

Supporting Information

OXIDATIVE REARRANGEMENT OF BENZYLAMINES TO 4*H*-3,1-BENZOXAZINES VIA Cu/Mn-PROMOTED INTRAMOLECULAR C–H AMINATION/ELECTROCYCLIC REACTION CASCADE

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Kinetic Studies

All deuterium-labeling experiments were carried out under the conventional heating conditions with an oil bath, because under microwave-assisted conditions the reaction proceeded in the course of the preheating time, and the conversion at an early stage was difficult to monitor.

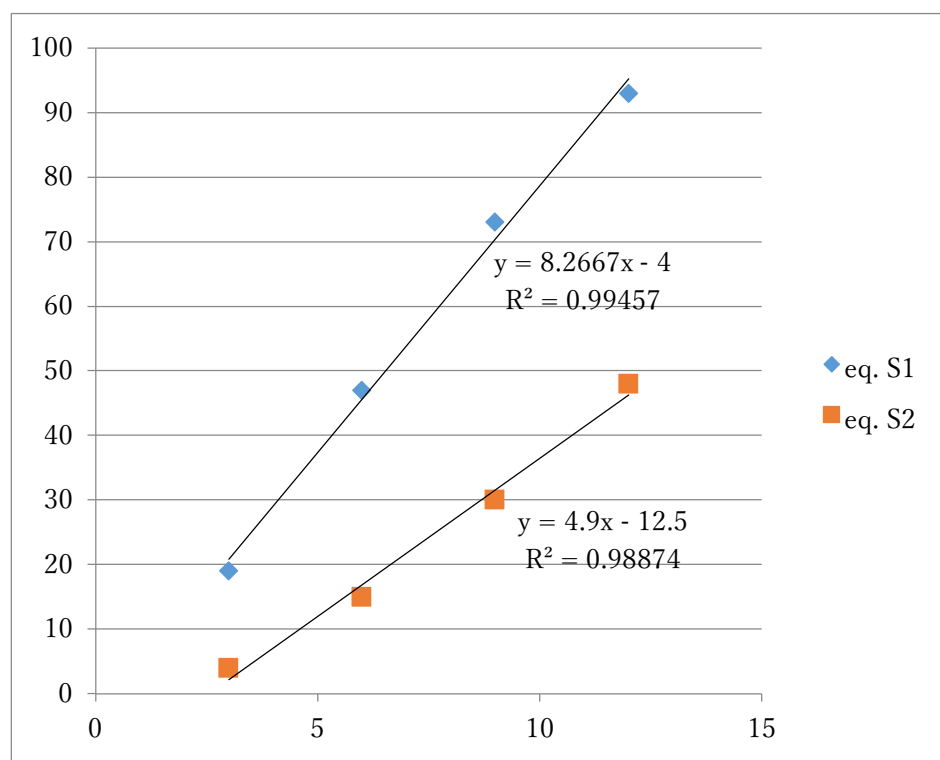
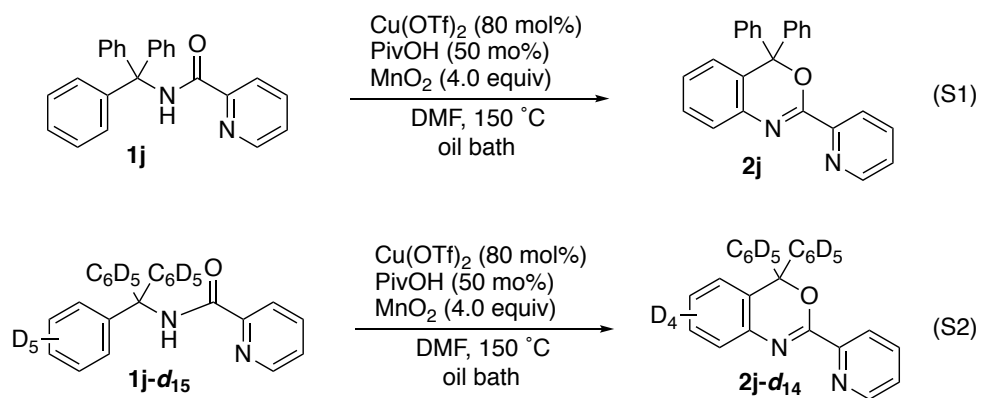


Figure S1. Reaction profiles of eqs. S1 and S2

According to the above data, the KIE value is calculated to be $8.2667/4.9 \doteq 1.7$.

ORTEP Drawings

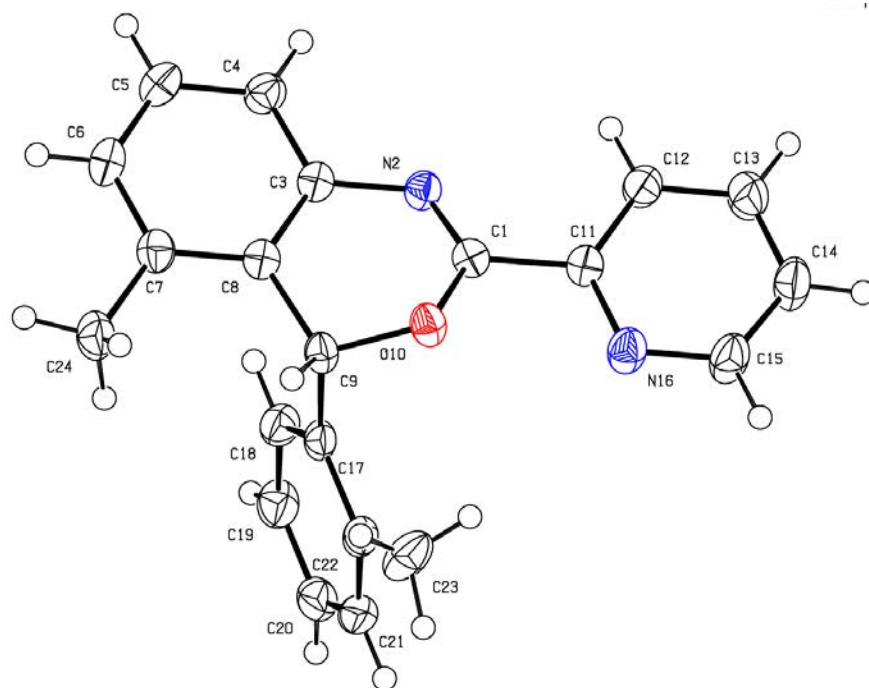


Figure S2. ORTEP Drawing of **21** (CCDC 1816027, 50% thermal ellipsoid, recrystallized from hexane/CH₂Cl₂)

