Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

$PhI(OAc)_2$-Mediated Intramolecular Oxidative C-N Coupling and Detosylative Aromatization: an Access to Indolo[2,3-*b*]quinolines

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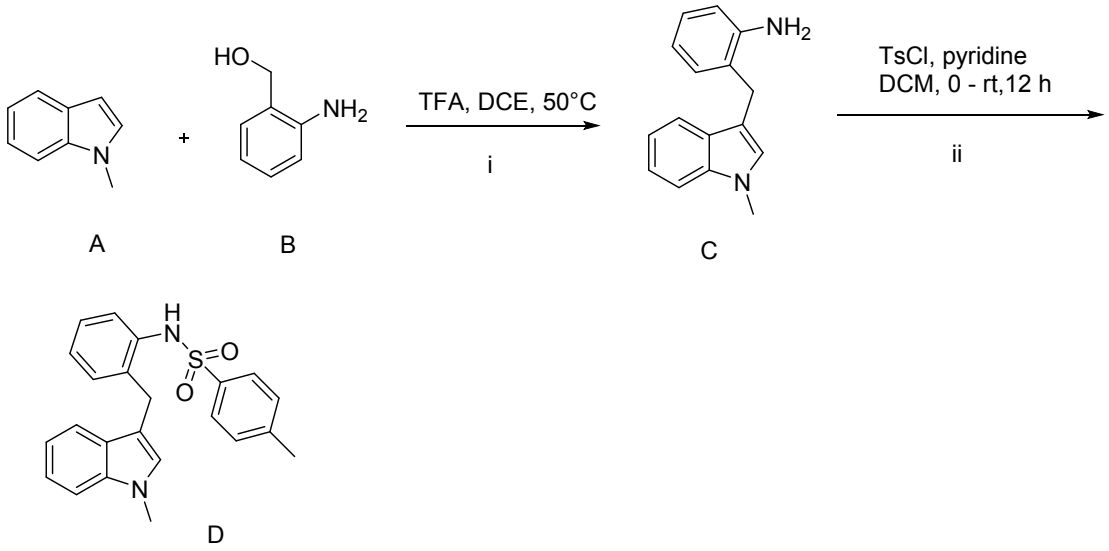
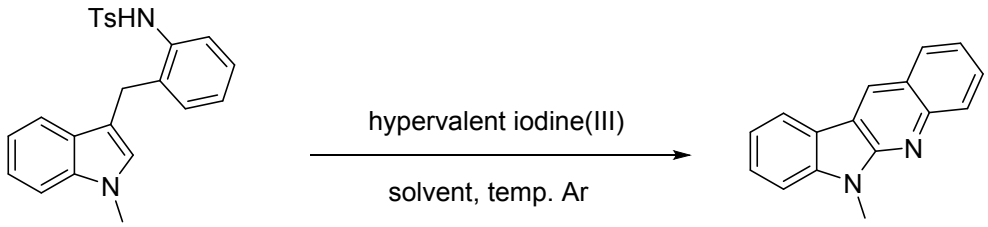
I. Preparation of Starting Materials



(i) To a solution of A (1.0 equiv) and (2-aminophenyl)-methanol B (2.0 equiv) in DCE was added TFA (30 mol%) at room temperature. The resulting solution was stirred at 50 ^{o}C for 12 h. After the reaction was completed (monitored by TLC), the reaction was quenched with saturated aqueous $NaHCO_3$, then diluted with DCM and washed with brine. The organic phase was dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product C.

(ii) The intermediate C (1.0 equiv) was dissolved in dry DCM and the solution was cooled to 0 ^{o}C. Pyridine (1.3 equiv) and TsCl (1.2 equiv) were then added dropwise. The reaction mixture was warmed to room temperature and stirred at this temperature for 12 h until TLC analysis showed a complete consumption of the starting material. HCl (1 N) was added and the organic layer was washed with water. The aqueous layer was extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product D.

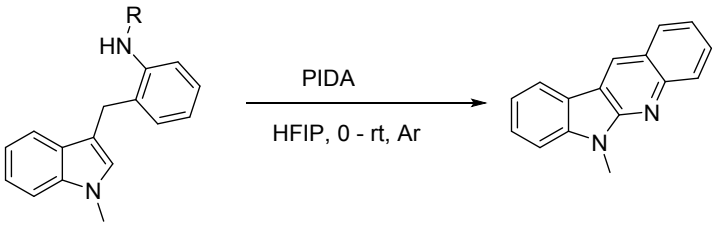
II. Optimization of the Reaction Conditions[a]



Entry	Oxidant	Solvent	Temp. (℃)	Additive	Yield (%)[b]
1	PIDA	DCM	rt	-	10
2	PIFA	DCM	rt	-	trace
3	PIDA	DCE	rt	-	22
4	PIDA	THF	rt	-	28
5	PIDA	dioxane	rt	-	19
6	PIDA	$PhCF_3$	rt	-	16
7	PIDA	TFE	rt	-	51
8	PIDA	HFIP	rt	-	67
9	PIDA	HFIP	0	-	15
10[c]	PIDA	HFIP	rt	-	43
11	PIDA	HFIP	0 - rt	-	82
12[d]	PIDA	HFIP	0 - rt	CS_2CO_3	73

[a]Reaction condition: 1a (0.2 mmol), Oxidant (0.24 mmol), in Ar, solvent (2 mL) was added at rt and stirred for 12 h. [b]Isolated yield in parentheses [c] PIDA was 4.0 mmol. [d]Cs_2CO_3 is 0.24 mmol.

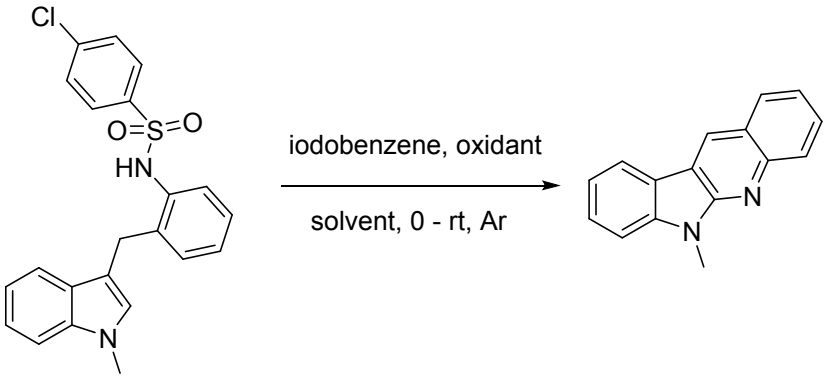
Screening of protecting group R [a]



Entry	Oxidant	Solvent	Temp. (℃)	R	Yield (%)[b]
13	PIDA	HFIP	0 - rt	benzenesulfonyl	73
14	PIDA	HFIP	0 - rt	4-chlorobenzenesulfonyl	86
15	PIDA	HFIP	0 - rt	4-fluorobenzenesulfonyl	75
16	PIDA	HFIP	0 - rt	methylsulfonyl	74
17	PIDA	HFIP	0 – rt	acetyl	trace

[a]Reaction condition: 1 (0.2 mmol), PIDA (0.24 mmol), in Ar, HFIP (2 mL) was added at 0 °C，then temperature was increased to rt stirred for 12 h. [b]Isolated yield in parentheses.

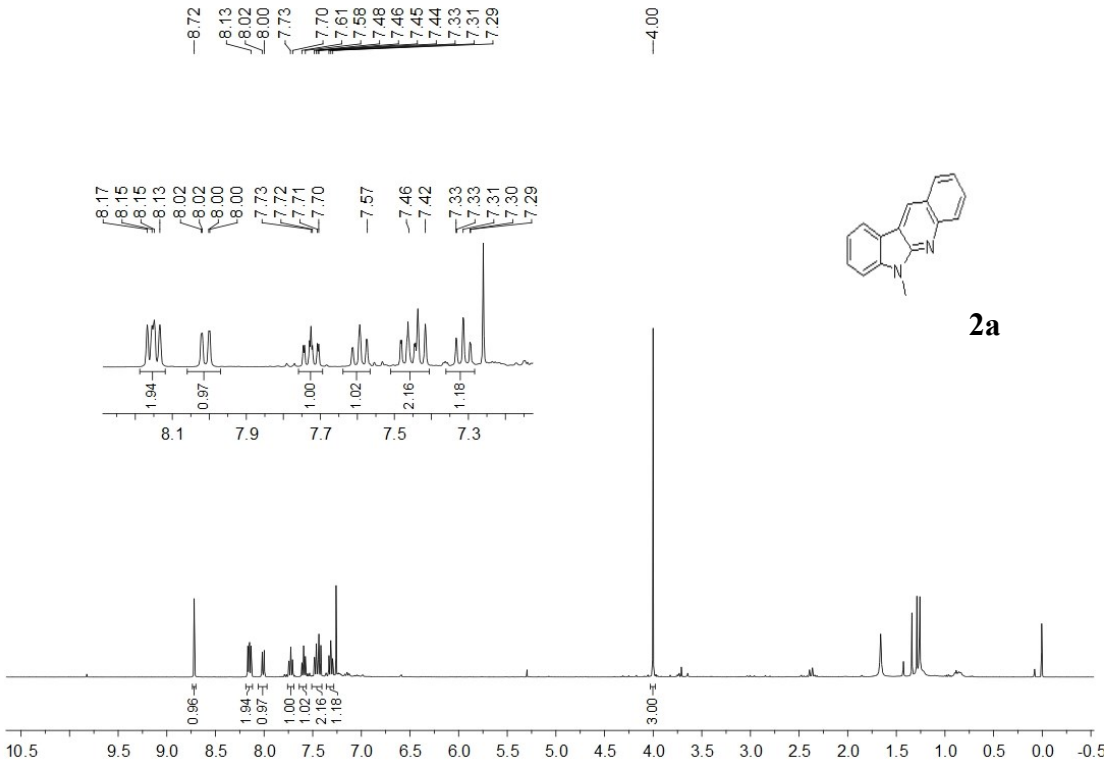
Screening of oxidant and solvent [a]



Entry	Oxidant	Solvent	Temp. (℃)	Additive	Yield (%) [b]
18	H_2O_2	DCM	0 - rt	-	--
29	*m*-CPBA	DCM	0 - rt	-	--
20	*m*-CPBA	CF_3CH_2OH	0 - rt	-	23
21	*m*-CPBA	HFIP	0 - rt	-	25

[a]Reaction condition: 1 (0.2 mmol), iodobenzene (0.06 mmol), oxidant (0.24 mmol) in Ar, solvent (2 mL) was added at 0 ℃， then temperature was increased to rt and stirred for 12 h. [b]Isolated yield in parentheses.

III. Copies of ^{1}H and ^{13}C NMR Spectra



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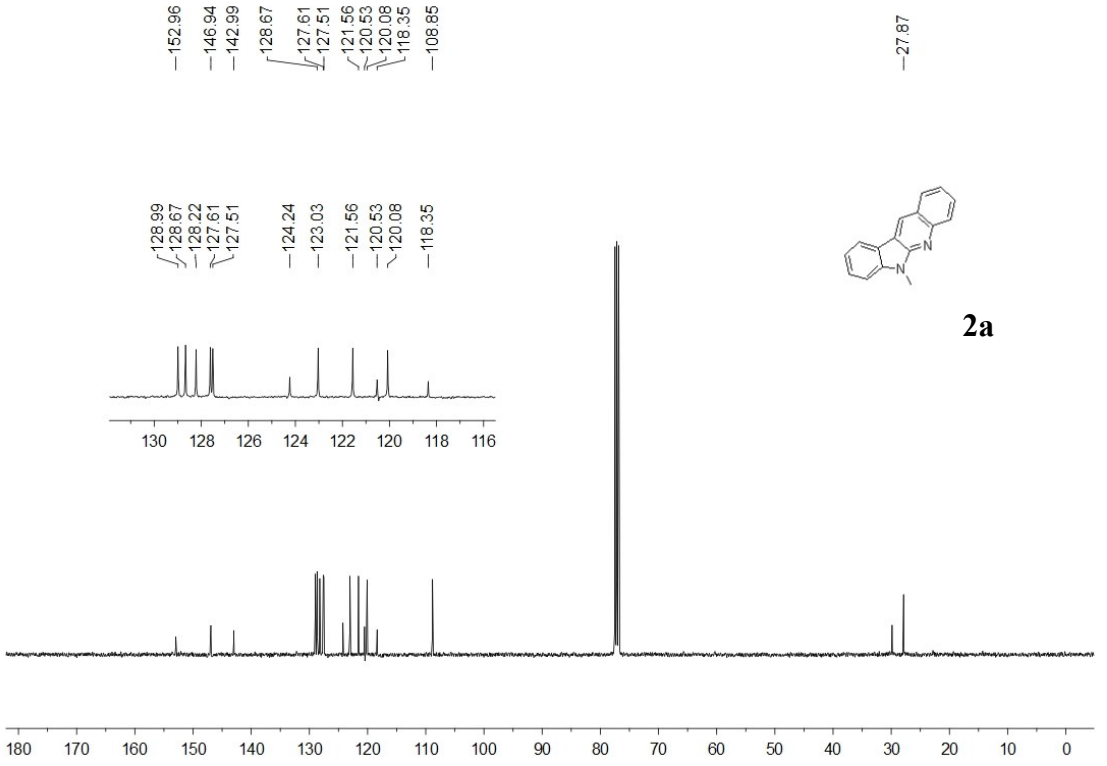

