

Supporting Information for

Organocatalytic [4+2] Cyclizations of *para*-Quinone Methide

Derivatives with Isocyanates

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E-mail: fshi@jsnu.edu.cn; gf2016@jsnu.edu.cn.

^b*School of Chemistry and Chemical Engineering, Hunan University of Science and Technology,*

Xiangtan, 411201, P. R. China, Email: yinchunjiao@hnust.edu.cn.

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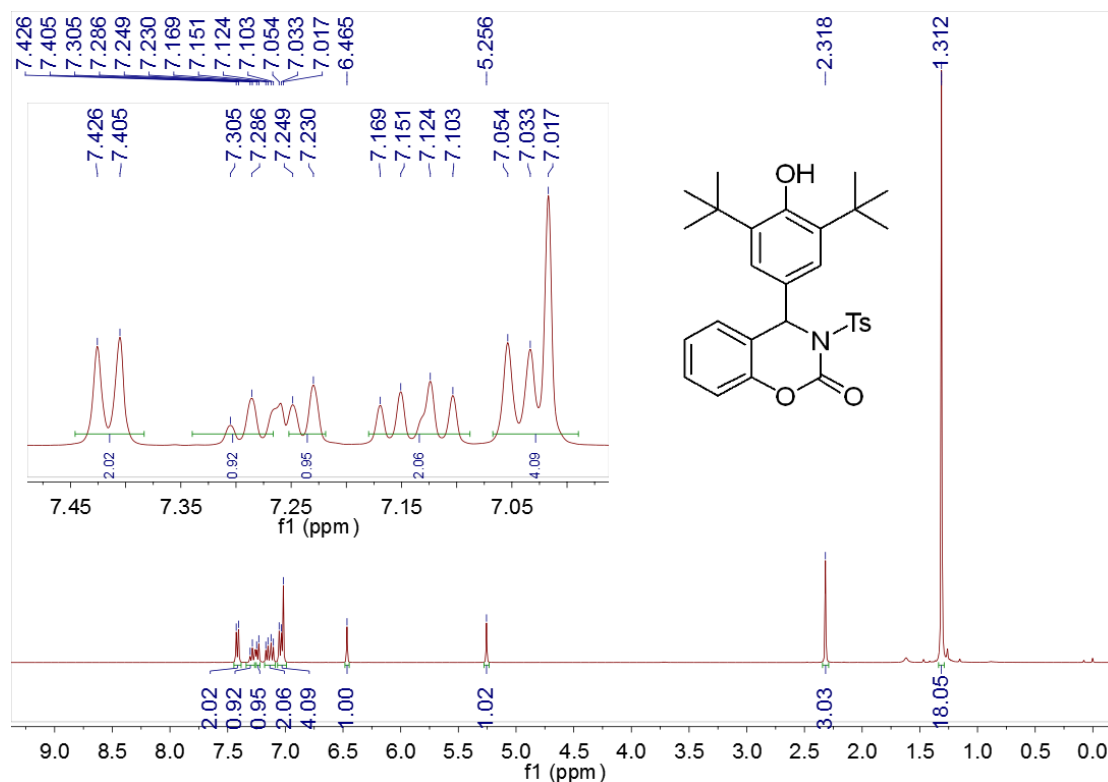
1. NMR spectra of products 3 and 6 (S2-S29)

2. HPLC copies of chiral product 3a (S30)

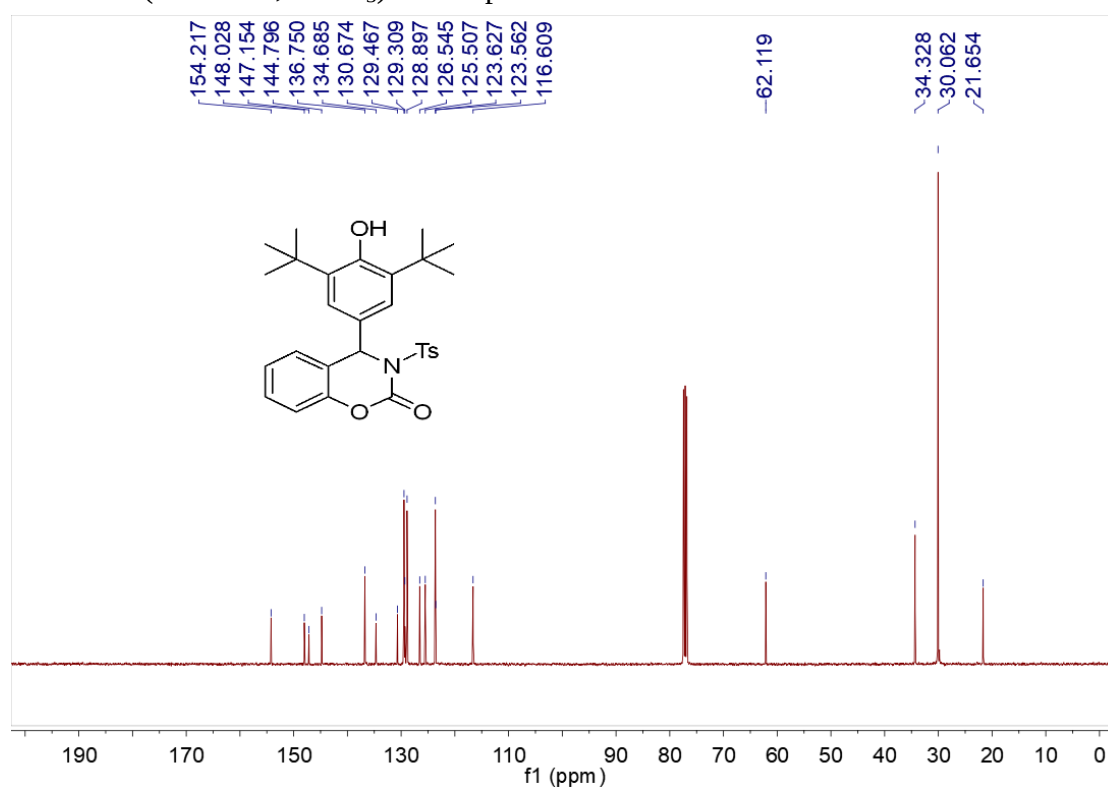
3. X-ray single crystal data for compound 3a (S31-S32)

1. NMR spectra of products 3 and 6

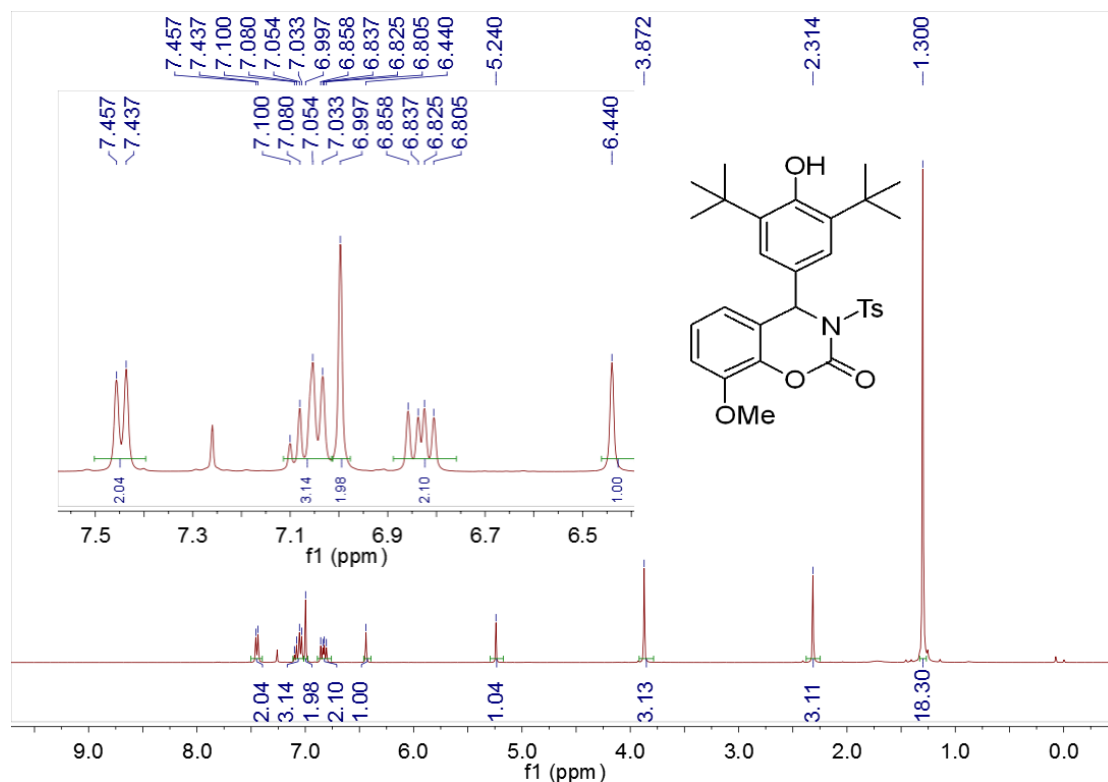
^1H NMR (400 MHz, CDCl_3) of compound **3a**:



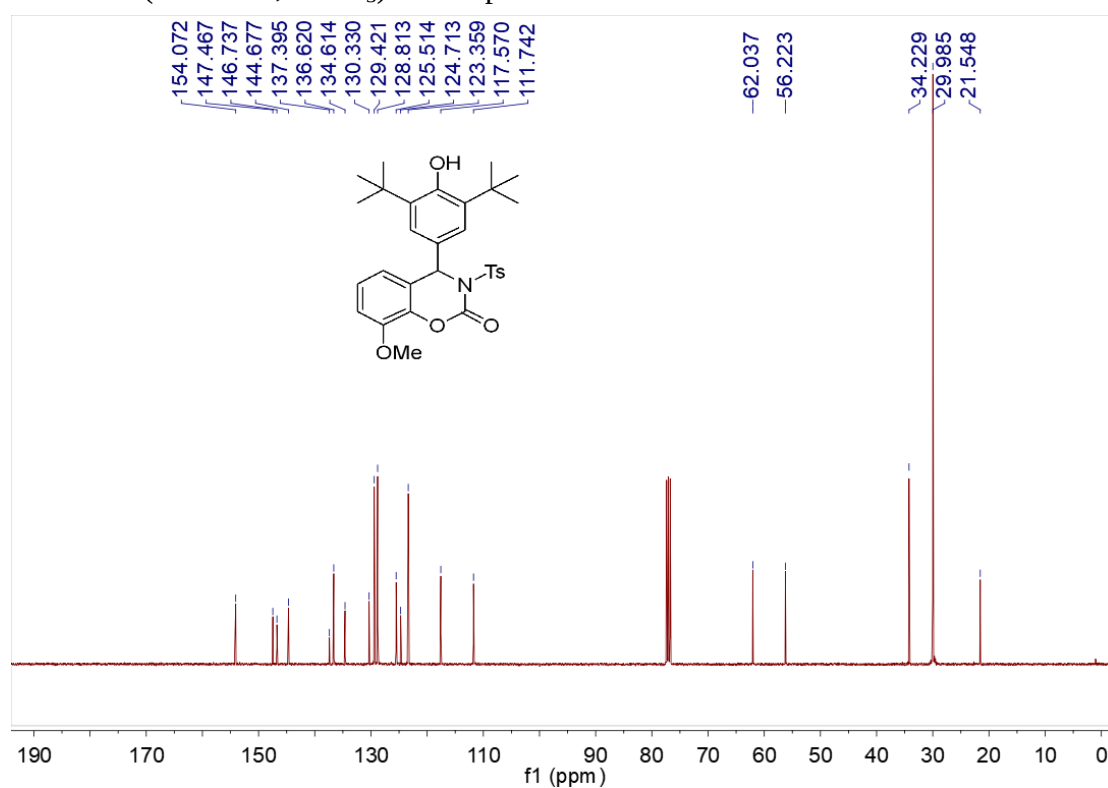
^{13}C NMR (100 MHz, CDCl_3) of compound **3a**:



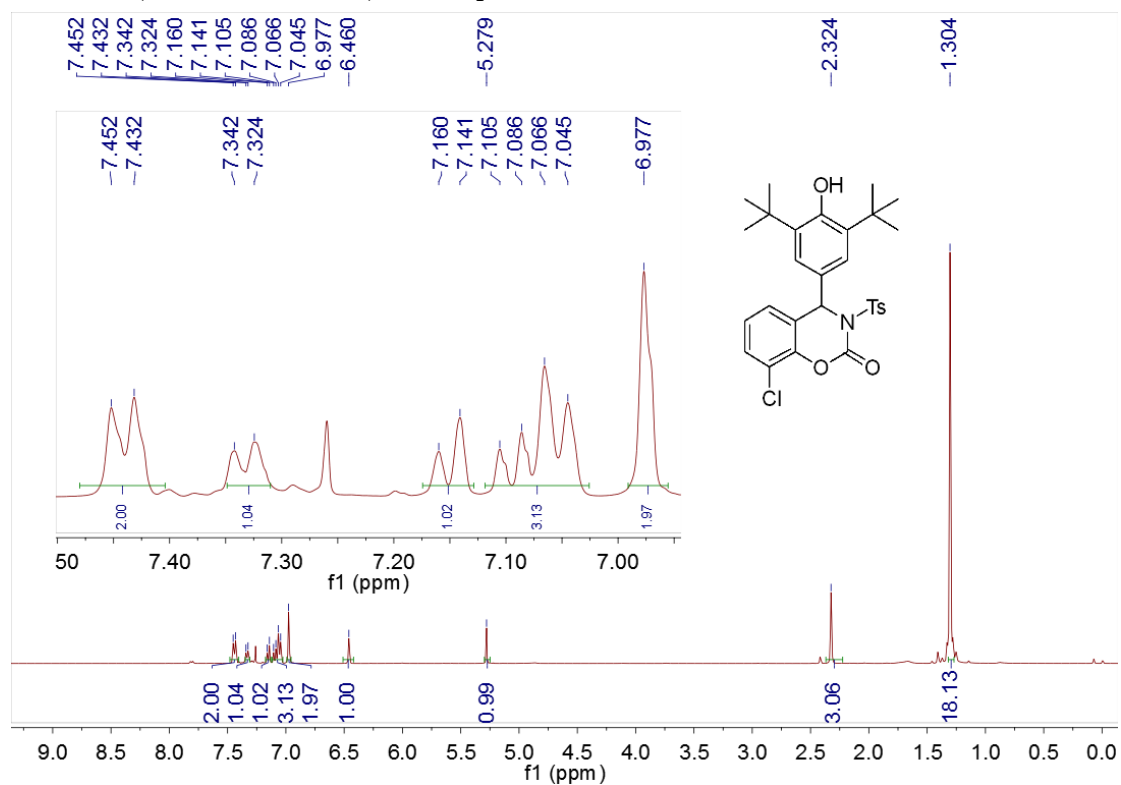
^1H NMR (400 MHz, CDCl_3) of compound **3b**:



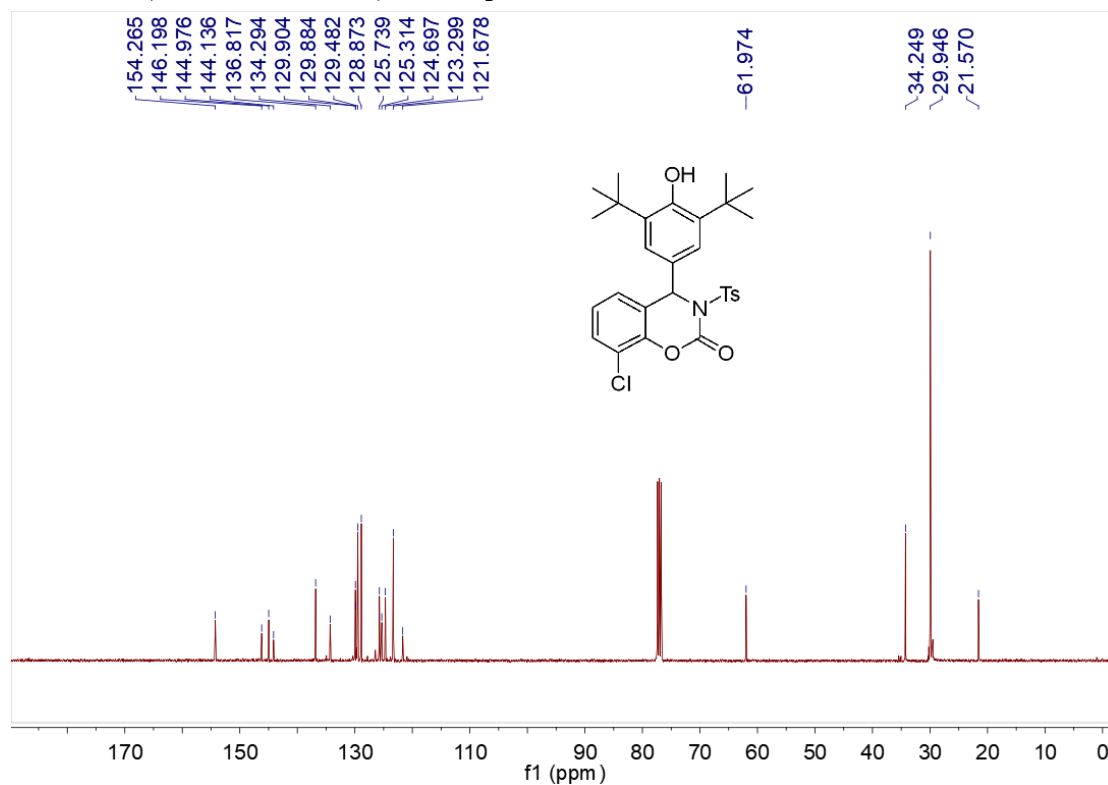
^{13}C NMR (100 MHz, CDCl_3) of compound **3b**:



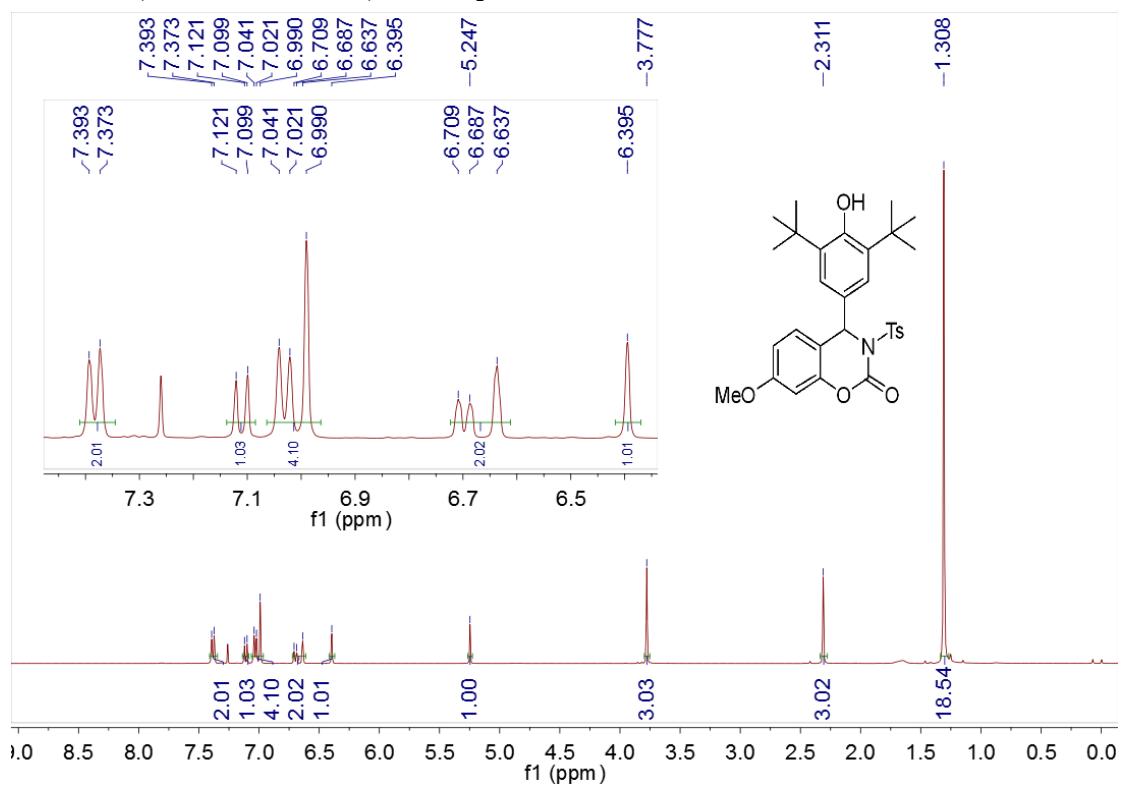
^1H NMR (400 MHz, CDCl_3) of compound **3c**:



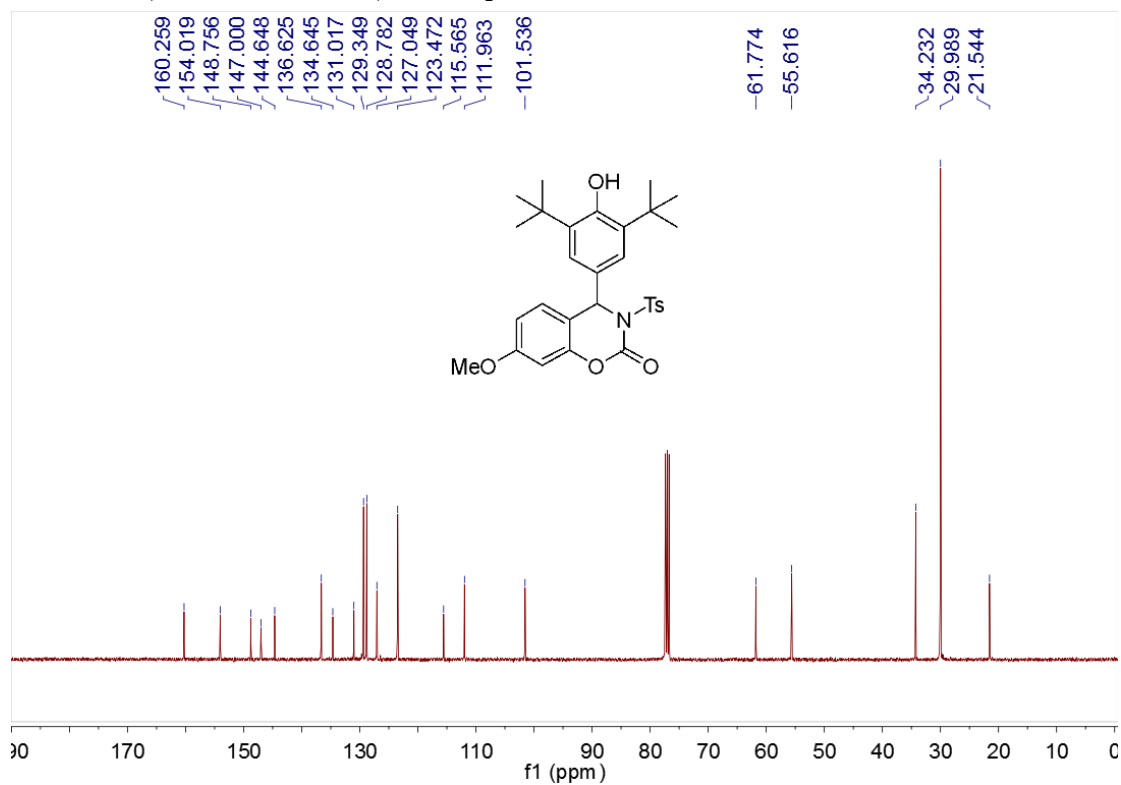
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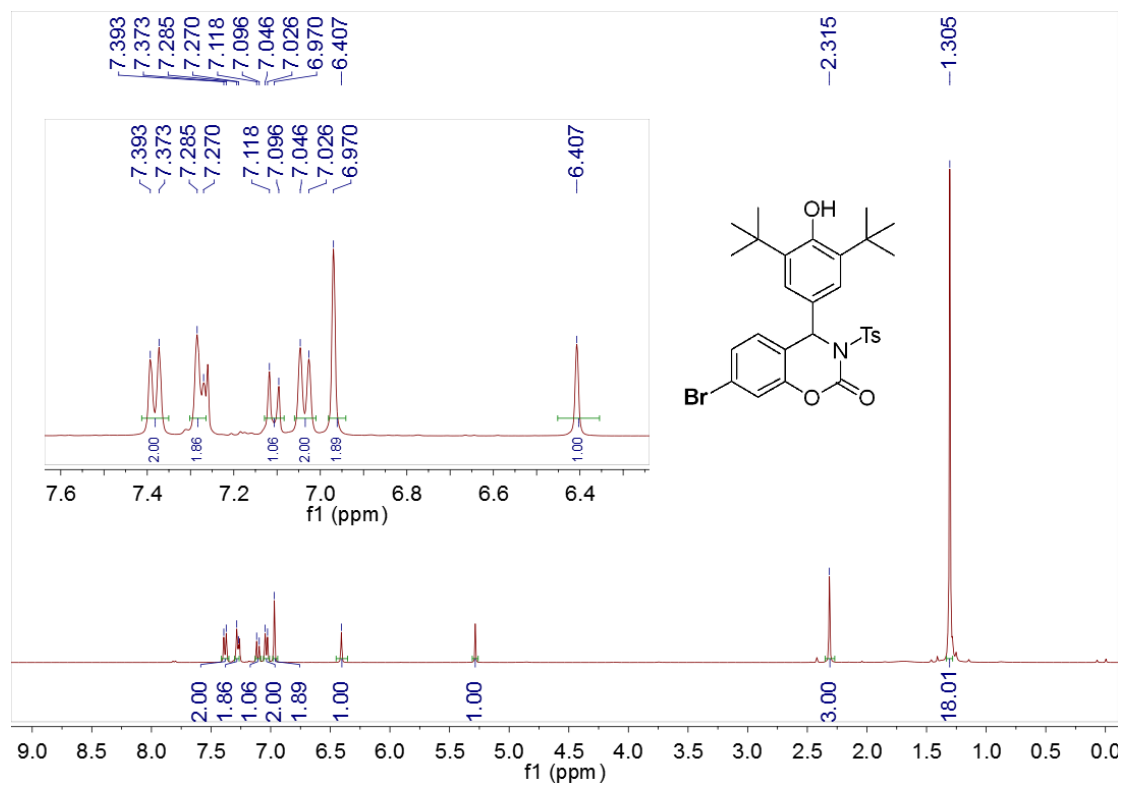
^1H NMR (400 MHz, CDCl_3) of compound **3d**:



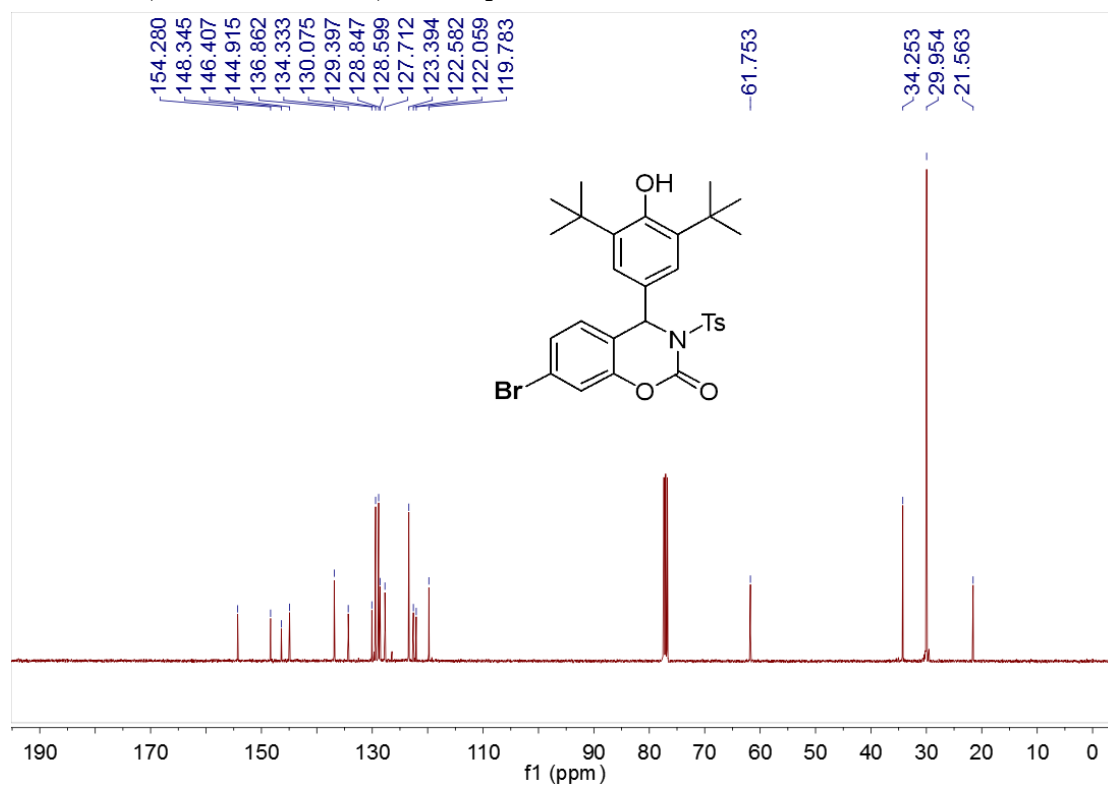
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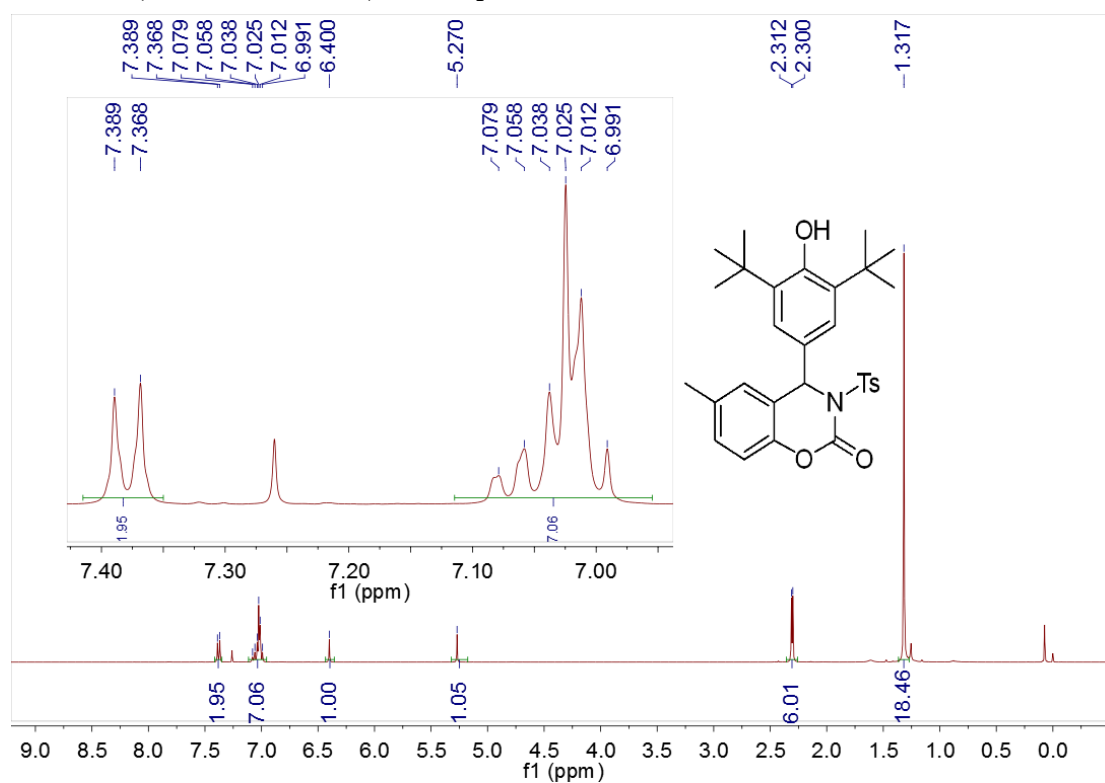
^1H NMR (400 MHz, CDCl_3) of compound **3e**:



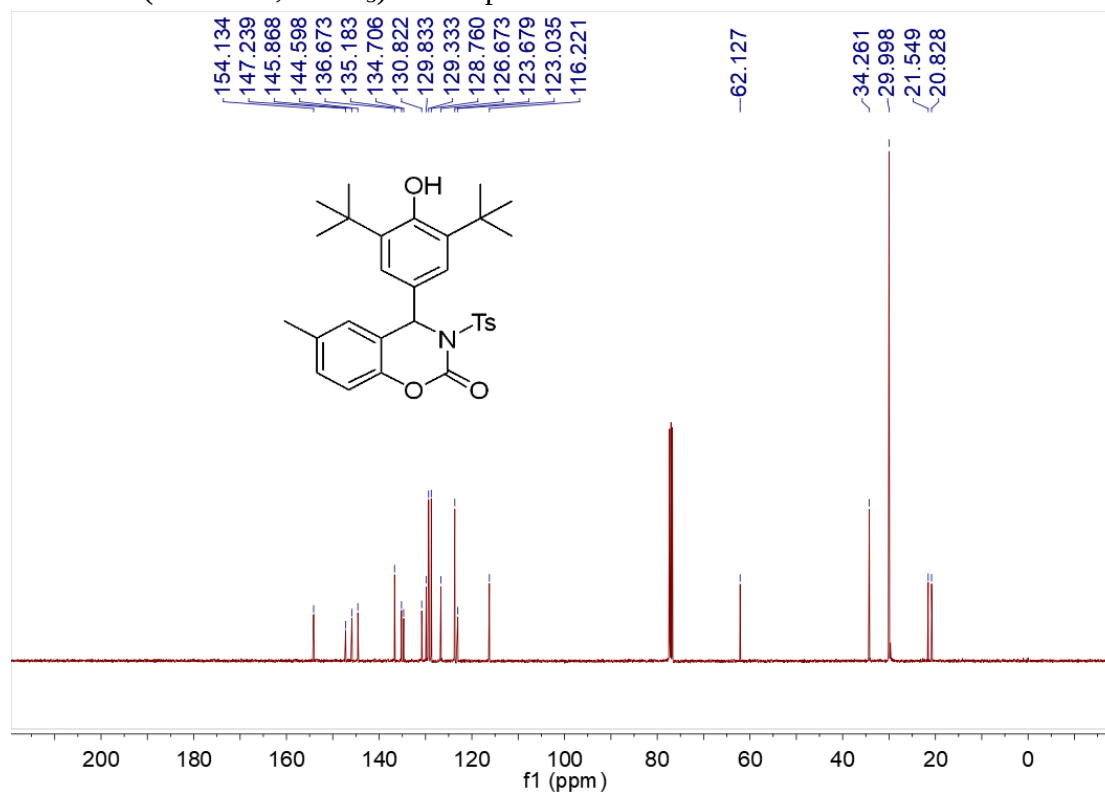
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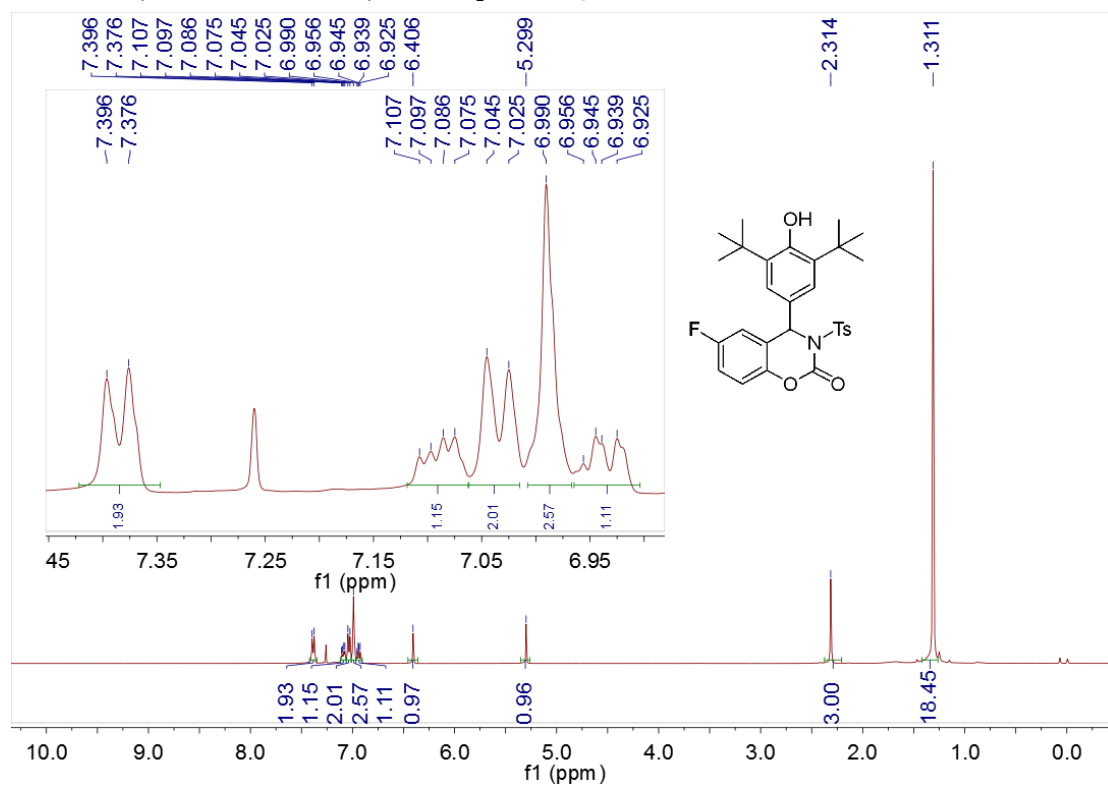
^1H NMR (400 MHz, CDCl_3) of compound **3f**:



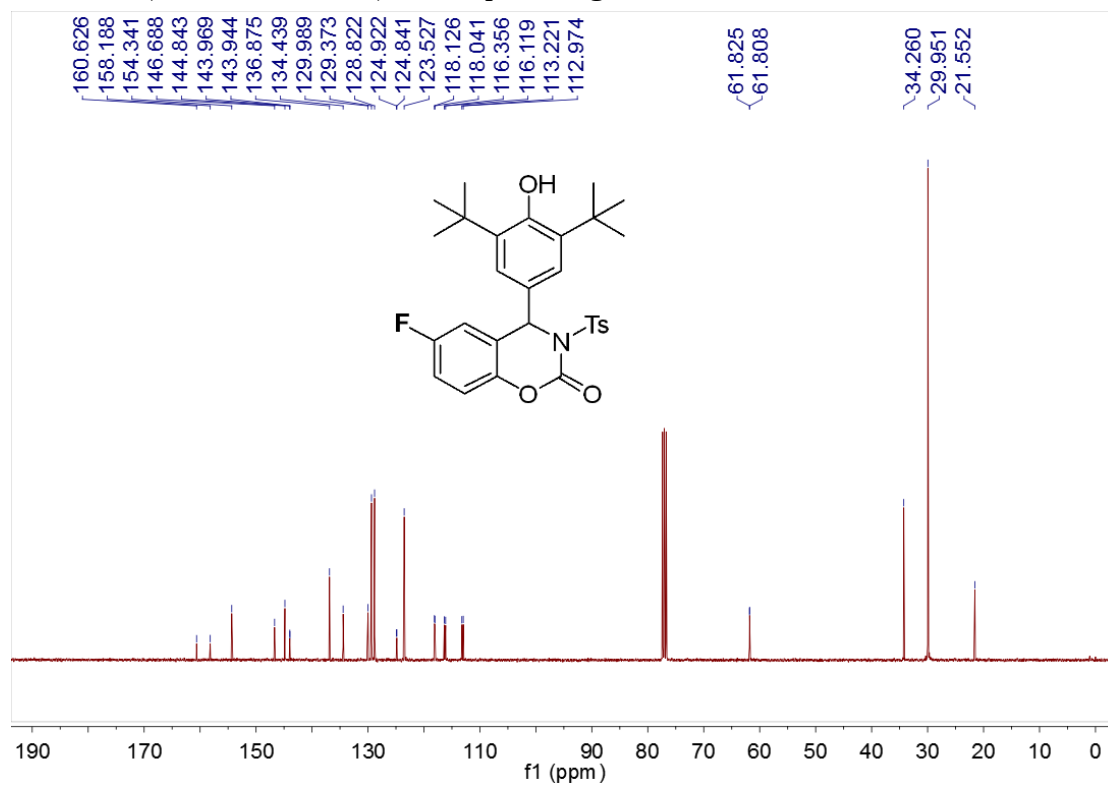
^{13}C NMR (100 MHz, CDCl_3) of compound **3f**:



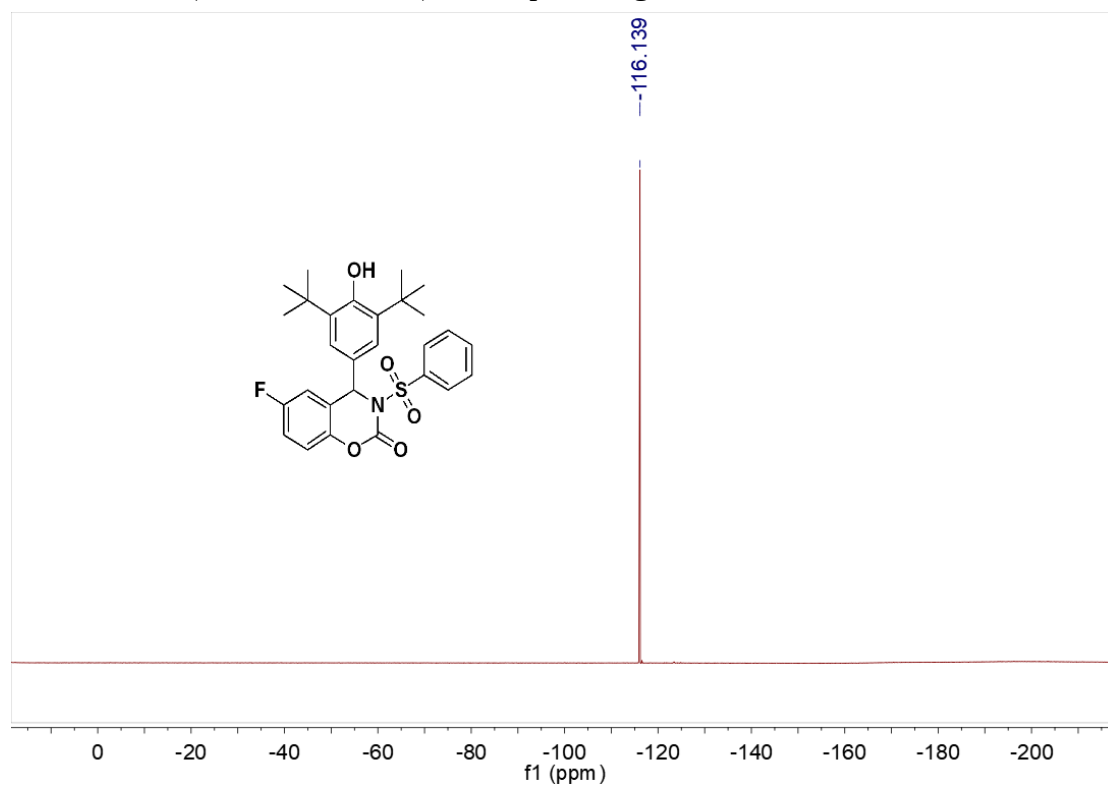
^1H NMR (400 MHz, CDCl_3) of compound **3g**:



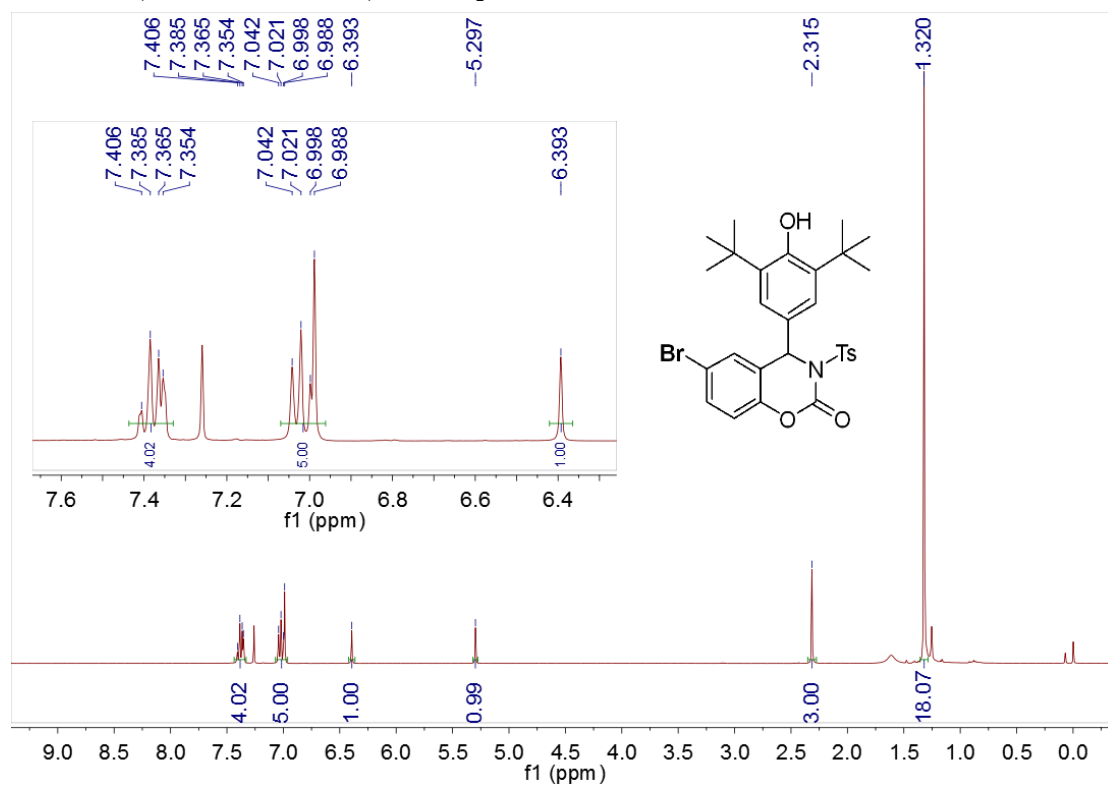
^{13}C NMR (100 MHz, CDCl_3) of compound **3g**:



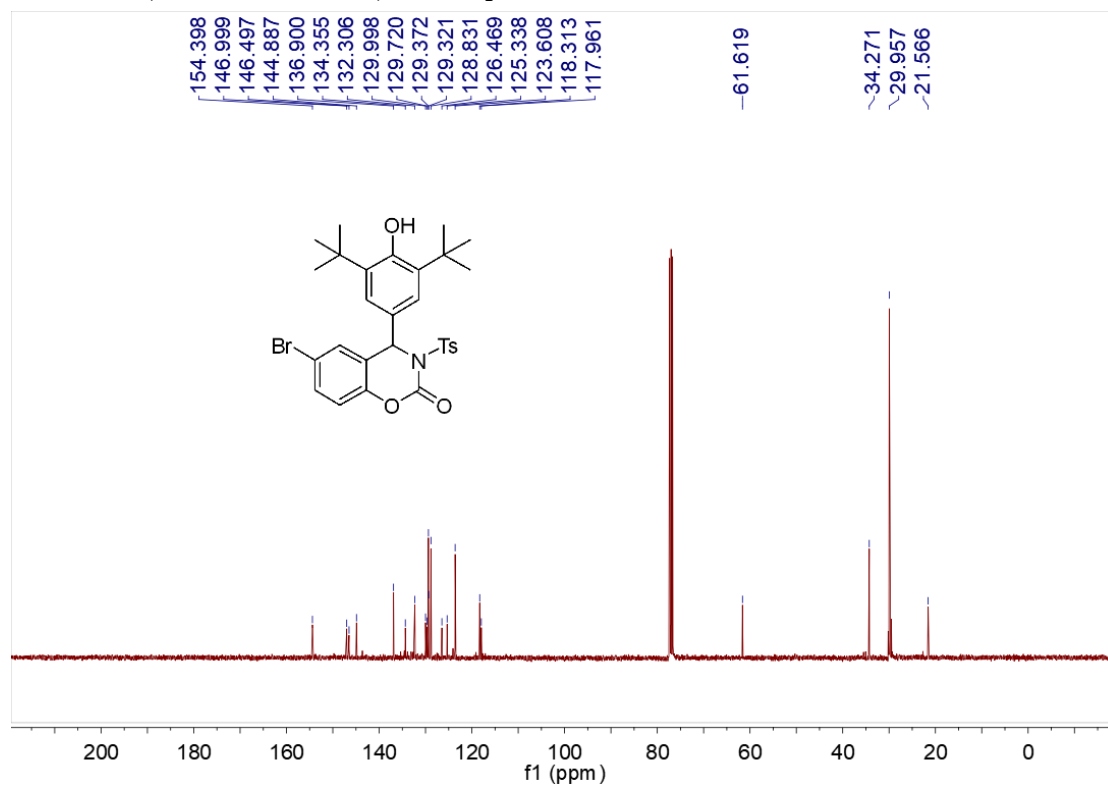
^{19}F NMR (376 MHz, CDCl_3) of compound **3g**:



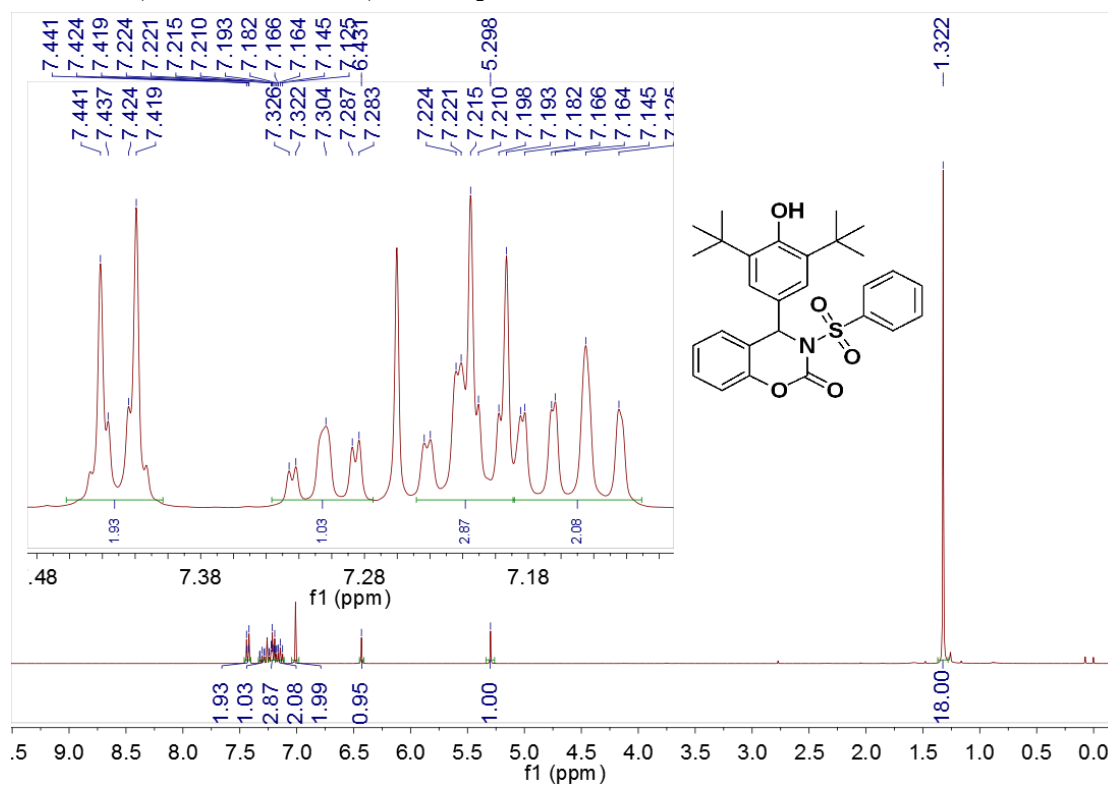
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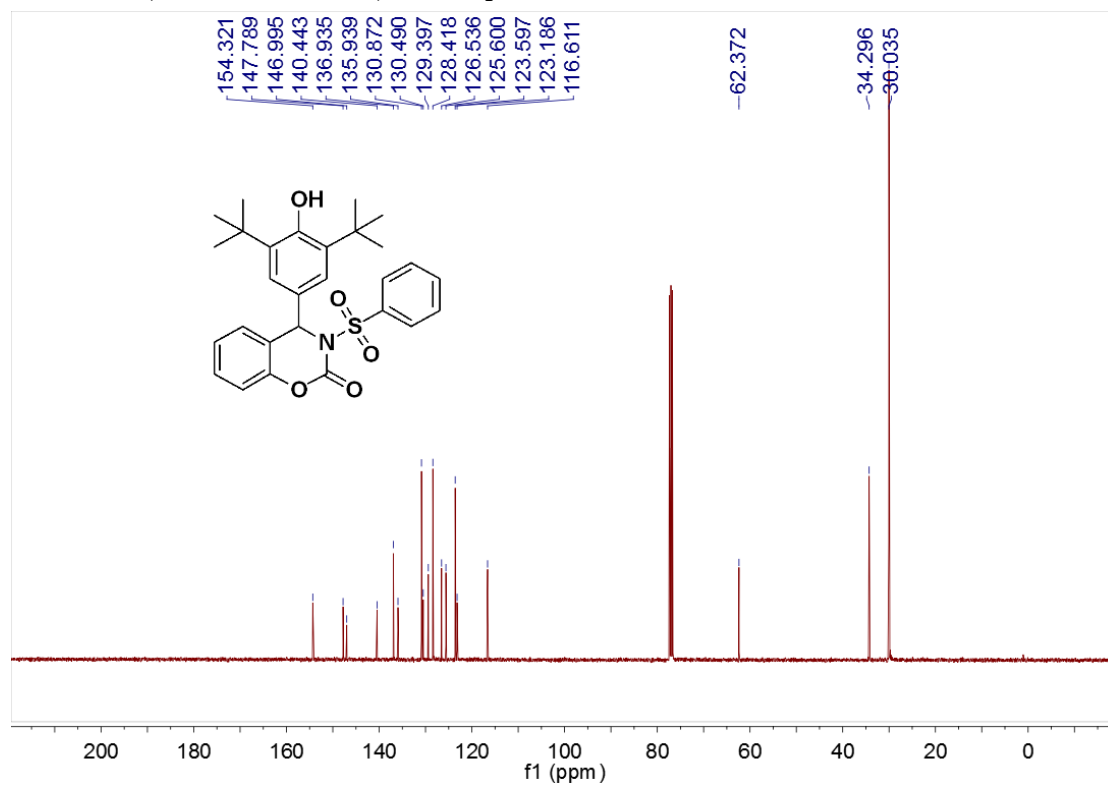
^{13}C NMR (100 MHz, CDCl_3) of compound **3h**:



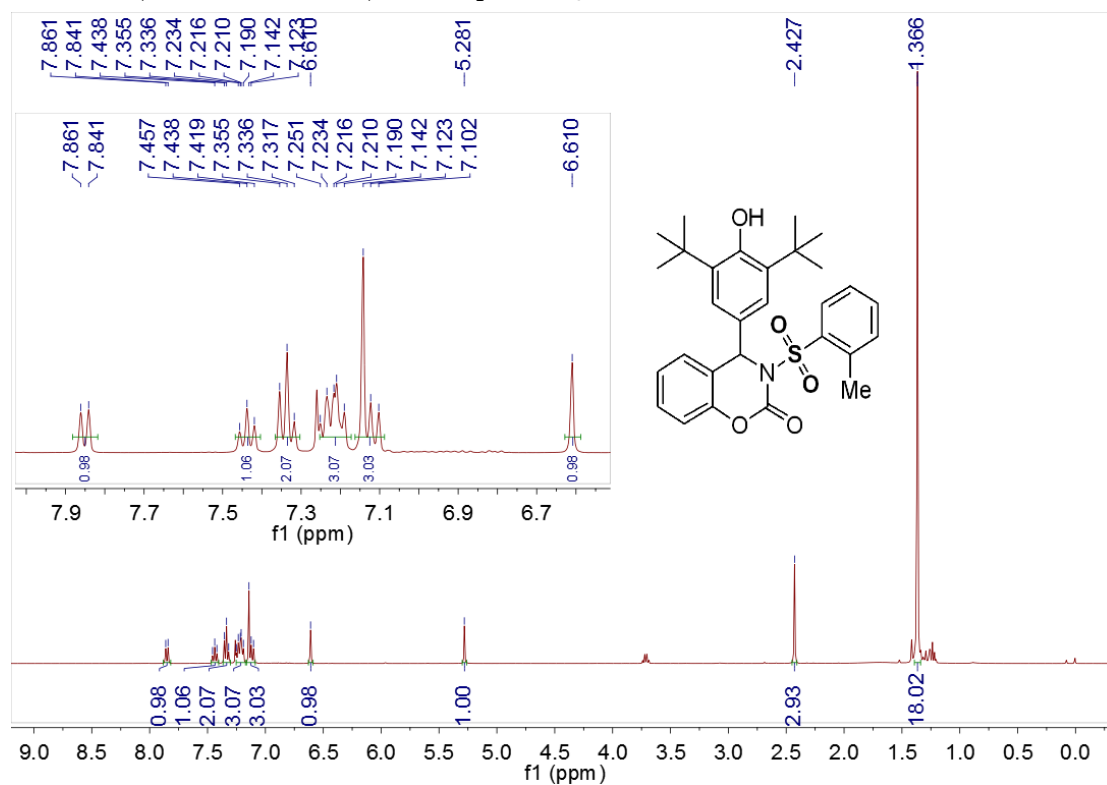
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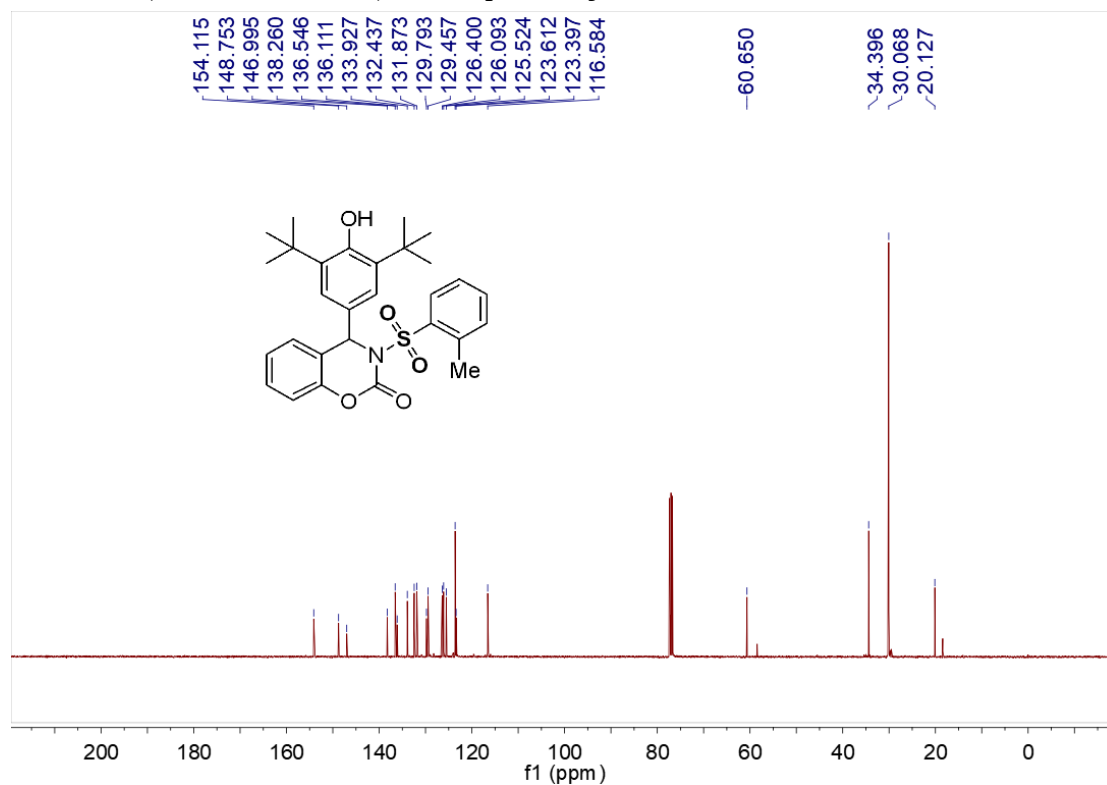
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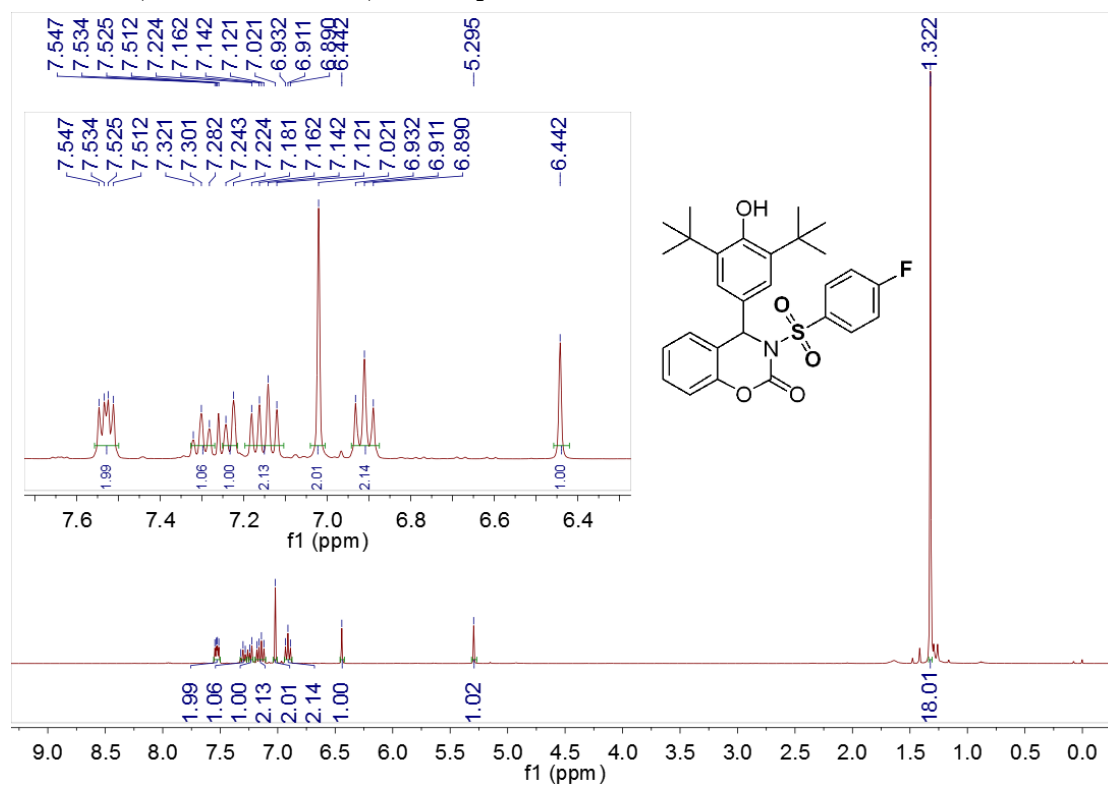
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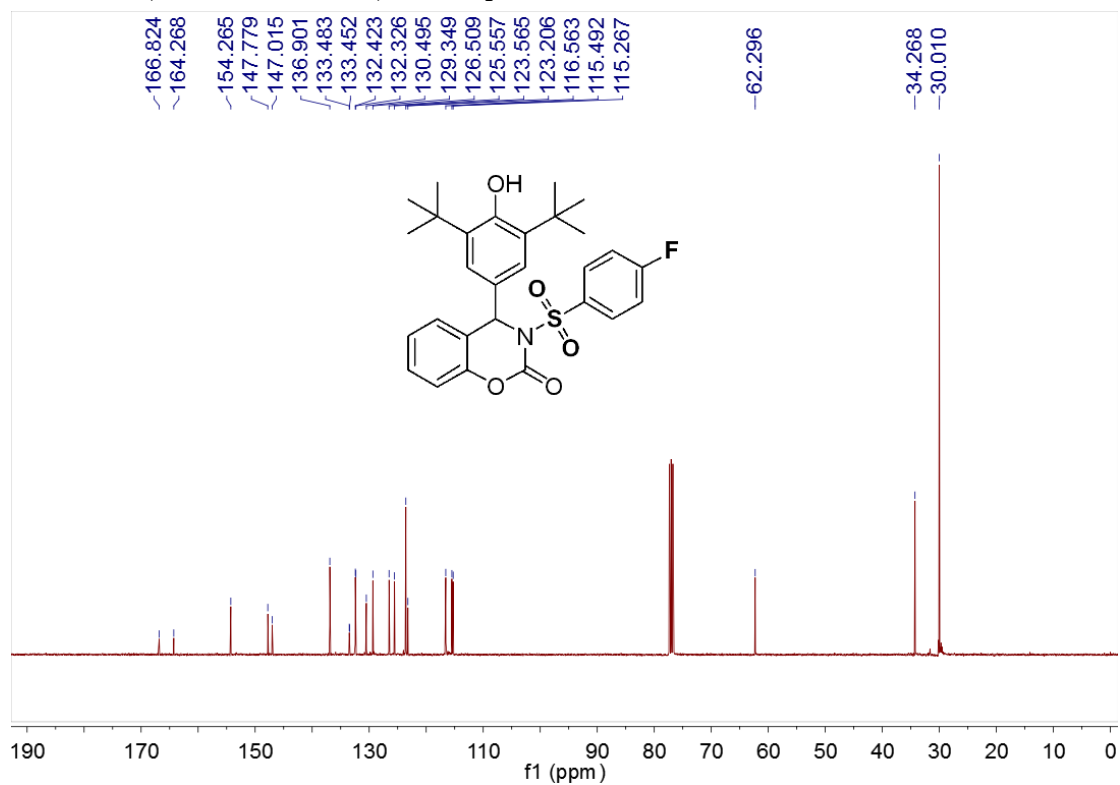
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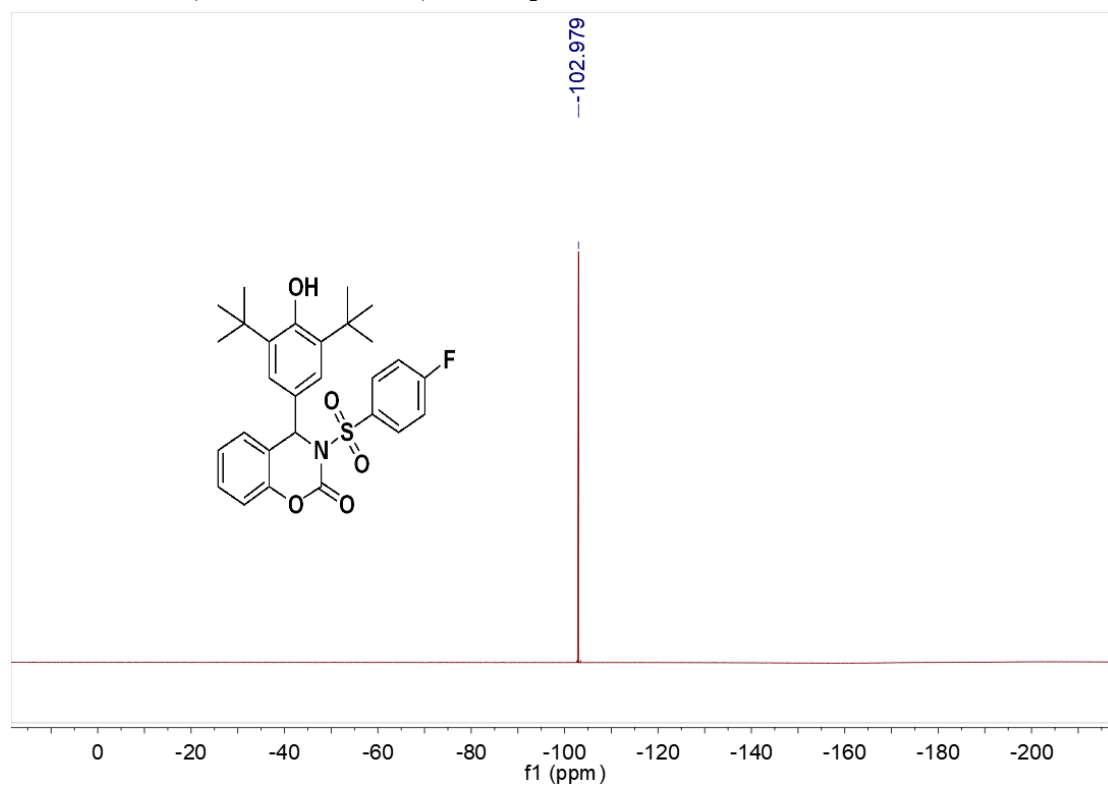
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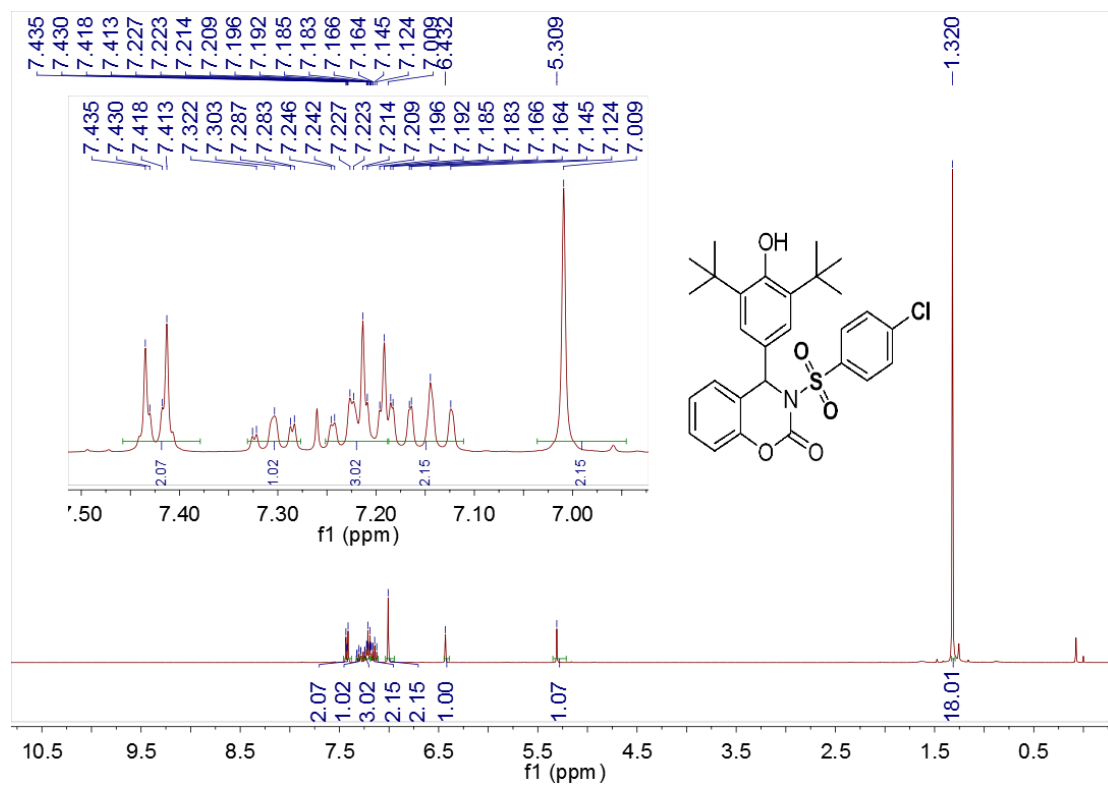
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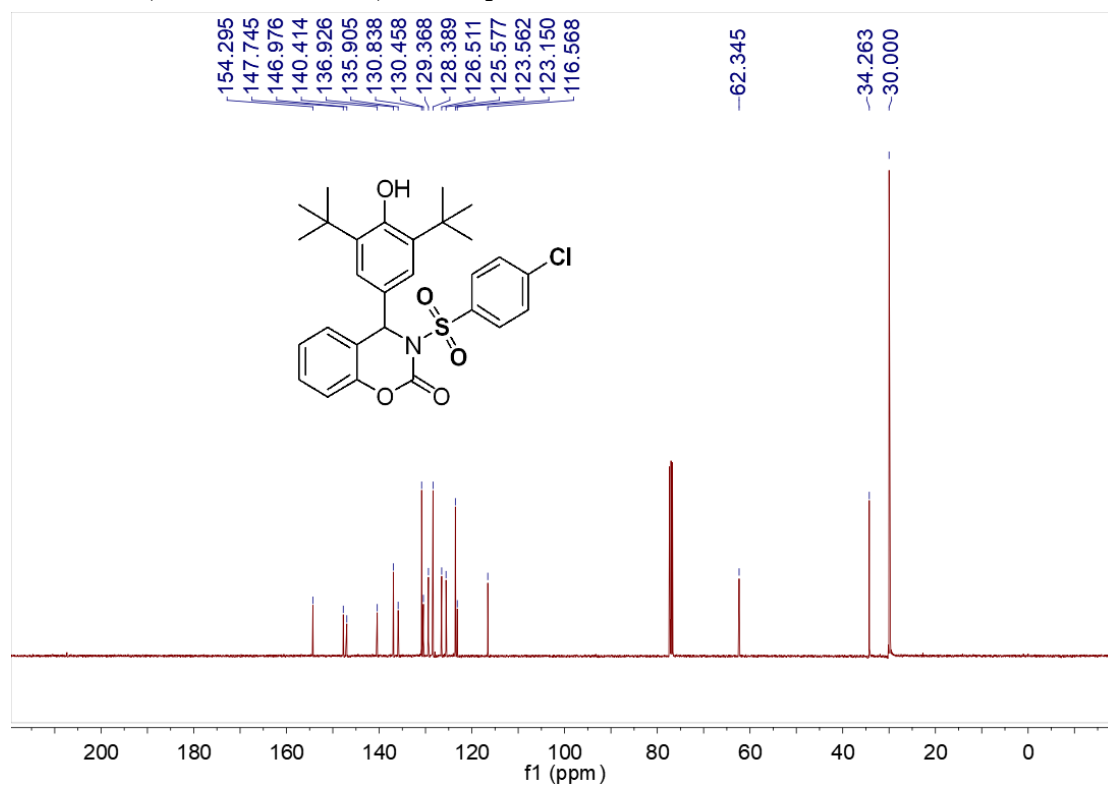
^{19}F NMR (376 MHz, CDCl_3) of compound **3k**:



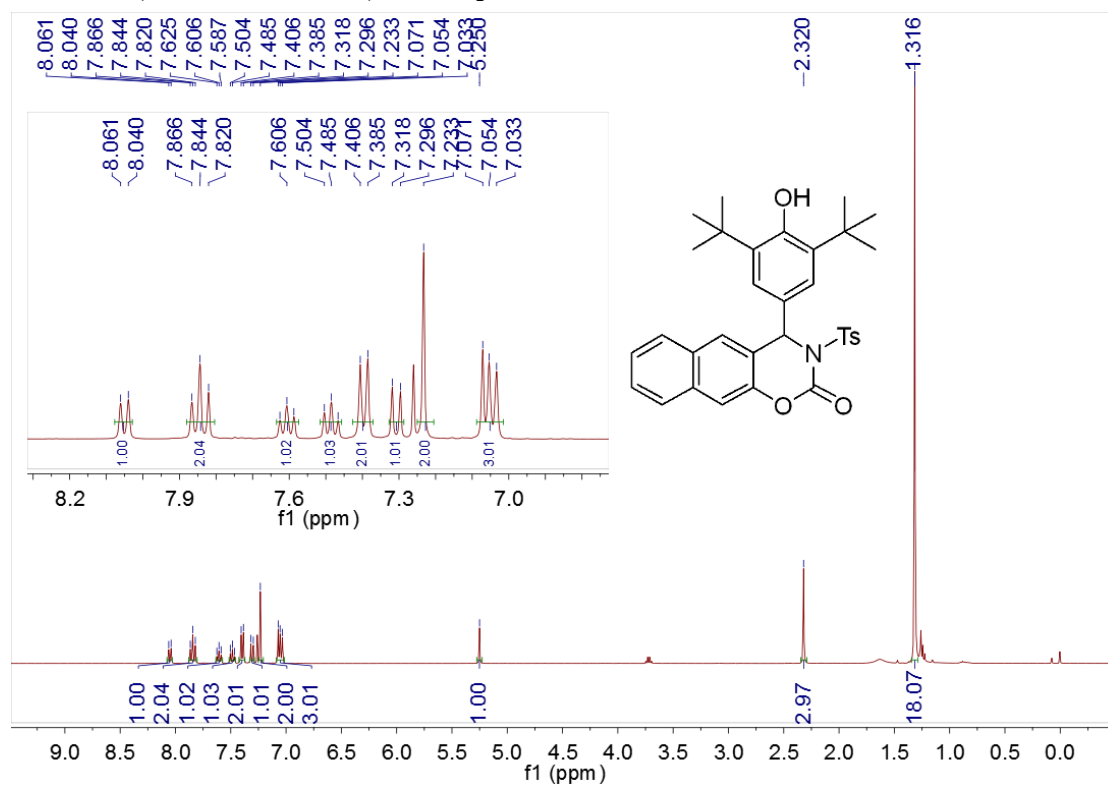
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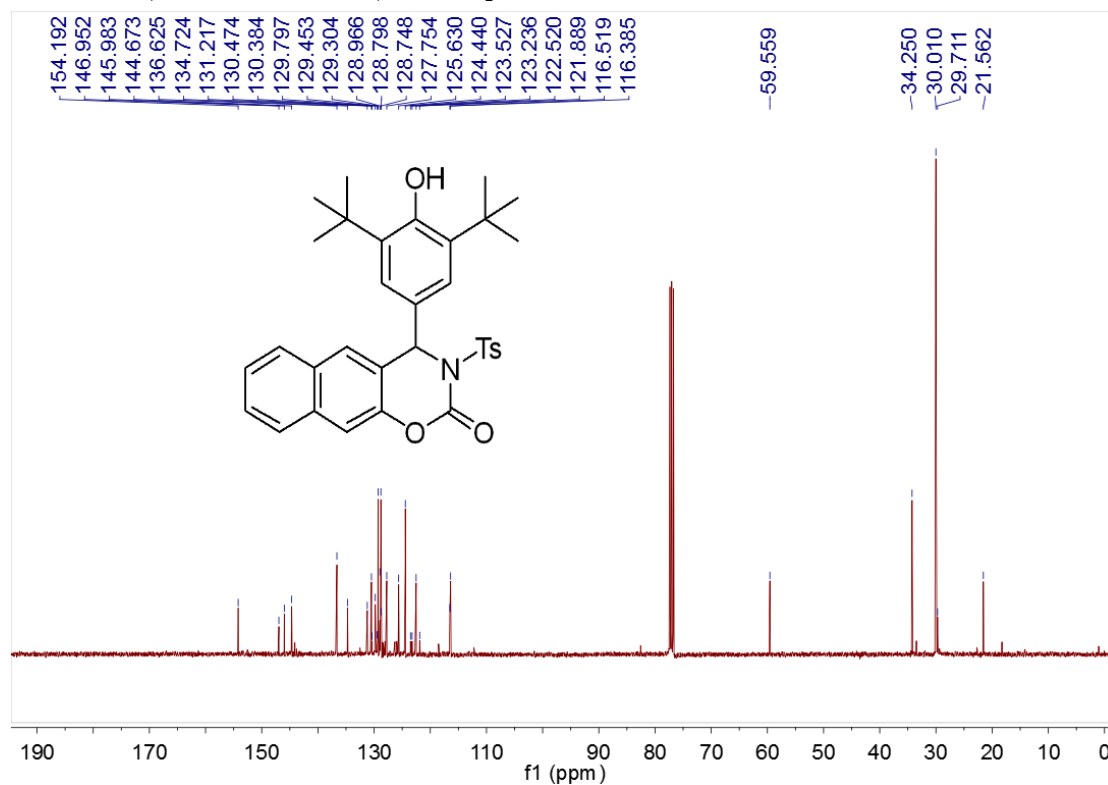
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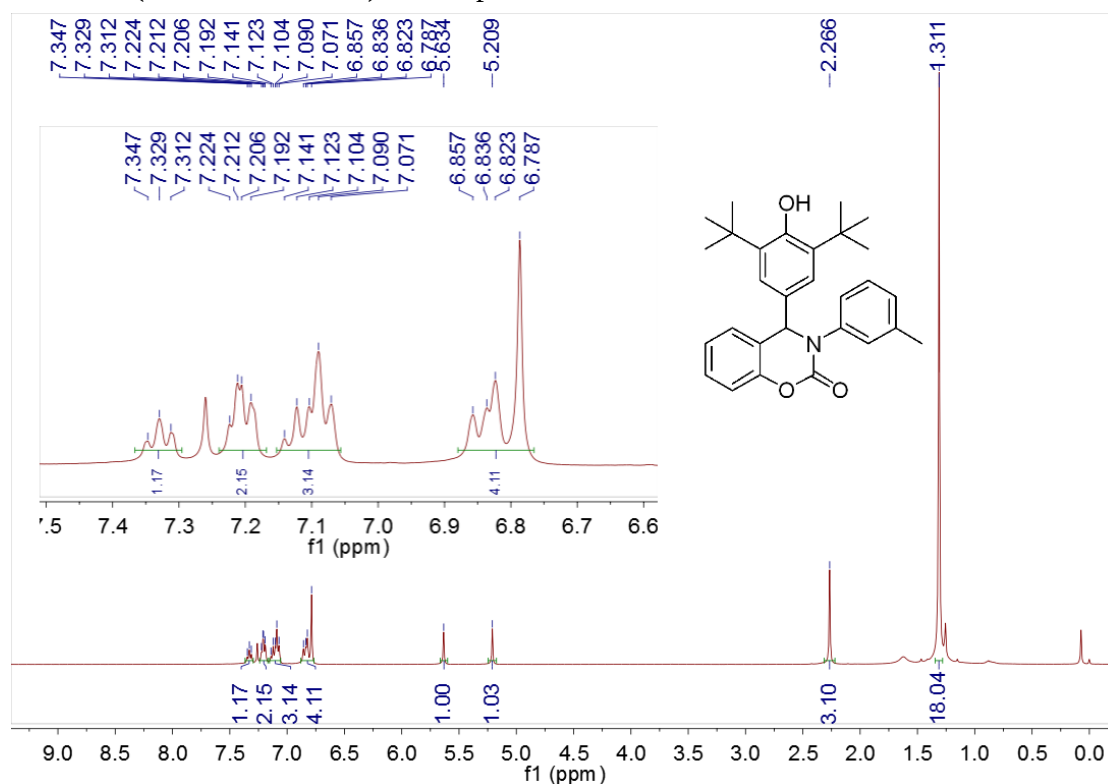
^1H NMR (400 MHz, CDCl_3) of compound **3m**:



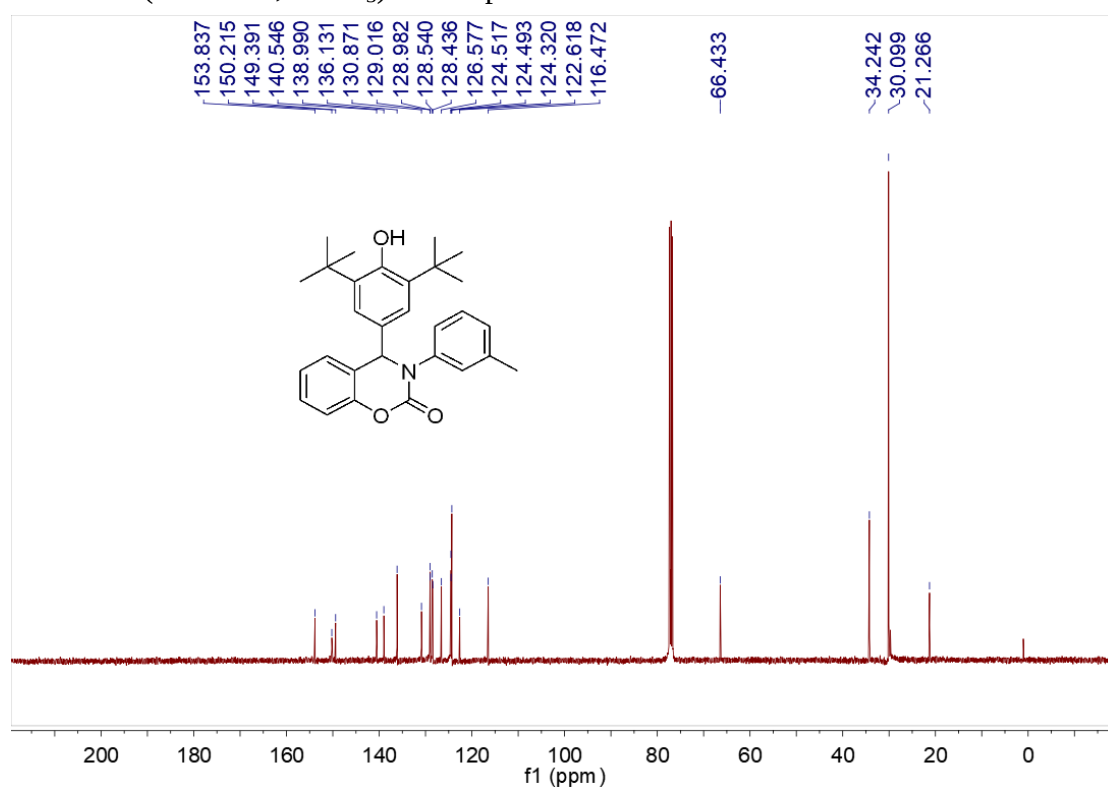
^{13}C NMR (100 MHz, CDCl_3) of compound **3m**:



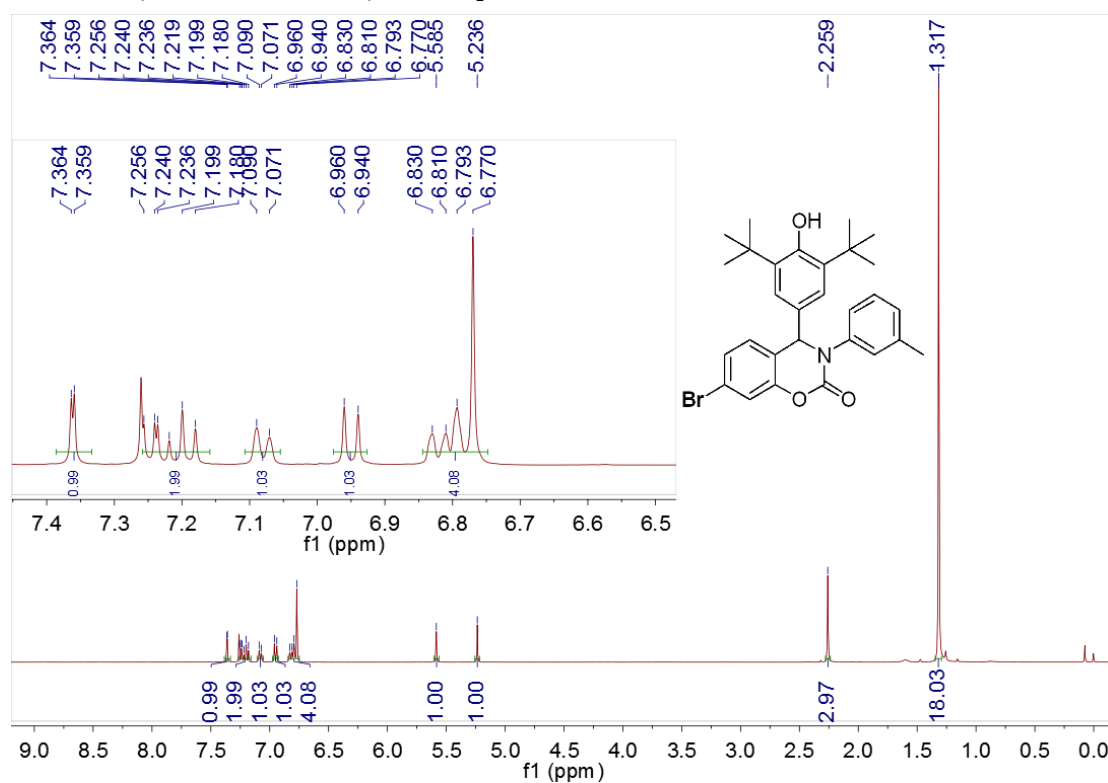
^1H NMR (400 MHz, CDCl_3) of compound **6a**:



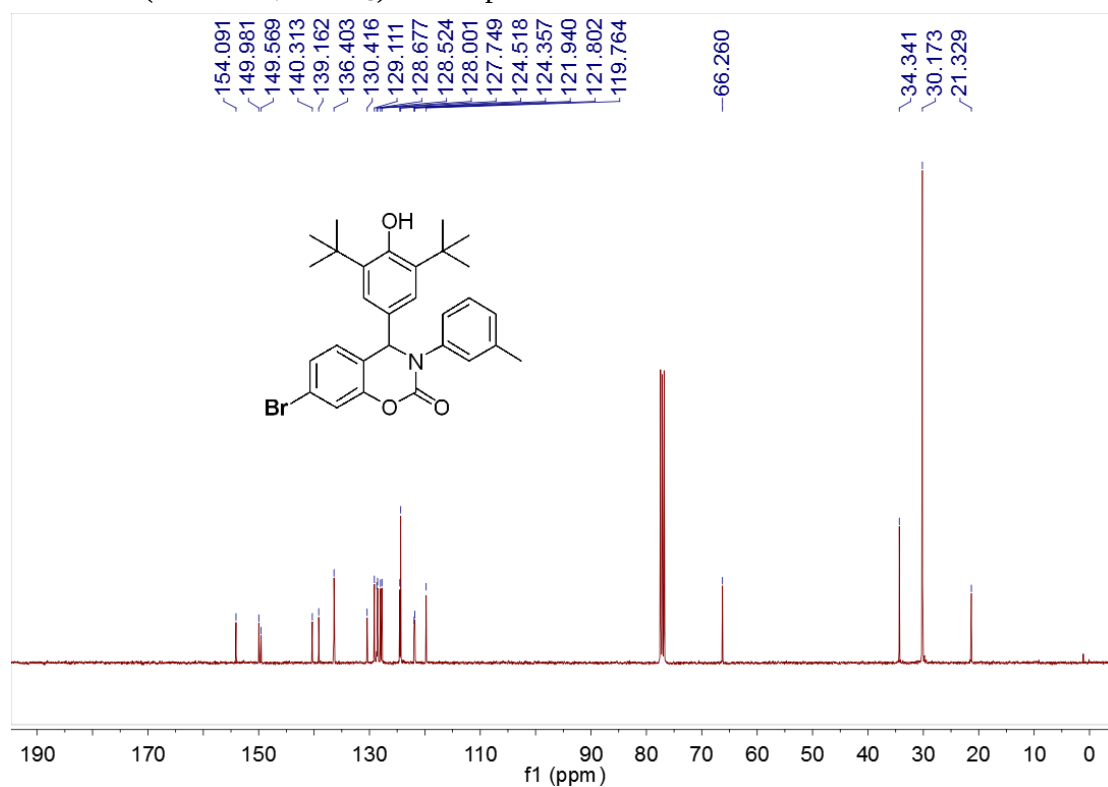
^{13}C NMR (100 MHz, CDCl_3) of compound **6a**:



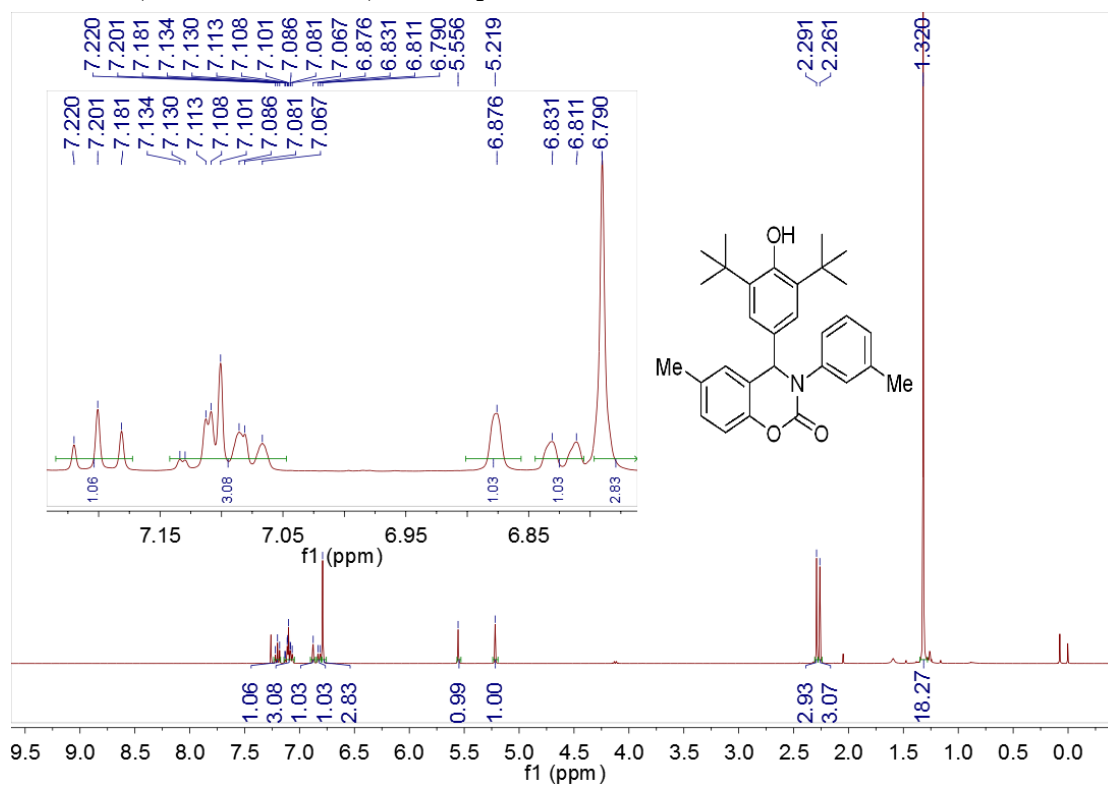
^1H NMR (400 MHz, CDCl_3) of compound **6b**:



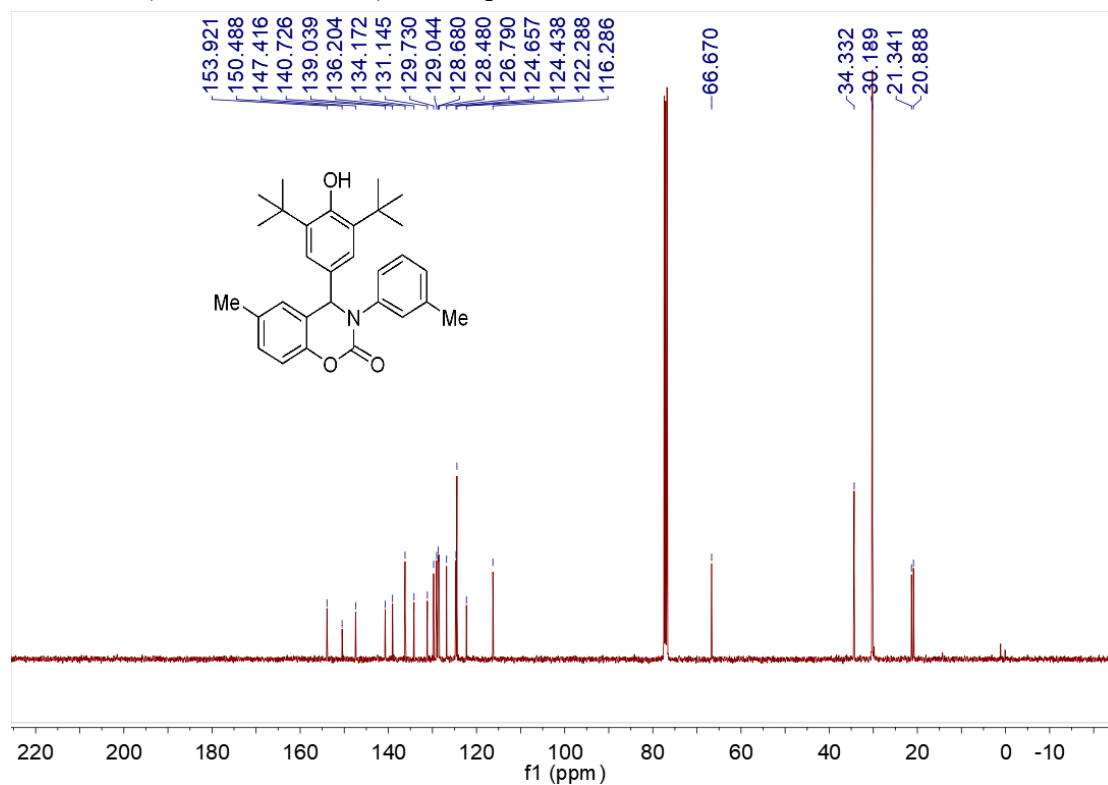
^{13}C NMR (100 MHz, CDCl_3) of compound **6b**:



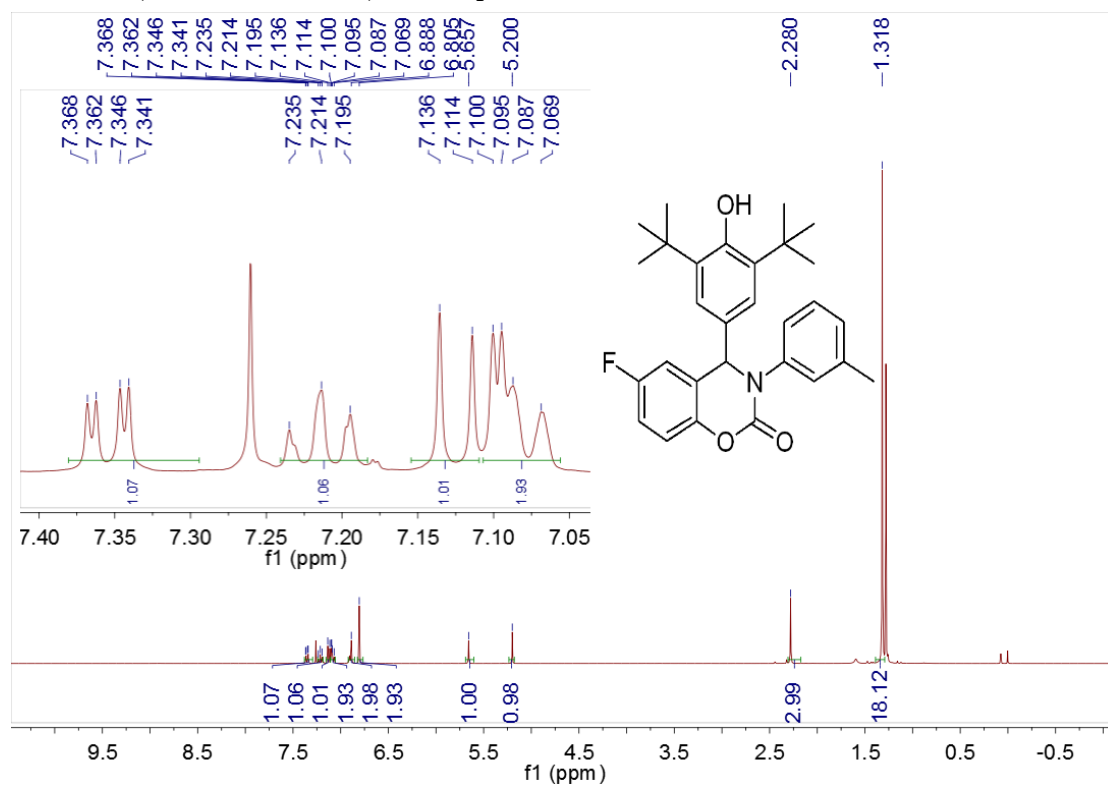
^1H NMR (400 MHz, CDCl_3) of compound **6c**:



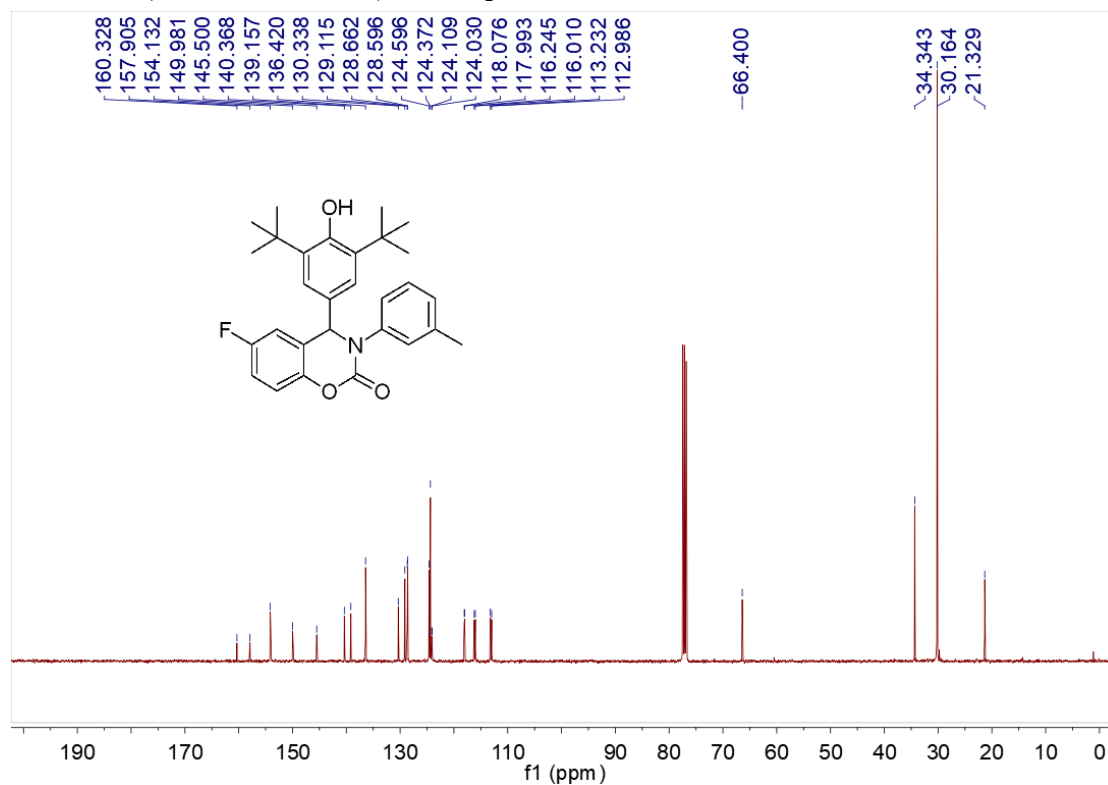
^{13}C NMR (100 MHz, CDCl_3) of compound **6c**:



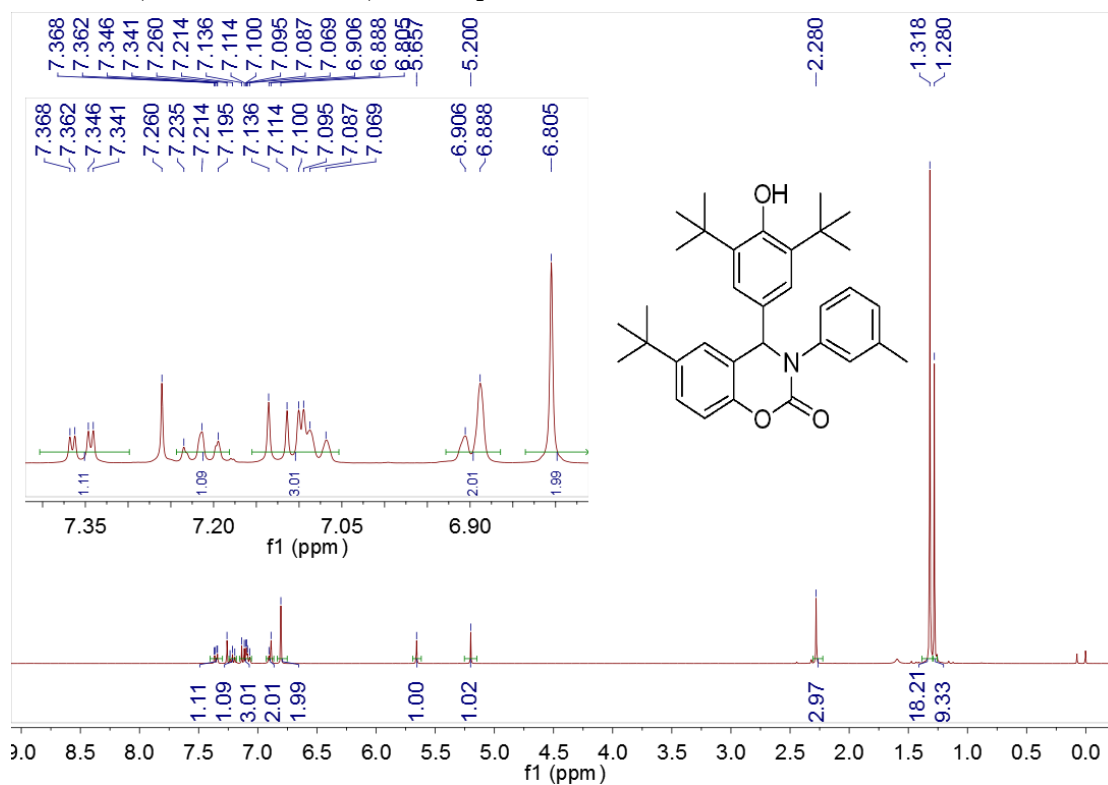
^1H NMR (400 MHz, CDCl_3) of compound **6d**:



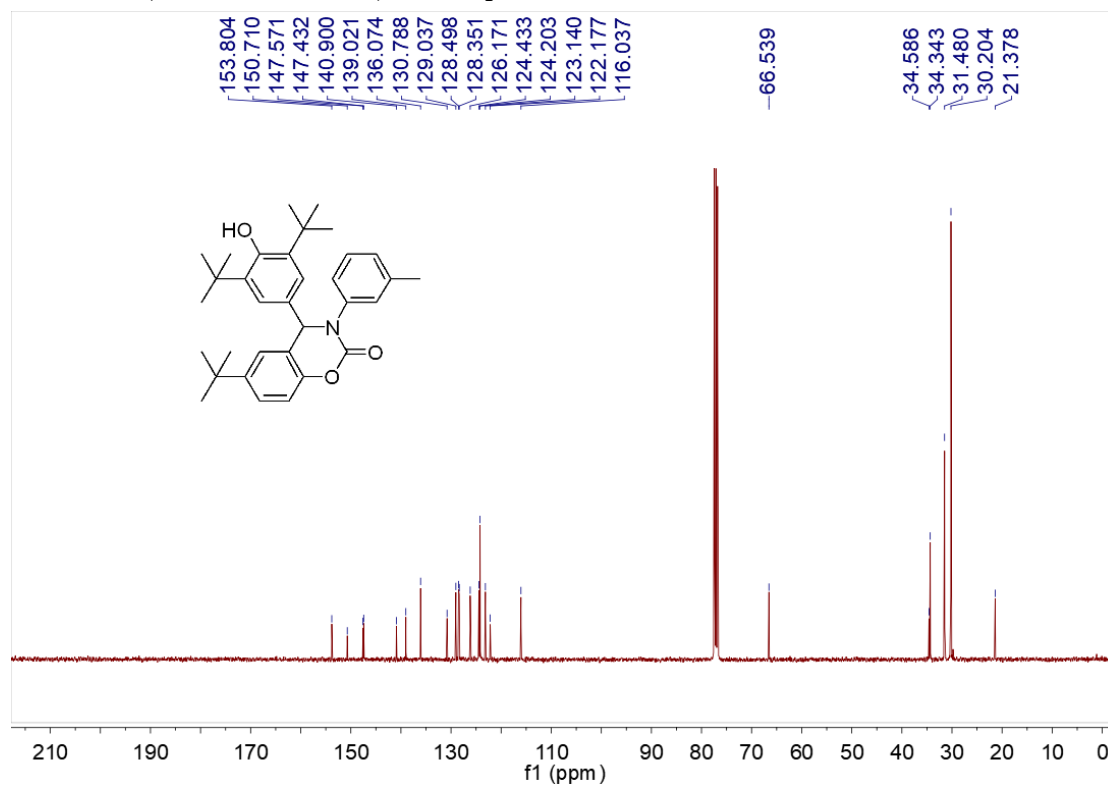
^{13}C NMR (100 MHz, CDCl_3) of compound **6d**:



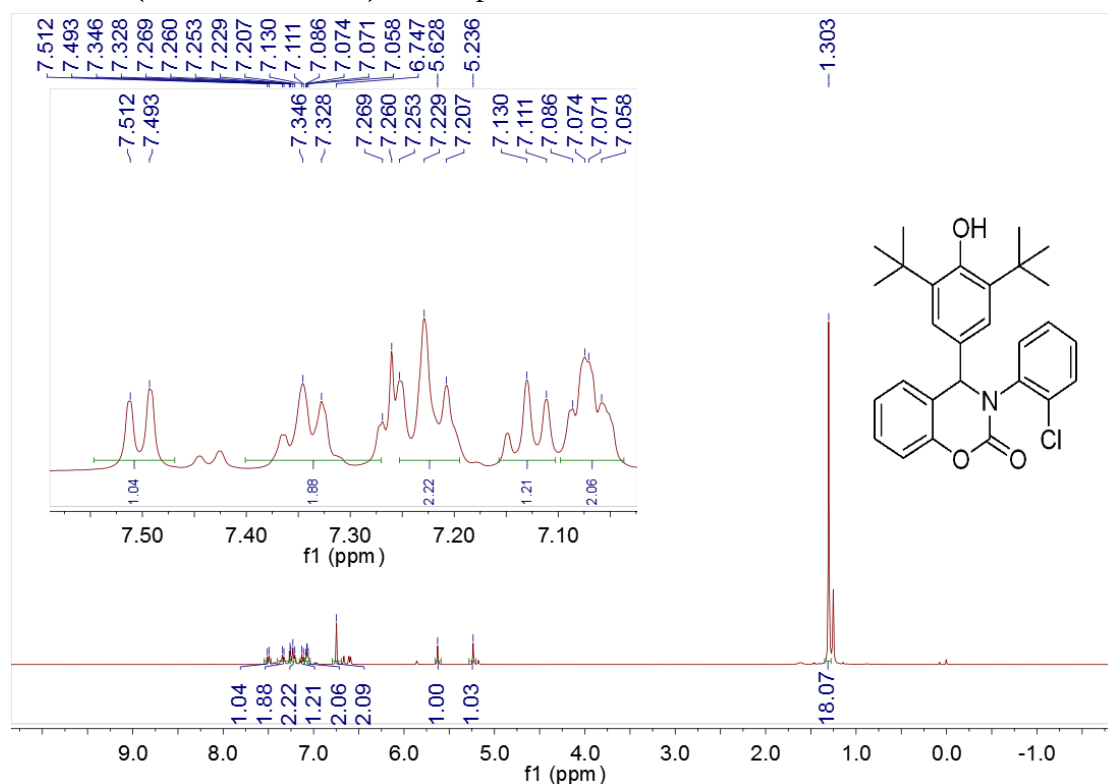
^1H NMR (400 MHz, CDCl_3) of compound **6e**:



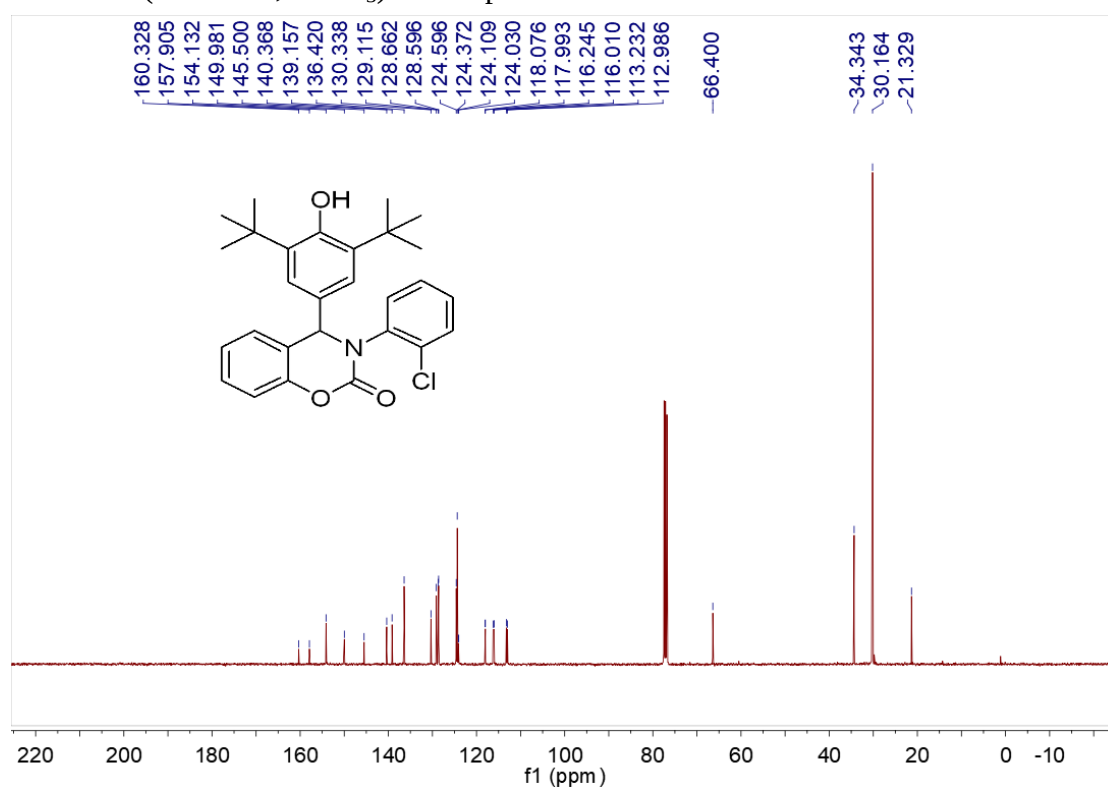
^{13}C NMR (100 MHz, CDCl_3) of compound **6e**:



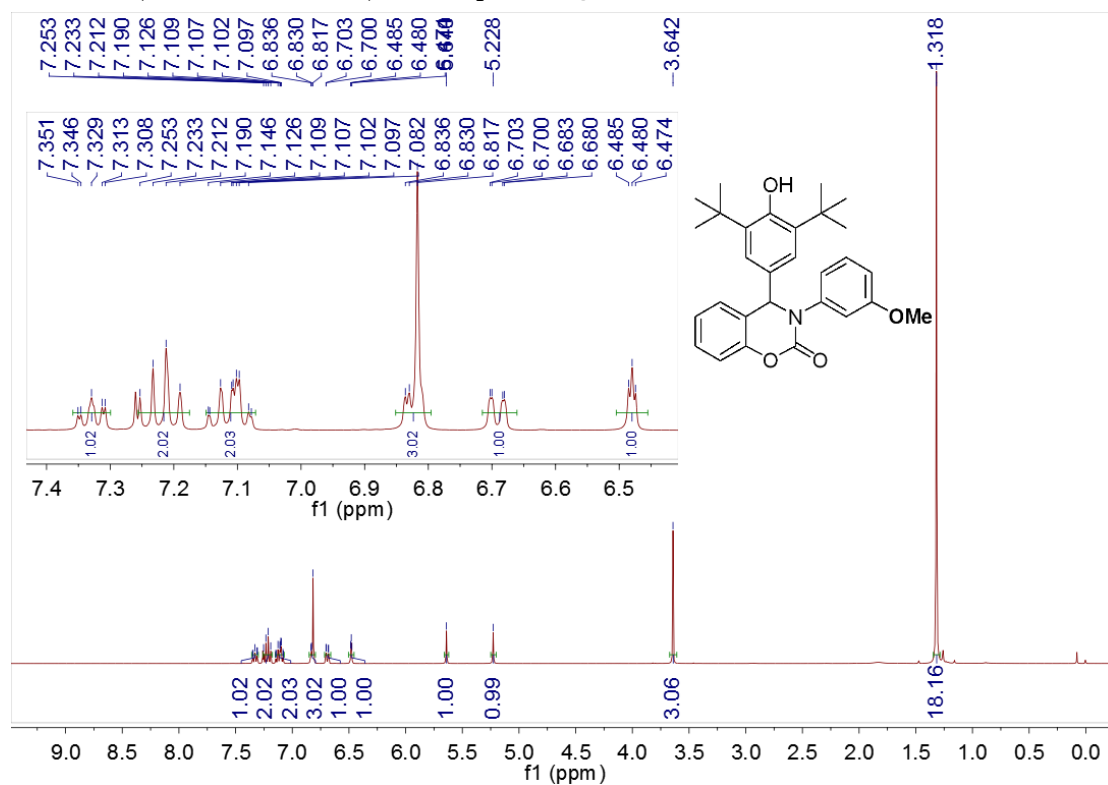
^1H NMR (400 MHz, CDCl_3) of compound **6f**:



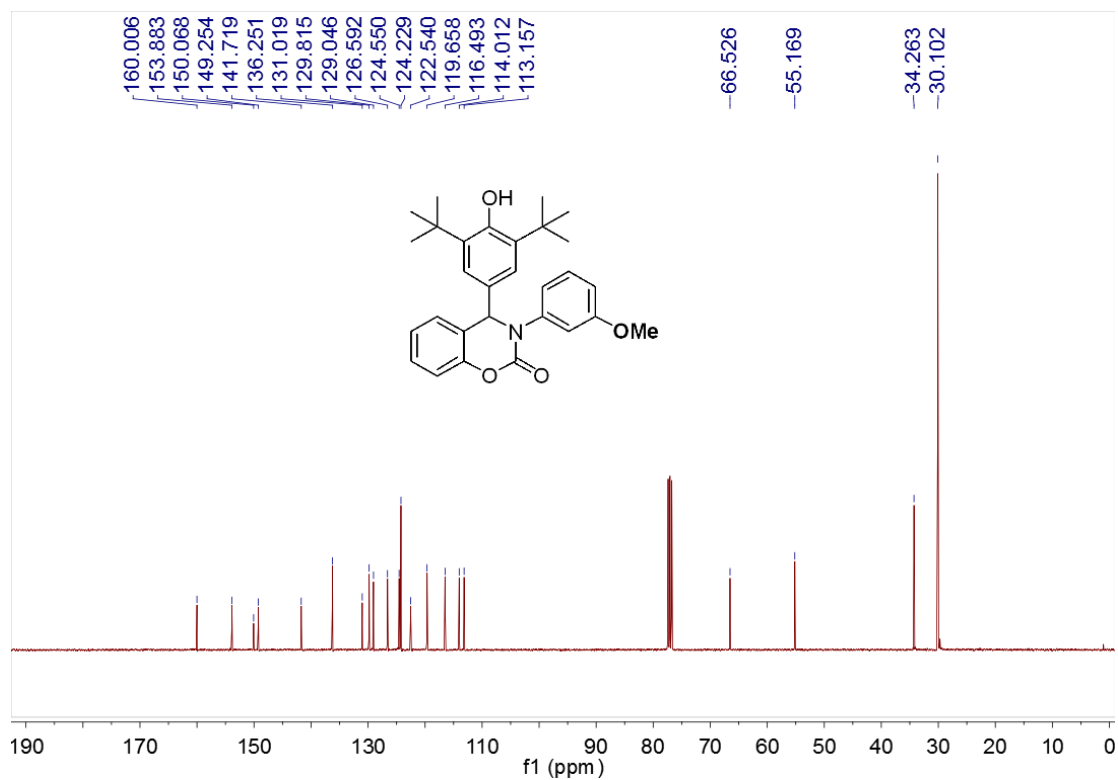
^{13}C NMR (100 MHz, CDCl_3) of compound **6f**



