

Supporting Information for

Highly Regioselective α -Formylation and α -Acylation of
BODIPY Dyes *via* Tandem Cross-Dehydrogenative
Coupling with *in situ* Deprotection

Fan Lv,^a Yang Yu,^a Erhong Hao,^{a,} Changjiang Yu,^a Hua Wang,^a Noël Boens^{b,*}*
and Lijuan Jiao^{a}*

^a The Key Laboratory of Functional Molecular Solids, Ministry of Education; School of Chemistry and Materials Science, Anhui Normal University, Wuhu, China 241000.

^b Department of Chemistry, KU Leuven (Katholieke Universiteit Leuven), Celestijnenlaan 200f, 3001 Leuven, Belgium.

* Correspondence authors. E-mail: jiao421@ahnu.edu.cn, haoehong@ahnu.edu.cn,
Noel.Boens@kuleuven.be

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1. Synthesis of compounds **1a-d** and **2a-f**

BODIPYs **1a-d** (Figure S1) were synthesized according to literature procedures.¹ Compounds **2a** and **2b** (Figure S1) are commercial reagents. Compounds **2c-f** (Figure S1) were prepared from the aldol condensation reaction of aldehyde and ethylene glycol by following literature procedures.² Compound 2-phenyl-1,3-dioxolane **2d** was used as an example to show the **general procedure for the preparation of 2-substituted 1,3-dioxolanes 2c-f.** To benzaldehyde (5.0 g, 27.0 mmol) in 30 mL of anhydrous toluene was added *p*-toluenesulfonic acid (22 mg, 0.1 mmol) and ethylene glycol (2.5 g, 40.3 mmol) at 120 °C. The reaction mixture was refluxed for 24 h. Upon completion, the reaction mixture was cooled to room temperature and was washed three times with saturated NaHCO₃ solution (50 mL) and brine (50 mL), dried over Na₂SO₄, filtered, and evaporated to provide crude products **2c-f** in 87%-96% yields.

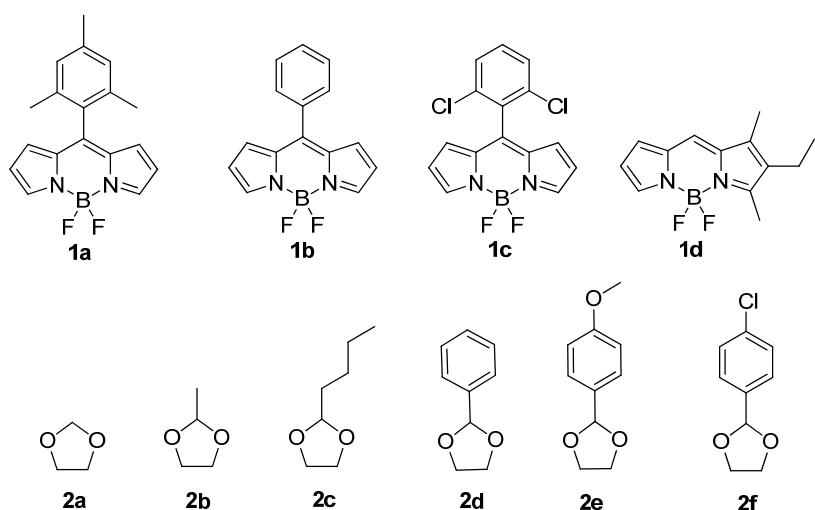
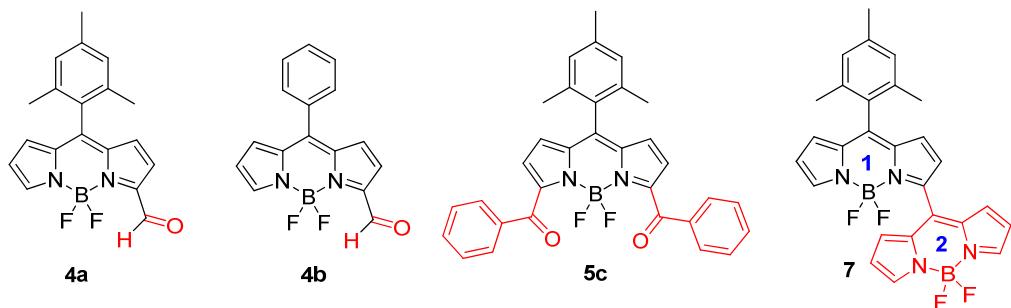


Figure S1. Chemical structure of BODIPYs **1a-d**, 1,3-dioxolane **2a** and its derivatives **2b-f.**

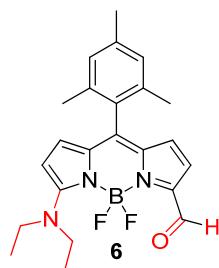
2. Table S1. Selected Geometrical Parameters of 4a, 4b, 5c and 7 obtained from crystallography



	4a	4b	5c	7
B-N bond distances (Å)	1.5483(39) 1.5476(28)	1.542(31) 1.546(37)	1.5416(27) 1.5531(23)	1.5608(78) (1) 1.5702(91) (1) 1.5466(66) (2) 1.5348(78) (2)
dihedral angles between <i>meso</i> -aryl group and dipyrin core (deg)	75.774(70)	55.066(79)	80.372(40)	83.133(129)
dihedral angles of two pyrrole rings in dipyrin core (deg)	9.838(90)	2.722(130)	19.303(68)	6.137(142) (1) 12.067(235) (2)
dihedral angles between two central BN ₂ C ₃ six-membered rings	/	/	/	61.919(94)

3. Photophysical properties

3.1 Table S2: Photophysical properties of **6 in different solvents at room temperature.**



solvent	$\lambda_{\text{abs}}^{\text{max}}$ [nm]	$\lambda_{\text{em}}^{\text{max}}$ [nm]	$\log \epsilon^{\text{a}}$	Φ^{b}	Stokes shift [cm ⁻¹] ^c
cyclohexane	481	560	4.59	0.18	2930
toluene	477	556	4.63	0.01	2980
CHCl ₃	472	548	4.57	0.006	2940
THF	467	532	4.48	0.005	2620
CH ₃ CN	461	525	4.48	0.003	2640
MeOH	467	519	4.48	0.002	2150

^a Molar absorption coefficient at $\lambda_{\text{abs}}^{\text{max}}$. ^b Fluorescence quantum yields determined using fluorescein ($\Phi = 0.90$ in 0.1 N NaOH aqueous solution) as standard. ^c Stokes shift values rounded to nearest 10 cm⁻¹.

3.2 UV-vis absorption and fluorescence emission spectra of **6 recorded in various solvents.**

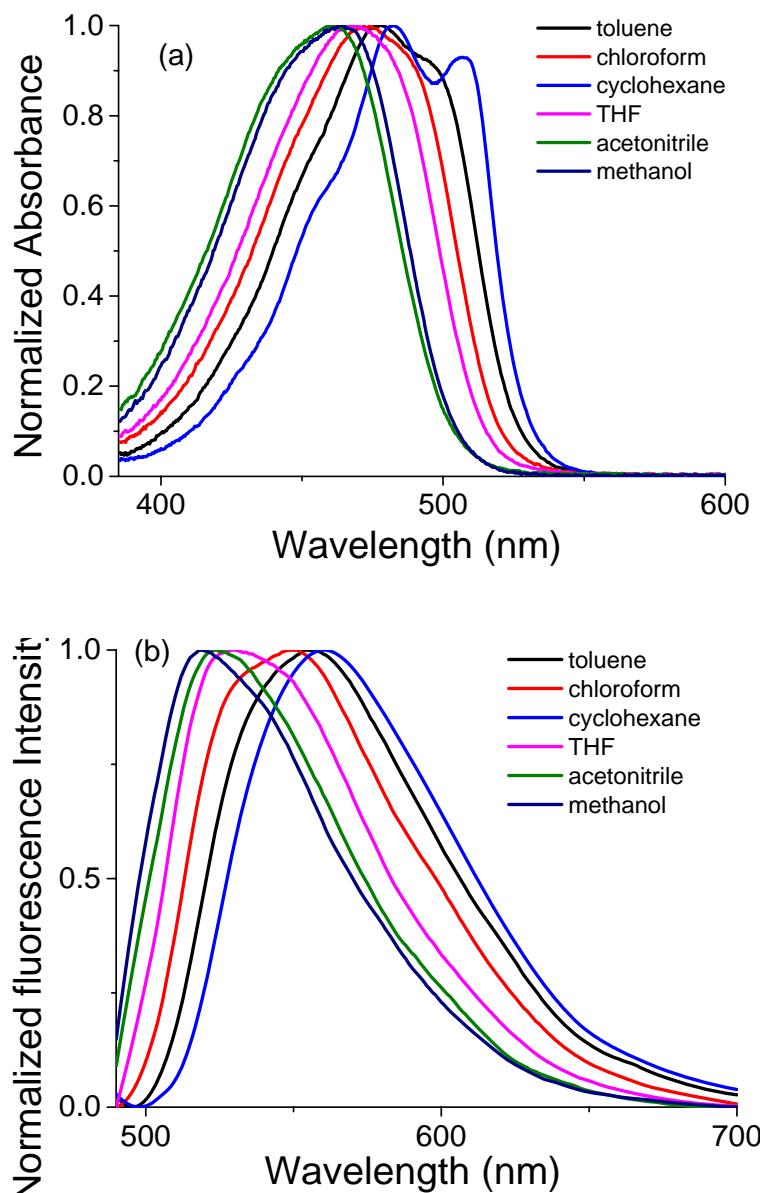


Figure S2. Absorption (a) and fluorescence emission (b) spectra of **6** recorded in different solvents (excitation at 460 nm).

3.3 UV-vis absorption and fluorescence emission spectra recorded in dichloromethane (excitation at 480 nm).

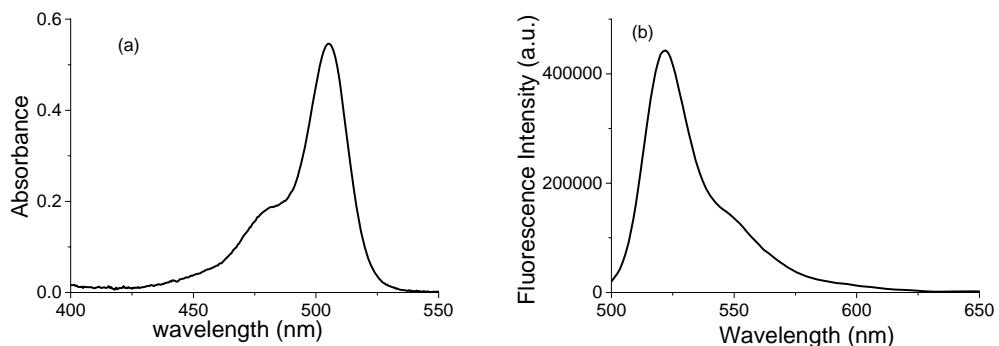


Figure S3. Absorption (a) and fluorescence emission (b) spectra of **3a**.

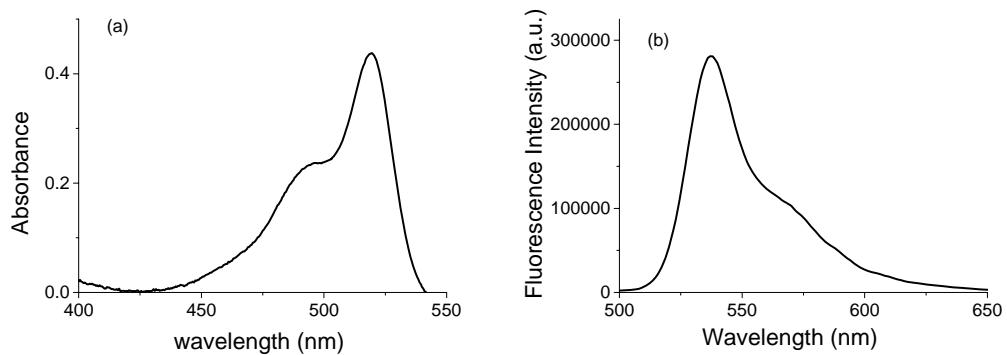


Figure S4. Absorption (a) and fluorescence emission (b) spectra of **4a**.

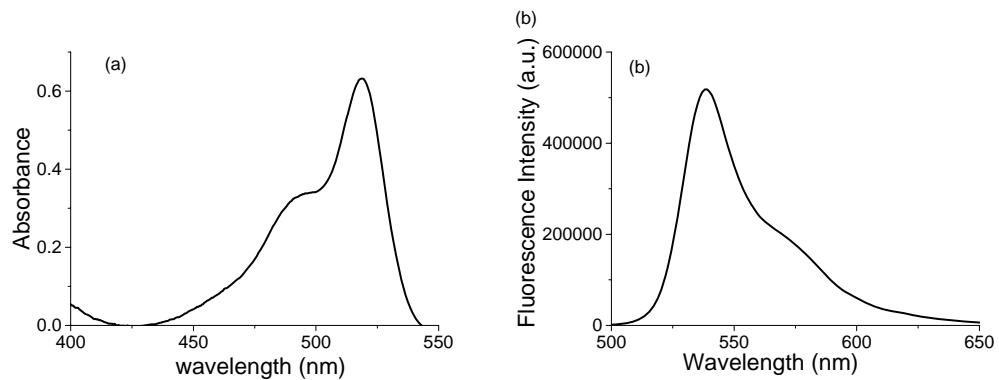


Figure S5. Absorption (a) and fluorescence emission (b) spectra of **4b**.

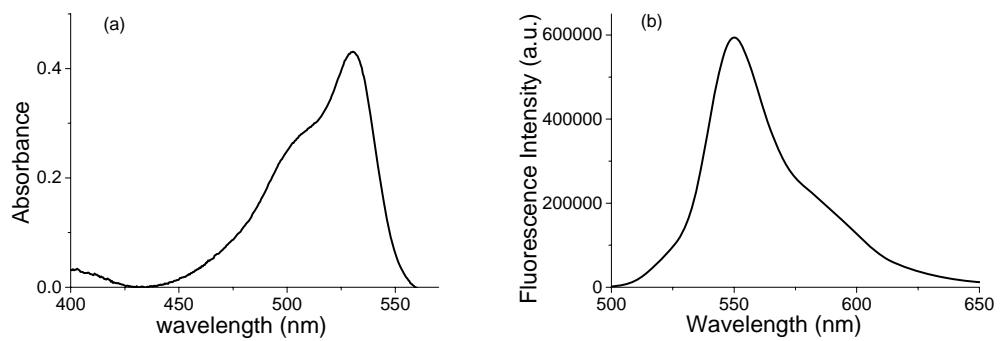


Figure S6. Absorption (a) and fluorescence emission (b) spectra of **4c**.

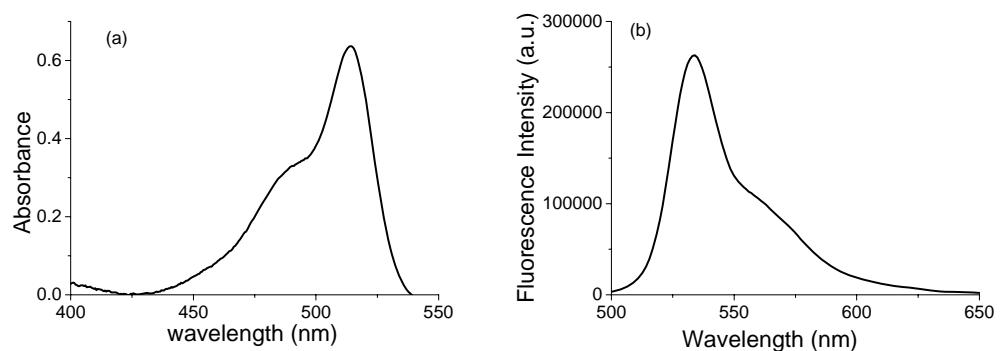


Figure S7. Absorption (a) and fluorescence emission (b) spectra of **4d**.

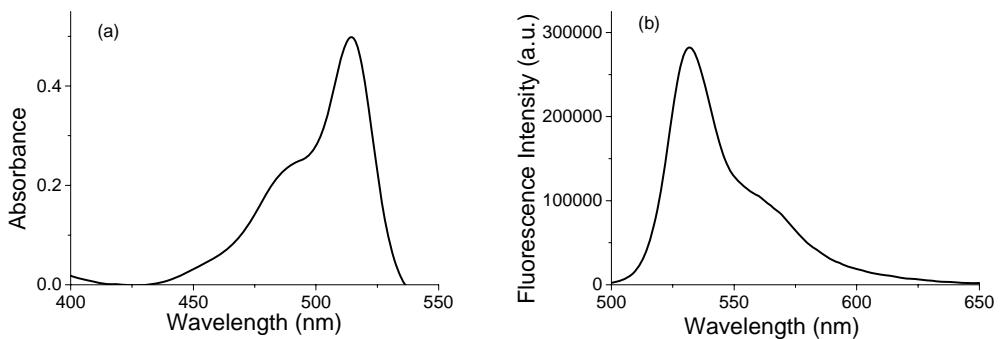


Figure S8. Absorption (a) and fluorescence emission (b) spectra of **4e**.

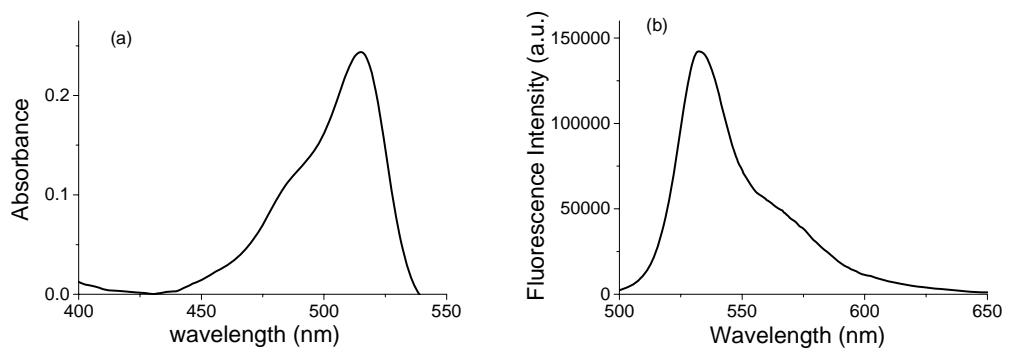


Figure S9. Absorption (a) and fluorescence emission (b) spectra of **4f**.

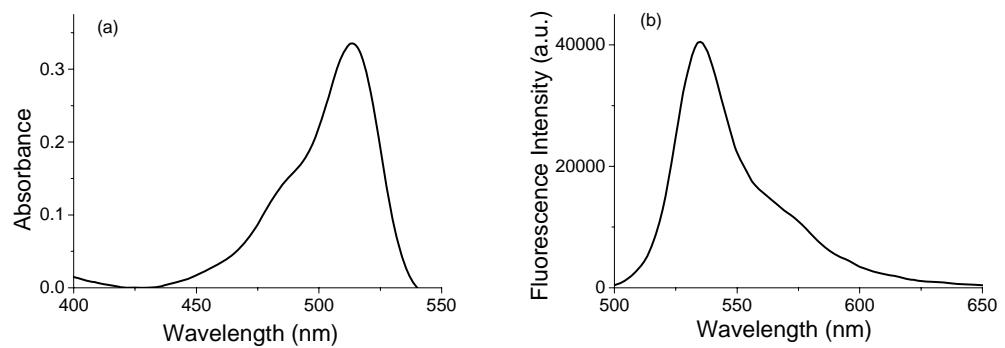


Figure S10. Absorption (a) and fluorescence emission (b) spectra of **4g**.

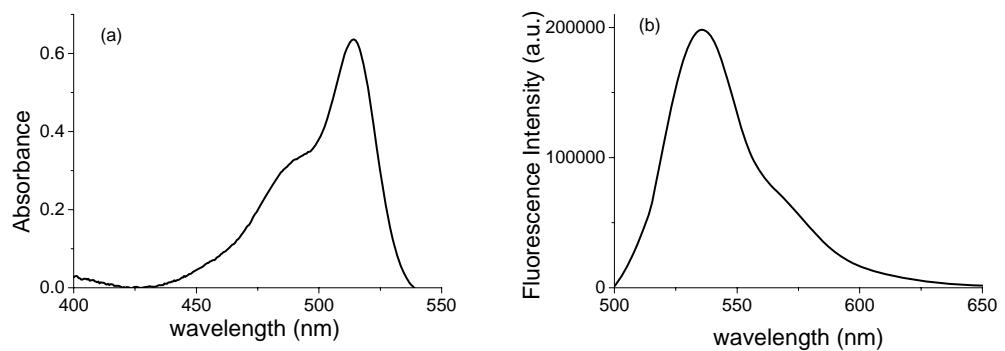


Figure S11. Absorption (a) and fluorescence emission (b) spectra of **4h**.

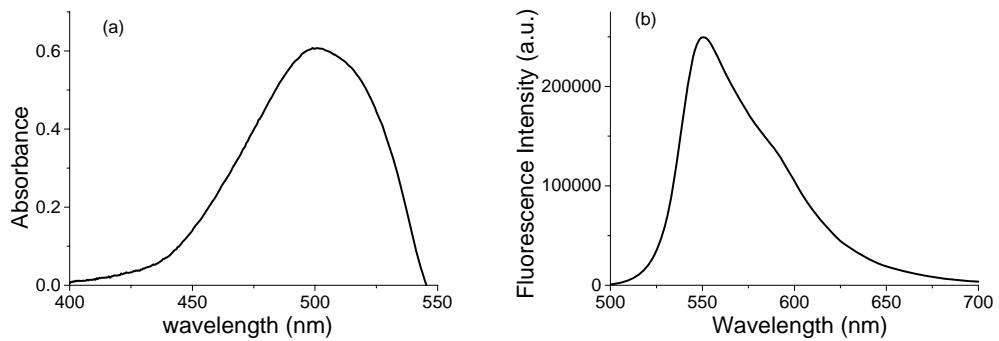


Figure S12. Absorption (a) and fluorescence emission (b) spectra of **4i**.

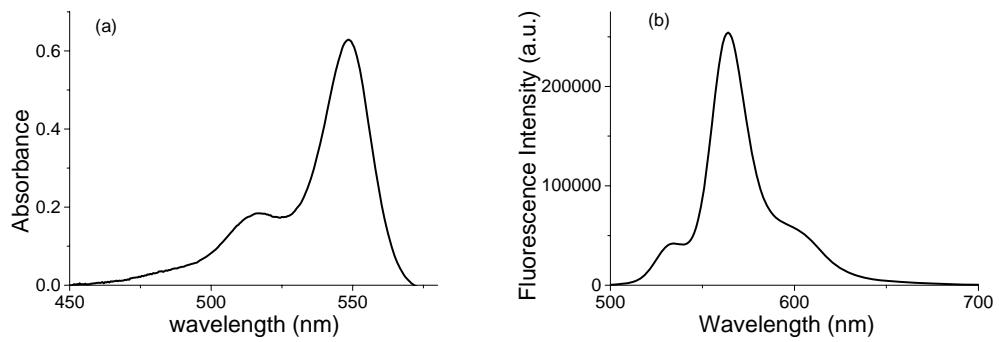


Figure S13. Absorption (a) and fluorescence emission (b) spectra of **5a**.

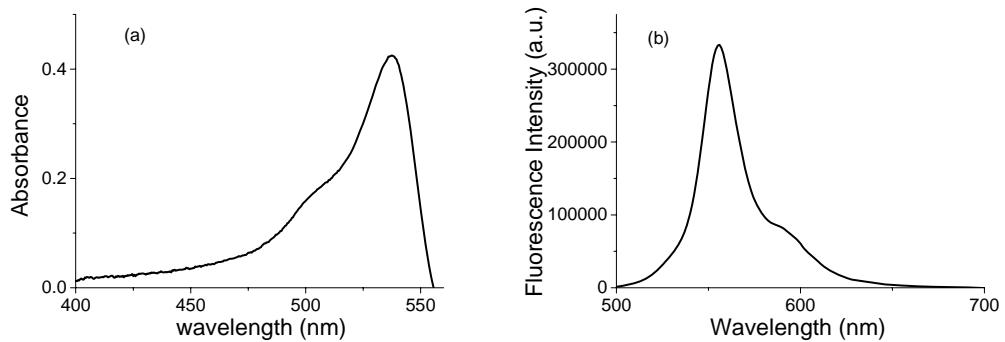


Figure S14. Absorption (a) and fluorescence emission (b) spectra of **5b**.

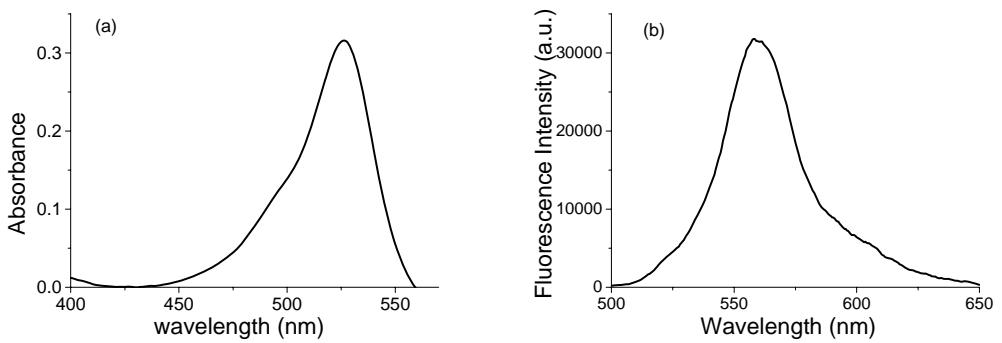


Figure S15. Absorption (a) and fluorescence emission (b) spectra of **5c**.

