

## **Supporting Information**

# **Manganese-Catalyzed Synthesis of Quaternary Peroxides: Application in Catalytic Deperoxidation and Rearrangement Reactions**

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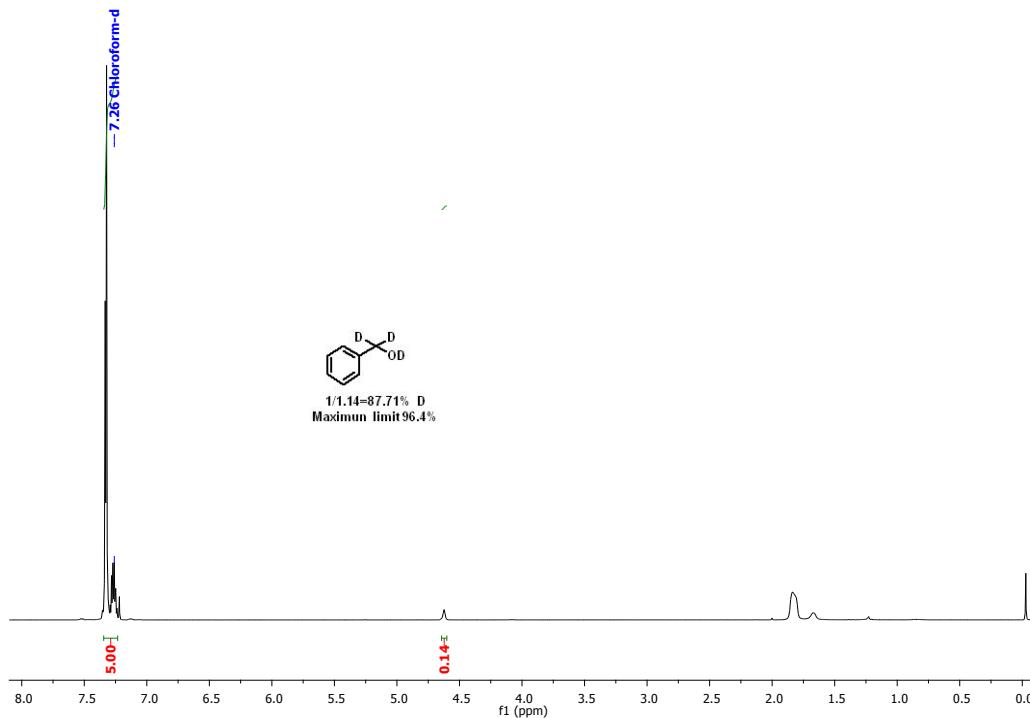
Dr. Homi Bhabha Road, Pashan, Pune - 411008, India.

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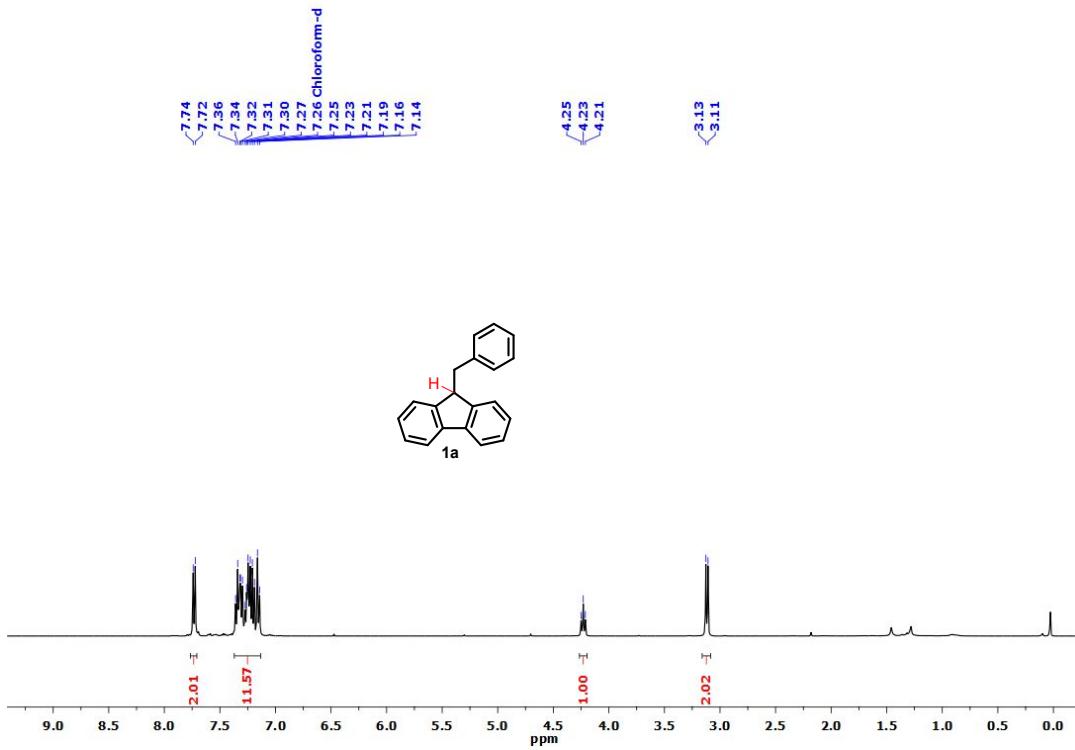
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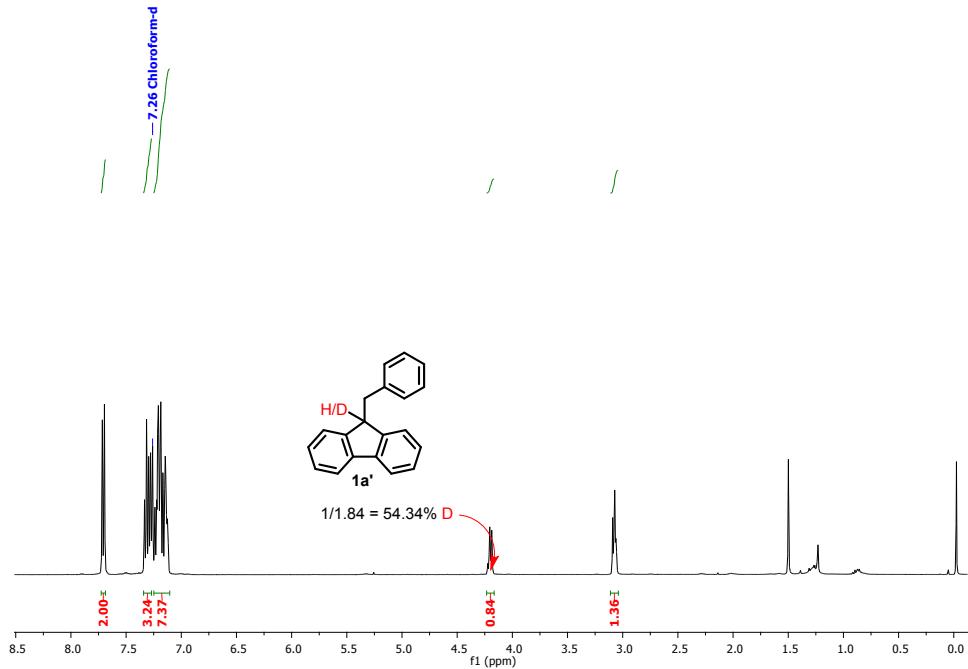
## 1. Deuteration experiments:



**Figure S1.** <sup>1</sup>H NMR of deuterated benzyl alcohol at 400 MHz in CDCl<sub>3</sub>

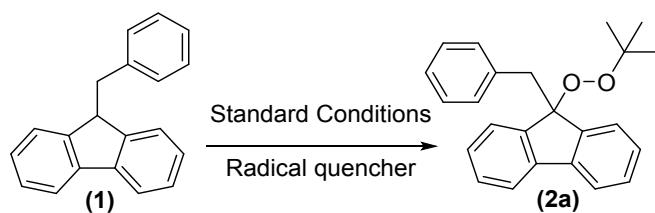
**<sup>1</sup>H-NMR spectra for the deuterated 9-benzyl-9H-fluorene:**





**Figure S2.**  $^1\text{H}$  NMR of Compound **1a** & **1a'** at 400 MHz in  $\text{CDCl}_3$

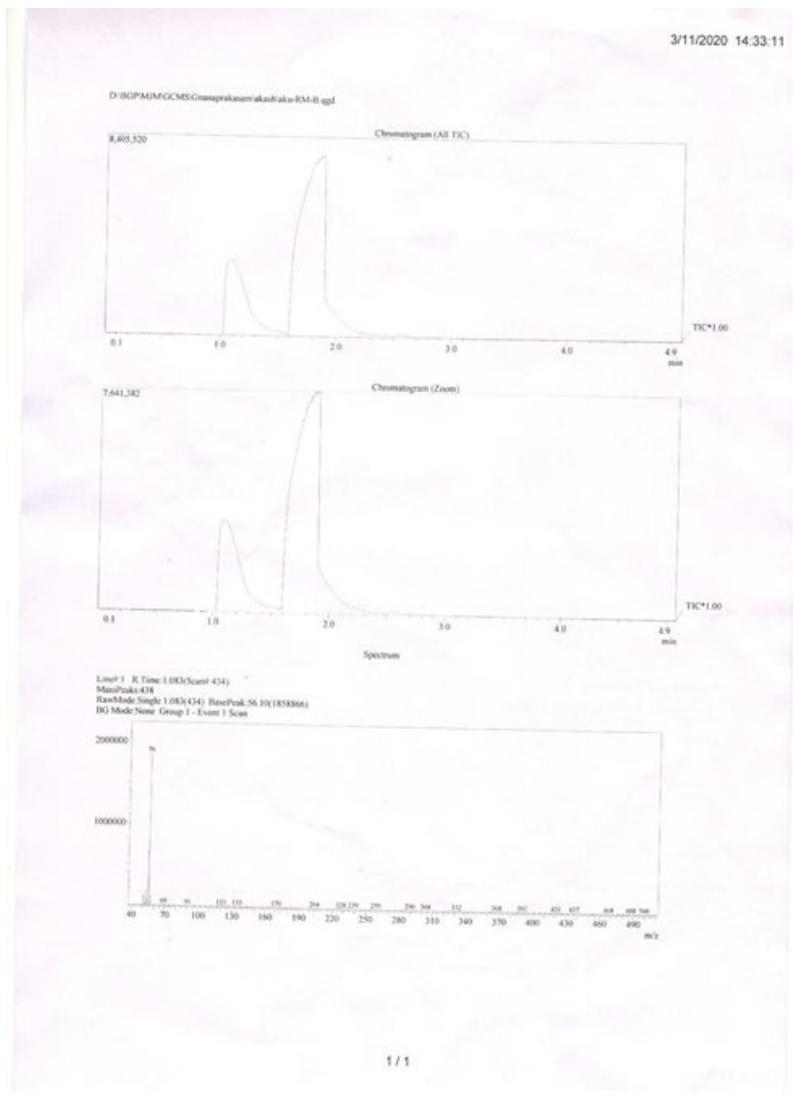
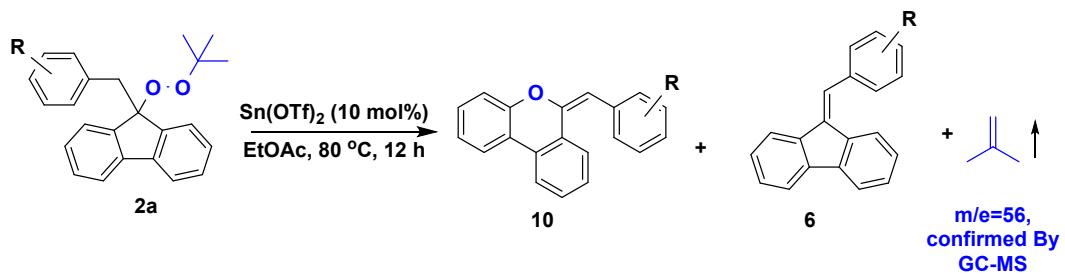
## 2. Radical quenching experiment:



Entry	Radical quencher (5 equiv.)	(%) Yield (2a)	(%) Starting Material Recovered (1)
1	None	85	-
2	TEMPO	80	-
3	1,1-diphenylethylene	68	15
4	$\alpha$ -methylstyrene	65	5
5	O <sub>2</sub>	85	-

**Reaction conditions:** In a 20 mL re-sealable vial was added Mn(OAc)<sub>3</sub>.2H<sub>2</sub>O (0.0125 mmol, 3 mg, 5 mol%) and 2,2'-bipyridine (0.0125 mmol, 2 mg, 5 mol% ) in acetonitrile 2 mL was stirred at room temperature for 20–30 min. To the deep-brown solution was added 9-benzyl-9H-fluorene (64 mg, 0.25 mmol, 1 equiv), 5.0-6.0 M *tert*-butyl hydroperoxide (TBHP) in decane solution (1.0 mmol, 90 mg, 4 equiv) and finally 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (5 equiv) or 1,1-diphenylethylene (5 equiv) or  $\alpha$ -methylstyrene (5 equiv) or molecular oxygen was added and resulting solution was stirred at room temperature for 4 h. Volatile component was evaporated using a vacuum. The residue was directly purified by silica gel column chromatography (EtOAc: n-hexane = 1:99) to afford 80, 68, 65, and 85% yield of the product **2a** respectively.

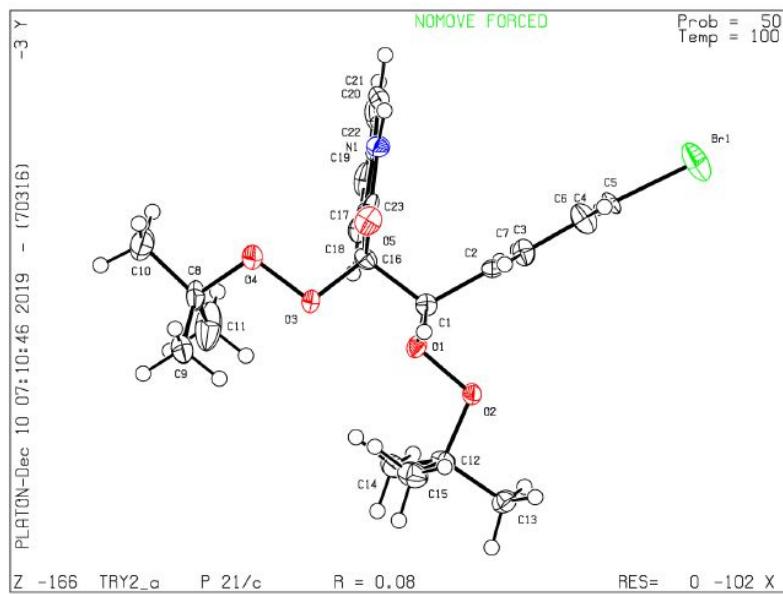
### 3. Detection of isobutylene gas using GC-MS:



**Figure S3.** GC-MS spectra of gaseous phase of reaction mixture. After reaction completion, the gaseous component was taken using Gas tight syringe and directly injected in the GC-MS instrument

#### 4. Crystallographic data:

X-ray structure for entry (9e):

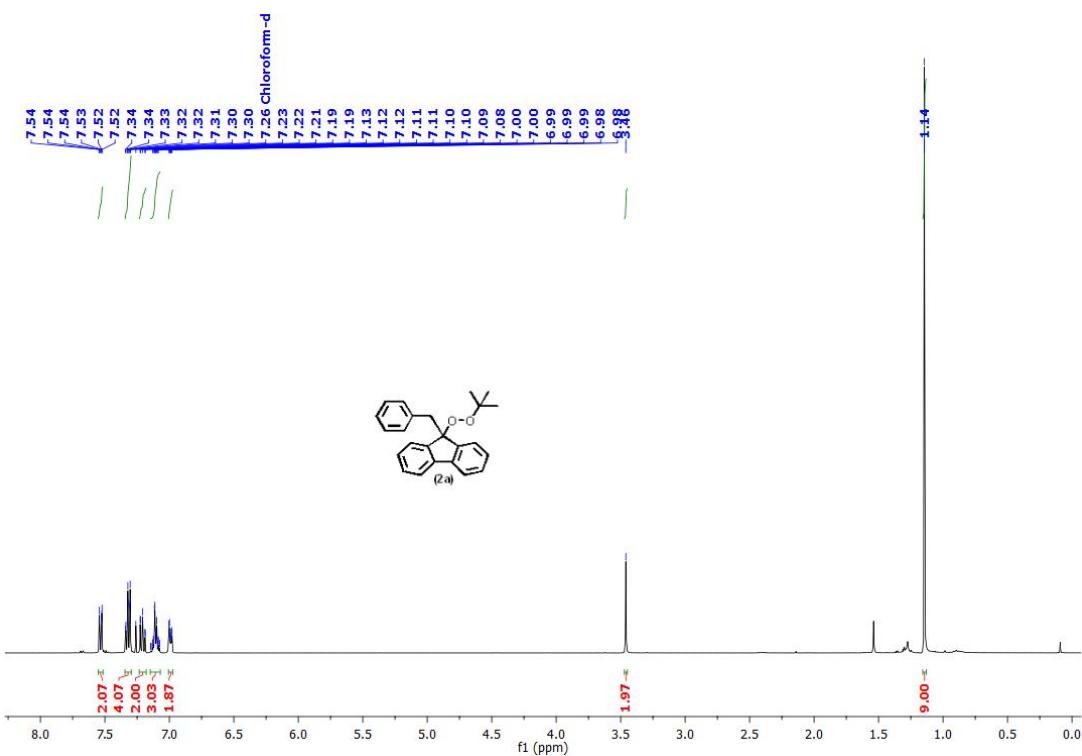


**Figure S4:** An ORTEP showing the crystal structure of **9e** with displacement ellipsoids drawn at the 50% probability level

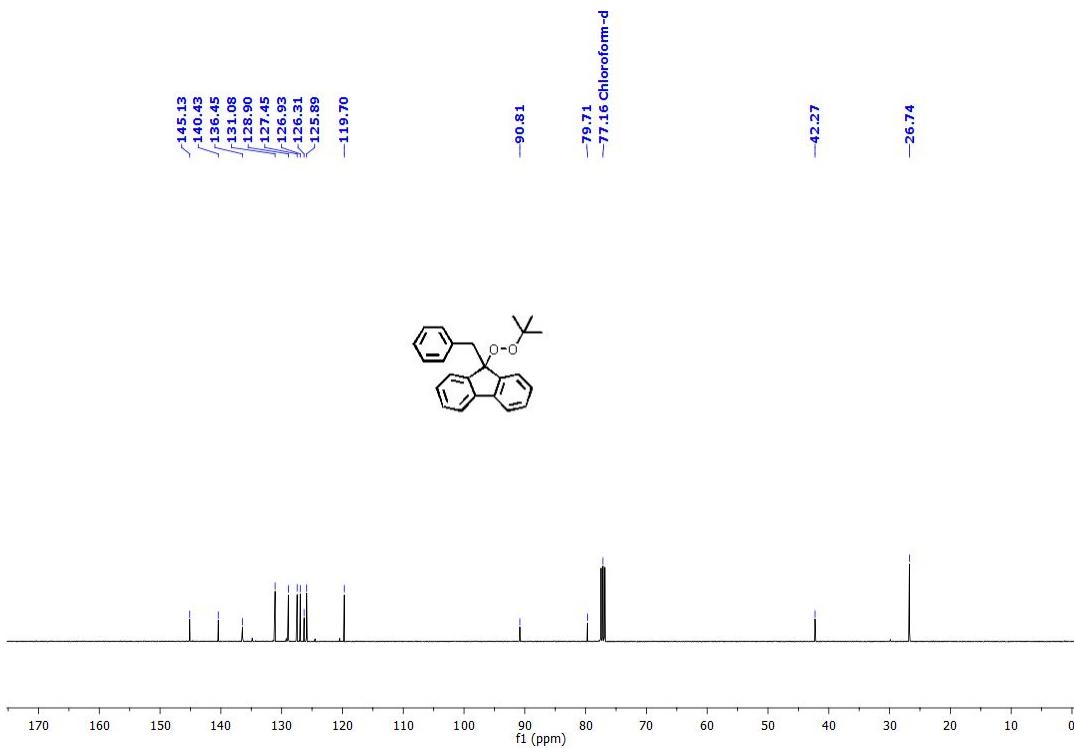
**Solvent and method for the crystal growth:** The crystal was grown using dichloromethane and pet ether (2:1) as a solvent by slow evaporation. A needle shaped single crystal was mounted on a loop with applying small amount of a paraffin oil.

**Crystal data for the compound 9e:**  $C_{23}H_{28}BrNO_5$ , Volume = 2318.9 (2), Monoclinic, space group P 21/C with  $a = 10.6710(6)$  Å,  $b = 22.8755(15)$  Å,  $c = 9.5065 (6)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 92.152^\circ$ ,  $\gamma = 90^\circ$ ,  $T = 273$  K,  $z = 4$ ,  $F(000) = 992$ , Absorption coefficient = 2.687, radiation wavelength ( $\lambda$ ) = 1.54178 Å, reflections were collected on a Brucker APEX-II, 3286 observed reflections  $I > 2\lambda s(I)$ .

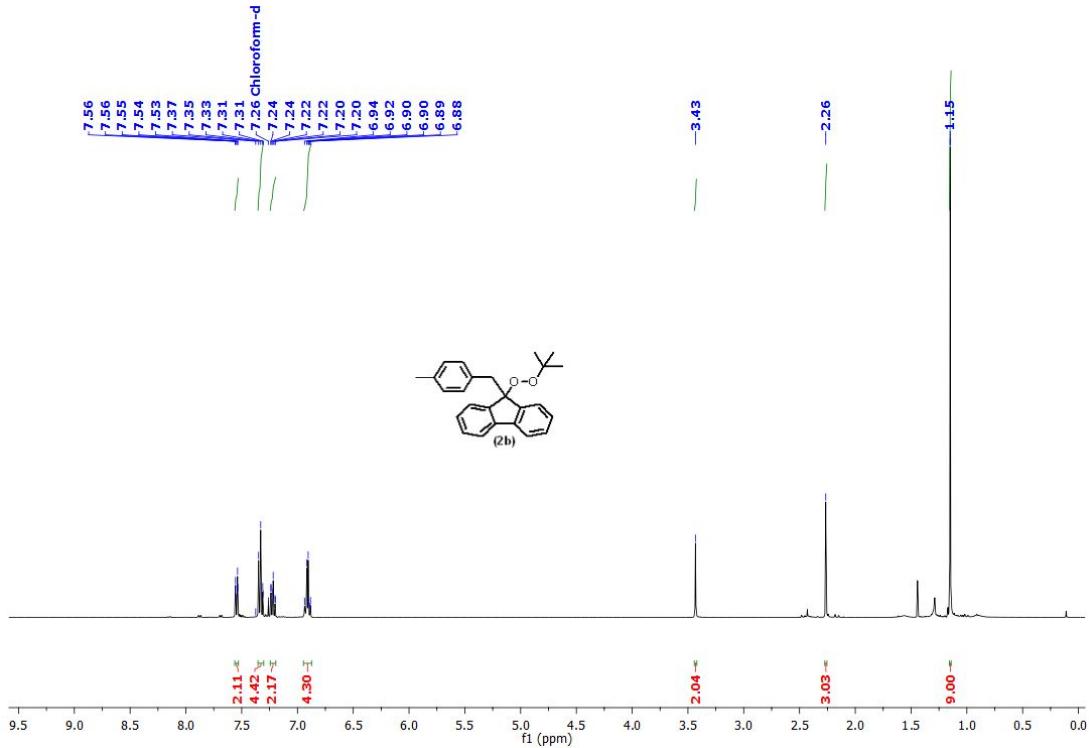
## **5. Copies of NMR Spectra:**



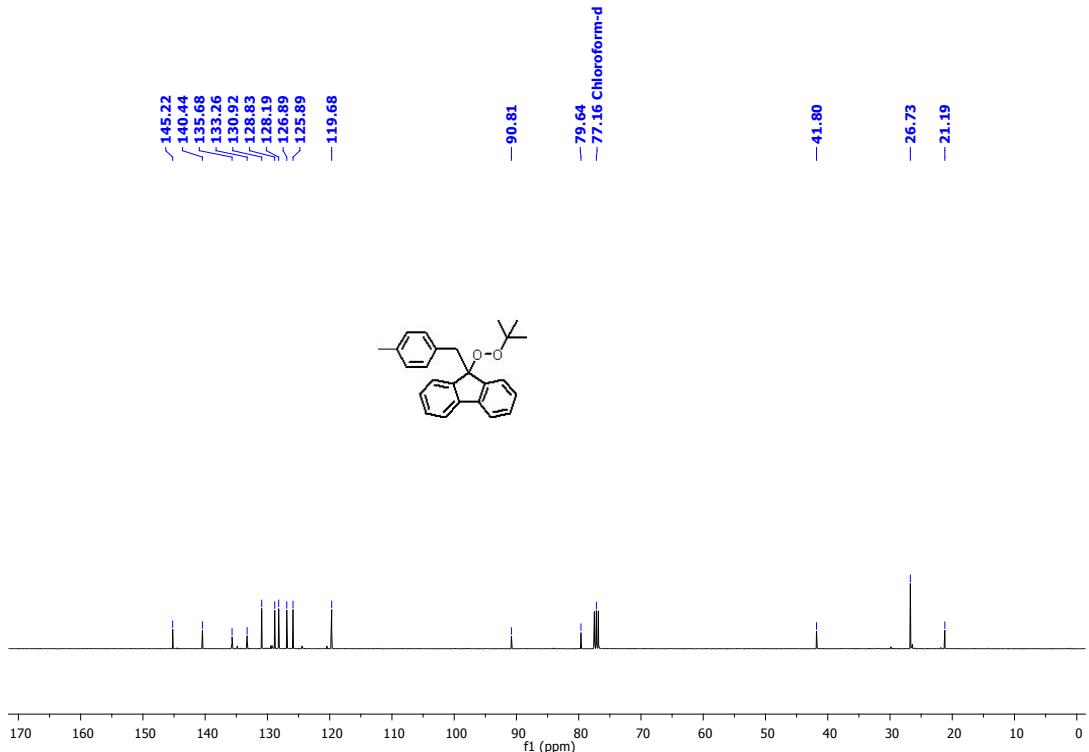
**Figure S5.**  $^1\text{H}$  NMR of Compound **2a** at 400 MHz in  $\text{CDCl}_3$



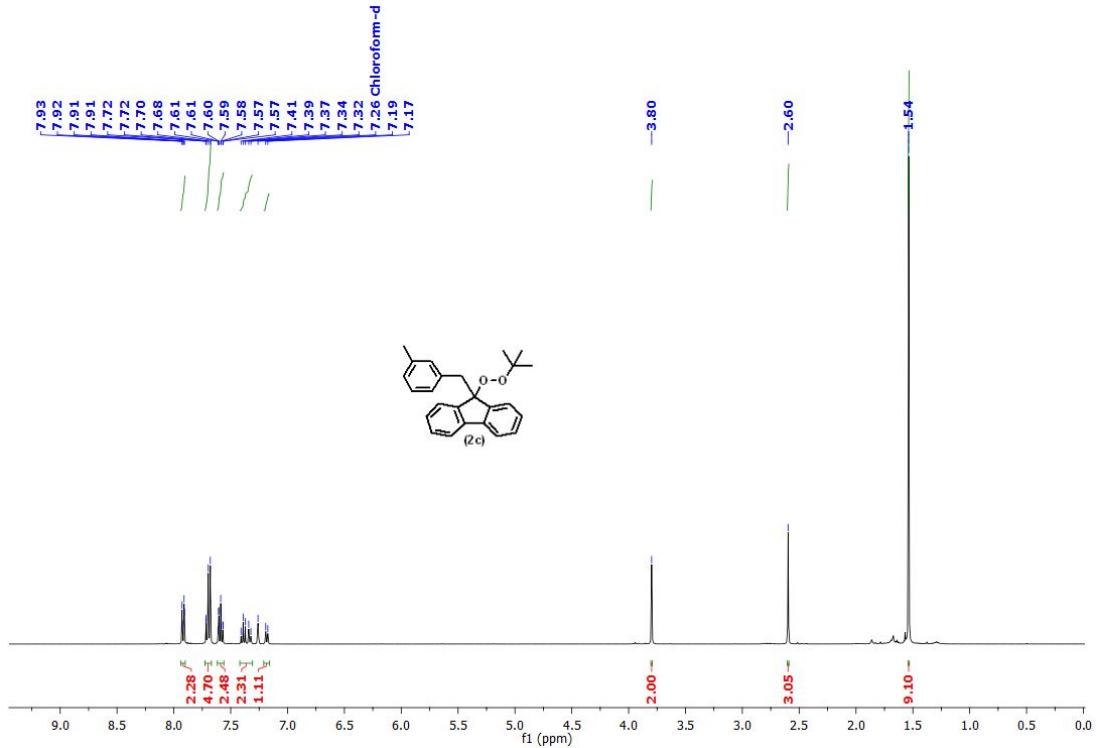
**Figure S6.**  $^{13}\text{C}$  NMR of Compound **2a** at 100 MHz in  $\text{CDCl}_3$



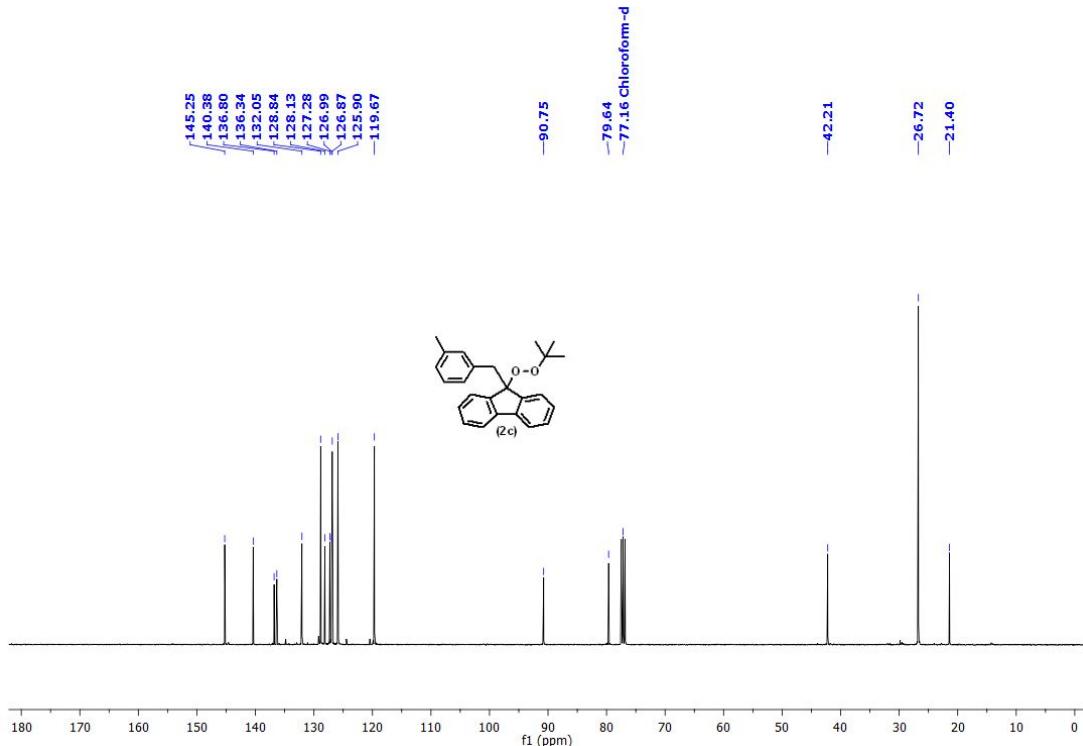
**Figure S7.**  $^1\text{H}$  NMR of Compound **2b** at 400 MHz in  $\text{CDCl}_3$



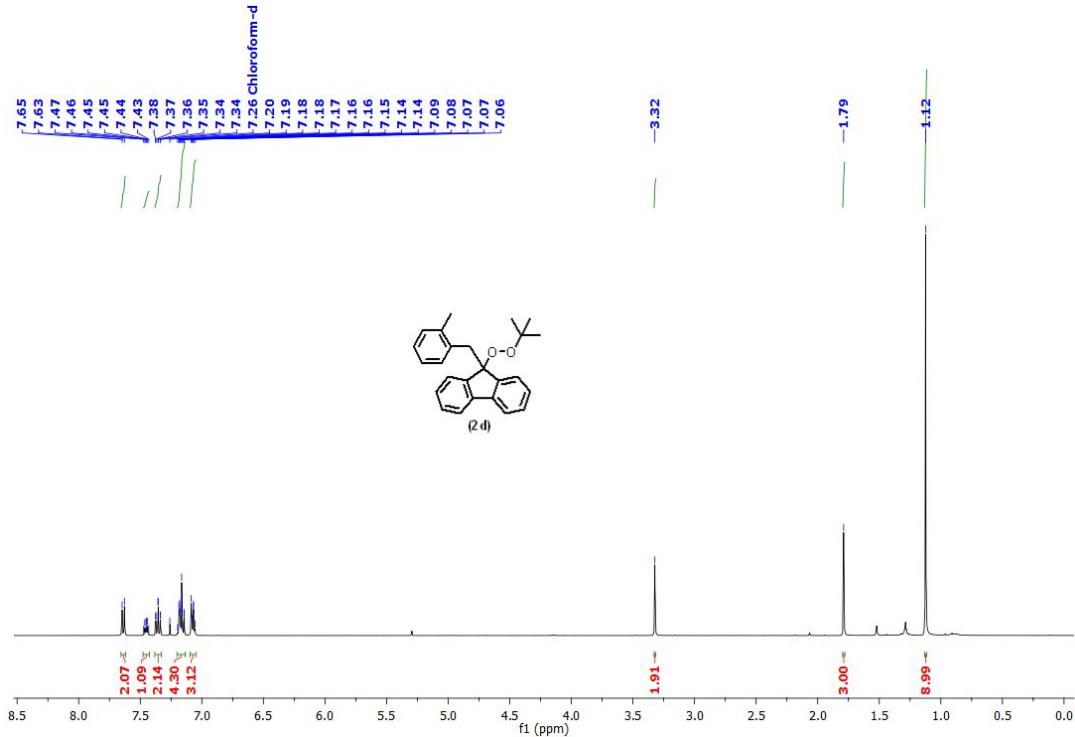
**Figure S8.**  $^{13}\text{C}$  NMR of Compound **2b** at 100 MHz in  $\text{CDCl}_3$



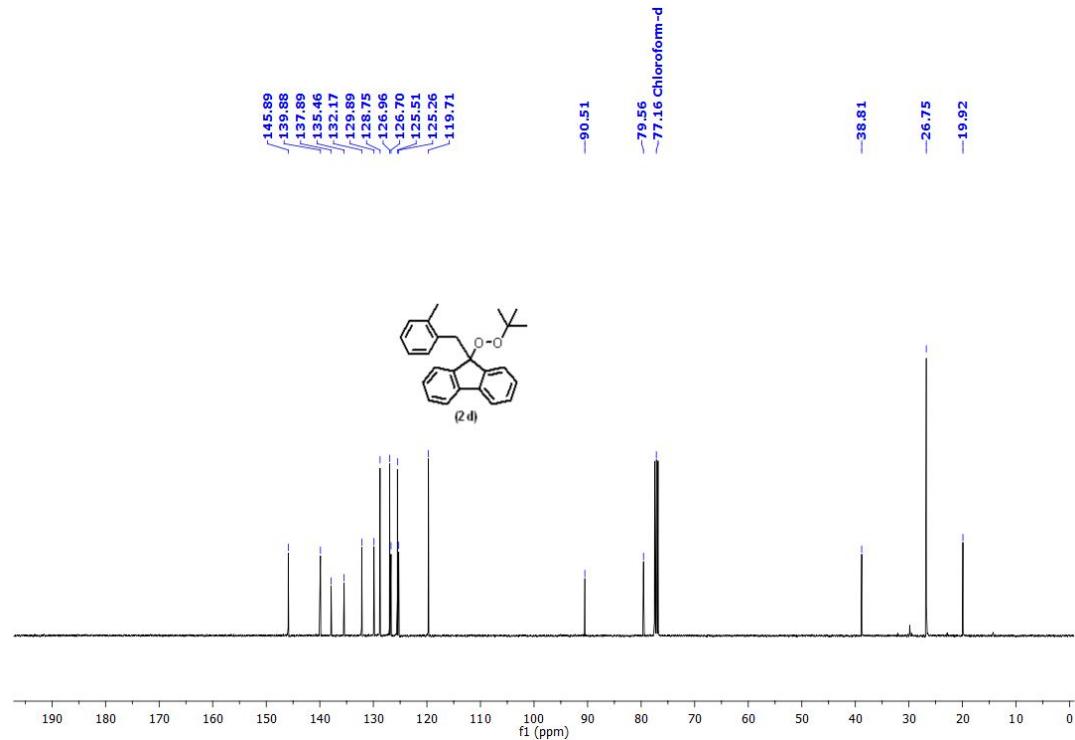
**Figure S9.**  $^1\text{H}$  NMR of Compound **2c** at 400 MHz in  $\text{CDCl}_3$



