

## Diversity-Oriented Synthesis of Chromone Inden-1-one fused Cyclopentadienylides and C-acylated Chromone Adducts via Allylic Phosphorus Ylides

Durga Prasad Gurram, Gangababu Marri, Naveen Jothimani, Yi-Ru Chen, Wenwei Lin\*

Department of Chemistry, National Taiwan Normal University, 88, Sec. 4, Tingchow Road, Taipei 11677, Taiwan R.O.C.

### Contents

I. General Information	S2
II. Preliminary studies	S3
III. Plausible reaction mechanism for compound <b>6</b>	S3
IV. Detailed optimization of compound <b>5aa</b>	S4
V. Typical procedures for the preparation of New compounds	S5
VI. Characterization of all Compounds	S6
VII. X-ray Crystallographic Data	S40
VIII. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR, $^{19}\text{F}$ NMR, and $^{31}\text{P}$ NMR Spectra of All Products	S43

## I. General Information

### a) Materials and reagents

All reactions were carried out under argon atmosphere in oven-dried glassware with magnetic stirring. All solvents and reagents were used as purchased from commercial suppliers without further purification. Triethylamine ( $\text{Et}_3\text{N}$ ) was freshly distilled from calcium hydride under argon atmosphere and stored over 4 Å molecular sieves. Starting materials which were not commercially available were synthesized according to the previously reported methods.

### b) Instrumentation

**Thin layer chromatography (TLC):** TLC analyses were performed on precoated aluminum-backed silica gel plate (Merck 60 F254, 0.2 mm thickness) which was visualized by fluorescence quenching.

**Flash Column Chromatography:** The crude products were purified on silica gel (Merck Kieselgel 60 230-400 mesh).

**NMR Spectroscopy:**  $^1\text{H}$ ,  $^{13}\text{C}\{\text{H}\}$ ,  $^{19}\text{F}\{\text{H}\}$ , and  $^{31}\text{P}\{\text{H}\}$ -NMR spectra were recorded on an Oxford JEOL 400 MHz spectrometer, a Bruker Ascend 400 MHz spectrometer (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$ , 376 MHz for  $^{19}\text{F}$ , and 162 MHz for  $^{31}\text{P}$ ). All NMR spectra were recorded at 299 K unless otherwise noted. Chemical shifts are reported in  $\delta$  ppm referenced to an internal standard, such as TMS for  $^1\text{H}$ -NMR ( $\delta = 0.0$  ppm),  $\text{CDCl}_3$  for  $^{13}\text{C}$ -NMR ( $\delta = 77.0$  ppm),  $\text{CD}_2\text{Cl}_2$  for  $^{13}\text{C}$ -NMR ( $\delta = 53.5$  ppm). The following abbreviations were used to explain the multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), m (multiplet), brs (broad singlet), dd (doublet of doublet), td (triplet of doublet), dtd (doublet of triplet of doublet) and p (pseudo). Coupling constants ( $J$ ) are reported in Hertz (Hz).

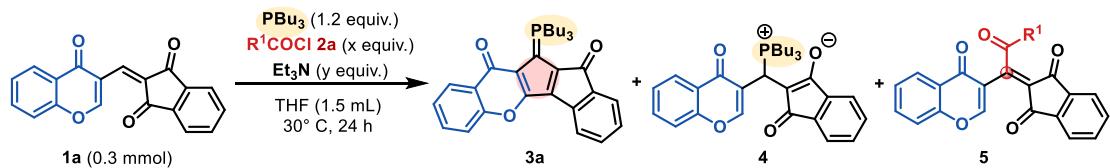
**Single Crystal X-Ray Diffraction:** The X-ray diffraction measurements were carried out at 200 K or 224 K on either a Bruker D8 Venture or a Bruker KAPPA APEX II CCD area detector system equipped with a graphite monochromator, a Mo-K $\alpha$  fine-focus sealed tube ( $k = 0.71073$  Å) or a Cu-K $\alpha$  fine-focus sealed tube ( $k = 1.54178$  Å).

**Melting Point:** Melting points were measured on a hot stage melting point apparatus and were uncorrected.

**High-Resolution Mass Spectrometry (HRMS):** HRMS were recorded on Waters XeVo G2-S QToF using ESI (TOF analyzer) or JEOL JMS-700 using EI (double-focusing magnetic sector). UltrafileXtreme MALDI-TOF/TOF using MALDI (Bruker

Daltonik, Bremen, Germany).

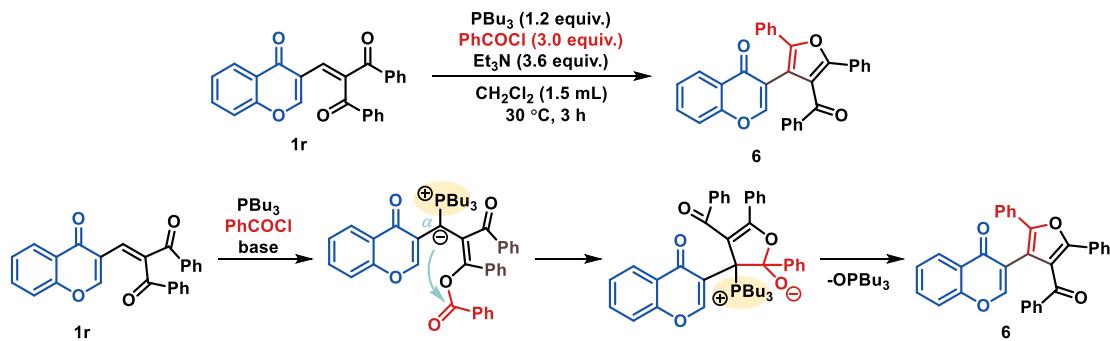
## II. Preliminary studies



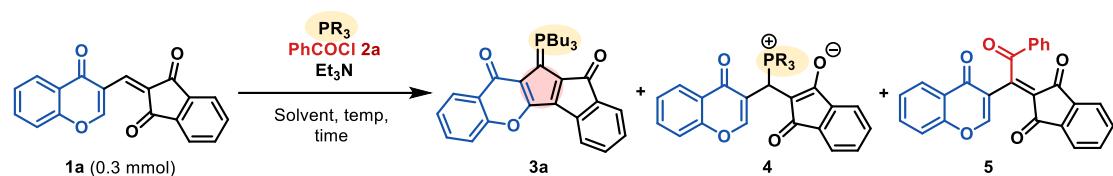
entry	$\text{R}^1\text{COCl}$ (x equiv.)	$\text{Et}_3\text{N}$ (y equiv.)	t (h)	<b>3a</b> (%) <sup>a</sup>	<b>5/4</b> (%) <sup>a</sup>
1	PhCOCl (1.5)	1.8	24	37	5/42
2	4-Me-BzCl (1.5)	1.8	24	29	2/55
3	4-OMePhCl (1.5)	1.8	24	32	3/57
4	4-NO <sub>2</sub> PhCl (1.5)	1.8	24	20	7/45
5	(Boc) <sub>2</sub> O (1.5)	1.8	24	0	0/93
6 <sup>c</sup>	PhCOCl (1.5)	1.8	24	27	4/60
7	PhCOCl (2.5)	2.8	22	50	20/15
8	PhCOCl (3.0)	3.6	24	57	13/0

<sup>a</sup>Yield of the products **3a**, **4** & **5** were determined by <sup>1</sup>H NMR analysis of the crude reaction mixture using triphenyl methane as an internal standard. <sup>b</sup>Reaction carried out at 60 °C.

## III. Reaction conditions and plausible reaction mechanism for compound 6.



#### IV. Detailed optimization of compound **5aa**.<sup>a</sup>

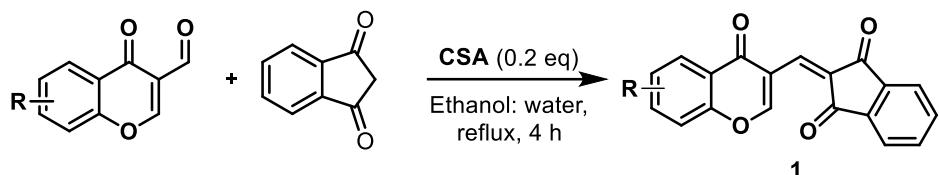


entry	<b>PR<sub>3</sub></b> (mol%)	<b>PhCOCl</b> (eqiuv.)	<b>Base</b> (eqiuv.)	<b>Solvent</b> (mL)	<b>t</b> (h)	<b>5aa</b> (%) <sup>b</sup>	<b>1a/4</b> (%) <sup>b</sup>
1	MePPh <sub>2</sub> (120)	3.0	Et <sub>3</sub> N (3.6)	THF	5	81	0
2	MePPh <sub>2</sub> (20)	3.0	Et <sub>3</sub> N (3.6)	THF	0.5	99	0
3	MePPh <sub>2</sub> (20)	1.2	Et <sub>3</sub> N (1.3)	THF	3	71	18
4	Me <sub>2</sub> PPh (20)	1.2	Et <sub>3</sub> N (1.3)	THF	0.5	88	0(6)
5	Et <sub>2</sub> PPh (20)	1.2	Et <sub>3</sub> N (1.3)	THF	3	39	38
6	EtPPh <sub>2</sub> (20)	1.2	Et <sub>3</sub> N (1.3)	THF	3	36	49
7	PBu <sub>3</sub> (20)	1.2	Et <sub>3</sub> N (1.3)	THF	4	36	32(4)
8	PPh <sub>3</sub> (20)	1.2	Et <sub>3</sub> N (1.3)	THF	24	0	86
9	Me <sub>2</sub> PPh (20)	1.2	Et <sub>3</sub> N (1.3)	Et <sub>2</sub> O	0.5	0	24(0)
10	Me <sub>2</sub> PPh (20)	1.2	Et <sub>3</sub> N (1.3)	CH <sub>3</sub> CN	3	28	40(13)
11	Me <sub>2</sub> PPh (20)	1.2	Et <sub>3</sub> N (1.3)	toluene	18	47	34(18)
12	Me <sub>2</sub> PPh (20)	1.2	Et <sub>3</sub> N (1.3)	DCM	3	53	22(8)
13	Me <sub>2</sub> PPh (20)	1.2	Et <sub>3</sub> N (1.3)	DCE	3	57	17(10)
14	Me <sub>2</sub> PPh (20)	1.2	Et <sub>3</sub> N (1.3)	EtOAc	18	53	30(17)
15	Me <sub>2</sub> PPh (20)	1.2	DIPEA (1.3)	THF	0.5	87	0
16	Me <sub>2</sub> PPh (20)	1.2	DBU (1.3)	THF	5	11	3(8)
17	Me <sub>2</sub> PPh (20)	1.2	DMAP (1.3)	THF	0.5	0	35(13)
18	Me <sub>2</sub> PPh (20)	1.2	Et <sub>3</sub> N (1.5)	THF	2	87	(10)
19	Me <sub>2</sub> PPh (20)	1.3	Et <sub>3</sub> N (1.5)	THF	0.5	88	(5)
20	Me <sub>2</sub> PPh (20)	1.2	Et <sub>3</sub> N (1.3)	THF (0.75)	5	87	(6)
21	Me <sub>2</sub> PPh (10)	1.2	Et <sub>3</sub> N (1.3)	THF	2	74	16(4)
22 <sup>c</sup>	Me <sub>2</sub> PPh (20)	1.2	Et <sub>3</sub> N (1.3)	THF	2	89	0

<sup>a</sup>Unless otherwise specified, all reactions were carried out with **1a** (0.3 mmol), **PhCOCl 2a**, **Base** and **PR<sub>3</sub>**, in the given anhydrous solvent (1.5 mL) under argon atmosphere at 30 °C. <sup>b</sup>Yield of the products **5aa** & **4**, **1a**

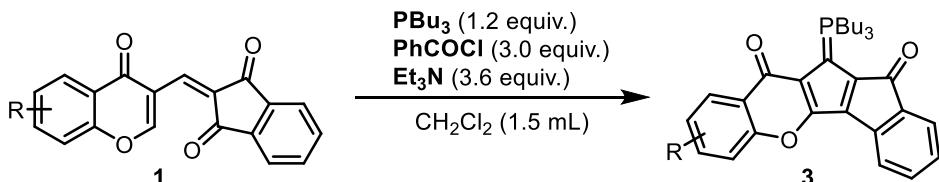
were determined by  $^1\text{H}$  NMR analysis of the crude reaction mixture using triphenyl methane as an internal standard.<sup>c</sup> Reaction carried out at 60 °C.

### V. a) Typical Procedure for the Preparation of compound 1 (TP-A)



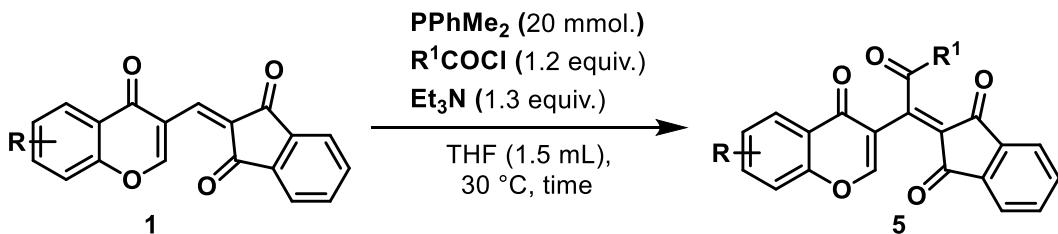
Following the reported procedure<sup>1</sup>, a round-bottomed flask equipped with a magnetic stir bar was charged with 3-Formylchromone<sup>2</sup> (5.0 mmol.), 1,3-indanedione (1.0 equiv.), and ( $\pm$ )-Camphor-10-Sulfonic Acid (CSA) (0.2 equiv.) in water: EtOH (1:1) at 80 °C in an oil bath for 4 h. After that, the resulting mixture was filtered under a vacuum and the residue was washed with methanol (2 times) then ethyl ether (2 times) to obtain product **1**.

### b) Typical Procedure for the Preparation of compound 3 (TP-B).



A dry and argon-flushed 10 mL Schlenk flask equipped with a magnetic stir bar was charged with **1** (0.3 mmol.),  $\text{PBu}_3$  (1.2 equiv.),  $\text{PhCOCl}$  **2a** (3.0 equiv.), and  $\text{Et}_3\text{N}$  (3.6 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (1.5 mL) at 30 °C. After completion of the reaction, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (4 mL), and the organic phase was washed with sodium bicarbonate solution. The resulted organic layer was dried over sodium sulfate and filtered through filter paper then the organic solution was concentrated under vacuum. Further, the crude reaction mixture was purified by flash column chromatography on silica gel to obtain the desired products **3**.

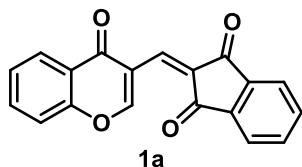
### c) Typical Procedure for the Preparation of compound 5 (TP-C).



A dry and argon-flushed 10 mL Schlenk flask equipped with a magnetic stir bar was charged with compound **1** (0.3 mmol.), PPhMe<sub>2</sub> (0.2 equiv.), R<sup>1</sup>COCl (1.2 equiv.), and Et<sub>3</sub>N (1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C. After completion of the reaction, the solvent was removed under vacuum and the crude residue was subjected to flash column chromatography on silica gel to obtain the desired products **5**.

## VI. Characterization of all Compounds

### **2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a**.**



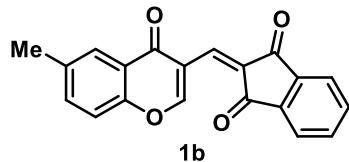
Following the **TP-A**, **1a** was obtained from 4-oxo-4H-chromene-3-carbaldehyde (0.87 g, 5.0 mmol), 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), and CSA (0.23 g, 0.2 equiv.). The residue was filtered under vacuum and obtain **1a** as a pale yellow solid (1.2 g, 80% yield). R<sub>f</sub> = 0.50 (Hexanes:EtOAc = 7:3) : mp.: 277.3-278.5 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.40 (s, 1H), 8.44 (s, 1H), 8.32 (dd, J = 8.1, 1.6 Hz, 1H), 8.08-7.98 (m, 2H), 7.89-7.80 (m, 2H), 7.75 (dtd, J = 8.7, 7.2, 1.7 Hz, 1H), 7.57 (dd, J = 8.4, 0.5 Hz, 1H), 7.50 (dtd, J = 9.1, 7.2, 0.9 Hz, 1H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 190.2, 189.0, 175.3, 163.4, 156.1, 142.1, 140.4, 136.5, 135.6, 135.4, 134.5, 129.4, 126.7, 126.4, 124.0, 123.6, 123.4, 118.6, 118.7.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>19</sub>H<sub>11</sub>O<sub>4</sub>: 302.0579 found: 302.0600.

### **2-(5-methyl-2-phenylbenzofuran-3-yl)-1-oxo-1H-inden-3-yl pivalate **1b**.**



Following the **TP-A**, **1b** was obtained from 6-methyl-4-oxo-4H-chromene-3-carbaldehyde (0.94 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1b** as a pale green solid (1.1 g, 70%). R<sub>f</sub> = 0.50 (Hexanes:EtOAc = 8:2) ; mp.: 228.2-229.4 °C.

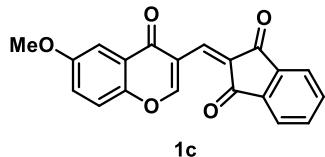
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.37 (s, 1H), 8.43 (pd, J = 0.6 Hz, 1H), 8.09 (pd, J = 1.1 Hz, 1H), 8.06-7.97 (m, 2H), 7.87-7.79 (d, 2H), 7.54 (d, J = 8.7, 2.2 Hz, 1H), 7.45 (pd, J = 8.5 Hz, 1H), 2.49 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 190.2, 189.1, 175.3, 163.4, 154.3, 142.1, 140.3, 136.8, 136.6, 135.6, 135.5, 135.3, 129.1, 126.0, 123.6, 123.5, 123.3, 118.4, 118.3,

20.9.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>: 316.0736 found: 316.0737.

**2-(5-methoxy-2-phenylbenzofuran-3-yl)-1-oxo-1H-inden-3-yl pivalate 1c.**



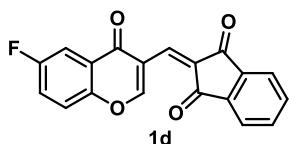
Following the **TP-A**, **1c** was obtained from 6-methoxy-4-oxo-4H-chromene-3-carbaldehyde (1.02 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1c** as a pale green solid (1.2 g, 72%). R<sub>f</sub> = 0.38 (Hexanes:EtOAc = 7:3); mp.: 266.7-267.7 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.37 (s, 1H), 8.46 (s, 1H), 8.08-7.96 (m, 2H), 7.89-7.89 (m, 2H), 7.68 (d, J = 3.1 Hz, 1H), 7.49 (pd, J = 9.1 Hz, 1H), 7.32 (dd, J = 9.1, 3.1 Hz, 1H), 3.93 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 190.2, 189.2, 175.2, 163.1, 157.8, 150.8, 142.1, 140.3, 136.9, 135.5, 135.3, 129.1, 124.8, 124.3, 123.5, 123.4, 120.0, 117.8, 105.9, 50.1.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>20</sub>H<sub>12</sub>O<sub>5</sub>: 332.0685 found: 332.0677.

**2-((6-fluoro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione 1d.**



Following the **TP-A**, **1d** was obtained from 6-fluoro-4-oxo-4H-chromene-3-carbaldehyde (0.96 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1d** as a half-white solid (1.1 g, 68%). R<sub>f</sub> = 0.40 (Hexanes:EtOAc = 8:2); mp.: 265.8-266.9 °C

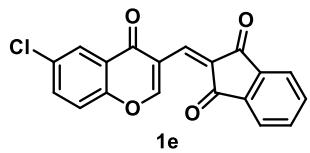
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.39 (d, J = 0.6 Hz, 1H), 8.39 (s, 1H), 8.06-8.00 (m, 2H), 7.96 (dd, J = 8.6, 3.1 Hz, 1H), 7.88-7.80 (m, 2H), 7.60 (dd, J = 9.1, 4.1 Hz, 1H), 7.51-7.43 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 190.1, 188.9, 174.1, 163.2, 154.8, 142.2, 140.4, 137.5, 135.7, 135.5, 129.8, 129.3, 125.2, 123.6, 123.5, 120.5, 119.9, 118.7.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ/ppm: -112.9.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>19</sub>H<sub>9</sub>FO<sub>4</sub>: 320.0485 found: 320.0466.

**2-((6-chloro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione 1e.**



Following the **TP-A**, **1e** was obtained from 6-chloro-4-oxo-4H-chromene-3-carbaldehyde (1.04 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1e** as a half-white solid (1.0 g, 60%).  $R_f = 0.40$  (Hexanes:EtOAc = 8:2); mp.: 271.2-272.3 °C.

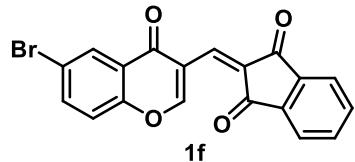
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 10.37 (s, 1H), 8.38 (s, 1H), 8.28 (d,  $J = 2.6$  Hz, 1H), 8.06-7.99 (m, 2H), 7.89-7.82 (m, 2H), 7.69 (dd,  $J = 8.7, 2.6$  Hz, 1H), 7.53 (d,  $J = 8.9$  Hz, 1H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 190.1, 188.9, 174.1, 163.2, 154.8, 142.2, 140.4, 137.5, 135.7, 135.5, 129.8, 129.3, 125.2, 123.6, 123.5, 120.5, 119.9, 118.7.

**HRMS** (EI) m/z:  $[\text{M}]^+$  calcd for  $\text{C}_{19}\text{H}_9^{35}\text{ClO}_4$ : 336.0189 found: 336.0197.

**HRMS** (EI) m/z:  $[\text{M}]^+$  calcd for  $\text{C}_{19}\text{H}_9^{37}\text{ClO}_4$ : 338.0160 found: 338.0156.

### 2-((6-bromo-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1f**.



Following the **TP-A**, **1f** was obtained from 6-bromo-4-oxo-4H-chromene-3-carbaldehyde (1.25 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1f** as a pale green solid (1.0 g, 52%).  $R_f = 0.38$  (Hexanes:EtOAc = 9:1); mp.: 264.4-265.6 °C

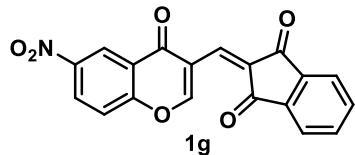
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 10.37 (s, 1H), 8.45 (d,  $J = 2.4$  Hz, 1H), 8.37 (s, 1H), 8.07-7.97 (m, 2H), 7.90-7.80 (m, 3H), 7.47 (d,  $J = 8.9$  Hz, 1H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 190.1, 188.9, 174.1, 163.2, 154.8, 142.2, 140.4, 137.5, 135.7, 135.5, 129.8, 129.3, 125.2, 123.6, 123.5, 120.5, 119.9, 118.7.

**HRMS** (EI) m/z:  $[\text{M}]^+$  calcd for  $\text{C}_{19}\text{H}_9^{79}\text{BrO}_4$ : 379.9684 found: 379.9700.

**HRMS** (EI) m/z:  $[\text{M}]^+$  calcd for  $\text{C}_{19}\text{H}_9^{81}\text{BrO}_4$ : 381.9664 found: 381.9627.

### 2-((6-nitro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1g**.

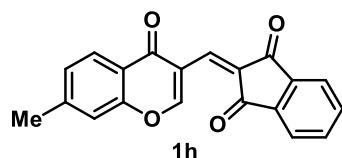


Following the **TP-A**, **1g** was obtained from 6-nitro-4-oxo-4H-chromene-3-

carbaldehyde (1.09 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1g** as a pale yellow solid (1.3 g, 76%).  $R_f = 0.45$  (Hexanes:EtOAc = 6:4) ; mp.: 309.2-310.5 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.39 (s, 1H), 9.19 (d, *J* = 2.7 Hz, 1H), 8.58 (dd, *J* = 9.7, 2.8 Hz, 1H), 8.34 (s, 1H), 8.08-8.02 (m, 2H), 7.90-7.84 (m, 2H), 7.74 (d, *J* = 9.1 Hz, 1H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 190.1, 188.5, 174.0, 162.8, 158.8, 145.5, 142.2, 140.5, 135.9, 135.6, 134.4, 130.8, 128.7, 123.1, 123.8, 123.6, 123.3, 120., 119. **HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>19</sub>H<sub>9</sub>NO<sub>6</sub>: 347.0430 found: 347.0425.

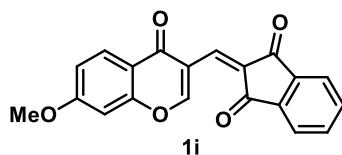
### 2-((7-methyl-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1h**.



Following the **TP-B**, **1h** was obtained from 7-methyl-4-oxo-4H-chromene-3-carbaldehyde (0.94 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1h** as a half-white solid (1.25 g, 80%).  $R_f = 0.45$  (Hexanes:EtOAc = 8:2) ; mp.: 224.4-225.6 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.34 (s, 1H), 8.40 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 8.06-7.94 (m, 2H), 7.87-7.78 (m, 2H), 7.33 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 2.51 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 190.1, 189.1, 175.1, 163.3, 156.1, 146.1, 142.0, 136.6, 135.5, 135.3, 129.0, 127.8, 126.3, 123.4, 123.3, 121.6, 118.4, 118.3, 21.8. **HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>: 316.0736 found: 316.0752.

### 2-((7-methoxy-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1i**.

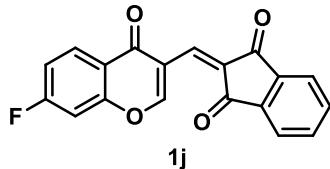


Following the **TP-B**, **1i** was obtained from 7-methoxy-4-oxo-4H-chromene-3-carbaldehyde (1.02 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1i** as a half-white solid (1.1 g, 68%).  $R_f = 0.45$  (Hexanes:EtOAc = 7:2) ; mp.: 268.8-269.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.34 (s, 1H), 8.44 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 1H) 8.09-7.97 (m, 2H), 7.89-7.77 (m, 2H), 7.04 (dd, *J* = 9.2, 2.5 Hz, 1H), 6.94 (d, *J* = 2.3 Hz, 1H), 3.64 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>) δ/ppm: 190.3, 189.1, 174.5, 164.7, 163.1, 157.8, 142.1, 140.4, 136.8, 135.5, 135.3, 129.2, 128.1, 123.5, 123.3, 118.6, 117.7, 115.4, 101.0, 55.9.

HRMS (EI) m/z: [M]<sup>+</sup> calcd for C<sub>20</sub>H<sub>12</sub>O<sub>5</sub>: 332.0685 found: 332.0668.

### 2-((7-fluoro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1j**.



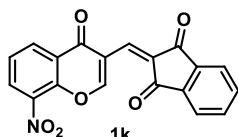
Following the TP-A, **1j** was obtained from 7-fluoro-4-oxo-4H-chromene-3-carbaldehyde (0.96 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1j** as a half-white solid (1.1 g, 76%). R<sub>f</sub> = 0.48 (Hexanes:EtOAc = 8:2); mp.: 284.3-285.5 °C.  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.36 (s, 1H), 8.39 (s, 1H), 8.34 (dd, J = 10, 6.2 Hz, 1H), 8.08-7.99 (m, 2H), 7.87-7.82 (m, 2H), 7.33-7.16 (m, 3H).

<sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>) δ/ppm: 190.1, 188.9, 174.3, 167.3, 164.8, 163.2, 157.1 (d, J<sub>C-F</sub> = 13.3 Hz) 142.2, 140.4, 135.8, 135.7, 135.5, 129.8, 129.1, 123.6, 123.4, 120.8, 118.7, 115.1 (d, J<sub>C-F</sub> = 22.8 Hz), 105.4 (d, J<sub>C-F</sub> = 24.5 Hz).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ/ppm: -100.9.

HRMS (EI) m/z: [M]<sup>+</sup> calcd for C<sub>19</sub>H<sub>9</sub>FO<sub>4</sub>: 320.0485 found: 320.0464.

### 2-((8-nitro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1k**.



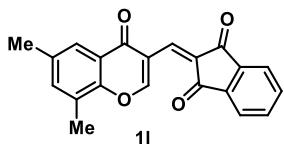
Following the TP-A, **1k** was obtained from 8-nitro-4-oxo-4H-chromene-3-carbaldehyde (1.1 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1k** as a brown solid (1.3 g, 76%). R<sub>f</sub> = 0.50 (Hexanes:EtOAc = 7:3); mp.: 249.3-250.8 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.40 (s, 1H), 7.54 (d, J = 8.1, 1.7 Hz, 1H), 7.54 (d, J = 8.2, 1.6 Hz, 1H), 8.31 (s, 1H), 8.08-8.01 (m, 2H), 7.92-7.82 (d, 2H), 7.62 (t, J = 7.9 Hz, 1H).

<sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.7, 188.6, 173.5, 162.3, 148.3, 142.2, 140.5, 139.2, 135.9, 135.7, 133.9, 132.3, 130.9, 130.3, 125.6, 125.5, 123.7, 123.6, 119.3.

HRMS (EI) m/z: [M]<sup>+</sup> calcd for C<sub>19</sub>H<sub>9</sub>NO<sub>6</sub>: 347.0430 found: 347.0423.

**2-((6,8-dimethyl-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1l**.**



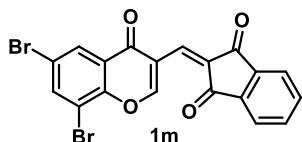
Following the **TP-A**, **1l** was obtained from 6,8-dimethyl-4-oxo-4H-chromene-3-carbaldehyde (1.0 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1l** as a pale green solid (1.05 g, 64%).  $R_f = 0.45$  (Hexanes:EtOAc = 7:3) ; mp.: 296.6-297.8 °C.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 10.41 (s, 1H), 8.46 (s, 1H), 8.06-7.98 (m, 2H), 7.94 (pd,  $J = 0.8$  Hz, 1H), 7.87-7.79 (m, 2H), 7.39 (pd,  $J = 0.9$  Hz, 1H), 2.51 (s, 3H), 2.44 (s, 3H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 190.3, 189.2, 175.7, 163.1, 152.9, 142.1, 140.3, 137.1, 136.8, 135.9, 135.5, 135.3, 128.9, 127.8, 127.6, 123.6, 123.5, 123.3, 118.2, 20.9, 15.3.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{14}\text{O}_4$ : 330.0892 found: 330.0864.

**2-((6,8-dibromo-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1m**.**



Following the **TP-A**, **1m** was obtained from 6,8-dibromo-4-oxo-4H-chromene-3-carbaldehyde (1.65 mg, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1m** as a pale green solid (1.2 g, 55%).  $R_f = 0.50$  (Hexanes/EtOAc = 7:3) ; mp: 302.5-303.6 °C.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 10.41 (s, 1H), 8.39 (d,  $J = 2.5$  Hz, 1H, 1H), 8.33 (s, 1H), 8.09 (d,  $J = 2.2$  Hz, 1H), 8.07-8.00 (m, 2H), 7.90-7.82 (m, 2H).

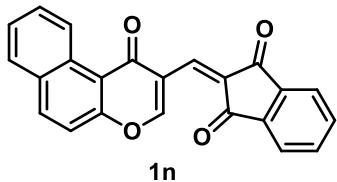
**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 189.9, 188.7, 173.7, 162.8, 151.9, 142.2, 140.4, 140.2, 135.8, 135.6, 134.6, 130.4, 128.6, 128.6, 125.9, 123.7, 123.6, 119.8, 118.7, 133.4.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{19}\text{H}_8^{79}\text{Br}^{79}\text{Br O}_4$ : 457.8789 found: 457.8772.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{19}\text{H}_8^{79}\text{Br}^{81}\text{BrO}_4$ : 459.8769 found: 459.8758.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{19}\text{H}_8^{81}\text{Br}^{81}\text{Br O}_4$ : 461.8748 found: 461.8722.

**2-((1-oxo-1H-benzo[f]chromen-2-yl)methylene)-1H-indene-1,3(2H)-dione **1n**.**



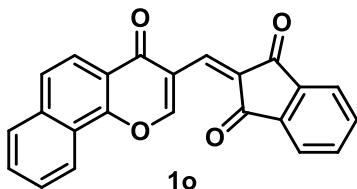
Following the TP-A, **1n** was obtained from 1-oxo-1H-benzo[f]chromene-2-carbaldehyde (1.1 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1n** as a half-white solid (1.3 g, 76%).  $R_f = 0.38$  (Hexanes:EtOAc = 8:2) ; mp.: 297.4-298.5 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.56 (s, 1H), 8.61-8.53 (m, 1H), 8.49 (s, 1H), 8.24 (d, *J*= 8.7 Hz, 1H), 8.09-8.01 (m, 2H), 8.00-7.93 (m, 1H), 7.89-7.82 (m, 3H), 7.78-7.69 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 190.2, 189.1, 176.7, 160.9, 157.4, 142.2, 140.4, 136.9, 136.4, 135.6, 135.4, 131.1, 130.6, 129.8, 129.6, 127.3, 127.2, 123.6, 123.4, 120.7, 117.5.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>23</sub>H<sub>12</sub>O<sub>4</sub>: 352.0736 found: 352.0741.

**2-((4-oxo-4H-benzo[h]chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1o**.**



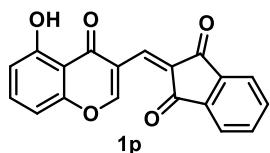
Following the TP-A, **1o** was obtained from 4-oxo-4H-benzo[h]chromene-3-carbaldehyde (1.1 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1o** as a yellow solid (1.4 g, 80%).  $R_f = 0.47$  (Hexanes/EtOAc = 8:2) ; mp.: 287.3-288.2 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.56 (s, 1H), 8.61-8.53 (m, 1H), 8.58 (s, 1H), 8.25 (d, *J*= 8.7 Hz, 1H), 8.81-8.01 (m, 2H), 7.99-7.93 (m, 1H), 7.87-7.82 (m, 3H), 7.79-7.69 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 190.2, 188.9, 175.1, 162.3, 153.6, 142.2, 140.4, 136.3, 136.2, 135.6, 135.4, 129.8, 129.7, 128.2, 127.6, 126.4, 123.9, 123.6, 123.4, 122.3, 121.3, 120.4, 119.7.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>23</sub>H<sub>12</sub>O<sub>4</sub>: 352.0736 found: 352.0719.

**2-((5-hydroxy-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1p**.**

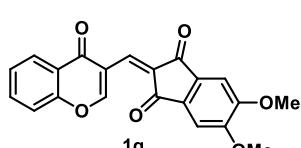


Following the **TP-A**, **1p** was obtained from 5-hydroxy-4-oxo-4H-chromene-3-carbaldehyde (0.95 g, 5.0 mmol), and 1H-indene-1,3(2H)-dione (0.73 g, 1.0 equiv.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1p** as a yellow solid (1.2 g, 75%).  $R_f = 0.43$  (Hexanes:EtOAc = 7:3); mp.: 249.1-250.2 °C.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 12.31 (s, 1H), 10.38 (s, 1H), 8.31 (s, 1H), 8.13-7.97 (m, 2H) 7.90-7.77 (m, 2H), 7.60 (t,  $J = 8.3$  Hz, 1H), 7.01 (pd,  $J = 8.4, 0.6$  Hz, 1H), 6.89 (pd,  $J = 8.4, 0.6$  Hz, 1H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 190.1, 188.8, 180.6, 164.2, 161.5, 156.1, 142.1, 140.4, 136.4, 135.7, 135.5, 134.3, 129.6, 123.6, 123.5, 117.3, 112.9, 110.7, 107.7. **HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{10}\text{O}_5$ : 318.0528 found: 318.0517.

**5,6-dimethoxy-2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1q**.**



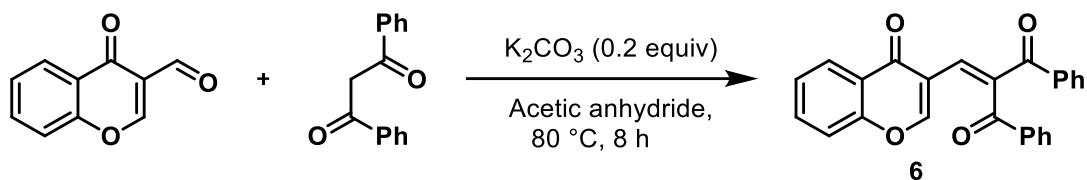
Following the **TP-A**, **1q** was obtained from 4-oxo-4H-chromene-3-carbaldehyde (0.87 g, 5.0 mmol), and 5,6-dimethoxy-1H-indene-1,3(2H)-dione (1.03 g, 5.0 mmol.), CSA (0.23 g, 0.2 equiv.). The residue was filtered under a vacuum and obtain **1q** as a yellow solid (1.2 g, 68%).  $R_f = 0.49$  (Hexanes:EtOAc = 5:5); mp.: 271.7-272.8 °C.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 10.28 (s, 1H), 8.33 (d,  $J = 7.8$  Hz, 1H), 8.26 (s, 1H), 7.74 (t,  $J = 8.3$  Hz, 1H), 7.56 (d,  $J = 8.5$  Hz, 1H), 7.48 (t,  $J = 7.8$  Hz, 1H), 7.04 (d,  $J = 11.4$  Hz, 1H), 7.33 (s, 2H), 4.03 (s, 6H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 196.6, 162.7, 155.9, 138.4, 134.3, 133.1, 126.6, 126.2, 118.6, 118.5, 103.9, 103.8, 103.2, 56.7, 44.7.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{14}\text{O}_6$ : 362.0790 found: 362.0775.

**2-((4-oxo-4H-chromen-3-yl)methylene)-1,3-diphenylpropane-1,3-dione **6**.**

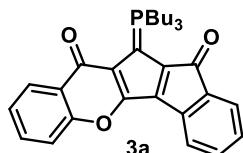


Following the reported procedure,<sup>3</sup> A 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with 4-oxo-4H-chromene-3-carbaldehyde (0.87 g, 5.0 mmol.), 1,3-diphenylpropane-1,3-dione (1.6 g, 1.5 equiv.),  $\text{K}_3\text{CO}_3$  (0.69 g, 0.2 equiv.) and acetic anhydride (30.0 mL). The reaction mixture was stirred for 8 h at 80 °C. After completion of the reaction, the residue was purified by column chromatography ( $\text{SiO}_2$ , Hexanes:EtOAc = 65:35) to give **6** as a half-white solid (1.45 g, 76%).  $R_f$  = 0.45 (Hexanes:EtOAc = 7:3); mp.: 177.0-178.1 °C.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 8.26 (d,  $J$  = 0.7 Hz, 1H), 8.17 (d,  $J$  = 8.2, 1.8 Hz, 1H), 8.00-7.91 (m, 4H), 7.68 (d,  $J$  = 0.9 Hz, 1H), 7.67-7.56 (m, 2H), 7.55-7.47 (m, 3H), 7.45-7.36 (m, 4H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 190.1, 188.8, 180.6, 164.2, 161.5, 156.1, 142.1, 140.4, 136.4, 135.7, 135.5, 134.3, 129.6, 123.6, 123.5, 117.3, 112.9, 110.7, 107.7. **HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{25}\text{H}_{16}\text{O}_4$ : 380.1049 found: 380.1068.

**11-(tributyl- $\lambda^5$ -phosphanylidene)-10H-benzo[5,6]pentaleno[1,2-b]chromene-10,12(11H)-dione **3a**.**



ollowing the **TP-B**, **3a** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol),  $\text{PBu}_3$  (88.8  $\mu\text{L}$ , 1.2 equiv.), benzoyl chloride **2a** (104.5  $\mu\text{L}$ , 3.0 equiv.) and  $\text{Et}_3\text{N}$  (150.5  $\mu\text{L}$ , 3.6 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (1.5 mL) at 30 °C for 8 h. After workup, the residue was purified by column chromatography ( $\text{SiO}_2$ , Hexanes:EtOAc = 70:30) to give **3a** as a dark red solid (135.0 mg, 92%).  $R_f$  = 0.30 (Hexanes:EtOAc = 9:1); mp.: 184.2-185.1 °C.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 8.23 (dd,  $J$  = 7.9, 1.9 Hz 1H), 7.57 (dtd,  $J$  = 9.0, 7.0, 1.7, Hz 1H), 7.46-7.44 (m, 1H), 7.33 (d,  $J$  = 7.2 Hz 1H), 7.29-7.25 (m, 1H), 6.94-6.88 (m, 1H), 2.73-2.54 (m, 6H), 1.48-1.44 (m, 12H), 0.93-0.89 (t,  $J$  = 8.0 Hz, 9H).

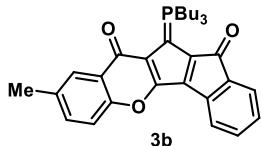
**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 189.7, 174.2, 156.3, 146.1 (d,  ${}^2J_{\text{C-P}} = 12.4$  Hz), 141.3, 139.3, 134.4, (d,  ${}^3J_{\text{C-P}} = 9.4$  Hz), 133.8, 132.3, 126.1, 124.7, 123.3, 122.8, 122.6 (d,  ${}^2J_{\text{C-P}} = 10.5$  Hz), 122.5, 122.3, (d,  ${}^3J_{\text{C-P}} = 12.7$  Hz), 118.9, 117.5, 82.8, (d,  ${}^1J_{\text{C-P}} = 102.9$  Hz), 24.1, (d,  ${}^3J_{\text{C-P}} = 4.0$  Hz), 23.8, (d,  ${}^2J_{\text{C-P}} = 16.0$  Hz), 21.3, (d,  ${}^1J_{\text{C-P}} = 52.3$

Hz), 13.5.

**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 22.0.

**HRMS** (EI) m/z:  $[\text{M}]^+$  calcd for  $\text{C}_{31}\text{H}_{35}\text{O}_3\text{P}$ : 486.2324 found: 486.2310.

**8-methyl-11-(tributyl- $\lambda^5$ -phosphanylidene)-10H-benzo[5,6]pentalenzo[1,2-b]chromene-10,12(11H)-dione 3b.**



Following the **TP-B**, **3b** was obtained from 2-((6-methyl-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1b** (94.89 mg, 0.3 mmol),  $\text{PBu}_3$  (88.8  $\mu\text{L}$ , 1.2 equiv.), **2a** (104.5  $\mu\text{L}$ , 3.0 equiv.), and  $\text{Et}_3\text{N}$  (150.5  $\mu\text{L}$ , 3.6 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (1.5 mL) at 30 °C for 48 h. After workup, the residue was purified by column chromatography ( $\text{SiO}_2$ , Hexanes:EtOAc = 70:30) to give **3b** as a dark red solid (138.0 mg, 90%).  $R_f = 0.45$  (Hexanes:EtOAc = 8:2); mp.: 179.9–181.1 °C.

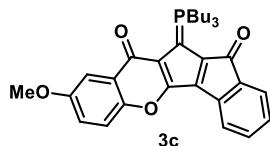
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 8.03 (s, 1H), 7.40–7.30 (m, 3H), 7.28–7.20 (m, 2H), 6.95–6.85 (m, 1H), 2.70–2.58 (m, 6H), 2.43 (s, 3H), 1.53–1.39 (m, 12H), 0.92 (t,  $J = 6.7$  Hz, 9H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 189.6, 174.3, 154.5, 146.3 (d,  $^2J_{\text{C-P}} = 11.9$  Hz), 141.3, 139.2, 139.1, 135.4 (d,  $^3J_{\text{C-P}} = 9.7$  Hz), 133.8, 133.4, 132.0, 125.6, 124.5, 123.2, 122.4 (d,  $^3J_{\text{C-P}} = 10.6$  Hz), 122.3 (d,  $^2J_{\text{C-P}} = 11.2$  Hz), 121.2, 118.9, 117.2, 82.0 (d,  $^1J_{\text{C-P}} = 104.2$  Hz), 24.1 (d,  $^3J_{\text{C-P}} = 3.9$  Hz), 23.7 (d,  $^2J_{\text{C-P}} = 15.7$  Hz), 21.5 (d,  $^1J_{\text{C-P}} = 52.7$  Hz), 20.7, 13.5.

**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 22.0.

**HRMS** (EI) m/z:  $[\text{M}]^+$  calcd for  $\text{C}_{32}\text{H}_{37}\text{O}_3\text{P}$ : 500.2480 found: 500.2462.

**8-methoxy-11-(tributyl- $\lambda^5$ -phosphanylidene)-10H-benzo[5,6]pentalenzo[1,2-b]chromene-10,12(11H)-dione 3c.**



Following the **TP-B**, **3c** was obtained from 2-((6-methoxy-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1c** (99.69 mg, 0.3 mmol),  $\text{PBu}_3$  (88.8  $\mu\text{L}$ , 1.2 equiv.), benzoyl chloride **2a** (104.5  $\mu\text{L}$ , 3.0 equiv.), and  $\text{Et}_3\text{N}$  (150.5  $\mu\text{L}$ , 3.6 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (1.5 mL) at 30 °C for 24 h. After workup, the residue was purified by column chromatography ( $\text{SiO}_2$ , Hexanes:EtOAc = 70:30) to give **3c** as a dark red

solid (114.5 mg, 73%).  $R_f$ = 0.45 (Hexanes:EtOAc = 8:2); mp.: 115.3-116.2 °C.

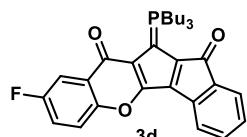
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 7.65 (d,  $J$  = 3.2 Hz, 1H), 7.38 (d,  $J$  = 9.1, 1H), 7.31 (d,  $J$  = 7.3 Hz, 1H), 7.28-7.21 (m, 1H), 7.18 (dd,  $J$  = 9.1, 3.2 Hz, 1H), 6.94-6.86 (m, 1H), 2.75-2.53 (m, 6H), 1.55-1.37 (m, 12H), 0.91 (t,  $J$  = 6.7 Hz, 9H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 189.7, 173.9, 155.2, 151.1, 146.5 (d,  $^2J_{\text{C-P}}$  = 12.1 Hz), 141.4, 139.2, 134.6 (d,  $^3J_{\text{C-P}}$  = 9.9 Hz), 133.8, 124.6, 123.2, 122.9, 122.4 (d,  $^3J_{\text{C-P}}$  = 10.4 Hz), 122.1 (d,  $^2J_{\text{C-P}}$  = 12.3 Hz), 121.9, 118.9, 118.7, 105.9, 81.6 (d,  $^1J_{\text{C-P}}$  = 103.3 Hz), 55.8, 24.2 (d,  $^3J_{\text{C-P}}$  = 3.8 Hz), 23.8 (d,  $^2J_{\text{C-P}}$  = 15.8 Hz), 21.5 (d,  $^1J_{\text{C-P}}$  = 52.8 Hz), 13.5.

**$^{31}\text{P NMR}$**  (162 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 21.9.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{32}\text{H}_{37}\text{O}_4\text{P}$ : 516.2429 found: 516.2454.

**8-fluoro-11-(tributyl- $\lambda^5$ -phosphanylidene)-10H-benzo[5,6]pentaleno[1,2-b]chromene-10,12(11H)-dione 3d.**



Following the **TP-B**, **3d** was obtained from 2-((6-fluoro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1d** (96.01 mg, 0.3 mmol),  $\text{PBu}_3$  (88.8  $\mu\text{L}$ , 1.2 equiv.), benzoyl chloride **2a** (104.5  $\mu\text{L}$ , 3.0 equiv.), and  $\text{Et}_3\text{N}$  (150.5  $\mu\text{L}$ , 3.6 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (1.5 mL) at 30 °C for 8 h. After workup, the residue was purified by column chromatography ( $\text{SiO}_2$ , Hexanes:EtOAc = 70:30) to give **3d** as a dark red solid (135.0 mg, 89%).  $R_f$ = 0.46 (Hexanes:EtOAc = 9:1); mp.: 169.7-170.5 °C

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 7.87 (dd,  $J$  = 9.0, 3.1 Hz, 1H), 7.43 (dd,  $J$  = 9.1, 4.3 Hz, 1H), 7.34 (d,  $J$  = 7.4 Hz, 1H), 7.3-7.28 (m, 1H), 7.3-7.2 (m, 1H), 6.94-6.90 (td,  $J$  = 6.9, 2.0 Hz, 1H), 2.80-2.52 (m, 6H), 1.55-1.37 (m, 12H), 0.92 (t,  $J$  = 6.9 Hz, 9H).

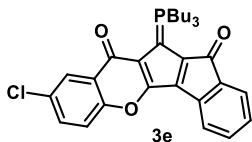
**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 189.7, 173.2, 159.5, 157.1, 152.4, 146.2, , (d,  $^2J_{\text{C-P}}$  = 12.0 Hz), 141.2, 139.1, 134.9, (d,  $^3J_{\text{C-P}}$  = 9.6 Hz), 133.9, 124.8, 123.7, (d,  $J_{\text{C-F}}$  = 6.7 Hz), 123.4, 122.3, (d,  $^3J_{\text{C-P}}$  = 10.6 Hz), 121.5, (d,  $^2J_{\text{C-P}}$  = 12.2 Hz), 120.0 (d,  $J_{\text{C-F}}$  = 25.2 Hz), 119.8, 119.0, 118.9, 111.0 (d,  $J_{\text{C-F}}$  = 23.7 Hz), 81.1 (d,  $^1J_{\text{C-P}}$  = 103.0 Hz), 24.1 (d,  $^3J_{\text{C-P}}$  = 3.9 Hz), 23.8 (d,  $^2J_{\text{C-P}}$  = 15.8 Hz), 21.4 , (d,  $^1J_{\text{C-P}}$  = 52.5 Hz), 13.5.

**$^{31}\text{P NMR}$**  (162 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 22.1.

**$^{19}\text{F NMR}$**  (376 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : -119.9.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{31}\text{H}_{34}\text{O}_3\text{PF}$ : 504.2230 found: 504.2198.

**8-chloro-11-(tributyl- $\lambda^5$ -phosphanylidene)-10H-benzo[5,6]pentalenol[1,2-b]chromene-10,12(11H)-dione 3e.**



Following the **TP-B**, **3e** was obtained from 2-((6-chloro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1e** (101.02 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 μL, 1.2 equiv.), benzoyl chloride **2a** (104.5 μL, 3.0 equiv.), and Et<sub>3</sub>N (150.5 μL, 3.6 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 8 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **3e** as a dark red solid (141.2 mg, 90%). R<sub>f</sub> = 0.55 (Hexanes:EtOAc = 9:1); mp.: 161.7–162.8 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.20 (d, J = 2.6 Hz, 1H), 7.50 (dd, J = 8.9, 2.6 Hz, 1H), 7.4 (d, J = 8.8 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 6.90 (td, J = 7.2, 1.7 Hz, 1H), 2.70–2.55 (m, 6H), 1.54–1.37 (m, 12H), 0.92 (t, J = 6.9 Hz, 9H).

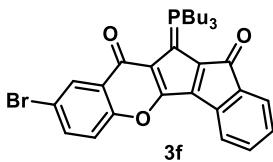
**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.6, 172.8, 154.6, 146.1 (d, <sup>2</sup>J<sub>C-P</sub> = 12.7 Hz), 141.2, 139.1, 135.0 (d, <sup>3</sup>J<sub>C-P</sub> = 9.6 Hz), 133.9, 132.1, 128.1, 125.7, 124.8, 123.9, 123.4, 122.4 (d, <sup>3</sup>J<sub>C-P</sub> = 10.8 Hz), 121.7 (d, <sup>2</sup>J<sub>C-P</sub> = 12.3 Hz), 119.1, 119.0, 82.5 (d, <sup>1</sup>J<sub>C-P</sub> = 102.7 Hz), 24.1 (d, <sup>3</sup>J<sub>C-P</sub> = 4.1 Hz), 23.7 (d, <sup>2</sup>J<sub>C-P</sub> = 15.7 Hz), 21.7 (d, <sup>1</sup>J<sub>C-P</sub> = 52.8 Hz), 13.5.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ/ppm: 22.2.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>31</sub>H<sub>34</sub>O<sub>3</sub>P<sup>35</sup>Cl: 520.1934 found: 520.1919.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>31</sub>H<sub>34</sub>O<sub>3</sub>P<sup>37</sup>Cl: 522.1905 found: 522.1904.

**8-bromo-11-(tributyl- $\lambda^5$ -phosphanylidene)-10H-benzo[5,6]pentalenol[1,2-b]chromene-10,12(11H)-dione 3f.**



Following the **TP-B**, **3f** was obtained from 2-((6-bromo-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1f** (114.4 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 μL, 1.2 equiv.), benzoyl chloride **2a** (104.5 μL, 3.0 equiv.), and Et<sub>3</sub>N (150.5 μL, 3.6 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 8 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **3f** as a dark red solid (148.2 mg, 87%). R<sub>f</sub> = 0.50 (Hexanes:EtOAc = 8:2); mp.: 170.3–171.2 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.36 (d, J = 2.5 Hz, 1H), 7.63 (dd, J = 8.8, 2.6 Hz, 1H), 7.35–7.34 (m, 1H), 7.33 (s, 1H), 6.94–6.90 (td, J = 14.1, 7.1 Hz, 1H), 2.71–2.53 (m,

6H), 1.54-1.36 (m, 12H), 0.92 (t,  $J$  = 6.9 Hz, 9H).

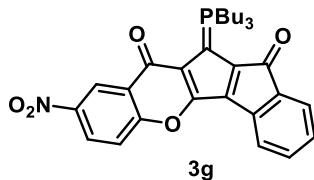
**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 189.6, 172.7, 155.0, 145.9 (d,  $^2J_{\text{C-P}}$  = 11.6 Hz), 141.1, 139.1, 135.0 (d,  $^3J_{\text{C-P}}$  = 9.4 Hz), 134.9, 133.9, 128.8, 124.3, 124.3, 123.4, 122.4 (d,  $^2J_{\text{C-P}}$  = 10.5 Hz), 121.6 (d,  $^3J_{\text{C-P}}$  = 11.93 Hz), 119.3, 119.1, 115.5, 83.1 (d,  $^1J_{\text{C-P}}$  = 101.8 Hz), 24.1 (d,  $^3J_{\text{C-P}}$  = 3.8 Hz), 23.8 (d,  $^2J_{\text{C-P}}$  = 15.4 Hz), 21.4 (d,  $^1J_{\text{C-P}}$  = 52.7 Hz), 13.5.

**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 22.2.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{31}\text{H}_{34}\text{O}_3\text{P}^{79}\text{Br}$ : 564.1429 found: 564.1411.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{31}\text{H}_{34}\text{O}_3\text{P}^{81}\text{Br}$ : 566.1408 found: 566.1397.

**8-nitro-11-(tributyl- $\lambda^5$ -phosphanylidene)-4c,10a,11,11a-tetrahydro-10H-benzo[5,6]pentaleno[1,2-b]chromene-10,12(4bH)-dione 3g.**



Following the **TP-B**, **3g** was obtained from 2-((6-nitro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1g** (104.18 mg, 0.3 mmol),  $\text{PBu}_3$  (88.8  $\mu\text{L}$ , 1.2 equiv.), benzoyl chloride **2a** (104.5  $\mu\text{L}$ , 3.0 equiv.), and  $\text{Et}_3\text{N}$  (150.5  $\mu\text{L}$ , 3.6 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (1.5 mL) at 30 °C for 8 h. After workup, the residue was purified by column chromatography ( $\text{SiO}_2$ , Hexanes:  $\text{EtOAc}$  = 70:30) to give **3g** as a dark red solid (128.0 mg, 80%).  $R_f$  = 0.50 (Hexanes:  $\text{EtOAc}$  = 8:2); mp.: 212.5-213.6 °C.

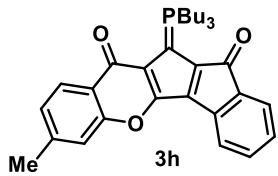
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 9.15 (d,  $J$  = 2.8 Hz, 1H), 8.40 (dd,  $J$  = 9.1, 2.9 Hz, 1H), 7.54 (d,  $J$  = 9.2 Hz, 1H), 7.36 (d,  $J$  = 7.4 Hz, 1H), 7.34-7.24 (m, 1H), 6.97 (td,  $J$  = 7.3, 1.2 Hz, 1H), 2.76-2.56 (m, 6H), 1.57-1.39 (m, 12H), 0.93 (t,  $J$  = 6.8 Hz, 9H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 189.5, 172.0, 159.4, 146.3 (d,  $^2J_{\text{C-P}}$  = 11.7 Hz), 143.1, 140.7, 139.1, 135.3 (d,  $^3J_{\text{C-P}}$  = 9.4 Hz), 134.1, 126.6, 125.2, 123.6, 123.3, 122.9, 122.7 (d,  $^3J_{\text{C-P}}$  = 10.4 Hz), 121.2 (d,  $^2J_{\text{C-P}}$  = 12.3 Hz), 119.3, 118.6, 83.5 (d,  $^1J_{\text{C-P}}$  = 102.2 Hz), 24.1 (d,  $^3J_{\text{C-P}}$  = 4.0 Hz), 23.3 (d,  $^2J_{\text{C-P}}$  = 15.8 Hz), 21.7 (d,  $^1J_{\text{C-P}}$  = 52.3 Hz), 13.5.

**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 22.7.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{31}\text{H}_{34}\text{NO}_5\text{P}$ : 531.2175 found: 531.2171.

**7-methyl-11-(tributyl- $\lambda^5$ -phosphanylidene)-10H-benzo[5,6]pentaleno[1,2-b]chromene-10,12(11H)-dione 3h.**



Following the **TP-B**, **3h** was obtained from 2-((7-methyl-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1h** (94.89 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 μL, 1.2 equiv.), benzoyl chloride **2a** (104.5 μL, 3.0 equiv.), and Et<sub>3</sub>N (150.5 μL, 3.6 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 48 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **3h** as a dark red solid (113.5 mg, 75%). R<sub>f</sub> = 0.48 (Hexanes:EtOAc = 8:2); mp.: 157.2–158.2 °C.

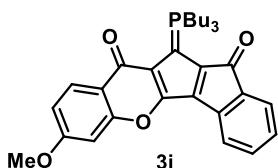
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.11 (d, J = 8.1 Hz, 1H), 7.32 (d, J = 7.2 Hz 1H), 7.28–7.20 (m, 3H), 7.09 (d, J = 8.1 Hz, 1H), 6.96–6.85 (m, 1H), 2.74–2.55 (m, 6H), 2.47 (s, 3H), 1.55–1.36 (m, 12H), 0.91 (t, J = 6.8 Hz, 9H).

<sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.6, 174.3, 156.4, 146.1 (d, <sup>3</sup>J<sub>C-P</sub> = 12.2 Hz), 143.3, 141.4, 141.3, 139.3, 134.0 (d, <sup>2</sup>J<sub>C-P</sub> = 9.9 Hz), 133.7, 125.8, 124.6, 123.9, 123.2, 122.6 (d, <sup>2</sup>J<sub>C-P</sub> = 10.3 Hz), 122.3 (d, <sup>3</sup>J<sub>C-P</sub> = 12.2 Hz), 120.4, 118.9, 117.4, 82.2 (d, <sup>1</sup>J<sub>C-P</sub> = 103.7 Hz), 24.1 (d, <sup>3</sup>J<sub>C-P</sub> = 3.8 Hz), 23.8 (d, <sup>2</sup>J<sub>C-P</sub> = 15.6 Hz), 21.7 (d, <sup>1</sup>J<sub>C-P</sub> = 52.9 Hz), 21.2, 13.5.

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ/ppm: 21.9.

HRMS (EI) m/z: [M]<sup>+</sup> calcd for C<sub>32</sub>H<sub>37</sub>O<sub>3</sub>P: 500.2480 found: 500.2492.

### 7-methoxy-11-(tributyl-phosphanylidene)-10H-benzo[5,6]pentalen-10,12(11H)-dione **3i**.



Following the **TP-B**, **3i** was obtained from 2-((7-methoxy-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1i** (99.69 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 μL, 1.2 equiv.), benzoyl chloride **2a** (104.5 μL, 3.0 equiv.), and Et<sub>3</sub>N (150.5 μL, 3.6 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 24 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 75:25) to give **3i** as a dark red solid (109.0 mg, 70%). R<sub>f</sub> = 0.38 (Hexanes:EtOAc = 8:2); mp.: 152.9–153.8 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.13 (d, J = 8.8 Hz, 1H), 7.32 (d, J = 7.1 Hz 1H), 7.26–7.21 (m, 3H), 6.96–6.80 (m, 3H), 3.91 (s, 3H), 2.7–2.55 (m, 6H), 1.53–1.37 (m, 12H), 0.91 (t, J = 6.7 Hz, 9H).

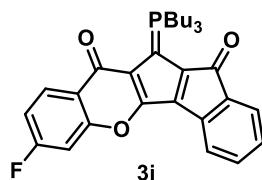
<sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.5, 174.1, 163.3, 158.0, 146.1 (d, <sup>3</sup>J<sub>C-P</sub> = 12.1 Hz), 141.3, 139.4, 133.6, 133.4 (d, <sup>2</sup>J<sub>C-P</sub> = 9.8 Hz), 127.4, 124.6, 123.2, 122.6 (d,

$^2J_{C-P} = 10.5$  Hz), 122.2 (d,  $^3J_{C-P} = 12.1$  Hz), 118.9, 116.6, 111.5, 100.2, 82.2 (d,  $^1J_{C-P} = 103.3$  Hz), 55.7, 24.2 (d,  $^3J_{C-P} = 3.4$  Hz), 23.8 (d,  $^2J_{C-P} = 15.8$  Hz), 21.5 (d,  $^1J_{C-P} = 53.1$  Hz).

**$^{31}P$  NMR** (162 MHz, CDCl<sub>3</sub>) δ/ppm: 22.0.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>32</sub>H<sub>37</sub>O<sub>4</sub>P: 516.2429 found: 516.2416.

**7-fluoro-11-(tributyl-λ<sup>5</sup>-phosphanylidene)-10H-benzo[5,6]pentalenzo[1,2-b]chromene-10,12(11H)-dione 3j.**



Following the **TP-B**, **3j** was obtained from 2-((7-fluoro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1j** (96.08 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 μL, 1.2 equiv.), benzoyl chloride **2a** (104.5 μL, 3.0 equiv.), and Et<sub>3</sub>N (150.5 μL, 3.6 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 24 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **3j** as a dark red solid (132.1 mg, 87%). R<sub>f</sub> = 0.50 (Hexanes:EtOAc = 8:2); mp.: 150.9–151.8 °C.

**$^1H$  NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.23 (dd,  $J = 8.9, 6.6$  Hz, 1H), 7.33 (d,  $J = 7.3$  Hz 1H), 7.30–7.20 (m, 2H), 6.96 (dd,  $J = 9.6, 2.4$  Hz, 1H), 7.99 (td,  $J = 8.2, 2.4$  Hz, 1H), 6.92 (td,  $J = 7.1, 1.6$  Hz, 1H), 2.76–2.53 (m, 6H), 1.58–1.36 (m, 12H), 0.92 (t,  $J = 6.8$  Hz, 9H).

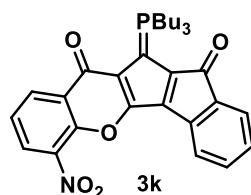
**$^{13}C\{^1H\}$ -NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.5, 173.4, 166.3, 163.8, 157.3 (d,  $J_{C-F} = 13.2$  Hz), 146.1 (d,  $^3J_{C-P} = 11.8$  Hz) 141.1, 139.2, 134.2 (d,  $^2J_{C-P} = 9.7$  Hz), 133.8, 128.3 (d,  $J_{C-F} = 10.6$  Hz), 124.8, 123.3, 122.5 (d,  $^2J_{C-P} = 10.8$  Hz) 121.7 (d,  $^3J_{C-P} = 12.2$  Hz) 119.6, 119.0, 110.9 (d,  $^2J_{C-P} = 22.2$  Hz), 103.9 (d,  $^2J_{C-P} = 25.2$  Hz), 82.5 (d,  $^1J_{C-P} = 103.2$  Hz), 24.1 (d,  $^3J_{C-P} = 3.8$  Hz), 23.8 (d,  $^2J_{C-P} = 15.7$  Hz), 21.4 (d,  $^1J_{C-P} = 52.6$  Hz), 13.5.

**$^{31}P$  NMR** (162 MHz, CDCl<sub>3</sub>) δ/ppm: 22.3.

**$^{19}F$  NMR** (376 MHz, CDCl<sub>3</sub>) δ/ppm: -106.4.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>31</sub>H<sub>34</sub>O<sub>3</sub>PF: 504.2230 found: 504.2215.

**6-nitro-11-(tributyl-λ<sup>5</sup>-phosphanylidene)-10H-benzo[5,6]pentalenzo[1,2-b]chromene-10,12(11H)-dione 3k.**



Following the **TP-B**, **3k** was obtained from 2-((8-nitro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1k** (104.18 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 µL, 1.2 equiv.), benzoyl chloride **2a** (104.5 µL, 3.0 equiv.), and Et<sub>3</sub>N (150.5 µL, 3.6 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 3 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **3k** as a dark red solid (138.0 mg, 86%). R<sub>f</sub> = 0.33 (Hexanes:EtOAc = 8:2); mp.: 179.7–180.8 °C.

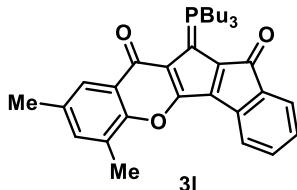
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.53 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.38 (dd, *J* = 7.9, 1.7 Hz), 7.38–7.28 (m, 4H), 6.96 (td, *J* = 7.2, 2.1 Hz, 1H), 2.71–2.56 (m, 6H), 1.55–1.39 (m, 12H), 0.92 (t, *J* = 6.6 Hz, 9H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.6, 171.7, 148.8, 144.5 (d, <sup>3</sup>J<sub>C-P</sub> = 11.8 Hz), 140.6, 138.9, 138.5, 135.6 (d, <sup>2</sup>J<sub>C-P</sub> = 9.6 Hz), 134.3, 132.1, 128.4, 125.3, 125.2, 123.4, 123.1 (d, <sup>3</sup>J<sub>C-P</sub> = 10.5 Hz), 121.3, 120.8 (d, <sup>2</sup>J<sub>C-P</sub> = 12.4 Hz), 119.6, 81.1 (d, <sup>1</sup>J<sub>C-P</sub> = 102.6 Hz), 24.1 (d, <sup>3</sup>J<sub>C-P</sub> = 3.9 Hz), 23.5 (d, <sup>2</sup>J<sub>C-P</sub> = 15.8 Hz), 21.2 (d, <sup>1</sup>J<sub>C-P</sub> = 52.6 Hz), 13.5.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ/ppm: 22.6.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>31</sub>H<sub>34</sub>NO<sub>5</sub>P: 531.2175 found: 531.2159.

### 6,8-dimethyl-11-(tributyl-λ<sup>5</sup>-phosphanylidene)-10H-benzo[5,6]pentalenol[1,2-b]chromene-10,12(11H)-dione **3l**.



Following the **TP-B**, **3l** was obtained from 2-((6,8-dimethyl-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1l** (330.3 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 µL, 1.2 equiv.), benzoyl chloride **2a** (104.5 µL, 3.0 equiv.) and Et<sub>3</sub>N (150.5 µL, 3.6 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 24 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **3l** as a dark red solid (116.0 mg, 75%). R<sub>f</sub> = 0.50 (Hexanes:EtOAc = 8:2); mp.: 211.1–212.3 °C.

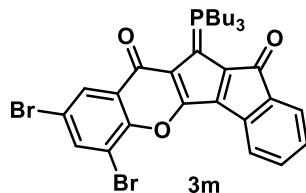
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 7.88 (d, *J* = 1.4 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.28–7.21 (m, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 6.90 (dd, *J* = 7.3, 0.82 Hz, 1H), 2.73–2.58 (m, 6H), 2.53(s, 3H), 2.40 (s, 3H), 1.57–1.36 (m, 12H), 0.91 (t, *J* = 6.8 Hz 9H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.7, 174.7, 152.8, 146.3 (d, <sup>2</sup>J<sub>C-P</sub> = 12.1 Hz), 141.4, 139.3, 134.6, 134.1 (d, <sup>3</sup>J<sub>C-P</sub> = 9.8 Hz), 133.7, 131.4, 126.2, 124.5, 123.2, 122.6 (d, <sup>3</sup>J<sub>C-P</sub> = 10.9 Hz), 122.1 (d, <sup>2</sup>J<sub>C-P</sub> = 12.2 Hz), 122.0, 118.8, 82.3 (d, <sup>1</sup>J<sub>C-P</sub> = 103.7 Hz), 24.2 (d, <sup>3</sup>J<sub>C-P</sub> = 3.7 Hz), 23.8 (d, <sup>2</sup>J<sub>C-P</sub> = 15.7 Hz), 21.5 (d, <sup>1</sup>J<sub>C-P</sub> = 53.7 Hz), 20.7, 15.7, 13.5.

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ/ppm: 21.9.

HRMS (EI) m/z: [M]<sup>+</sup> calcd for C<sub>33</sub>H<sub>39</sub>O<sub>3</sub>P: 514.2637 found: 514.2618.

**6,8-dibromo-11-(tributyl-λ<sup>5</sup>-phosphanylidene)-10H-benzo[5,6]pentaleno[1,2-b]chromene-10,12(11H)-dione 3m.**



Following the TP-B, **3m** was obtained from 2-((6,8-dibromo-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1m** (138.02 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 μL, 1.2 equiv.), benzoyl chloride **2a** (104.5 μL, 3.0 equiv.), and Et<sub>3</sub>N (150.5 μL, 3.6 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 8 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexane:EtOAc = 75:25) to give **3m** as a dark red solid (165.0 mg, 85%). R<sub>f</sub> = 0.40 (Hexanes:EtOAc = 9:1); mp.: 214.2–215.5 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.30 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 2.3 Hz, 1H), 7.35 (d, J = 7.4 Hz, 1H), 7.32–7.27 (m, 2H), 6.99–6.90 (m, 1H), 2.73–2.49 (m, 6H), 1.58–1.35 (m, 12H), 0.91 (t, J = 6.7 Hz, 9H).

<sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.7, 171.8, 151.6, 145.3 (d, <sup>2</sup>J<sub>C-P</sub> = 11.8 Hz), 140.9, 140.8, 139.0, 137.5, 135.4 (d, <sup>3</sup>J<sub>C-P</sub> = 9.6 Hz), 134.1, 128.3, 125.1, 125.0, 123.5, 122.8 (d, <sup>3</sup>J<sub>C-P</sub> = 10.5 Hz), 120.8 (d, <sup>2</sup>J<sub>C-P</sub> = 12.4 Hz), 119.4, 115.1, 112.0, 82.8 (d, <sup>1</sup>J<sub>C-P</sub> = 102.8 Hz), 24.1 (d, <sup>3</sup>J<sub>C-P</sub> = 4.1 Hz), 23.8 (d, <sup>2</sup>J<sub>C-P</sub> = 15.8 Hz), 21.3 (d, <sup>1</sup>J<sub>C-P</sub> = 52.8 Hz), 13.5.

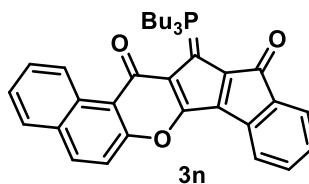
<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ/ppm: 22.4.

HRMS (EI) m/z: [M]<sup>+</sup> calcd for C<sub>31</sub>H<sub>33</sub><sup>79</sup>Br<sup>79</sup>Br O<sub>3</sub>P: 642.0534 found: 642.0519.

HRMS (EI) m/z: [M]<sup>+</sup> calcd for C<sub>31</sub>H<sub>33</sub><sup>79</sup>Br<sup>81</sup>BrO<sub>4</sub>P: 644.0514 found: 644.0522.

HRMS (EI) m/z: [M]<sup>+</sup> calcd for C<sub>31</sub>H<sub>33</sub><sup>81</sup>Br<sup>81</sup>Br O<sub>4</sub>P: 646.0493 found: 646.0487.

**13-(tributyl-λ<sup>5</sup>-phosphanylidene)-12H-benzo[f]benzo[5,6]pentaleno[1,2-b]chromene-12,14(13H)-dione 3n.**



Following the TP-B, **3n** was obtained from 2-((1-oxo-1H-benzo[f]chromen-2-yl)methylene)-1H-indene-1,3(2H)-dione **1n** (105.7 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 μL, 1.2 equiv.), benzoyl chloride **2a** (104.5 μL, 3.0 equiv.), and Et<sub>3</sub>N (150.5 μL, 3.6 equiv.) in

anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 48 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **3n** as a dark red solid (85.1 mg, 52%). R<sub>f</sub> = 0.53 (Hexanes:EtOAc = 7:3); mp.: 189.4-190.3 °C.

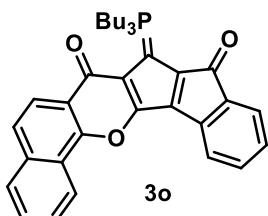
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 10.17 (d, J = 8.7 Hz, 1H), 7.98 (d, J = 9.1 Hz 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.9 Hz, 1H), 7.57 (d, J = 9.1 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 7.3 Hz, 1H), 7.29-7.20 (m, 2H), 6.95-6.85 (m, 1H), 2.79-2.59 (m, 6H), 1.55-1.40 (m, 12H), 0.92 (t, J = 6.7 Hz, 9H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.6, 177.2, 157.3, 144.7 (d, <sup>3</sup>J<sub>C-P</sub> = 12.0 Hz), 141.3, 141.2, 139.4, 133.8, 133.7, 133.4 (d, <sup>2</sup>J<sub>C-P</sub> = 10.0 Hz), 132.2, 130.2, 128.1, 126.9, 125.2 (d, <sup>2</sup>J<sub>C-P</sub> = 11.4 Hz), 124.9, 124.6, 123.2, 122.7, (d, <sup>3</sup>J<sub>C-P</sub> = 10.6 Hz), 118.7, 118.6, 114.7, 81.2 (d, <sup>1</sup>J<sub>C-P</sub> = 104.5 Hz), 24.3 (d, <sup>3</sup>J<sub>C-P</sub> = 3.9 Hz), 23.8 (d, <sup>2</sup>J<sub>C-P</sub> = 15.7 Hz), 21.8 (d, <sup>1</sup>J<sub>C-P</sub> = 53.7 Hz), 13.6.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ/ppm: 21.9.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>35</sub>H<sub>37</sub>O<sub>3</sub>P: 536.2480 found: 536.2464.

**8-(tributyl-λ<sup>5</sup>-phosphanylidene)-7H-benzo[h]benzo[5,6]pentaleno[1,2-b]chromene-7,9(8H)-dione **3o**.**



Following the **TP-B**, **3o** was obtained from 2-((4-oxo-4H-benzo[h]chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1o** (105.72 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 μL, 1.2 equiv.), benzoyl chloride **2a** (104.5 μL, 3.0 equiv.), and Et<sub>3</sub>N (150.5 μL, 3.6 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 24 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 75:25) to give **3o** as a dark red solid (118.0 mg, 73%). R<sub>f</sub> = 0.50 (Hexanes:EtOAc = 8:2); mp.: 191.3-192.1 °C.

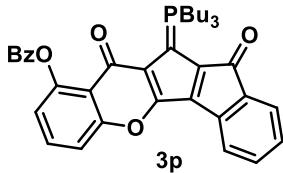
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.69-8.61 (m, 1H), 8.23 (d, J = 8.7 Hz, 1H), 7.94-7.84 (m, 1H), 7.73-7.60 (m, 3H), 7.42-7.29 (m, 3H), 6.94 (td, J = 7.4, 1.0 Hz, 1H), 2.79-2.56 (m, 6H), 1.62-1.37 (m, 12H), 0.91 (t, J = 6.9 Hz, 9H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.7, 174.4, 153.1, 145.9 (d, <sup>3</sup>J<sub>C-P</sub> = 12.2 Hz), 141.3, 139.6, 135.6, 133.9 (d, <sup>2</sup>J<sub>C-P</sub> = 9.9 Hz), 133.8, 128.3, 127.8, 126.3, 124.8, 124.4, 123.3, 123.1 (d, <sup>2</sup>J<sub>C-P</sub> = 10.3 Hz), 122.9 (d, <sup>3</sup>J<sub>C-P</sub> = 12.3 Hz), 122.7, 122.4, 121.9, 118.9, 117.9, 81.7 (d, <sup>1</sup>J<sub>C-P</sub> = 104.0 Hz), 24.2 (d, <sup>3</sup>J<sub>C-P</sub> = 3.9 Hz), 23.8 (d, <sup>2</sup>J<sub>C-P</sub> = 15.7 Hz), 21.6 (d, <sup>3</sup>J<sub>C-P</sub> = 53.3 Hz), 13.5.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ/ppm: 22.1.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>35</sub>H<sub>37</sub>O<sub>3</sub>P: 536.2480 found: 536.2489.

**10,12-dioxo-11-(tributyl- $\lambda^5$ -phosphanylidene)-11,12-dihydro-10H-benzo[5,6]pentaleno[1,2-b]chromen-9-yl benzoate 3p.**



Following the **TP-B**, **3p** was obtained from 2-((5-hydroxy-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1p** (95.40 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 µL, 1.2 equiv.), benzoyl chloride **2a** (156.83 µL, 4.5 equiv.) and Et<sub>3</sub>N (192.30 µL, 4.6 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 24 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 80:20) to give **3p** as a dark red solid (128.0 mg, 70%). R<sub>f</sub> = 0.40 (Hexanes:EtOAc = 9:1); mp.: 190.8-191.5 °C.