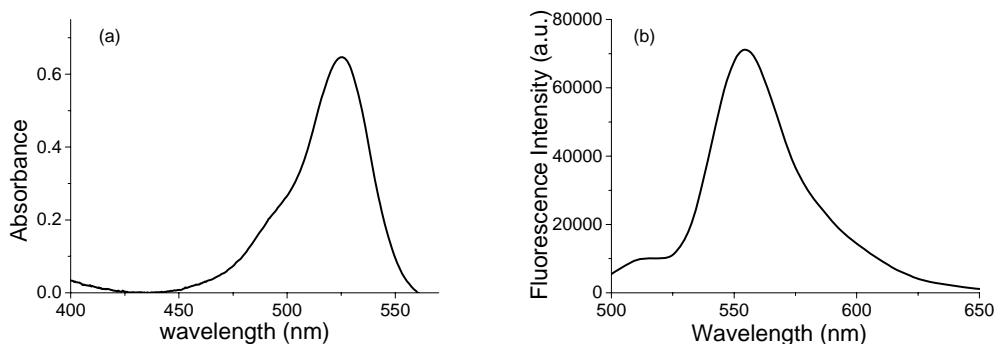


Figure S16. Absorption (a) and fluorescence emission (b) spectra of **5d**.

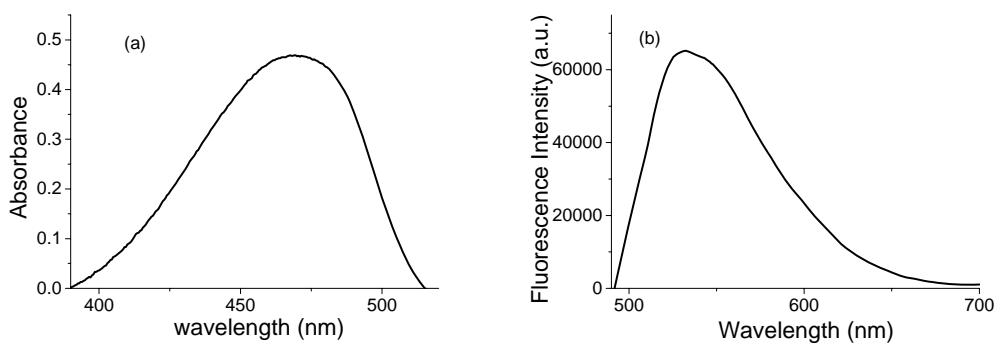


Figure S17. Absorption (a) and fluorescence emission (b) spectra of **6**.

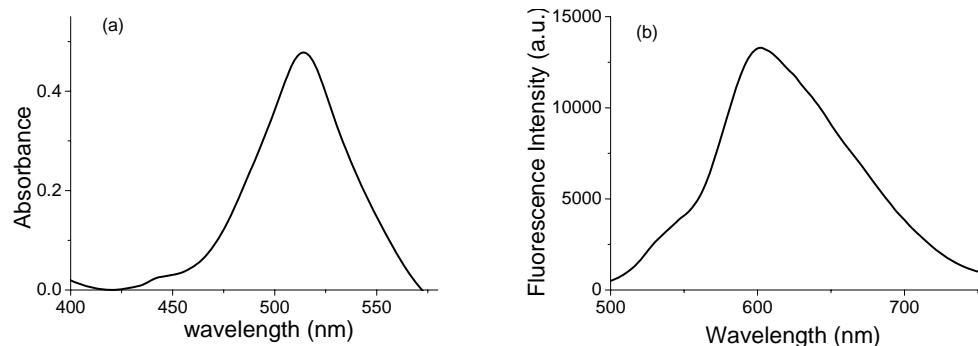


Figure S18. Absorption (a) and fluorescence emission (b) spectra of **7**.

3.4 Photooxidation of 1,3-diphenylisobenzofuran (DPBF) with BODIPY dimer 7

Singlet oxygen (${}^1\text{O}_2$) quantum yields Φ_Δ of the triplet photosensitizers were calculated according to a modified literature method.³ The irradiation wavelength for the samples and the reference was the same using a 532 nm laser. The absorbance of DPBF was adjusted around 1.4 at 416 nm in toluene, and the absorbance of the photosensitizer **7** was adjusted to 0.2-0.3 at the irradiation wavelength. The photooxidation of DPBF was monitored at 60 s intervals. The quantum yields of singlet oxygen generation (Φ_Δ) were calculated according to equation (S2), using Rose Bengal ($\Phi_\Delta = 0.80$ in MeOH) as the reference,

$$\Phi_\Delta^{\text{sam}} = \Phi_\Delta^{\text{std}} \frac{m^{\text{sam}} F^{\text{std}}}{m^{\text{std}} F^{\text{sam}}} \quad (\text{S1})$$

where the superscripts *sam* and *std* designate BODIPY dimer **7** and the standard Rose Bengal, respectively; Φ_Δ is the quantum yield of singlet oxygen; m is the slope of a plot of difference in change in absorbance of DPBF (at 416 nm) with the irradiation time and F is the absorption correction factor, which is given by $F = 1 - 10^{-A}$ (A is the absorbance at the irradiation wavelength).

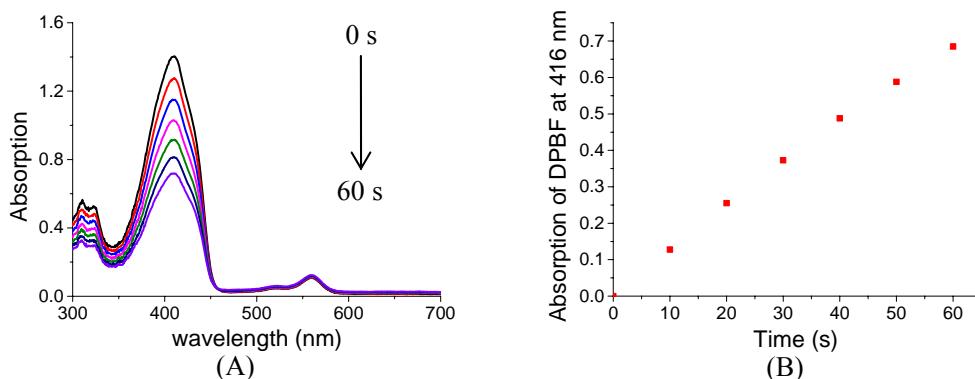
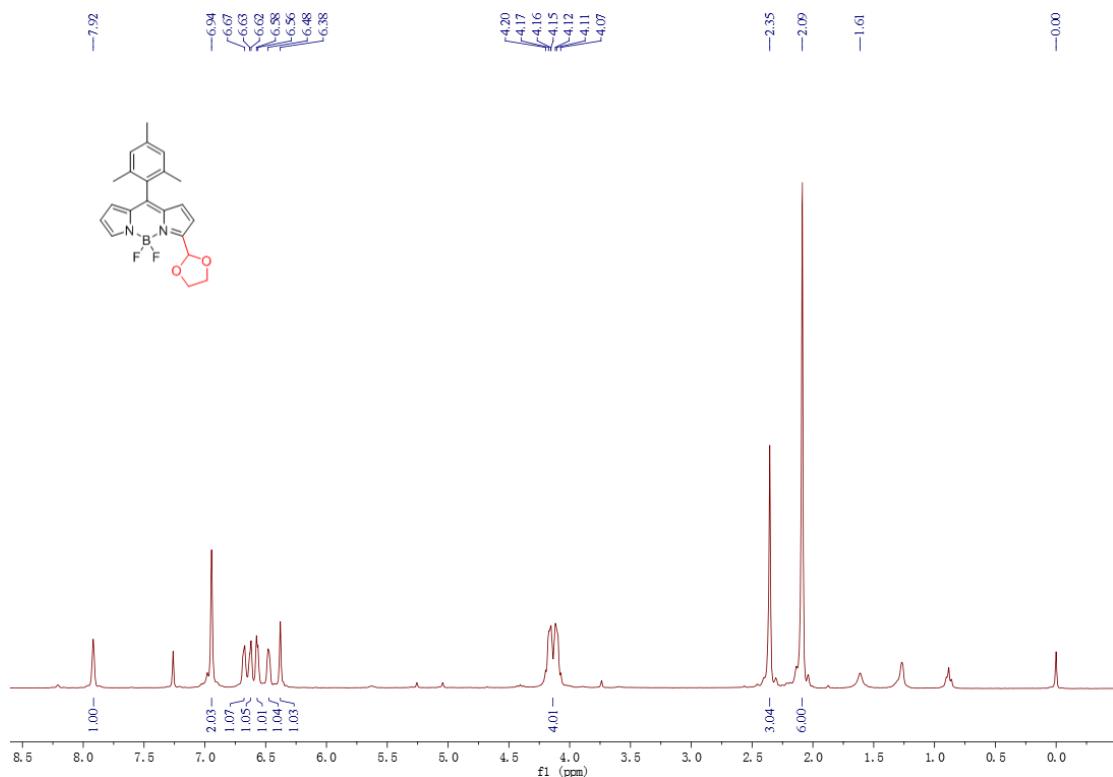


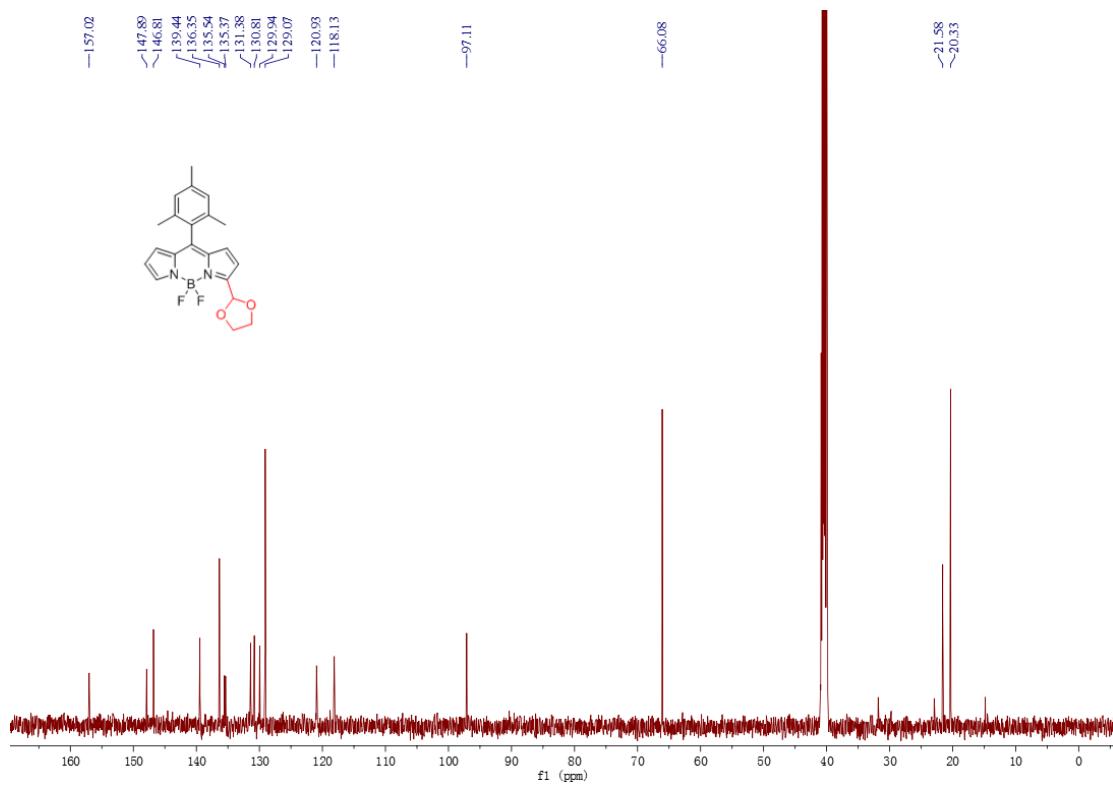
Figure S19. (A) Changes in the absorption spectrum of **DPBF** upon irradiation in the presence of Rose Bengal (**RB**) in methanol (recorded at 10 s intervals). (B) Plot of change in absorbance of DPBF at 416 nm vs irradiation time ($\lambda_{\text{irr}} = 532$ nm) in the presence of Rose Bengal (**RB**) in methanol.

