

## Vinylogous Michael addition-triggered Quadruple Cascade for the Enantioselective Generation of Multiple Quaternary Stereocenters

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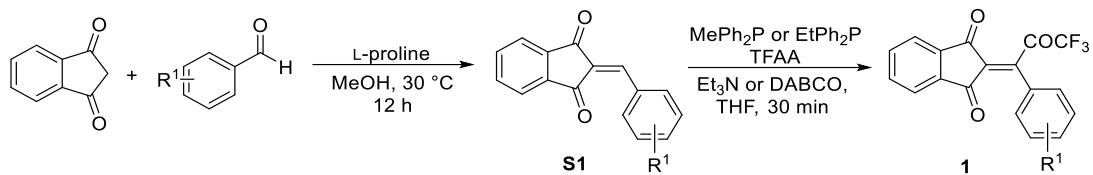
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## **I. General Information**

All solvents and reagents were used as purchased from commercial suppliers without further purification. Starting materials and catalysts which were not commercially available were synthesized by the previously reported methods. Analytical thin layer chromatography (TLC) was performed on precoated alumina-backed silica gel plates (Merck 60 F254, 0.2 mm thickness) which were developed using UV fluorescence and iodine. Flash-chromatography was performed on silica gel (Merck Kieselgel 60 Å 230-400 mesh). Melting points were measured on a hotstage meting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 500 spectrometer and only selected peaks are shown. <sup>1</sup>H-NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer, while <sup>13</sup>C-NMR spectra were recorded on a 100 MHz instrument. Chemical shifts are reported in δ ppm referenced to an internal TMS standard for <sup>1</sup>H-NMR and chloroform-d ( $\delta = 77.0$  ppm) for <sup>13</sup>C-NMR. In some cases, while the chloroform-d couldn't dissolve the analyst well, the acetone-d<sub>6</sub> was applied instead. The chemical shifts refer to an internal acetone-d<sub>6</sub> standard for <sup>1</sup>H-NMR ( $\delta = 2.05$  ppm) and for <sup>13</sup>C-NMR ( $\delta = 29.8$  ppm). HRMS spectra were recorded on JEOL SX-102A. For transferring liquids on a microliter scale, a micropipette (VITLAB C121) of 2-20 μL capacity was used. The X-ray diffraction measurements were carried out at 298 K on a KAPPA APEX II CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ( $k = 0.71073$  Å). Optical rotations were measured in CH<sub>2</sub>Cl<sub>2</sub> on a JASCO co. DIP-1000 digital polarimeter with a 50 mm cell (c given in g/100 mL). The known fully substituted substituted enones **1a**, and **1c-II** were synthesized following the procedure reported earlier by our group.<sup>1,2</sup> The compound **1b** and other oxindole derived vinylogous nucleophiles **2a-2p** were synthesized following the procedure mentioned in this supporting information.

## **II. Experimental procedures**

## General Synthesis of 1:



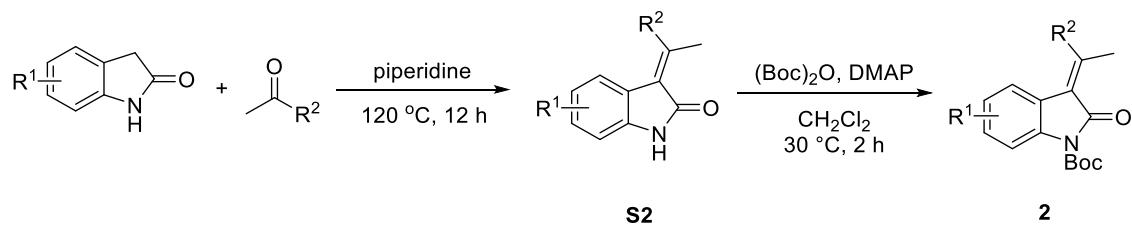
## **General procedure A (GP-A) for the preparation of S1:**

A dry and argon-flushed 50 mL round-bottomed flask equipped with a magnetic stir bar was sequentially charged with 1,3-indanedione (10.0 mmol), L-proline (0.3 equiv), appropriately substituted benzaldehyde (1.1 equiv) and methanol (20 mL). The reaction mixture was stirred for 12 hours at 30 °C. Thereafter, the resulting slurry was filtered and the residue was washed with methanol until it was free from any residual starting materials to get the pure product **S1**.

## **General procedure B (GP-B) for the preparation of 1:**

A dry and nitrogen-flushed 25 mL round-bottomed flask, equipped with a magnetic stirring bar and a septum, was sequentially charged with a solution of **S1** (1.5 mmol), EtPh<sub>2</sub>P (0.15 equiv), TFAA (1.3 equiv) and Et<sub>3</sub>N (1.4 equiv) in THF (7.5 mL). The reaction mixture was stirred for 30 minutes at 30 °C. Thereafter, the solvent was removed by evaporation *in vacuo*. Purification by flash chromatography furnished **1**.

### General synthesis of 2:



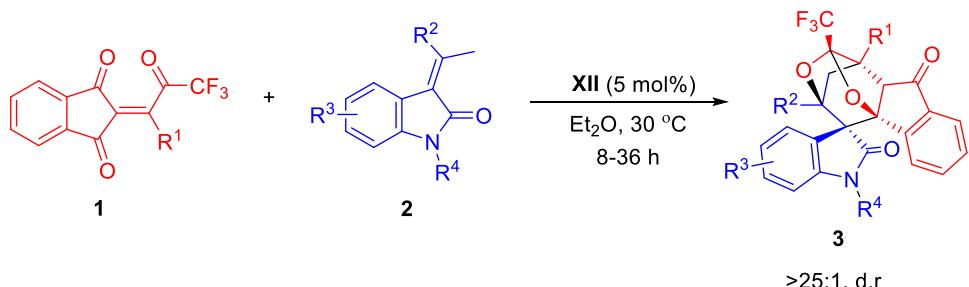
## **General procedure C (GP-C) for the preparation of S2:**

An ace pressure tube with a magnetic stir bar was sequentially with indolin-2-one (10.0 mmol) in piperidine (0.8 equiv), acetophenone derivative (3.0 equiv) and the resulting mixture was heated to 160 °C for 12 hours. Upon completion of reaction, the resulting dark solution was cooled to 30 °C and stirred for 30 min. The crude residue was purified by silica gel flash chromatography (Hexanes/EtOAc =1:9) to obtain **S2**.

**General procedure D (GP-D) for the preparation of 2:**

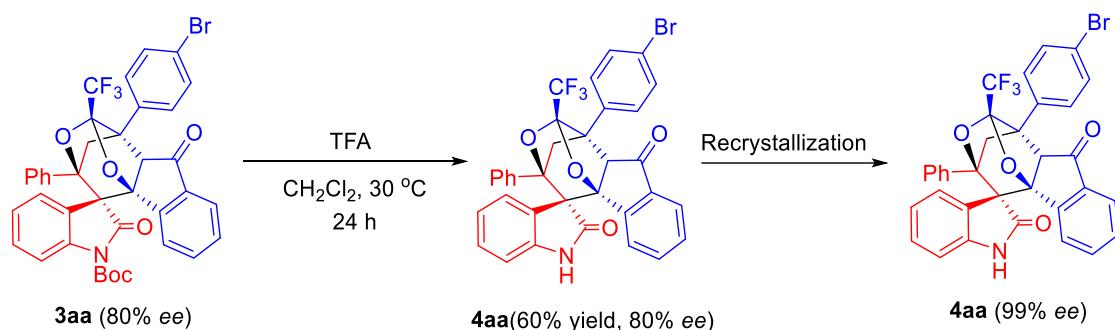
To a solution of **S2** (5 mmol) in DCM (20 mL) was added a solution of  $(\text{Boc})_2\text{O}$  (1.1 equiv) diluted in DCM (5 mL) and DMAP (0.5 equiv) and stirred for 2 hours. Then the reaction mixture was concentrated *in vacuo* and the residue was purified by silica gel flash chromatography (Hexanes/DCM = 5: 1) to obtain **2**.

**General experimental procedure E for the synthesis of cascade product 3:**



A capped glass vial equipped with a magnetic stir bar was charged with **1** (0.1 mmol), **2** (1.0 equiv), catalyst **QN-T** (5 mol%) and  $\text{Et}_2\text{O}$  (0.5 mL) and stirred at  $30^\circ\text{C}$ . The progress of the reaction was monitored by TLC and  $^1\text{H}$  NMR data analysis. After the completion of reaction, 2N HCl (2 mL) was added and extracted twice with DCM (2.5 mL). The combined organic extracts were concentrated *in vacuo* and the residue was subjected to flash column chromatography over silica gel (hexanes/ethyl acetate) to afford pure adduct **3**.

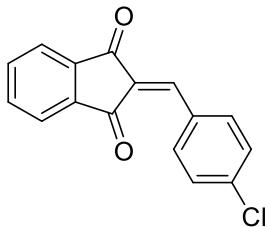
**Typical experimental procedure for the deprotection of 3aa:**



To a solution of enantiomerically enriched **3aa** (0.053 mmol, 39.5 mg, 80% ee) in DCM (0.5 mL) was added TFA (1.0 equiv, 4.06  $\mu\text{L}$ ) and the reaction mixture was stirred at  $30^\circ\text{C}$  for 24 hours. Afterwards, the reaction mixture was directly subjected to flash column chromatography on silica gel ( $\text{EtOAc}/\text{Hex} = 1:6$ ) to afford **4aa** as a white solid (60% yield, 20.5 mg).

### III. Analytical data for all new compounds

#### **2-(4-Chlorobenzylidene)-1*H*-indene-1,3(2*H*)-dione (**S1b**)**



Following the GP-A, **S1b** was obtained as a green solid (2.42 g, 90% yield) from 1,3-indanedione (1.46 g, 10.0 mmol), L-proline (0.345 g, 0.3 equiv) and 4-chlorobenzaldehyde (1.54 g, 1.1 equiv) in methanol (20.0 mL) at 30 °C after 12 hours.  $R_f = 0.37$  (DCM/Hex = 1/1), mp.: 180.8-182.0 °C.

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 8.43 (d,  $J = 8.6$  Hz, 2H), 8.00-8.03 (m, 2H), 7.82-7.84 (m, 3H), 7.48 (d,  $J = 8.5$  Hz, 2H).

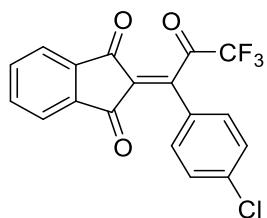
**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 190.0, 189.0, 145.2, 142.5, 140.1, 139.5, 135.5, 135.3, 131.5, 129.4, 129.1, 123.41, 123.40.

**IR (KBr)**  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3085, 1689, 1592, 830, 733.

**HRMS (EI)** calcd for  $\text{C}_{16}\text{H}_9^{35}\text{ClO}_2$ , [M] (268.0291) found: 268.0292 (100).

**HRMS (EI)** calcd for  $\text{C}_{16}\text{H}_9^{37}\text{ClO}_2$ , [M] (270.0262) found: 270.0267 (28).

#### **2-(1-(4-Chlorophenyl)-3,3,3-trifluoro-2-oxopropylidene)-1*H*-indene-1,3(2*H*)-dione (**1b**)**



Following the GP-B, **1b** was obtained as a green solid (0.492 g, 90%) from **S1b** (0.403 g, 1.5 mmol),  $\text{EtPh}_2\text{P}$  (46.9  $\mu\text{L}$ , 0.15 equiv), TFAA (273.7  $\mu\text{L}$ , 1.3 equiv) and  $\text{Et}_3\text{N}$  (298.1  $\mu\text{L}$ , 1.4 equiv) in THF (7.5 mL) at 30 °C after 30 minutes and purification by flash chromatography (DCM/Hex = 1/3)

$R_f = 0.41$  (DCM/Hex = 1/1), mp.: 141.0-141.1 °C.

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 8.00-8.03 (m, 2H), 7.87-7.93 (m, 2H), 7.61 (d,  $J = 8.7$  Hz, 2H), 7.49 (d,  $J = 8.6$  Hz, 2H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 189.2, 187.2 (q,  $J = 38.6$  Hz), 185.6, 149.8, 143.3, 139.44, 139.36, 136.7, 136.3, 131.7, 130.8, 129.2, 125.7, 124.04, 124.02, 115.1

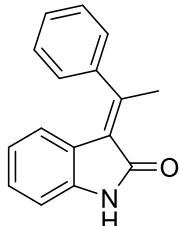
(q,  $J = 291.7$  Hz).

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 1745, 1690, 1617, 1588, 1218, 749.

**HRMS** (EI) for C<sub>18</sub>H<sub>8</sub><sup>35</sup>ClF<sub>3</sub>O<sub>3</sub>, [M] (364.0114) found: 364.0115 (100).

**HRMS** (EI) for C<sub>18</sub>H<sub>8</sub><sup>37</sup>ClF<sub>3</sub>O<sub>3</sub>, [M] (366.0085) found: 366.010 (33).

**(E)-3-(1-Phenylethylidene)indolin-2-one (S2a)**



Following the GP-C, **S2a** was obtained as an orange solid (1.60 g, 68% yield) from indolin-2-one (1.30 g, 10.0 mmol), piperidine (0.7 mL, 0.8 equiv) and acetophenone (3.5 mL, 3.0 equiv).

$R_f = 0.70$  (EtOAc/Hex = 1/4), mp.: 194.9-195.6 °C.

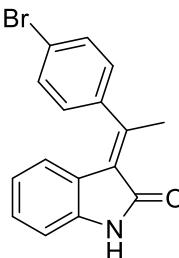
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 9.11 (s, 1H), 7.40-7.53 (m, 3H), 7.29 (dd,  $J = 7.6, 1.4$  Hz, 2H), 7.07 (pt,  $J = 7.6$  Hz, 1H), 6.84 (d,  $J = 7.6$  Hz, 1H), 6.61 (pt,  $J = 7.6$  Hz, 1H), 6.13 (d,  $J = 7.6$  Hz, 1H), 2.81 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 170.5, 155.6, 143.1, 139.9, 129.3, 128.5, 128.2, 126.6, 124.0, 123.5, 123.2, 121.4, 109.6, 23.0.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3200, 1694, 1611, 1464, 1331, 1220.

**HRMS** (ESI) for C<sub>16</sub>H<sub>14</sub>NO, [M+H]<sup>+</sup> (236.1070) found: 236.1075.

**(E)-3-(1-(4-Bromophenyl)ethylidene)indolin-2-one (S2b)**



Following the GP-C, **S2b** was obtained as a yellow solid (1.96 g, 62% yield) from indolin-2-one (1.33 g, 10.0 mmol), piperidine (0.7 mL, 0.8 equiv) and 4'-bromoacetophenone (4.1 mL, 3.0 equiv).

$R_f = 0.27$  (EtOAc/Hex = 1/4), mp.: 230.4-230.7 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 8.63 (s, 1H), 7.62 (dt,  $J = 8.4$  Hz, 2.1 Hz, 2H), 7.19 (d,  $J = 8.4, 2.2$  Hz, 2H), 7.10 (td,  $J = 7.6, 0.7$  Hz, 1H), 6.83 (d,  $J = 7.8$  Hz,

1H), 6.67 (td,  $J = 7.7$ , 0.8 Hz, 1H), 6.23 (d,  $J = 7.9$  Hz, 1H), 2.76 (s, 3H).

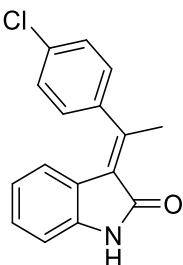
**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 170.0, 153.6, 141.7, 139.7, 132.4, 128.4, 124.1, 123.1, 123.0, 122.5, 121.4, 109.5, 22.6.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3154, 3072, 2826, 1690, 1610, 1466, 1333, 1226, 1094, 823, 748, 540.

**HRMS** (ESI) for  $\text{C}_{16}\text{H}_{13}\text{NO}^{79}\text{Br}$ ,  $[\text{M}+\text{H}]^+$  (314.0175) found: 314.0179 (100).

**HRMS** (ESI) for  $\text{C}_{16}\text{H}_{13}\text{NO}^{81}\text{Br}$ ,  $[\text{M}+\text{H}]^+$  (316.0155) found: 316.0161 (99).

**(E)-3-(1-(4-Chlorophenyl)ethylidene)indolin-2-one (S2c)**



Following the GP-C, **S2c** was obtained as a yellow solid (1.96 g, 73% yield) from indolin-2-one (1.30 g, 10.0 mmol), piperidine (0.7 mL, 0.8 equiv) and 4'-chloroacetophenone (4.0 mL, 3.0 equiv).

$R_f = 0.27$  (EtOAc/Hex = 1/4), mp.: 194.5-194.7 °C.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 9.07 (s, 1H), 7.46 (d,  $J = 8.4$  Hz, 2H), 7.25 (d,  $J = 8.3$  Hz, 2H), 7.10 (t,  $J = 7.7$  Hz, 1H), 6.85 (d,  $J = 7.8$  Hz, 1H), 6.66 (t,  $J = 7.6$  Hz, 1H), 6.23 (d,  $J = 7.5$  Hz, 1H), 2.77 (s, 3H).

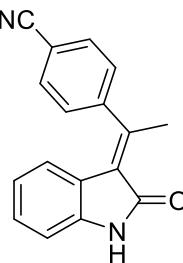
**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 170.1, 153.7, 141.2, 139.8, 134.4, 129.5, 128.4, 128.1, 124.2, 123.0, 121.4, 109.5, 22.7.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3176, 3076, 2905, 2808, 1688, 1611, 1466, 1331, 1226, 1096, 785, 747.

**HRMS** (ESI) for  $\text{C}_{16}\text{H}_{13}\text{NO}^{35}\text{Cl}$ ,  $[\text{M}+\text{H}]^+$  (270.0680) found: 270.0686 (100).

**HRMS** (ESI) for  $\text{C}_{16}\text{H}_{13}\text{NO}^{37}\text{Cl}$ ,  $[\text{M}+\text{H}]^+$  (272.0651) found: 272.0682 (39).

**(E)-4-(1-(2-Oxoindolin-3-ylidene)ethyl)benzonitrile (S2d)**



Following the GP-C, **S2d** was obtained as an orange solid (0.28 g, 11% yield) from

indolin-2-one (1.30 g, 10.0 mmol), piperidine (0.7 mL, 0.8 equiv) and 4-acetylbenzonitrile (4.3 mL, 3.0 equiv).

$R_f = 0.15$  (EtOAc/Hex = 1/4), mp.: 249.9–250.0 °C.

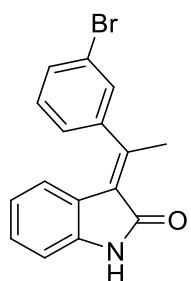
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 8.16 (s, 1H), 7.81 (dt,  $J = 8.2, 1.8$  Hz, 2H), 7.44 (dt,  $J = 8.3, 2.2$  Hz, 2H), 7.12 (td,  $J = 8.0, 0.7$  Hz, 1H), 6.65 (td,  $J = 7.7, 0.9$  Hz, 1H), 6.05 (d,  $J = 7.8$  Hz, 1H), 2.78 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 169.2, 151.8, 147.5, 139.8, 133.2, 129.0, 127.6, 124.4, 123.0, 122.6, 121.6, 118.4, 112.4, 109.6, 22.2.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3175, 3085, 2896, 2817, 1692, 1613, 1603, 1466, 1331, 1226, 1189, 843, 752.

**HRMS** (ESI) for  $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}$ ,  $[\text{M}+\text{H}]^+$  (261.1022) found: 261.1031.

#### (E)-3-(1-(3-Bromophenyl)ethylidene)indolin-2-one (S2e)



Following the GP-C, **S2e** was obtained as a yellow solid (3.06 g, 98% yield) from indolin-2-one (1.30 g, 10.0 mmol), piperidine (0.7 mL, 0.8 equiv) and 3'-bromoacetophenone (4.1 mL, 3.0 equiv).

$R_f = 0.30$  (EtOAc/Hex = 1/4), mp.: 171.7–172.1 °C.

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 9.15 (s, 1H), 7.58 (d,  $J = 8.0$  Hz, 1H), 7.44 (s, 1H), 7.36 (t,  $J = 7.8$  Hz, 1H), 7.23 (d,  $J = 7.6$  Hz, 1H), 7.10 (t,  $J = 7.7$  Hz, 1H), 6.86 (d,  $J = 7.7$  Hz, 1H), 6.66 (t,  $J = 7.7$  Hz, 1H), 6.17 (d,  $J = 8.0$  Hz, 1H), 2.77 (s, 3H).

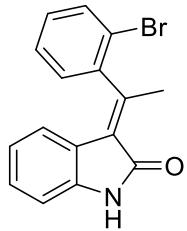
**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 170.1, 153.0, 144.8, 140.0, 131.4, 130.8, 129.5, 128.5, 125.2, 124.3, 123.1, 123.0, 121.4, 109.6, 22.6.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3204, 3081, 1697, 1613, 1466, 1333, 1226, 1107, 789, 748, 693, 546.

**HRMS** (ESI) for  $\text{C}_{16}\text{H}_{13}\text{NO}^{79}\text{Br}$ ,  $[\text{M}+\text{H}]^+$  (314.0175) found: 314.0182 (100).

**HRMS** (ESI) for  $\text{C}_{16}\text{H}_{13}\text{NO}^{81}\text{Br}$ ,  $[\text{M}+\text{H}]^+$  (316.0155) found: 316.0163 (98).

#### (E)-3-(1-(2-Bromophenyl)ethylidene)indolin-2-one (S2f)



Following the GP-C, **S2f** was obtained as a yellow solid (1.00 g, 32% yield) from indolin-2-one (1.30 g, 10.0 mmol), piperidine (0.7 mL, 0.8 equiv) and 2'-bromoacetophenone (4.1 mL, 3.0 equiv).

$R_f = 0.32$  (EtOAc/Hex = 1/4), mp.: 178.2-178.9 °C.

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 8.58 (s, 1H), 7.73 (dd,  $J = 7.5, 0.6$  Hz, 1H), 7.44 (td,  $J = 7.5, 0.9$  Hz, 1H), 7.32 (td,  $J = 7.7, 1.6$  Hz, 1H), 7.19 (dd,  $J = 7.5, 1.6$  Hz, 1H), 7.09 (td,  $J = 7.5, 0.6$  Hz, 1H), 6.83 (d,  $J = 7.8$  Hz, 1H), 6.63 (td,  $J = 7.7, 0.9$  Hz, 1H), 5.86 (d,  $J = 7.8$  Hz, 1H), 2.77 (s, 3H).

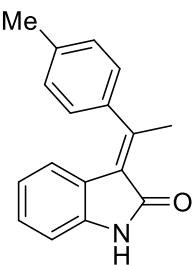
**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 169.8, 152.9, 143.2, 139.7, 133.5, 129.6, 128.5, 128.4, 127.9, 124.7, 123.1, 122.8, 121.7, 120.1, 109.4, 21.4.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3224, 3068, 2930, 1698, 1636, 1617, 1590, 1465, 1427, 1334, 1225, 1006, 784, 584.

**HRMS** (ESI) for  $\text{C}_{16}\text{H}_{13}\text{NO}^{79}\text{Br}$ ,  $[\text{M}+\text{H}]^+$  (314.0175) found: 314.0182 (100).

**HRMS** (ESI) for  $\text{C}_{16}\text{H}_{13}\text{NO}^{81}\text{Br}$ ,  $[\text{M}+\text{H}]^+$  (316.0155) found: 316.0162 (99).

#### (E)-3-(1-(*p*-Tolyl)ethylidene)indolin-2-one (**S2g**)



Following the GP-C, **S2g** was obtained as a yellow solid (1.64 g, 67% yield) from indolin-2-one (1.30 g, 10.0 mmol), piperidine (0.7 mL, 0.8 equiv) and 4'-methylacetophenone (4.2 mL, 3.0 equiv).

$R_f = 0.32$  (EtOAc/Hex = 1/4), mp.: 194.7-195.0 °C.

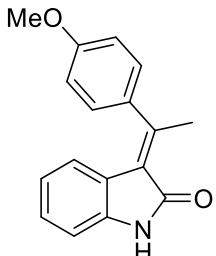
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 8.65 (s, 1H), 7.28 (d,  $J = 7.8$  Hz, 2H), 7.20 (d,  $J = 7.8$  Hz, 2H), 7.01 (t,  $J = 7.6$  Hz, 1H), 6.82 (d,  $J = 7.7$  Hz, 1H), 6.63 (t,  $J = 7.7$  Hz, 1H), 6.26 (d,  $J = 7.5$  Hz, 1H), 2.79 (s, 3H), 2.45 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 170.1, 155.9, 140.0, 139.6, 138.3, 129.8, 128.0, 126.5, 123.59, 123.55, 123.1, 121.2, 109.2, 33.0, 21.4.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3198, 3081, 2914, 1692, 1612, 1467, 1333, 1227, 1106, 817m 736.

**HRMS** (ESI) for C<sub>17</sub>H<sub>16</sub>NO, [M+H]<sup>+</sup> (250.1226) found: 250.1232.

**(E)-3-(1-(4-Methoxyphenyl)ethylidene)indolin-2-one (S2h)**



Following the GP-C, **S2h** was obtained as a yellow solid (1.72 g, 65% yield) from indolin-2-one (1.30 g, 10.0 mmol), piperidine (0.7 mL, 0.8 equiv) and 4'-methoxyacetophenone (4.2 mL, 3.0 equiv).

R<sub>f</sub> = 0.22 (EtOAc/Hex = 1/4); mp.: 182.8-183.4 °C.

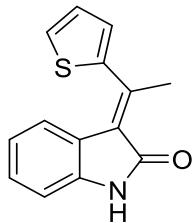
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.90 (s, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 7.9 Hz, 1H), 6.65 (t, J = 7.7 Hz, 1H), 6.36 (d, J = 7.8 Hz, 1H), 3.89 (s, 3H), 2.79 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 170.3, 159.8, 155.6, 139.6, 135.1, 128.3, 127.9, 123.7, 123.6, 122.9, 121.2, 114.4, 109.3, 55.3, 23.0.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3185, 3076, 2967, 2839, 1691, 1612, 1509, 1467, 1334, 1246, 1179, 829, 749, 573.

**HRMS** (ESI) for C<sub>17</sub>H<sub>16</sub>NO<sub>2</sub>, [M+H]<sup>+</sup> (266.1176) found: 266.1183.

**(E)-3-(1-(Thiophen-2-yl)ethylidene)indolin-2-one (S2i)**



Following the GP-C, **S2i** was obtained as a yellow solid (0.56 g, 24% yield) from indolin-2-one (1.30 g, 10.0 mmol), piperidine (0.7 mL, 0.8 equiv) and 2-acetylthiophene (3.2 mL, 3.0 equiv).

R<sub>f</sub> = 0.31 (EtOAc/Hex = 1/4), mp.: 193.0-194.0 °C.

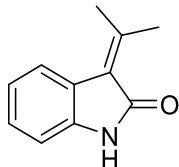
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 7.90 (s, 1H), 7.50 (d, J = 4.9 Hz, 1H), 7.18 (dd, J = 3.3, 0.5 Hz, 1H), 7.09-7.14 (m, 2H), 6.80 (d, J = 7.8 Hz, 1H), 6.70-6.76 (m, 2H), 2.81 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 169.8, 147.4, 143.7, 139.7, 128.6, 127.5, 127.3, 126.6, 125.4, 123.2, 122.9, 121.4, 109.4, 23.9.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3163, 3046, 2901, 2817, 1692, 1611, 1465, 1335, 1227, 748, 706.

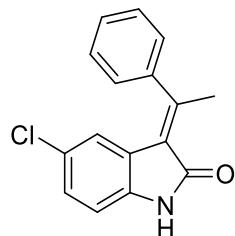
**HRMS** (ESI) for C<sub>14</sub>H<sub>12</sub>NOS, [M+H]<sup>+</sup> (242.0634) found: 242.0641.

### 3-(propan-2-ylidene)indolin-2-one (**S2j**)



Prepared according to the literature report.<sup>3</sup>

### (E)-5-Chloro-3-(1-phenylethylidene)indolin-2-one (**S2k**)



Following the GP-C, **S2k** was obtained as an orange solid (0.81 g, 30% yield) from 5-chlorooxindole (1.70 g, 10.0 mmol), piperidine (0.7 mL, 0.8 equiv) and acetophenone (3.5 mL, 3.0 equiv).

R<sub>f</sub> = 0.25 (EtOAc/Hex = 1/4), mp.: 188.2-188.5 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 9.42 (s, 1H), 7.44-7.54 (m, 3H), 7.25 (dd, J = 7.6, 1.4 Hz, 2H), 7.07 (dd, J = 7.6 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.04 (d, J = 7.6 Hz, 1H), 2.79 (s, 3H).

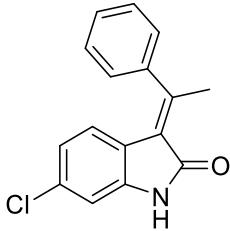
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 170.2, 157.6, 142.2, 138.2, 129.3, 128.8, 127.8, 126.5, 126.2, 124.7, 123.3, 123.2, 110.3, 22.9.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3173, 3081, 2940, 2843, 1698, 1616, 1467, 1438, 1303, 1221, 1077, 814, 761.

**HRMS** (ESI) for C<sub>16</sub>H<sub>13</sub>NO<sup>35</sup>Cl, [M+H]<sup>+</sup> (270.0680) found: 270.0687 (100).

**HRMS** (ESI) for C<sub>16</sub>H<sub>13</sub>NO<sup>37</sup>Cl, [M+H]<sup>+</sup> (272.0651) found: 272.0662 (33).

### (E)-6-Chloro-3-(1-phenylethylidene)indolin-2-one (**S2l**)



Following the GP-C, **S2l** was obtained as a yellow solid (1.19 g, 44% yield) from 6-chloro-2-oxindole (1.70 g, 10.0 mmol), piperidine (0.7 mL, 0.8 equiv) and acetophenone (3.5 mL, 3.0 equiv).

$R_f = 0.42$  (EtOAc/Hex = 1/4), mp.: 199.9-200.1 °C.

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 8.91 (s, 1H), 7.43-7.52 (m, 3H), 7.27 (dd,  $J$  = 7.7, 1.6 Hz, 2H), 6.85 (d,  $J$  = 1.8 Hz, 1H), 6.58 (dd,  $J$  = 8.4, 1.7 Hz, 1H), 6.03 (d,  $J$  = 8.4 Hz, 1H), 2.80 (s, 3H).

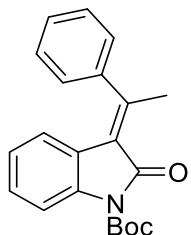
**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 170.1, 156.4, 142.6, 140.5, 133.6, 129.2, 128.6, 126.3, 124.0, 123.0, 121.8, 121.3, 109.8, 22.9.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3117, 3032, 1692, 1607, 1443, 1323, 1228, 1066, 812, 717, 698.

**HRMS** (ESI) for  $\text{C}_{16}\text{H}_{13}\text{NO}^{35}\text{Cl}$ ,  $[\text{M}+\text{H}]^+$  (270.0680) found: 270.0686 (100).

**HRMS** (ESI) for  $\text{C}_{16}\text{H}_{13}\text{NO}^{37}\text{Cl}$ ,  $[\text{M}+2+\text{H}]^+$  (272.0651) found: 272.0660 (33).

**tert-butyl(E)-2-oxo-3-(1-phenylethylidene)indoline-1-carboxylate (2a):**



Following the GP-D, **2a** was obtained as a yellow solid (1.31 g, 58% yield) from **S2a** (1.60 g, 6.76 mmol),  $(\text{Boc})_2\text{O}$  (2.0 mL, 1.2 equiv) and DMAP (417.5 mg, 0.5 equiv) in DCM (22.0 mL).

$R_f = 0.23$  (EtOAc/Hex = 1/20), mp.: 75.1-76.3 °C.

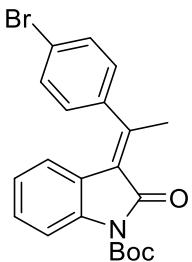
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 7.81 (d,  $J$  = 7.9 Hz, 1H), 7.41-7.52 (m, 3H), 7.25 (dd,  $J$  = 7.9, 1.3 Hz, 2H), 7.15 (td,  $J$  = 7.9, 1.3 Hz, 1H), 6.72 (td,  $J$  = 7.9, 1.3 Hz, 1H), 6.18 (d,  $J$  = 7.9 Hz, 1H), 2.78 (s, 3H), 1.68 (s, 9H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 166.3, 156.7, 149.7, 143.1, 138.4, 129.5, 128.7, 128.4, 126.4, 123.4, 123.2, 122.8, 122.6, 114.5, 84.2, 28.3, 23.9.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 2980, 1725, 1600, 1462, 1353, 1304, 1153, 1094.

**HRMS** (ESI) for  $\text{C}_{21}\text{H}_{21}\text{NO}_3\text{Na}$ ,  $[\text{M}+\text{Na}]^+$  (358.1414) found: 358.1420.

**tert-Butyl-(E)-3-(1-(4-bromophenyl)ethylidene)-2-oxoindoline-1-carboxylate (2b)**



Following the GP-D, **2b** was obtained as a yellow solid (0.65 g, 79%) from **S2b** (0.63 g, 2.0 mmol), (Boc)<sub>2</sub>O (0.6 mL, 1.2 equiv) and DMAP (122.2 mg, 0.5 equiv) in DCM (22.0 mL).

$R_f = 0.27$  (EtOAc/Hex = 1/40), mp.: 113.0-113.9 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 7.82 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.17 (pt, *J* = 7.8 Hz, 1H), 7.15 (pd, *J* = 8.2 Hz, 2H), 6.78 (t, *J* = 7.7 Hz, 1H), 6.28 (d, *J* = 7.8 Hz, 1H), 2.74 (s, 3H), 1.67 (s, 9H).

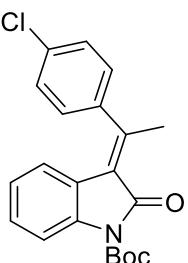
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 165.9, 154.5, 149.4, 141.7, 138.3, 132.6, 128.7, 128.2, 123.3, 122.74, 122.66, 122.6, 122.5, 114.5, 84.1, 28.1, 23.5.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3081, 2983, 2923, 1780, 1741, 1623, 1603, 1480, 1463, 1369, 1350, 1302, 1254, 1154, 1096, 788, 749, 450.

**HRMS** (ESI) for C<sub>21</sub>H<sub>20</sub>NO<sub>3</sub>Na<sup>79</sup>Br, [M+Na]<sup>+</sup> (436.0519) found: 436.0529 (99).

**HRMS** (ESI) for C<sub>21</sub>H<sub>20</sub>NO<sub>3</sub>Na<sup>81</sup>Br, [M+Na]<sup>+</sup> (438.0498) found: 438.0511 (100).

**tert-Butyl-(E)-3-(1-(4-chlorophenyl)ethylidene)-2-oxoindoline-1-carboxylate (2c)**



Following the GP-D, **2c** was obtained as a yellow solid (0.81 g, 55%) from **S2c** (1.10 g, 4.0 mmol), (Boc)<sub>2</sub>O (1.1 mL, 1.2 equiv) and DMAP (246.8 mg, 0.5 equiv) in DCM (44.0 mL).

$R_f = 0.30$  (EtOAc/Hex = 1/40), mp.: 125.7-126.0 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 7.82 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.17 (t, *J* = 8.1, 1H), 6.77 (t, *J* = 7.6, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 2.75 (s, 3H), 1.68 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 165.9, 154.6, 149.4, 141.2, 138.3, 134.5,

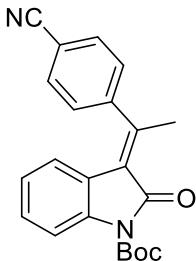
123.0, 128.5, 128.0, 123.3, 122.8, 122.7, 122.5, 114.5, 84.1, 28.1, 23.6.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3094, 2983, 2940, 1780, 1744, 1625, 1601, 1463, 1369, 1350, 1302, 1254, 1154, 1096, 788, 750, 554.

**HRMS** (ESI) for C<sub>21</sub>H<sub>20</sub>NO<sub>3</sub>Na<sup>35</sup>Cl, [M+Na]<sup>+</sup> (392.1024) found: 392.1031 (100).

**HRMS** (ESI) for C<sub>21</sub>H<sub>20</sub>NO<sub>3</sub>Na<sup>37</sup>Cl, [M+Na]<sup>+</sup> (394.0994) found: 394.1008 (34).

**tert-Butyl (E)-3-(1-(4-cyanophenyl)ethylidene)-2-oxoindoline-1-carboxylate (2d)**



Following the GP-D, **2d** was obtained as a yellow solid (0.40 g, 30%) from **S2d** (1.30 g, 3.7 mmol), (Boc)<sub>2</sub>O (1.0 mL, 1.2 equiv) and DMAP (228.3 mg, 0.5 equiv) in DCM (40.0 mL).

R<sub>f</sub> = 0.05 (EtOAc/Hex = 1/40), mp.: 175.5-175.7 °C.

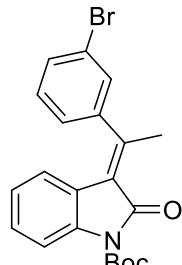
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 7.79-7.84 (m, 3H), 7.40 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 7.9, 1H), 6.76 (t, J = 7.7 Hz, 1H), 6.09 (d, J = 8.0 Hz, 1H), 2.76 (s, 3H), 1.68 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 165.6, 152.6, 149.3, 147.5, 138.6, 133.3, 129.0, 127.5, 123.4, 123.2, 122.4, 122.1, 118.3, 114.7, 112.5, 84.3, 28.1, 23.1.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 2982, 2927, 2231, 1779, 1740, 1603, 1463, 1349, 1302, 1253, 1153, 1097, 842, 749.

**HRMS** (ESI) for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>Na, [M+Na]<sup>+</sup> (383.1366) found: 383.1374.

**tert-Butyl-(E)-3-(1-(3-bromophenyl)ethylidene)-2-oxoindoline-1-carboxylate (2e)**



Following the GP-D, **2e** was obtained as a yellow solid (0.65 g, 78%) from **S2e** (0.63 g, 2.0 mmol), (Boc)<sub>2</sub>O (0.6 mL, 1.2 equiv) and DMAP (122.2 mg, 0.5 equiv) in DCM (22.0 mL).

R<sub>f</sub> = 0.28 (EtOAc/Hex = 1/40), mp.: 54.0-55.0 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 7.82 (d, *J* = 8.2 Hz, 1H), 7.59 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.41 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.16-7.20 (m, 2H), 6.78 (t, *J* = 7.7 Hz, 1H), 6.22 (d, *J* = 7.5 Hz, 1H), 2.75 (s, 3H), 1.67 (s, 9H).

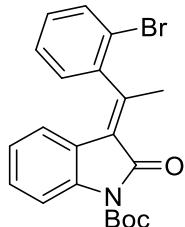
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 165.9, 153.9, 149.4, 144.8, 138.4, 131.6, 131.0, 129.3, 128.7, 125.1, 123.4, 123.3, 122.9, 122.7, 122.5, 114.6, 84.2, 28.2, 23.5.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3085, 2983, 2927, 1781, 1736, 1602, 1463, 1369, 1349, 1303, 1253, 1153, 1096, 788, 748, 461.

**HRMS** (ESI) for C<sub>21</sub>H<sub>20</sub>NO<sub>3</sub>Na<sup>79</sup>Br, [M+Na]<sup>+</sup> (436.0519) found: 436.0525 (99).

**HRMS** (ESI) for C<sub>21</sub>H<sub>20</sub>NO<sub>3</sub>Na<sup>81</sup>Br, [M+Na]<sup>+</sup> (438.0498) found: 438.0507 (100).

#### **tert-Butyl-(E)-3-(1-(2-bromophenyl)ethylidene)-2-oxoindoline-1-carboxylate (2f)**



Following the GP-D, **2f** was obtained as a white solid (0.76 g, 61%) from **S2f** (0.94 g, 3.0 mmol), (Boc)<sub>2</sub>O (0.9 mL, 1.2 equiv) and DMAP (183.3 mg, 0.5 equiv) in DCM (33.0 mL).

R<sub>f</sub> = 0.30 (EtOAc/Hex = 1/40), mp.: 56.5-56.7 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 7.83 (d, *J* = 8.2 Hz, 1H), 7.72 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.12-7.22 (m, 2H), 6.75 (t, *J* = 7.7 Hz, 1H), 5.93 (d, *J* = 7.8 Hz, 1H), 2.75 (s, 3H), 1.67 (s, 9H).

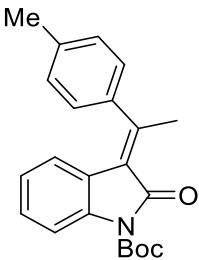
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 165.9, 153.9, 149.5, 143.2, 138.3, 133.6, 129.7, 128.6, 128.5, 127.6, 123.9, 123.7, 123.3, 122.6, 122.3, 120.0, 114.5, 84.1, 28.2, 22.3.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3072, 2981, 2927, 1783, 1744, 1603, 1463, 1369, 1351, 1302, 1254, 1153, 1096, 746, 598.

**HRMS** (ESI) for C<sub>21</sub>H<sub>20</sub>NO<sub>3</sub>Na<sup>79</sup>Br, [M+Na]<sup>+</sup> (436.0519) found: 436.0525 (100).

**HRMS** (ESI) for C<sub>21</sub>H<sub>20</sub>NO<sub>3</sub>Na<sup>81</sup>Br, [M+Na]<sup>+</sup> (438.0498) found: 438.0508 (99).

#### **tert-Butyl (E)-2-oxo-3-(1-(*p*-tolyl)ethylidene)indoline-1-carboxylate (2g)**



Following the GP-D, **2g** was obtained as a yellow solid (0.18 g, 58%) from **S2g** (1.30 g, 0.9 mmol), (Boc)<sub>2</sub>O (0.25 mL, 1.2 equiv) and DMAP (55.5 mg, 0.5 equiv) in DCM (10.0 mL).

$R_f = 0.33$  (EtOAc/Hex = 1/40), mp.: 70.4-71.2 °C.

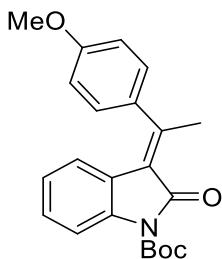
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 7.81 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.12-7.16 (m, 3H), 6.74 (t, *J* = 7.7, 1H), 6.31 (dd, *J* = 7.9 Hz, 1H), 2.76 (s, 3H), 2.43 (s, 3H), 1.68 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 166.1, 156.8, 149.5, 139.8, 138.5, 138.0, 129.8, 128.0, 126.3, 123.1, 122.5, 122.2, 114.3, 83.8, 28.1, 23.8, 21.3.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 2981, 2929, 1781, 1740, 1601, 1463, 1368, 1350, 1302, 1282, 1253, 1154, 1095, 1002, 970, 845, 818, 787, 748, 703.

**HRMS** (EI) for C<sub>22</sub>H<sub>23</sub>NO<sub>3</sub>, [M] (349.1678) found: 349.1678.

**tert-Butyl (E)-3-(1-(4-methoxyphenyl)ethylidene)-2-oxoindoline-1-carboxylate  
(2h)**



Following the GP-D, **2h** was obtained as a yellow solid (0.45 g, 49%) from **S2h** (0.91 g, 2.5 mmol), (Boc)<sub>2</sub>O (0.7 mL, 1.2 equiv) and DMAP (0.15 g, 0.5 equiv) in DCM (28.0 mL).

$R_f = 0.17$  (EtOAc/Hex = 1/40), mp.: 99.0-100.0 °C.

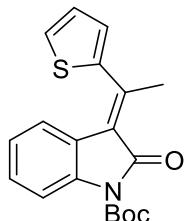
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 7.81 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.0 (d, *J* = 8.4 Hz, 2H), 6.76 (t, *J* = 7.7 Hz, 1H), 6.4 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 2.76 (s, 3H), 1.67 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 166.1, 160.0, 156.7, 149.5, 138.0, 135.0, 128.1, 128.0, 123.2, 123.1, 122.4, 122.2, 114.5, 114.3, 83.8, 55.3, 28.1, 23.9.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 2983, 2931, 1779, 1738, 1601, 1510, 1476, 1463, 1369, 1350, 1303, 1250, 1154, 1095, 835, 748.

**HRMS** (ESI) for C<sub>22</sub>H<sub>23</sub>NO<sub>4</sub>Na, [M+Na]<sup>+</sup> (388.1519) found: 388.1526.

**tert-Butyl (E)-2-oxo-3-(1-(thiophen-2-yl)ethylidene)indoline-1-carboxylate (2i)**



Following the GP-D, **2i** was obtained as a yellow solid (0.79 g, 58%) from **S2i** (1.36 g, 4.0 mmol), (Boc)<sub>2</sub>O (2.3 mL, 1.2 equiv) and DMAP (0.62 g, 0.5 equiv) in DCM (22.0 mL).

R<sub>f</sub> = 0.30 (EtOAc/Hex = 1/40), mp.: 121.6-122.5 °C.

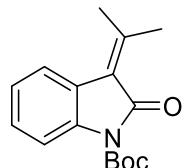
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ ppm: 7.82 (d, J = 8.2 Hz, 1H), 7.51 (d, J = 4.9 Hz, 1H), 7.19 (t, J = 7.7 Hz, 1H), 7.11-7.15 (m, 2H), 6.83 (t, J = 7.7 Hz, 1H), 6.76 (d, J = 7.8, 1.3 Hz, 1H), 2.80 (s, 3H), 1.67 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ ppm: 165.8, 149.5, 148.3, 143.7, 138.3, 128.7, 127.7, 126.6, 124.1, 123.3, 122.9, 122.4, 114.5, 84.1, 28.2, 24.8.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 2979, 1737, 1601, 1458, 1344, 1301, 1254, 1153, 1096, 747, 706.

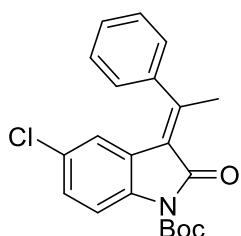
**HRMS** (ESI) for C<sub>19</sub>H<sub>19</sub>NO<sub>3</sub>NaS, [M+Na]<sup>+</sup> (364.0978) found: 364.0986.

**tert-Butyl 2-oxo-3-(propan-2-ylidene)indoline-1-carboxylate (2j)**



Prepared following the reported method.<sup>3</sup>

**tert-Butyl-(E)-5-chloro-2-oxo-3-(1-phenylethylidene)indoline-1-carboxylate (2k)**



Following the GP-D, **2k** was obtained as a yellow colored solid (786.1 mg, 97%) from **S2k** (0.81 g, 2.2 mmol), (Boc)<sub>2</sub>O (0.62 mL, 1.2 equiv) and DMAP (0.14 g, 0.5 equiv)

in DCM (24.0 mL).

$R_f$  = 0.30 (EtOAc/Hex = 1/40), mp.: 165.9–166.9 °C.

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 7.77 (d,  $J$  = 8.8 Hz, 1H), 7.46–7.53 (m, 3H), 7.23 (dd,  $J$  = 7.0, 1.2 Hz, 2H), 7.11 (dd,  $J$  = 9.0, 1.6 Hz, 1H), 6.07 (d,  $J$  = 1.3 Hz, 1H), 2.79 (s, 3H), 1.67 (s, 9H).

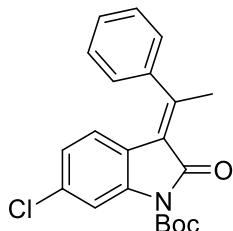
**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 165.5, 158.6, 149.4, 142.3, 136.6, 129.5, 129.0, 128.7, 128.0, 126.0, 124.4, 122.7, 121.7, 115.5, 84.3, 28.2, 23.8.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 2979, 1780, 1746, 1624, 1466, 1369, 1338, 1297, 1271, 1155, 1118, 819, 768, 563.

**HRMS** (EI) for  $\text{C}_{21}\text{H}_{20}^{35}\text{ClNO}_3$ , [M] (369.1132) found: 369.1130 (100).

**HRMS** (EI) for  $\text{C}_{21}\text{H}_{20}^{37}\text{ClNO}_3$ , [M] (371.1102) found: 371.1103 (42).

#### **tert-Butyl (E)-6-chloro-2-oxo-3-(1-phenylethylidene)indoline-1-carboxylate (2l)**



Following the GP-D, **2l** was obtained as a yellow solid (0.295 g, 39%) from **S2l** (0.73 g, 2.0 mmol),  $(\text{Boc})_2\text{O}$  (0.6 mL, 1.2 equiv) and DMAP (0.12 g, 0.5 equiv) in DCM (22.0 mL).

$R_f$  = 0.32 (EtOAc/Hex = 1/40), mp.: 114.7–115.9 °C.

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 7.89 (d,  $J$  = 2.0 Hz, 1H), 7.43–7.51 (m, 3H), 7.23 (dd,  $J$  = 7.8, 1.7 Hz, 2H), 6.70 (dd,  $J$  = 8.5, 2.0 Hz, 1H), 6.07 (d,  $J$  = 8.5 Hz, 1H), 2.77 (s, 3H), 1.68 (s, 9H).

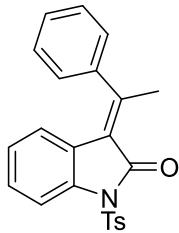
**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 165.6, 157.2, 149.3, 142.6, 138.9, 133.9, 129.4, 128.7, 126.2, 123.38, 123.37, 121.7, 121.4, 115.0, 84.5, 28.1, 23.7.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 2979, 2927, 1781, 1744, 1728, 1599, 1468, 1427, 1369, 1347, 1301, 1277, 1248, 1152, 1114, 818, 763, 547.

**HRMS** (EI) for  $\text{C}_{21}\text{H}_{20}^{35}\text{ClNO}_3$ , [M] (369.1132) found: 369.1130 (100).

**HRMS** (EI) for  $\text{C}_{21}\text{H}_{20}^{37}\text{ClNO}_3$ , [M] (371.1102) found: 371.1103 (37).

#### **(E)-3-(1-Phenylethylidene)-1-tosylindolin-2-one (2m)**



A dry argon-flushed 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with **S2a** (0.470 g, 2.0 mmol) in anhydrous THF (22.0 mL), then NaH (72.0 mg, 1.5 equiv) and TsCl (1.16 g, 3.0 equiv) were added to the flask with iced-bath and stirred for 12 hours. Afterwards, the reaction mixture was concentrated *in vacuo* and the residue was purified by silica gel flash chromatography (EtOAc/Hex = 1:5) to obtain **2m** as a yellow solid (0.236 g, 30%).

$R_f$  = 0.4 (EtOAc/Hex = 1/5), mp.: 196.8–197.1 °C.

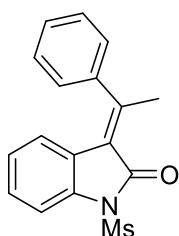
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 8.03 (d,  $J$  = 8.1 Hz, 2H), 7.95 (d,  $J$  = 8.2 Hz, 1H), 7.45–7.41 (m, 3H), 7.33 (d,  $J$  = 7.8 Hz, 2H), 7.16–7.20 (m, 3H), 6.73 (t,  $J$  = 7.7 Hz, 1H), 6.17 (d,  $J$  = 8.0 Hz, 1H), 2.69 (s, 3H), 2.42 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 166.0, 158.0, 145.3, 142.3, 137.5, 135.8, 129.7, 129.3, 128.7, 128.7, 127.9, 126.0, 123.6, 123.2, 123.0, 121.5, 113.0, 23.7, 21.7.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 2909, 1736, 1618, 1376, 1243, 1179.

**HRMS** (ESI) for  $\text{C}_{23}\text{H}_{20}\text{NO}_3\text{S}$ ,  $[\text{M}+\text{H}]^+$  (390.1158) found: 390.1164.

#### (*E*)-1-(Methylsulfonyl)-3-(1-phenylethylidene)indolin-2-one (**2n**)



A dry argon-flushed 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with **S2a** (0.470 g, 2.0 mmol) in anhydrous THF (22.0 mL) and then NaH (72.0 mg, 1.5 equiv) and MsCl (312.7  $\mu\text{L}$ , 2.0 equiv) were added to the flask with iced-bath and stirred overnight. Then the reaction mixture was concentrated *in vacuo* and the residue was purified by silica gel flash chromatography (Hexanes/EtOAc = 1:7) to afford **2n** as a yellow solid (0.820 g, 13%).

$R_f$  = 0.375 (EtOAc/Hex = 1/7), mp.: 137.4–138.0 °C.

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 7.78 (d,  $J$  = 8.3 Hz, 1H), 7.53–7.45 (m, 3H), 7.26 (dd,  $J$  = 7.6, 2.1 Hz, 2H), 7.15 (t,  $J$  = 7.9 Hz, 1H), 6.76 (t,  $J$  = 7.7 Hz, 1H), 6.23 (d,

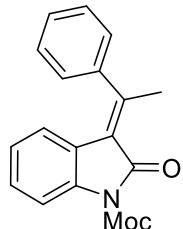
$J = 7.8$  Hz, 1H), 3.48 (s, 3H), 2.79 (s, 3H).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 167.0, 158.9, 142.2, 137.2, 129.4, 128.9, 128.7, 126.0, 123.8, 123.0, 122.9, 113.0, 41.8, 23.8.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3438, 3048, 3022, 2939, 1944, 1911, 1876, 1804, 1732, 1624, 1560, 1491, 1457, 1441, 1356, 1324, 1158, 743, 701.

**HRMS** (ESI) for  $\text{C}_{17}\text{H}_{16}\text{NO}_3\text{S}$ ,  $[\text{M}+\text{H}]^+$  (314.0845) found: 314.0853.

**(E)-Methyl-2-oxo-3-(1-phenylethylidene)indoline-1-carboxylate (2o):**



To a solution of **S2a** (0.235 g, 1.0 mmol) in  $\text{CH}_3\text{CN}$  (7.0 mL) was added a solution of (Moc)<sub>2</sub>O (0.2 mL, 2.0 equiv) in  $\text{CH}_3\text{CN}$  (3.0 mL) and DMAP (36.7 mg, 0.3 equiv) and stirred for 4 hours. Then the reaction mixture was quenched with 2N HCl (5 mL) and extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried over anhydrous  $\text{MgSO}_4$ , filtered and then concentrated *in vacuo* and the residue was purified by silica gel flash chromatography (EtOAc/Hex = 1:15) to obtain **2o** as a yellow solid (0.161 g, 55%).

$R_f = 0.4$  (EtOAc/Hex = 1/5), mp.: 138.9-139.5 °C.

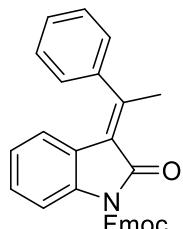
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 7.90 (d,  $J = 8.2$  Hz, 1H), 7.48-7.43 (m, 3H), 7.24 (d,  $J = 7.2$  Hz, 2H), 7.14 (t,  $J = 7.8$  Hz, 1H), 6.73 (t,  $J = 7.6$  Hz, 1H), 6.19 (d,  $J = 7.8$  Hz, 1H), 4.03 (s, 3H), 2.77 (s, 3H).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 165.6, 157.0, 151.6, 142.5, 137.6, 129.1, 128.5, 128.2, 126.1, 123.4, 123.0, 122.4, 122.0, 114.4, 53.5, 23.6.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 2954, 1736, 1618, 1303, 1247.

**HRMS** (ESI) for  $\text{C}_{18}\text{H}_{15}\text{NO}_3\text{Na}$ ,  $[\text{M}+\text{Na}]^+$  (316.0944) found: 316.0952.

**(E)-(9*H*-Fluoren-9-yl)methyl-2-oxo-3-(1-phenylethylidene)indoline-1-carboxylate (2p)**



A dry and argon-flushed 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with **S2a** (0.470 g, 2.0 mmol) in anhydrous THF (22.0 mL) and then NaH (72.0 mg, 1.5 equiv) and FmocCl (791.9 mg, 1.5 equiv) were added to the flask with iced-bath and stirred overnight. Then the reaction mixture was concentrated *in vacuo* and the residue was purified by silica gel flash chromatography (EtOAc/Hex = 1:7) to obtain **2p** as a yellow solid (0.532 g, 58%).

$R_f$  = 0.5 (EtOAc/Hex = 1/7), mp.: 173.6-174.4 °C.

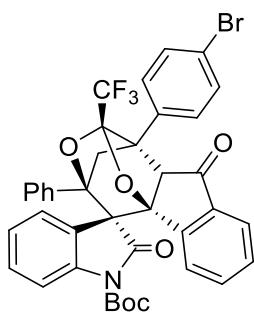
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 7.82 (d,  $J$  = 7.4 Hz, 2H), 7.79 (d,  $J$  = 7.5 Hz, 2H), 7.62 (d,  $J$  = 8.4 Hz, 1H), 7.52-7.46 (m, 3H), 7.43 (t,  $J$  = 7.3 Hz, 2H), 7.35 (td,  $J$  = 7.5, 1.3 Hz, 2H), 7.28 (dd,  $J$  = 7.8, 1.5 Hz, 2H), 7.07 (td,  $J$  = 8.4, 0.9 Hz, 1H), 6.73 (td,  $J$  = 7.7, 0.9 Hz, 1H), 6.19 (d,  $J$  = 7.5 Hz, 1H), 4.73 (d,  $J$  = 7.0 Hz, 2H), 4.46 (t,  $J$  = 7.0, 1H), 2.84 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 165.8, 157.3, 151.2, 143.5, 142.8, 141.4, 137.7, 129.4, 128.6, 128.4, 127.9, 127.3, 126.3, 125.4, 123.6, 123.2, 122.7, 122.2, 120.0, 114.6, 68.9, 46.7, 23.9.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3464, 3054, 3026, 2972, 2952, 2928, 2893, 1952, 1904, 1882, 1782, 1734, 1623, 1601, 1463, 1451, 1383, 758, 702.

**HRMS** (ESI) for  $\text{C}_{31}\text{H}_{23}\text{NO}_3\text{Na}$ ,  $[\text{M}+\text{Na}]^+$  (480.1570) found: 480.1580.

**tert-Butyl (2'*R*,3*R*,3a'*S*,3b'*R*,8b'*S*,9a'*R*)-3a'-(4-bromophenyl)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8*b*]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3aa)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 8 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc /Hex = 1/15), **3aa** was obtained as a white solid (60.3 mg, 81%).

$R_f$  = 0.50 (/Hex = 1/5), mp.: 195.7-196.4 °C,  $[\alpha]_D^{23} = 1.1$  ( $c = 0.5$  in  $\text{CH}_2\text{Cl}_2$ ),

**HPLC:** 81% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.00

mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 5.15$  min,  $t_{\text{major}} = 7.30$  min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.17 (d,  $J = 7.5$ , 1.3 Hz, 1H), 7.76 (d,  $J = 7.5$  Hz, 1H), 7.58 (d,  $J = 7.7$ , 0.7 Hz, 1H), 7.54-7.56 (d, 2H), 7.49-7.50 (d, 2H), 7.46 (td,  $J = 7.5$ , 0.6 Hz, 1H), 7.38 (td,  $J = 7.8$ , 1.4 Hz, 1H), 7.31 (td,  $J = 7.6$ , 0.9 Hz, 1H), 7.29 (td,  $J = 7.6$ , 1.0 Hz, 1H), 7.17 (m, 1H), 7.07-7.14 (m, 4H), 6.17 (d,  $J = 7.6$  Hz, 1H), 4.67 (s, 1H), 3.86 (d,  $J = 12.0$  Hz, 1H), 2.78 (d,  $J = 12.4$  Hz, 1H), 1.54 (s, 9H).

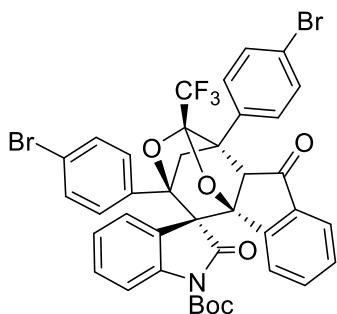
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 197.3, 172.3, 148.2, 143.8, 139.3, 137.5, 135.4, 134.9, 132.2, 131.5, 131.2 (q,  $J = 2.1$  Hz), 130.8, 129.8, 128.9, 128.7, 127.8, 125.7, 125.6, 125.1, 124.4, 122.7, 120.6 (q,  $J = 282.2$  Hz), 114.5, 113.5 (q,  $J = 34.5$  Hz), 90.7, 89.3, 85.2, 64.9, 62.9, 56.8, 47.0, 28.1.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 2984, 1793, 1736, 1605, 1466, 1151, 1079, 761.

**HRMS** (ESI) for C<sub>39</sub>H<sub>29</sub><sup>79</sup>BrF<sub>3</sub>NO<sub>6</sub>Na, [M+Na]<sup>+</sup> (766.1023) found: 766.1027.

**HRMS** (ESI) for C<sub>39</sub>H<sub>29</sub><sup>81</sup>BrF<sub>3</sub>NO<sub>6</sub>Na, [M+Na]<sup>+</sup> (768.1002) found: 768.1008.

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-2',3a'-bis(4-bromophenyl)-2,4'-dioxo-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-b]indeno[2,1-d]furan]-1-carboxylate (3ab)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2b** (41.4 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 12 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ab** was obtained as a white solid (73.2 mg, 86%).

R<sub>f</sub> = 0.52 (EtOAc/Hex = 1/5), mp.: 207.5-208.8 °C,  $[\alpha]_D^{25} = 25.3$  ( $c = 0.5$  in CH<sub>2</sub>Cl<sub>2</sub>),

**HPLC:** 84% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 5.52$  min,  $t_{\text{major}} = 8.24$  min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.14 (d,  $J = 7.6$  Hz, 1H), 7.75 (d,  $J = 7.6$  Hz, 1H), 7.60 (d,  $J = 7.6$  Hz, 1H), 7.60 (d,  $J = 8.2$  Hz, 2H), 7.39-7.48 (m, 4H), 7.32 (t,  $J = 7.6$  Hz, 1H), 7.29 (t,  $J = 7.5$  Hz, 1H), 7.24 (d,  $J = 9.1$  Hz, 2H), 7.00 (d,  $J = 8.8$  Hz, 2H), 6.13 (d,  $J = 7.5$  Hz, 1H), 4.62 (s, 1H), 3.82 (d,  $J = 12.0$  Hz, 1H), 2.73 (d,  $J = 12.0$

Hz, 1H), 1.55 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 196.9, 172.1, 147.8, 143.4, 139.1, 137.3, 134.8, 134.4, 131.8, 131.40, 131.00, 130.99, 130.8, 130.7, 130.0, 128.7, 127.3, 125.14, 125.12, 125.05, 124.5, 124.2, 122.9, 122.6, 120.3 (q, *J* = 282.0 Hz), 114.6, 113.4 (q, *J* = 34.5 Hz), 90.5, 88.7, 85.4, 64.7, 62.6, 56.5, 46.8, 28.0.

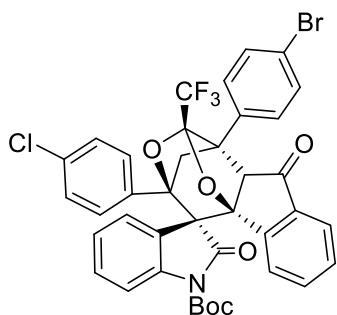
**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3107, 2945, 2839, 1787, 1736, 1471, 1395, 1342, 1309, 1248, 1187, 1150, 077, 1048, 823, 761, 614, 518.

**HRMS** (ESI) for C<sub>39</sub>H<sub>28</sub>NO<sub>6</sub><sup>79</sup>Br<sub>2</sub>F<sub>3</sub>Na, [M+Na]<sup>+</sup> (844.0128) found: 844.0132 (50).

**HRMS** (ESI) for C<sub>39</sub>H<sub>28</sub>NO<sub>6</sub><sup>79</sup>Br<sup>81</sup>B<sub>r</sub>F<sub>3</sub>Na, [M+Na]<sup>+</sup> (846.0107) found: 846.0107 (100).

**HRMS** (ESI) for C<sub>39</sub>H<sub>28</sub>NO<sub>6</sub><sup>81</sup>Br<sub>2</sub>F<sub>3</sub>Na, [M+Na]<sup>+</sup> (848.0087) found: 848.0099 (55).

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-3a'-(4-bromophenyl)-2'-(4-chlorophenyl)-2,4'-dioxo-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-b]lindeno[2,1-d]furan]-1-carboxylate (3ac)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2c** (36.9 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 14 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ac** was obtained as a white solid (71.0 mg, 88%).

R<sub>f</sub> = 0.60 (EtOAc/Hex = 1/5), mp.: 194.3-195.4 °C, [α]<sub>D</sub><sup>25</sup> = 38.0 (*c* = 0.5 in CH<sub>2</sub>Cl<sub>2</sub>),

**HPLC:** 82% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.00 mL/min, λ = 246 nm, t<sub>minor</sub> = 5.71 min, t<sub>major</sub> = 8.57 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.15 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.54-7.56 (m, 2H), 7.40-7.49 (m, 4H), 7.32 (pt, *J* = 7.3 Hz, 1H), 7.29 (pt, *J* = 7.1 Hz, 1H), 7.04-7.10 (m, 4H), 6.15 (d, *J* = 7.6 Hz, 1H), 4.64 (s, 1H), 3.84 (d, *J* = 11.9 Hz, 1H), 2.74 (d, *J* = 11.9 Hz, 1H), 1.56 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 196.9, 172.0, 147.8, 143.4, 139.1, 137.3, 134.8, 134.6, 133.9, 131.8, 131.4, 131.0, 130.6, 129.9, 128.7, 127.8, 125.1, 125.14,

125.09, 125.01, 124.1, 122.6, 120.2 (q,  $J = 282.0$  Hz), 114.5, 113.4 (q,  $J = 34.6$  Hz), 90.5, 88.7, 85.3, 64.7, 62.5, 56.5, 46.8, 27.9.

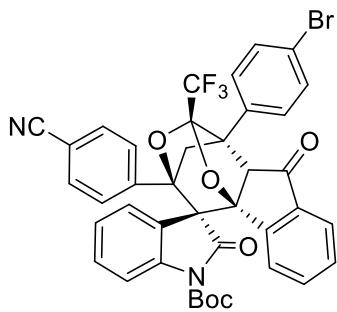
**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 2975, 2932, 1786, 1738, 1605, 1495, 1478, 1466, 1371, 1342, 1312, 1289, 1250, 1187, 1150, 1078, 1050, 914, 880, 824, 761, 613, 519.

**HRMS** (ESI) for C<sub>39</sub>H<sub>28</sub>NO<sub>6</sub><sup>35</sup>Cl<sup>79</sup>BrF<sub>3</sub>Na, [M+Na]<sup>+</sup> (800.0633) found: 800.0637 (71).

**HRMS** (ESI) for C<sub>39</sub>H<sub>28</sub>NO<sub>6</sub><sup>35</sup>Cl<sup>81</sup>BrF<sub>3</sub>Na, [M+Na]<sup>+</sup> (802.0612) found: 802.0626 (100).

**HRMS** (ESI) for C<sub>39</sub>H<sub>28</sub>NO<sub>6</sub><sup>37</sup>Cl<sup>81</sup>BrF<sub>3</sub>Na, [M+Na]<sup>+</sup> (804.0583) found: 804.0614 (29).

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-3a'-(4-bromophenyl)-2'-(4-cyanophenyl)-2,4'-dioxo-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-b]indeno[2,1-d]furan]-1-carboxylate (3ad)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2d** (36.0 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 12 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ad** was obtained as a white solid (51.8 mg, 65%).

R<sub>f</sub> = 0.40 (EtOAc/Hex = 1/5), mp.: 173.1-174.6 °C,  $[\alpha]_D^{25} = 48.9$  ( $c = 0.5$  in CH<sub>2</sub>Cl<sub>2</sub>),

**HPLC:** 98% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min,  $\lambda = 246$  nm, t<sub>minor</sub> = 9.16 min, t<sub>major</sub> = 18.93 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.14 (d,  $J = 7.6$  Hz, 1H), 7.76 (d,  $J = 7.6$  Hz, 1H), 7.67 (d,  $J = 8.1$  Hz, 1H), 7.55 (d,  $J = 8.7$  Hz, 2H), 7.45-7.49 (m, 3H), 7.42 (t,  $J = 7.9$  Hz, 1H), 7.29-7.35 (m, 4H), 7.05 (d,  $J = 7.8$  Hz, 1H), 6.97 (t,  $J = 7.8$  Hz, 1H), 6.17 (d,  $J = 8.0$  Hz, 1H), 4.65 (s, 1H), 3.84 (d,  $J = 11.9$  Hz, 1H), 2.75 (d,  $J = 12.0$  Hz, 1H), 1.57 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 197.0, 171.8, 148.0, 143.4, 139.1, 137.5, 137.3, 134.9, 131.8, 131.7, 131.4, 131.01, 131.00, 130.7, 130.0, 129.2, 128.7, 125.14, 125.08, 125.06, 124.3, 124.2, 122.6, 121.9, 120.3 (q,  $J = 282.1$  Hz), 114.4, 113.3 (q,  $J = 34.7$  Hz), 90.6, 88.4, 85.4, 64.7, 62.5, 56.5, 46.7, 28.0.

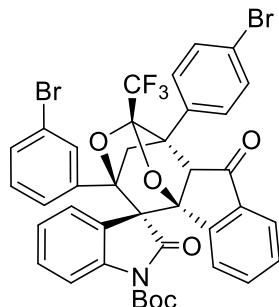
**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3081, 2982, 2936, 2232, 1786, 1739, 1605, 1480, 1371, 1342, 1311,

1289, 1252, 1187, 1150, 1077, 1050, 833, 767, 614.

**HRMS** (ESI) for  $C_{40}H_{28}N_2O_6F_3Na^{79}Br$ ,  $[M+Na]^+$  (791.0975) found: 791.0981 (93).

**HRMS** (ESI) for  $C_{40}H_{28}N_2O_6F_3Na^{81}Br$ ,  $[M+Na]^+$  (793.0955) found: 793.0969 (100).

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-2'-(3-bromophenyl)-3a'-(4-bromophenyl)-2,4'-dioxo-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-(2,8b)methanofuro[2,3-b]indeno[2,1-d]furan]-1-carboxylate (3ae)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2e** (41.4 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 9 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ae** was obtained as a white solid (54.5 mg, 64%).

$R_f = 0.52$  (EtOAc/Hex = 1/5), mp.: 189.5-192.1 °C,  $[\alpha]_D^{25} = 45.6$  ( $c = 0.5$  in  $CH_2Cl_2$ ),

**HPLC:** 82% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 5.14$  min,  $t_{\text{major}} = 7.11$  min.

**<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ , 25 °C)  $\delta/\text{ppm}$ : 8.14 (d,  $J = 7.6$  Hz, 1H), 7.76 (d,  $J = 7.6$  Hz, 1H), 7.66 (d,  $J = 8.1$  Hz, 1H), 7.55 (d,  $J = 8.7$  Hz, 2H), 7.44-7.49 (m, 3H), 7.42 (t,  $J = 9.2$  Hz, 1H), 7.25-7.39 (m, 4H), 7.05 d,  $J = 7.8$  Hz, 1H), 7.0 (t,  $J = 7.8$  Hz, 1H), 6.17 (d,  $J = 8.0$  Hz, 1H), 4.65 (s, 1H), 3.84 (d,  $J = 11.9$  Hz, 1H), 2.75 (d,  $J = 11.9$  Hz, 1H), 1.57 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz,  $CDCl_3$ , 25 °C)  $\delta/\text{ppm}$ : 197.0, 171.8, 148.0, 143.4, 139.1, 137.5, 137.3, 134.9, 131.8, 131.7, 131.4, 131.0, 131.00, 130.69, 130.00, 129.2, 128.7, 125.2, 125.08, 125.06, 124.5, 124.3, 124.2, 121.9, 121.7, 120.3 (q,  $J = 282.1$  Hz), 114.4, 113.3 (q,  $J = 34.7$  Hz), 90.6, 88.4, 85.4, 64.7, 62.5, 56.5, 46.7, 28.0.

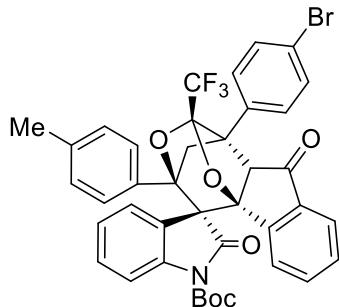
**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3085, 2984, 2933, 1787, 1738, 1605, 1495, 1478, 1466, 1395, 1371, 1343, 289, 1255, 1204, 1187, 1150, 1078, 1050, 1035, 881, 837, 787, 761, 747, 519.

**HRMS** (ESI) for  $C_{39}H_{28}NO_6^{79}Br_2F_3Na$ ,  $[M+Na]^+$  (844.0128) found: 844.0135 (49).

**HRMS** (ESI) for  $C_{39}H_{28}NO_6^{79}Br^{81}F_3Na$ ,  $[M+Na]^+$  (846.0107) found: 846.0117 (100).

**HRMS** (ESI) for  $C_{39}H_{28}NO_6^{81}Br_2F_3Na$ ,  $[M+Na]^+$  (848.0087) found: 848.0111 (57).

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-3a'-(4-bromophenyl)-2,4'-dioxo-2'-(p-tolyl)-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-b]indeno[2,1-d]furan]-1-carboxylate (3ag)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2g** (34.9 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 12 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ag** was obtained as a white solid (58.5 mg, 73%).

$R_f = 0.55$  (EtOAc/Hex = 1/5), mp.: 178.8-179.9 °C,  $[\alpha]_D^{25} = 38.2$  ( $c = 0.5$  in  $CH_2Cl_2$ ),

**HPLC:** 71% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 5.49$  min,  $t_{\text{major}} = 7.01$  min.

**<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ , 25 °C)  $\delta$ /ppm: 8.16 (d,  $J = 7.5$  Hz, 1H), 7.75 (d,  $J = 7.6$  Hz, 1H), 7.60 (d,  $J = 8.1$  Hz, 1H), 7.53-7.56 (m, 2H), 7.44-7.49 (m, 3H), 7.39 (t,  $J = 7.8$  Hz, 1H), 7.31 (t,  $J = 7.6$  Hz, 1H), 7.28 (t,  $J = 7.4$  Hz, 1H), 6.98 (d,  $J = 8.0$  Hz, 2H), 6.90 (d,  $J = 8.4$  Hz, 2H), 6.14 (d,  $J = 7.7$  Hz, 1H), 4.65 (s, 1H), 3.83 (d,  $J = 11.9$  Hz, 1H), 2.74 (d,  $J = 11.9$  Hz, 1H), 2.22, (s, 3H), 1.54 (s, 9H).

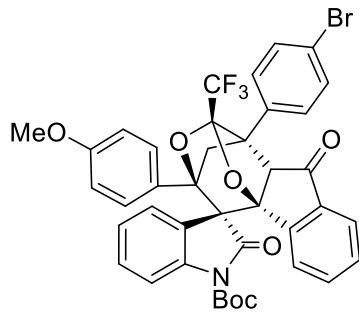
**<sup>13</sup>C NMR** (100 MHz,  $CDCl_3$ , 25 °C)  $\delta$ /ppm: 197.2, 172.3, 148.0, 143.7, 139.2, 138.3, 137.4, 134.7, 132.5, 132.1, 131.3, 131.1, 130.6, 129.6, 128.7, 128.3, 125.6, 125.4, 124.96, 124.95, 124.2, 122.5, 120.4 (q,  $J = 281.9$  Hz), 114.4, 113.4 (q,  $J = 34.7$  Hz), 90.5, 89.1, 84.9, 64.7, 62.7, 56.7, 47.0, 27.9, 21.0.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3059, 2980, 2930, 1787, 1736, 1605, 1466, 1371, 1343, 1310, 1290, 1255, 1184, 1150, 1077, 1050, 871, 758, 615.

**HRMS** (ESI) for  $C_{40}H_{31}NO_6F_3Na^{79}Br$ ,  $[M+Na]^+$  (780.1179) found: 780.1184 (92).

**HRMS** (ESI) for  $C_{40}H_{31}NO_6F_3Na^{81}Br$ ,  $[M+Na]^+$  (782.1159) found: 782.1173 (100).

**tert-Butyl(2'R,3R,3a'S,3b'R,8b'S,9a'R)-3a'-(4-bromophenyl)-2'-(4-methoxyphenyl)-2,4'-dioxo-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-b]indeno[2,1-d]furan]-1-carboxylate (3ah)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2h** (36.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 9 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ah** was obtained as a white solid (65.0 mg, 81%).

$R_f = 0.42$  (EtOAc/Hex = 1/5), mp.: 148.9–149.7 °C,  $[\alpha]_D^{25} = 33.9$  ( $c = 0.5$  in CH<sub>2</sub>Cl<sub>2</sub>).

**HPLC:** 68% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 6.89$  min,  $t_{\text{major}} = 9.01$  min.

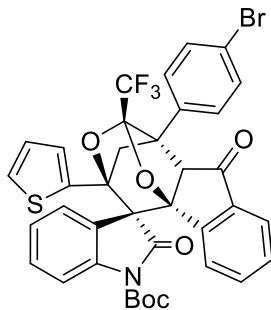
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 8.15 (d,  $J = 7.5$  Hz, 1H), 7.7 (d,  $J = 8.0$  Hz, 1H), 7.6 (d,  $J = 8.0$  Hz, 1H), 7.54 (d,  $J = 8.4$  Hz, 2H), 7.48 (d,  $J = 8.4$  Hz, 2H), 7.45 (t,  $J = 7.7$  Hz, 1H), 7.39 (t,  $J = 8.0$  Hz, 1H), 7.31 (d,  $J = 7.5$  Hz, 1H), 7.28 (t,  $J = 7.5$  Hz, 1H), 7.01 (d,  $J = 8.8$  Hz, 2H), 6.61 (d,  $J = 8.8$  Hz, 2H), 6.15 (d,  $J = 8.0$  Hz, 1H), 4.63 (s, 1H), 3.84 (d,  $J = 12.0$  Hz, 1H), 3.70 (s, 3H), 2.73 (d,  $J = 12.0$  Hz, 1H), 1.55 (s, 9H).  
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 197.2, 172.3, 159.5, 148.1, 143.7, 139.3, 137.4, 134.8, 132.2, 131.3, 131.1, 130.6, 129.7, 128.7, 127.7, 127.0, 125.7, 124.99, 124.97, 124.3, 131.2 (q,  $J = 2.1$  Hz), 130.8, 129.8, 128.9, 128.7, 127.8, 125.7, 125.6, 125.1, 124.4, 122.5, 120.4 (q,  $J = 282.2$  Hz), 114.5, 113.5 (q,  $J = 33.9$  Hz), 113.0, 90.5, 89.0, 85.0, 64.8, 62.8, 56.9, 55.2, 47.2, 28.0.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3072, 2934, 2852, 1785, 1736, 1606, 1517, 1495, 1478, 1466, 1342, 1305, 1254, 1182, 1150, 1077, 834, 761, 612.

**HRMS** (ESI) for C<sub>40</sub>H<sub>31</sub>NO<sub>7</sub>F<sub>3</sub>Na<sup>79</sup>Br, [M+Na]<sup>+</sup> (796.1128) found: 796.1125 (97).

**HRMS** (ESI) for C<sub>40</sub>H<sub>31</sub>NO<sub>7</sub>F<sub>3</sub>Na<sup>81</sup>Br, [M+Na]<sup>+</sup> (798.1108) found: 798.1113 (100).

**tert-Butyl (2'*S*,3*S*,3*a'**S*,3*b'**R*,8*b'**S*,9*a'**S*)-3*a*'-(4-bromophenyl)-2,4'-dioxo-2'-(thiophen-2-yl)-9*a*'-(trifluoromethyl)-2',3',3*a*',3*b*',4',9*a*'-hexahydrospiro[indoline-3,10'-[2,8*b*]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3ai)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2i** (34.1 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 8 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ai** was obtained as a white solid (68.3 mg, 91%).

$R_f = 0.47$  (EtOAc/Hex = 1/5), mp.: 197.2-198.5 °C,  $[\alpha]_D^{25} = 20.7$  ( $c = 0.5$  in CH<sub>2</sub>Cl<sub>2</sub>), **HPLC:** 34% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 98:2, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 7.59$  min,  $t_{\text{major}} = 12.56$  min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 8.16 (d,  $J = 7.3$  Hz, 1H), 7.75 (d,  $J = 7.6$  Hz, 1H), 7.72 (d,  $J = 8.2$  Hz, 1H), 7.56 (d,  $J = 8.7$  Hz, 2H), 7.45-7.50 (m, 2H), 7.33 (t,  $J = 7.6$  Hz, 2H), 7.07-7.26 (m, 5H), 6.17 (d,  $J = 7.7$  Hz, 1H), 4.58 (s, 1H), 3.86 (d,  $J = 11.9$  Hz, 1H), 2.89 (d,  $J = 12.4$  Hz, 1H), 1.55 (s, 9H).

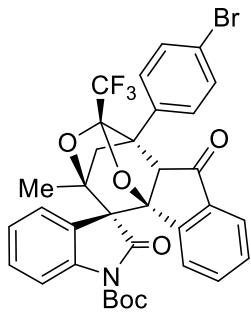
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 196.9, 171.7, 148.1, 143.4, 139.7, 137.3, 137.2, 134.8, 131.8, 131.4, 131.04, 131.02, 130.7, 130.0, 128.9, 126.3, 126.0, 125.6, 125.0, 124.2, 120.2 (q,  $J = 281.9$  Hz), 114.6, 113.7 (q,  $J = 34.7$  Hz), 90.5, 87.6, 85.1, 64.8, 62.3, 57.0, 48.2, 28.0.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3076, 2980, 2936, 1787, 1736, 1605, 1466, 1397, 1342, 1312, 1289, 1253, 1186, 1150, 1076, 1033, 837, 761, 704, 633, 519.

**HRMS** (ESI) for C<sub>37</sub>H<sub>27</sub>NO<sub>6</sub>F<sub>3</sub>NaS<sup>79</sup>Br, [M+Na]<sup>+</sup> (772.0587) found: 772.0590 (91).

**HRMS** (ESI) for C<sub>37</sub>H<sub>27</sub>NO<sub>6</sub>F<sub>3</sub>NaS<sup>81</sup>Br, [M+Na]<sup>+</sup> (774.0566) found: 774.0573 (100).

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-3a'-(4-bromophenyl)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-b]indeno[2,1-d]furan]-1-carboxylate (3aj)**



Following the GP-E, **1a** (163.7 mg, 0.4 mmol), **2j** (109.3 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (2.0 mL) and stirred for 24 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:5), **3aj** was obtained as a purple solid (71.0 mg, 26%).

