Electronic supplementary information

New Synthetic Pathway Leading to Oxospirochlorins

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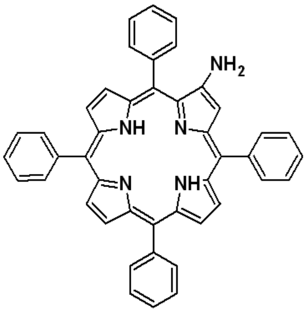
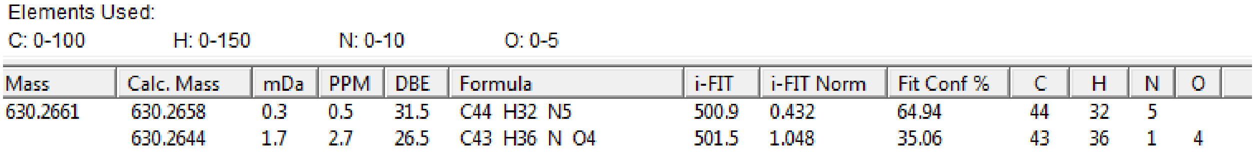
Contents

1. Mass spectrometry

Accurate mass measurements of the $[M + H]^+$ ions of amine **2a** and imino-ketone **3a** formed during MS measurement:

Compound 2a





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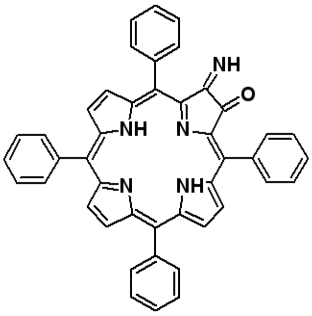
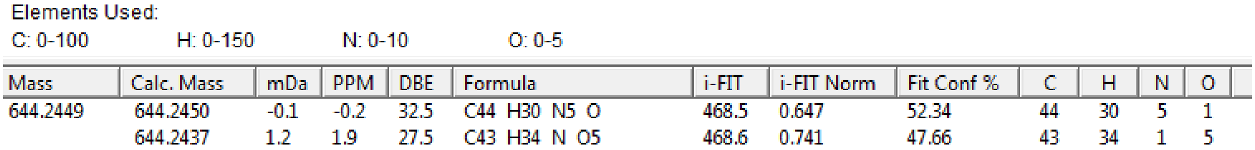
Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O
630.2661	630.2658	0.3	0.5	31.5	C44 H32 N5	500.9	0.432	64.94	44	32	5	
	630.2644	1.7	2.7	26.5	C43 H36 N O4	501.5	1.048	35.06	43	36	1	4

Compound 3a



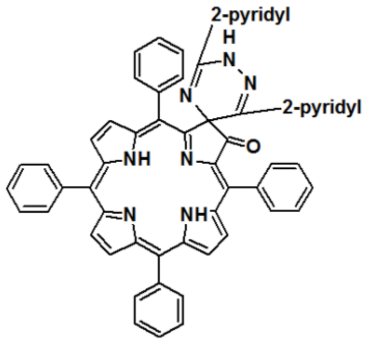


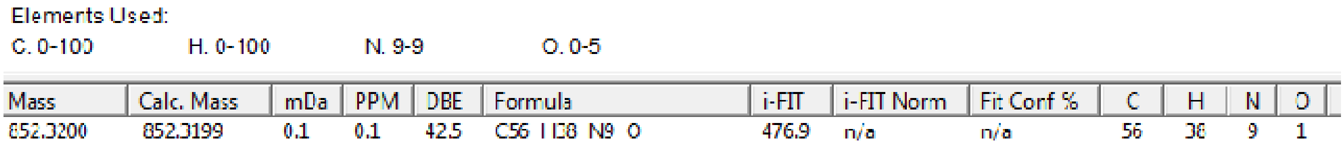
Elements Used:
C: 0-100 H: 0-150 N: 0-10 O: 0-5

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O
644.2449	644.2450	-0.1	-0.2	32.5	C44 H30 N5 O	468.5	0.647	52.34	44	30	5	1
	644.2437	1.2	1.9	27.5	C43 H34 N O5	468.6	0.741	47.66	43	34	1	5

HR MS of obtained oxospirochlorins

Compound 6a

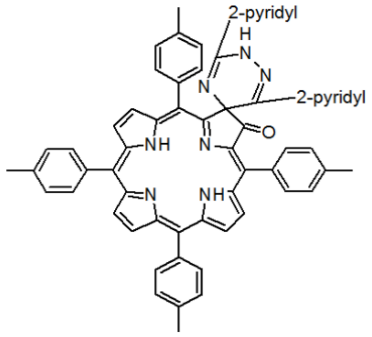


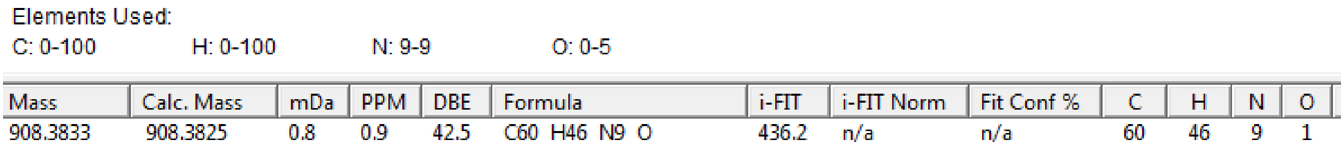


Elements Used:
C: 0-100 H: 0-100 N: 9-9 O: 0-5

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O
852.3200	852.3199	0.1	0.1	42.5	C56 H38 N9 O	476.9	n/a	n/a	56	38	9	1

Compound 6b

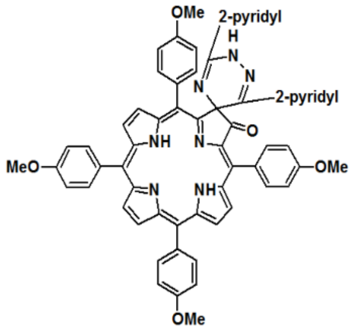


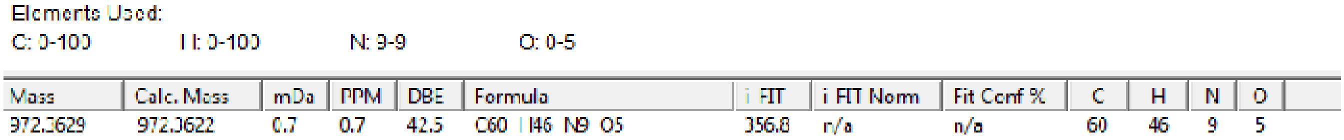


Elements Used:
C: 0-100 H: 0-100 N: 9-9 O: 0-5

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O
908.3833	908.3825	0.8	0.9	42.5	C60 H46 N9 O	436.2	n/a	n/a	60	46	9	1

Compound 6c

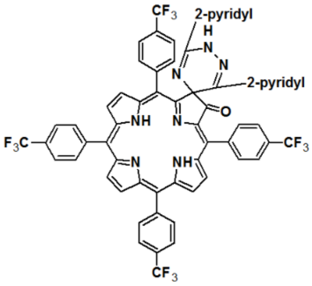


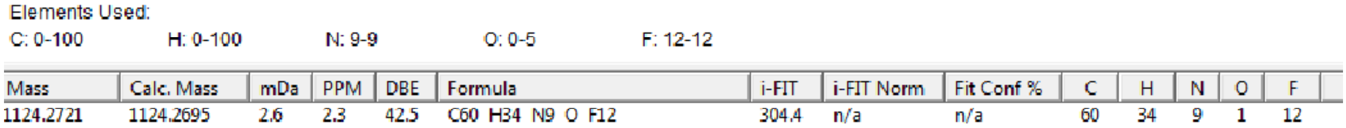


Elements Used:
C: 0-100 H: 0-100 N: 9-9 O: 0-5

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O
972.3629	972.3622	0.7	0.7	42.5	C60 H46 N9 O5	356.8	n/a	n/a	60	46	9	5

Compound 6d





Elements Used:
C: 0-100 H: 0-100 N: 9-9 O: 0-5 F: 12-12

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O	F
1124.2721	1124.2695	2.6	2.3	42.5	C60 H34 N9 O F12	304.4	n/a	n/a	60	34	9	1	12

2. Theoretical calculations

Table S1 Numerical results of calculated FMO energies (HOMO and LUMO) using LC-ωHPBE/aug-cc-pVTZ after optimization at PBE1PBE/6-311+G(d,p)level.[1]

Model	**Energy [kJ/mol]**	
	HOMO	**LUMO**
5	-33.25	-2.14
3a	-26.19	-5.61
3b	-25.81	-5.25
3c	-25.49	-5.12
3d	-28.03	-7.48
3e	-28.94	-8.66
3f	-26.59	-6.20

3. NMR spectra of obtained compounds

3a. Compound 6a

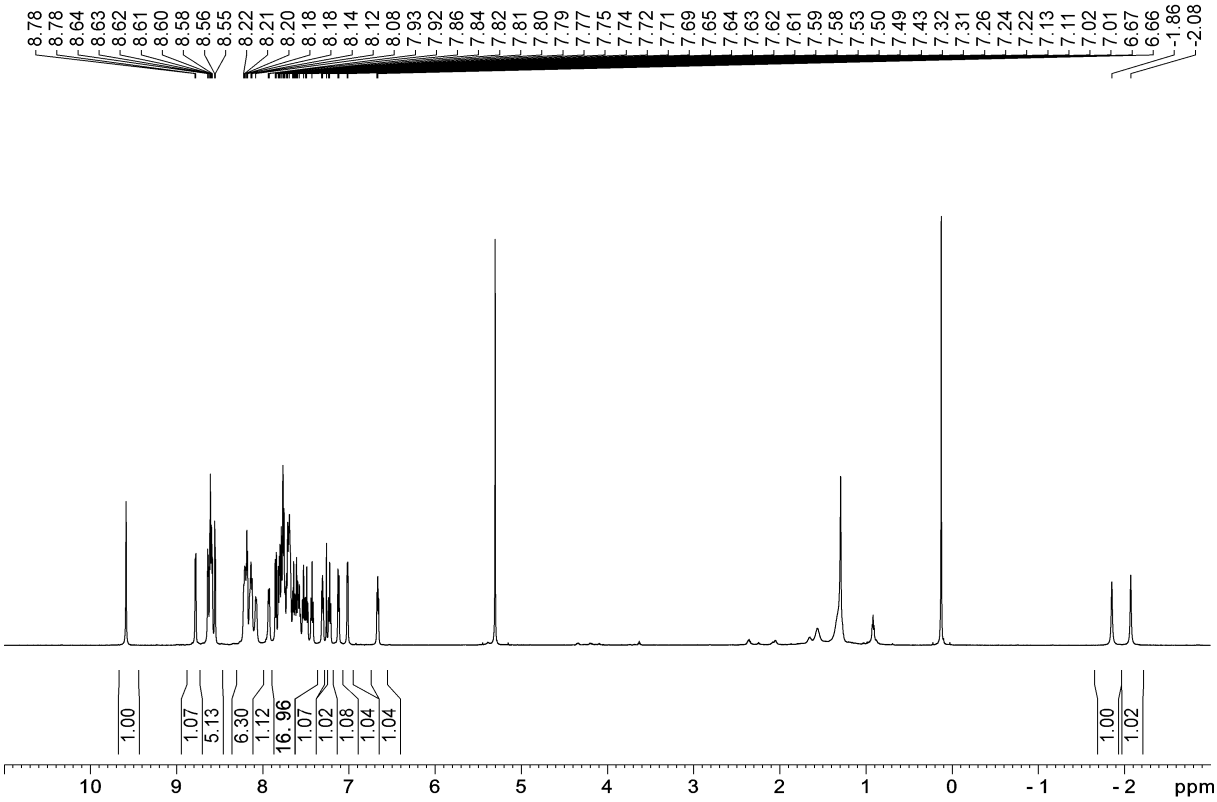


Fig. S1. ^{1}H NMR spectrum in $CDCl_3$ of compound **6a.**

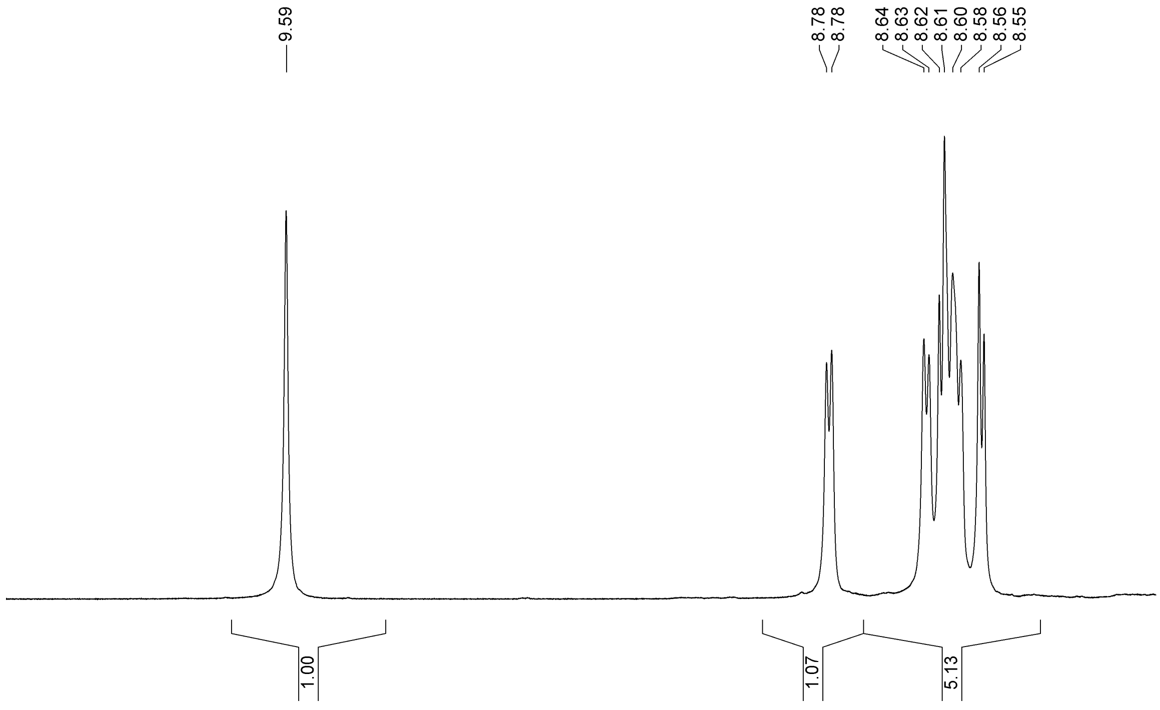


Fig. S2. ^{1}H NMR spectrum in $CDCl_3$ of compound **6a** (expansion of 8.4 – 10.0 ppm region).