4. NMR and HRMS spectra of all new compounds

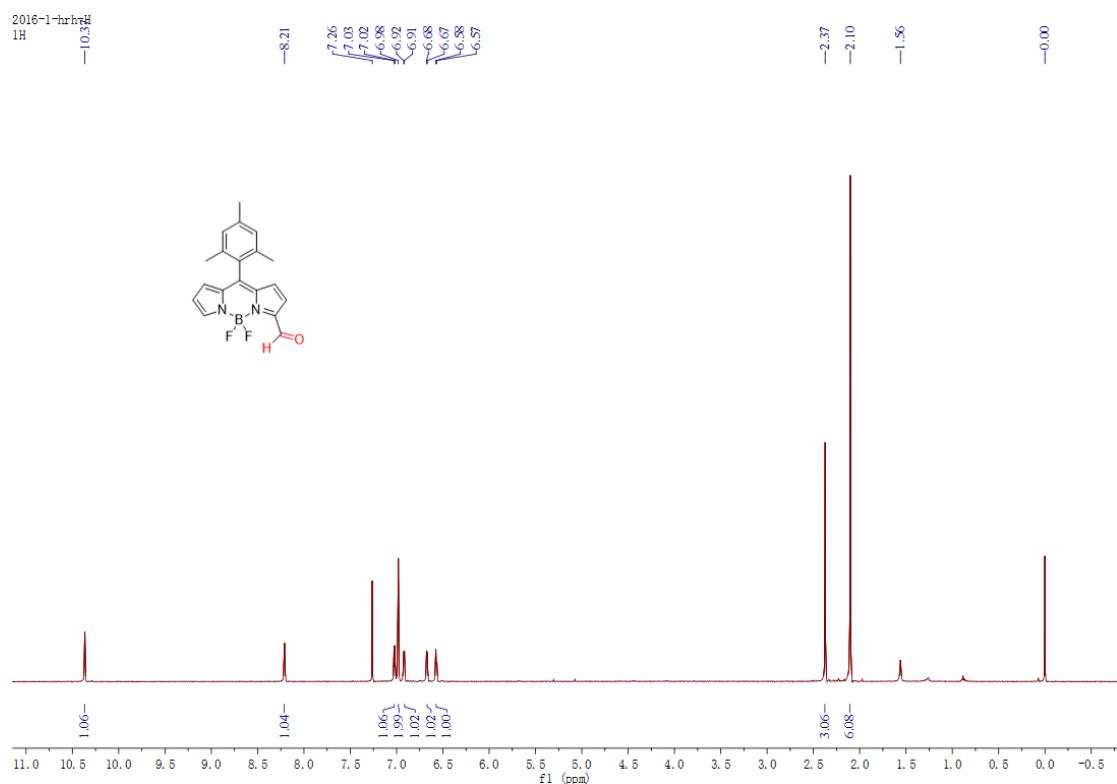
¹H NMR spectrum of **3a** in CDCl₃



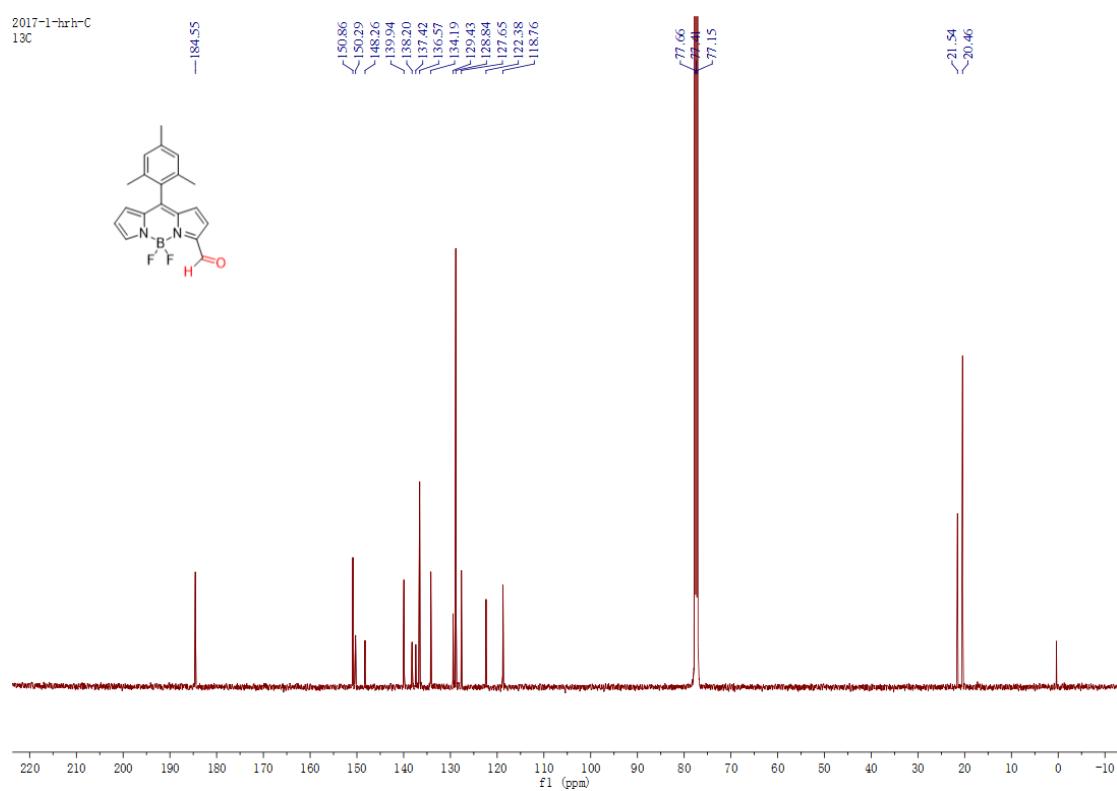
¹³C NMR spectrum of **3a** in *d*₆-DMSO



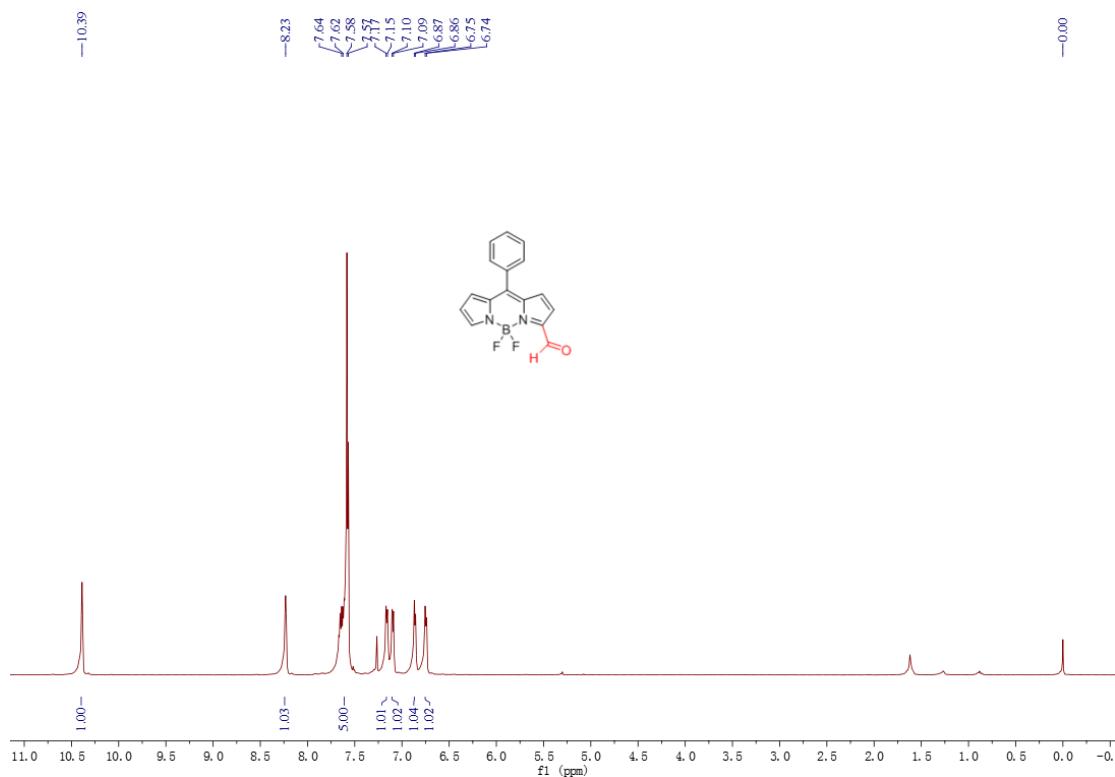
¹H NMR spectrum of **4a** in CDCl₃



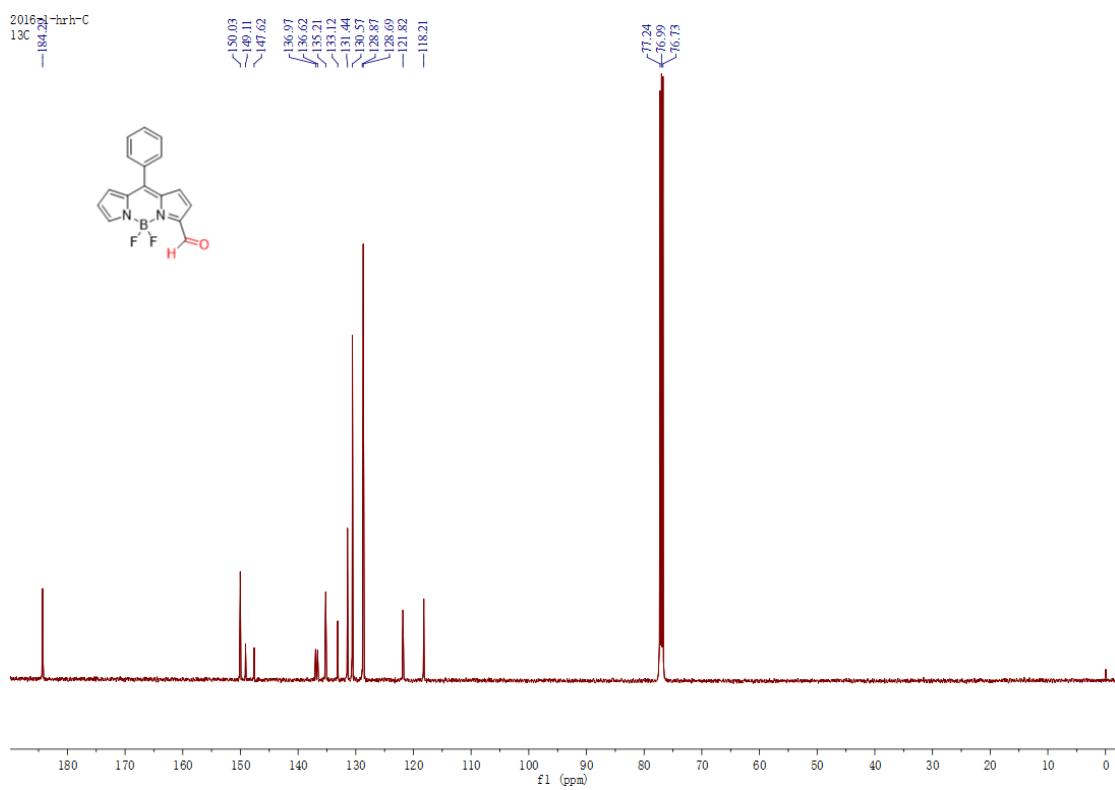
¹³C NMR spectrum of **4a** in CDCl₃



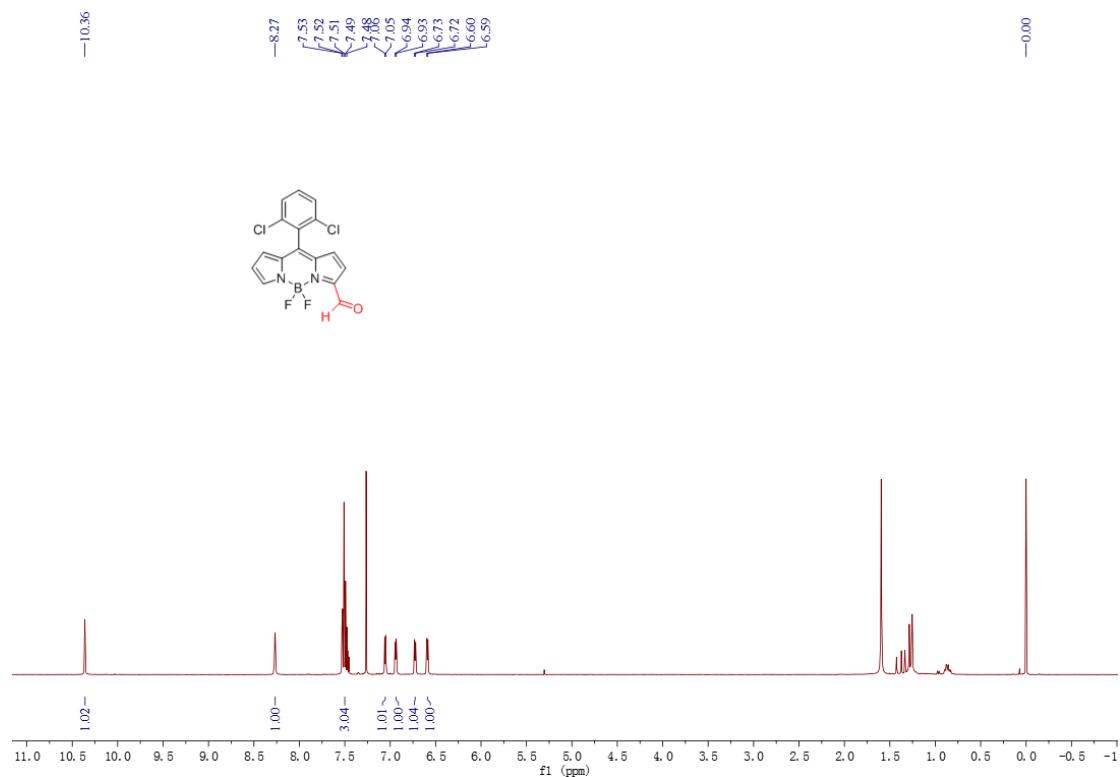
¹H NMR spectrum of **4b** in CDCl₃



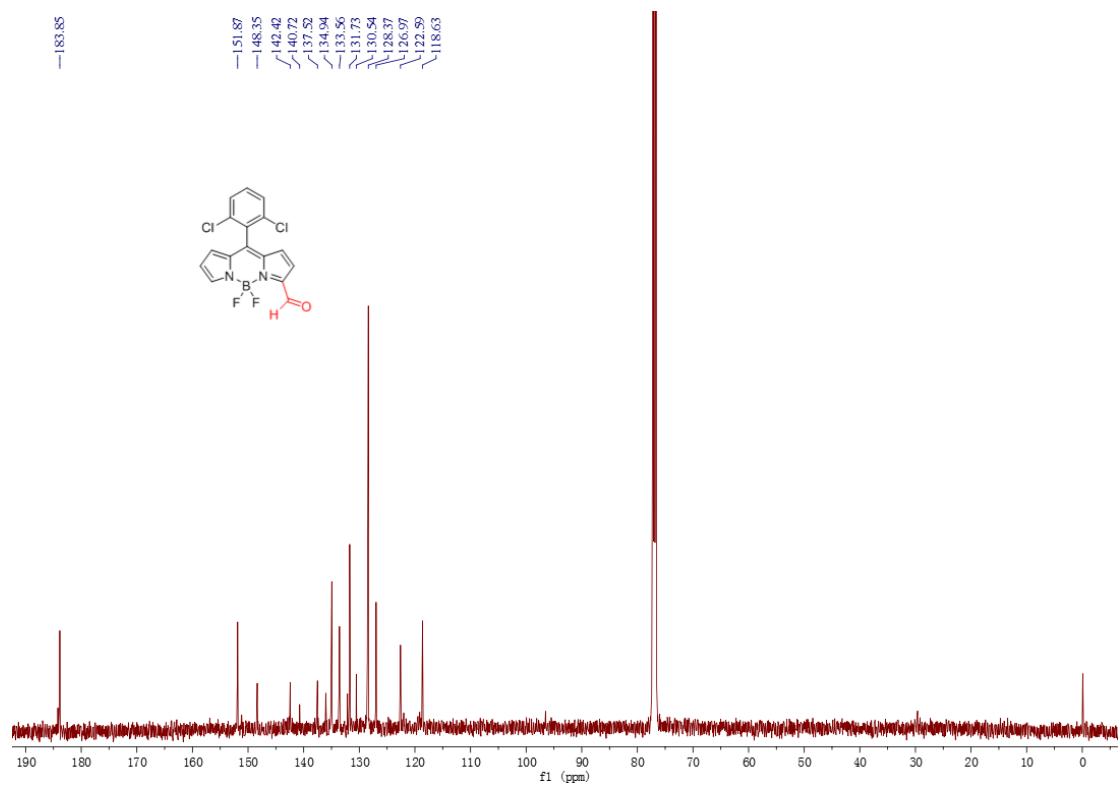
¹³C NMR spectrum of **4b** in CDCl₃



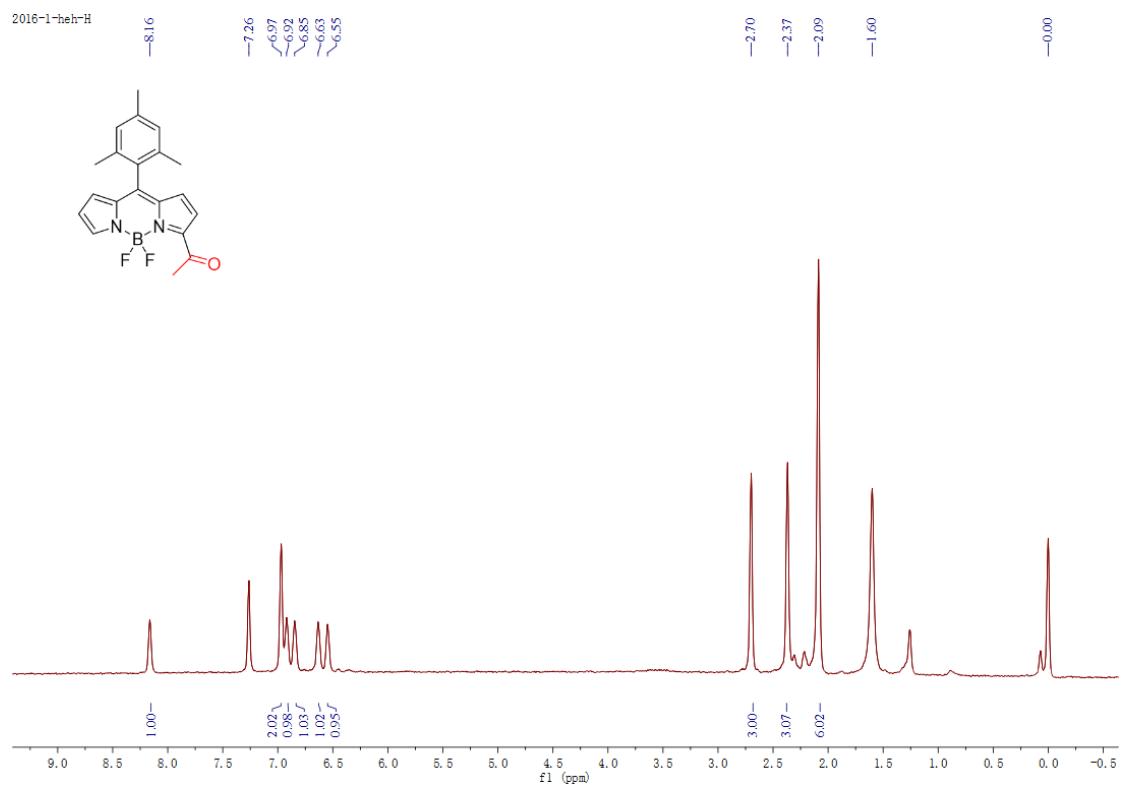
¹H NMR spectrum of **4c** in CDCl₃



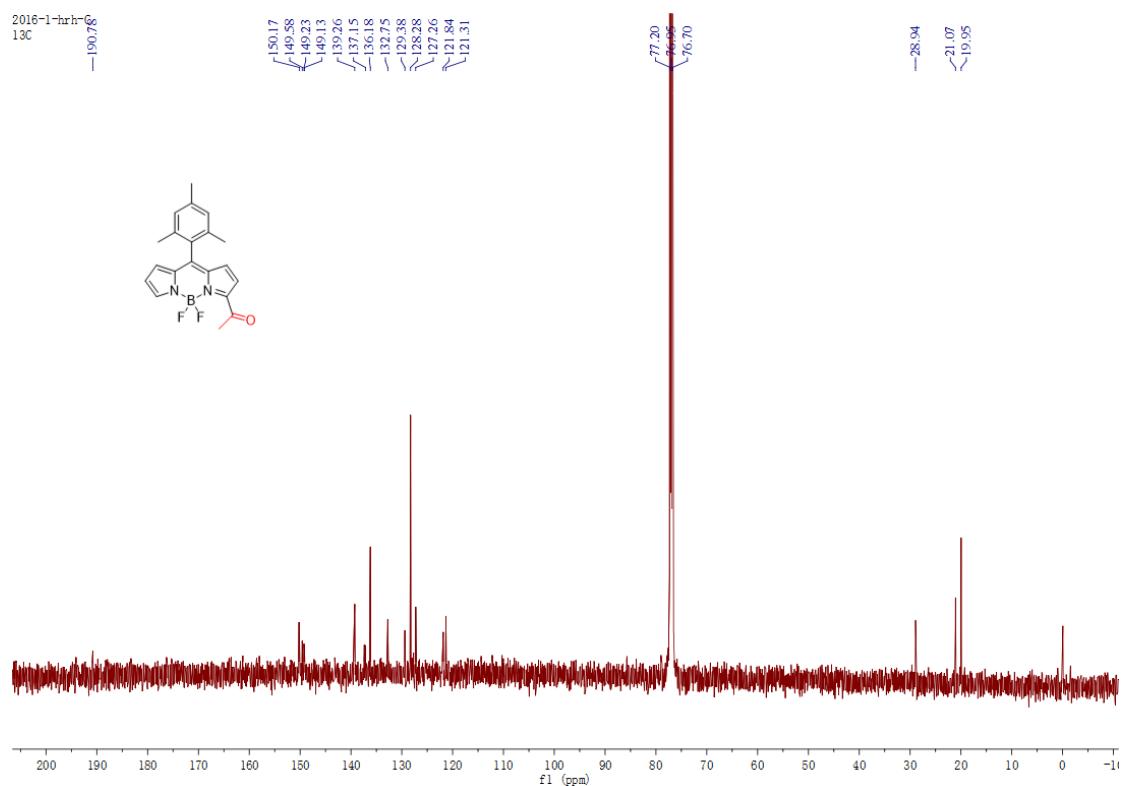
¹³C NMR spectrum of **4c** in CDCl₃



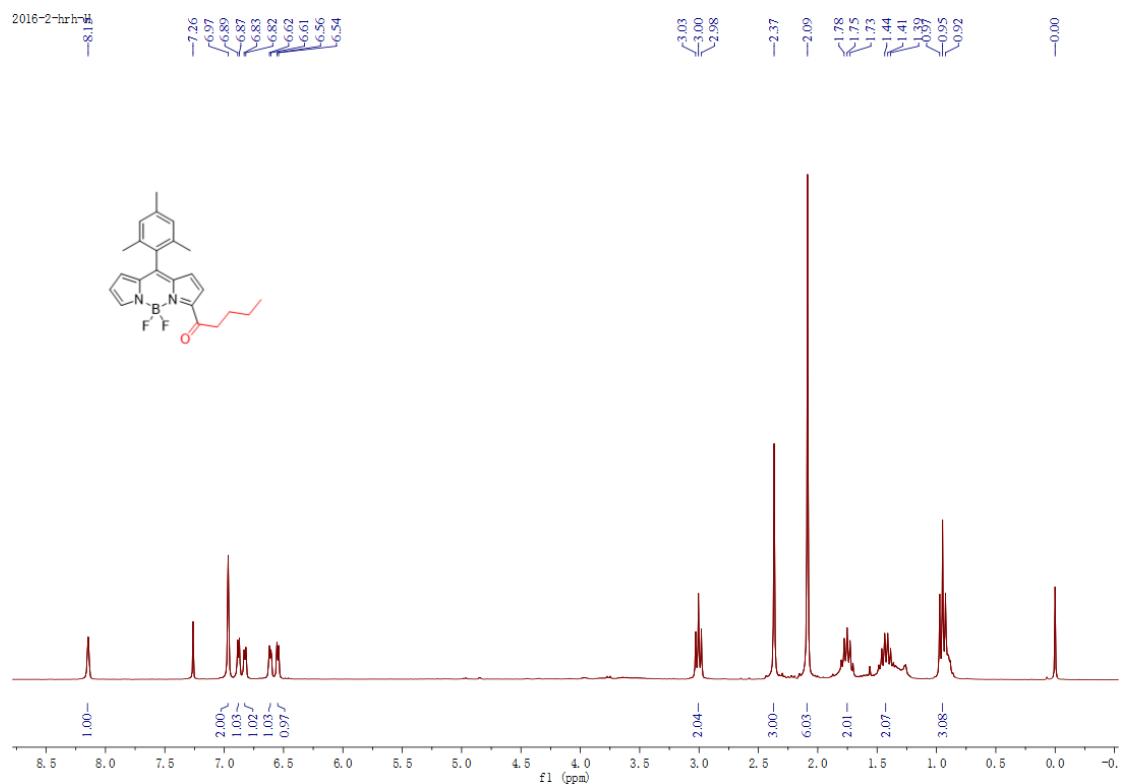
¹H NMR spectrum of **4d** in CDCl₃



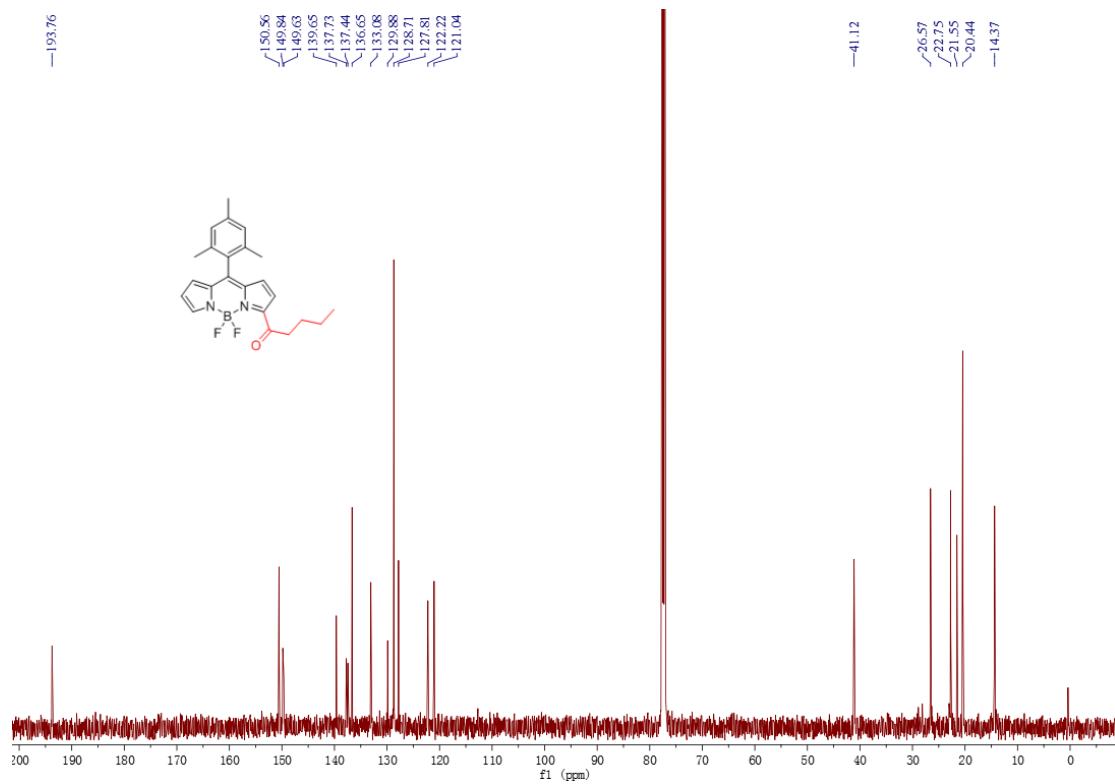
¹³C NMR spectrum of **4d** in CDCl₃



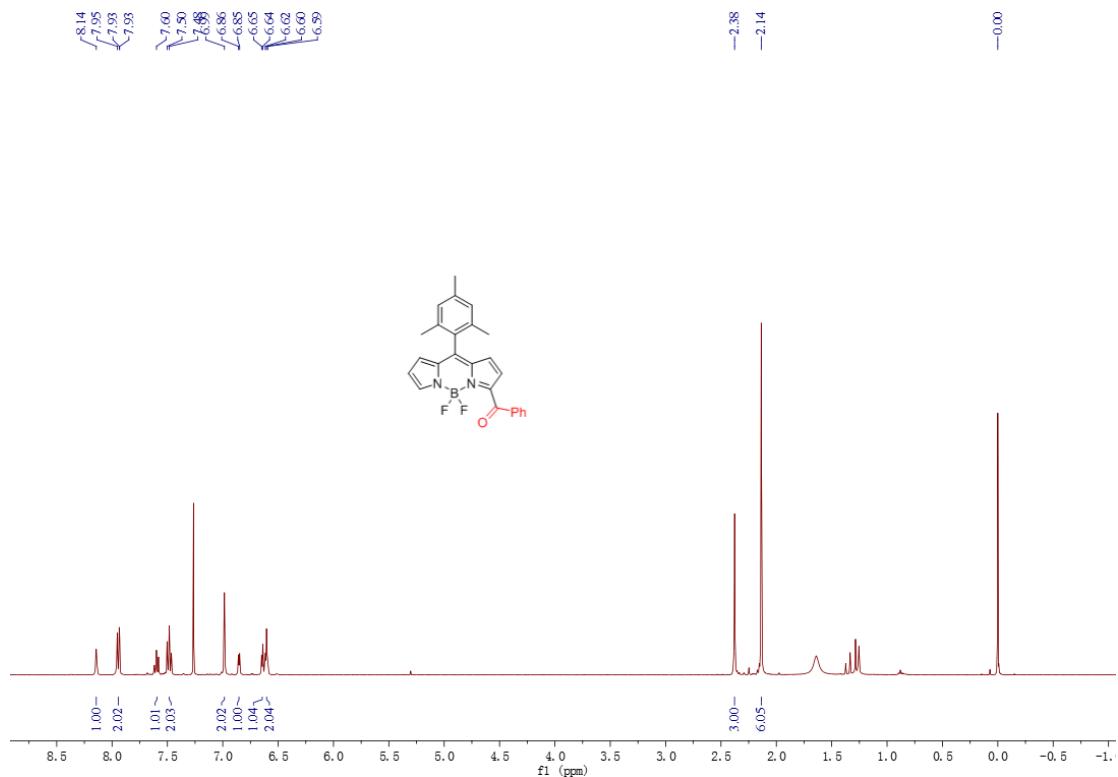
¹H NMR spectrum of **4e** in CDCl₃