$R_f = 0.37$  (EtOAc/Hex = 1/5), mp.: 271.0-272.0 °C,  $[\alpha]_D^{22} = 8.2$  ( $c = 0.5$  in CHCl<sub>3</sub>),

**HPLC:** 34% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.00 mL/min,  $\lambda = 241$  nm,  $t_{\text{minor}} = 5.65$  min,  $t_{\text{major}} = 10.93$  min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 8.05 (d,  $J = 7.7$  Hz, 1H), 8.01 (d,  $J = 8.2$  Hz, 1H), 7.72 (d,  $J = 7.5$  Hz, 1H), 7.61 – 7.52 (m, 3H), 7.48-7.41 (m, 3H), 7.37 (d,  $J = 8.0$  Hz, 1H), 7.29 (t,  $J = 7.7$  Hz, 1H), 6.11 (d,  $J = 7.7$  Hz, 1H), 4.37 (s, 1H), 3.40 (d,  $J = 11.9$  Hz, 1H), 2.51 (d,  $J = 12.0$  Hz, 1H), 1.60 (s, 9H), 1.19 (s, 3H).

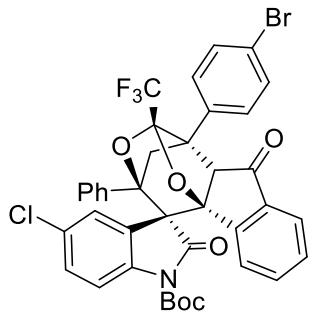
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 197.1, 171.9, 148.4, 143.5, 139.8, 137.4, 134.8, 132.1, 131.2, 131.0, 129.9, 128.6, 126.1, 125.6, 125.0, 124.0, 122.4, 120.3 (q,  $J = 281.8$  Hz), 114.8, 113.4 (q,  $J = 34.3$  Hz), 90.2, 86.0, 85.6, 65.0, 62.2, 55.5, 47.9, 28.0, 19.0.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 2985, 2936, 1785, 1736, 1605, 1466, 1371, 1342, 1309, 1289, 1253, 1179, 1149, 1086, 1054, 838, 759, 512.

**HRMS** (ESI) for C<sub>34</sub>H<sub>27</sub>NO<sub>6</sub><sup>79</sup>BrF<sub>3</sub>Na, [M+Na]<sup>+</sup> (704.0866) found: 704.0872 (91).

**HRMS** (ESI) for C<sub>34</sub>H<sub>27</sub>NO<sub>6</sub><sup>81</sup>BrF<sub>3</sub>Na, [M+Na]<sup>+</sup> (706.0846) found: 774.0877 (100).

**tert-Butyl (2'*R*,3*R*,3a'*S*,3b'*R*,8b'*S*,9a'*R*)-3a'-(4-bromophenyl)-5-chloro-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8*b*]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3ak)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2k** (36.9 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 36 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ak** was obtained as a white solid (67.0 mg, 86%).

$R_f$ =0.45 (EtOAc/Hex = 1/5), mp.: 217.8-217.9 °C,  $[\alpha]_D^{25} = 33.0$  ( $c = 0.5$  in  $\text{CH}_2\text{Cl}_2$ ),

**HPLC:** 65% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 98:2, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 7.57$  min,  $t_{\text{major}} = 10.78$  min.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 8.16 (s, 1H), 7.76 (d,  $J = 7.5$  Hz, 1H), 7.46-7.58 (m, 6H), 7.37 (dd,  $J = 9.9, 0.9$  Hz, 1H), 7.33 (t,  $J = 7.6$  Hz, 1H), 7.19-7.20 (m, 1H), 7.12-7.15 (m, 4H), 6.25 (d,  $J = 7.5$  Hz, 1H), 4.65 (s, 1H), 3.85 (d,  $J = 12.4$  Hz, 1H), 2.79 (d,  $J = 12.4$  Hz, 1H), 1.54 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 196.8, 171.5, 147.7, 143.2, 137.7, 137.3, 134.9, 134.9, 131.8, 131.5, 131.0, 130.6, 130.5, 129.7, 128.7, 128.7, 127.8, 127.2, 125.4, 125.1, 124.1, 122.6, 120.2 (q,  $J = 281.7$  Hz), 115.6, 113.4 (q,  $J = 34.5$  Hz), 90.3, 89.1, 85.4, 64.6, 62.7, 56.8, 46.9, 28.0.

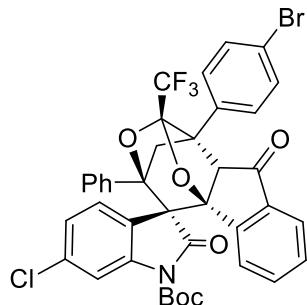
**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3072, 2983, 2927, 1788, 1736, 1604, 1497, 1473, 1447, 1395, 1371, 1334, 1297, 1248, 1189, 1151, 1076, 821, 763, 520.

**HRMS** (ESI) for  $\text{C}_{39}\text{H}_{28}\text{NO}_6\text{Na}^{35}\text{Cl}^{79}\text{BrF}_3$ ,  $[\text{M}+\text{Na}]^+$  (800.0633) found: 800.0637 (71).

**HRMS** (ESI) for  $\text{C}_{39}\text{H}_{28}\text{NO}_6\text{Na}^{35}\text{Cl}^{81}\text{BrF}_3$ ,  $[\text{M}+\text{Na}]^+$  (802.0612) found: 802.0621 (100).

**HRMS** (ESI) for  $\text{C}_{39}\text{H}_{28}\text{NO}_6\text{Na}^{37}\text{Cl}^{81}\text{BrF}_3$ ,  $[\text{M}+\text{Na}]^+$  (804.0583) found: 804.0610 (31).

**tert-Butyl (2'*R*,3*R*,3a'*S*,3b'*R*,8b'*S*,9a'*R*)-3a'-(4-bromophenyl)-6-chloro-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8*b*]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3al)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2l** (36.9 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 8 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3al** was obtained as a white solid (68.5 mg, 88%).

$R_f = 0.52$  (EtOAc/Hex = 1/5), mp.: 216.2-217.4 °C,  $[\alpha]_D^{25} = 47.1$  ( $c = 0.5$  in CH<sub>2</sub>Cl<sub>2</sub>),

**HPLC:** 81% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 98:2, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 6.50$  min,  $t_{\text{major}} = 11.46$  min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 8.09 (d,  $J = 8.3$  Hz, 1H), 7.76 (d,  $J = 7.6$  Hz, 1H), 7.69 (d,  $J = 1.4$  Hz, 1H), 7.54 (d,  $J = 8.6$  Hz, 2H), 7.45-7.49 (m, 3H), 7.33 (t,  $J = 7.7$  Hz, 1H), 7.31 (dd,  $J = 7.9, 0.8$  Hz, 1H), 7.19-7.23 (m, 1H), 7.14 (t,  $J = 7.6$  Hz, 2H), 7.10 (d,  $J = 7.5$  Hz, 2H), 6.24 (d,  $J = 7.7$  Hz, 1H), 4.63 (s, 1H), 3.83 (d,  $J = 12.4$  Hz, 1H), 2.78 (d,  $J = 11.9$  Hz, 1H), 1.55 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 196.8, 171.7, 147.7, 143.3, 139.9, 137.2, 135.7, 135.0, 131.8, 131.4, 131.0, 130.6, 129.4, 128.7, 127.7, 125.4, 125.08, 125.05, 124.0, 123.9, 122.5, 120.2 (q,  $J = 281.9$  Hz), 115.1, 113.3 (q,  $J = 34.6$  Hz), 90.4, 85.5, 64.6, 62.7, 56.6, 46.9, 27.9.

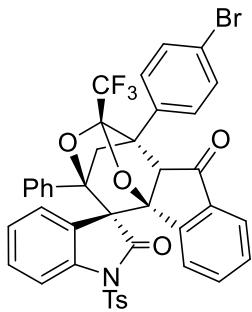
**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3085, 2980, 2940, 1791, 1739, 1604, 1498, 1474, 1454, 1395, 1371, 1338, 1287, 1248, 1188, 1149, 1078, 1034, 840, 764, 616, 520.

**HRMS** (ESI) for C<sub>39</sub>H<sub>27</sub>NO<sub>6</sub>F<sub>3</sub><sup>35</sup>Cl<sup>79</sup>Br, [M-H]<sup>+</sup> (776.0668) found: 776.0662 (74).

**HRMS** (ESI) for C<sub>39</sub>H<sub>27</sub>NO<sub>6</sub>F<sub>3</sub><sup>35</sup>Cl<sup>81</sup>Br, [M-H]<sup>+</sup> (778.0647) found: 778.0656 (100).

**HRMS** (ESI) for C<sub>39</sub>H<sub>27</sub>NO<sub>6</sub>F<sub>3</sub><sup>37</sup>Cl<sup>81</sup>Br, [M-H]<sup>+</sup> (780.0617) found: 780.0680 (29).

**(2'*R*,3*R*,3a'*S*,3b'*R*,8b'*S*,9a'*R*)-3a'-(4-Bromophenyl)-2'-phenyl-1-tosyl-9a'-trifluoromethyl)-2',3',3a',9a'-tetrahydrospiro[indoline-3,10'-(2,8*b*]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-2,4'(3b'*H*)-dione (3am)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2m** (38.9 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 40 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:5), **3am** was obtained as a yellow solid (48.7 mg, 61%).

$R_f = 0.2$  (EtOAc/Hex = 1/5), mp.: 268.1-268.6 °C,  $[\alpha]_D^{26} = 26.2$  ( $c = 0.5$  in CH<sub>2</sub>Cl<sub>2</sub>),

**HPLC:** 14% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 7.68$  min,  $t_{\text{major}} = 10.24$  min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 8.13 (d,  $J = 7.5$  Hz, 1H), 7.79 (d,  $J = 7.9$  Hz, 1H), 7.68 (d,  $J = 8.4$  Hz, 3H), 7.53 (d,  $J = 8.8$  Hz, 2H), 7.44-7.37 (m, 4H), 7.33 (t,  $J = 7.0$  Hz, 1H), 7.13-7.05 (m, 4H), 6.98-6.96 (m, 4H), 5.88 (d,  $J = 7.9$  Hz, 1H), 4.46 (s, 1H), 3.75 (d,  $J = 11.9$  Hz, 1H), 2.72 (d,  $J = 12.3$  Hz, 1H), 2.37 (s, 3H).

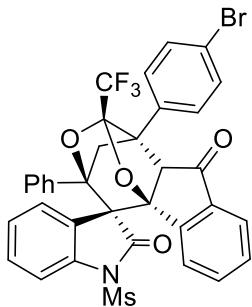
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 196.7, 172.0, 145.8, 143.0, 138.7, 137.2, 135.2, 134.6, 134.5, 131.8, 131.0, 130.9, 130.7, 130.2, 129.6, 129.3, 128.4, 128.0, 127.8, 125.7, 125.4, 125.0, 123.6, 122.6, 120.3 (q,  $J = 282.1$  Hz), 113.4 (q,  $J = 34.4$  Hz), 113.0, 90.5, 88.8, 64.6, 62.4, 56.6, 47.3, 21.7.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3069, 2934, 1732, 1603, 1464, 1388, 1237, 1192, 1091, 1077, 1032, 571.

**HRMS** (ESI) for C<sub>41</sub>H<sub>28</sub>NO<sub>6</sub>F<sub>3</sub>S<sup>79</sup>Br, [M+H]<sup>+</sup> (798.0767) found: 798.0772.

**HRMS** (ESI) for C<sub>41</sub>H<sub>28</sub>NO<sub>6</sub>F<sub>3</sub>S<sup>81</sup>Br, [M+H]<sup>+</sup> (800.0747) found: 800.0757.

**(2'*R*,3*R*,3a'*S*,3b'*R*,8b'*S*,9a'*R*)-3a'-(4-Bromophenyl)-1-(methylsulfonyl)-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',9a'-tetrahydrospiro[indoline-3,10'-[2,8b]methano-furo[2,3-*b*]indeno[2,1-*d*]furan]-2,4'(3b'H)-dione (3an)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2n** (31.3 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 40 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc /Hex = 1/15), **3an** was obtained as a yellow solid (66.5 mg, 92%).

$R_f = 0.15$  (EtOAc/Hex = 1/5), mp.: 168.8-169.4 °C,  $[\alpha]_D^{26} = 16.3$  ( $c = 0.5$  in CH<sub>2</sub>Cl<sub>2</sub>),

**HPLC:** 80% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 38.00$  min,  $t_{\text{major}} = 22.33$  min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 8.22 (d,  $J = 7.1$  Hz, 1H), 7.88 (d,  $J = 7.5$  Hz, 1H), 7.61-7.47 (m, 6H), 7.43 (td,  $J = 7.8, 1.3$  Hz, 1H), 7.38 (t,  $J = 7.5$  Hz, 1H), 7.33 (t,  $J = 7.5$  Hz, 1H), 7.24-7.21 (m, 1H), 7.18-7.13 (m, 4H), 6.16 (d,  $J = 7.5$  Hz, 1H), 4.49 (s, 1H), 3.86 (d,  $J = 11.9$  Hz, 1H), 3.01 (s, 3H), 2.85 (d,  $J = 12.4$ , 1H).

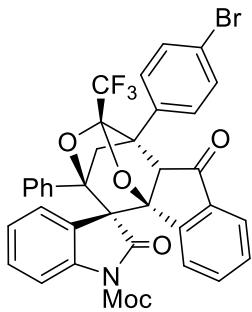
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 196.6, 172.8, 143.1, 138.4, 137.3, 135.2, 135.0, 131.7, 131.6, 131.0, 130.9, 130.7, 130.3, 129.5, 129.0, 128.0, 125.9, 125.6, 125.4, 125.3, 123.7, 122.7, 120.2 (q,  $J = 281.9$  Hz), 113.5 (q,  $J = 34.7$  Hz), 112.9, 90.5, 89.0, 64.5, 62.5, 57.0, 47.1, 41.2.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3454, 3062, 2989, 1918, 1816, 1733, 1604, 1464, 1375, 1329, 1304, 1262, 1240, 1183, 1168, 1077, 762, 740, 704.

**HRMS** (ESI) for C<sub>35</sub>H<sub>24</sub>NO<sub>6</sub>F<sub>3</sub>S<sup>79</sup>Br, [M+H]<sup>+</sup> (722.0454) found: 722.0460.

**HRMS** (ESI) for C<sub>35</sub>H<sub>24</sub>NO<sub>6</sub>F<sub>3</sub>S<sup>81</sup>Br, [M+H]<sup>+</sup> (724.0434) found: 724.0446.

**Methyl (2'*R*,3*R*,3a'*S*,3b'*R*,8b'*S*,9a'*R*)-3a'-(4-bromophenyl)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3ao)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2o** (29.3 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 17 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc /Hex = 1/15), **3ao** was obtained as a yellow solid (61.8 mg, 88%).

$R_f = 0.15$  (EtOAc/Hex = 1/5), mp.: 241.7-242.4 °C,  $[\alpha]_D^{25} = 77.5$  ( $c = 0.5$  in CH<sub>2</sub>Cl<sub>2</sub>), **HPLC:** 64% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 16.07$  min,  $t_{\text{major}} = 22.6$  min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 8.19 (d,  $J = 7.7$  Hz, 1H), 7.76 (d,  $J = 7.5$  Hz, 1H), 7.69 (d,  $J = 7.9$  Hz, 1H), 7.56 (d,  $J = 8.6$  Hz, 2H), 7.52-7.46 (m, 3H), 7.42 (td,  $J = 9.3, 1.3$  Hz, 1H), 7.35 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.29 (td,  $J = 8.5, 1.0$  Hz, 1H), 7.21-7.08 (m, 5H), 6.14 (t,  $J = 8.1$  Hz, 1H), 4.61 (s, 1H), 3.91 (s, 3H), 3.86 (d,  $J = 11.8$  Hz, 1H), 2.80 (t,  $J = 12.2$  Hz, 1H).

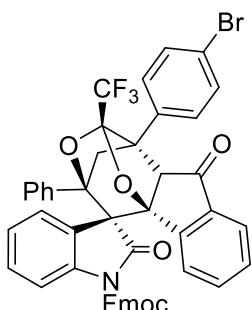
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 197.0, 172.1, 150.3, 143.4, 138.7, 137.3, 135.3, 134.9, 131.8, 131.4, 131.0, 130.7, 129.9, 128.9, 128.7, 127.8, 125.55, 125.50, 125.4, 125.1, 124.0, 122.6, 114.4, 90.6, 89.1, 64.6, 62.5, 56.9, 54.2, 47.0.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3059, 2934, 1743, 1605, 1242, 1186, 1078, 617.

**HRMS** (ESI) for C<sub>36</sub>H<sub>24</sub>NO<sub>6</sub><sup>79</sup>BrF<sub>3</sub>, [M+H]<sup>+</sup> (702.0734) found: 702.0734.

**HRMS** (ESI) for C<sub>36</sub>H<sub>24</sub>NO<sub>6</sub><sup>81</sup>BrF<sub>3</sub>, [M+H]<sup>+</sup> (704.0713) found: 704.0712.

**(9H-Fluoren-9-yl) methyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-3a'-(4-bromophenyl)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-(2,8b)methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3ap)**



Following the GP-E, **1a** (40.9 mg, 0.1 mmol), **2p** (45.7 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 15 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc /Hex = 1/15), **3ap** was obtained as a yellow solid (67.7 mg, 70%).

$R_f = 0.25$  (EtOAc/Hex = 1/7), mp.: 161.7-162.5 °C,  $[\alpha]_D^{25} = 36.9$  ( $c = 0.5$  in  $\text{CH}_2\text{Cl}_2$ ),

**HPLC:** 75% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 85:15, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 9.49$  min,  $t_{\text{major}} = 14.14$  min.

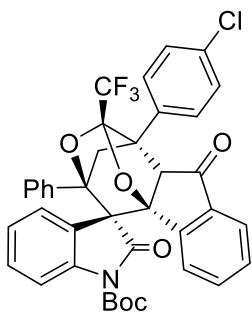
**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 8.18 (dd,  $J = 7.1, 1.8$  Hz, 1H), 7.79-7.76 (m, 3H), 7.59-7.56 (m, 3H), 7.54-7.50 (m, 3H), 7.48-7.36 (m, 4H), 7.35-7.22 (m, 5H), 7.16-7.05 (m, 5H), 6.11 (d,  $J = 7.7$  Hz, 1H), 4.67 (s, 1H), 4.64 (dd,  $J = 10.6, 6.5$  Hz, 1H), 4.52 (dd,  $J = 10.6, 7.3$  Hz, 1H), 4.29 (t,  $J = 6.8$  Hz, 1H), 3.91 (d,  $J = 11.9$  Hz, 1H), 2.83 (d,  $J = 11.9$  Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 197.0, 172.1, 149.6, 143.4, 143.2, 142.8, 141.4, 141.3, 138.6, 137.4, 135.3, 134.9, 131.9, 131.4, 131.1, 130.7, 129.9, 128.9, 128.7, 128.1, 127.8, 127.3, 127.2, 125.5, 125.4, 125.1, 124.9, 124.1, 122.6, 120.3 (q,  $J = 281.7$  Hz), 120.2, 114.5, 113.4 (q,  $J = 34.5$  Hz), 90.6, 89.1, 69.3, 64.7, 62.6, 57.0, 47.1, 46.4. **IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3450, 3068, 2954, 2926, 2855, 1955, 1925, 1789, 1739, 1606, 1254, 1224, 1204, 1187, 1078, 1035, 759, 741, 703.

**HRMS** (ESI) for  $\text{C}_{49}\text{H}_{31}\text{NO}_6\text{F}_3\text{Na}^{79}\text{Br}$ ,  $[\text{M}+\text{Na}]^+$  (888.1179) found: 888.1187.

**HRMS** (ESI) for  $\text{C}_{49}\text{H}_{31}\text{NO}_6\text{F}_3\text{Na}^{81}\text{Br}$ ,  $[\text{M}+\text{Na}]^+$  (890.1159) found: 890.1174.

**tert-Butyl (2'*R*,3*R*,3a'*S*,3b'*R*,8b'*S*,9a'*R*)-3a'-(4-chlorophenyl)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8*b*]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3ba)**



Following the GP-E, **1b** (36.5 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 12 hours at 30 °C. After quenching the reaction, the mixture purification by flash chromatography (EtOAc/Hex = 1:15), **3ba** was obtained as a yellow solid (45.5 mg, 65%).

$R_f = 0.50$  (EtOAc/Hex = 1/5), mp.: 154.1-154.7 °C,  $[\alpha]_D^{25} = 49.1$  ( $c = 0.5$  in  $\text{CH}_2\text{Cl}_2$ ),  
**HPLC:** 81% ee, Chiralpak IA column, *n*-hexane/EtOH = 98:2, flow rate = 0.80 mL/min,  
 $\lambda = 246$  nm,  $t_{\text{minor}} = 7.17$  min,  $t_{\text{major}} = 11.03$  min.

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 8.17 (d,  $J = 7.6$  Hz, 1H), 7.76 (d,  $J = 7.5$  Hz, 1H), 7.55-7.59 (m, 3H), 7.46 (td,  $J = 7.5, 0.8$  Hz, 1H), 7.36-7.41 (m, 3H), 7.31 (t,  $J = 7.5$  Hz, 1H), 7.28 (td,  $J = 7.6, 0.9$  Hz, 1H), 7.14-7.20 (m, 1H), 7.08-7.13 (m, 4H), 6.17 (d,  $J = 8.2$  Hz, 1H), 4.67 (s, 1H), 3.87 (d,  $J = 11.9$  Hz, 1H), 2.79 (d,  $J = 12.3$  Hz, 1H), 1.54 (s, 9H).

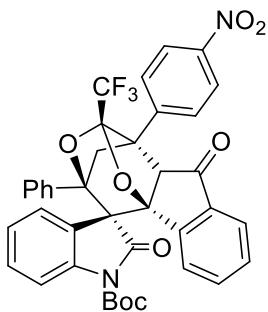
**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta/\text{ppm}$ : 197.2, 172.2, 148.0, 143.6, 139.1, 137.4, 135.3, 134.8, 134.2, 131.5, 131.3, 130.8, 129.7, 128.7, 128.5, 127.9, 127.7, 127.6, 127.3, 125.5, 125.0, 124.2, 120.4 (q,  $J = 285.2$  Hz), 114.4, 113.4 (q,  $J = 34.5$  Hz), 90.5, 89.1, 85.0, 76.7, 64.6, 62.7, 56.7, 46.9, 28.0.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 2982, 2933, 1786, 1736, 1605, 1499, 1480, 1466, 1393, 1371, 1343, 1310, 1288, 1255, 1185, 1150, 1081, 1034, 838, 763, 702.

**HRMS** (ESI) for  $\text{C}_{39}\text{H}_{29}\text{NO}_6\text{F}_3\text{Na}^{35}\text{Cl}$ ,  $[\text{M}+\text{Na}]^+$  (722.1528) found: 722.1533.

**HRMS** (ESI) for  $\text{C}_{39}\text{H}_{29}\text{NO}_6\text{F}_3\text{Na}^{37}\text{Cl}$ ,  $[\text{M}+\text{Na}]^+$  (724.1498) found: 724.1523.

**tert-Butyl (2'*R*,3*R*,3a'S,3b'R,8b'S,9a'R)-3a'-(4-nitrophenyl)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3ca)**



Following the GP-E, **1c** (37.5 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 24 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ca** was obtained as a white solid (37.6 mg, 54%).

$R_f = 0.37$  (EtOAc/Hex = 1/5), mp.: 194.4-195.0 °C,  $[\alpha]_D^{25} = 47.7$  ( $c = 0.5$  in  $\text{CH}_2\text{Cl}_2$ ),  
**HPLC:** 77% ee, Chiralpak IA column, *n*-hexane/EtOH = 95:5, flow rate = 1.00 mL/min,  
 $\lambda = 246$  nm,  $t_{\text{minor}} = 8.10$  min,  $t_{\text{major}} = 14.34$  min.

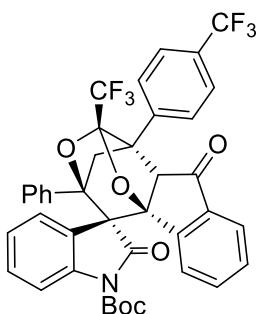
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.28 (d, *J* = 9.0 Hz, 2H), 8.16 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.38 (td, *J* = 7.9, 1.2 Hz, 1H), 7.30-7.35 (m, 2H), 7.16-7.22 (m, 1H), 7.12-7.15 (m, 4H), 6.19 (d, *J* = 7.7 Hz, 1H), 4.75 (s, 1H), 3.96 (d, *J* = 11.9 Hz, 1H), 2.82 (d, *J* = 12.0 Hz, 1H), 1.55 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 197.0, 172.1, 147.9, 147.5, 143.5, 140.6, 139.1, 137.1, 134.98, 134.94, 131.5, 130.4, 130.4, 129.8, 128.7, 128.6, 127.7, 125.5, 125.2, 125.1, 124.3, 122.5, 120.2 (q, *J* = 282.9 Hz), 114.4, 113.4 (q, *J* = 34.7 Hz), 90.7, 89.3, 85.1, 65.1, 62.6, 56.6, 47.1, 27.9.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 2982, 2934, 1752, 1738, 1605, 1523, 1479, 1466, 1371, 1347, 1313, 1288, 1252, 1188, 1150, 1082, 1050, 1033, 1000, 855, 770, 755, 700.

**HRMS** (ESI) calcd for C<sub>39</sub>H<sub>28</sub>N<sub>2</sub>O<sub>8</sub>F<sub>3</sub>, [M-H]<sup>+</sup> (709.1803) found: 709.1793.

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-3a'-(4-(trifluoromethyl)phenyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-b]indeno[2,1-d]furan]-1-carboxylate (3da)**



Following the GP-E, **1d** (39.8 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 11 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3da** was obtained as a white solid (63.4 mg, 85%).

R<sub>f</sub> = 0.50 (EtOAc/Hex = 1/5), mp.: 186.6-187.5 °C, [α]<sub>D</sub><sup>20</sup> = 3.1 (*c* = 0.5 in CH<sub>2</sub>Cl<sub>2</sub>),

**HPLC:** 75% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.00 mL/min, λ = 246 nm, t<sub>minor</sub> = 4.87 min, t<sub>major</sub> = 6.46 min.

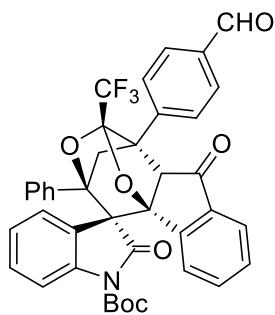
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.17 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.80-7.73 (m, 3H), 7.65-7.71 (m, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.46 (pt, *J* = 7.5 Hz, 1H), 7.39 (td, *J* = 8.0, 1.1 Hz, 1H), 7.26-7.32 (td, *J* = 7.6, 0.9 Hz, 1H), 7.29 (pt, *J* = 8.1 Hz, 1H), 7.21-7.14 (m, 1H), 7.08-7.15 (m, 4H), 6.18 (d, *J* = 7.5 Hz, 1H), 4.73 (s, 1H), 3.92 (d, *J* = 12.0 Hz, 1H), 2.82 (d, *J* = 12.0 Hz, 1H), 1.55 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 197.2, 172.3, 148.1, 143.7, 139.3, 137.5, 137.3, 135.3, 135.0, 131.5, 130.3 (q, *J* = 32.6 Hz), 129.9, 128.8, 128.7, 127.8, 125.7, 125.5, 125.2, 124.5 (q, *J* = 3.7 Hz), 124.4, 124.2 (q, *J* = 272.1 Hz), 120.5 (q, *J* = 281.9 Hz), 114.6, 113.6 (q, *J* = 34.7 Hz), 90.8, 89.4, 85.2, 65.2, 62.9, 56.8, 47.2, 28.1.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 2981, 1788, 1740, 1606, 1329, 1151, 1073, 767.

**HRMS** (ESI) for C<sub>40</sub>H<sub>29</sub>F<sub>6</sub>NO<sub>6</sub>Na, [M+Na]<sup>+</sup> (756.1791) found: 756.1790.

**tert-Butyl (2'*R*,3*R*,3a'*S*,3b'*R*,8b'*S*,9a'*R*)-3a'-(4-formylphenyl)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3ea)**



Following the GP-E, **1e** (35.8 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 48 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ea** was obtained as a yellow solid (42.3 mg, 61%).

R<sub>f</sub> = 0.25 (EtOAc/Hex = 1/5), mp.: 214.7-215.4 °C, [α]<sub>D</sub><sup>25</sup> = 58.9 (*c* = 0.5 in CH<sub>2</sub>Cl<sub>2</sub>),

**HPLC:** 80% ee, Chiralpak IA column, *n*-hexane/EtOH = 95:5, flow rate = 1.00 mL/min, λ = 246 nm, t<sub>minor</sub> = 9.66 min, t<sub>major</sub> = 16.65 min.

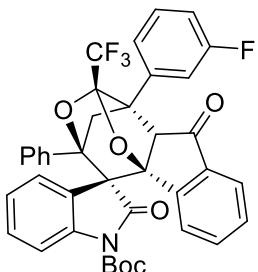
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 10.08 (s, 1H), 8.17 (d, *J* = 7.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.28-7.34 (m, 2H), 7.16-7.20 (m, 1H), 7.09-7.13 (m, 4H), 6.19 (d, *J* = 7.5 Hz, 1H), 4.74 (s, 1H), 3.94 (d, *J* = 12.0 Hz, 1H), 2.84 (d, *J* = 12.4 Hz, 1H), 1.55 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 197.0, 192.0, 172.1, 148.0, 143.5, 140.0, 139.1, 137.3, 135.8, 135.1, 134.9, 131.4, 130.0, 129.8, 128.7, 128.6, 128.4, 127.6, 125.5, 125.4, 125.0, 124.2, 120.3 (q, *J* = 282.0 Hz), 114.4, 113.5 (q, *J* = 34.8 Hz), 90.7, 89.2, 85.1, 65.4, 62.8, 56.7, 47.0, 27.9.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3063, 2983, 2931, 2738, 1786, 1736, 1708, 1608, 1478, 1466, 1391, 1371, 1342, 1312, 1288, 1250, 1186, 1150, 1081, 1033, 1001, 839, 763, 739, 717, 700.

**HRMS** (ESI) for  $C_{40}H_{30}NO_7NaF_3$ ,  $[M+Na]^+$  (716.1867) found: 716.1873.

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-3a'-(3-fluorophenyl)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-b]indeno[2,1-d]furan]-1-carboxylate (3fa)**



Following the GP-E, **1f** (34.8 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 24 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3fa** was obtained as a yellow solid (48.4 mg, 68%).

$R_f = 0.47$  (EtOAc/Hex = 1/5), mp.: 156.0-157.2 °C,  $[\alpha]_D^{25} = 50.6$  ( $c = 0.5$  in  $CH_2Cl_2$ ),

**HPLC:** 77% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 99:1, flow rate = 0.80 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 7.90$  min,  $t_{\text{major}} = 19.01$  min.

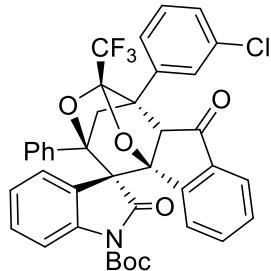
**<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ , 25 °C)  $\delta$ /ppm: 8.18 (dd,  $J = 7.5, 1.0$  Hz, 1H), 7.76 (d,  $J = 7.5$  Hz, 1H), 7.58 (d,  $J = 8.0$  Hz, 1H), 7.46 (td,  $J = 7.5, 0.8$  Hz, 1H), 7.36-7.43 (m, 4H), 7.31 (td,  $J = 7.5, 1.3$  Hz, 1H), 7.28 (td,  $J = 7.5, 1.2$  Hz, 1H), 7.15-7.19 (m, 1H), 7.08-7.14 (m, 5H), 6.17 (d,  $J = 7.8$  Hz, 1H), 4.70 (s, 1H), 3.89 (d,  $J = 11.8$  Hz, 1H), 2.79 (d,  $J = 12.3$  Hz, 1H), 1.54 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz,  $CDCl_3$ , 25 °C)  $\delta$ /ppm: 196.9, 172.2, 163.3, 160.9, 148.0, 143.6, 139.1, 137.4, 135.6, 135.5, 135.3, 134.7, 131.3, 129.7, 129.4, 128.8 (q), 128.7, 128.5, 128.3, 127.6, 125.5, 125.2, 125.00, 124.97, 124.2, 123.2, 120.4 (q,  $J = 281.9$  Hz), 116.7, 116.5, 115.1, 114.9, 114.3, 113.4 (q,  $J = 34.6$  Hz), 90.5, 89.1, 85.0, 64.9, 62.8, 56.7, 47.0, 27.9.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 2983, 2935, 1786, 1736, 1606, 1591, 1478, 1466, 1393, 1371, 1342, 1311, 1289, 1251, 1203, 1176, 1150, 1084, 1033, 763, 702.

**HRMS** (ESI) for  $C_{39}H_{29}NO_6F_4Na$ ,  $[M+Na]^+$  (706.1823) found: 706.1824.

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-3a'-(3-chlorophenyl)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-b]indeno[2,1-d]furan]-1-carboxylate (3ga)**



Following the GP-E, **1g** (36.5 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 12 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ga** was obtained as a yellow solid (46.2 mg, 66%).

$R_f = 0.50$  (EtOAc/Hex = 1/5), mp.: 151.3-152.5 °C,  $[\alpha]_D^{25} = 47.5$  ( $c = 0.5$  in CH<sub>2</sub>Cl<sub>2</sub>), **HPLC:** 80% ee, Chiralpak IA column, *n*-hexane/EtOH = 98:2, flow rate = 0.7 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 7.81$  min,  $t_{\text{major}} = 10.46$  min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 8.17 (d,  $J = 7.7$ , 0.9 Hz, 1H), 7.77 (d,  $J = 7.6$  Hz, 1H), 7.58 (d,  $J = 8.1$  Hz, 1H), 7.62 (s, 1H), 7.58 (d,  $J = 8.1$  Hz, 1H), 7.31 (td,  $J = 7.5$ , 0.8 Hz, 1H), 7.35-7.41 (m, 3H), 7.26-7.33 (m, 2H), 7.15-7.20 (m, 1H), 7.08-7.14 (m, 4H), 6.17 (d,  $J = 7.7$  Hz, 1H), 4.69 (s, 1H), 3.88 (d,  $J = 11.9$  Hz, 1H), 2.79 (d,  $J = 12.3$  Hz, 1H), 1.54 (s, 9H).

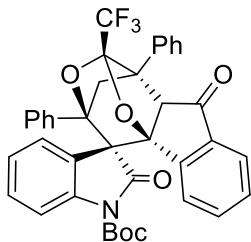
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 197.0, 172.1, 148.0, 143.6, 139.1, 137.4, 135.2, 135.1, 134.7, 133.5, 131.3, 129.7, 129.2, 128.9, 128.7, 128.5, 128.2, 128.0, 127.8, 127.6, 125.5, 125.0, 125.0, 124.2, 120.3 (q,  $J = 282.1$  Hz), 114.4, 113.4 (q,  $J = 34.6$  Hz), 90.5, 89.2, 85.2, 85.0, 84.8, 64.8, 62.7, 56.7, 46.9, 28.0.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3062, 2982, 2934, 1786, 1736, 1603, 1479, 1466, 1393, 1371, 1342, 1312, 1289, 1255, 1203, 1187, 1150, 1080, 1050, 1034, 1002, 763, 741, 701, 615.

**HRMS** (ESI) for C<sub>39</sub>H<sub>29</sub>NO<sub>6</sub>F<sub>3</sub>Na<sup>35</sup>Cl, [M+Na]<sup>+</sup> (722.1528) found: 722.1525.

**HRMS** (ESI) for C<sub>39</sub>H<sub>29</sub>NO<sub>6</sub>F<sub>3</sub>Na<sup>37</sup>Cl, [M+Na]<sup>+</sup> (724.1498) found: 724.1511.

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-2,4'-dioxo-2',3a'-diphenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3ha)**



Following the GP-E, **1h** (33.0 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 15 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ha** was obtained as a yellow solid (45.8 mg, 66%).

$R_f = 0.50$  (EtOAc/Hex = 1/5), mp.: 144.5-144.8 °C,  $[\alpha]_D^{25} = 50.1$  ( $c = 0.5$  in CH<sub>2</sub>Cl<sub>2</sub>),

**HPLC:** 80% ee, Chiralpak IA column, *n*-hexane/EtOH = 98:2, flow rate = 0.80 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 7.09$  min,  $t_{\text{major}} = 10.58$  min.

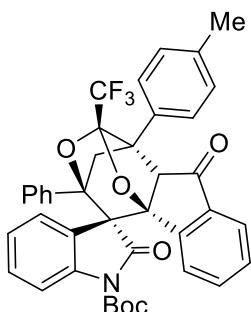
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta/\text{ppm}$ : 8.20 (d,  $J = 7.4$  Hz, 1H), 7.75 (d,  $J = 7.5$  Hz, 1H), 7.62 (d,  $J = 7.2$  Hz, 2H), 7.58 (d,  $J = 8.0$  Hz, 1H), 7.36-7.46 (m, 5H), 7.25-7.33 (m, 2H), 7.08-7.17 (m, 5H), 6.17 (d,  $J = 7.9$  Hz, 1H), 4.70 (s, 1H), 3.88 (d,  $J = 12.4$ , 1H), 2.85 (d,  $J = 12.0$ , 1H), 1.54 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta/\text{ppm}$ : 197.1, 172.2, 148.0, 143.7, 139.1, 137.5, 135.5, 134.6, 132.9, 131.2, 129.6, 129.3 (q,  $J = 2.0$  Hz), 128.8, 128.4, 128.2, 128.1, 127.9, 127.7, 127.5, 127.4, 125.6, 125.5, 124.9, 124.7, 120.4 (q,  $J = 281.9$  Hz), 114.3, 113.5 (q,  $J = 34.5$  Hz), 90.5, 89.1, 84.9, 65.1, 62.9, 56.7, 46.8, 28.0.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3062, 2982, 2934, 1786, 1736, 1605, 1478, 1466, 1392, 1371, 1342, 1311, 1289, 1255, 1204, 1183, 1150, 1080, 1034, 840, 757.

**HRMS** (ESI) for C<sub>39</sub>H<sub>30</sub>NO<sub>6</sub>F<sub>3</sub>Na, [M+Na]<sup>+</sup> (688.1917) found: 688.1915.

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-2,4'-dioxo-2'-phenyl-3a'-(*p*-tolyl)-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8*b*]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3ia)**



Following the GP-E, **1i** (34.4 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 6 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ia** was obtained as a white solid (54.4 mg, 80%).

$R_f = 0.50$  (EtOAc/Hex = 1/5), mp.: 187.9–188.8 °C,  $[\alpha]_D^{23} = 6.4$  ( $c = 0.5$  in  $\text{CH}_2\text{Cl}_2$ ),

**HPLC:** 80% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.00 mL/min,  $\lambda = 246$  nm,  $t_{\text{minor}} = 4.82$  min,  $t_{\text{major}} = 6.44$  min.

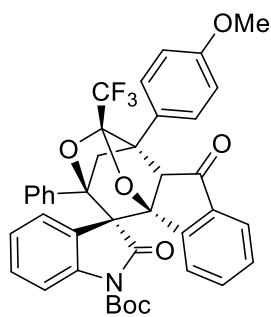
**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 8.19 (dd,  $J = 7.5, 1.3$  Hz, 1H), 7.75 (d,  $J = 7.5$  Hz, 1H), 7.57 (d,  $J = 8.0$  Hz, 1H), 7.49 (d,  $J = 8.1$  Hz, 2H), 7.45 (pt,  $J = 7.6$  Hz, 1H), 7.38 (td,  $J = 7.9, 1.3$  Hz, 1H), 7.32 (d,  $J = 7.7$  Hz, 1H), 7.28 (d,  $J = 7.4$  Hz, 1H), 7.23 (d,  $J = 8.2$  Hz, 2H), 7.20–7.06 (m, 5H), 6.16 (d,  $J = 7.5$  Hz, 1H), 4.65 (s, 1H), 3.85 (d,  $J = 12.1$  Hz, 1H), 2.84 (d,  $J = 12.1$  Hz, 1H), 2.40 (s, 3H), 1.54 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 197.4, 172.4, 148.2, 143.9, 139.3, 137.9, 137.7, 135.7, 134.7, 131.3, 129.9, 129.7, 129.3 (q,  $J = 2.1$  Hz), 129.0, 128.6, 128.4, 127.7, 125.9, 125.7, 125.0, 124.3, 120.7 (q,  $J = 281.6$  Hz), 114.4, 113.7 (q,  $J = 34.4$  Hz), 90.6, 89.2, 85.1, 64.9, 63.1, 56.9, 46.9, 28.1, 21.2.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 2981, 1737, 1606, 1151, 1081, 762.

**HRMS** (ESI) for  $\text{C}_{40}\text{H}_{32}\text{F}_3\text{NO}_6\text{Na}$ ,  $[\text{M}+\text{Na}]^+$  (702.2074) found: 702.2075.

**tert-Butyl (2'*R*,3*R*,3a'*S*,3b'*R*,8b'*S*,9a'*R*)-3a'-(4-methoxyphenyl)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8*b*]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3ja)**



Following the GP-E, **1j** (36.0 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 12 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ja** was obtained as a white solid (56.3 mg, 81%).

$R_f = 0.37$  (EtOAc/Hex = 1/5), mp.: 154.4–155.1 °C,  $[\alpha]_D^{25} = 53.9$  ( $c = 0.5$  in  $\text{CH}_2\text{Cl}_2$ ),

**HPLC:** 84% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 97:3, flow rate = 0.70 mL/min,  $\lambda$  = 246 nm,  $t_{\text{minor}} = 11.75$  min,  $t_{\text{major}} = 14.05$  min.

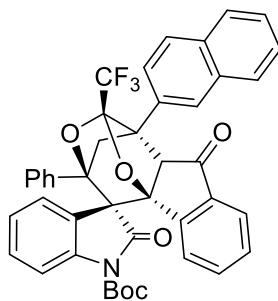
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 8.19 (d,  $J$  = 7.5 Hz, 1H), 7.76 (d,  $J$  = 7.5 Hz, 1H), 7.52-7.58 (m, 3H), 7.45 (t,  $J$  = 7.5 Hz, 1H), 7.37 (td,  $J$  = 7.8, 1.2 Hz, 1H), 7.30 (td,  $J$  = 7.5, 0.8 Hz, 2H), 7.27 (td,  $J$  = 7.5, 0.8 Hz, 1H), 7.08-7.18 (m, 5H), 6.95 (d,  $J$  = 8.9 Hz, 2H), 6.16 (d,  $J$  = 7.9 Hz, 1H), 4.64 (s, 1H), 3.86 (s, 3H), 2.83 (d,  $J$  = 12.1 Hz, 1H), 1.54 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 197.4, 172.3, 159.3, 148.1, 143.8, 139.2, 137.6, 135.6, 134.6, 131.2, 130.6, 129.6, 128.8, 128.4, 127.6, 125.7, 125.6, 124.9, 124.7, 124.2, 120.5 (q,  $J$  = 281.0 Hz), 114.3, 113.4 (q,  $J$  = 37.3 Hz), 90.4, 89.1, 84.9, 64.5, 62.9, 56.8, 55.2, 46.8, 28.0.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3059, 2982, 2934, 2840, 1786, 1739, 1606, 1519, 1479, 1466, 1393, 1371, 1343, 1310, 1290, 1257, 1203, 1183, 1150, 1081, 1034, 1001, 837, 764, 741, 703.

**HRMS** (ESI) for C<sub>40</sub>H<sub>32</sub>NO<sub>7</sub>NaF<sub>3</sub>, [M+Na]<sup>+</sup> (718.2023) found: 718.2026.

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-3a'-(naphthalen-2-yl)-2,4'-dioxo-2'-phenyl-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3ka)**



Following the GP-E, **1k** (38.0 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 15 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3ka** was obtained as a yellow solid (49.1 mg, 70%).

R<sub>f</sub> = 0.45 (EtOAc/Hex = 1/5), mp.: 200.2-200.7 °C,  $[\alpha]_D^{25} = 58.6$  (*c* = 0.5 in CH<sub>2</sub>Cl<sub>2</sub>),

**HPLC:** 84% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 0.70 mL/min,  $\lambda$  = 246 nm,  $t_{\text{minor}} = 7.59$  min,  $t_{\text{major}} = 11.31$  min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$ /ppm: 8.22 (d,  $J$  = 7.5 Hz, 1H), 8.12 (s, 1H), 7.86-7.90 (m, 3H), 7.77 (d,  $J$  = 7.5 Hz, 1H), 7.72 (d,  $J$  = 8.6 Hz, 1H), 7.60 (d,  $J$  = 8.0 Hz, 1H), 7.43-7.52 (m, 3H), 7.38 (td,  $J$  = 7.9, 1.1 Hz, 1H), 7.26-7.34 (m, 2H), 7.10-7.18 (m,

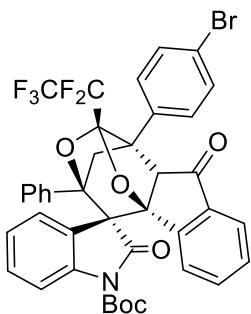
5H), 6.19 (d,  $J$  = 7.9 Hz, 1H), 4.78 (s, 1H), 4.00 (d,  $J$  = 11.9 Hz, 1H), 3.01 (d,  $J$  = 12.3 Hz, 1H), 1.54 (s, 9H).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 197.2, 172.2, 148.1, 143.8, 139.2, 137.5, 135.5, 134.7, 132.9, 132.8, 131.2, 130.8, 129.6, 128.8, 128.5, 128.4, 127.9, 127.8, 127.6, 127.4, 126.4, 126.0, 125.64, 125.58, 125.99, 125.95, 124.2, 120.5 (q,  $J$  = 282.0 Hz), 114.3, 113.5 (q,  $J$  = 34.6 Hz), 90.6, 89.2, 84.9, 65.4, 63.3, 56.8, 47.0, 28.0.

**IR** (KBr)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3059, 2981, 2934, 1786, 1736, 1605, 1478, 1466, 1393, 1371, 1343, 1311, 1288, 1248, 1203, 1184, 1150, 1079, 1033, 839, 764, 703, 479.

**HRMS** (ESI) for  $\text{C}_{43}\text{H}_{32}\text{NO}_6\text{F}_3\text{Na}$ ,  $[\text{M}+\text{Na}]^+$  (738.2074) found: 738.2070.

**tert-Butyl (2'*R*,3*R*,3a'*S*,3b'*R*,8b'*S*,9a'*R*)-3a'-(4-bromophenyl)-2,4'-dioxo-9a'-(perfluoroethyl)-2'-phenyl-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-*b*]indeno[2,1-*d*]furan]-1-carboxylate (3la)**



Following the GP-E, **1l** (45.9 mg, 0.1 mmol), **2a** (33.5 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 36 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3la** was obtained as a yellow solid (46.2 mg, 59%).

$R_f$  = 0.45 (EtOAc/Hex = 1/5), mp.: 156.1–156.7 °C,  $[\alpha]_D^{25}$  = 51.7 ( $c$  = 0.5 in  $\text{CH}_2\text{Cl}_2$ ),

**HPLC:** 82% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 99:1, flow rate = 1.00 mL/min,  $\lambda$  = 246 nm,  $t_{\text{minor}}$  = 7.19 min,  $t_{\text{major}}$  = 14.29 min.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 8.12 (d,  $J$  = 7.5, 0.8 Hz, 1H), 7.76 (d,  $J$  = 7.6 Hz, 1H), 7.49–7.59 (m, 5H), 7.46 (td,  $J$  = 7.9, 0.7 Hz, 1H), 7.37 (td,  $J$  = 7.5, 1.3 Hz, 1H), 7.26–7.32 (m, 2H), 7.15–7.20 (m, 1H), 7.01–7.11 (m, 4H), 6.15 (d,  $J$  = 7.8 Hz, 1H), 4.68 (s, 1H), 3.86 (d,  $J$  = 11.9 Hz, 1H), 2.77 (d,  $J$  = 11.9 Hz, 1H), 1.55 (s, 9H).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ /ppm: 197.1, 172.2, 148.0, 143.6, 139.1, 137.4, 133.5, 134.8, 132.1, 131.40, 131.36, 131.3, 130.5, 129.7, 128.5, 128.0, 127.6, 125.4, 125.4, 125.39, 125.35, 124.3, 122.4, 118.5 (qt,  $J$  = 291.0 Hz, 33.2 Hz), 114.4, 113.4 (t,  $J$  = 31.7 Hz), 110.4 (tq,  $J$  = 262.7 Hz, 38.0 Hz), 90.8, 89.8, 85.1, 66.6, 62.1, 56.7, 46.1,

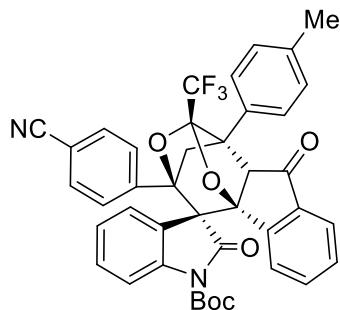
28.0.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 3076, 2980, 2927, 1787, 1736, 1603, 1590, 1478, 1466, 1392, 1371, 1343, 1311, 1289, 1251, 1204, 1176, 1150, 1084, 1033, 1004, 840, 763, 702.

**HRMS** (ESI) for C<sub>40</sub>H<sub>29</sub>NO<sub>6</sub>Na<sup>79</sup>BrF<sub>5</sub>, [M+Na]<sup>+</sup> (816.0991) found: 816.0985.

**HRMS** (ESI) for C<sub>40</sub>H<sub>29</sub>NO<sub>6</sub>Na<sup>81</sup>BrF<sub>5</sub>, [M+Na]<sup>+</sup> (818.0971) found: 818.0957.

**tert-Butyl (2'R,3R,3a'S,3b'R,8b'S,9a'R)-2'-(4-cyanophenyl)-2,4'-dioxo-3a'-(p-tolyl)-9a'-(trifluoromethyl)-2',3',3a',3b',4',9a'-hexahydrospiro[indoline-3,10'-[2,8b]methanofuro[2,3-b]indeno[2,1-d]furan]-1-carboxylate (3id)**



Following the GP-E, **1i** (36.0 mg, 0.1 mmol), **2d** (36.0 mg, 1.0 equiv) and catalyst **QN-T** (5 mol%) were mixed in diethyl ether (0.5 mL) and stirred for 12 hours at 30 °C. After quenching the reaction and purification by flash chromatography (EtOAc/Hex = 1:15), **3id** was obtained as a yellow solid (63.4 mg, 90%).

R<sub>f</sub> = 0.43 (EtOAc/Hex = 1/5), mp.: 217.0-218.2 °C, [α]<sub>D</sub><sup>27</sup> = 45.6 (c = 0.5 in CH<sub>2</sub>Cl<sub>2</sub>),

**HPLC:** 88% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 98:2, flow rate = 1.00 mL/min, λ = 246 nm, t<sub>minor</sub> = 15.27 min, t<sub>major</sub> = 18.41 min.

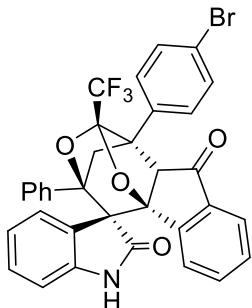
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.16 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.40-7.49 (m, 6H), 7.23-7.35 (m, 6H), 6.14 (d, *J* = 7.9 Hz, 1H), 4.62 (s, 1H), 3.85 (d, *J* = 11.9 Hz, 1H), 2.81 (d, *J* = 11.9 Hz, 1H), 2.40 (s, 3H), 1.56 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 196.7, 171.9, 147.7, 143.3, 140.6, 138.9, 138.1, 137.4, 134.7, 131.4, 130.1, 129.2, 129.1, 128.7, 128.3, 126.5, 125.2, 125.1, 124.9, 124.0, 120.3 (q, *J* = 281.9 Hz), 118.1, 114.5, 113.4 (q, *J* = 34.7 Hz), 112.5, 90.5, 88.5, 85.6, 64.8, 62.7, 56.4, 46.4, 28.0, 21.1.

**IR** (KBr)  $\tilde{\nu}$  (cm<sup>-1</sup>): 2982, 2932, 2231, 1786, 1738, 1605, 1465, 1392, 1371, 1342, 1311, 1288, 1253, 1184, 1149, 1080, 1050, 1029, 1000, 914, 834, 767, 733, 706, 615, 516.

**HRMS** (ESI) for C<sub>41</sub>H<sub>31</sub>N<sub>2</sub>O<sub>6</sub>NaF<sub>3</sub>, [M+Na]<sup>+</sup> (727.2026) found: 727.2032.

**(2'R,3R,3a'S,3b'R,8b'S,9a'R)-3a'-(4-Bromophenyl)-2'-phenyl-9a'-  
(trifluoromethyl)-2',3',3a',9a'-tetrahydrospiro[indoline-3,10'-  
[2,8b]methanofuro[2,3-b]indeno[2,1-d]furan]-2,4'(3b'H)-dione (4aa)**



Following the GP-E, **3aa** (39.5 mg, 0.053 mmol, 80% ee) was dissolved in DCM (0.5 mL) at 30 °C and TFA (4.06 µL, 1.0 equiv) was added. After 24 hours, the mixture was directly subjected to flash chromatography (EtOAc/Hex = 1:6) to afford **4aa** as a white solid (20.5 mg, 60%).

R<sub>f</sub> = 0.70 (EtOAc/Hex = 1/1), mp.: 173.8-174.6 °C, [α]<sub>D</sub><sup>20</sup> = 35.4 (c = 0.5 in CH<sub>2</sub>Cl<sub>2</sub>), **HPLC:** 99% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ = 246 nm, t<sub>minor</sub> = 29.76 min, t<sub>major</sub> = 37.23 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.09 (d, *J* = 7.5 Hz, 1H), 7.83 (brs, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.50-7.56 (m, 2H), 7.46-7.50 (m, 2H), 7.44 (pt, *J* = 7.5 Hz, 1H), 7.29 (pt, *J* = 7.6 Hz, 1H), 7.26 (pt, *J* = 7.0 Hz, 1H), 7.23-7.05 (m, 6H), 6.67 (d, *J* = 7.7 Hz, 1H), 6.16 (d, *J* = 7.7 Hz, 1H), 4.62 (s, 1H), 3.89 (d, *J* = 11.8 Hz, 1H), 2.75 (d, *J* = 11.8 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 197.7, 174.5, 143.9, 139.8, 137.4, 135.9, 134.9, 132.2, 131.4, 131.2 (q, *J* = 2.2 Hz), 130.7, 129.7, 129.5, 128.4, 127.8, 127.3, 126.0, 125.1, 124.3, 123.5, 122.6, 120.6 (q, *J* = 281.9 Hz), 113.6 (q, *J* = 34.5 Hz), 109.6, 90.6, 88.8, 64.9, 62.4, 57.0, 47.2.

**IR** (KBr) ν (cm<sup>-1</sup>): 3276, 3063, 2925, 1716, 1620, 1472, 1327, 1264, 1189, 1077, 1036;

**HRMS** (ESI) for C<sub>34</sub>H<sub>20</sub><sup>79</sup>BrF<sub>3</sub>NO<sub>4</sub>, [M-H]<sup>-</sup> (642.0533) found: 642.0532.

**HRMS** (ESI) for C<sub>34</sub>H<sub>20</sub><sup>81</sup>BrF<sub>3</sub>NO<sub>4</sub>, [M-H]<sup>-</sup> (644.0512) found: 644.0516.

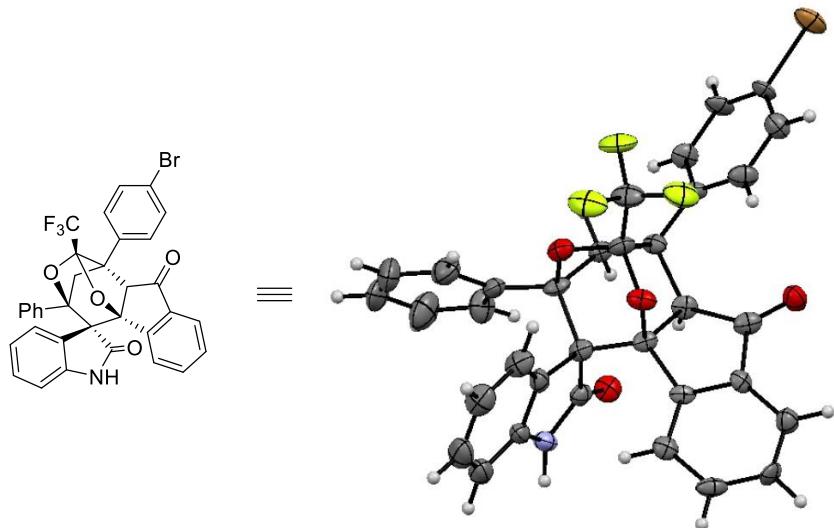
#### IV. References

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- 2 C.-J. Lee, C.-N. Sheu, C.-C. Tsai, Z.-Z. Wu and W. Lin, *Chem. Commun.*, 2014, **50**, 5304.

3. G. Rassu, V. Zambrano, R. Tanca, A. Sartori, L. Battistini, F. Zanardi, C. Curti and G. Casiraghi, *Eur. J. Org. Chem.*, 2012, **2012**, 466.

### V. X-ray crystallographic data for 4aa

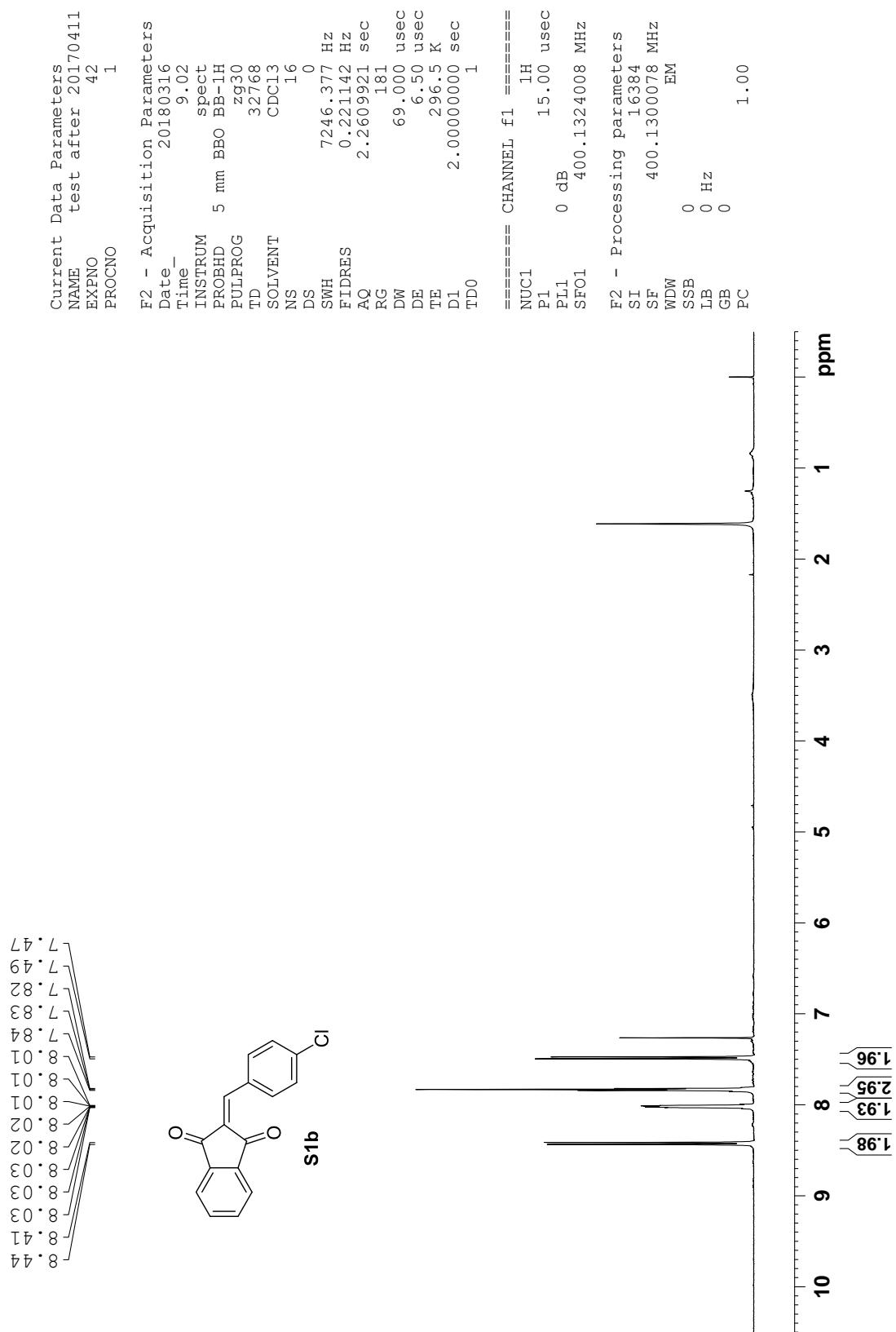
**4aa** (CCDC no. 1528078): The thermal ellipsoid drawn at 30% probability level.

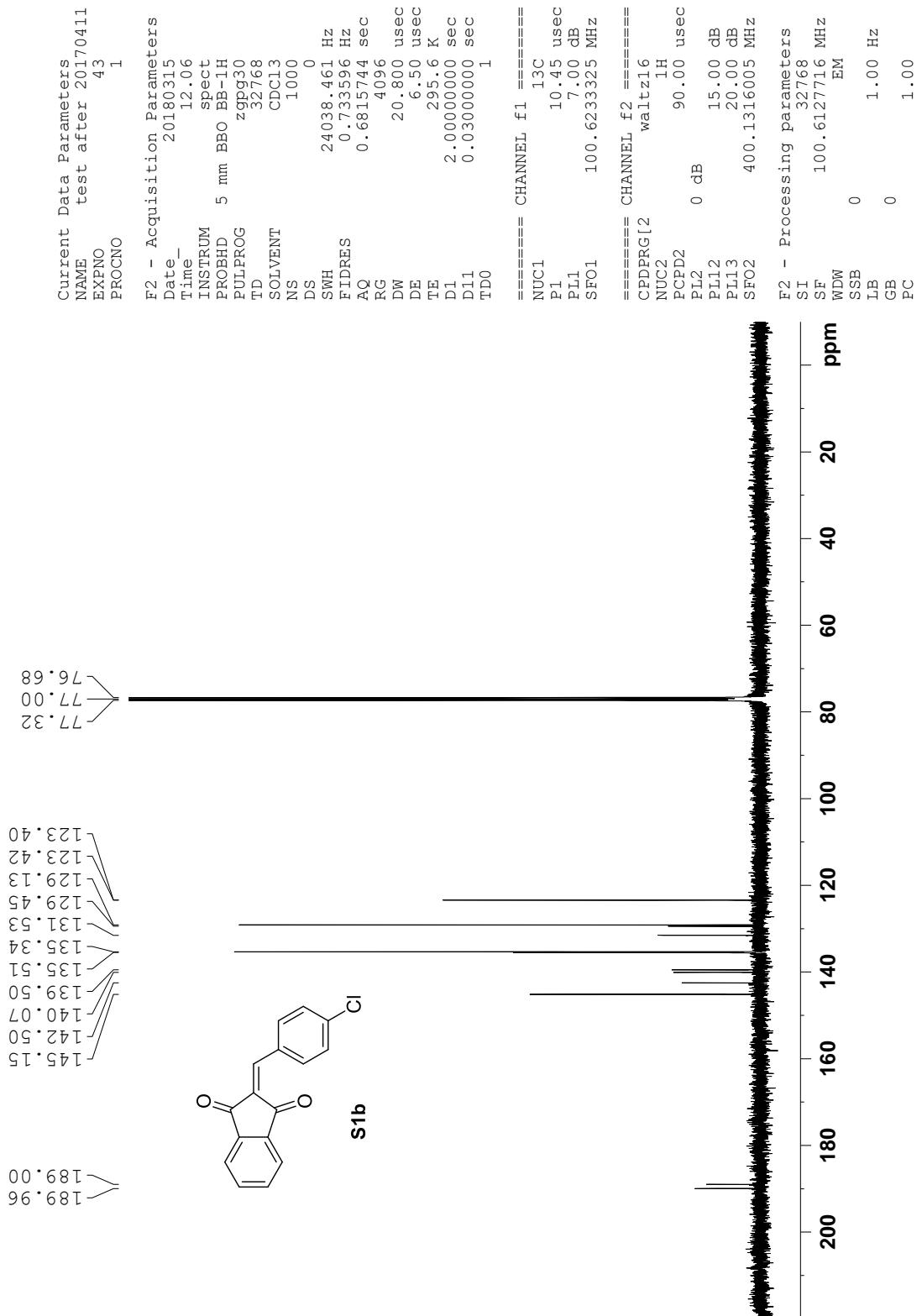


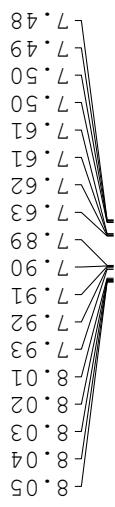
Empirical formula	C34 H21 Br F3 N O4	
Formula weight	644.43	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C 2 2 21	
Unit cell dimensions	a = 13.3813(11) Å	α= 90°.
	b = 16.8878(11) Å	β= 90°.
	c = 27.600(2) Å	γ = 90°.
Volume	6237.0(8) Å³	
Z	8	
Density (calculated)	1.373 Mg/m³	
Absorption coefficient	1.373 mm⁻¹	
F(000)	2608	
Crystal size	0.29 x 0.17 x 0.01 mm³	
Theta range for data collection	2.41 to 25.05°.	
Index ranges	-15<=h<=15, -20<=k<=19, -32<=l<=32	
Reflections collected	43388	
Independent reflections	5508 [R(int) = 0.1148]	

Completeness to theta = 25.05°	99.6 %
Absorption correction	multi-scan
Max. and min. transmission	0.9864 and 0.6915
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5508 / 0 / 388
Goodness-of-fit on F <sup>2</sup>	1.132
Final R indices [I>2sigma(I)]	R1 = 0.0694, wR2 = 0.1358
R indices (all data)	R1 = 0.0859, wR2 = 0.1419
Absolute structure parameter	0.047(13)
Largest diff. peak and hole	0.573 and -0.626 e.Å <sup>-3</sup>

**VI.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra for all new compounds**



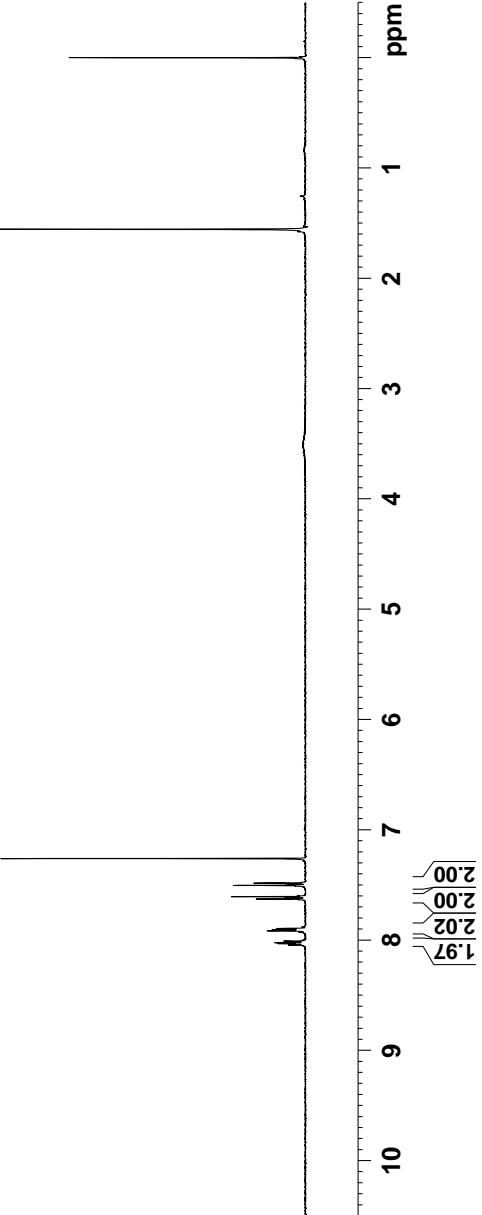


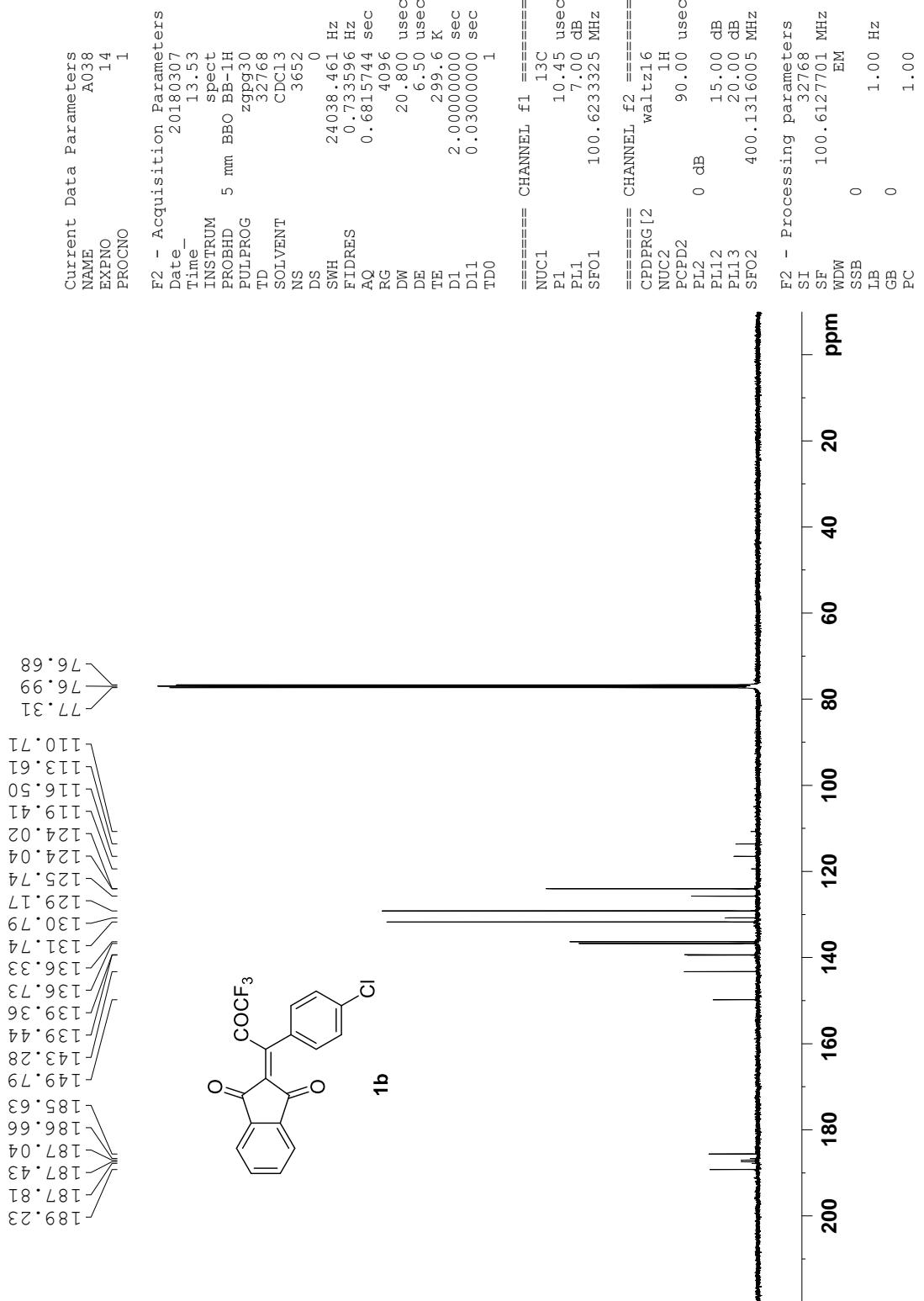


Current Data Parameters  
NAME A038  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date 20160905  
Time 20.46  
INSTRUM spect  
PROBHD BB-1H  
PULPROG zg30  
TD 32768  
SOLVENT CDCl<sub>3</sub>  
NS 16  
DS 0  
SWH 7246.377 Hz  
FIDRES 0.221142 Hz  
AQ 2.2609921 sec  
RG 456.1  
DW 69.000 usec  
DE 6.50 usec  
TE 297.0 K  
D1 2.0000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.40 usec  
PL1 1.80 dB  
SFO1 400.1324008 MHz  
  
F2 - Processing parameters  
SI 16384  
SF 400.1300089 MHz  
WDW EM  
SSB 0  
LB 0 Hz  
GB 0  
PC 1.00





Current Data Parameters

NAME	NH-oxindole
EXPNO	22
PROCNO	1

F2 - Acquisition Parameters

Date	20170206
Time	12.07
INSTRUM	
PROBHD	5 mm BBO BB-1H
PULPROG	Zg30
TD	32768
SOLVENT	CDC13
NS	8
DS	0
SWH	7246.377 Hz
FIDRES	0.221142 Hz
AQ	2.2609921 sec
RG	114
DW	69.000 usec
DE	6.50 usec
TE	296.9 K
DI	2.0000000 sec
TD0	1

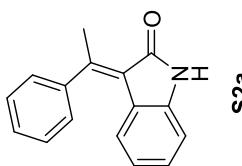
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NUC1	1H
P1	14.40 usec
PL1	1.80 dB
SFO1	400.1324008 MHz

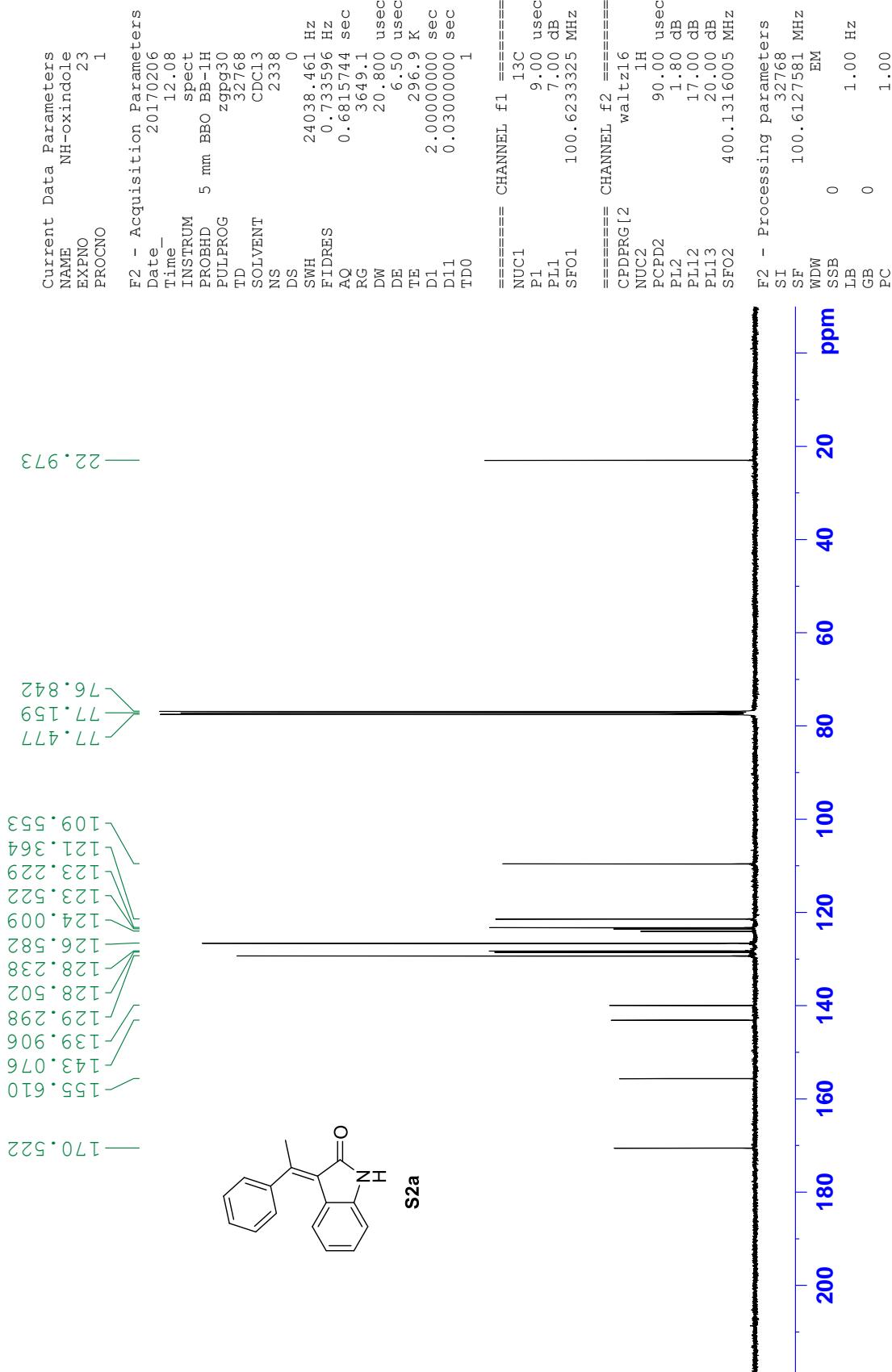
F2 - Processing parameters

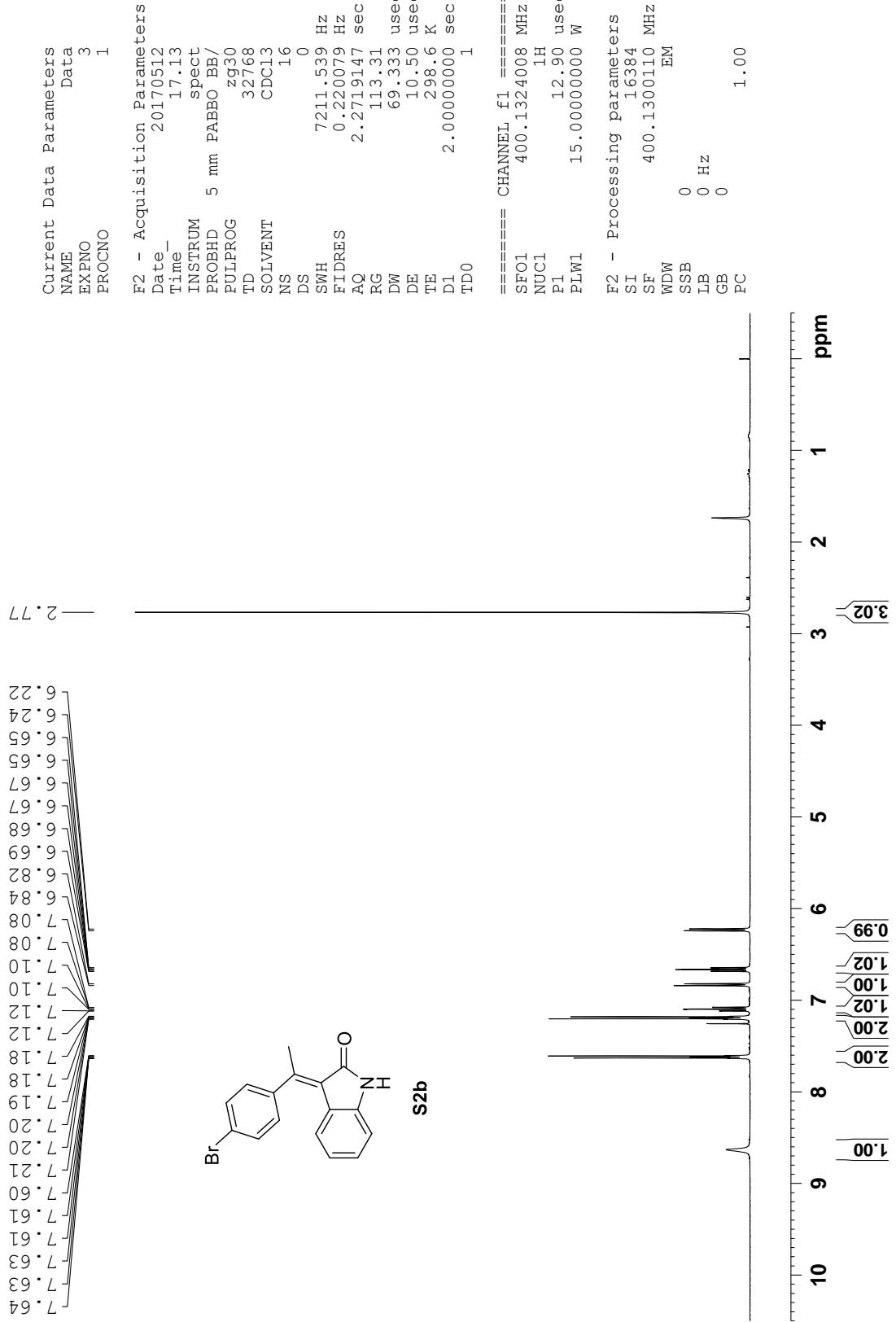
SI	16384
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WDW	EM
SSB	0
LB	0 Hz
GB	0
PC	1.00

