

Regiospecific Inverse Electron Demand Diels-Alder Reaction of 7-Methylcoumarin-4-azadienes

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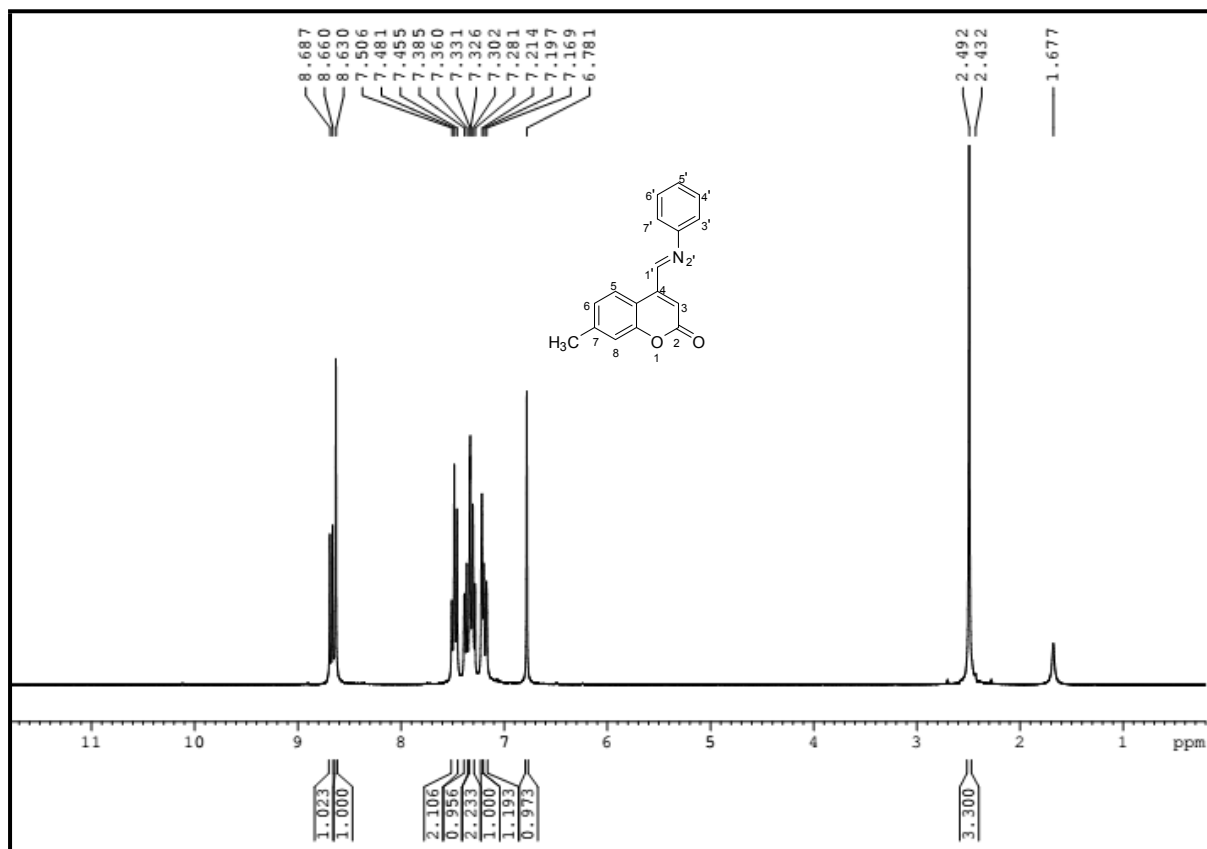
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Supporting Info

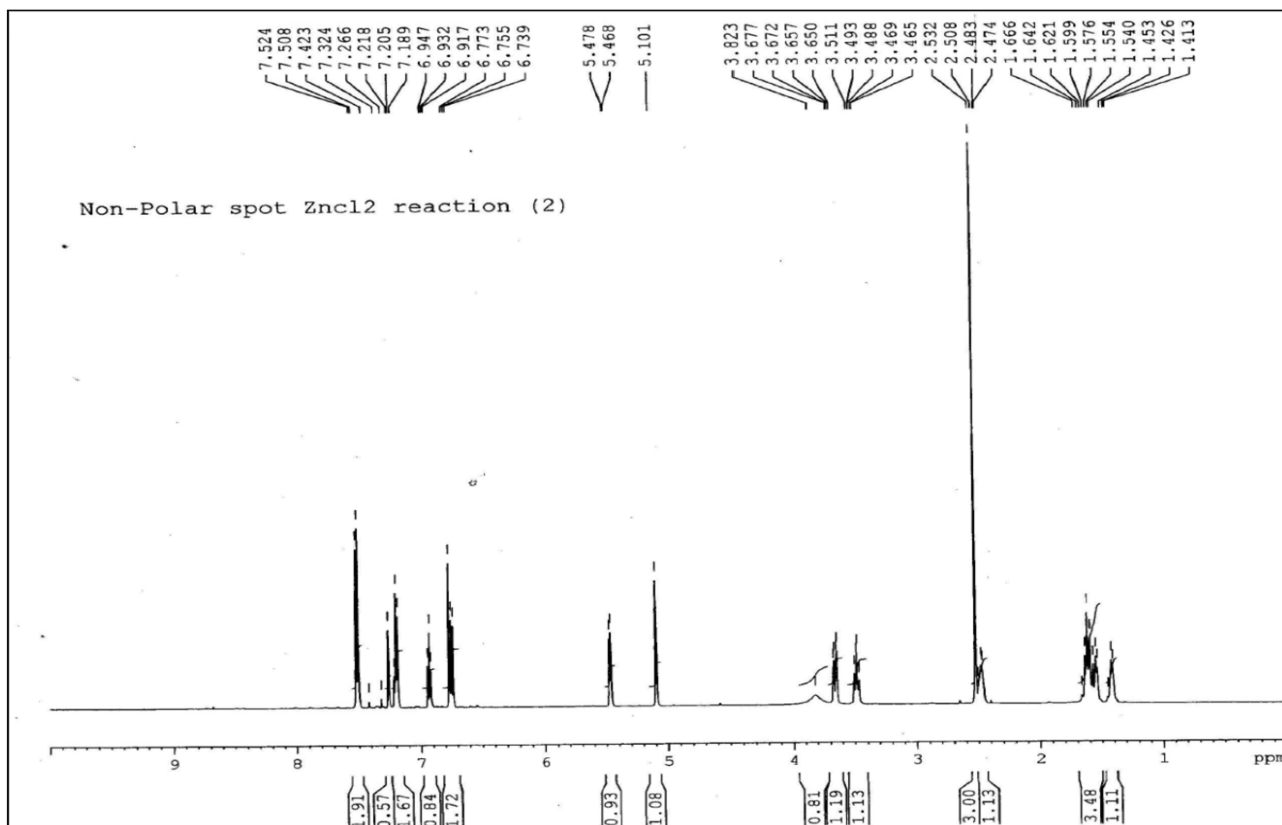
1. ¹H and ¹³C NMR Spectra

2-21

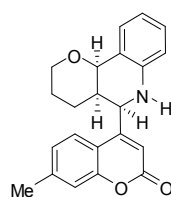
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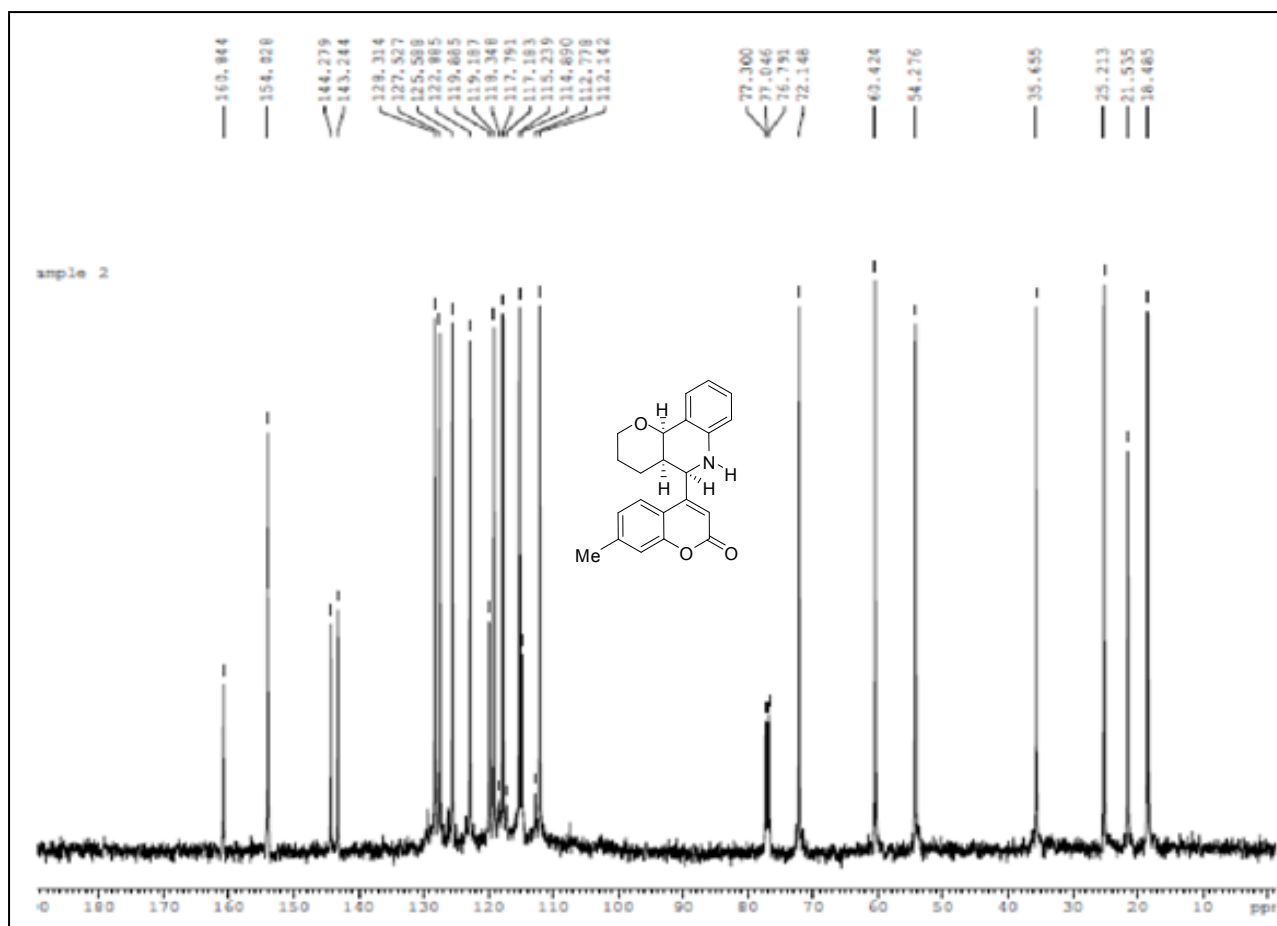


¹H NMR spectrum (CDCl₃, 300 MHz) of 7-methyl-coumarin-4-azadiene (**1a**)

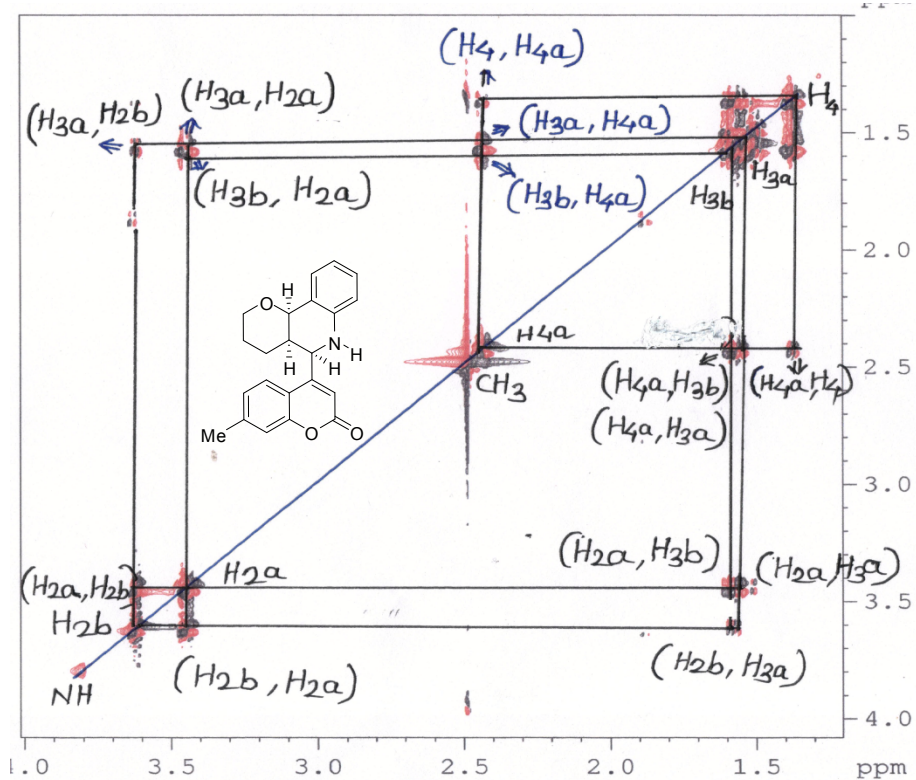
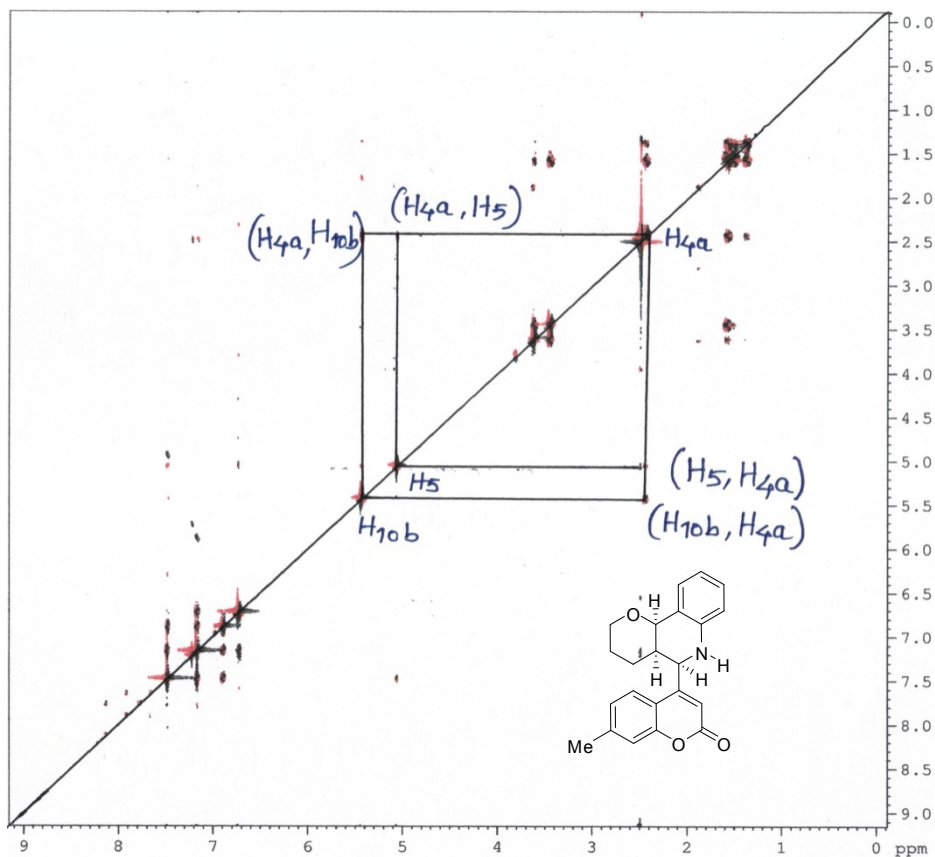