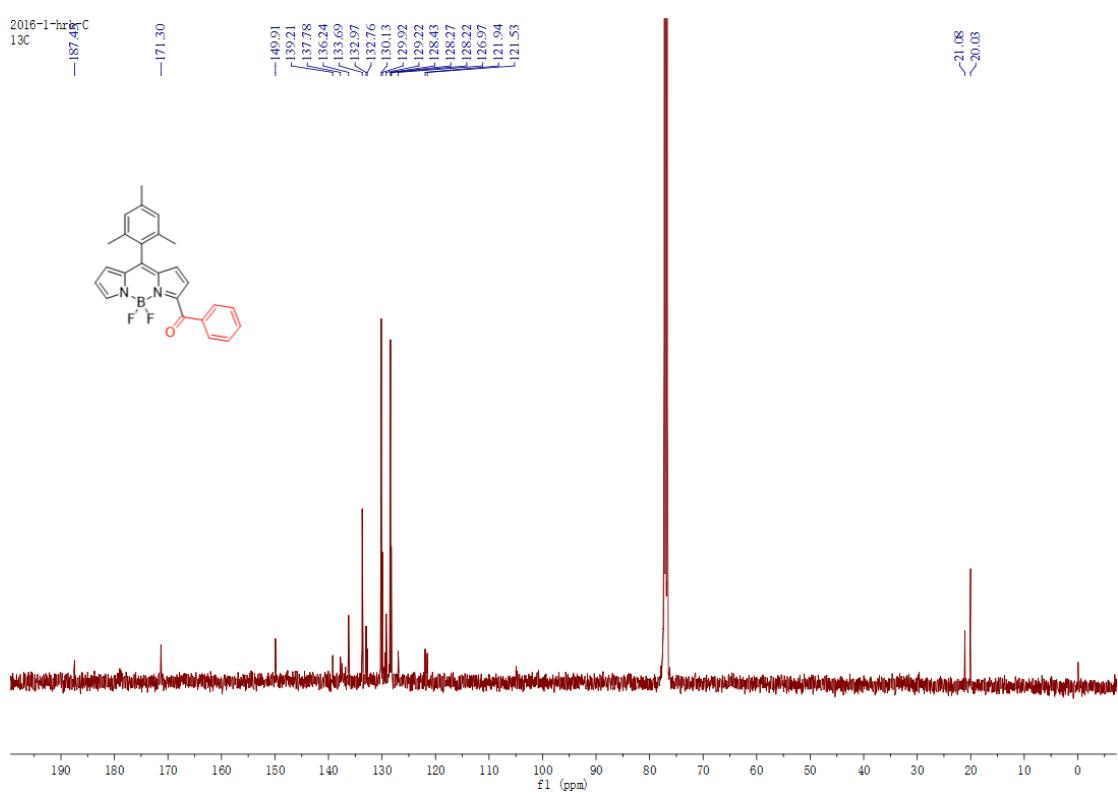
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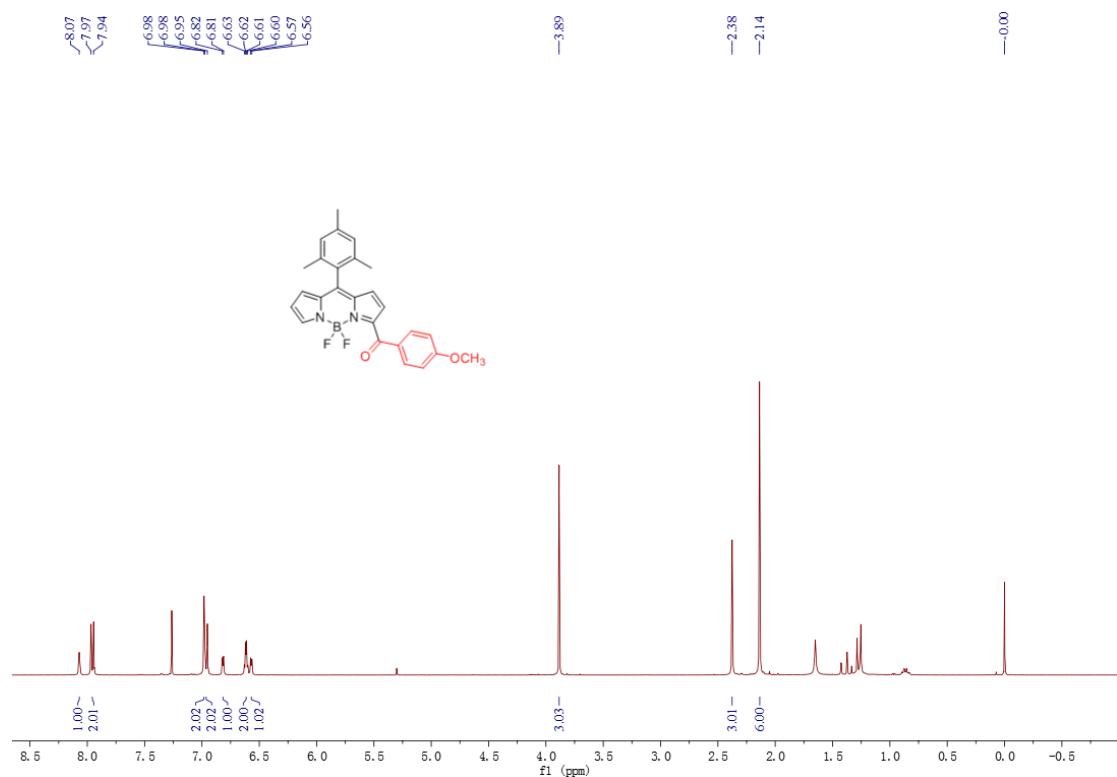
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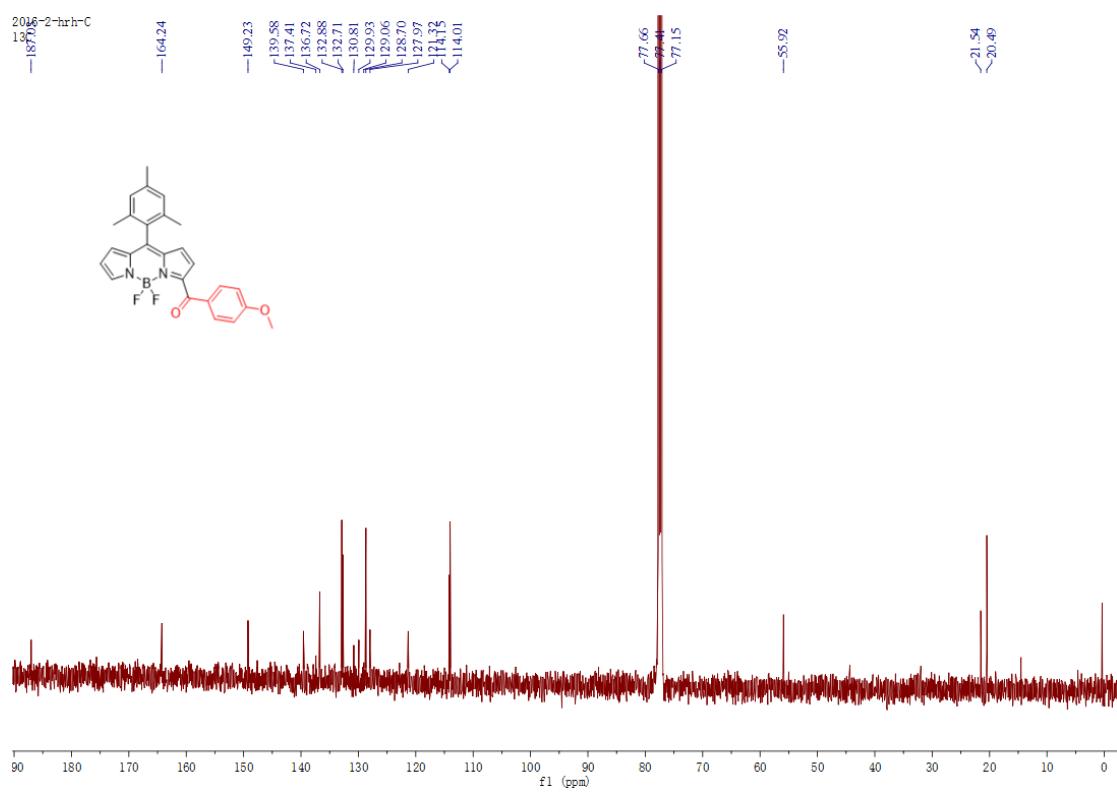
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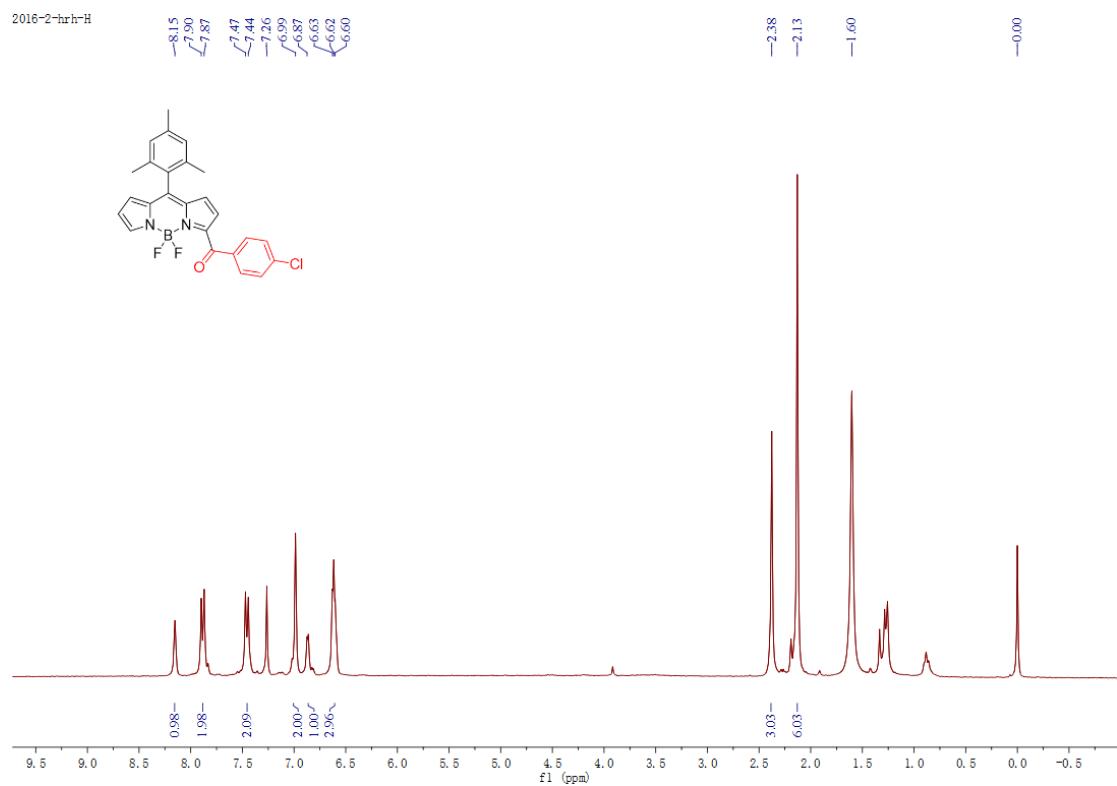
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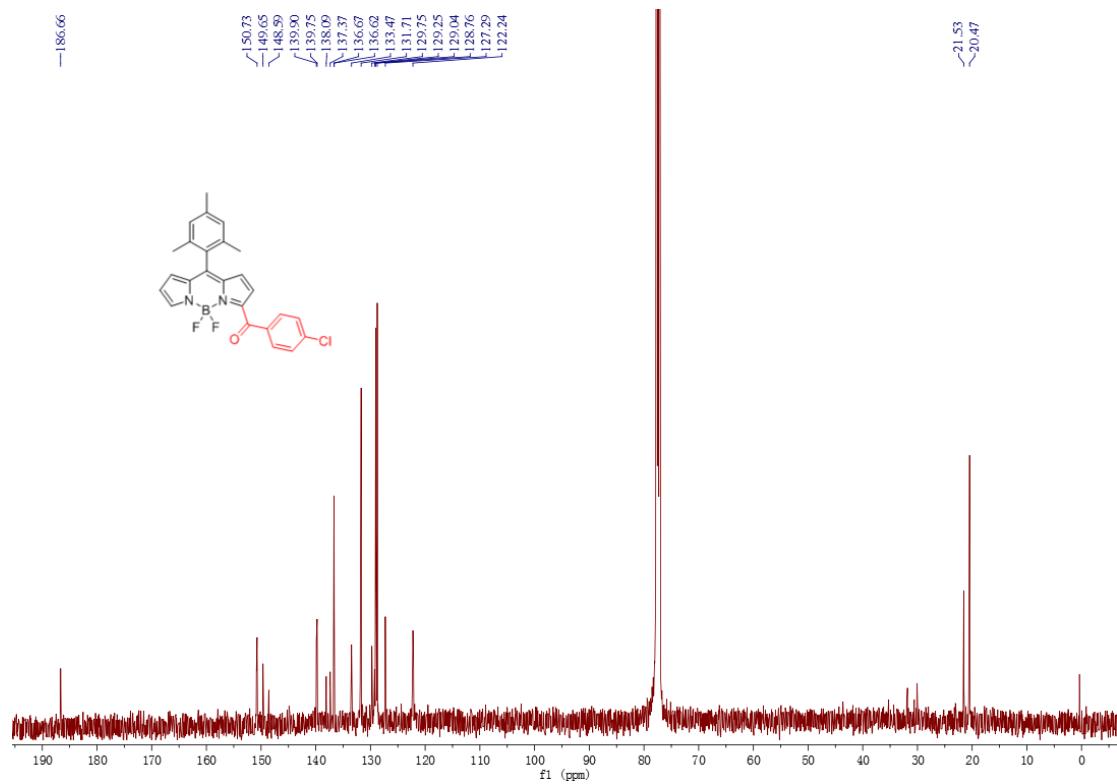
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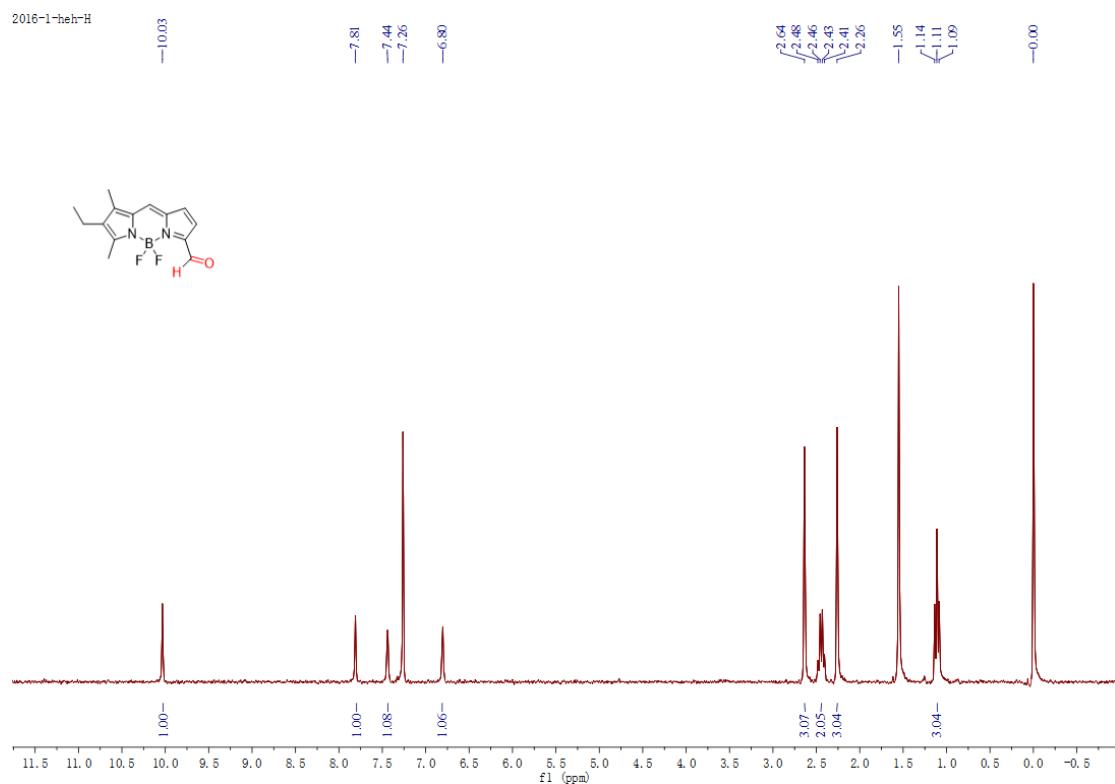
¹H NMR spectrum of **4h** in CDCl₃



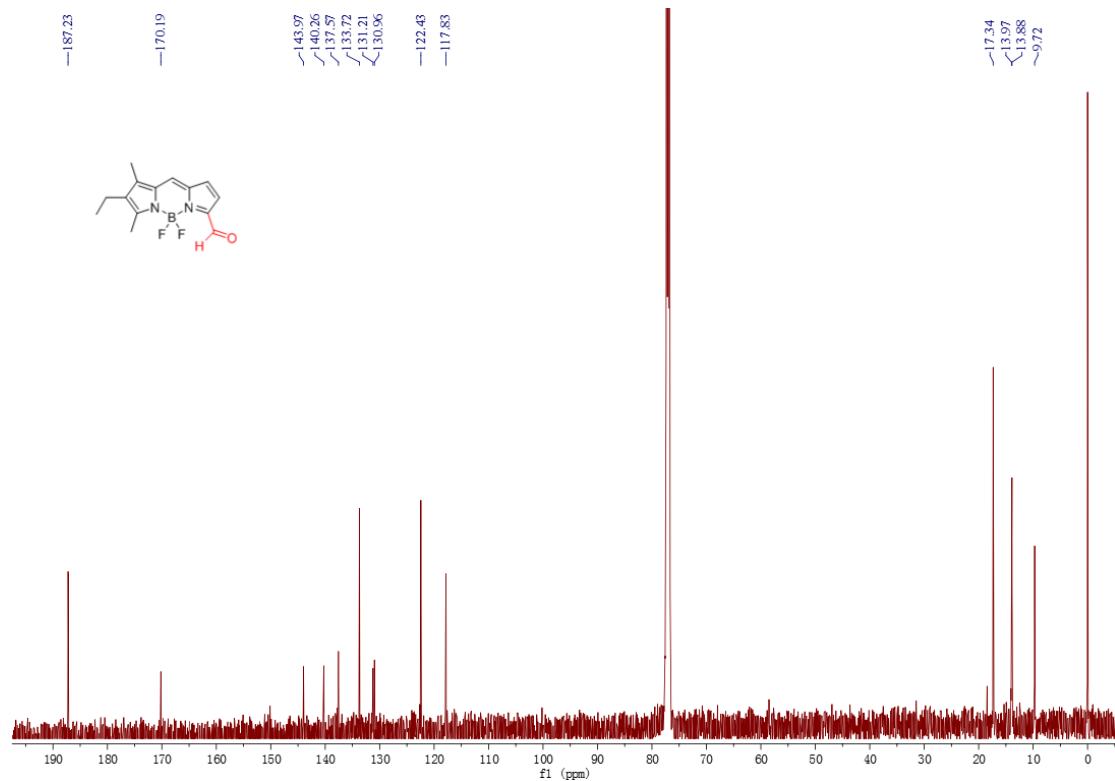
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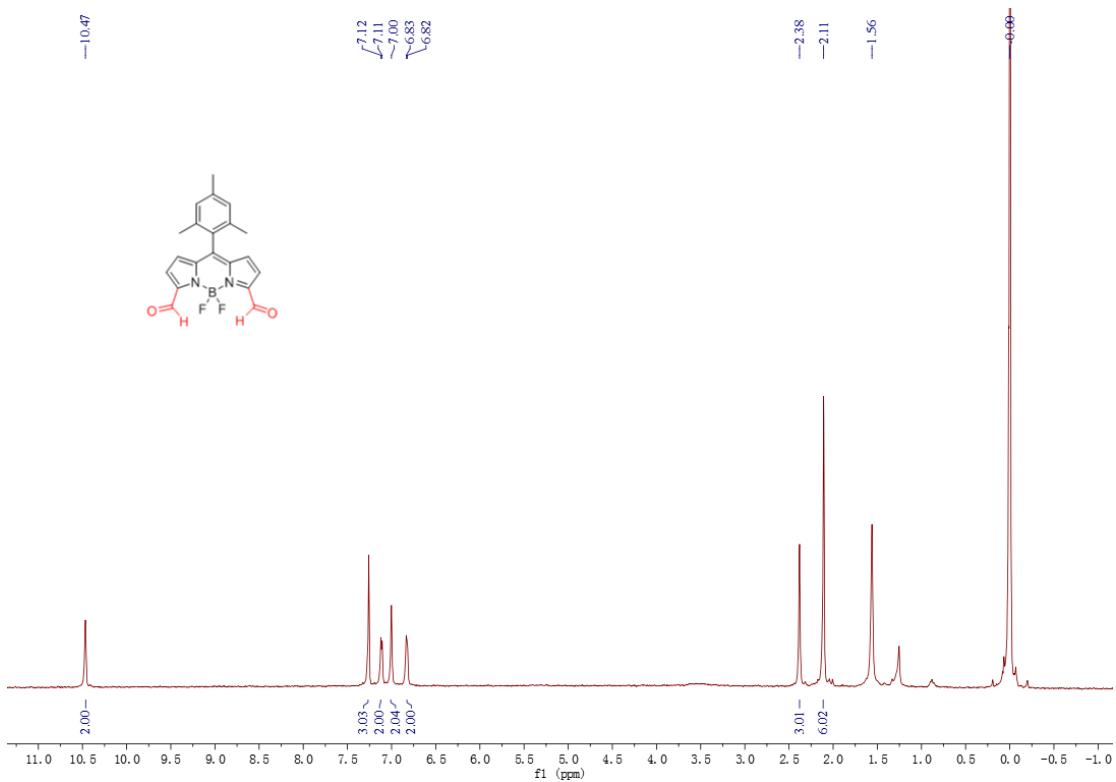
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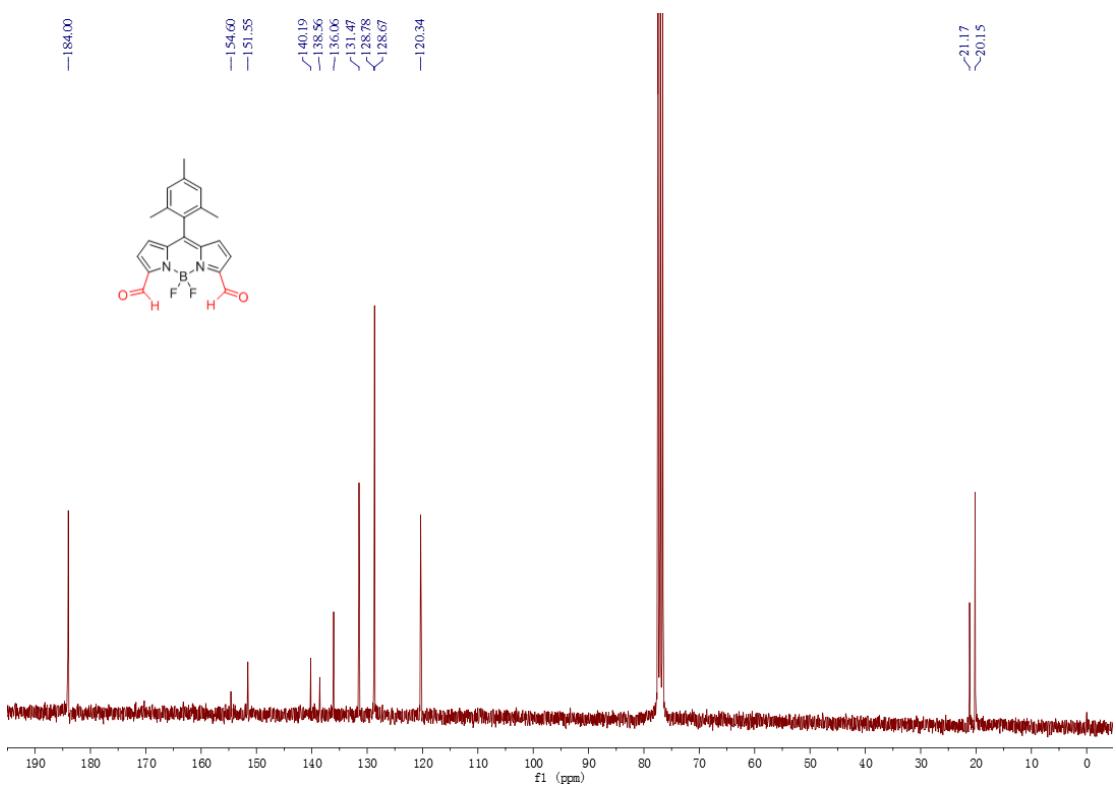
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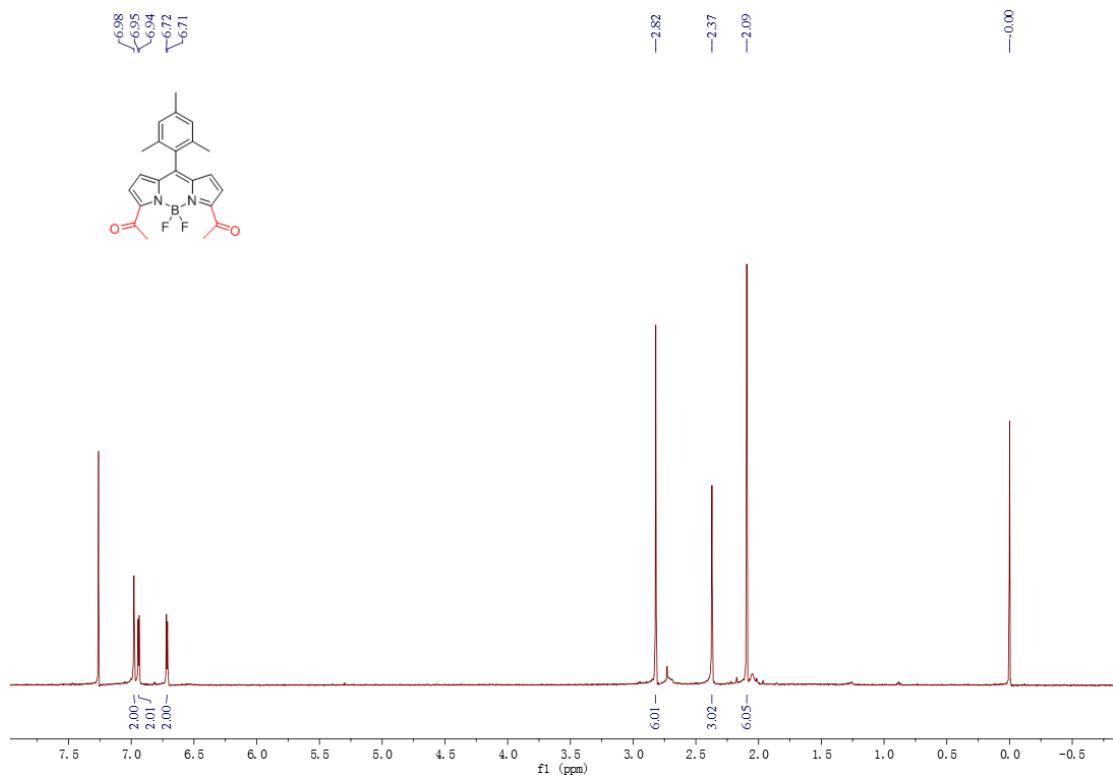
¹H NMR spectrum of **5a** in CDCl₃