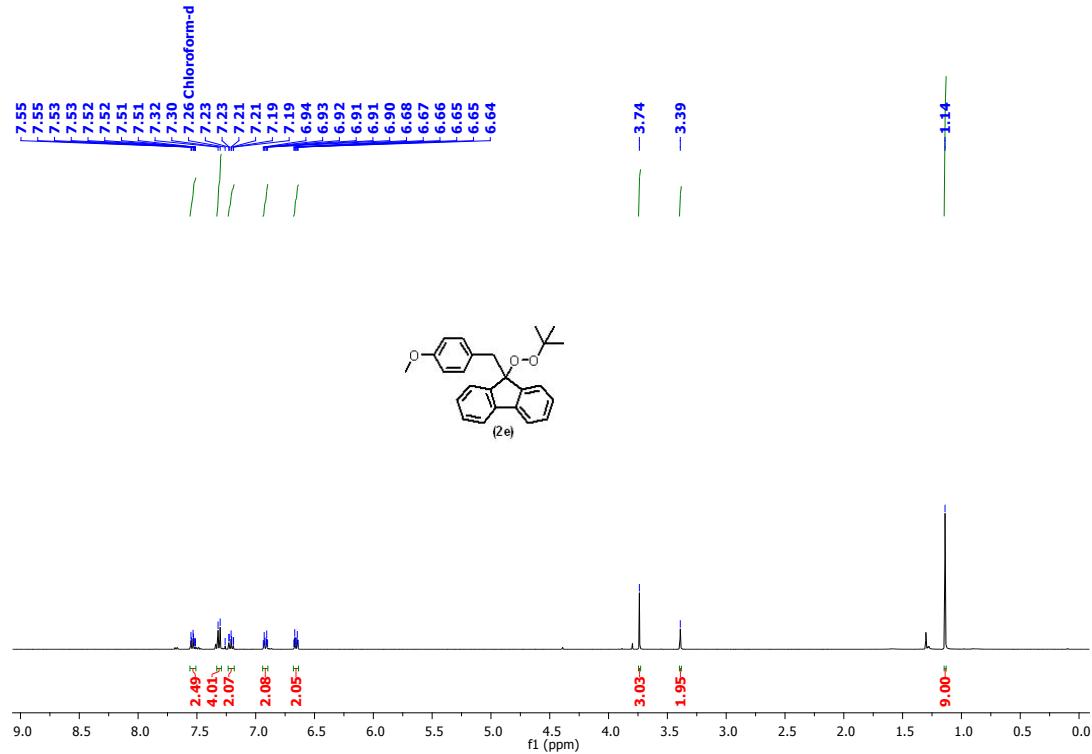
**Figure S10.**  $^{13}\text{C}$  NMR of Compound **2c** at 100 MHz in  $\text{CDCl}_3$



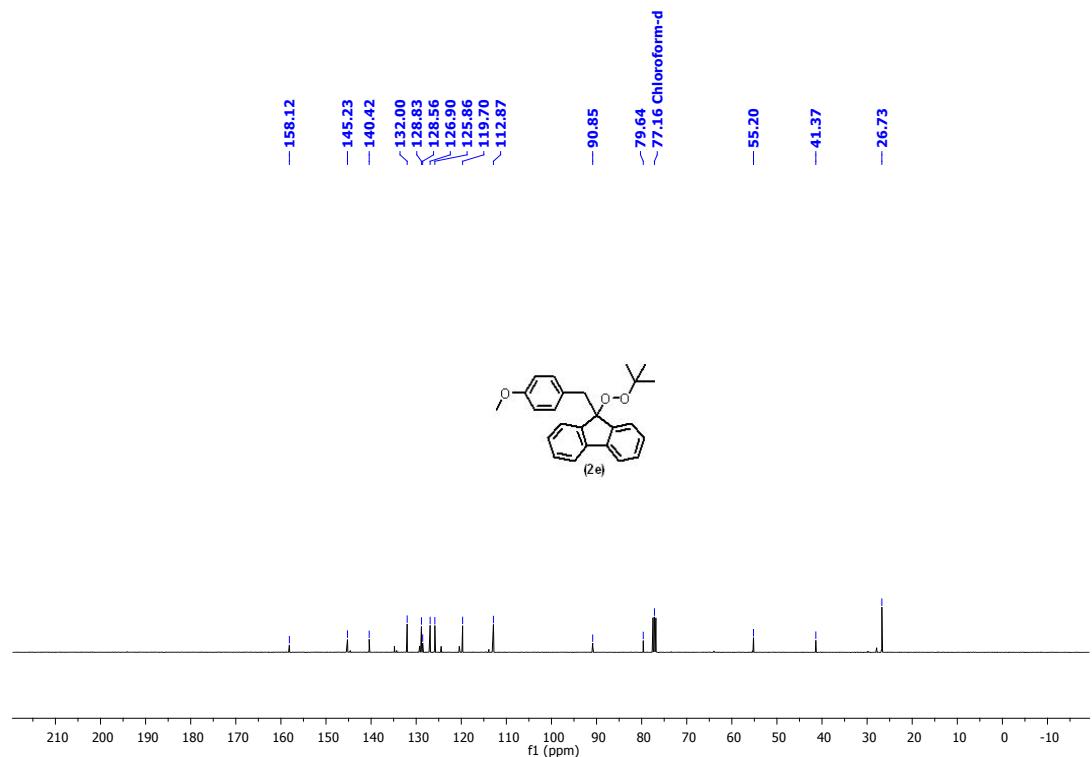
**Figure S11.**  $^1\text{H}$  NMR of Compound **2d** at 400 MHz in  $\text{CDCl}_3$



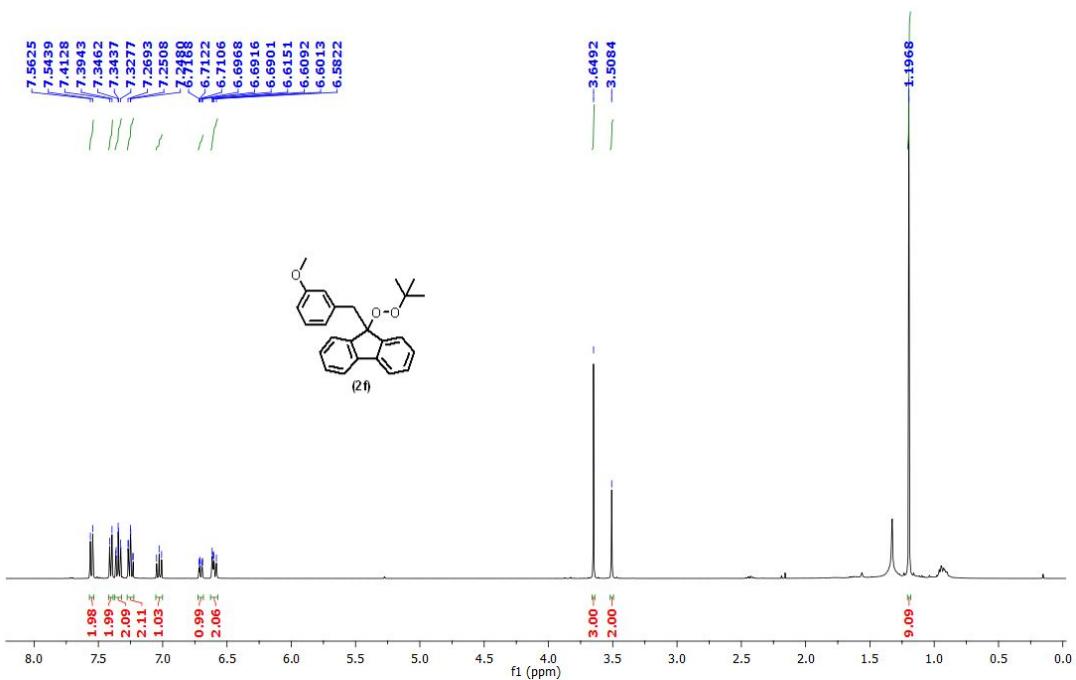
**Figure S12.**  $^{13}\text{C}$  NMR of Compound **2d** at 100 MHz in  $\text{CDCl}_3$



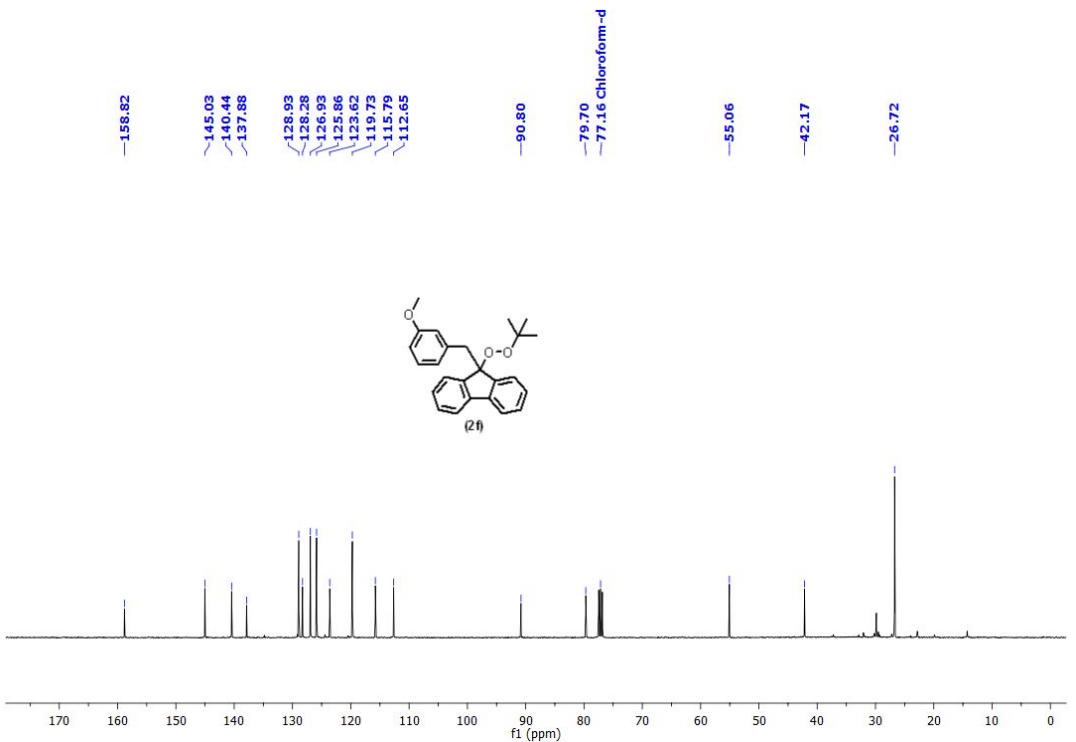
**Figure S13.**  $^1\text{H}$  NMR of Compound **2e** at 400 MHz in  $\text{CDCl}_3$



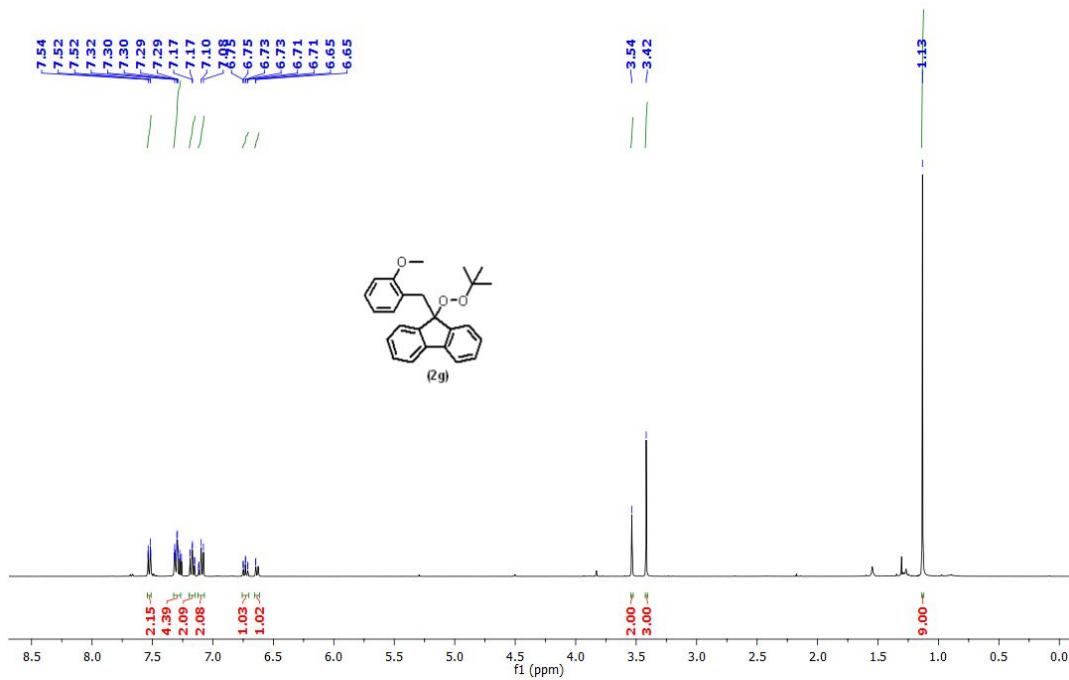
**Figure S14.**  $^{13}\text{C}$  NMR of Compound **2e** at 100 MHz in  $\text{CDCl}_3$



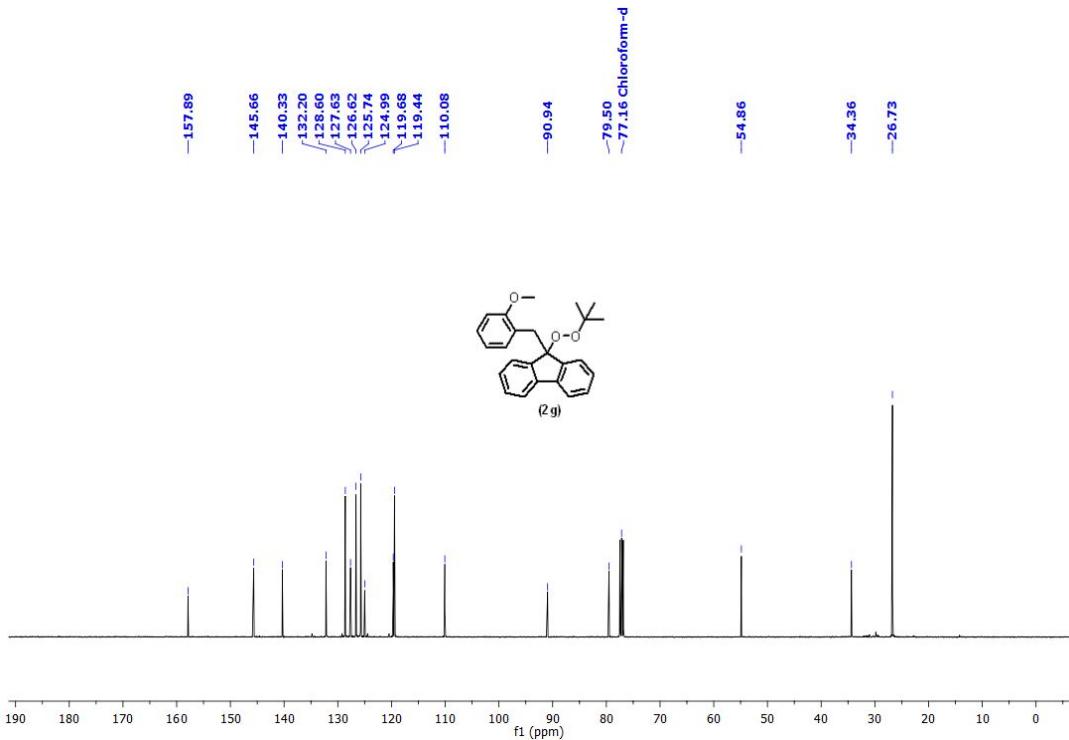
**Figure S15.**  $^1\text{H}$  NMR of Compound **2f** at 400 MHz in  $\text{CDCl}_3$



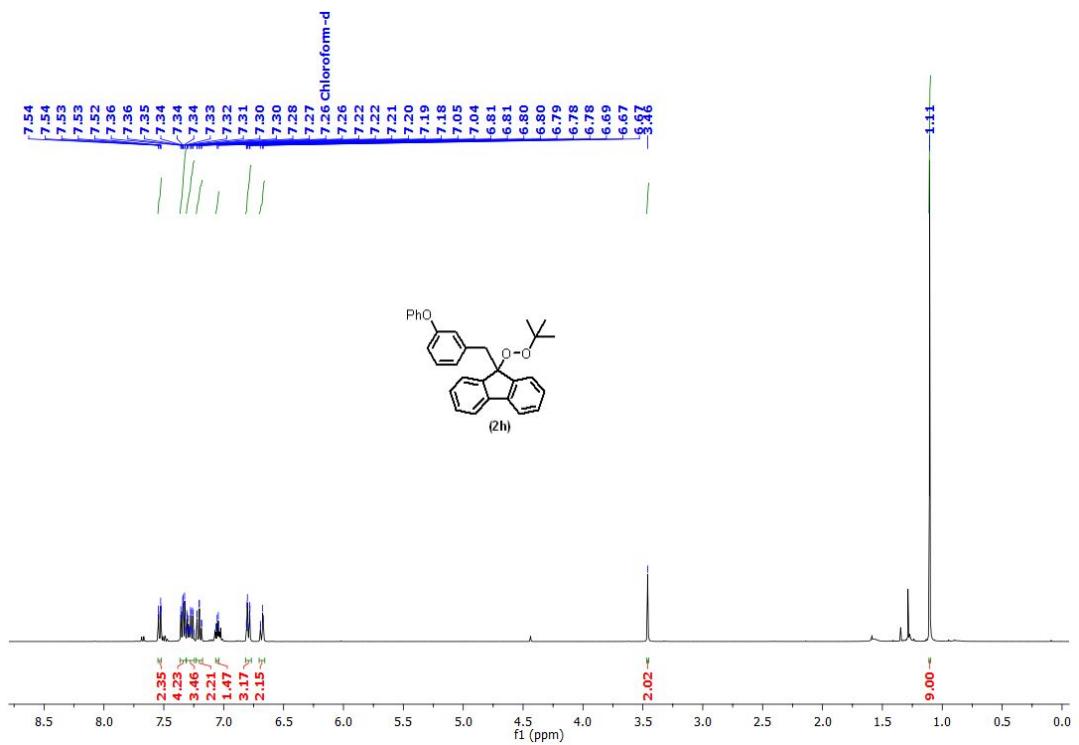
**Figure S16.**  $^{13}\text{C}$  NMR of Compound **2f** at 100 MHz in  $\text{CDCl}_3$



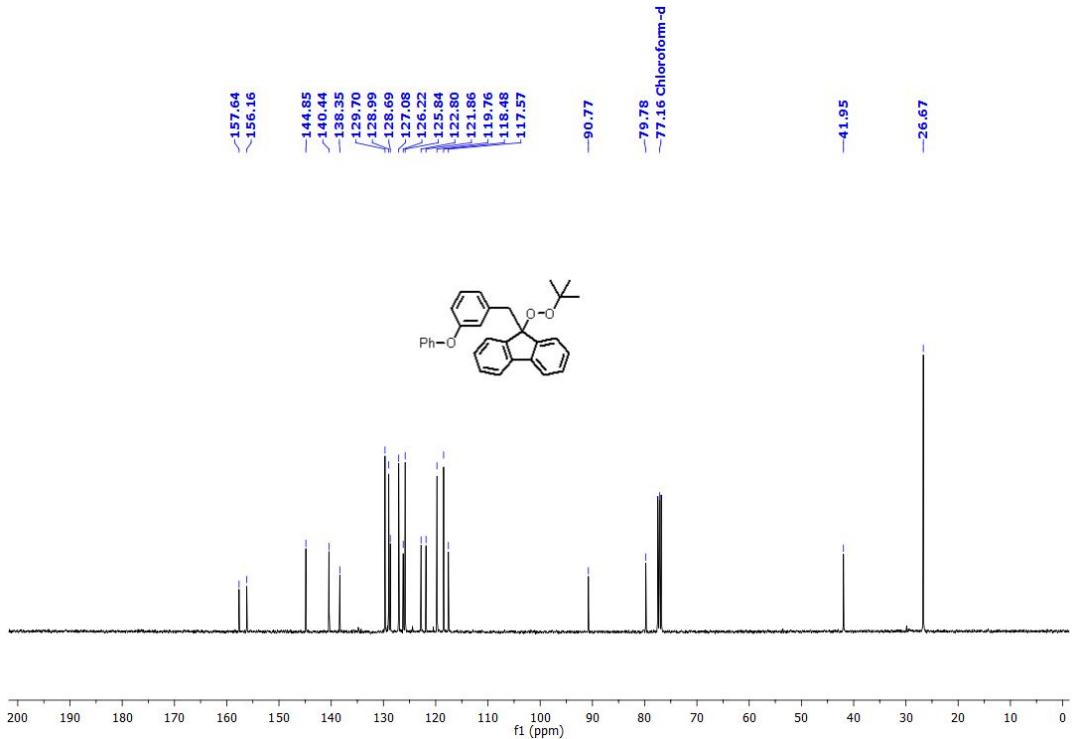
**Figure S17.**  $^1\text{H}$  NMR of Compound **2g** at 400 MHz in  $\text{CDCl}_3$



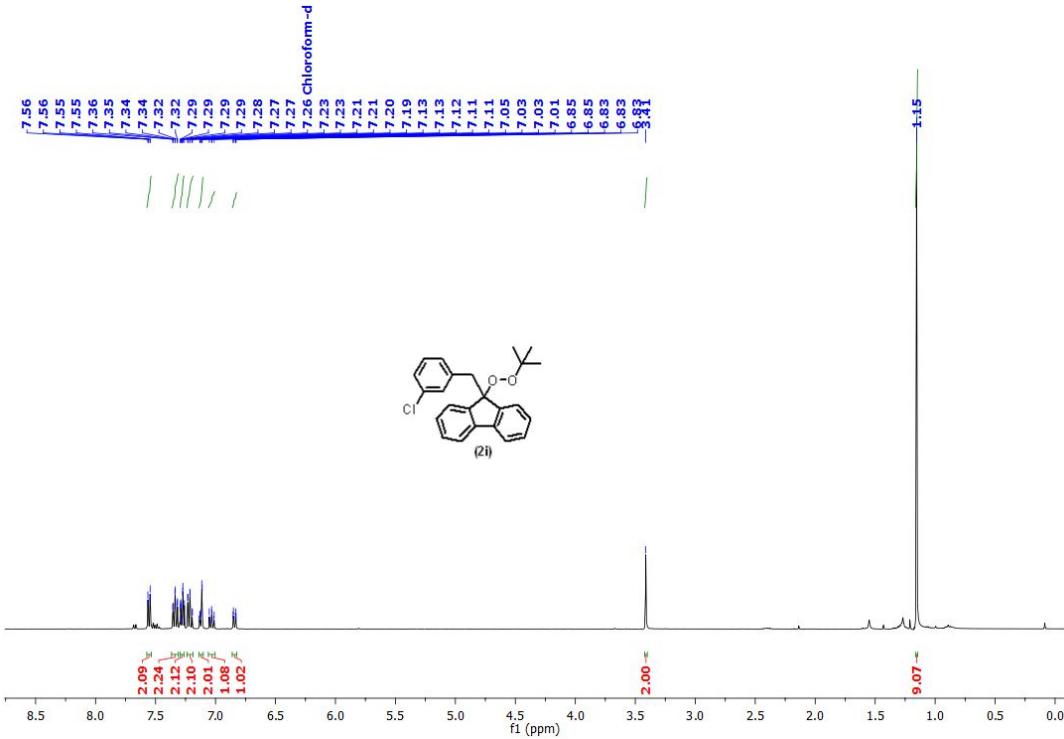
**Figure S18.**  $^{13}\text{C}$  NMR of Compound **2g** at 100 MHz in  $\text{CDCl}_3$



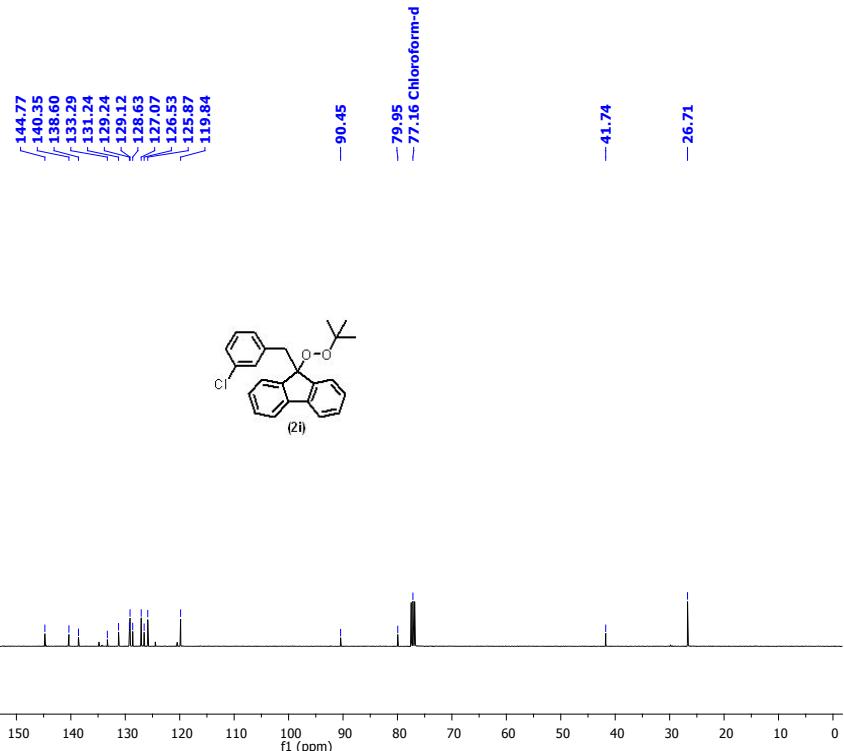
**Figure S19.**  $^1\text{H}$  NMR of Compound **2h** at 400 MHz in  $\text{CDCl}_3$



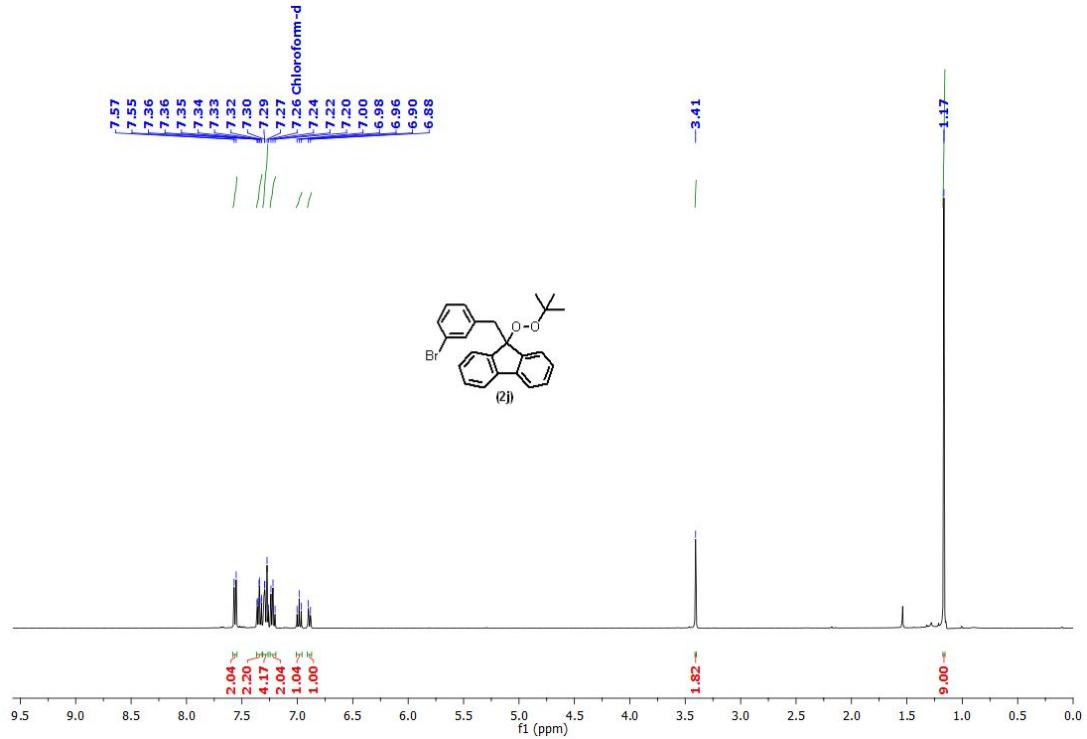
**Figure S20.**  $^{13}\text{C}$  NMR of Compound **2h** at 100 MHz in  $\text{CDCl}_3$



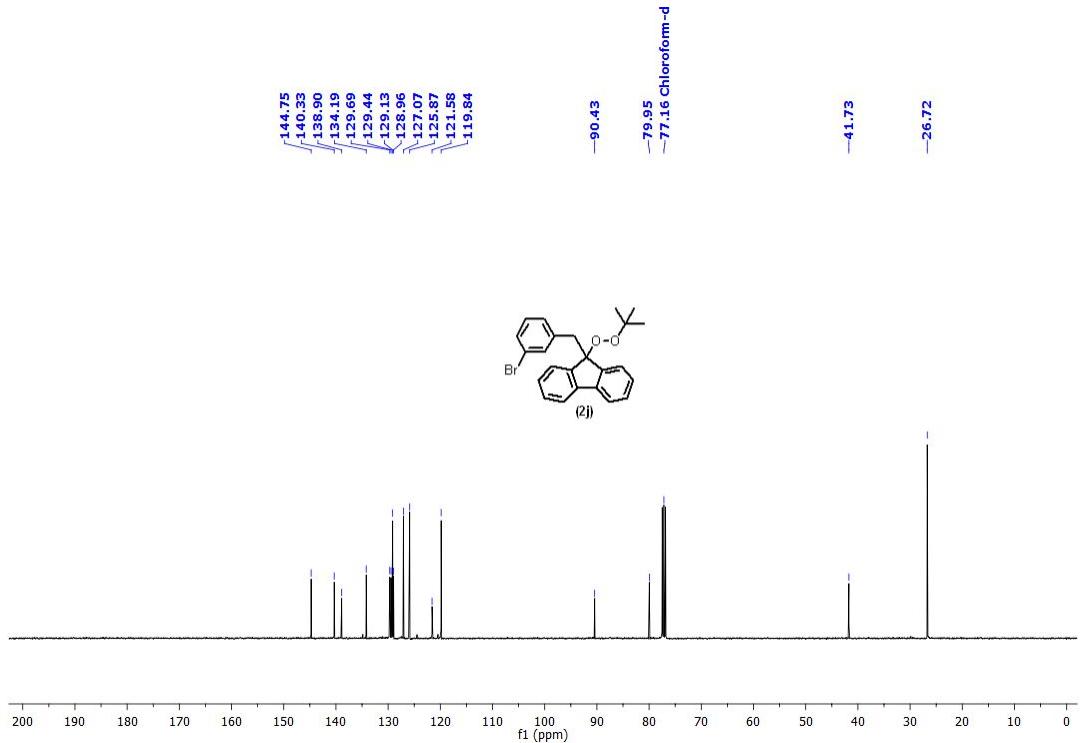
**Figure S21.** <sup>1</sup>H NMR of Compound 2i at 400 MHz in CDCl<sub>3</sub>



**Figure S22.** <sup>13</sup>C NMR of Compound 2i at 100 MHz in CDCl<sub>3</sub>



**Figure S23.**  $^1\text{H}$  NMR of Compound **2j** at 400 MHz in  $\text{CDCl}_3$



**Figure S24.**  $^{13}\text{C}$  NMR of Compound **2j** at 100 MHz in  $\text{CDCl}_3$

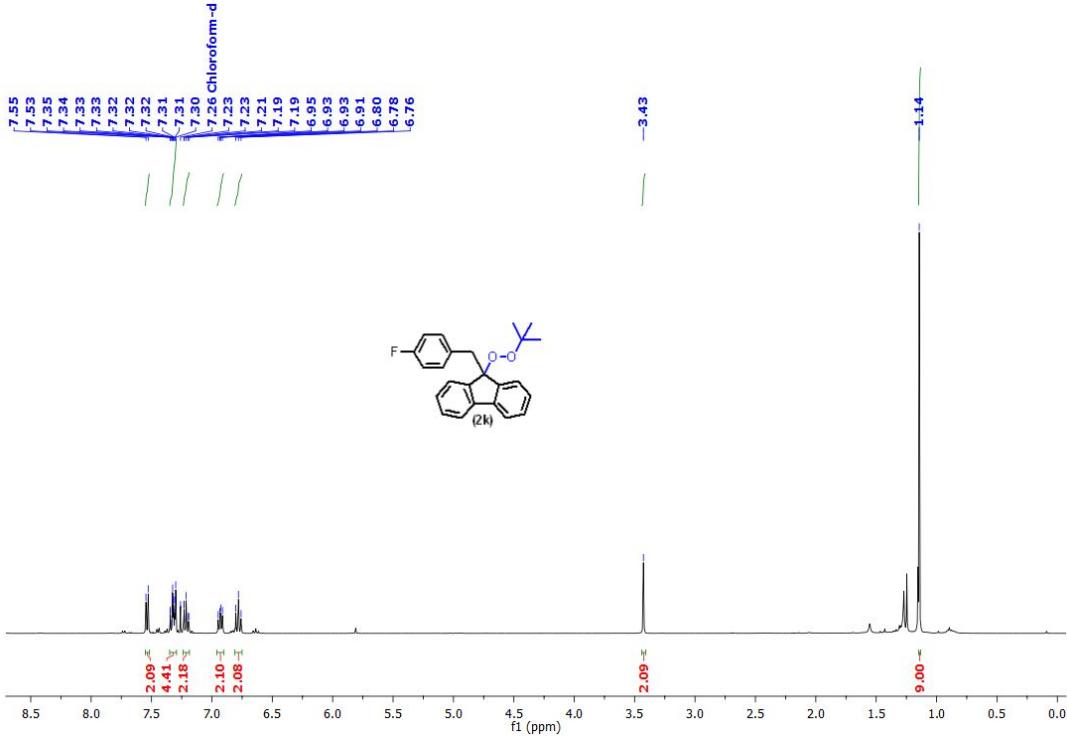


Figure S25.  $^1\text{H}$  NMR of Compound **2k** at 400 MHz in  $\text{CDCl}_3$

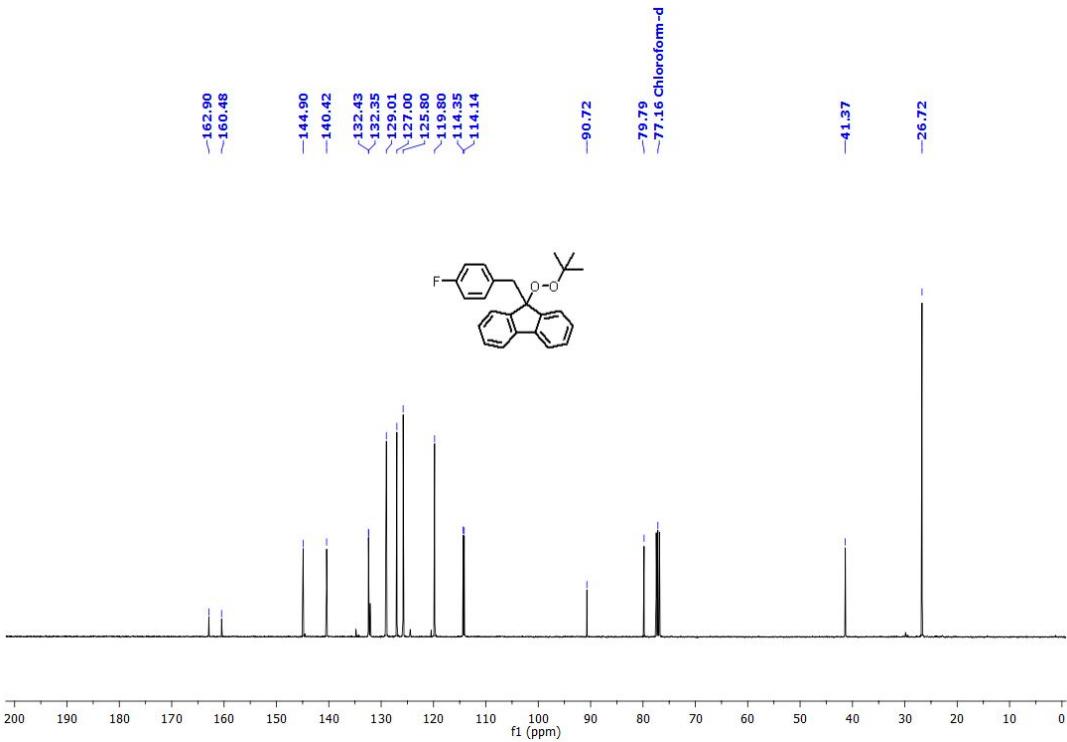
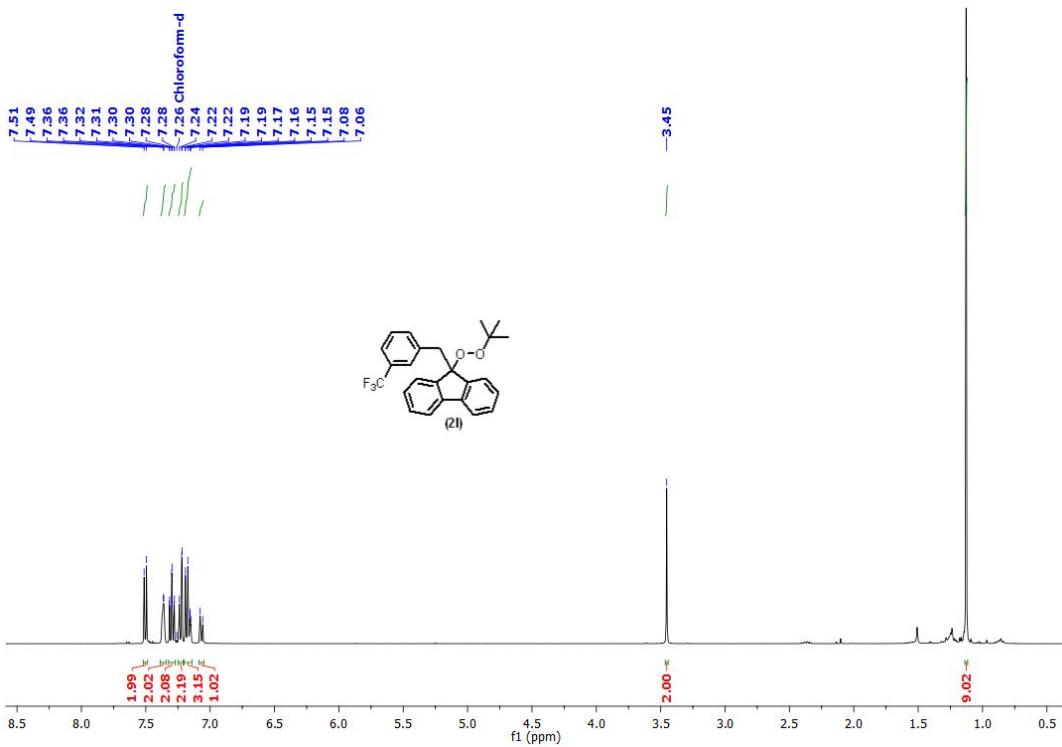
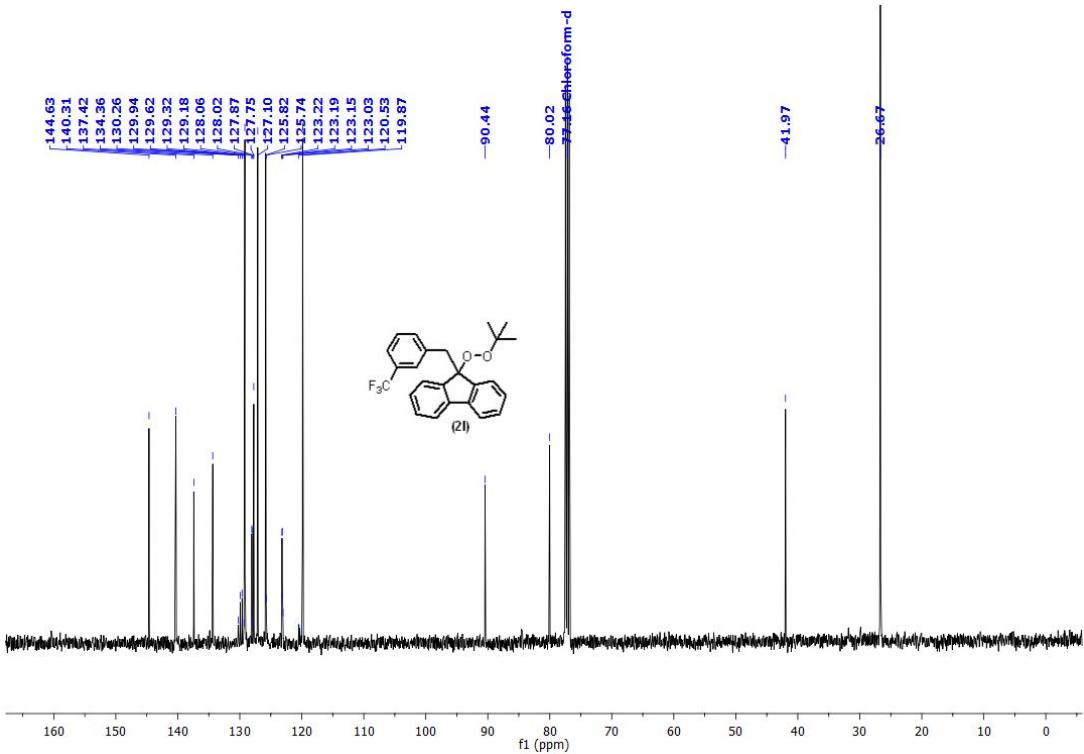


