

Contents class Wintersemester 2017/18 (Modern Applications of NMR Spectroscopy)

Structure Elucidation in Organic and Inorganic Chemistry: Methods and Examples.

Class 3 – Dec. 20th

ADEQUATE: Differentiation of substituents in natural products

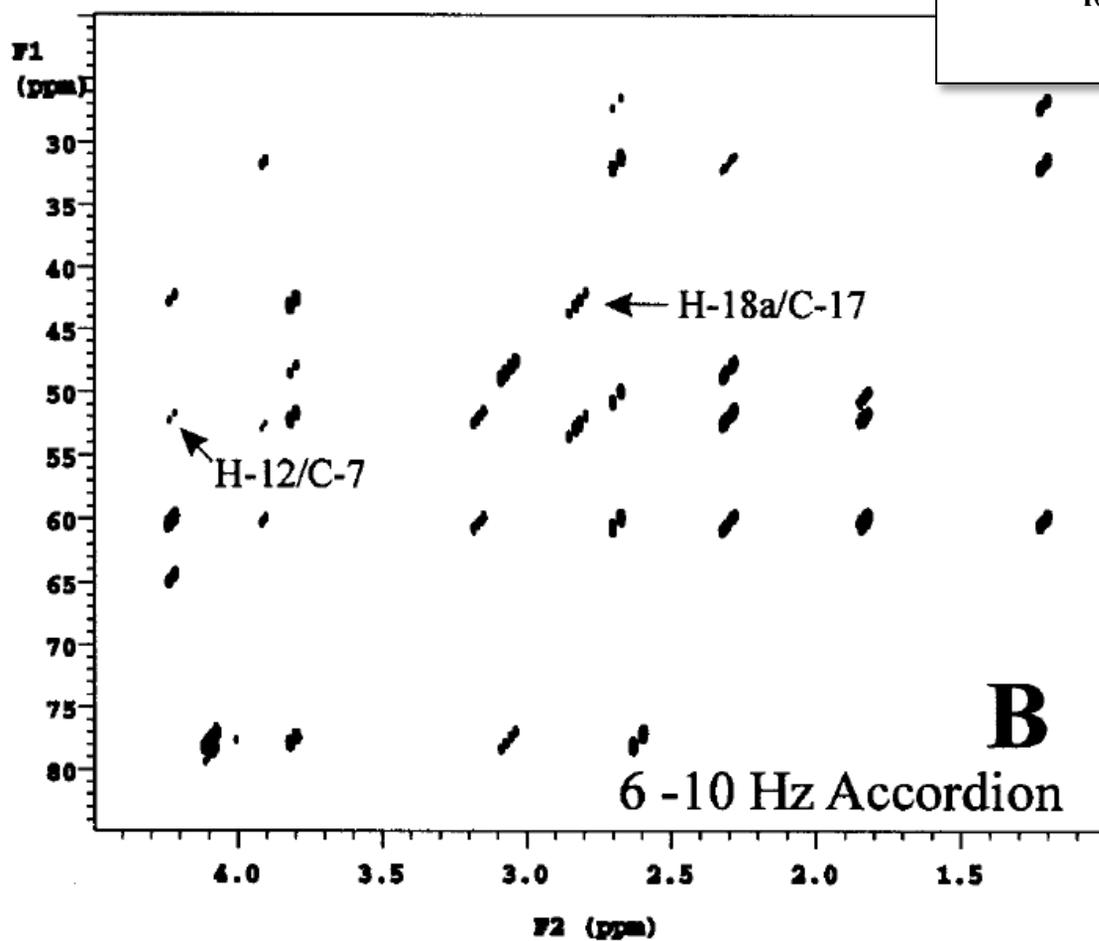
