

Supporting information for:

A pyrene-based N-heterocyclic carbene: study of its coordination chemistry and stereoelectronic properties

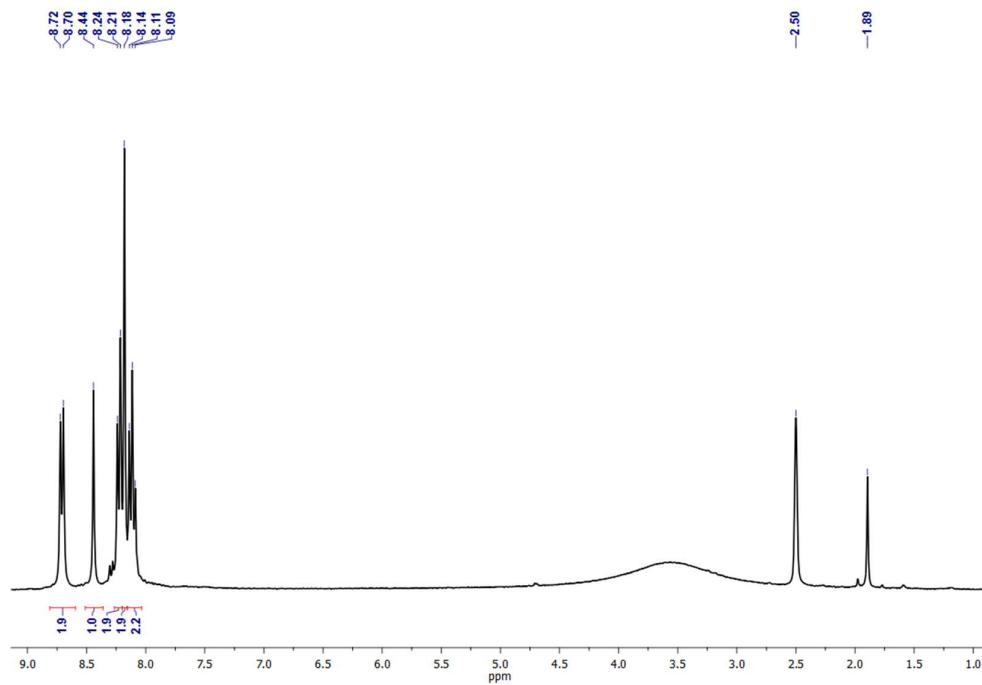
Hugo Valdés, Macarena Poyatos and Eduardo Peris

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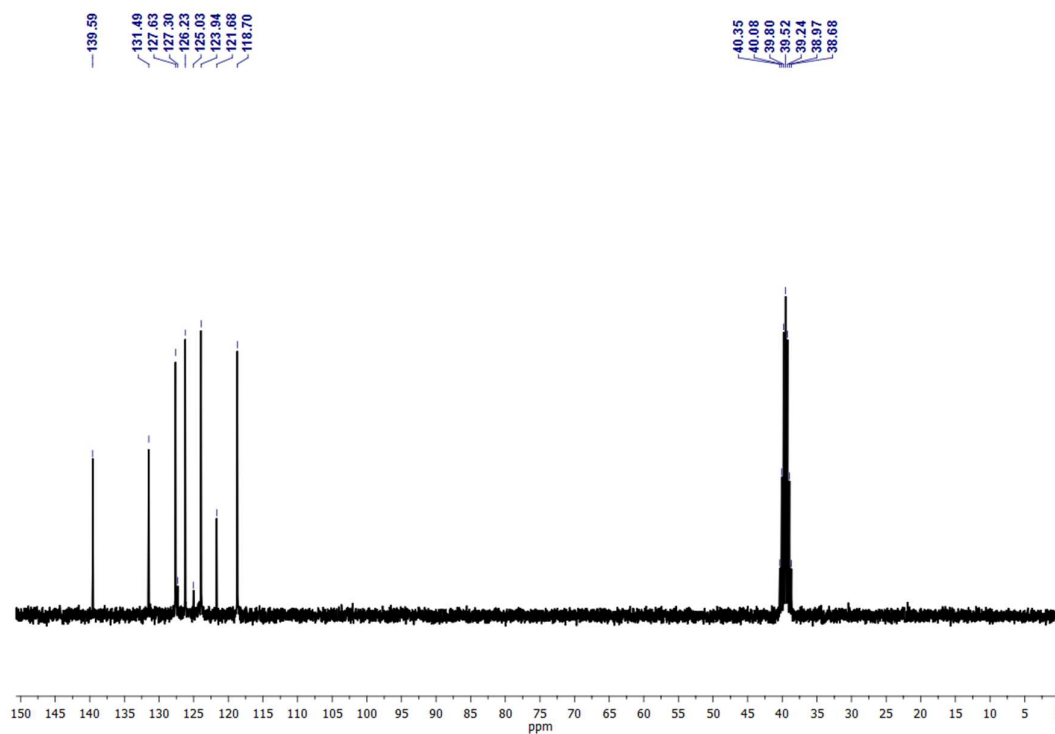
1. Spectra