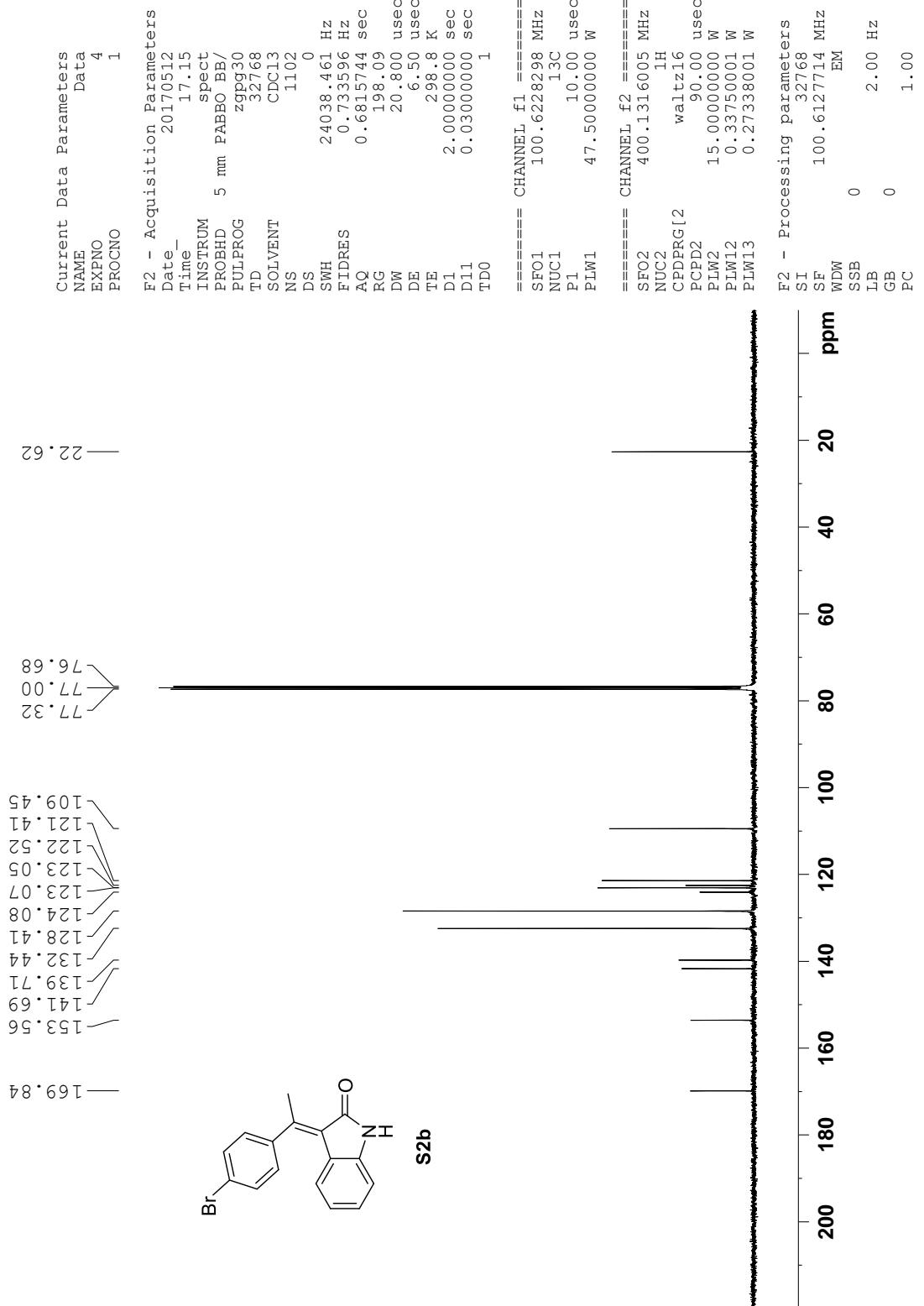
**S2a**



S2a







9.07 —  
7.47 —  
7.26 —  
7.12 —  
7.08 —  
7.04 —  
7.00 —  
6.86 —  
6.68 —  
6.64 —  
6.60 —  
6.22 —

— 2.77 —

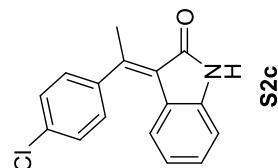
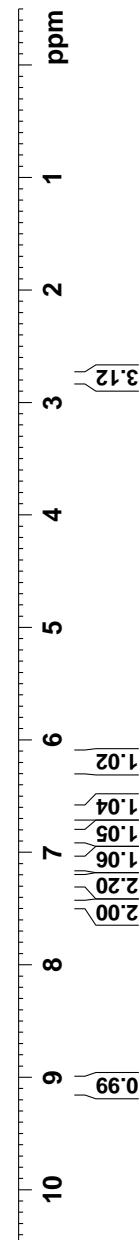
Current Data Parameters  
NAME A173  
EXPNO 14  
PROCNO 1

F2 - Acquisition Parameters

Date 20180314  
Time 18.00  
INSTRUM spect  
PROBHD 5 mm BBO BB-1H  
PULPROG zg30  
TD 32768  
SOLVENT CDCl3  
NS 16  
DS 0  
SWH 7246.377 Hz  
FIDRES 0.2221142 Hz  
AQ 2.2609921 sec  
RG 114  
DW 69.000 usec  
DE 6.50 usec  
TE 295.2 K  
D1 2.0000000 sec  
TDO 1

===== CHANNEL f1 =====

NUC1 1H  
P1 15.00 usec  
PL1 0 dB  
SFO1 400.1324008 MHz  
SI 16384  
SF 400.1300118 MHz  
WDW EM  
SSB 0  
LB 0 Hz  
GB 0  
PC 1.00



— 22.68 —

Current Data Parameters  
NAME A173  
EXPNO 15  
PROCNO 1

F2 - Acquisition Parameters  
Date 20180314  
Time 18.01  
INSTRUM spect  
PROBHD 5 mm BBO BB-1H  
PULPROG zgpp30  
TD 32768

SOLVENT CDC13  
NS 1640  
DS 0  
SWH 24038.461 Hz  
ETDRES 0.73596 Hz  
AQ 0.6815744 sec

RG 4096  
DW 20.800 usec  
DE 6.50 usec  
TE 295.2 K  
D1 2.0000000 sec  
D11 0.03000000 sec  
TDO 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 10.45 usec  
PL1 7.00 dB  
SFO1 100.6233325 MHz

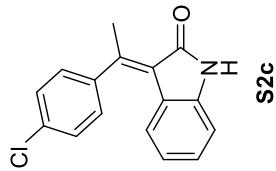
===== CHANNEL f2 =====  
CPDPG[2] waitz16  
NUC2 1H  
PCPD2 90.00 usec  
PL2 0 dB  
PL1.2 15.00 dB  
PL1.3 20.00 dB  
SFO2 400.1316005 MHz

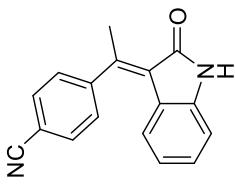
F2 - Processing parameters  
SI 32768  
SF 100.6127731 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.00

— 77.32 —

109.54  
121.36  
123.02  
124.23  
128.13  
128.40  
129.47  
134.38  
139.80  
141.19  
153.66

— 170.10 —



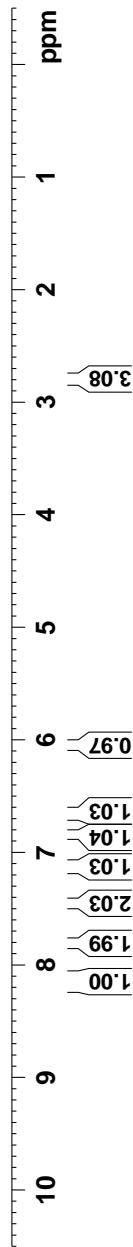


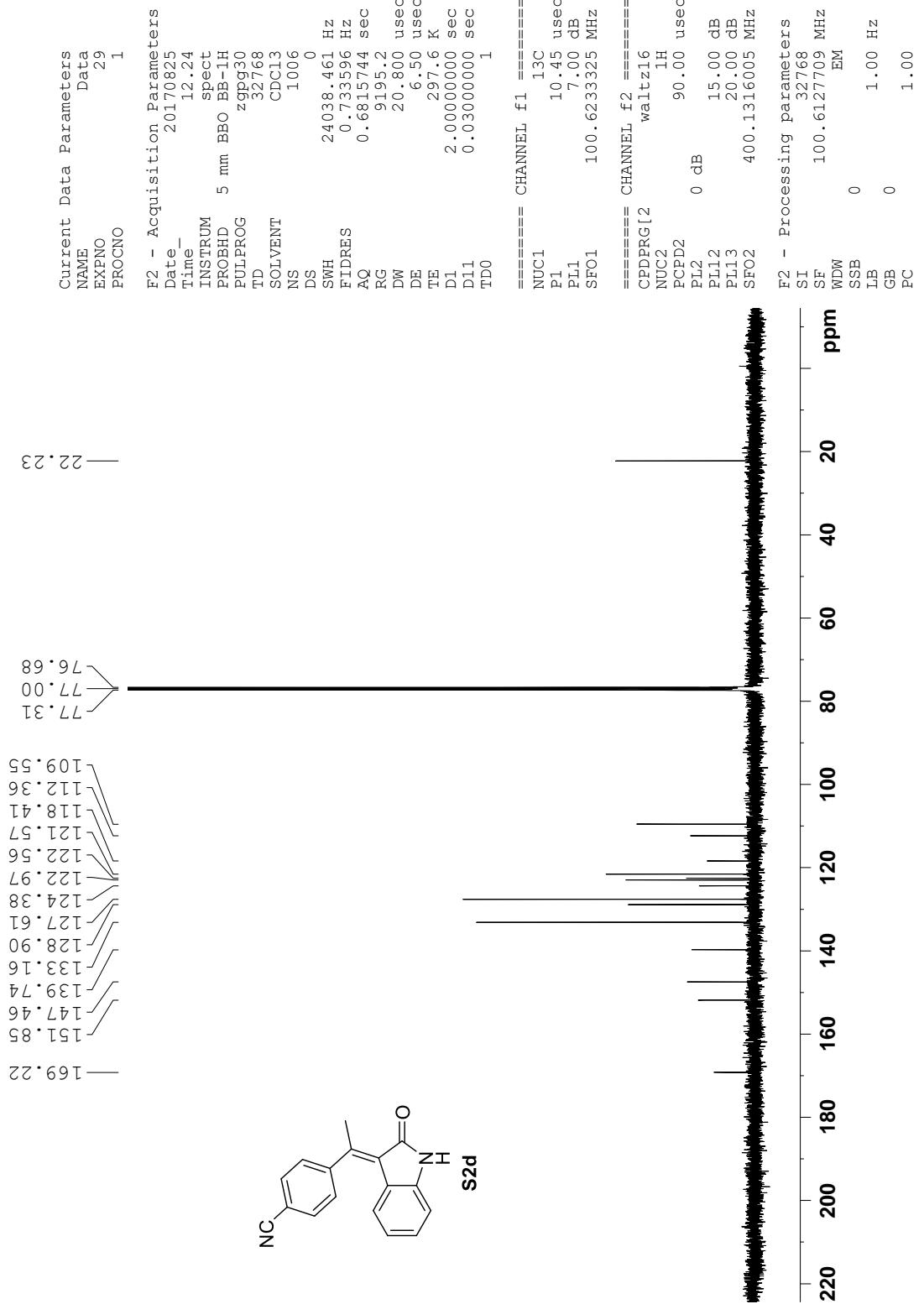
2.78

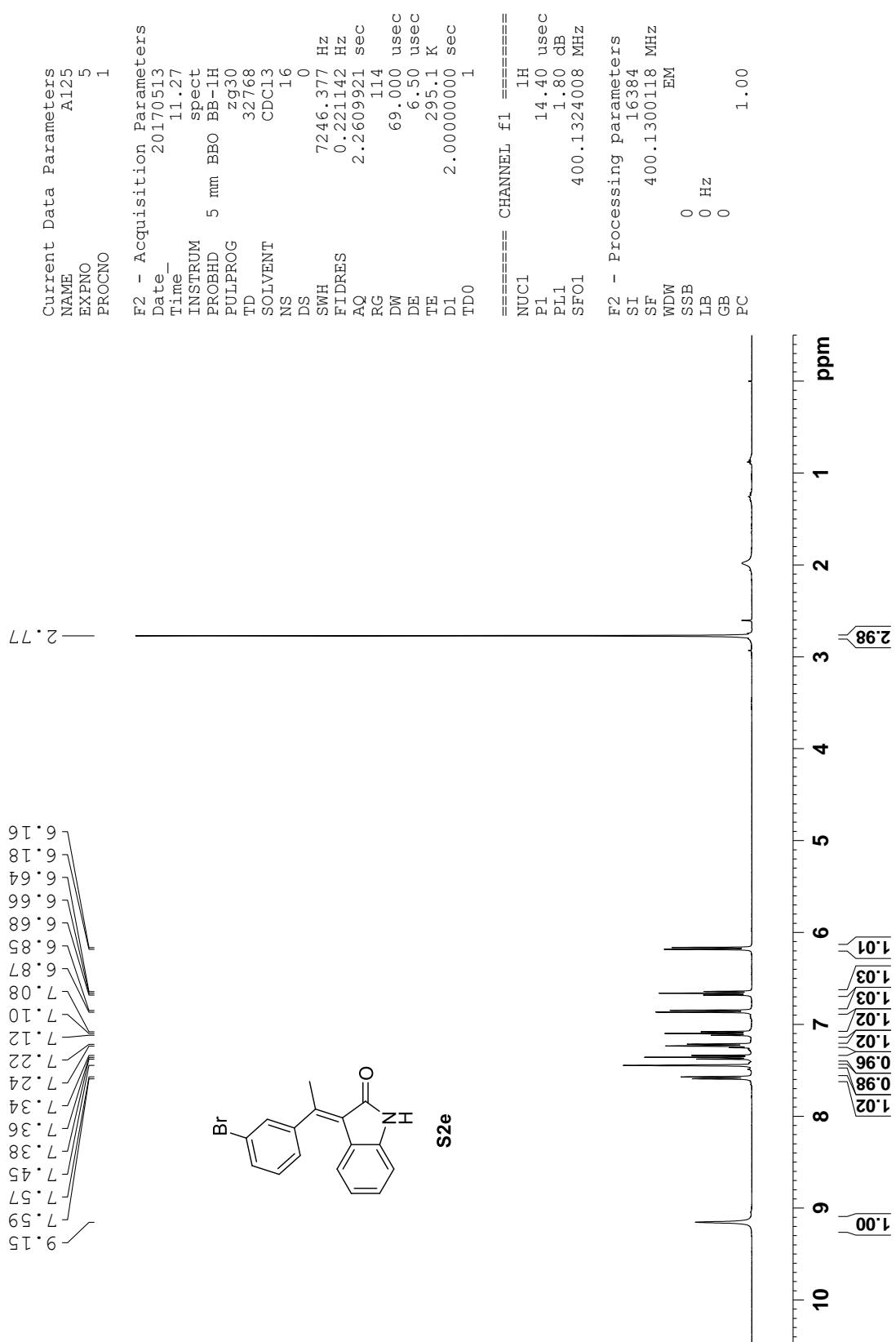
Current Data Parameters  
NAME A187  
EXPNO 8  
PROCNO 1

F2 - Acquisition Parameters  
Date 20180131  
Time 18.05  
INSTRUM spect  
PROBHD 5 mm BBO BB-1H  
PULPROG zg30  
TD 32768  
SOLVENT CDCl3  
NS 16  
DS 0  
SWH 7246.377 Hz  
FIDRES 0.221142 Hz  
AQ 2.260921 sec  
RG 114  
DW 69.000 usec  
DE 6.50 usec  
TE 294.6 K  
D1 2.0000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.00 usec  
PL1 0 dB  
SF01 400.1324008 MHz  
F2 - Processing parameters  
SI 16384  
SF 400.1300078 MHz  
WDW EM  
SSB 0  
LB 0 Hz  
GB 0  
PC 1.00

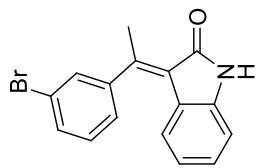






— 22.56 —  
 — 77.32 —  
 — 76.68 —

109.57  
 121.44  
 122.90  
 123.09  
 124.33  
 125.22  
 128.49  
 129.46  
 130.83  
 131.40  
 139.88  
 144.78  
 152.96  
 170.06