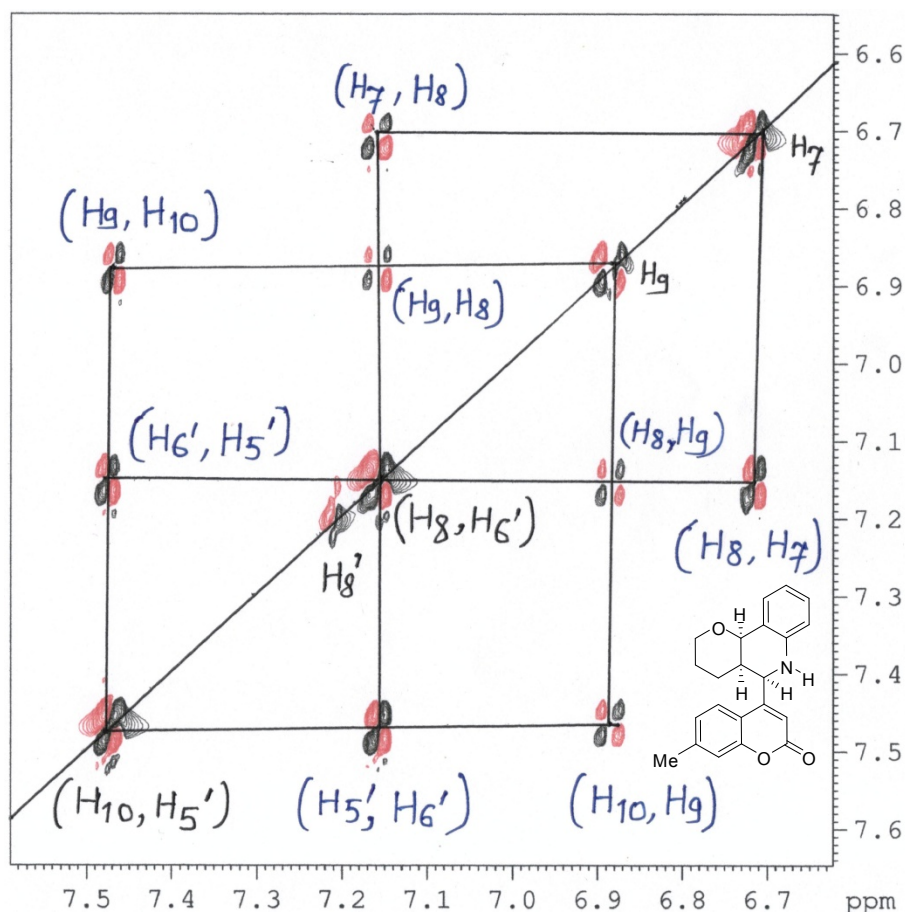
¹H NMR (500 MHz) spectrum of **11a**





^{13}C NMR (125 MHz) spectrum of **11a**

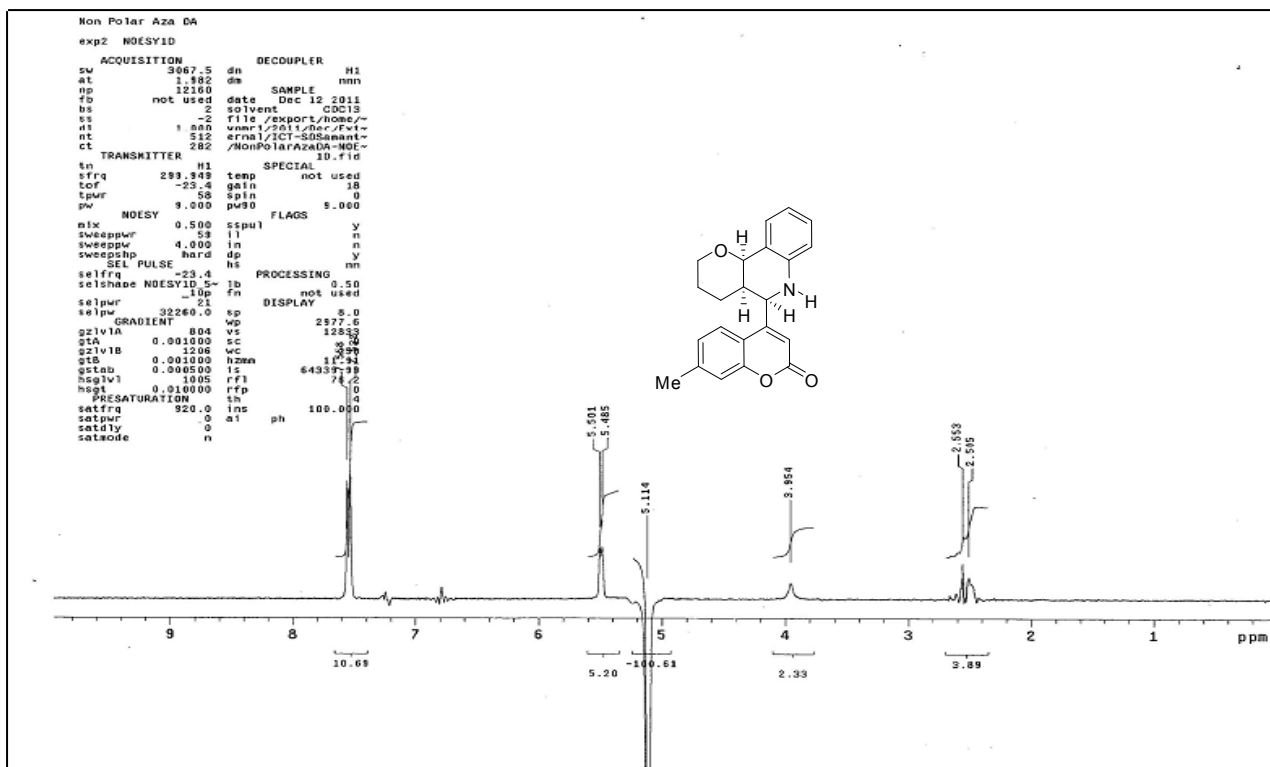




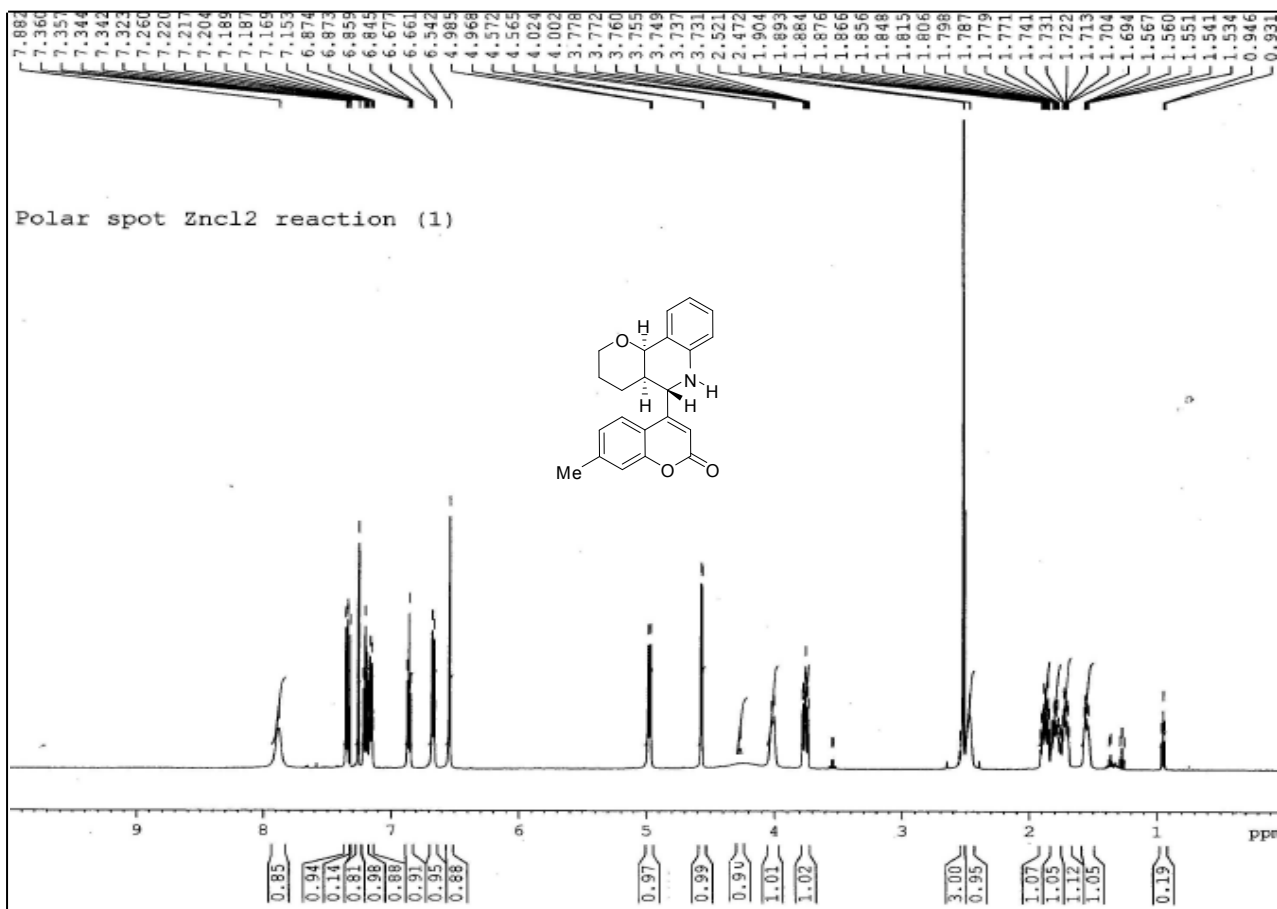
(c) DQF-COSY zoomed spectrum of **11a (A)**

Table S1 Diagonal peaks and their corresponding off-diagonal peaks of **11a (A)**

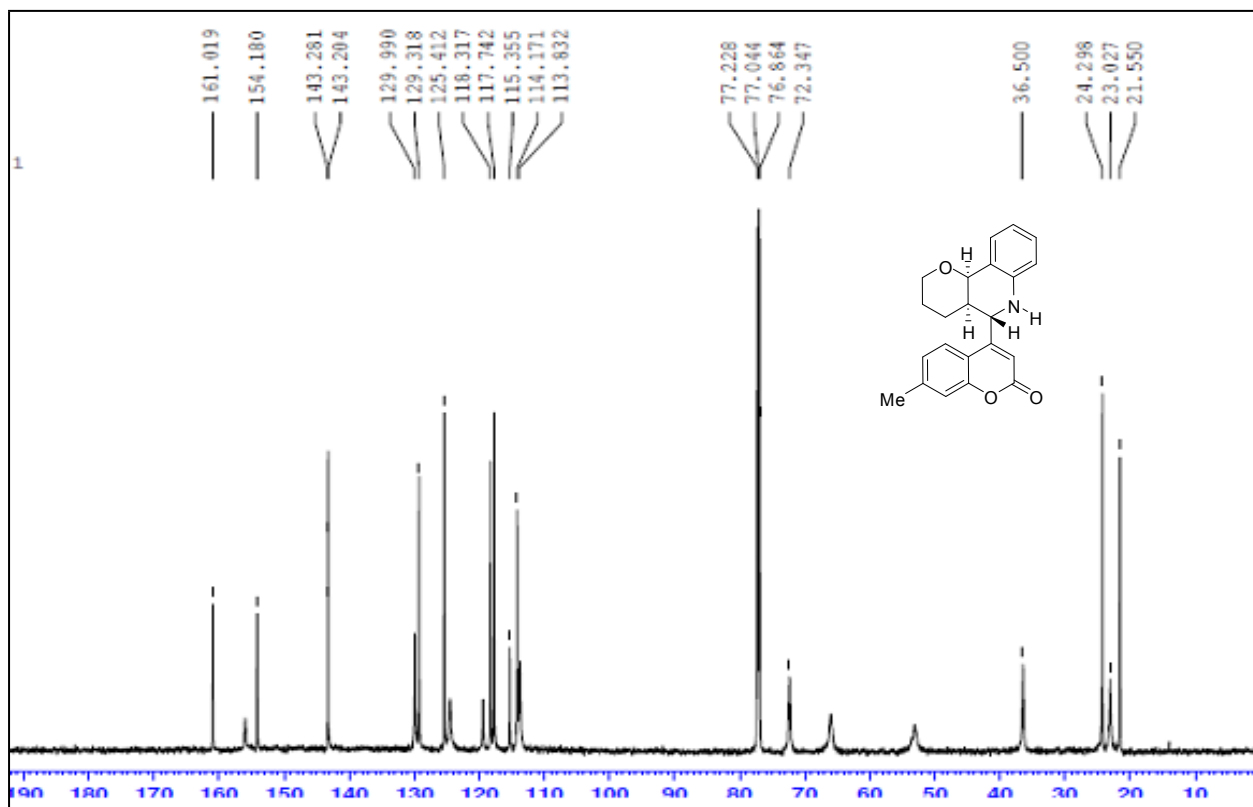
Entry	Diagonal peak	Off-diagonal peaks	Entry	Diagonal Peak	Off-diagonal peaks
1	H ₄	(H ₄ , H _{4a}) (H ₄ , H _{3a})	10	H _{10b}	(H _{10b} , H _{4a})
2	H _{3a}	(H _{3a} , H ₄) (H _{3a} , H _{4a}) (H _{3a} , H _{2a}) (H _{3a} , H _{2b})	11	H ₁₀	(H ₁₀ , H ₉)
3	H _{3b}	(H _{3b} , H _{2a}) (H _{3b} , H _{4a}) (H _{3b} , H _{2b})	12	H _{3'}	-
4	H _{4a}	(H _{4a} , H ₄) (H _{4a} , H ₅) (H _{4a} , H _{10b})	13	H ₈	(H ₈ , H ₇), (H ₈ , H ₉)
5	CH ₃	-	14	H _{6'}	(H _{6'} , H _{5'})
6	H _{2a}	(H _{2a} , H _{3a}), (H _{2a} , H _{3b}) (H _{2a} , H _{2b})	15	H ₉	(H ₉ , H ₈), (H ₉ , H ₁₀)
7	H _{2b}	(H _{2b} , H _{3a}), (H _{2b} , H _{2a})	16	H _{8'}	-
8	NH	-	17	H ₇	(H ₇ , H ₈)
9	H ₅	(H ₅ , H _{4a})	18	H _{5'}	(H _{5'} , H _{6'})