1.1. Spectroscopic data of **2**

^1H NMR spectrum of **2** in $\text{DMSO}-d_6$

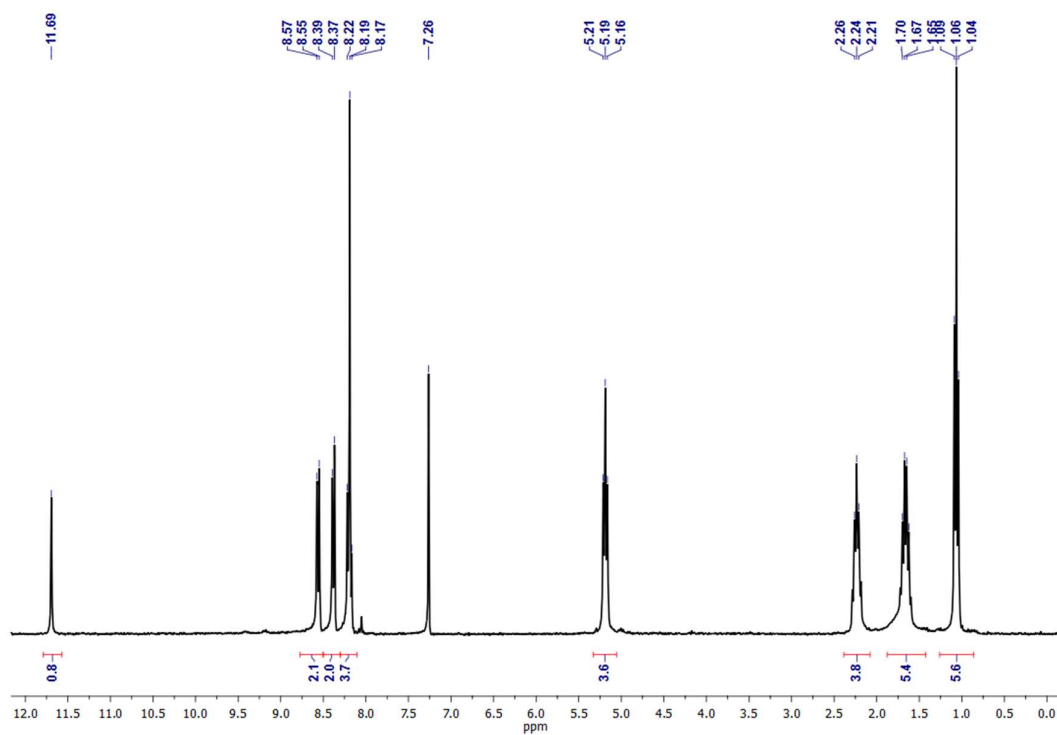


^{13}C NMR spectrum of **2** in $\text{DMSO}-d_6$

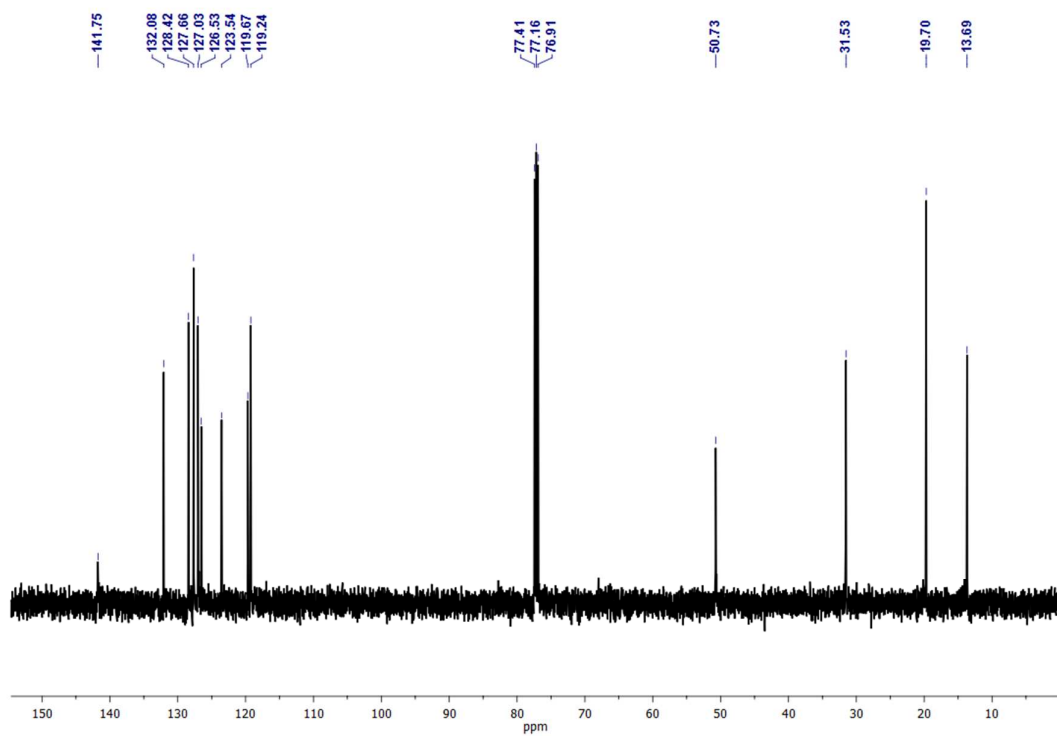


1.2. Spectroscopic data of **3**

^1H NMR spectrum of **3** in CDCl_3

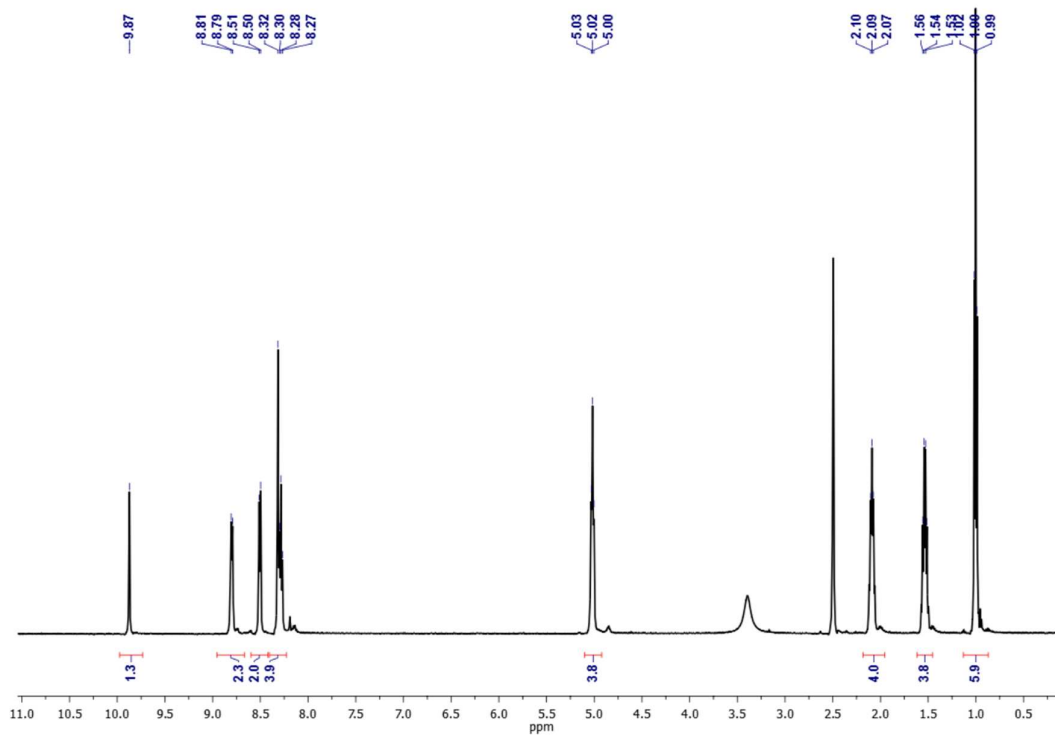


^{13}C NMR spectrum of **3** in CDCl_3