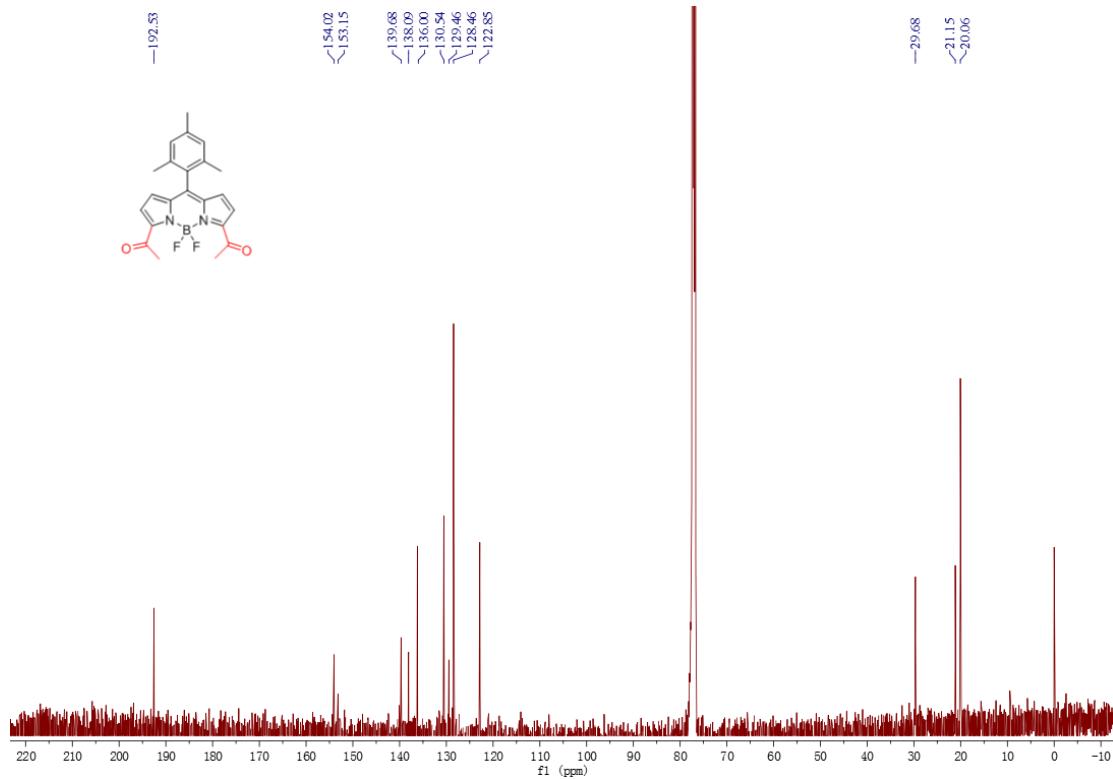
¹³C NMR spectrum of **5a** in CDCl₃



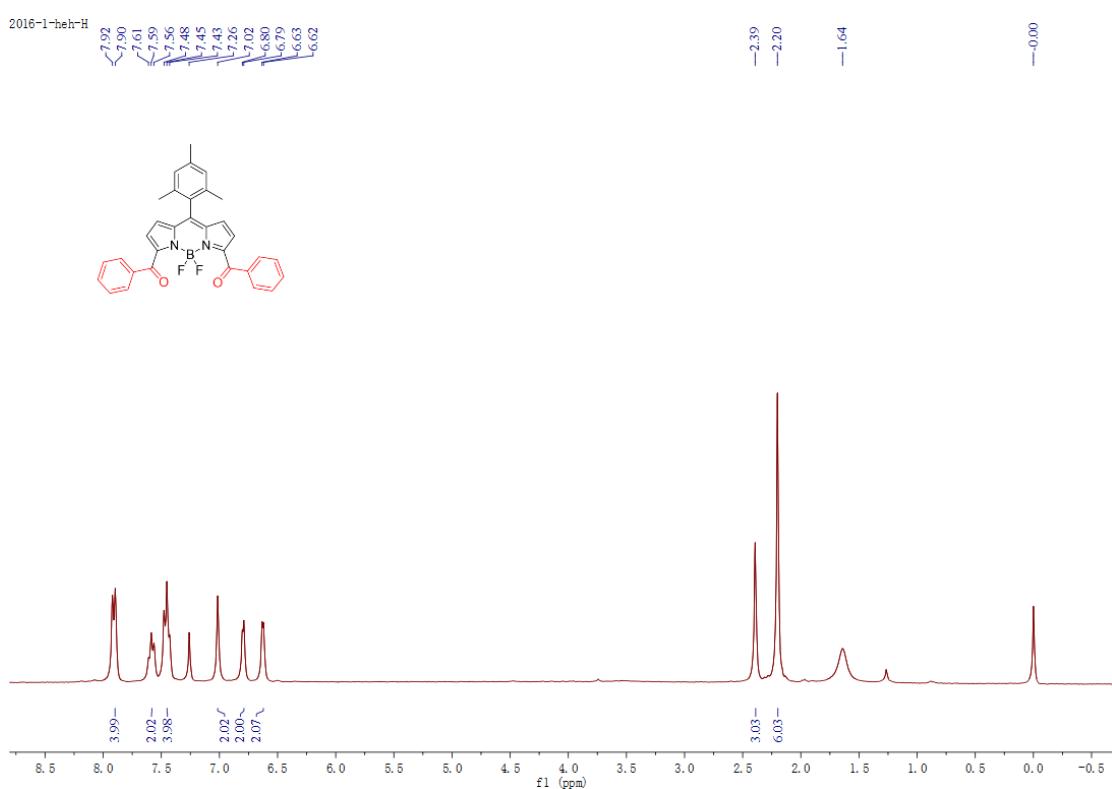
¹H NMR spectrum of **5b** in CDCl₃



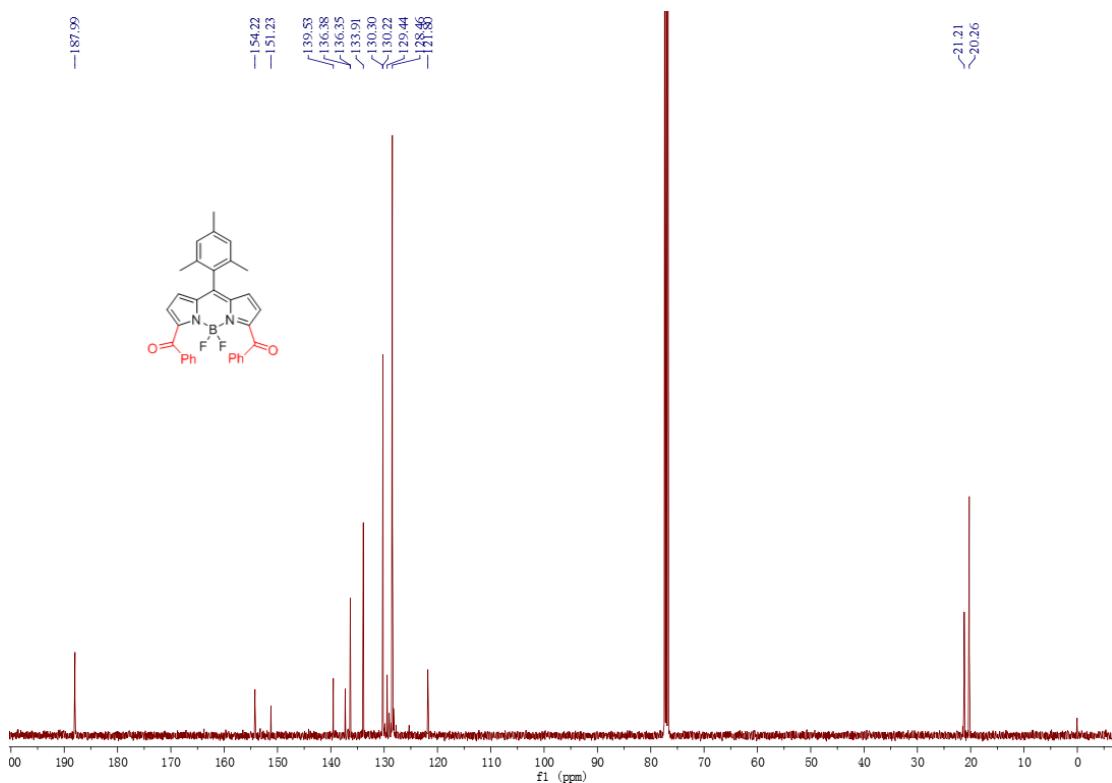
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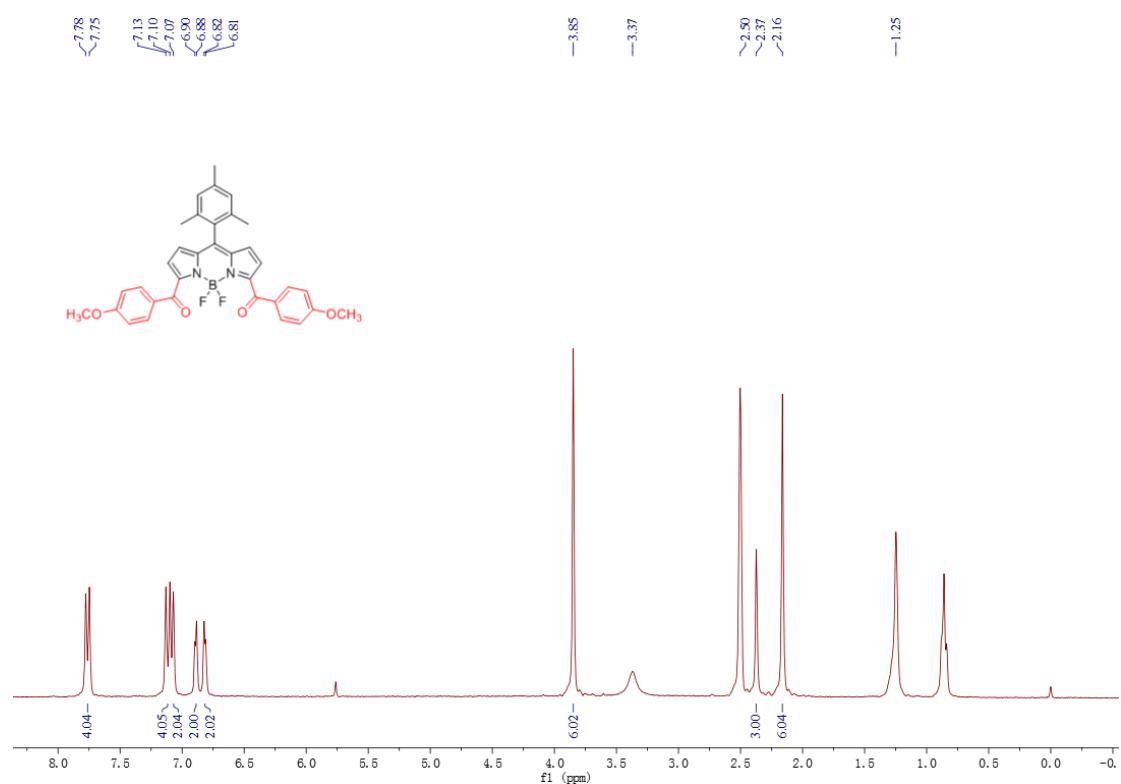
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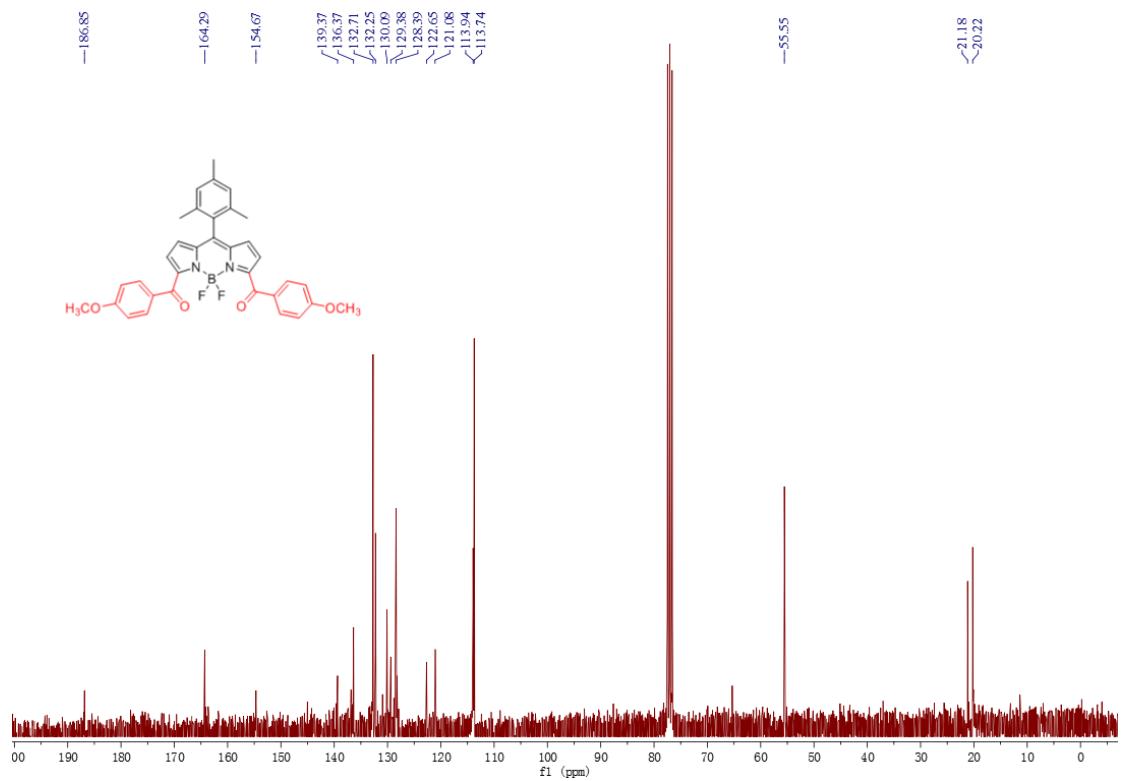
¹³C NMR spectrum of **5c** in CDCl₃



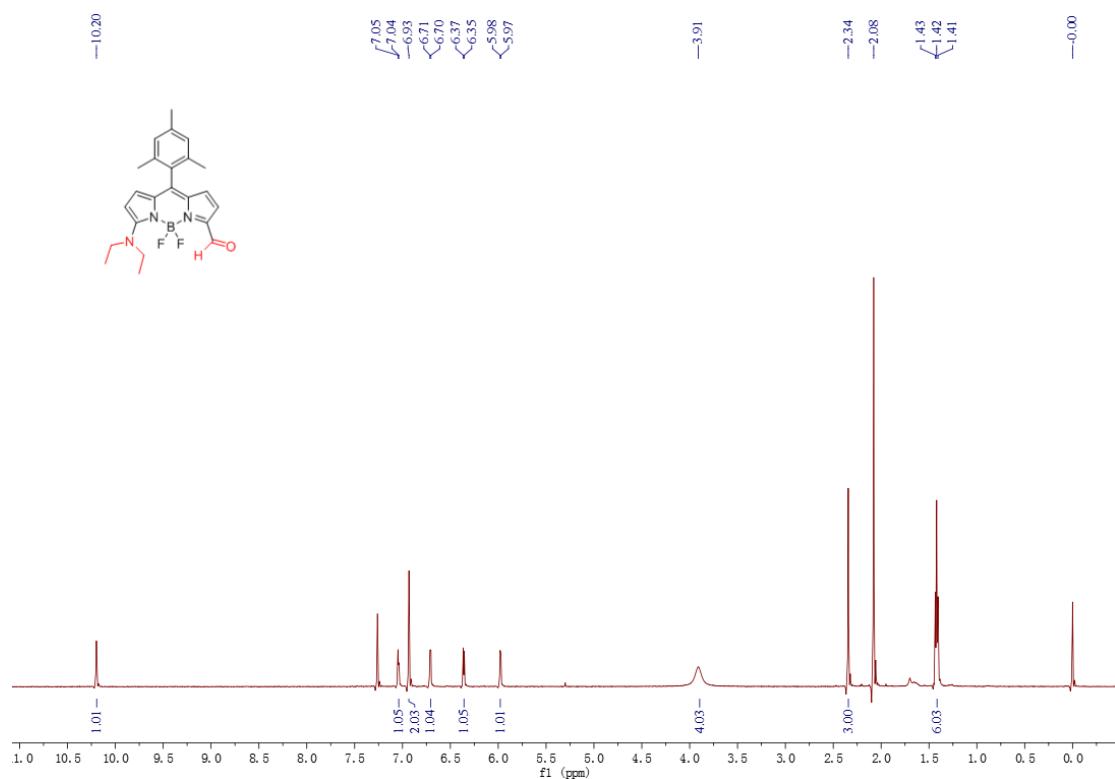
¹H NMR spectrum of **5d** in DMSO



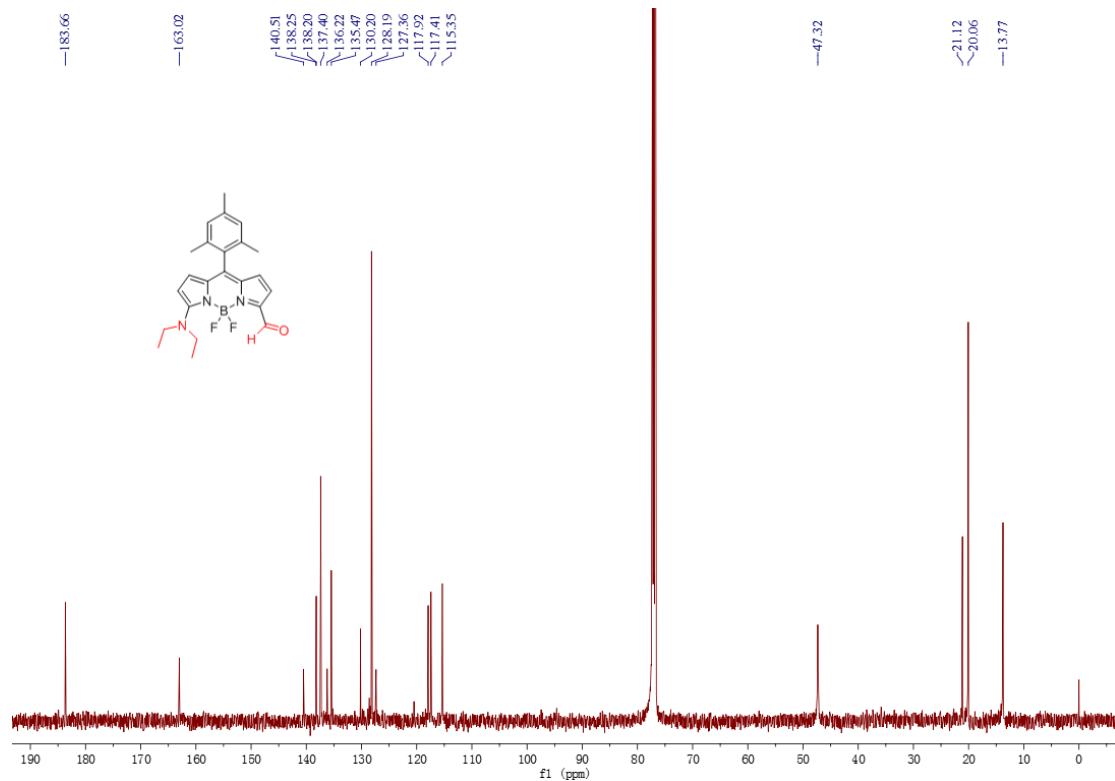
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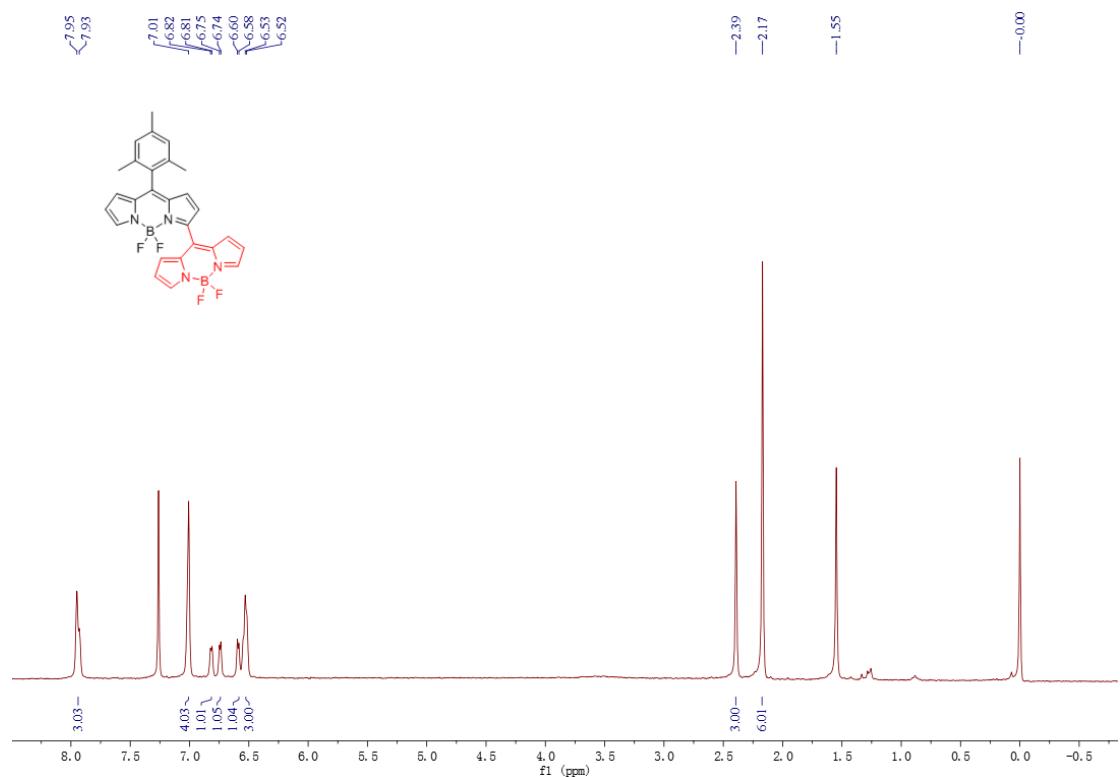
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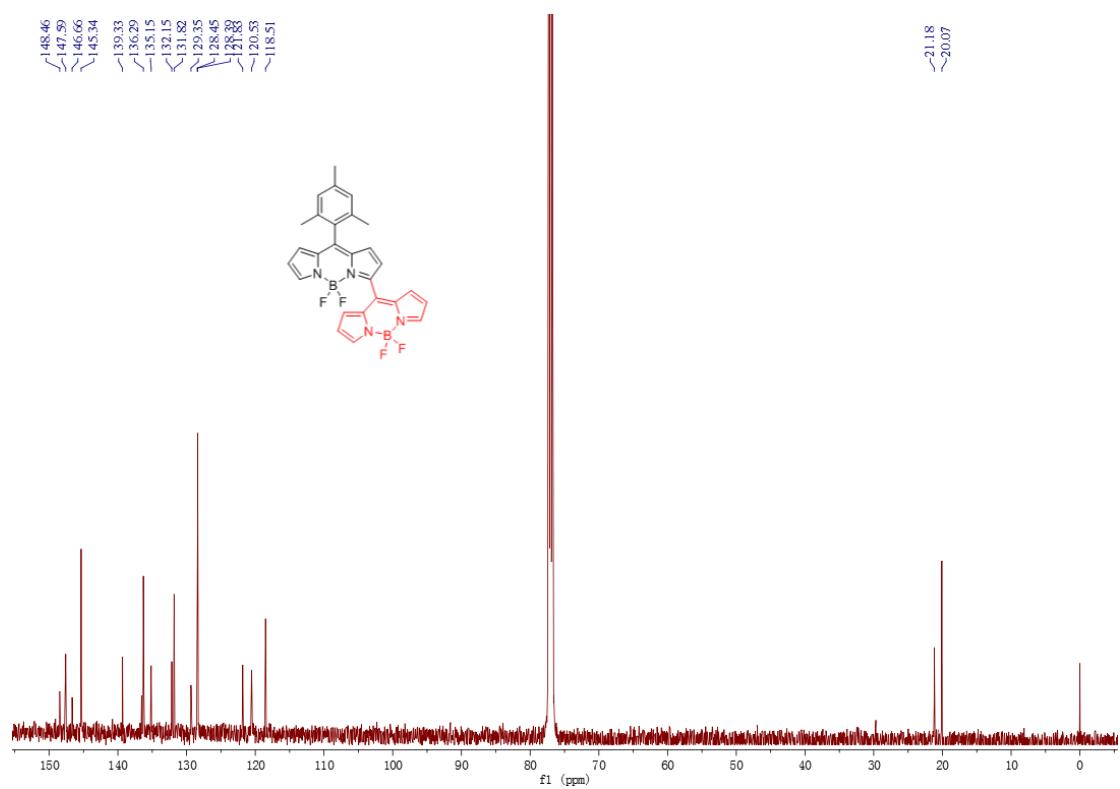
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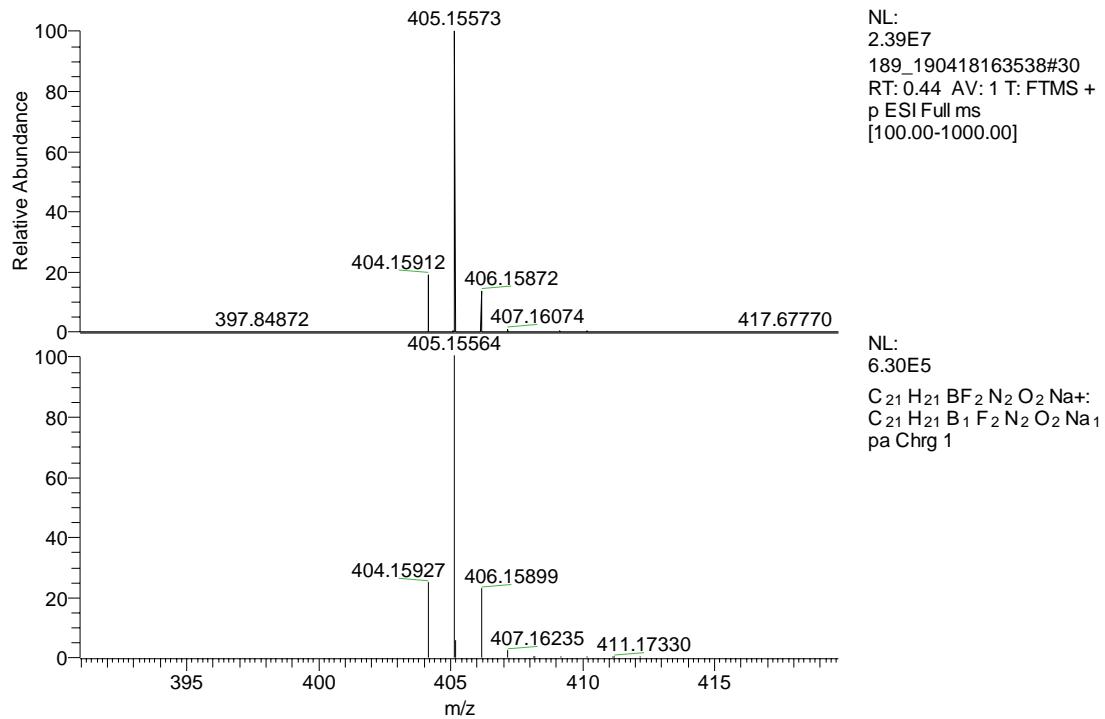
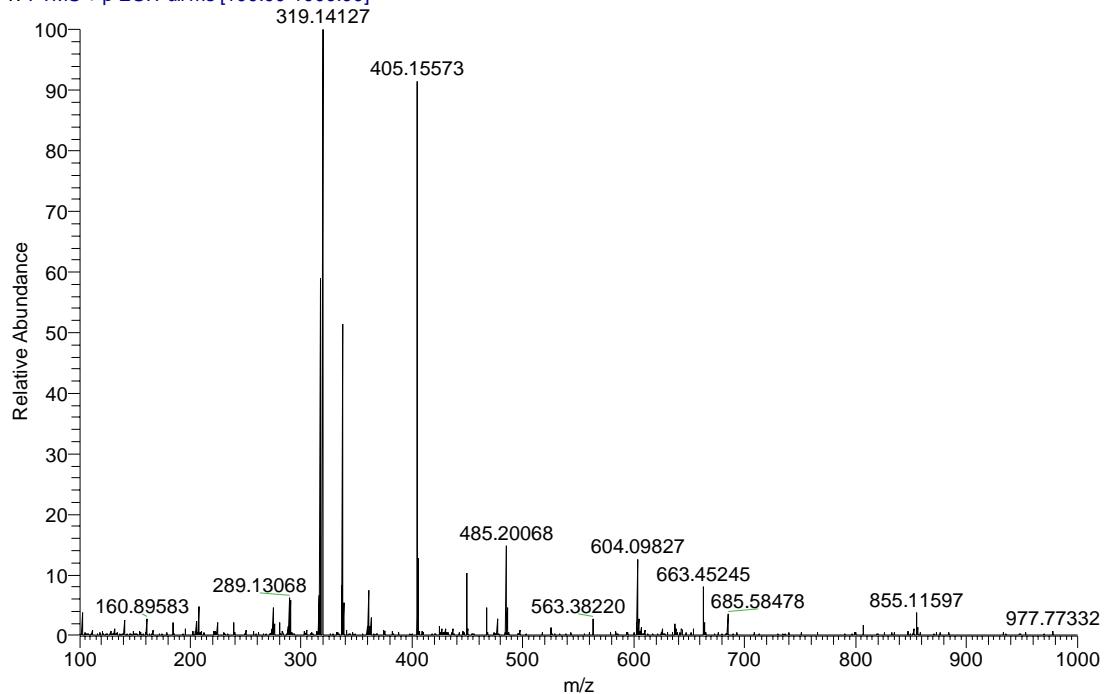