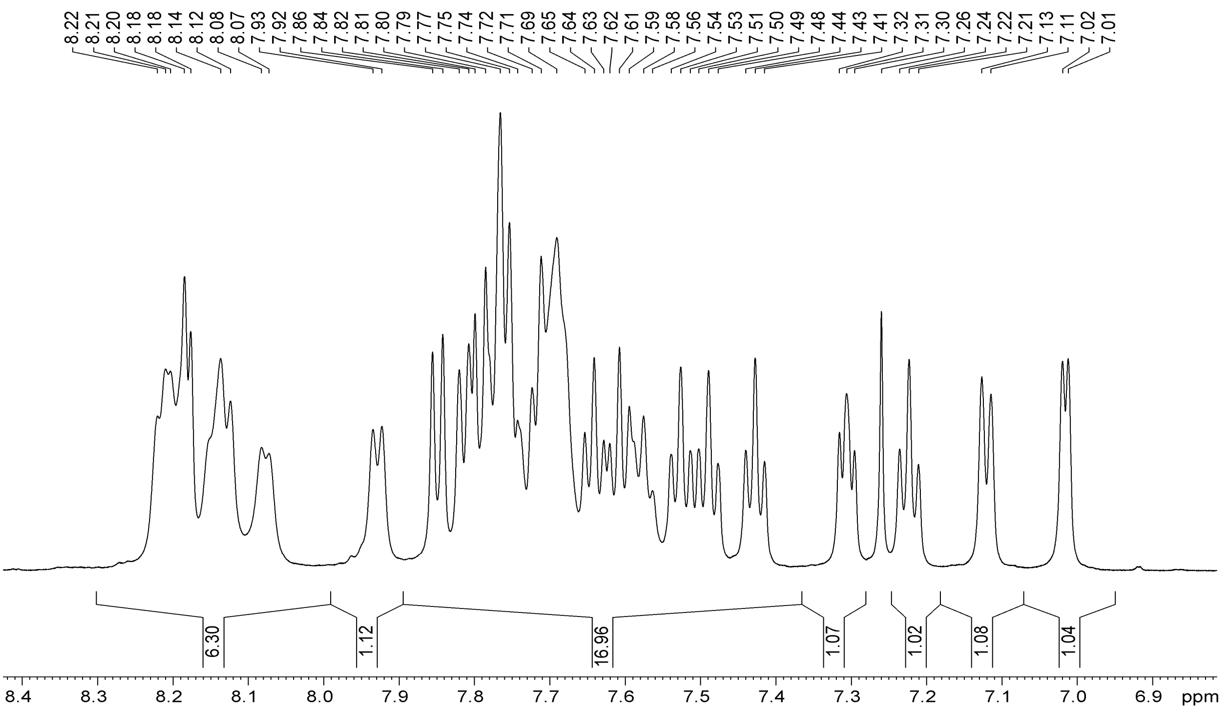


Fig. S3. ^{1}H NMR spectrum in $CDCl_3$ of compound **6a** (expansion of 6.9 – 8.4 ppm region).

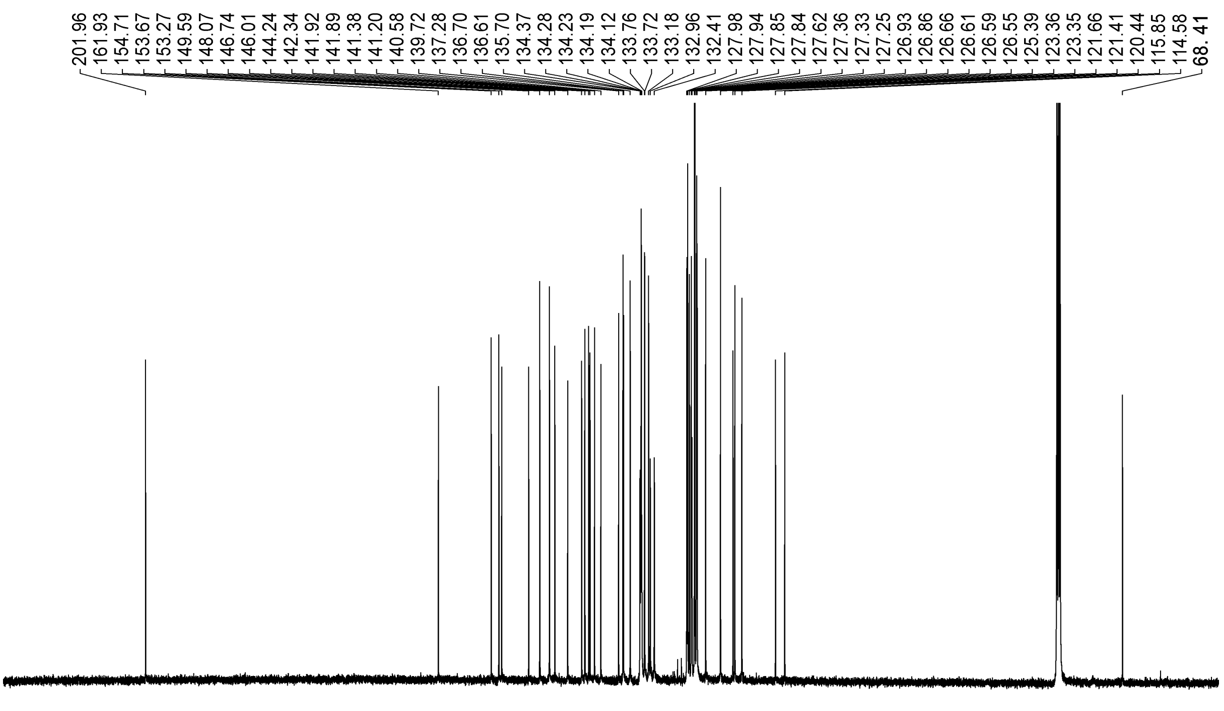


Fig. S4. ^{13}C NMR spectrum in $CDCl_3$ of compound **6a.**

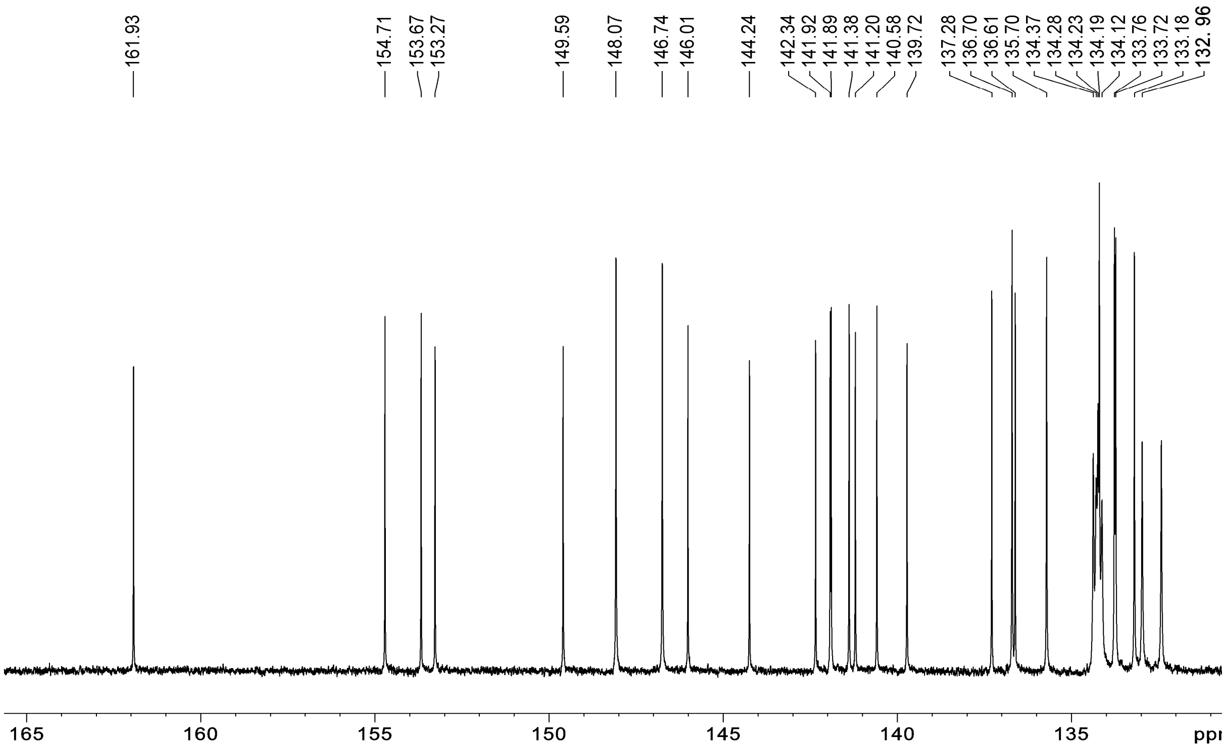


Fig. S5. ^{13}C NMR spectrum in $CDCl_3$ of compound **6a** (expansion of 130-165 ppm region).

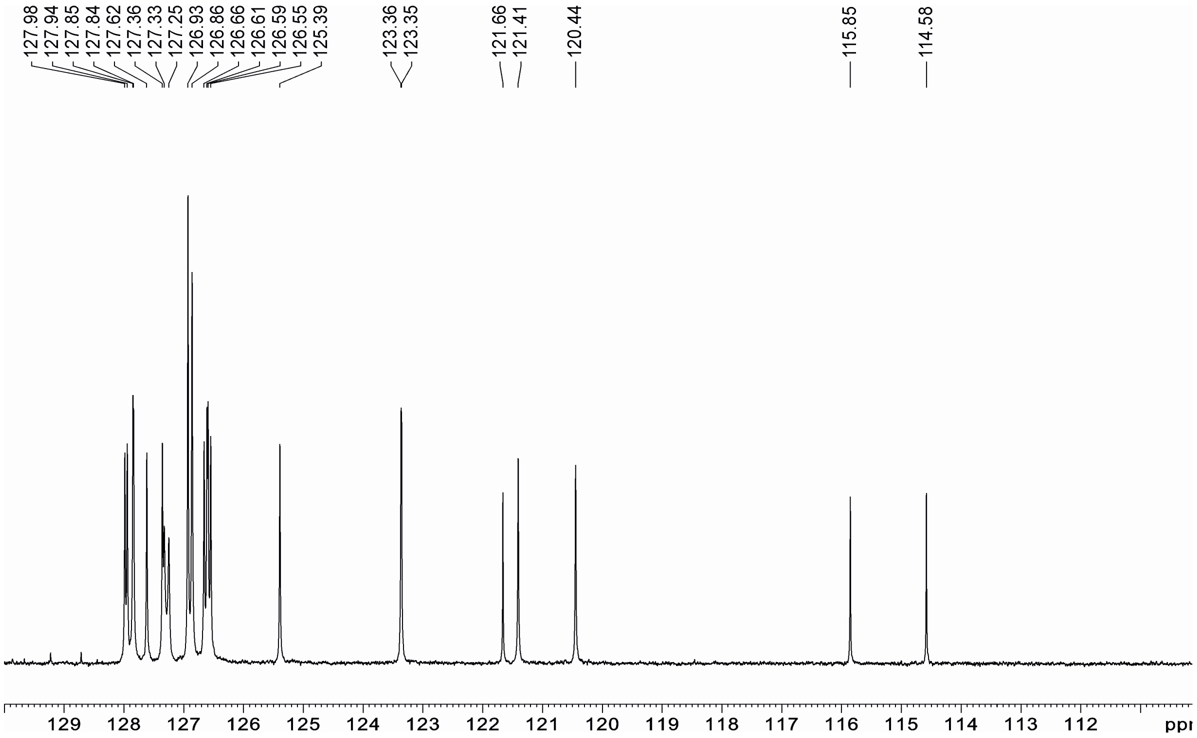


Fig. S6. ^{13}C NMR spectrum in $CDCl_3$ of compound **6a (**expansion of 111-130 ppm region).

