

Preparation of Functional Benzofurans and Indoles via Chemoselective Intramolecular Wittig Reactions

Yu-Ting Lee, Yeong-Jiunn Jang, Siang-en Syu,
Shu-Chi Chou, Chia-Jui Lee, and Wenwei Lin*

Department of Chemistry, National Taiwan Normal University
No. 88, Section 4, Tingchow Road, Taipei 116, Taiwan, ROC

Fax: (+886) 02 29354249

e-mail: wenweilin@ntnu.edu.tw

Supporting Information

Index

I. General Information	S2
II. Studies of reaction mechanism.....	S2
III. Typical procedure for syntheses of benzofuran 4, 4', 26 (TP 1 for Table 1 and Scheme 5), indole 17, 18, 19, 20 (TP 2 for Table 2) and benzothiophene 22 (TP 3 for Scheme 4)	S4
IV. Typical procedure for deacylation of 4, 4', 26 (TP 4 for Table 1 and Scheme 5)	S6
V. Typical procedure for syntheses of 9, 10, 11, 12 (TP 5 for Table 2), 21 (TP 6 for Scheme 4)	S7
VI. Spectra data of compounds.....	S10
VII. Spectra of ^1H , ^{13}C , and ^{31}P NMR.....	S89
VIII. Spectra of X-ray crystallography 4a, 4'q, 8, 17e, 18d, 19a, 20a, 20b, and 22b.....	S316

I. General Information:

All reactions were carried out under a nitrogen atmosphere in dried glassware. The starting materials purchased from commercial sources were used without further purification. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was freshly distilled from calcium hydride under nitrogen and degased under argon. Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by $^1\text{H-NMR}$. Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Flash chromatography was performed using Merck silica gel 60. The temperature of our RT condition ranges from 28 to 30 °C.

II. Studies of reaction mechanism:

The following reaction demonstrated that the reaction pathway via 1,4-addition of Bu_3P toward **1a** followed by acylation of benzoyl chloride **2a** can be observed in the crude ^1H NMR studies in comparison with pure ^1H NMR spectra of **8** (**Step 1, Figure 1**). After the addition of Et_3N , **8** was successfully converted into the desired functional benzofuran **4a** (**Step 2, Figure 1**).

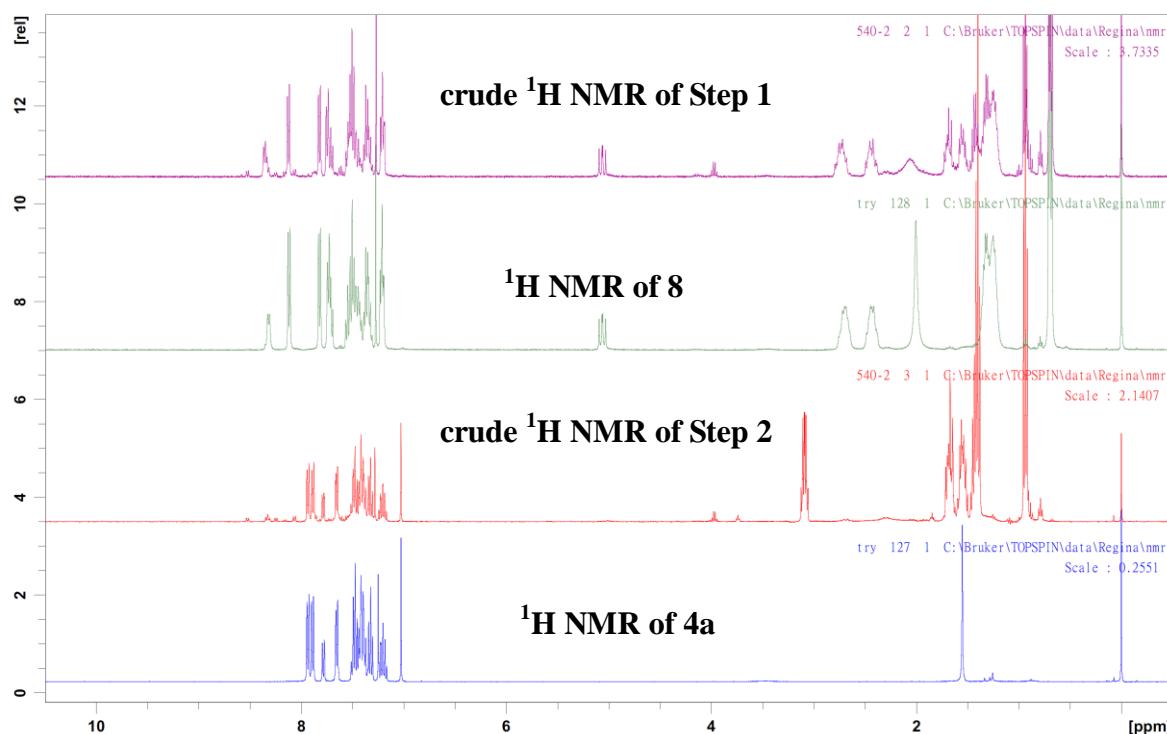
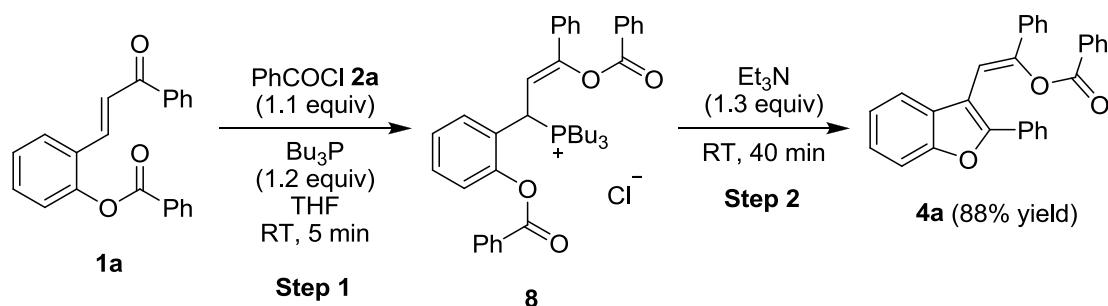


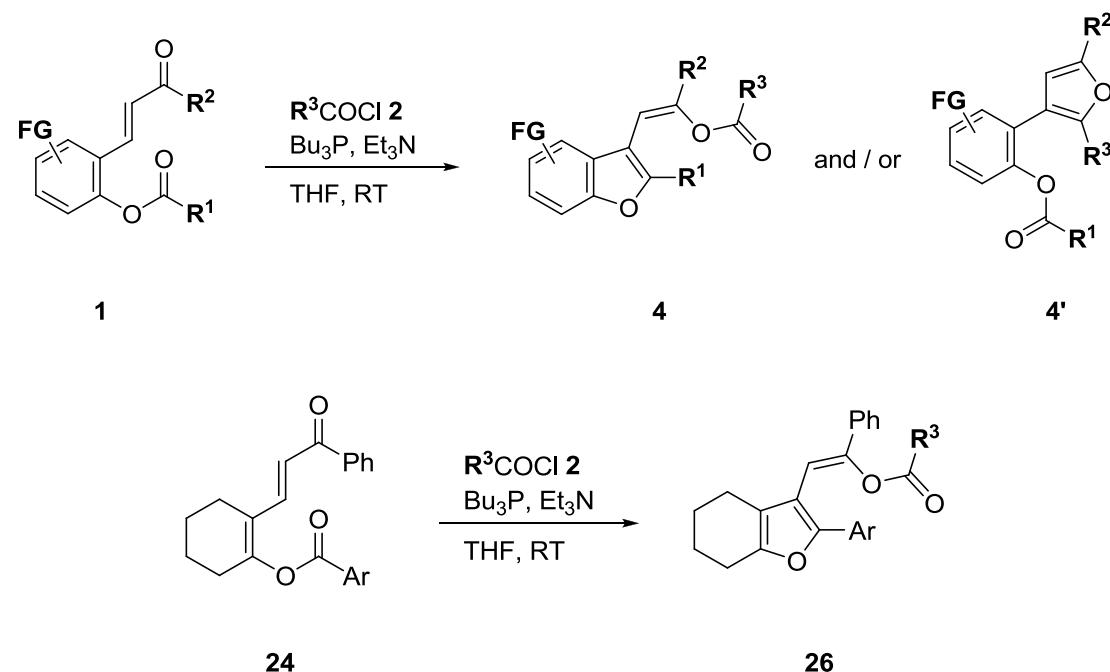
Figure 1

Step 1: A dry and nitrogen-flushed 10-mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **1a** (112.0 mg, 0.5 mmol) in dry THF (1 mL). Benzoyl chloride **2a** (64 μL , 1.1 equiv) and Bu_3P (150 μL , 1.2 equiv) was added, and the reaction mixture was stirred for 5 min at room temperature. The formation of **8** was observed in the crude ^1H NMR spectrum.

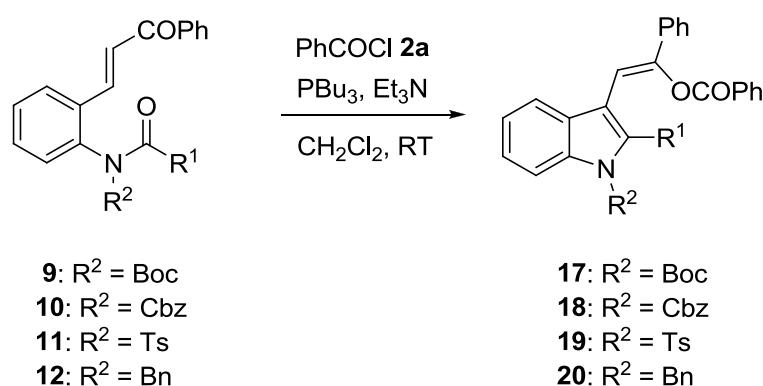
Step 2: followed by step 1, NEt_3 (91 μL , 1.3 equiv) was added to the reaction mixture and the resulting mixture was stirred for 40 min. The formation of expected product **4a** was observed in the crude ^1H NMR spectrum. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished **4a** (183.1

mg, 88%).

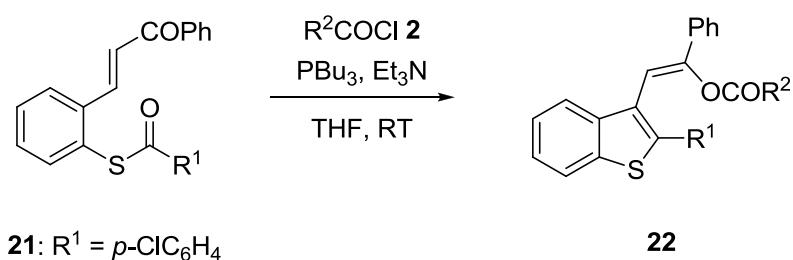
III. Typical procedure for syntheses of benzofuran **4, **4'**, **26** (TP 1 for Table 1 and Scheme 5), indole **17**, **18**, **19**, **20** (TP 2 for Table 2) and benzothiophene **22** (TP 3 for Scheme 4)**



TP 1: A dry and nitrogen-flushed 10-mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **1** or **24** (0.5 mmol) in dry THF (1 mL). Acyl chloride **2** (1.1 equiv), Bu₃P (150.0 μ L, 1.2 equiv), and NEt₃ (91.0 μ L, 1.3 equiv) was added, and the reaction mixture was stirred for the indicated time at room temperature. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished **4**, **4'**, **26**.

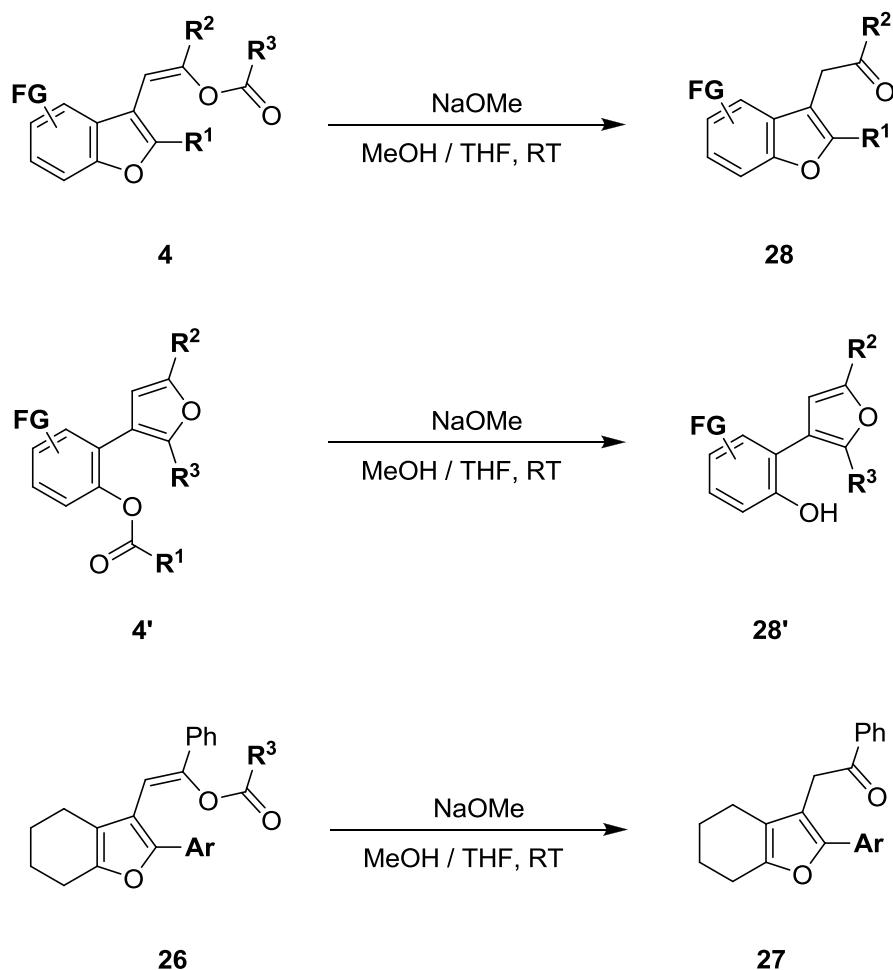


TP 2: A dry and nitrogen-flushed 10-mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **9-12** (0.3 mmol) in dry CH_2Cl_2 (0.6 mL). Benzoyl chloride **2a** (38 μL , 1.1 equiv), Bu_3P (1.2 or 1.3 equiv) and NEt_3 (54 μL , 1.3 equiv) was added, and the reaction mixture was stirred for the indicated time at RT. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished **17-20**.



TP 3: A dry and nitrogen-flushed 10-mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **21** (0.5 mmol) in dry THF (1 mL). Acyl chloride **2** (1.1 equiv), Bu_3P (150 μL , 1.2 equiv) and NEt_3 (91 μL , 1.3 equiv) was added, and the reaction mixture was stirred for the indicated time at RT. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished **22**.

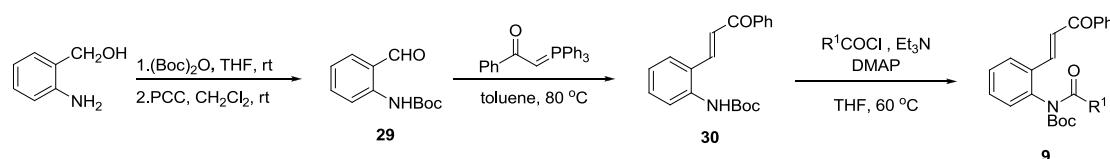
IV. Typical procedure for deacylation of **4, **4'**, **26** (TP 4 for Table 1 and Scheme 5)**



TP4:

A dry and nitrogen-flushed 10-mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **4**, **4'**, **26** (0.2 mmol) in MeOH/THF (0.1/0.1 mL). NaOMe (13 mg, 1.2 equiv) was added, and the reaction mixture was stirred for 5 h at RT. Then the crude product was neutralized by addition of 1M aq. HCl solution and extracted by dichloromethane, and the organic layer was dried by MgSO₄ and then evaporated. Purification by flash chromatography furnished **28**, **28'**, **27**.

V. Typical procedure for syntheses of 9, 10, 11, 12 (TP 5 for Table 2), 21 (TP 6 for Scheme 4)

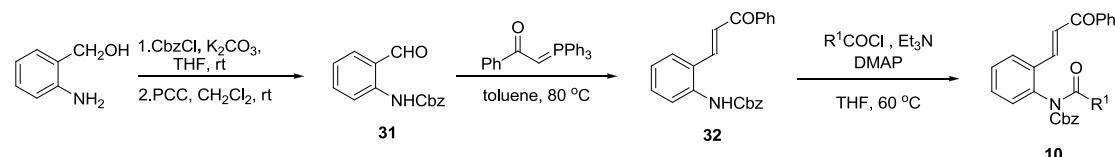


TP 5:

29¹: A dry and nitrogen-flushed 100-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 2-aminobenzyl alcohol (2.46 g, 20 mmol) in dry THF (66 mL). (Boc)₂O (4.79 g, 1.1 equiv) was added, and the reaction mixture was stirred for 12 h at room temperature. Thereafter, the solvent was removed by evaporation in vacuo. Without purification, the crude product was dissolved in dichloromethane (50 mL) and then PCC (5.173 g, 1.2 equiv) was added. The reaction mixture was stirred for 4 h at room temperature and then filtered through Celite 545 followed by washing with CH₂Cl₂. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography (ethyl acetate/hexanes: 1/10) furnished **29** (3.54 g, 80%).

30: A dry and nitrogen-flushed 100-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of **29** (3.23 g, 10 mmol) in toluene (50 mL). 1-phenyl-2-(triphenylphosphoranylidene)ethanone (4.18 g, 1.1 equiv) was added, and the reaction mixture was stirred for 12 h at 80 °C. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography (ethyl acetate/hexanes: 1/6) furnished **30** (2.58 g, 80%).

9: A dry and nitrogen-flushed 25-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of **30** (0.96 g, 3 mmol) and DMAP (36.6 mg, 0.1 equiv) in dry THF (7.5 mL). Acyl chloride or Ac₂O (1.05 equiv) and NEt₃ (0.5 mL, 1.2 equiv) was added, and the reaction mixture was stirred for 12 h at 60 °C. Then the crude product was dissolved in ethyl acetate and washed with sat. NaHCO₃(aq), and the organic layer was dried by MgSO₄ and then evaporated. Purification by flash chromatography furnished **9**.

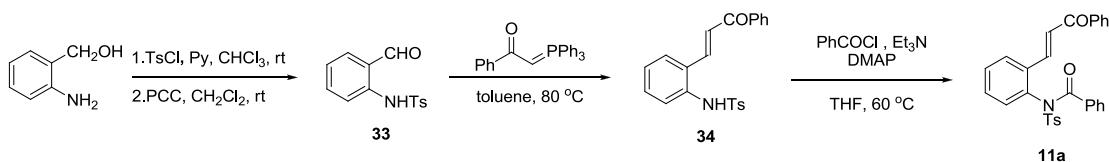


¹ Thielges, S.; Meddah, E.; Bisseret, P.; Eustache, J. *Tetrahedron Lett.* **2004**, *45*, 907.

31²: A dry and nitrogen-flushed 100-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 2-aminobenzyl alcohol (2.46 g, 20 mmol) in dry THF (66 mL). CbzCl (3.74 g, 1.1 equiv) and K₂CO₃ (27.6 g, 10 equiv) was added, and the reaction mixture was stirred for 12 h at room temperature. Then the crude product was dissolved in ethyl acetate and washed with sat. NaHCO₃(aq), and the organic layer was dried by MgSO₄ and then evaporated. Without purification, the crude product was dissolved in dichloromethane (50 mL) and then PCC (5.173 g, 1.2 equiv) was added. The reaction mixture was stirred for 4 h at room temperature and then filtered through Celite 545 followed by washing with CH₂Cl₂. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography (ethyl acetate/hexanes: 1/10) furnished **31** (4.34 g, 85%).

32: A dry and nitrogen-flushed 100-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of **31** (2.55 g, 10 mmol) in toluene (50 mL). 1-phenyl-2-(triphenylphosphoranylidene)ethanone (4.18 g, 1.1 equiv) was added, and the reaction mixture was stirred for 12 h at 80 °C. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography (ethyl acetate/hexanes: 1/6) furnished **32** (2.86 g, 80%).

10: A dry and nitrogen-flushed 25-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of **32** (1.07 g, 3 mmol) and DMAP (36.6 mg, 0.1 equiv) in dry THF (7.5 mL). Acyl chloride (1.05 equiv) and NEt₃ (0.5 mL, 1.2 equiv) was added, and the reaction mixture was stirred for 12 h at 60 °C. Then the crude product was dissolved in ethyl acetate and washed with sat. NaHCO₃(aq), and the organic layer was dried by MgSO₄ and then evaporated. Purification by flash chromatography furnished **10**.



33³: A dry and nitrogen-flushed 250-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 2-aminobenzyl alcohol (2.46 g, 20 mmol) in CHCl₃ (100 mL). TsCl (4.18 g, 1.1 equiv) and pyridine (0.1 mL) was added, and the reaction mixture was stirred for 12 h at room temperature. Thereafter, the solvent was removed by evaporation in vacuo. Without purification, the crude

² Waibel, M.; Hasserodt, J. *Tetrahedron Lett.* **2009**, *50*, 2767.

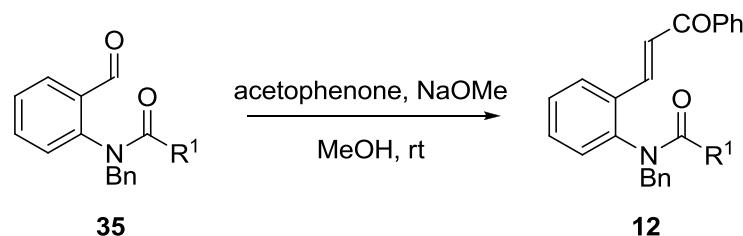
³ López, M. V.; Bermejo, M. R.; Vázquez, M. E.; Taglietti, A.; Zaragoza, G.; Pedrido, R.; Martínez-Calvo, M. *Org. Biomol. Chem.* **2010**, *8*, 357.

product was dissolved in dichloromethane (50 mL) and then PCC (5.173 g, 1.2 equiv) was added. The reaction mixture was stirred for 4 h at room temperature and then filtered through Celite 545 followed by washing with CH_2Cl_2 . Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography (dichloromethane/hexanes: 2/1) furnished **33** (5.34 g, 97%).

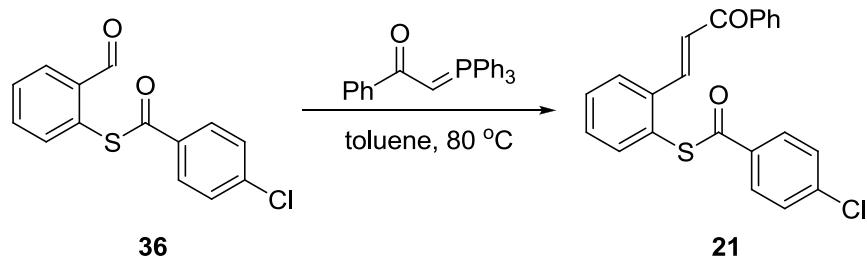
34: A dry and nitrogen-flushed 100-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of **33** (2.75 g, 10 mmol) in toluene (50 mL). 1-phenyl-2-(triphenylphosphoranylidene)ethanone (4.18 g, 1.1 equiv) was added, and the reaction mixture was stirred for 12 h at 80 °C. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography (dichloromethane/hexanes: 6/1) furnished **34** (3.02 g, 80%).

11a: A dry and nitrogen-flushed 25-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of **34** (1.07 g, 3 mmol) and DMAP (36.6 mg, 0.1 equiv) in dry THF (7.5 mL). Benzoyl chloride (0.37 mL, 1.05 equiv) and NEt_3 (0.5 mL, 1.2 equiv) was added, and the reaction mixture was stirred for 12 h at 60 °C. Then the crude product was dissolved in ethyl acetate and washed with sat. NaHCO_3 (aq), and the organic layer was dried by MgSO_4 and then evaporated.

Washed by *n*-pentane furnished **11a** as yellow solid (1.36 g, 94%).



12: A dry and nitrogen-flushed 25-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of **35**⁴ (3 mmol) in MeOH (10 mL). Acetophenone (0.39 g, 1.1 equiv) and NaOMe (0.32 g, 2 equiv) was added, and the reaction mixture was stirred for 12 h at room temperature. Then the crude product was dissolved in ethyl acetate and washed with sat. NaHCO_3 (aq), and the organic layer was dried by MgSO_4 and then evaporated. Purification by flash chromatography furnished **12**.



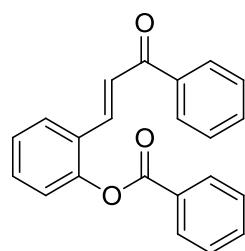
⁴ Syu, S.; Lee, Y.-T.; Jang, Y.-J.; Lin, W. *Org. Lett.* **2011**, *13*, 2970.

TP 6:

21: A dry and nitrogen-flushed 25-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of **36⁴** (0.41 g, 1.5 mmol) in toluene (7.5 mL). 1-phenyl-2-(triphenylphosphoranylidene)ethanone (0.63 g, 1.1 equiv) was added, and the reaction mixture was stirred for 12 h at 80 °C. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished **21**.

VI. Spectra data of compounds

Synthesis of (*E*)-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl benzoate (1a):



The compound **1a** was obtained as white solid (321.5 g, 98%) according to the reported procedure⁴.

R_f 0.2 (ethyl acetate/hexanes: 1/25); mp.: 108.5-109.1 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 8.26 (*pseudo* d, 2H, *J* = 7.2 Hz), 7.93 (d, 1H, *J* = 15.8 Hz), 7.87 (*pseudo* d, 2H, *J* = 7.2 Hz), 7.81 (*pseudo* d, 1H, *J* = 7.8 Hz), 7.69 (*pseudo* t, 1H, *J* = 7.4 Hz), 7.53-7.47 (m, 5H), 7.37 (*pseudo* t, 3H, *J* = 7.6 Hz), 7.30 (*pseudo* d, 1H, *J* = 8.1 Hz).

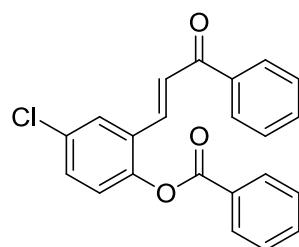
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 190.4, 164.8, 149.3, 138.4, 137.8, 133.9, 132.7, 131.3, 130.3, 128.9, 128.8, 128.5, 128.4, 127.9, 126.4, 124.3, 123.4.

MS (70eV, EI) *m/z* (%): 328 [M]⁺ (5), 223 (3), 207 (28), 118 (5), 105 (100), 77 (28).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 1727 (s), 1664 (s), 1598 (s), 1211 (m), 1089 (w), 1052 (w).

HRMS (ESI) for C₂₂H₁₆O₃Na, [M+Na]⁺ (351.0997) found: 351.1012.

Synthesis of (*E*)-4-chloro-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl benzoate (1b):



The compound **1b** was obtained as white solid (325.8 g, 90%) according to the reported procedure⁴.

R_f 0.2 (ethyl acetate/hexanes: 1/25); mp.: 133.1-133.3 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.25 (*pseudo d*, 2H, J = 7.5 Hz), 7.92 (*pseudo d*, 2H, J = 7.3 Hz), 7.84 (d, 1H, J = 15.8 Hz), 7.77 (d, 1H, J = 2.4 Hz), 7.68 (*pseudo t*, 1H, J = 7.5 Hz), 7.54-7.52 (m, 4H), 7.41-7.38 (m, 3H), 7.24 (d, 1H, J = 8.6 Hz).

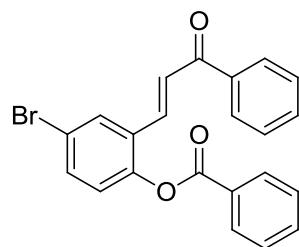
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 189.8, 164.6, 148.3, 137.6, 136.8, 134.1, 133.0, 131.9, 130.1, 130.5, 130.3, 129.5, 128.8, 128.6, 128.5, 127.8, 125.2, 124.8.

MS (70eV, EI) m/z (%): 364 [M+2]⁺ (1), 362 [M]⁺ (3), 240 (5), 179 (1), 152 (5), 105 (100), 77 (35).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 1727 (s), 1664 (s), 1598 (s), 1211 (m), 1089 (w), 1052 (w).

HRMS (ESI) for C₂₂H₁₅ClO₃Na, [M+Na]⁺ (385.0607) found: 385.0601.

Synthesis of (*E*)-4-bromo-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl benzoate (**1c**):



The compound **1c** was obtained as white solid (345.1 g, 85%) according to the reported procedure⁴.

R_f 0.2 (ethyl acetate/hexanes: 1/25); mp.: 142.8-143.4 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.23 (*pseudo d*, 2H, J = 7.6 Hz), 7.92-7.89 (m, 3H), 7.82 (d, 1H, J = 15.8 Hz), 7.67 (t, 1H, J = 7.7 Hz), 7.54-7.51 (m,

5H), 7.40 (*pseudo* t, 2H, $J = 7.7$ Hz), 7.17 (d, 1H, $J = 8.4$ Hz).

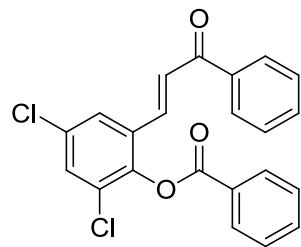
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 189.8, 164.5, 148.9, 137.6, 136.6, 134.1, 133.9, 133.0, 130.8, 130.3, 130.0, 128.8, 128.6, 128.5, 128.4, 125.2, 125.1, 119.6.

MS (70eV, EI) m/z (%): 408 [$\text{M}+2]^+$ (2), 406 [$\text{M}]^+$ (2), 285 (8), 196 (2), 105 (100), 77 (32).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3040 (w), 1734 (s), 1660 (w), 1612 (m), 1233 (s), 1048 (m), 680 (m).

HRMS (ESI) for $\text{C}_{22}\text{H}_{15}\text{BrO}_3\text{Na}$, $[\text{M}+\text{Na}]^+$ (406.0205) found: 406.0210.

Synthesis of (*E*)-2,4-dichloro-6-(3-oxo-3-phenylprop-1-en-1-yl)phenyl benzoate (1d):



The compound **1d** was obtained as white solid (368.3 g, 93%) according to the reported procedure⁴.

R_f 0.2 (ethyl acetate/hexanes: 1/25); mp.: 148.7-149.2 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.25 (*pseudo* d, 2H, $J = 7.3$ Hz), 7.88 (*pseudo* d, 2H, $J = 7.2$ Hz), 7.71-7.67 (m, 3H), 7.54-7.52 (m, 5H), 7.40 (*pseudo* t, 2H, $J = 7.4$ Hz).

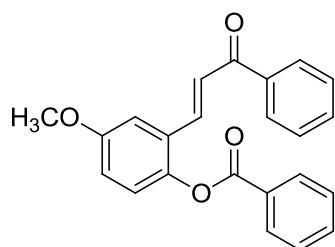
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 189.4, 163.6, 145.1, 137.3, 136.0, 134.3, 133.1, 132.2, 131.5, 131.0, 130.5, 129.5, 128.8, 128.6, 128.5, 127.8, 126.3, 126.1.

MS (70eV, EI) m/z (%): 398 [$\text{M}+2]^+$ (3), 396 [$\text{M}]^+$ (3), 275 (3), 105 (100), 77 (28).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3077 (w), 1734 (s), 1664 (m), 1601 (s), 1211 (m), 1048 (m), 687 (s).

HRMS (ESI) for $\text{C}_{22}\text{H}_{14}\text{Cl}_2\text{O}_3\text{Na}$, $[\text{M}+\text{Na}]^+$ (419.0218) found: 419.0219.

Synthesis of (*E*)-4-methoxy-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl benzoate (1e):



The compound **1e** was obtained as white solid (293.6 g, 82%) according to the reported procedure⁴.

R_f 0.2 (ethyl acetate/hexanes: 1/25); mp.: 123.2-123.9 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.24 (*pseudo d*, 2H, $J = 7.3$ Hz), 7.84-7.79 (m, 3H), 7.68 (*pseudo t*, 1H, $J = 7.5$ Hz), 7.52-7.47 (m, 4H), 7.38 (t, 2H, $J = 7.8$ Hz), 7.29 (d, 1H, $J = 2.9$ Hz), 7.20 (d, 1H, $J = 8.8$ Hz), 7.04 (dd, 1H, $J = 8.9, 3.0$ Hz), 3.88 (s, 3H).

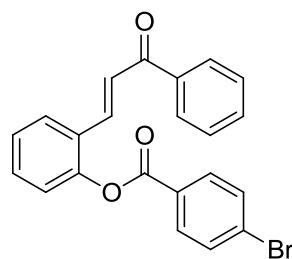
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 190.4, 165.2, 157.5, 143.6, 138.5, 137.8, 133.9, 132.7, 130.3, 130.0, 128.7, 128.5, 128.4, 128.1, 124.5, 124.2, 117.0, 112.7, 55.7.

MS (70eV, EI) m/z (%): 358 [M]⁺ (3), 237 (18), 148 (3), 105 (100), 77 (38).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 2841(w), 1734 (s), 1664 (m), 1609 (s), 1262 (s), 1240 (w), 1059 (m), 1037(w).

HRMS (ESI) for $\text{C}_{23}\text{H}_{18}\text{O}_4\text{Na}$, [M+Na]⁺ (381.1103) found: 381.1072.

Synthesis of (*E*)-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl 4-bromobenzoate (**1f**):



The compound **1f** was obtained as white solid (385.7 g, 95%) according to the reported procedure⁴.

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 132.5-133.8 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.10 (*pseudo d*, 2H, $J = 8.6$ Hz), 7.89-7.87 (m, 3H), 7.80 (*pseudo d*, 1H, $J = 7.8$ Hz), 7.68 (*pseudo d*, 2H, $J = 8.8$ Hz),

7.52-7.47 (m, 3H), 7.38-7.31 (m, 3H), 7.28 (*pseudo* d, 1H, *J* = 8.1 Hz).

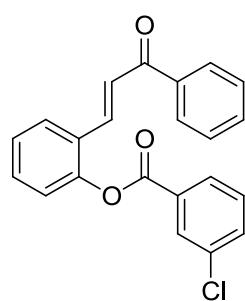
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 190.1, 164.0, 149.7, 137.9, 137.8, 132.7, 132.1, 131.6, 131.3, 129.2, 128.4, 128.4, 128.2, 127.8, 126.5, 124.2, 123.2.

MS (70eV, EI) *m/z* (%): 408 [M+2]⁺ (4), 406 [M]⁺ (5), 207 (70), 183 (100), 155 (23), 105 (32), 77 (23).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 1738 (s), 1660 (s), 1601 (s), 1214 (s), 1070 (m), 680 (m).

HRMS (ESI) for C₂₂H₁₅BrO₃Na, [M+2+Na]⁺ (429.0103) found: 431.0085.

Synthesis of (*E*)-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl 3-chlorobenzoate (**1g**):



The compound **1g** was obtained as white solid (325.8 g, 90%) according to the reported procedure⁴.

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 115.6-115.8 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 8.23 (*pseudo* s, 1H), 8.14 (*pseudo* d, 1H, *J* = 7.7 Hz), 7.90-7.87 (m, 3H), 7.82 (*pseudo* d, 1H, *J* = 7.7 Hz), 7.67 (*pseudo* d, 1H, *J* = 8.1 Hz), 7.53-7.48 (m, 4H), 7.39-7.36 (m, 3H), 7.28 (*pseudo* d, 1H, *J* = 7.3 Hz).

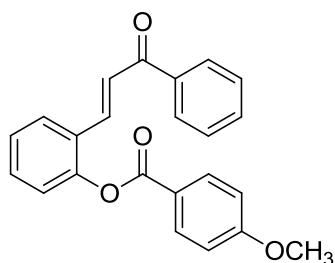
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 190.3, 163.7, 149.7, 138.1, 137.8, 135.0, 134.0, 132.9, 131.4, 130.6, 130.3, 130.1, 128.6, 128.5, 128.4, 128.3, 127.9, 126.7, 124.5, 123.2.

MS (70eV, EI) *m/z* (%): 364 [M+2]⁺ (2), 362 [M]⁺ (5), 207 (50), 139 (100), 77 (18).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 1734 (s), 1660 (s), 1572 (s), 1214 (w), 1074 (m), 735 (m).

HRMS (ESI) for C₂₂H₁₅ClO₃Na, [M+Na]⁺ (385.0607) found: 385.0612.

Synthesis of (*E*)-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl 4-methoxybenzoate (**1h**):



The compound **1h** was obtained as white solid (311.5 g, 87%) according to the reported procedure⁴.