¹³C NMR spectrum of **7** in CDCl₃



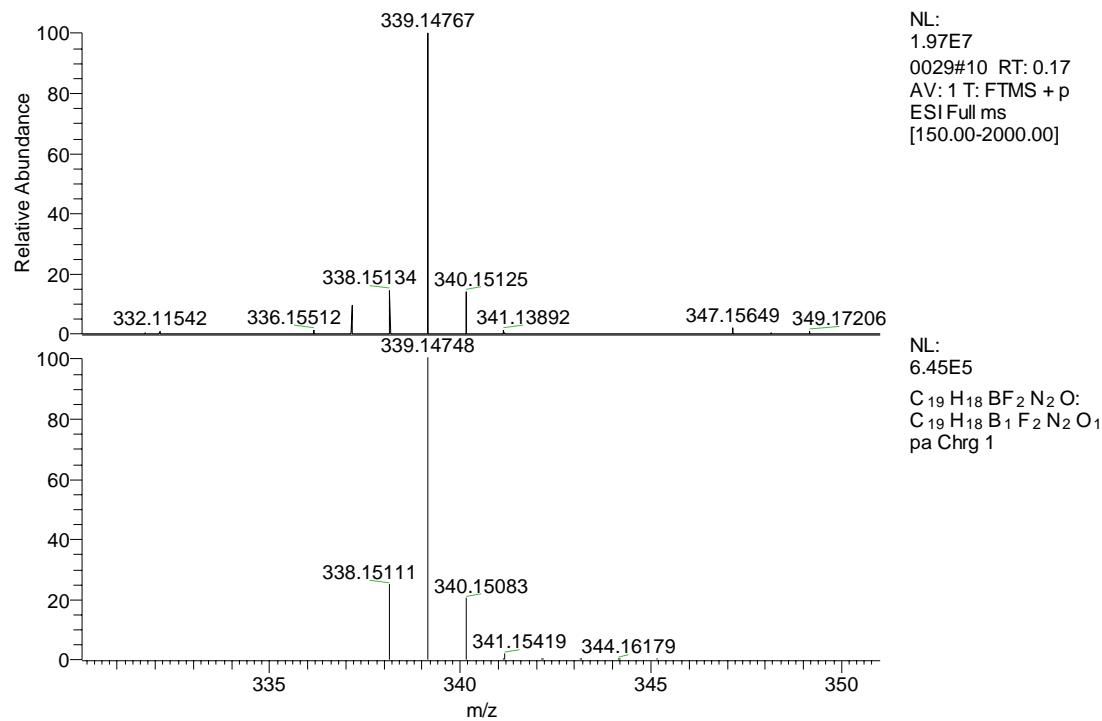
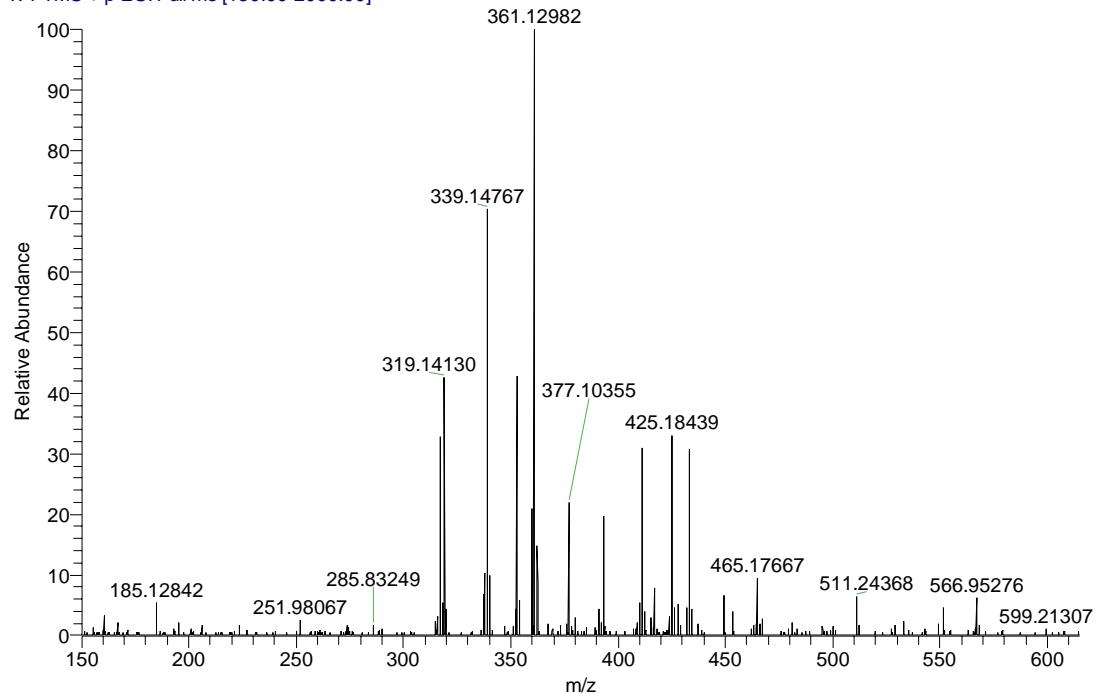
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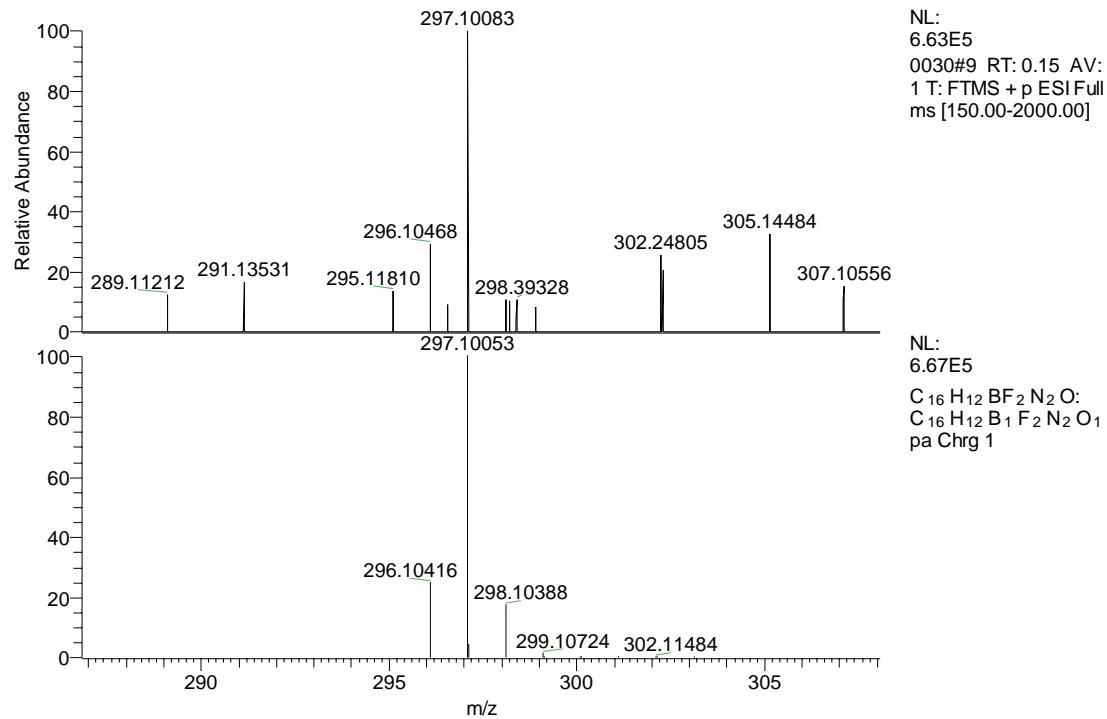
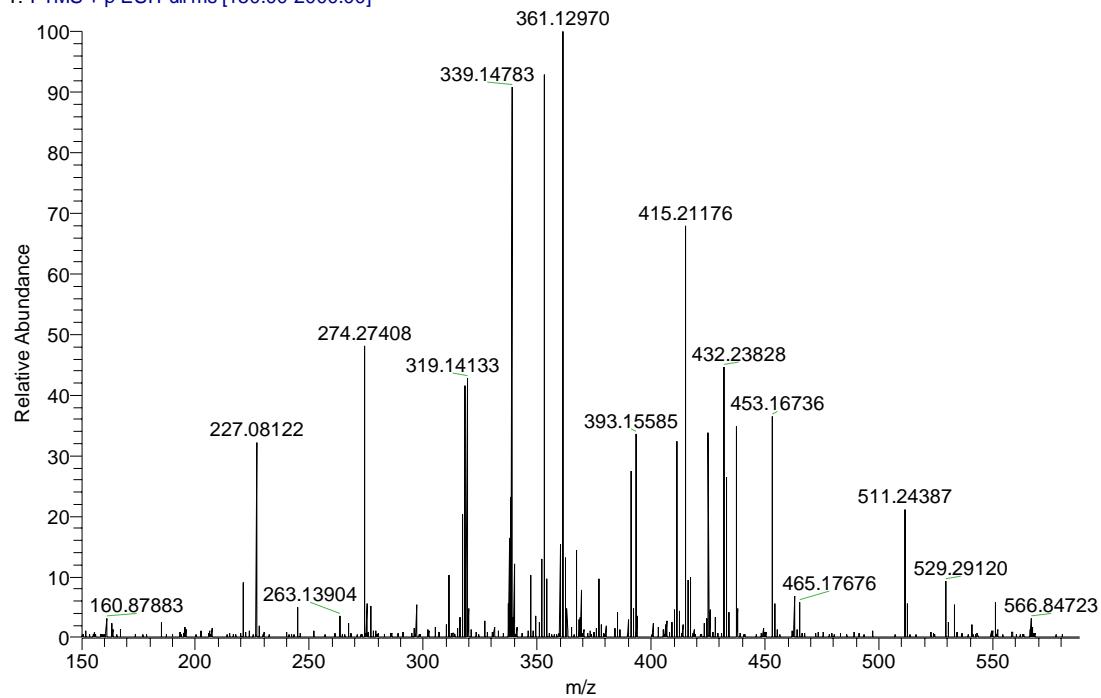
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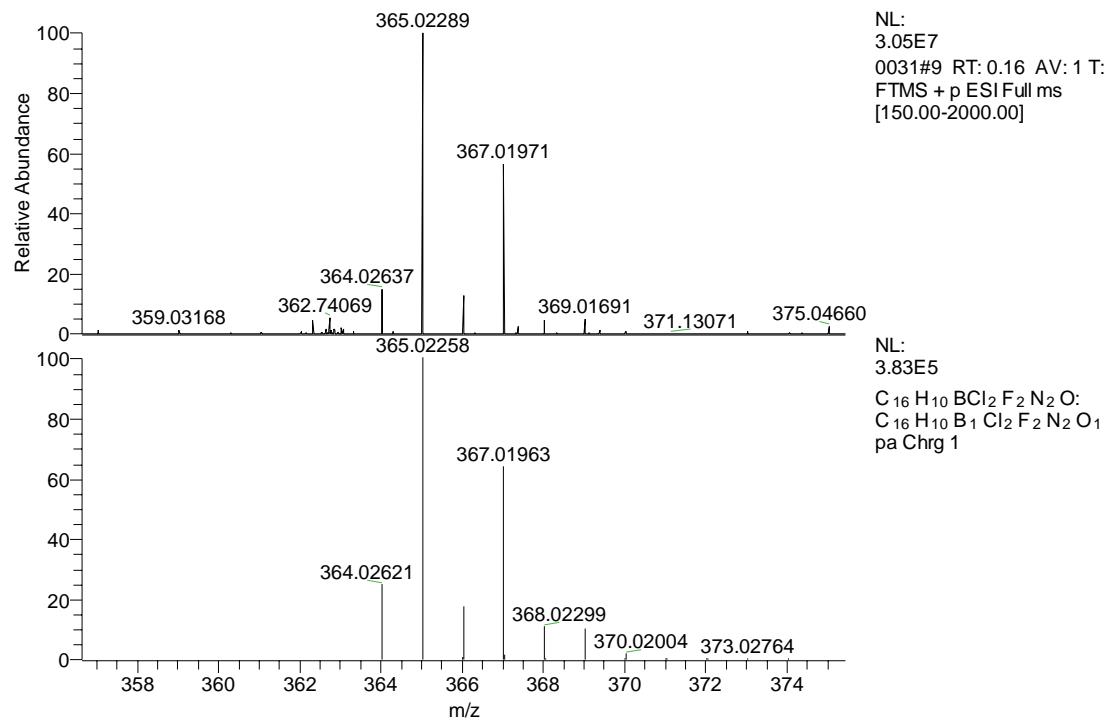
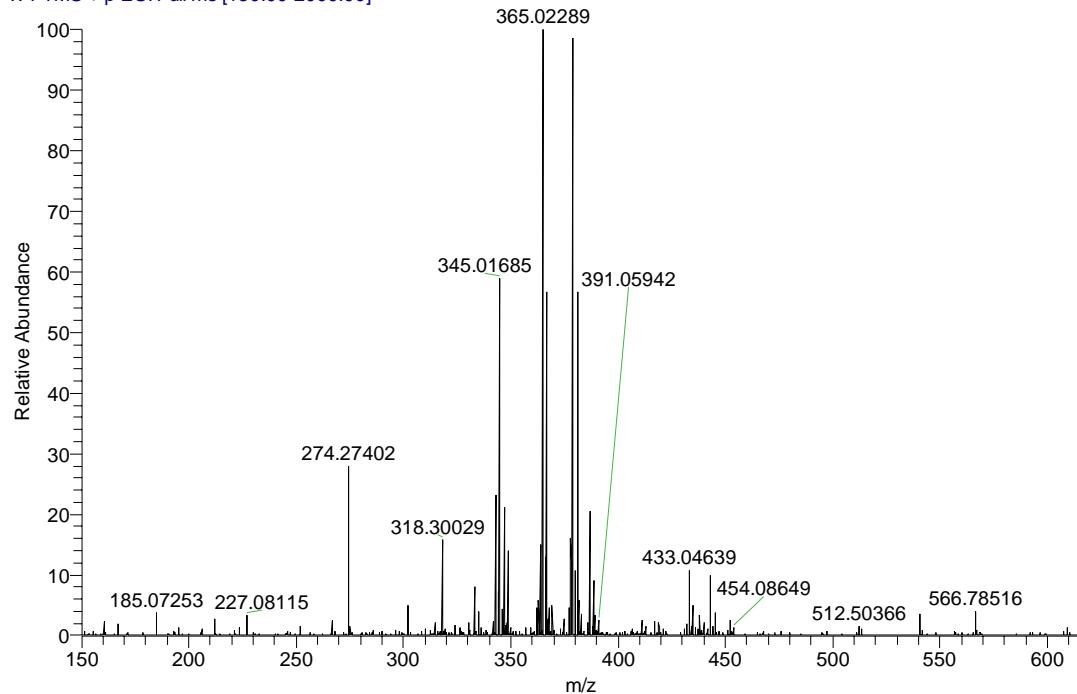
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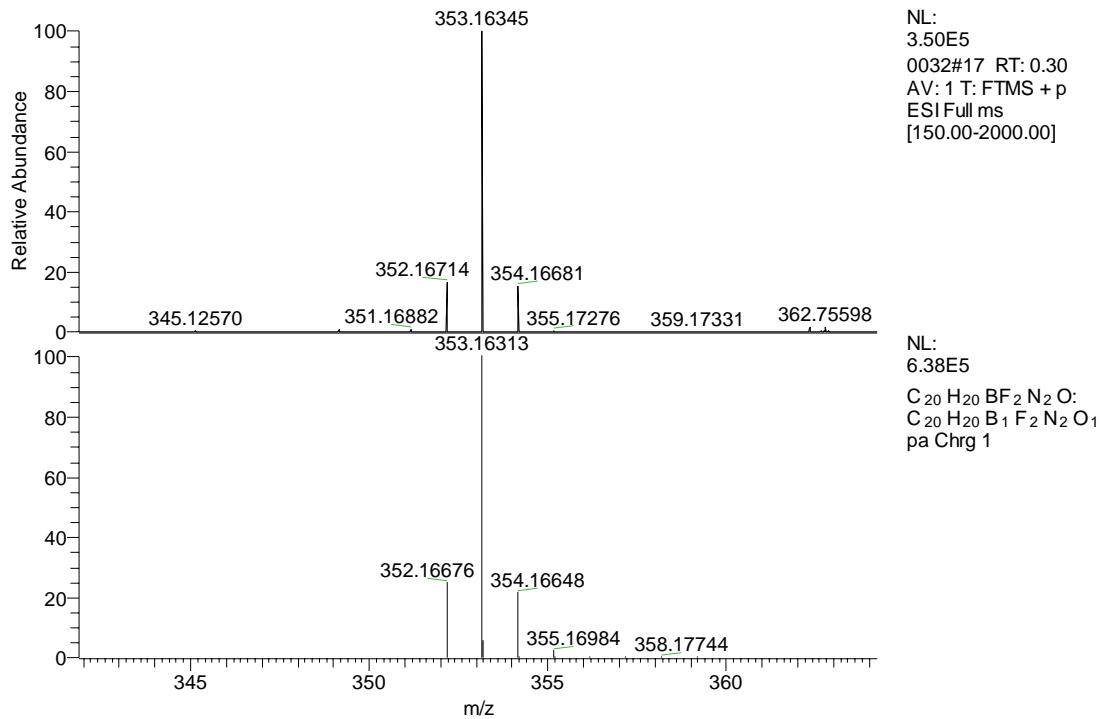
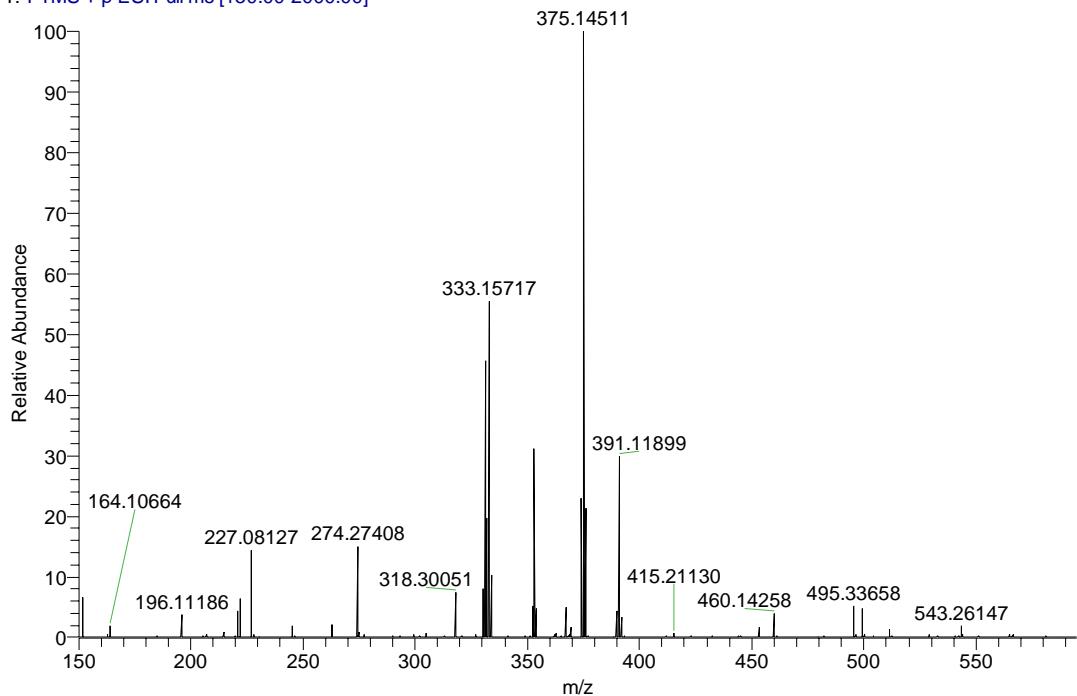
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T: FTMS + p ESI Full ms [150.00-2000.00]



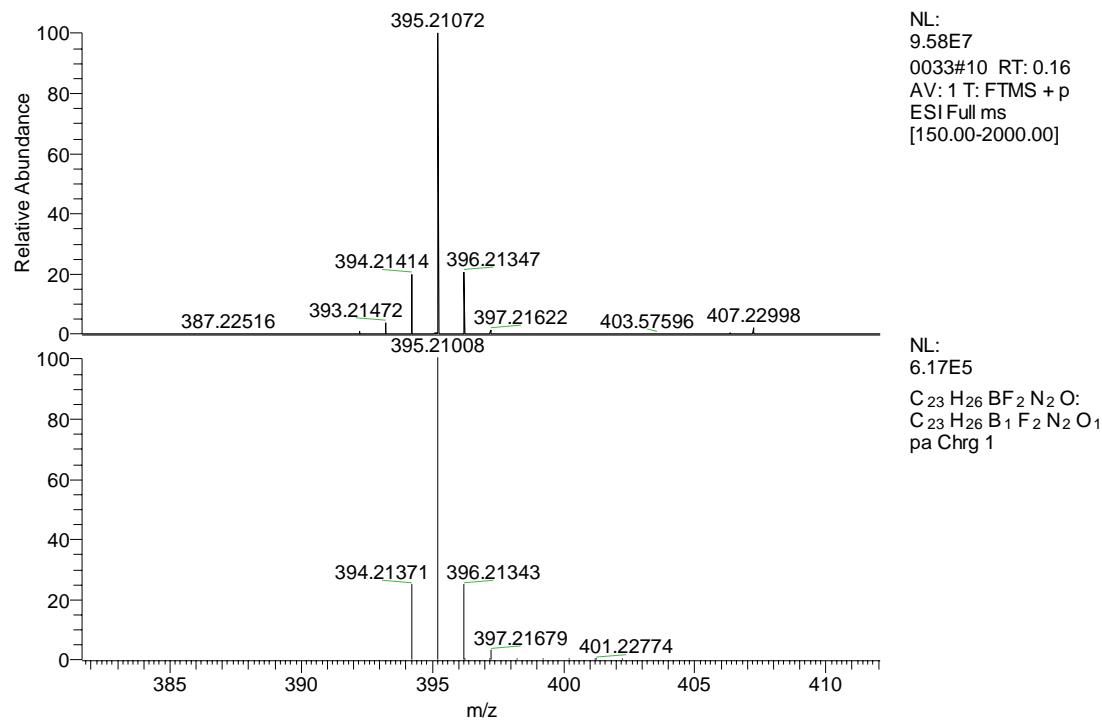
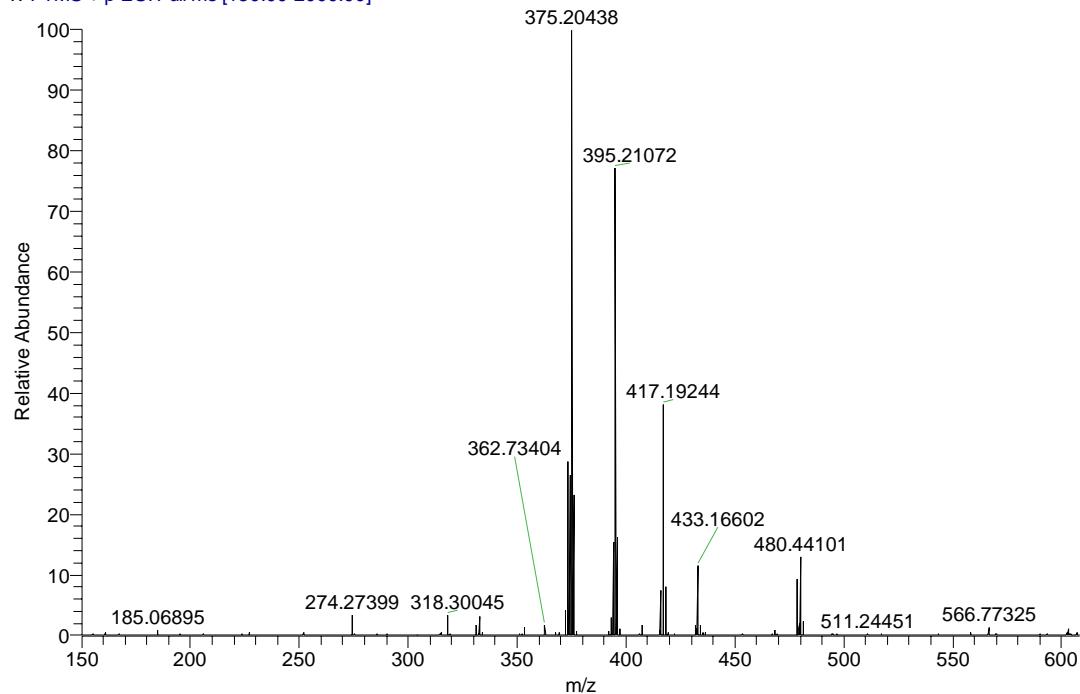
HRMS for **4d**

0032 #17 RT: 0.30 AV: 1 NL: 1.12E6
T: FTMS + p ESI Full ms [150.00-2000.00]