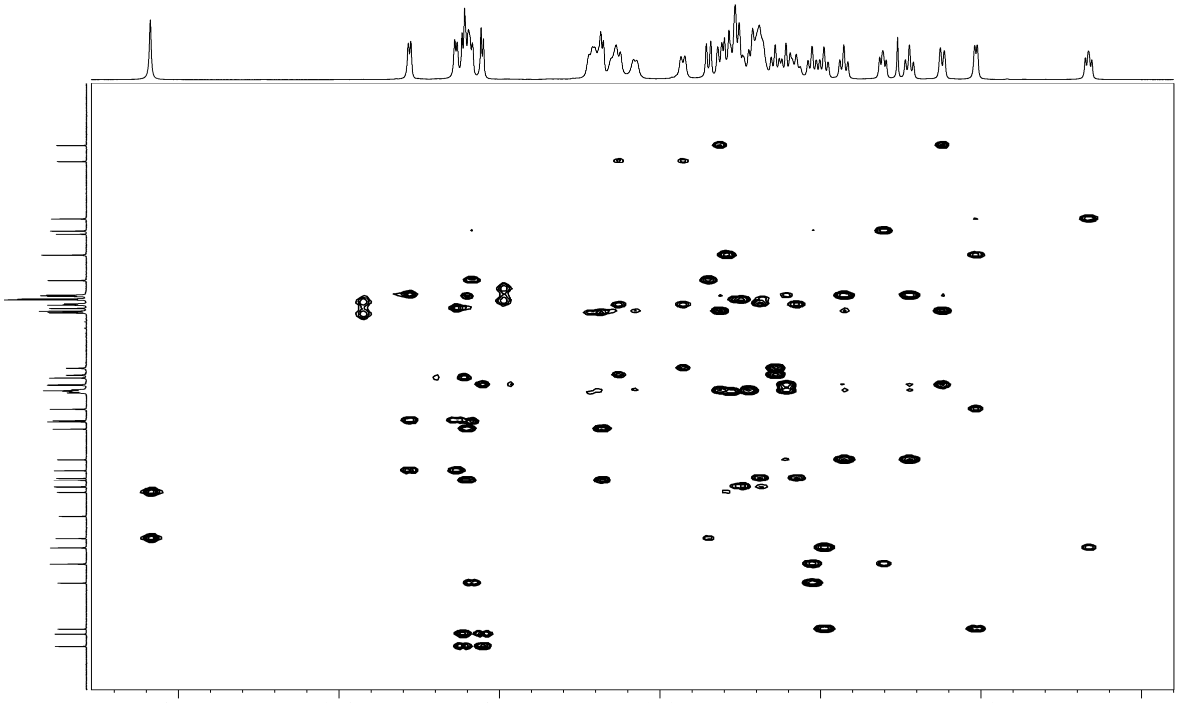


Fig. S7. ^{1}H-^{13}C HMBC NMR spectrum in $CDCl_3$ of compound **6a.**

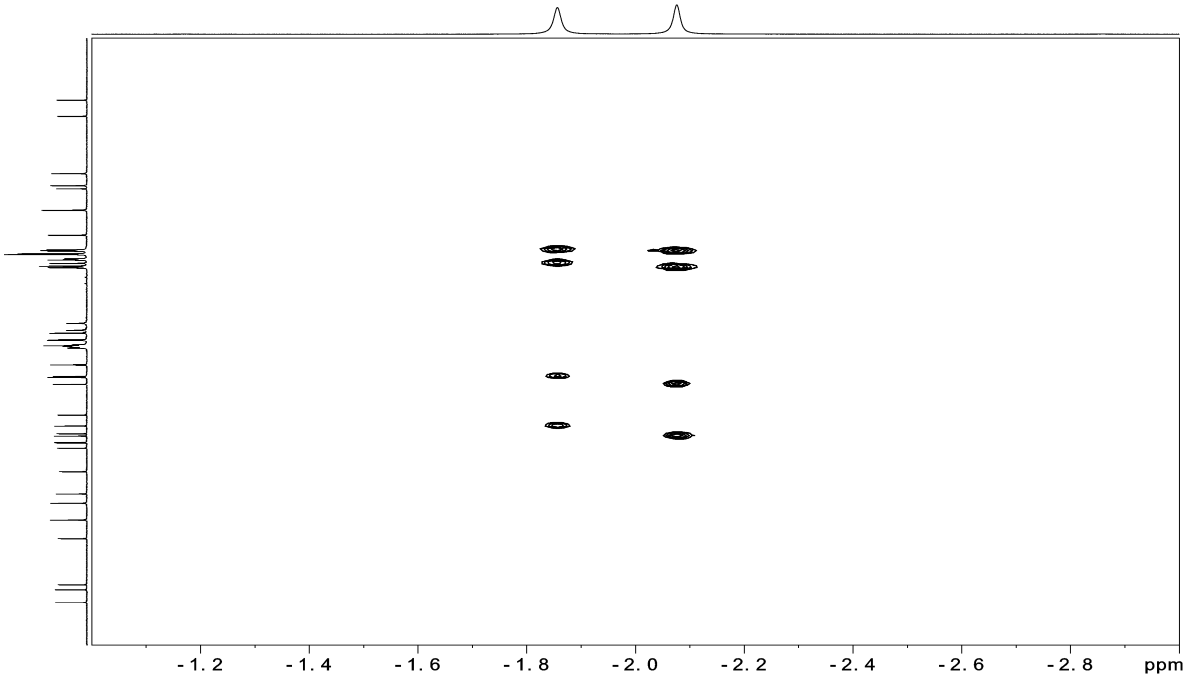


Fig. S8. ^{1}H-^{13}C HMBC NMR spectrum in $CDCl_3$ of compound **6a.**

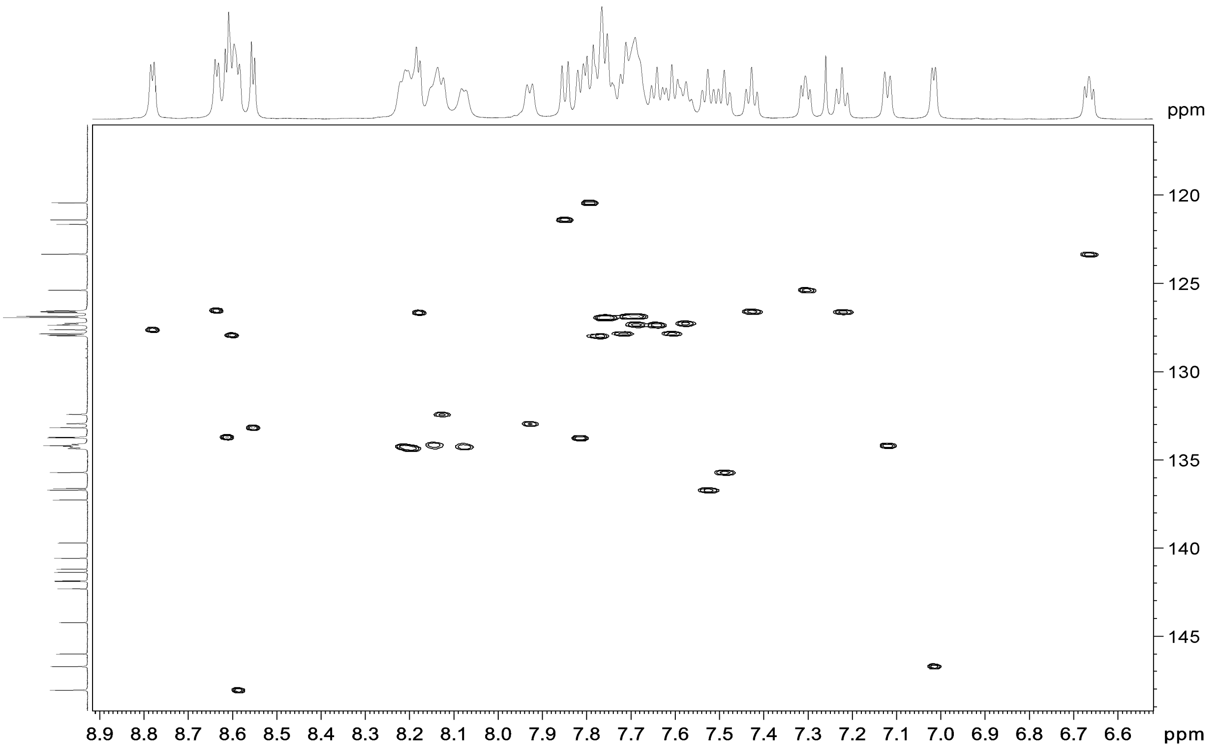


Fig. S9. ^{1}H-^{13}C HSQC NMR spectrum in $CDCl_3$ of compound **6a.**

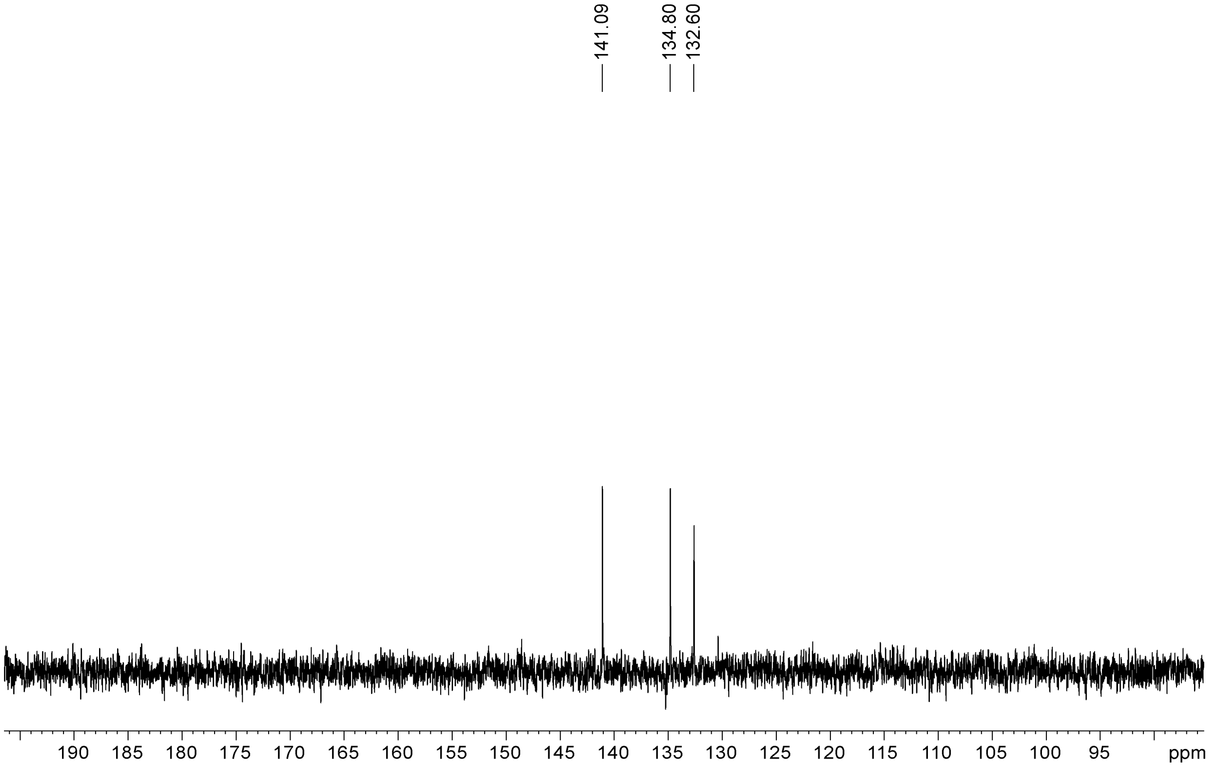


Fig. S10. ^{15}N INEPT NMR spectrum in $CDCl_3$ of compound **6a.**

3b. Compound 6b

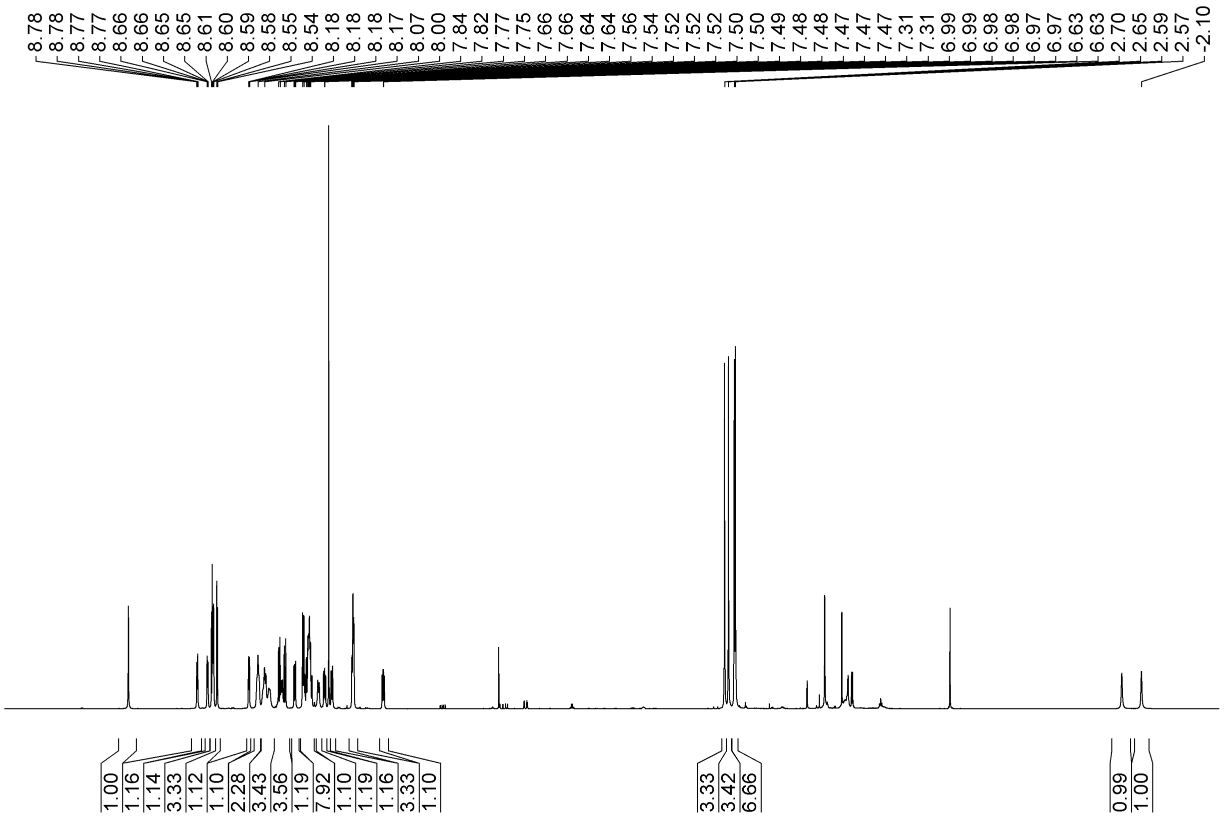


Fig. S11. ^{1}H NMR spectrum in CDCl$_3$ of compound **6b.**

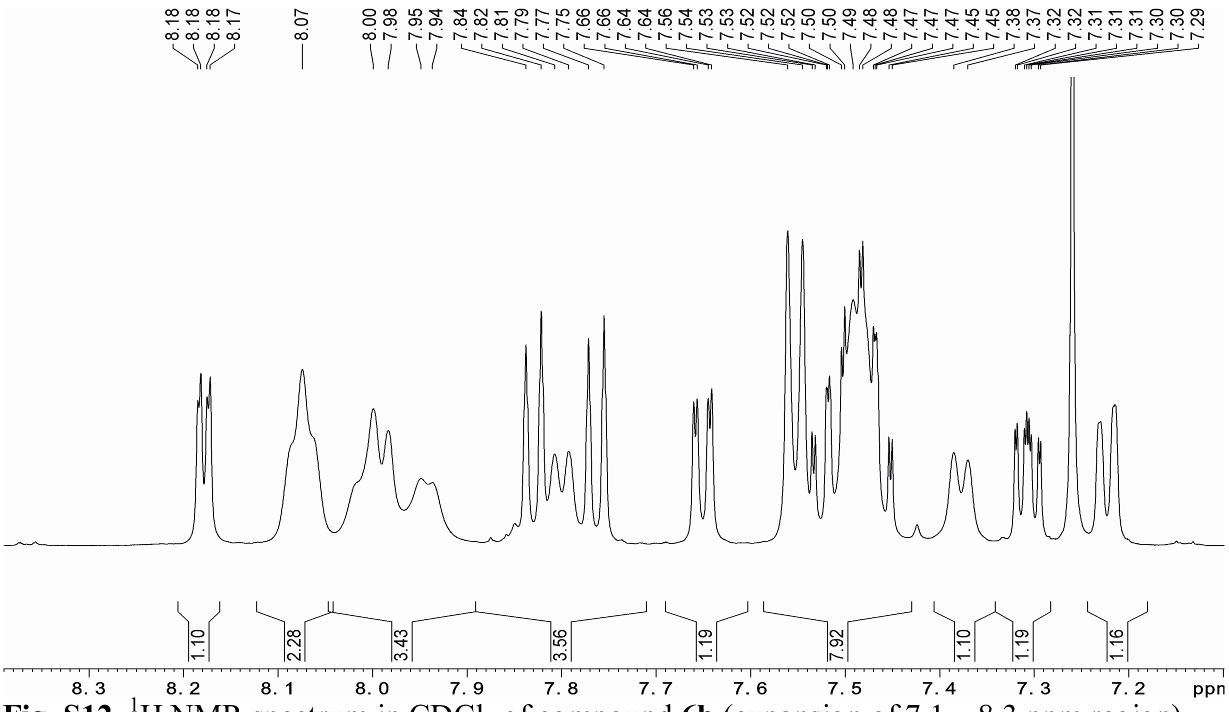


Fig. S12. ^{1}H NMR spectrum in CDCl$_3$ of compound **6b** (expansion of 7.1 – 8.3 ppm region).