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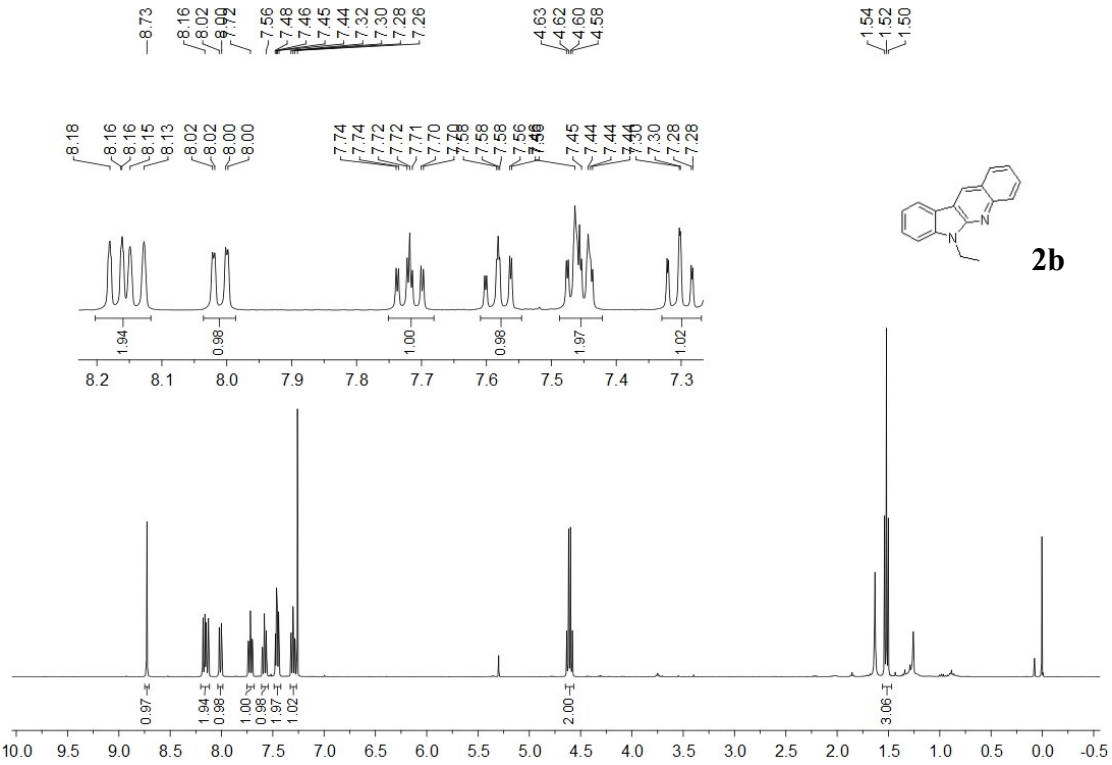
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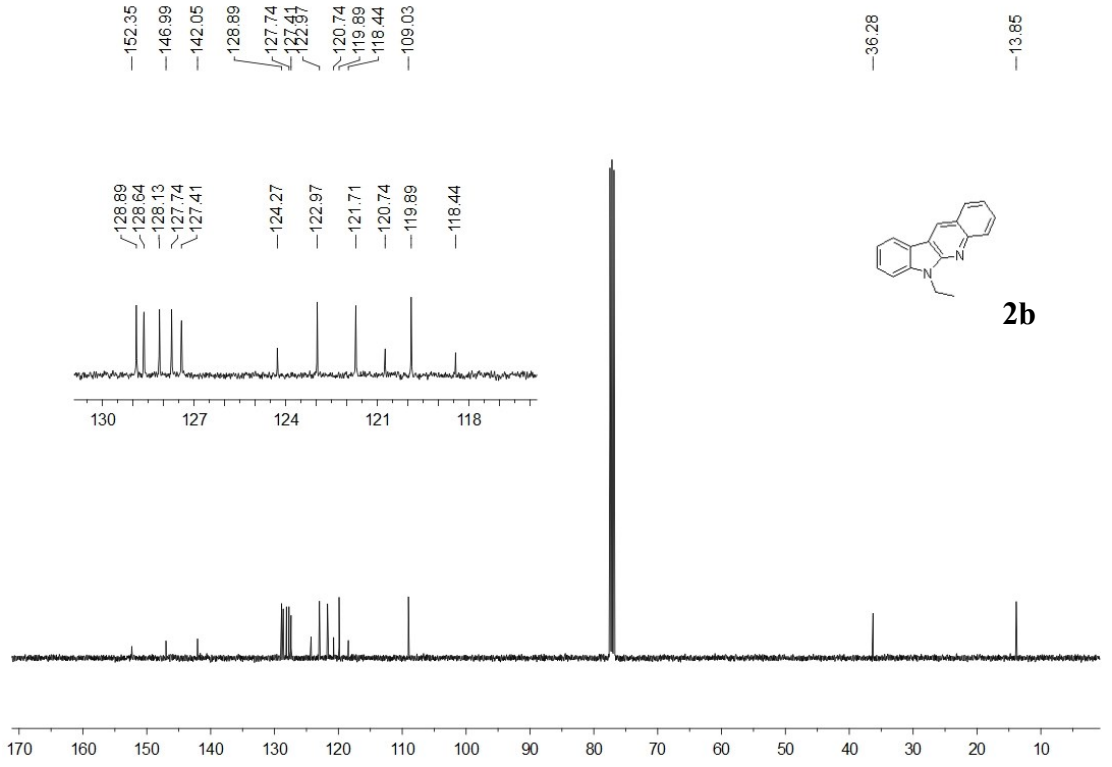
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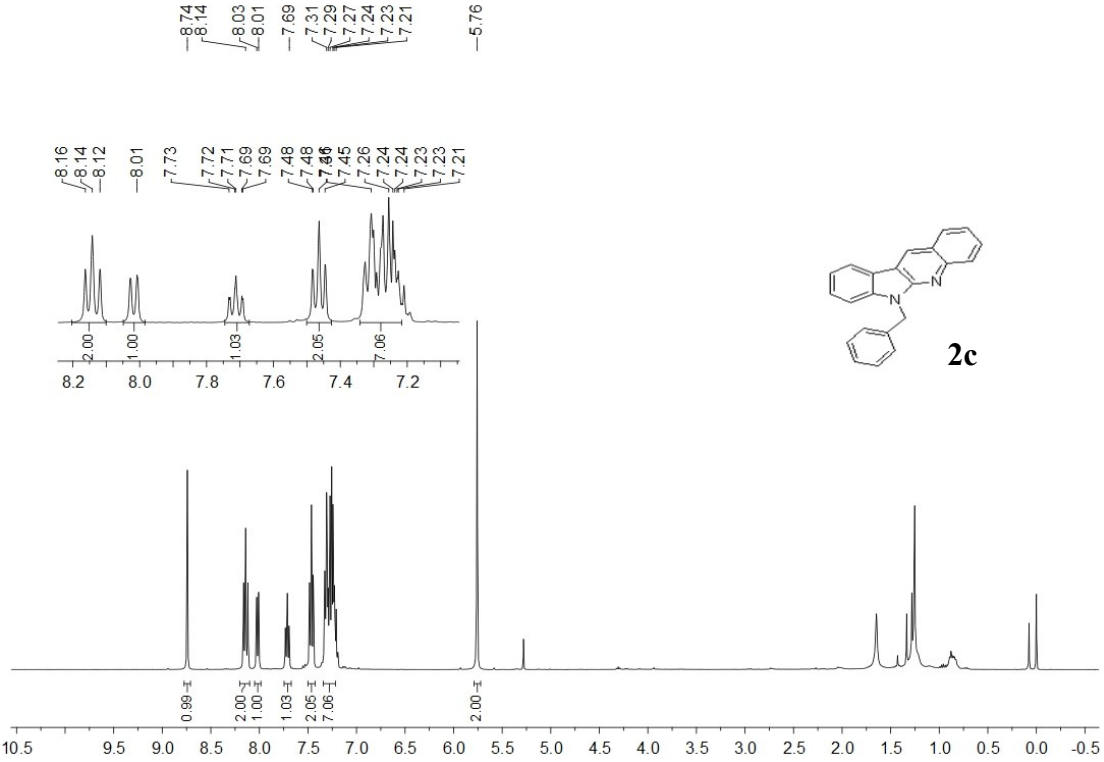
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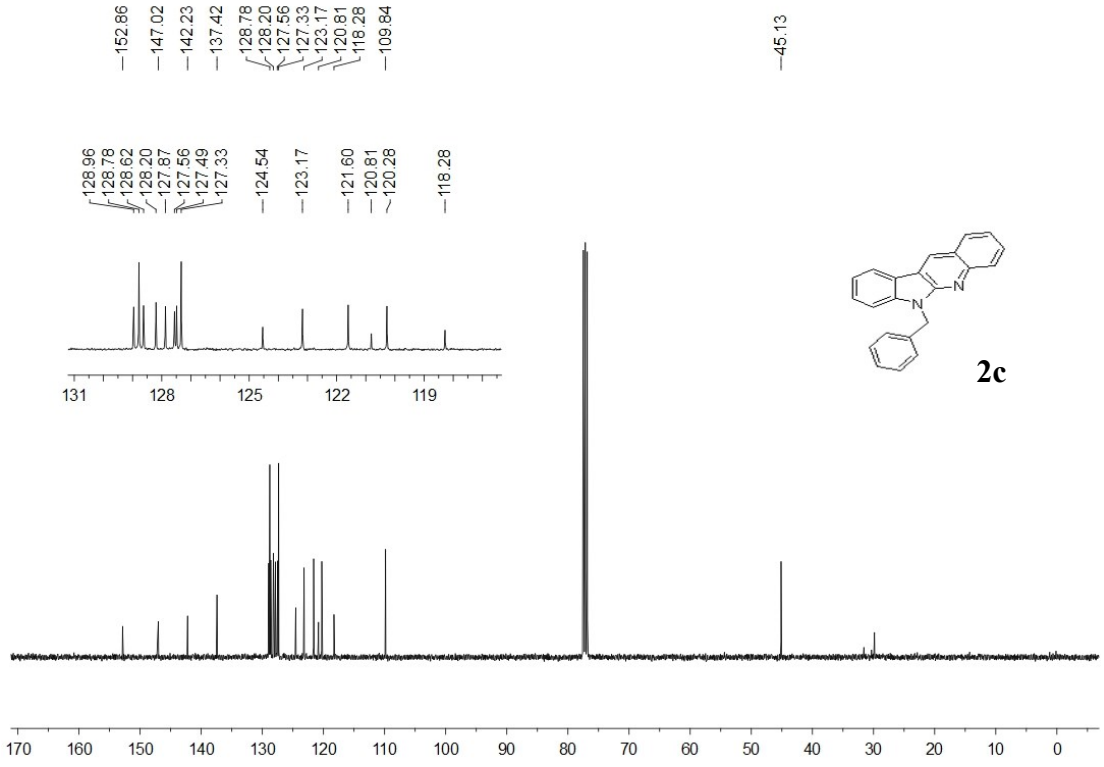
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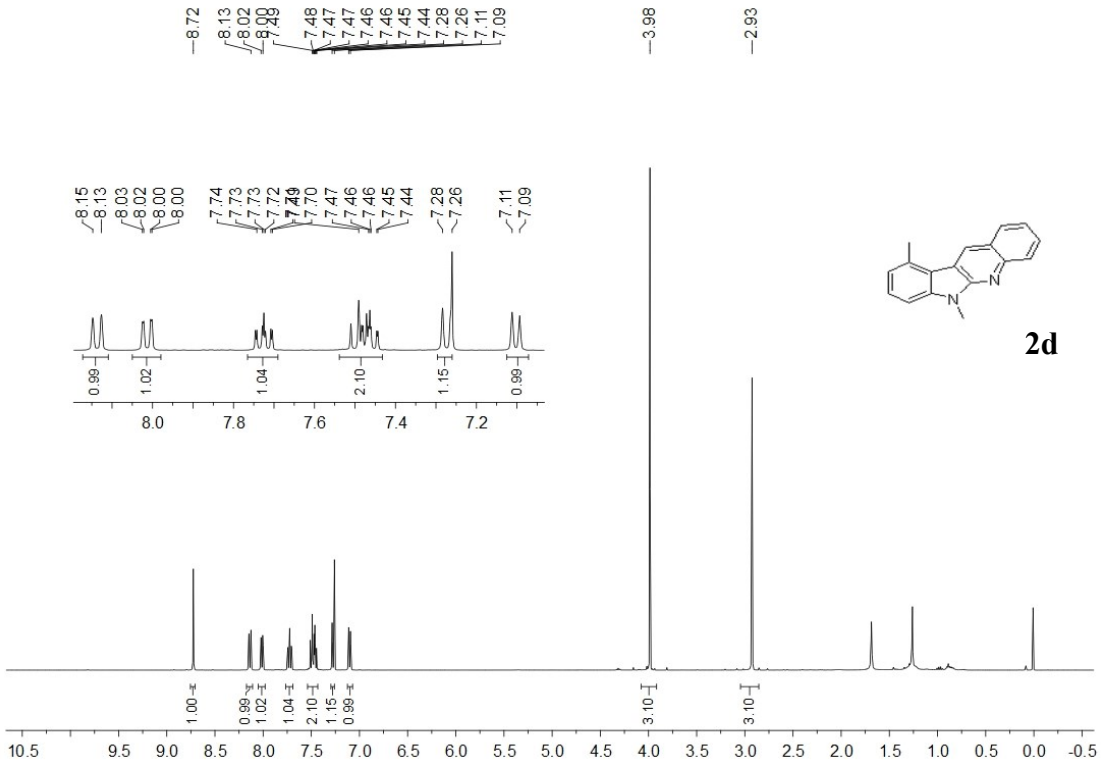
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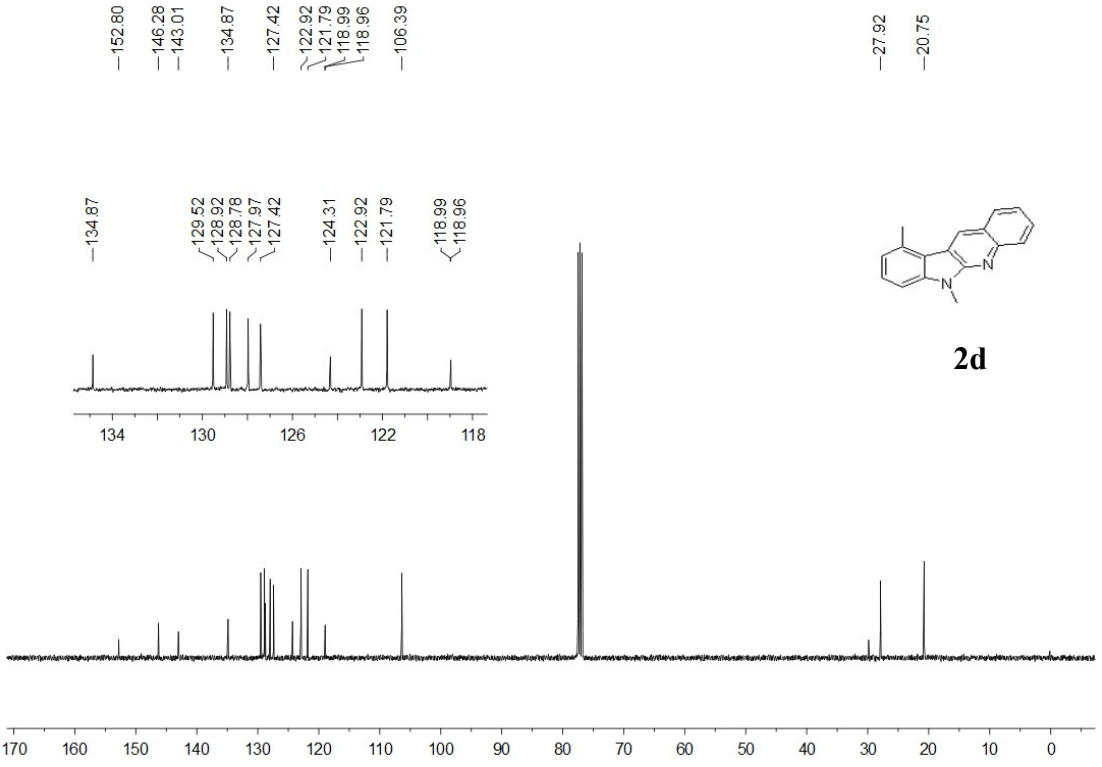
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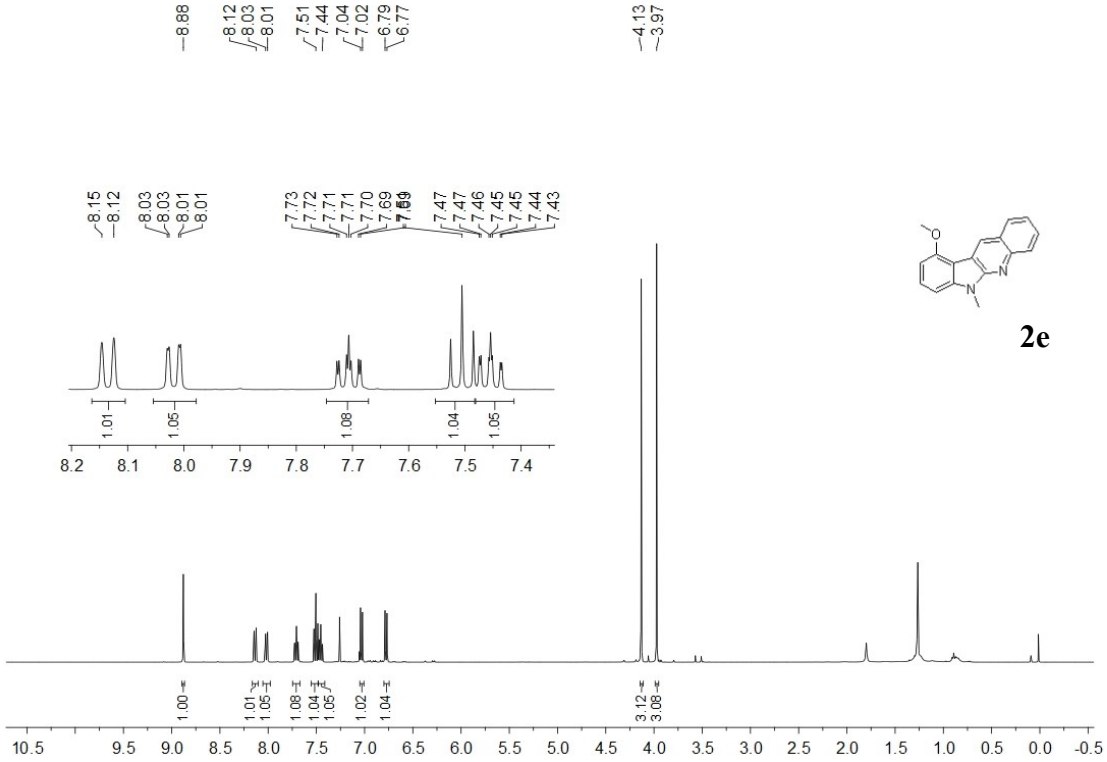