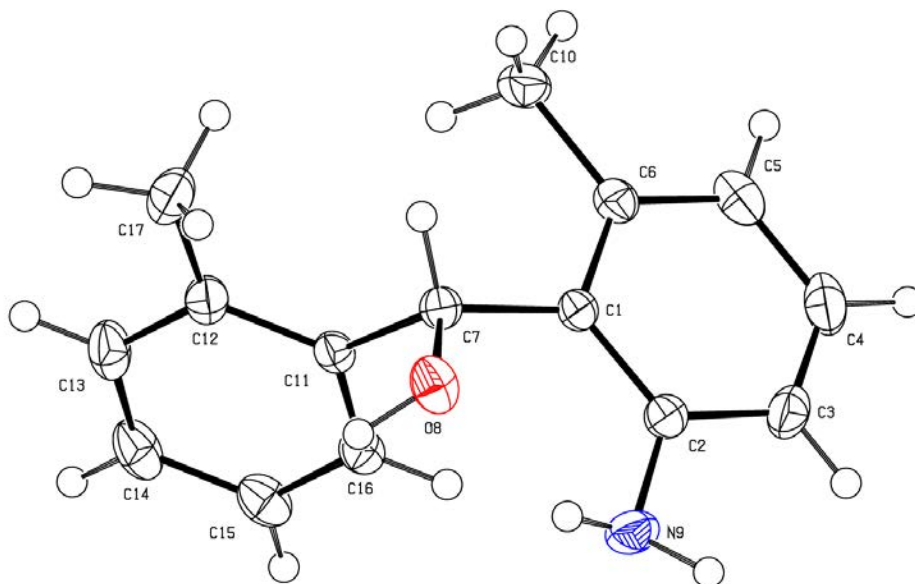
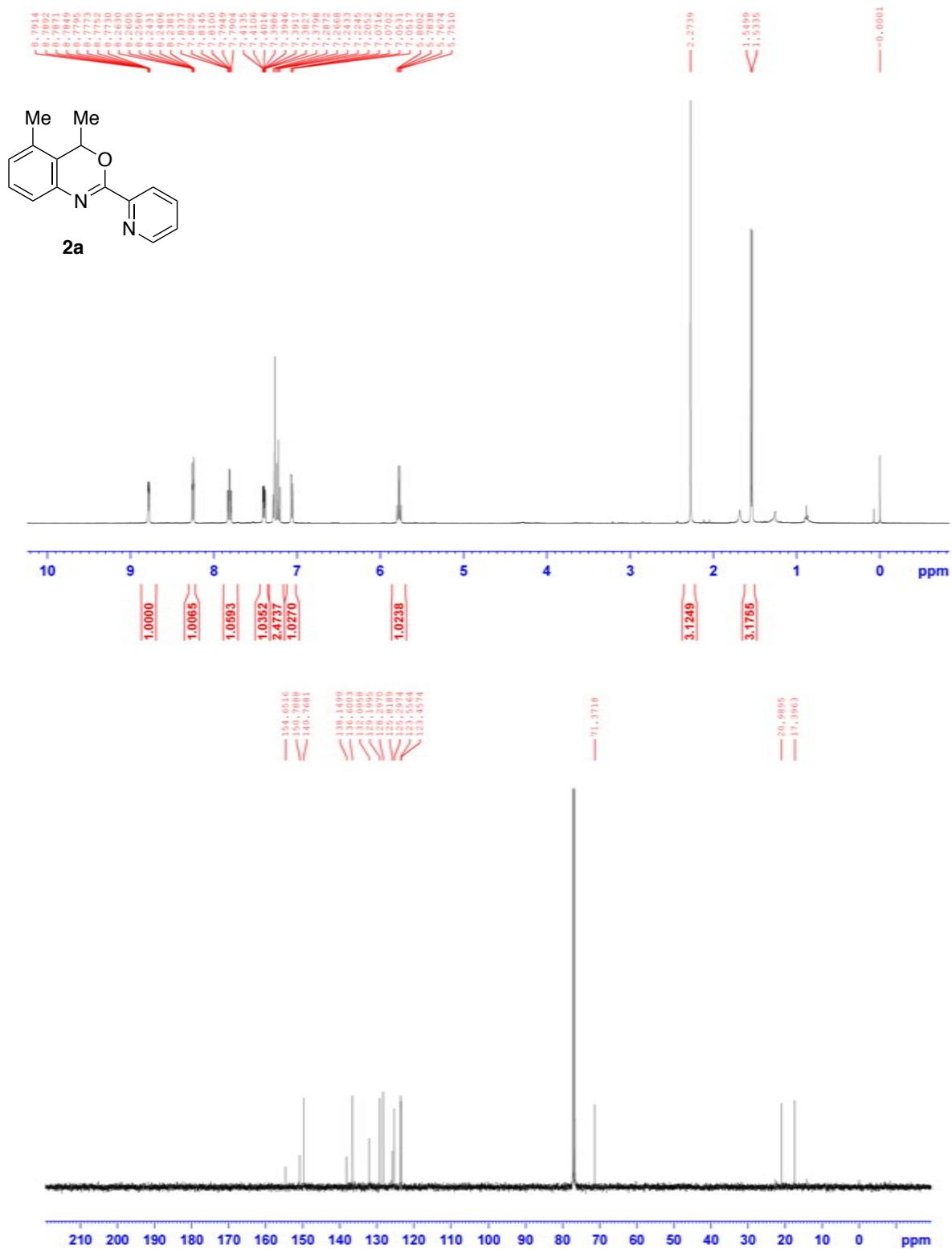