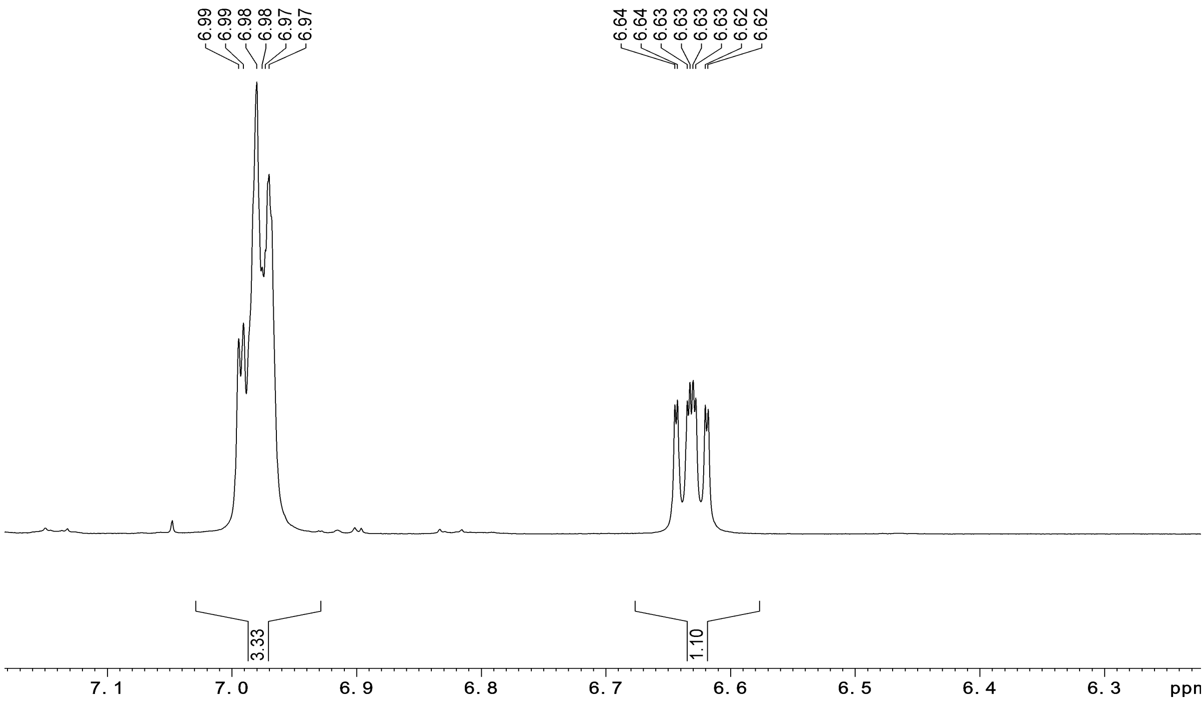


Fig. S13. ^{1}HNMR spectrum in $CDCl_3$ of compound **6b** (expansion of 6.3 – 7.1 ppm region).

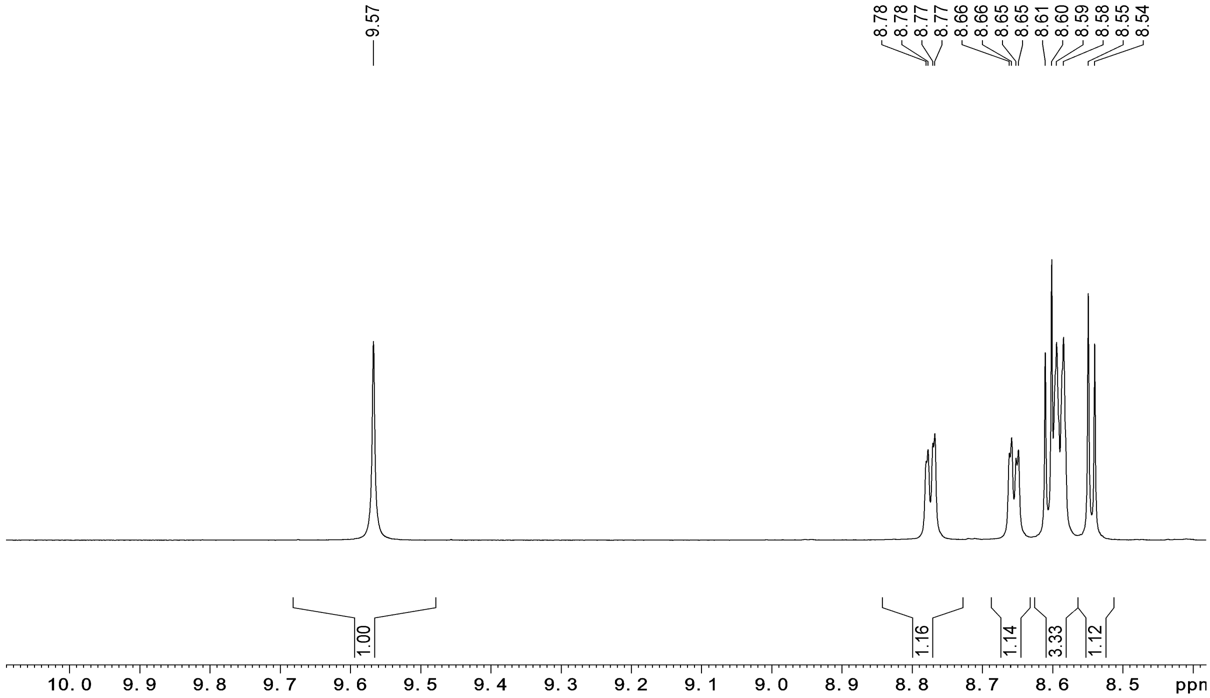


Fig. S14. ^{1}H NMR spectrum in $CDCl_3$ of compound **6b** (expansion of 8.5 – 10.0 ppm region).

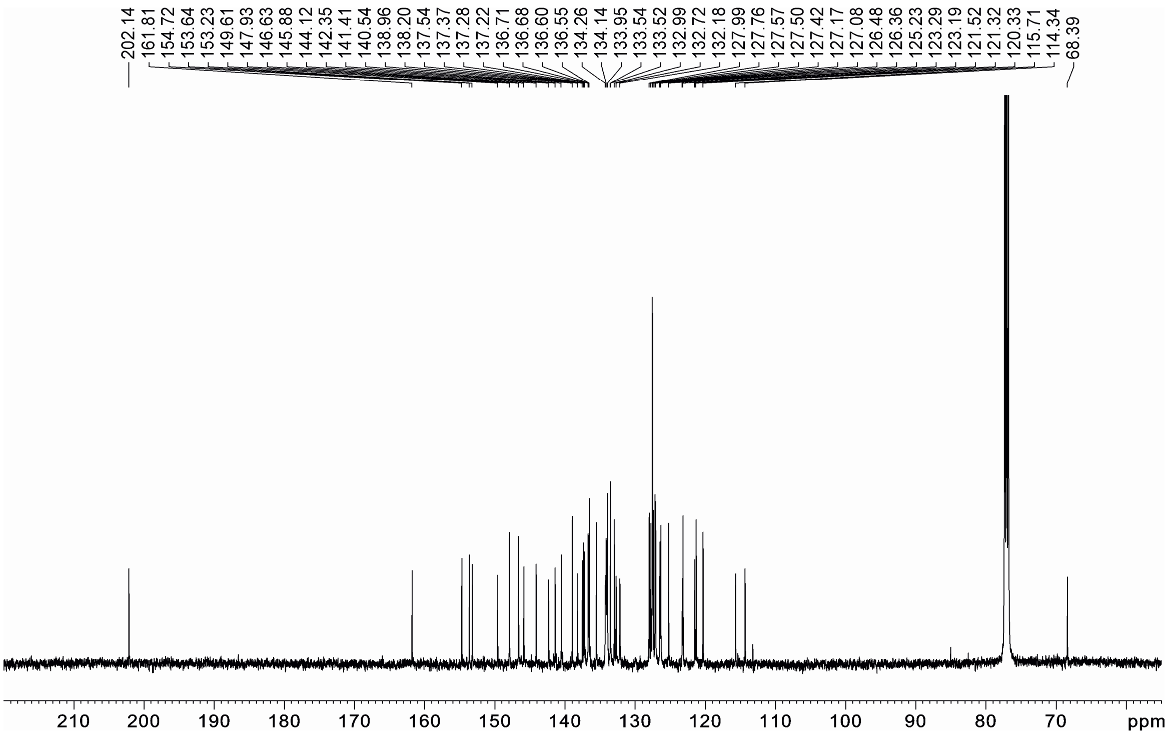


Fig. S15. ^{13}CNMR spectrum in CDCl$_3$ of compound **6b.**

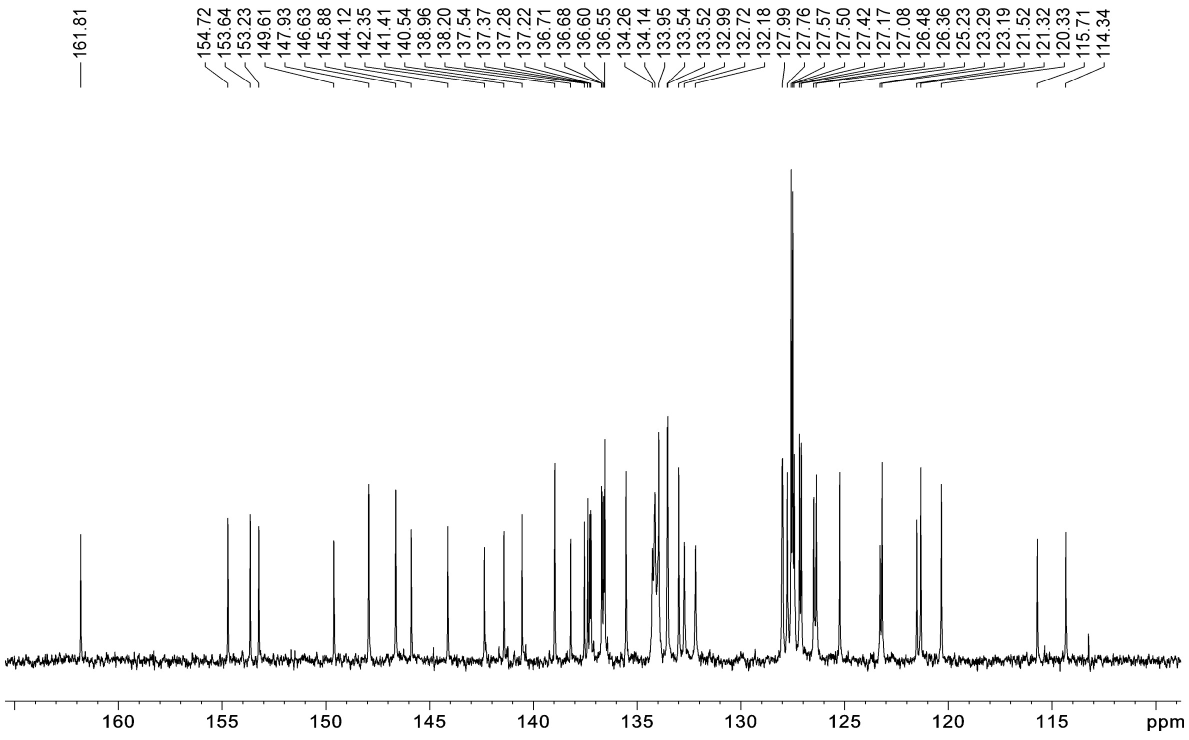


Fig. S16. ^{13}C NMR spectrum in CDCl$_3$ of compound **6b** (expansion of 110 – 165 ppm region).

