

*Caracterización de
cristales moleculares
por RMN de sólidos*

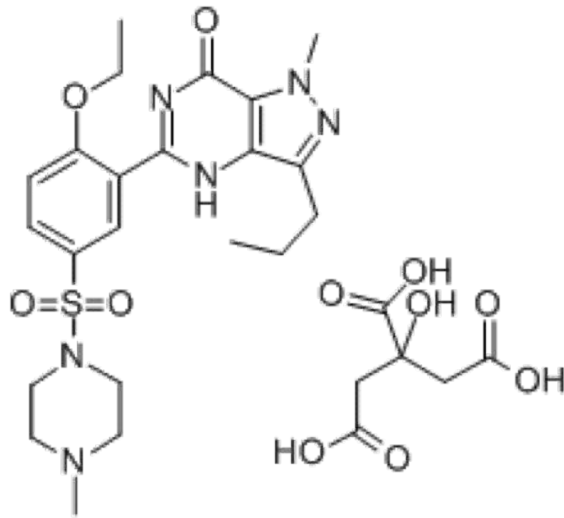
Braulio Rodriguez-Molina, PhD
IQ-UNAM



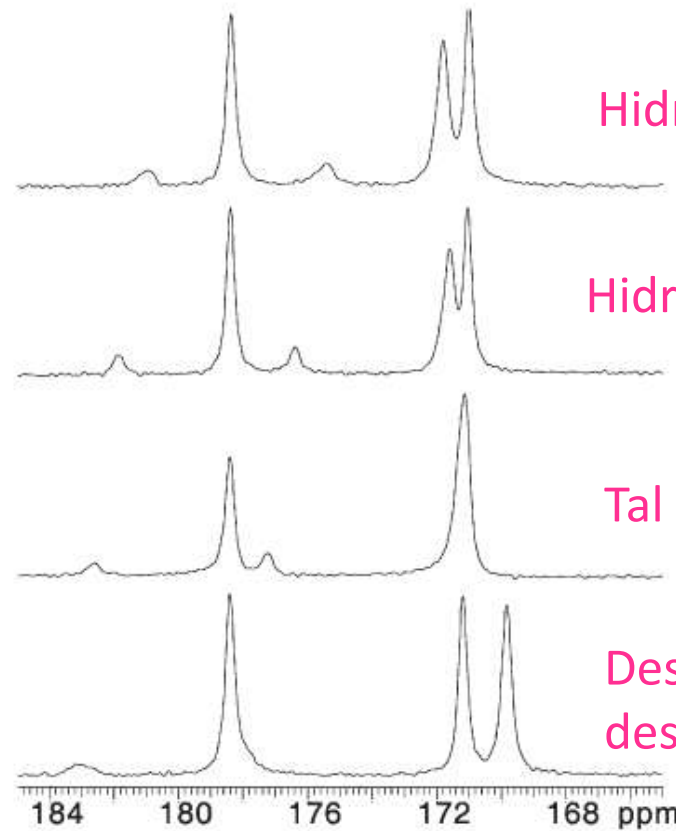
RMN de sólidos como herramienta valiosa de caracterización

- ✓ Identificación de polimorfos
- ✓ Transformaciones inducidas (temperatura, luz)
- ✓ Movimiento al interior de los cristales

Estudio de hidratos por RMN de sólidos



El agua se asocia con uno de los grupos carboxilo del citrato



Hidratado por 7 días a 88% RH

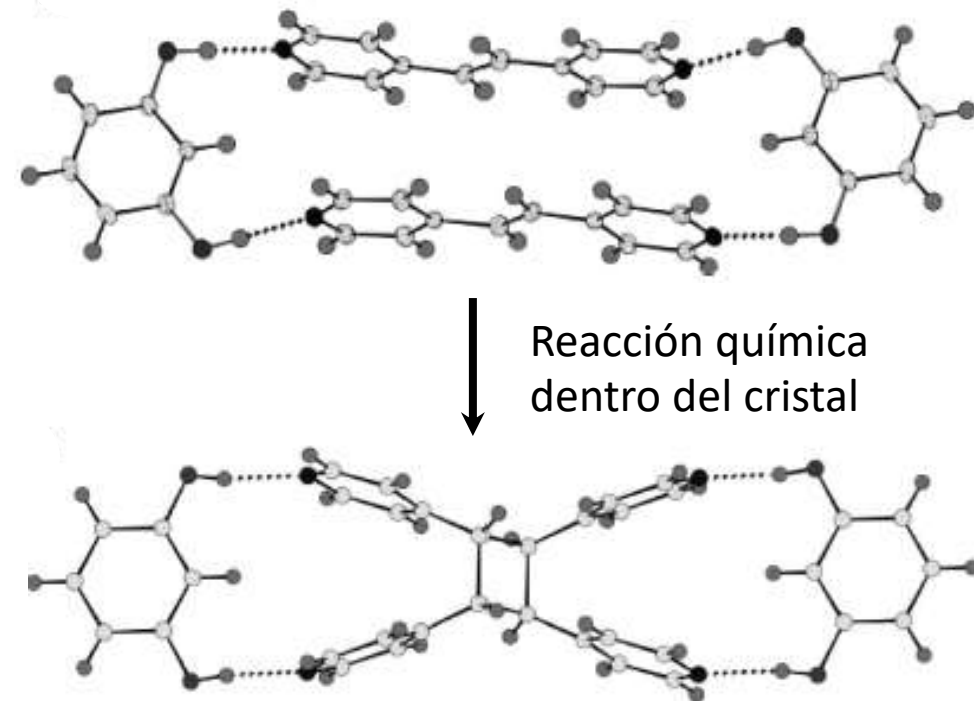
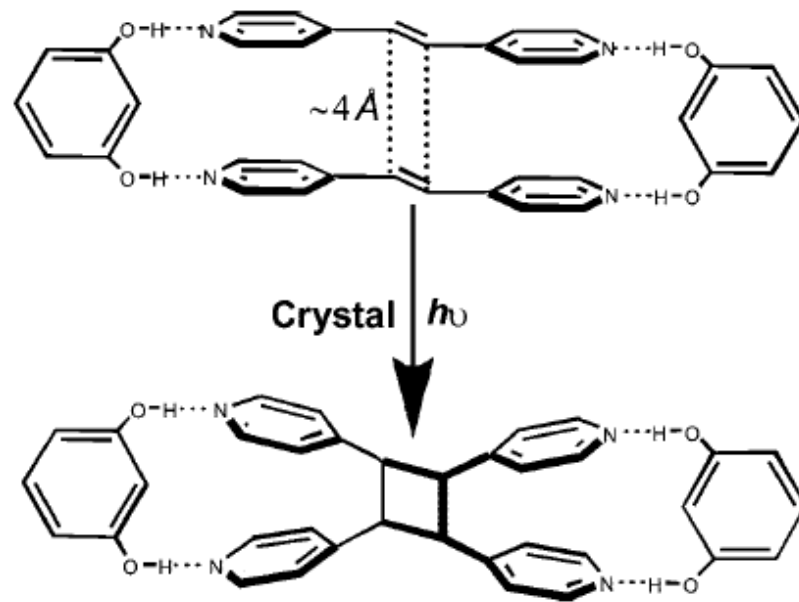
Hidratado por 3.5 días a 88% RH

Tal y como fue recibido

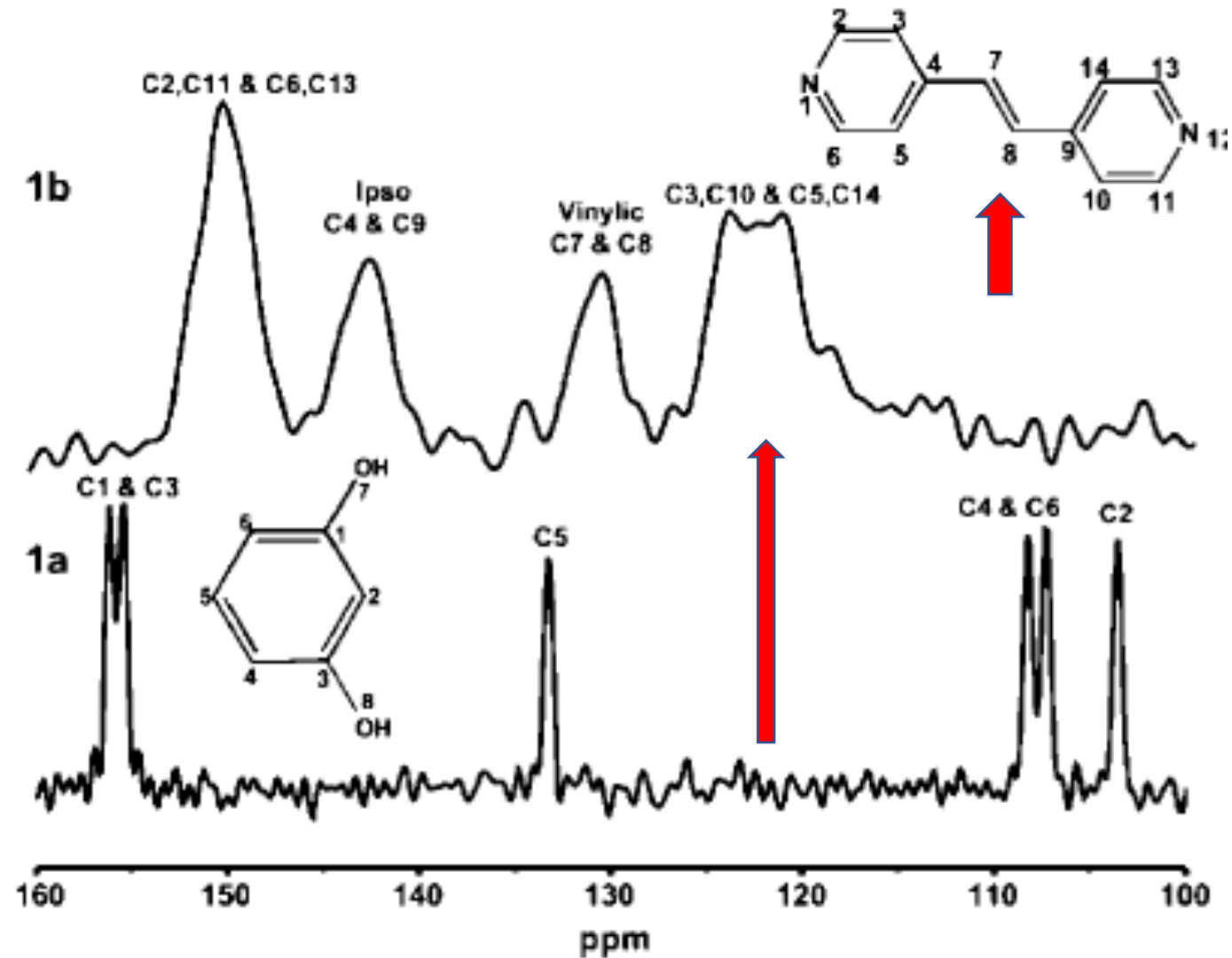
Deshidratado sobre un agente desecante por 7 días