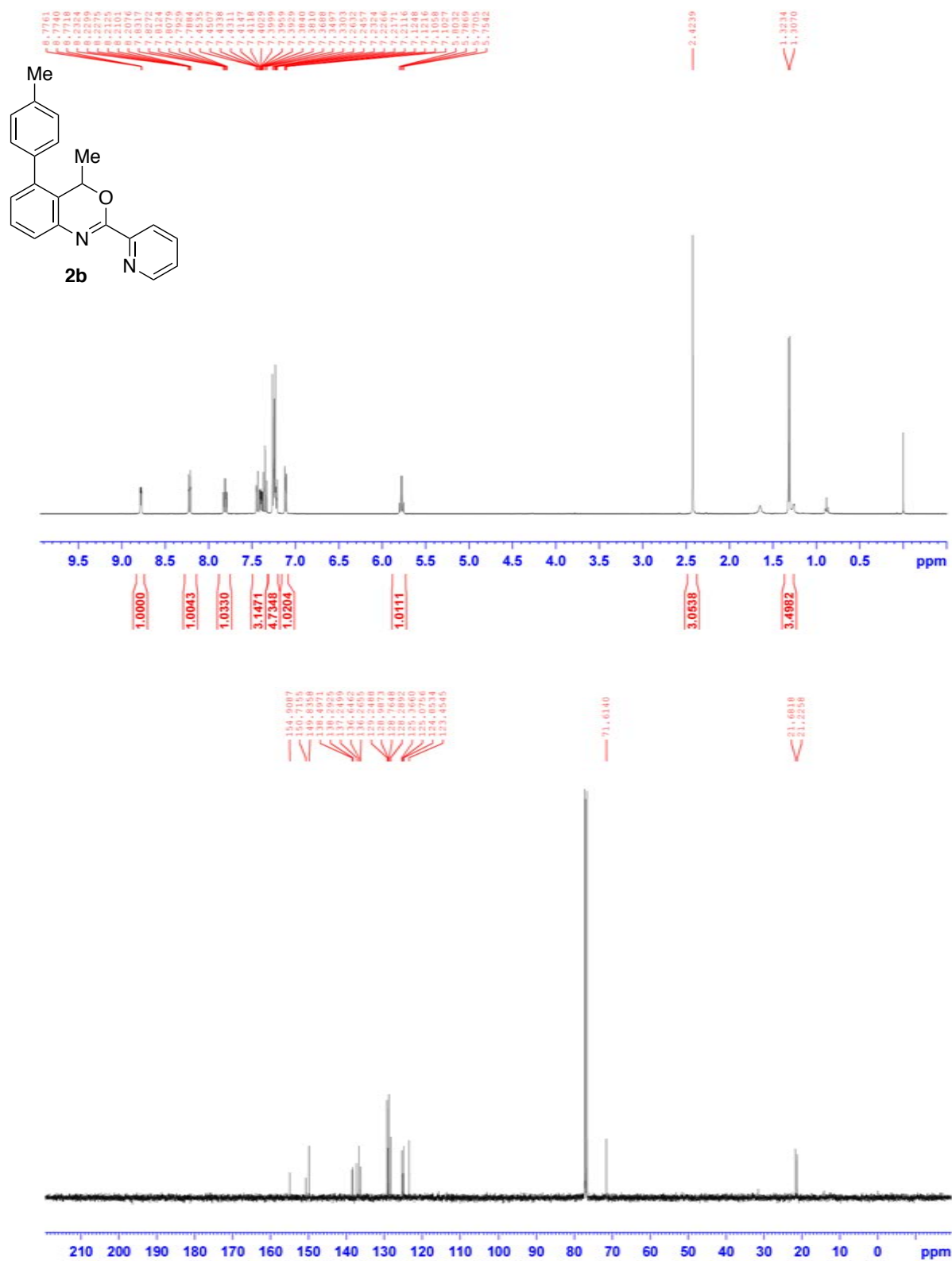
Figure S3. ORTEP Drawing of **31** (CCDC 1816028, 50% thermal ellipsoid, recrystallized from hexane/CH₂Cl₂)

^1H , ^{13}C , and ^{19}F NMR Spectra of Products

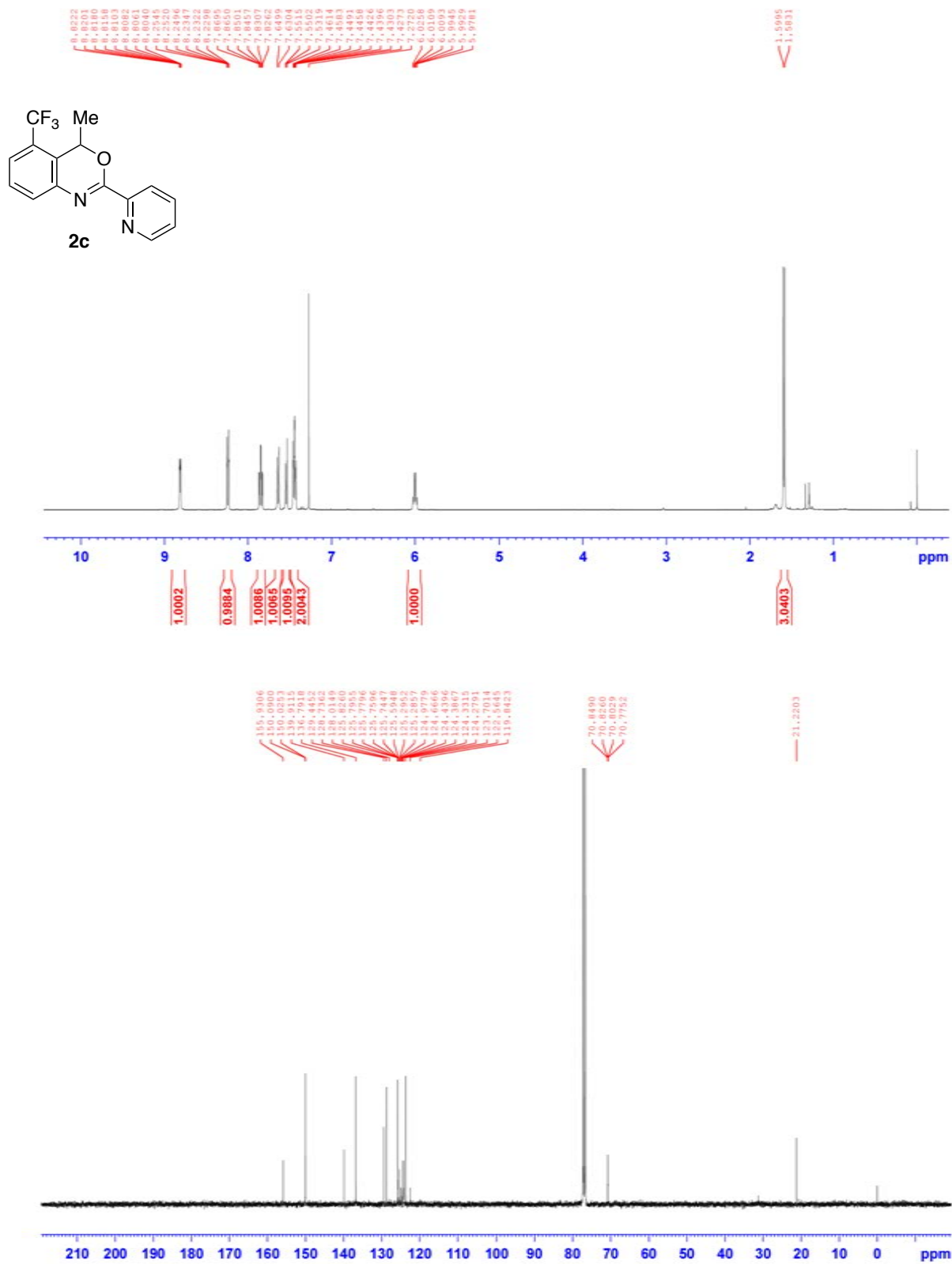
[^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2a**]