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 90.5-91.1 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.20 (*pseudo d*, 2H, J = 8.4 Hz), 7.93 (d, 1H, J = 16.1 Hz), 7.87 (*pseudo d*, 2H, J = 7.7 Hz), 7.80 (*pseudo d*, 1H, J = 7.7 Hz), 7.54-7.46 (m, 3H), 7.38-7.27 (m, 4H), 7.01 (*pseudo d*, 2H, J = 8.4 Hz), 3.89 (s, 3H).

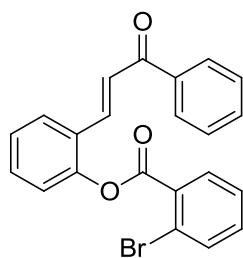
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 190.4, 164.5, 164.2, 150.1, 138.6, 137.9, 132.7, 132.5, 131.2, 128.5, 128.4, 127.9, 126.3, 124.2, 123.5, 121.2, 114.1, 55.5.

MS (70eV, EI) m/z (%): 358 [M]⁺ (2), 207 (10), 135 (100), 77 (15).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 1723 (s), 1660 (m), 1601 (s), 1211 (m), 1089 (w).

HRMS (ESI) for C₂₃H₁₈O₄Na, [M+Na]⁺ (381.1103) found: 381.1095.

Synthesis of (*E*)-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl 2-bromobenzoate (**1i**):



The compound **1i** was obtained as white solid (324.8 g, 80%) according to the reported procedure⁴.

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 82.5-83.1 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.06 (*pseudo d*, 1H, J = 6.6 Hz), 7.97 (d, 1H, J = 15.8 Hz), 7.92 (*pseudo d*, 2H, J = 7.2 Hz), 7.82 (*pseudo d*, 1H, J = 7.7 Hz), 7.76 (*pseudo d*, 1H, J = 7.2 Hz), 7.49-7.41 (m, 7H), 7.35-7.33 (m, 2H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 190.4, 164.2, 149.7, 138.2, 137.9, 134.7, 133.4, 132.8, 131.8, 131.3, 128.5, 128.5, 128.2, 128.1, 127.8, 127.5, 126.6, 124.5,

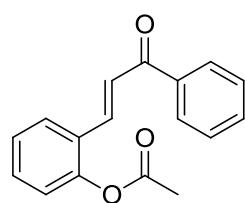
123.6, 122.4.

MS (70eV, EI) m/z (%): 408 [$M+2]^+$ (2), 406 [$M]^+$ (2), 302 (2), 223 (1), 207 (10), 183 (100), 118 (23), 105 (35), 77 (15).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3062 (w), 1741 (s), 1660 (m), 1601 (s), 1207 (m), 1015 (w), 683 (m).

HRMS (ESI) for $\text{C}_{22}\text{H}_{15}\text{O}_3\text{BrNa}$, $[\text{M}+\text{Na}]^+$ (429.0094) found: 429.0102.

Synthesis of (*E*)-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl acetate (1j**):**



The compound **1j** was obtained as white solid (172.9 g, 65%) according to the reported procedure⁴.

R_f 0.3 (ethyl acetate/hexanes: 1/20); mp.: 67.9–68.3 °C

¹H-NMR (400 MHz, CDCl_3 , 25 °C) δ /ppm: 8.01 (*pseudo d*, 2H, $J = 7.4$ Hz), 7.87 (d, 1H, $J = 15.8$ Hz), 7.78 (*pseudo d*, 1H, $J = 6.6$ Hz), 7.59 (*pseudo t*, 1H, $J = 7.4$ Hz), 7.52–7.49 (m, 3H), 7.44 (*pseudo t*, 1H, $J = 7.7$ Hz), 7.31 (*pseudo t*, 1H, $J = 7.6$ Hz), 7.16 (*pseudo d*, 1H, $J = 8.1$ Hz), 2.38 (s, 3H).

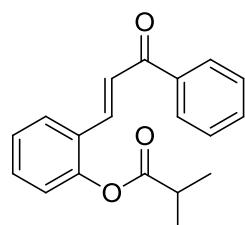
¹³C-NMR (100 MHz, CDCl_3 , 25 °C) δ /ppm: 190.3, 169.2, 149.8, 38.0, 133.0, 131.4, 128.7, 128.6, 127.7, 127.6, 126.4, 124.1, 123.2, 21.0.

MS (70eV, EI) m/z (%): 266 [$M]^+$ (8), 224 (55), 207 (100), 165 (8), 147 (62), 105 (82), 77 (67).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3040 (w), 1760 (s), 1657 (s), 1605 (s), 1203 (s), 1041 (w).

HRMS (ESI) for $\text{C}_{17}\text{H}_{14}\text{O}_3\text{Na}$, $[\text{M}+\text{Na}]^+$ (289.0841) found: 289.0853.

Synthesis of (*E*)-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl isobutyrate (1k**):**



The compound **1k** was obtained as white solid (229.3 g, 78%) according to the reported procedure⁴.

R_f 0.4 (ethyl acetate/hexanes: 1/20); mp.: 67.9-68.3 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.98 (*pseudo* d, 2H, J = 7.4 Hz), 7.87 (d, 1H, J = 15.8 Hz), 7.76 (*pseudo* d, 1H, J = 7.6 Hz), 7.57 (*pseudo* t, 1H, J = 7.4 Hz), 7.49-7.47 (m, 3H), 7.40 (*pseudo* t, 1H, J = 7.7 Hz), 7.27 (*pseudo* t, 1H, J = 8.0 Hz), 7.11 (*pseudo* d, 1H, J = 8.4 Hz), 2.87 (heptet, 1H, J = 7.0 Hz), 1.29 (d, 6H, J = 7.5 Hz).

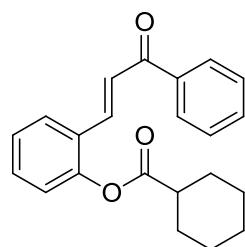
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 190.4, 175.3, 150.0, 138.0, 138.0, 137.9, 132.8, 131.3, 128.7, 128.5, 127.8, 127.3, 126.2, 124.0, 123.2, 34.3, 19.0.

MS (70eV, EI) m/z (%): 294 [M]⁺ (5), 224 (40), 207 (100), 165 (10), 147 (32), 118 (48), 105 (78), 77 (72).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3070 (w), 2878 (w), 1752 (s), 1657 (m), 1609 (s), 1211 (s), 1041 (w).

HRMS (ESI) for C₁₉H₁₈O₃Na, [M+Na]⁺ (317.1154) found: 317.1160.

Synthesis of (*E*)-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl cyclohexanecarboxylate (**1l**):



The compound **1l** was obtained as white solid (273.9 g, 82%) according to the reported procedure⁴.

R_f 0.4 (ethyl acetate/hexanes: 1/20); mp.: 55.1-56.2 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.98 (*pseudo* d, 2H, J = 7.6 Hz), 7.87 (d, 1H, J = 15.8 Hz), 7.76 (*pseudo* d, 1H, J = 7.7 Hz), 7.57 (*pseudo* t, 1H, J = 7.0 Hz), 7.49-7.46 (m, 3H), 7.41 (*pseudo* t, 1H, J = 7.6 Hz), 7.28 (*pseudo* t, 1H, J = 7.6 Hz), 7.10 (*pseudo* d, 1H, J = 8.0 Hz), 2.64 (tt, 1H, J = 11.3, 3.6 Hz), 2.08 (*pseudo* d, 2H, J = 10.4 Hz), 1.81 (*pseudo* d, 2H, J = 12.8 Hz), 1.63-1.55 (m, 3H), 1.33-1.26 (m, 3H).

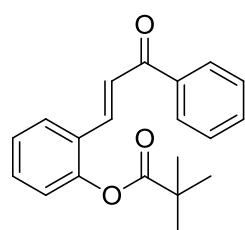
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 190.6, 174.2, 150.0, 138.1, 138.0, 132.7, 131.3, 128.6, 128.5, 127.7, 127.3, 126.1, 124.0, 123.2, 43.2, 28.9, 25.6, 25.3.

MS (70eV, EI) m/z (%): 334 [M]⁺ (5), 229 (2), 224 (35), 207 (70), 147 (17), 118 (28), 105 (50), 83 (100).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055(w), 2922 (m), 2856 (w), 1752 (s), 1660 (s), 1598 (s), 1214 (s), 1089 (m).

HRMS (ESI) for C₂₂H₂₂O₃Na, [M+Na]⁺ (357.1467) found: 357.1468.

Synthesis of (*E*)-2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl pivalate (1m):



The compound **1m** was obtained as white solid (224.8 g, 73%) according to the reported procedure⁴.

R_f 0.4 (ethyl acetate/hexanes: 1/20); mp.: 114.8-115.6 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.98 (*pseudo* d, 2H, *J* = 7.1 Hz), 7.87 (d, 1H, *J* = 15.8 Hz), 7.78 (*pseudo* d, 1H, *J* = 7.9 Hz), 7.59 (*pseudo* t, 1H, *J* = 7.3 Hz), 7.46-7.41 (m, 4H), 7.28-7.26 (m, 1H), 7.09 (*pseudo* d, 1H, *J* = 8.0 Hz), 1.38 (s, 9H).

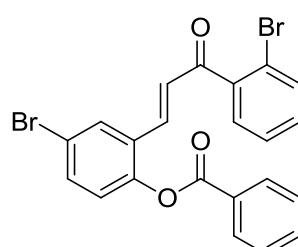
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 190.6, 176.8, 150.2, 138.0, 137.9, 132.8, 131.3, 128.6, 127.9, 127.1, 126.2, 124.2, 123.1, 39.3, 27.2.

MS (70eV, EI) m/z (%): 308 [M]⁺ (6), 224 (15), 207 (50), 118 (25), 105 (42), 77 (35), 57 (100).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055(w), 2870 (w), 1745 (s), 1660 (s), 1601 (s), 1214 (s), 1015 (m).

HRMS (ESI) for C₂₀H₂₀O₃Na, [M+Na]⁺ (331.1310) found: 331.1321.

Synthesis of (*E*)-4-bromo-2-(3-(2-bromophenyl)-3-oxoprop-1-en-1-yl)phenyl benzoate (1n):



The compound **1n** was obtained as white solid (425.9 g, 88%) according to the reported procedure⁴.

R_f 0.3 (ethyl acetate/hexanes: 1/25); mp.: 119.4–119.6 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.09 (*pseudo d*, 2H, $J = 7.3$ Hz), 7.87 (d, 1H, $J = 2.2$ Hz), 7.68 (*pseudo t*, 1H, $J = 7.5$ Hz), 7.59 (dd, 1H, $J = 8.6, 2.3$ Hz), 7.48–7.44 (m, 4H), 7.29 (dd, 1H, $J = 7.3, 1.9$ Hz), 7.18–7.15 (m, 3H), 7.06 (d, 1H, $J = 16.2$ Hz).

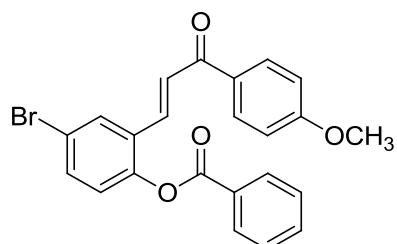
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 194.1, 164.4, 148.8, 140.5, 138.4, 134.3, 134.1, 133.2, 131.3, 130.4, 130.2, 129.3, 129.0, 128.7, 128.4, 127.2, 125.0, 119.6, 119.4.

MS (70eV, EI) m/z (%): 488 [M+4]⁺ (1), 486 [M+2]⁺ (3), 484 [M]⁺ (1), 365 (8), 182 (5), 105 (100), 77 (22).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm⁻¹): 3085 (w), 1738 (s), 1657 (m), 1598 (s), 1214 (m), 1059 (m), 698 (m).

HRMS (ESI) for $\text{C}_{22}\text{H}_{14}\text{Br}_2\text{O}_3\text{N}_a$, [M+Na]⁺ (506.9207) found: 506.9199

Synthesis of (*E*)-4-bromo-2-(3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)phenyl benzoate (1o**):**



The compound **1o** was obtained as white solid (405.5 g, 93%) according to the reported procedure⁴.

R_f 0.3 (ethyl acetate/hexanes: 1/25); mp.: 151.3–152.0 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.24 (*pseudo d*, 2H, $J = 7.3$ Hz), 7.93–7.90 (m, 3H), 7.80 (d, 1H, $J = 15.8$ Hz), 7.68 (*pseudo t*, 1H, $J = 7.4$ Hz), 7.53–7.51 (m, 4H), 7.17 (d, 1H, $J = 8.7$ Hz), 6.87 (*pseudo d*, 2H, $J = 8.8$ Hz), 3.86 (s, 3H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 188.0, 164.6, 163.6, 148.8, 135.8, 134.1, 133.7, 130.9, 130.8, 130.6, 130.4, 130.2, 128.8, 128.6, 125.2, 125.1, 119.6, 113.9,

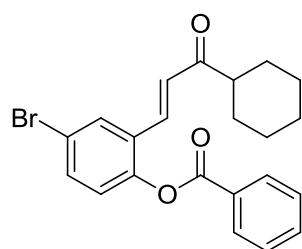
55.5.

MS (70eV, EI) m/z (%): 438 [$M+2]^+$ (2), 436 [$M]^+$ (2), 317 (15), 315 (25), 135 (15,), 105 (100), 77 (25).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 2841 (w), 1741 (s), 1660 (m), 1601 (s), 1218 (s), 1056 (w), 698 (m).

HRMS (ESI) for $\text{C}_{23}\text{H}_{17}\text{BrO}_4\text{N}_a$, $[M+\text{Na}]^+$ (459.0208) found: 459.0210

Synthesis of (*E*)-4-bromo-2-(3-cyclohexyl-3-oxoprop-1-en-1-yl)phenyl benzoate (1p**):**



The compound **1p** was obtained as white solid (207.9 g, 92%) according to the reported procedure⁴.

R_f 0.3 (ethyl acetate/hexanes: 1/25); mp.: 129.5-132.4 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.19 (*pseudo* d, 2H, $J = 8.5$ Hz), 7.83 (d, 1H, $J = 2.3$ Hz), 7.66-7.60 (m, 2H), 7.55-7.53 (m, 3H), 7.16 (*pseudo* d, 1H, $J = 8.7$ Hz), 6.81 (d, 1H, $J = 16.0$ Hz), 2.50 (*pseudo* tt, 1H, $J = 11.2, 6.5$ Hz), 1.79-1.75 (m, 4H), 1.63 (*pseudo* s, 1H), 1.25-1.12 (m, 5H).

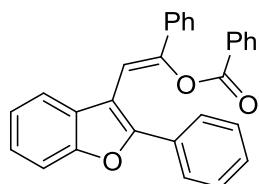
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 202.2, 164.6, 148.8, 134.2, 134.0, 133.7, 130.5, 129.8, 128.8, 128.6, 127.4, 125.0, 119.5, 49.8, 28.4, 25.8, 25.6.

MS (70eV, EI) m/z (%): 226 (100), 224 (100), 118 (78), 89 (28), 54 (23).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3070 (w), 2848 (w), 1738 (m), 1686 (w), 1590 (w), 1218 (s), 1082 (w), 650 (m).

HRMS (EI) for $\text{C}_{22}\text{H}_{21}\text{BrO}_3$, $[M]^+$ (412.0674) found: 412.0671.

Synthesis of (*Z*)-1-phenyl-2-(2-phenylbenzofuran-3-yl)vinyl benzoate (4a**):**



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl benzoate (**1a**) (164.1 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu₃ (150.0 μ L, 1.2 equiv) and NEt₃ (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 40 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4a** as white solid (185.1 mg, 89%).

R_f 0.3 (ethyl acetate/hexanes: 1/25); mp.: 140.6-141.1 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.93 (*pseudo* d, 2H, *J* = 8.6 Hz), 7.88 (*pseudo* d, 2H, *J* = 7.3 Hz), 7.77 (*pseudo* d, 1H, *J* = 7.3 Hz), 7.65 (*pseudo* d, 2H, *J* = 6.7 Hz), 7.48-7.46 (m, 3H), 7.40-7.37 (m, 5H), 7.33 (*pseudo* t, 2H, *J* = 7.8 Hz), 7.20-7.17 (m, 2H), 7.02 (s, 1H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 163.8, 154.2, 152.9, 148.5, 134.9, 133.3, 131.0, 130.1, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 127.5, 124.9, 124.5, 122.7, 121.5, 111.0, 110.7, 108.4.

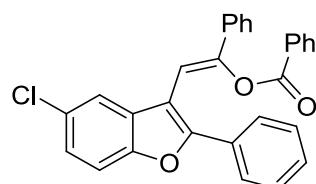
MS (70eV, EI) *m/z* (%): 416 [M]⁺ (22), 311 (8), 206 (8), 105 (100), 77 (30).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3047 (w), 1730 (m), 1605 (w), 1240 (s), 1082 (m).

HRMS (ESI) for C₂₉H₂₀O₃Na, [M+Na]⁺ (439.1310) found: 439.1326.

CCDC: 865909

Synthesis of (*Z*)-2-(5-chloro-2-phenylbenzofuran-3-yl)-1-phenylvinyl benzoate (**4b**):



Prepared according to **TP 1** from (*E*)-4-chloro-2-(3-oxo-3-phenylprop-1-enyl)phenyl benzoate (**1b**) (181.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu₃ (150.0 μ L, 1.2 equiv) and NEt₃ (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 20 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4b** as white solid (207.0 mg, 92%).

R_f 0.3 (ethyl acetate/hexanes: 1/25); mp.: 145.2-145.9 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.98 (*pseudo* d, 2H, *J* = 7.1 Hz), 7.91 (*pseudo* d, 2H, *J* = 8.6 Hz), 7.80 (d, 1H, *J* = 2.0 Hz), 7.67 (*pseudo* d, 2H, *J* = 7.9 Hz), 7.51-7.48(m, 3H), 7.41-7.37 (m, 6H), 7.33 (*pseudo* d, 1H, *J* = 8.6 Hz), 7.16 (*pseudo*

dd, 1H, $J = 8.7, 2.1$ Hz), 7.00 (s, 1H).

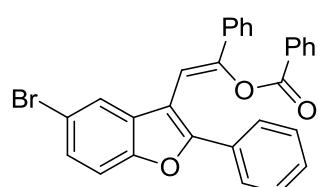
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 163.6, 154.4, 152.5, 148.6, 134.6, 133.5, 130.4, 130.2, 129.4, 129.1, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 127.6, 124.9, 124.6, 121.5, 112.0, 110.4, 107.7.

MS (70eV, EI) m/z (%): 452 [$\text{M}+2]^+$ (6), 450 [$\text{M}]^+$ (15), 239 (5), 105 (100), 77 (20).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3040 (w), 1730 (s), 1598 (m), 1229 (s), 1063 (s), 691 (s).

HRMS (ESI) for $\text{C}_{29}\text{H}_{19}\text{ClO}_3\text{Na}$, $[\text{M}+\text{Na}]^+$ (473.0920) found: 473.0924.

Synthesis of (Z)-2-(5-bromo-2-phenylbenzofuran-3-yl)-1-phenylvinyl benzoate (4c):



Prepared according to **TP 1** from (*E*)-4-bromo-2-(3-oxo-3-phenylprop-1-enyl)phenyl benzoate (**1c**) (203.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μL , 1.1 equiv), PBu_3 (150.0 μL , 1.2 equiv) and NEt_3 (91.0 μL , 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 20 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4c** as white solid (219.9 mg, 89%).

R_f 0.4 (ethyl acetate/hexanes: 1/25); mp.: 154.8–155.3 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.00 (*pseudo d*, 3H, $J = 7.0$ Hz), 7.91 (*pseudo d*, 2H, $J = 7.5$ Hz), 7.66 (*pseudo d*, 2H, $J = 6.8$ Hz), 7.52–7.48 (m, 3H), 7.41–7.37 (m, 6H), 7.30 (*pseudo s*, 2H), 7.00 (s, 1H).

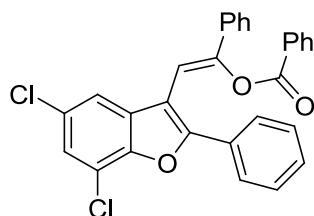
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 163.6, 154.2, 152.9, 148.6, 134.5, 133.5, 130.3, 130.2, 130.0, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 127.6, 127.2, 124.9, 124.6, 115.8, 112.5, 110.2, 107.7.

MS (70eV, EI) m/z (%): 496 [$\text{M}+2]^+$ (11), 494 [$\text{M}]^+$ (10), 105 (100), 77 (20).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3047 (w), 1734 (s), 1653 (w), 1233 (s), 1063 (s), 683 (s).

HRMS (EI) for $\text{C}_{29}\text{H}_{19}\text{BrO}_3$, $[\text{M}]^+$ (494.0518) found: 494.0518.

Synthesis of (Z)-2-(5,7-dichloro-2-phenylbenzofuran-3-yl)-1-phenylvinyl benzoate (4d):



Prepared according to **TP** **1** from (*E*)-2,4-dichloro-6-(3-oxo-3-phenylprop-1-enyl)phenyl benzoate (**1d**) (198.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu_3 (150.0 μ L, 1.2 equiv) and NEt_3 (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 10 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4d** as white solid (218.0 mg, 90%).

R_f 0.4 (ethyl acetate/hexanes: 1/25); mp.: 177.4–178.0 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 7.94 (*pseudo* d, 4H, $J = 6.3$ Hz), 7.71 (d, 1H, $J = 1.8$ Hz), 7.65–7.64 (*pseudo* dd, 2H, $J = 8.0, 1.5$ Hz), 7.53–7.49 (m, 3H), 7.41–7.39 (m, 6H), 7.20 (d, 1H, $J = 1.8$ Hz), 7.00 (s, 1H).

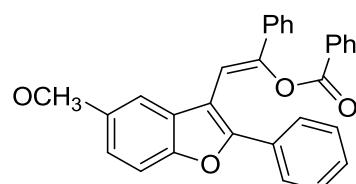
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 163.5, 155.0, 149.1, 148.6, 134.4, 133.6, 130.5, 130.2, 129.9, 129.5, 129.2, 128.8, 128.5, 127.8, 125.0, 124.5, 120.1, 117.0, 110.8, 107.2.

MS (70eV, EI) m/z (%): 486 [$\text{M}+2$]⁺ (3), 484 [M]⁺ (5), 105 (100), 77 (20).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 1727 (s), 1657 (w), 1233 (s), 1082 (s), 761 (s).

HRMS (EI) for $\text{C}_{29}\text{H}_{18}\text{Cl}_2\text{O}_3$, [M]⁺ (484.0633) found: 484.0637.

Synthesis of (*Z*)-2-(5-methoxy-2-phenylbenzofuran-3-yl)-1-phenylvinyl benzoate (**4e**):



Prepared according to **TP** **1** from (*E*)-4-methoxy-2-(3-oxo-3-phenylprop-1-enyl)phenyl benzoate (**1e**) (179.1 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu_3 (150.0 μ L, 1.2 equiv) and NEt_3 (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 60 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **4e** as white solid (194.0 mg, 87%).

R_f 0.4 (ethyl acetate/hexanes: 1/20); mp.: 152.4-154.4 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 7.91-7.90 (m, 4H), 7.65 (*pseudo* dd, 2H, J = 8.1, 1.3 Hz), 7.42-7.31 (m, 10H), 7.18 (d, 1H, J = 2.5 Hz), 6.98 (s, 1H), 6.81 (*pseudo* d, 4H, J = 6.3 Hz dd, 1H, J = 8.9, 2.6 Hz), 3.76 (s, 3H).

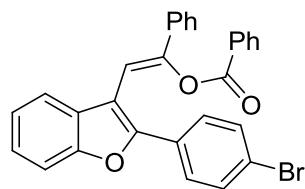
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 163.9, 155.9, 153.7, 149.1, 148.3, 134.9, 133.4, 131.0, 130.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 127.4, 124.9, 113.7, 111.5, 110.9, 108.5, 103.6, 55.8.

MS (70eV, EI) m/z (%): 446 [M]⁺ (23), 340 (11), 105 (100), 77 (23).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3040 (w), 2826 (w), 1730 (s), 1657 (w), 1236 (s), 1063 (s).

HRMS (ESI) for $\text{C}_{30}\text{H}_{22}\text{O}_4$, [M+Na]⁺ (469.1416) found: 469.1425.

Synthesis of (Z)-2-(2-(4-bromophenyl)benzofuran-3-yl)-1-phenylvinyl benzoate (**4f**):



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl 4-bromobenzoate (**1f**) (203.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μL , 1.1 equiv), PBu_3 (150.0 μL , 1.2 equiv) and NEt_3 (91.0 μL , 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 60 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4f** as white solid (224.8 mg, 91%).

R_f 0.4 (ethyl acetate/hexanes: 1/25); mp.: 133.4-134.1 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 7.86 (*pseudo* d, 2H, J = 7.1 Hz), 7.77-7.76 (m, 3H), 7.65 (*pseudo* d, 2H, J = 8.2 Hz), 7.58 (*pseudo* d, 2H, J = 8.6 Hz), 7.50 (*pseudo* t, 1H, J = 7.5 Hz), 7.41-7.38 (m, 4H), 7.33 (*pseudo* t, 2H, J = 7.8 Hz), 7.20-7.18 (m, 2H), 7.20 (s, 1H).

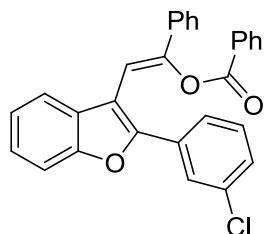
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 163.7, 154.1, 151.5, 148.8, 134.6, 133.4, 131.8, 130.0, 129.8, 129.0, 128.8, 128.7, 128.3, 128.3, 124.9, 124.8, 122.9, 122.8, 121.3, 111.2, 111.0, 107.8.

MS (70eV, EI) m/z (%): 496 [M+2]⁺ (7), 494 [M]⁺ (7), 105(100), 77 (18).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 1730 (s), 1646 (w), 1240 (s), 1078 (m), 687 (s).

HRMS (ESI) for $\text{C}_{29}\text{H}_{19}\text{BrO}_3\text{Na}$, [M+Na]⁺ (517.0416) found: 517.0433.

Synthesis of (Z)-2-(2-(3-chlorophenyl)benzofuran-3-yl)-1-phenylvinyl benzoate (4g):



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl 3-chlorobenzoate (**1g**) (181.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu_3 (150.0 μ L, 1.2 equiv) and NEt_3 (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 40 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **4g** as white solid (202.5 mg, 90%).

R_f 0.4 (ethyl acetate/hexanes: 1/20); mp.: 129.6–129.9 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ /ppm: 7.89 (*pseudo s*, 1H), 7.83 (m, 3H), 7.77 (*pseudo d*, 1H, J = 6.6 Hz), 7.66 (*pseudo d*, 2H, J = 6.6 Hz), 7.51 (*pseudo t*, 1H, J = 7.5 Hz), 7.38–7.31 (m, 8H), 7.23 (m, 2H), 6.99 (s, 1H).

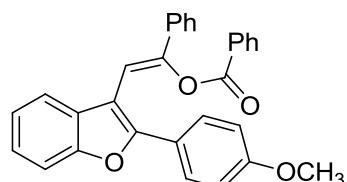
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ /ppm: 163.7, 154.1, 151.0, 149.0, 134.7, 133.4, 132.7, 130.0, 129.9, 129.0, 128.8, 128.7, 128.5, 128.3, 127.0, 125.6, 125.0, 124.9, 122.9, 121.5, 111.6, 111.1, 107.7.

MS (70eV, EI) m/z (%): 452 [$\text{M}+2$]⁺ (3), 450 [M]⁺ (10), 105(100), 77 (18).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 1730 (s), 1638 (w), 1236 (s), 1059 (m), 750 (s)

HRMS (ESI) for $\text{C}_{29}\text{H}_{19}\text{ClO}_3\text{Na}$, [$\text{M}+\text{Na}$]⁺ (473.0920) found: 473.0918.

Synthesis of (Z)-2-(2-(4-methoxyphenyl)benzofuran-3-yl)-1-phenylvinyl benzoate (4h):



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl 4-methoxybenzoate (**1h**) (179.1 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu_3 (150.0 μ L, 1.2 equiv) and NEt_3 (91.0 μ L, 1.3 equiv) in THF (1.0 mL)

[reaction condition: RT for 70 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **4h** as white solid (165.0 mg, 74%).

R_f 0.3 (ethyl acetate/hexanes: 1/20); mp.: 142.2-142.9°C.

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.92 (*pseudo d*, 2H, J = 7.6 Hz), 7.84 (*pseudo d*, 2H, J = 8.5 Hz), 7.76-7.74 (m, 1H), 7.63 (*pseudo d*, 2H, J = 7.3 Hz), 7.37-7.28 (m, 7H), 7.16-7.15 (m, 2H), 6.95 (m, 3H), 3.81 (s, 3H)

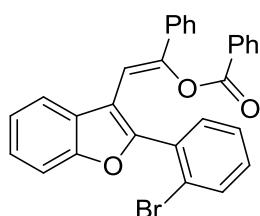
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 163.9, 160.2, 154.1, 153.2, 148.2, 135.0, 133.4, 130.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.4, 124.9, 124.2, 123.7, 122.7, 121.3, 114.3, 110.9, 109.4, 108.7, 55.4.

MS (70eV, EI) m/z (%): 446 [M]⁺ (38), 341 (25), 235 (5), 105 (100), 77 (22).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3047 (w), 2833 (w), 1727 (s), 1642 (w), 1240 (s), 1082 (m).

HRMS (ESI) for C₃₀H₂₂O₄Na, [M+Na]⁺ (469.1416) found: 469.1427.

Synthesis of (Z)-2-(2-(2-bromophenyl)benzofuran-3-yl)-1-phenylvinyl benzoate (**4i**):



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl 2-bromobenzoate (**1i**) (203.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu₃ (150.0 μ L, 1.2 equiv) and NEt₃ (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 60 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4i** as white solid (197.6 mg, 80%).

R_f 0.4 (ethyl acetate/hexanes: 1/25); mp.: 82.1-82.9°C.

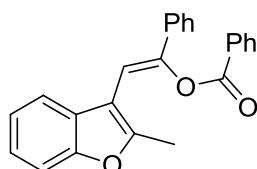
¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.93 (*pseudo d*, 2H, J = 7.1 Hz), 7.83 (*pseudo d*, 1H, J = 8.0 Hz), 7.63-7.61 (m, 2H), 7.54-7.52 (m, 3H), 7.46 (*pseudo d*, 1H, J = 8.2 Hz), 7.35-7.30 (m, 6H), 7.24-7.22 (m, 2H), 7.18 (*pseudo t*, 1H, J = 7.4 Hz), 6.83 (s, 1H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 163.6, 154.5, 152.5, 147.8, 135.1, 133.5, 133.4, 133.1, 131.9, 130.6, 130.2, 128.9, 128.7, 128.7, 128.3, 127.4, 127.2, 124.9, 124.8, 123.2, 122.7, 121.6, 113.2, 111.3, 107.8.

MS (70eV, EI) m/z (%): 496 [M+2]⁺ (2), 494[M]⁺ (2), 185 (2), 105 (100), 77 (40).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3047 (w), 1730 (s), 1657 (w), 1236 (s), 1059 (m), 691 (m).
HRMS (ESI) for $\text{C}_{29}\text{H}_{19}\text{BrO}_3\text{Na}, [\text{M}+\text{Na}]^+$ (517.0415) found: 517.0424.

Synthesis of (Z)-2-(2-methylbenzofuran-3-yl)-1-phenylvinyl benzoate (4j):



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl acetate (**1j**) (133.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μL , 1.1 equiv), PBu_3 (150.0 μL , 1.2 equiv) and NEt_3 (91.0 μL , 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 40 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4j** as white solid (141.6 mg, 80%).

R_f 0.4 (ethyl acetate/hexanes: 1/25); mp.: 129.6–129.9 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.07 (*pseudo d*, 2H, $J = 7.9$ Hz), 7.62–7.58 (m, 3H), 7.51 (*pseudo t*, 1H, $J = 7.2$ Hz), 7.34–7.28 (m, 6H), 7.09–7.03 (m, 2H), 6.81 (s, 1H), 2.45 (s, 3H).

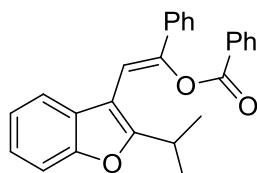
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 164.1, 154.2, 153.7, 147.2, 135.3, 133.7, 130.2, 129.2, 128.8, 128.8, 128.6, 128.1, 124.9, 123.6, 12.6, 120.6, 110.7, 110.6, 107.7, 13.5.

MS (70eV, EI) m/z (%): 354 [$\text{M}]^+$ (15), 223 (8), 144 (3), 105 (100), 77 (23).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3047 (w), 2826 (w), 1734 (s), 1649 (w), 1236 (m), 1063 (m).

HRMS (ESI) for $\text{C}_{24}\text{H}_{18}\text{O}_3\text{Na}, [\text{M}+\text{Na}]^+$ (377.1154) found: 377.1163.

Synthesis of (Z)-2-(2-isopropylbenzofuran-3-yl)-1-phenylvinyl benzoate (4k):



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl isobutyrate (**1k**) (147.1 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μL , 1.1 equiv), PBu_3 (150.0 μL , 1.2 equiv) and NEt_3 (91.0 μL , 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 90 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4k** as white solid (141.6 mg, 80%).

acetate/hexanes: 1/25) yielded **4k** as white solid (149.0 mg, 78%).

R_f 0.4 (ethyl acetate/hexanes: 1/25); mp.: 122.5-129.9 °C.

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.01 (*pseudo* d, 2H, J = 8.1 Hz), 7.66 (*pseudo* d, 1H, J = 7.5 Hz), 7.60 (*pseudo* d, 2H, J = 8.3 Hz), 7.47 (*pseudo* t, 1H, J = 7.5 Hz), 7.34-7.28 (m, 6H), 7.09 (*pseudo* quintet, 2H, J = 8.2 Hz), 6.86 (s, 1H), 3.29 (septet, 1H, J = 6.9 Hz), 1.32 (d, 6H, J = 6.6 Hz).

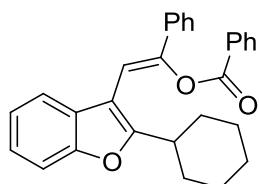
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 163.9, 161.5, 153.9, 147.2, 135.1, 133.4, 130.1, 129.1, 128.6, 128.6, 128.3, 127.8, 124.8, 123.3, 122.2, 120.9, 110.6, 108.2, 107.6, 27.3, 21.1.

MS (70eV, EI) m/z (%): 382 [M]⁺ (8), 128 (5), 105 (100), 77 (50).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3040(w), 2870 (w), 1723 (s), 1660 (w), 1240 (m), 1085 (m).

HRMS (ESI) for C₂₆H₂₂O₃Na, [M+Na]⁺ (405.1457) found: 405.1469.

Synthesis of (Z)-2-(2-cyclohexylbenzofuran-3-yl)-1-phenylvinyl benzoate (4l):



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl cyclohexanecarboxylate (**1l**) (167.1 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu₃ (150.0 μ L, 1.2 equiv) and NEt₃ (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 90 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4l** as white solid (149.8 mg, 71%).

R_f 0.4 (ethyl acetate/hexanes: 1/25); mp.: 116.8-117.2 °C.

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.04 (*pseudo* d, 2H, J = 7.2 Hz), 7.63-7.61 (m, 3H), 7.51 (*pseudo* t, 1H, J = 7.5 Hz), 7.36-7.32 (m, 6H), 7.09-7.00 (m, 2H), 6.84 (s, 1H), 2.92 (t, 1H, J = 11.5 Hz), 1.83 (t, 4H, J = 13.4 Hz), 1.68-1.62 (m, 3H), 1.31-1.24 (m, 3H).

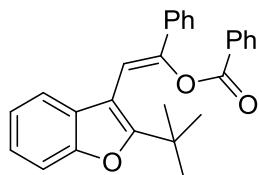
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 163.9, 161.1, 153.9, 147.1, 135.1, 133.2, 133.4, 130.2, 129.2, 128.7, 128.6, 128.4, 127.9, 124.9, 123.3, 122.2, 120.9, 110.6, 108.4, 107.7, 37.1, 31.2, 26.2, 25.8.

MS (70eV, EI) m/z (%): 422 [M]⁺ (18), 423 [M+1]⁺ (10), 317 (8), 105 (100), 77 (22).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 3025 (w), 2922 (m), 2848 (w), 1727 (s), 1660 (w), 1240 (s), 1085 (m).

HRMS (ESI) for C₂₉H₂₆O₃Na, [M+Na]⁺ (445.1780) found: 445.1756.

Synthesis of (Z)-2-(2-(tert-butyl)benzofuran-3-yl)-1-phenylvinyl benzoate (4m):



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl pivalate (**1m**) (154.1 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu₃ (150.0 μ L, 1.2 equiv) and NEt₃ (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 7 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4m** as white solid (106.9 mg, 54%).