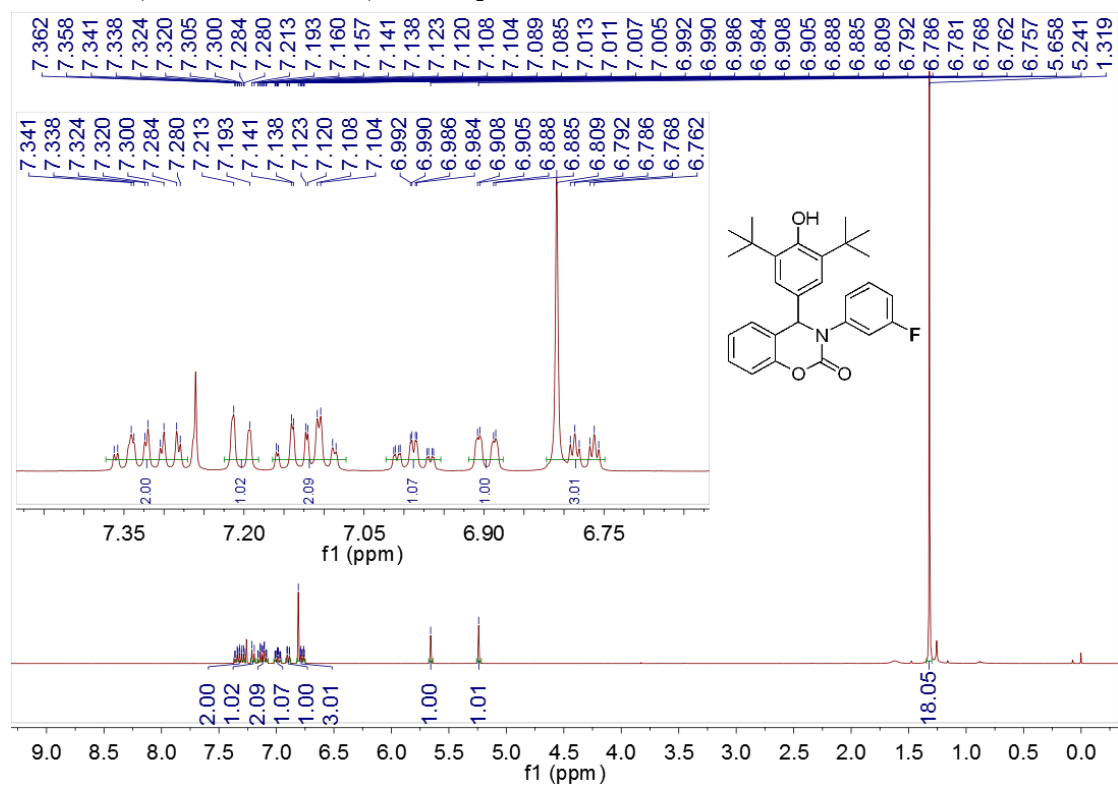
^1H NMR (400 MHz, CDCl_3) of compound **6g**:



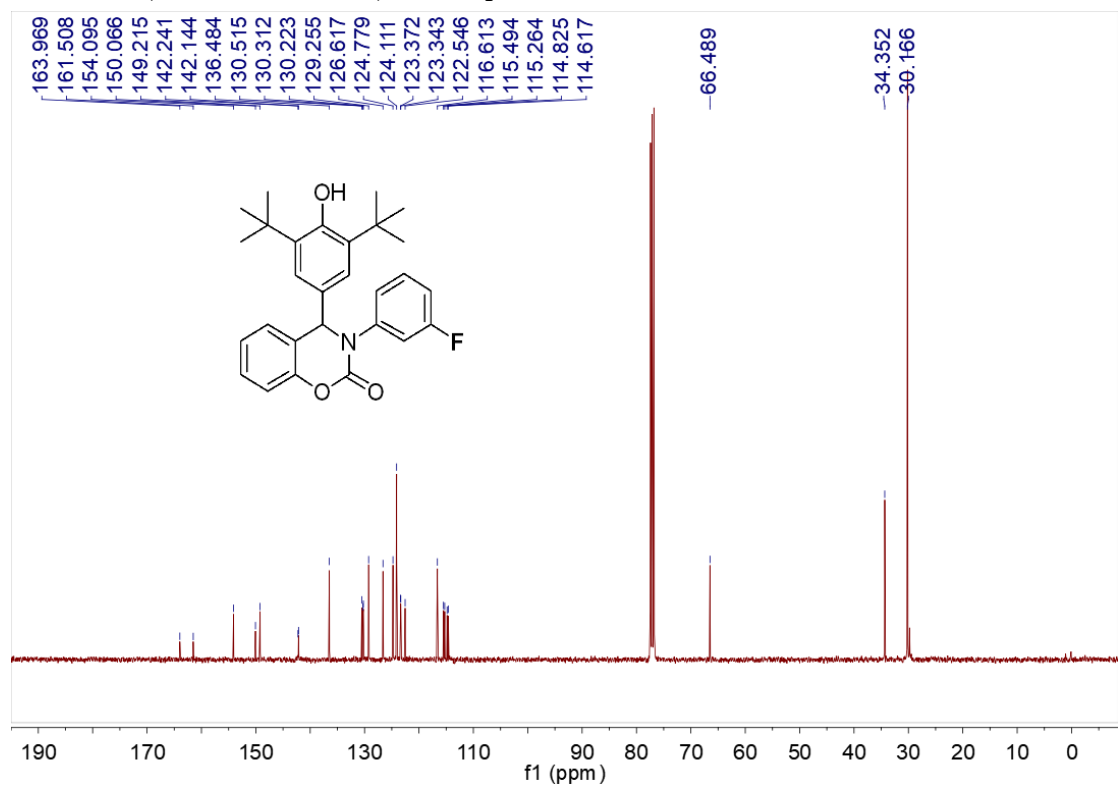
^{13}C NMR (100 MHz, CDCl_3) of compound **6g**:



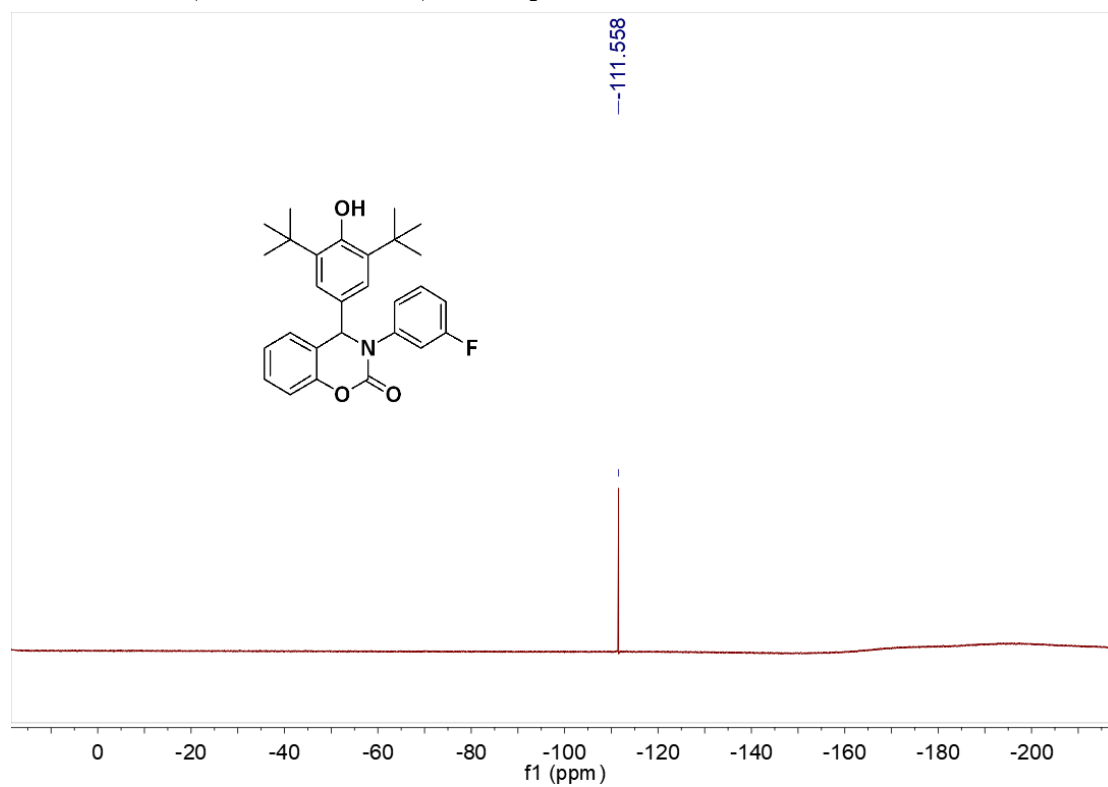
^1H NMR (400 MHz, CDCl_3) of compound **6h**:



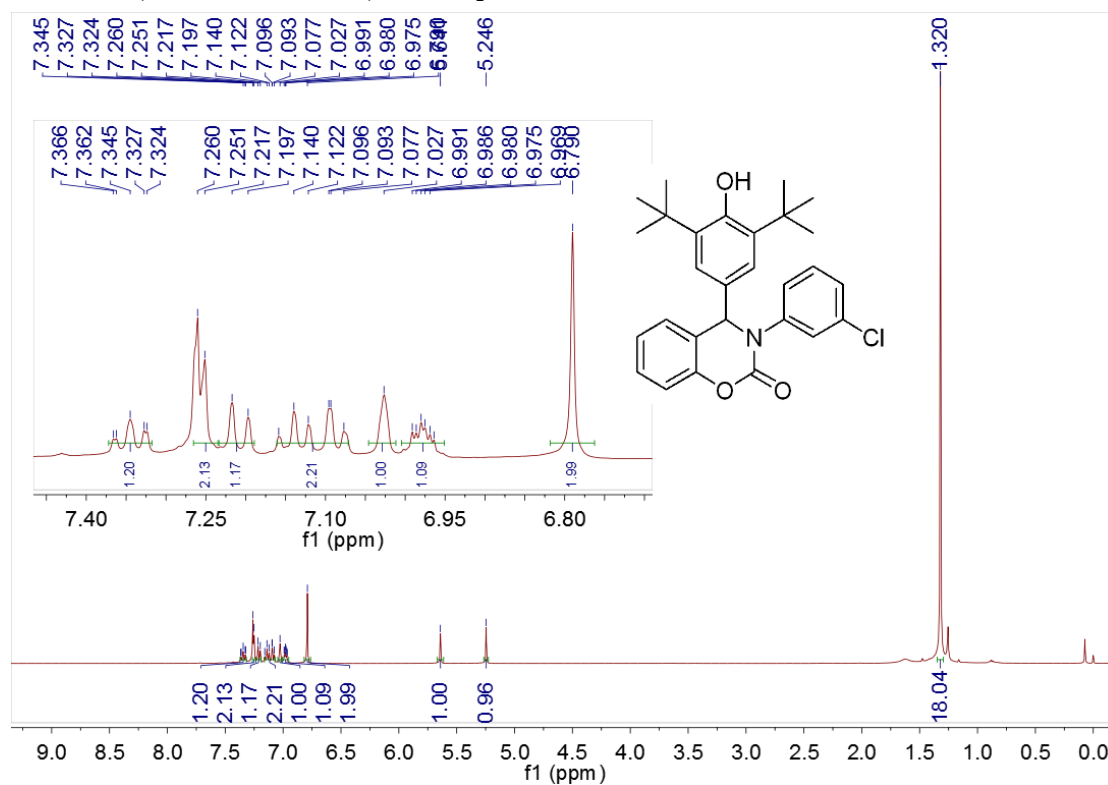
^{13}C NMR (100 MHz, CDCl_3) of compound **6h**:



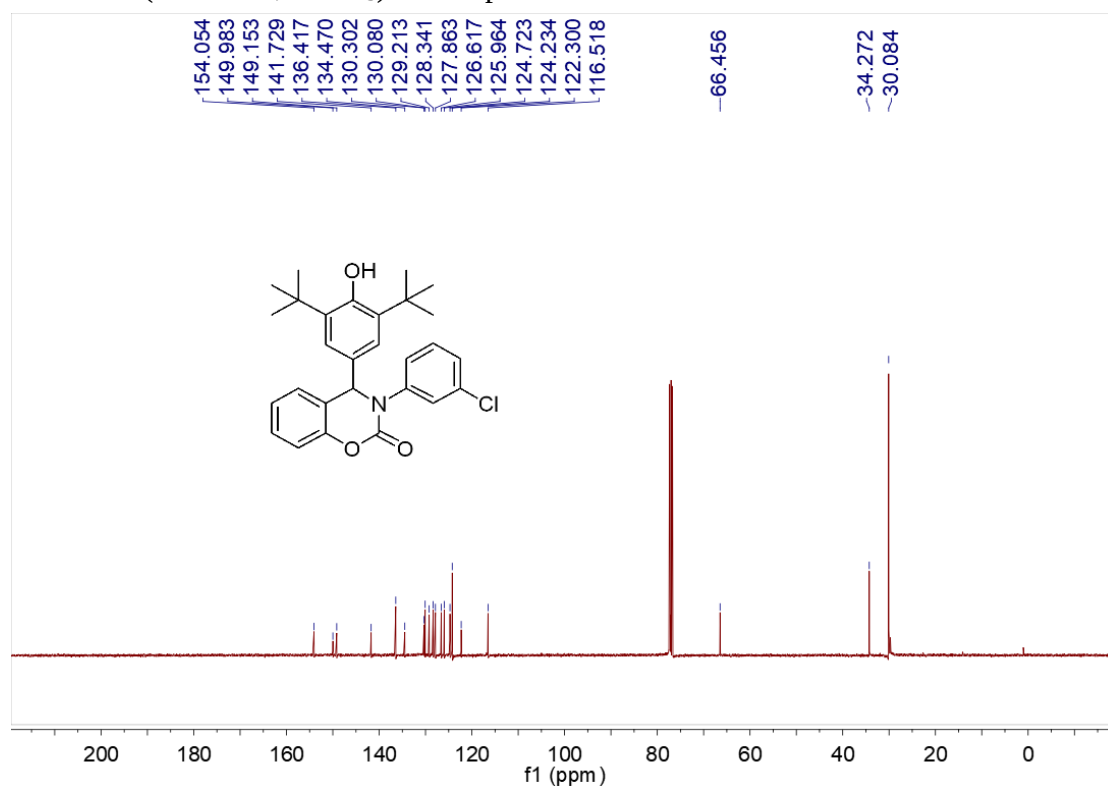
^{19}F NMR (376 MHz, CDCl_3) of compound **6h**:



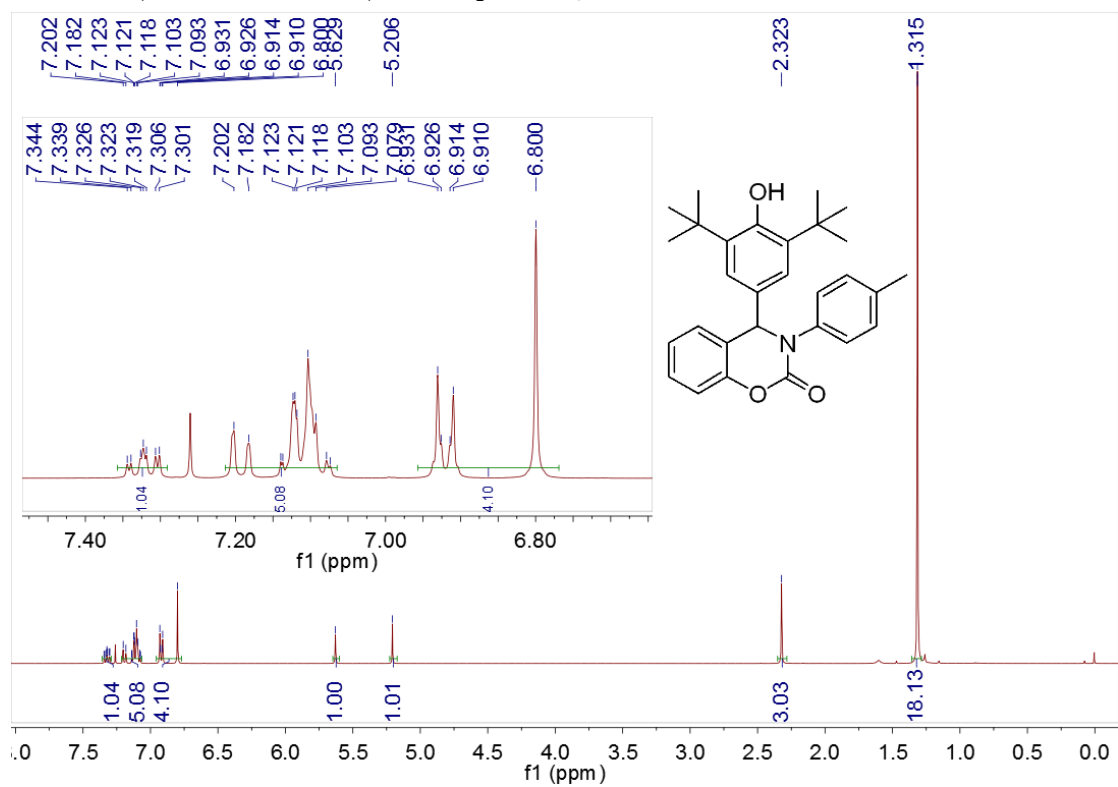
^1H NMR (400 MHz, CDCl_3) of compound **6i**:



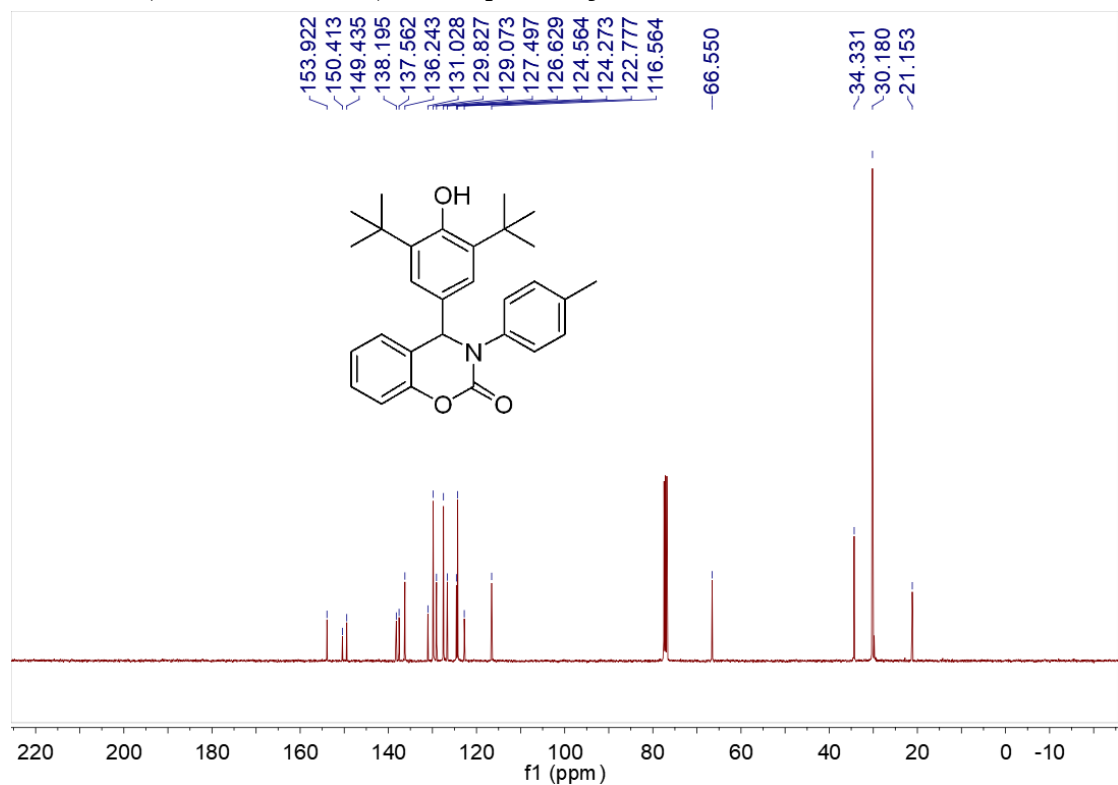
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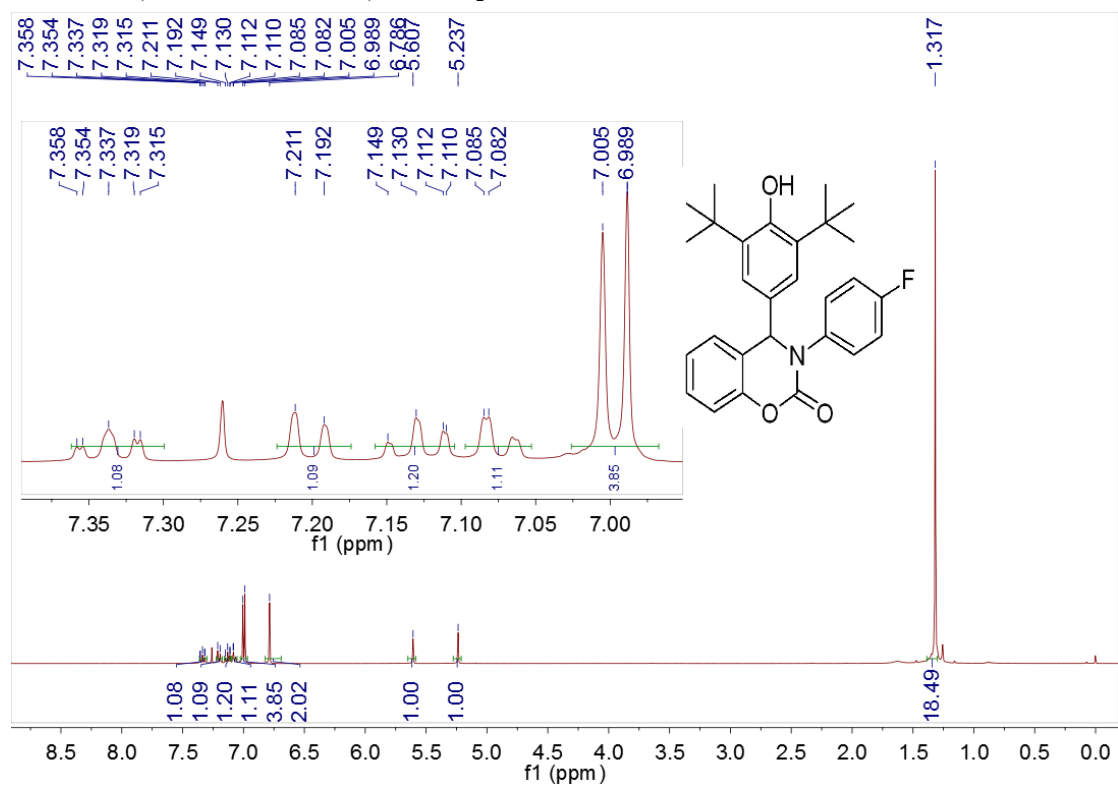
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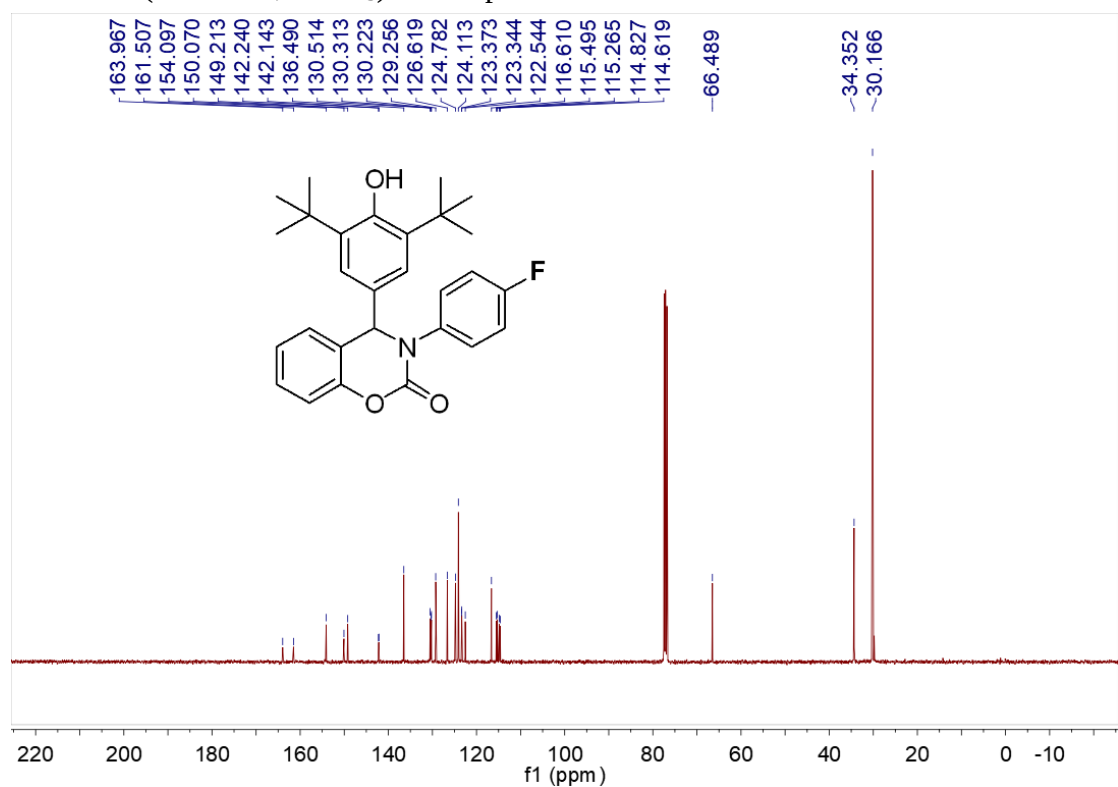
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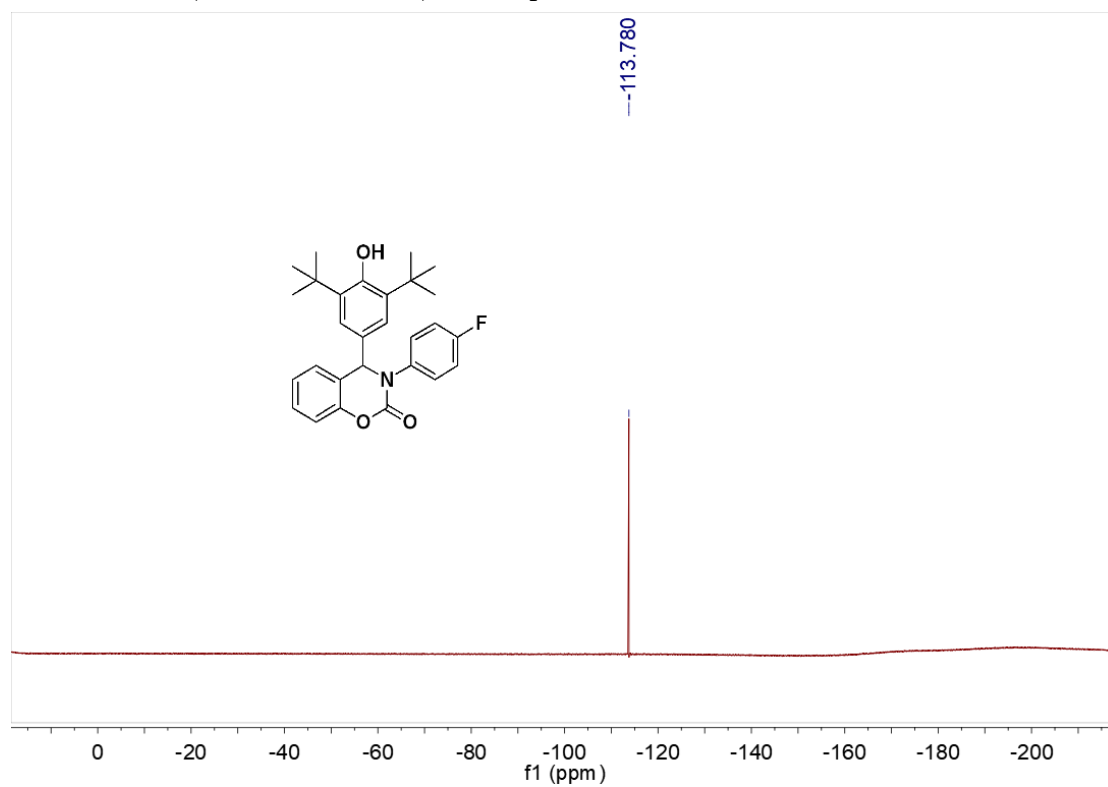
^1H NMR (400 MHz, CDCl_3) of compound **6k**:



^{13}C NMR (100 MHz, CDCl_3) of compound **6k**:

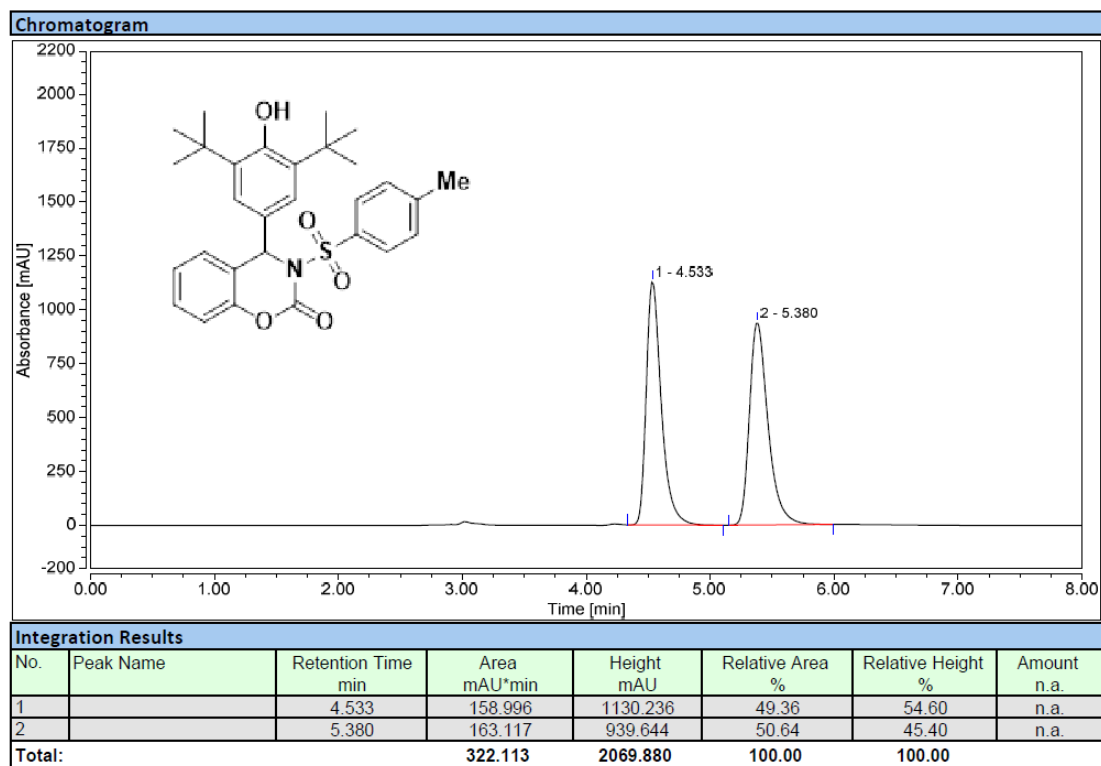


^{19}F NMR (376 MHz, CDCl_3) of compound **6k**:

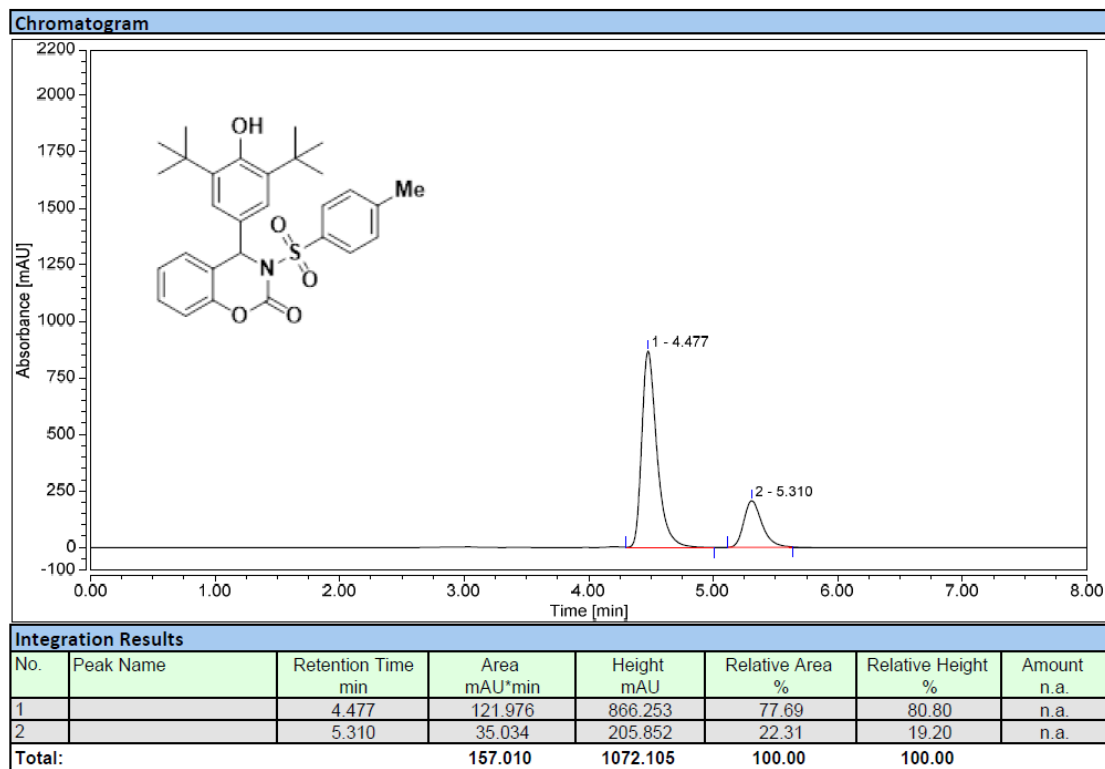


2. HPLC copies of chiral product 3a

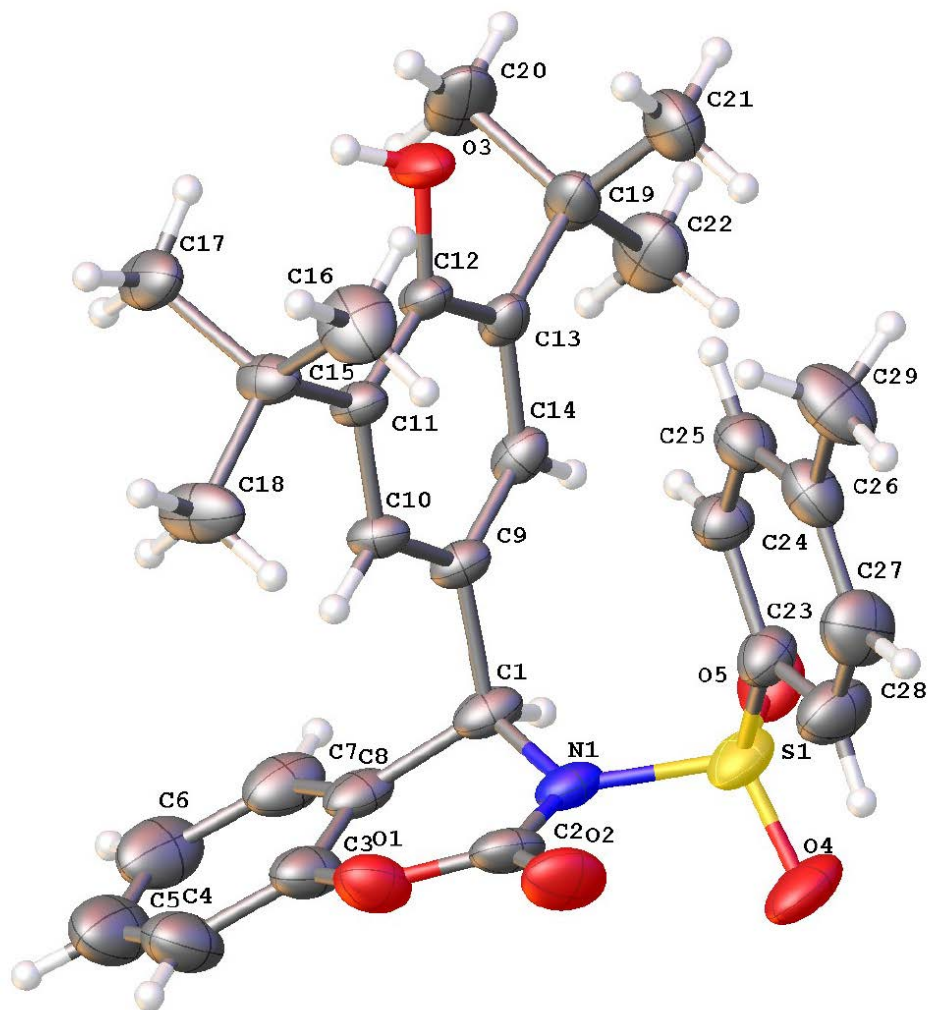
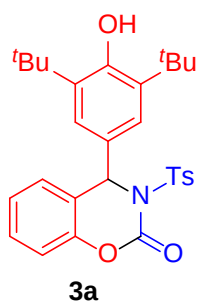
Racemic:



Enantioselective:



3. X-ray single crystal data for compound 3a



CCDC 1910017

The thermal ellipsoid was drawn at the 30% probability level.

Empirical formula C₂₉ H₃₃ N O₅ S

Formula weight 507.62

Temperature 296(2) K

Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.9129(11) Å alpha = 90 deg. b = 13.7709(13) Å beta = 102.2440(10) deg. c = 18.7714(18) Å gamma = 90 deg.
Volume	2756.8(5) Å ³
Z, Calculated density	4, 1.223 Mg/m ³
Absorption coefficient	0.155 mm ⁻¹
F(000)	1080
Crystal size	0.60 x 0.50 x 0.50 mm
Theta range for data collection	2.40 to 27.48 deg.
Limiting indices	-14 ≤ h ≤ 11, -15 ≤ k ≤ 17, -17 ≤ l ≤ 24
Reflections collected / unique	16031 / 6186 [R(int) = 0.0247]
Completeness to theta = 27.48	97.8 %
Absorption correction	None
Max. and min. transmission	0.9265 and 0.9127
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6186 / 1 / 333
Goodness-of-fit on F ²	1.048
Final R indices [I > 2sigma(I)]	R1 = 0.0626, wR2 = 0.1737
R indices (all data)	R1 = 0.0910, wR2 = 0.1972
Largest diff. peak and hole	0.322 and -0.731 e.Å ⁻³