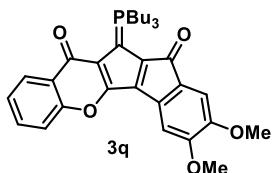
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.26 (d, J = 7.3 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.57-7.47 (m, 3H), 7.39 (d, J = 8.5 Hz, 1H), 7.30 (d, J = 7.3 Hz, 1H), 7.27-7.28 (m, 2H), 6.98 (d, J = 7.6 Hz, 1H), 7.39 (dd, J = 7.1, 1.6 Hz, 1H), 2.51-2.34 (m, 6H), 1.58-1.28 (m, 12H), 0.86 (t, J = 6.8 Hz, 9H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.5, 173.4, 165.4, 157.7, 150.2, 144.9 (d, <sup>2</sup>J<sub>C-P</sub> = 11.8 Hz), 141.3, 141.2, 139.3, 133.8 (d, <sup>3</sup>J<sub>C-P</sub> = 11.8 Hz), 133.7, 132.8, 131.6, 130.8, 130.3, 128.2, 124.6, 123.3 (d, <sup>3</sup>J<sub>C-P</sub> = 12.3 Hz), 123.2, 122.3 (d, <sup>2</sup>J<sub>C-P</sub> = 12.2 Hz), 118.9, 116.9, 115.9, 82.4 (d, <sup>1</sup>J<sub>C-P</sub> = 103.5 Hz), 24.1 (d, <sup>3</sup>J<sub>C-P</sub> = 3.9 Hz), 23.8 (d, <sup>2</sup>J<sub>C-P</sub> = 15.9 Hz), 21.5 (d, <sup>1</sup>J<sub>C-P</sub> = 53.0 Hz), 13.5.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ/ppm: 21.6.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>38</sub>H<sub>39</sub>O<sub>5</sub>P: 606.2535 found: 606.2524.

**2,3-dimethoxy-11-(tributyl- $\lambda^5$ -phosphanylidene)-10H-benzo[5,6]pentaleno[1,2-b]chromene-10,12(11H)-dione 3q.**



Following the **TP-B**, **3q** was obtained 5,6-dimethoxy-2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1q** (108.7 mg, 0.3 mmol), PBu<sub>3</sub> (88.8 µL, 1.2 equiv.), benzoyl chloride **2a** (104.5 µL, 3.0 equiv.) and Et<sub>3</sub>N (150.5 µL, 3.6 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at 30 °C for 3 h. After workup, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 72:25) to give **3q** as a reddish brown solid (90.0 mg, 55%). R<sub>f</sub> = 0.38 (Hexanes/EtOAc = 8:2); mp.: 160.7-161.7 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.23 (dd, J = 7.9, 1.6 Hz, 1H), 7.56 (dtd, J = 8.9,

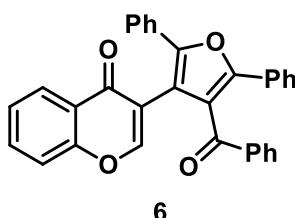
7.5, 1.7 Hz, 1H), 7.27 (dd,  $J$  = 7.5, 0.7 Hz, 1H), 6.98 (s, 1H), 6.83 (s, 1H), 4.03 (s, 3H), 3.86 (s, 3H), 2.71-2.55 (m, 6H), 1.57-1.38 (m, 12H), 0.92 (t,  $J$  = 6.7 Hz, 9H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 189.2, 173.6, 156.2, 153.9, 146.4, 145.6 (d,  $^2J_{\text{C-P}} = 11.9$  Hz), 136.7, 135.3 (d,  $^3J_{\text{C-P}} = 9.6$  Hz), 132.0, 131.2, 126.1, 122.8, 122.5, 121.4 (d,  $^2J_{\text{C-P}} = 12.1$  Hz), 120.5 (d,  $^3J_{\text{C-P}} = 10.7$  Hz), 117.3, 107.9, 103.4, 82.9 (d,  $^1J_{\text{C-P}} = 103.2$  Hz), 56.3, 56.2, 24.2 (d,  $^3J_{\text{C-P}} = 3.8$  Hz), 23.8 (d,  $^2J_{\text{C-P}} = 15.7$  Hz), 21.4 (d,  $^1J_{\text{C-P}} = 52.8$  Hz), 13.5.

**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 22.0.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{33}\text{H}_{39}\text{O}_5\text{P}$ : 546.2535. found: 546.2538.

### 3-(4-benzoyl-2,5-diphenylfuran-3-yl)-4H-chromen-4-one **6**.



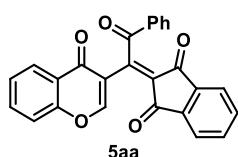
Following the **TP-B**, **6** was obtained 2-((4-oxo-4H-chromen-3-yl)methylene)-1,3-diphenylpropane-1,3-dione **1r** (114.1 mg, 0.3 mmol),  $\text{PBu}_3$  (88.8 $\mu\text{L}$ , 1.2 equiv.), benzoyl chloride **2a** (104.5  $\mu\text{L}$ , 3.0 equiv.) and  $\text{Et}_3\text{N}$  (150.5  $\mu\text{L}$ , 3.6 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (1.5 mL) at 30 °C for 3 h. After workup, the residue was purified by column chromatography ( $\text{SiO}_2$ , Hexanes:EtOAc = 70:30) to give **6** as a half-white solid (99.0 mg, 75%).  $R_f = 0.38$  (Hexanes/EtOAc = 8:2); mp.: 115.8-116.8 °C.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 8.16 (dd,  $J$  = 7.9, 1.6 Hz, 1H), 8.02 (s, 1H), 7.86 (dd,  $J$  = 8.3, 1.4 Hz, 1H), 7.73-7.62 (m, 3H), 7.55-7.48 (m, 2H), 7.44 (d,  $J$  = 8.4, Hz, 1H), 7.40-7.28 (m, 5H), 7.27-7.18 (m, 5H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 192.4, 175.6, 156.2, 154.9, 152.6, 150.5, 137.2, 133.6, 132.9, 129.8, 129.7, 129.2, 128.6, 128.6, 128.2, 128.1, 127.1, 126.2, 126.1, 125.1, 123.8, 123.8, 118.0, 117.4, 113.8.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{32}\text{H}_{20}\text{O}_4\text{P}$ : 468.1362. found: 468.1352.

### 2-(2-oxo-1-(4-oxo-4H-chromen-3-yl)-2-phenylethylidene)-1H-indene-1,3(2H)-dione **5aa**.



Following the **TP-C**, **5aa** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol),  $\text{Me}_2\text{PhP}$  (8.54 $\mu\text{L}$ , 0.2 equiv.),

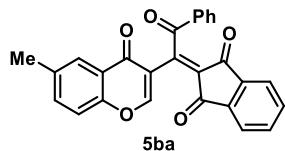
benzoyl chloride **2a** (41.82  $\mu$ L, 1.2 equiv.), and Et<sub>3</sub>N (54.36  $\mu$ L, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 0.5 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5aa** as a pale yellow solid (110.0 mg, 90%). R<sub>f</sub> = 0.41 (Hexanes:EtOAc = 7:3); mp.: 248.2–248.5 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.30 (s, 1H), 8.29 (dd, *J* = 7.9, 1.5 Hz 1H), 8.11 (dd, *J* = 7.3, 1.2 Hz 1H), 7.96–7.92 (m, 1H), 7.89–7.84 (m, 1H), 7.84–7.74 (m, 2H), 7.70 (dtd, *J* = 9.0, 7.3, 1.6 Hz, 1H), 7.57 (t, *J* = 7.4 Hz 1H), 7.50–7.41 (m, 4H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 195.4, 187.6, 187.3, 173.0, 155.9, 155.4, 146.2, 142.6, 140.7, 135.8, 132.7, 134.9, 134.3, 134.2, 131.6, 129.0, 128.9, 126.6, 126.0, 123.7, 123.6, 123.5, 118.4, 118.2.

**HRMS** (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>14</sub>O<sub>5</sub>: 407.0919 found: 407.0916.

### 2-(1-(6-methyl-4-oxo-4H-chromen-3-yl)-2-oxo-2-phenylethylidene)-1H-indene-1,3(2H)-dione **5ba**.



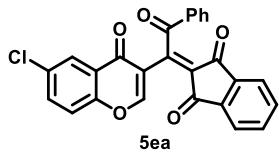
Following the TP-C, **5ba** was obtained from 2-((6-methyl-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1b** (94.89 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54  $\mu$ L, 0.2 equiv.), benzoyl chloride **2a** (41.82  $\mu$ L, 1.2 equiv.), and Et<sub>3</sub>N (54.36  $\mu$ L, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 3 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5ba** as a pale yellow solid (101.0 mg, 80%). R<sub>f</sub> = 0.45 (Hexanes:EtOAc = 7:3); mp.: 290.3–291.2 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.27 (s, 1H), 8.14–8.07 (m, 3H), 7.95 (dd, *J* = 6.1, 1.5 Hz, 1H), 7.90–7.85 (m, 1H), 7.83–7.75 (m, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.52 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 1H), 2.50 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 195.4, 187.8, 187.4, 173.1, 155.3, 154.2, 146.5, 142.7, 140.8, 136.2, 135.8, 135.6, 135.5, 135.1, 134.2, 131.5, 129.1, 128.9, 126.0, 123.7, 123.6, 123.4, 118.2, 117.9, 20.9.

**HRMS** (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>16</sub>O<sub>5</sub>: 420.0998 found: 420.0989.

### 2-(1-(6-chloro-4-oxo-4H-chromen-3-yl)-2-oxo-2-phenylethylidene)-1H-indene-1,3(2H)-dione **5ea**.



Following the **TP-C**, **5ea** was obtained from 2-((6-chloro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1e** (101.02 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 μL, 0.2 equiv.), benzoyl chloride **2a** (41.82 μL, 1.2 equiv.), and Et<sub>3</sub>N (54.36 μL, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 0.5 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5ea** as a pale yellow solid (95.0 mg, 72%). R<sub>f</sub> = 0.45 (Hexanes:EtOAc = 7:3); mp.: 270.1–271.2 °C.

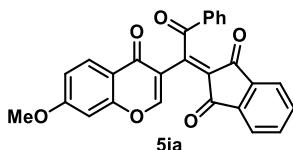
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.29 (s, 1H), 8.27 (dd, J = 2.6 Hz, 1H), 8.12–8.07 (m, 2H), 7.99–7.95 (m, 1H), 7.91–7.87 (m, 1H), 7.85–7.77 (m, 2H), 7.70 (dd, J = 9.4, 2.7 Hz, 1H), 7.62–7.56 (m, 1H), 7.51–7.43 (m, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 195.3, 187.6, 187.3, 171.9, 155.2, 154.3, 145.4, 142.6, 140.8, 135.9, 135.7, 134.9, 134.5, 134.4, 132.1, 131.8, 129.1, 128.9, 126.1, 124.6, 123.7, 123.6, 119.9, 118.4.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>13</sub><sup>35</sup>Cl O<sub>5</sub>: 440.0452 found: 440.0434.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>13</sub><sup>37</sup>Cl O<sub>5</sub>: 442.0422 found: 442.0436.

### 2-(1-(7-methoxy-4-oxo-4H-chromen-3-yl)-2-oxo-2-phenylethylidene)-1H-indene-1,3(2H)-dione **5ia**.



Following the **TP-C**, **5ia** was obtained from 2-((7-methoxy-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1i** (99.69 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 μL, 0.2 equiv.), benzoyl chloride **2a** (41.82 μL, 1.2 equiv.), and Et<sub>3</sub>N (54.36 μL, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 2 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5ia** as a pale yellow solid (82.0 mg, 62%). R<sub>f</sub> = 0.40 (Hexanes:EtOAc = 7:3); mp.: 268.8–269.3 °C.

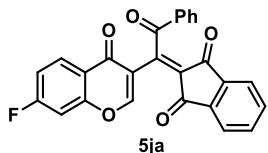
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.23 (s, 1H), 8.19 (d, J = 8.9 Hz, 1H), 8.14–8.07 (m, 2H), 7.99–7.95 (m, 1H), 7.90–7.86 (m, 1H), 7.85–7.74 (m, 2H), 7.62–7.54 (m, 1H), 7.50–7.43 (m, 2H), 7.02 (dd, J = 9.1, 2.3 Hz, 1H), 6.87 (d, J = 2.4 Hz, 1H), 3.91 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 195.5, 187.8, 187.4, 172.3, 164.6, 157.7, 155.1, 146.6, 142.7, 140.8, 135.8, 135.6, 135.1, 134.1, 131.6, 129.1, 128.9, 128.1, 123.7,

123.6, 118.5, 117.6, 115.2, 100.5, 55.9.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>27</sub>H<sub>16</sub>O<sub>6</sub>: 436.0947 found: 436.0966.

**2-(1-(7-fluoro-4-oxo-4H-chromen-3-yl)-2-oxo-2-phenylethylidene)-1H-indene-1,3(2H)-dione 5ja.**



Following the **TP-C**, **5ja** was obtained from 2-((7-fluoro-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1j** (96.08 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 μL, 0.2 equiv.), benzoyl chloride **2a** (41.82 μL, 1.2 equiv.), and Et<sub>3</sub>N (54.36 μL, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 0.5 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5ja** as a pale yellow solid (95.4 mg, 75%). R<sub>f</sub> = 0.43 (Hexanes:EtOAc = 7:3); mp.: 223.5–224.5 °C.

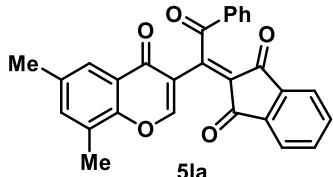
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.3 (dd, J = 8.7, 6.3 Hz, 1H), 8.29 (s, 1H), 8.11 (d, J = 7.8 Hz, 2H), 7.96 (dd, J = 6.4, 1.3 Hz, 1H), 7.93–7.85 (m, 1H), 7.85–7.75 (m, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.24–7.15 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 195.3, 187.7, 187.3, 172.2, 167.2, 164.6, 157.9 (d, J<sub>C-F</sub> = 13.3 Hz), 155.2, 145.6, 142.6, 140.8, 135.9, 135.8, 134.9, 134.3, 131.8, 129.1 (d, J<sub>C-F</sub> = 10.9 Hz), 129.1, 128.9, 123.8, 123.7, 120.7, 120.6, 118.7, 114.8 (d, J<sub>C-F</sub> = 22.8 Hz), 105.0 (d, J<sub>C-F</sub> = 25.6 Hz).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ/ppm: -101.3.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>13</sub>O<sub>5</sub>F: 424.0747 found: 424.0745.

**2-(1-(6,8-dimethyl-4-oxo-4H-chromen-3-yl)-2-oxo-2-phenylethylidene)-1H-indene-1,3(2H)-dione 5la.**



Following the **TP-C**, **5la** was obtained from 2-((6,8-dimethyl-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1l** (99.10 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 μL, 0.2 equiv.), benzoyl chloride **2a** (41.82 μL, 1.2 equiv.), and Et<sub>3</sub>N (54.36 μL, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 0.5 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5la** as a pale yellow solid (105.1 mg, 80%). R<sub>f</sub> = 0.53 (Hexanes:EtOAc = 7:3); mp.:

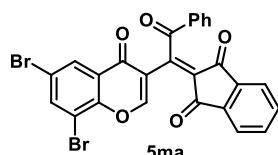
304.1-305.2 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.32 (s, 1H), 8.10 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.99-7.93 (m, 1H), 7.92 (d, *J* = 0.8 Hz, 1H), 7.89-7.85 (m, 1H), 7.83-7.75 (m, 2H), 7.60-7.53 (m, 1H), 7.50-7.42 (m, 2H), 7.36 (s, 1H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 195.4, 187.9, 187.4, 173.4, 155.2, 152.8, 146.8, 142.7, 140.8, 136.5, 135.8, 135.6, 135.5, 135.1, 134.1, 131.4, 129.1, 128.9, 127.4, 123.7, 123.6, 123.5, 123.4, 117.9, 20.9, 15.3.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>28</sub>H<sub>18</sub>O<sub>5</sub>: 434.1154 found: 434.1163.

**2-(1-(6,8-dibromo-4-oxo-4H-chromen-3-yl)-2-oxo-2-phenylethylidene)-1H-indene-1,3(2H)-dione 5ma.**



Following the **TP-C**, **5ma** was obtained from 2-((6,8-dibromo-4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1m** (138.04 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 μL, 0.2 equiv.), benzoyl chloride **2a** (41.82 μL, 1.2 equiv.), and Et<sub>3</sub>N (54.36 μL, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 0.5 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5ma** as a pale yellow solid (85.0 mg, 50%). R<sub>f</sub> = 0.30 (Hexanes:EtOAc = 7:3); mp.: 269.1-270.5 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.41-8.34 (m, 2H), 8.12-8.04 (m, 3H), 7.98-7.94 (m, 1H), 7.92-7.87 (m, 1Hz), 7.86-7.77 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H).

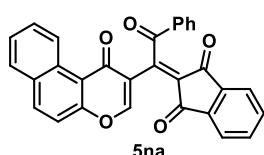
**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 194.9, 187.4, 187.3, 171.4, 154.8, 151.6, 144.6, 142.6, 140.9, 140.0, 136.0, 135.9, 134.8, 134.4, 132.1, 129.1, 129.0, 128.7, 125.7, 123.8, 119.4, 118.6, 113.1.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>12</sub><sup>79</sup>Br<sup>79</sup>BrO<sub>5</sub>: 561.9051 found: 561.9042.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>12</sub><sup>79</sup>Br<sup>81</sup>BrO<sub>5</sub>: 563.9031 found: 563.9021.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>12</sub><sup>81</sup>Br<sup>81</sup>Br O<sub>5</sub>: 565.9011 found: 565.9024.

**2-(2-oxo-1-(1-oxo-1H-benzo[f]chromen-2-yl)-2-phenylethylidene)-1H-indene-1,3(2H)-dione 5na.**



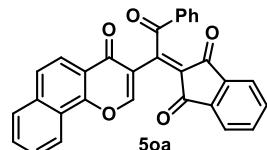
Following the **TP-C**, **5na** was obtained from 2-((1-oxo-1H-benzo[f]chromen-2-yl)methylene)-1H-indene-1,3(2H)-dione **1n** (105.70 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 μL, 0.2 equiv.), benzoyl chloride **2a** (41.82 μL, 1.2 equiv.), and Et<sub>3</sub>N (54.36 μL, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 2 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 65:35) to give **5na** as a pale yellow solid (97.0 mg, 74%). R<sub>f</sub> = 0.45 (Hexanes:EtOAc = 7:3); mp.: 264.5-265.6 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 9.94 (d, J = 8.7 Hz, 1H), 8.32 (s, 1H), 8.23-8.20 (m, 2H), 8.12 (d, J = 9.1 Hz, 1H), 7.97-7.94 (m, 1H), 7.92 (d, J = 7.4 Hz, 1H), 7.90-7.86 (m, 1H), 7.84-7.72 (m, 3H), 7.63 (dt, J = 8.78, 7.2, 1.2 Hz, 1H), 7.60-7.55 (m, 1H), 7.53-7.44 (m, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 195.5, 187.9, 187.3, 174.7, 157.2, 152.9, 146.8, 142.7, 140.8, 136.1, 135.8, 135.6, 135.2, 134.2, 134.3, 131.6, 131.0, 130.6, 129.6, 129.2, 128.9, 128.3, 127.2, 126.9, 123.7, 123.6, 120.9, 117.4, 117.3.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>30</sub>H<sub>16</sub>O<sub>5</sub>: 456.0998 found: 456.1010.

### 2-(2-oxo-1-(4-oxo-4H-benzo[h]chromen-3-yl)-2-phenylethylidene)-1H-indene-1,3(2H)-dione **5oa**.



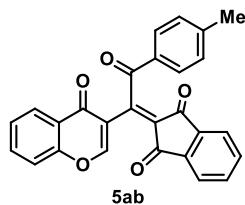
Following the **TP-C**, **5oa** was obtained from 2-((1-oxo-1H-benzo[f]chromen-2-yl)methylene)-1H-indene-1,3(2H)-dione **1o** (105.70 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 μL, 0.2 equiv.), benzoyl chloride **2a** (41.82 μL, 1.2 equiv.), and Et<sub>3</sub>N (54.36 μL, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 0.5 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 75:25) to give **5oa** as a pale yellow solid (98.0 mg, 75%). R<sub>f</sub> = 0.40 (Hexanes:EtOAc = 7:3); mp.: 180.2-181.5 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.50 (s, 1H), 8.45 (d, J = 8.2 Hz, 1H), 8.21 (d, J = 8.7 Hz, 1H), 8.18-8.12 (m, 2H), 8.0-7.95 (m, 1H), 7.93 (d, J = 7.7 Hz, 1H), 7.91-7.87 (m, 1H), 7.85-7.76 (m, 3H), 7.75-7.64 (m, 2H), 7.80 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 195.5, 187.8, 187.3, 172.8, 154.4, 153.5, 146.2, 142.7, 140.8, 136.0, 135.8, 135.7, 135.0, 134.2, 131.8, 129.7, 129.1, 128.9, 128.1, 127.1, 127.5, 126.1, 123.8, 123.7, 123.7, 122.2, 121.1, 120.2, 119.7.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>30</sub>H<sub>16</sub>O<sub>5</sub>: 456.0998 found: 456.0983.

**2-(2-oxo-1-(4-oxo-4H-chromen-3-yl)-2-(p-tolyl)ethylidene)-1H-indene-1,3(2H)-dione 5ab.**



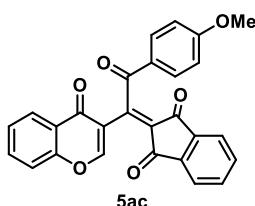
Following the **TP-C**, **5ab** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 μL, 1.2 equiv.), 4-methylbenzoyl chloride **2b** (52.35 μL, 1.2 equiv.), and Et<sub>3</sub>N (54.36 μL, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 0.5 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 80:20) to give **5ab** as a pale yellow solid (109.0 mg, 86%). R<sub>f</sub> = 0.40 (Hexanes:EtOAc = 90:10); mp.: 284.1-285.0 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.35-8.25 (m, 2H), 8.00 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 6.6 Hz, 1H), 7.91-7.85 (m, 1H), 7.84-7.75 (m, 2H), 7.71 (td, J = 6.7, 1.0 Hz, 1H), 7.54-7.41 (m, 2H), 7.30-7.22 (m, 2H), 2.37 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 194.9, 187.8, 187.4, 172.9, 155.9, 155.2, 146.4, 145.3, 142.6, 140.8, 135.8, 135.6, 134.2, 132.6, 131.4, 129.7, 129.2, 126.7, 125.9, 123.8, 123.7, 123.6, 118.6, 118.2, 21.8.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>27</sub>H<sub>16</sub>O<sub>5</sub>: 420.0998 found: 420.0989.

**2-(2-(4-methoxyphenyl)-2-oxo-1-(4-oxo-4H-chromen-3-yl)ethylidene)-1H-indene-1,3(2H)-dione 5ac.**



Following the **TP-C**, **5ac** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 μL, 0.2 equiv.), 4-methoxy benzoyl chloride **2c** (52.8 μL, 1.2 equiv.), and Et<sub>3</sub>N (54.36 μL, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 3 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5ac** as a pale yellow solid (115.0 mg, 88%). R<sub>f</sub> = 0.36 (Hexanes:EtOAc = 7:3); mp.: 251.9-252.8 °C.

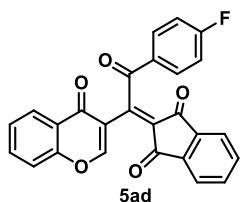
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.33-8.27 (m, 1H), 8.16-8.05 (m, 2H), 7.99-7.93 (m, 1H), 7.92-7.87 (m, 1H), 7.84-7.77 (m, 2H), 7.71 (dtd, J = 9.4, 7.7, 1.7 Hz, 1H),

7.51-7.43 (m, 2H), 6.97-6.88 (m, 2H), 3.83 (s, 3H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 193.8, 187.8, 187.5, 173.0, 164.5, 156.0, 154.9, 146.4, 142.6, 140.9, 135.8, 135.6, 134.2, 131.6, 131.3, 128.2, 126.7, 125.9, 123.8, 123.7, 123.6, 118.8, 118.2, 114.4, 55.5.

**HRMS** (EI) m/z:  $[\text{M}]^+$  calcd for  $\text{C}_{27}\text{H}_{16}\text{O}_6$ : 436.0947 found: 436.0945.

**2-(2-oxo-1-(4-oxo-4H-benzo[h]chromen-3-yl)-2-phenylethylidene)-1H-indene-1,3(2H)-dione 5ad.**



Following the **TP-C**, **5ad** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol),  $\text{Me}_2\text{PhP}$  (8.54  $\mu\text{L}$ , 0.2 equiv.), 4-fluorobenzoyl chloride **2d** (42.59  $\mu\text{L}$ , 1.2 equiv.), and  $\text{Et}_3\text{N}$  (54.36  $\mu\text{L}$ , 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 0.5 h. After completion of the reaction, the residue was purified by column chromatography ( $\text{SiO}_2$ , Hexanes:EtOAc = 70:30) to give **5ad** as a pale yellow solid (110.0 mg, 86%).  $R_f = 0.45$  (Hexanes:EtOAc = 7:3); mp.: 267.4-268.5 °C.

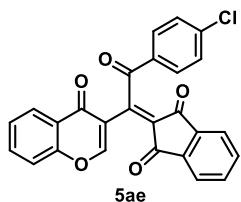
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 8.30 (s, 1H), 8.29 (dd,  $J = 8.0, 1.6$  Hz, 1H), 8.18-8.11 (m, 2H), 7.99-7.94 (m, 1H), 7.86-7.78 (m, 2H), 7.73 (td,  $J = 9.5, 6.9, 1.7$  Hz, 1H), 7.58 (t,  $J = 7.5$  Hz, 1H), 7.75-7.45 (m, 2H), 7.19-7.10 (m, 2H).

**$^{13}\text{C}\{\text{H}\}$ -NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 193.8, 187.8, 187.2, 173.3, 167.6, 167.6, 165.1, 155.9, 155.5, 145.9, 142.6, 140.7, 135.9 (d,  $J_{\text{C}-\text{F}} = 17.2$  Hz), 134.3, 131.8, 131.7, 131.6, 126.6, 126.1, 123.7, 123.6, 118.3, 118.3, 116.2 (d,  $J_{\text{C}-\text{F}} = 23.2$  Hz).

**$^{19}\text{F NMR}$**  (376 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: -102.8.

**HRMS** (EI) m/z:  $[\text{M}]^+$  calcd for  $\text{C}_{26}\text{H}_{13}\text{O}_5\text{F}$ : 424.0747 found: 424.0764.

**2-(2-(4-chlorophenyl)-2-oxo-1-(4-oxo-4H-chromen-3-yl)ethylidene)-1H-indene-1,3(2H)-dione 5ae.**



Following the **TP-C**, **5ae** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol),  $\text{Me}_2\text{PhP}$  (8.54  $\mu\text{L}$ , 0.2 equiv.), 4-

chlorobenzoyl chloride **2e** (41.82  $\mu$ L, 1.2 equiv.), and Et<sub>3</sub>N (54.36  $\mu$ L, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 2 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5ae** as a pale yellow solid (121.1 mg, 92%). R<sub>f</sub> = 0.53 (Hexanes:EtOAc = 7:3); mp.: 196.4–197.5 °C.

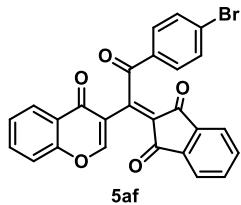
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.32 (s, 1H), 8.27 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.17–8.03 (m, 2H), 7.97–7.95 (m, 1H), 7.91–7.87 (m, 1H), 7.87–7.78 (m, 2H), 7.76–7.69 (m, 1H), 7.49 (t, *J* = 8.6 Hz, 2H), 7.46–7.41 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 194.3, 187.8, 187.2, 173.3, 155.9, 155.8, 145.9, 142.6, 140.7, 140.6, 135.9, 135.8, 134.4, 133.6, 131.6, 131.5, 130.3, 129.3, 128.8, 126.6, 126.1, 123.8, 123.7, 123.6, 118.3, 118.2.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>13</sub><sup>35</sup>ClO<sub>5</sub>: 440.0452 found: 440.0431.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>13</sub><sup>37</sup>ClO<sub>5</sub>: 442.0422 found: 442.0396.

**2-(2-(4-bromophenyl)-2-oxo-1-(4-oxo-4H-chromen-3-yl)ethylidene)-1H-indene-1,3(2H)-dione **5af**.**



Following the TP-C, **5af** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54  $\mu$ L, 0.2 equiv.), 4-bromobenzoyl chloride **2f** (49.09 mg, 1.2 equiv.), and Et<sub>3</sub>N (54.36  $\mu$ L, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 0.5 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5af** as a pale yellow solid (110.0 mg, 75%). R<sub>f</sub> = 0.50 (Hexanes:EtOAc = 65: 35); mp.: 236.5–237.8 °C.

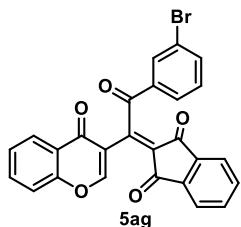
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.32 (s, 1H), 8.28 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 3H), 7.92–7.76 (m, 1H), 7.86–7.77 (m, 2H), 7.73 (dtd, *J* = 8.7, 6.7, 1.5 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.53–7.44 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 194.5, 187.8, 187.2, 173.3, 155.9, 155.9, 145.9, 142.7, 140.7, 135.9, 135.8, 134.4, 134.1, 132.3, 131.7, 130.4, 129.5, 126.6, 126.1, 123.8, 123.6, 123.7, 118.3, 118.2.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>13</sub><sup>79</sup>BrO<sub>5</sub>: 483.9946 found: 483.9971.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>13</sub><sup>81</sup>BrO<sub>5</sub>: 485.9926 found: 485.9979.

**2-(2-(3-bromophenyl)-2-oxo-1-(4-oxo-4H-chromen-3-yl)ethylidene)-1H-indene-1,3(2H)-dione 5ag.**



Following the **TP-C**, **5ag** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 μL, 0.2 equiv.), 3-bromobenzoyl chloride **2g** (47.53 μL, 1.2 equiv.), and Et<sub>3</sub>N (54.36 μL, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 0.5 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5ag** as a pale yellow solid (120.0 mg, 82%). R<sub>f</sub> = 0.48 (Hexanes:EtOAc = 7:3); mp.: 250.1-251.3 °C.

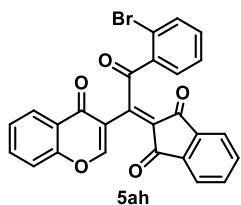
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.32 (s, 1H), 8.31-8.34 (m, 2H), 8.01-7.95 (m, 2H), 7.98-7.86 (m, 1H), 7.85-7.77 (m, 2H), 7.72 (dtd, J = 9.2, 7.7, 1.7 Hz, 1H), 7.78-7.66 (m, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.56-7.44 (m, 1H), 7.32 (t, J = 7.9 Hz, 1H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 194.2, 187.8, 187.1, 173.3, 156.2, 155.9, 145.9, 142.7, 140.6, 136.9, 136.8, 135.9, 135.8, 134.4, 131.7, 131.3, 130.4, 127.9, 126.6, 126.1, 123.8, 123.7, 123.2, 118.3, 118.1.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>13</sub><sup>79</sup>BrO<sub>5</sub>: 483.9946 found: 483.9931.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>13</sub><sup>81</sup>BrO<sub>5</sub>: 485.9926 found: 485.9912.

**2-(2-(2-bromophenyl)-2-oxo-1-(4-oxo-4H-chromen-3-yl)ethylidene)-1H-indene-1,3(2H)-dione 5ah.**



Following the **TP-C**, **5ah** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 μL, 0.2 equiv.), 2-bromobenzoyl chloride **2h** (59.49 μL, 1.2 equiv.), and Et<sub>3</sub>N (54.36 μL, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 2 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5ah** as a pale yellow solid (113.0 mg, 77%). R<sub>f</sub> = 0.38 (Hexanes:EtOAc = 7:3); mp.: 242.2-243.3 °C.

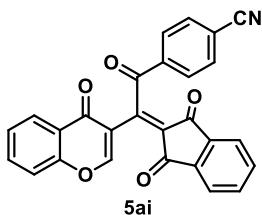
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.48 (s, 1H), 8.26 (dd, J = 8.0, 1.4 Hz, 1H), 8.08

(dd,  $J = 7.5, 1.9$  Hz, 1H), 7.99-7.92 (m, 1H), 7.91-7.86 (m, 1H), 7.85-7.78 (m, 2H), 7.75-7.70 (m, 1H), 7.53 (d,  $J = 8.3$  Hz, 1H), 7.47 (t,  $J = 7.9$  Hz, 1H), 7.42-7.31 (m, 2H).  $^{13}\text{C}\{\text{H}\}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 193.7, 188.0, 187.5, 173.6, 157.2, 155.9, 147.0, 142.5, 140.5, 135.8, 135.7, 135.4, 134.8, 134.4, 133.6, 133.3, 130.8, 127.4, 126.6, 126.1, 123.8, 123.7, 122.2, 118.4, 118.3.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{26}\text{H}_{13}{^{79}\text{BrO}_5}$ : 483.9946 found: 483.9935.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for  $\text{C}_{26}\text{H}_{13}{^{81}\text{BrO}_5}$ : 485.9926 found: 485.9921.

#### 4-(2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-2-(4-oxo-4H-chromen-3-yl)acetyl)benzonitrile **5ai**.



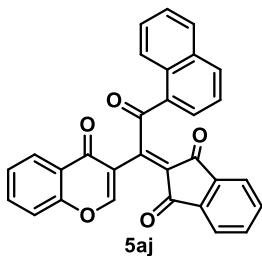
Following the **TP-C**, **5ai** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol),  $\text{Me}_2\text{PhP}$  (8.54  $\mu\text{L}$ , 0.2 equiv.), 4-cyanobenzoyl chloride **2i** (59.0 mg, 1.2 equiv.), and  $\text{Et}_3\text{N}$  (54.36  $\mu\text{L}$ , 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 2 h. After completion of the reaction, the residue was purified by column chromatography ( $\text{SiO}_2$ , Hexanes:EtOAc = 65:35) to give **5ai** as a yellow solid (84.0 mg, 65%).  $R_f = 0.50$  (Hexanes:EtOAc = 5:5); mp.: 265.1-266.1 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 8.42 (s, 1H), 8.27-8.16 (m, 3H), 7.99 (d,  $J = 7.1$  Hz, 1H), 7.90-7.80 (m, 3H), 7.79-7.71 (m, 3H), 7.54 (d,  $J = 8.5$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 1H).

$^{13}\text{C}\{\text{H}\}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 194.3, 187.9, 187.0, 173.9, 157.4, 155.9, 146.1, 142.6, 140.4, 138.6, 136.2, 136.0, 134.6, 132.6, 131.7, 129.1, 126.5, 126.3, 126.5, 126.3, 123.9, 123.7, 123.6, 118.3, 117.9, 116.7.

**HRMS** (MALDI) m/z: [M+H]<sup>+</sup> calcd for  $\text{C}_{27}\text{H}_{14}\text{NO}_5$ : 432.0872 found: 432.0867.

#### 2-(2-(naphthalen-1-yl)-2-oxo-1-(4-oxo-4H-chromen-3-yl)ethylidene)-1H-indene-1,3(2H)-dione **5aj**.



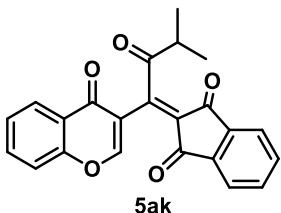
Following the **TP-C**, **5aj** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 $\mu$ L, 0.2 equiv.), 1-naphthoyl chloride **2j** (54.24  $\mu$ L, 1.2 equiv.), and Et<sub>3</sub>N (54.36  $\mu$ L, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 2 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 75:25) to give **5aj** as a pale yellow solid (117.0 mg, 85%). R<sub>f</sub> = 0.43 (Hexanes:EtOAc = 7:3); mp.: 190.3-191.5 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 9.43 (d, *J* = 6.8 Hz, 1H), 8.41 (s, 1H), 8.34 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.26 (d, *J* = 7.1 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 7.4 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.85-7.67 (m, 5H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.51-7.41 (m, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 197.1, 188.1, 187.7, 173.1, 156.0, 154.7, 146.9, 142.7, 140.8, 135.7, 135.6, 135.2, 134.2, 134.0, 133.7, 131.0, 130.9, 130.7, 129.2, 128.6, 126.8, 126.7, 126.2, 125.9, 124.7, 123.8, 123.7, 123.6, 119.2, 118.2.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>27</sub>H<sub>16</sub>O<sub>5</sub>: 456.0998 found: 456.0984.

### 2-(3-methyl-2-oxo-1-(4-oxo-4H-chromen-3-yl)butylidene)-1H-indene-1,3(2H)-dione **5ak**.



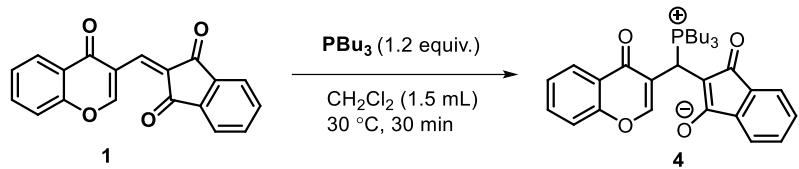
Following the **TP-C**, **5ak** was obtained from 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol), Me<sub>2</sub>PhP (8.54 $\mu$ L, 0.2 equiv.), isobutyryl chloride **2k** (37.7  $\mu$ L, 1.2 equiv.), and Et<sub>3</sub>N (54.36  $\mu$ L, 1.3 equiv.) in anhydrous THF (1.5 mL) at 30 °C for 0.5 h. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 70:30) to give **5ak** as a pale yellow solid (62.0 mg, 55%). R<sub>f</sub> = 0.48 (Hexanes:EtOAc = 7:3); mp.: 200.1-201.2 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.30 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.17 (s, 1H), 7.99-7.95 (m, 1H), 7.93-7.89 (m, 1H), 7.85-7.78 (m, 2H), 7.85-7.75 (m, 2H), 7.73 (td, *J* = 8.8, 7.4, 1.6 Hz, 1H), 7.53-7.45 (m, 2H), 3.13 (sep, *J* = 7.01 Hz, 1H), 1.26 (brs, 3H), 1.24 (brs, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 209.8, 188.5, 187.3, 173.1, 155.9, 154.4, 147.8, 142.5, 140.7, 135.9, 135.7, 134.2, 130.4, 126.7, 126.0, 123.7, 123.6, 123.5, 118.6, 118.2, 41.1, 17.6.

**HRMS** (EI) m/z: [M]<sup>+</sup> calcd for C<sub>23</sub>H<sub>16</sub>O<sub>5</sub>: 372.0998 found: 372.0981.

**1-oxo-2-((4-oxo-4H-chromen-3-yl)(tributylphosphonio)methyl)-1H-inden-3-olate 4**



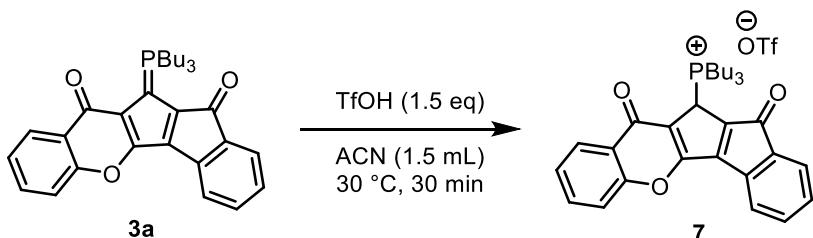
A 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **1a** (90.75 mg, 0.3 mmol),  $\text{PBu}_3$  ( $88.8\mu\text{L}$ , 1.2 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (15 mL). The reaction mixture was stirred for 30 minutes at 30 °C. After completion of the reaction, the residue was purified by column chromatography ( $\text{SiO}_2$ , DCM:MeOH = 90:10) to give **4** as a pale yellow solid (138.0 mg, 92%).  $R_f = 0.45$  (DCM:MeOH = 9.5:0.5); mp.: 227.1–228.4 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 8.86 (d,  $J = 3.8$  Hz, 1H), 8.21 (dtd,  $J = 8.6, 7.0, 1.6$  Hz, 1H), 7.47 (d,  $J = 8.4$  Hz, 1H), 7.43 (t,  $J = 7.4$  Hz, 1H), 7.40–7.36 (m, 2H), 7.35–7.23 (m, 2H), 5.35 (d,  $J = 18.5$  Hz, 1H), 2.38–2.13 (m, 6H), 1.66–1.34 (m, 12H), 0.87 (t,  $J = 7.3$  Hz, 9H).

$^{13}\text{C}\{\text{H}\}\text{-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 190.7, 190.6, 177.0, 159.2 (d,  ${}^2J_{\text{C-P}} = 6.2$  Hz), 156.2, 139.3, 133.9, 130.0, 125.7 (d,  ${}^2J_{\text{C-P}} = 29.7$  Hz), 123.1, 120.4, 118.3, 118.1, 96.5 (d,  ${}^3J_{\text{C-P}} = 3.3$  Hz), 27.6 (d,  ${}^1J_{\text{C-P}} = 64.7$  Hz), 25.2 (d,  ${}^2J_{\text{C-P}} = 46.9$  Hz), 24.8, 24.1, 23.9, 20.4 (d,  ${}^3J_{\text{C-P}} = 43.9$  Hz), 13.3.

$^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 36.9.

**HRMS (MALDI)** m/z: [M]<sup>+</sup> calcd for.  $\text{C}_{31}\text{H}_{37}\text{O}_4\text{P}$ : 504.2429 found: 504.2424.

**tributyl(10,12-dioxo-11,12-dihydro-10H-benzo[5,6]pentaleno[1,2-b]chromen-11-yl)phosphonium trifluoromethanesulfonate 7.**



A 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with 11-(tributyl- $\lambda^5$ -phosphorylidene)-10H-benzo[5,6]pentaleno[1,2-b]chromene-10,12(11H)-dione **3a** (90.75 mg, 0.15 mmol), Trifluoromethanesulfonic acid (1.2 equiv.) in acetonitrile (1.5 mL). The reaction mixture was stirred for 30 minutes at 30 °C and monitored by TLC. After completion of the reaction, the solvent was removed in *vacuo*.

and the crude compound was without purification to give **7** as a purple solid (85.0 mg, 90%).  $R_f = 0.35$  (Hexanes:EtOAc = 9:1); mp.: 170.9-171.8 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.61 (d,  $J = 8.1$  Hz, 1H), 7.86 (d,  $J = 7.6$  Hz, 1H), 7.69 (d,  $J = 8.3$  Hz, 1H), 7.65-7.43 (m, 4H), 7.22-7.09 (m, 1H), 2.87-2.54 (m, 6H), 1.71-1.35 (m, 12H), 0.94 (t,  $J = 6.8$  Hz, 9H).

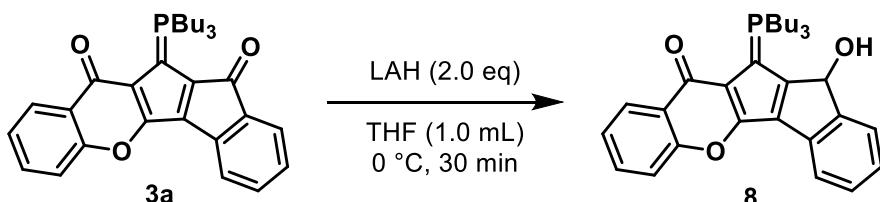
**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm: 189.0, 164.2, 155.8, 147.8 (d,  ${}^3J_{C-P} = 7.6$  Hz), 146.8 (d,  ${}^3J_{C-P} = 8.5$  Hz), 140.1, 138.4, 135.7, 135.3, 126.6, 125.9, 125.3, 125.1, 124.9, 120.9, 120.3 (q,  $J_{C-F} = 320.3$  Hz) 119.6 (d,  ${}^2J_{C-P} = 9.9$  Hz), 118.4 (d,  ${}^2J_{C-P} = 12.1$  Hz), 117.9, 114.9, 86.5 (d,  ${}^1J_{C-P} = 98.2$  Hz), 24.2 (d,  ${}^3J_{C-P} = 4.2$  Hz), 23.6 (d,  ${}^2J_{C-P} = 15.9$  Hz), 21.5, (d,  ${}^1J_{C-P} = 51.3$  Hz), 13.4.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ/ppm: 24.9.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ/ppm: -78.2.

**HRMS (MALDI)** m/z: [M+Na]<sup>+</sup> calcd for C<sub>32</sub>H<sub>36</sub>F<sub>3</sub>O<sub>6</sub>PSNa: 659.1820 found: 659.1814.

### 12-hydroxy-11-(tributyl-λ<sup>5</sup>-phosphanylidene)-11,12-dihydro-10H-benzo[5,6]pentaleno[1,2-b]chromen-10-one **8**.



A 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with LAH (11.0 mg, 2.0 equiv.) in anhydrous THF (0.5 mL) at 0 °C and 11-(tributyl-λ<sup>5</sup>-phosphanylidene)-10H-benzo[5,6]pentaleno[1,2-b]chromene-10,12(11H)-dione **3a** (73.0 mg, 0.15 mmol) dissolved in anhydrous THF (0.5 mL) adding to reaction mixture. The reaction mixture was stirred for 30 minutes at 0 °C and monitored by TLC. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 80:20) to give **8** as a yellow solid (59.0 mg, 80%).  $R_f = 0.38$  (Hexanes:EtOAc = 7:3); mp.: 172.9-173.8 °C.

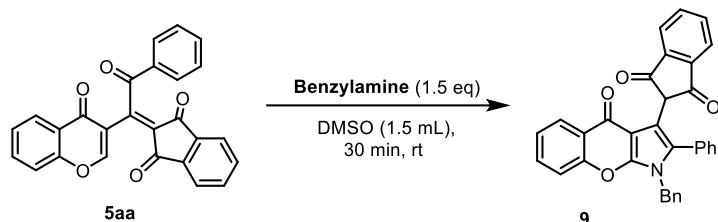
**<sup>1</sup>H NMR** (400 MHz, DMSO) δ/ppm: 8.18 (dd,  $J = 7.9, 1.2$  Hz, 1H), 7.65-7.59 (m, 1H), 7.58-7.54 (m, 1H), 7.43-7.36 (m, 2H), 7.31 (t,  $J = 7.2$  Hz, 1H), 7.23 (t,  $J = 7.4$  Hz, 1H), 6.98 (t,  $J = 7.4$  Hz, 1H), 5.60 (d,  $J = 8.8$  Hz, 1H), 5.38 (d,  $J = 8.8$  Hz, 1H), 2.68-2.50 (m, 6H), 1.54-1.26 (m, 12H), 0.84 (t,  $J = 6.9$  Hz, 1H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, DMSO) δ/ppm: 169.7, 154.8, 148.8, 148.6 (d,  ${}^3J_{C-P} = 9.6$  Hz), 144.8 (d,  ${}^2J_{C-P} = 11.5$  Hz), 137.8, 131.1, 128.1, 125.6, 124.7, 122.9, 122.6, 122.2, 117.4, 117.0, 116.4 (d,  ${}^2J_{C-P} = 13.4$  Hz), 115.7 (d,  ${}^3J_{C-P} = 12.5$  Hz), 74.8 (d,  ${}^1J_{C-P} = 107.4$  Hz), 70.6, 23.3 (d,  ${}^3J_{C-P} = 4.4$  Hz), 23.2 (d,  ${}^2J_{C-P} = 7.6$  Hz), 19.7 (d,  ${}^1J_{C-P} = 53.4$  Hz), 13.3.

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ/ppm: 22.1.

HRMS (MALDI) m/z: [M]<sup>+</sup> calcd for. C<sub>31</sub>H<sub>37</sub>O<sub>3</sub>P: 488.2480 found: 488.2475.

**2-(1-benzyl-4-oxo-2-phenyl-1,4-dihydrochromeno[2,3-b]pyrrol-3-yl)-1H-indene-1,3(2H)-dione 9.**



A 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with 2-((4-oxo-4H-chromen-3-yl)methylene)-1H-indene-1,3(2H)-dione **5aa** (61.0 mg, 0.15 mmol), and benzylamine (25.0 μL, 1.5 equiv.) in DMSO (0.75 mL). The reaction mixture was stirred for 30 minutes at 30 °C. After completion of the reaction, the residue was purified by column chromatography (SiO<sub>2</sub>, Hexanes:EtOAc = 65:35) to give **9** as an Off-white solid (56.0 mg, 75%). R<sub>f</sub> = 0.40 (Hexanes:EtOAc = 7:3); mp.: 211.0-212.2 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.11 (dd, J = 8.0, 1.5 Hz, 1H), 8.09-8.03 (m, 2H), 7.98-7.83 (m, 2H), 7.55 (td, J = 8.9, 6.8, 1.5 Hz, 1H), 7.52-7.46 (m, 2H), 7.45-7.37 (m, 4H), 7.34-7.24 (m, 4H), 7.07 (d, J = 6.8 Hz, 1H), 5.26 (s, 2H), 4.28 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>) δ/ppm: 198.1, 172.9, 154.2, 149.8, 142.3, 136.1, 135.2, 133.5, 132.4, 131.3, 129.2, 128.9, 128.8, 128.6, 127.9, 126.8, 126.7, 124.2, 123.3, 123.2, 117.2, 107.1, 104.3, 53.8, 46.8.

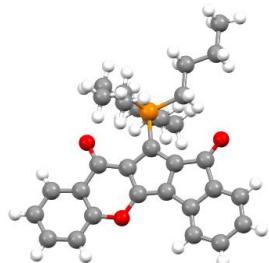
HRMS (EI) m/z: [M]<sup>+</sup> calcd for. C<sub>33</sub>H<sub>21</sub>NO<sub>4</sub>: 495.1471 found: 495.1457.

## References

1. D. Kumbhar, R. Patil, D. Patil, A. Patravale, D. Chandam, S. Jadhav, M. Deshmukh, *Synth. Commun.*, 2016, **46**, 85-92.
2. L. Pellegatti, S. L. Buchwald, *Org. Process Res. Dev.*, 2012, **16**, 1442-1448.
3. T. Lepitre, C. Denhez, M. Sanselme, M. Othman, A. M. Lawson, A Daich, *J. Org. Chem.*, 2016, **18**, 8837-8849.

## VII. X-ray crystallographic data for selected compounds

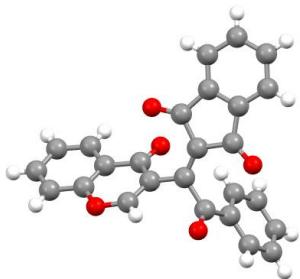
a) Crystal Data and Structure Refinement for compound **3a** (CCDC no. 2360174):



The purified compound **3a** was dissolved in a minimal amount of CH<sub>2</sub>Cl<sub>2</sub> in a glass vial. Hexanes were then added until the solution became turbid. The solution was allowed to slowly evaporate. After a few days, a dark red color crystals were obtained.

Empirical formula	C <sub>31</sub> H <sub>35</sub> O <sub>3</sub> P	
Formula weight	486.56	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.4838(16) Å	α= 90°.
	b = 21.180(2) Å	β= 96.690(4)°.
	c = 10.3247(11) Å	γ = 90°.
Volume	2711.4(5) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.192 Mg/m <sup>3</sup>	
Absorption coefficient	0.131 mm <sup>-1</sup>	
F(000)	1040	
Crystal size	0.24 x 0.21 x 0.02 mm <sup>3</sup>	
Theta range for data collection	2.53 to 25.06°.	
Index ranges	-14<=h<=14, -25<=k<=25, -12<=l<=12	
Reflections collected	25869	
Independent reflections	4800 [R(int) = 0.0956]	
Completeness to theta = 25.06°	99.8 % Absorption correction multi-scan	
Max. and min. transmission	0.9974 and 0.9693	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4800 / 0 / 319	
Goodness-of-fit on F <sup>2</sup>	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0534, wR2 = 0.1240	
R indices (all data)	R1 = 0.0872, wR2 = 0.1428	
Largest diff. peak and hole	0.214 and -0.345 e.Å <sup>-3</sup>	

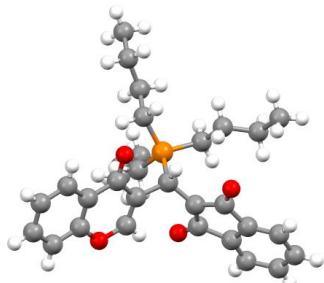
b) Crystal Data and Structure Refinement for compound **5aa** (CCDC no. 2360188):



The purified compound **5aa** was dissolved in a minimal amount of CH<sub>2</sub>Cl<sub>2</sub> in a glass vial. Hexanes were then added until the solution became turbid. The solution was allowed to slowly evaporate. After a few days, a pale yellow color crystals were obtained.

Empirical formula	C <sub>26</sub> H <sub>14</sub> O <sub>5</sub>	
Formula weight	406.37	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 19.4485(7) Å	α= 90°.
	b = 6.3637(2) Å	β= 105.2800(10)°.
	c = 15.7718(5) Å	γ = 90°.
Volume	1882.98(11) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.433 Mg/m <sup>3</sup>	
Absorption coefficient	0.100 mm <sup>-1</sup>	
F(000)	840	
Crystal size	0.41 x 0.20 x 0.04 mm <sup>3</sup>	
Theta range for data collection	2.68 to 25.10°.	
Index ranges	-23<=h<=23, -7<=k<=7, -18<=l<=18	
Reflections collected	19261	
Independent reflections	3344 [R(int) = 0.0838]	
Completeness to theta = 25.10°	99.3 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9960 and 0.9602	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	3344 / 0 / 280	
Goodness-of-fit on F <sup>2</sup>	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.1107	
R indices (all data)	R1 = 0.0584, wR2 = 0.1239	
Largest diff. peak and hole	0.219 and -0.184 e.Å <sup>-3</sup>	

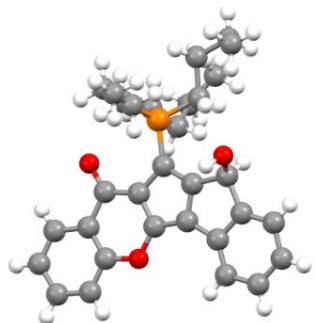
c) Crystal Data and Structure Refinement for compound **4** (CCDC no. 2360233):



The purified compound **4** was dissolved in a minimal amount of CH<sub>2</sub>Cl<sub>2</sub> in a glass vial. Hexanes were then added until the solution became turbid. The solution was allowed to slowly evaporate. After a few days, a pale yellow color crystals were obtained.

Empirical formula	C <sub>31</sub> H <sub>36</sub> O <sub>4</sub> P	
Formula weight	503.57	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.6734(4) Å	α= 90°.
	b = 14.6130(6) Å	β= 101.356(2)°.
	c = 19.9002(9) Å	γ = 90°.
Volume	2758.0(2) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.213 Mg/m <sup>3</sup>	
Absorption coefficient	0.133 mm <sup>-1</sup>	
F(000)	1076	
Crystal size	0.13 x 0.10 x 0.03 mm <sup>3</sup>	
Theta range for data collection	2.20 to 25.38°.	
Index ranges	-11≤h≤11, -17≤k≤17, -23≤l≤23	
Reflections collected	31956	
Independent reflections	5064 [R(int) = 0.0799]	
Completeness to theta = 25.38°	99.8 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9960 and 0.9829	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	5064 / 0 / 327	
Goodness-of-fit on F <sup>2</sup>	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0684, wR2 = 0.1967	
R indices (all data)	R1 = 0.1036, wR2 = 0.2344	
Largest diff. peak and hole	1.277 and -0.440 e.Å <sup>-3</sup>	

d) Crystal Data and Structure Refinement for compound **8** (CCDC no. 2363295):

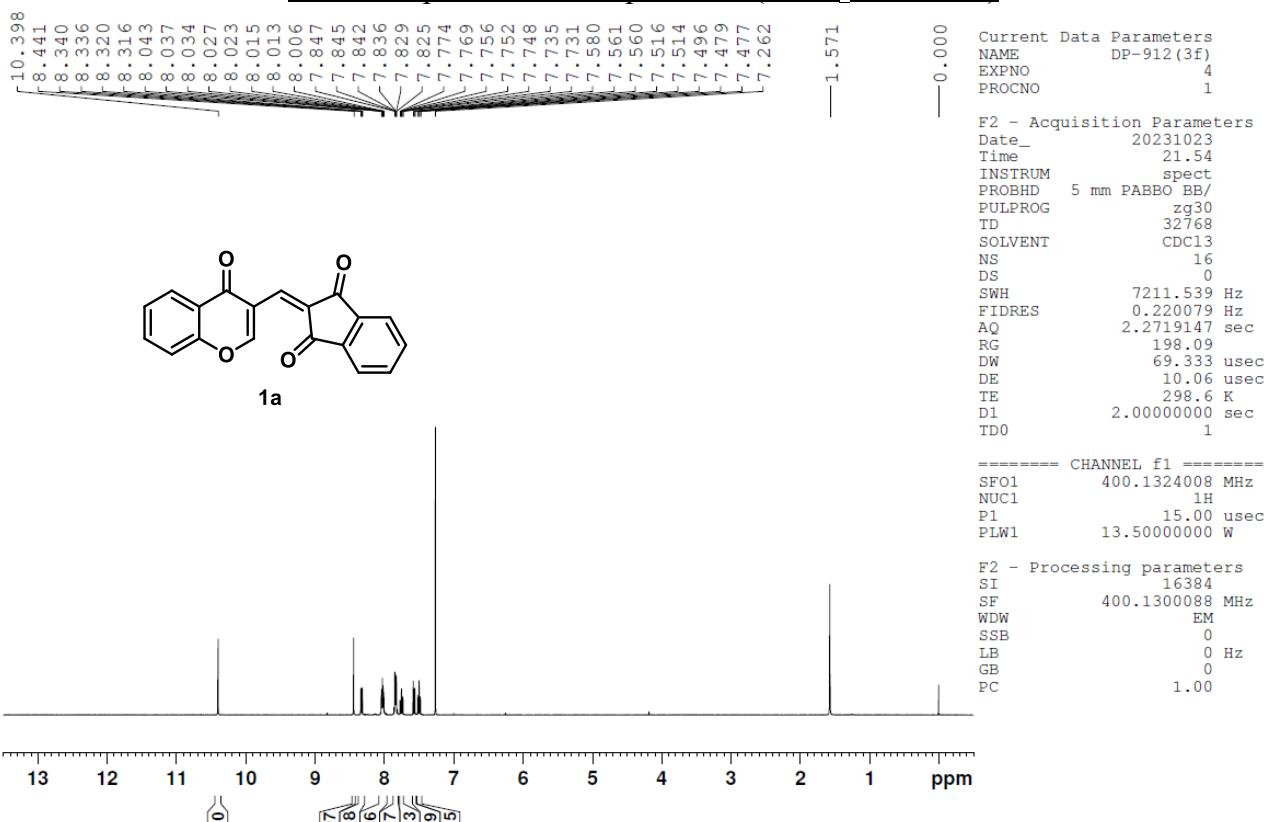


The purified compound **4** was dissolved in a minimal amount of CH<sub>2</sub>Cl<sub>2</sub> in a glass vial. Hexanes were then added until the solution became turbid. The solution was allowed to slowly evaporate. After a few days, a pale yellow color crystals were obtained.

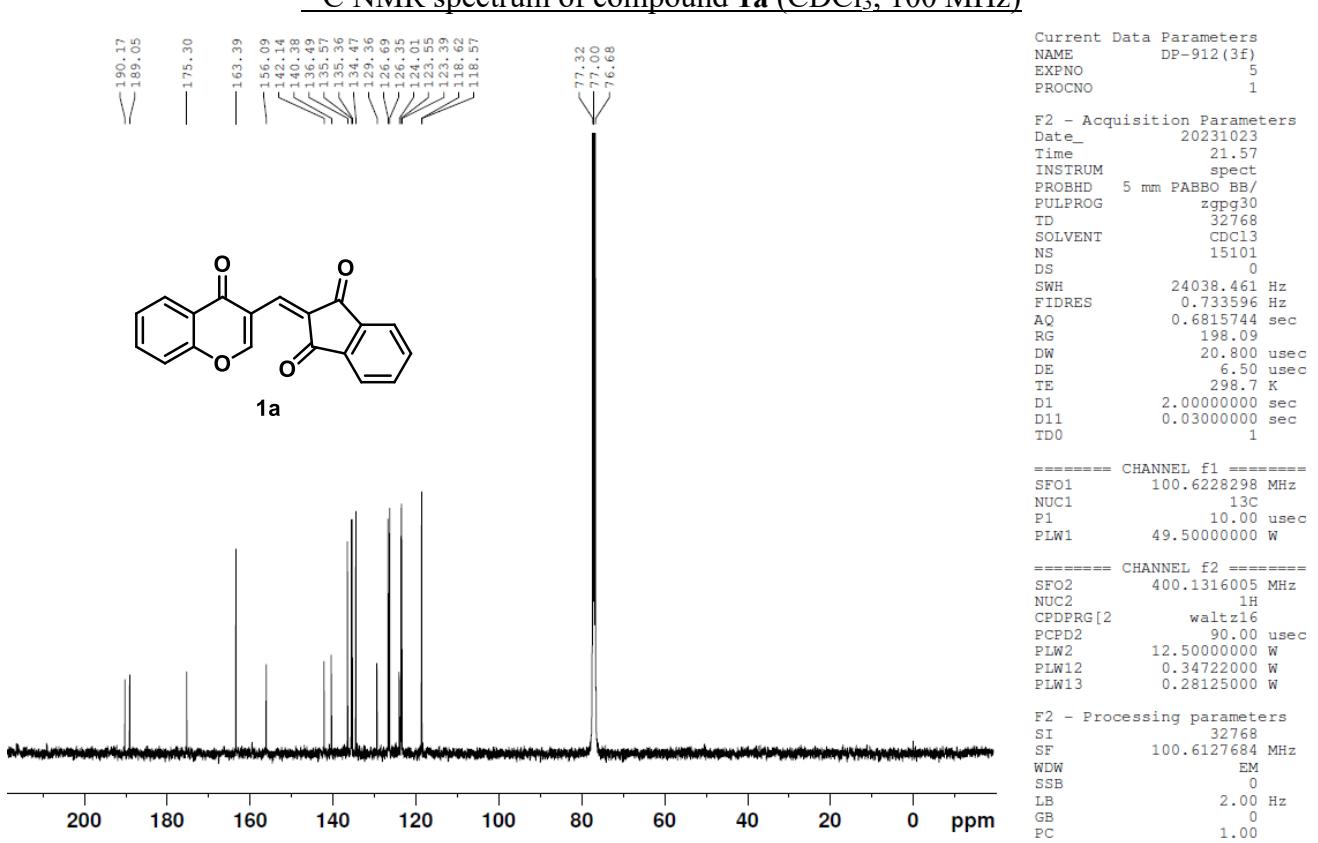
Empirical formula	C <sub>31</sub> H <sub>37</sub> O <sub>3</sub> P		
Formula weight	488.58		
Temperature	200(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P 21/n		
Unit cell dimensions	a = 11.3575(5) Å	α= 90°.	
	b = 11.1326(5) Å	β= 97.976(2)°.	
	c = 21.2159(11) Å	γ = 90°.	
Volume	2656.6(2) Å <sup>3</sup>		
Z	4		
Density (calculated)	1.222 Mg/m <sup>3</sup>		
Absorption coefficient	0.134 mm <sup>-1</sup>		
F(000)	1048		
Crystal size	0.22 x 0.09 x 0.03 mm <sup>3</sup>		
Theta range for data collection	2.07 to 25.05°.		
Index ranges	-13<=h<=13, -13<=k<=13, -25<=l<=23		
Reflections collected	24725		
Independent reflections	4697 [R(int) = 0.0721]		
Completeness to theta = 25.05°	99.9 %		
Absorption correction	None		
Max. and min. transmission	0.9960 and 0.9712		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	4697 / 0 / 319		
Goodness-of-fit on F <sup>2</sup>	1.029		
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1230		
R indices (all data)	R1 = 0.0590, wR2 = 0.1386		
Largest diff. peak and hole	0.199 and -0.331 e.Å <sup>-3</sup>		

### VIII. $^1\text{H}$ , $^{13}\text{C}$ NMR, $^{19}\text{F}$ NMR and $^{31}\text{P}$ NMR spectra for all compounds

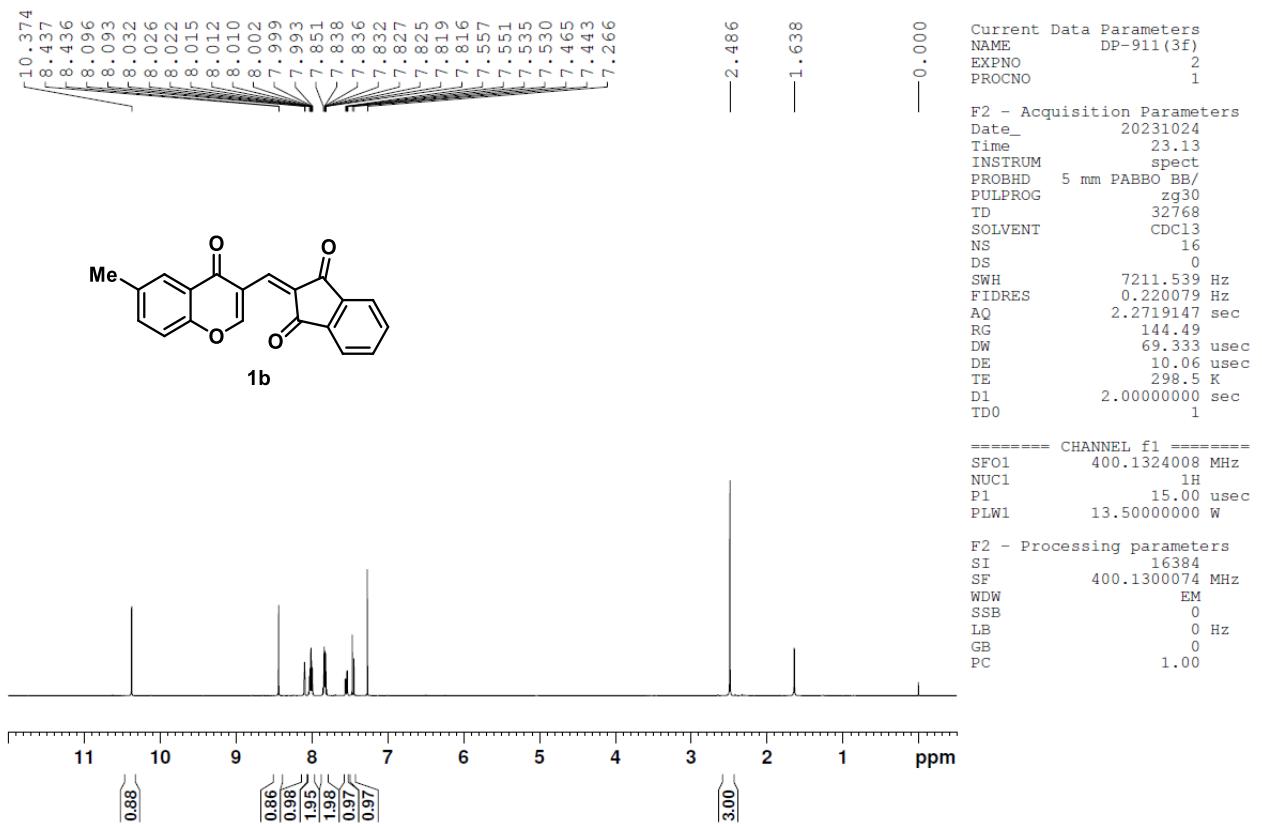
$^1\text{H}$  NMR spectrum of compound **1a** ( $\text{CDCl}_3$ , 400 MHz)



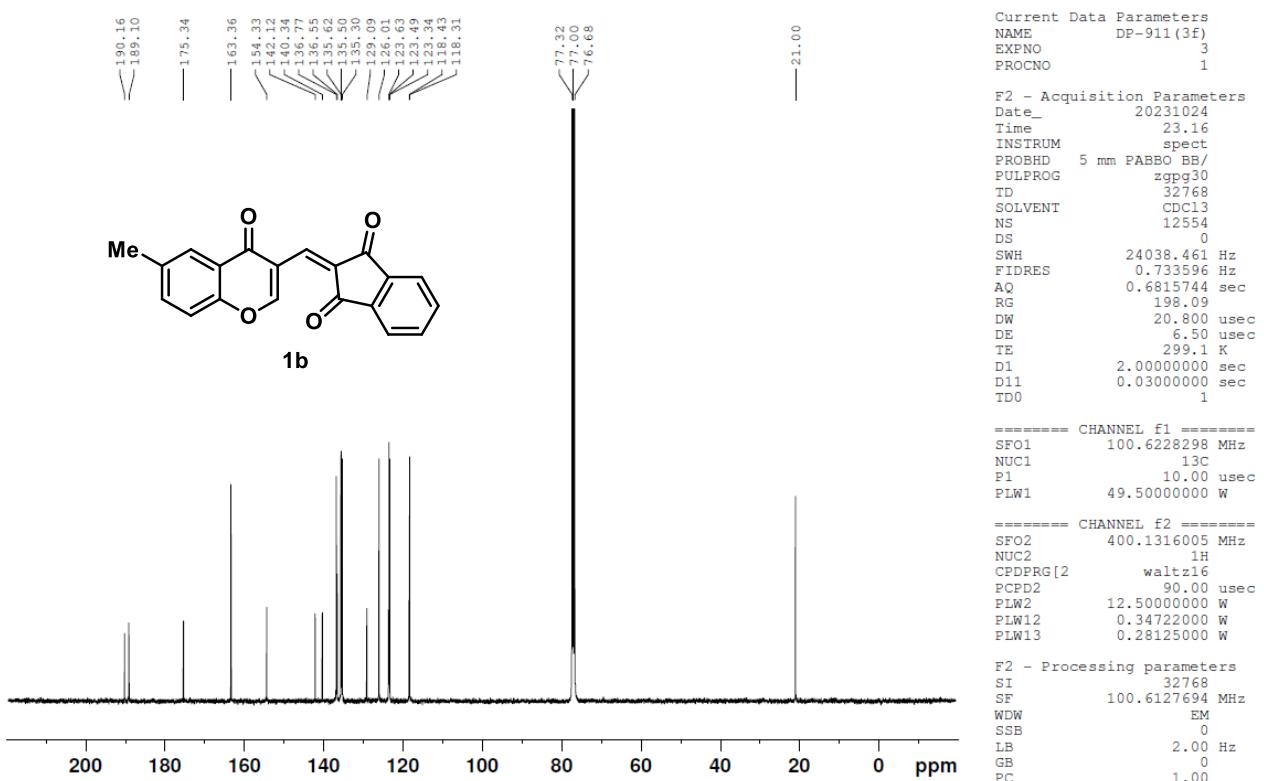
$^{13}\text{C}$  NMR spectrum of compound **1a** ( $\text{CDCl}_3$ , 100 MHz)



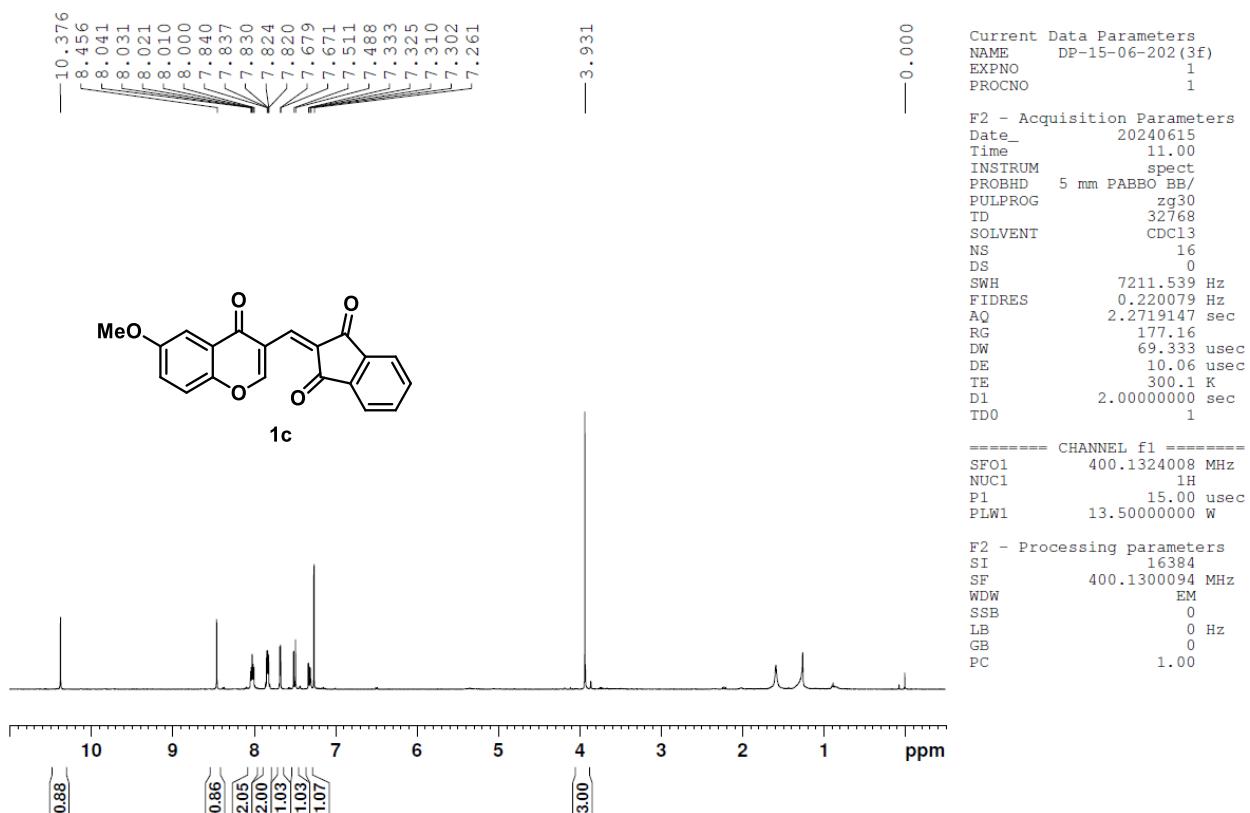
<sup>1</sup>H NMR spectrum of compound **1b** (CDCl<sub>3</sub>, 400 MHz)



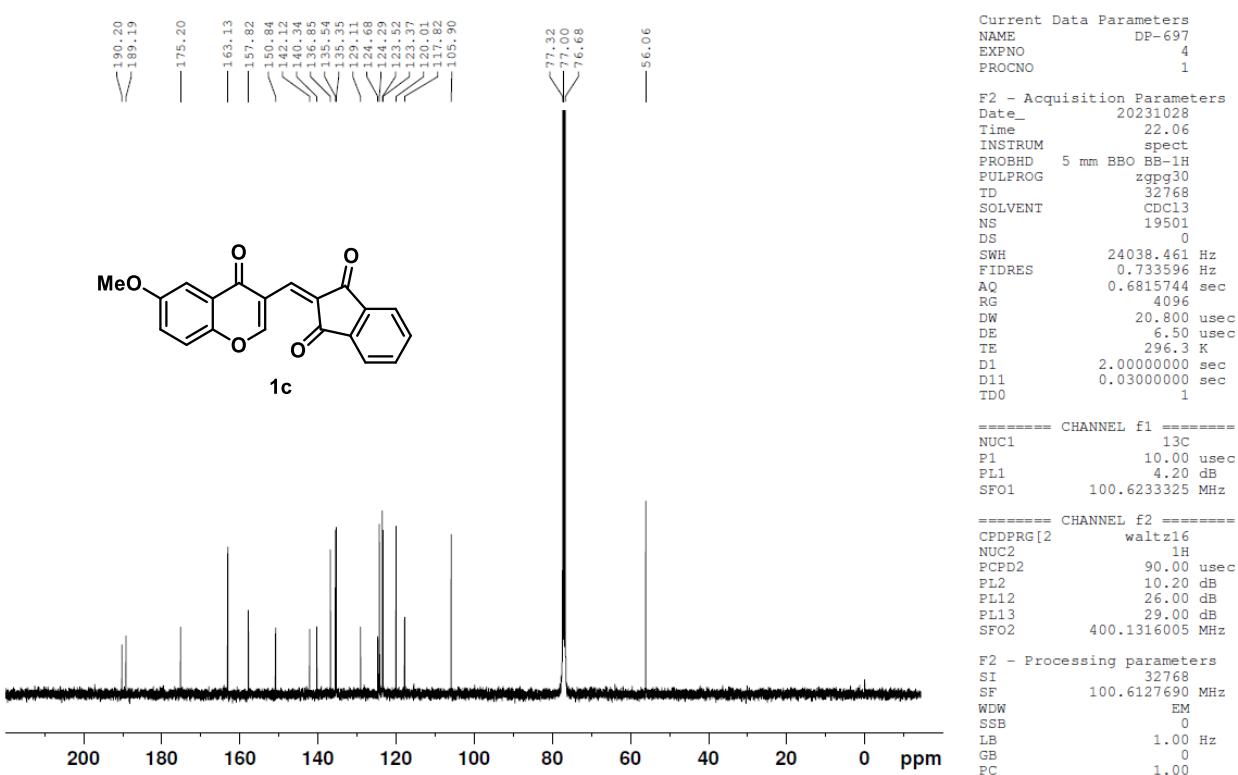
<sup>13</sup>C NMR spectrum of compound **1b** (CDCl<sub>3</sub>, 100 MHz)