R_f 0.4 (ethyl acetate/hexanes: 1/25); mp.: 147.7-148.2 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.84 (*pseudo* d, 2H, *J* = 4.2 Hz), 7.61 (*pseudo* d, 3H, *J* = 4.0 Hz), 7.40-7.33 (m, 4H), 7.27-7.25 (m, 3H), 7.14-7.10 (m, 2H), 6.97 (s, 1H), 1.46 (s, 9H).

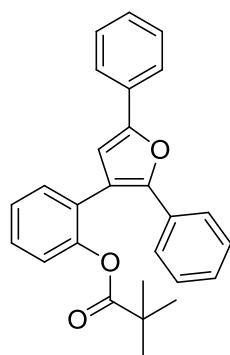
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 163.7, 162.2, 153.2, 147.9, 135.0, 133.1, 129.9, 129.1, 128.2, 124.9, 124.9, 123.3, 122.1, 120.8, 110.5, 108.9, 107.5, 34.5, 29.4.

MS (70eV, EI) *m/z* (%): 396 [M]⁺ (38), 133 (1), 105 (100), 77 (15).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3047 (w), 2856 (w), 1730 (s), 1657 (w), 1488 (m), 1236 (s), 1085 (m).

HRMS (ESI) for C₂₇H₂₄O₃Na, [M+Na]⁺ (419.1623) found: 419.1612.

Synthesis of 2-(2,5-diphenylfuran-3-yl)phenyl pivalate (4'm):



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl pivalate (**1m**) (154.1 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu₃ (150.0 μ L, 1.2 equiv) and NEt₃ (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 7 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4'm** as white solid (64.0 mg, 29%).

R_f 0.4 (ethyl acetate/hexanes: 1/25); mp.: 127.5-127.9 °C

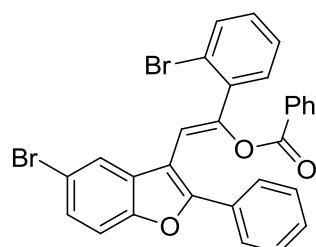
¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.73 (*pseudo* d, 2H, *J* = 7.7 Hz), 7.52 (*pseudo* d, 2H, *J* = 7.5 Hz), 7.40-7.37 (m, 4H), 7.28-7.25 (m, 5H), 7.22 (d, 1H, *J* = 7.4 Hz), 7.15 (*pseudo* d, 1H, *J* = 8.0 Hz), 6.72 (s, 1H), 1.07 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 176.7, 152.0, 149.2, 148.7, 131.4, 130.8, 130.5, 129.0, 128.8, 128.4, 128.0, 127.5, 127.4, 126.2, 125.4, 123.7, 122.9, 110.4, 38.9, 26.9.

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 2885 (w), 1727 (w), 1675 (s), 1211 (s), 1082 (w).

HRMS (ESI) for C₂₇H₂₄O₃Na, [M+Na]⁺ (419.1623) found: 419.1613.

Synthesis of (*Z*)-2-(5-bromo-2-phenylbenzofuran-3-yl)-1-(2-bromophenyl)vinyl benzoate (**4n**):



Prepared according to **TP 1** from (*E*)-4-bromo-2-(3-(2-bromophenyl)-3-oxoprop-1-enyl)phenyl benzoate (**1n**) (242.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu₃ (150.0 μ L, 1.2 equiv) and NEt₃ (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 10 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4n** as white solid (237.4 mg, 83%).

R_f 0.5 (ethyl acetate/hexanes: 1/25); mp.: 150.4-151.0 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.06 (*pseudo* s, 1H), 7.97 (*pseudo* d, 2H, *J* = 7.3 Hz), 7.88 (*pseudo* d, 2H, *J* = 7.8 Hz), 7.75 (*pseudo* d, 1H, *J* = 7.6 Hz), 7.64 (*pseudo* d, 1H, *J* = 8.1 Hz), 7.49 (*pseudo* t, 3H, *J* = 7.5 Hz), 7.41-7.39 (m, 2H), 7.33-7.30 (m, 4H), 7.27-7.23 (m, 1H), 6.63 (s, 1H).

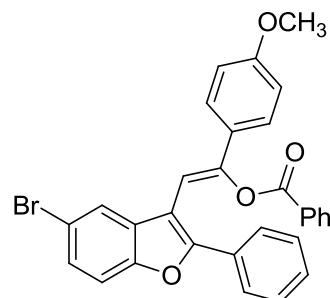
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 163.6, 154.0, 152.8, 148.3, 137.0, 133.5, 133.4, 131.3, 130.4, 130.3, 130.2, 129.1, 128.7, 128.6, 128.3, 127.6, 127.4, 127.3, 124.5, 122.0, 115.9, 112.5, 112.4, 109.5.

MS (70eV, EI) *m/z* (%): 574 [M+2]⁺ (3), 572 [M]⁺ (1), 183(3), 105 (100), 77 (30).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3047 (w), 1727 (m), 1236 (s), 1063 (s), 680 (s).

HRMS (ESI) for C₂₉H₁₈O₃Br₂Na, [M+Na]⁺ (594.9520) found: 594.9528.

Synthesis of (Z)-2-(5-bromo-2-phenylbenzofuran-3-yl)-1-(4-methoxyphenyl)vinyl benzoate (4o**):**



Prepared according to **TP** **1** from (E)-4-bromo-2-(3-(4-methoxyphenyl)-3-oxoprop-1-enyl)phenyl benzoate (**1o**) (218.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μL, 1.1 equiv), PBu₃ (150.0 μL, 1.2 equiv) and NEt₃ (91.0 μL, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 90 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4o** as white solid (191.3 mg, 73%).

R_f 0.5 (ethyl acetate/hexanes: 1/25); mp.: 138.0-139.6 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 7.99-7.96 (m, 3H), 7.91 (*pseudo* d, 2H, *J* = 1.4 Hz), 7.58 (*pseudo* d, 2H, *J* = 8.8 Hz), 7.49-7.45 (m, 3H), 7.39-7.36 (m, 3H), 6.93 (*pseudo* d, 2H, *J* = 8.8 Hz), 6.8 (s, 1H), 3.82 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 163.7, 160.3, 153.9, 152.9, 148.5, 133.5, 130.4, 130.3, 130.1, 129.0, 128.7, 128.6, 128.4, 127.6, 127.2, 126.4, 124.6, 115.7, 114.2, 112.4, 110.4, 105.6, 55.4.

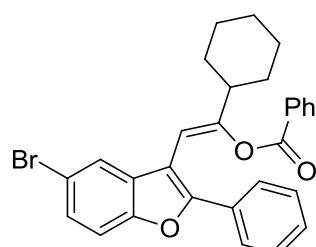
MS (70eV, EI) *m/z* (%): 526 [M+2]⁺ (5), 524 [M]⁺ (5), 176 (1), 105 (100), 77 (35).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3047 (w), 2833 (w), 1730 (s), 1660 (w), 1240 (s), 1082 (m), 687 (m).

HRMS (EI) for C₃₀H₂₁BrO₄, [M]⁺ (524.0623) found: 524.0618.

Synthesis of (Z)-2-(5-bromo-2-phenylbenzofuran-3-yl)-1-cyclohexylvinyl

benzoate (4p):



Prepared according to **TP 1** from (*E*)-4-bromo-2-(3-cyclohexyl-3-oxoprop-1-enyl)phenyl benzoate (**1b**) (206.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu_3 (150.0 μ L, 1.2 equiv) and NEt_3 (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 2 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4p** as white solid (212.5 mg, 85%).

R_f 0.5 (ethyl acetate/hexanes: 1/25); mp.: 130.2–130.4 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ /ppm: 7.90 (*pseudo* d, 2H, J = 7.6 Hz), 7.80 (*pseudo* t, 3H, J = 7.5 Hz), 7.49 (*pseudo* t, 3H, J = 7.5 Hz), 7.40–7.38 (m, 1H), 7.33 (*pseudo* t, 2H, J = 7.7 Hz), 7.26–7.24 (m, 2H), 6.19 (s, 1H), 2.49 (*pseudo* t, 1H, J = 11.1 Hz), 2.17 (m, 2H), 1.87 (*pseudo* d, 2H, J = 12.4 Hz), 1.74 (*pseudo* d, 1H, J = 12.4 Hz), 1.36–1.23 (m, 5H).

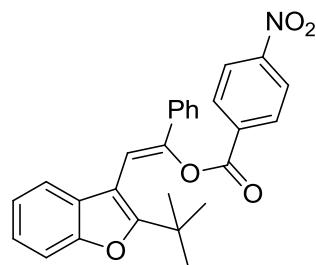
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ /ppm: 163.6, 156.8, 152.9, 152.7, 133.1, 130.6, 130.5, 129.9, 128.8, 128.6, 128.2, 127.3, 127.0, 124.2, 115.5, 112.3, 110.1, 105.1, 42.6, 31.0, 26.0.

MS (70eV, EI) m/z (%): 502 [$\text{M}+2$]⁺ (8) 500 [M]⁺ (8), 105(100), 77 (23).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3047 (w), 2848(w), 1730 (s), 1671 (w), 1236 (s), 1063 (m), 687 (m).

HRMS (ESI) for $\text{C}_{29}\text{H}_{25}\text{BrO}_3\text{Na}$, $[\text{M}+\text{Na}]^+$ (523.0885) found: 523.0889.

Synthesis of (*Z*)-2-(2-(tert-butyl)benzofuran-3-yl)-1-phenylvinyl 4-nitrobenzoate (4q**):**



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl pivalate (**1m**) (154.1 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu₃ (150.0 μ L, 1.2 equiv) and NEt₃ (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 40 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4q** as white solid (11.0 mg, 5%).

R_f 0.3 (ethyl acetate/hexanes: 1/25); mp.: 140.0-140.6°C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.11 (*pseudo* d, 2H, *J* = 8.9 Hz), 7.96 (*pseudo* d, 3H, *J* = 8.8 Hz), 7.61-7.59 (m, 2H), 7.28-7.25 (m, 1H), 7.42-7.38 (m, 3H), 7.30-7.29 (m, 1H), 7.18-7.16 (m, 2H), 1.47 (s, 9H)

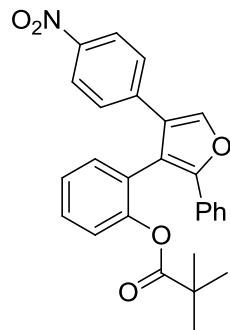
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 162.6, 162.0, 153.2, 150.6, 147.7, 134.4, 134.3, 130.9, 129.0, 128.8, 128.4, 124.8, 123.6, 123.4, 122.2, 120.5, 110.7, 109.2, 107.1, 34.6, 29.3.

MS (70eV, EI) *m/z* (%): 440 [M]⁺ (57), 291 (20), 234 (2), 150 (3), 105(100), 57 (5).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 2870(w), 1738 (s), 1609 (w), 1520 (s), 1343 (m), 1240 (s), 1085 (s).

HRMS (ESI) for C₂₇H₂₃NO₅Na, [M+Na]⁺ (419.1623) found: 419.1612.

Synthesis of 2-(4-(4-nitrophenyl)-2-phenylfuran-3-yl)phenyl pivalate (**4'q**):



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl pivalate (**1m**) (154.1 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu₃ (150.0 μ L, 1.2 equiv) and NEt₃ (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT

for 40 min]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4'q** as white solid (167.6 mg, 76%).

R_f 0.3 (ethyl acetate/hexanes: 1/25); mp.: 130.4-130.7°C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.12 (*pseudo* d, 2H, *J* = 9.0 Hz), 7.78 (*pseudo* d, 2H, *J* = 7.1 Hz), 7.63 (*pseudo* d, 2H, *J* = 9.0 Hz), 7.47-7.43 (m, 3H), 7.35-7.30 (m, 3H), 6.76-6.73 (*pseudo* d, 1H, *J* = 8.0 Hz), 6.97 (s, 1H), 1.04 (s, 9H)

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 176.6, 154.0, 149.0, 146.3, 146.1, 136.5, 131.0, 129.8, 129.7, 128.9, 128.4, 127.1, 126.5, 125.2, 124.1, 123.9, 123.4, 123.2, 111.0, 38.9, 26.8.

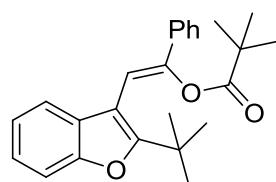
MS (70eV, EI) *m/z* (%): 441 [M]⁺ (100), 357 (70), 205(7), 85 (10), 57(70).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3047 (w), 2878(w), 1738 (s), 1598 (s), 1513 (s), 1336 (s), 1222(w), 1048 (w).

HRMS (ESI) for C₂₇H₂₃NO₅Na, [M+Na]⁺ (464.1474) found: 464.1441.

CCDC: 865911

Synthesis of (Z)-2-(2-(tert-butyl)benzofuran-3-yl)-1-phenylvinyl pivalate (4r):



Prepared according to **TP 1** from (*E*)-2-(3-oxo-3-phenylprop-1-enyl)phenyl pivalate (**1m**) (154.1 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu₃ (150.0 μ L, 1.2 equiv) and NEt₃ (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 30 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **4r** as white solid (133.5 mg, 71%).

R_f 0.4 (ethyl acetate/hexanes: 1/25); mp.: 115.7-118.1°C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.54 (*pseudo* d, 2H, *J* = 8.5 Hz), 7.38-7.31 (m, 5H), 7.14 (*pseudo* quintet, 2H, *J* = 5.4 Hz), 6.81 (s, 1H), 1.44 (s, 9H), 0.83 (s, 9H).

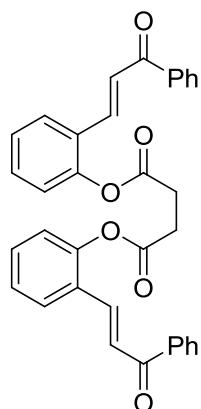
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 175.6, 161.9, 153.3, 148.5, 135.1, 129.2, 128.7, 124.8, 123.4, 122.1, 120.8, 110.4, 108.6, 107.3, 38.7, 34.5, 29.3, 26.6.

MS (70eV, EI) *m/z* (%): 376 [M]⁺ (72), 291 (25), 105(42), 85 (12), 57 (100).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 2870(w), 1741 (s), 1646 (w), 1266 (s), 1026 (w).

HRMS (ESI) for C₂₅H₂₈O₃Na, [M+Na]⁺ (399.1936) found: 399.1949.

Synthesis of bis(2-((E)-3-oxo-3-phenylprop-1-enyl)phenyl) succinate (5):



A dry and nitrogen-flushed 10-mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **37a** (224.1 mg, 1.0 mmol) in dry THF (6.6 mL). Succinyl chloride (58.0 μ L, 0.525 equiv) and NEt₃ (174.0 μ L, 1.25 equiv) was added, and the reaction mixture was stirred for 6 h at room temperature. Thereafter the resulting mixture was extracted with CH₂Cl₂ followed by washed with sat. NaHCO_{3(aq)}. The organic layer was dried over anhydrous MgSO₄ and then evaporated in vacuo. Purification by flash chromatography (ethyl acetate/hexanes: 1/4) yielded **5** as yellow oil (429.3 mg, 81%).

R_f 0.2 (ethyl acetate/hexanes: 1/4)

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.98 (*pseudo d*, 4H, *J* = 7.2 Hz), 7.86 (d, 2H, *J* = 16.0 Hz), 7.76 (*pseudo d*, 2H, *J* = 7.8 Hz), 7.57 (*pseudo t*, 2H, *J* = 7.2 Hz), 7.54-7.45 (m, 6H), 7.41 (*pseudo t*, 2H, *J* = 8.0 Hz), 7.29 (*pseudo t*, 2H, *J* = 7.8 Hz), 7.16 (*pseudo d*, 2H, *J* = 8.2 Hz), 3.10 (s, 4H).

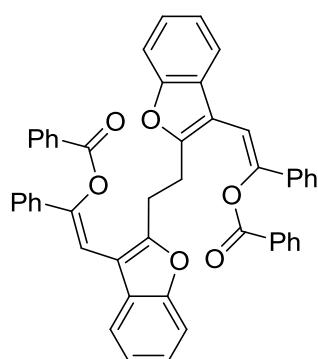
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 190.3, 170.4, 149.6, 138.0, 137.9, 132.9, 131.3, 128.6, 128.5, 127.7, 127.6, 126.5, 124.3, 123.2, 29.1.

MS (70eV, EI) *m/z* (%): 207 [M-323]⁺ (100), 147 (22), 105 (65), 57 (25).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3048 (w), 2915 (w), 1757 (s), 1660 (m), 1602 (s), 1211 (s), 1123 (s).

HRMS (ESI) for C₃₄H₂₆O₆Na, [M+Na]⁺ (553.1627) found: 553.1635.

Synthesis of (1Z,1'Z)-2,2'-(2,2'-(ethane-1,2-diyl)bis(benzofuran-3,2-diyl))bis(1-phenylethene-2,1-diyl) dibenzoate (7):



A dry and nitrogen-flushed 10-mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **5** (159.1 mg, 0.3 mmol) in dry THF (1.2 mL). Benzoyl chloride **2a** (77.0 μ L, 2.2 equiv), Bu₃P (180.0 μ L, 2.4 equiv), and NEt₃ (110.0 μ L, 2.6 equiv) was added, and the reaction mixture was stirred for 1h. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography (ethyl acetate/hexanes: 1/20) yielded **7** as white solid (165.3 mg, 78%).

R_f 0.2 (ethyl acetate/hexanes: 1/20); mp.: 158.5-159.0°C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.01 (*pseudo* d, 4H, *J* = 7.2 Hz), 7.62 (*pseudo* d, 2H, *J* = 7.6 Hz), 7.51 (*pseudo* t, 2H, *J* = 7.4 Hz), 7.39-7.22 (m, 16H), 7.16 (*pseudo* t, 2H, *J* = 7.6 Hz), 7.08 (*pseudo* t, 2H, *J* = 7.4 Hz), 6.52 (s, 2H), 3.30 (s, 4H).

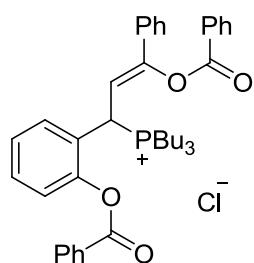
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 163.9, 155.1, 154.2, 147.5, 134.9, 133.4, 130.1, 129.1, 128.6, 128.5, 128.4, 127.7, 124.8, 123.8, 122.5, 121.1, 111.3, 110.8, 107.1, 26.0.

MS (70eV, EI) *m/z* (%): 185 [M-521]⁺ (38), 105 (100), 77 (30).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 2922 (w), 1734 (s), 1594 (w), 1450 (m), 1236 (s), 1082 (m), 1060 (m).

HRMS (ESI) for C₄₈H₃₄O₆Na, [M+Na]⁺ (729.2253) found: 729.2229.

Synthesis of (Z)-(3-(benzoyloxy)-1-(2-(benzoyloxy)phenyl)-3-phenylallyl) tributylphosphonium chloride (8):



A dry and nitrogen-flushed 10-mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **1a** (112.0 mg, 0.5 mmol) in dry THF (1 mL). Benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv) and Bu₃P (150.0 μ L, 1.2 equiv) were added, and the reaction mixture was stirred for 5 min at room temperature. Thereafter, the solvent was removed by evaporation in vacuo. The crude product was directly washed by pentane to afford **8**.

mp.: 155.0-155.7°C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.32 (*pseudo* d, 1H, *J* = 7.6 Hz), 8.12 (*pseudo* d, 2H, *J* = 7.6 Hz), 7.82 (*pseudo* d, 2H, *J* = 7.6 Hz), 7.77-7.67 (m, 3H), 7.58-7.40 (m, 6H), 7.40-7.30 (m, 3H), 7.25-7.15 (m, 3H), 5.06 (dd, 1H, *J* = 14.0, 11.2 Hz), 2.81-2.58 (m, 3H), 2.54-2.34 (m, 3H), 1.42-1.12 (m, 12H), 0.76-0.61 (m, 9H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 164.7, 164.0, 163.9, 150.4, 147.9, 147.8, 134.3, 134.2, 131.7, 130.1, 129.8, 129.7, 129.6, 129.5, 128.9, 128.7, 127.9, 127.8, 127.7, 127.6, 125.3, 123.2, 123.1, 109.7, 109.6, 30.1 (*J* = 46.0 Hz), 23.8 (*J* = 16.0 Hz), 23.7 (*J* = 5.0 Hz), 18.7 (*J* = 43.0 Hz), 13.1.

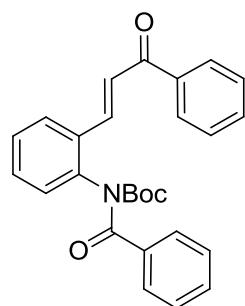
³¹P (200 MHz, CDCl₃, 25 °C) δ /ppm: 36.89.

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3049 (w), 2959 (m), 2878 (m), 1730 (s), 1598 (w), 1447 (m), 1240 (s), 1207 (s), 1082 (s), 1056 (s).

HRMS (ESI) for C₄₁H₄₈O₄P, [M-Cl]⁺ (635.3290) found: 635.3282.

CCDC: 865910

Synthesis of (*E*)-*tert*-butyl benzoyl(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (9a**):**



Prepared according to **TP 5** from (*E*)-*tert*-butyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**30**) (0.97 g, 3 mmol), benzoyl chloride (0.37 mL, 1.05 equiv), DMAP (36.6 mg, 0.1 equiv) and NEt₃ (0.36 mL, 1.2

equiv) in THF (7.5 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/6) yielded **9a** as white solid (1.09 g, 85%).

R_f 0.2 (ethyl acetate/hexanes: 1/6); mp.: 134.5-135.0°C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.98-7.94 (m, 3H), 7.85 (*pseudo* d, 1H, *J* = 7.4 Hz), 7.73 (*pseudo* d, 2H, *J* = 7.7 Hz), 7.54-7.48 (m, 9H), 7.31 (*pseudo* d, 1H, *J* = 7.7 Hz), 1.17 (s, 9H).

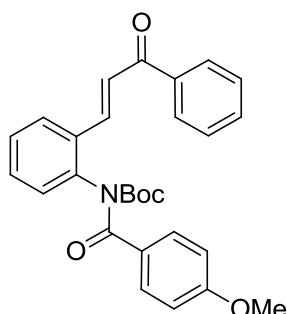
¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ /ppm: 190.4, 172.3, 152.8, 139.5, 138.8, 138.0, 136.6, 133.6, 132.8, 131.7, 131.1, 129.7, 128.9, 128.6, 128.5, 128.3, 128.0, 127.5, 125.1, 84.0, 27.3.

MS (70eV, EI) *m/z* (%): 327 [M-100]⁺ (8), 249 (8), 207 (27), 105 (100), 77 (40), 57 (56).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 2976 (w), 2928 (w), 1738 (s), 1680 (s), 1657 (m), 1604 (m), 1290 (m), 1152 (m).

HRMS (FAB) for C₂₇H₂₆NO₄, [M+H]⁺ (428.1862) found: 428.1860.

Synthesis of (*E*)-*tert*-butyl (4-methoxybenzoyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**9b**):



Prepared according to **TP 5** from (*E*)-*tert*-butyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**30**) (0.97 g, 3 mmol), 4-methoxybenzoyl chloride (0.41 mL, 1.05 equiv), DMAP (36.6 mg, 0.1 equiv) and NEt₃ (0.36 mL, 1.2 equiv) in THF (7.5 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/4) yielded **9b** as yellow solid (1.10 g, 80%).

R_f 0.2 (ethyl acetate/hexanes: 1/4); mp.: 128.5-129.0°C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.99-7.95 (m, 3H), 7.83 (*pseudo* d, 1H, *J* = 7.6 Hz), 7.73 (*pseudo* d, 2H, *J* = 8.7 Hz), 7.58-7.41 (m, 6H), 7.28 (*pseudo* d, 1H, *J* = 7.4 Hz), 6.93 (*pseudo* d, 2H, *J* = 8.7 Hz), 3.86 (s, 3H), 1.23 (s, 9H).

¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ /ppm: 190.4, 171.6, 162.7, 153.1, 139.7, 139.2,

138.0, 133.6, 132.7, 131.0, 130.7, 129.7, 128.6, 128.5, 128.4, 128.3, 127.4, 124.9, 113.6, 83.7, 55.4, 27.5.

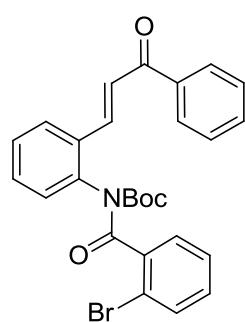
MS (70eV, EI) m/z (%): 357 [M-100]⁺ (4), 252 (6), 206 (10), 135 (100), 105 (14), 77 (23), 57 (23).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 2976 (m), 2918 (w), 1738 (s), 1676 (s), 1657 (m), 1604 (m), 1242 (m).

HRMS (EI) for $\mathbf{C}_{28}\mathbf{H}_{27}\mathbf{NO}_5$, [M]⁺ (457.1889) found: 457.1886.

Synthesis of (*E*)-*tert*-butyl

(2-bromobenzoyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**9c**):



Prepared according to **TP 5** from (*E*)-*tert*-butyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**30**) (0.97 g, 3 mmol), 2-bromobenzoyl chloride (0.39 mL, 1.05 equiv), DMAP (36.6 mg, 0.1 equiv) and NEt₃ (0.36 mL, 1.2 equiv) in THF (7.5 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/6) yielded **9c** as white solid (1.26 g, 83%).

R_f 0.2 (ethyl acetate/hexanes: 1/6); mp.: 149.0-149.5 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.00-7.93 (m, 3H), 7.87 (*pseudo* d, 1H, *J* = 7.8 Hz), 7.59-7.38 (m, 10H), 7.31-7.28 (m, 1H), 1.16 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 190.3, 169.8, 151.2, 139.7, 139.4, 138.0, 137.9, 133.4, 132.8, 132.5, 131.1, 130.6, 129.4, 129.0, 128.6, 128.5, 128.0, 127.4, 127.3, 124.9, 118.7, 84.5, 27.3.

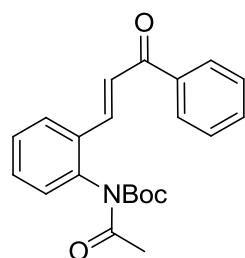
MS (70eV, EI) m/z (%): 405 [M-100]⁺ (6), 300 (14), 207 (35), 183 (100), 155 (34), 105 (68), 77 (52), 57 (88).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 2966 (w), 2918 (w), 1742 (s), 1671 (s), 1663 (s), 1600 (m), 1147 (m), 547 (m).

HRMS (FAB) for $\mathbf{C}_{27}\mathbf{H}_{25}\mathbf{NO}_5\mathbf{Br}$, [M+H]⁺ (506.0967) found: 506.0965.

Synthesis of (*E*)-*tert*-butyl

acetyl(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (9d):



Prepared according to **TP 5** from (*E*)-*tert*-butyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**30**) (0.97 g, 3 mmol), Ac₂O (0.42 mL, 1.05 equiv), DMAP (36.6 mg, 0.1 equiv) and NEt₃ (0.36 mL, 1.2 equiv) in THF (7.5 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/6) yielded **9d** as yellow oil (0.82 g, 75%).

R_f 0.3 (ethyl acetate/hexanes: 1/6)

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ/ppm: 7.99 (*pseudo* d, 2H, J = 8.0 Hz), 7.81 (*pseudo* dd, 1H, J = 7.6, 1.3 Hz), 7.68 (d, 1H, J = 15.7 Hz), 7.60 (*pseudo* t, 1H, J = 7.5 Hz), 7.54-7.48 (m, 5H), 7.04 (*pseudo* dd, 1H, J = 7.0, 1.0 Hz), 2.65 (s, 3H), 1.34 (s, 9H).

¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ/ppm: 190.2, 172.9, 152.2, 139.3, 138.8, 137.9, 132.9, 132.7, 130.9, 129.3, 128.6, 128.5, 128.4, 127.1, 124.5, 83.7, 27.7, 26.4.

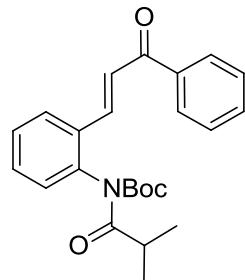
MS (70eV, EI) m/z (%): 265 [M-100]⁺ (6), 249 (14), 207 (45), 160 (18), 118 (30), 105 (36), 77 (25), 57 (100).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 2976 (m), 2928 (w), 1733 (s), 1700 (s), 1666 (m), 1604 (m), 1271 (m).

HRMS (FAB) for C₂₂H₂₄NO₄, [M+H]⁺ (366.1705) found: 366.1709.

Synthesis of (*E*)-*tert*-butyl

isobutyryl(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (9e):



Prepared according to **TP 5** from (*E*)-*tert*-butyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**30**) (0.97 g, 3 mmol), isobutyryl chloride (0.48 mL, 1.05 equiv), DMAP (36.6 mg, 0.1 equiv) and NEt₃ (0.36 mL, 1.2 equiv) in THF (7.5 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/6) yielded **9e** as white solid (0.94 g, 80%).

R_f 0.4 (ethyl acetate/hexanes: 1/6); mp.: 82.5-83.0 °C

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ/ppm: 7.97 (*pseudo* d, 2H, J = 8.0 Hz), 7.80 (*pseudo* dd, 1H, J = 8.0, 1.0 Hz), 7.72 (d, 1H, J = 15.7 Hz), 7.58 (*pseudo* t, 1H, J = 7.0 Hz), 7.50-7.38 (m, 5H), 7.04 (*pseudo* dd, 1H, J = 8.0, 1.0 Hz), 3.79 (septet, 1H, J = 6.8 Hz), 1.35 (s, 9H), 1.24 (d, 1H, J = 6.8 Hz), 1.23 (d, 1H, J = 6.8 Hz).

¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ/ppm: 190.3, 180.3, 152.1, 139.4, 139.3, 137.9, 132.8, 130.8, 129.3, 128.6, 128.5, 128.3, 127.0, 124.5, 83.5, 34.8, 27.7, 19.7, 19.4.

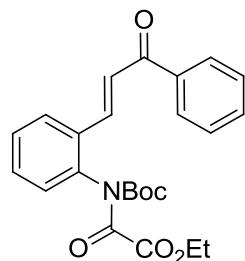
MS (70eV, EI) m/z (%): 293 [M-100]⁺ (4), 249 (16), 207 (76), 105 (42), 77 (21), 71 (23), 57 (100).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 2966 (m), 2928 (w), 1728 (s), 1700 (s), 1662 (m), 1600 (s), 1152 (m).

HRMS (EI) for C₂₄H₂₇NO₄, [M]⁺ (393.1940) found: 393.1937.

Synthesis of (*E*)-ethyl **2**-

((*tert*-butoxycarbonyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)amino)-2-oxoacetate (**9f**):



Prepared according to **TP 5** from (*E*)-*tert*-butyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**30**) (0.97 g, 3 mmol), ethyl oxalyl chloride (0.5 mL, 1.05 equiv), DMAP (36.6 mg, 0.1 equiv) and NEt₃ (0.36 mL, 1.2 equiv) in THF (7.5 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/6) yielded **9f** as yellow solid (0.51 g, 40%).

R_f 0.2 (ethyl acetate/hexanes: 1/6); mp.: 90.0-90.5 °C

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ/ppm: 7.97 (*pseudo* d, 2H, J = 7.0 Hz),

7.82-7.80 (m, 1H), 7.74 (d, 1H, $J = 15.7$ Hz), 7.58 (*pseudo t*, 1H, $J = 8.0$ Hz), 7.52-7.47 (m, 5H), 7.26-7.24 (m, 1H), (quartet, 2H, $J = 7.3$ Hz), 1.41-1.38 (m, 12H).

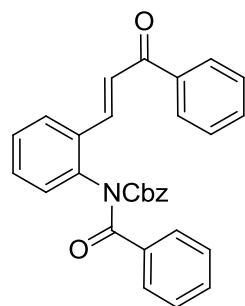
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 25 °C) δ/ppm : 190.1, 163.0, 161.2, 151.0, 138.7, 137.7, 134.9, 133.2, 132.9, 130.9, 129.5, 129.4, 128.6, 128.5, 128.1, 125.4, 85.8, 62.5, 27.6, 13.8.

MS (70eV, EI) m/z (%): 323 [$\text{M}-100$]⁺ (10), 250 (7), 144 (6), 105 (33), 77 (25), 57 (100).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 2985 (m), 2937 (w), 1752 (s), 1695 (s), 1662 (s), 1604 (m), 1290 (m), 1152 (m).

HRMS (FAB) for $\text{C}_{24}\text{H}_{26}\text{NO}_6$, [$\text{M}+\text{H}$]⁺ (424.1760) found: 424.1759.

Synthesis of (*E*)-benzyl benzoyl(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (10a):



Prepared according to **TP 5** from (*E*-benzyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**32**) (1.07 g, 3 mmol), benzoyl chloride (0.37 mL, 1.05 equiv), DMAP (36.6 mg, 0.1 equiv) and NEt_3 (0.36 mL, 1.2 equiv) in THF (7.5 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/6) yielded **10a** as yellow oil (1.18 g, 85%).

R_f 0.1 (ethyl acetate/hexanes: 1/6)

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25 °C) δ/ppm : 8.00-7.95 (m, 3H), 7.88-7.86 (m, 1H), 7.73 (*pseudo d*, 2H, $J = 8.0$ Hz), 7.60-7.40 (m, 9H), 7.33-7.31 (m, 1H), 7.29-7.22 (m, 3H), 7.04 (*pseudo d*, 2H, $J = 8.0$ Hz), 5.10 (s, 2H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 25 °C) δ/ppm : 190.2, 171.7, 154.1, 139.0, 138.1, 137.8, 135.3, 134.3, 133.5, 132.7, 131.9, 130.9, 129.7, 129.1, 128.5, 128.3, 128.2, 128.1, 128.0, 127.5, 125.3, 68.9.

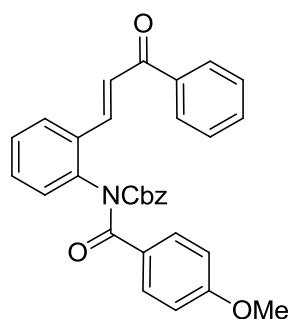
MS (70eV, EI) m/z (%): 207 [$\text{M}-254$]⁺ (7), 105 (100), 91 (57), 77 (42).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 3035 (w), 1740 (s), 1683 (s), 1601 (m), 1251 (m).

HRMS (MALDI) for $\text{C}_{30}\text{H}_{23}\text{NO}_4\text{Na}$, [$\text{M}+\text{Na}$]⁺ (484.1525) found: 484.1537.

Synthesis of (*E*)-benzyl

(4-methoxybenzoyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**10b**):



Prepared according to **TP 5** from (*E*-benzyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**32**) (1.07 g, 3 mmol), 4-methoxybenzoyl chloride (0.41 mL, 1.05 equiv), DMAP (36.6 mg, 0.1 equiv) and NEt₃ (0.36 mL, 1.2 equiv) in THF (7.5 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/6) yielded **10b** as yellow solid (1.18 g, 80%).

R_f 0.1 (ethyl acetate/hexanes: 1/6); mp.: 124.5–125.0 °C

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ/ppm: 7.95–7.90 (m, 3H), 7.82–7.81 (m, 1H), 7.68 (*pseudo* d, 2H, *J* = 8.7 Hz), 7.53 (*pseudo* t, 1H, *J* = 7.4 Hz), 7.46–7.41 (m, 5H), 7.33–7.31 (m, 4H), 7.73 (*pseudo* d, 2H, *J* = 8.0 Hz), 6.84 (*pseudo* d, 2H, *J* = 8.7 Hz), 5.08 (s, 2H), 3.82 (s, 3H).

¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ/ppm: 190.3, 171.0, 162.9, 154.4, 139.2, 138.5, 137.8, 134.6, 133.4, 132.7, 130.9, 130.8, 129.8, 128.9, 128.5, 128.3, 128.2, 128.0, 127.5, 127.1, 125.1, 113.6, 68.8, 55.3.

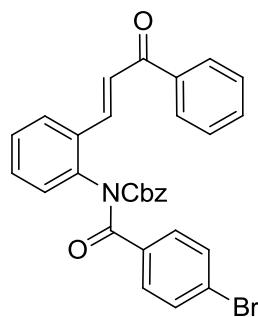
MS (70 eV, EI) *m/z* (%): 135 [M–356]⁺ (100), 107 (16), 91 (70), 77 (28).

IR (KBr) $\tilde{\nu}$ (cm^{−1}): 3052 (w), 2966 (w), 2928 (w), 1733 (s), 1700 (s), 1685 (s), 1638 (s), 1242 (m).

HRMS (MALDI) for C₃₁H₂₅NO₅Na, [M+Na]⁺ (514.1630) found: 514.1644.

Synthesis of (*E*)-benzyl

(4-bromobenzoyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**10c**):



Prepared according to **TP 5** from (E)-benzyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**32**) (1.07 g, 3 mmol), 4-bromobenzoyl chloride (0.69 g, 1.05 equiv), DMAP (36.6 mg, 0.1 equiv) and NEt₃ (0.36 mL, 1.2 equiv) in THF (7.5 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/6) yielded **10c** as yellow oil (1.37 g, 85%).