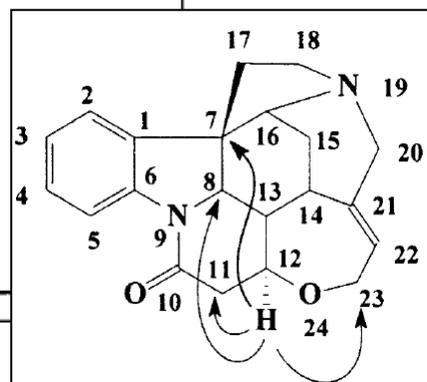
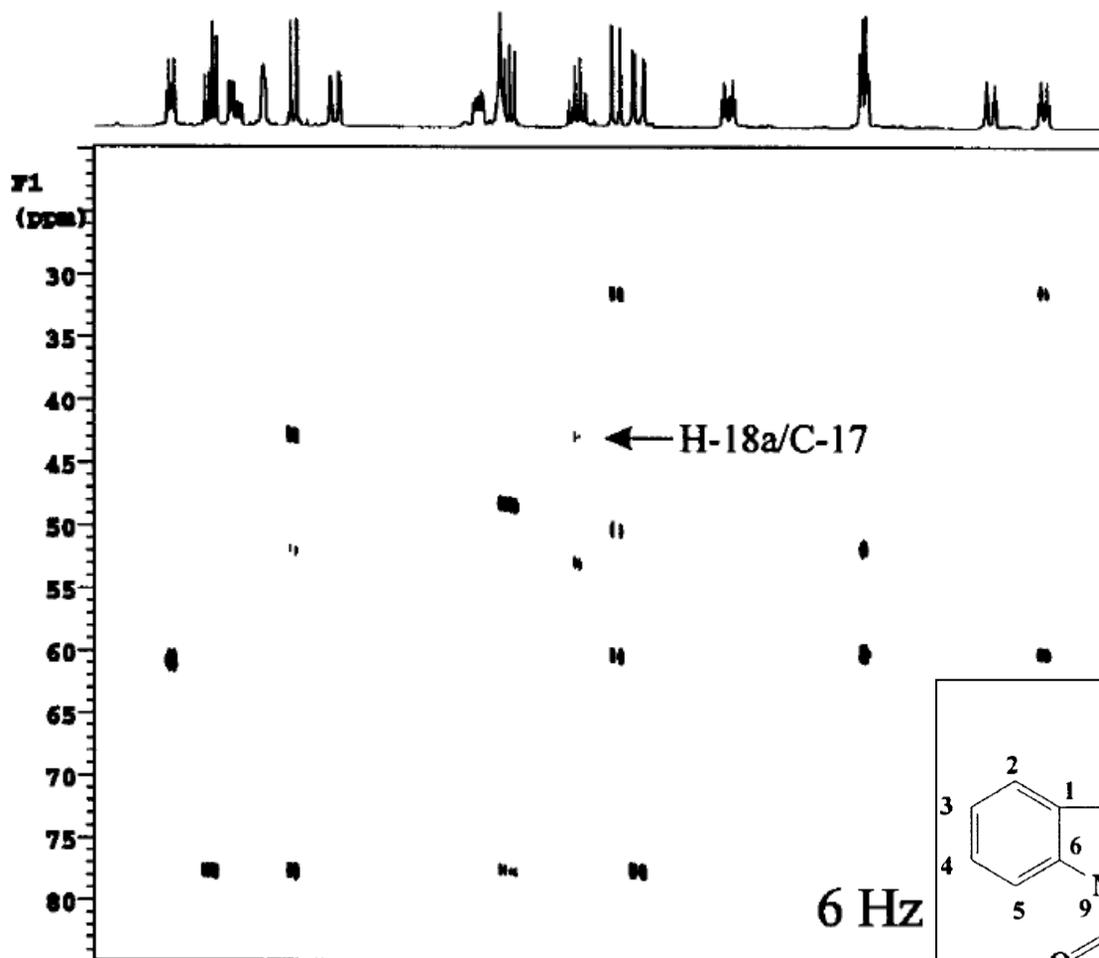
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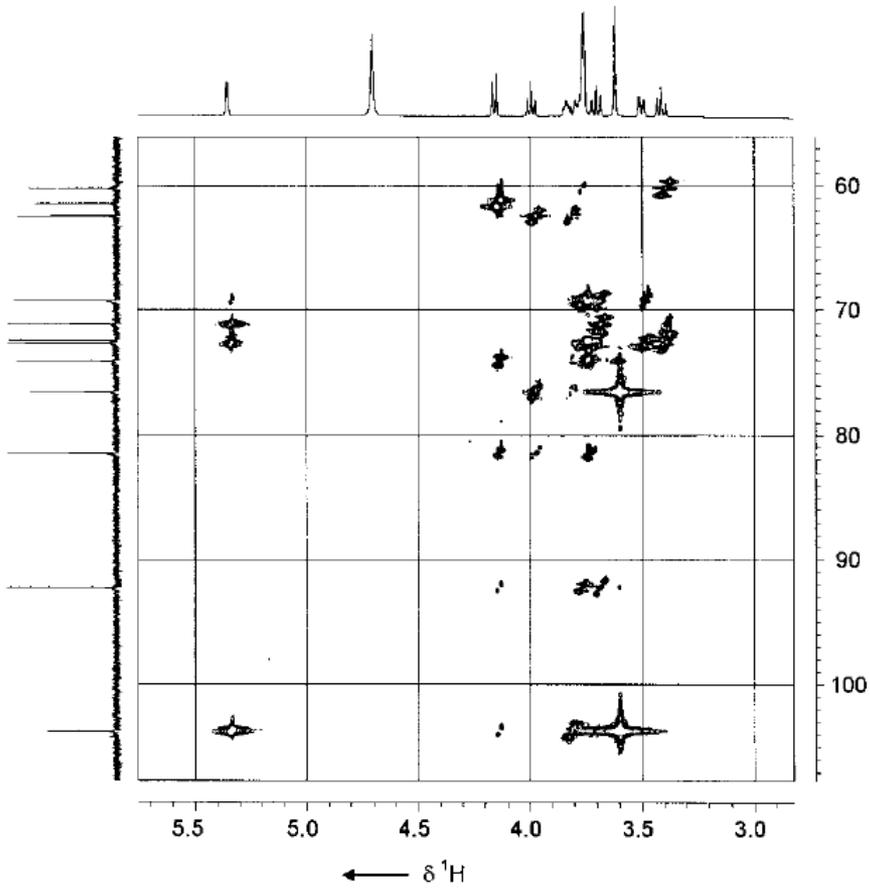
- Köck, *J. Nat. Prod.* **2008**, *53*, 13239 (application 1,1 and 1,n ADEQUATE)