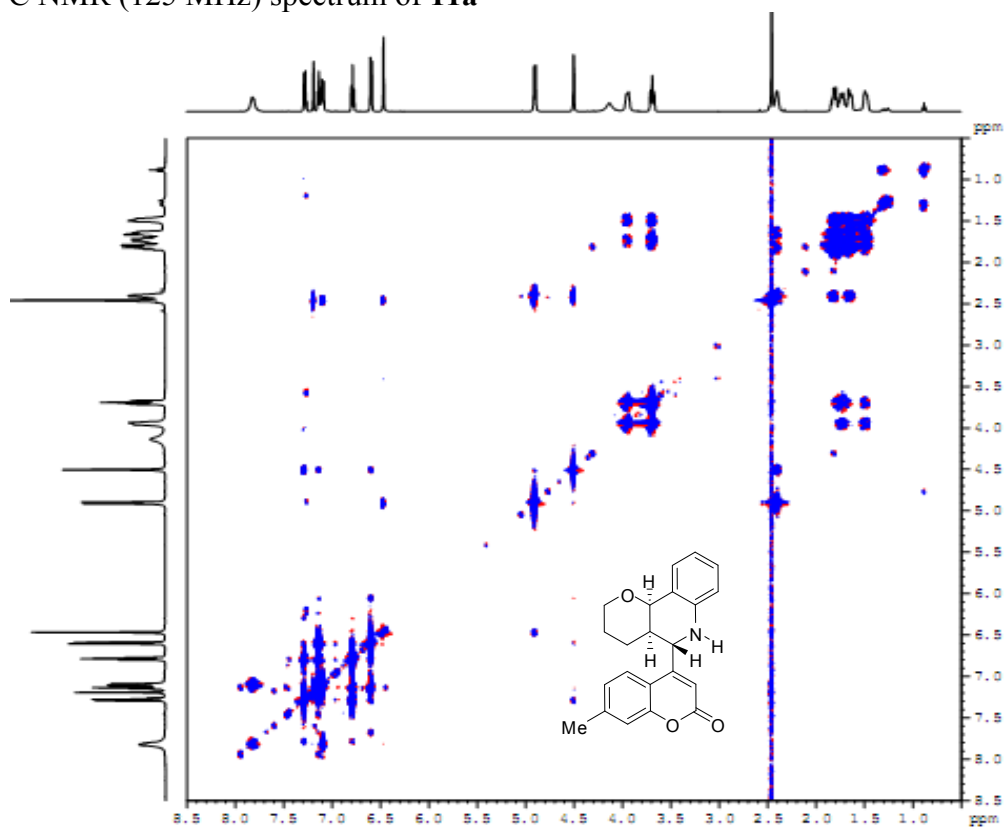
NOE spectrum of **11a**



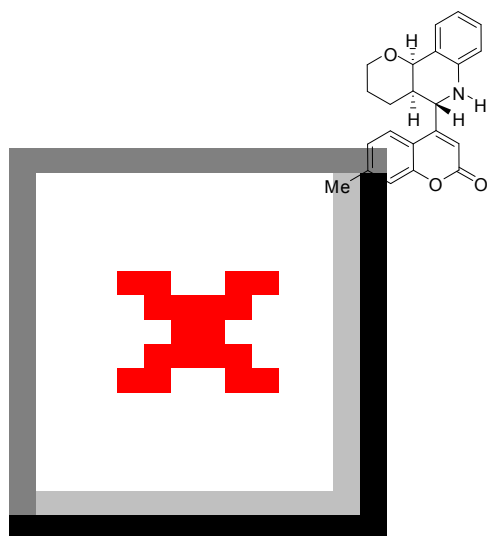
¹H NMR (500 MHz) spectrum of **11a'**



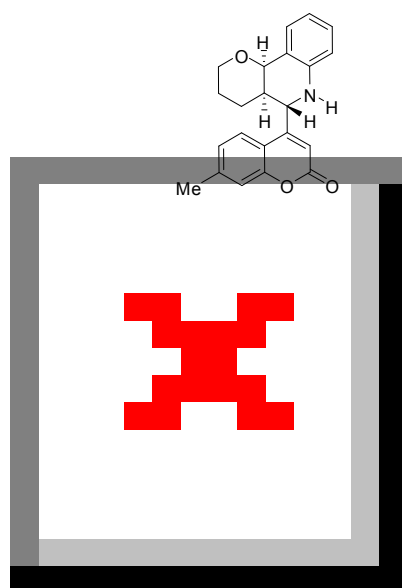
^{13}C NMR (125 MHz) spectrum of **11a'**



(a) DQF spectrum of **11a'** (B)-COSY



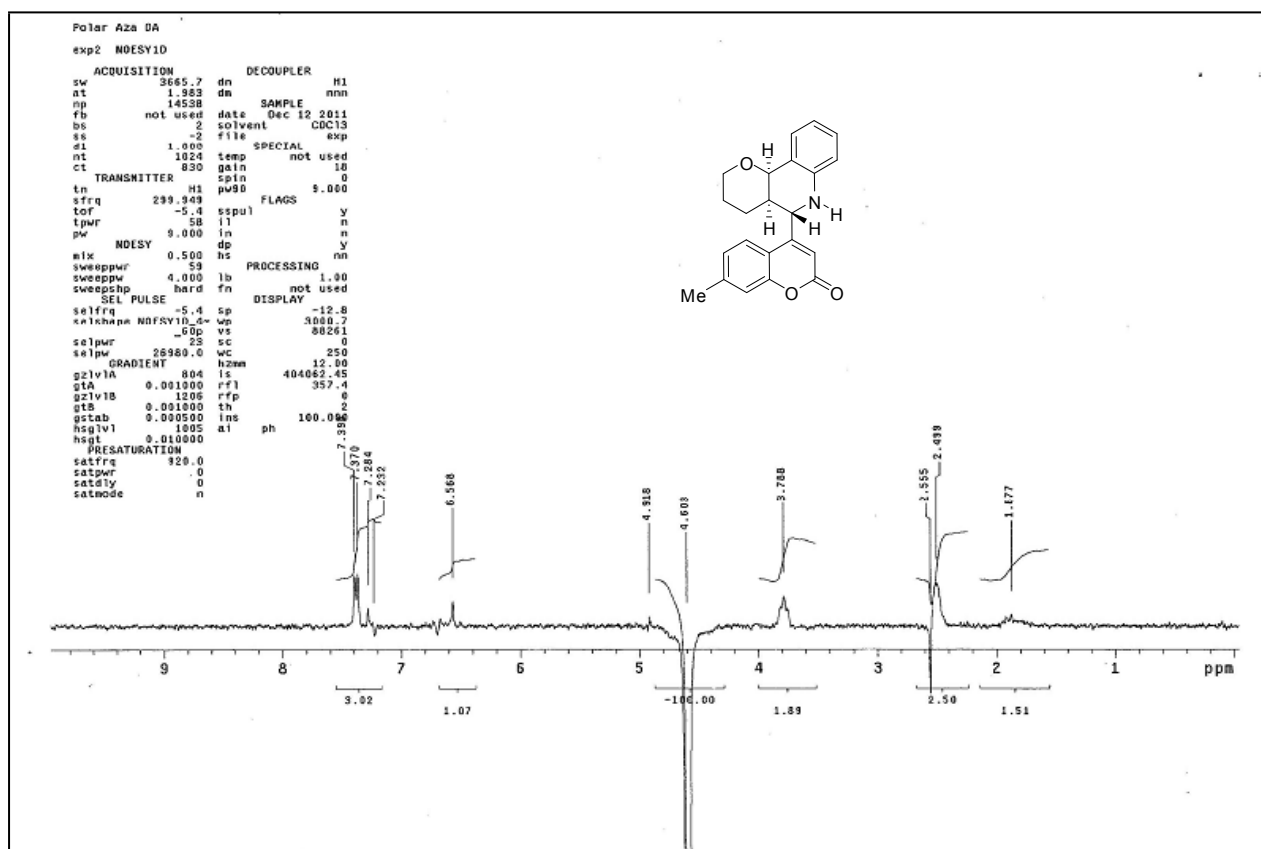
(b) DQF-COSY zoomed spectrum of 11a' (B)



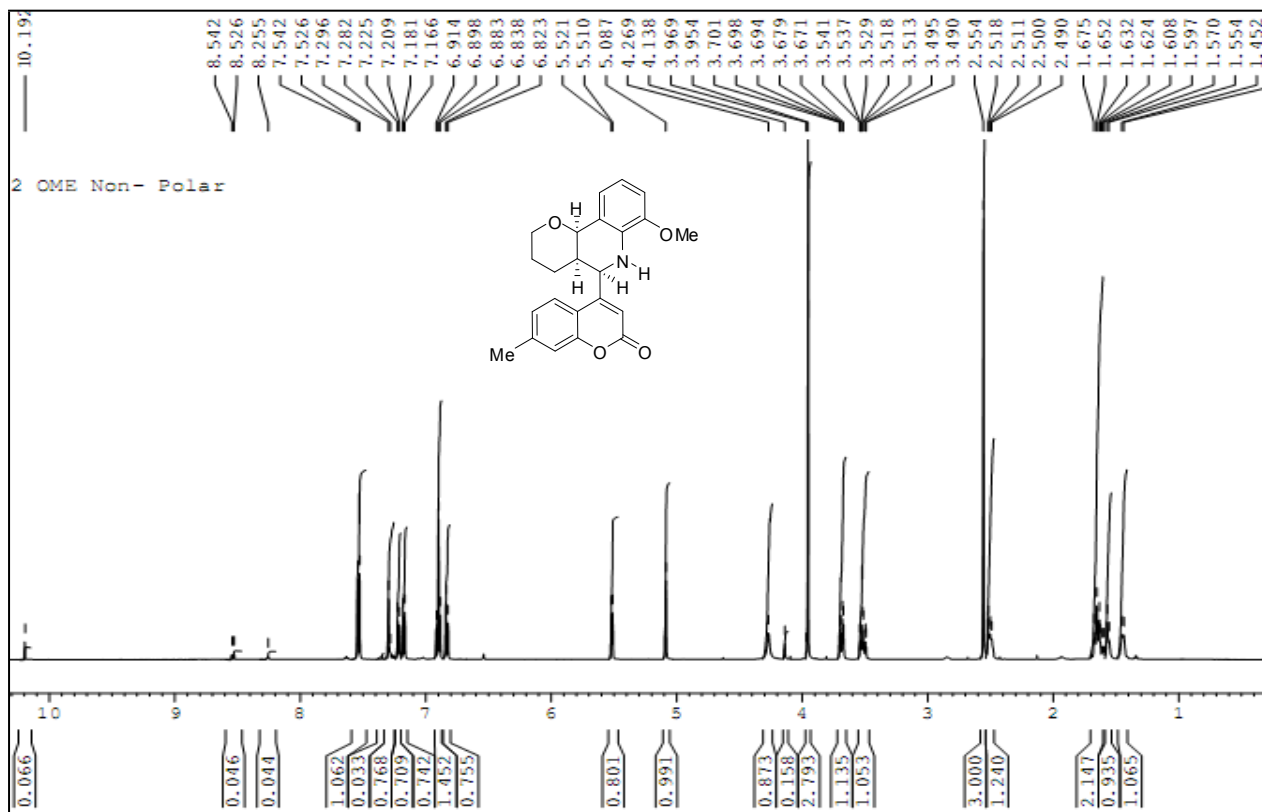
(c) DQF-COSY zoomed spectrum of 11a' (B)

Table S2 Diagonal peaks and their corresponding off-diagonal peaks of **11a'** (B)

