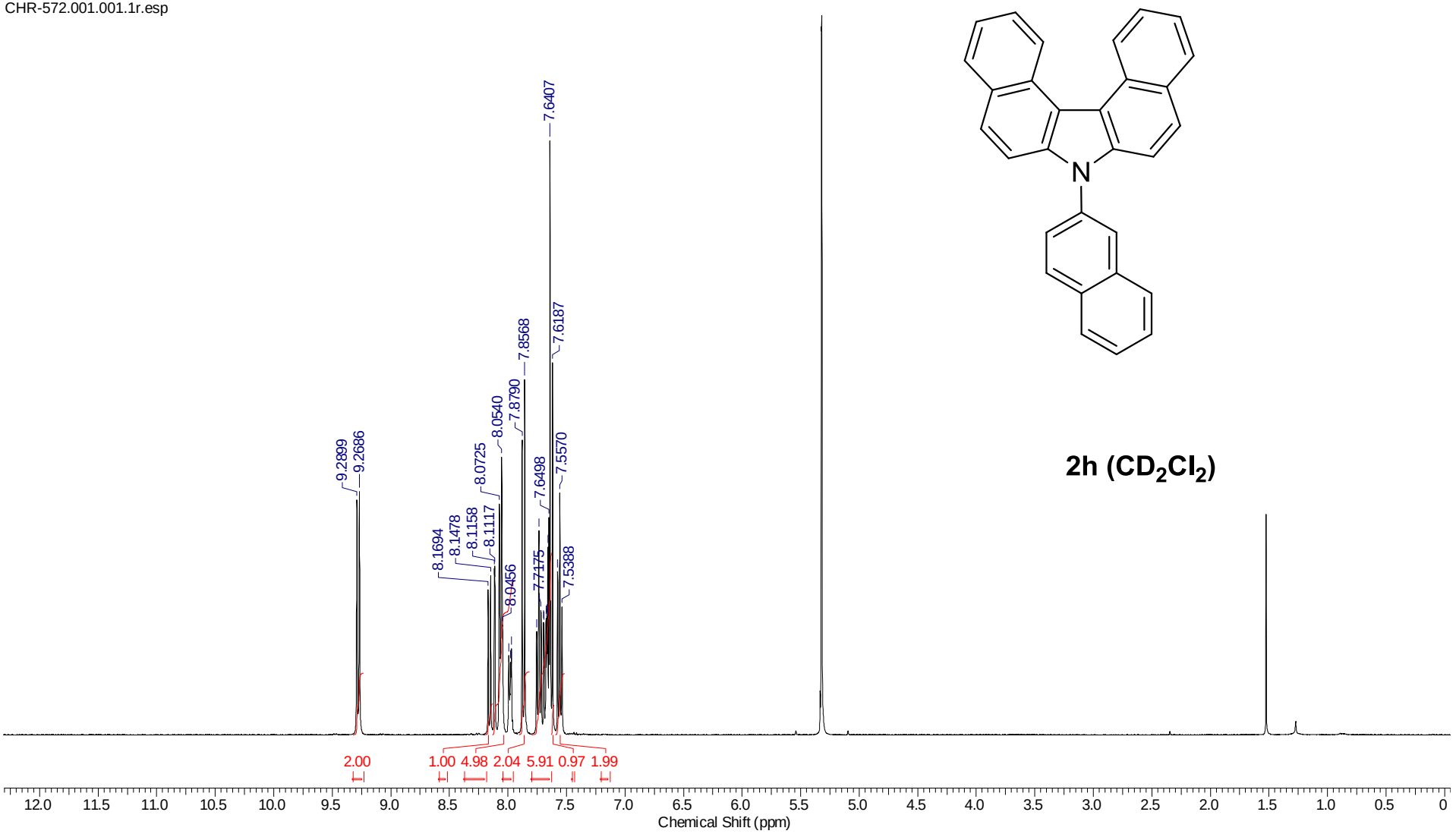

CHR-570-nPw.003.001.1r.esp
130.3324
128.6264
128.1888
126.1472
123.2745
113.7229
N
2g (CD_2Cl_2)
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

Dept Zoom:


CHR-570-nPw.003.001.1r.esp
130.3324
129.0127
128.6263
128.3638
128.1888
127.7076
127.1826
126.1472
125.2431
123.2745
113.7229
N
2g (CD_2Cl_2)
132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111 110 109 108
Chemical Shift (ppm)

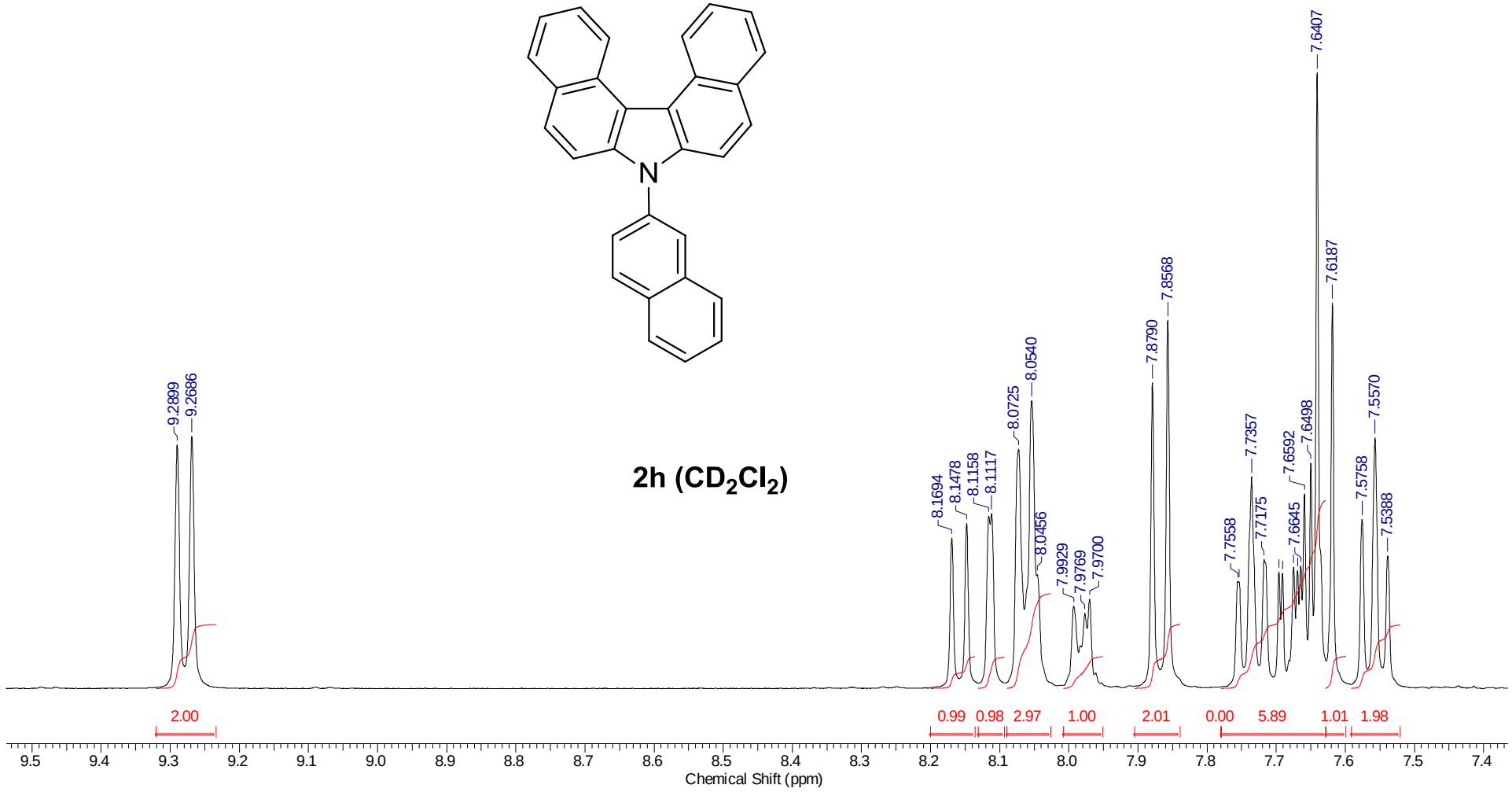
^{1}H:

CHR-572.001.001.1r.esp



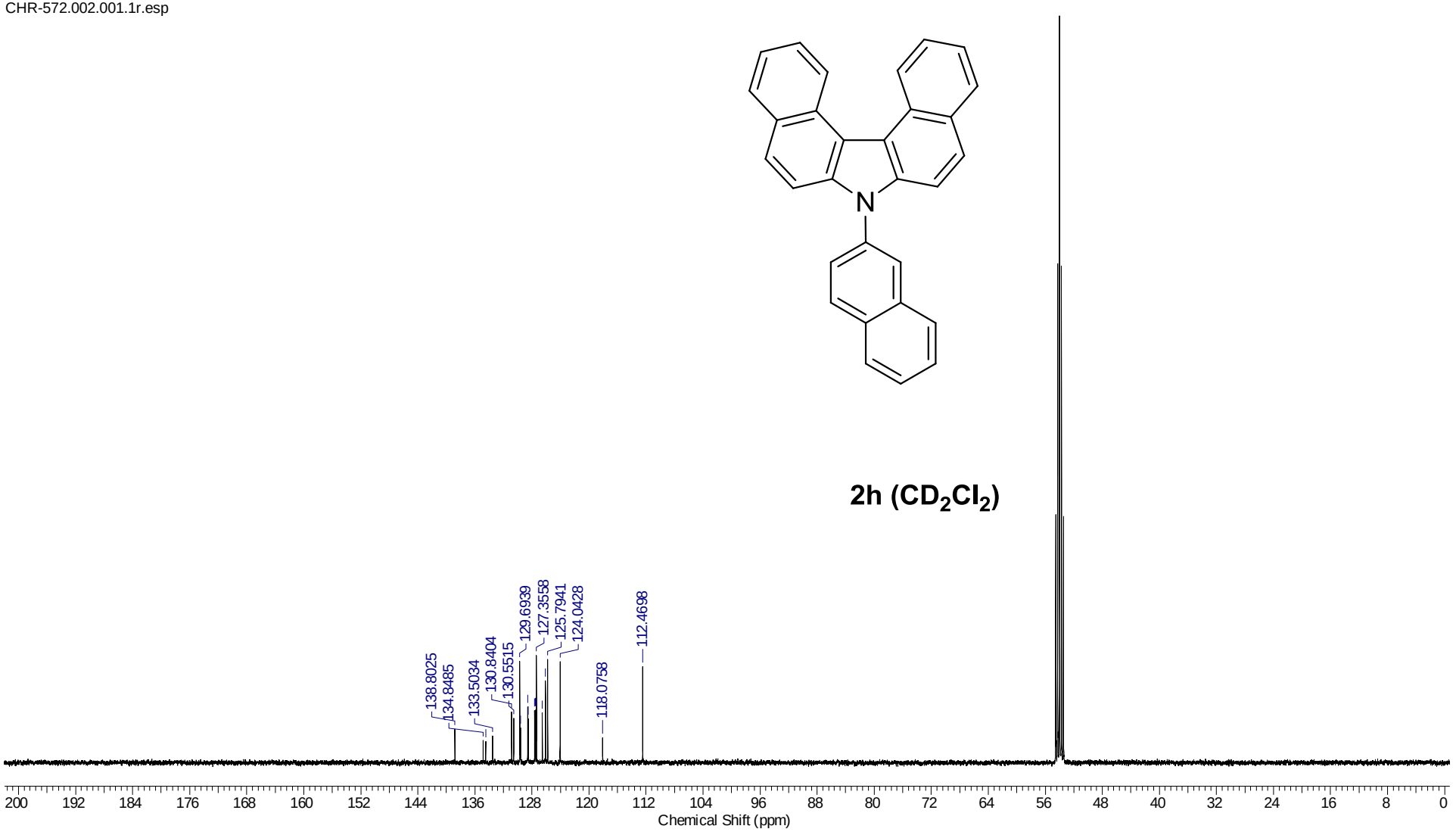
^{1}H Zoom:

CHR-572.001.001.1r.esp



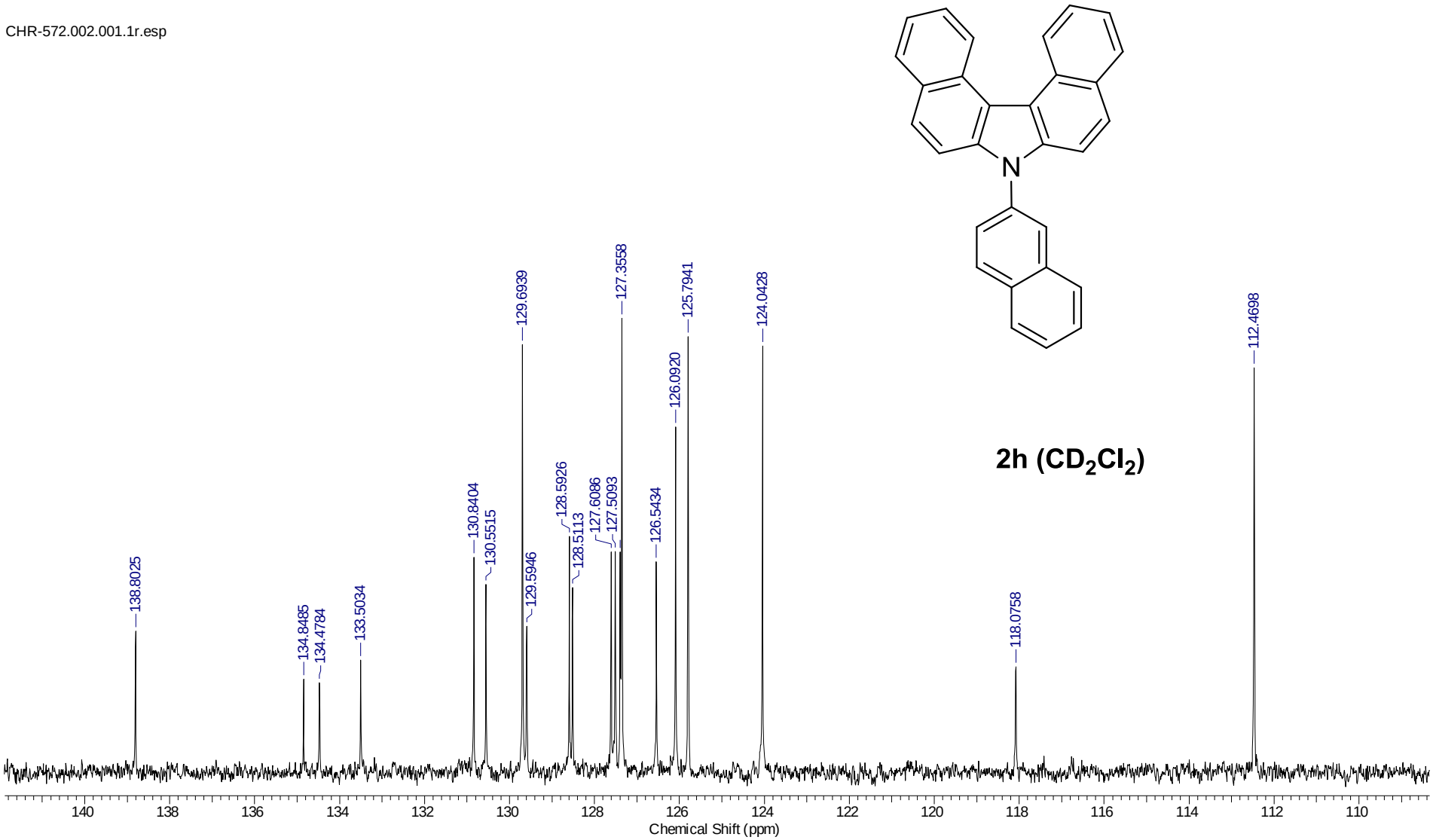
^{13}C:

CHR-572.002.001.1r.esp

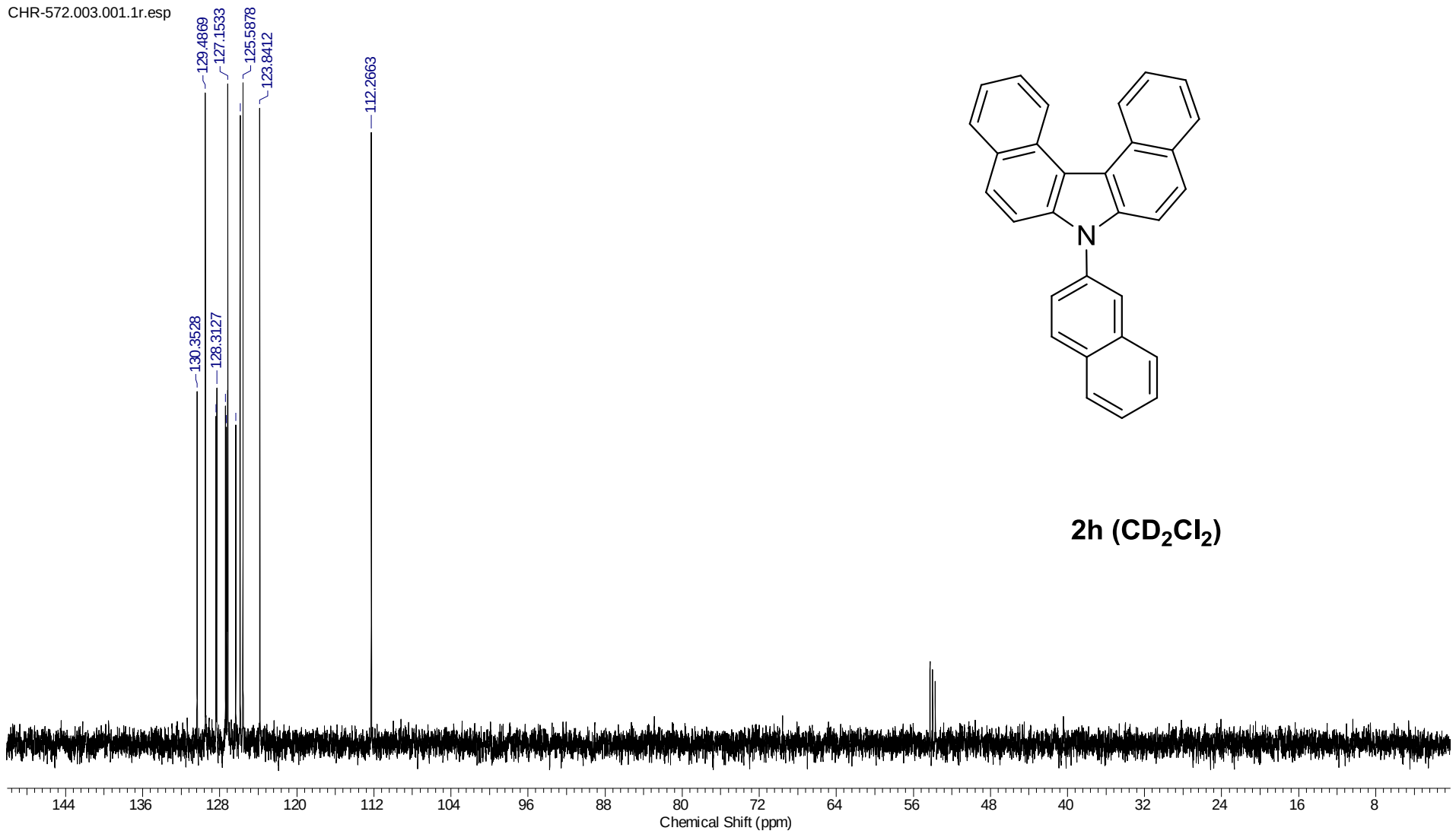


^{13}C Zoom:

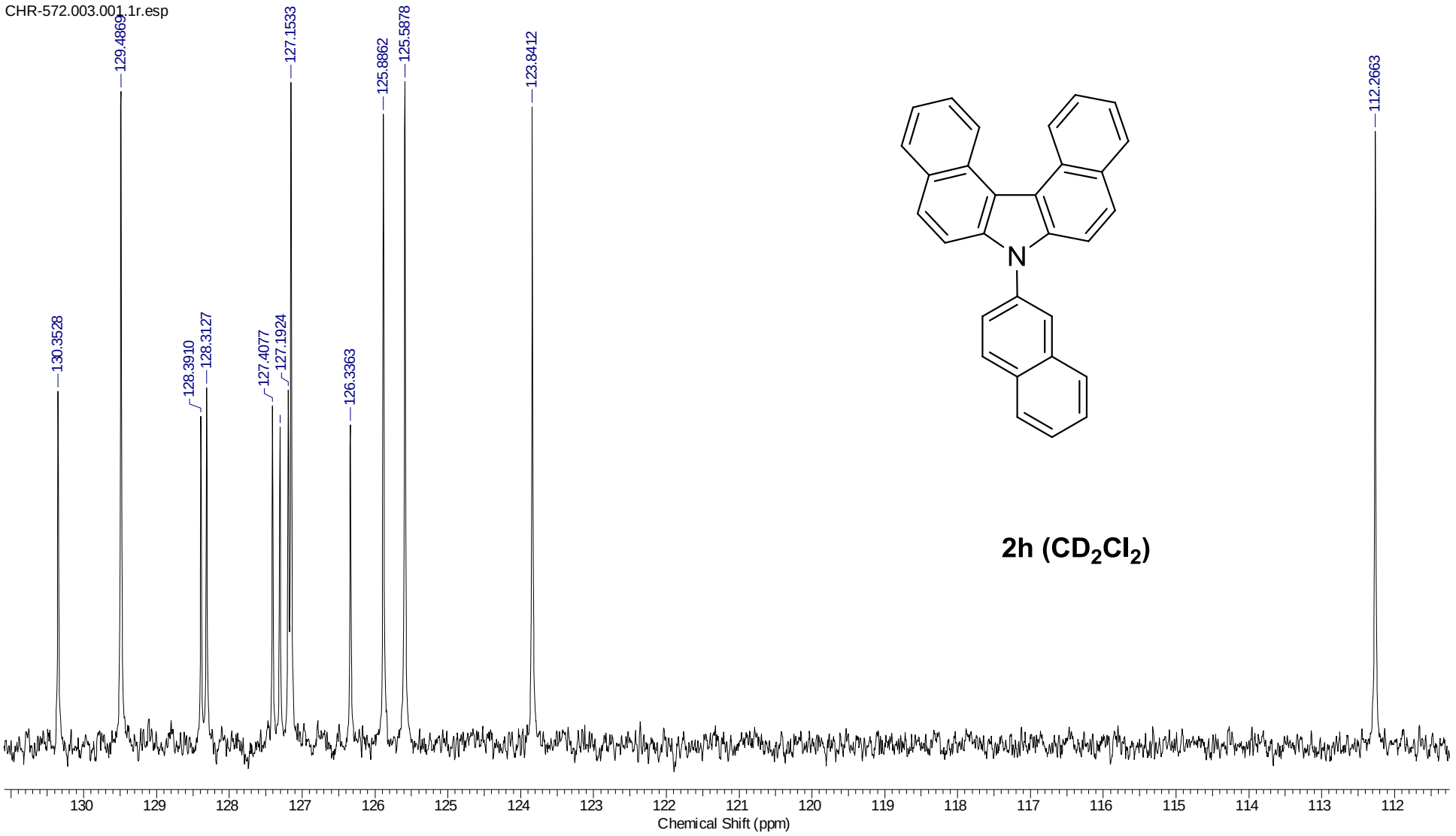
CHR-572.002.001.1r.esp



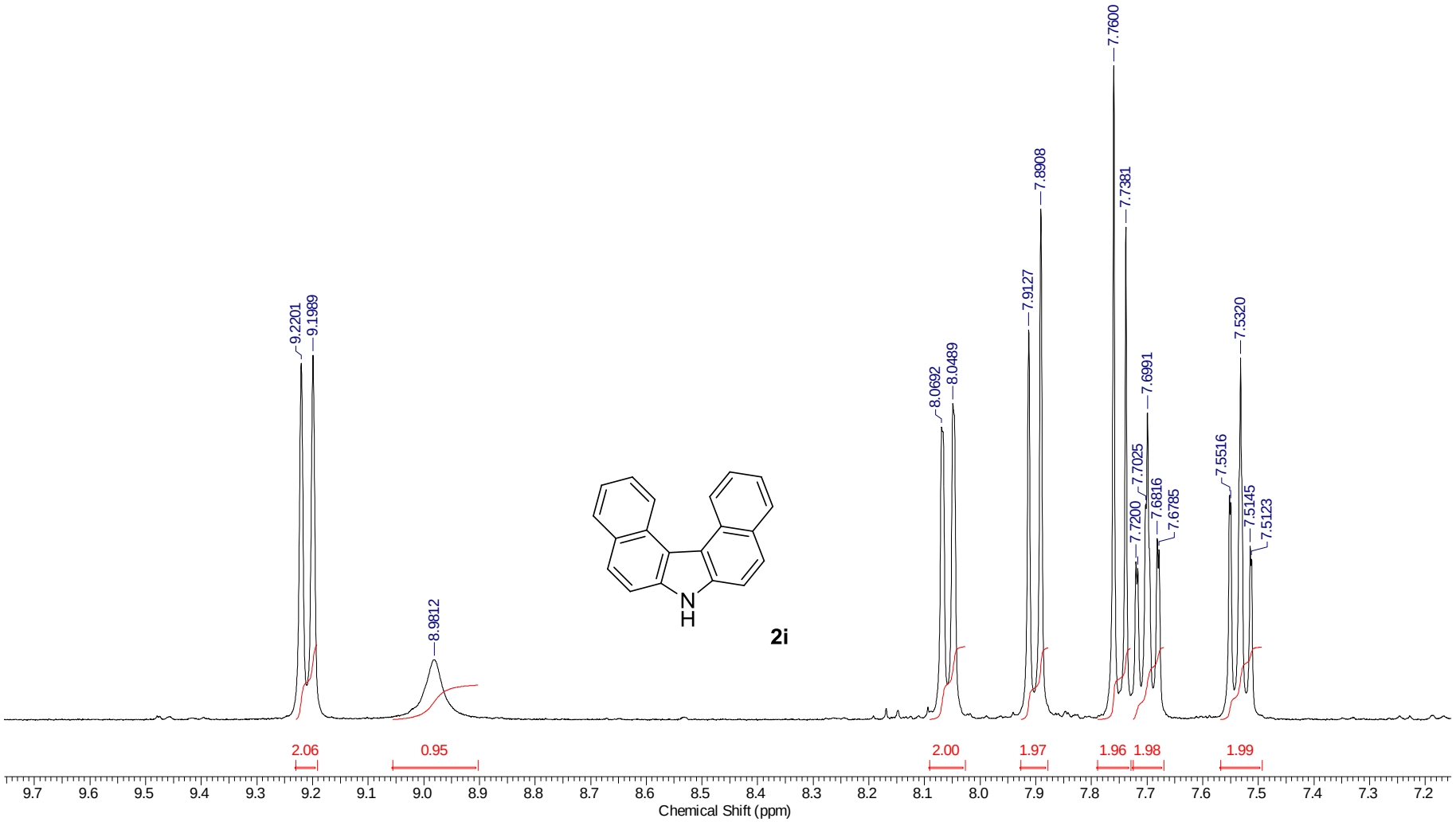
Dept:



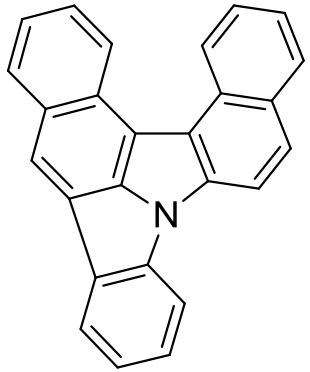
Dept Zoom:


CHR-572.003.001.1r.esp
129.4869
127.1533
125.8862
125.5878
123.8412
112.2663
130.3528
128.3910
128.3127
127.4077
127.1924
126.3363
N
2h (CD2Cl2)
130
129
128
127
126
125
124
123
122
121
120
119
118
117
116
115
114
113
112
Chemical Shift (ppm)

1H:


9.2201
9.1989
8.9812
8.0692
8.0489
7.9127
7.8908
7.7600
7.7381
7.6991
7.7025
7.7200
7.6816
7.6785
7.5516
7.5320
7.5145
7.5123
N
H
2i
2.06
0.95
2.00
1.97
1.96
1.98
1.99
Chemical Shift (ppm)

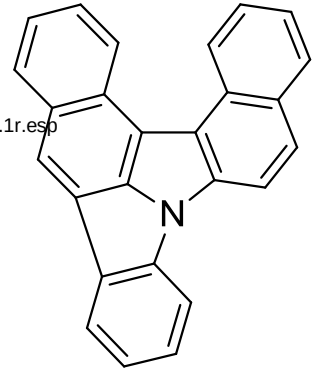
CHR-573-b-DMSO-d6.001.001.1r.esp



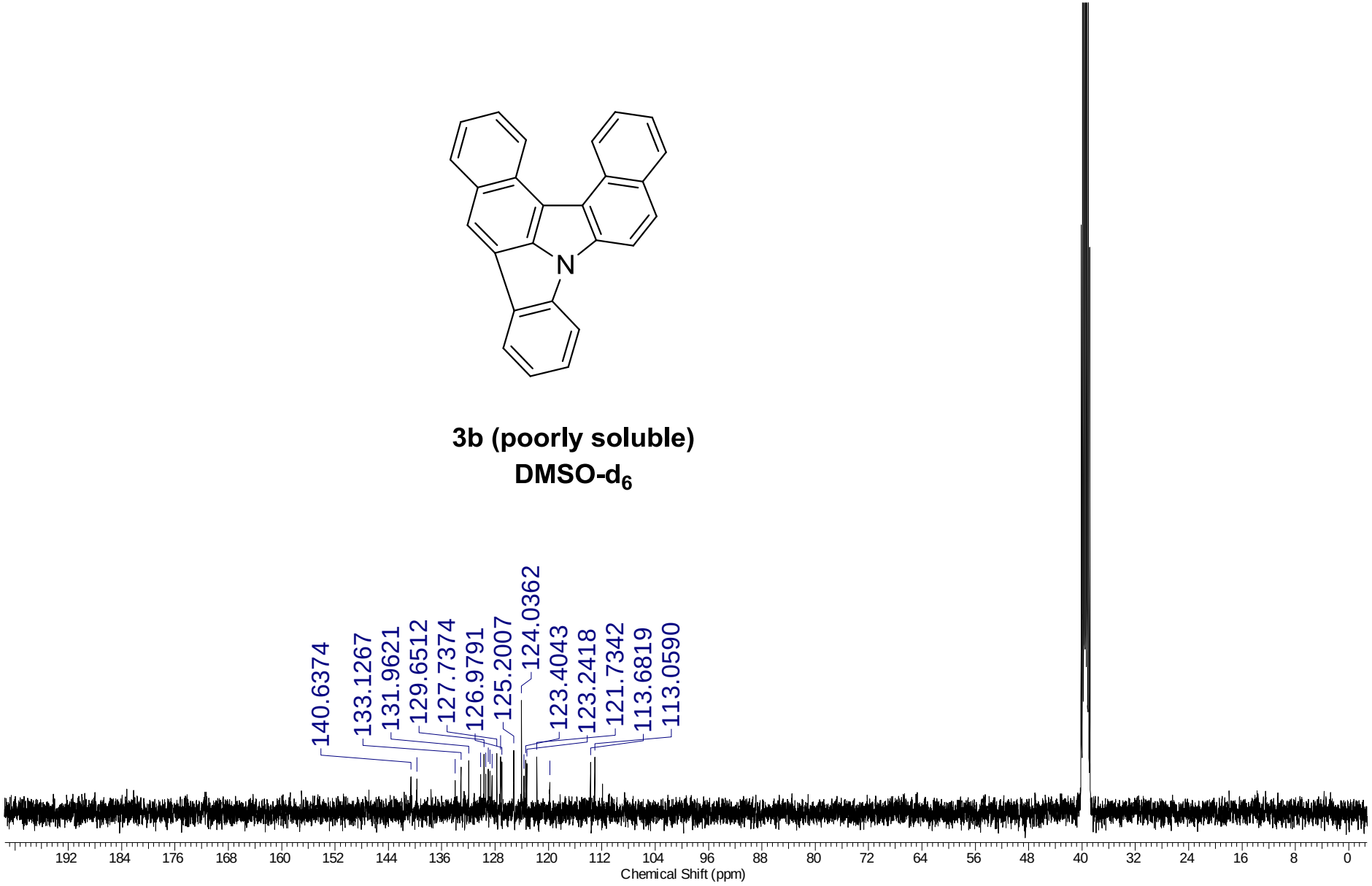
3b (poorly soluble)
DMSO-d_6

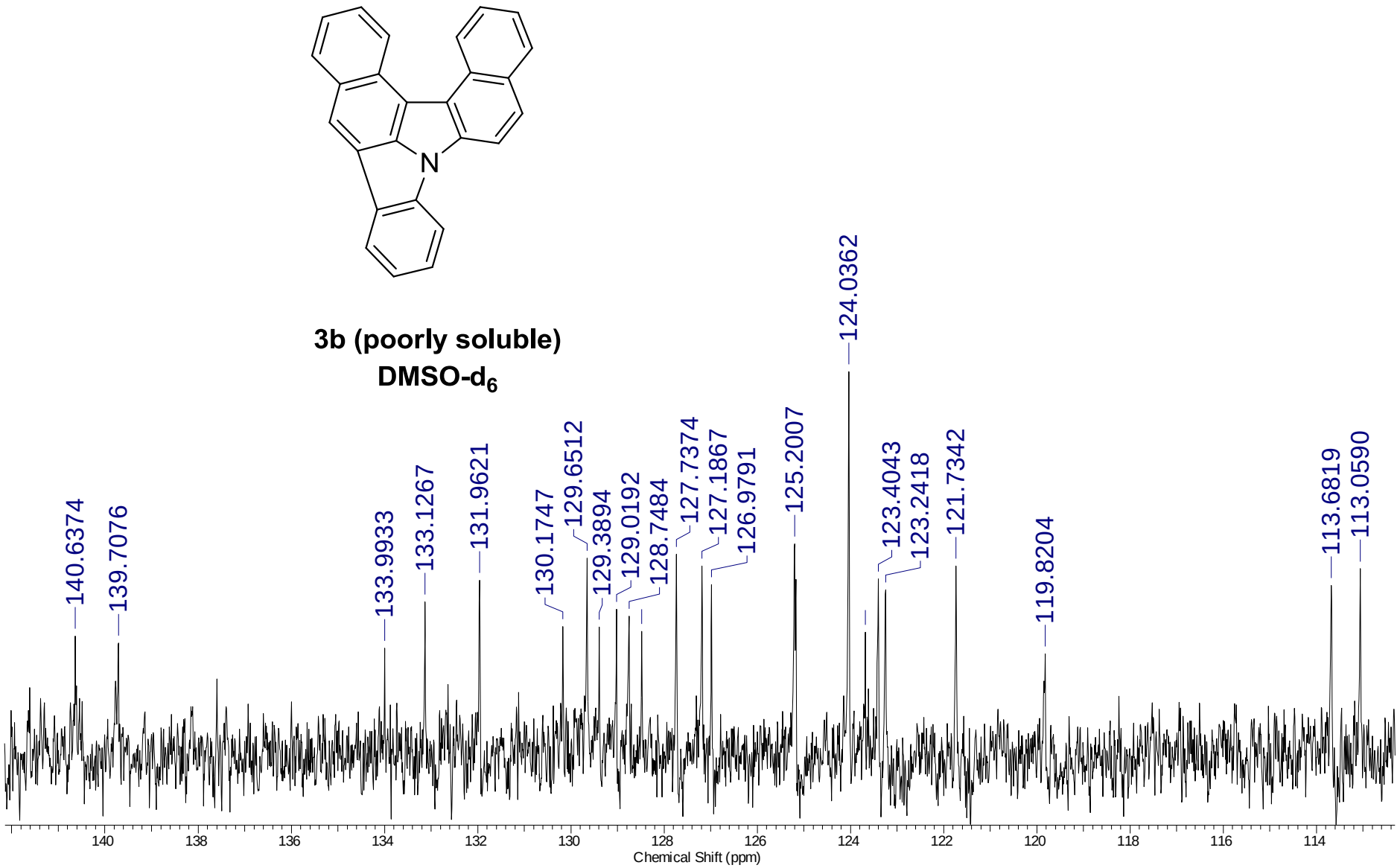
^{1}H Zoom:

CHR-573-b-DMSO-d6.001.001.1r.esp

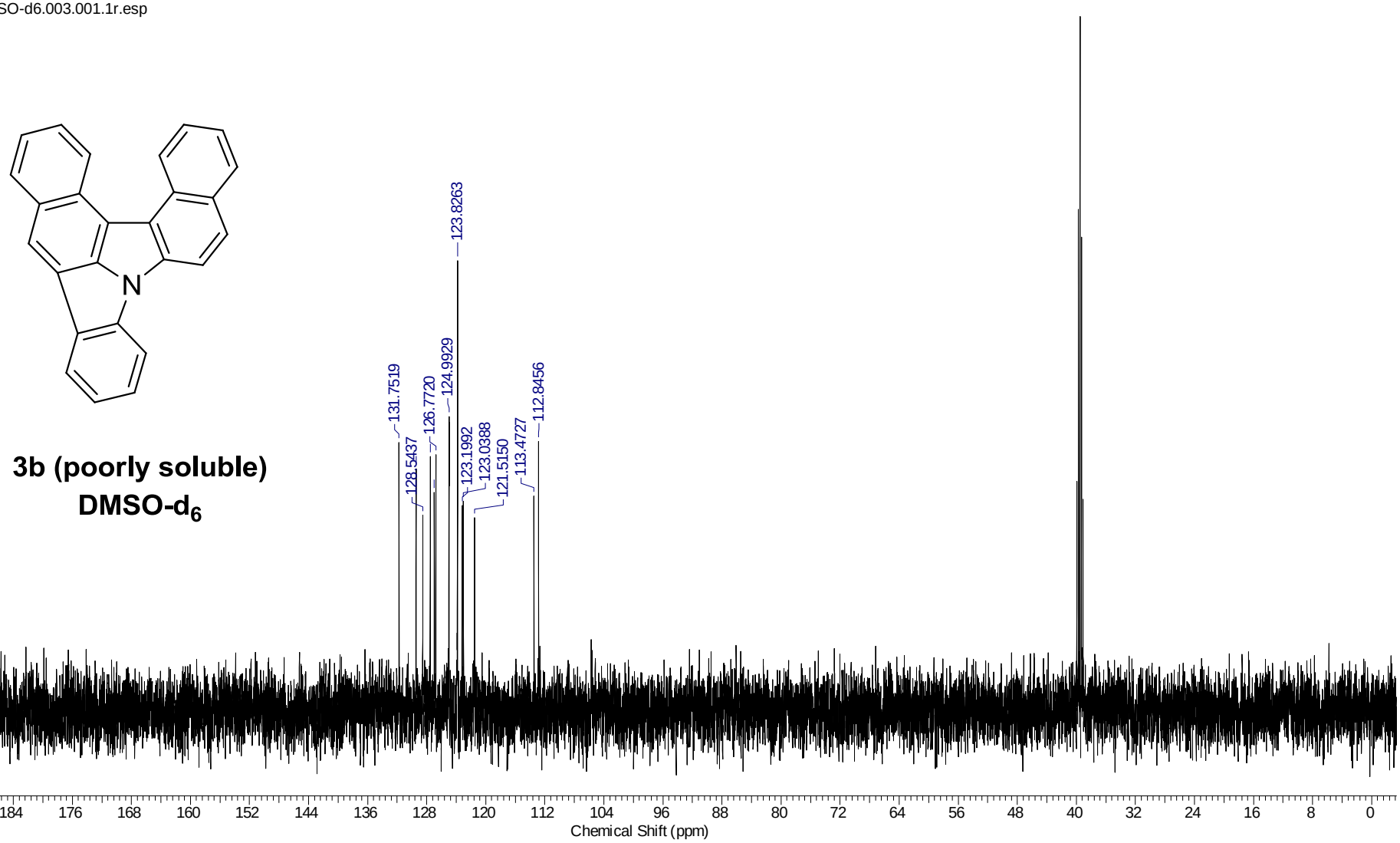


3b (poorly soluble)
DMSO-d_6


N
3b (poorly soluble)
DMSO-d6
140.6374
133.1267
131.9621
129.6512
127.7374
126.9791
125.2007
124.0362
123.4043
123.2418
121.7342
113.6819
113.0590
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