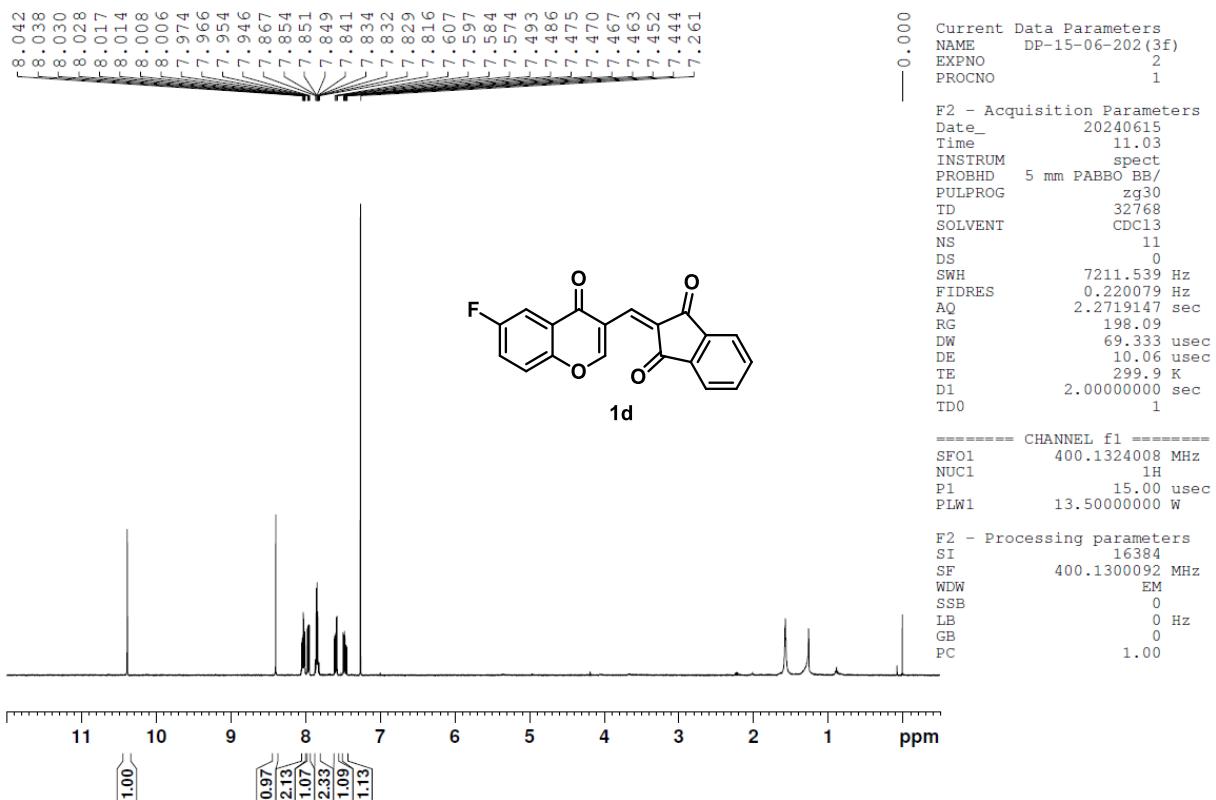
<sup>1</sup>H NMR spectrum of compound **1c** (CDCl<sub>3</sub>, 400 MHz)



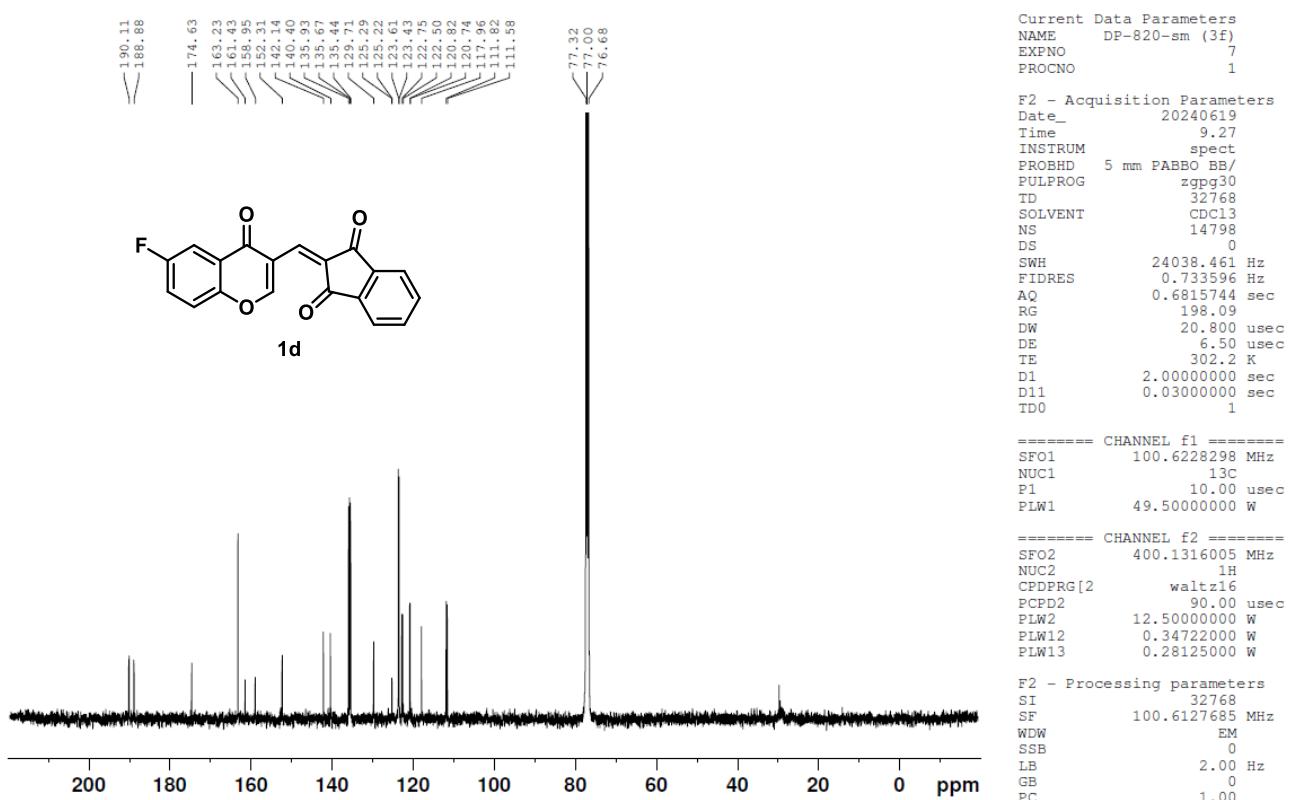
<sup>13</sup>C NMR spectrum of compound **1c** (CDCl<sub>3</sub>, 100 MHz)



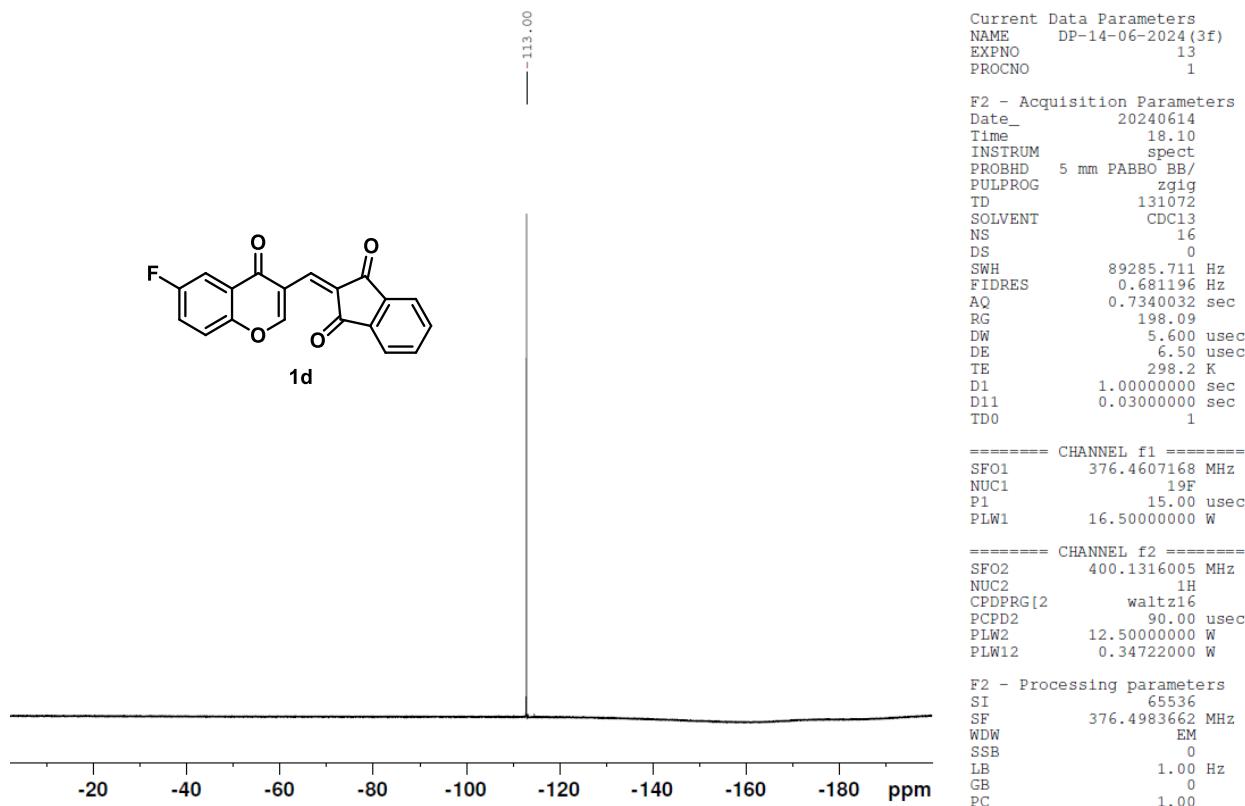
<sup>1</sup>H NMR spectrum of compound **1d** (CDCl<sub>3</sub>, 400 MHz)



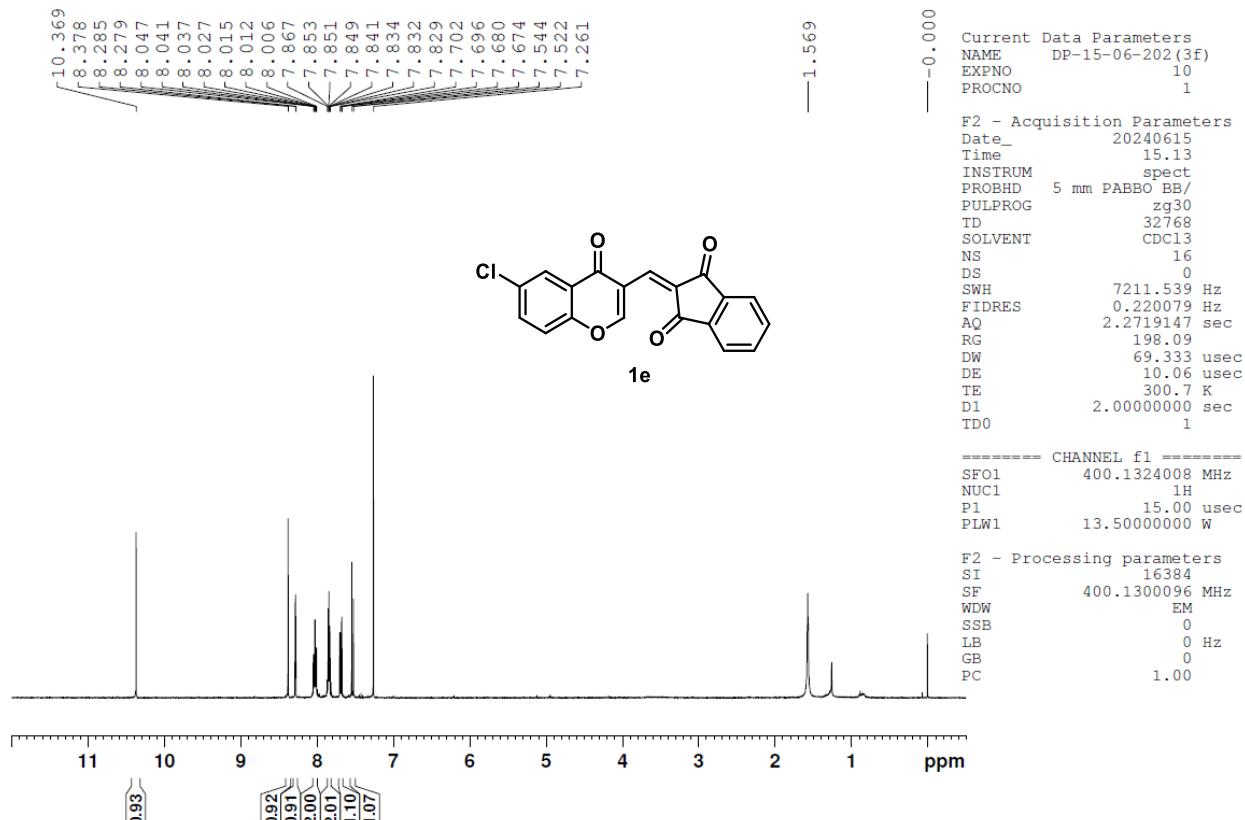
<sup>13</sup>C NMR spectrum of compound **1d** (CDCl<sub>3</sub>, 100 MHz)



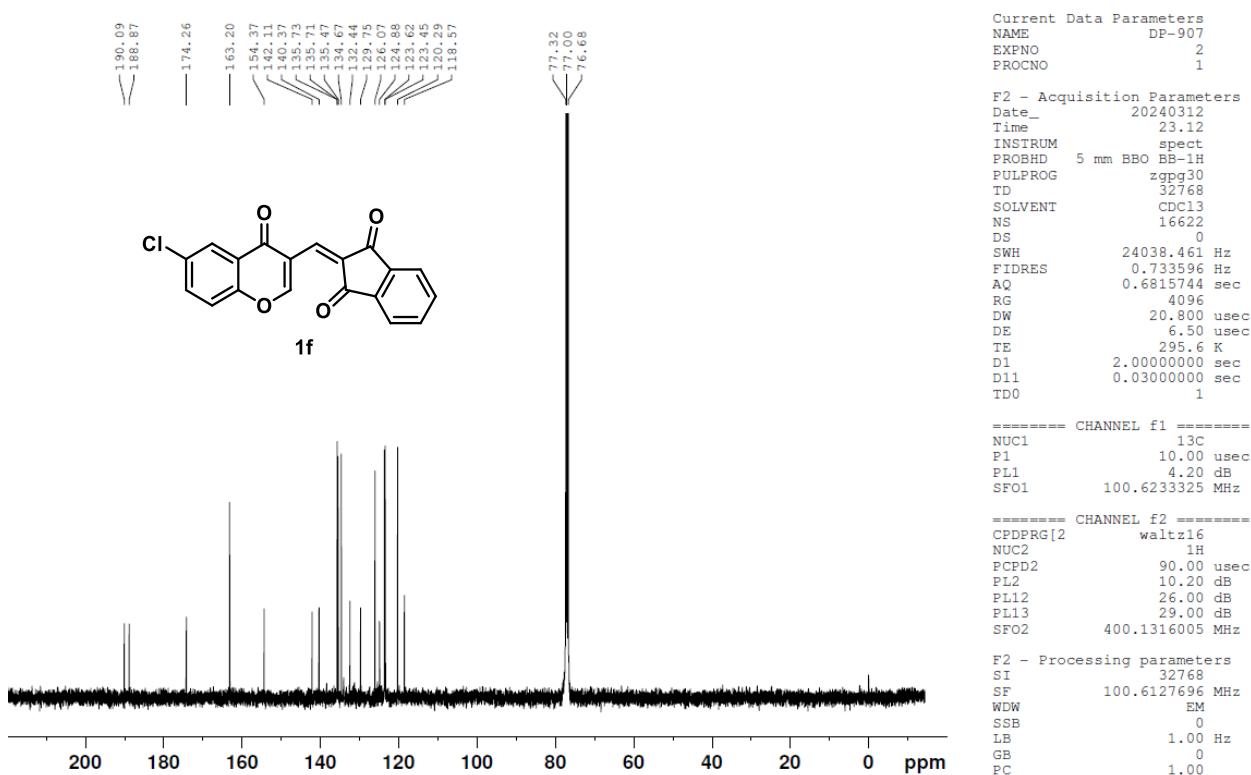
<sup>19</sup>F NMR spectrum of compound **1d** (CDCl<sub>3</sub>, 376 MHz)



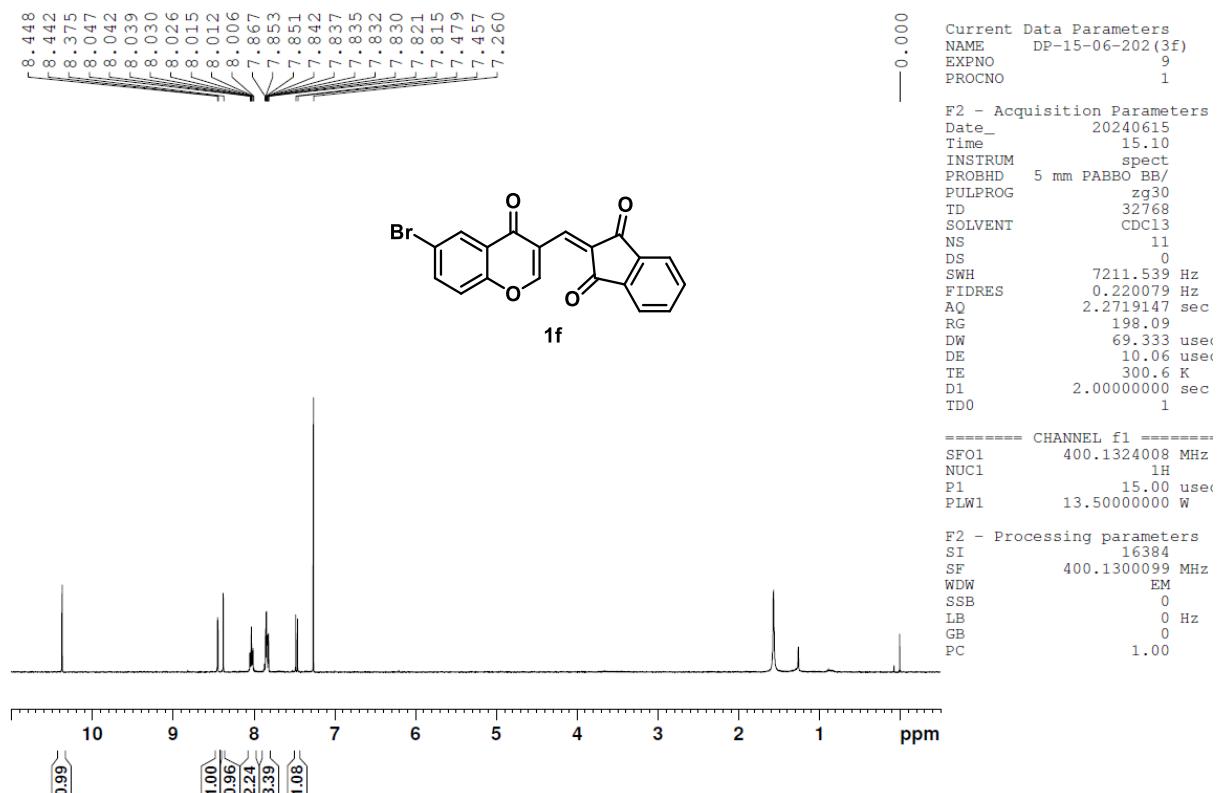
<sup>1</sup>H NMR spectrum of compound **1e** (CDCl<sub>3</sub>, 400 MHz)



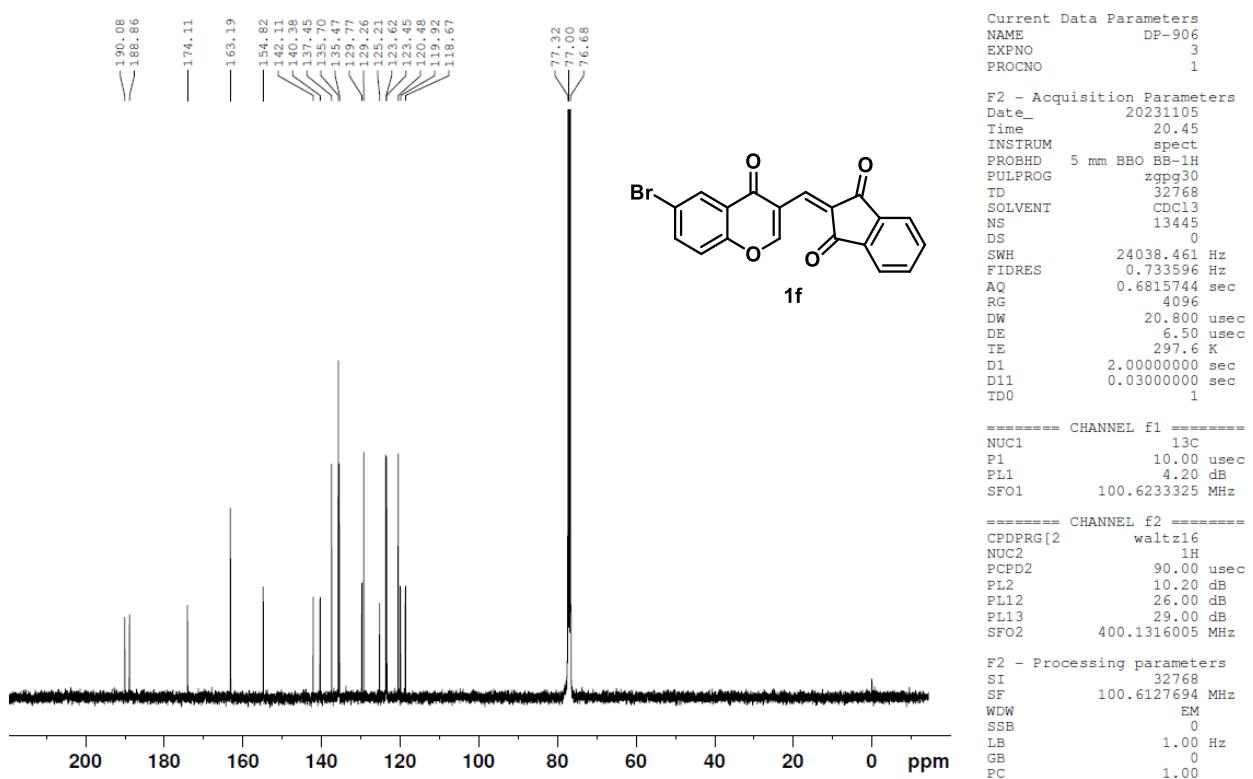
<sup>13</sup>C NMR spectrum of compound **1e** (CDCl<sub>3</sub>, 100 MHz)



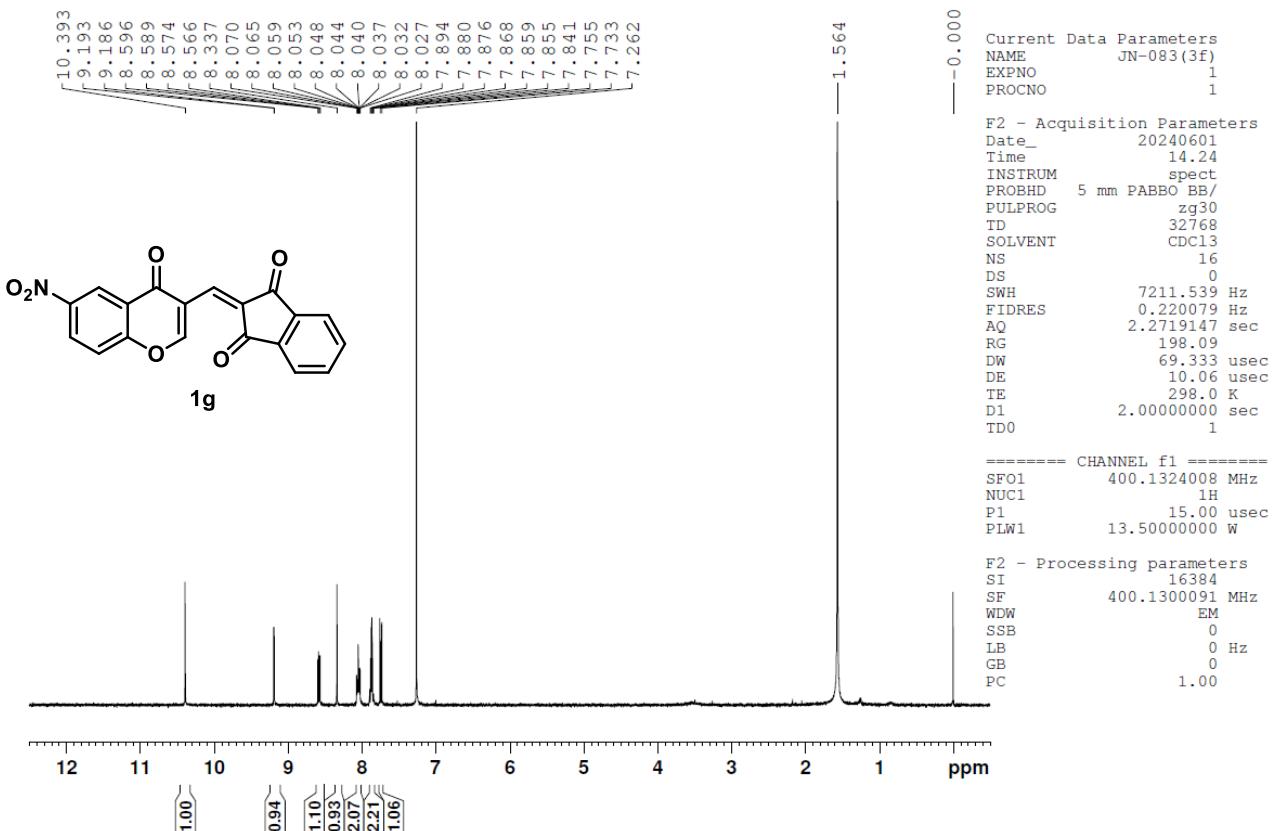
<sup>1</sup>H NMR spectrum of compound **1f** (CDCl<sub>3</sub>, 400 MHz)



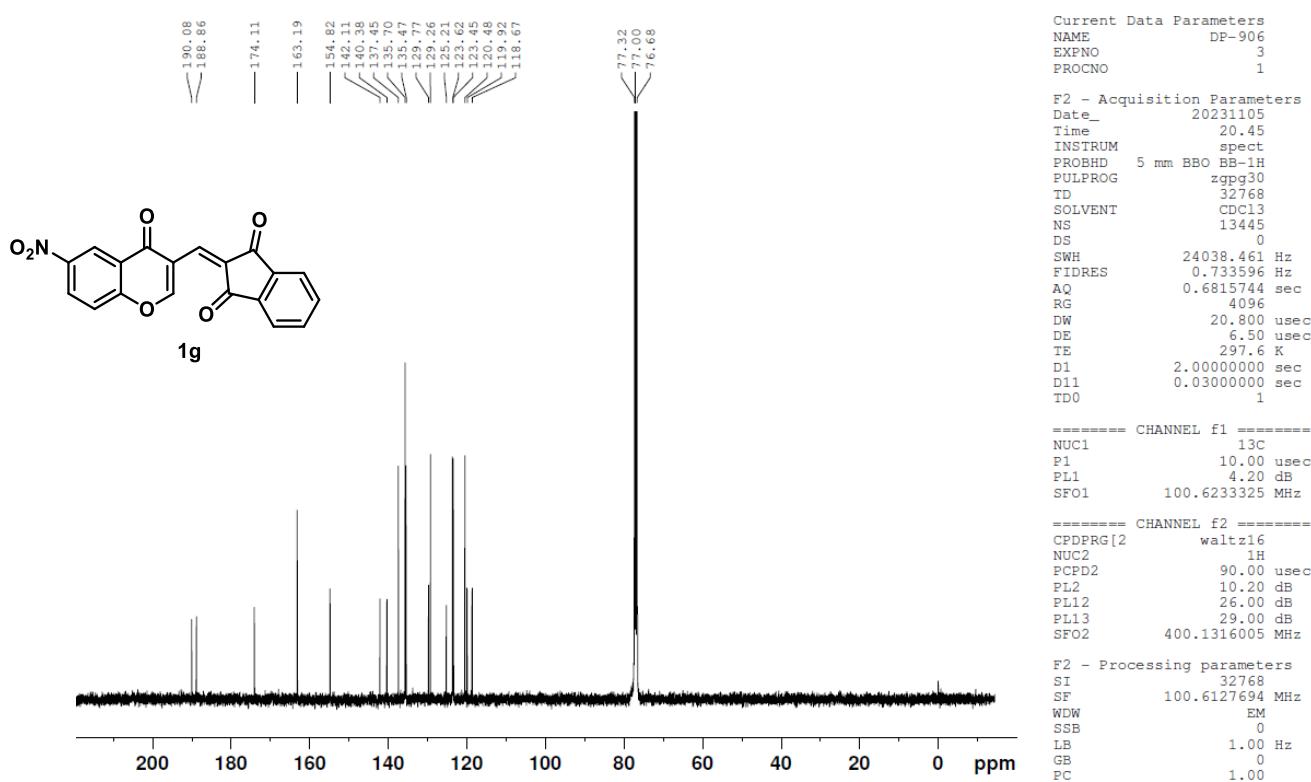
<sup>13</sup>C NMR spectrum of compound **1f** (CDCl<sub>3</sub>, 100 MHz)



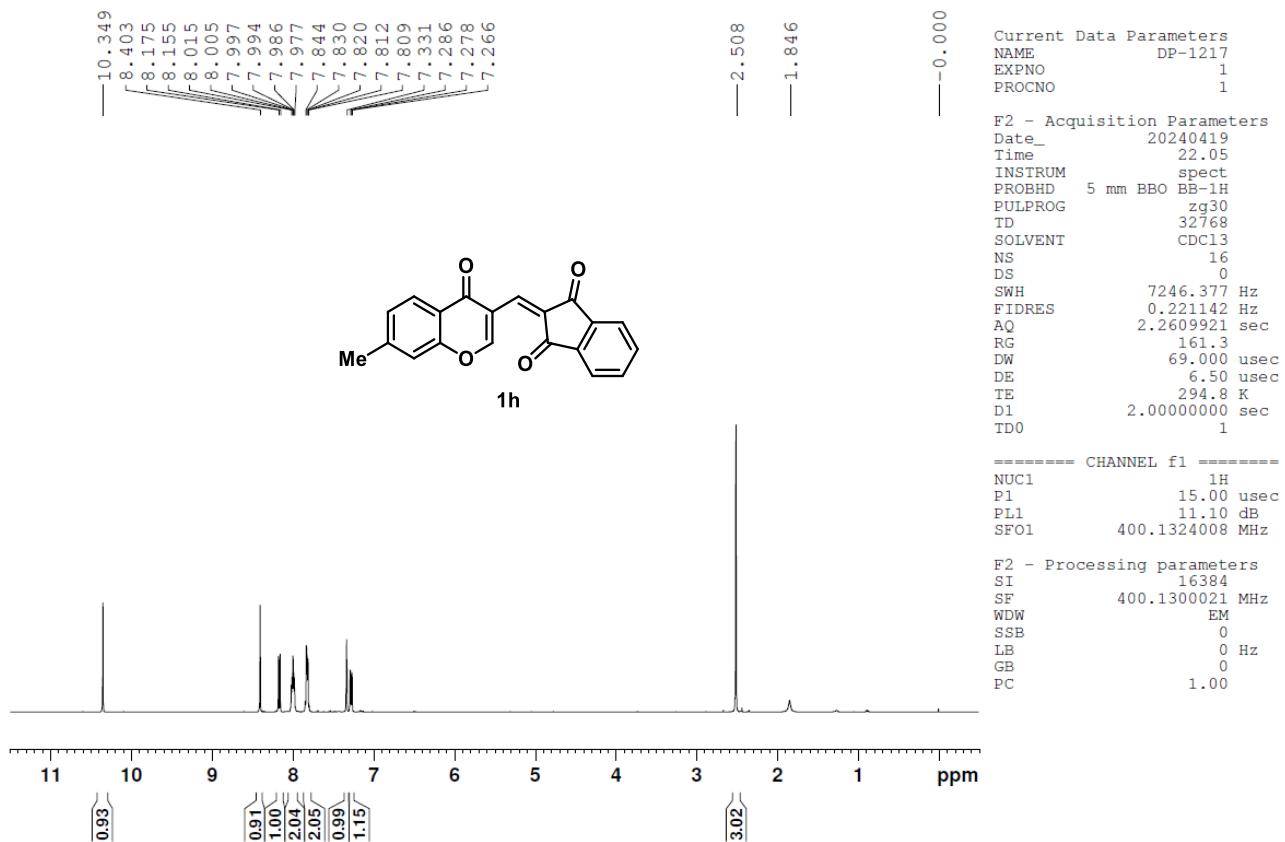
<sup>1</sup>H NMR spectrum of compound **1g** (CDCl<sub>3</sub>, 400 MHz)



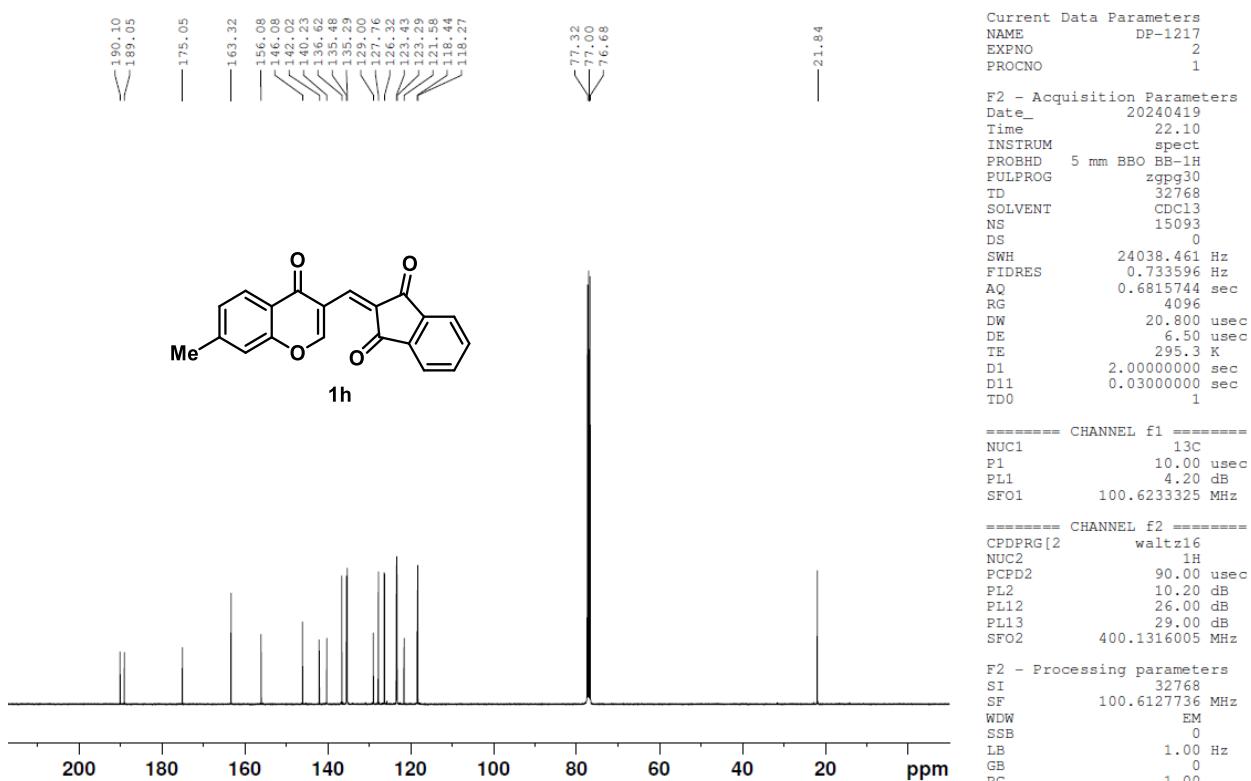
<sup>13</sup>C NMR spectrum of compound 1g (CDCl<sub>3</sub>, 100 MHz)



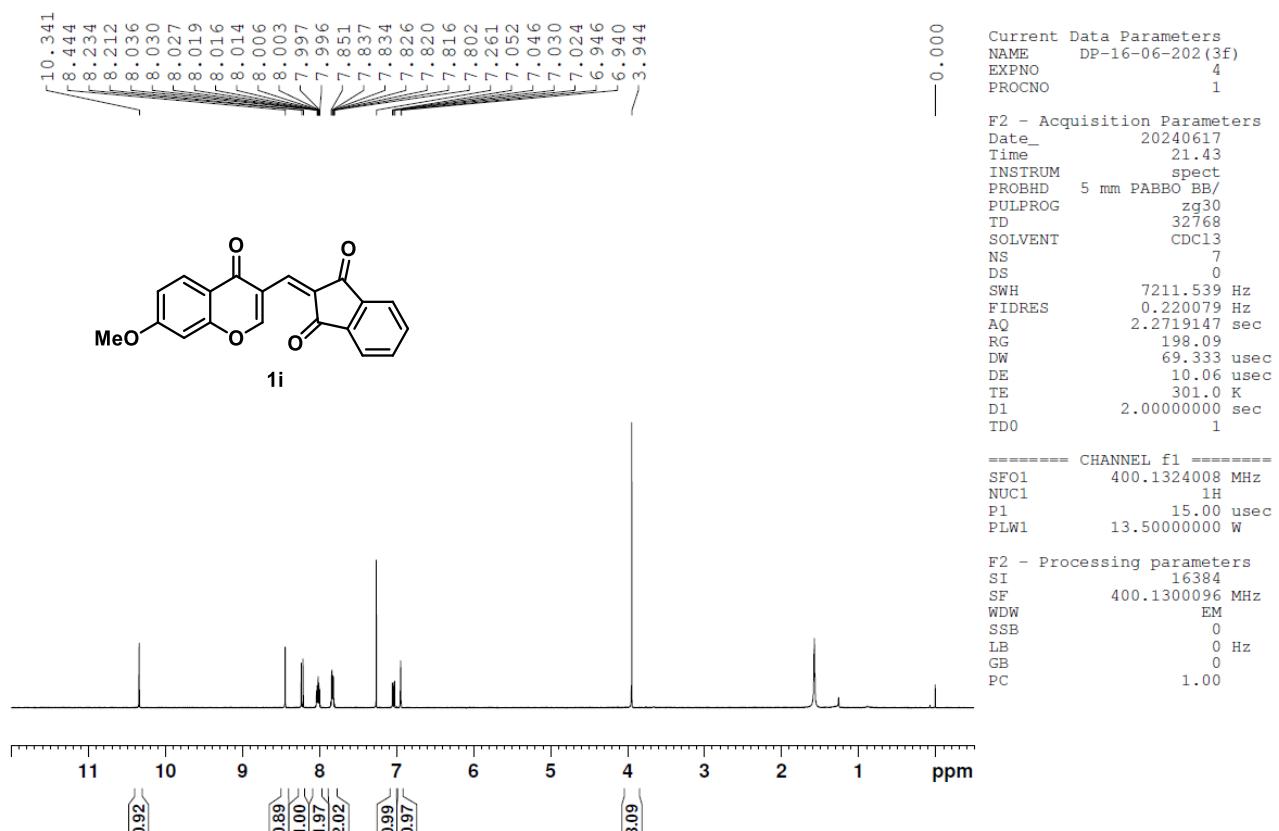
<sup>1</sup>H NMR spectrum of compound 1h (CDCl<sub>3</sub>, 400 MHz)



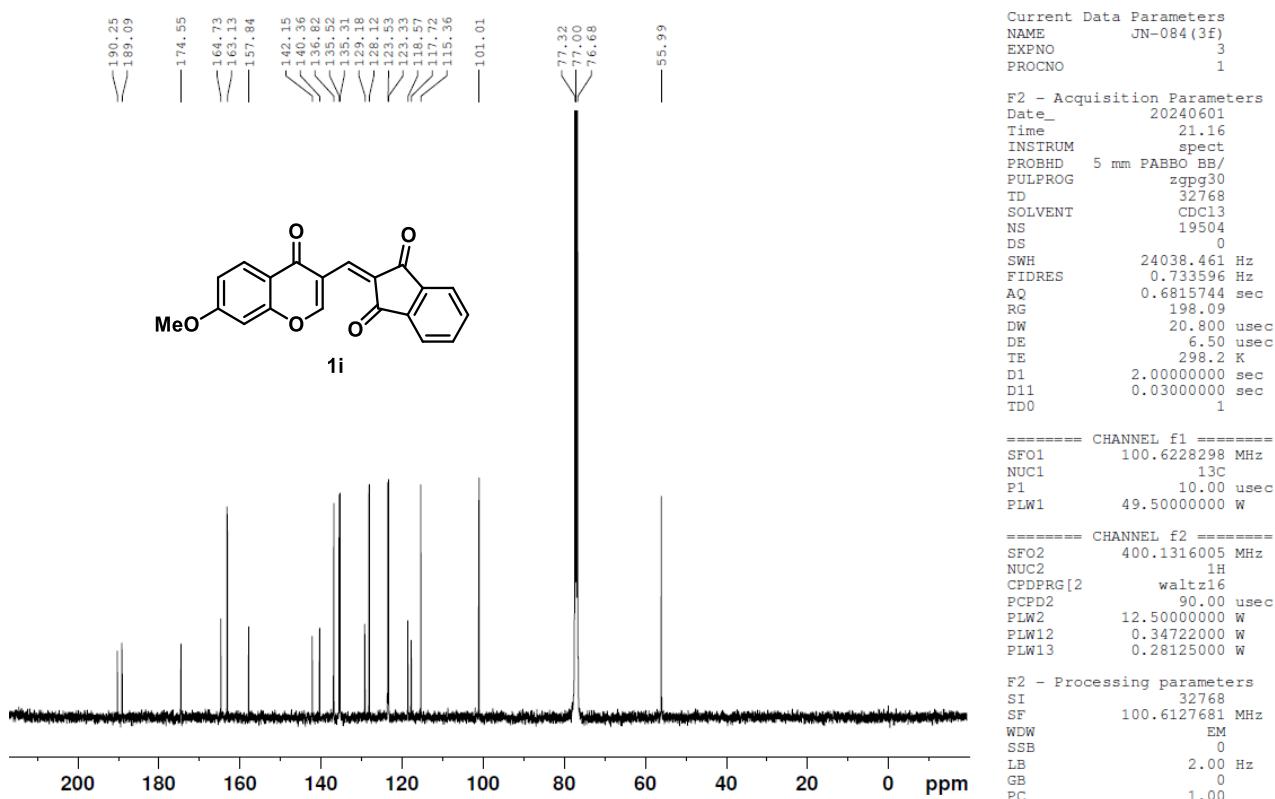
**<sup>13</sup>C NMR spectrum of compound **1h** (CDCl<sub>3</sub>, 100 MHz)**



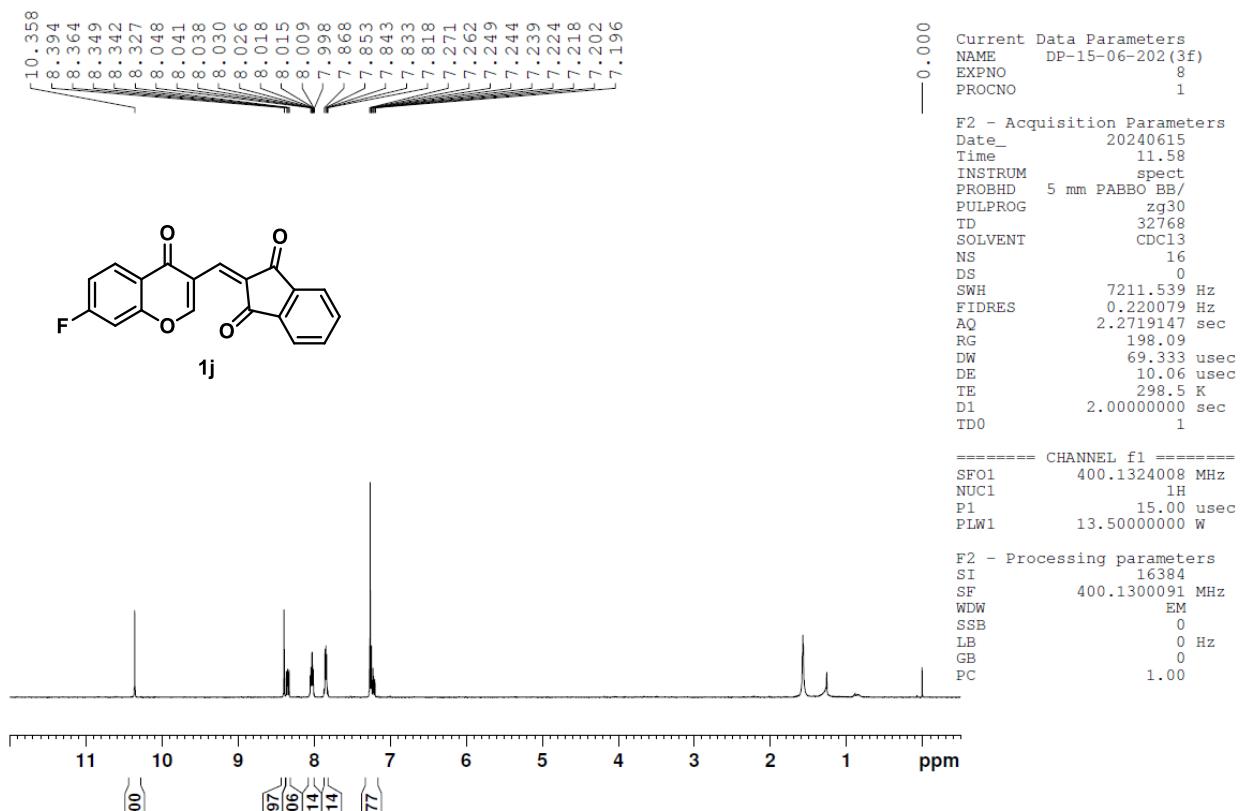
**<sup>1</sup>H NMR spectrum of compound **1i** (CDCl<sub>3</sub>, 400 MHz)**



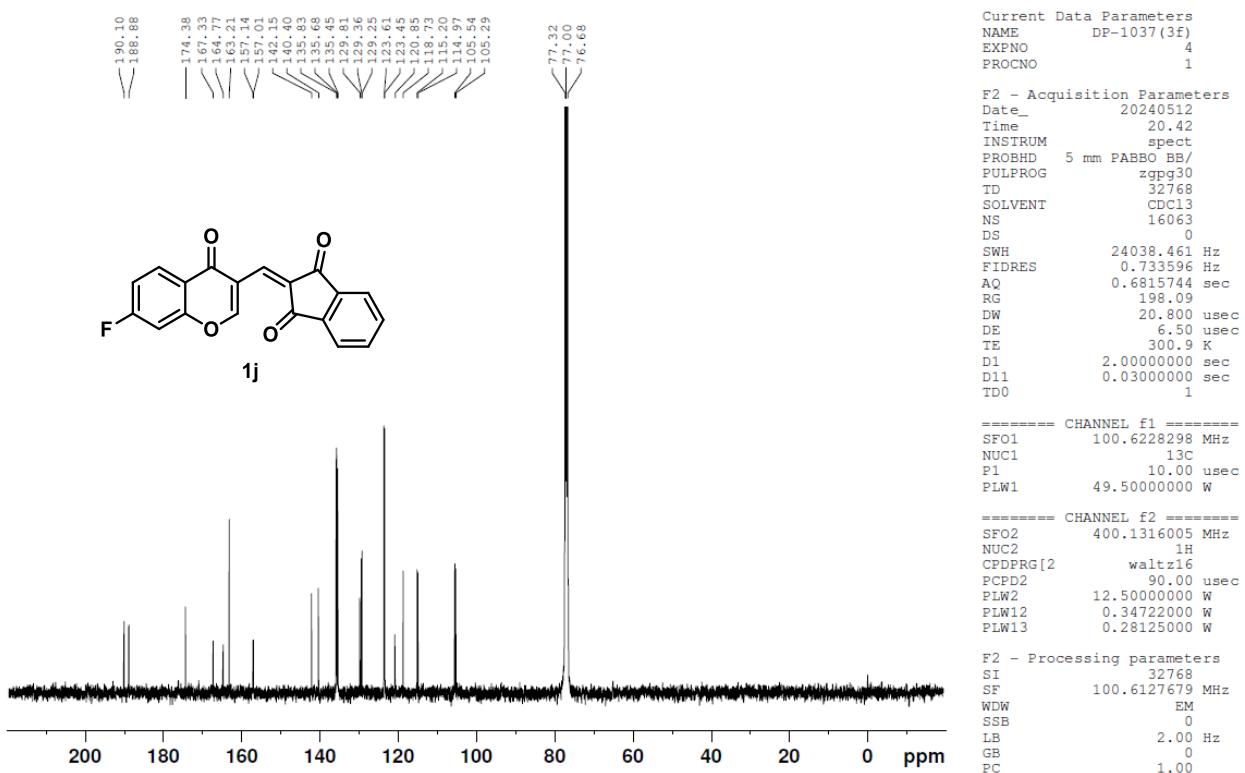
<sup>13</sup>C NMR spectrum of compound **1i** (CDCl<sub>3</sub>, 100 MHz)



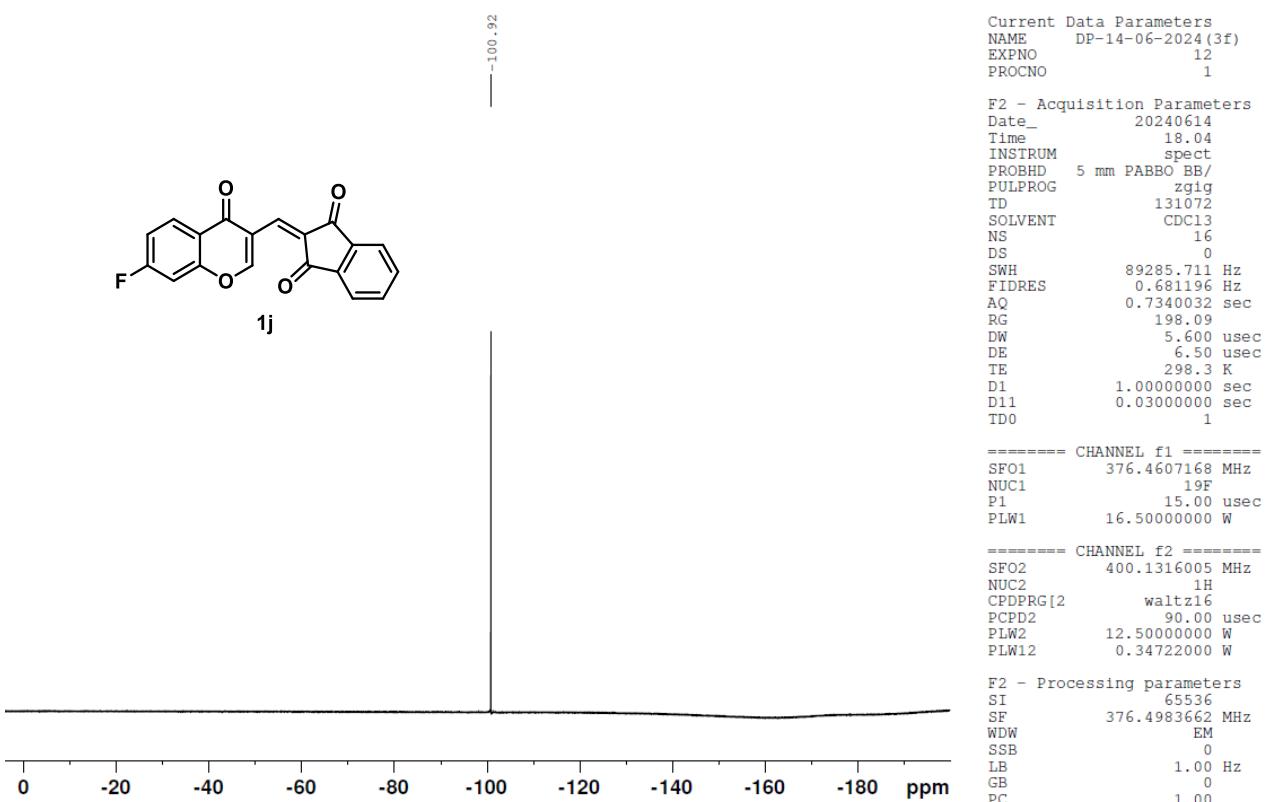
<sup>1</sup>H NMR spectrum of compound **1j** (CDCl<sub>3</sub>, 400 MHz)



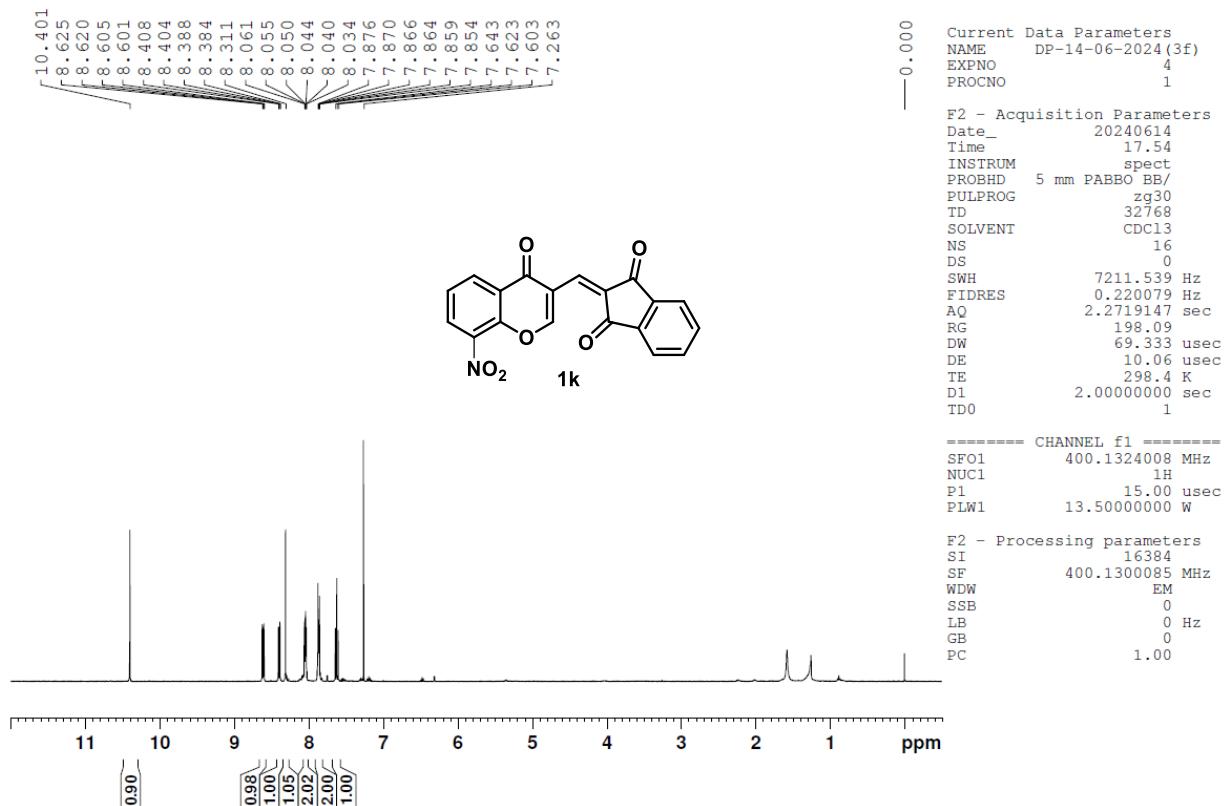
<sup>13</sup>C NMR spectrum of compound **1j** (CDCl<sub>3</sub>, 100 MHz)



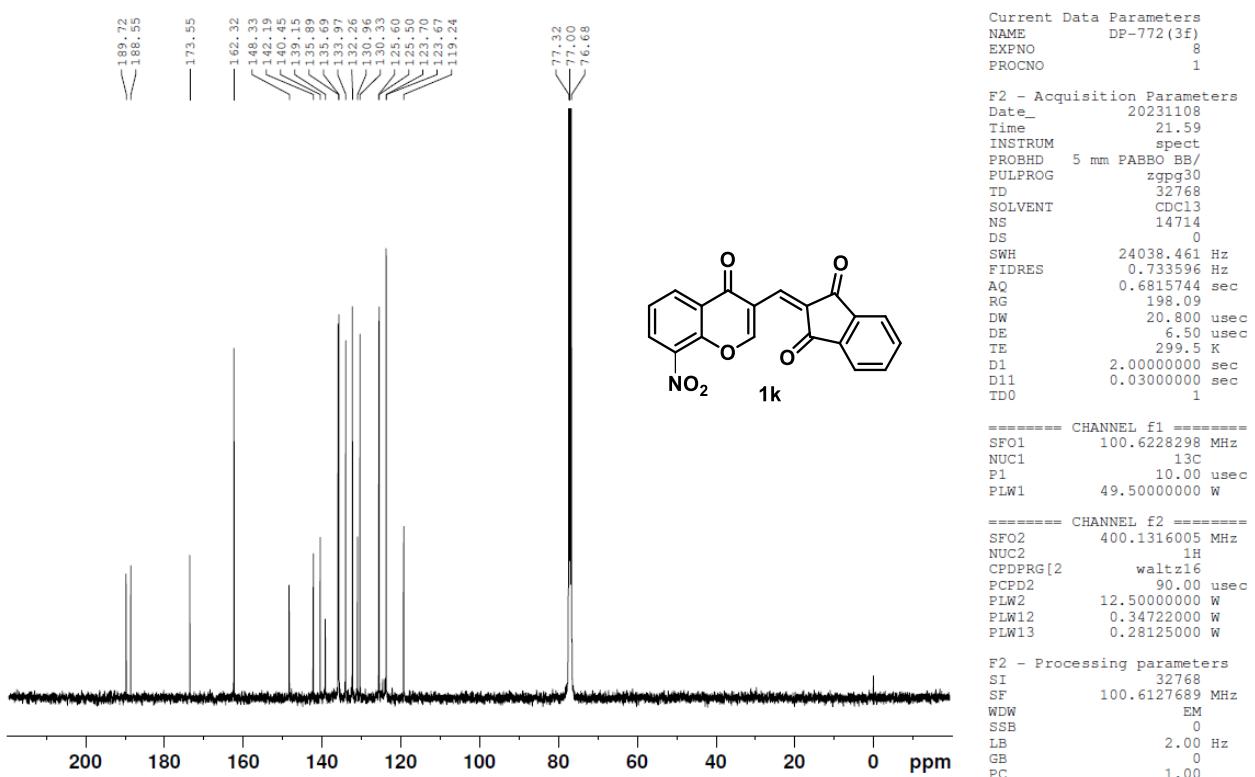
<sup>19</sup>F NMR spectrum of compound **1j** (CDCl<sub>3</sub>, 376 MHz)



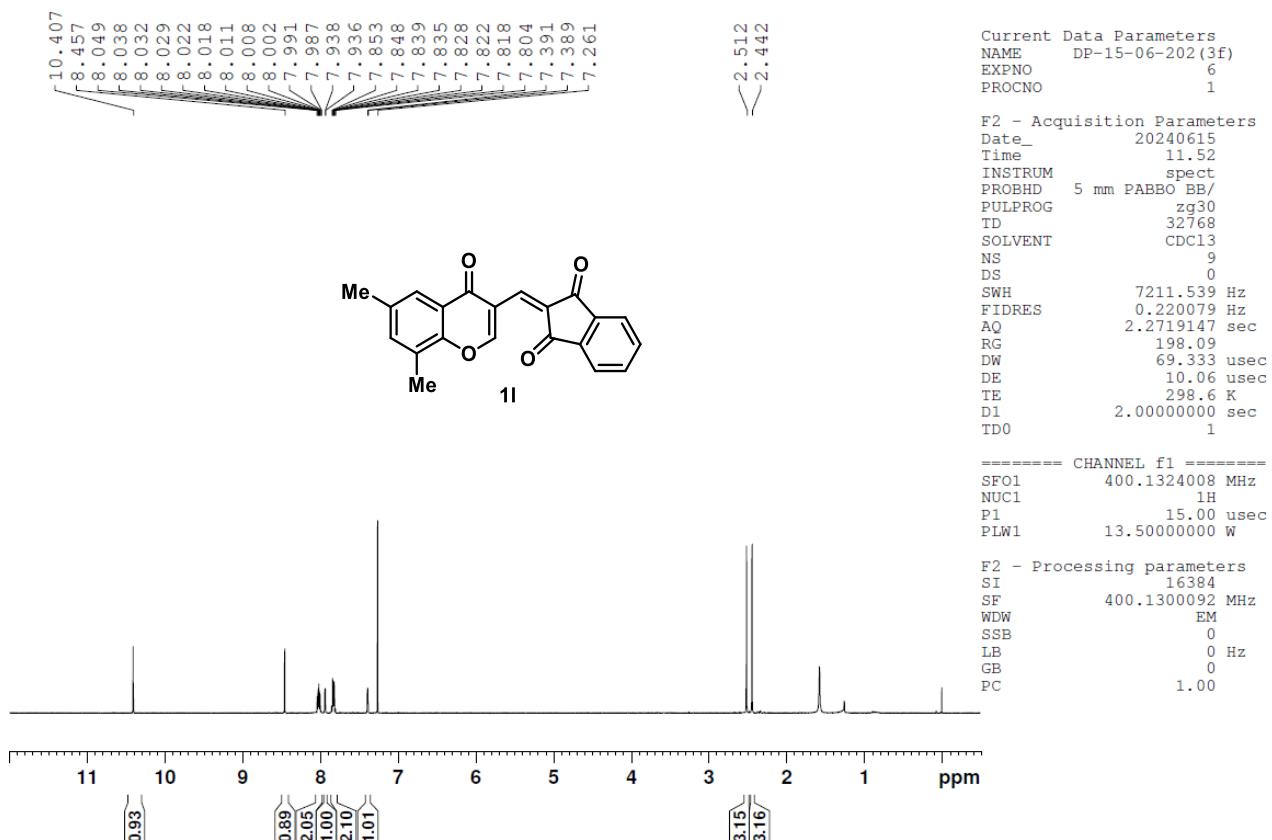
<sup>1</sup>H NMR spectrum of compound **1k** (CDCl<sub>3</sub>, 400 MHz)



<sup>13</sup>C NMR spectrum of compound **1k** (CDCl<sub>3</sub>, 100 MHz)



<sup>1</sup>H NMR spectrum of compound **1I** (CDCl<sub>3</sub>, 400 MHz)



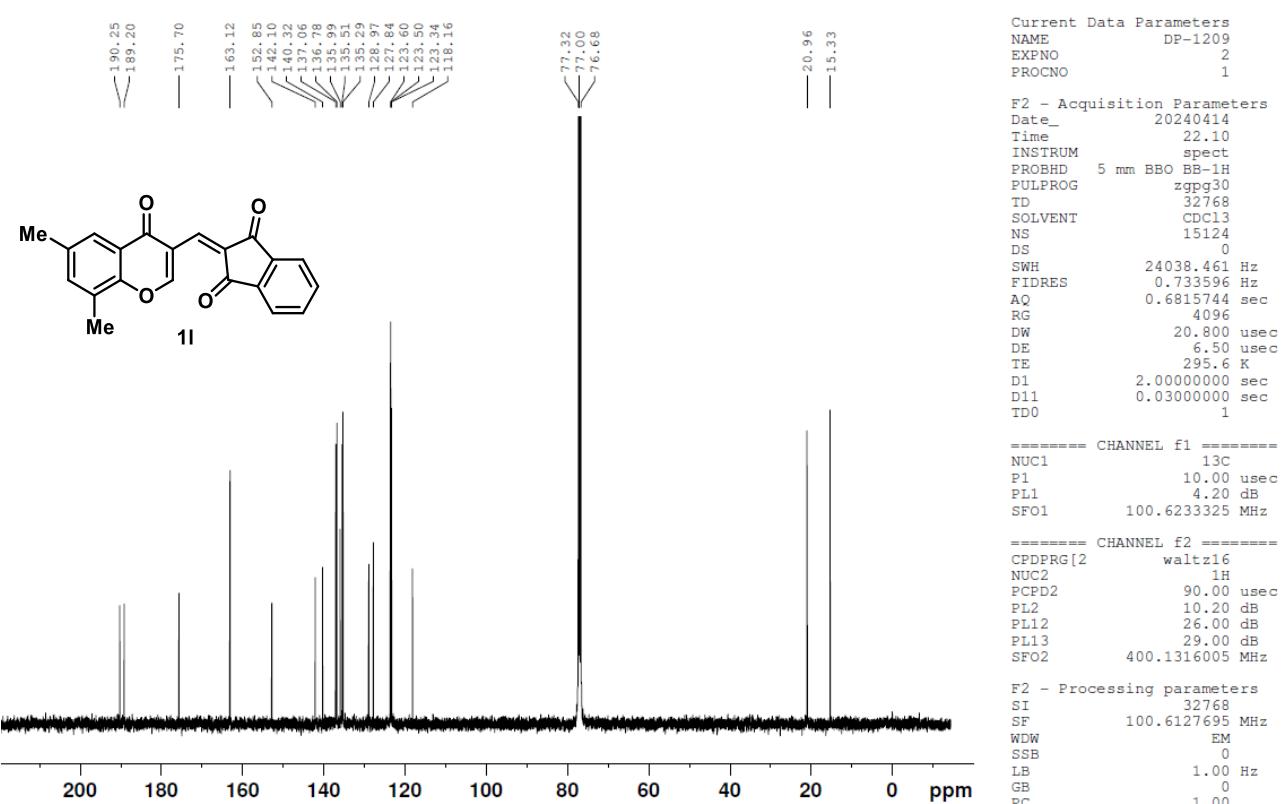
Current Data Parameters  
NAME DP-15-06-202 (3f)  
EXPNO 6  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20240615  
Time 11.52  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 32768  
SOLVENT CDCl<sub>3</sub>  
NS 9  
DS 0  
SWH 7211.539 Hz  
FIDRES 0.220079 Hz  
AQ 2.2719147 sec  
RG 198.09  
DW 69.333 usec  
DE 10.06 usec  
TE 298.6 K  
D1 2.0000000 sec  
TDO 1

===== CHANNEL f1 =====  
SFO1 400.1324008 MHz  
NUC1 1H  
P1 15.00 usec  
PLW1 13.5000000 W

F2 - Processing parameters  
SI 16384  
SF 400.1300092 MHz  
WDW EM  
SSB 0  
LB 0 Hz  
GB 0  
PC 1.00

<sup>13</sup>C NMR spectrum of compound **1I** (CDCl<sub>3</sub>, 100 MHz)



Current Data Parameters  
NAME DP-1209  
EXPNO 2  
PROCNO 1

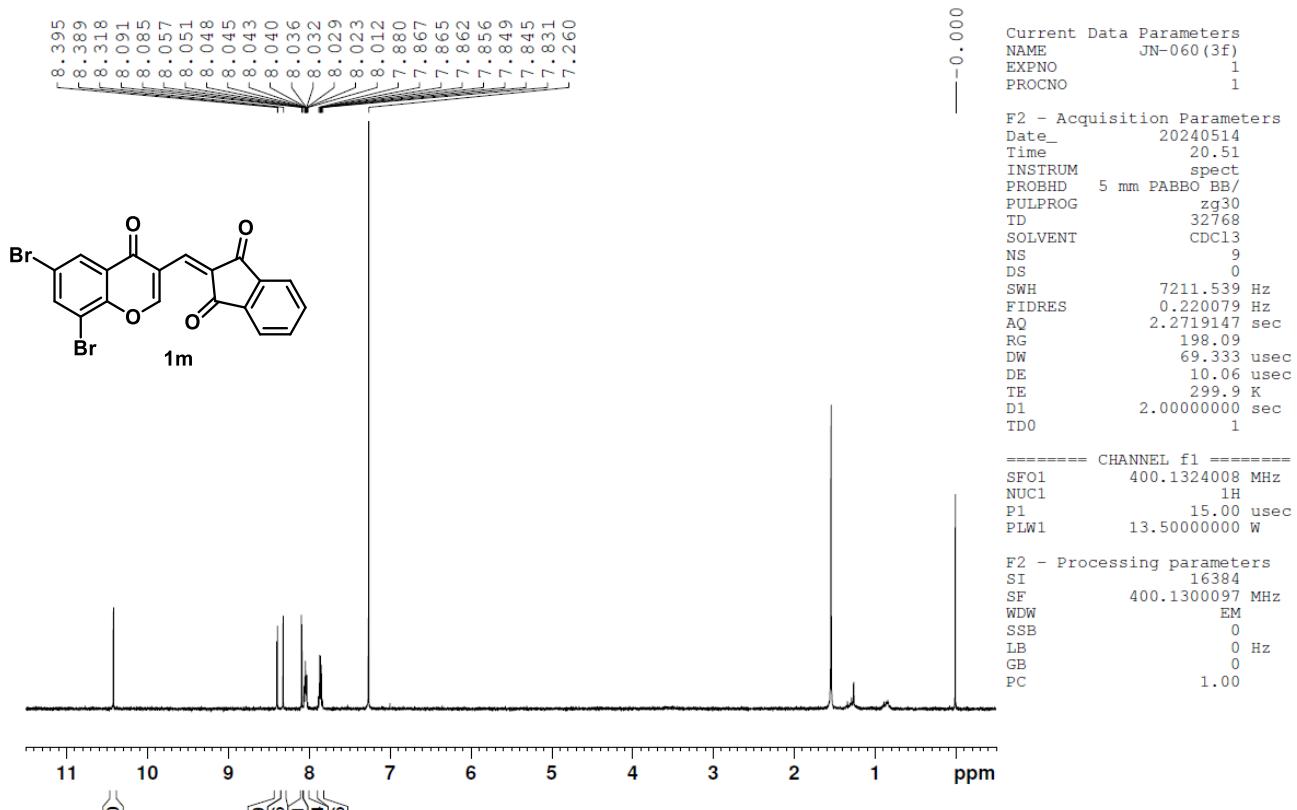
F2 - Acquisition Parameters  
Date\_ 20240414  
Time 22.10  
INSTRUM spect  
PROBHD 5 mm BBO BB-1H  
PULPROG zgpg30  
TD 32768  
SOLVENT CDCl<sub>3</sub>  
NS 15124  
DS 0  
SWH 24038.461 Hz  
FIDRES 0.733596 Hz  
AQ 0.6815744 sec  
RG 4096  
DW 20.800 usec  
DE 6.50 usec  
TE 295.6 K  
D1 2.0000000 sec  
D11 0.03000000 sec  
TDO 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 10.00 usec  
PL1 4.20 dB  
SFO1 100.6233325 MHz

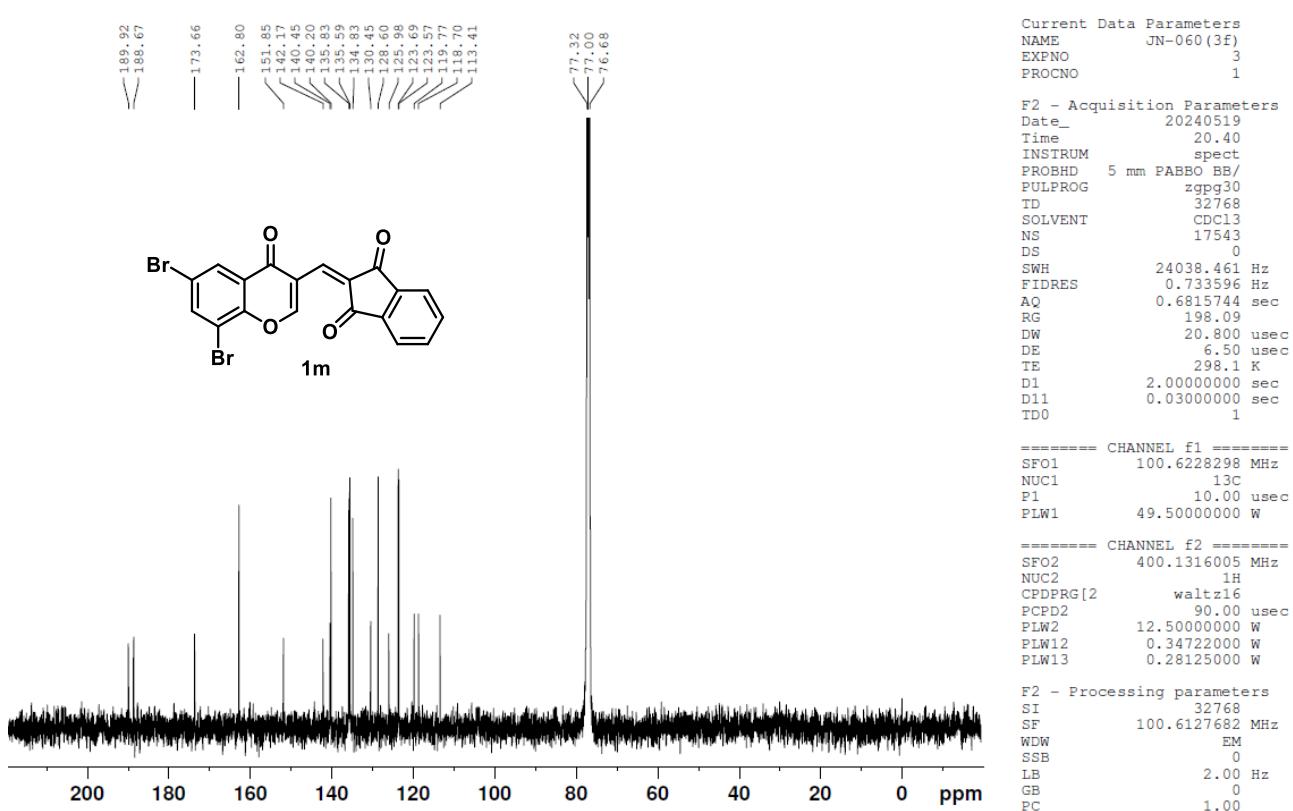
===== CHANNEL f2 =====  
CPDPGR[2] waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PL2 10.20 dB  
PL12 26.00 dB  
PL13 29.00 dB  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127695 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.00

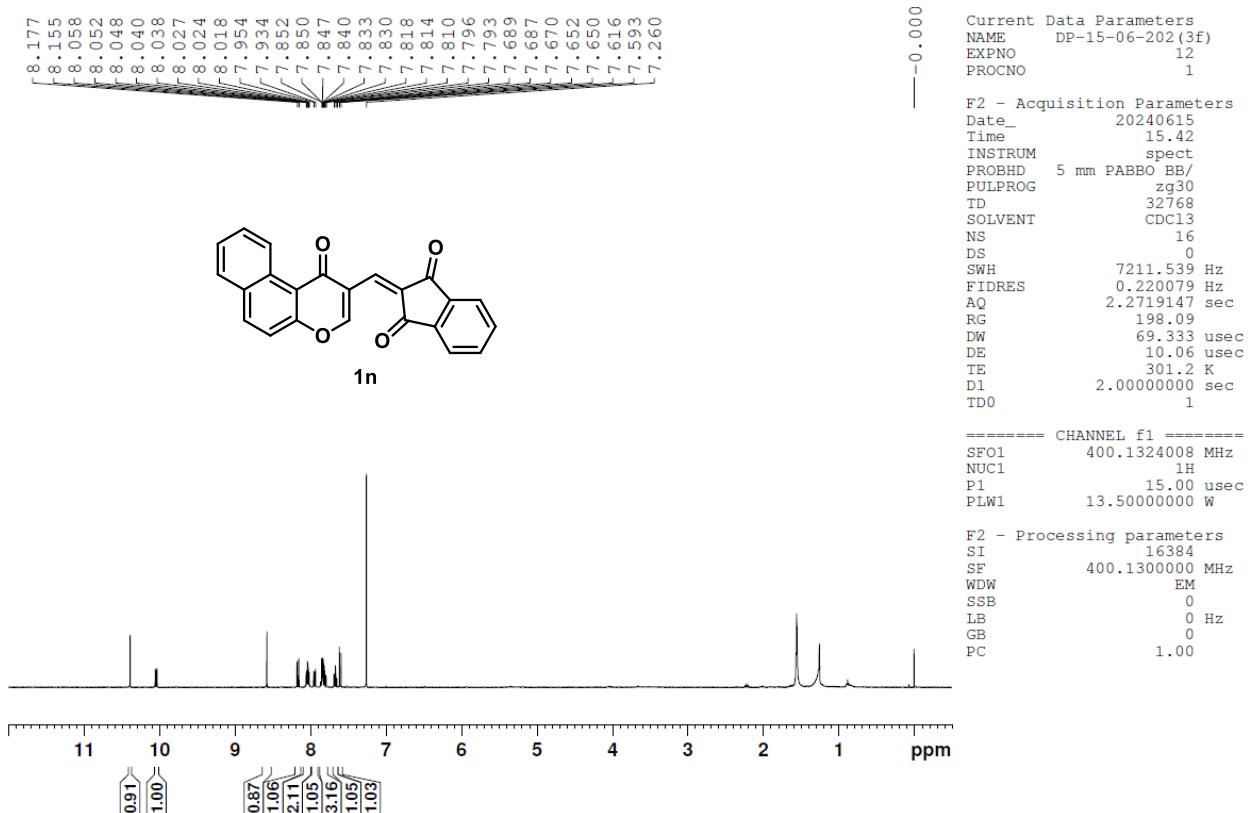
<sup>1</sup>H NMR spectrum of compound **1m** (CDCl<sub>3</sub>, 400 MHz)