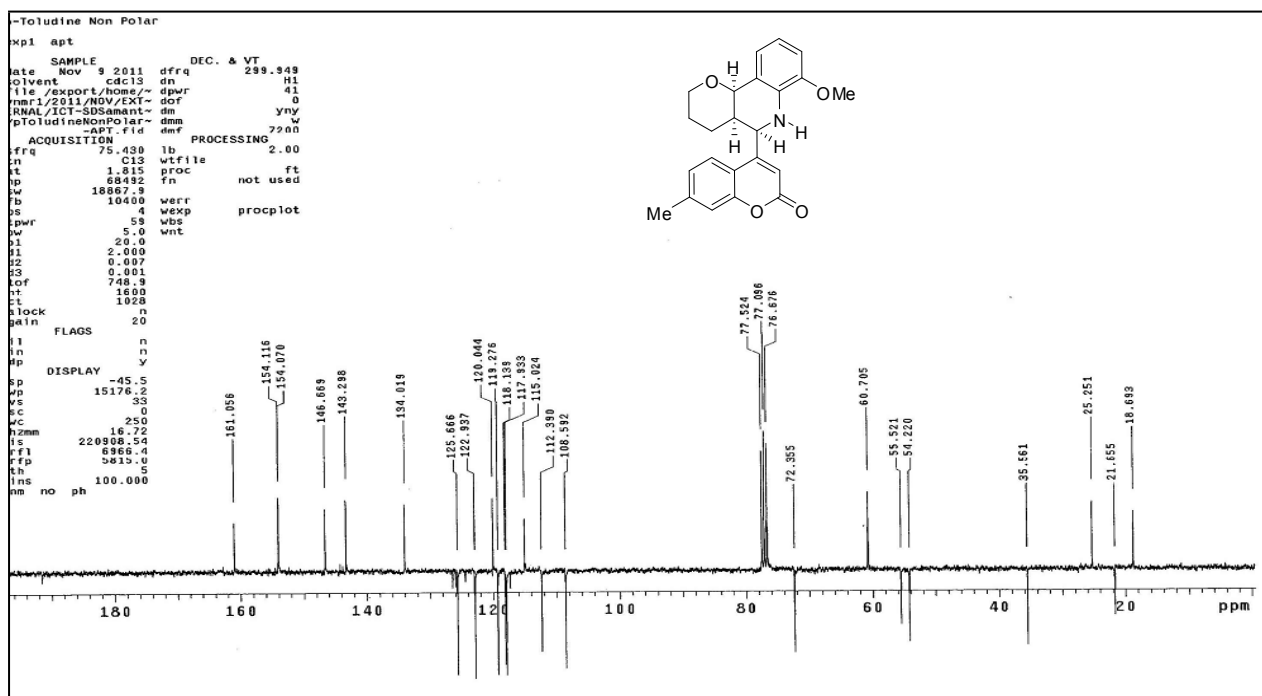
Entry	Diagonal peak	Off-diagonal peaks	Entry	Diagonal peak	Off-diagonal peaks
1	H _{3a}	(H _{3a} , H ₄) (H _{3a} , H _{2a})	10	H _{10b}	(H _{10b} , H _{4a})
2	H _{3b}	(H _{3b} , H _{2a})	11	H _{3'}	-
3	H ₄	(H ₄ , H _{4a})	12	H ₇	(H ₇ , H ₈)
4	H _{4a}	(H _{4a} , H ₄) (H _{4a} , H ₅) (H _{4a} , H _{10b})	13	H ₉	(H ₉ , H ₈), (H ₉ , H ₁₀)
5	CH ₃	-	14	H _{6'}	(H _{6'} , H _{5'})
6	H _{2a}	(H _{2a} , H _{3b}), (H _{2a} , H _{2b})	15	H ₈	(H ₈ , H ₇), (H ₈ , H ₉)
7	H _{2b}	(H _{2b} , H _{3a}), (H _{2b} , H _{2a})	16	H ₁₀	(H ₁₀ , H ₉)
8	NH	-	17	H _{8'}	-
9	H ₅	(H ₅ , H _{4a})	18	H _{5'}	(H _{5'} , H _{6'})



