Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

SUPPORTING INFORMATION

Molecular and Supported Ruthenium Complexes as Photoredox Oxidation Catalysts in Water

Enric Clerich,[a] *Syrine Affès,*[a] *Enriqueta Anticó,*[a] *Xavier Fontrodona,*[a] *Francesc Teixidor*[b] *and Isabel Romero**[a]

[a] Departament de Química and Serveis Tècnics de Recerca, Universitat de Girona, C/ M. Aurèlia Campmany, 69, E-17003 Girona, Spain.

[b] Institut de Ciencia de Materials de Barcelona, ICMAB-CSIC, Campus UAB, E-08193 Bellaterra, Spain.

Table S1. Crystallographic data for the X-ray diffraction of the *trans*-**2** and *cis*-**2** complexes.

Table S2. Selected bond lengths (Å) and angles (°) for of the *trans*-**2** and *cis*-**2** complexes.

Figure S1. Packing arrangement for isomer a) *trans*-**2** and b) *cis*-**2.**

Figure S2. IR spectra of a) *pypz-pyr*; b) *trans*-**2** and *cis*-**2;** c) *trans*-**3.**

Figure S3. NMR spectra of *pypz-pyr* (400 MHz, CD_2Cl_2): a) ^{1}H-NMR; b) ^{13}C-NMR; c) COSY; d) NOESY; e) ^{1}H-^{13}C HSQC.

Figure S4. NMR spectra of *trans*-**2**, 400 MHz, CD_6CO: a) DEPT b) COSY; c) NOESY; d) EXSY; e) HMBC H,N; f) HMBC; g) HSQC.

Figure S5. NMR spectra of *cis,*-**2**, 400 MHz CD_6CO: a) ^{13}C-NMR; b) DEPT; c) COSY; d) NOESY; e) TOCSY; f) HMBC; g) HSQC.

Figure S6. NMR spectra of *trans*-**3**, 400 MHz, MeOD: a) ^{1}H-NMR.

Figure S7. UV/Vis spectra of *trans*-**2** (solid line), *cis*-**2** (dotted line) in CH_2Cl_2 and *trans*-**3** (dashed line in phosphate buffer (pH=6.8)

Figure S8. CV of a) ligand *pyrz-pyr* in CH_2Cl_2 containing 0.1 M *n*-Bu_4NPF_6 (TBAH) vs SCE.and b) *trans*-**3** in phosphate buffer (pH=6.8); c) DPV of *trans*-**3.**

Figure S9. IR spectra of a) rGO (orange) and b) rGO@*trans*-**3** (blue).

Figure S10. SEM images of a) rGO support and b) rGO@*trans*-**3**.

Figure S11. DPV of rGO@*trans*-**2** in in CH_2Cl_2 containing 0.1 M *n*-Bu_4NPF_6 (TBAH) vs SCE.

Figure S12. Plot of yield as a function of time for the photoredox catalysis of 1-benzylalcohol using rGO-*trans*-**3** as photocatalyst. The blue curve shows the substract yield after 3h and 6 h of reaction time in presence of catalyst. The red curve shows the dependence of substract yield with the reaction time after the catalyst was removed at 3h. Conditions: rGO-*trans*-**3** (0,25 mM), substrate (25 mM), $Na_2S_2O_8$ (75 mM), 3ml water (phosphate buffer pH 6.8), 6h h of catalysis at RT. light irradiation using a lamp with λ= 400-700 nm.

Table S1. Crystallographic data for the X-ray diffraction of the *trans*-**2** and *cis*-**2** complexes.

	trans-**2**	*cis*-**2**
Empirical formula	$C_{40}H_{28}ClF_6N_6PRu.7/4CH_2Cl_2$	$C_{40}H_{28}ClF_6N_6PRu$
Formula weight	1026.42 g/mol	874.17 g/mol
Crystal system	monoclinic	tetragonal
Space group	P 1 21/n 1	P 4/n n c
a[Å]	15.550(9)	17.9714(15)
b[Å]	16.801(7)	17.9714(15)
c[Å]	16.104(8)	49.745(9)
α[º]	90	90
β[º]	103.032(19)	90
γ[º]	90	90
V [Å^3]	4099.(3)	16066.(4)
Formula Units/ cell	1	16
Temp. [K]	100(2)	100(2)
ρ_{calc}, [g/cm^{-3}]	1.657	1.446
μ[mm^{-1}]	0.783	0.561
Final R indices, [I>2σ(I)]	R_1 = 0.0542 wR_2 = 0.1274	R_1 = 0.1125 wR_2 = 0.2311
R indices [all data]	R_1 = 0.0632 wR_2 = 0.1369	R_1 = 0.1334 wR_2 = 0.2469

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

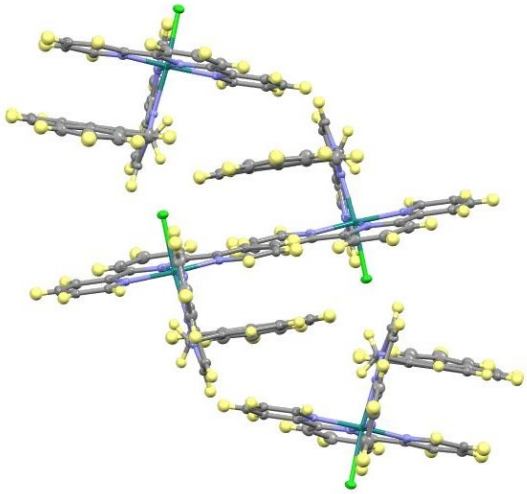
$wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{½}$, where $w = 1/[\sigma^2(Fo^2) + (0.0042P)^2]$ and $P=(F_o^2+2F_c^2)$

Table S2. Selected bond lengths (Å) and angles (°) for of the *trans*-**2** and *cis*-**2** complexes.

	trans-**2**	*cis*-**2**
Ru(1)-N(1)	2.099(3)	2.065(8)
Ru(1)-N(2)	2.056(3)	2.110(9)
Ru(1)-N(4)	2.069(3)	2.039(6)
Ru(1)-N(5)	1.954(3)	1.923(5)
Ru(1)-N(6)	2.063(3)	2.063(9)
Ru(1)-Cl(1)	2.3969(12)	2.417(3)
N(5)-Ru(1)-N(2)	103.02(11)	174.3(3)
N(2)-Ru(1)-N(6)	94.17(11)	100.5(4)
N(2)-Ru(1)-N(4)	90.31(11)	99.8(3)
N(5)-Ru(1)-N(1)	174.96(11)	96.9(3)
N(6)-Ru(1)-N(1)	94.61(11)	93.6(3)
N(5)-Ru(1)-Cl(1)	86.31(8)	85.4(2)
N(6)-Ru(1)-Cl(1)	89.78(8)	89.6(2)
N(1)-Ru(1)-Cl(1)	93.82(8)	176.3(2)
N(5)-Ru(1)-N(6)	80.35(12)	79.6(3)
N(5)-Ru(1)-N(4)	79.63(12)	79.9(3)
N(6)-Ru(1)-N(4)	159.99(11)	159.5(3)
N(2)-Ru(1)-N(1)	77.11(11)	77.5(3)
N(4)-Ru(1)-N(1)	105.40(12)	88.1(3)
N(2)-Ru(1)-Cl(1)	170.35(8)	100.3(2)
N(4)-Ru(1)-Cl(1)	88.95(8)	89.5(2)

Figure S1. Packing arrangement for isomer a) *trans*-**2** and b) *cis*-**2.**

a)



b)

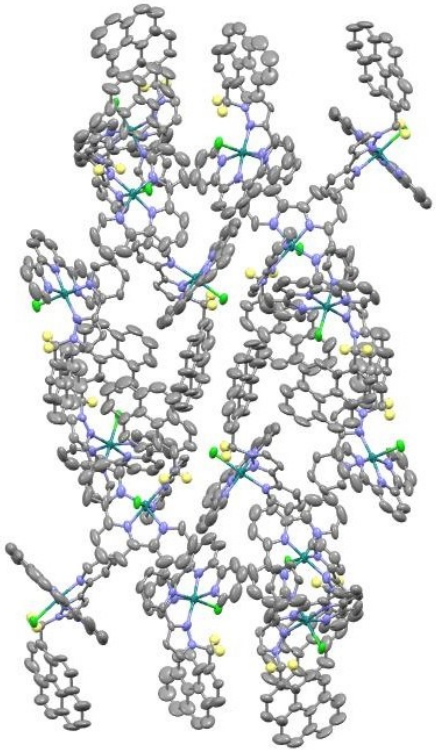
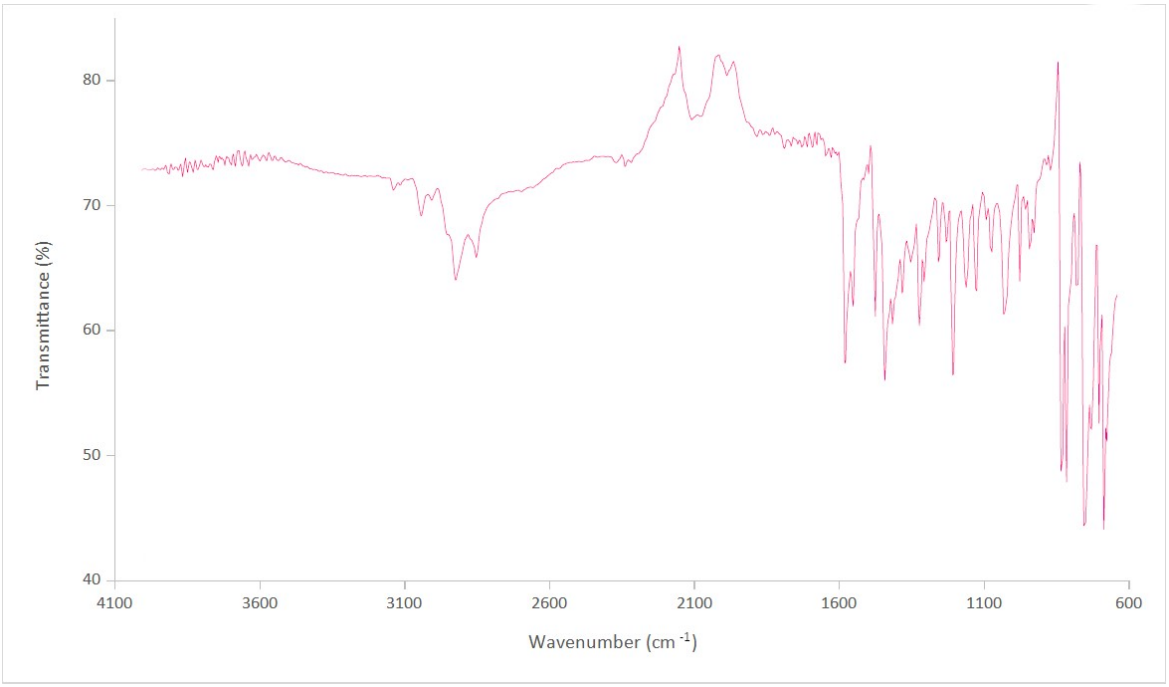
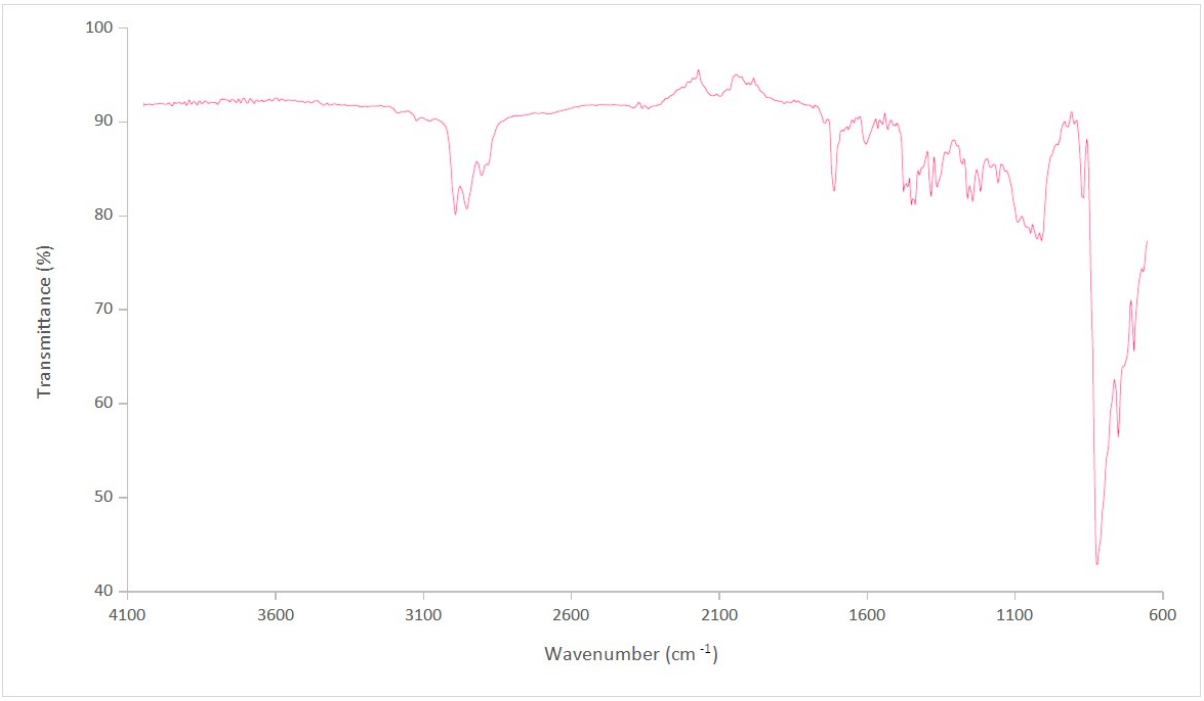


