Supplementary Information

Ru(II)-dmso Complexes containing Azole-based Ligands: Synthesis, Linkage Isomerism and Catalytic Behaviour

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Keywords: ruthenium /dmso complexes/ azole-based ligands / linkage isomerism / hydration catalysis.

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Table S1. Crystallographic data for complexes **2-5** and **6'**.

	2	**3**	**4**	**5**	**6'**
Empirical formula	$C_{10}H_{24}Cl_2N_2O_3RuS_3$	$C_9H_{21}Cl_2N_3O_5RuS_3$	$C_{10}H_{23}Cl_2F_3N_2O_4RuS_3$	$C_{13}H_{24}BrCl_2N_2O_4RuS_3$	$C_{11}H_{15}Cl_3N_3ORuS$
Formula weight	488.46	519.44	560.45	620.40	515.64
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P21/n	P 21/n	P2(1)/c	P21/c
a [Å]	8.8684(17)	8.396(7)	8.739(3)	12.493(6)	9.969(5)
b [Å]	14.240(3)	15.783(13)	23.299(7)	13.943(7)	16.673(8)
c [Å]	15.809(3)	14.403(12)	10.690(3)	16.522(6)	11.326(6)
α [º]	90	90	90	90	90
β [º]	102.331(3)	105.773(13)	93.393(6)	130.27(2)	96.414 (7)
γ [º]	90	90	90	90	90
V [Å^3]	1950.3(6)	1837(3)	2172.9(12)	2195.9(17)	1870.8(16)
Formula Units/ cell	4	4	4	4	4
Temp. [K]	298(2)	298(2)	298(2)	298(2)	100(2)
ρ_{calc}, [Mg/m^{-3}]	1.664	1.878	1.713	1.877	1.831
μ [mm^{-1}]	1.407	1.509	1.297	3.083	1.665
Final R indices, [I>2σ(I)]	R1=0.0256 wR2=0.0657	R1=0.0237 wR2=0.0608	R1=0.0390 wR2=0.1193	R1=0.0387 wR2=0.0985	R1 = 0.0400 wR2 = 0.1022
R indices [all data]	R1=0.0298 wR2=0.0681	R1=0.0259 wR2=0.0626	R1=0.0447 wR2=0.1229	R1=0.0523 wR2=0.1052	R1 = 0.0524 wR2 = 0.1111

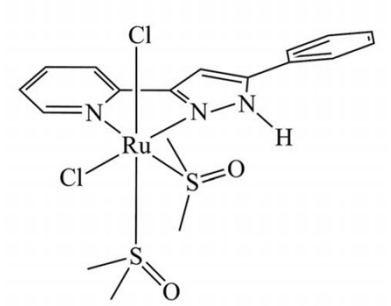
$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

$wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{½}$, where $w = 1/[\sigma^2(Fo^2) + (0.0042P)^2]$ and $P=(F_o^2+2F_c^2)$

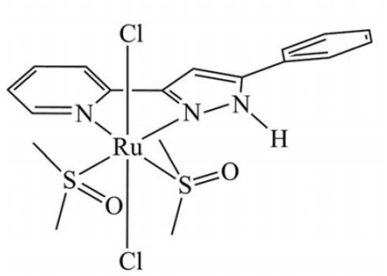
Table S2. Formulas used for the calculation of rate (k) and equilibrium (K) constants.

Equations	Description of parameters
$\frac{i_{c1}}{i_{c2}} = a \cdot \frac{1}{v} + K_{O-S}^{III}$ **(eq. 1)**	i_c = cathodic peak intensity (A) a = RT/nF, with: R = Boltzmann constant (J/(K·mol)) T= temperature (K) n = number of exchanged electrons F = Faraday constant (A·s/mol) υ = scan rate (V/s) K = equilibrium constant
$\sqrt{v} = \frac{1}{\frac{0.471}{K_{O-S}^{III}} \cdot \sqrt{\frac{nFl}{RT}}} \cdot \frac{i_d}{i_k} - \frac{1.02}{\frac{0.471}{K_{O-S}^{III}} \cdot \sqrt{\frac{nFl}{RT}}}$ **(eq. 2)**	i_d = diffusional current in the absence of a chemical reaction (= i_{a1}) i_k = measured peak current (= i_{c1}) $l = k_{O-S}^{III} + k_{S-O}^{III}$
$K^{II} = K^{III} + e^{\frac{F}{RT} \cdot \left(E_{Ru-S}^{0} - E_{Ru-O}^{0}\right)}$ **(eq. 3)**	E^0 = standard potential
$ln\left(\frac{i_{a1}}{\sqrt{v}}\right) = k_{O-S}^{II} \cdot \frac{1}{v} + b$ **(eq. 4)**	

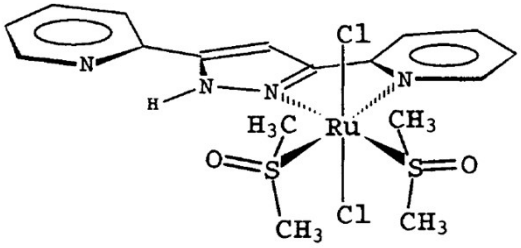
Scheme S1. Ru-dmso complexes gathered in entries 3-6 of Table 2.



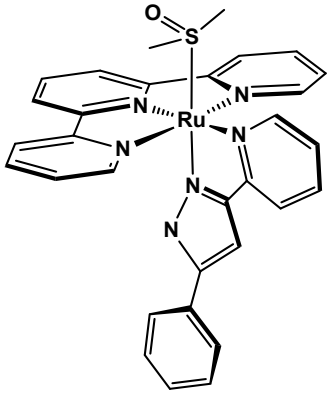
cis,*cis*-[$RuCl_2$(H3p)(dmso-S)$_2$]



trans,*cis*-[$RuCl_2$(H3p)(dmso-S)$_2$]



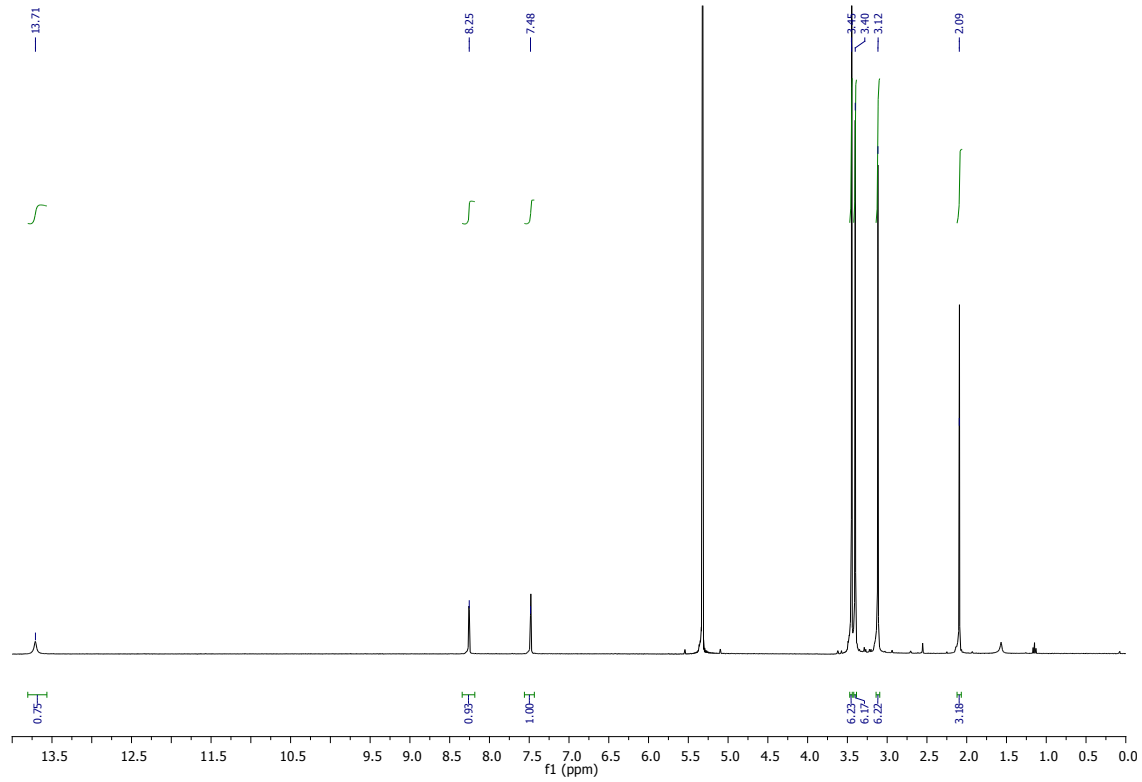
trans,cis-[$RuCl_2$(bpp)(dmso-S)$_2$]$^-$



out-[Ru(L^2)(trpy)(dmso-S)]$^+$

Figure S1. NMR spectra of **2**, 400 MHz, CD_2Cl_2: a) ^{1}H-NMR; b) ^{13}C-NMR; c) COSY; d) NOESY; e) ^{1}H-^{13}C HSQC, f) ^{1}H-^{13}C HMBC

a)



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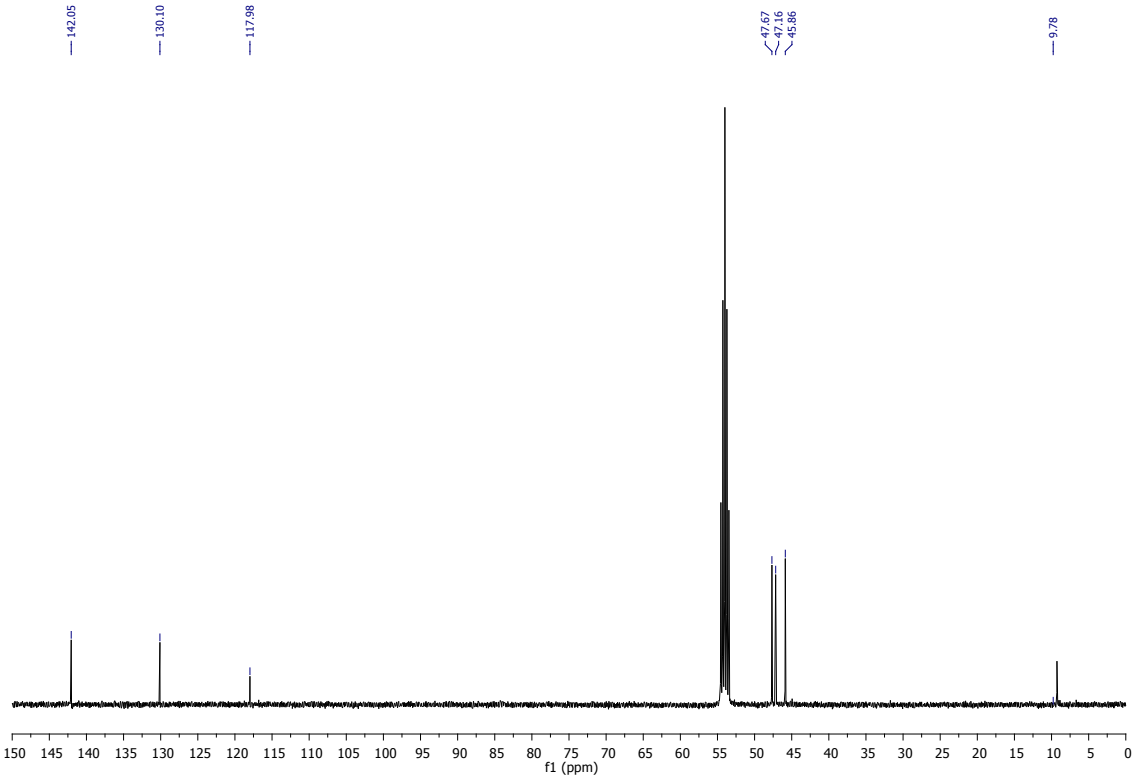
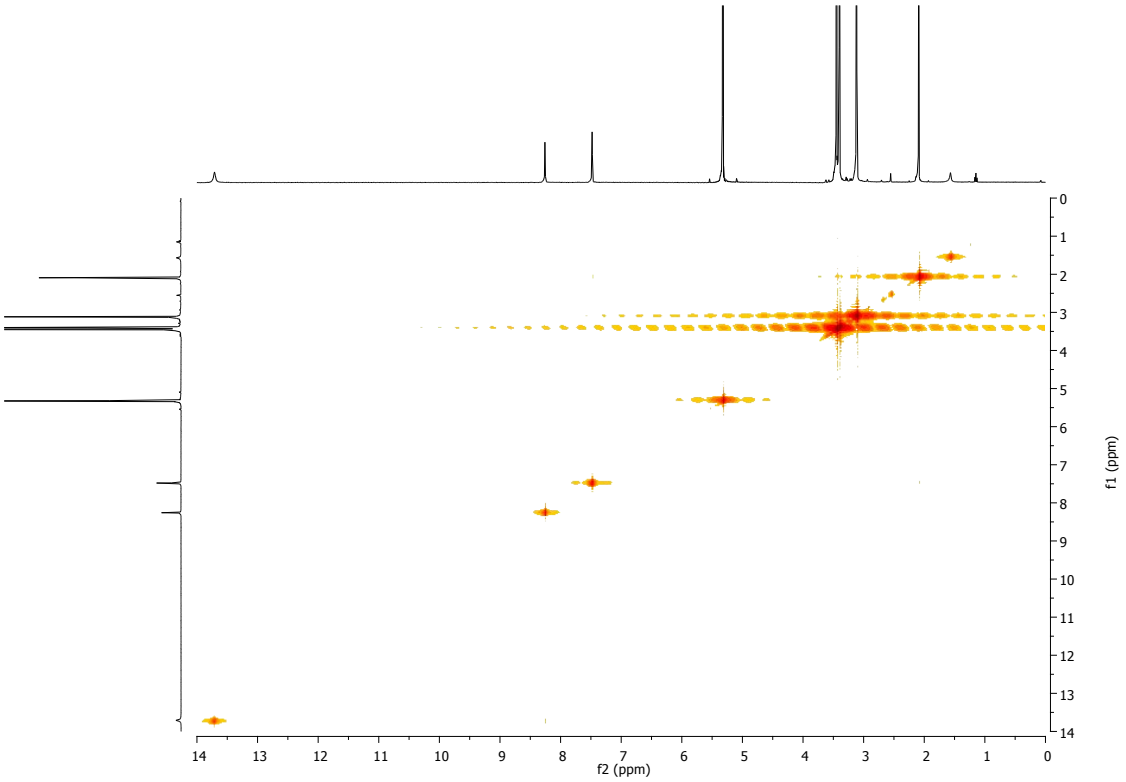