**S2e**

```

Current Data Parameters
NAME          Data
EXPNO        10
PROCNO       1

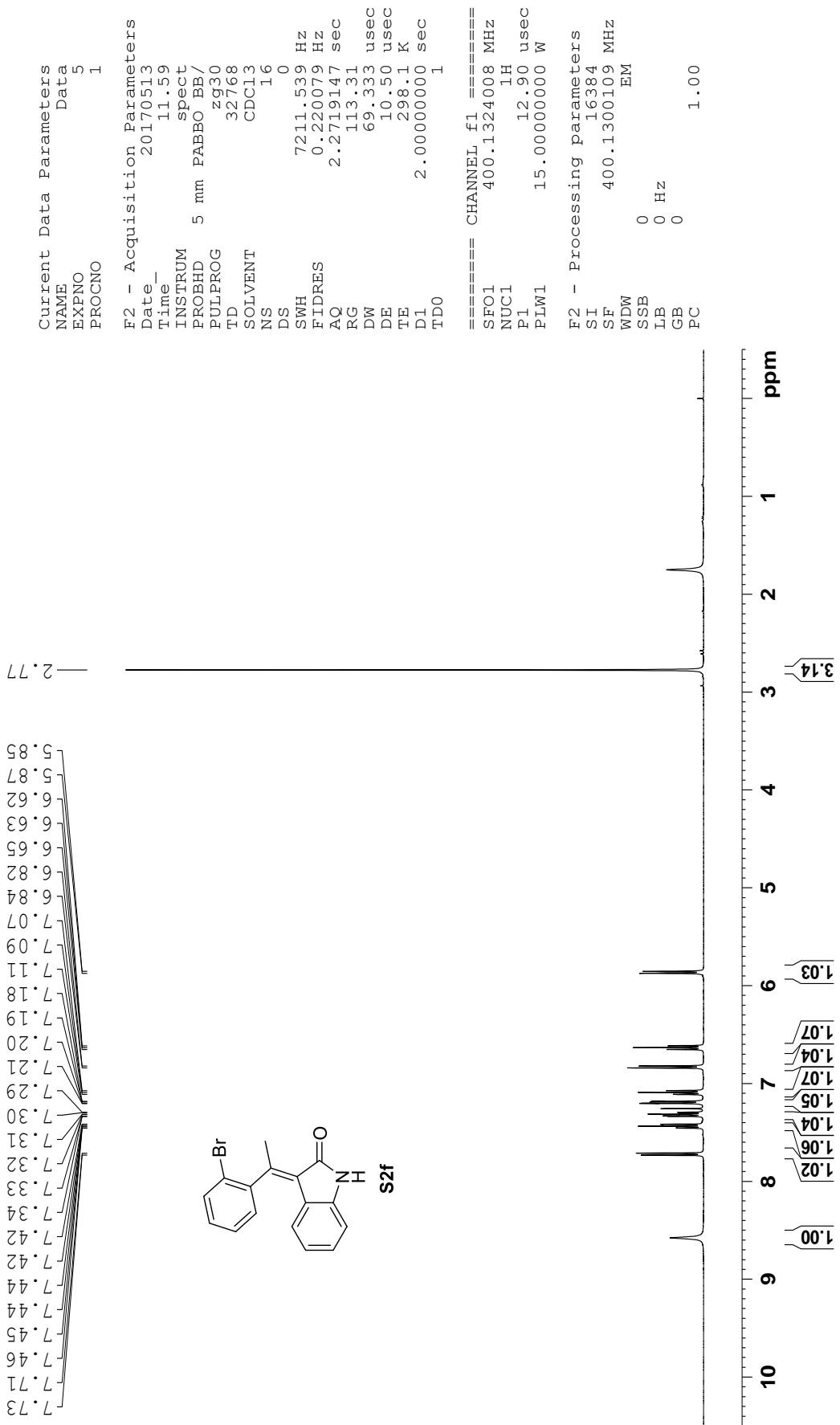
F2 - Acquisition Parameters
Date_        20170516
Time_        17.05
INSTRUM     spect
PROBHD      5 mm PABBO BB/
PULPROG    zgpg30
TD          32768
SOLVENT      CDCl3
NS           41
DS            0
SWH         24038.461 Hz
FIDRES     0.73596 Hz
AQ          0.6815744 sec
RG          198.09
DW          20.800 usec
DE          6.50 usec
TE          298.7 K
D1          2.0000000 sec
D11         0.03000000 sec
TD0          1

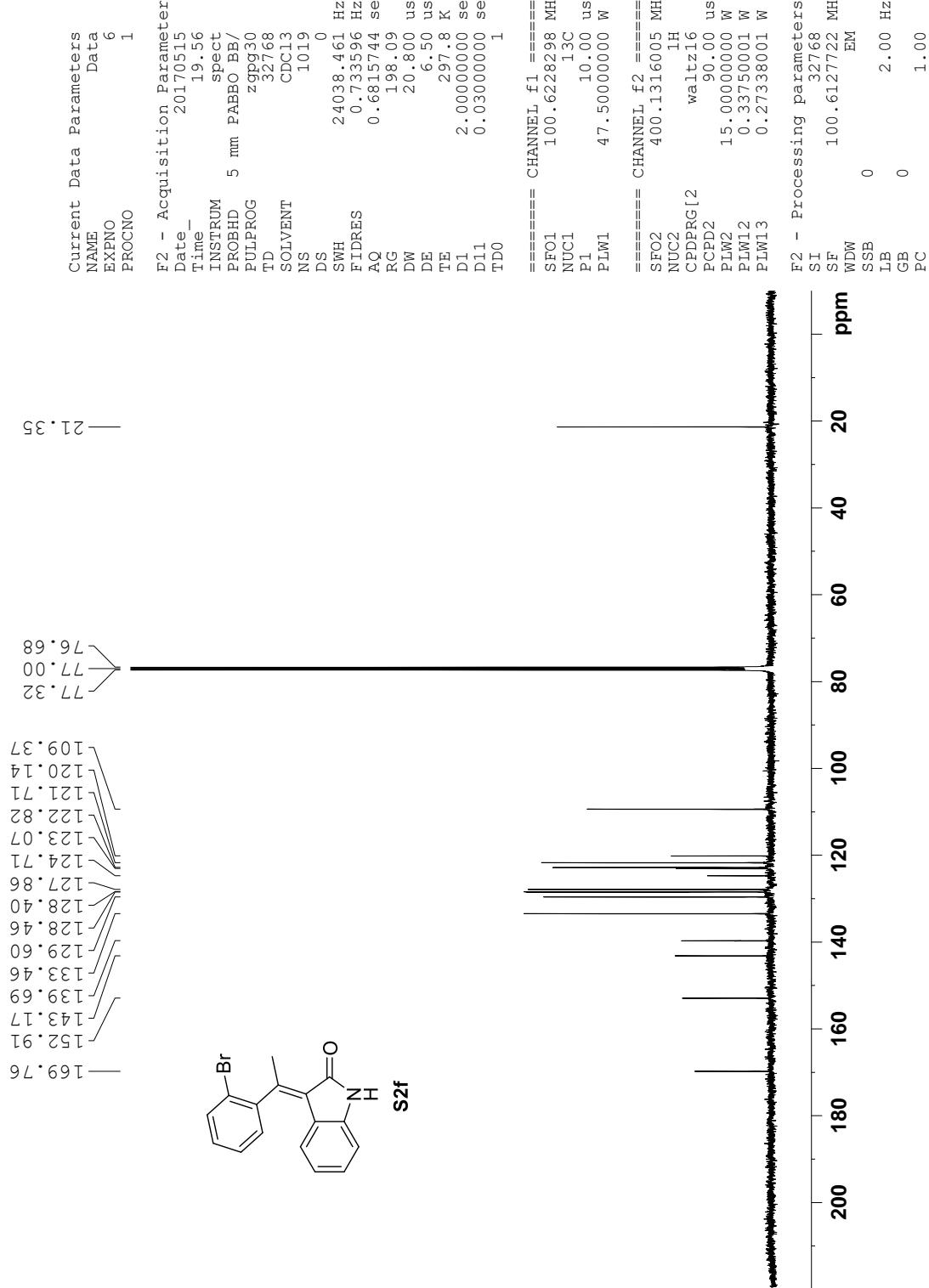
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CHANNEL f1
SFO1        100.6228298 MHz
NUC1         13C
P1          10.00 usec
PLW1        47.5000000 W

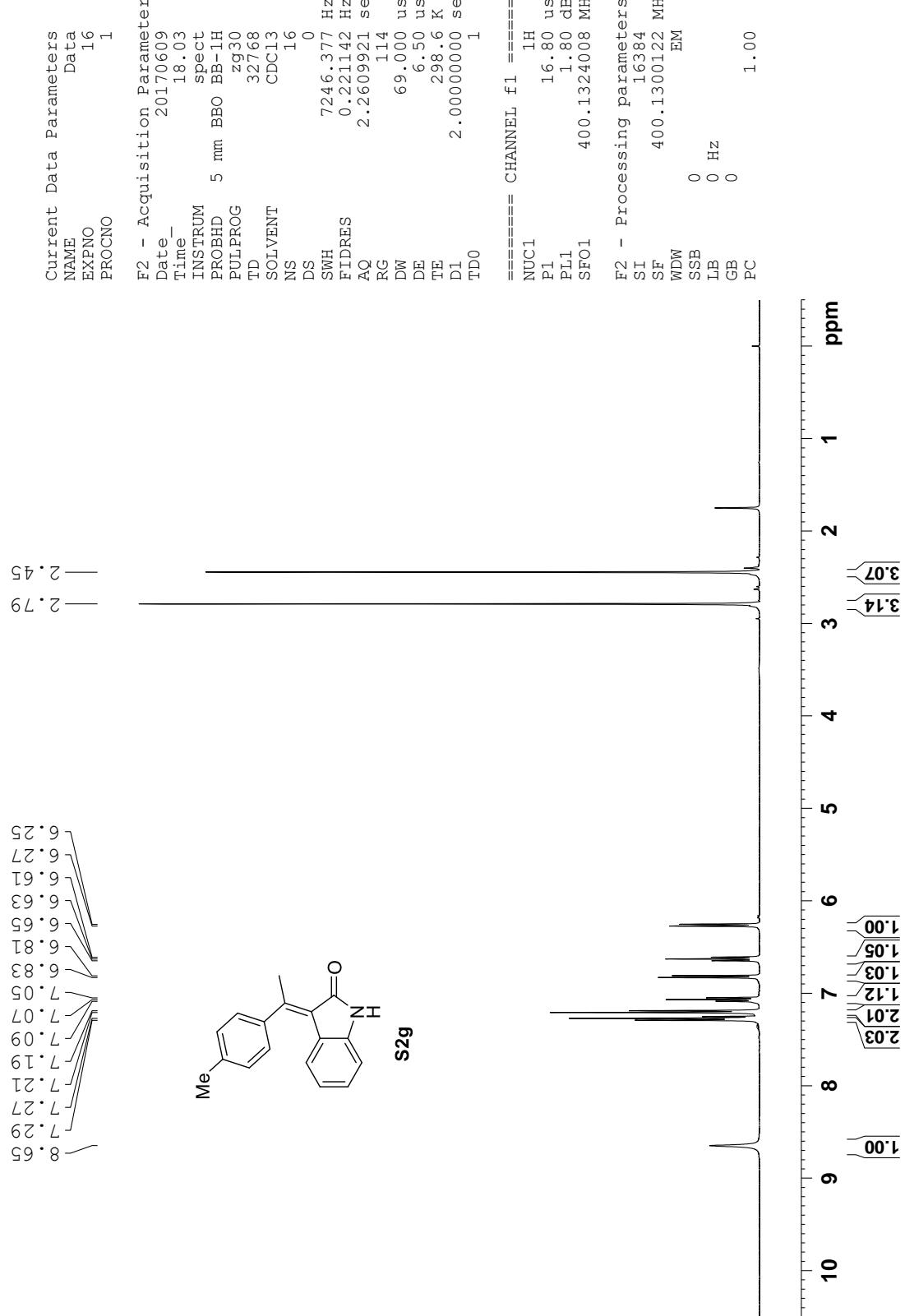
=====
CHANNEL f2
SFO2        400.1316005 MHz
NUC2         1H
CPDPRG[2]   waltz16
PCPD2       90.00 usec
PLW2        15.00000000 W
PLW12      0.33750001 W
PLW13      0.27338001 W

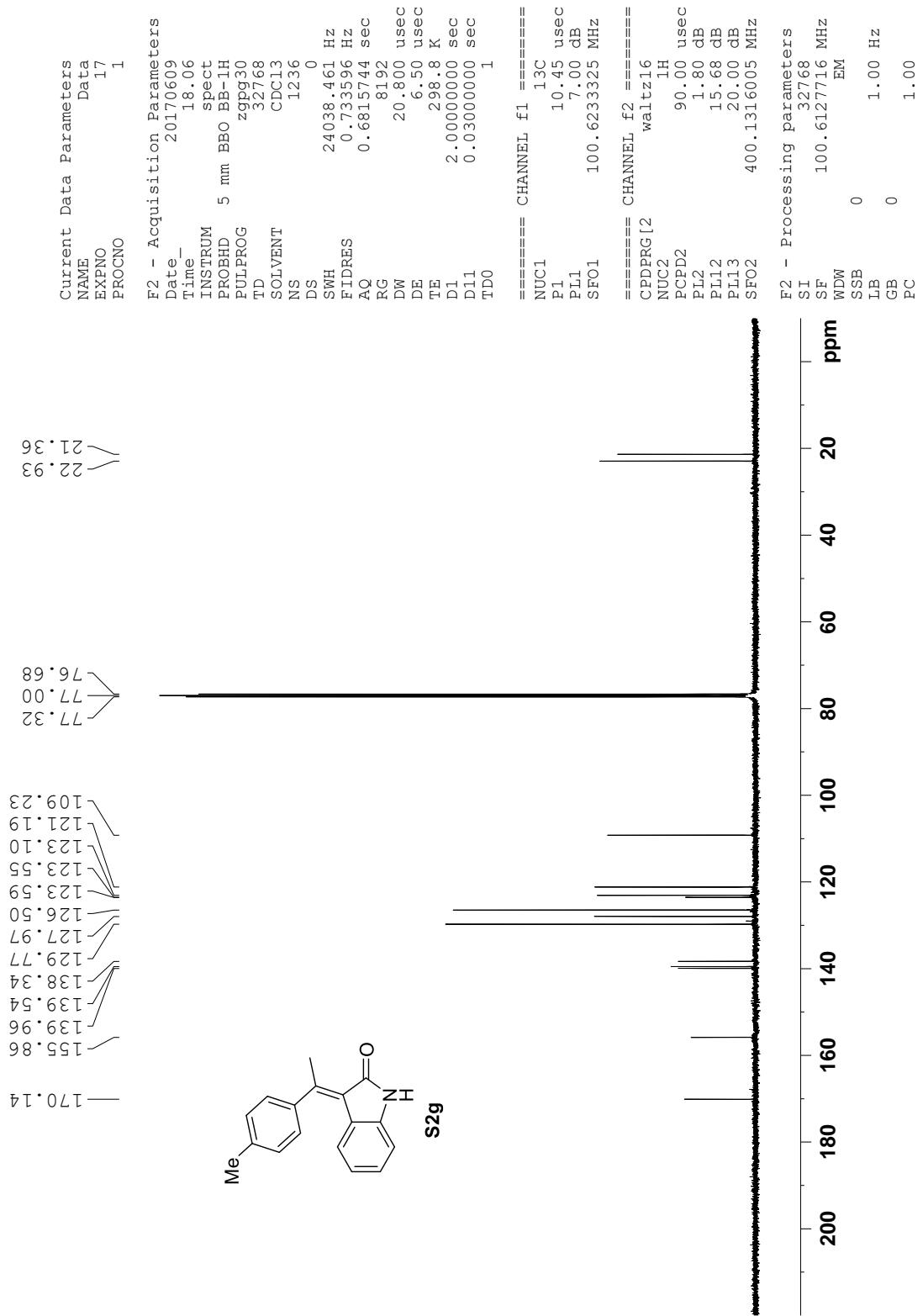
F2 - Processing parameters
SI            32768
SF          100.6127744 MHz
WDW           EM
SSB           0
LB            2.00 Hz
GB           0
PC           1.00

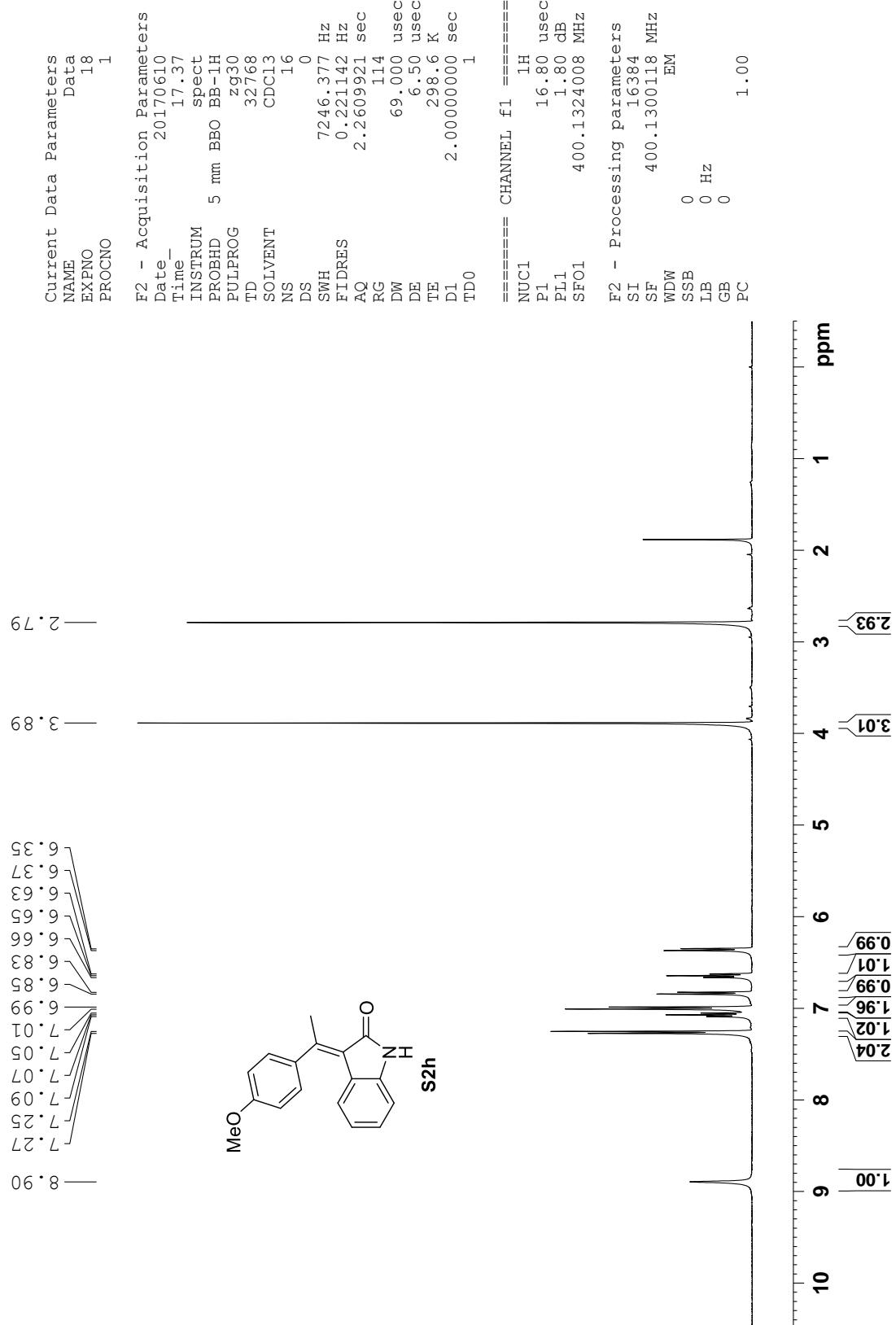
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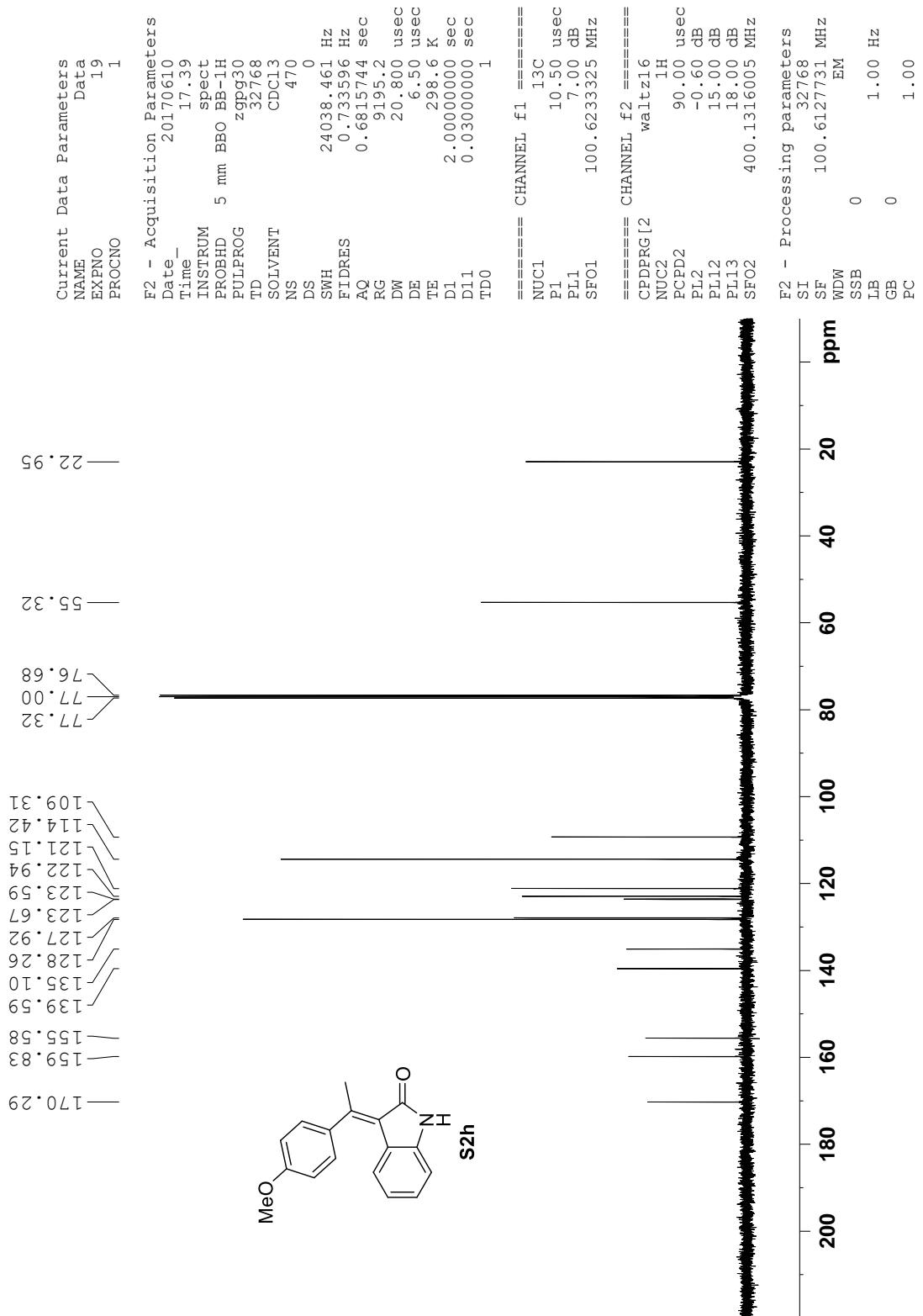






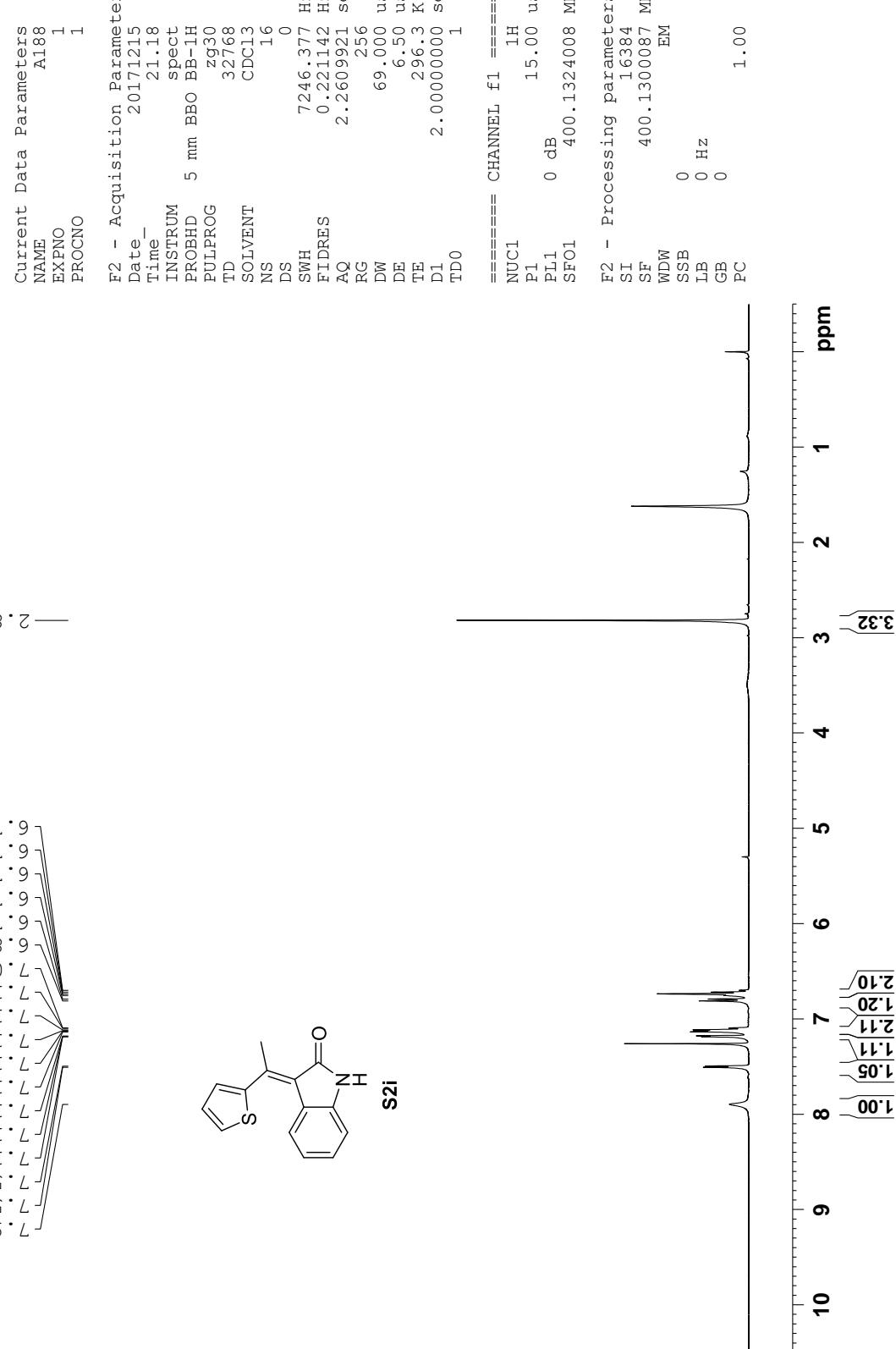


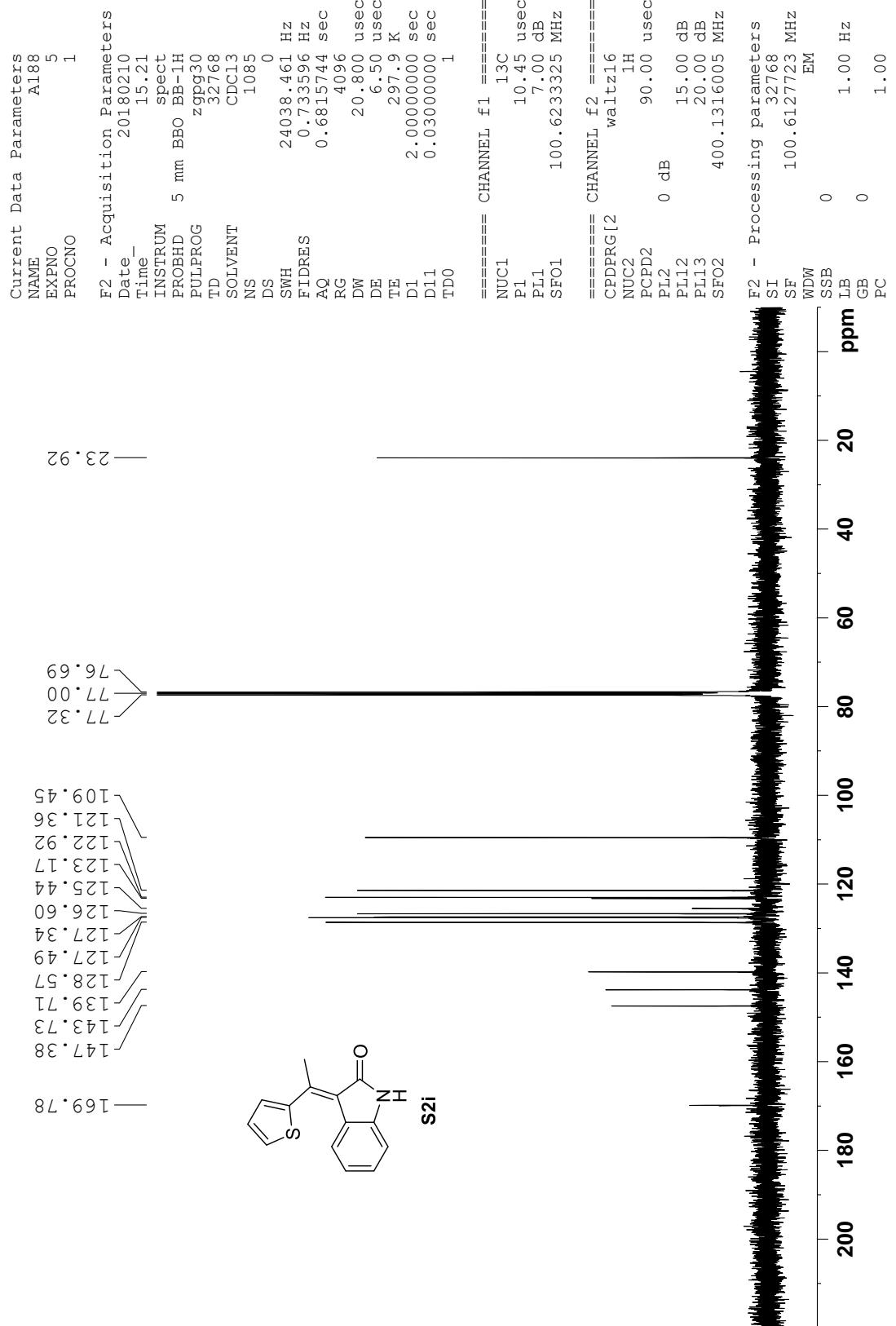


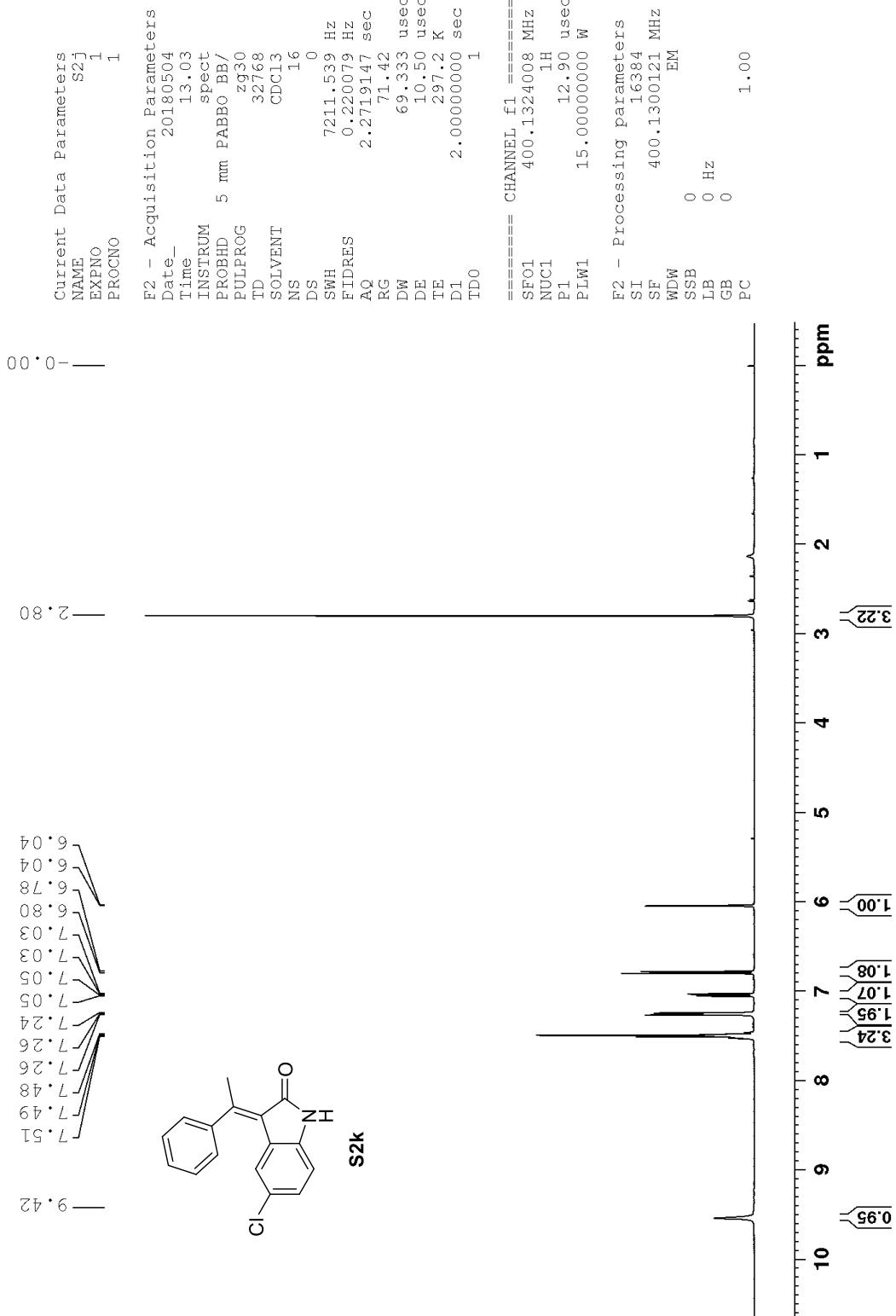


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 6.96  
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 7.94  
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 8.52  
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 8.84  
 8.86  
 8.88  
 8.90  
 8.92  
 8.94  
 8.96  
 8.98  
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 9.02  
 9.04  
 9.06  
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 9.42  
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 9.80  
 9.82  
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 10.00

— 2.82 —

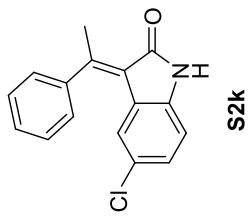






— 22.93 —

157.61  
142.19  
138.21  
129.30  
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110.35  
77.32  
76.68



— 170.23 —

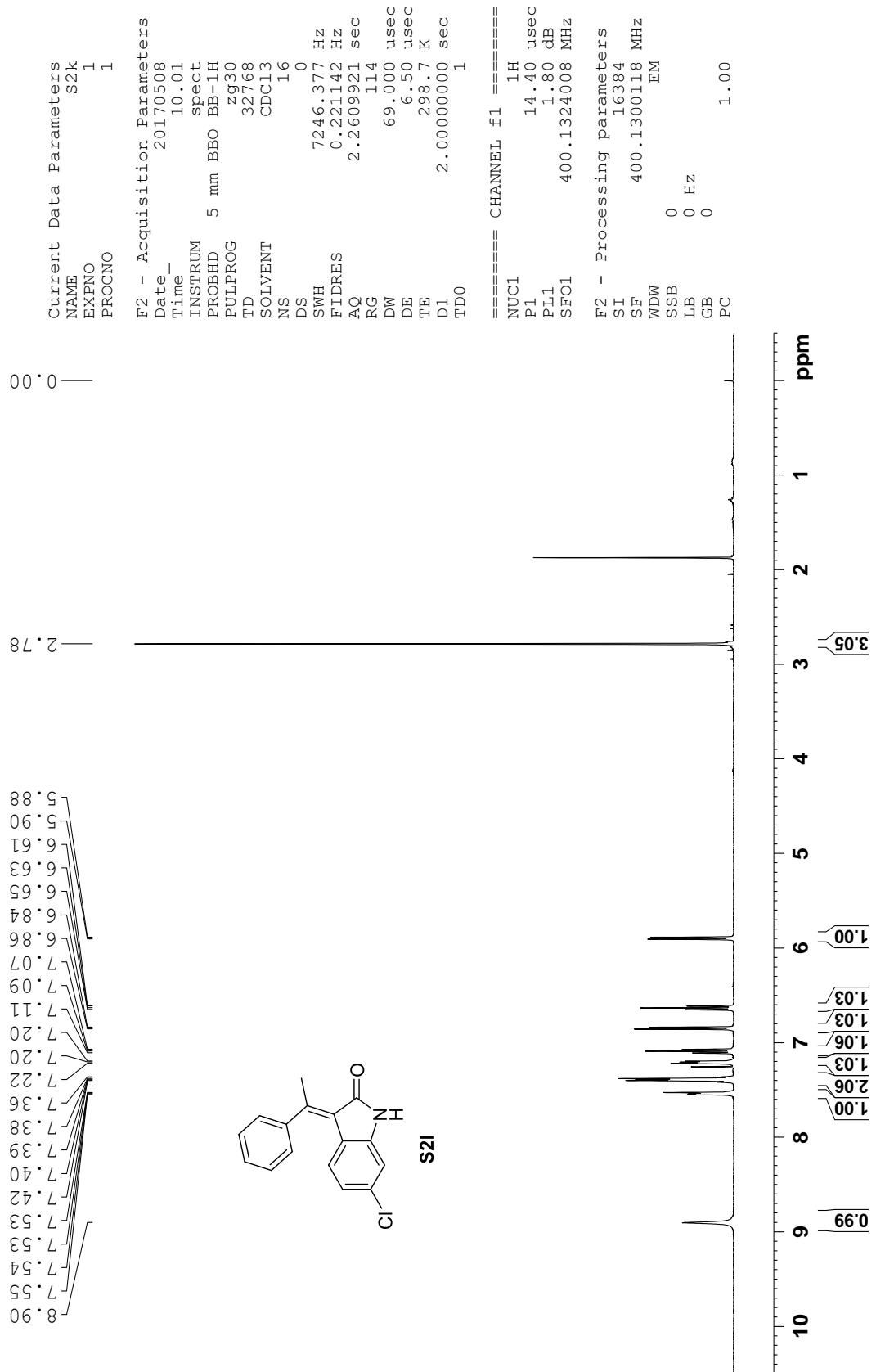
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PROCNO 1

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Time 13.04  
INSTRUM spect  
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PULPROG zgpp30  
TD 32768  
SOLVENT CDCl3  
NS 1000  
DS 0  
SWH 24038.461 Hz  
FIDRES 0.73596 Hz  
AQ 0.6815744 sec  
RG 198.09  
DW 20.800 usec  
DE 6.50 usec  
TE 297.3 K  
D1 2.0000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
SFO1 100.6228298 MHz  
NUC1 13C  
P1 10.00 usec  
PLW1 47.50000000 W  
===== CHANNEL f2 =====  
SFO2 400.1316005 MHz  
NUC2 1H  
CPDPRG [2  
PCPD2 90.00 usec  
PLW2 15.0000000 W  
PLW12 0.33750001 W  
PLW13 0.27338001 W

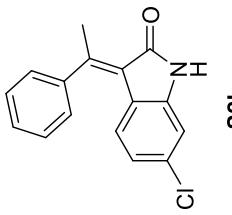
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SF 100.6127729 MHz  
WDW EM  
SSB 0  
LB 2.00 Hz  
GB 0  
PC 1.00





22.88

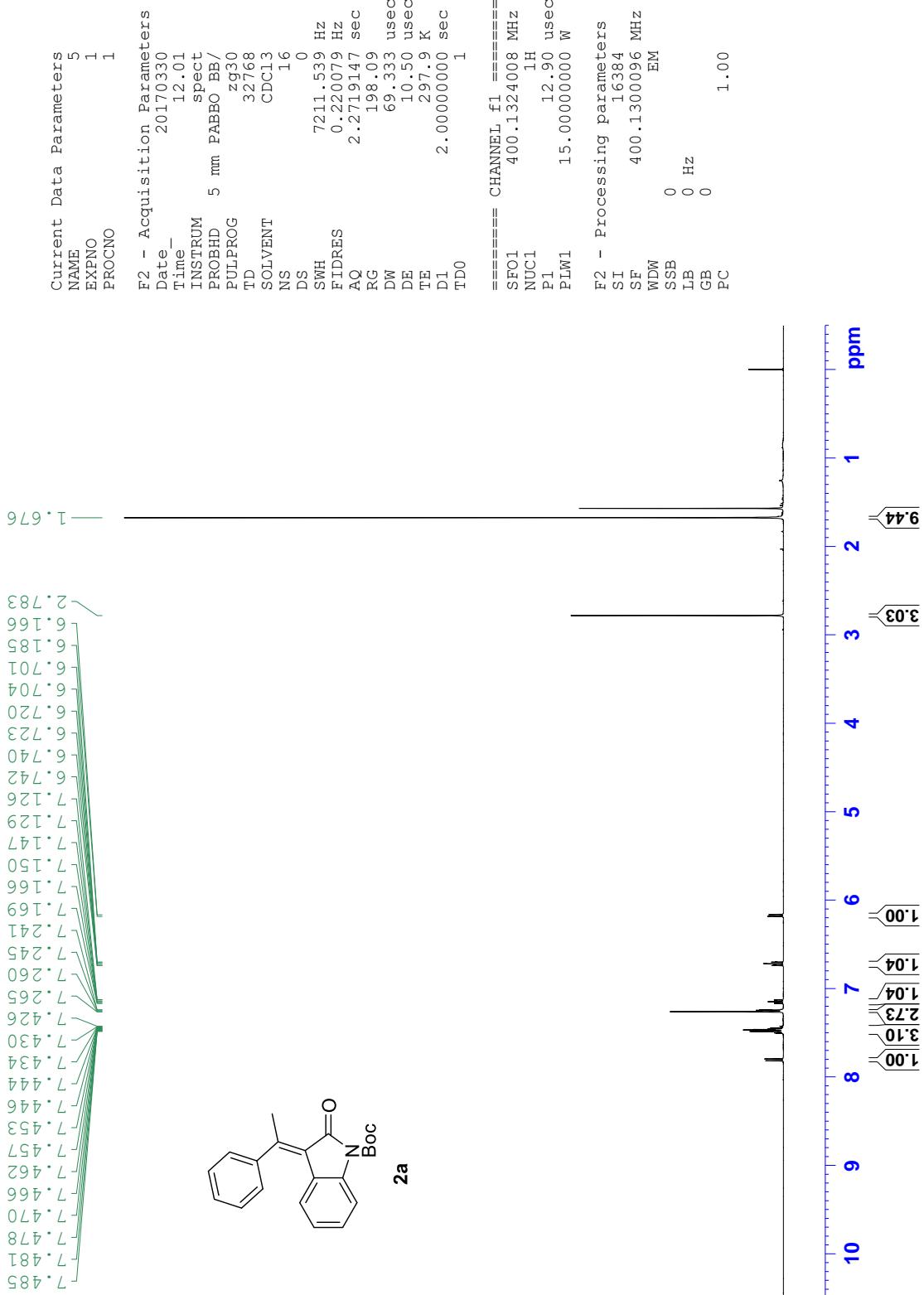
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170.06

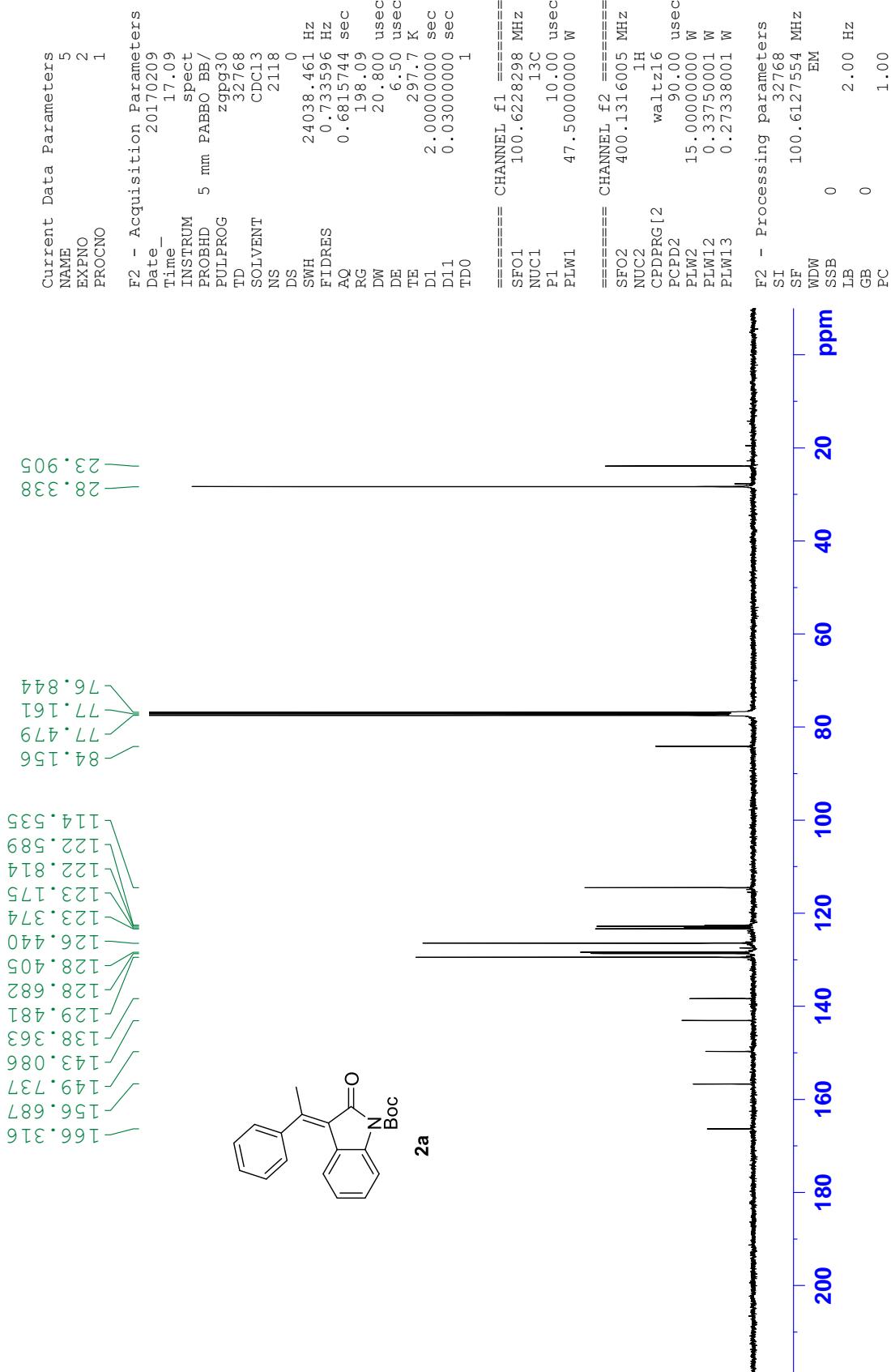


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NAME A261  
EXPNO 2  
PROCNO 1

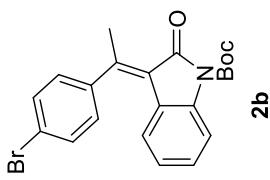
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Date 20171216  
Time 16.19  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgpg30  
TD 32768  
SOLVENT CDCl3  
NS 859  
DS 0  
SWH 24038.461 Hz  
FIDRES 0.733596 Hz  
AQ 0.6815744 sec  
RG 198.09  
DW 20.800 usec  
DE 6.50 usec  
TE 298.0 K  
D1 2.0000000 sec  
D11 0.03000000 sec  
TD0 1  
=====  
SFO1 100.6228298 MHz  
NUC1 13C  
P1 10.00 usec  
PLW1 47.5000000 W

===== CHANNEL f1 =====  
SFO1 400.1316005 MHz  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 90.00 usec  
PLW2 15.00000000 W  
PLW12 0.3375001 W  
PLW13 0.27338001 W  
  
===== CHANNEL f2 =====  
SFO2 400.1316005 MHz  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 90.00 usec  
PLW2 15.00000000 W  
PLW12 0.3375001 W  
PLW13 0.27338001 W  
  
F2 - Processing parameters  
SI 32768  
SF 100.6127714 MHz  
WDW 0  
SSB 2.00 Hz  
LB 0  
GB 1.00  
PC





6.27  
 6.29  
 6.76  
 6.78  
 6.80  
 7.14  