R_f 0.2 (ethyl acetate/hexanes: 1/6)

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ/ppm: 7.92-7.87 (m, 3H), 7.85-7.83 (m, 1H), 7.56 (*pseudo t*, 1H, *J* = 7.4 Hz), 7.52-7.43 (m, 9H), 7.27-7.22 (m, 4H), 7.01-7.00 (m, 2H), 5.07 (s, 2H).

¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ/ppm: 190.2, 170.9, 154.0, 138.8, 137.9, 137.8, 134.2, 133.4, 132.9, 131.6, 131.1, 129.7, 129.6, 129.2, 128.6, 128.5, 128.4, 128.2, 127.5, 126.8, 125.3, 69.2.

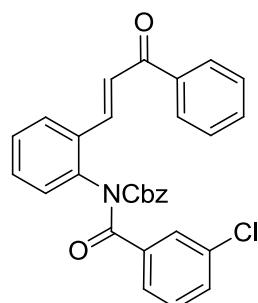
MS (70eV, EI) *m/z* (%): 404 [M-135]⁺ (82), 207 (28), 183 (55), 155 (14), 105 (100), 91 (92), 77 (96).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 3037 (w), 1743 (s), 1690 (s), 1608 (m), 1252 (m).

HRMS (MALDI) for C₃₀H₂₂BrNO₂Na, [M+Na]⁺ (562.0630) found: 562.0646.

Synthesis of (E)-benzyl

(3-chlorobenzoyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**10d**):



Prepared according to **TP 5** from (E)-benzyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**32**) (1.07 g, 3 mmol), 3-chlorobenzoyl chloride (0.58 mL, 1.05 equiv), DMAP (36.6 mg, 0.1 equiv) and NEt₃ (0.36 mL, 1.2 equiv) in THF (7.5 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/6) yielded **10d** as yellow oil (1.19 g, 80%).

R_f 0.2 (ethyl acetate/hexanes: 1/6)

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ/ppm: 7.92-7.87 (m, 3H), 7.83-7.81 (m, 1H), 7.65-7.64 (m, 1H), 7.55-7.51 (m, 2H), 7.48-7.41 (m, 6H), 7.28-7.20 (m, 5H), 7.00-6.98 (m, 2H), 5.05 (s, 2H).

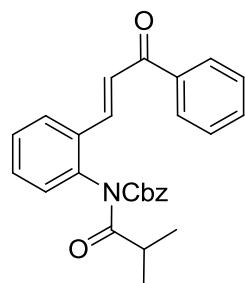
¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ/ppm: 190.0, 170.4, 153.8, 138.6, 137.6, 137.1, 134.4, 134.1, 133.4, 132.8, 131.7, 131.0, 129.5, 129.4, 129.2, 128.5, 128.4, 128.3, 128.0, 127.9, 127.5, 125.8, 125.3, 69.1.

MS (70eV, EI) *m/z* (%): 360 [M-135]⁺ (3), 207 (15), 139 (38), 105 (44), 91 (100), 77 (12).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 3033 (w), 1738 (s), 1690 (s), 1662 (s), 1604 (m), 1252 (m), 738 (s).

HRMS (MALDI) for C₃₀H₂₂ClNO₄Na, [M+Na]⁺ (518.1135) found: 518.1147.

Synthesis of (E)-benzyl isobutyryl(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**10e**):



Prepared according to **TP 5** from (E)-benzyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**32**) (1.07 g, 3 mmol), isobutyryl chloride (0.48 mL, 1.05 equiv), DMAP (36.6 mg, 0.1 equiv) and NEt₃ (0.36 mL, 1.2 equiv) in THF (7.5 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/6) yielded **10e** as yellow solid (0.83 g, 65%).

R_f 0.3 (ethyl acetate/hexanes: 1/6); mp.: 124.5-125.0 °C

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ/ppm: 7.90 (*pseudo* d, 2H, *J* = 8.2 Hz), 7.82-7.81 (m, 1H), 8.00 (d, 1H, *J* = 15.6 Hz), 7.57 (*pseudo* t, 1H, *J* = 7.5 Hz),

7.49-7.44 (m, 4H), , 7.04 (d, 1H, $J = 15.6$ Hz), 7.24-7.22 (m, 3H), 7.12-7.11 (m, 1H), 7.09-7.07 (m, 2H), 5.18-5.11 (m, 2H), 3.85 (septet, 1H, $J = 6.8$ Hz), 1.22 (*pseudo t*, 6H, $J = 6.8$ Hz).

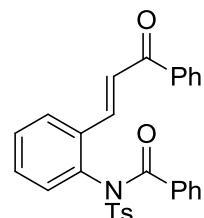
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 25 °C) δ/ppm : 190.1, 180.2, 153.2, 138.8, 138.4, 137.8, 135.0, 133.0, 132.8, 130.9, 129.4, 128.8, 128.6, 128.5, 128.4, 128.3, 127.5, 127.2, 124.8, 68.4, 34.9, 19.7, 19.2.

MS (70eV, EI) m/z (%): 207 [M-200]⁺ (11), 135 (5), 105 (44), 91 (100), 77 (8).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 3033 (w), 2995 (w), 2966 (w), 1738 (s), 1704 (s), 1661 (m), 1604 (m), 1247 (m).

HRMS (MALDI) for $\text{C}_{27}\text{H}_{25}\text{NO}_4\text{Na}$, [M+Na]⁺ (450.1682) found: 450.1692.

Synthesis of (*E*)-N-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)-N-tosylbenzamide (11a)



R_f 0.3 (ethyl acetate/hexanes: 1/5); mp.: 177.5-178.2 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.04-7.92 (m, 4H), 7.77-7.67 (m, 2H), 7.63-7.56 (m, 1H), 7.54-7.47 (m, 2H), 7.44-7.18 (m, 9H), 7.15-7.04 (m, 2H), 2.35 (s, 3H)

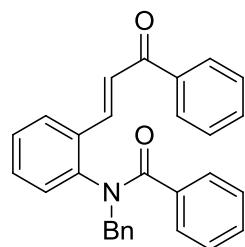
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 190.3, 169.6, 145.4, 139.0, 137.5, 136.7, 135.2, 134.8, 133.8, 133.0, 132.4, 131.6, 130.7, 130.0, 129.9, 129.4, 128.7, 127.9, 127.8, 125.8, 21.7

MS (70eV, EI) m/z (%): 155 [M-326]⁺ (13), 430 , 105 (100), 77 (48).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 2922 (w), 1690 (m), 1631 (s), 1590 (m), 1362 (s), 1166 (s), .

HRMS (ESI) for $\text{C}_{29}\text{H}_{23}\text{NO}_4\text{SNa}$, [M+Na]⁺ (504.1245) found: 504.1223.

Synthesis of (*E*)-N-benzyl-N-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)benzamide (12a):



Prepared according to **TP 5** from *N*-benzyl-*N*-(2-formylphenyl)benzamide (**35a**) (94.6 mg, 3 mmol) Acetophenone (0.39 ml, 1.1 equiv) and sodium methoxide (324.0 mg, 2 equiv) in MeOH (10 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/5) yielded **12a** as yellow solid (519.2 mg, 41 %).

R_f 0.1(ethyl acetate/hexanes: 1/10); mp.: 168.3-169.0 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 7.92 (*pseudo d*, 2H, $J = 7.4$ Hz), 7.66 (d, 1H, $J = 15.7$), 7.61-7.44 (m, 4H), 7.34-7.11 (m, 10H), 7.11-6.98 (m, 2H), 6.95-6.85 (m, 1H), 5.38 (d, 1H, $J = 13.9$ Hz), 4.80 (d, 1H, $J = 13.9$ Hz).

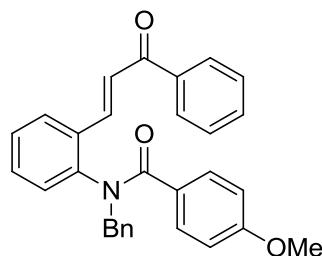
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 189.9, 170.4, 142.3, 139.5, 137.7, 136.3, 135.6, 132.8, 132.7, 130.6, 130.3, 129.6, 129.3, 128.6, 128.5, 128.4, 127.9, 127.7, 127.6, 127.5, 124.5, 53.8.

MS (70eV, EI) m/z (%): 417 [$\text{M}]^+$ (7), 312 (35), 105 (100), 77 (22).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 3026 (w), 2900 (w), 1661 (s), 1642 (s), 1598 (s), 1314 (s), 1215 (s).

HRMS (ESI) for $\text{C}_{29}\text{H}_{23}\text{NO}_2\text{Na}$, $[\text{M}+\text{Na}]^+$ (440.1626) found: 440.1613.

Synthesis of
(E)-*N*-benzyl-4-methoxy-*N*-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)benzamide
(12b):



Prepared according to **TP 5** from *N*-benzyl-*N*-(2-formylphenyl)-4-methoxybenzamide (**35b**) (103.5 mg, 3 mmol) Acetophenone (0.39 ml, 1.1 equiv) and sodium methoxide

(324.0 mg, 2 equiv) in MeOH (10 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/5) yielded **12b** as yellow solid (617.1 mg, 46 %).

R_f 0.1 (ethyl acetate/hexanes: 1/10); mp.: 131.3-133.8 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.90 (d, 2H, J = 7.9 Hz), 7.68-7.45 (m, 5H), 7.35-7.08 (m, 10H), 6.94 (s, 1H), 6.69-6.45 (m, 2H), 5.33 (d, 1H, J = 14.0 Hz), 4.82 (d, 1H, J = 14.0 Hz), 3.64 (s, 3H).

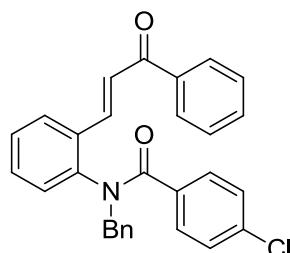
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 189.7, 169.3, 142.1, 139.2, 137.7, 136.2, 135.8, 134.2, 133.1, 132.9, 131.0, 130.2, 129.9, 129.5, 128.7, 128.5, 128.4, 128.3, 127.9, 124.7, 54.1.

MS (70eV, EI) m/z (%): 447 [M]⁺ (4), 342 (11), 312 (22), 135 (100), 105 (25), 91 (8).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3055 (m), 3011 (m), 2959 (m), 2930 (m), 1661 (s), 1631 (s), 1602 (s), 1248 (s), 1211 (s), 1178 (s).

HRMS (ESI) for C₃₀H₂₅NO₃Na, [M+Na]⁺ (470.1732) found: 470.1717.

**Synthesis of
(E)-N-benzyl-4-chloro-N-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)benzamide
(12c):**



Prepared according to **TP 5** from *N*-benzyl-4-chloro-*N*-(2-formylphenyl)benzamide (**35c**) (104.7 mg, 3 mmol) Acetophenone (0.39 ml, 1.1 equiv) and sodium methoxide (324.0 mg, 2 equiv) in MeOH (10 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/5) yielded **12c** as yellow solid (816.2 mg, 71 %).

R_f 0.1 (ethyl acetate/hexanes: 1/10); mp.: 108.2-110.3 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.92 (d, 2H, J = 7.4 Hz), 7.64-7.53 (m, 3H), 7.53-7.46 (m, 2H), 7.31-7.13 (m, 10H), 7.10-6.97 (m, 2H), 6.98-6.89 (m, 1H), 5.32 (d, 1H, J = 14.0), 4.84 (d, 1H, J = 14.0).

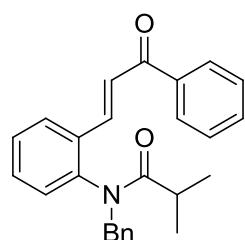
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 189.6, 169.2, 142.0, 139.0, 137.6, 136.0, 135.7, 134.0, 132.9, 132.8, 130.8, 130.0, 129.8, 129.3, 128.6, 128.4, 128.3, 128.1, 127.7, 124.6, 53.9.

MS (70eV, EI) m/z (%): 451 [M]⁺ (7), 346 (10), 312 (26), 263 (12), 139 (72), 105 (100), 91 (29), 77 (17).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3063 (w), 3026 (w), 2945 (w), 1657 (s), 1639 (s), 1602 (s), 1325 (s), 1274 (s), 1215 (s), 735 (s).

HRMS (ESI) for $\mathbf{C}_{29}\mathbf{H}_{22}\mathbf{ClNO}_2\mathbf{Na}$, [M+Na]⁺ (474.1237) found: 474.1217

Synthesis of
(E)-N-benzyl-N-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)isobutyramide (12d):



Prepared according to **TP 5** from *N*-benzyl-*N*-(2-formylphenyl)isobutyramide (**35d**) (84.3 mg, 3 mmol) Acetophenone (0.39 ml, 1.1 equiv) and sodium methoxide (324.0 mg, 2 equiv) in MeOH (10 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/) yielded **12d** as solid (0.34g, 34%).

R_f 0.1 (ethyl acetate/hexanes: 1/10); mp.: 131.1-132.8 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.94 (pseudo d, 2H, J = 7.5 Hz), 7.78 (pseudo d, 1H, J = 7.6 Hz), 7.64-7.55 (m, 2H), 7.55-7.46 (m, 2H), 7.44-7.30 (m, 3H), 7.22-7.09 (m, 5H), 6.89 (pseudo d, 1H, J = 7.8 Hz), 5.21 (d, 1H, J = 14.0), 4.47 (d, 1H, J = 14.0), 2.28 (pseudo quintet, 1H, J = 6.6 Hz), 1.10-0.97 (m, 6H).

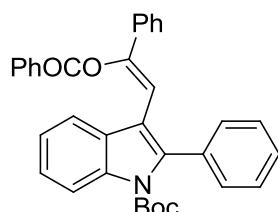
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 189.8, 177.0, 141.5, 138.9, 137.6, 136.6, 133.3, 132.8, 131.0, 130.1, 129.3, 128.6, 128.4, 128.2, 127.9, 127.4, 124.7, 52.7, 31.7, 19.8, 19.3.

MS (70eV, EI) m/z (%): 463 [M]⁺ (2), 311 (19), 278 (7), 207 (17), 105 (100), 91 (52), 77 (13), 71 (14).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 3026 (w), 2959 (w), 2923 (w), 2871 (w), 1642 (s), 1602 (s), 1576 (m), 1247 (m), 1215 (s).

HRMS (EI) for $\mathbf{C}_{26}\mathbf{H}_{25}\mathbf{NO}_2$, [M+H]⁺ (384.1964) found: 384.1983.

Synthesis of (Z)-*tert*-butyl 3-(2-(benzoyloxy)-2-phenylvinyl)-2-phenyl-1*H*-indole-1-carboxylate (17a):



Prepared according to **TP 2** from (*E*)-*tert*-butyl benzoyl(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**9a**) (132.6 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.0 μ L, 1.1 equiv), PBu₃ (90.0 μ L, 1.2 equiv) and NEt₃ (54.0 μ L, 1.3 equiv) in CH₂Cl₂ (0.6 mL) [reaction condition: RT for 1.5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **17a** as white solid (123.6 mg, 80%).

R_f 0.3 (ethyl acetate/hexanes: 1/10); mp.: 186.0–187.0 °C

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ /ppm: 8.18 (*pseudo* d, 1H, *J* = 8.0 Hz), 8.05 (*pseudo* d, 2H, *J* = 7.3 Hz), 7.87 (*pseudo* d, 1H, *J* = 7.5 Hz), 7.53 (*pseudo* t, 1H, *J* = 7.5 Hz), 7.50–7.47 (m, 4H), 7.45–7.37 (m, 5H), 7.34–7.26 (m, 4H), 7.21 (*pseudo* t, 1H, *J* = 7.5 Hz), 6.58 (s, 1H), 1.24 (s, 9H).

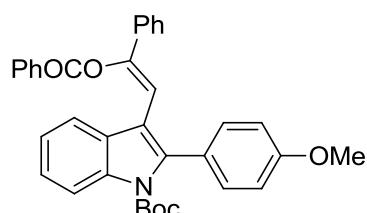
¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ /ppm: 163.8, 150.0, 147.3, 138.2, 136.9, 135.1, 133.8, 133.3, 130.2, 130.1, 129.2, 128.6, 128.4, 128.3, 127.8, 127.7, 127.6, 124.7, 124.5, 122.7, 121.3, 115.5, 115.0, 109.9, 83.5, 27.4.

MS (70eV, EI) *m/z* (%): 515 [M]⁺ (5), 459 (12), 415 (6), 354 (4), 310 (14), 282 (7), 204 (14), 105 (100), 77 (21), 57 (38).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 2976 (m), 2926 (w), 1738 (s), 1233 (m), 1147 (m).

HRMS (MALDI) for C₃₄H₂₉NO₄Na, [M+Na]⁺ (538.1995) found: 538.2004.

Synthesis of (*Z*)-*tert*-butyl 3-(2-(benzoyloxy)-2-phenylvinyl)-2-(4-methoxyphenyl)-1*H*-indole-1-carboxylate (**17b**):



Prepared according to **TP 2** from (*E*)-*tert*-butyl (4-methoxybenzoyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**9b**) (137.2 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.0 μ L, 1.1 equiv), PBu₃ (90.0 μ L, 1.2

equiv) and NEt₃ (54.0 μL, 1.3 equiv) in CH₂Cl₂ (0.6 mL) [reaction condition: RT for 1.5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **17b** as yellow solid (125.9 mg, 77%).

R_f 0.2 (ethyl acetate/hexanes: 1/10); mp.: 147.5-148.0 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 8.15 (*pseudo d*, 1H, *J* = 8.0 Hz), 8.05 (*pseudo d*, 2H, *J* = 7.8 Hz), 7.85 (*pseudo d*, 1H, *J* = 7.6 Hz), 7.54-7.49 (m, 3H), 7.42-7.18 (m, 9H), 6.97 (*pseudo d*, 2H, *J* = 8.5 Hz), 6.58 (s, 1H), 1.30 (s, 9H).

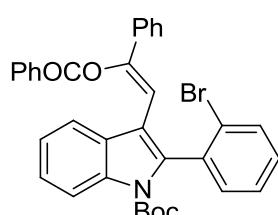
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 163.8, 159.4, 150.1, 147.1, 138.3, 136.8, 135.2, 133.3, 131.4, 130.2, 129.3, 128.6, 128.3, 127.7, 126.1, 124.7, 124.3, 122.6, 121.2, 115.2, 115.0, 113.3, 110.1, 83.4, 55.3, 27.6.

MS (70eV, EI) *m/z* (%): 545 [M]⁺ (2), 489 (7), 445 (16), 340 (32), 312 (12), 234 (8), 105 (100), 77 (35), 57 (22).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3067 (w), 2966 (m), 2932 (w), 1737 (s), 1728 (s), 1235 (m).

HRMS (MALDI) for C₃₅H₃₁NO₅Na, [M+Na]⁺ (568.2100) found: 568.2114.

Synthesis of (*Z*)-*tert*-butyl 3-(2-(benzoyloxy)-2-phenylvinyl)-2-(2-bromophenyl)-1*H*-indole-1-carboxylate (**17c**):



Prepared according to **TP 2** from (E)-*tert*-butyl (2-bromobenzoyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**9c**) (151.5 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.0 μL, 1.1 equiv), PBu₃ (90.0 μL, 1.2 equiv) and NEt₃ (54.0 μL, 1.3 equiv) in CH₂Cl₂ (0.6 mL) [reaction condition: RT for 3.0 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **17c** as yellow solid (119.2 mg, 67%).

R_f 0.3 (ethyl acetate/hexanes: 1/10); mp.: 77.0-77.5 °C

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ/ppm: 8.25 (*pseudo d*, 1H, *J* = 8.3 Hz), 8.02 (*pseudo d*, 2H, *J* = 7.3 Hz), 7.86 (*pseudo d*, 1H, *J* = 7.8 Hz), 7.63 (*pseudo d*, 1H, *J* = 7.6 Hz), 7.55-7.51 (m, 2H), 7.46-7.44 (m, 2H), 7.41-7.37 (m, 3H), 7.33-7.27 (m, 5H), 7.20 (*pseudo t*, 1H, *J* = 7.5 Hz), 6.47 (s, 1H), 1.26 (s, 9H).

¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ/ppm: 163.7, 149.6, 147.5, 136.4, 136.2, 135.6,

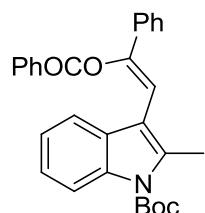
135.1, 133.3, 132.9, 132.2, 130.2, 129.6, 129.2, 128.6, 128.5, 128.3, 127.3, 127.2, 124.9, 124.8, 124.5, 122.6, 121.5, 116.0, 115.4, 109.1, 83.3, 27.5.

MS (70eV, EI) m/z (%): 595 [M+2]⁺ (4), 593 [M]⁺ (4), 537 (7), 493 (6), 388 (22), 360 (2), 282 (8), 105 (100), 77 (22), 57 (38).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3052 (w), 2976 (m), 2928 (w), 1733 (s), 1233 (m), 571 (w).

HRMS (MALDI) for C₃₄H₂₈BrNO₄Na, [M+Na]⁺ (616.1100) found: 616.1116.

Synthesis of (Z)-tert-butyl 3-(2-(benzoyloxy)-2-phenylvinyl)-2-methyl-1*H*-indole-1-carboxylate (17d):



Prepared according to **TP 2** from (E)-tert-butyl acetyl(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**9d**) (109.5 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.0 μ L, 1.1 equiv), PBu₃ (90.0 μ L, 1.2 equiv) and NEt₃ (54.0 μ L, 1.3 equiv) in CH₂Cl₂ (0.6 mL) [reaction condition: RT for 3.0 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **17d** as colorless oil (102.0 mg, 75%).

R_f 0.3 (ethyl acetate/hexanes: 1/10)

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ /ppm: 8.05-8.01 (m, 3H), 7.63-7.62 (m, 3H), 7.53 (pseudo t, 1H, *J* = 7.5 Hz), 7.41-7.33 (m, 5H), 7.21-7.16 (m, 2H), 6.89 (s, 1H), 1.63 (s, 9H).

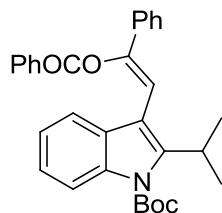
¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ /ppm: 164.0, 150.5, 147.8, 135.8, 135.6, 135.2, 133.3, 130.1, 129.2, 128.6, 128.5, 128.4, 128.3, 124.9, 123.5, 122.6, 119.5, 115.1, 113.6, 109.0, 83.8, 28.2, 15.5.

MS (70eV, EI) m/z (%): 453 [M]⁺ (20), 397 (54), 292 (24), 248 (48), 220 (22), 105 (100), 77 (23), 57 (44).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3052 (w), 2976 (m), 2918 (w), 1733 (s), 1238 (m).

HRMS (MALDI) for C₂₉H₂₇NO₄Na, [M+Na]⁺ (476.1838) found: 476.1854.

Synthesis of (Z)-tert-butyl 3-(2-(benzoyloxy)-2-phenylvinyl)-2-isopropyl-1*H*-indole-1-carboxylate (17e):



Prepared according to **TP 2** from (*E*)-*tert*-butyl isobutyryl(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**9e**) (118.0 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.0 μ L, 1.1 equiv), PBu_3 (90.0 μ L, 1.2 equiv) and NEt_3 (54.0 μ L, 1.3 equiv) in CH_2Cl_2 (0.6 mL) [reaction condition: RT for 5.0 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **17e** as yellow solid (115.5 mg, 80%).

R_f 0.4 (ethyl acetate/hexanes: 1/10); mp.: 139.0-139.5 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25 °C) δ /ppm: 7.91 (*pseudo* d, 1H, J = 7.8 Hz), 7.87 (*pseudo* d, 2H, J = 7.3 Hz), 7.65-7.62 (m, 3H), 7.46 (*pseudo* t, 1H, J = 7.5 Hz), 7.41-7.38 (m, 2H), 7.50-7.47 (m, 1H), 7.30 (*pseudo* t, 2H, J = 7.8 Hz), 7.22-7.15 (m, 2H), 6.98 (s, 1H), 3.93 (septet, 1H, J = 7.1 Hz), 1.67 (s, 9H), 1.48 (d, 6H, J = 7.1 Hz).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 25 °C) δ /ppm: 163.8, 150.5, 147.6, 144.5, 135.6, 135.2, 133.1, 130.0, 129.3, 128.7, 128.6, 128.2, 124.9, 123.4, 122.2, 120.1, 114.9, 112.4, 110.1, 84.0, 28.2, 27.7, 22.0.

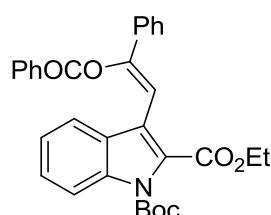
MS (70eV, EI) m/z (%): 481 [$\text{M}]^+$ (7), 425 (12), 381 (3), 320 (7), 276 (18), 248 (4), 170 (5), 105 (100), 77 (21), 57 (38).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3062 (w), 2976 (m), 2937 (w), 1734 (s), 1720 (s), 1237 (m).

HRMS (MALDI) for $\text{C}_{31}\text{H}_{31}\text{NO}_4\text{Na}$, $[\text{M}+\text{Na}]^+$ (504.2151) found: 504.2165.

CCDC: 876493

Synthesis of (*Z*)-1-*tert*-butyl 2-ethyl 3-(2-(benzoyloxy)-2-phenylvinyl)-1*H*-indole-1,2-dicarboxylate (**17f**):



Prepared according to **TP 2** from (*E*)-ethyl 2-((*tert*-butoxycarbonyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)amino)-2-oxoaceta

te (**9f**) (127.0 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.0 μ L, 1.1 equiv), PBu_3 (90.0 μ L, 1.2 equiv) and NEt_3 (54.0 μ L, 1.3 equiv) in CH_2Cl_2 (0.6 mL) [reaction condition: RT for 2.0 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **17f** as yellow solid (107.4 mg, 70%).

R_f 0.1 (ethyl acetate/hexanes: 1/10); mp.: 134.0-134.5°C

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25 °C) δ/ppm : 8.00 (*pseudo d*, 1H, $J = 8.4$ Hz), 7.97 (*pseudo d*, 2H, $J = 7.2$ Hz), 7.80 (*pseudo d*, 1H, $J = 7.9$ Hz), 7.62-7.61 (m, 2H), 7.51 (*pseudo t*, 1H, $J = 7.4$ Hz), 7.41-7.34 (m, 4H), 7.33-7.30 (m, 1H), 7.18 (*pseudo t*, 1H, $J = 7.7$ Hz), 7.08 (s, 1H), 4.41 (quartet, 2H, $J = 7.2$ Hz), 1.61 (s, 9H), 1.36 (t, 3H, $J = 7.1$ Hz).

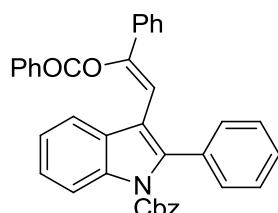
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 25 °C) δ/ppm : 163.8, 162.2, 149.2, 149.0, 136.5, 135.0, 133.4, 130.1, 129.0, 128.9, 128.7, 128.3, 128.0, 127.0, 126.6, 125.1, 123.0, 122.3, 120.0, 114.7, 107.7, 84.7, 61.5, 27.9, 14.2.

MS (70eV, EI) m/z (%): 481 [$\text{M}-31$]⁺ (7), 425 (9), 381 (2), 320 (12), 276 (18), 248 (6), 207 (12), 135 (10), 105 (100), 91 (29), 77 (26), 57 (24).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3062 (w), 2976 (m), 2928 (w), 1733 (s), 1238 (m).

HRMS (MALDI) for $\text{C}_{31}\text{H}_{29}\text{NO}_6\text{Na}$, $[\text{M}+\text{Na}]^+$ (534.1893) found: 534.1905.

Synthesis of (*Z*)-benzyl 3-(2-(benzoyloxy)-2-phenylvinyl)-2-phenyl-*1H*-indole-1-carboxylate (**18a**):



Prepared according to **TP 2** from (E)-benzyl benzoyl(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**10a**) (138.3 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.0 μ L, 1.1 equiv), PBu_3 (90.0 μ L, 1.2 equiv) and NEt_3 (54.0 μ L, 1.3 equiv) in CH_2Cl_2 (0.6 mL) [reaction condition: RT for 2.0 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **18a** as yellow solid (135.1 mg, 82%).

R_f 0.2 (ethyl acetate/hexanes: 1/10); mp.: 66.5-67.0°C

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25 °C) δ/ppm : 8.15 (*pseudo d*, 1H, $J = 7.6$ Hz), 8.02 (*pseudo d*, 2H, $J = 7.4$ Hz), 7.85 (*pseudo d*, 1H, $J = 8.2$ Hz), 7.53-7.46 (m, 5H),

7.39-7.21 (m, 13H), 7.00 (*pseudo* d, 2H, $J = 6.7$ Hz), 6.56 (s, 1H), 5.16 (s, 2H).

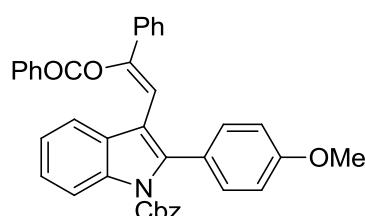
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 25 °C) δ/ppm : 163.7, 151.4, 147.7, 138.1, 136.8, 135.0, 134.4, 133.3, 133.0, 130.2, 129.1, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 124.8, 123.1, 121.4, 116.5, 115.3, 109.6, 68.7.

MS (70eV, EI) m/z (%): 549 [M]⁺ (18), 414 (4), 400 (14), 204 (6), 105 (100), 91 (94), 77 (20).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3052 (w), 3033 (w), 2947 (w), 1733 (s), 1238 (m).

HRMS (MALDI) for $\text{C}_{37}\text{H}_{27}\text{NO}_4\text{Na}$, [M+Na]⁺ (572.1838) found: 572.1852.

Synthesis of (Z)-benzyl 3-(2-(benzoyloxy)-2-phenylvinyl)-2-(4-methoxyphenyl)-1*H*-indole-1-carboxylate (18b):



Prepared according to **TP 2** from (E)-benzyl (4-methoxybenzoyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**10b**) (147.4 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.0 μL , 1.1 equiv), PBu_3 (90.0 μL , 1.2 equiv) and NEt_3 (54.0 μL , 1.3 equiv) in CH_2Cl_2 (0.6 mL) [reaction condition: RT for 2.0 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **18b** as white solid (126.8 mg, 73%).

R_f 0.2 (ethyl acetate/hexanes: 1/10); mp.: 78.0-78.5 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25 °C) δ/ppm : 8.13 (*pseudo* d, 1H, $J = 7.5$ Hz), 8.03 (*pseudo* d, 2H, $J = 7.6$ Hz), 7.84 (*pseudo* d, 1H, $J = 7.0$ Hz), 7.53-7.49 (m, 3H), 7.50-7.47 (m, 12H), 7.06 (*pseudo* d, 2H, $J = 7.0$ Hz), 6.86 (*pseudo* d, 2H, $J = 8.6$ Hz), 6.57 (s, 1H), 5.18 (s, 2H), 3.83 (s, 3H).

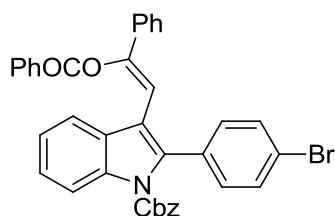
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 25 °C) δ/ppm : 163.8, 159.4, 151.5, 147.4, 138.2, 136.7, 135.0, 134.4, 133.3, 131.5, 130.2, 129.1, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 125.2, 124.7, 124.5, 123.0, 121.3, 116.1, 115.3, 113.2, 109.8, 68.7, 55.2.

MS (70eV, EI) m/z (%): 579 [M]⁺ (6), 430 (8) 105 (85), 91 (100), 77 (23).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3024 (w), 3004 (w), 2947 (w), 1733 (s), 1723 (s), 1238 (m), 1176 (m).

HRMS (MALDI) for $\text{C}_{28}\text{H}_{29}\text{NO}_5\text{Na}$, [M+Na]⁺ (602.1944) found: 602.1958.

**Synthesis of (*Z*)-benzyl 3-(2-(benzoyloxy)-2-phenylvinyl)-2-(4-bromophenyl)-
1H-indole-1-carboxylate (18c):**



Prepared according to **TP 2** from (E)-benzyl (4-bromobenzoyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**10c**) (161.7 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.0 μ L, 1.1 equiv), PBu₃ (90.0 μ L, 1.2 equiv) and NEt₃ (54.0 μ L, 1.3 equiv) in CH₂Cl₂ (0.6 mL) [reaction condition: RT for 1.5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **18c** as yellow solid (150.5 mg, 80%).

R_f 0.3 (ethyl acetate/hexanes: 1/10); mp.: 133.0–133.5 °C

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ /ppm: 8.16 (*pseudo* d, 1H, *J* = 8.0 Hz), 8.00 (*pseudo* d, 2H, *J* = 7.8 Hz), 7.83 (*pseudo* d, 1H, *J* = 7.8 Hz), 7.54–7.48 (m, 3H), 7.41–7.22 (m, 14H), 7.04 (*pseudo* d, 2H, *J* = 6.8 Hz), 6.52 (s, 1H), 5.17 (s, 2H).

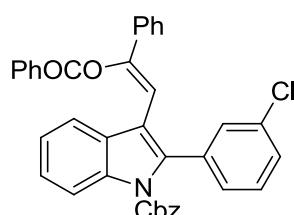
¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ /ppm: 163.7, 151.3, 148.1, 136.8, 136.6, 134.8, 134.0, 133.4, 131.9, 131.7, 130.9, 130.2, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 125.0, 124.8, 123.2, 122.4, 121.4, 116.9, 115.4, 109.1, 69.0.

MS (70eV, EI) *m/z* (%): 478 [M-149]⁺ (4), 203 (4), 105 (100), 91 (84), 77 (18).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3043 (w), 1738 (s), 1219 (m), 1057 (m), 581 (w).

HRMS (MALDI) for C₃₇H₂₆NO₅Na, [M+Na]⁺ (650.0943) found: 650.0958.

**Synthesis of (*Z*)-benzyl 3-(2-(benzoyloxy)-2-phenylvinyl)-2-(3-chlorophenyl)-
1H-indole-1-carboxylate (18d):**



Prepared according to **TP 2** from (E)-benzyl (3-chlorobenzoyl)(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**10d**)

(148.5 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.0 μ L, 1.1 equiv), PBu_3 (90.0 μ L, 1.2 equiv) and NEt_3 (54.0 μ L, 1.3 equiv) in CH_2Cl_2 (0.6 mL) [reaction condition: RT for 1.5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **18d** as yellow solid (138.2 mg, 79%).

R_f 0.3 (ethyl acetate/hexanes: 1/10); mp.: 154.0-154.5°C

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25 °C) δ/ppm : 8.16 (*pseudo d*, 1H, $J = 8.1$ Hz), 8.00 (*pseudo d*, 2H, $J = 7.8$ Hz), 7.83 (*pseudo d*, 1H, $J = 7.9$ Hz), 7.54-7.49 (m, 3H), 7.41-7.22 (m, 14H), 7.08-7.07 (m, 2H), 6.53 (s, 1H), 5.16 (s, 2H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 25 °C) δ/ppm : 163.6, 151.2, 148.2, 136.7, 136.1, 134.8, 134.7, 134.1, 133.6, 133.3, 130.1, 130.0, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 125.1, 124.8, 123.2, 121.4, 117.1, 115.4, 108.9, 68.9.

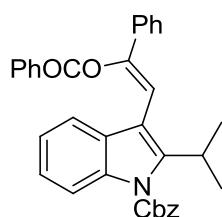
MS (70eV, EI) m/z (%): 585 [$\text{M}+2$]⁺ (2), 583 [M]⁺ (6), 433 (65), 105 (100), 91 (71), 77 (24).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3062 (w), 3033 (w), 2937 (w), 1733 (s), 1233 (m), 752 (m).

HRMS (MALDI) for $\text{C}_{37}\text{H}_{26}\text{ClNO}_4$, [$\text{M}+\text{Na}$]⁺ (606.1448) found: 606.1463.

CCDC: 876492

Synthesis of (*Z*)-benzyl 3-(2-(benzoyloxy)-2-phenylvinyl)-2-isopropyl-1*H*-indole-1-carboxylate (**18e**):



Prepared according to **TP 2** from (*E*)-benzyl isobutyryl(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (**10e**) (128.2 mg, 0.3 mmol), benzoyl chloride (**3a**) (38.0 μ L, 1.1 equiv), PBu_3 (90.0 μ L, 1.2 equiv) and NEt_3 (54.0 μ L, 1.3 equiv) in CH_2Cl_2 (0.6 mL) [reaction condition: RT for 1.5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **18e** as yellow solid (115.9 mg, 75%) and **18'e** as yellow oil (4.6 mg, 3%).