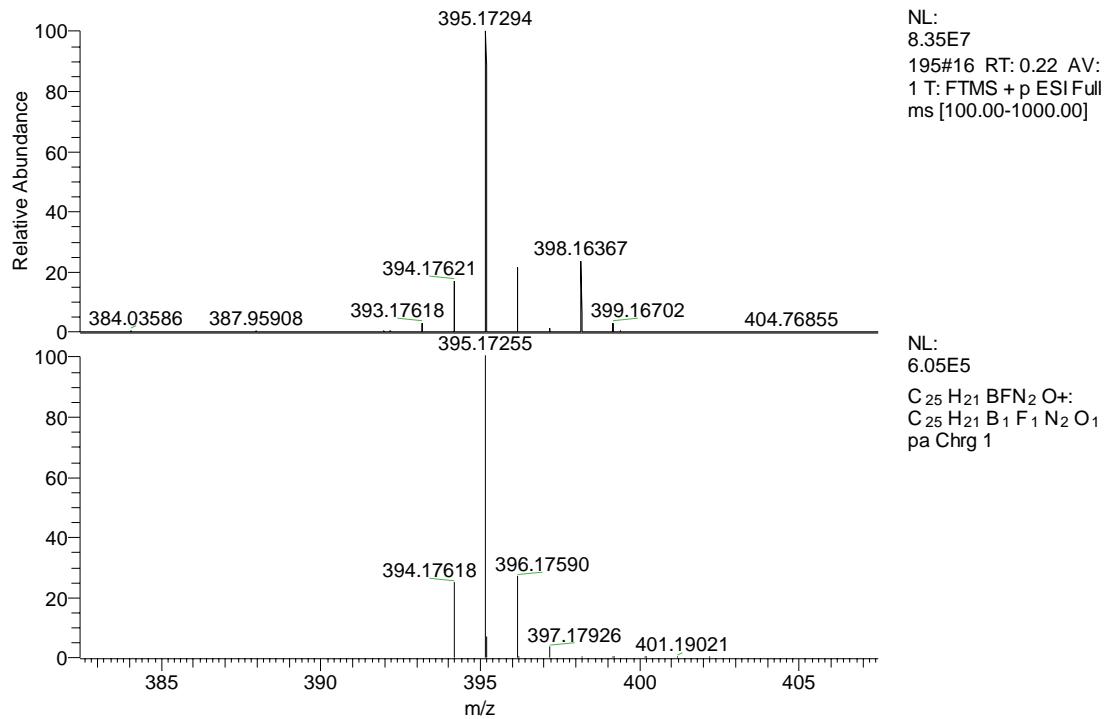
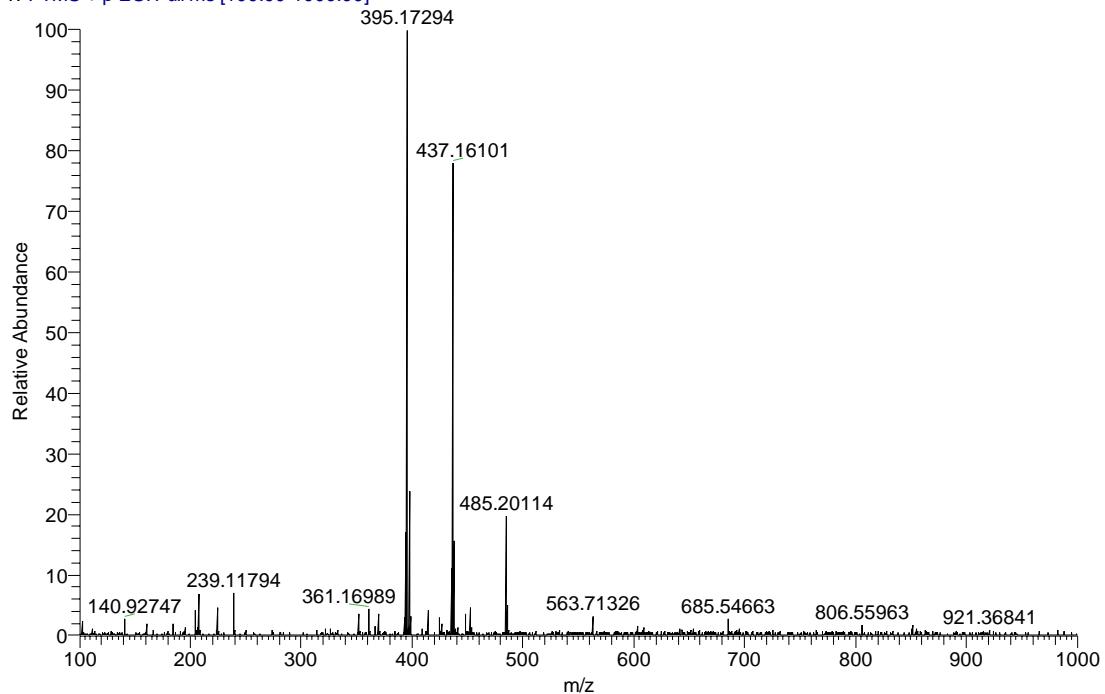
HRMS for **4e**

0033 #10 RT: 0.16 AV: 1 NL: 1.24E8
T: FTMS + p ESI Full ms [150.00-2000.00]



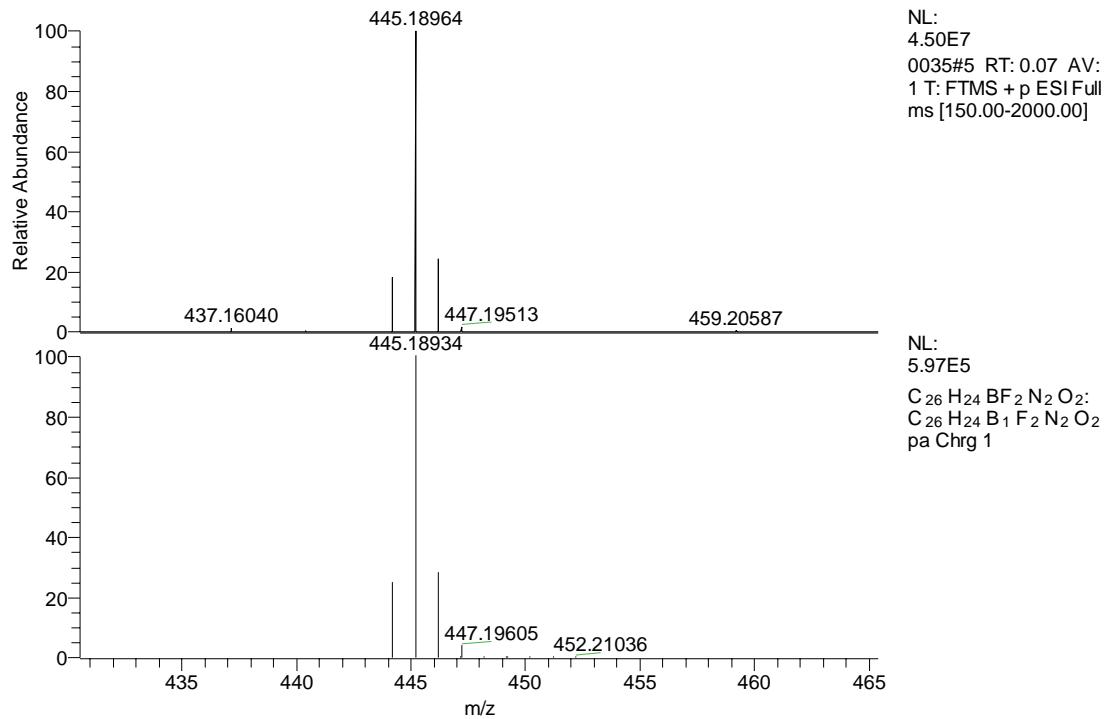
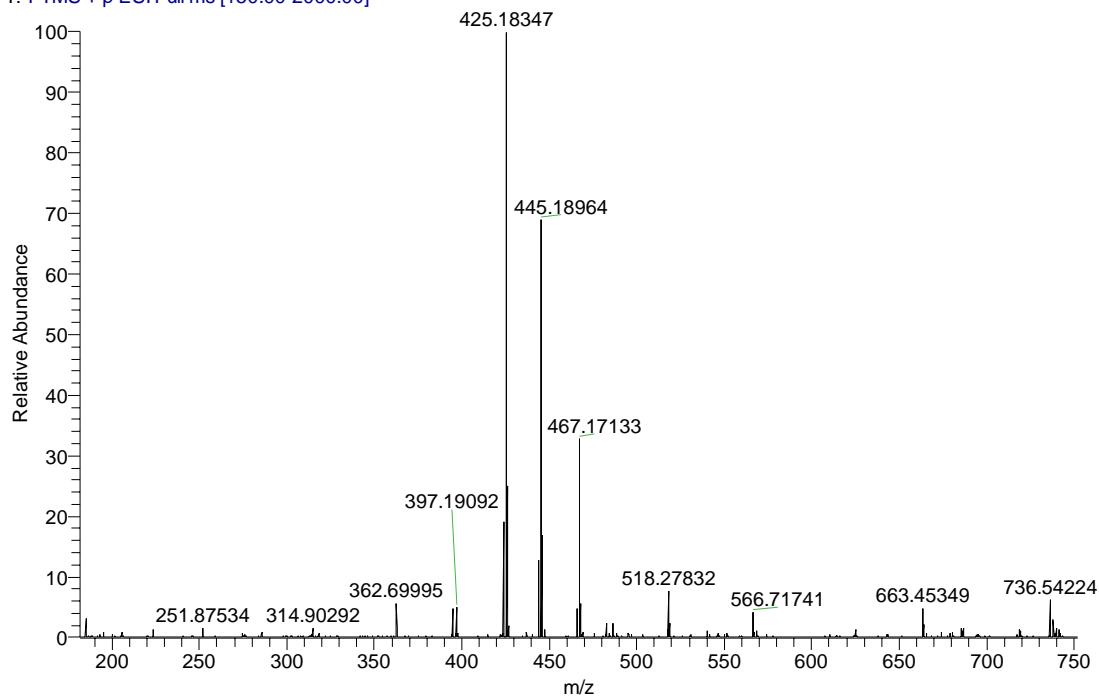
HRMS for **4f**

195 #16 RT: 0.22 AV: 1 NL: 8.35E7
T: FTMS + p ESI Full ms [100.00-1000.00]



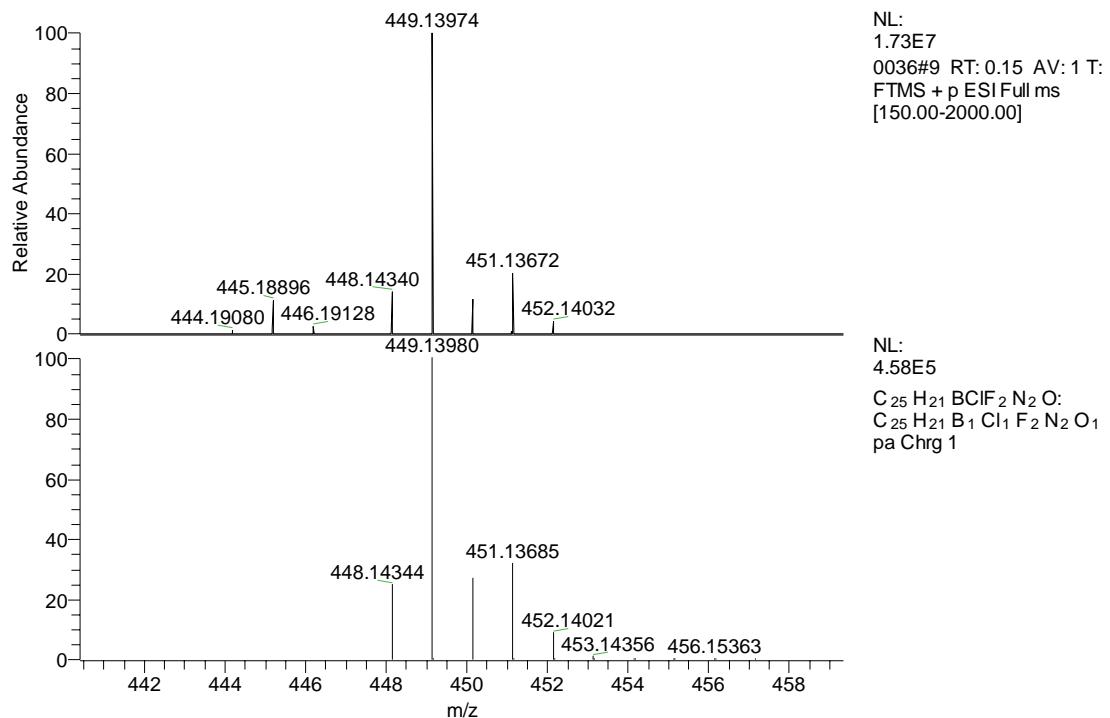
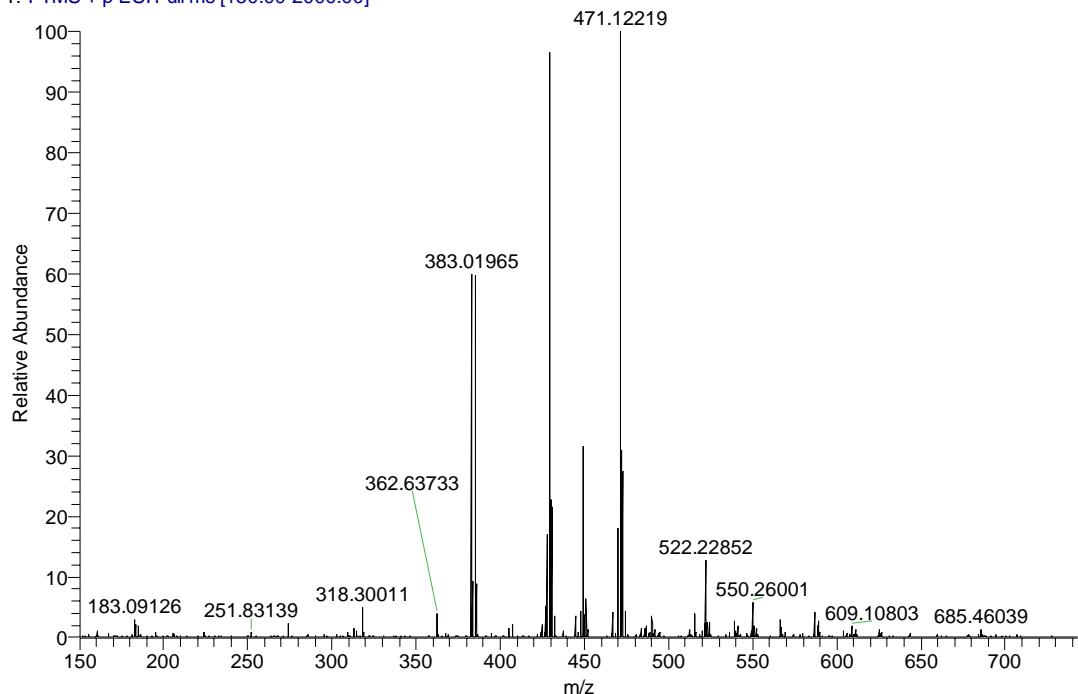
HRMS for **4g**

0035 #5 RT: 0.07 AV: 1 NL: 6.53E7
T: FTMS + p ESI Full ms [150.00-2000.00]



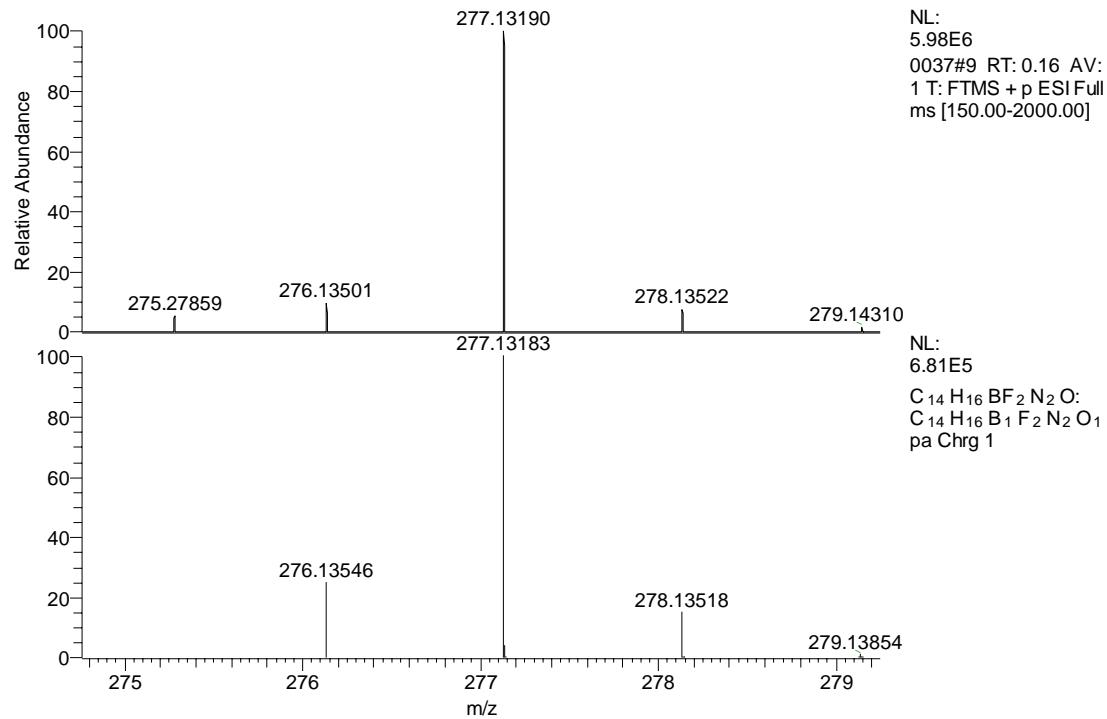
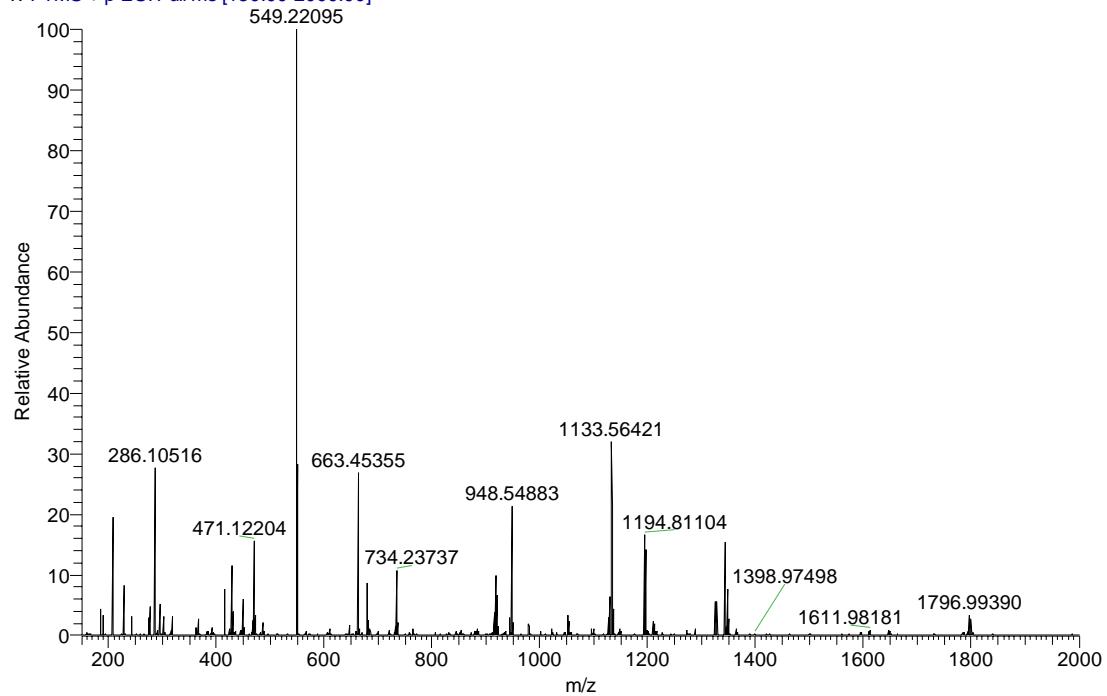
HRMS for **4h**

0036 #9 RT: 0.15 AV: 1 NL: 5.46E7
T: FTMS + p ESI Full ms [150.00-2000.00]



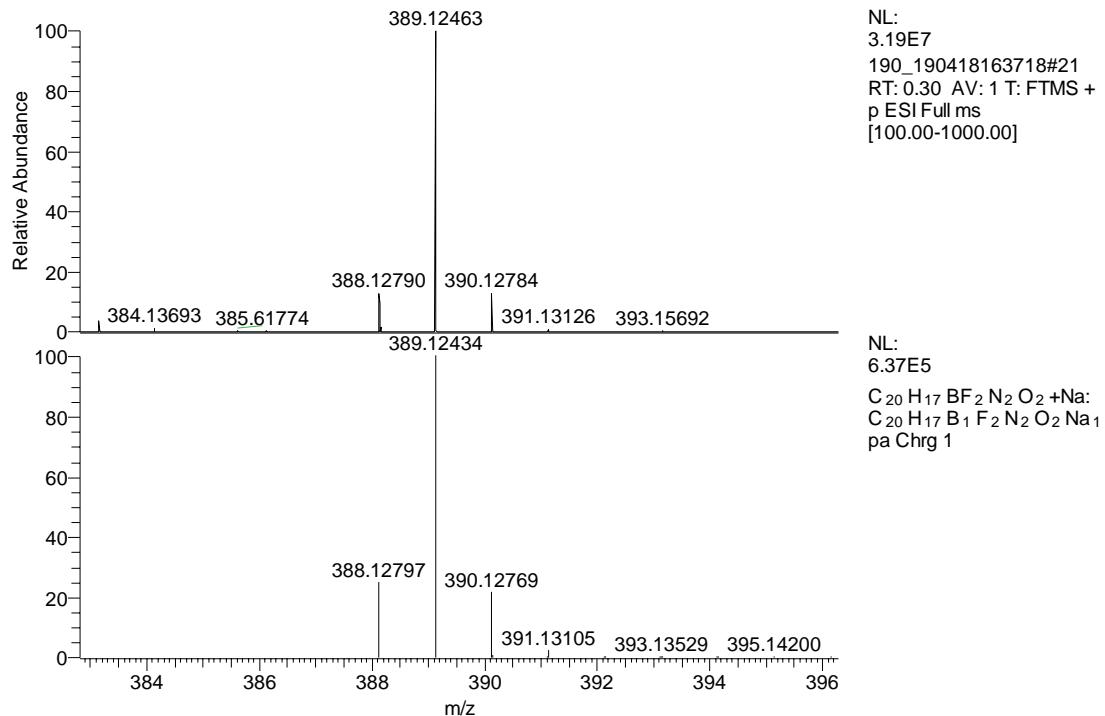
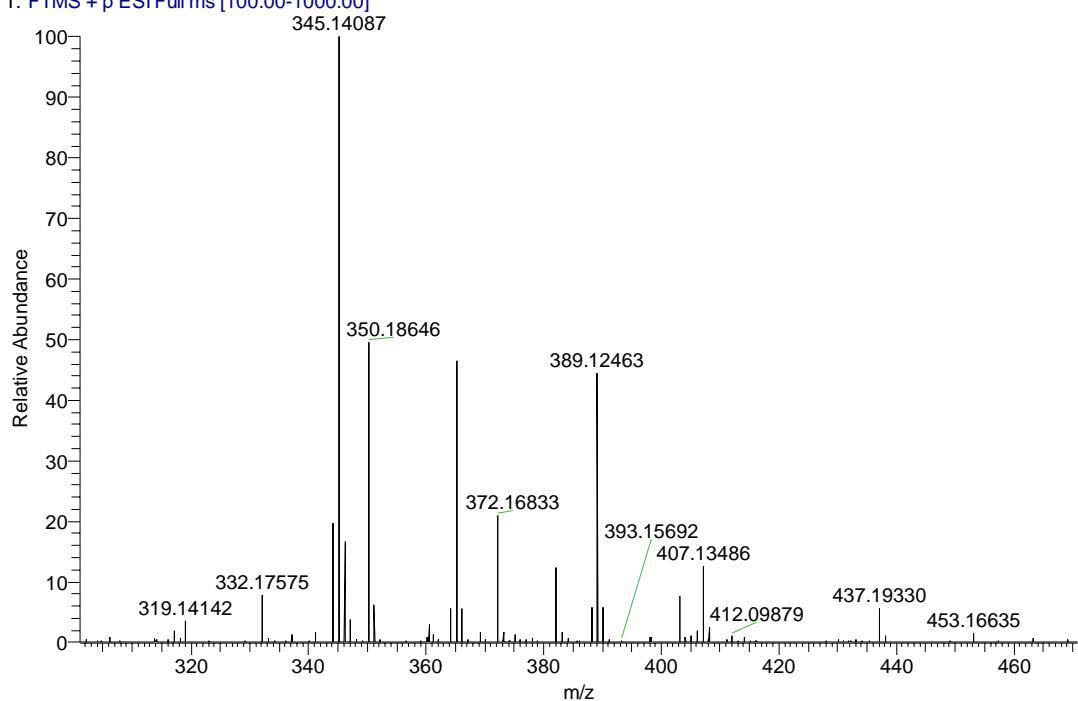
HRMS for **4i**

0037 #9 RT: 0.16 AV: 1 NL: 1.27E8
T: FTMS + p ESI Full ms [150.00-2000.00]