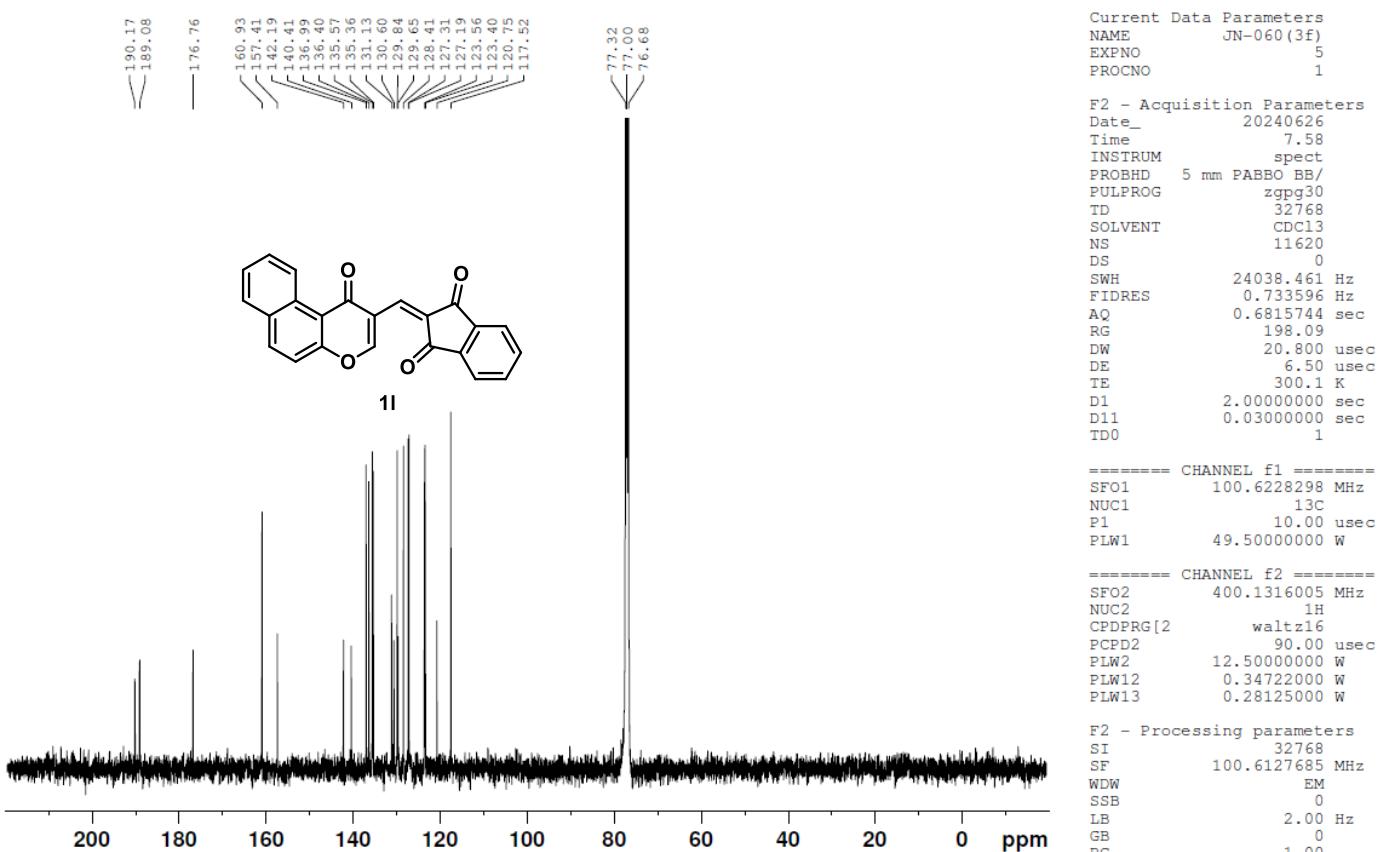
<sup>13</sup>C NMR spectrum of compound **1m** (CDCl<sub>3</sub>, 100 MHz)



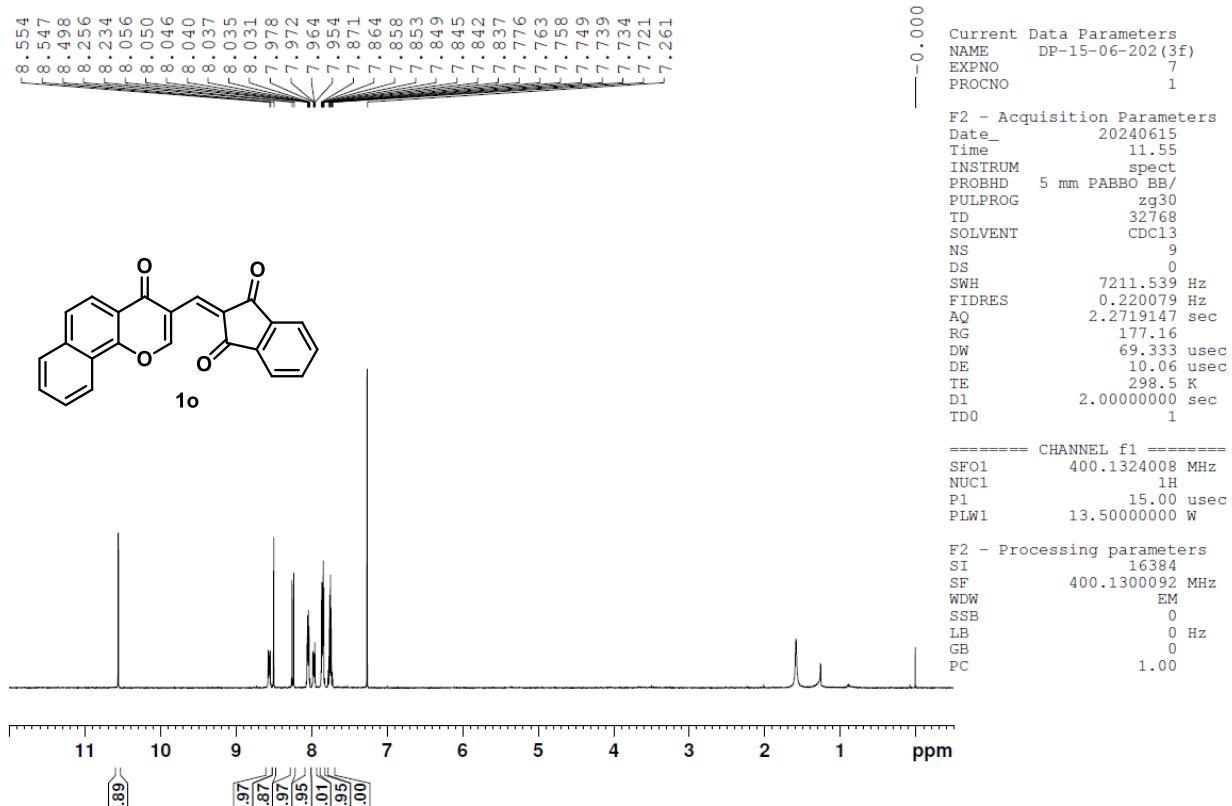
<sup>1</sup>H NMR spectrum of compound **1n** (CDCl<sub>3</sub>, 400 MHz)



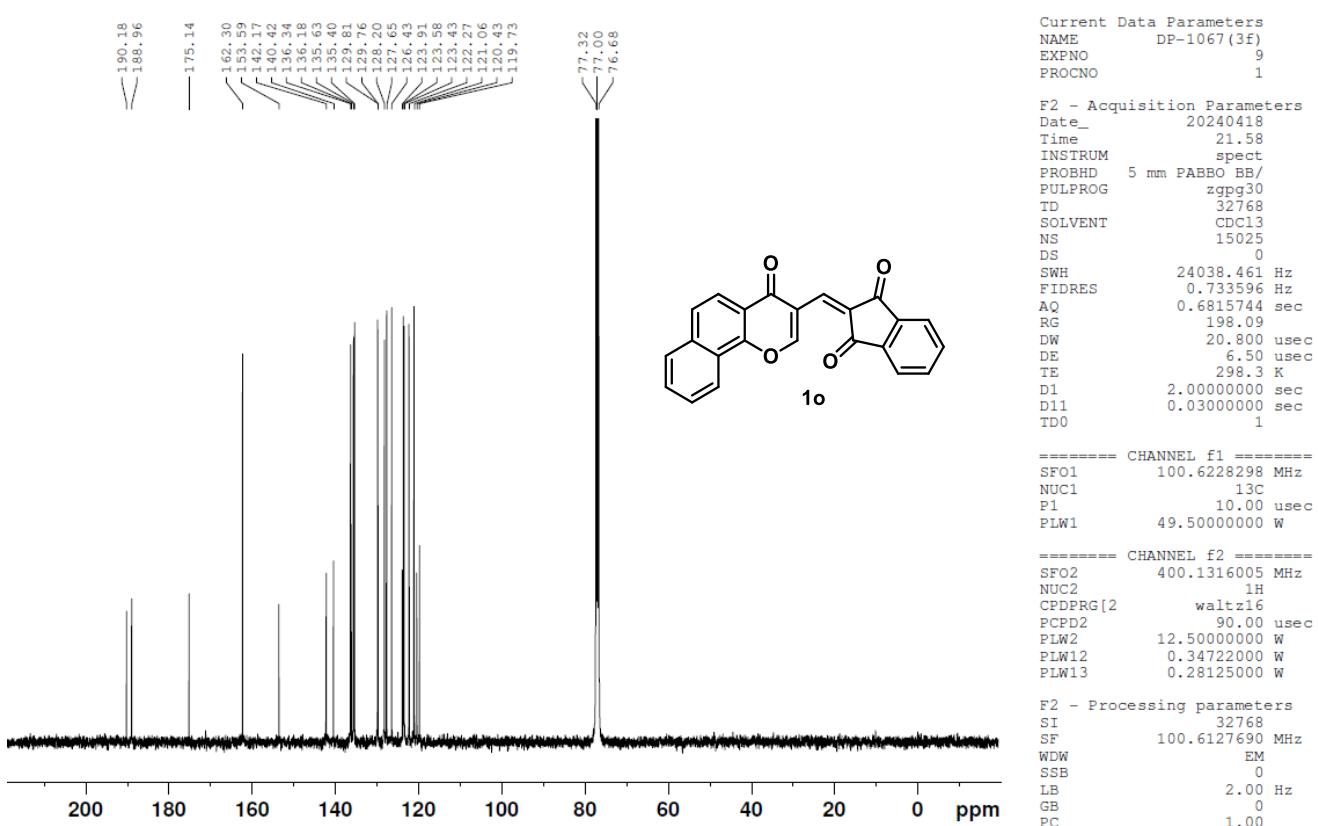
<sup>13</sup>C NMR spectrum of compound **1n** (CDCl<sub>3</sub>, 100 MHz)



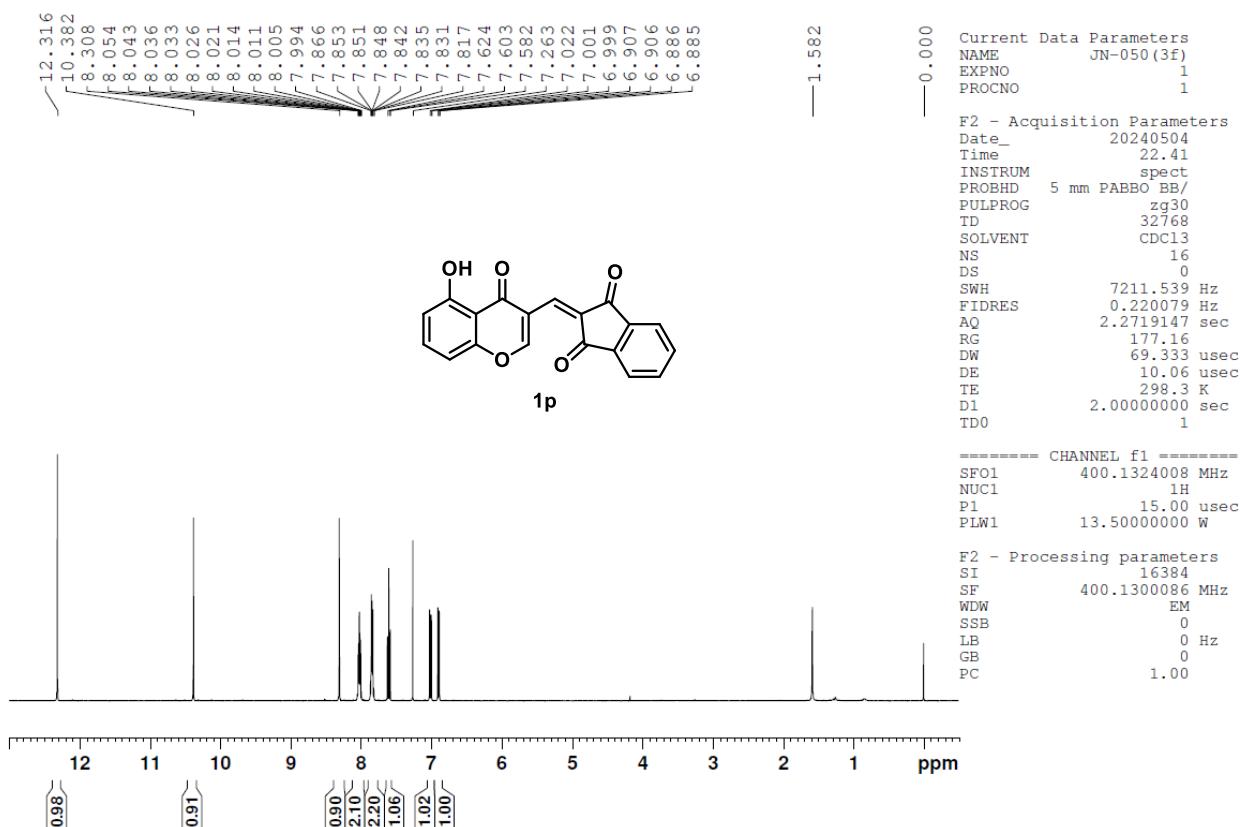
<sup>1</sup>H NMR spectrum of compound **1o** (CDCl<sub>3</sub>, 400 MHz)



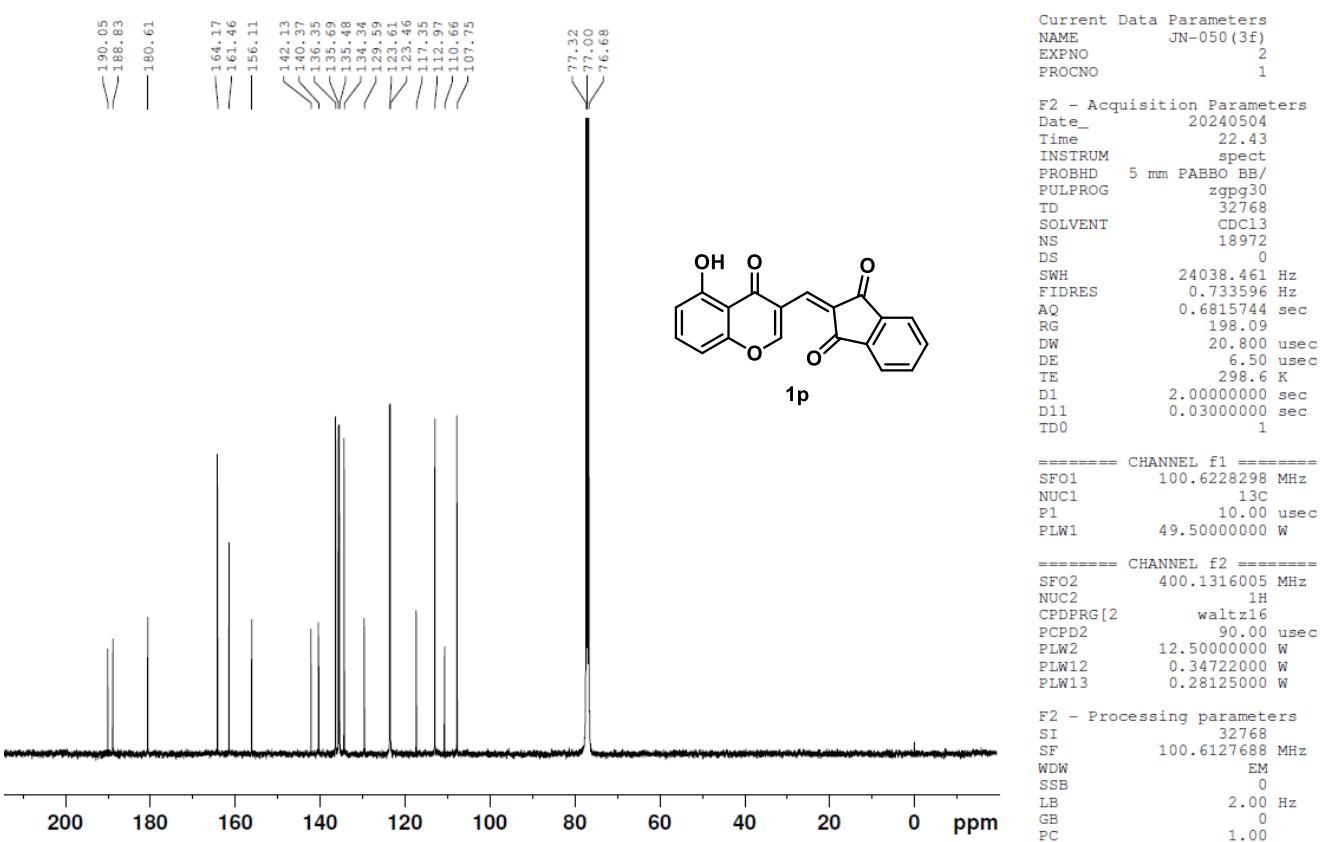
<sup>13</sup>C NMR spectrum of compound **1o** (CDCl<sub>3</sub>, 100 MHz)



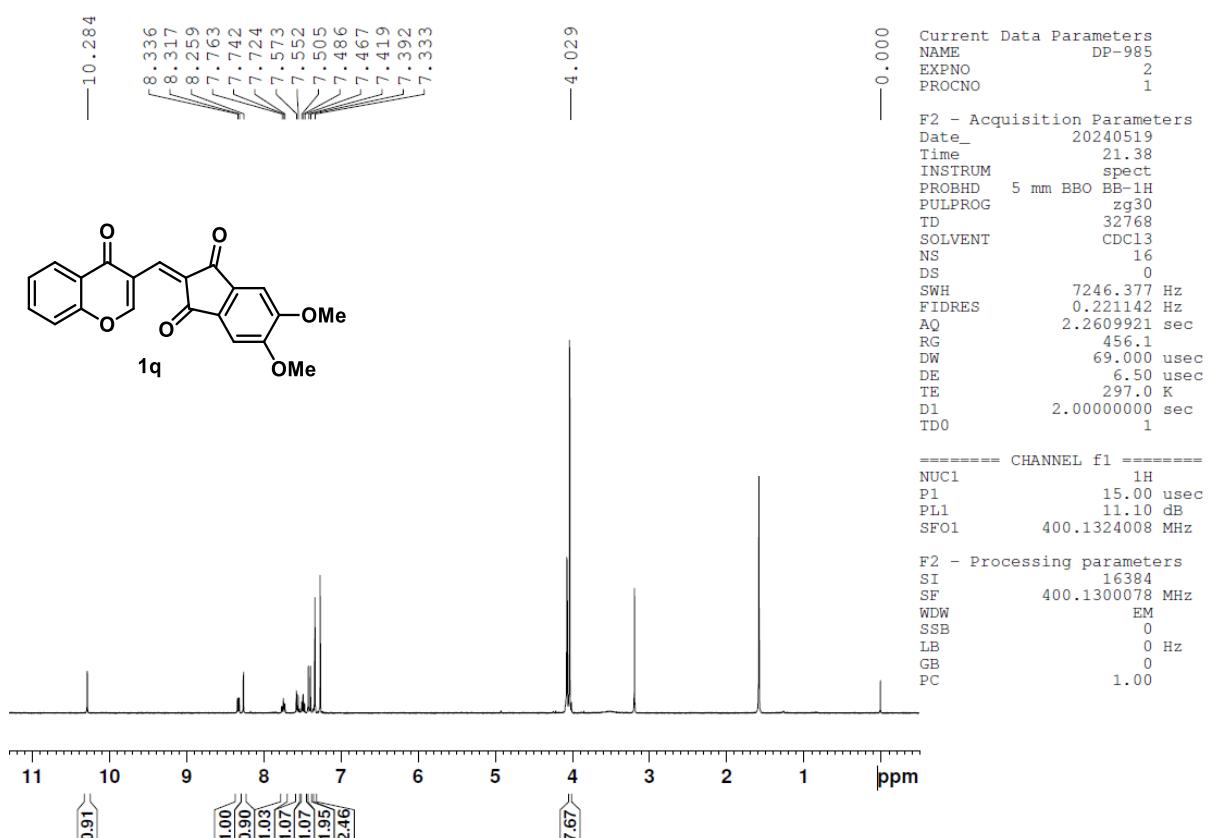
<sup>1</sup>H NMR spectrum of compound **1p** (CDCl<sub>3</sub>, 400 MHz)



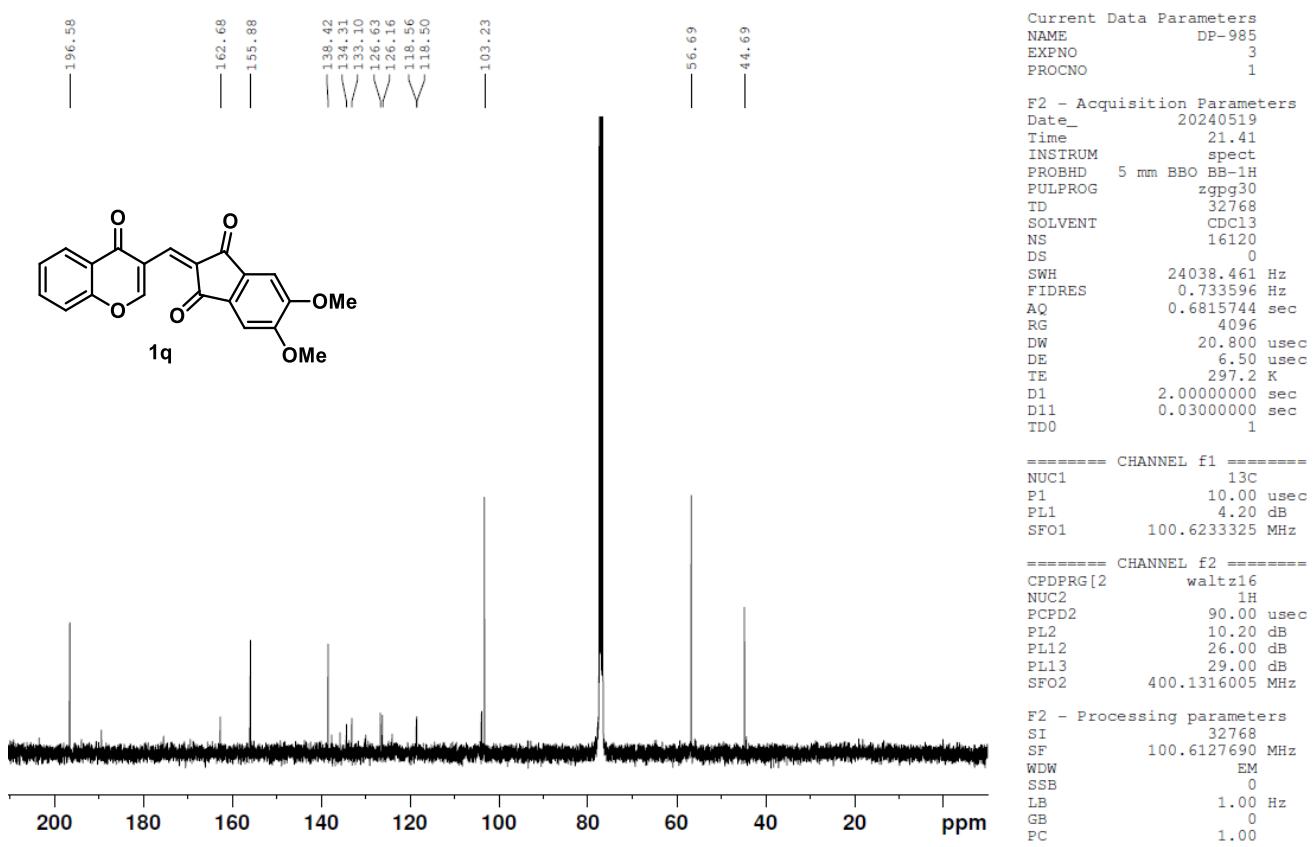
<sup>13</sup>C NMR spectrum of compound **1p** (CDCl<sub>3</sub>, 100 MHz)



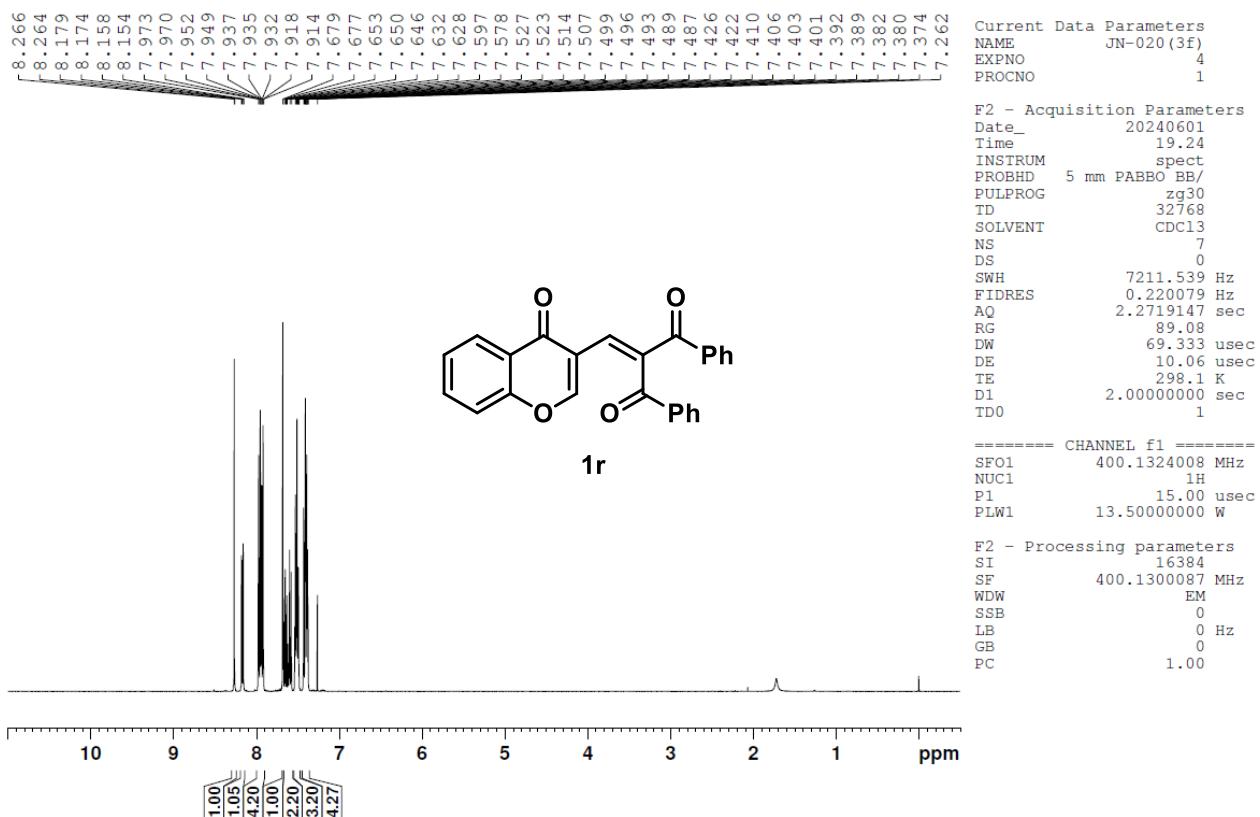
<sup>1</sup>H NMR spectrum of compound **1q** (CDCl<sub>3</sub>, 400 MHz)



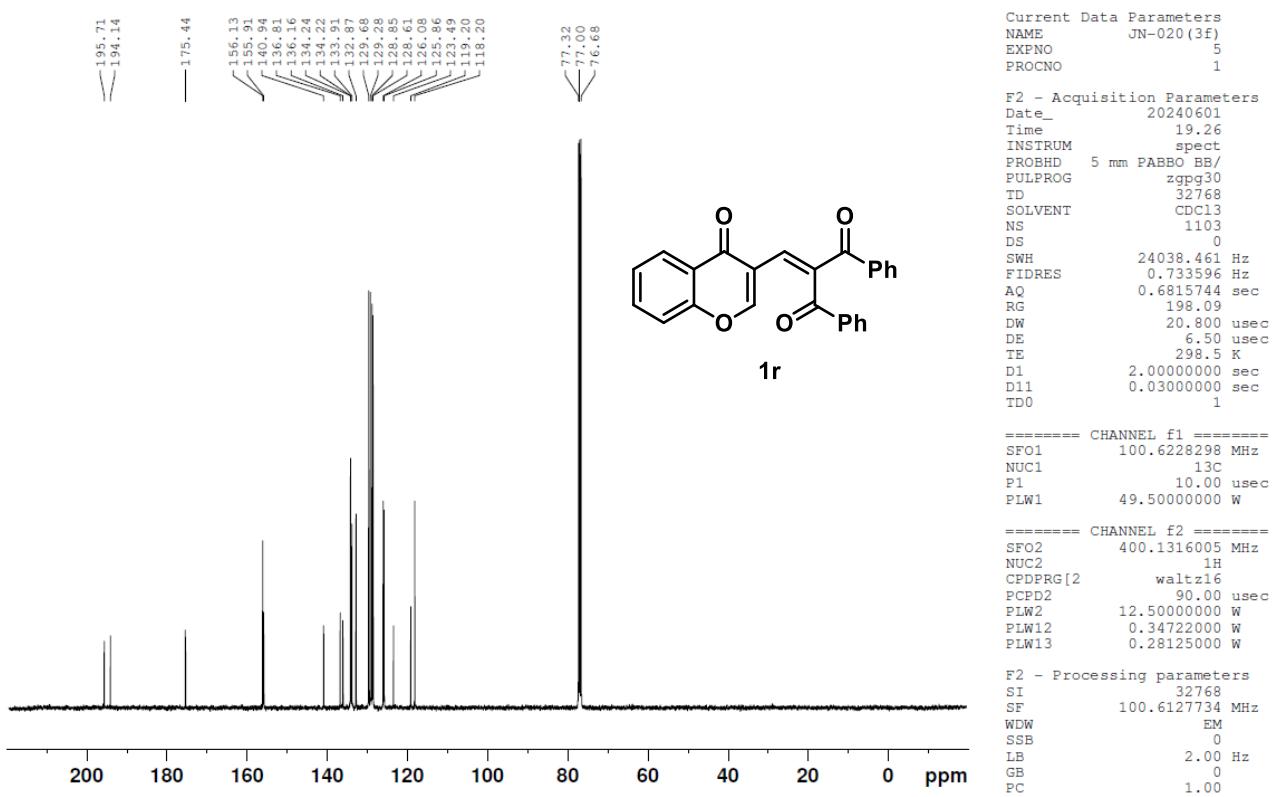
<sup>13</sup>C NMR spectrum of compound **1q** (CDCl<sub>3</sub>, 100 MHz)



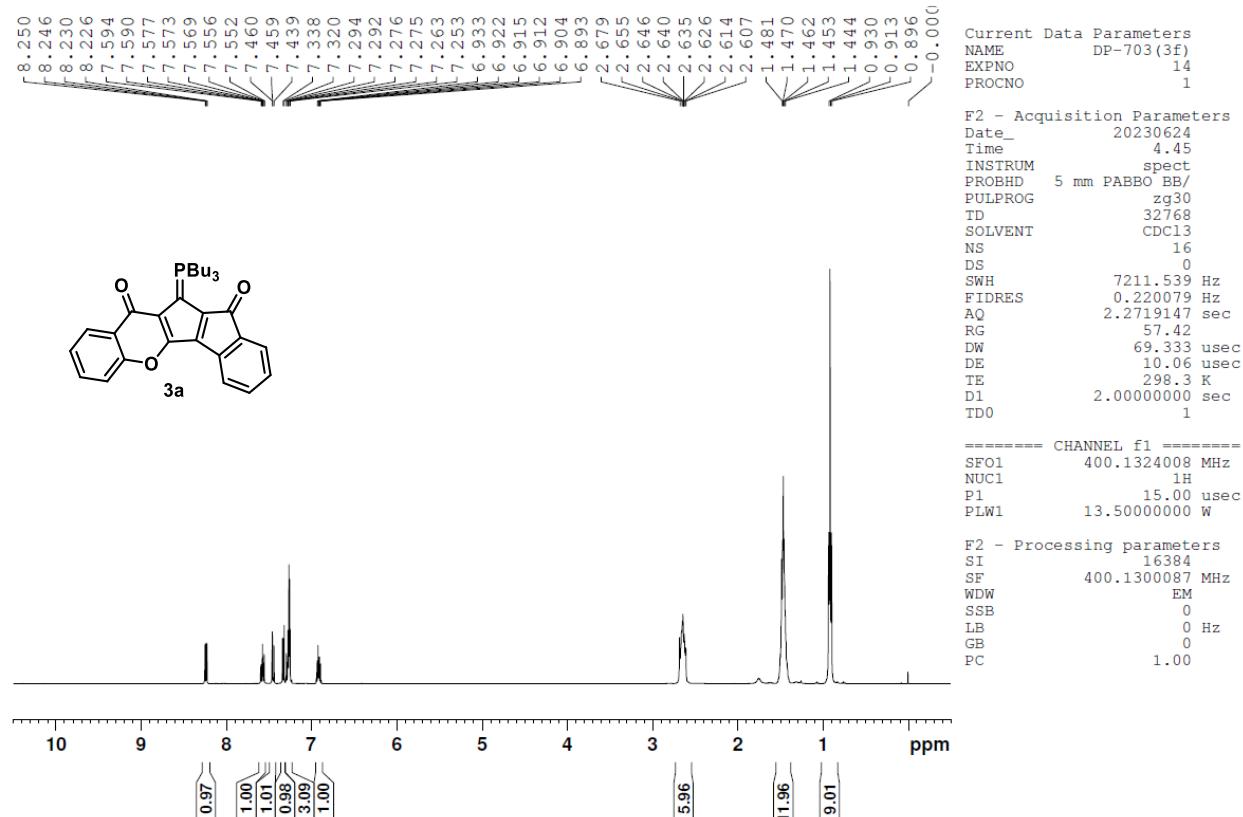
<sup>1</sup>H NMR spectrum of compound **1r** (CDCl<sub>3</sub>, 400 MHz)



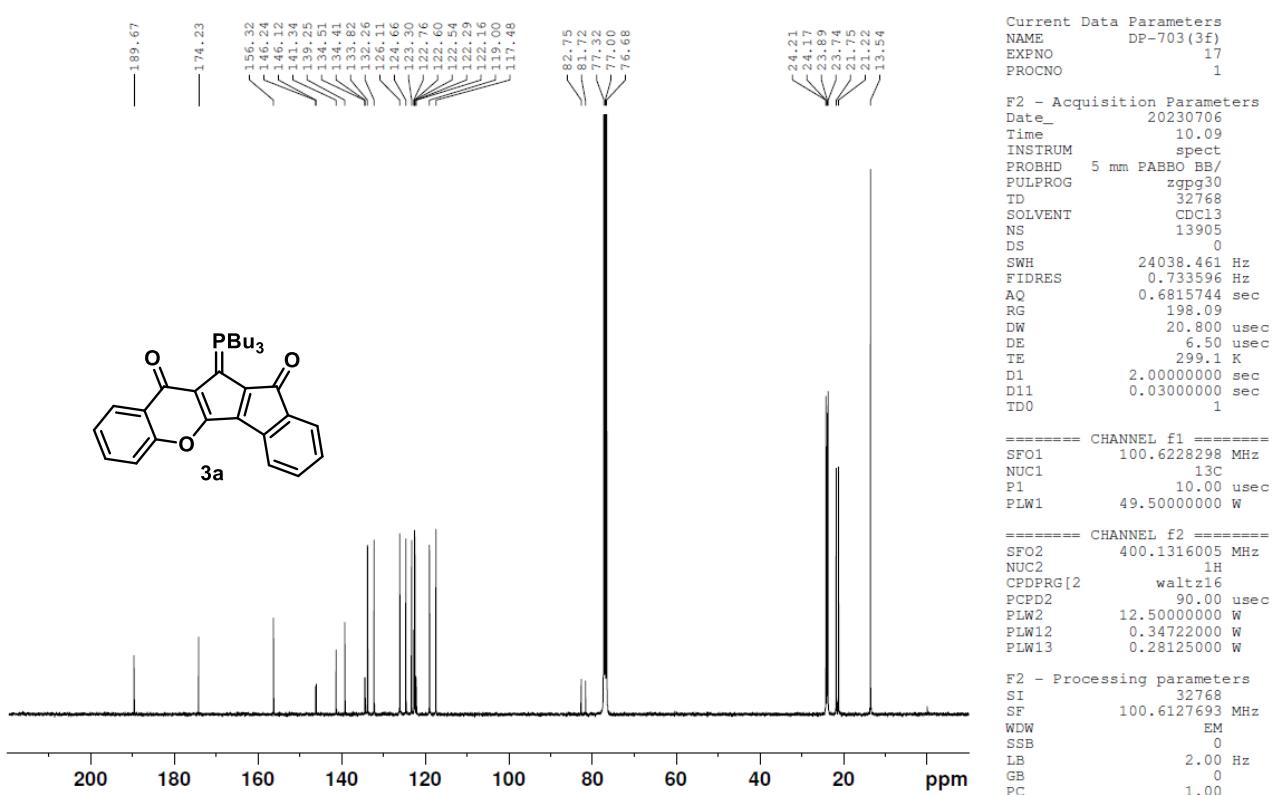
<sup>13</sup>C NMR spectrum of compound **1r** (CDCl<sub>3</sub>, 100 MHz)



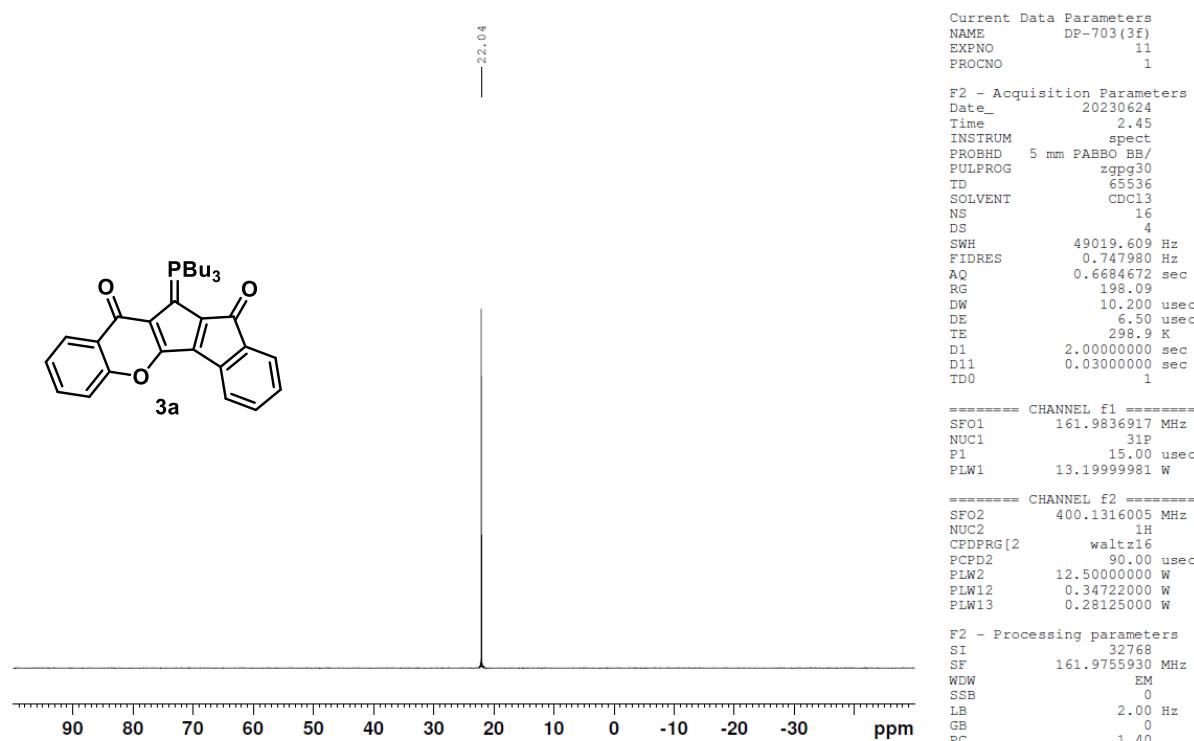
<sup>1</sup>H NMR spectrum of compound 3a (CDCl<sub>3</sub>, 400 MHz)



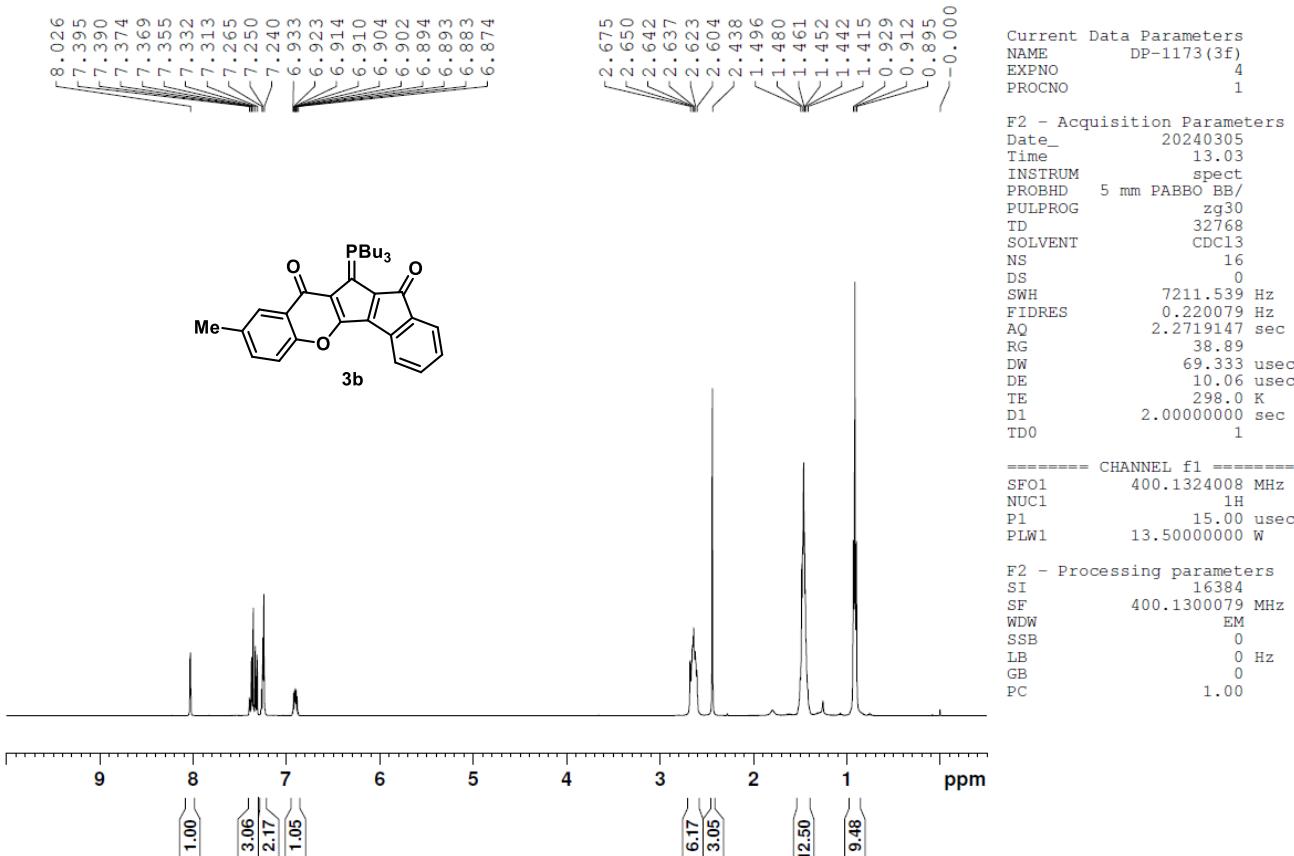
<sup>13</sup>C NMR spectrum of compound **3a** (CDCl<sub>3</sub>, 100 MHz)



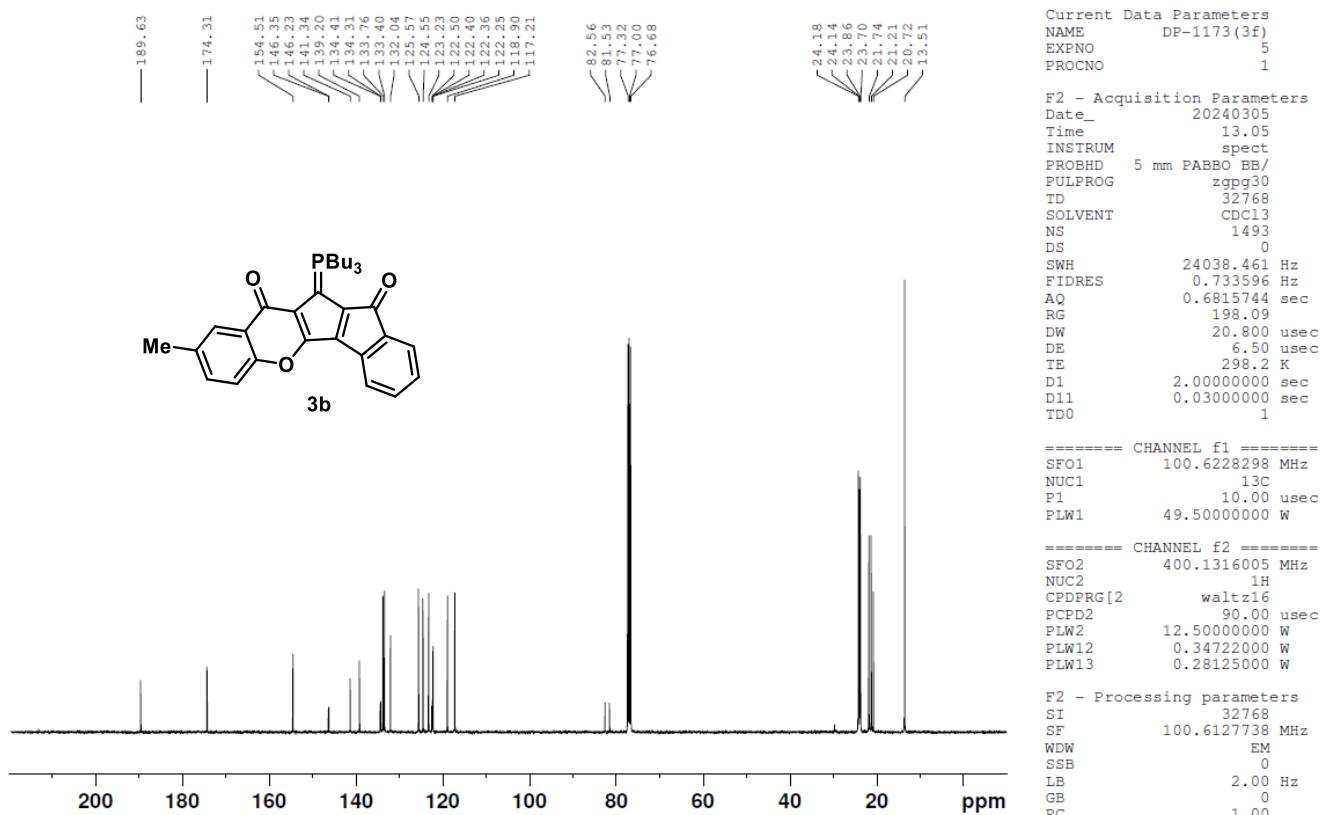
<sup>31</sup>P NMR spectrum of compound 3a (CDCl<sub>3</sub>, 162 MHz)



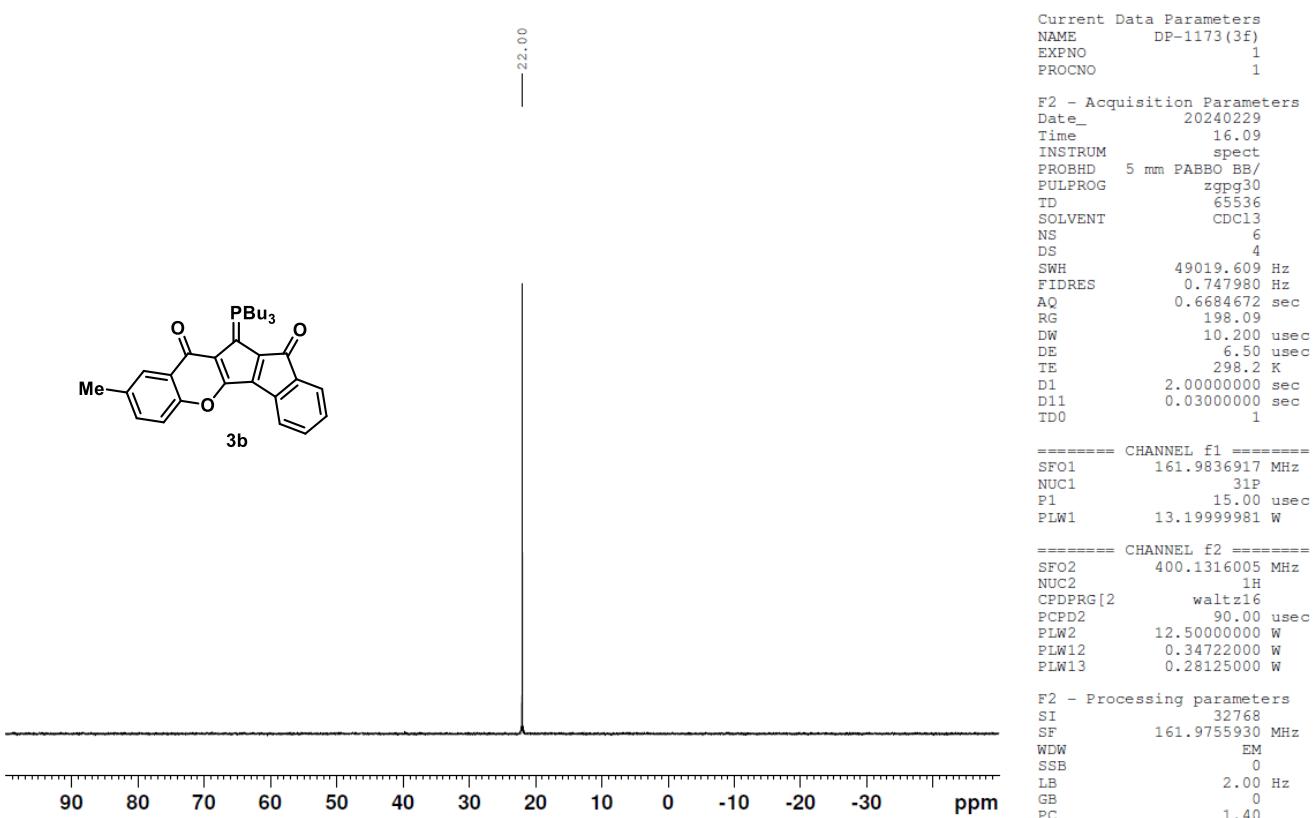
<sup>1</sup>H NMR spectrum of compound 3b (CDCl<sub>3</sub>, 400 MHz)



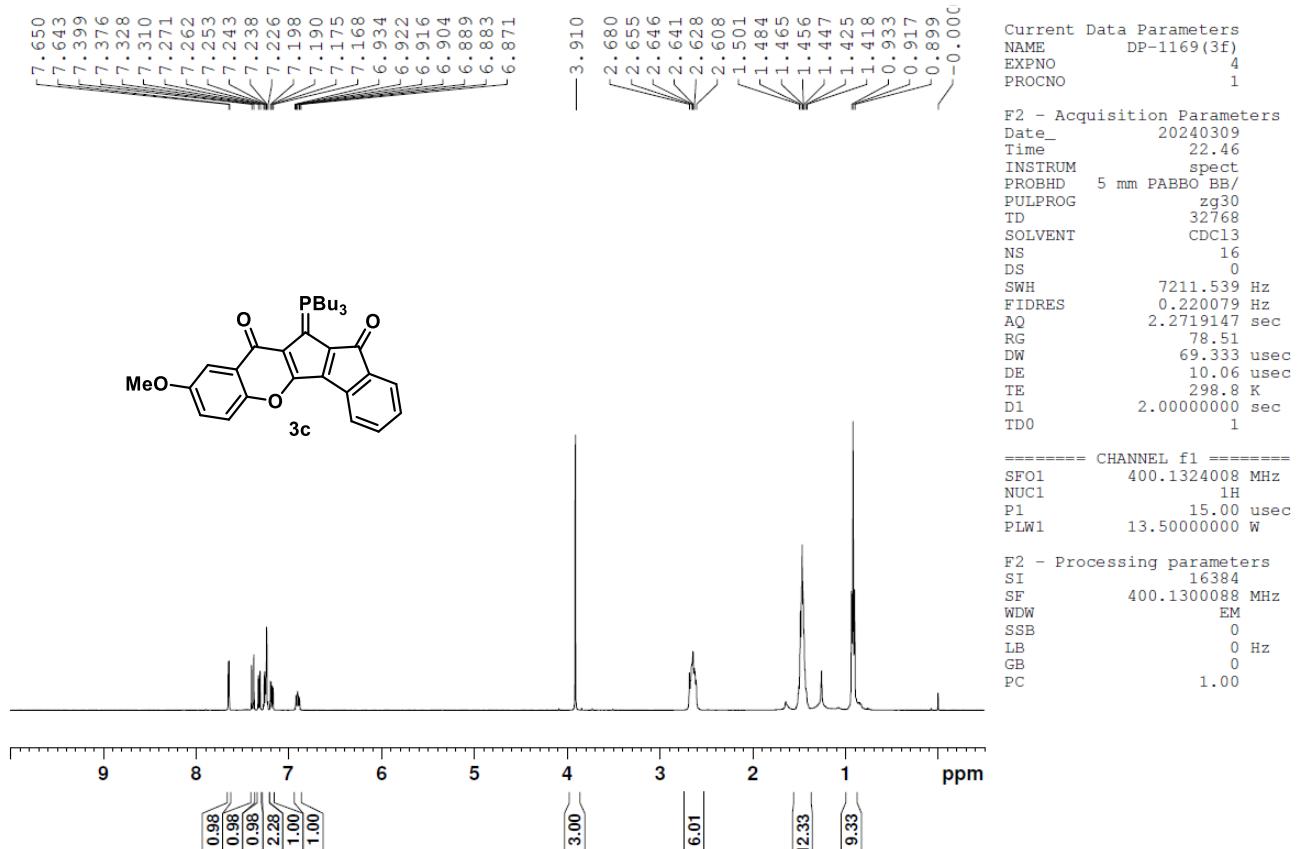
<sup>13</sup>C NMR spectrum of compound 3b (CDCl<sub>3</sub>, 100 MHz)



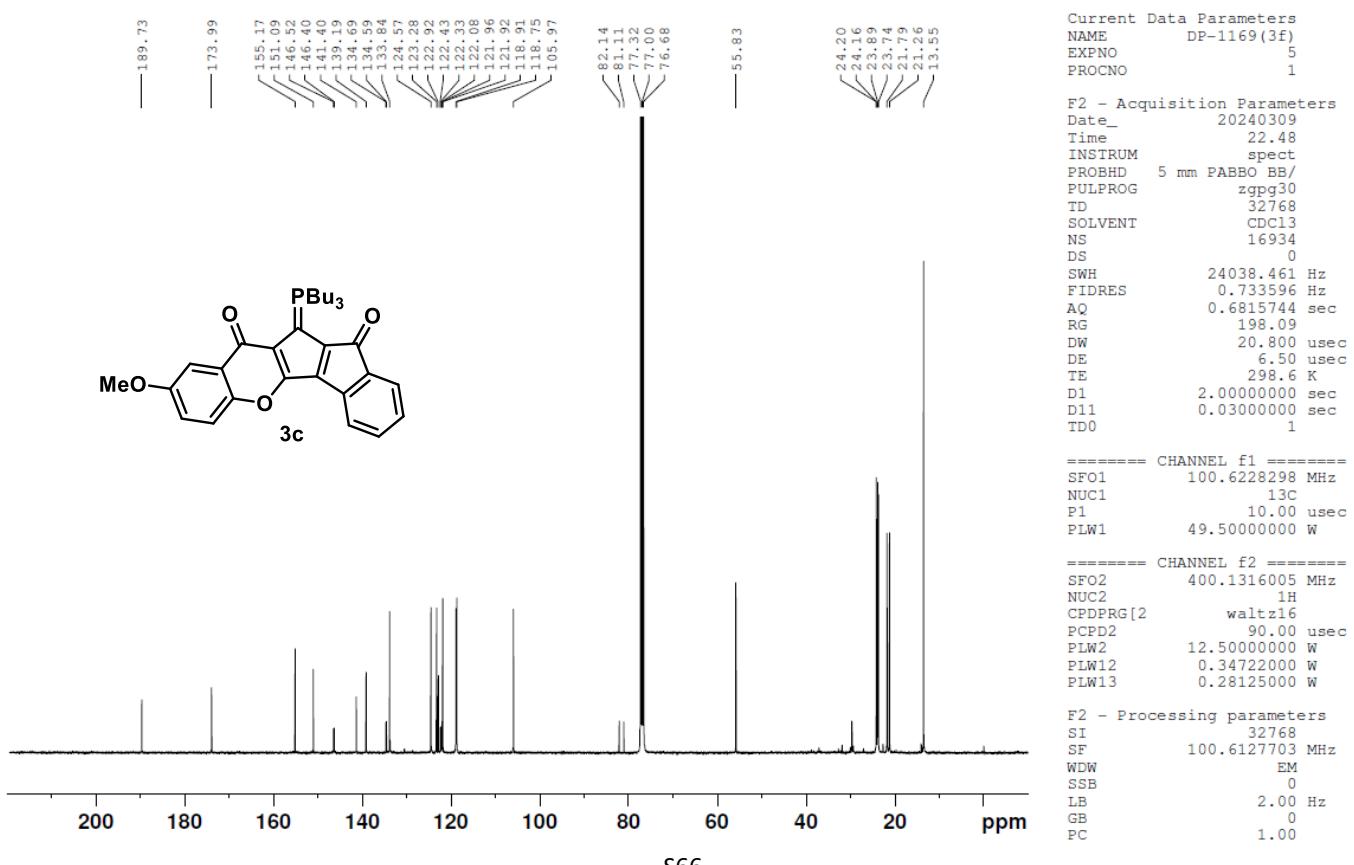
<sup>31</sup>P NMR spectrum of compound 3b (CDCl<sub>3</sub>, 162 MHz)



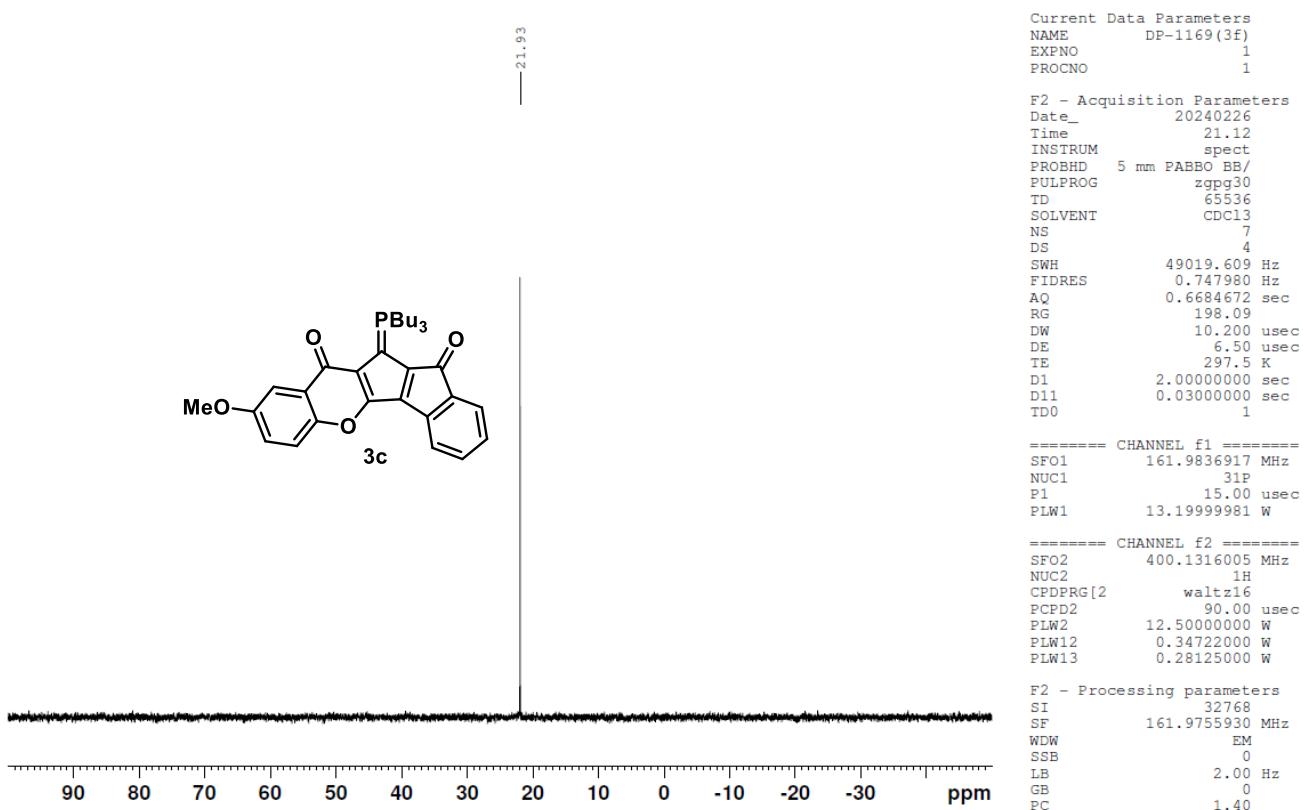
<sup>1</sup>H NMR spectrum of compound 3c (CDCl<sub>3</sub>, 400 MHz)



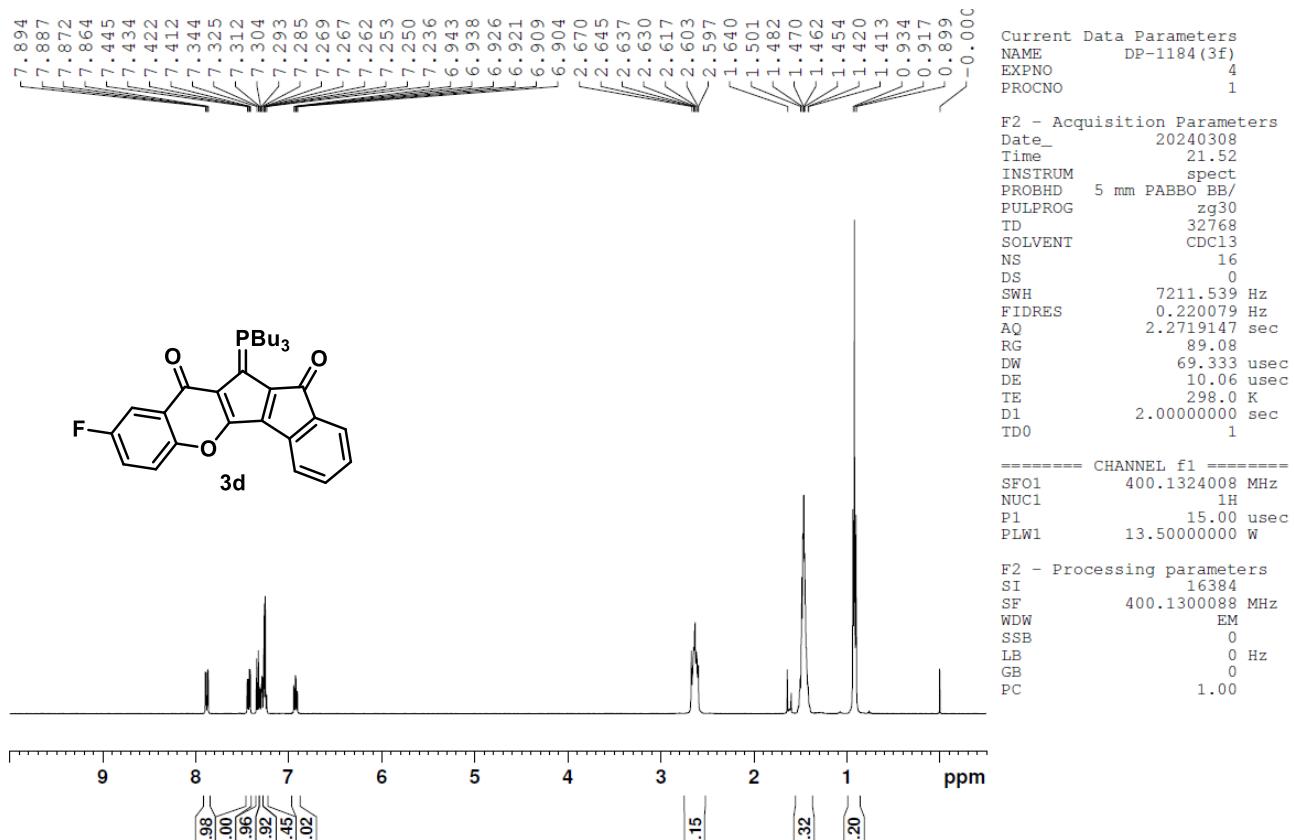
<sup>13</sup>C NMR spectrum of compound 3c (CDCl<sub>3</sub>, 100 MHz)



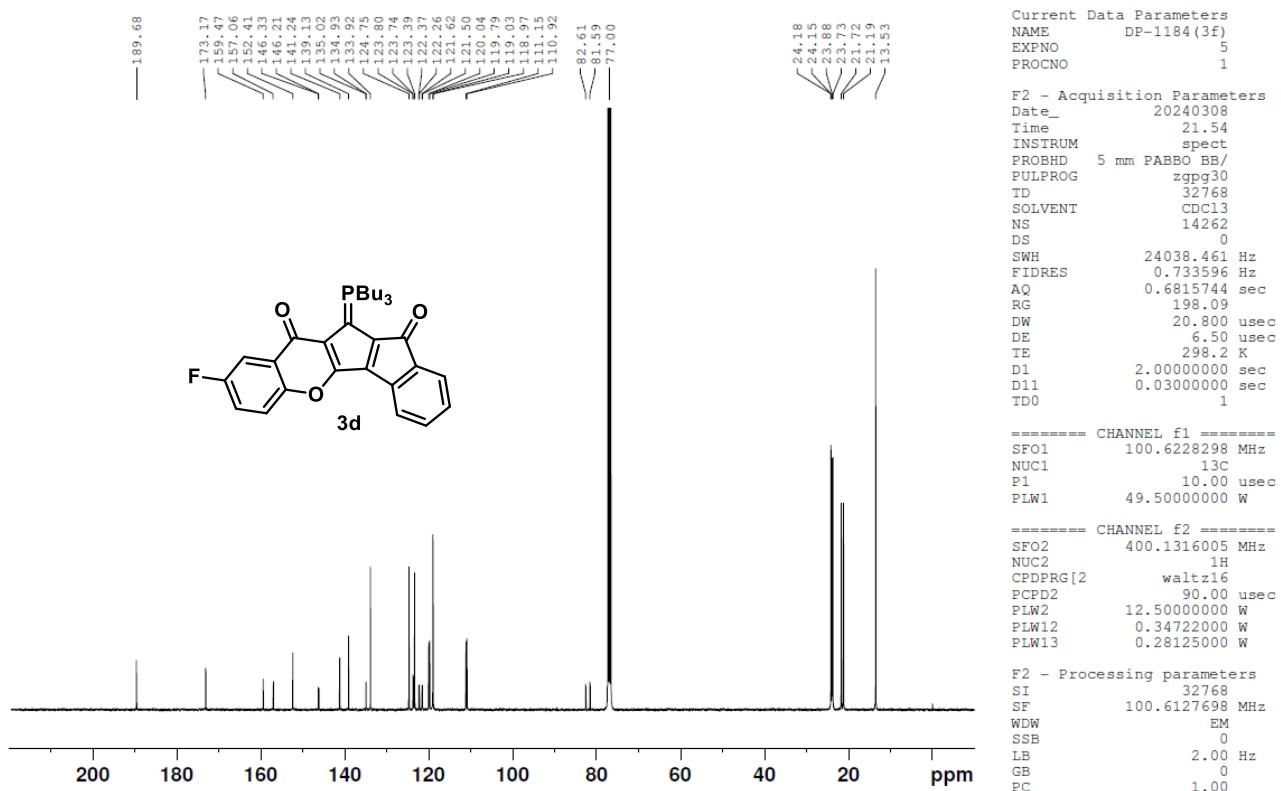
<sup>31</sup>P NMR spectrum of compound 3c (CDCl<sub>3</sub>, 162 MHz)



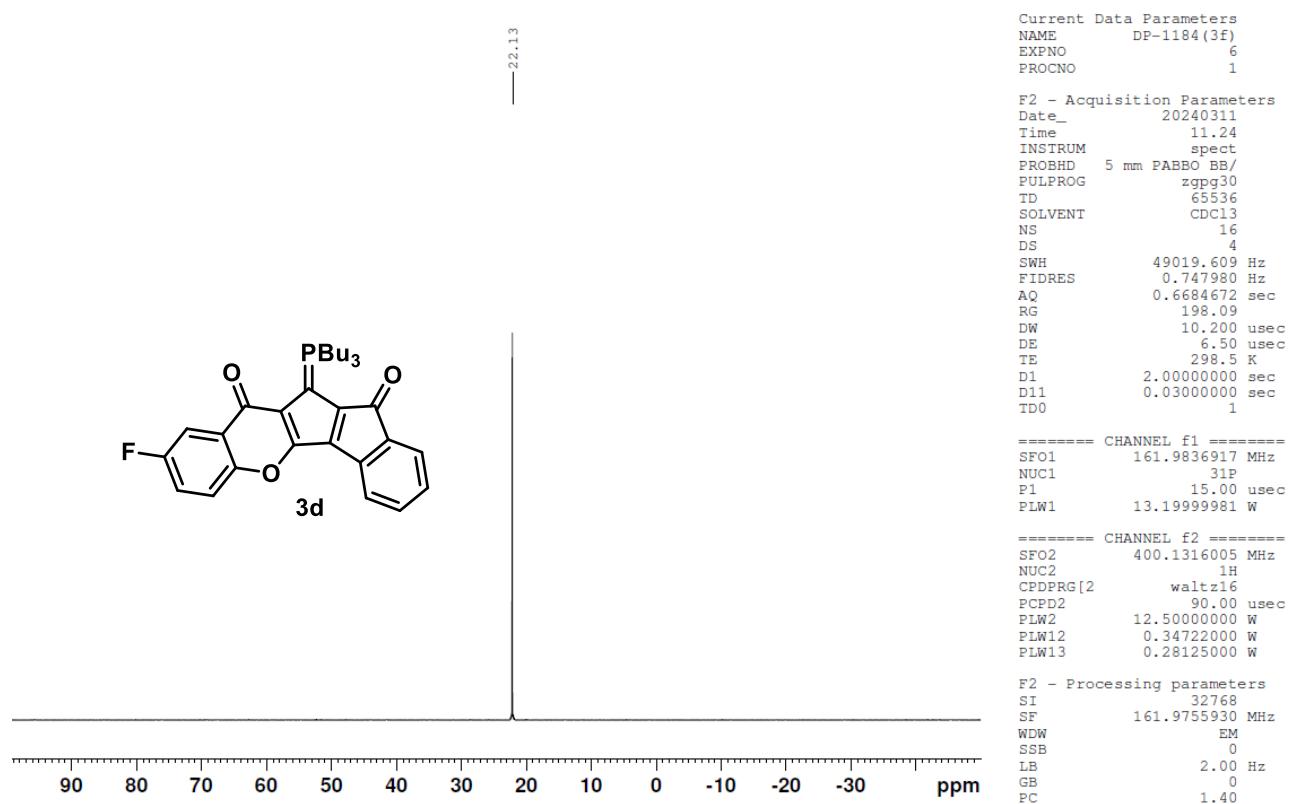
<sup>1</sup>H NMR spectrum of compound 3d (CDCl<sub>3</sub>, 400 MHz)



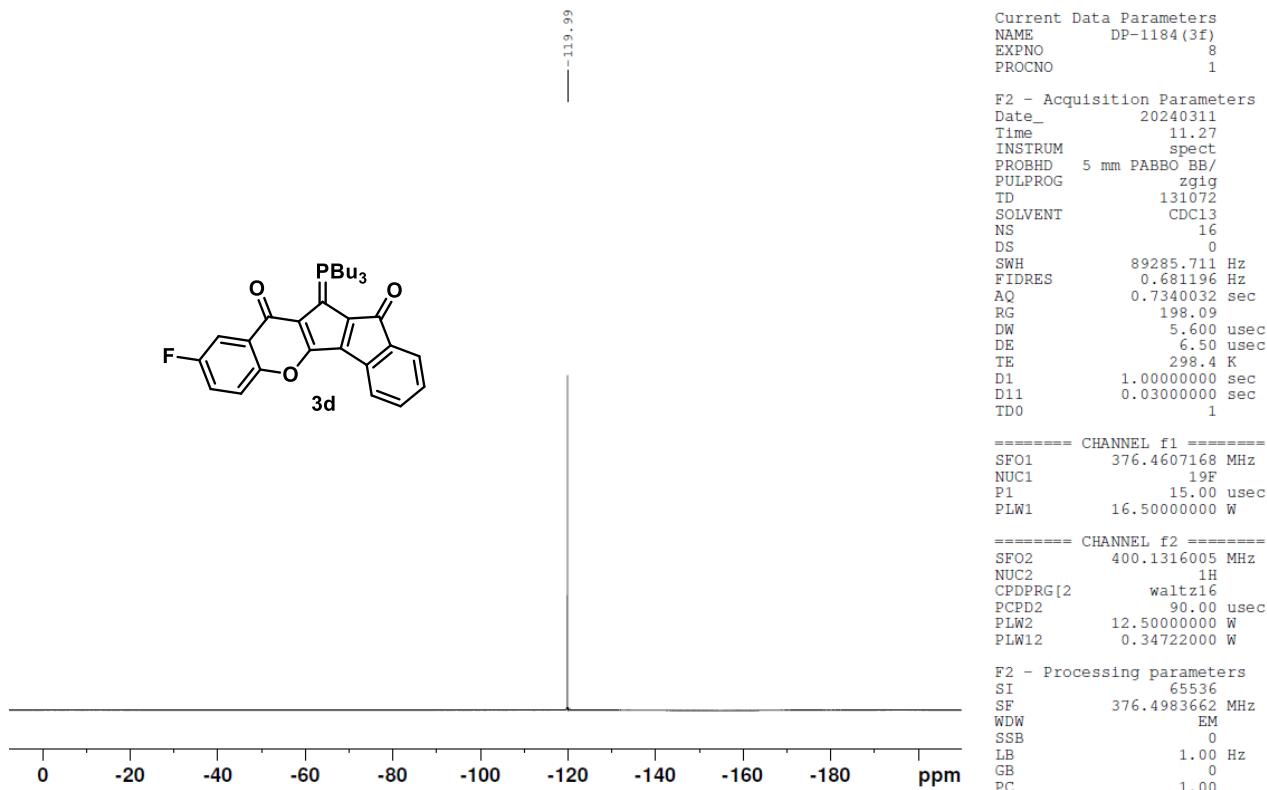
**<sup>13</sup>C NMR spectrum of compound 3d (CDCl<sub>3</sub>, 100 MHz)**