R_f 0.3 (ethyl acetate/hexanes: 1/10); mp.: 63.0-63.5°C

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25 °C) δ/ppm : 7.89 (*pseudo d*, 1H, $J = 8.3$ Hz), 7.84 (*pseudo d*, 2H, $J = 7.6$ Hz), 7.62 (*pseudo d*, 3H, $J = 7.3$ Hz), 7.49-7.44 (m, 3H), 7.41-7.35 (m, 6H), 7.28 (*pseudo t*, 2H, $J = 7.8$ Hz), 7.20 (*pseudo t*, 1H, $J = 7.4$ Hz),

7.14 (*pseudo t*, 1H, $J = 7.4$ Hz), 6.96 (s, 1H), 5.44 (s, 2H), 3.95 (septet, 2H, $J = 7.1$ Hz), 1.43 (d, 6H, $J = 7.1$ Hz).

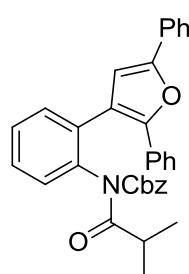
^{13}C -NMR (125 MHz, CDCl_3 , 25 °C) δ /ppm: 163.8, 151.8, 148.0, 144.5, 135.5, 135.1, 134.9, 133.1, 130.0, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 124.9, 123.8, 122.6, 120.2, 115.3, 113.3, 109.8, 68.9, 27.7, 21.9.

MS (70eV, EI) m/z (%): 514 [M-1]⁺ (6), 366 (4), 260 (2), 105 (100), 91 (76), 77 (28).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 3033 (w), 2956 (m), 2928 (w), 1733 (s), 1233 (m).

HRMS (MALDI) for $\text{C}_{34}\text{H}_{29}\text{NO}_4\text{Na}$, [M+Na]⁺ (538.1995) found: 538.2005.

benzyl (2-(2,5-diphenylfuran-3-yl)phenyl)(isobutyryl)carbamate (18'e):



R_f 0.2 (ethyl acetate/hexanes: 1/10)

^1H -NMR (400 MHz, CDCl_3 , 25 °C) δ /ppm: 7.63-7.57 (m, 3H), 7.52 (*pseudo t*, 1H, $J = 7.6$ Hz), 7.44-7.42 (m, 2H), 7.31-7.25 (m, 6H), 7.15 (*pseudo dt*, 1H, $J = 7.6, 1.0$ Hz), 7.09-6.99 (m, 4H), 6.75 (*pseudo d*, 2H, $J = 7.4$ Hz), 6.22 (s, 1H), 3.54-3.47 (m, 2H), 3.37 (d, 1H, $J = 12.5$ Hz), 0.95 (d, 2H, $J = 6.6$ Hz), 0.91 (d, 2H, $J = 6.6$ Hz).

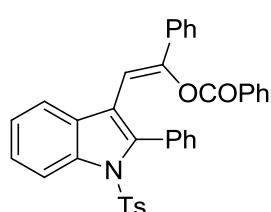
^{13}C -NMR (100 MHz, CDCl_3 , 25 °C) δ /ppm: 177.8, 177.7, 162.5, 149.4, 140.2, 134.2, 133.8, 133.7, 130.7, 129.9, 129.6, 129.1, 128.6, 128.3, 128.1, 127.8, 127.2, 125.0, 124.9, 123.8, 117.9, 116.4, 54.0, 46.3, 34.5, 18.9, 18.5.

MS (70eV, EI) m/z (%): 515 [M]⁺ (1), 424 (2), 220 (1), 105 (100), 77 (23).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 2966 (w), 2922 (w), 1749 (s), 1708 (m), 1251 (s).

HRMS (ESI) for $\text{C}_{34}\text{H}_{29}\text{NO}_4\text{Na}$, [M+Na]⁺ (538.1994) found: 538.1992.

Synthesis of (Z)-1-phenyl-2-(2-phenyl-1-tosyl-1*H*-indol-3-yl)vinyl benzoate (19a)



Prepared according to **TP** **2** from (*E*)-*N*-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)-*N*-tosylbenzamide (**11a**) (144.3 mg, 0.3 mmol), benzoyl chloride (**2a**) (39.0 μ L, 1.1 equiv), PBu₃ (90.0 μ L, 1.2 equiv) and NEt₃ (54.0 μ L, 1.3 equiv) in CH₂Cl₂ (0.6 mL) [reaction condition: RT for 8 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/30) yielded **19a** as white solid (123.6 mg, 80%).

R_f 0.3 (ethyl acetate/hexanes: 1/25); mp.: 189.4-190.1 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.23 (d, 1H, *J* = 7.7 Hz), 7.78-7.61 (m, 5H), 7.55-7.40 (m, 6H), 7.37-7.21 (m, 7H), 7.12 (d, 2H, *J* = 8.3 Hz), 6.81 (d, 2H, *J* = 8.2 Hz), 6.50 (s, 1H), 2.14 (s, 3H)

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 163.4, 148.5, 144.1, 139.5, 138.0, 134.6, 134.3, 133.2, 131.8, 131.4, 129.8, 129.5, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 128.2, 127.4, 126.5, 125.1, 124.8, 124.2, 121.6, 119.6, 116.8, 109.2, 21.5

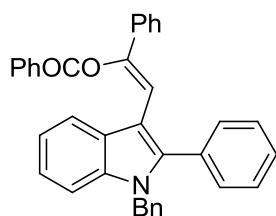
MS (70eV, EI) *m/z* (%): 769 [M]⁺ (17), 105 (100), 77 (19).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 2922 (w), 1730 (s), 1598 (w), 1443 (m), 1380 (m), 1174 (s).

HRMS (ESI) for C₃₆H₂₇NO₄SNa, [M+Na]⁺ (592.1558) found: 592.1555.

CCDC: 869630

Synthesis of (*Z*)-2-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-1-phenylvinyl benzoate (**20a**):



Prepared according to **TP** **2** from (*E*)-*N*-benzyl-*N*-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)benzamide (**12a**) (125.2 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.3 μ L, 1.1 equiv), PBu₃ (90.0 μ L, 1.2 equiv) and NEt₃ (54.2 μ L, 1.3 equiv) in CH₂Cl₂ (0.6 mL) [reaction condition: RT for 3.0 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/30) yielded **20a** as yellow solid (133.4 mg, 88%).

R_f 0.4 (ethyl acetate/hexanes: 1/10); mp.: 203.4-204.3 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.07 (*pseudo* d, 2H, *J* = 7.1 Hz),

7.99-7.93 (m, 1H), 7.57-7.45 (m, 5H), 7.43-7.17 (m, 11H), 7.11-7.02 (m, 3H), 6.97-6.90 (m, 2H), 6.88 (s, 1H), 5.28 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 163.9, 144.8, 140.5, 137.9, 137.3, 135.7, 133.1, 131.3, 130.8, 130.2, 129.5, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 127.1, 126.2, 125.8, 124.4, 122.2, 121.7, 120.2, 111.2, 110.4, 109.3, 47.9.

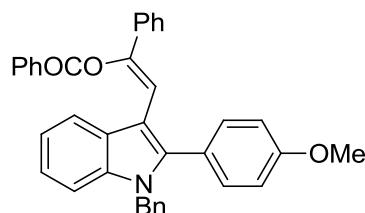
MS (70eV, EI) *m/z* (%): 505 [M]⁺ (48), 105 (100), 91 (42), 77 (33)

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 3026 (w), 2923 (w), 1727 (s), 1598 (w), 1241 (s), 1089 (s).

HRMS (ESI) for C₃₆H₂₇NO₂Na, [M+Na]⁺ (528.1939) found: 528.1935.

CCDC: 866846

Synthesis of (Z)-2-(1-benzyl-2-(4-methoxyphenyl)-1*H*-indol-3-yl)-1-phenylvinyl benzoate (20b):



Prepared according to **TP 2** from (*E*)-N-benzyl-4-methoxy-N-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)benzamide (**12b**) (134.2 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.3 μL, 1.1 equiv), PBu₃ (90.0 μL, 1.2 equiv) and NEt₃ (54.2 μL, 1.3 equiv) in CH₂Cl₂ (0.6 mL) [reaction condition: RT for 4.0 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/30) yielded **20b** as yellow solid (131.7 mg, 82%).

R_f 0.3 (ethyl acetate/hexanes: 1/10); mp.: 212.2-214.1 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 8.07 (*pseudo* d, 2H, *J* = 7.8 Hz), 8.00-7.90 (m, 1H), 7.58-7.46 (m, 3H), 7.45-7.15 (m, 10H), 7.09-6.99 (m, 3H), 6.97-6.84 (m, 5H), 5.25 (s, 2H), 3.80 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 164.0, 159.8, 144.6, 140.6, 138.1, 137.2, 135.8, 133.1, 132.1, 130.2, 129.6, 128.7, 128.6, 128.2, 127.8, 127.1, 126.3, 125.8, 124.4, 123.5, 122.1, 121.6, 120.2, 114.0, 111.4, 110.4, 109.0, 55.3, 47.8.

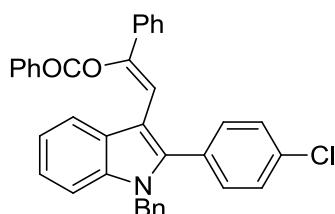
MS (70eV, EI) *m/z* (%): 535 [M]⁺ (26), 430 (60), 105 (100), 91 (57), 77 (38).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 3018 (w), 2996(w), 2930 (w), 1727 (s), 1609 (m), 1637 (s), 1086 (s).

HRMS (ESI) for C₃₇H₂₉NO₃Na, [M+Na]⁺ (558.2045) found: 558.2046.

CCDC: 866847

Synthesis of (*Z*)-2-(1-benzyl-2-(4-chlorophenyl)-1*H*-indol-3-yl)-1-phenylvinyl benzoate (20c**):**



Prepared according to **TP 2** from (*E*)-*N*-benzyl-4-chloro-*N*-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)benzamide (**12c**) (135.3 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.3 µL, 1.1 equiv), PBu₃ (90.0 µL, 1.2 equiv) and NEt₃ (54.2 µL, 1.3 equiv) in CH₂Cl₂ (0.6 mL) [reaction condition: RT for 2.0 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/30) yielded **20c** as yellow solid (144.0 mg, 89%).

R_f 0.5 (ethyl acetate/hexanes: 1/10); mp.: 139.3-139.9 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 8.03 (*pseudo* d, 2H, *J* = 7.4 Hz), 7.98-7.89 (m, 1H), 7.62-7.47 (m, 3H), 7.46-7.25 (m, 9H), 7.25-7.16 (m, 3H), 7.14-7.03 (m, 3H), 6.96-6.86 (m, 2H), 6.85 (s, 1H), 5.24 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 164.0, 145.5, 139.0, 137.9, 137.6, 135.7, 134.7, 133.3, 132.1, 130.3, 129.9, 129.5, 128.9, 128.8, 128.4, 128.2, 127.4, 126.4, 125.9, 124.6, 122.7, 121.8, 120.6, 110.8, 110.6, 109.9, 48.0.

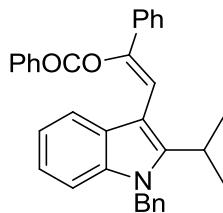
MS (70eV, EI) *m/z* (%): 539 [M]⁺ (42), 434 (88), 105 (68), 91 (100), 77 (18).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 3026 (w), 2923 (w), 1727 (s), 1598 (w), 1237 (s), 1082 (s), 1064 (m), 706 (m).

HRMS (ESI) for C₃₆H₂₆ClNO₂Na, [M+Na]⁺ (562.1550) found: 562.1529.

CCDC: 866849

Synthesis of (*Z*)-2-(1-benzyl-2-isopropyl-1*H*-indol-3-yl)-1-phenylvinyl benzoate (20d**):**



Prepared according to **TP** **2** from
(*E*)-*N*-benzyl-*N*-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)isobutyramide (**12d**)
(115.0 mg, 0.3 mmol), benzoyl chloride (**2a**) (38.3 μ L, 1.1 equiv), PBu₃ (90.0 μ L, 1.2 equiv) and NEt₃ (54.2 μ L, 1.3 equiv) in CH₂Cl₂ (0.6 mL) [reaction condition: RT for 24.0 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/40) yielded **20d** as yellow liquid (17.0 mg, 12%) and **20d'** as white powder (70.7 mg, 50%).

R_f 0.4 (ethyl acetate/hexanes: 1/10)

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.92 (*pseudo* d, 2H, *J* = 7.8 Hz), 7.77 (*pseudo* d, 1H, *J* = 7.6 Hz), 7.64 (*pseudo* d, 2H, *J* = 7.6 Hz), 7.46 (*pseudo* t, 1H, *J* = 7.4 Hz), 7.39 (*pseudo* t, 2H, *J* = 7.5 Hz), 7.35-7.26 (m, 3H), 7.25-7.10 (m, 4H), 7.10-6.98 (m, 3H), 6.82-6.74 (m, 2H), 5.34 (s, 2H), 3.22 (septet, 1H, *J* = 6.9 Hz), 1.36 (d, 6H, *J* = 7.1 Hz).

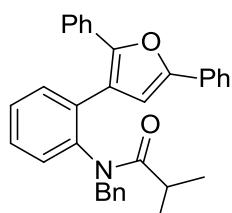
¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ /ppm: 164.0, 145.8, 144.0, 137.9, 136.4, 135.6, 132.9, 130.0, 129.5, 128.6, 128.1, 128.0, 127.1, 126.9, 125.6, 124.6, 124.6, 121.2, 120.6, 119.7, 110.9, 109.3, 106.0, 46.7, 29.7, 26.6, 22.0.

MS (70eV, EI) *m/z* (%): 471 [M]⁺ (66), 366 (86), 105 (63), 91 (100), 77 (26).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 2959 (m), 2923 (m), 1731 (m), 1642 (s), 1237 (m), 1086 (m).

HRMS (ESI) for C₃₃H₂₉NO₂Na, [M+Na]⁺ (494.2096) found: 494.2107.

N-benzyl-*N*-(2-(2,5-diphenylfuran-3-yl)phenyl)isobutyramide (20d'):



R_f 0.3 (ethyl acetate/hexanes: 1/10) mp.: 160.9-161.4 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.71 (*pseudo* d, 2H, *J* = 7.7 Hz), 7.59-7.45 (m, 3H), 7.41 (*pseudo* t, 2H, *J* = 7.6 Hz), 7.36-7.15 (m, 9H), 7.15-7.05 (m, 2H), 6.87 (*pseudo* d, 1H, *J* = 7.8 Hz), 6.55 (s, 1H), 5.45 (*pseudo* d, 1H, *J* = 14.4 Hz), 3.72 (d,

1H, $J = 14.4$ Hz), 2.52 (septet, 1H, $J = 6.6$ Hz), 1.08 (d, 3H, $J = 6.7$ Hz), 1.01 (d, 3H, $J = 6.5$ Hz).

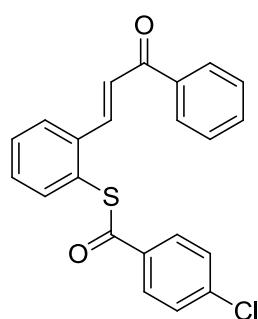
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 177.2, 152.8, 148.4, 140.6, 137.8, 132.7, 132.5, 130.6, 130.2, 130.1, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 127.8, 127.6, 127.1, 125.3, 123.9, 120.7, 108.9, 51.7, 31.6, 20.6, 19.1.

MS (70eV, EI) m/z (%): 471 [M]⁺ (68), 400 (22), 105 (70), 91 (100), 77 (24).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3063 (w), 3026 (w), 2967 (m), 2930 (m), 1650 (s), 1594 (m), 1403 (m), 1248 (m), 1215 (m).

HRMS (ESI) for $\text{C}_{33}\text{H}_{29}\text{NO}_2\text{Na}$, [M+Na]⁺ (494.2096) found: 494.2097.

**Synthesis of (*E*)-S-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)
4-chlorobenzothioate (21):**



R_f 0.3 (EA /hexanes: 1/20); mp.: 81.1-81.3 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.13 (d, 1H, $J = 16.0$ Hz), 7.97-7.94 (m, 4H), 7.90 (*pseudo* d, 1H, $J = 8.0$ Hz), 7.58 (*pseudo* d, 1H, $J = 8.0$ Hz), 7.55-7.45 (m, 6H), 7.42-7.38 (m, 2H).

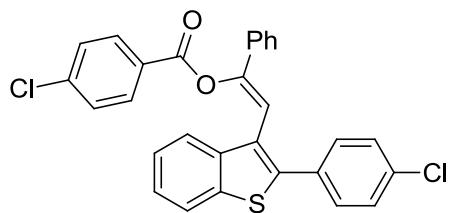
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 190.5, 187.8, 141.9, 140.3, 139.1, 137.8, 137.2, 134.6, 132.8, 130.6, 130.5, 129.1, 128.9, 128.6, 128.5, 128.4, 127.4, 124.9.

MS (70eV, EI) m/z (%): 239 [M-139]⁺ (7.7), 138 (100), 105 (80), 77 (23).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3055 (m), 1793 (m), 1672 (s), 1203 (m), 894 (m), 753 (w).

HRMS (ESI) for $\text{C}_{29}\text{H}_{18}\text{ClO}_2\text{SNa}$, [M+Na]⁺ (401.0379) found: 401.0377.

**Synthesis of 2-(2-(4-chlorophenyl)benzo[b]thiophen-3-yl)-1-phenylvinyl
4-chlorobenzoate (22a):**



Prepared according to **TP 3** from (*Z*)-S-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl) 4-chlorobenzothioate (**21**) (378.0 mg, 0.3 mmol), 4-chlorophenyl chloride (**2a**) (42 μ L, 1.1 equiv), PBu_3 (91.5 μ L, 1.2 equiv) and NEt_3 (54 μ L, 1.3 equiv) in THF (0.6 mL) [reaction condition: RT for 1.5 h]. Purification by flash-chromatography (Dichloromethane /hexanes: 1/2) yielded **22a** as white solid (141.2 mg, 94%).

R_f 0.3 (Dichloromethane /hexanes: 1/2); mp.: 179.0–180.0 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ /ppm: 7.92 (*pseudo d*, 1H, J = 8.0 Hz), 7.75 (*pseudo d*, 1H, J = 8.0 Hz), 7.71–7.69 (m, 4H), 7.60–7.57 (m, 2H), 7.42–7.38 (m, 6H), 7.33–7.28 (m, 2H) 6.91 (s, 1H).

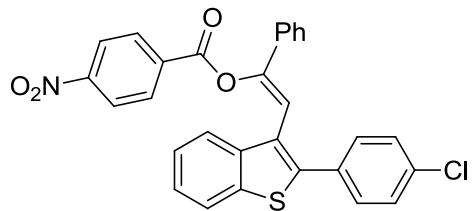
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ /ppm: 162.8, 148.7, 140.1, 139.9, 138.9, 138.7, 134.5, 134.4, 133.1, 131.3, 130.6, 129.1, 128.9, 128.8, 128.6, 127.1, 125.8, 124.9, 124.7, 124.4, 123.9, 122.1, 110.9.

MS (70eV, EI) m/z (%): 499 [$\text{M}-1$]⁺ (17), 139 (73), 221 (17), 105 (100), 77 (9).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 1730 (s), 1240 (s), 1085 (s), 750 (s).

HRMS (ESI) for $\text{C}_{29}\text{H}_{18}\text{ClO}_2\text{SNa}$, $[\text{M}+\text{Na}]^+$ (523.0302) found: 523.0316.

Synthesis of 2-(2-(4-chlorophenyl)benzo[b]thiophen-3-yl)-1-phenylvinyl 4-nitrobenzoate (**22b**):



Prepared according to **TP 3** from (*Z*)-S-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl) 4-nitrobenzothioate (**21**) (378.0 mg, 0.3 mmol), 4-nitrophenyl chloride (**2a**) (61.3 mg, 1.1 equiv), PBu_3 (91.5 μ L, 1.2 equiv) and NEt_3 (54 μ L, 1.3 equiv) in THF (0.6 mL) [reaction condition: RT for 1.5 h]. Purification by flash-chromatography (EA /hexanes: 1/20) yielded **22b** as white solid (104.3 mg, 68%).

R_f 0.3 (Dichloromethane /hexanes: 1/2); mp.: 190.3-191.3 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.09 (*pseudo d*, 2H, J = 8.6 Hz), 7.91-7.88 (m, 2H), 7.70 (*pseudo d*, 1H, J = 8.0 Hz), 7.67 (*pseudo d*, 2H, J = 8.4 Hz), 7.59-7.58 (m, 2H), 7.41-7.27 (m, 7H), 6.93 (s, 1H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 161.9, 150.6, 148.6, 140.4, 138.7, 138.7, 134.5, 134.0, 133.9, 132.9, 131.0, 130.5, 129.3, 128.9, 128.8, 125.4, 124.8, 124.7, 124.4, 123.7, 123.3, 122.2, 111.1.

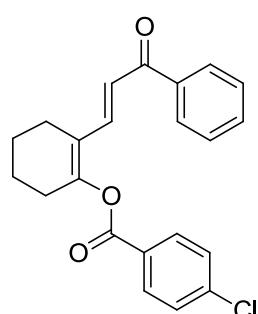
MS (70eV, EI) m/z (%): 511[M-1]⁺ (100), 361 (19), 255 (26), 150 (12).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3055 (m), 1734 (s), 1528 (s), 1244 (m), 1028 (s), 750 (s).

HRMS (ESI) for $\text{C}_{29}\text{H}_{18}\text{ClO}_2\text{SNa}$, [M+Na]⁺ (534.0543) found: 534.0538.

CCDC: 876151

Synthesis of (E)-2-(3-oxo-3-phenylprop-1-en-1-yl)cyclohex-1-en-1-yl 4-chlorobenzoate (24):



Prepared according to **TP 5** from 2-formylcyclohex-1-en-1-yl 4-chlorobenzoate (**38**) (2.6 g, 10 mmol), benzoyl chloride (1.2 mL, 1.05 equiv) and NEt_3 (1.7 mL, 1.2 equiv) in THF (20 mL). Purification by flash-chromatography (ethyl acetate/hexanes: 1/20) yielded **24** as yellow oil (0.73 g, 20%).

R_f 0.4 (ethyl acetate/hexanes: 1/20)

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.04 (d, 2H, J = 8.4 Hz), 7.89 (d, 2H, J = 7.1 Hz), 7.77 (d, 2H, J = 15.5 Hz), 7.54-7.38 (m, 5H), 6.92 (d, 1H, J = 15.5 Hz), 2.50-2.42 (m, 4H), 1.88-1.78 (m, 4H).

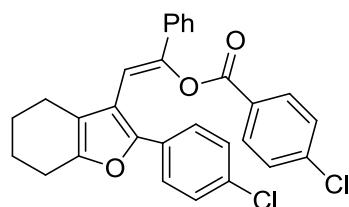
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 190.8, 163.6, 153.7, 140.2, 138.8, 138.2, 132.5, 131.4, 129.0, 128.4, 128.3, 127.5, 122.2, 121.1, 28.6, 24.3, 22.3, 21.7.

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3049 (w), 1730 (s), 1664 (m), 1590 (s), 1089 (s), 753(w).

HRMS (ESI) for $\text{C}_{22}\text{H}_{19}\text{ClO}_3\text{Na}$, [M+Na]⁺ (389.0920) found: 389.0929.

Synthesis of

(Z)-2-(2-(4-chlorophenyl)-4,5,6,7-tetrahydrobenzofuran-3-yl)-1-phenylvinyl 4-chlorobenzoate (26a):



Prepared according to **TP 1** from (E)-2-(3-oxo-3-phenylprop-1-en-1-yl)cyclohex-1-en-1-yl 4-chlorobenzoate (**24**) (132.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu_3 (150.0 μ L, 1.2 equiv) and NEt_3 (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 4 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **26a** as yellow oil (199.8 mg, 88%).

R_f 0.3 (ethyl acetate/hexanes: 1/25)

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 7.77 (d, 2H, J = 8.4 Hz), 7.59 (d, 2H, J = 7.1 Hz), 7.53 (d, 2H, J = 15.5 Hz), 7.42-7.33 (m, 5H), 7.34-7.28 (m, 2H), 6.72 (s, 1H), 2.62-2.54 (m, 2H), 2.50-2.42 (m, 2H), 1.84-1.74 (m, 2H), 1.74-1.65 (m, 2H).

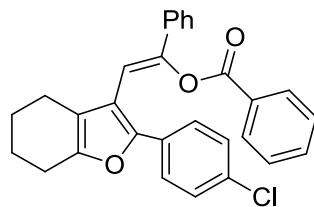
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 162.8, 150.8, 147.4, 147.3, 140.0, 134.8, 132.6, 131.3, 130.4, 128.8, 128.5, 127.5, 127.0, 124.7, 119.4, 115.4, 109.1, 23.2, 22.9, 22.8, 21.7.

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3062 (w), 1738 (s), 1675 (s), 1598 (w), 1236 (s), 1085 (s), 757 (w).

HRMS (ESI) for $\text{C}_{29}\text{H}_{23}\text{ClO}_3\text{Na}$, $[\text{M}+\text{Na}]^+$ (477.1233) found: 477.1243.

Synthesis of

(Z)-2-(2-(4-chlorophenyl)-4,5,6,7-tetrahydrobenzofuran-3-yl)-1-phenylvinyl benzoate (26b):



Prepared according to **TP 1** from (E)-2-(3-oxo-3-phenylprop-1-en-1-yl)cyclohex-1-en-1-yl 4-chlorobenzoate (**24**)

(132.0 mg, 0.5 mmol), benzoyl chloride (**2a**) (64.0 μ L, 1.1 equiv), PBu_3 (150.0 μ L, 1.2 equiv) and NEt_3 (91.0 μ L, 1.3 equiv) in THF (1.0 mL) [reaction condition: RT for 4 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **26b** as yellow oil (186.2 mg, 82%).

R_f 0.3 (ethyl acetate/hexanes: 1/25)

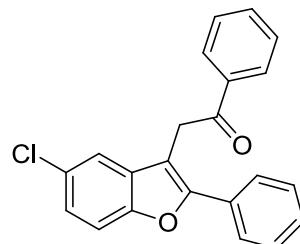
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 7.87 (d, 2H, $J = 8.4$ Hz), 7.63-7.52 (m, 5H), 7.44-7.32 (m, 5H), 7.54-7.38 (m, 5H), 7.32-7.27 (m, 2H), 6.71 (s, 1H), 2.60-2.52 (m, 2H), 2.52-2.43 (m, 2H), 1.82-1.72 (m, 2H), 1.72-1.63 (m, 2H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 163.7, 150.7, 147.6, 147.3, 135.0, 133.4, 132.5, 130.4, 130.0, 129.1, 128.7, 128.6, 128.5, 128.4, 127.0, 124.7, 119.5, 115.5, 109.0, 23.2, 23.0, 22.8, 21.8.

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3070 (w), 1738 (s), 1590 (m), 1244 (s), 1074 (s), 753 (m).

HRMS (ESI) for $\text{C}_{29}\text{H}_{23}\text{ClO}_3\text{Na}$, $[\text{M}+\text{Na}]^+$ (477.1233) found: 477.1243.

Synthesis of 2-(5-chloro-2-phenylbenzofuran-3-yl)-1-phenylethanone (**28b**):



Prepared according to **TP 4** from (*Z*)-2-(5-chloro-2-phenylbenzofuran-3-yl)-1-phenylvinyl benzoate (**4b**) (90.0 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28b** as white solid (60.9 mg, 88%).

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 133.1-133.3 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 7.98 (*pseudo* d, 2H, $J = 8.6$ Hz), 7.65 (*pseudo* d, 2H, $J = 7.1$ Hz), 7.59 (*pseudo* t, 1H, $J = 7.4$ Hz), 7.42-7.37 (m, 7H), 7.21 (*pseudo* dd, 1H, $J = 8.7, 1.9$ Hz), 4.48 (s, 2H).

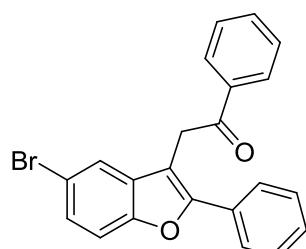
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 195.8, 154.4, 152.5, 136.2, 133.6, 131.5, 130.1, 129.0, 128.8, 128.7, 127.3, 124.6, 119.3, 112.2, 108.9, 34.6.

MS (70 eV, EI) m/z (%): 348 $[\text{M}+2]^+$ (12), 346 $[\text{M}]^+$ (35), 241 (18), 205(10), 105 (100), 77 (36).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3062 (w), 2892 (w), 1686 (s), 1587 (w), 1207 (m), 1067 (w), 687 (s).

HRMS (ESI) for $\text{C}_{22}\text{H}_{15}\text{ClO}_2\text{Na}$, $[\text{M}+\text{Na}]^+$ (369.0658) found: 369.0667.

Synthesis of 2-(5-bromo-2-phenylbenzofuran-3-yl)-1-phenylethanone (28c):



Prepared according to **TP 4** from (*Z*)-2-(5-bromo-2-phenylbenzofuran-3-yl)-1-phenylvinyl benzoate (**4c**) (98.8 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28c** as white solid (60.9 mg, 88%).

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 142.8- 143.4 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ /ppm: 8.03 (*pseudo d*, 2H, $J = 8.5$ Hz), 7.66 (*pseudo d*, 2H, $J = 8.4$ Hz), 7.60 (*pseudo t*, 1H, $J = 7.4$ Hz), 7.53 (*pseudo s*, 1H), 7.45-7.39 (m, 5H), 7.36 (s, 2H), 4.50 (s, 2H).

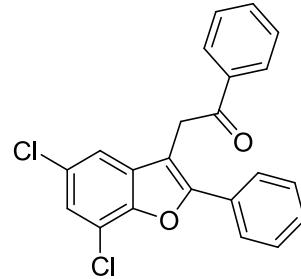
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ /ppm: 195.8, 154.3, 152.8, 136.2, 133.6, 132.2, 130.1, 130.1, 129.0, 128.8, 128.7, 128.3, 127.4, 122.4, 115.8, 112.7, 108.7, 34.7.

MS (70eV, EI) m/z (%): 392 $[\text{M}+2]^+$ (20), 390 $[\text{M}]^+$ (20), 287 (15), 205(15), 105 (100), 77 (36).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 2892 (w), 1682 (s), 1590 (m), 1211 (s), 1063 (m), 750(s).

HRMS (ESI) for $\text{C}_{22}\text{H}_{15}\text{BrO}_2\text{Na}$, $[\text{M}+\text{Na}]^+$ (413.0153) found: 413.0142.

Synthesis of 2-(5,7-dichloro-2-phenylbenzofuran-3-yl)-1-phenylethanone (28d):



Prepared according to **TP** **4** from (*Z*)-2-(5,7-dichloro-2-phenylbenzofuran-3-yl)-1-phenylvinyl benzoate (**4d**) (96.8 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28d** as white solid (64.6 mg, 85%).

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 177.0–177.6 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.00 (*pseudo d*, 2H, $J = 7.2$ Hz), 7.68 (*pseudo d*, 2H, $J = 7.2$ Hz), 7.61 (*pseudo t*, 1H, $J = 7.4$ Hz), 7.45–7.39 (m, 5H), 7.28 (*pseudo s*, 1H), 4.47 (s, 2H).

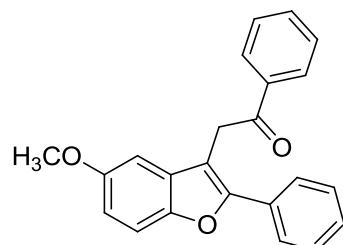
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 195.4, 155.3, 148.6, 136.1, 133.7, 132.5, 129.5, 129.4, 128.9, 128.3, 127.5, 124.5, 118.1, 117.3, 109.5, 34.7.

MS (70 eV, EI) m/z (%): 384 [$\text{M}+4$]⁺ (1), 382 [$\text{M}+2$]⁺ (5), 380 [M]⁺ (8), 275 (3), 105 (100), 77 (36).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3062 (w), 2892 (w), 1671 (s), 1576 (m), 1211 (s), 1067 (m), 683 (s).

HRMS (EI) for $\text{C}_{22}\text{H}_{14}\text{Cl}_2\text{O}_2\text{Na}$, [$\text{M}+\text{Na}$]⁺ (380.0371) found: 380.0371.

Synthesis of 2-(5-methoxy-2-phenylbenzofuran-3-yl)-1-phenylethanone (**28e**):



Prepared according to **TP** **4** from (*Z*)-2-(5-methoxy-2-phenylbenzofuran-3-yl)-1-phenylvinyl benzoate (**4e**) (89.2 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction

condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28e** as white solid (60.9 mg, 89%).

R_f 0.2 (ethyl acetate/hexanes: 1/15); mp.: 153.1-154.1 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.02 (*pseudo d*, 2H, J = 7.2 Hz), 7.68 (*pseudo d*, 2H, J = 7.1 Hz), 7.57 (*pseudo t*, 1H, J = 7.5 Hz), 7.45 (*pseudo q*, 4H, J = 7.7 Hz), 7.37-7.36 (m, 2H), 6.88-6.86 (m, 2H), 4.50 (s, 2H), 3.03 (s, 3H).

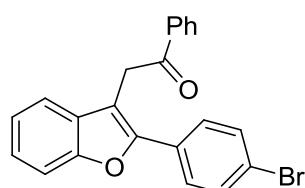
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 196.3, 156.0, 153.8, 149.1, 136.4, 133.4, 130.7, 128.8, 128.7, 128.6, 128.4, 127.3, 113.3, 111.6, 109.3, 102.2, 55.9, 35.0.

MS (70eV, EI) m/z (%): 342 [M]⁺ (88), 237(100), 105 (100), 77 (62).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 2826 (w), 1679 (s), 1598 (m), 1211 (s), 1059 (m).

HRMS (ESI) for C₂₃H₁₈O₃Na, [M+Na]⁺ (365.1154) found: 365.1162.

Synthesis of 2-(2-(4-bromophenyl)benzofuran-3-yl)-1-phenylethanone (**28f**):



Prepared according to **TP 4** from (Z)-2-(2-(4-bromophenyl)benzofuran-3-yl)-1-phenylvinyl benzoate (**4f**) (98.8 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28f** as white solid (71.8 mg, 92%).

R_f 0.3 (ethyl acetate/hexanes: 1/20); mp.: 130.7-131.4 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.01 (*pseudo d*, 2H, J = 7.6 Hz), 7.58-7.55 (m, 5H), 7.42-7.39 (m, 4H), 7.28 (*pseudo t*, 1H, J = 7.5 Hz), 7.19 (*pseudo t*, 1H, J = 7.5 Hz), 4.49 (s, 2H).

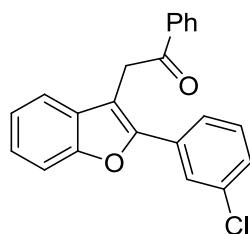
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 196.0, 154.0, 151.3, 136.3, 133.5, 131.9, 130.0, 129.5, 128.7, 128.6, 128.3, 124.8, 122.8, 122.7, 119.6, 111.2, 109.8, 34.6.

MS (70eV, EI) m/z (%): 392 [M+2]⁺ (22), 390 [M]⁺ (22), 284(10), 206 (26), 176 (18), 105 (100), 77 (50).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 2900 (w), 1675 (s), 1590 (m), 1207 (s), 1070 (m), 735(s).

HRMS (EI) for C₂₂H₁₅BrO₂, [M]⁺ (390.0255) found: 390.0249.

Synthesis of 2-(2-(3-chlorophenyl)benzofuran-3-yl)-1-phenylethanone (28g):



Prepared according to **TP 4** from (*Z*)-2-(2-(3-chlorophenyl)benzofuran-3-yl)-1-phenylvinyl benzoate (**4g**) (90.0 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28g** as white solid (65.7 mg, 95%).

R_f 0.3 (ethyl acetate/hexanes: 1/20); mp.: 126.2-126.8°C

1H -NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.04 (*pseudo* d, 2H, *J* = 7.8 Hz), 7.72 (*pseudo* s, 1H), 7.61 (*pseudo* t, 1H, *J* = 7.46 Hz), 7.55-7.54 (m, 1H), 7.47-7.42 (m, 4H), 7.33-7.29 (m, 3H), 7.22-7.20 (m, 1H), 4.54 (s, 2H).

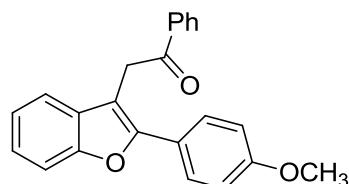
^{13}C -NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 196.0, 154.1, 151.4, 136.4, 134.8, 133.5, 132.4, 130.0, 129.9, 128.8, 128.7, 128.6, 128.4, 127.3, 127.2, 125.2, 125.0, 122.9, 119.8, 111.3, 110.3, 34.7.

MS (70eV, EI) *m/z* (%): 348 [M+2]⁺ (7), 346 [M]⁺ (18), 241(8), 206 (12), 105 (100), 77 (28).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 2892 (w), 1679 (s), 1587 (m), 1211 (s), 1056 (m), 683 (s).