Figure S2. IR spectra of a) *pypz-pyr*; b) *trans*-**2** and *cis*-**2;** c) *trans*-**3**.

a)



b)



c)

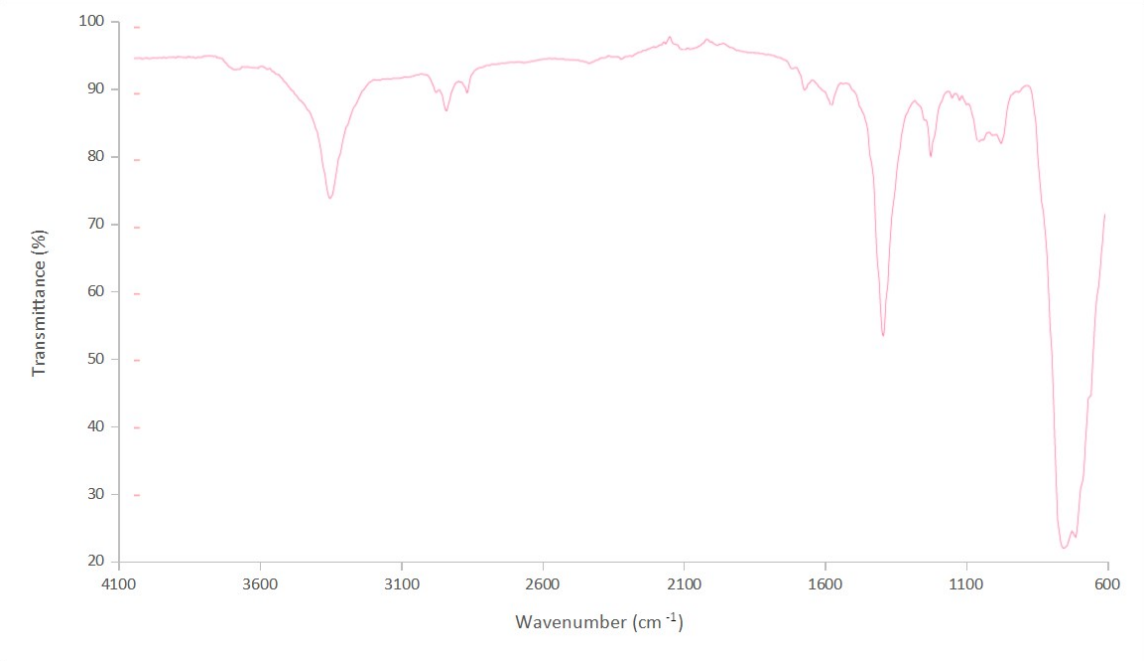
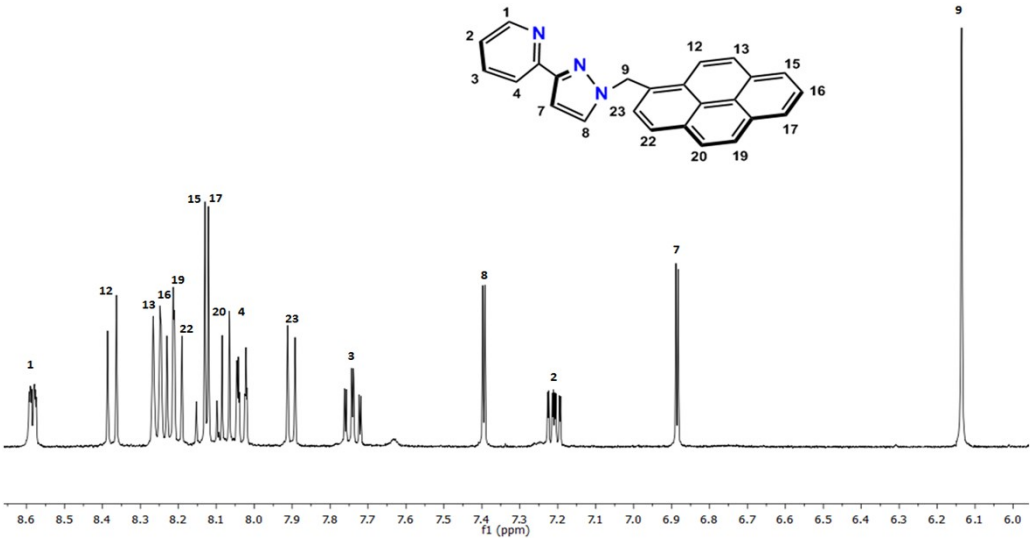
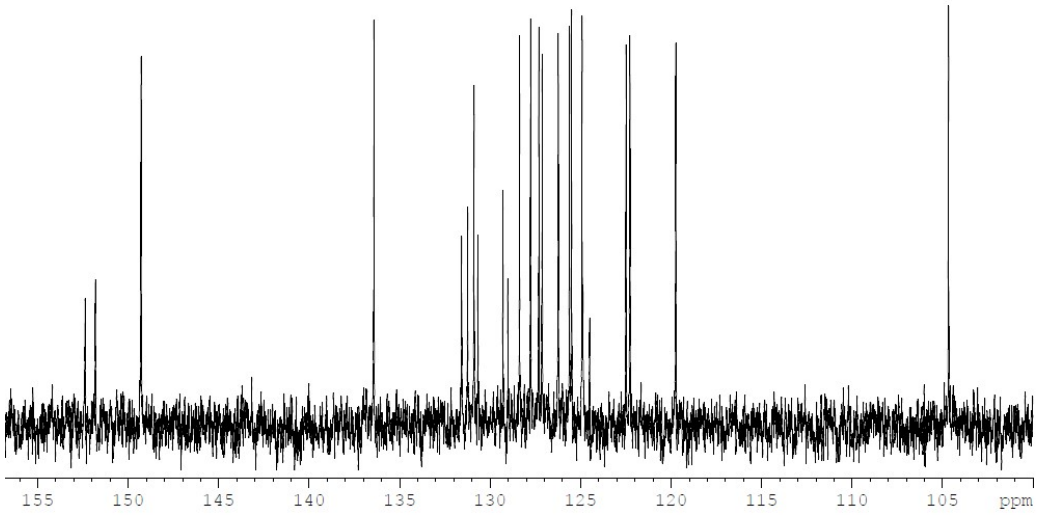

100
90
80
70
60
50
40
30
20
Transmittance (%)
4100
3600
3100
2600
2100
1600
1100
600
Wavenumber (cm -1)

Figure S3. NMR spectra of *pypz-pyr* (400 MHz, CD_2Cl_2): a) ^{1}H-NMR; b) ^{13}C-NMR; c) COSY; d) NOESY; e) ^{1}H-^{13}C HSQC.