c)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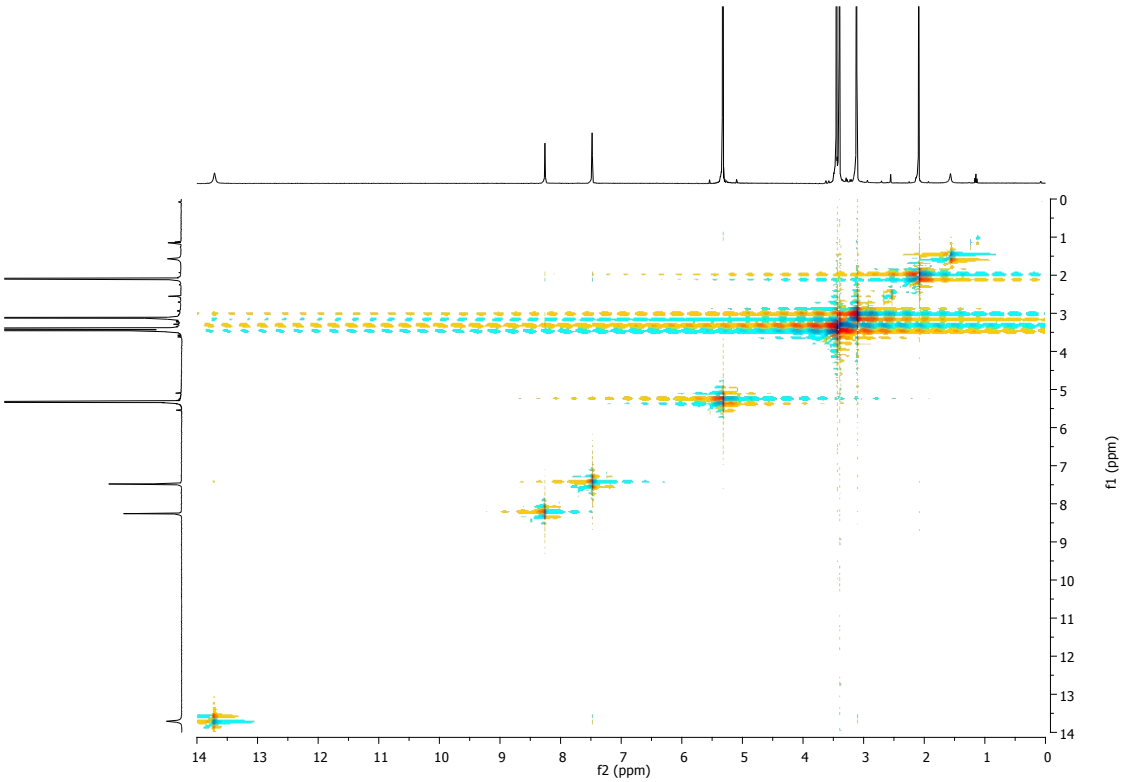
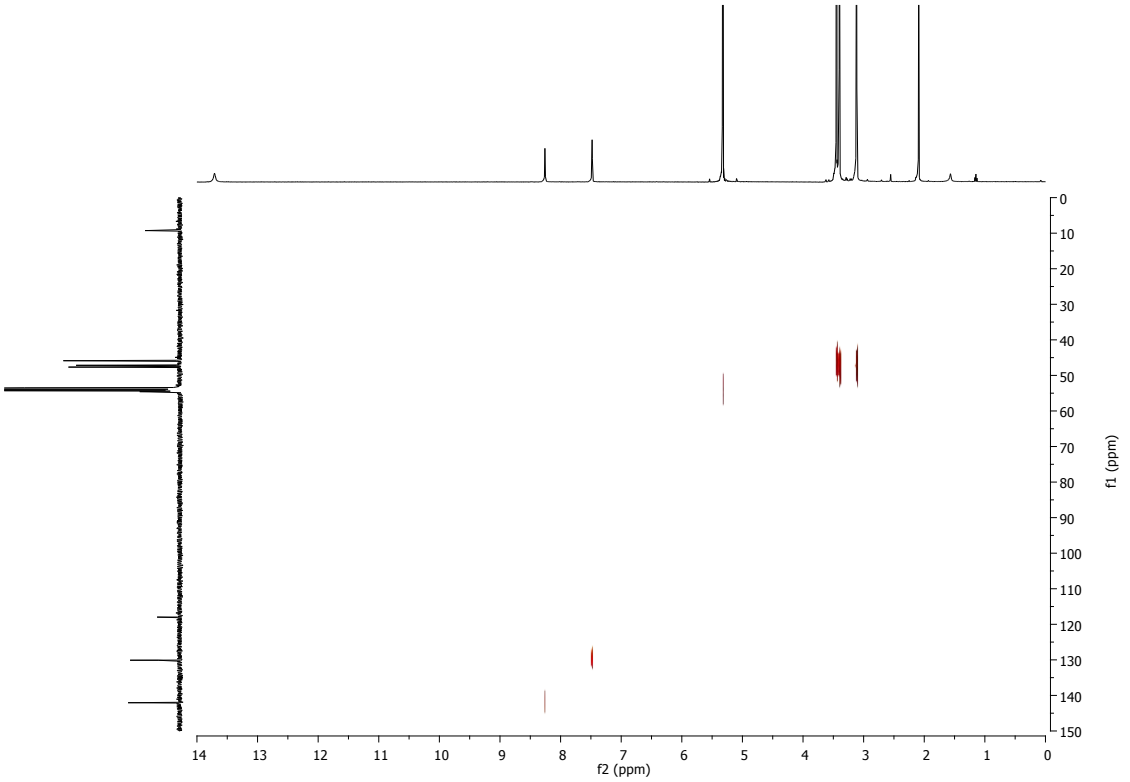
f2 (ppm)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
f1 (ppm)

d)


14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f2 (ppm)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
f1 (ppm)

e)



f)

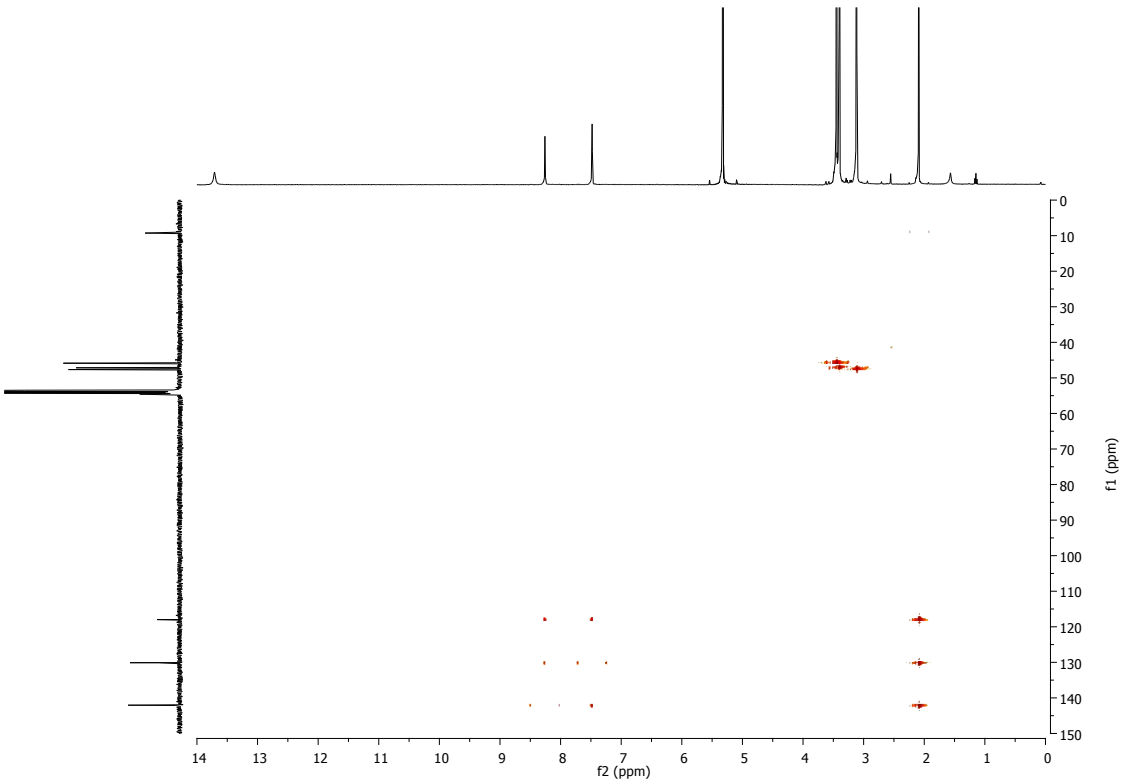
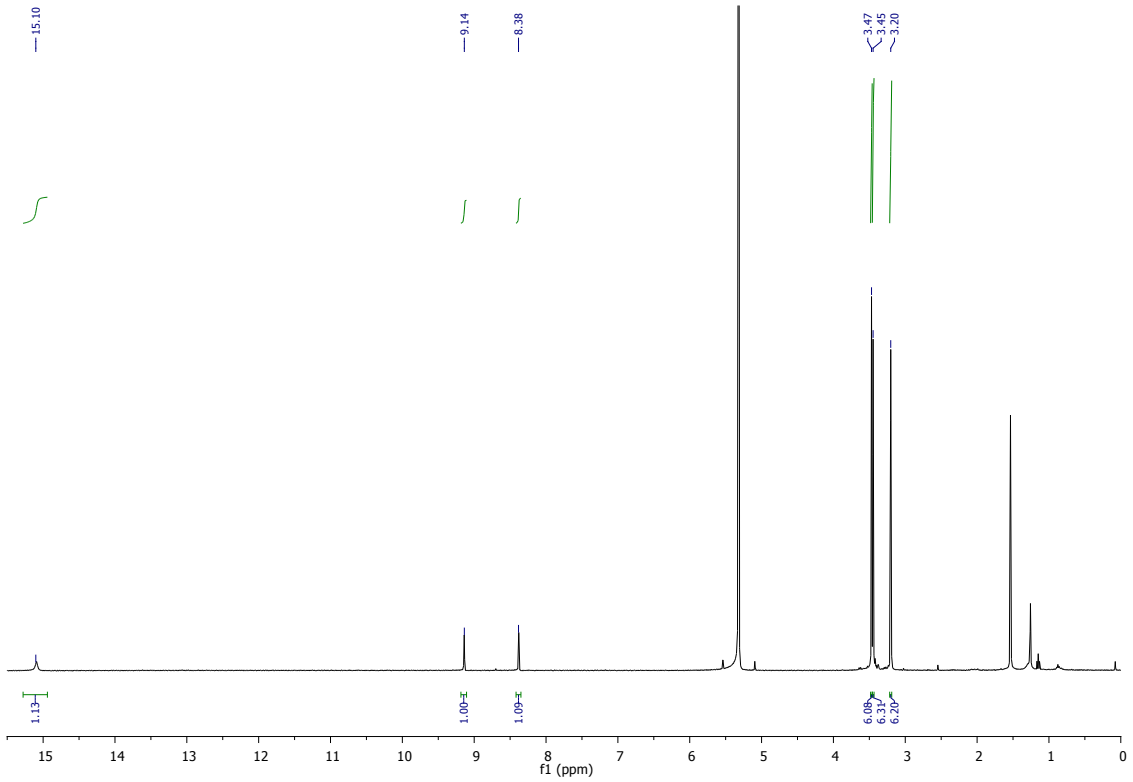


Figure S2. NMR spectra of **3**, 300 MHz, CD_2Cl_2: a) ^{1}H-NMR; b) ^{13}C-NMR; c) COSY; d) NOESY; e) ^{1}H-^{13}C HSQC, f) ^{1}H-^{13}C HMBC

a)