HRMS (ESI) for C₂₂H₁₅ClO₂Na, [M+Na]⁺ (369.0658) found: 369.0668.

Synthesis of 2-(2-(4-methoxyphenyl)benzofuran-3-yl)-1-phenylethanone (28h):



Prepared according to **TP 4** from (*Z*)-2-(2-(4-methoxyphenyl)benzofuran-3-yl)-1-phenylvinyl benzoate (**4h**) (89.2 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction

condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **278h** as white solid (56.7 mg, 83%).

R_f 0.3 (ethyl acetate/hexanes: 1/20); mp.: 121.3-122.0°C

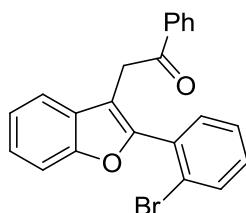
¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.02 (*pseudo* d, 2H, *J* = 7.8 Hz), 7.66 (*pseudo* d, 2H, *J* = 7.8 Hz), 7.57 (*pseudo* t, 1H, *J* = 7.46 Hz), 7.44-7.40 (m, 4H), 7.26-7.25 (m, 1H), 7.17-7.11 (m, 1H), 7.22-7.20 (m, 1H), 6.91 (*pseudo* d, 2H, *J* = 7.8 Hz), 4.52 (s, 2H), 3.88 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 196.5, 160.0, 153.9, 153.1, 136.5, 133.4, 130.2, 128.8, 128.7, 128.4, 124.1, 123.3, 122.6, 119.4, 114.3, 111.0, 107.9, 55.3, 35.0. MS (70eV, EI) *m/z* (%): 342 [M]⁺ (63), 265 (3), 249 (18), 237 (100), 105 (23), 77 (21).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3084 (w), 2922 (w), 1682 (s), 1590 (m), 1214 (m), 1089 (m).

HRMS (ESI) for C₂₃H₁₈O₃, [M]⁺ (343.1334) found: 343.1329.

Synthesis of 2-(2-(2-bromophenyl)benzofuran-3-yl)-1-phenylethanone (**28i**):



Prepared according to **TP 4** from (Z)-2-(2-(2-bromophenyl)benzofuran-3-yl)-1-phenylvinyl benzoate (**4i**) (98.8 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28i** as white solid (67.9 mg, 87%).

R_f 0.3 (ethyl acetate/hexanes: 1/20); mp.: 110.8-112.3°C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.90 (*pseudo* d, 2H, *J* = 7.2 Hz), 7.72 (*pseudo* d, 1H, *J* = 8.0 Hz), 7.51-7.48 (m, 4H), 7.40 (*pseudo* t, 3H, *J* = 7.8 Hz), 7.33 (*pseudo* t, 2H, *J* = 7.6 Hz), 7.25 (*pseudo* t, 1H, *J* = 7.4 Hz), 4.30 (s, 2H).

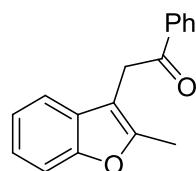
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 196.1, 154.5, 152.0, 136.3, 133.4, 132.7, 131.6, 131.0, 128.9, 128.6, 127.4, 124.7, 124.2, 122.8, 120.4, 111.8, 111.4, 35.0. MS (70eV, EI) *m/z* (%): 392 [M+2]⁺ (16), 390 [M]⁺ (18), 311(2), 206 (24), 105 (100), 77 (18).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 2915 (s), 2848 (m), 1690 (m), 1211 (w), 1026 (m),

739 (s).

HRMS (ESI) for $C_{22}H_{15}BrO_2Na$, $[M+Na]^+$ (413.0153) found: 413.0128.

Synthesis of 2-(2-methylbenzofuran-3-yl)-1-phenylethanone (28j):



Prepared according to **TP 4** from (*Z*)-2-(2-methylbenzofuran-3-yl)-1-phenylvinyl benzoate (**4j**) (70.8 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28j** as white solid (40.5 mg, 81%).

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 120.1-120.3 °C

1H -NMR (400 MHz, $CDCl_3$, 25 °C) δ /ppm: 8.04 (*pseudo* d, 2H, J = 7.2 Hz), 7.57 (*pseudo* t, 1H, J = 7.4 Hz), 7.47 (*pseudo* t, 2H, J = 7.6 Hz), 7.38-7.37 (m, 2H), 7.18 (*pseudo* quint, 2H, J = 6.9 Hz), 4.25 (s, 2H), 2.41 (s, 3H).

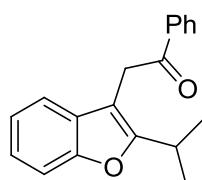
^{13}C -NMR (100 MHz, $CDCl_3$, 25 °C) δ /ppm: 196.3, 154.0, 152.4, 136.6, 133.2, 129.3, 128.7, 128.3, 128.3, 122.4, 118.8, 110.7, 108.0, 34.1, 12.3.

MS (70 eV, EI) m/z (%): 250 [$M]^+$ (18), 145 (62), 105 (100), 77 (68).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 2900 (w), 1675 (s), 1590 (w), 1211 (m), 1078 (w).

HRMS (ESI) for $C_{17}H_{14}O_2Na$, $[M+Na]^+$ (273.0891) found: 273.0866.

Synthesis of 2-(2-isopropylbenzofuran-3-yl)-1-phenylethanone (28k):



Prepared according to **TP 4** from (*Z*)-2-(2-isopropylbenzofuran-3-yl)-1-phenylvinyl benzoate (**4k**) (76.4 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28k** as white solid (48.9 mg, 88%).

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 100.8-101.3 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 8.07 (*pseudo* d, 2H, *J* = 7.6 Hz), 7.59 (*pseudo* t, 1H, *J* = 7.4 Hz), 7.50 (*pseudo* t, 2H, *J* = 7.6 Hz), 7.43-7.40 (m, 2H), 7.21 (*pseudo* quint, 2H, *J* = 7.7 Hz), 4.29 (s, 2H), 3.19 (heptet, 1H, *J* = 6.9 Hz), 1.32 (d, 6H, *J* = 7.0 Hz).

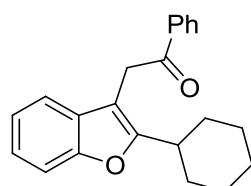
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 196.6, 160.4, 153.9, 136.6, 133.3, 129.4, 128.68, 128.4, 123.3, 122.3, 119.0, 110.8, 105.8, 34.0, 26.7, 21.1.

MS (70eV, EI) *m/z* (%): 278 [M]⁺ (22), 173 (57), 158 (15), 105 (100), 77 (55).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3062 (w), 2870 (w), 1679 (s), 1594 (w), 1214 (m), 1041 (w).

HRMS (ESI) for C₁₉H₁₈O₂Na, [M+Na]⁺ (301.1204) found: 301.1224.

Synthesis of 2-(2-cyclohexylbenzofuran-3-yl)-1-phenylethanone (28l):



Prepared according to **TP 4** from (*Z*)-2-(2-cyclohexylbenzofuran-3-yl)-1-phenylvinyl benzoate (**4l**) (84.4 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28l** as white solid (54.7 mg, 86%).

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 133.4-134.5 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 8.03 (*pseudo* d, 2H, *J* = 7.8 Hz), 7.57 (*pseudo* t, 1H, *J* = 7.1 Hz), 7.47 (*pseudo* t, 2H, *J* = 7.4 Hz), 7.36 (*pseudo* d, 2H, *J* = 7.6 Hz), 7.17 (*pseudo* quint, 2H, *J* = 7.6 Hz), 4.27 (s, 2H), 2.75 (*pseudo* t, 1H, *J* = 11.5 Hz), 1.78-1.68 (m, 7H), 1.31-1.25 (m, 3H)

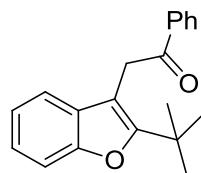
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 196.6, 159.9, 153.8, 136.6, 133.2, 129.3, 128.6, 128.3, 123.2, 122.2, 119.0, 110.8, 106.0, 36.6, 34.0, 31.2, 26.4, 25.8.

MS (70eV, EI) *m/z* (%): 318 [M]⁺ (30), 213 (30), 131 (30), 105(100), 77 (55).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 2915 (s), 2856 (m), 1679 (s), 1594 (w), 1211 (m), 1085 (w).

HRMS (ESI) for C₂₂H₂₂O₂Na, [M+Na]⁺ (341.1517) found: 341.1482.

Synthesis of 2-(2-(tert-butyl)benzofuran-3-yl)-1-phenylethanone (28m):



Prepared according to **TP 4** from (*Z*)-2-(2-(tert-butyl)benzofuran-3-yl)-1-phenylvinyl benzoate (**4m**) (79.2 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28m** as white solid (50.2 mg, 86%).

R_f 0.3 (ethyl acetate/hexanes: 1/20); mp.: 120.3–120.5 °C

1H -NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.08 (*pseudo* d, 2H, *J* = 7.6 Hz), 7.61 (*pseudo* t, 1H, *J* = 7.4 Hz), 7.51 (*pseudo* t, 2H, *J* = 7.6 Hz), 7.41 (*pseudo* d, 1H, *J* = 8.1 Hz), 7.25–7.24 (m, 1H), 7.20 (*pseudo* t, 1H, *J* = 7.6 Hz), 7.12 (*pseudo* t, 1H, *J* = 7.4 Hz), 4.51 (s, 2H), 1.4 (s, 9H)

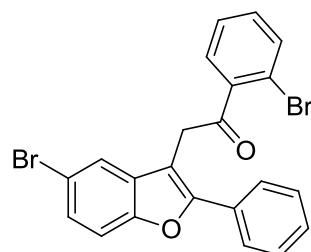
^{13}C -NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 196.5, 161.8, 153.0, 136.8, 133.3, 130.7, 128.7, 128.2, 123.3, 122.0, 118.4, 110.7, 105.6, 34.4, 29.5.

MS (70 eV, EI) *m/z* (%): 292 [M]⁺ (100), 187 (92), 145 (18), 105 (100), 77 (34).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3055 (w), 2959 (m), 2878 (w), 1690 (s), 1598 (w), 1207 (s), 1096 (m).

HRMS (ESI) for C₂₀H₂₀O₂Na, [M+Na]⁺ (315.1361) found: 315.1367.

Synthesis of 2-(5-bromo-2-phenylbenzofuran-3-yl)-1-(2-bromophenyl)ethanone (**28n**):



Prepared according to **TP 4** from (*Z*)-2-(5-bromo-2-phenylbenzofuran-3-yl)-1-(2-bromophenyl)vinyl benzoate (**4n**) (114.4 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28n** as white solid (75.8 mg, 81%).

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 91.1-92.0 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 7.67 (*pseudo d*, 2H, $J = 8.4$ Hz), 7.59 (*pseudo d*, 1H, $J = 6.6$ Hz), 7.53 (*pseudo s*, 1H), 7.40-7.34 (m, 5H), 7.29-7.25 (m, 3H,), 4.44 (s, 2H).

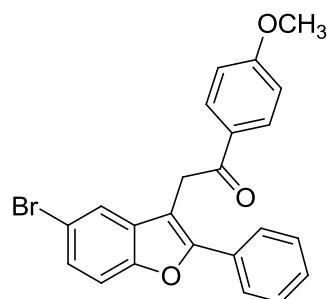
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 200.0, 154.6, 152.7, 141.1, 133.6, 131.8, 131.8, 129.8, 129.1, 128.5, 127.5, 127.4, 127.3, 122.4, 118.5, 115.8, 112.6, 107.8, 38.7.

MS (70eV, EI) m/z (%): 472 [$\text{M}+4$]⁺ (16), 470 [$\text{M}+2$]⁺ (38), 468 [M]⁺ (18), 285(43), 183 (100), 155 (30), 105 (12), 77 (21).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 2892 (w), 1694 (s), 1583 (w), 1258 (m), 1056 (w), 680 (m).

HRMS (ESI) for $\text{C}_{22}\text{H}_{14}\text{Br}_2\text{O}_2\text{Na}$, [$\text{M}+\text{Na}$]⁺ (490.9258) found: 490.9238.

Synthesis of 2-(5-bromo-2-phenylbenzofuran-3-yl)-1-(4-methoxyphenyl)ethanone (28o):



Prepared according to **TP 4** from (*Z*)-2-(5-bromo-2-phenylbenzofuran-3-yl)-1-(4-methoxyphenyl)vinyl benzoate (**4o**) (104.8 g, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28o** as white solid (69.7 mg, 83%).

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 136.9-137.4 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.02 (*pseudo d*, 2H, $J = 8.6$ Hz), 7.68 (*pseudo d*, 2H, $J = 7.5$ Hz), 7.56 (*pseudo s*, 1H), 7.41-7.37 (m, 5H), 6.93 (*pseudo d*, 2H, $J = 8.7$ Hz), 4.45 (s, 2H), 3.88 (s, 3H).

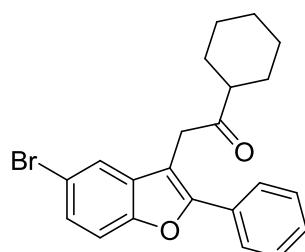
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 194.4, 163.9, 154.2, 152.9, 132.2, 130.7, 130.2, 129.3, 129.0, 128.8, 127.4, 127.3, 122.5, 115.8, 114.0, 112.6, 109.1, 55.5, 34.3.

MS (70eV, EI) m/z (%): 422 [$\text{M}+2$]⁺ (5), 420 [M]⁺ (5), 285(3), 208 (3), 135 (100), 77 (8).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3062 (w), 2907 (w), 2856 (w), 1671 (m), 1598 (s), 1218 (m), 1026 (w).

HRMS (ESI) for $\text{C}_{23}\text{H}_{17}\text{BrO}_3\text{Na}$, $[\text{M}+\text{Na}]^+$ (443.0259) found: 443.0257.

Synthesis of 2-(5-bromo-2-phenylbenzofuran-3-yl)-1-cyclohexylethanone (28p):



Prepared according to **TP 4** from (*Z*)-2-(5-bromo-2-phenylbenzofuran-3-yl)-1-cyclohexylvinyl benzoate (**4p**) (100.0 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28p** as white solid (71.3 mg, 90%).

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 144.7-145.1 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 7.66 (*pseudo d*, 2H, $J = 7.5$ Hz), 7.52 (s, 1H), 7.47 (*pseudo t*, 2H, $J = 7.5$ Hz), 7.39-7.36 (m, 3H), 3.90 (s, 2H), 2.56 (*pseudo t*, 1H, $J = 11.5$ Hz), 1.90 (*pseudo d*, 2H, $J = 13.4$ Hz), 1.81 (*pseudo d*, 2H, $J = 9.6$ Hz), 1.68 (*pseudo s*, 1H), 1.45 (*pseudo quartet*, 2H, $J = 11.7$ Hz), 1.27-1.20 (m, 3H)

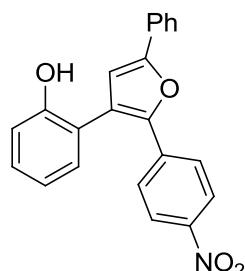
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 209.8, 154.2, 152.8, 132.1, 130.1, 129.0, 128.8, 127.4, 127.3, 122.1, 115.9, 112.7, 108.7, 50.3, 36.7, 28.7, 25.7, 25.6.

MS (70eV, EI) m/z (%): 398 $[\text{M}+2]^+$ (40), 396 $[\text{M}]^+$ (38), 285(36), 205 (25), 176 (22), 111 (42), 83 (100).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3055 (w), 2915 (m), 2848 (w), 1701 (s), 1587 (w), 1258 (w), 1063 (w), 683 (m).

HRMS (ESI) for $\text{C}_{22}\text{H}_{21}\text{BrO}_2\text{Na}$, $[\text{M}+2+\text{Na}]^+$ (419.0623) found: 421.0624.

Synthesis of 2-(2-(4-nitrophenyl)-5-phenylfuran-3-yl)phenol (28'q):



Prepared according to **TP 4** from (*Z*)-2-(2-(tert-butyl)benzofuran-3-yl)-1-phenylvinyl 4-nitrobenzoate (**4'q**) (88.0 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/15) yielded **28'q** as white solid (68.1 mg, 86%).

R_f 0.3 (ethyl acetate/hexanes: 1/15); mp.: 174.8–175.8 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.12 (*pseudo d*, 2H, $J = 8.8$ Hz) 7.78 (*pseudo d*, 2H, $J = 7.4$ Hz), 7.67 (*pseudo d*, 2H, $J = 8.8$ Hz), 7.47 (*pseudo t*, 2H, $J = 7.5$ Hz), 7.37 (*pseudo t*, 2H, $J = 7.5$ Hz), 7.30–7.28 (m, 1H), 7.03 (*pseudo d*, 2H, $J = 5.6$ Hz), 6.83 (s, 1H), 5.00 (s, 1H).

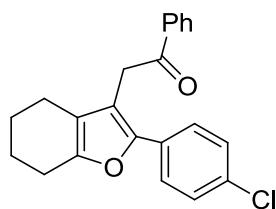
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 155.2, 152.9, 146.5, 146.3, 136.2, 130.5, 130.4, 129.4, 129.0, 124.9, 124.3, 124.0, 122.4, 121.3, 119.5, 116.1, 110.7

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3675 (m), 1502 (m), 1325 (s), 1225 (w), 1107 (m).

HRMS (ESI) for $\text{C}_{22}\text{H}_{15}\text{NO}_4\text{Na}$, $[\text{M}+\text{H}]^+$ (358.1079) found: 358.1062.

Synthesis of

2-(2-(4-chlorophenyl)-4,5,6,7-tetrahydrobenzofuran-3-yl)-1-phenylethanone (27):



Prepared according to **TP 6** from (*Z*)-2-(2-(4-chlorophenyl)-4,5,6,7-tetrahydrobenzofuran-3-yl)-1-phenylvinyl 4-chlorobenzoate (**26a**) (90.8 mg, 0.2 mmol) and NaOMe (13.0 mg, 1.2 equiv) in MeOH/THF (0.1/0.1 mL) [reaction condition: RT for 5 h]. Purification by flash-chromatography (ethyl acetate/hexanes: 1/25) yielded **27** as yellow oil (60.9 mg, 87%).

R_f 0.3 (ethyl acetate/hexanes: 1/25)

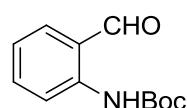
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 8.00 (d, 2H, J = 8.4 Hz), 7.59 (t, 1H, J = 8.4 Hz), 7.48 (t, 2H, J = 8.4 Hz), 7.41 (d, 2H, J = 8.4 Hz), 7.31 (d, 2H, J = 8.4 Hz), 7.42 (s, 2H), 2.68-2.62 (m, 2H), 2.32-2.25 (m, 2H), 1.90-1.81 (m, 2H), 1.79-1.69 (m, 2H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 196.7, 150.6, 147.6, 136.6, 133.3, 132.6, 130.1, 128.8, 128.7, 128.3, 126.9, 120.0, 114.2, 34.9, 23.2, 22.9, 22.8, 20.8.

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3062 (w), 1664 (m), 1587 (s), 1255 (w), 1096 (m), 757 (w).

HRMS (ESI) for $\text{C}_{22}\text{H}_{19}\text{ClO}_2\text{Na}$, $[\text{M}+\text{Na}]^+$ (373.0971) found: 373.0970.

Synthesis of *tert*-butyl (2-formylphenyl)carbamate (29):



R_f 0.5 (ethyl acetate/hexanes: 1/10); mp.: 85.0-85.5 °C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 10.39 (brs, 1H), 9.90 (s, 1H), 8.46 (d, 1H, J = 8.5 Hz), 7.62 (dd, 1H, J = 7.7, 1.6 Hz), 7.87 (dt, 1H, J = 8.0, 1.3 Hz), 7.53 (dt, 1H, J = 7.7, 1.3 Hz), 1.54 (s, 9H).

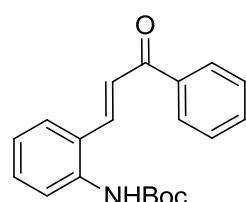
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 195.0, 152.9, 141.8, 136.1, 135.9, 121.5, 121.2, 118.3, 81.0, 28.3.

MS (70eV, EI) m/z (%): 221 [$\text{M}]^+$ (10), 121 (28), 93 (54), 57 (100).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3291 (s), 2976 (m), 2822 (m), 2746 (m), 1723 (s), 1666 (s), 1147 (m).

HRMS (EI) for $\text{C}_{12}\text{H}_{15}\text{NO}_3$, $[\text{M}]^+$ (221.1052) found: 221.1052.

Synthesis of (*E*)-*tert*-butyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (30):



R_f 0.4 (ethyl acetate/hexanes: 1/6); mp.: 98.0-98.5 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 8.06-7.98 (m, 3H), 7.86 (d, 1H, *J* = 8.1 Hz), 7.66 (d, 1H, *J* = 8.0 Hz), 7.62-7.59 (m, 1H), 7.55-7.50 (m, 3H), 7.87 (t, 1H, *J* = 7.8 Hz), 7.15 (t, 1H, *J* = 7.5 Hz), 6.60 (s, 1H), 1.53 (s, 9H).

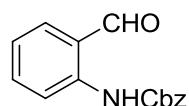
¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ/ppm: 189.8, 152.9, 139.2, 137.9, 137.2, 133.0, 131.0, 128.6, 128.5, 127.2, 126.4, 124.3, 123.9, 122.9, 81.0, 28.2.

MS (70eV, EI) *m/z* (%): 223 [M-100]⁺ (6), 206 (31), 117 (12), 105 (18), 77 (24), 57 (100).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3253 (s), 3062 (w), 2976 (m), 1723 (s), 1652 (m), 1600 (m), 1152 (m).

HRMS (MALDI) for C₂₀H₂₁NO₃Na, [M+Na]⁺ (346.1420) found: 346.1431.

Synthesis of benzyl (2-formylphenyl)carbamate (31):



R_f 0.3 (ethyl acetate/hexanes: 1/10); mp.: 66.0-66.5 °C

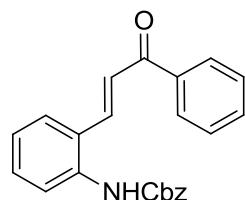
¹H-NMR (500 MHz, CDCl₃, 25 °C) δ/ppm: 10.67 (brs, 1H), 9.86 (s, 1H), 8.46 (d, 1H, *J* = 8.5 Hz), 7.60 (dd, 1H, *J* = 7.7, 1.5 Hz), 7.56 (dt, 1H, *J* = 8.5, 1.5 Hz), 7.43-7.41 (m, 2H), 7.39-7.35 (m, 2H), 7.34-7.31 (m, 1H), 7.14 (t, 1H, *J* = 7.5 Hz), 5.22 (s, 2H).

¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ/ppm: 194.9, 153.4, 141.0, 135.9, 135.8, 135.7, 128.5, 128.2, 128.1, 121.9, 121.3, 118.2, 67.0.

MS (70eV, EI) *m/z* (%): 255 [M]⁺ (6), 164 (3), 120 (7), 91 (100).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3272 (w), 3033 (w), 2956 (w), 2870 (w), 2765 (w), 1723 (s), 1666 (s), 12909 (m).

Synthesis of (*E*)-benzyl (2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (32):



R_f 0.3 (ethyl acetate/hexanes: 1/6); mp.: 142.0-142.5 °C

¹H-NMR (500 MHz, CDCl₃, 25 °C) δ/ppm: 8.01 (d, 2H, *J* = 8.0 Hz), 7.97 (d, 1H, *J* = 15.5 Hz), 7.86 (brs, 1H), 7.65 (d, 1H, *J* = 7.8 Hz), 7.60-7.57 (m, 1H), 7.51-7.48 (m,

3H), 7.43-7.32 (m, 6H), 7.19 (t, 1H, $J = 7.6$ Hz), 6.87 (brs, 1H), 5.22 (s, 2H).

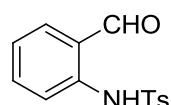
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 25 °C) δ/ppm : 189.8, 153.7, 138.9, 137.9, 136.6, 135.8, 133.0, 132.1, 132.0, 131.1, 128.7, 128.6, 128.5, 128.4, 127.4, 124.9, 124.5, 123.1, 67.4.

MS (70eV, EI) m/z (%): 222 [$\text{M}-135$]⁺ (6), 207 (12), 105 (34), 91 (100), 77 (22).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3291 (s), 3062 (s), 2985 (w), 3033 (w), 2947 (w), 1700 (s), 1661 (s), 1600 (m), 1238 (m).

HRMS (MALDI) for $\text{C}_{23}\text{H}_{19}\text{NO}_3\text{Na}$, $[\text{M}+\text{Na}]^+$ (380.1263) found: 380.1271.

Synthesis of N-(2-formylphenyl)-4-methylbenzenesulfonamide (33)



R_f 0.3 (ethyl acetate/hexanes: 1/8) ; mp.: 134.8-135.7°C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 10.80 (s, 1H), 9.82 (s, 1H), 7.76(d, 2H, $J = 8.2$ Hz), 7.67 (d, 1H, $J = 8.4$ Hz), 7.59 (pseudo d, 1H, $J = 9.1, 0.7$ Hz), 7.54-7.46 (m, 1H), 7.23 (d, 2H, $J = 8.2$), 7.16 (t, 1H, $J = 7.5$ Hz), 2.35 (s, 3H)

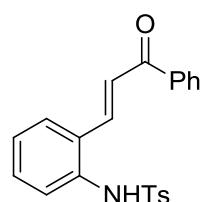
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ/ppm : 195.0, 144.1, 139.7, 136.2, 136.1, 135.7, 129.7, 127.1, 122.9, 121.7, 117.5, 21.4

S (70eV, EI) m/z (%): 275 [$\text{M}]^+$ (18), 120 (100), 90 (58).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3129(m), 3062 (w), 2915 (w), 2856 (w), 2752 (w), 1668 (s), 1336 (s), 1155 (m).

HRMS (ESI) for $\text{C}_{14}\text{H}_{13}\text{NO}_3\text{SNa}$, $[\text{M}+\text{Na}]^+$ (298.0514) found: 298.0508.

Synthesis of (E)-4-methyl-N-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl) Benzenesulfonamide (34)



R_f 0.3 (ethyl acetate/hexanes: 1/5) ; mp.: 176.7-177.1°C

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ/ppm : 7.95 (d, 2H, $J = 7.2$ Hz), 7.71 (d, 1H, $J =$

15.5 Hz), 7.63–7.45 (m, 7H), 7.39 (t, 1H, J = 7.1 Hz), 7.34–7.24 (m, 2H), 7.20 (d, 1H, J = 15.5 Hz), 7.11 (d, 2H, J = 8.1 Hz), 2.14 (s, 3H)

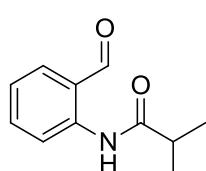
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ /ppm: 190.0, 143.9, 139.1, 137.6, 135.9, 135.3, 133.1, 131.1, 131.0, 129.7, 128.7, 128.6, 127.7, 127.3, 127.2, 124.3, 21.3

MS (70eV, EI) m/z (%): 222 [M-155]⁺ (13), 117 (13), 105 (100), 77 (30).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm⁻¹): 3180(s), 3047 (w), 2915 (s), 1653 (m), 1590 (s), 1340 (s), 1152 (s)

HRMS (ESI) for $\text{C}_{22}\text{H}_{19}\text{NO}_3\text{SNa}$, [M+Na]⁺ (400.0983) found: 400.0964.

Synthesis of *N*-(2-formylphenyl)isobutyramide :



A 25-mL Schlenk flask, equipped with a magnetic stirring bar, was charged with a solution of 2-amino benzyl alcohol (1231.5 mg, 10 mmol) in THF (33 mL). Benzoyl chloride (1.2 mL, 1.1 equiv) and triethylamine (1.7 mL, 1.2 equiv) was added, and the reaction mixture was stirred for 12 h at room temperature. Then the crude product was dissolved in ethyl acetate and washed with sat. NaHCO_3 (aq), and the organic layer was dried by MgSO_4 and then evaporated. Without purification, the crude product was dissolved in CH_2Cl_2 (25 mL) and then PCC (2587.0 mg, 1.2 equiv) was added. The reaction mixture was stirred for 4 h under room temperature and then filtered through Celite 545 and silica gel followed by washing with CH_2Cl_2 . The solvent was removed by evaporation and purification by flash chromatography (ethyl acetate/hexanes: 1/10) yielded *N*-(2-formylphenyl)isobutyramide as yellow liquid (1158 mg, 58%).

R_f 0.4 (ethyl acetate/hexanes:1/10)

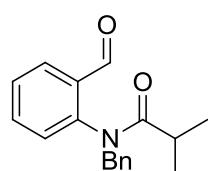
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ /ppm: 11.20 (s, 1H), 9.92 (s, 1H), 8.77 (pseudo d, 1H, J = 8.4 Hz), 7.67 (pseudo dd, 1H, J = 7.6 Hz, J = 1.4 Hz), 7.60 (pseudo t, 1H, J = 8.1 Hz), 7.21(pseudo t, 1H, J = 7.5 Hz), 2.64 (septet, 1H, J = 7.0 Hz), 1.30 (d, 6H, J = 7.0).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ /ppm: 195.4, 176.6, 141.1, 136.0, 135.9, 122.6, 121.6, 119.7, 37.2, 19.3.

MS (70eV, EI) m/z (%): 192 [M+1]⁺ (65), 121 (22), 93 (38), 71 (100).

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 2959 (m), 2915 (m), 1650 (s), 1609 (m), 1285 (m), 1189 (m).

Synthesis of *N*-benzyl-*N*-(2-formylphenyl)isobutyramide (35d):



A 25-mL Schlenk flask, equipped with a magnetic stirring bar, was charged with a solution of *N*-(2-formylphenyl)isobutyramide (955.0 mg, 5 mmol) and sodium hydride (240.0 mg, 1.2 equiv) in DMF (10 mL). After stirred for 30 minutes at 0 °C, benzyl bromide (374.0 µL, 1.2 equiv) was added, and the reaction mixture was stirred for 12 h under room temperature. Then the crude product was dissolved in ethyl acetate and washed with water. The organic layer was dried by MgSO₄ and then evaporated. Purification by flash chromatography (ethyl acetate/hexanes: 1/8) yielded **31d** as yellow liquid (431.9 mg, 31%).

R_f 0.2 (ethyl acetate/hexanes: 1/10)

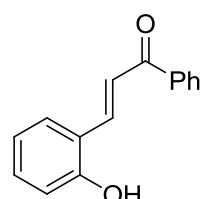
¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 9.72 (s, 1H), 7.92 (*pseudo* dd, 1H, J = 7.7 Hz, J = 1.5 Hz), 7.61 (*pseudo* td, 1H, J = 7.6 Hz, J = 1.6 Hz), 7.50 (*pseudo* t, 1H, J = 7.5 Hz), 7.28-7.19 (m, 3H), 7.18-7.10 (m, 2H), 7.06 (*pseudo* d, 1H, J = 7.9 Hz), 4.99 (d, 1H, J = 14.0 Hz), 4.84 (d, 1H, J = 14.0 Hz), 2.29 (septet, 1H, J = 6.7 Hz), 1.10-0.97 (m, 6H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 189.0, 176.8, 143.9, 136.0, 135.2, 133.1, 130.0, 129.6, 129.3, 128.7, 128.4, 127.8, 53.5, 31.8, 19.8, 19.0.

MS (70eV, EI) *m/z* (%): 282 [M]⁺ (3), 210 (100), 91 (28), 71 (4)

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3026 (w), 2967 (m) 2841 (m), 1690 (s), 1653 (s), 1392 (s), 1244 (s).

Synthesis of (*E*)-3-(2-hydroxyphenyl)-1-phenylprop-2-en-1-one (37a):



The compound **37a** was obtained as yellow solid according to the reported

procedure⁵.

mp.: 154.0-154.3 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 8.19 (*pseudo d*, 1H, *J* = 15.8 Hz), 8.05 (*pseudo d*, 2H, *J* = 7.8 Hz), 7.72 (d, 1H, *J* = 15.8 Hz), 7.60 (*pseudo t*, 2H, *J* = 7.8 Hz), 7.51 (*pseudo t*, 2H, *J* = 7.4 Hz), 7.32-7.24 (m, 1H), 7.00-6.90 (m, 2H), 6.63 (s, 1H).

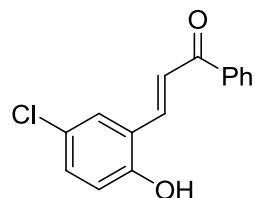
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 191.8, 155.6, 140.8, 138.3, 132.7, 131.8, 129.5, 128.6, 128.6, 122.9, 122.3, 121.0, 116.6.

MS (70eV, EI) *m/z* (%): 224 [M]⁺ (75), 207 (100), 147 (60), 105 (46).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3188 (brs), 2944 (w), 1639 (s), 1561 (s), 1230 (s).

HRMS (EI) for C₁₅H₁₃O₂, [M+H]⁺ (225.0916) found: 225.0921.

Synthesis of (*E*)-3-(5-chloro-2-hydroxyphenyl)-1-phenylprop-2-en-1-one (37b):



The compound **37b** was obtained as yellow solid according to the reported procedure⁵.

mp.: 174.2-174.4 °C

¹H-NMR (400 MHz, *d*⁶-DMSO, 25 °C) δ/ppm: 10.55 (s, 1H), 8.15 (*pseudo d*, 2H, *J* = 7.2 Hz), 8.06-7.90 (m, 3H), 7.66 (*pseudo t*, 1H, *J* = 7.2 Hz), 7.57 (*pseudo t*, 2H, *J* = 7.6 Hz), 7.30 (dd, 1H, *J* = 8.8, 2.4 Hz), 6.95 (*pseudo d*, 1H, *J* = 8.8 Hz).

¹³C-NMR (100 MHz, *d*⁶-DMSO, 25 °C) δ/ppm: 189.2, 155.9, 137.7, 137.6, 133.0, 131.3, 128.7, 128.5, 127.5, 123.2, 123.1, 122.1, 117.8.

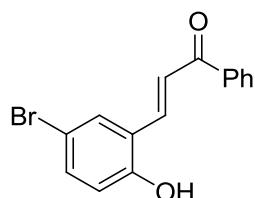
MS (70eV, EI) *m/z* (%): 260 [M+2]⁺ (29), 258 [M]⁺ (83), 243 (30), 241 (95), 183 (17), 181 (55), 154 (8), 152 (24), 105 (100).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3143 (brs), 2937 (w), 1635 (s), 1565 (s), 1270 (s).

HRMS (EI) for C₁₅H₁₂O₂Cl, [M+H]⁺ (259.0526) found: 259.0528.

Synthesis of (*E*)-3-(5-bromo-2-hydroxyphenyl)-1-phenylprop-2-en-1-one (37c):

⁵ Liao, Q.; Fu, H.; Wang, C.; Yao, J. *Angew. Chem. Int. Ed.* **2011**, *50*, 4942.



The compound **37c** was obtained as yellow solid according to the reported procedure⁵.

mp.: 163.7-164.2 °C

¹H-NMR (400 MHz, d^6 -DMSO, 25 °C) δ /ppm: 10.57 (s, 1H), 8.20-8.09 (m, 3H), 8.05-7.90 (m, 2H), 7.65 (*pseudo t*, 1H, J = 7.2 Hz), 7.55 (*pseudo t*, 2H, J = 7.2 Hz), 7.40 (dd, 1H, J = 8.8, 2.4 Hz), 6.90 (*pseudo d*, 1H, J = 8.8 Hz).

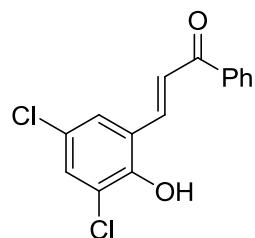
¹³C-NMR (100 MHz, d^6 -DMSO, 25 °C) δ /ppm: 189.2, 156.4, 137.7, 137.6, 134.2, 133.0, 130.4, 128.7, 128.5, 123.7, 122.0, 118.3, 110.9.

MS (70eV, EI) m/z (%): 304 [M+2]⁺ (85), 302 [M]⁺ (85), 287 (82), 285 (95), 227 (50), 225 (53), 198 (20), 196 (20), 118 (43), 105 (100).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3099 (brs), 2944 (w), 1639 (s), 1561 (s), 1270 (s).

HRMS (EI) for C₁₅H₁₂O₂Br, [M+H]⁺ (303.0021) found: 303.0023.

Synthesis of (*E*)-3-(3,5-dichloro-2-hydroxyphenyl)-1-phenylprop-2-en-1-one (37d):



The compound **37d** was obtained as yellow solid according to the reported procedure⁵.

mp.: 182.2-182.4 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 8.03 (*pseudo d*, 2H, J = 7.6 Hz), 7.97 (d, 1H, J = 15.8 Hz), 7.70 (d, 1H, J = 15.8 Hz), 7.60 (*pseudo t*, 1H, J = 7.6 Hz), 7.55-7.48 (m, 3H), 7.38 (*pseudo d*, 1H, J = 2.4 Hz), 6.18 (s, 1H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ /ppm: 190.3, 149.5, 137.9, 137.7, 133.0, 129.7, 128.7, 128.6, 127.8, 125.7, 125.1, 124.4, 121.5.