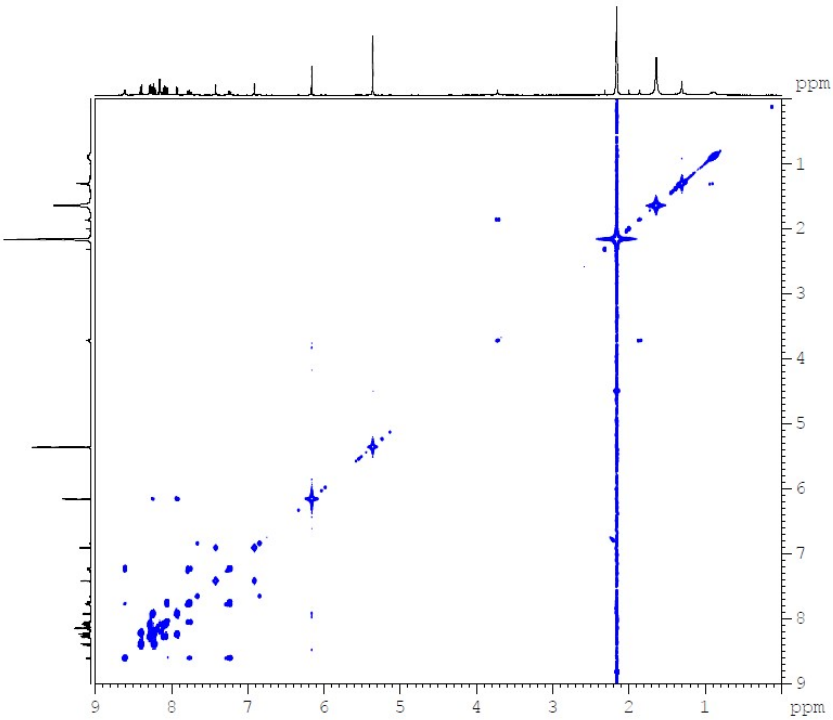
a)



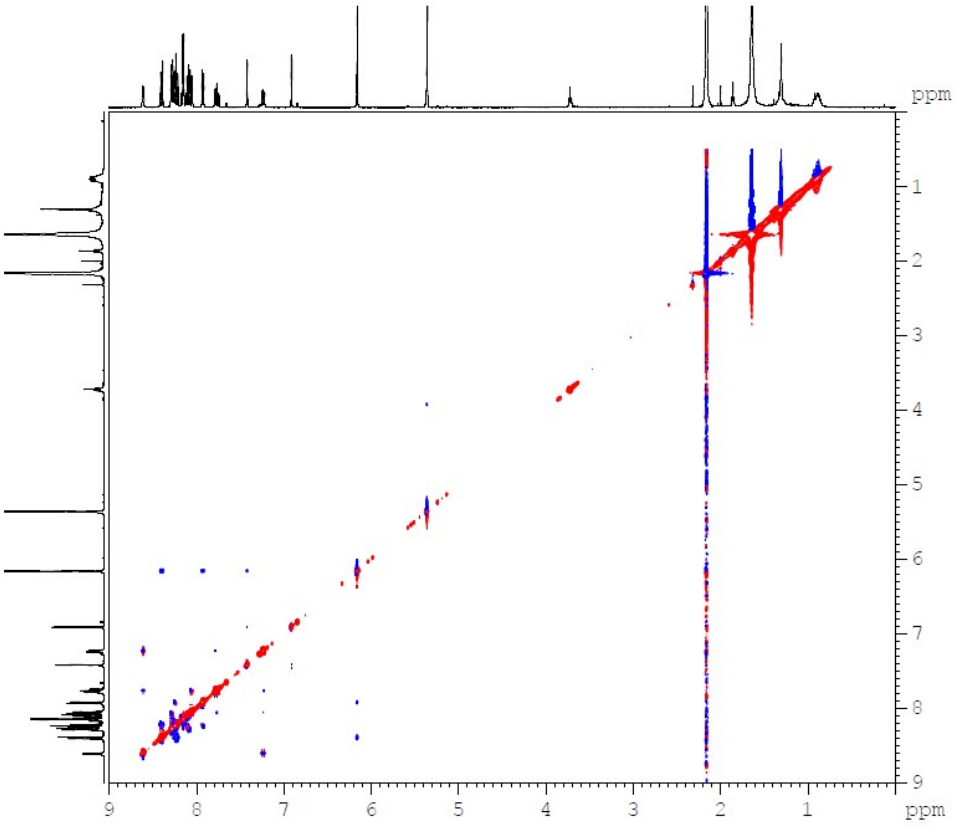
b)



c)



d)



e)

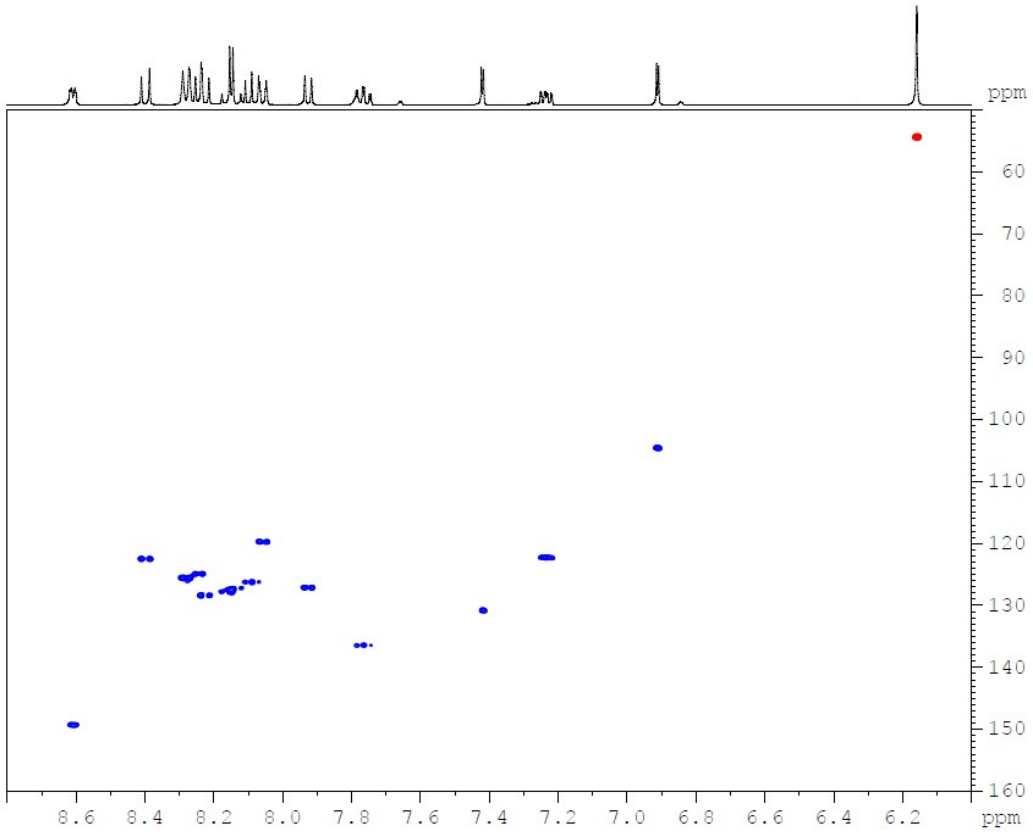
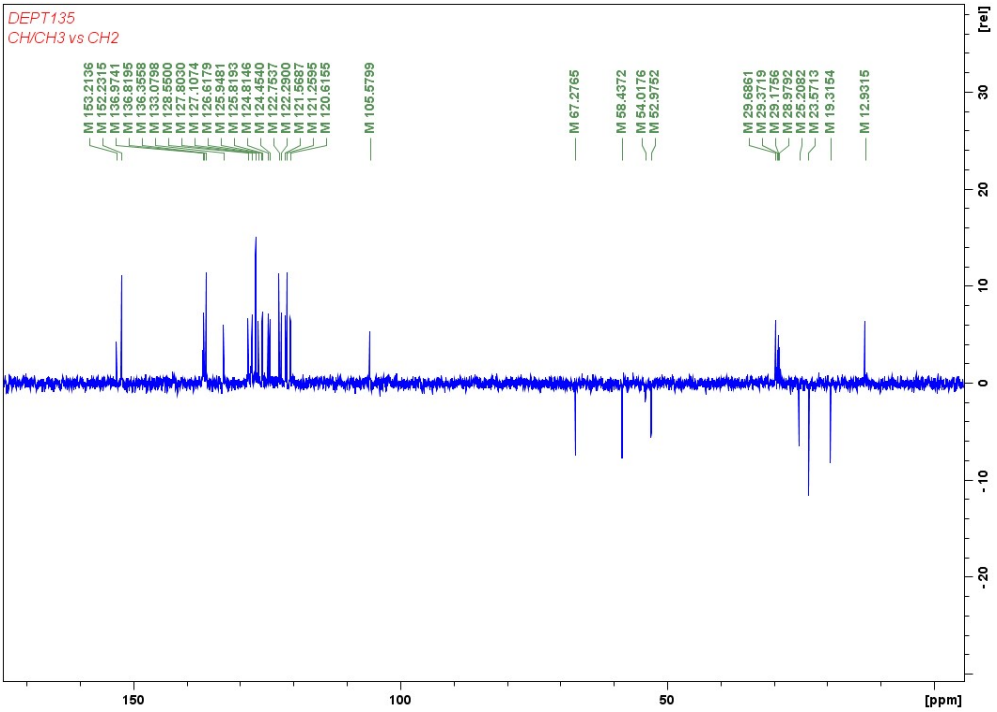
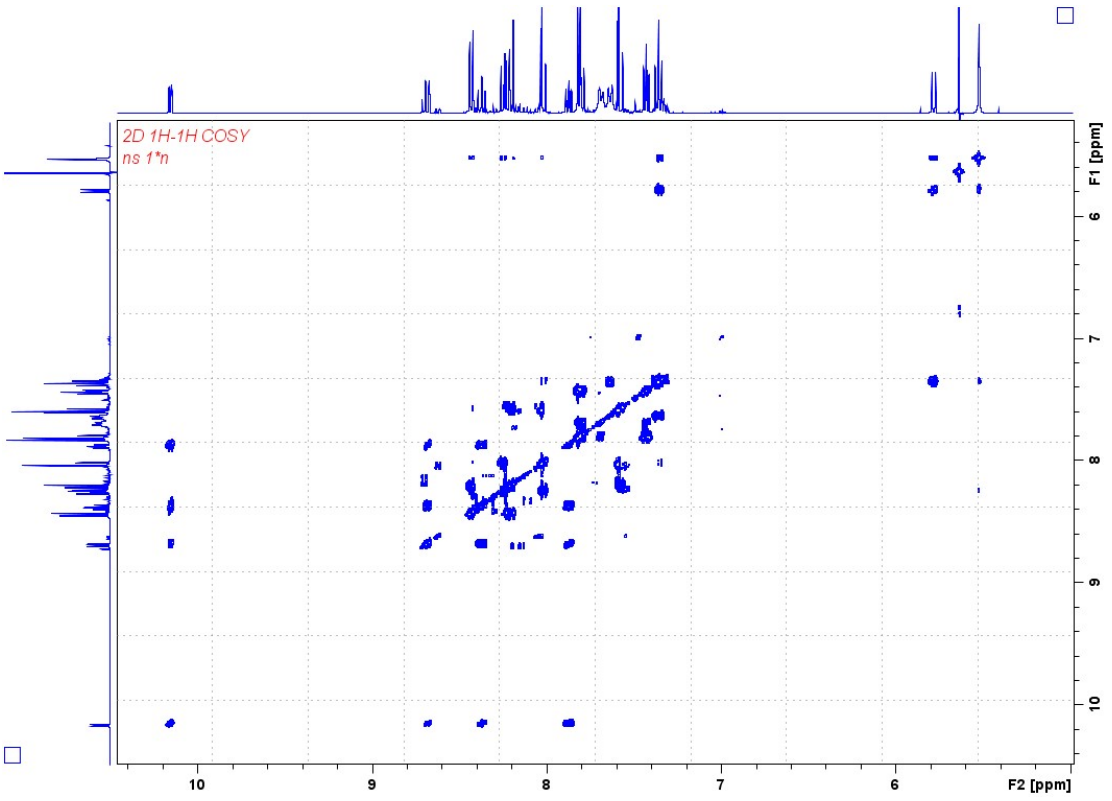

ppm
60
70
80
90
100
110
120
130
140
150
160
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm

Figure S4. NMR spectra of *trans*-**2**, 400 MHz, CD_6CO: a) DEPT b) COSY; c) NOESY; d) EXSY; e) HMBC H,N; f) HMBC H,C; g) HSQC H,C

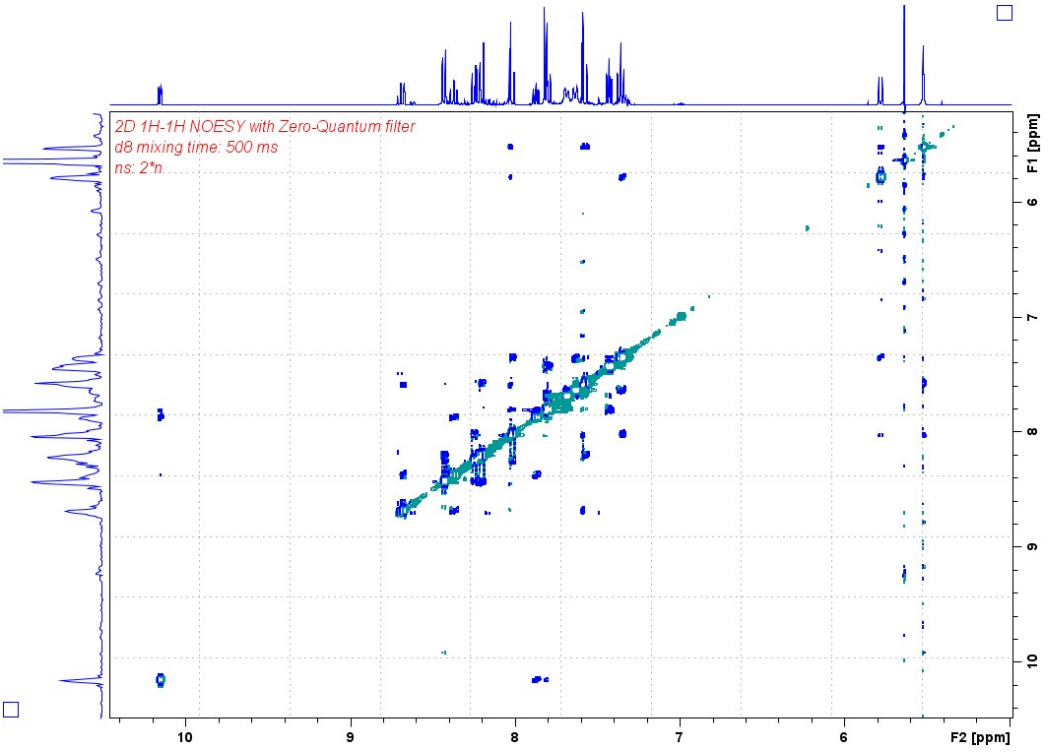
a)



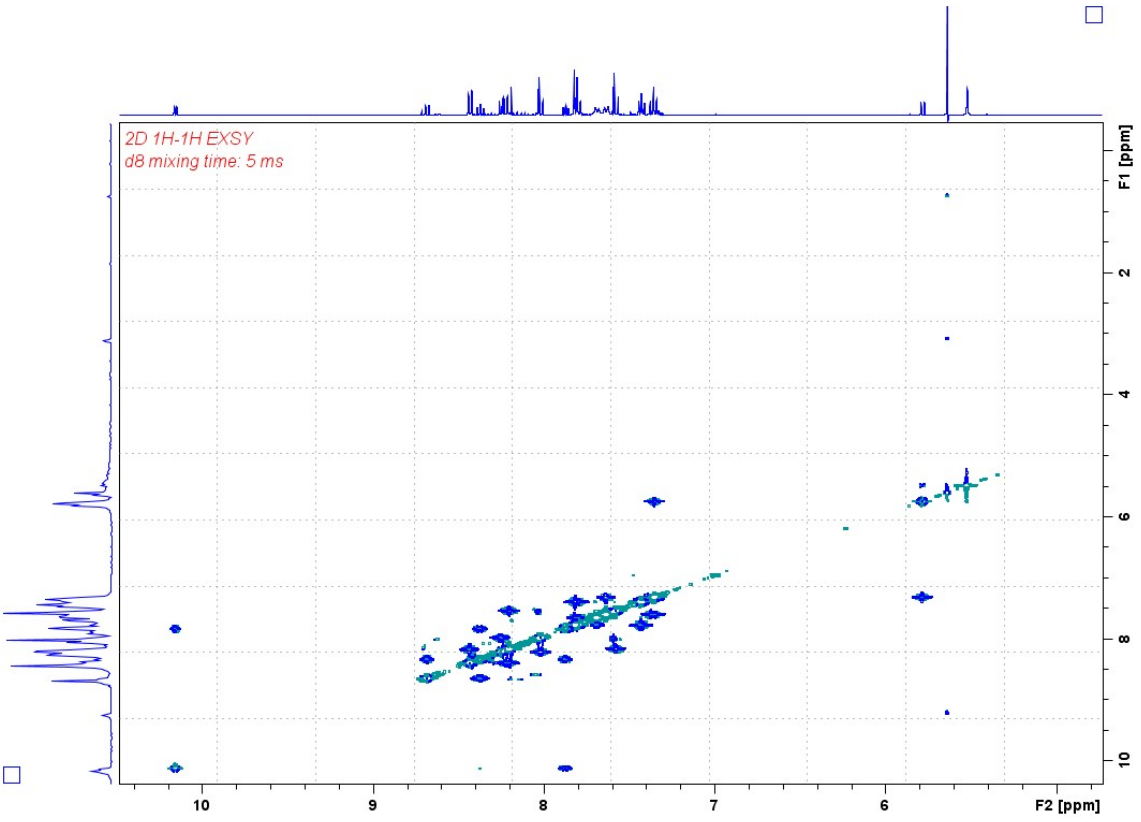
b)



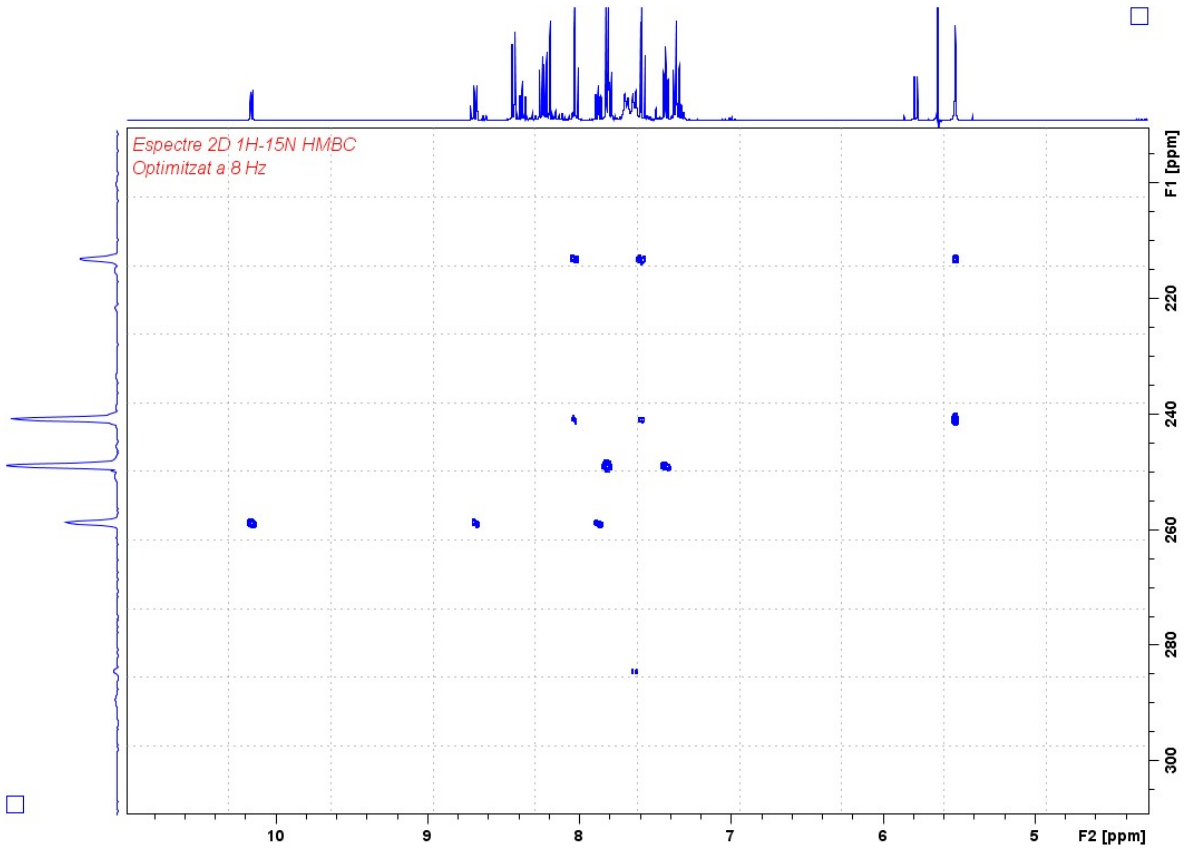
c)


2D 1H-1H NOESY with Zero-Quantum filter
d8 mixing time: 500 ms
ns: 2*n
F1 [ppm]
F2 [ppm]