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 7.18  
 7.20  
 7.63  
 7.65  
 7.81  
 7.83



1.67  
 2.75

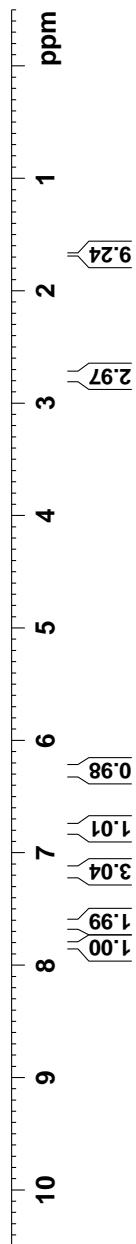
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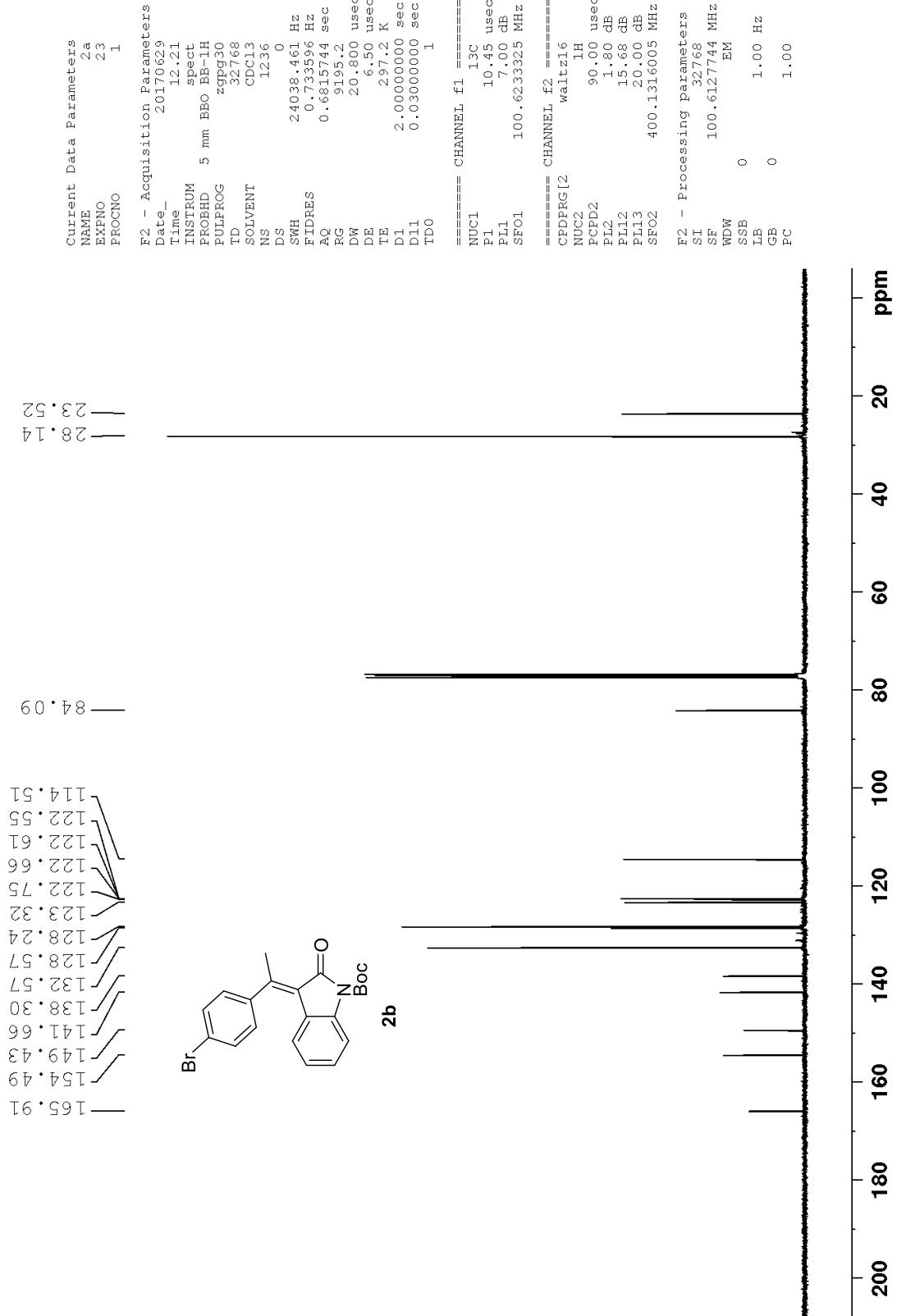
F2 - Acquisition Parameters

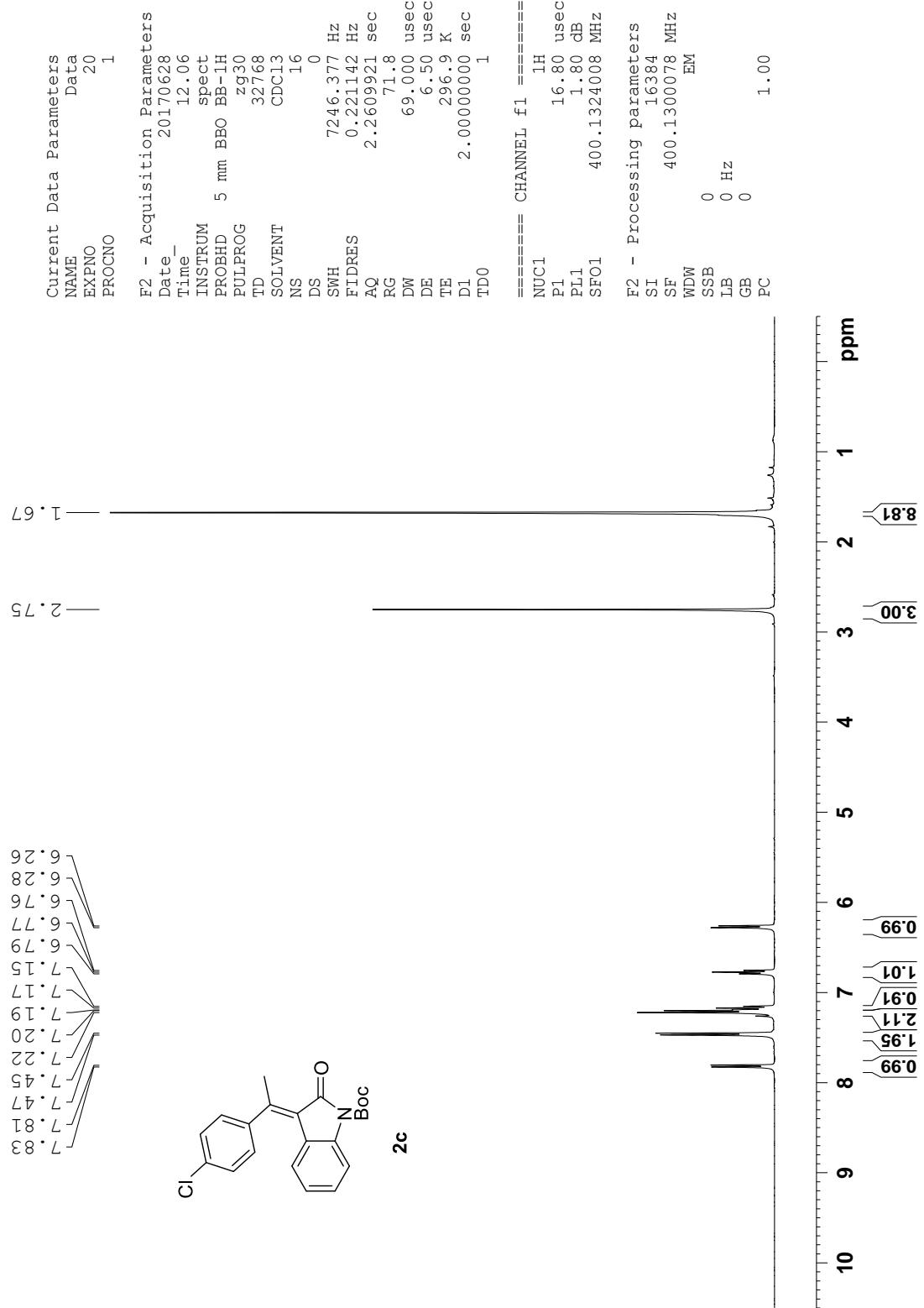
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 PROBHD 5 mm BBO BB-1H  
 PULPROG 3g30  
 TD 32768  
 SOLVENT CDCl3  
 NS 16  
 DS 0  
 SWH 7246.377 Hz  
 FIDRES 0.221142 Hz  
 AQ 2.260921 sec  
 RG 114  
 DW 69.000 usec  
 DE 6.50 usec  
 TE 297.0 K  
 D1 2.0000000 sec  
 TDO 1

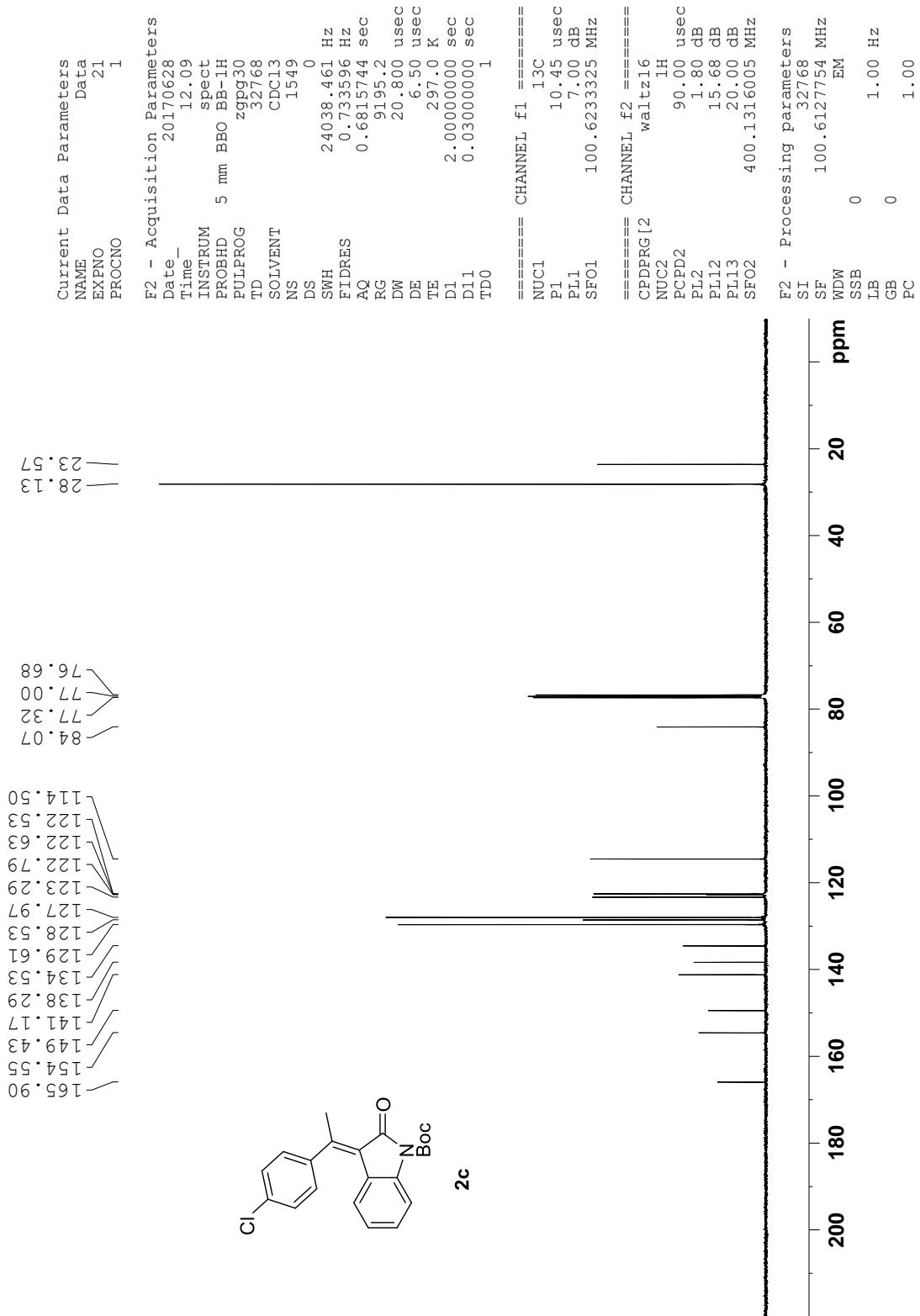
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 SF01 400.1324008 MHz  
 WDW EM  
 SSB 0  
 LB 0 Hz  
 GB 0  
 PC 1.00



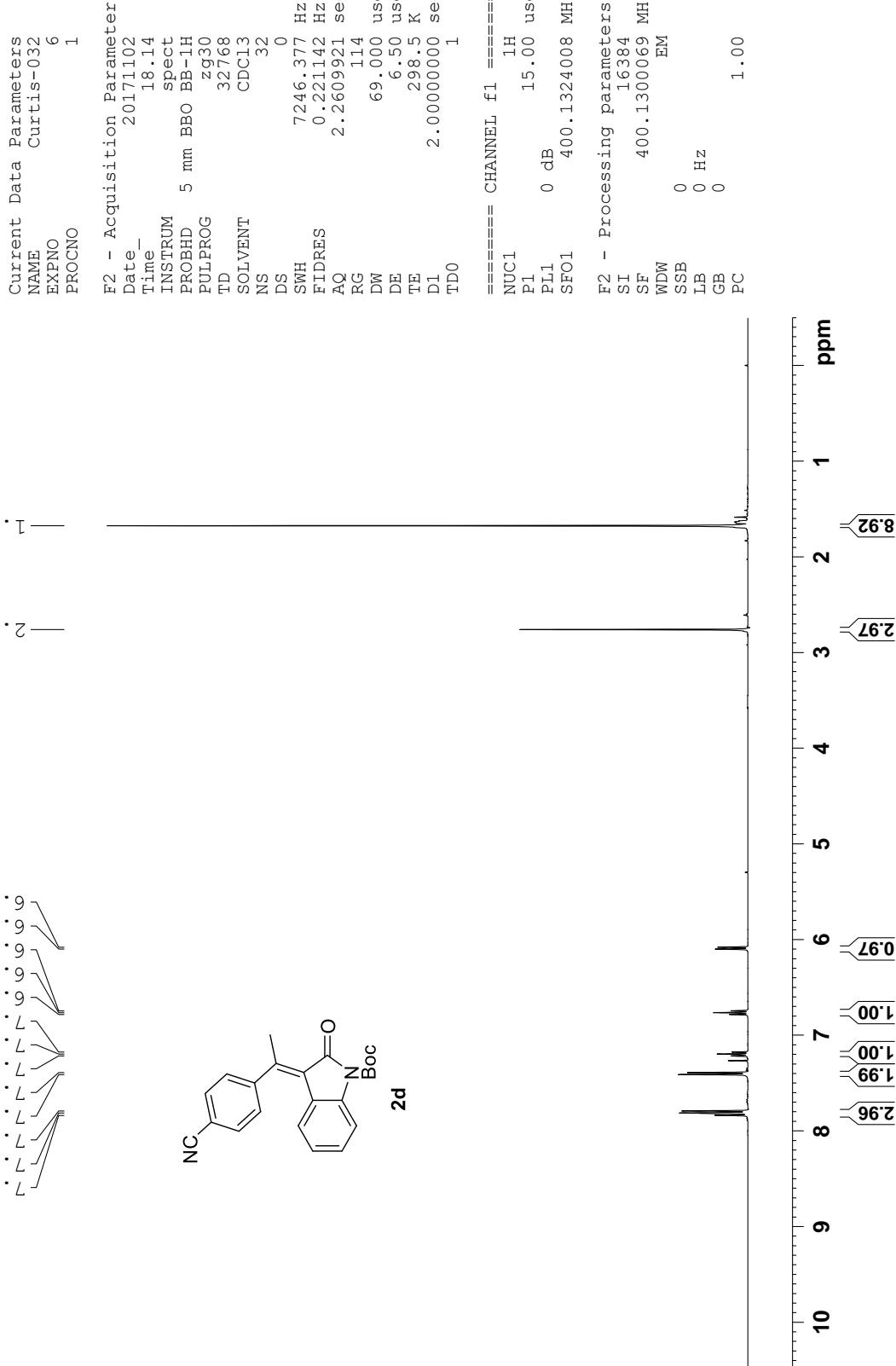
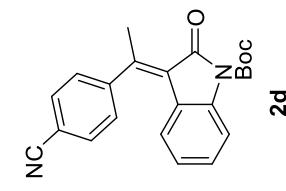


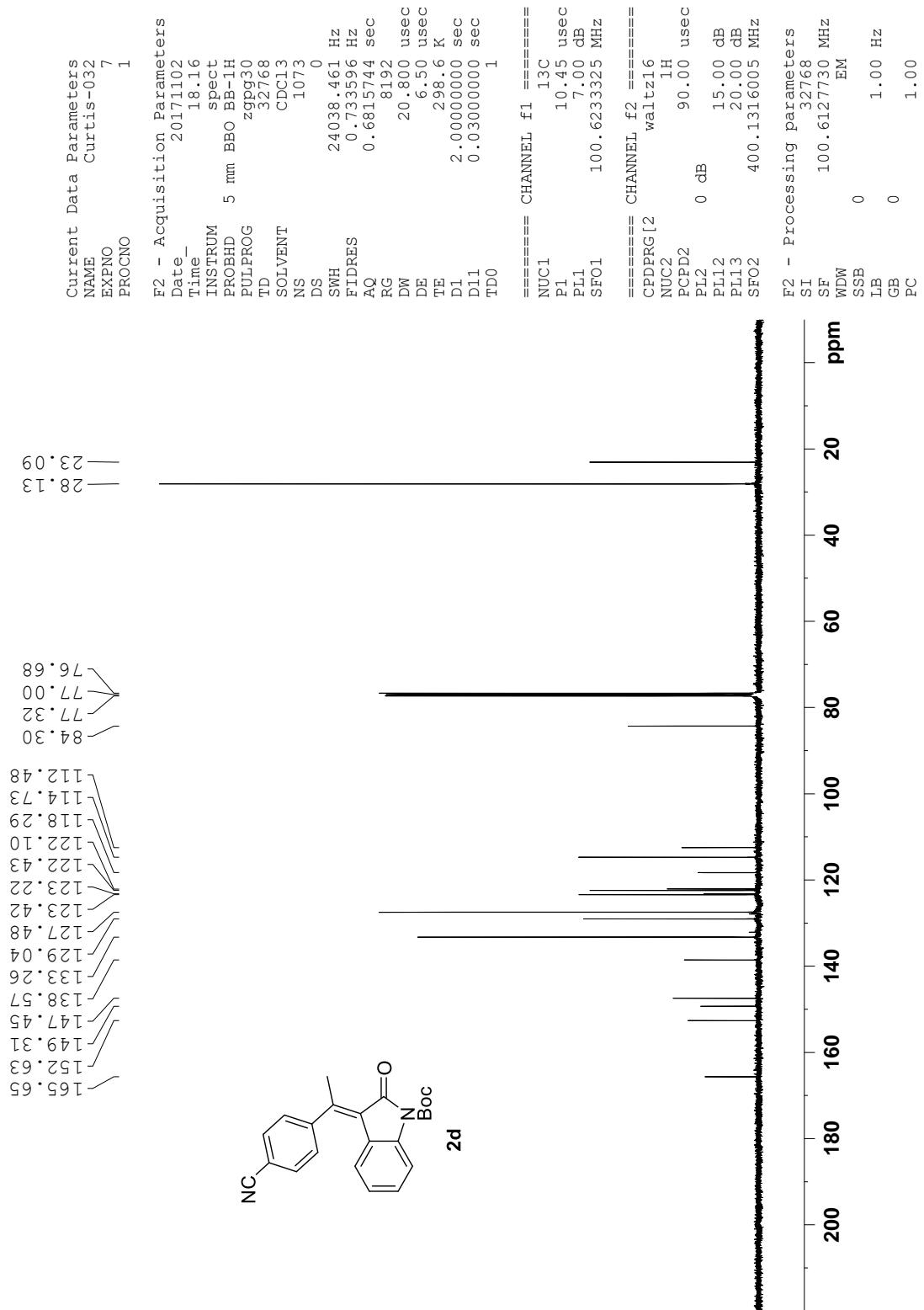


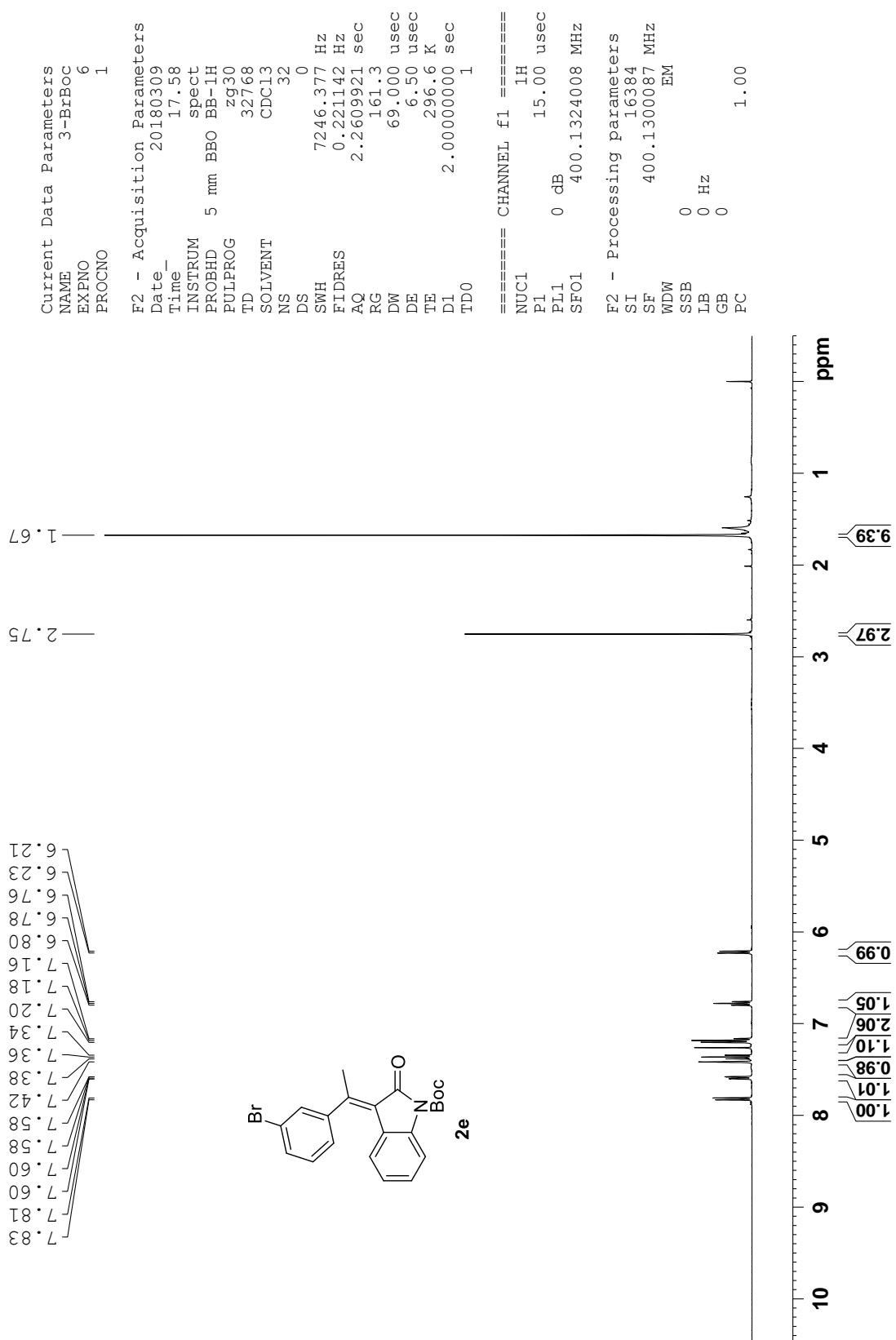


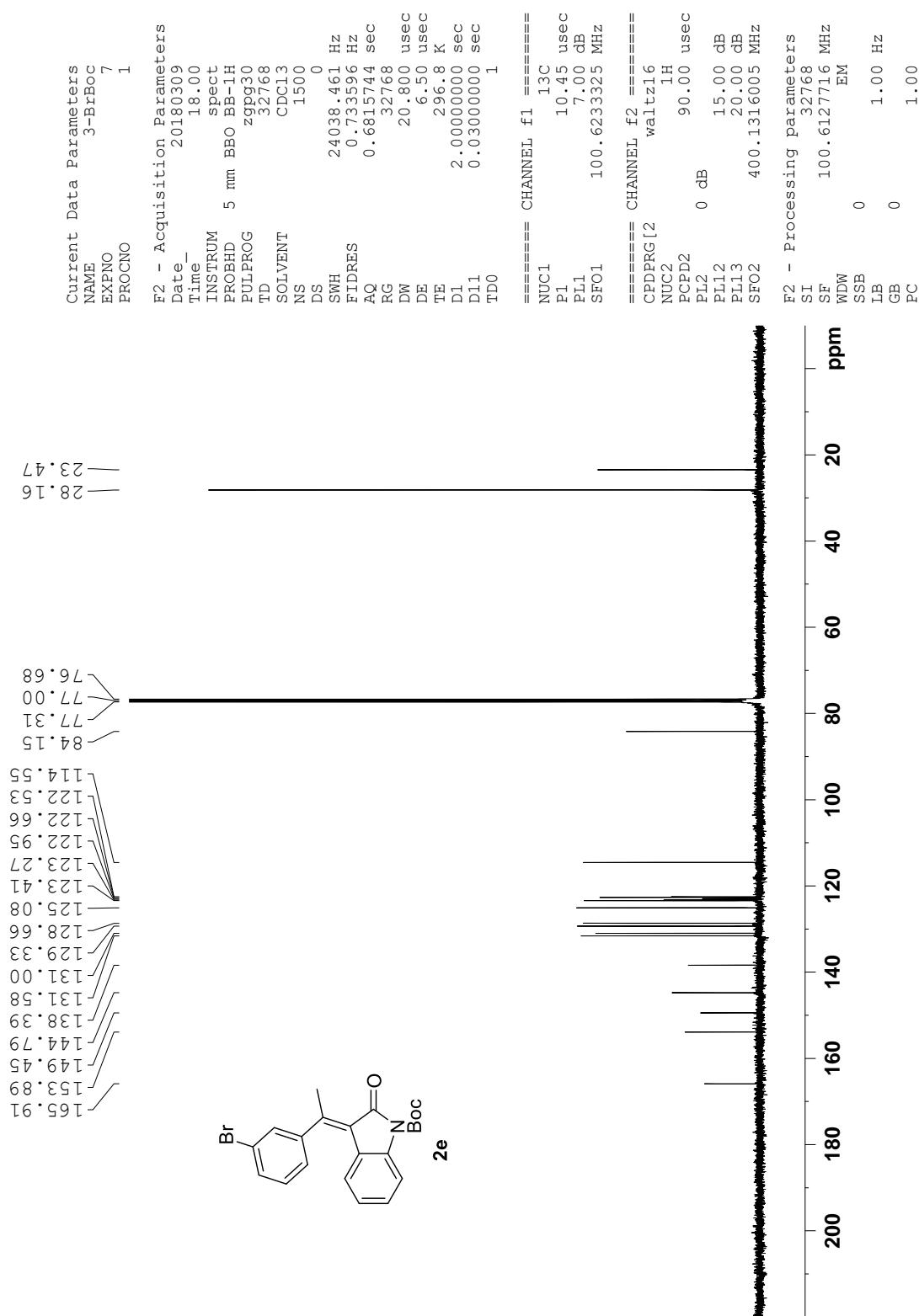
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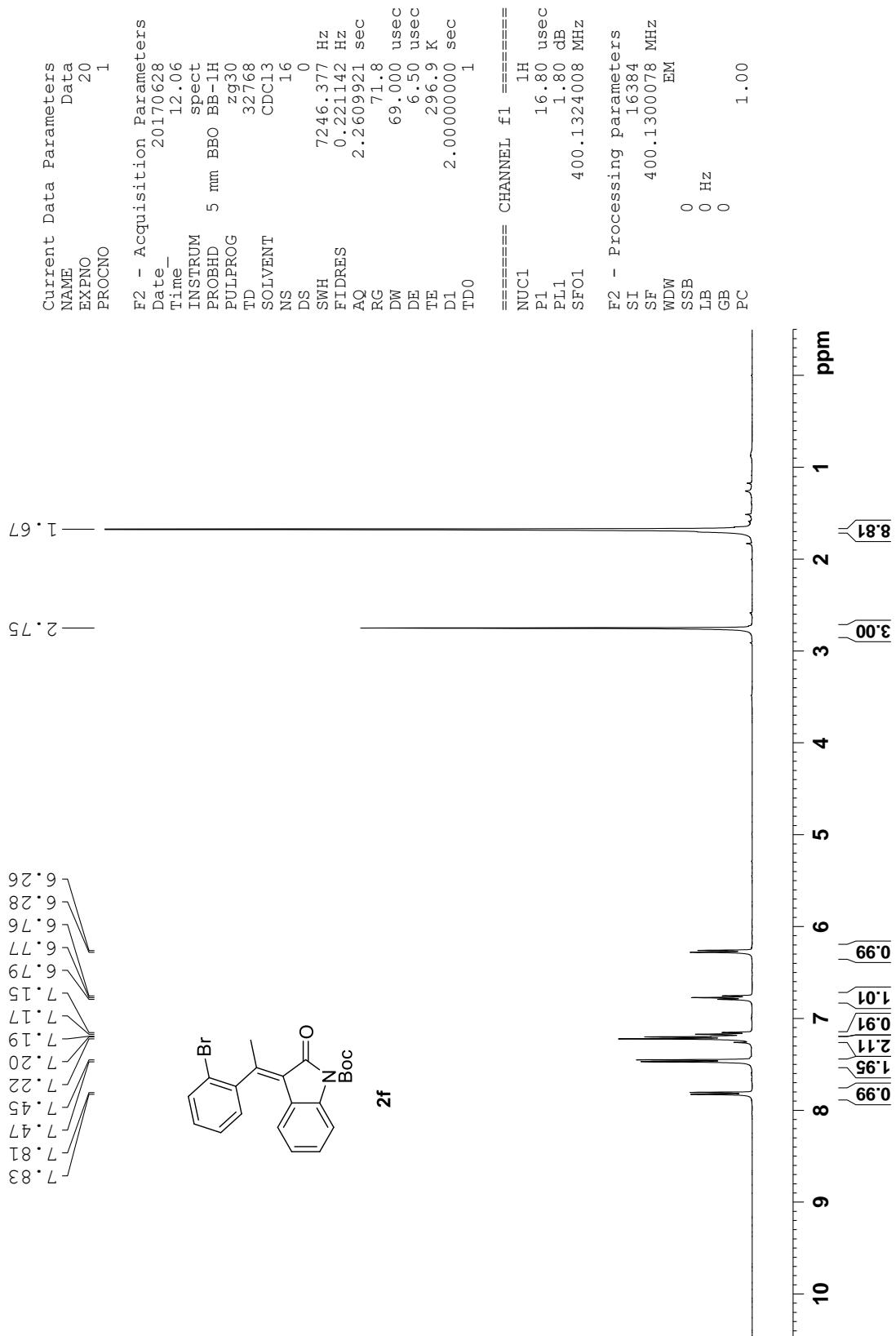
1.68  
 2.76

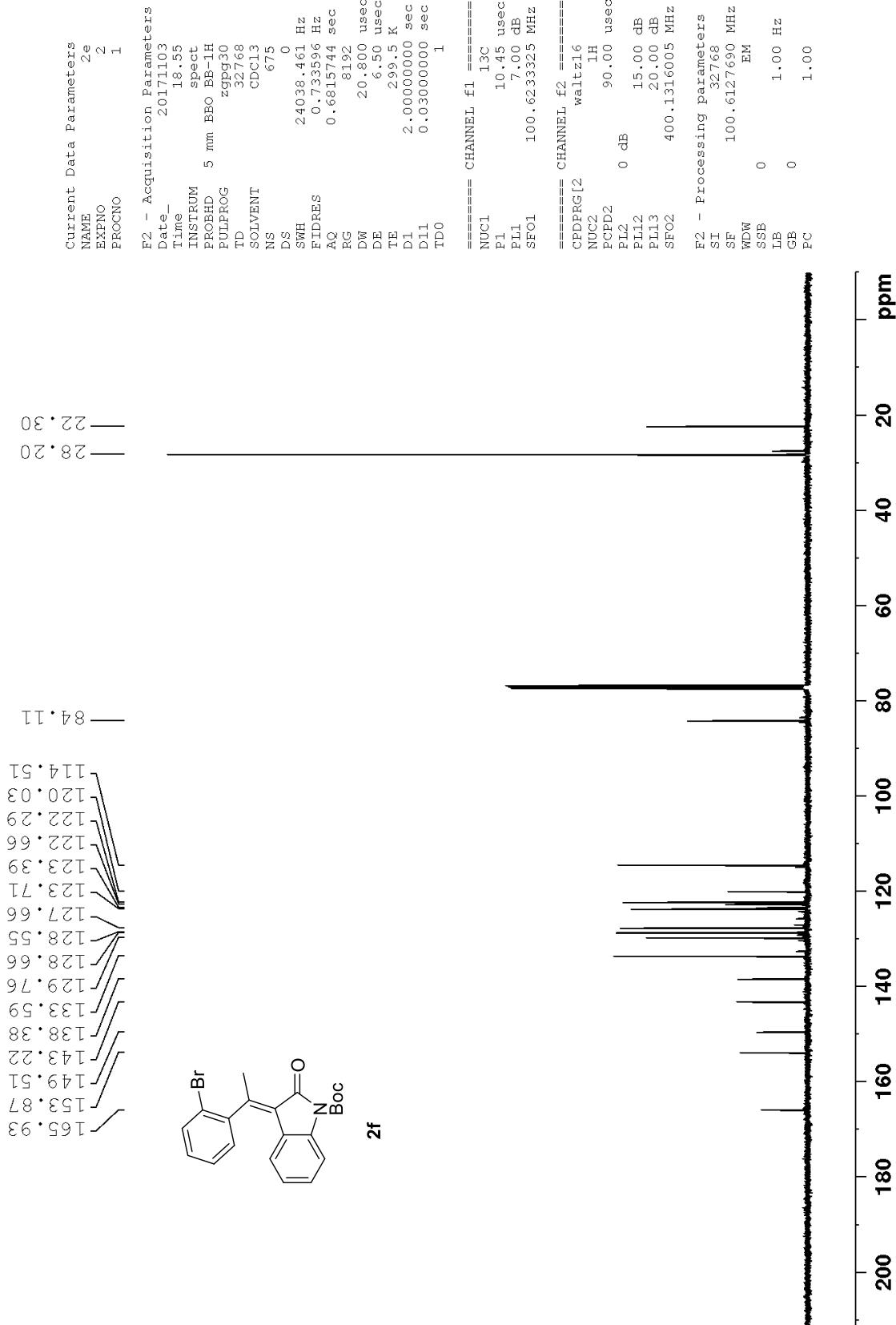


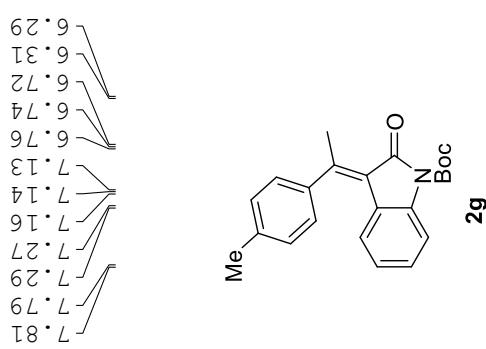












1.67  
2.44  
2.76  
2.79

Current Data Parameters  
NAME Curtis-081  
EXNO 2  
PROCNO 1

F2 - Acquisition Parameters

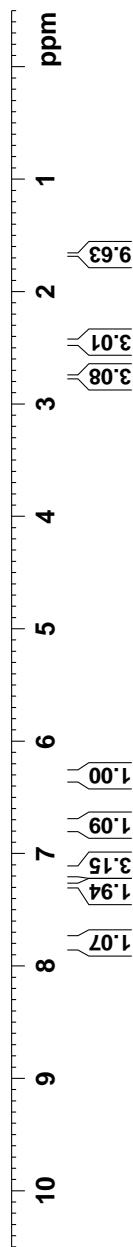
Date 20180310  
Time 10.49  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 32768  
SOLVENT CDCl3  
NS 32  
DS 0  
SWH 7211.539 Hz  
FIDRES 0.220079 Hz  
AQ 2.2719147 sec  
RG 4.01  
DW 69.333 usec  
DE 10.50 usec  
TE 297.7 K  
D1 2.0000000 sec  
TDD0 1

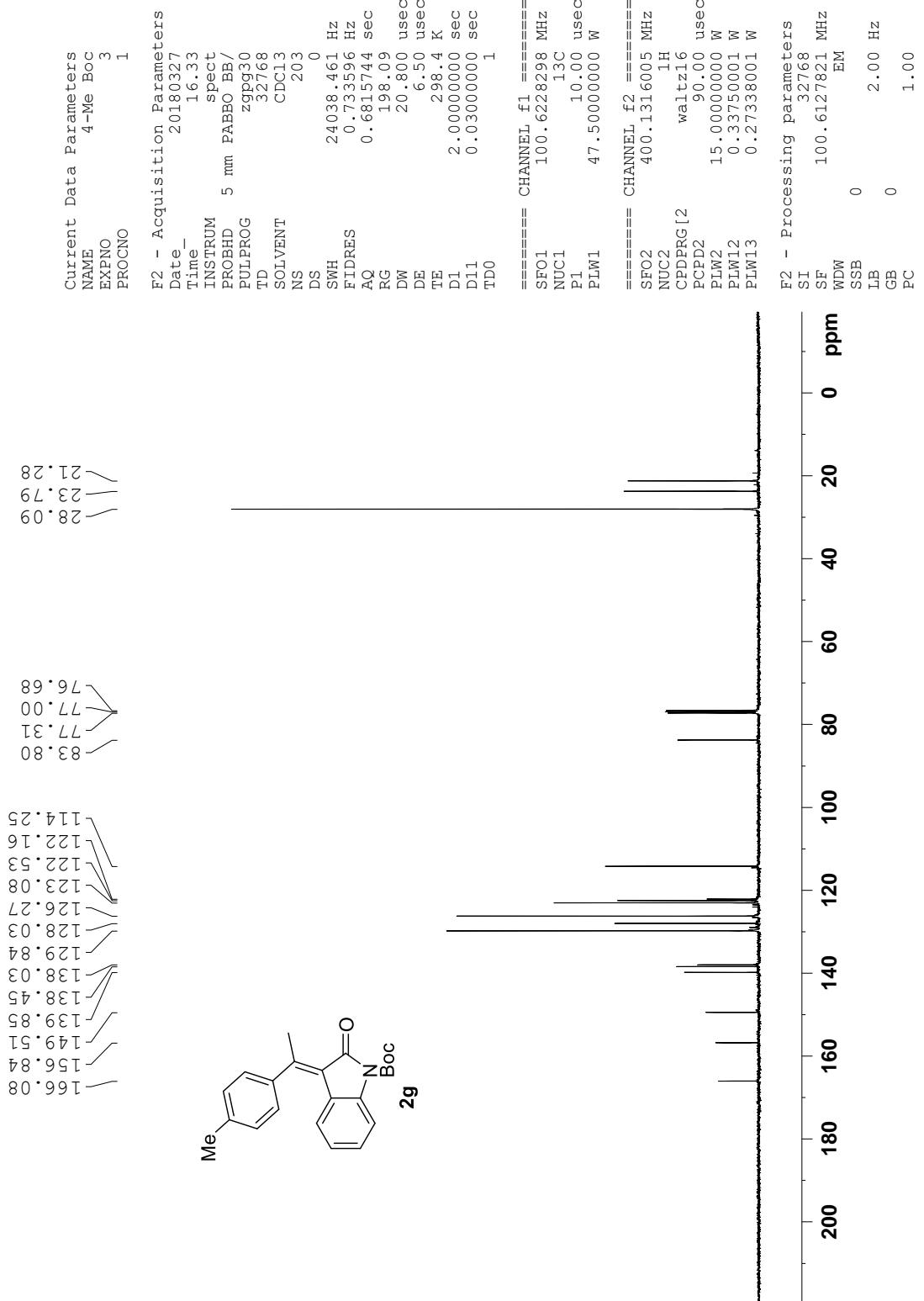
===== CHANNEL f1 =====

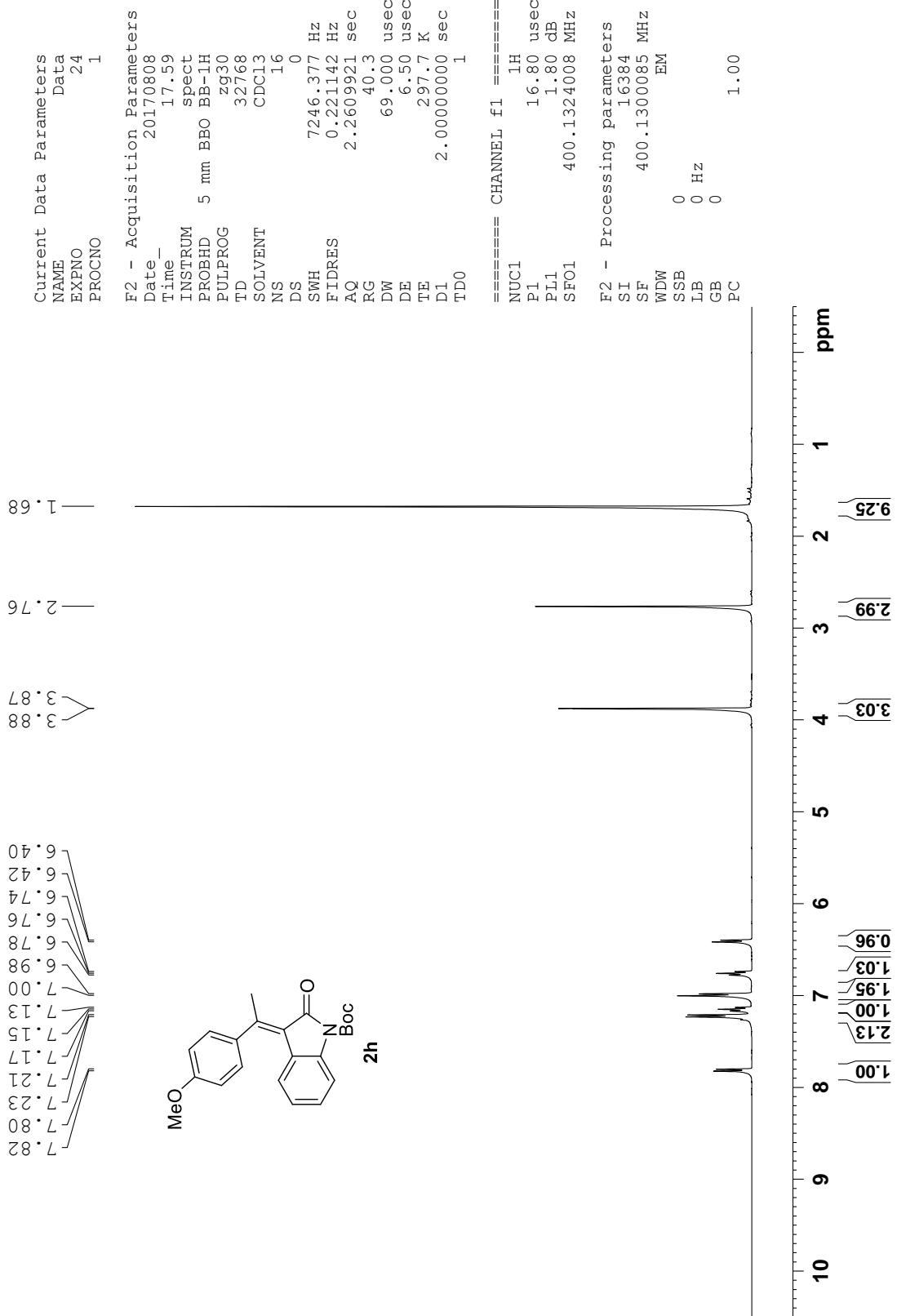
SFO1 400.1324008 MHz  
NUC1 1H  
P1 12.90 usec  
PLW1 15.00000000 W

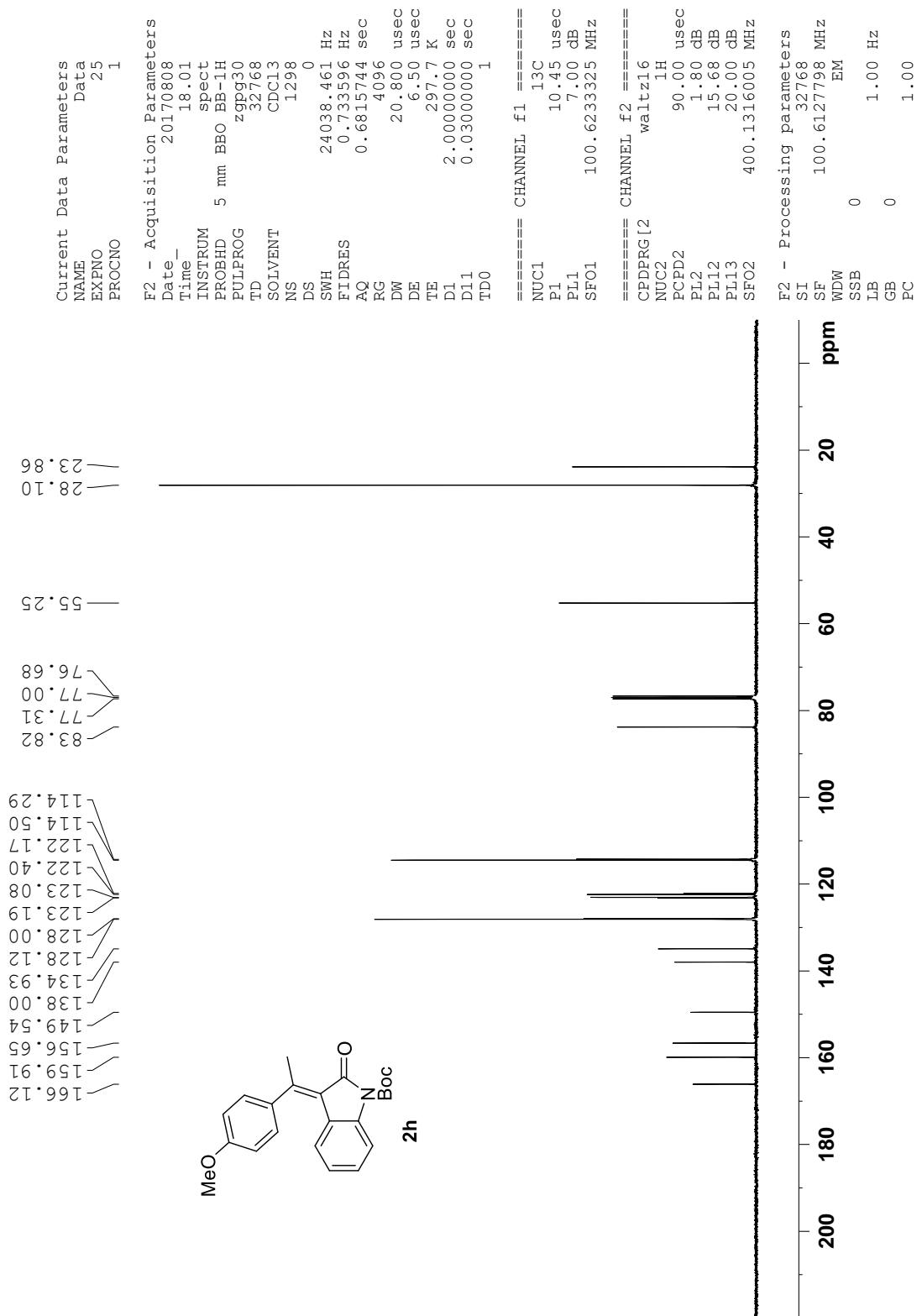
F2 - Processing parameters

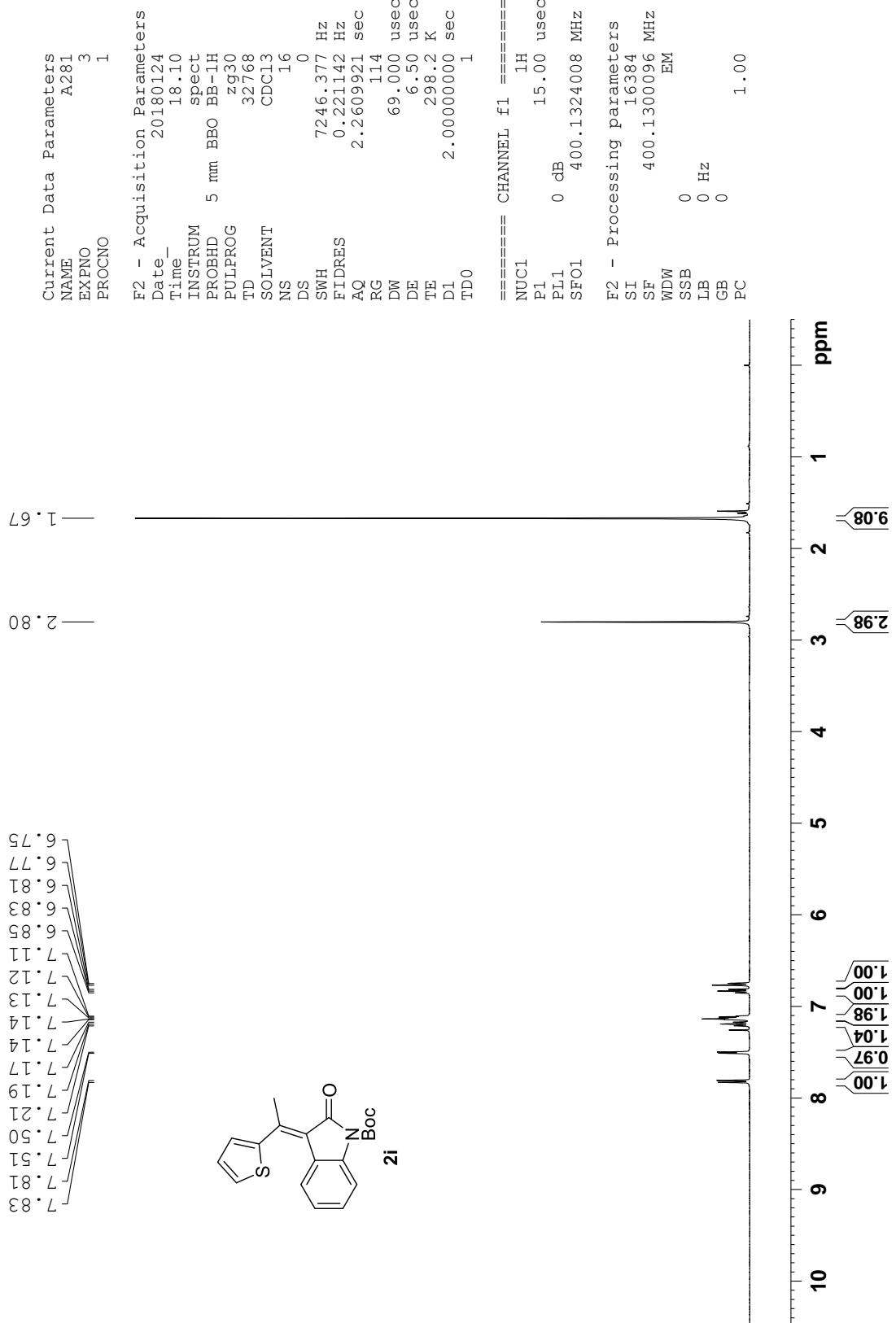
SI 16384  
SF 400.1300105 MHz  
WDW EM  
SSB 0  
LB 0 Hz  
GB 0  
PC 1.00

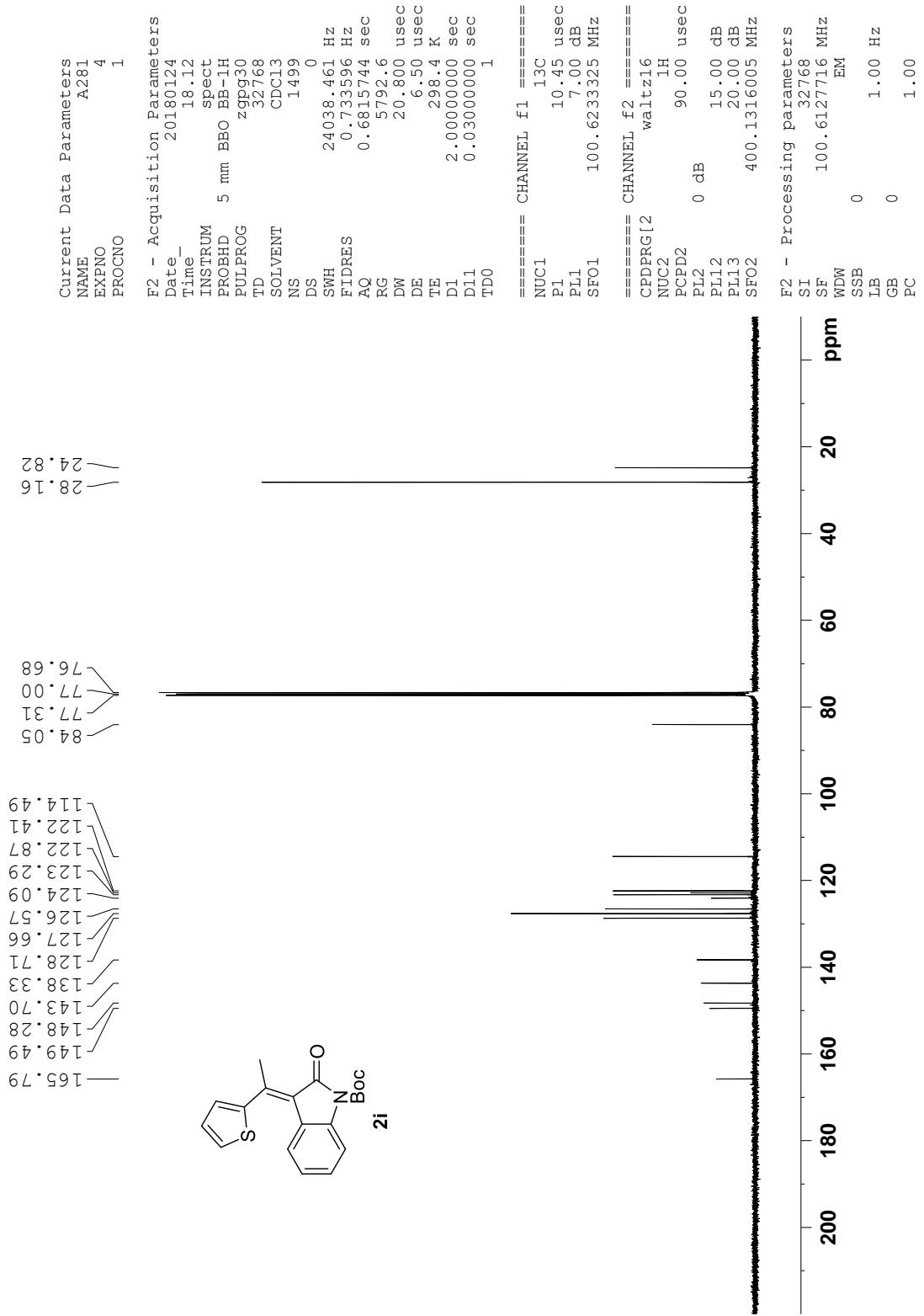


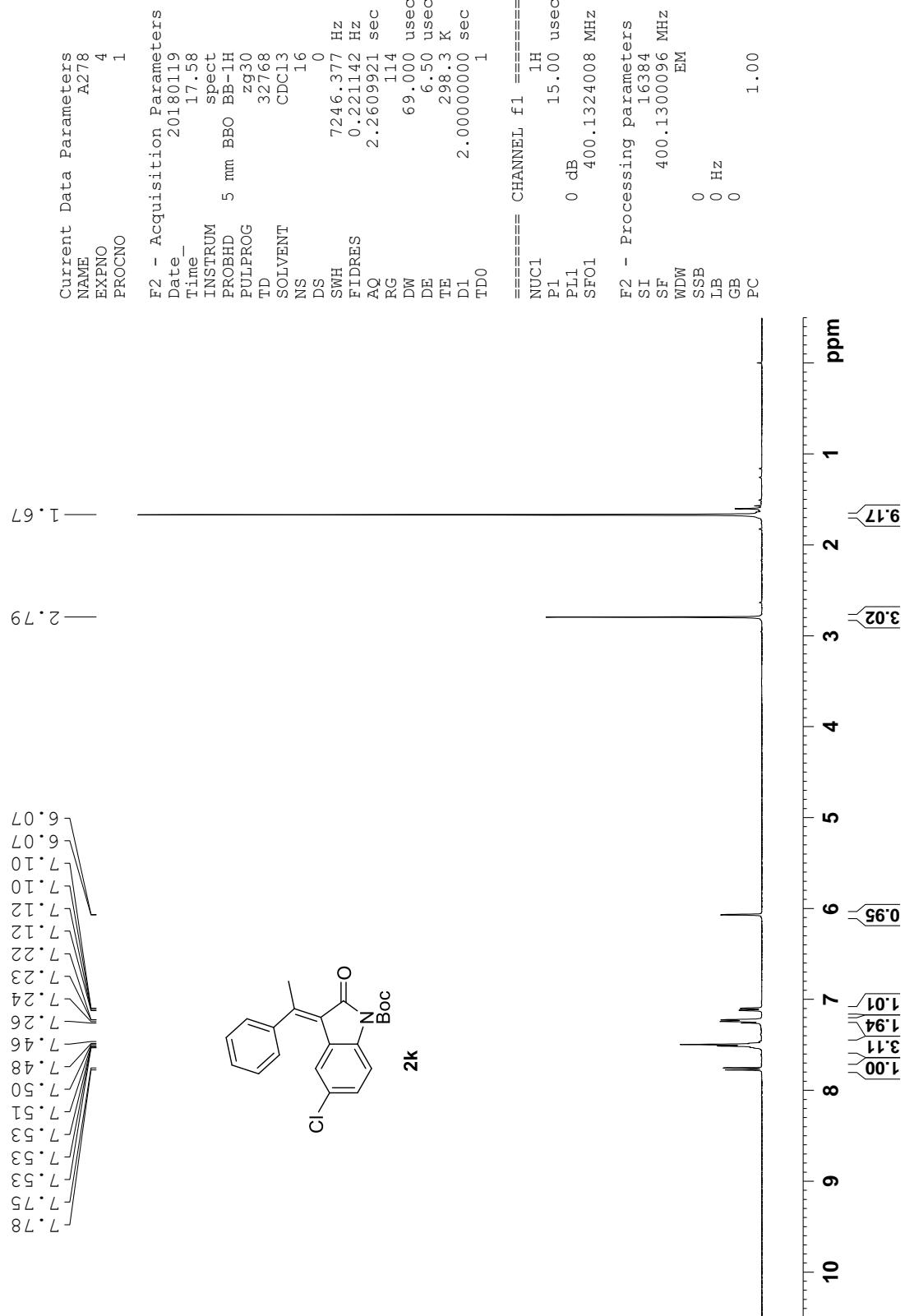


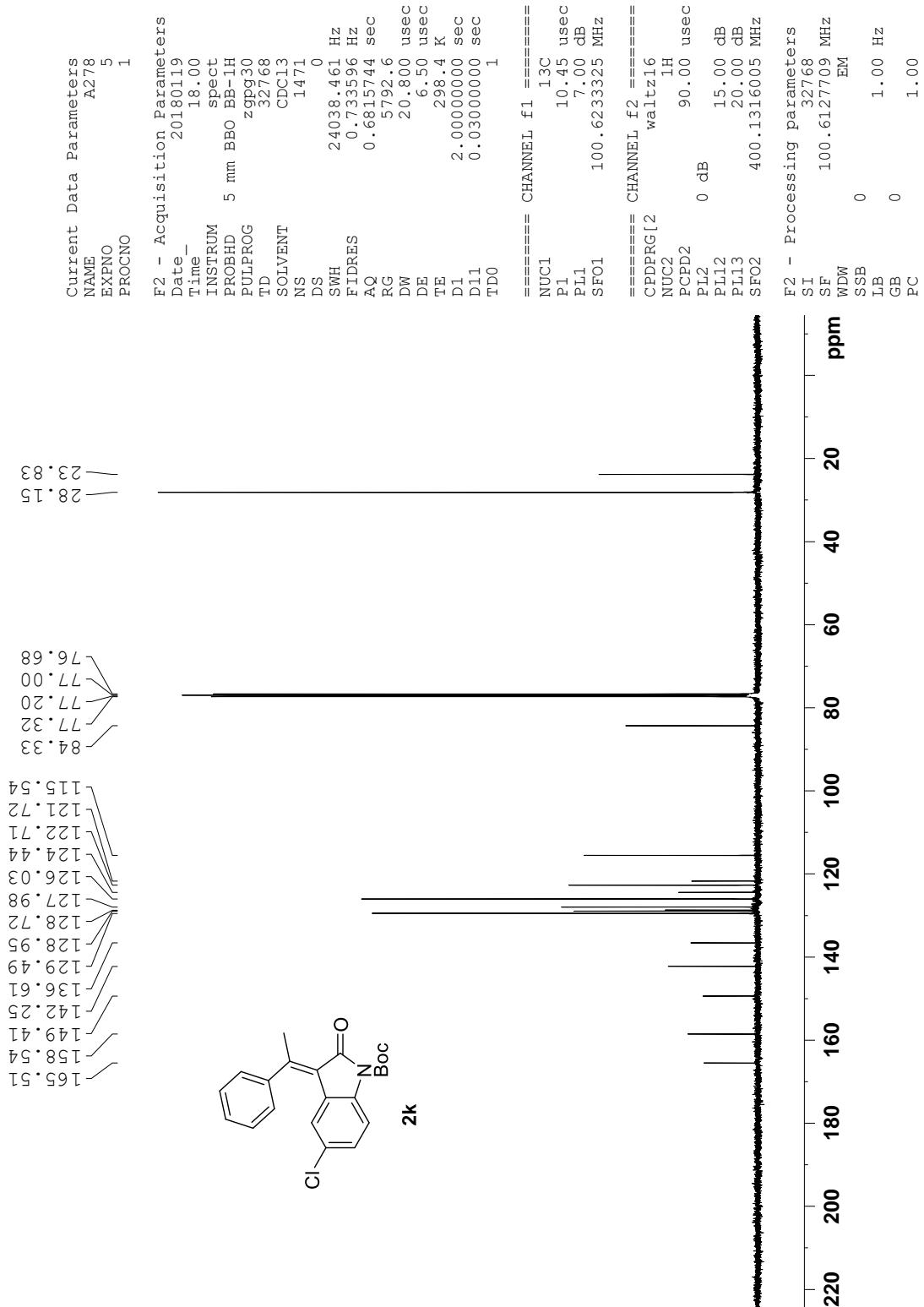


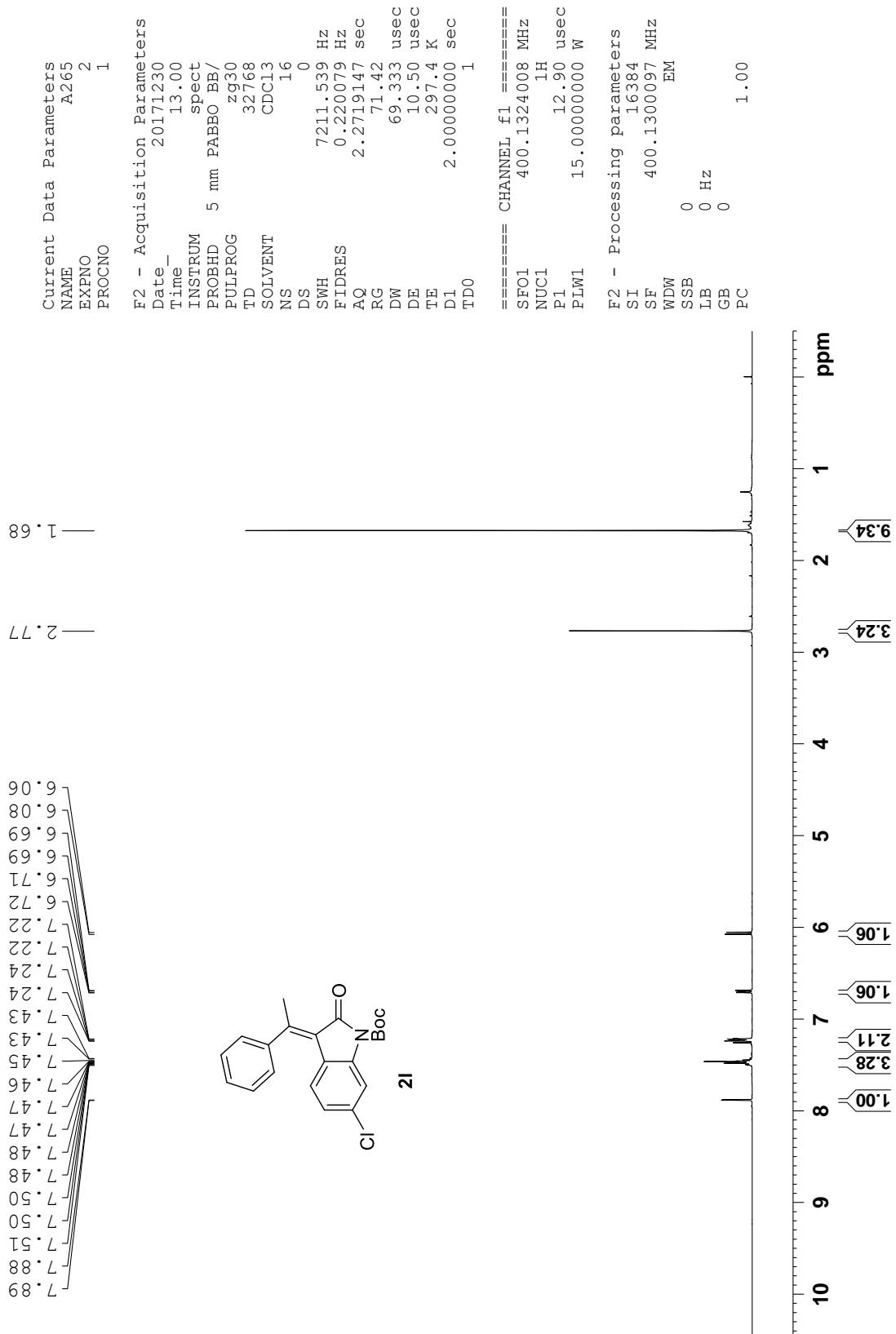






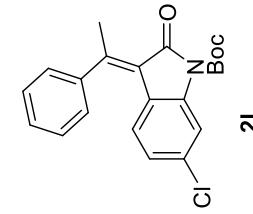






28.12  
23.73

165.65  
149.33  
157.23  
142.59  
138.90  
133.90  
129.41  
128.74  
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121.70  
121.45  
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84.49  
77.68  
77.00  
76.68

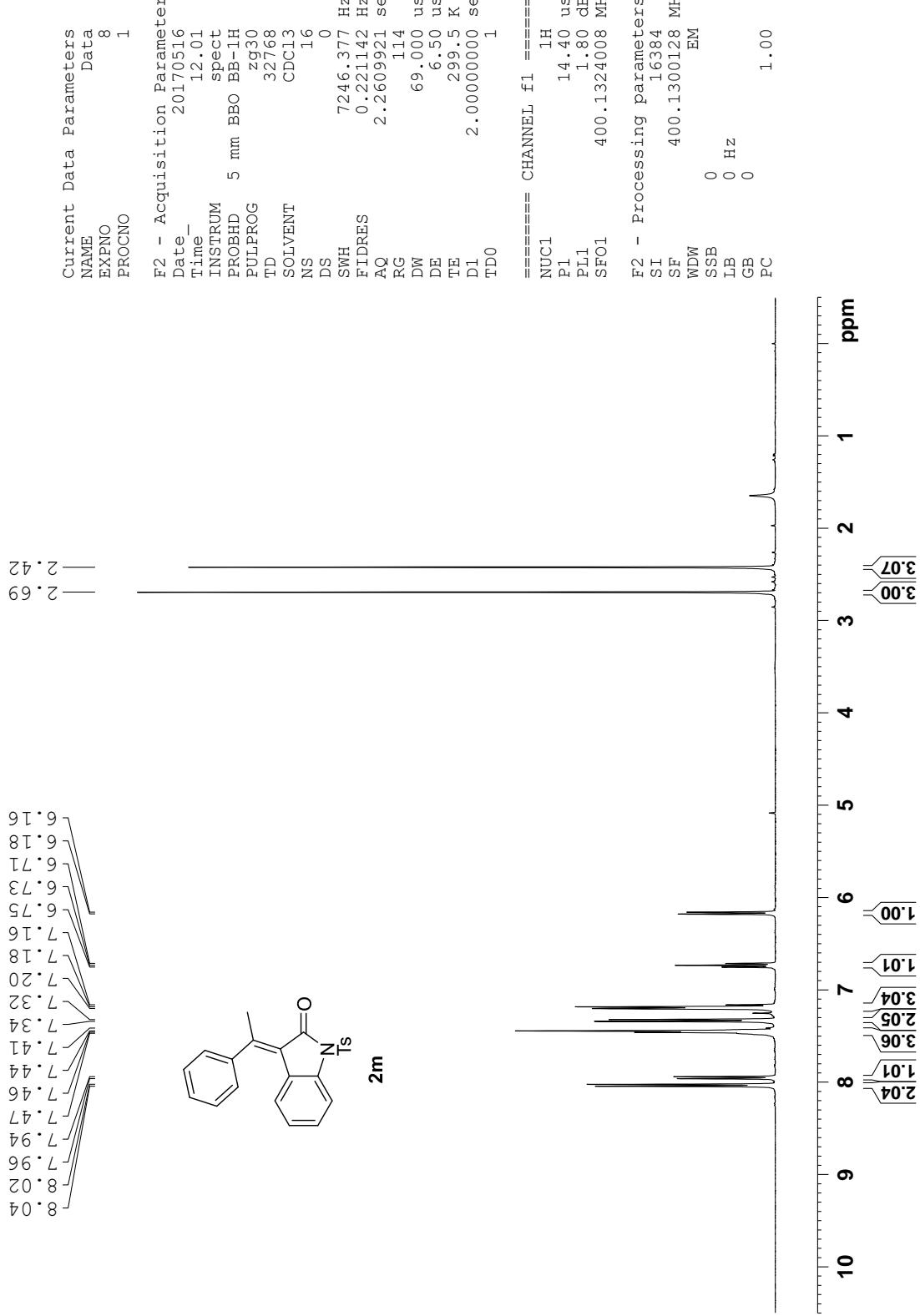


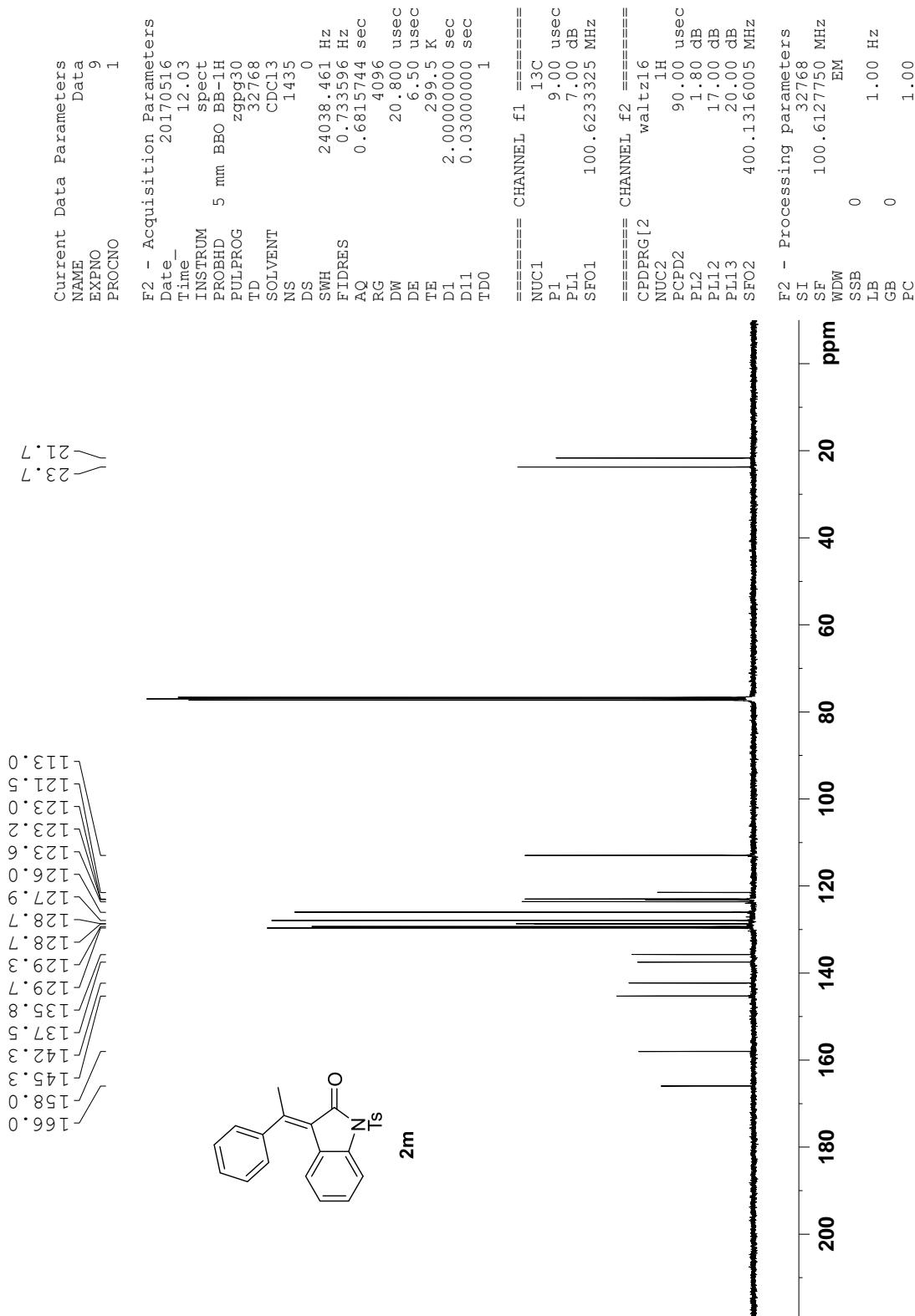
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Date 20171230  
Time 13.01  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgpp30  
TD 32768

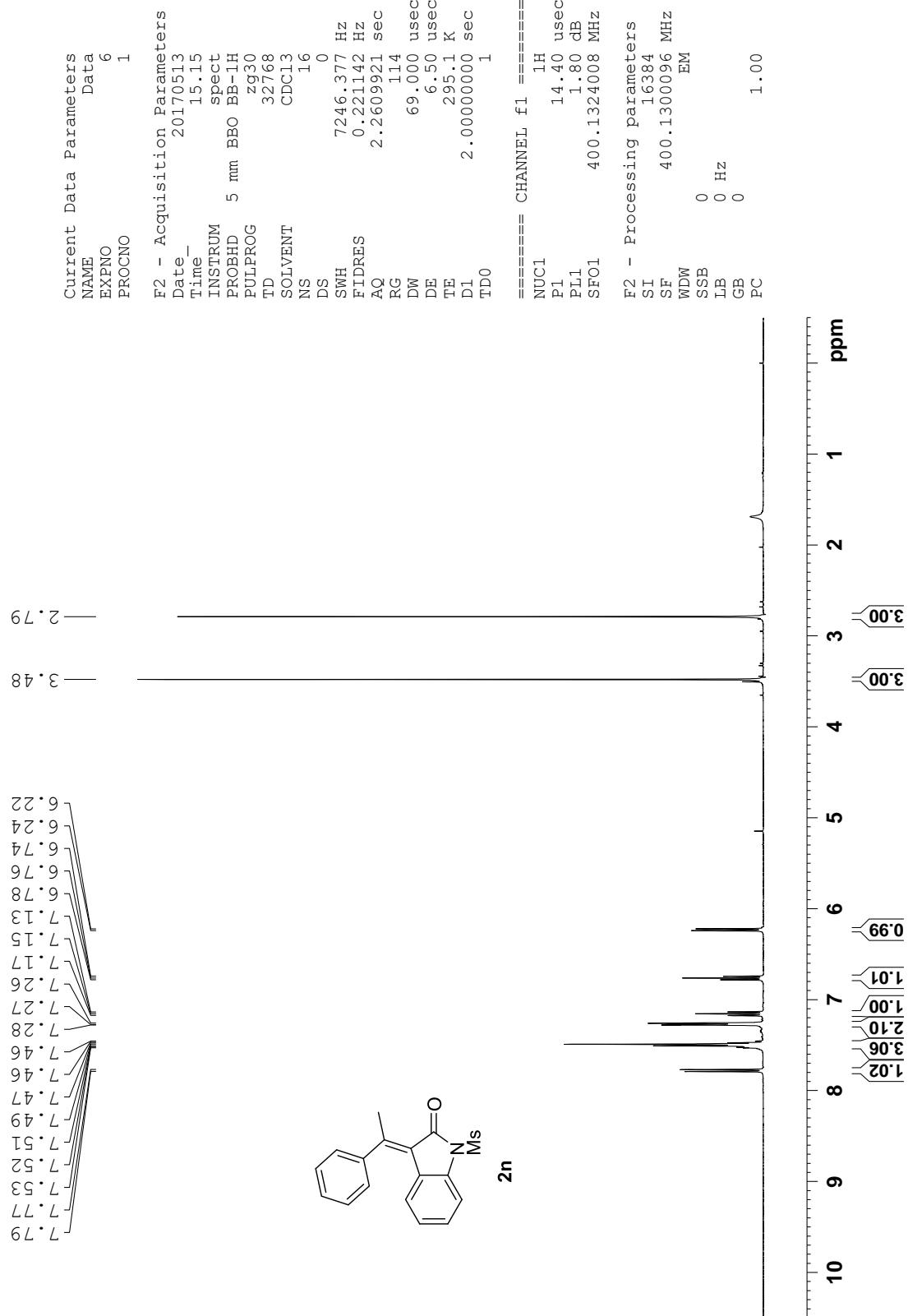
SOLVENT CDCl3  
NS 1.185  
DS 0  
SWH 24038.461 Hz  
FIDRES 0.73596 Hz  
AQ 0.6815744 sec  
RG 198.09  
DW 20.800 usec  
DE 6.50 usec  
TE 297.6 K  
D1 2.0000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
SFO1 100.6228298 MHz  
NUC1 13C  
P1 10.00 usec  
PLW1 47.50000000 W  
===== CHANNEL f2 =====  
SFO2 400.1316005 MHz  
NUC2 1H  
CPDPRG [2  
PCPD2 waltz16  
PLW2 90.00 usec  
PLW12 15.0000000 W  
PLW13 0.33750001 W  
0.27338001 W

F2 - Processing parameters  
SI 32768  
SF 100.6127721 MHz  
WDW EM  
SSB 0  
LB 2.00 Hz  
GB 0  
PC 1.00







113.0  
 122.9  
 123.8  
 123.0  
 126.0  
 128.7  
 128.9  
 128.4  
 129.2  
 137.2  
 142.2  
 158.9  
 167.0

23.8  
 41.8

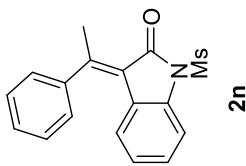
Current Data Parameters  
 NAME Data 7  
 EXPNO 1  
 PROCNO

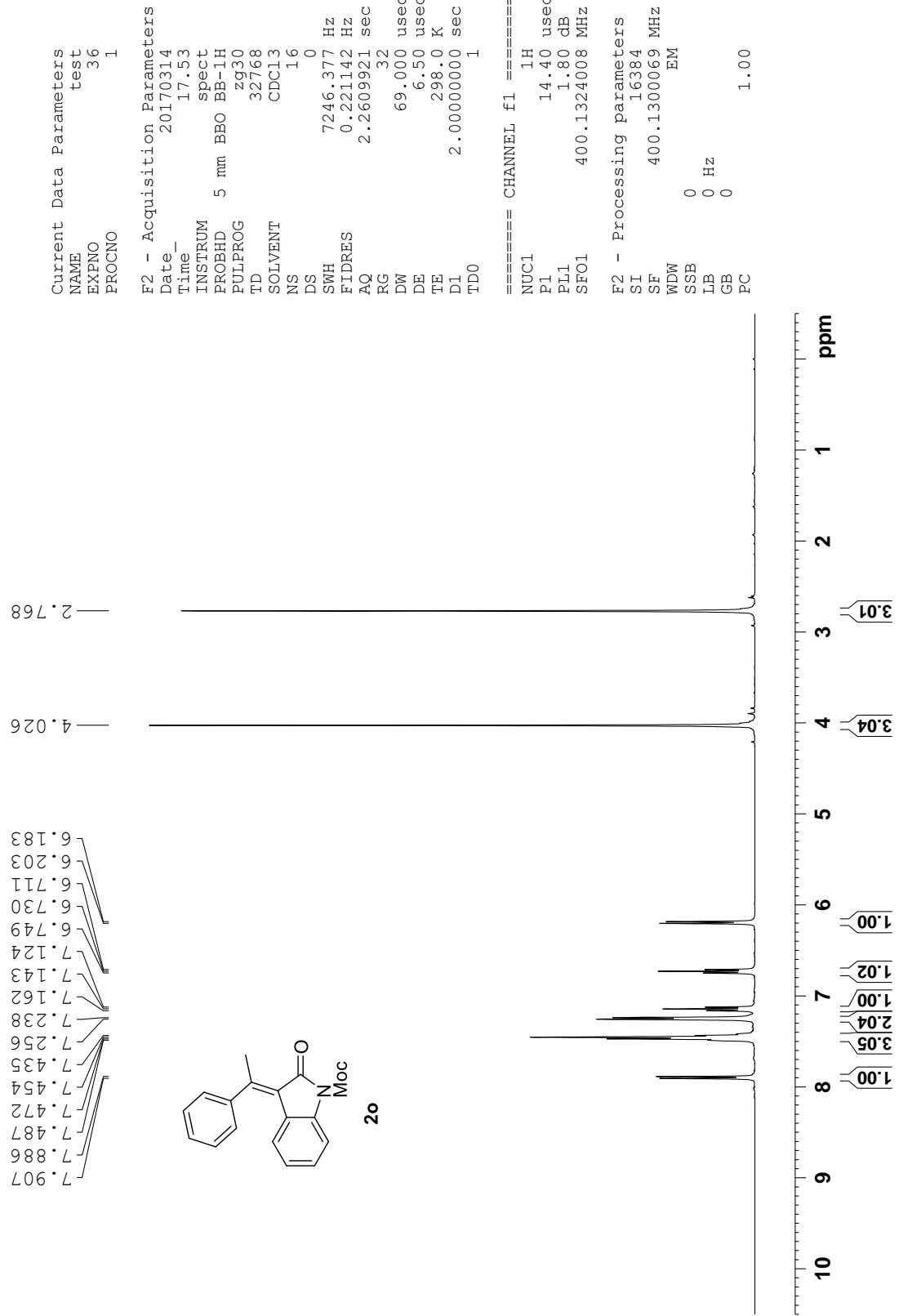
F2 - Acquisition Parameters  
 Date 20170513  
 Time 15:16  
 INSTRUM spect  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zqppg30  
 TD 32768  
 SOLVENT CDCl3  
 NS 1136  
 DS 0  
 SWH 24038.461 Hz  
 FIDRES 0.733596 Hz  
 AQ 0.6815744 sec  
 RG 9195.2  
 DW 20.800 usec  
 DE 6.50 usec  
 TE 295.1 K  
 D1 2.0000000 sec  
 D11 0.03000000 sec  
 TDO 1

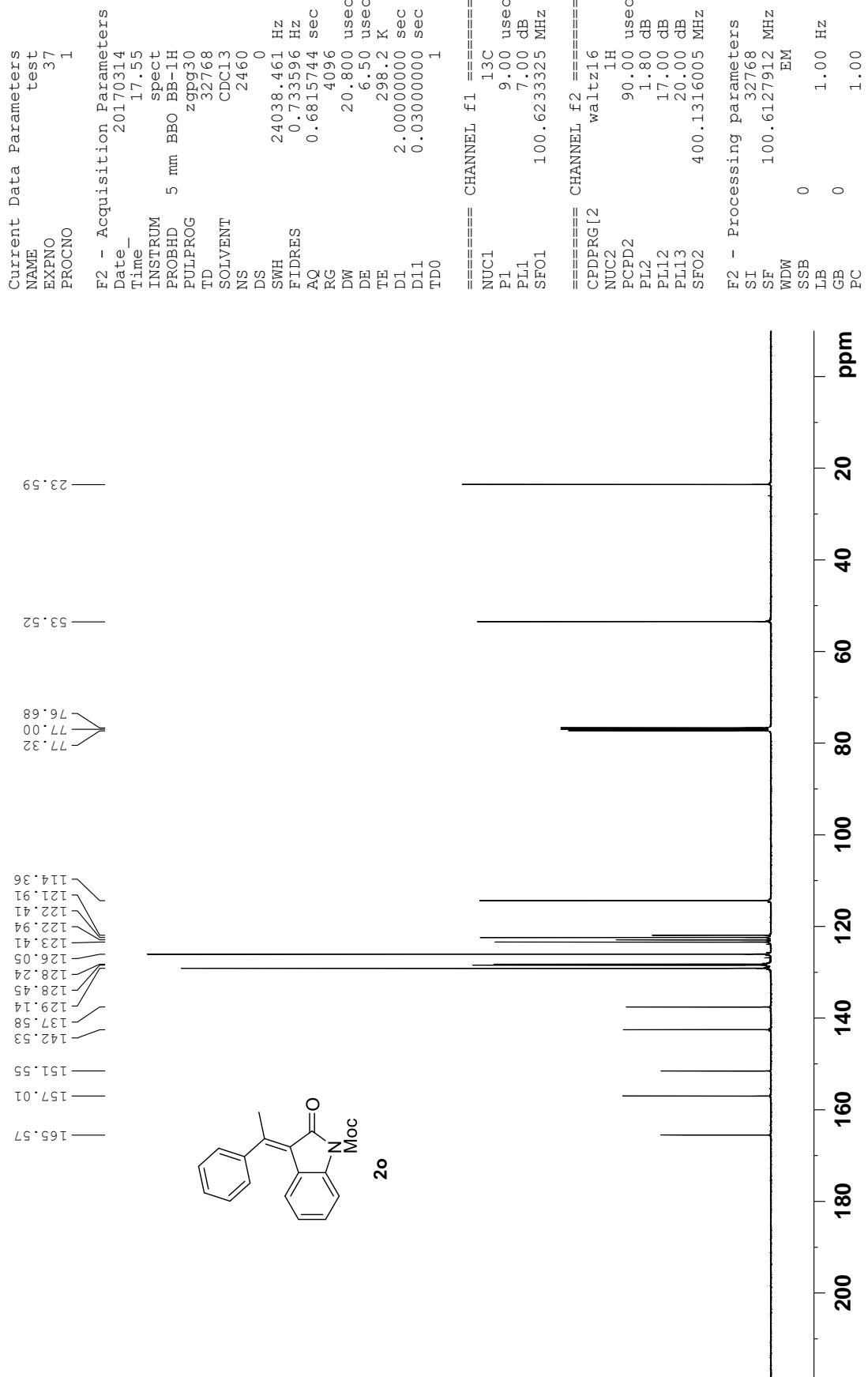
===== CHANNEL f1 =====  
 NUC1 13C  
 P1 9.00 usec  
 PL1 7.00 dB  
 SFO1 100.6233325 MHz

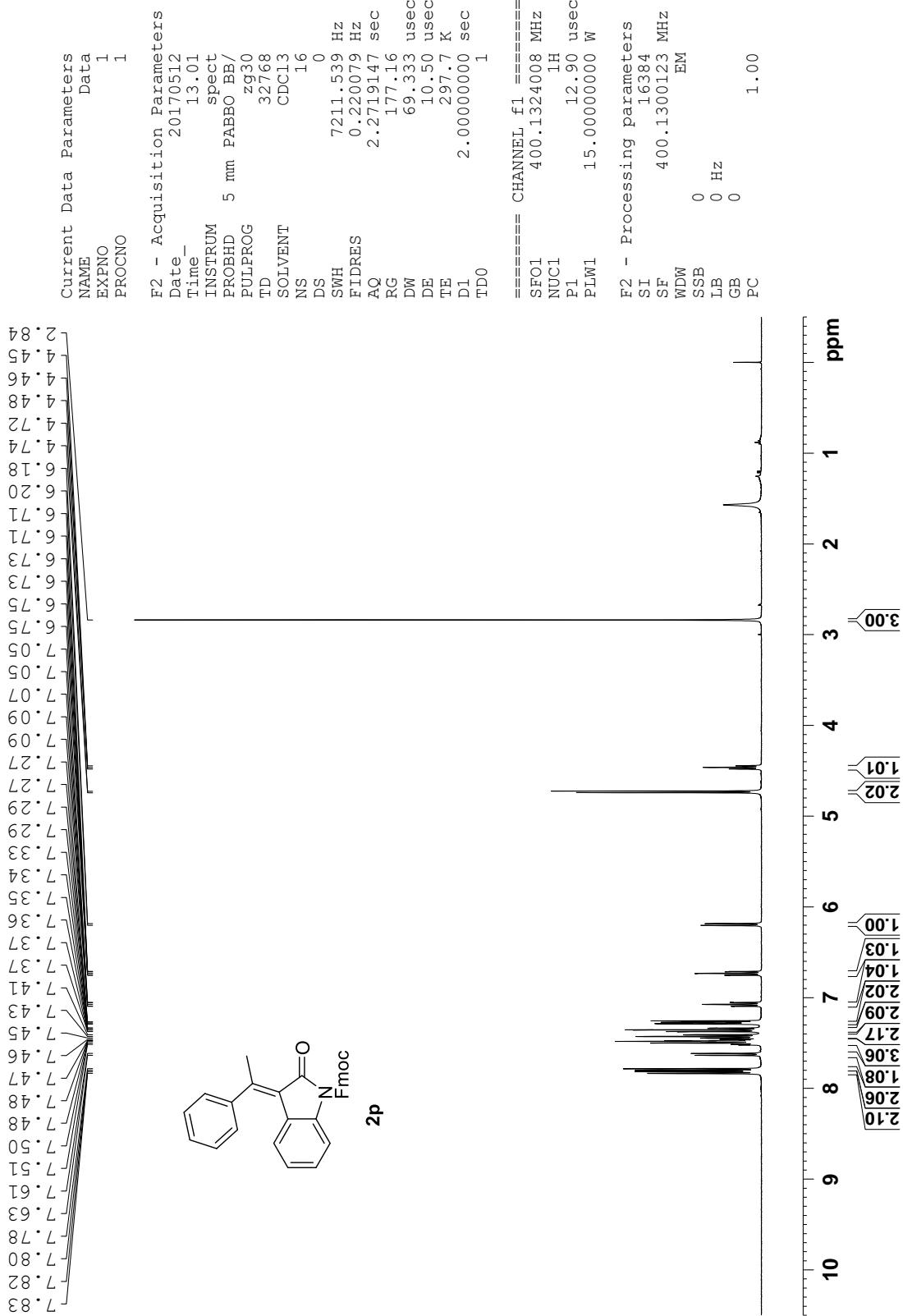
===== CHANNEL f2 =====  
 CPDPRG[2] waltz16  
 NUC2 1H  
 PCPD2 90.00 usec  
 PL2 1.80 dB  
 PLL2 17.00 dB  
 PL13 20.00 dB  
 SFO2 400.1316005 MHz

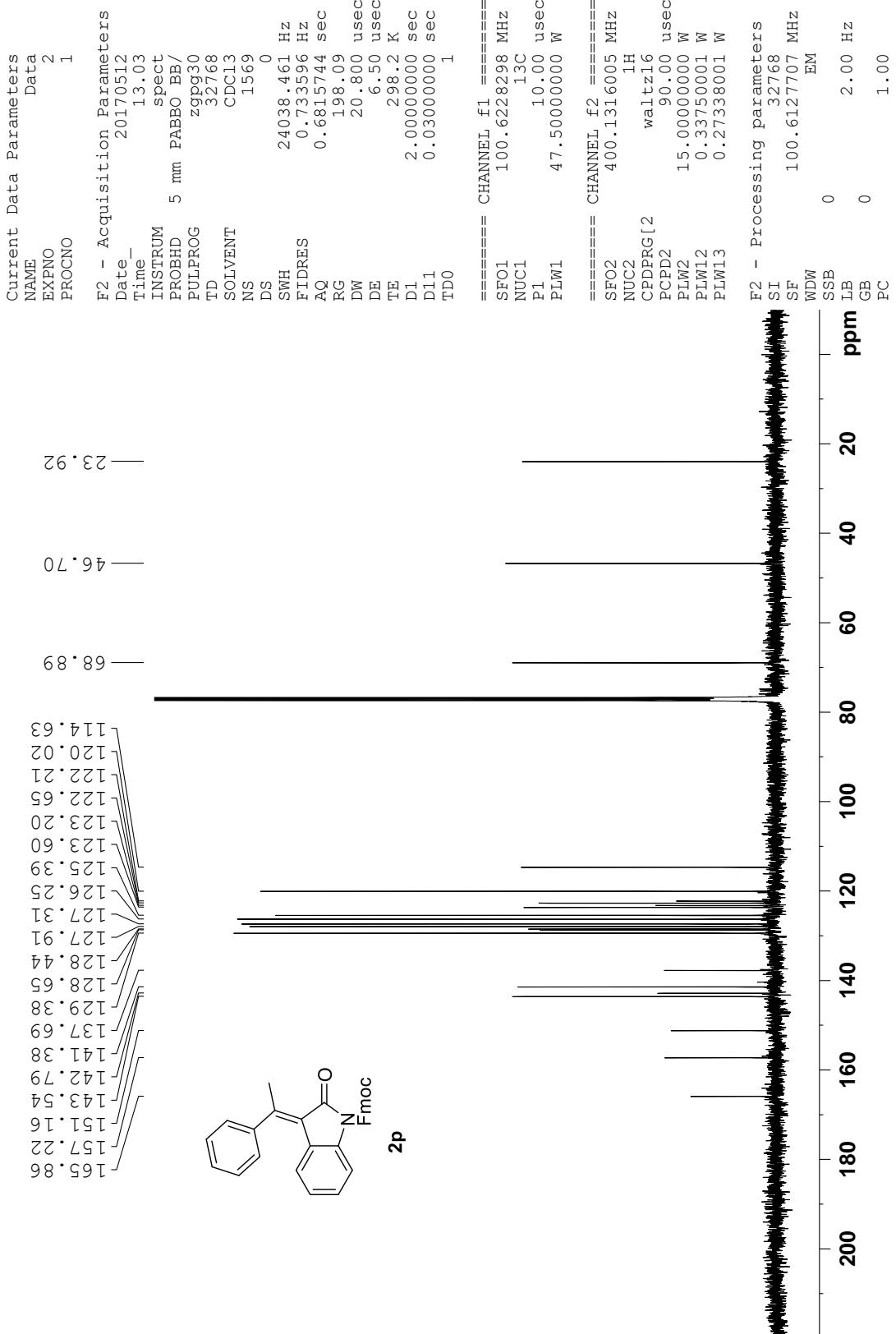
F2 - Processing parameters  
 SI 32768  