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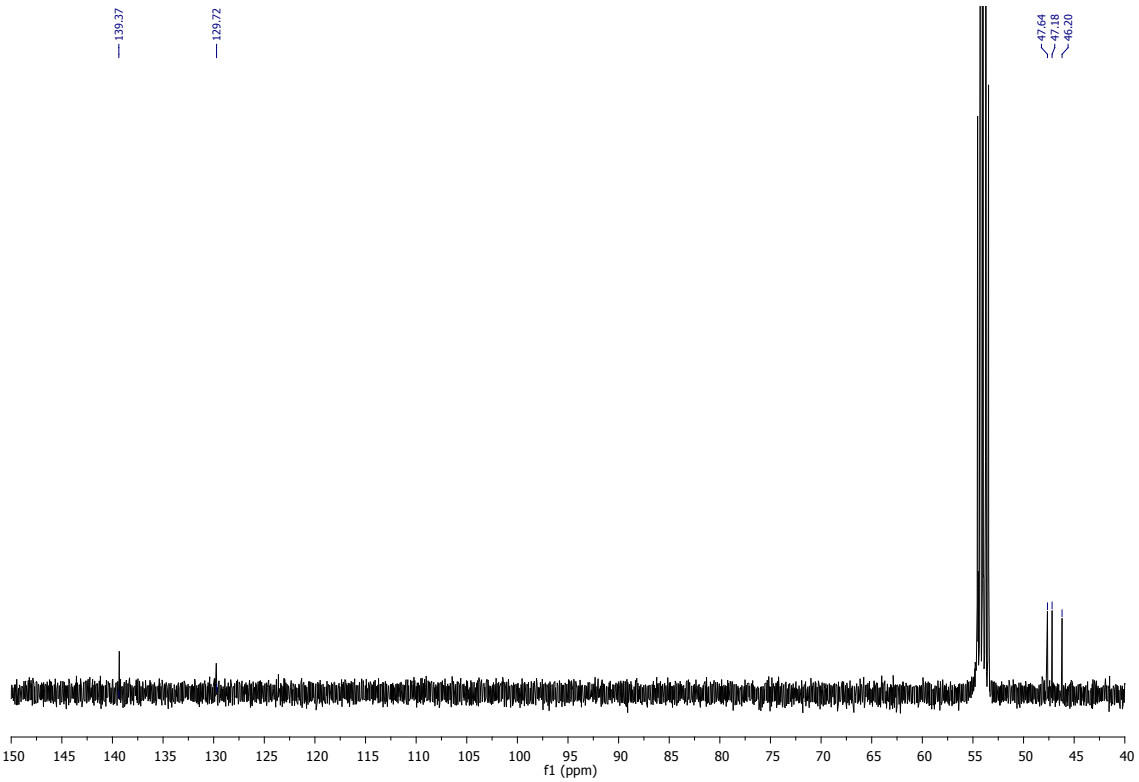
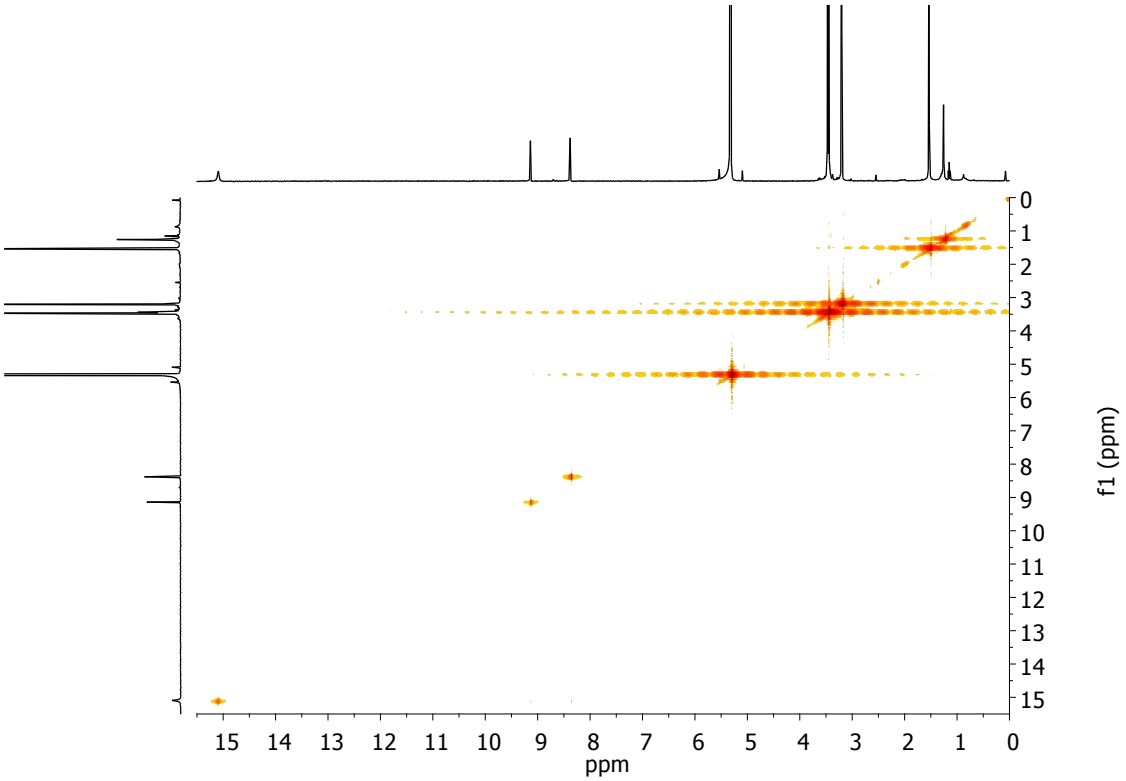
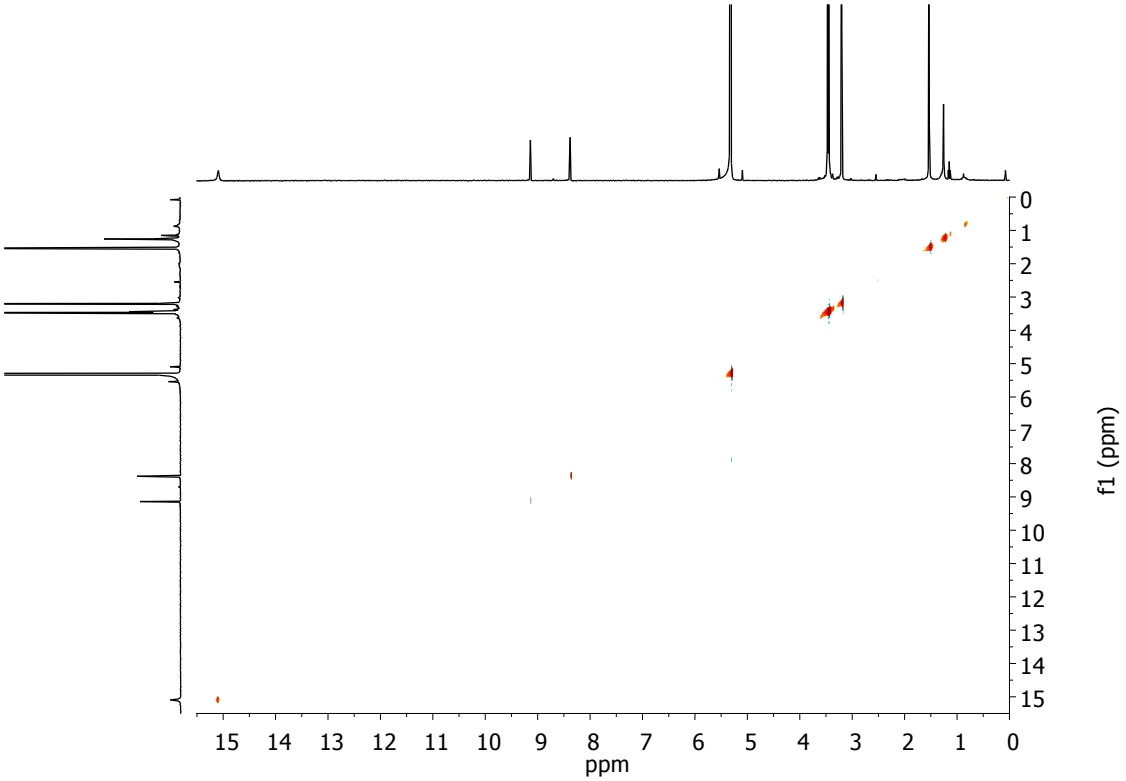


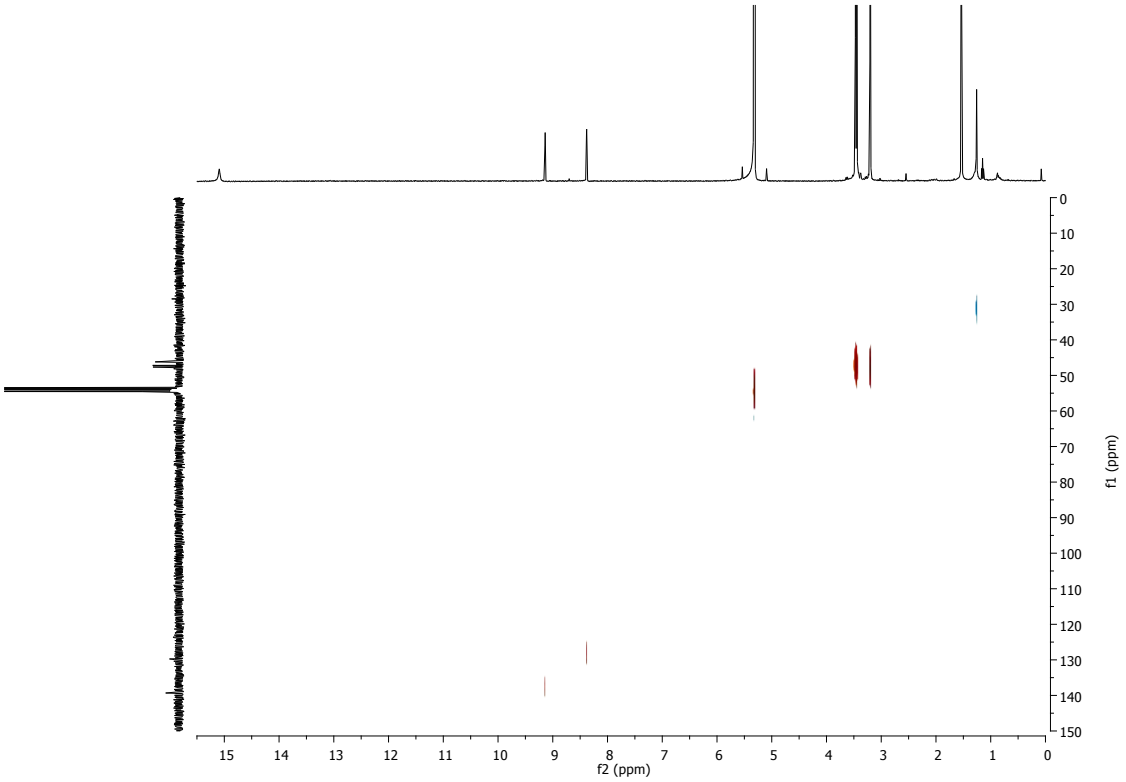
c)


0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
f1 (ppm)
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm

d)


0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
f1 (ppm)
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm

e)



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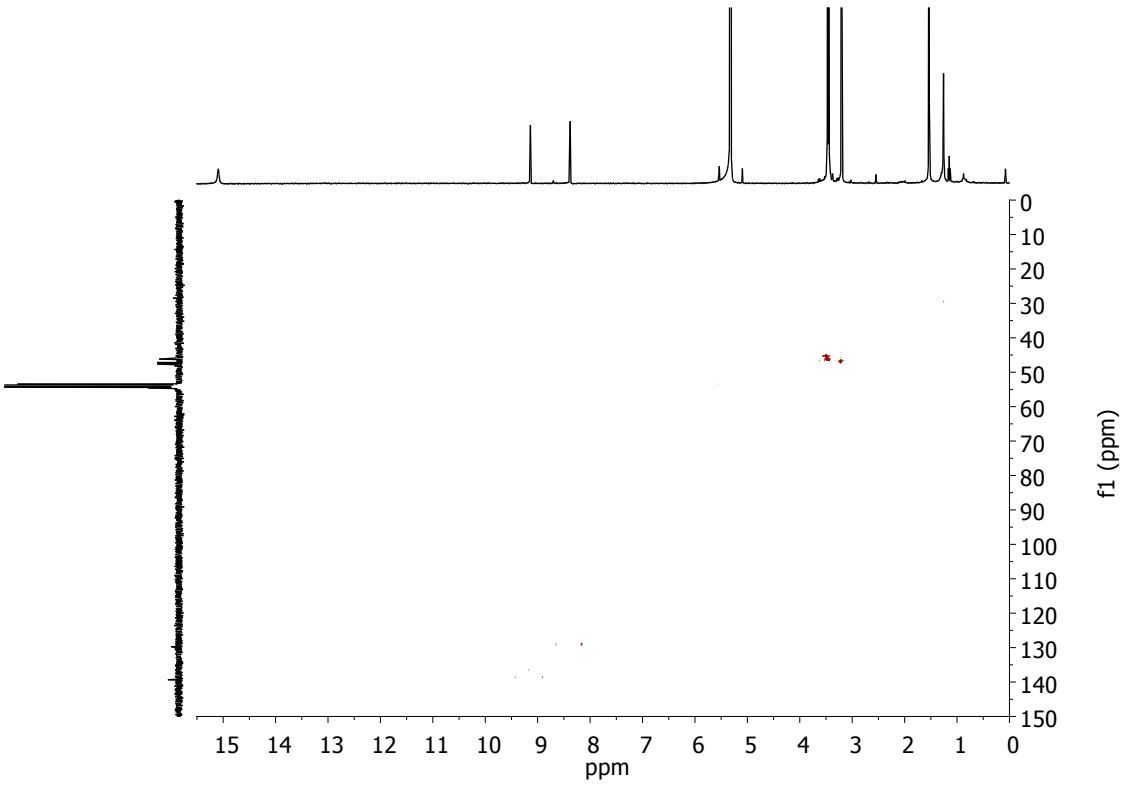
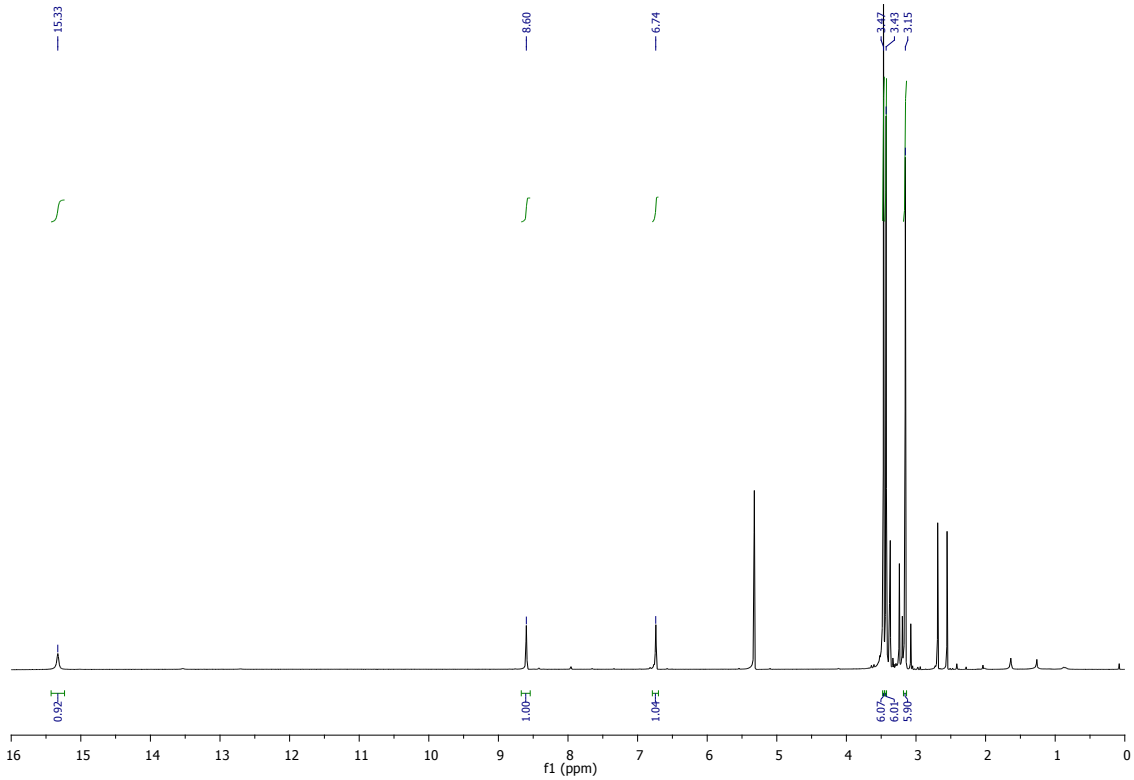
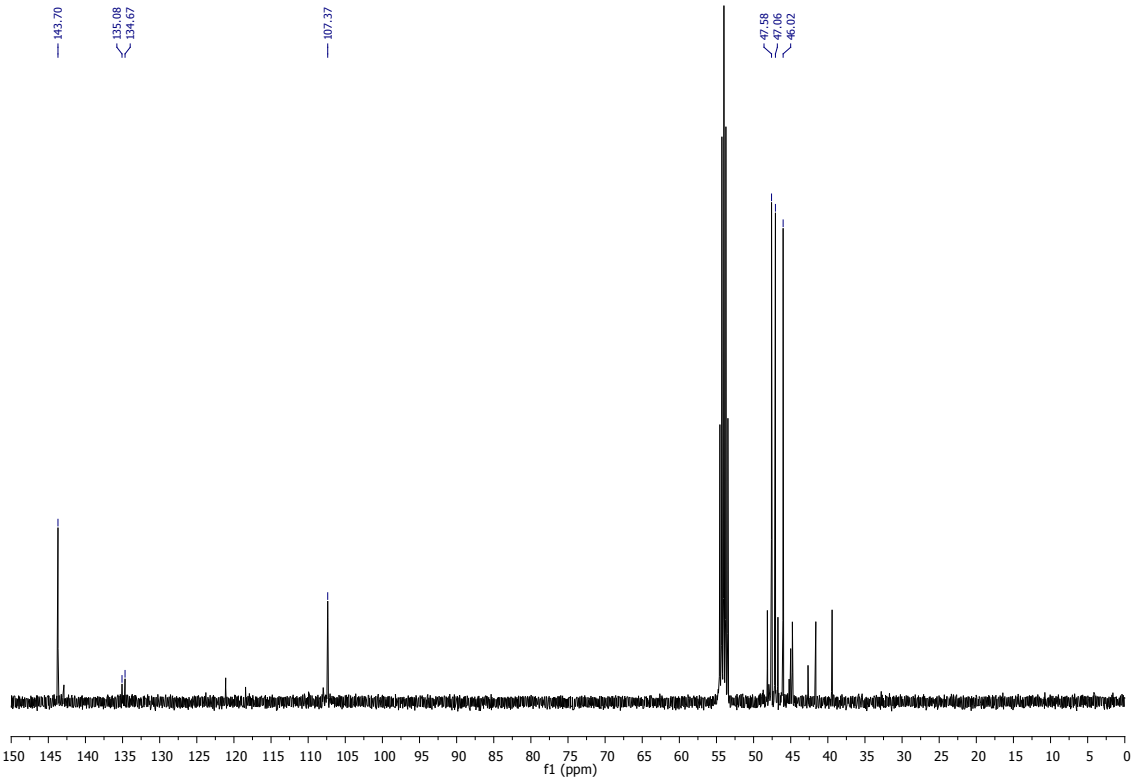