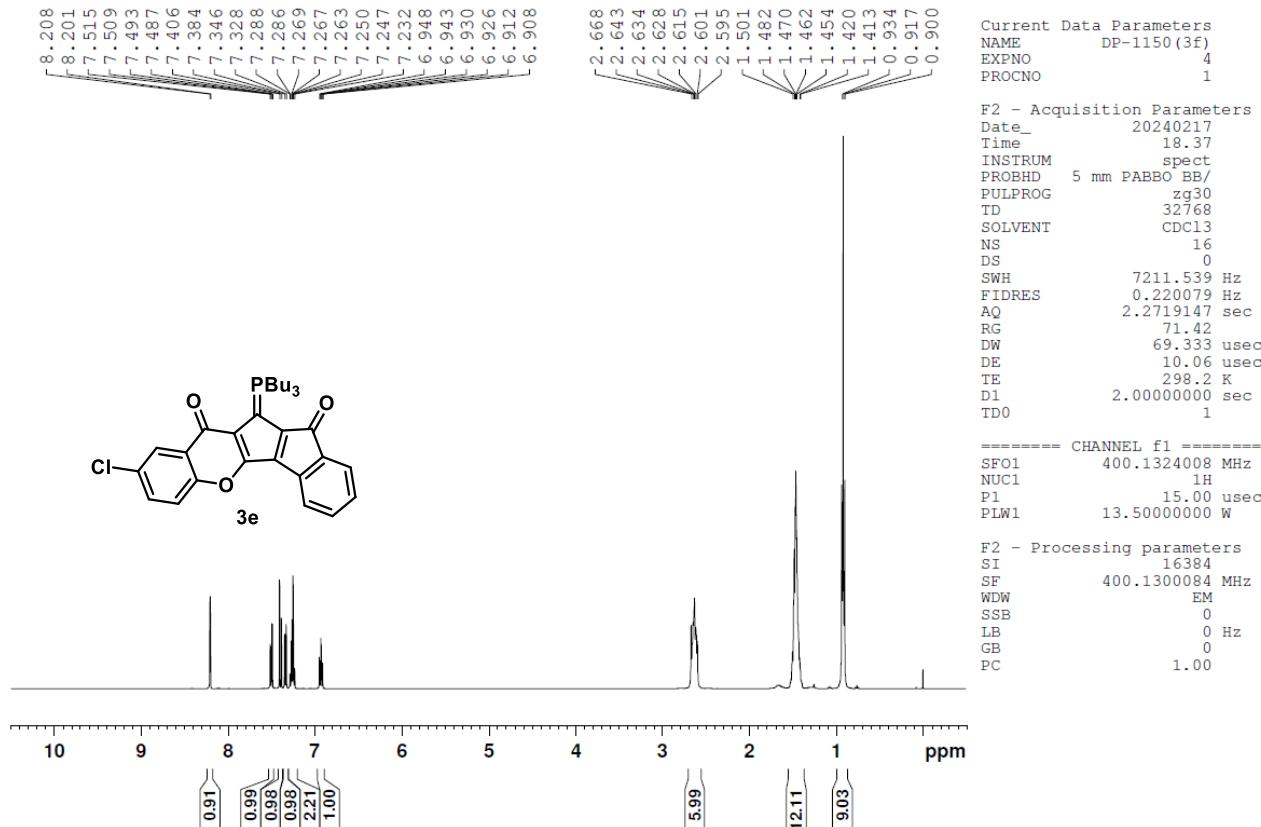
**<sup>31</sup>P NMR spectrum of compound 3d (CDCl<sub>3</sub>, 162 MHz)**



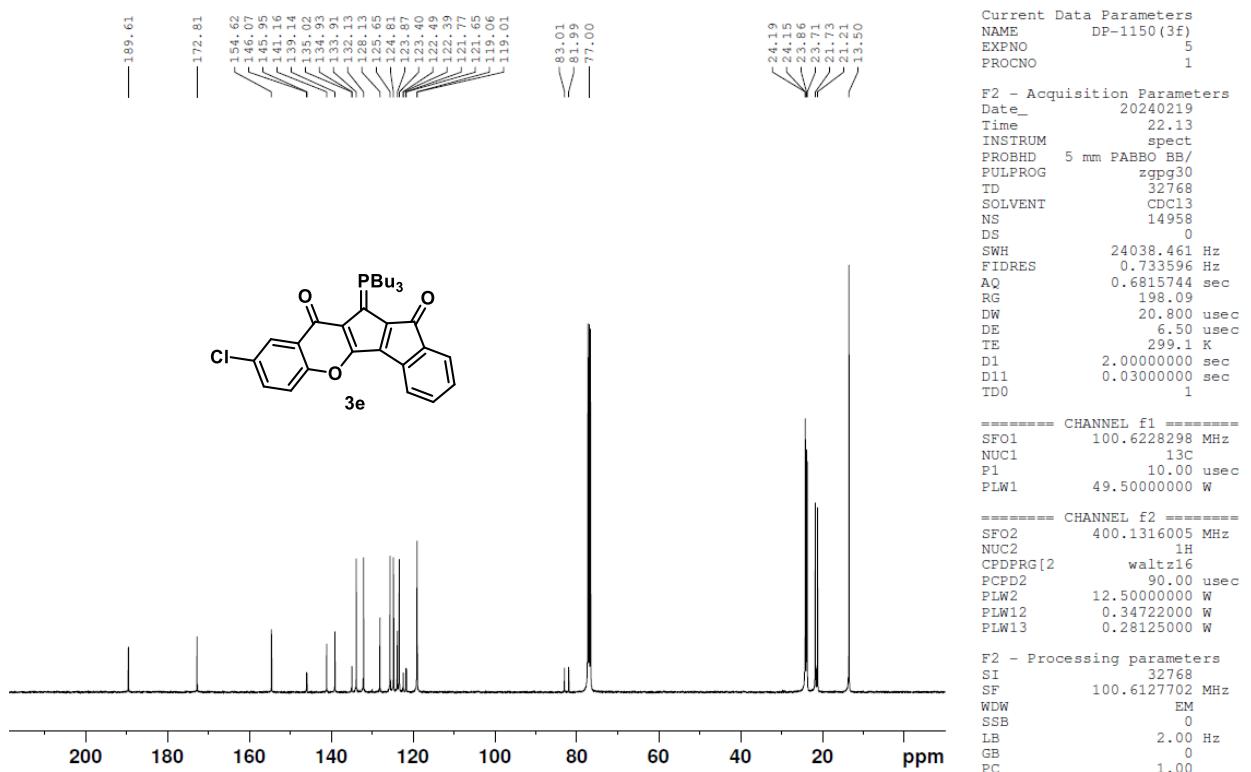
<sup>19</sup>F NMR spectrum of compound **3d** (CDCl<sub>3</sub>, 376 MHz)



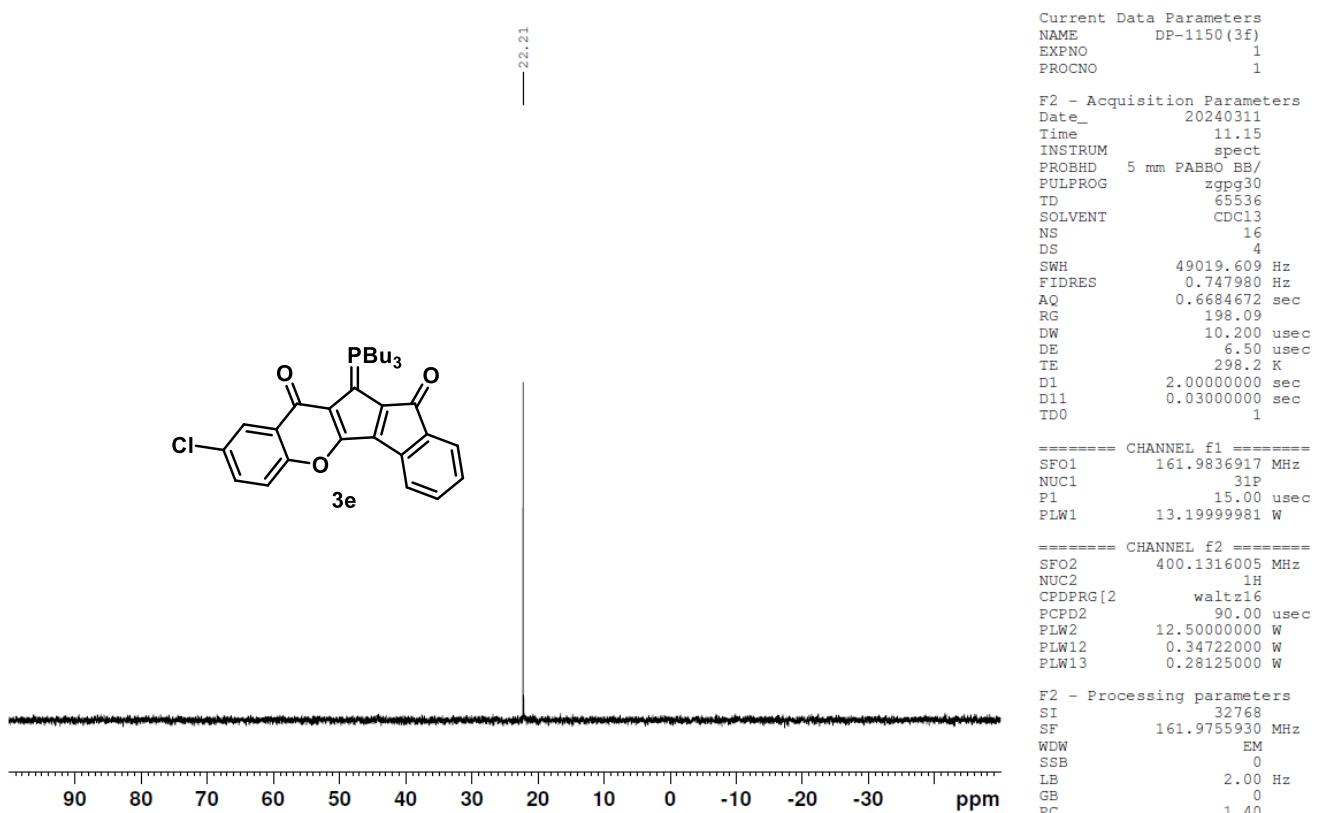
<sup>1</sup>H NMR spectrum of compound **3e** (CDCl<sub>3</sub>, 400 MHz)



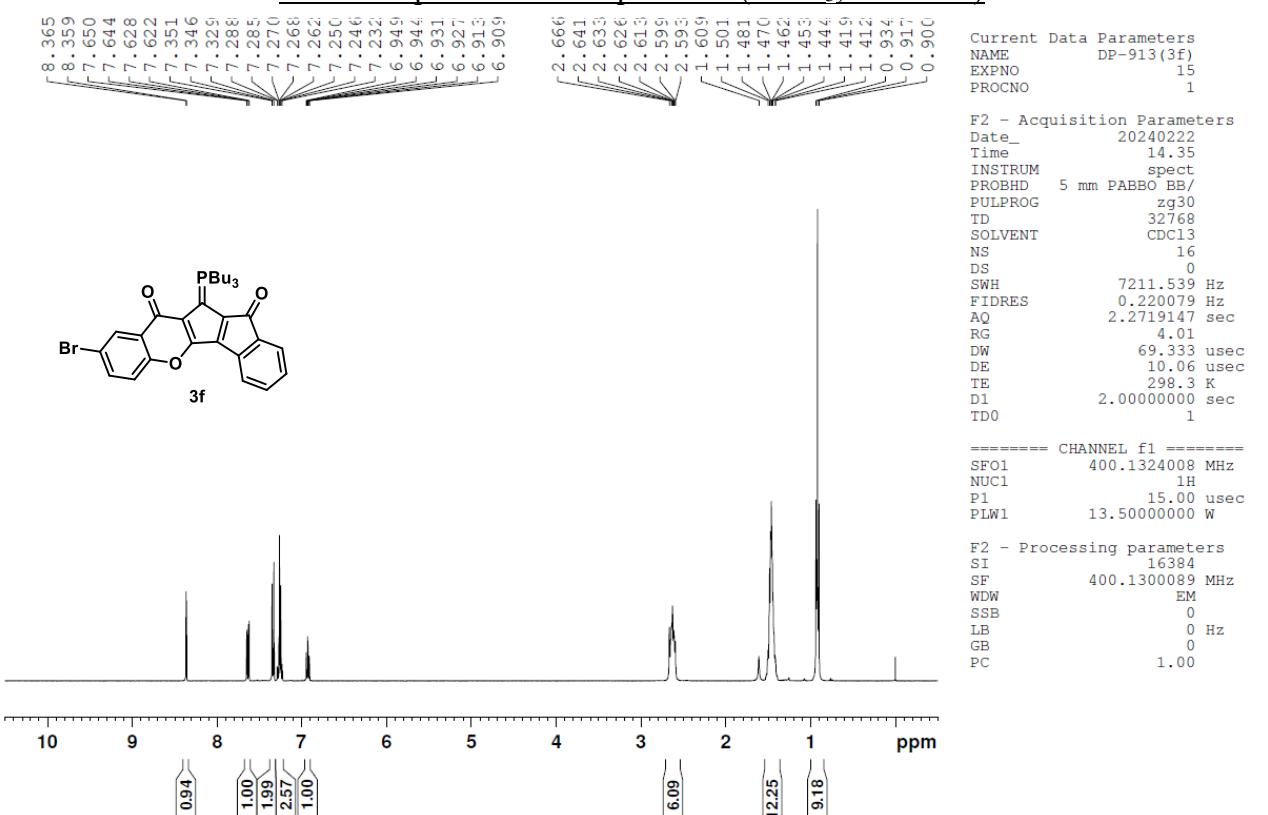
<sup>13</sup>C NMR spectrum of compound 3e (CDCl<sub>3</sub>, 100 MHz)



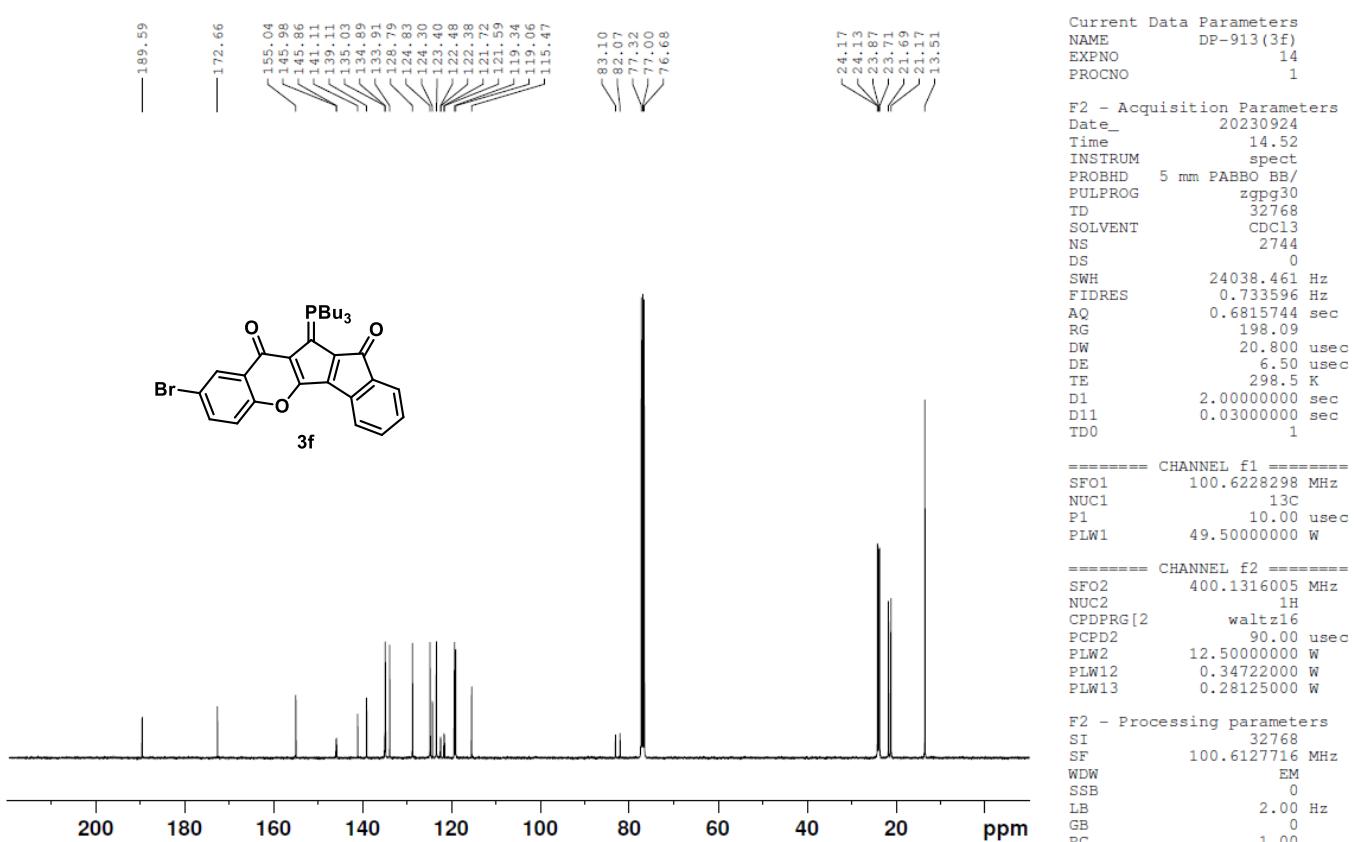
<sup>31</sup>P NMR spectrum of compound 3e (CDCl<sub>3</sub>, 162 MHz)



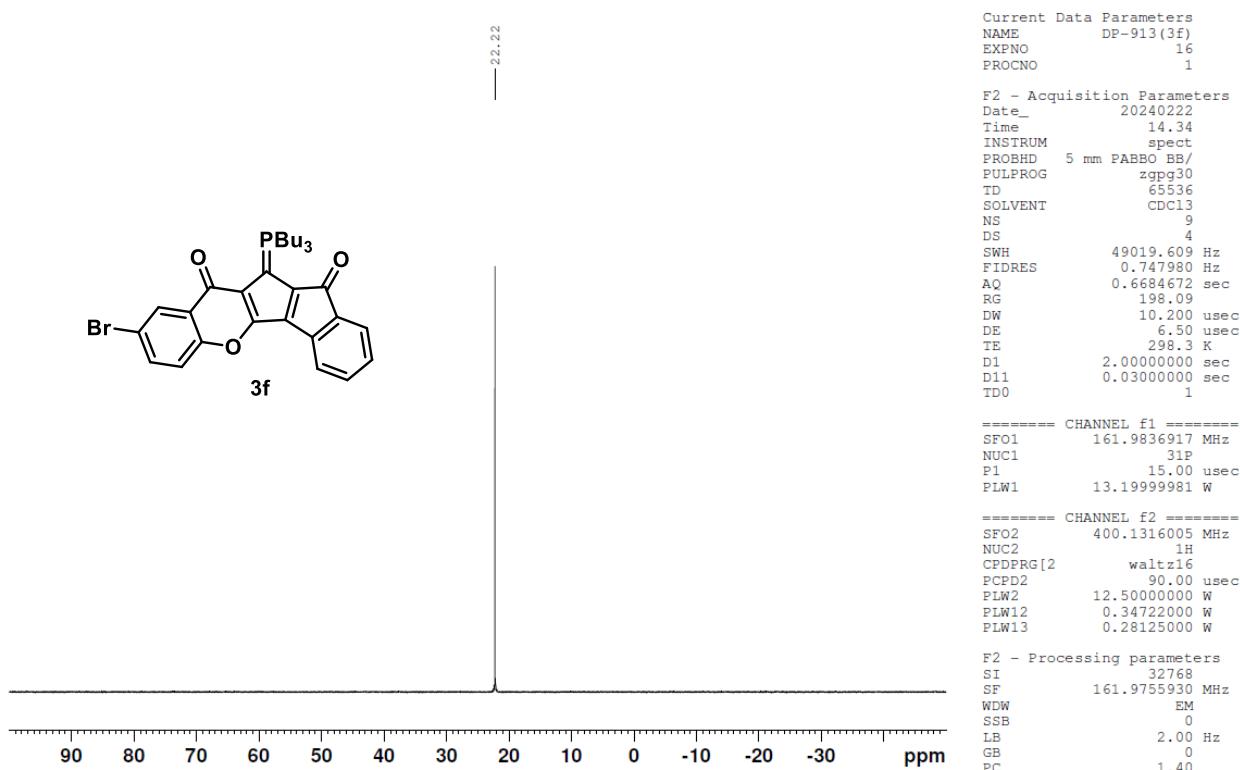
<sup>1</sup>H NMR spectrum of compound 3f (CDCl<sub>3</sub>, 400 MHz)



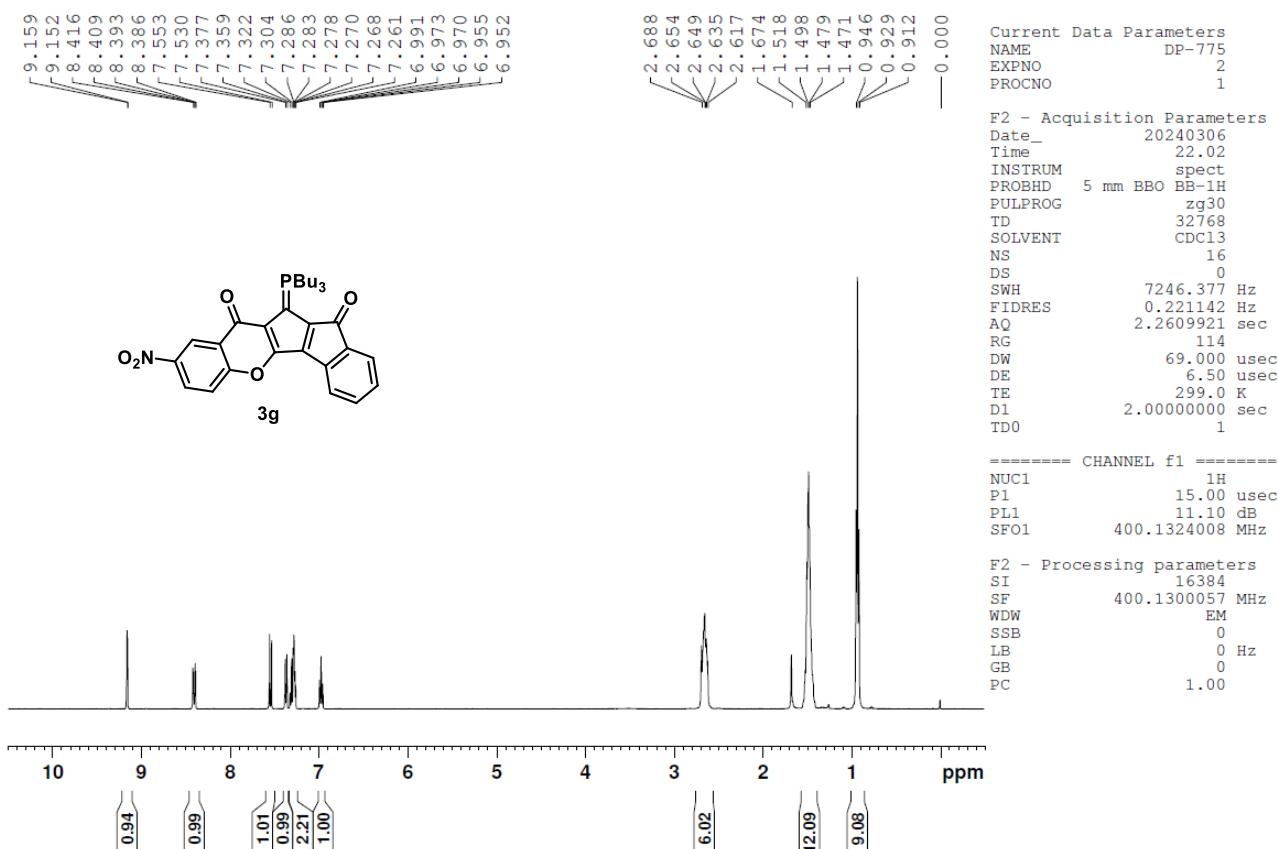
<sup>13</sup>C NMR spectrum of compound 3f (CDCl<sub>3</sub>, 100 MHz)



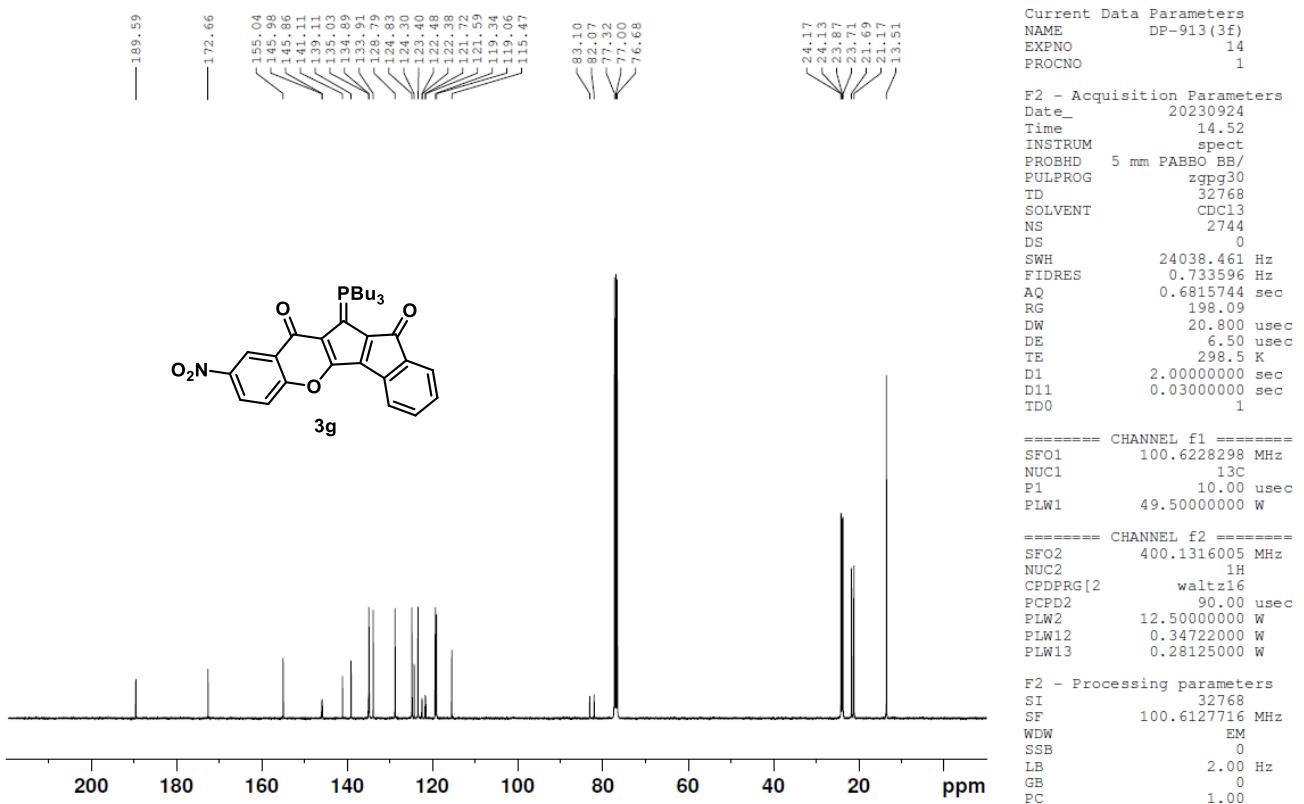
<sup>31</sup>P NMR spectrum of compound **3f** (CDCl<sub>3</sub>, 162 MHz)



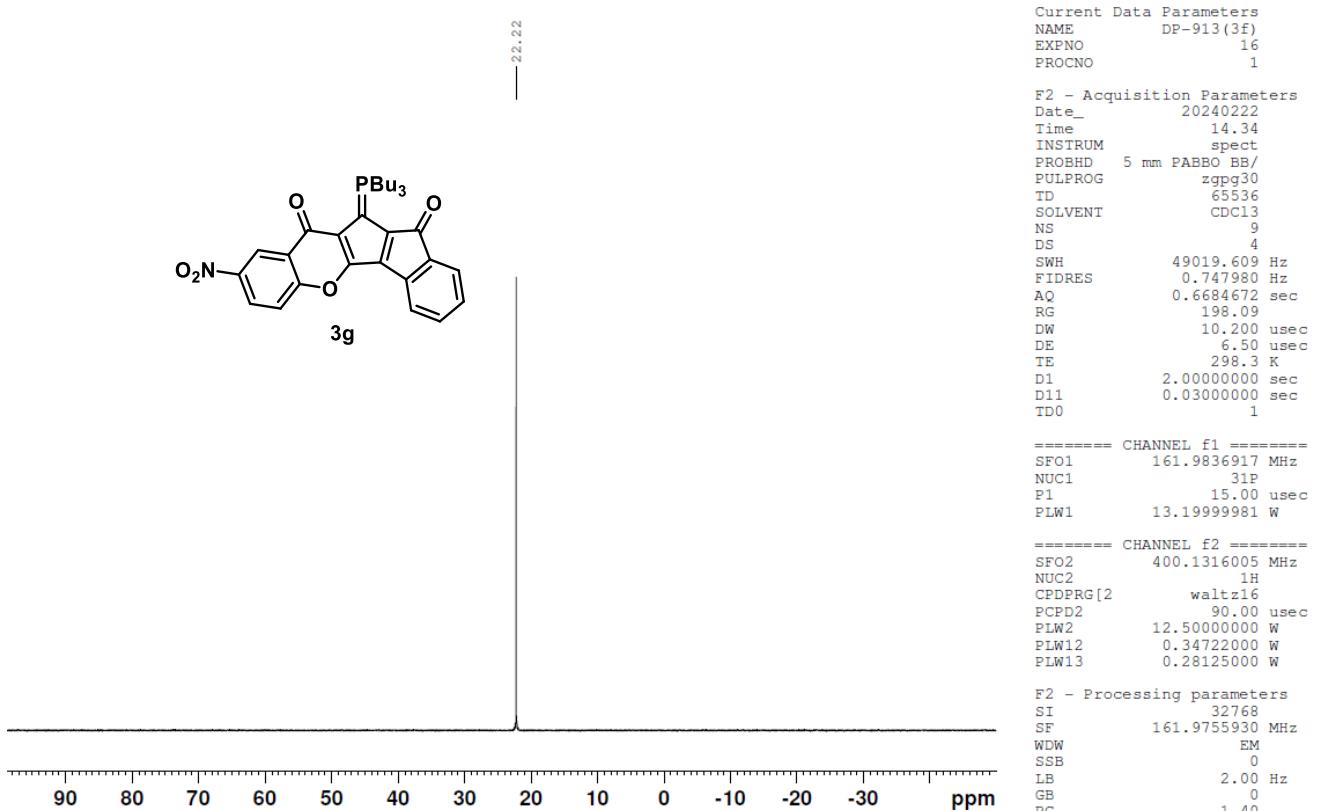
<sup>1</sup>H NMR spectrum of compound **3g** (CDCl<sub>3</sub>, 400 MHz)



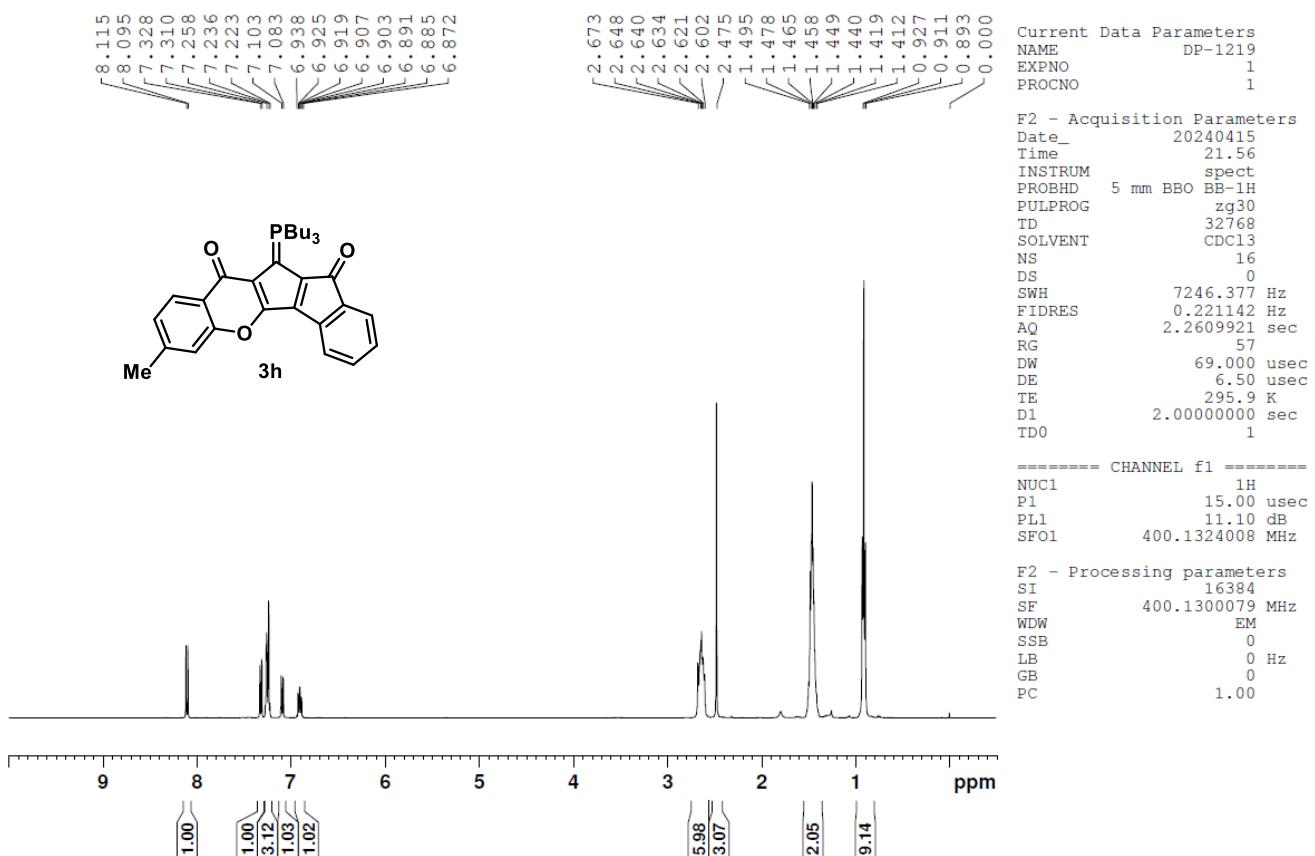
<sup>13</sup>C NMR spectrum of compound 3g (CDCl<sub>3</sub>, 100 MHz)



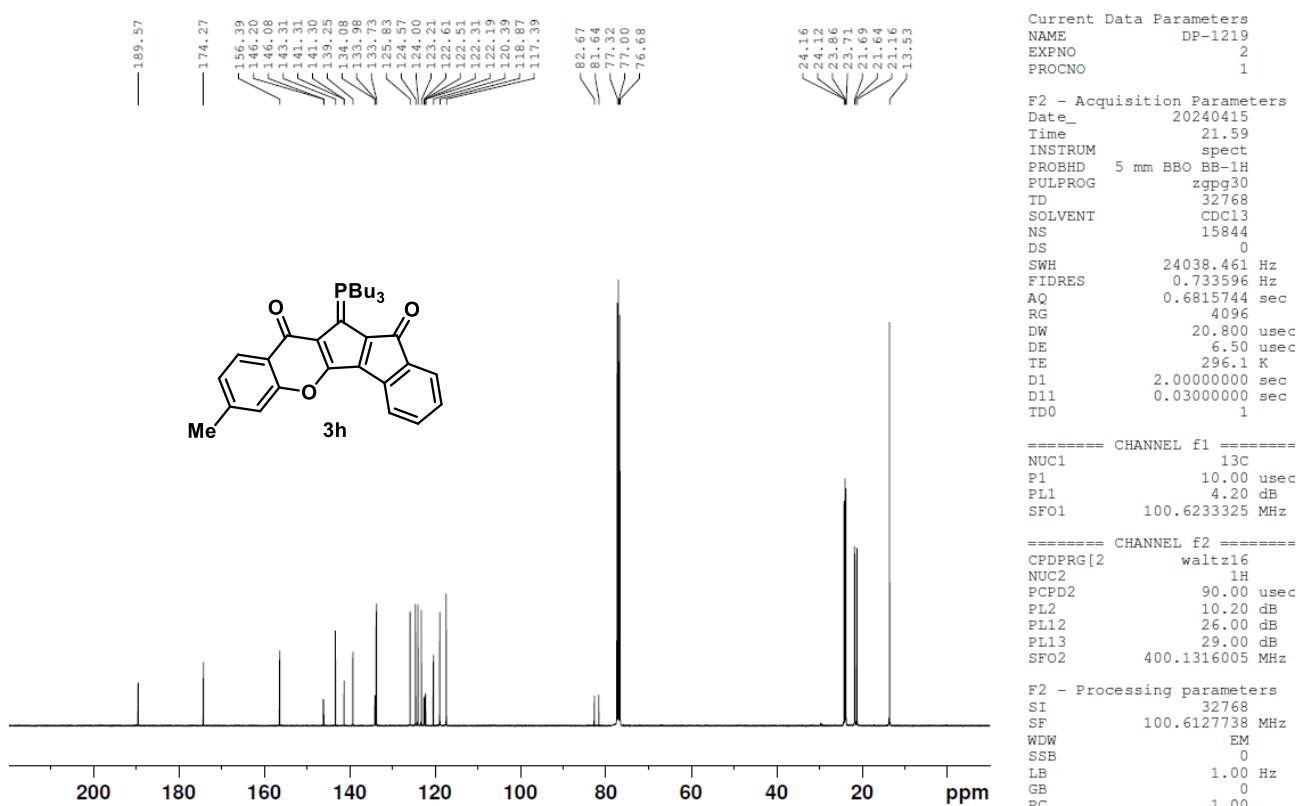
<sup>31</sup>P NMR spectrum of compound 3g (CDCl<sub>3</sub>, 162 MHz)



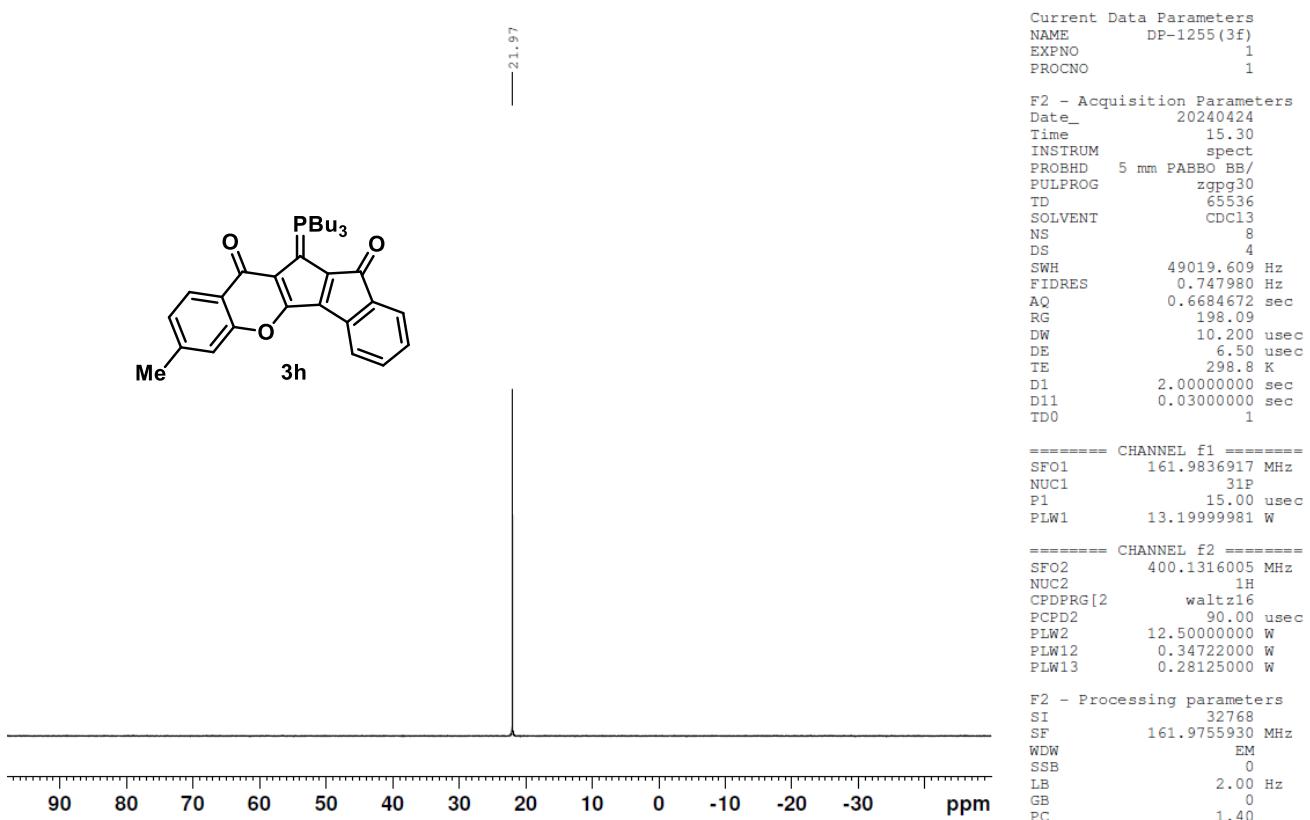
<sup>1</sup>H NMR spectrum of compound 3h (CDCl<sub>3</sub>, 400 MHz)



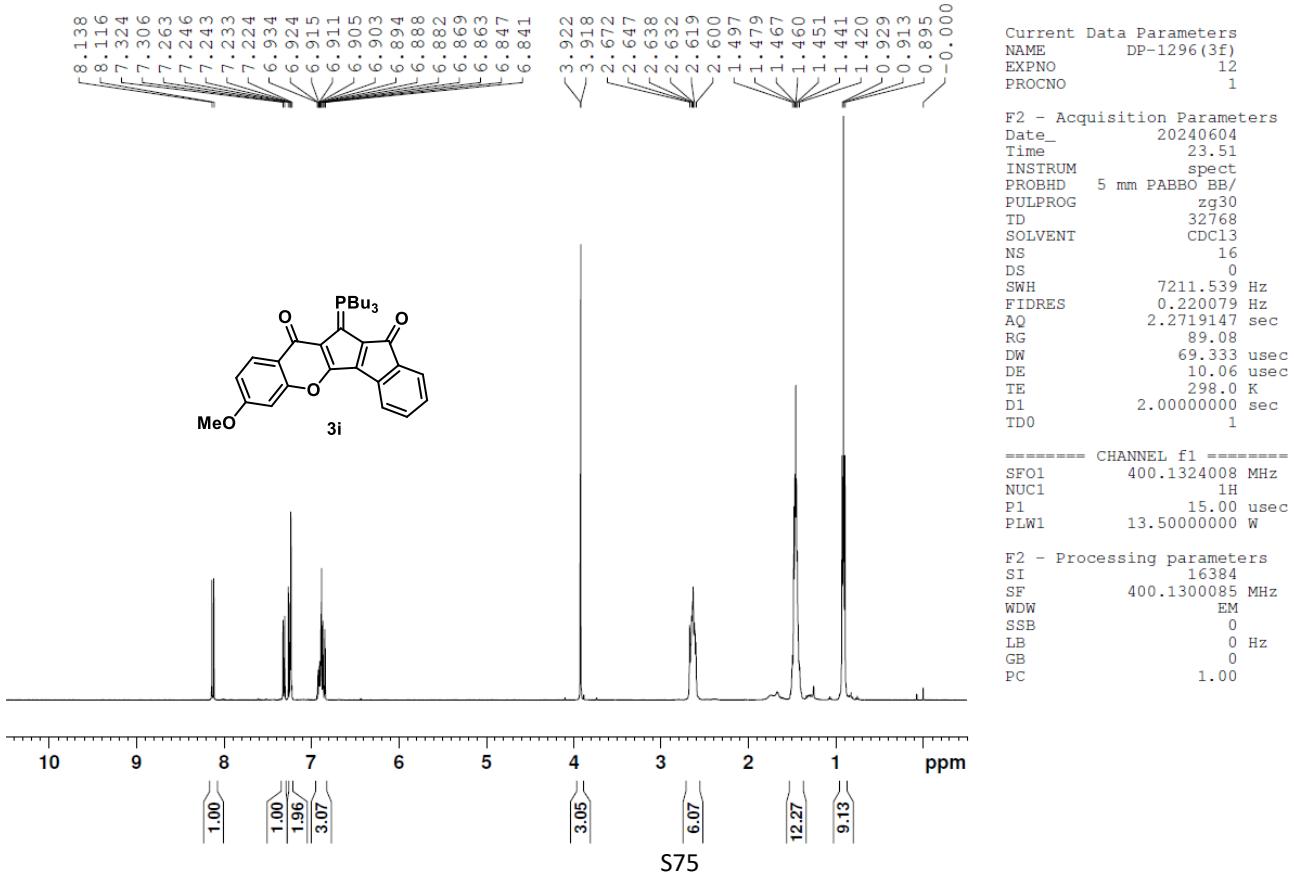
<sup>13</sup>C NMR spectrum of compound 3h (CDCl<sub>3</sub>, 100 MHz)



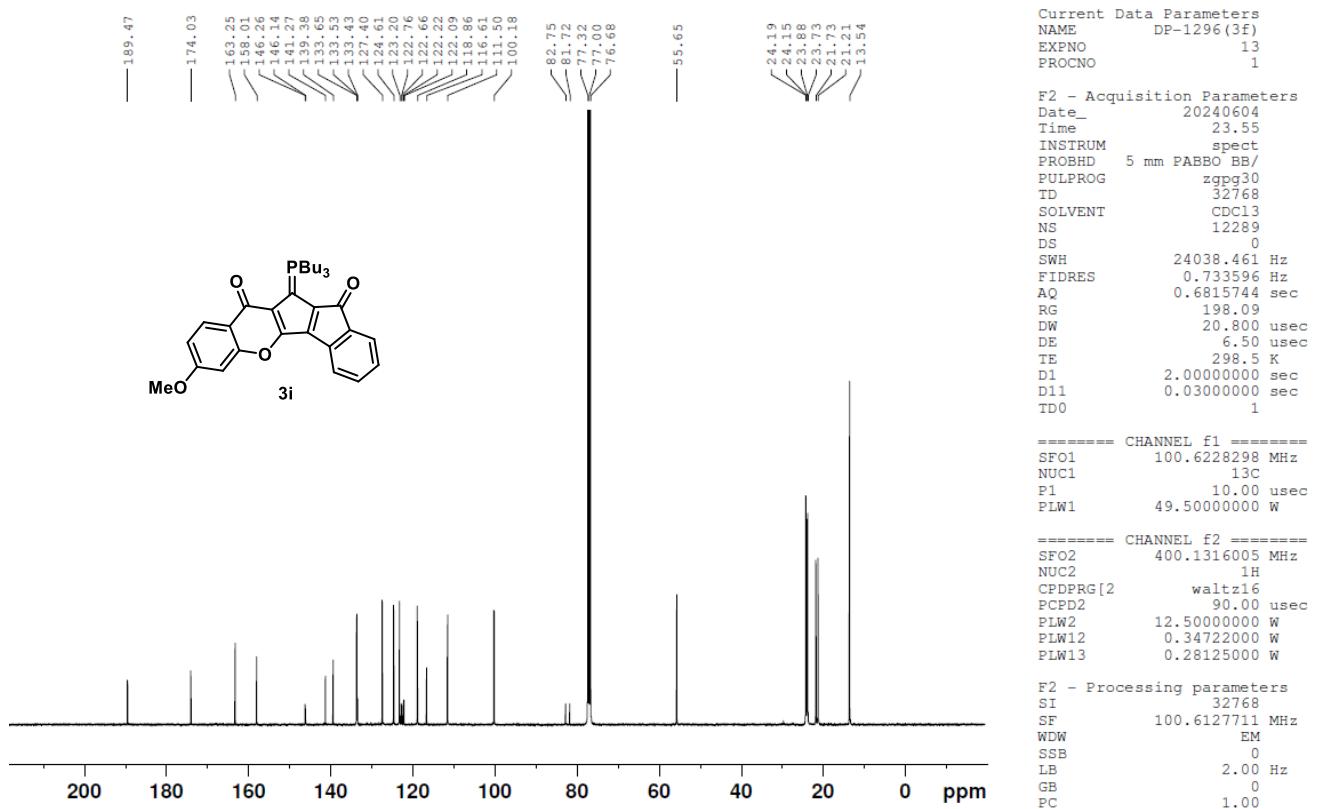
<sup>31</sup>P NMR spectrum of compound 3h (CDCl<sub>3</sub>, 162 MHz)



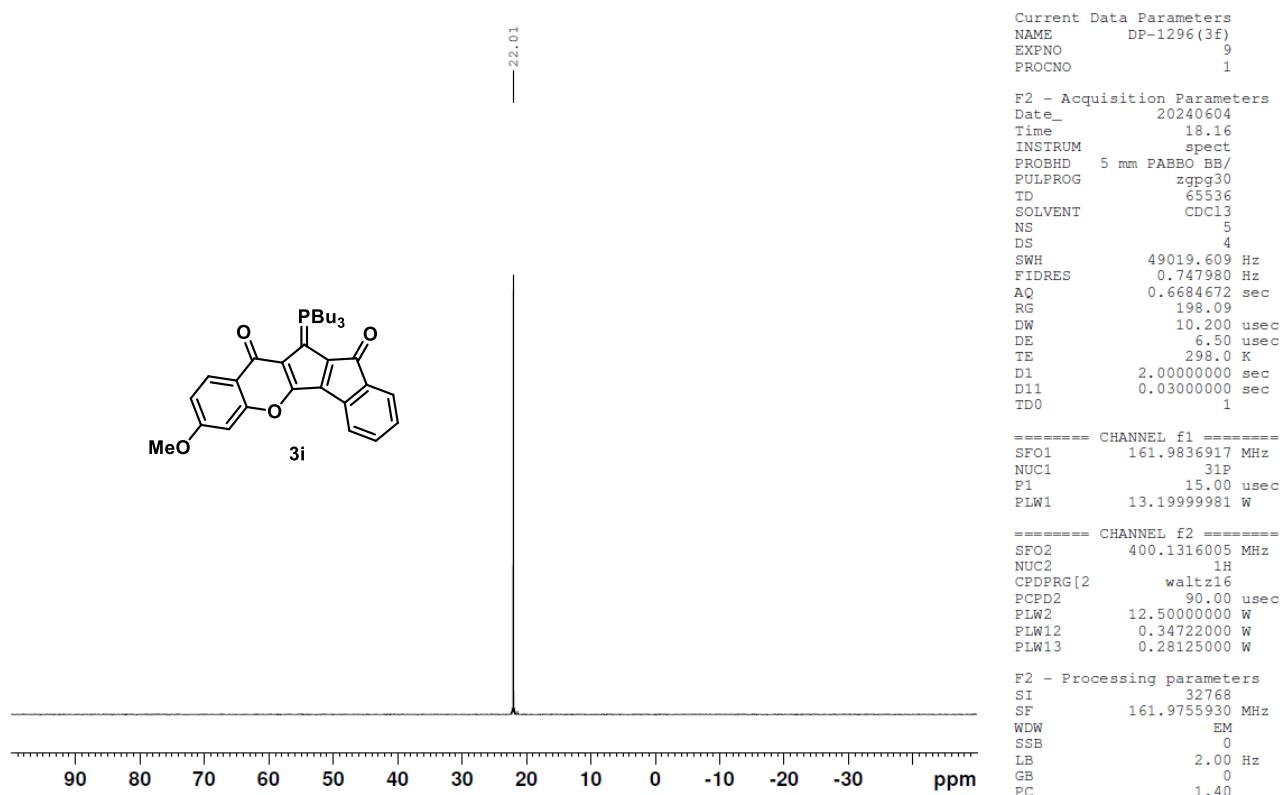
<sup>1</sup>H NMR spectrum of compound 3i (CDCl<sub>3</sub>, 400 MHz)



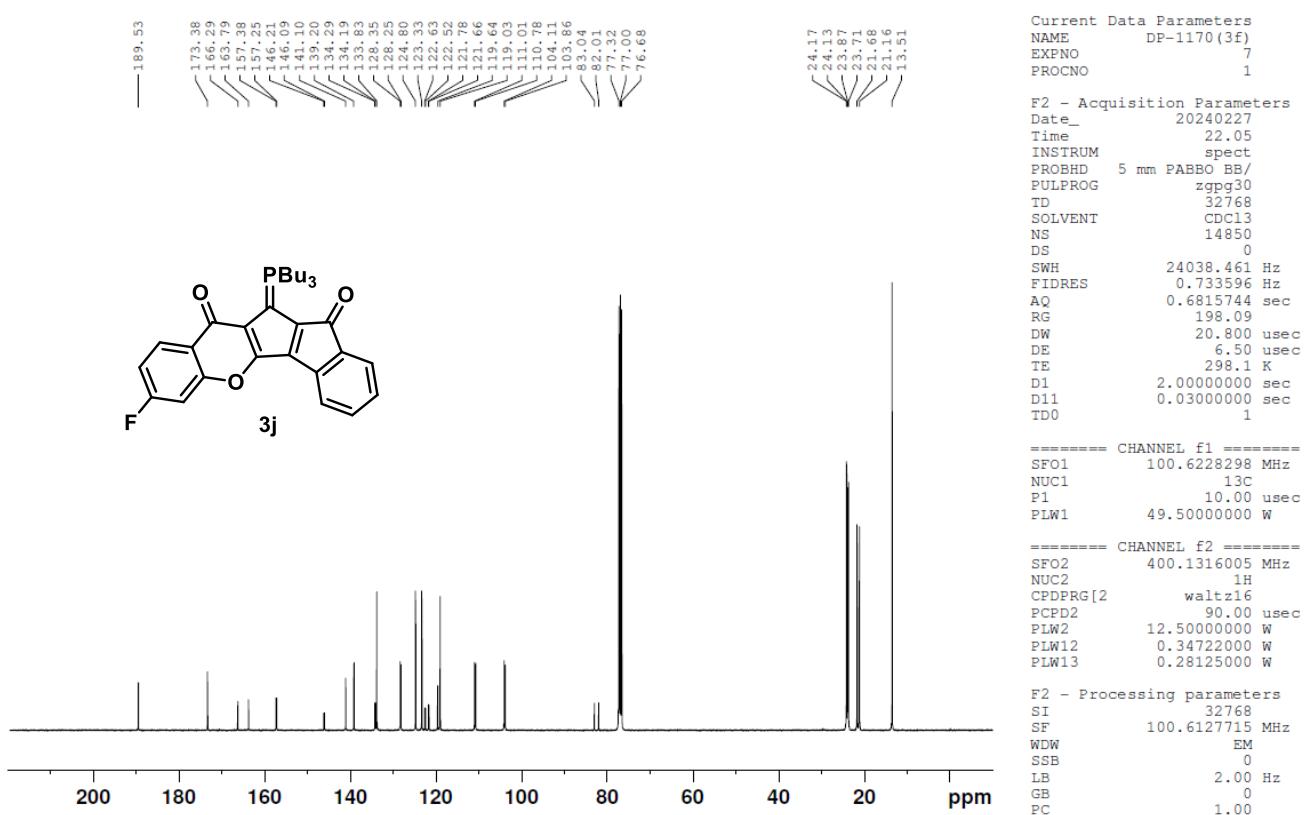
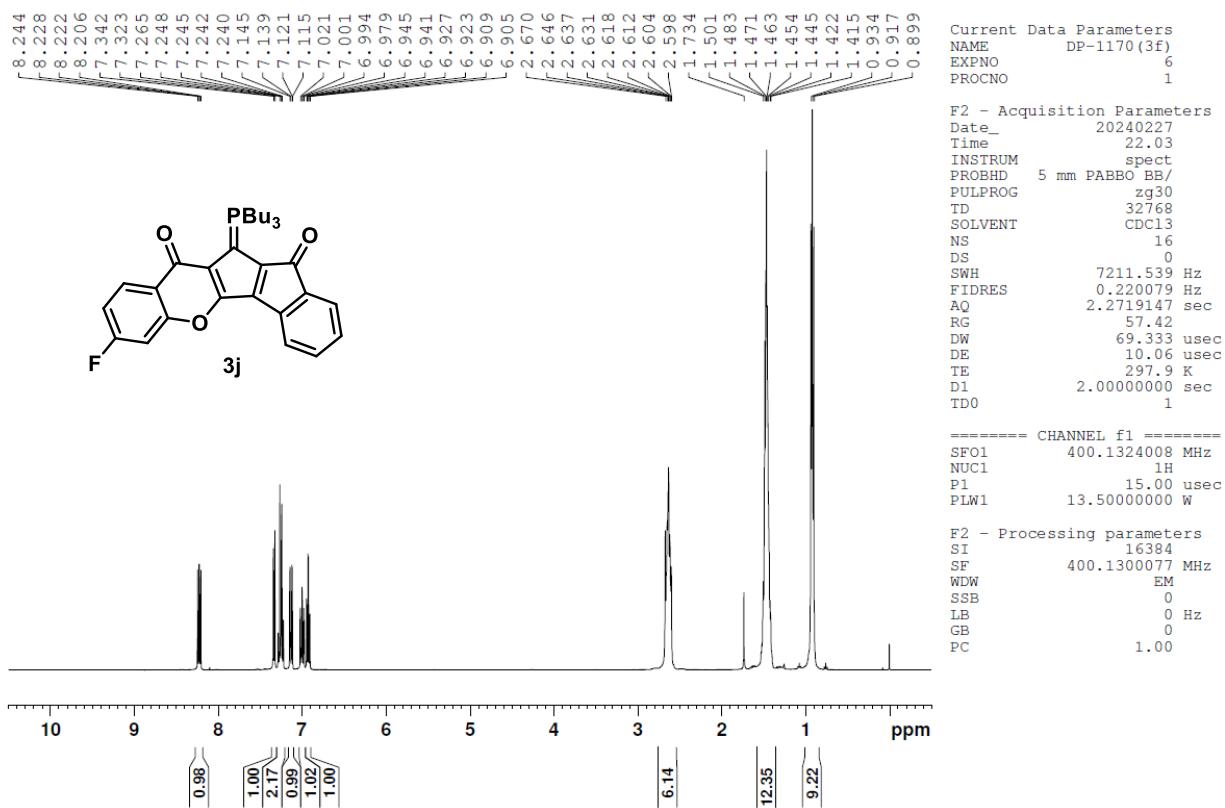
<sup>13</sup>C NMR spectrum of compound 3i (CDCl<sub>3</sub>, 100 MHz)



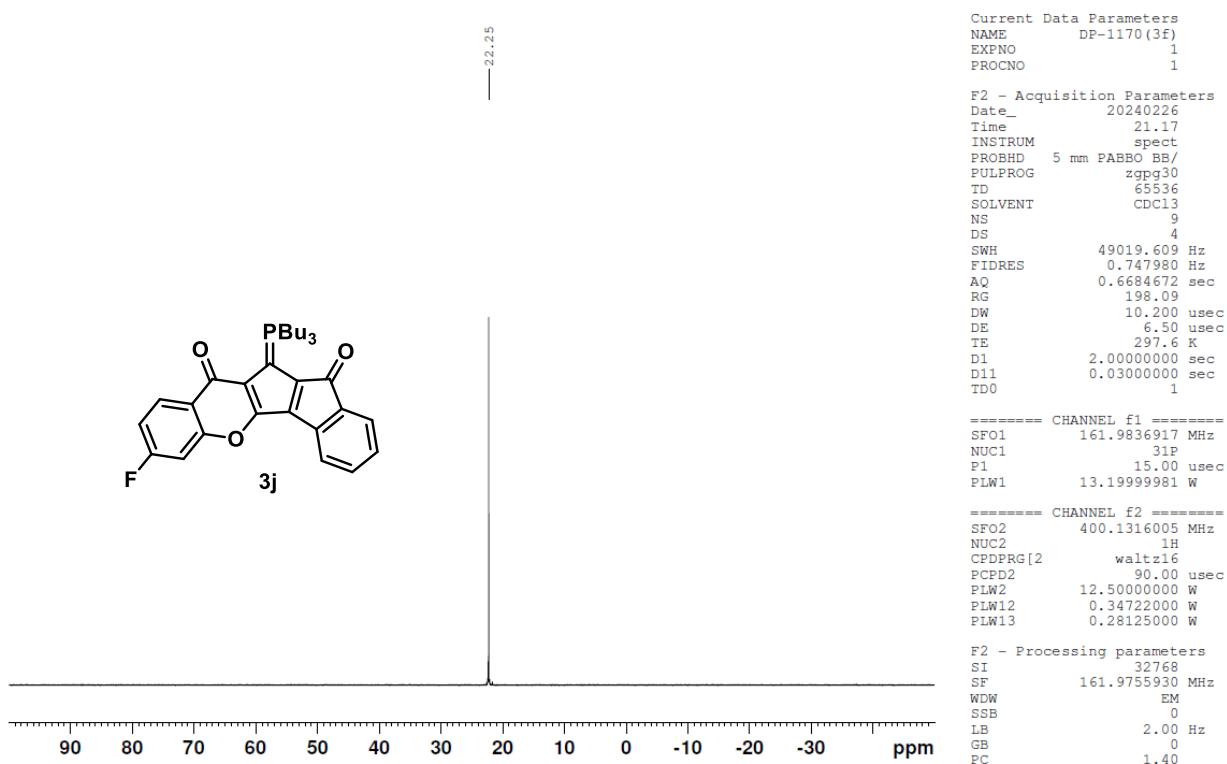
<sup>31</sup>P NMR spectrum of compound 3i (CDCl<sub>3</sub>, 162 MHz)



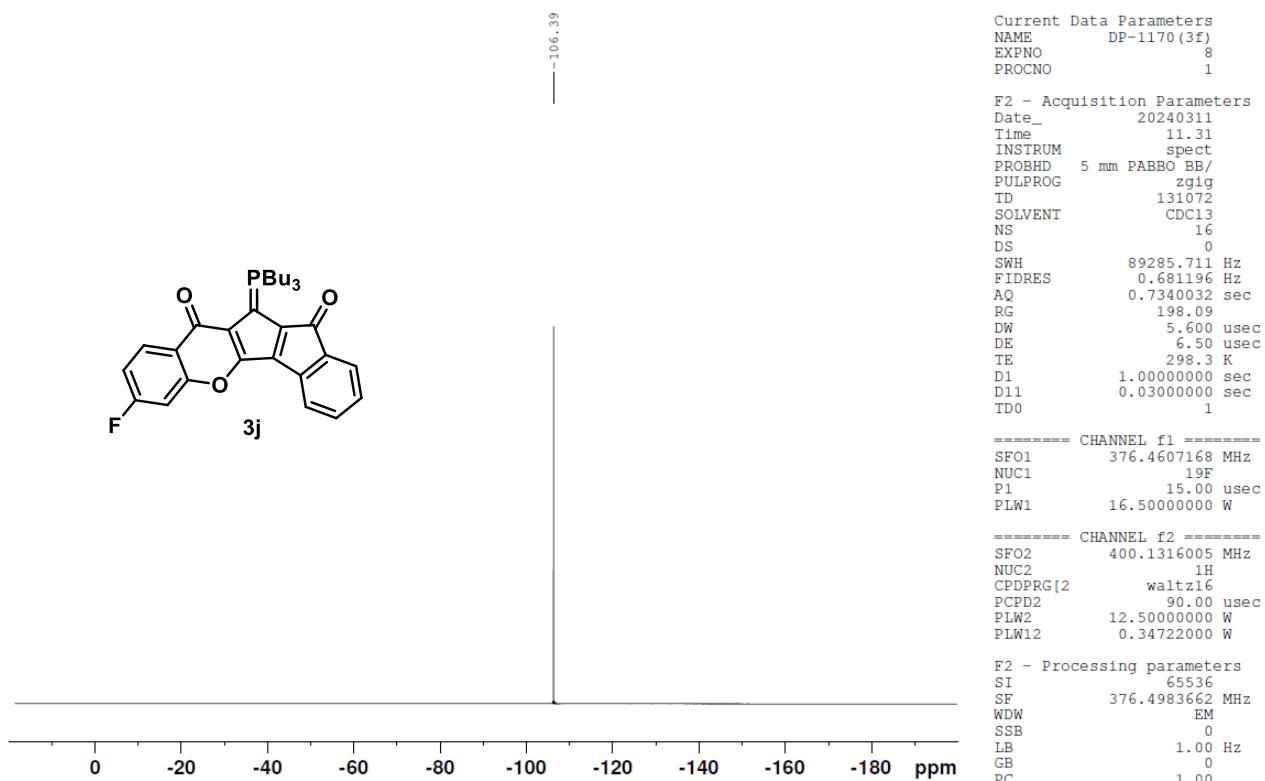
<sup>1</sup>H NMR spectrum of compound 3j (CDCl<sub>3</sub>, 400 MHz)



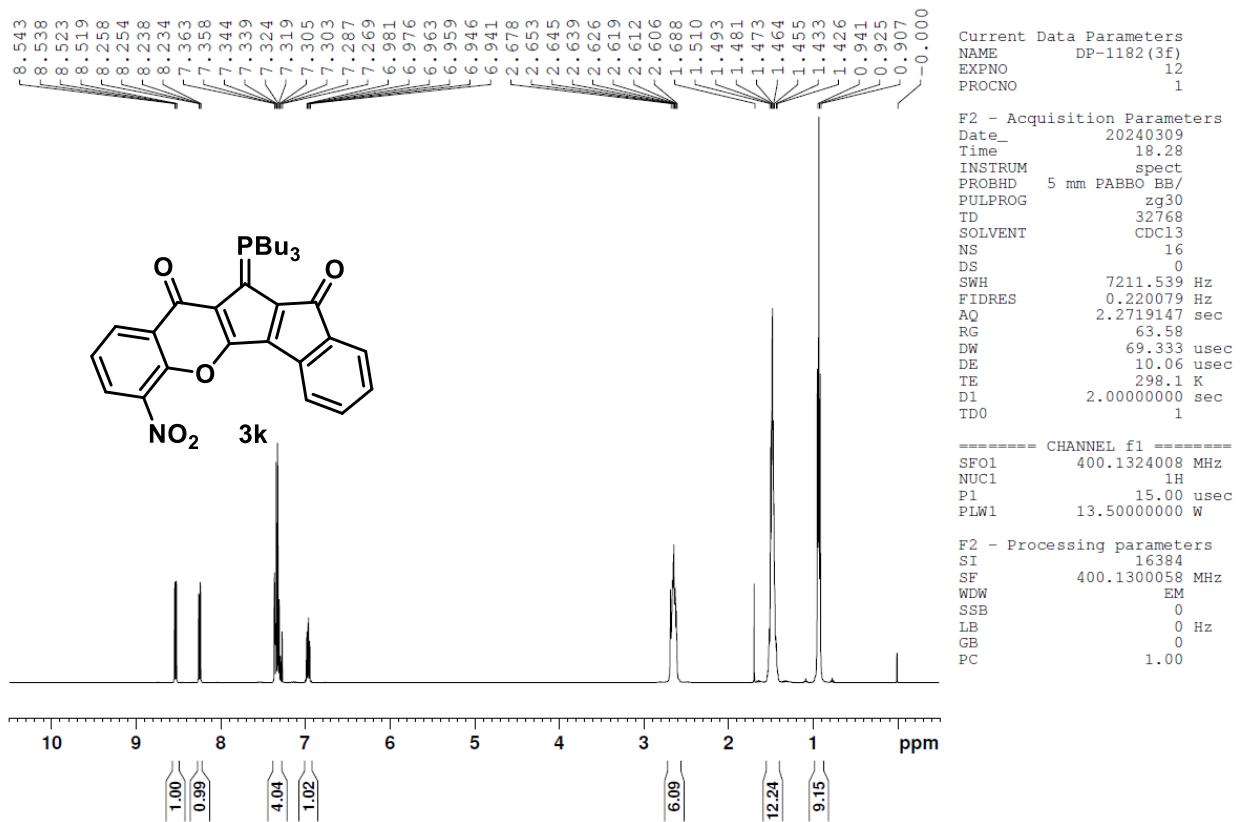
<sup>31</sup>P NMR spectrum of compound 3j (CDCl<sub>3</sub>, 162 MHz)



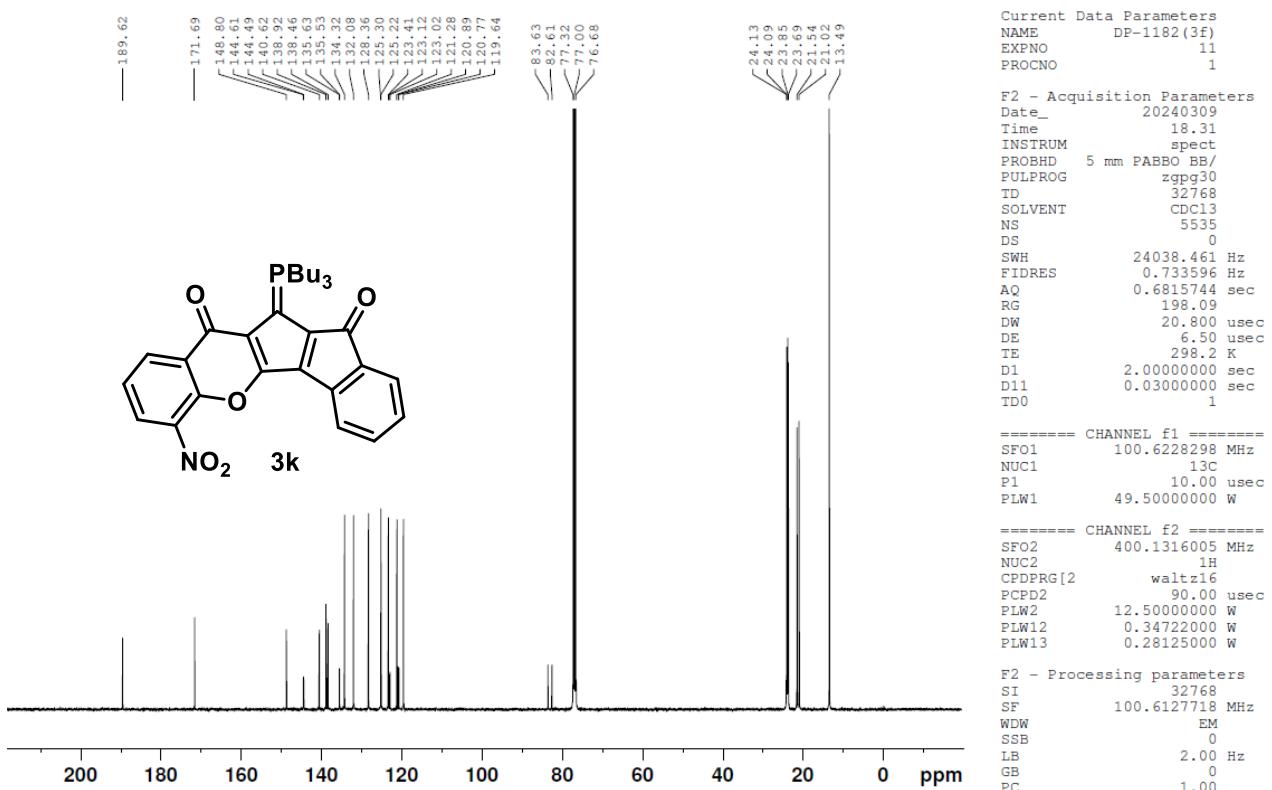
<sup>19</sup>F NMR spectrum of compound 3j (CDCl<sub>3</sub>, 376 MHz)



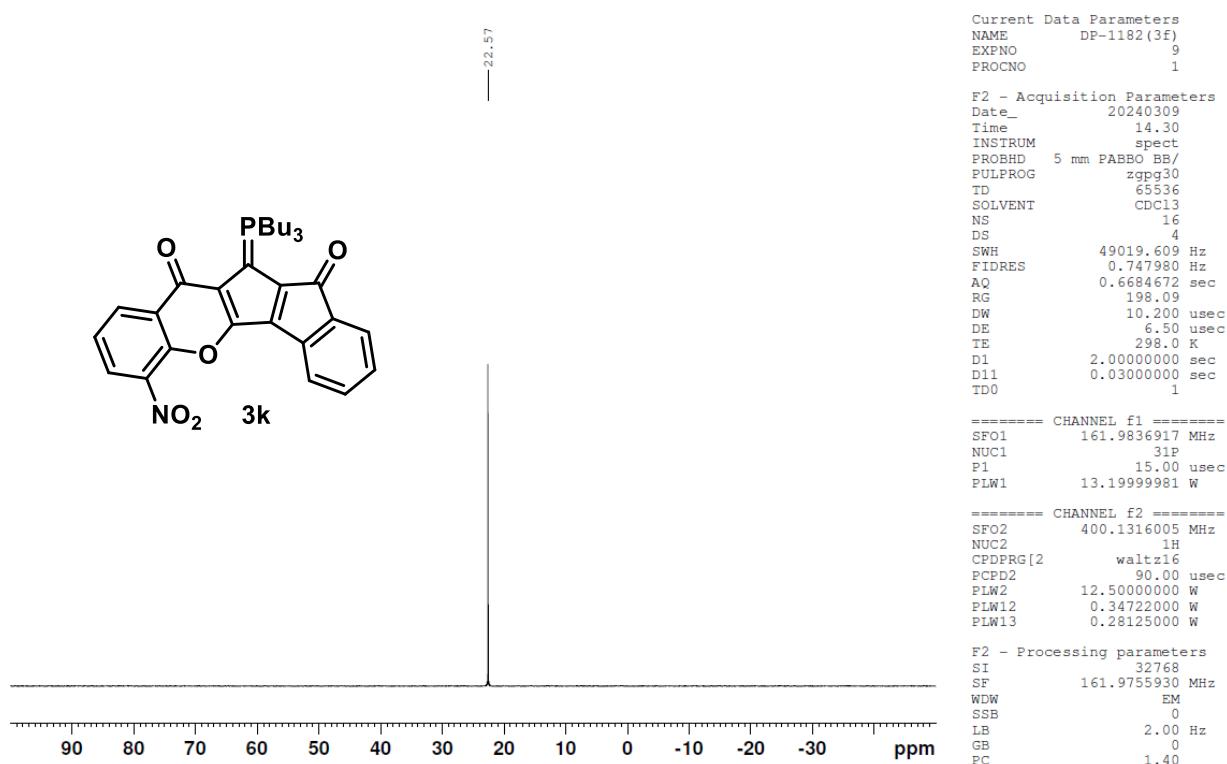
<sup>1</sup>H NMR spectrum of compound 3k (CDCl<sub>3</sub>, 400 MHz)



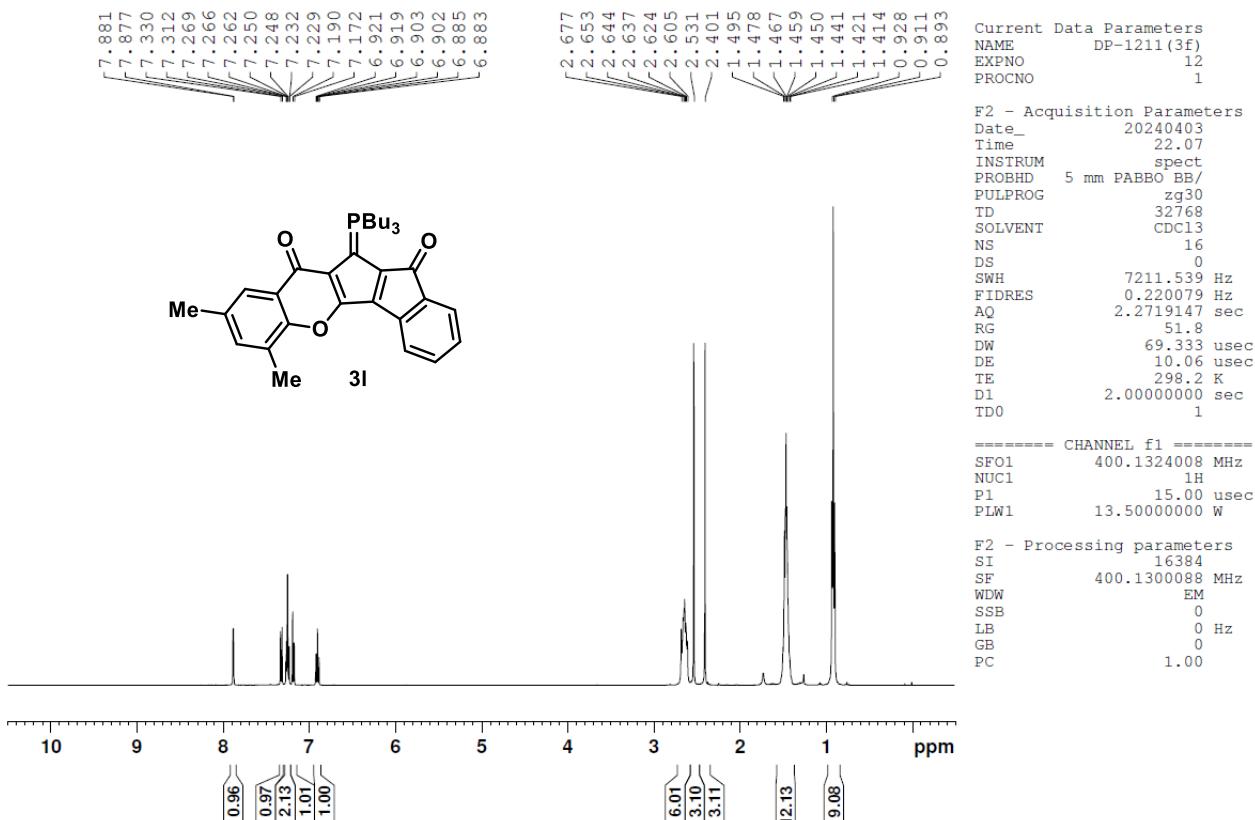
<sup>13</sup>C NMR spectrum of compound 3k (CDCl<sub>3</sub>, 100 MHz)