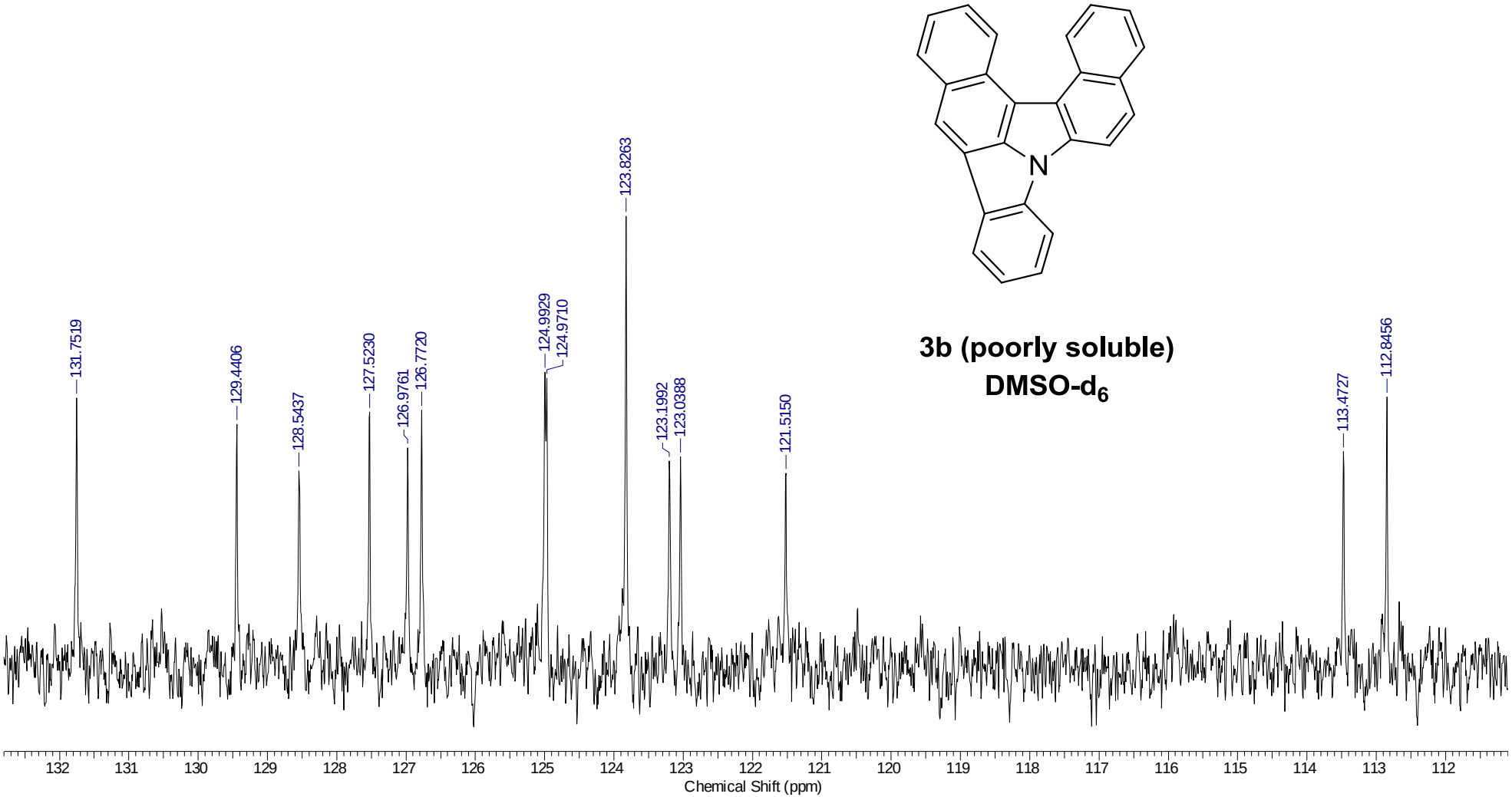

N
3b (poorly soluble)
DMSO-d6
140.6374
139.7076
133.9933
133.1267
131.9621
130.1747
129.6512
129.3894
129.0192
128.7484
127.7374
127.1867
126.9791
125.2007
124.0362
123.4043
123.2418
121.7342
119.8204
113.6819
113.0590
140
138
136
134
132
130
128
126
124
122
120
118
116
114
Chemical Shift (ppm)

CHR-573-b-DMSO-d6.003.001.1r.esp



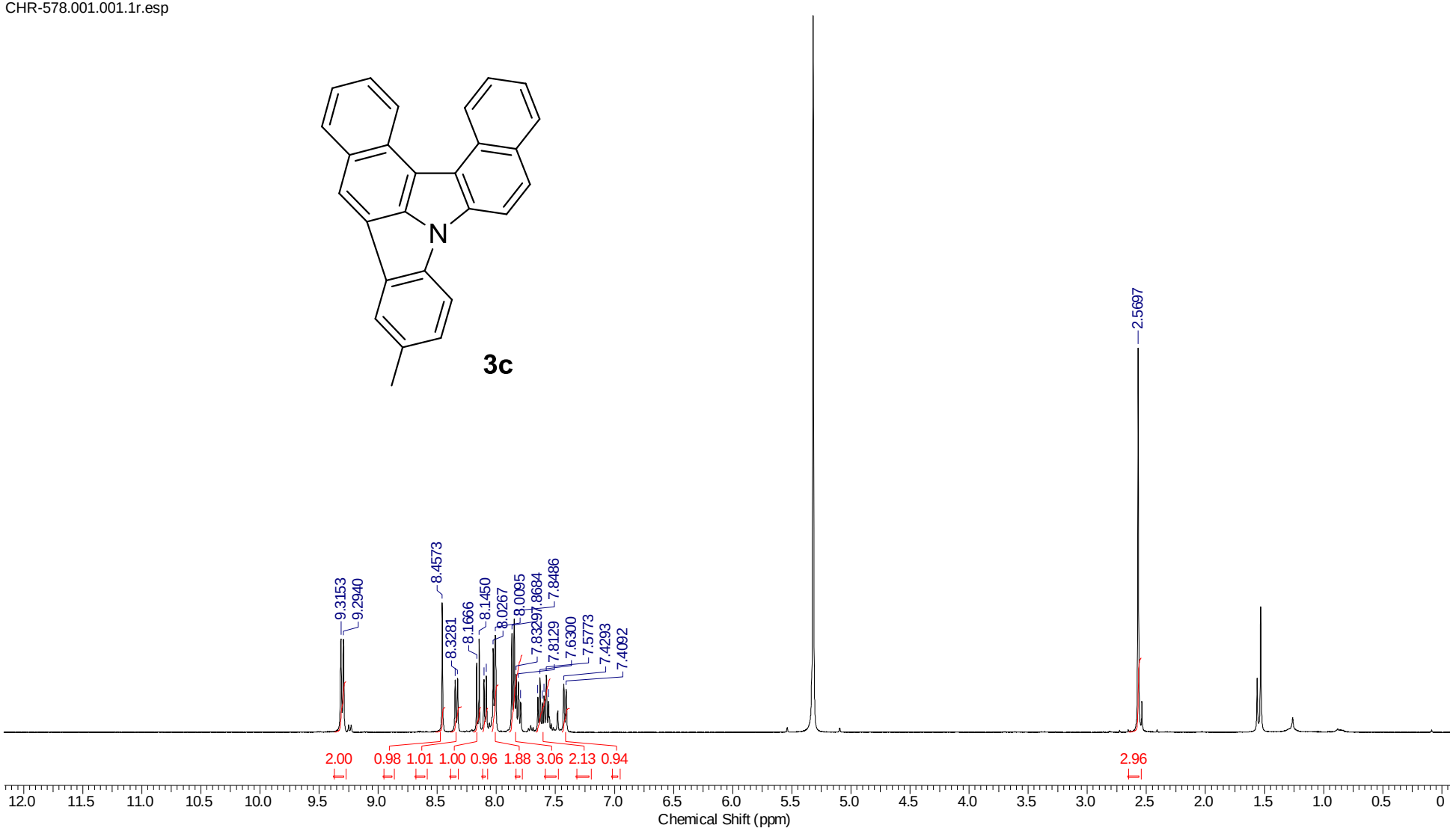
Dept Zoom: *Difficulties to dissolve*

CHR-573-b-DMSO-d6.003.001.1r.esp



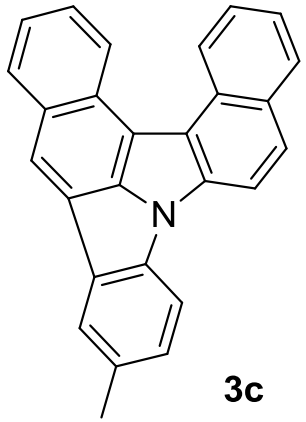
^{1}H:

CHR-578.001.001.1r.esp

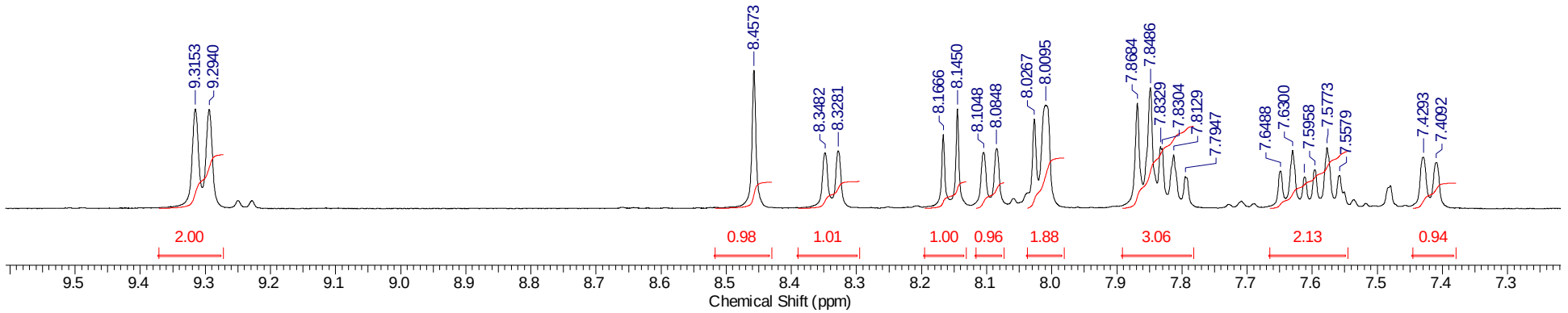


^{1}H Zoom:

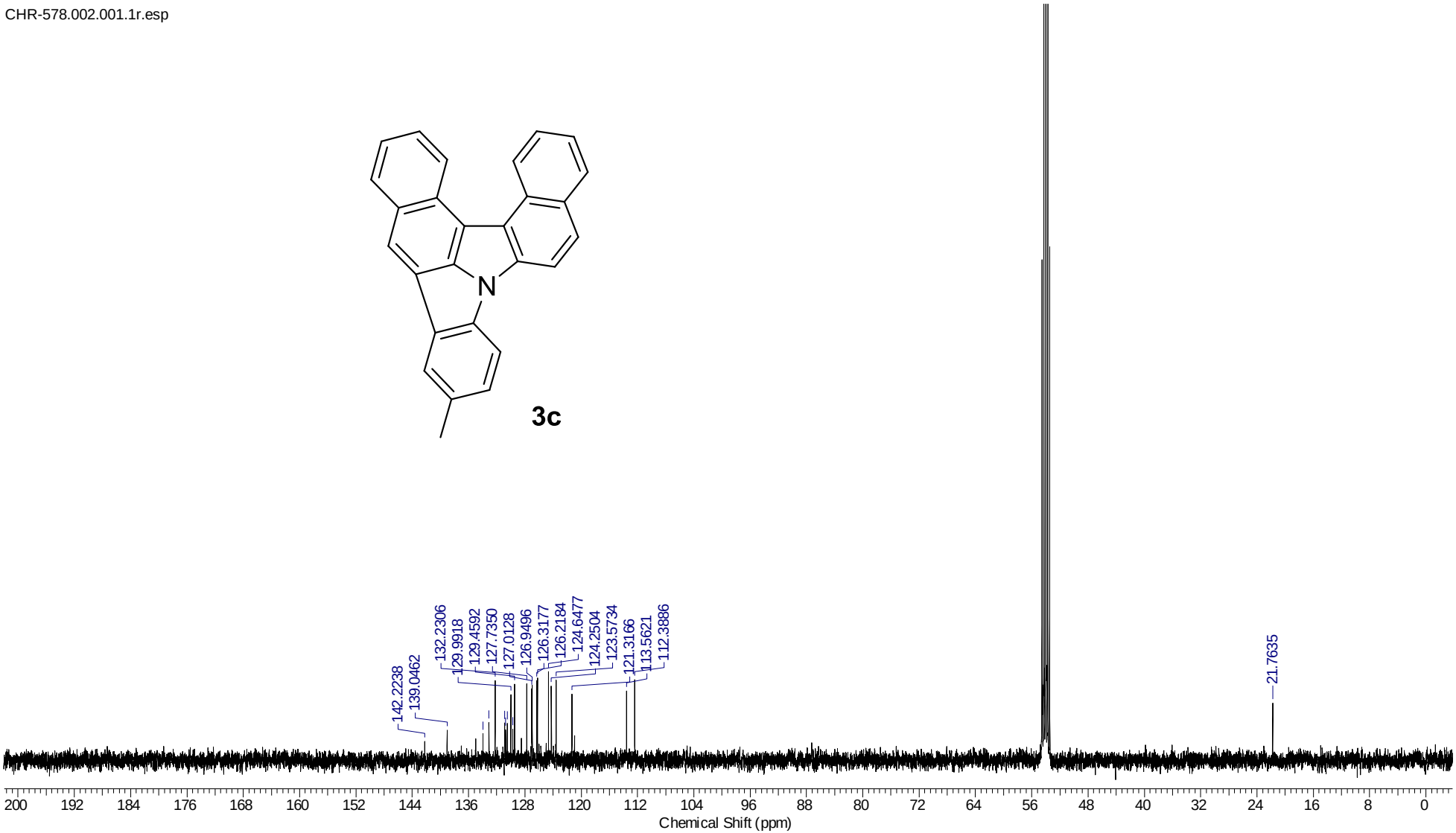
CHR-578.001.001.1r.esp



3c

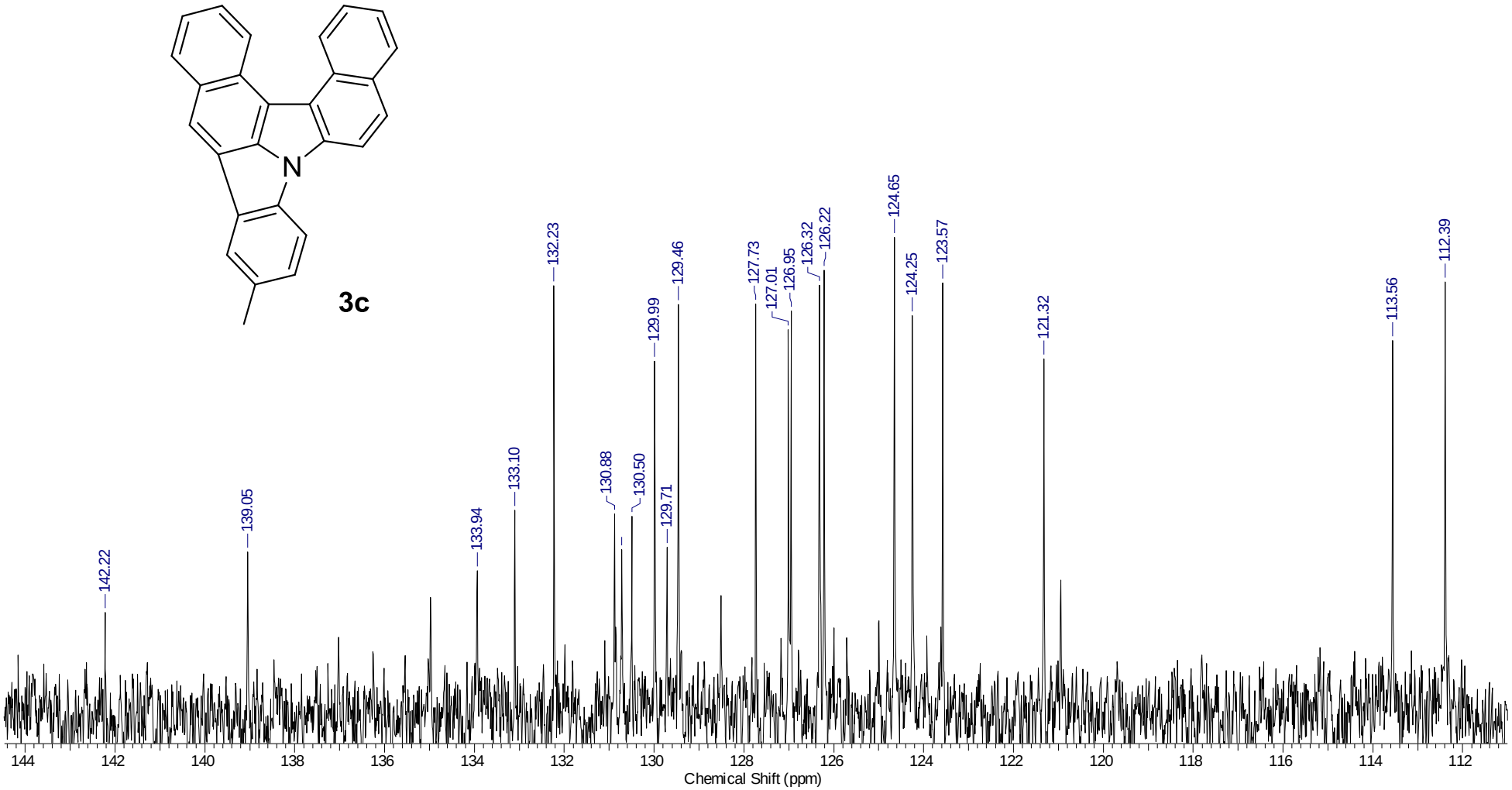


^{13}C:

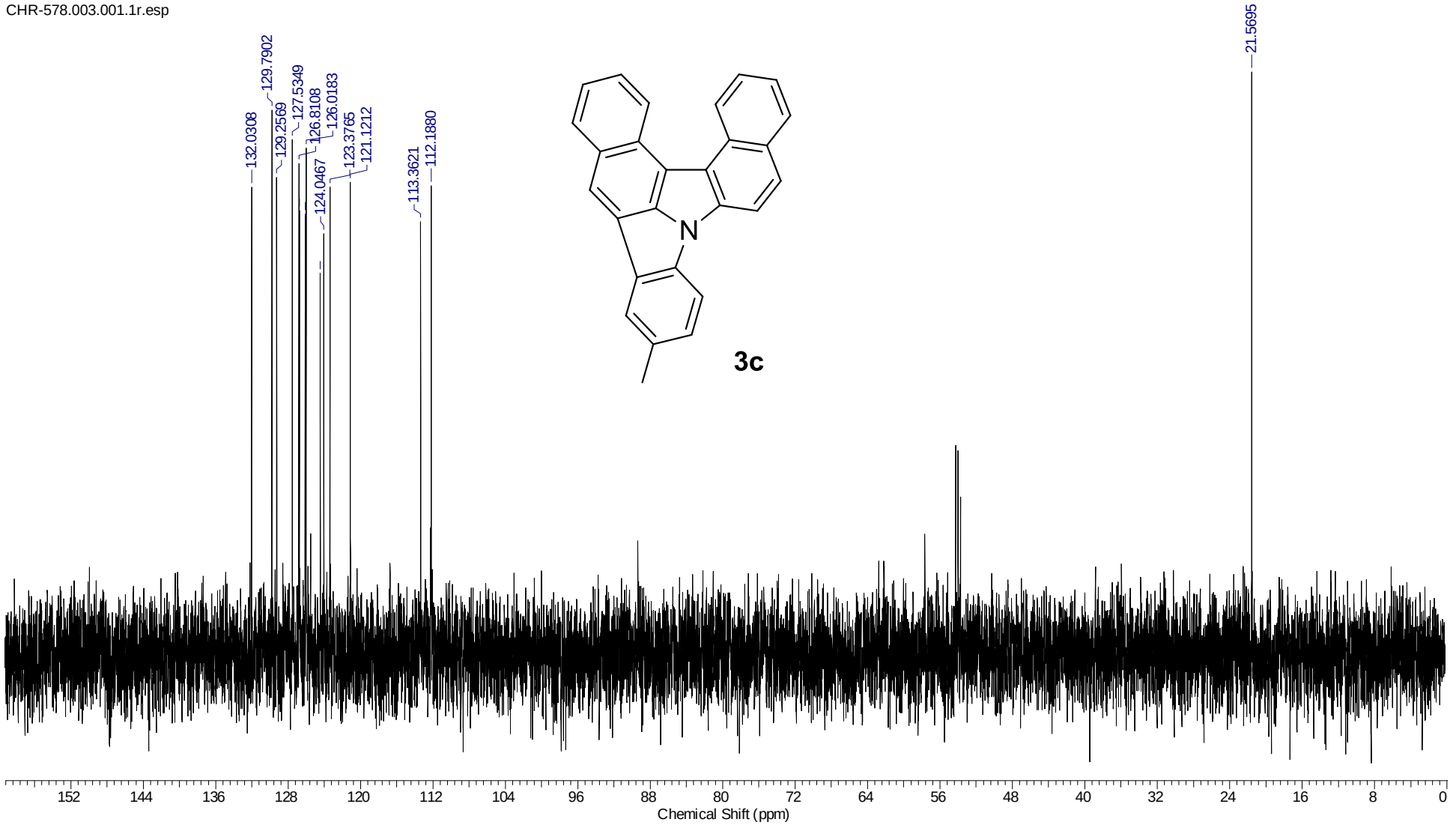

CHR-578.002.001.1r.esp
N
3c
142.2238
139.0462
132.2306
129.9918
129.4592
127.7350
127.0128
126.9496
126.3177
126.2184
124.6477
124.2504
123.5734
121.3166
113.5621
112.3886
21.7635
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

^{13}C Zoom:

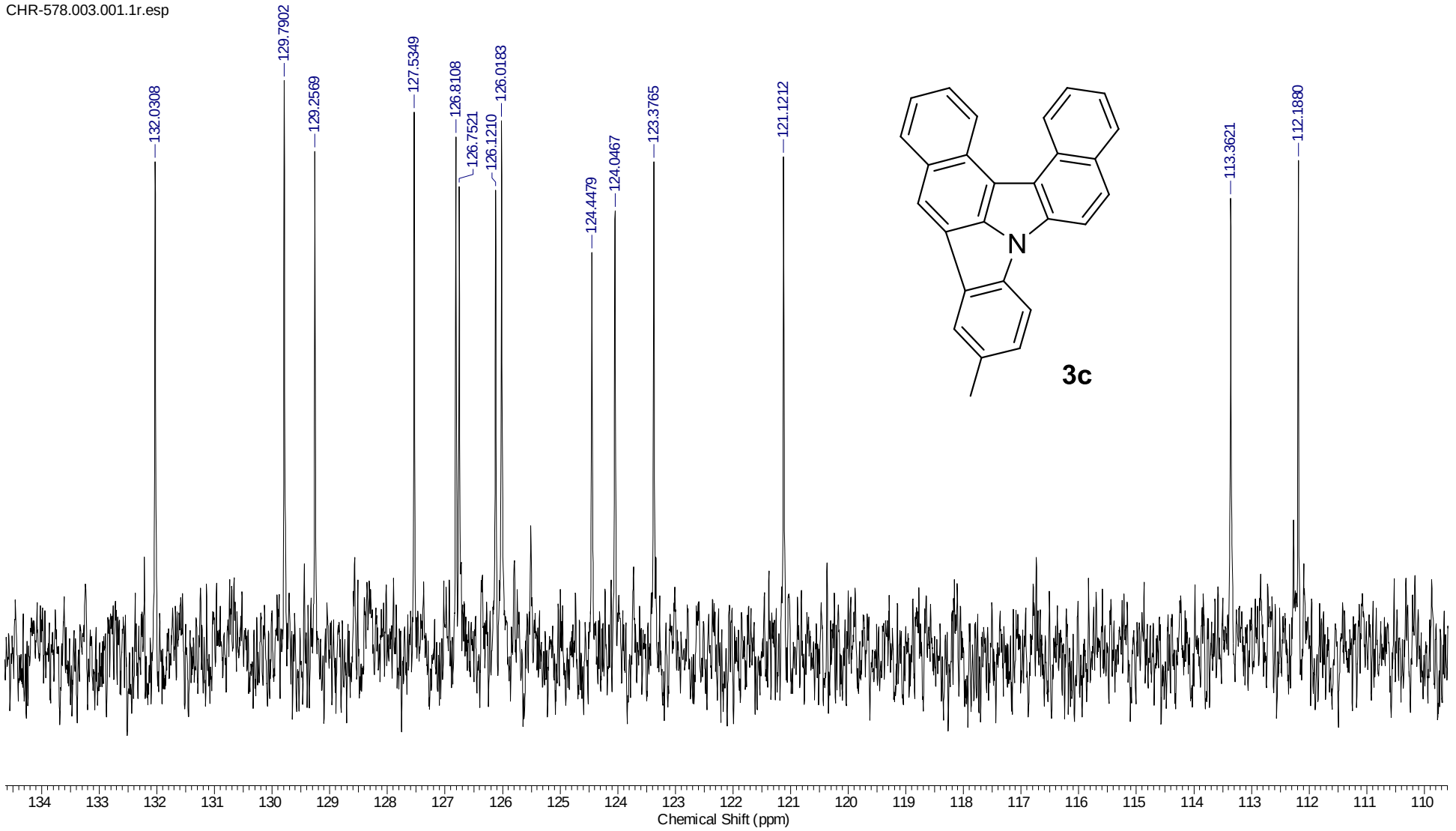
CHR-578.002.001.1r.esp



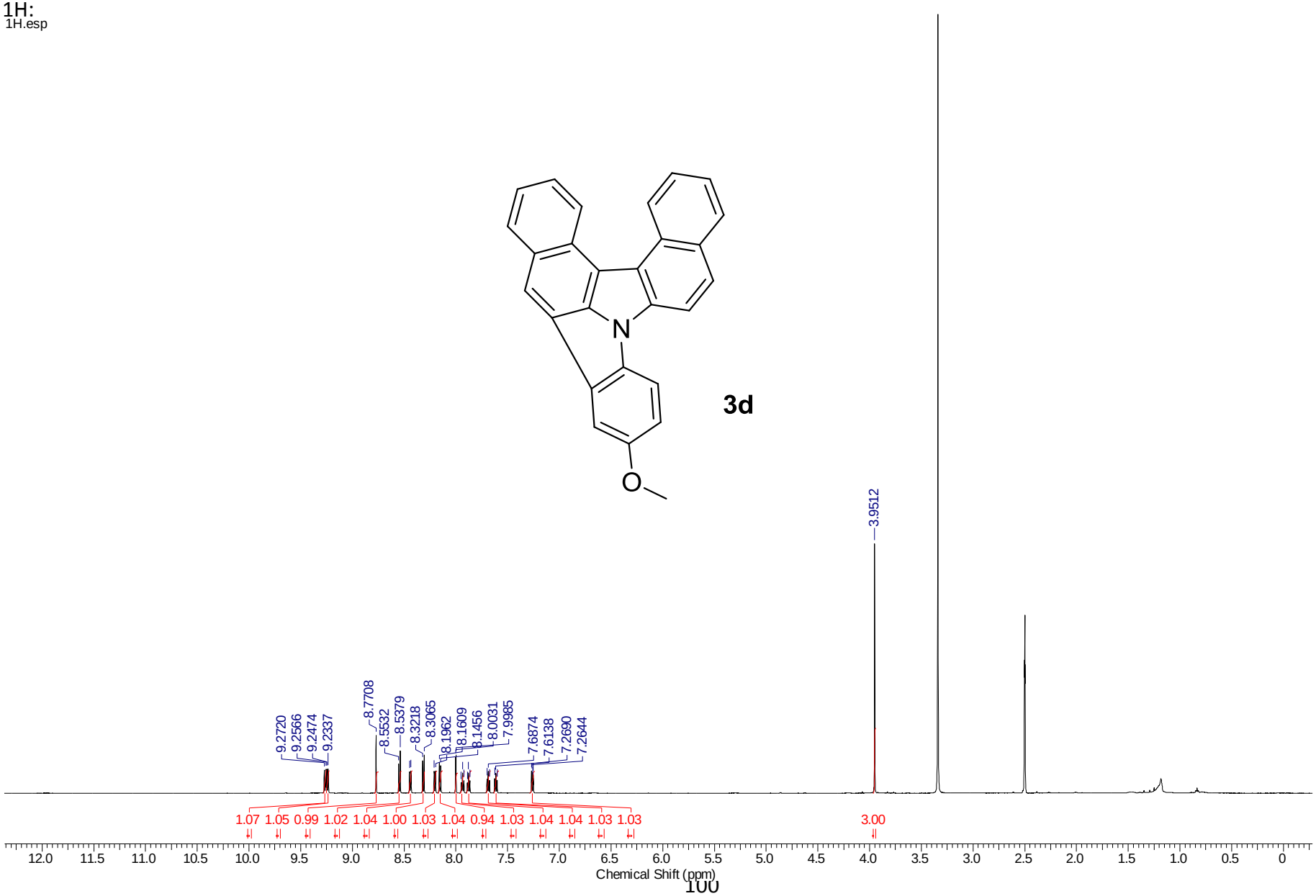
Dept:


CHR-578.003.001.1r.esp
132.0308
129.7902
129.2569
127.5349
126.8108
126.0183
124.0467
123.3765
121.1212
113.3621
112.1880
21.5695
N
3c
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

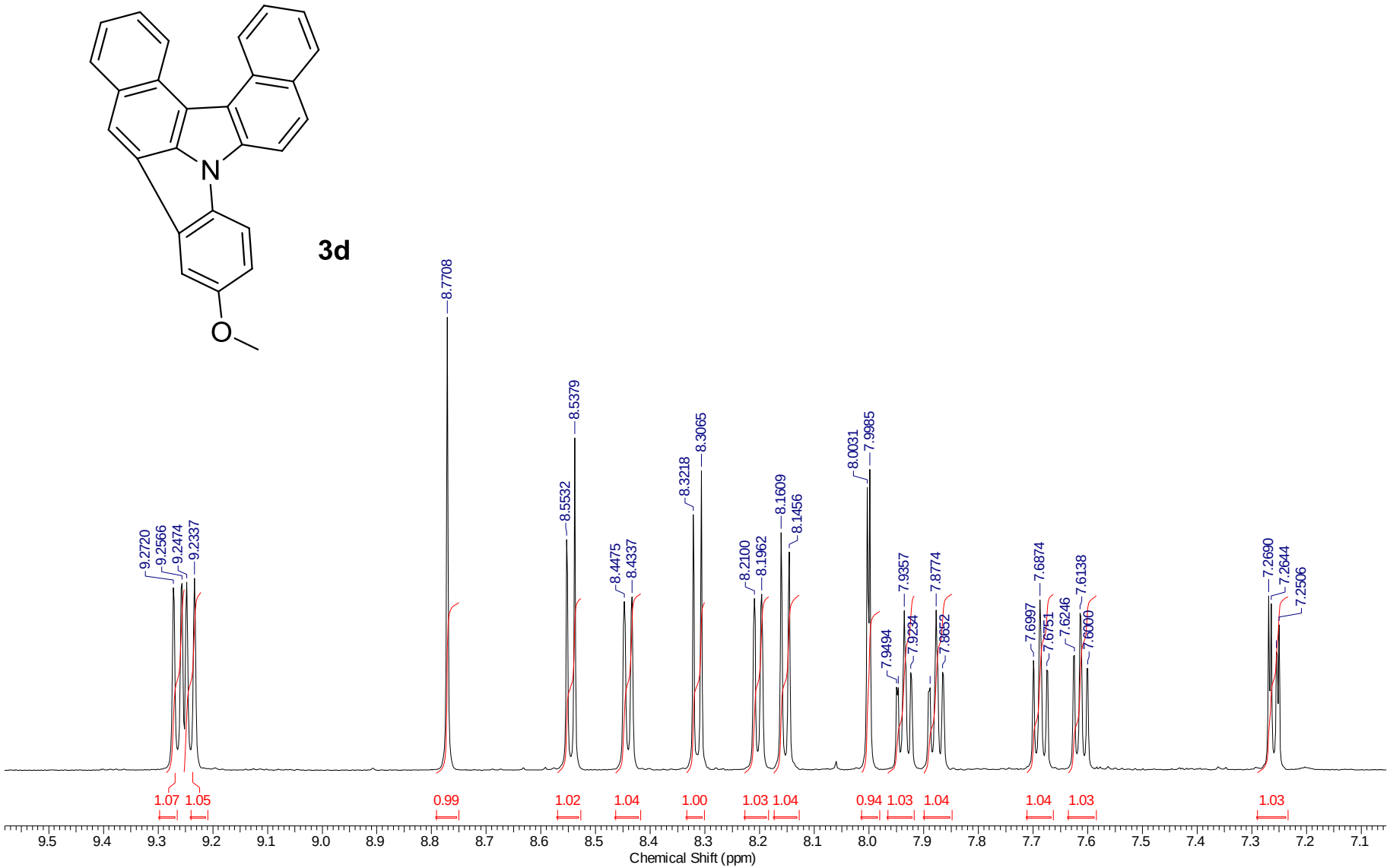
Dept Zoom:


CHR-578.003.001.1r.esp
132.0308
129.7902
129.2569
127.5349
126.8108
126.7521
126.1210
126.0183
124.4479
124.0467
123.3765
121.1212
113.3621
112.1880
N
3c
134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111 110
Chemical Shift (ppm)

1H:
1H.esp

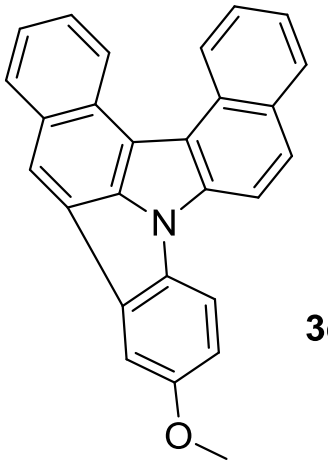

N
O
3d
9.2720
9.2566
9.2474
9.2337
8.7708
8.5532
8.5379
8.3218
8.3065
8.1962
8.1609
8.1456
8.0031
7.9985
7.6874
7.6138
7.2690
7.2644
3.9512
1.07 1.05 0.99 1.02 1.04 1.00 1.03 1.04 0.94 1.03 1.04 1.04 1.03 1.03
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

1H-Zoom:
1H.esp



13C:

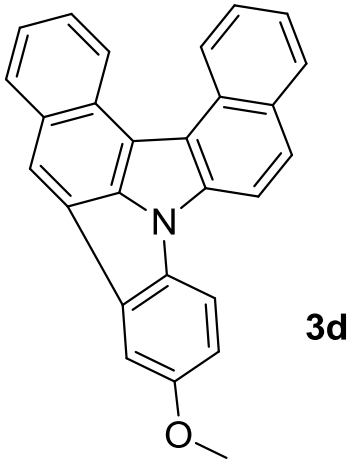
13C.esp



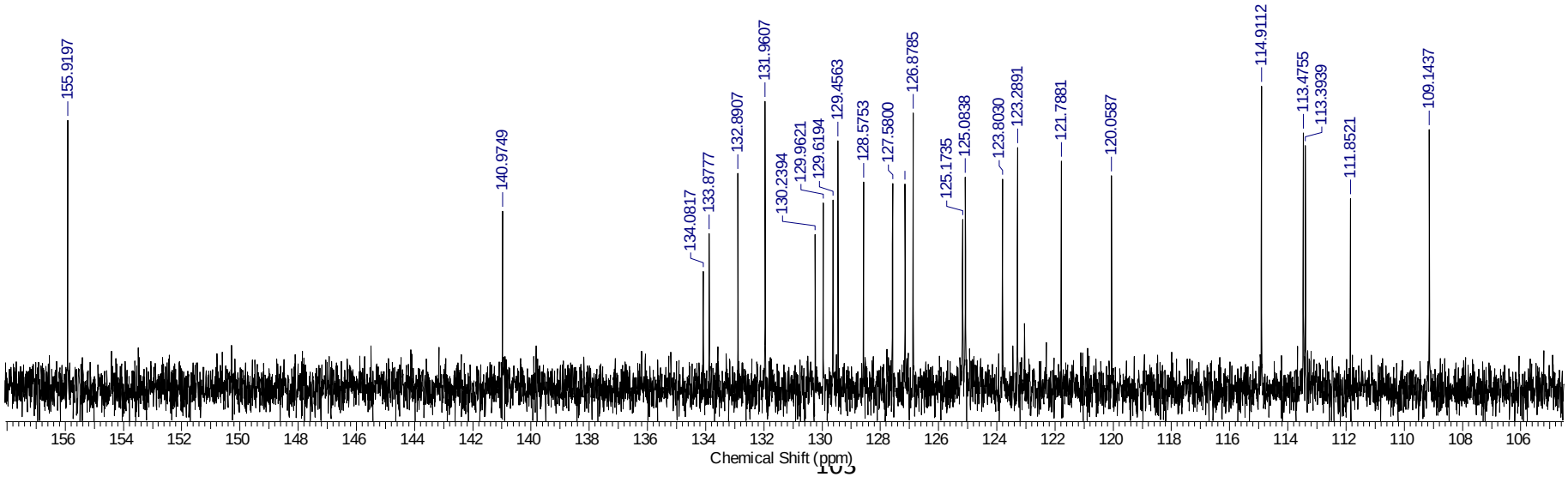
3d

13C-Zoom:

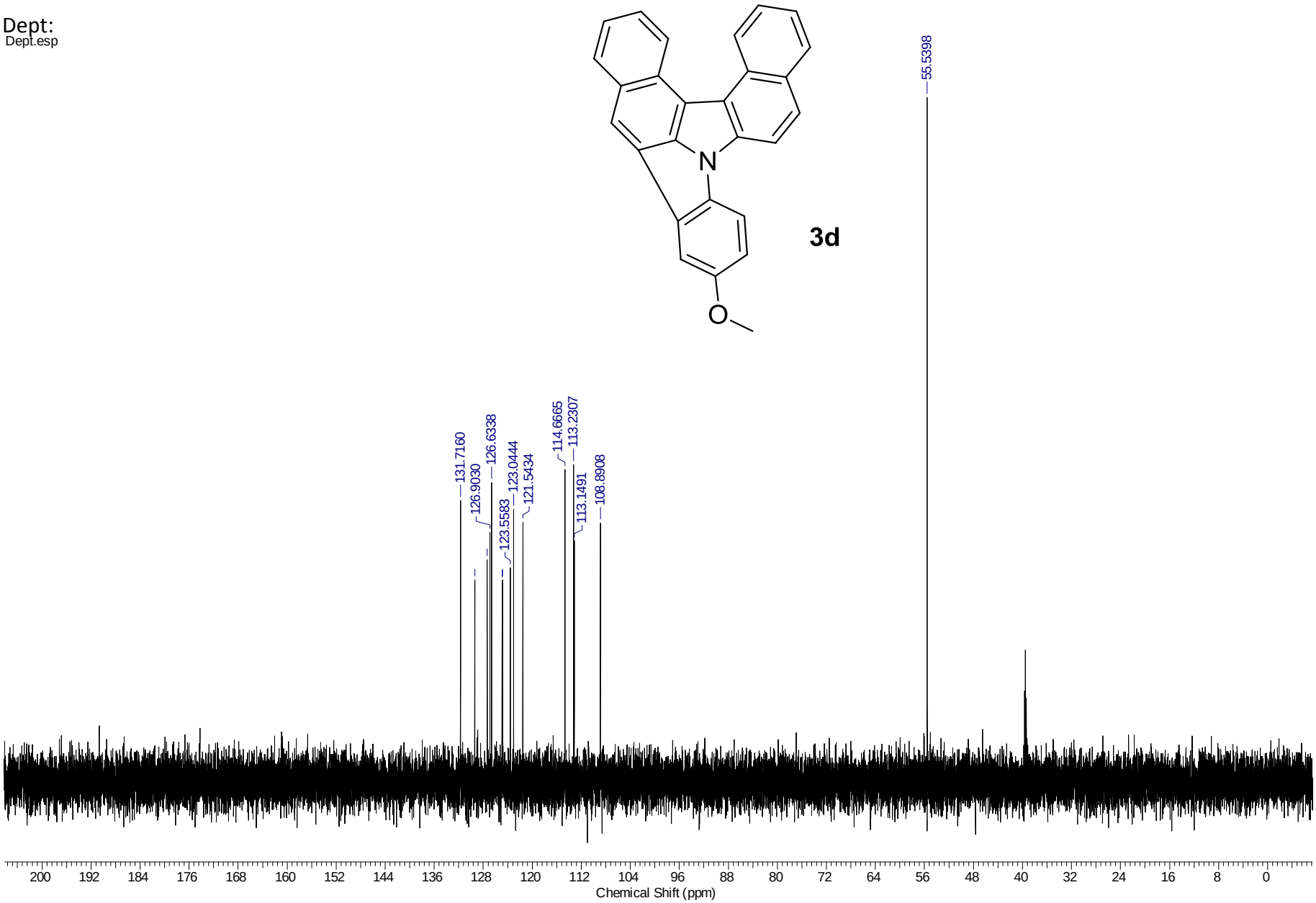
13C.esp



3d

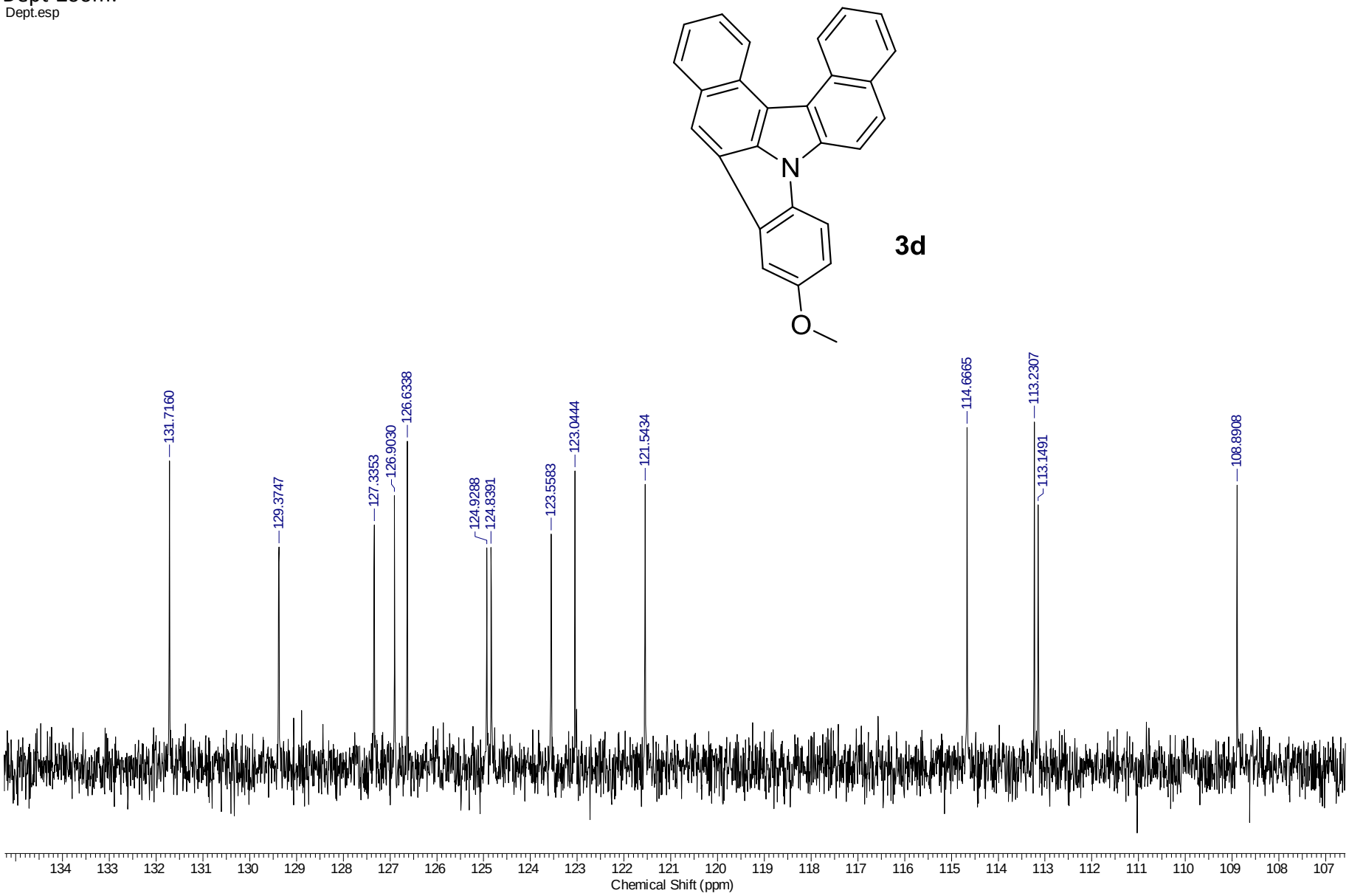


Dept:
Dept.esp



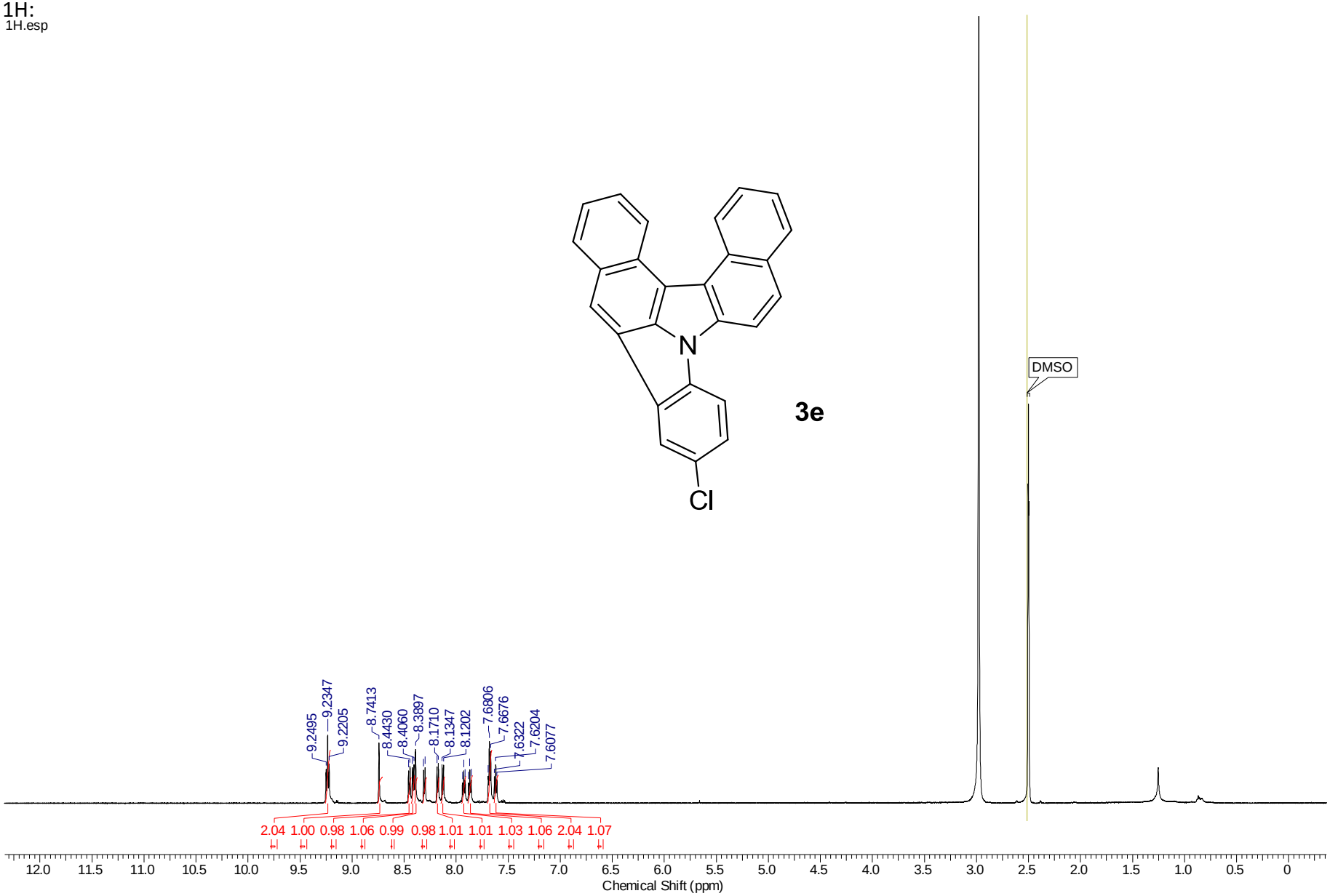
Dept-Zoom:

Dept.esp

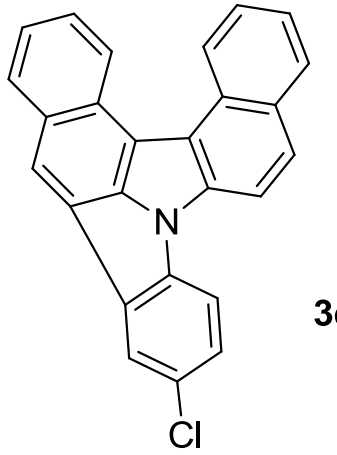


1H:

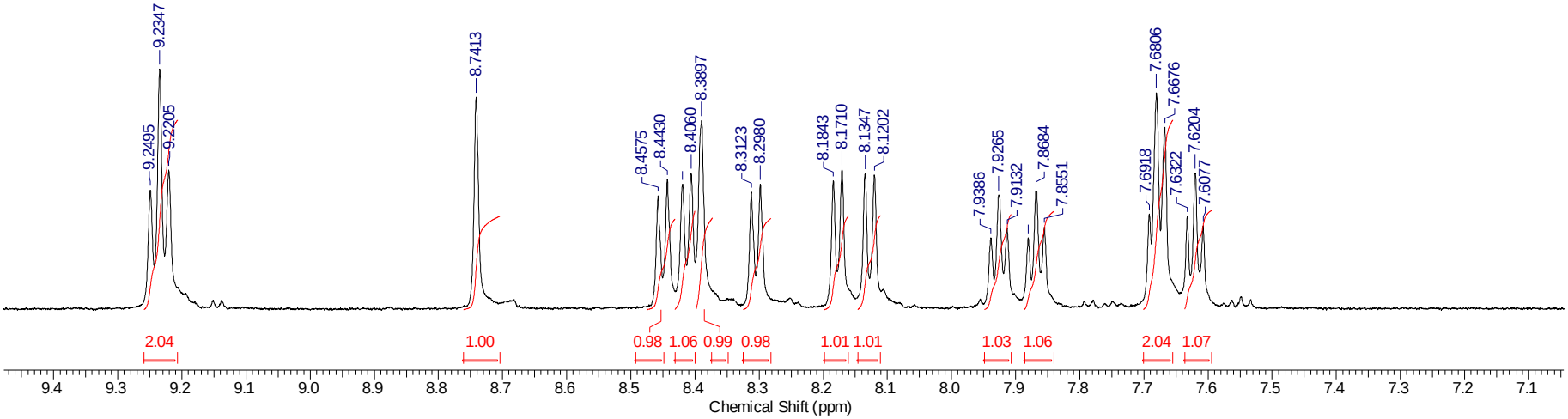
1H.esp


N
Cl
3e
DMSO
9.2495
9.2347
9.2205
8.7413
8.4430
8.4060
8.3897
8.1710
8.1347
8.1202
7.6806
7.6676
7.6322
7.6204
7.6077
2.04 1.00 0.98 1.06 0.99 0.98 1.01 1.01 1.03 1.06 2.04 1.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

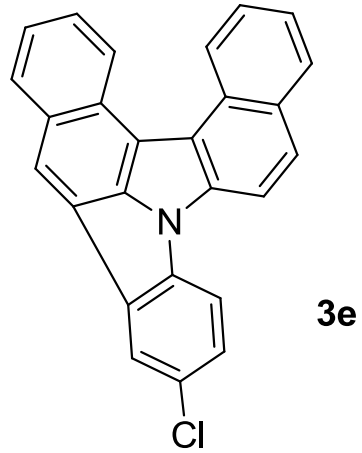
1H-Zoom:
1H.esp



3e



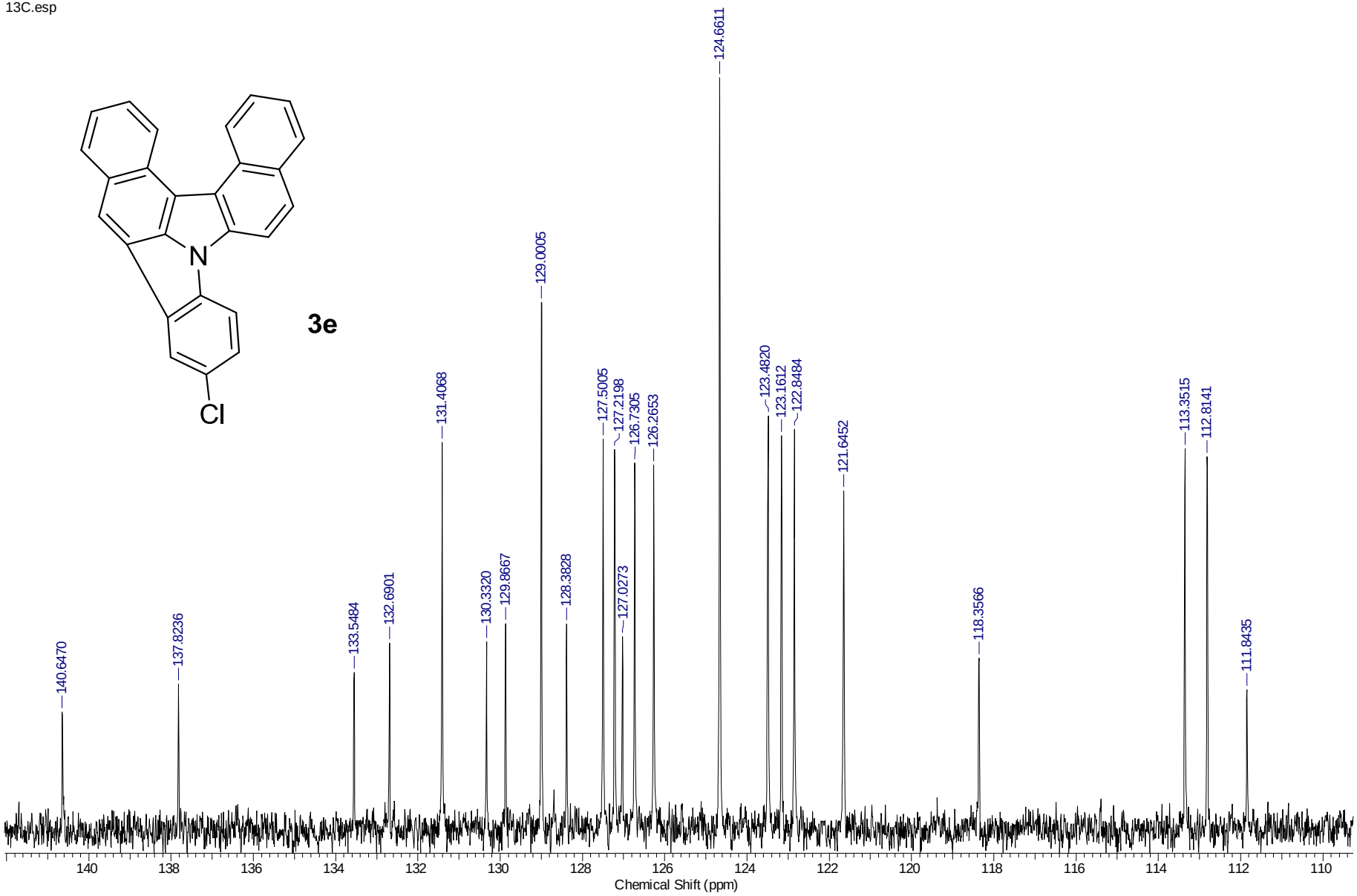
13C:
13C.esp



3e

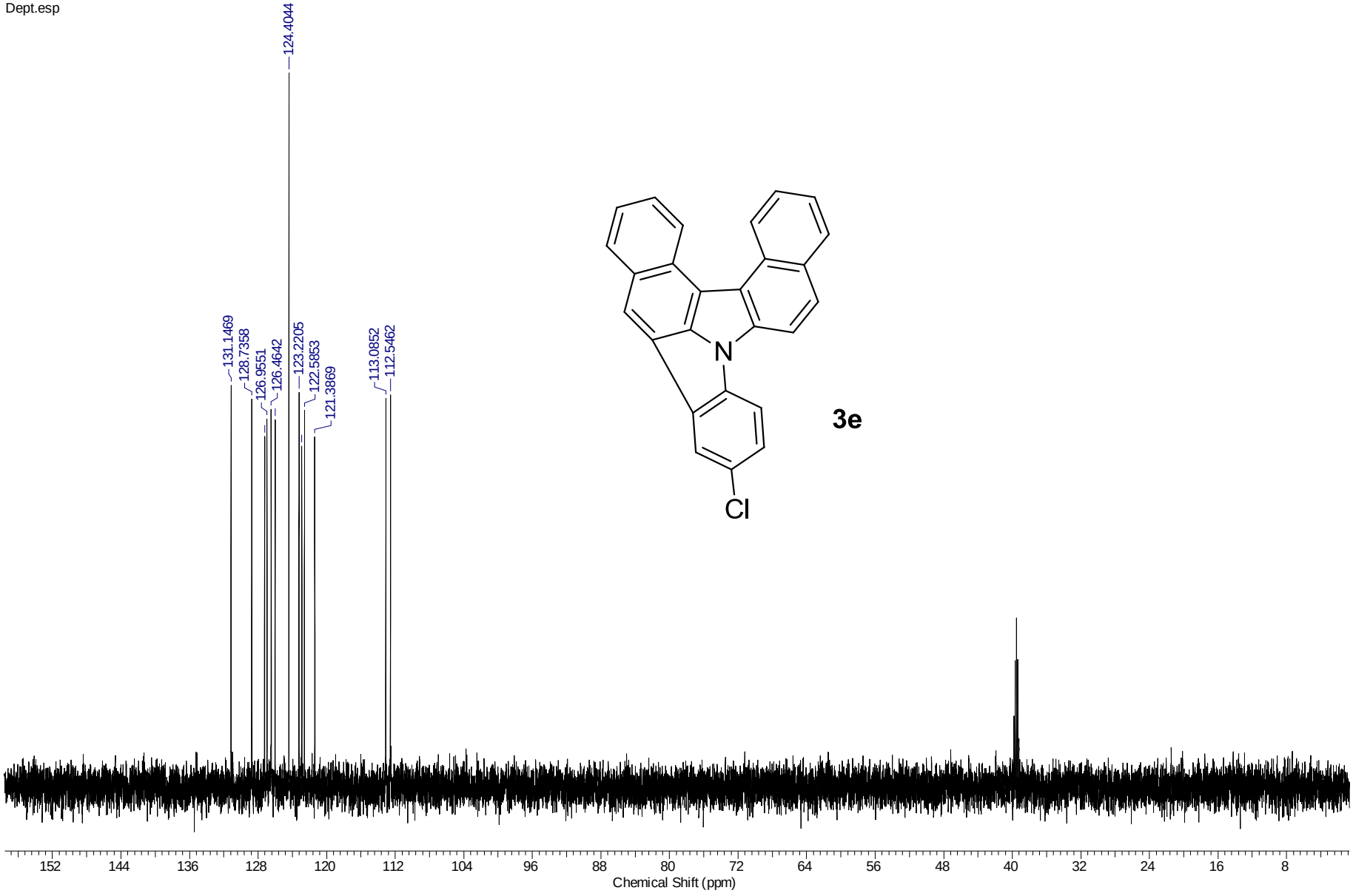
13C-Zoom:

13C.esp

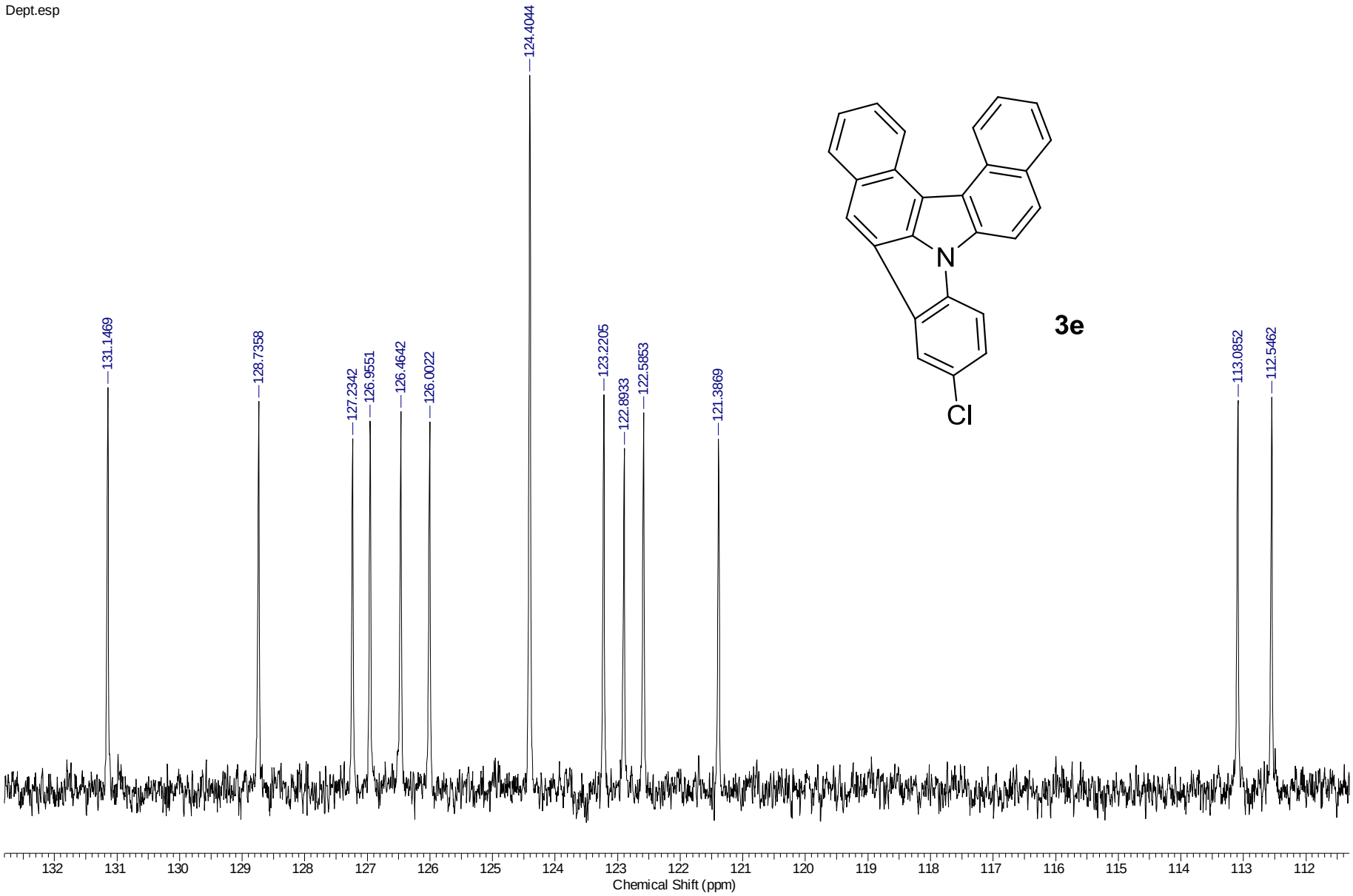


Dept:

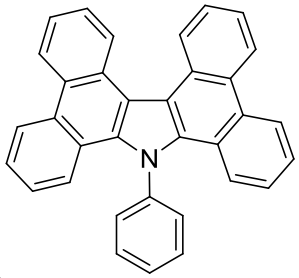
Dept.esp



Dept-Zoom:


Dept.esp
131.1469
128.7358
127.2342
126.9551
126.4642
126.0022
124.4044
123.2205
122.8933
122.5853
121.3869
113.0852
112.5462
N
Cl
3e
132
131
130
129
128
127
126
125
124
123
122
121
120
119
118
117
116
115
114
113
112
Chemical Shift (ppm)

1.5 XYZ-Coordinates, UV/VIS/Luminsescence Spectra, and HOMO/LUMO Orbitals

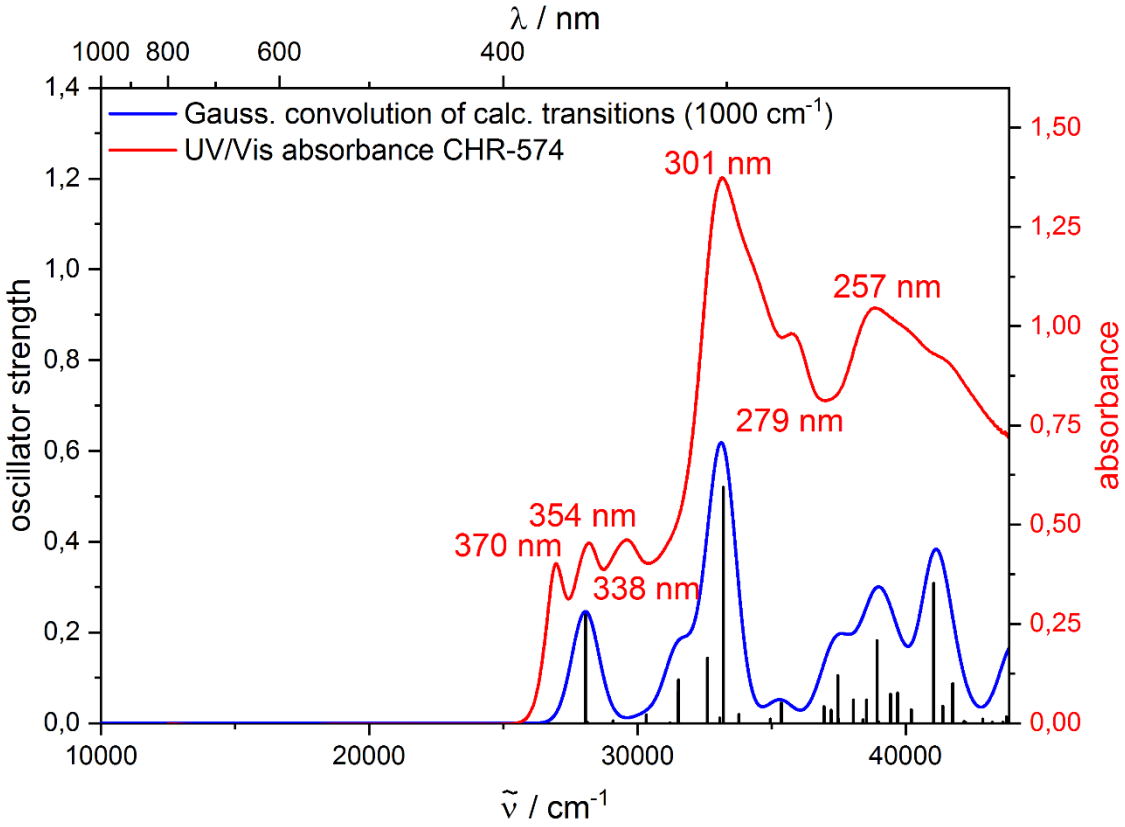


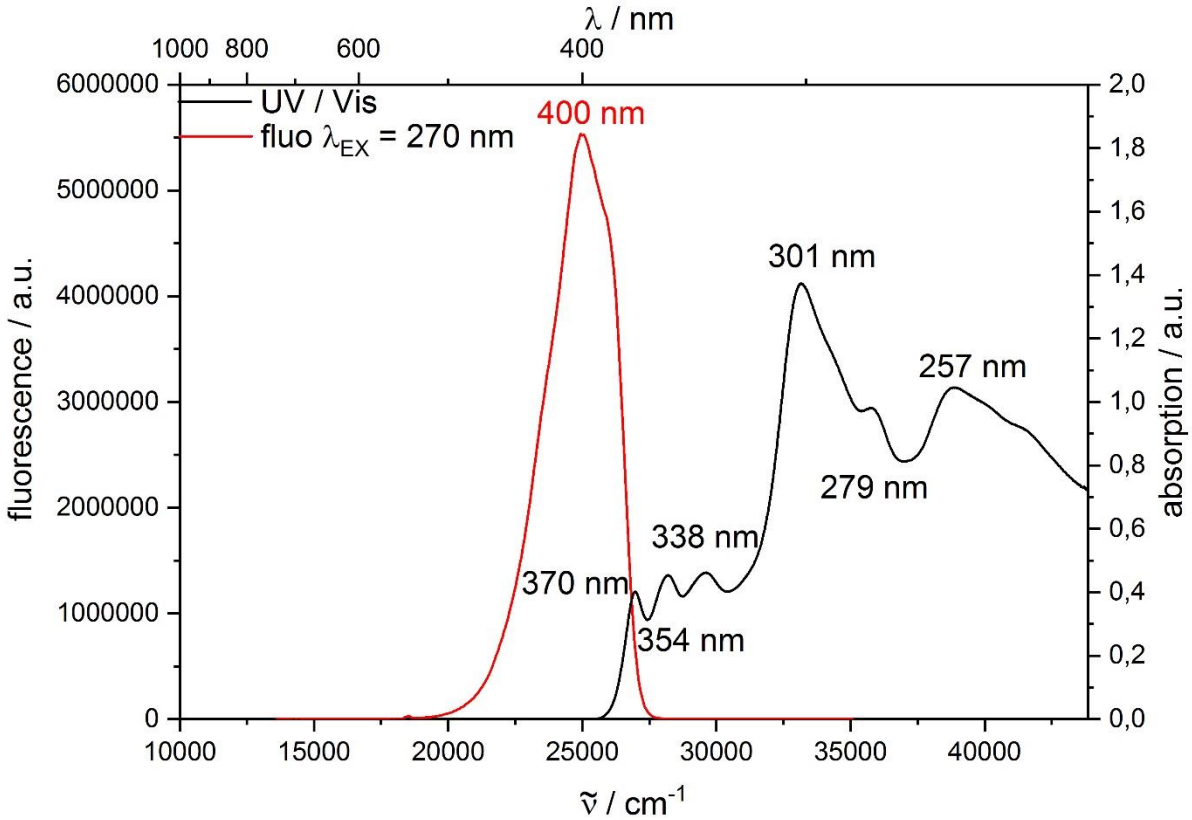
2a

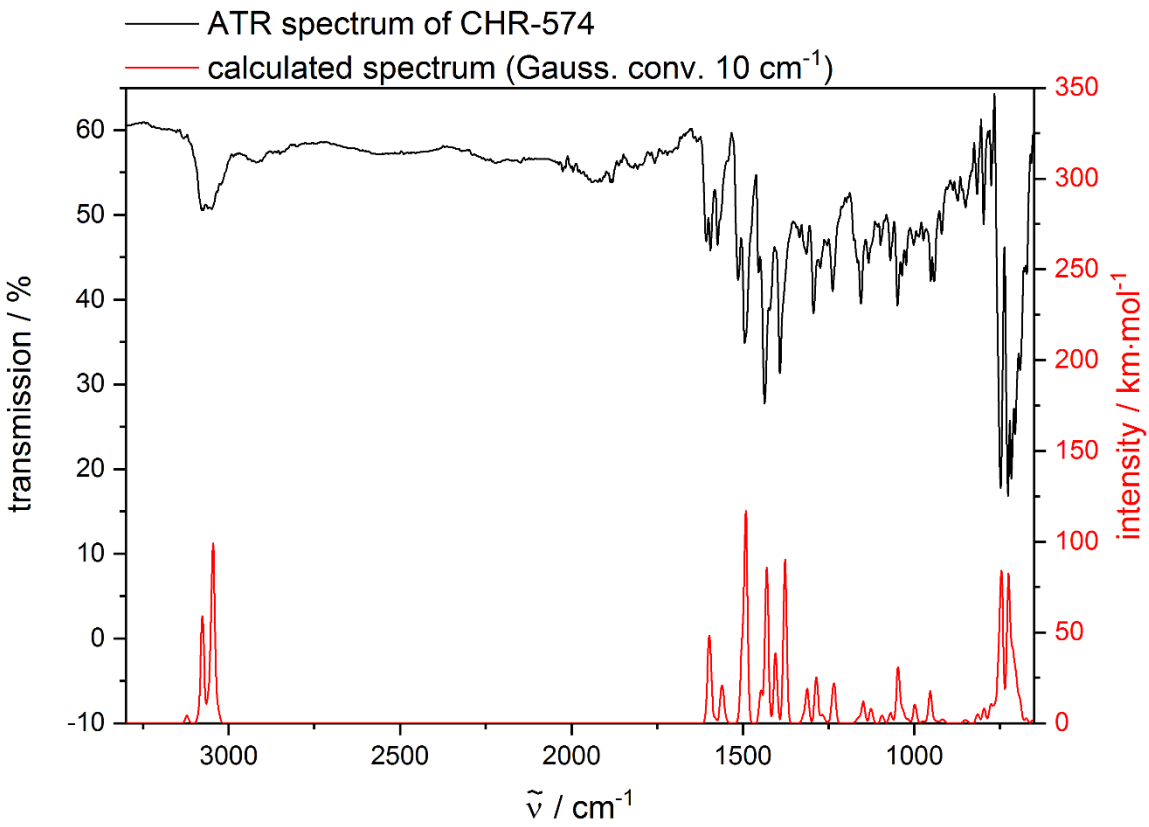
56

C	-4.01501	-2.70137	-0.52949
C	-3.63812	-3.95239	-0.96501
C	-1.33259	-3.29764	-0.83002
C	-3.06831	-1.70750	-0.21700
C	-1.69066	-2.03356	-0.32288
C	-2.28254	-4.24464	-1.13895
H	-5.06934	-2.47658	-0.46615
C	-3.47304	-0.35315	0.13896
H	-4.39212	-4.69091	-1.20526
H	-1.97680	-5.20486	-1.53488
H	-0.29260	-3.51388	-1.01582
C	-2.51113	0.69851	0.19484
C	-1.13255	0.32503	0.02323
C	-0.71831	-1.00680	-0.04238
C	-4.81704	-0.04001	0.40810
C	-2.95763	2.00434	0.48943
N	0.00024	1.13383	-0.00086
C	0.71755	-1.00720	0.04227
C	1.13256	0.32432	-0.02438
C	1.68940	-2.03433	0.32322
C	2.51131	0.69695	-0.19632
C	3.06722	-1.70912	0.21695
C	3.47270	-0.35513	-0.13966
C	4.01335	-2.70352	0.52959
H	5.06781	-2.47951	0.46583

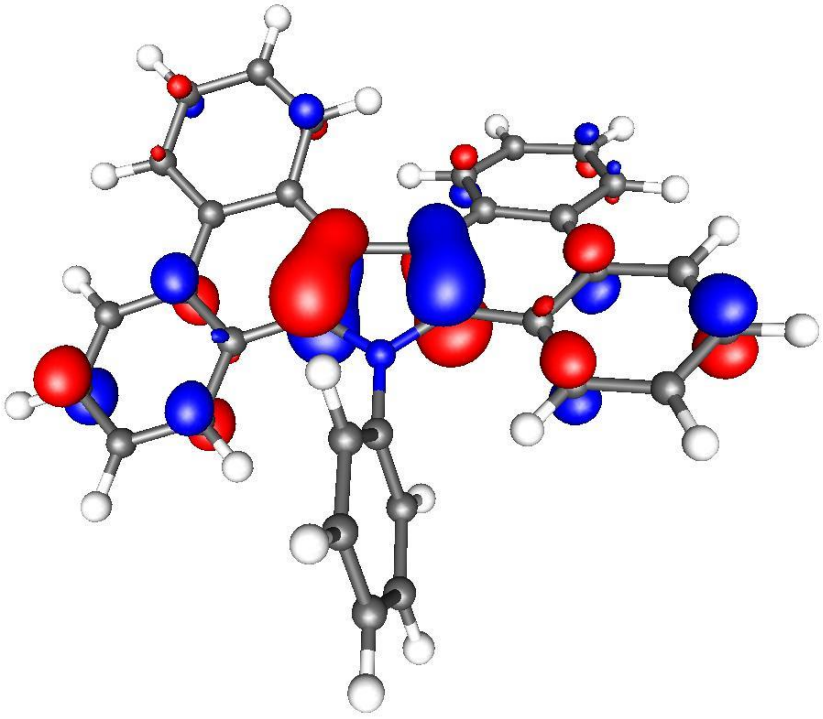
C	1.33065	-3.29795	0.83102
C	3.63577	-3.95410	0.96574
C	2.28006	-4.24541	1.14018
H	4.38935	-4.69304	1.20599
H	1.97379	-5.20522	1.53668
C	4.81690	-0.04264	-0.40858
C	2.95836	2.00241	-0.49168
H	0.29056	-3.51344	1.01710
C	0.29870	3.24589	1.17029
C	0.30116	4.63447	1.16857
C	0.00220	5.33077	0.00195
C	0.00085	2.55836	0.00013
C	-0.29747	4.63631	-1.16558
C	-0.29636	3.24773	-1.16913
H	0.52718	2.68697	2.06790
H	0.53366	5.17294	2.07817
H	0.00278	6.41315	0.00267
H	-0.52940	5.17620	-2.07448
H	-0.52541	2.69021	-2.06746
C	5.22691	1.23980	-0.69855
H	5.55506	-0.83051	-0.40652
C	4.28690	2.27119	-0.73380
H	2.25474	2.81309	-0.55431
H	6.27019	1.44098	-0.90524
H	4.59284	3.28324	-0.96654
C	-4.28598	2.27376	0.73180
H	-2.25373	2.81485	0.55116
C	-5.22642	1.24272	0.69752
H	-5.55547	-0.82766	0.40669
H	-4.59151	3.28610	0.96381
H	-6.26953	1.44446	0.90450


λ / nm
1000 800 600 400
Gauss. convolution of calc. transitions (1000 cm-1)
UV/Vis absorbance CHR-574
301 nm
257 nm
279 nm
354 nm
370 nm
338 nm
oscillator strength
absorbance
ν̃ / cm-1

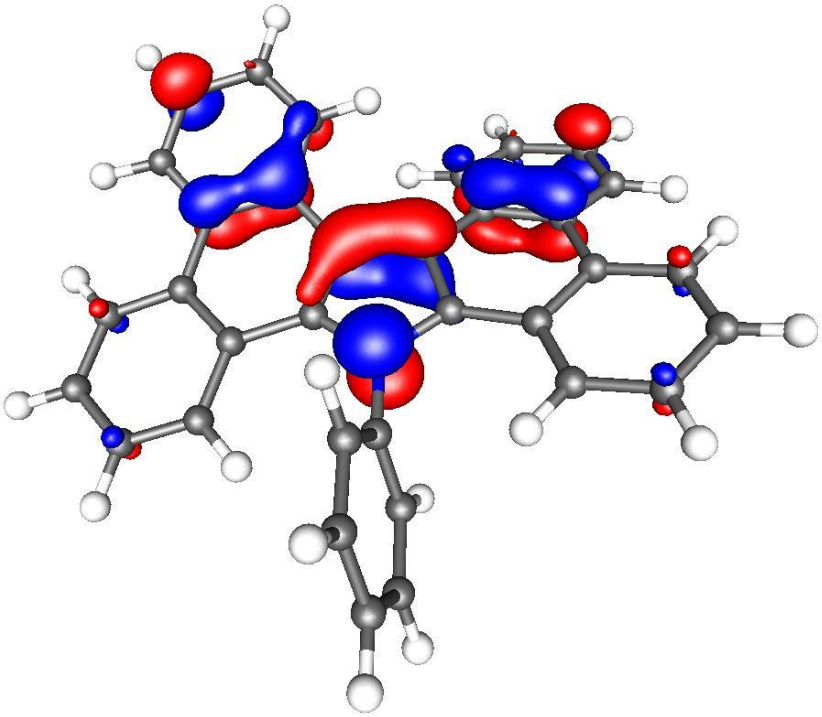

λ / nm
1000 800 600 400
UV / Vis
fluo λEX = 270 nm
400 nm
301 nm
257 nm
279 nm
338 nm
370 nm
354 nm
fluorescence / a.u.
absorption / a.u.
ν̃ / cm-1


ATR spectrum of CHR-574
calculated spectrum (Gauss. conv. 10 cm-1)
transmission / %
intensity / km·mol-1
ν̃ / cm-1
60
50
40
30
20
10
0
-10
350
300
250
200
150
100
50
0
3000
2500
2000
1500
1000