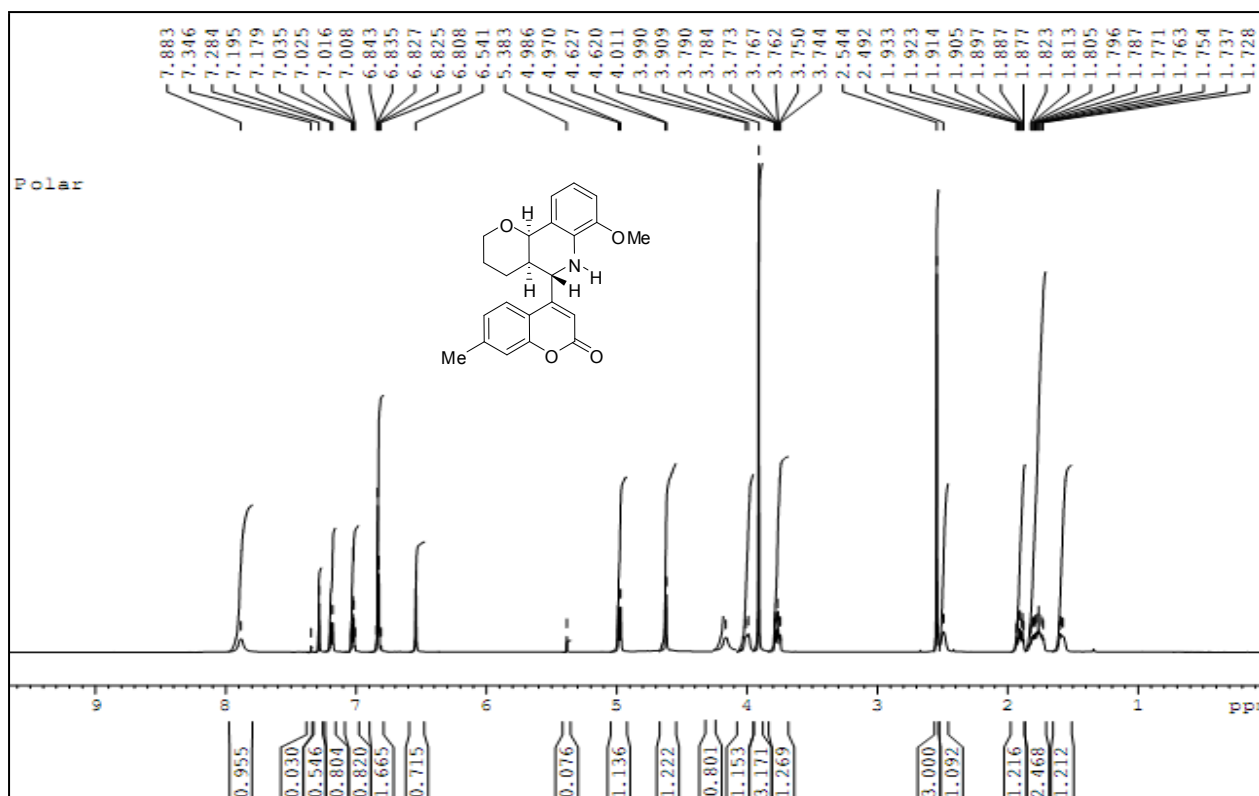
NOE spectrum of **11a'**



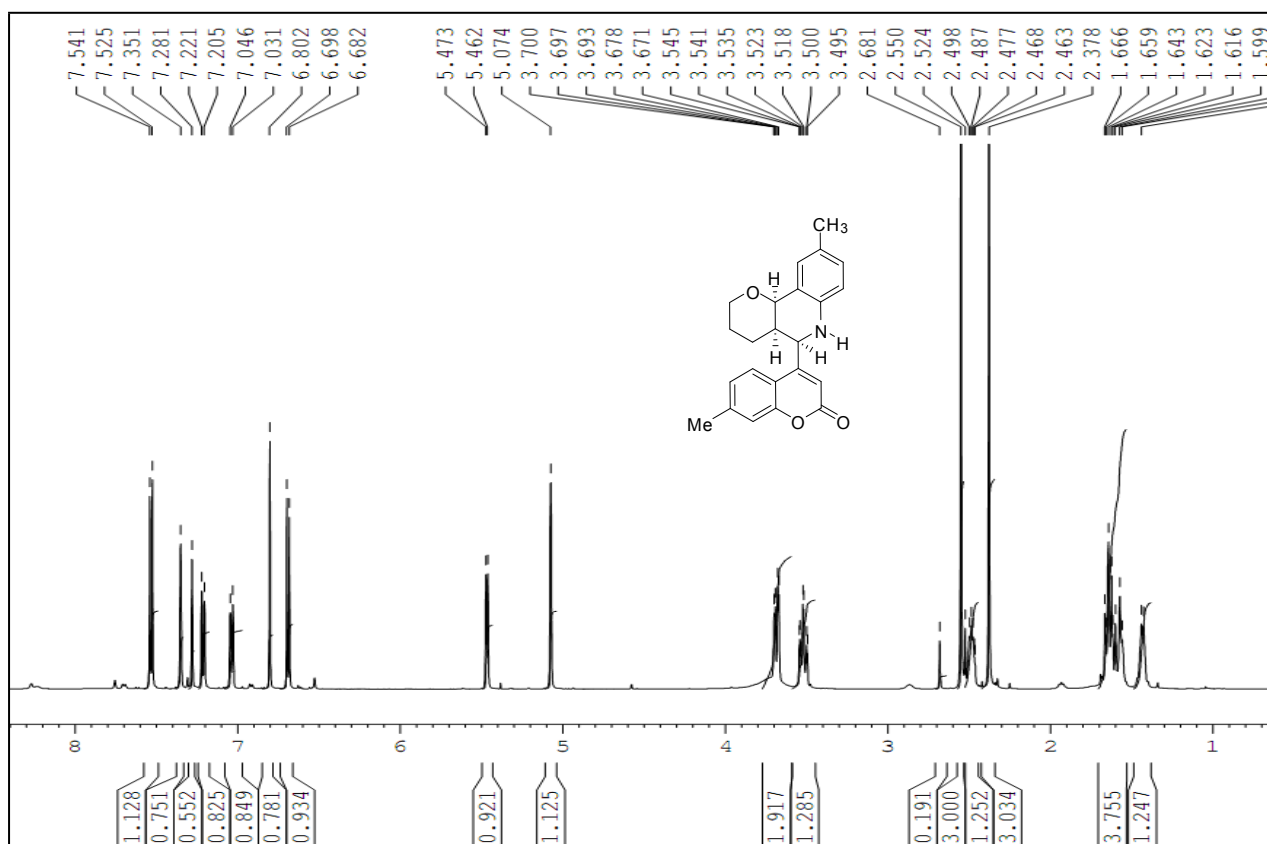
^1H NMR (500 MHz) spectrum of **12a**



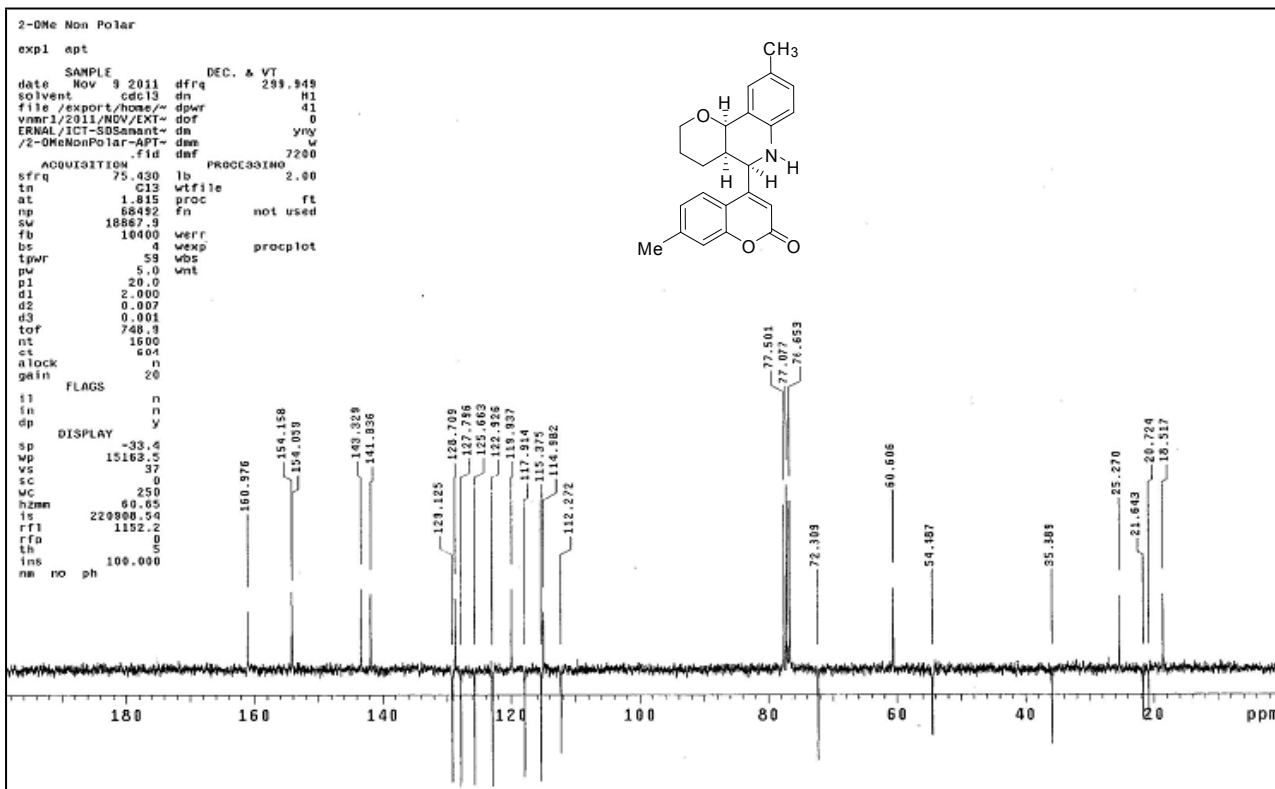
^{13}C NMR (75 MHz) spectrum of **12a**



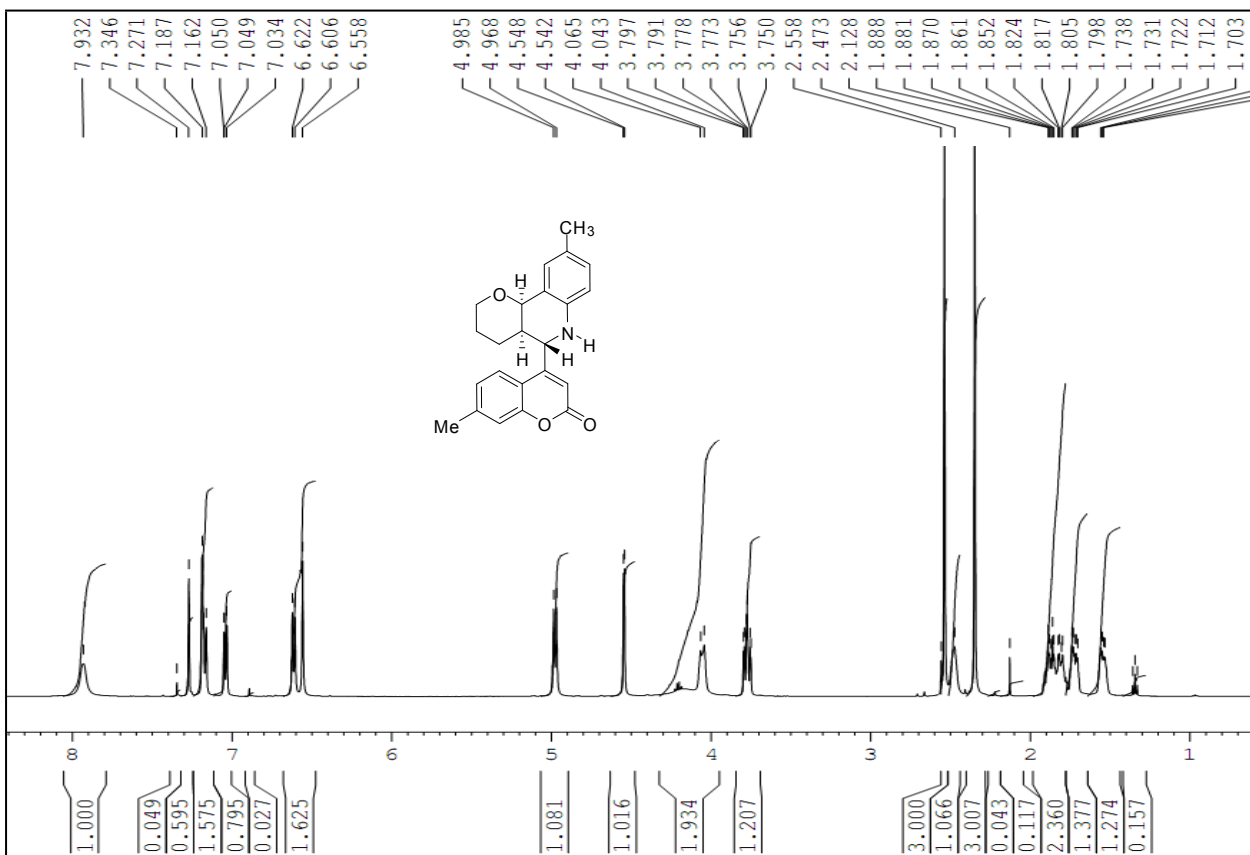
¹H NMR (500 MHz) spectrum of **12a'**



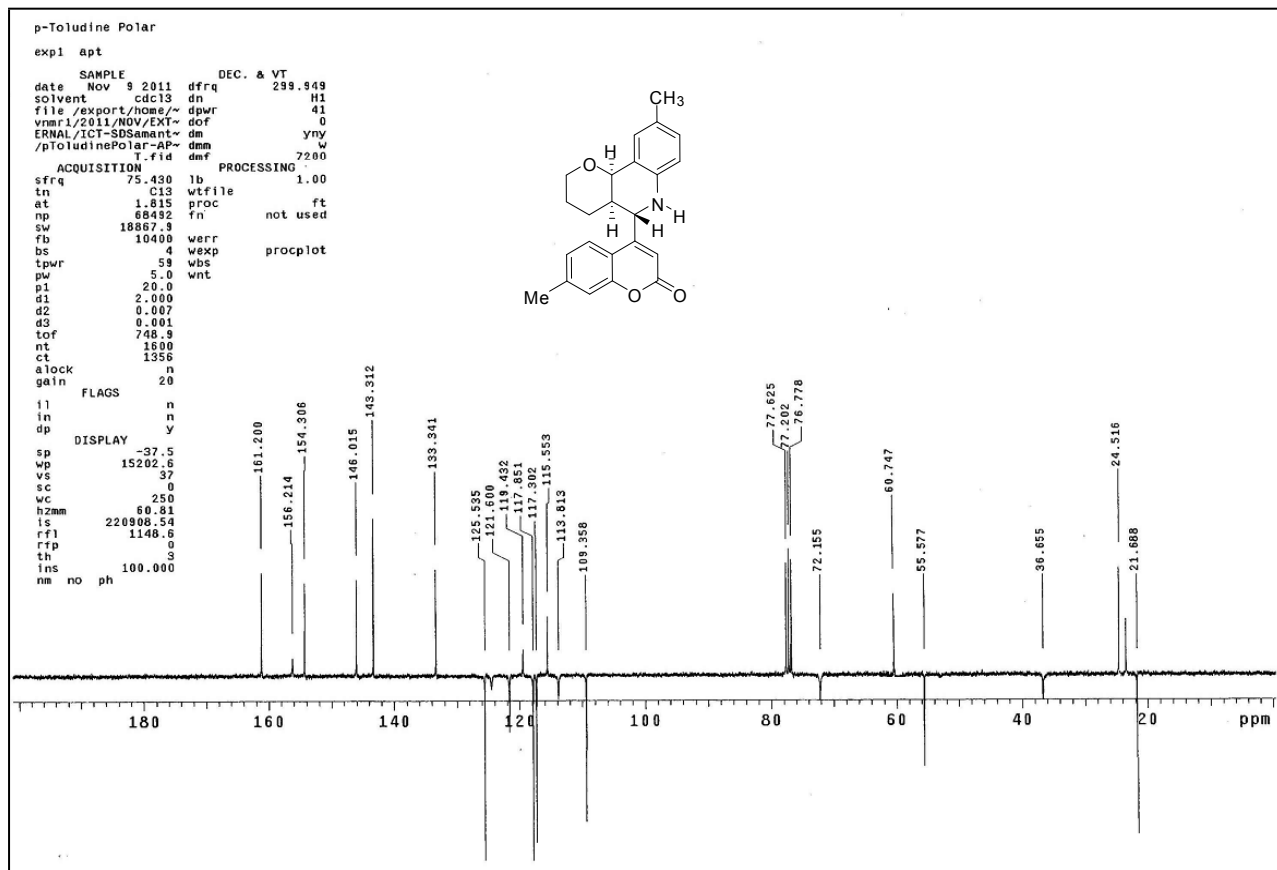
¹H NMR (500 MHz) spectrum of **13a**



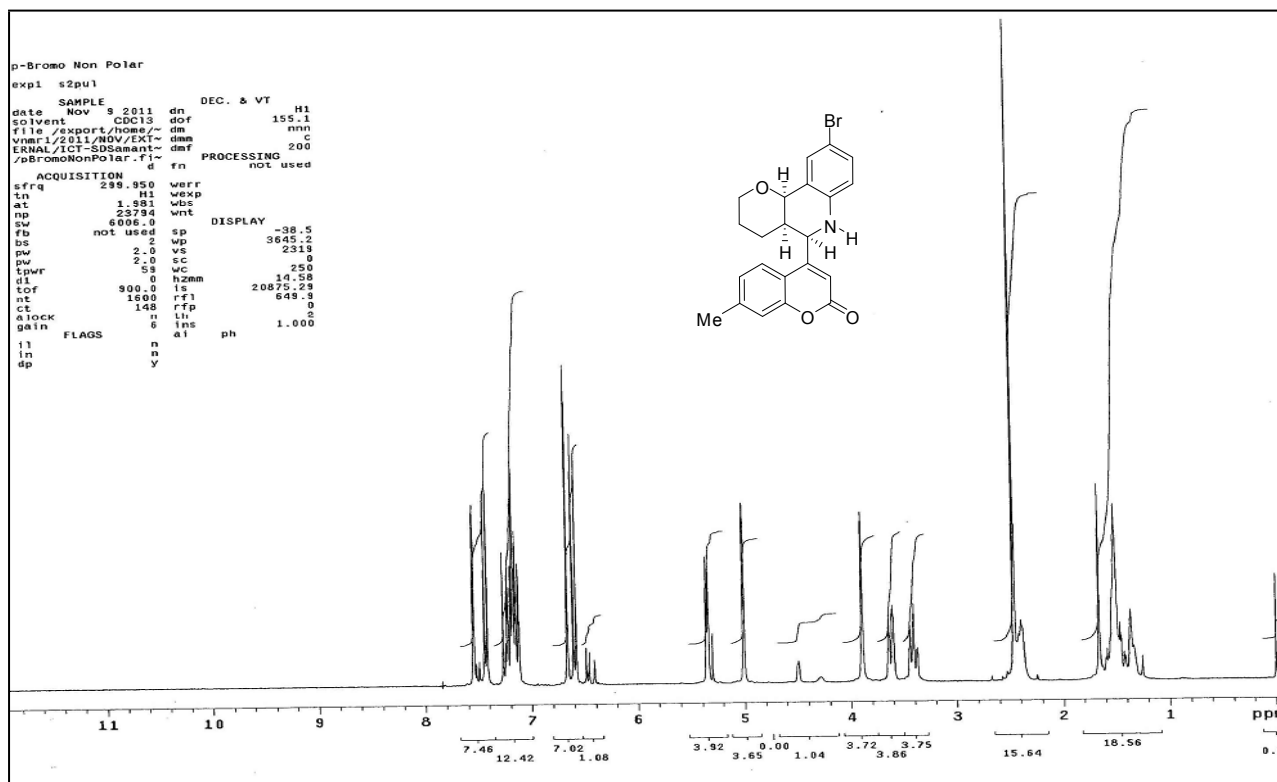
^{13}C NMR (75 MHz) spectrum of **13a**