HMBC: Variations and related experiments for long range H,C correlation – Ir-HMBC variations of ACCORDION-type experiments (ACCORD-, IMPEACH- and CIGAR-HMBC), discrimination of 2J vs. 3J (H2BC, $^2J, ^3J$ -HMBC) and 'extreme' long range correlations (2Q-HMBC, Ir-HSQMBC)

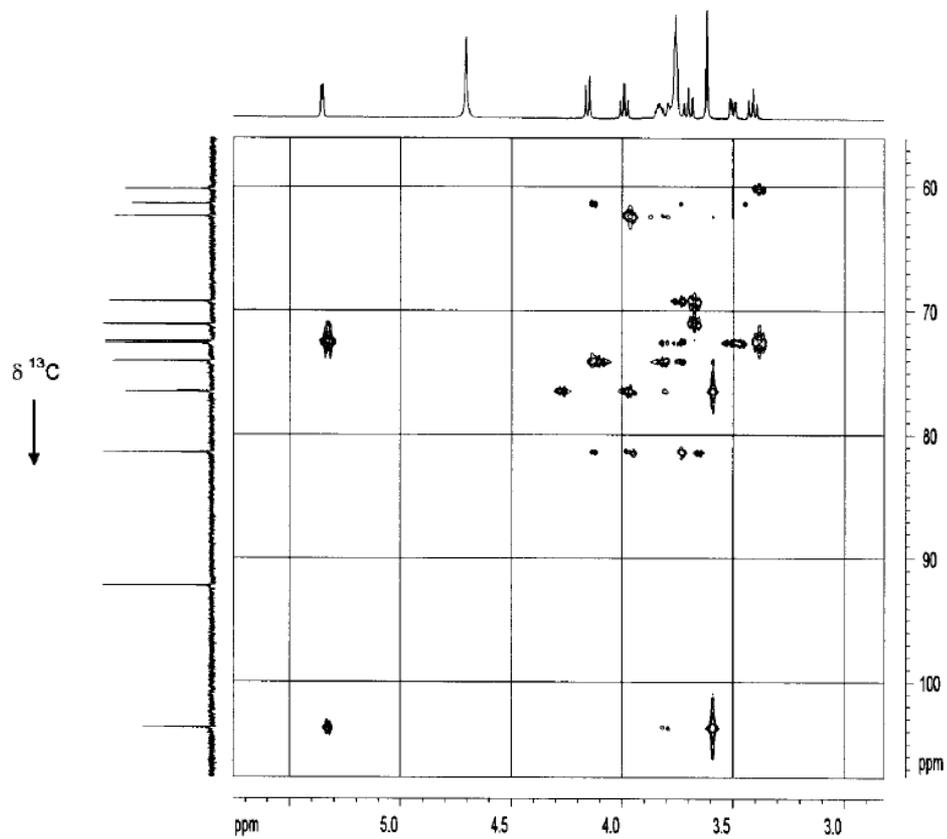
References:

- Furrer, *Concepts Magn. Reson. Part A* **2015**, *44A(5)*, 227 (discussion of HMBC and related experiments, series of four articles published 2012, 2012, 2015 and 2015)
- Sørensen, *J. Magn. Reson.* **1997**, *124*, 245 (2Q-HMBC)
- Sørensen, *J. Am. Chem. Soc.* **2005**, *127*, 6154 (H2BC)
- Williamson, *J. Org. Chem.* **2014**, *79*, 3887 (IrHSQMBC applied to cervinomycin A)

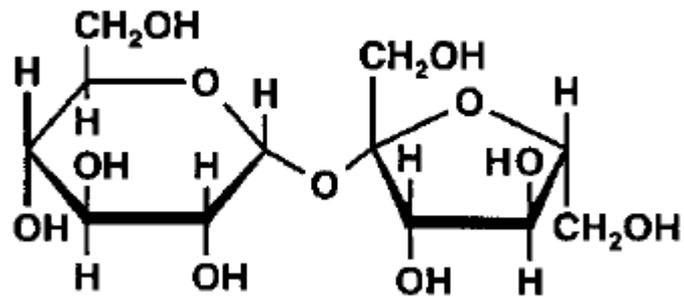


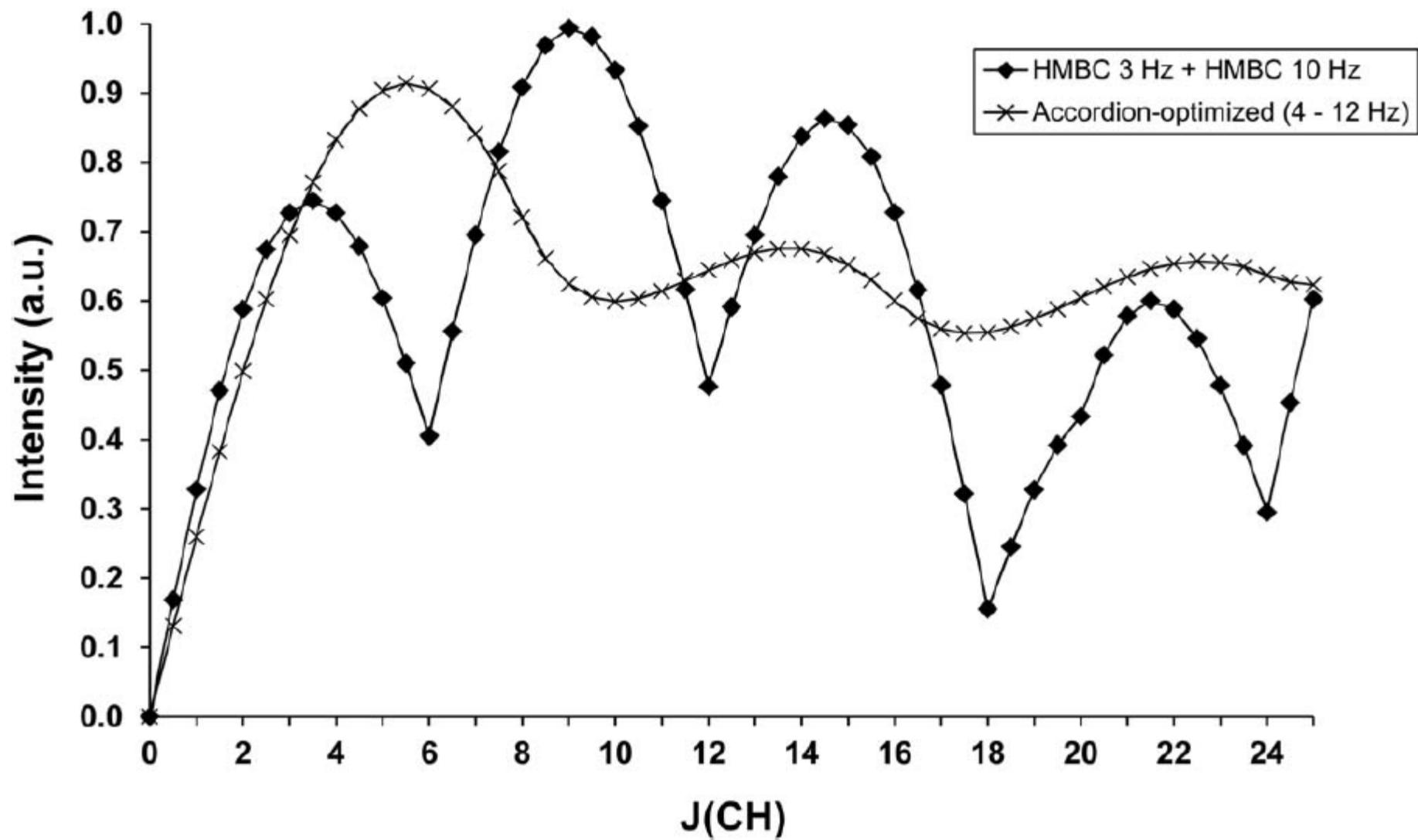


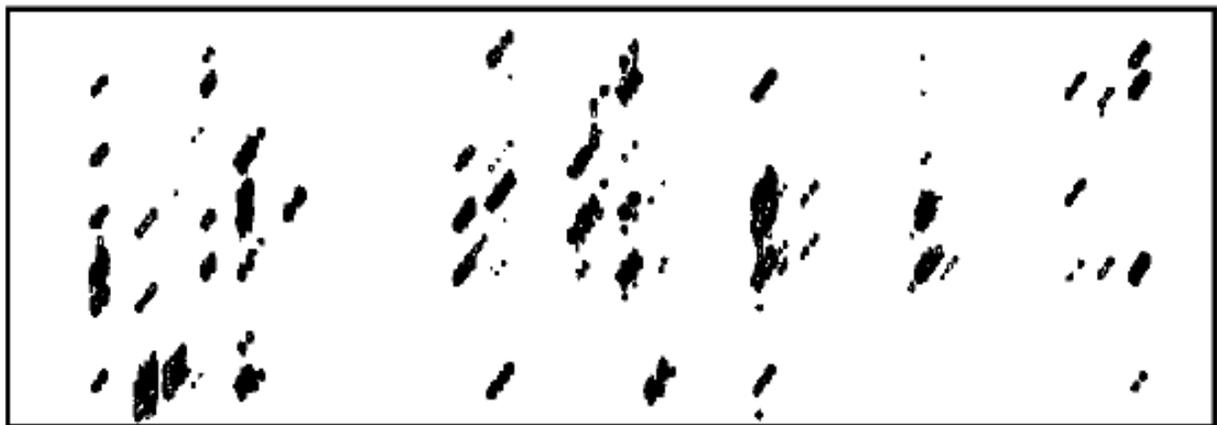
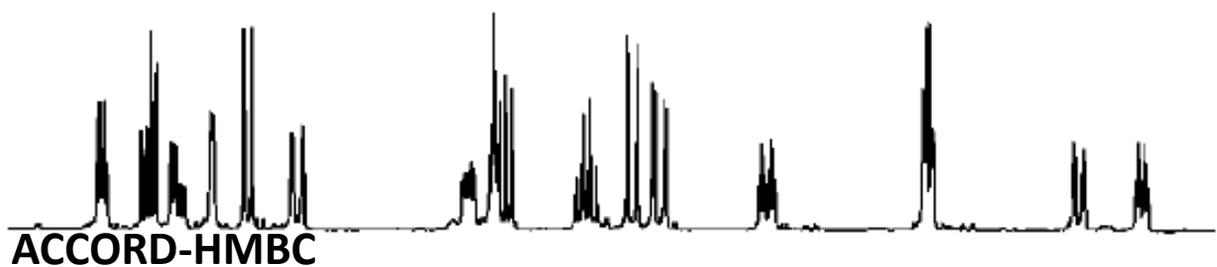
ACCORD-HMBC