3c. Compound 6c

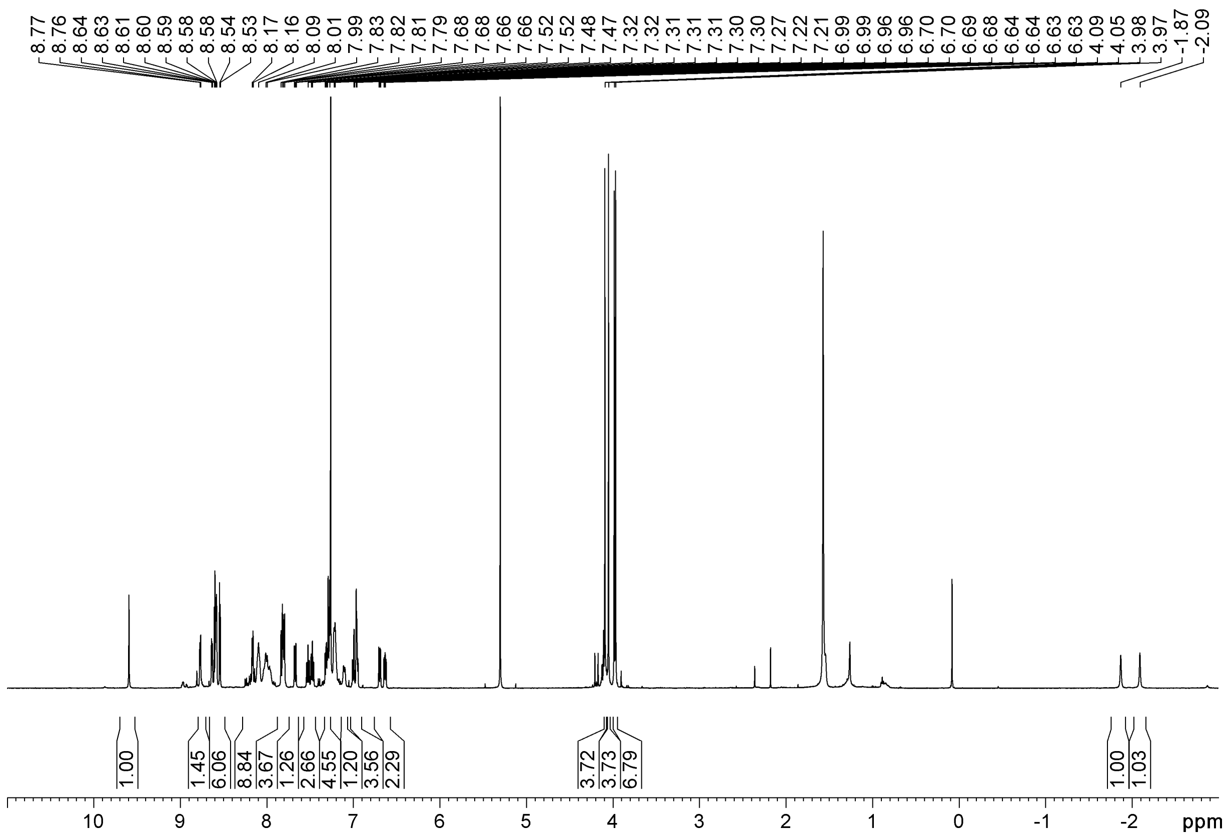


Fig. S17. ^{1}H NMR spectrum in CDCl$_3$ of compound **6c.**

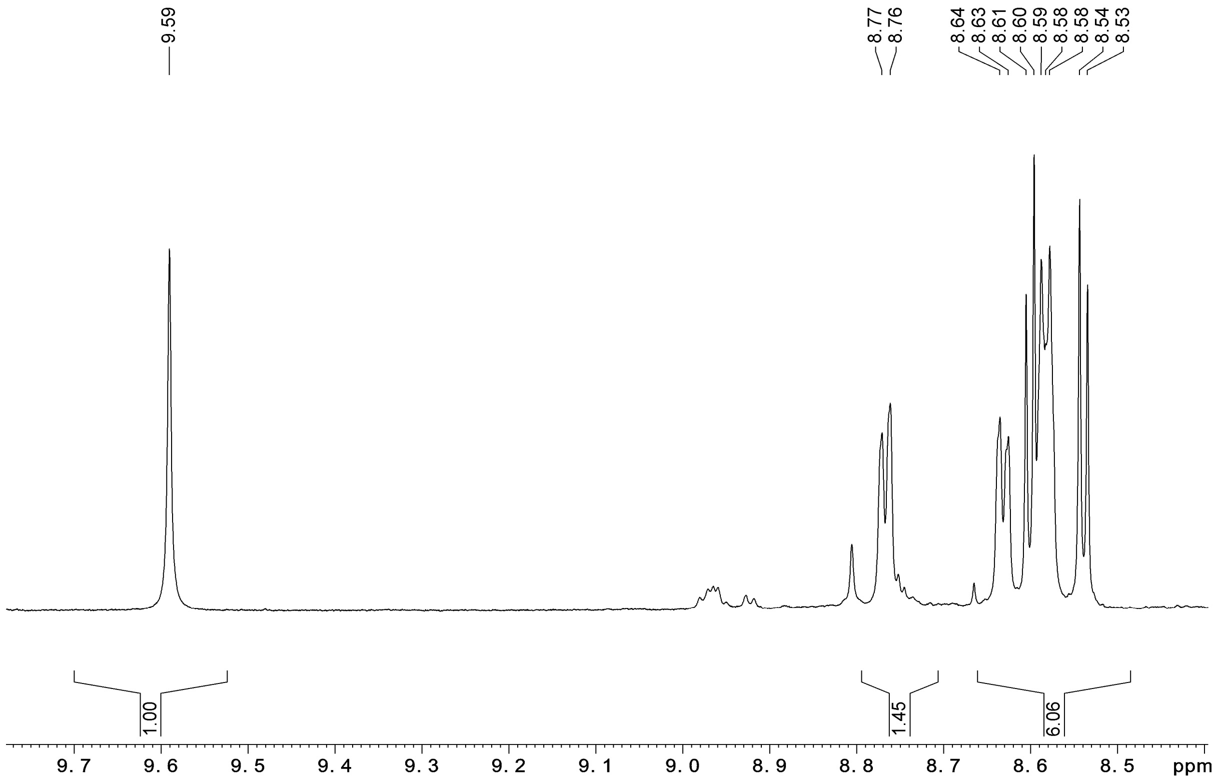


Fig. S18. ^{1}H NMR spectrum in CDCl$_3$ of compound **6c** (expansion of 8.5– 9.7 ppm region).

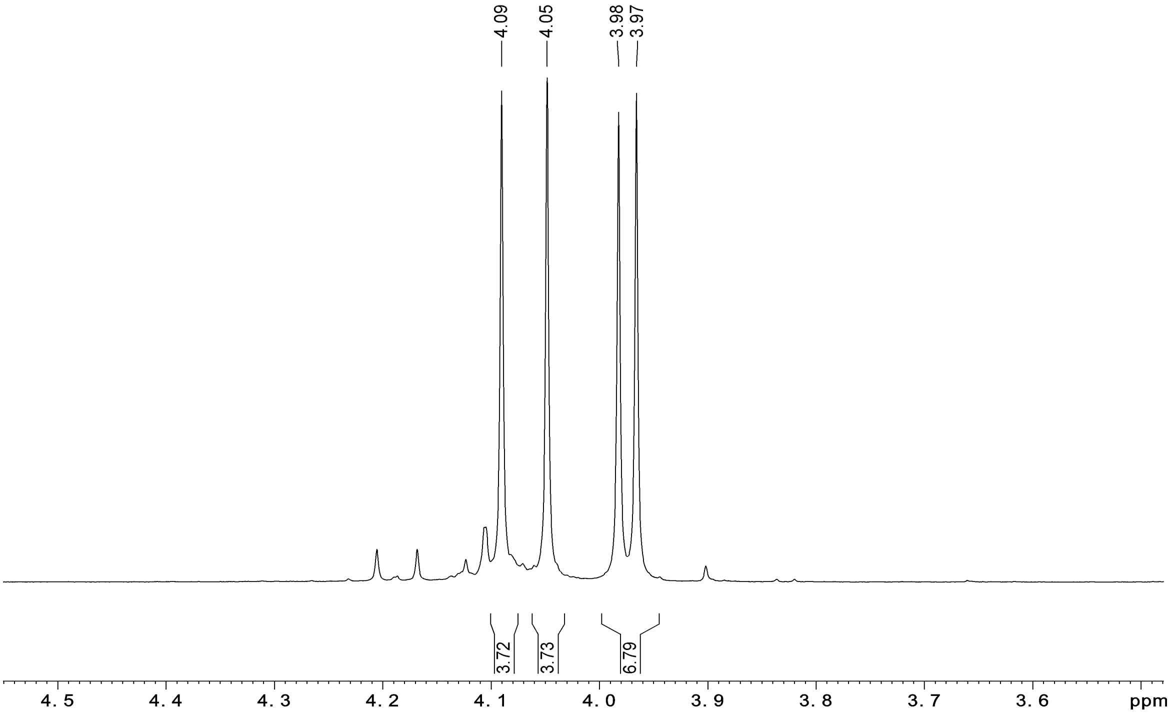


Fig. S19. ^{1}H NMR spectrum in $CDCl_3$ of compound **6c** (expansion of 3.6 – 4.5 ppm region).

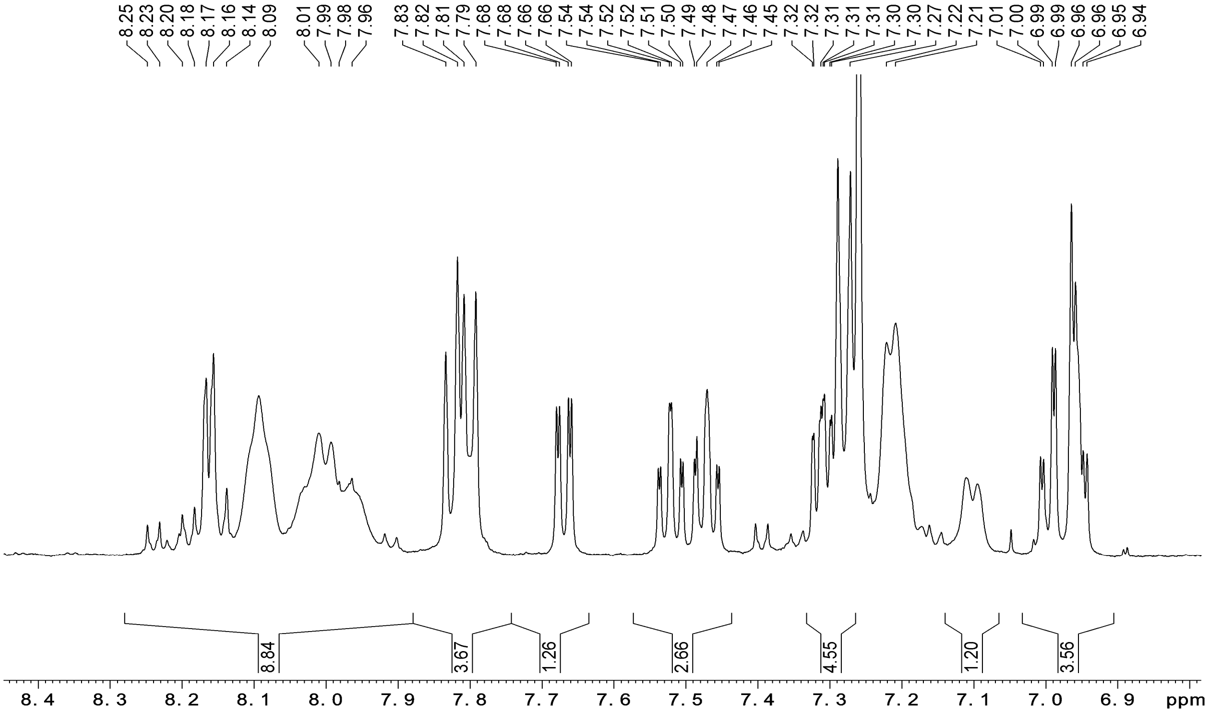


Fig. S20. ^{1}H NMR spectrum in $CDCl_3$ of compound **6c** (expansion of 6.8 – 8.4 ppm region).

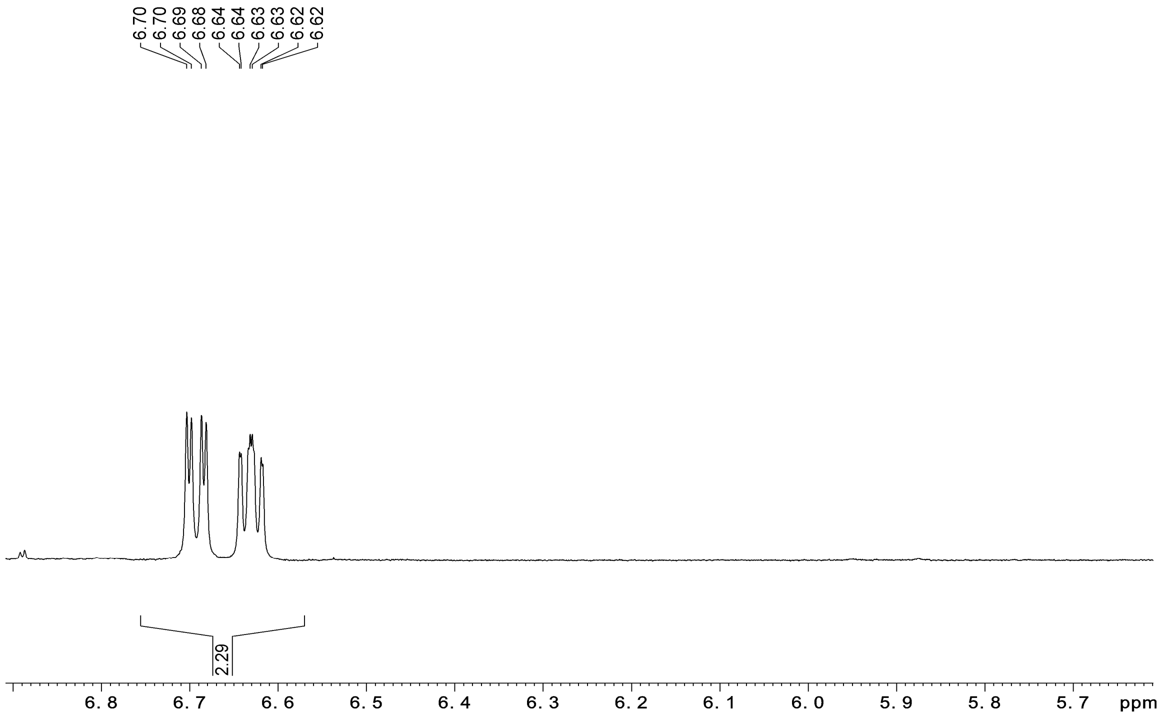


Fig. S21. ^{1}H NMR spectrum in $CDCl_3$ of compound **6c** (expansion of 5.7– 6.9 ppm region).

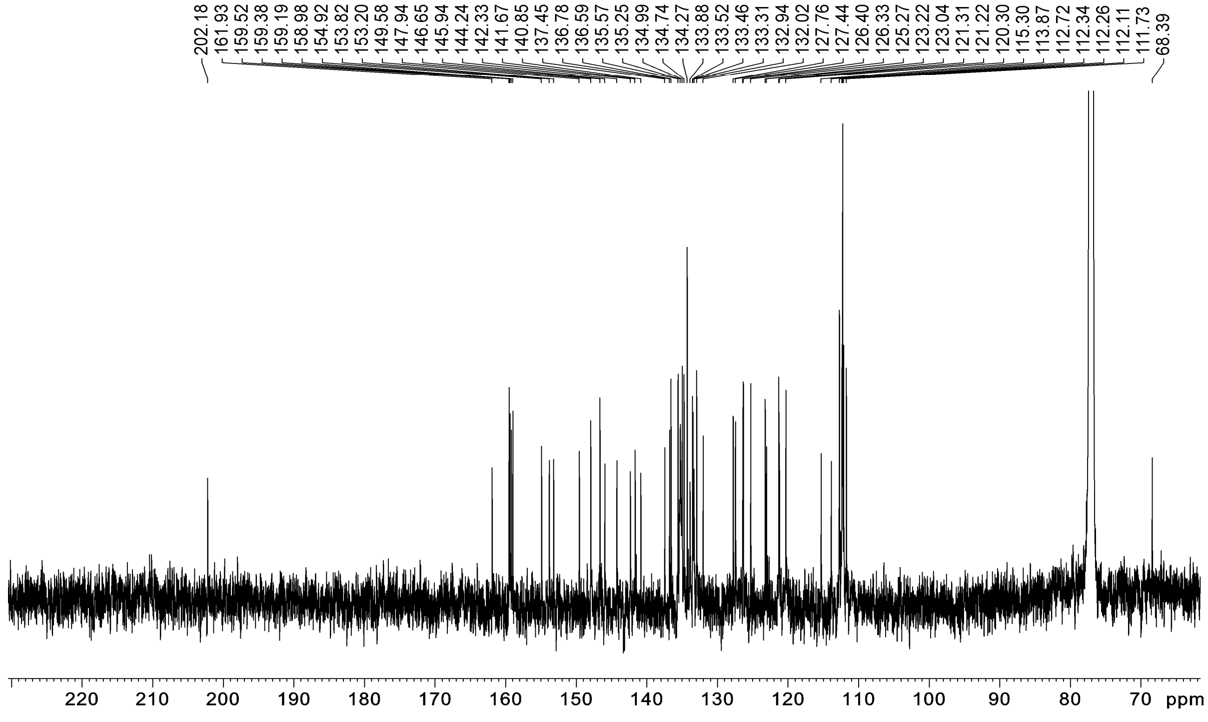


Fig. S22. ^{13}C NMR spectrum in $CDCl_3$ of compound **6c**.