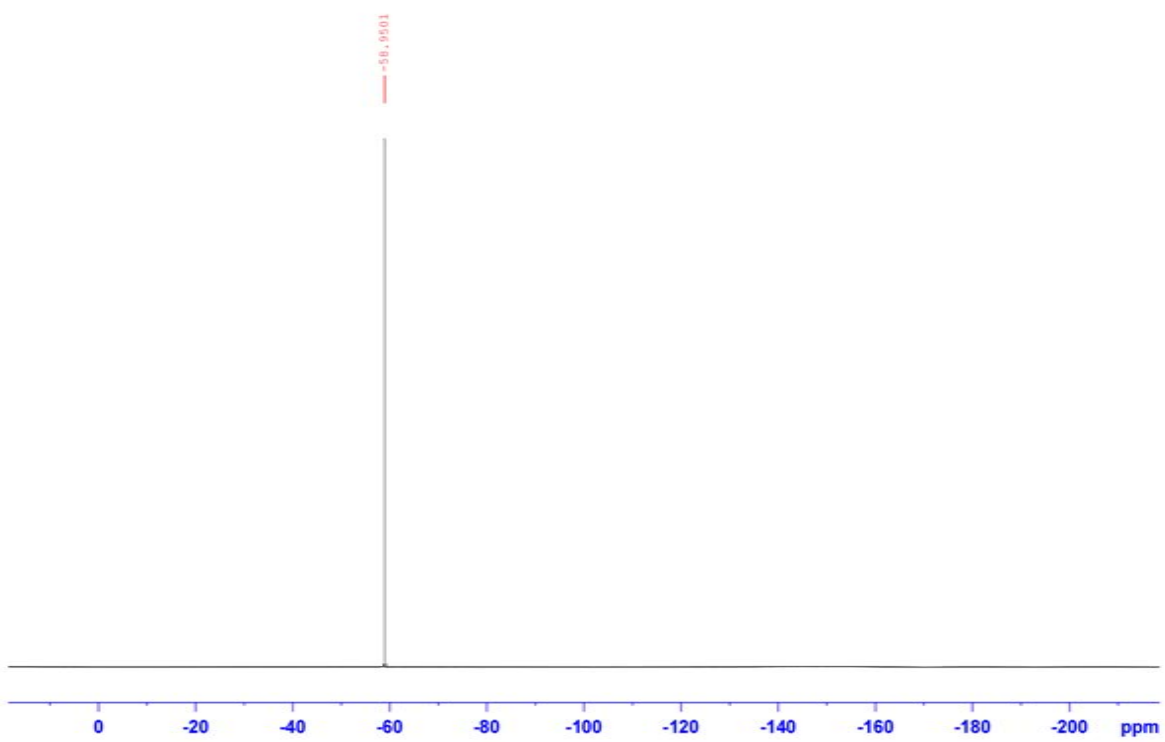


[¹H and ¹³C{¹H}] spectra NMR of **2b**

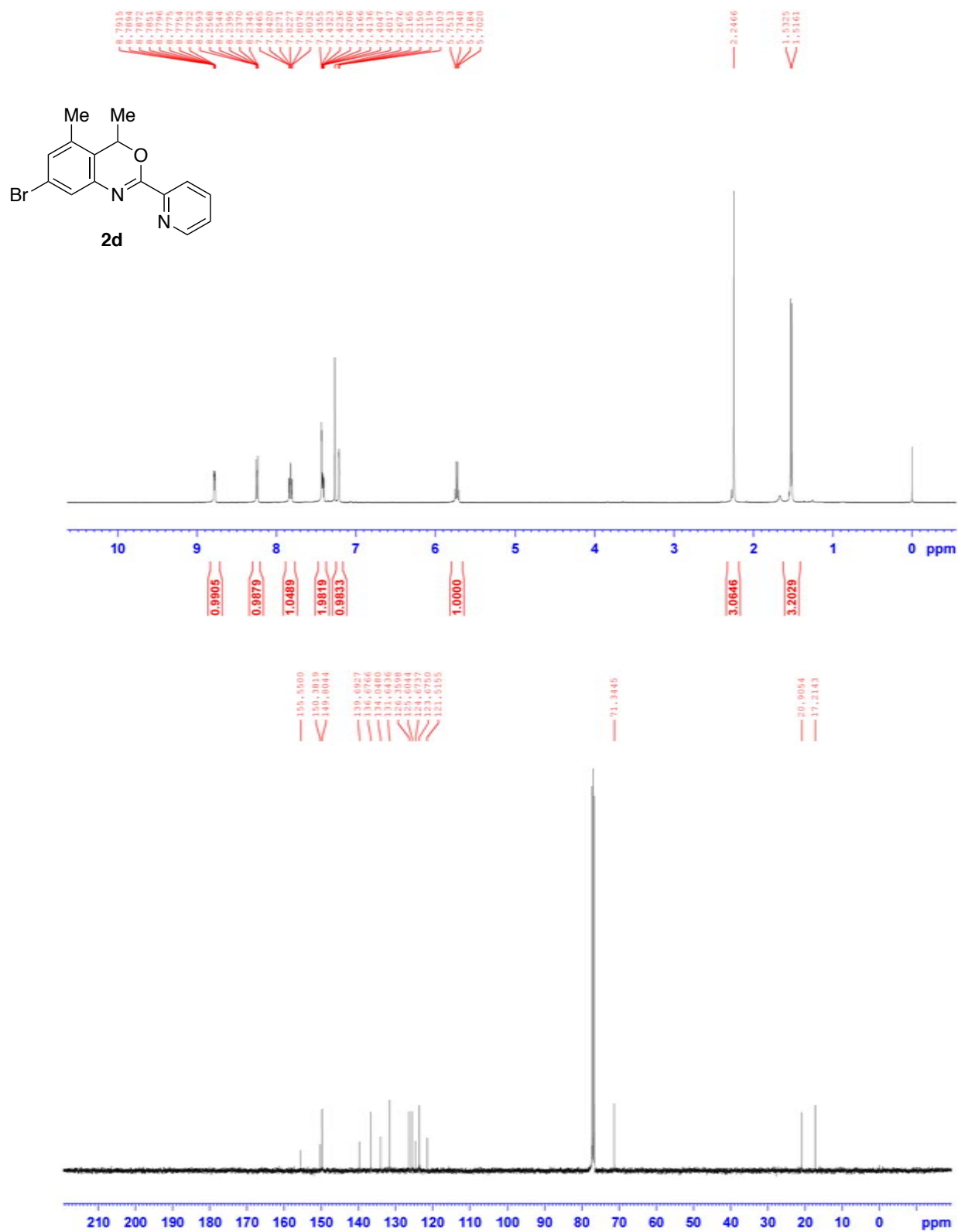


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of **2c**