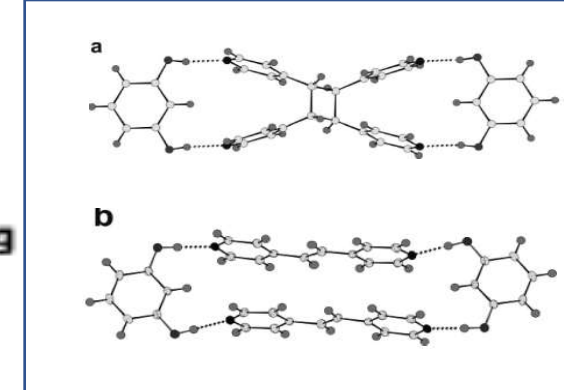
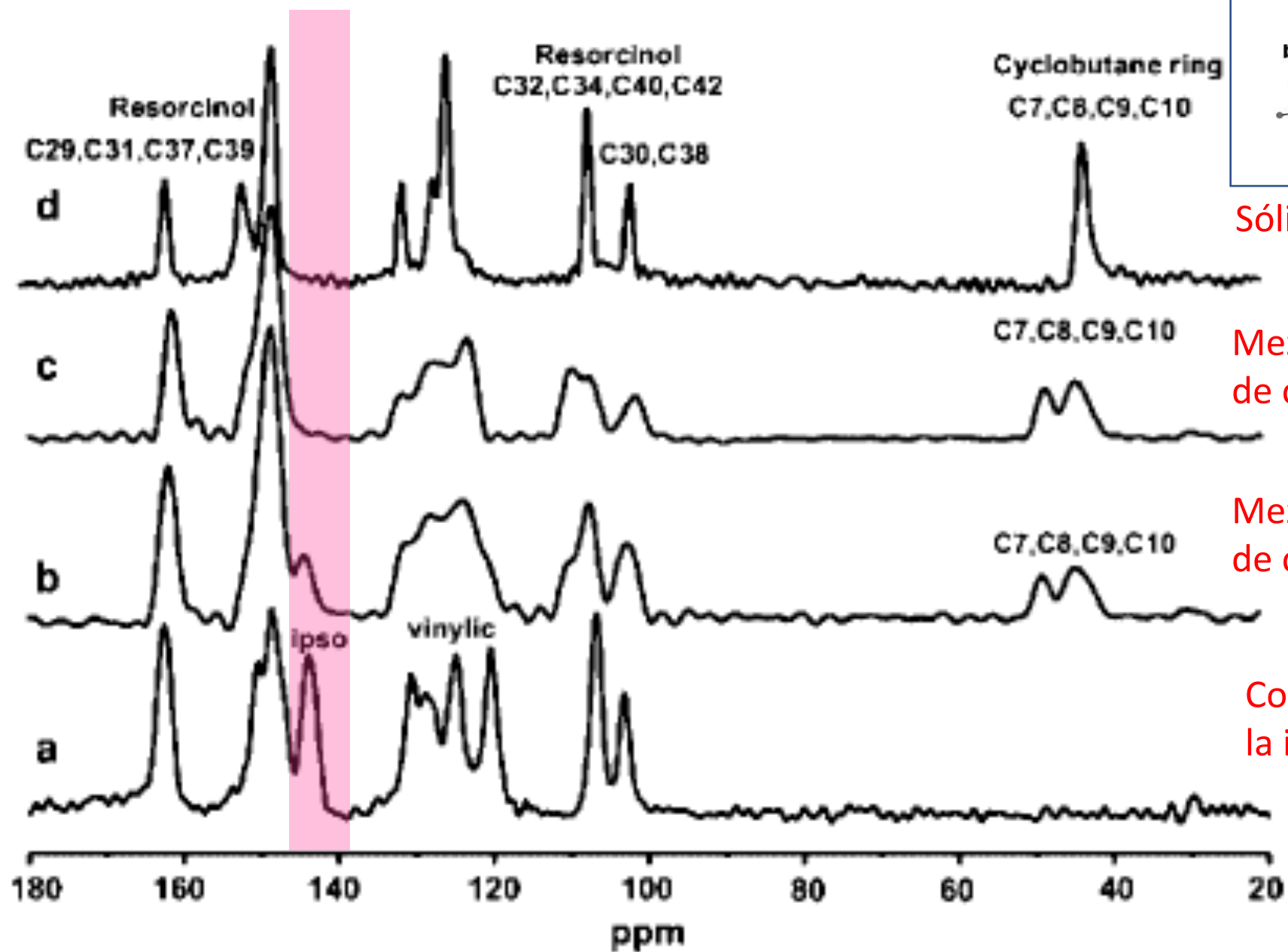
^{13}C CPMAS de diferentes hidratos del citrato de sildenafil