Figure S3. NMR spectra of **4**, 300 MHz, CD_2Cl_2: a) ^{1}H-NMR; b) ^{13}C-NMR; c) COSY; d) NOESY; e) ^{1}H-^{13}C HSQC, f) ^{1}H-^{13}C HMBC

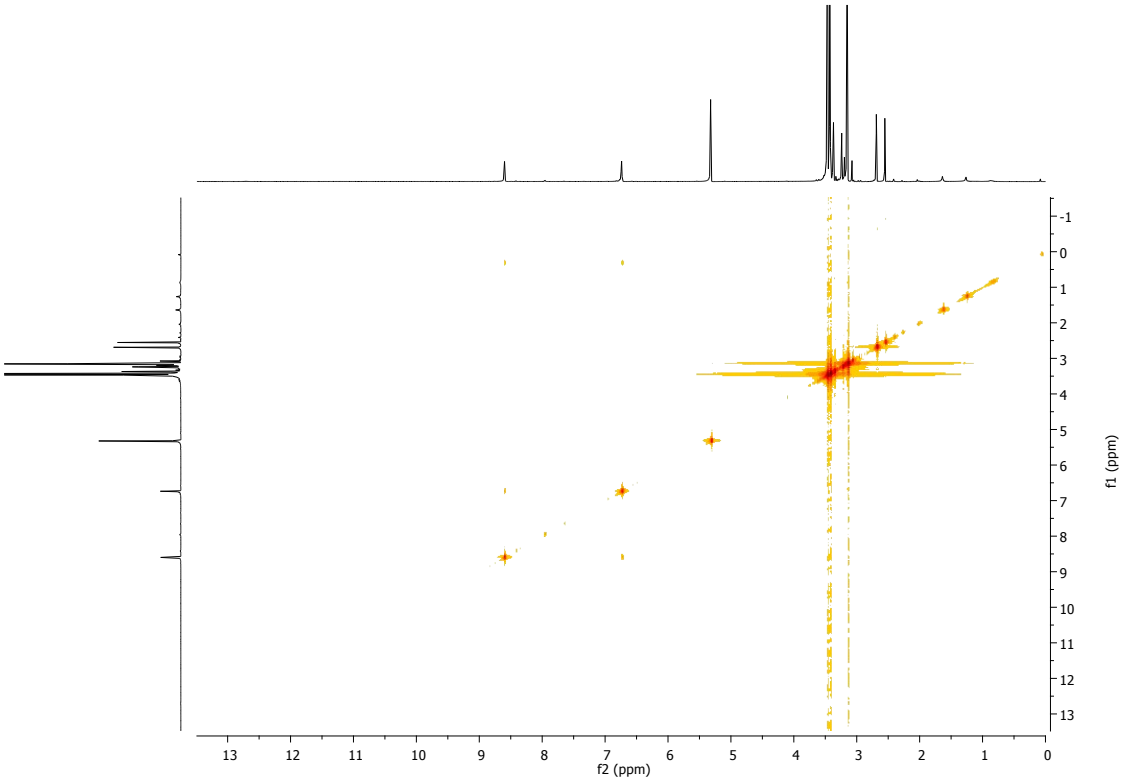
a)



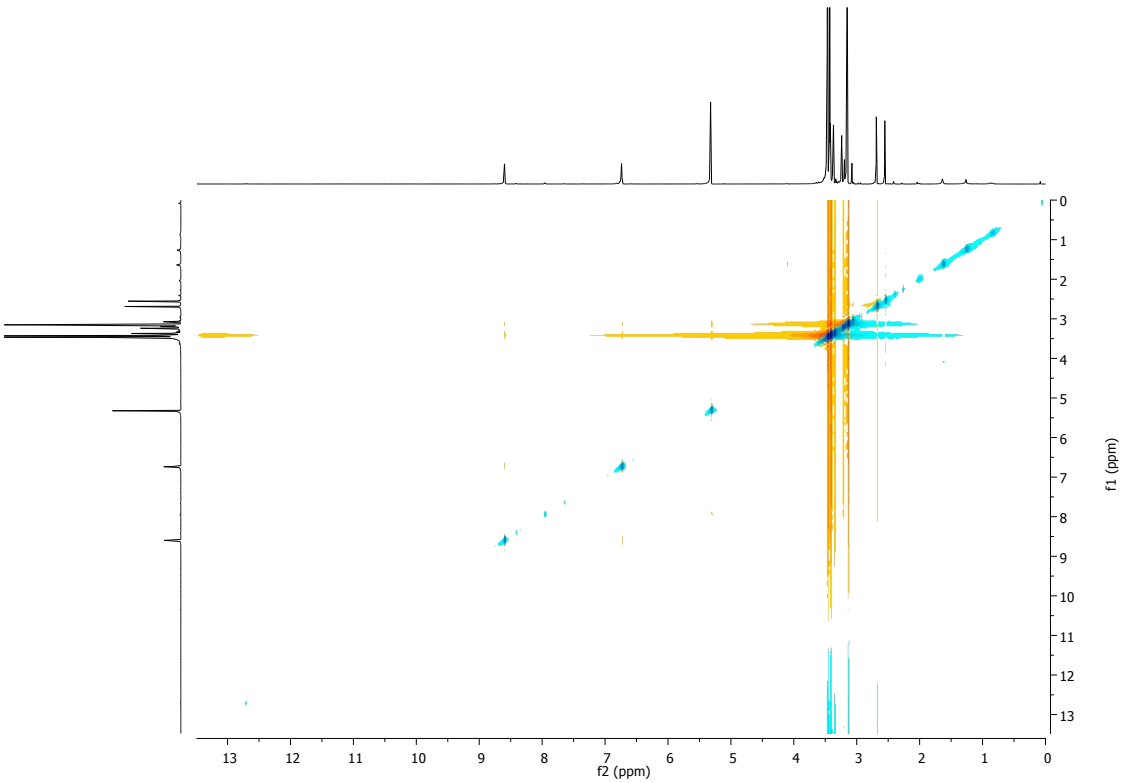
b)



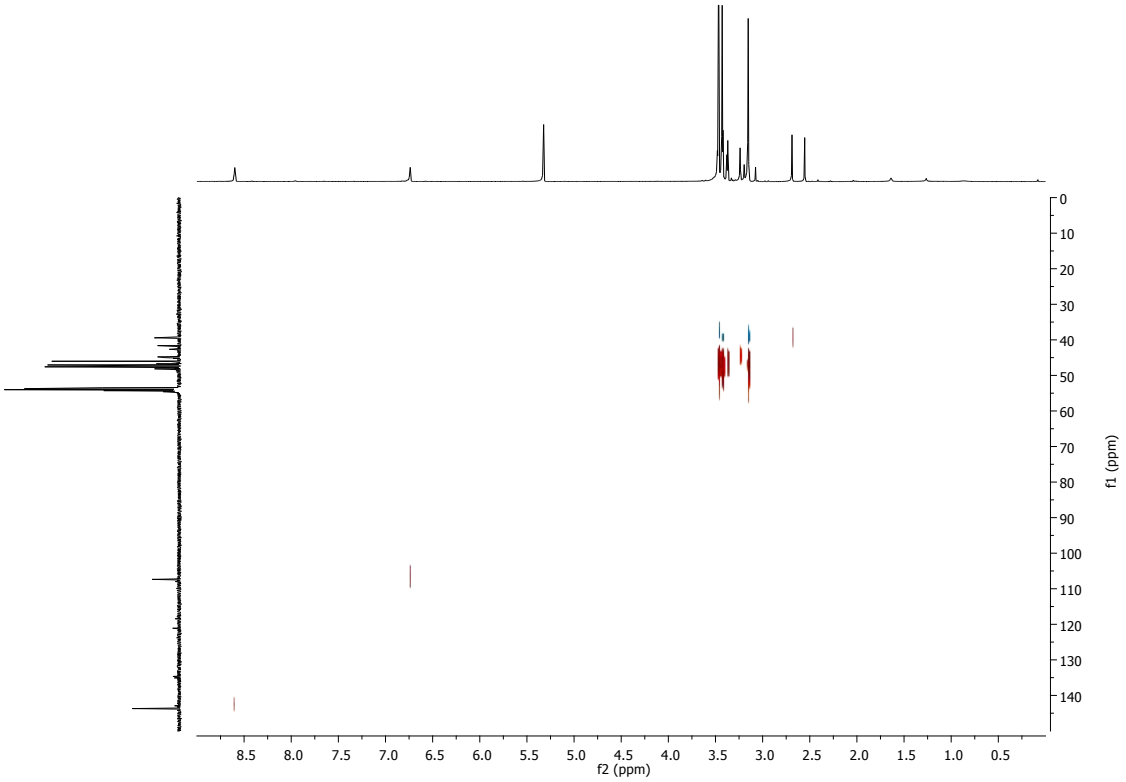
c)



d)



e)



f)

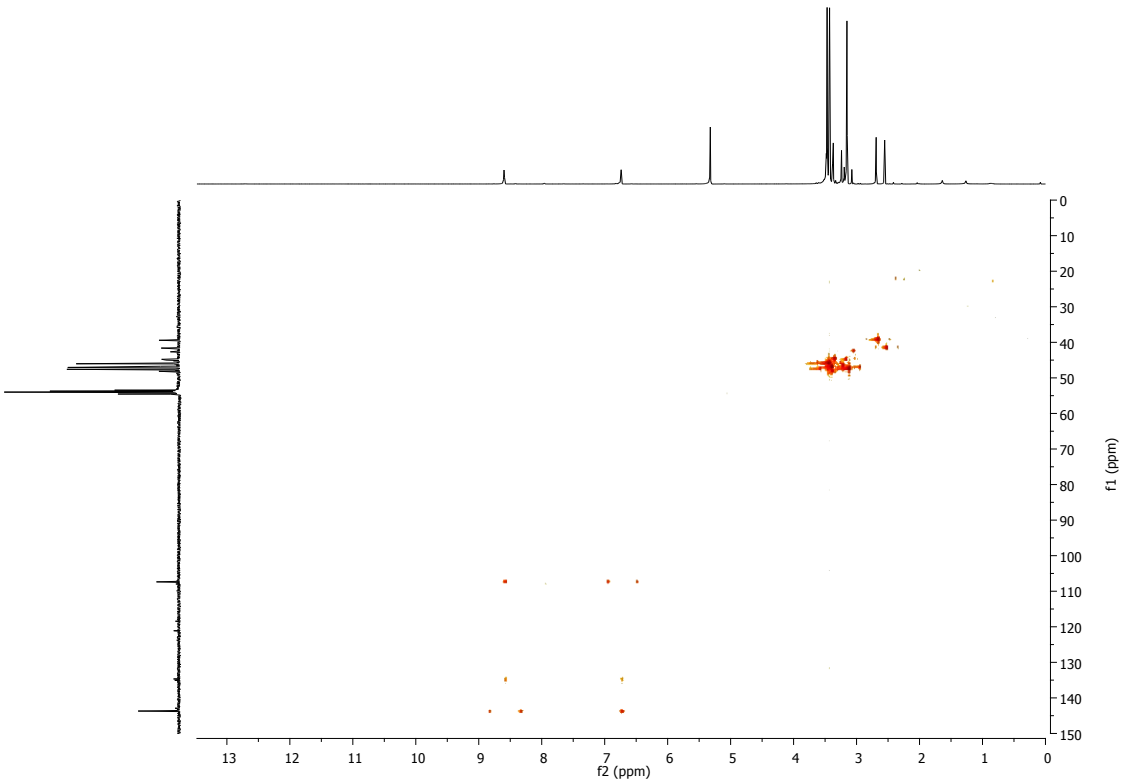
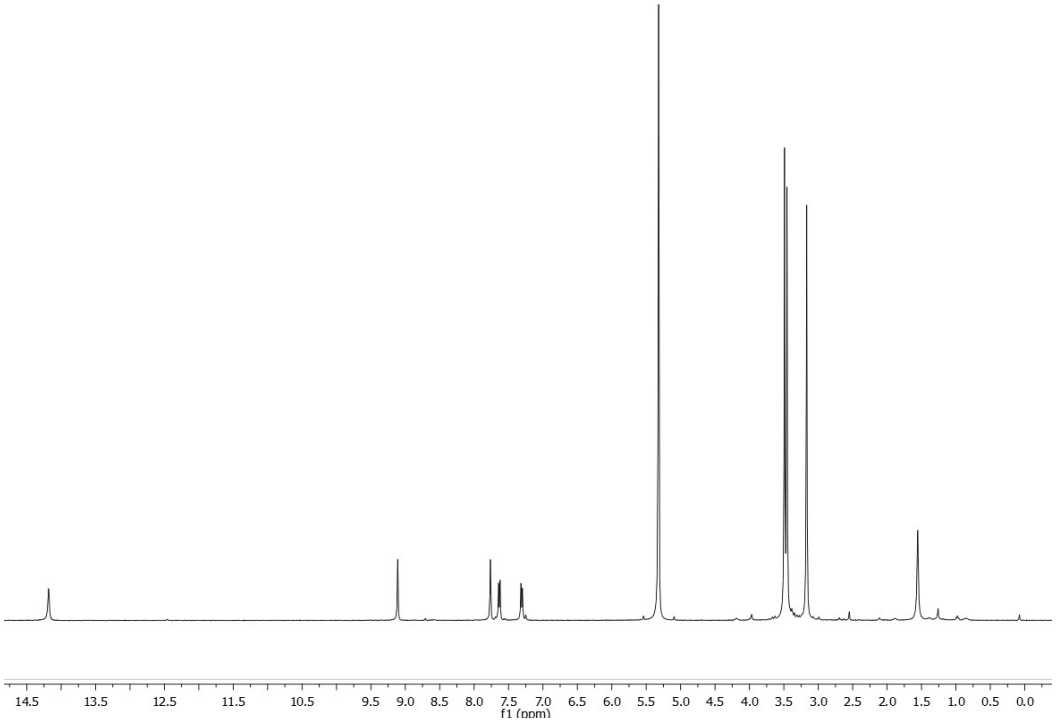
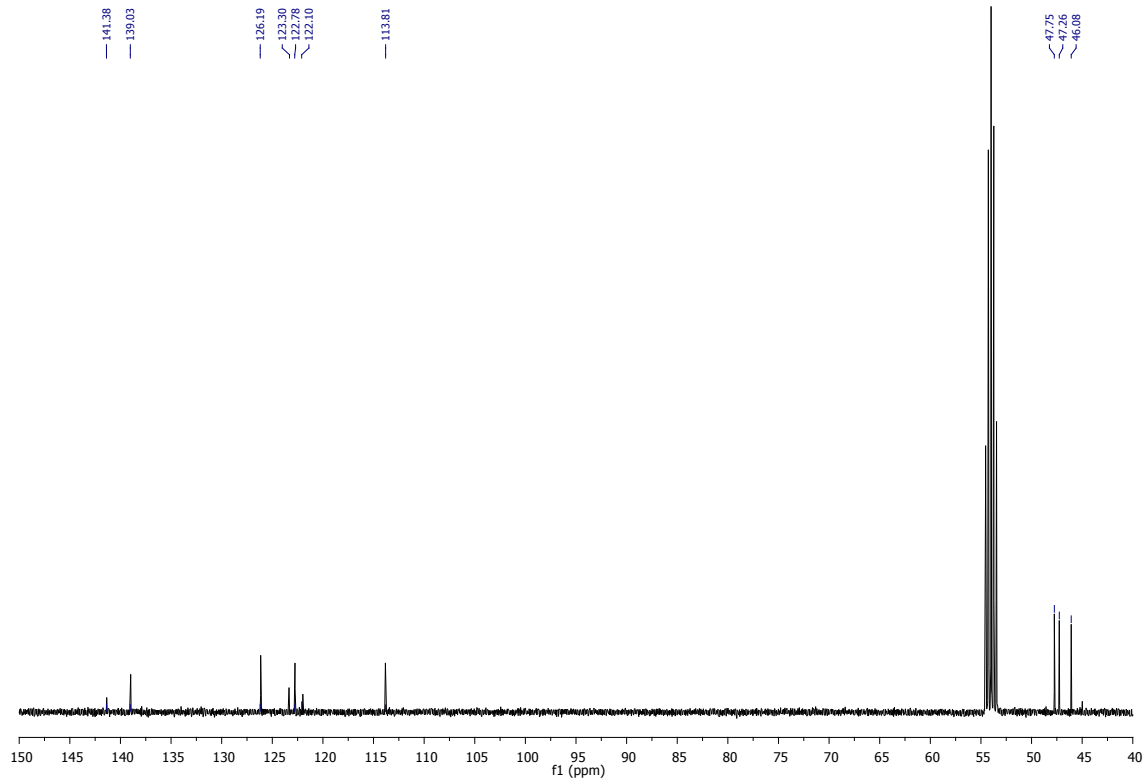