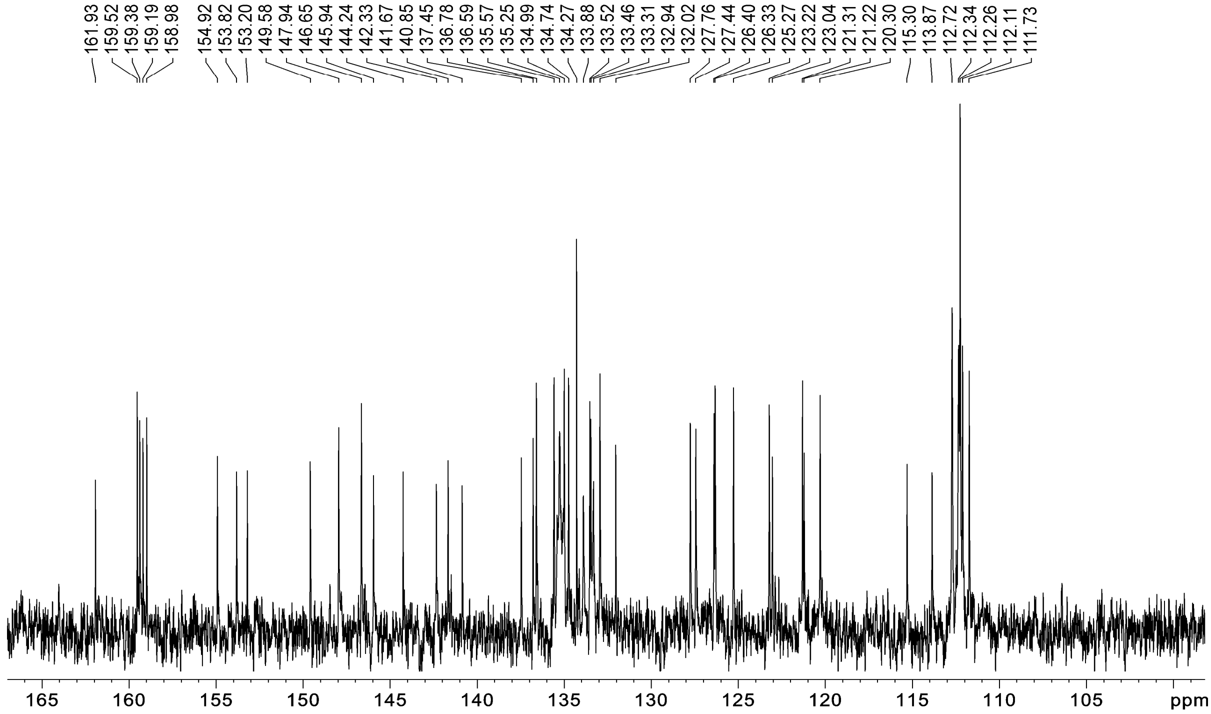


Fig. S23. ^{13}CNMR spectrum in $CDCl_3$ of compound **6c** (expansion of 105 – 165 ppm region).

3d. Compound 6d

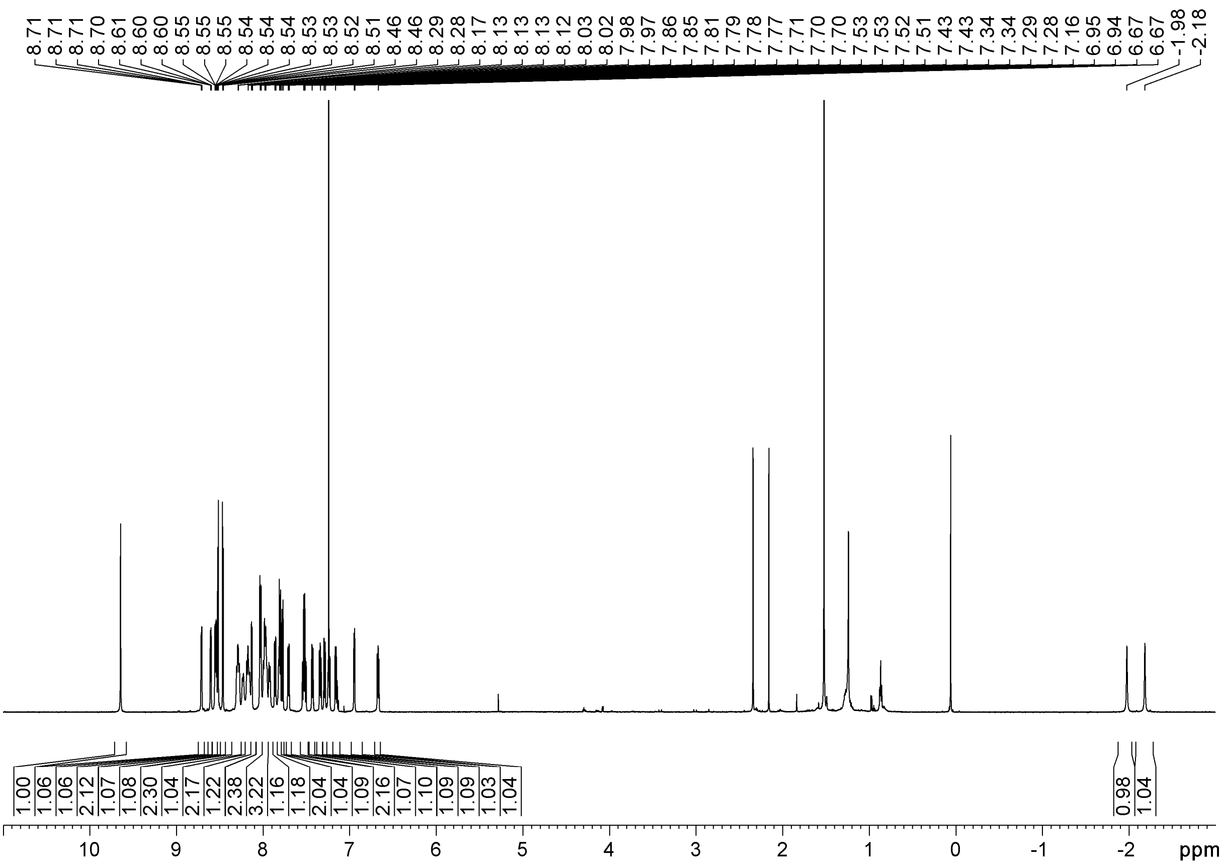


Fig. S24. ^{1}HNMR spectrum in CDCl$_3$ of compound **6d.**

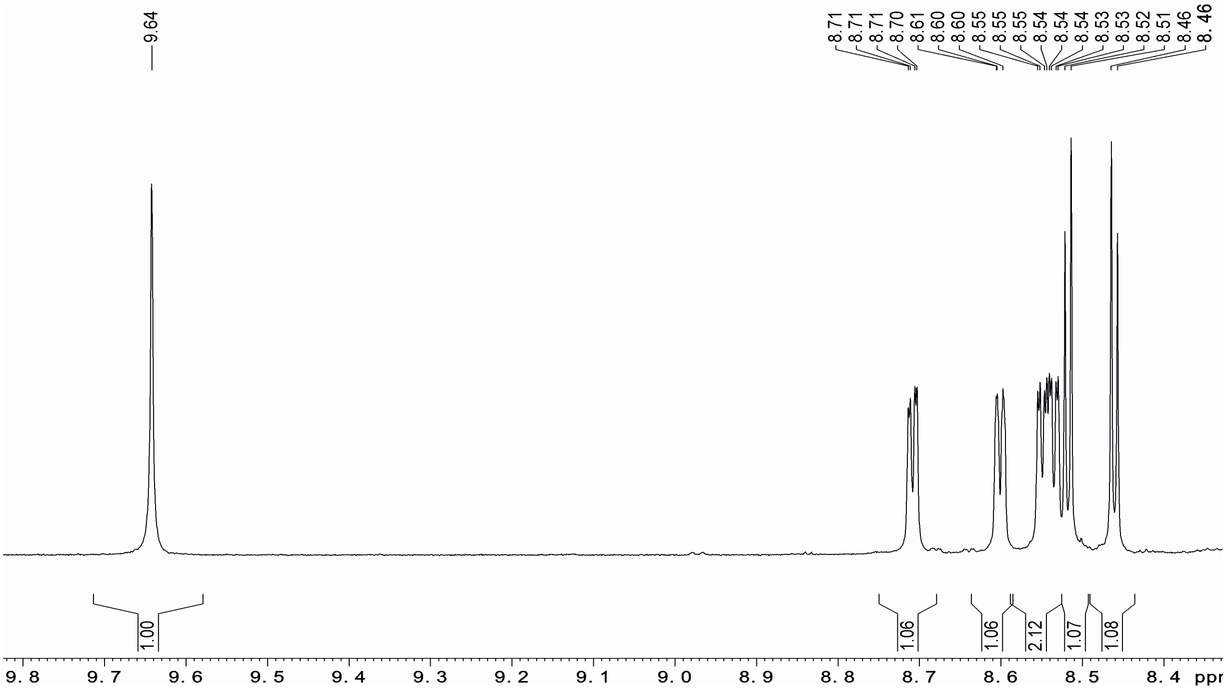


Fig. S25. ^{1}H NMR spectrum in CDCl$_3$ of compound **6d** (expansion of 8.4– 9.8 ppm region).

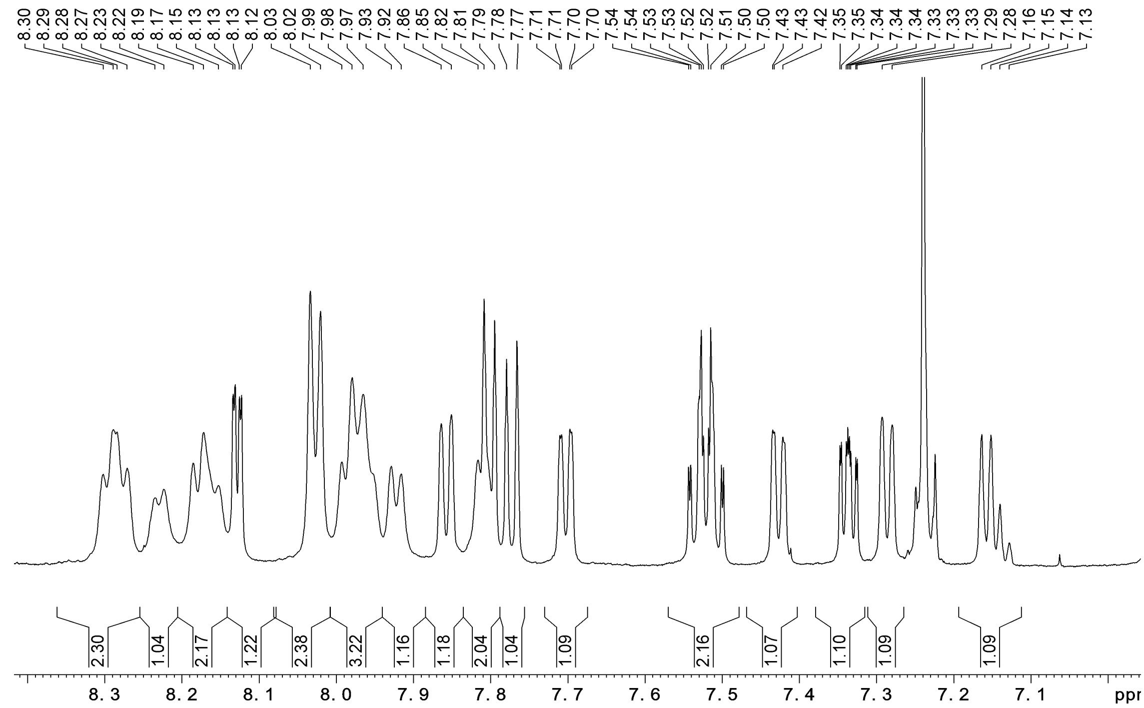


Fig. S26. ^{1}H NMR spectrum in $CDCl_3$ of compound **6d** (expansion of 7.0 – 8.4 ppm region).

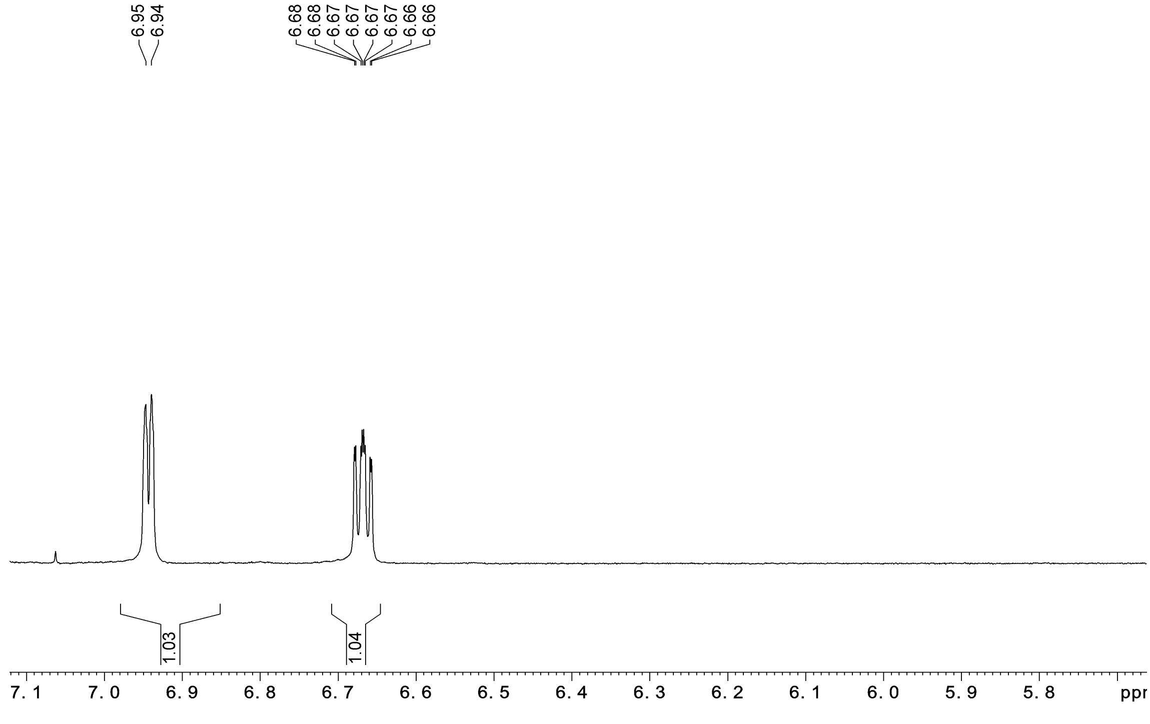


Fig. S27. ^{1}H NMR spectrum in $CDCl_3$ of compound **6d** (expansion of 5.7– 7.1 ppm region).