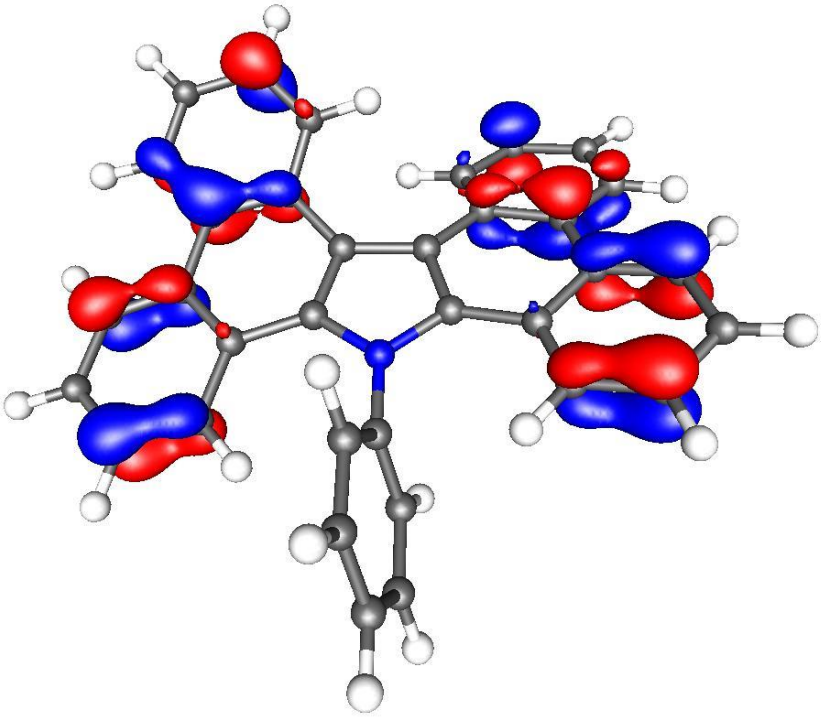
HOMO 0 eV



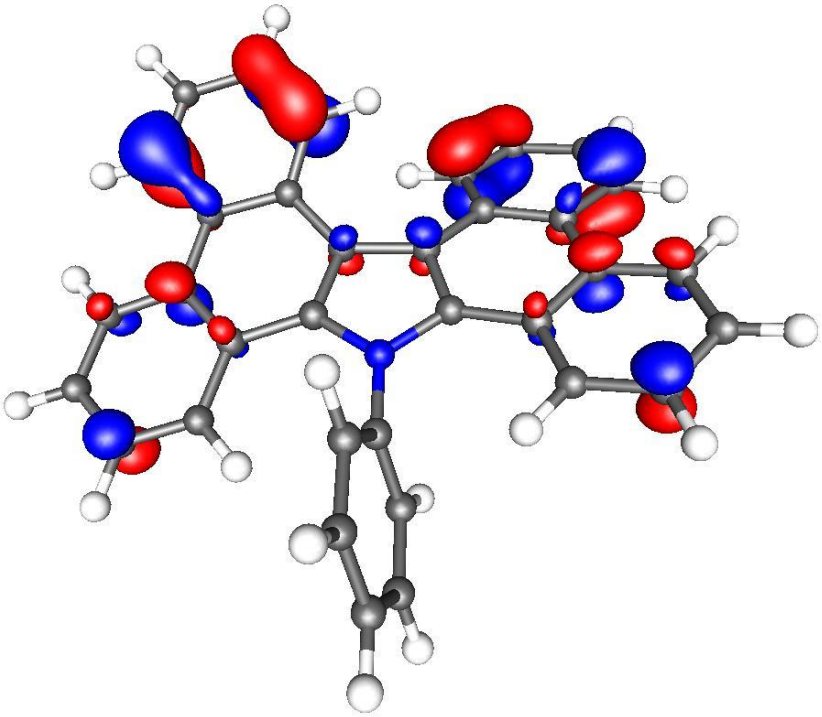
HOMO-1 -0.32 eV



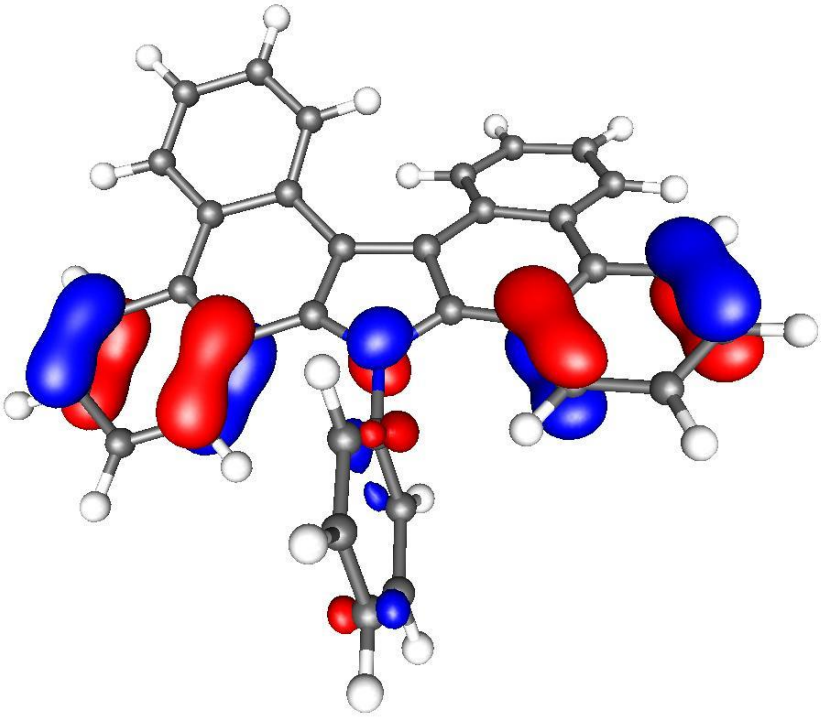
HOMO-2 -0.90 eV



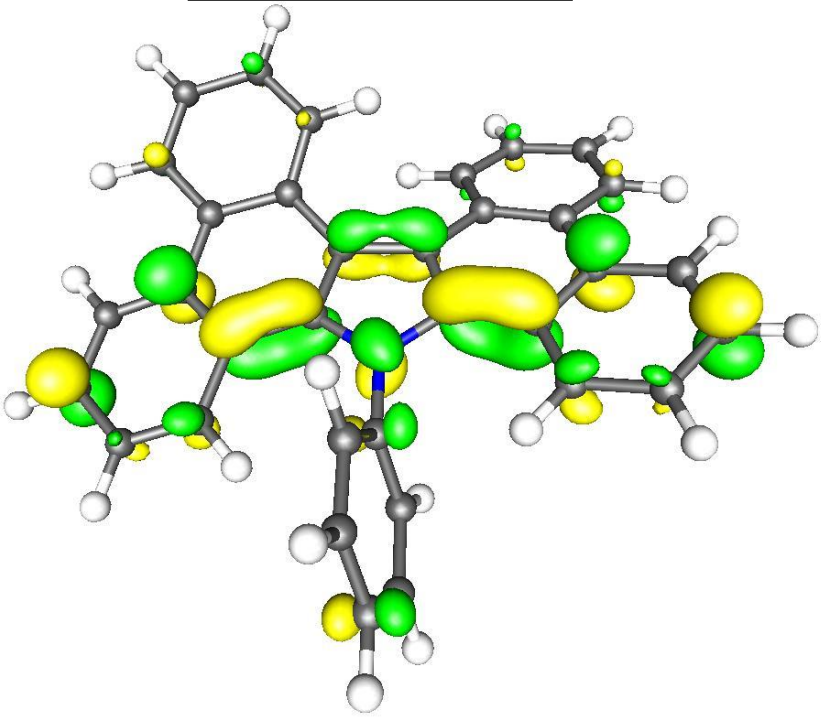
HOMO-3 -0.95 eV



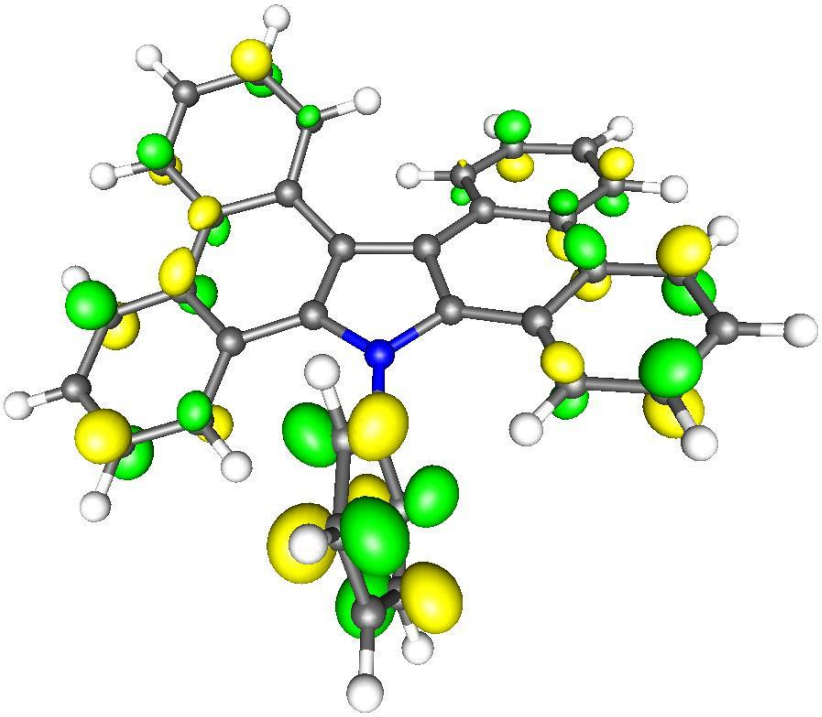
HOMO-4 -1.76 eV



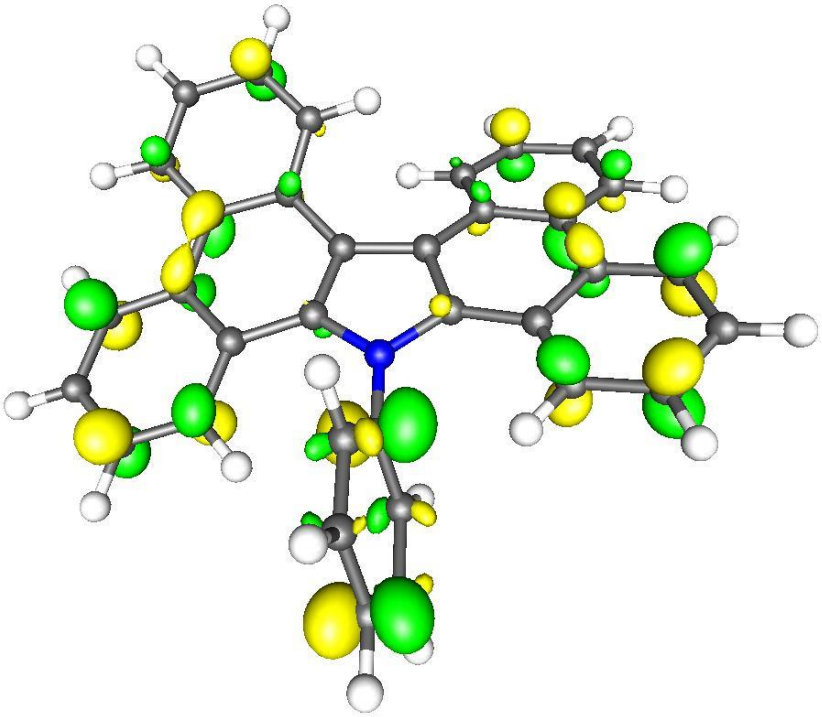
LUMO 3.95 eV



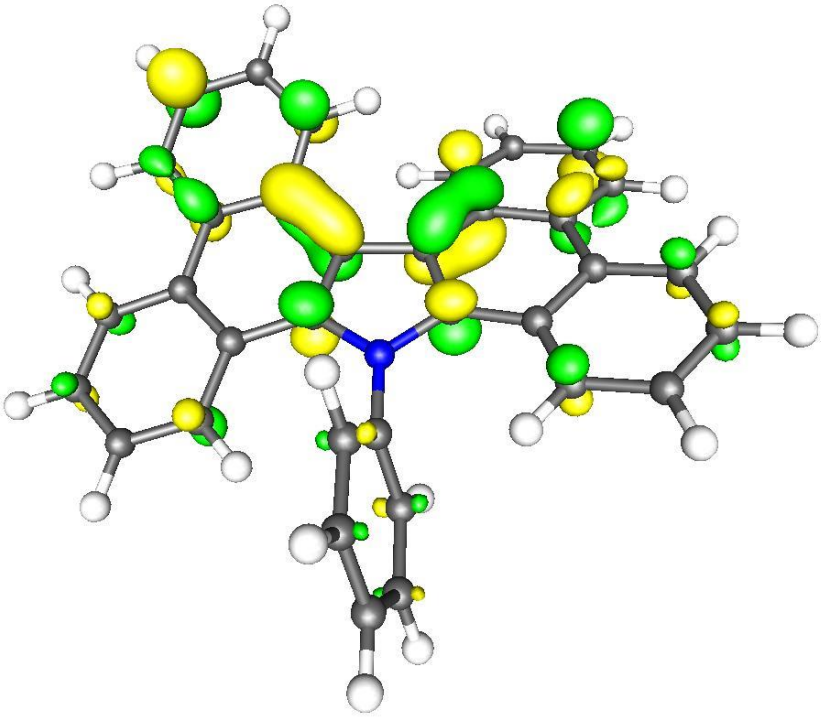
LUMO+1 4.11 eV



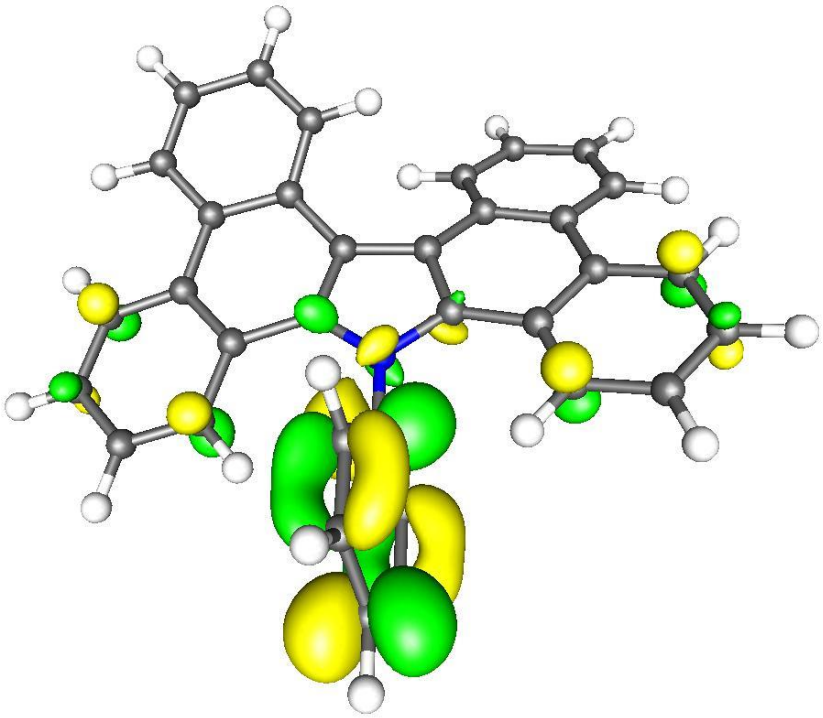
LUMO+2 4.23 eV

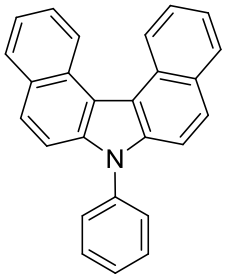


LUMO+3 4.32 eV



LUMO+4 4.38 eV



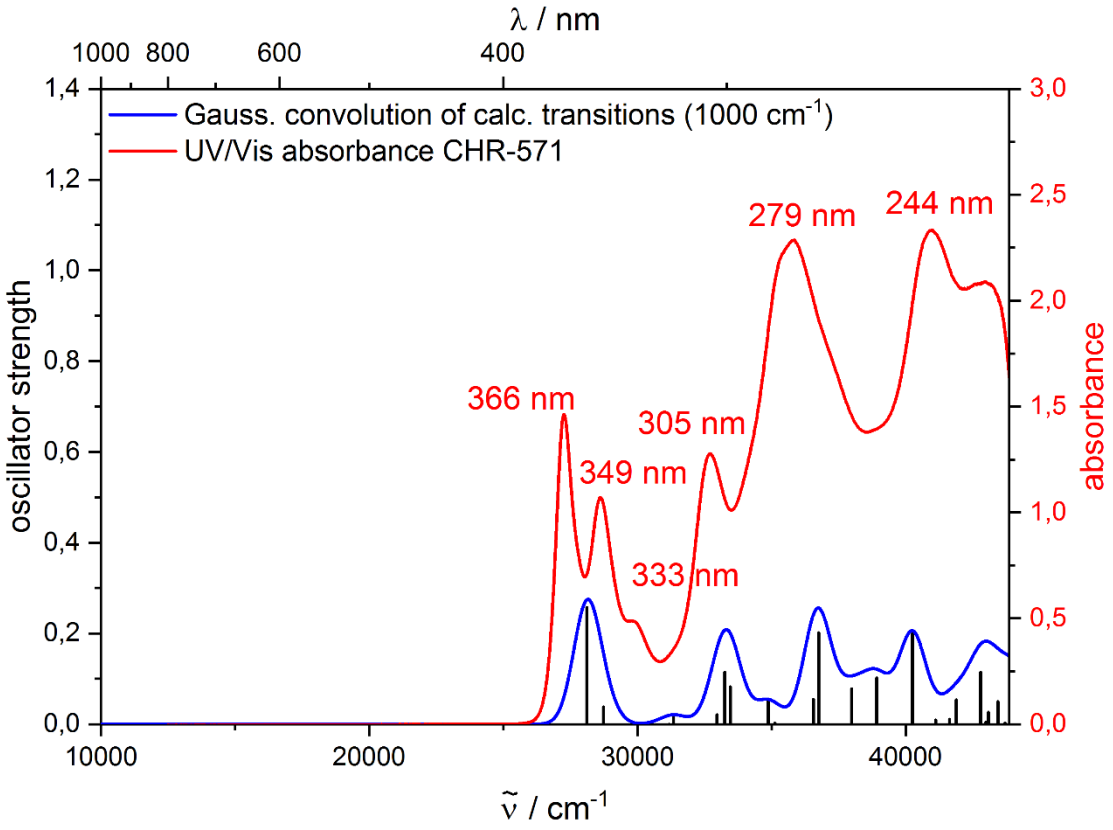


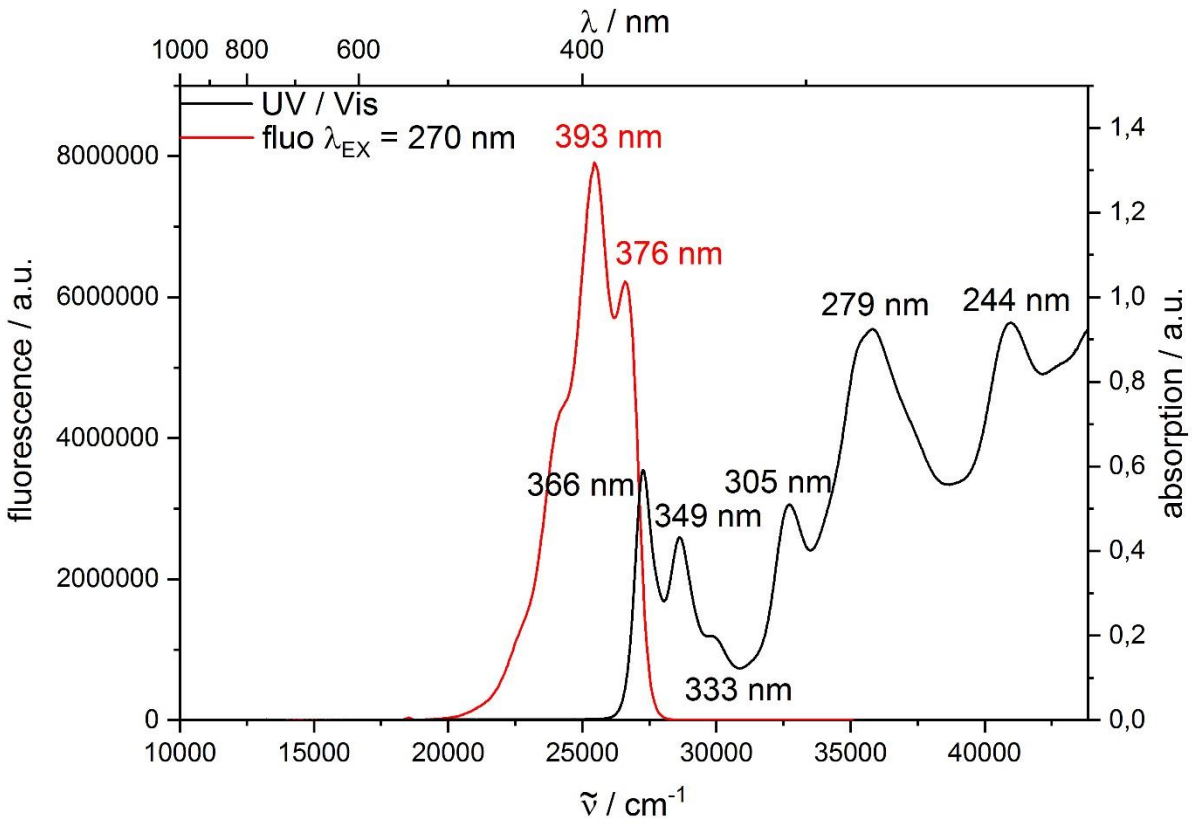
2b

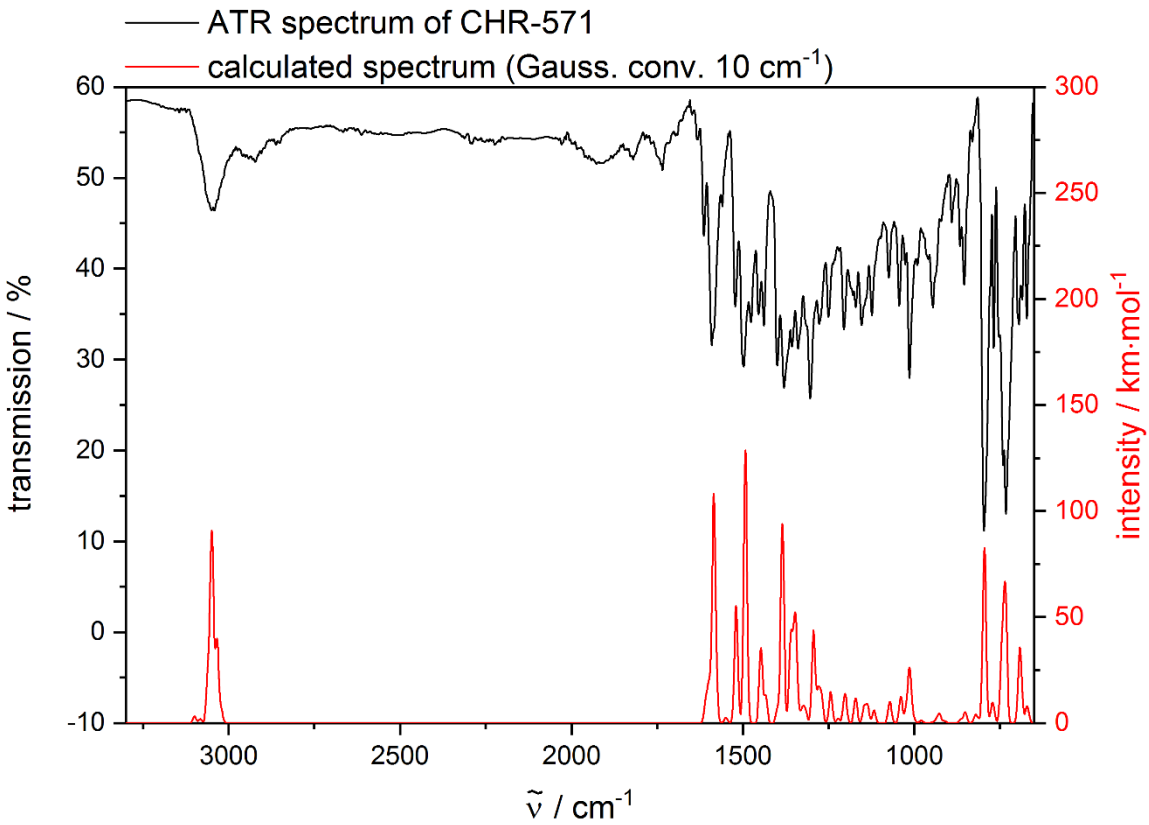
44

C	2.16902	-4.14745	0.02792
C	3.47554	-3.89026	-0.30187
C	2.96372	-1.53899	-0.50514
C	1.21233	-3.11091	0.10418
C	1.62849	-1.75486	-0.09613
C	3.86298	-2.57381	-0.60315
H	1.84076	-5.16415	0.20985
C	-0.16238	-3.42068	0.29829
H	4.19443	-4.69703	-0.36486
H	4.87547	-2.37114	-0.92926
H	3.27328	-0.54801	-0.79363
C	-1.12532	-2.45380	0.25381
C	-0.71108	-1.11825	0.10786
C	0.63871	-0.72517	0.02624
H	-0.44167	-4.45847	0.43144
H	-2.17507	-2.70008	0.33057
N	-1.52046	-0.00008	-0.00022
C	0.63865	0.72519	-0.02641
C	-0.71116	1.11816	-0.10818
C	1.62834	1.75495	0.09608
C	-1.12548	2.45368	-0.25415
C	1.21210	3.11097	-0.10424
C	-0.16262	3.42063	-0.29849
C	2.16869	4.14759	-0.02785
H	1.84036	5.16427	-0.20979
C	2.96355	1.53918	0.50524

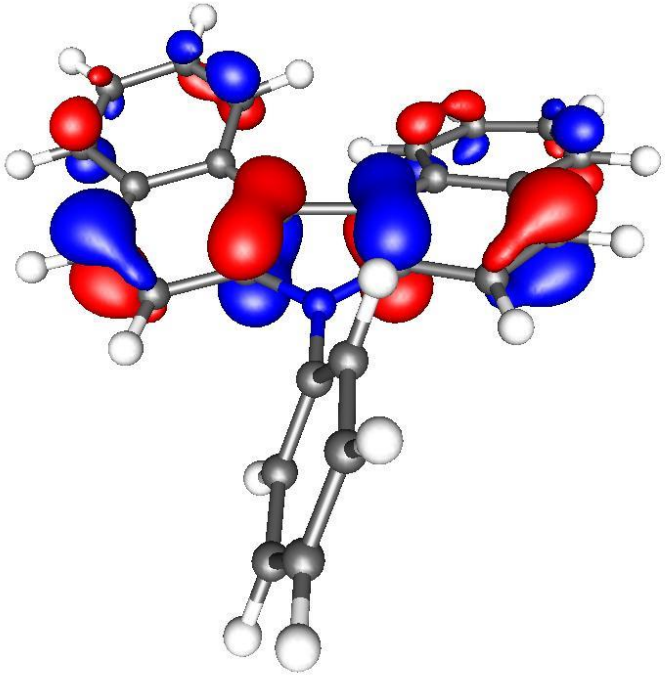
C	3.47519	3.89050	0.30209
C	3.86271	2.57408	0.60338
H	4.19401	4.69733	0.36518
H	4.87518	2.37147	0.92960
H	-0.44198	4.45841	-0.43165
H	-2.17525	2.69988	-0.33101
H	3.27316	0.54822	0.79374
C	-3.63338	-0.44530	1.12114
C	-5.02217	-0.45217	1.11506
C	-5.71941	-0.00012	0.00027
C	-2.93876	-0.00011	-0.00006
C	-5.02244	0.45194	-1.11469
C	-3.63364	0.44507	-1.12109
H	-3.08013	-0.77679	1.98977
H	-5.55986	-0.79990	1.98778
H	-6.80175	-0.00012	0.00040
H	-5.56033	0.79967	-1.98729
H	-3.08060	0.77655	-1.98986



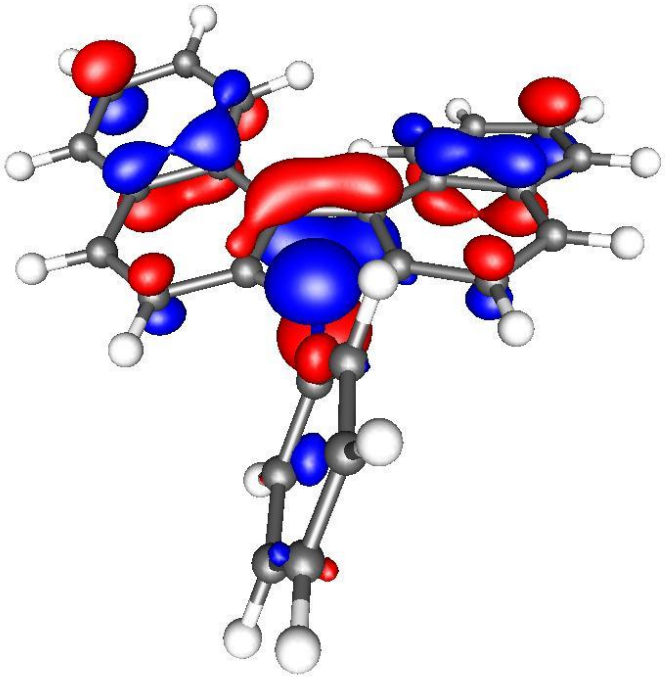

λ / nm
1000 800 600 400
UV / Vis
fluo λEX = 270 nm
393 nm
376 nm
279 nm
244 nm
366 nm
305 nm
349 nm
333 nm
fluorescence / a.u.
absorption / a.u.
8000000
6000000
4000000
2000000
0
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
10000 15000 20000 25000 30000 35000 40000
ν̃ / cm-1


ATR spectrum of CHR-571
calculated spectrum (Gauss. conv. 10 cm-1)
transmission / %
intensity / km·mol-1
60
50
40
30
20
10
0
-10
300
250
200
150
100
50
0
3000 2500 2000 1500 1000
ν̃ / cm-1