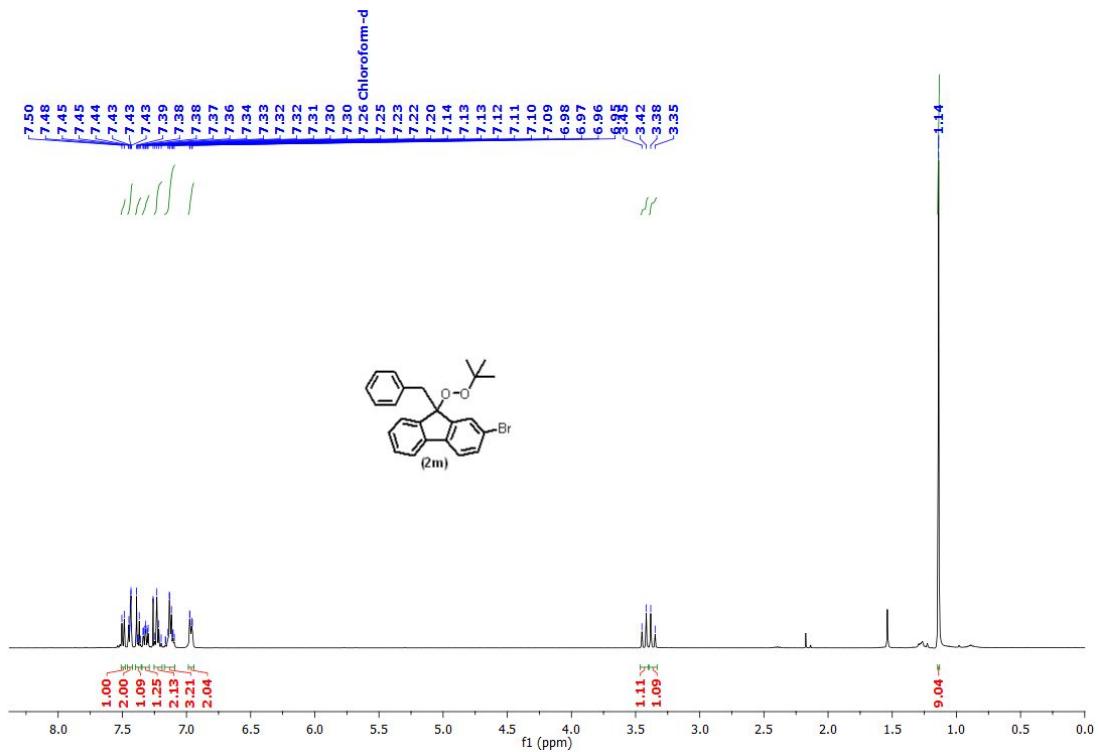
Figure S26.  $^{13}\text{C}$  NMR of Compound **2k** at 100 MHz in  $\text{CDCl}_3$



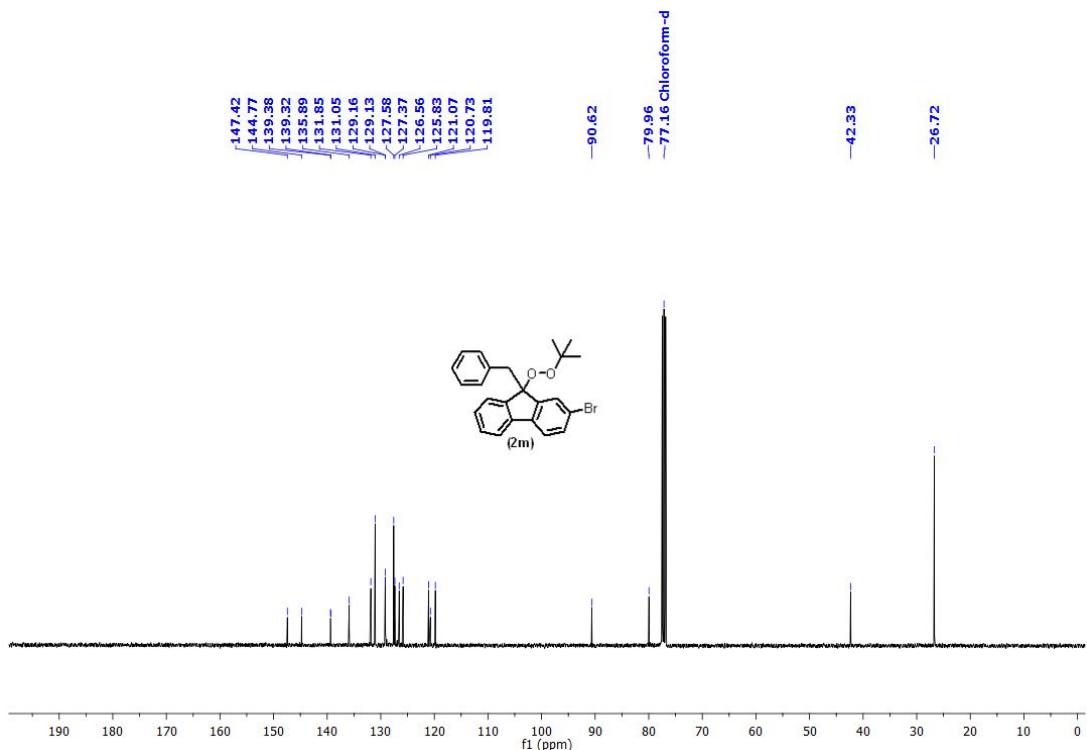
**Figure S27.**  $^1\text{H}$  NMR of Compound **2l** at 400 MHz in  $\text{CDCl}_3$



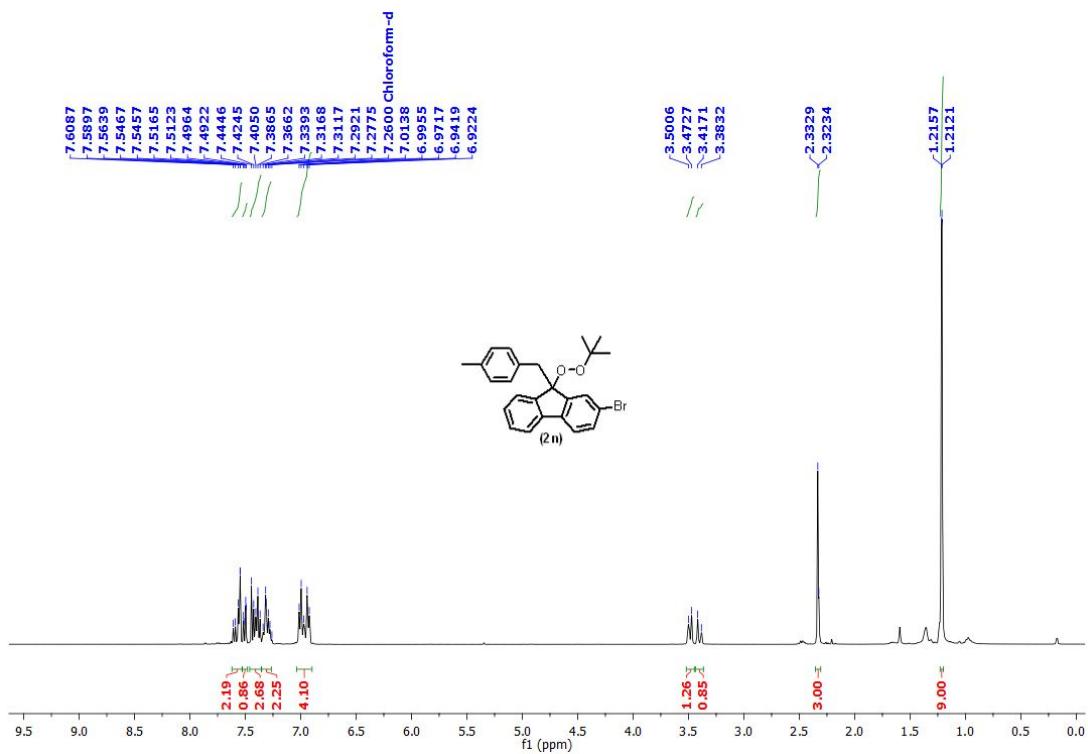
**Figure S28.**  $^{13}\text{C}$  NMR of Compound **2l** at 100 MHz in  $\text{CDCl}_3$



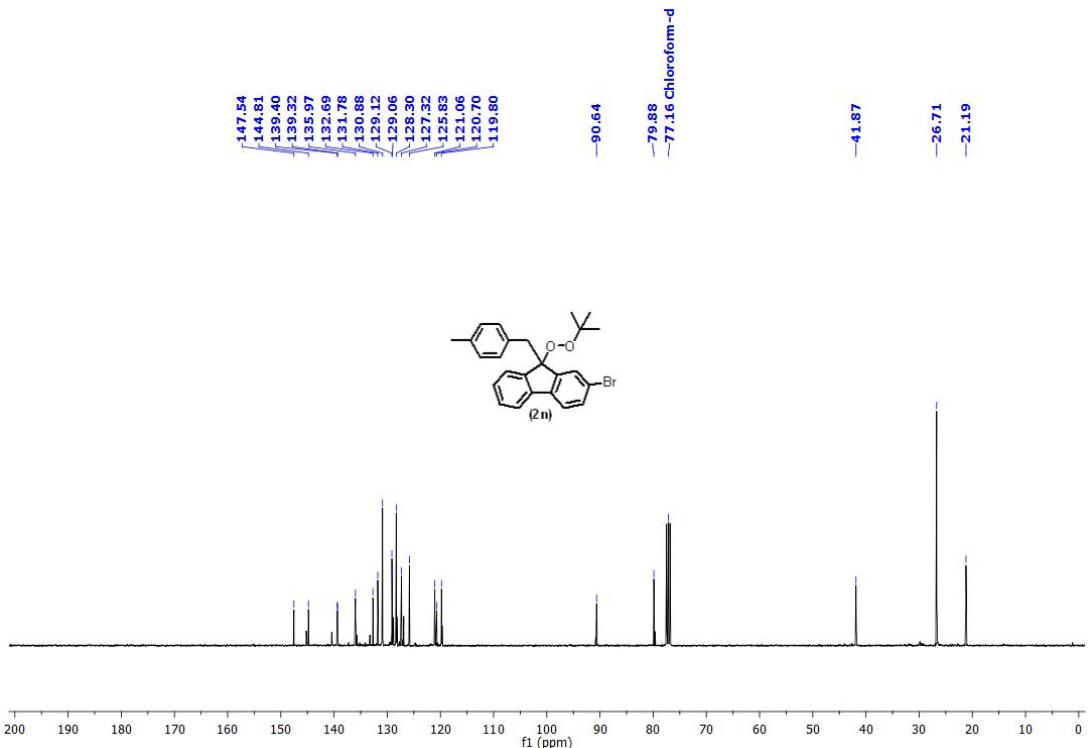
**Figure S29.**  $^1\text{H}$  NMR of Compound **2m** at 400 MHz in  $\text{CDCl}_3$



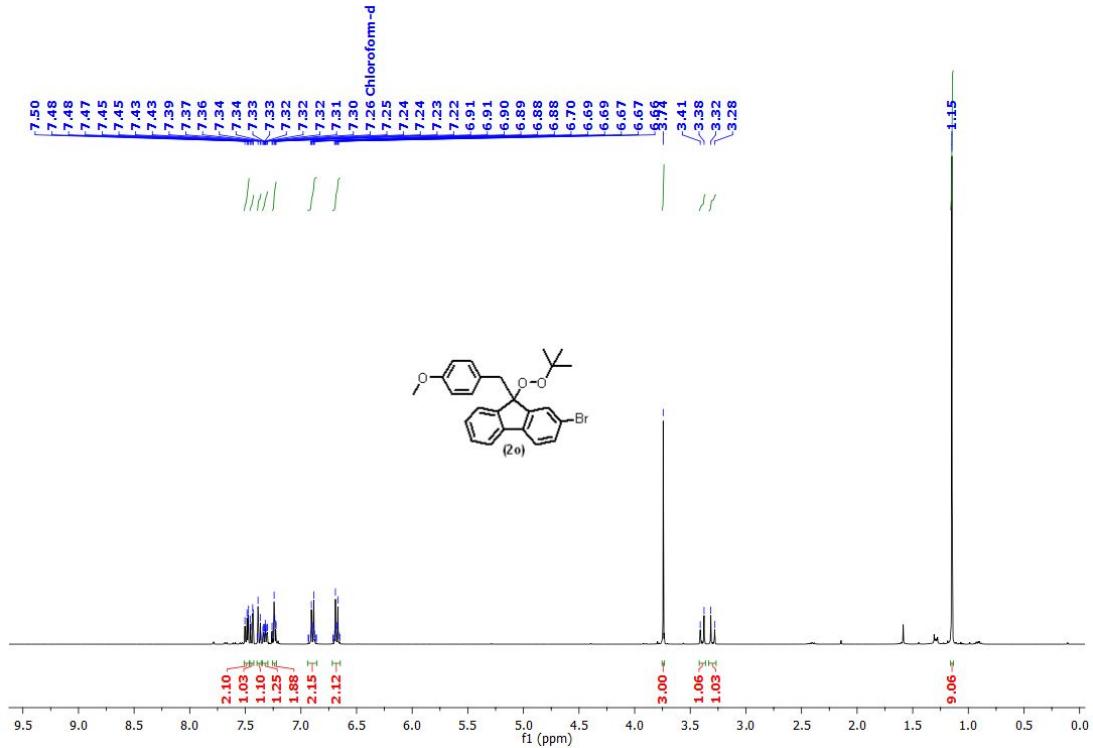
**Figure S30.**  $^{13}\text{C}$  NMR of Compound **2m** at 100 MHz in  $\text{CDCl}_3$



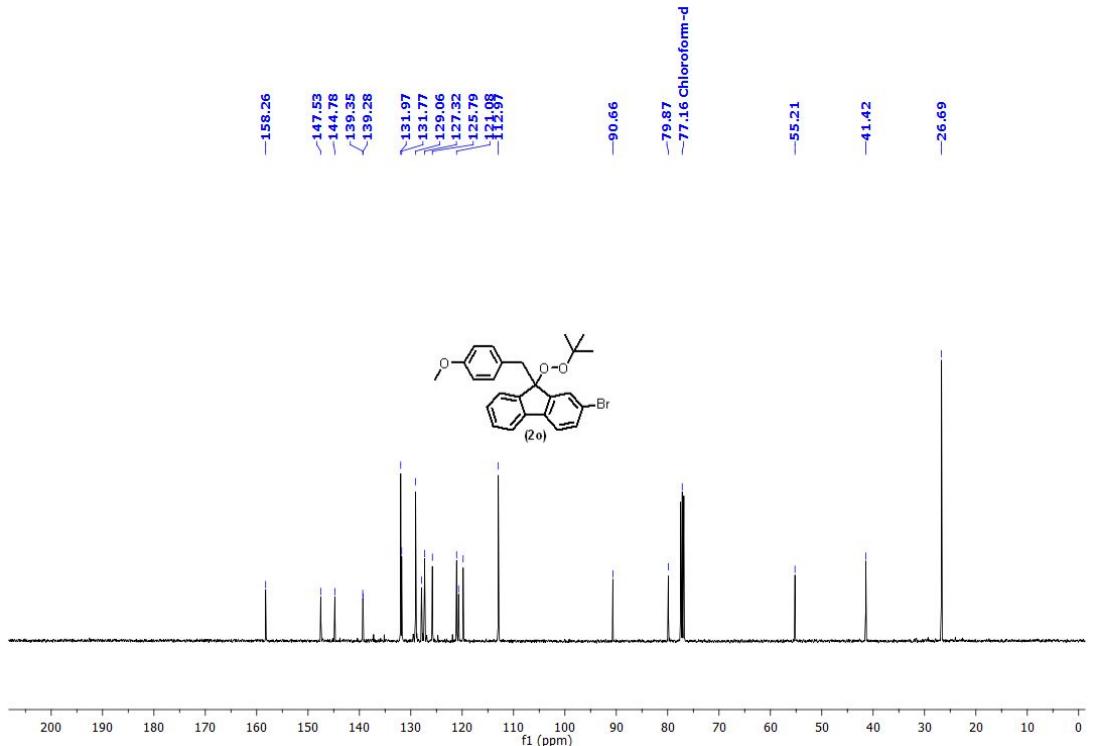
**Figure S31.**  $^1\text{H}$  NMR of Compound **2n** at 400 MHz in  $\text{CDCl}_3$



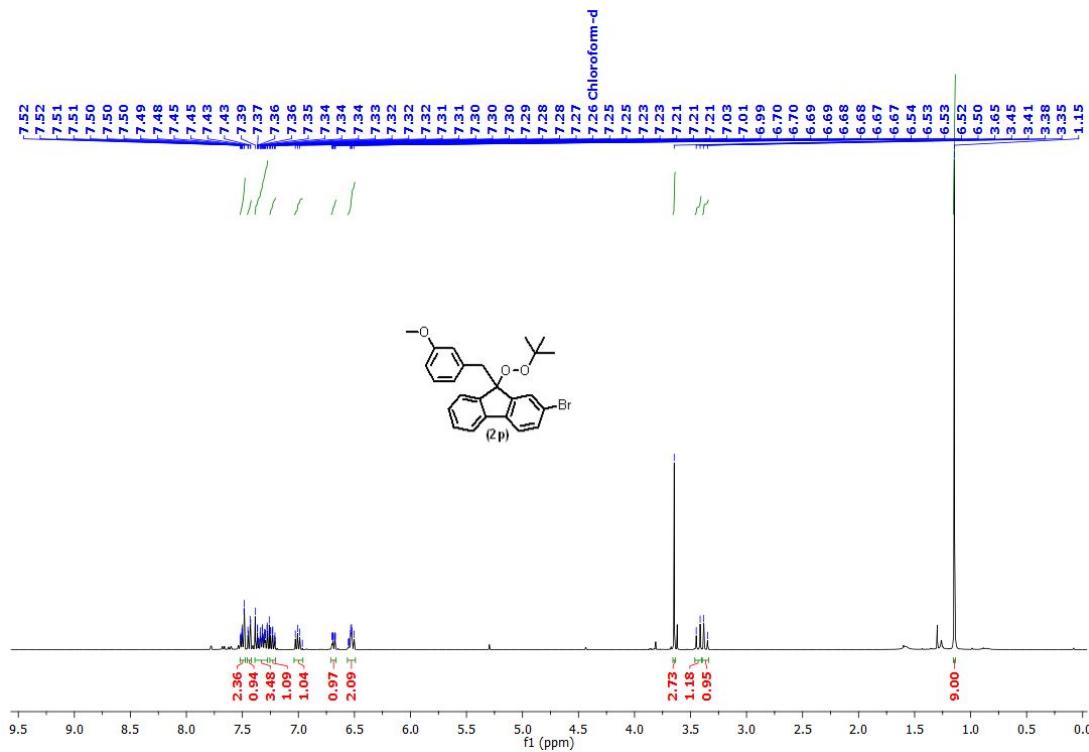
**Figure S32.**  $^{13}\text{C}$  NMR of Compound **2n** at 100 MHz in  $\text{CDCl}_3$



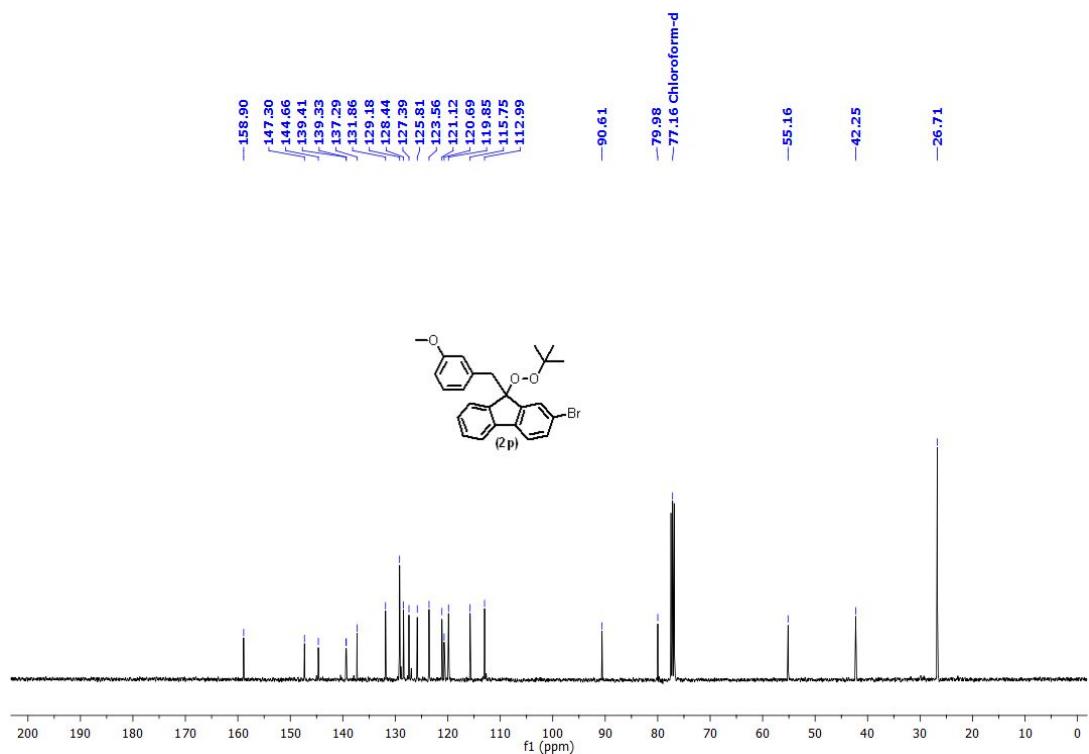
**Figure S33.**  $^1\text{H}$  NMR of Compound **2o** at 400 MHz in  $\text{CDCl}_3$



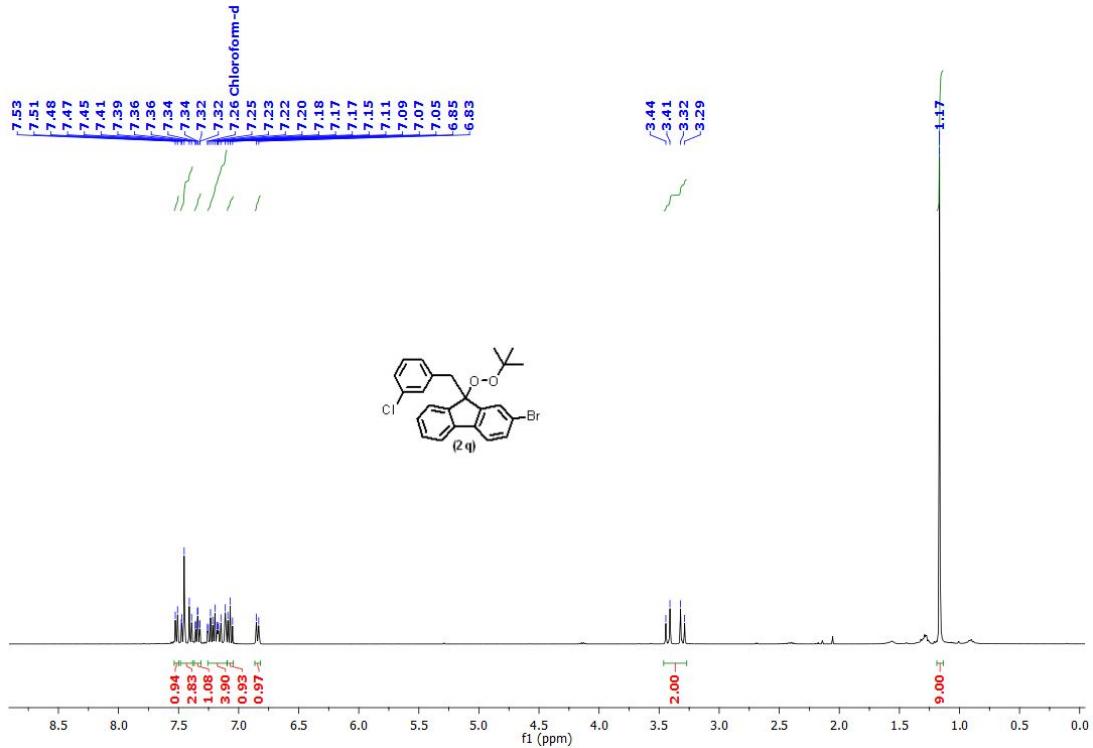
**Figure S34.**  $^{13}\text{C}$  NMR of Compound **2o** at 100 MHz in  $\text{CDCl}_3$



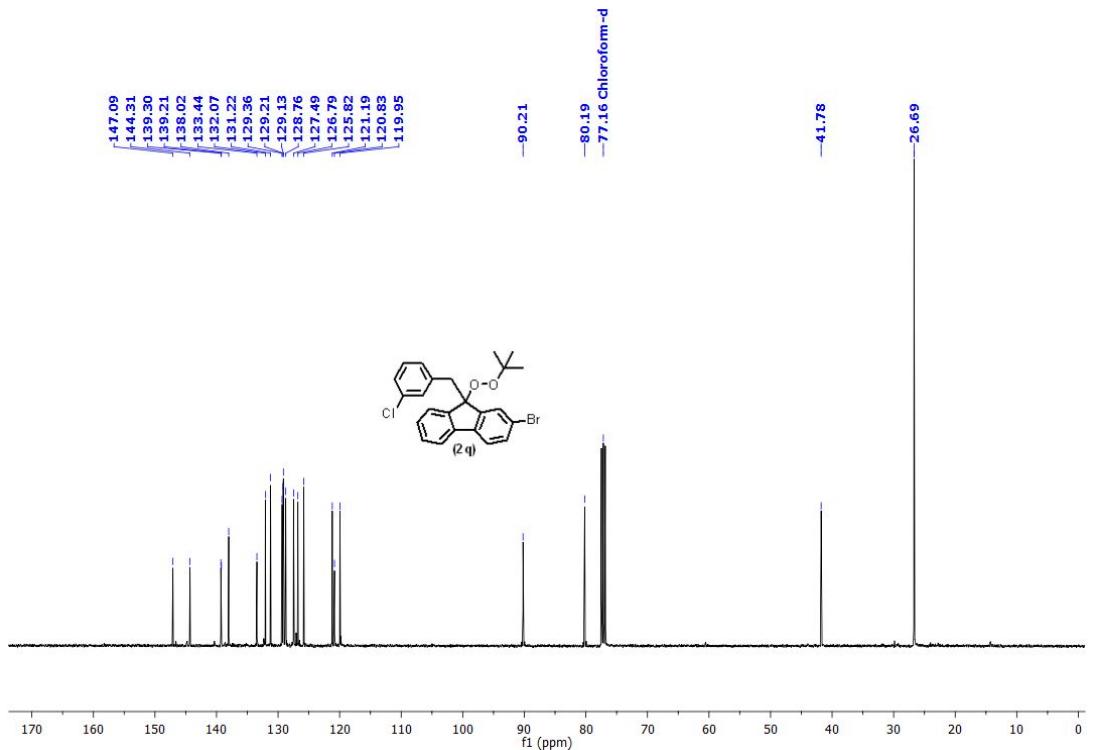
**Figure S35.**  $^1\text{H}$  NMR of Compound **2p** at 400 MHz in  $\text{CDCl}_3$



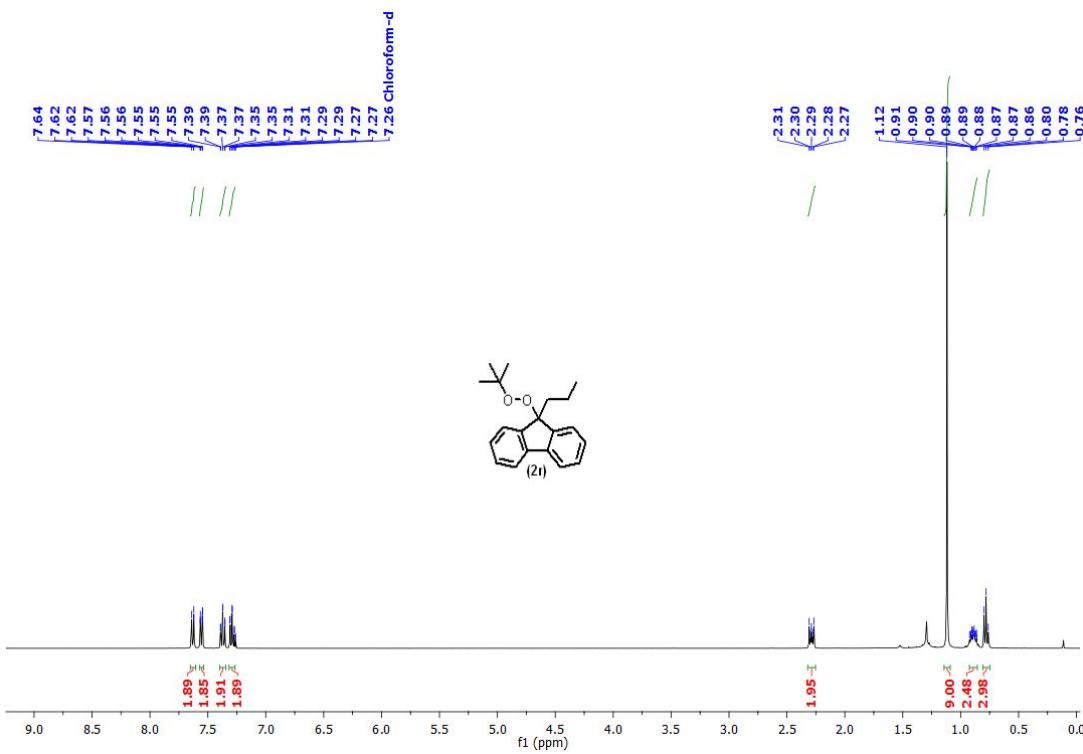
**Figure S36.**  $^{13}\text{C}$  NMR of Compound **2p** at 100 MHz in  $\text{CDCl}_3$



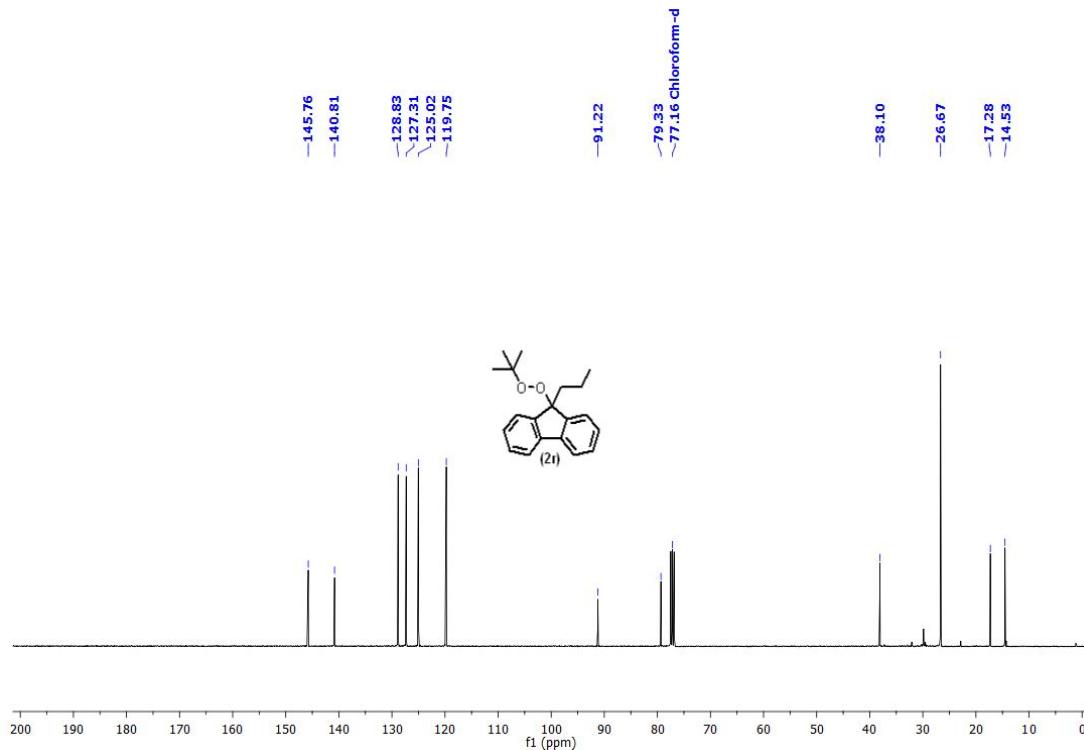
**Figure S37.**  $^1\text{H}$  NMR of Compound **2q** at 400 MHz in  $\text{CDCl}_3$



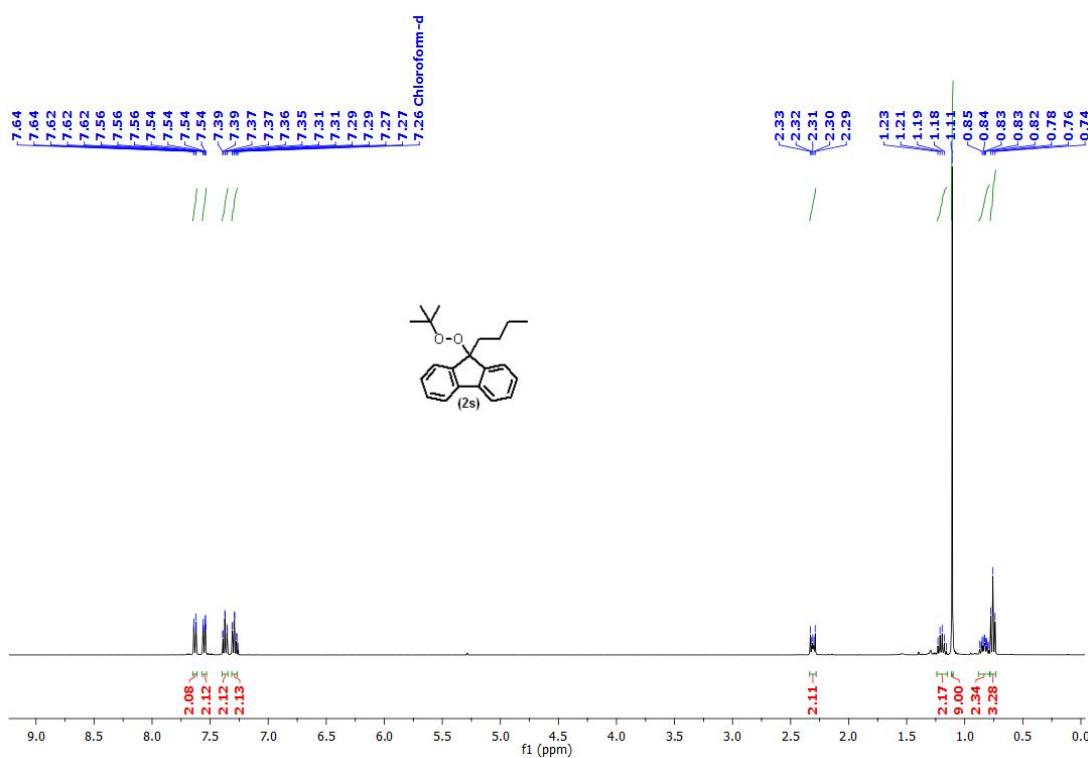
**Figure S38.**  $^{13}\text{C}$  NMR of Compound **2q** at 100 MHz in  $\text{CDCl}_3$