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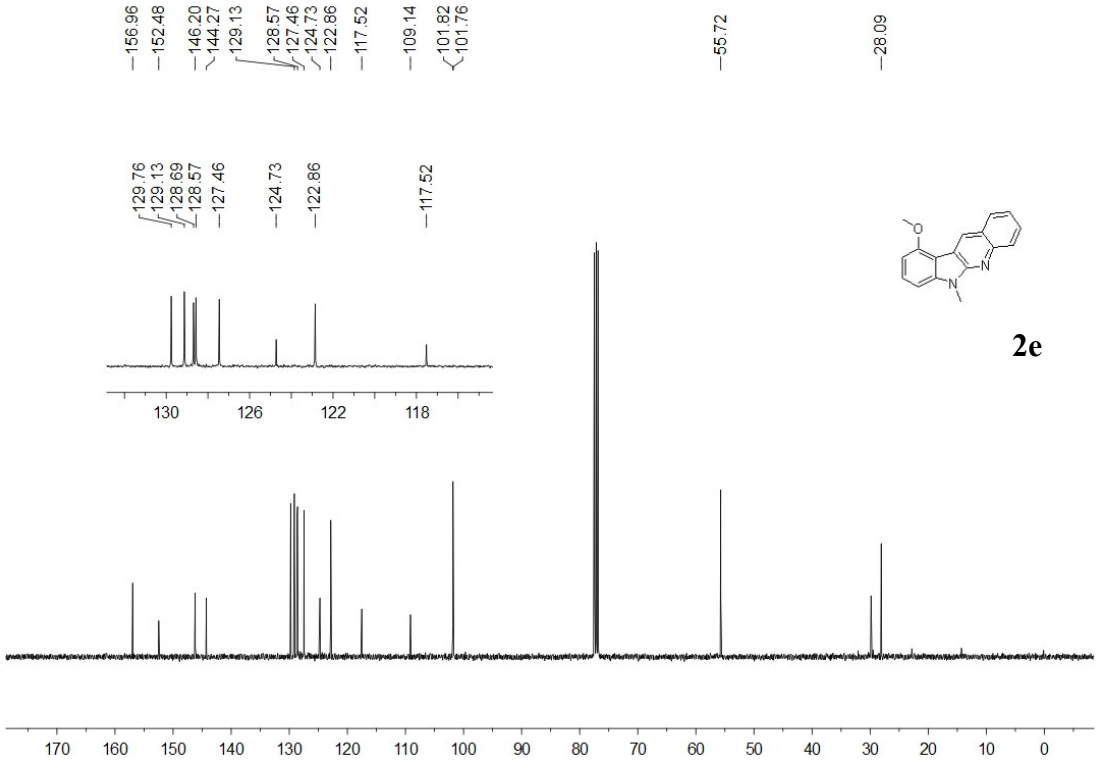
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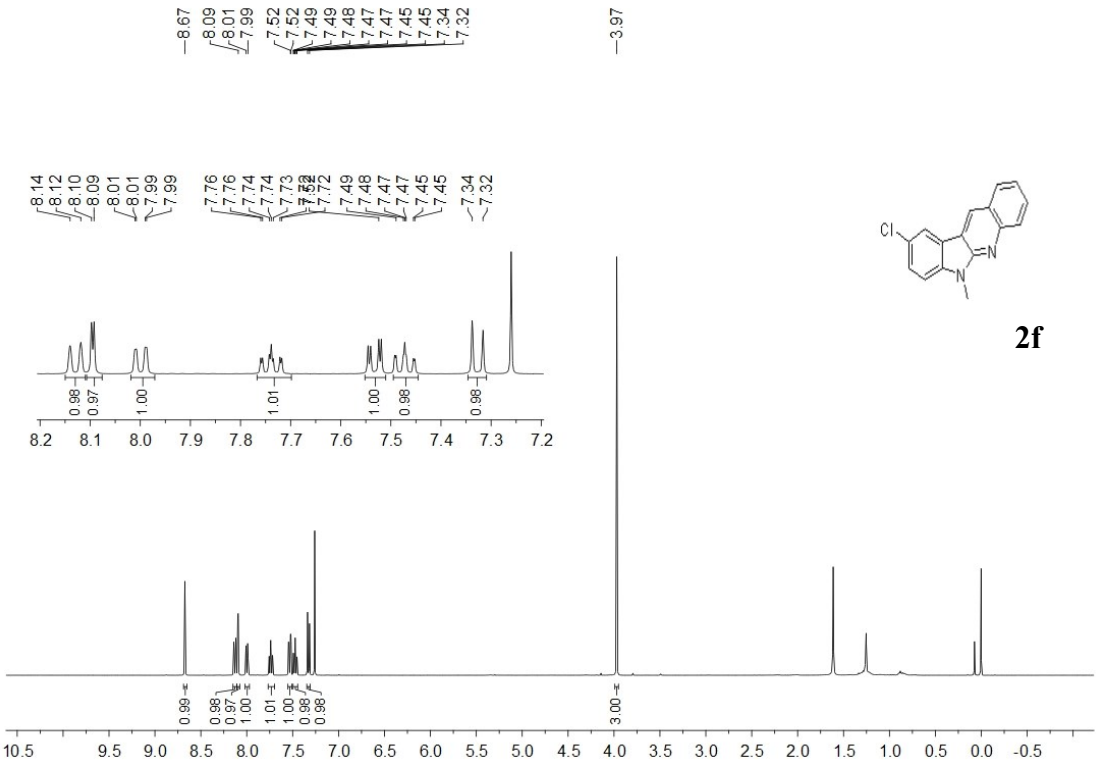
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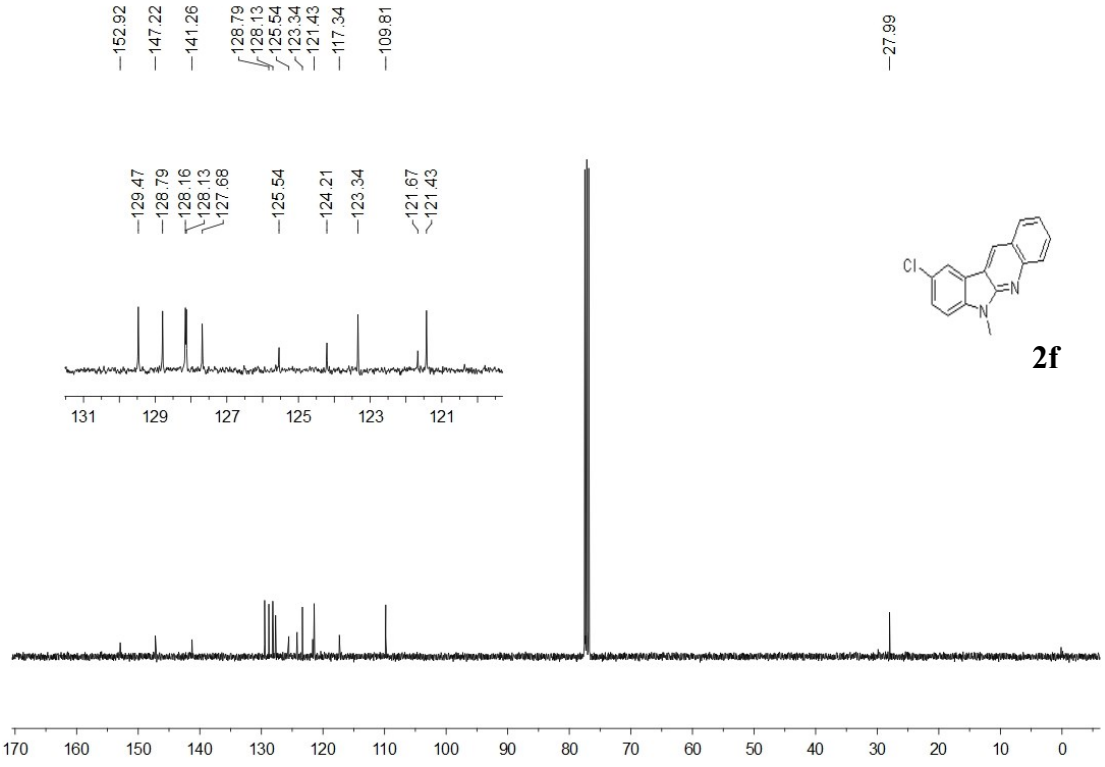
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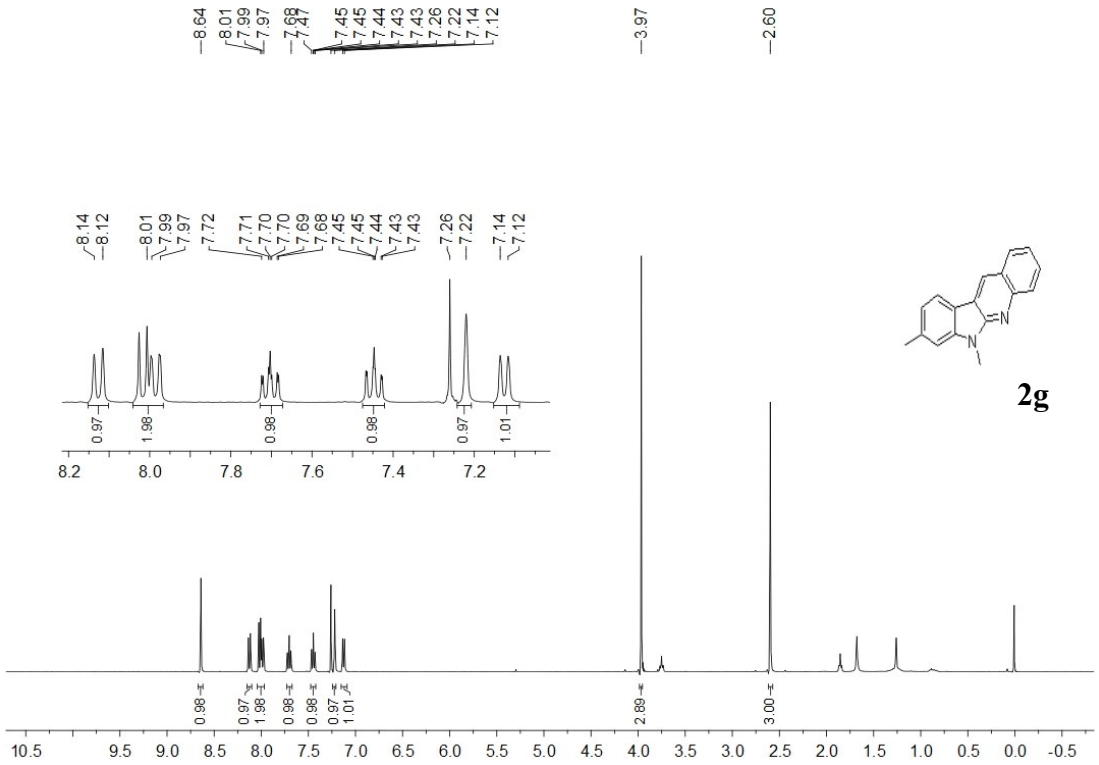
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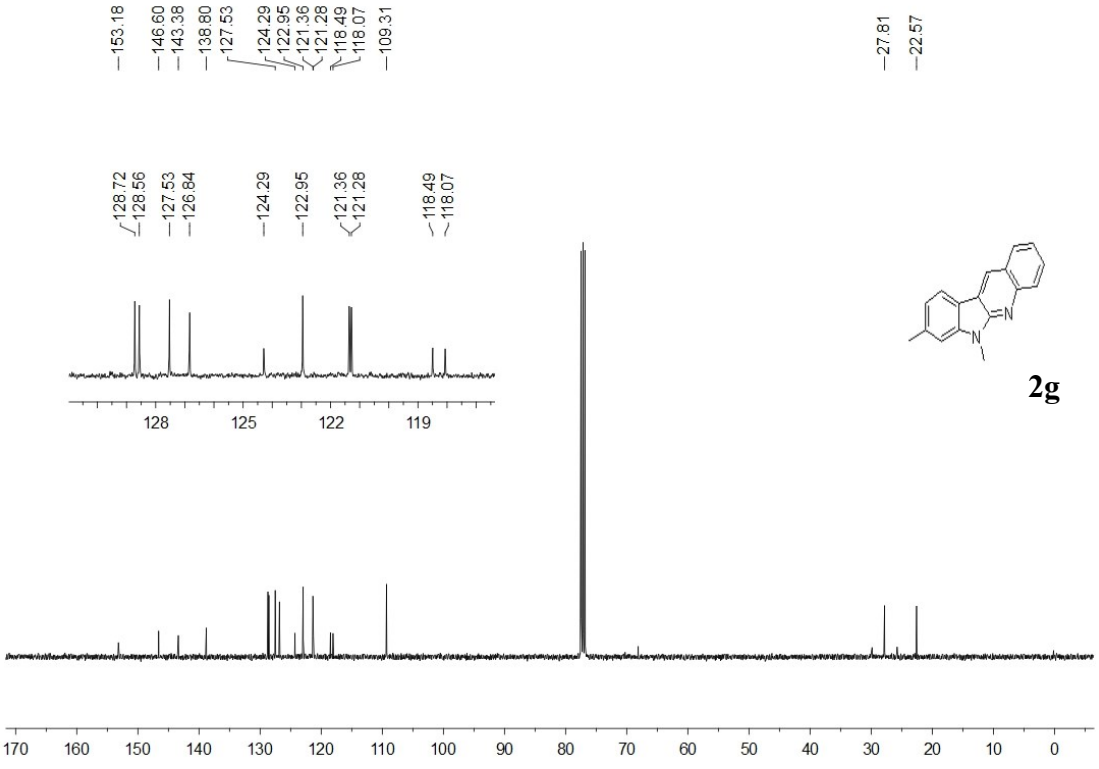
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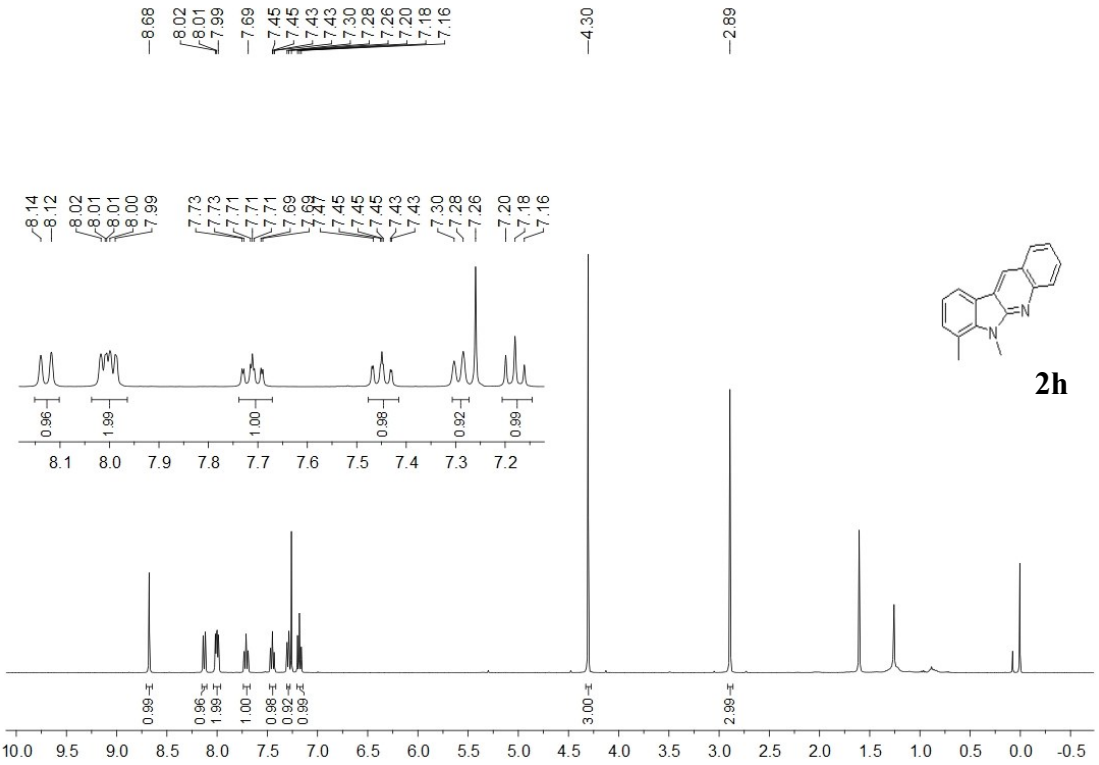