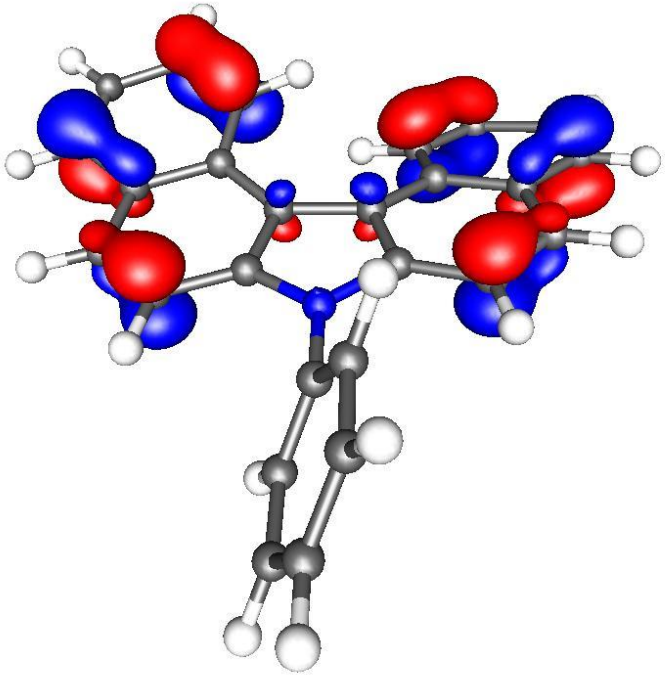
HOMO 0 eV



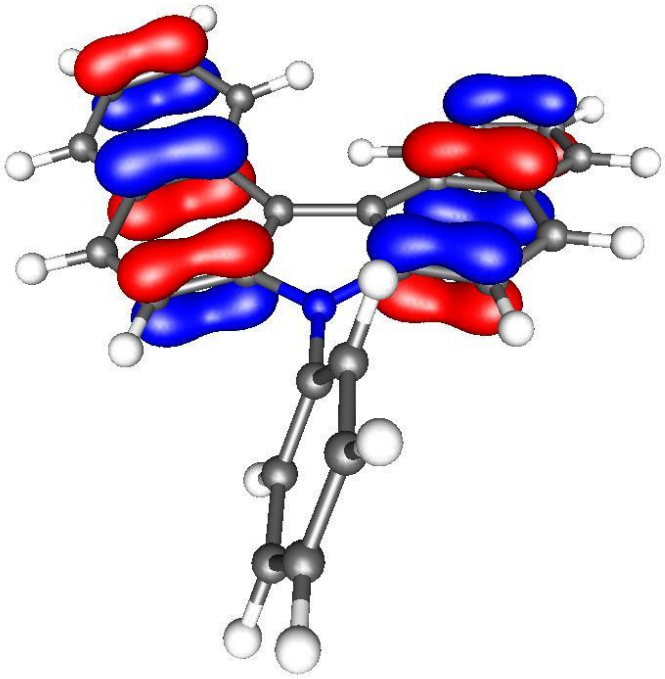
HOMO-1 -0.33 eV



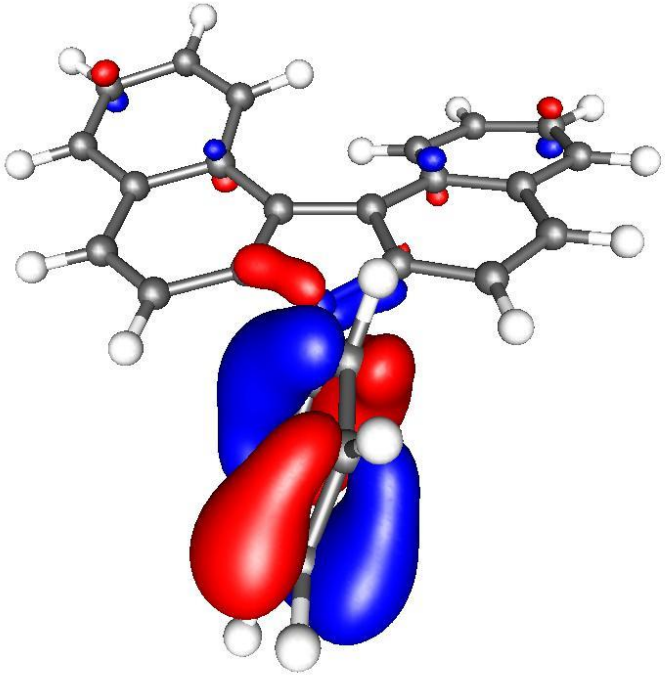
HOMO-2 -1.05 eV



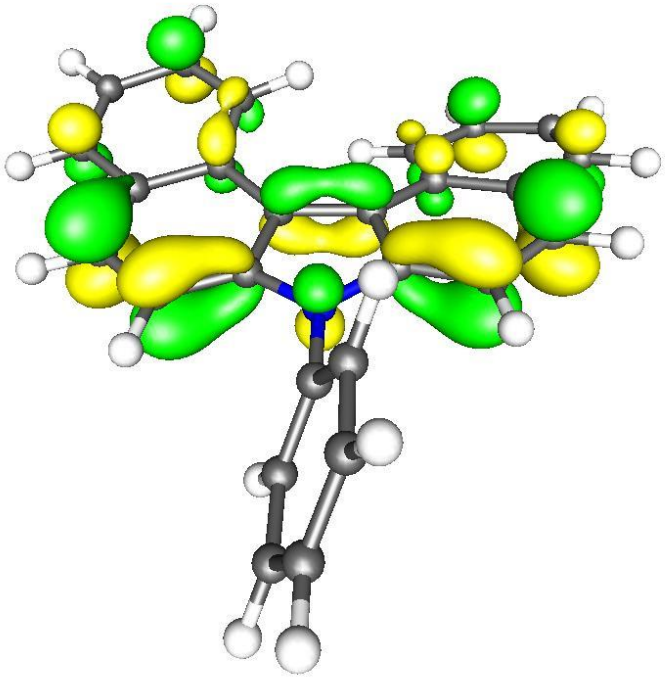
HOMO-3 -1.42 eV



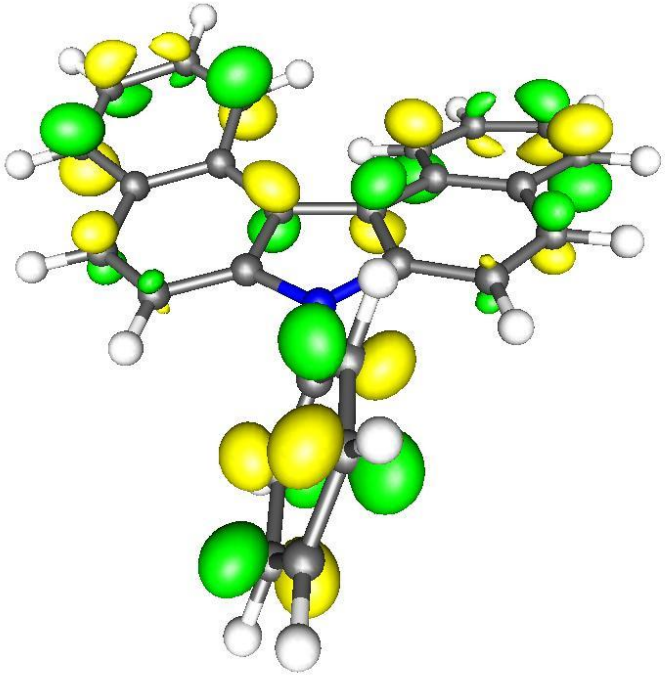
HOMO-4 -2.0 eV



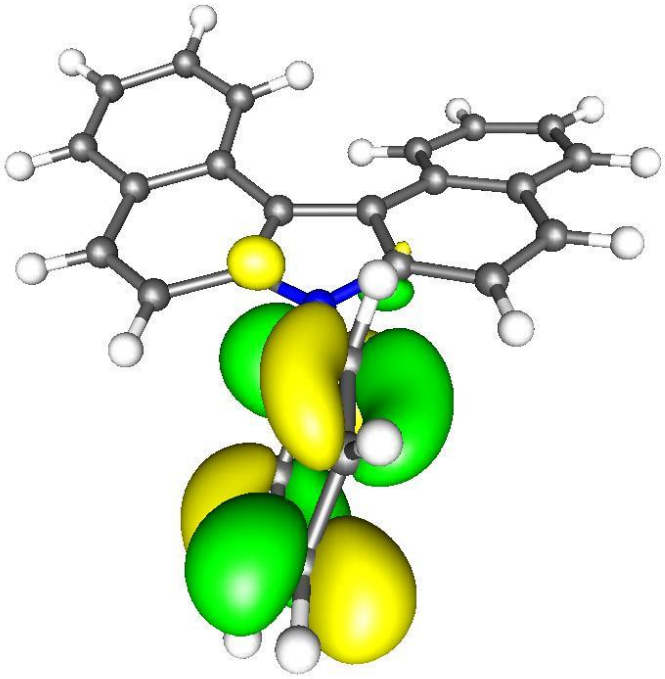
LUMO 3.89 eV



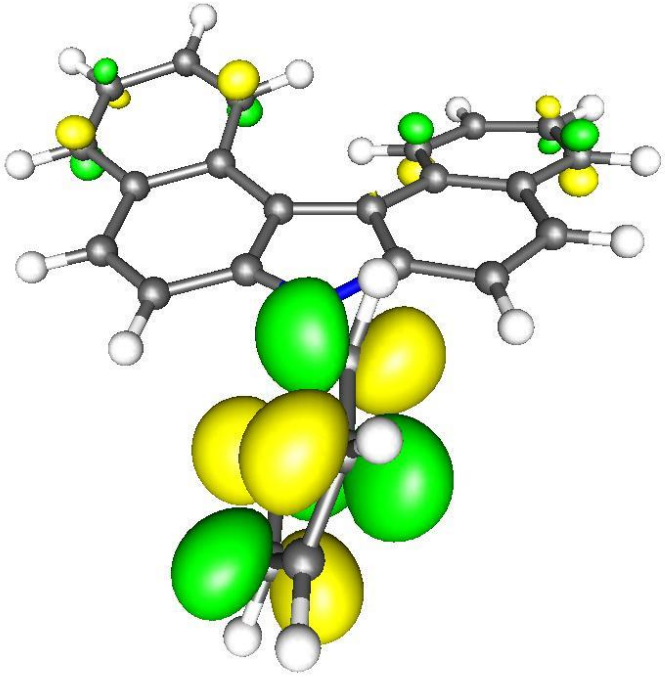
LUMO+1 4.37 eV



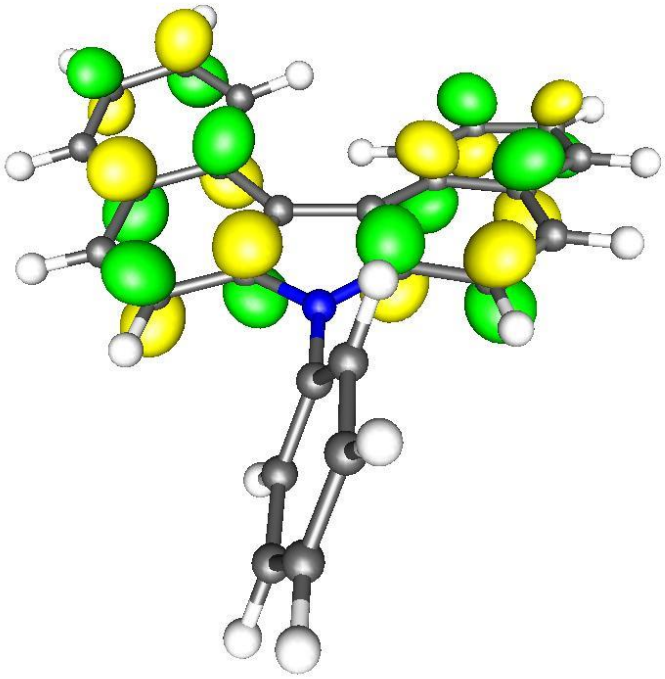
LUMO+2 4.45 eV

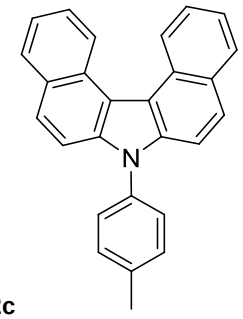


LUMO+3 4.60 eV



LUMO+4 5.00 eV



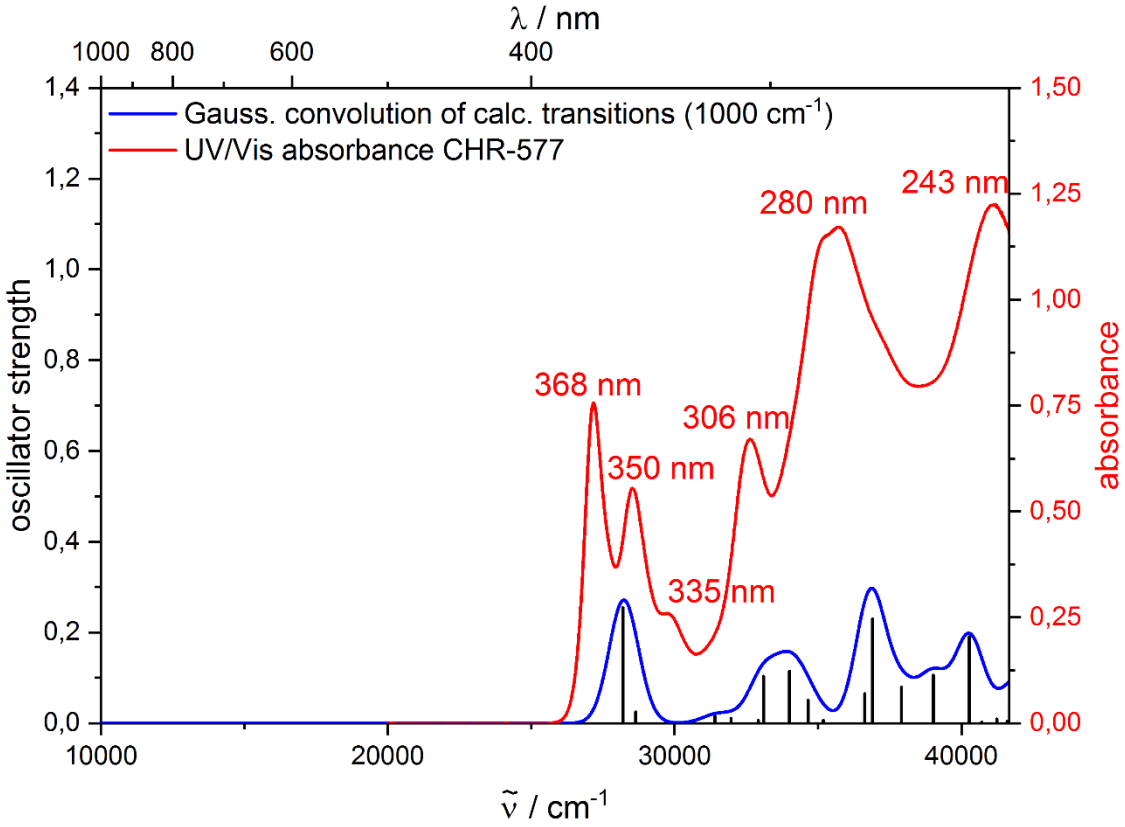


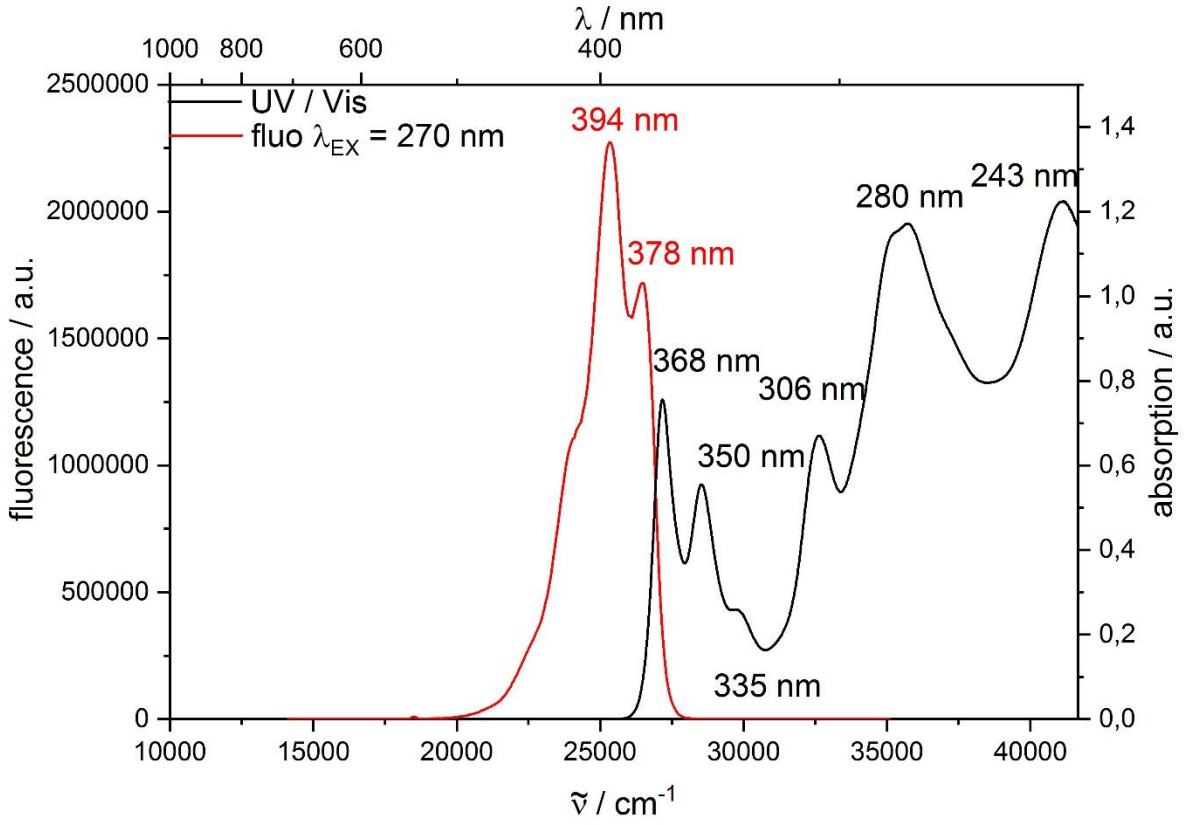
2c

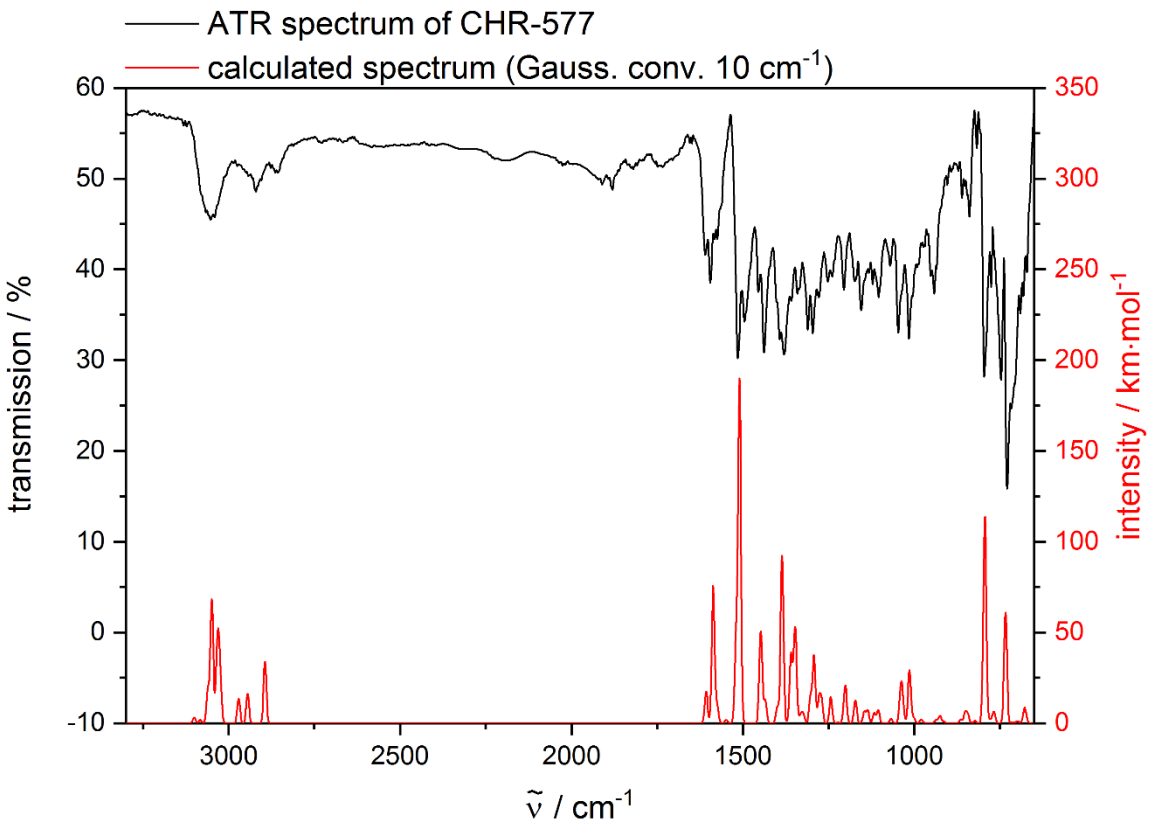
47

C	-2.47787	4.15222	0.03155
C	-3.78566	3.89898	-0.29660
C	-3.28037	1.54655	-0.50212
C	-1.52384	3.11321	0.10585
C	-1.94389	1.75824	-0.09500
C	-4.17709	2.58383	-0.59813
H	-2.14658	5.16789	0.21395
C	-0.14811	3.41930	0.29941
H	-4.50235	4.70786	-0.35789
H	-5.19062	2.38399	-0.92283
H	-3.59306	0.55660	-0.79082
C	0.81215	2.44988	0.25338
C	0.39431	1.11568	0.10572
C	-0.95678	0.72573	0.02548
H	0.13364	4.45630	0.43393
H	1.86286	2.69223	0.33090
N	1.20109	-0.00344	-0.00138
C	-0.95957	-0.72451	-0.02671
C	0.39000	-1.11964	-0.10743
C	-1.95063	-1.75319	0.09429
C	0.80264	-2.45550	-0.25454
C	-1.53588	-3.10982	-0.10626
C	-0.16135	-3.42124	-0.29994
C	-2.49387	-4.14513	-0.03137
H	-2.16654	-5.16213	-0.21354
C	-3.28615	-1.53623	0.50178

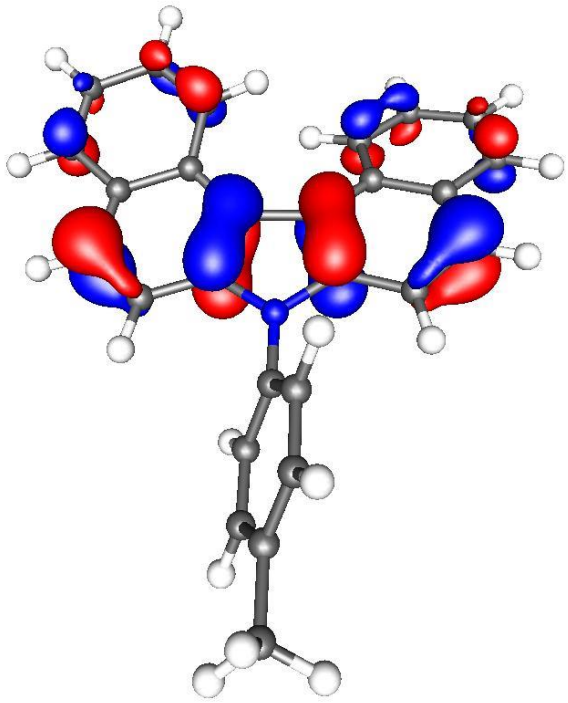
C	-3.80058	-3.88675	0.29712
C	-4.18684	-2.57003	0.59839
H	-4.52035	-4.69285	0.35890
H	-5.19948	-2.36618	0.92338
H	0.11648	-4.45935	-0.43400
H	1.85239	-2.70198	-0.33206
H	-3.59494	-0.54500	0.79029
C	3.31913	0.41340	1.12706
C	4.70648	0.41522	1.12042
C	5.42494	-0.01268	0.00336
C	2.62002	-0.00559	-0.00052
C	4.70776	-0.44146	-1.11326
C	3.31972	-0.43088	-1.12447
H	2.77022	0.72840	2.00475
H	5.24115	0.74160	2.00463
C	6.92885	0.01419	-0.00439
H	5.24278	-0.77972	-1.99267
H	2.77206	-0.75036	-2.00133
H	7.33591	-0.72641	-0.69368
H	7.33478	-0.18355	0.98871
H	7.29893	0.99416	-0.31950


λ / nm
1000 800 600 400
Gauss. convolution of calc. transitions (1000 cm-1)
UV/Vis absorbance CHR-577
oscillator strength
absorbance
368 nm
350 nm
335 nm
306 nm
280 nm
243 nm
ν̃ / cm-1

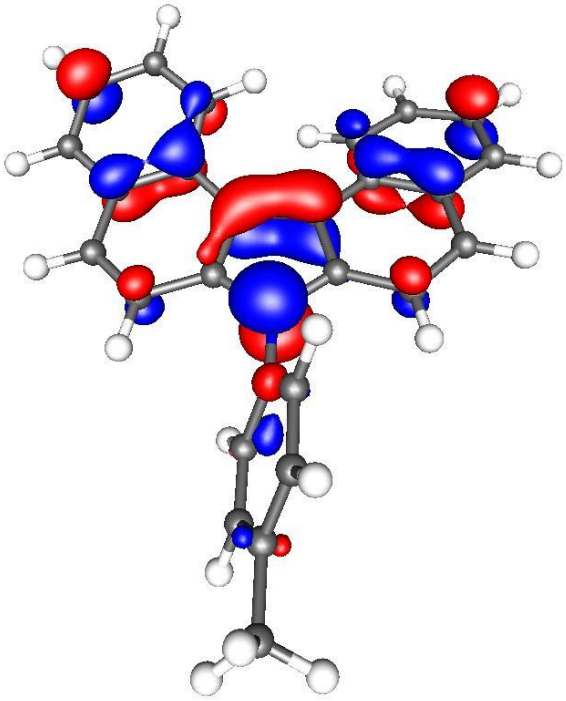

λ / nm
1000 800 600 400
UV / Vis
fluo λEX = 270 nm
fluorescence / a.u.
absorption / a.u.
394 nm
378 nm
368 nm
350 nm
335 nm
306 nm
280 nm
243 nm
ν̃ / cm-1


ATR spectrum of CHR-577
calculated spectrum (Gauss. conv. 10 cm-1)
transmission / %
intensity / km·mol-1
ν̃ / cm-1
60
50
40
30
20
10
0
-10
350
300
250
200
150
100
50
0
3000
2500
2000
1500
1000

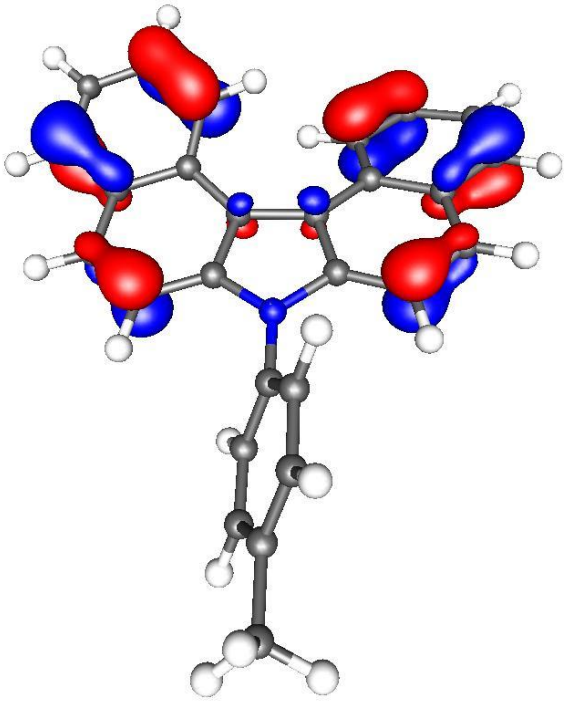
HOMO 0 eV



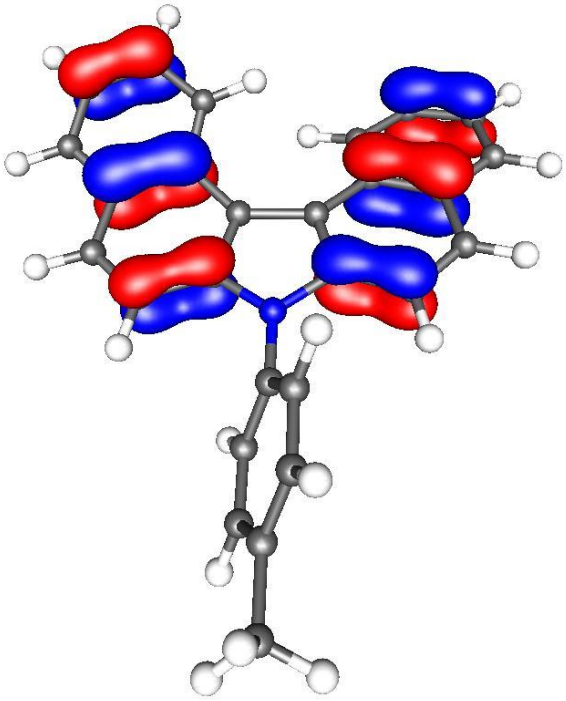
HOMO-1 -0.30 eV



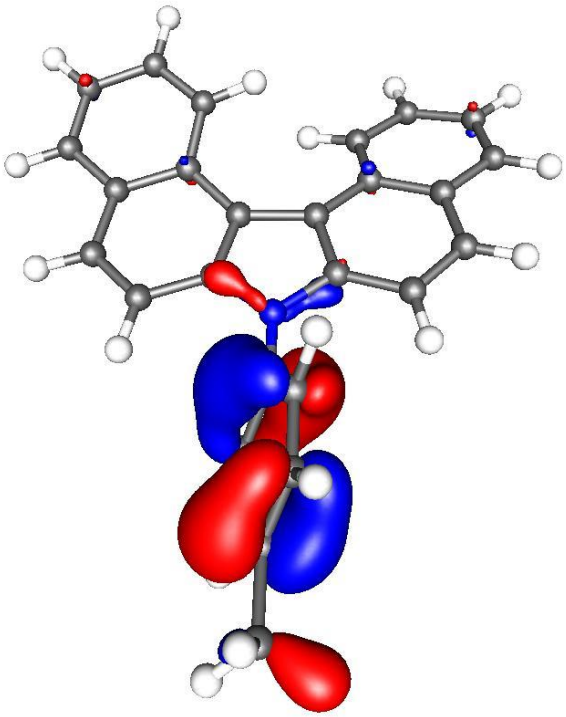
HOMO-2 -1.05 eV



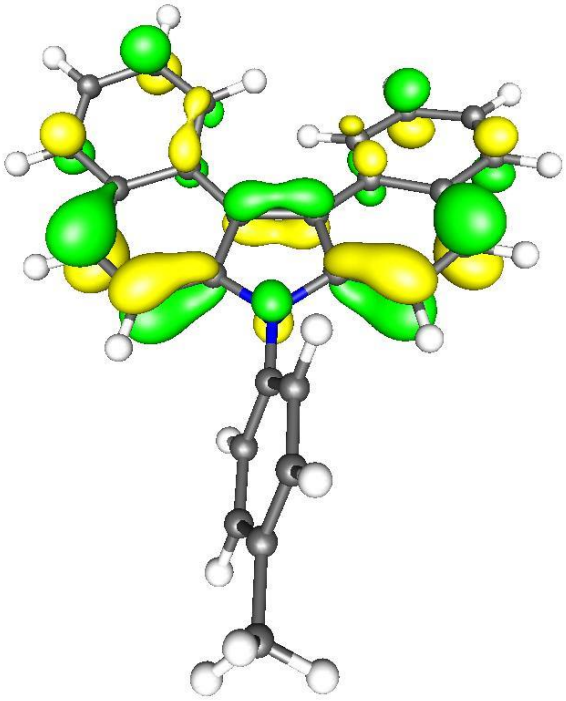
HOMO-3 -1.42



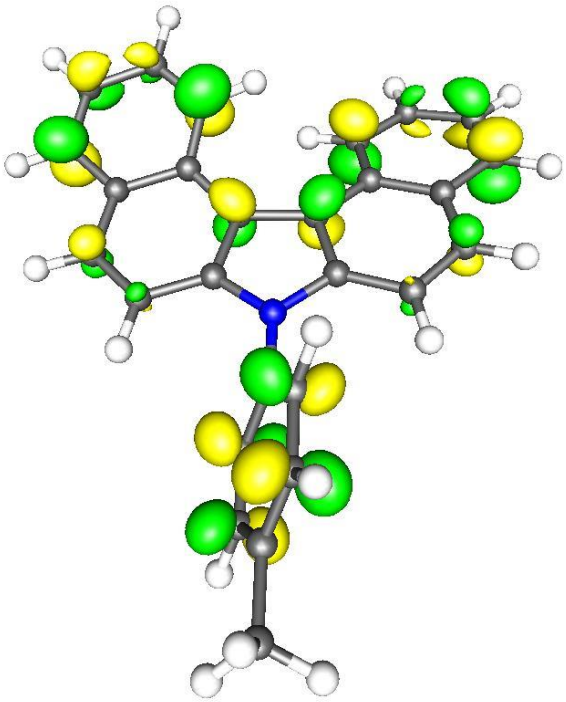
HOMO-4 -1.79 eV



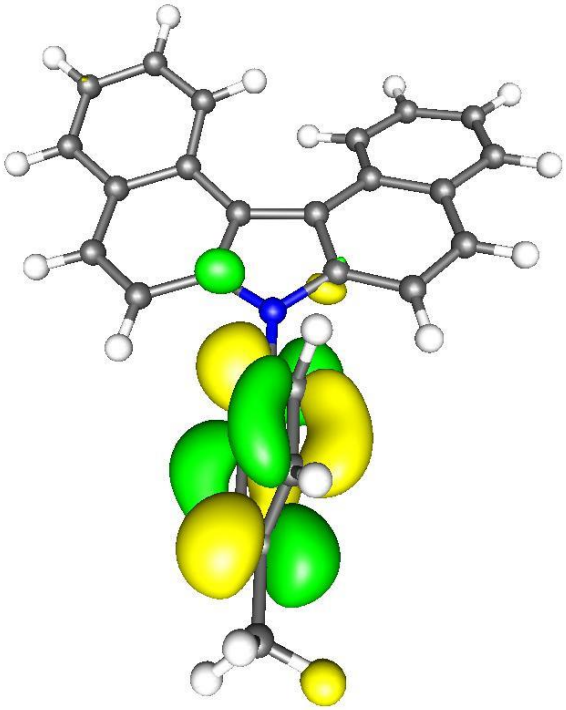
LUMO 3.91 eV



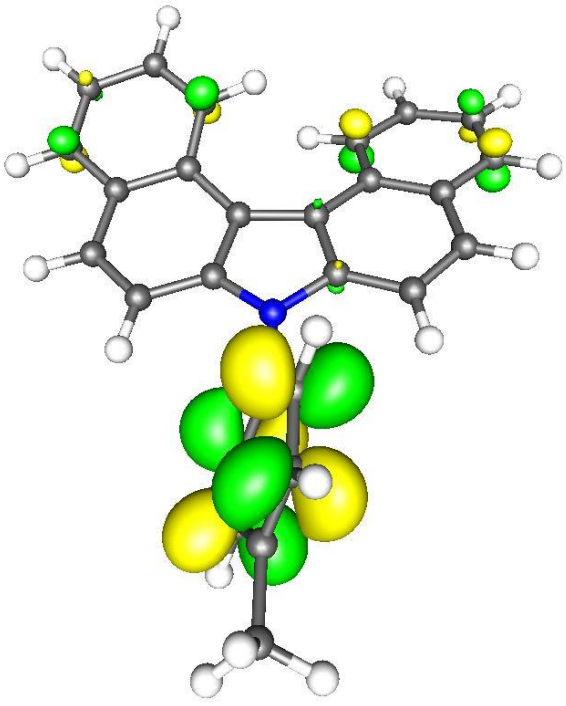
LUMO+1 4.36 eV



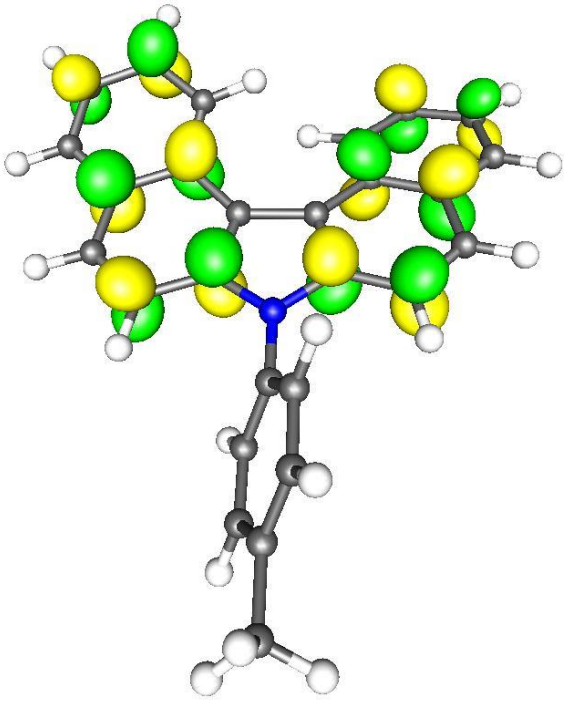
LUMO+2 4.52 eV

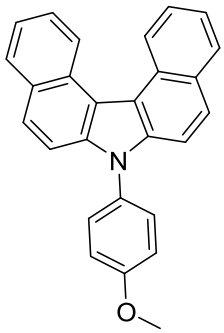


LUMO+3 4.62 eV



LUMO+4 5.01 eV



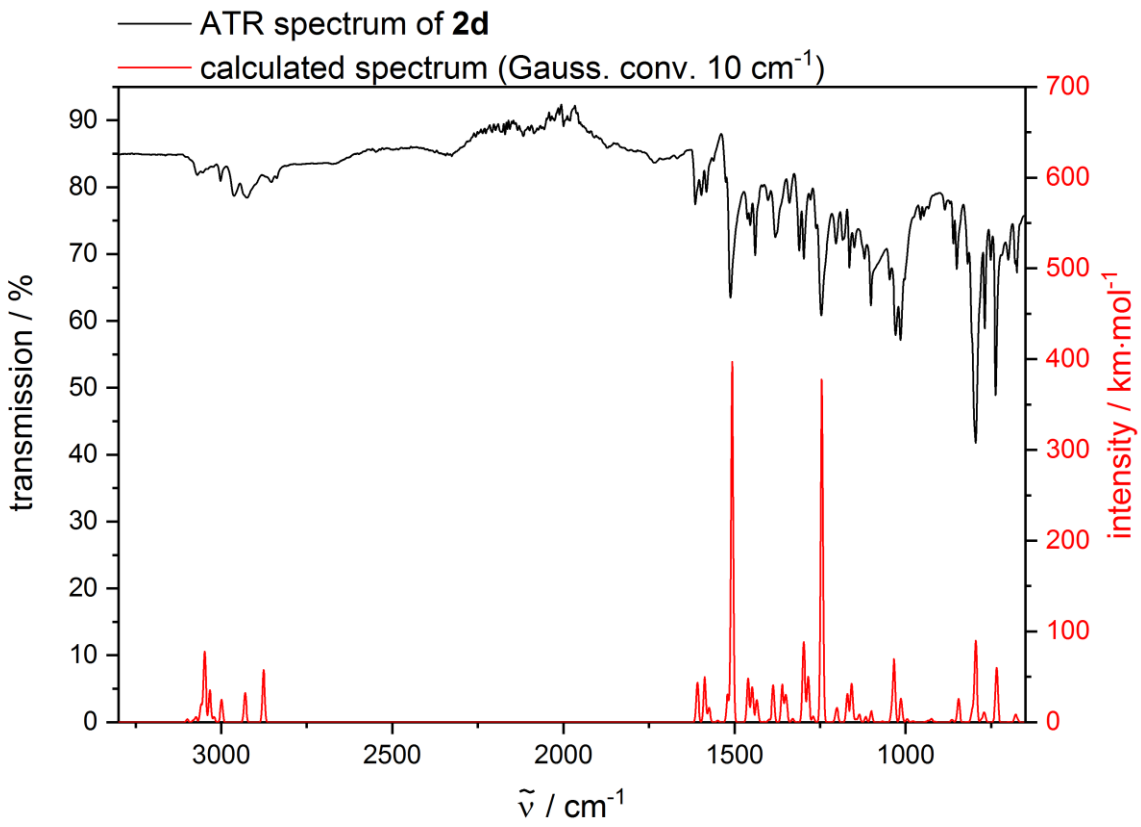


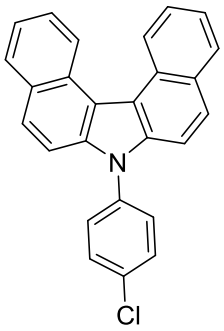
2d

48

C	-2.6483218	4.2046077	0.1894736
C	-3.9550676	4.0102263	-0.1810633
C	-3.5210285	1.6540785	-0.4826610
C	-1.7303065	3.1324497	0.2382431
C	-2.1881266	1.8034850	-0.0387675
C	-4.3816282	2.7238638	-0.5507775
H	-2.2900984	5.1991300	0.4288865
C	-0.3529822	3.3817570	0.4947213
H	-4.6437480	4.8444183	-0.2208436
H	-5.3933959	2.5725586	-0.9058646
H	-3.8580636	0.6884991	-0.8223455
C	0.5774322	2.3853624	0.4227386
C	0.1244717	1.0778479	0.1740727
C	-1.2363813	0.7348458	0.0523876
H	-0.0452753	4.3982038	0.7068241
H	1.6307847	2.5829167	0.5664187
N	0.8981764	-0.0624667	0.0551207
C	-1.2837902	-0.7120134	-0.0396484
C	0.0545725	-1.1474450	-0.0994117
C	-2.3095142	-1.7129017	0.0069020
C	0.4282346	-2.4835358	-0.3272349
C	-1.9312510	-3.0707985	-0.2491223
C	-0.5638193	-3.4143213	-0.4418011
C	-2.9216022	-4.0777082	-0.2429345
H	-2.6213998	-5.0950535	-0.4655204
C	-3.6481452	-1.4716620	0.3889742
C	-4.2276446	-3.7935686	0.0670805

C	-4.5819933	-2.4800431	0.4170288
H	-4.9726787	-4.5788049	0.0751578
H	-5.5962964	-2.2591139	0.7252981
H	-0.3167753	-4.4501282	-0.6390826
H	1.4710687	-2.7534018	-0.4218908
H	-3.9338029	-0.4844362	0.7132872
C	3.0648044	0.5593609	-0.8647141
C	4.4550862	0.5294876	-0.8272165
C	5.1030769	-0.1978246	0.1704457
C	2.3155405	-0.1111196	0.0914829
C	4.3489070	-0.8817921	1.1279267
C	2.9685151	-0.8305903	1.0927281
H	2.5569107	1.1094095	-1.6459466
H	5.0146202	1.0622359	-1.5814632
O	6.4516824	-0.2995438	0.2939270
H	4.8683015	-1.4359748	1.8981509
H	2.3834182	-1.3458192	1.8430093
C	7.2678382	0.3782414	-0.6473823
H	8.2948642	0.1671164	-0.3597431
H	7.0969343	1.4584207	-0.6172598
H	7.0926787	0.0117023	-1.6631590


ATR spectrum of **2d**
calculated spectrum (Gauss. conv. 10 cm-1)
transmission / %
intensity / km·mol-1
ν̃ / cm-1
90
80
70
60
50
40
30
20
10
0
700
600
500
400
300
200
100
0
3000
2500
2000
1500
1000

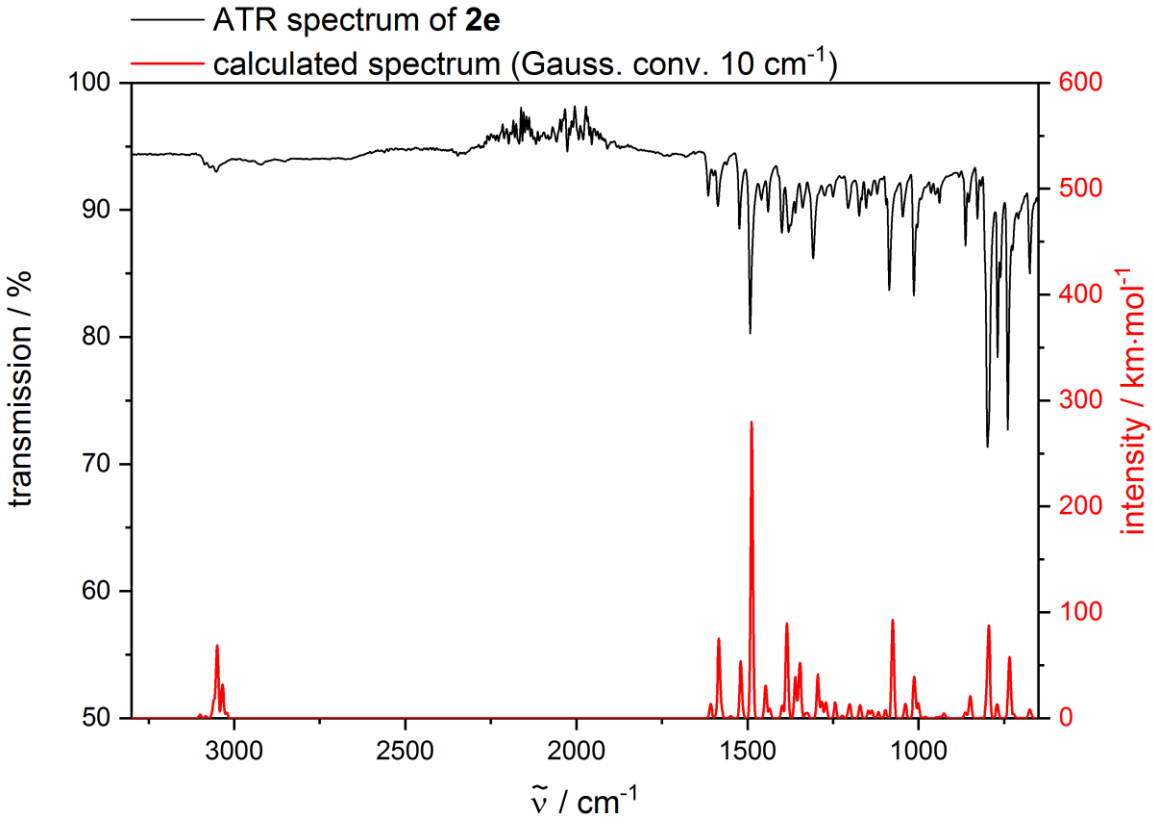


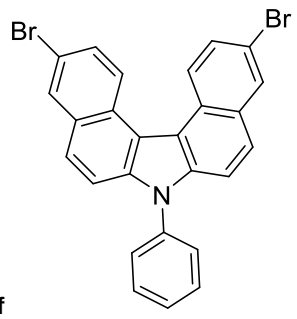
2e

44

C	2.7814340	4.1408210	-0.2030202
C	4.0876754	3.8978635	0.1388673
C	3.5753545	1.5580784	0.4456984
C	1.8244742	3.1024772	-0.2336453
C	2.2396872	1.7573946	0.0309682
C	4.4751526	2.5959377	0.4971524
H	2.4544863	5.1482163	-0.4327513
C	0.4522898	3.4014387	-0.4606771
H	4.8069440	4.7062963	0.1654079
H	5.4880369	2.4074419	0.8304154
H	3.8843954	0.5801536	0.7764953
C	-0.5119037	2.4392011	-0.3691066
C	-0.1012836	1.1160997	-0.1292522
C	1.2477778	0.7243618	-0.0411065
H	0.1764321	4.4281517	-0.6666100
H	-1.5590886	2.6775539	-0.4935730
N	-0.9119470	-0.0000333	0.0002438
C	1.2478118	-0.7243455	0.0412880
C	-0.1012226	-1.1161352	0.1296115
C	2.2397490	-1.7573415	-0.0309445
C	-0.5117634	-2.4392572	0.3694903
C	1.8246201	-3.1024454	0.2336931
C	0.4524772	-3.4014622	0.4609075
C	2.7816105	-4.1407558	0.2028995
H	2.4547307	-5.1481684	0.4326508
C	3.5753483	-1.5579690	-0.4458660
C	4.0877927	-3.8977454	-0.1391770

C	4.4751730	-2.5957972	-0.4974844
H	4.8070837	-4.7061538	-0.1658487
H	5.4880006	-2.4072589	-0.8308958
H	0.1766858	-4.4281906	0.6668524
H	-1.5589247	-2.6776472	0.4940891
H	3.8843075	-0.5800251	-0.7766823
C	-3.0258750	0.7580751	0.9359524
C	-4.4132211	0.7677119	0.9332678
C	-5.0973731	-0.0000584	-0.0000779
C	-2.3268410	-0.0000772	0.0001560
C	-4.4130718	-0.7678574	-0.9332914
C	-3.0257255	-0.7582421	-0.9357419
H	-2.4787465	1.3351583	1.6691371
H	-4.9615659	1.3540075	1.6570915
Cl	-6.8400145	0.0000197	-0.0002823
H	-4.9613027	-1.3541367	-1.6572149
H	-2.4784830	-1.3353296	-1.6688380



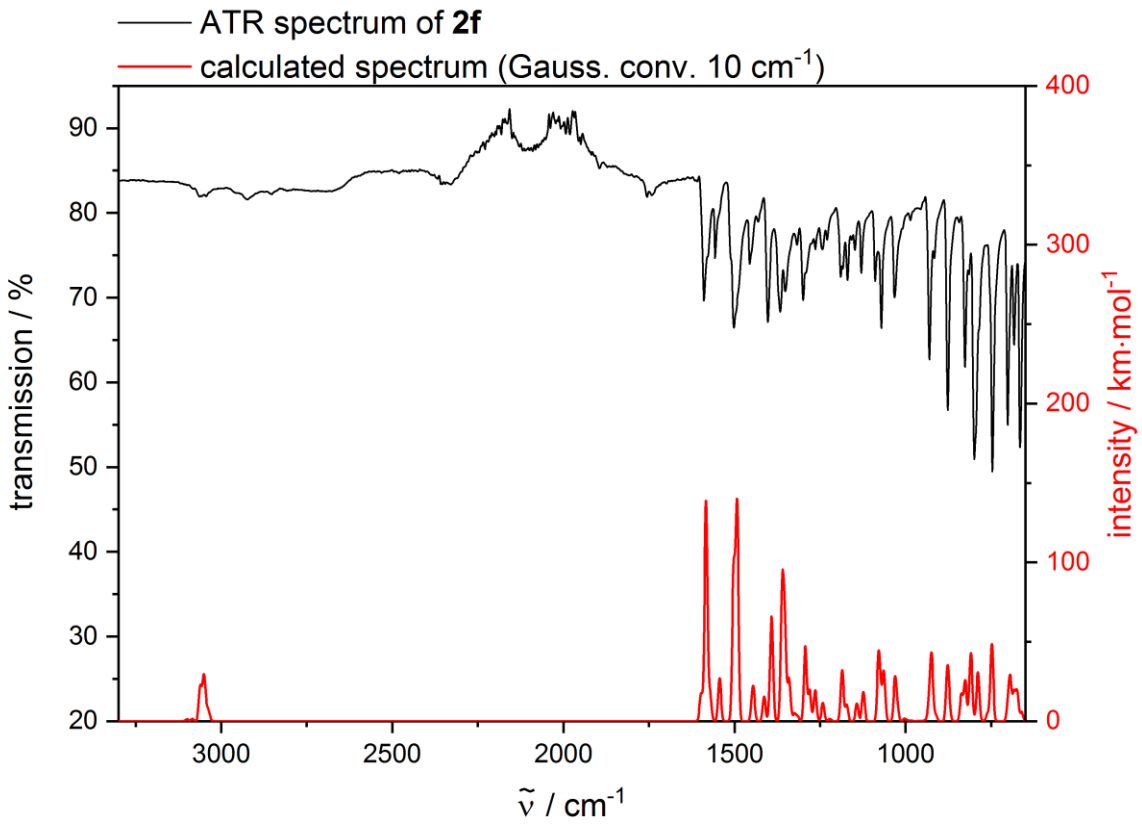


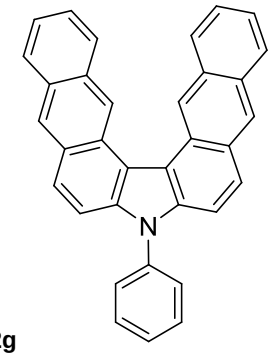
2f

44

C	4.1392585	-0.8595469	-0.2923618
C	3.8864337	-2.1597591	0.0526071
C	1.5682044	-1.6599726	0.4075369
C	3.0953074	0.0917247	-0.2989241
C	1.7563767	-0.3238648	-0.0092413
C	2.6012396	-2.5652589	0.4395899
H	5.1431452	-0.5413255	-0.5392277
C	3.3913125	1.4643844	-0.5304877
Br	5.3047133	-3.4393414	0.0613823
H	2.4304546	-3.5787281	0.7738797
H	0.5998578	-1.9739796	0.7612920
C	2.4300349	2.4269429	-0.4188892
C	1.1116845	2.0169904	-0.1535270
C	0.7224941	0.6667127	-0.0578388
H	4.4135395	1.7404910	-0.7557388
H	2.6650081	3.4746212	-0.5451831
N	0.0003871	2.8267351	-0.0004831
C	-0.7224523	0.6669415	0.0567384
C	-1.1112212	2.0173775	0.1523859
C	-1.7566036	-0.3232689	0.0084342
C	-2.4293896	2.4276932	0.4178876
C	-3.0953081	0.0926457	0.2984304
C	-3.3909120	1.4653703	0.5298465
C	-4.1395125	-0.8584895	0.2923307
H	-5.1431821	-0.5399608	0.5396773
C	-1.5688678	-1.6595234	-0.4084225
C	-3.8870797	-2.1587220	-0.0525985

C	-2.6020023	-2.5645653	-0.4399911
Br	-5.3057111	-3.4379261	-0.0606627
H	-2.4317144	-3.5781306	-0.7742532
H	-4.4130294	1.7417985	0.7551987
H	-2.6641098	3.4754485	0.5440085
H	-0.6007006	-1.9735331	-0.7627140
C	0.7607164	4.9390234	0.9377513
C	0.7654004	6.3277561	0.9300312
C	0.0012009	7.0249377	0.0009315
C	0.0006972	4.2453661	-0.0000025
C	-0.7632737	6.3286603	-0.9286185
C	-0.7590983	4.9399295	-0.9372601
H	1.3362900	4.3862858	1.6682656
H	1.3577065	6.8653022	1.6592869
H	0.0014074	8.1072287	0.0012931
H	-1.3553971	6.8669102	-1.6575041
H	-1.3349027	4.3878794	-1.6681173