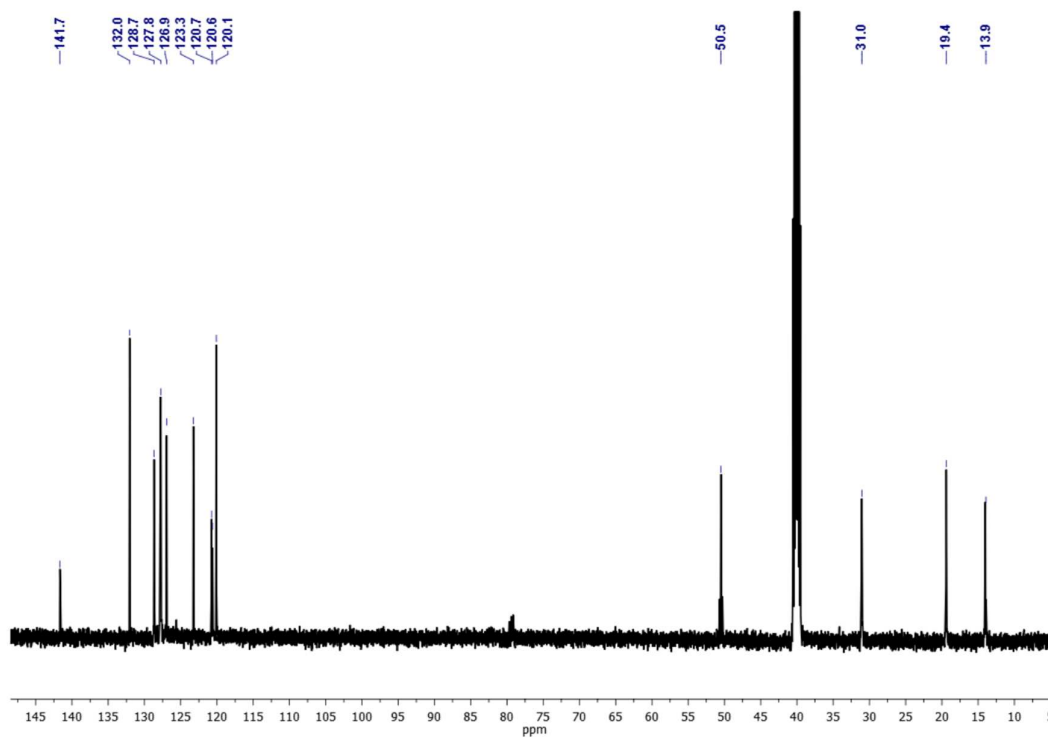


1.3. Spectroscopic data of **4**

^1H NMR spectrum of **4** in $\text{DMSO}-d_6$

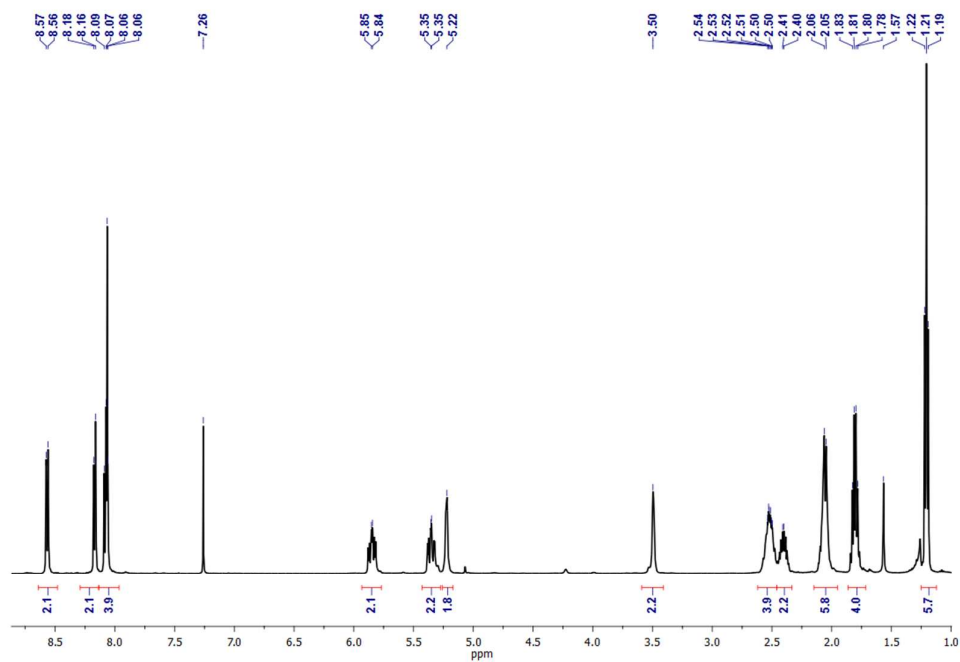


^{13}C NMR spectrum of **4** in $\text{DMSO}-d_6$

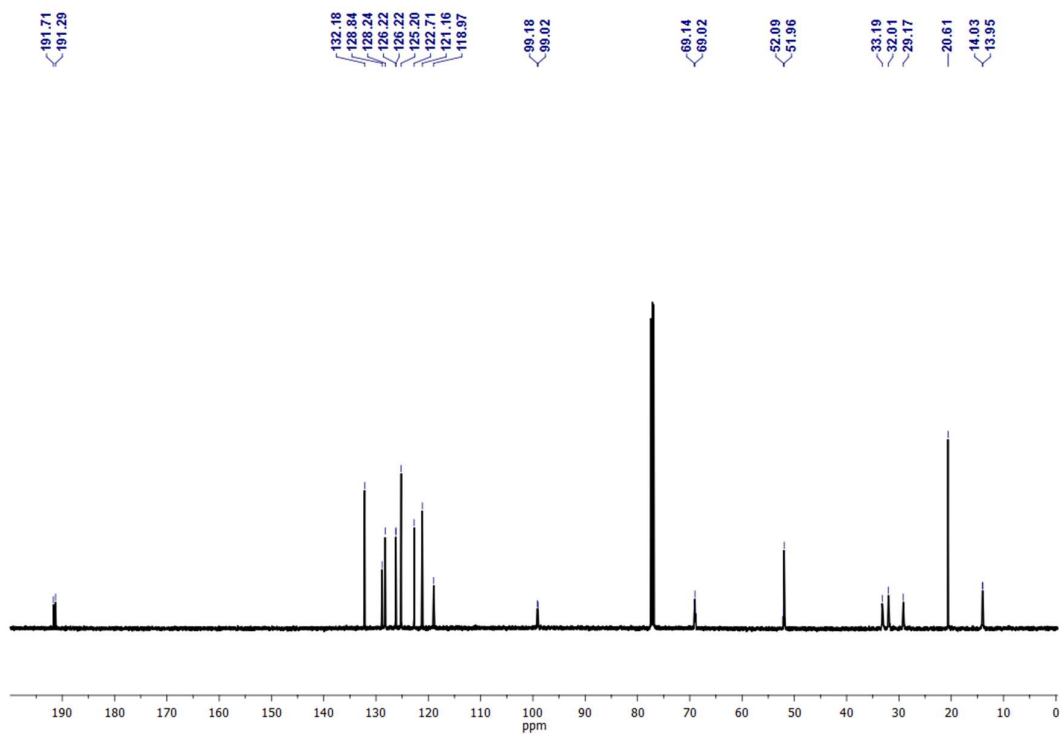


1.4. Spectroscopic data of **5a**

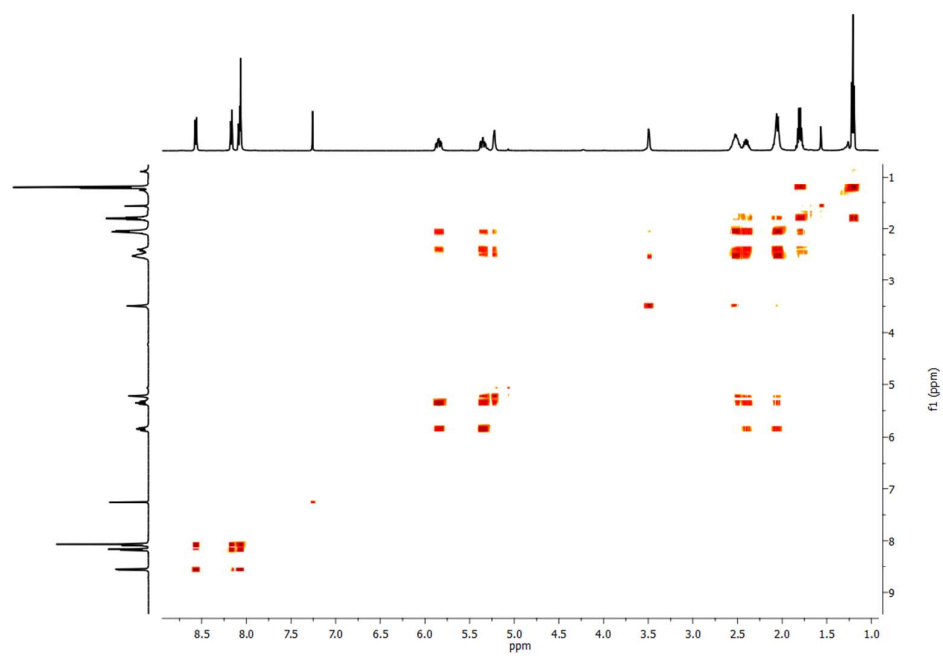
^1H NMR spectrum of **5a** in CDCl_3



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