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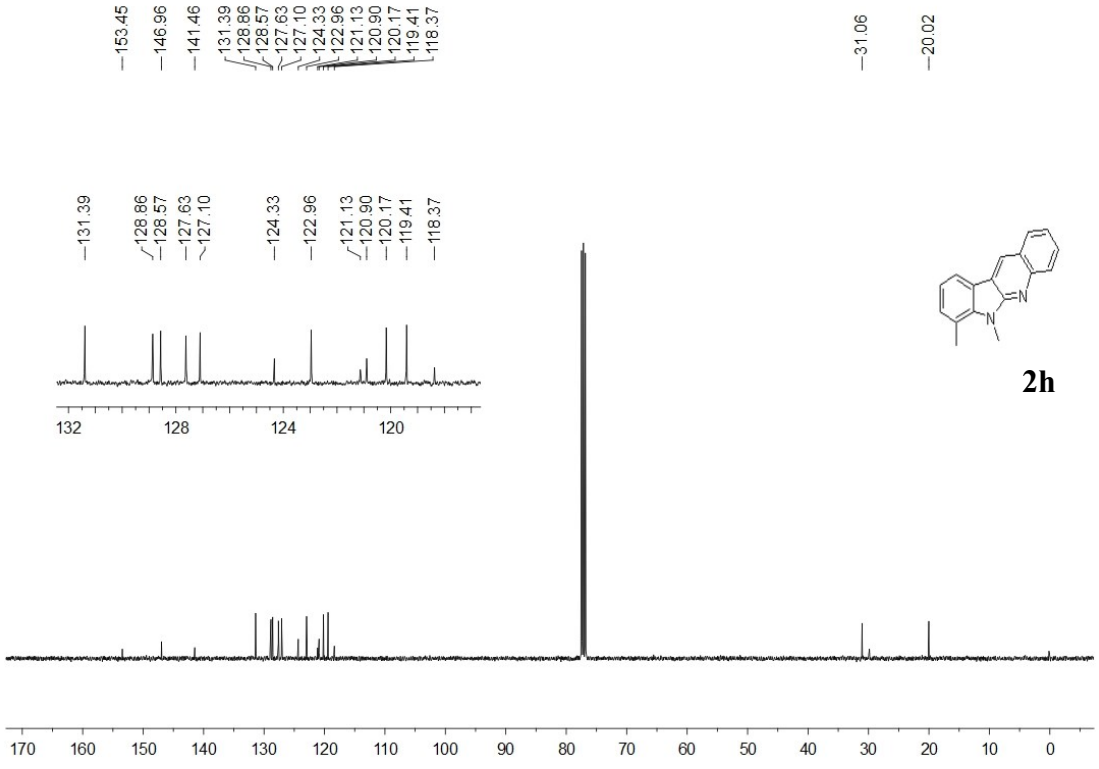
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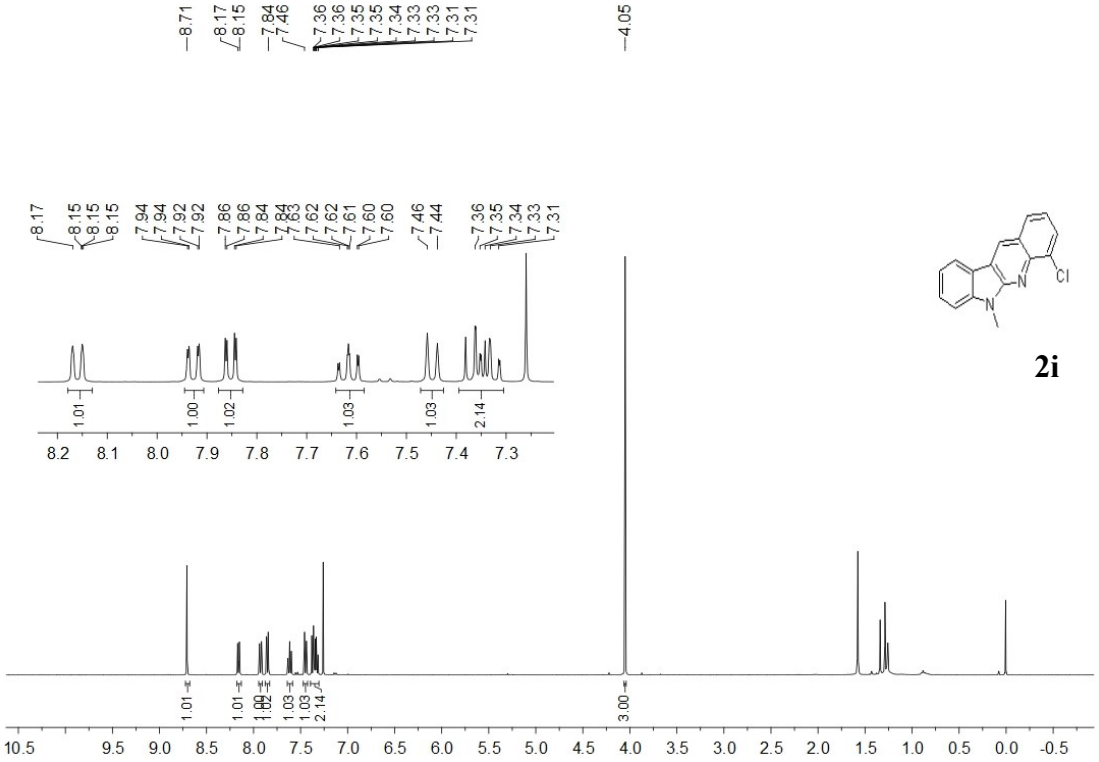
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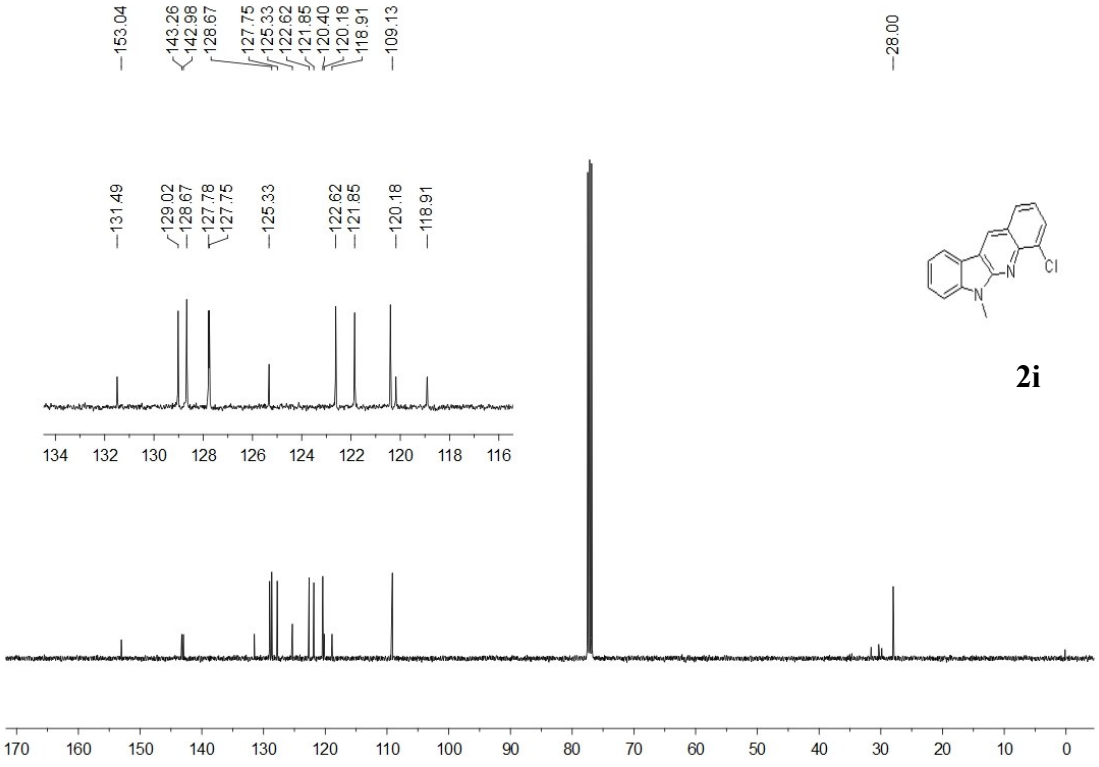
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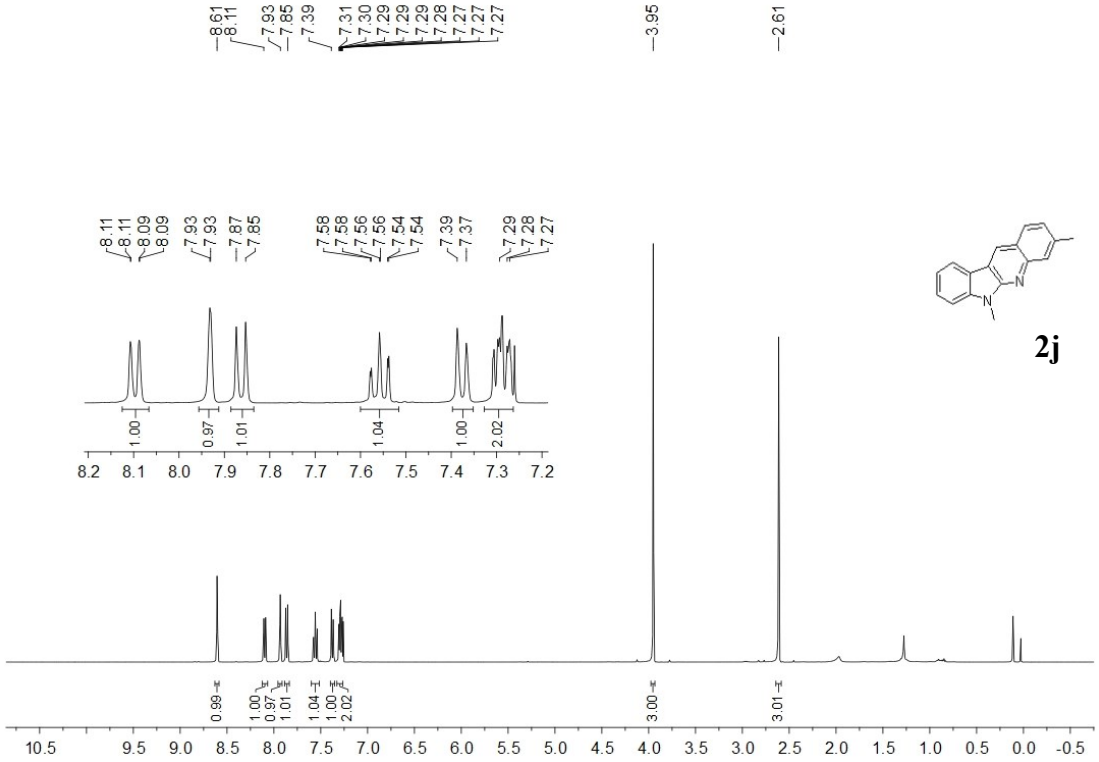
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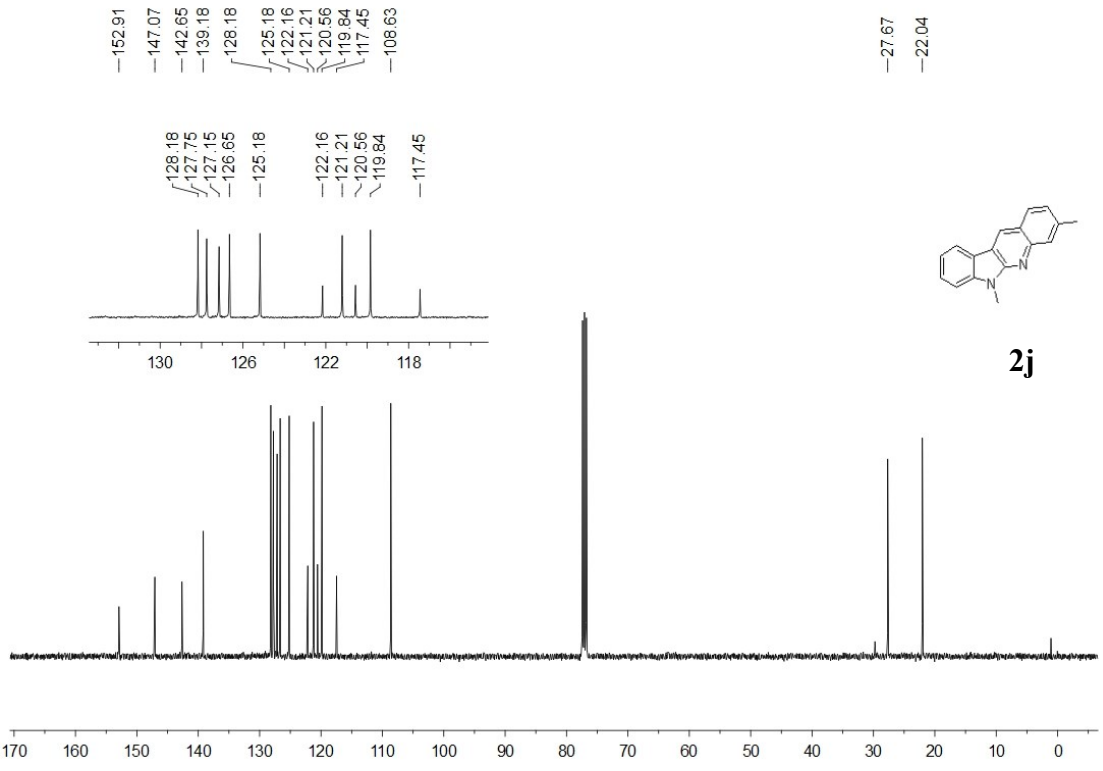
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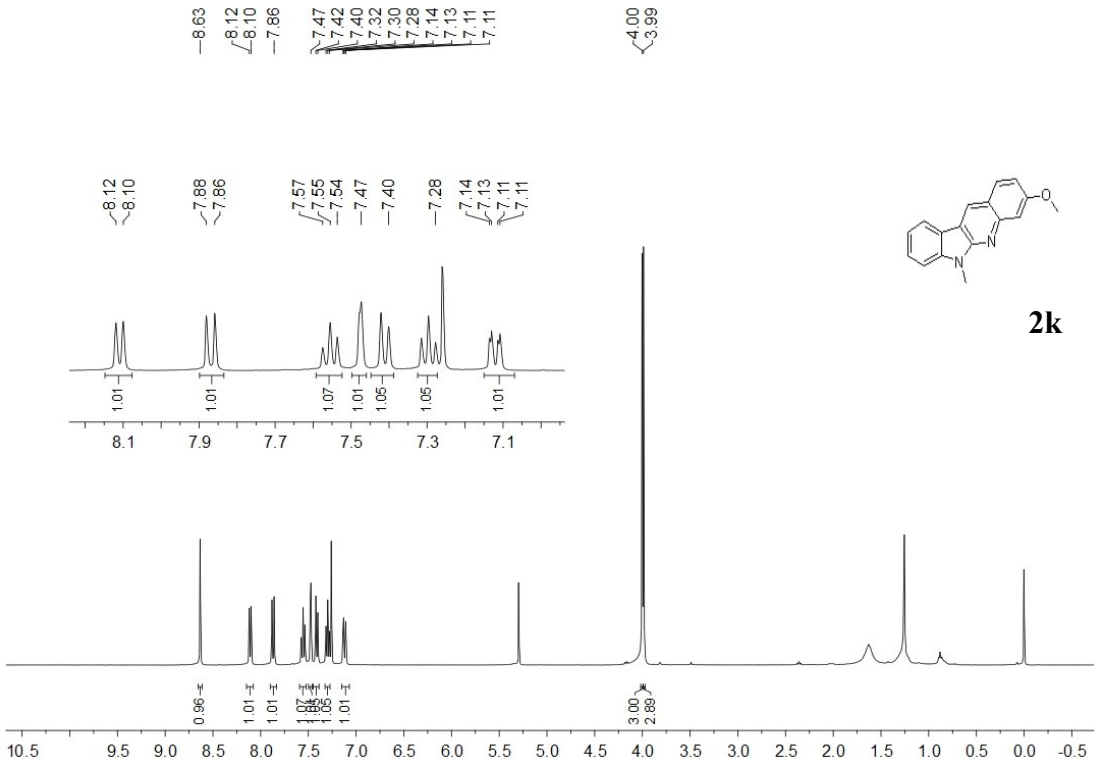
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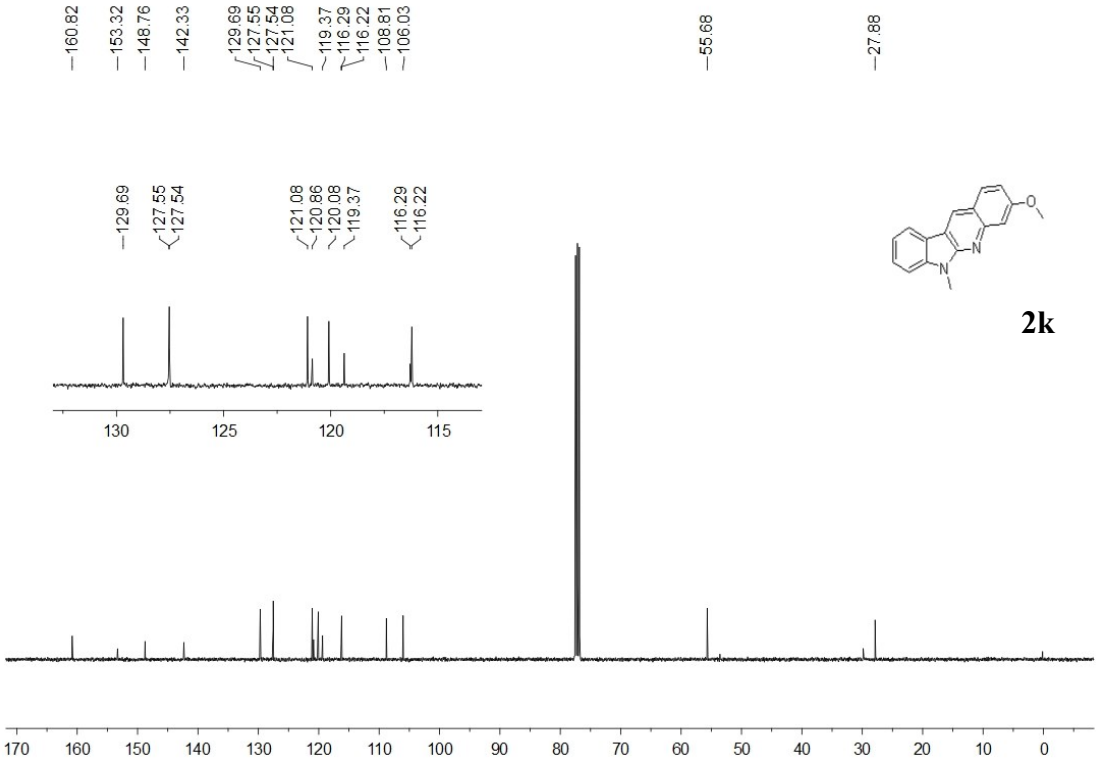