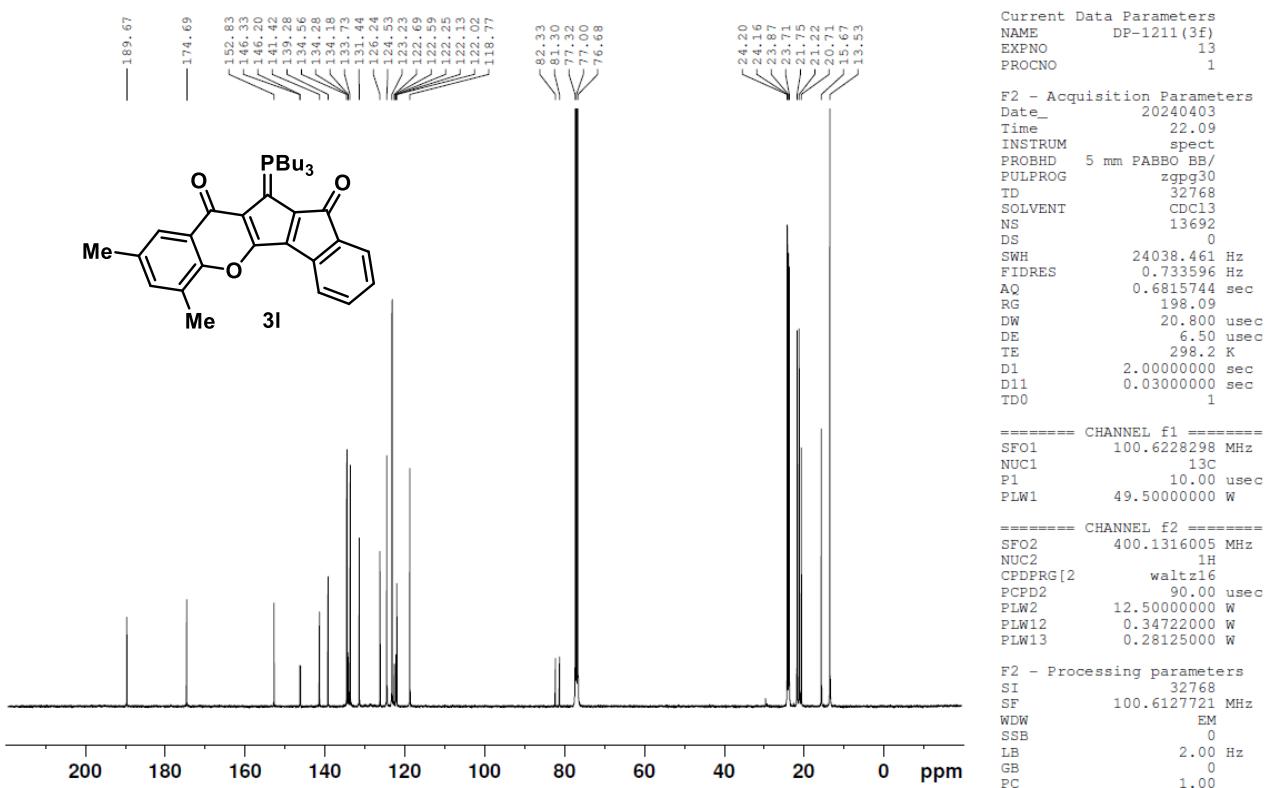
<sup>31</sup>P NMR spectrum of compound **3k** (CDCl<sub>3</sub>, 162 MHz)



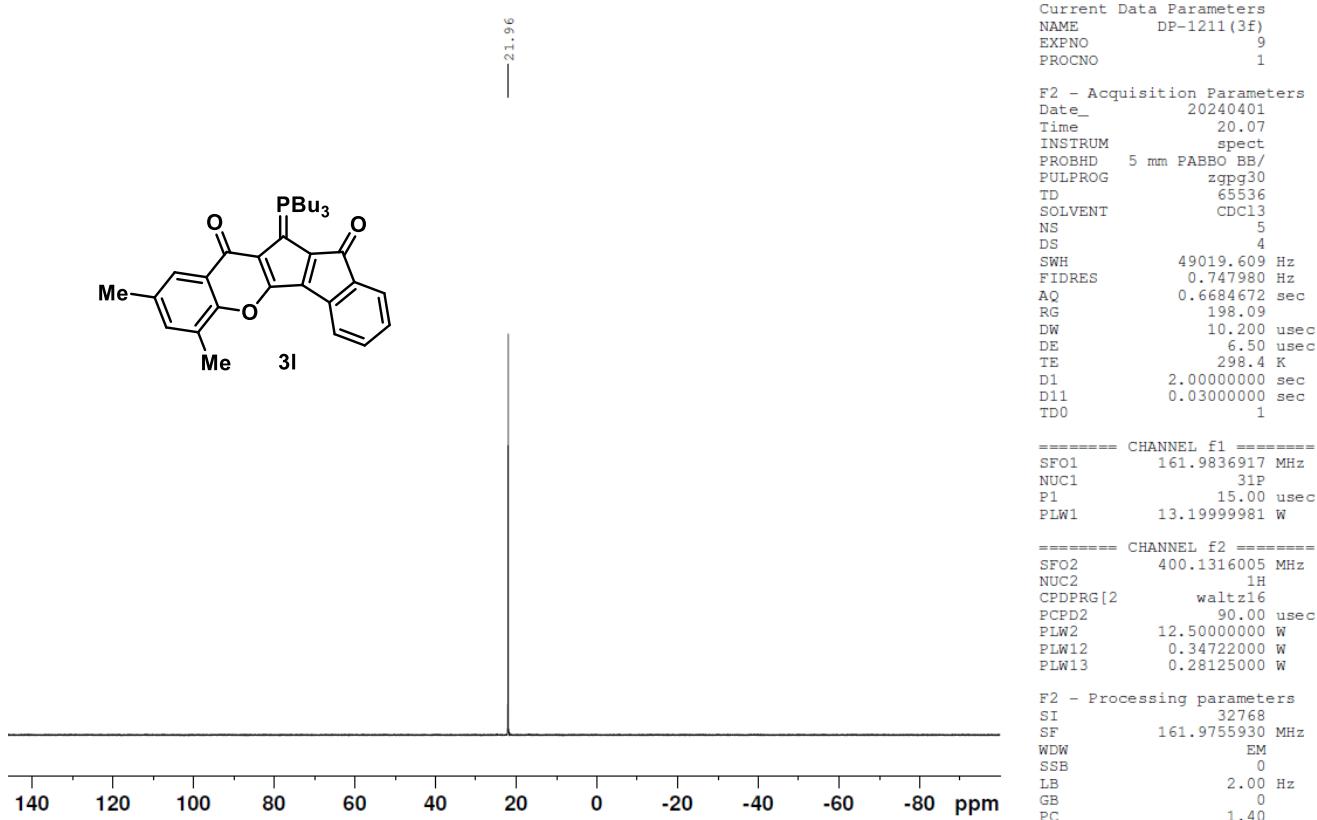
<sup>1</sup>H NMR spectrum of compound **3l** (CDCl<sub>3</sub>, 400 MHz)



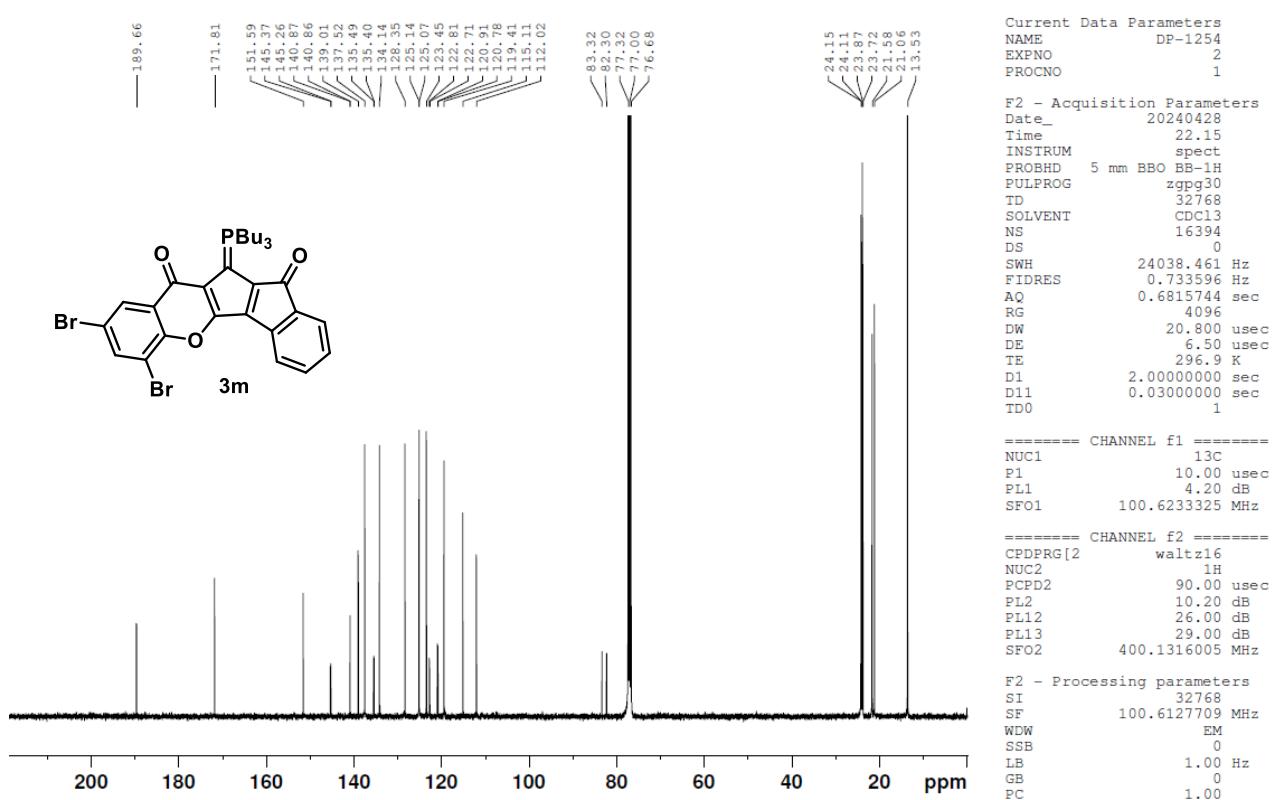
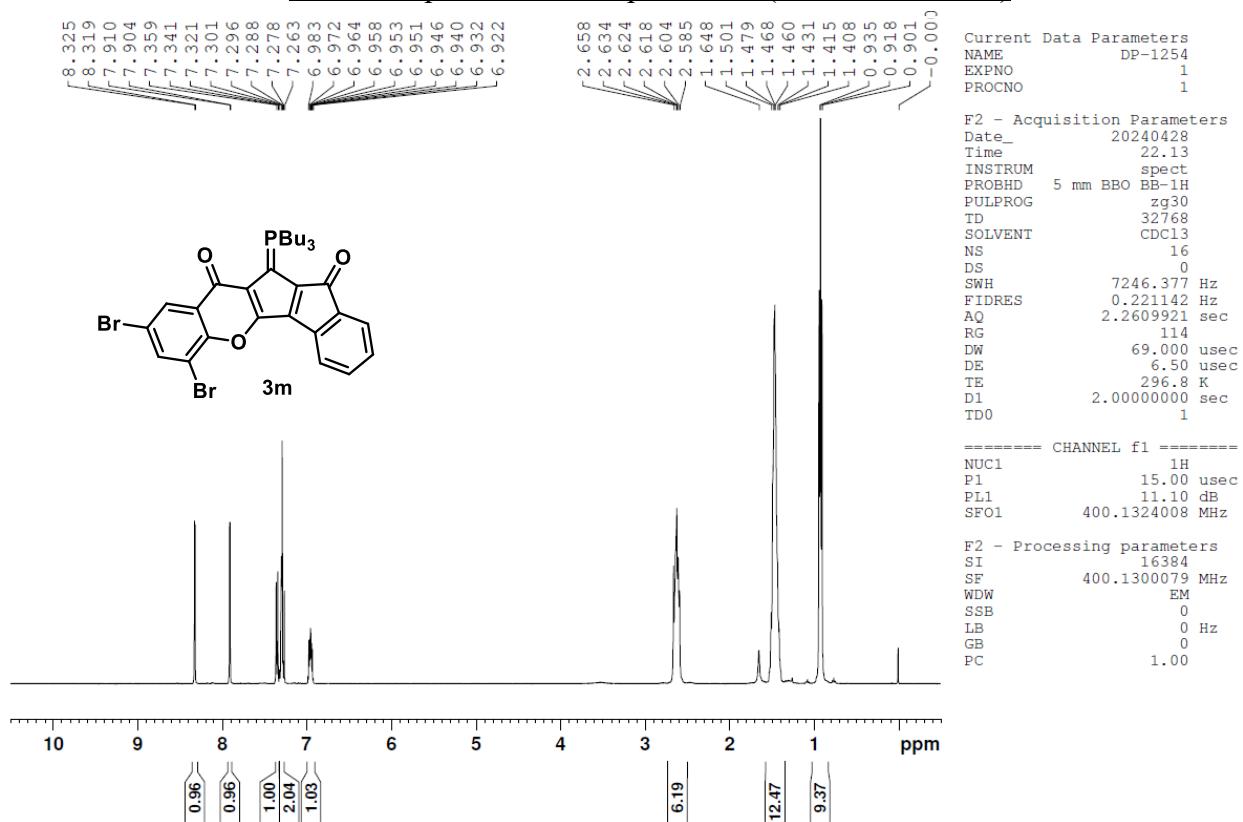
<sup>13</sup>C NMR spectrum of compound 3I (CDCl<sub>3</sub>, 100 MHz)



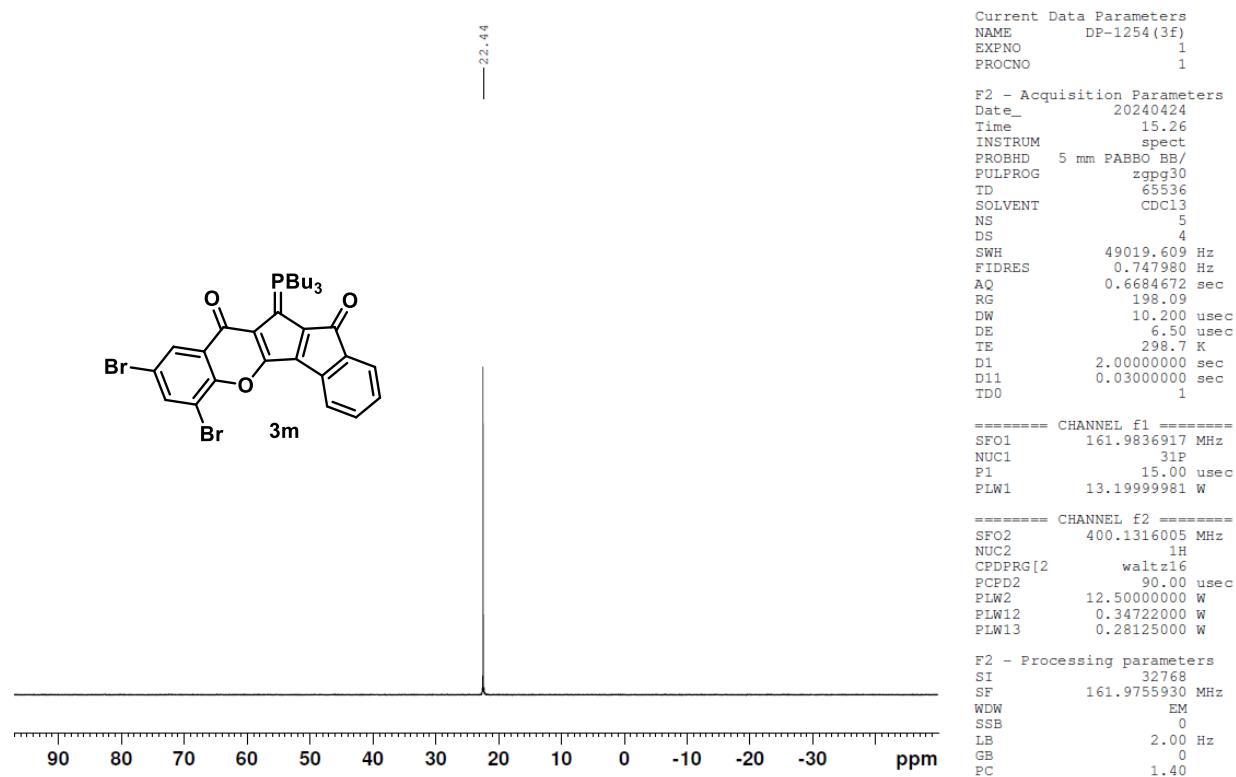
<sup>31</sup>P NMR spectrum of compound 3I (CDCl<sub>3</sub>, 162 MHz)



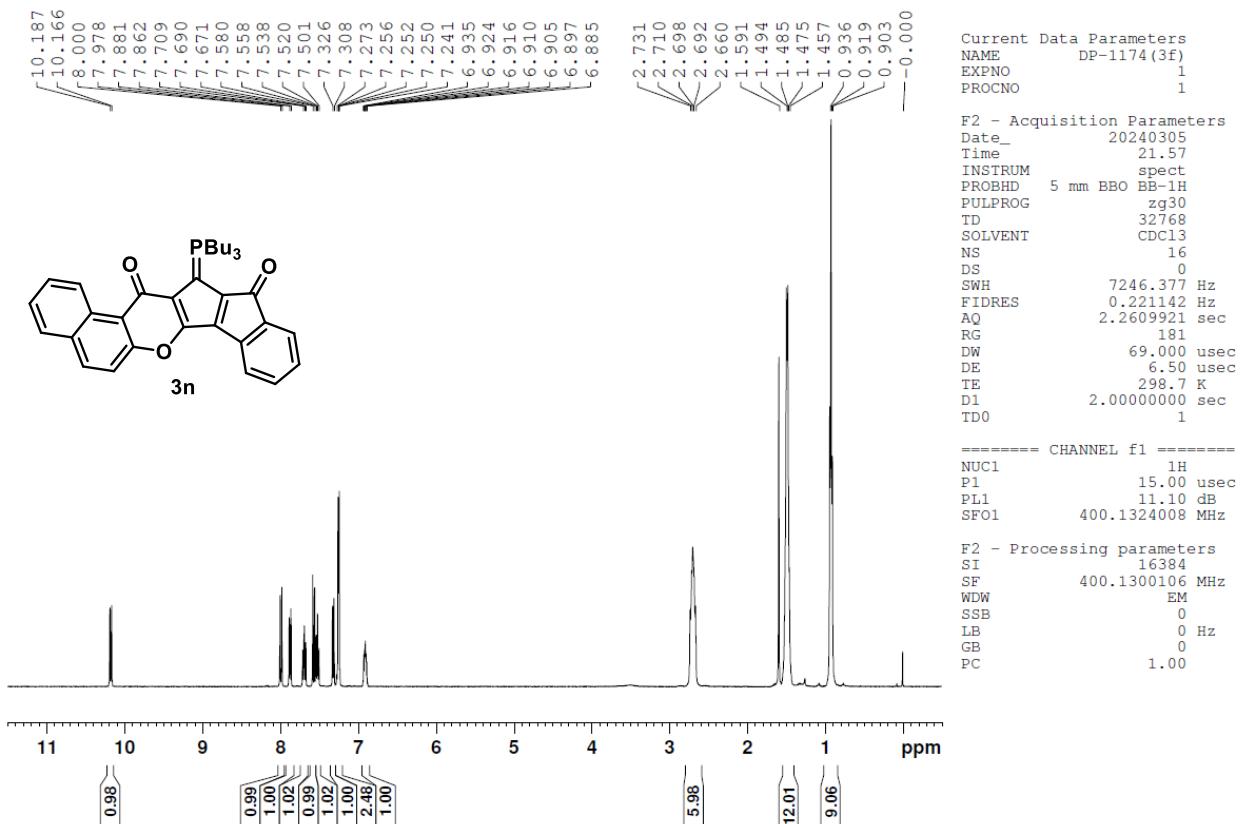
<sup>1</sup>H NMR spectrum of compound 3m (CDCl<sub>3</sub>, 400 MHz)



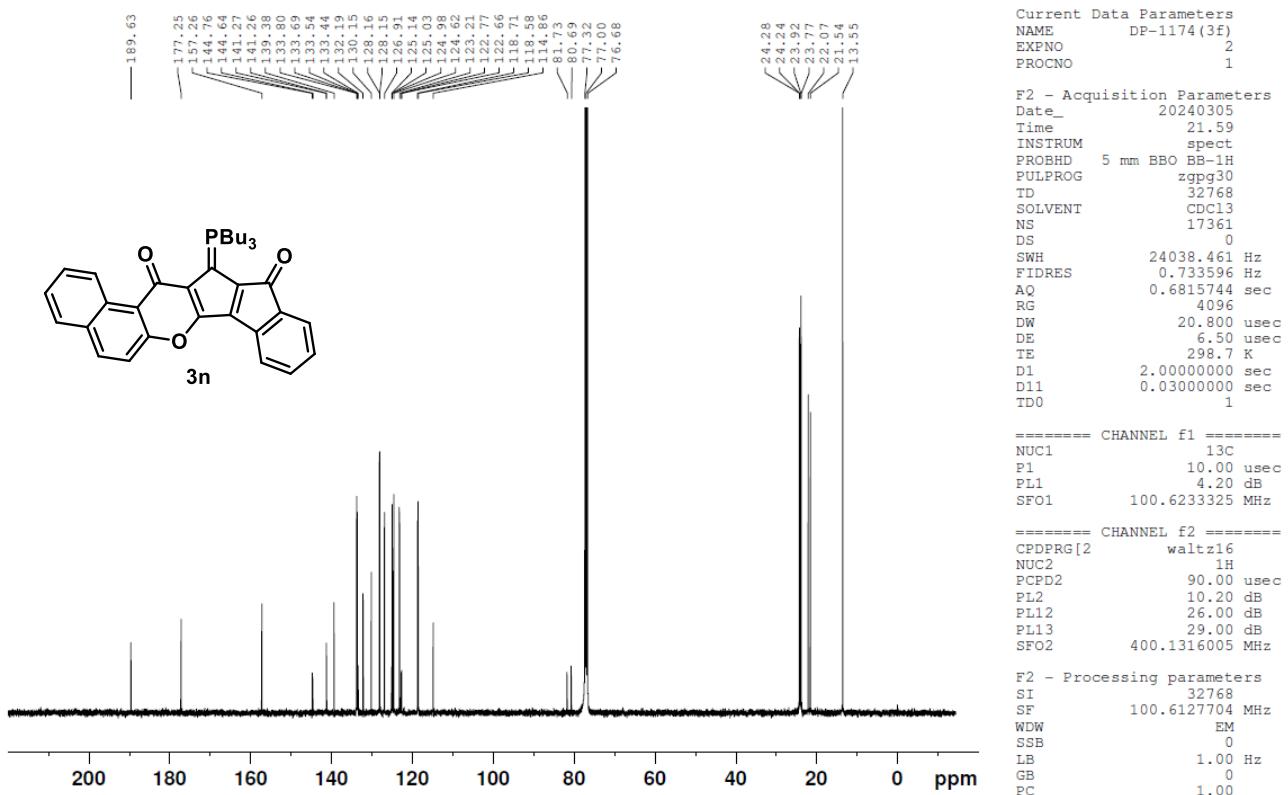
<sup>31</sup>P NMR spectrum of compound 3m (CDCl<sub>3</sub>, 162 MHz)



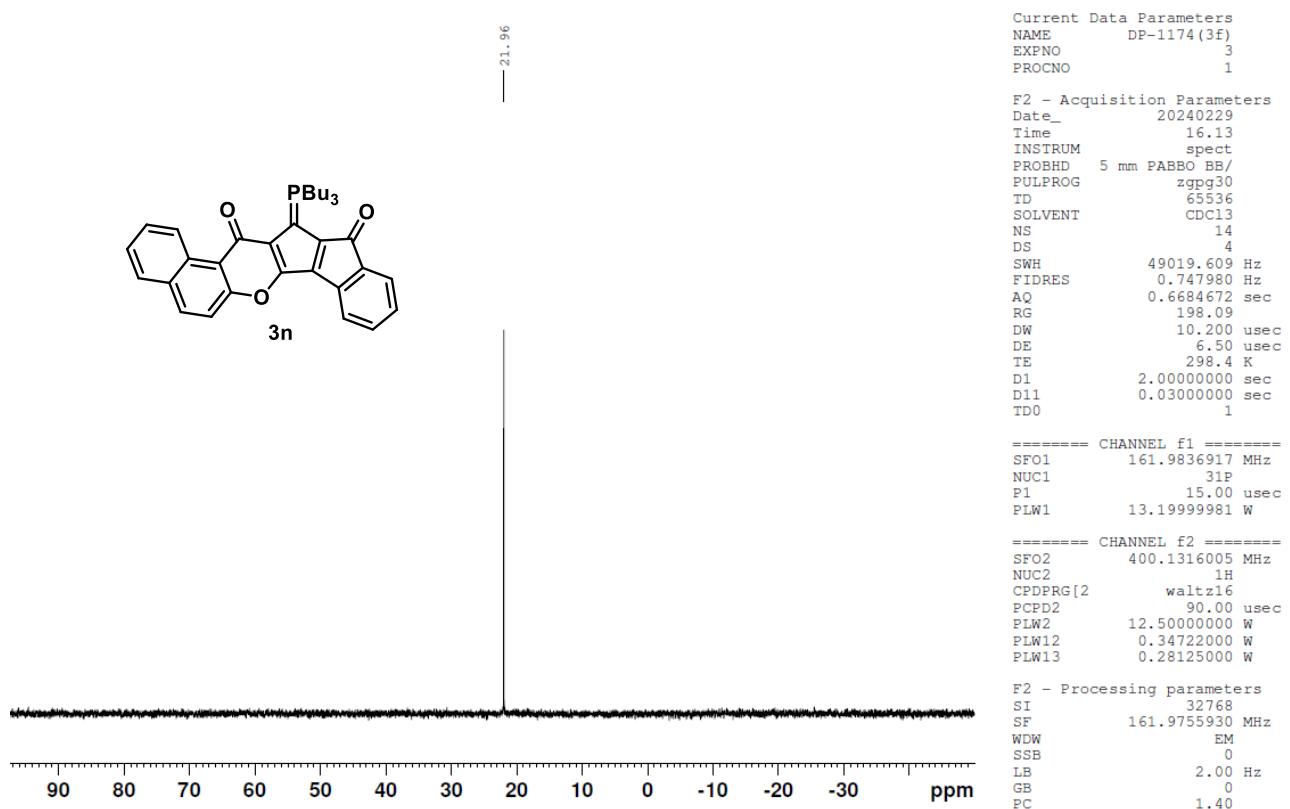
<sup>1</sup>H NMR spectrum of compound 3n (CDCl<sub>3</sub>, 400 MHz)



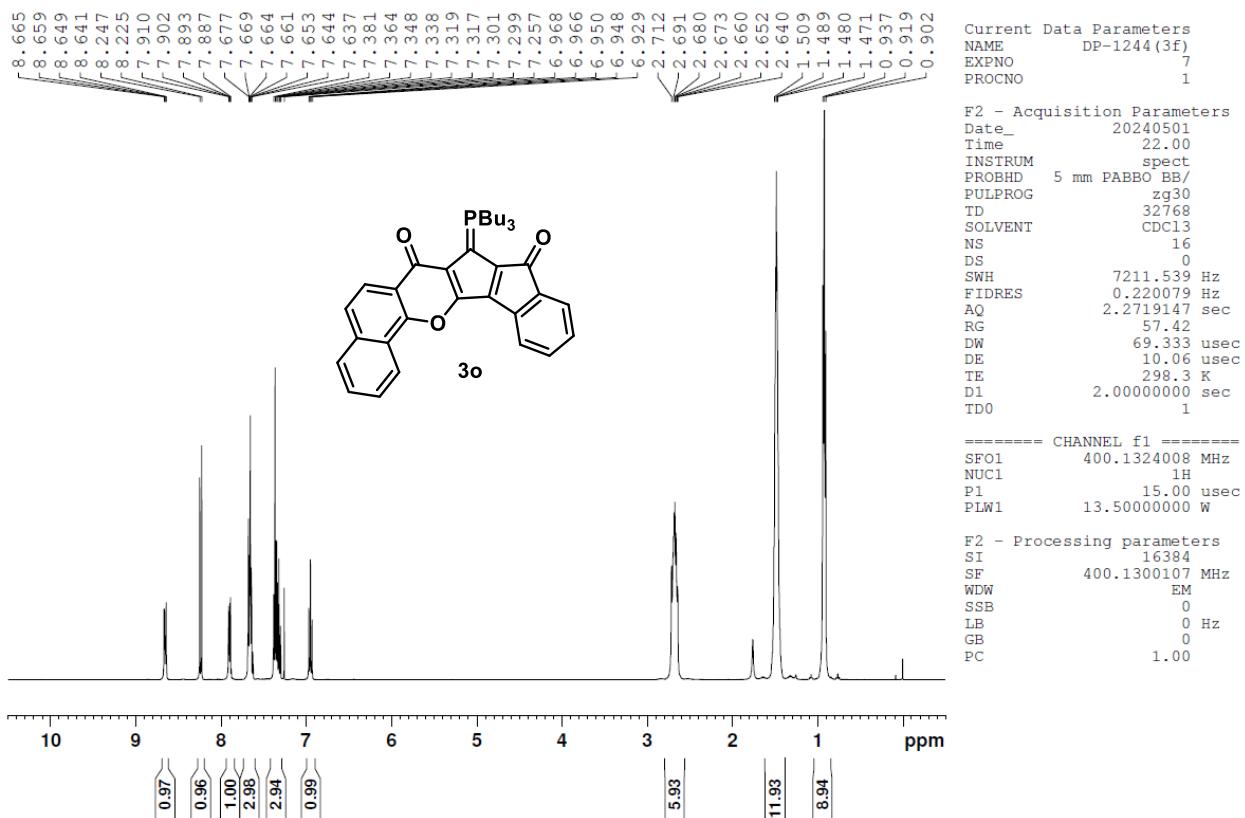
<sup>13</sup>C NMR spectrum of compound 3n (CDCl<sub>3</sub>, 100 MHz)



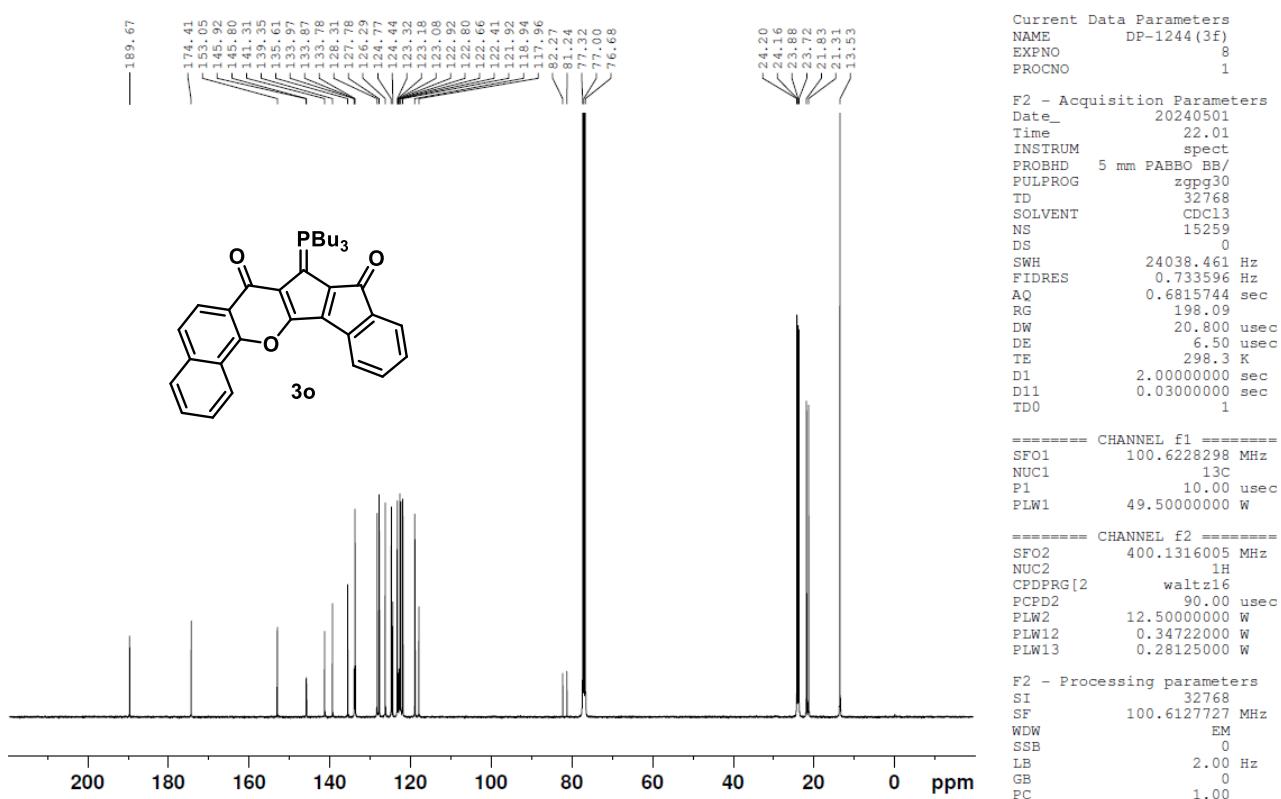
<sup>31</sup>P NMR spectrum of compound 3n (CDCl<sub>3</sub>, 162 MHz)



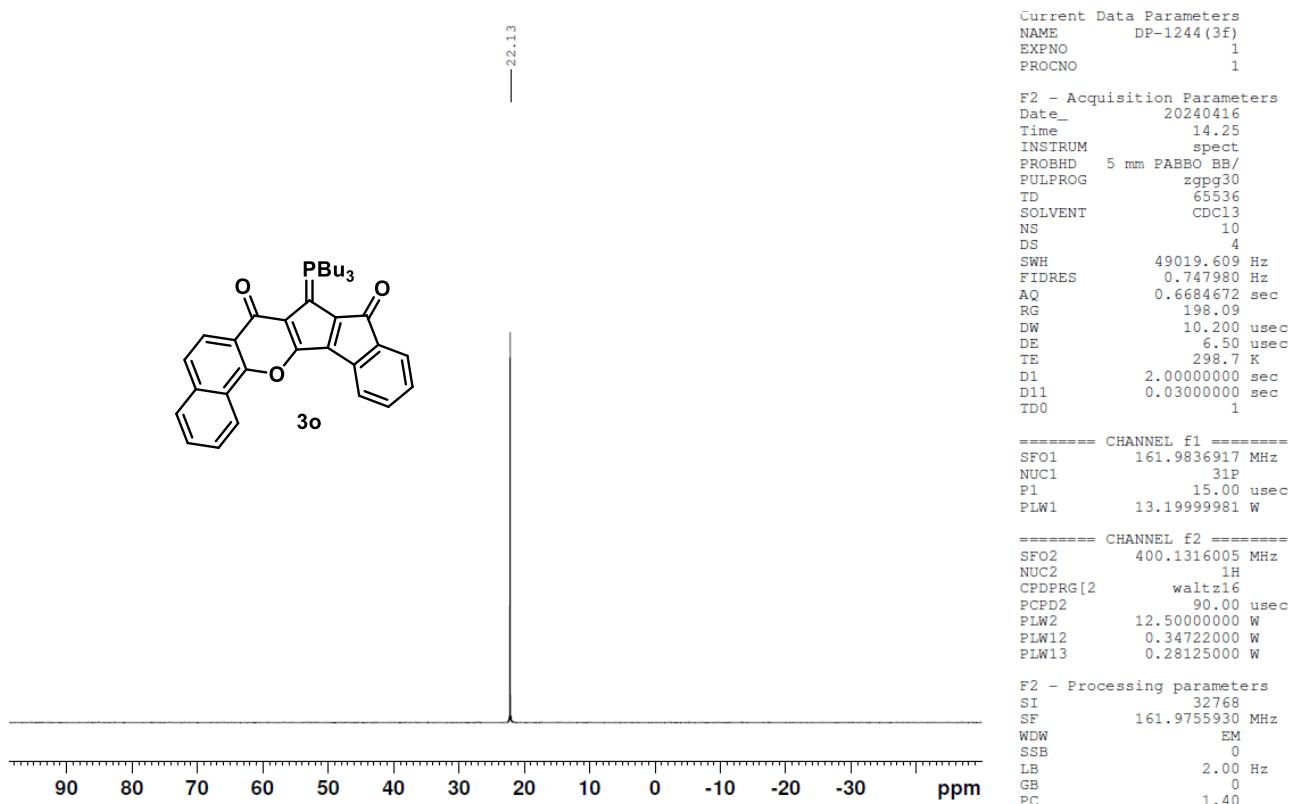
<sup>1</sup>H NMR spectrum of compound **3o** (CDCl<sub>3</sub>, 400 MHz)



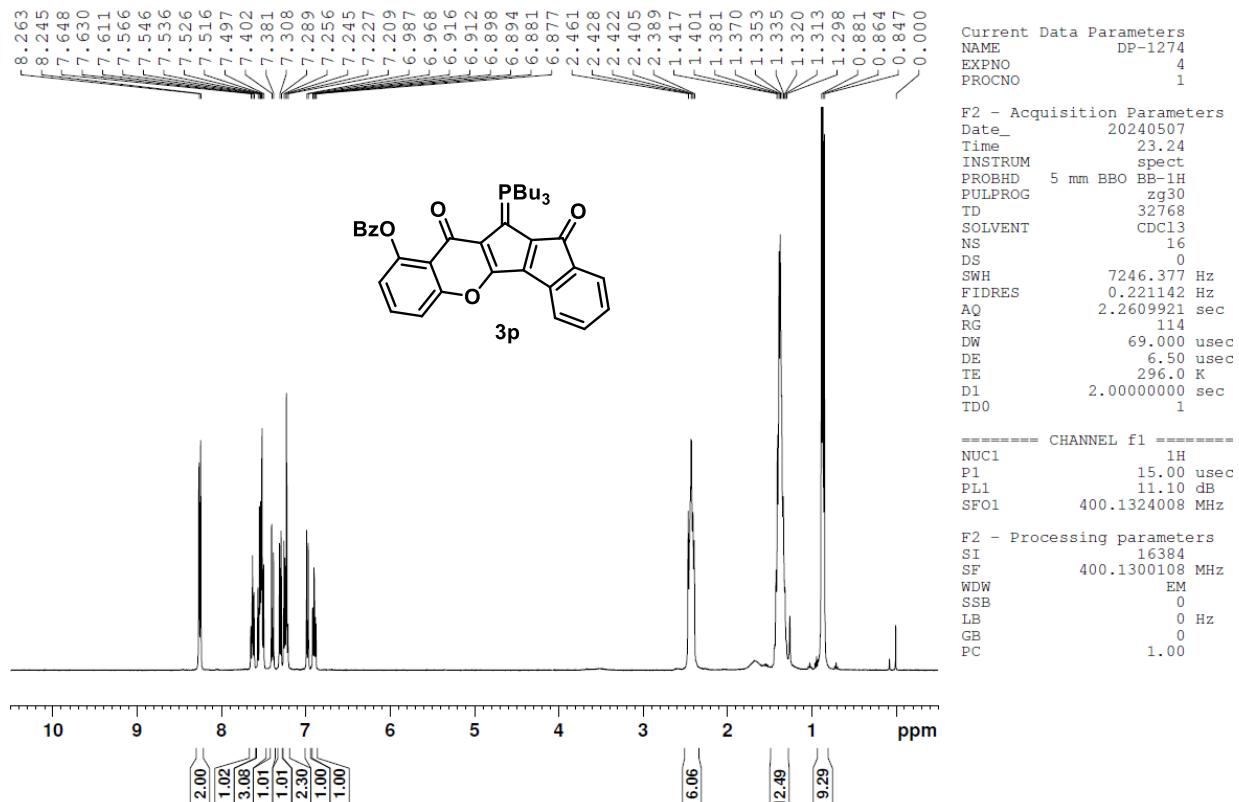
<sup>13</sup>C NMR spectrum of compound **3o** (CDCl<sub>3</sub>, 100 MHz)



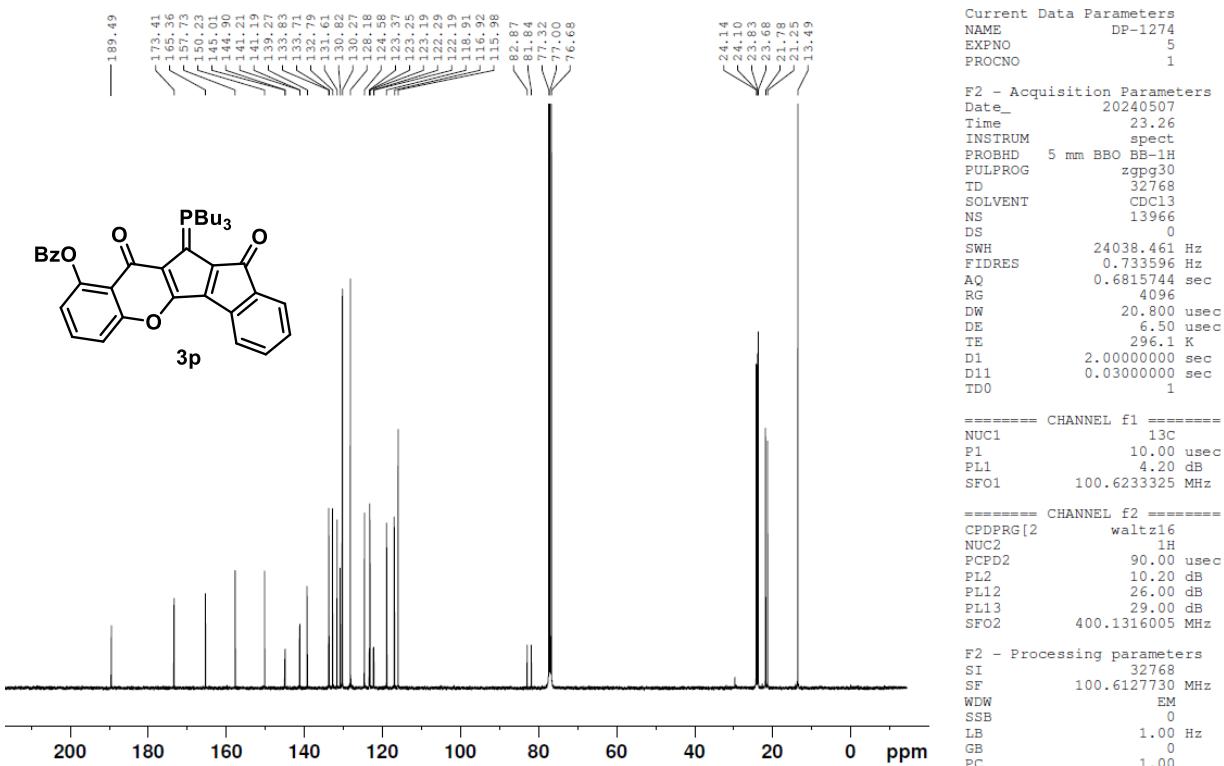
<sup>31</sup>P NMR spectrum of compound **3o** (CDCl<sub>3</sub>, 162 MHz)



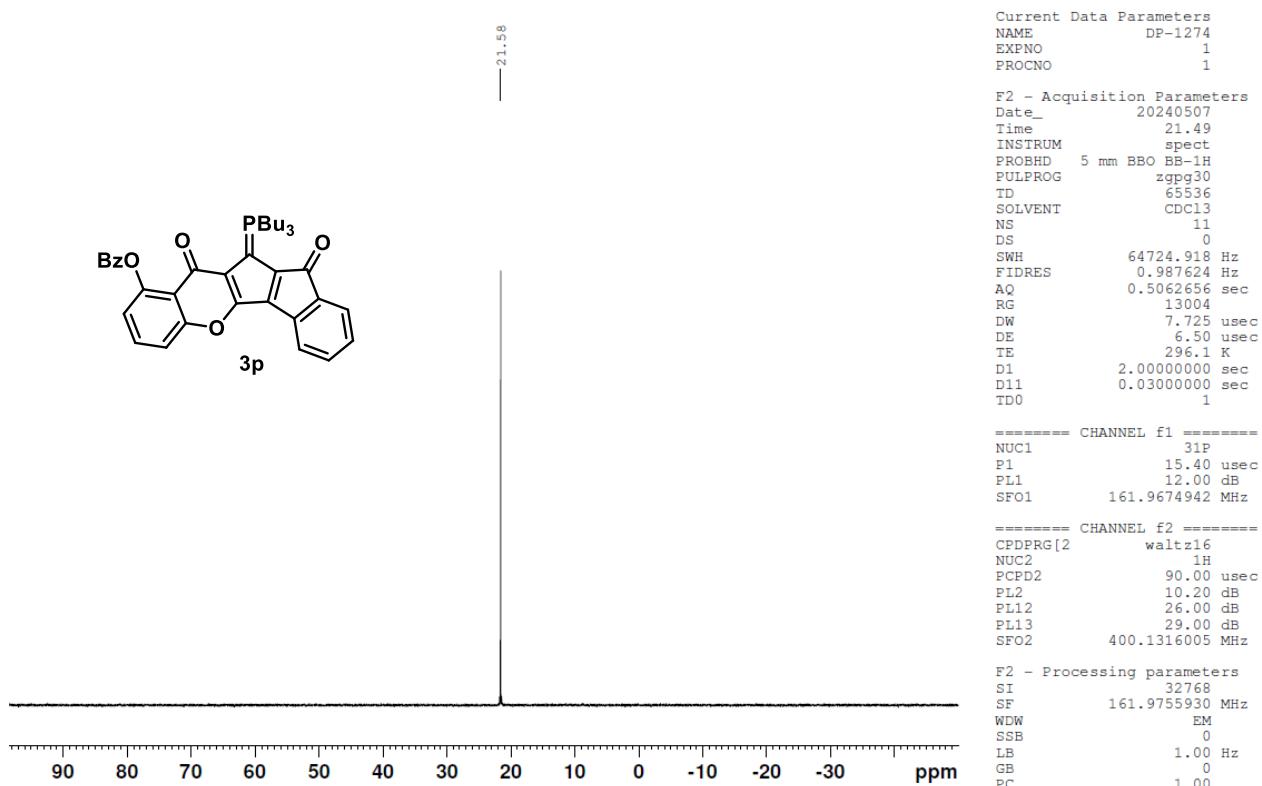
<sup>1</sup>H NMR spectrum of compound **3p** (CDCl<sub>3</sub>, 400 MHz)



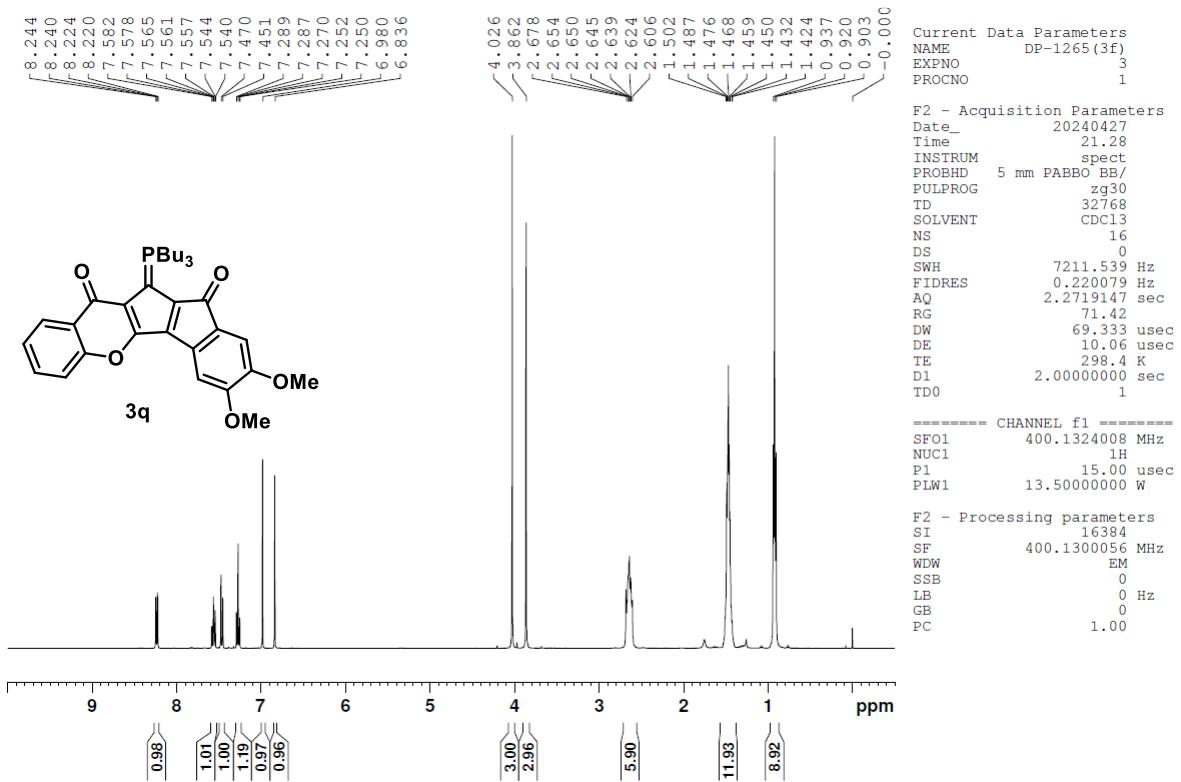
<sup>13</sup>C NMR spectrum of compound 3p (CDCl<sub>3</sub>, 100 MHz)



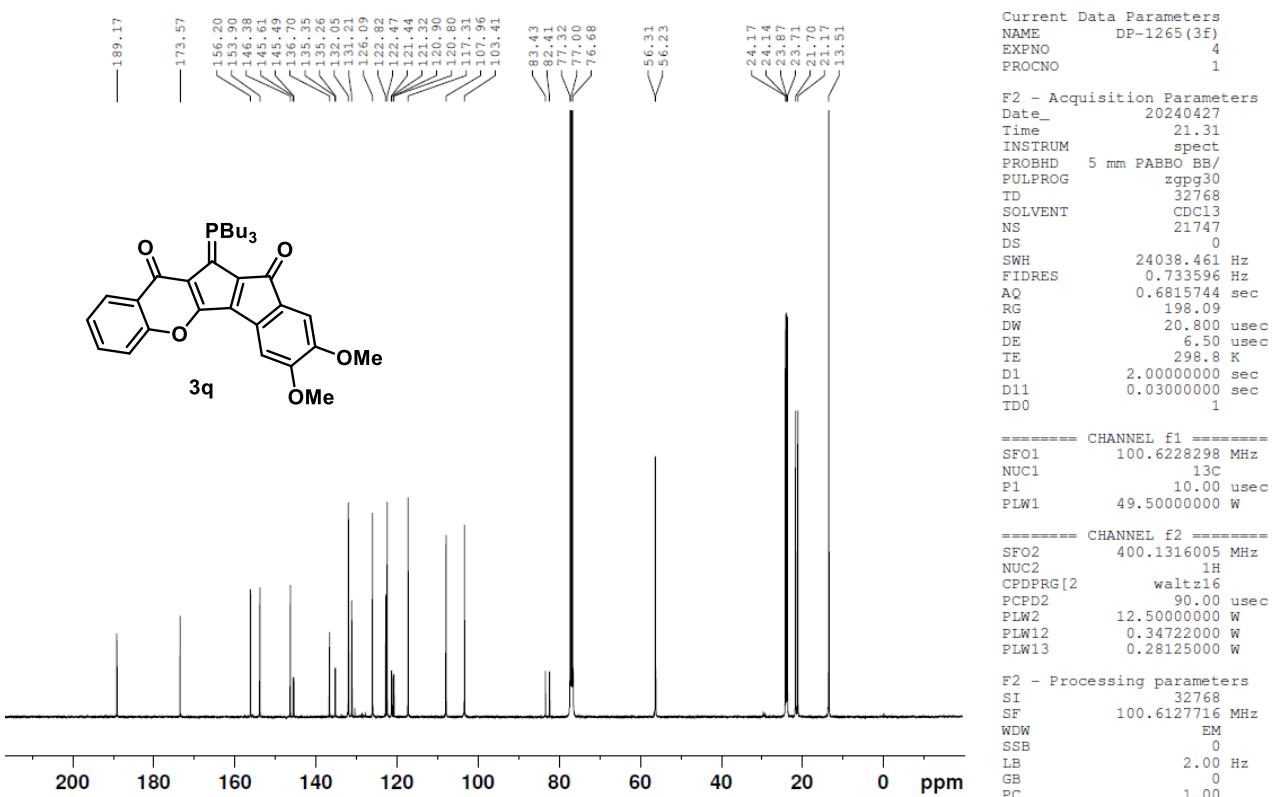
<sup>31</sup>P NMR spectrum of compound 3p (CDCl<sub>3</sub>, 162 MHz)



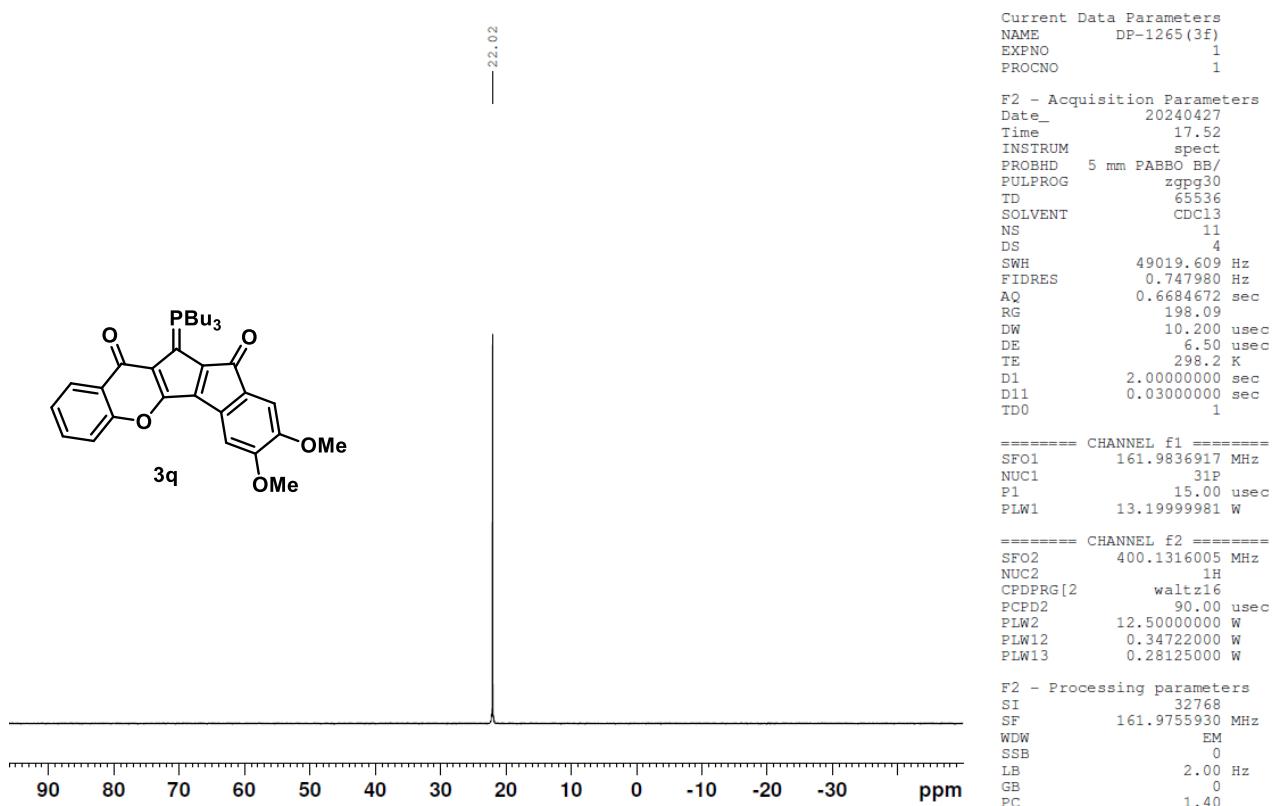
<sup>1</sup>H NMR spectrum of compound 3q (CDCl<sub>3</sub>, 400 MHz)



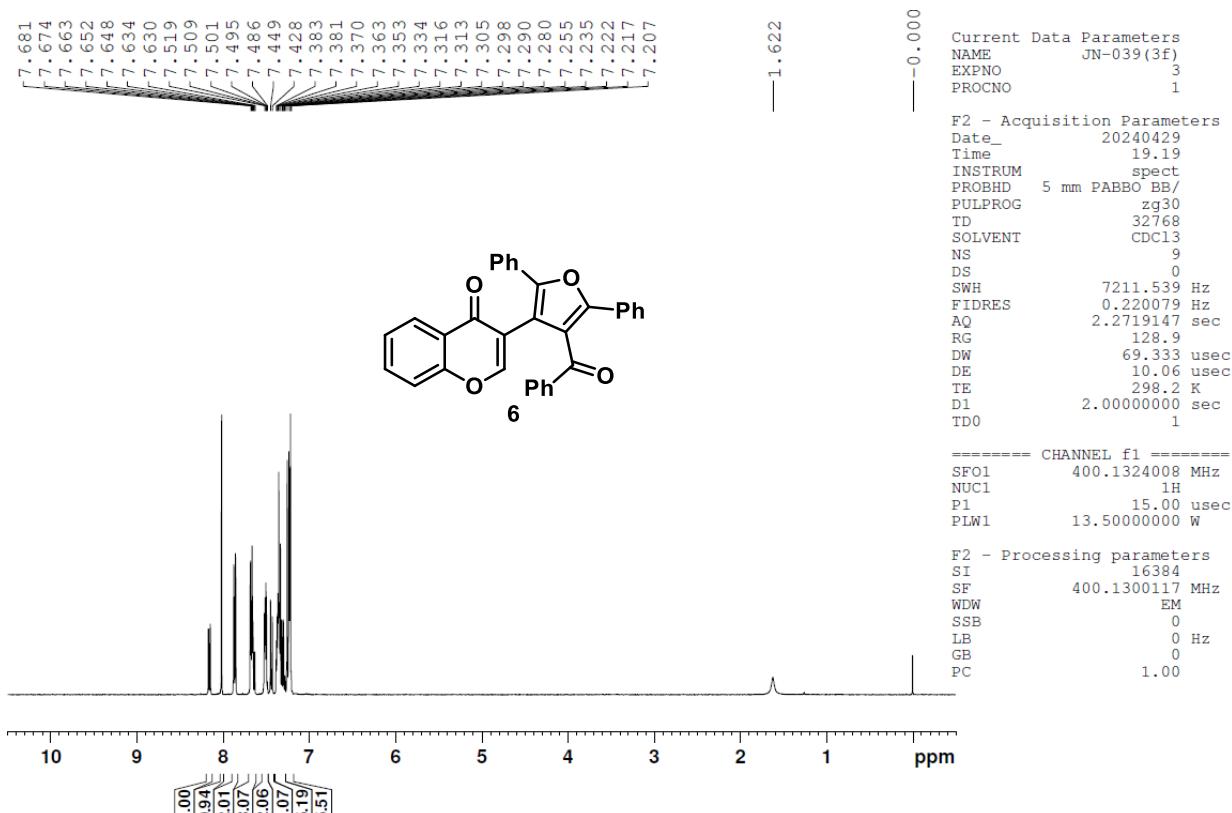
<sup>13</sup>C NMR spectrum of compound 3q (CDCl<sub>3</sub>, 100 MHz)



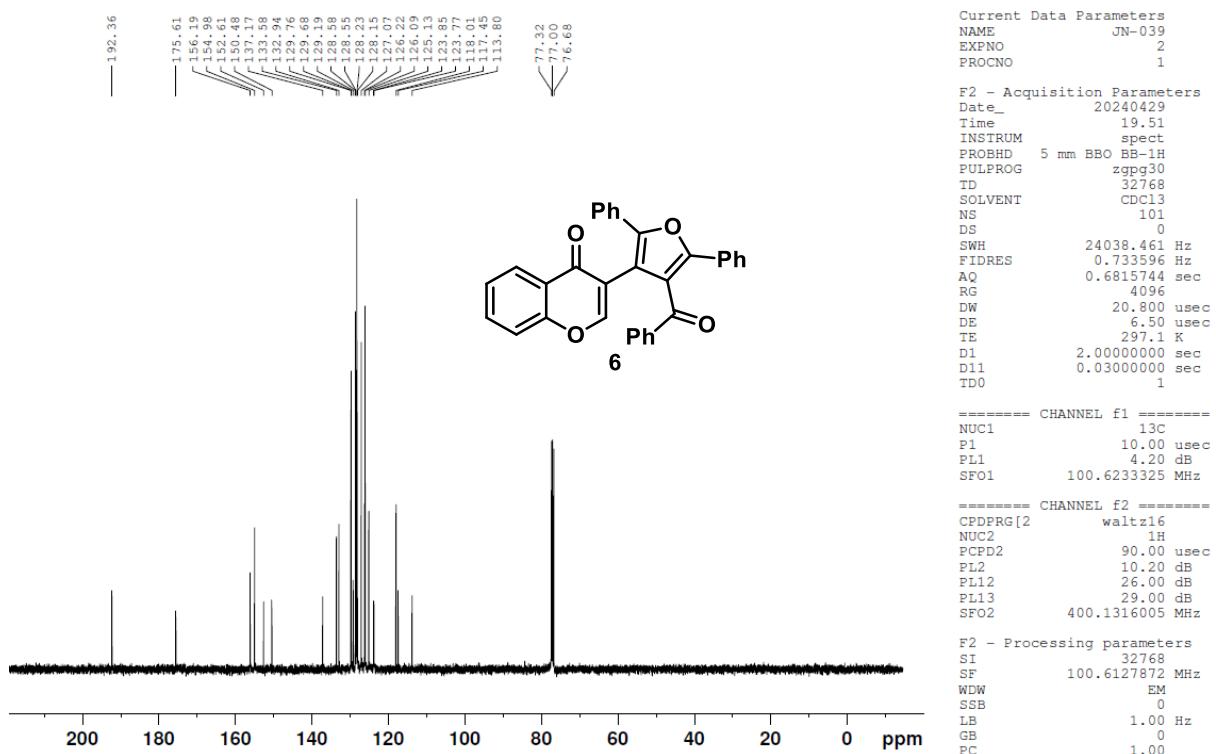
<sup>31</sup>P NMR spectrum of compound 3q (CDCl<sub>3</sub>, 162 MHz)



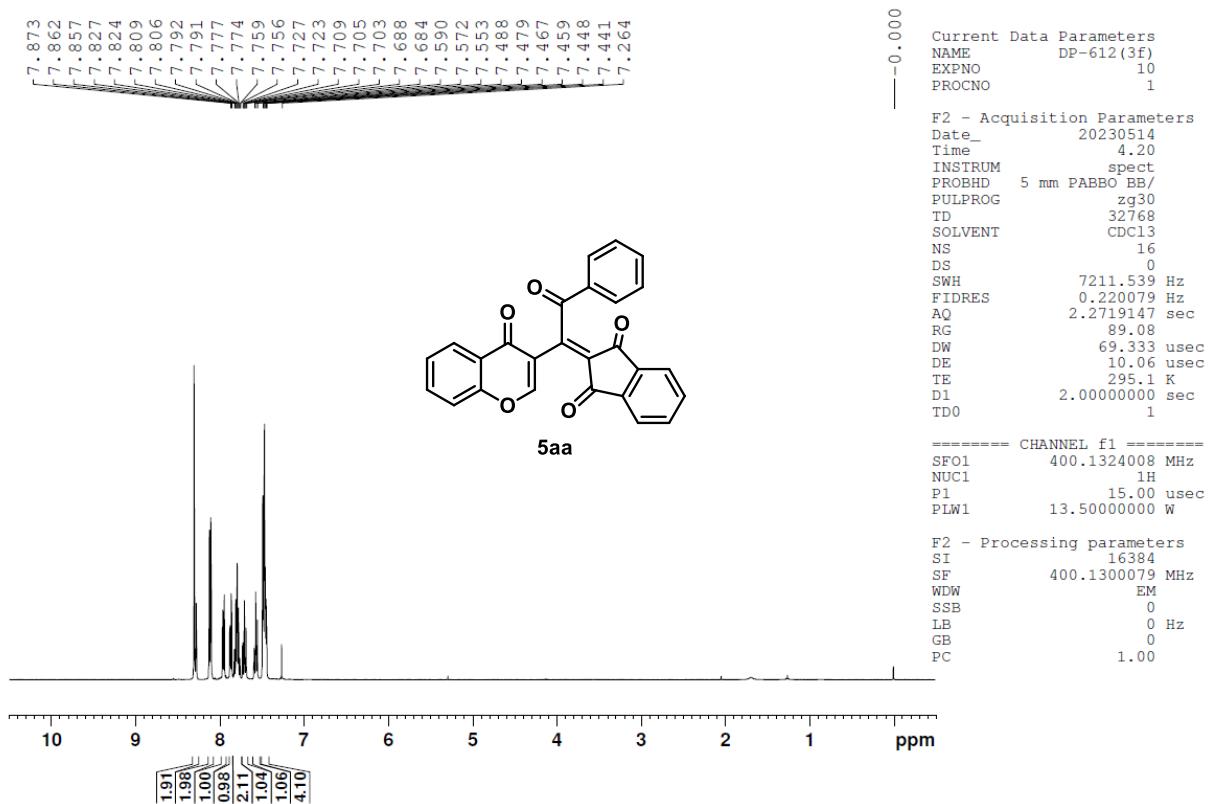
<sup>1</sup>H NMR spectrum of compound 6 (CDCl<sub>3</sub>, 400 MHz)



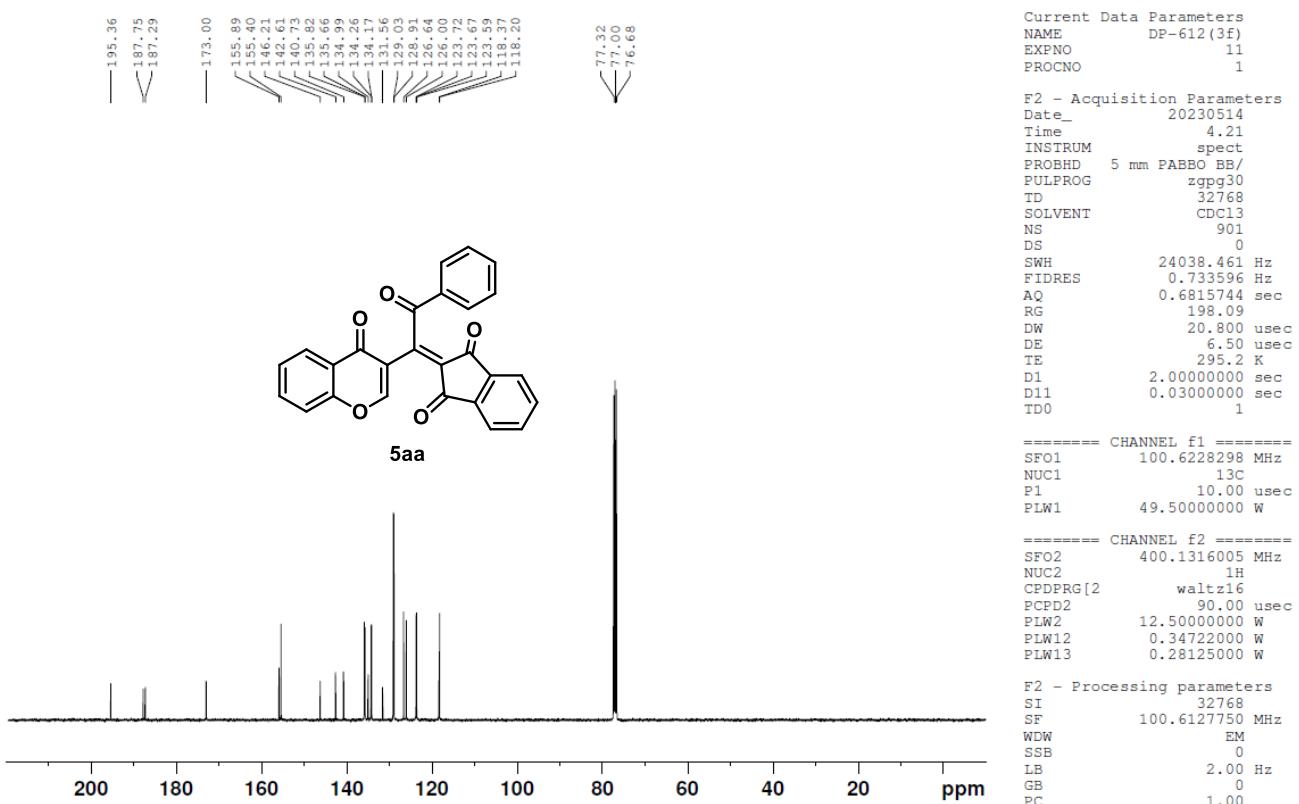
<sup>13</sup>C NMR spectrum of compound 6 (CDCl<sub>3</sub>, 100 MHz)



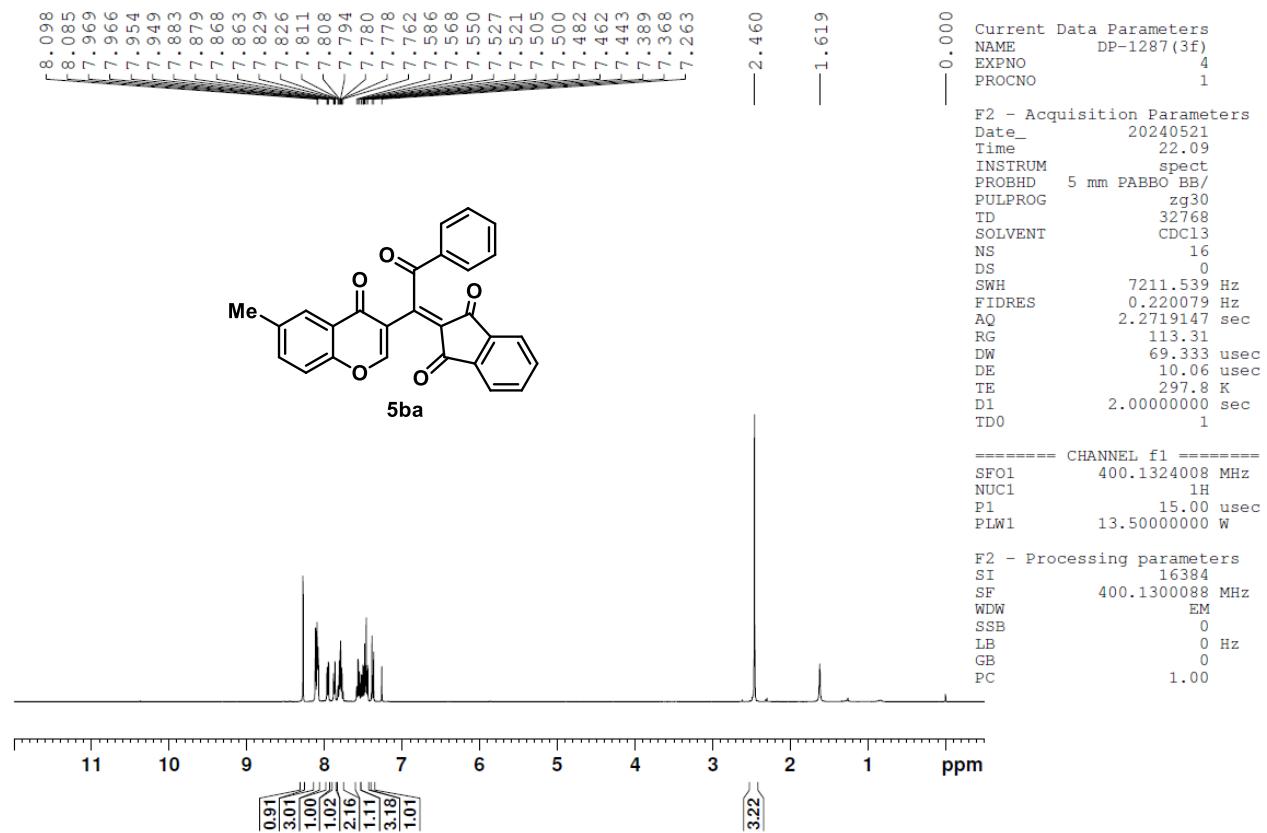
**<sup>1</sup>H NMR spectrum of compound 5aa (CDCl<sub>3</sub>, 400 MHz)**



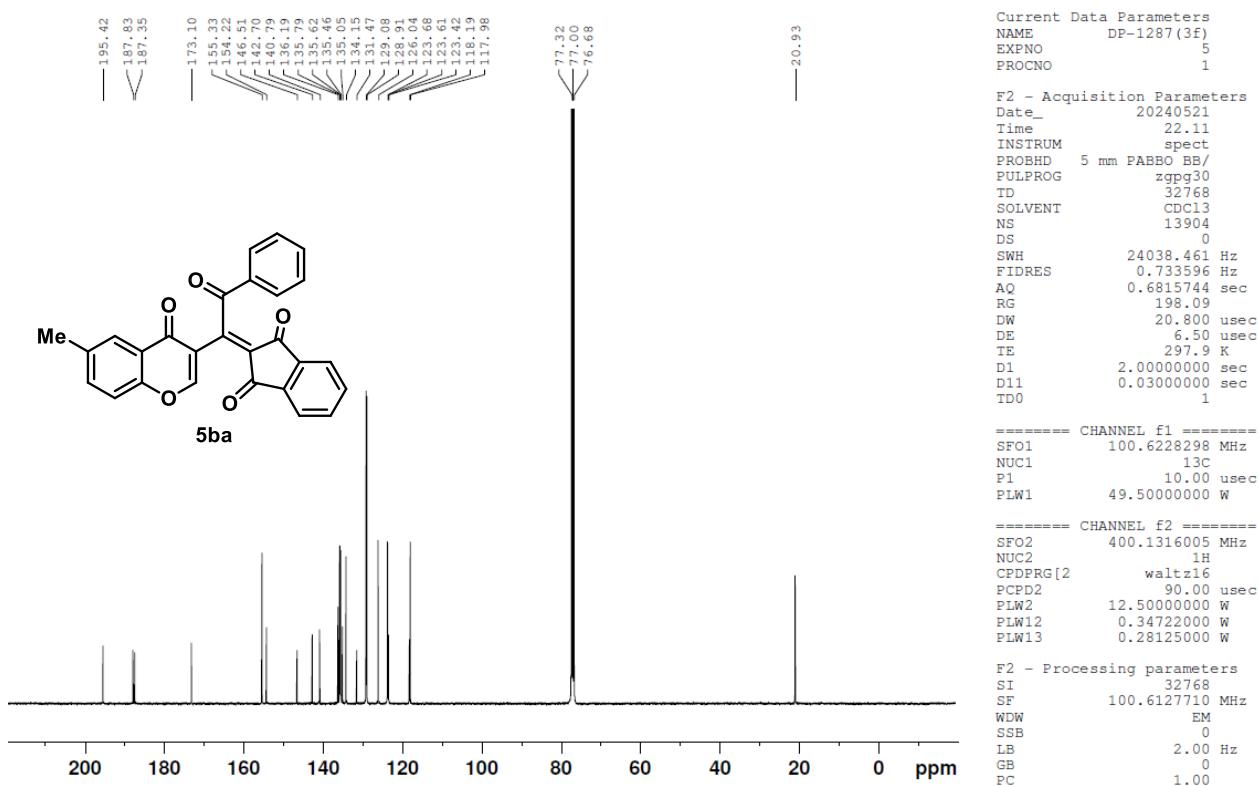
**<sup>13</sup>C NMR spectrum of compound 5aa (CDCl<sub>3</sub>, 100 MHz)**



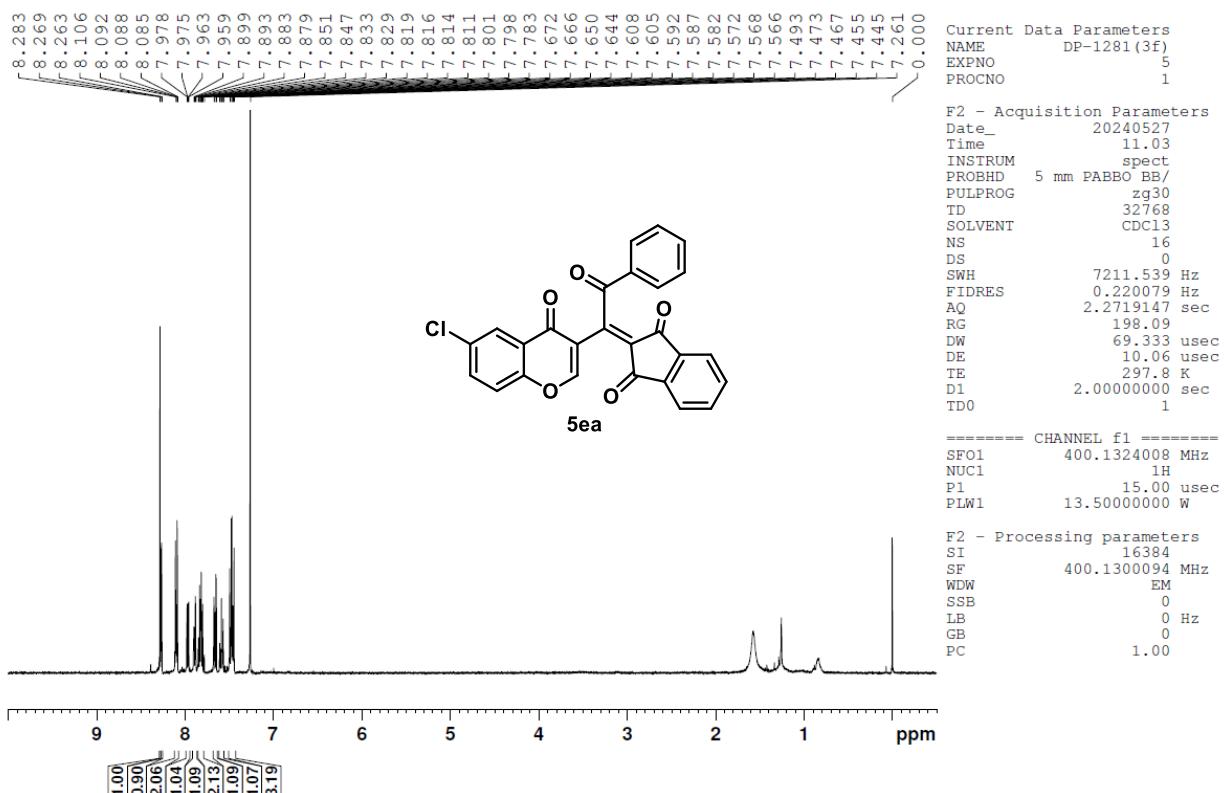
<sup>1</sup>H NMR spectrum of compound **5ba** (CDCl<sub>3</sub>, 400 MHz)