Figure S4. NMR spectra of **5**, 300 MHz, CD_2Cl_2: a) ^{1}H-NMR; b) ^{13}C-NMR; c) COSY; d) NOESY; e) ^{1}H-^{13}C HSQC, f) ^{1}H-^{13}C HMBC, g) ^{1}H-NMR with presence of the minor isomer.

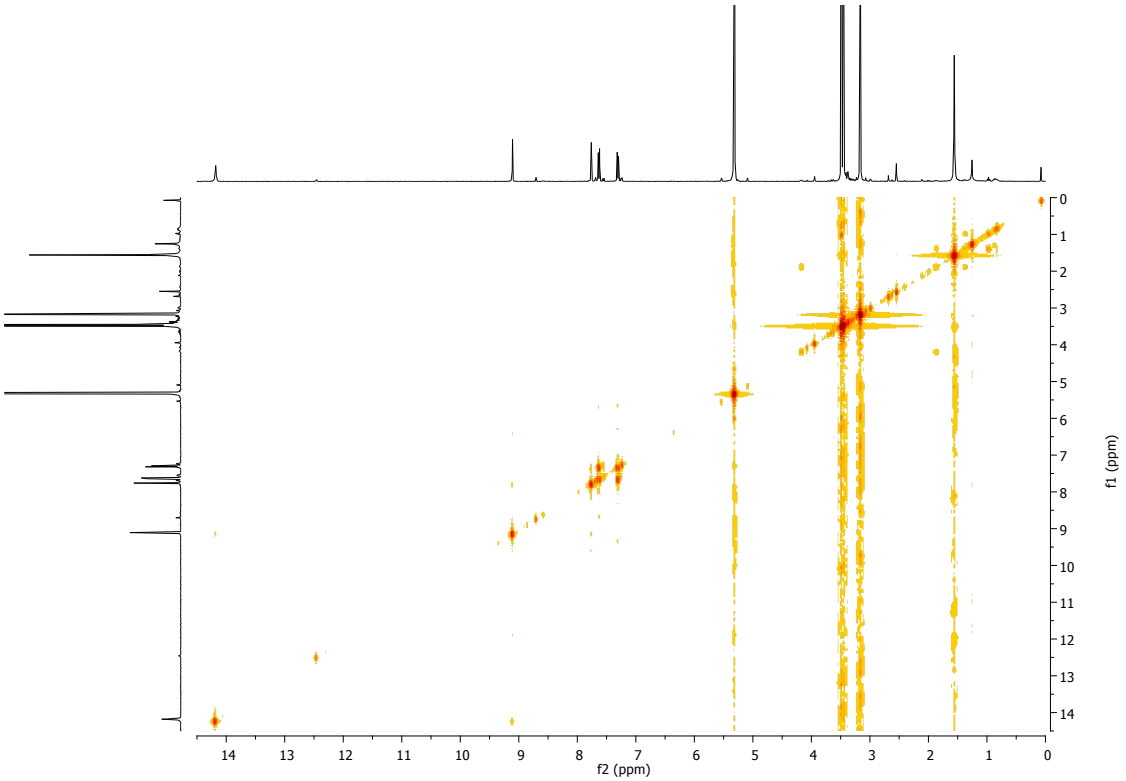
a)



b)



c)



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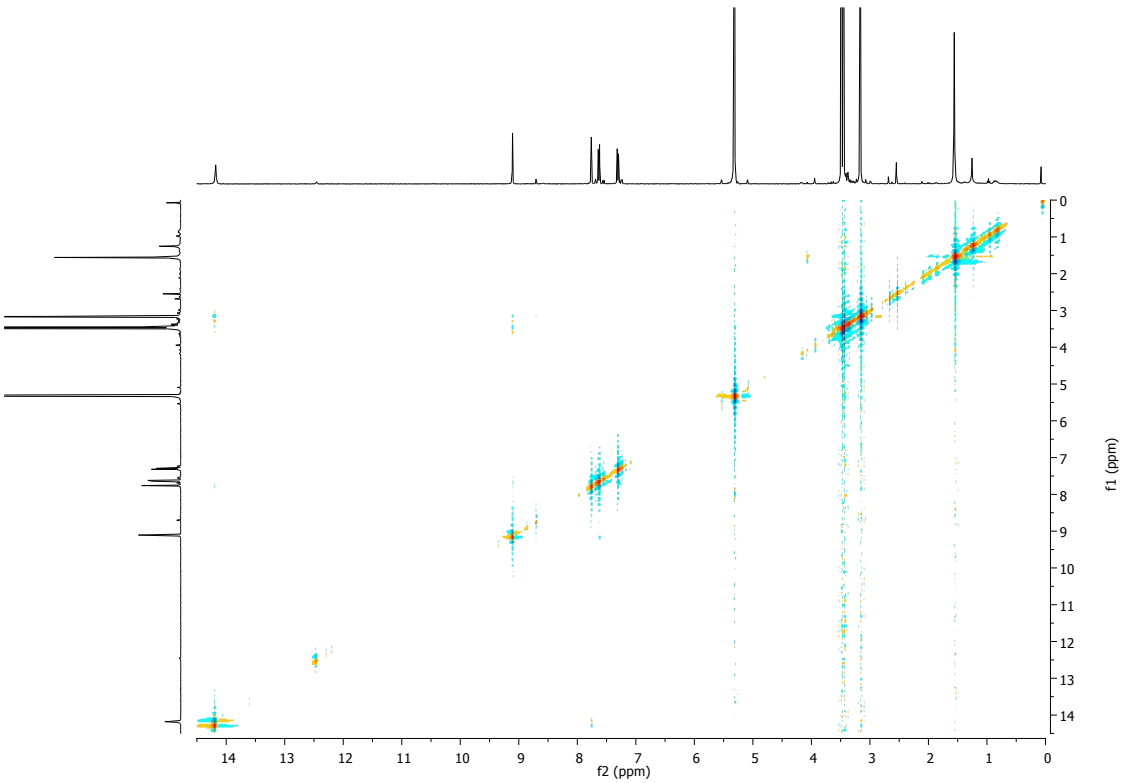
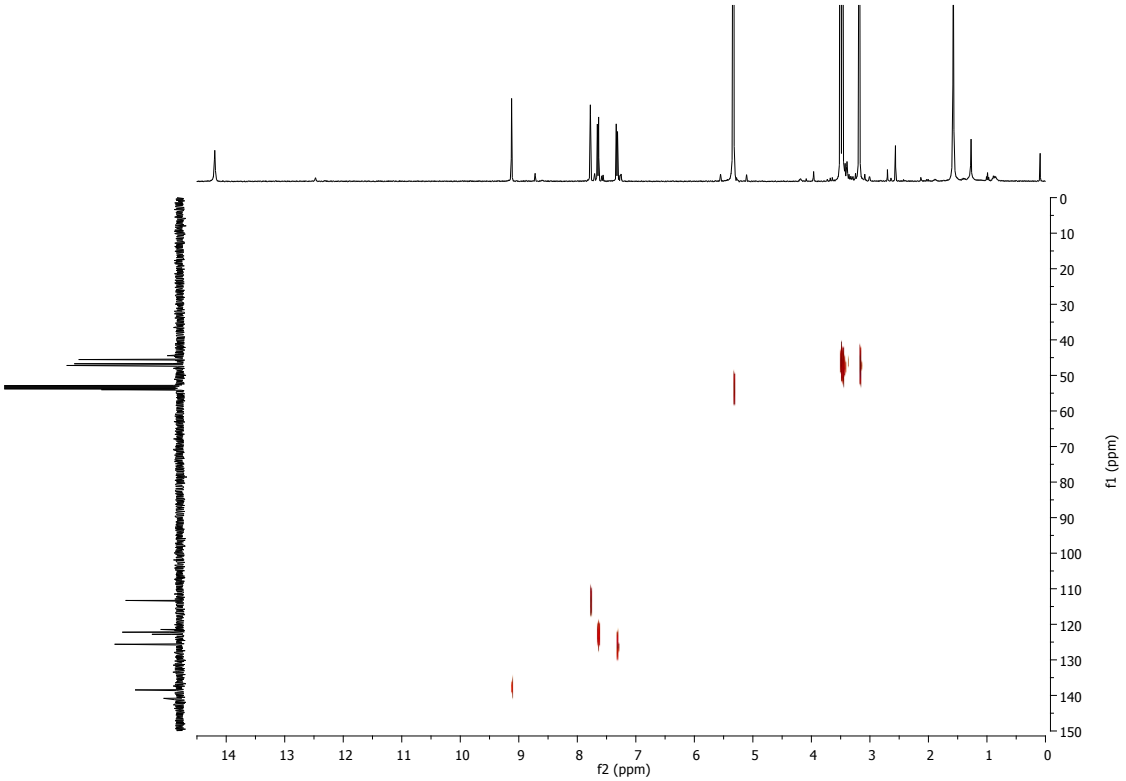
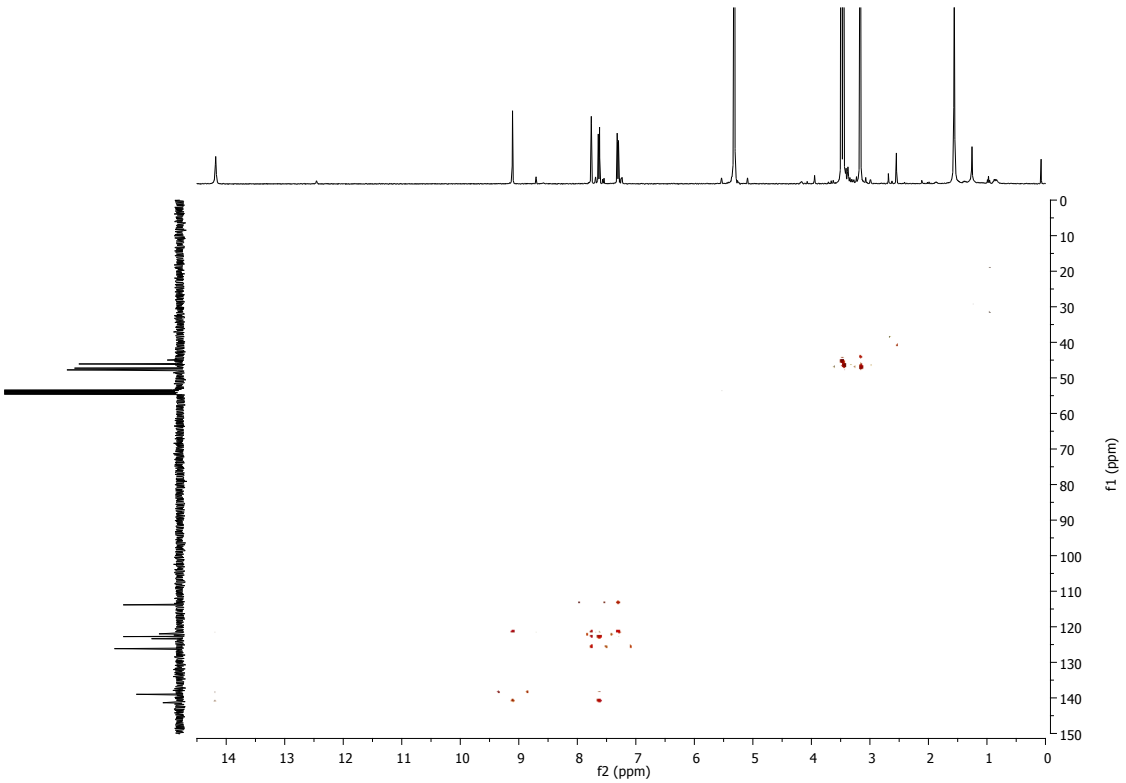


e)



f)



g)

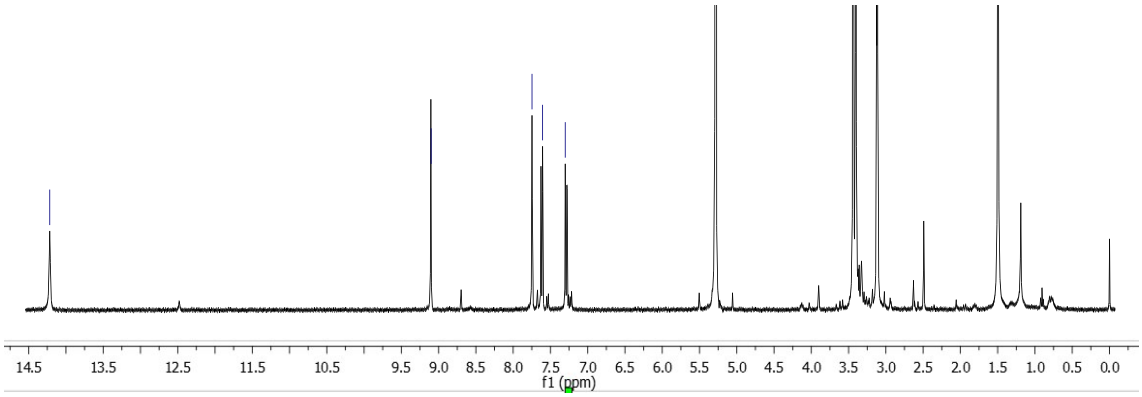

14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Figure S5. UV-visible spectra of **2** (blue), **3** (green), **4** (grey) and **5** (red) in CH_2Cl_2