Foto-transformaciones SC-SC



^{13}C CPMAS de los precursors individuales





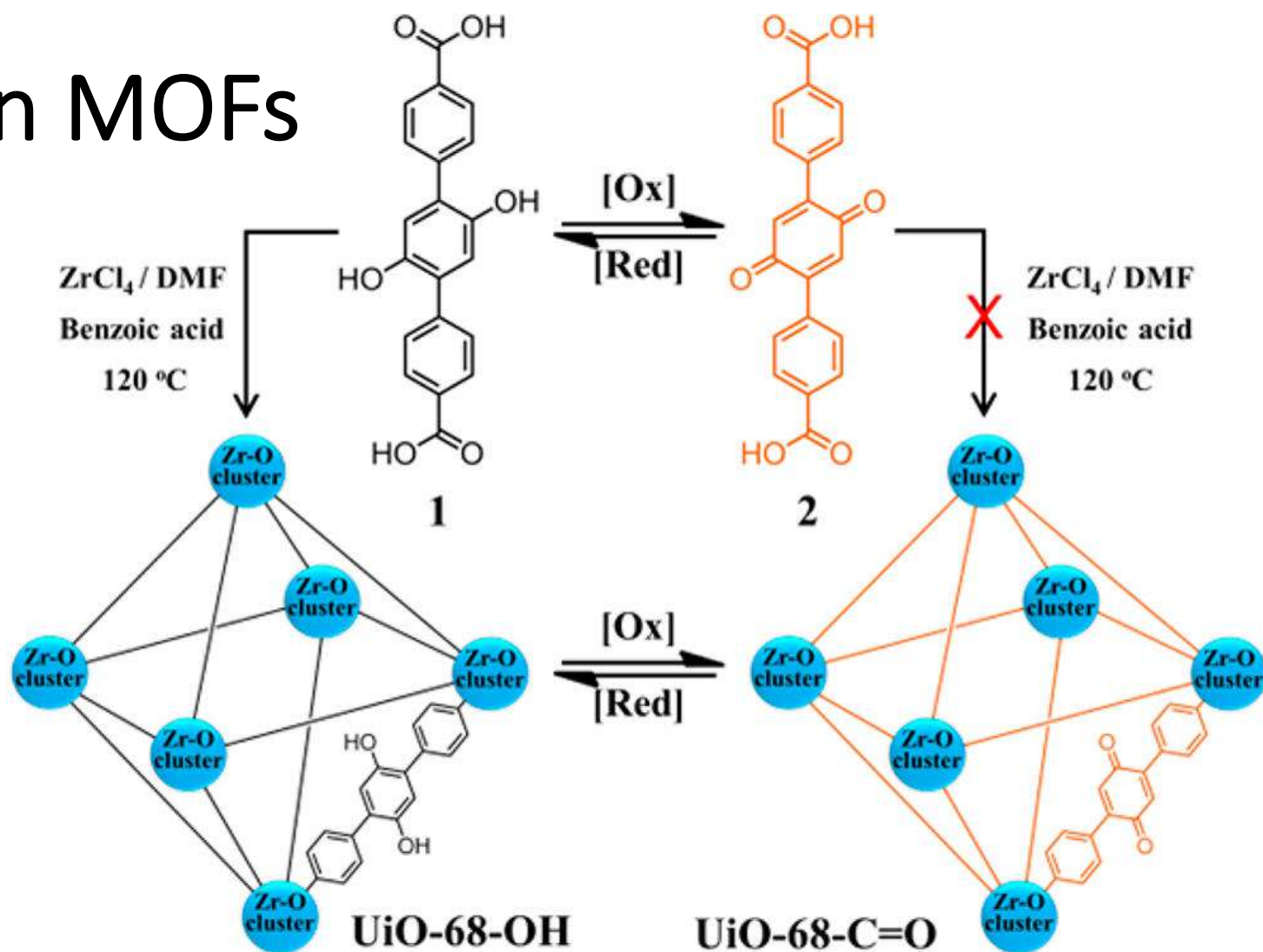
Sólido Recristalizado

Mezcla con 100% de conversión

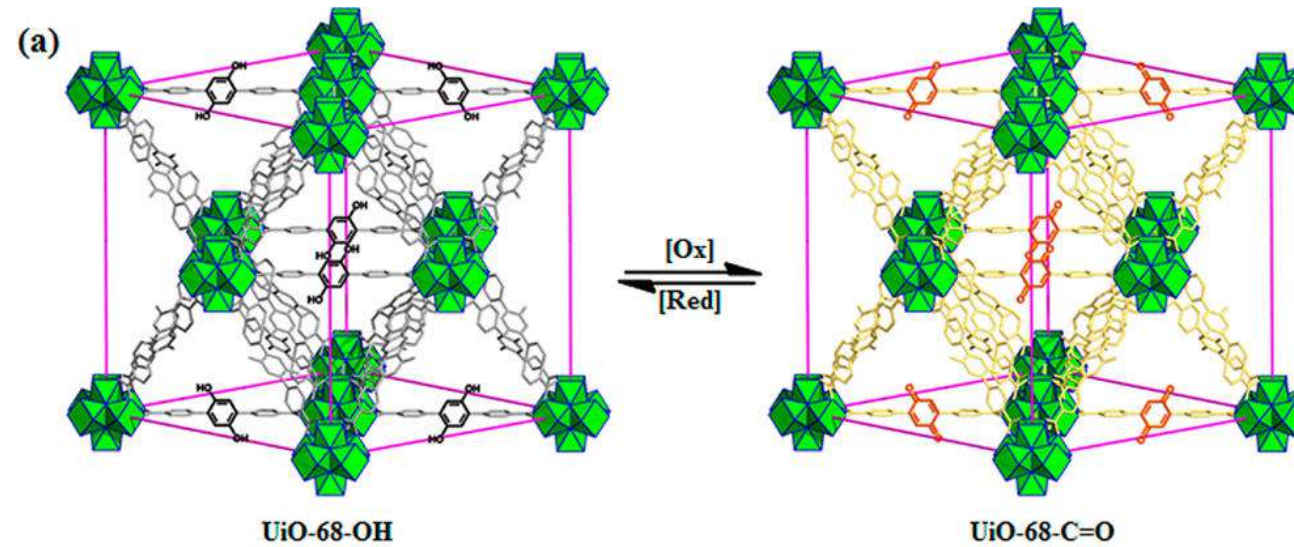
Mezcla con 50% de conversión

Co-cristal antes de la irradiación

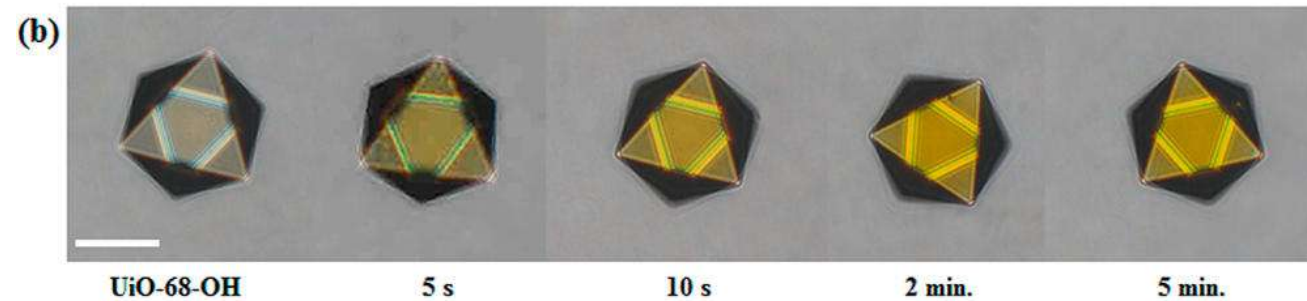
Redox en MOFs



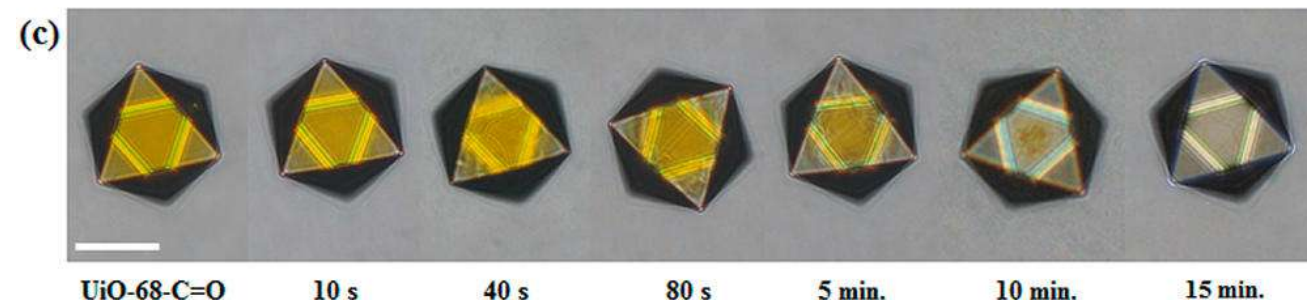
Proceso redox en MOFs



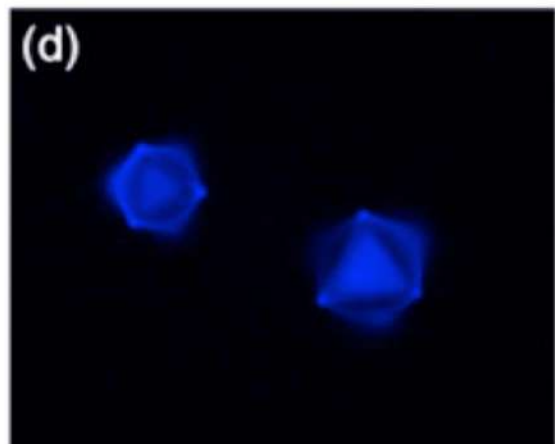
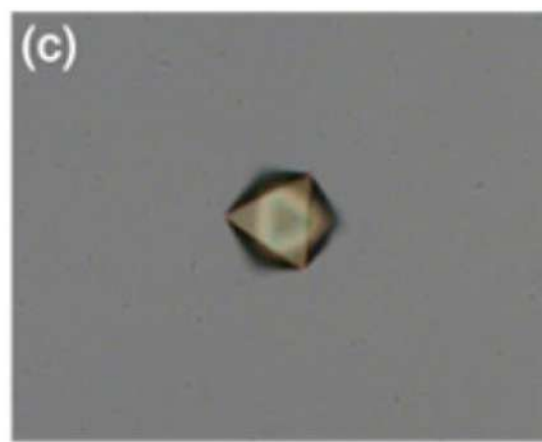
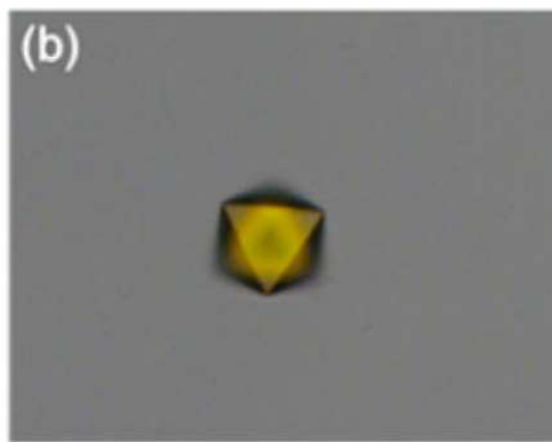
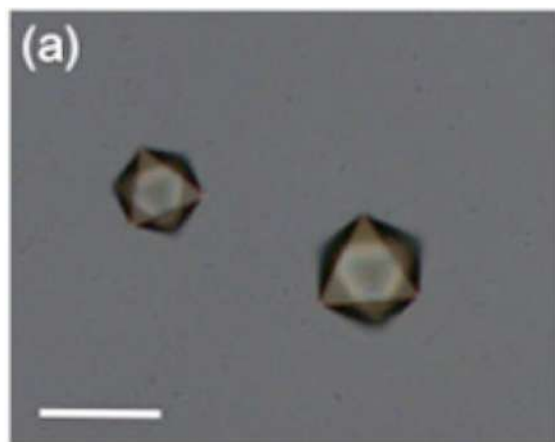
Oxidación



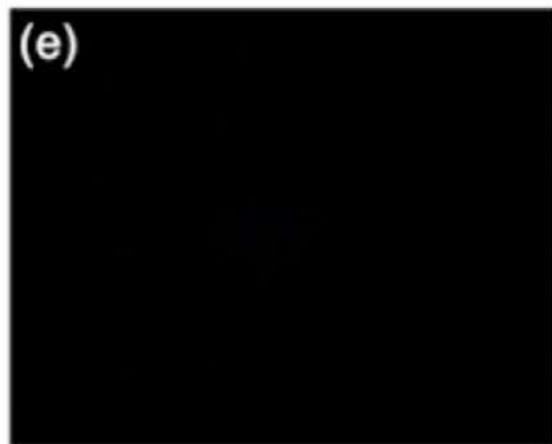
Reducción



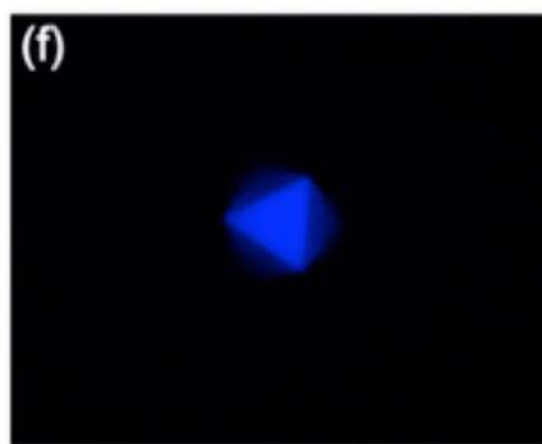
Cambios en fluorescencia



UiO-68-OH

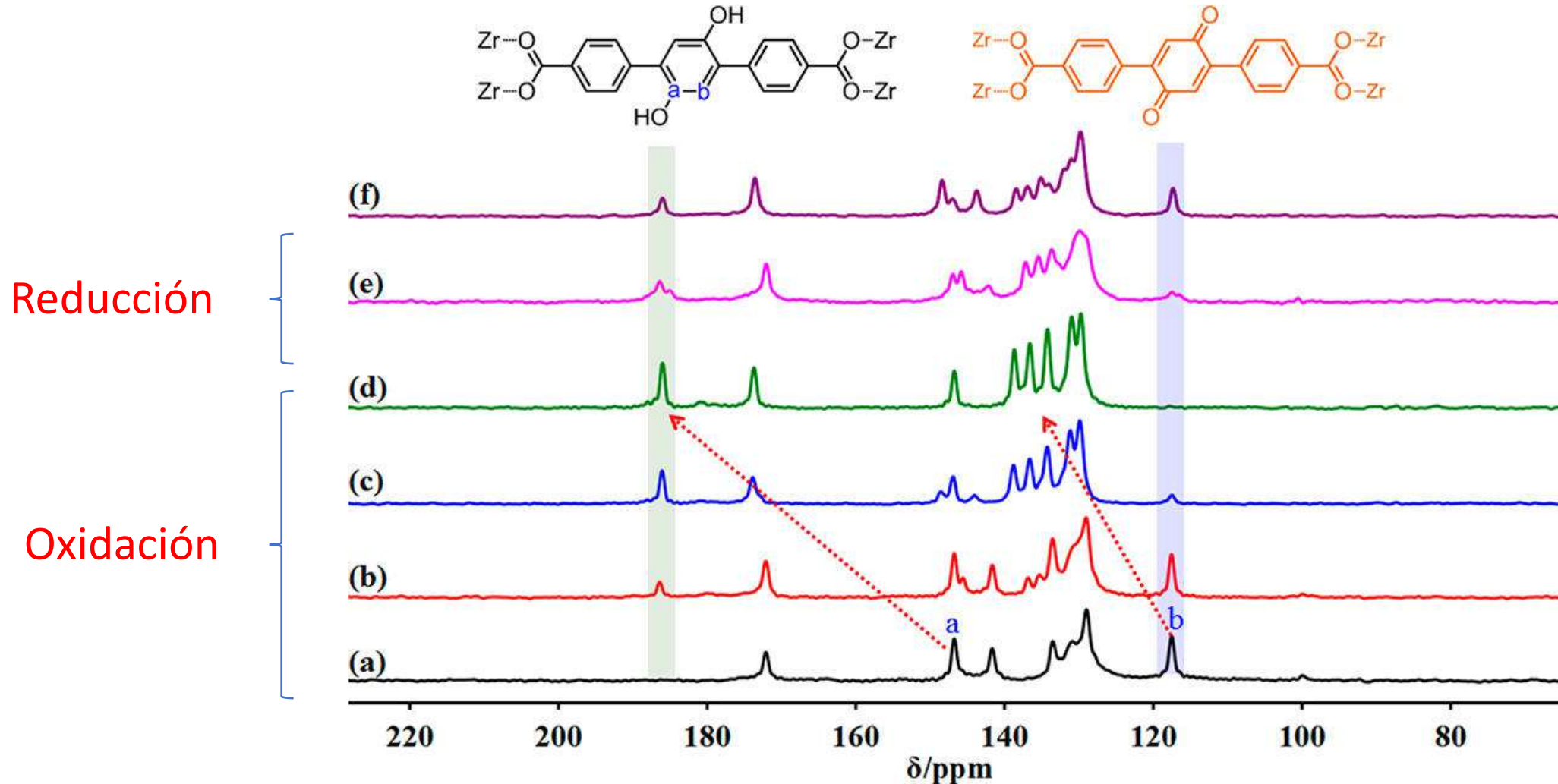


UiO-68-C=O



UiO-68-OH(R)

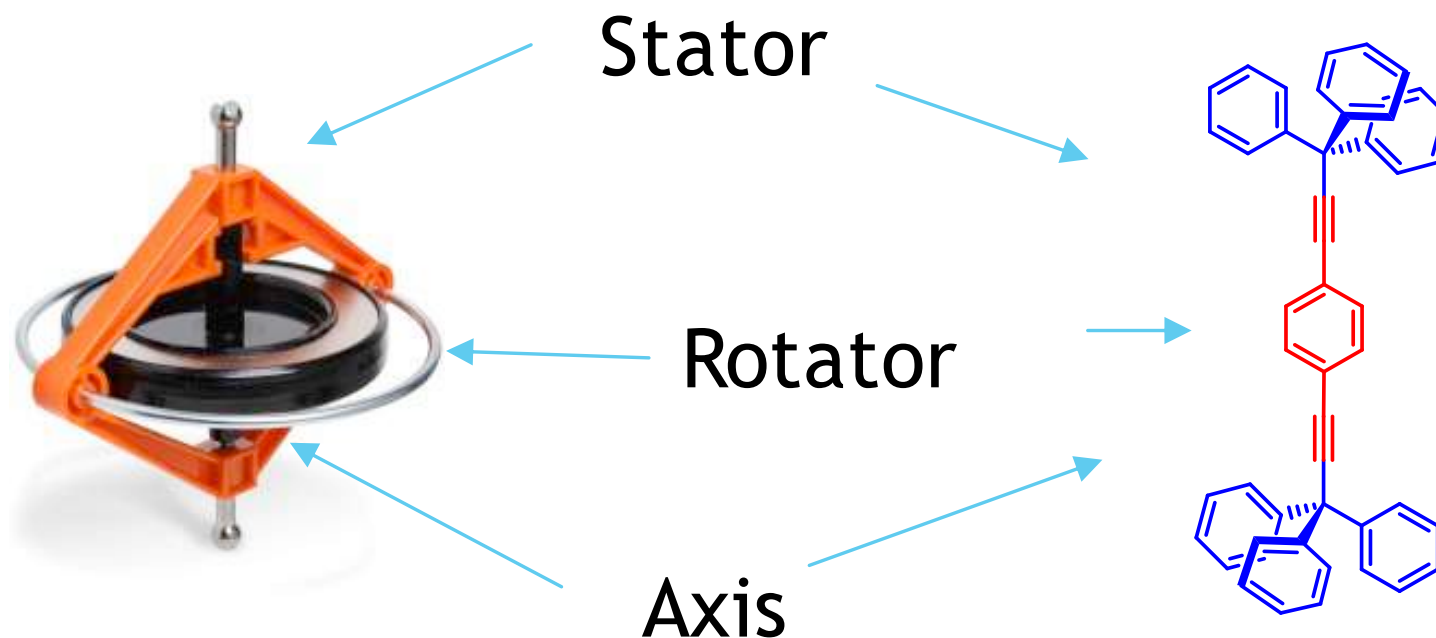
Seguimiento y reversibilidad de de la reacción en MOFs



Movimiento al interior de los cristales

¿Cómo perdemos el tiempo en el lab?