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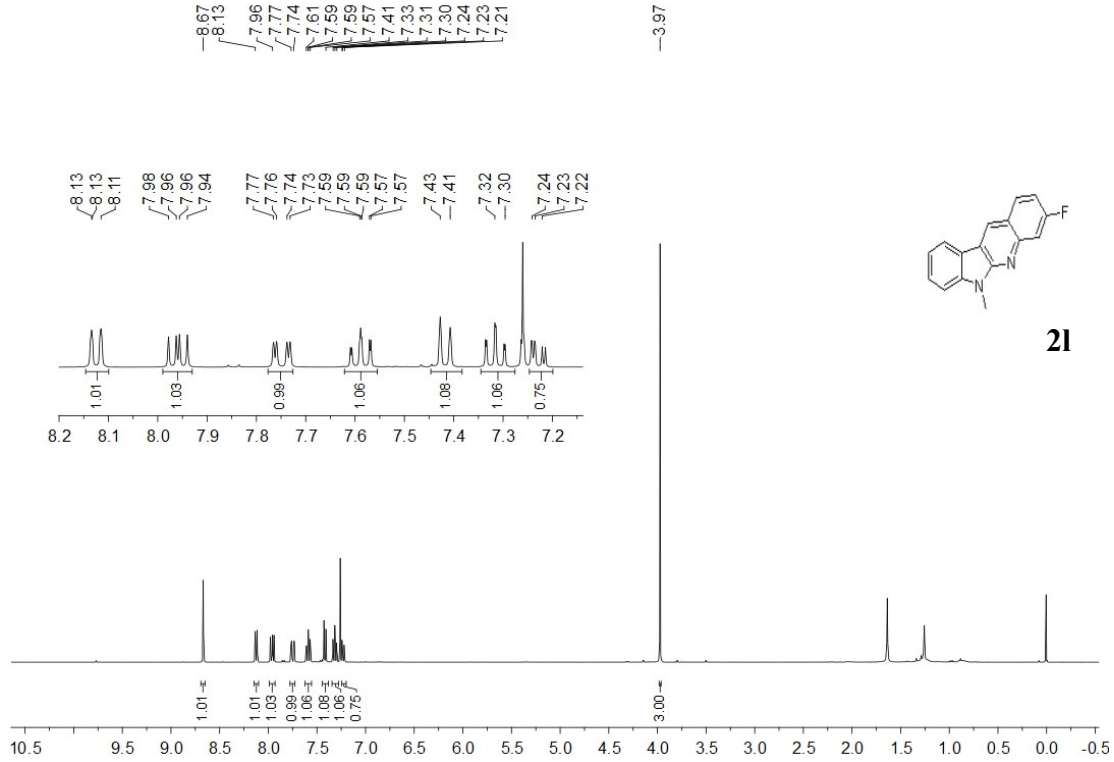
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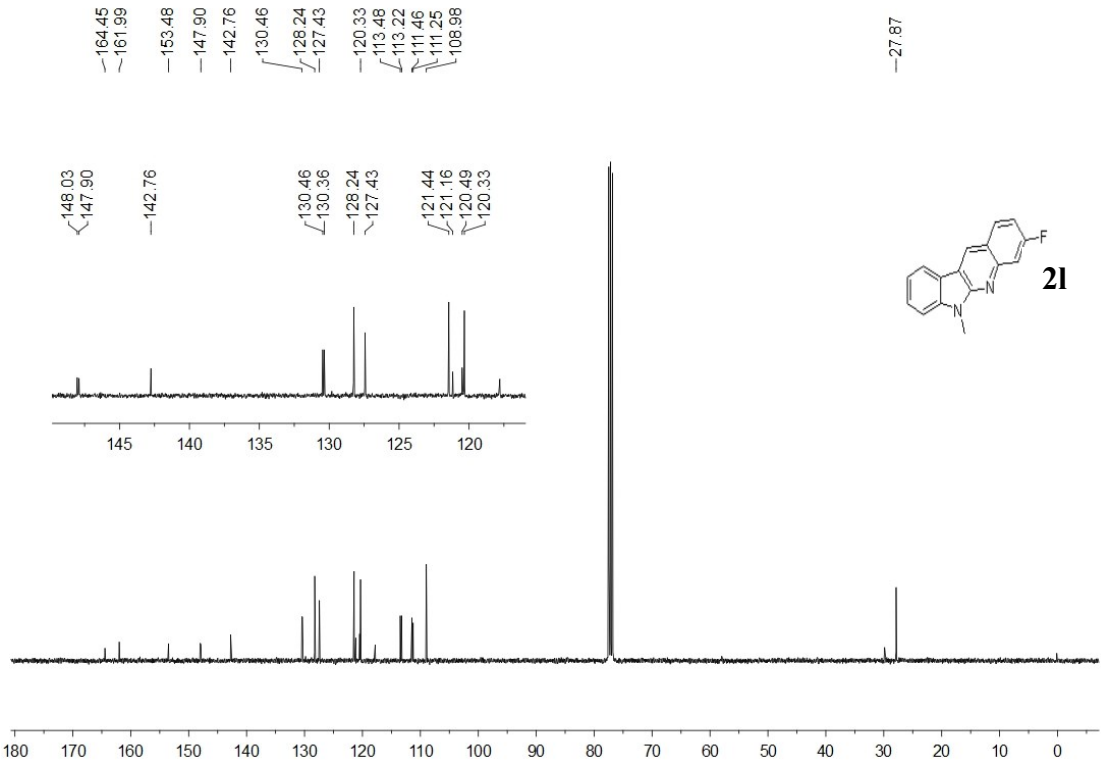
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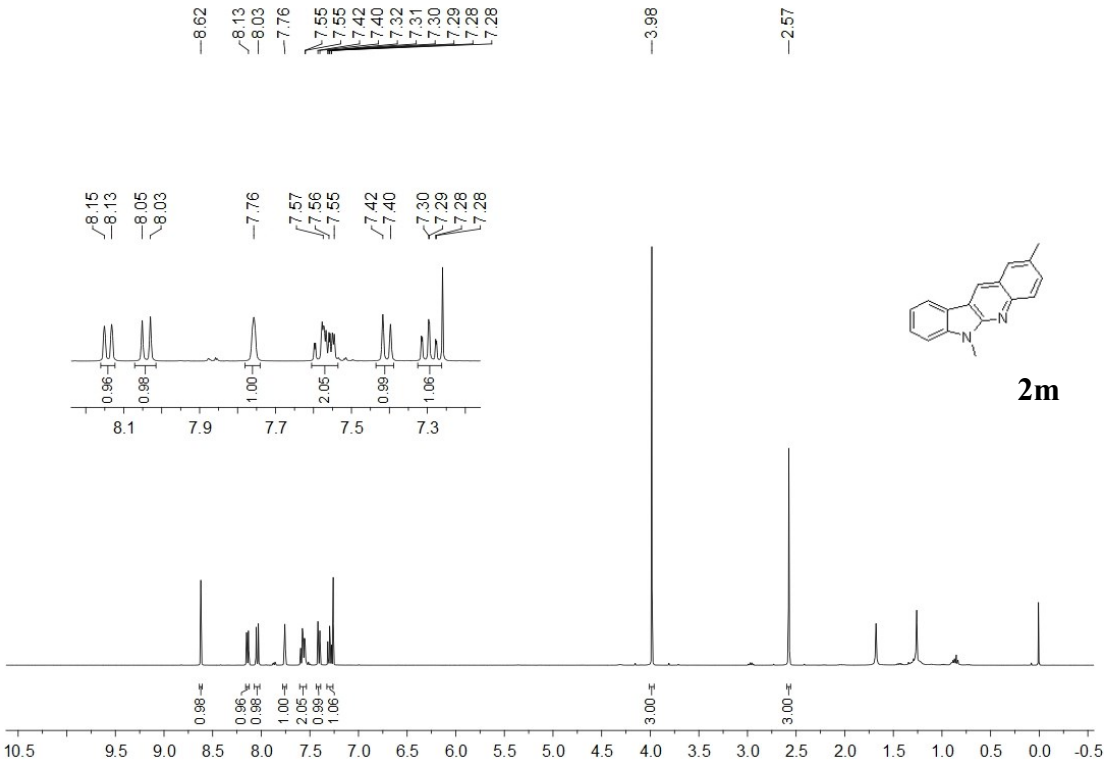
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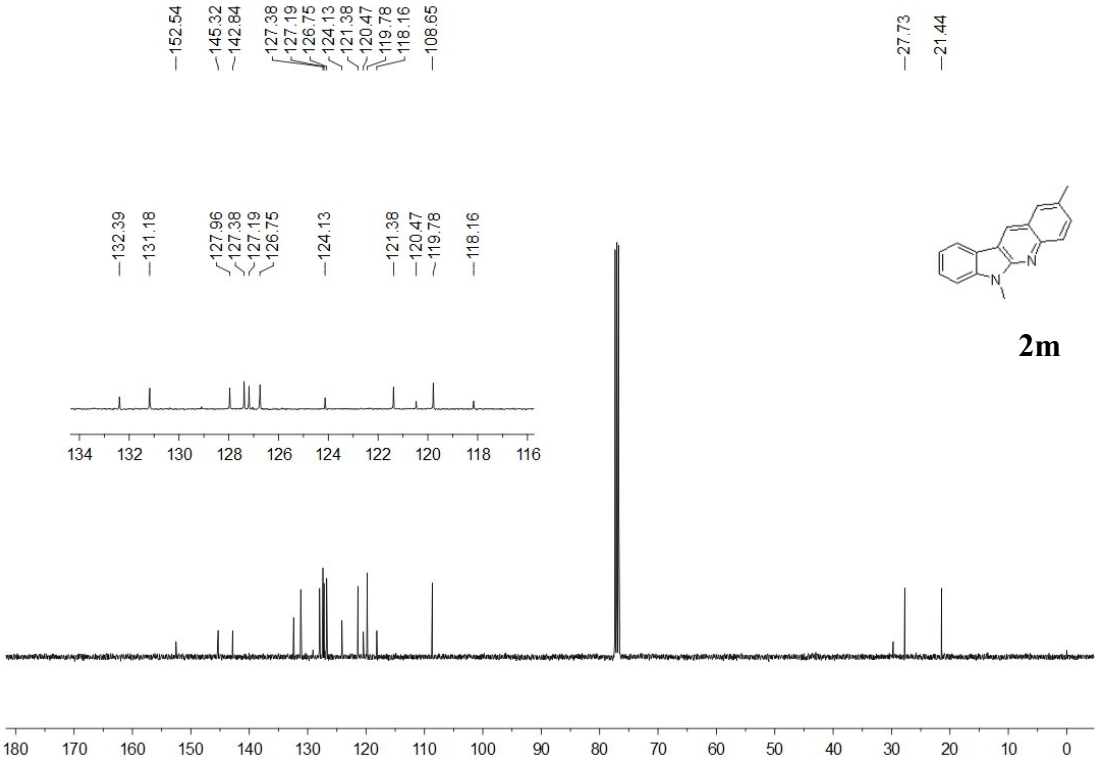
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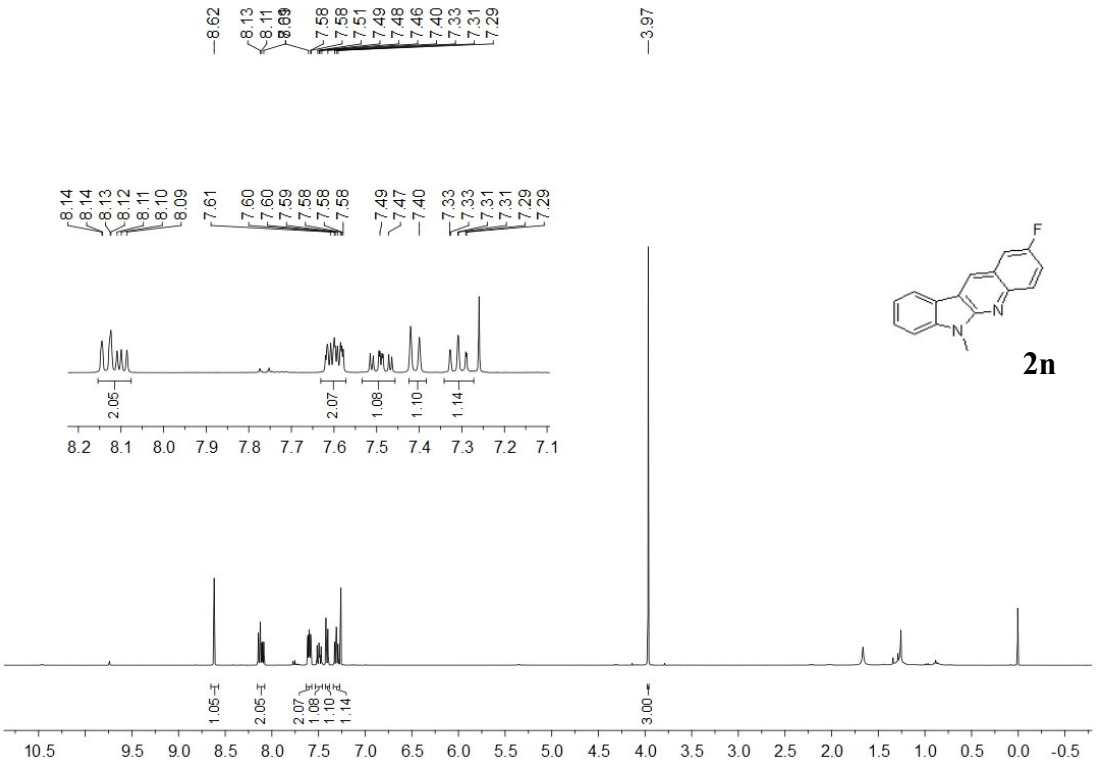
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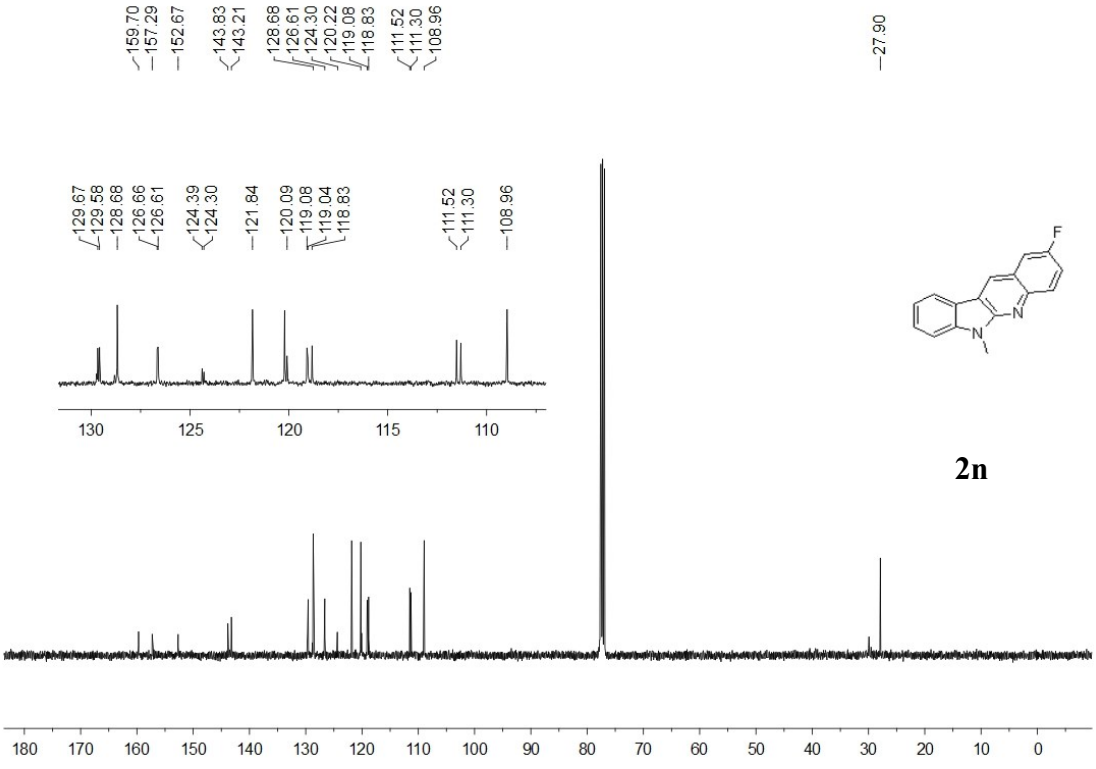
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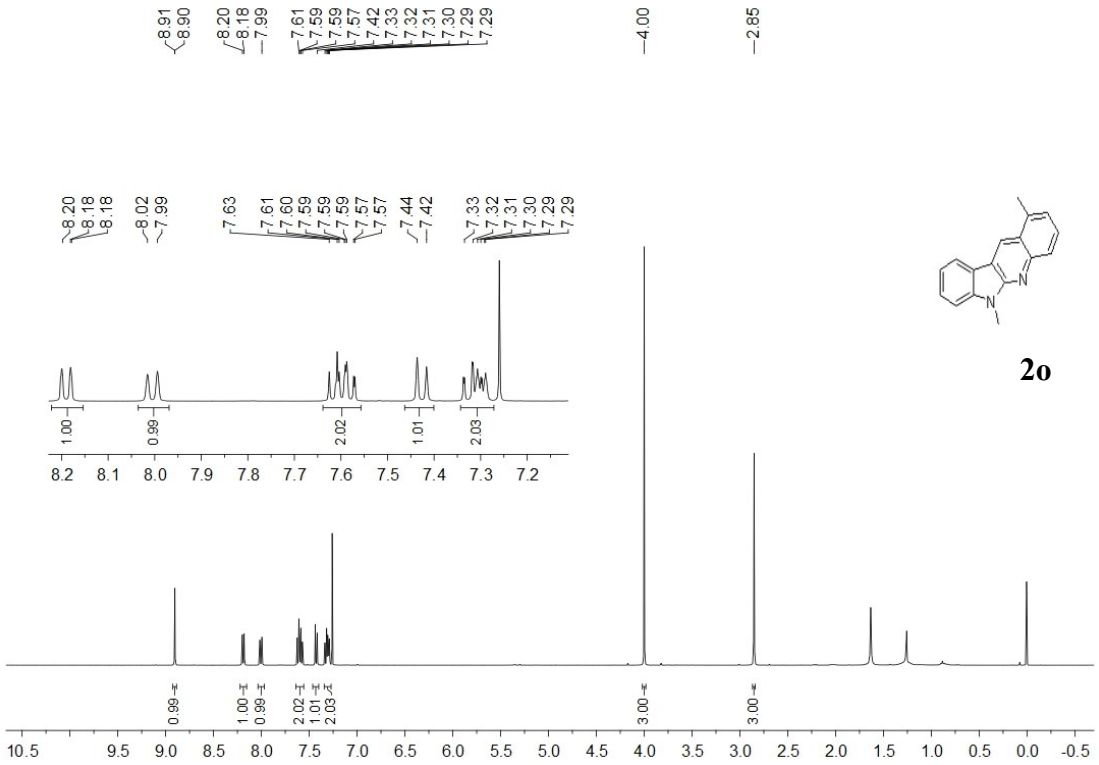