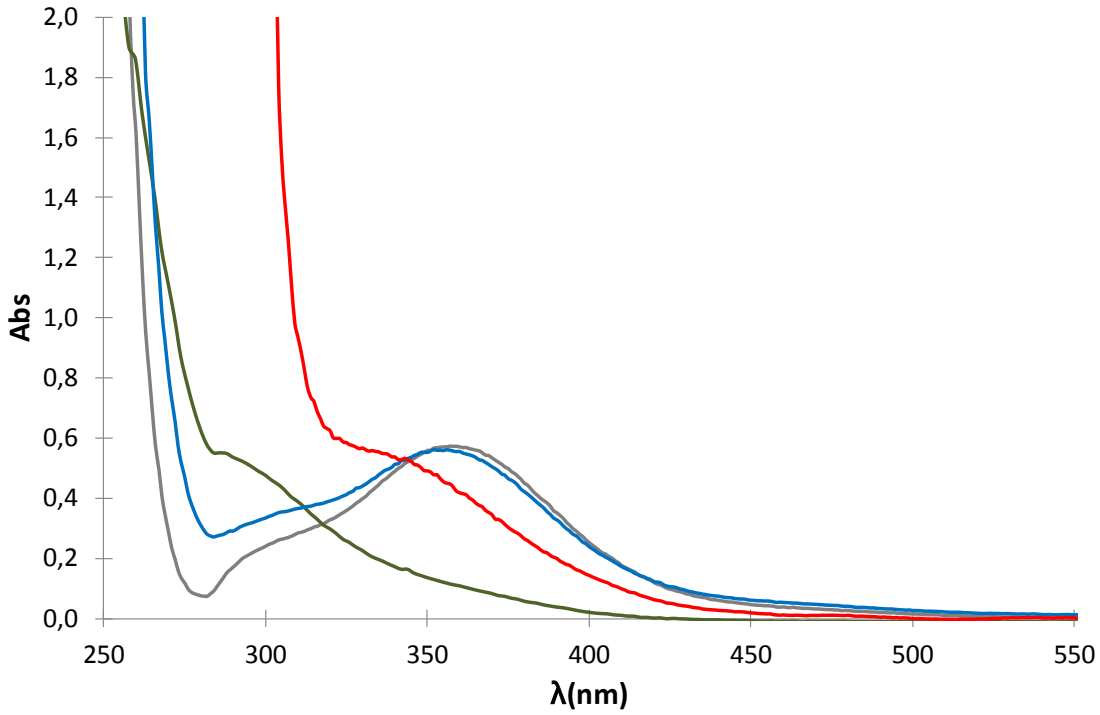


Figure S6. CV of a) **3** (blue), **4** (black) and **5** (orange) in CH_3CN + 0.1 M TBAH.

a)

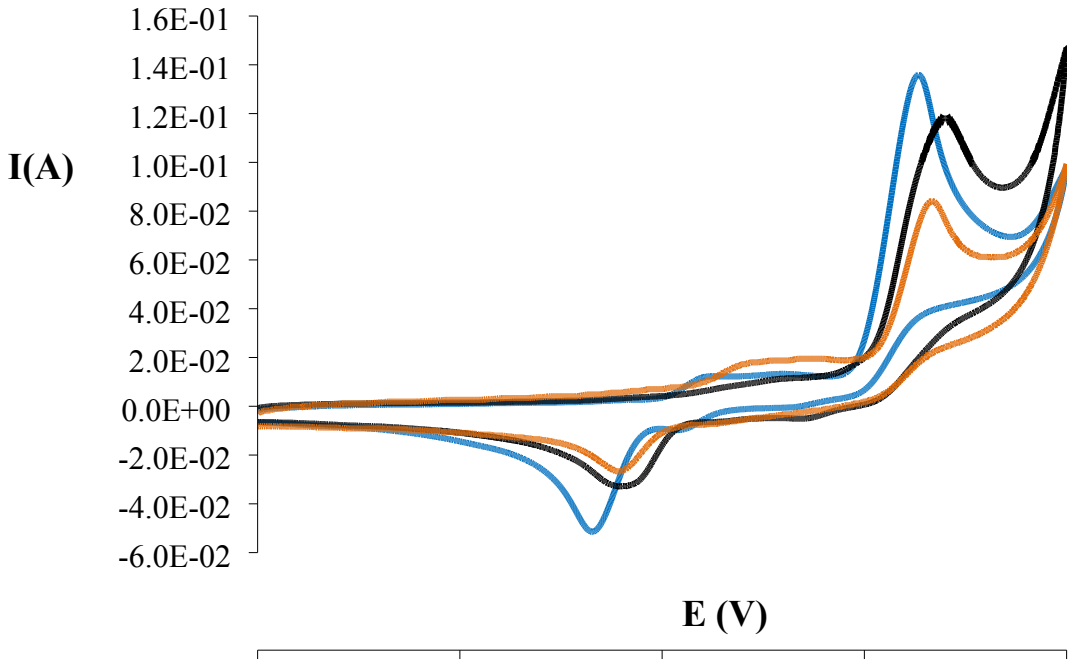
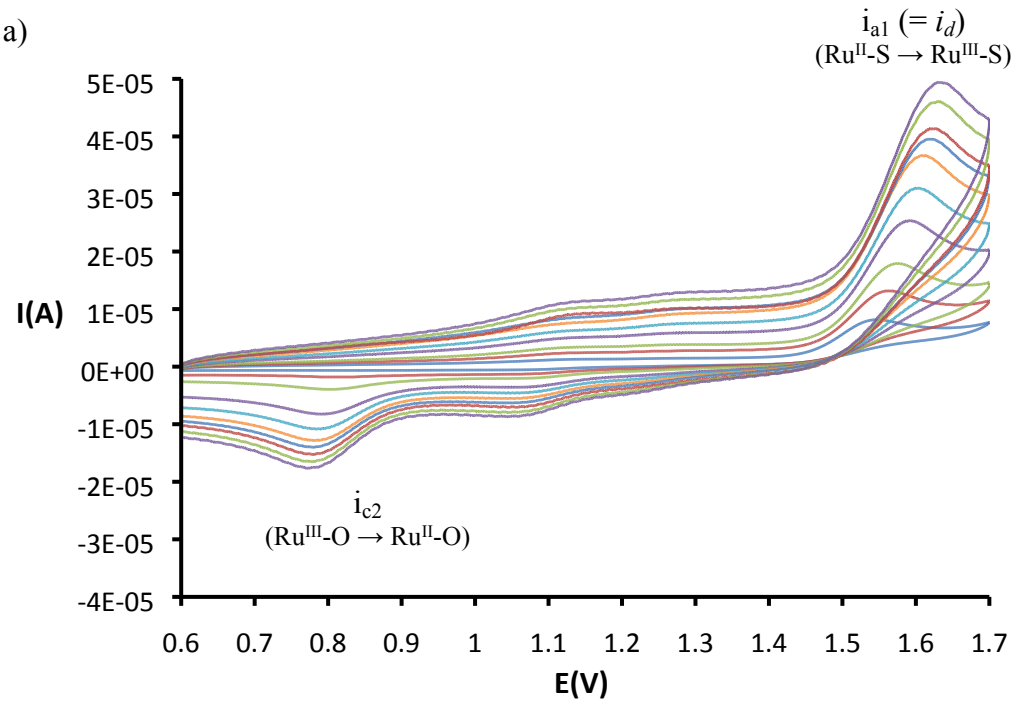


Figure S7. CV registered in CH_2Cl_2 (TBAH, 0.1M) vs Ag/AgCl starting the scanning potential at E_{init} = 0.6 for **2** and 0 V for **6** at scan rates between 0.20 and 8 V/s (equilibration time = 2 s). a) complex **2**, b) complex **6**.

a)



b)

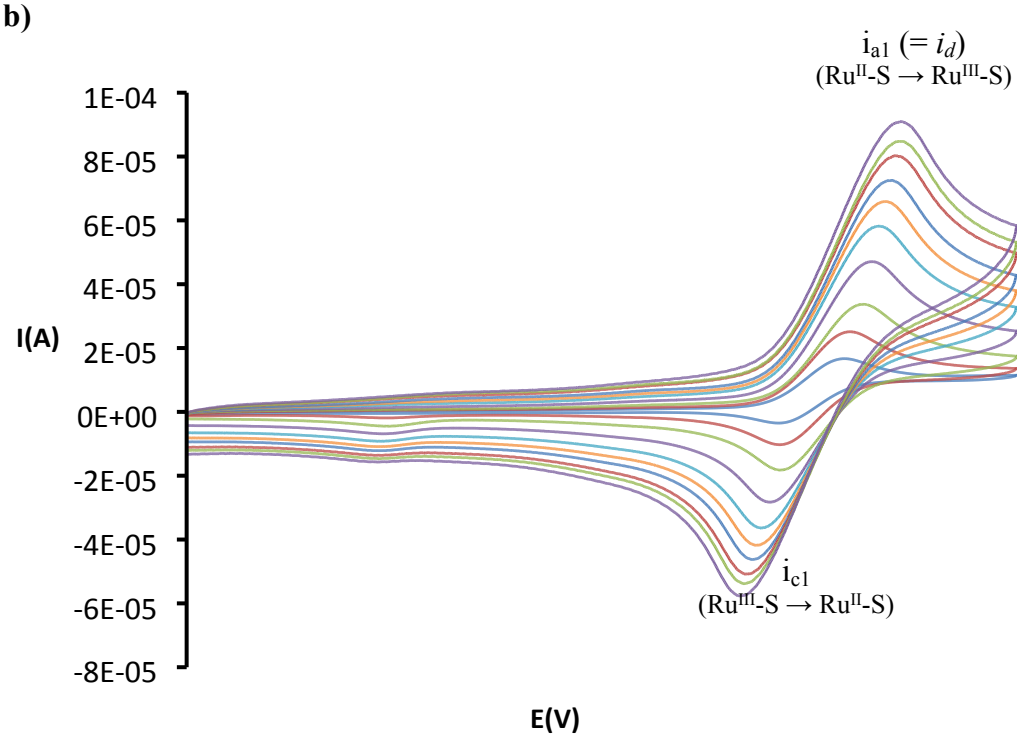


Figure S8. Plot of i_{C1}/i_{C2} vs. 1/υ to obtain $K^{III}_{O\text{-}S}$ for complex **2.**

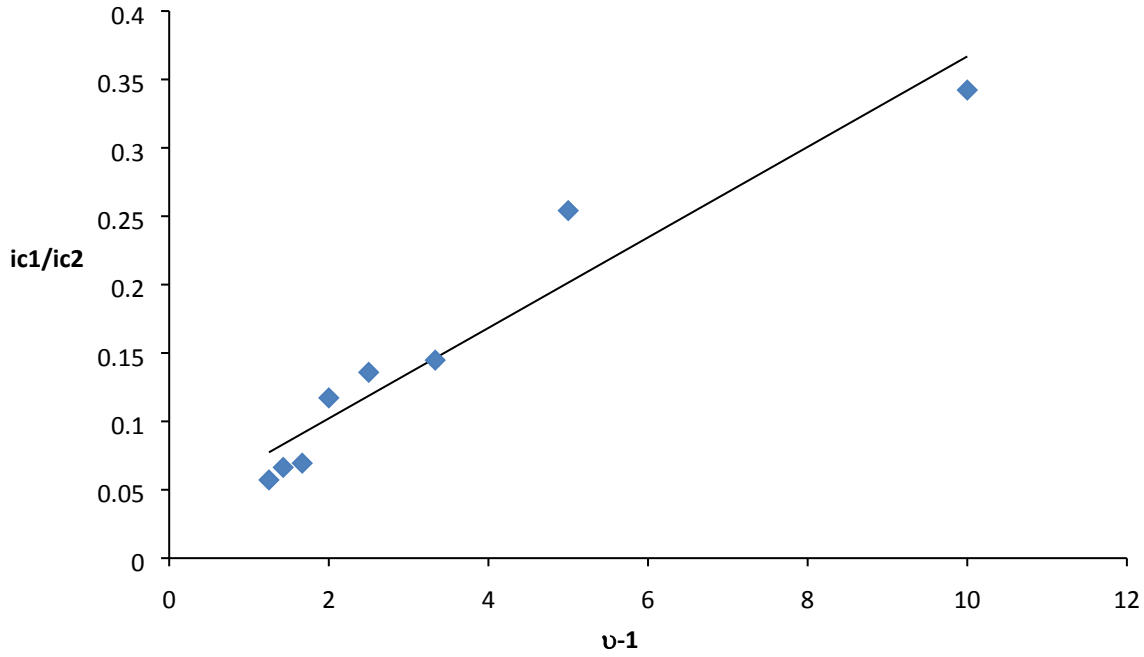


Figure S9. Plot of i_{C1}/i_{C2} vs. 1/υ to obtain $K^{III}_{O\text{-}S}$ for complex **6.**

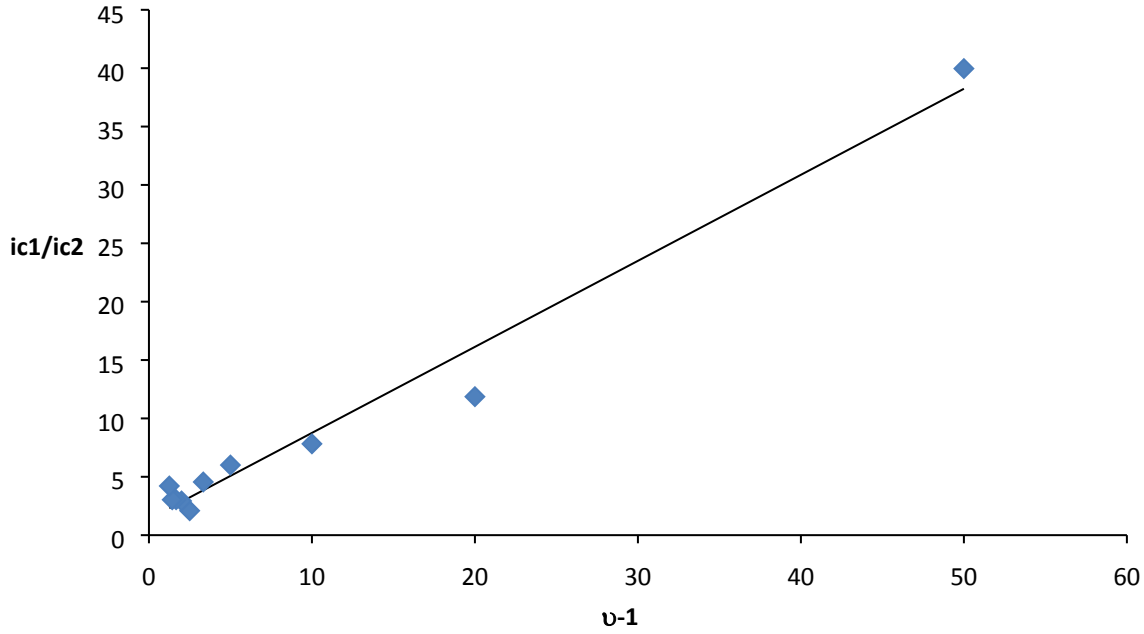


Figure S10. Plot of $\upsilon^{1/2}$ vs. i_d/i_k to obtain $k^{III}_{S\rightarrow O}$ and $k^{III}_{O\rightarrow S}$ for complex **2**.