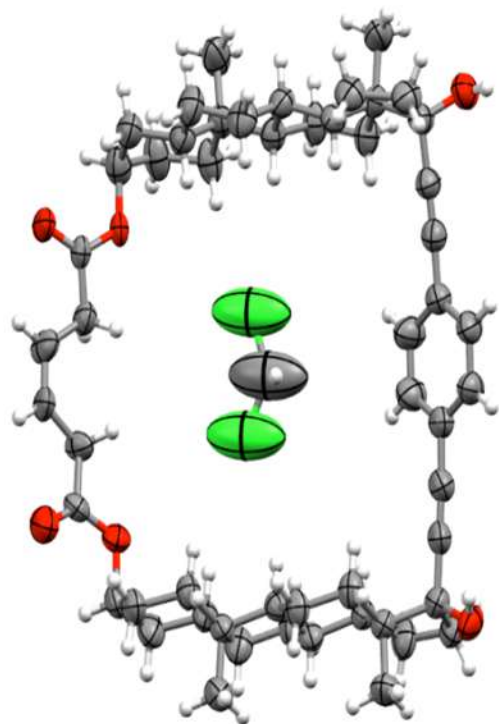
Rotores moleculares cristalinos



Vogelsberg, C. S.; Garcia-Garibay, M. A. *Chem. Soc. Rev.*, **2012**, 41, 1892.

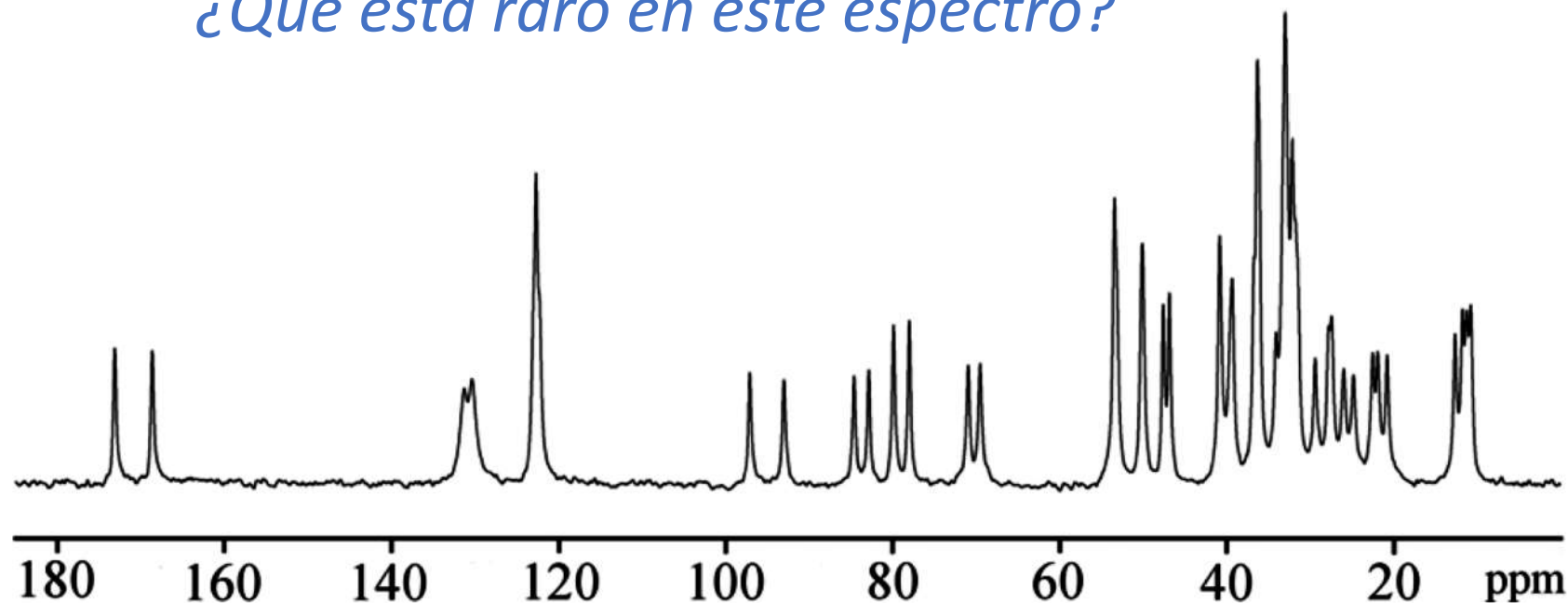
Rodríguez-Molina, B.; Ochoa, M. E. ; Farfán, N.; Santillán, R.; Garcia-Garibay, M. A. *J. Org. Chem.*, **2009**, 74, 8554

Un poco de historia...



$Z'=1$

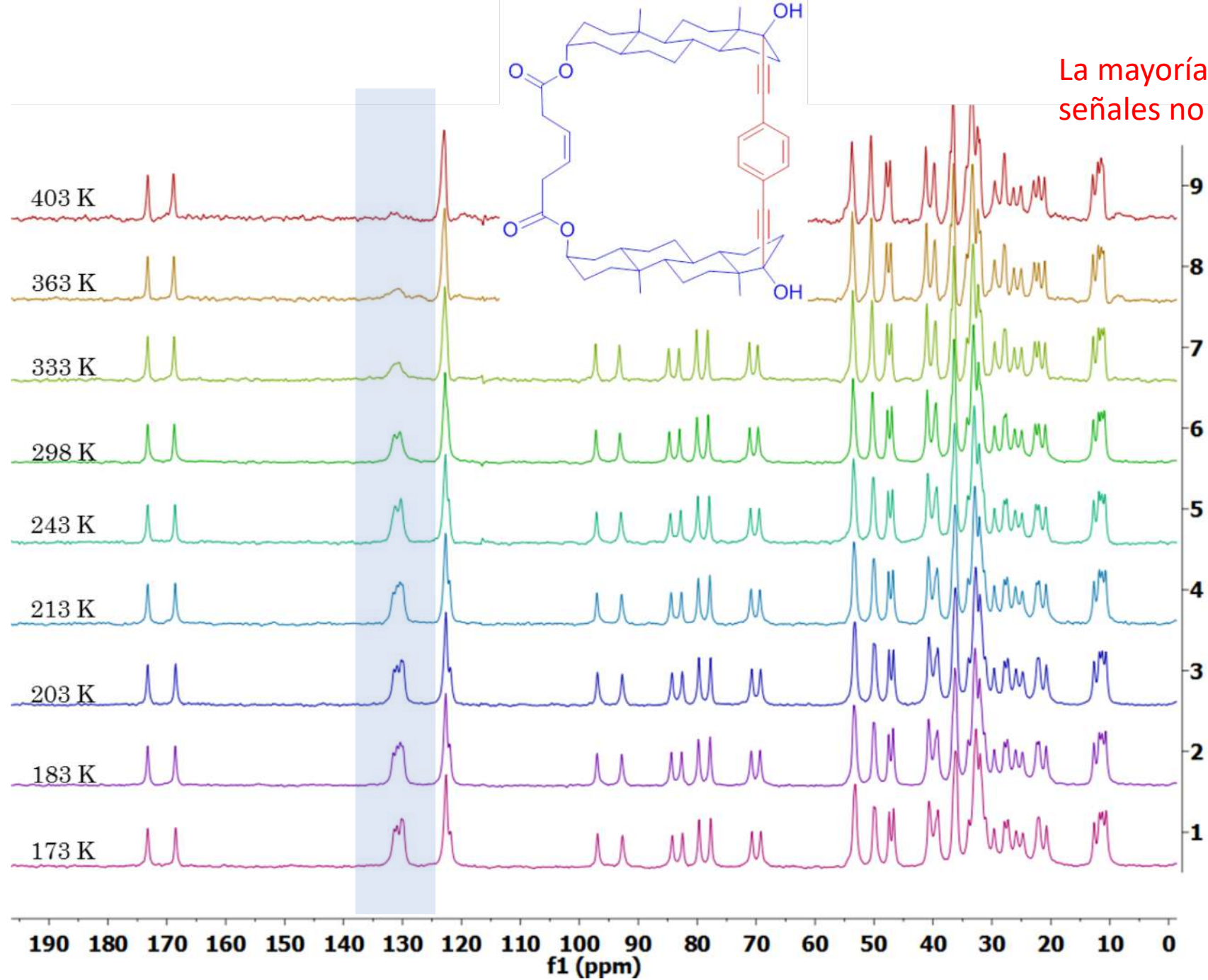
¿Qué está raro en este espectro?

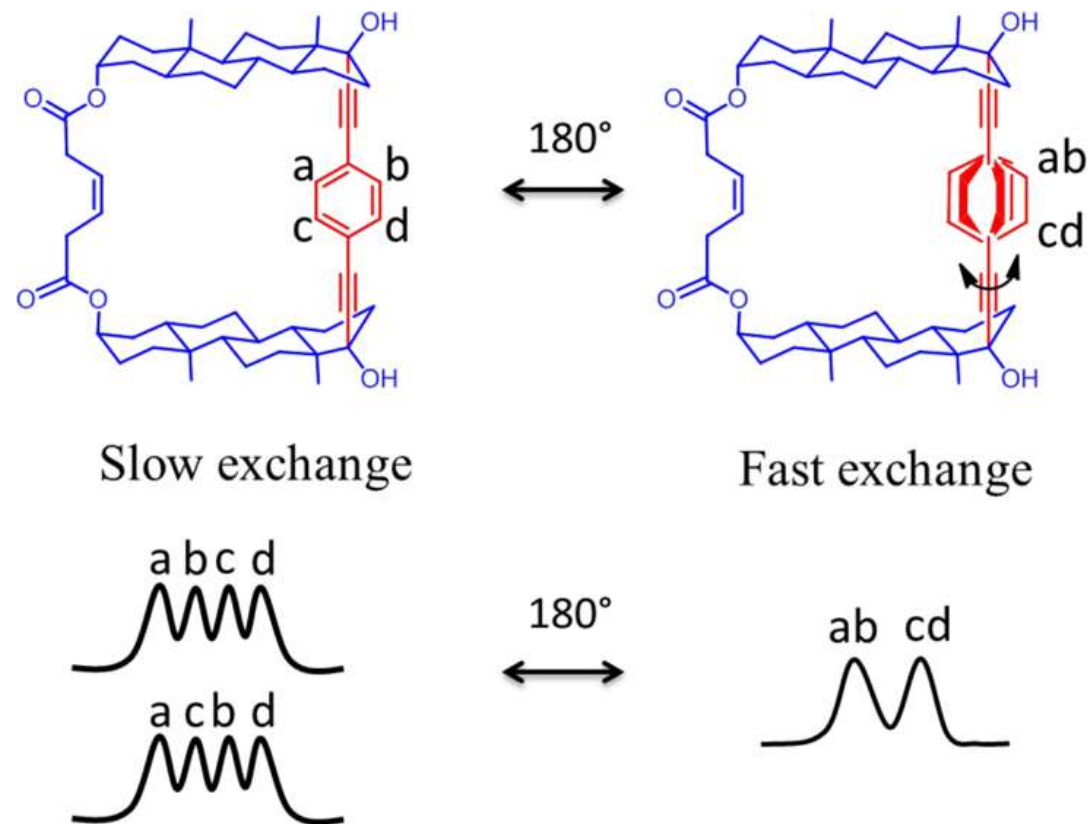
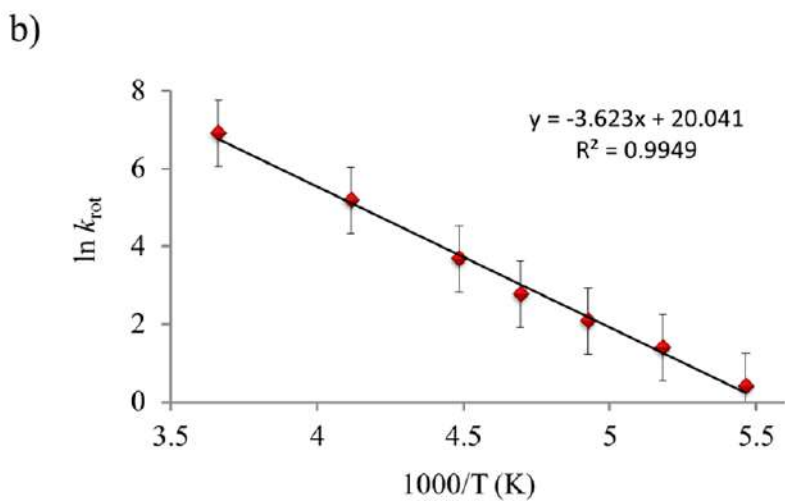
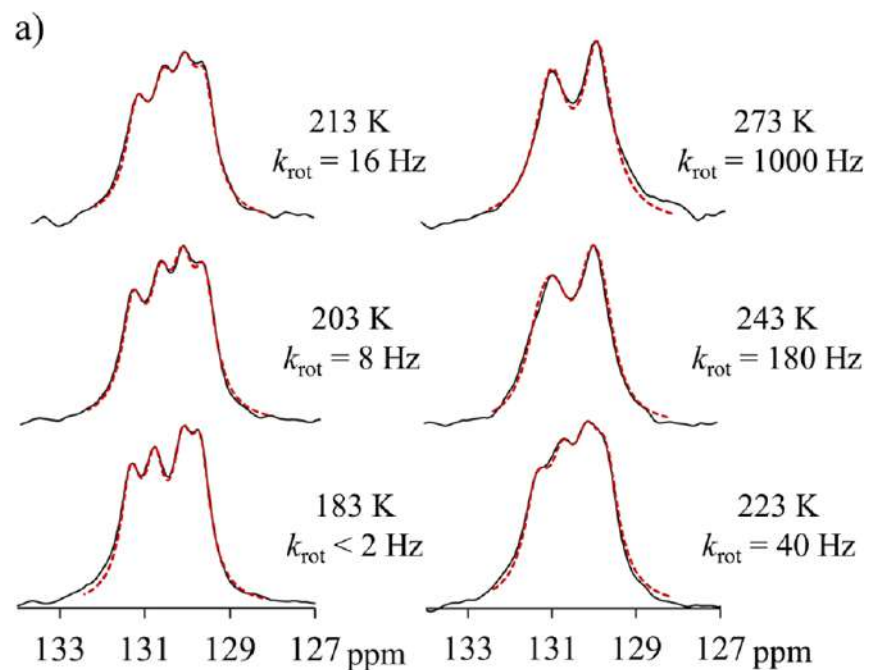