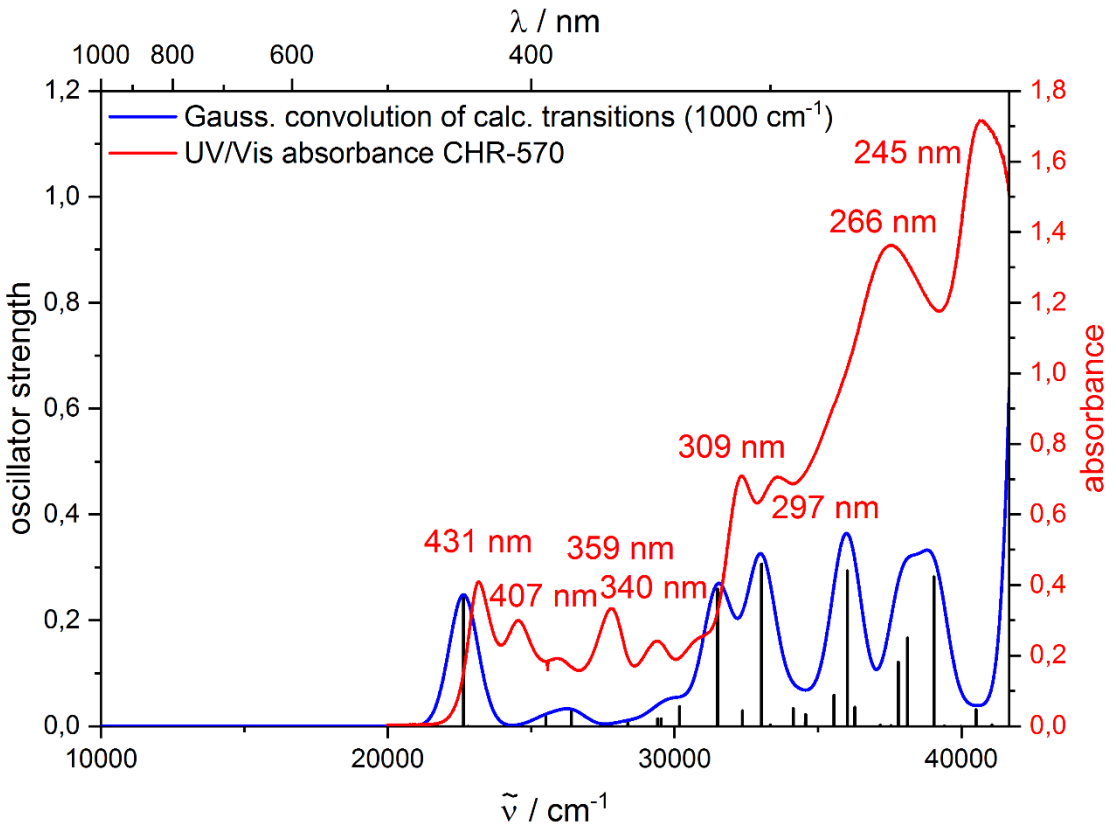


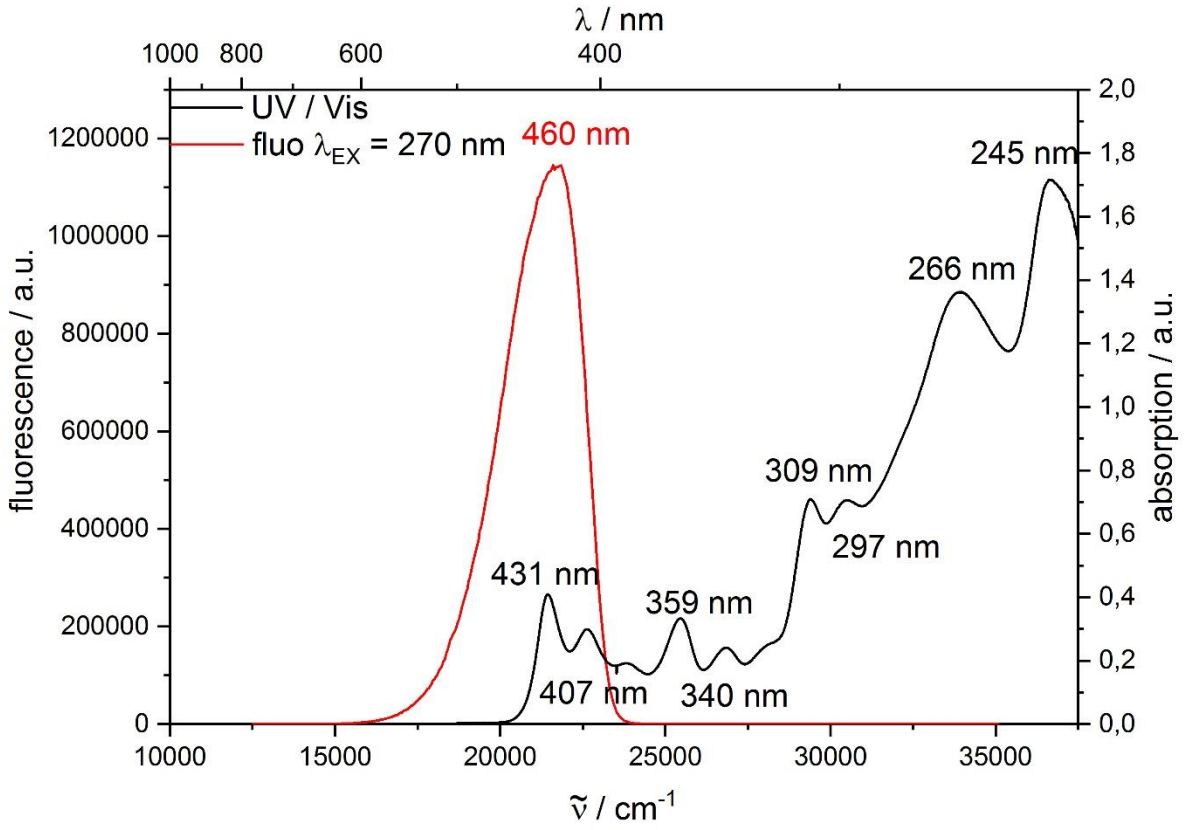
2g

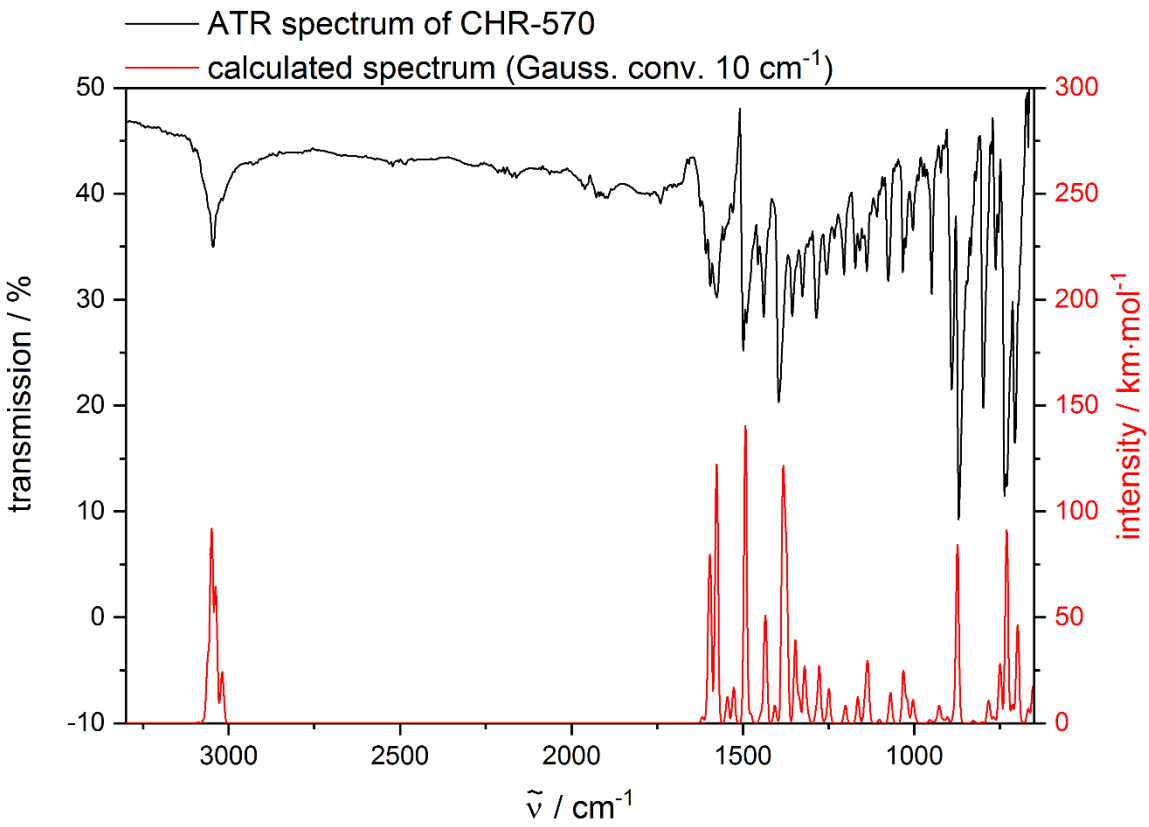
56

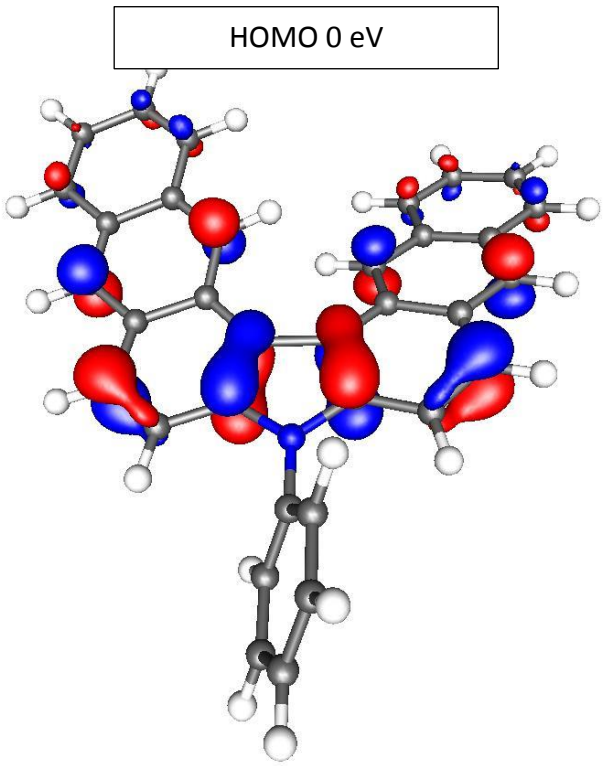
C	0.91160	-4.13290	0.36706
C	2.24960	-3.92414	0.02849
C	1.71217	-1.57326	-0.37732
C	-0.02604	-3.10482	0.35066
C	0.39743	-1.75699	0.03718
C	2.64861	-2.61219	-0.38752
H	0.58293	-5.13524	0.61877
C	-1.41187	-3.39285	0.55771
H	2.02833	-0.60872	-0.74109
C	-2.36704	-2.43315	0.42966
C	-1.94778	-1.10692	0.18332
C	-0.60207	-0.71880	0.07823
H	-1.69348	-4.41636	0.77085
H	-3.41817	-2.66857	0.52171
N	-2.75615	0.00003	0.00001
C	-0.60209	0.71889	-0.07797
C	-1.94779	1.10701	-0.18313
C	0.39738	1.75710	-0.03687
C	-2.36708	2.43323	-0.42946
C	-0.02609	3.10492	-0.35039
C	-1.41191	3.39295	-0.55746
C	0.91158	4.13298	-0.36683
H	0.58290	5.13534	-0.61841
C	1.71203	1.57336	0.37782
C	2.24957	3.92415	-0.02832

C	2.64856	2.61226	0.38791
C	3.99504	2.40714	0.79707
H	-1.69351	4.41646	-0.77061
H	-3.41822	2.66862	-0.52156
H	2.02804	0.60890	0.74193
C	-4.86946	-0.35273	1.15366
C	-6.25828	-0.35979	1.14793
C	-6.95512	-0.00006	-0.00026
C	-4.17546	0.00001	-0.00009
C	-6.25816	0.35971	-1.14836
C	-4.86933	0.35274	-1.15391
H	-4.31598	-0.61271	2.04617
H	-6.79614	-0.63541	2.04591
H	-8.03746	-0.00009	-0.00033
H	-6.79592	0.63530	-2.04641
H	-4.31576	0.61274	-2.04636
H	5.92079	-3.26118	-1.08559
H	5.23355	-5.52829	-0.34026
C	4.89727	-3.43212	-0.77639
C	4.50469	-4.72776	-0.35110
C	3.99512	-2.40712	-0.79674
H	4.29323	-1.41654	-1.11967
C	3.21745	-4.96576	0.03700
H	2.91182	-5.95568	0.35490
C	4.89746	3.43189	0.77586
C	4.50496	4.72748	0.35032
H	5.92109	3.26091	1.08463
H	4.29330	1.41651	1.11966
C	3.21763	4.96567	-0.03735
H	5.23406	5.52779	0.33883
H	2.91207	5.95552	-0.35549

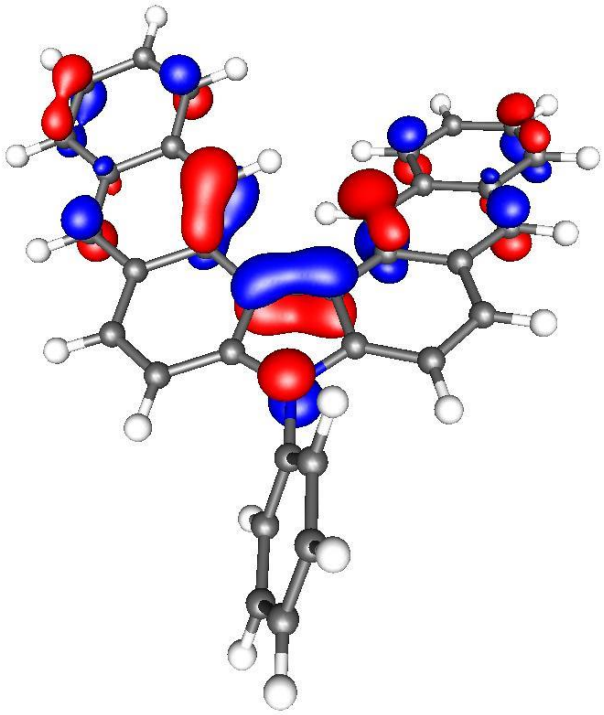

λ / nm
1000 800 600 400
Gauss. convolution of calc. transitions (1000 cm-1)
UV/Vis absorbance CHR-570
245 nm
266 nm
309 nm
297 nm
431 nm
359 nm
407 nm
340 nm
oscillator strength
absorbance
10000 20000 30000 40000
ν̃ / cm-1


λ / nm
1000 800 600 400
UV / Vis
fluo λEX = 270 nm
460 nm
245 nm
266 nm
309 nm
297 nm
431 nm
359 nm
407 nm
340 nm
fluorescence / a.u.
absorption / a.u.
10000 15000 20000 25000 30000 35000
ν̃ / cm-1

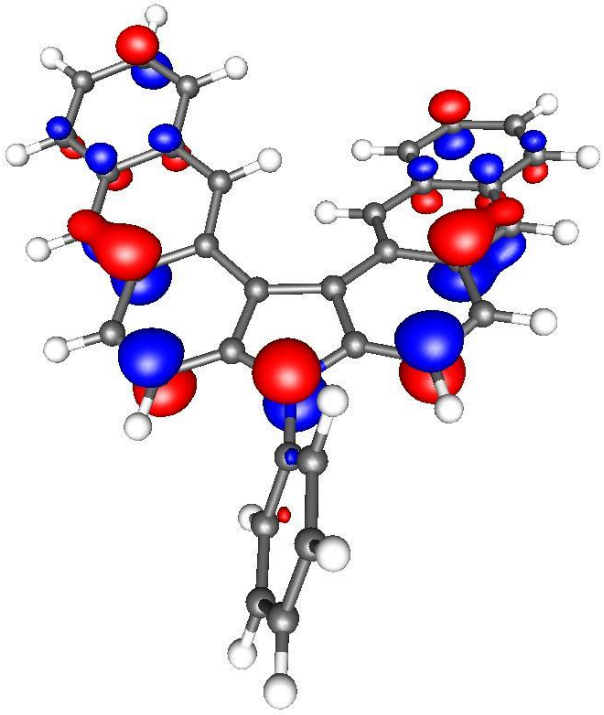

ATR spectrum of CHR-570
calculated spectrum (Gauss. conv. 10 cm-1)
transmission / %
intensity / km·mol-1
ν̃ / cm-1
50
40
30
20
10
0
-10
300
250
200
150
100
50
0
3000
2500
2000
1500
1000


HOMO 0 eV

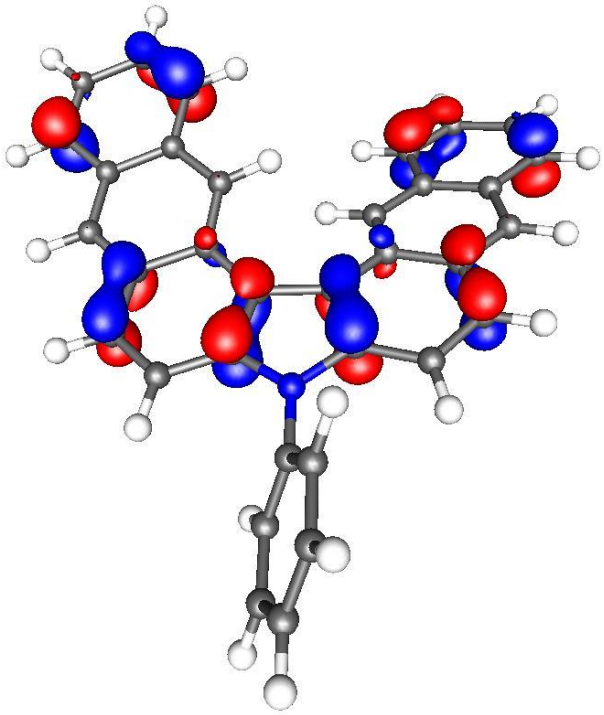
HOMO-1 -0.46 eV



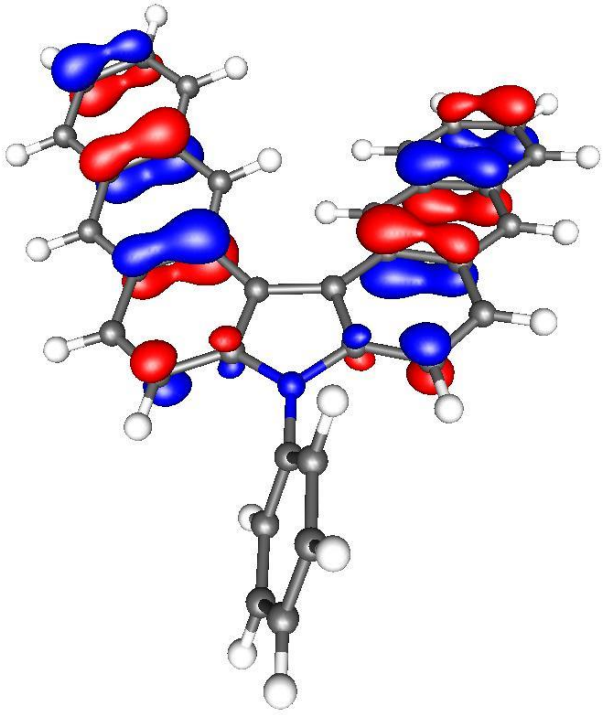
HOMO-2 -0.99 eV



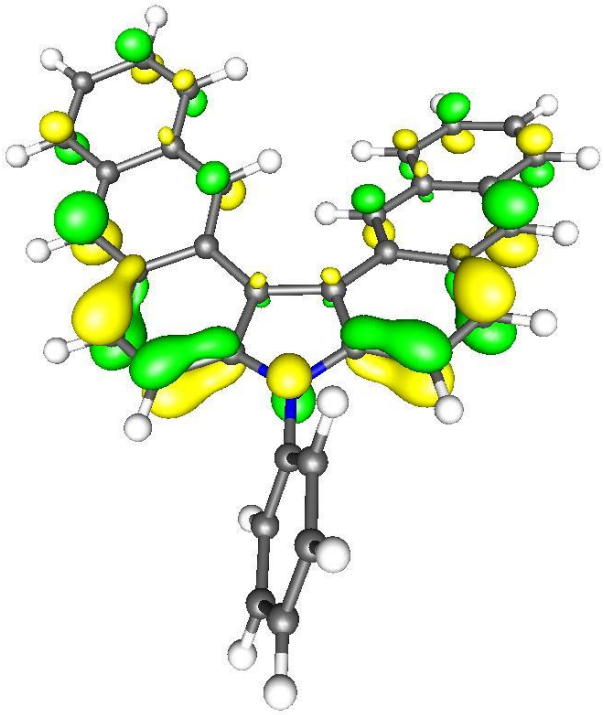
HOMO-3 -1.62 eV



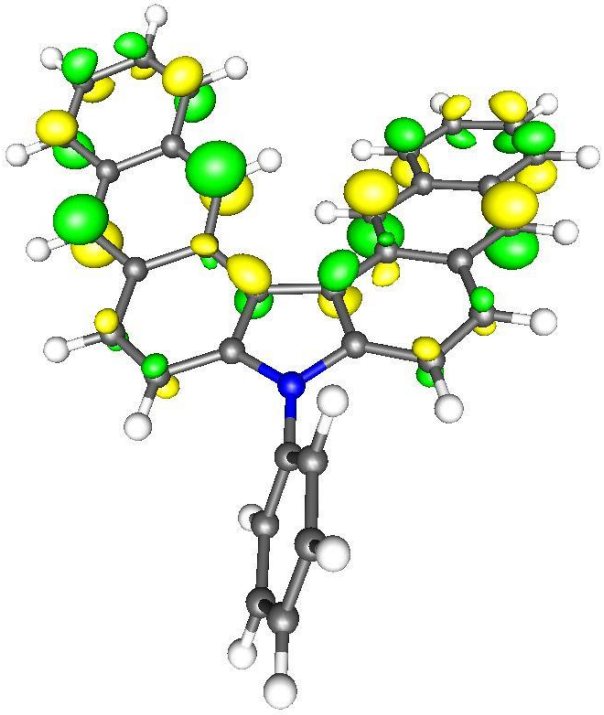
HOMO-4 -1.67 eV



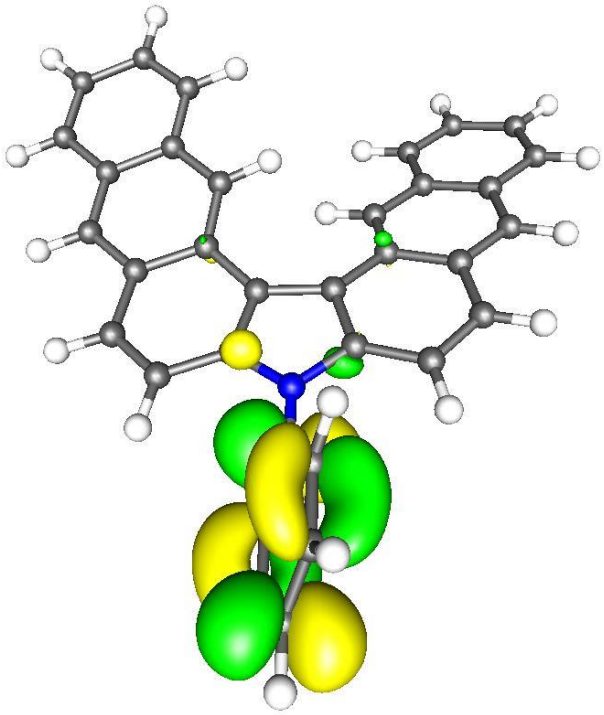
LUMO 3.19 eV



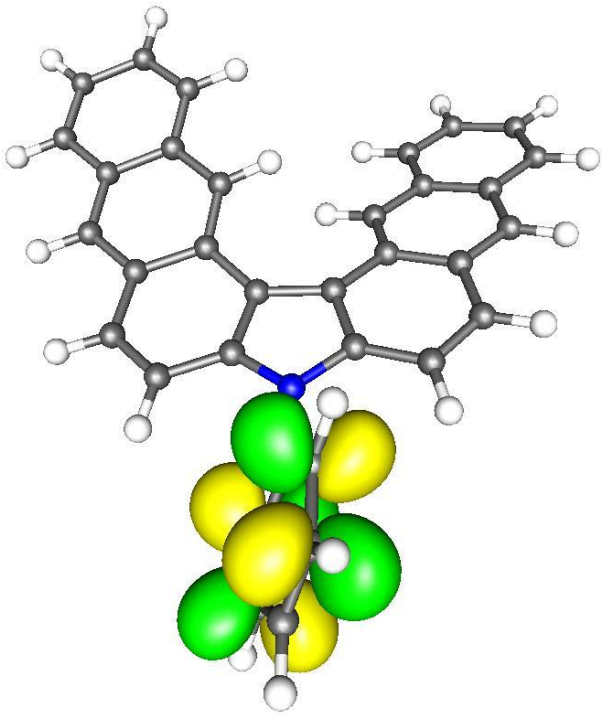
LUMO+1 3.30 eV



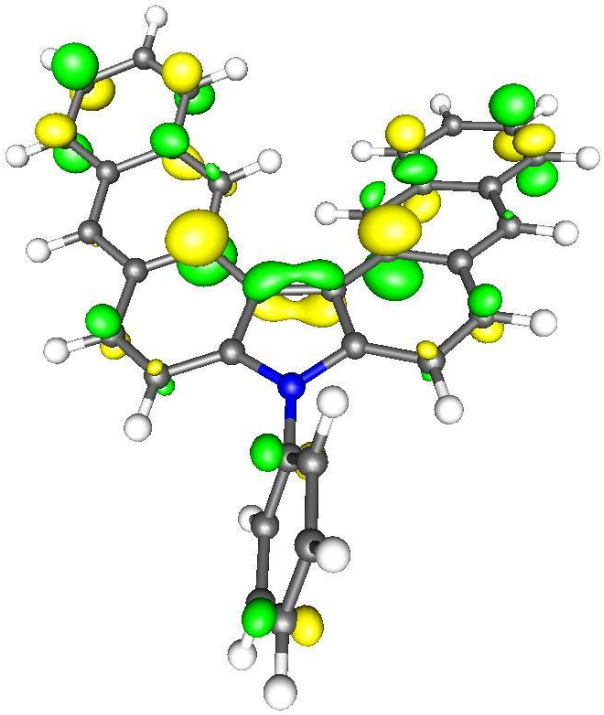
LUMO+2 4.05 eV

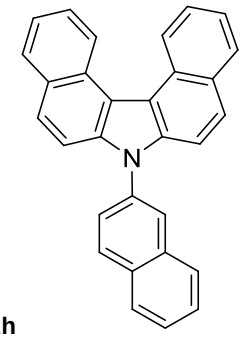


LUMO+3 4.14 eV



LUMO+4 4.42 eV



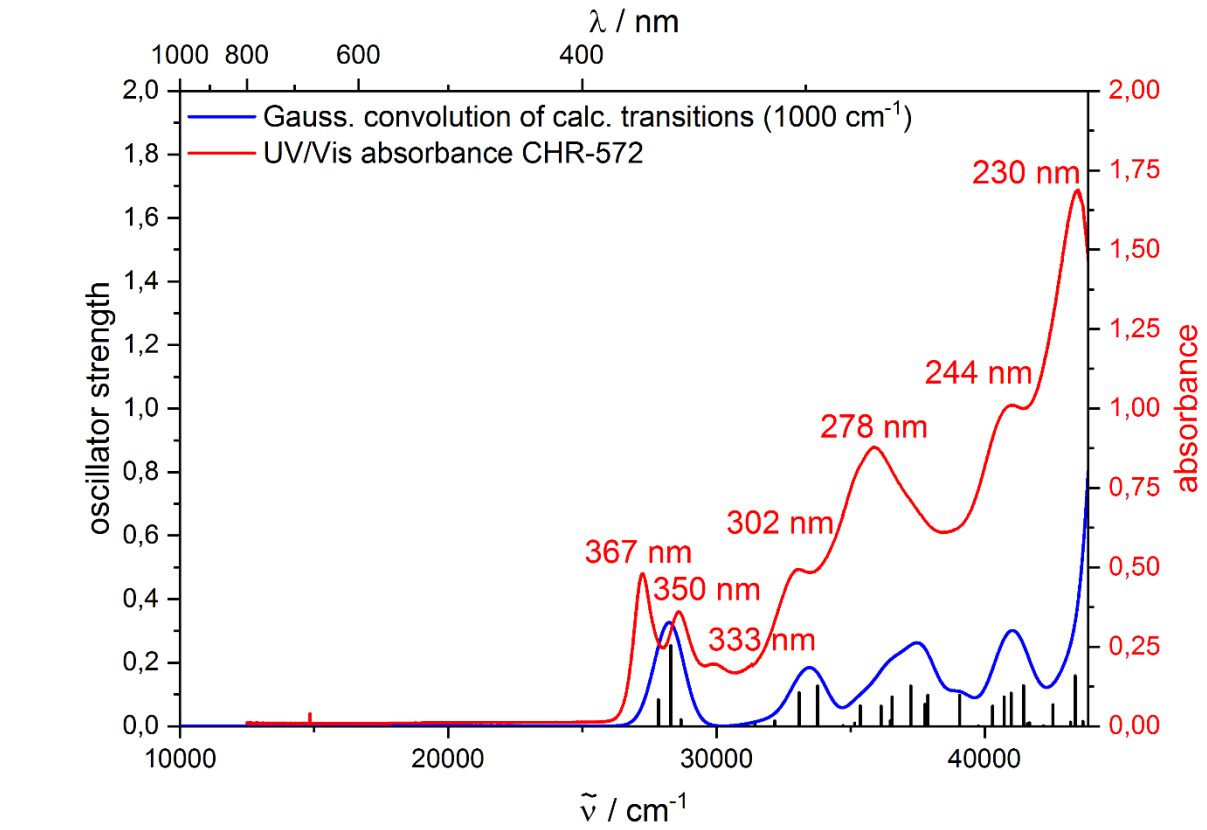


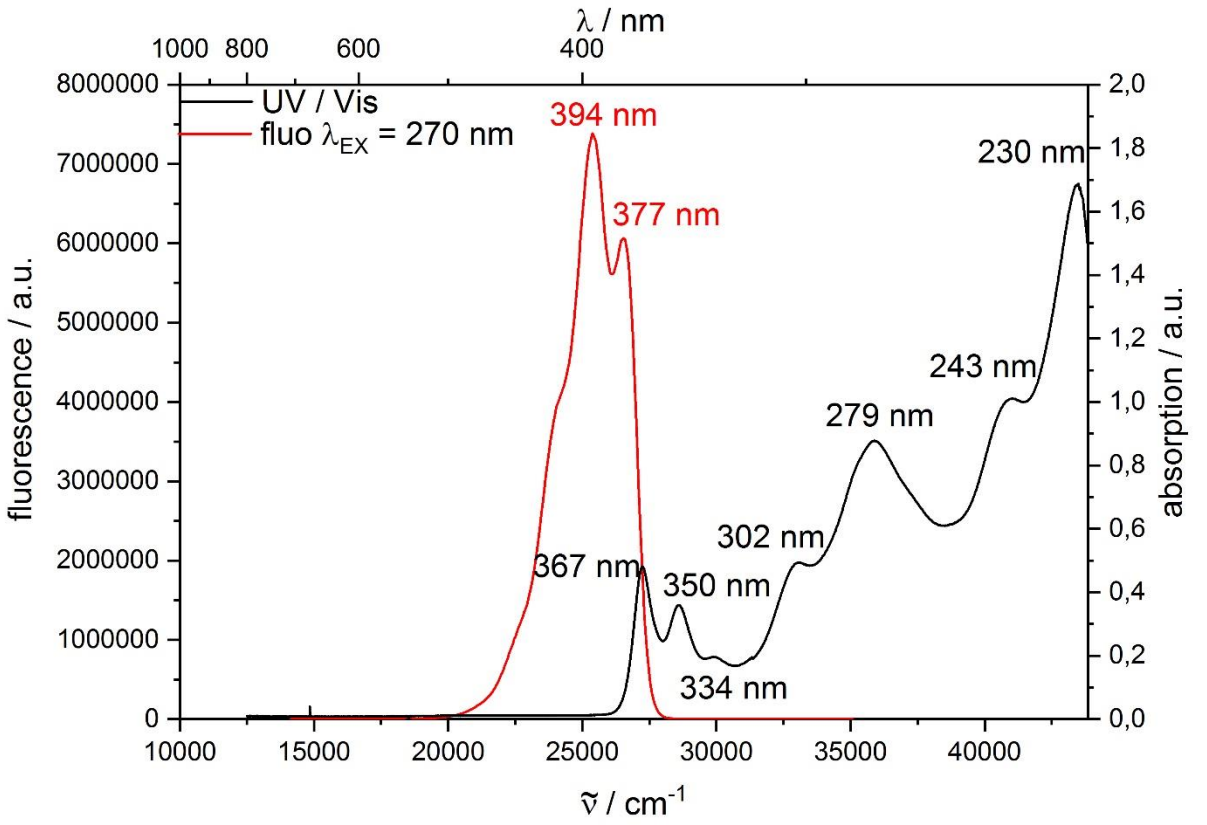
2h

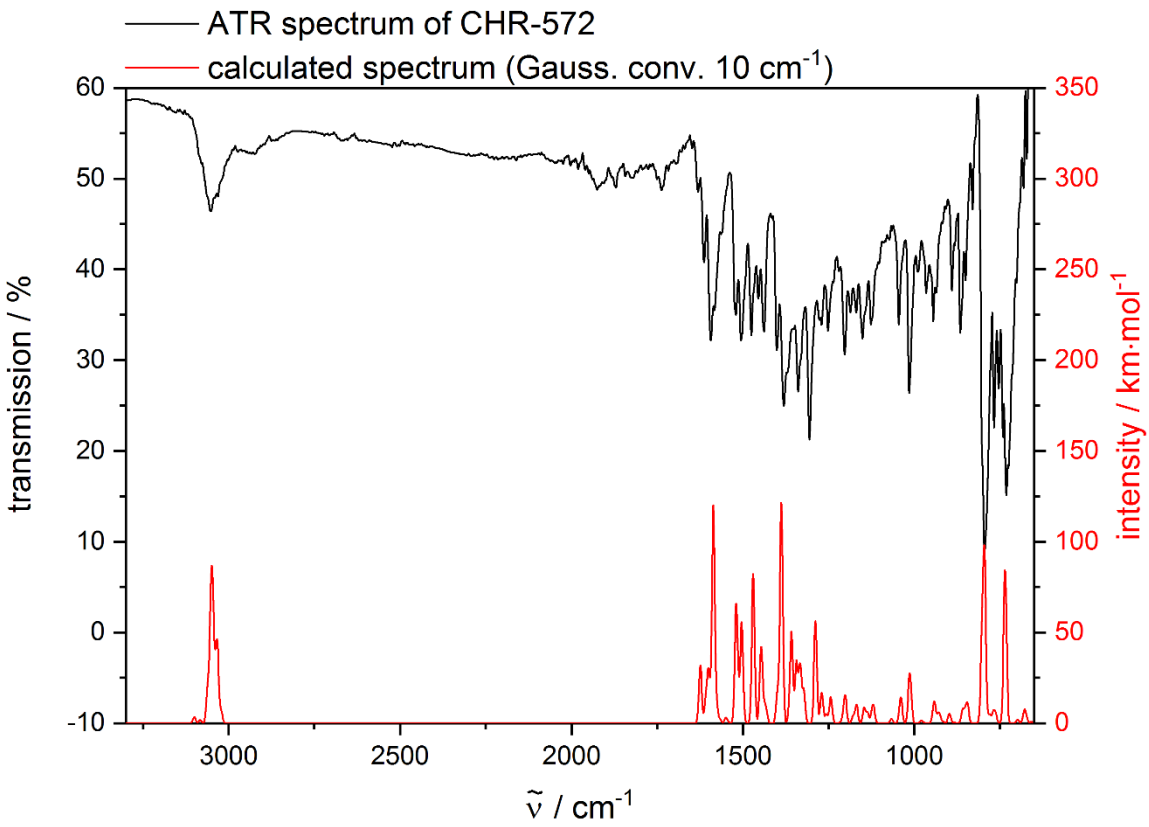
50

C	-3.31482	-4.03513	0.15712
C	-4.57357	-3.69268	0.58145
C	-3.91137	-1.37251	0.68069
C	-2.30866	-3.05999	-0.02175
C	-2.62784	-1.67714	0.17422
C	-4.85851	-2.34898	0.87673
H	-3.06166	-5.07348	-0.02264
C	-0.97413	-3.45647	-0.31335
H	-5.33077	-4.45327	0.72234
H	-5.82819	-2.07868	1.27574
H	-4.13884	-0.35853	0.96573
C	0.04420	-2.54863	-0.36865
C	-0.27901	-1.18759	-0.22805
C	-1.59272	-0.71191	-0.05247
H	-0.76725	-4.51201	-0.43906
H	1.06875	-2.86003	-0.51720
N	0.60081	-0.11915	-0.21151
C	-1.50297	0.73667	-0.03698
C	-0.13016	1.04882	-0.06995
C	-2.43732	1.82153	-0.10820
C	0.37163	2.35966	0.00954
C	-1.92799	3.15390	0.02460
C	-0.52644	3.38370	0.10339
C	-2.82530	4.24447	-0.00333
H	-2.42453	5.24302	0.12666
C	-3.81115	1.67830	-0.40628

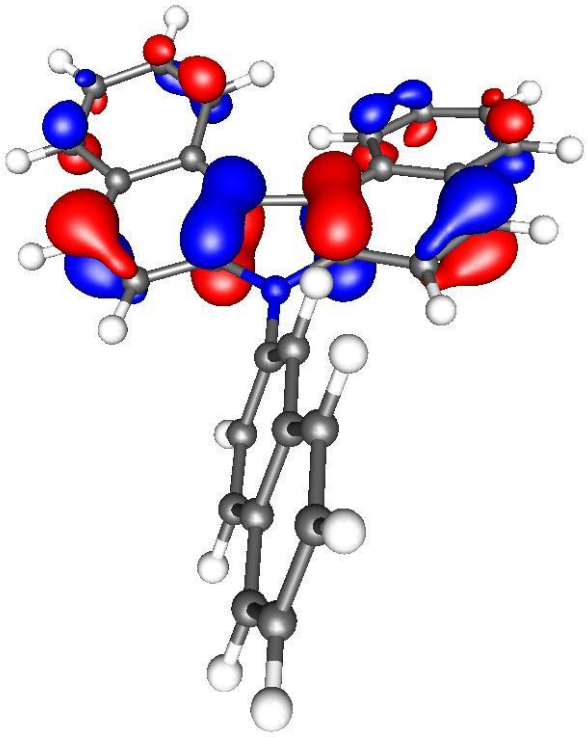
C	-4.16671	4.05992	-0.22388
C	-4.65326	2.76329	-0.46036
H	-4.83978	4.90723	-0.25133
H	-5.69856	2.61530	-0.70130
H	-0.17707	4.40528	0.18788
H	1.43681	2.54336	-0.00070
H	-4.20018	0.70203	-0.64430
C	2.57452	-0.73355	-1.51297
C	3.93354	-0.82120	-1.64553
C	4.79777	-0.37742	-0.61614
C	2.01095	-0.20815	-0.32768
C	4.22555	0.16152	0.57468
C	2.81861	0.22307	0.69312
H	1.91479	-1.05383	-2.30823
H	4.36590	-1.22177	-2.55441
C	6.20606	-0.44718	-0.72776
C	5.08560	0.60560	1.60729
H	2.37474	0.61211	1.60069
C	7.01236	-0.00773	0.28958
C	6.44625	0.52277	1.46840
H	6.63784	-0.85508	-1.63387
H	8.08896	-0.06622	0.19310
H	4.64842	1.01182	2.51141
H	7.09434	0.86514	2.26509


λ / nm
1000 800 600 400
Gauss. convolution of calc. transitions (1000 cm-1)
UV/Vis absorbance CHR-572
oscillator strength
absorbance
230 nm
244 nm
278 nm
302 nm
367 nm
350 nm
333 nm
ν̃ / cm-1

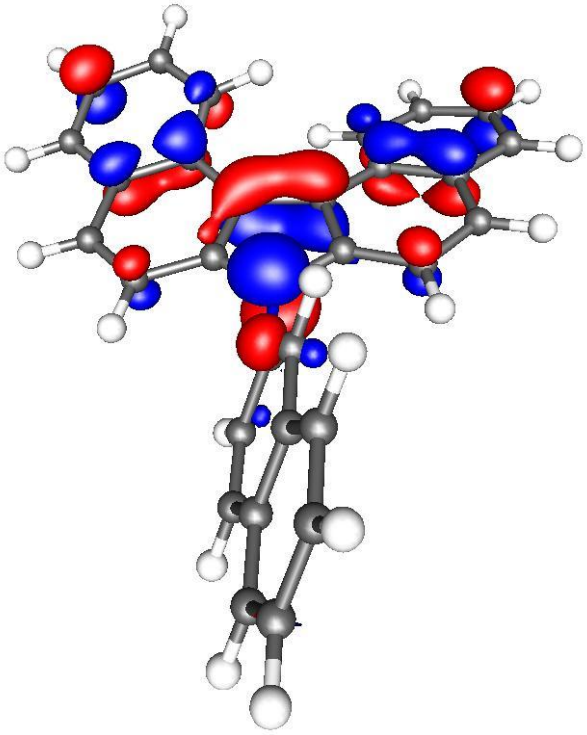

λ / nm
1000 800 600 400
UV / Vis
fluo λEX = 270 nm
fluorescence / a.u.
absorption / a.u.
394 nm
377 nm
230 nm
243 nm
279 nm
302 nm
367 nm
350 nm
334 nm
ν̃ / cm-1