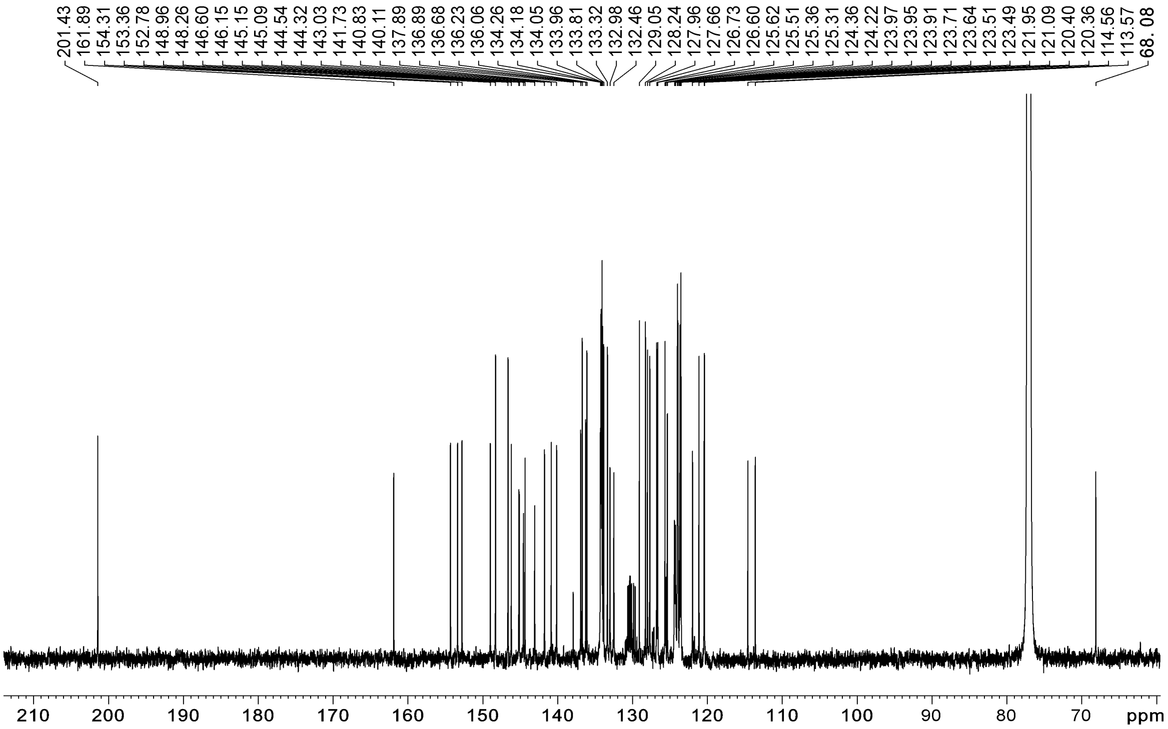


Fig. S28. ^{13}C NMR spectrum in CDCl$_3$ of compound **6d.**

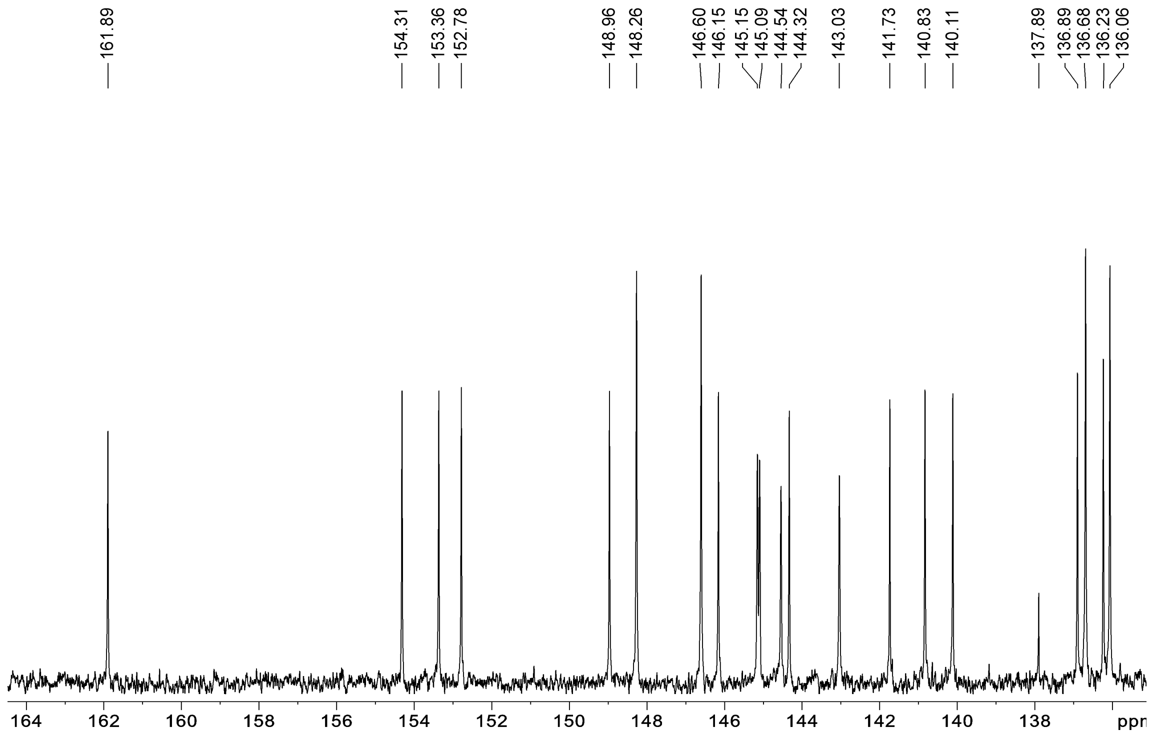


Fig. S29. ^{13}CNMR spectrum in CDCl$_3$ of compound **6d** (expansion of 137-164 ppm region).

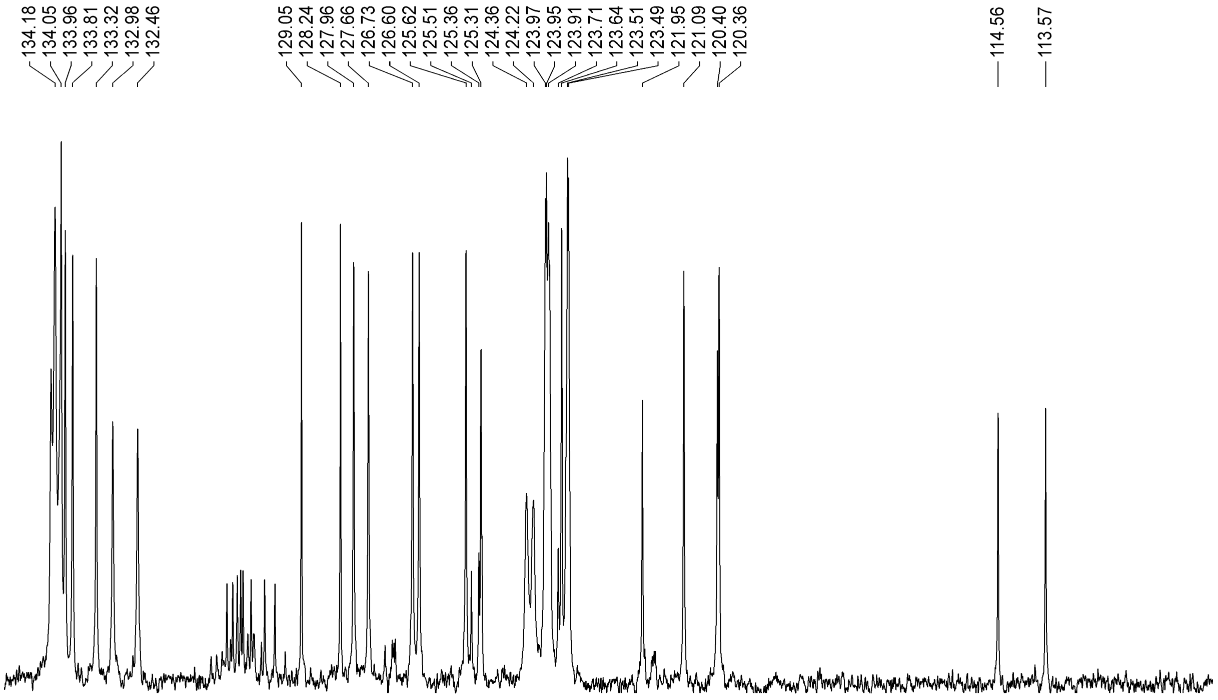


Fig. S30. ^{13}CNMR spectrum in CDCl$_3$ of compound **6d** (expansion of 111– 134 ppm region).

4. Crystallographic Data

4a. Single crystal X-ray measurements.

Single crystal diffraction experiments for **6a** were carried out on Oxford SuperNova single-crystal diffractometer with micro source CuKα radiation (λ = 1.5418 Å) and a Titan detector. The plate crystal of dimensions 0.18x0.09x0.02 was glued do a glass capillary by epoxy glue and measured at room temperature. The absorption correction was performed based on the crystal shape, orientation and absorption coefficient. Diffraction data collection, cell refinement, data reduction, and absorption correction were performed using the CrysAlis PRO program (Oxford Diffraction). The structure was solved by direct methods SHELXS and refined using full-matrix least-squares methods SHELX 2015 implemented in OLEX2 package.[2] The hydrogen atoms ware set geometrically and refined as riding with the thermal parameter equal to 1.2 of the thermal vibration of the parental atom. The two hydrogen atoms connected with internal nitrogens of the chlorin ring were found on the difference Fourier map and refined without any geometrical restrains with isotropic thermal parameters. Two disordered moieties were detected in the structure: the phenyl ring in the vicinity of 1,2,4-triazine ring and a solvent dichloromethane molecule. Both disordered fragments were modeled in two positions with the fractional occupation factors summing to one. The vibration of phenyl ring can be described as a swing of the pendulum in the ring plane. The dichloromethane molecule oscillates around the axis passing thought the CL1 atom and the middle of the C60-Cl2 bond. The structure was validated by CheckCif (http://checkcif.iucr.org/) and deposited in CCDC under accession number 1573589.

4b. Molecule description.

The molecule of **6a** contains two main approximately planar systems perpendicular to each other. One of them, the chlorin ring, is connect with the other the 1,2,4-triazine ring, by a spiro C7 atom. The tetra phenyl chlorin moiety is slightly bound around the axis passing through the N2, N4 unprotonated nitrogen atoms. Two of four phenyl rings connected to the chlorin ring located in the vicinity of the modified pyrrole ring are perpendicular to it, while the other two, more distant from the modification, are angular. The disordered phenyl is parallel to the 1,2,4-triazine ring and the short distance between these two aromatic systems allows $\pi - \pi$ interaction. One of the two pirydin-2-yl rings connected to the triazine ring is approximately coplanar with it and the other is slightly twisted. Only two nitrogens of the chlorin ring are protonated the positions of them were found from experimental data. The low no restricted isotropic thermal parameters and stabile position during refinement indicate that even in room temperature external proton exchange between nitrogen atoms doesn't occurs in a crystal.

The compound **6a** crystallizes from dichloromethane in triclinic form in centrosymetric P-1 space group. The independent unit contains one molecule of **6a** and one molecule of crystallization solvent dichloromethane. Two independent units related by center of symmetry fill unit cell. The molecules of **6a** interact in crystal lattice mostly by hydrophobic contacts. The two solvent molecules are located close to each other in cage created by network of **6a**. They are related by symmetry and interact each other, the contact with host molecule are by weak hydrogen bond between carbon hydrogen and ketone oxygen, and Van der Waals contact of disordered CL7 atom with disordered phenyl ring. In both positions carbon hydrogens of dichloromethane with fractional occupancy are able to create contact.