Czajkowska-Szczykowska, D.; **Rodríguez-Molina, B.**; Magaña-Vergara, N. E.; Santillan, R.; Morzycki, J. W.; Garcia-Garibay, M. A. *J. Org. Chem.* **2012**, 77, 9970

Alta
temperatura

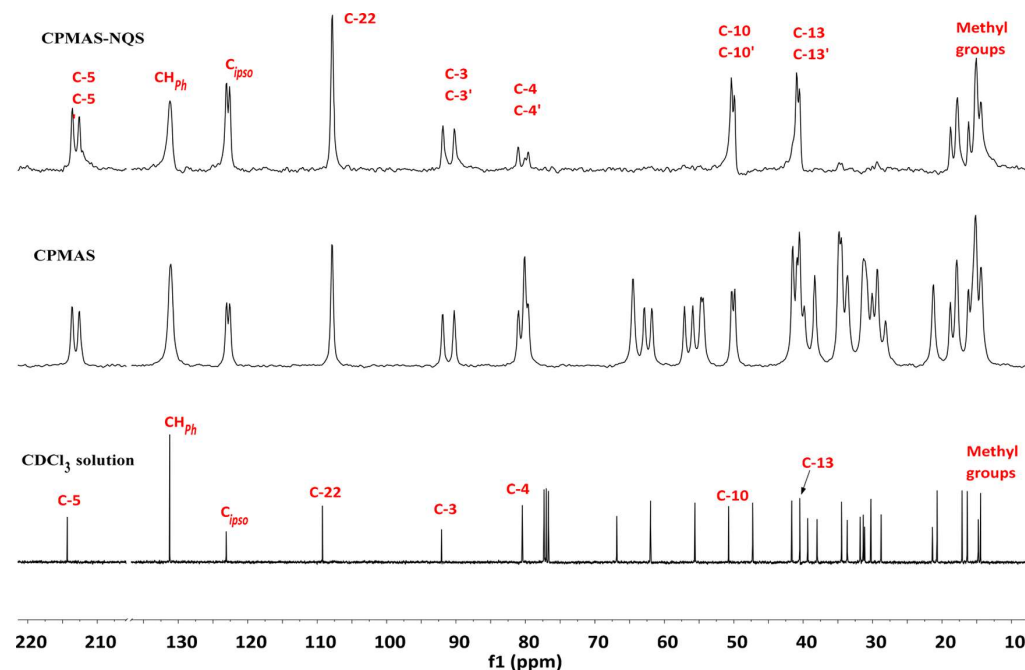
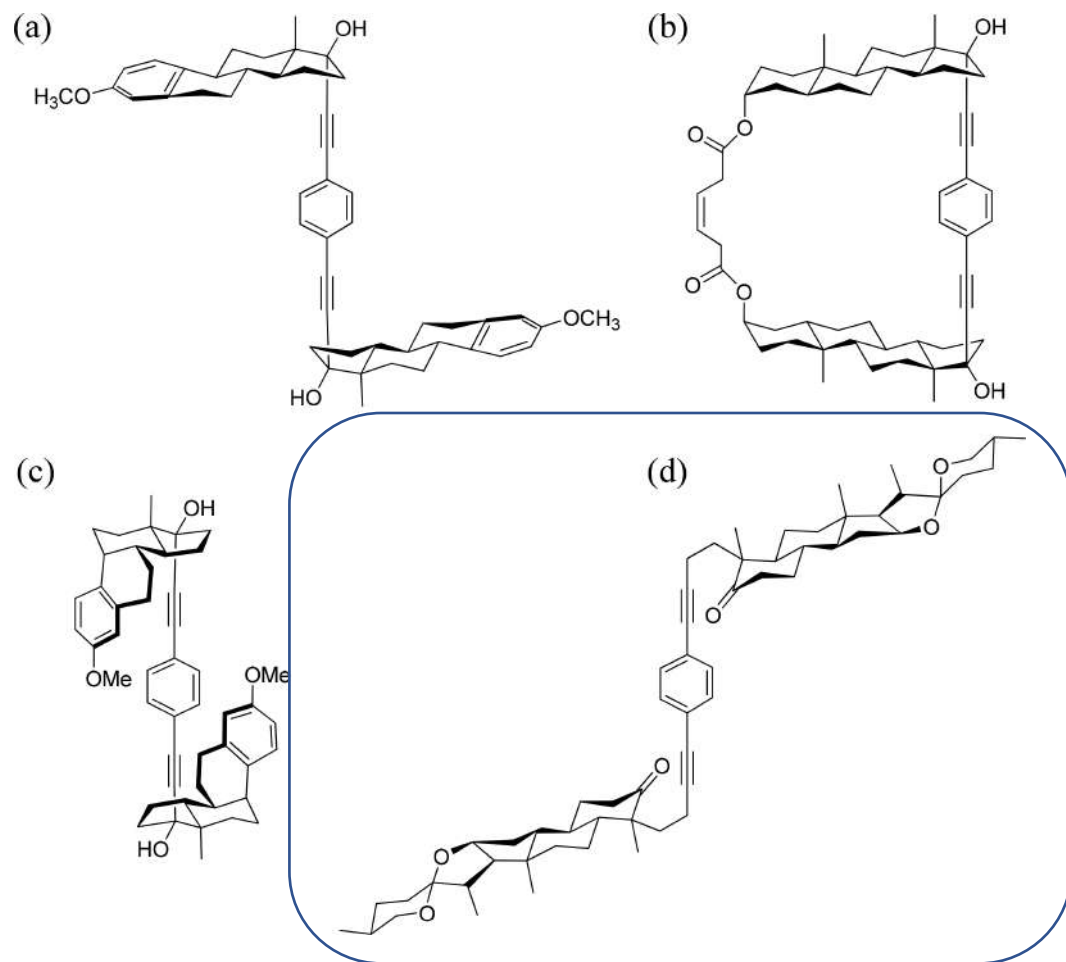
Baja
temperatura





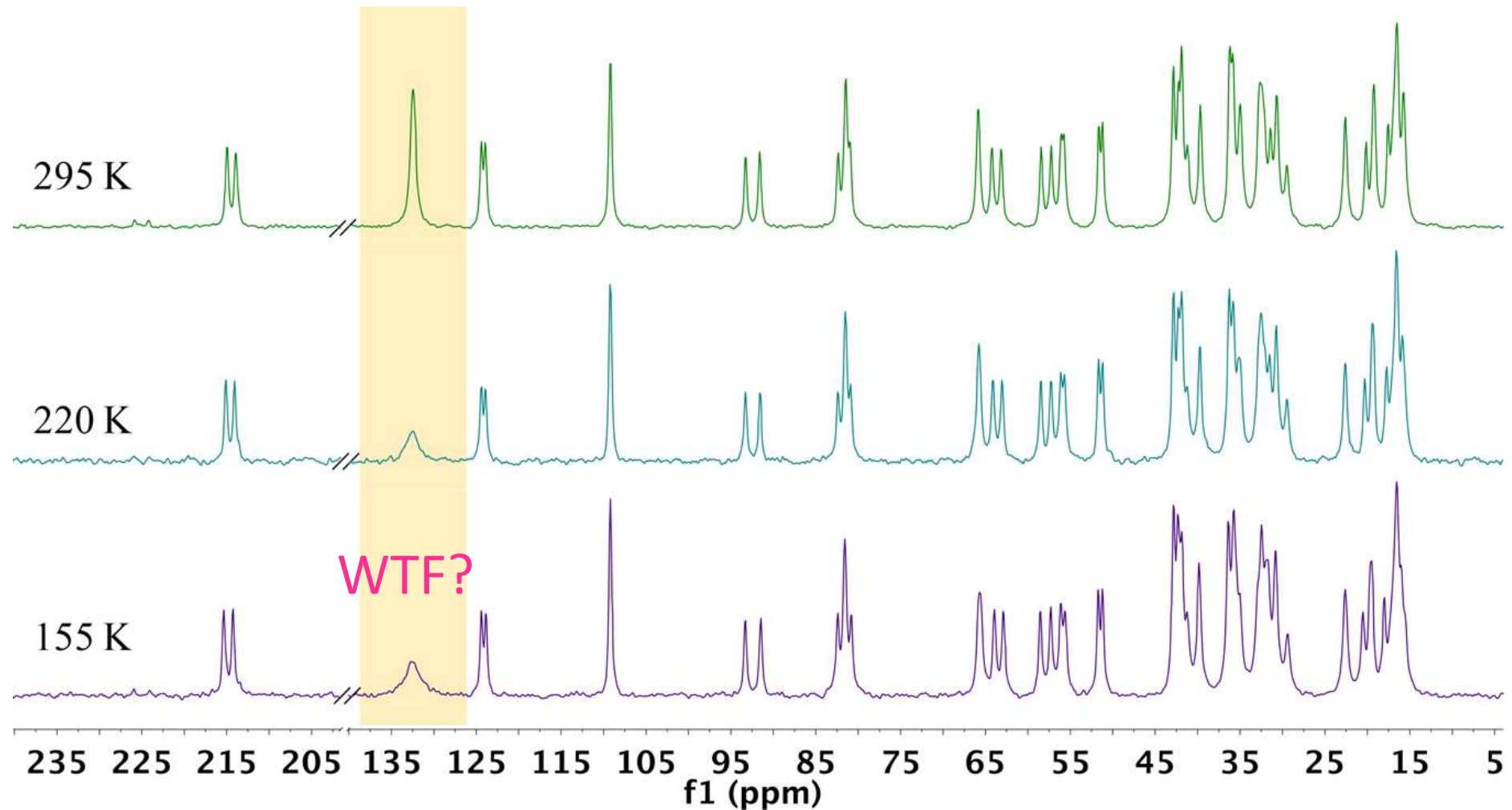
Czajkowska-Szczykowska, D.; **Rodríguez-Molina, B.**; Magaña-Vergara, N. E.; Santillan, R.; Morzycki, J. W.; Garcia-Garibay, M. A. *J. Org. Chem.* **2012**, 77, 9970

Rotores de esteroide 4a generación



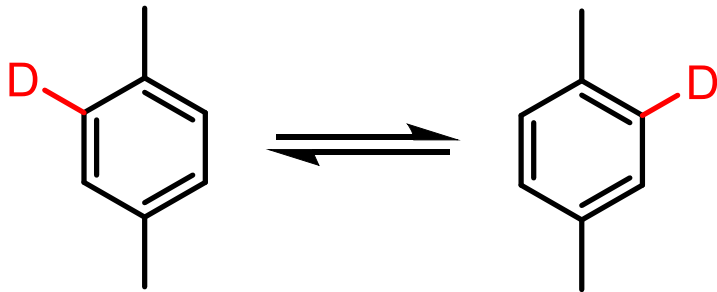
Mayorquin-Torres, Martha Cristina; Colin-Molina, Abraham; Pérez-Estrada, Salvador; Galano, Annia, **Rodríguez-Molina, B.**; Iglesias-Arteaga, Martín A.* *J. Org. Chem.* **2018**, 83, 3768.