HMBC



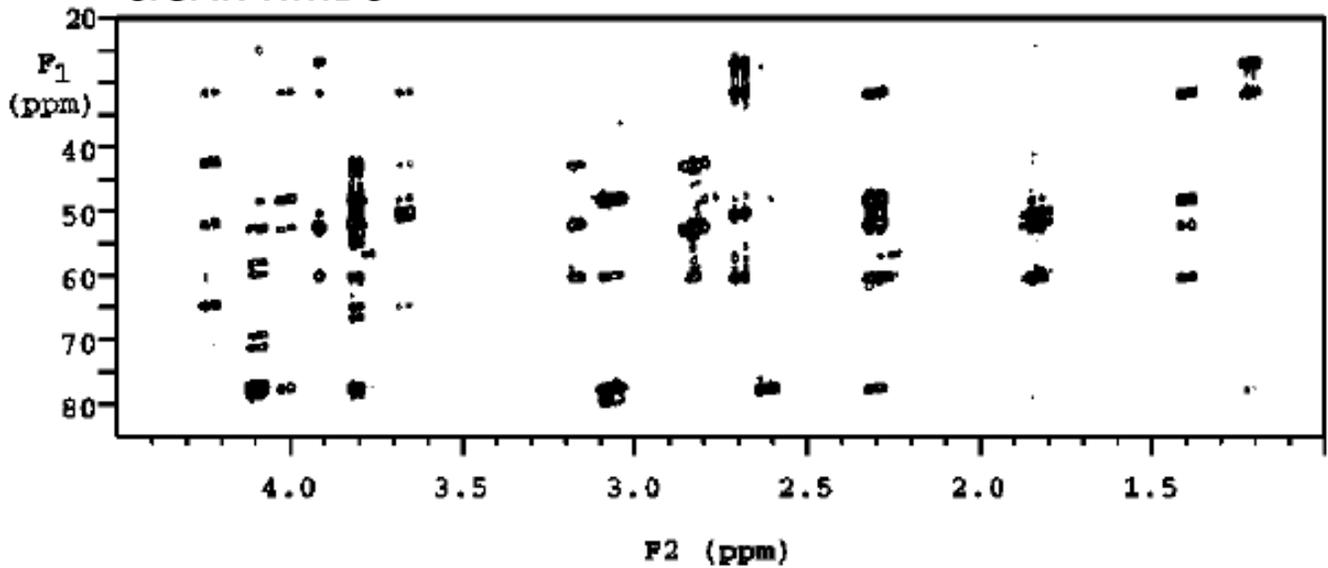


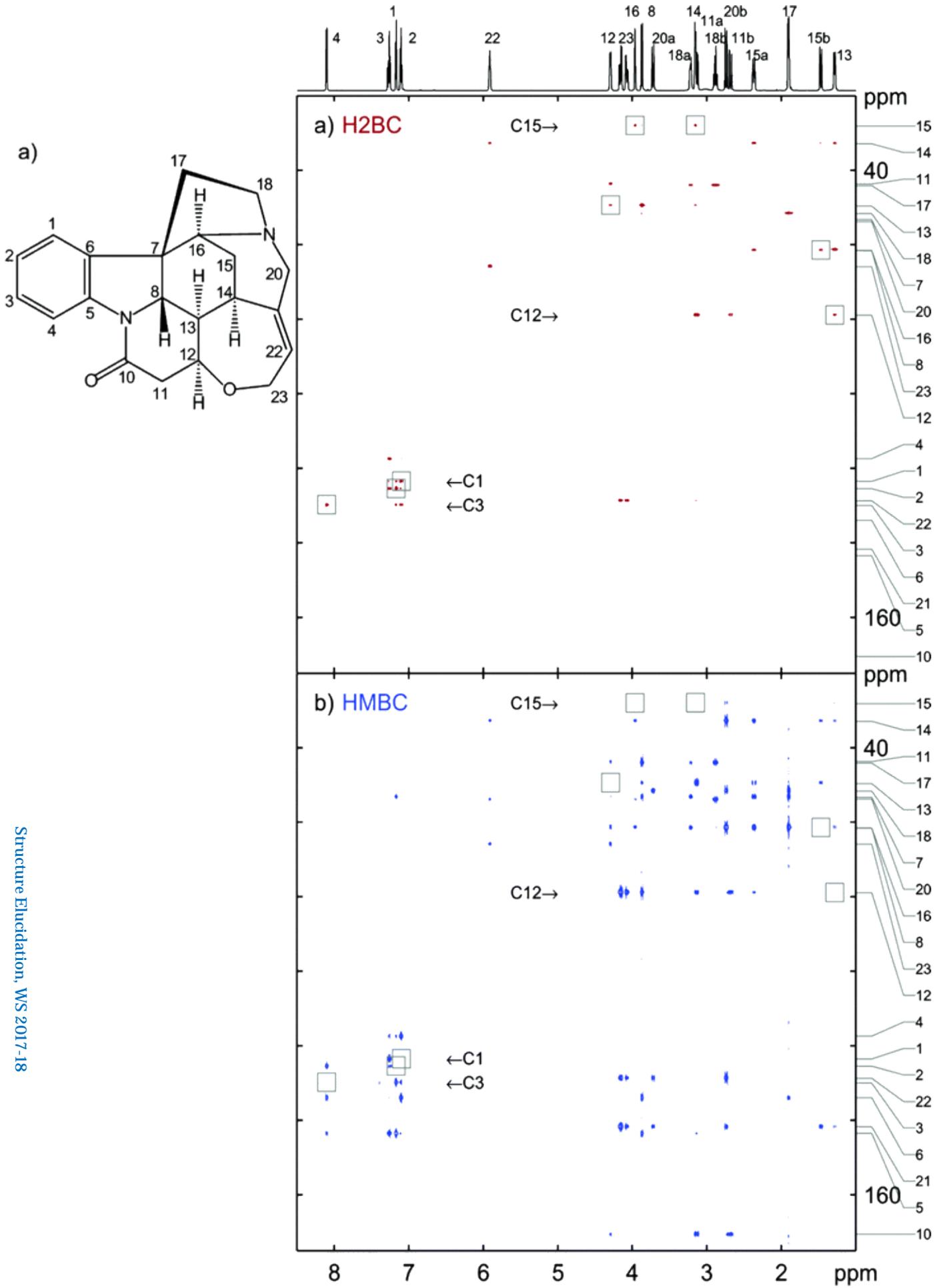


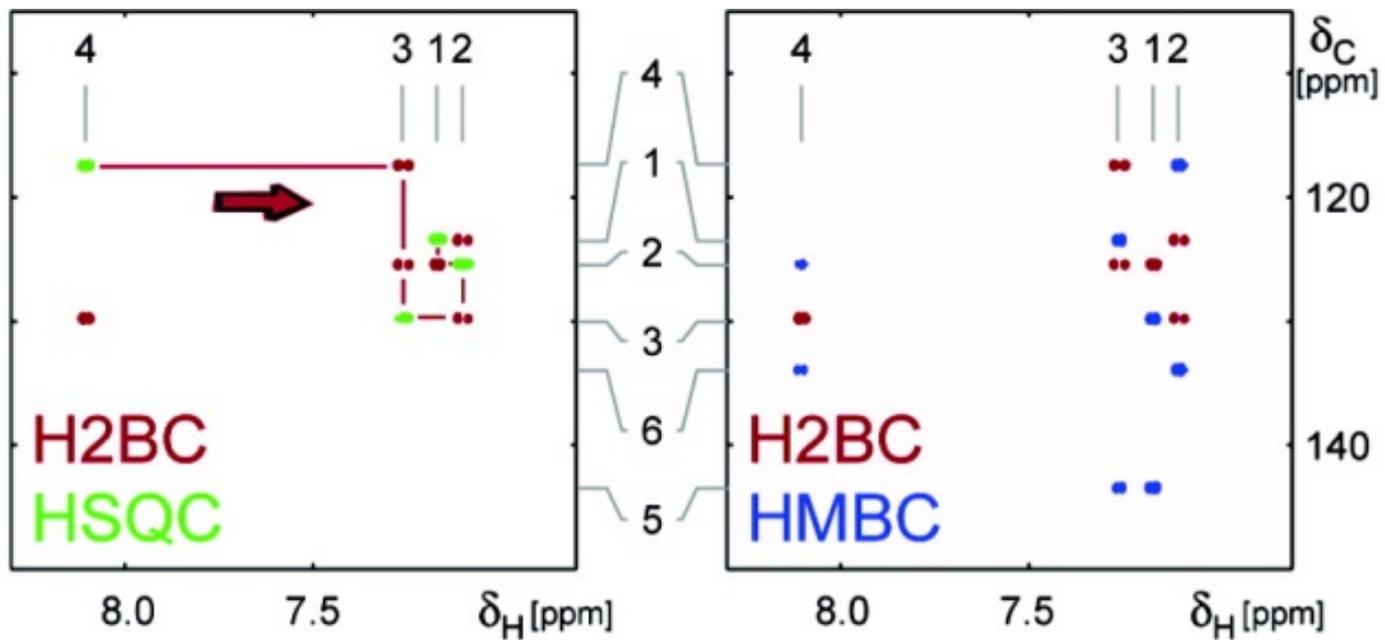
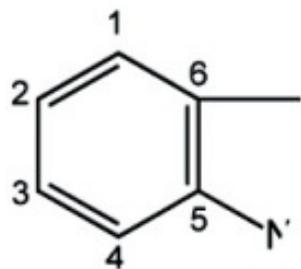
IMPEACH-HMBC