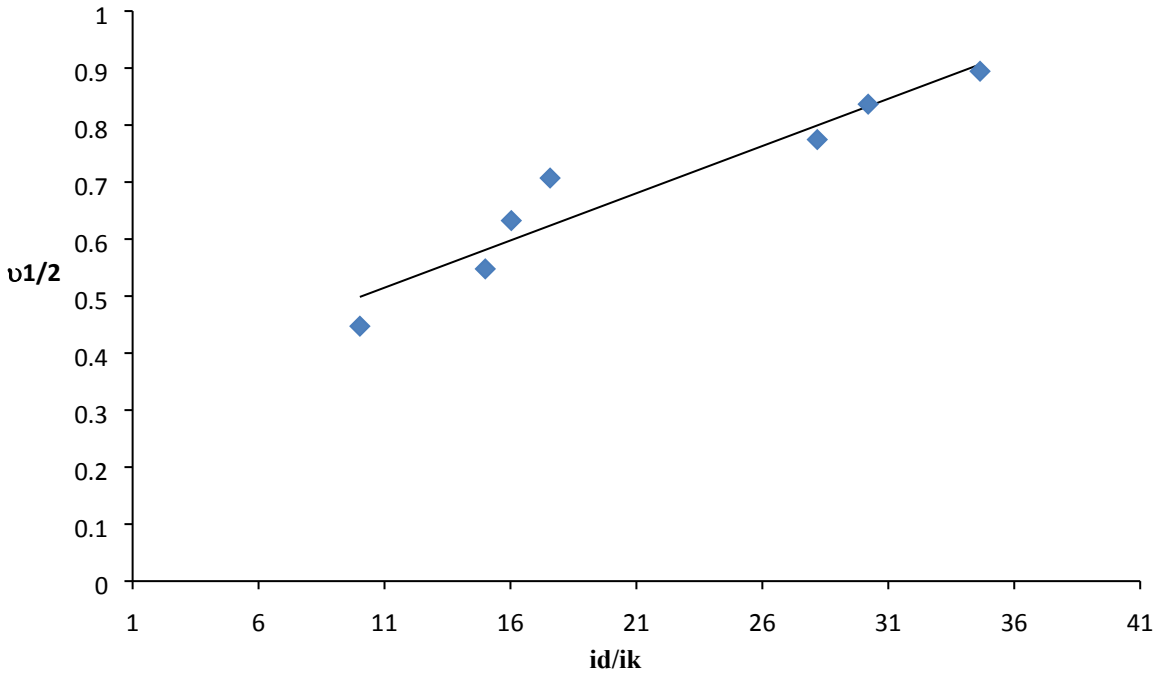


Figure S11. Plot of $\upsilon^{1/2}$ vs. i_d/i_k to obtain $k^{III}_{S\rightarrow O}$ and $k^{III}_{O\rightarrow S}$ for complex **6**.

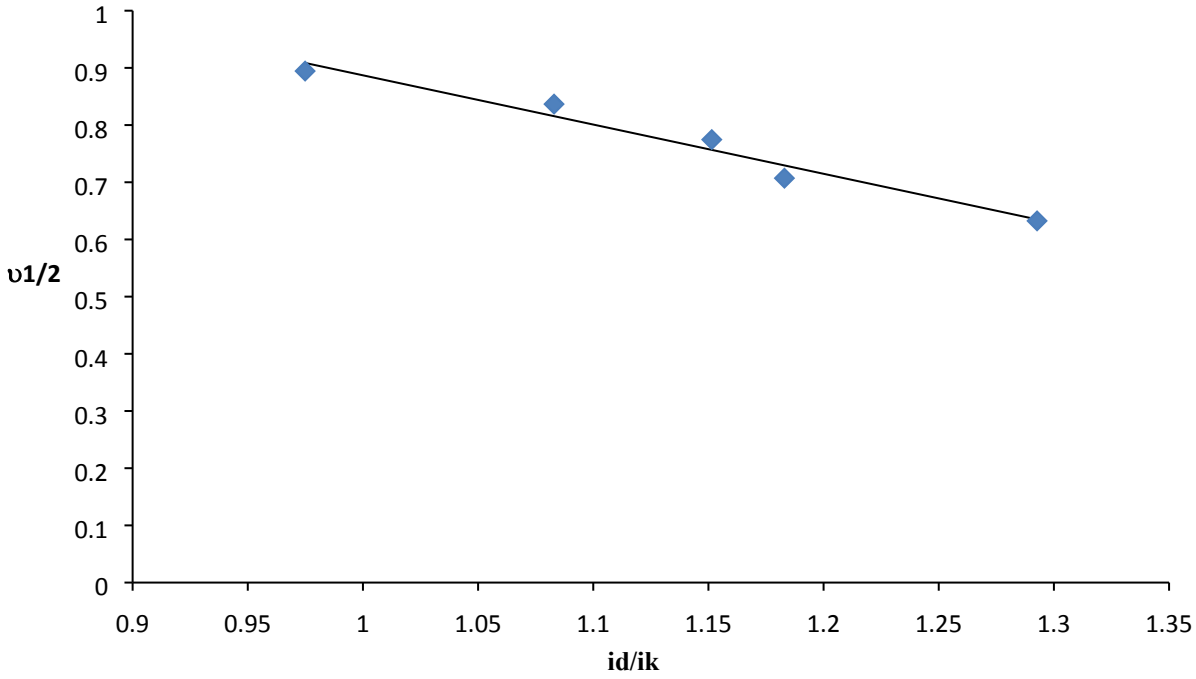


Figure S12. Plot of $\ln(i_{a1}/\upsilon^{1/2})$ vs. $1/\upsilon$ to obtain $k^{II}_{O\rightarrow S}$ for complex **2**

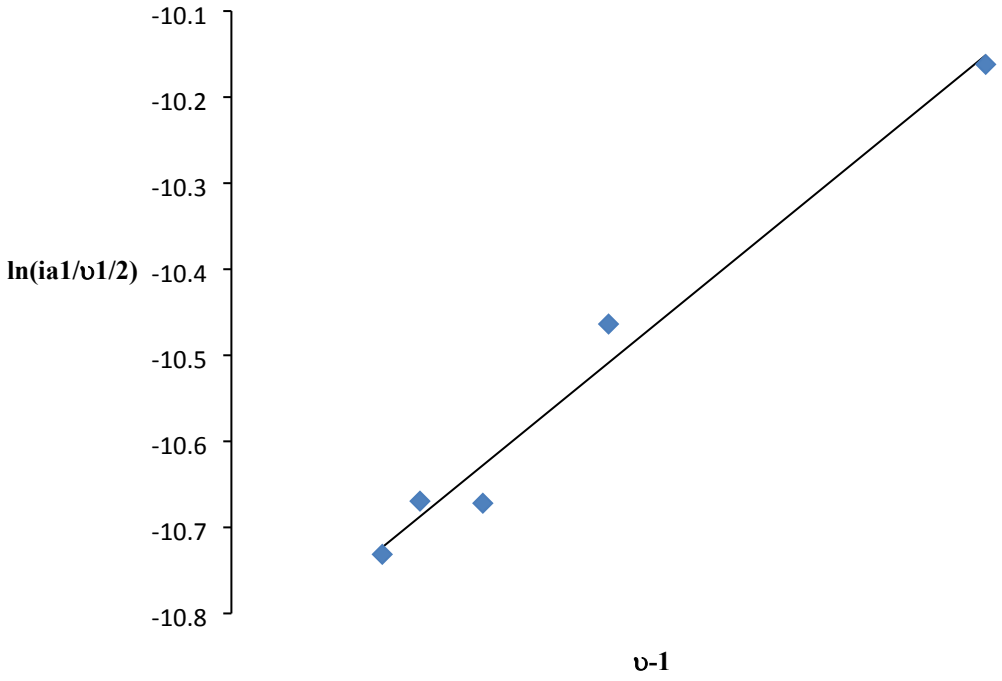


Figure S13. Plot of $\ln(i_{a1}/\upsilon^{1/2})$ vs. $1/\upsilon$ to obtain $k^{II}_{O\rightarrow S}$ for complex **6**

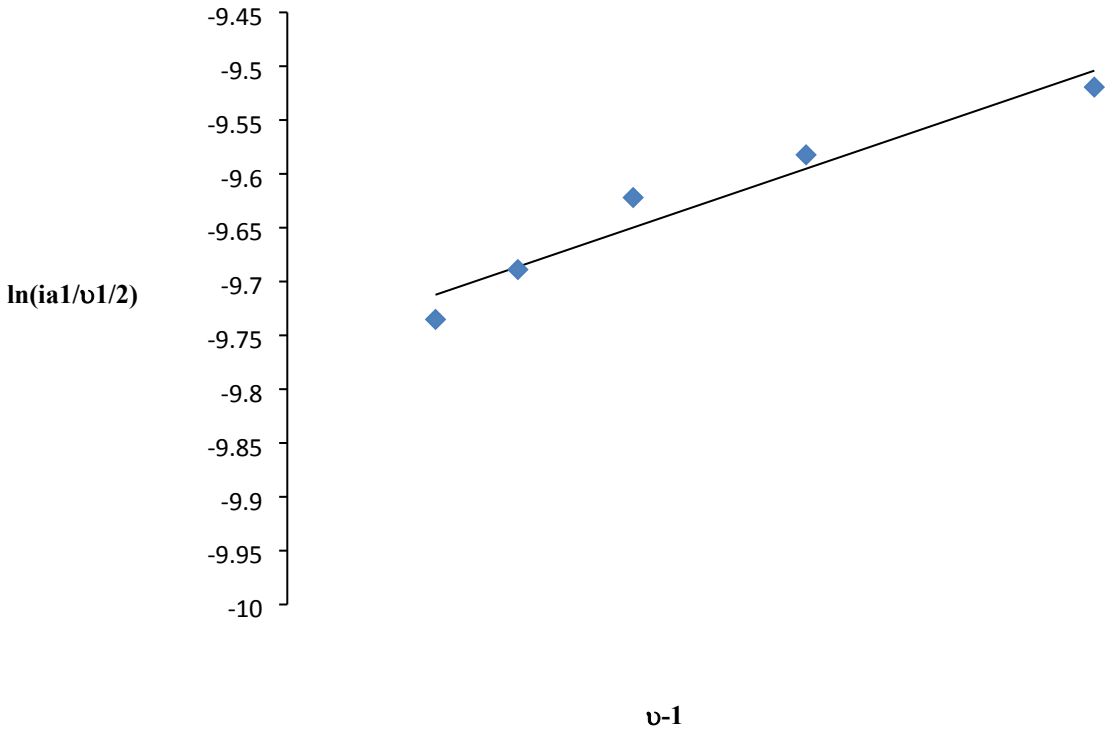


Figure S14. NMR spectra of **2** in CH_3CN after irradiation at t = a) 0, b) 45 and c) 90 minutes.

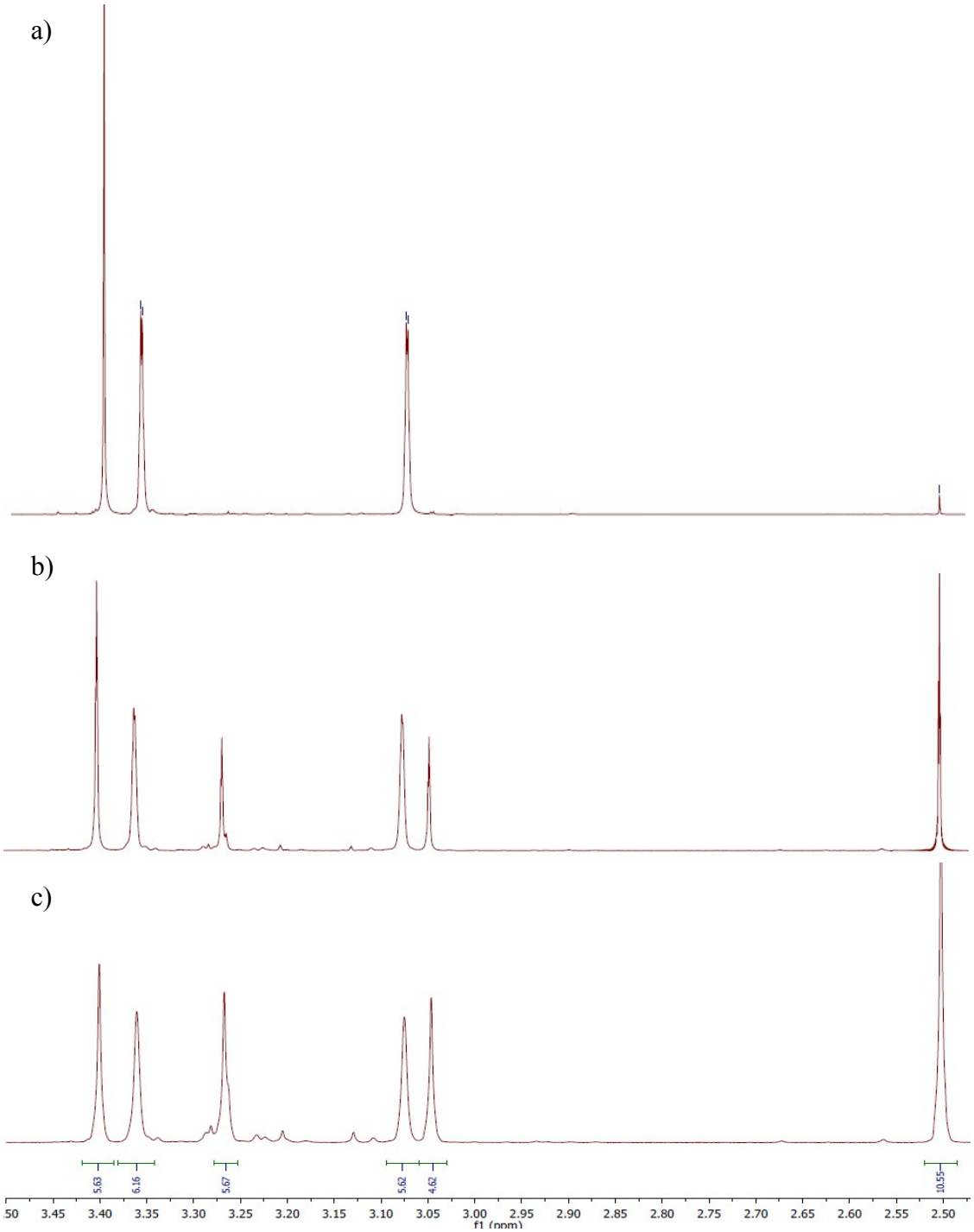


Figure S15. CV of **2** in CH_3CN + 0.1 M TBAH after irradiation during 90 minutes.