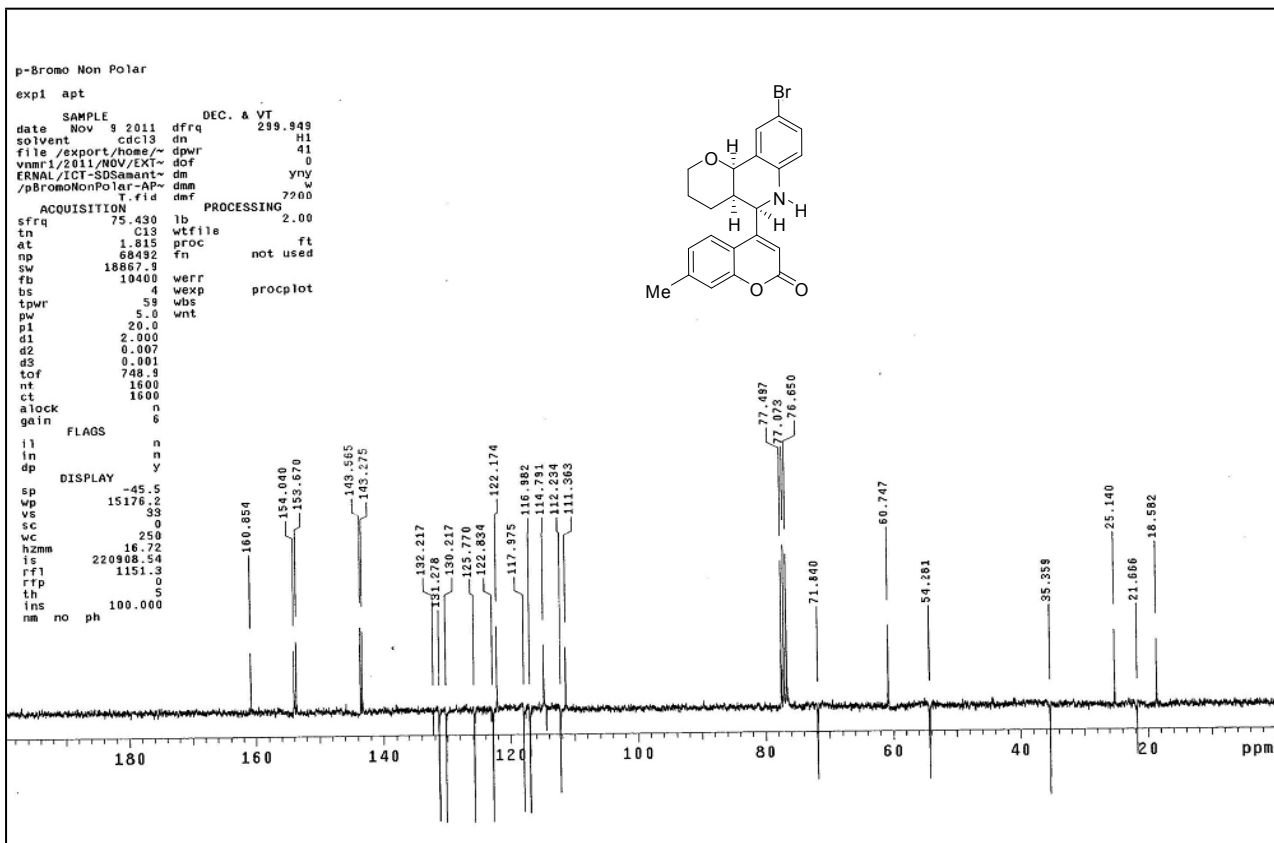
^1H NMR (500 MHz) spectrum of **13a'**



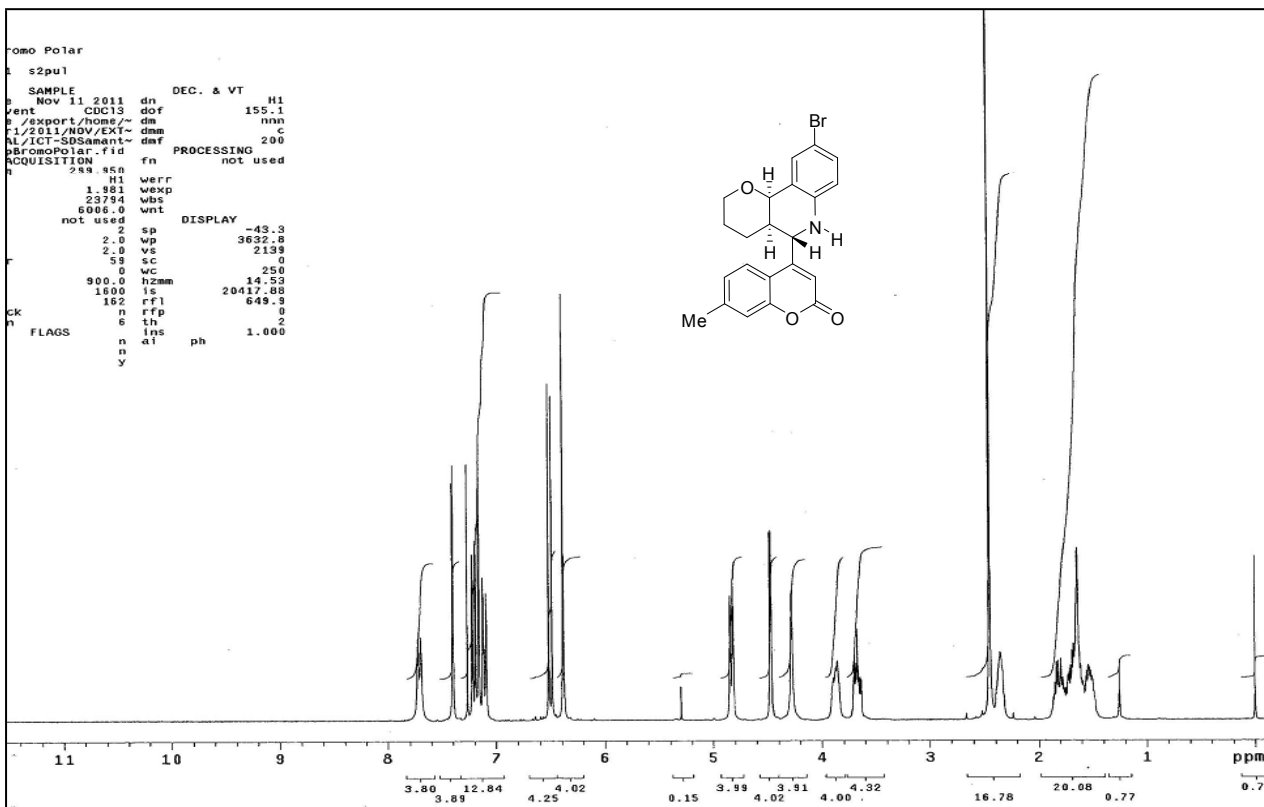
¹³C NMR (75 MHz) spectrum of **13a'**



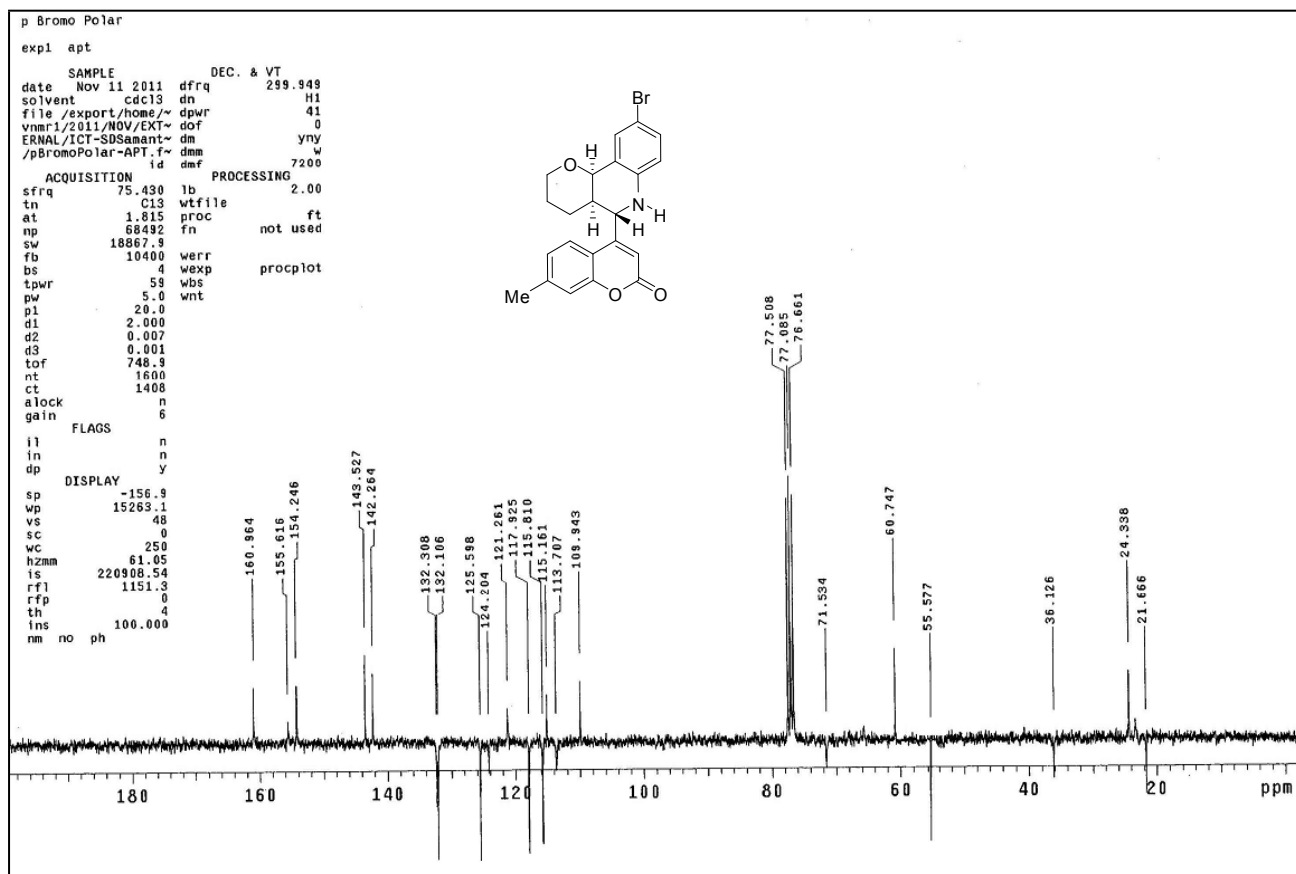
¹H NMR (300 MHz) spectrum of **14a**



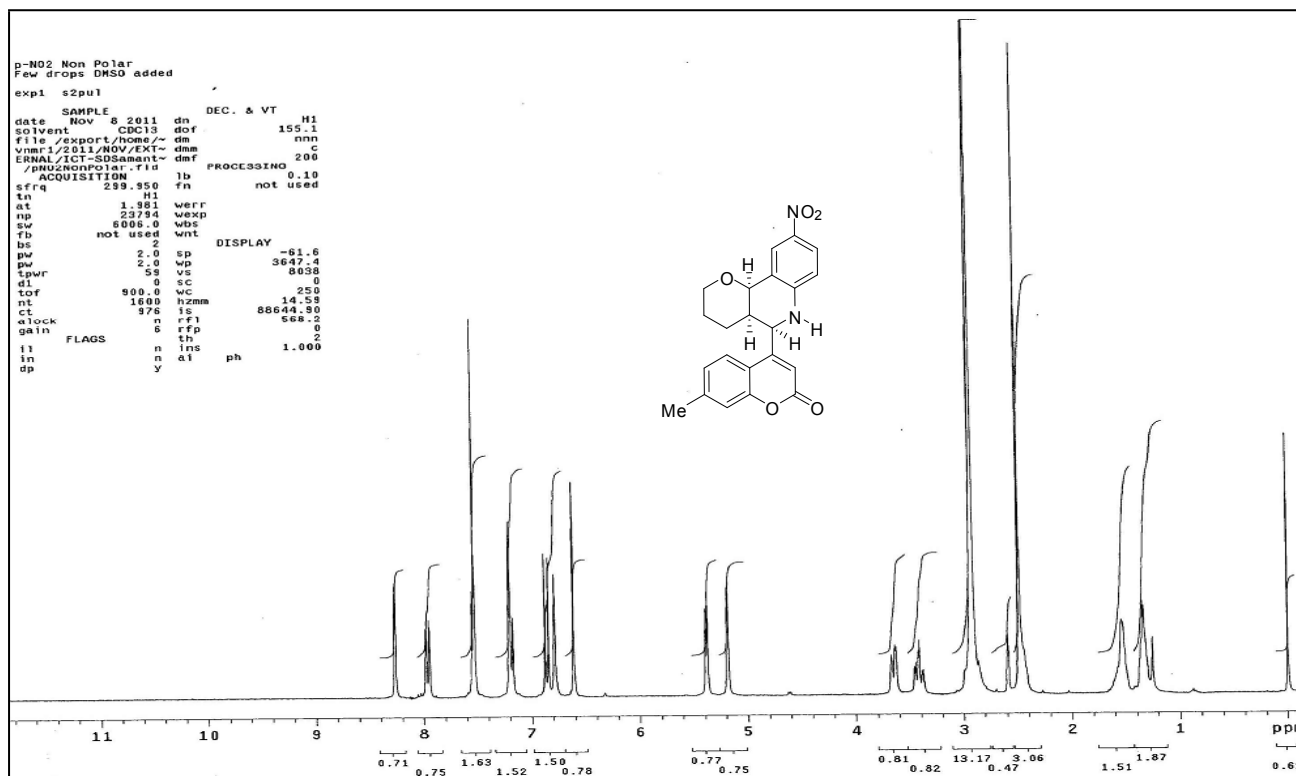
¹³C NMR (75 MHz) spectrum of 14a



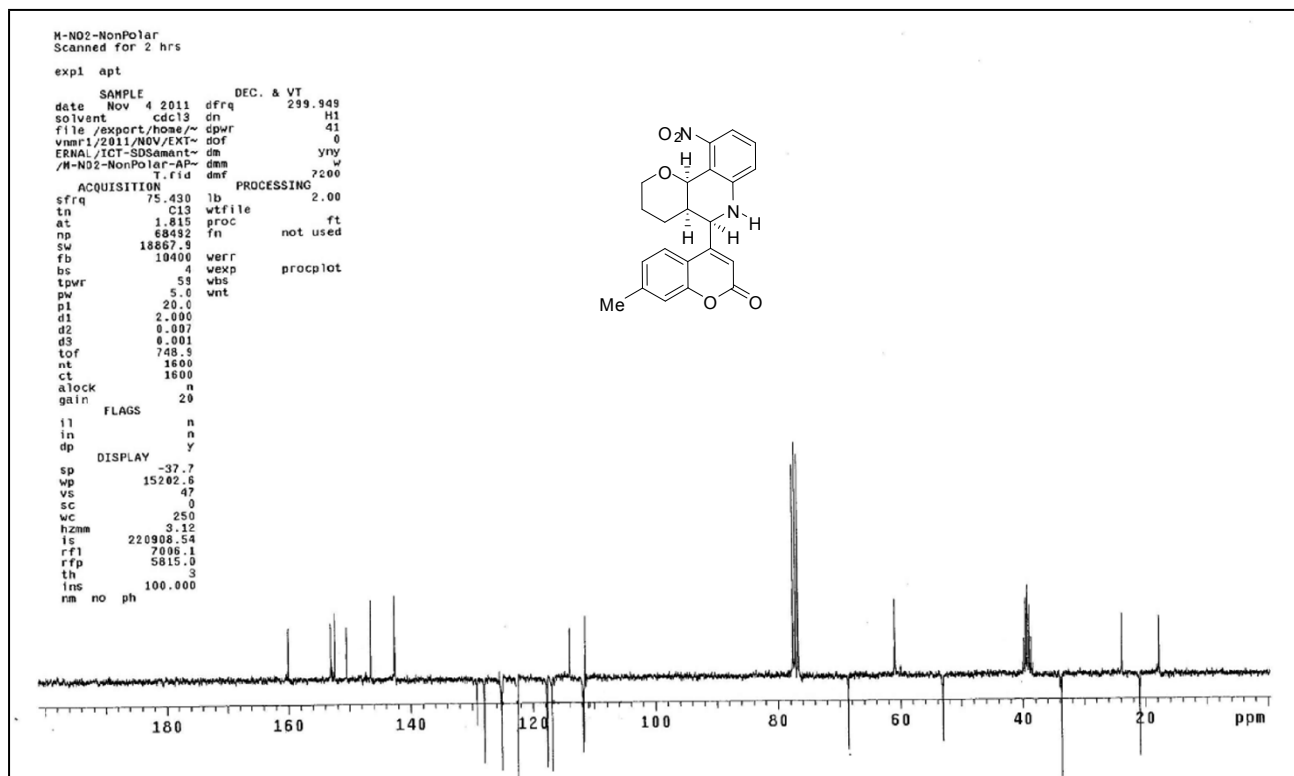
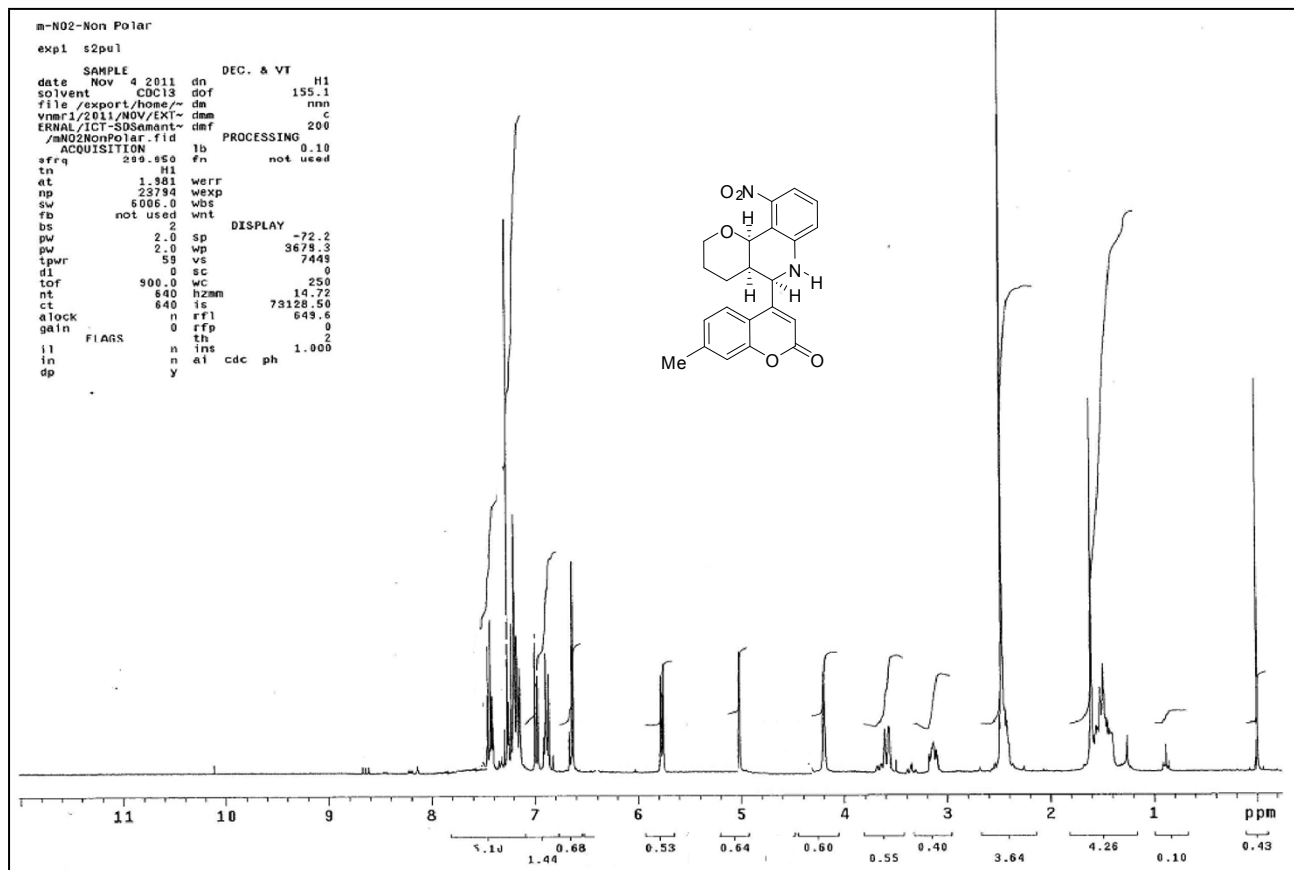
¹H NMR (300 MHz) spectrum of 14a'