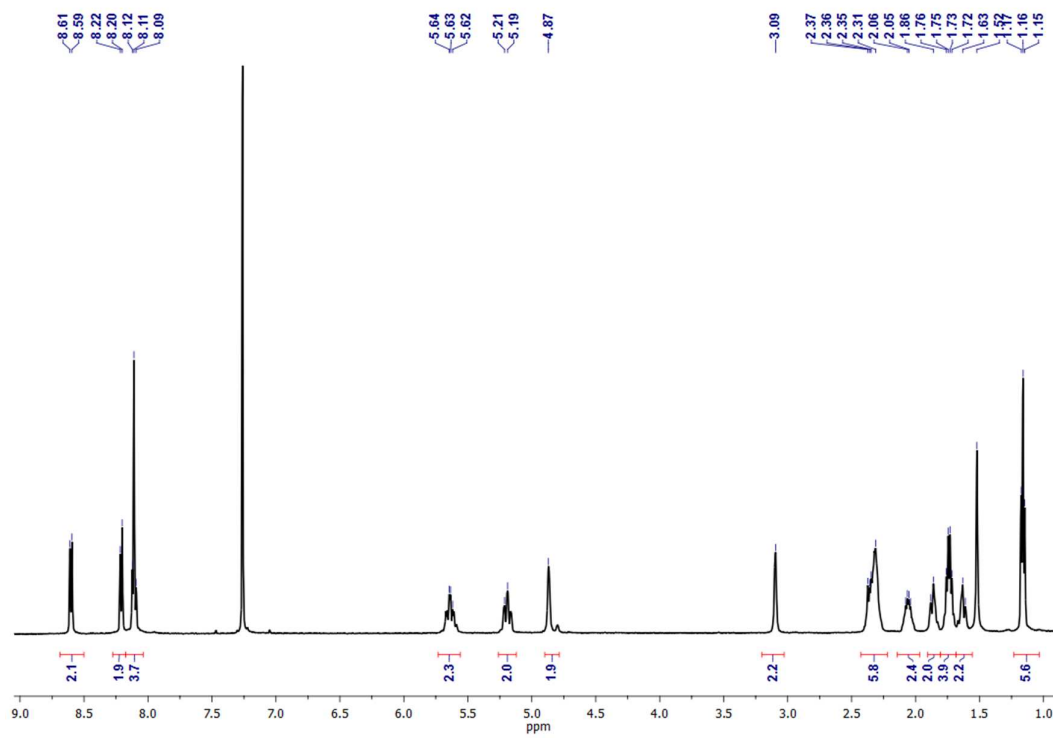


^1H - ^1H COSY NMR spectrum of **5a** in CDCl_3

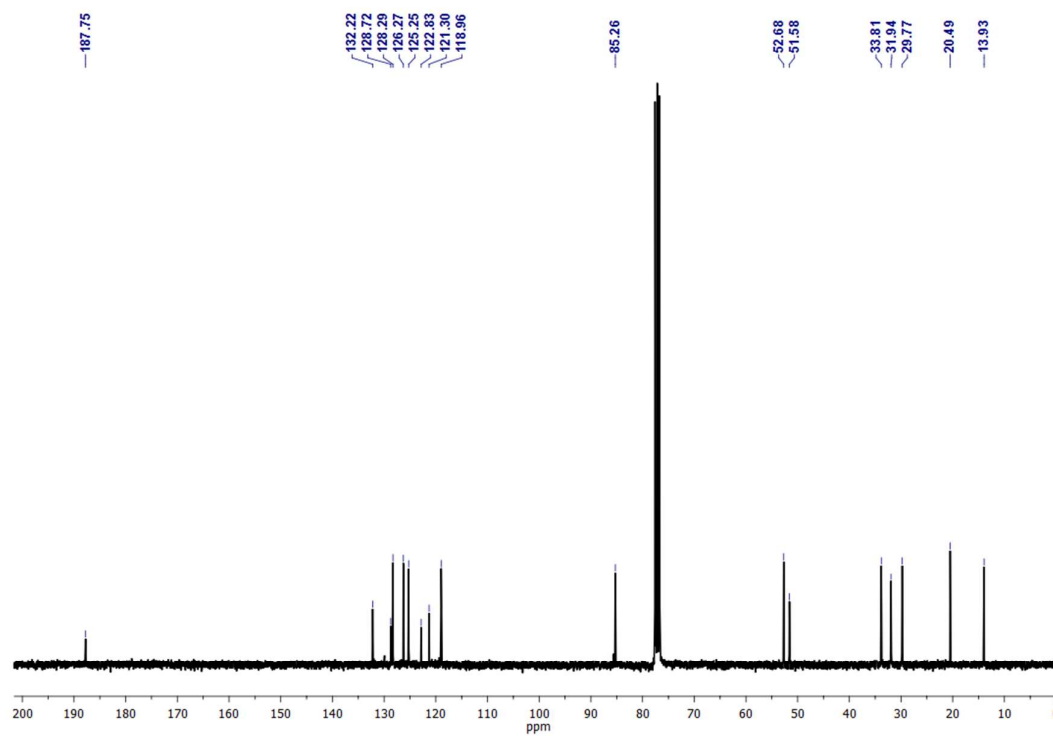


1.5. Spectroscopic data of **6a**

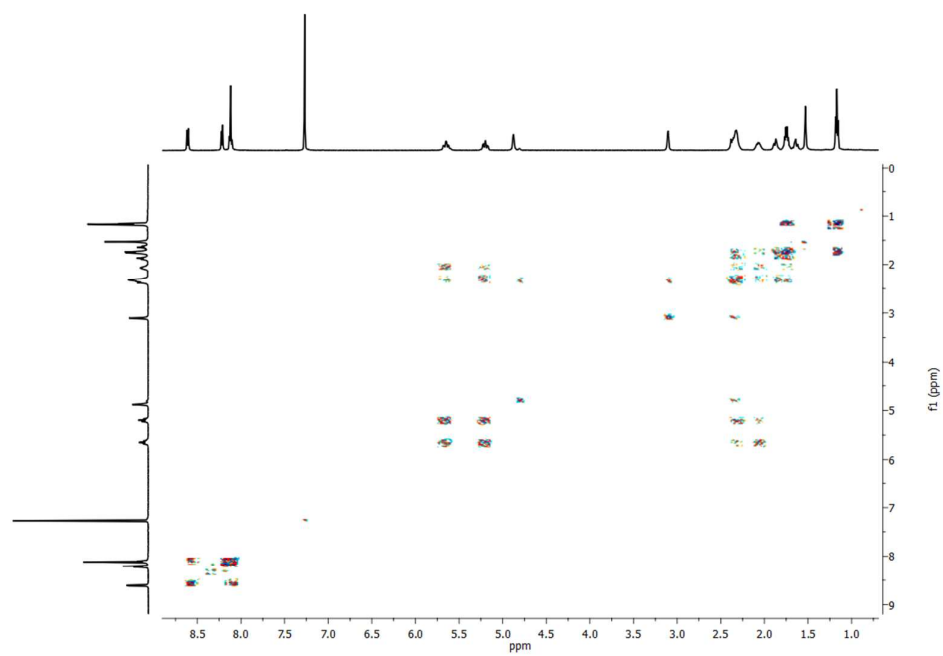
^1H NMR spectrum of **6a** in CDCl_3



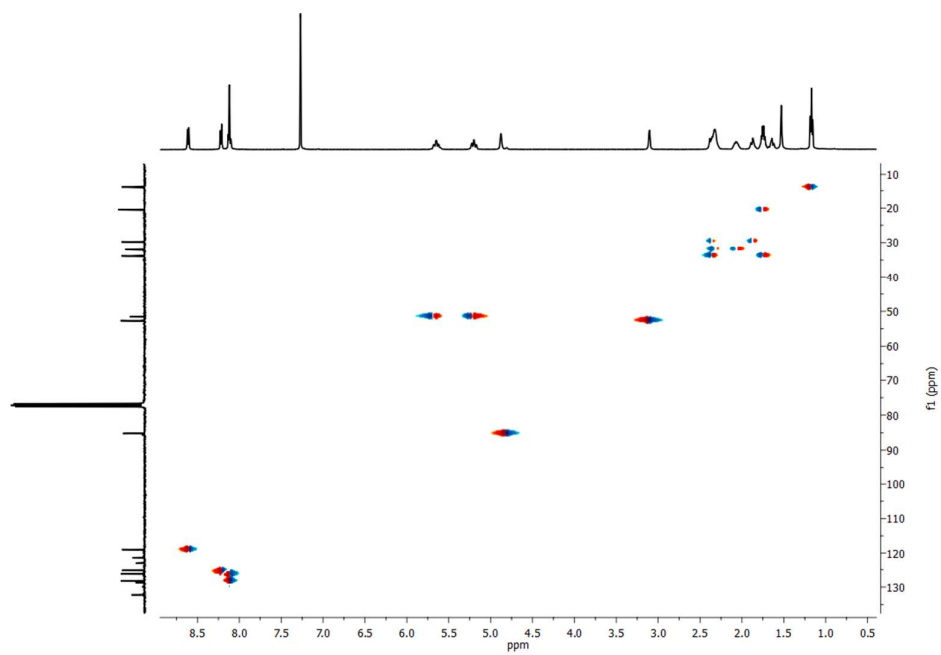
^{13}C NMR spectrum of **6a** in CDCl_3



^1H - ^1H COSY NMR spectrum of **6a** in CDCl_3