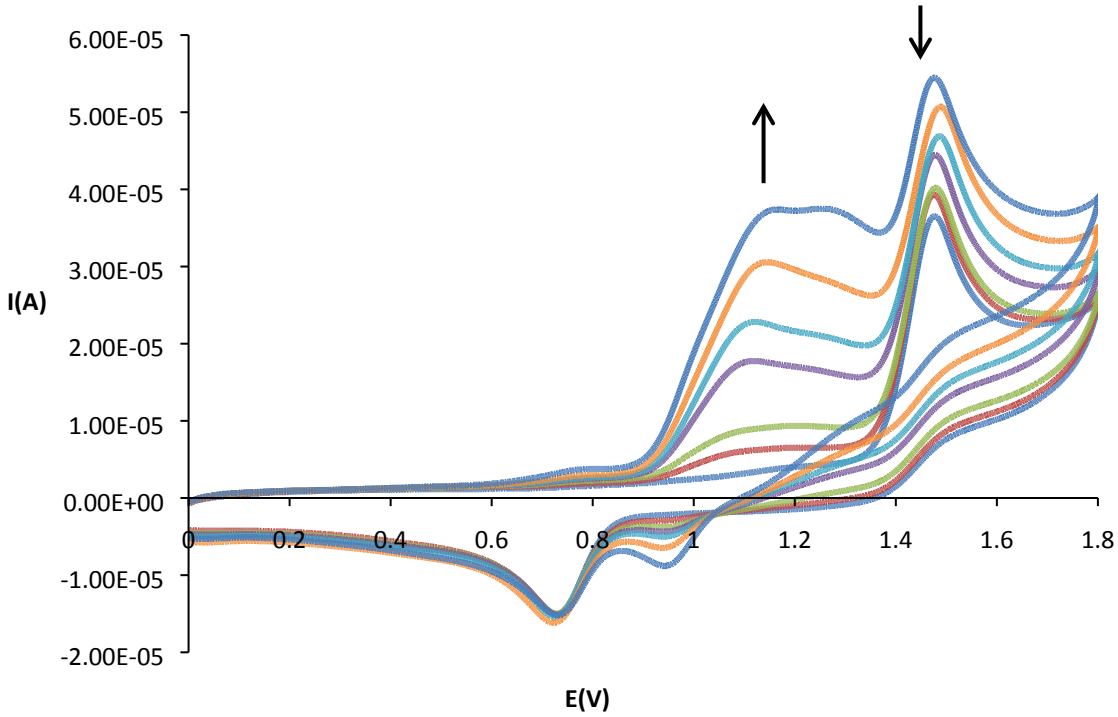


Figure S16. CV of **6'** in CH_2Cl_2 + 0.1 M TBAH.

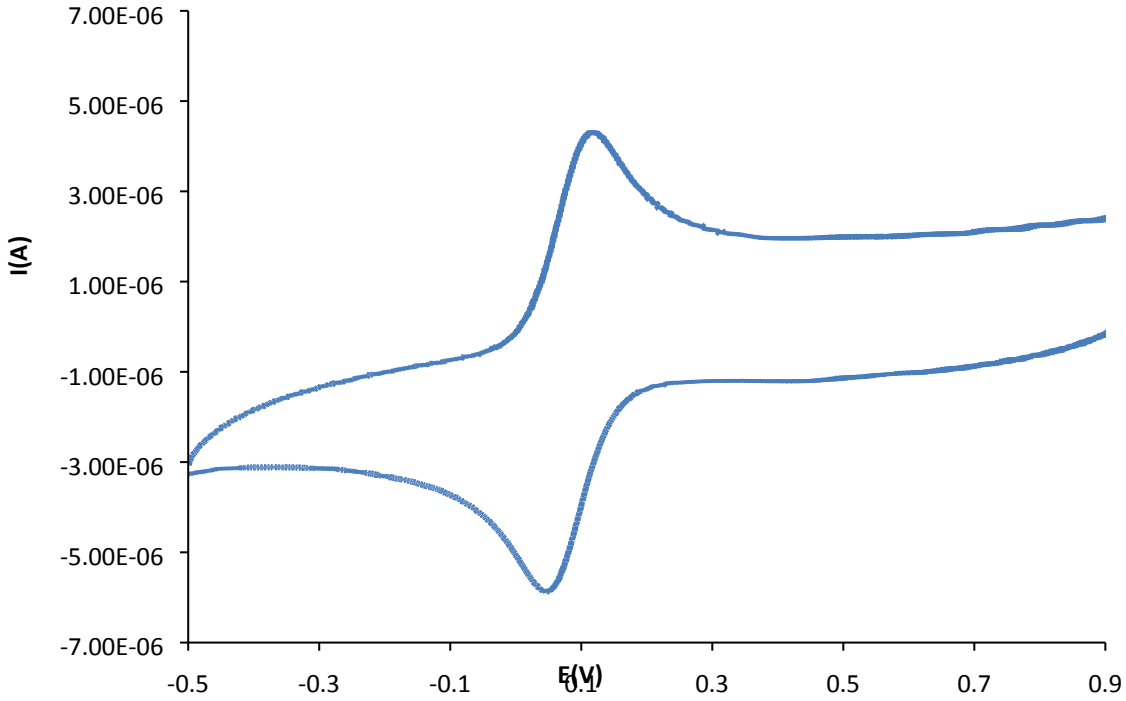


Figure S17. Successive UV-visible spectra obtained after irradiation of a solution of complex **6** in $CHCl_3$ during 60 min, to generate complex **6'**.

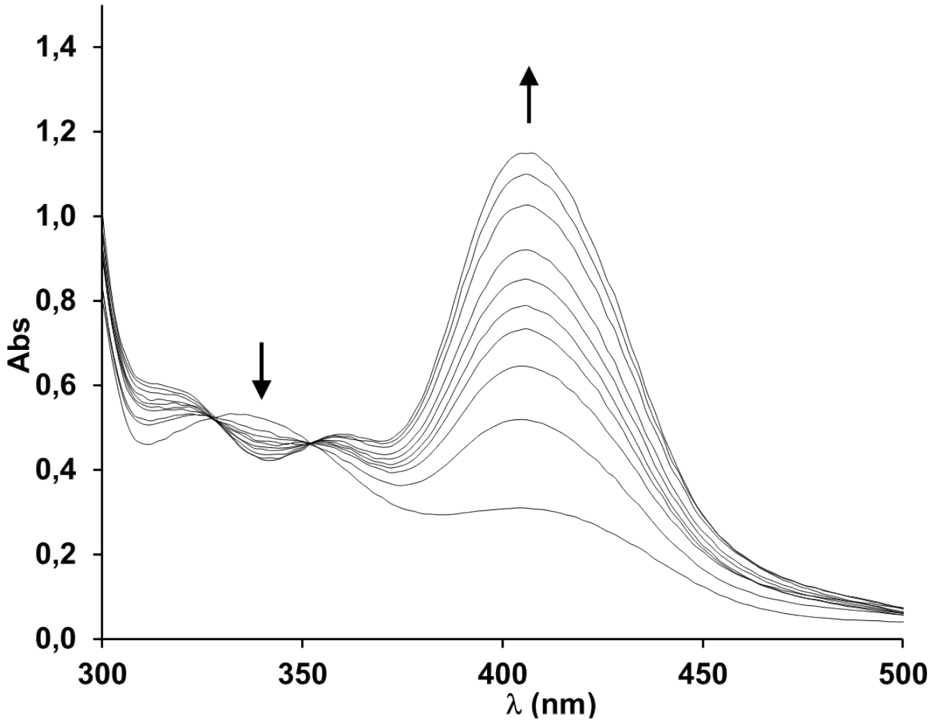


Figure S18. Successive UV-visible spectra obtained after irradiation of a solution of complex **2** in $CHCl_3$ during 24 h, to generate complex **2"**.

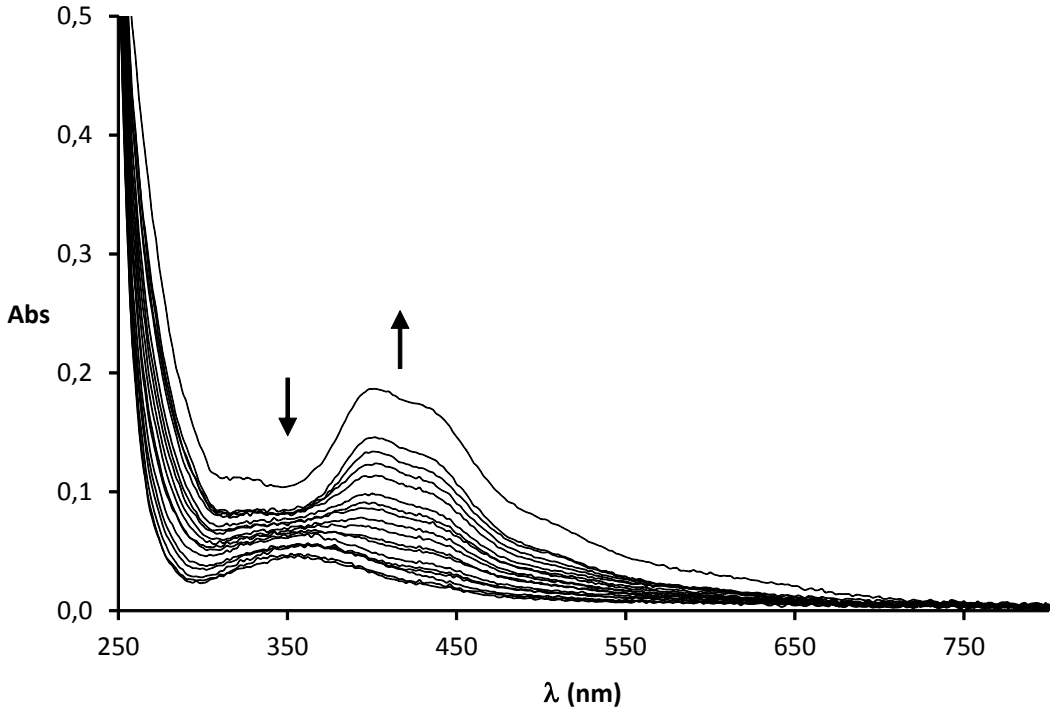


Figure S19. CV of **2"** in CH_2Cl_2 + 0.1 M TBAH after irradiation.

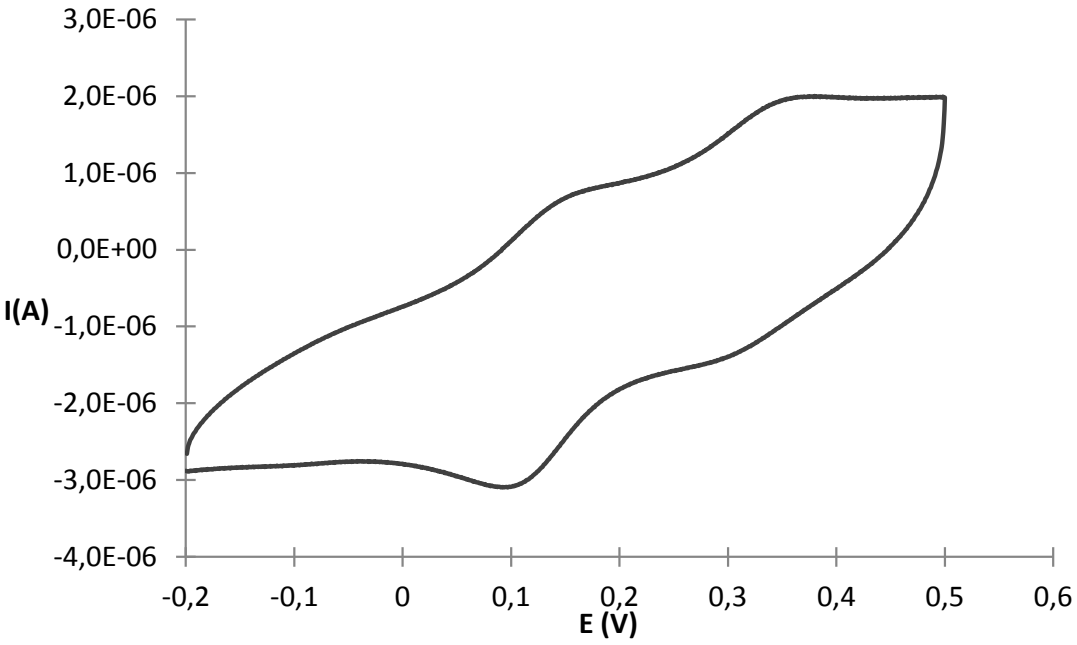


Figure S20. UV-vis monitoring of complex **2** in water at 80ºC: main figure, spectra registered for 30 minutes; inset, evolution of the band at 516 nm up to 150 minutes.

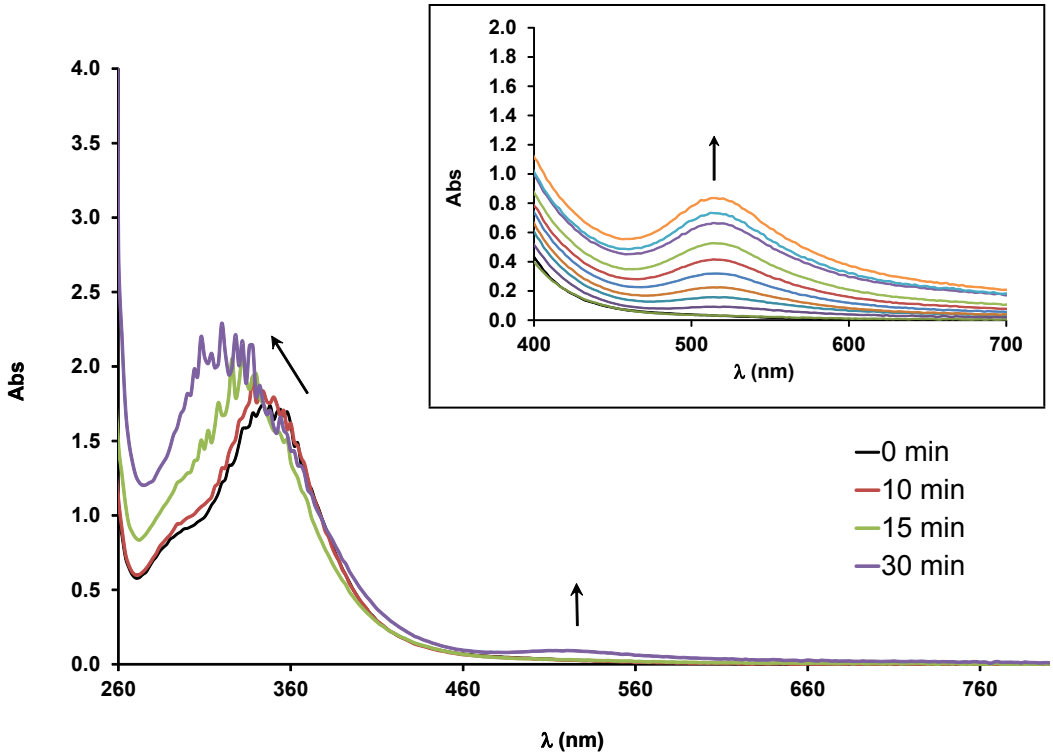


Figure S21. Red, ^{1}H-NMR spectrum of complex **2** registered in D_2O. Black, ^{1}H-NMR spectrum of complex **2** after 150 minutes in water solution at 80ºC.