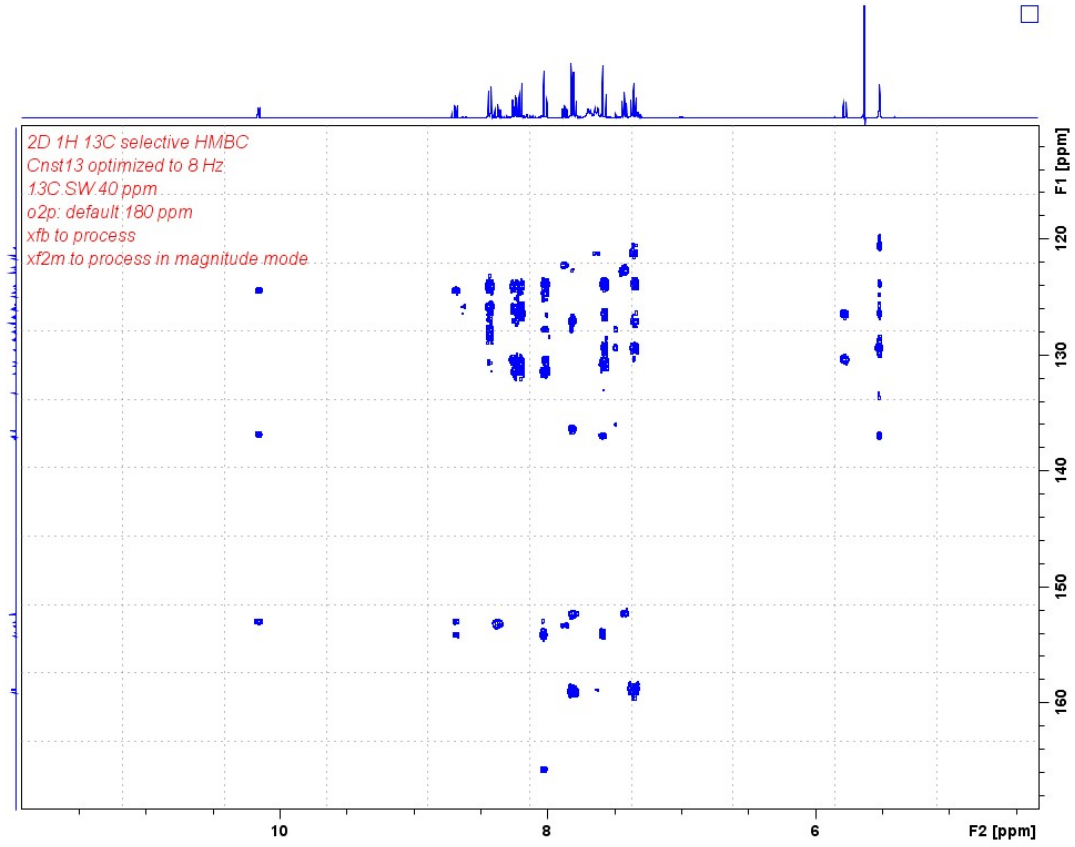
d)


2D 1H-1H EXSY
d8 mixing time: 5 ms
F1 [ppm]
F2 [ppm]

e)


Espectre 2D 1H-15N HMBC
Optimitzat a 8 Hz
F1 [ppm]
220
240
260
280
300
10
9
8
7
6
5
F2 [ppm]

f)


2D 1H 13C selective HMBC
Cnst13 optimized to 8 Hz
13C SW 40 ppm
o2p: default 180 ppm
xfb to process
xf2m to process in magnitude mode
F1 [ppm]
120
130
140
150
160
10
8
6
F2 [ppm]

g)

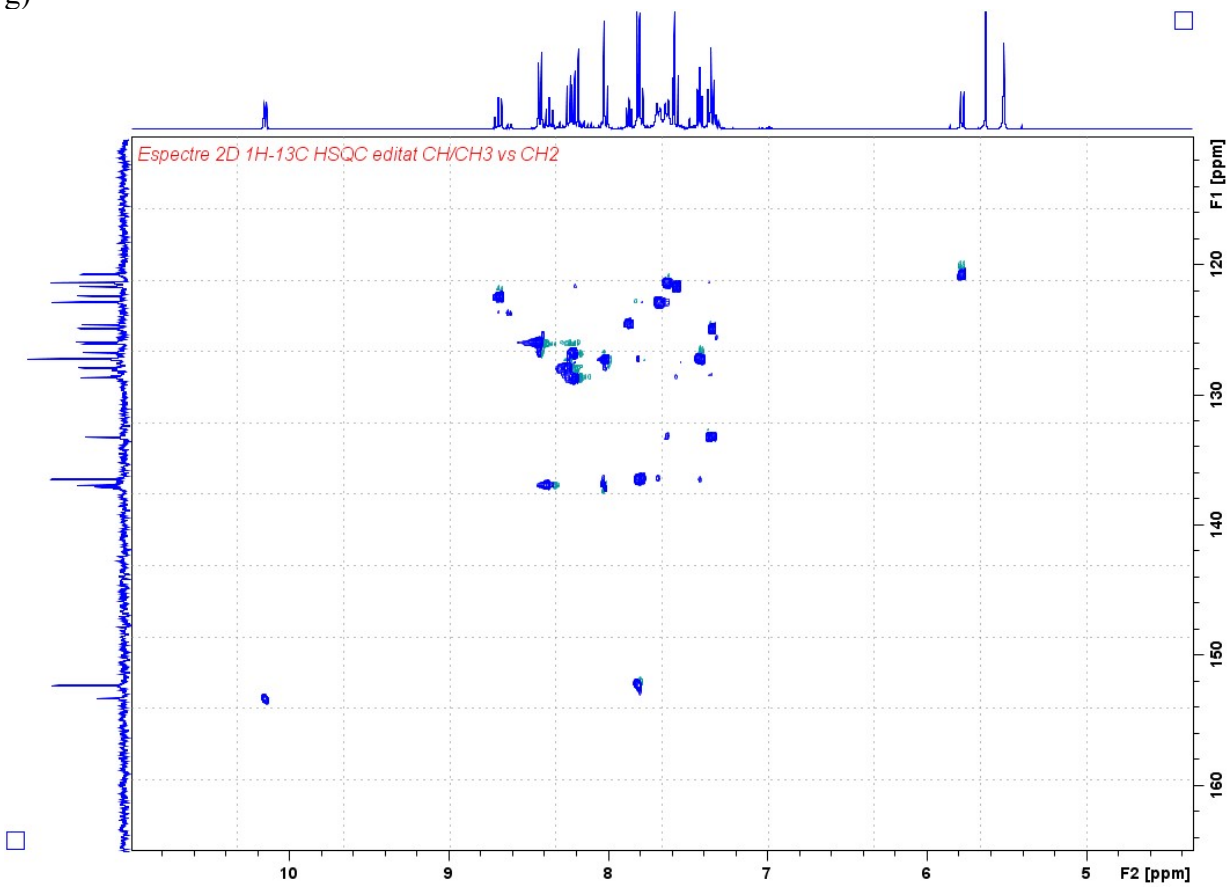
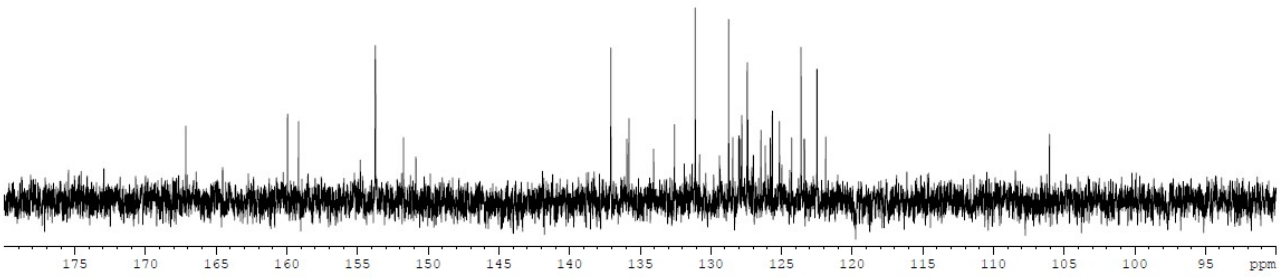
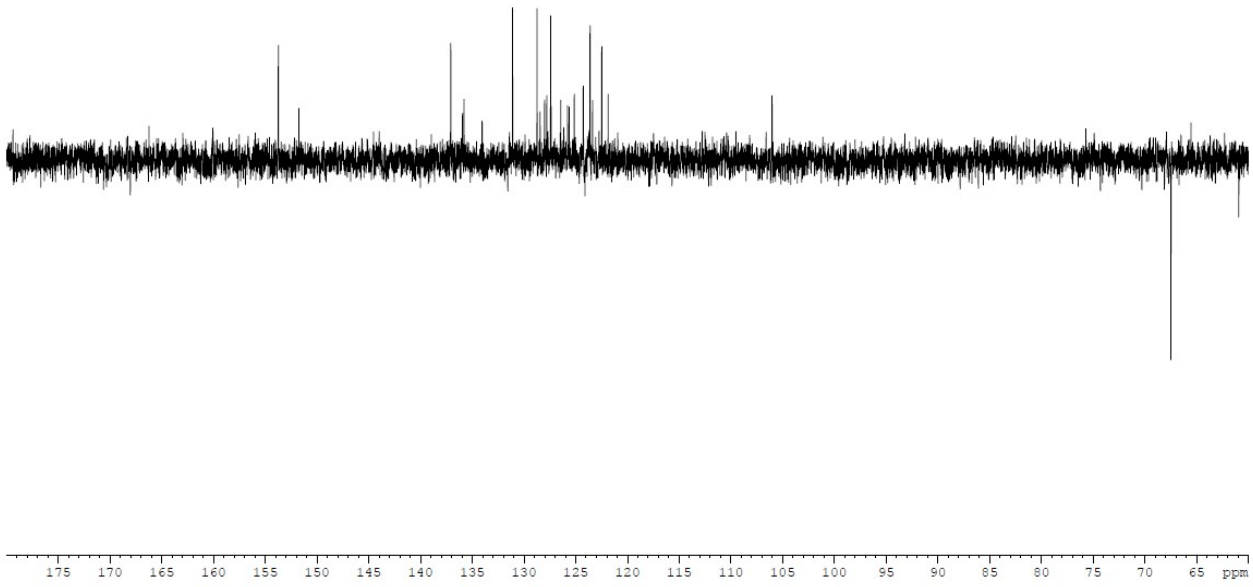

Espectre 2D 1H-13C HSQC editat CH/CH3 vs CH2
F1 [ppm]
120
130
140
150
160
10
9
8
7
6
5
F2 [ppm]

Figure S5. NMR spectra of *cis,*-**2**, 400 MHz, CD_6CO: a) ^{13}C-NMR; b) DEPT; c) COSY; d) NOESY; e) TOCSY; f) HMBC H,C; g) HSQC H,C

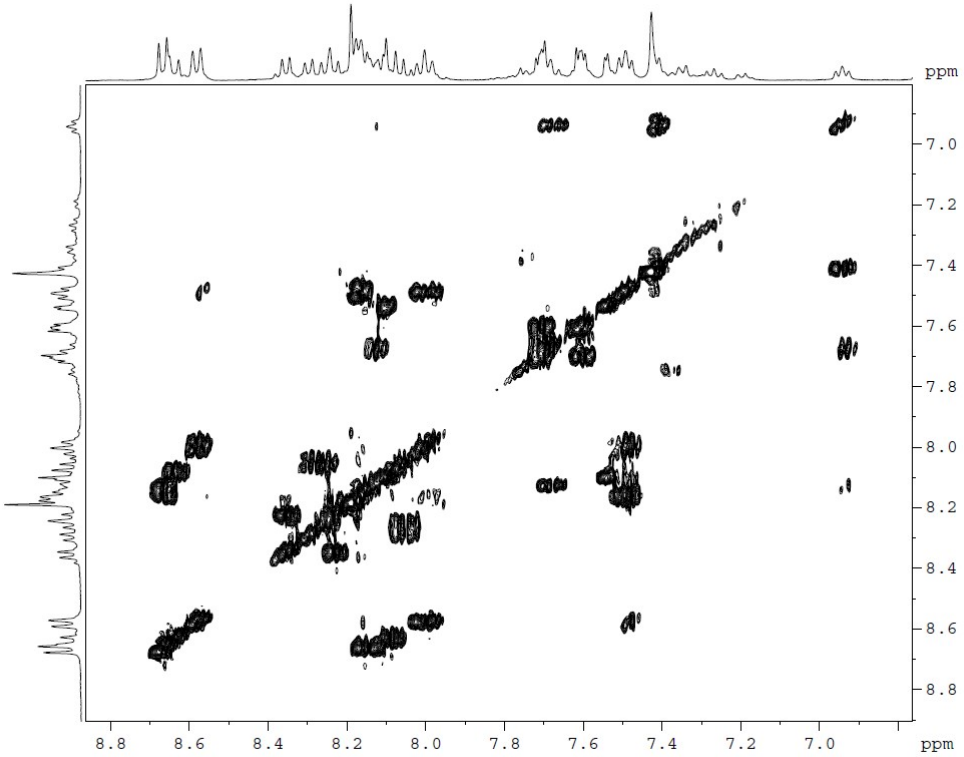
a)