 SF 100.6127757 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.00

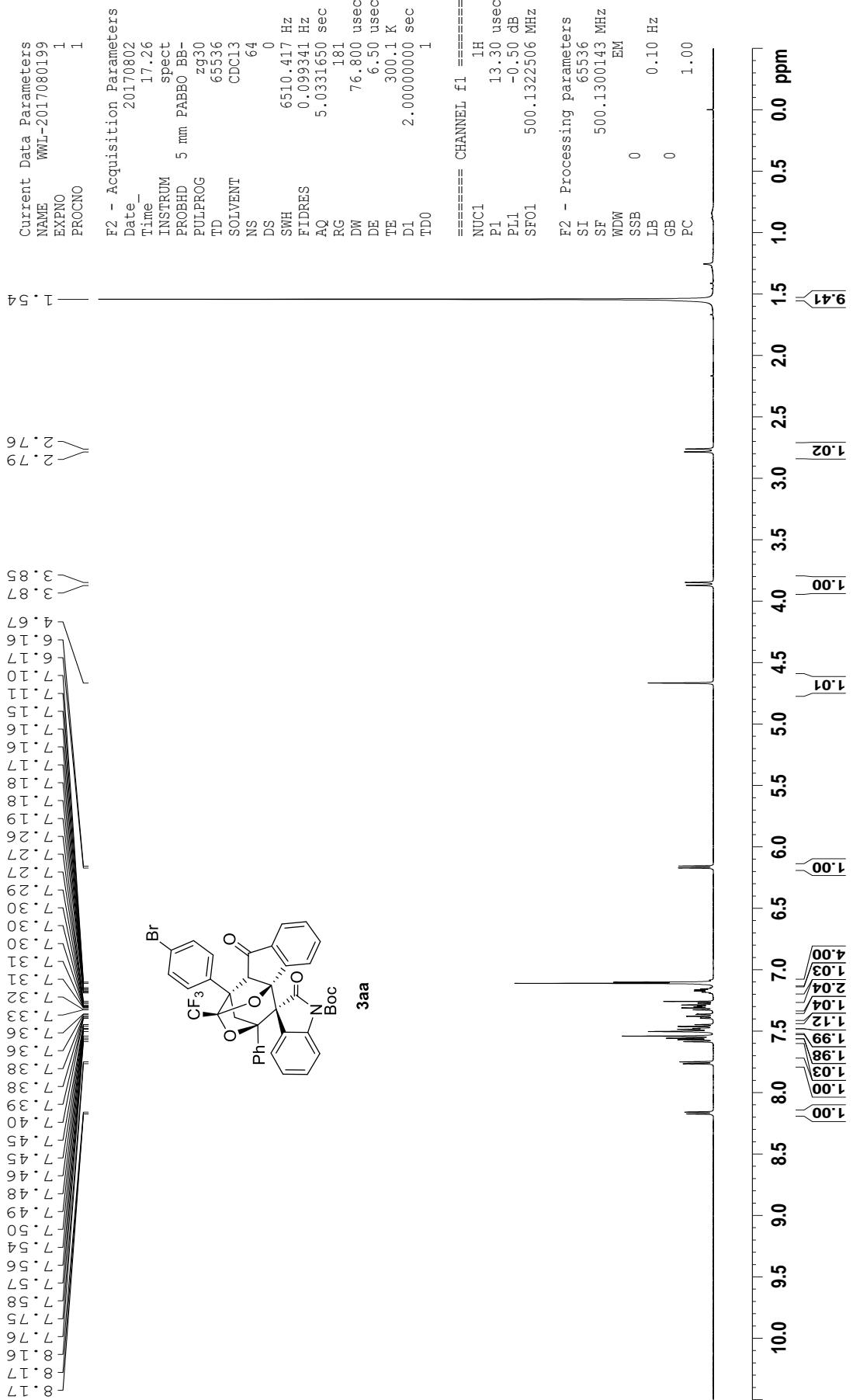


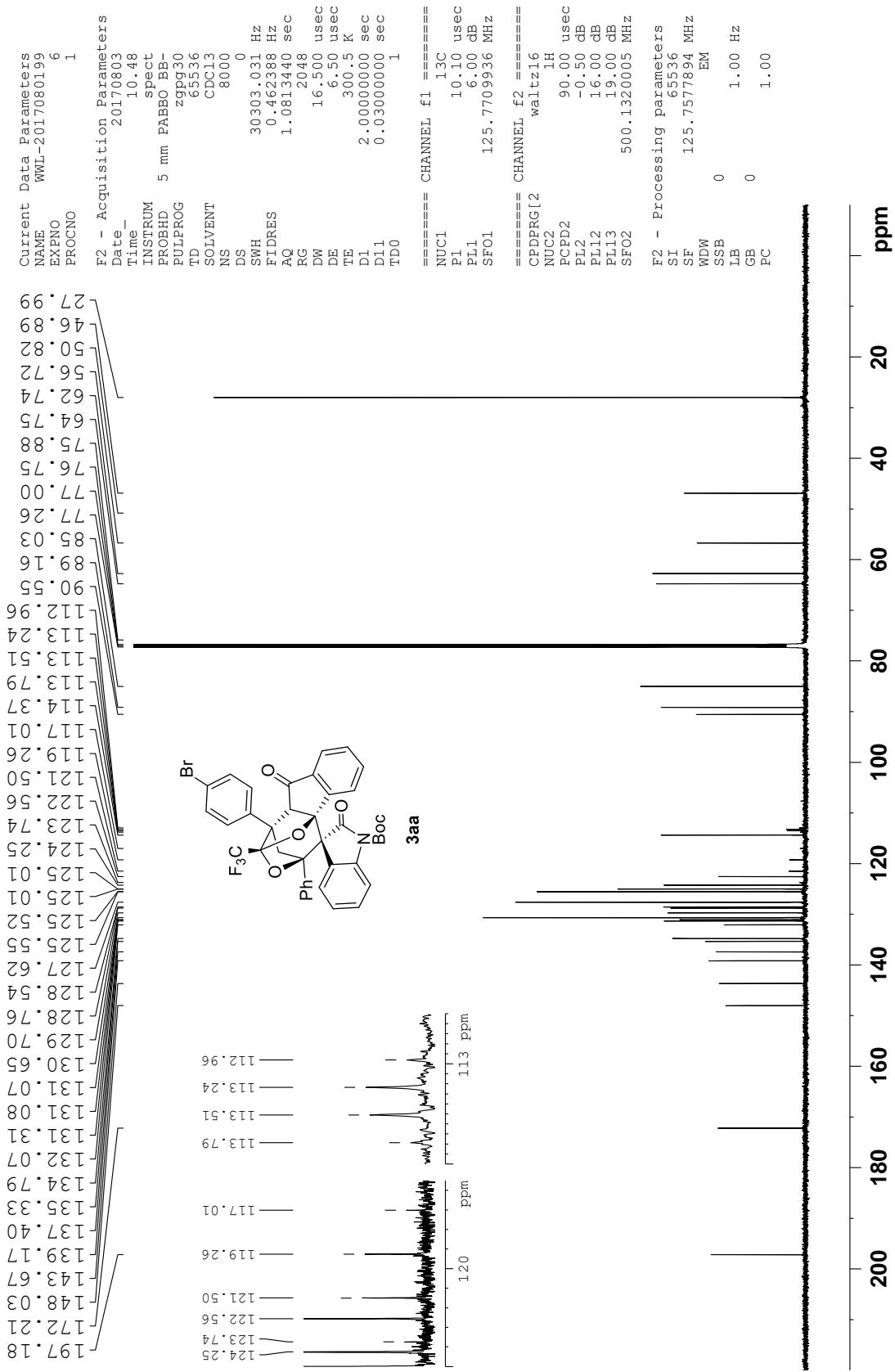


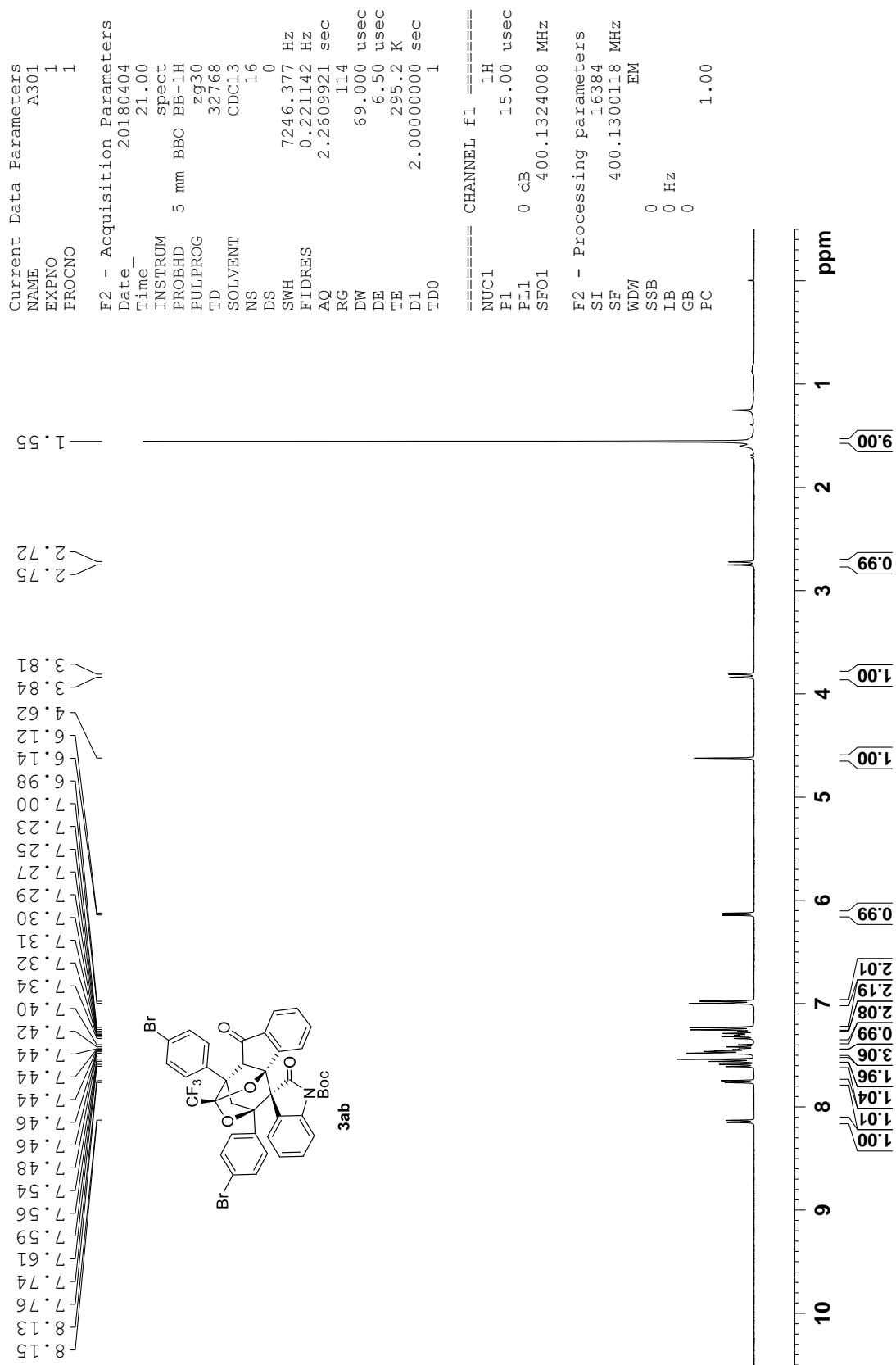


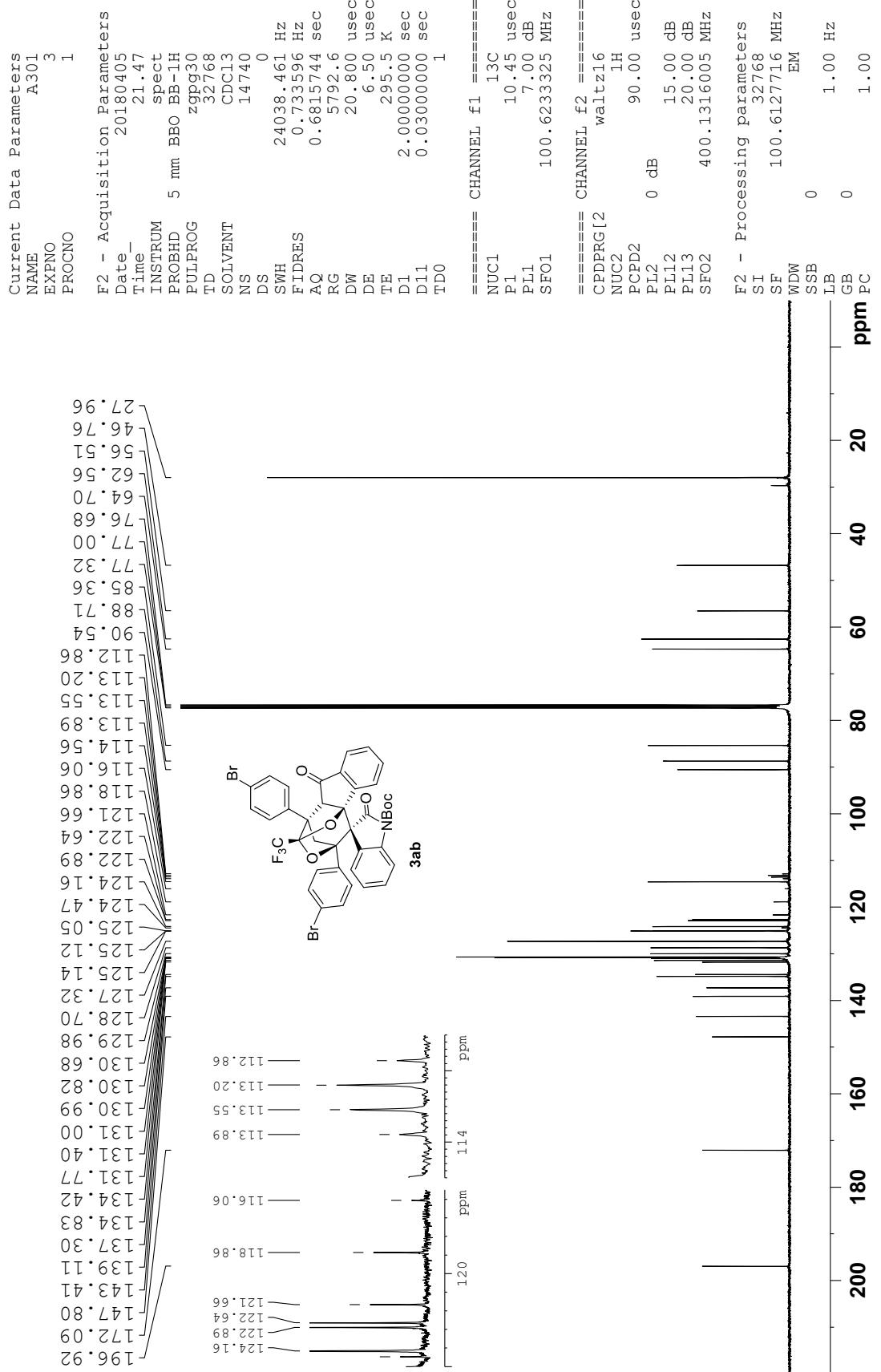


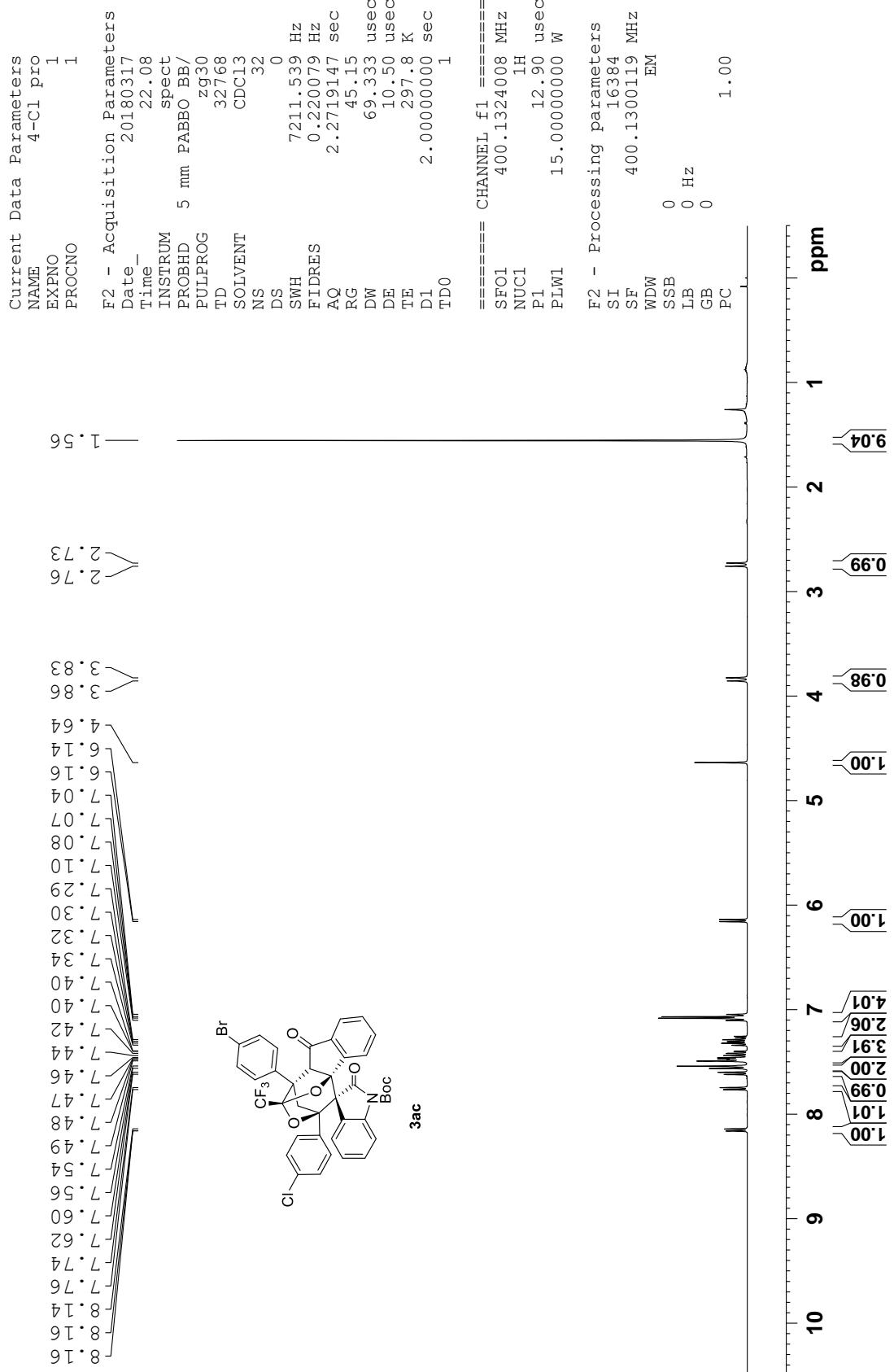


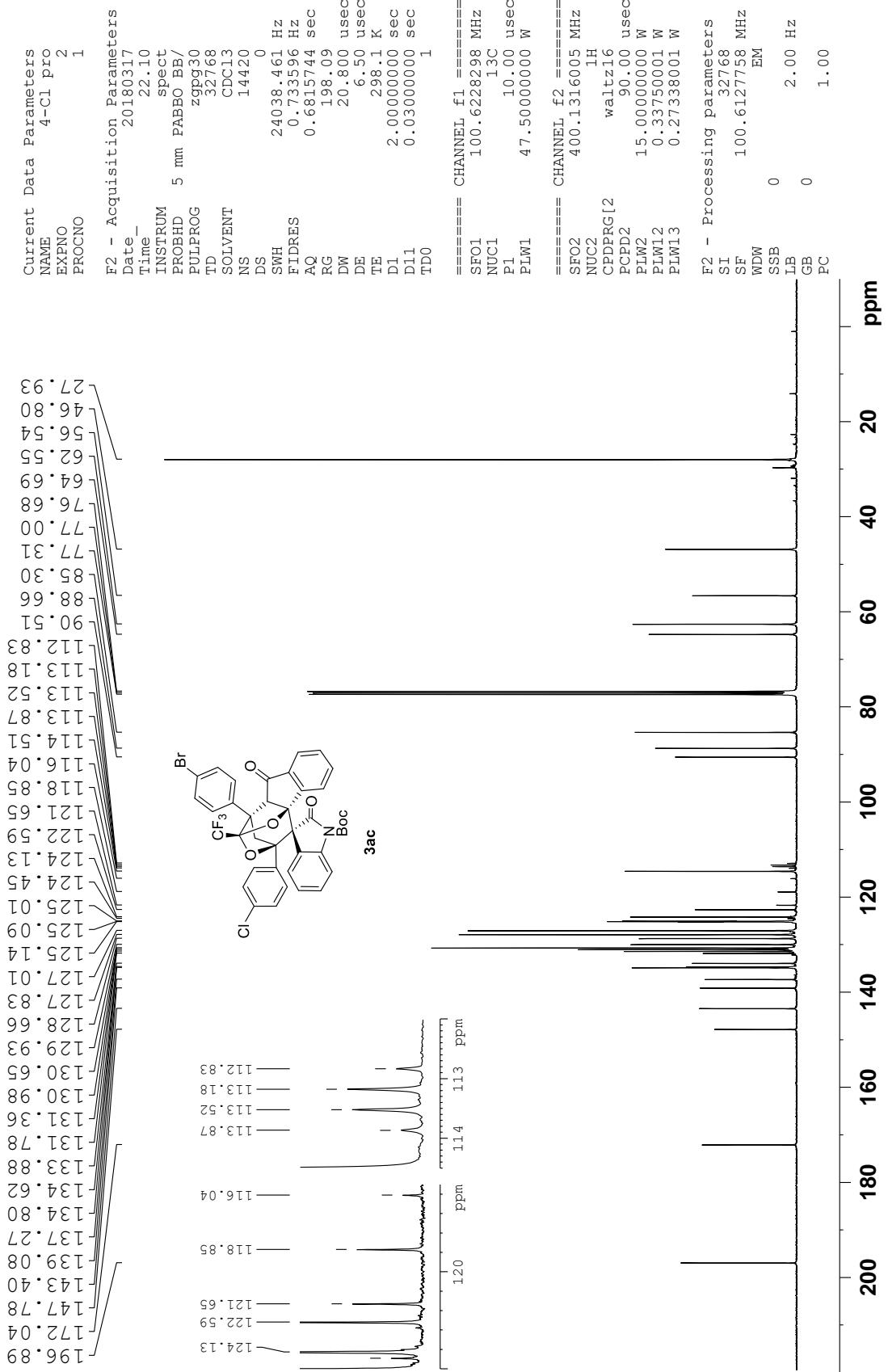


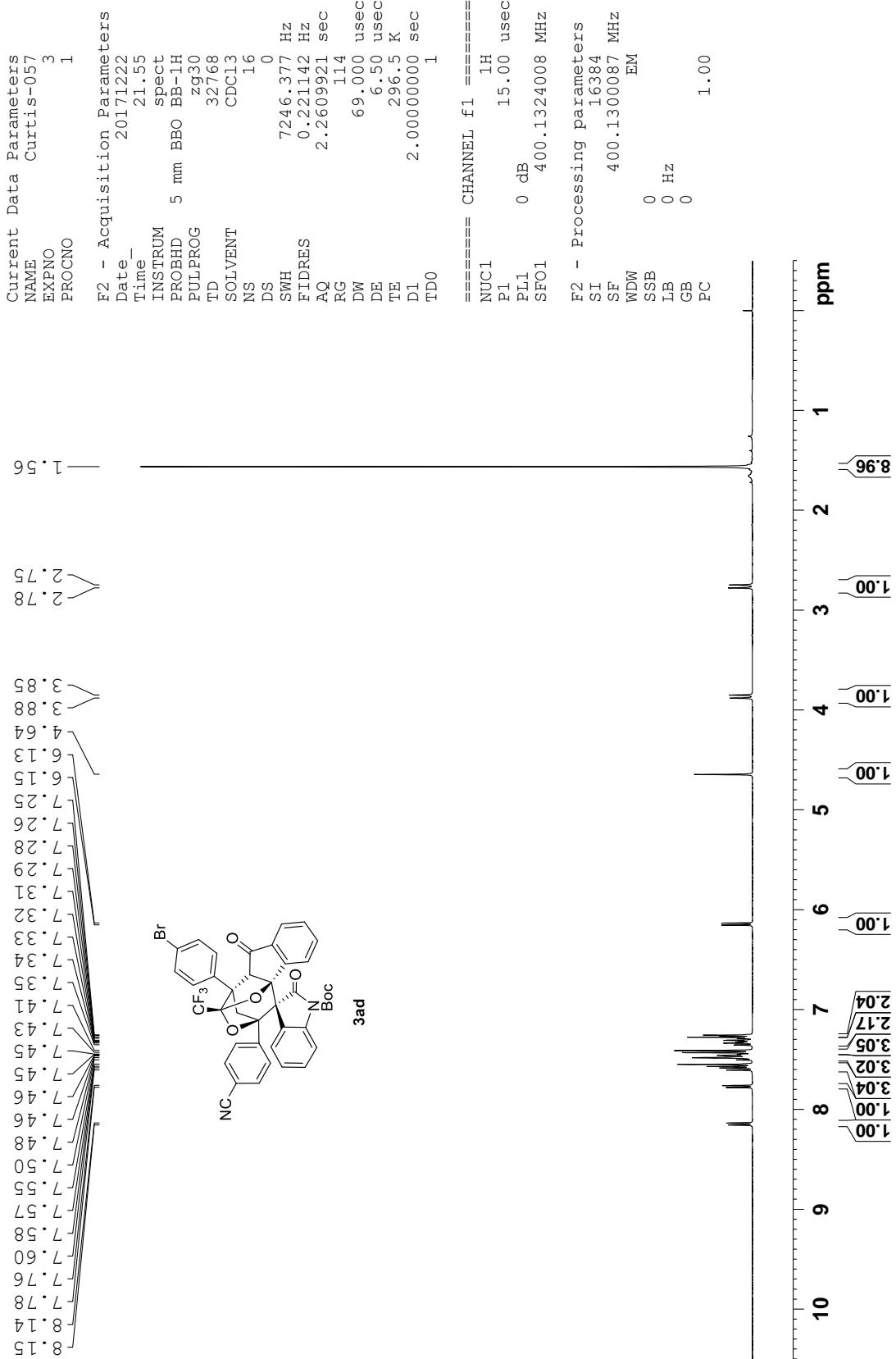


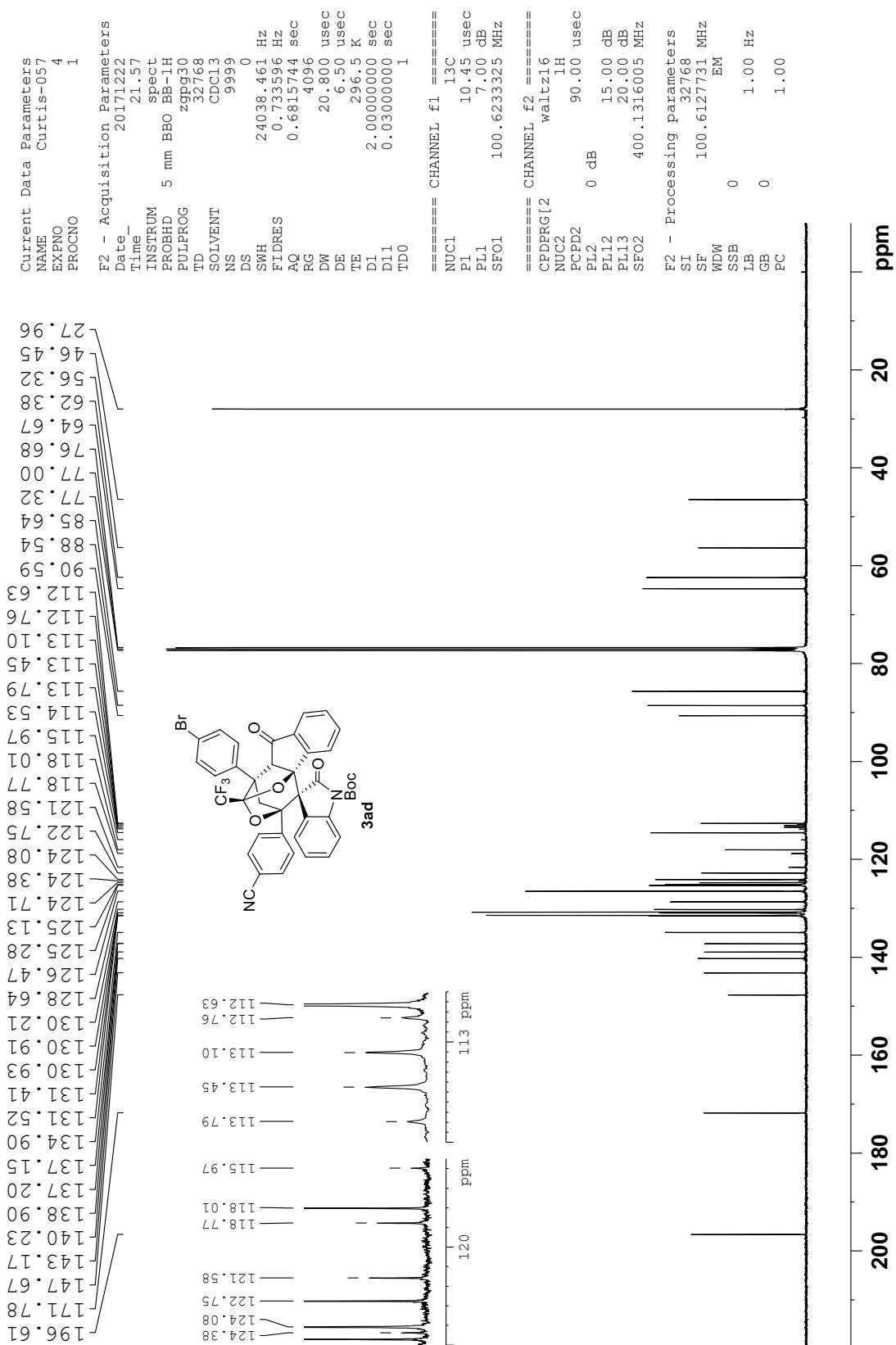


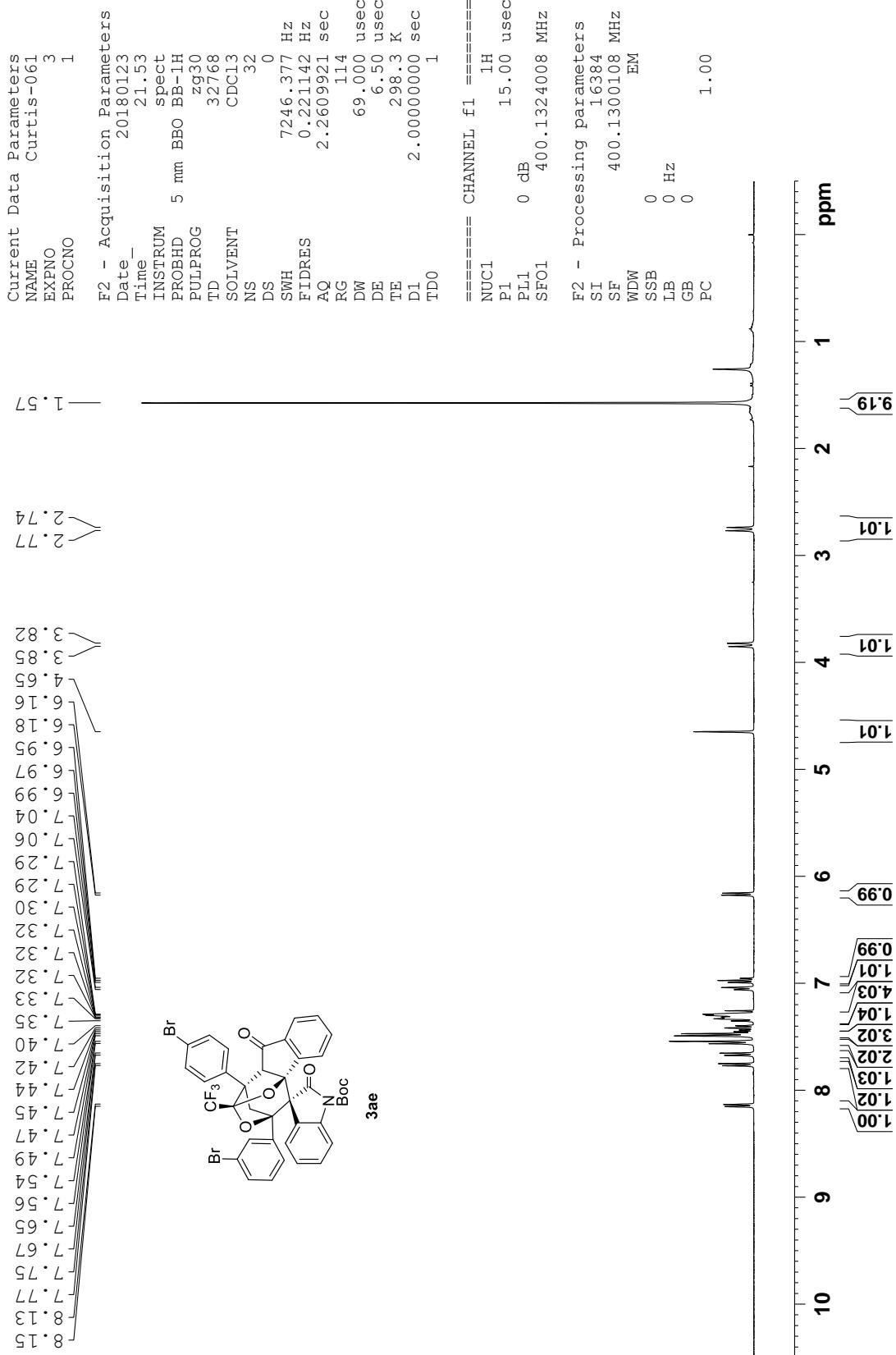


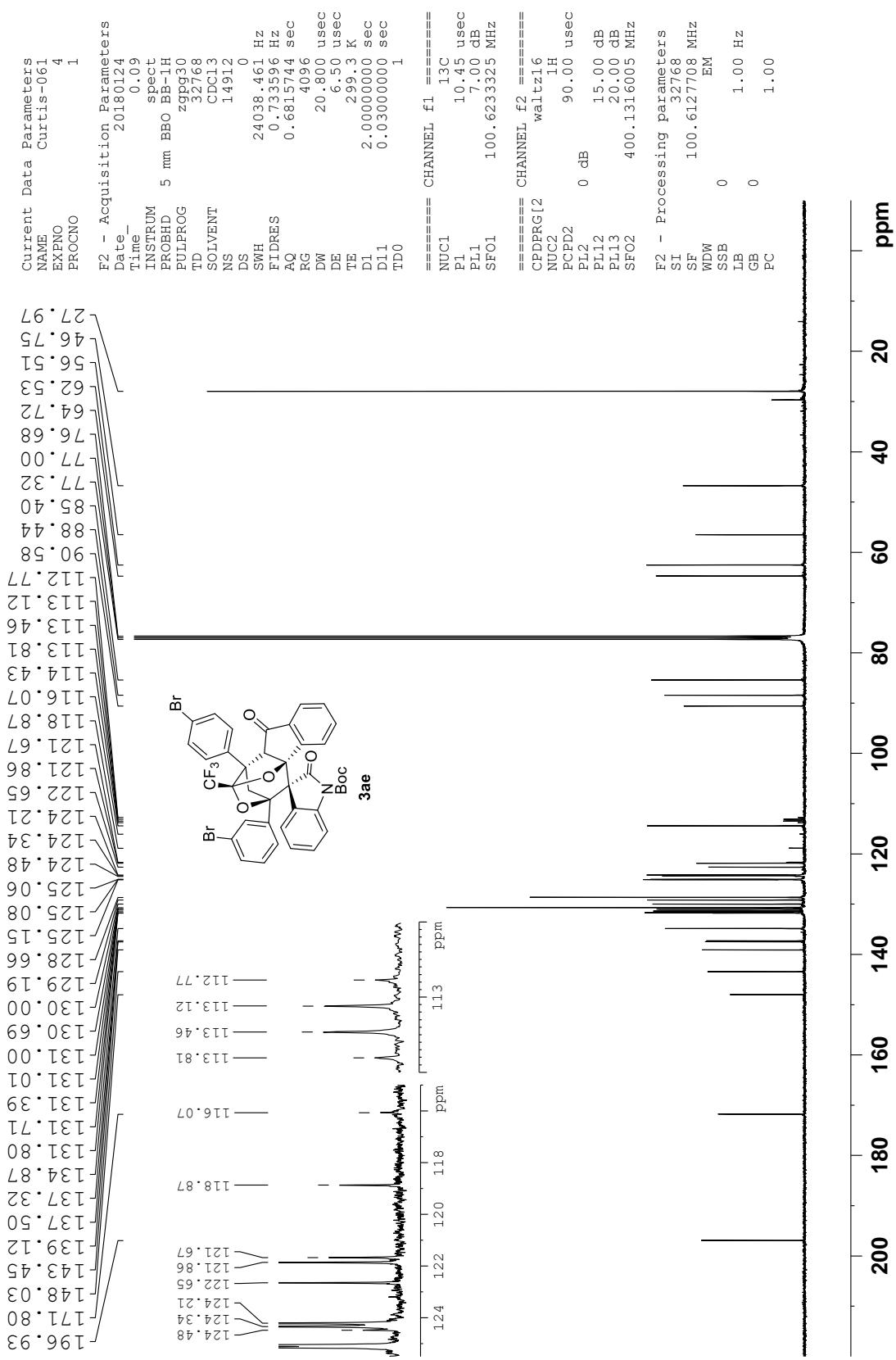


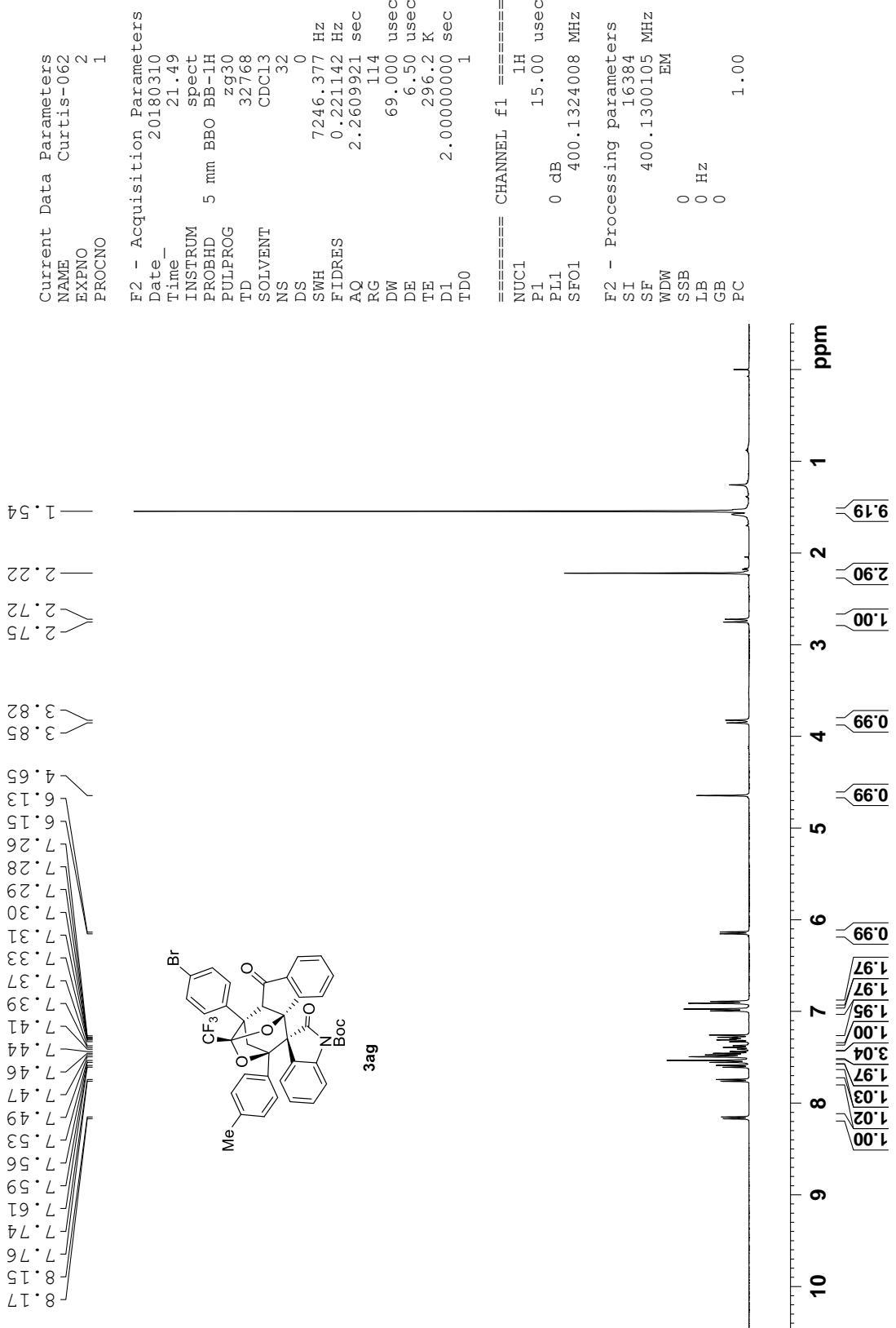


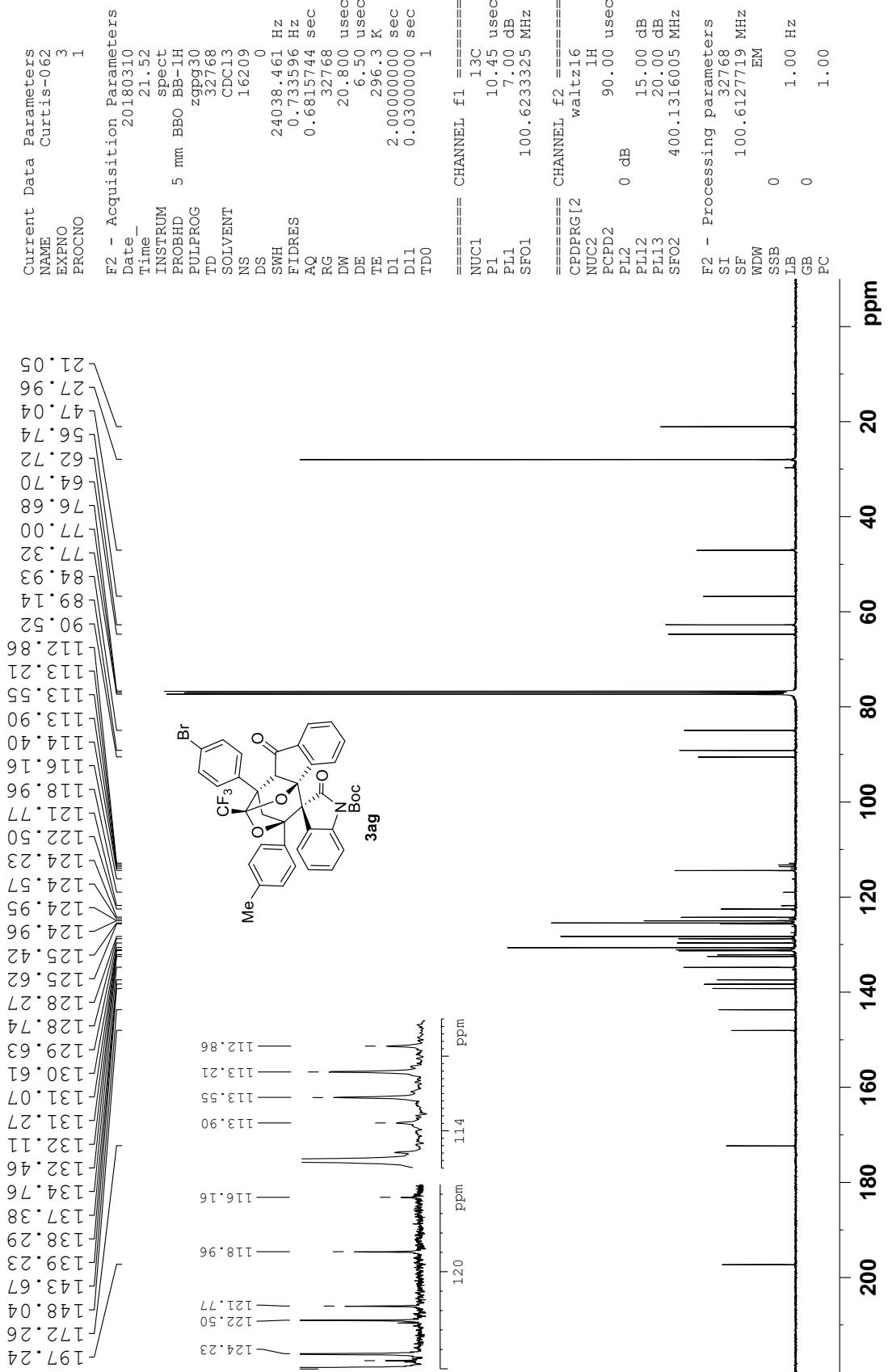


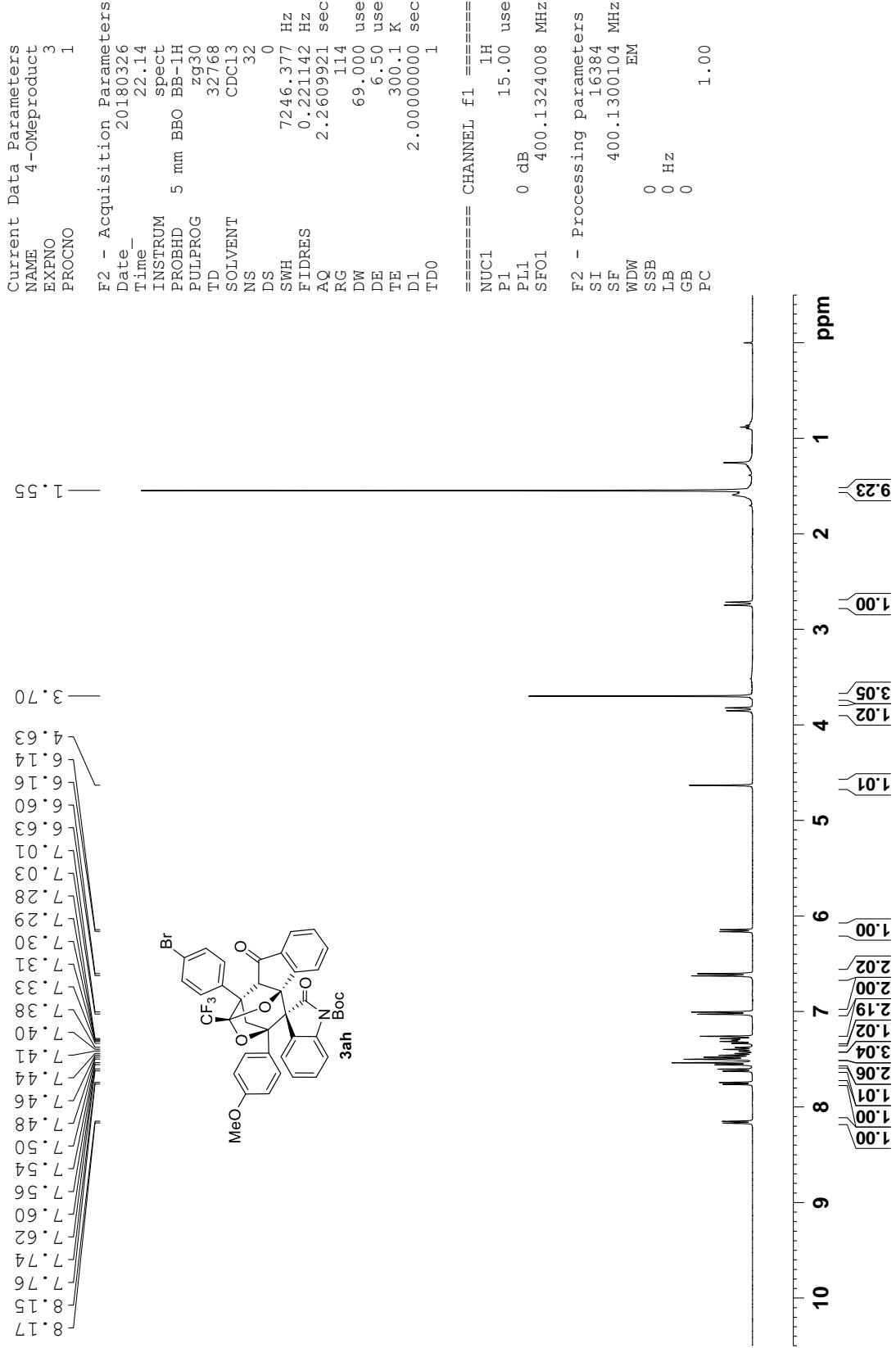


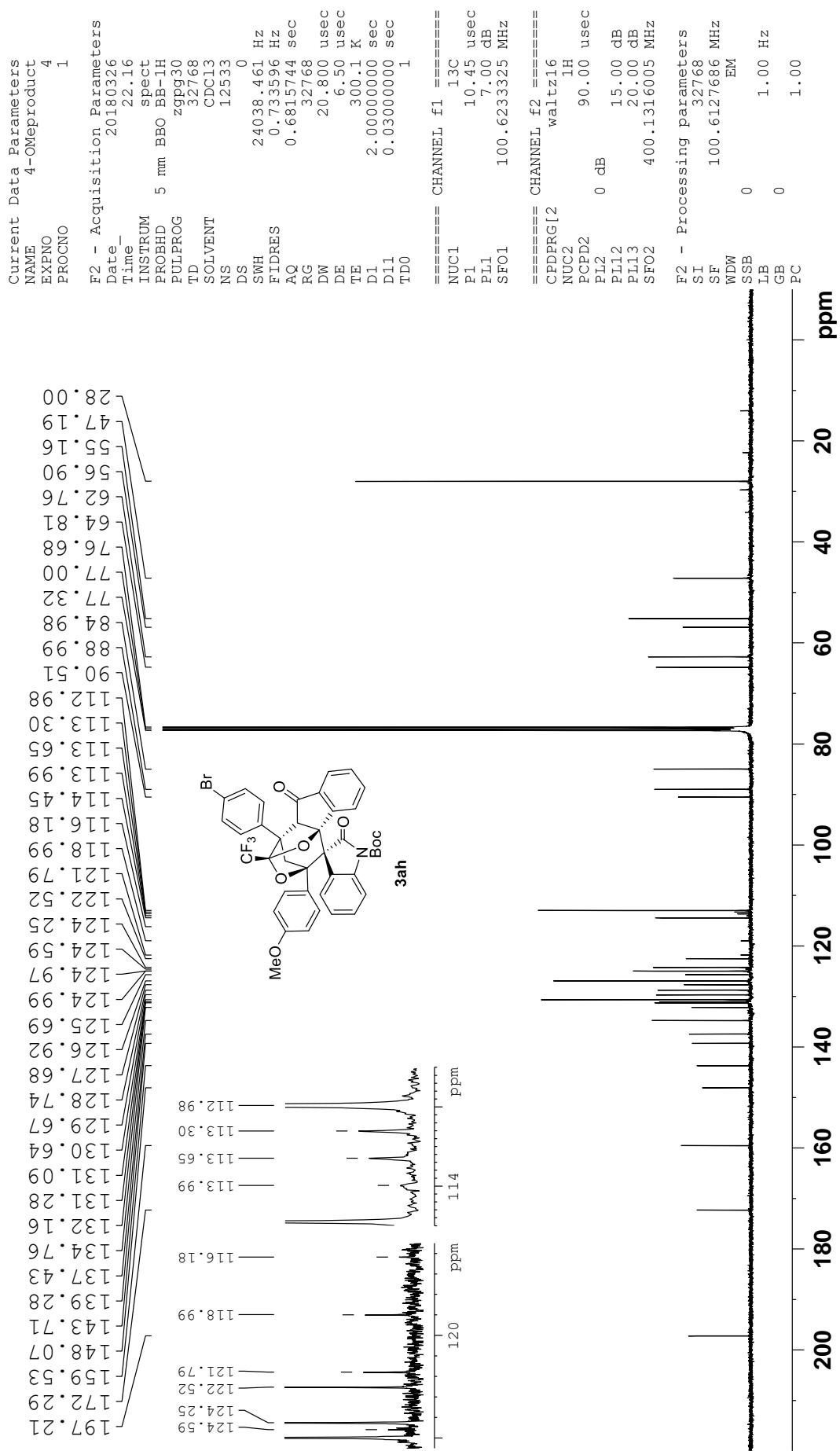


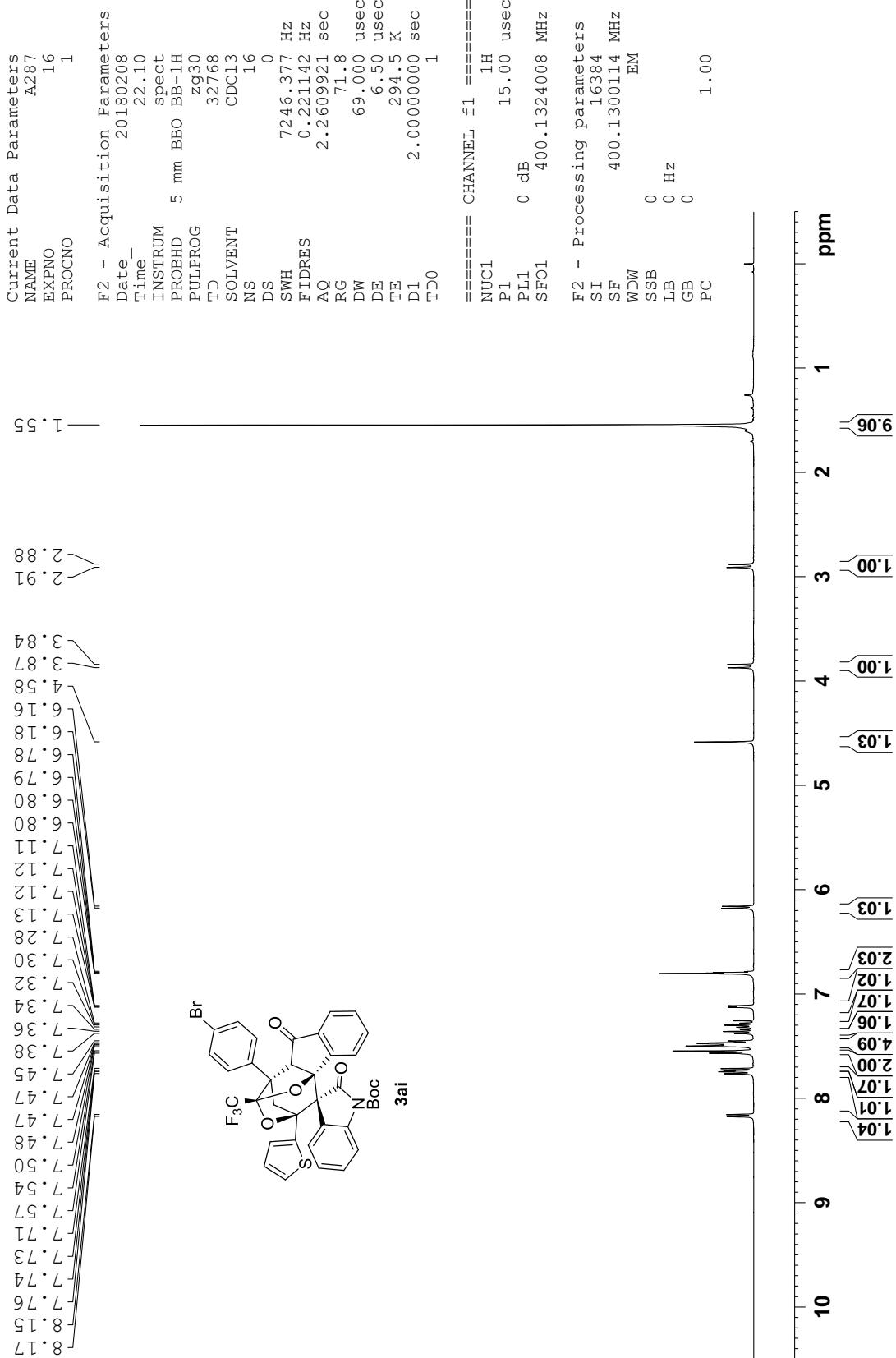


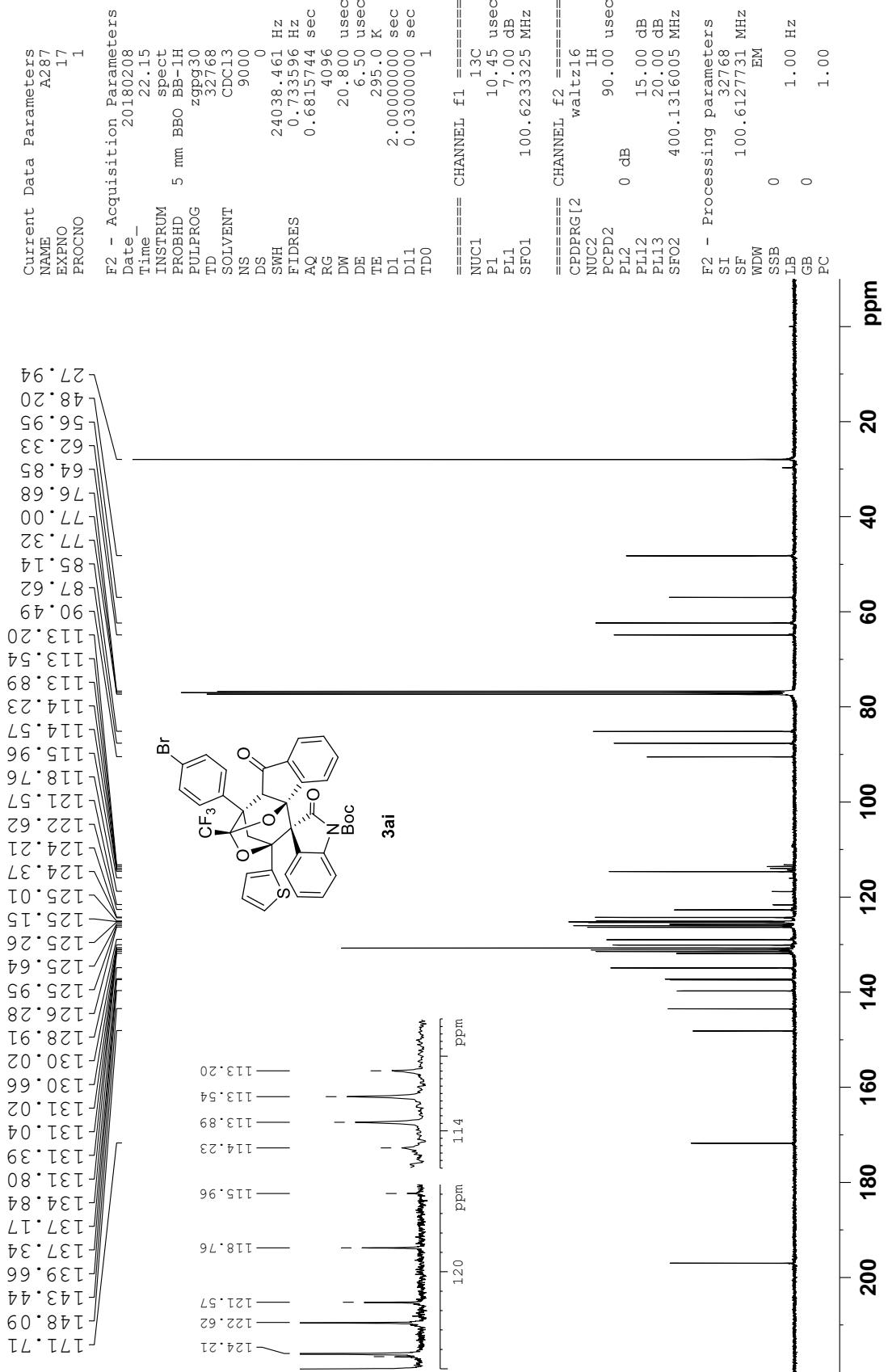


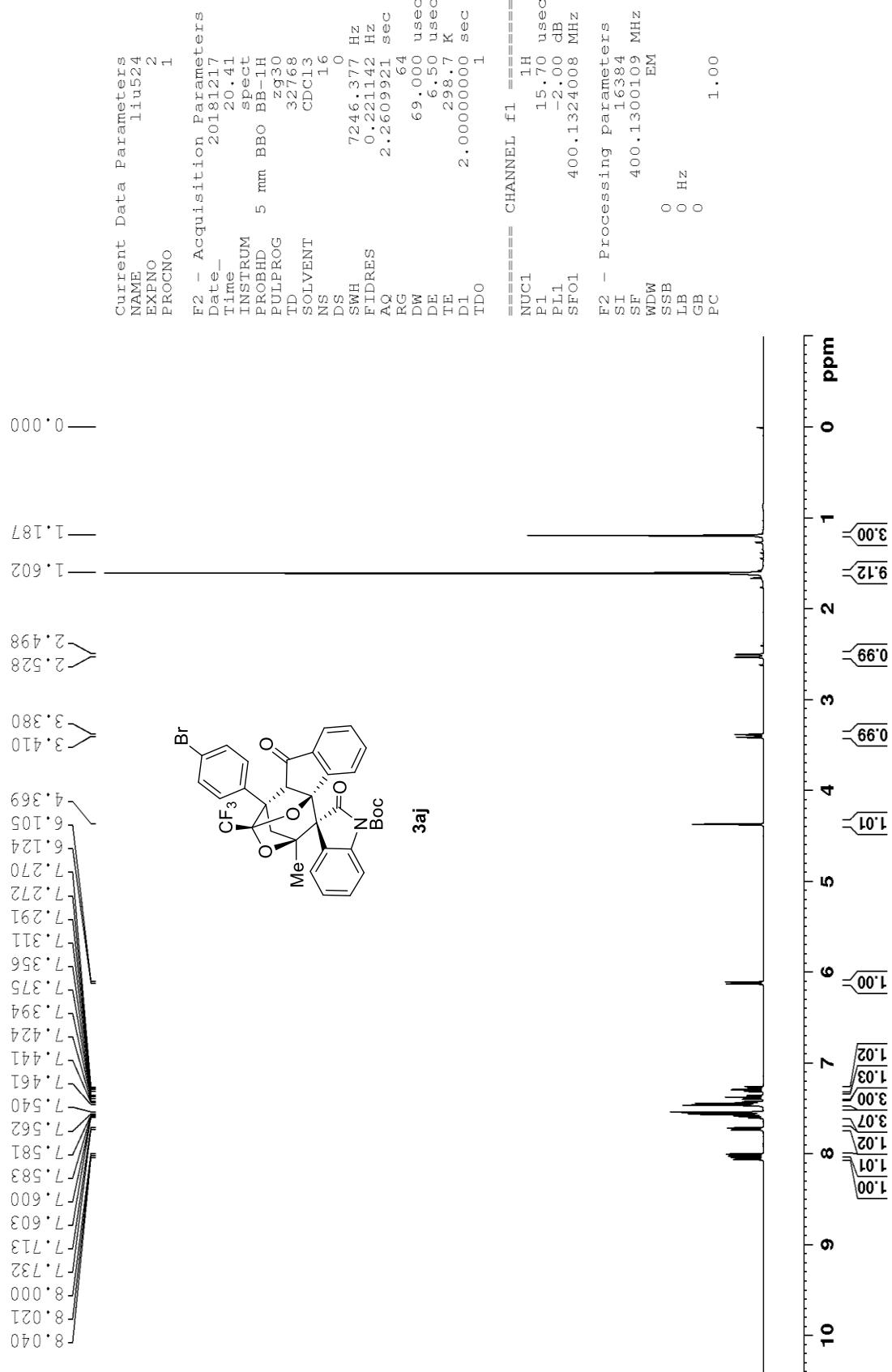


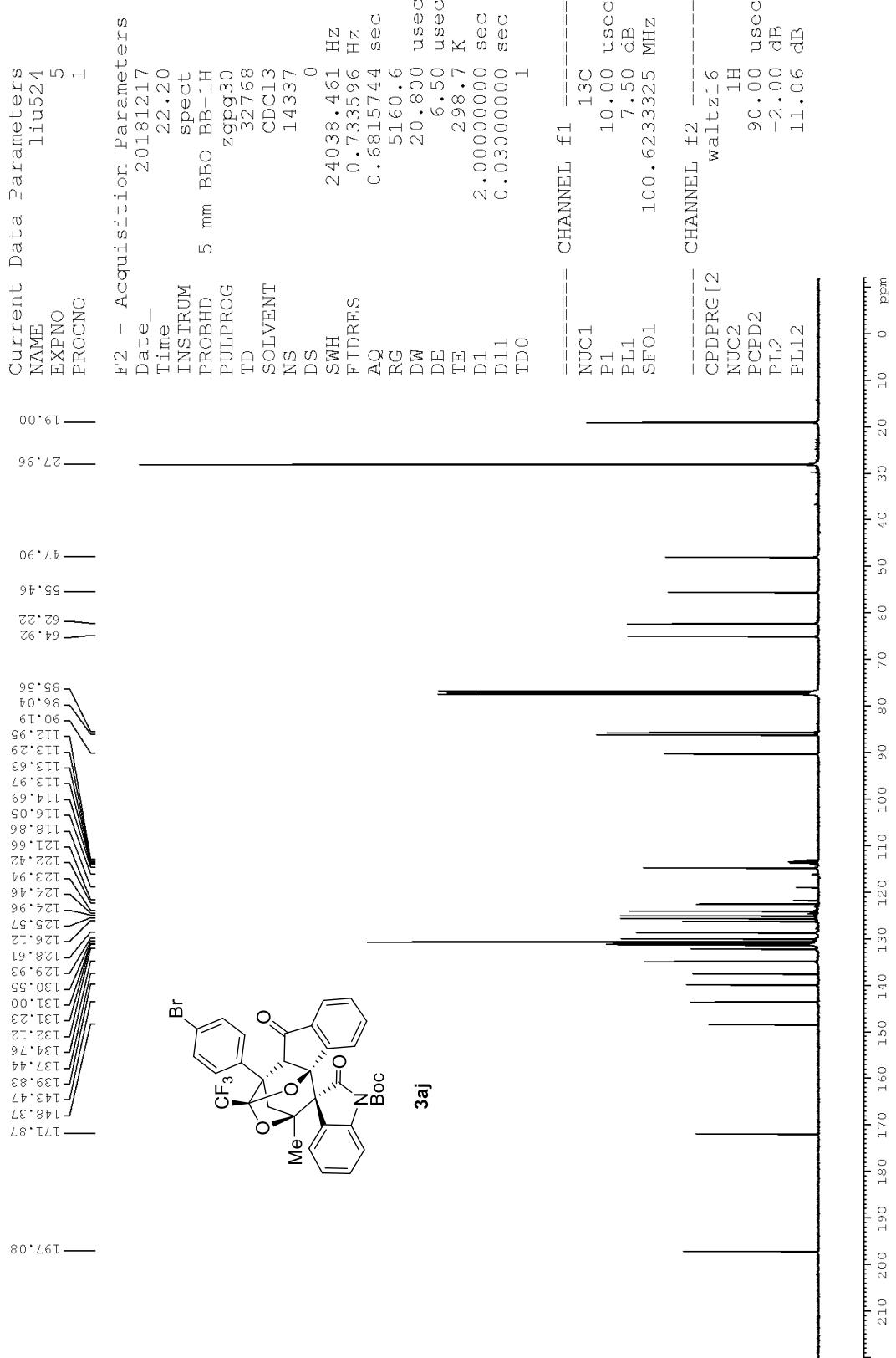


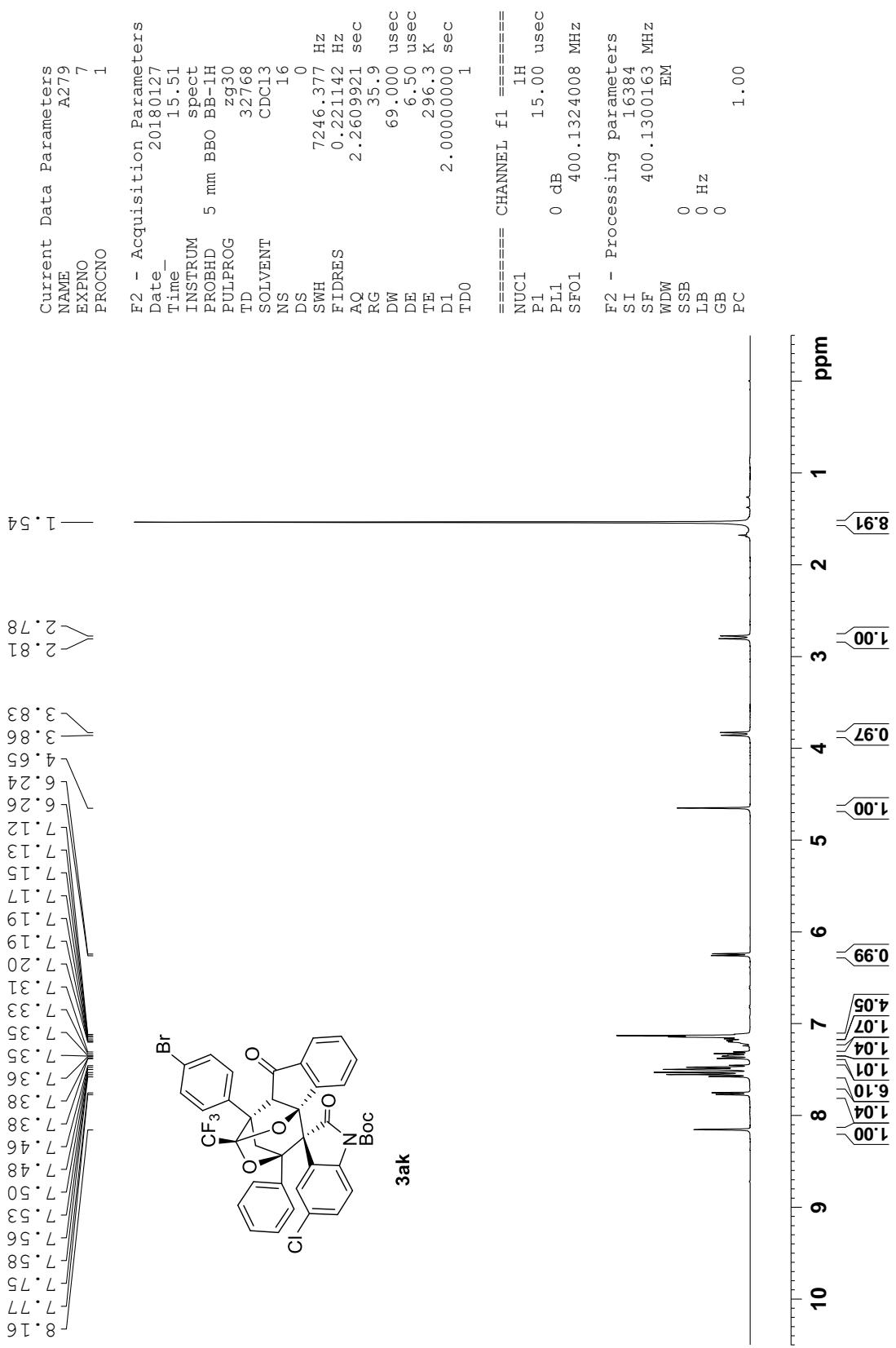


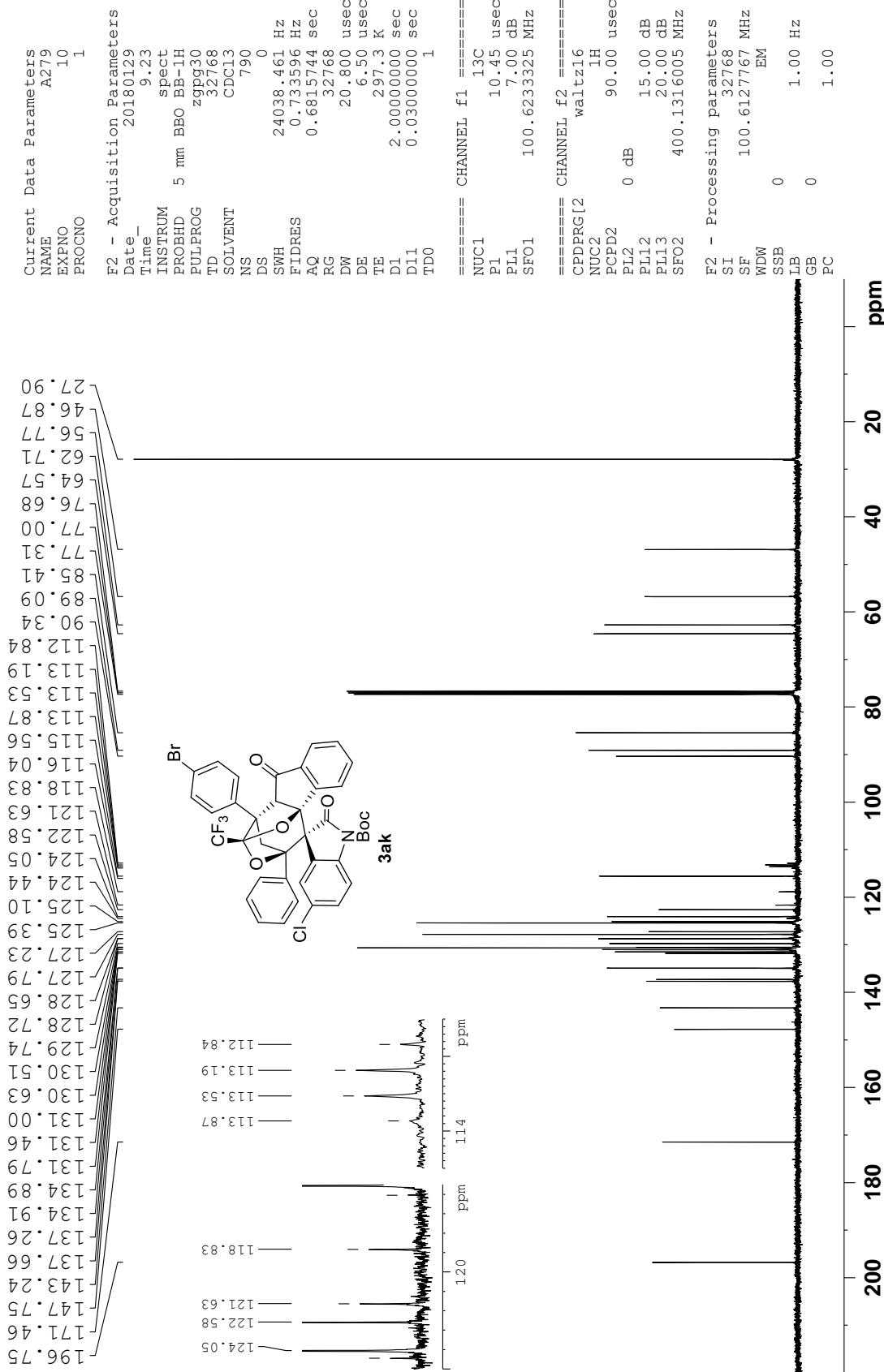


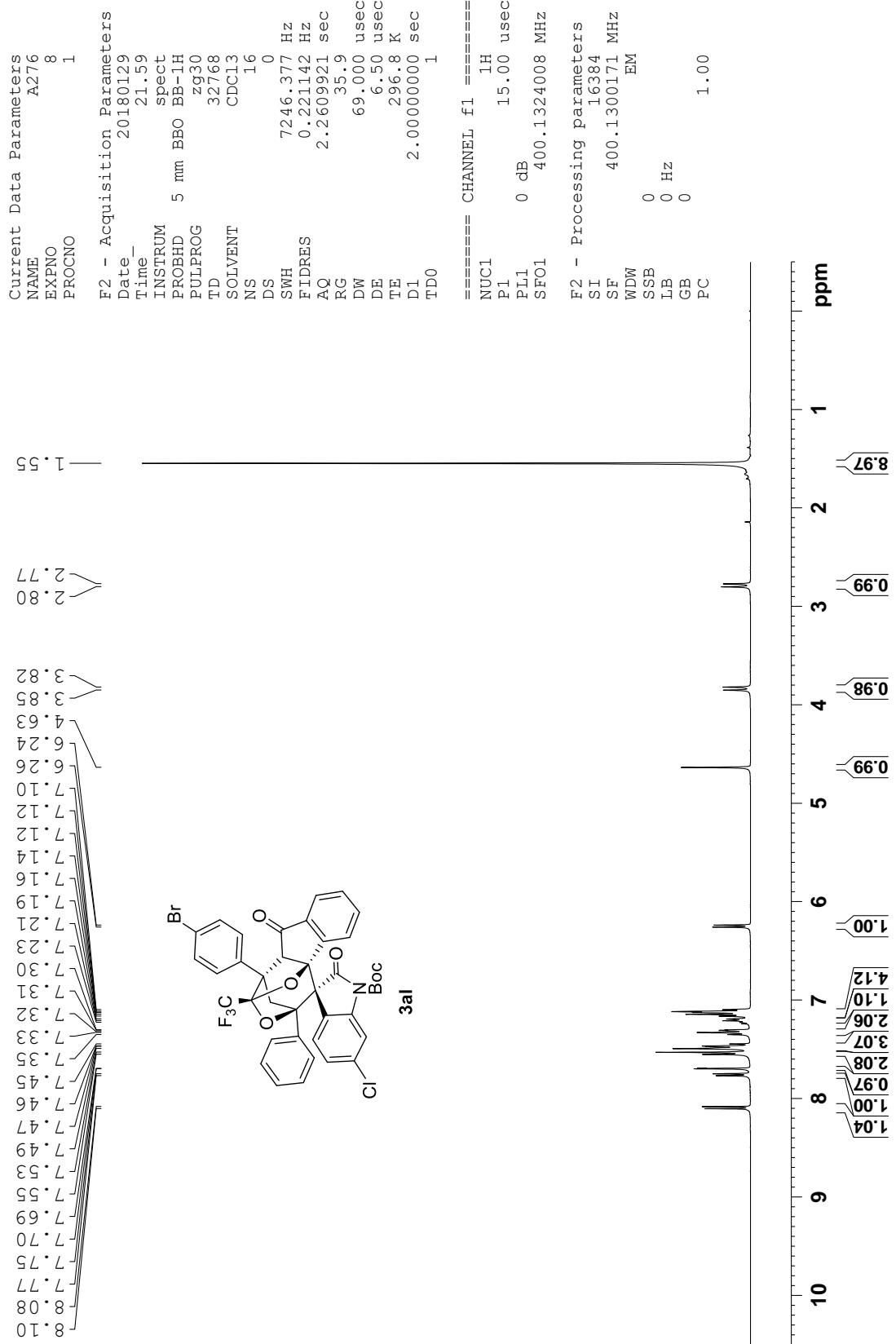


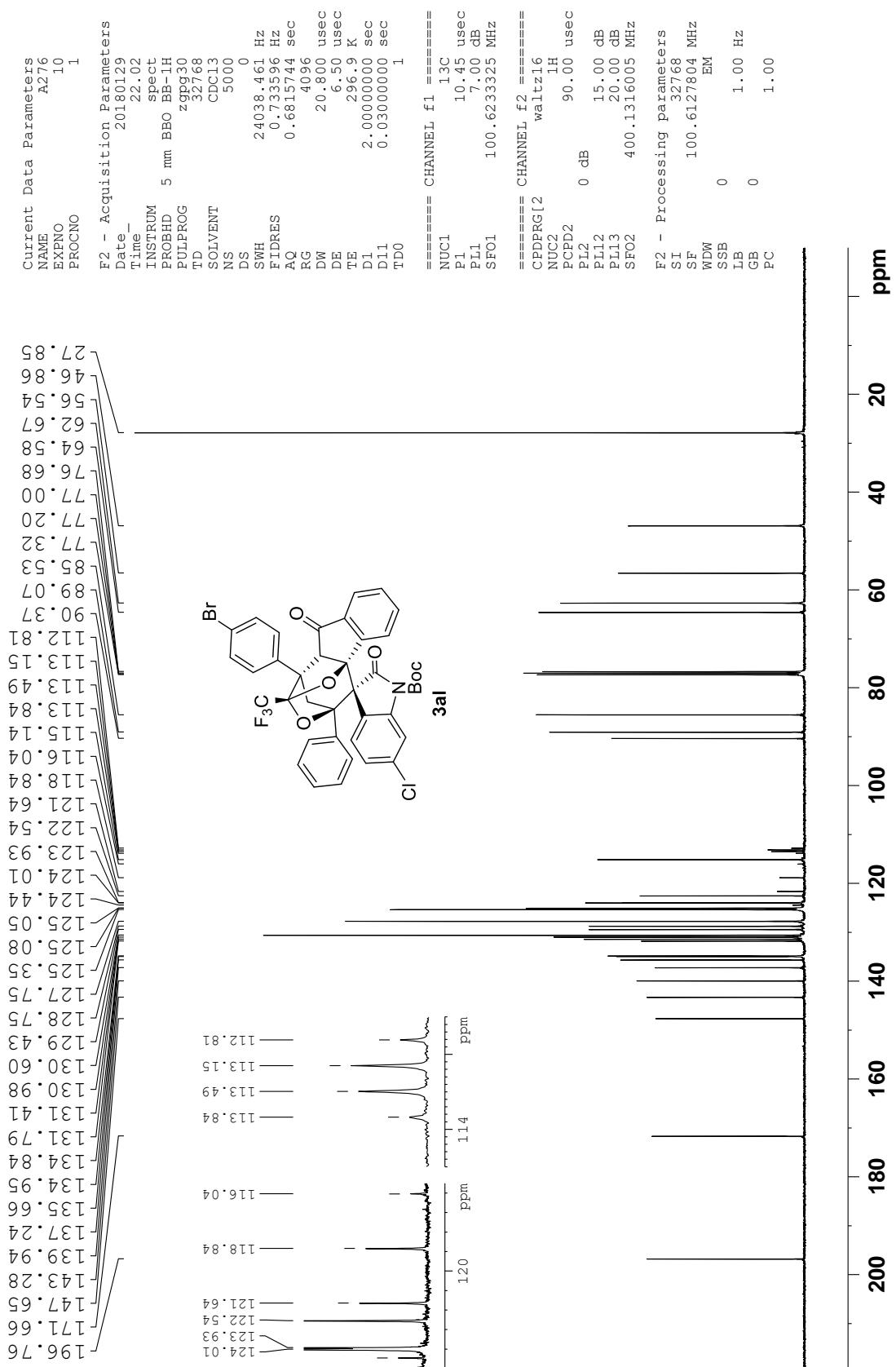


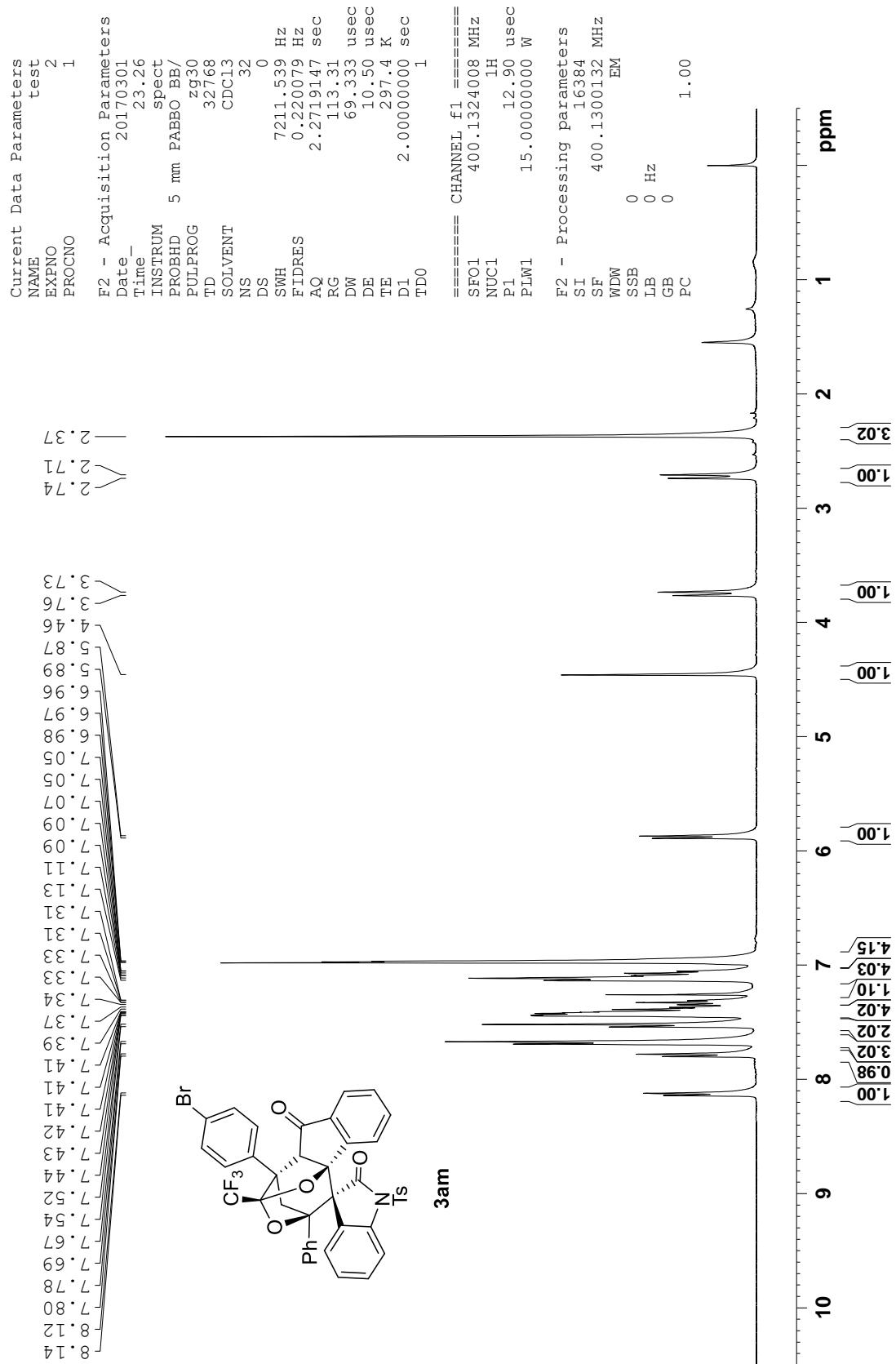


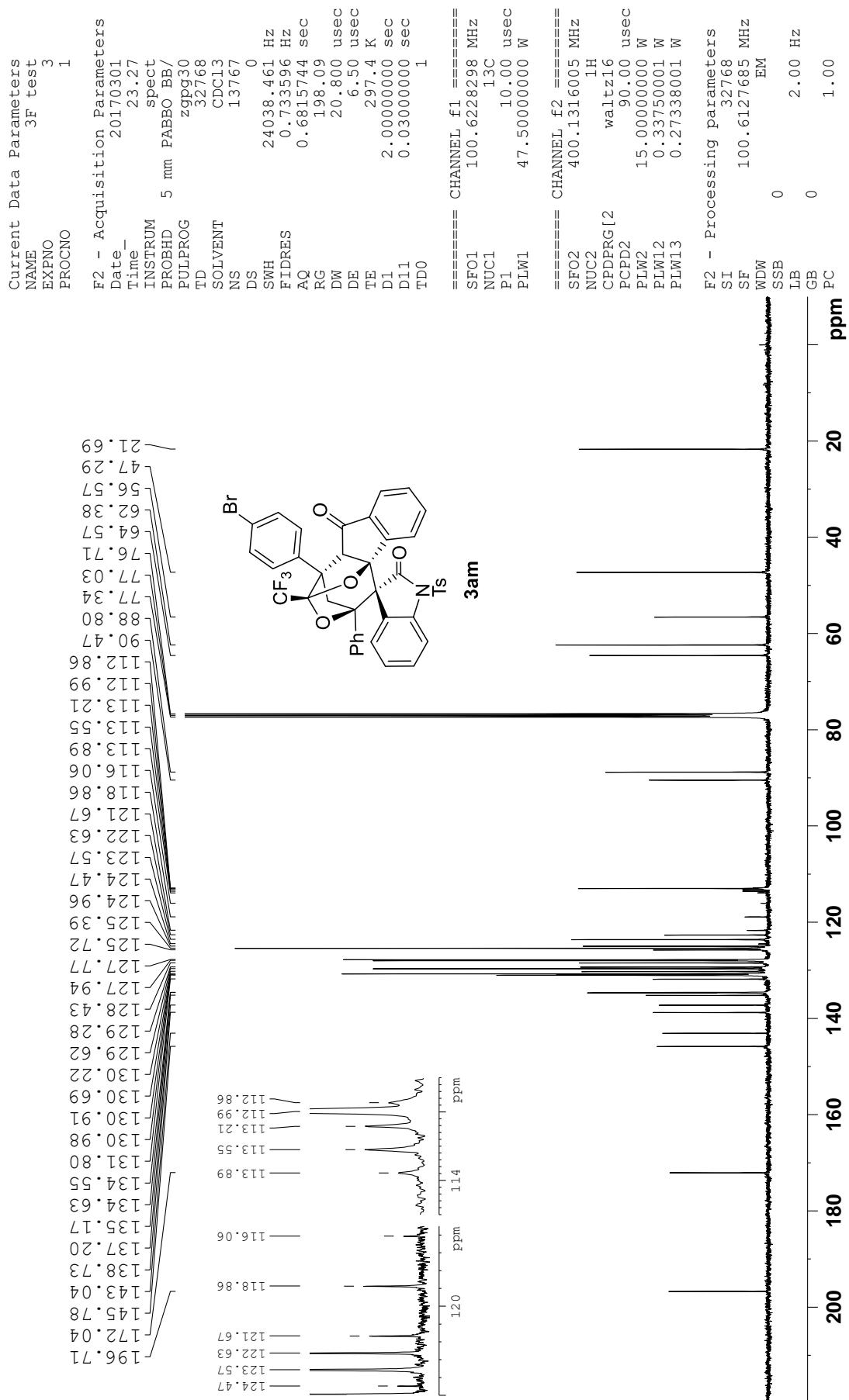


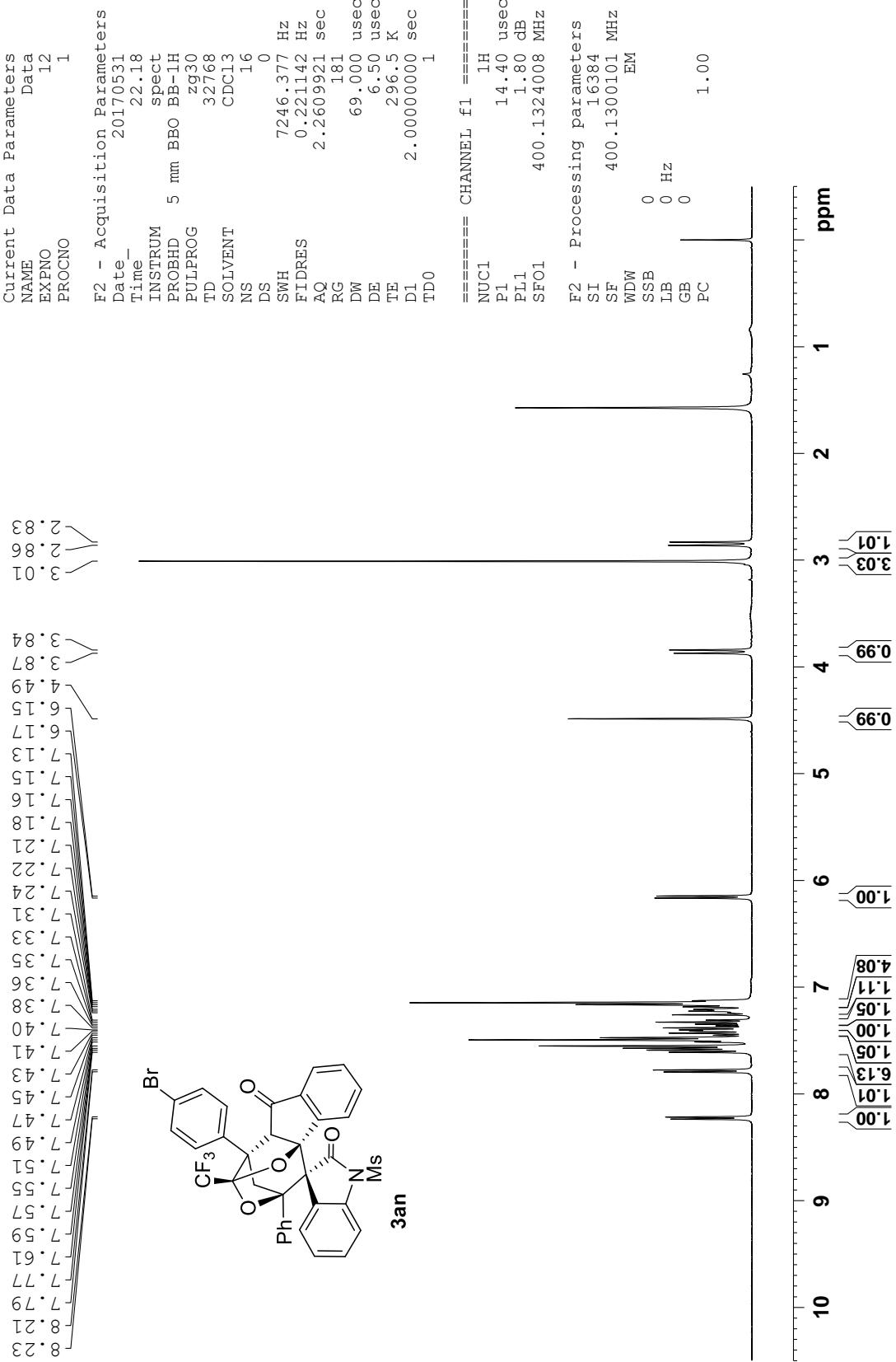


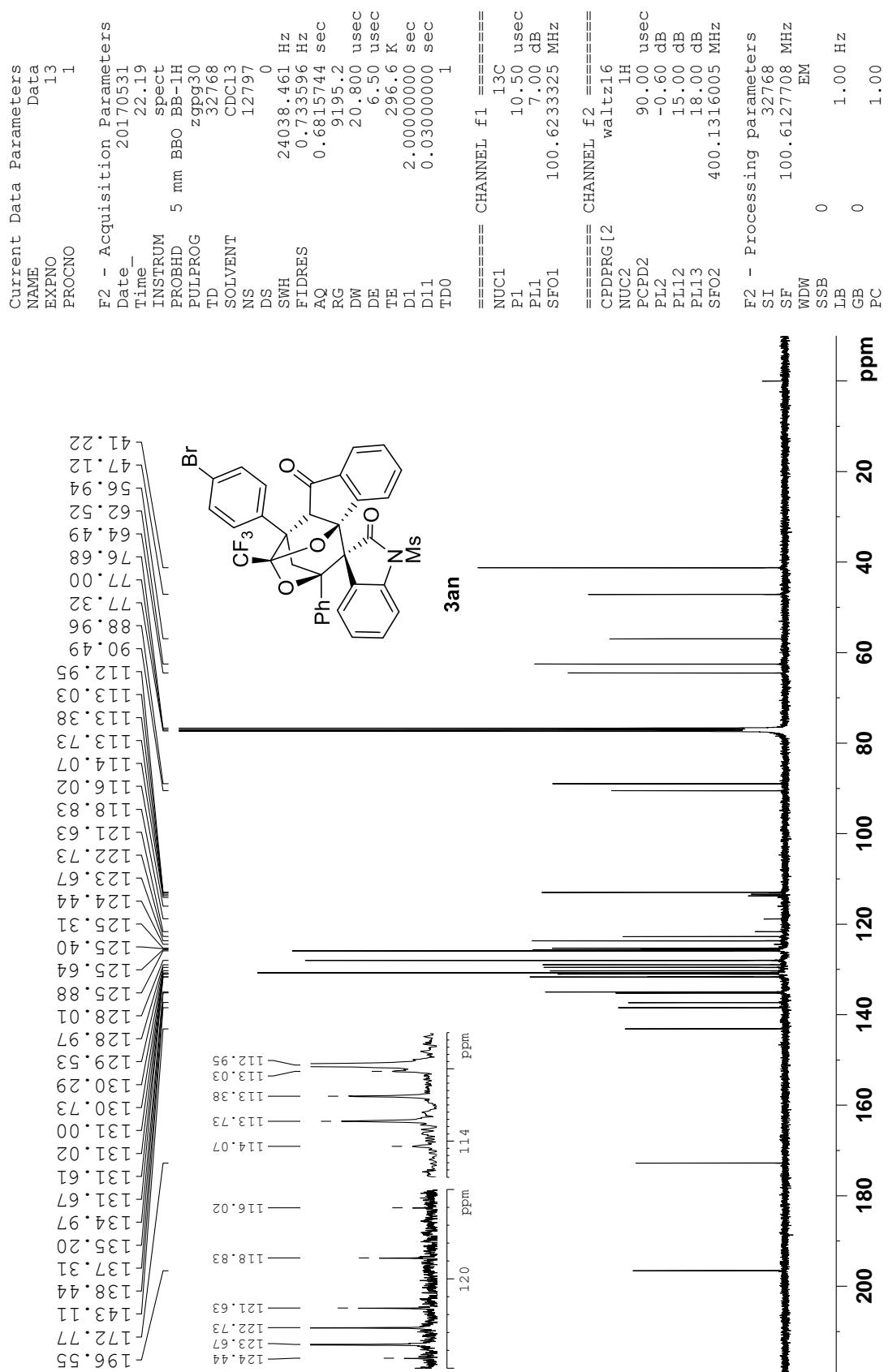


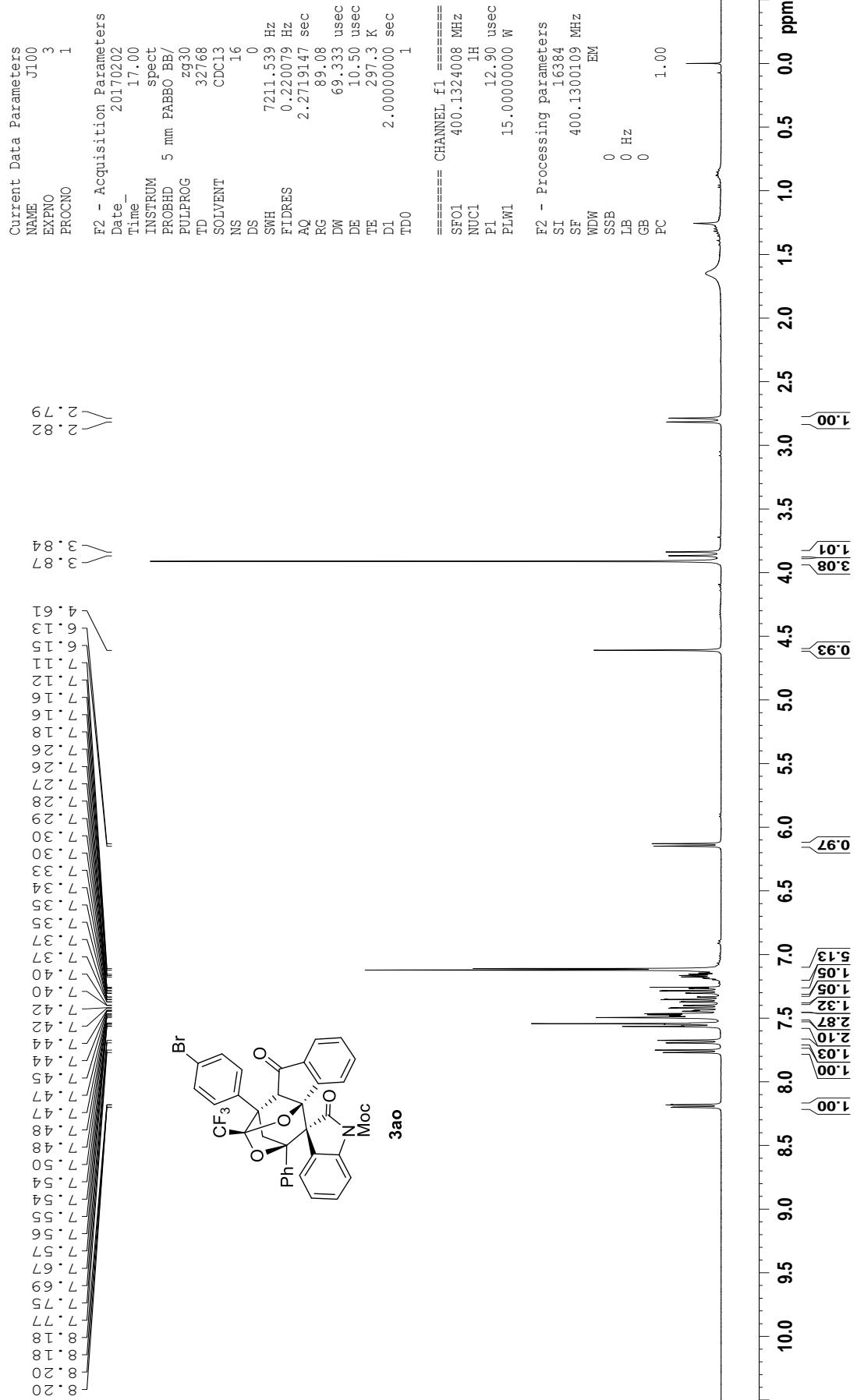


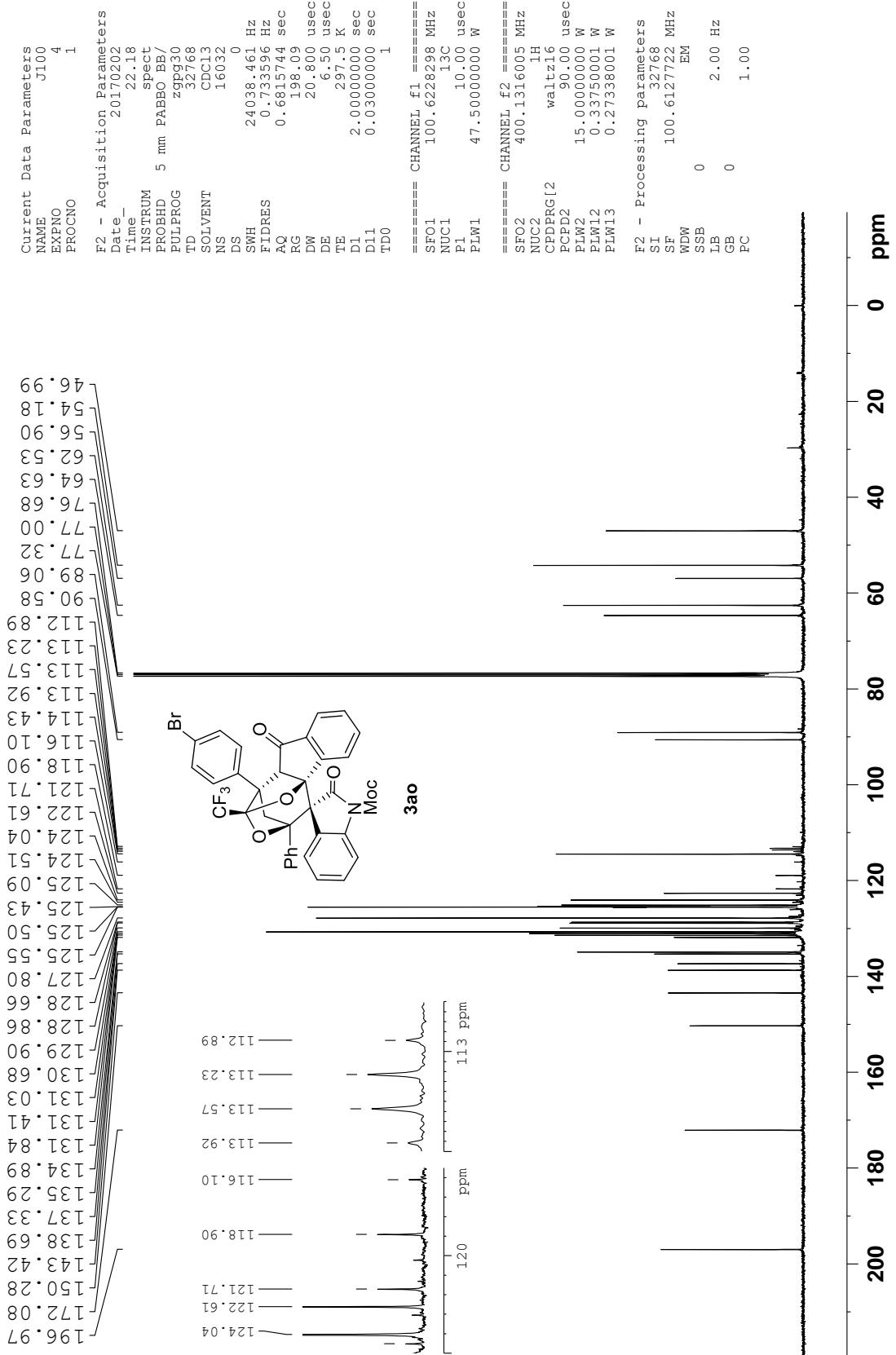


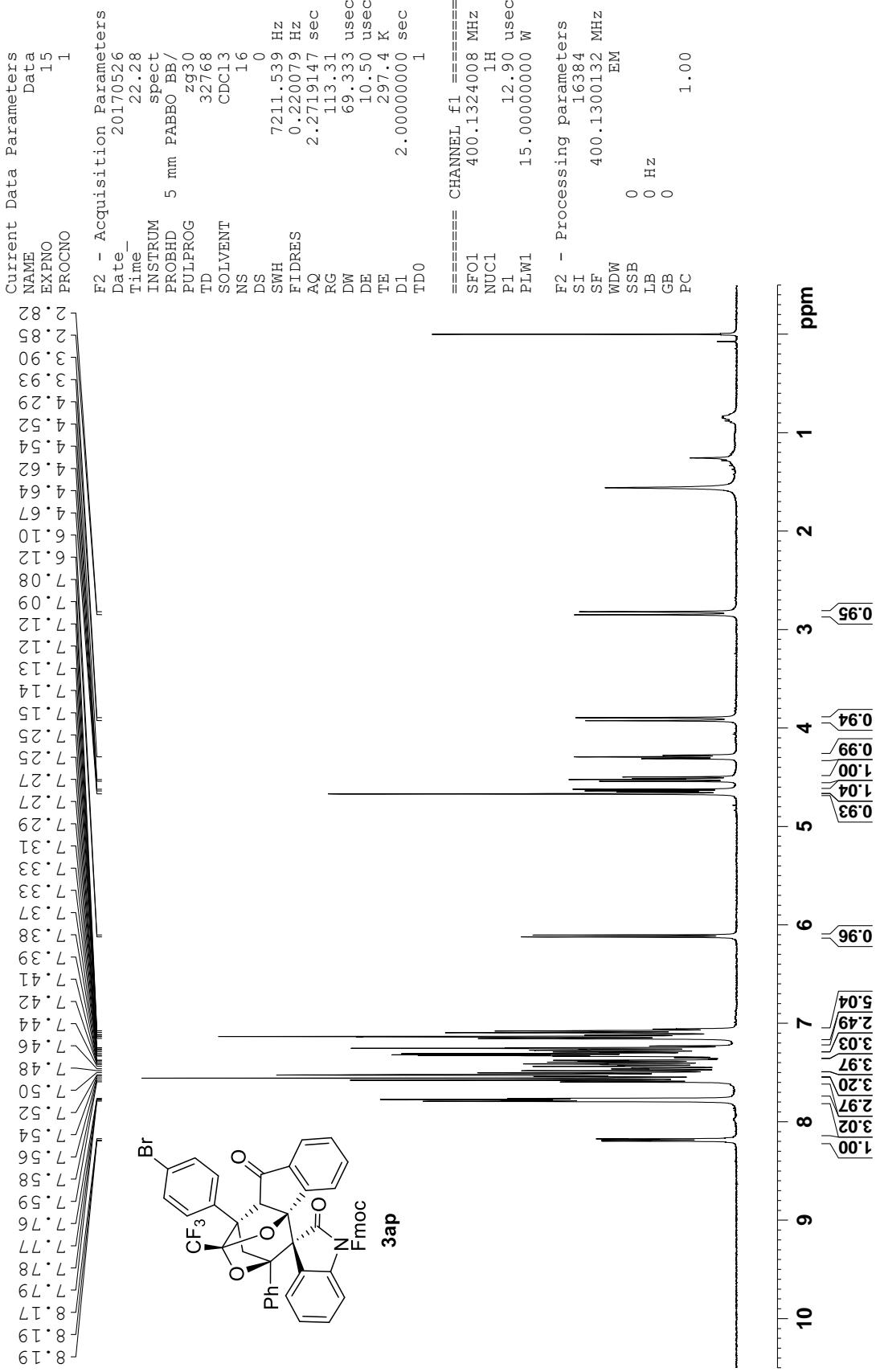


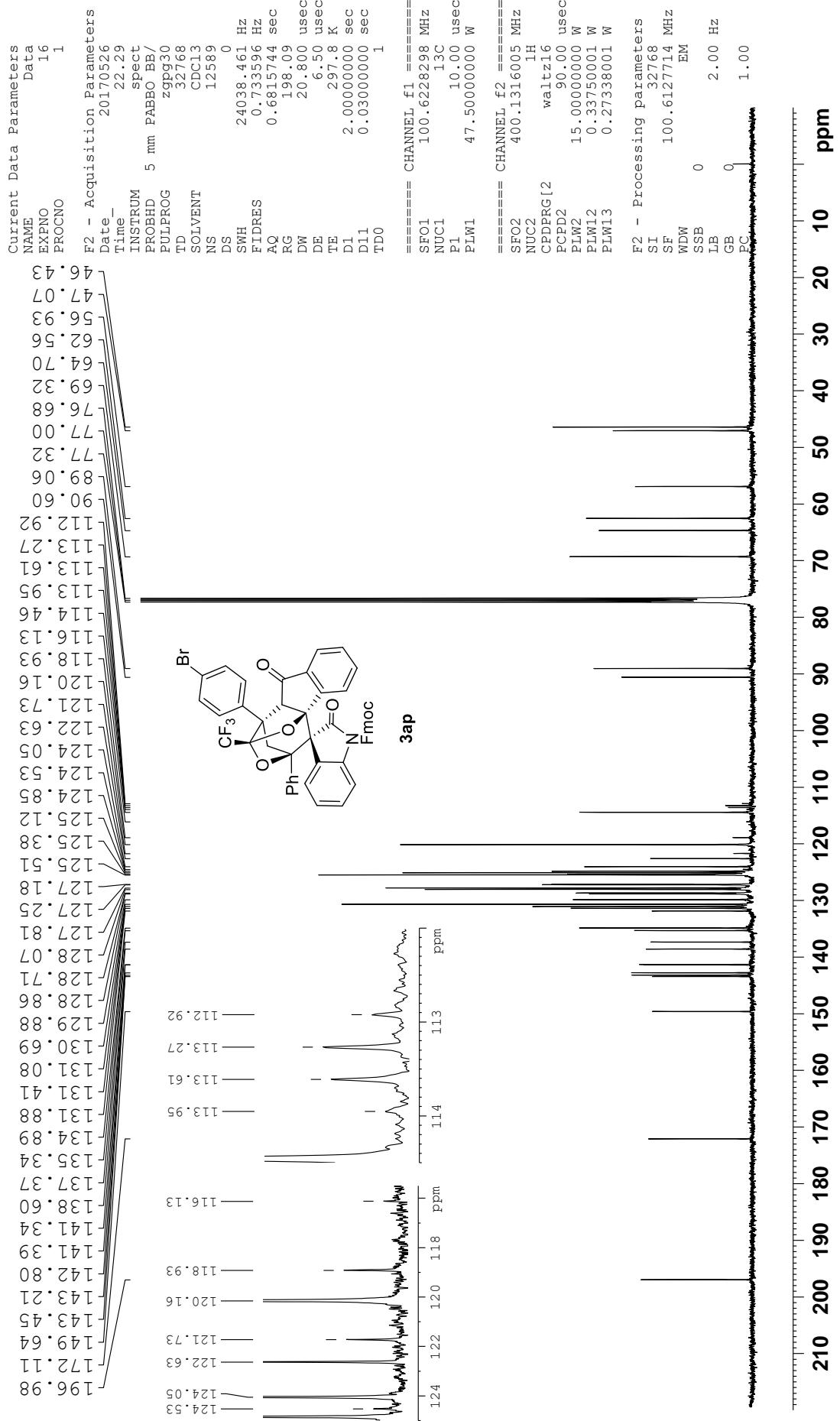


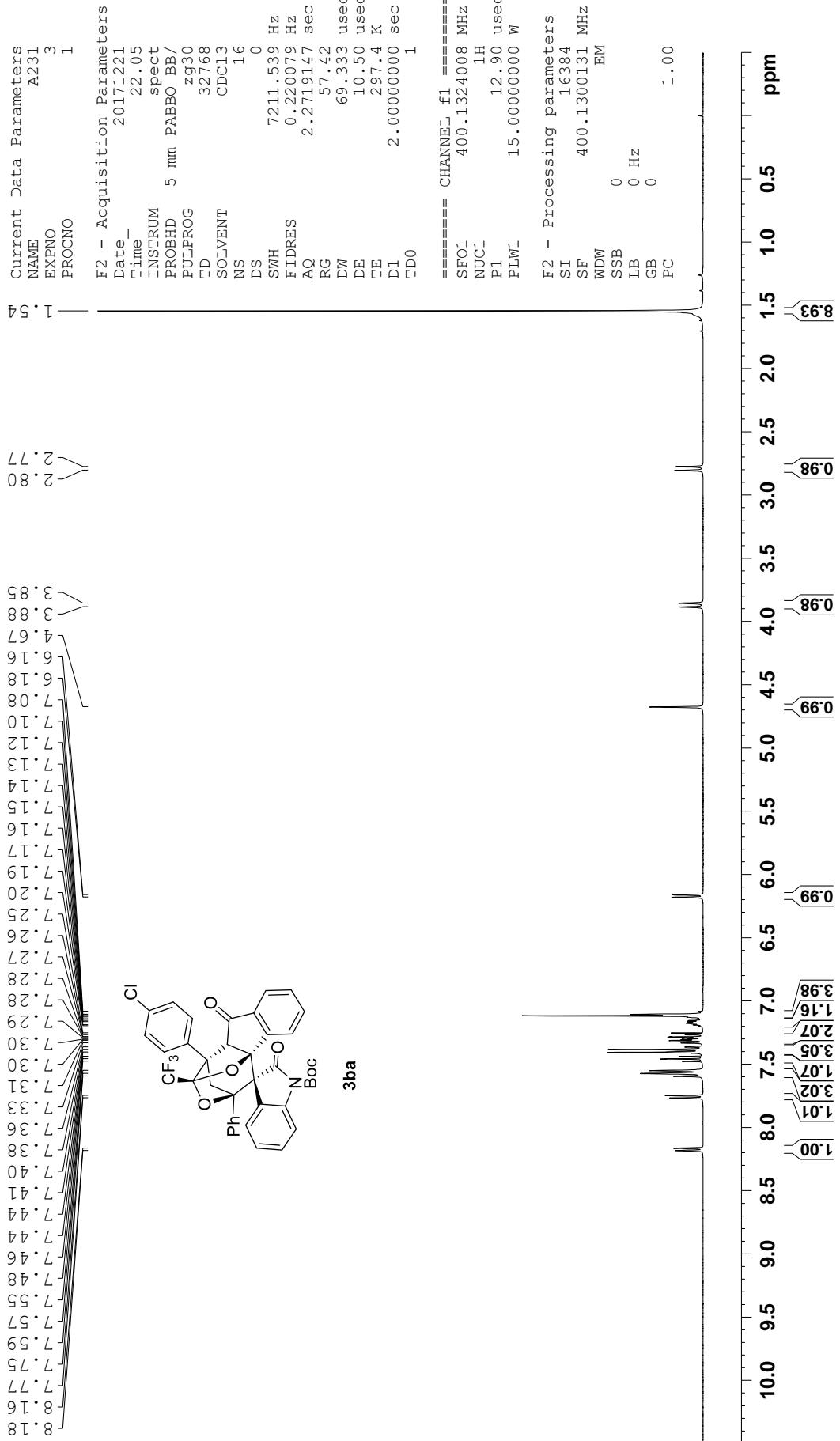


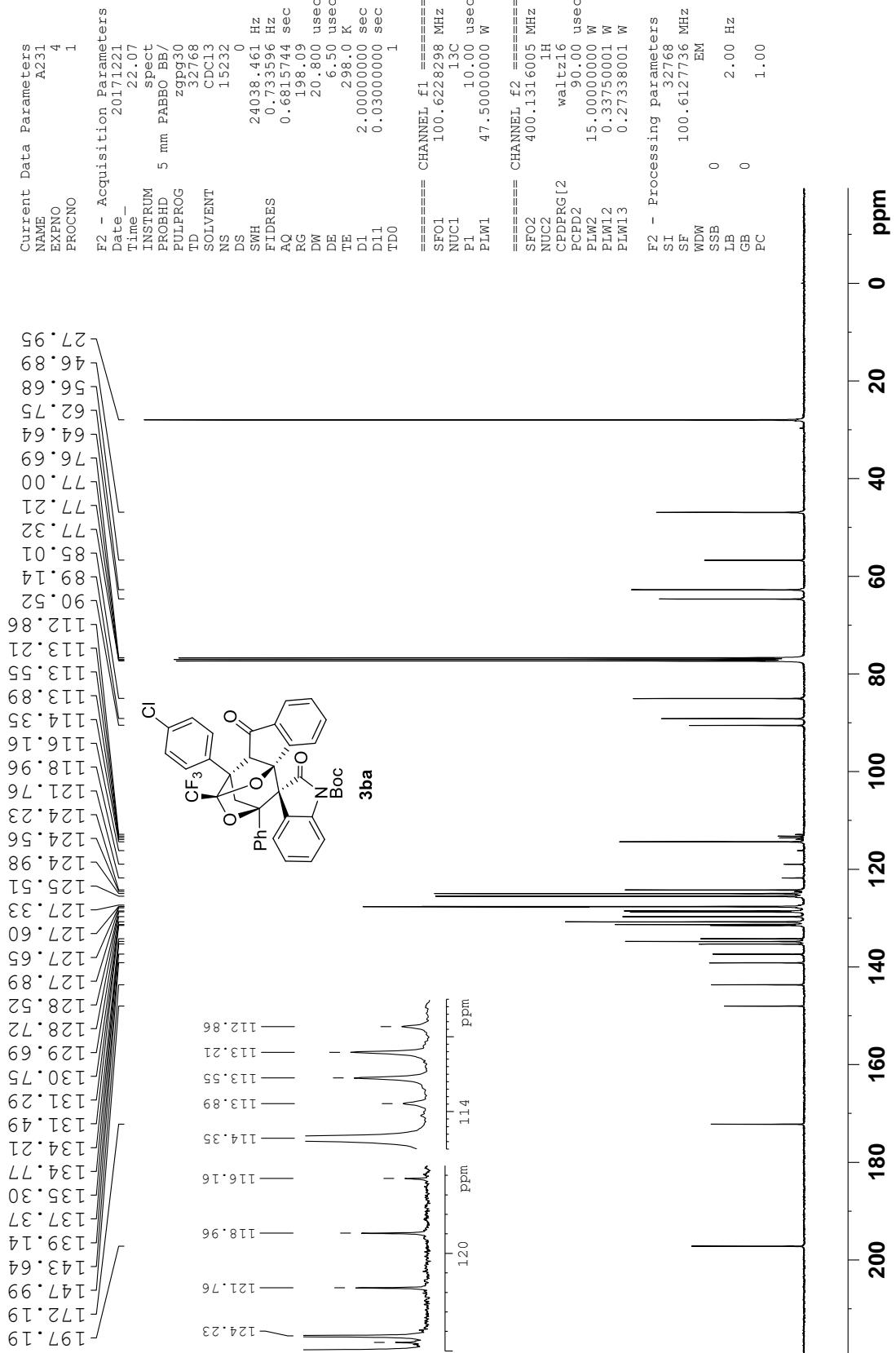


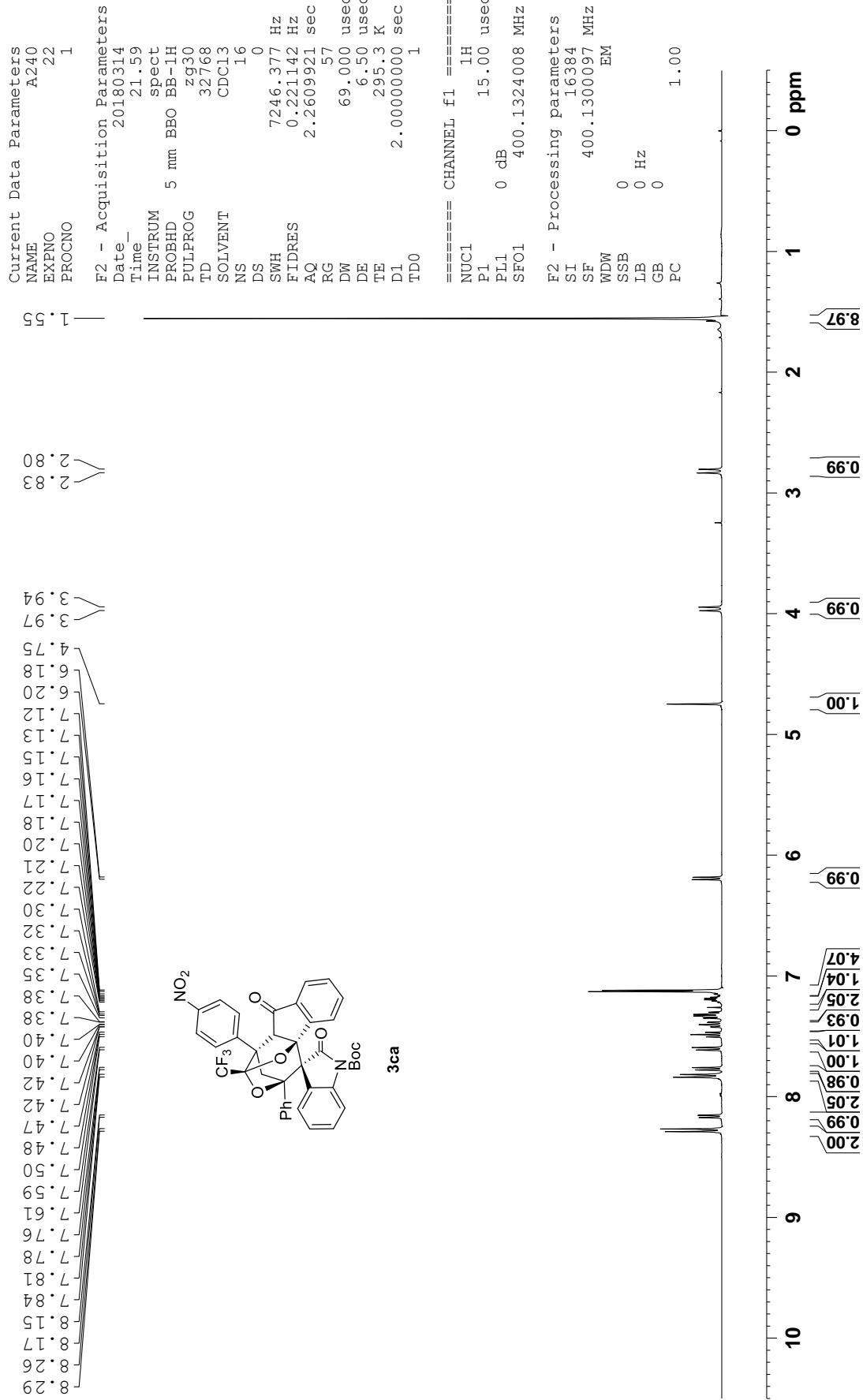


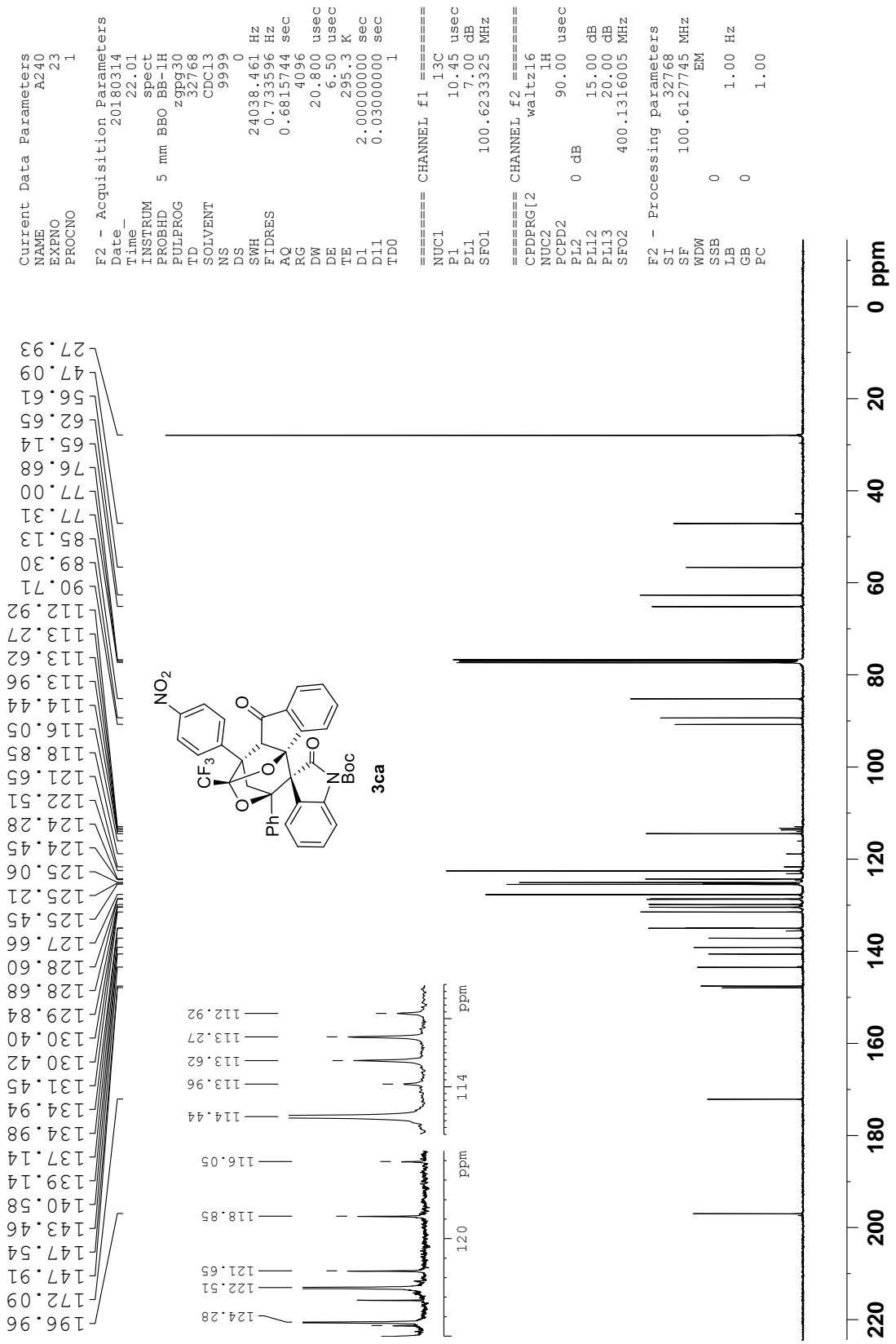


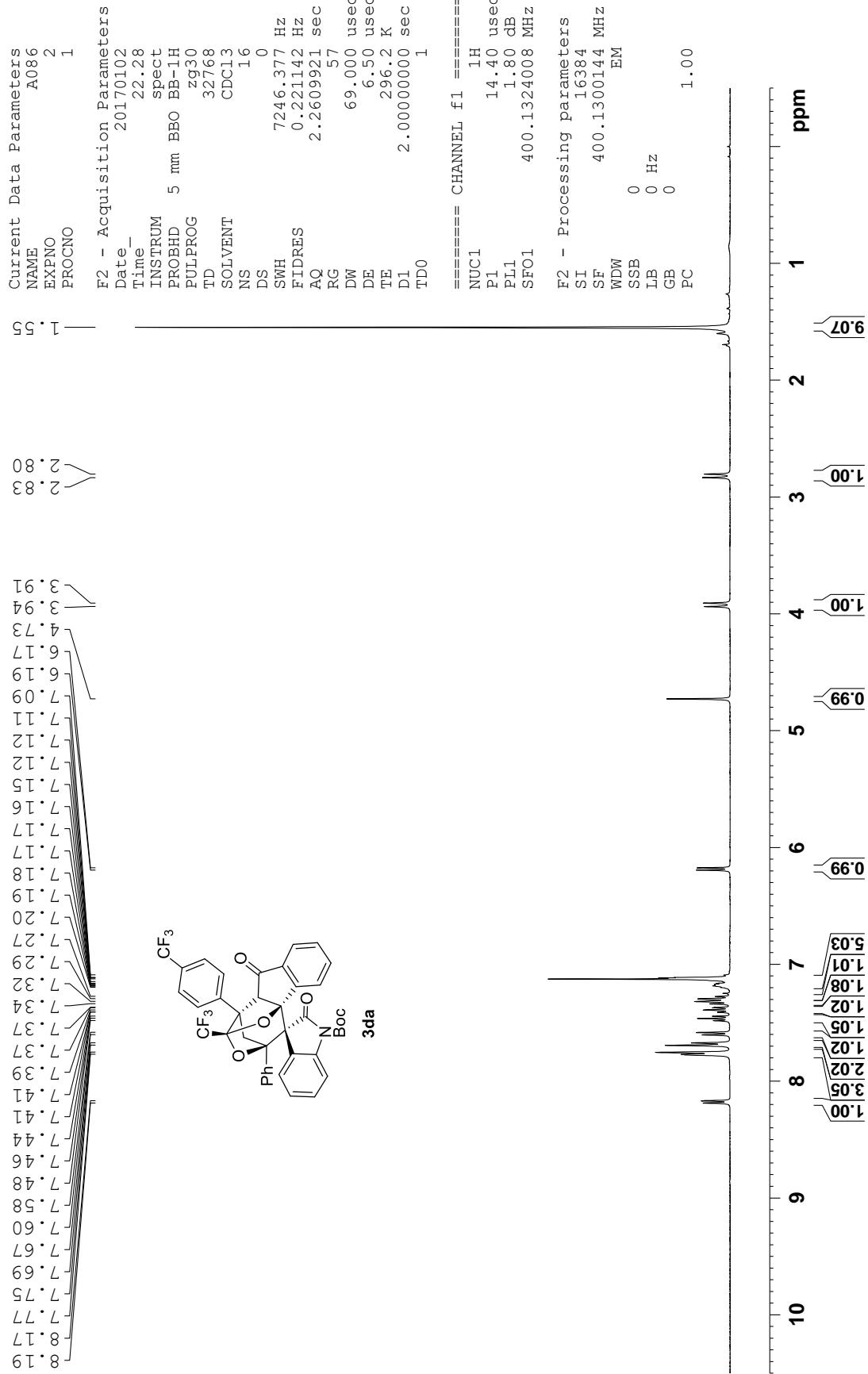


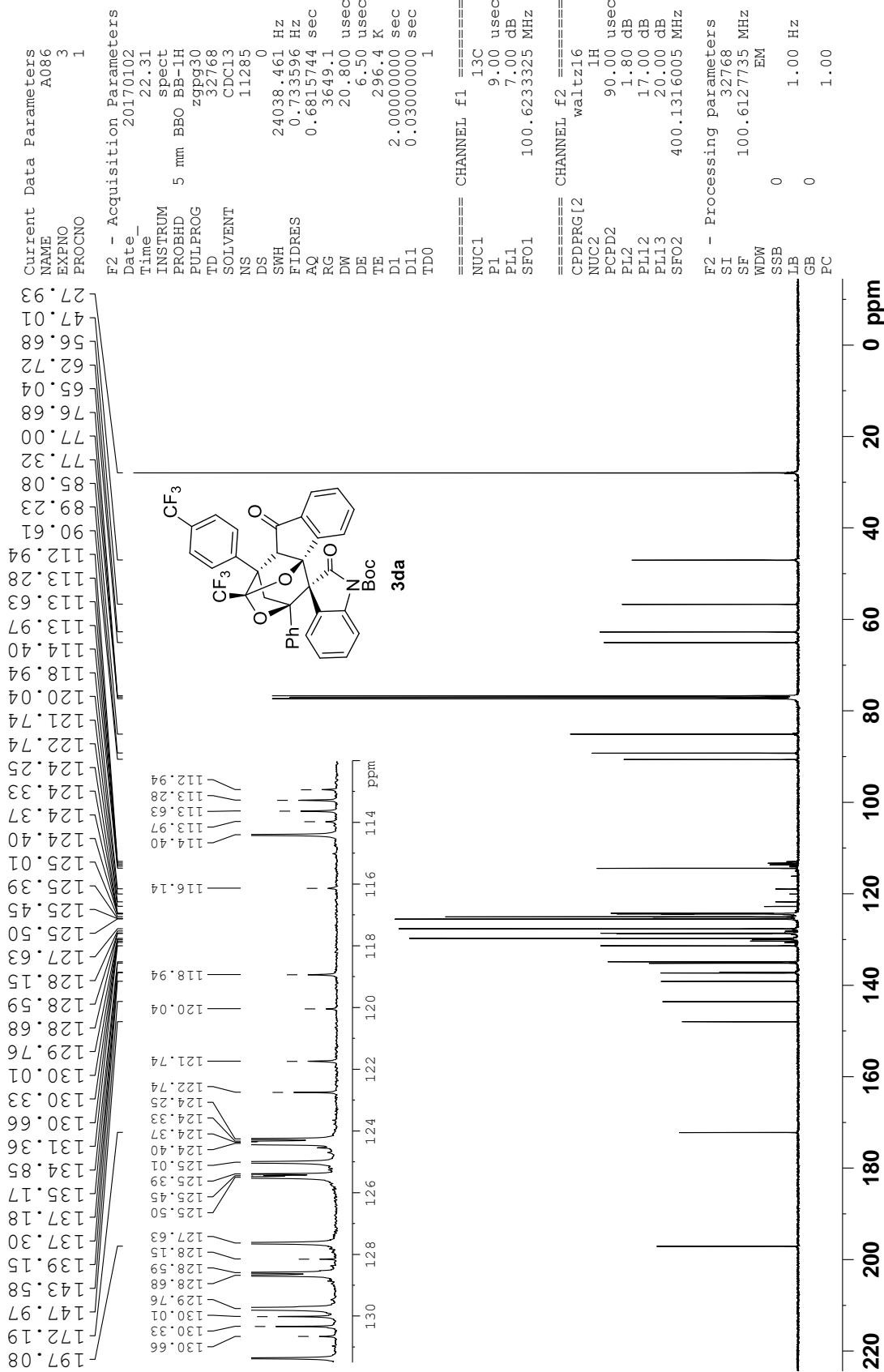


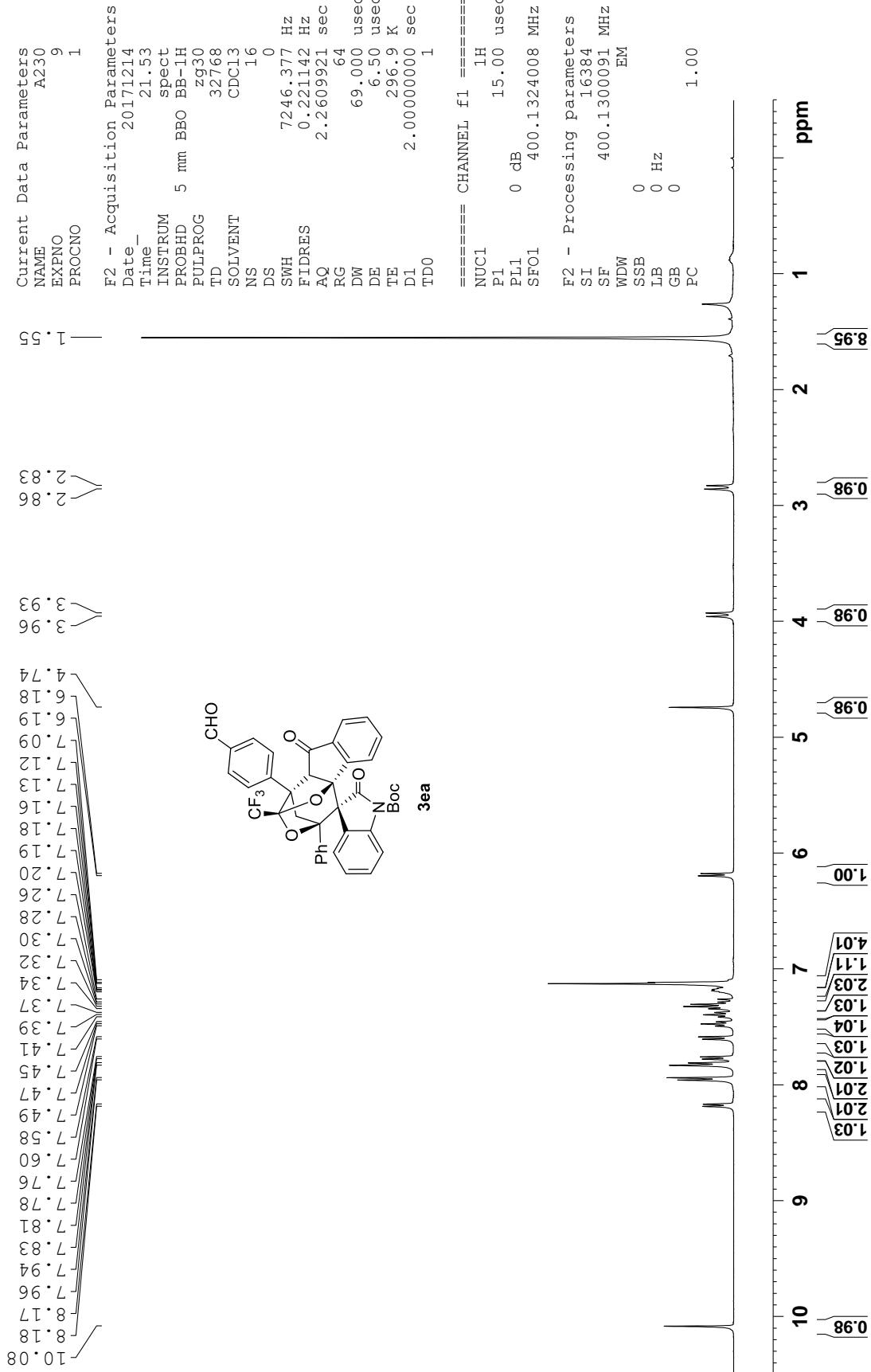


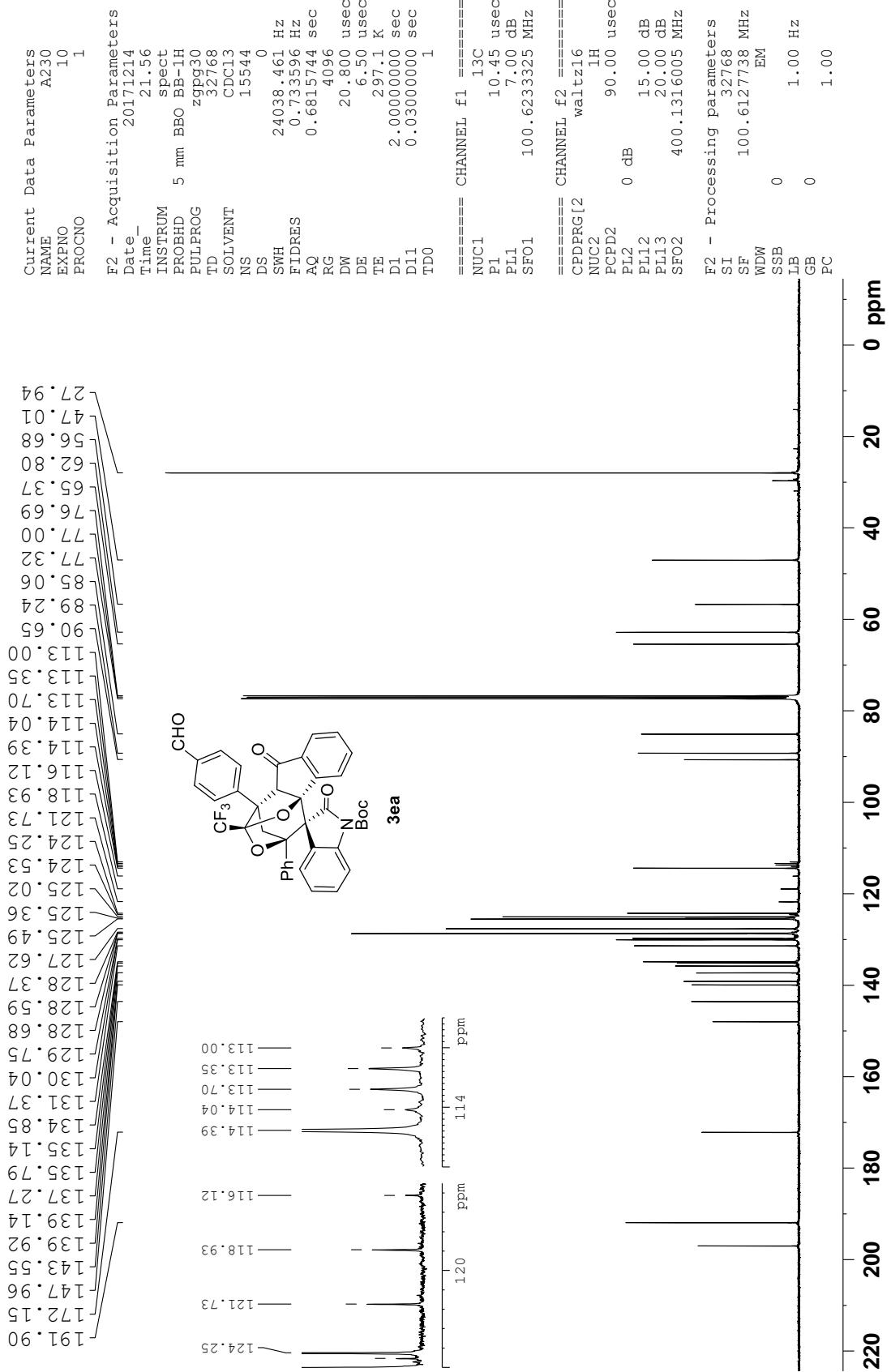


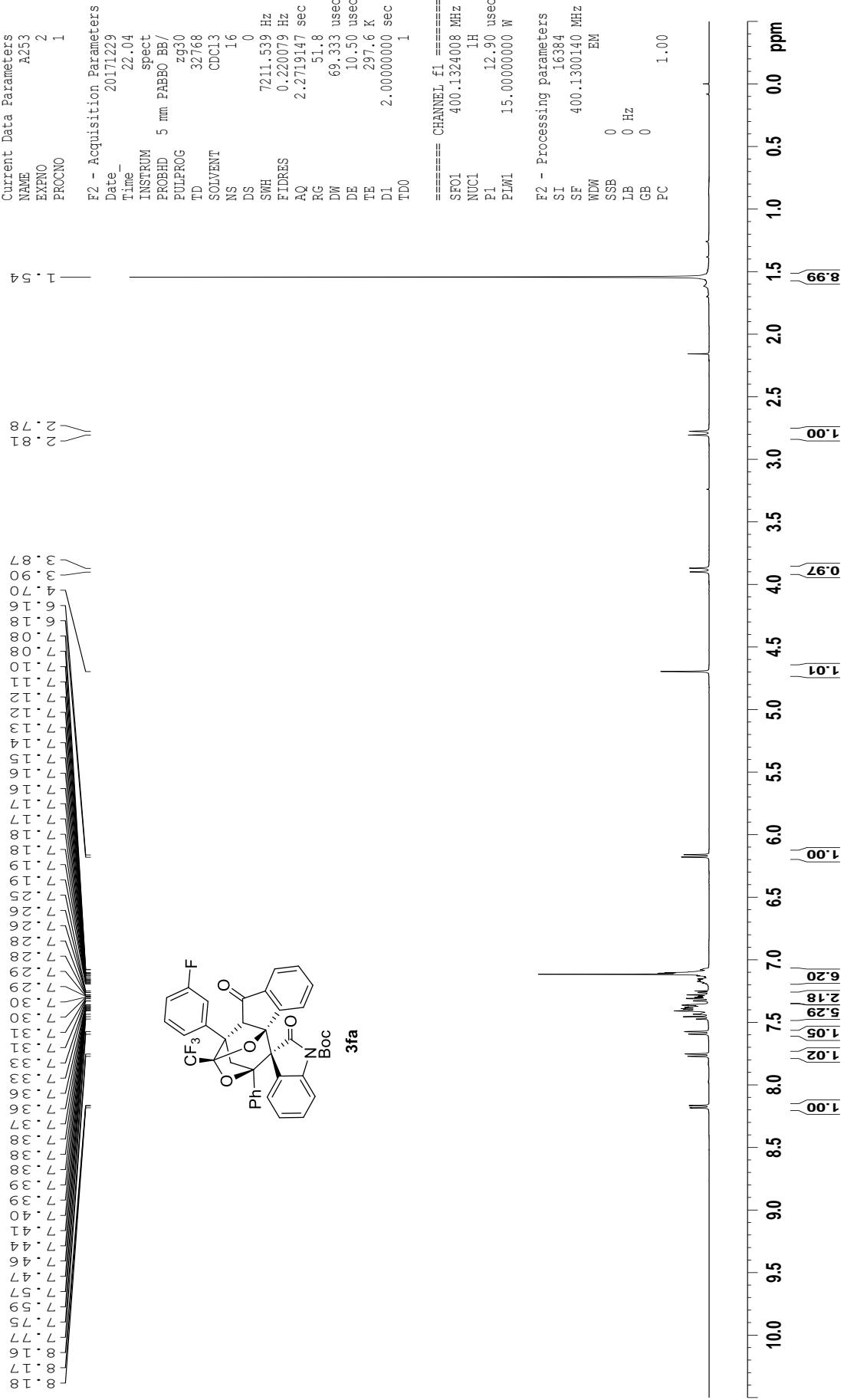


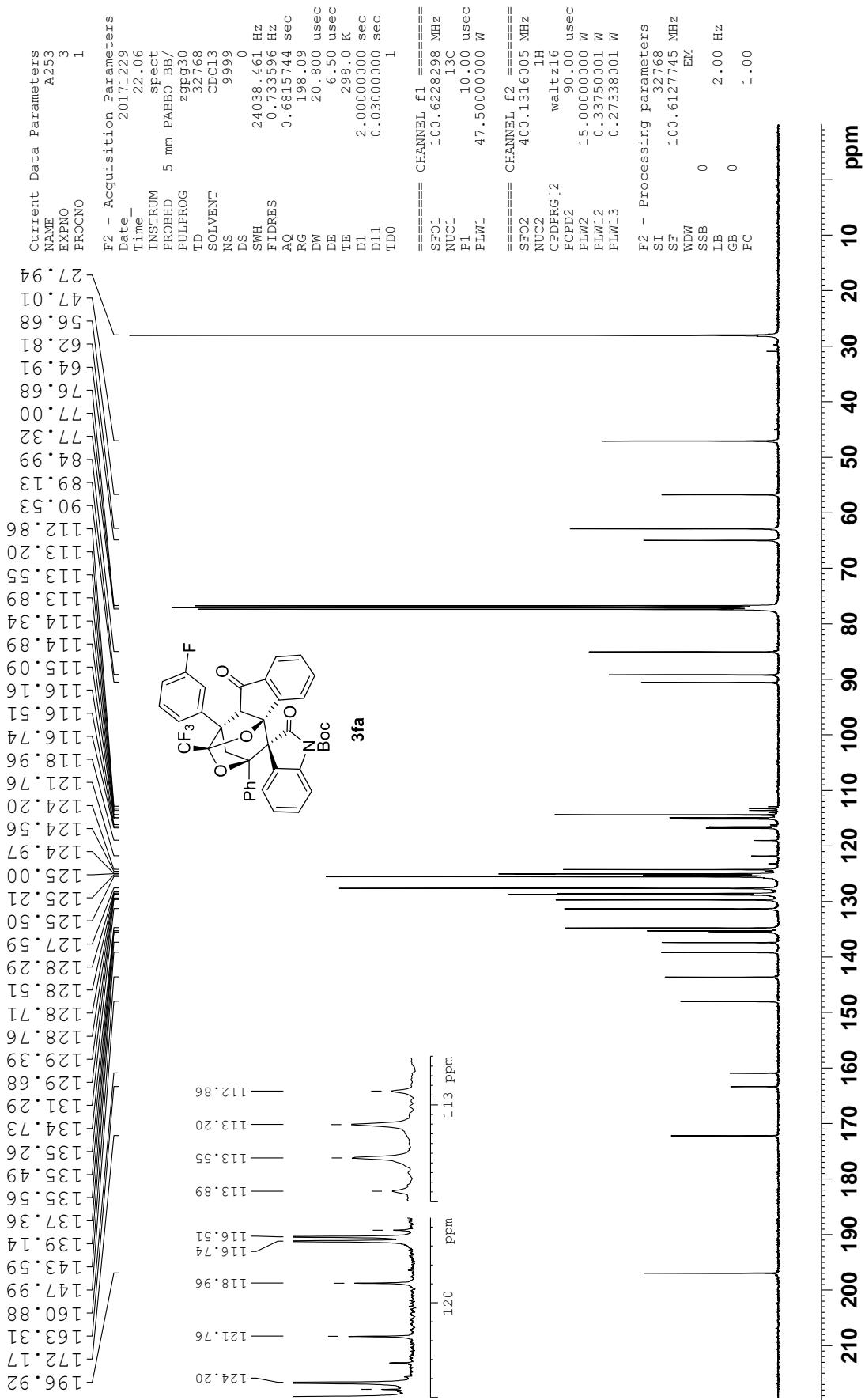


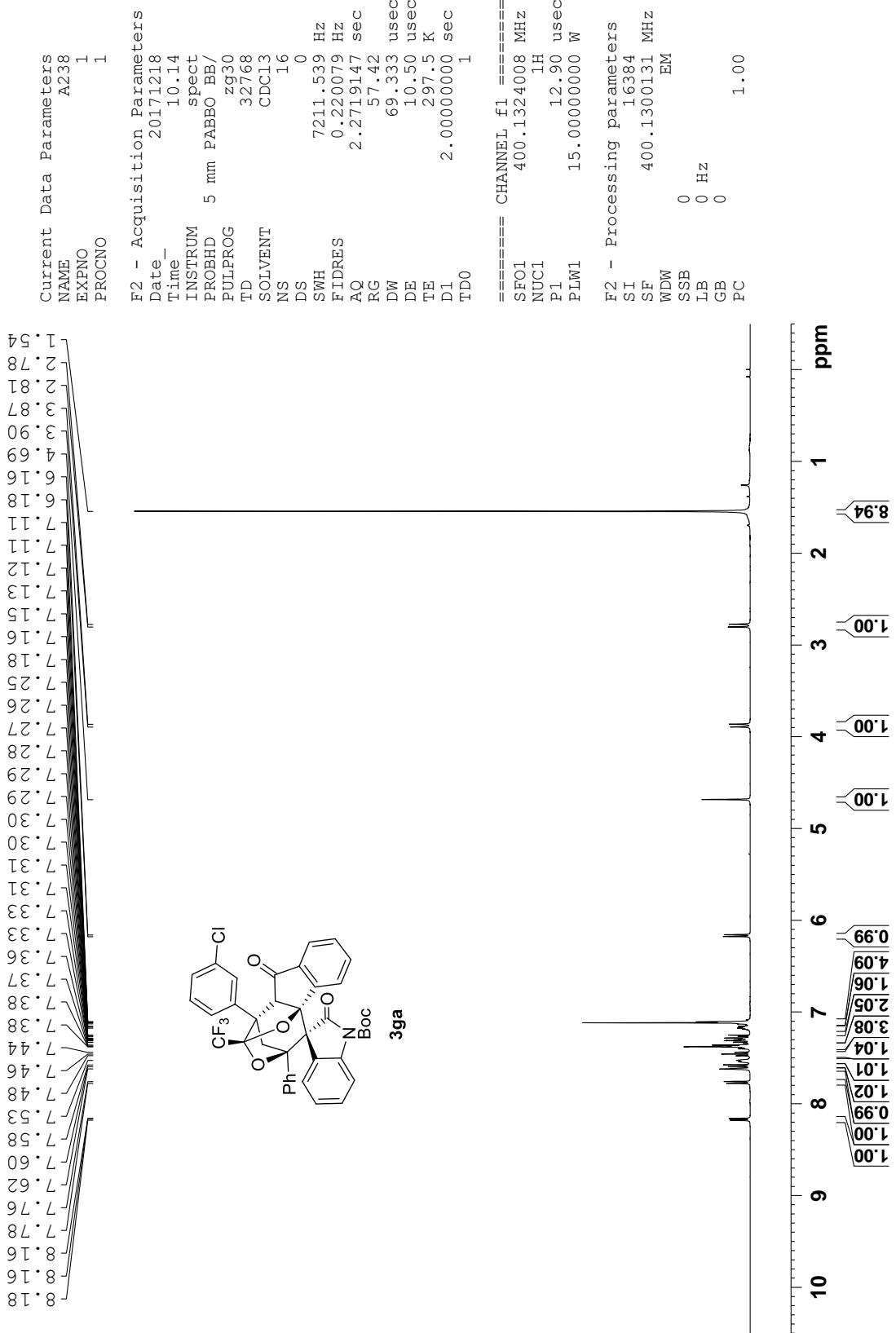


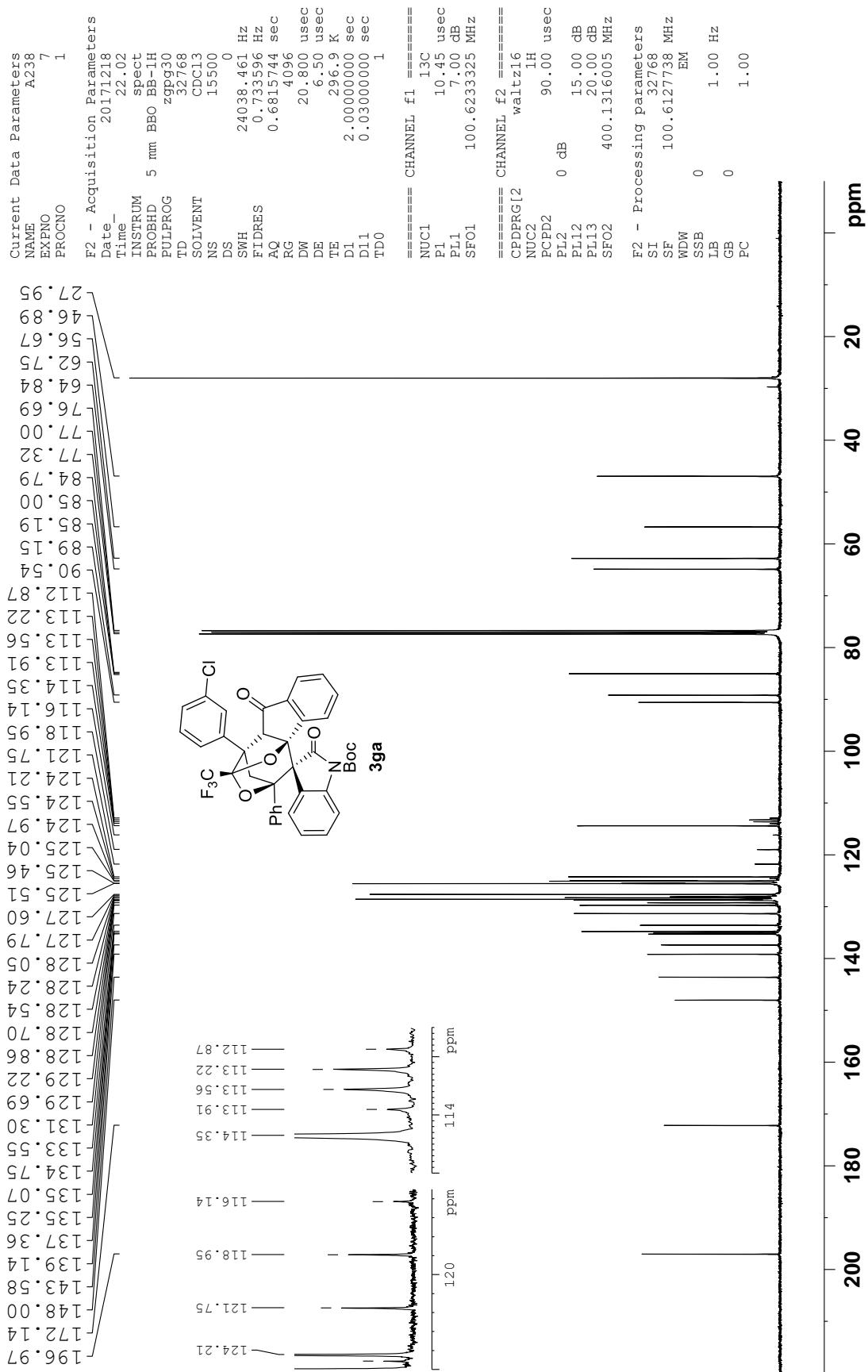


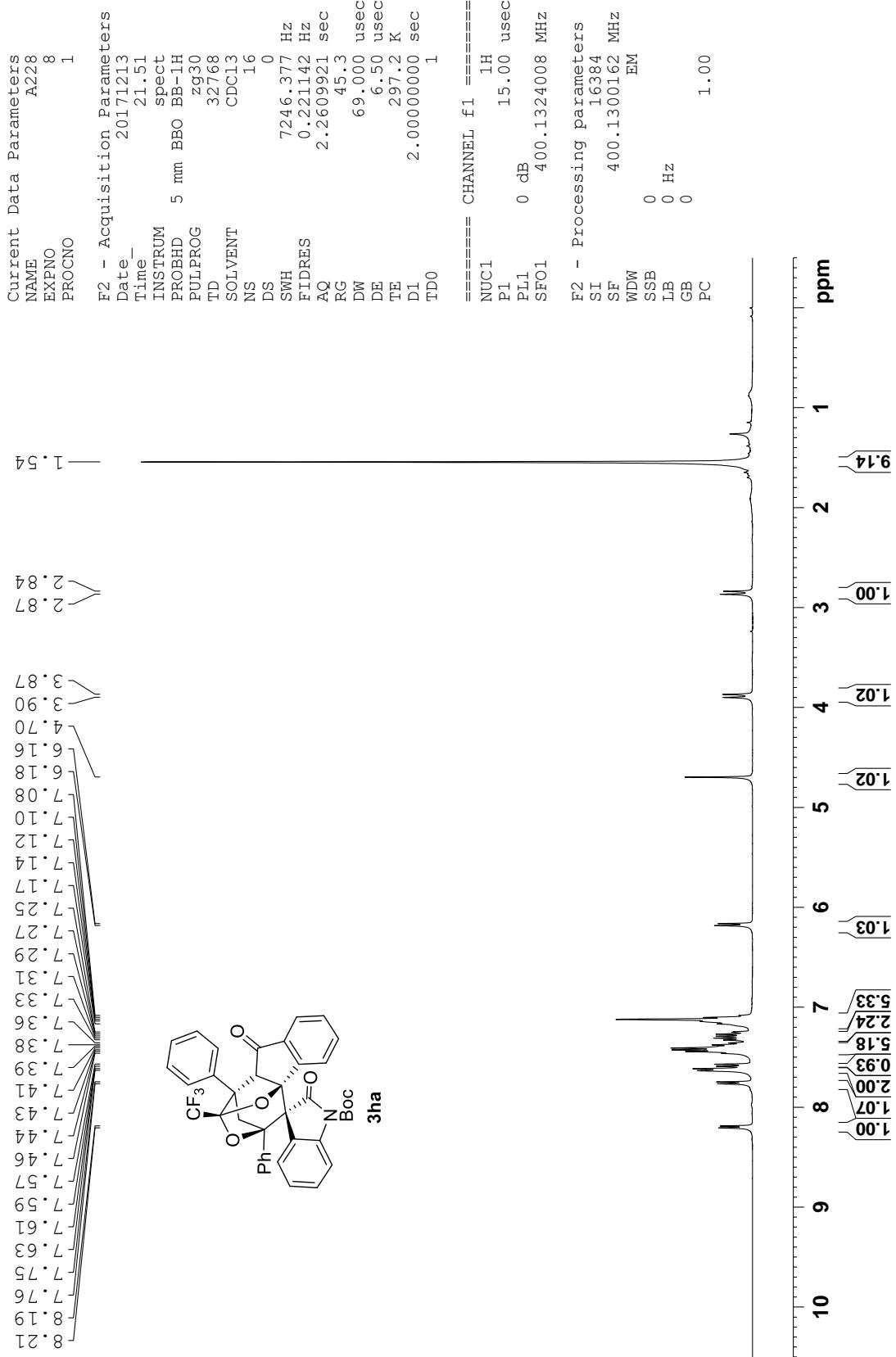


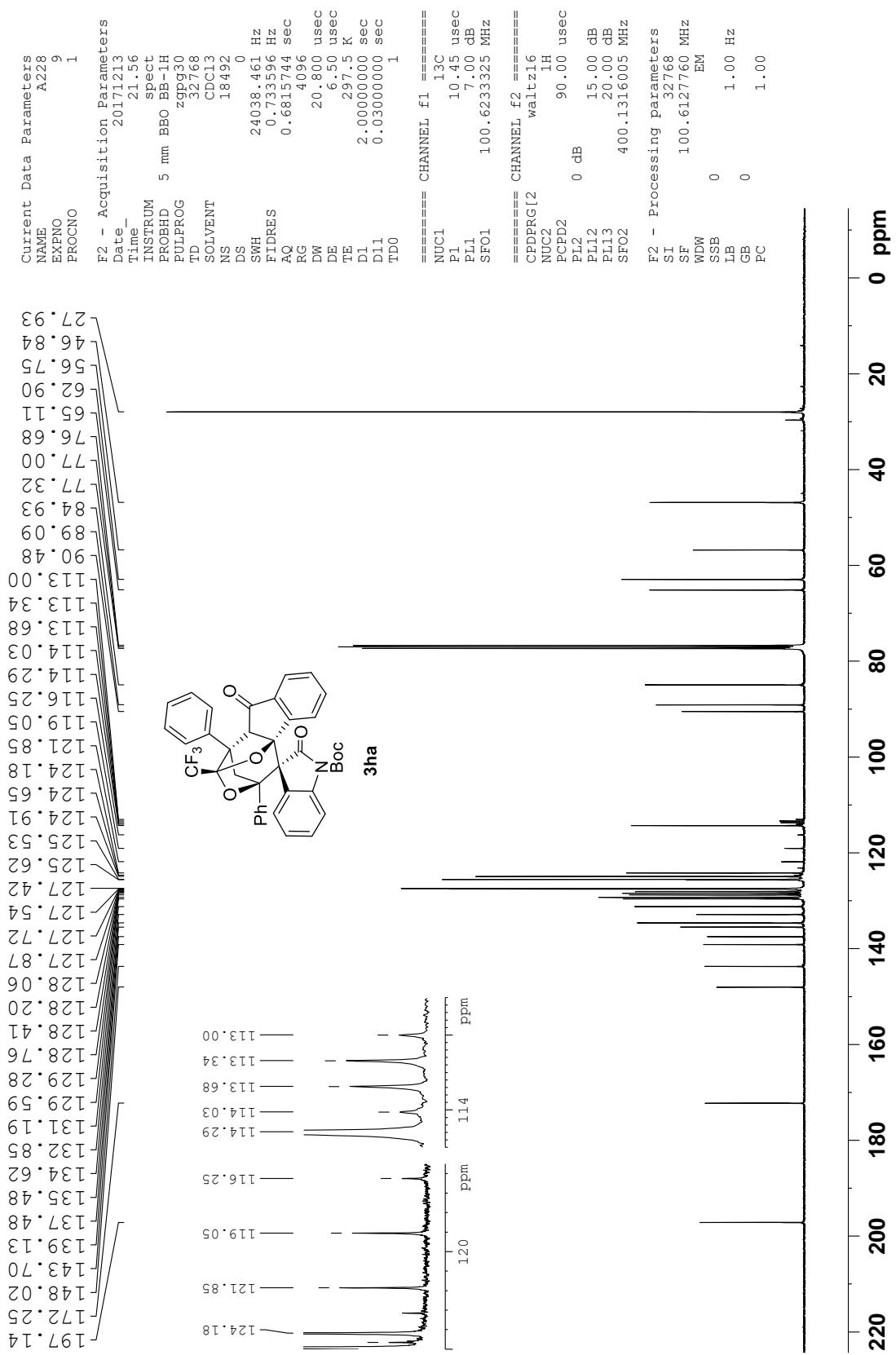


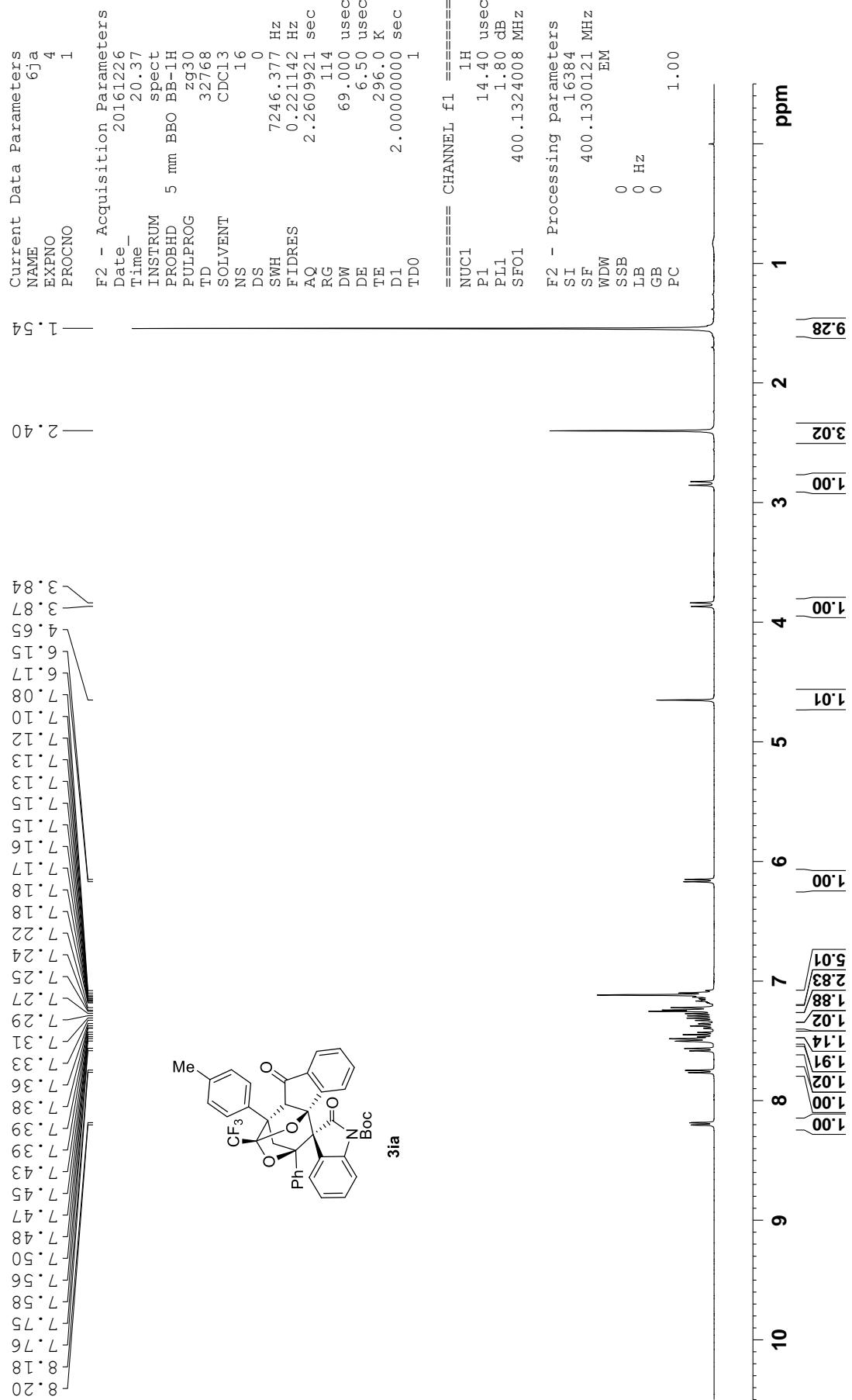


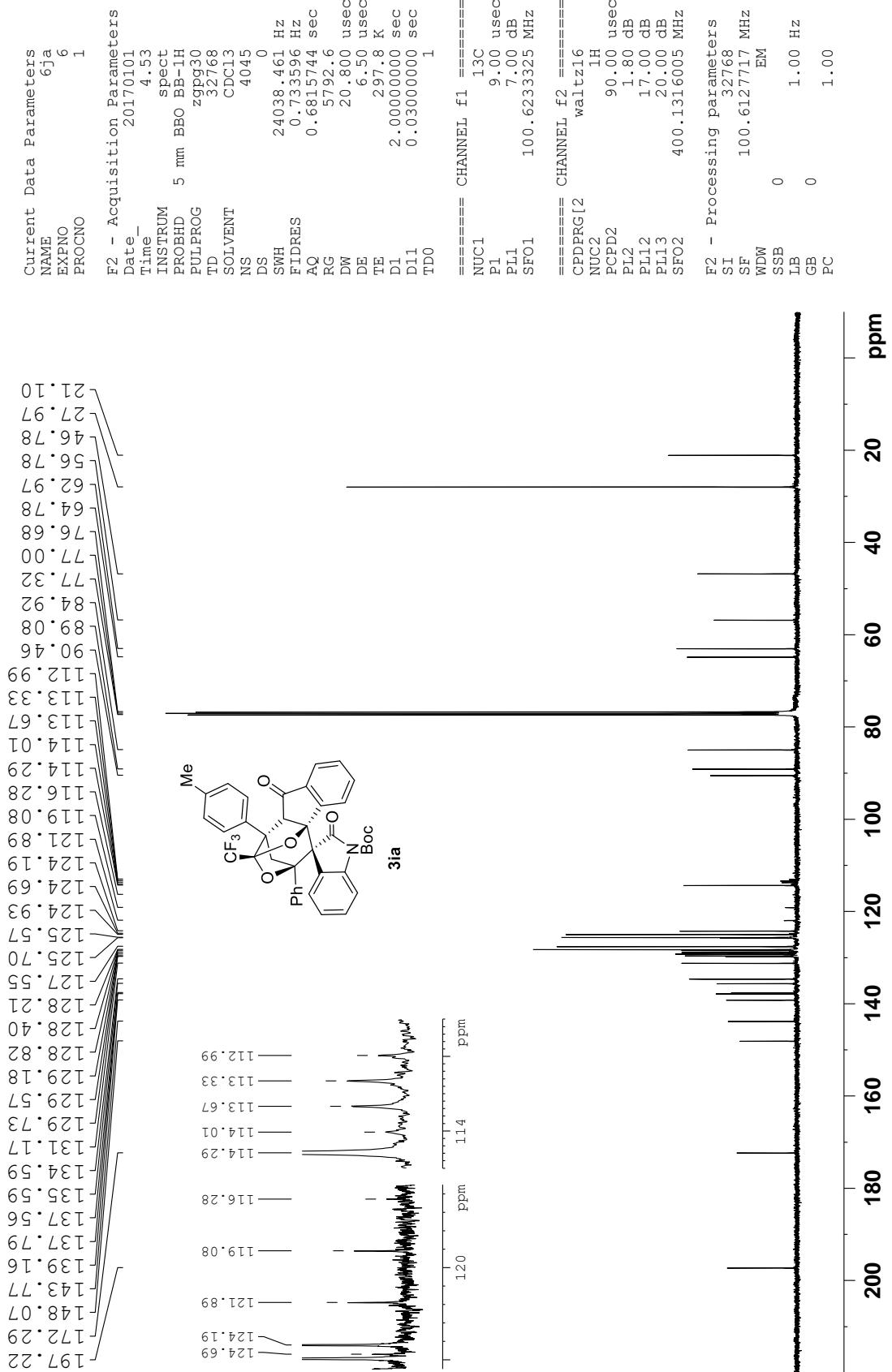


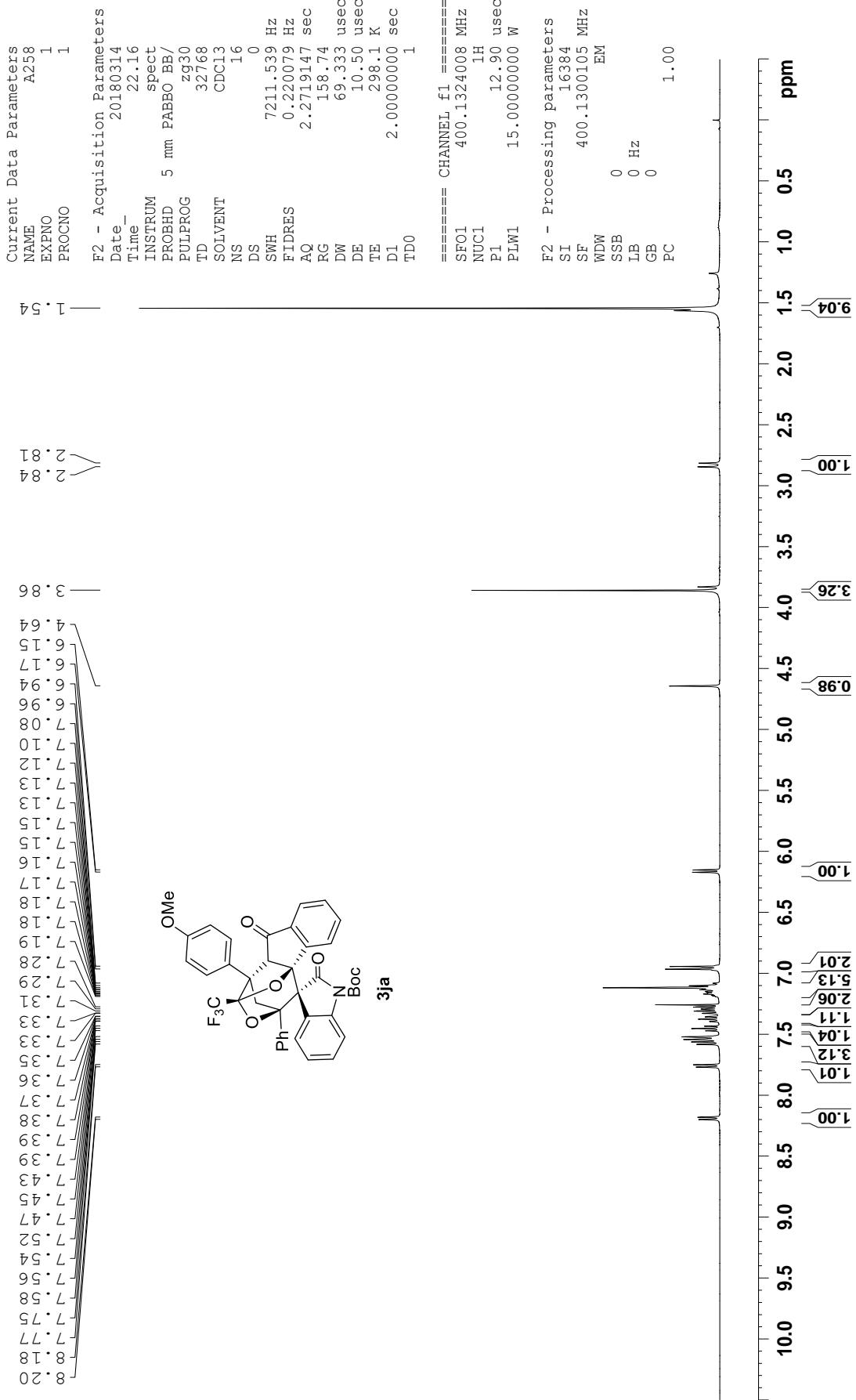


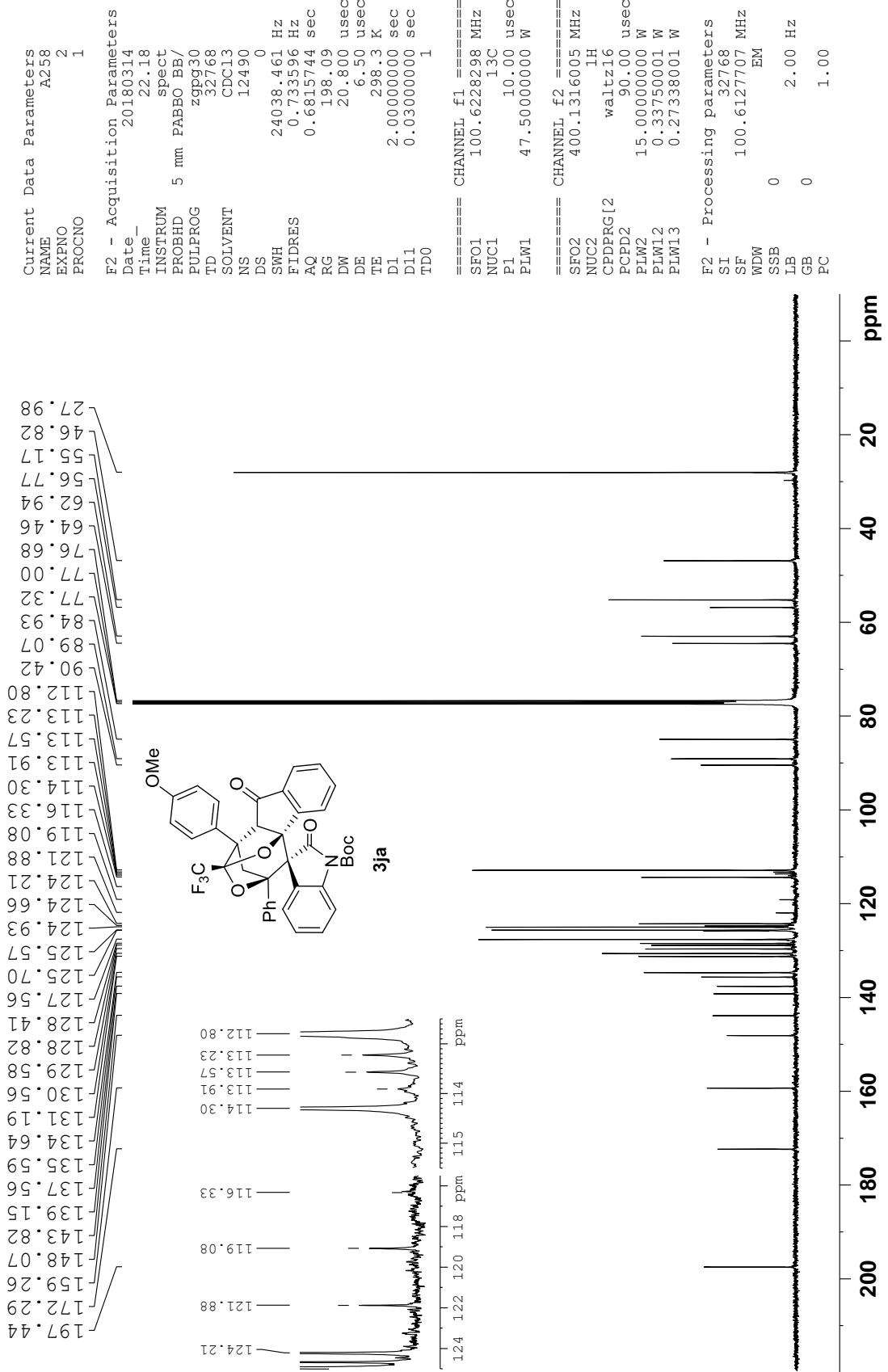


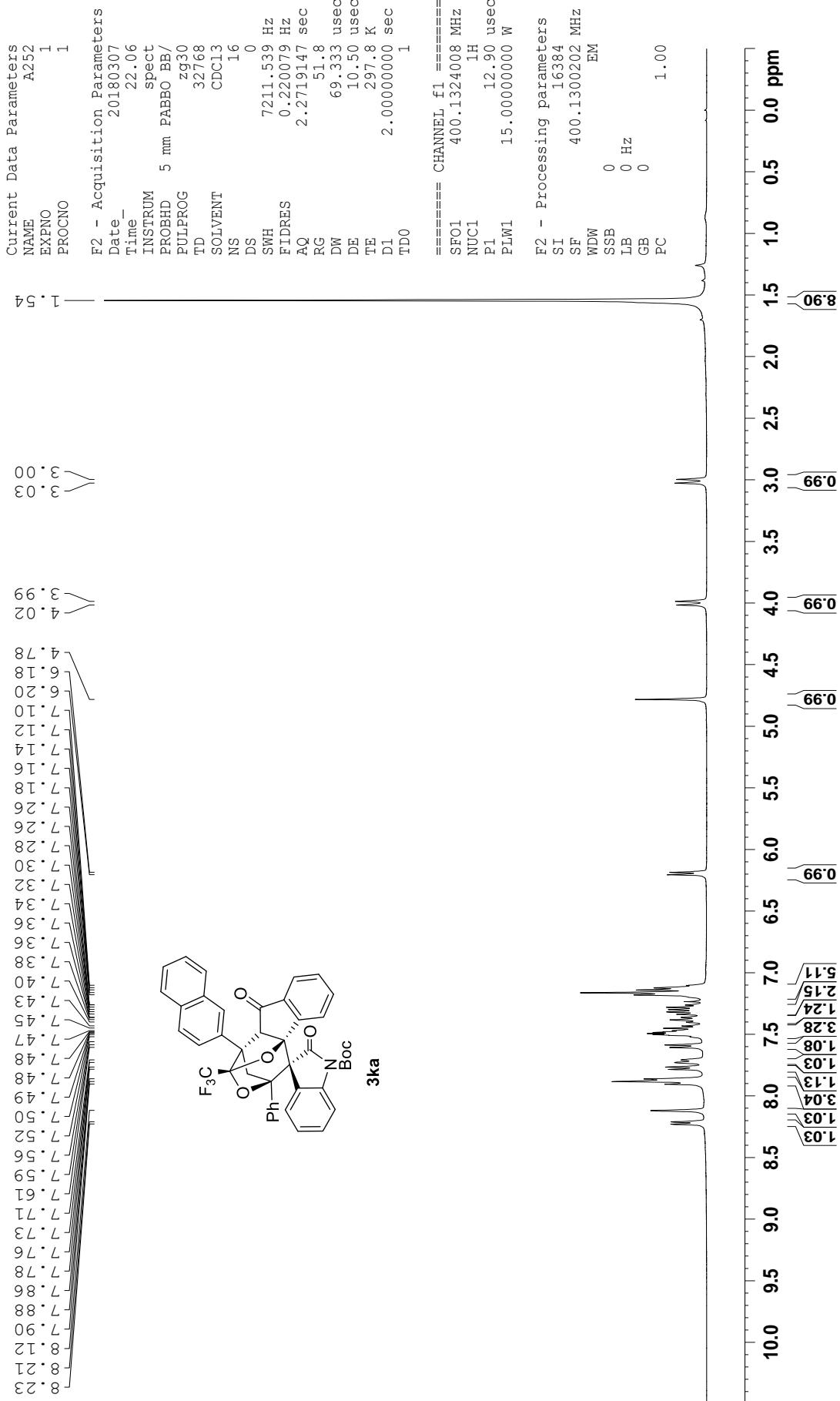


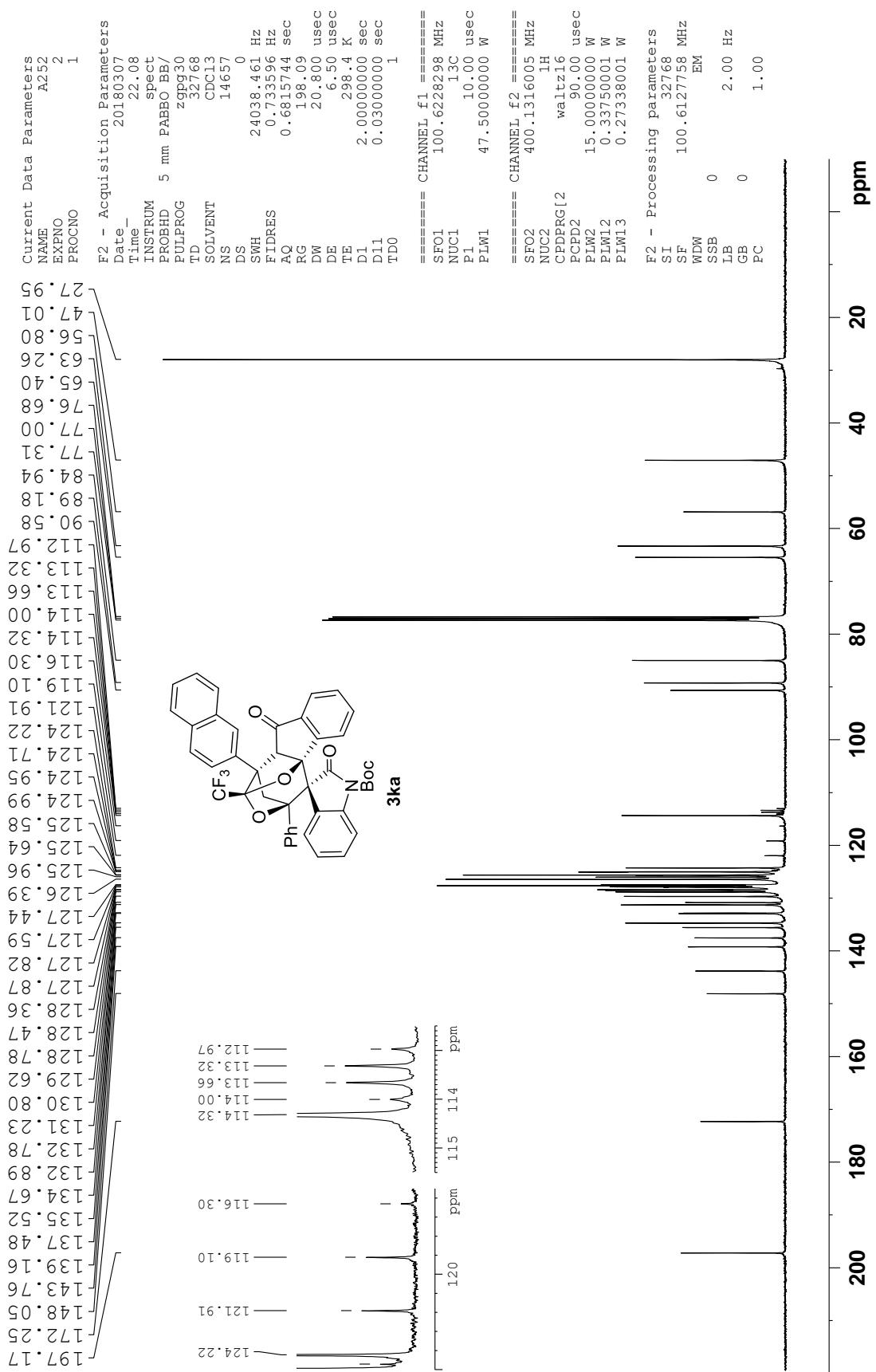


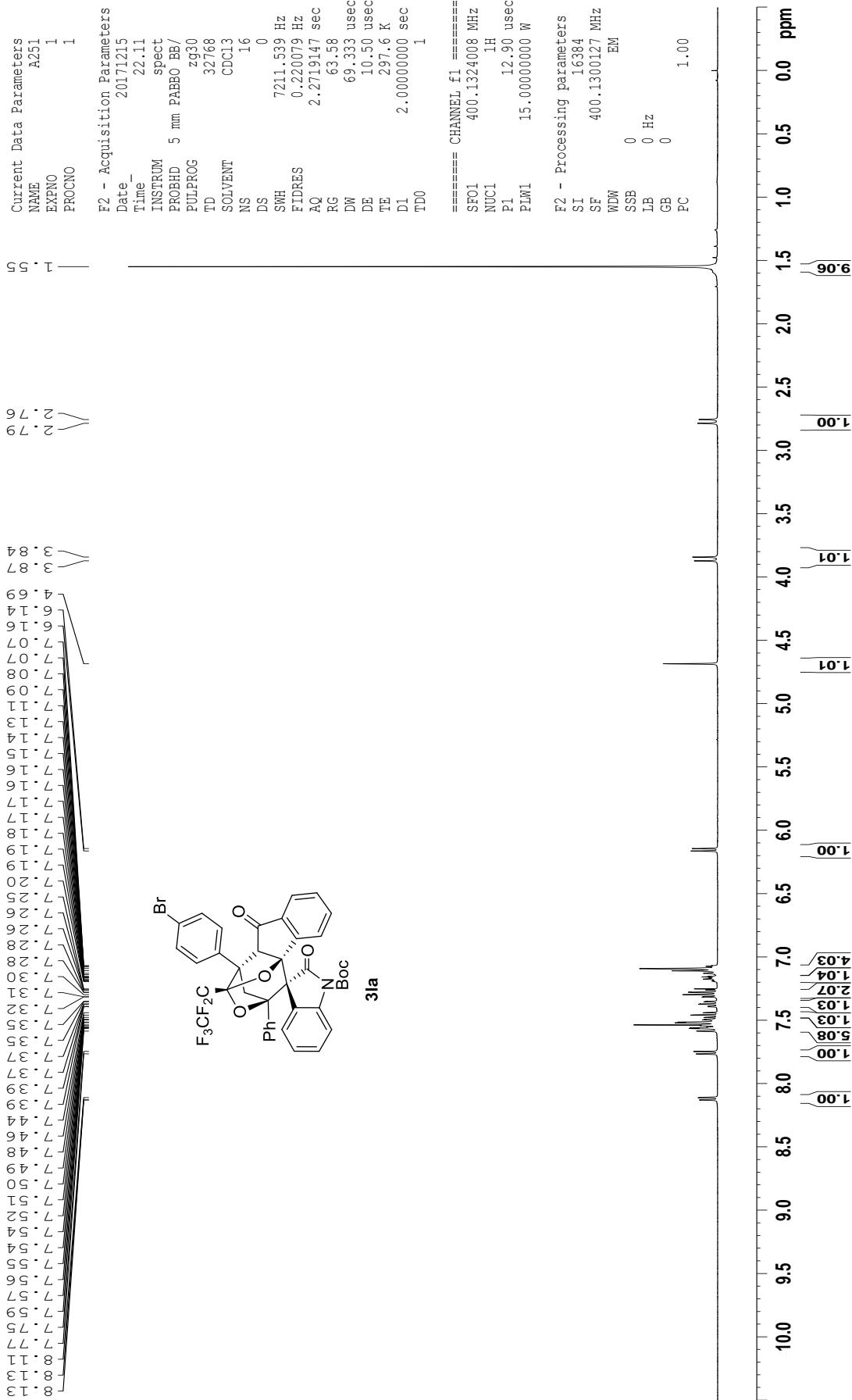


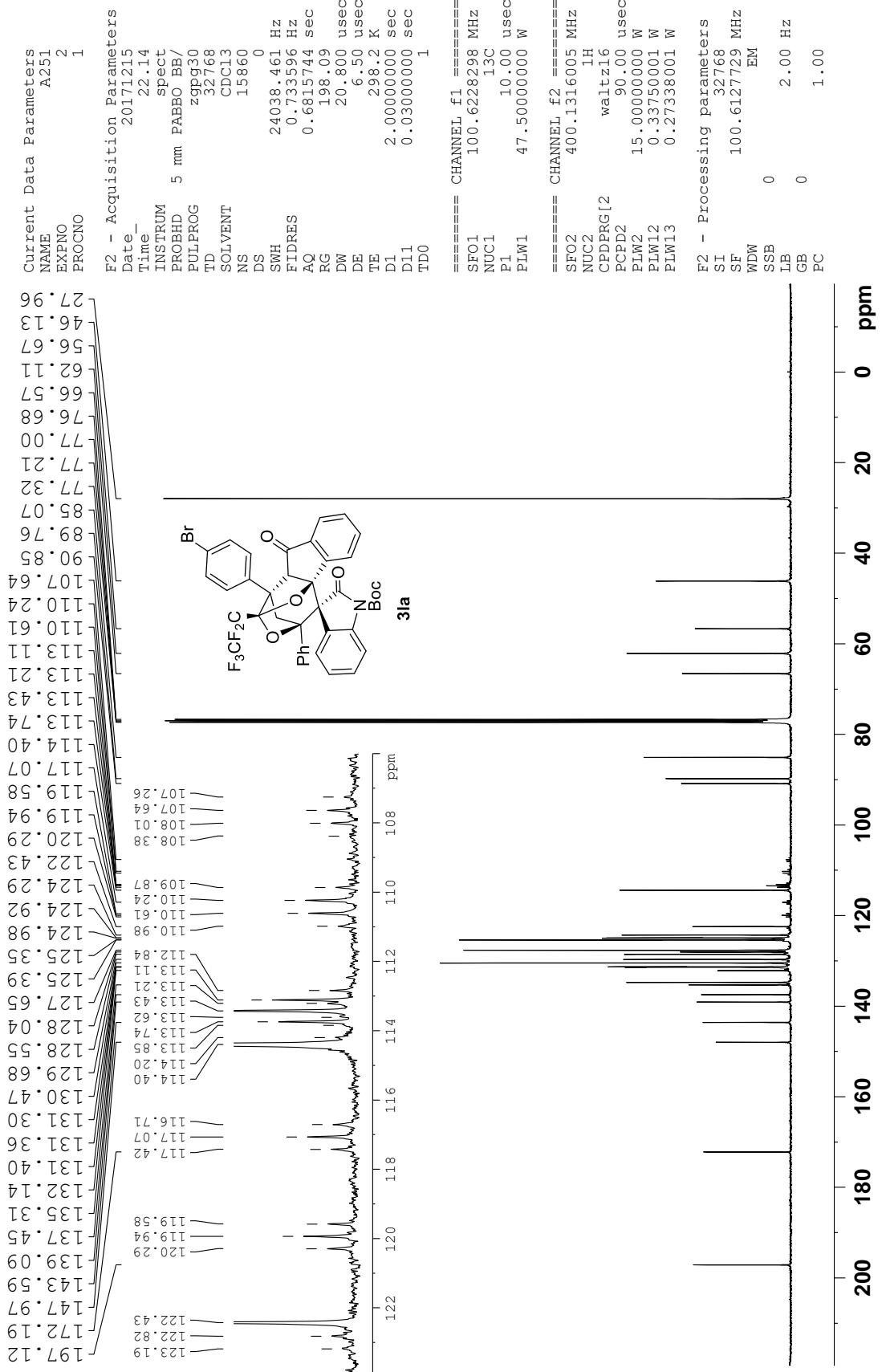


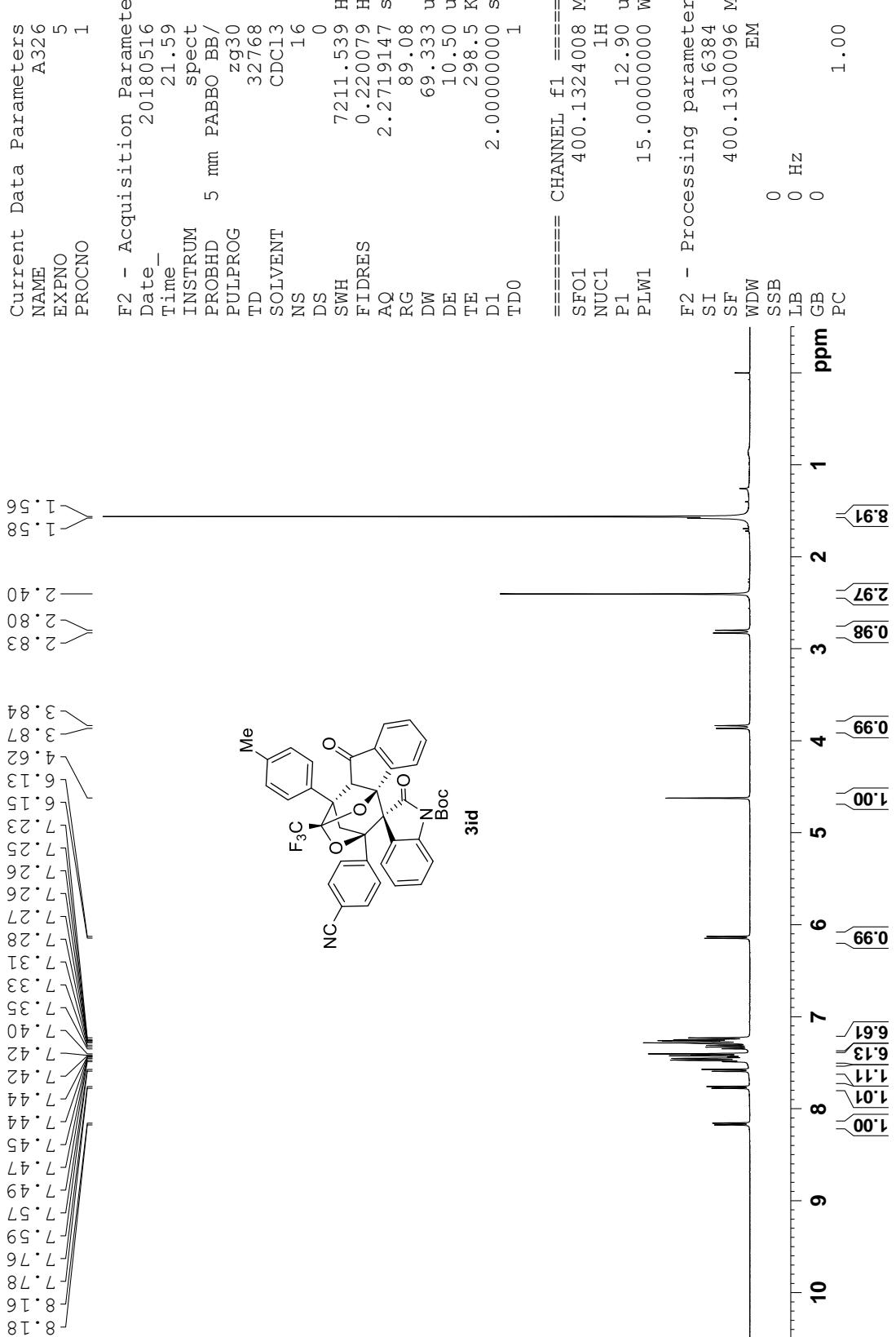


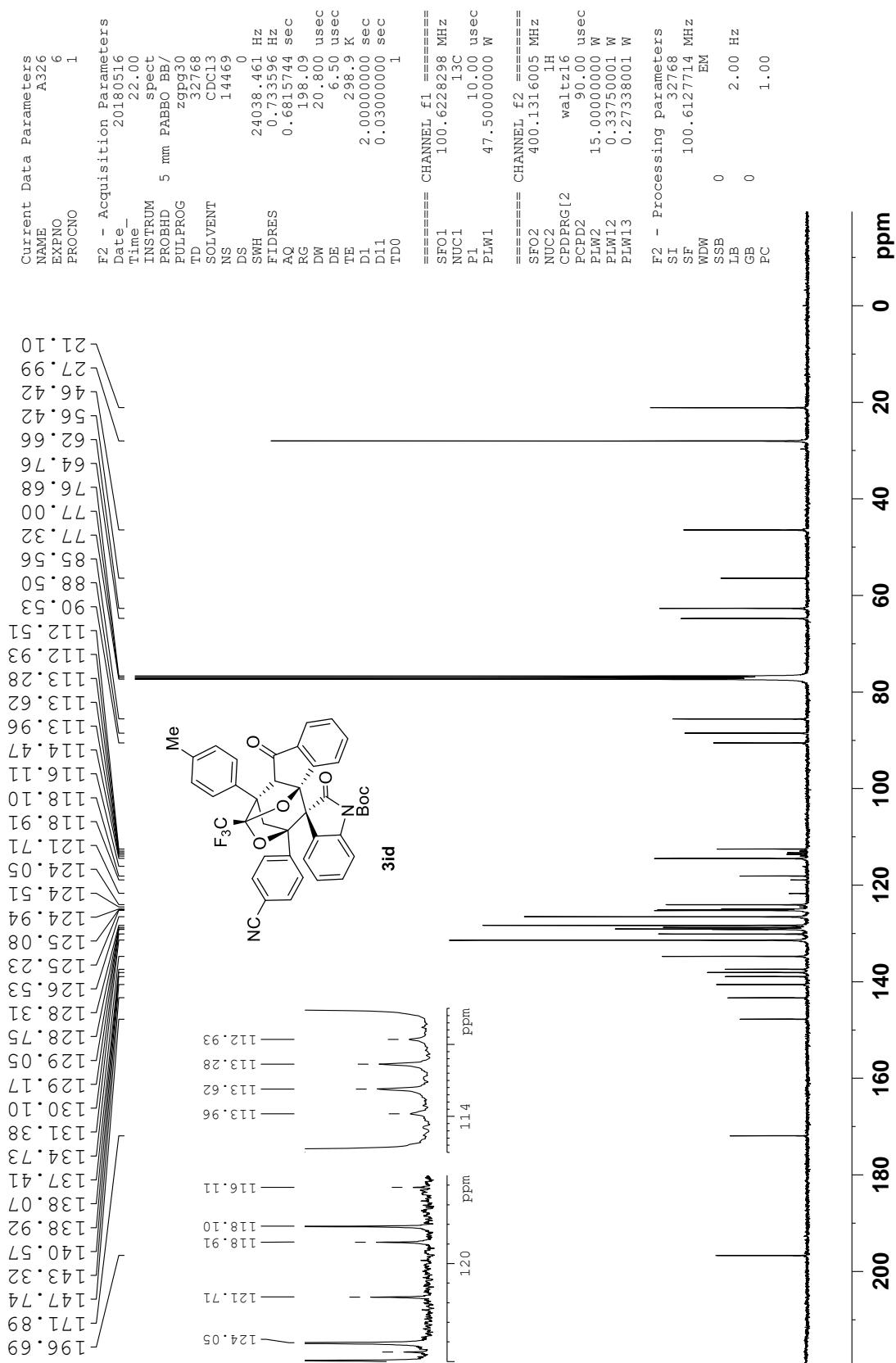


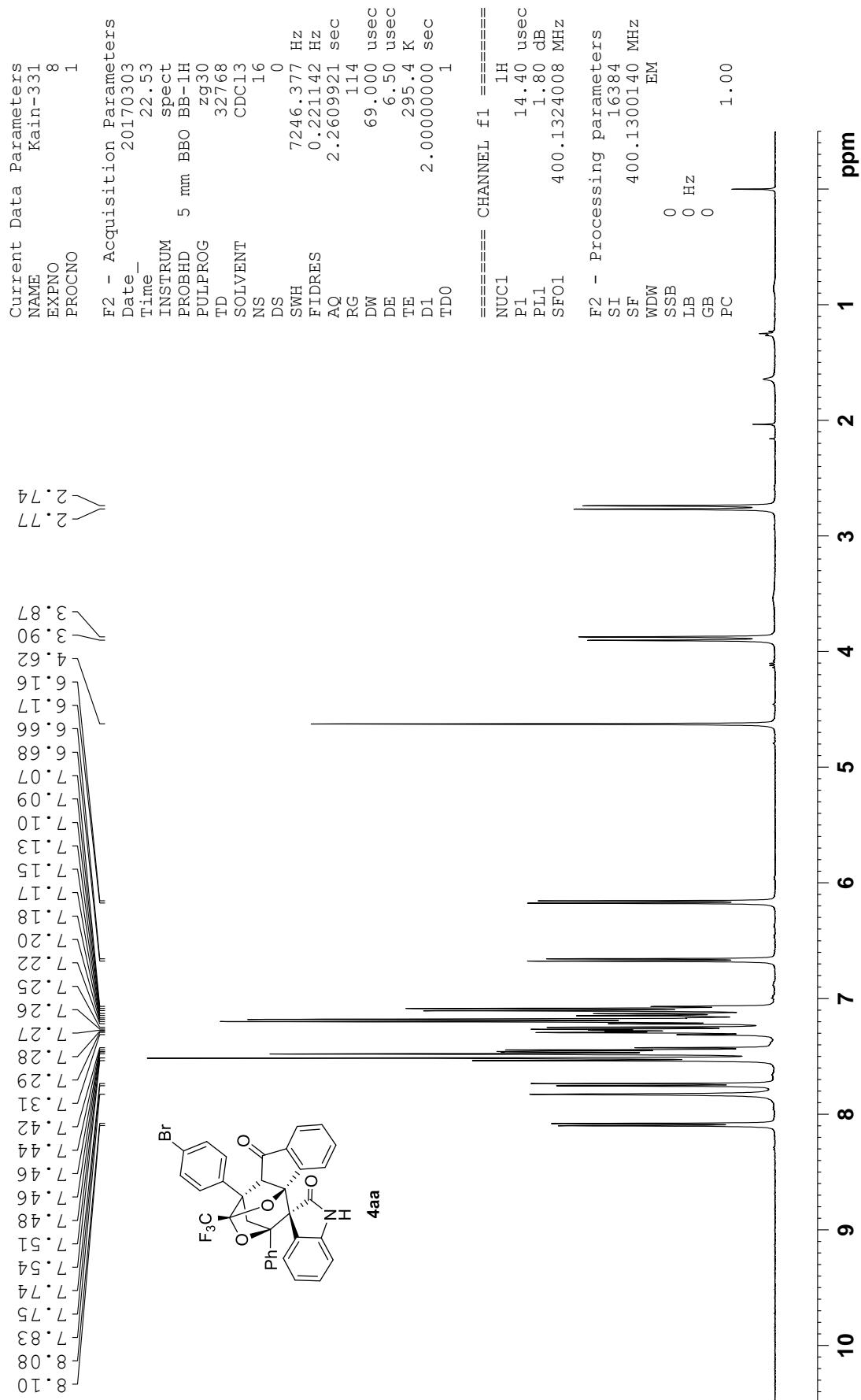


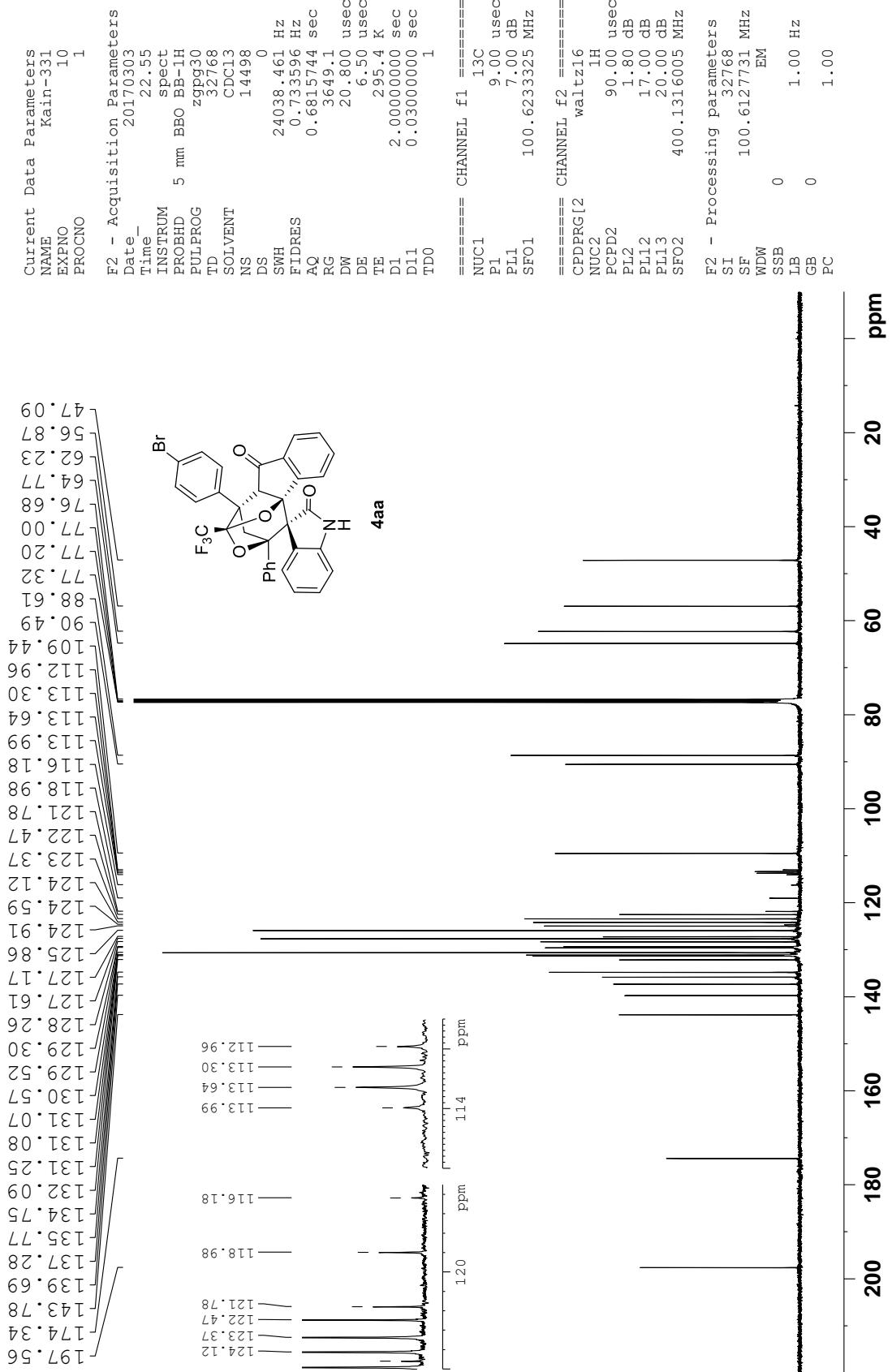








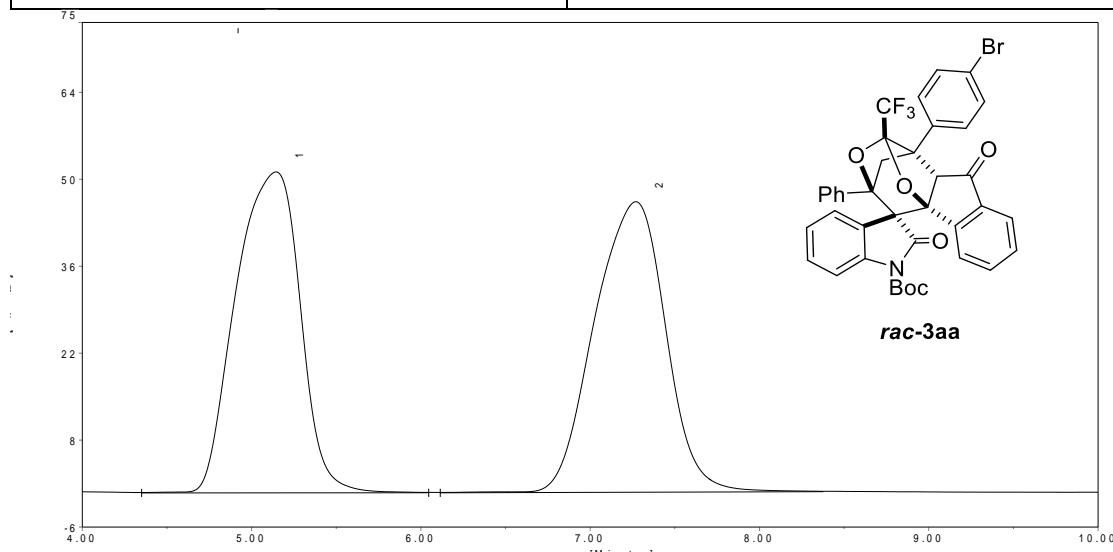




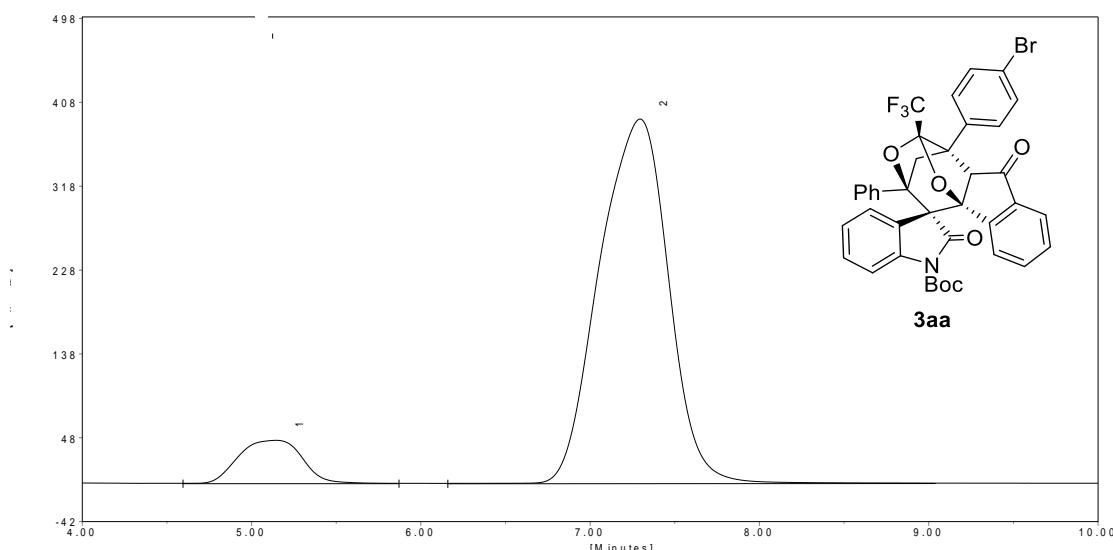
## VII. HPLC chromatograms of adducts 3

HPLC Chromatogram for **3aa**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=95:5	Detector: UV 246 nm



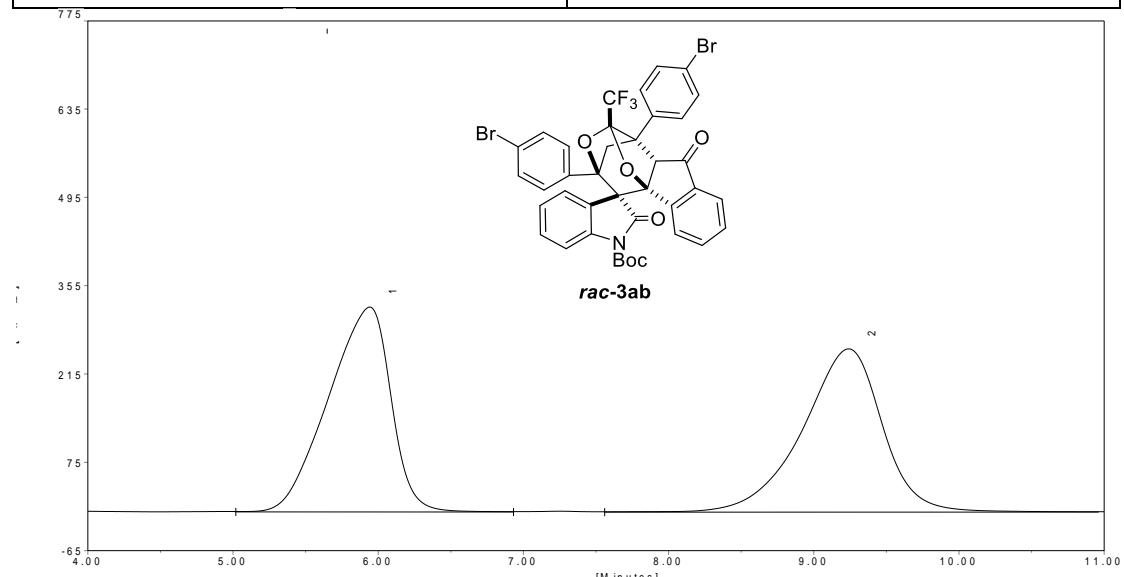
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.15	51.61	1361.43	49.9944
7.27	646.72	1361.73	50.0056



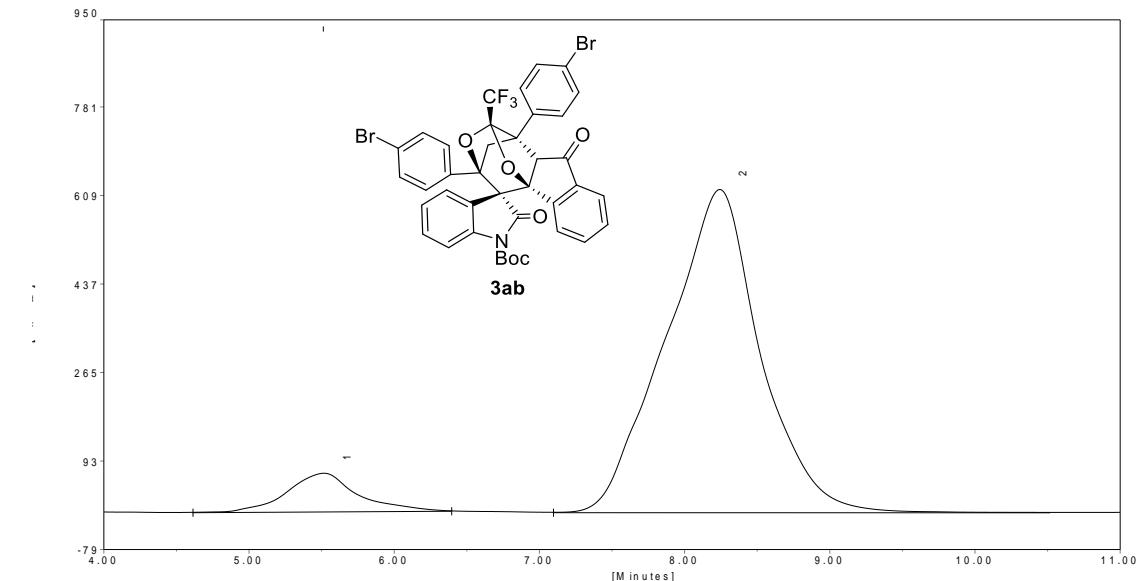
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.15	46.12	1192.36	9.7235
7.30	390.92	11070.23	90.2765

HPLC Chromatogram for **3ab**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 95: 5	Detector: UV 246 nm



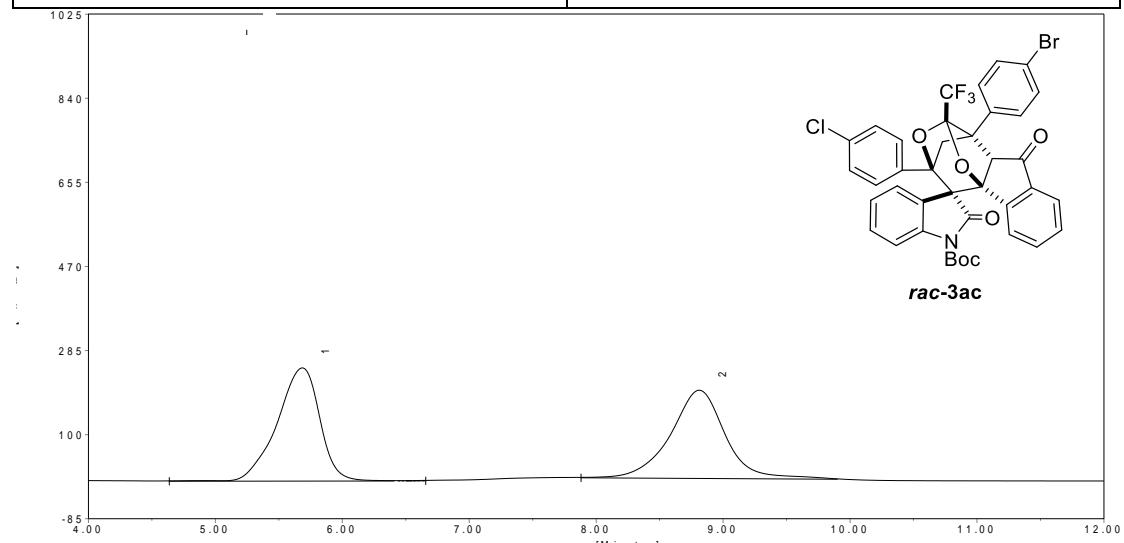
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.94	324.18	9668.60	49.6126
9.24	258.20	9819.59	50.3874



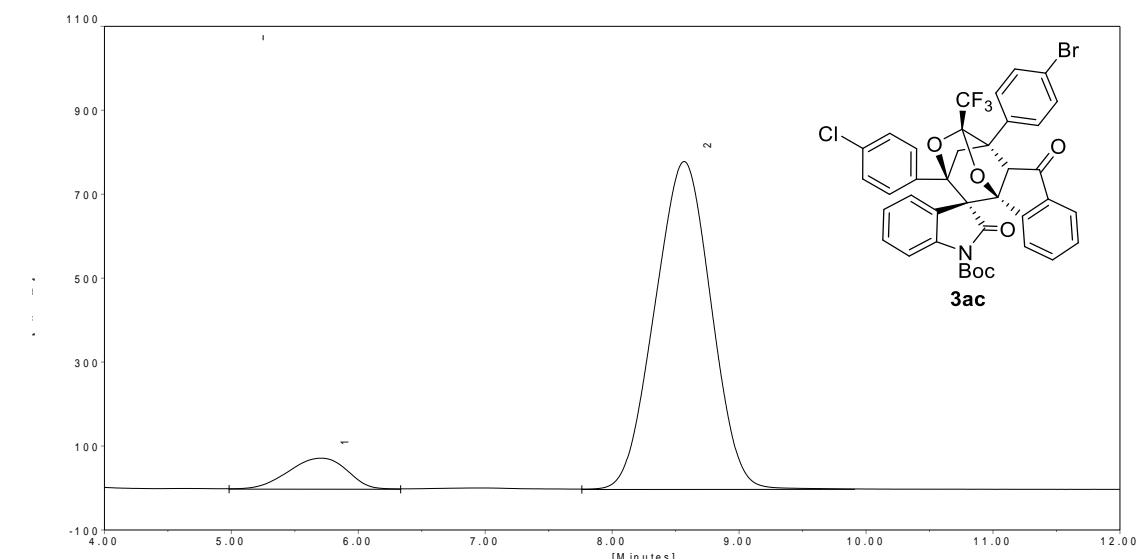
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.52	74.50	2487.44	8.1037
8.24	627.23	28207.59	91.8963

HPLC Chromatogram for **3ac**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 95: 5	Detector: UV 246 nm

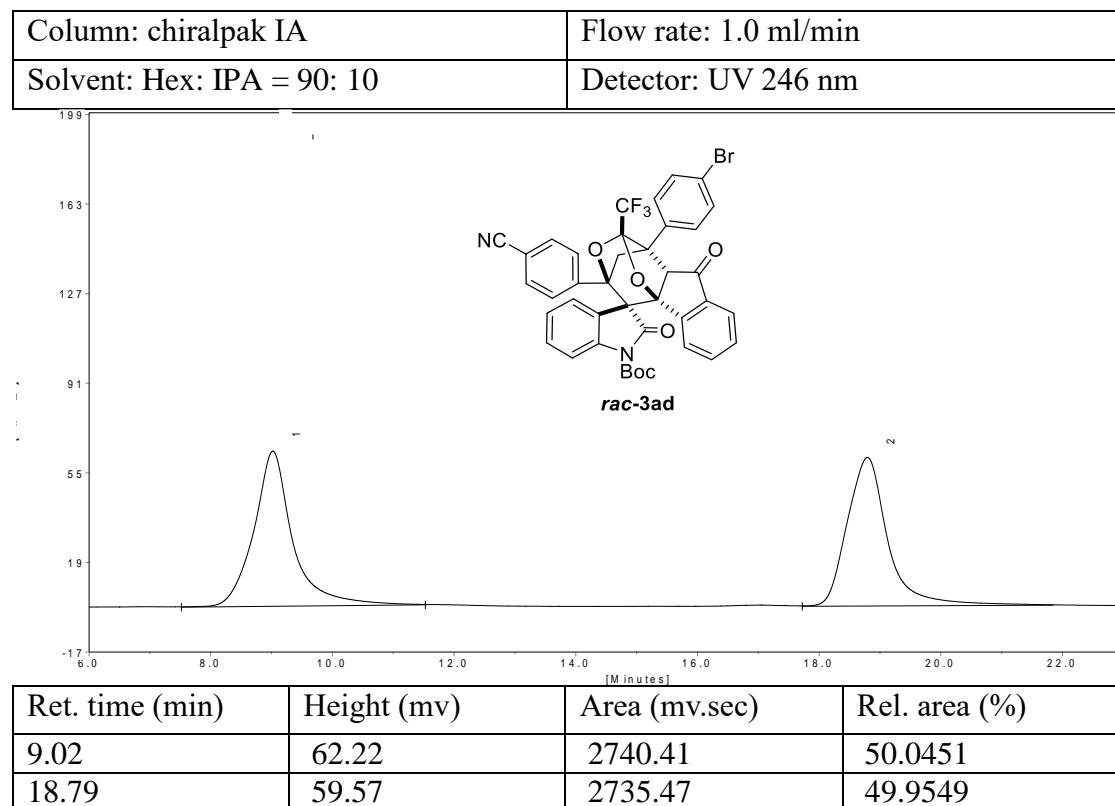


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.69	248.01	5726.70	49.9672
8.81	193.28	5734.21	50.0328

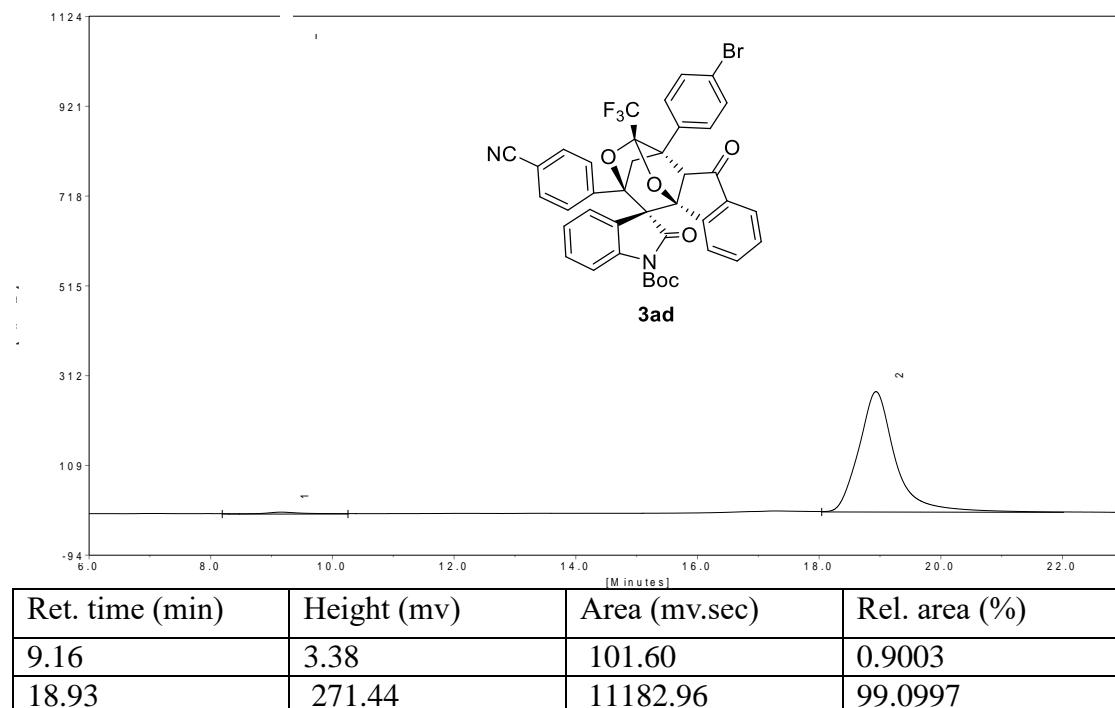


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.71	72.97	2317.94	8.8132
8.57	780.32	23982.73	91.1868

HPLC Chromatogram for **3ad**



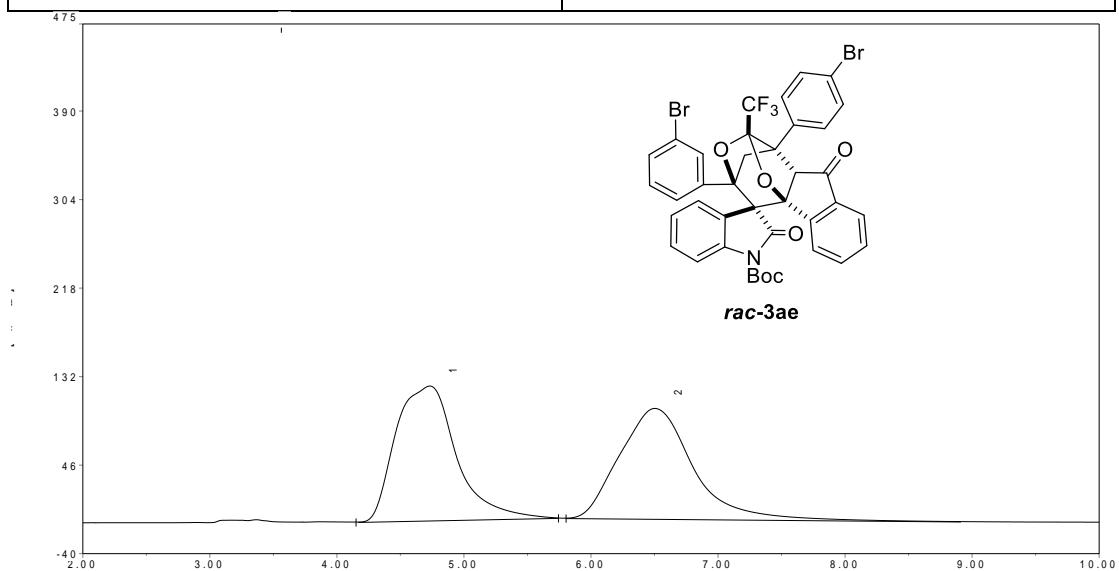
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
9.02	62.22	2740.41	50.0451
18.79	59.57	2735.47	49.9549



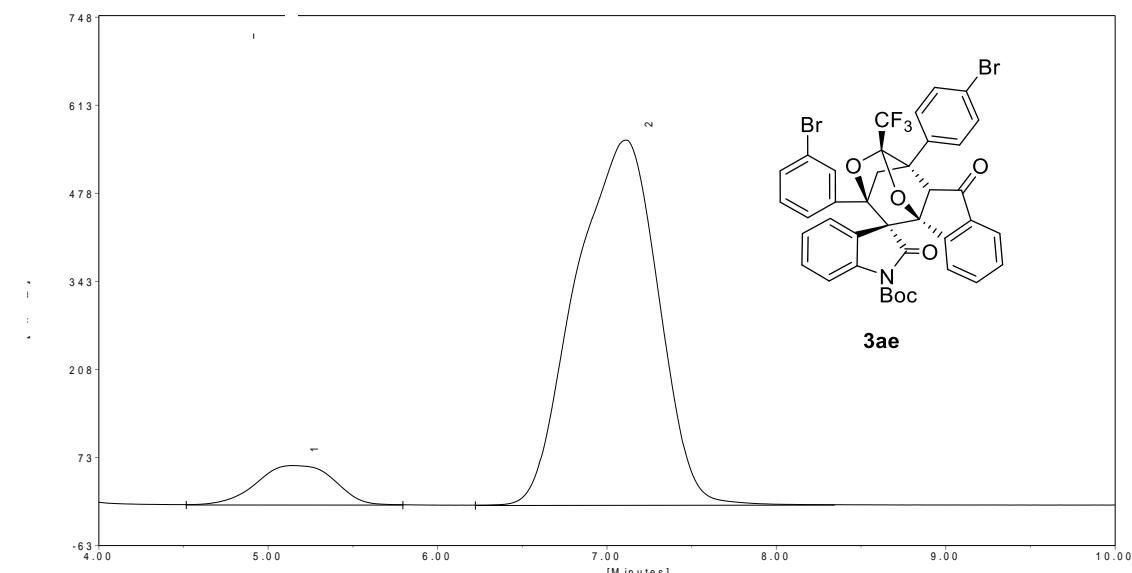
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
9.16	3.38	101.60	0.9003
18.93	271.44	11182.96	99.0997

HPLC Chromatogram for **3ae**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 95: 5	Detector: UV 246 nm

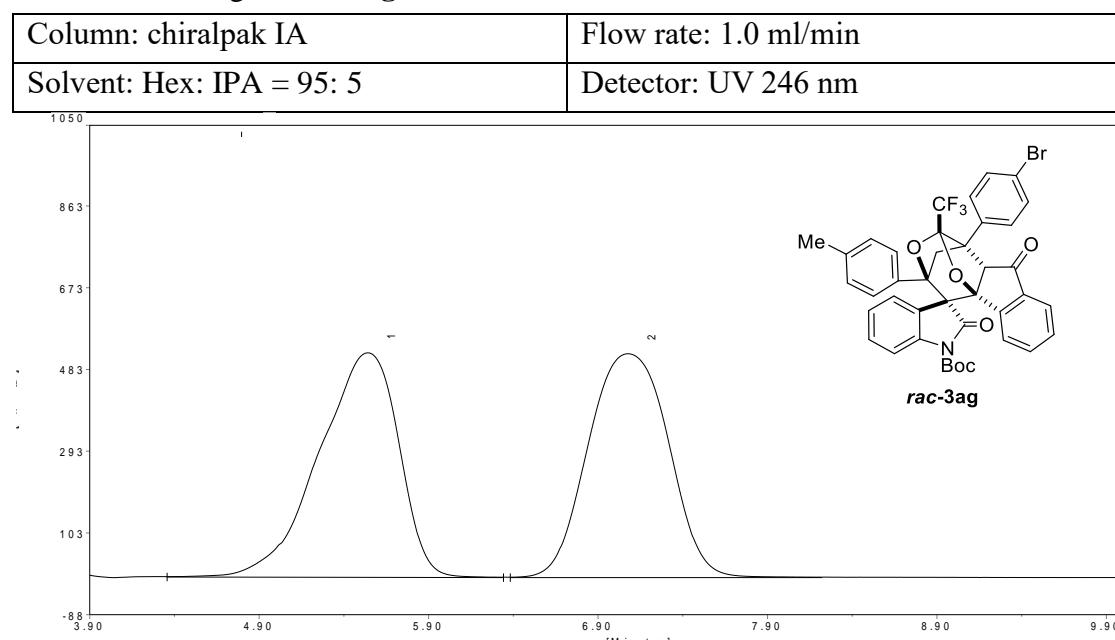