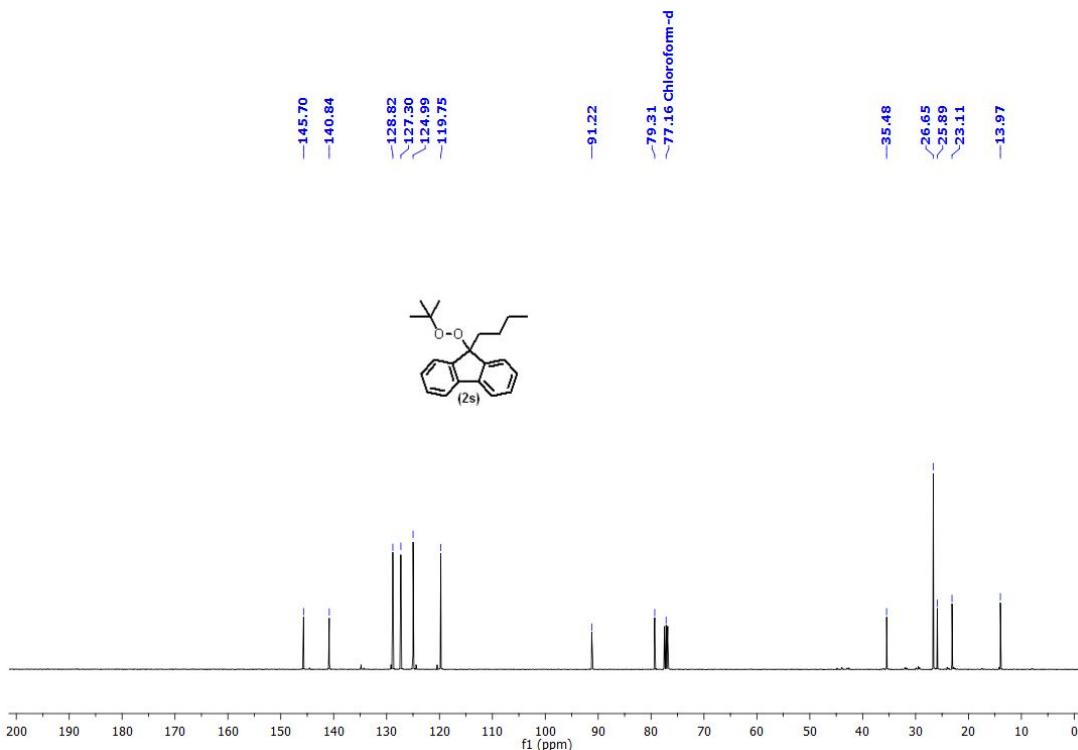
**Figure S39.**  $^1\text{H}$  NMR of Compound **2r** at 400 MHz in  $\text{CDCl}_3$



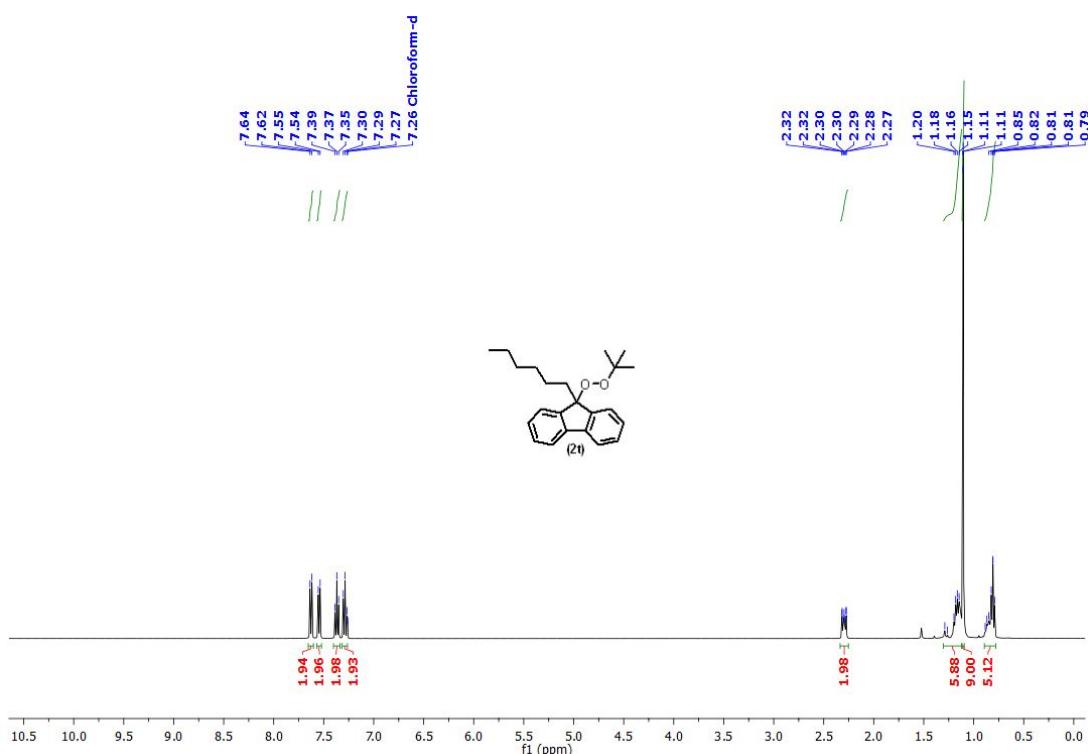
**Figure S40.**  $^{13}\text{C}$  NMR of Compound **2r** at 100 MHz in  $\text{CDCl}_3$



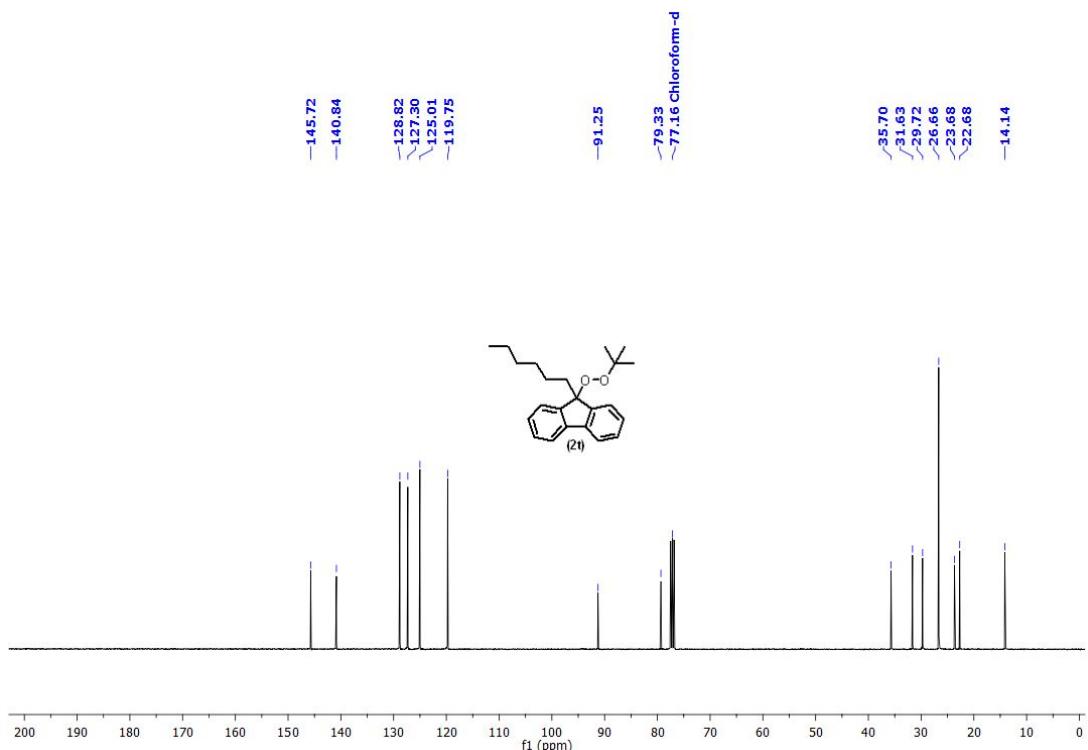
**Figure S41.**  $^1\text{H}$  NMR of Compound **2s** at 400 MHz in  $\text{CDCl}_3$



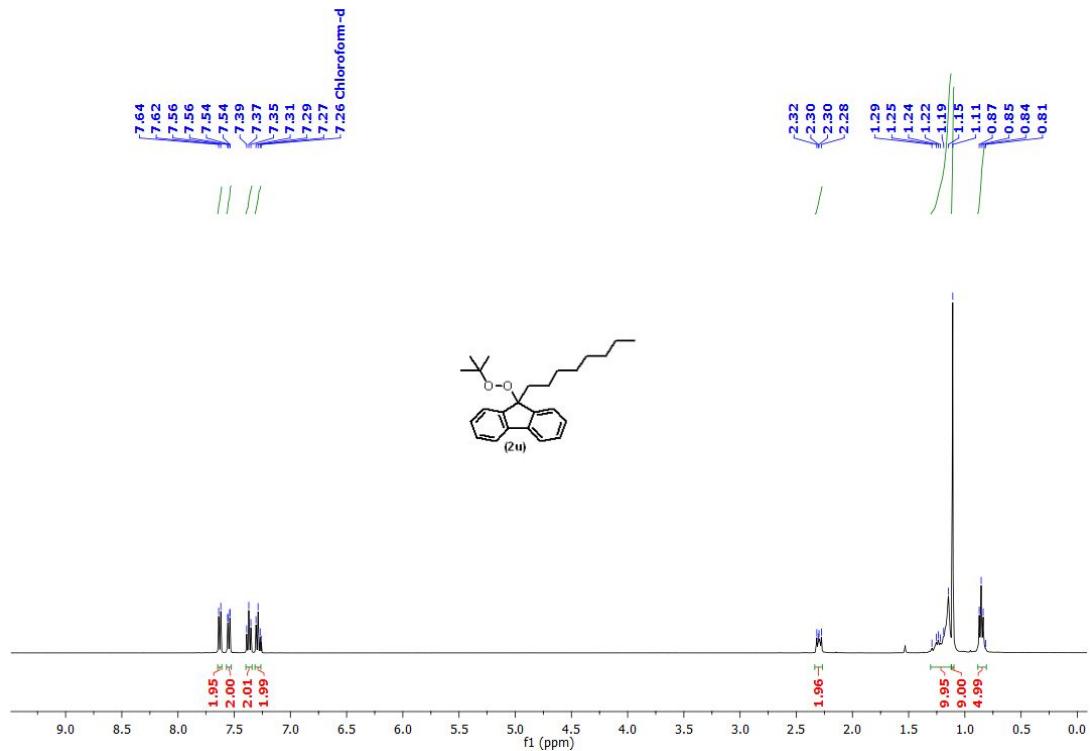
**Figure S42.**  $^{13}\text{C}$  NMR of Compound **2s** at 100 MHz in  $\text{CDCl}_3$



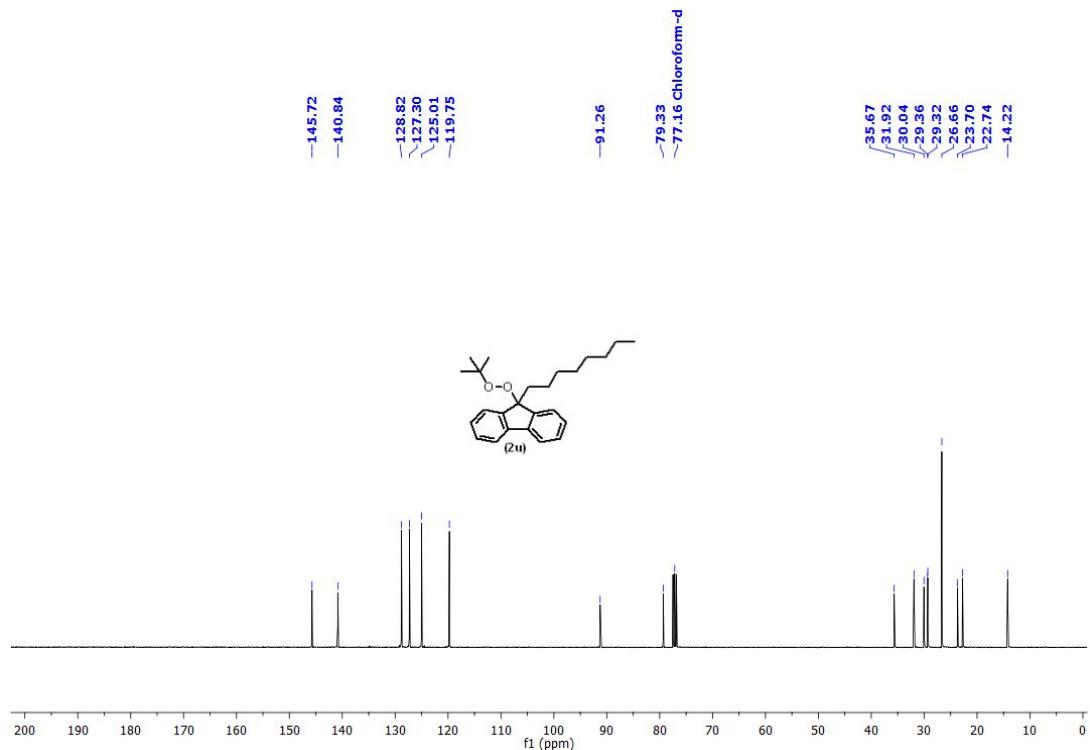
**Figure S43.**  $^1\text{H}$  NMR of Compound **2t** at 400 MHz in  $\text{CDCl}_3$



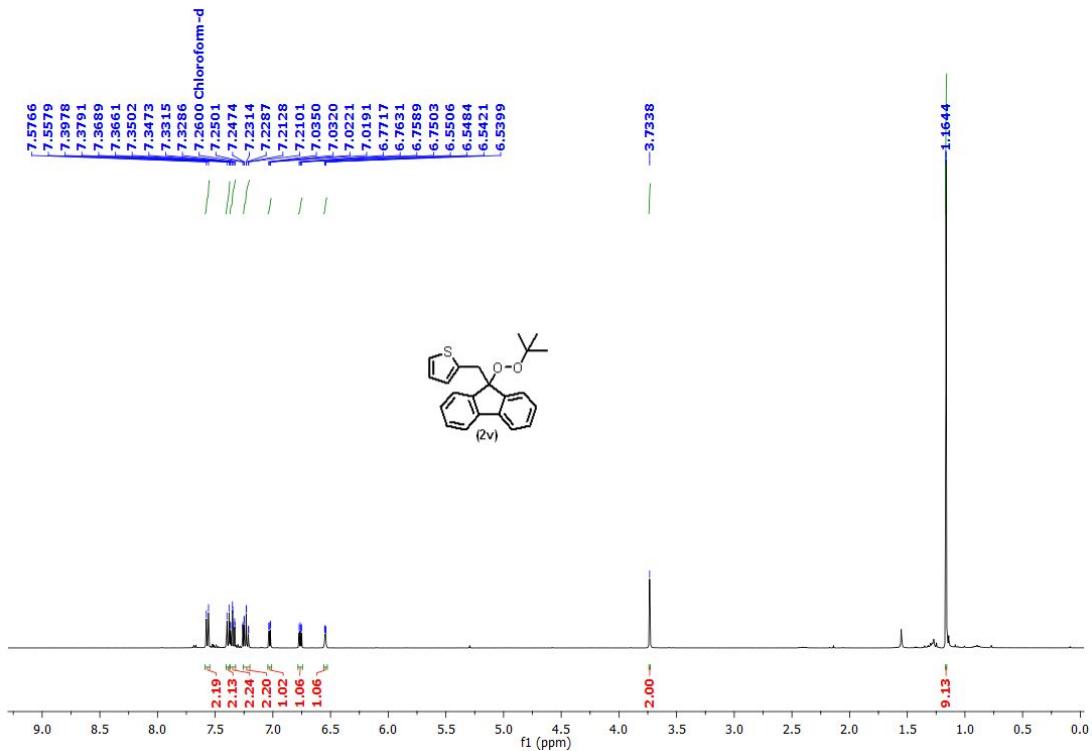
**Figure S44.**  $^{13}\text{C}$  NMR of Compound **2t** at 100 MHz in  $\text{CDCl}_3$



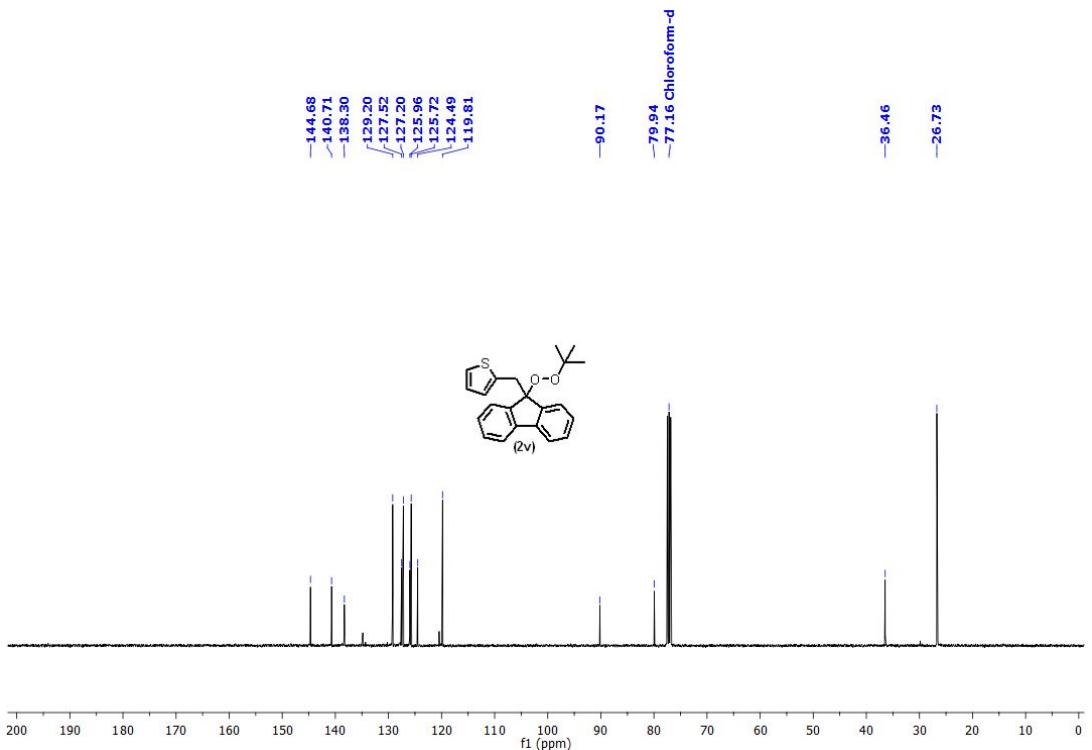
**Figure S45.**  $^1\text{H}$  NMR of Compound **2u** at 400 MHz in  $\text{CDCl}_3$



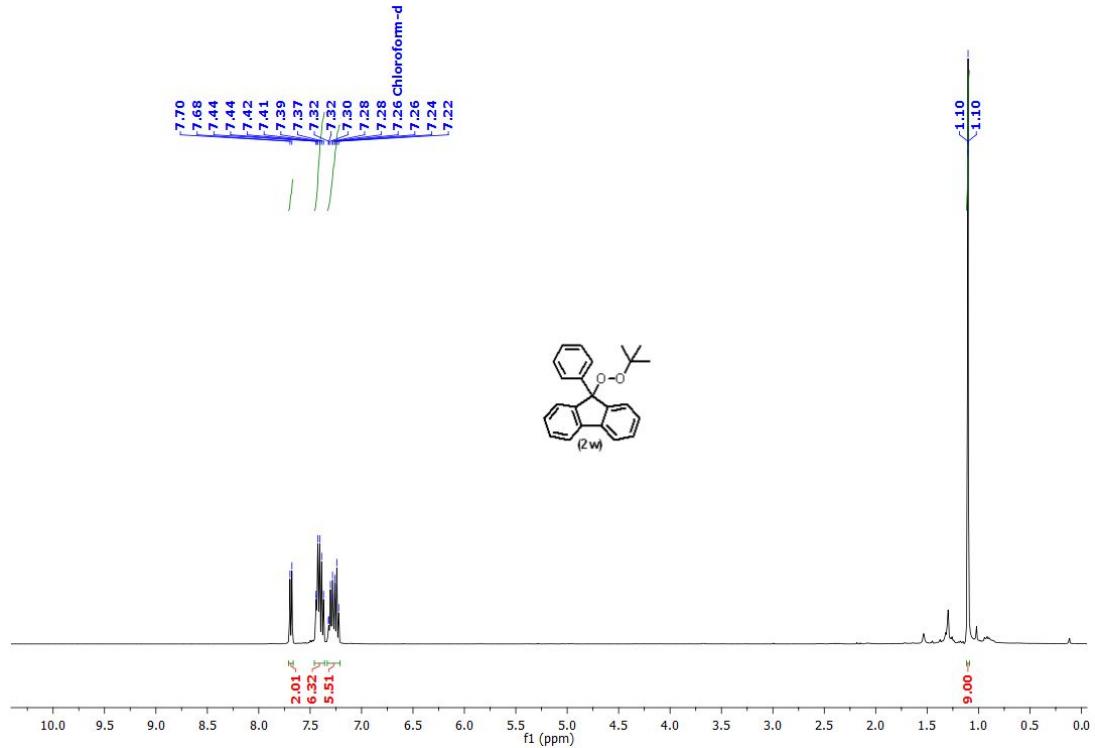
**Figure S46.**  $^{13}\text{C}$  NMR of Compound **2u** at 100 MHz in  $\text{CDCl}_3$



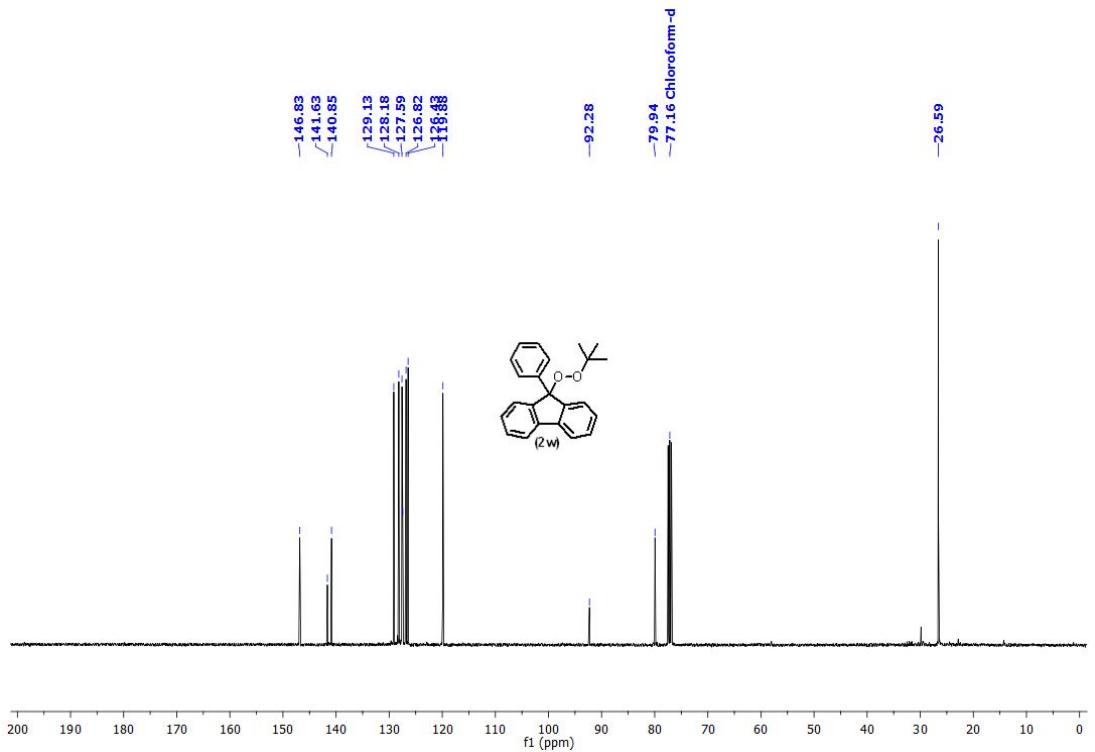
**Figure S47.**  $^1\text{H}$  NMR of Compound **2v** at 400 MHz in  $\text{CDCl}_3$



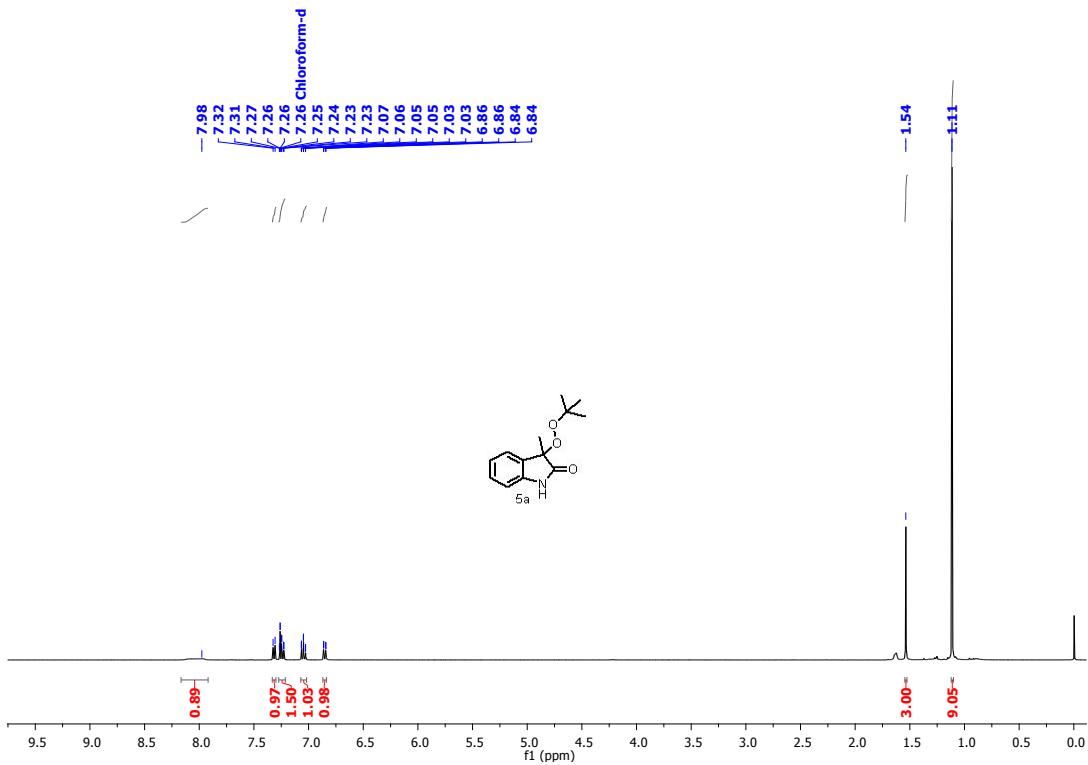
**Figure S48.**  $^{13}\text{C}$  NMR of Compound **2v** at 100 MHz in  $\text{CDCl}_3$



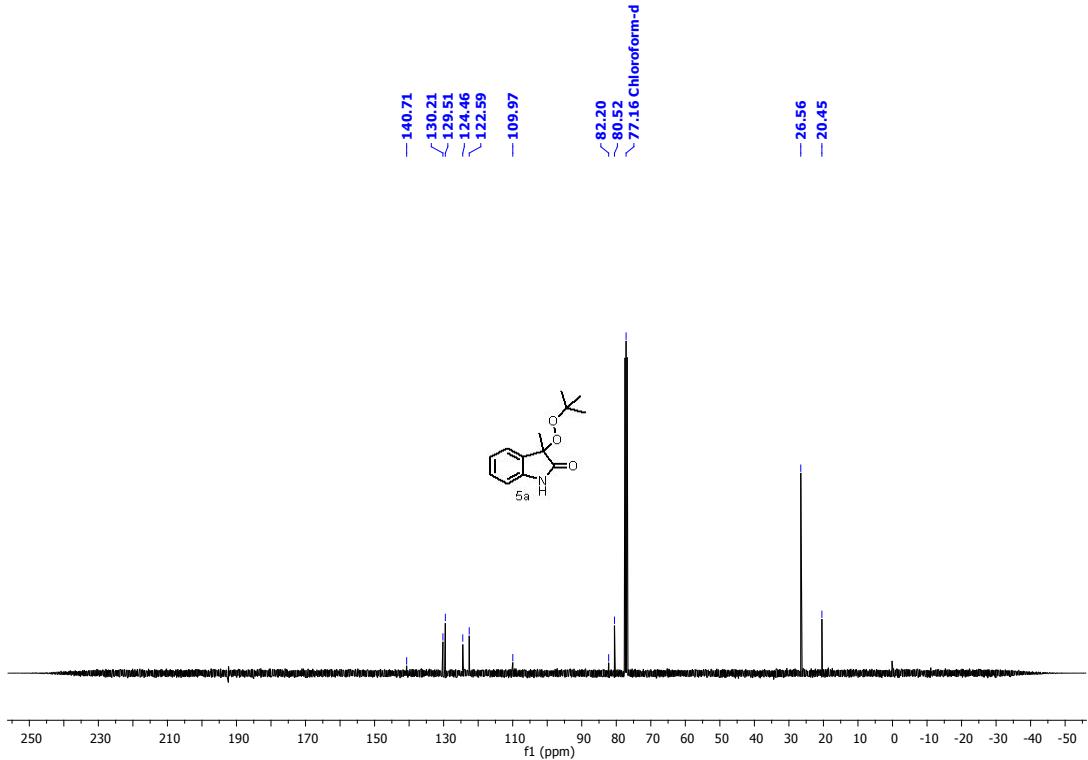
**Figure S49.**  $^1\text{H}$  NMR of Compound **2w** at 400 MHz in  $\text{CDCl}_3$



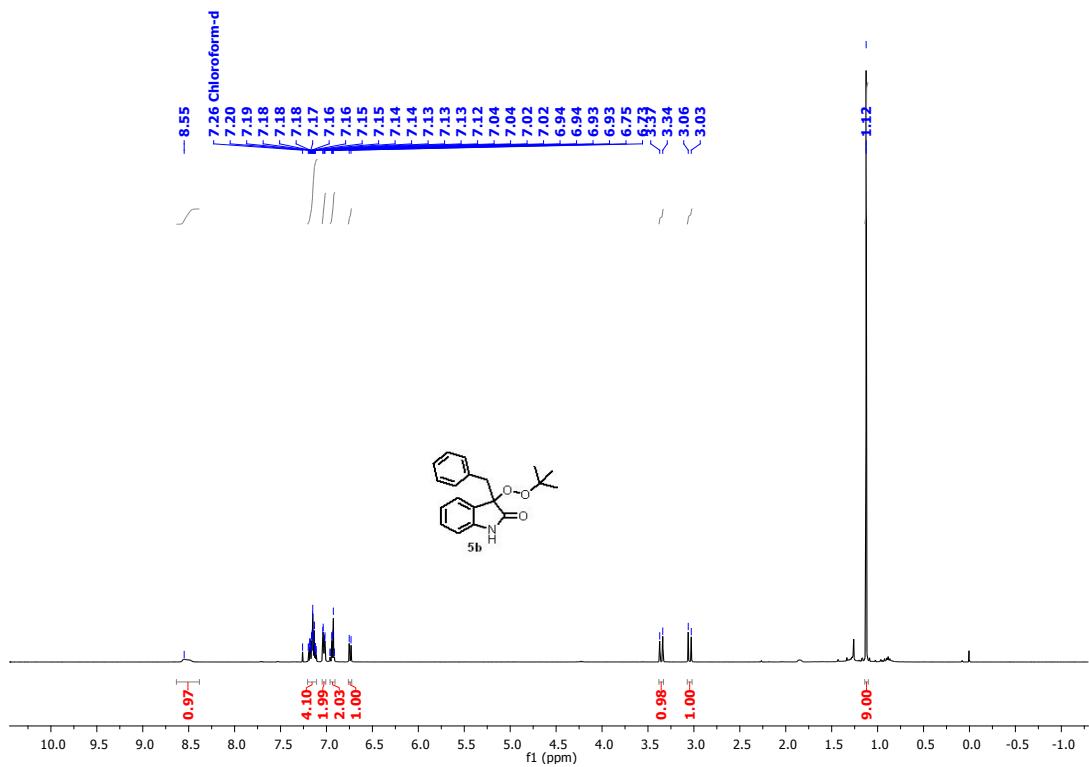
**Figure S50.**  $^{13}\text{C}$  NMR of Compound **2w** at 100 MHz in  $\text{CDCl}_3$



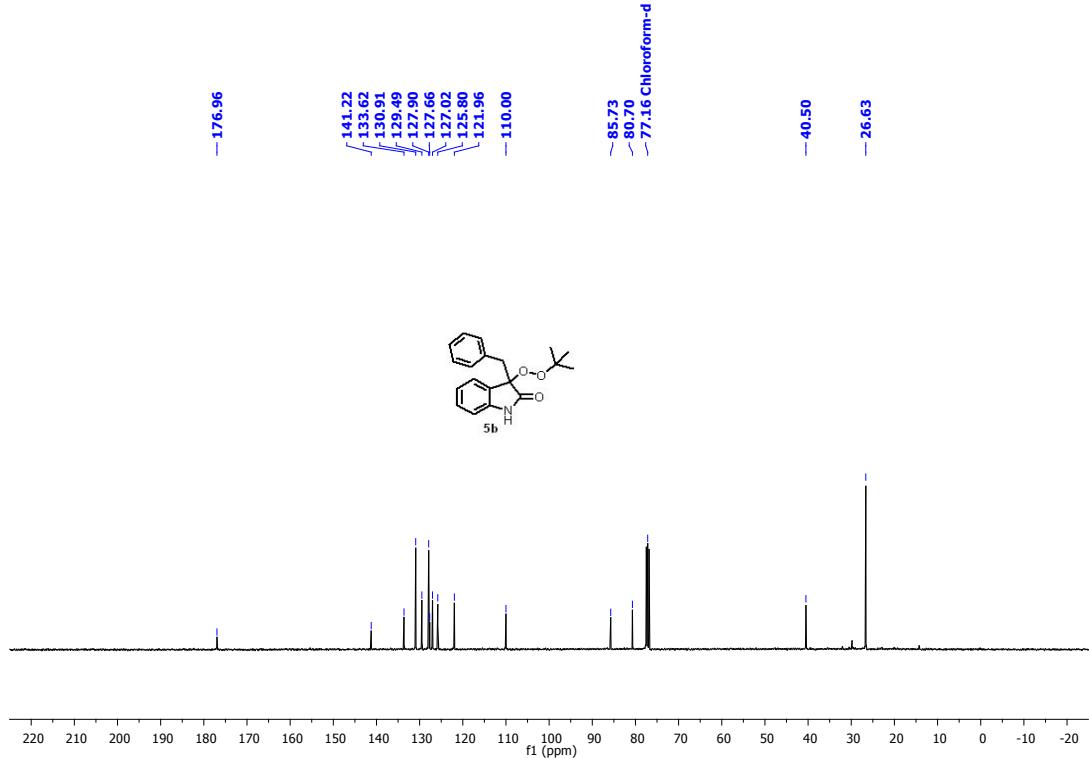
**Figure S51.**  $^1\text{H}$  NMR of Compound 5a at 400 MHz in  $\text{CDCl}_3$



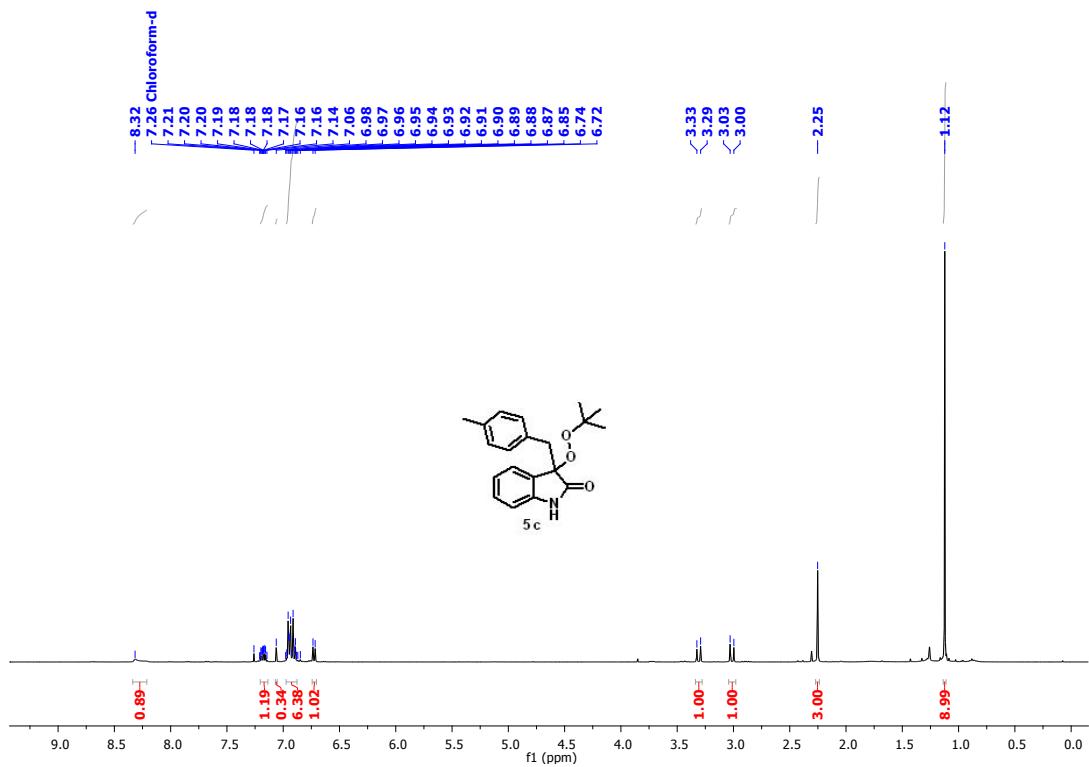
**Figure S52.**  $^{13}\text{C}$  NMR of Compound 5a at 100 MHz in  $\text{CDCl}_3$