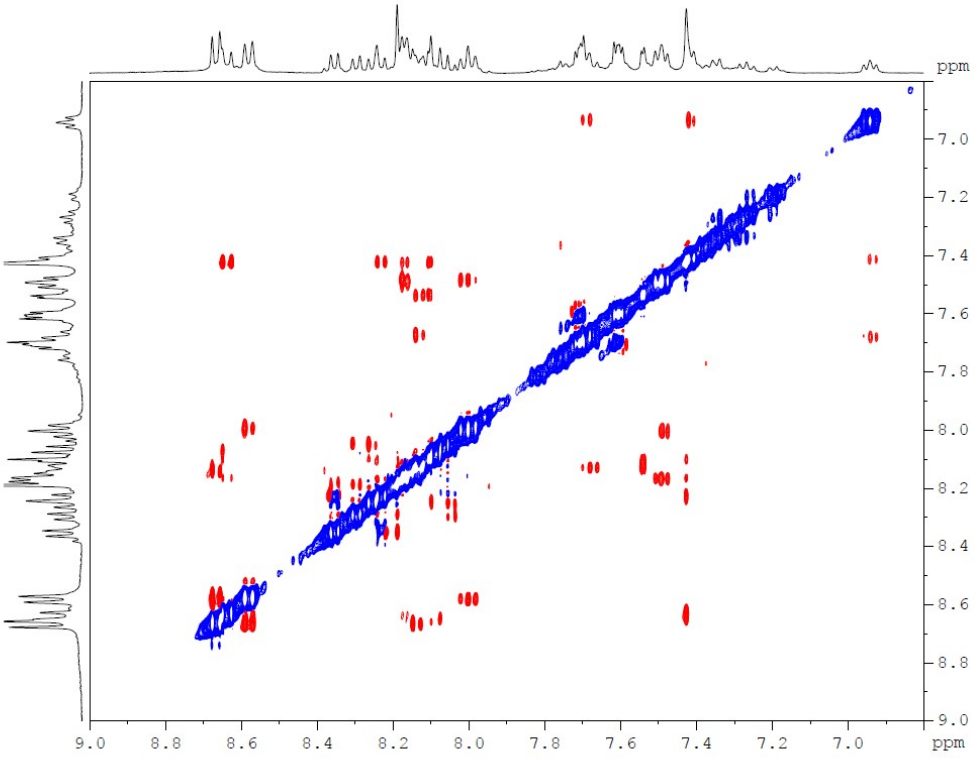
b)



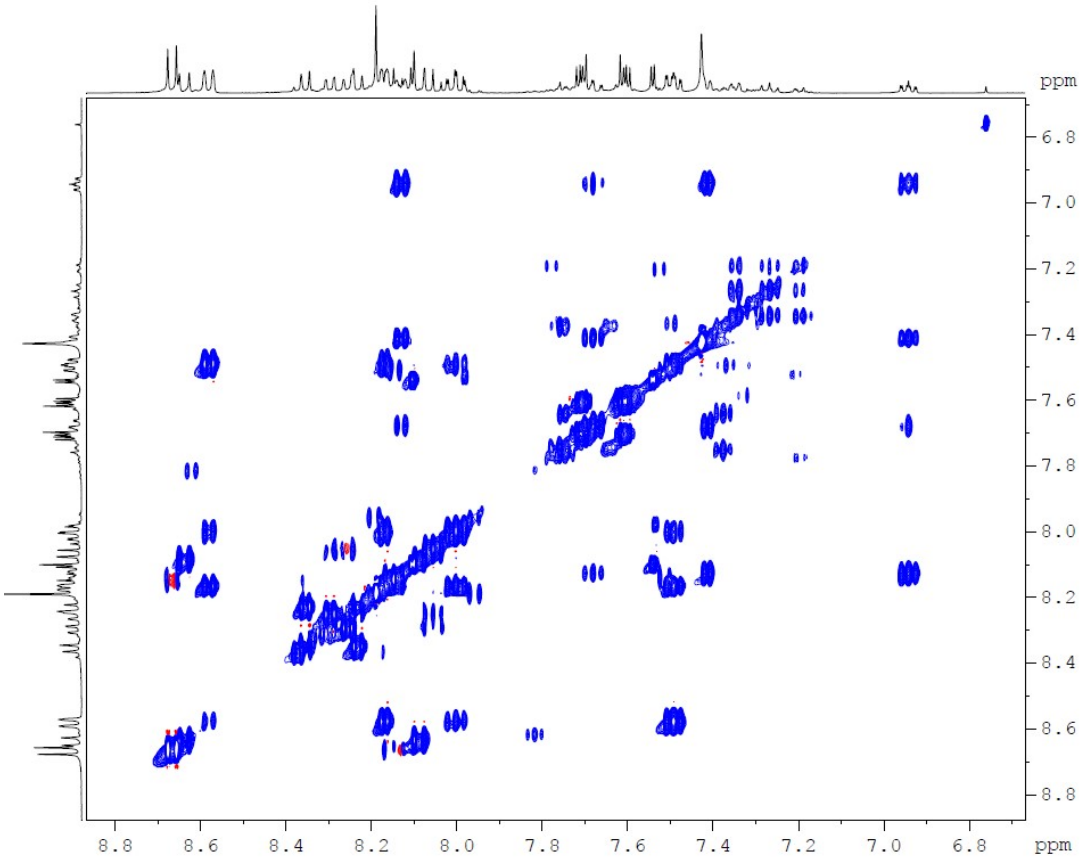
c)


ppm
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm

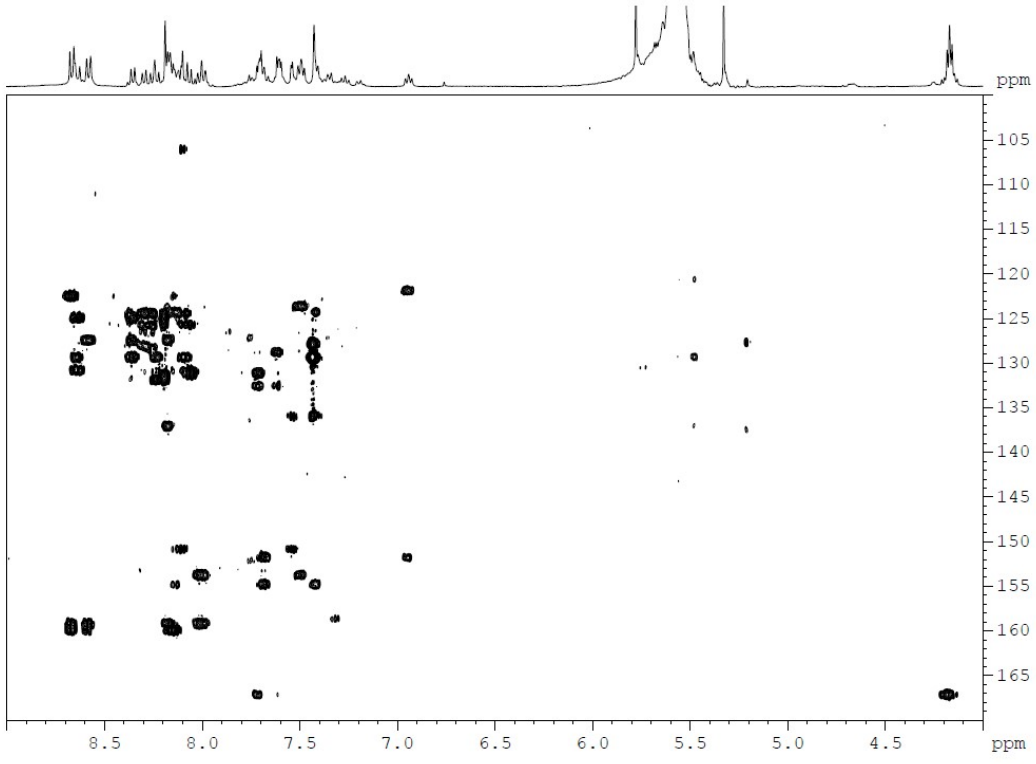
d)


ppm
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
9.0
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm

e)


ppm
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm

f)


ppm
105
110
115
120
125
130
135
140
145
150
155
160
165
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 ppm

g)

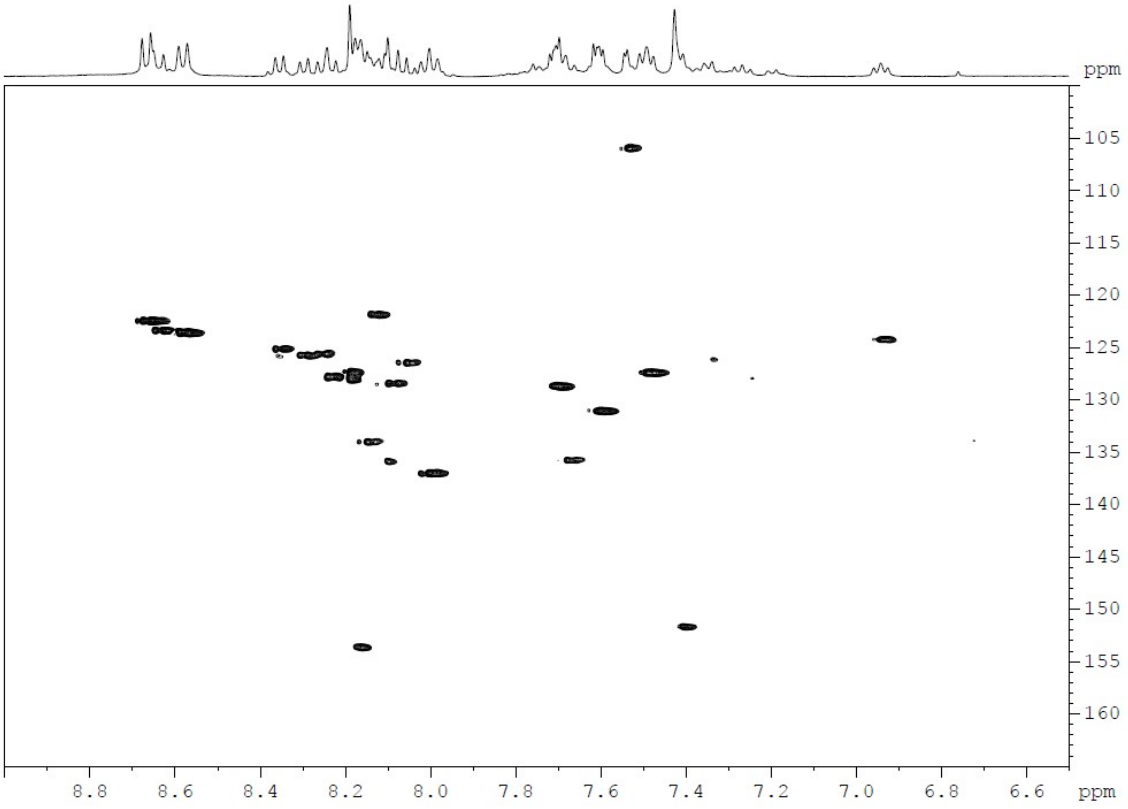

ppm
105
110
115
120
125
130
135
140
145
150
155
160
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
ppm