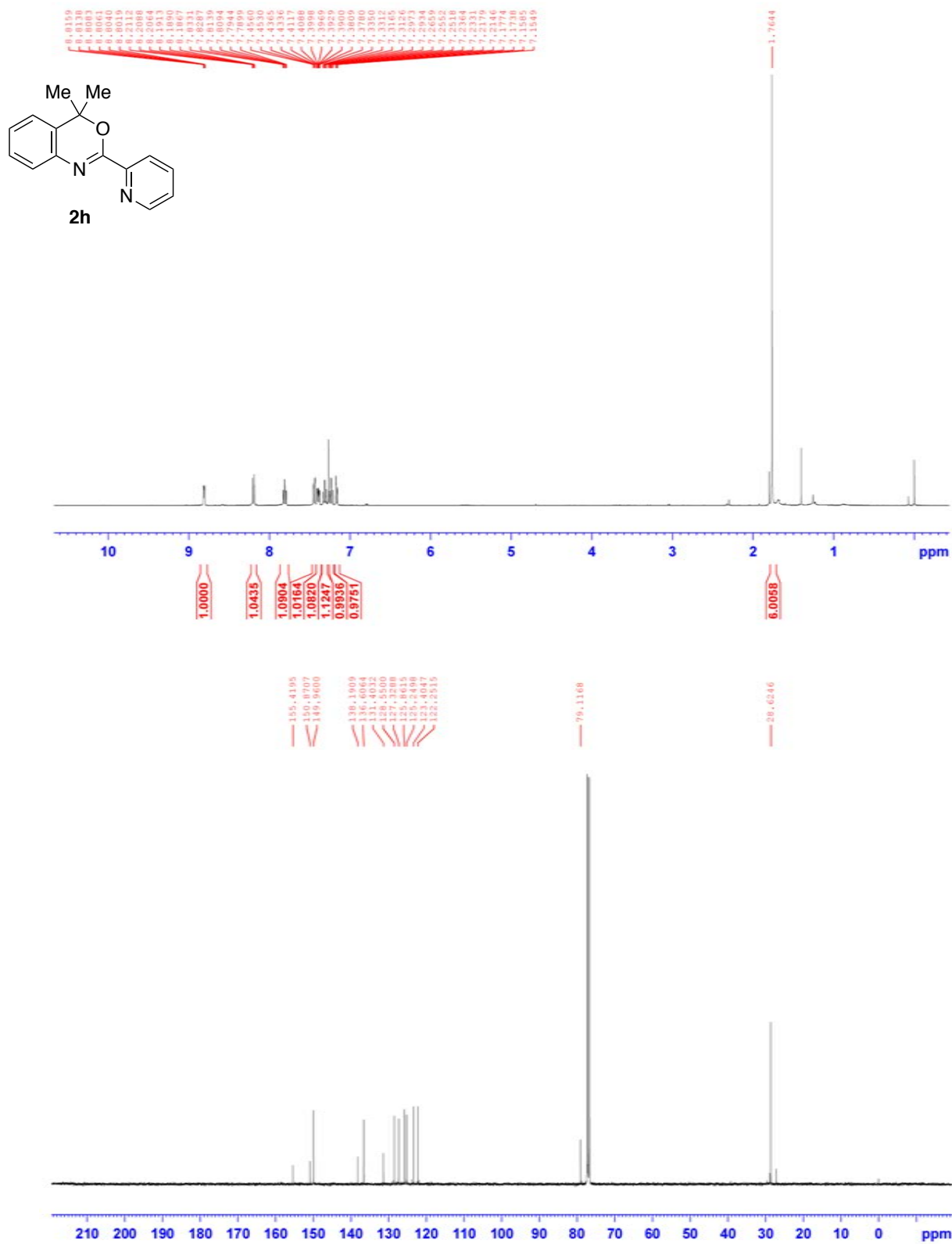




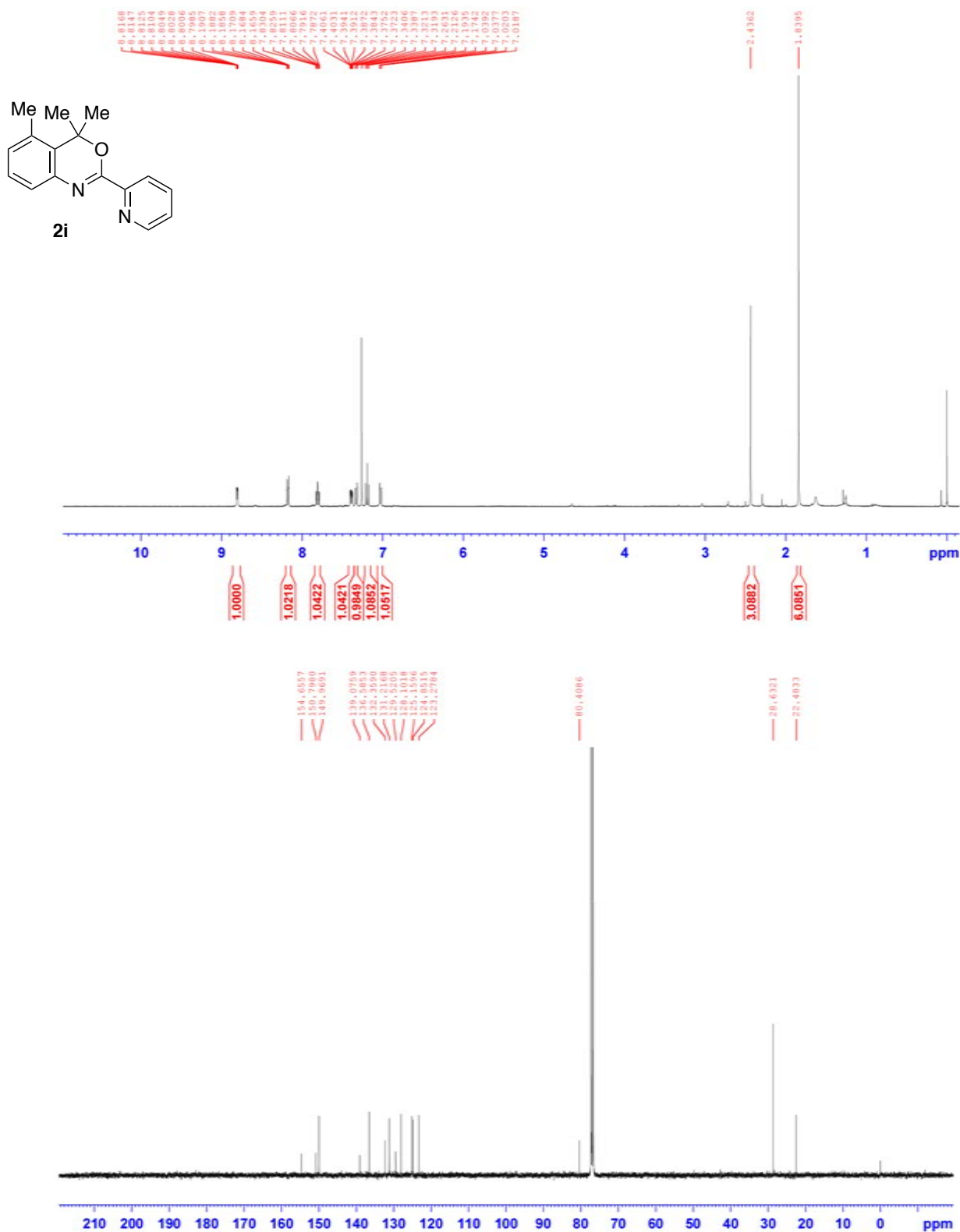
[¹H and ¹³C{¹H}] NMR spectra of **2d**