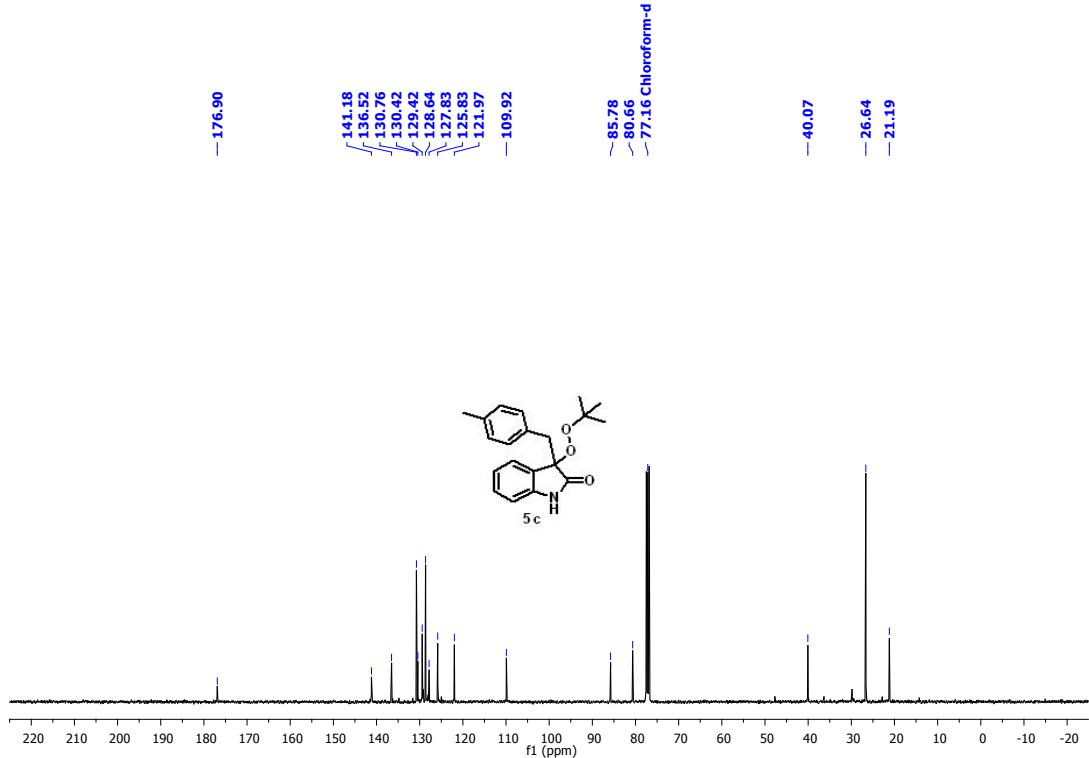
**Figure S53.**  $^1\text{H}$  NMR of Compound **5b** at 400 MHz in  $\text{CDCl}_3$



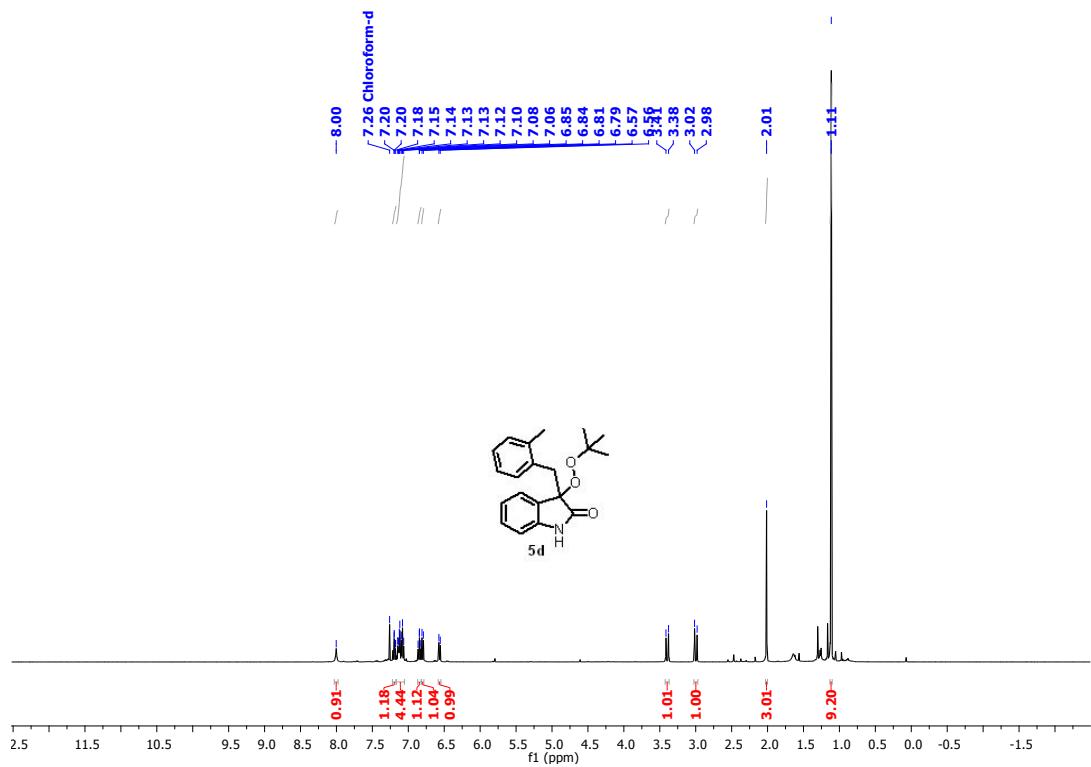
**Figure S54.**  $^{13}\text{C}$  NMR of Compound **5b** at 100 MHz in  $\text{CDCl}_3$



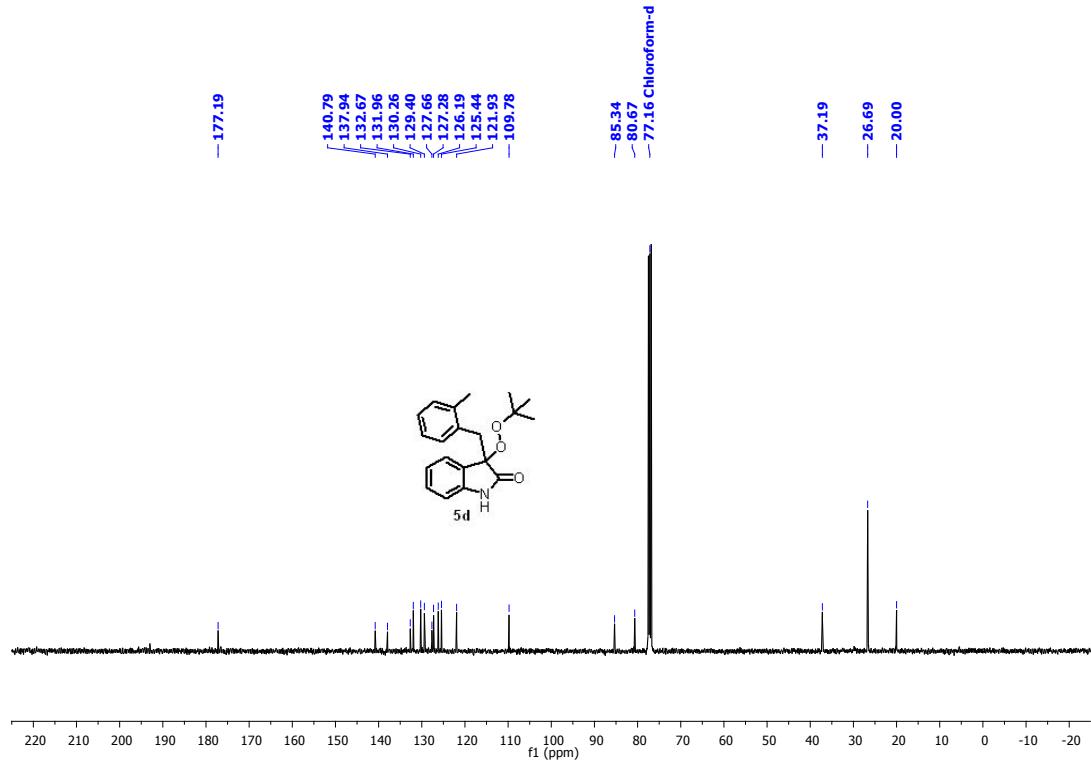
**Figure S55.**  $^1\text{H}$  NMR of Compound 5c at 400 MHz in  $\text{CDCl}_3$



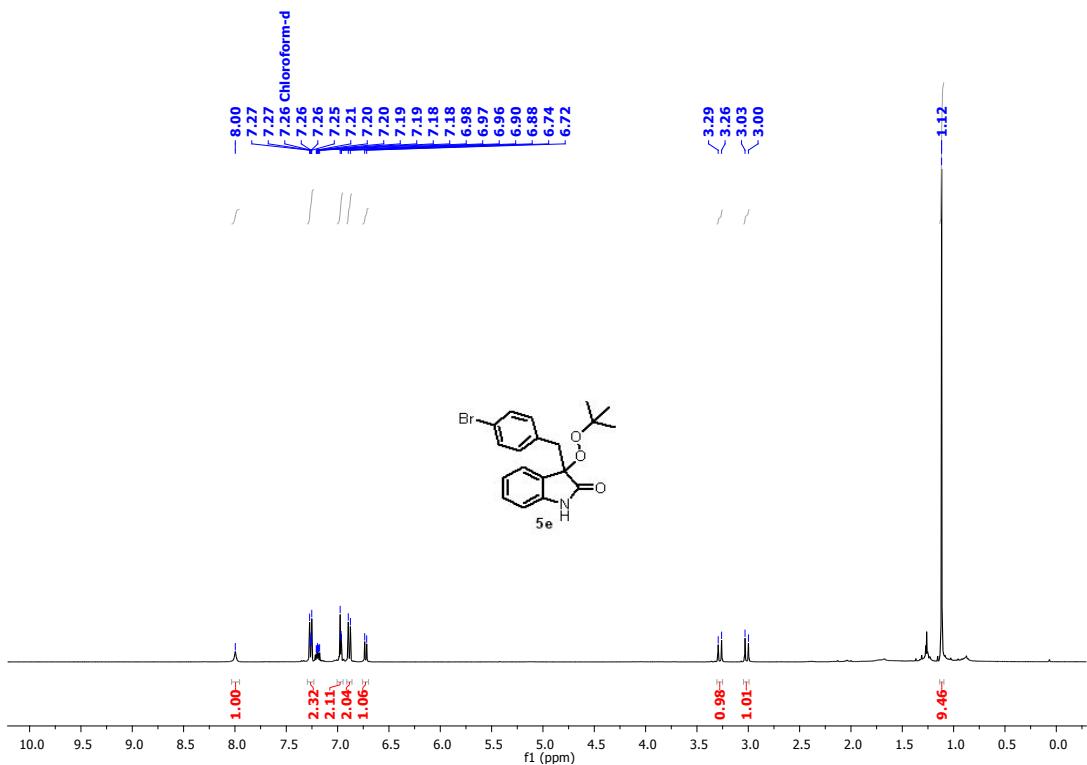
**Figure S56.**  $^{13}\text{C}$  NMR of Compound 5c at 100 MHz in  $\text{CDCl}_3$



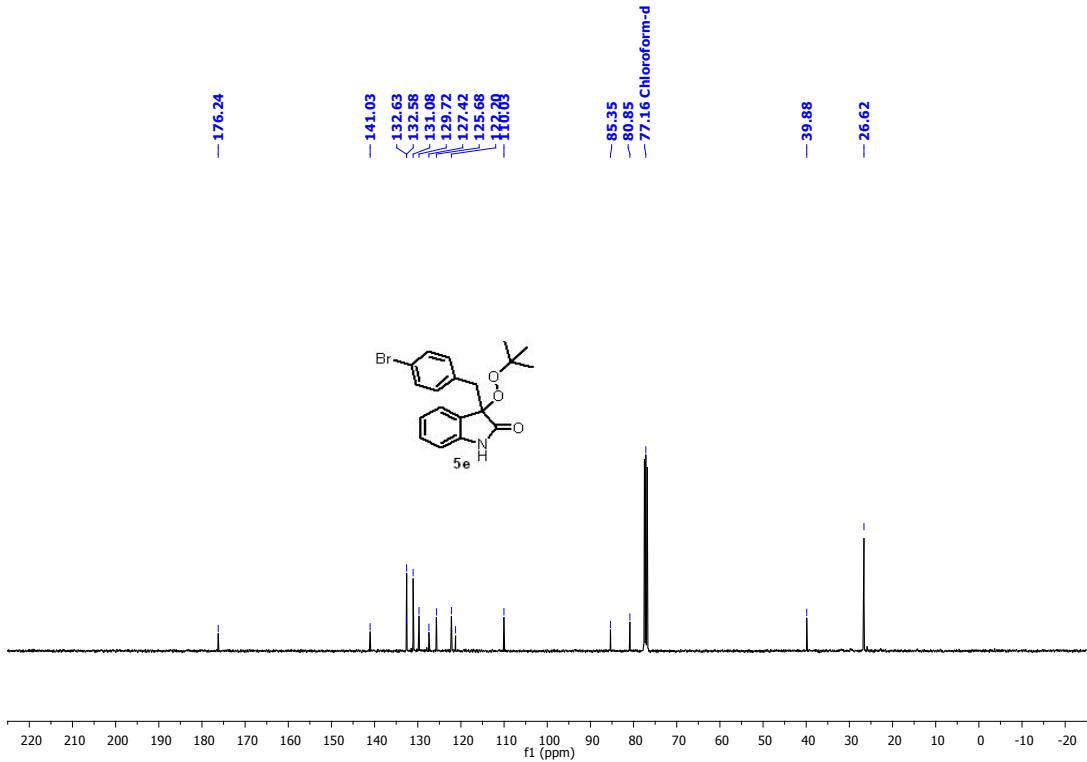
**Figure S57.**  $^1\text{H}$  NMR of Compound **5d** at 400 MHz in  $\text{CDCl}_3$



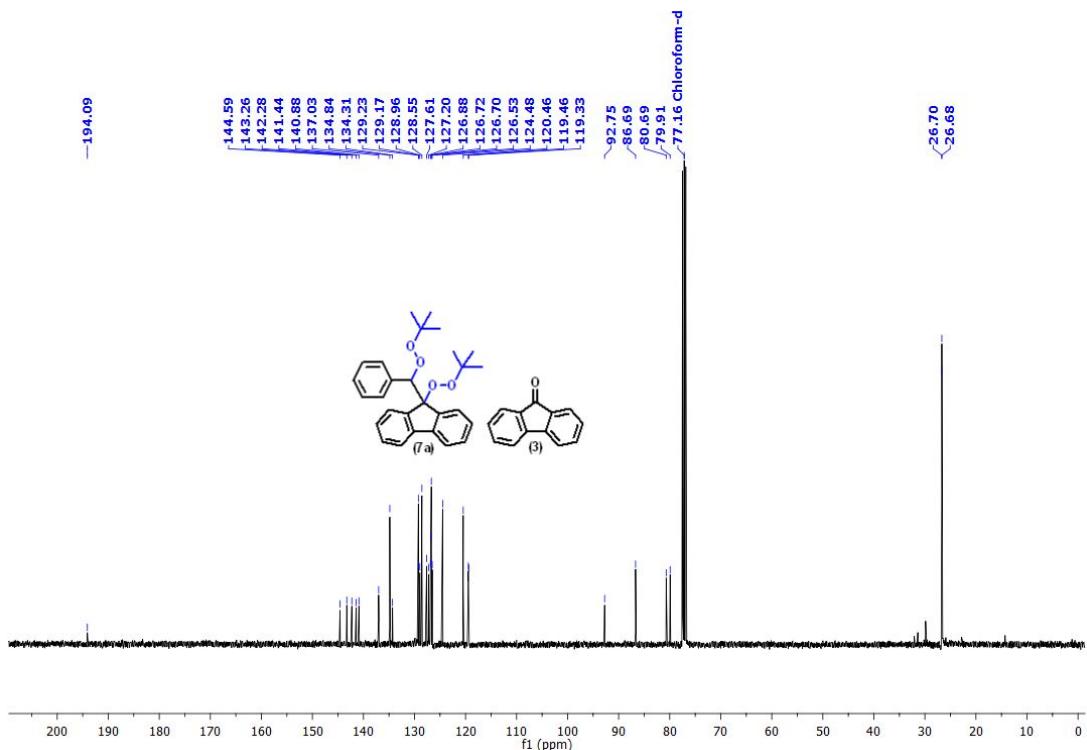
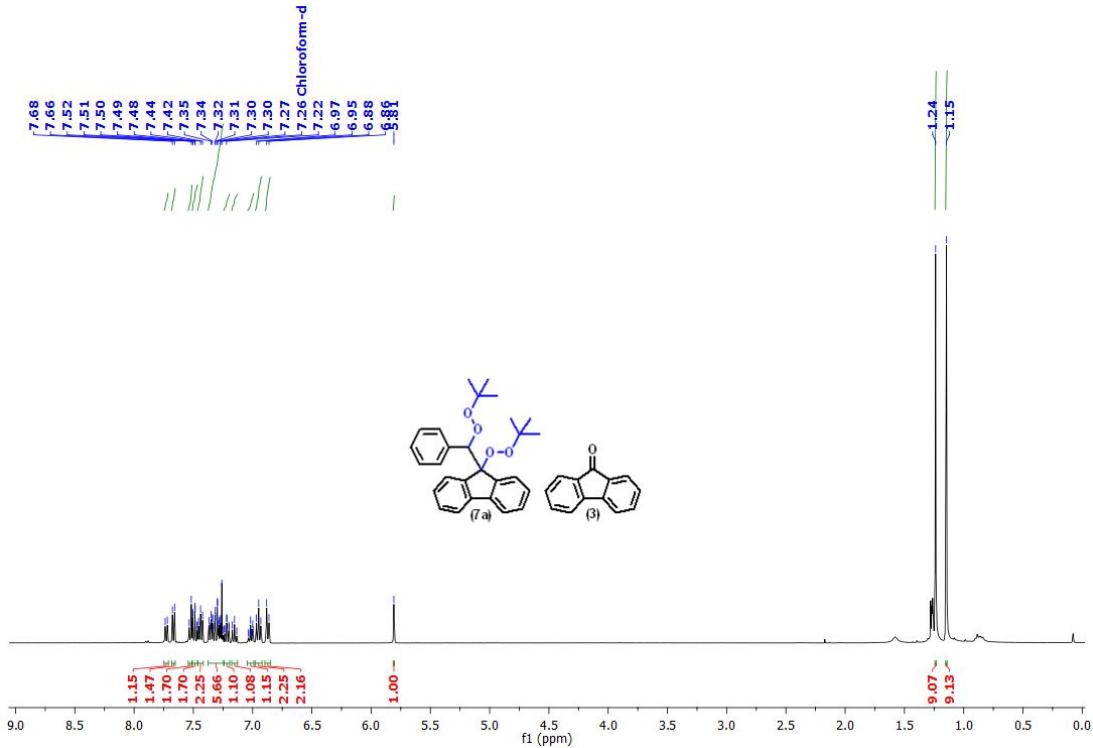
**Figure S58.**  $^{13}\text{C}$  NMR of Compound **5d** at 100 MHz in  $\text{CDCl}_3$



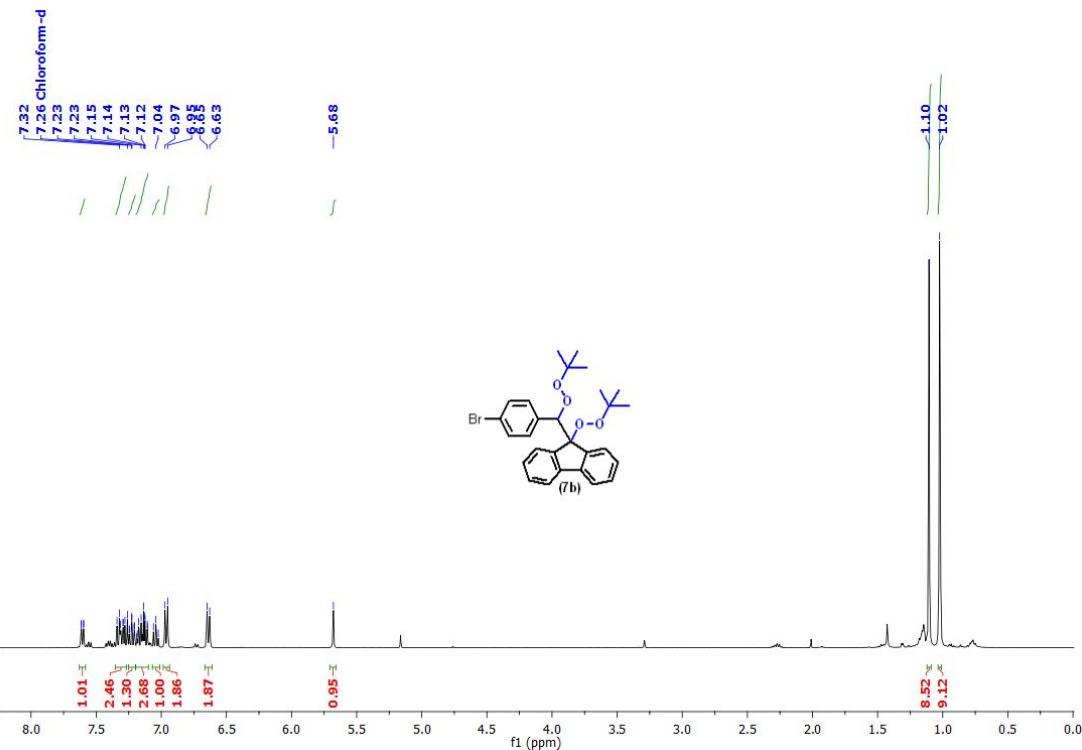
**Figure S59.**  $^1\text{H}$  NMR of Compound **5e** at 400 MHz in  $\text{CDCl}_3$



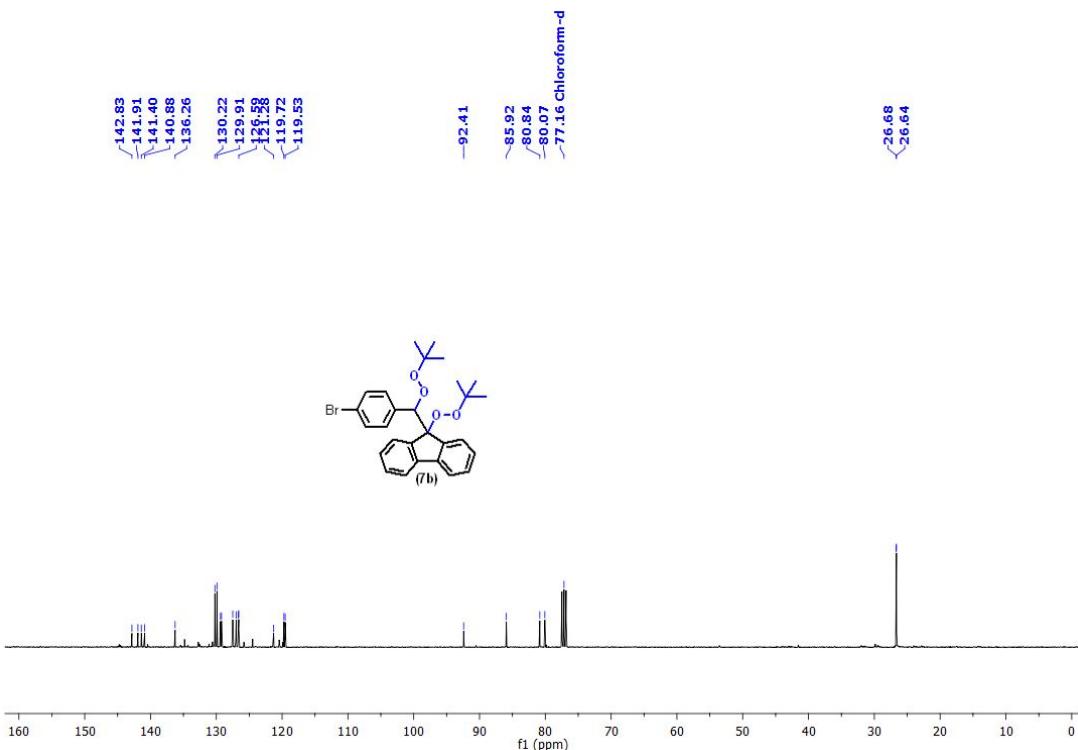
**Figure S60.**  $^{13}\text{C}$  NMR of Compound **5e** at 100 MHz in  $\text{CDCl}_3$



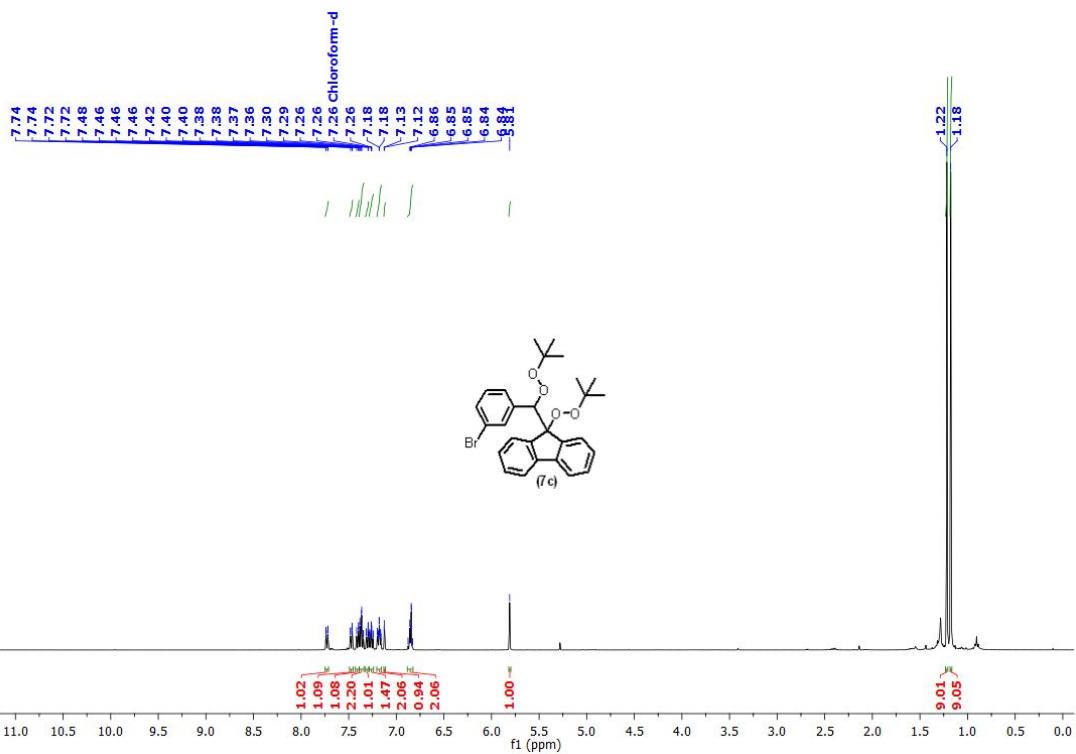
**Figure S62.**  $^{13}\text{C}$  NMR of Compound **7a** at 100 MHz in  $\text{CDCl}_3$



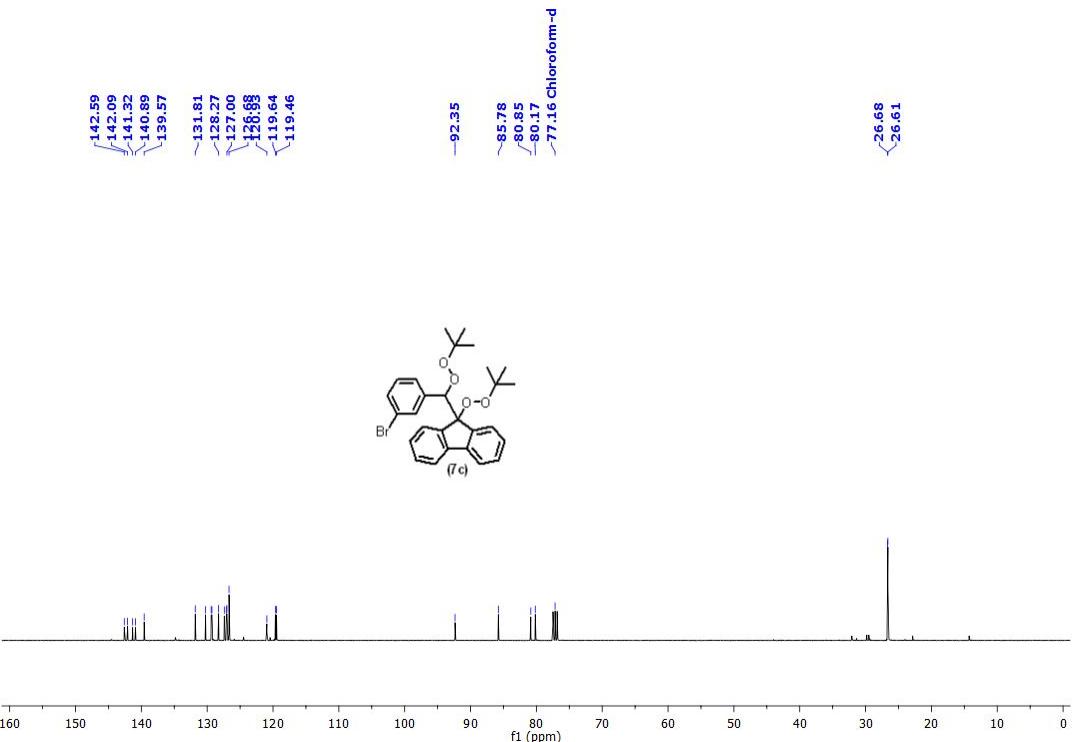
**Figure S63.**  $^1\text{H}$  NMR of Compound **7b** at 400 MHz in  $\text{CDCl}_3$



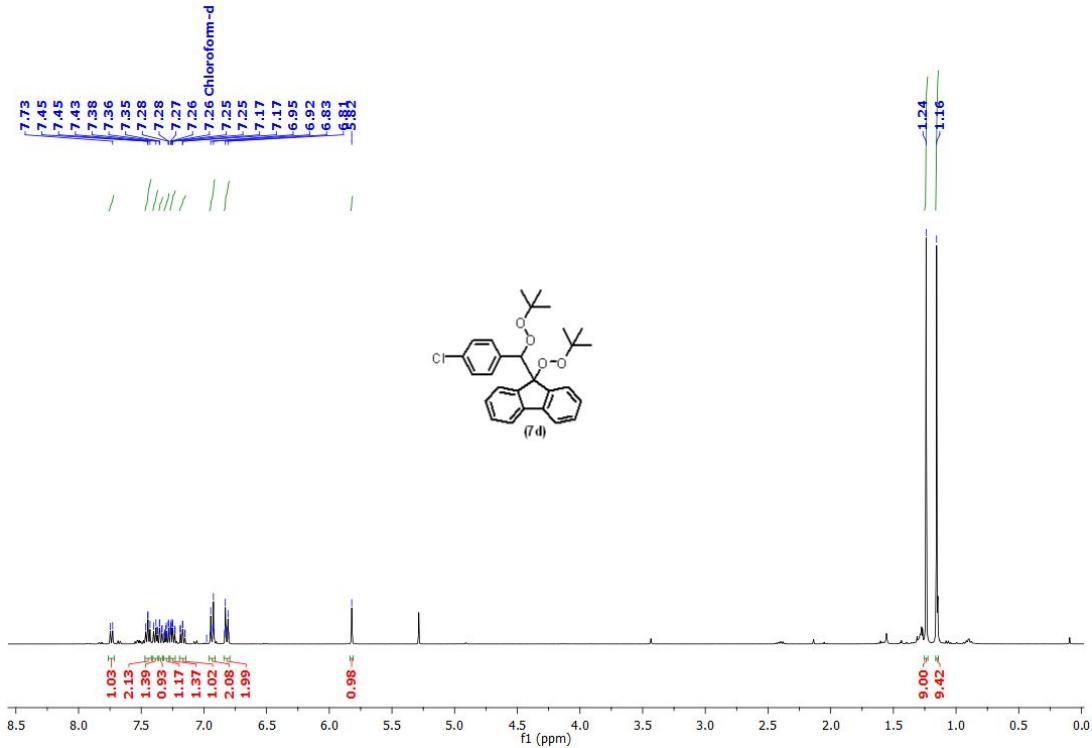
**Figure S64.**  $^{13}\text{C}$  NMR of Compound **7b** at 100 MHz in  $\text{CDCl}_3$



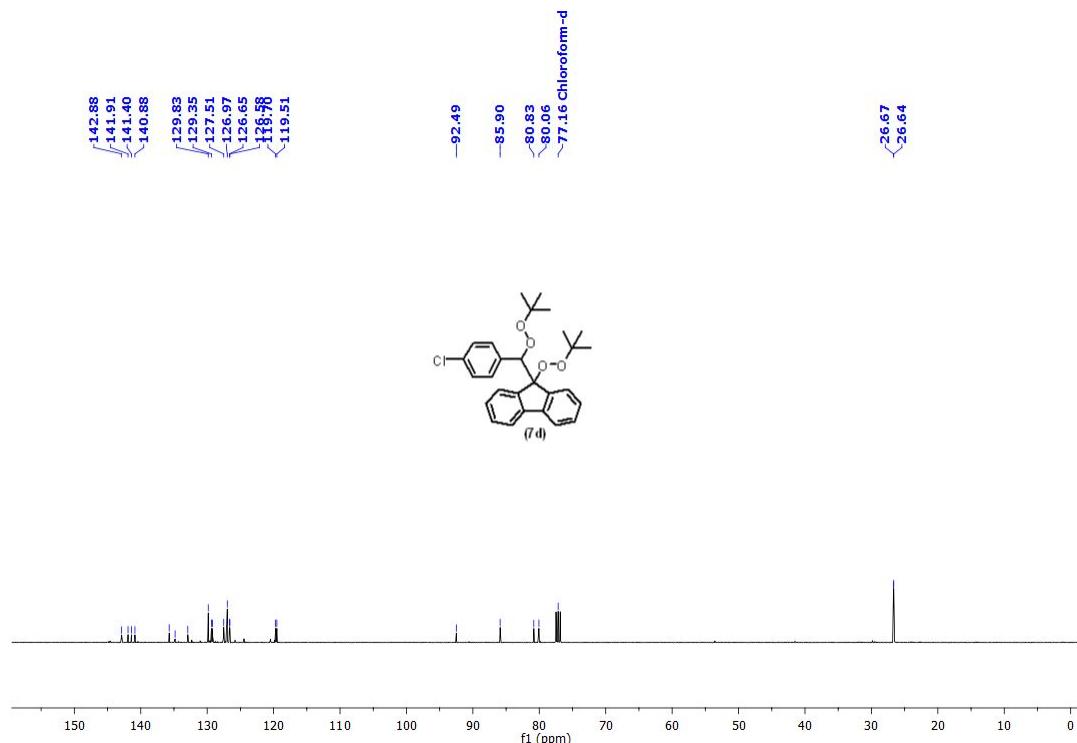
**Figure S65.** <sup>1</sup>H NMR of Compound 7c at 400 MHz in CDCl<sub>3</sub>



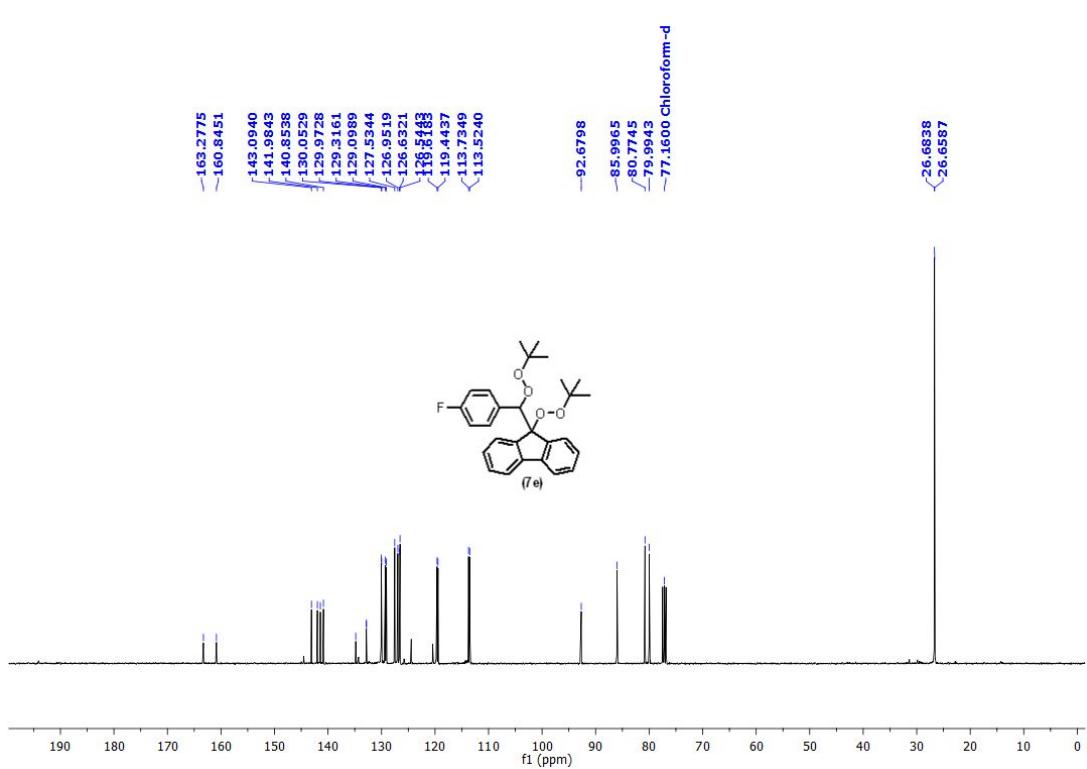
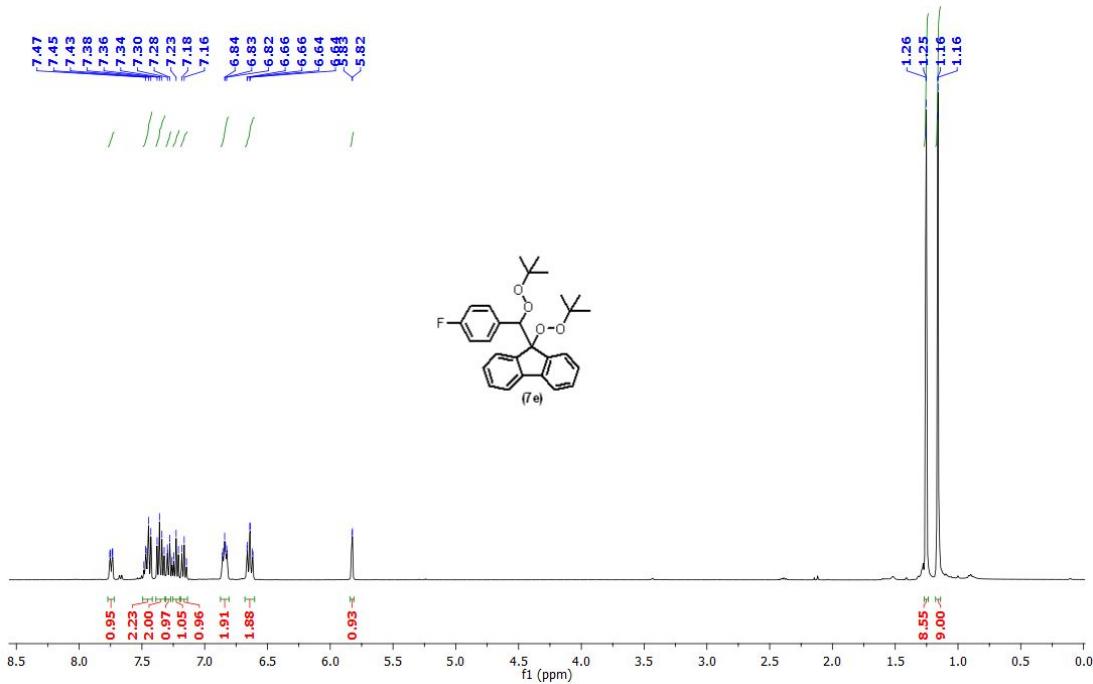
**Figure S66.** <sup>13</sup>C NMR of Compound 7c at 100 MHz in CDCl<sub>3</sub>