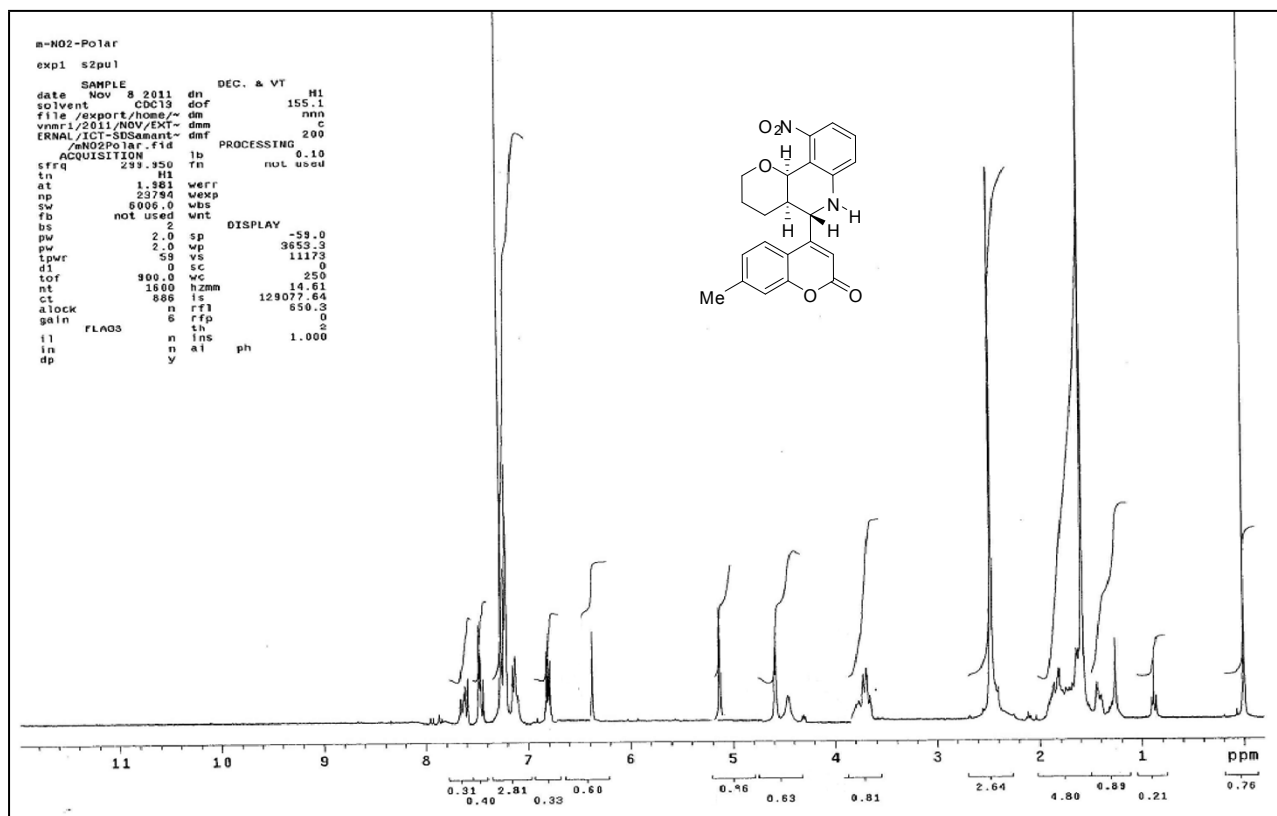


¹³C NMR (75 MHz) spectrum of **14a**

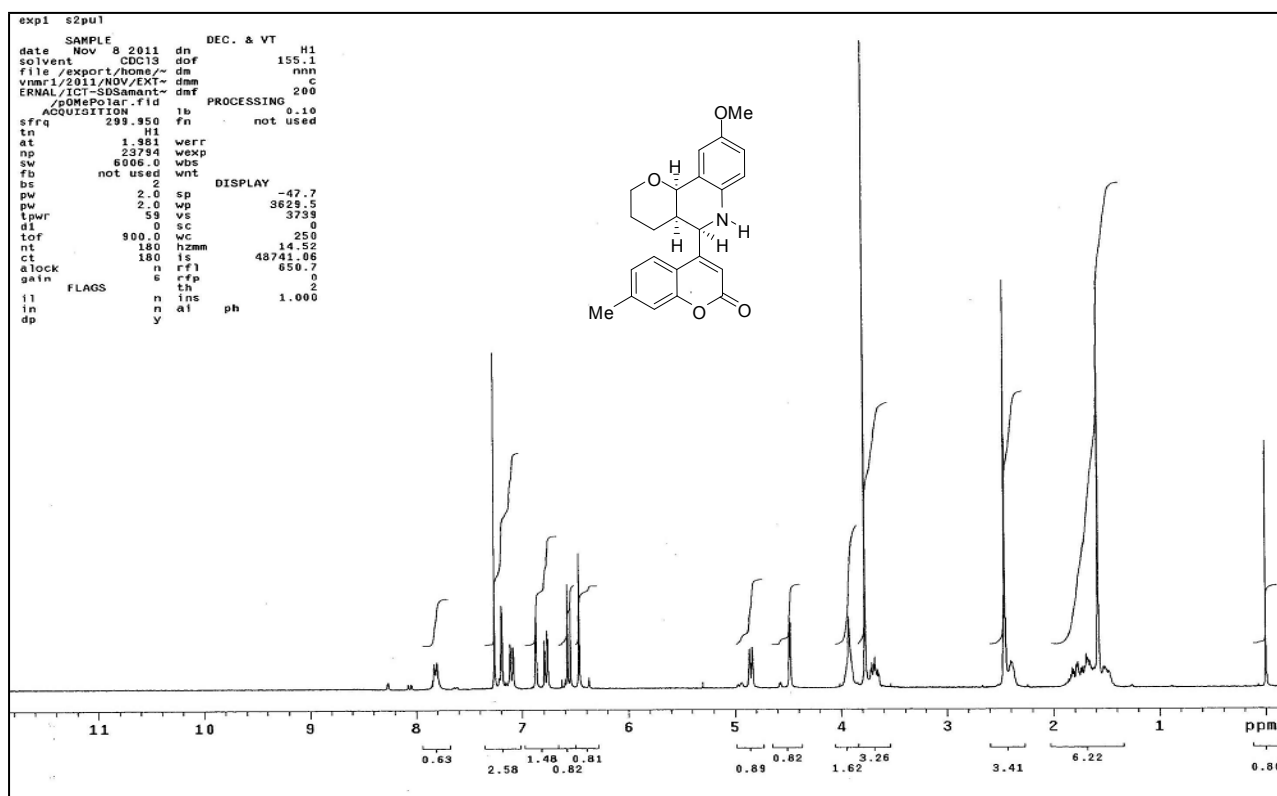


¹H NMR (300 MHz) spectrum of **15a**

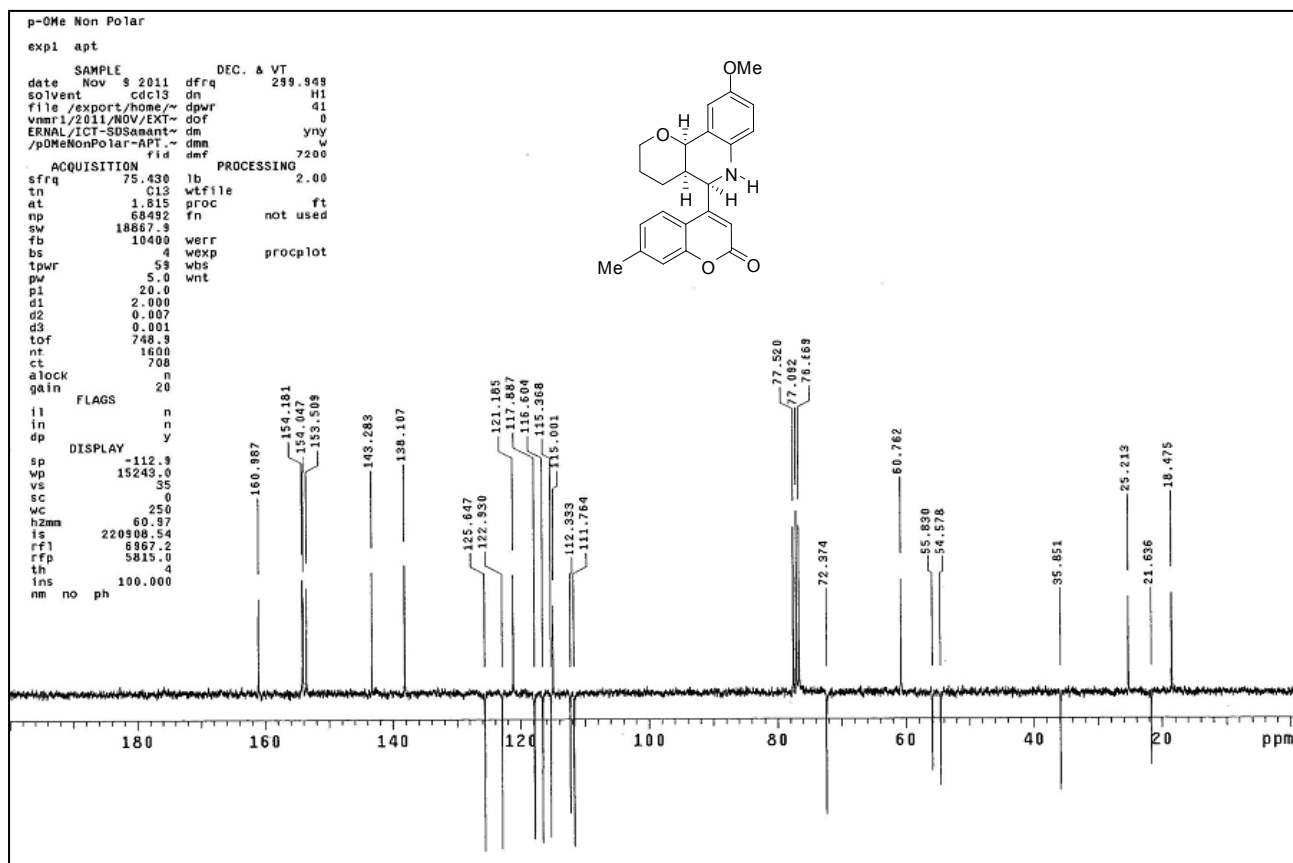




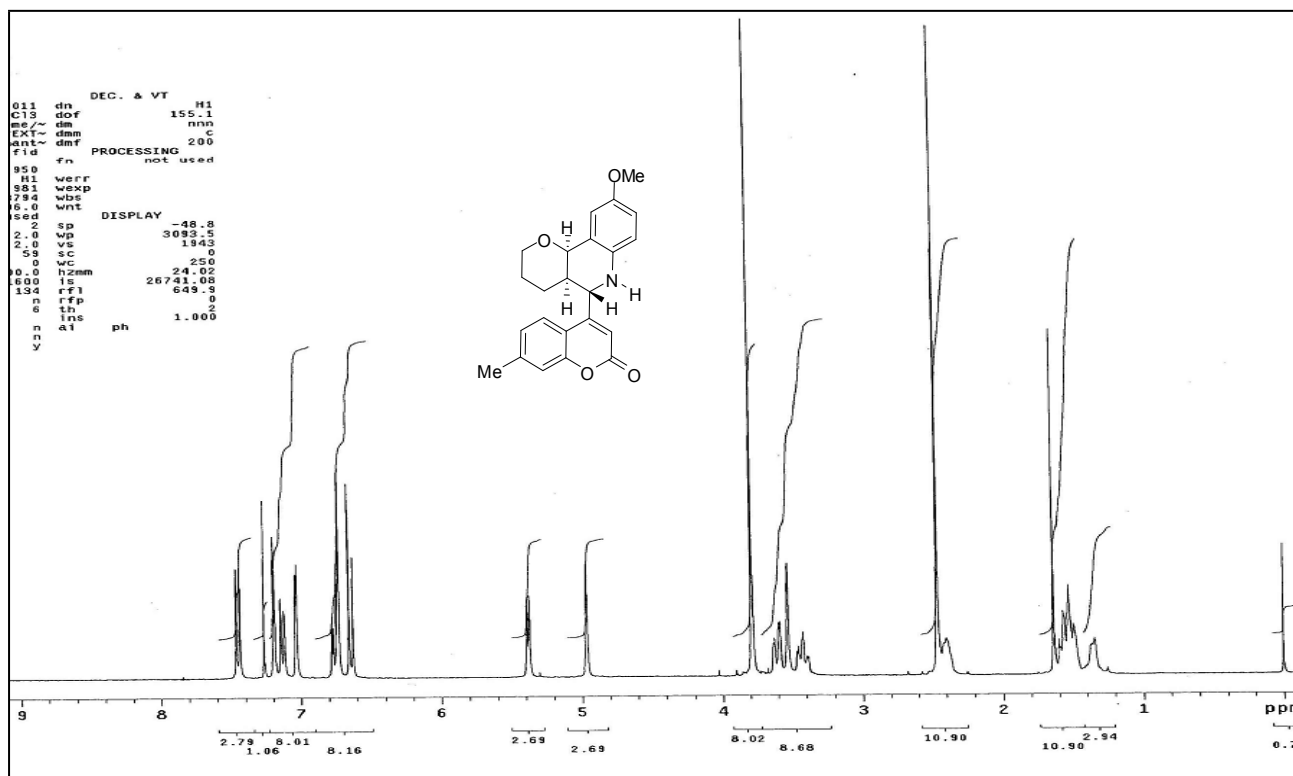
¹H NMR (300 MHz) spectrum of **16a'**



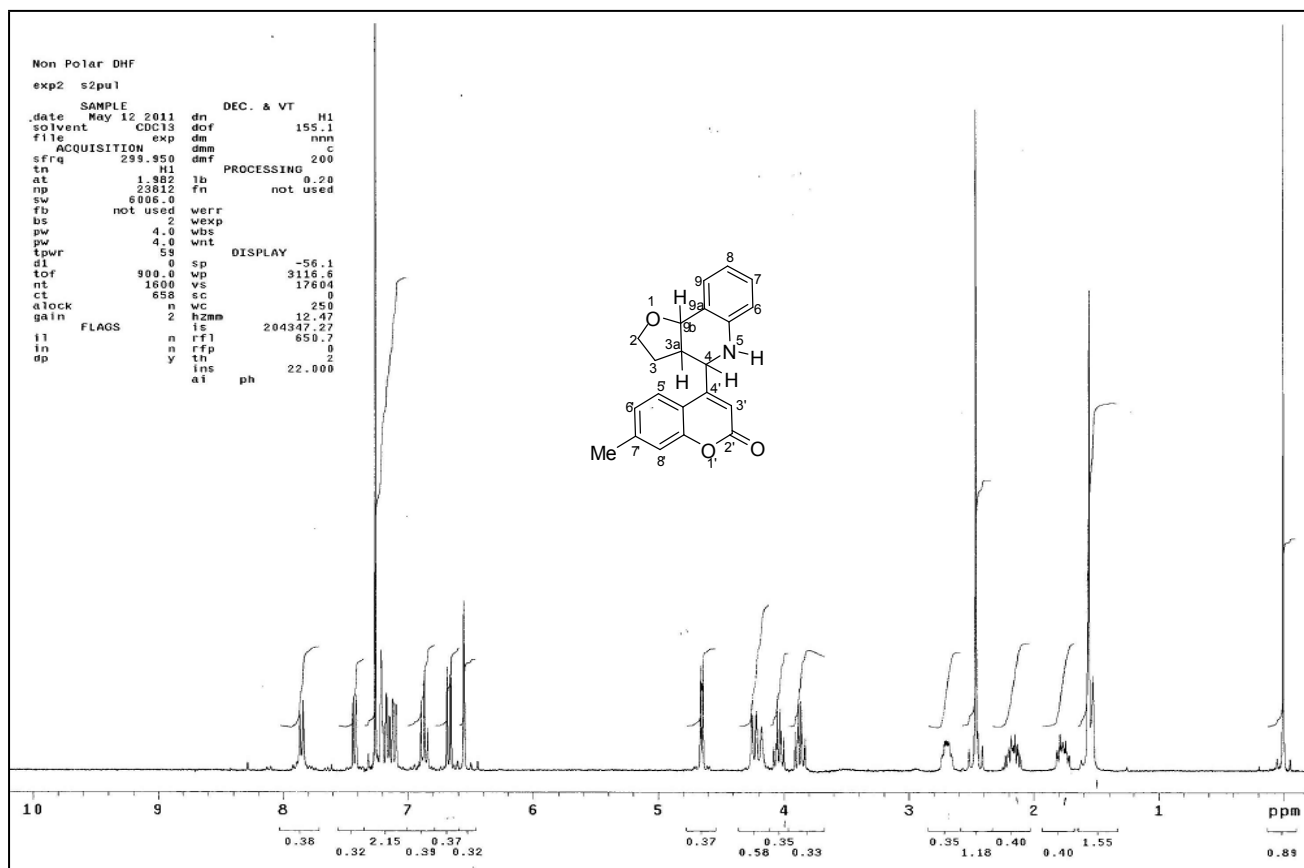
¹H NMR (300 MHz) spectrum of **17a**