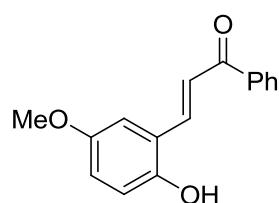
MS (70eV, EI) m/z (%): 296 [M+4]⁺ (6), 294 [M+2]⁺ (38), 292 [M]⁺ (58), 279 (5), 277

(30), 275 (45), 219 (4), 217 (23), 215 (35), 188 (6), 186 (9), 105 (100).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3276 (brs), 2900 (w), 1657 (s), 1564 (s), 1211 (s).

HRMS (EI) for $\mathbf{C}_{15}\mathbf{H}_{10}\mathbf{O}_2\mathbf{Cl}_2$, $[\mathbf{M}]^+$ (292.0058) found: 292.0054.

Synthesis of (*E*)-3-(2-hydroxy-5-methoxyphenyl)-1-phenylprop-2-en-1-one (37e):



The compound **37e** was obtained as yellow solid according to the reported procedure⁵.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C) δ /ppm: 8.17 (d, 1H, $J = 12.6$ Hz), 8.02 (*pseudo* d, 2H, $J = 6.8$ Hz), 7.66 (d, 1H, $J = 12.6$ Hz), 7.58 (*pseudo* d, 1H, $J = 6.0$ Hz), 7.49 (*pseudo* d, 2H, $J = 6.0$ Hz), 7.08 (*pseudo* d, 1H, $J = 2.0$ Hz), 6.90-6.82 (m, 2H), 3.79 (s, 3H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C) δ /ppm: 192.1, 153.4, 150.5, 141.2, 138.2, 132.8, 128.7, 128.6, 122.7, 122.5, 118.4, 117.7, 113.0, 55.9.

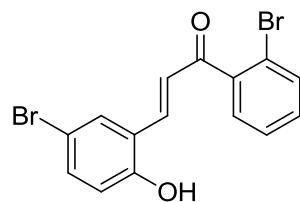
MS (70eV, EI) m/z (%): 254 $[\mathbf{M}]^+$ (100), 237 (88), 177 (27), 149 (29), 105 (68).

IR (CH_2Cl_2) $\tilde{\nu}$ (cm^{-1}): 3254 (brs), 2930 (w), 1650 (m), 1583 (s), 1207 (s).

HRMS (EI) for $\mathbf{C}_{16}\mathbf{H}_{14}\mathbf{O}_3$, $[\mathbf{M}]^+$ (254.0943) found: 254.0943.

Synthesis of

(*E*)-3-(5-bromo-2-hydroxyphenyl)-1-(2-bromophenyl)prop-2-en-1-one (37n):



The compound **37n** was obtained as yellow solid according to the reported procedure⁵.

mp.: 156.8-157.3 °C

$^1\text{H-NMR}$ (400 MHz, MeOD , 25 °C) δ /ppm: 7.64-7.61 (m, 3H), 7.41-7.33 (m, 4H),

7.17 (d, 1H, $J = 16.2$ Hz), 6.78 (*pseudo* d, 1H, $J = 8.7$ Hz).

$^{13}\text{C-NMR}$ (100 MHz, MeOD, 25 °C) δ/ppm : 197.3, 157.5, 143.0, 141.9, 135.4, 134.0, 132.2, 131.8, 129.7, 128.2, 127.3, 124.2, 119.7, 118.6, 112.1.

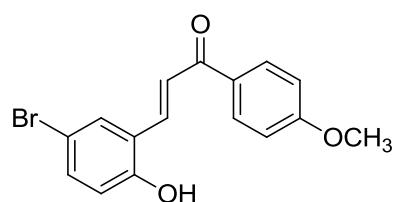
MS (70eV, EI) m/z (%): 384 [M+2]⁺ (20), 382 [M]⁺ (30), 301 (10), 227 (35), 183 (100), 155 (55), 118 (100), 89 (83), 76 (32).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3276 (m), 2922 (m), 1646 (s), 1568 (s), 1115 (s), 676(w).

HRMS (ESI) for **C₁₅H₁₀Br₂O₂Na, [M+Na]⁺** (380.9126) found: 380.9128.

Synthesis of

(E)-3-(5-bromo-2-hydroxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (37o):



The compound **37o** was obtained as yellow solid according to the reported procedure⁵.

mp.: 177.0-177.3 °C

$^1\text{H-NMR}$ (400 MHz, CDCl₃, 25 °C) δ/ppm : 8.08-8.05 (m, 3H), 7.73 (*pseudo* s, 1H), 7.63 (*pseudo* d, 1H, $J = 15.8$ Hz), 7.37 (*pseudo* d, 1H, $J = 8.5$ Hz), 6.99 (*pseudo* d, 2H, $J = 8.8$ Hz), 6.83 (*pseudo* d, 1H, $J = 8.5$ Hz), 6.55 (s, 1H), 3.90 (s, 3H).

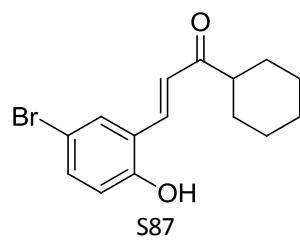
$^{13}\text{C-NMR}$ (100 MHz, MeOD, 25 °C) δ/ppm : 192.1, 166.2, 158.7, 140.7, 136.0, 133.2, 133.0, 126.3, 124.5, 119.8, 115.9, 113.4, 56.9.

MS (70eV, EI) m/z (%): 334 [M+2]⁺ (20), 332 [M]⁺ (5), 315 (18), 135 (100), 108 (30), 77 (20).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3217 (w), 2952 (w), 1624 (s), 1587 (s), 1126 (w).

HRMS (ESI) for **C₁₆H₁₃BrO₃Na, [M+Na]⁺** (354.9941) found: 354.9941.

Synthesis of (E)-3-(5-bromo-2-hydroxyphenyl)-1-cyclohexylprop-2-en-1-one (37p):



The compound **37p** was obtained as yellow solid according to the reported procedure⁵.

mp.: 175.0-175.7 °C

¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 8.03 (*pseudo* s, 1H), 7.93 (d, 1H, *J* = 16.2 Hz), 7.62 (d, 1H, *J* = 2.3 Hz), 7.34 (*pseudo* dd, 1H, *J* = 8.6, 2.3 Hz), 6.99 (d, 1H, *J* = 16.2 Hz), 6.84 (*pseudo* d, 1H, *J* = 8.7 Hz), 2.72 (*pseudo* t, 1H, *J* = 11.1 Hz), 1.91-1.71 (m, 6H), 1.35-1.14 (m, 5H).

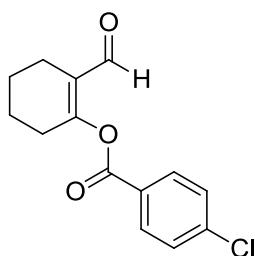
¹³C-NMR (100 MHz, MeOD, 25 °C) δ/ppm: 207.1, 158.5, 139.2, 135.9, 132.8, 127.2, 125.8, 119.7, 113.3, 51.1, 30.8, 27.8, 27.6.

MS (70eV, EI) *m/z* (%): 310 [M+2]⁺ (8), 308 [M]⁺ (8), 227 (100), 224 (62), 118 (70), 55 (23).

IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3276 (m), 2929 (s), 1646 (w), 1568 (m), 1111 (w).

HRMS (EI) for C₁₅H₁₇BrO₂, [M]⁺ (308.0412) found: 308.0409.

Synthesis of 2-formylcyclohex-1-en-1-yl 4-chlorobenzoate (38):



The compound **38** was obtained as white solid (224.5 g, 85%) according to the reported procedure⁴.

R_f 0.3 (ethyl acetate/hexanes: 1/20); mp.: 132.5-133.1 °C

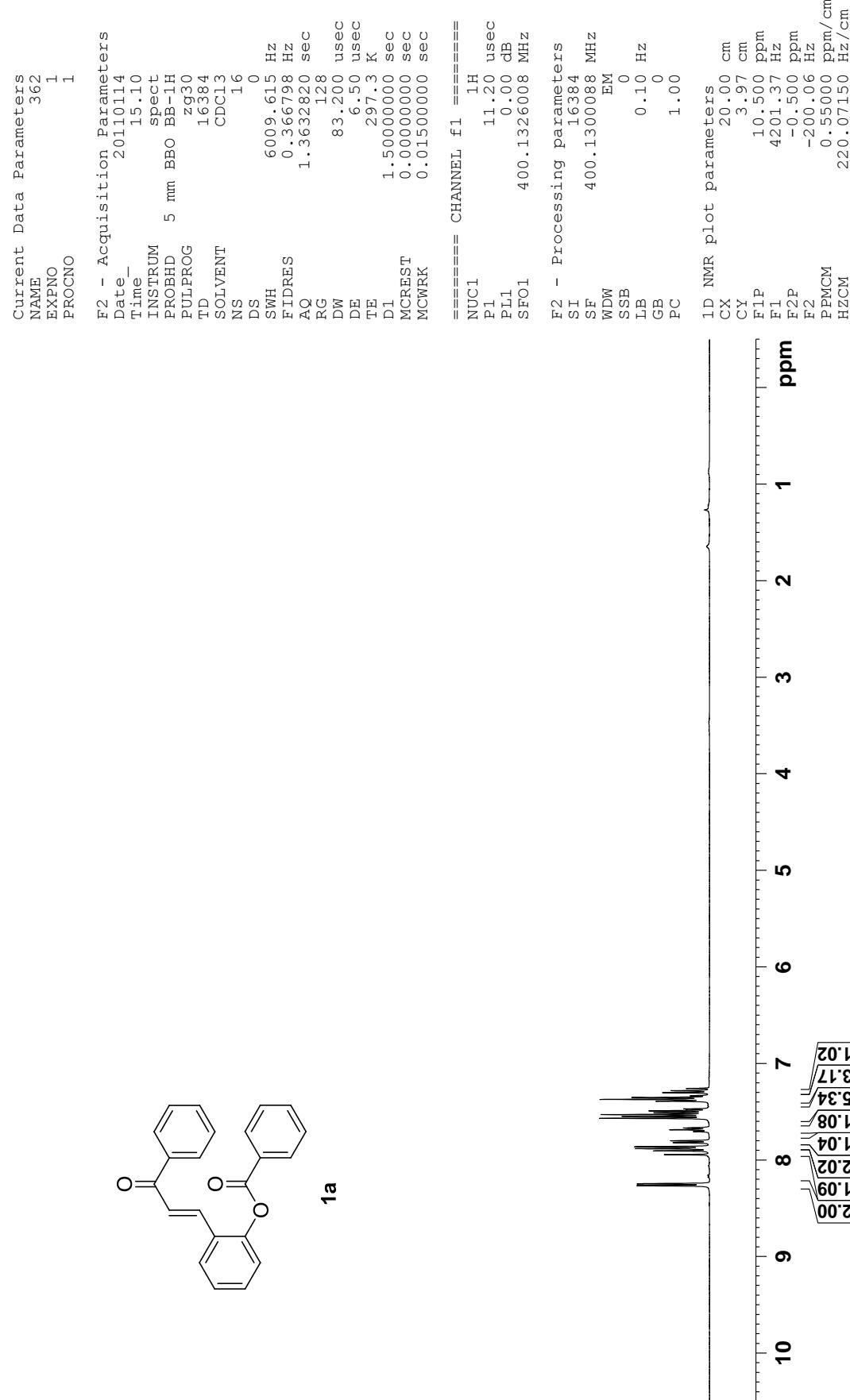
¹H-NMR (400 MHz, CDCl₃, 25 °C) δ/ppm: 8.21 (s, 1H), 7.98 (d, 2H, *J* = 8.2 Hz), 7.37 (d, 2H, *J* = 8.1 Hz), 2.70-2.62 (m, 2H), 2.43-2.37 (m, 2H), 1.87-1.78 (m, 2H), 1.78-1.69 (m, 2H).

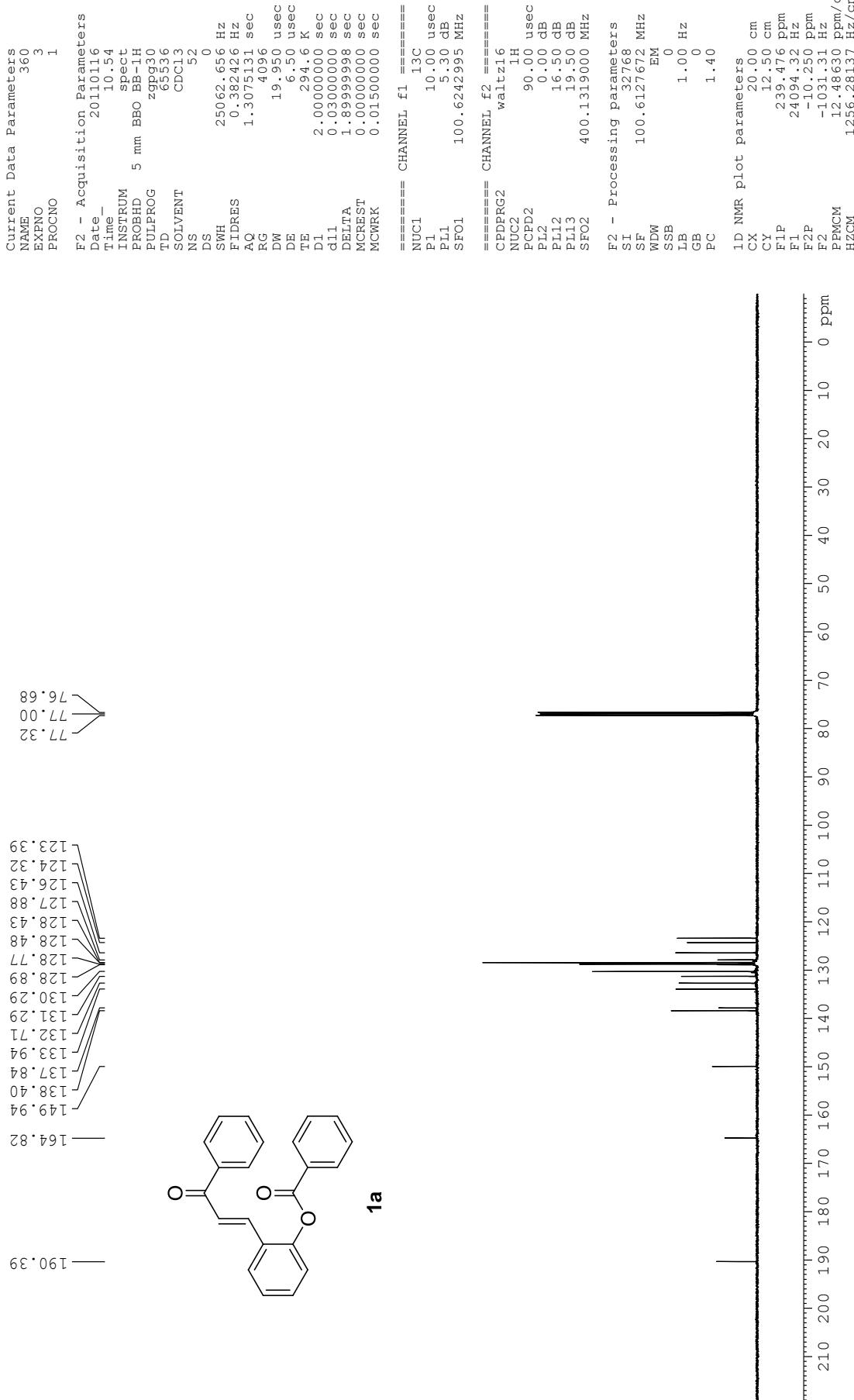
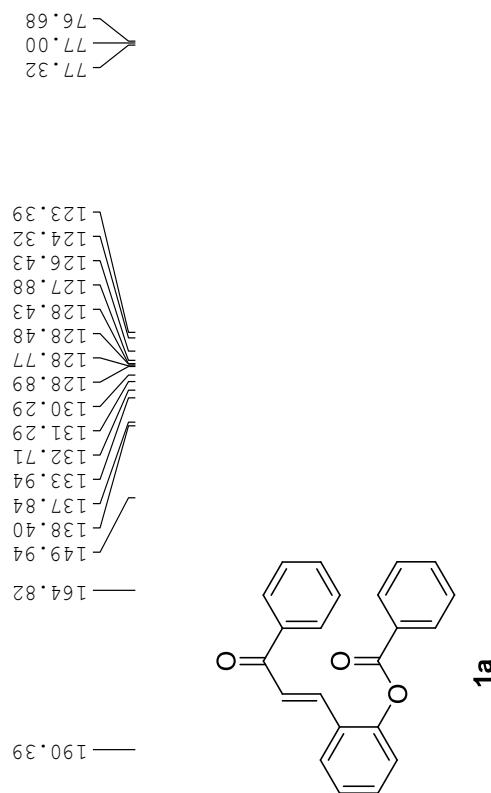
¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ/ppm: 200.3, 161.9, 141.5, 140.8, 131.5, 129.1, 126.8, 122.3, 40.3, 24.5, 23.1, 22.7.

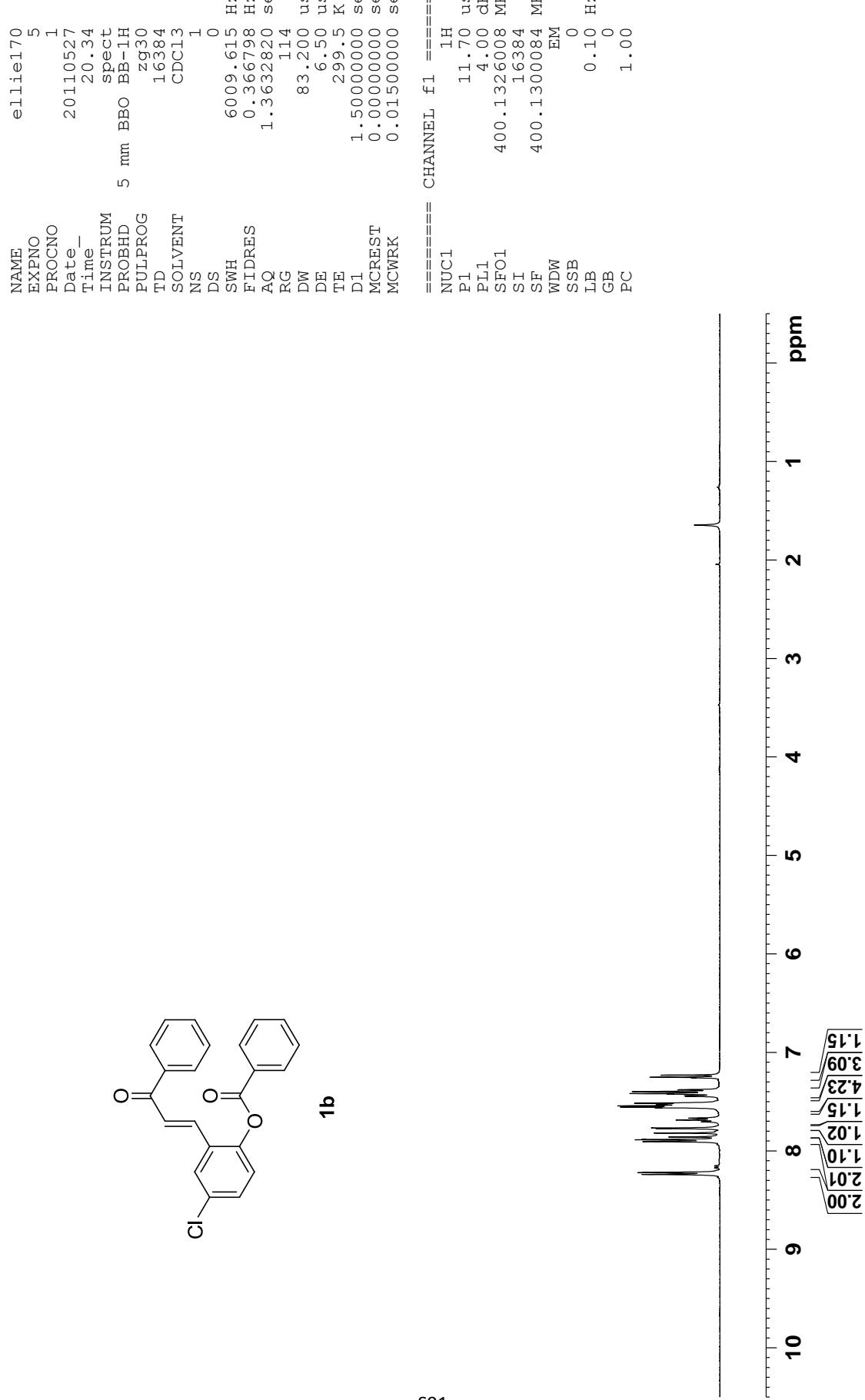
IR (CH₂Cl₂) $\tilde{\nu}$ (cm⁻¹): 3092 (w), 1741 (m), 1620 (s), 1251 (m), 1089 (m), 753 (w).

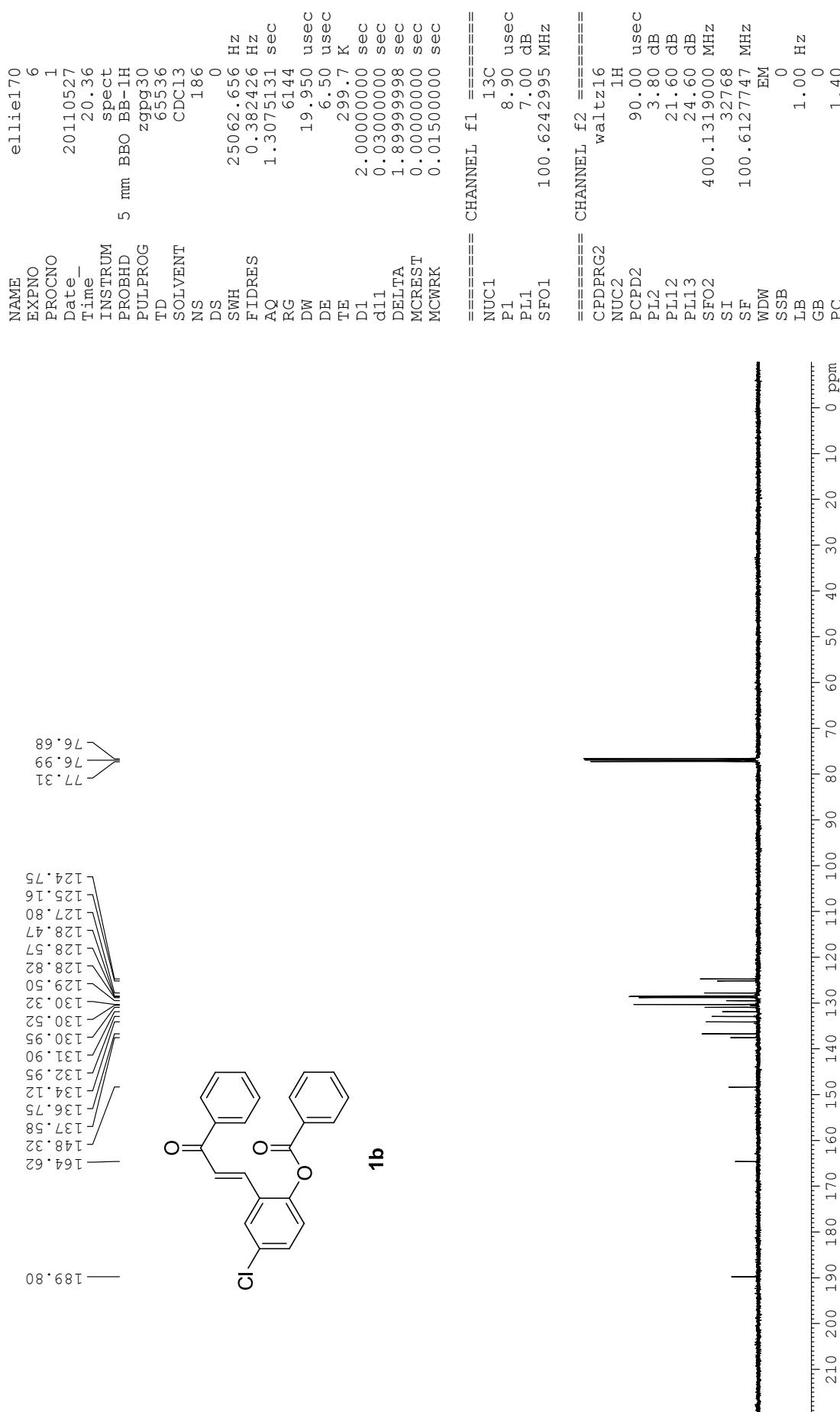
HRMS (ESI) for C₁₄H₁₃ClO₃Na, [M+Na]⁺ (287.0451) found: 287.0475.

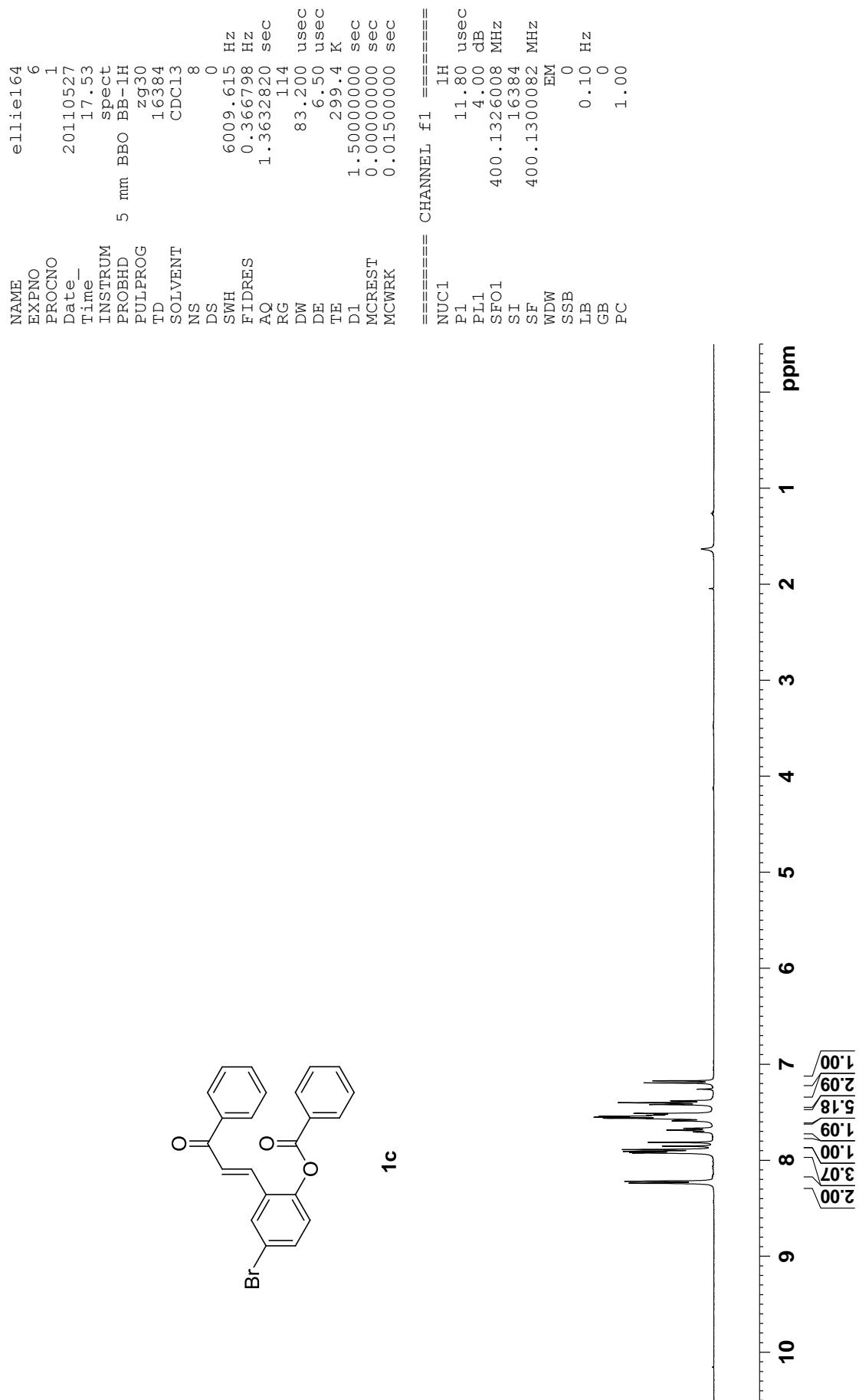
VII. Spectra of ^1H , ^{13}C , and ^{31}P NMR