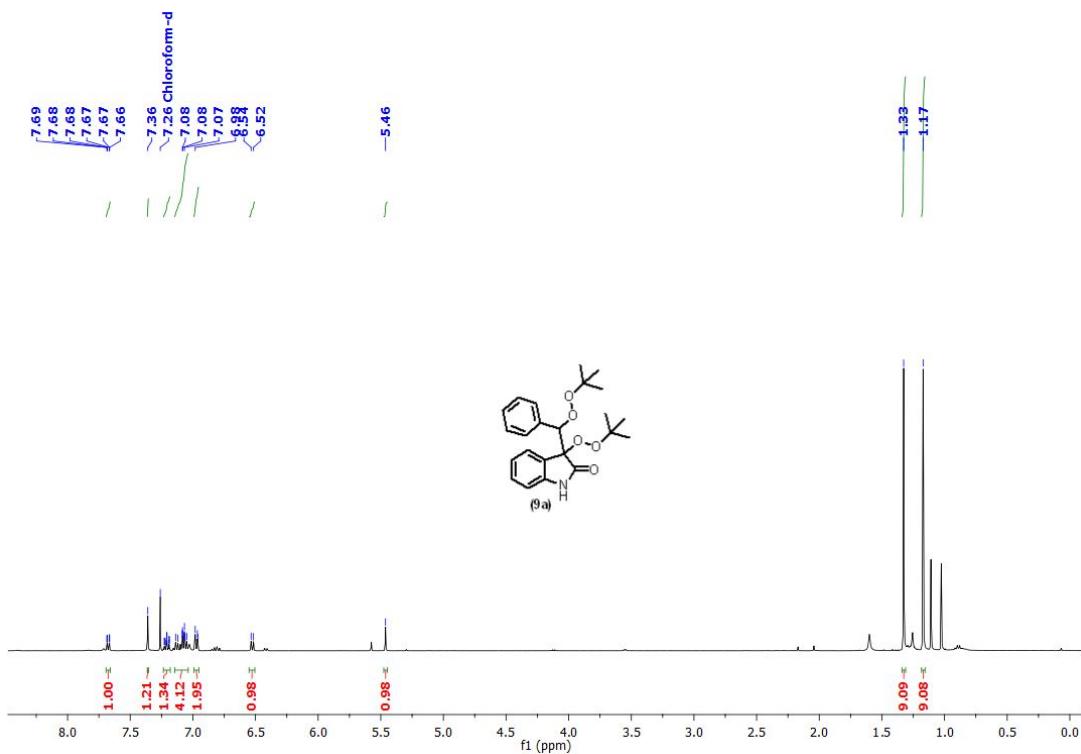


**Figure S67.**  $^1\text{H}$  NMR of Compound **7d** at 400 MHz in  $\text{CDCl}_3$

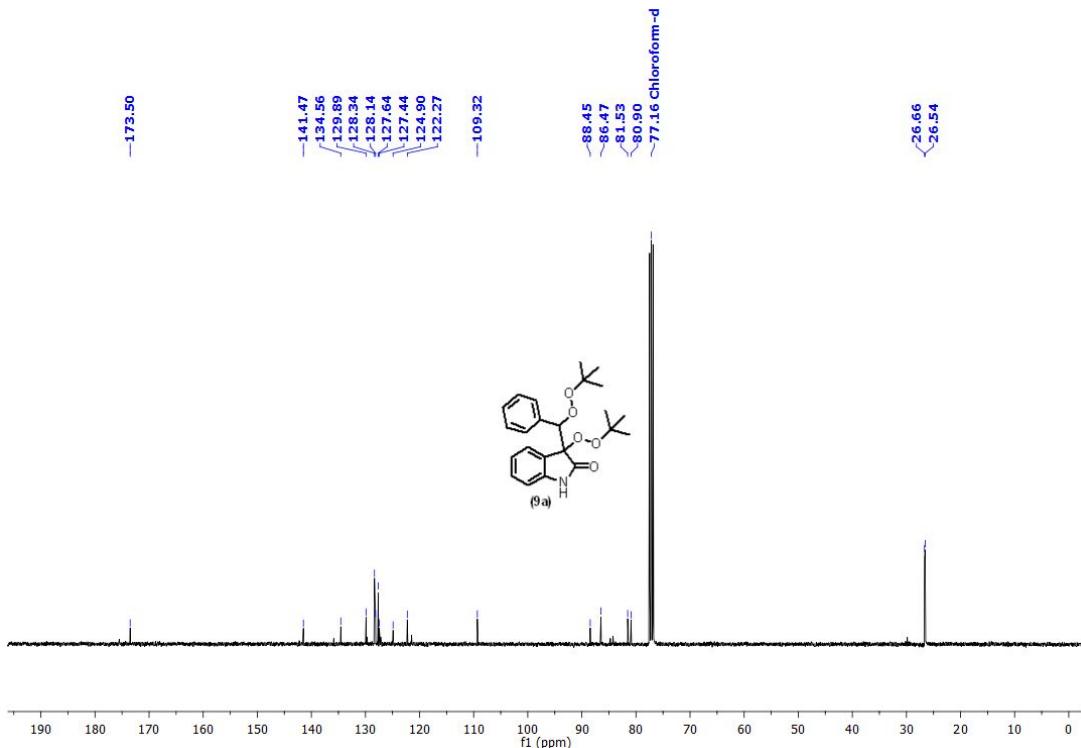


**Figure S68.**  $^{13}\text{C}$  NMR of Compound **7d** at 100 MHz in  $\text{CDCl}_3$

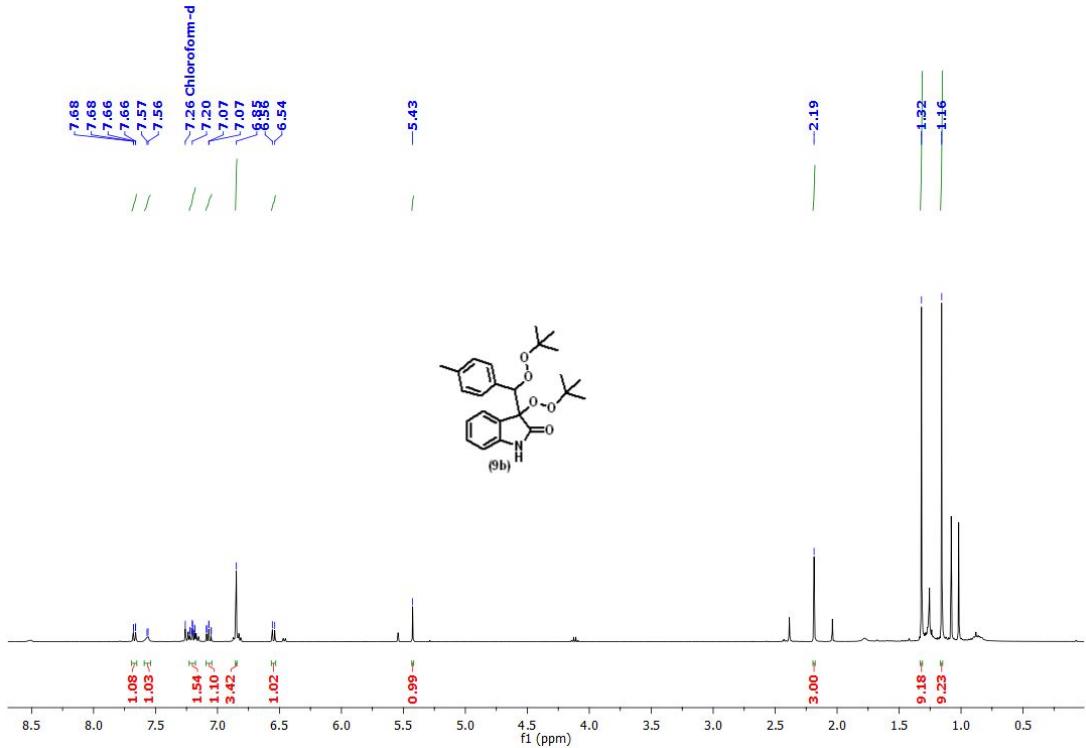




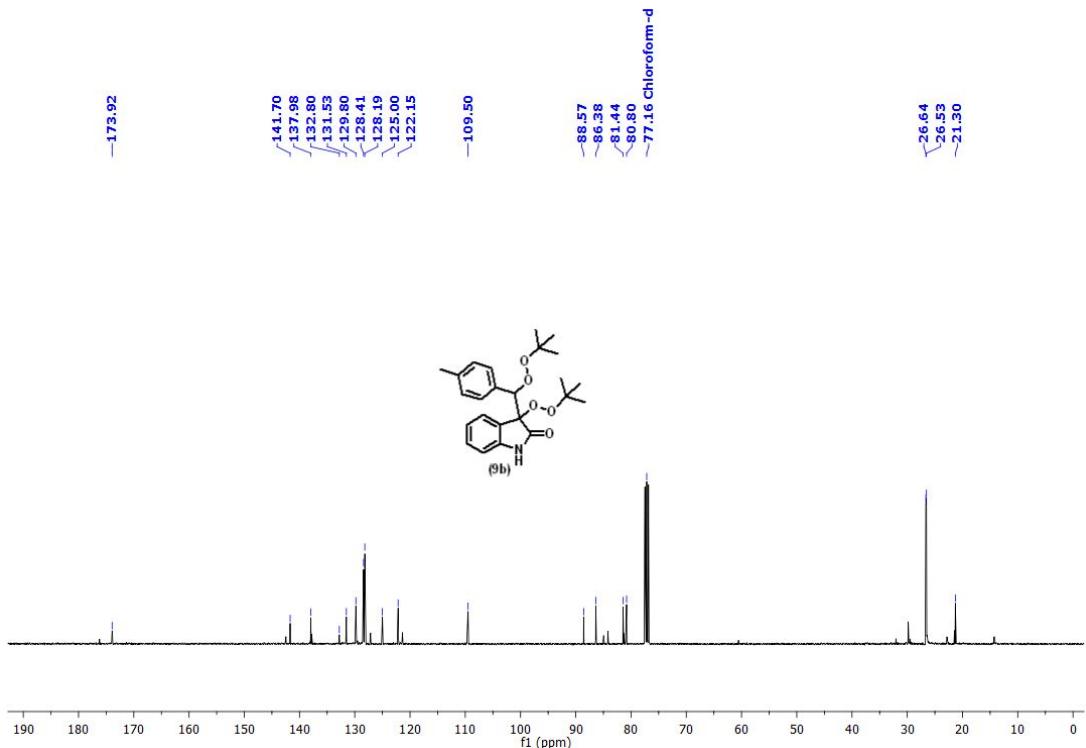
**Figure S71.**  $^1\text{H}$  NMR of Compound **9a** at 400 MHz in  $\text{CDCl}_3$



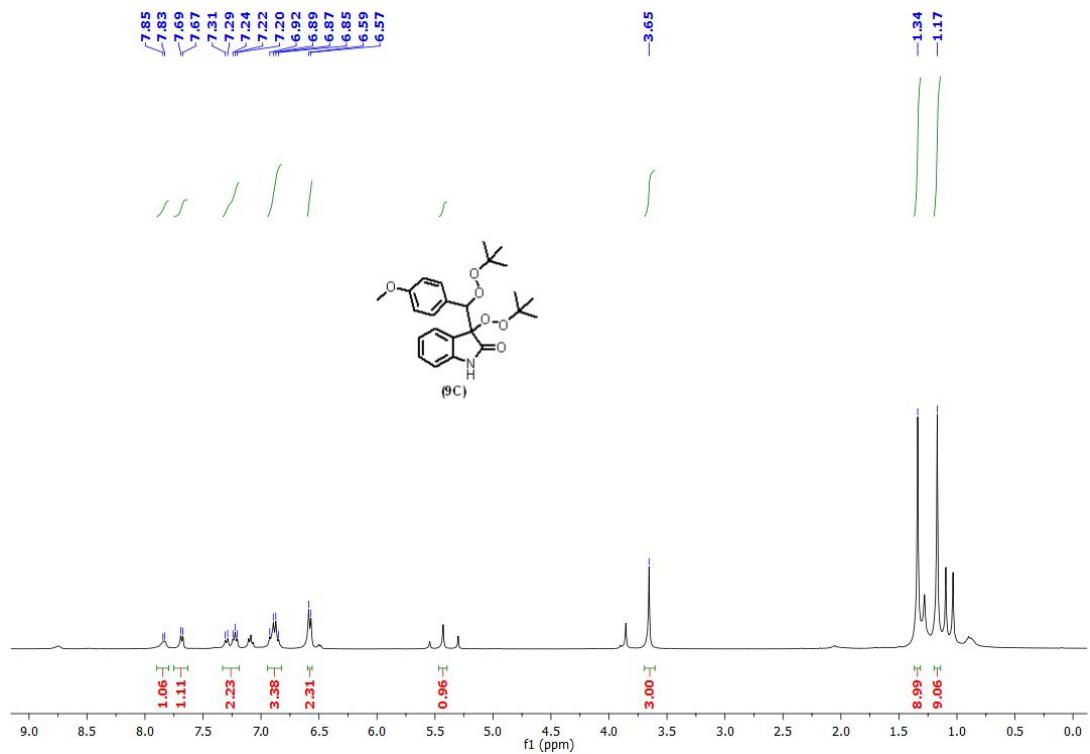
**Figure S72.**  $^{13}\text{C}$  NMR of Compound **9a** at 100 MHz in  $\text{CDCl}_3$



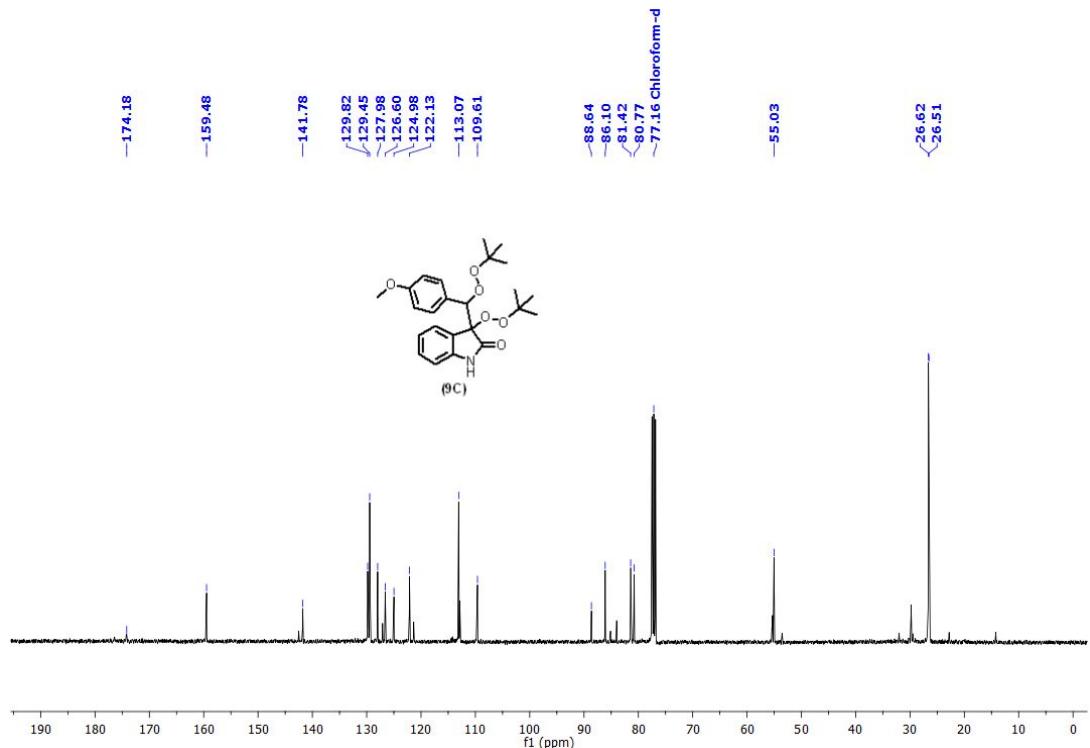
**Figure S73.**  $^1\text{H}$  NMR of Compound **9b** at 400 MHz in  $\text{CDCl}_3$



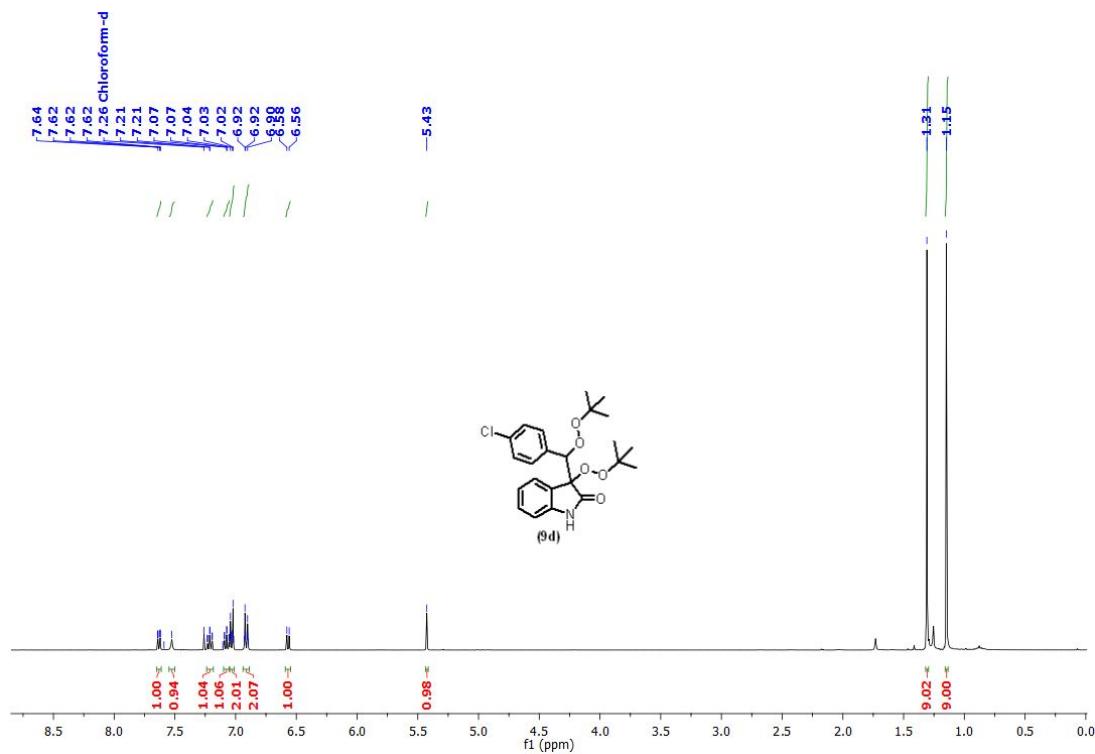
**Figure S74.**  $^{13}\text{C}$  NMR of Compound **9b** at 100 MHz in  $\text{CDCl}_3$



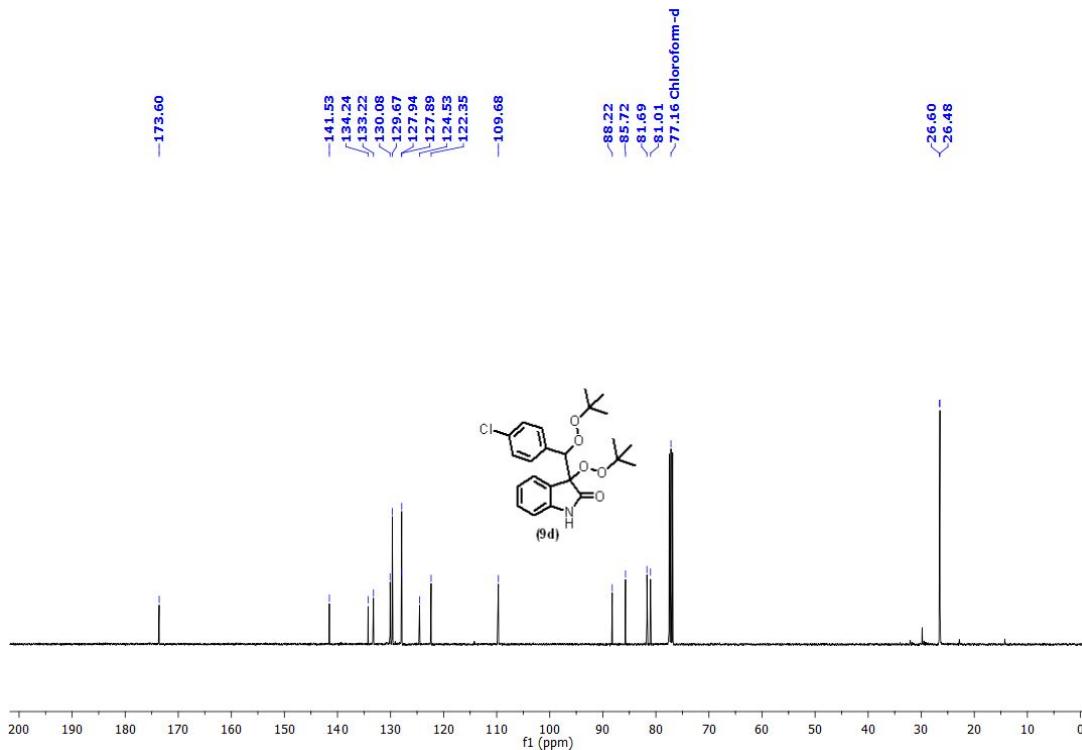
**Figure S75.** <sup>1</sup>H NMR of Compound 9c at 400 MHz in CDCl<sub>3</sub>



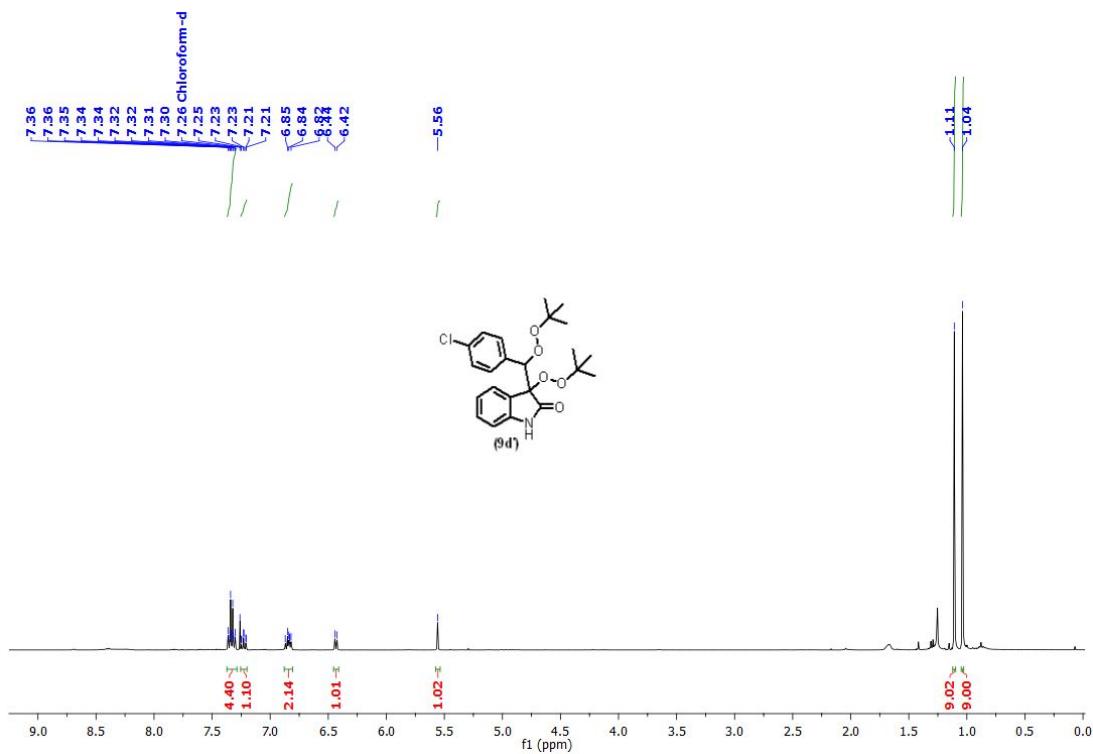
**Figure S76.** <sup>13</sup>C NMR of Compound 9c at 100 MHz in CDCl<sub>3</sub>



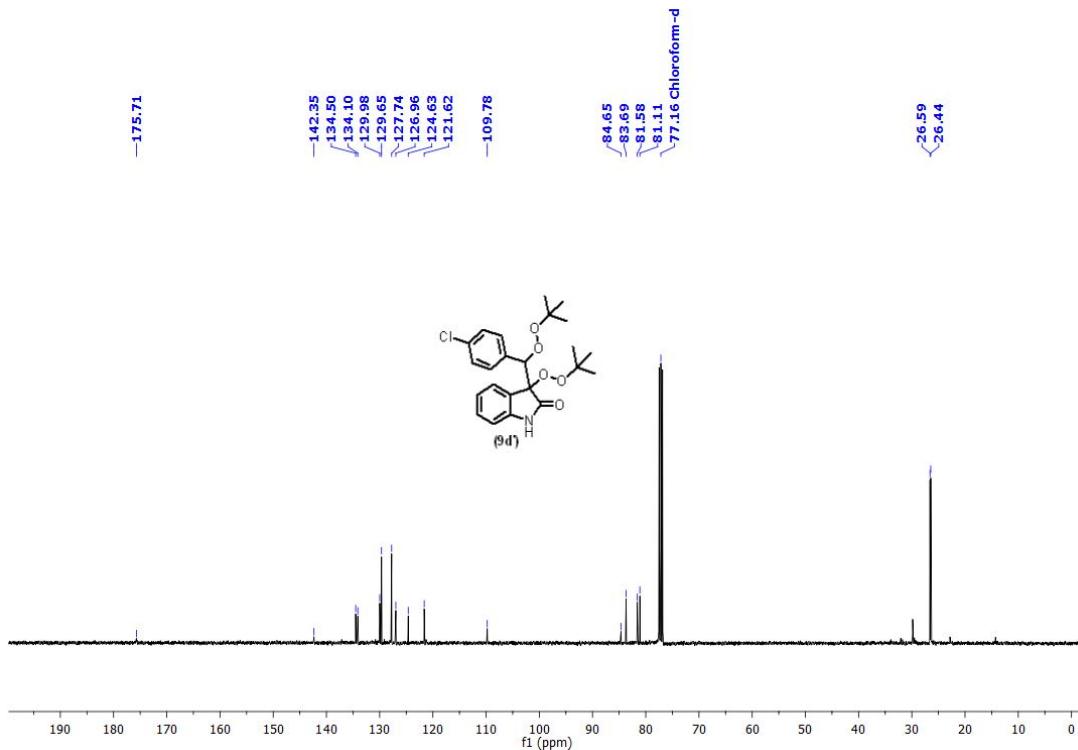
**Figure S77.**  $^1\text{H}$  NMR of Compound **9d** at 400 MHz in  $\text{CDCl}_3$



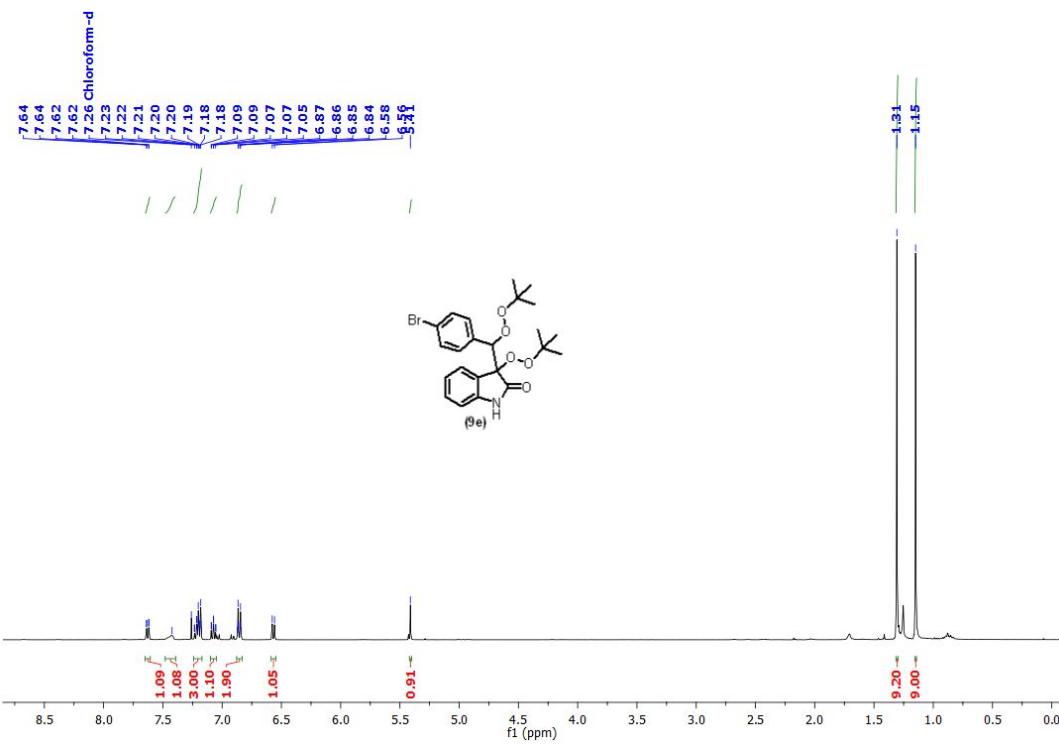
**Figure S78.**  $^{13}\text{C}$  NMR of Compound **9d** at 100 MHz in  $\text{CDCl}_3$



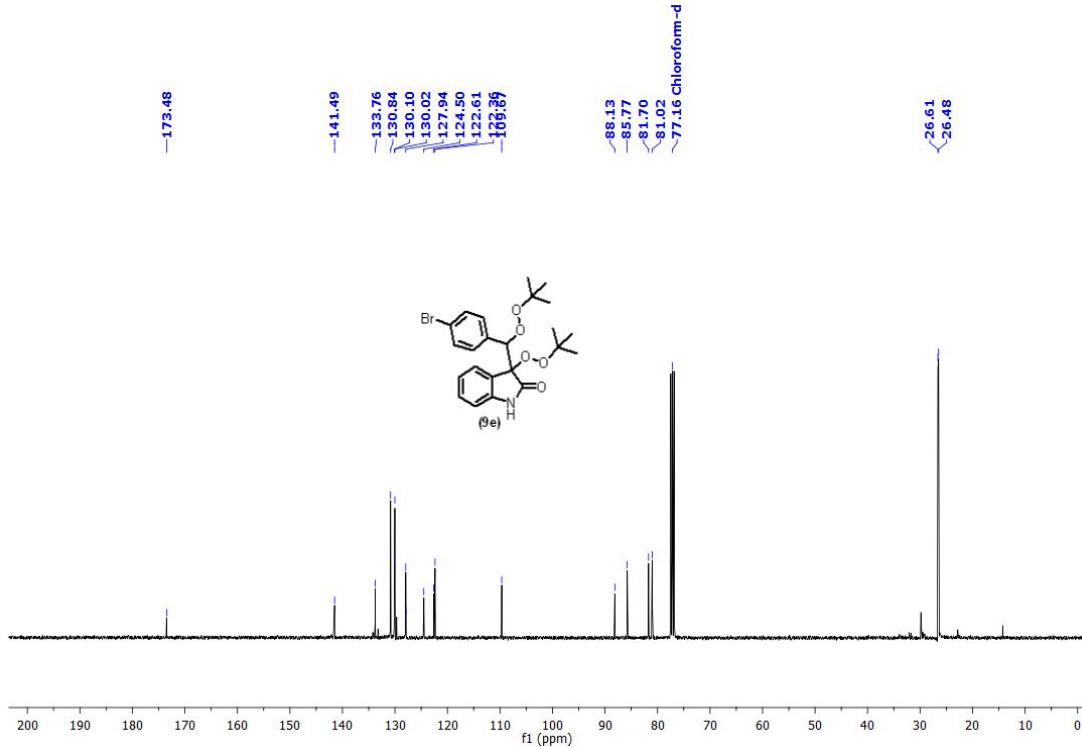
**Figure S79.** <sup>1</sup>H NMR of Compound 9d' at 400 MHz in CDCl<sub>3</sub>



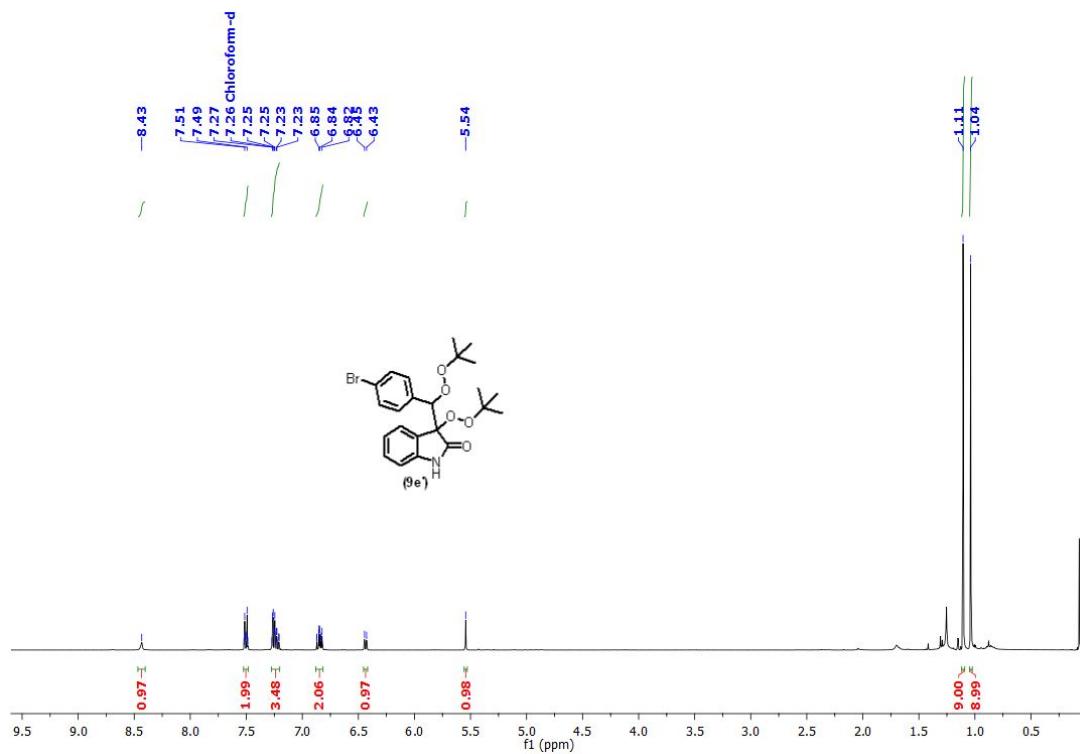
**Figure S80.** <sup>13</sup>C NMR of Compound 9d' at 100 MHz in CDCl<sub>3</sub>



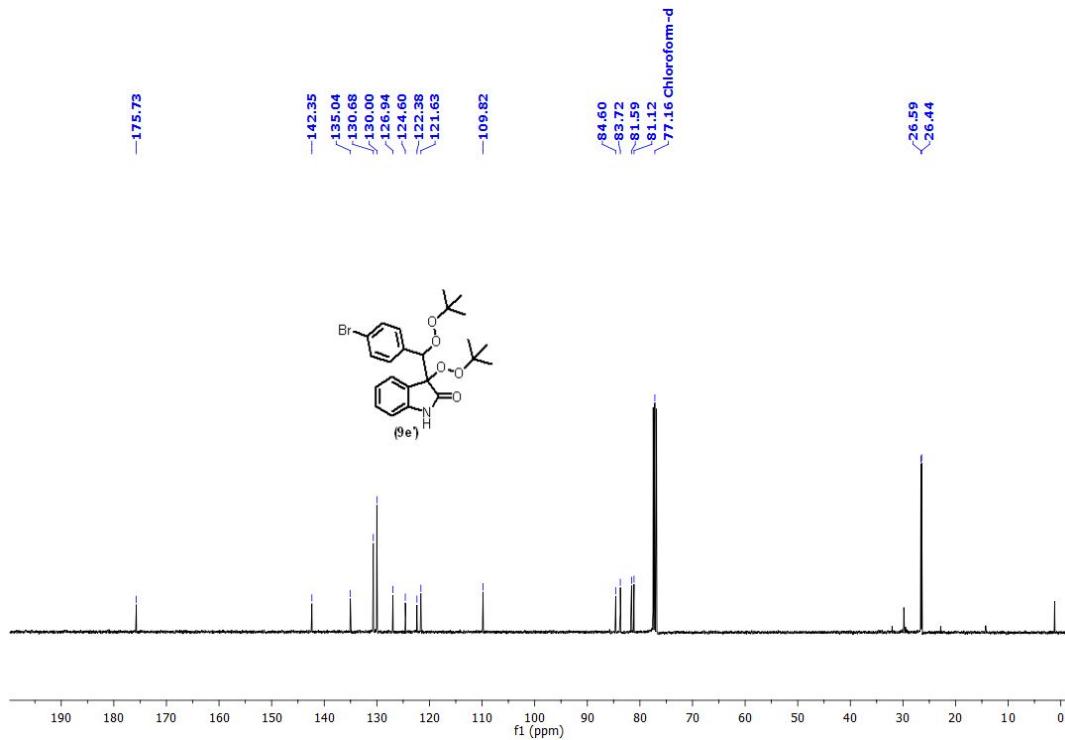
**Figure S81.**  $^1\text{H}$  NMR of Compound **9e** at 400 MHz in  $\text{CDCl}_3$