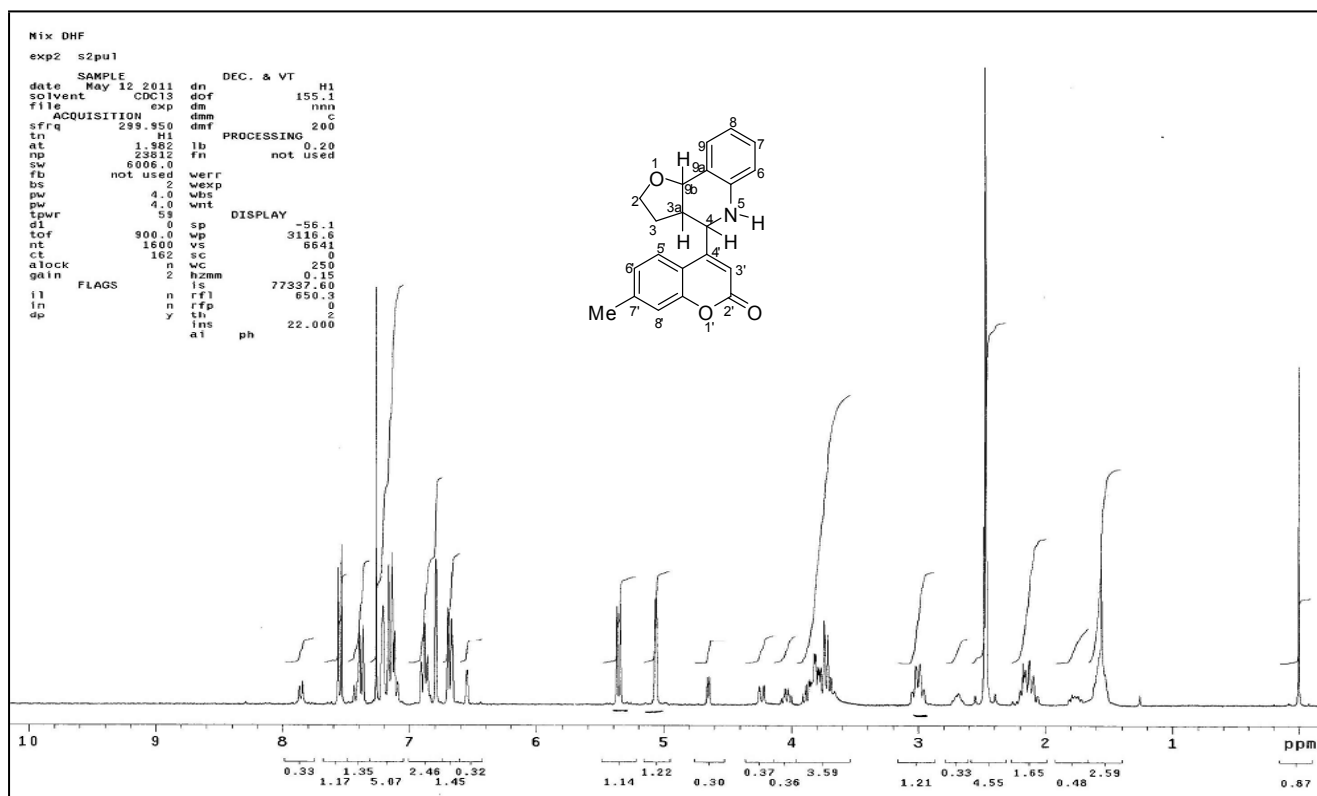
¹³C NMR (75 MHz) spectrum of **17a**



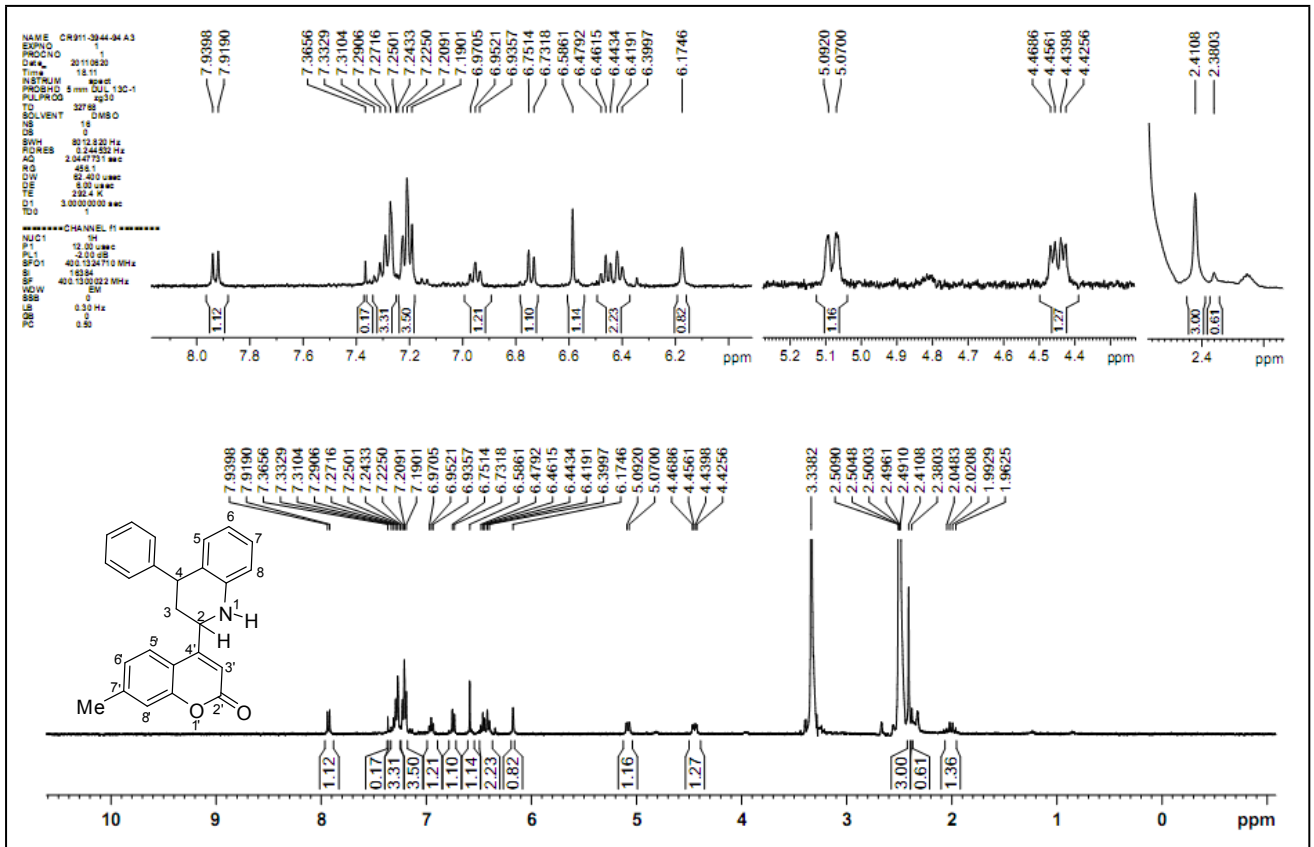
¹H NMR (300 MHz) spectrum of **17a**



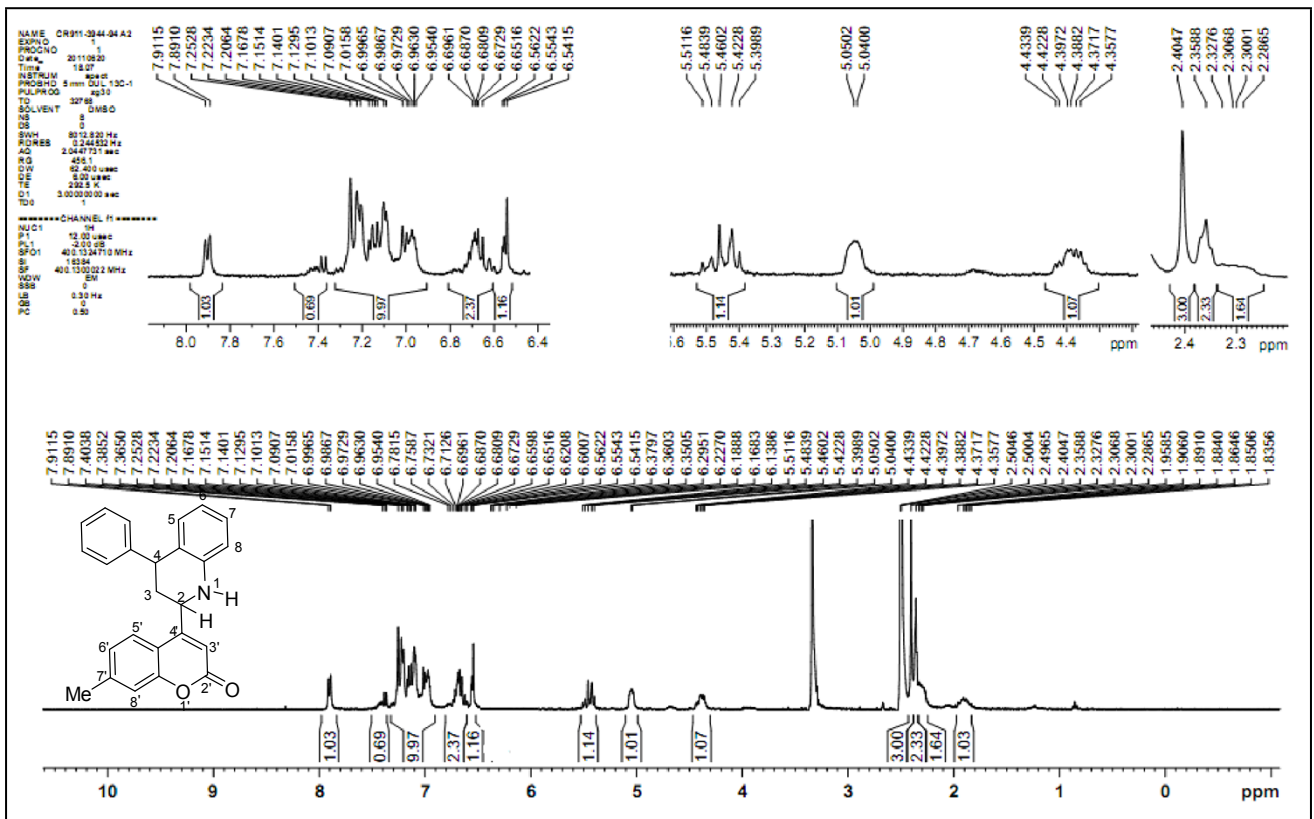
¹H NMR (300 MHz) spectrum of **20a**



¹H NMR (300 MHz) spectrum of mixture of **20a** + **20a'**



¹H NMR (400 MHz) spectrum of 21a



¹H NMR (400 MHz) spectrum of 21a'