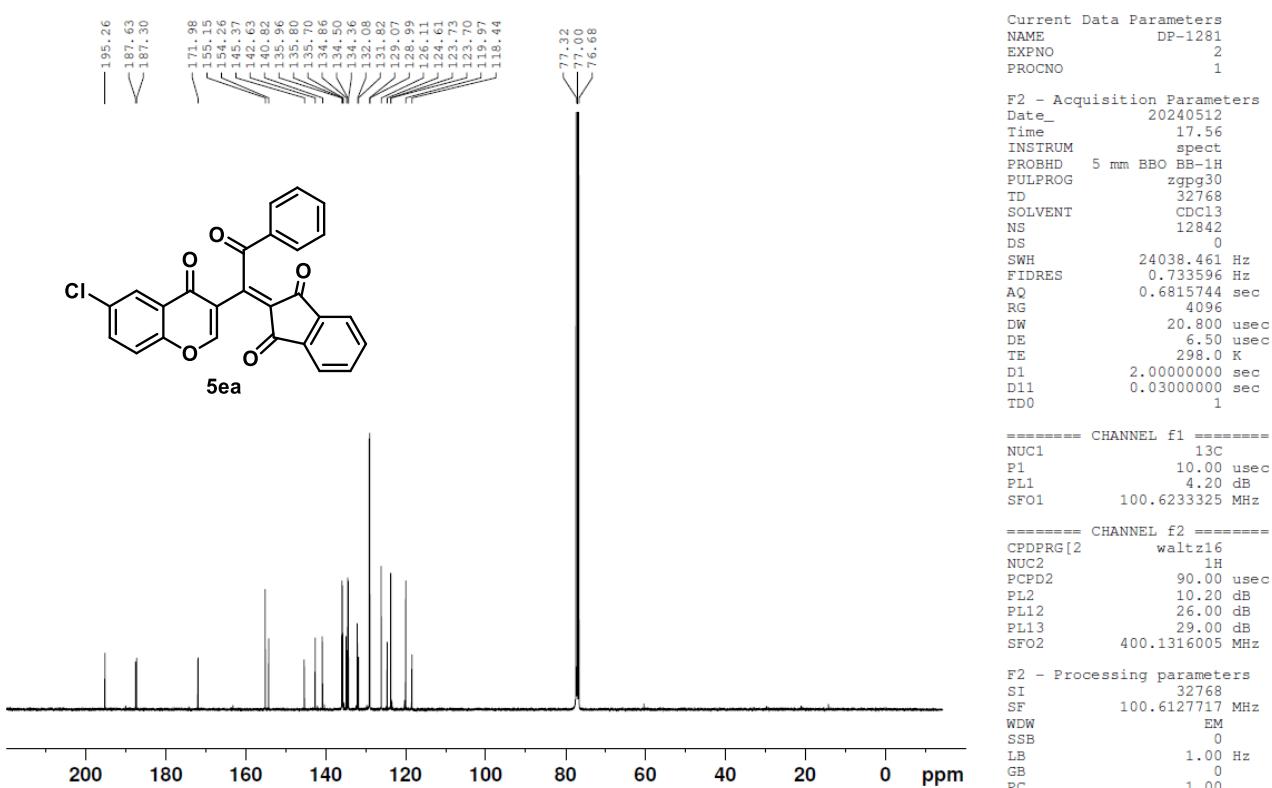
<sup>13</sup>C NMR spectrum of compound **5ba** (CDCl<sub>3</sub>, 100 MHz)



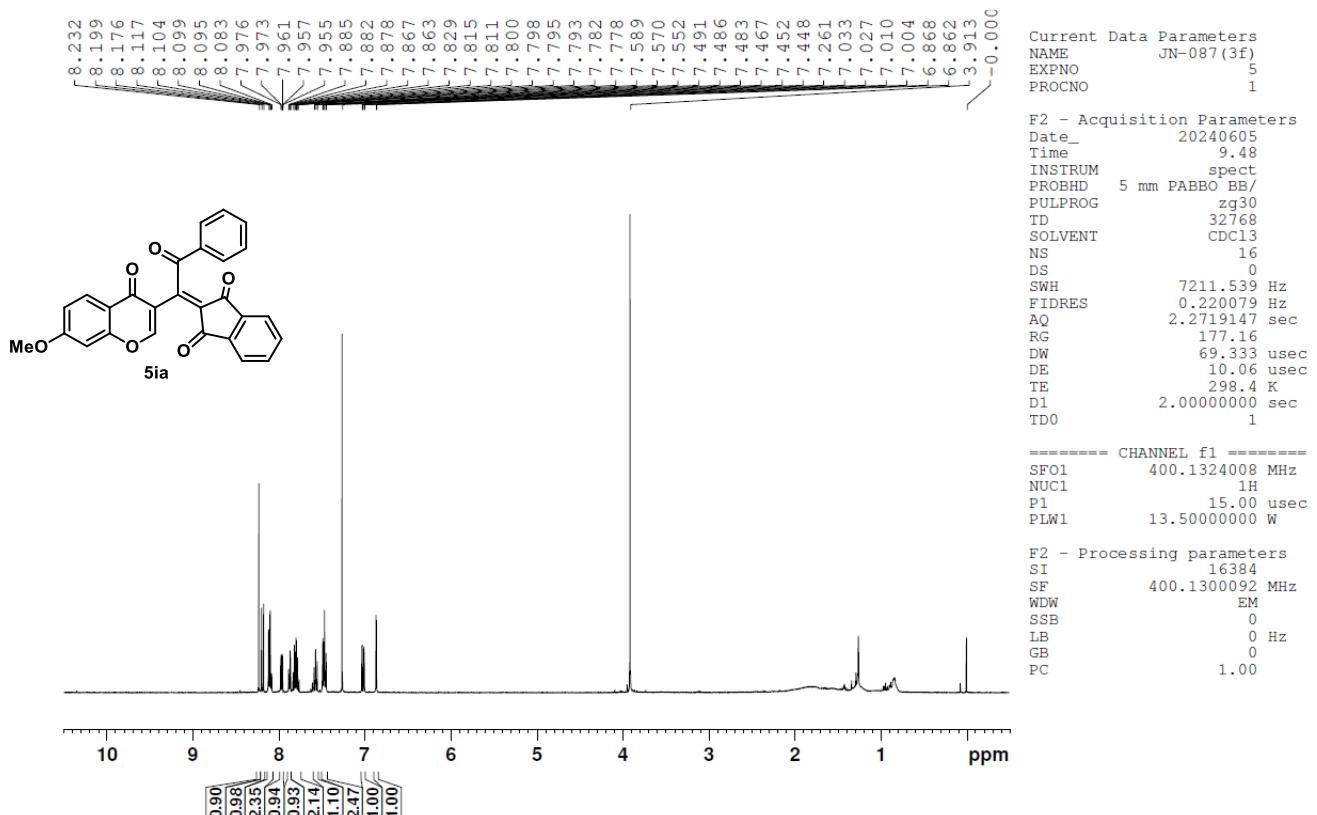
<sup>1</sup>H NMR spectrum of compound 5ea (CDCl<sub>3</sub>, 400 MHz)



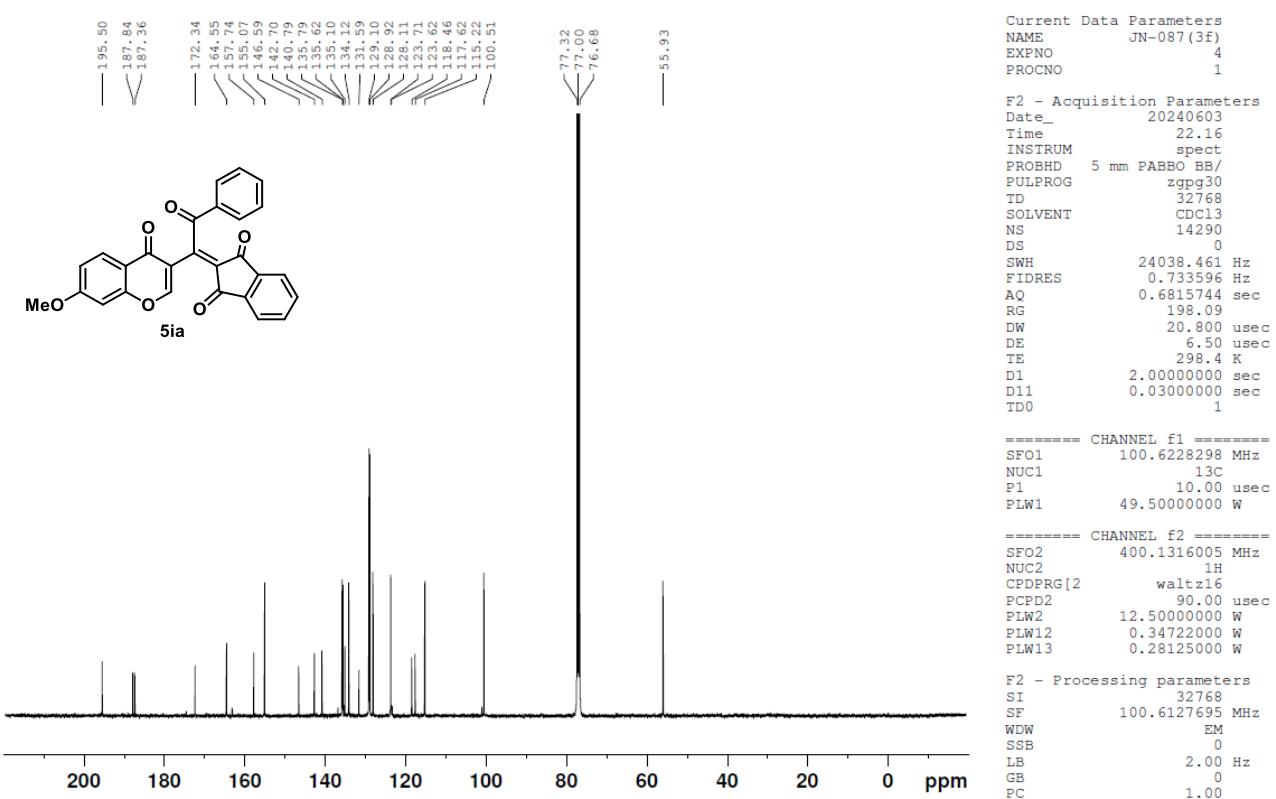
<sup>13</sup>C NMR spectrum of compound 5ea (CDCl<sub>3</sub>, 100 MHz)



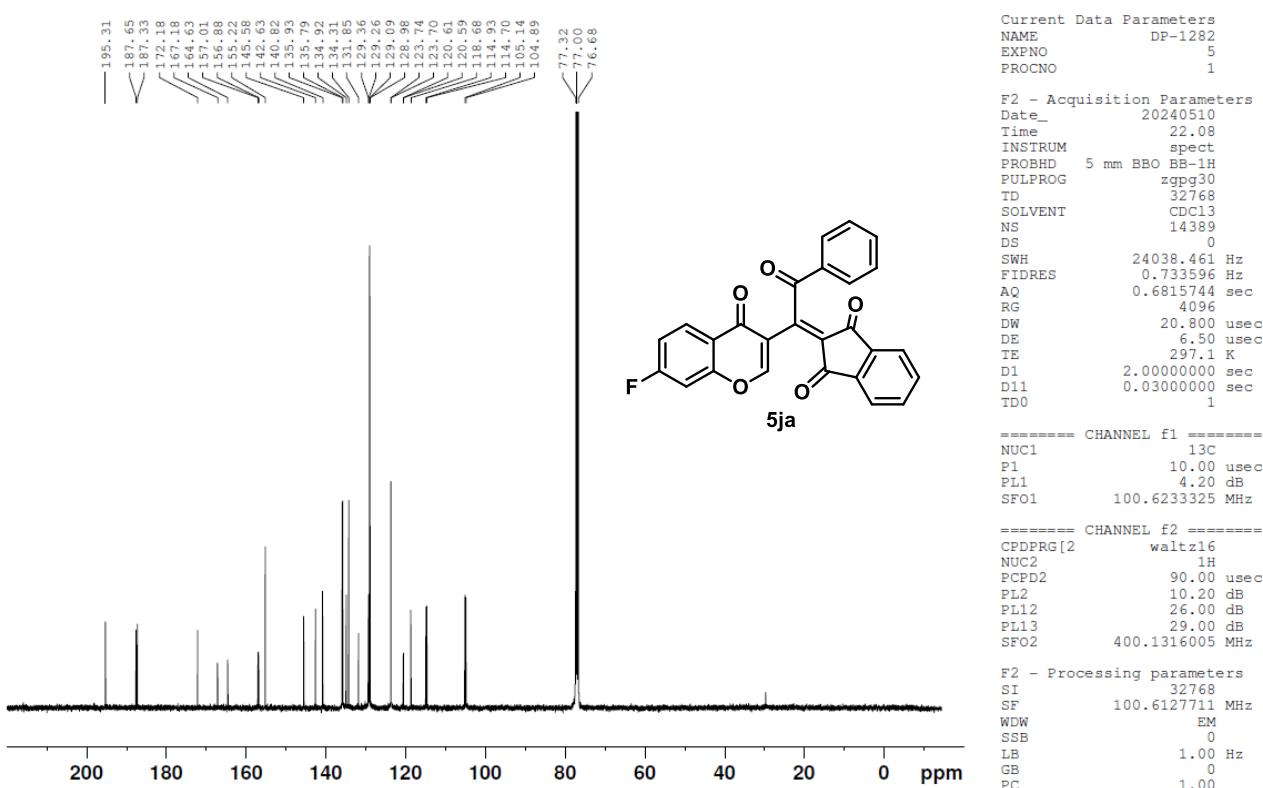
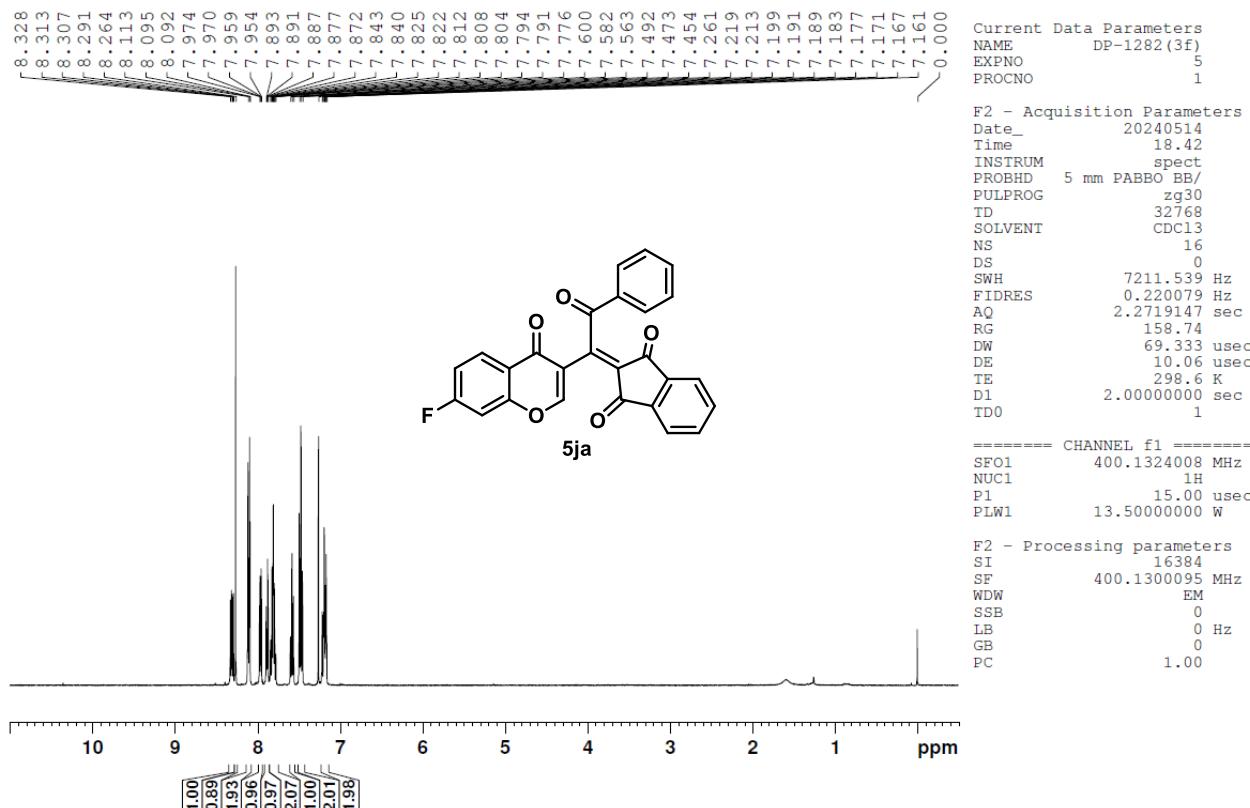
<sup>1</sup>H NMR spectrum of compound 5ia (CDCl<sub>3</sub>, 400 MHz)



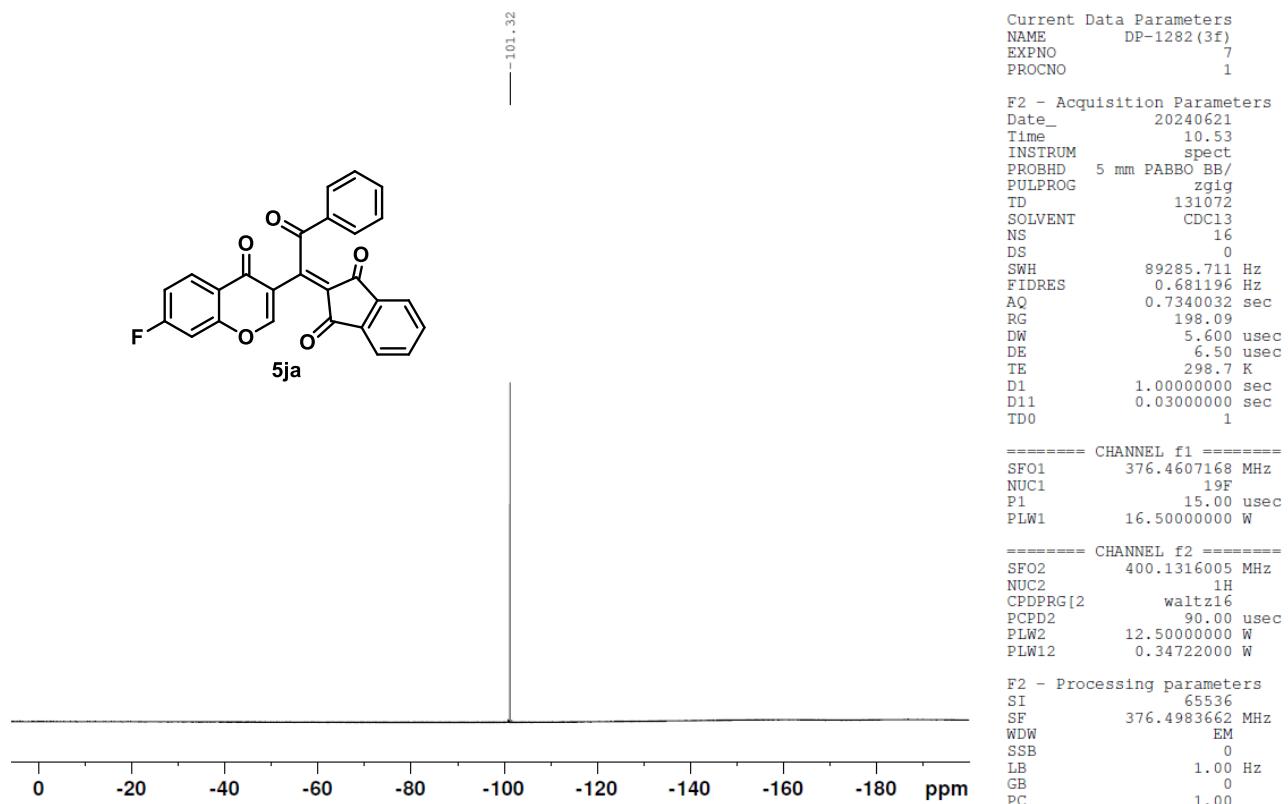
<sup>13</sup>C NMR spectrum of compound 5ia (CDCl<sub>3</sub>, 100 MHz)



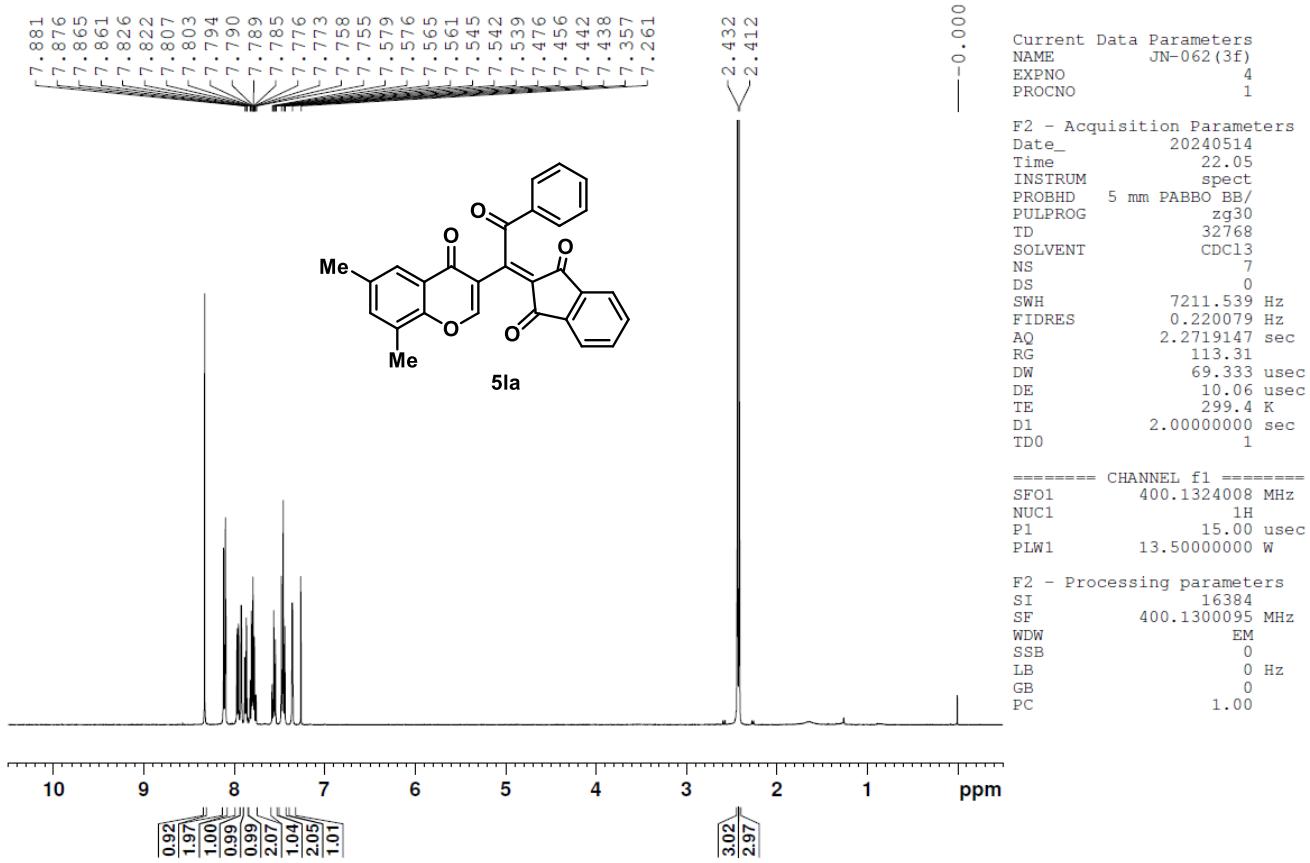
<sup>1</sup>H NMR spectrum of compound 5ja (CDCl<sub>3</sub>, 400 MHz)



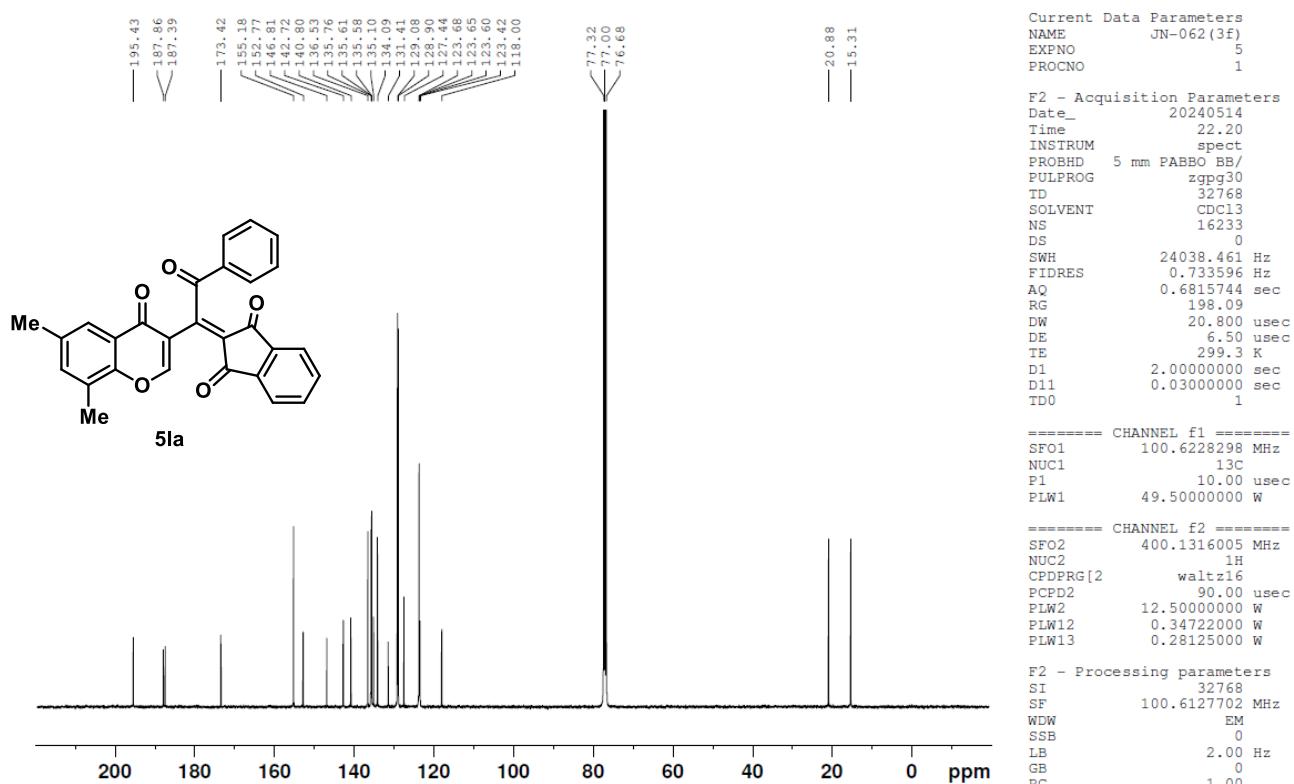
<sup>19</sup>F NMR spectrum of compound 5ja (CDCl<sub>3</sub>, 376 MHz)



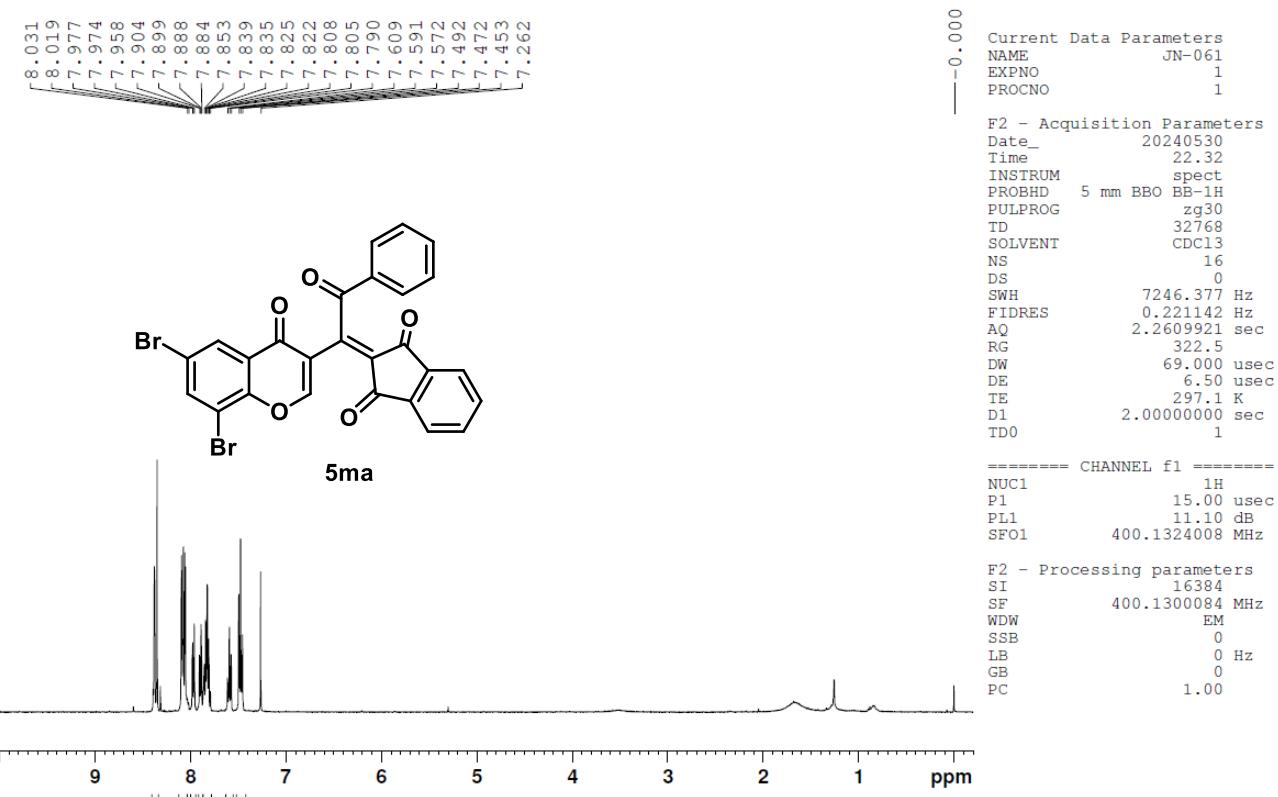
<sup>1</sup>H NMR spectrum of compound **5la** (CDCl<sub>3</sub>, 400 MHz)



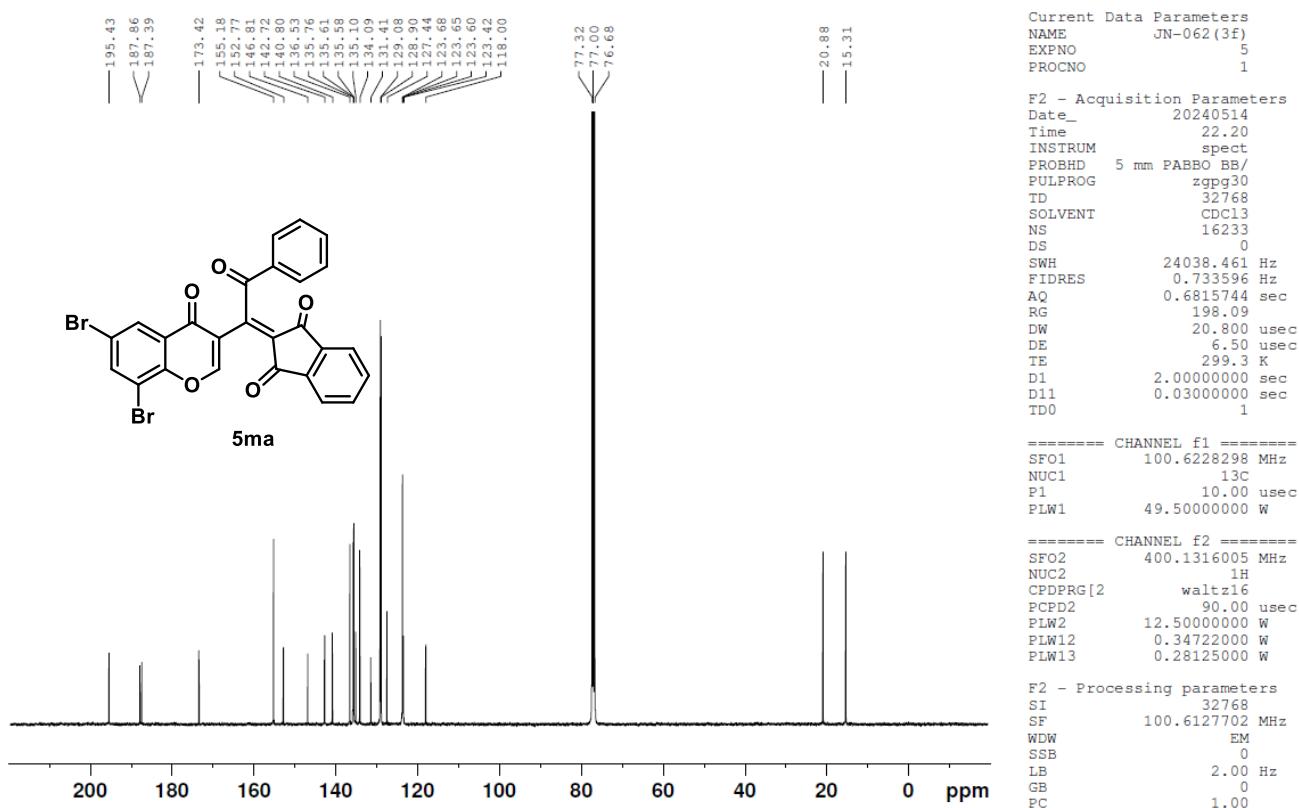
<sup>13</sup>C NMR spectrum of compound **5la** (CDCl<sub>3</sub>, 100 MHz)



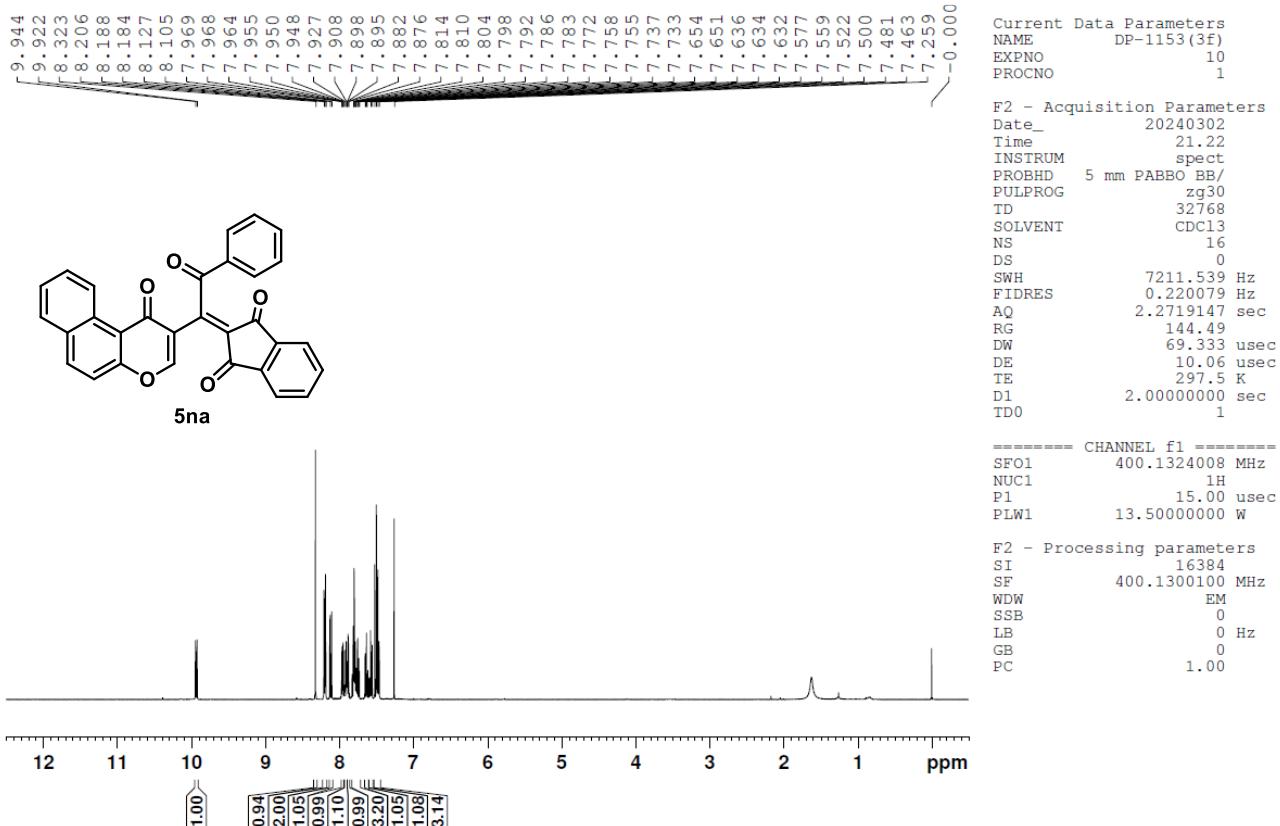
<sup>1</sup>H NMR spectrum of compound **5ma** (CDCl<sub>3</sub>, 400 MHz)



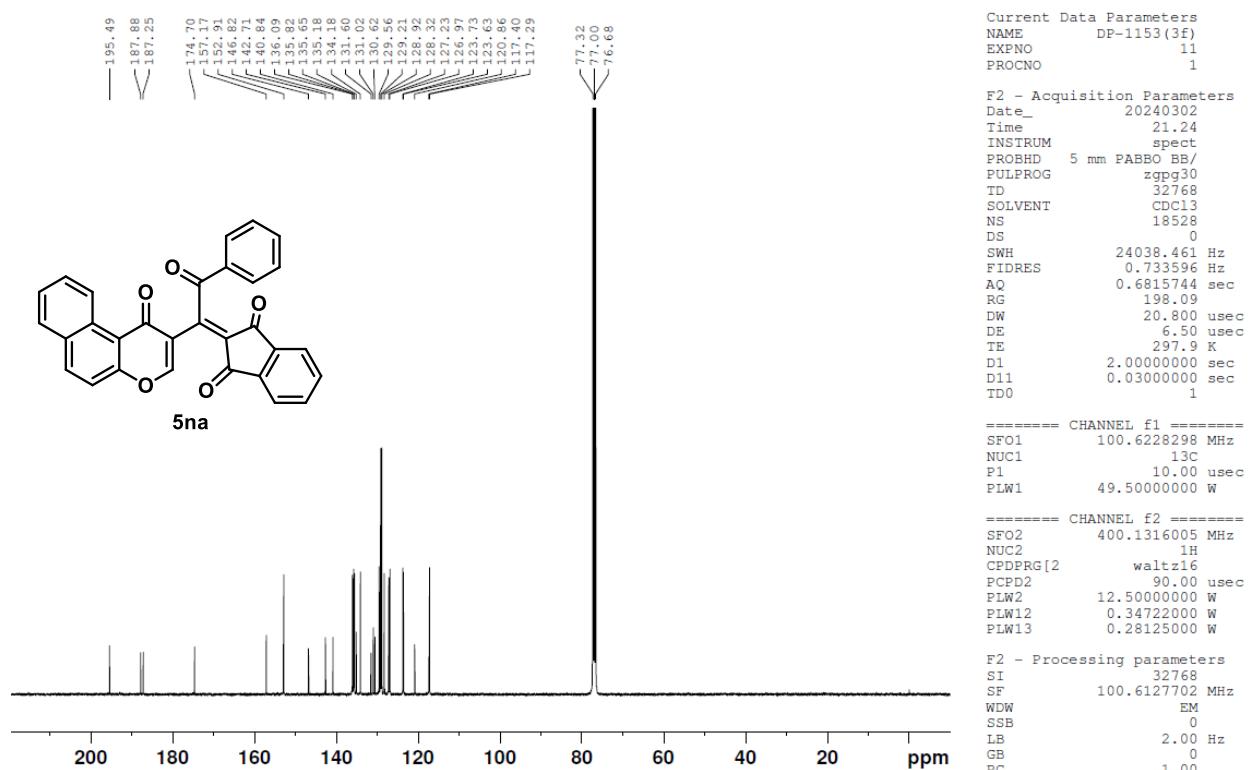
<sup>13</sup>C NMR spectrum of compound **5ma** (CDCl<sub>3</sub>, 100 MHz)



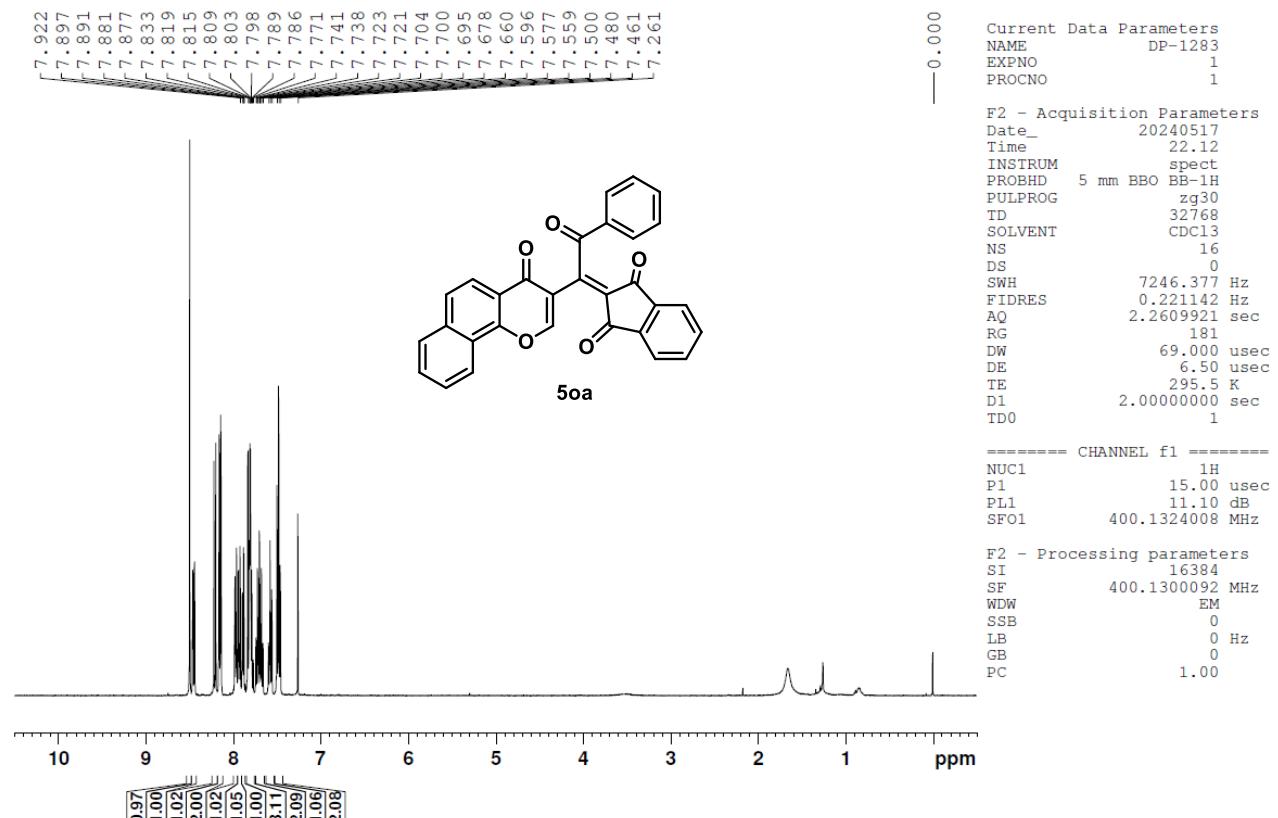
**<sup>1</sup>H NMR spectrum of compound 5na (CDCl<sub>3</sub>, 400 MHz)**



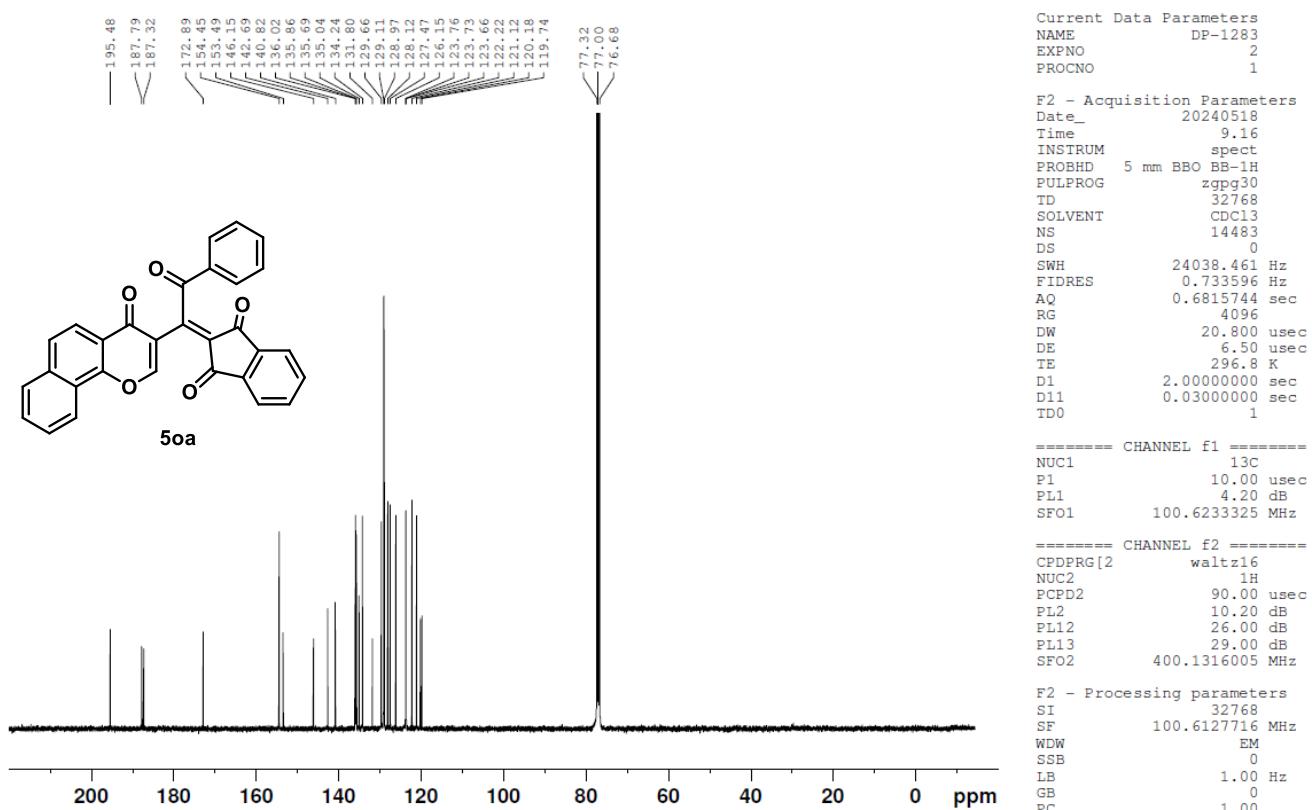
**<sup>13</sup>C NMR spectrum of compound 5na (CDCl<sub>3</sub>, 100 MHz)**



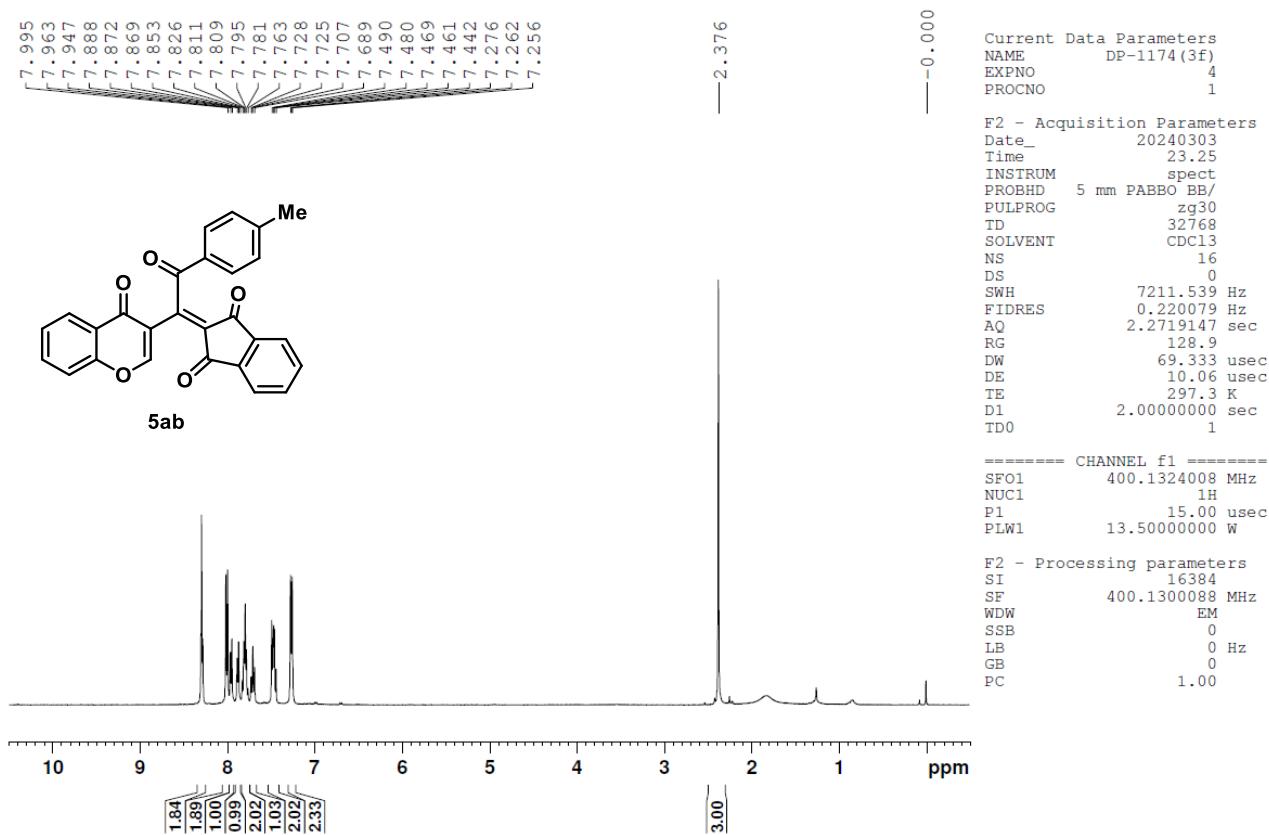
<sup>1</sup>H NMR spectrum of compound 5a (CDCl<sub>3</sub>, 400 MHz)



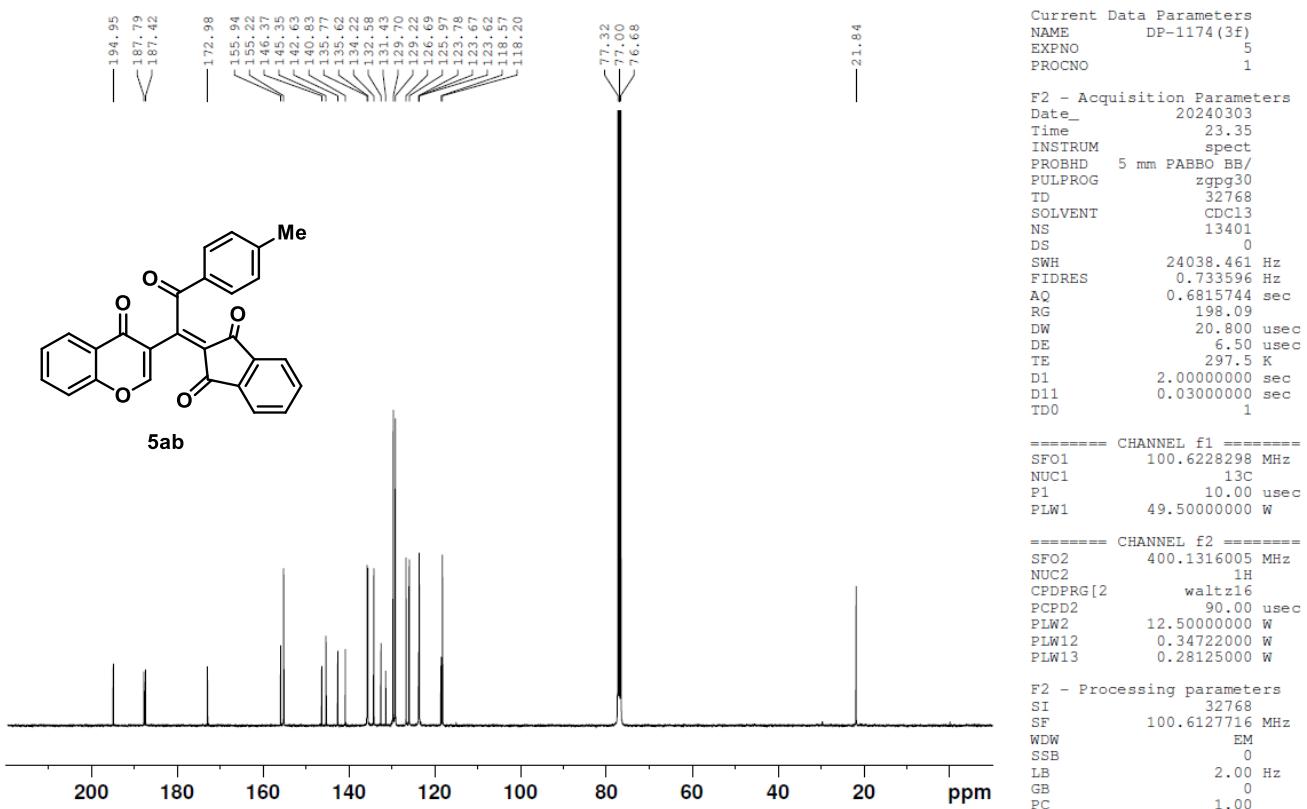
<sup>13</sup>C NMR spectrum of compound 5a (CDCl<sub>3</sub>, 100 MHz)



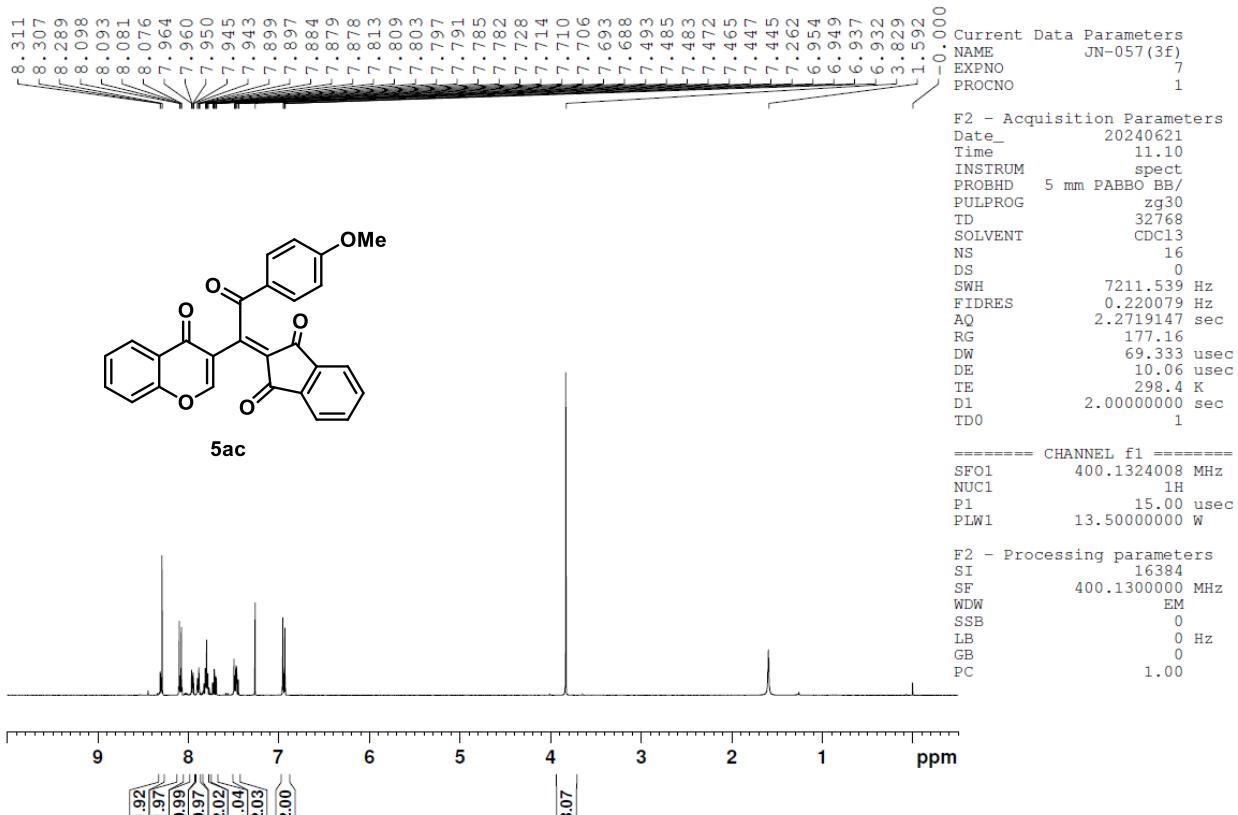
<sup>1</sup>H NMR spectrum of compound **5ab** (CDCl<sub>3</sub>, 400 MHz)



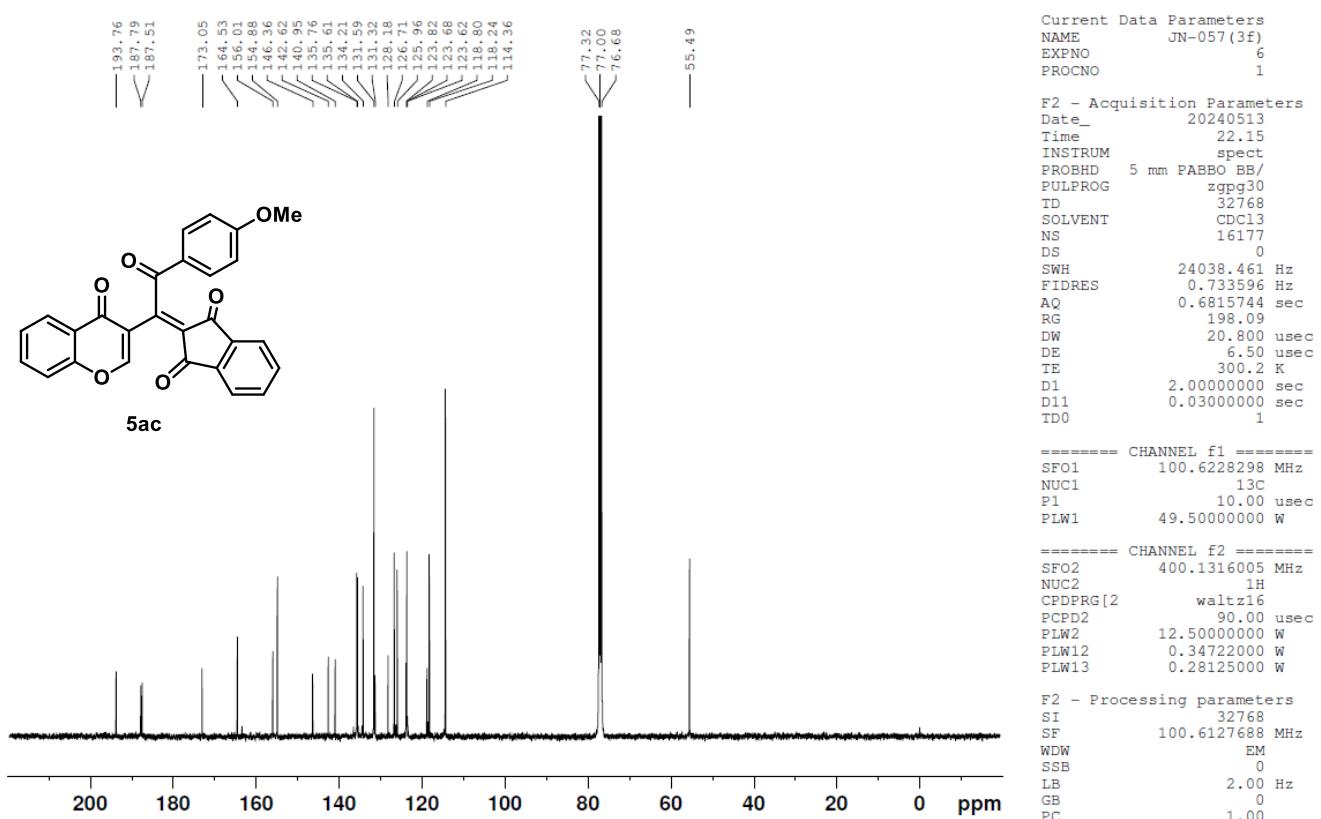
<sup>13</sup>C NMR spectrum of compound **5ab** (CDCl<sub>3</sub>, 100 MHz)



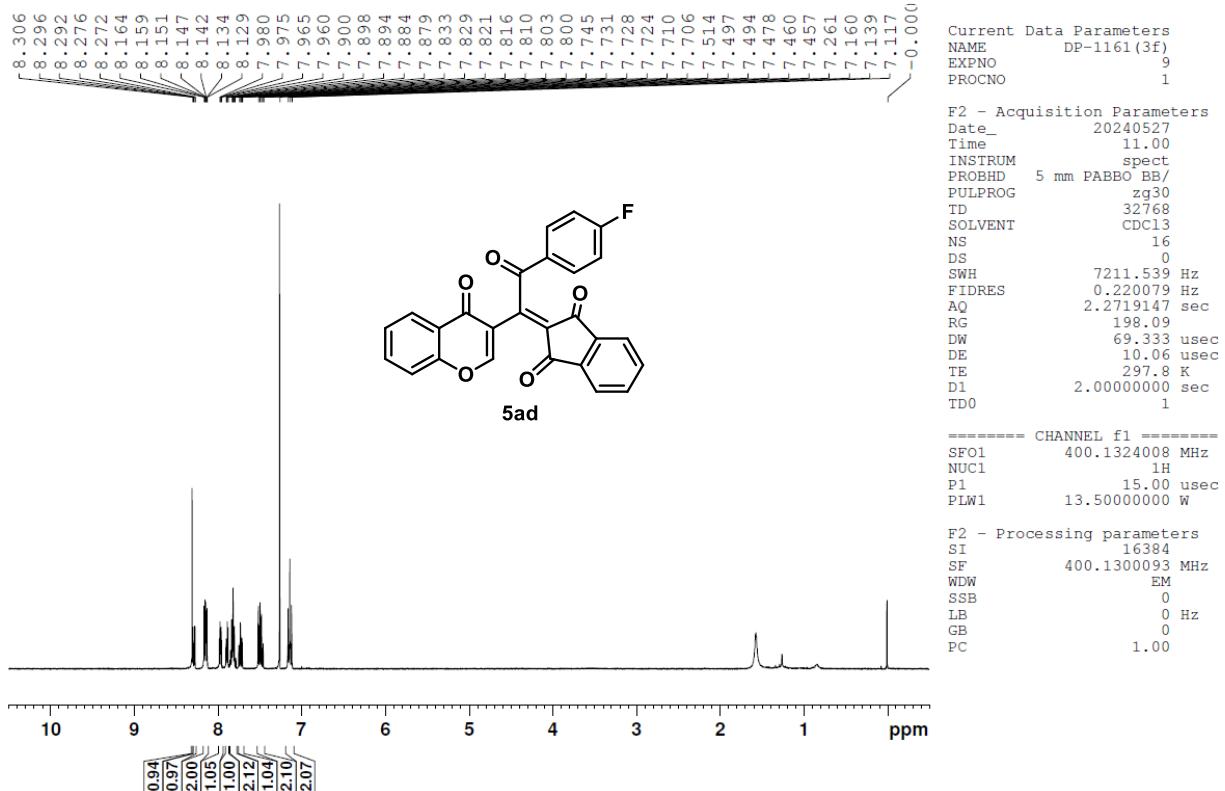
<sup>13</sup>C NMR spectrum of compound 5ac (CDCl<sub>3</sub>, 400 MHz)



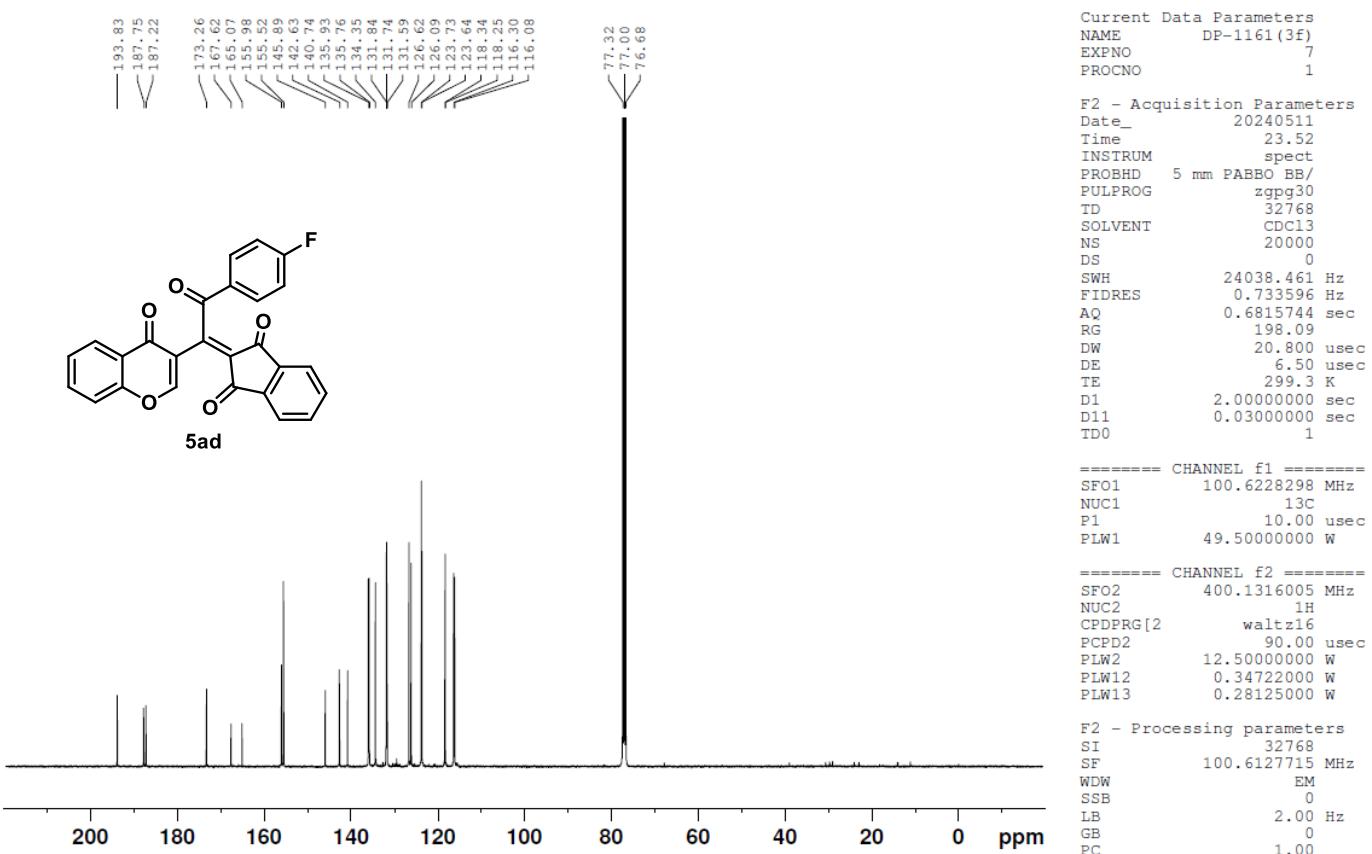
<sup>13</sup>C NMR spectrum of compound 5ac (CDCl<sub>3</sub>, 100 MHz)



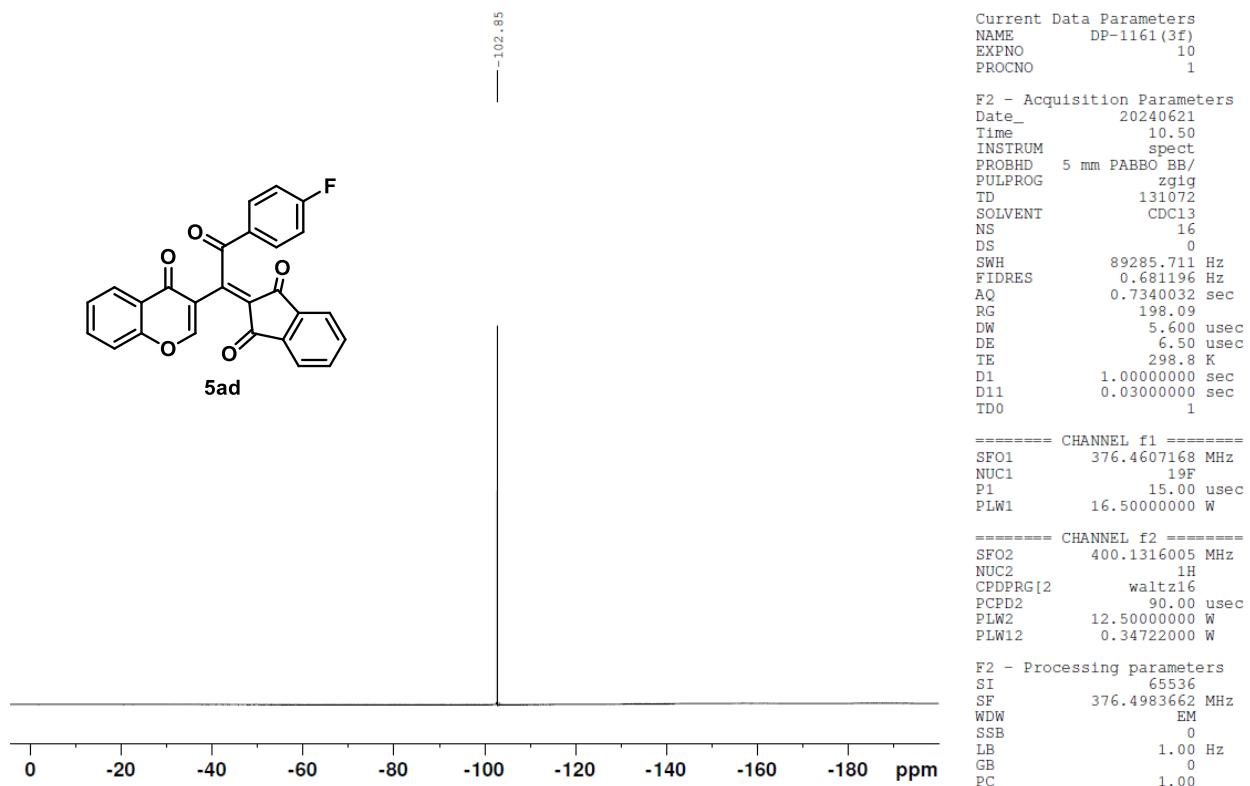
<sup>1</sup>H NMR spectrum of compound 5ad (CDCl<sub>3</sub>, 400 MHz)



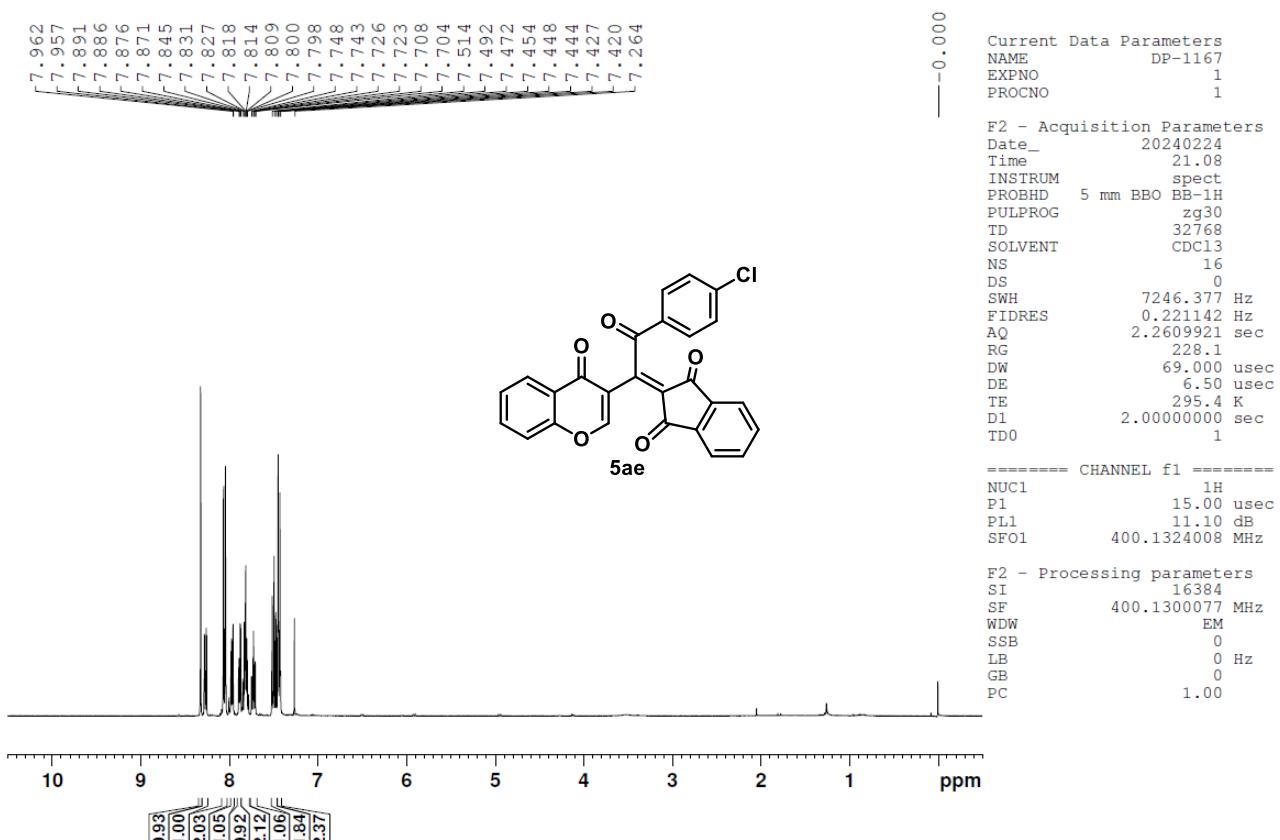
<sup>13</sup>C NMR spectrum of compound 5ad (CDCl<sub>3</sub>, 100 MHz)



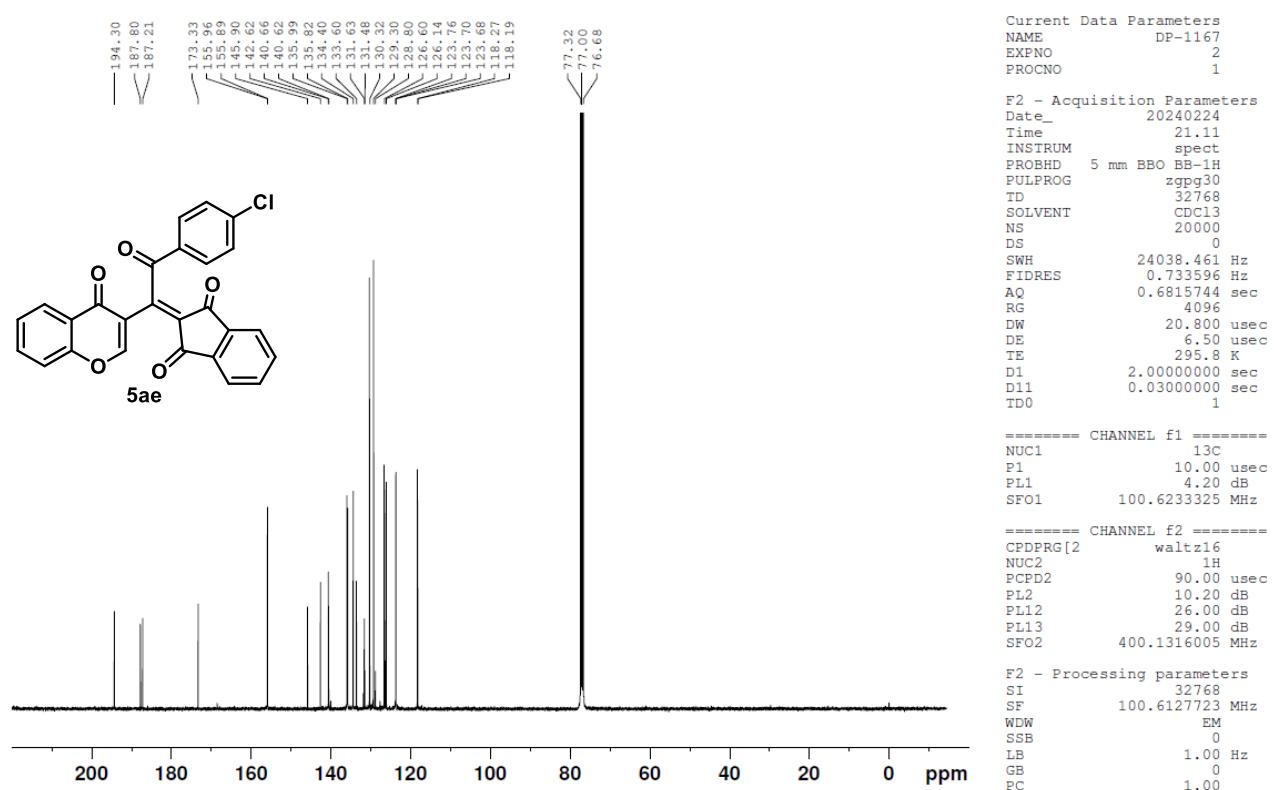
<sup>19</sup>F NMR spectrum of compound 5ad (CDCl<sub>3</sub>, 376 MHz)