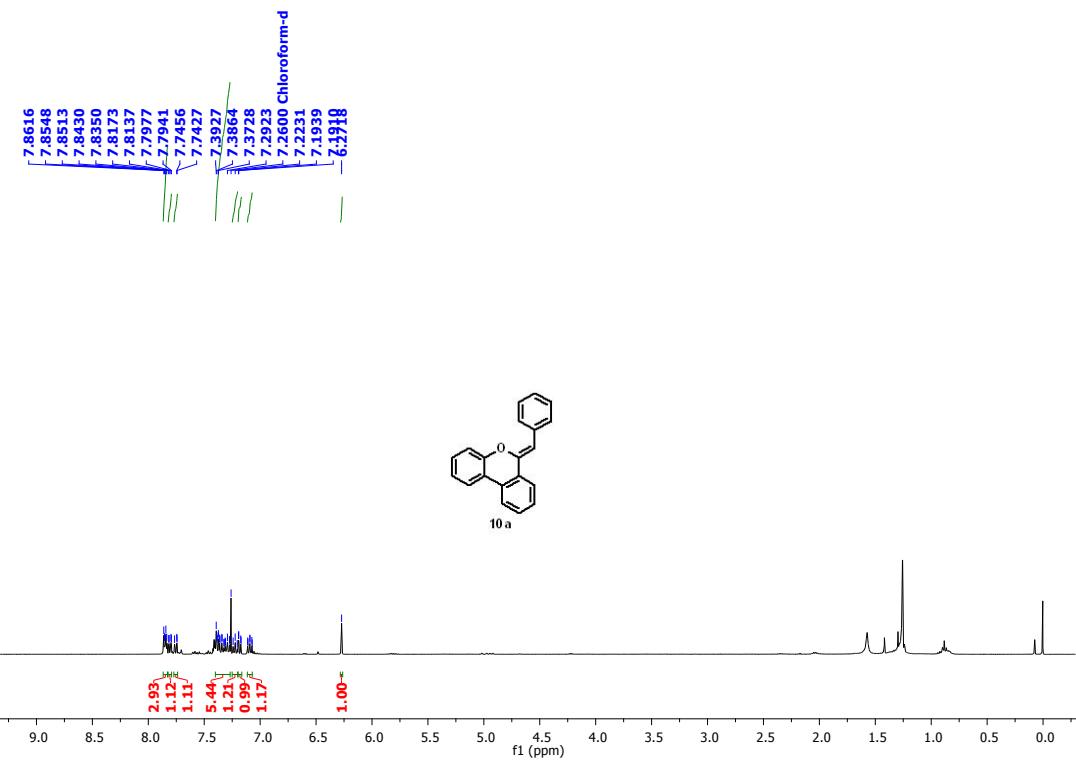
**Figure S82.**  $^{13}\text{C}$  NMR of Compound **9e** at 100 MHz in  $\text{CDCl}_3$



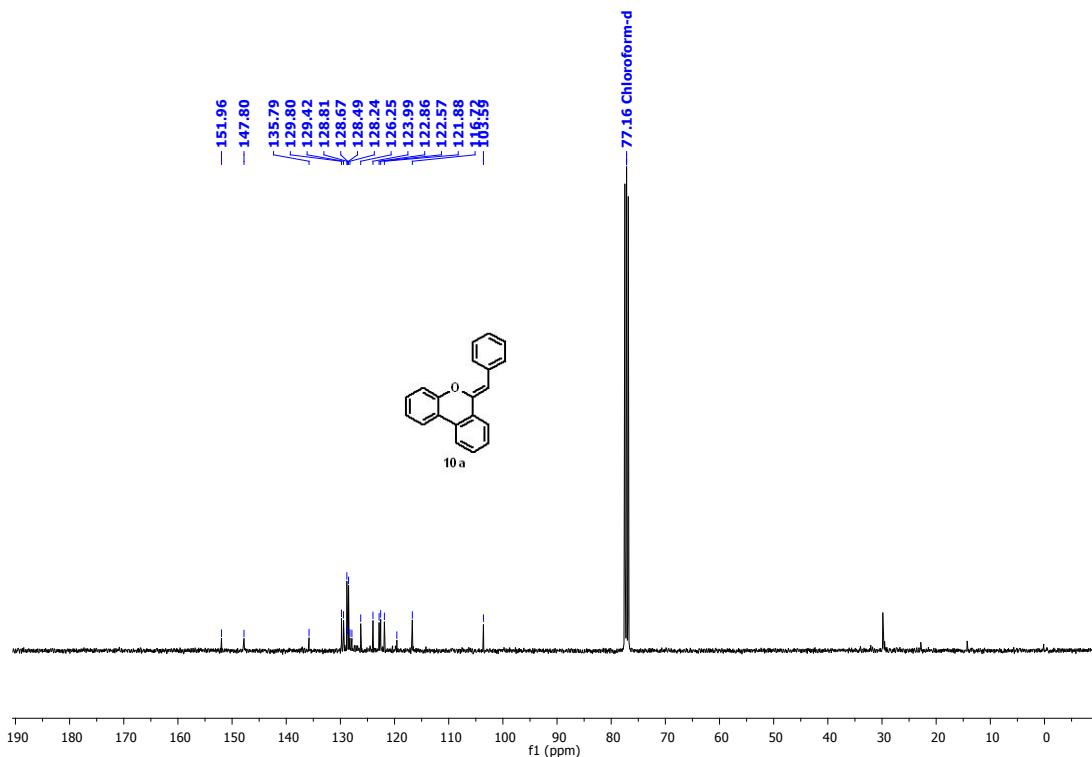
**Figure S83.**  $^1\text{H}$  NMR of Compound **9e'** at 400 MHz in  $\text{CDCl}_3$



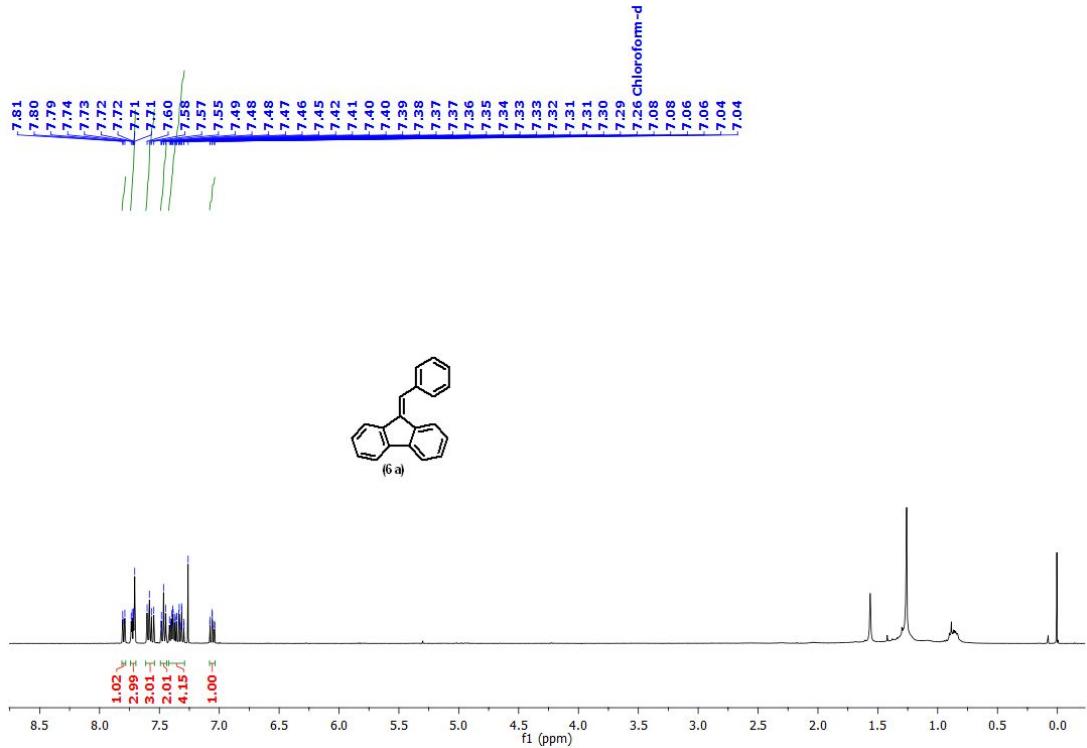
**Figure S84.**  $^{13}\text{C}$  NMR of Compound **9e'** at 100 MHz in  $\text{CDCl}_3$



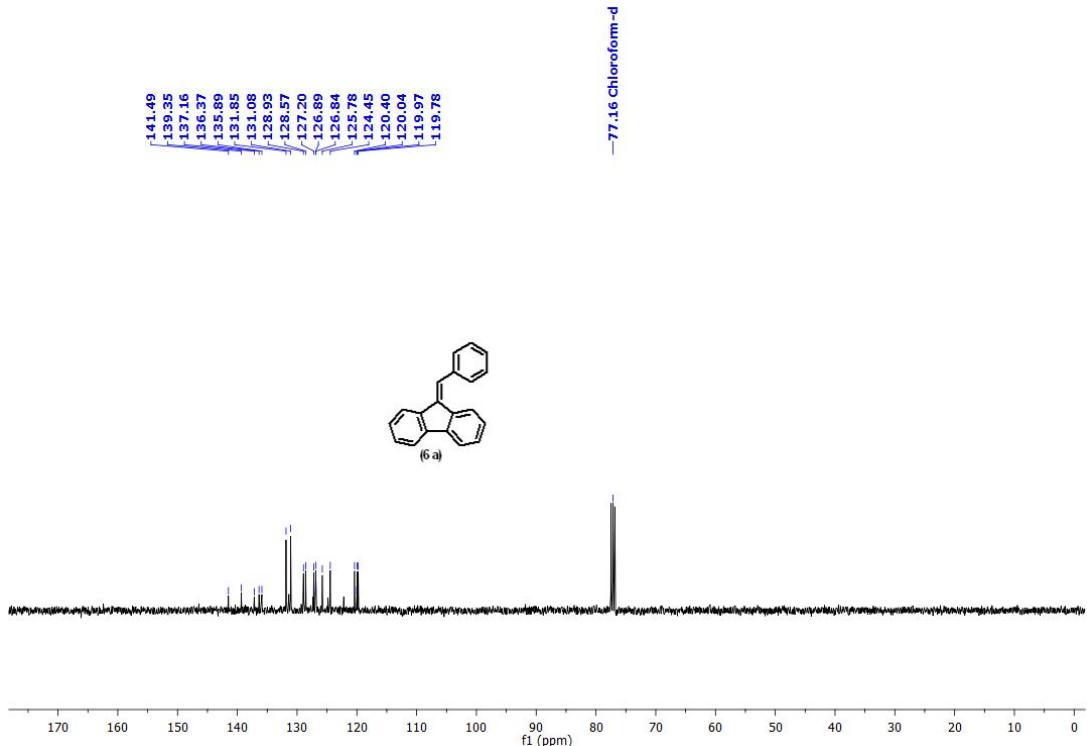
**Figure S85.**  $^1\text{H}$  NMR of Compound **10a** at 400 MHz in  $\text{CDCl}_3$



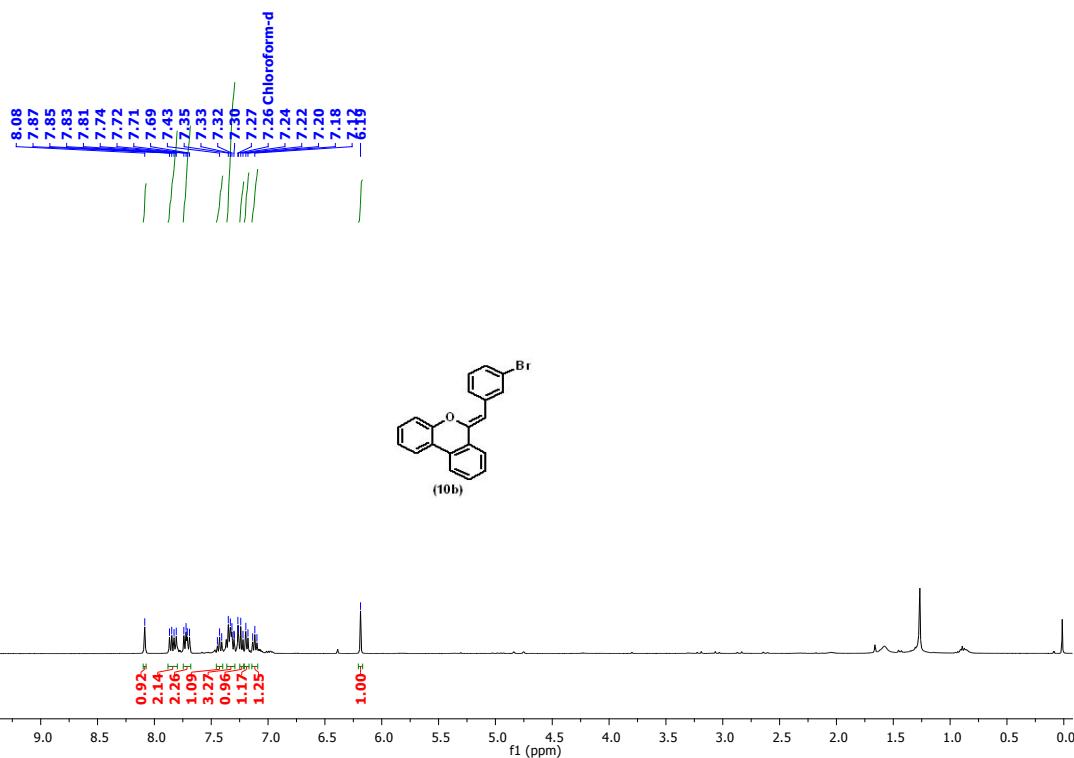
**Figure S86.**  $^{13}\text{C}$  NMR of Compound **10a** at 100 MHz in  $\text{CDCl}_3$



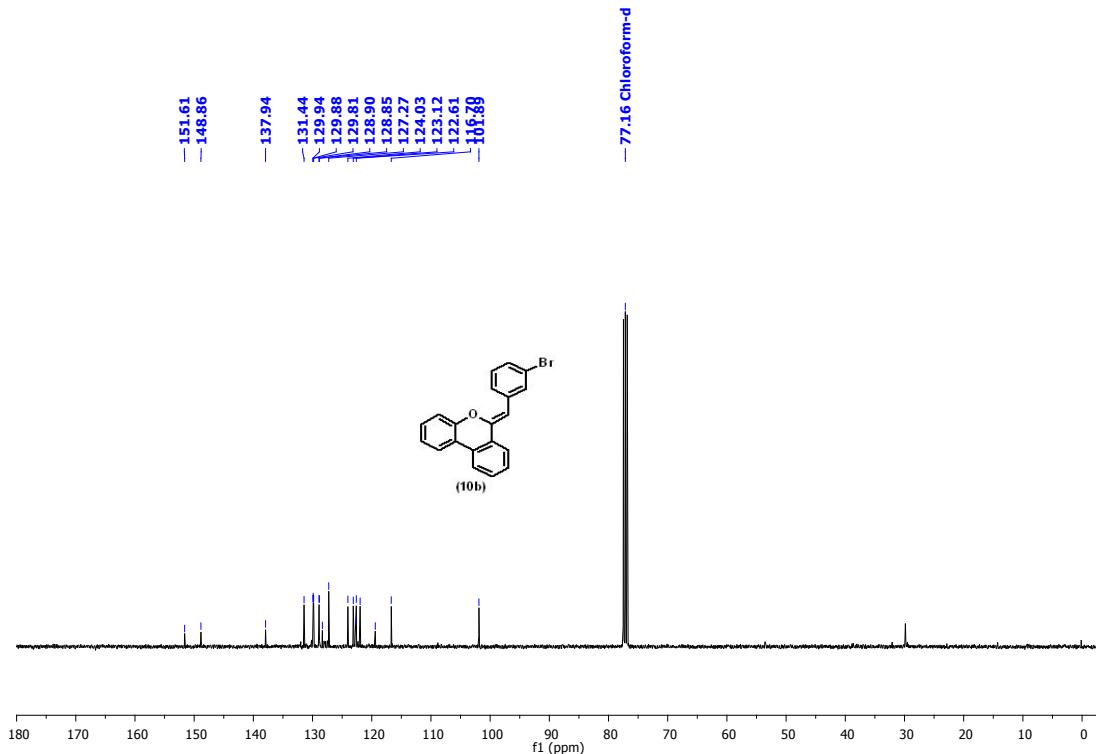
**Figure S87.**  $^1\text{H}$  NMR of Compound **6a** at 400 MHz in  $\text{CDCl}_3$



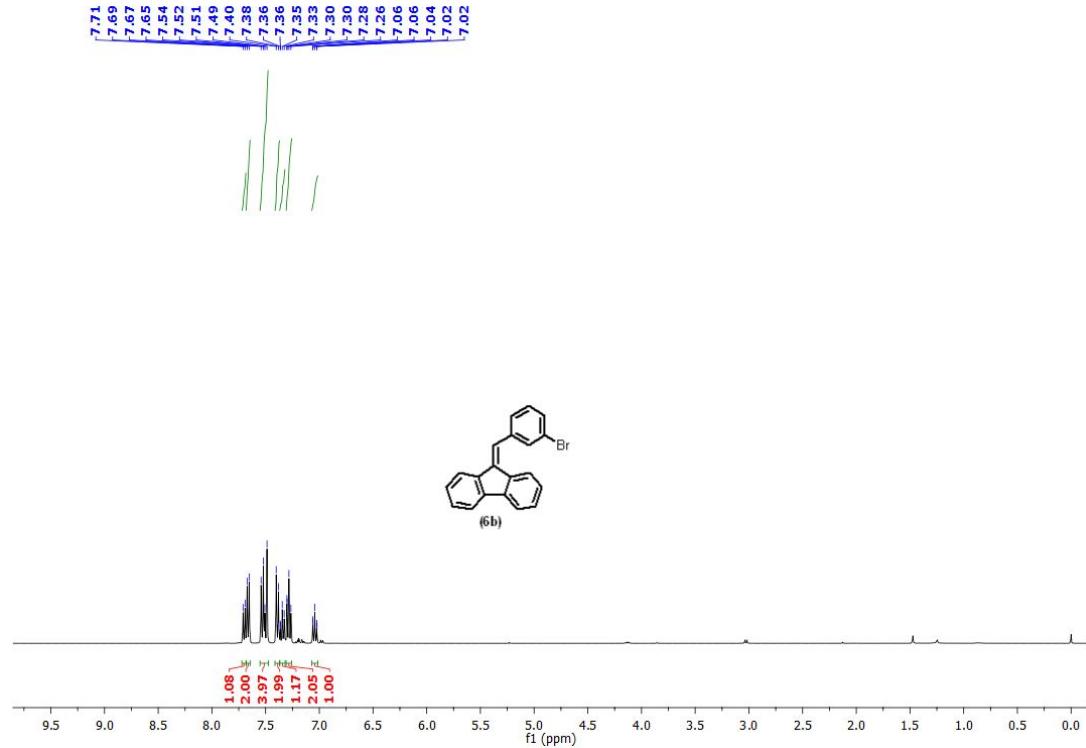
**Figure S88.**  $^{13}\text{C}$  NMR of Compound **6a** at 100 MHz in  $\text{CDCl}_3$



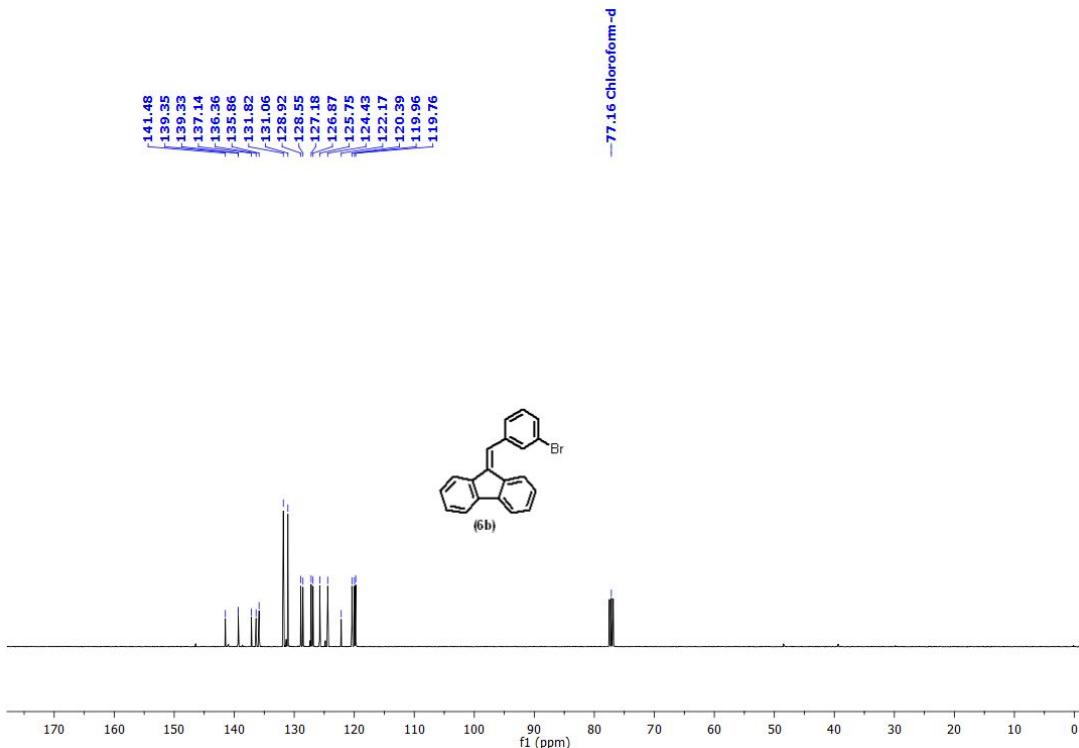
**Figure S89.**  $^1\text{H}$  NMR of Compound **10b** at 400 MHz in  $\text{CDCl}_3$



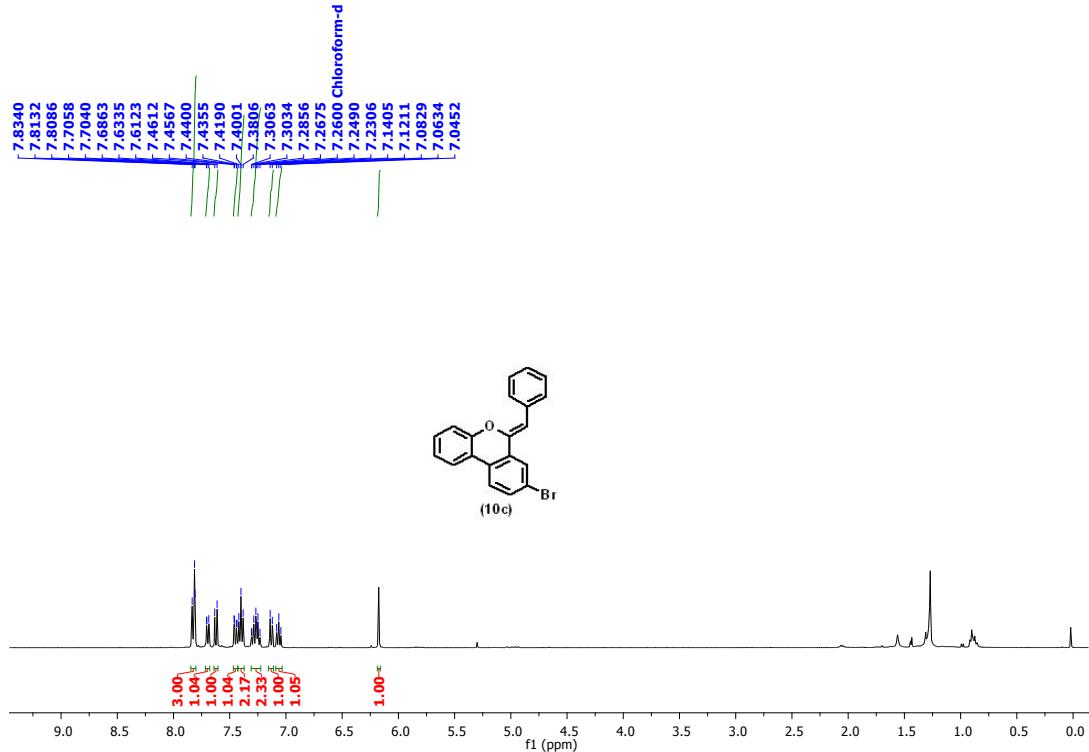
**Figure S90.**  $^{13}\text{C}$  NMR of Compound **10b** at 100 MHz in  $\text{CDCl}_3$



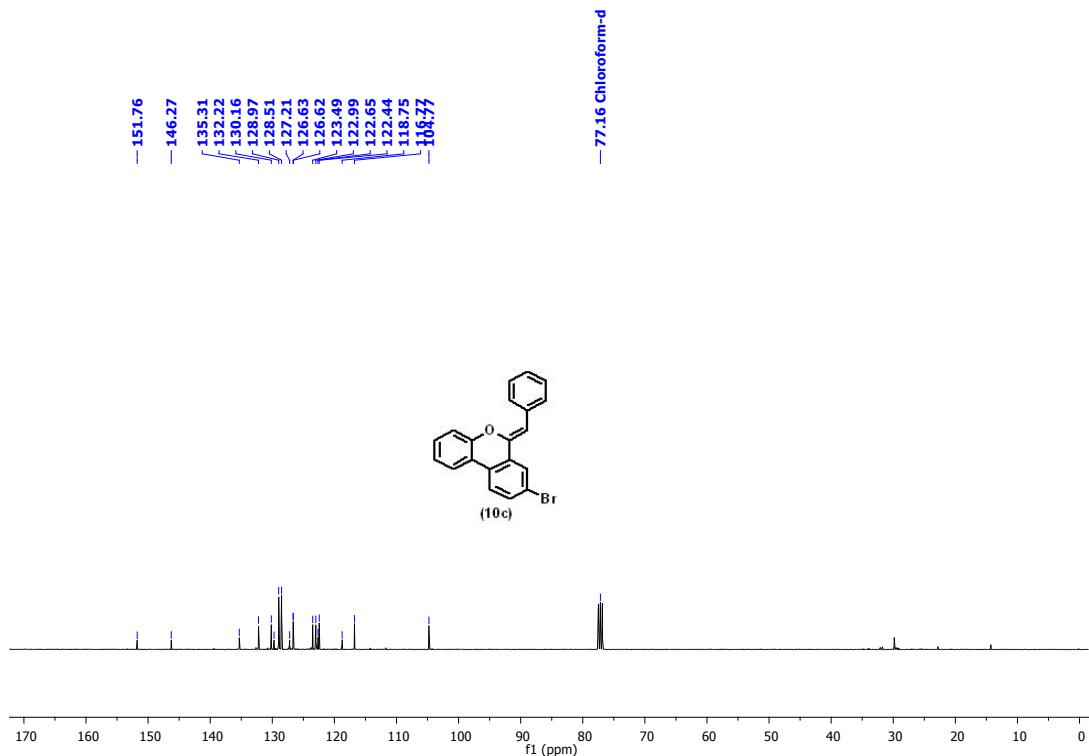
**Figure S91.**  $^1\text{H}$  NMR of Compound **6b** at 400 MHz in  $\text{CDCl}_3$



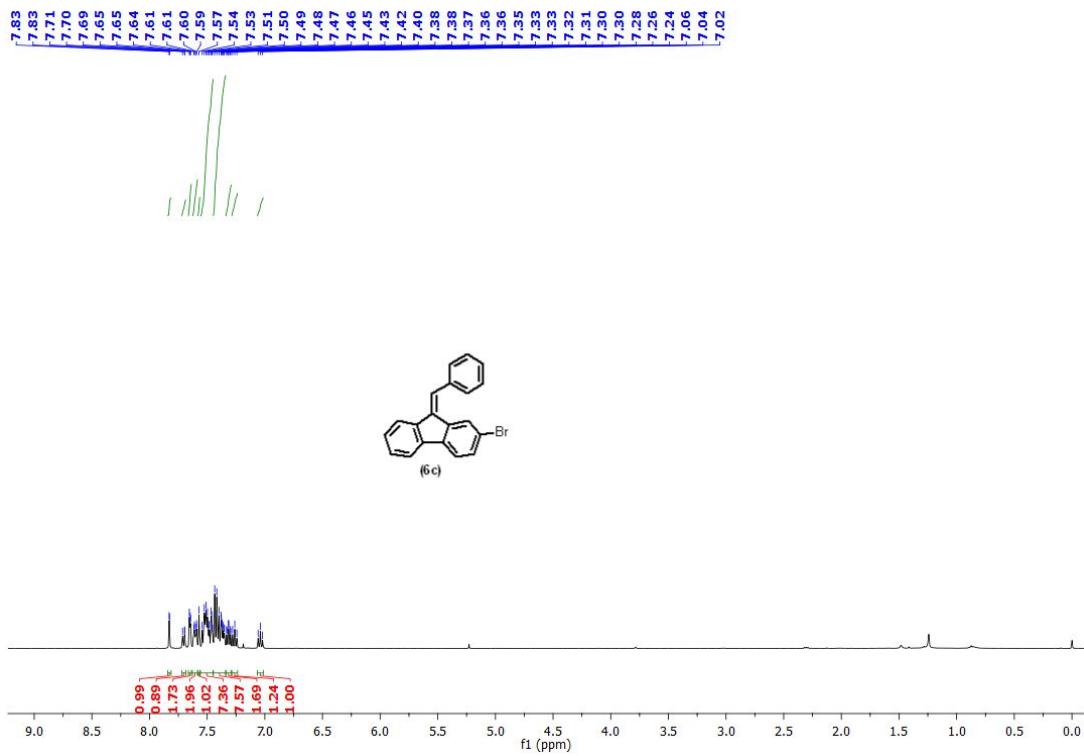
**Figure S92.**  $^{13}\text{C}$  NMR of Compound **6b** at 100 MHz in  $\text{CDCl}_3$



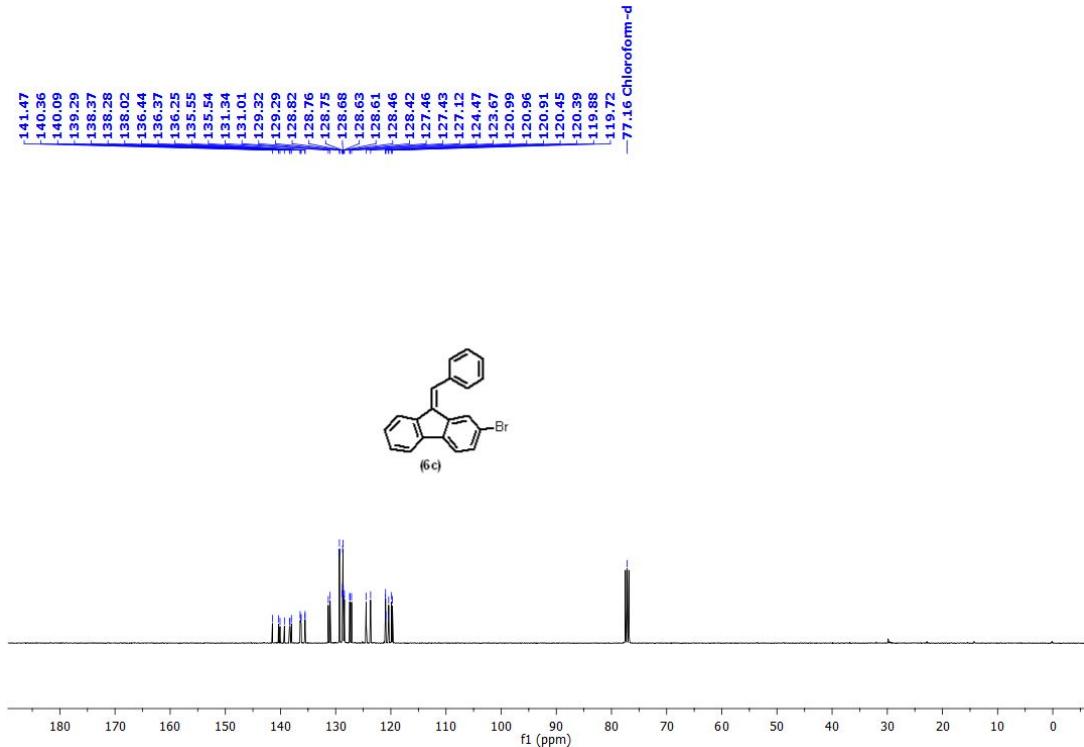
**Figure S93.**  $^1\text{H}$  NMR of Compound **10c** at 400 MHz in  $\text{CDCl}_3$



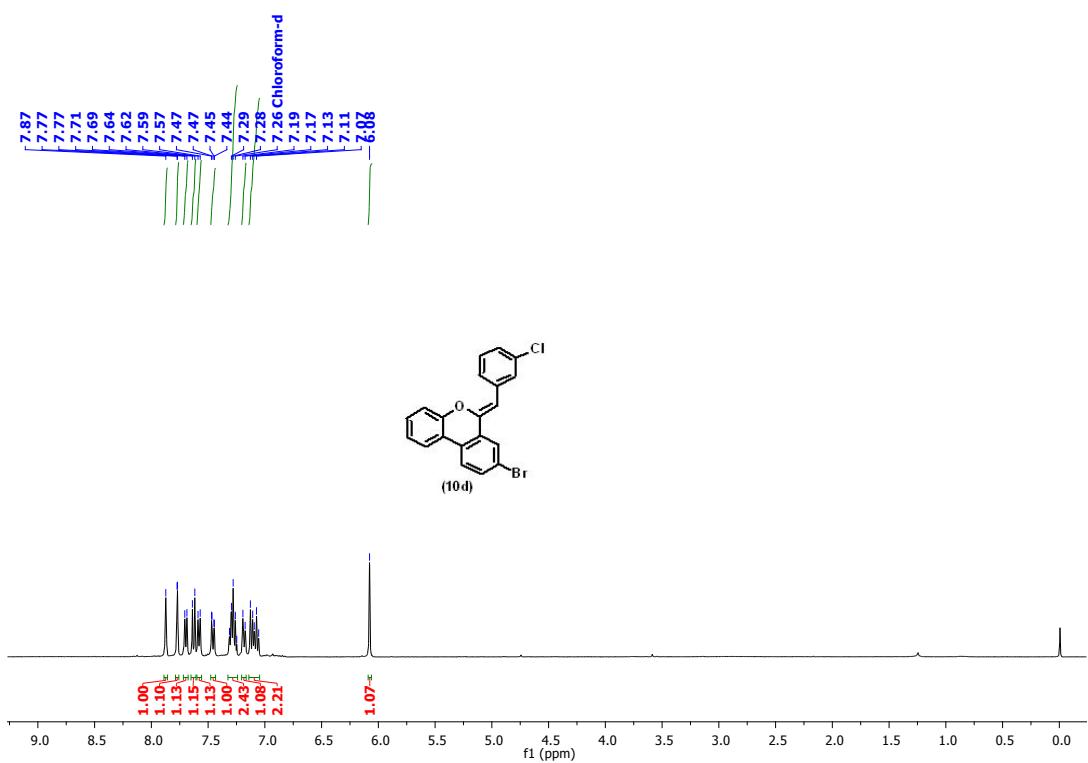
**Figure S94.**  $^{13}\text{C}$  NMR of Compound **10c** at 100 MHz in  $\text{CDCl}_3$



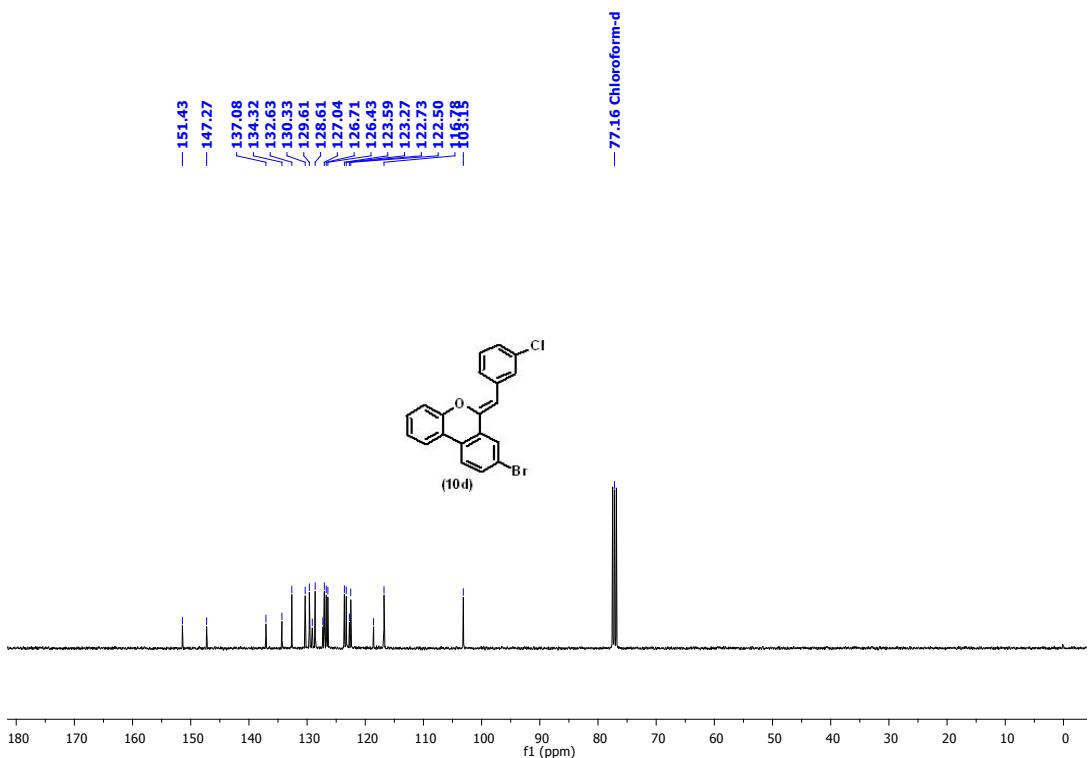
**Figure S95.**  $^1\text{H}$  NMR of Compound **6c** at 400 MHz in  $\text{CDCl}_3$