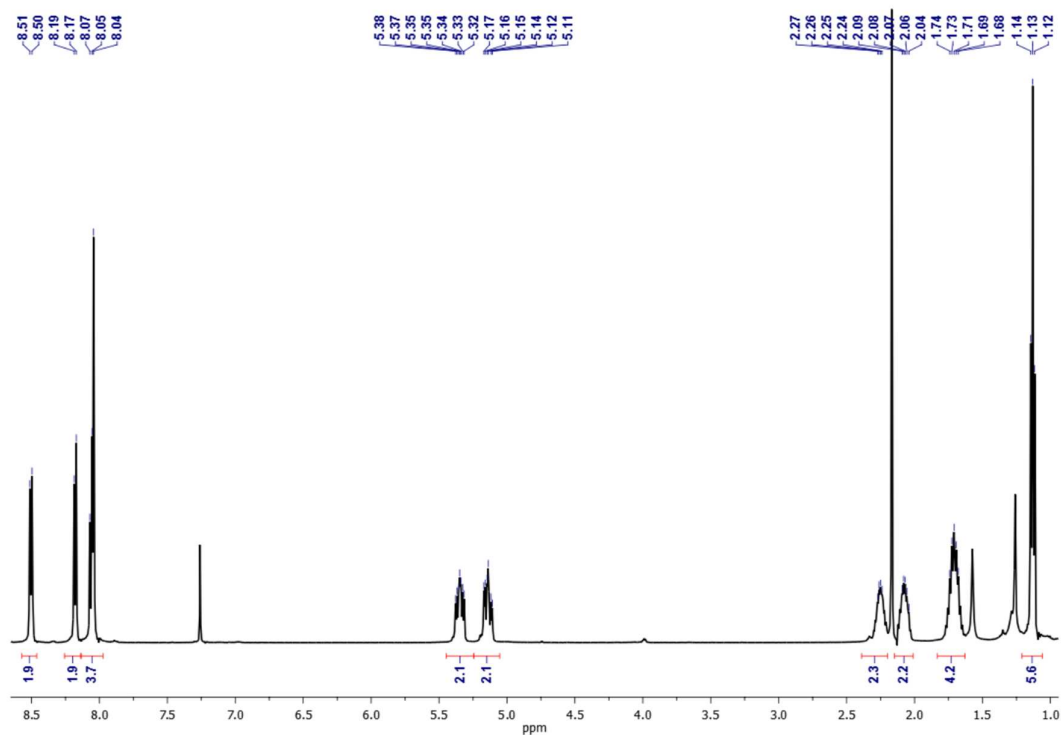


^{13}C - ^1H HSQC NMR spectrum of **6a** in CDCl_3

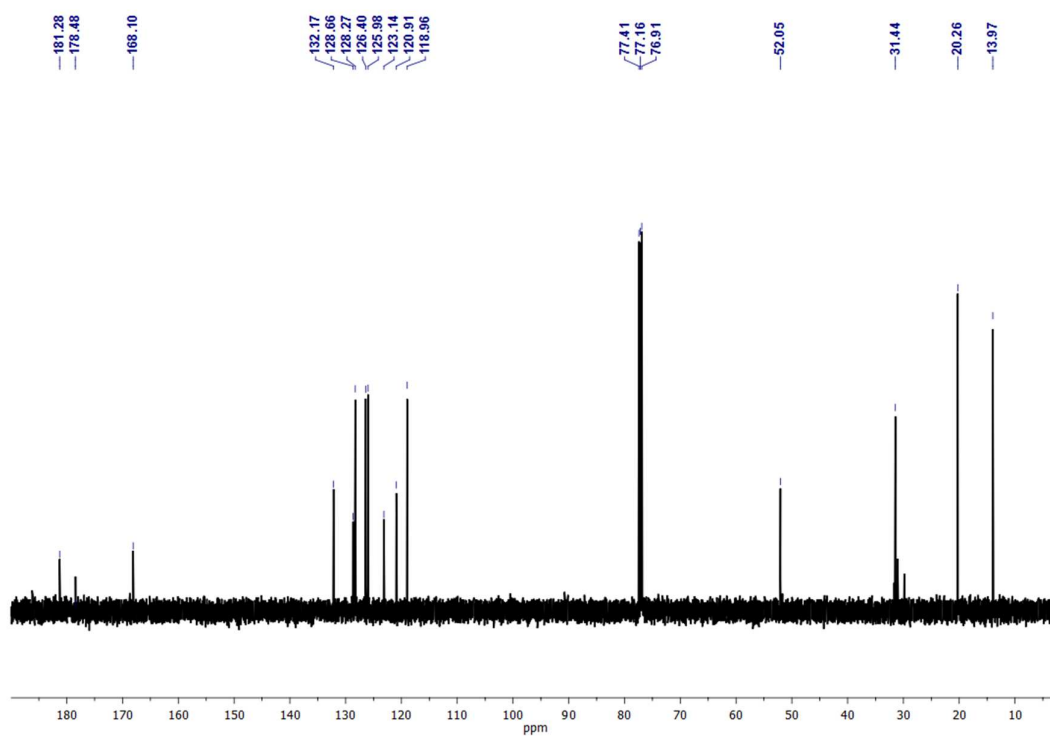


1.6. Spectroscopic data of 7

^1H NMR spectrum of 7 in CDCl_3

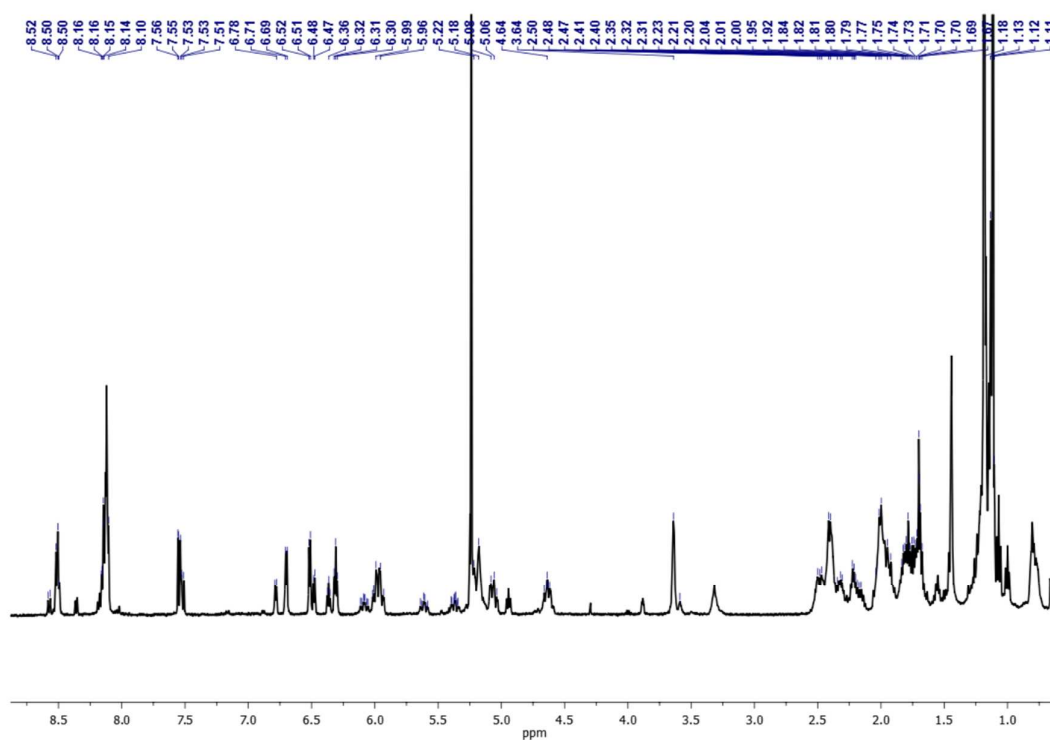


^{13}C NMR spectrum of 7 in CDCl_3

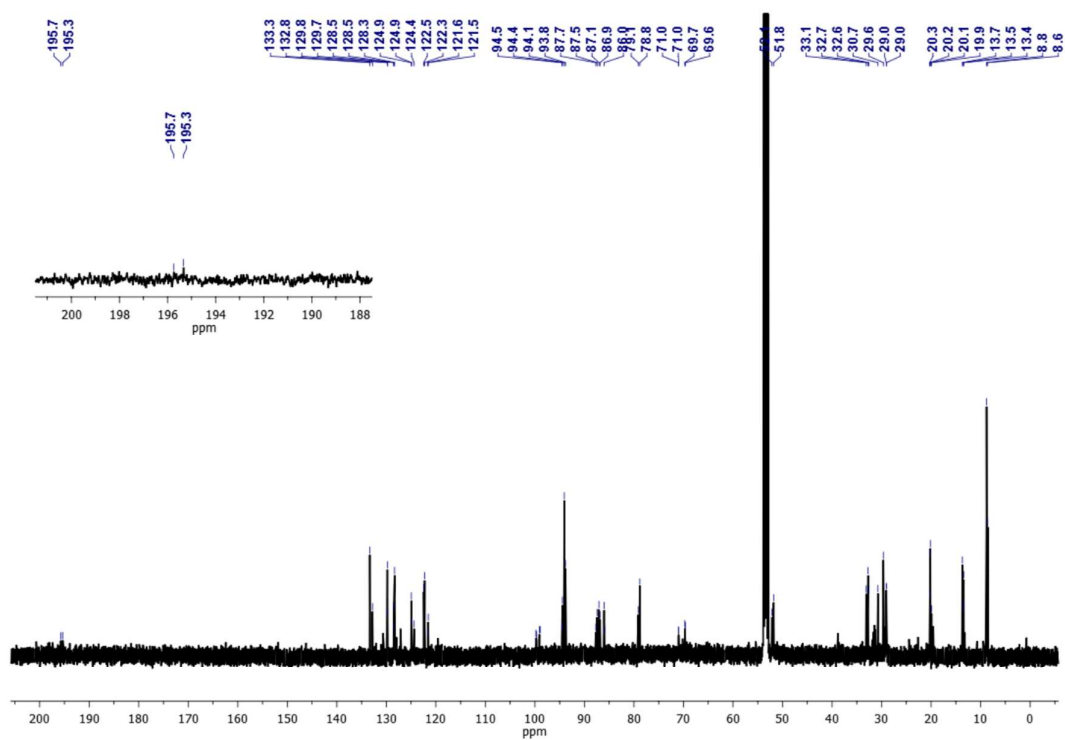


1.7. Spectroscopic data of **8b**