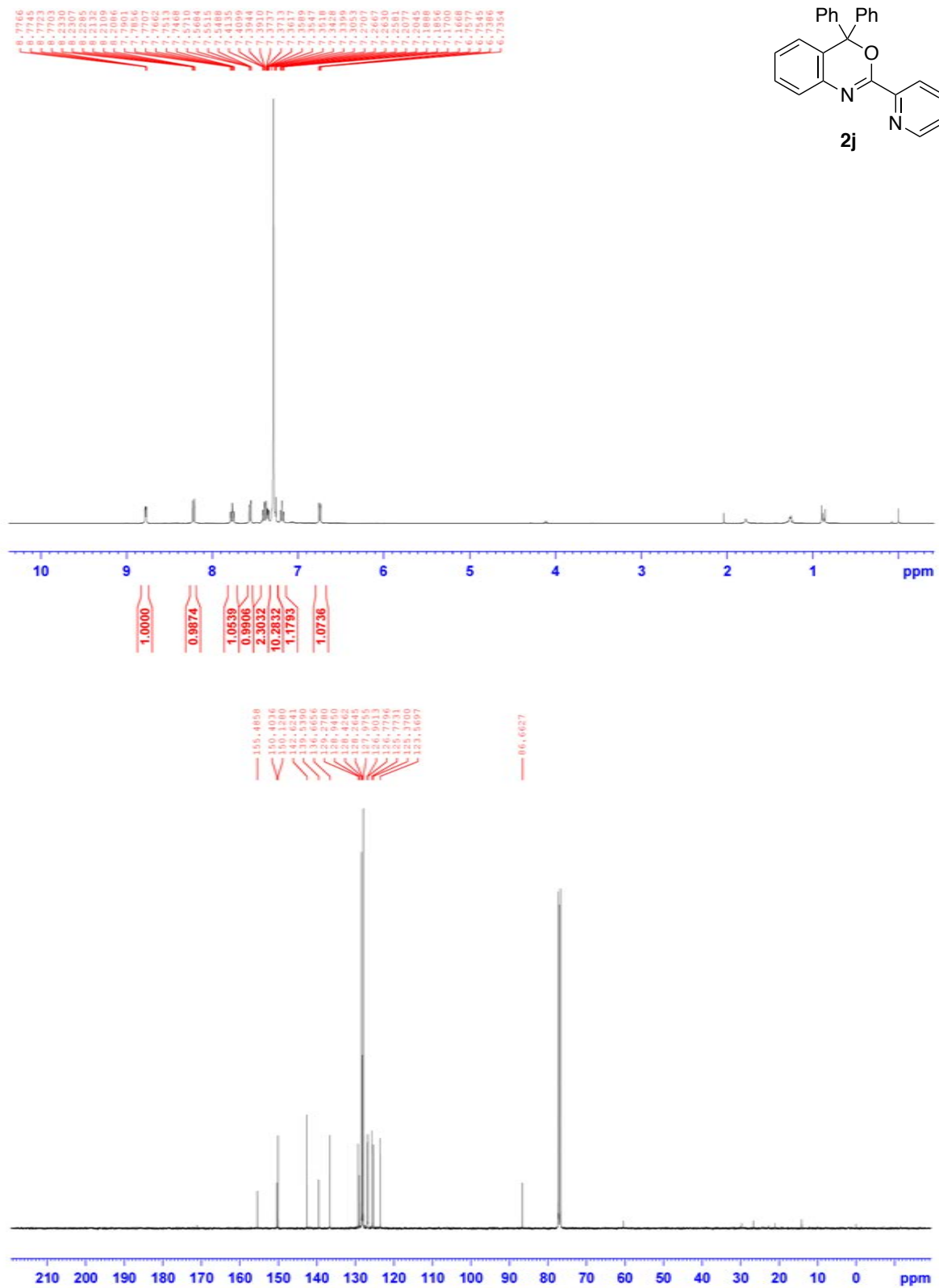
^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2h**



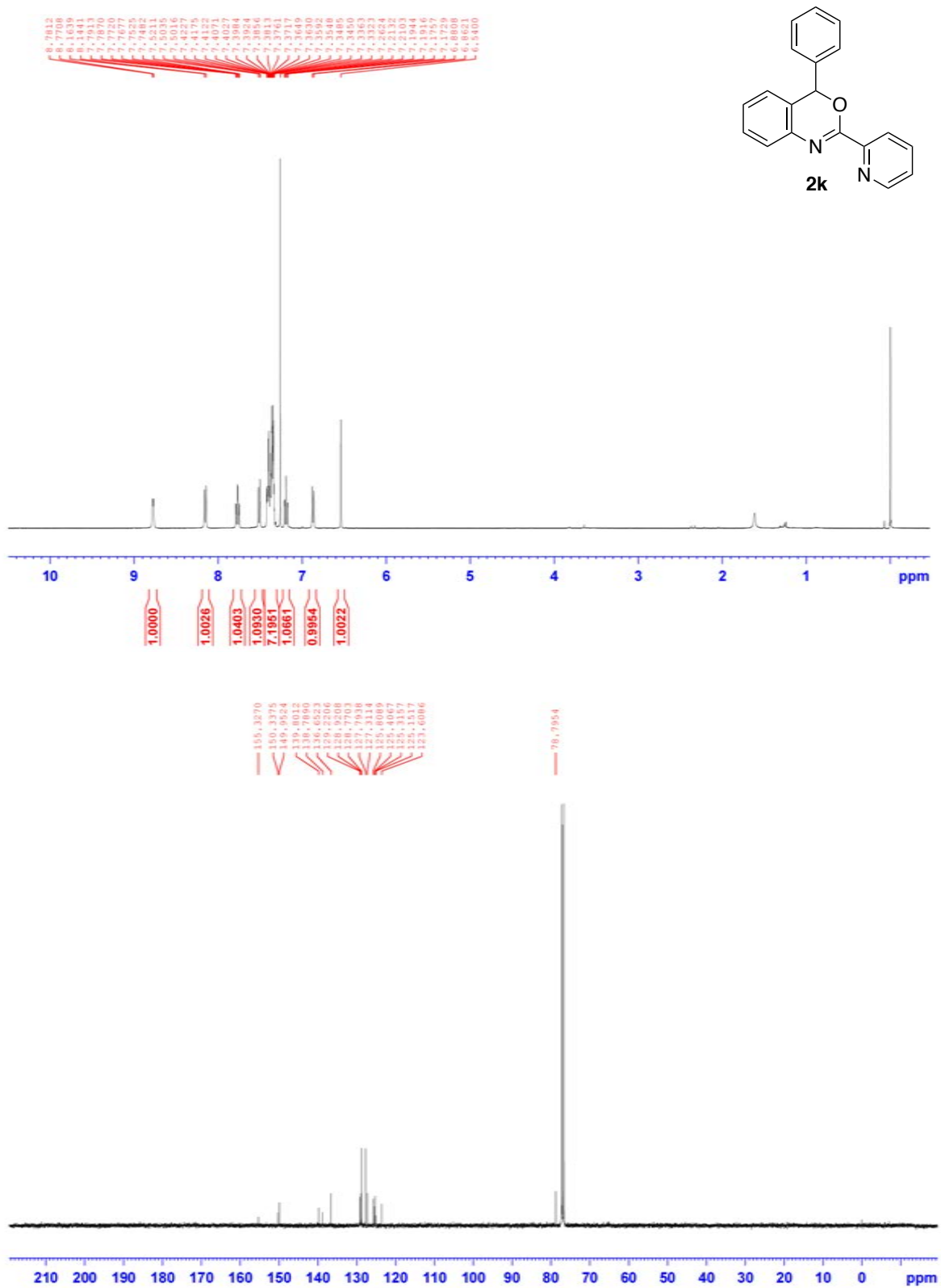
[¹H and ¹³C{¹H} NMR spectra of **2i**]