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
4.73	132.13	4539.39	49.1617
6.50	110.36	4694.19	50.8383

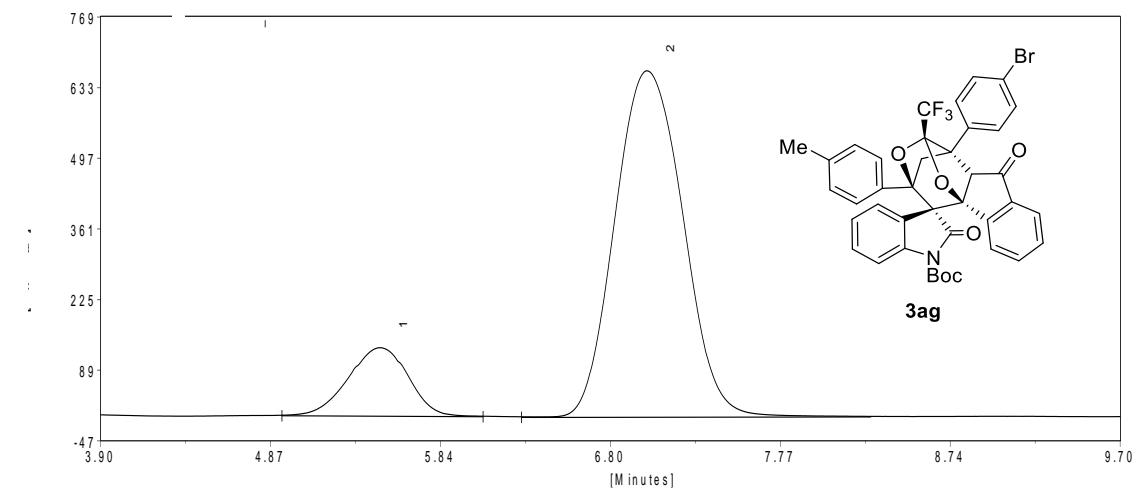


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.14	59.94	1889.23	9.0818
7.11	559.24	18913.15	90.9182

HPLC Chromatogram for **3ag**



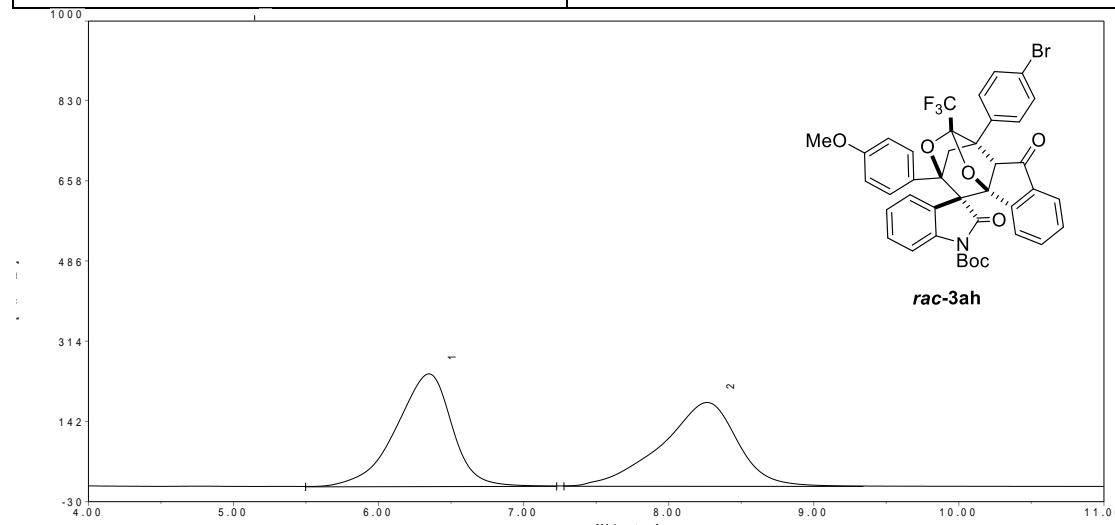
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.54	520.92	16998.70	49.9007
7.08	519.41	17066.35	50.0993



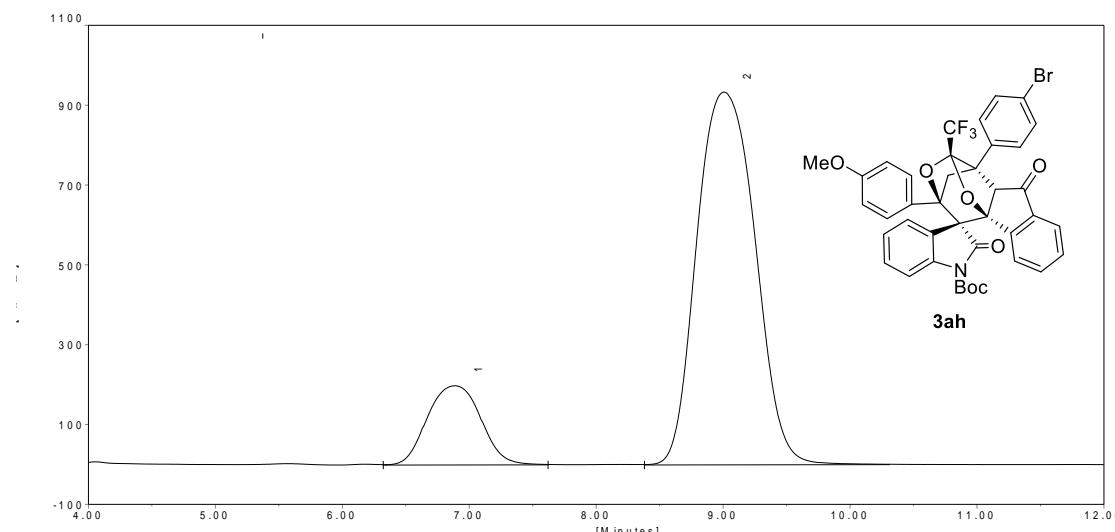
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.49	130.89	3086.93	14.7378
7.01	665.89	17858.78	85.2622

HPLC Chromatogram for **3ah**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 95: 5	Detector: UV 246 nm



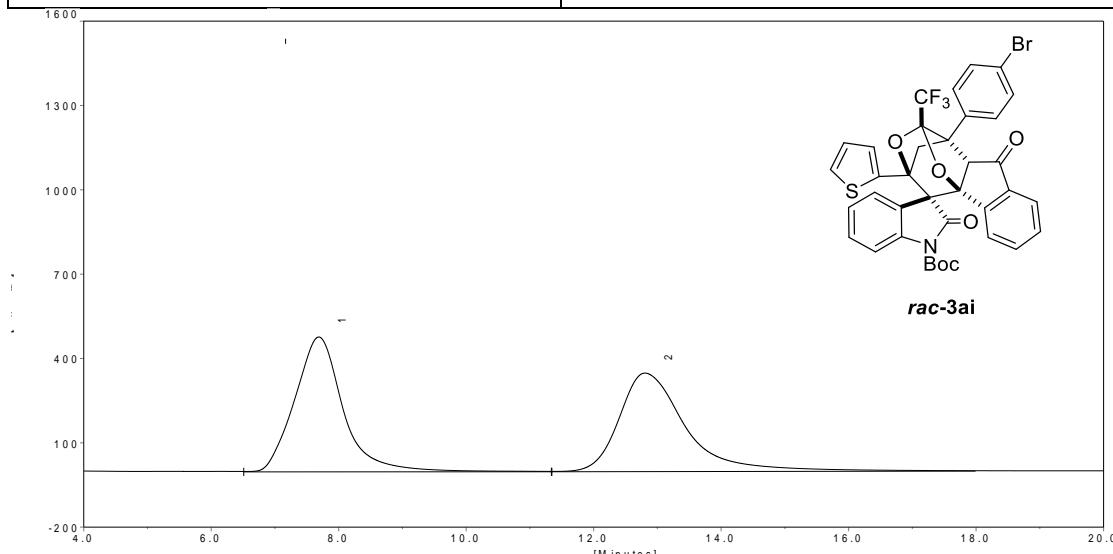
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
6.35	240.73	6438.76	49.9649
8.26	178.93	6447.80	50.0351



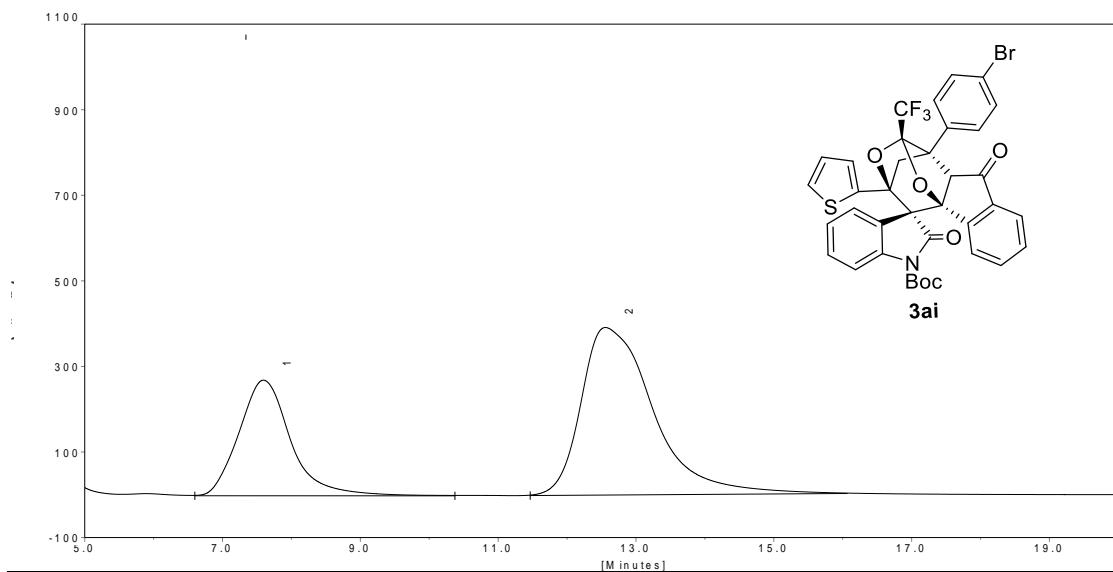
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
6.89	197.48	5728.72	16.1475
9.01	932.90	29748.74	83.8525

HPLC Chromatogram for **3ai**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 98: 2	Detector: UV 246 nm

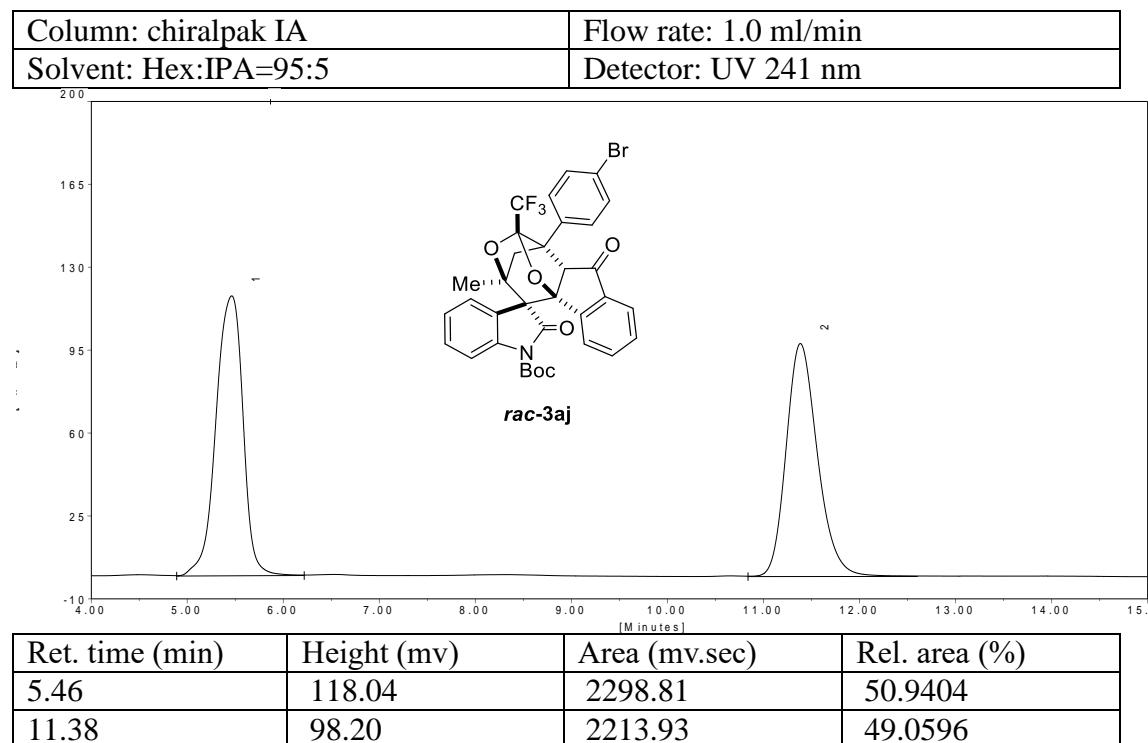


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
7.69	478.15	24901.30	50.0539
12.81	348.55	24847.68	49.9461

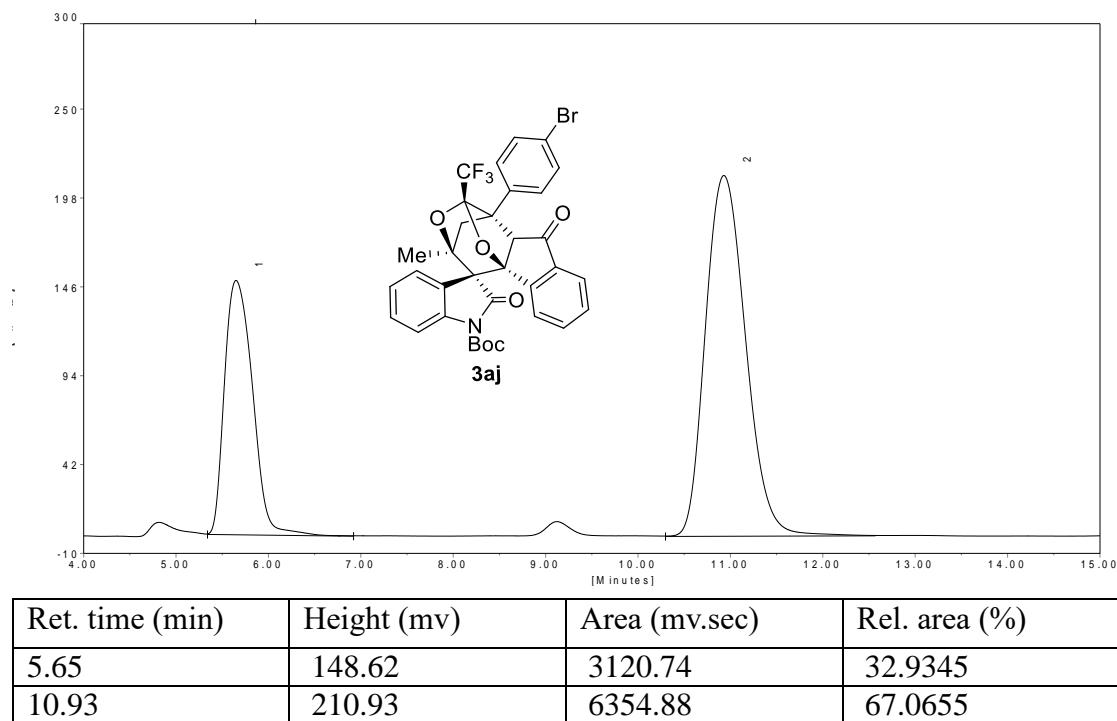


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
7.59	269.34	13920.60	32.9209
12.56	390.68	28364.34	67.0791

HPLC Chromatogram for **3aj**



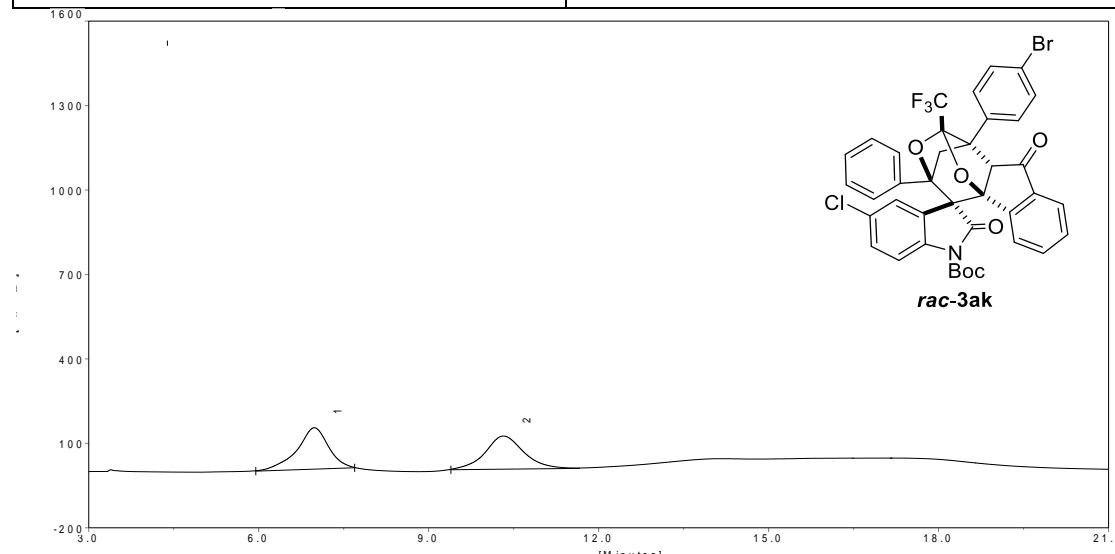
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.46	118.04	2298.81	50.9404
11.38	98.20	2213.93	49.0596



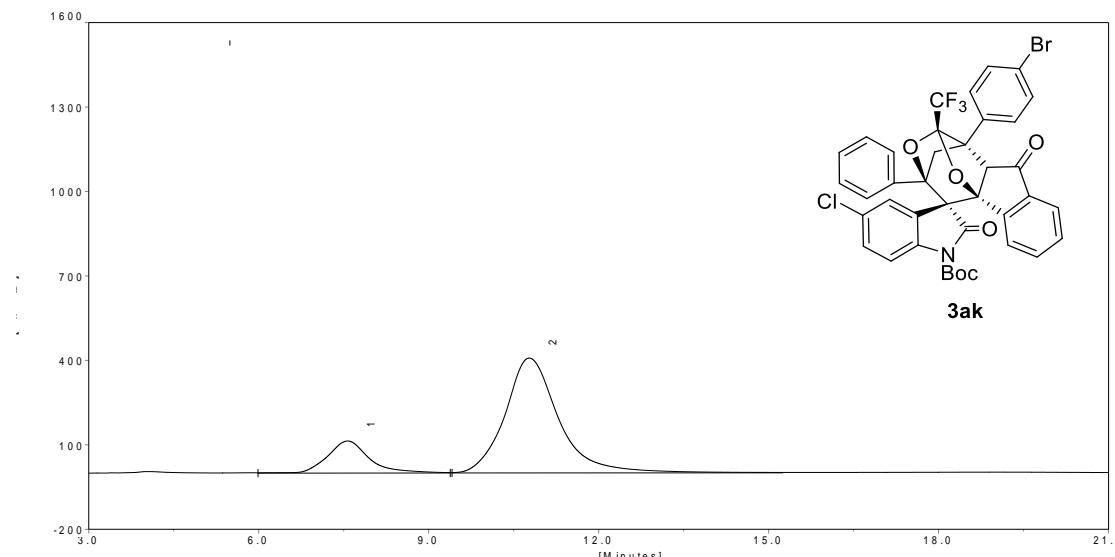
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.65	148.62	3120.74	32.9345
10.93	210.93	6354.88	67.0655

HPLC Chromatogram for **3ak**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 98: 2	Detector: UV 246 nm



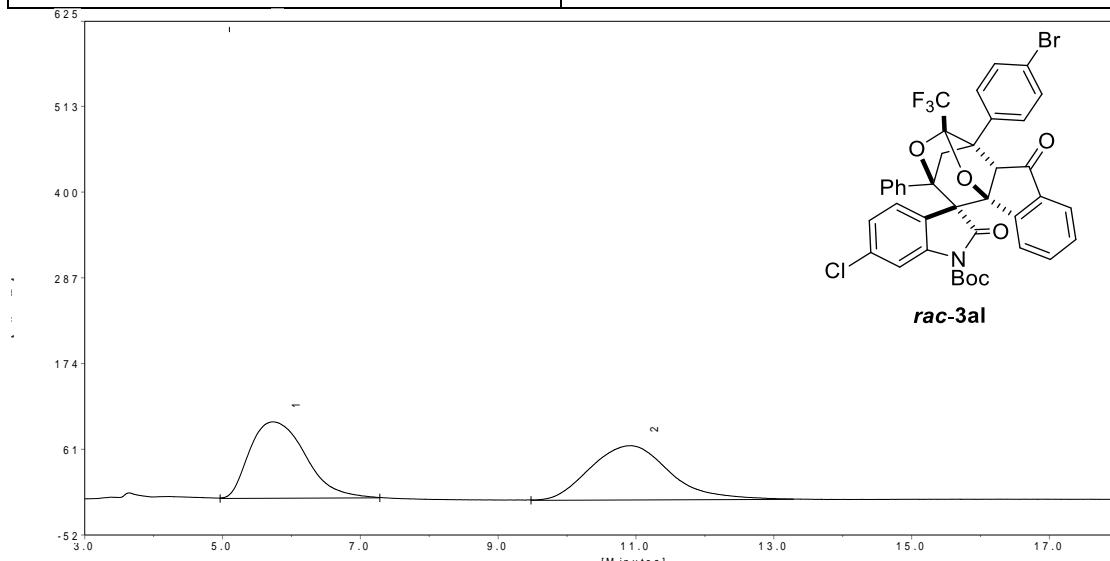
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
6.98	145.75	5565.29	50.6782
10.32	116.49	5416.33	49.3218



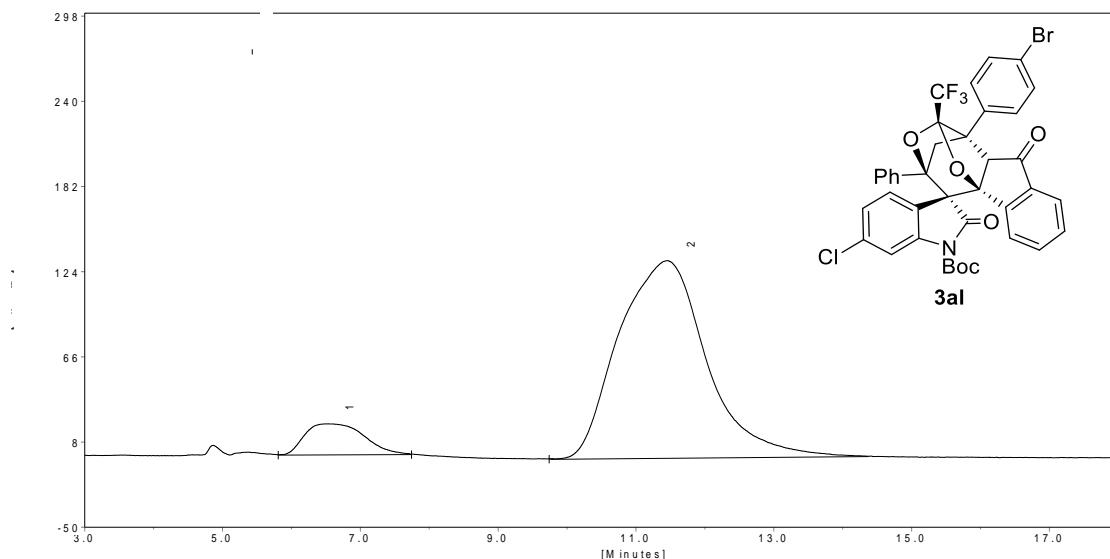
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
7.57	112.58	5584.76	17.3961
10.78	406.67	26518.82	82.6039

HPLC Chromatogram for **3al**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 98: 2	Detector: UV 246 nm

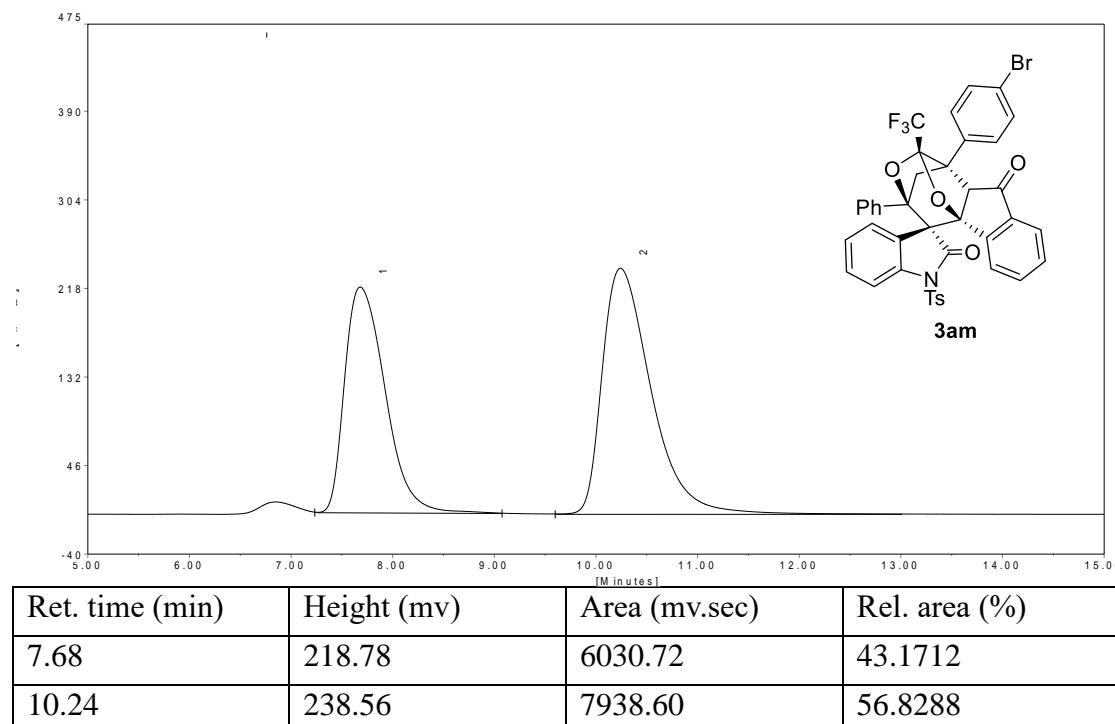
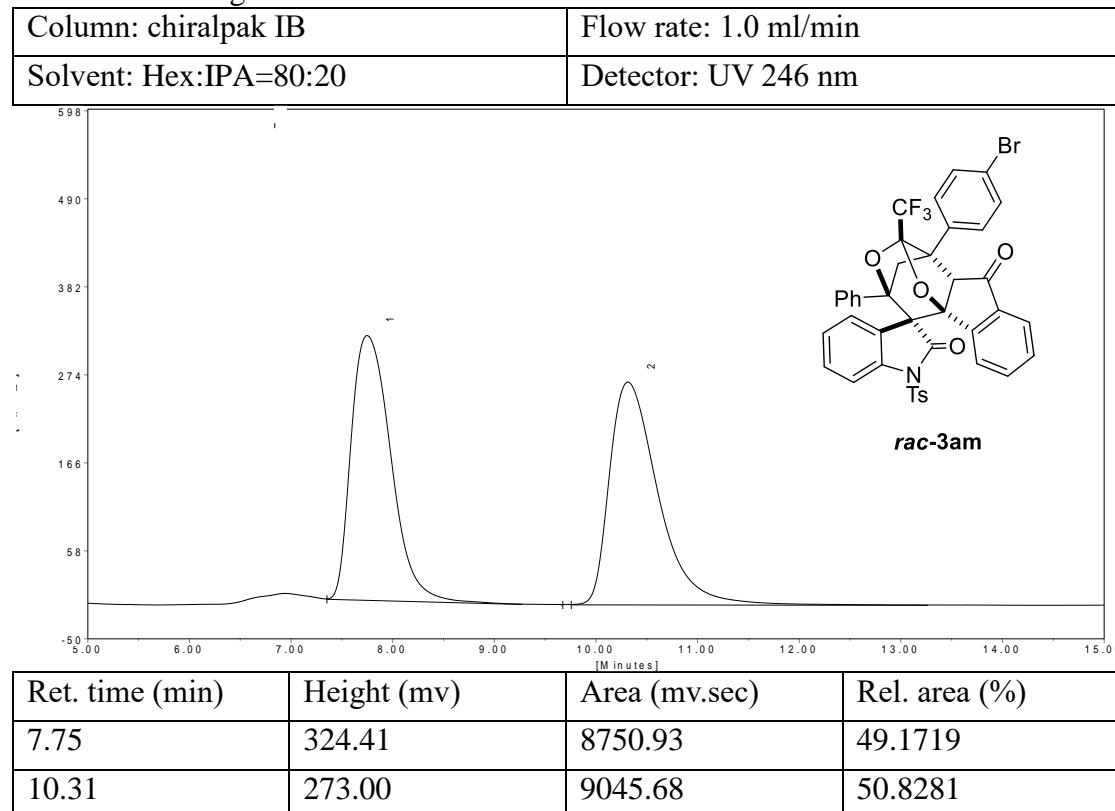


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
5.72	100.18	5616.95	49.9638
10.92	70.94	5625.09	50.0362



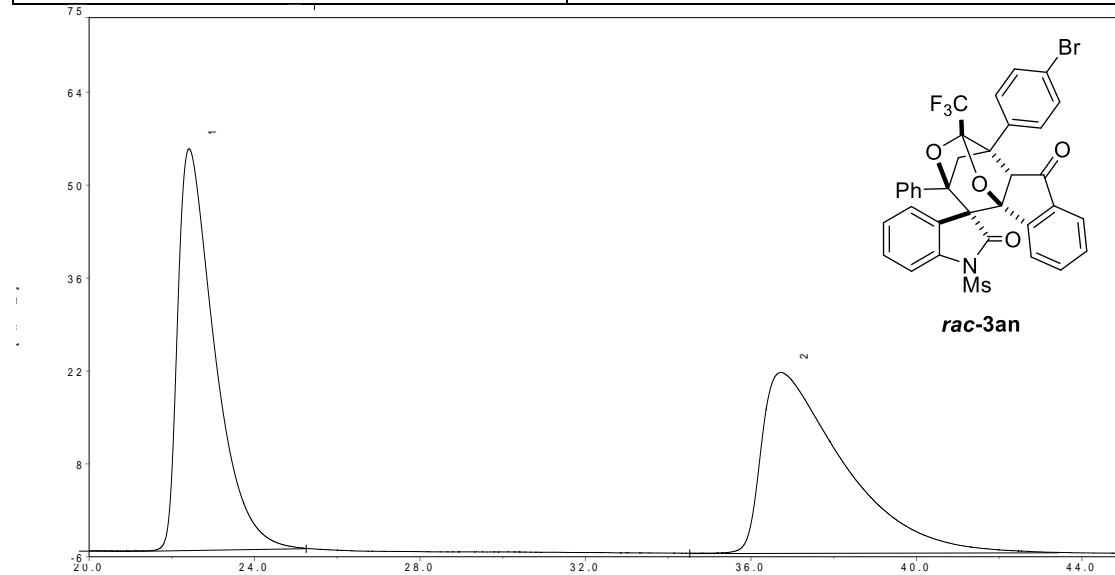
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
6.50	20.86	1231.48	9.4235
11.46	134.20	11836.80	90.5765

HPLC Chromatogram for **3am**

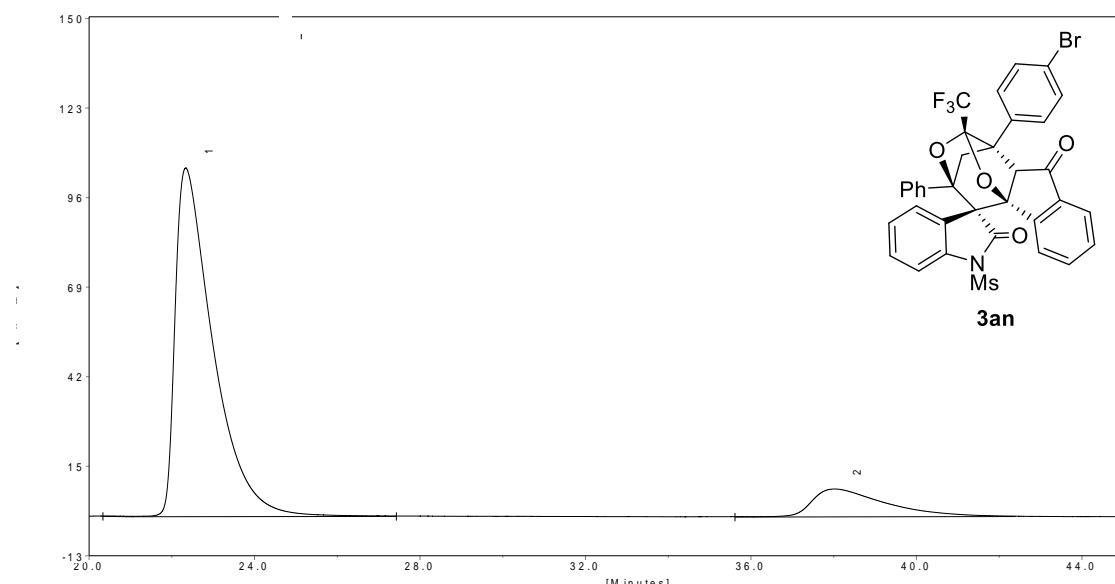


HPLC Chromatogram for **3an**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=80:20	Detector: UV 246 nm



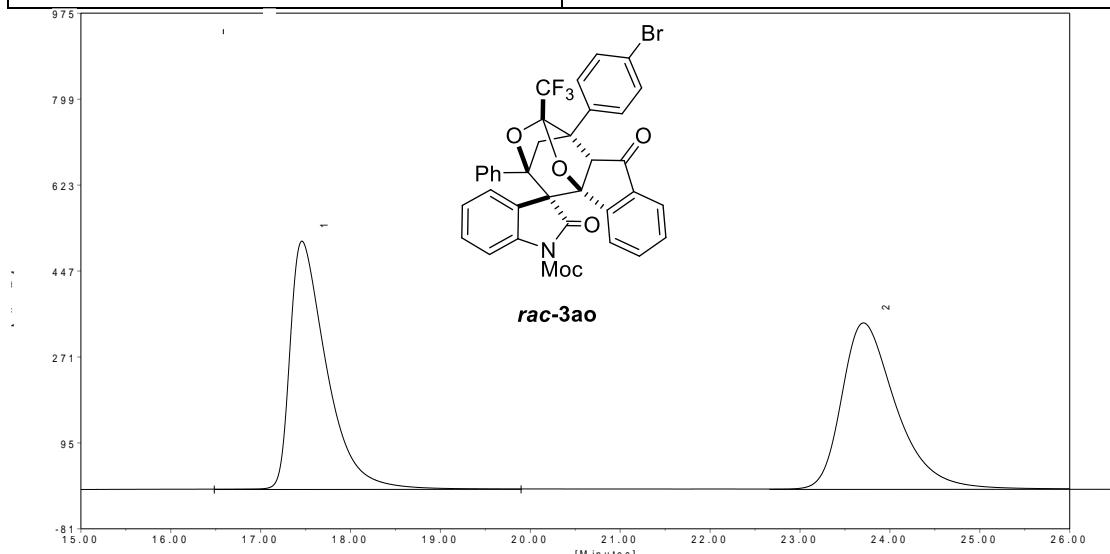
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
22.42	60.42	3715.95	49.8213
36.72	27.21	3742.61	50.1787



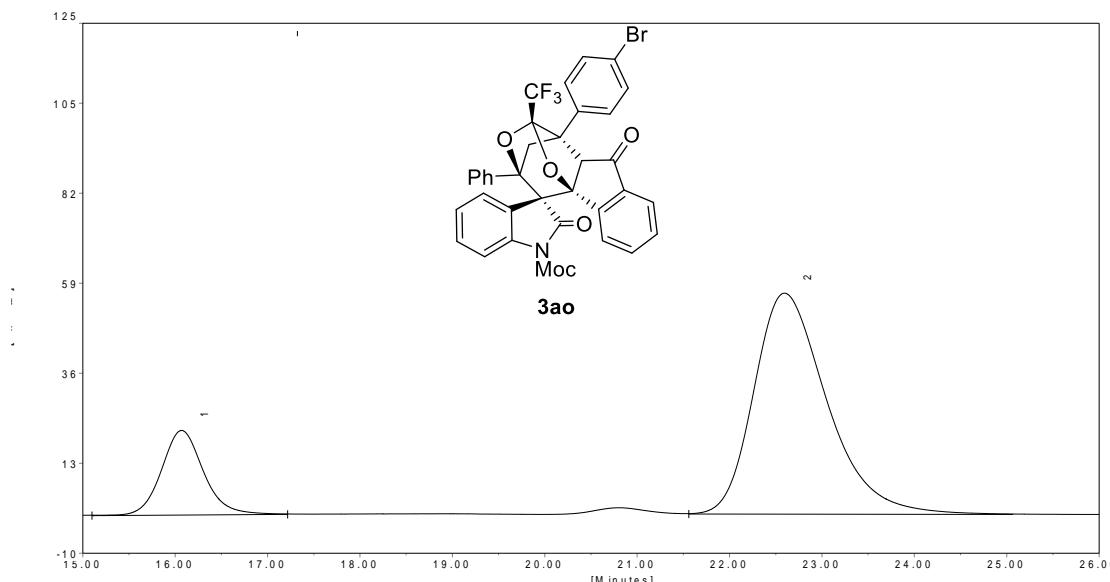
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
22.33	104.93	6619.58	86.9557
38.00	8.29	993.01	13.0443

HPLC Chromatogram for **3ao**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=95:5	Detector: UV 246 nm

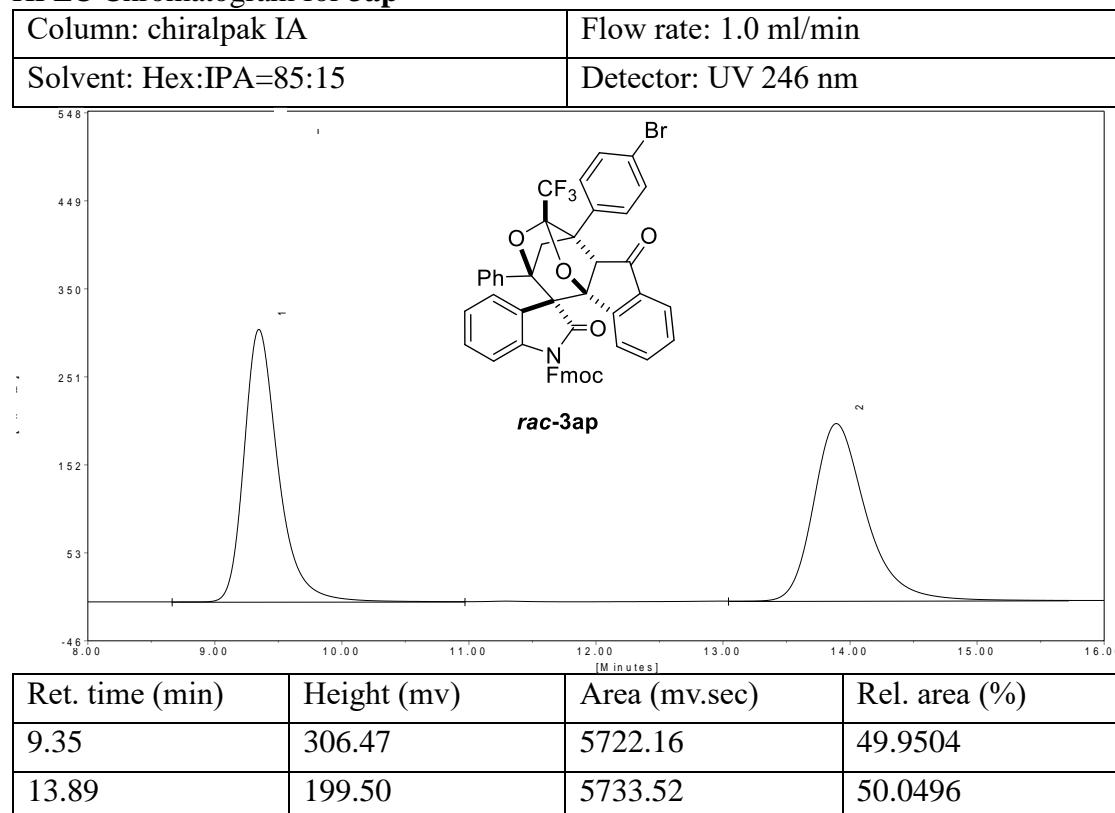


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
17.46	508.00	14301.21	50.0350
23.71	340.26	14281.18	49.9650

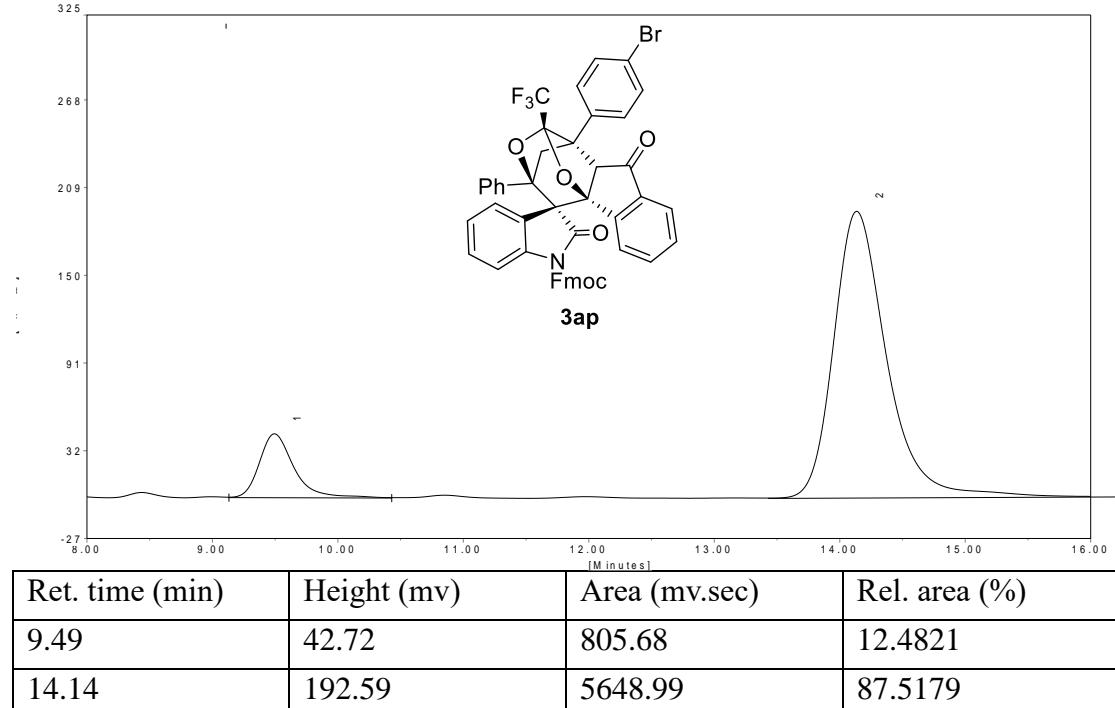


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
16.07	21.51	670.09	17.8569
22.60	56.36	3082.47	82.1431

HPLC Chromatogram for **3ap**



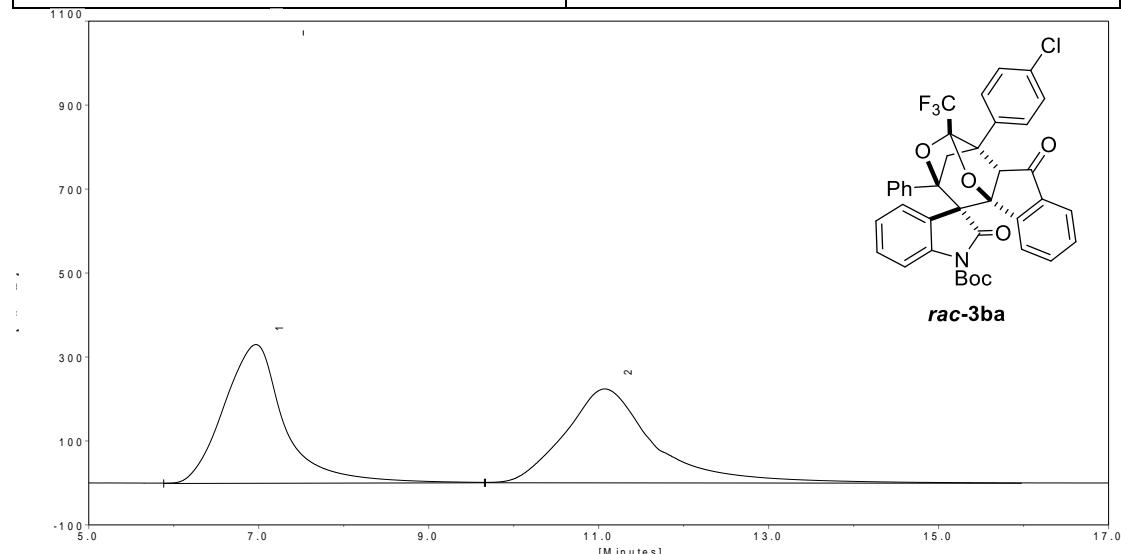
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
9.35	306.47	5722.16	49.9504
13.89	199.50	5733.52	50.0496



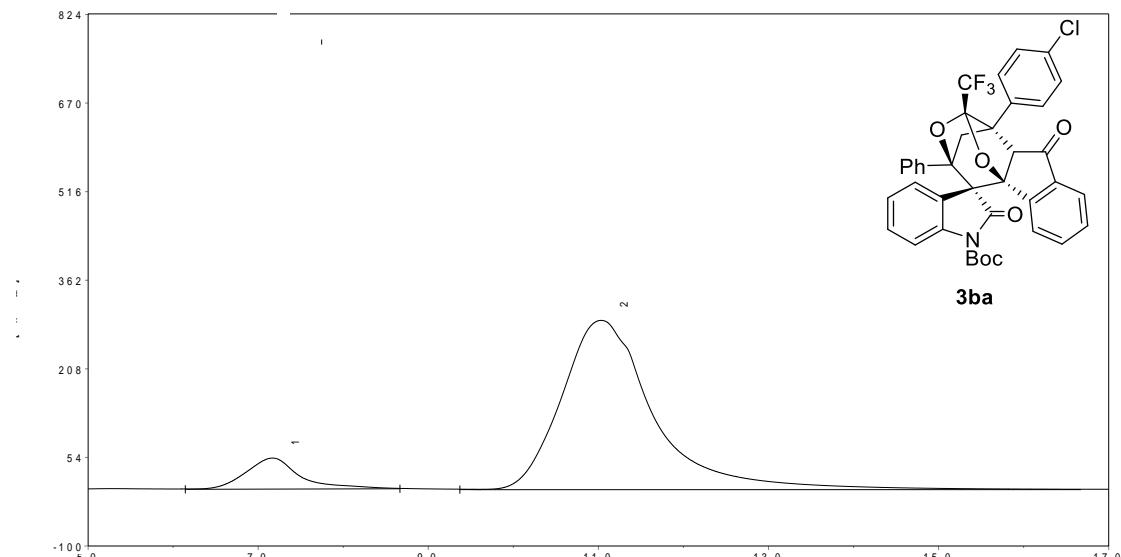
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
9.49	42.72	805.68	12.4821
14.14	192.59	5648.99	87.5179

HPLC Chromatogram for **3ba**

Column: chiralpak IA	Flow rate: 0.8 ml/min
Solvent: Hex: EtOH = 98:2	Detector: UV 246 nm



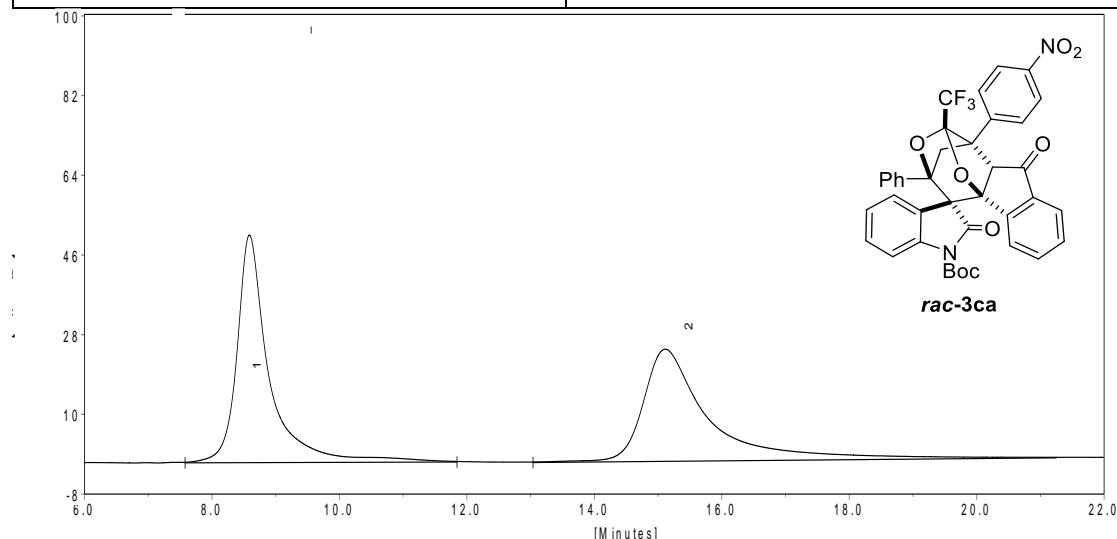
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
6.97	329.49	16209.50	50.0869
11.07	222.79	16153.28	49.9131



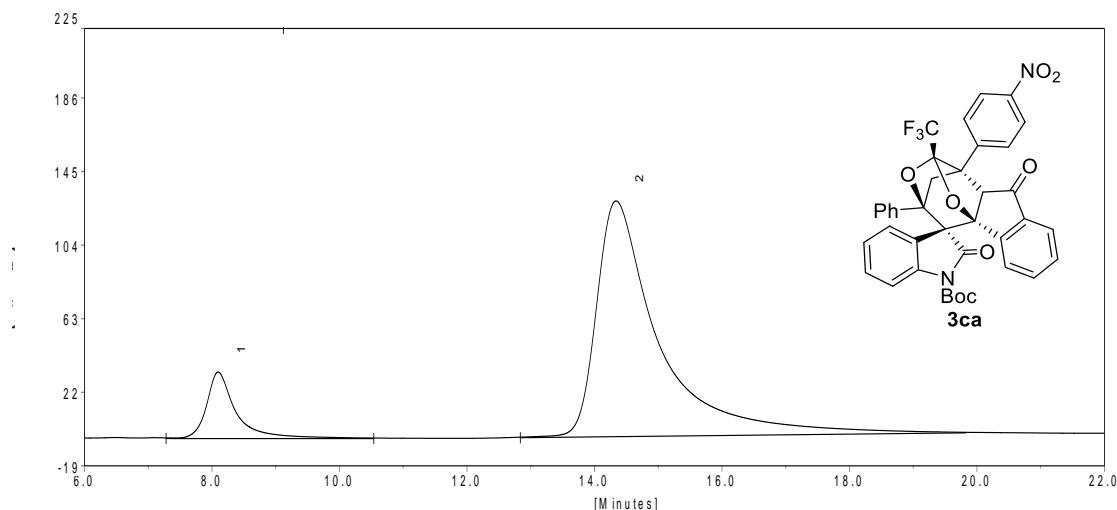
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
7.17	53.29	2299.49	9.4650
11.03	293.45	21995.19	90.5350