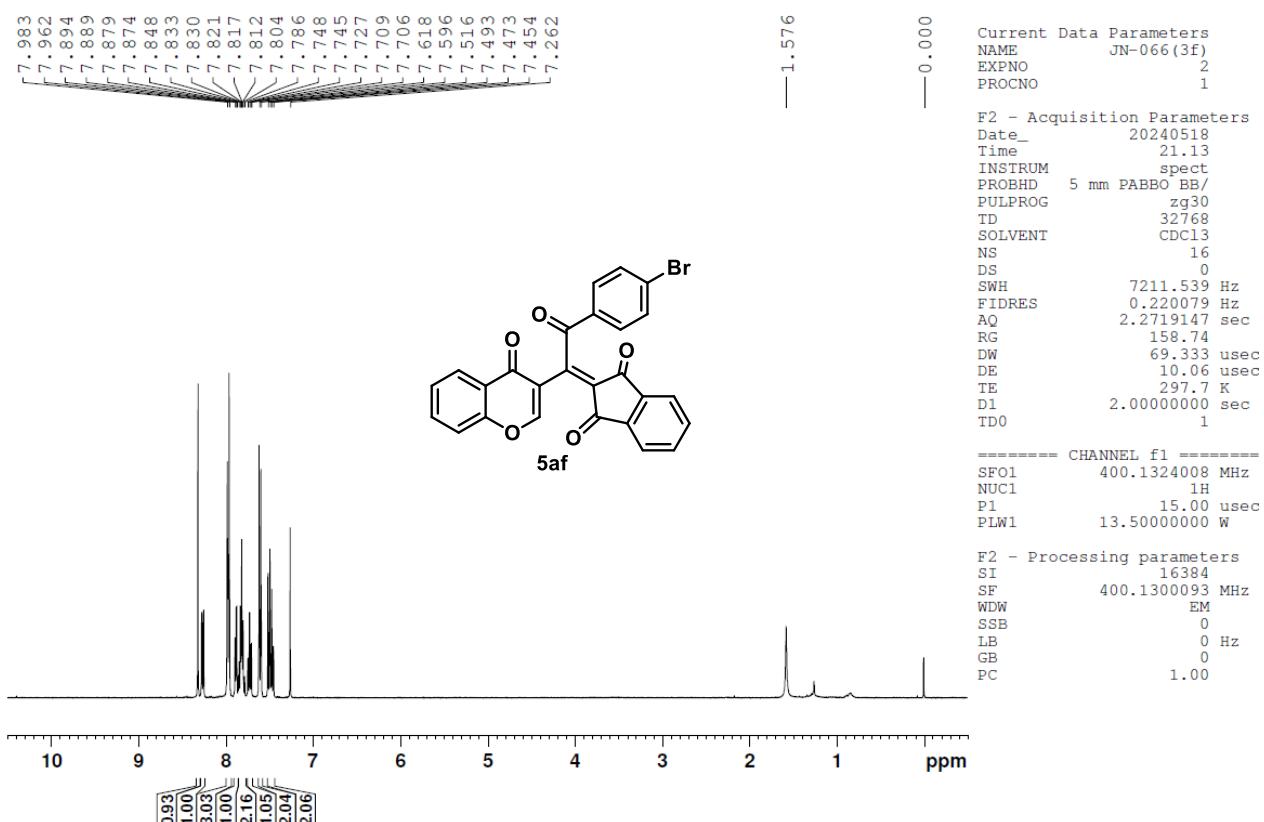
<sup>1</sup>H NMR spectrum of compound 5ae (CDCl<sub>3</sub>, 400 MHz)



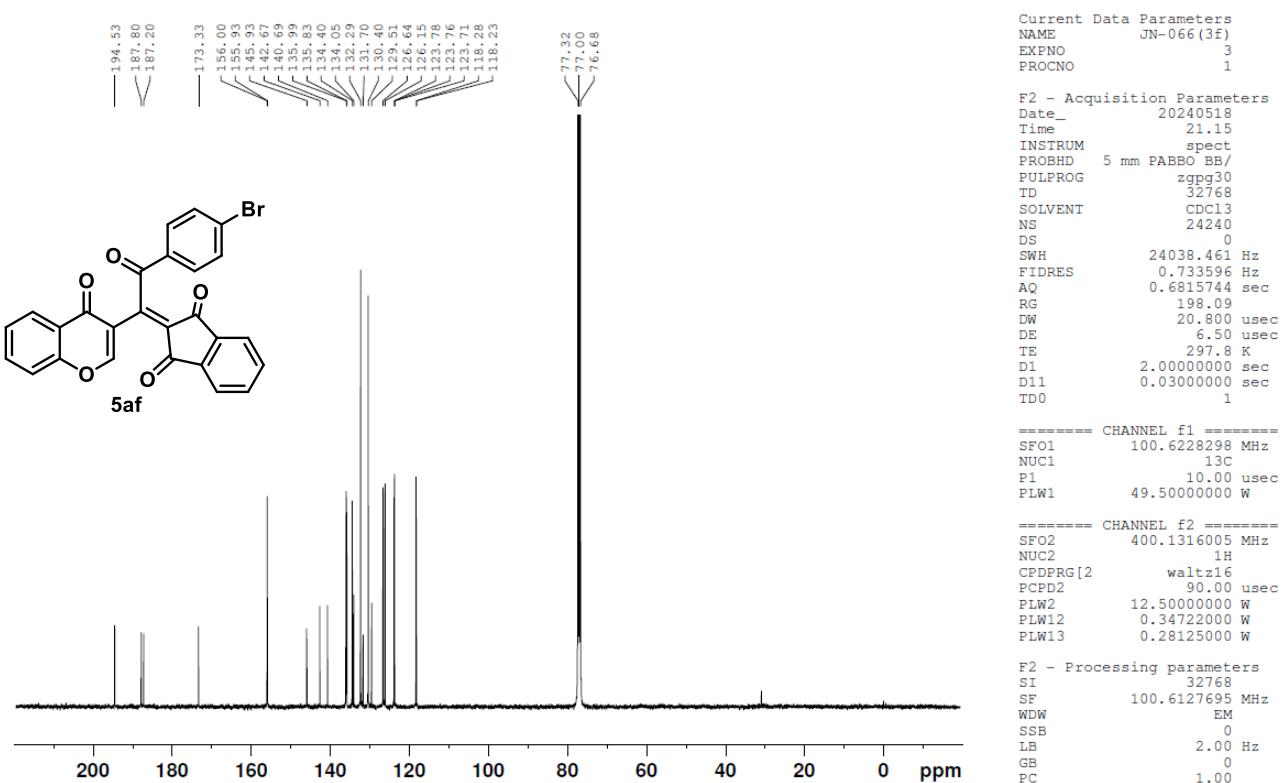
<sup>13</sup>C NMR spectrum of compound 5ae (CDCl<sub>3</sub>, 100 MHz)



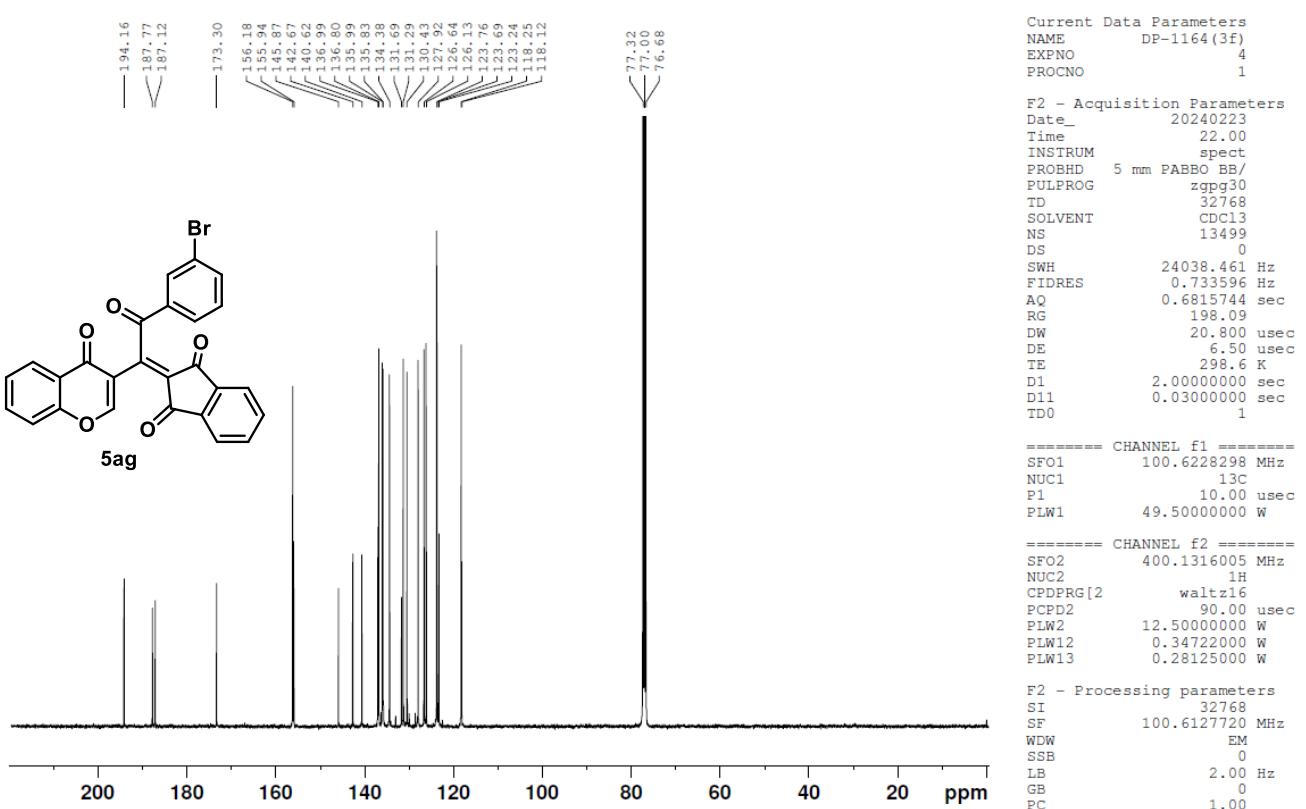
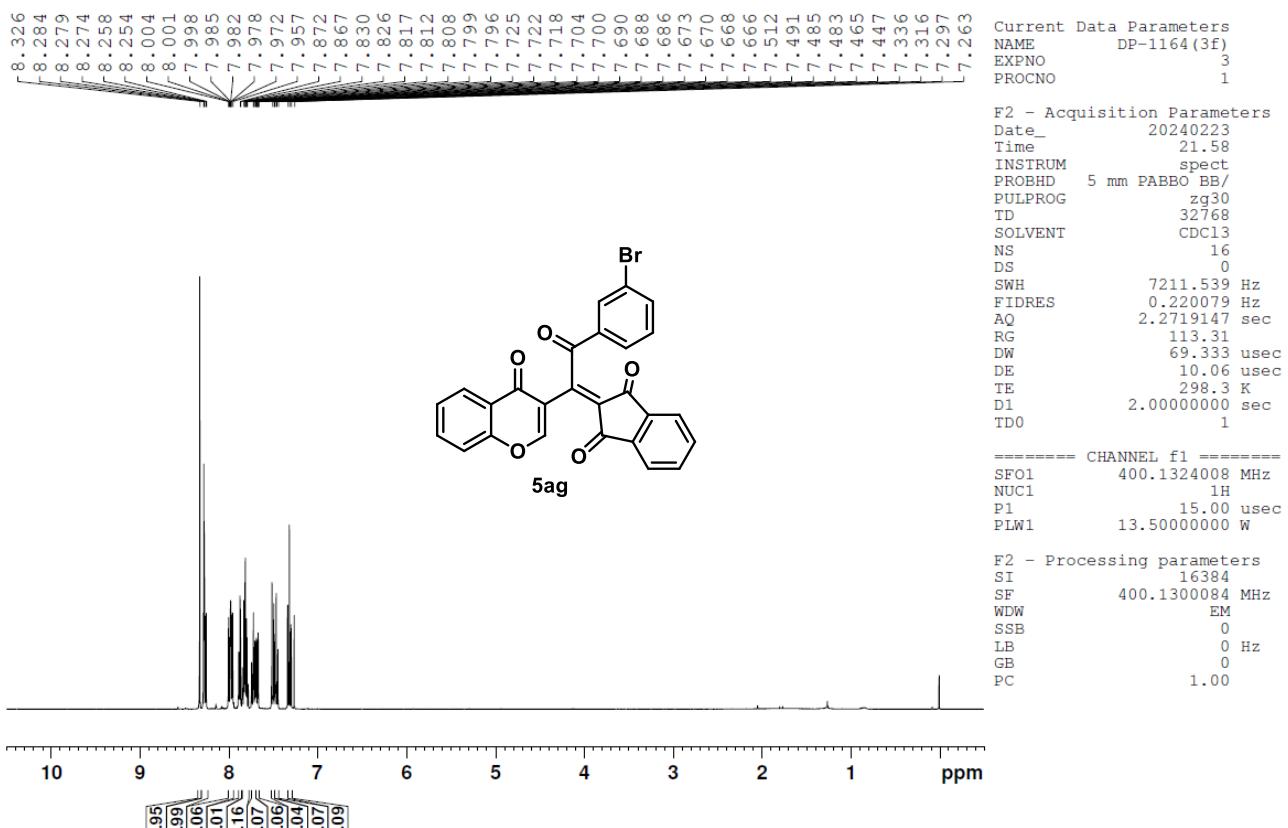
<sup>1</sup>H NMR spectrum of compound **5af** (CDCl<sub>3</sub>, 400 MHz)



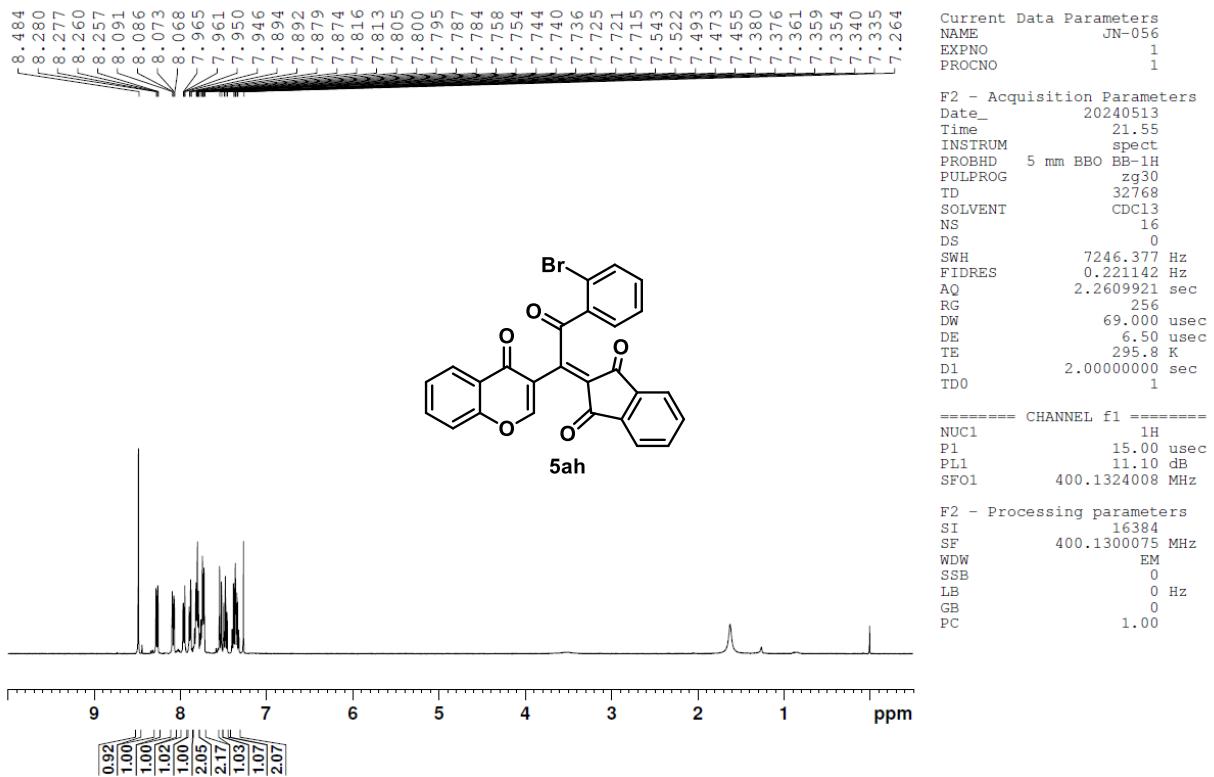
<sup>13</sup>C NMR spectrum of compound **5af** (CDCl<sub>3</sub>, 100 MHz)



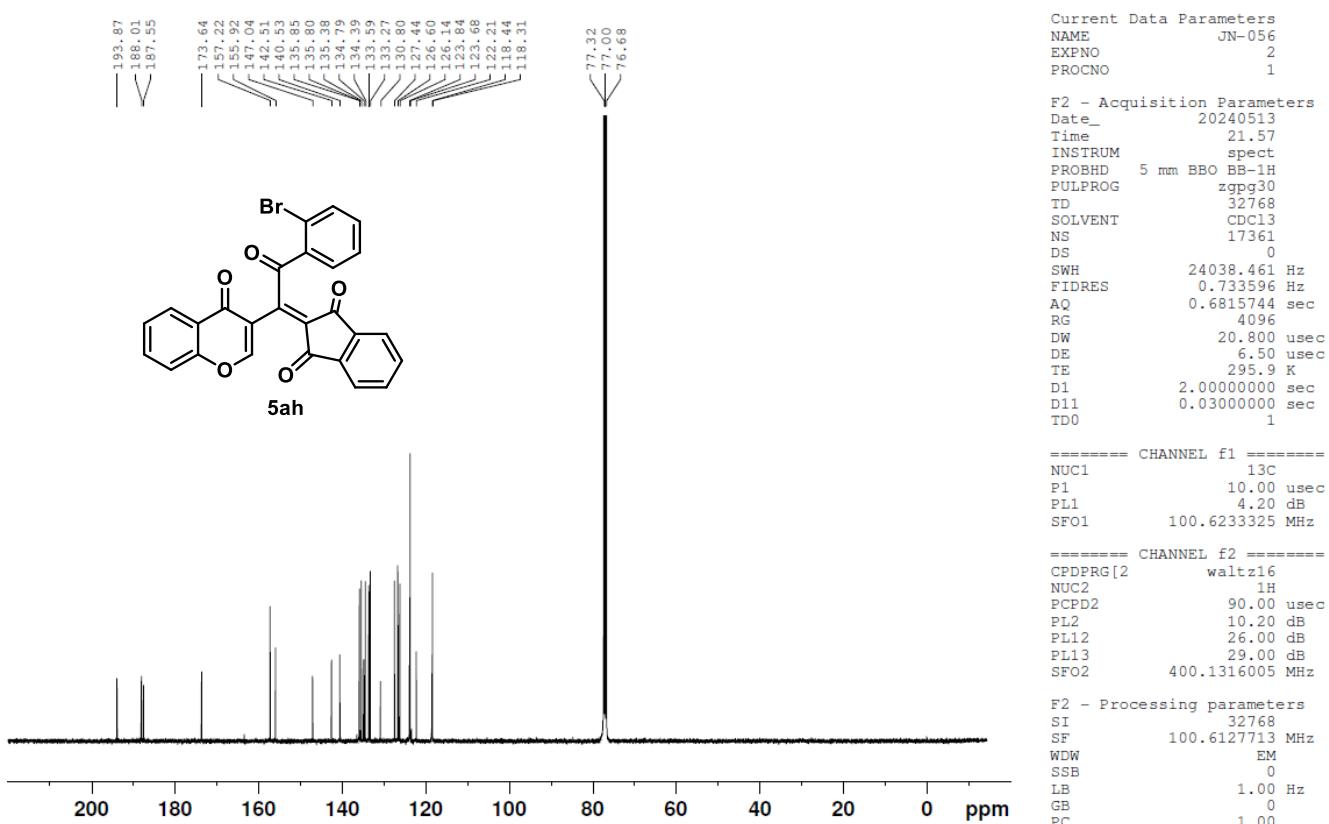
<sup>1</sup>H NMR spectrum of compound **5ag** (CDCl<sub>3</sub>, 400 MHz)



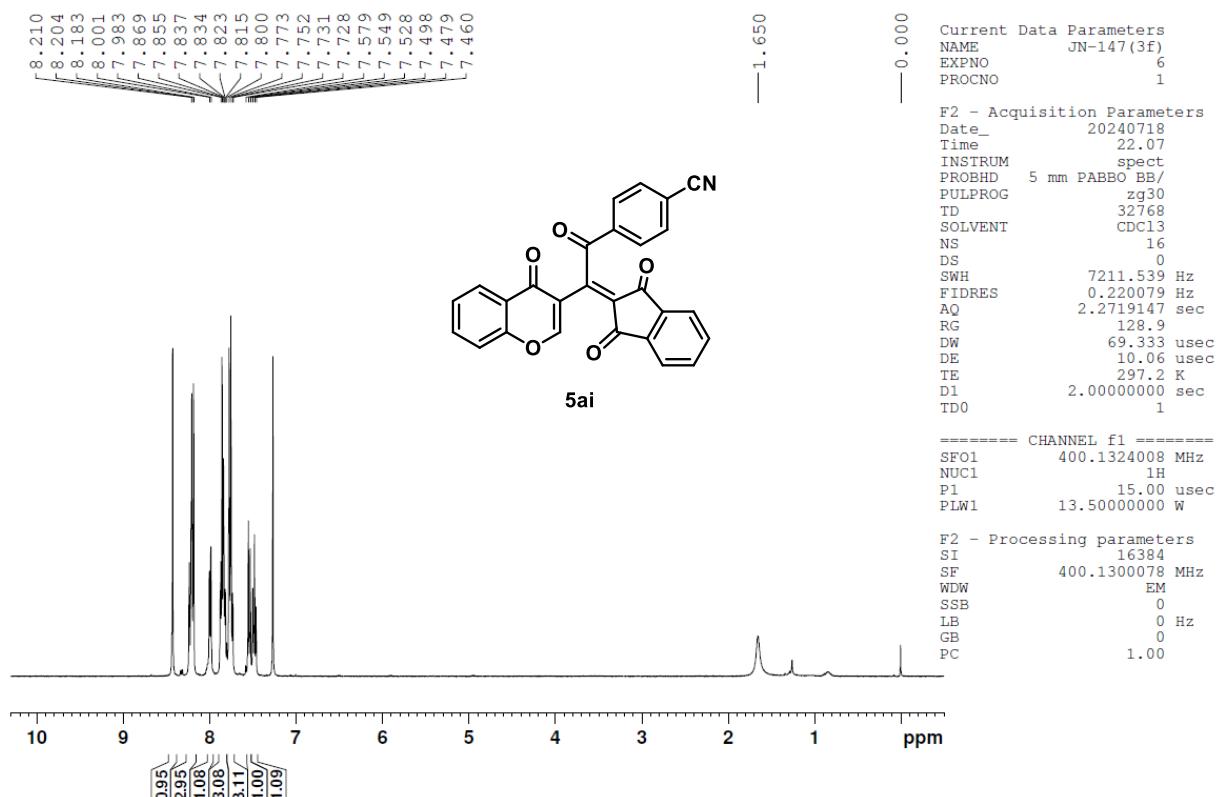
<sup>1</sup>H NMR spectrum of compound **5ah** (CDCl<sub>3</sub>, 400 MHz)



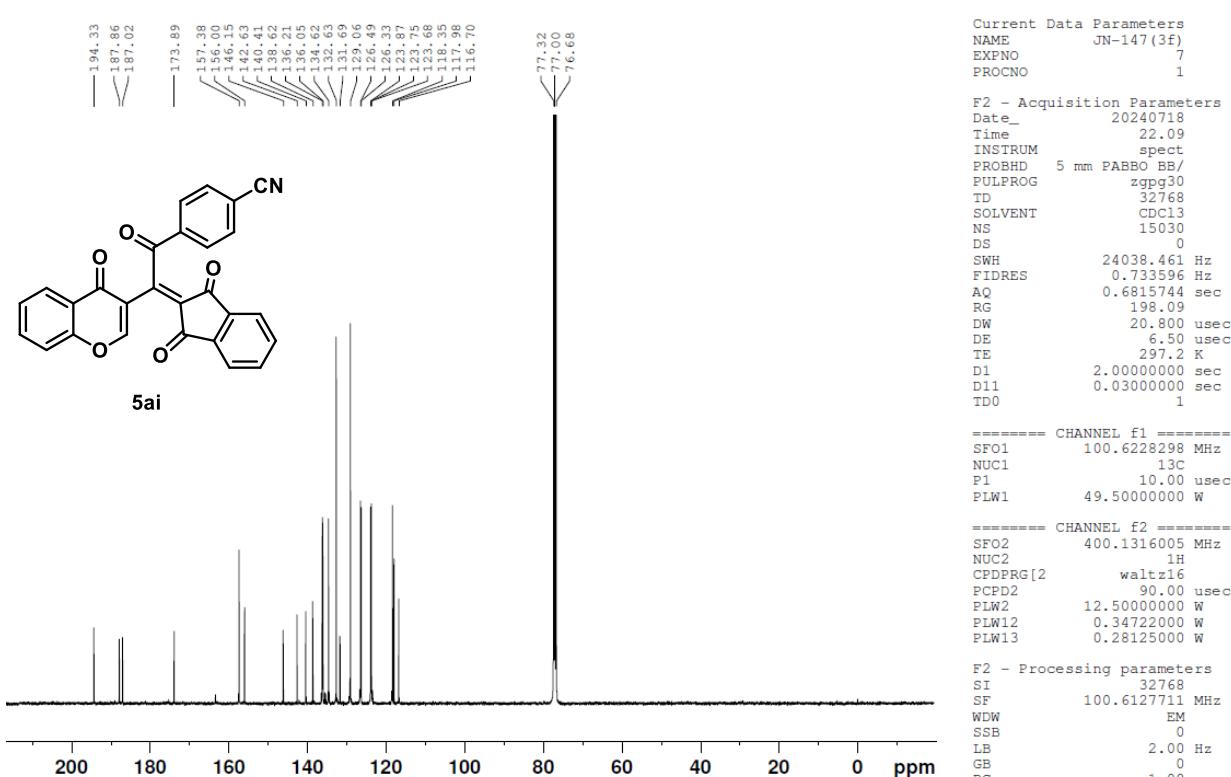
<sup>13</sup>C NMR spectrum of compound **5ah** (CDCl<sub>3</sub>, 100 MHz)



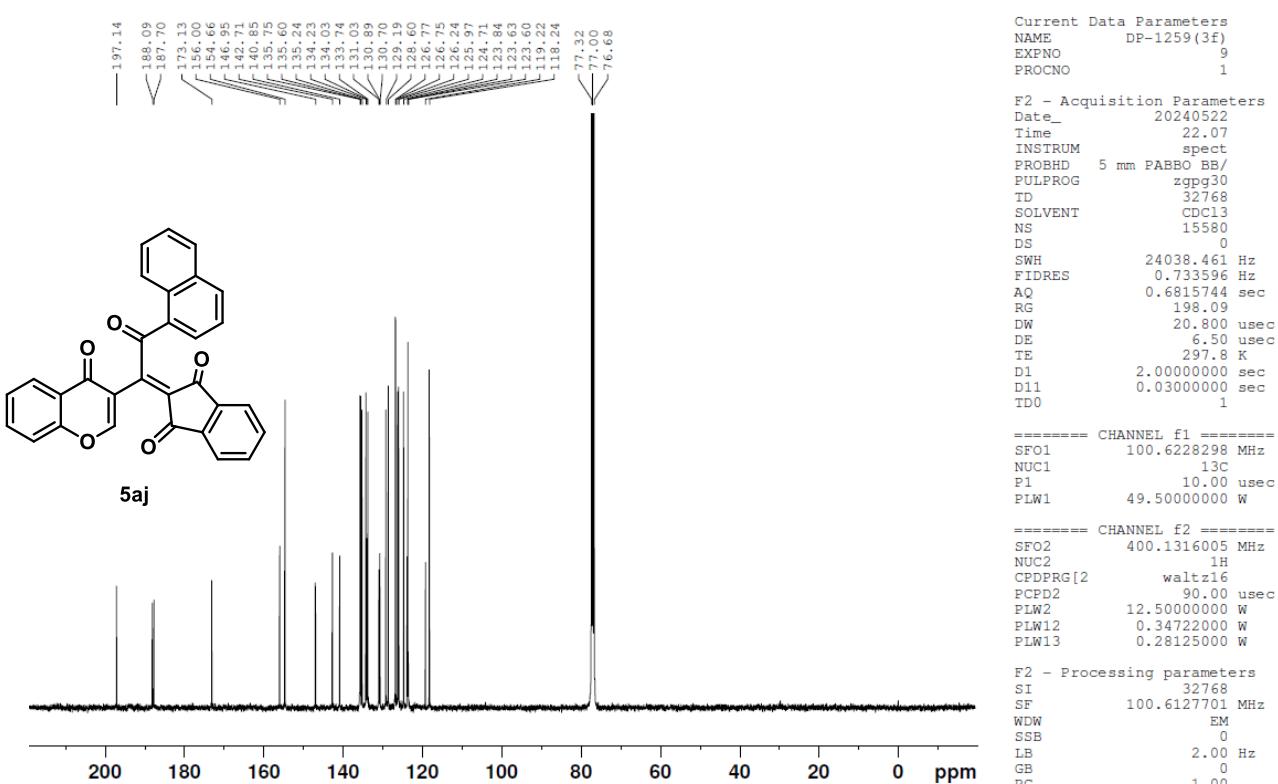
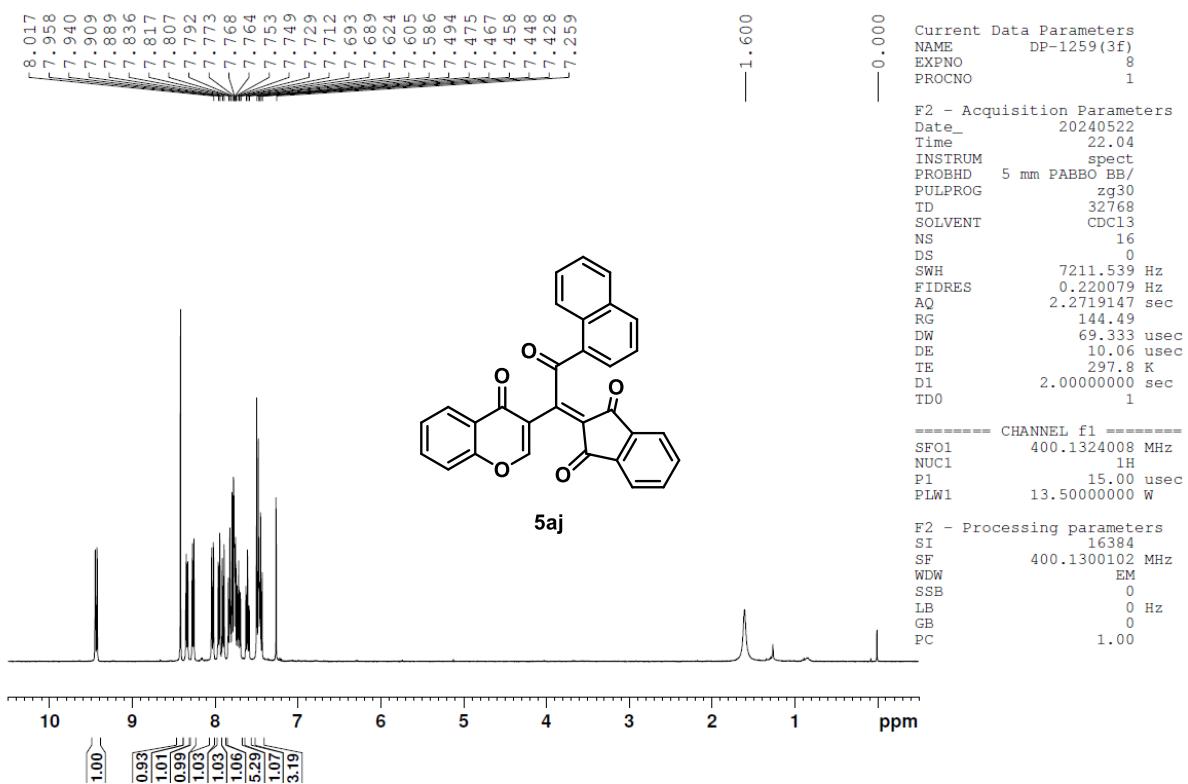
<sup>1</sup>H NMR spectrum of compound 5ai (CDCl<sub>3</sub>, 400 MHz)



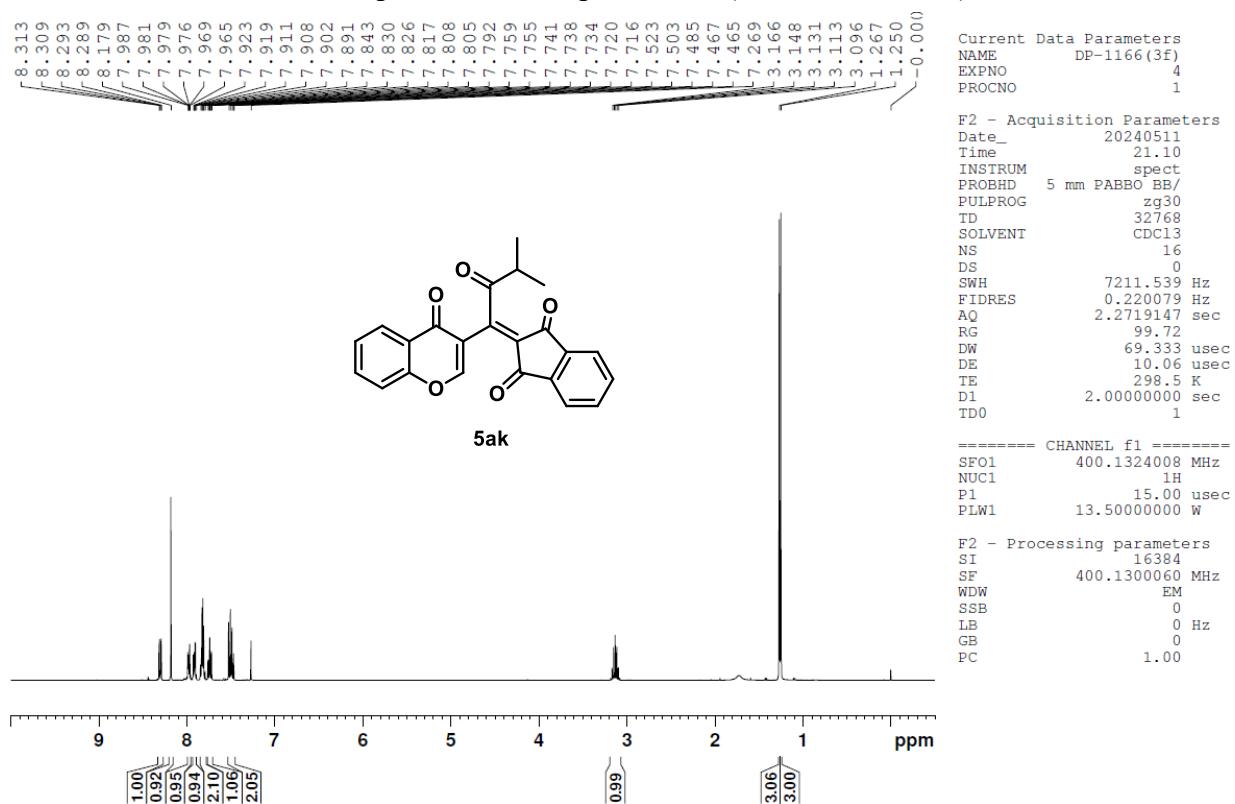
<sup>13</sup>C NMR spectrum of compound 5ai (CDCl<sub>3</sub>, 100 MHz)



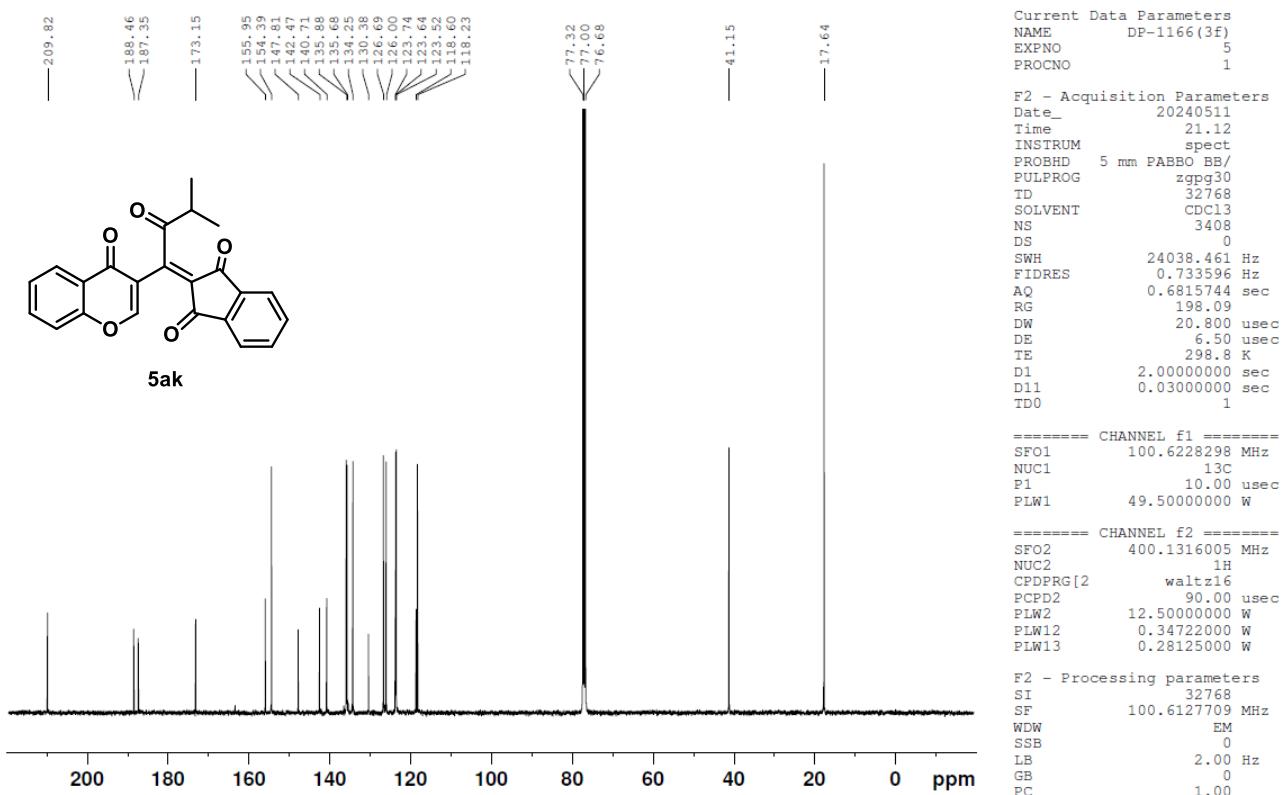
<sup>1</sup>H NMR spectrum of compound 5aj (CDCl<sub>3</sub>, 400 MHz)



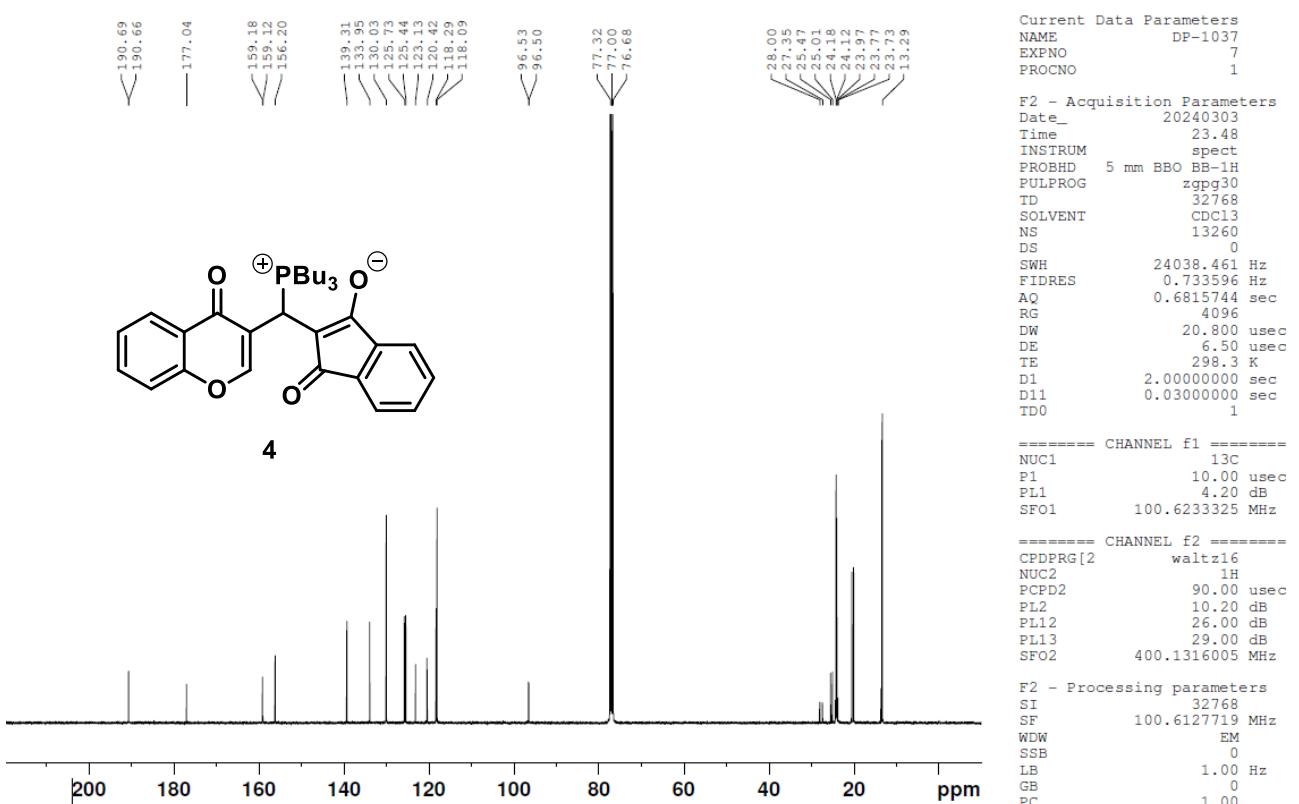
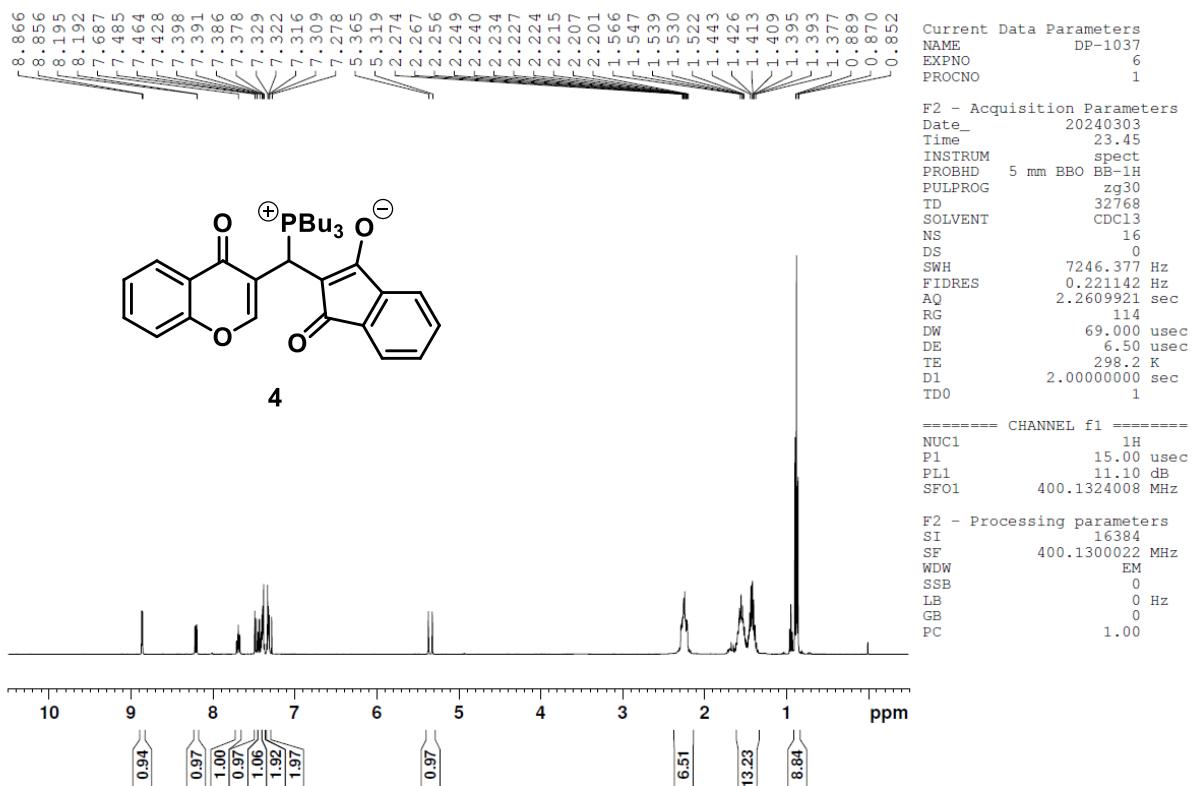
<sup>1</sup>H NMR spectrum of compound 5ak (CDCl<sub>3</sub>, 400 MHz)



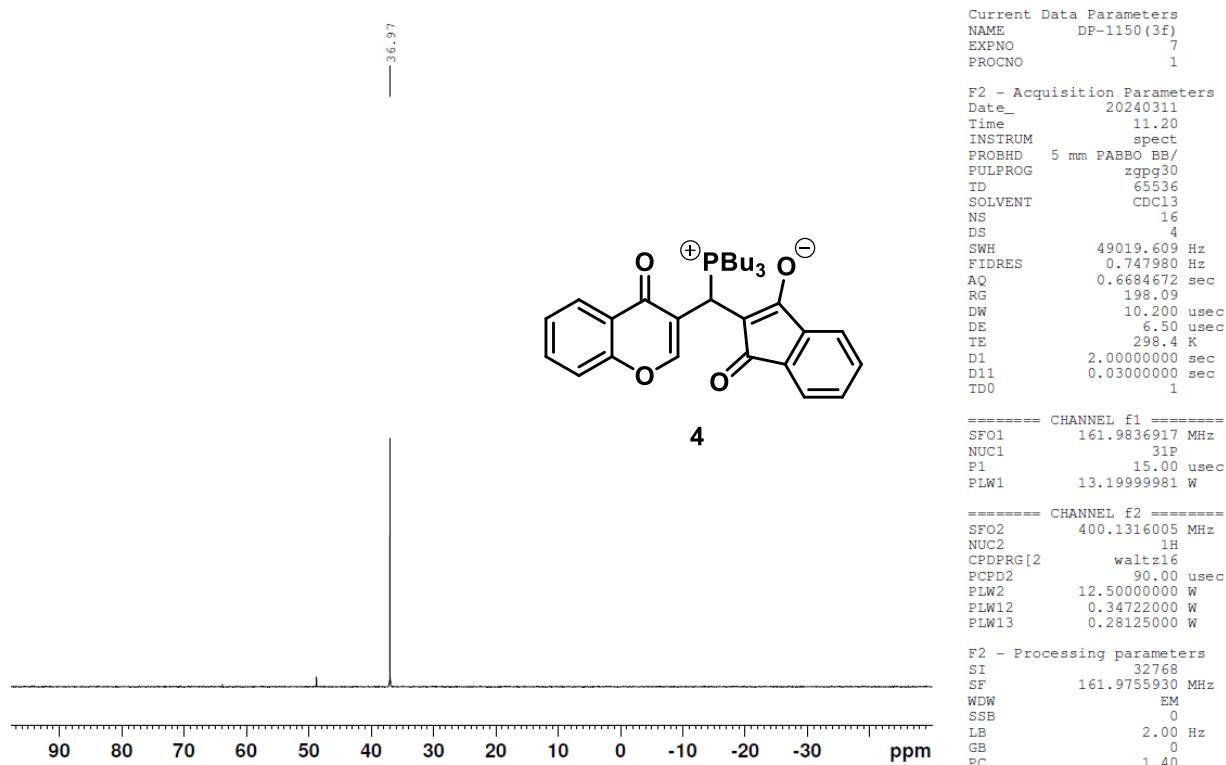
<sup>13</sup>C NMR spectrum of compound 5ak (CDCl<sub>3</sub>, 100 MHz)



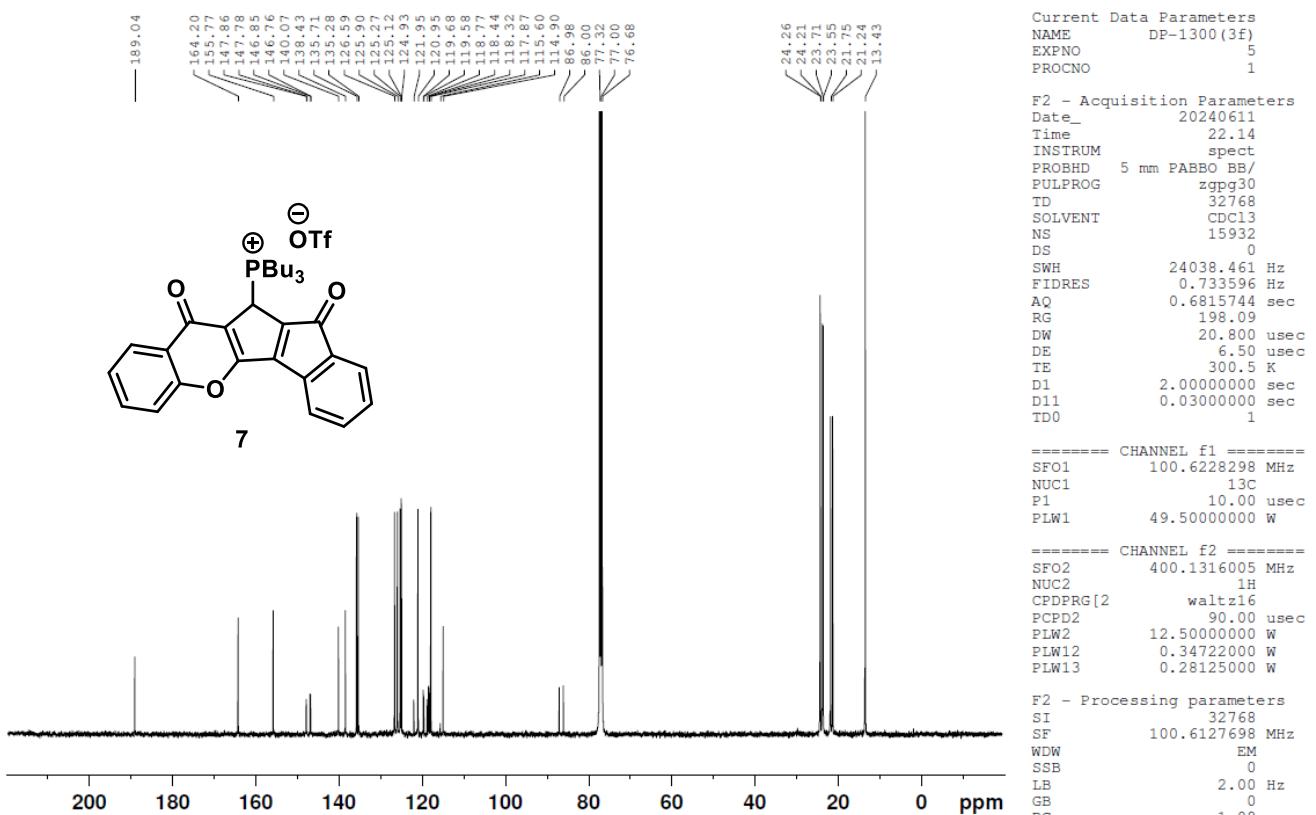
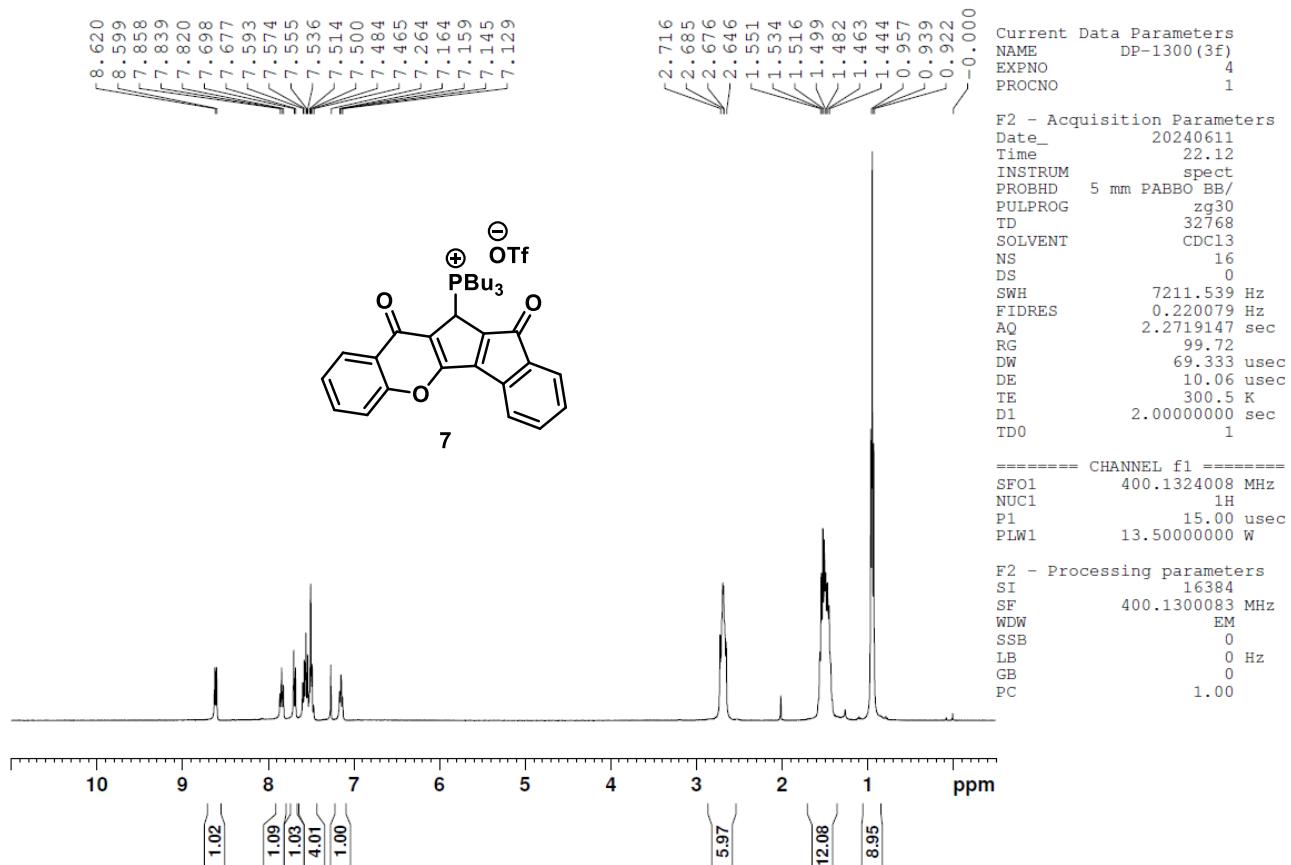
<sup>1</sup>H NMR spectrum of compound 4 (CDCl<sub>3</sub>, 400 MHz)



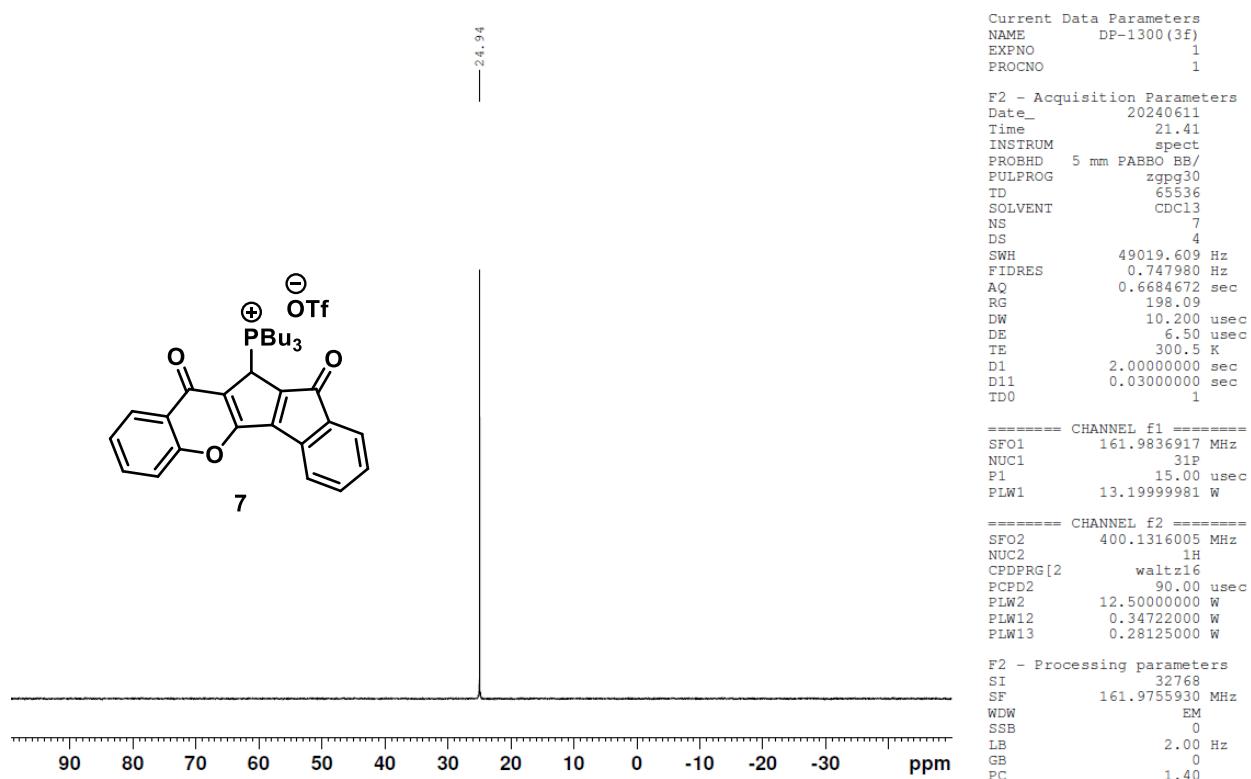
<sup>31</sup>P NMR spectrum of compound 4 (CDCl<sub>3</sub>, 162 MHz)



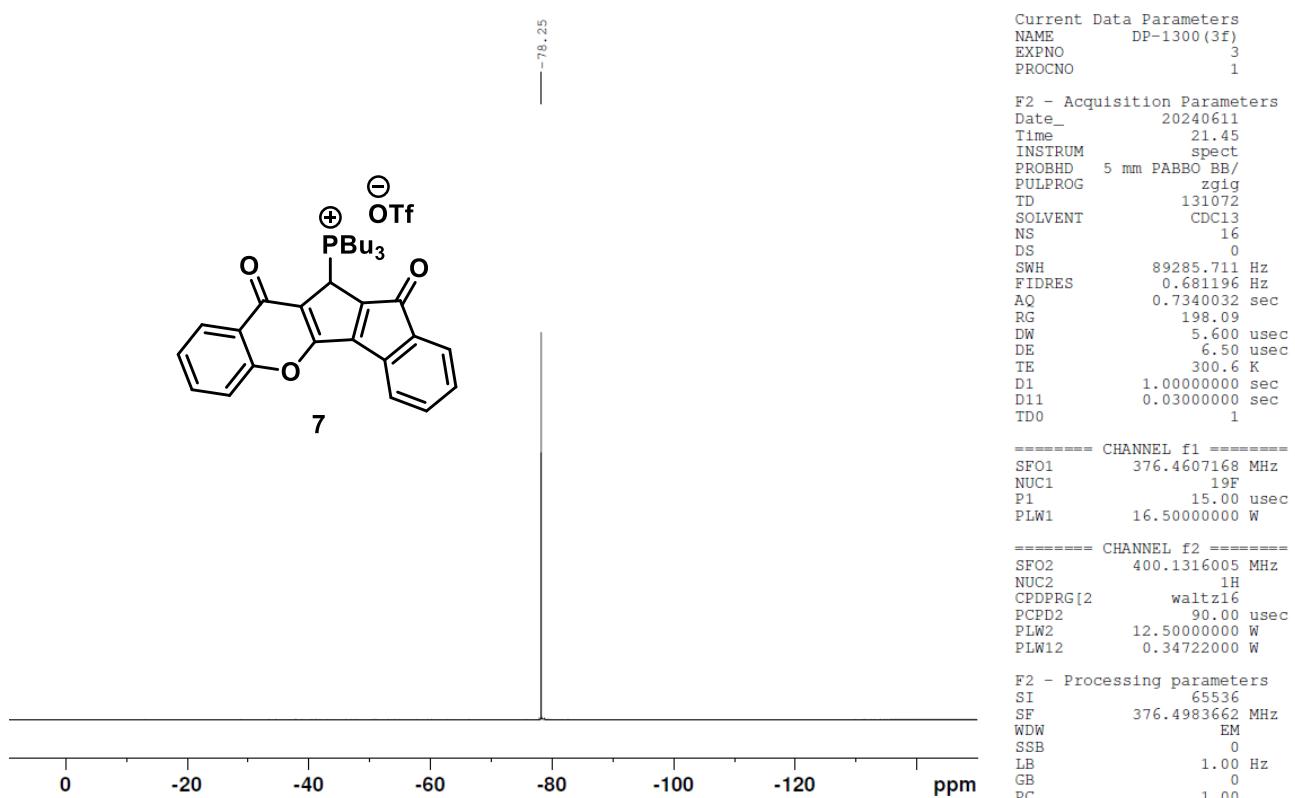
<sup>1</sup>H NMR spectrum of compound 7 (CDCl<sub>3</sub>, 400 MHz)



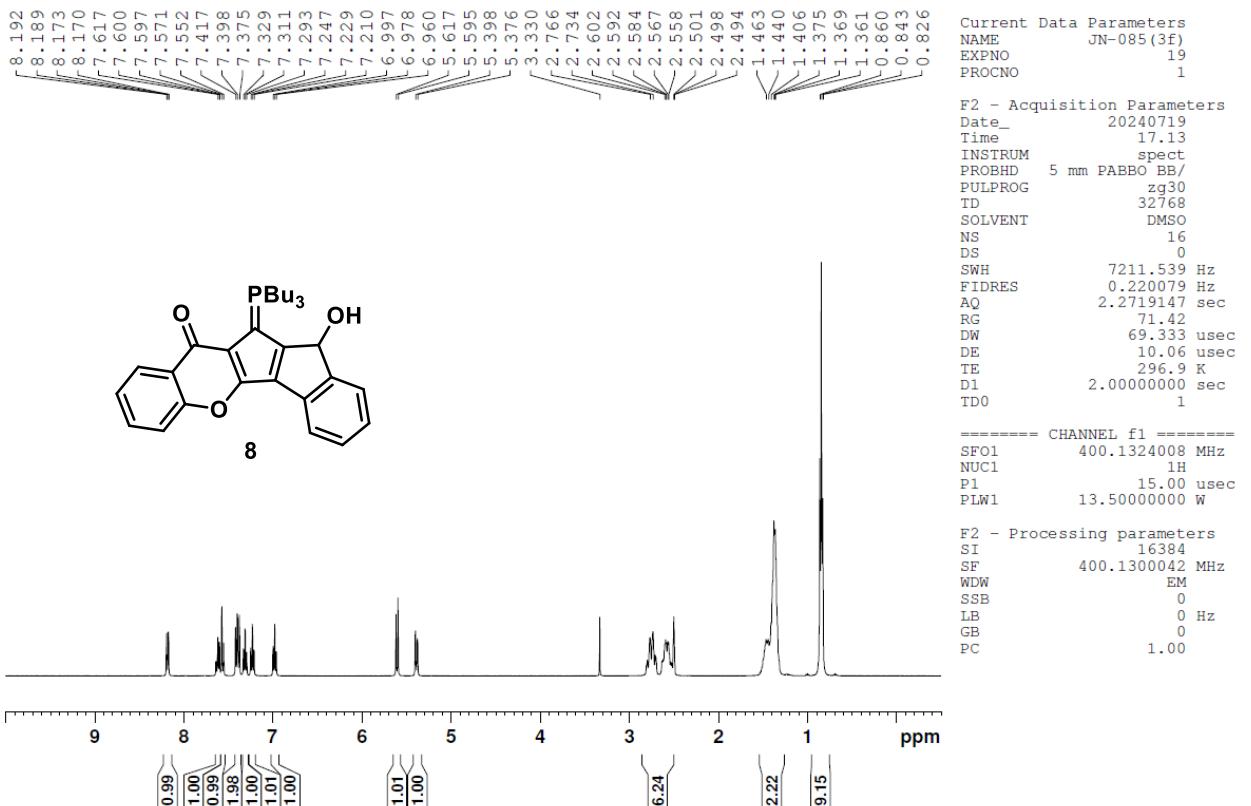
<sup>31</sup>P NMR spectrum of compound 7 (CDCl<sub>3</sub>, 162 MHz)



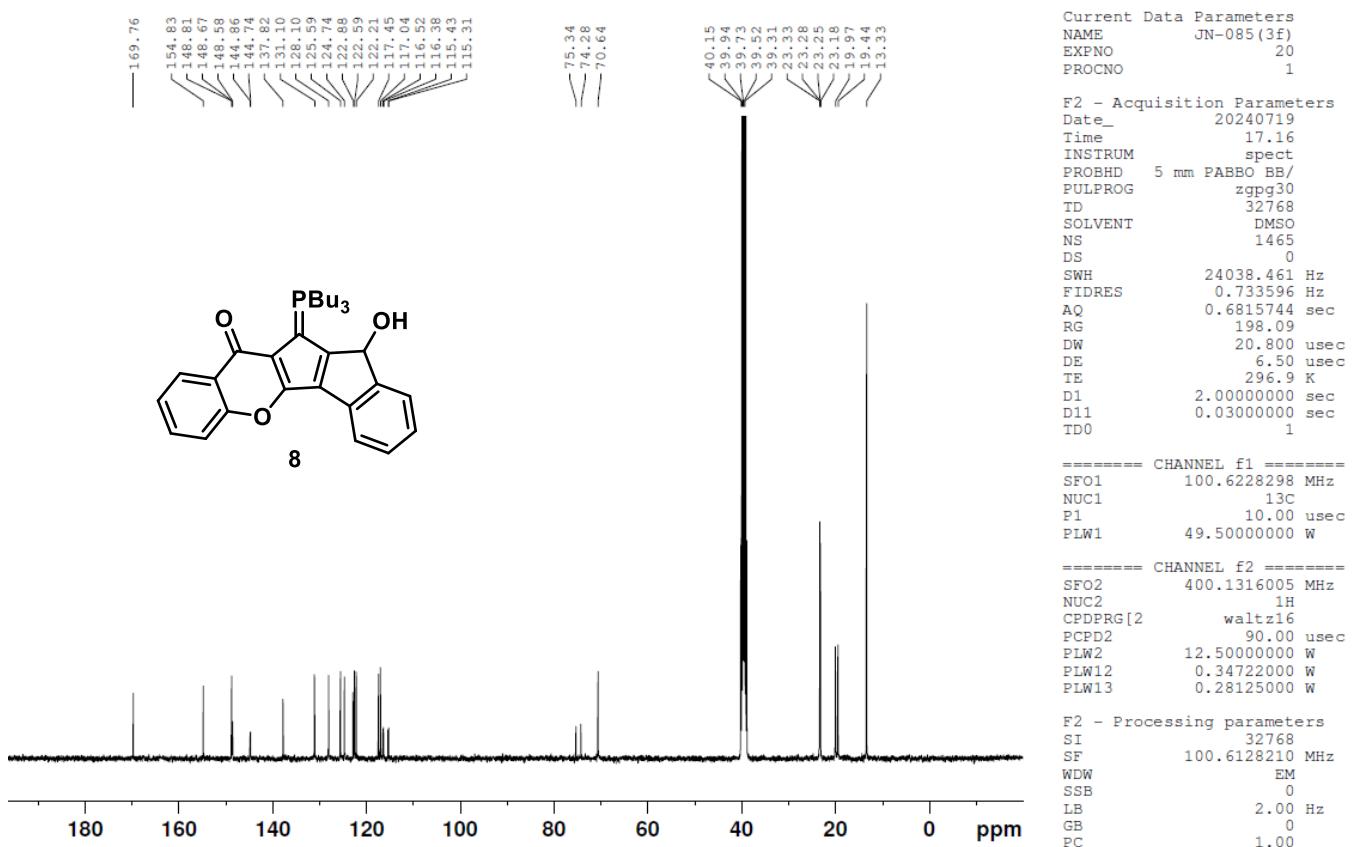
<sup>19</sup>F NMR spectrum of compound 7 (CDCl<sub>3</sub>, 376 MHz)



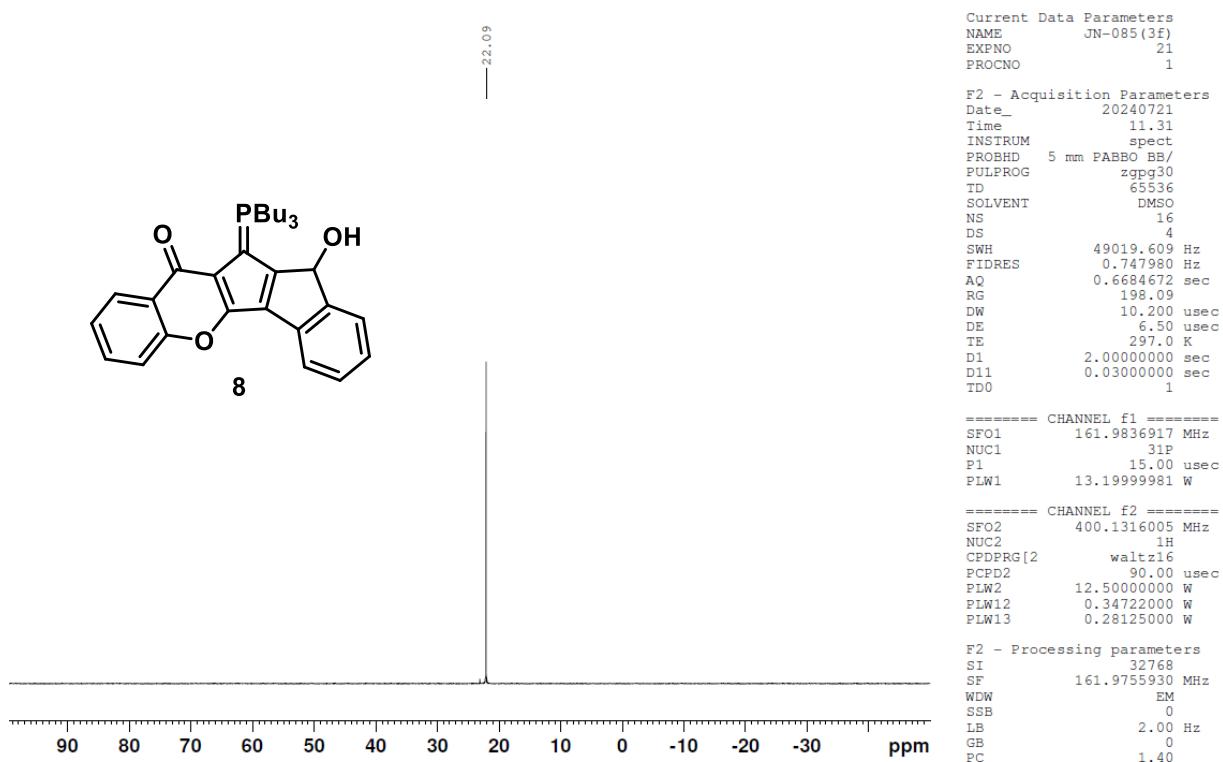
<sup>1</sup>H NMR spectrum of compound 8 (DMSO, 400 MHz)



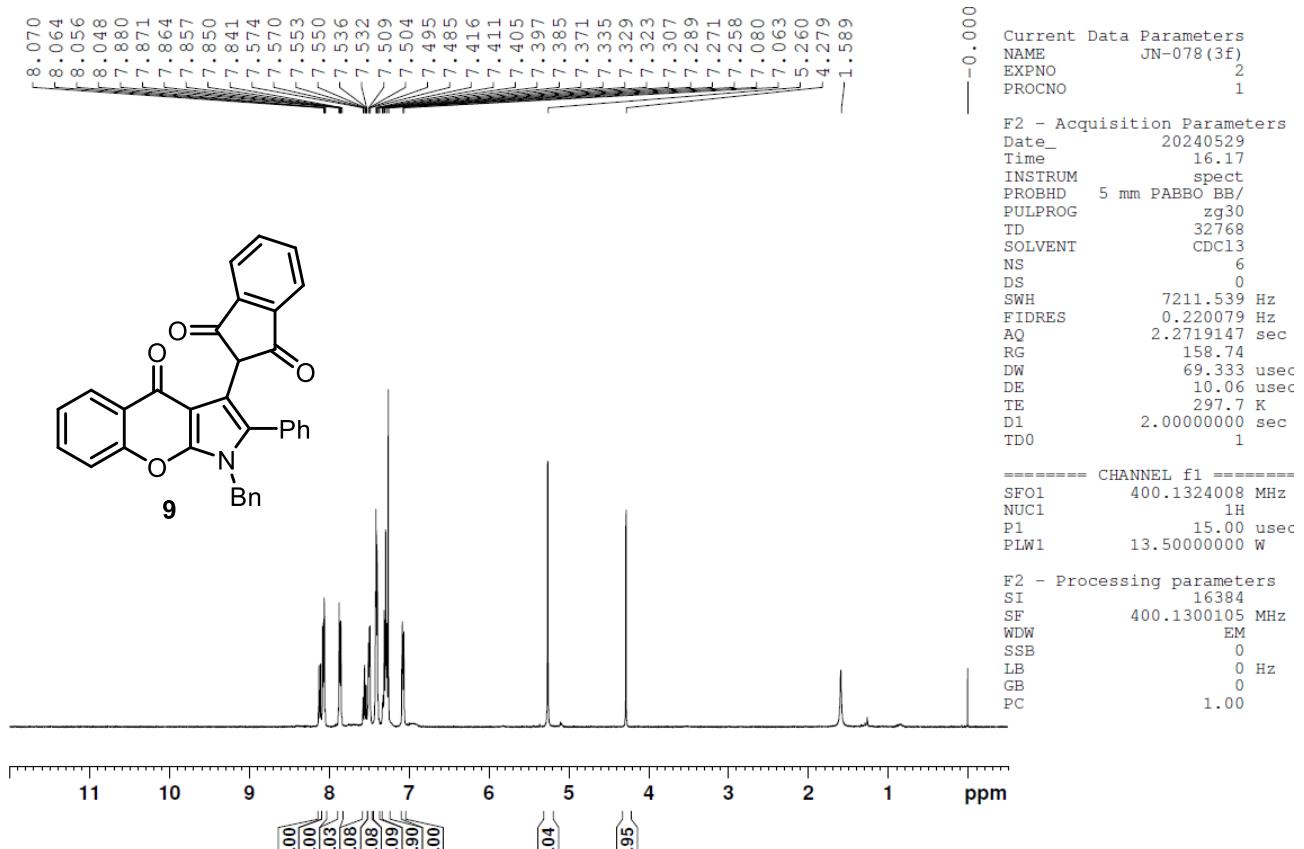
<sup>13</sup>C NMR spectrum of compound 8 (DMSO, 100 MHz)



<sup>31</sup>P NMR spectrum of compound 8 (DMSO, 162 MHz)



<sup>1</sup>H NMR spectrum of compound 9 (CDCl<sub>3</sub>, 400 MHz)



<sup>13</sup>C NMR spectrum of compound 9 (CDCl<sub>3</sub>, 100 MHz)