Cuando VT ^{13}C CPMAS no es suficiente



¿Cómo se mide un movimiento más rápido en cristales?

Sintetizar derivados deuterados



Measure the internal dynamics in the MHz frequency by solid state ^2H Nuclear Magnetic Resonance

ULTRAFAST!

FAST

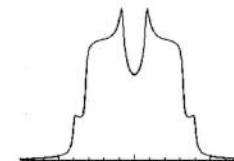
SLOW

Lineshape analysis

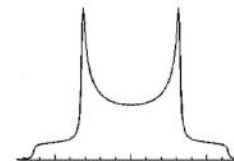
Temperature



> 10 MHz



~ 6 MHz

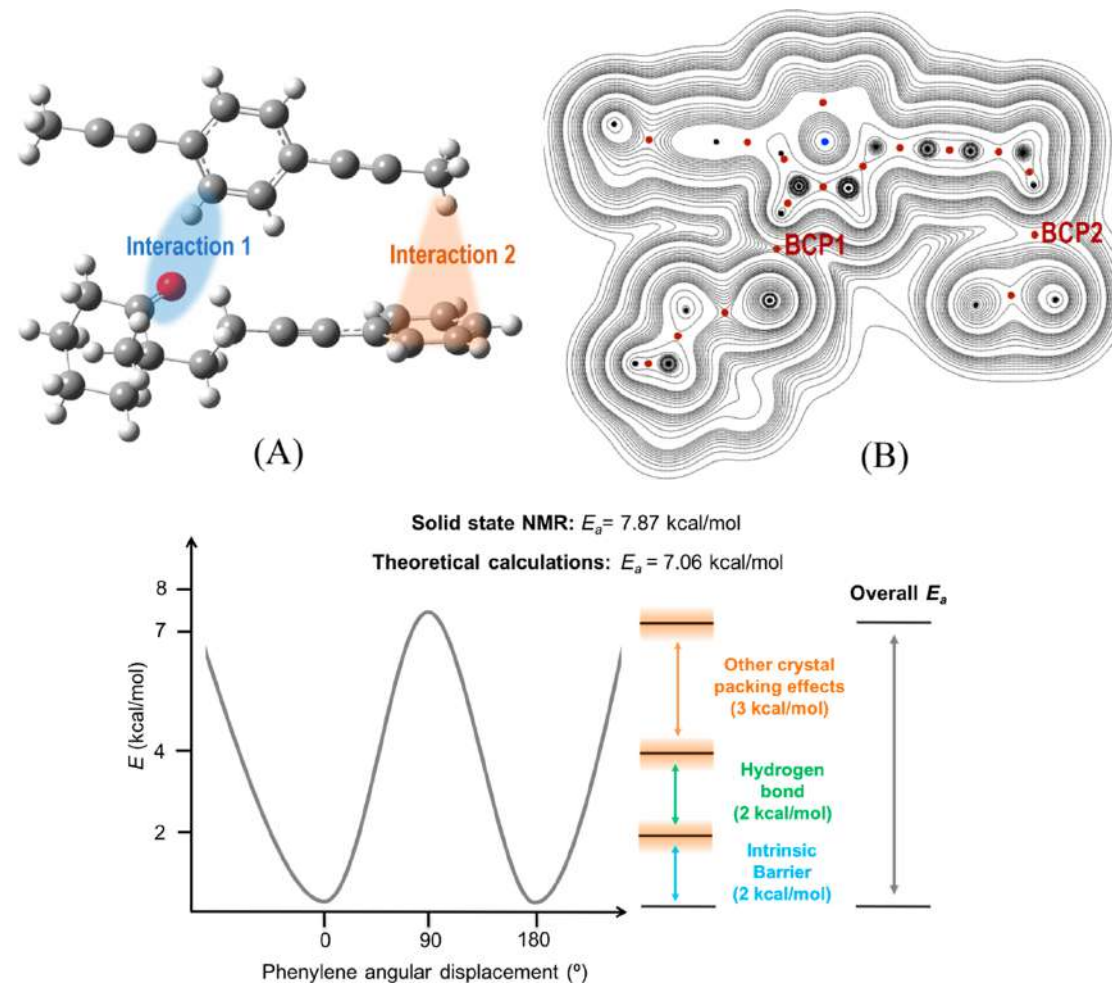
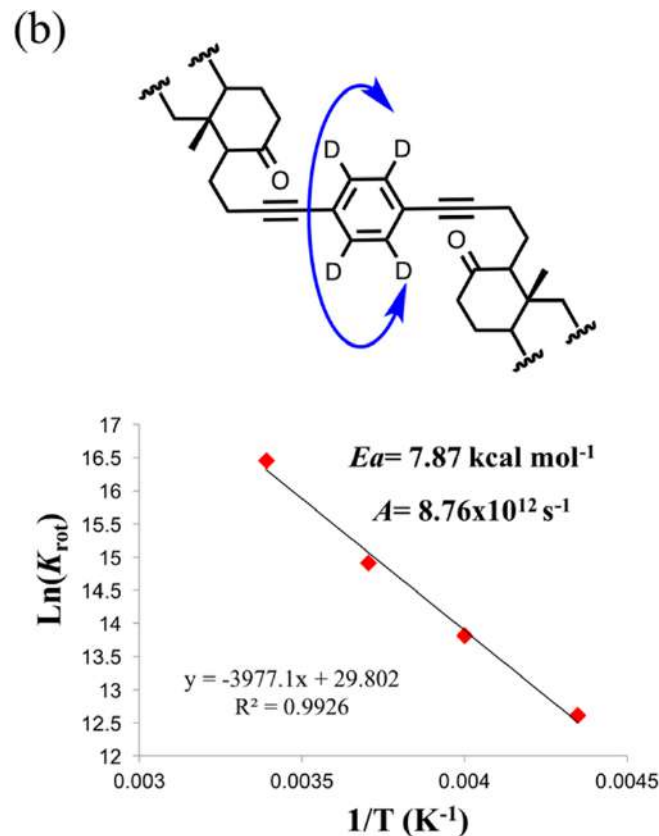
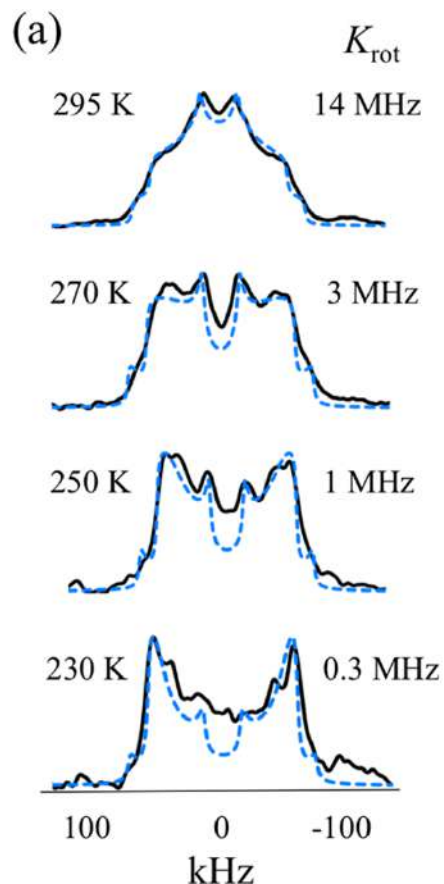


< 0.1 MHz



a) Nishikiori, S. I.; Soma, T.; Iwamoto, T. *J. Incl. Phenom. Mole. Recogn. Chem.*, **1997**, 27, 233. b) Macho, V; Brombacher, L; Spiess, H. W. *Appl. Magn. Reson.*, **2001**, 20, 405.

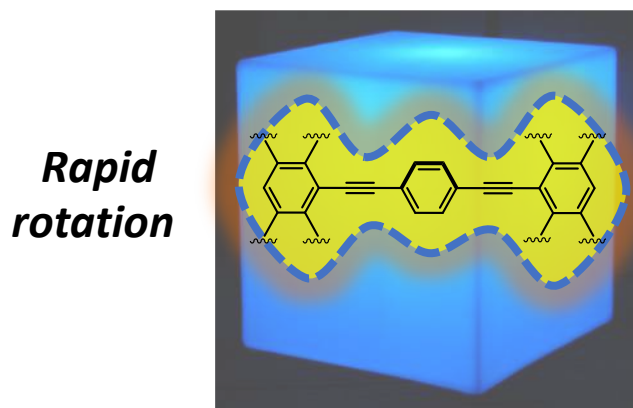
Mediciones de muestra deuterada



Mayorquin-Torres, Martha Cristina; Colin-Molina, Abraham; Pérez-Estrada, Salvador; Galano, Annia, **Rodríguez-Molina, B.**; Iglesias-Arteaga, Martín A. *J. Org. Chem.* **2018**, 83, 3768.

Our interest

- Design and synthesize conjugated crystalline materials with synergistic solid-state properties, including, but not limited to, intramolecular motion, fluorescence, gas sorption and more.