^1H NMR spectrum of **8b** in CD_2Cl_2

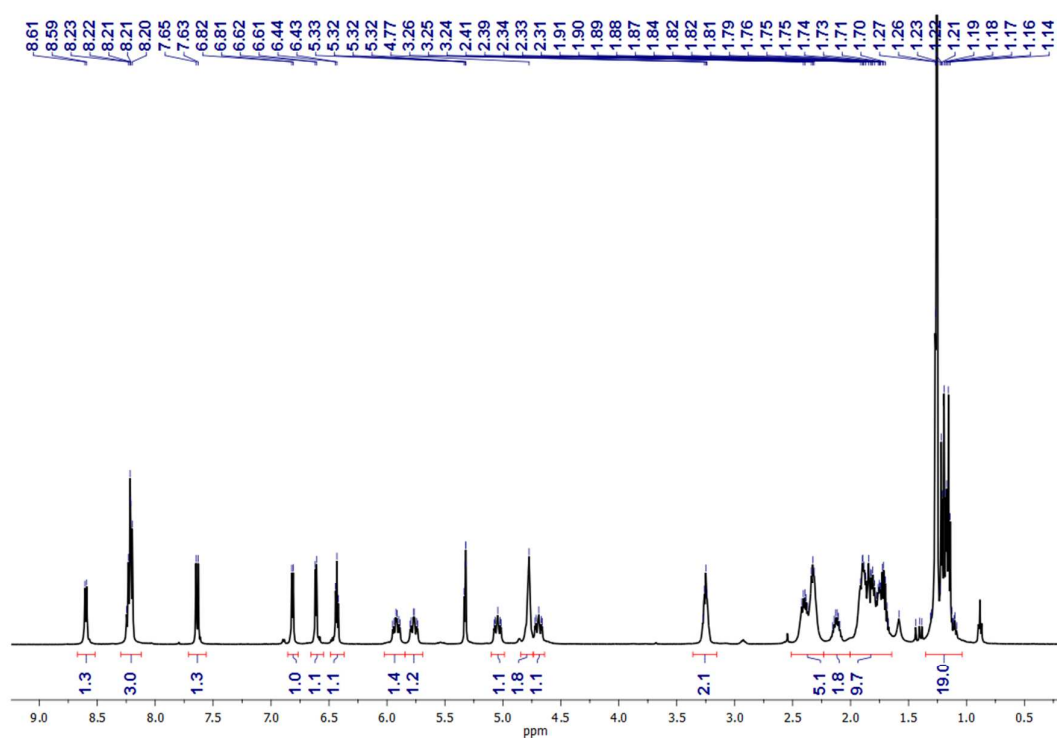


^{13}C NMR spectrum of **8b** in CD_2Cl_2

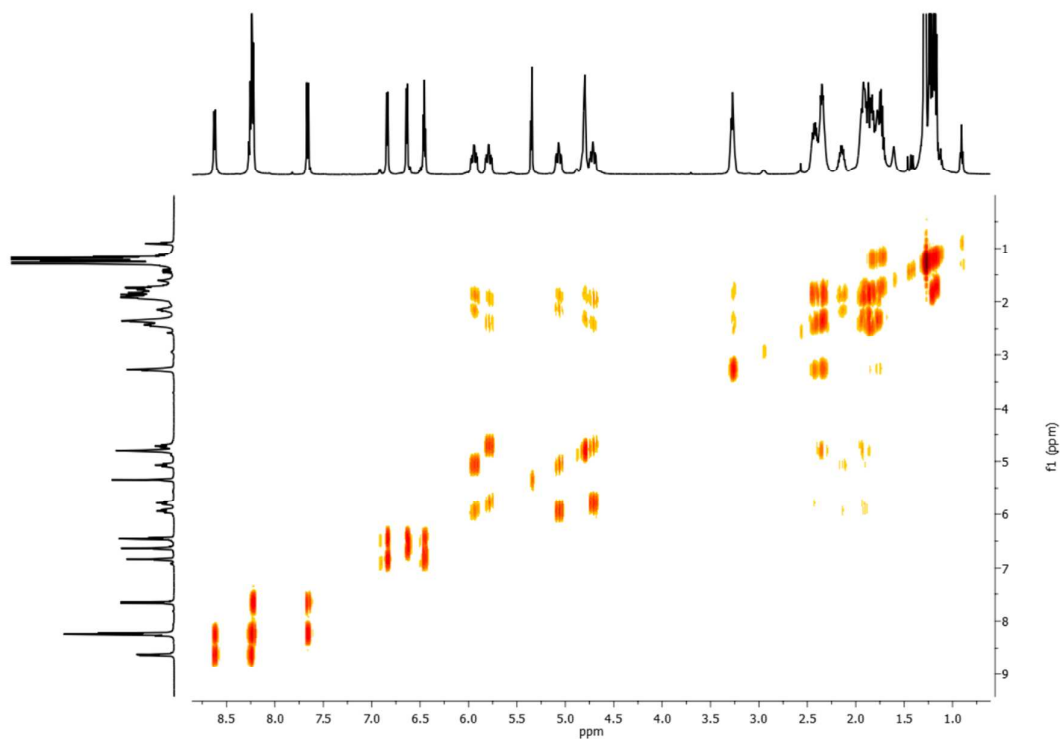


1.8. Spectroscopic data of **9a**

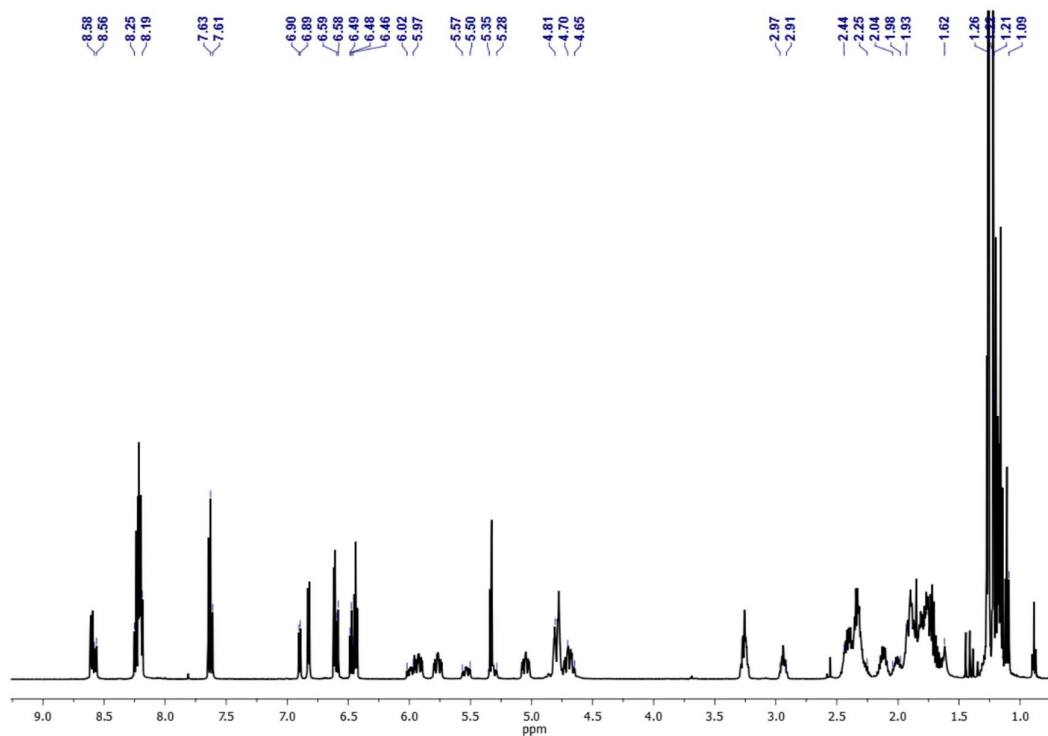
^1H NMR spectrum of **9a** (*syn* isomer) in CD_2Cl_2



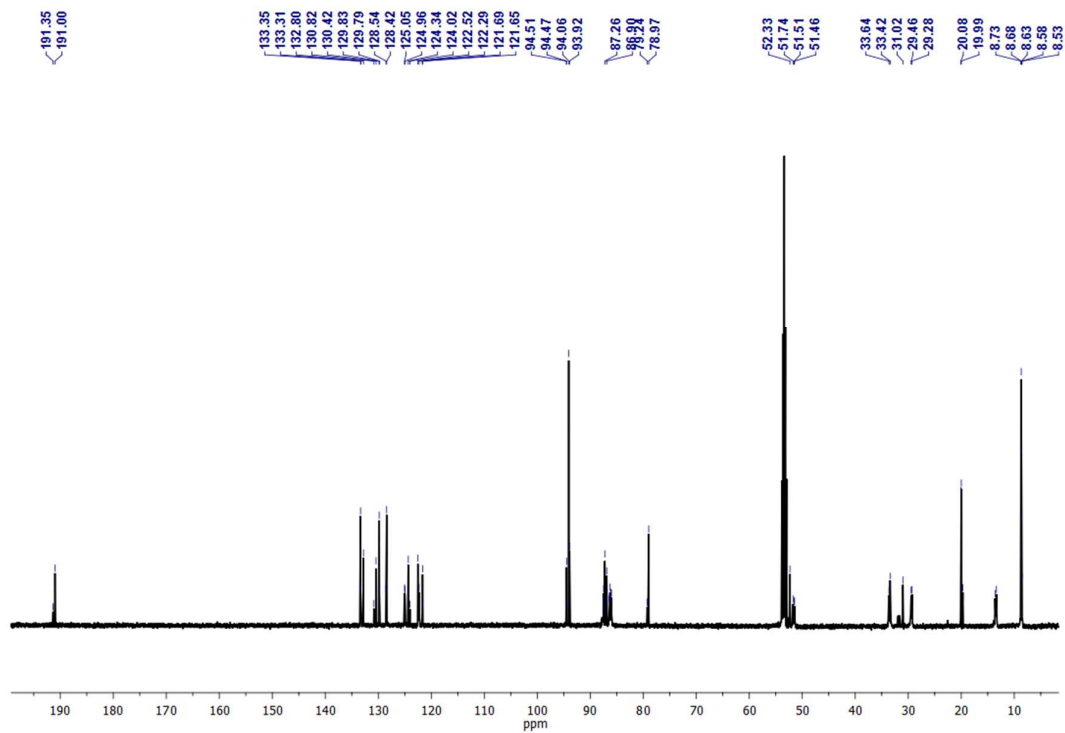
^1H - ^1H COSY NMR spectrum of **9a** (*syn* isomer) in CD_2Cl_2