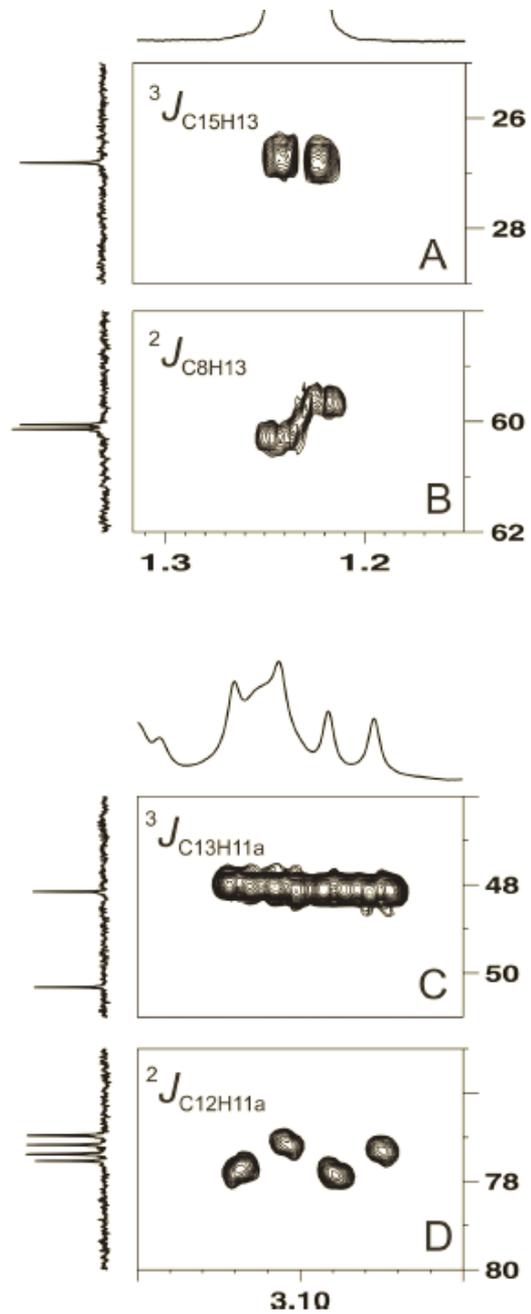
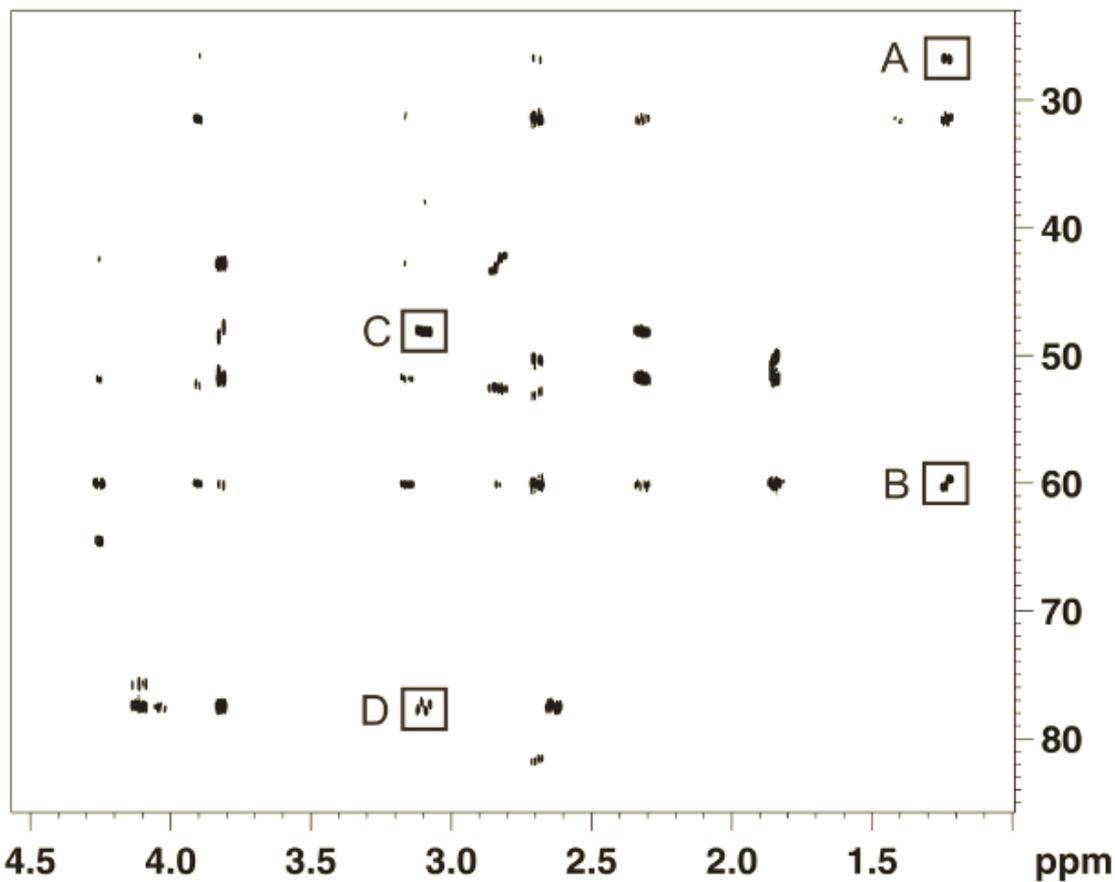
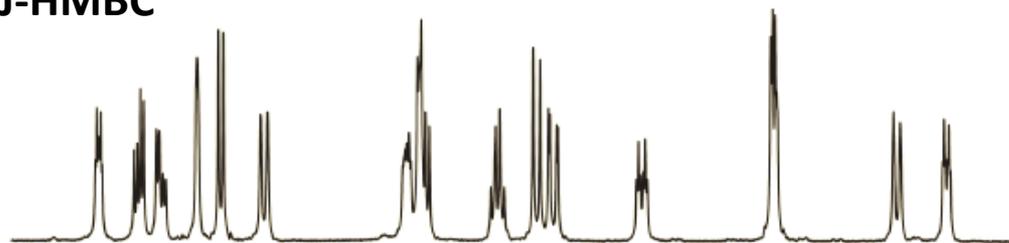
CIGAR-HMBC