ATR spectrum of CHR-572
calculated spectrum (Gauss. conv. 10 cm-1)
transmission / %
intensity / km·mol-1
ν̃ / cm-1
60
50
40
30
20
10
0
-10
350
300
250
200
150
100
50
0
3000
2500
2000
1500
1000

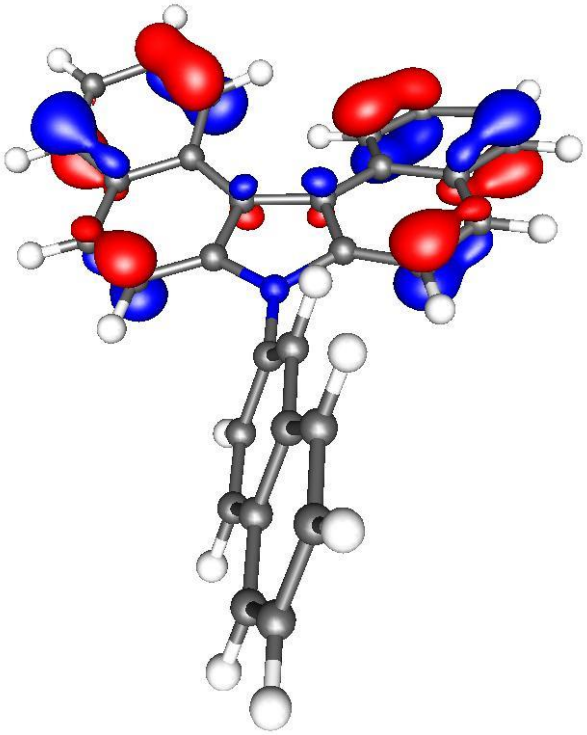
HOMO 0 eV



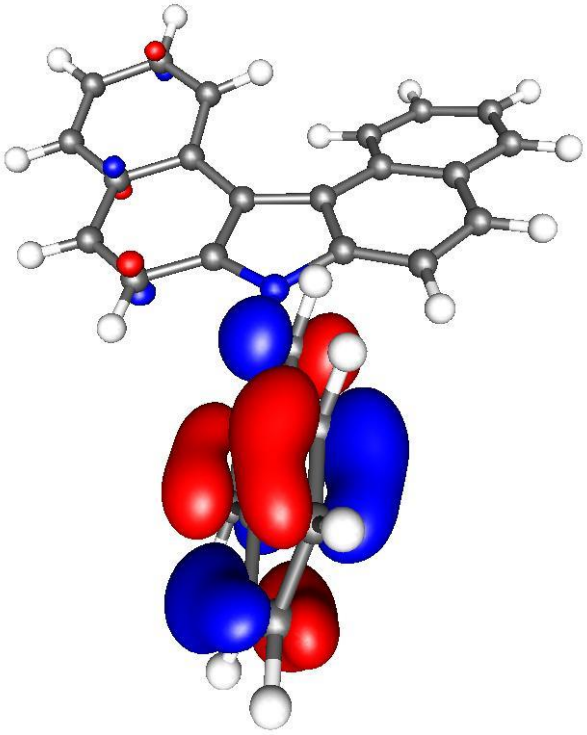
HOMO-1 -0.29 eV



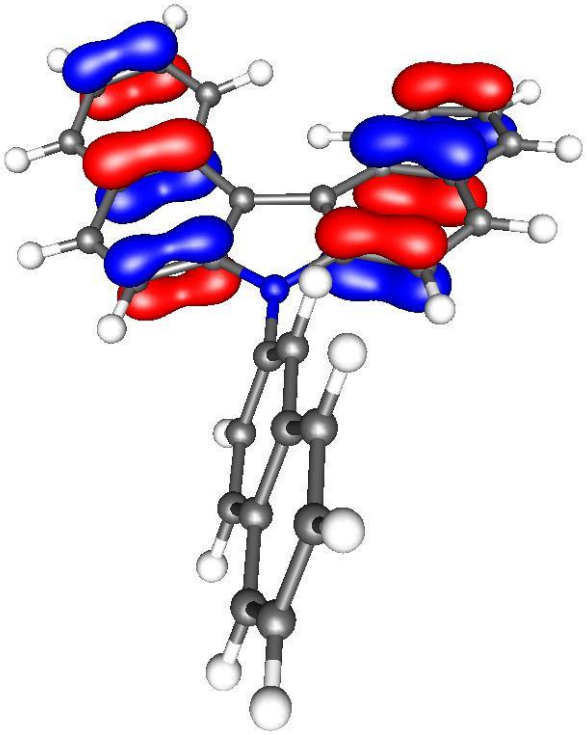
HOMO-2 -1.04 eV



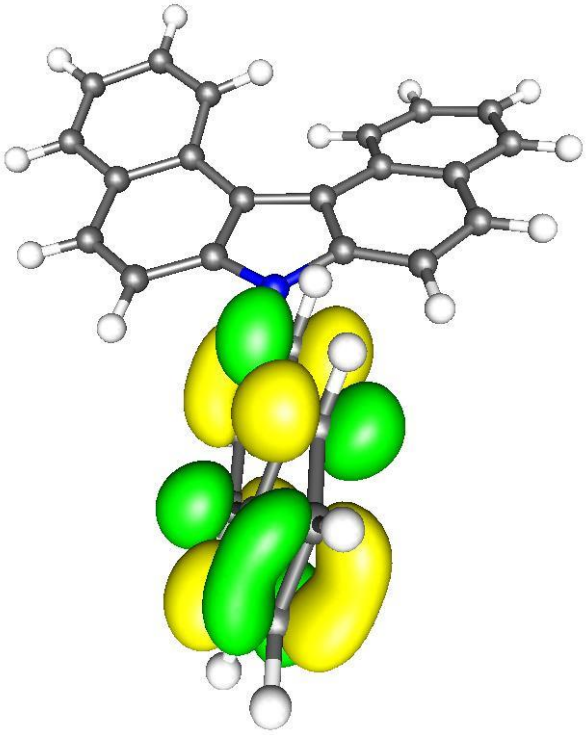
HOMO-3 -1.10 eV



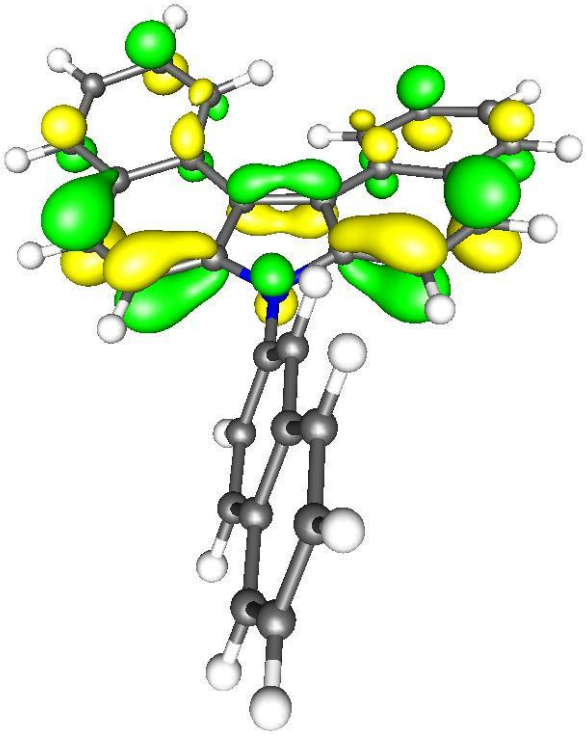
HOMO-4 -1.43 eV



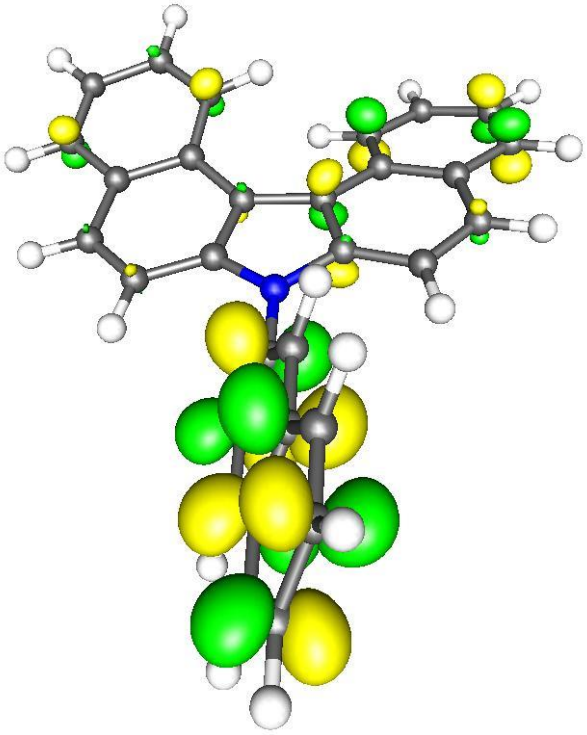
LUMO 3.69 eV



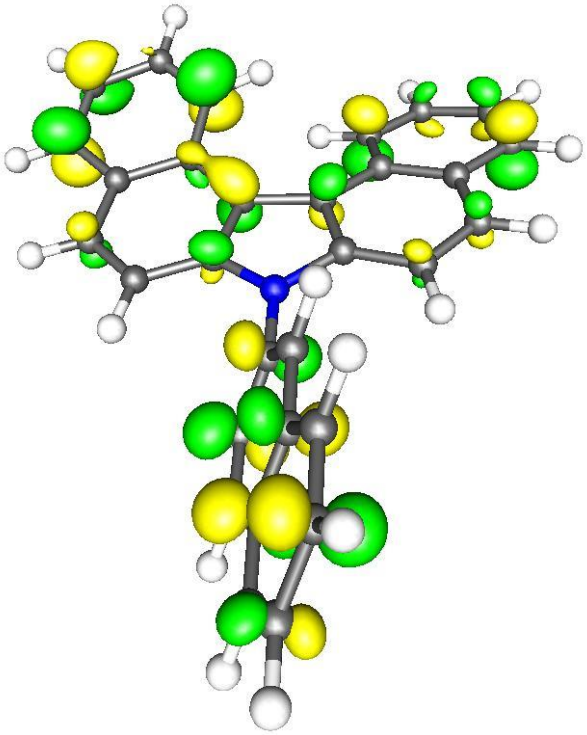
LUMO+1 3.91 eV



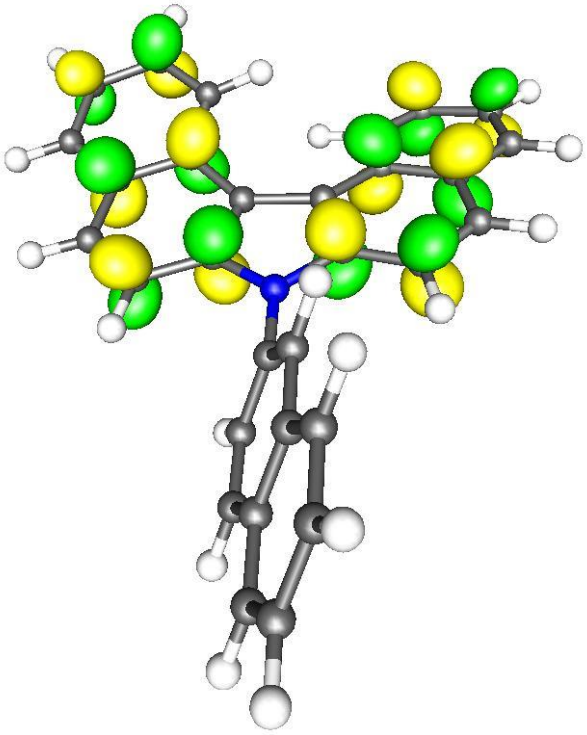
LUMO+2 4.38 eV

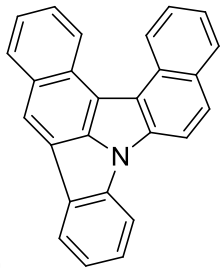


LUMO+3 4.47 eV



LUMO+4 5.01 eV



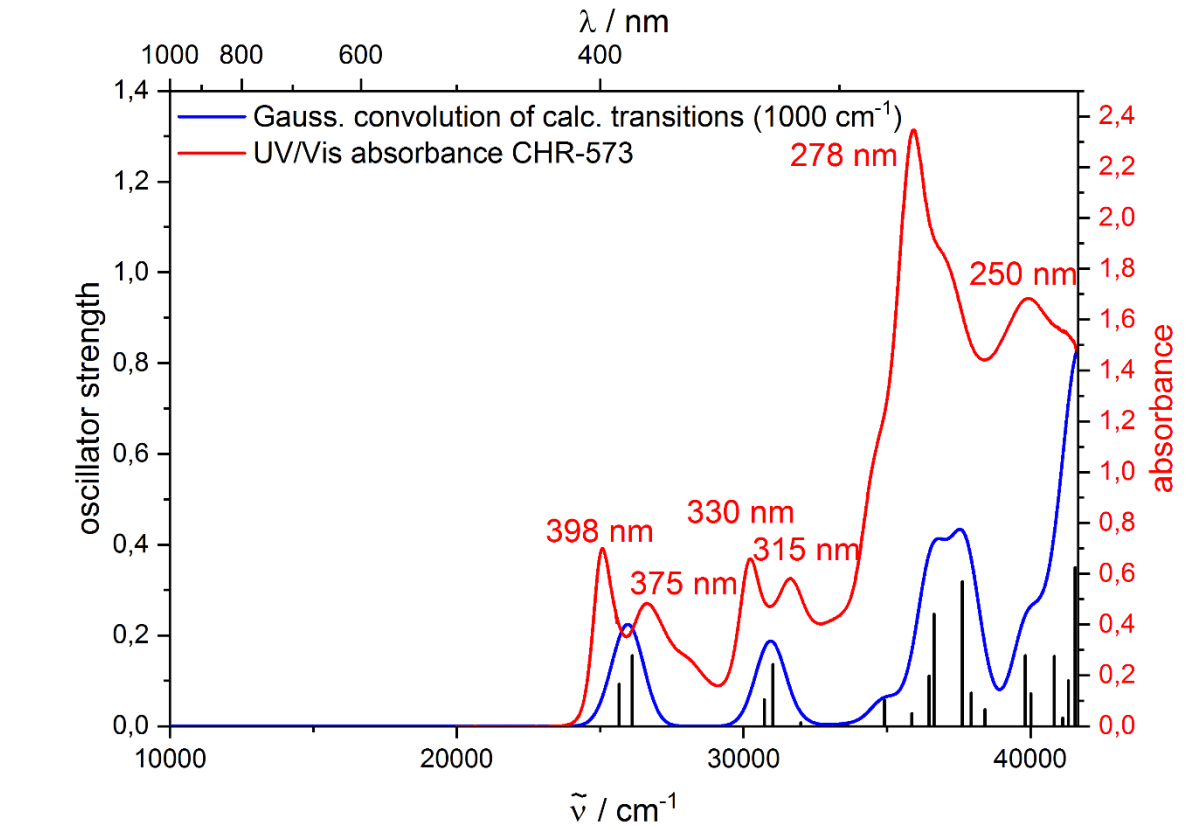


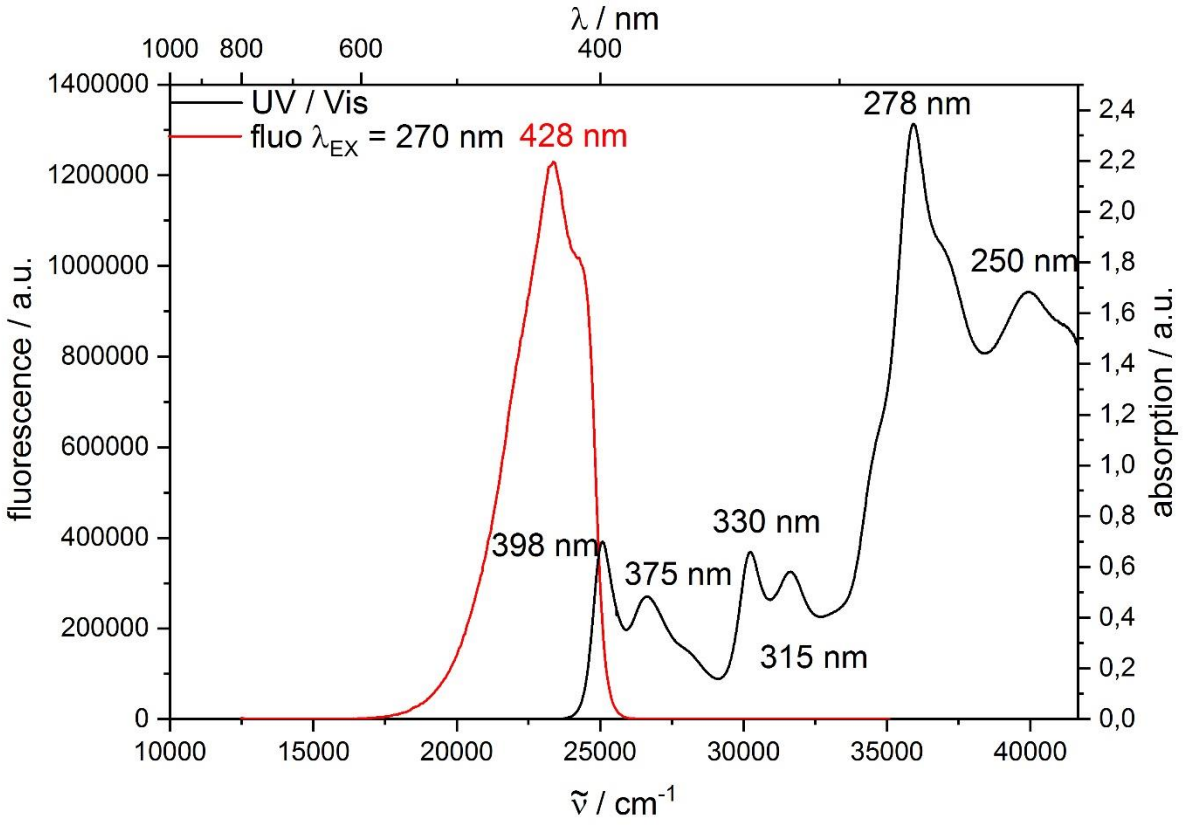
3b

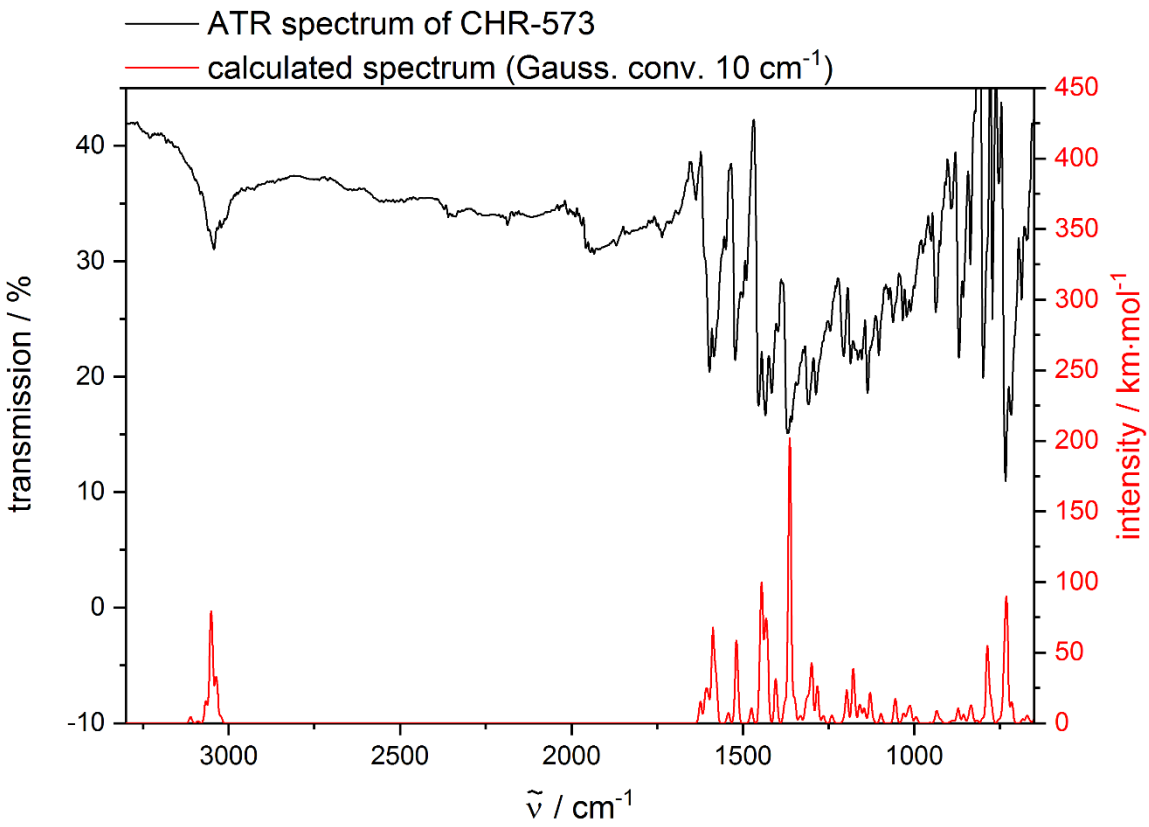
42

C	0.84450	4.28961	0.04453
C	-0.32823	4.97567	-0.13462
C	-1.53083	2.88903	-0.28280
C	0.89176	2.87480	0.06822
C	-0.35778	2.13896	-0.04743
C	-1.52301	4.26208	-0.32461
H	1.77716	4.83045	0.15384
C	2.17369	2.24401	0.15480
H	-0.33116	6.05783	-0.15502
H	-2.44540	4.79586	-0.51607
H	-2.45386	2.36902	-0.47852
C	2.24290	0.87457	0.11098
C	1.00401	0.23417	0.04571
C	-0.28758	0.70496	0.01259
H	3.05247	2.87317	0.22163
N	1.10615	-1.12024	-0.02260
C	-1.09506	-0.52601	-0.02469
C	-0.18705	-1.62206	-0.09234
C	-2.48840	-0.82683	0.05187
C	-0.59225	-2.95644	-0.22461
C	-2.89820	-2.19110	-0.11773
C	-1.93358	-3.22088	-0.27016
C	-4.27583	-2.50764	-0.08268
H	-4.56911	-3.53978	-0.23407
C	-3.49088	0.12270	0.35467
C	-5.22333	-1.54742	0.15982
C	-4.81851	-0.22316	0.40585

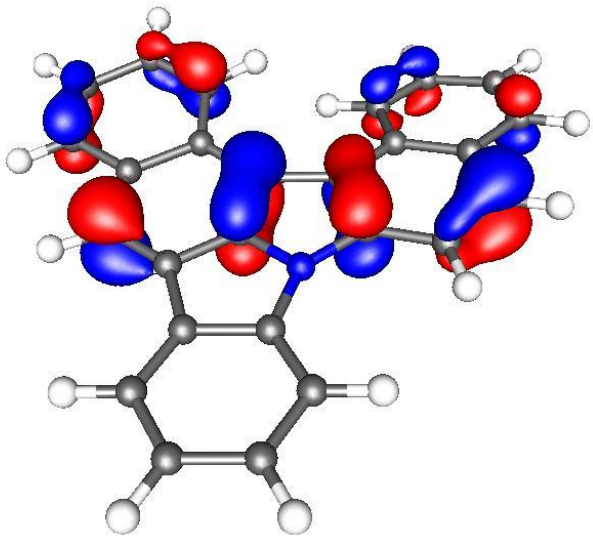
H	-6.27331	-1.80854	0.18947
H	-5.55813	0.52859	0.65141
H	-2.28199	-4.23887	-0.39182
H	0.13864	-3.74931	-0.30095
H	-3.20110	1.13016	0.60134
C	3.21082	-0.22799	0.08907
C	4.59604	-0.28201	0.13052
C	5.23199	-1.52044	0.08136
C	2.47040	-1.44968	-0.00228
C	4.49319	-2.69854	-0.00886
C	3.09961	-2.68003	-0.05233
H	5.17624	0.62948	0.19997
H	6.31244	-1.56932	0.11338
H	5.00836	-3.64968	-0.04561
H	2.53536	-3.59949	-0.11986


λ / nm
1000 800 600 400
Gauss. convolution of calc. transitions (1000 cm-1)
UV/Vis absorbance CHR-573
278 nm
250 nm
330 nm
315 nm
398 nm
375 nm
oscillator strength
absorbance
ν̃ / cm-1

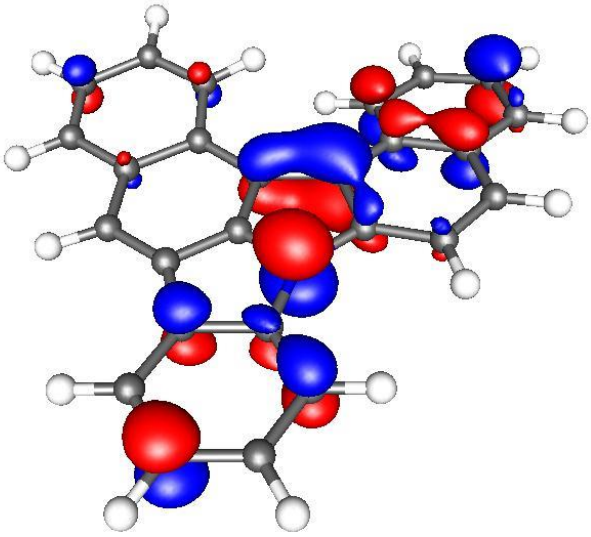

λ / nm
1000 800 600 400
UV / Vis
fluo λEX = 270 nm
428 nm
278 nm
250 nm
330 nm
398 nm
375 nm
315 nm
fluorescence / a.u.
absorption / a.u.
ν̃ / cm-1


ATR spectrum of CHR-573
calculated spectrum (Gauss. conv. 10 cm-1)
transmission / %
intensity / km·mol-1
ν̃ / cm-1
40
30
20
10
0
-10
450
400
350
300
250
200
150
100
50
0
3000
2500
2000
1500
1000

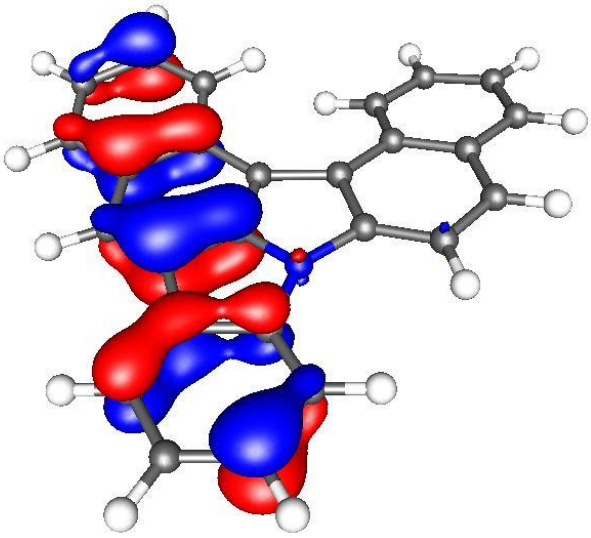
HOMO 0 eV



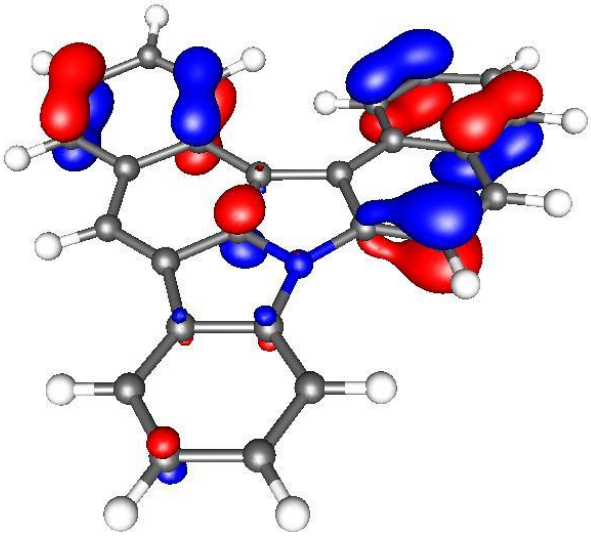
HOMO-1 -0.26 eV



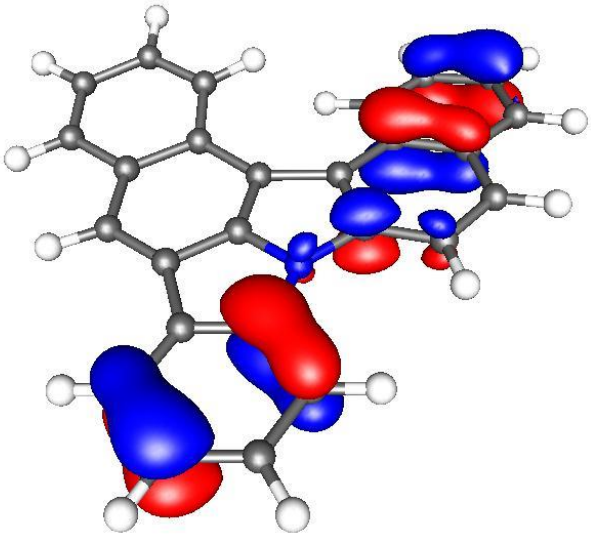
HOMO-2 -0.83 eV



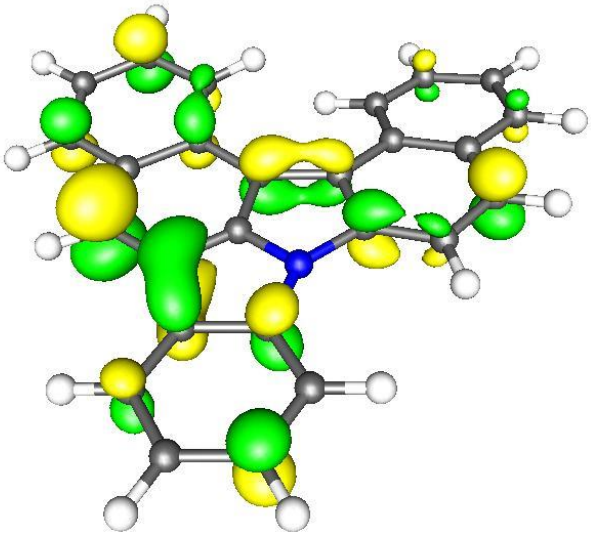
HOMO-3 -1.26 eV



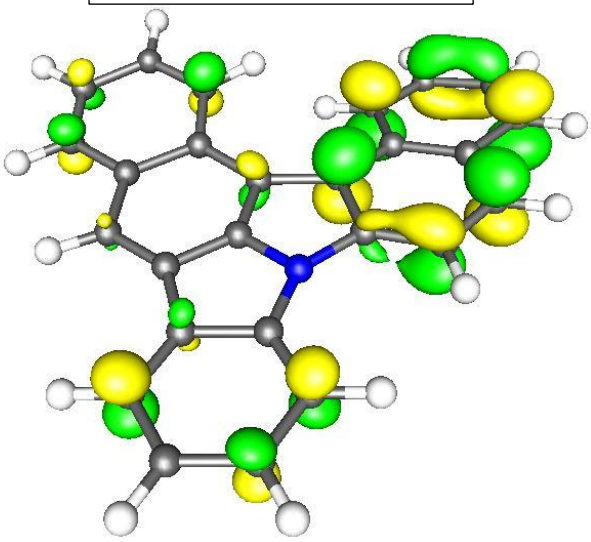
HOMO-4 -1.70 eV



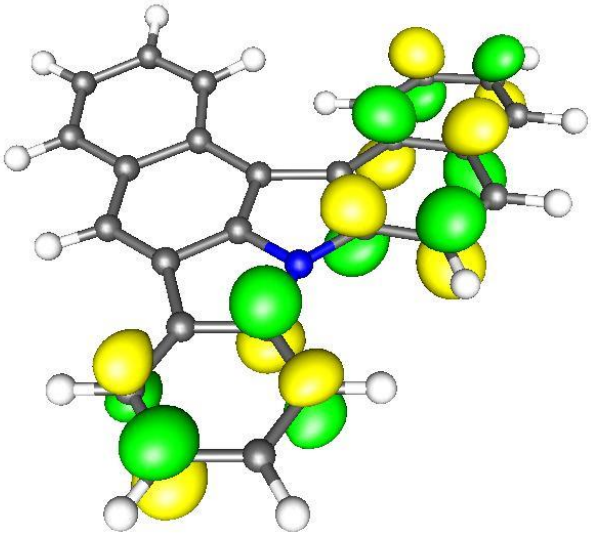
LUMO 3.38 eV



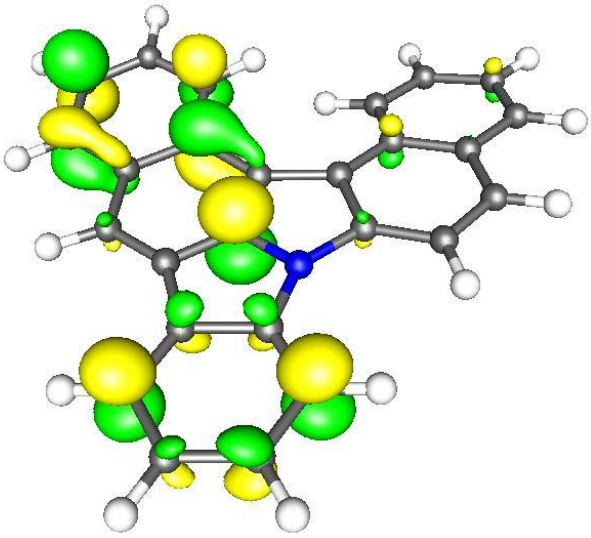
LUMO+1 4.12 eV



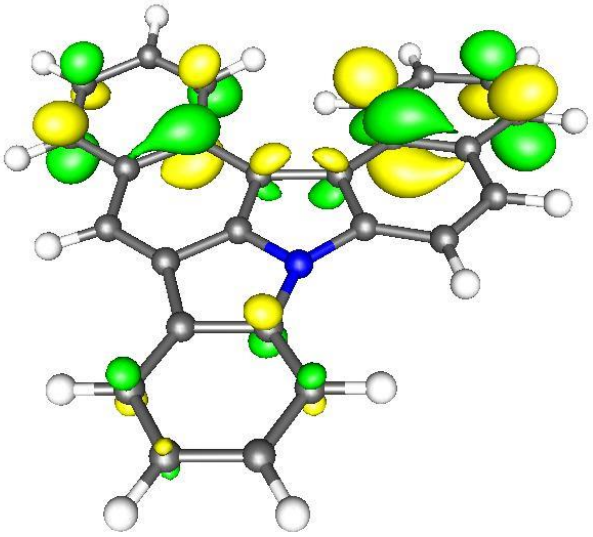
LUMO+2 4.75 eV

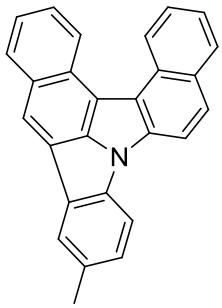


LUMO+3 4.83 eV



LUMO+4 5.29 eV



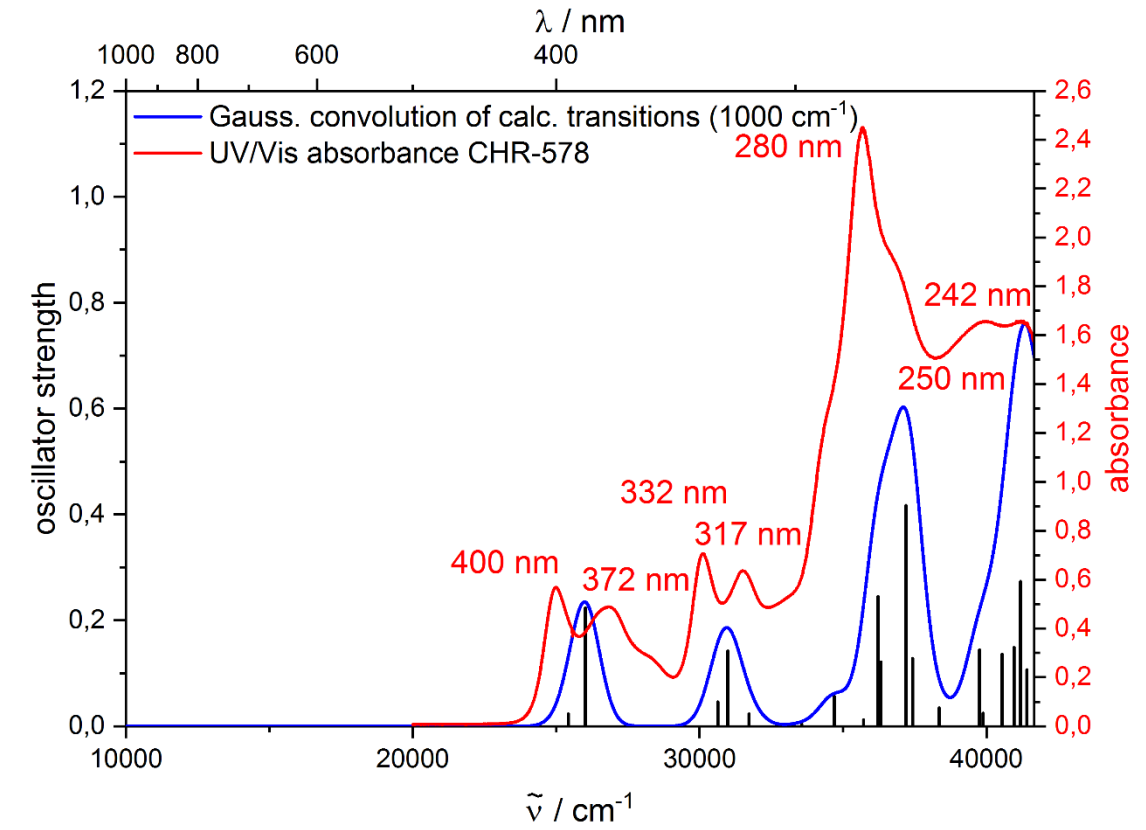


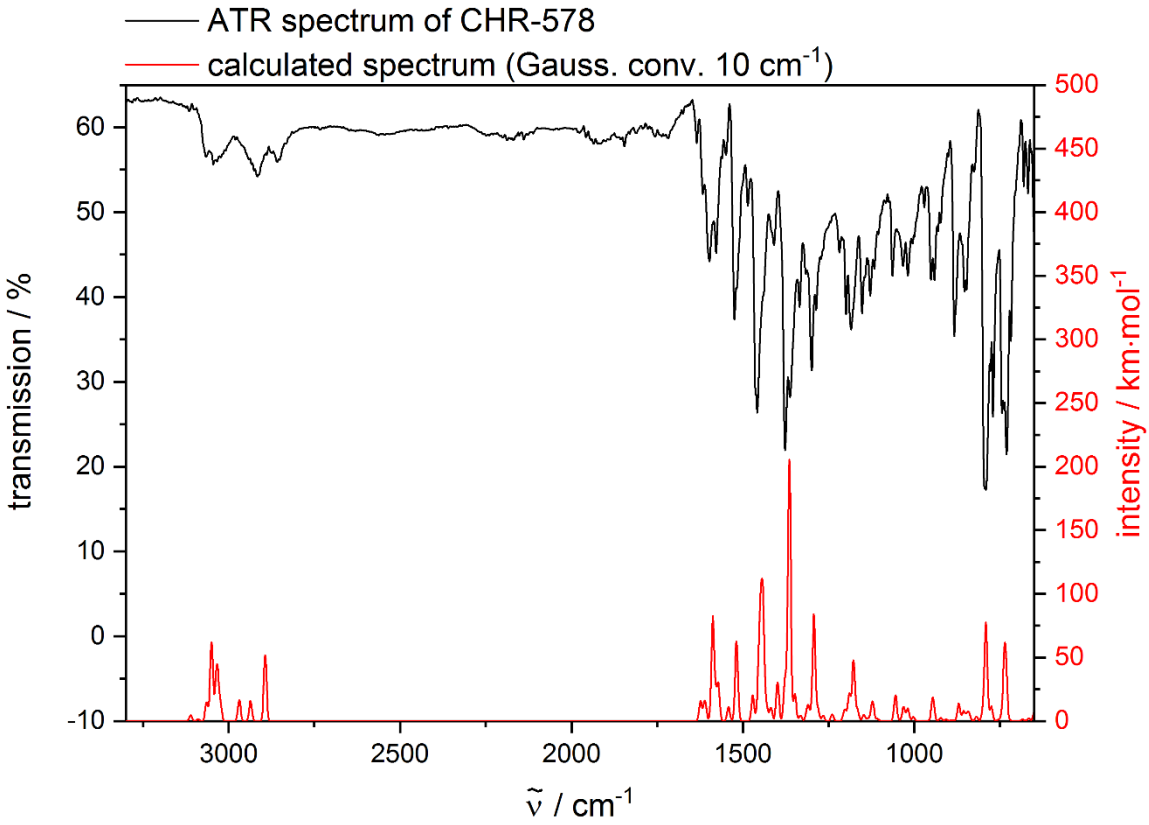
3c

45

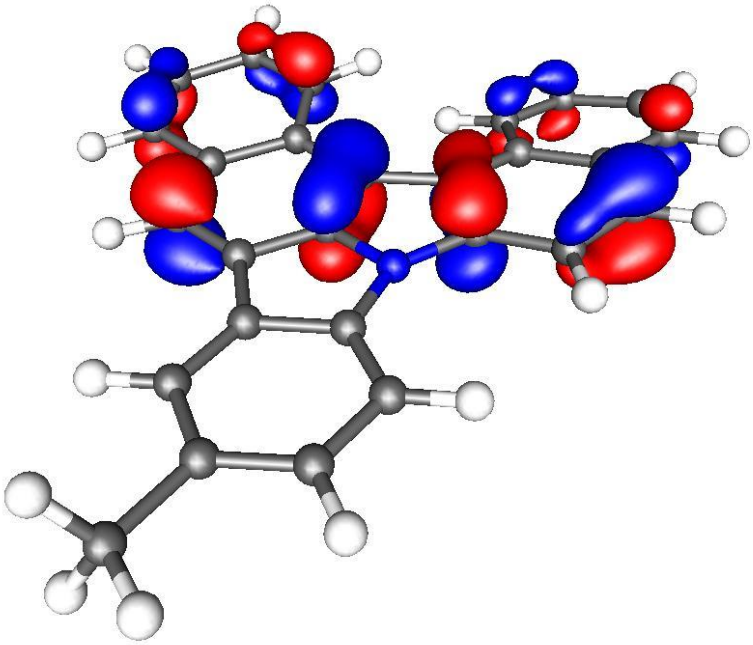
C	0.10802	4.38789	0.04102
C	-1.12797	4.95448	-0.13173
C	-2.11789	2.75883	-0.27608
C	0.29555	2.98497	0.06340
C	-0.87512	2.12879	-0.04728
C	-2.24683	4.12603	-0.31632
H	0.98294	5.01868	0.14602
C	1.63451	2.48436	0.14360
H	-1.23827	6.03105	-0.15110
H	-3.21877	4.56554	-0.50223
H	-2.98579	2.14998	-0.46787
C	1.83914	1.12884	0.09879
C	0.66946	0.36812	0.03911
C	-0.66283	0.70857	0.01105
H	2.44639	3.19815	0.20630
N	0.90487	-0.96916	-0.03039
C	-1.34426	-0.59601	-0.02448
C	-0.33134	-1.59632	-0.09651
C	-2.70042	-1.03457	0.05579
C	-0.60206	-2.96459	-0.22907
C	-2.97253	-2.43289	-0.11418
C	-1.91038	-3.36141	-0.27067
C	-4.31151	-2.88540	-0.07563
H	-4.50057	-3.94165	-0.22689
C	-3.79212	-0.19030	0.36195
C	-5.34975	-2.02482	0.17002