^1H NMR spectrum of **9a** (mixture of isomers *syn* and *anti*) in CD_2Cl_2

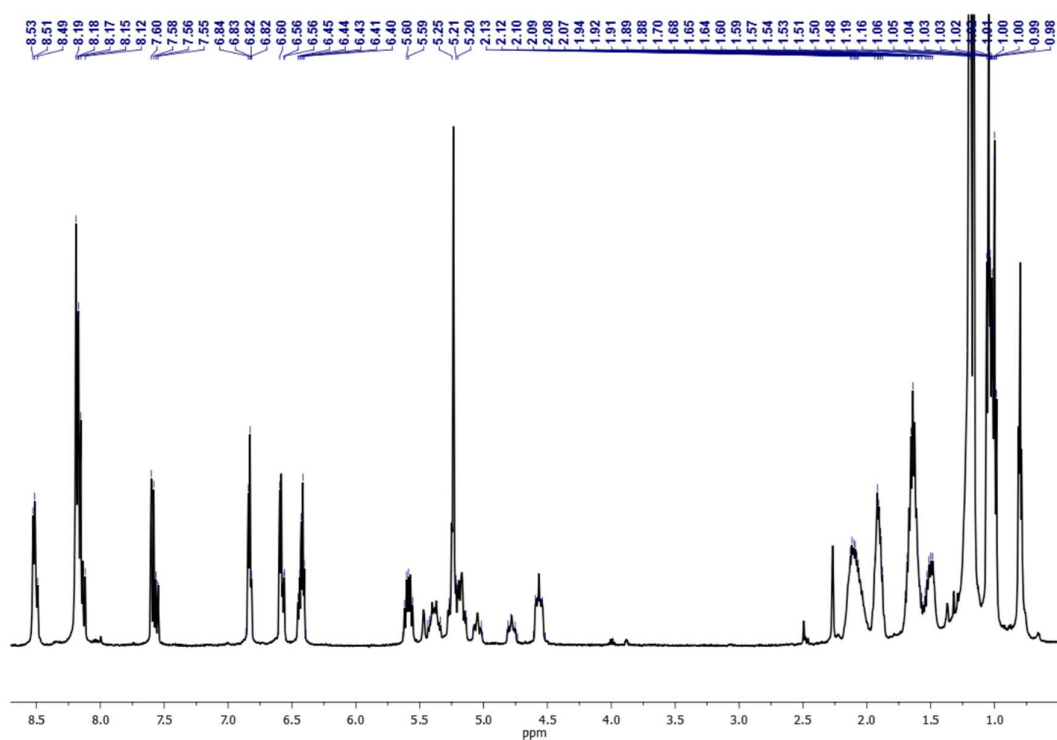


^{13}C NMR spectrum of **9a** (mixture of isomers *syn* and *anti*) in CD_2Cl_2

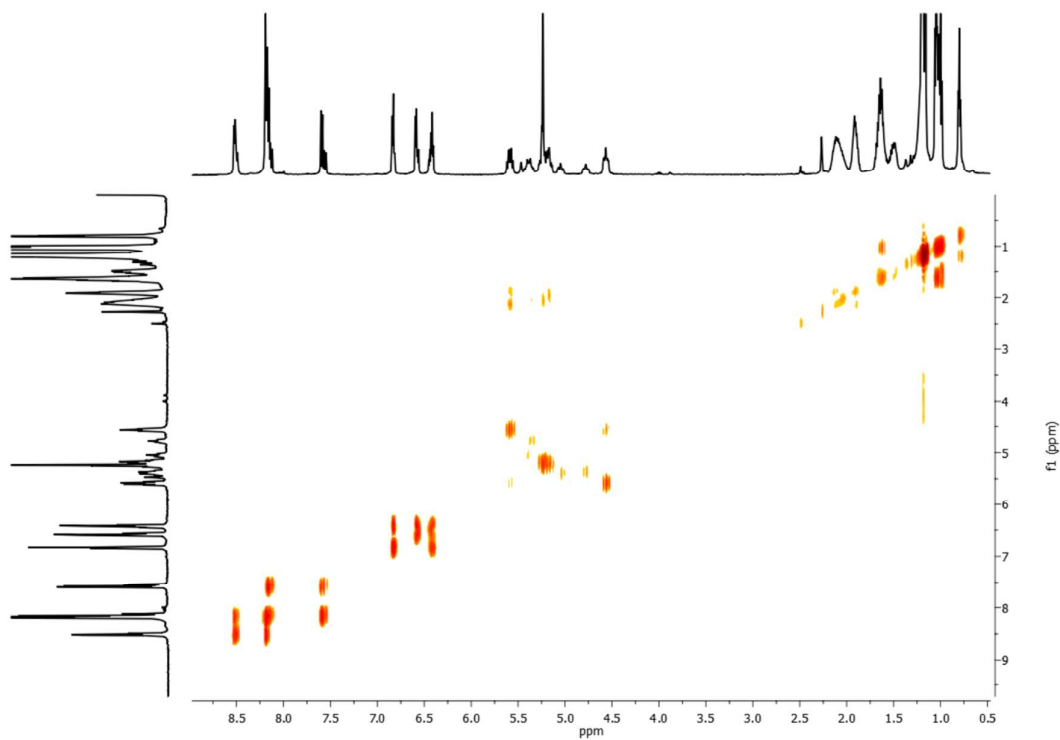


1.9. Spectroscopic data of **10**

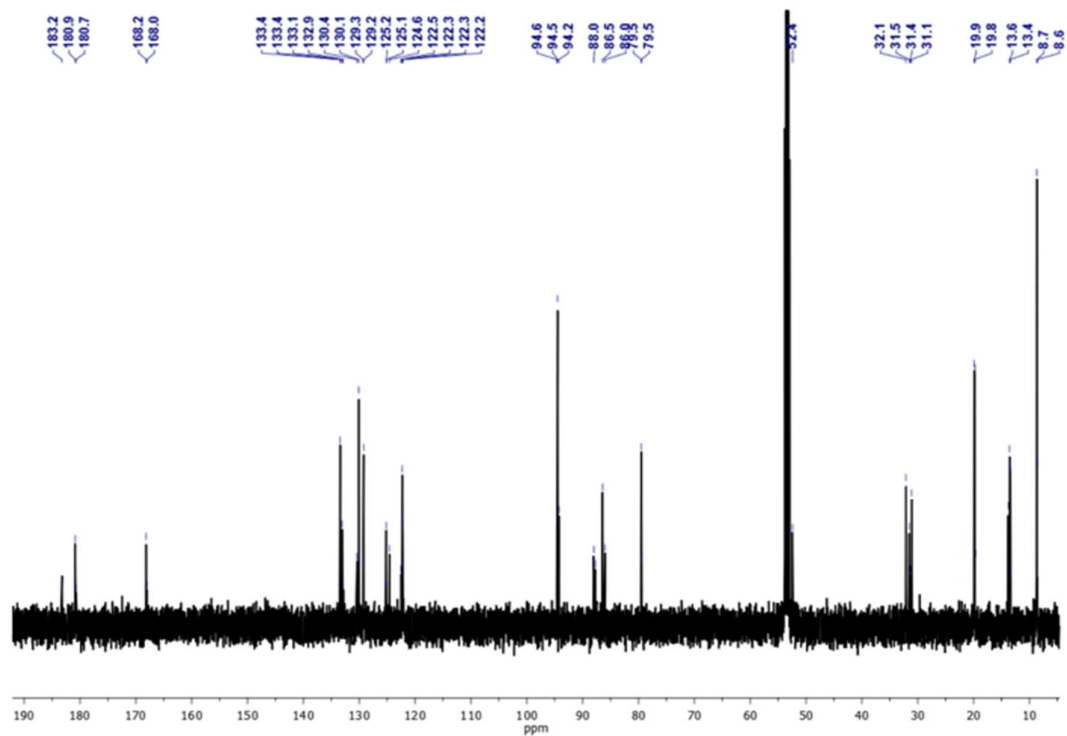
^1H NMR spectrum of **10** (mixture of isomers *syn* and *anti*) in CD_2Cl_2



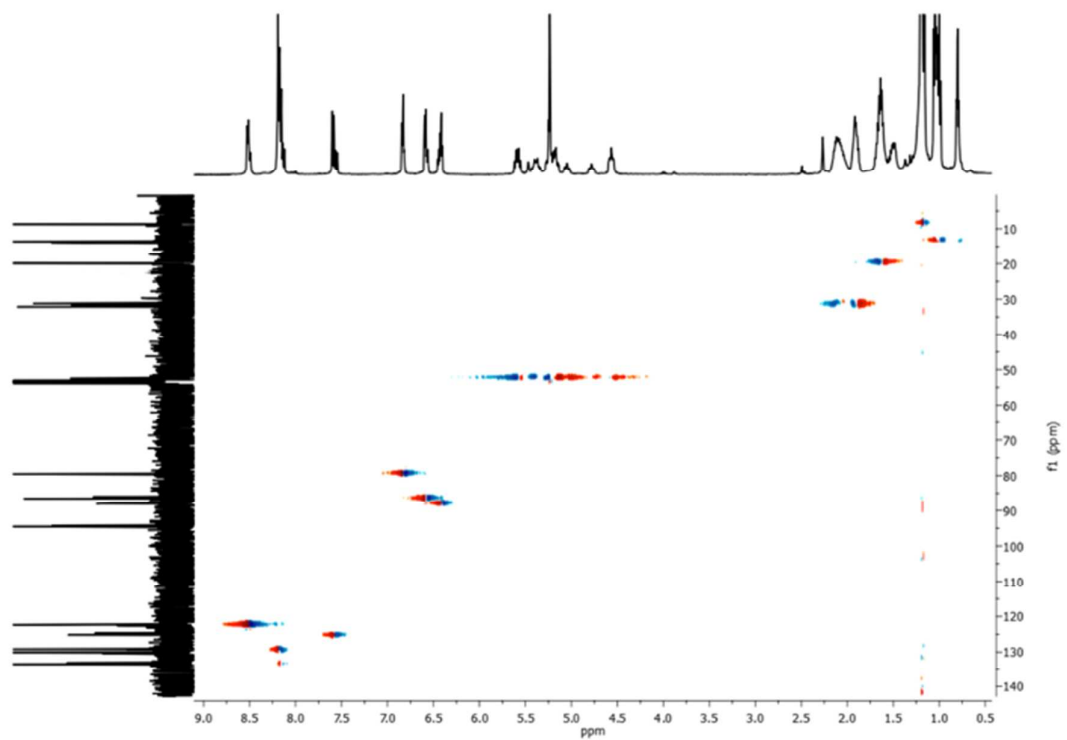
^1H - ^1H COSY NMR spectrum of **10** (mixture of isomers *syn* and *anti*) in CD_2Cl_2