4c. Crystal data and structural refinement for compound 6a

Crystal data and structural refinement for 8-oxo-7-spiro((3,6-dipirydin-2-yl)-2,5-dihydro-1,2,4-triazinyl)5,10,15,20-tetraphenyl chlorin, dichloromethane cocrystal (solvate)

Empirical formula	$C_{56}H_{37}N_9O * CH_2Cl_2$
Formula weight, M	936.87
Crystal system	triclinic
Space group	*P-1*
a (Å)	9.5173(5)
b (Å)	13.2143(7)
c (Å)	20.606(1)
α (°)	105.758(4)
β (°)	92.806(4)
γ (°)	107.008(5)
Volume V ($Å^3$)	2361.7(2)
Z	2
Dcal, (g/cm^3)	1.317
Radiation	CuKα
Absorption coefficient, μ(mm^{-1})	1.651
F(*000*)	972.0
Crystal size (mm^3)	0.18 x 0.08 x 0.02
T (K)	293(1)
□-range for data collection (°)	2.250 - 75.188
Limiting indices	-10 □≤ h ≤ 11, -14 ≤ k ≤ 16, -25 ≤ l ≤ 24
Unique reflections	9369 (R_{int} = 0.0425)
Goodness-of-fit on Fo2	1.026
Data/restraints/parameters	9369/90/705
Weights (w/p)	0.123/0.383
Final R indices [$F_o > 4\sigma(F_o)$]	$R_1^a = 0.0751$, $wR_2^b = 0.2020$
R indices (all data)	$R_1 = 0.1109$, $wR_2 = 0.2445$
Highest peak and deepest hole (eÅ-3)	0.287 and -0.637
CCDC accession number	1573589

5. Absorption spectroscopy

Table S2 Molar absorbance coefficient from experimental data (dichloromethane, room temperature)

Oxospirochlorin	Soret band [nm]	Molar absorbance coefficient [dm^3·mol^{-1}·cm^{-1}]
6a	429	197 235
6b	430	384 035
6c	432	306 045
6d	426	334 842

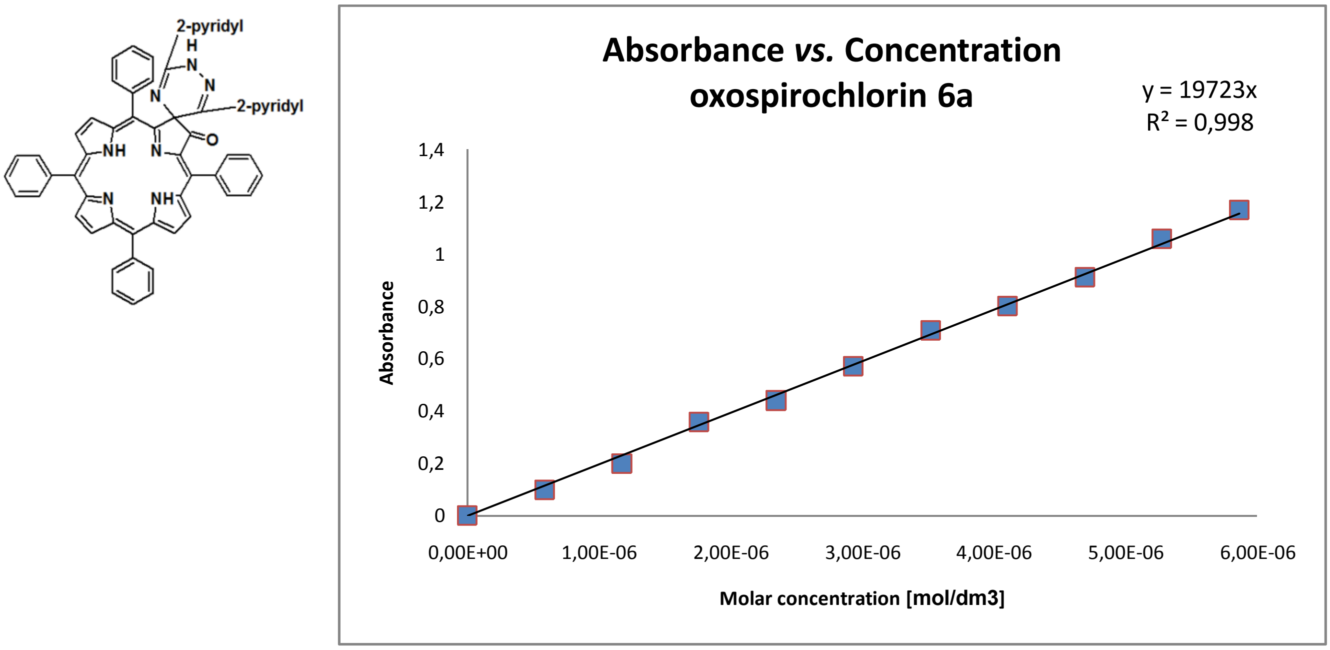


Fig. S31. Absorbance *vs*. Concentration Calibration Curve for oxospirochlorin **6a**in dichloromethane.

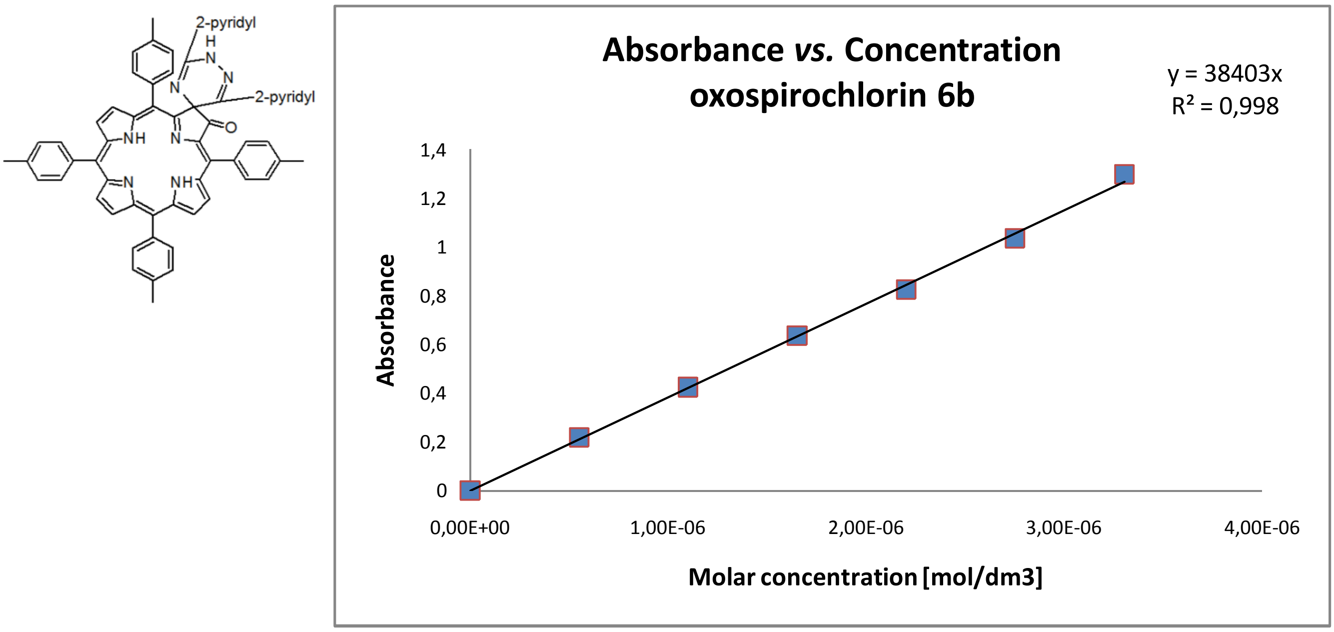


Fig. S32. Absorbance *vs*. Concentration Calibration Curve for oxospirochlorin **6b** in dichloromethane.

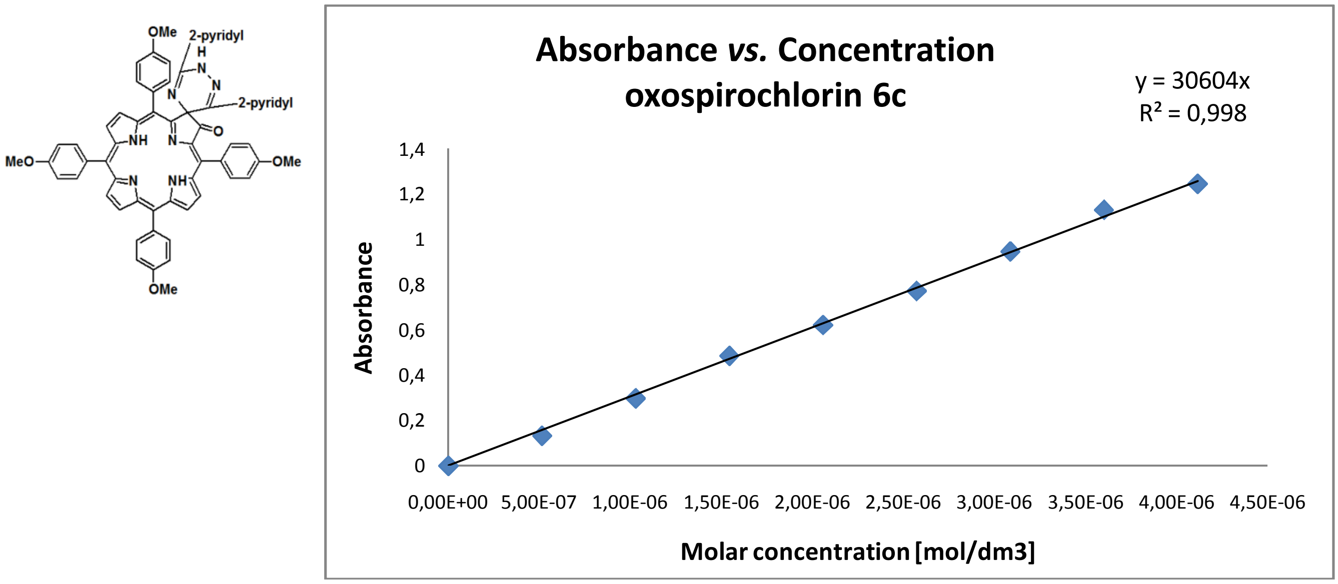


Fig. S33. Absorbance *vs.* Concentration Calibration Curve for oxospirochlorin **6c** in dichloromethane.

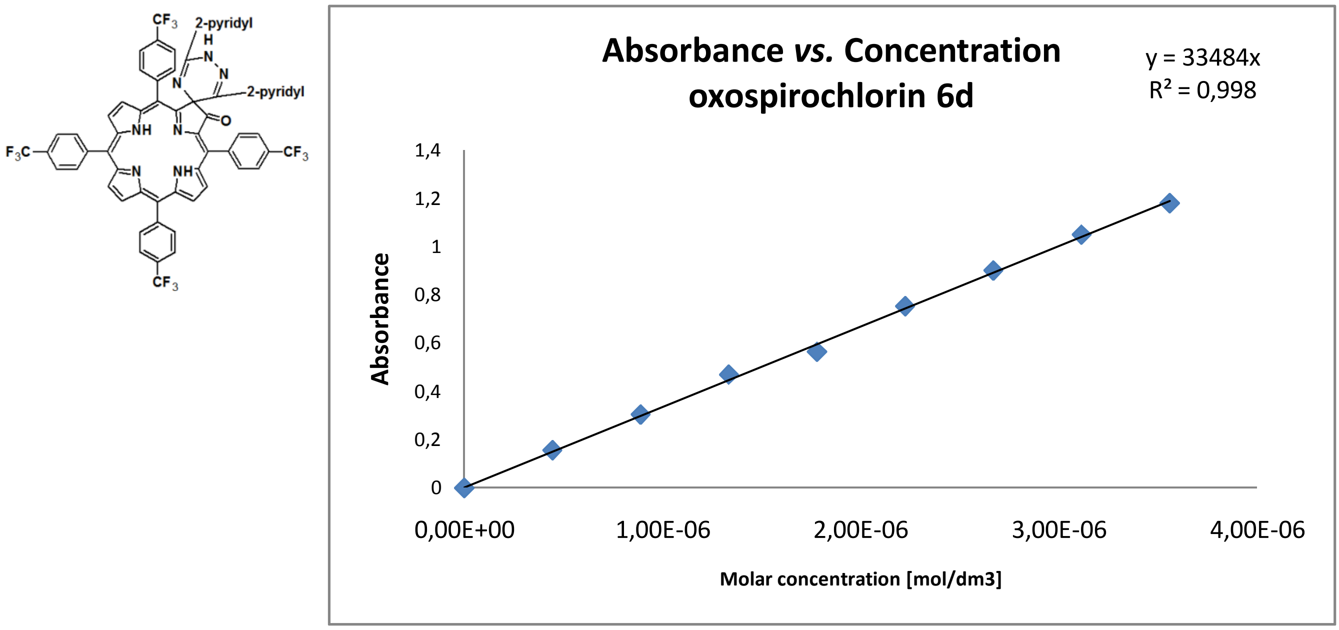


Fig. S34. Absorbance *vs.* Concentration Calibration Curve for oxospirochlorin **6d** in dichloromethane.

6. IR spectrum

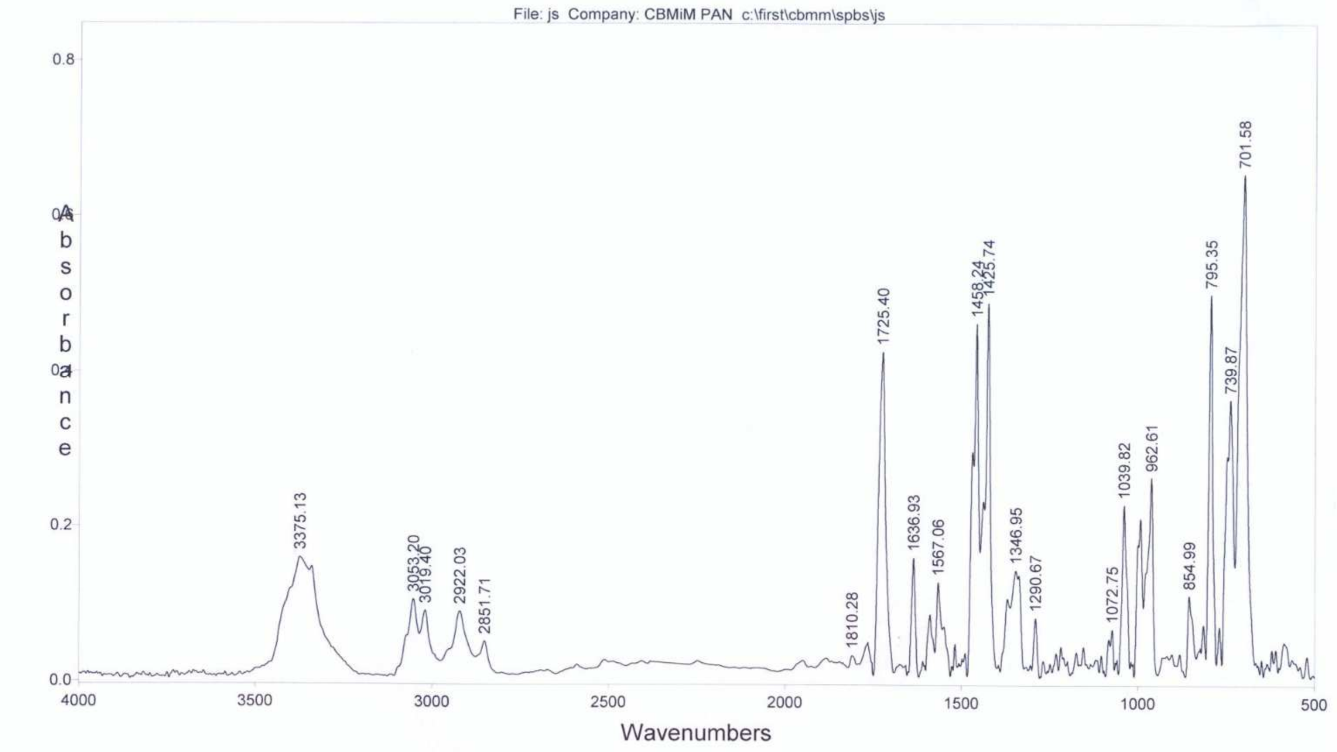


Fig. S35. IR spectrum of compound **6a.**

8. References

1. R. A. Kendall, T. H. Dunning Jr. and R. J. Harrison, J. *Chem. Phys.* 1992, **96**, 6796.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339.