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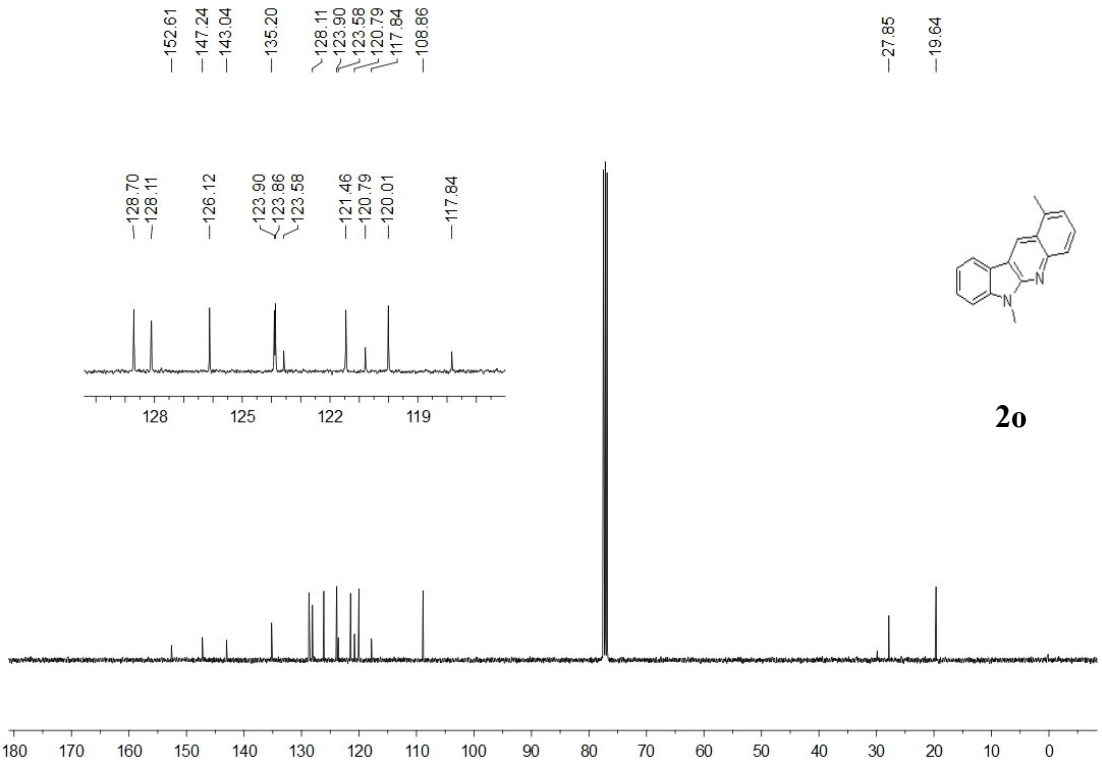
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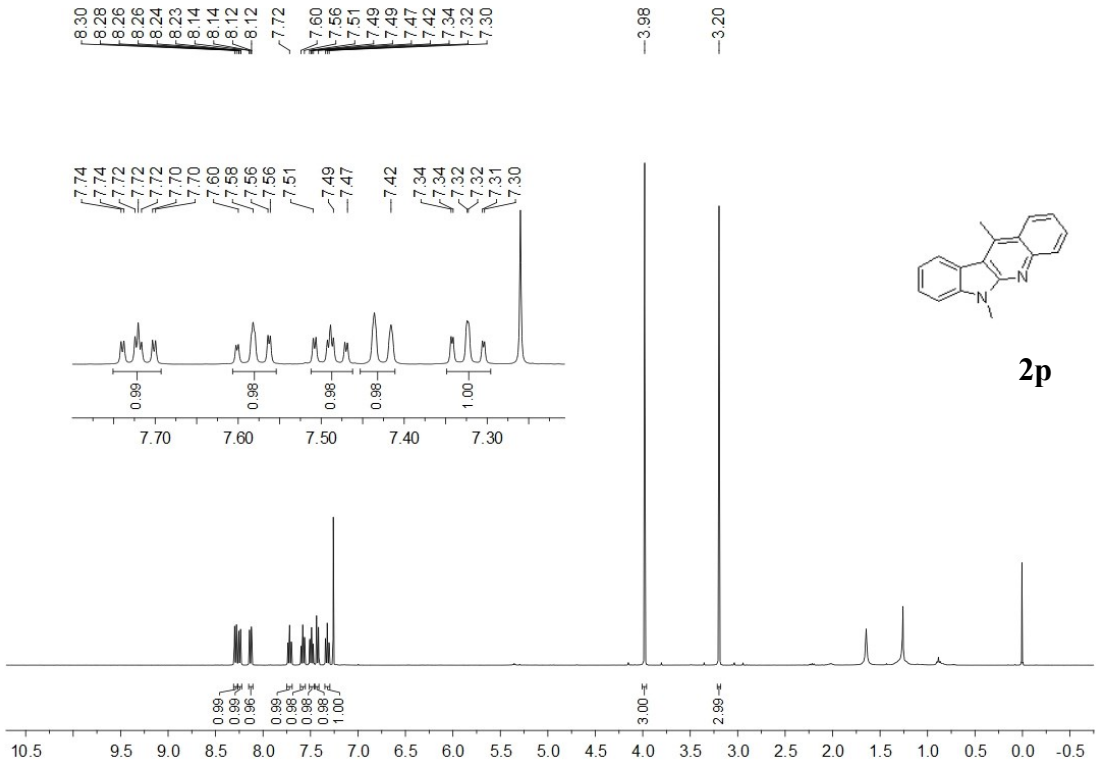
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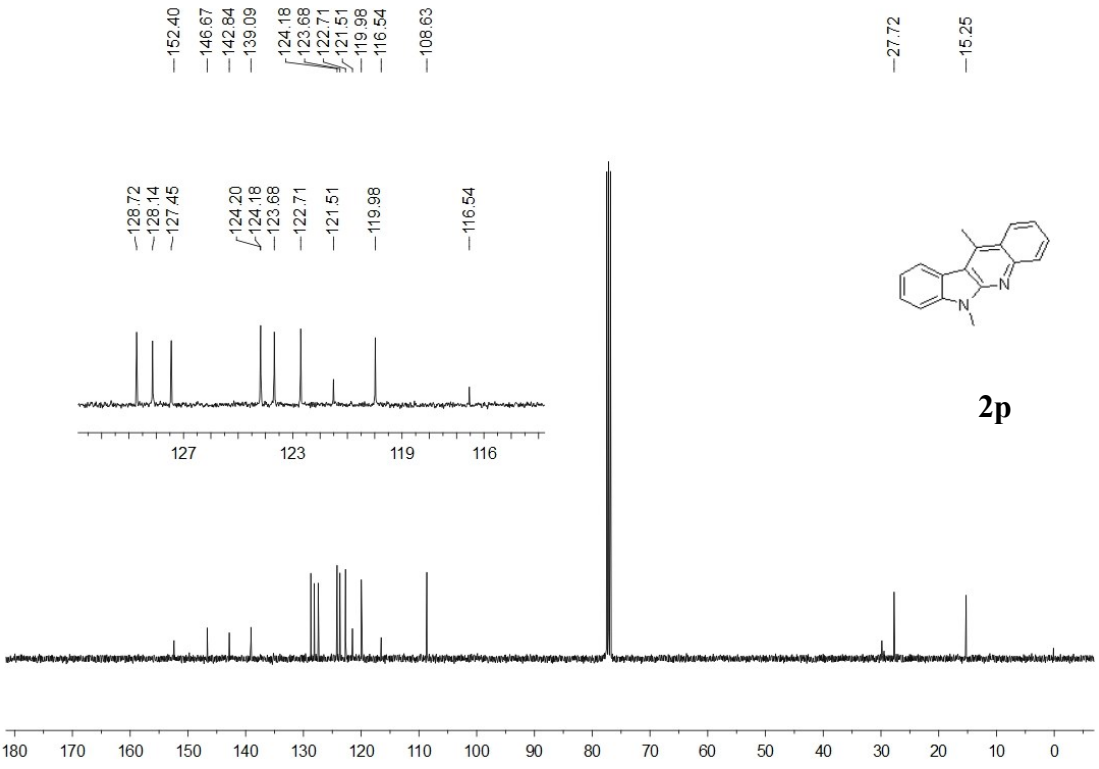
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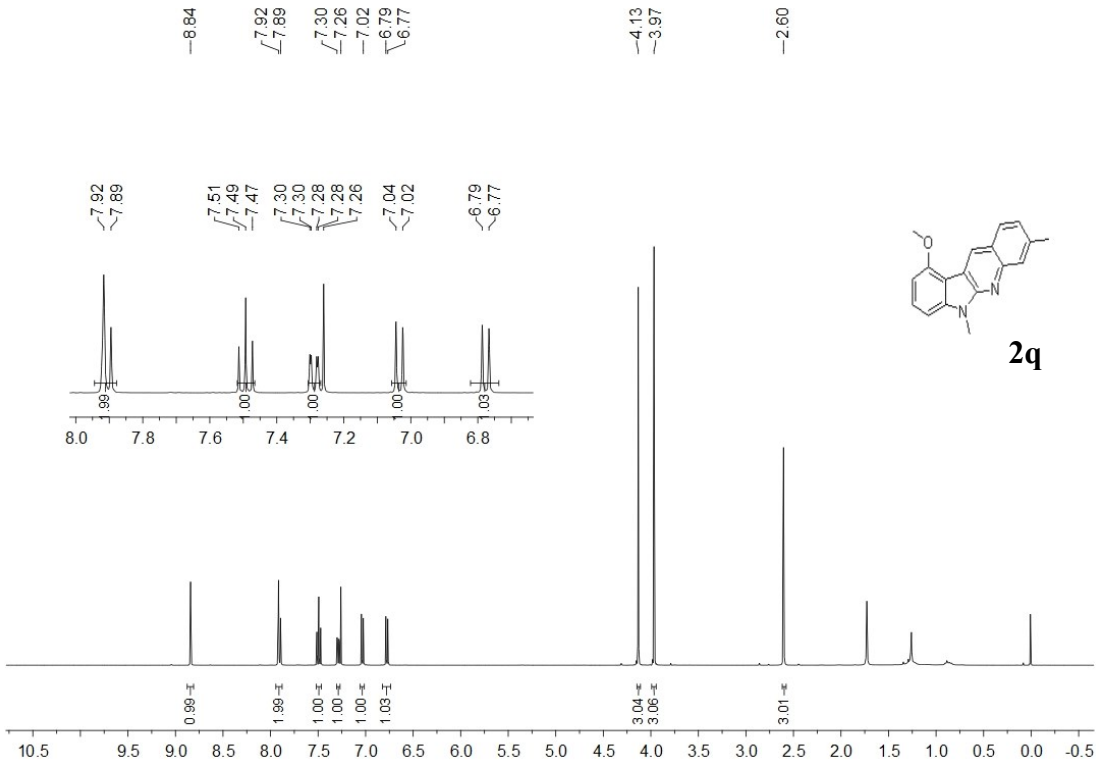
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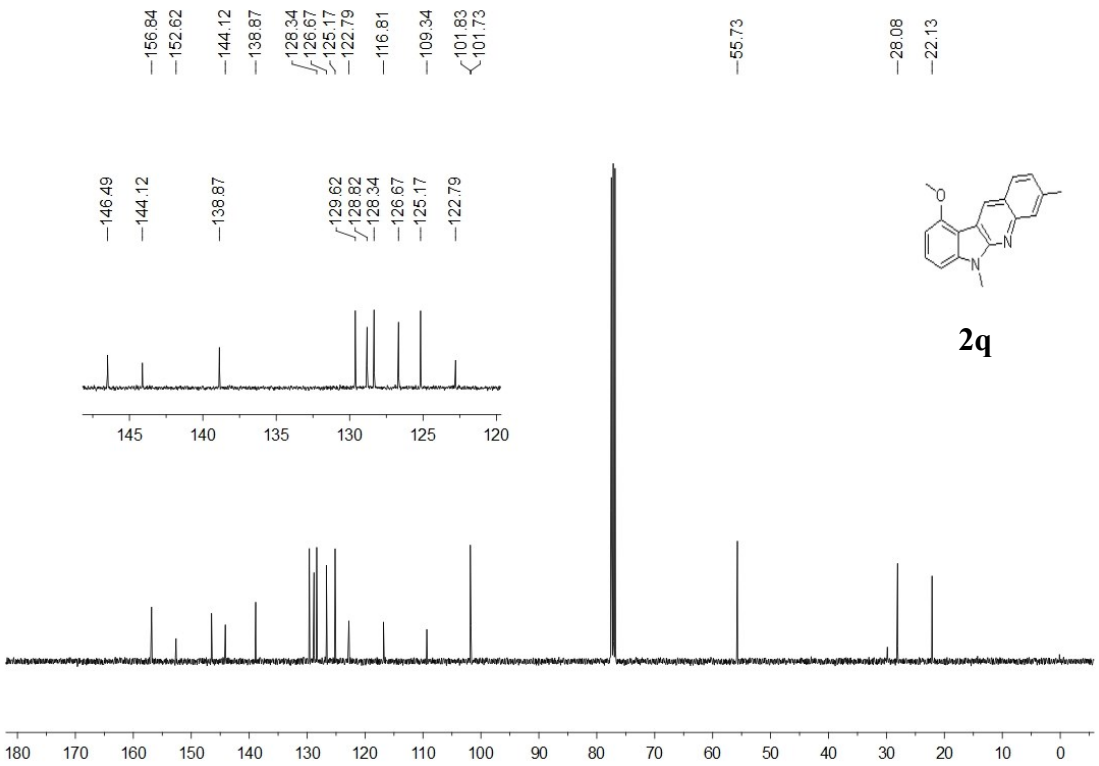
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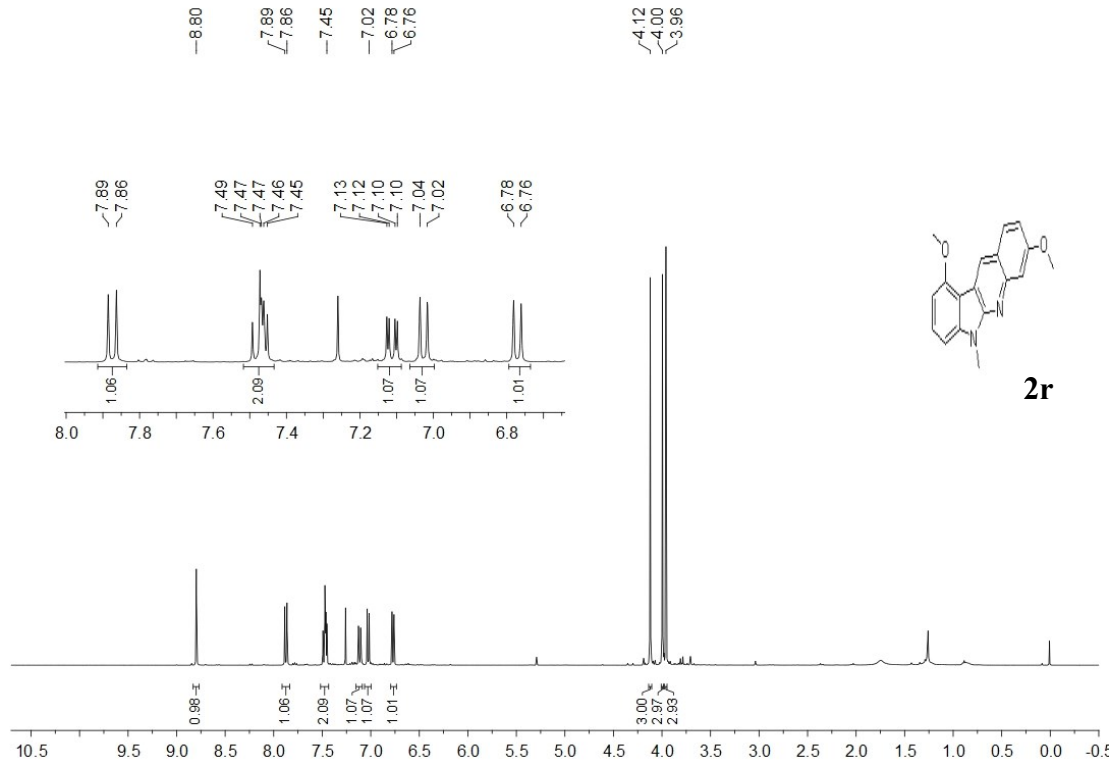