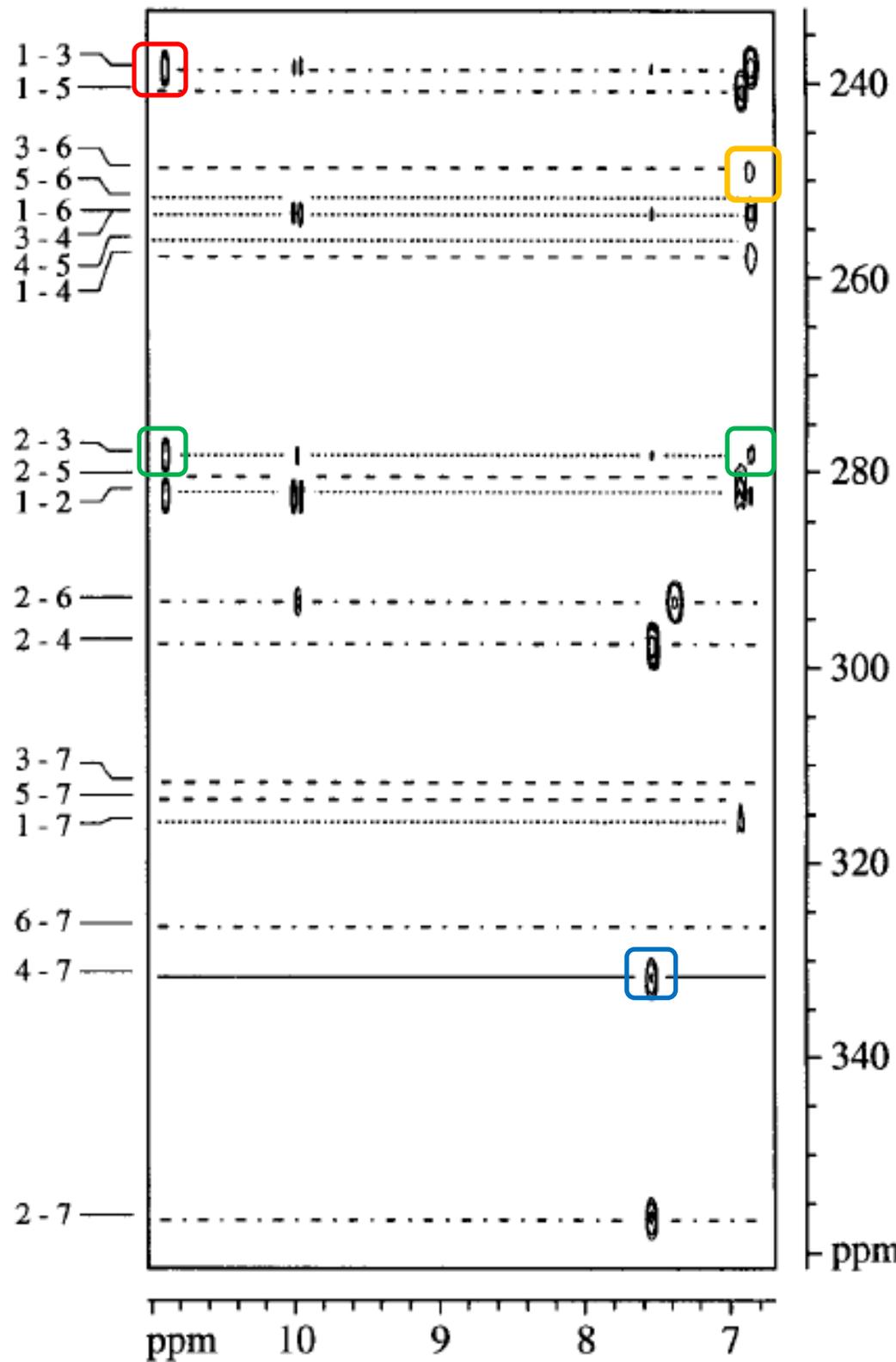
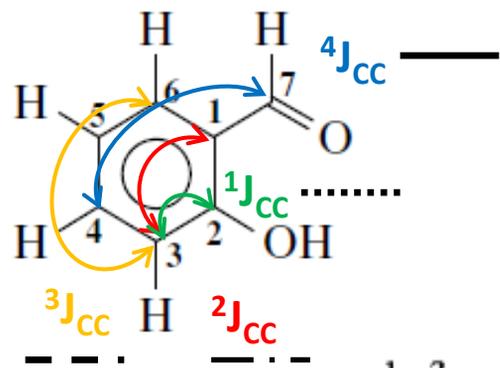