Emissive

Appropriate external stimuli

Possible applications

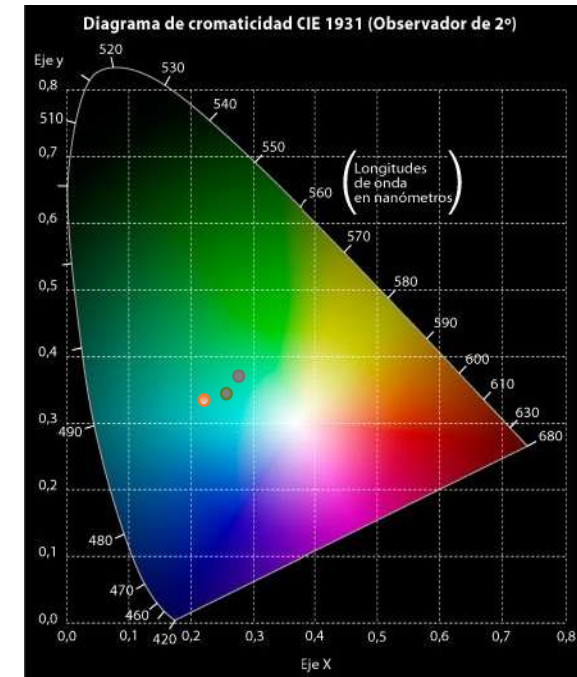


OLEDs

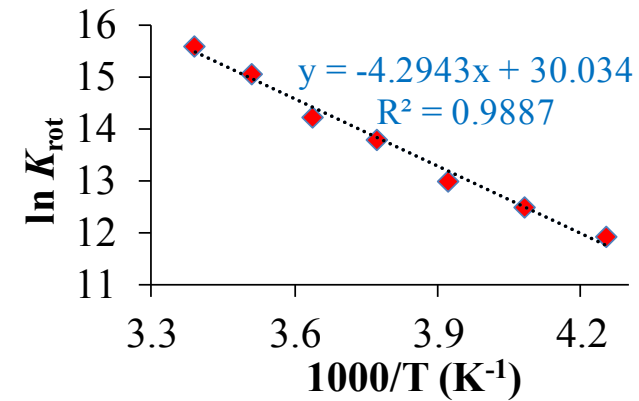
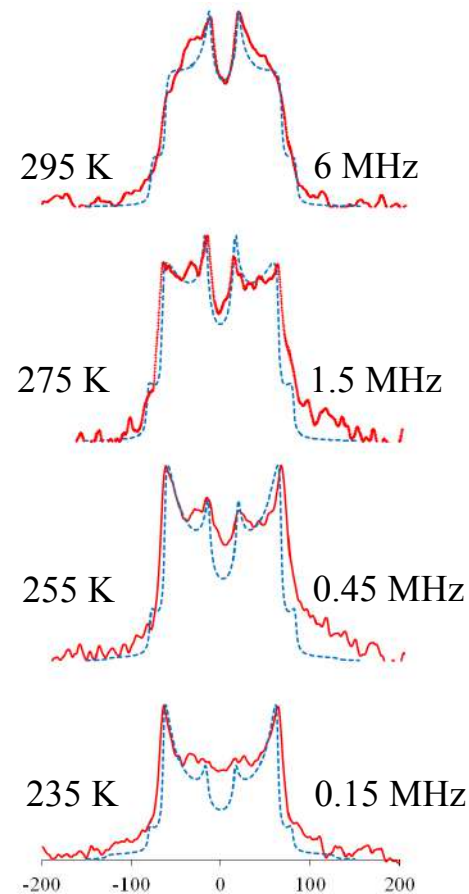
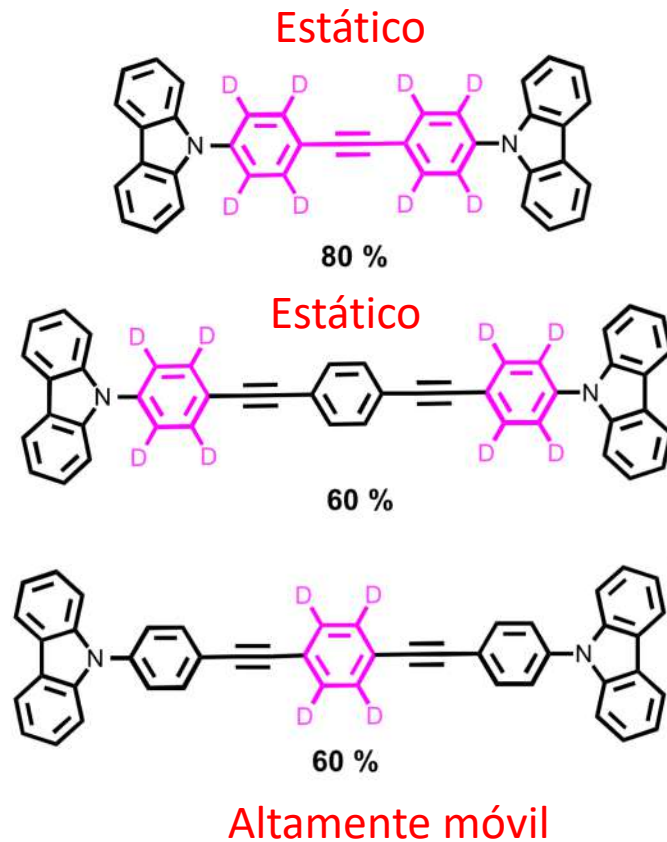


Solid state sensors

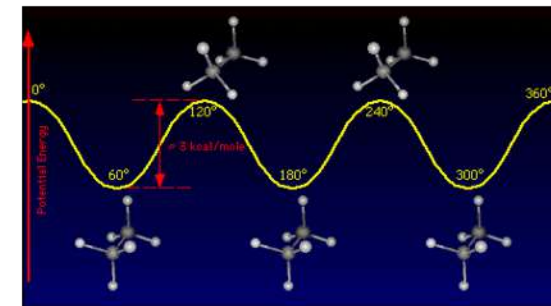
¿Cuál sería un uso de los rotores? OLEDs y WOLEDs



Rotores fluorescentes



Activation barrier to rotation:
8.5 kcal/mol



Activation barrier to rotation:
Aprox. 3 kcal/mol

Aguilar-Granda, A.; Pérez-Estrada, S.; Roa, Arian E.; Rodriguez-Hernandez, J.; Hernandez-Ortega, S.; Rodríguez, M.; **Rodríguez-Molina, B.** *Crystal Growth & Design*, **2016**, *16*, 3435.

Rotates alright, but does it show emission in the solid state?

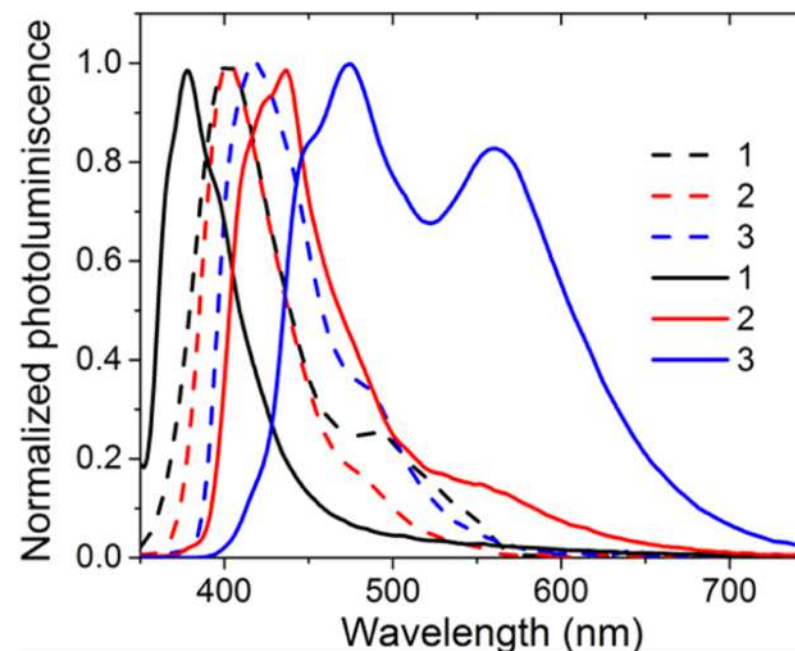
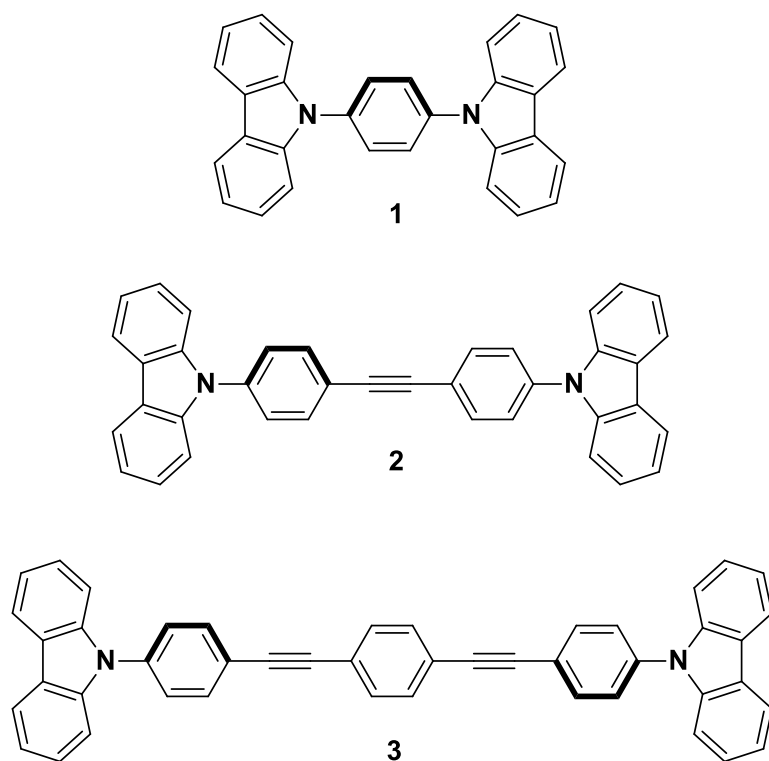
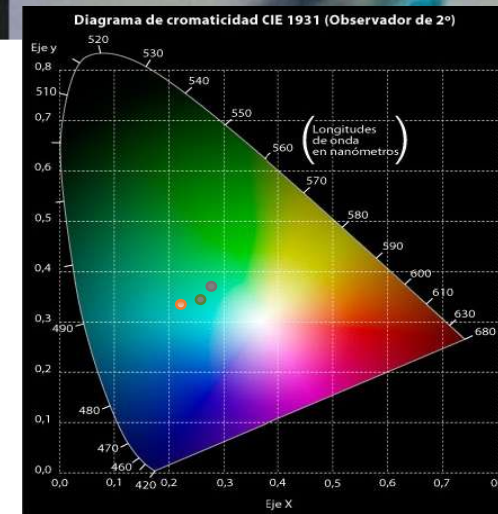
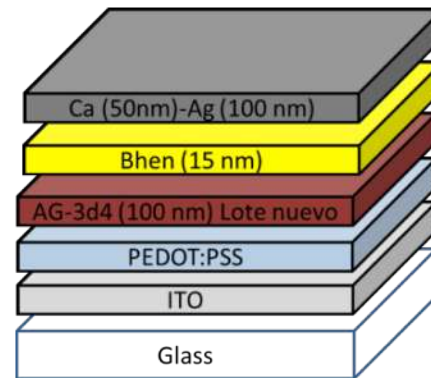
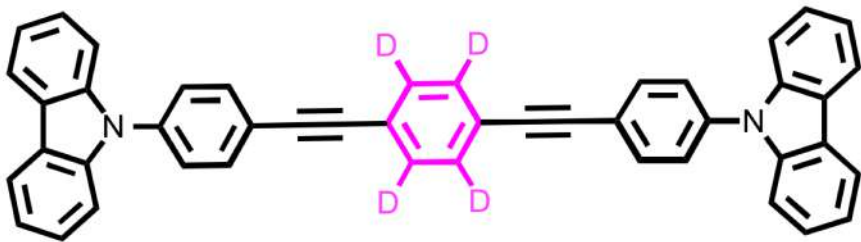


Table 2. Optical Properties of Compounds 1–3

compound	λ_{max} (nm) abs	λ_{em} (nm) PL in solution	Stokes shift (cm^{-1})	Φ solution	Φ powder
1	292	401	9.31×10^3	0.56	0.09
2	341	402	4.45×10^3	0.18	0.09
3	343	417	5.17×10^3	0.06	0.28