HPLC Chromatogram for **3ca**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 95:5	Detector: UV 246 nm



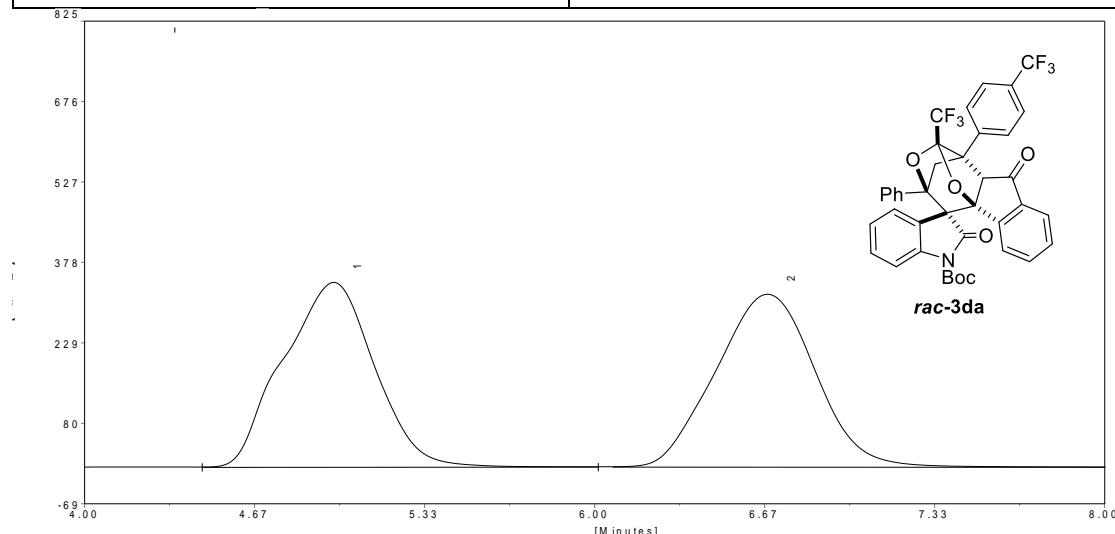
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
8.34	16.70	1786.19	50.0771
15.12	25.23	1780.69	49.9229



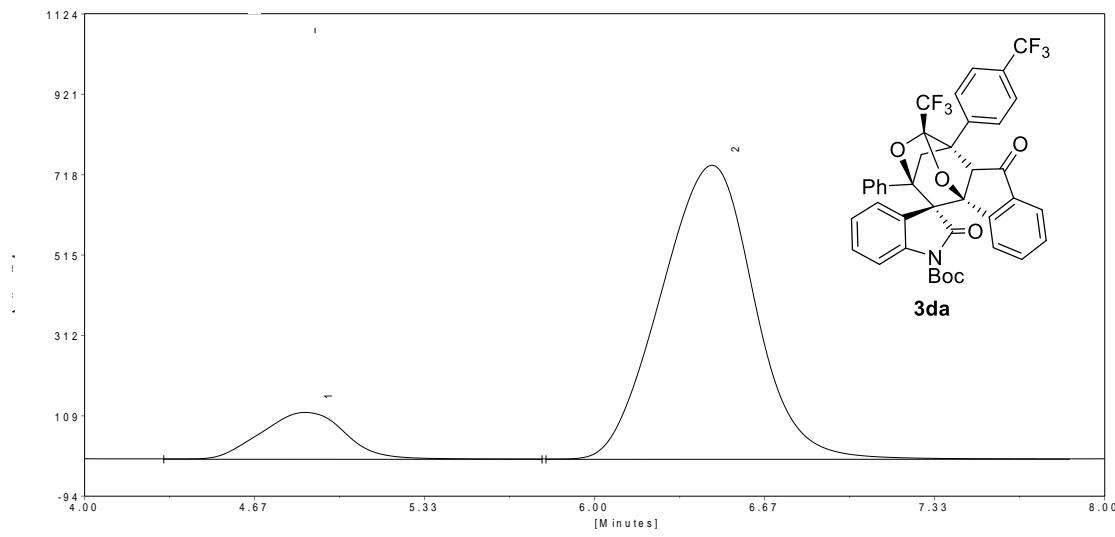
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
8.10	36.73	1145.16	11.3935
14.34	131.08	8905.78	88.6065

HPLC Chromatogram for **3da**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 95:5	Detector: UV 246 nm

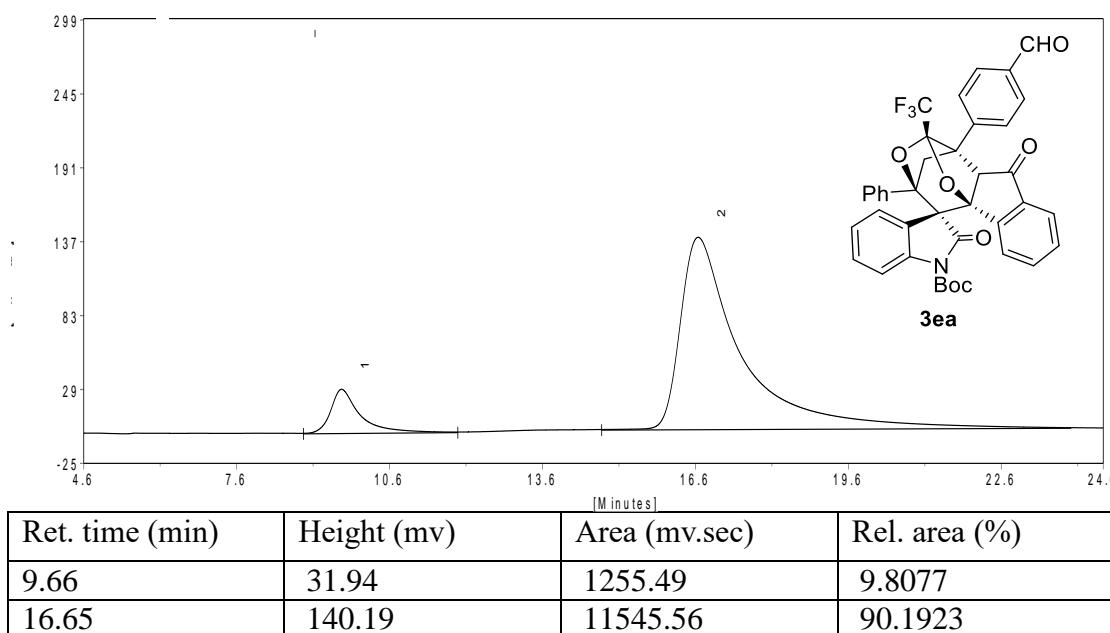
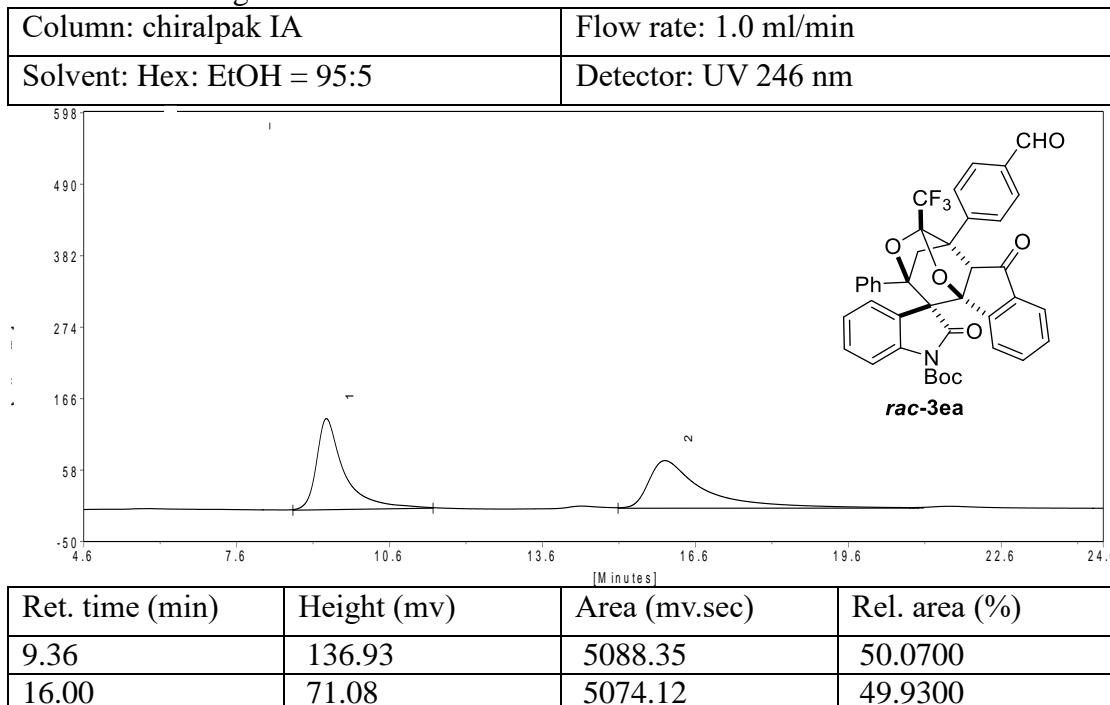


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
4.46	4.98	341.75	49.5791
6.07	6.68	319.44	50.4209

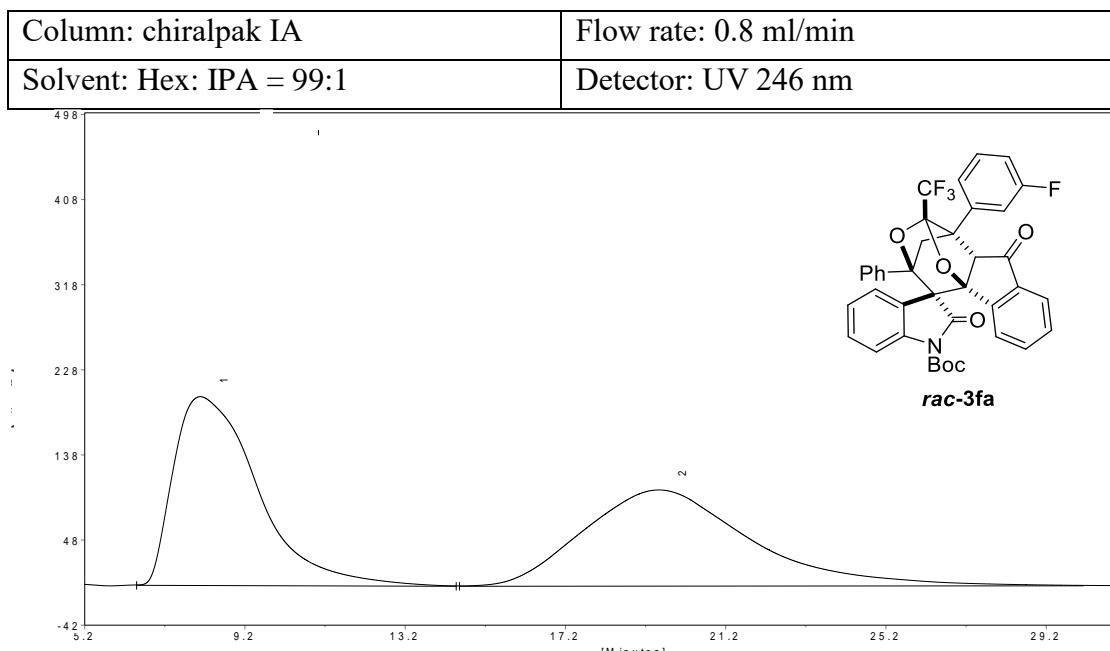


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
4.87	117.32	2659.29	12.3541
6.46	741.76	18866.19	87.6459

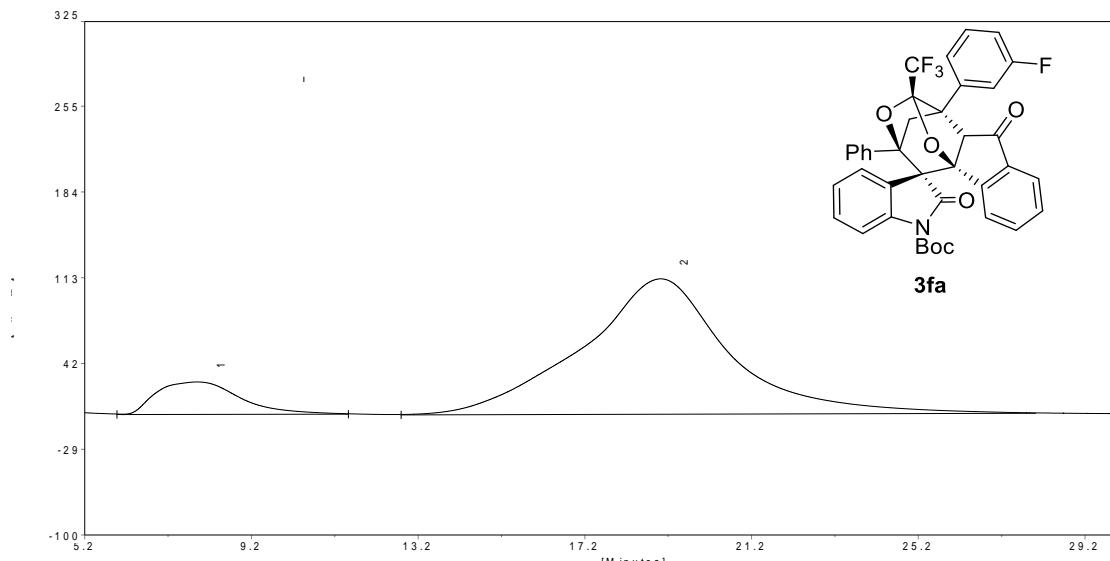
HPLC Chromatogram for **3ea**



HPLC Chromatogram for **3fa**



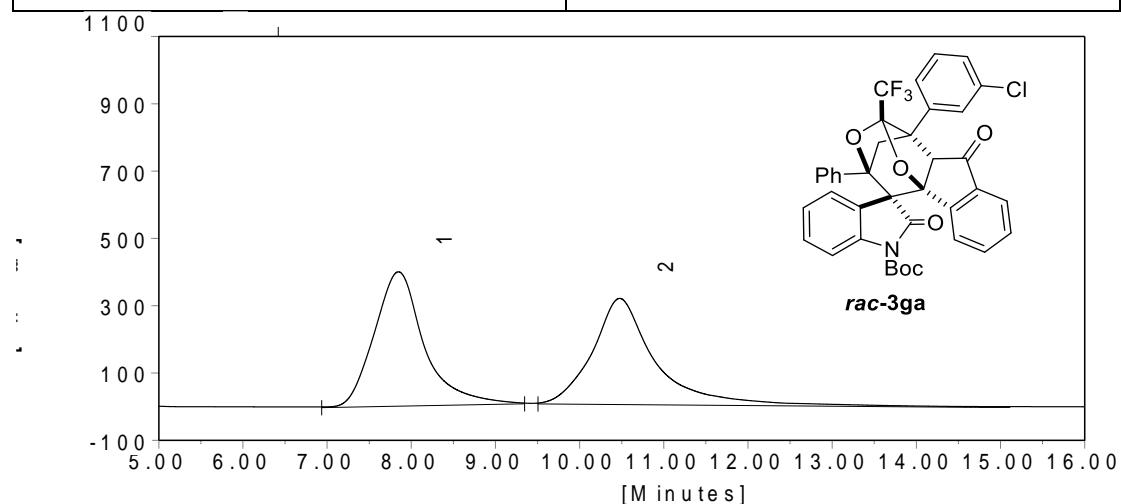
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
8.09	199.25	29006.59	50.0656
19.53	101.26	28930.59	49.9344



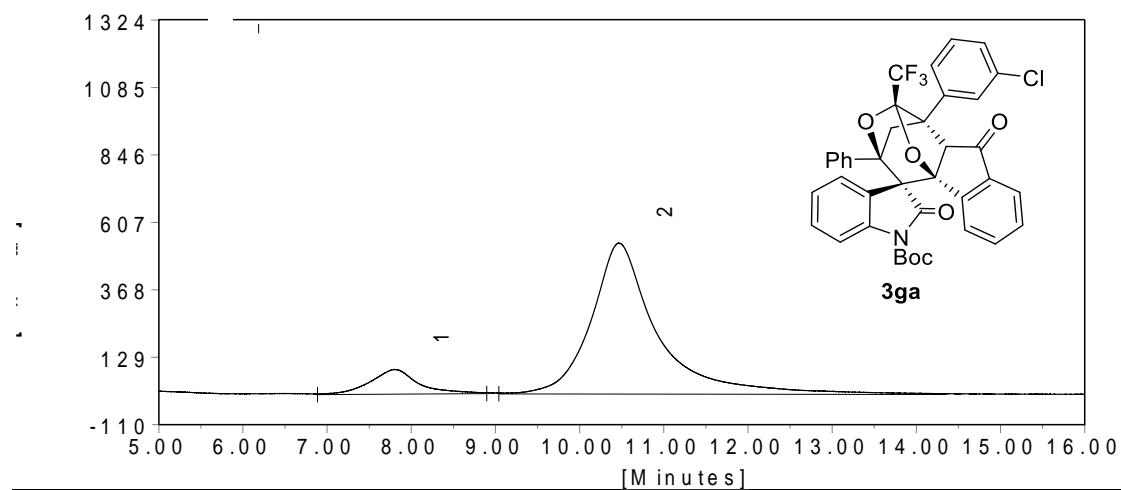
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
7.90	26.48	3618.58	11.7278
19.01	111.75	27236.05	88.2722

HPLC Chromatogram for **3ga**

Column: chiralpak IA	Flow rate: 0.7 ml/min
Solvent: Hex: EtOH = 98:2	Detector: UV 246 nm



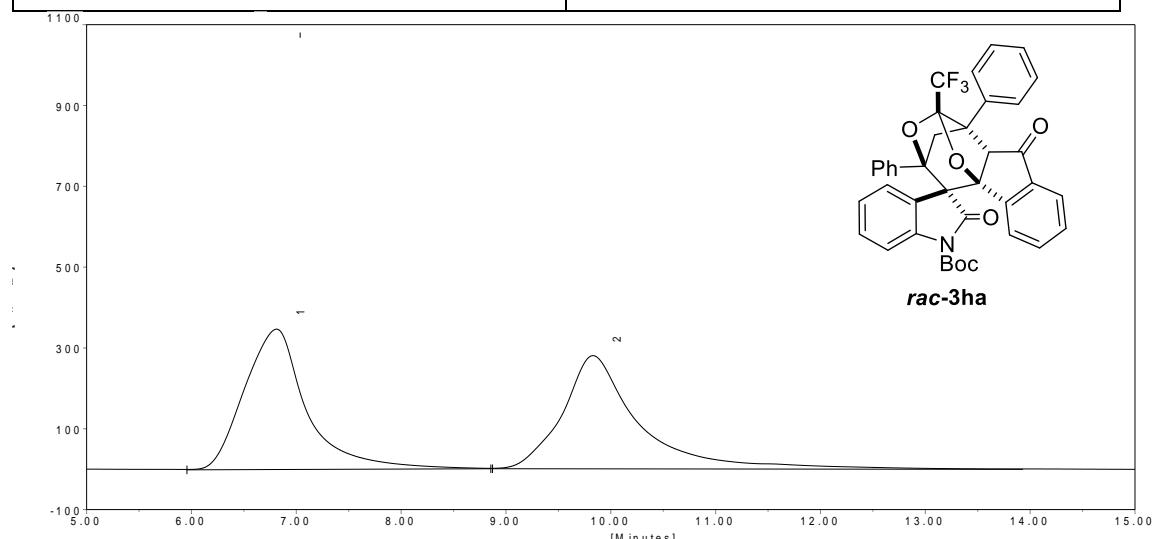
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
7.85	397.05	16115.25	50.3743
10.48	312.97	15875.75	49.6257



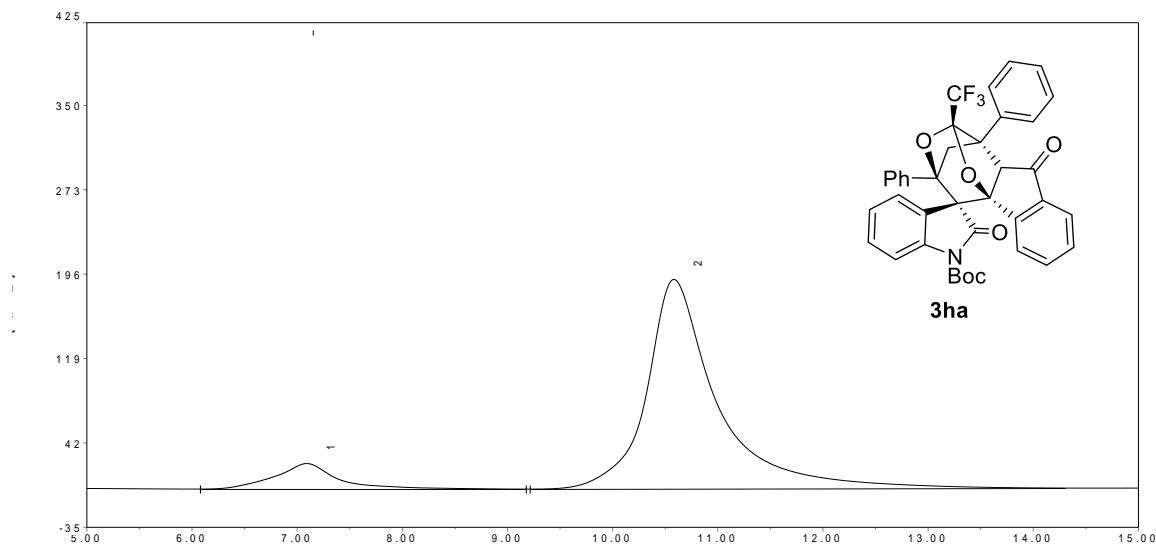
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
7.81	84.65	3159.01	9.9774
10.46	531.69	28502.74	90.0226

HPLC Chromatogram for **3ha**

Column: chiralpak IA	Flow rate: 0.8 ml/min
Solvent: Hex: EtOH = 98:2	Detector: UV 246 nm



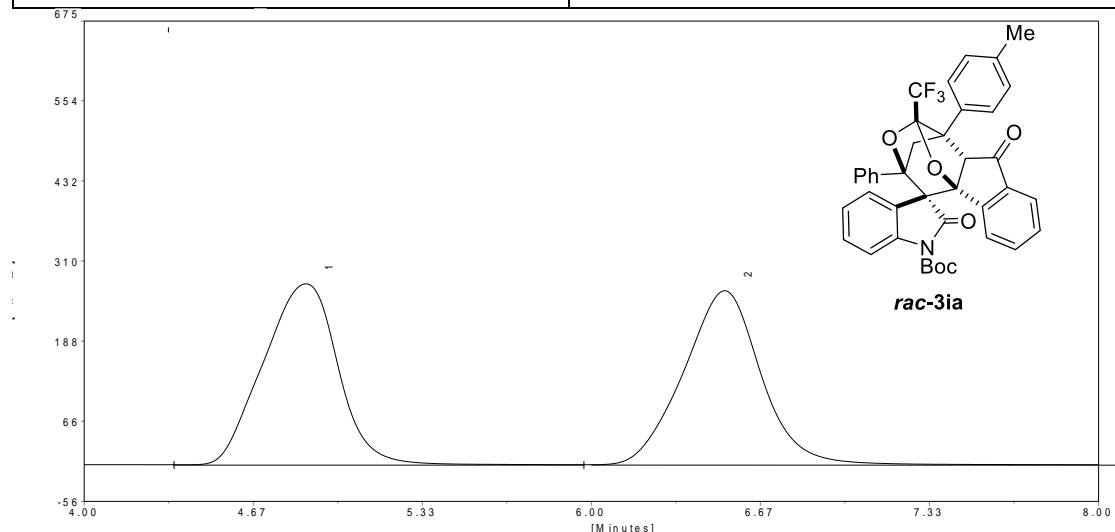
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
6.81	346.35	14208.50	50.3844
9.83	279.11	13991.70	49.6156



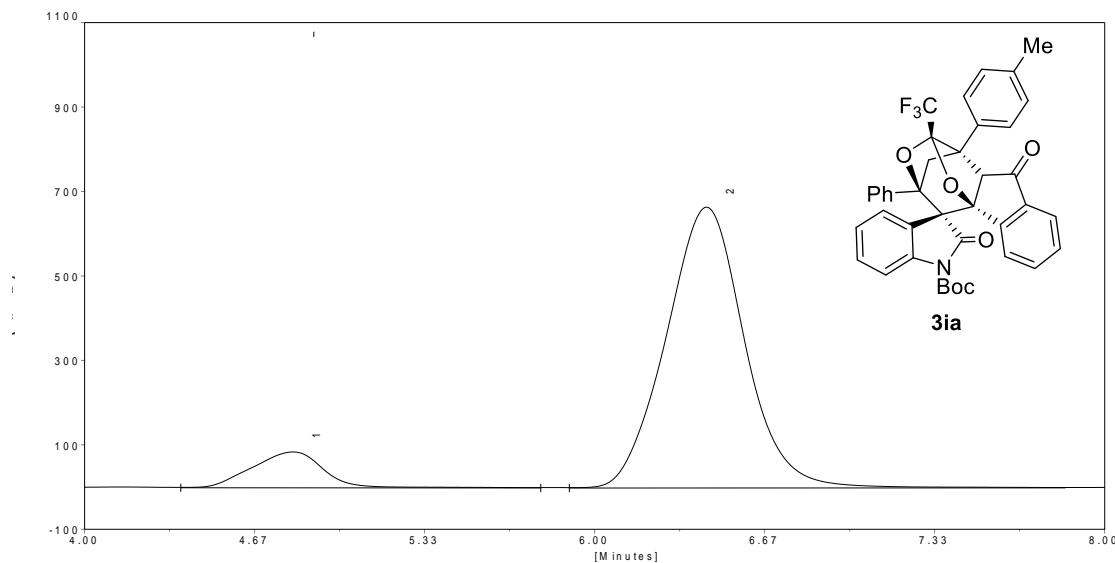
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
7.09	23.29	973.86	9.8111
10.58	191.06	8952.28	90.1889

HPLC Chromatogram for **3ia**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 95:5	Detector: UV 246 nm



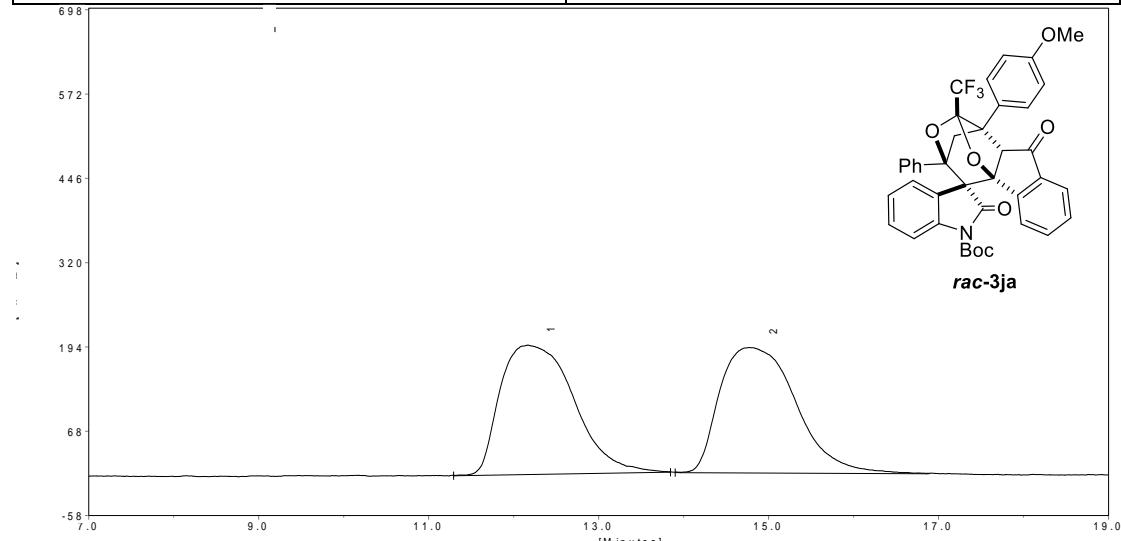
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
4.87	274.27	5530.35	50.4672
6.53	262.36	5427.95	49.5328



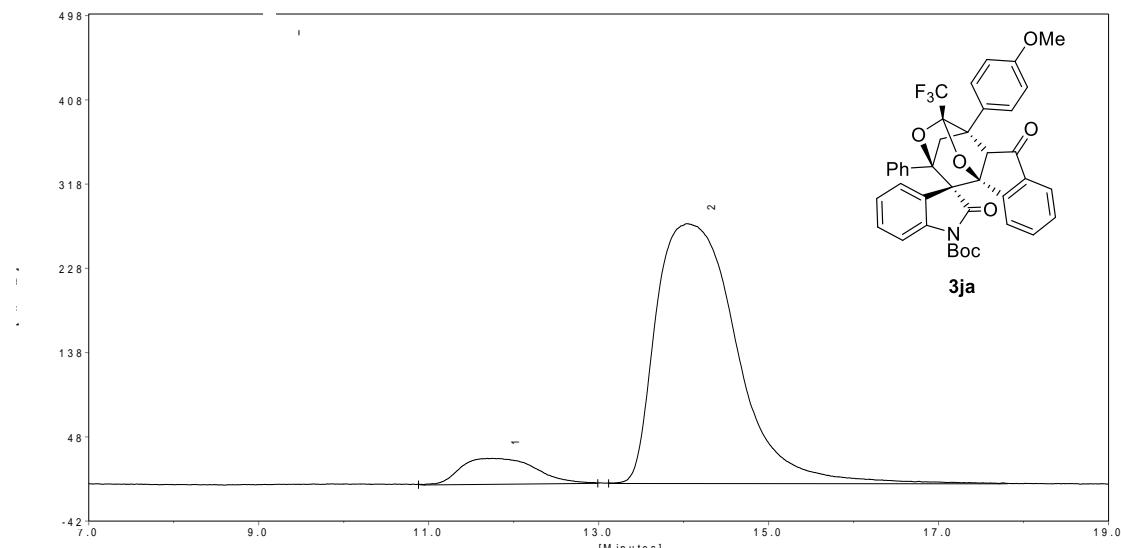
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
4.82	84.00	1596.96	10.1614
6.44	664.03	14118.90	89.8386

HPLC Chromatogram for **3ja**

Column: chiralpak IA	Flow rate: 0.7 ml/min
Solvent: Hex: IPA = 97:3	Detector: UV 246 nm



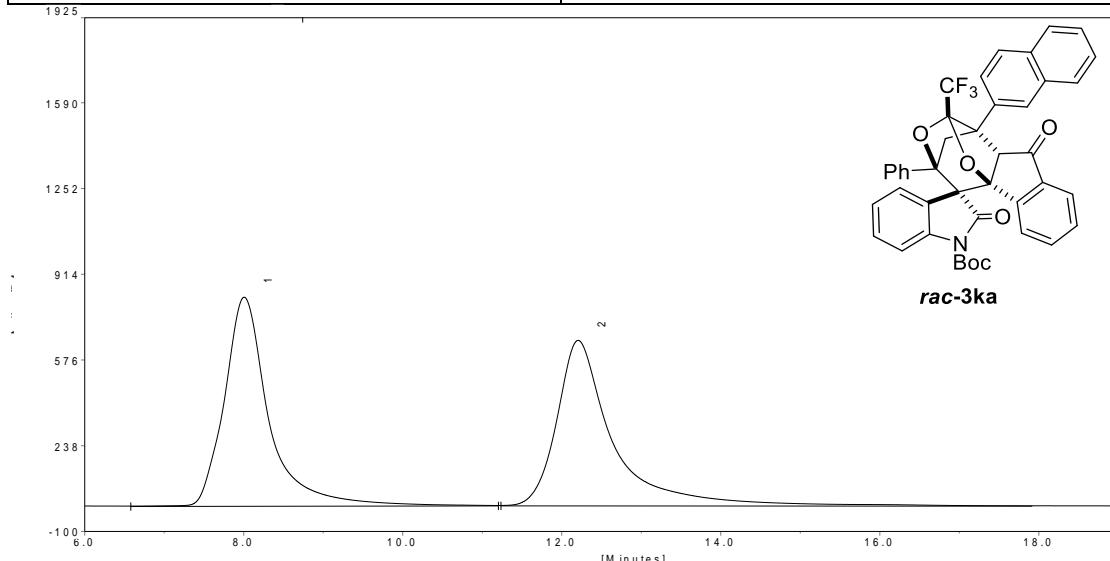
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.17	192.78	11541.64	49.9166
14.78	186.90	11580.20	50.0834



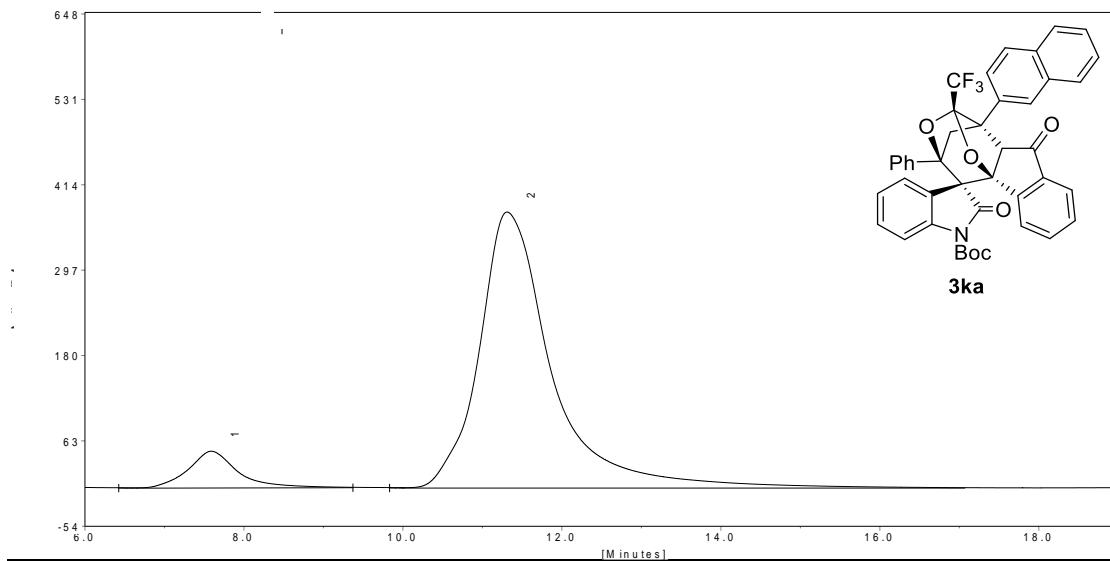
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
11.75	27.13	1617.95	8.1559
14.05	277.10	18219.89	91.8441

HPLC Chromatogram for **3ka**

Column: chiralpak IA	Flow rate: 0.7 ml/min
Solvent: Hex: EtOH = 95:5	Detector: UV 246 nm

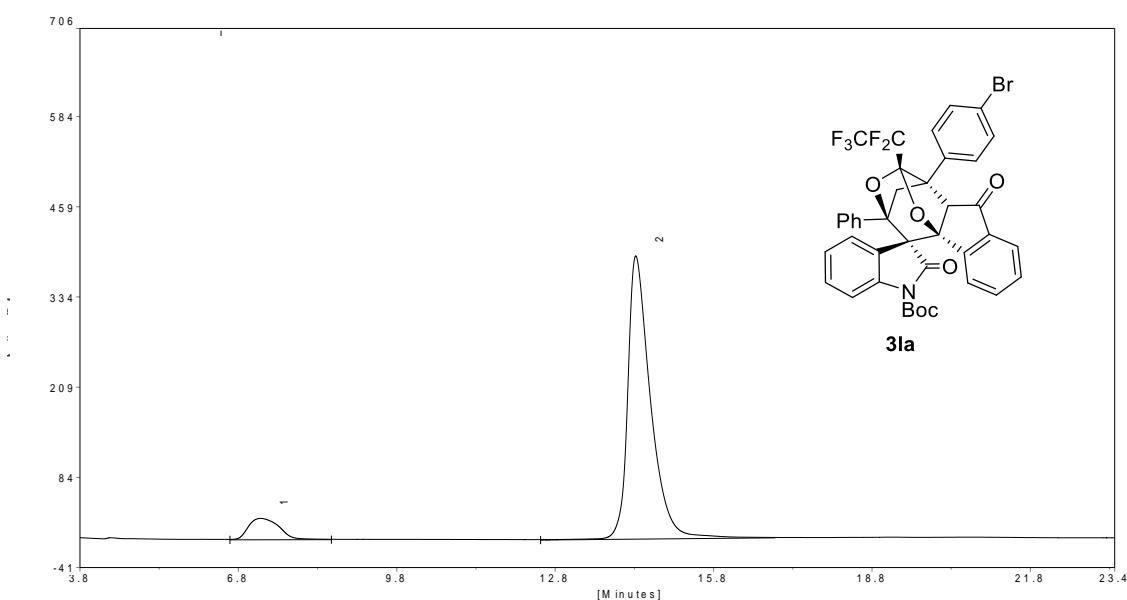
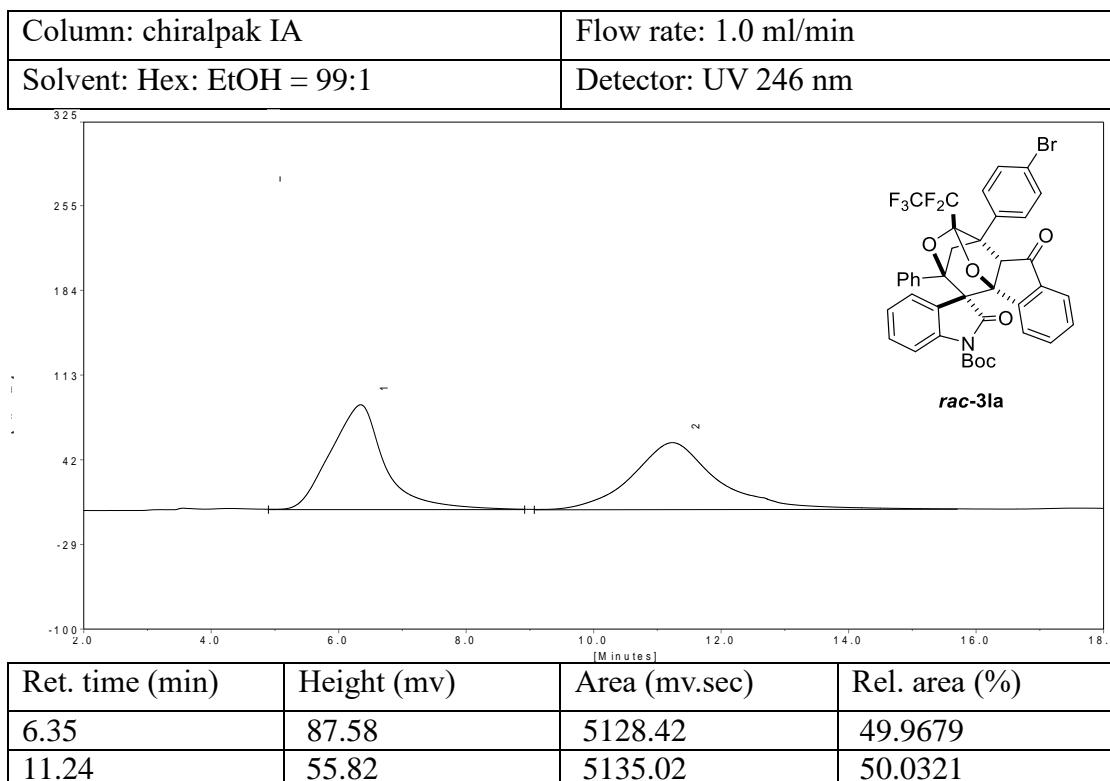


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
8.01	822.63	31873.01	50.0252
12.21	650.87	31840.84	49.9748



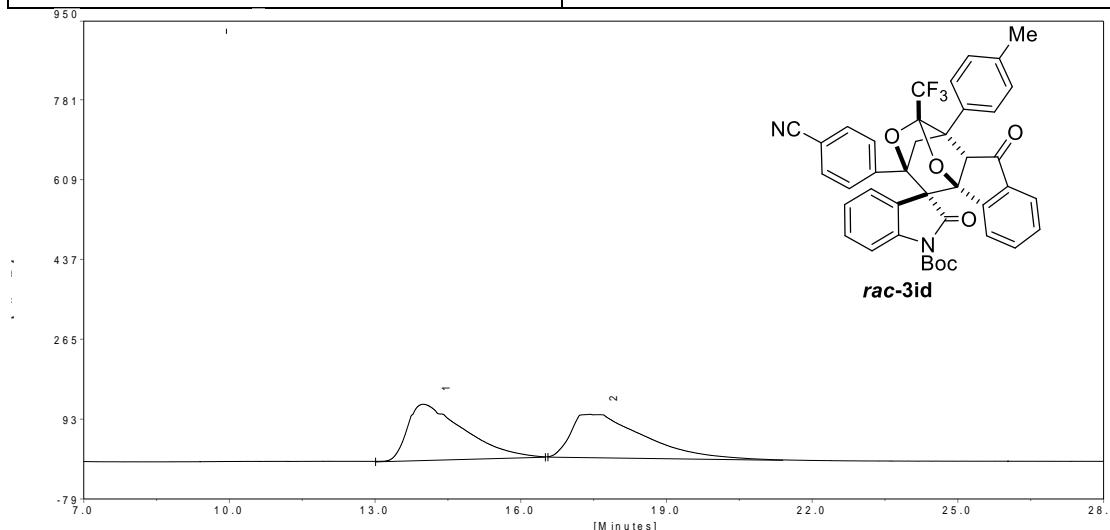
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
7.59	49.85	2111.82	8.1323
11.31	377.58	23856.37	91.8677

HPLC Chromatogram for **3la**

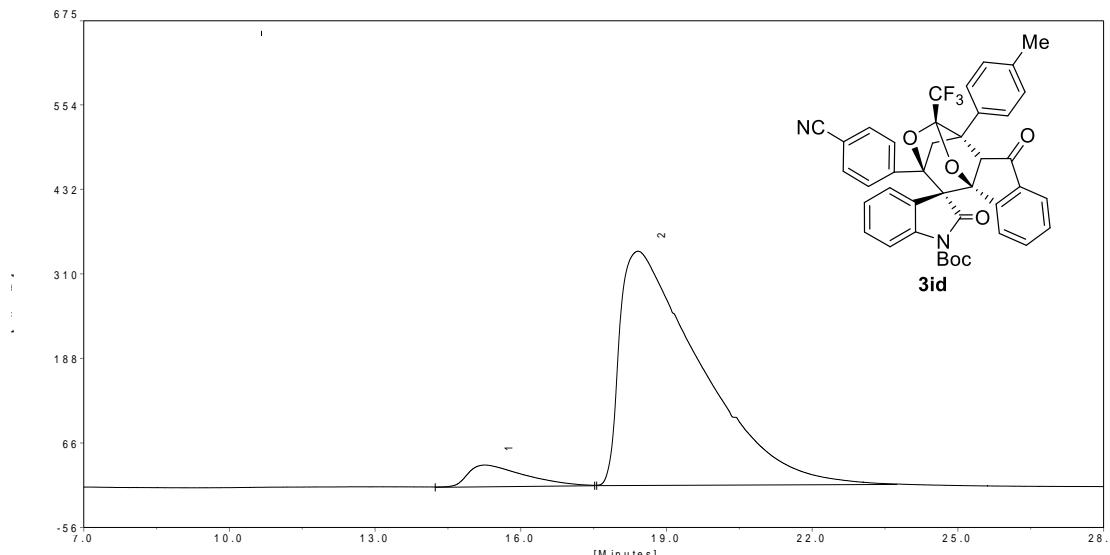


HPLC Chromatogram for **3id**

Column: chiralpak IB	Flow rate: 0.8 ml/min
Solvent: Hex: IPA = 98: 2	Detector: UV 246 nm



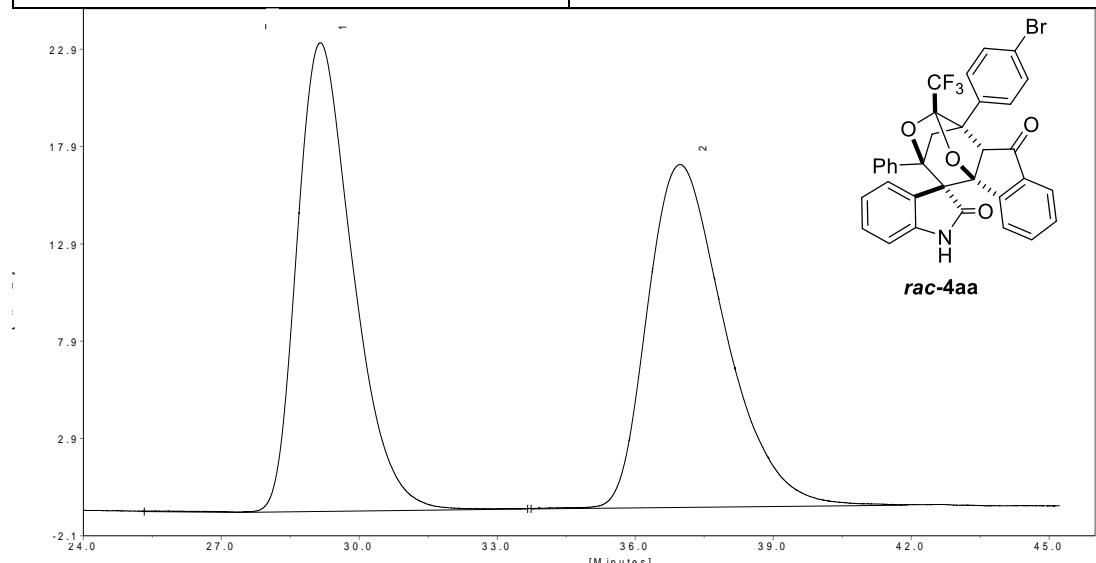
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
13.98	120.25	9609.41	50.0299
17.43	92.60	9597.94	49.9701



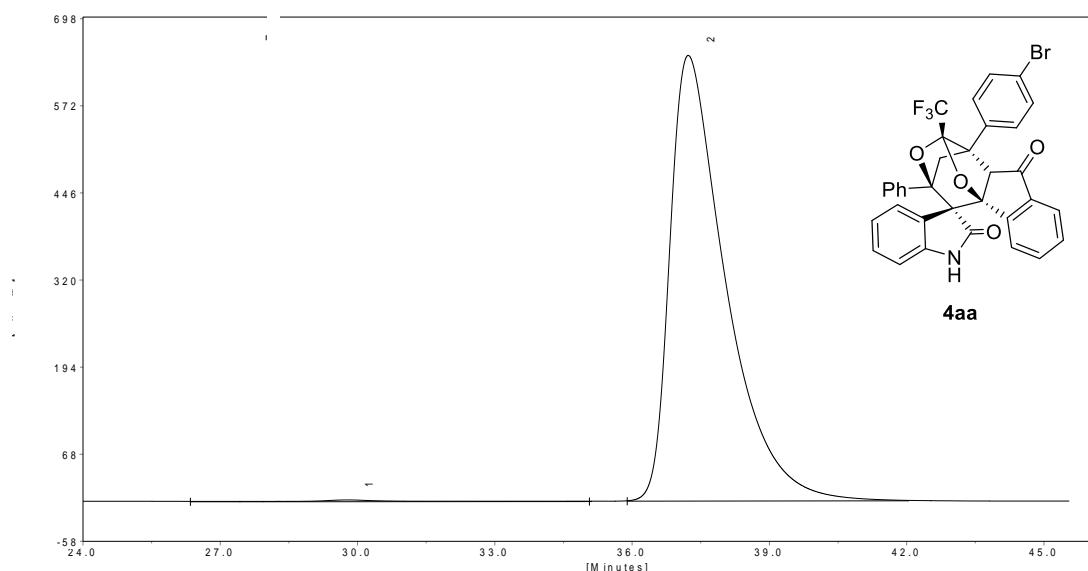
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
15.27	30.89	2428.99	5.8407
18.41	337.58	39158.60	94.1593

HPLC Chromatogram for **4aa**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex: IPA=90:10	Detector: UV 246 nm



Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
29.14	24.00	2000.28	49.2727
36.97	17.60	2059.33	50.7273



Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
29.76	1.94	129.87	0.2377
37.23	644.17	54499.39	99.7623