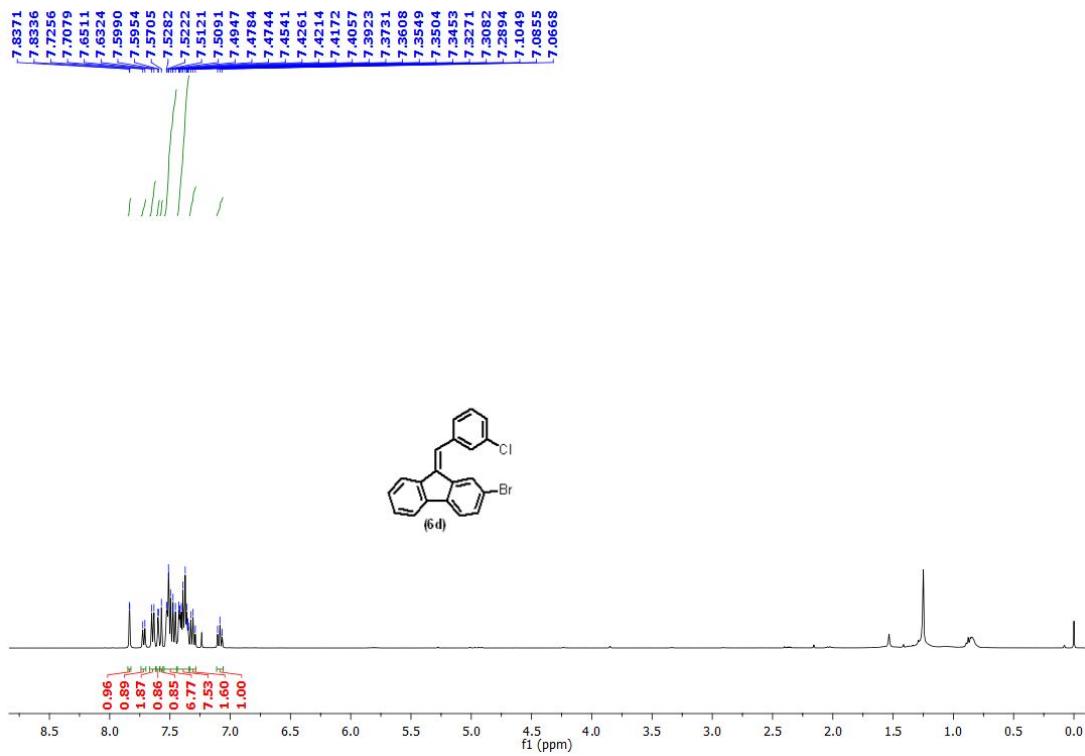
**Figure S96.**  $^{13}\text{C}$  NMR of Compound **6c** at 100 MHz in  $\text{CDCl}_3$



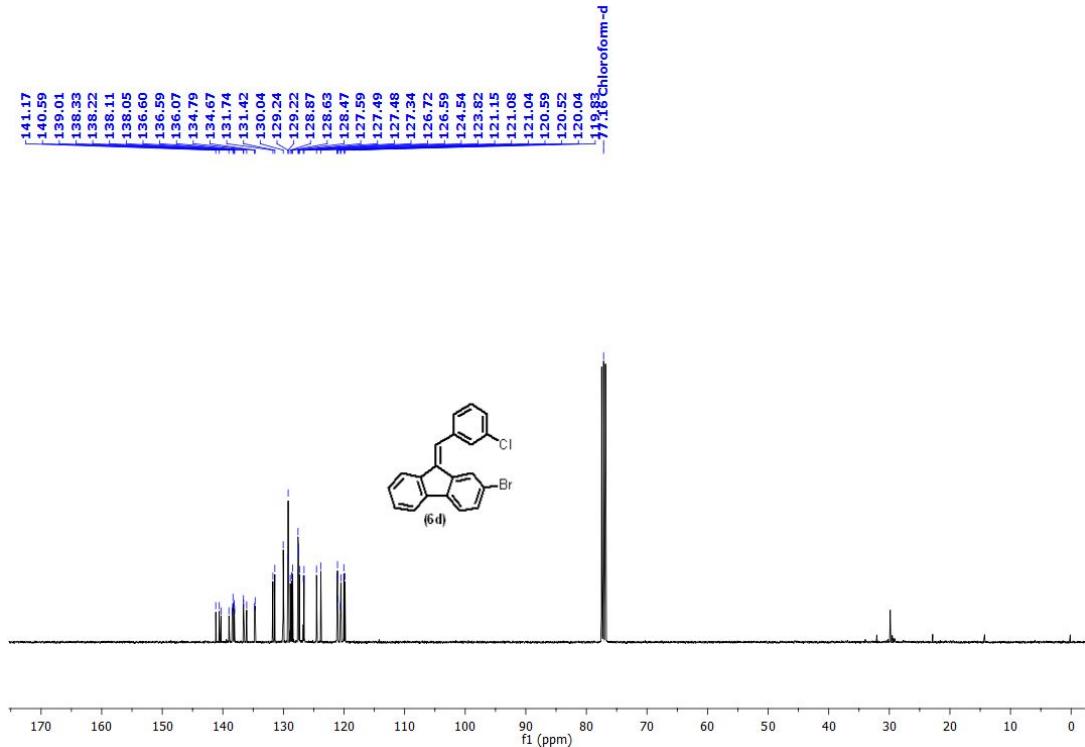
**Figure S97.**  $^1\text{H}$  NMR of Compound **10d** at 400 MHz in  $\text{CDCl}_3$



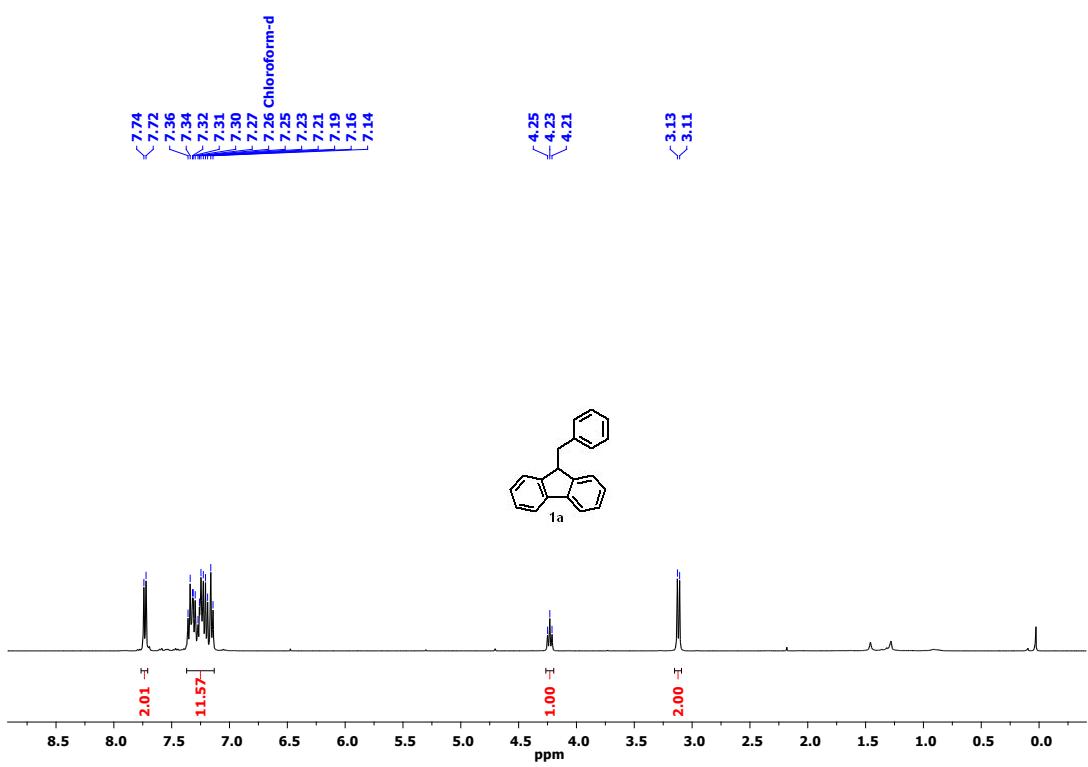
**Figure S98.**  $^{13}\text{C}$  NMR of Compound **10d** at 100 MHz in  $\text{CDCl}_3$



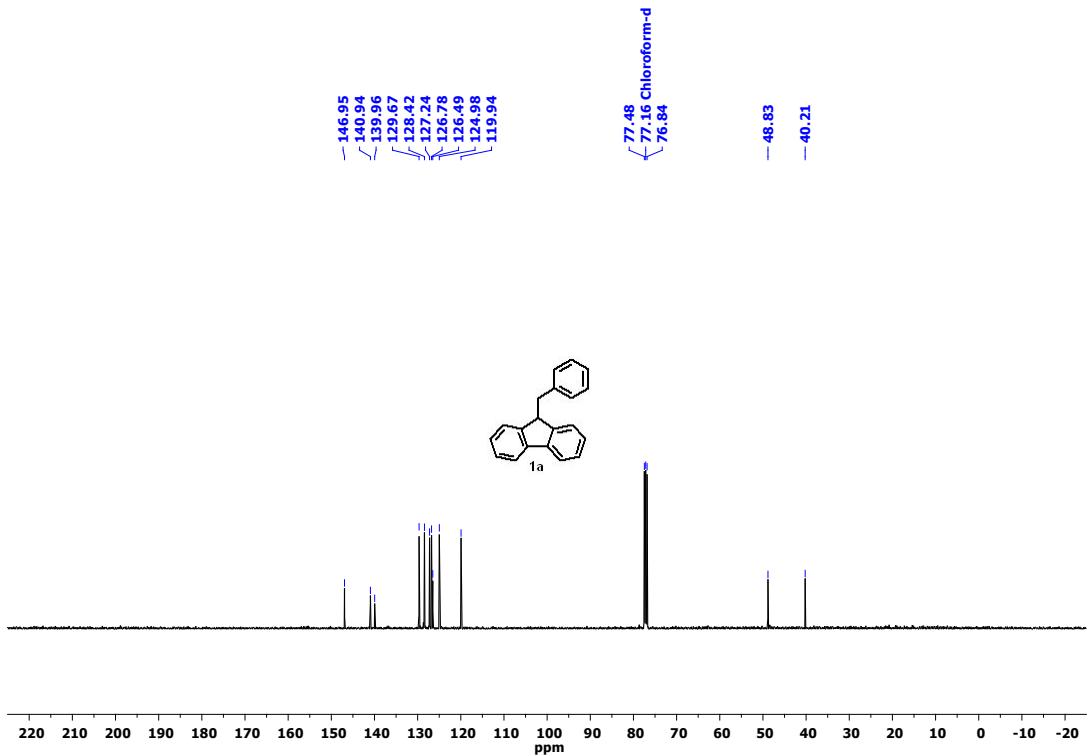
**Figure S99.**  $^1\text{H}$  NMR of Compound **6d** at 400 MHz in  $\text{CDCl}_3$



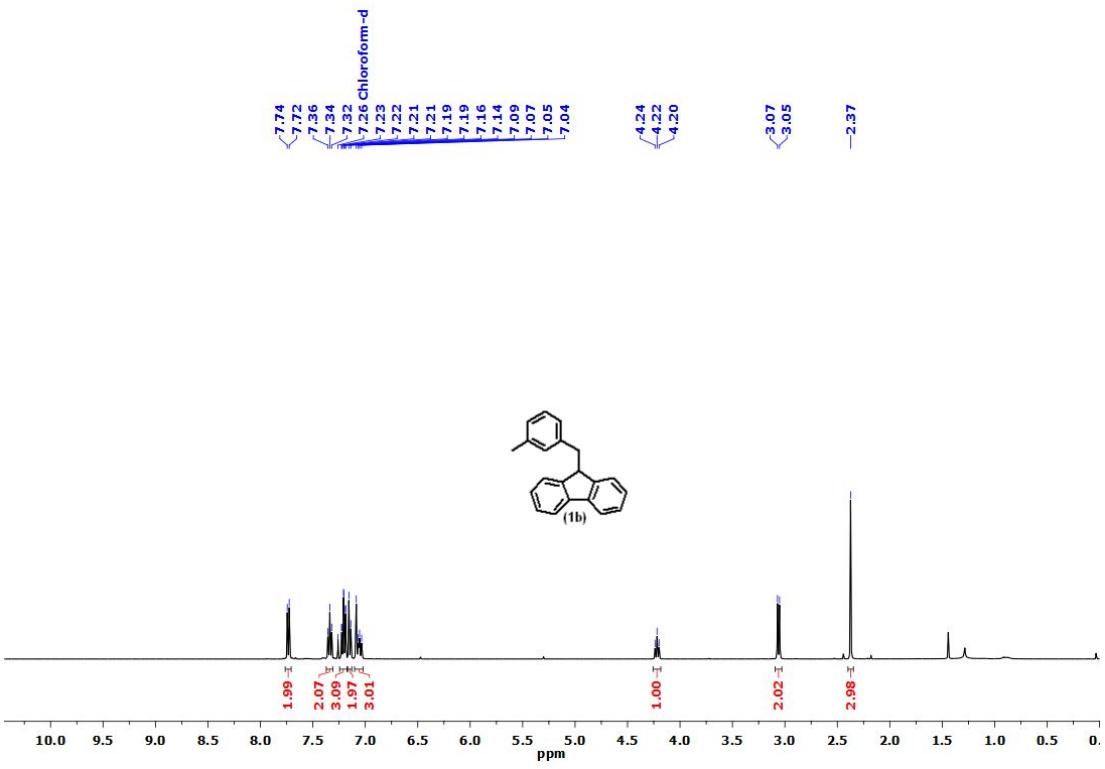
**Figure S100.**  $^{13}\text{C}$  NMR of Compound **6d** at 100 MHz in  $\text{CDCl}_3$



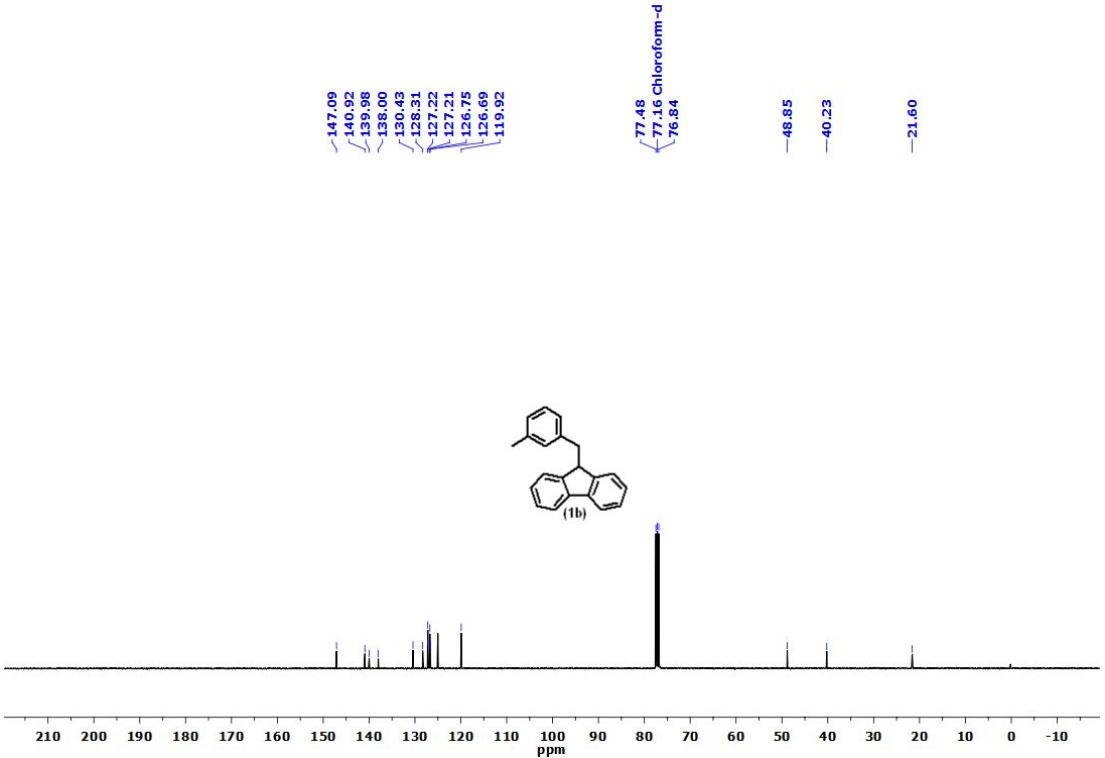
**Figure S101.**  $^1\text{H}$  NMR of Compound **1a** at 400 MHz in  $\text{CDCl}_3$



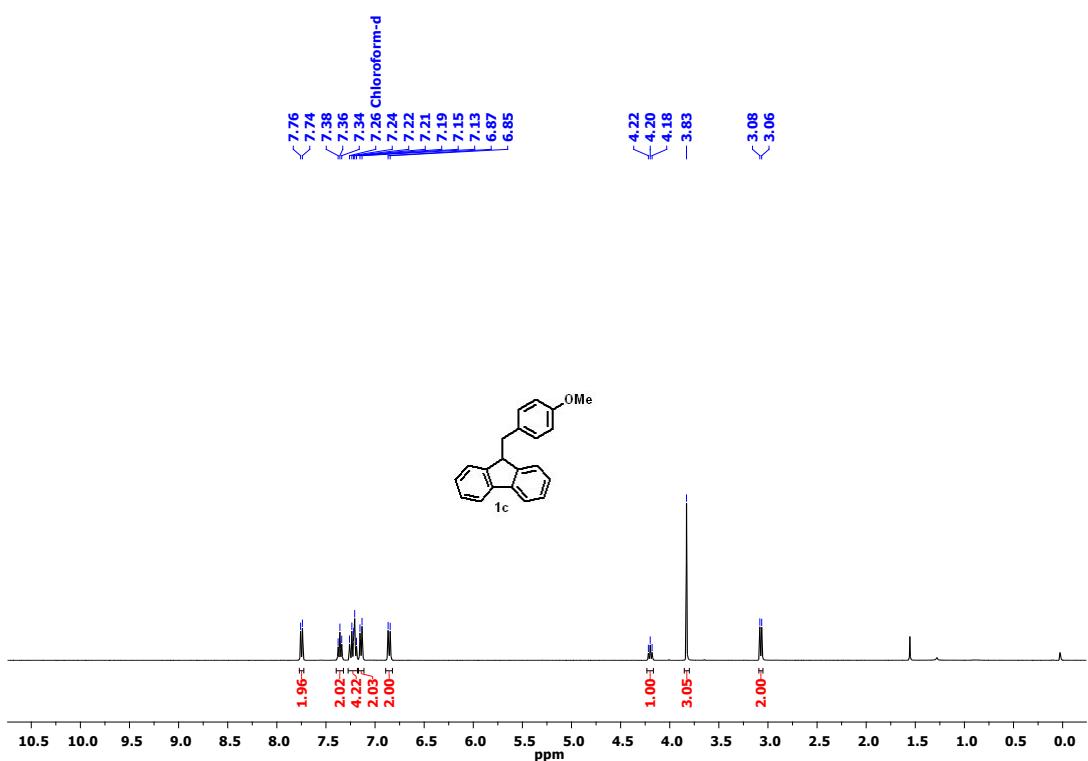
**Figure S102.**  $^{13}\text{C}$  NMR of Compound **1a** at 100 MHz in  $\text{CDCl}_3$



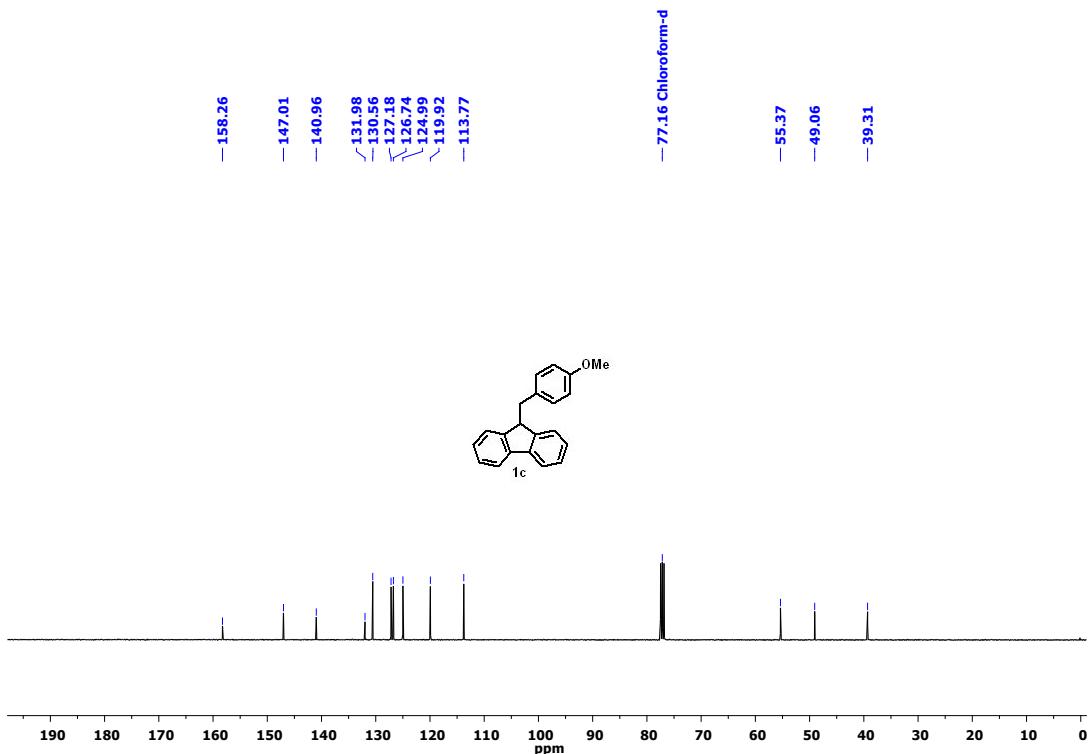
**Figure S103.**  $^1\text{H}$  NMR of Compound **1b** at 400 MHz in  $\text{CDCl}_3$



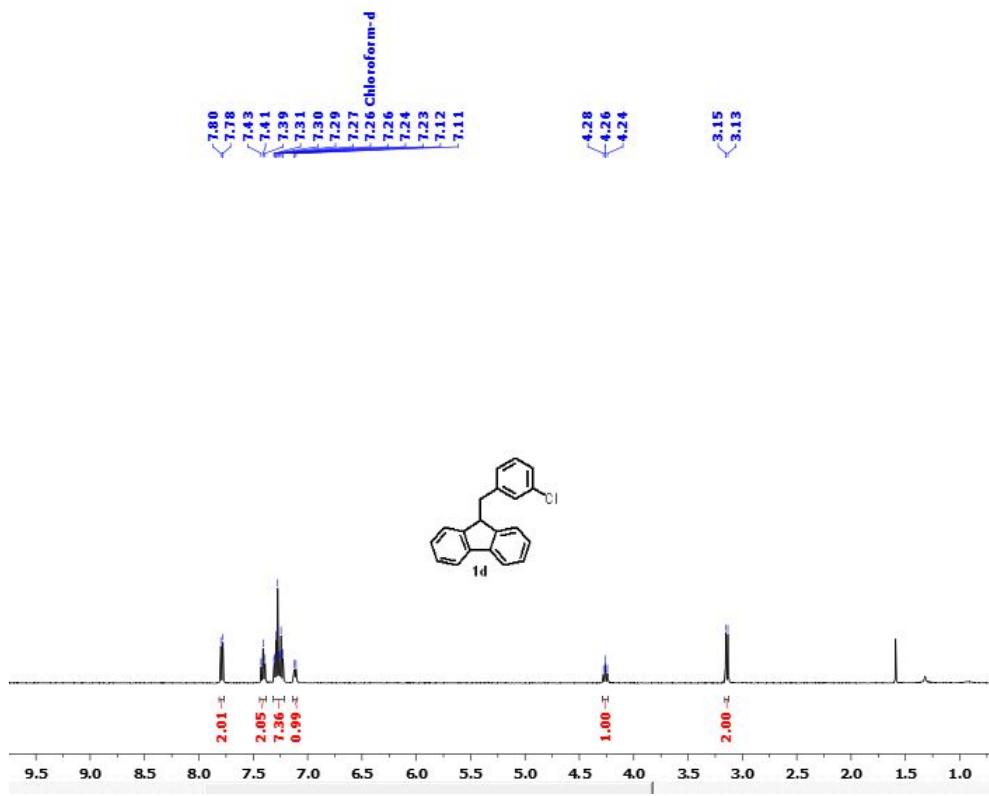
**Figure S104.**  $^{13}\text{C}$  NMR of Compound **1b** at 100 MHz in  $\text{CDCl}_3$



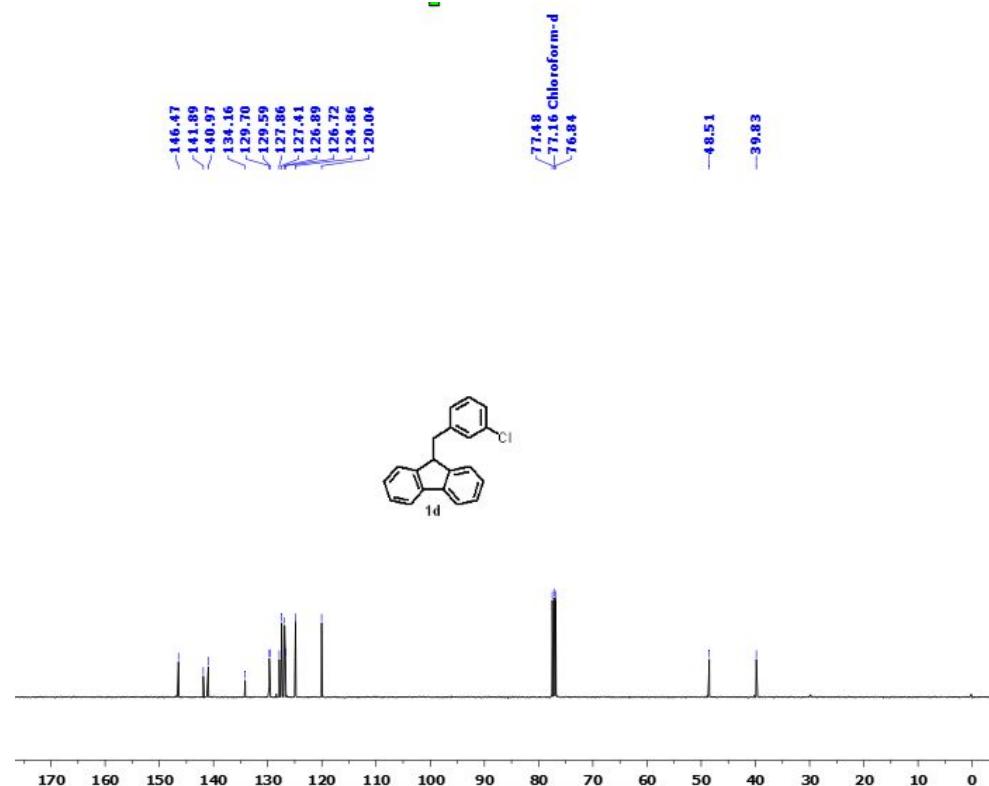
**Figure S105.**  $^1\text{H}$  NMR of Compound **1c** at 400 MHz in  $\text{CDCl}_3$



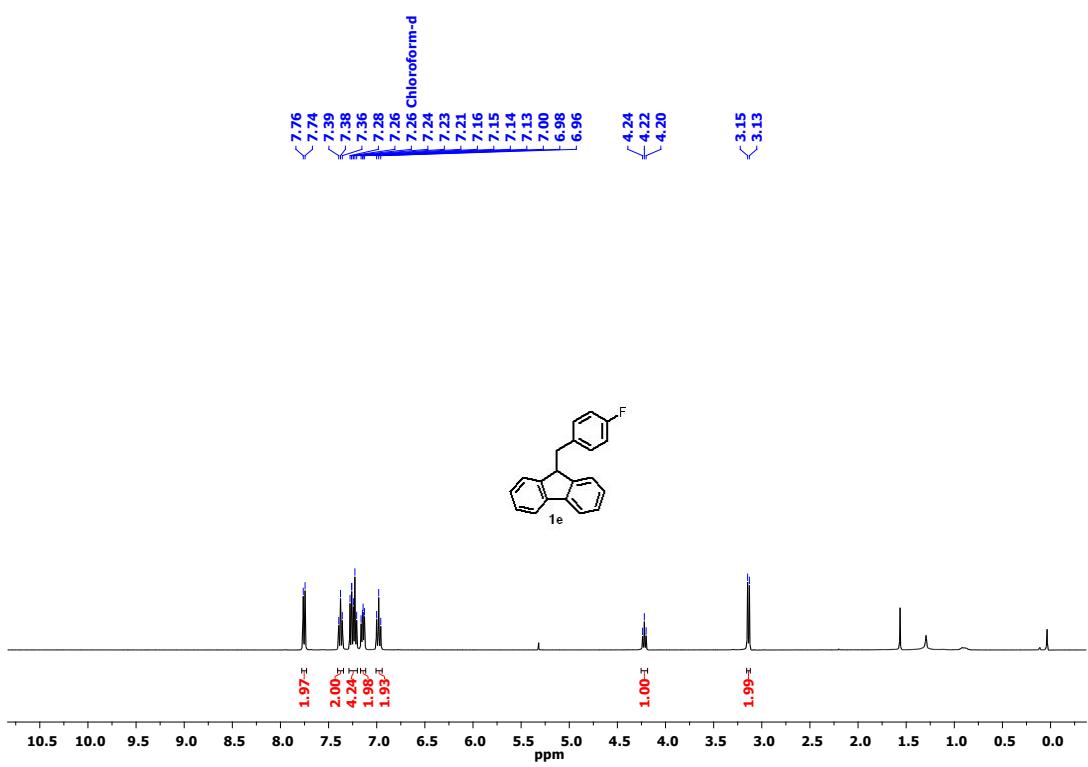
**Figure S106.**  $^{13}\text{C}$  NMR of Compound **1c** at 100 MHz in  $\text{CDCl}_3$



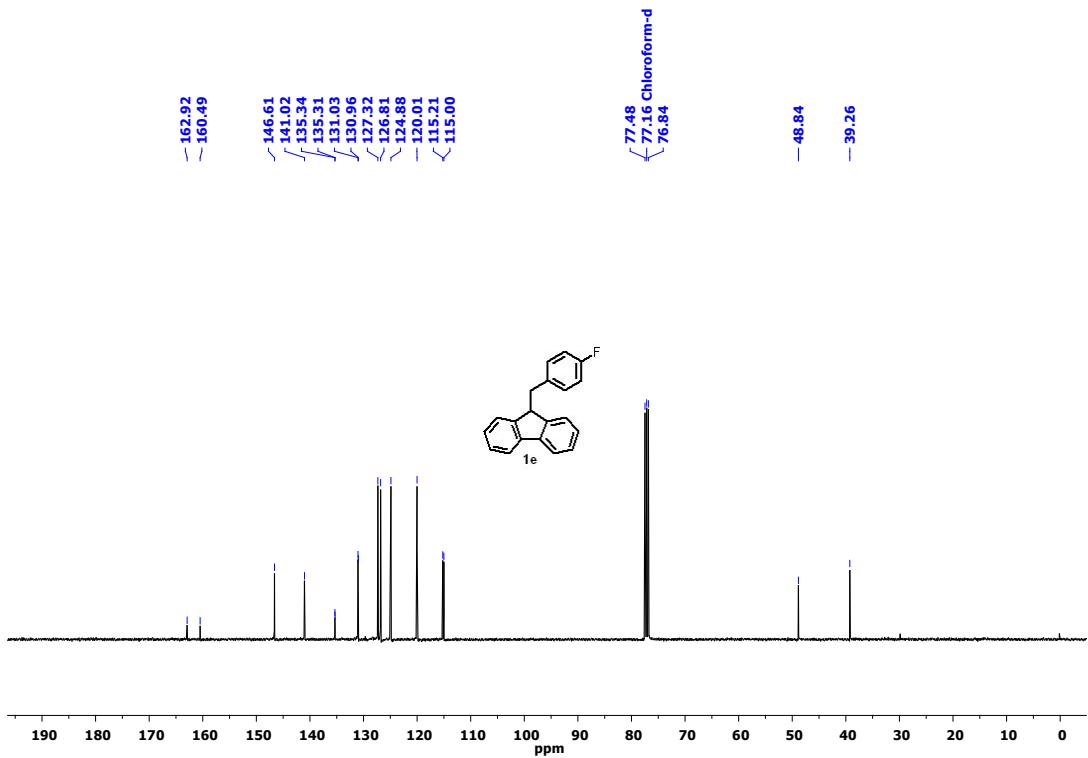
**Figure S107.**  $^1\text{H}$  NMR of Compound **1d** at 400 MHz in  $\text{CDCl}_3$



**Figure S108.**  $^{13}\text{C}$  NMR of Compound **1d** at 100 MHz in  $\text{CDCl}_3$

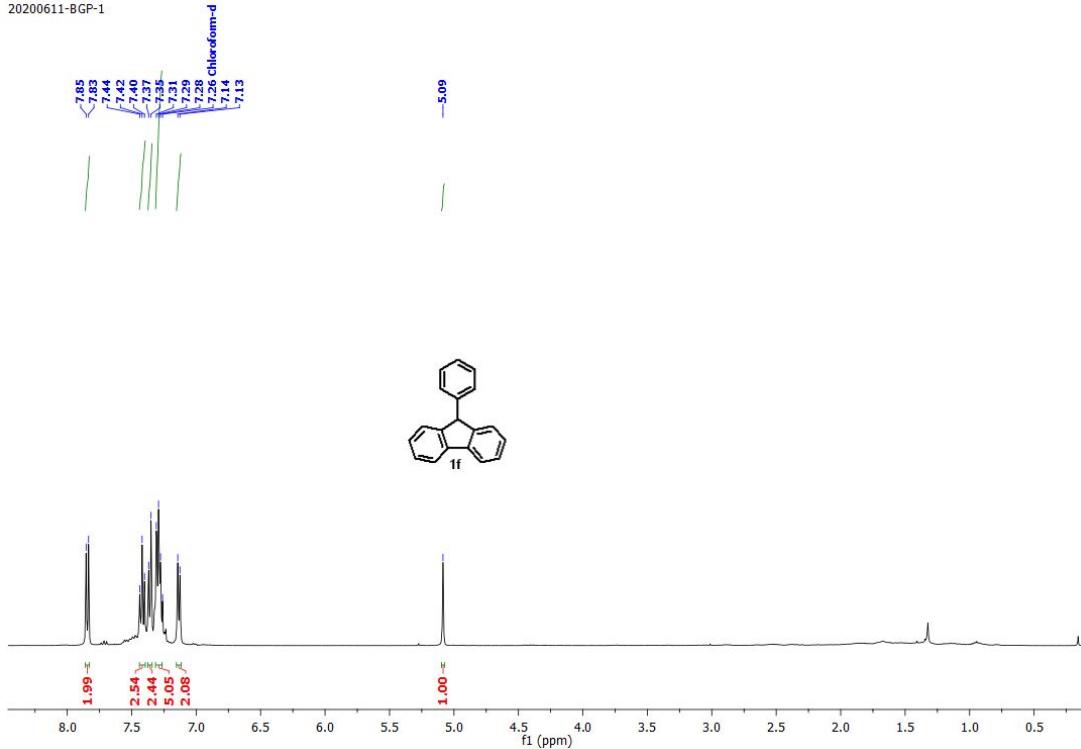


**Figure S109.**  $^1\text{H}$  NMR of Compound **1e** at 400 MHz in  $\text{CDCl}_3$



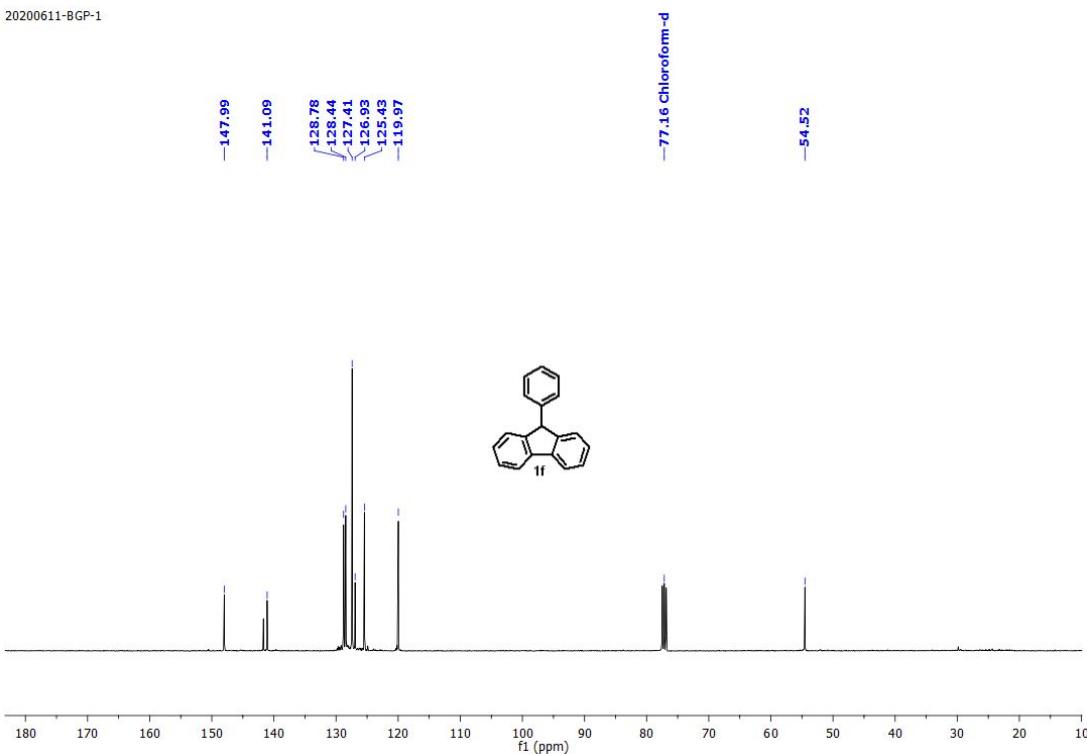
**Figure S110.**  $^{13}\text{C}$  NMR of Compound **1e** at 100 MHz in  $\text{CDCl}_3$

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**Figure S111.** <sup>1</sup>H NMR of Compound 1f at 400 MHz in CDCl<sub>3</sub>

20200611-BGP-1



**Figure S112.** <sup>13</sup>C NMR of Compound 1f at 100 MHz in CDCl<sub>3</sub>