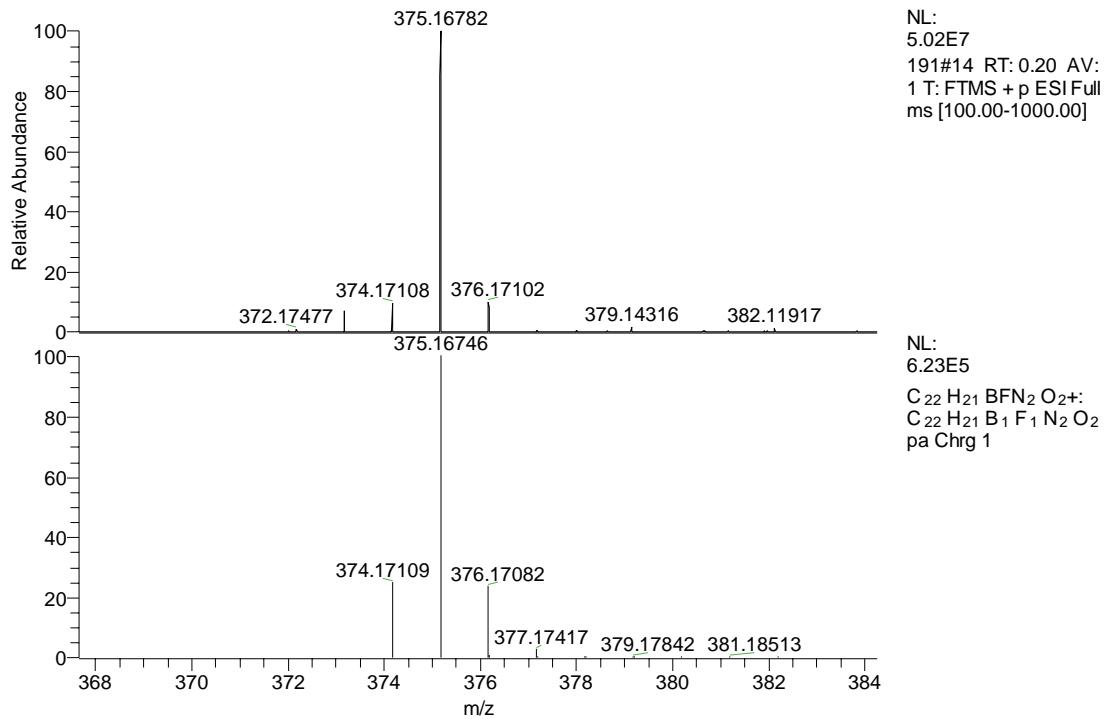
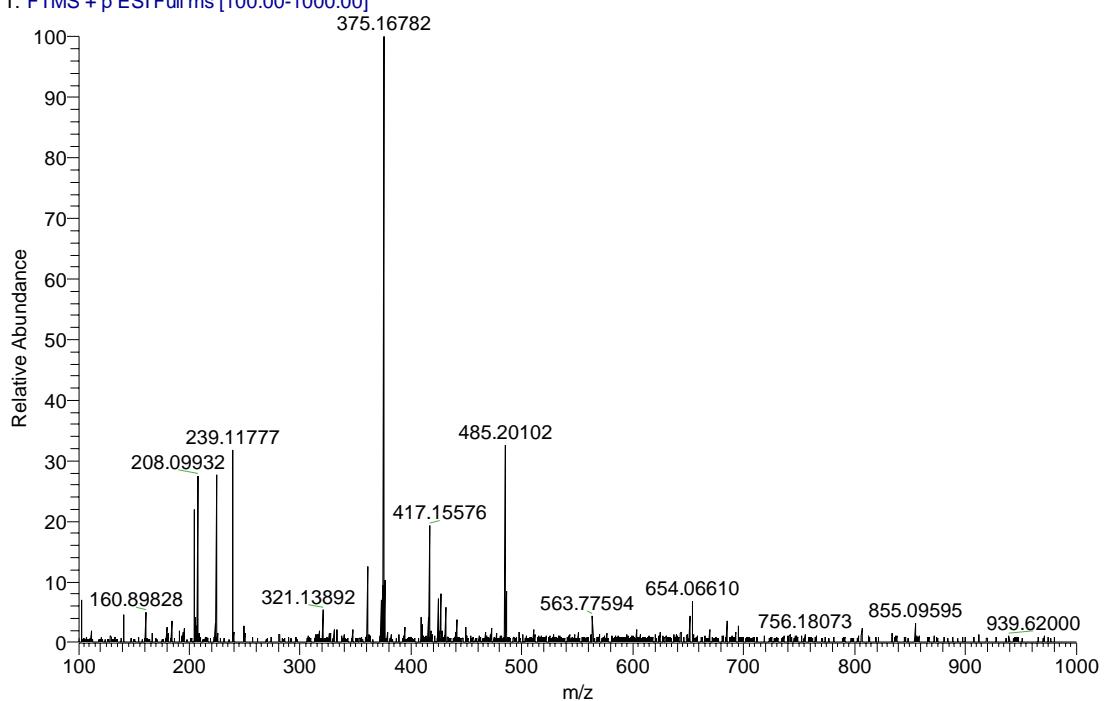
HRMS for **5a**

190_190418163718 #21 RT: 0.30 AV: 1 NL: 7.16E7
T: FTMS + p ESI Full ms [100.00-1000.00]



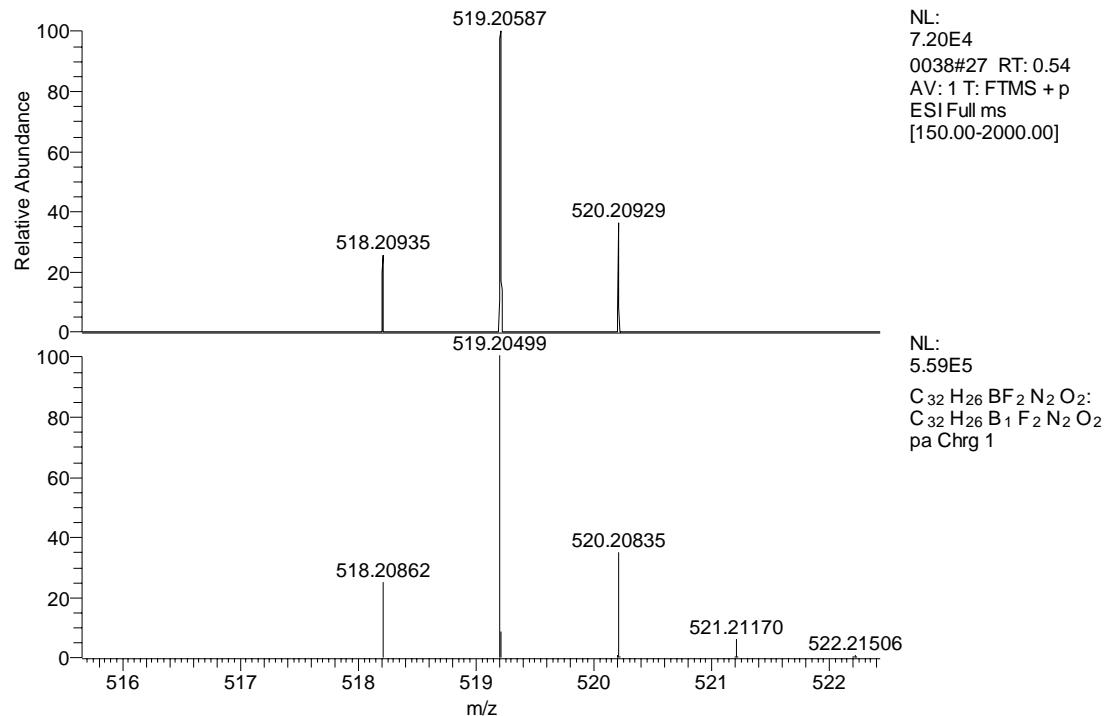
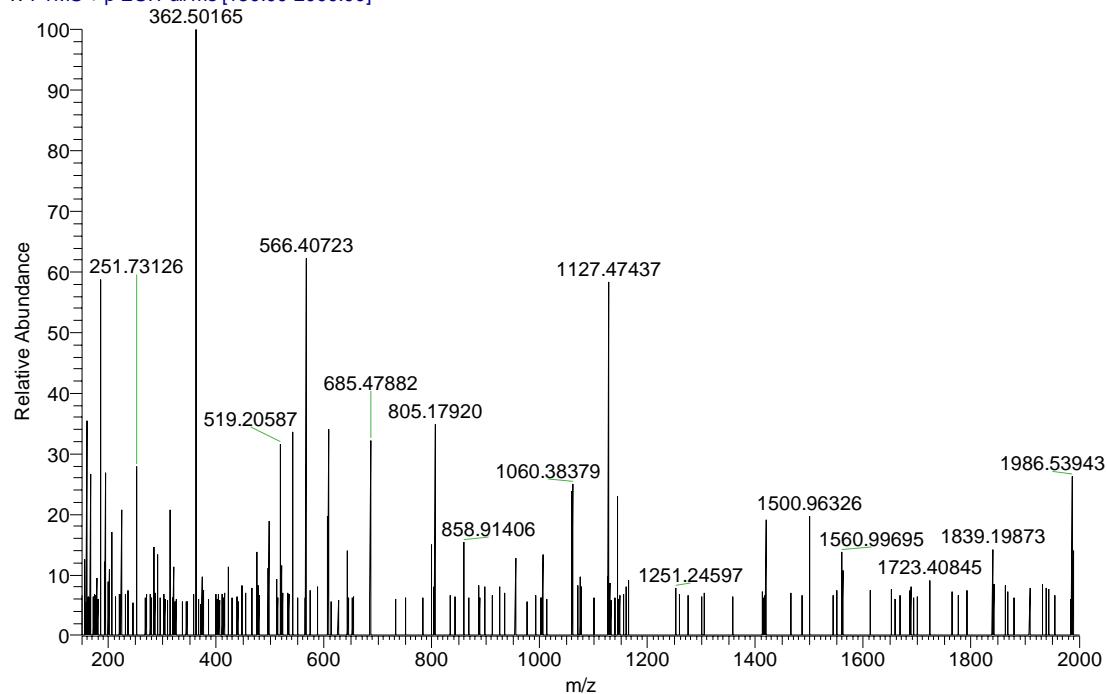
HRMS for **5b**

191 #14 RT: 0.20 AV: 1 NL: 5.02E7
T: FTMS + p ESI Full ms [100.00-1000.00]



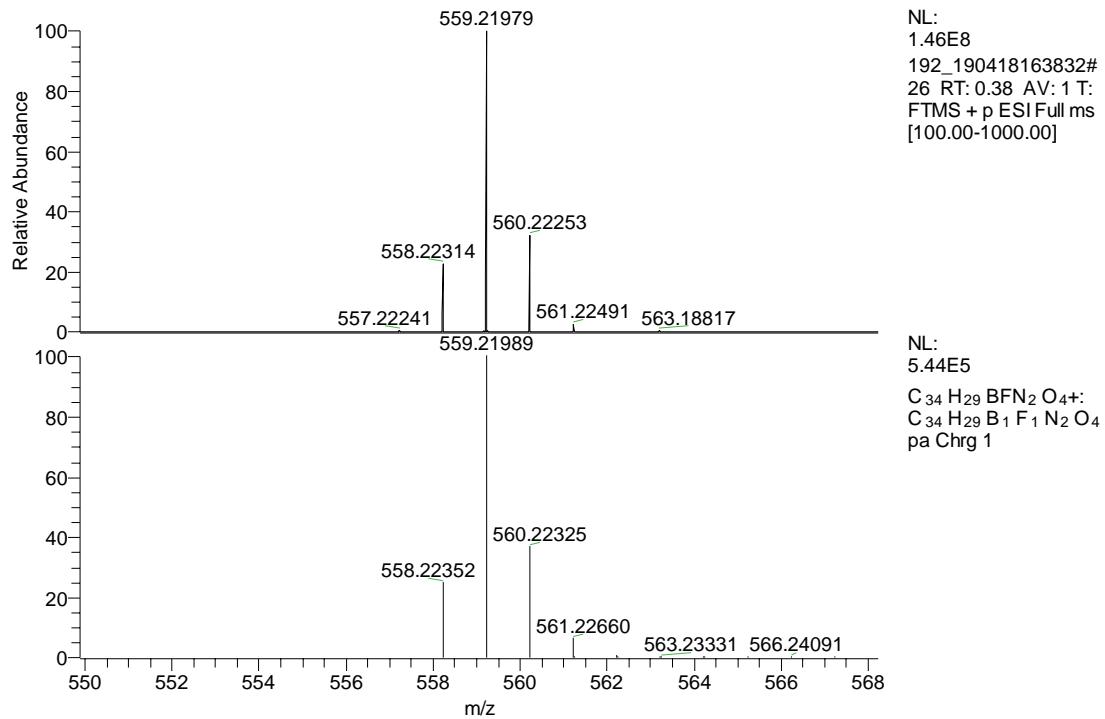
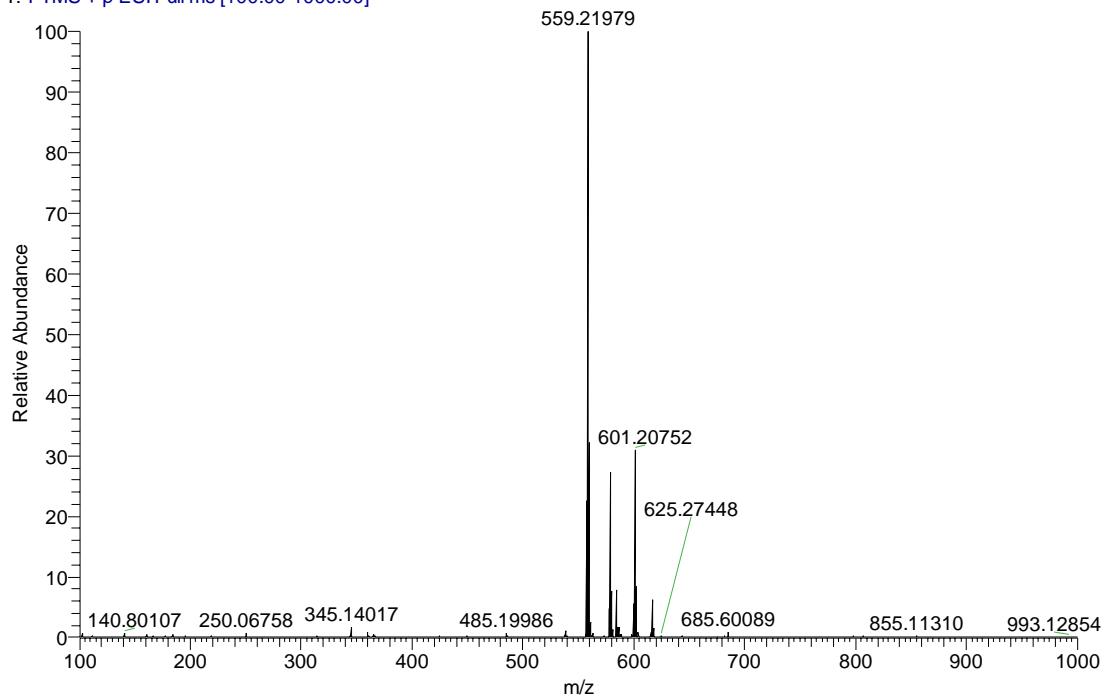
HRMS for **5c**

0038 #27 RT: 0.54 AV: 1 NL: 2.29E5
T: FTMS + p ESI Full ms [150.00-2000.00]



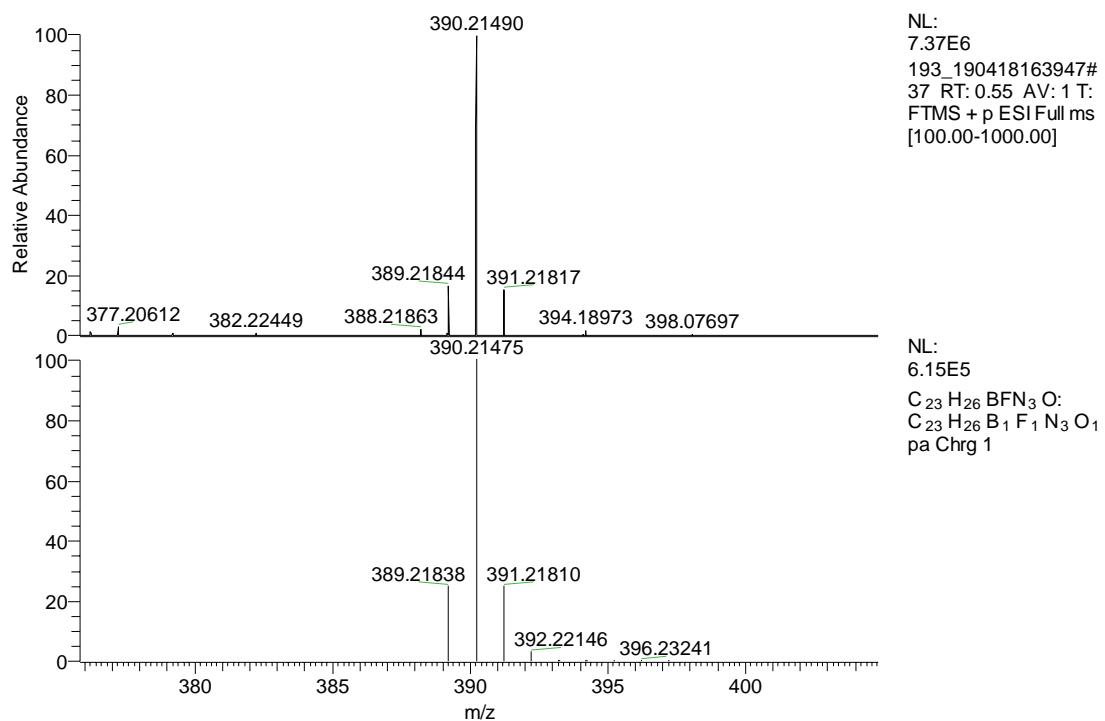
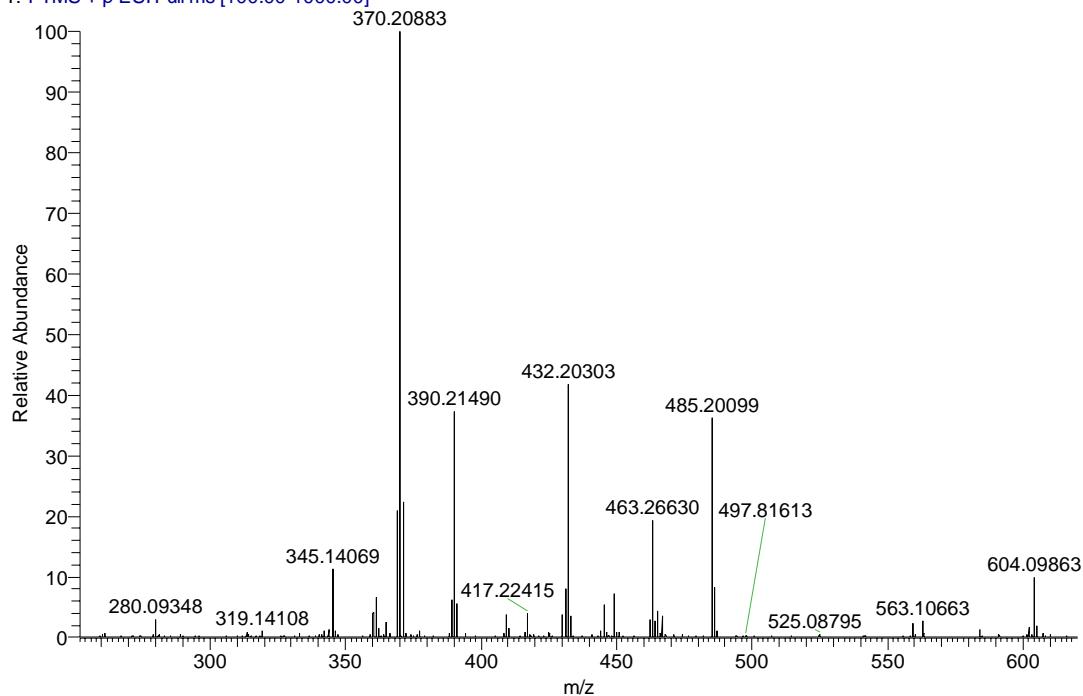
HRMS for **5d**

192_190418163832 #26 RT: 0.38 AV: 1 NL: 1.46E8
T: FTMS + p ESI Full ms [100.00-1000.00]



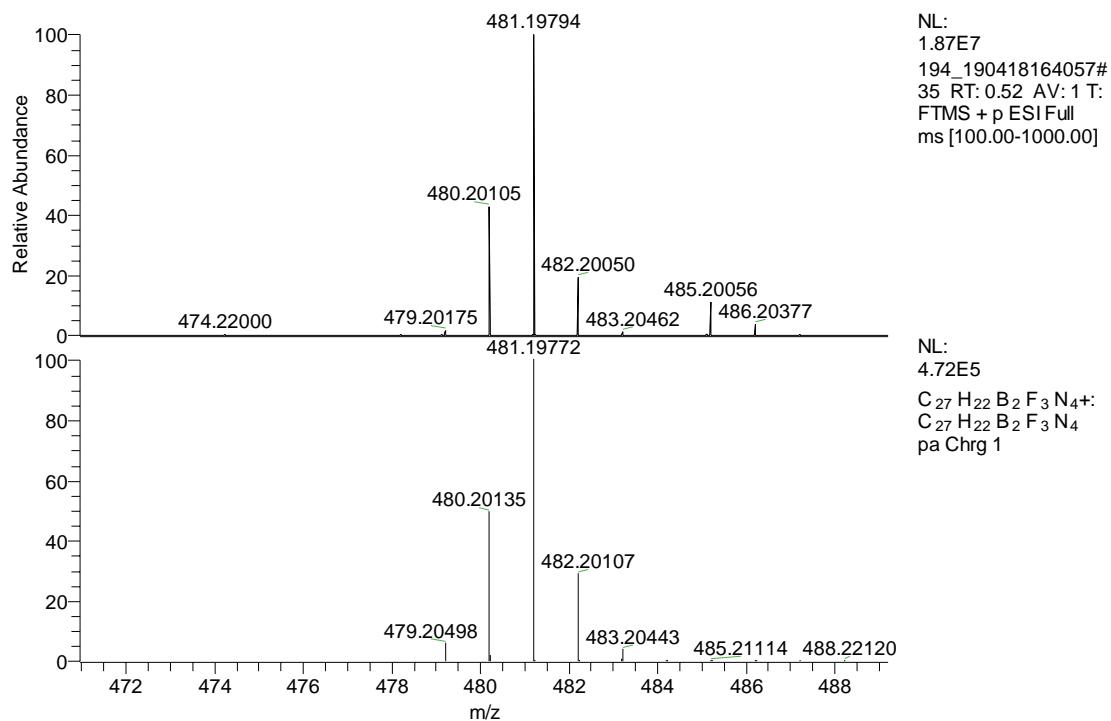
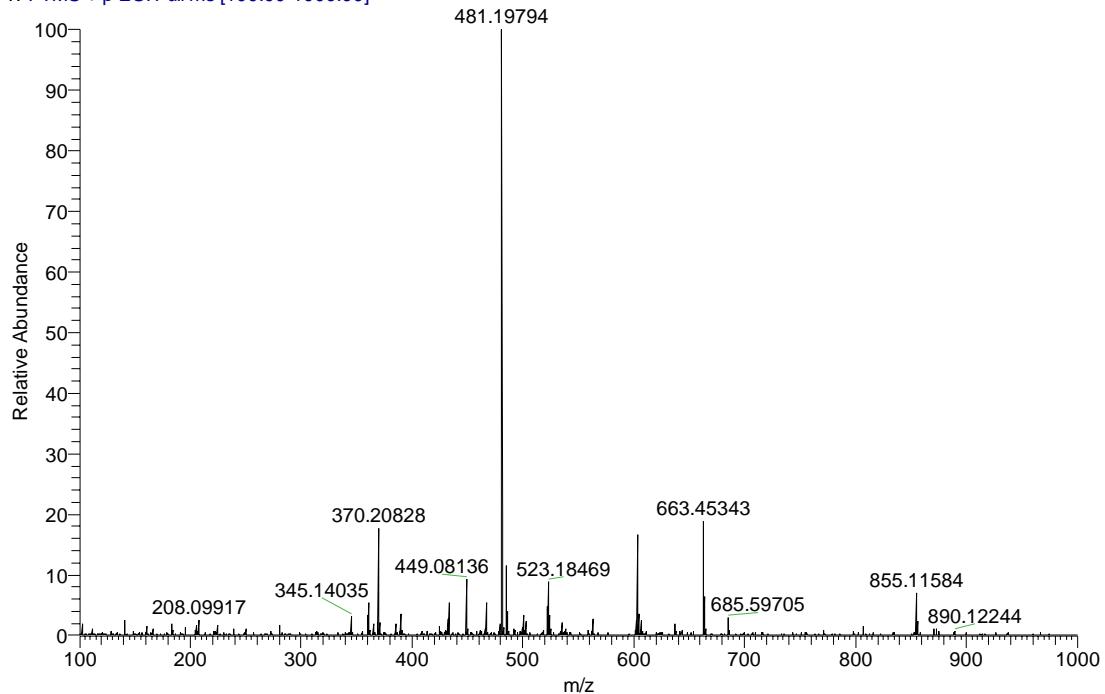
HRMS for 6

193_190418163947 #37 RT: 0.55 AV: 1 NL: 1.98E7
T: FTMS + p ESI Full ms [100.00-1000.00]



HRMS for 7

194_190418164057 #35 RT: 0.52 AV: 1 NL: 1.87E7
T: FTMS + p ESI Full ms [100.00-1000.00]



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