^{13}C NMR spectrum of **10** (mixture of isomers *syn* and *anti*) in CD_2Cl_2

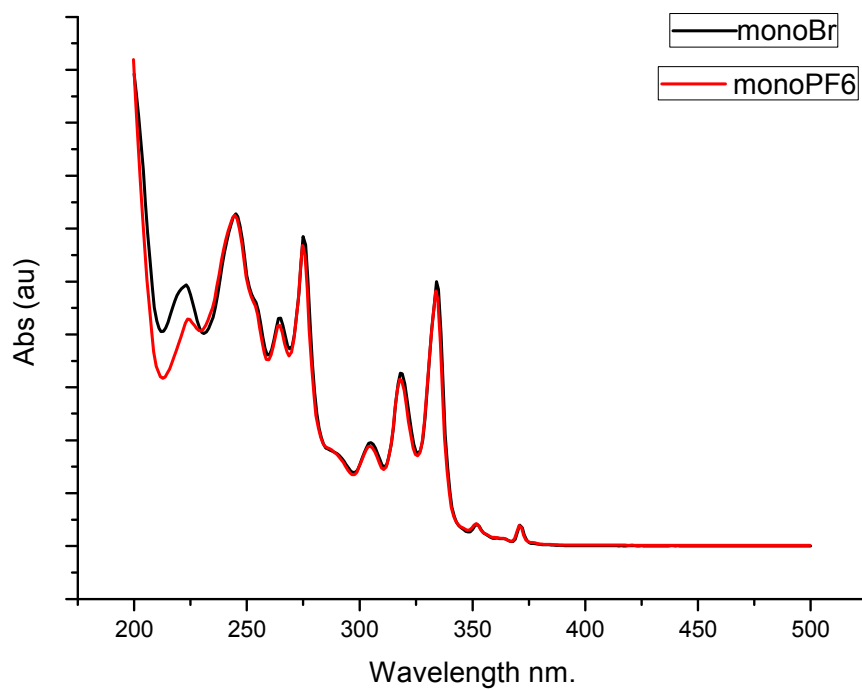


^{13}C - ^1H HSQC NMR spectrum of **10** (mixture of isomers *syn* and *anti*) in CD_2Cl_2

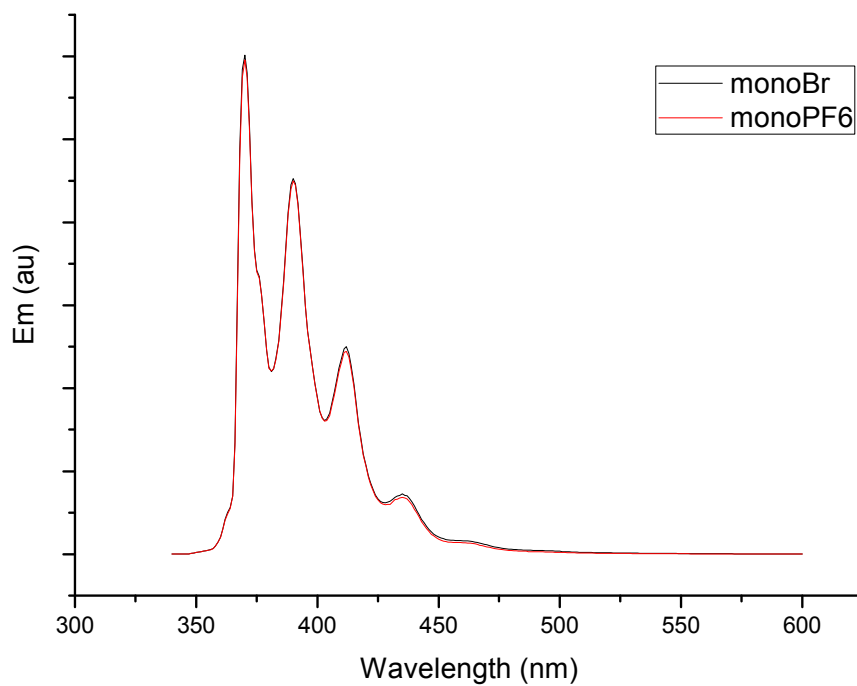


2. UV-Vis absorption and emission spectra of **3** and **4**

2.1. UV-Vis absorption spectra of **3** (monoBr) and **4** (monoPF6) recorded using MeCN under ambient conditions.



2.2. Emission spectra of **3** (monoBr) and **4** (monoPF6) recorded using degassed MeCN



Supplementary Table S1. Photophysical properties of **3** and **4**

Compound	λ_{max} (nm) ($\log(\epsilon)$) ^a	Φ_f ^b
3	245 (4.50), 275 (4.47)	0.31
4	245 (4.59), 275 (4.55)	0.28

^aMesurements were performed in MeCN under ambient conditions. Molar extinction coefficients (ϵ , in $\text{M}^{-1}\text{cm}^{-1}$) were determined from Beer's law plots. ^bEmission quantum yield was measured in degassed MeCN, with recrystallized anthracene in degassed EtOH as standard ($\Phi_f = 0.27$), exciting at 317 nm.

3. X-Ray Crystallography

Crystals suitable for X-ray study were obtained by slow diffusion of hexane into a concentrated solution of the complex in chloroform (**3**, **5a**, **6b**) or dichloromethane (**9b**). Diffraction data was collected on a Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Single crystals were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Absorption corrections based on the multiscan method were applied.¹ The structure was solved by direct methods in SHELXS-97 and refined by the full-matrix method based on F^2 with the program SHELXL-97² using the OLEX software package.³ Key details of the crystal and structure refinement data are summarized in Supplementary Table S1.

Supplementary Table S2. Summary of crystal data, data collection, and structure refinement details

	3	5a	6b	9b
Empirical formula	$\text{C}_{25}\text{H}_{27}\text{BrN}_2$	$\text{C}_{99}\text{H}_{114}\text{Cl}_3\text{N}_6\text{Rh}_3$	$\text{C}_{33}\text{H}_{38}\text{BrIrN}_2$	$\text{C}_{43}\text{H}_{53}\text{BrF}_6\text{IrN}_2\text{PRu}$
Formula weight	435.39	1803.04	734.76	1116.02
Temperature	293(2)	199.95(10)	200.00(10)	200.1(2)
Crystal System	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P-1$
a/ $\text{\AA}$	8.2162(3)	18.20666(12)	9.3221(3)	11.8980(3)
b/ $\text{\AA}$	12.5197(4)	21.18239(13)	21.3617(5)	12.2223(4)
c/ $\text{\AA}$	19.5121(8)	21.55681(15)	14.4693(4)	17.2260(4)
$\alpha/^\circ$	90	90	90	96.493(3)
$\beta/^\circ$	93.037(4)	90.7989(6)	101.674(3)	101.866(2)

$\gamma/^\circ$	90	90	90	118.496(3)
Volume/ $\text{\AA}^3$	2004.27(14)	8312.80(9)	2821.75(14)	2088.52(12)
Z	4	4	4	2
Density (calculated)/ mg/mm^3	1.443	1.441	1.730	1.775
Absorption coefficient/ mm^{-1}	2.064	6.045	6.172	4.599
F(000)	904.0	3744.0	1448.0	1100.0
Crystal size/ mm^3	$0.055 \times 0.135 \times$ 0.239	$0.238 \times 0.149 \times$ 0.116	0.3379×0.1486 $\times 0.1169$	$0.1472 \times 0.1353 \times$ 0.0549
Theta range for data collection	5.936 to 58.934 $^\circ$	5.85 to 145.32 $^\circ$	5.75 to 58.986 $^\circ$	5.424 to 59.05 $^\circ$
Index ranges	$-10 \leq h \leq 11,$ $-15 \leq k \leq 17,$ $-26 \leq l \leq 26$	$-22 \leq h \leq 22,$ $-25 \leq k \leq 26,$ $-26 \leq l \leq 25$	$-11 \leq h \leq 12,$ $-29 \leq k \leq 28,$ $-19 \leq l \leq 18$	$-15 \leq h \leq 16,$ $-16 \leq k \leq 16,$ $-23 \leq l \leq 23$
Reflections collected	20273	7771	22604	45967
Independent reflections	5092 [R(int) = 0.0541]	16357 [R(int) = 0.0378]	6991 [R(int) = 0.0370]	10643 [R(int) = 0.0519]
Data / restraints / parameters	5092/0/255	16357/2/1035	6991/0/336	10643/0/512
Goodness-of-fit on F^2	1.111	1.107	0.928	1.082
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0511,$ $wR_2 = 0.1311$	$R_1 = 0.0546,$ $wR_2 = 0.1550$	$R_1 = 0.0380,$ $wR_2 = 0.0891$	$R_1 = 0.0433,$ $wR_2 = 0.0890$
R indices (all data)	$R_1 = 0.0765,$ $wR_2 = 0.1459$	$R_1 = 0.0720,$ $wR_2 = 0.1691$	$R_1 = 0.0598,$ $wR_2 = 0.1053$	$R_1 = 0.0753,$ $wR_2 = 0.1069$
Largest diff. peak and hole/ $\text{e.}\text{\AA}^{-3}$	0.81 and -0.52	2.37 and -1.36	1.42 to -1.29	2.40 to -1.42

4. References

1. Clark, R. C.; Reid, J. S., *Acta Crystallogr. Sect. A* **1995**, *51*, 887-897.
2. Sheldrick, G. M., *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., *J. Appl. Crystallogr.* **2009**, *42*, 339-341.