C	-5.07855	-0.66697	0.41607
H	-6.36830	-2.38963	0.20216
H	-5.88886	0.00713	0.66401
H	-2.15617	-4.40895	-0.39224
H	0.20461	-3.67994	-0.30871
H	-3.60389	0.84092	0.60897
C	2.91271	0.12772	0.07177
C	4.29415	0.21483	0.10689
C	5.07593	-0.94398	0.05497
C	2.29694	-1.16079	-0.01714
C	4.44220	-2.18489	-0.03271
C	3.05313	-2.31414	-0.07018
H	4.77341	1.18478	0.17424
C	6.57813	-0.84524	0.09358
H	5.04916	-3.08112	-0.07253
H	2.59293	-3.29008	-0.13558
H	7.04035	-1.83120	0.04504
H	6.92023	-0.36031	1.01143
H	6.95859	-0.25584	-0.74458

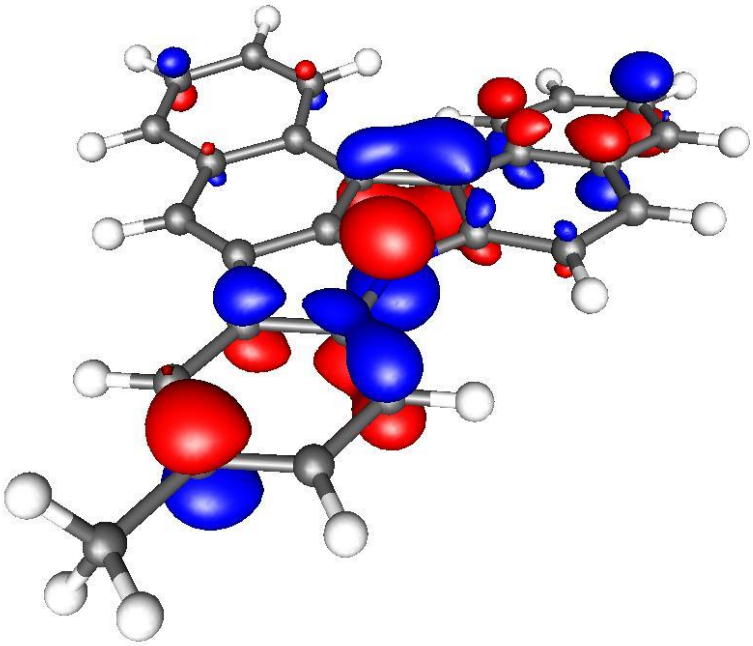

λ / nm
1000
800
600
400
Gauss. convolution of calc. transitions (1000 cm-1)
UV/Vis absorbance CHR-578
280 nm
242 nm
250 nm
332 nm
317 nm
400 nm
372 nm
oscillator strength
absorbance
ν̃ / cm-1


ATR spectrum of CHR-578
calculated spectrum (Gauss. conv. 10 cm-1)
transmission / %
intensity / km·mol-1
ν̃ / cm-1

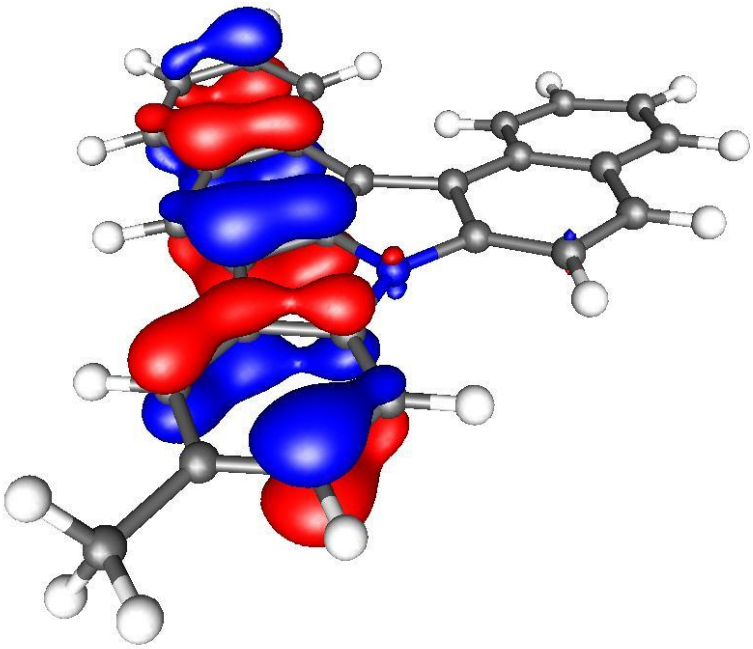
HOMO 0 eV



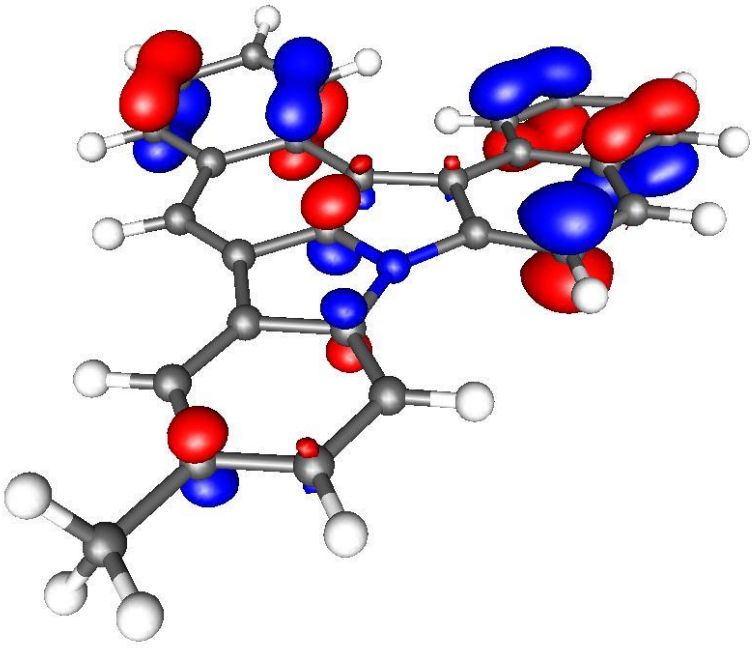
HOMO-1 -0.19 eV



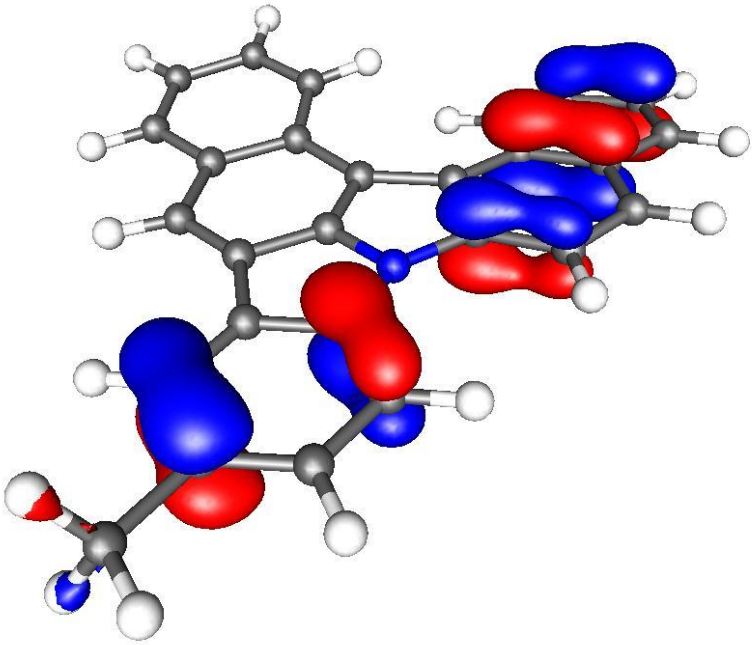
HOMO-2 -0.73 eV



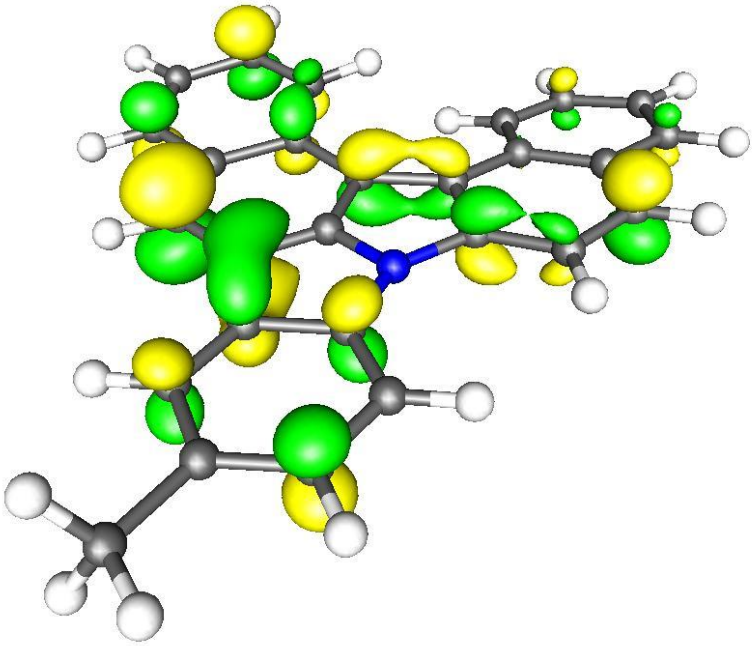
HOMO-3 -1.18 eV



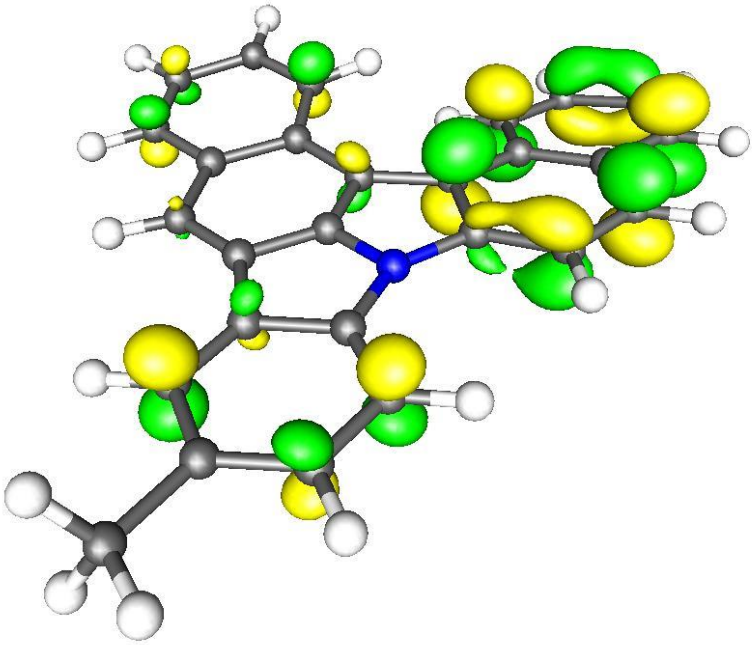
HOMO-4 -1.53 eV



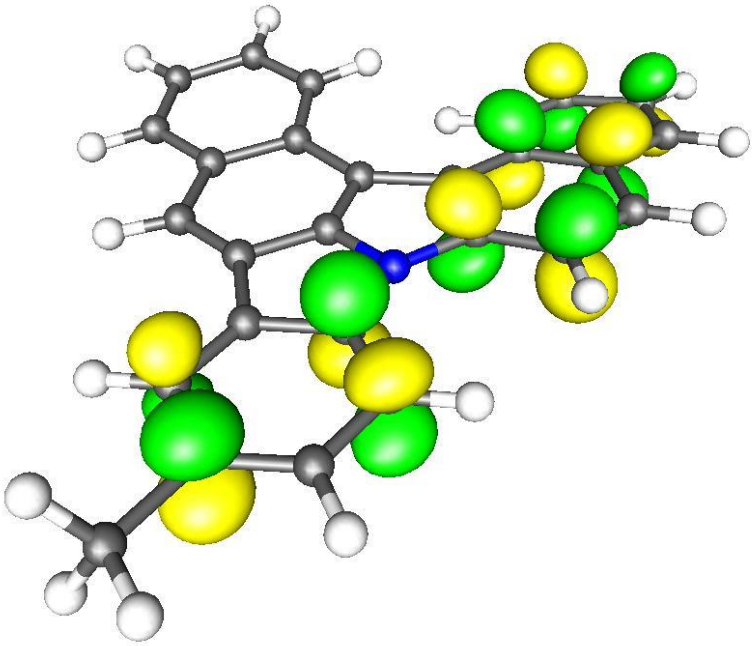
LUMO 3.59 eV



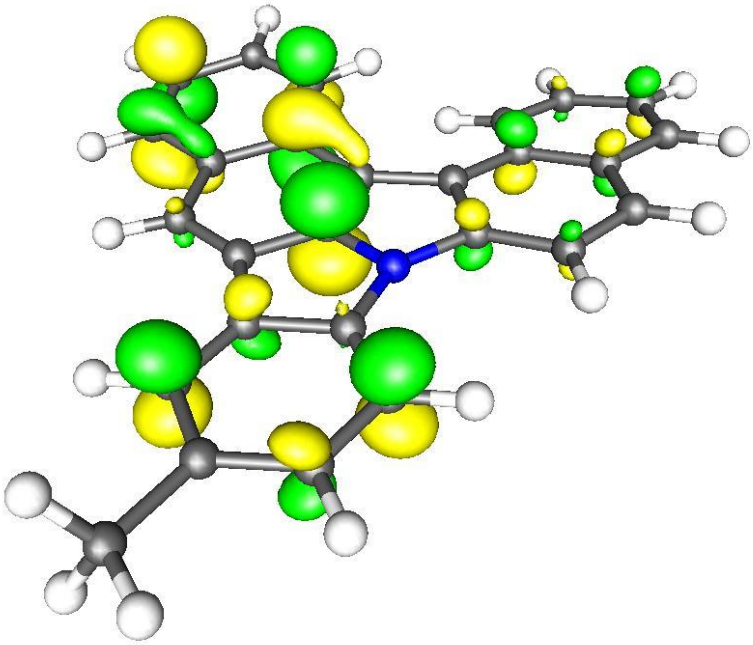
LUMO+1 4.33 eV



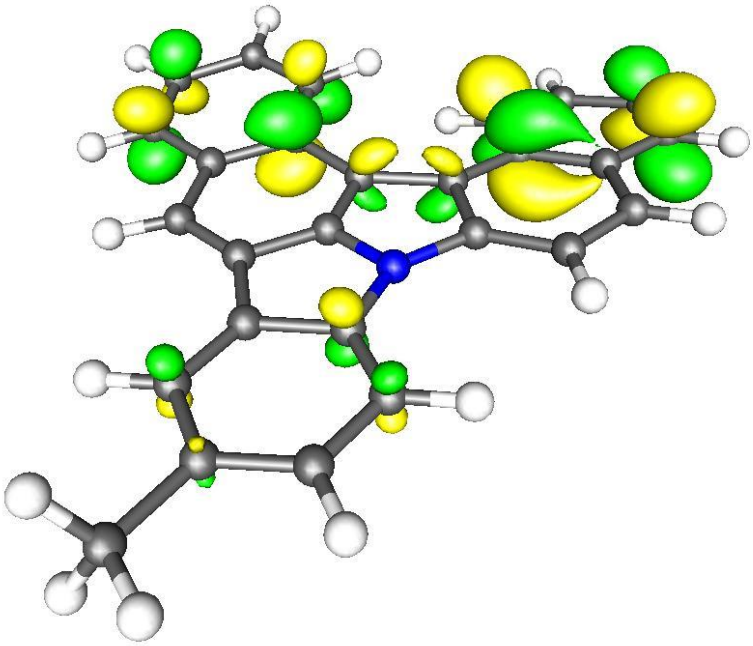
LUMO+2 4.82 eV

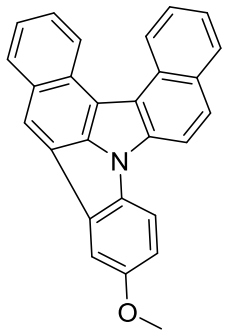


LUMO+3 4.92 eV



LUMO+4 5.41 eV



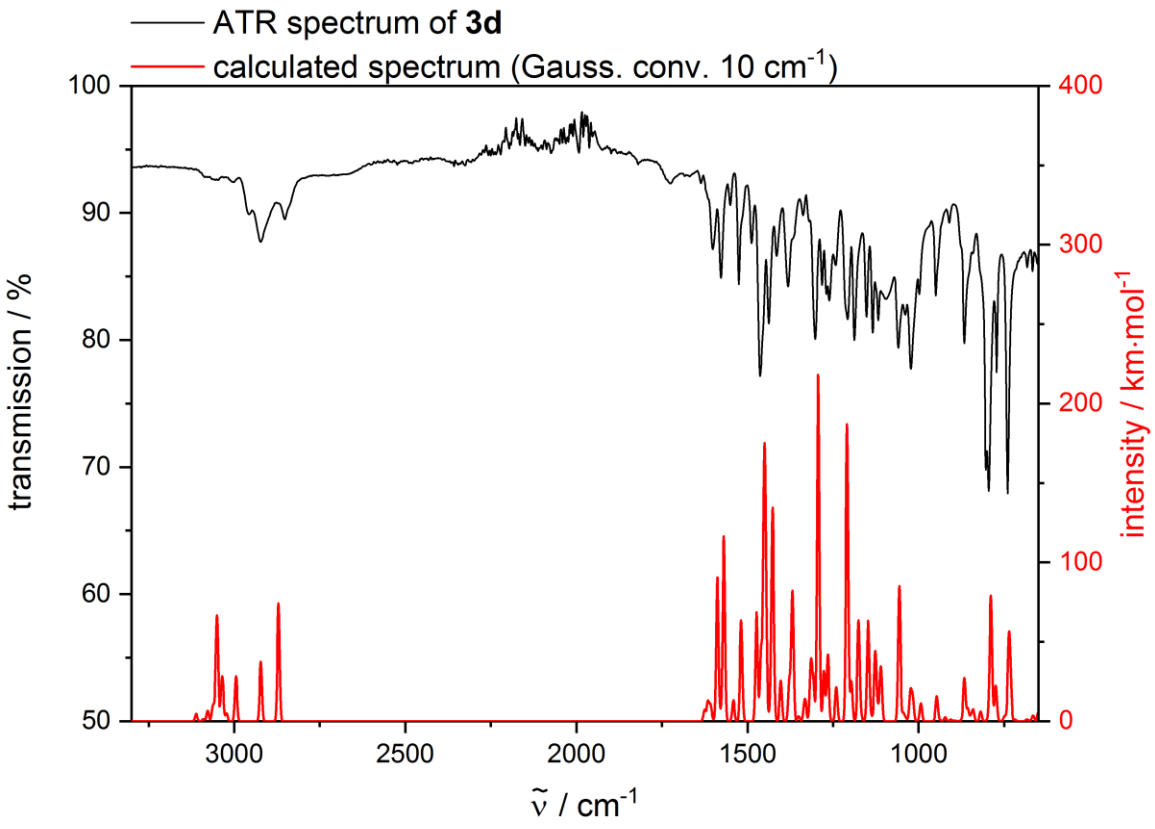


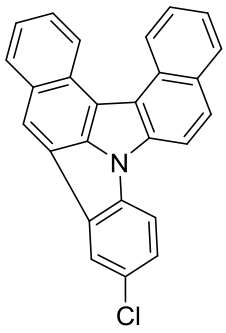
3d

46

C	0.6009339	4.4351761	-0.0411231
C	1.8844711	4.8841590	0.1307501
C	2.6654826	2.6055630	0.2734467
C	0.2837864	3.0558682	-0.0639731
C	1.3693613	2.0940331	0.0453363
C	2.9212127	3.9548351	0.3140873
H	-0.2116374	5.1445872	-0.1451874
C	-1.0962135	2.6824277	-0.1427236
H	2.0946498	5.9457129	0.1505585
H	3.9300803	4.3016773	0.4993467
H	3.4731018	1.9185224	0.4641774
C	-1.4255076	1.3520781	-0.0988760
C	-0.3326749	0.4840991	-0.0413803
C	1.0261130	0.6995775	-0.0133877
H	-1.8386050	3.4683168	-0.2033136
N	-0.6907643	-0.8246106	0.0282602
C	1.5831084	-0.6619506	0.0233871
C	0.4803213	-1.5634895	0.0950271
C	2.8923234	-1.2256318	-0.0559791
C	0.6225953	-2.9513173	0.2277266
C	3.0325563	-2.6431646	0.1143948
C	1.8880075	-3.4684272	0.2700909
C	4.3232131	-3.2190151	0.0771431
H	4.4123099	-4.2883609	0.2287181
C	4.0586532	-0.4876037	-0.3614388
C	5.4379163	-2.4596163	-0.1675304
C	5.2949943	-1.0825237	-0.4140681

H	6.4178445	-2.9182132	-0.1985831
H	6.1649388	-0.4870305	-0.6612622
H	2.0349927	-4.5343628	0.3917604
H	-0.2471824	-3.5886423	0.3070291
H	3.9683177	0.5566226	-0.6089965
C	-2.5892077	0.4569313	-0.0695045
C	-3.9517158	0.6813265	-0.1021077
C	-4.8273732	-0.4084277	-0.0476343
C	-2.0972609	-0.8852342	0.0181970
C	-4.3356962	-1.7119965	0.0386684
C	-2.9597064	-1.9578349	0.0722776
H	-4.3625123	1.6800095	-0.1680323
O	-6.1539250	-0.0937144	-0.0856295
H	-5.0124662	-2.5518637	0.0799581
H	-2.5950209	-2.9733283	0.1364472
C	-7.0978062	-1.1481095	-0.0341364
H	-8.0768581	-0.6765230	-0.0762848
H	-7.0103104	-1.7182906	0.8960856
H	-6.9862193	-1.8272367	-0.8852248





3e

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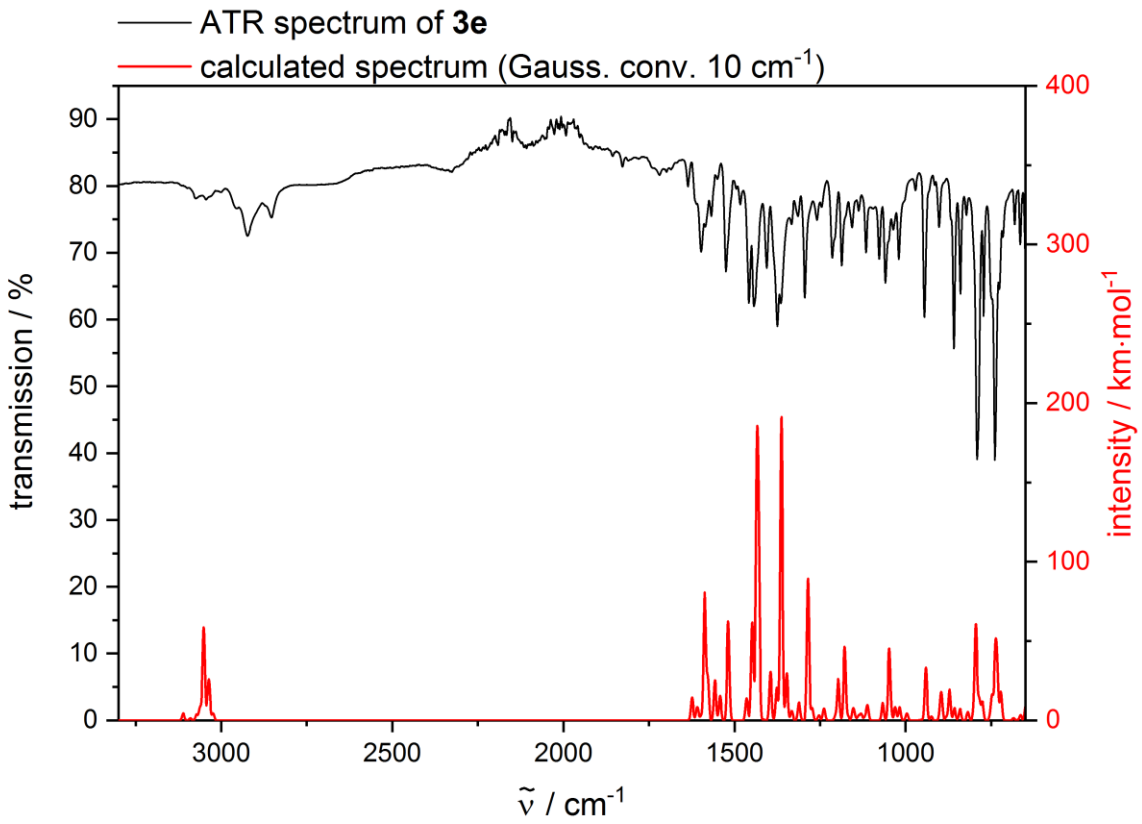
C	-0.3409203	4.4147525	0.0394937
C	-1.5976136	4.9328345	-0.1321331
C	-2.5038188	2.7007672	-0.2747961
C	-0.1000852	3.0196009	0.0620736
C	-1.2375453	2.1188074	-0.0465490
C	-2.6842354	4.0617418	-0.3155922
H	0.5092724	5.0785355	0.1433132
C	1.2564262	2.5717091	0.1396570
H	-1.7494971	6.0042285	-0.1520004
H	-3.6721895	4.4639941	-0.5011637
H	-3.3479659	2.0592025	-0.4655966
C	1.5112937	1.2242296	0.0951846
C	0.3724683	0.4190748	0.0387703
C	-0.9715435	0.7082062	0.0123878
H	2.0410995	3.3152546	0.2000629
N	0.6591391	-0.9086975	-0.0321292
C	-1.6027552	-0.6221052	-0.0234427
C	-0.5538664	-1.5832849	-0.0972694
C	-2.9414141	-1.1110555	0.0581979
C	-0.7720893	-2.9604295	-0.2303762
C	-3.1607275	-2.5183296	-0.1129334
C	-2.0647576	-3.4060255	-0.2712194
C	-4.4817284	-3.0210334	-0.0733699
H	-4.6313127	-4.0834005	-0.2255947
C	-4.0632540	-0.3085460	0.3672706
C	-5.5508807	-2.2001477	0.1746729
C	-5.3306064	-0.8333940	0.4224412

H	-6.5549506	-2.6028769	0.2077426
H	-6.1653424	-0.1907802	0.6726687
H	-2.2708849	-4.4619595	-0.3934583
H	0.0602780	-3.6455001	-0.3113218
H	-3.9135842	0.7285672	0.6158837
C	2.6203954	0.2650800	0.0638998
C	3.9983169	0.4115162	0.0945157
C	4.7875388	-0.7323205	0.0371435
C	2.0542305	-1.0467376	-0.0237942
C	4.2340131	-2.0061605	-0.0491972
C	2.8514142	-2.1749369	-0.0807767
H	4.4575336	1.3879304	0.1604194
Cl	6.5260035	-0.5648307	0.0743962
H	4.8860707	-2.8668516	-0.0911181
H	2.4259063	-3.1662221	-0.1452237

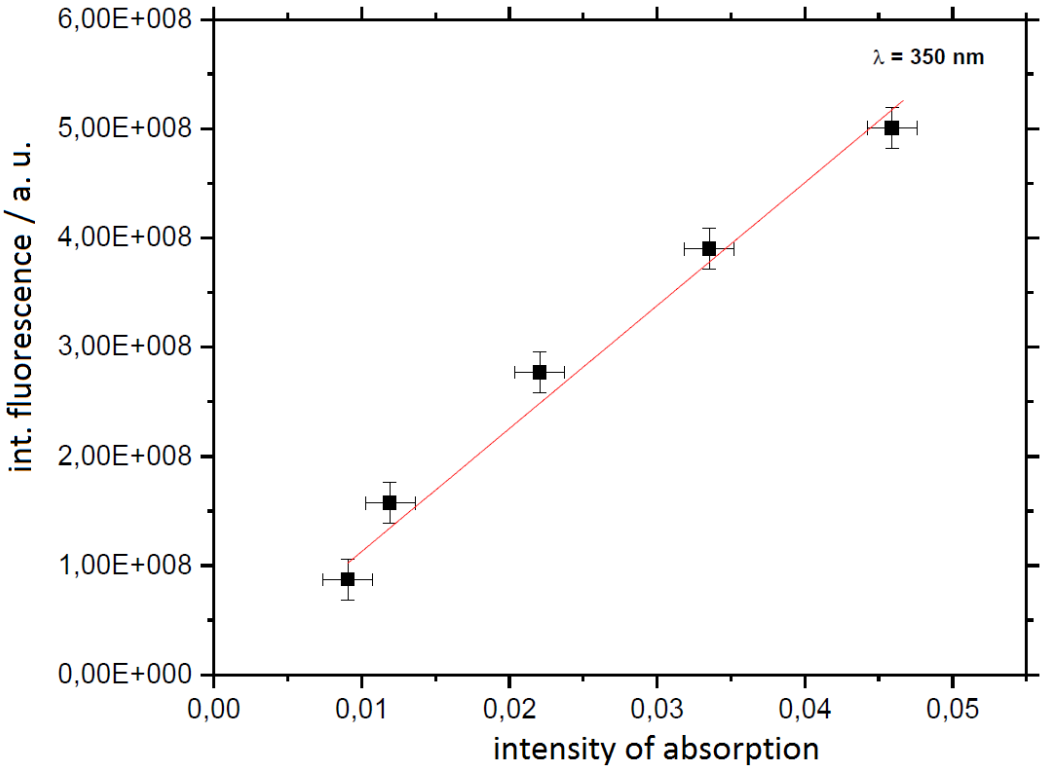


1.6 Determination of quantum yields

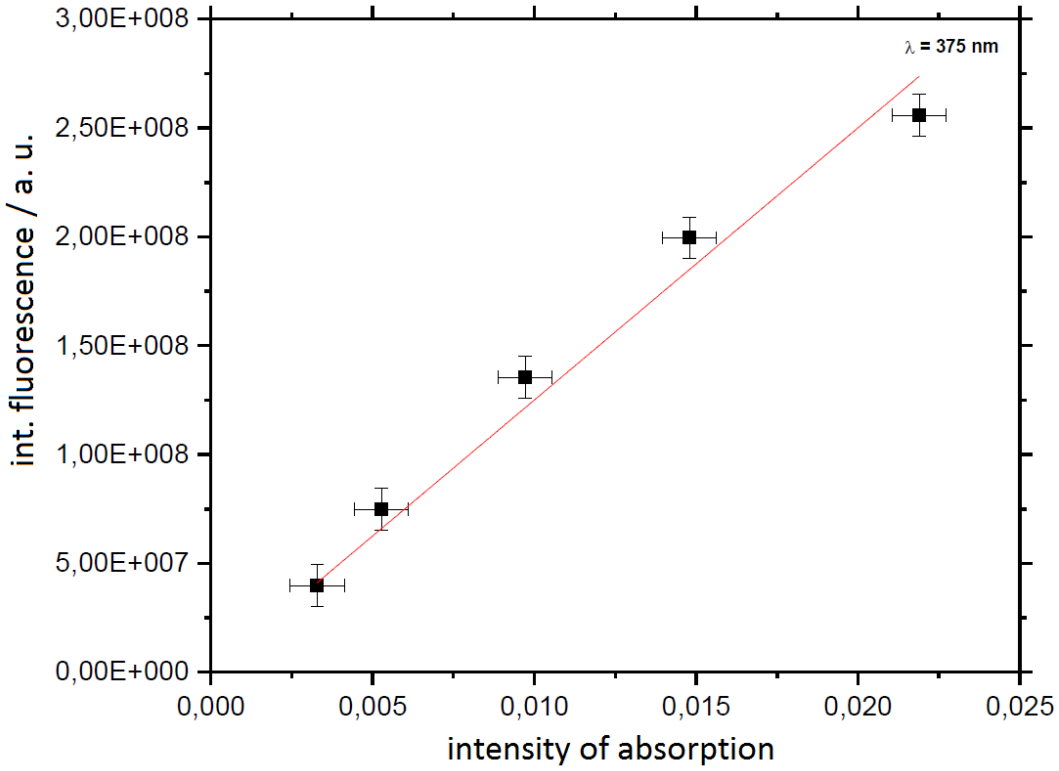
In this work the quantum yield ϕ is obtained by a relative method. The unknown quantum yield of an analysed substance *i* is determined by comparison with a substance serving as standard *S* with a known quantum yield. The standards chosen in this work are POPOP (λ_{EX} = 330 – 375 nm) and tryptophan (λ_{EX} = 277 / 280 nm). These substances are suitable, since the excitation wavelengths (for the fluorescence spectra) of the investigated species and standards must be identical. With each of the samples and standards a master solution was prepared, which was stirred overnight to homogenize the sample completely. For the absorbance measurements a subsequent dilution of 5 different concentrations are taken into account. The absorbance of the global maximum was approximately between 0.01 and 0.1 OD. The samples had a concentration range of 10^{-6} – 10^{-7} mol/l. To avoid effects due to impurities, uvasol grade solvents as well as doubly destilled water were used. The observed absorption maxima were chosen for subsequent fluorescence measurements of using the same concentration. No concentration effects were found. The fluorescence spectra of the samples and standards were integrated and were plotted against the intensity of the absorption to get the gradient of the straight line. To calculate the quantum yield ϕ_i, the following equation was used (Grad=Gradient, n refractions index of the solvent).

$$\phi_i = \phi_S \cdot \frac{Grad_i}{Grad_S} \cdot \frac{n_i^2}{n_S^2}$$

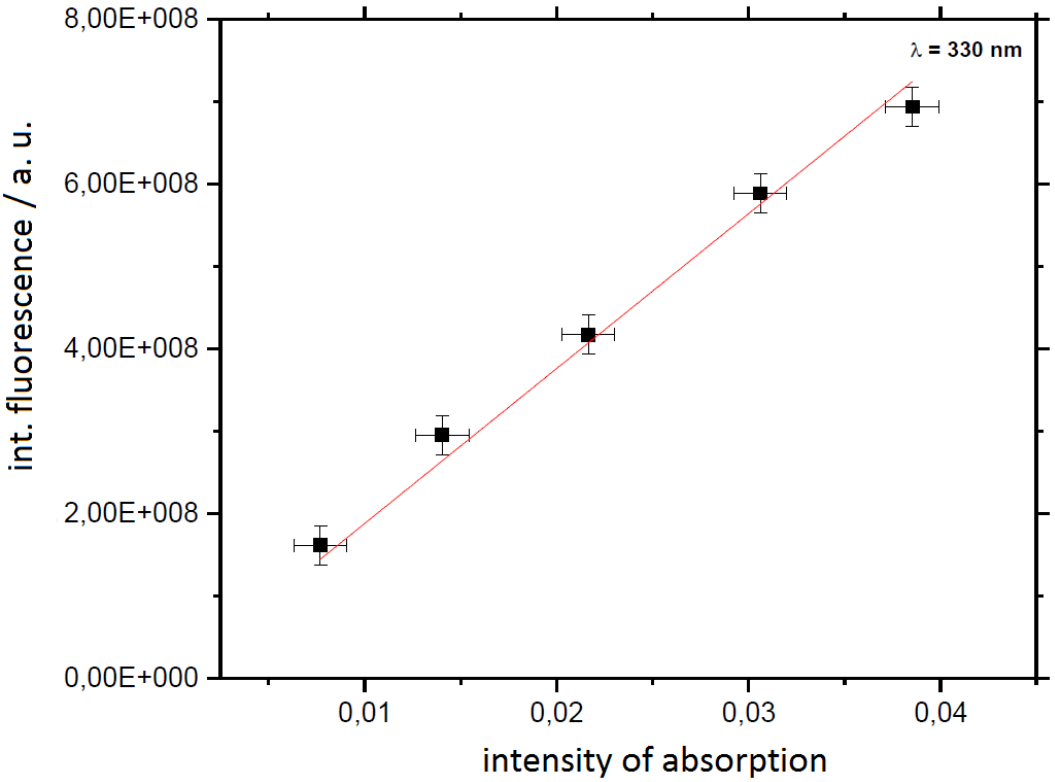
The obtained absorption spectra were measured by a Lambda® 900 spectrometer (PerkinElmer); for fluorescence measurements a Fluorolog® 3-22τ spectrometer (Horiba scientific) was used.



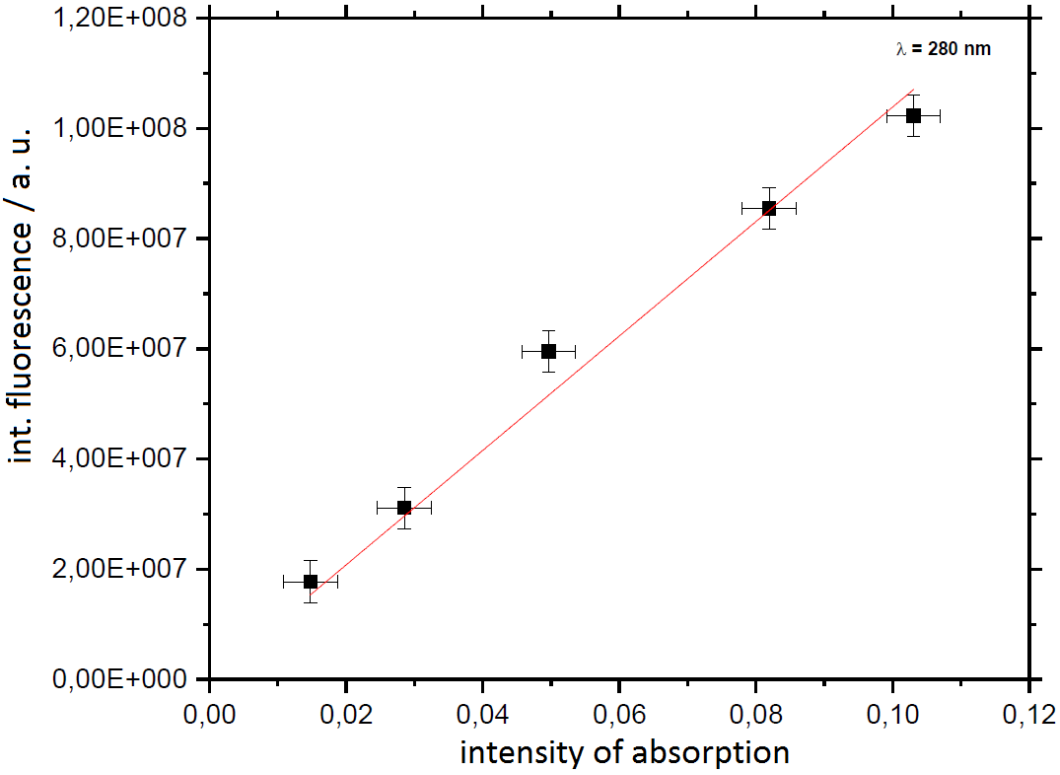
Integrated fluorescence vs. absorption intensity (OD) for **2b**.



Integrated fluorescence vs. absorption intensity (OD) for **3b**.



Integrated fluorescence vs. absorption intensity (OD) for POPOP.



Integrated fluorescence vs. absorption intensity (OD) for tryptophan.