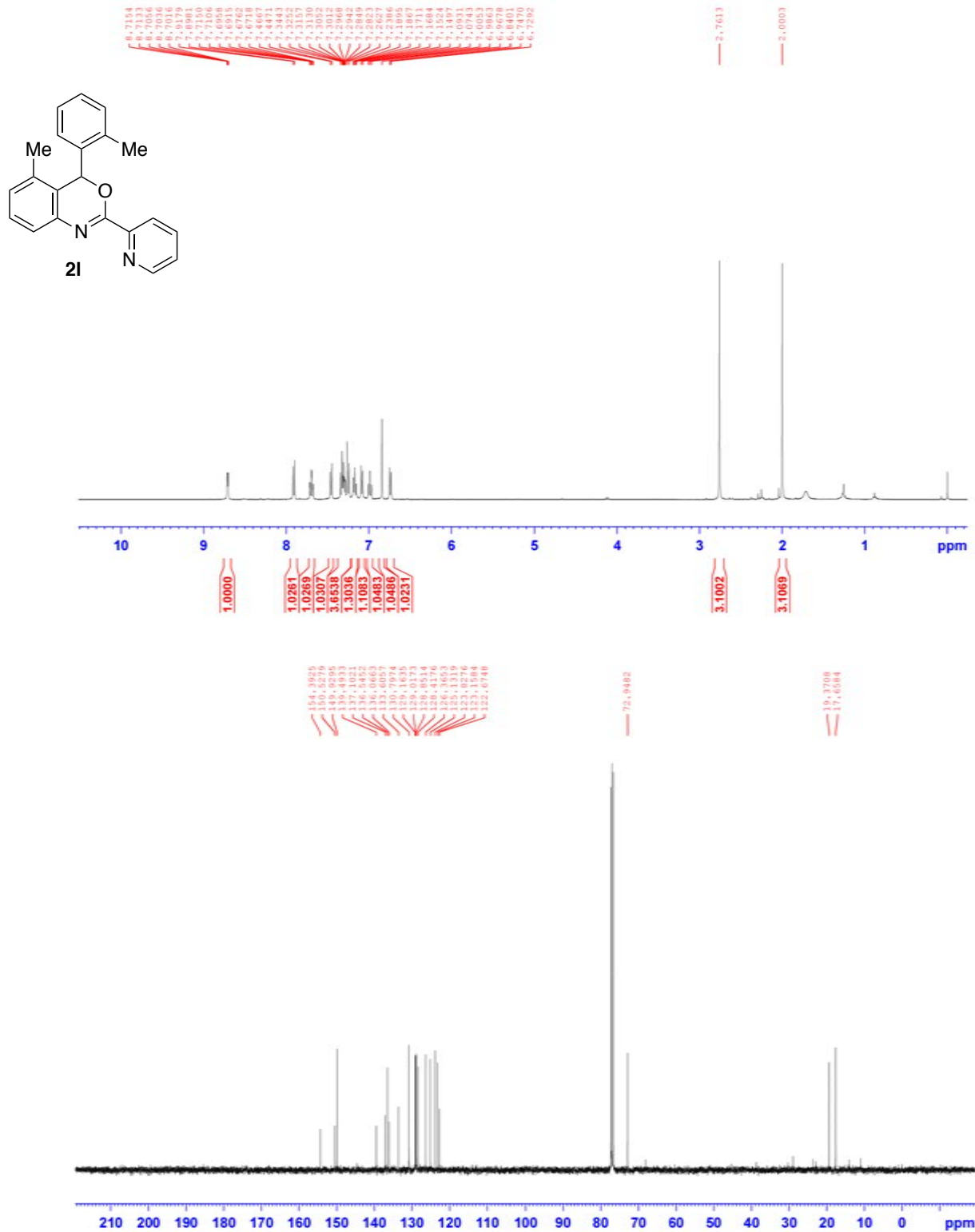
[¹H and ¹³C{¹H}] NMR spectra of **2j**



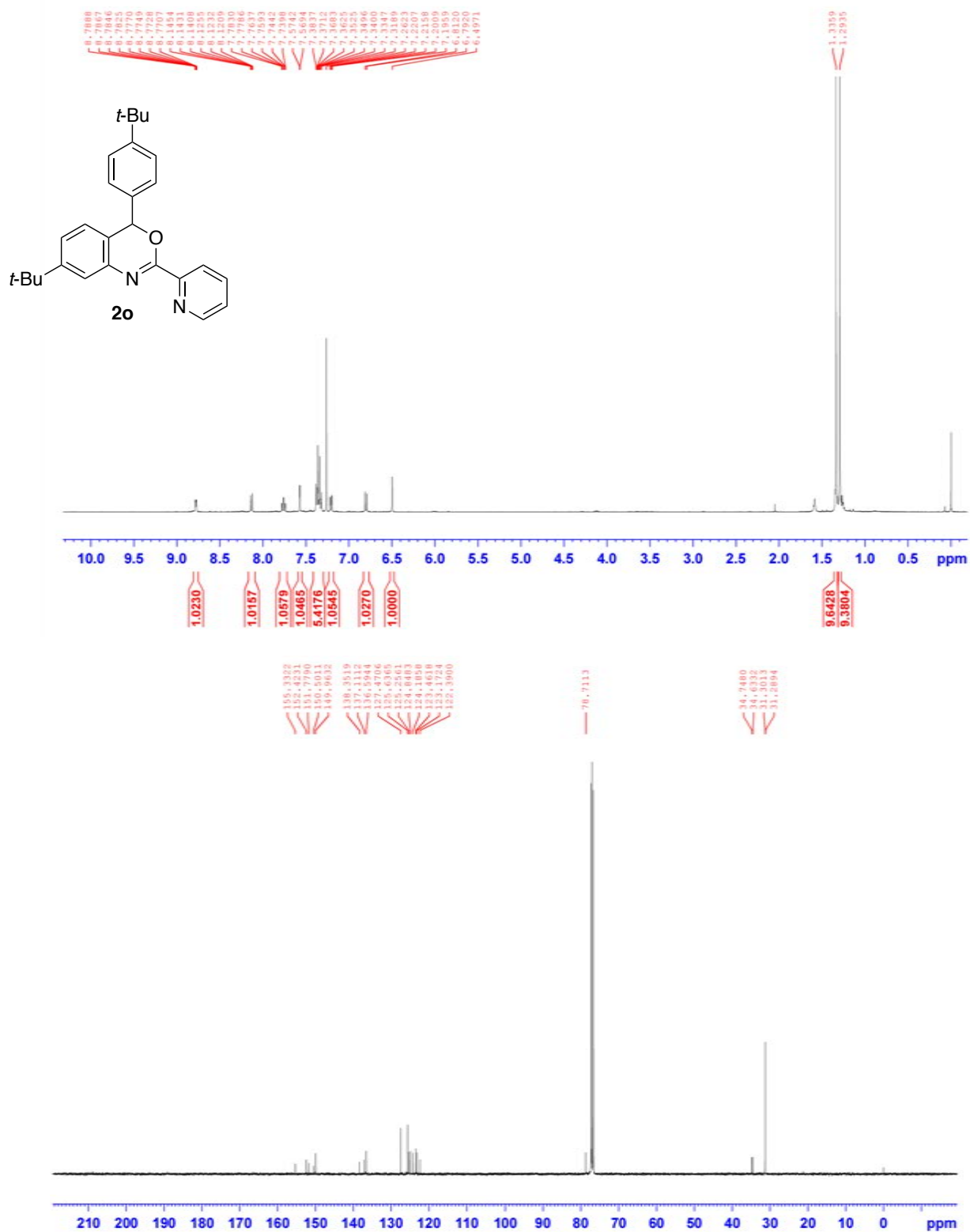
[¹H and ¹³C{¹H} NMR spectra of **2k**]