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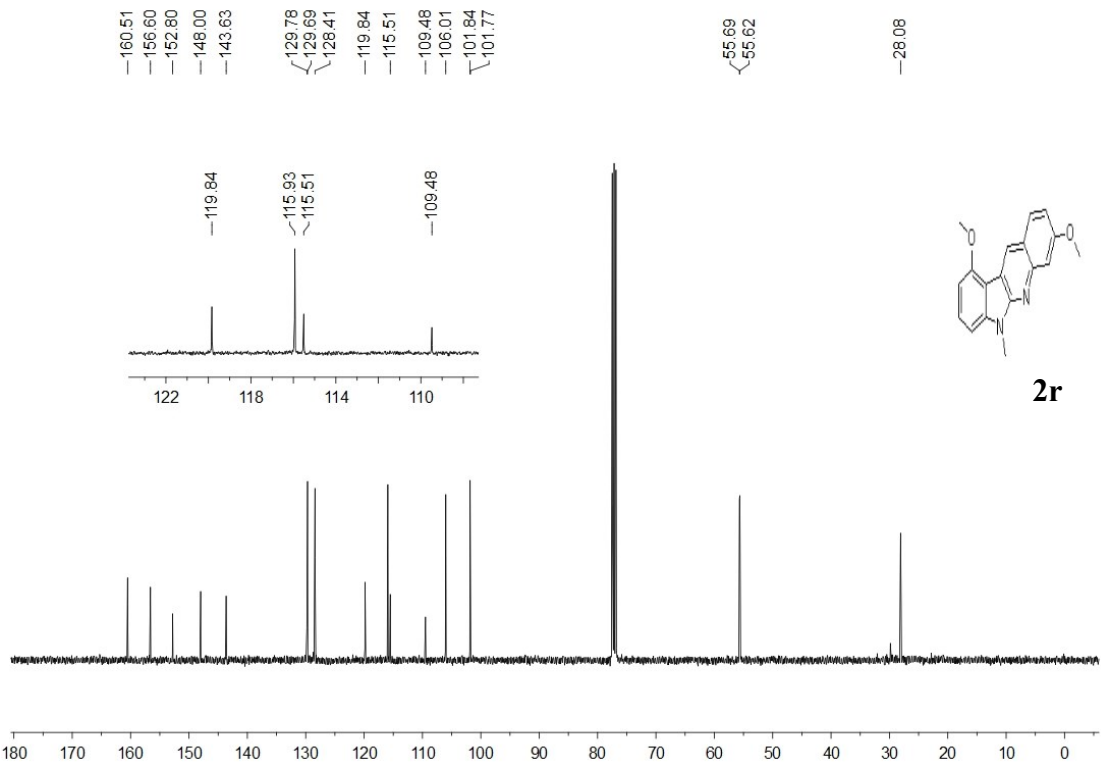
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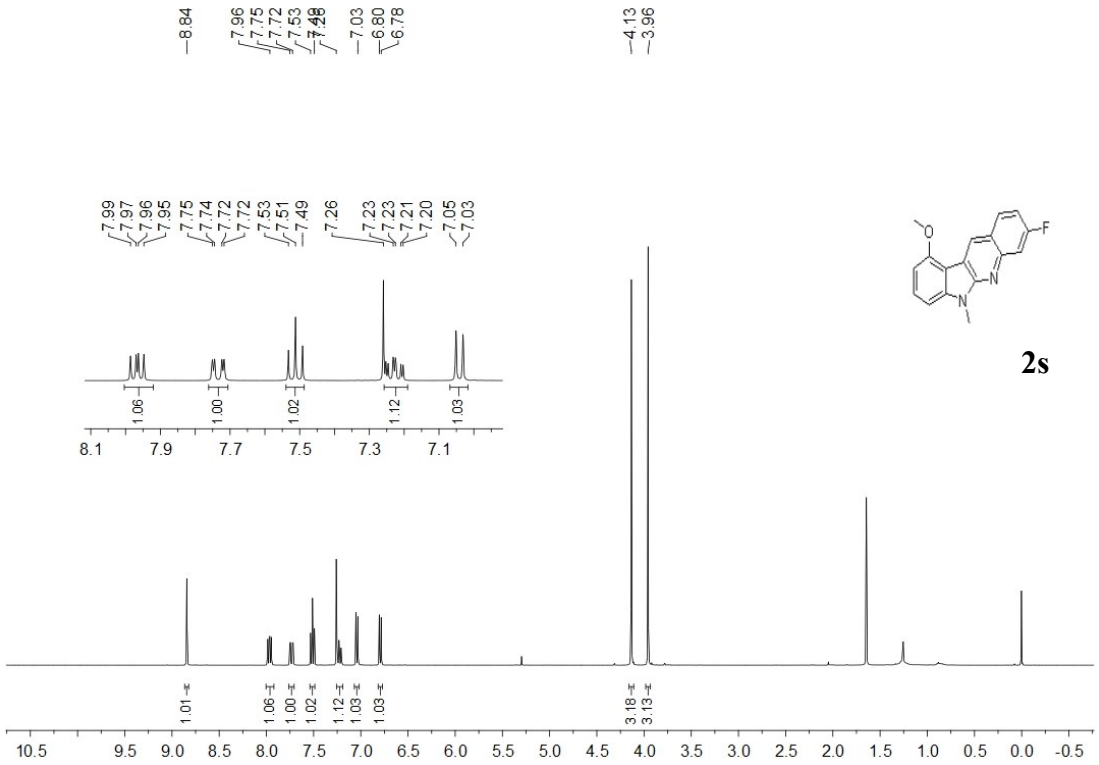
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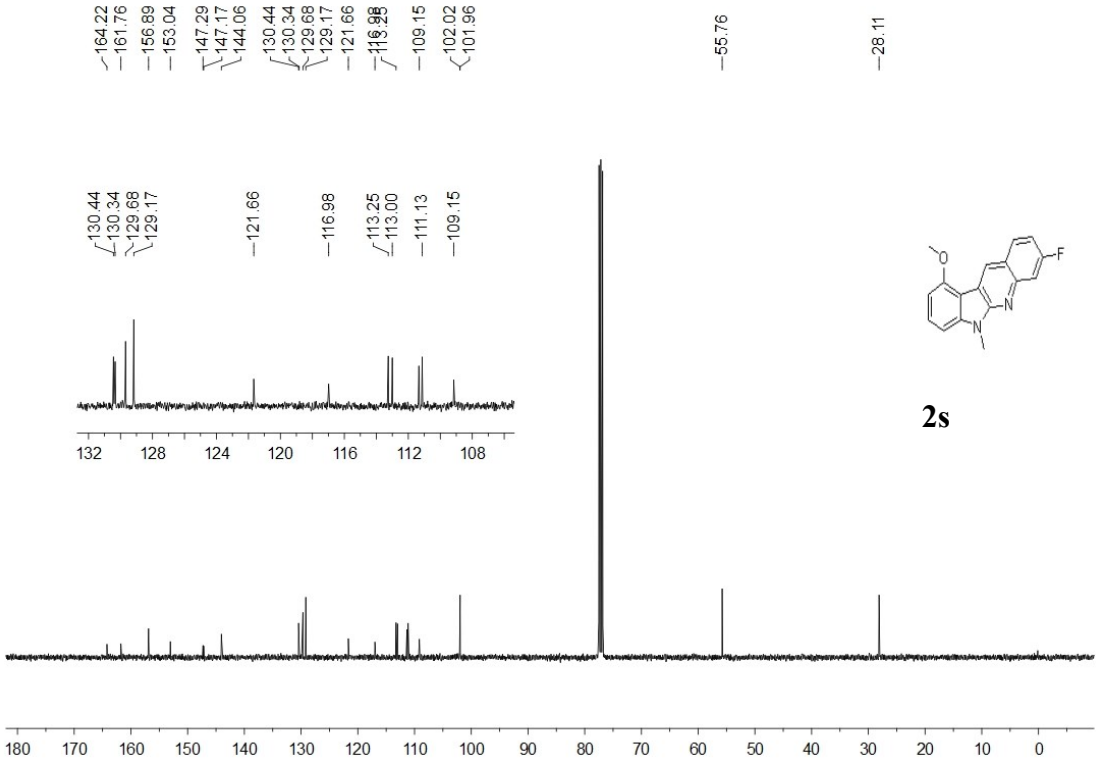
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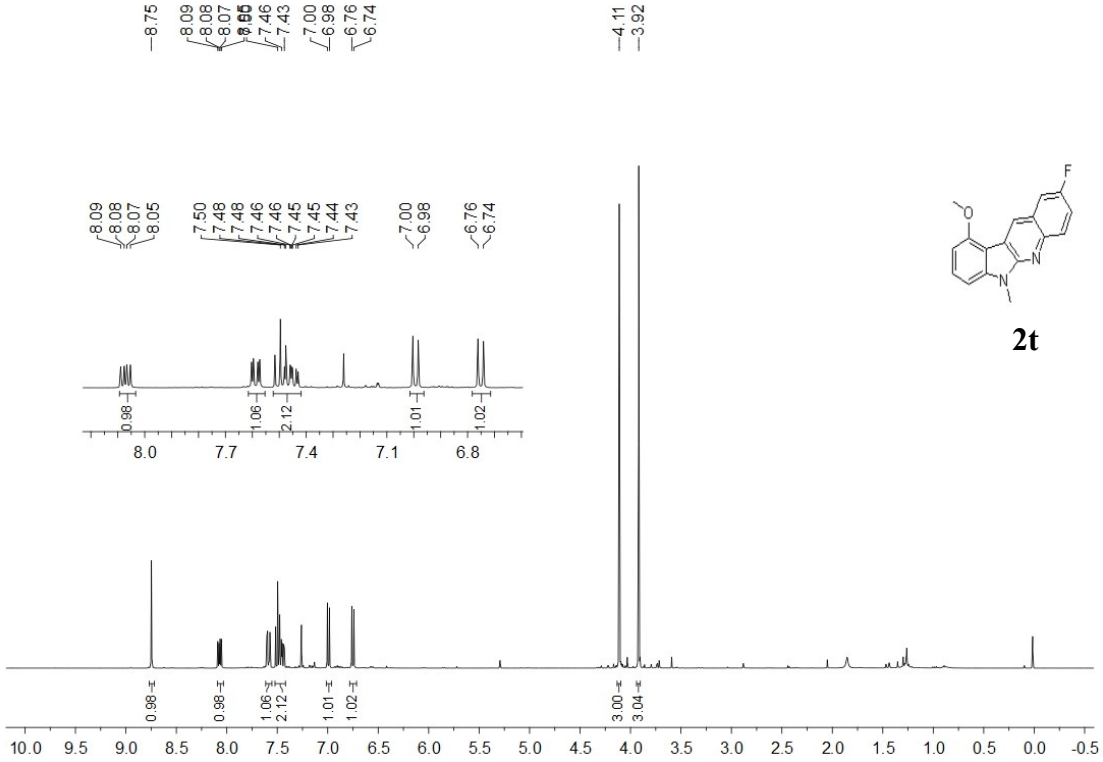
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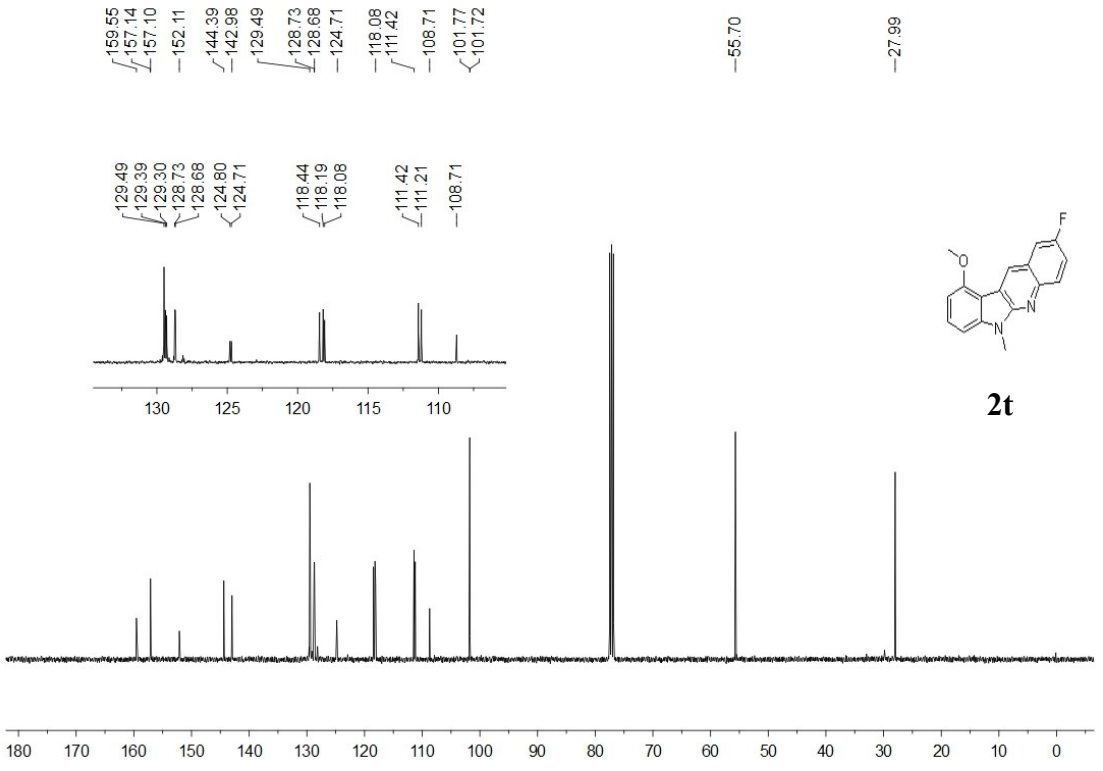
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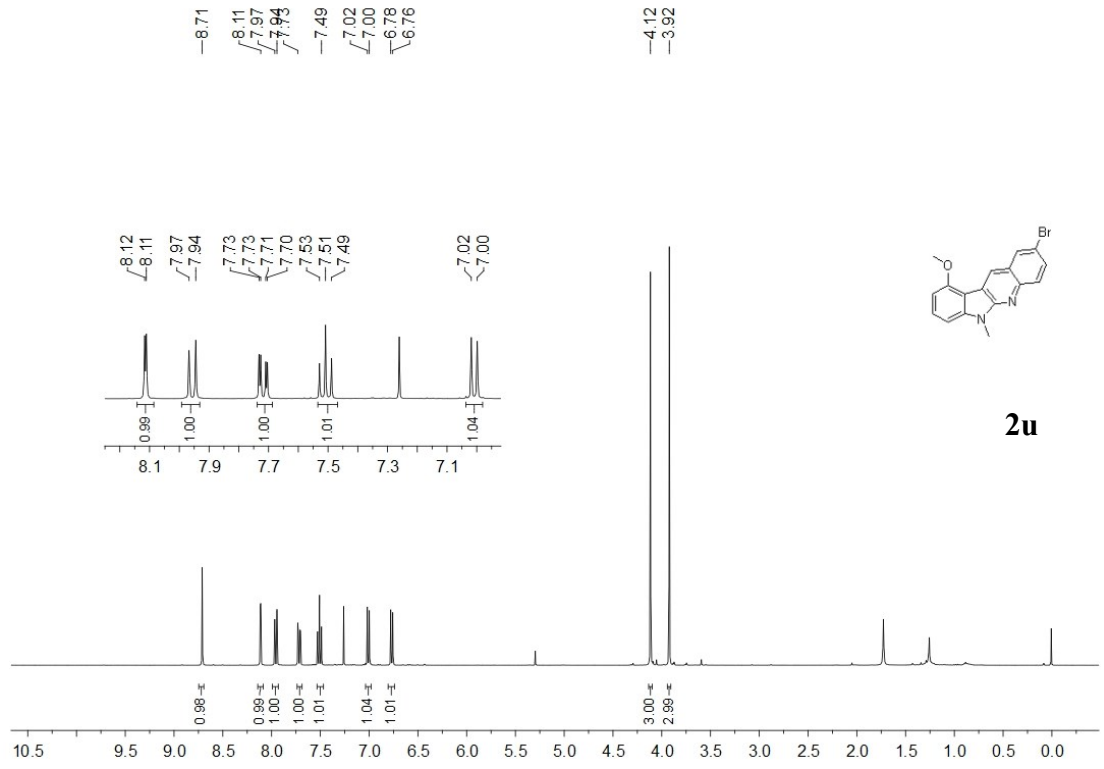
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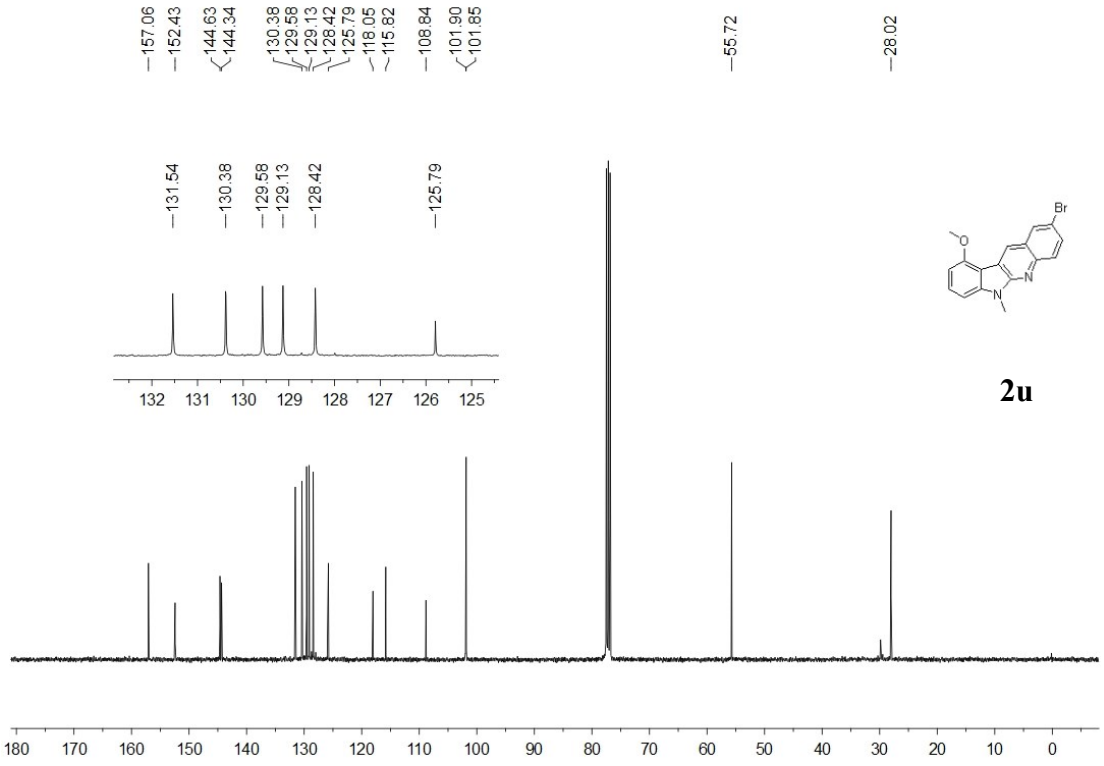