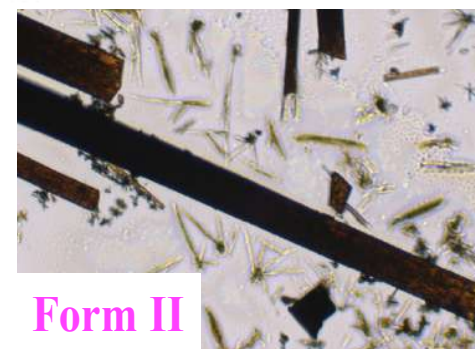
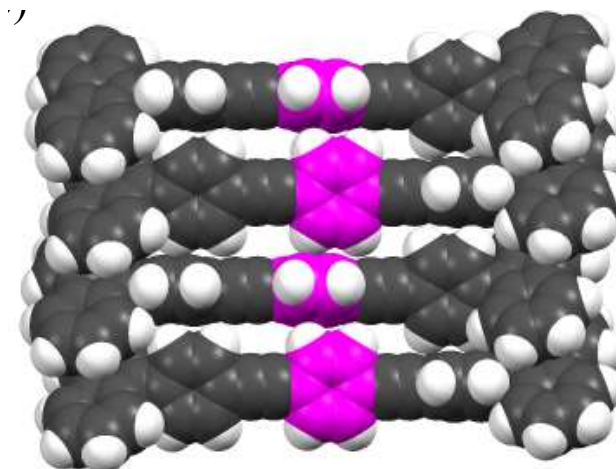
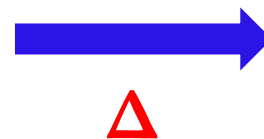
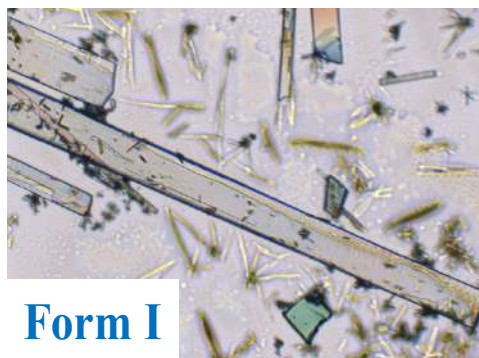
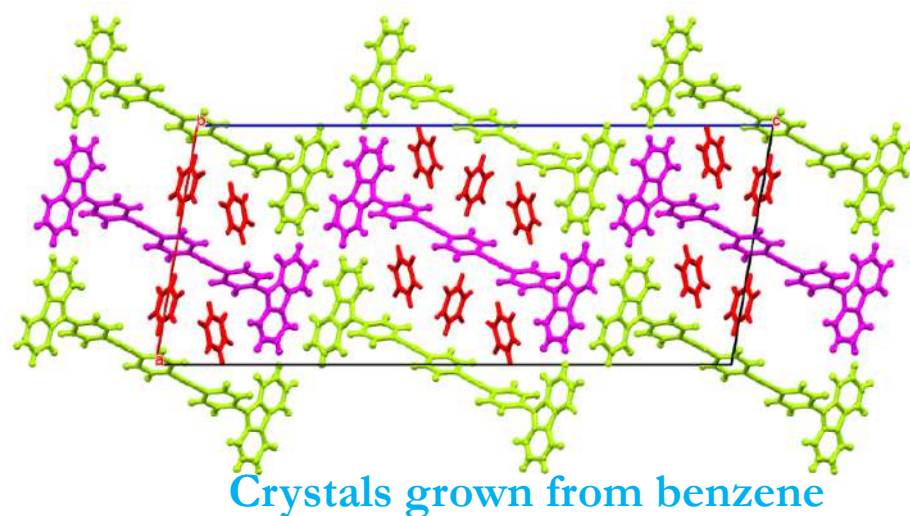
Aguilar-Granda, A.; Pérez-Estrada, S.; Roa, Arian E.; Rodriguez-Hernandez, J.; Hernandez-Ortega, S.; Rodríguez, M.; **Rodríguez-Molina, B.** *Crystal Growth & Design*, **2016**, *16*, 3435.

Dispositivos de luz blanca (OLEDs)



Bernal, W.; Barbosa, O.; Aguilar-Granda, A.; Rodríguez, M.; **Rodríguez-Molina, B. sometido**

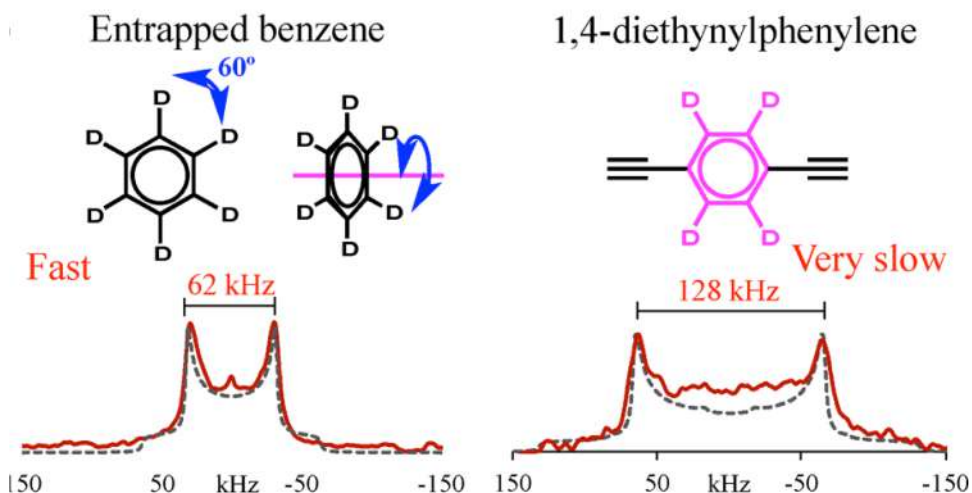
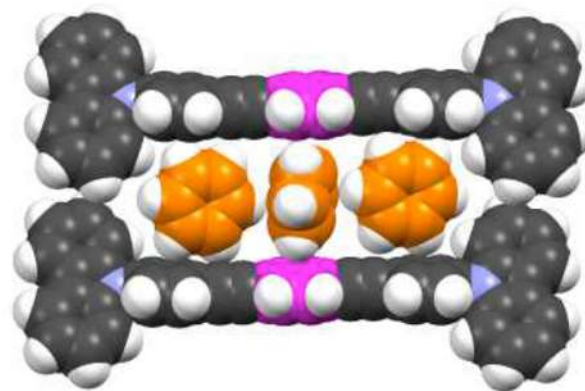
Desolvatación de cristales



Highly stable

Aguilar-Granda, A.; Pérez-Estrada, S.; Sánchez-González, E.; Álvarez, J. R.; Hernández-Ortega, S.; Ibarra, I. A. **Rodríguez-Molina, B.** *J. Am. Chem. Soc.* **2017**, 139, 7549

¿Qué pasa cuando el benceno se encuentra dentro del cristal?



Aguilar-Granda, A.; Pérez-Estrada, S.; Sánchez-González, E.; Álvarez, J. R.; Hernández-Ortega, S.; Ibarra, I. A. **Rodríguez-Molina, B.** *J. Am. Chem. Soc.* **2017**, 139, 7549

Bibliografía

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- *NMR crystallography*. Robin K. Harris, Roderick E. Wasylshen, Melinda J. Duer. Chichester, United Kingdom. Wiley, 2009.
- *Solid state NMR: basic principles & practice*. David C. Apperley, Robin K. Harris & Paul Hodgkinson, New York. Momentum Press, 2012.
- *Solid-state NMR in materials science: principles and applications*. Vladimir I. Bakhmutov, Boca Raton, Florida. CRC Press, 2012.
- *Introduction to solid-state NMR spectroscopy*. Melinda J. Duer. Oxford, United Kingdom. Blackwell, 2004.
- *Structure elucidation in organic chemistry: the search for the right tools*. María-Magdalena Cid, Jorge Bravo. Weinheim, Germany : Wiley-VCH Verlag GmbH & Co, KGaA, 2015.

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Dazaet Galicia

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Dr. Luis D. Miranda (IQ-UNAM)

Dra. Rosa L. Santillan (CINVESTAV)

Dr. Salvador Pérez Estrada (UAEH)

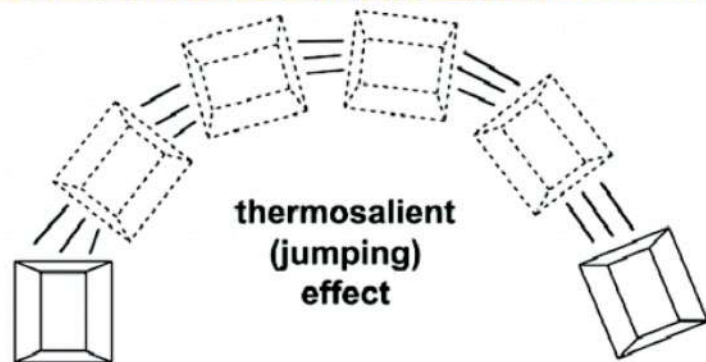
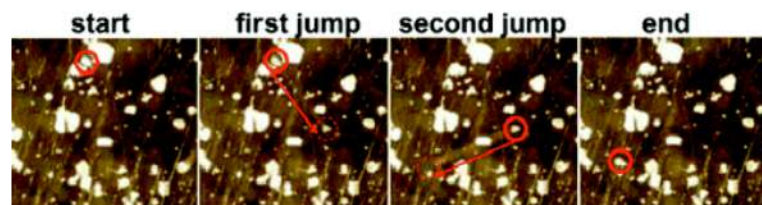


Miembros anteriores:

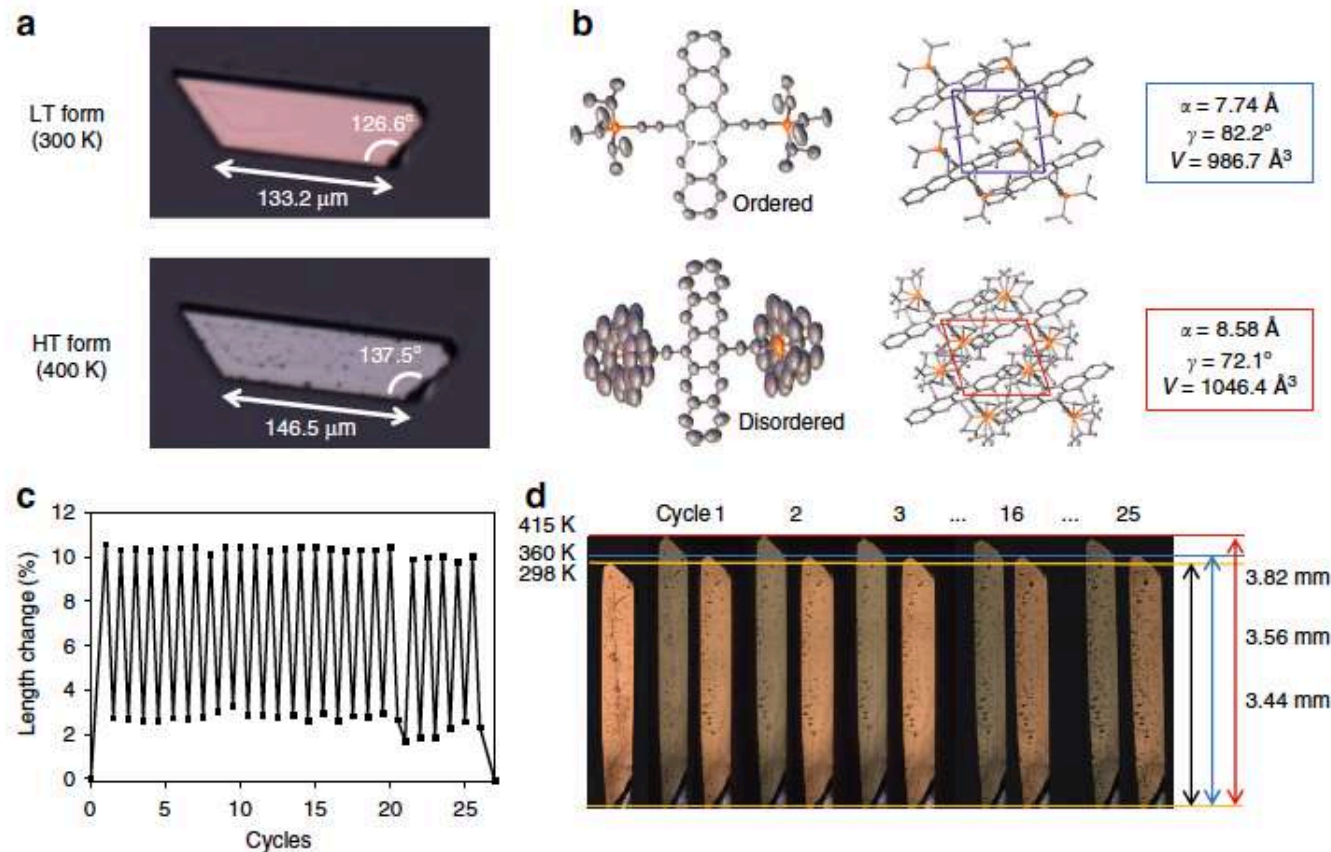
Dr. Andrés Aguilar-Granda

Q. Julio Morán Muñoz

Thermosalient effect · “*jumping crystals*”



2010



2018

Naumov, et. al. *J. Am. Chem. Soc.*, **2010**, 132, 14191

Chung, H, et. el. *Nature Communications*, **2018**, 18, 278.