Figure S6. NMR spectra of *trans*-**3**, 400 MHz, MeOD: a) ^{1}H-NMR

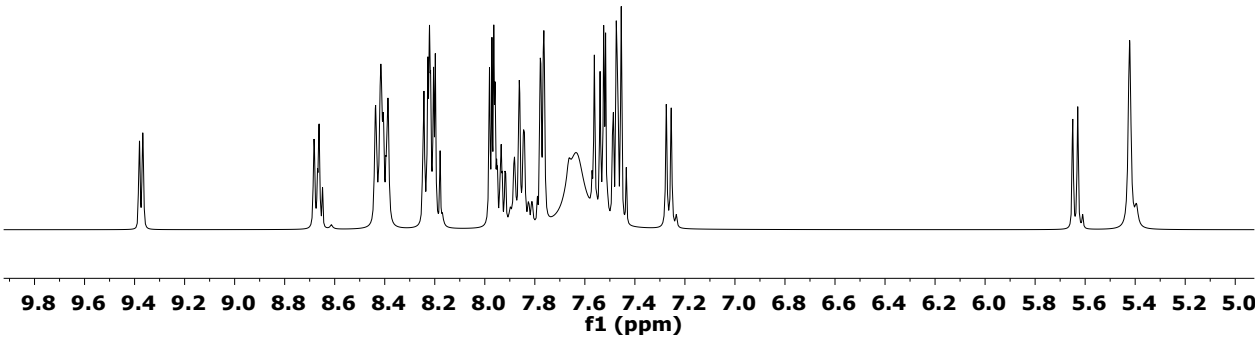


Figure S7. UV/Vis spectra of *trans*-**2** (solid line), *cis*-**2** (dotted line) in CH_2Cl_2 and *trans*-**3** (dashed line in phosphate buffer (pH=6.8)

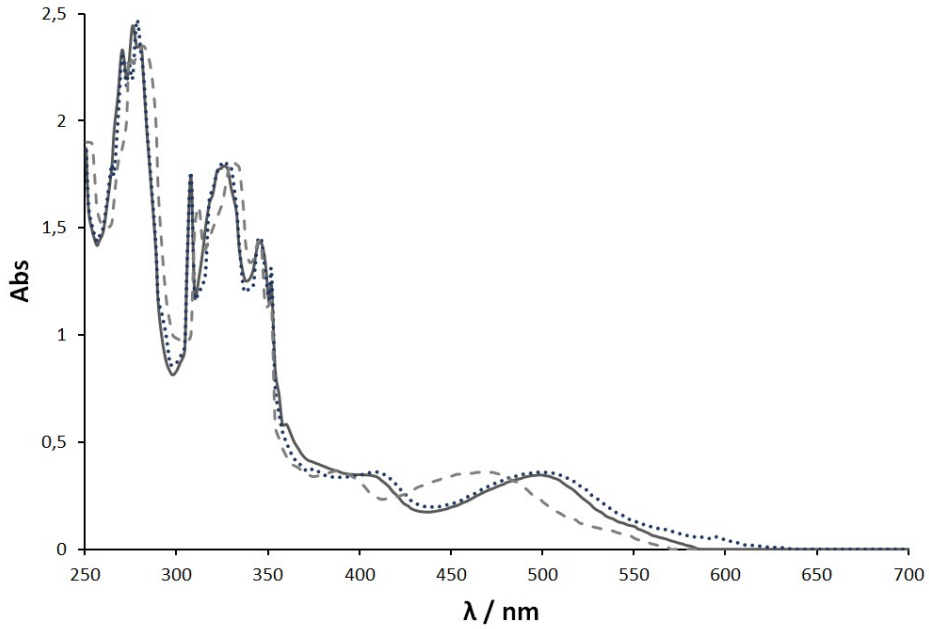
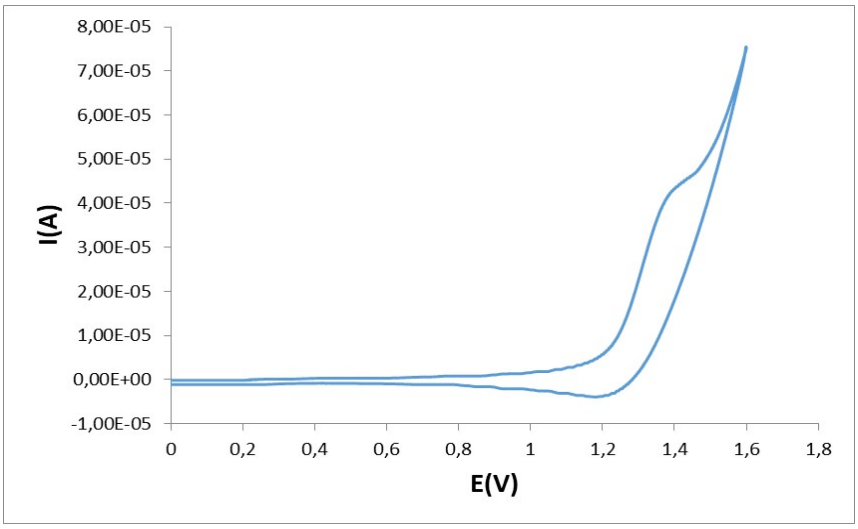
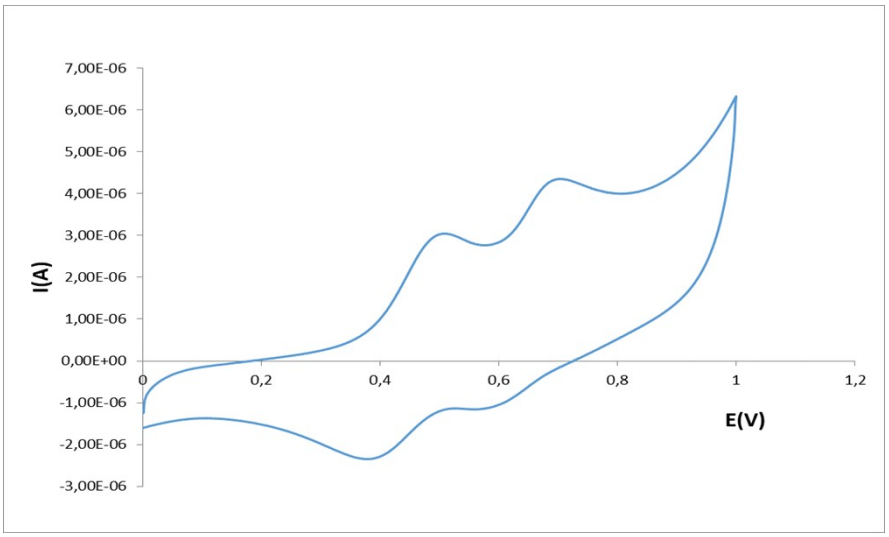


Figure S8. CV of a) ligand **pyrz-pyr** in CH_2Cl_2 containing 0.1 M *n*-Bu_4NPF_6 (TBAH) vs SCE.and b) *trans*-**3** in phosphate buffer (pH=6.8); c) DPV of *trans*-**3**

a)



b)



c)

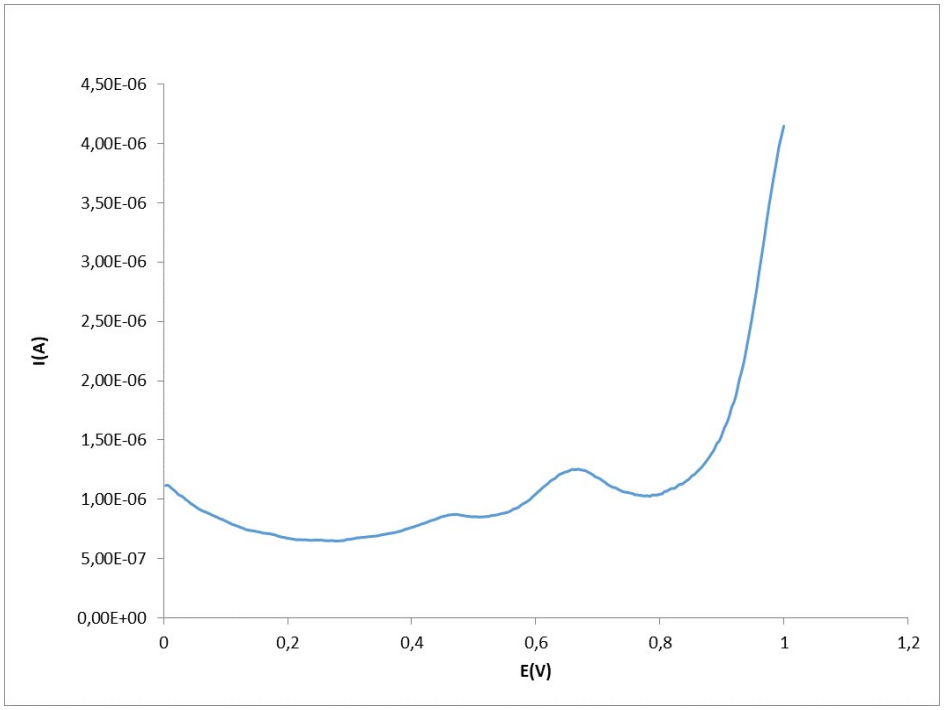

4,50E-06
4,00E-06
3,50E-06
3,00E-06
2,50E-06
2,00E-06
1,50E-06
1,00E-06
5,00E-07
0,00E+00
I(A)
0
0,2
0,4
0,6
0,8
1
1,2
E(V)