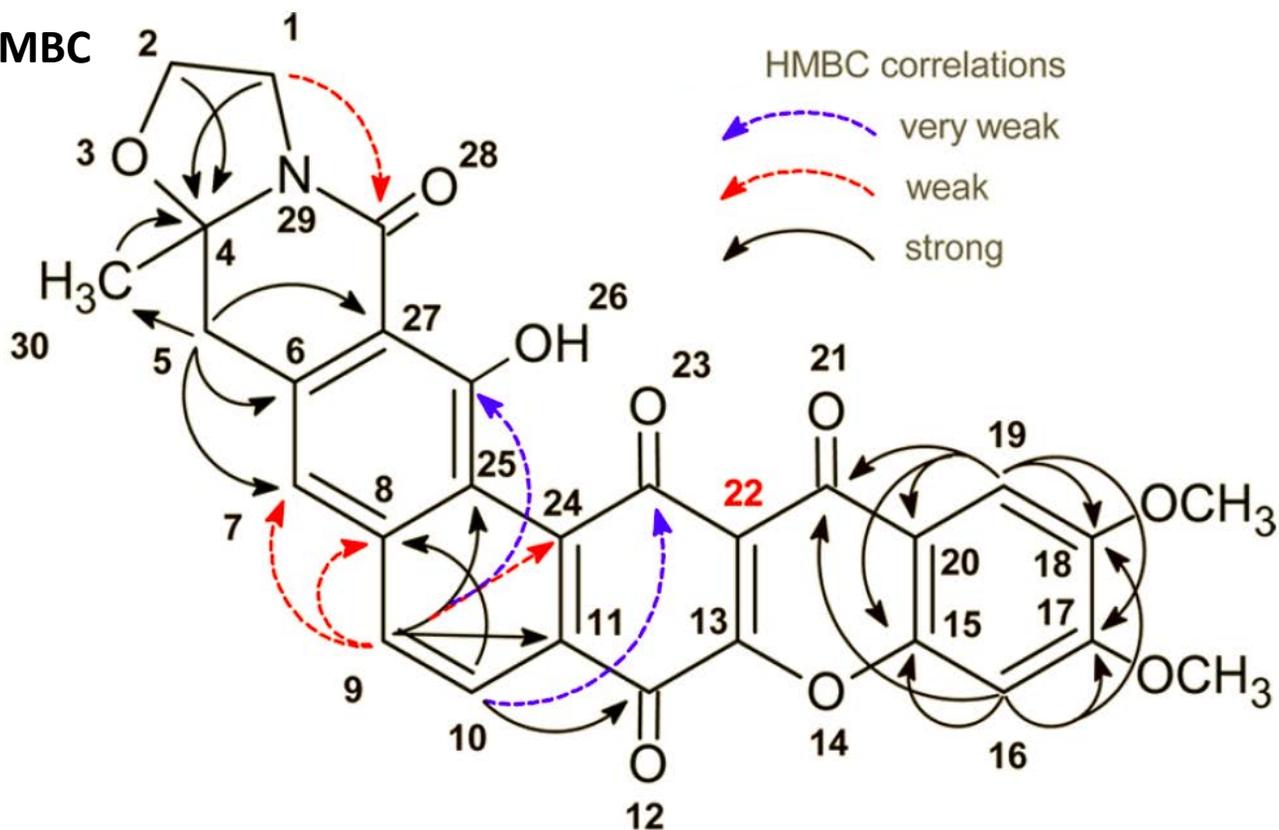


$^2J, ^3J$ -HMBC

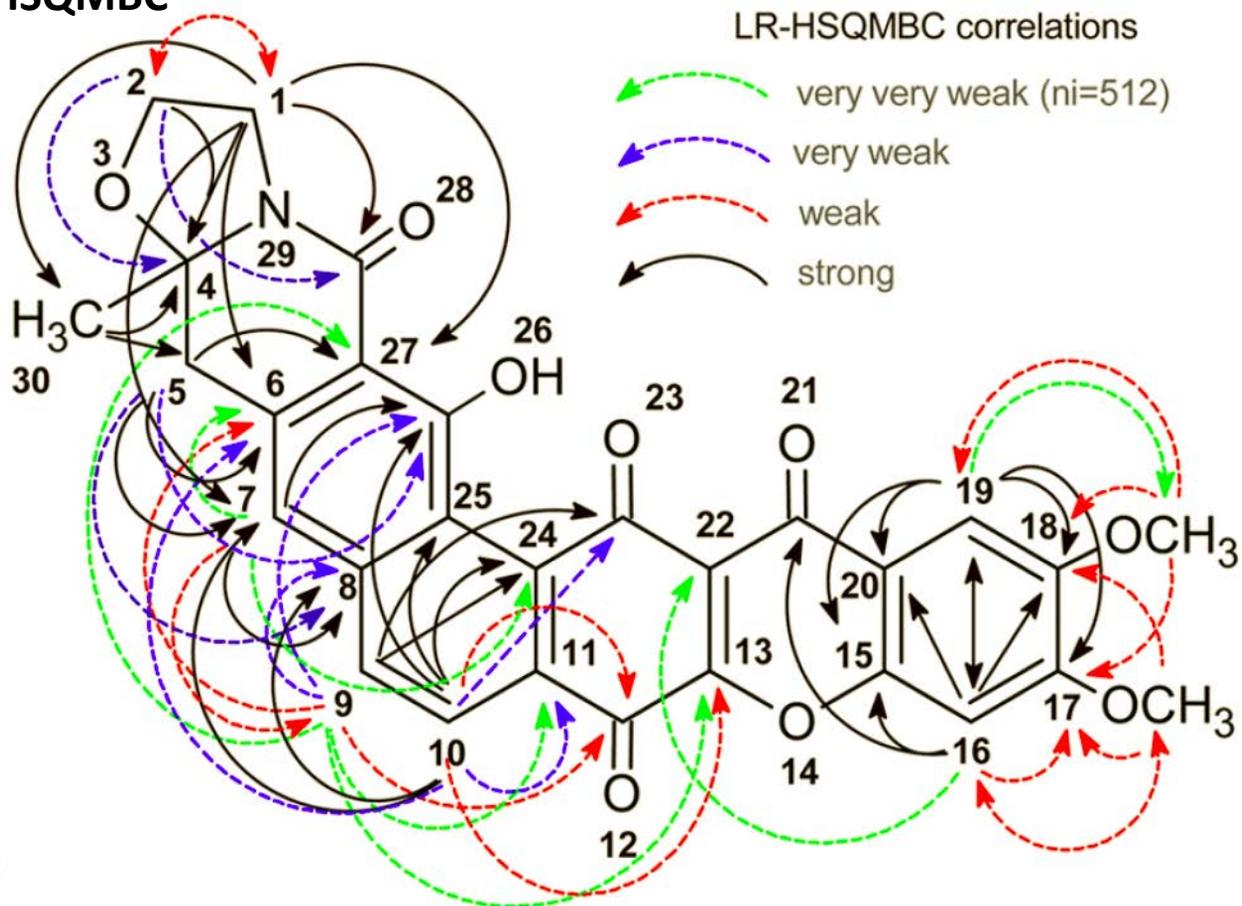




HMBC



Ir-HSQMBC



Experiment	Type of correlation	Sensitivity	Limitations
HMBC	$^2J_{CH}, ^3J_{CH}$ (mainly)	high	No differentiation between 2J and 3J , breakthrough of 1J , limited access to very long range correlations ($\geq ^4J$)
H2BC	$^2J_{CH}$	high	$^3J_{HH}$ required for correlations (does not include quaternary carbons)
$^2J, ^3J$ -HMBC	$^2J_{CH}, ^3J_{CH}$ (mainly) with editing	medium	$^3J_{HH}$ required for correlations (does not include quaternary carbons), $^4J_{HH}$ might intrude
ACCORDION-type HMBC (ACCORD, IMPEACH, CIGAR)	$^2J_{CH}, ^3J_{CH}, ^4J_{CH}$ (mainly), covers a range of couplings	medium-high	Skewed signals, scaling factor, no differentiation between types of long range correlation
2Q-HMBC	$^1J_{CC}$ up to $^4J_{CC}$, through HMBC by $^2J_{CH}$ and $^3J_{CH}$	low	If $^nJ_{CH}$ too small, no cross peak – results in DQ dimension as combined correlated chemical shifts
Ir-HSQMBC	$^2J_{CH}, ^3J_{CH}, ^4J_{CH}$ (mainly, but up to $^6J_{CH}$)	high	No differentiation between types of long range correlation