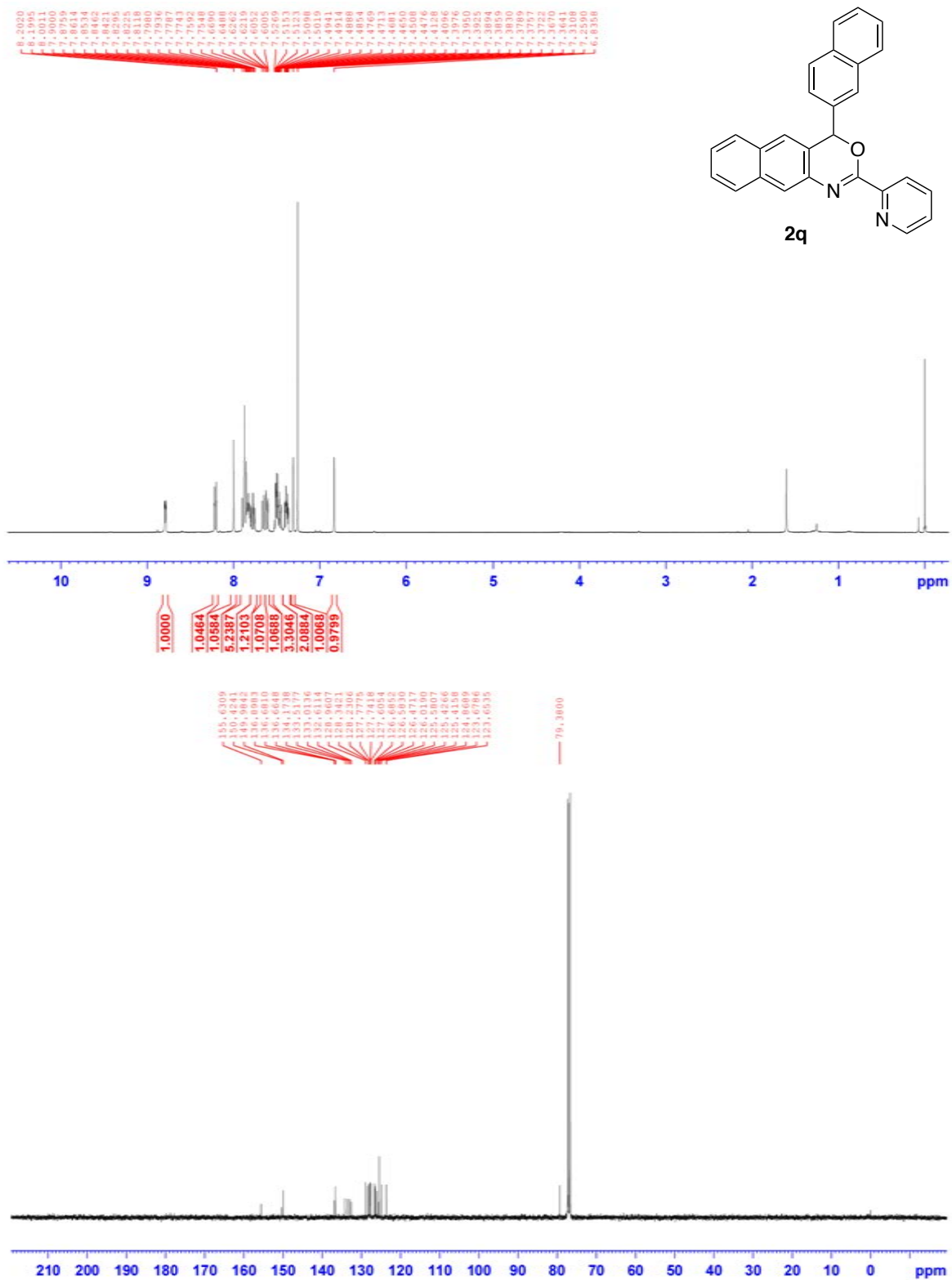
[¹H and ¹³C{¹H} NMR spectra of **2I**]



[¹H and ¹³C{¹H} NMR spectra of **2o**]



[¹H and ¹³C{¹H} NMR spectra of **2q**]



[¹H and ¹³C{¹H} NMR spectra of **3I**]