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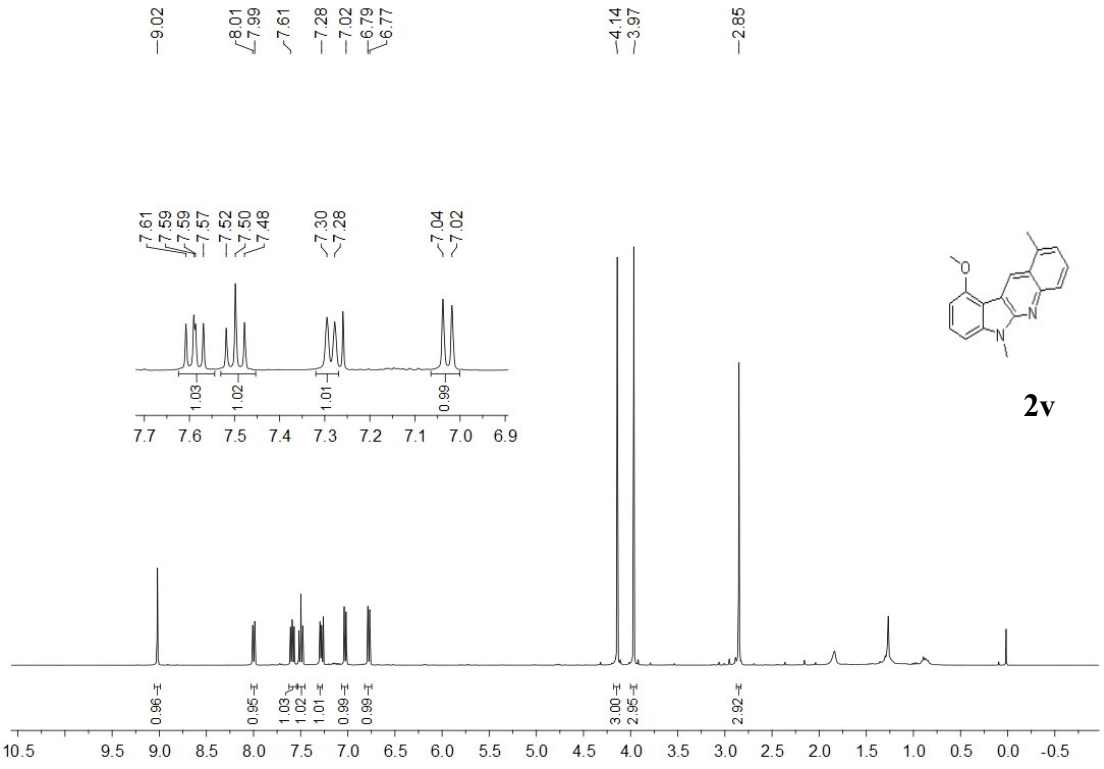
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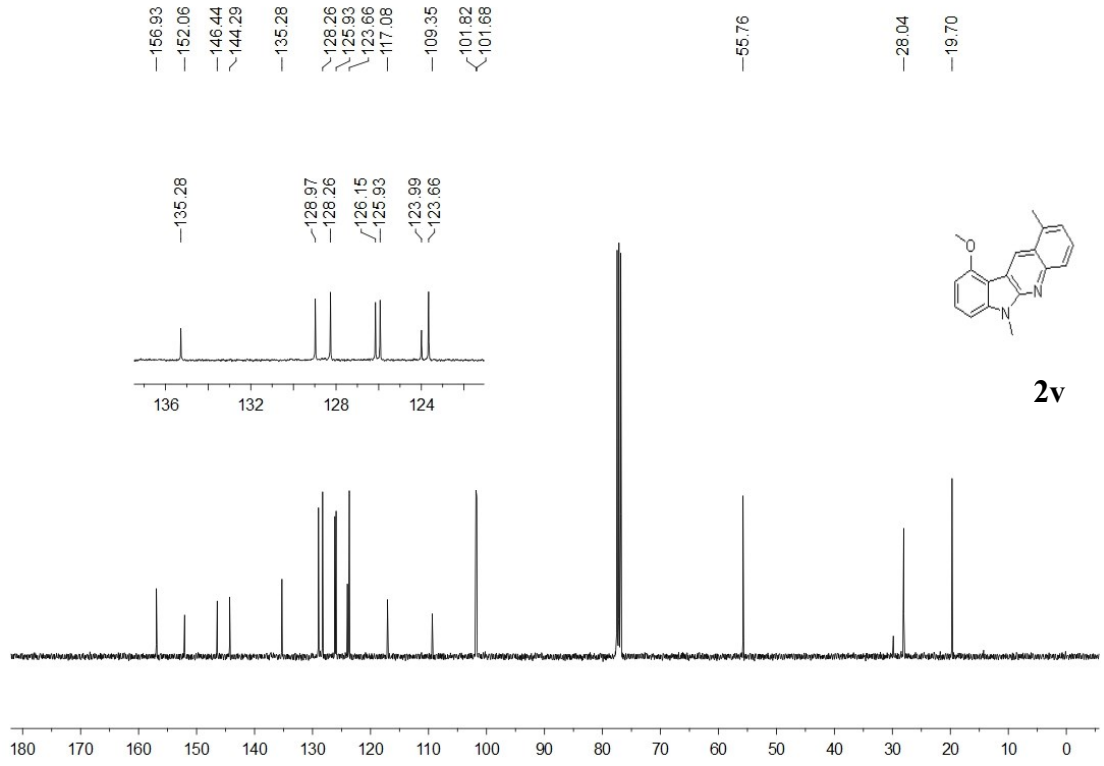
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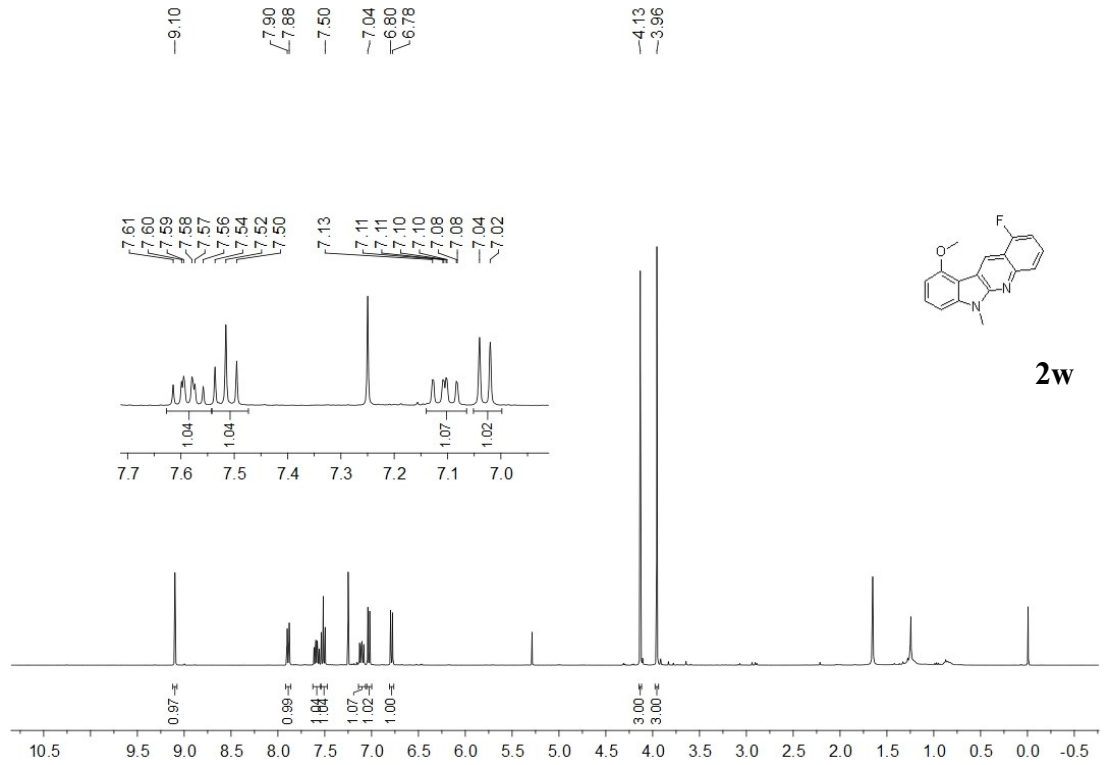
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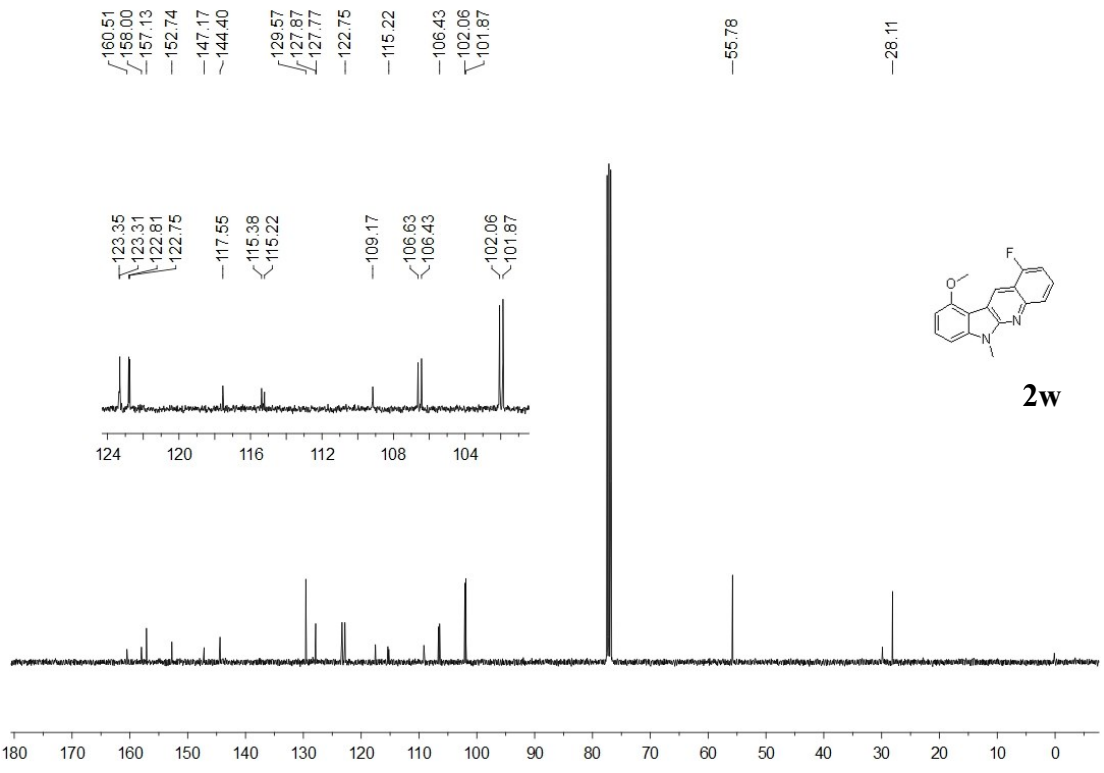
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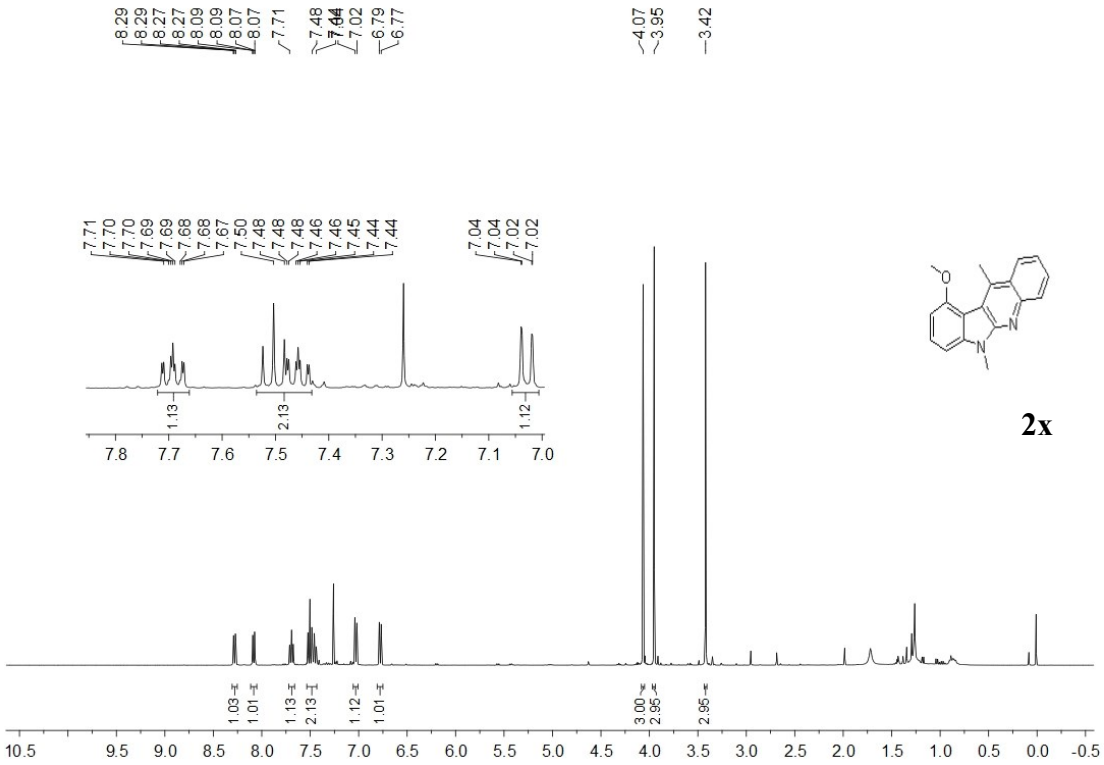
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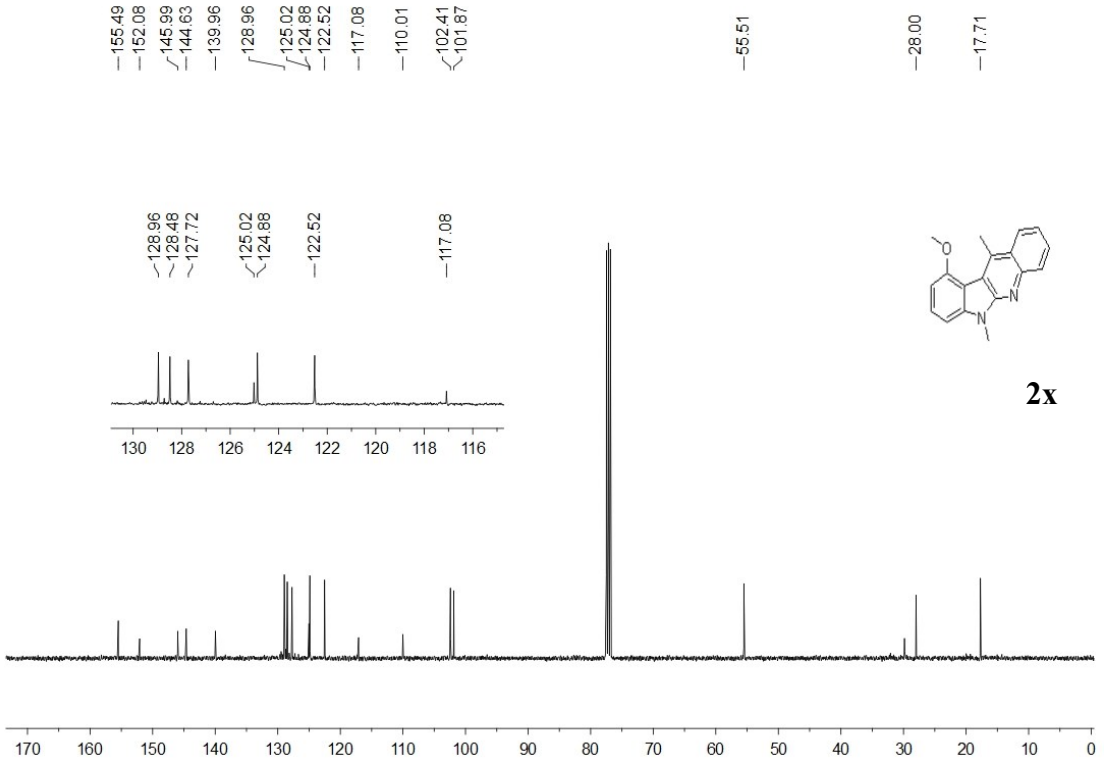
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2x