Figure S9. IR spectra of a) rGO (orange), b) rGO@*trans*-**3** (blue)

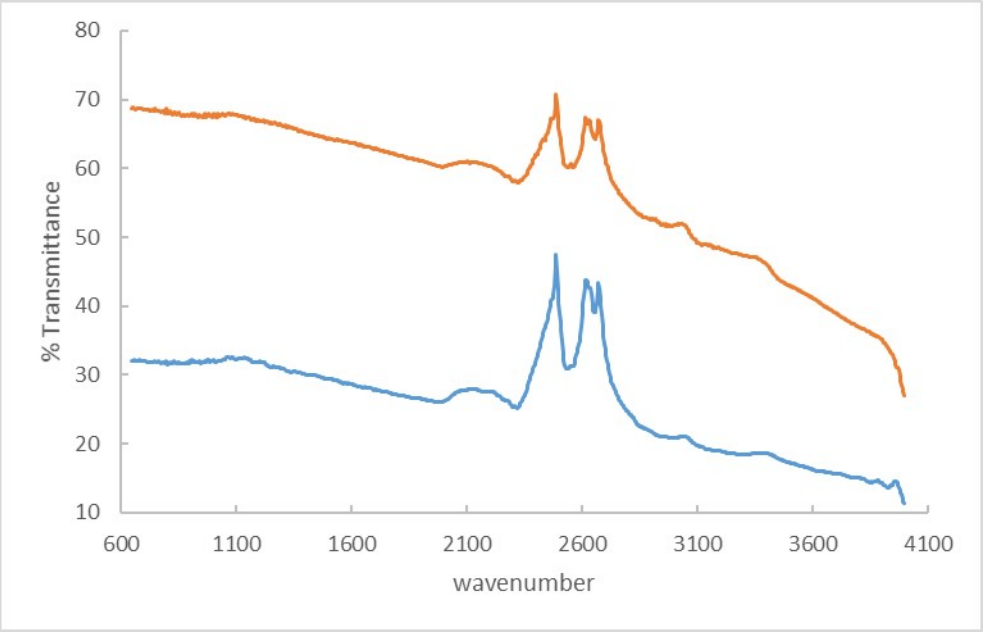
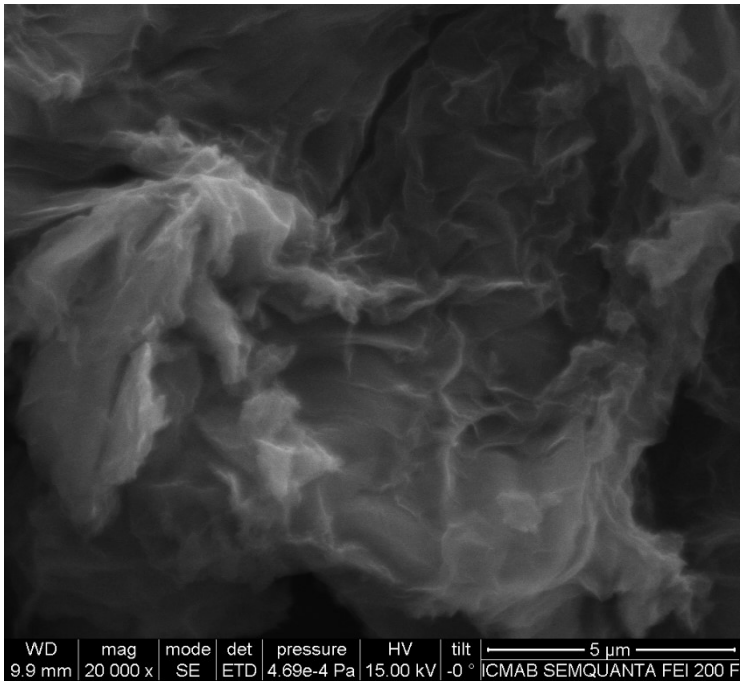
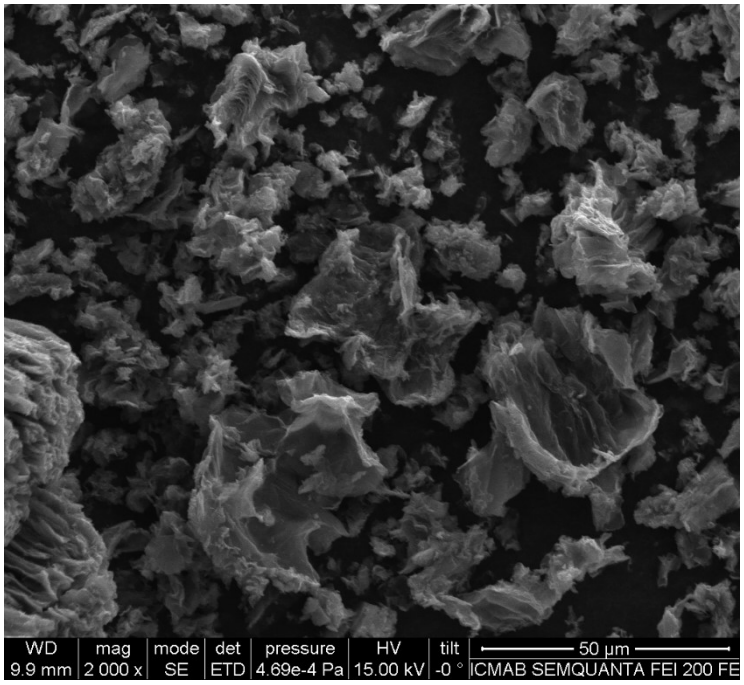


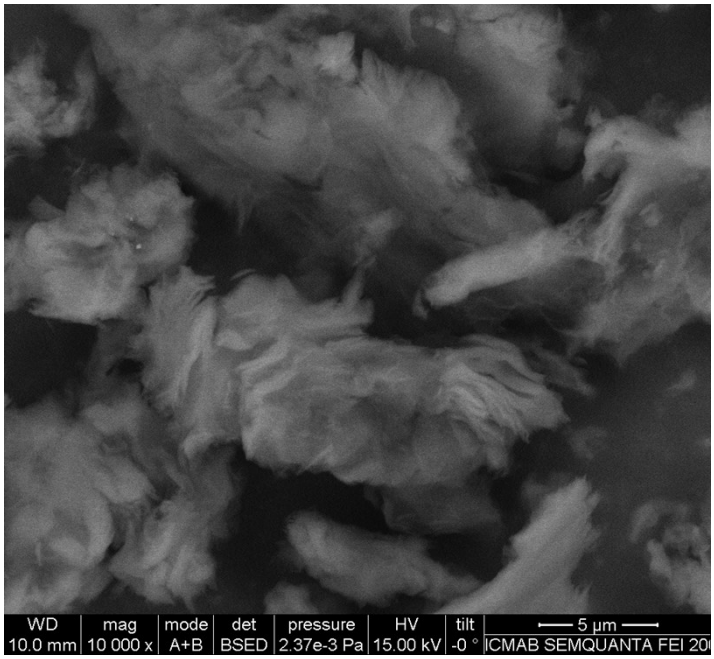
Figure S10. SEM images of a) rGO support and b) rGO@*trans*-**3**.

a)





b)


WD
10.0 mm
mag
10 000 x
mode
A+B
det
BSED
pressure
2.37e-3 Pa
HV
15.00 kV
tilt
-0 °
5 µm
ICMAB SEMQUANTA FEI 20

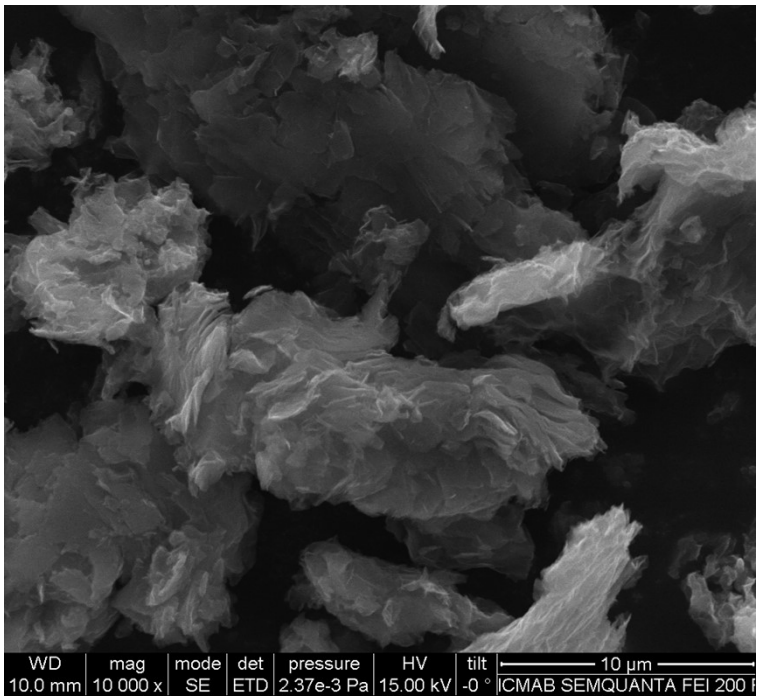

WD
10.0 mm
mag
10 000 x
mode
SE
det
ETD
pressure
2.37e-3 Pa
HV
15.00 kV
tilt
-0 °
10 µm
ICMAB SEMQUANTA FEI 200

Figure S11. DPV of **rGO@*trans*-2** in in CH_2Cl_2 containing 0.1 M *n*-Bu_4NPF_6 (TBAH) vs SCE.

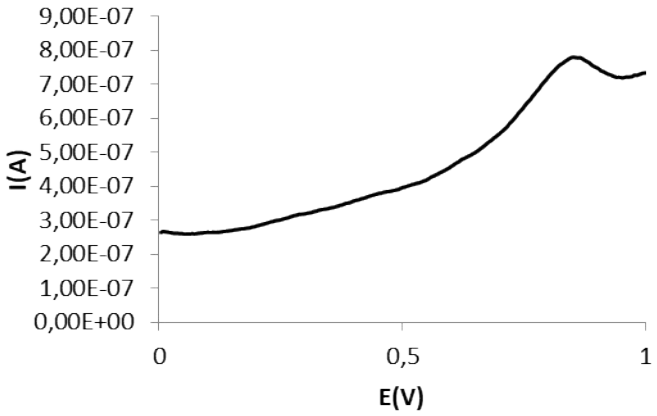


Figure S12. Plot of yield as a function of time for the photoredox catalysis of 1-benzylalcohol using rGO-*trans*-**3** as photocatalyst. The blue curve shows the substract yield after 3h and 6 h of reaction time in presence of catalyst. The red curve shows the dependence of substract yield with the reaction time after the catalyst was removed at 3h. Conditions: rGO-*trans*-**3** (0,25 mM), substrate (25 mM), $Na_2S_2O_8$ (75 mM), 3ml water (phosphate buffer pH 6.8), 6h h of catalysis at RT. light irradiation using a lamp with λ= 400-700 nm.