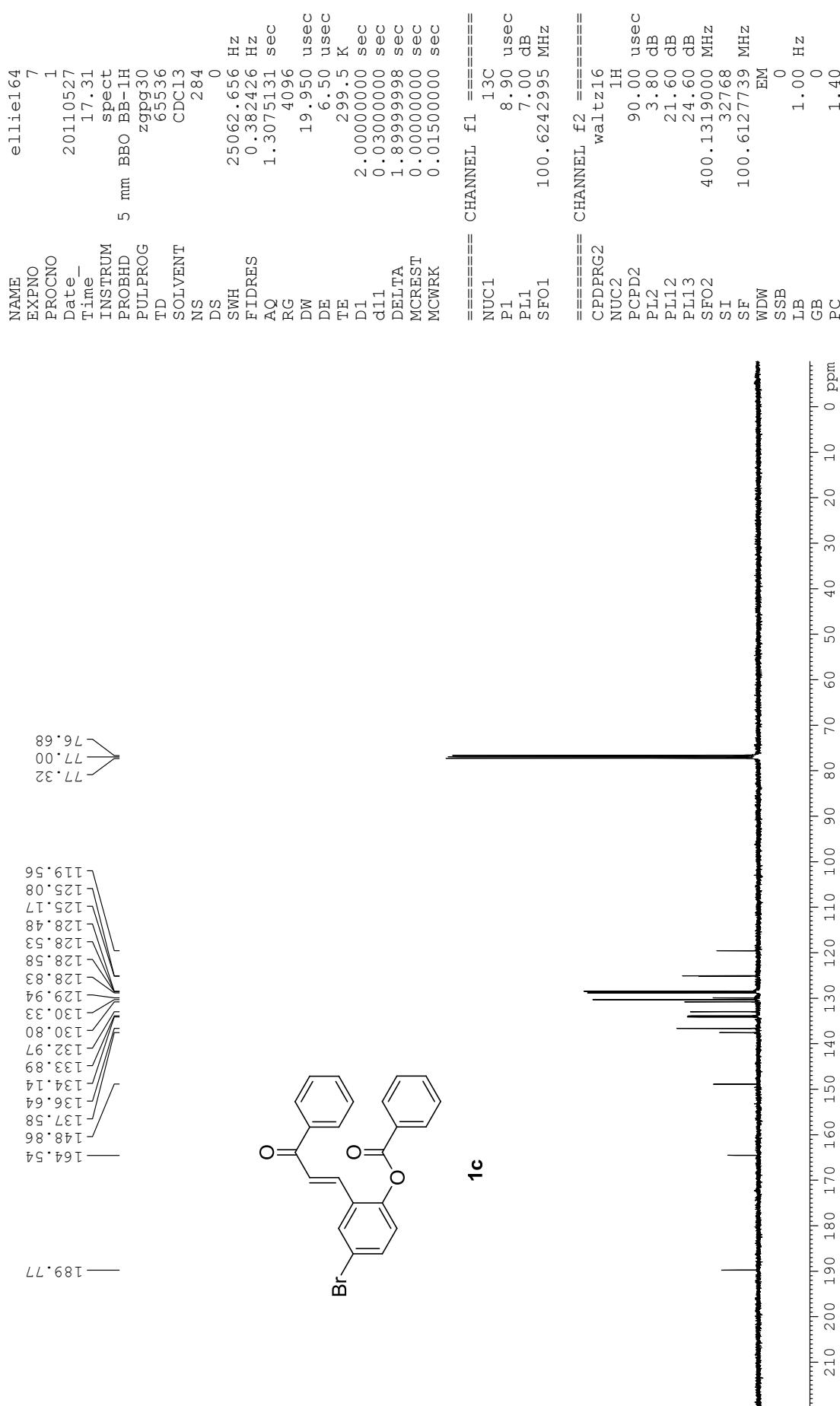


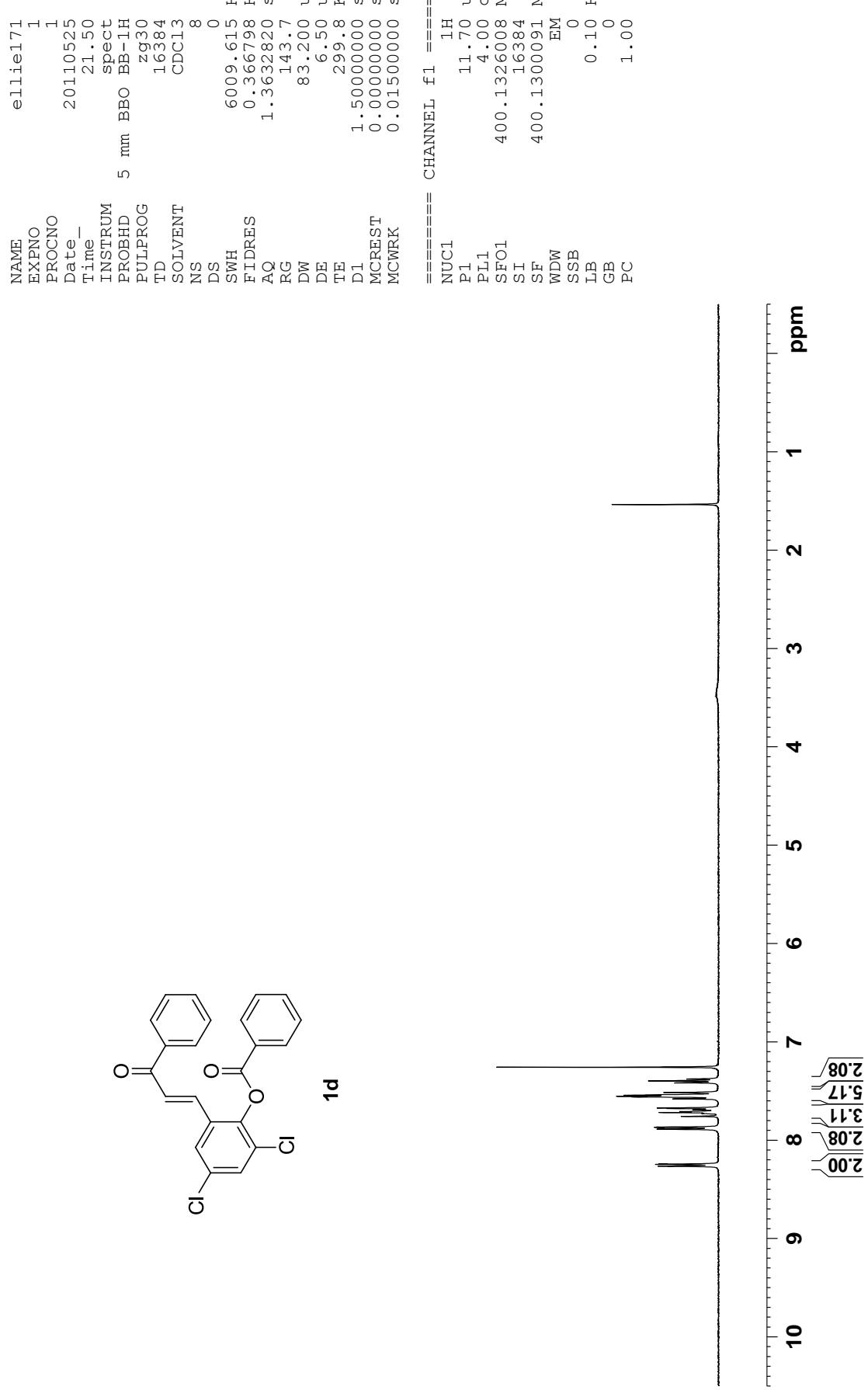


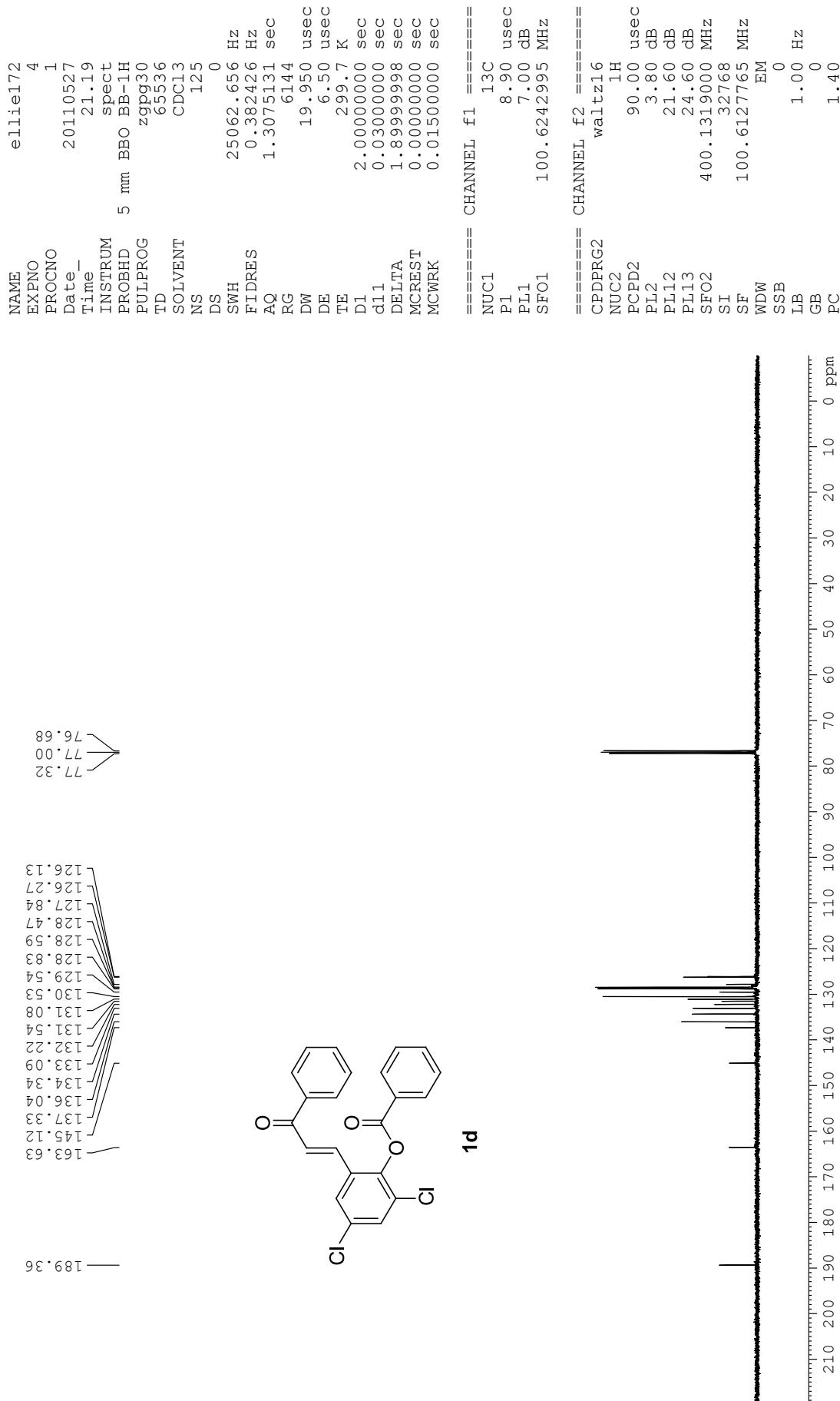


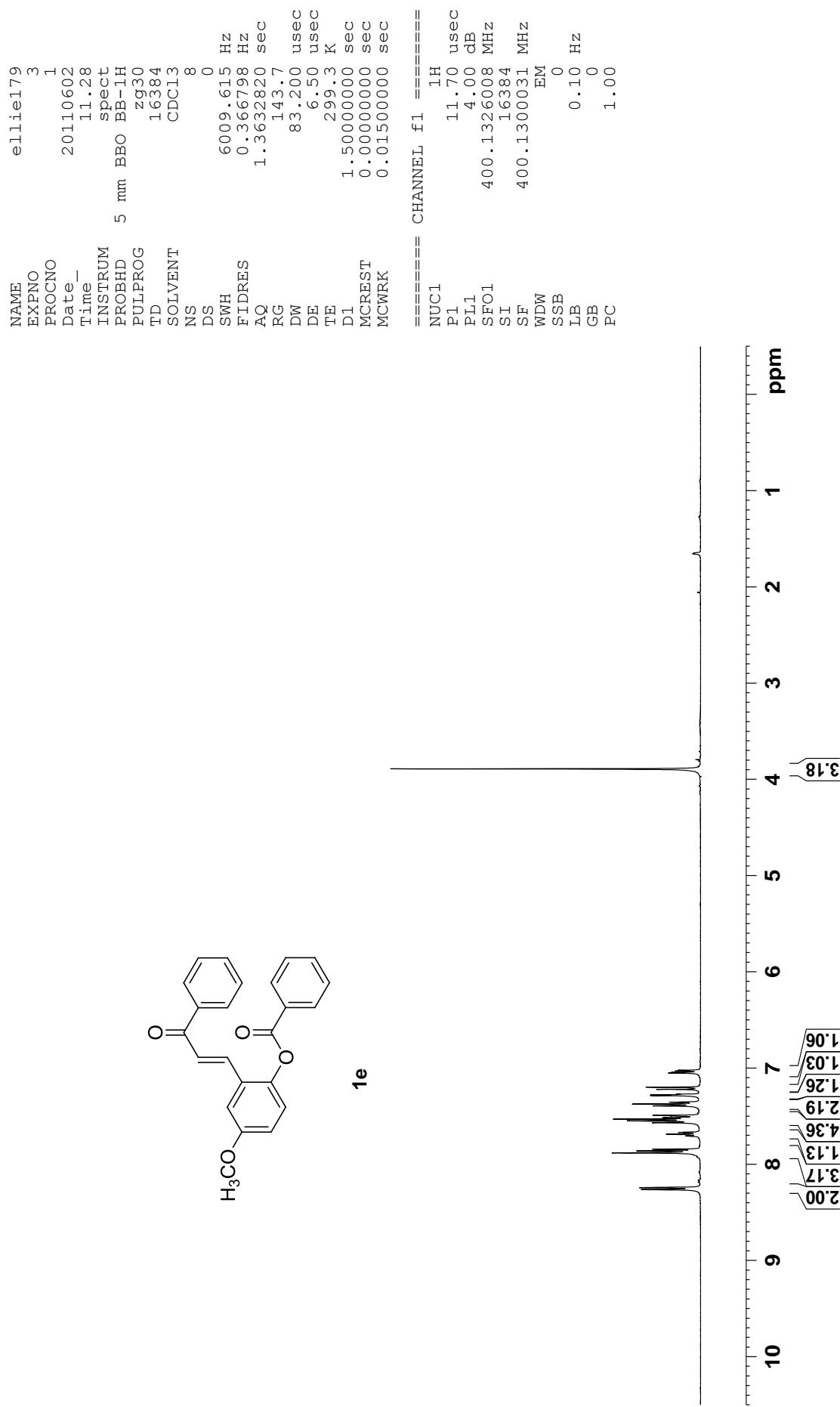


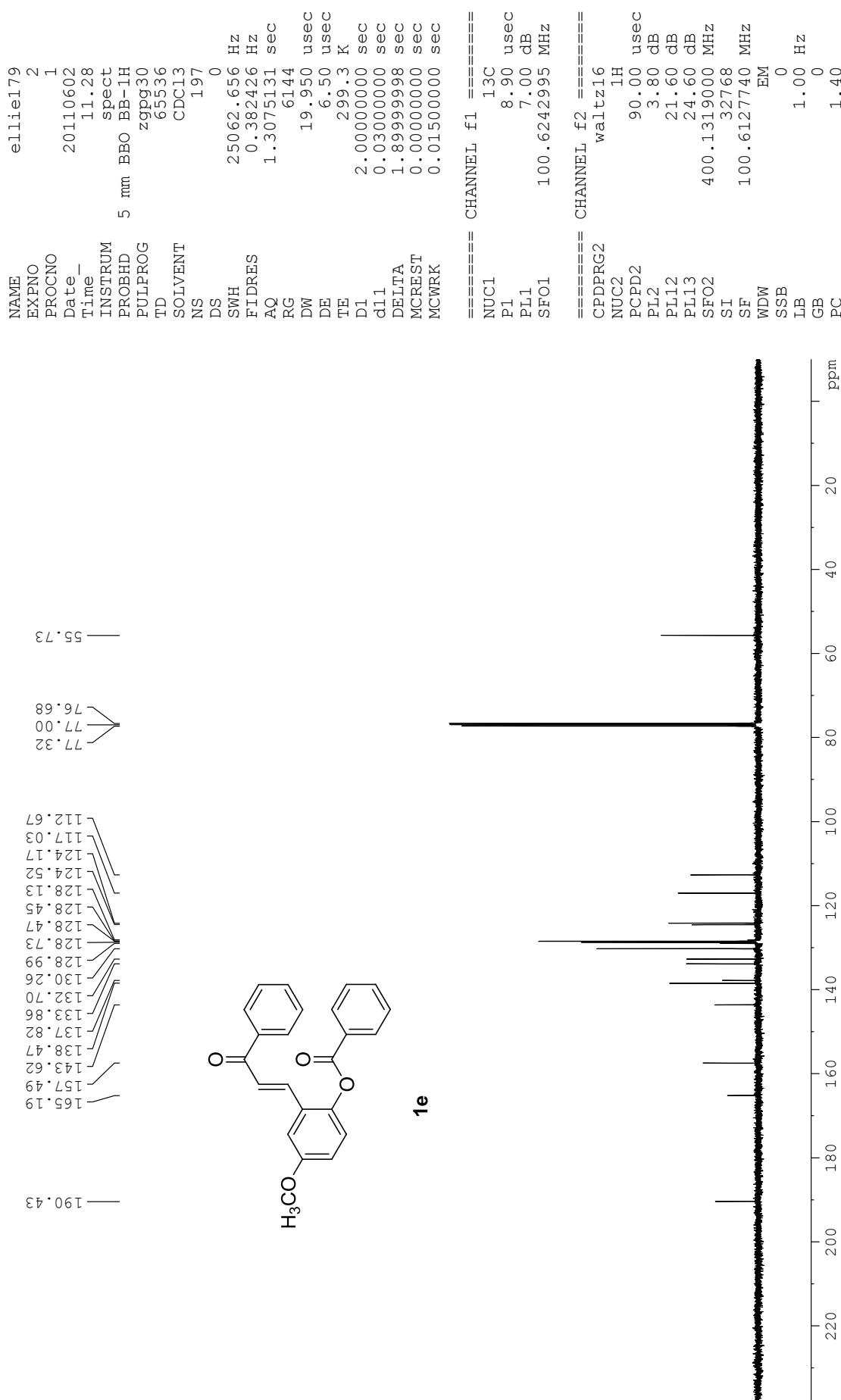


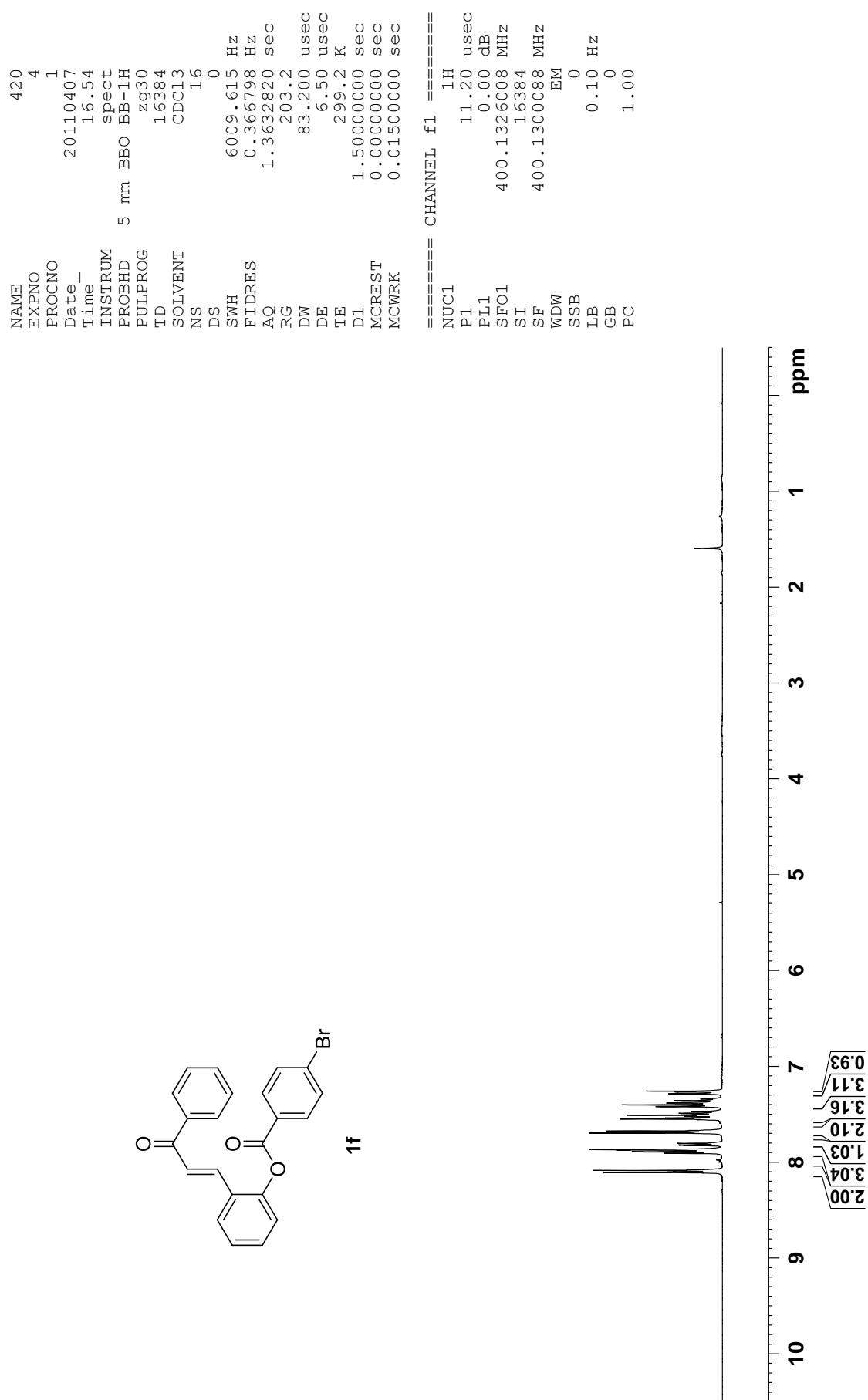


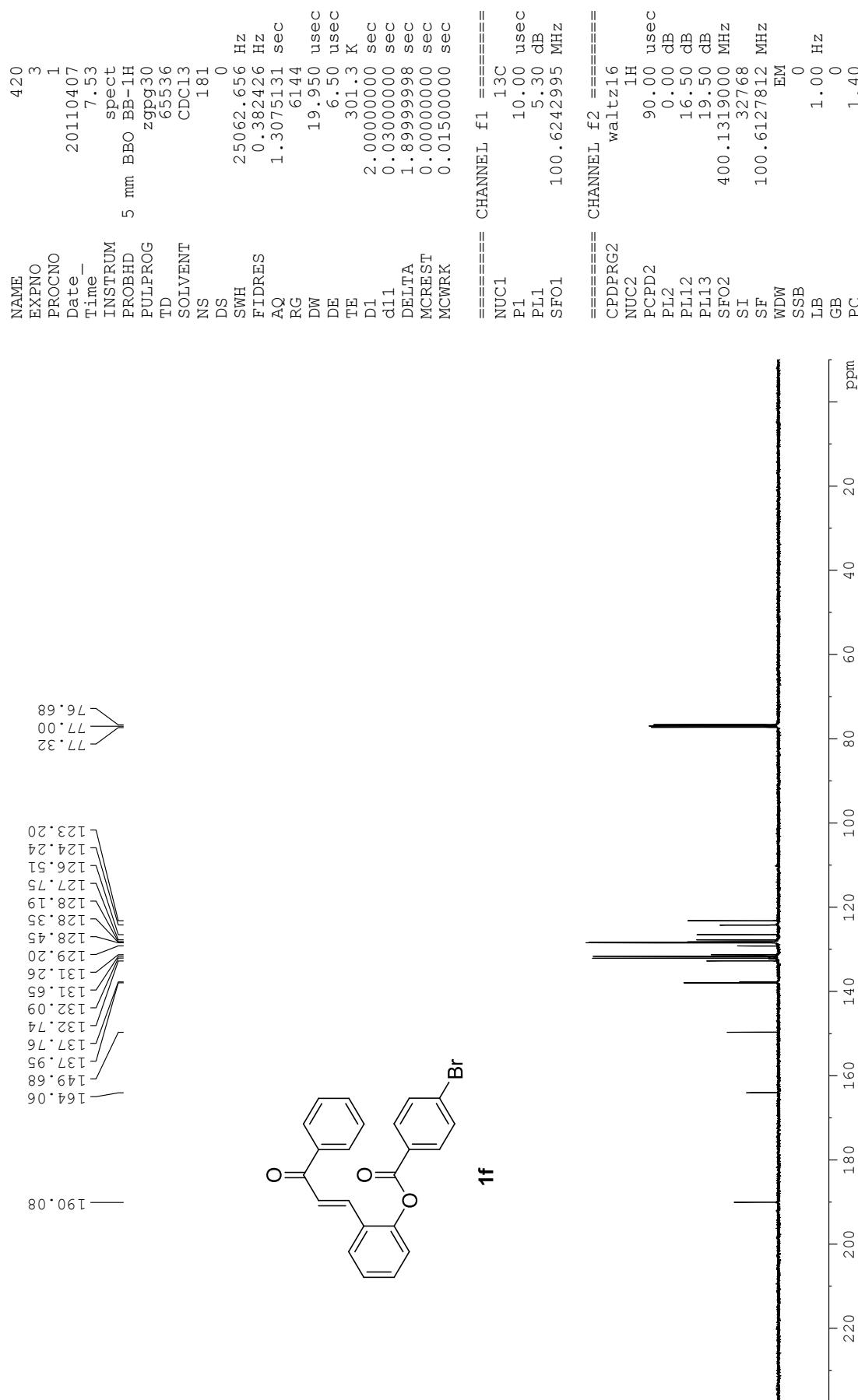


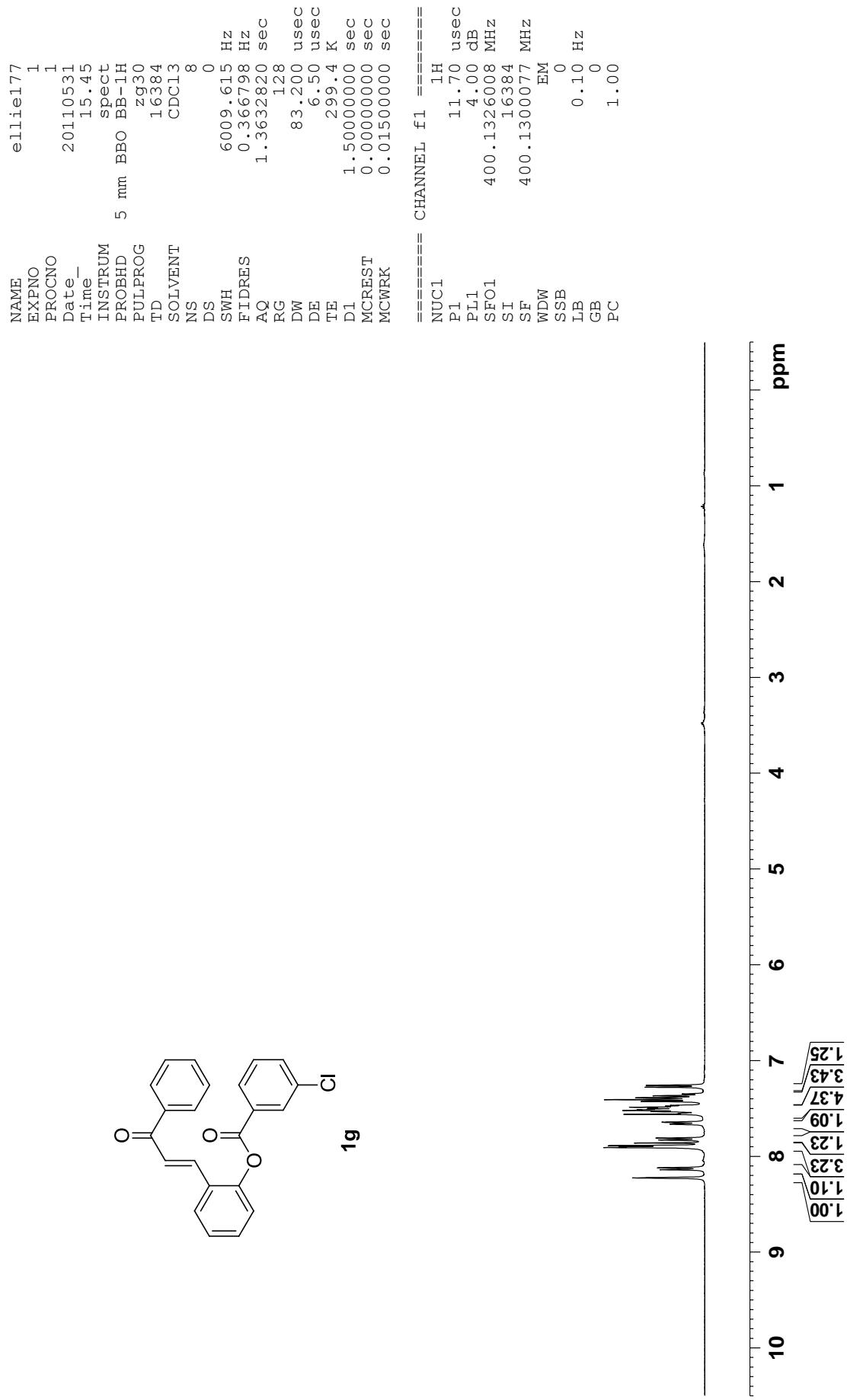


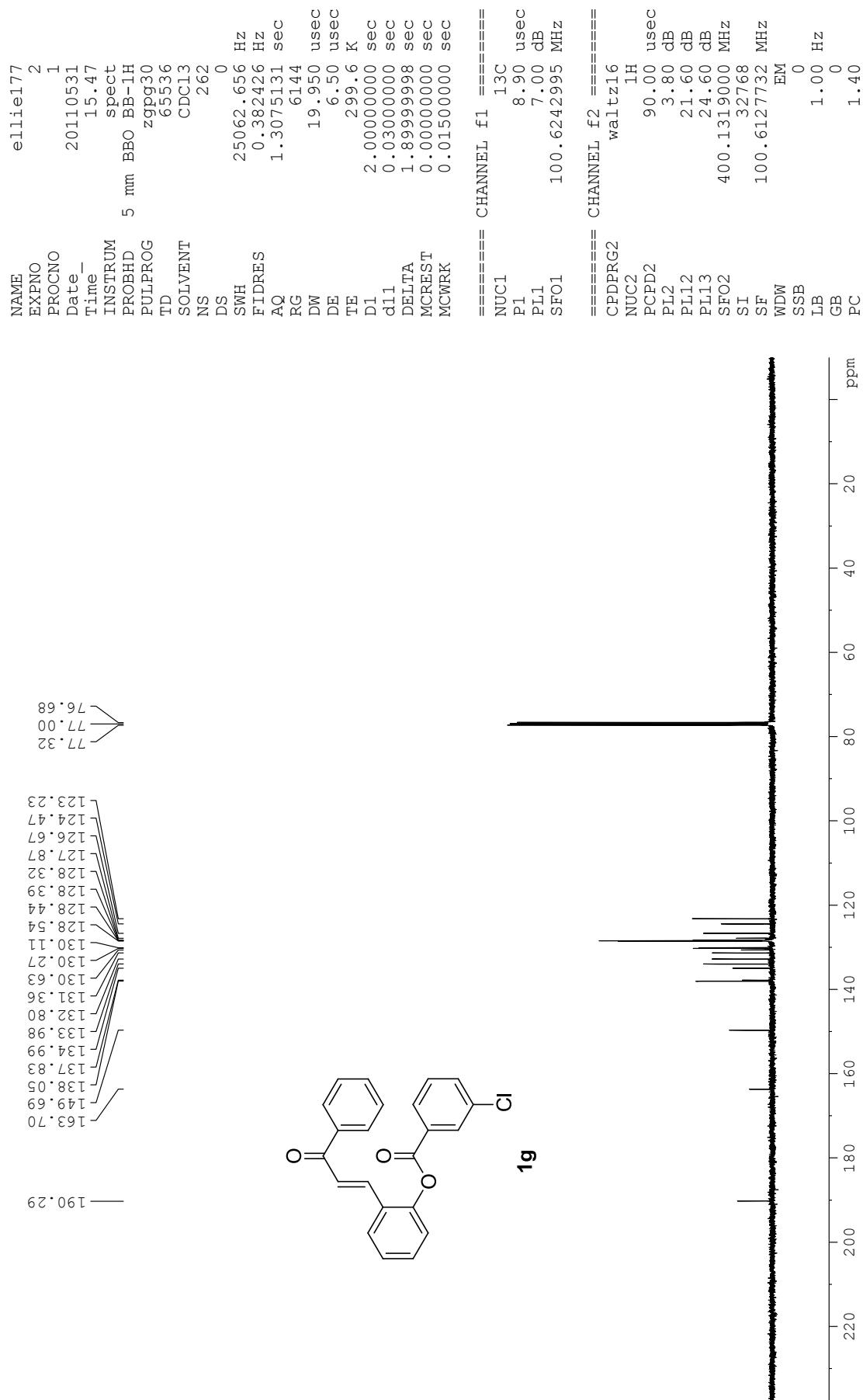


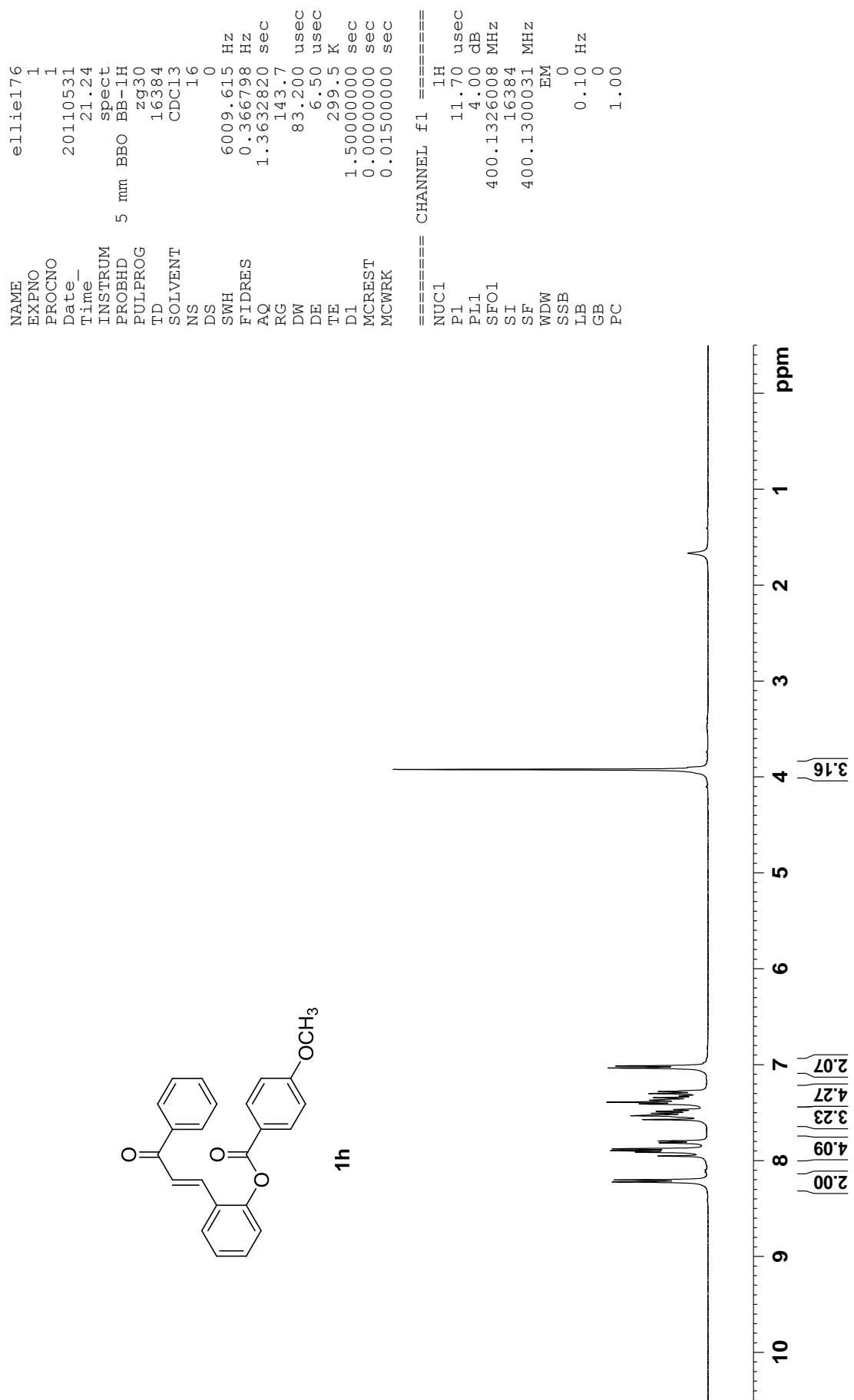


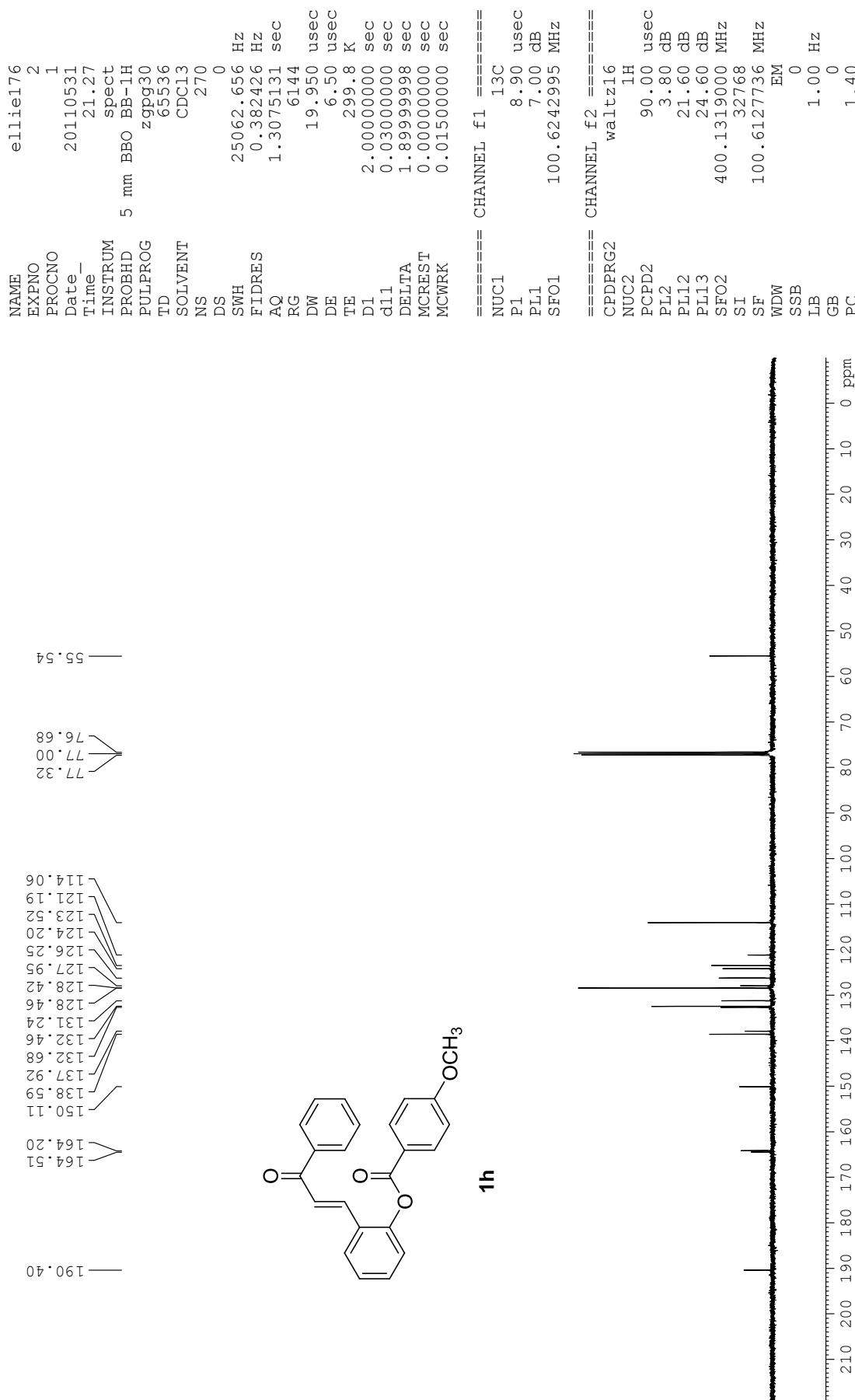


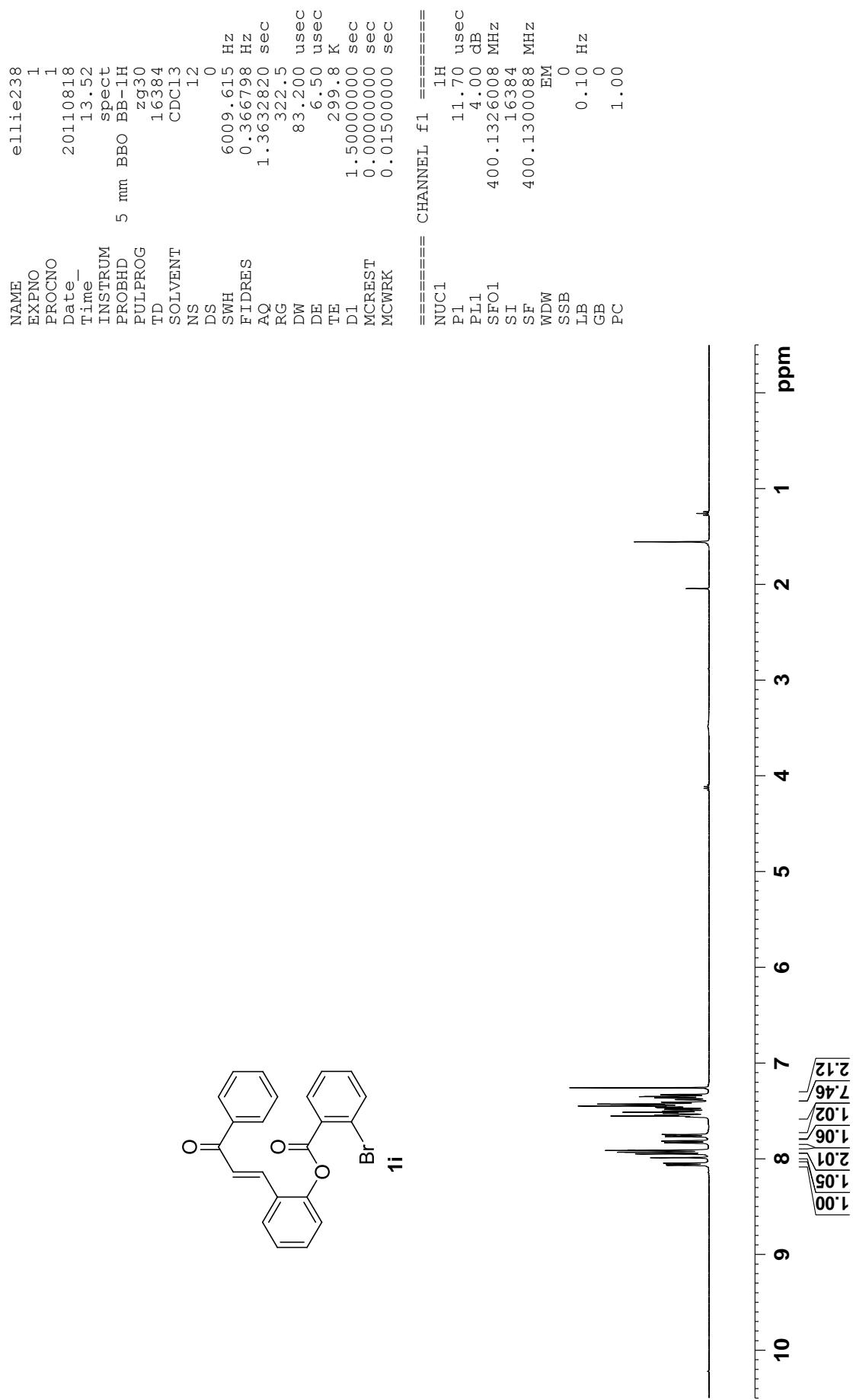


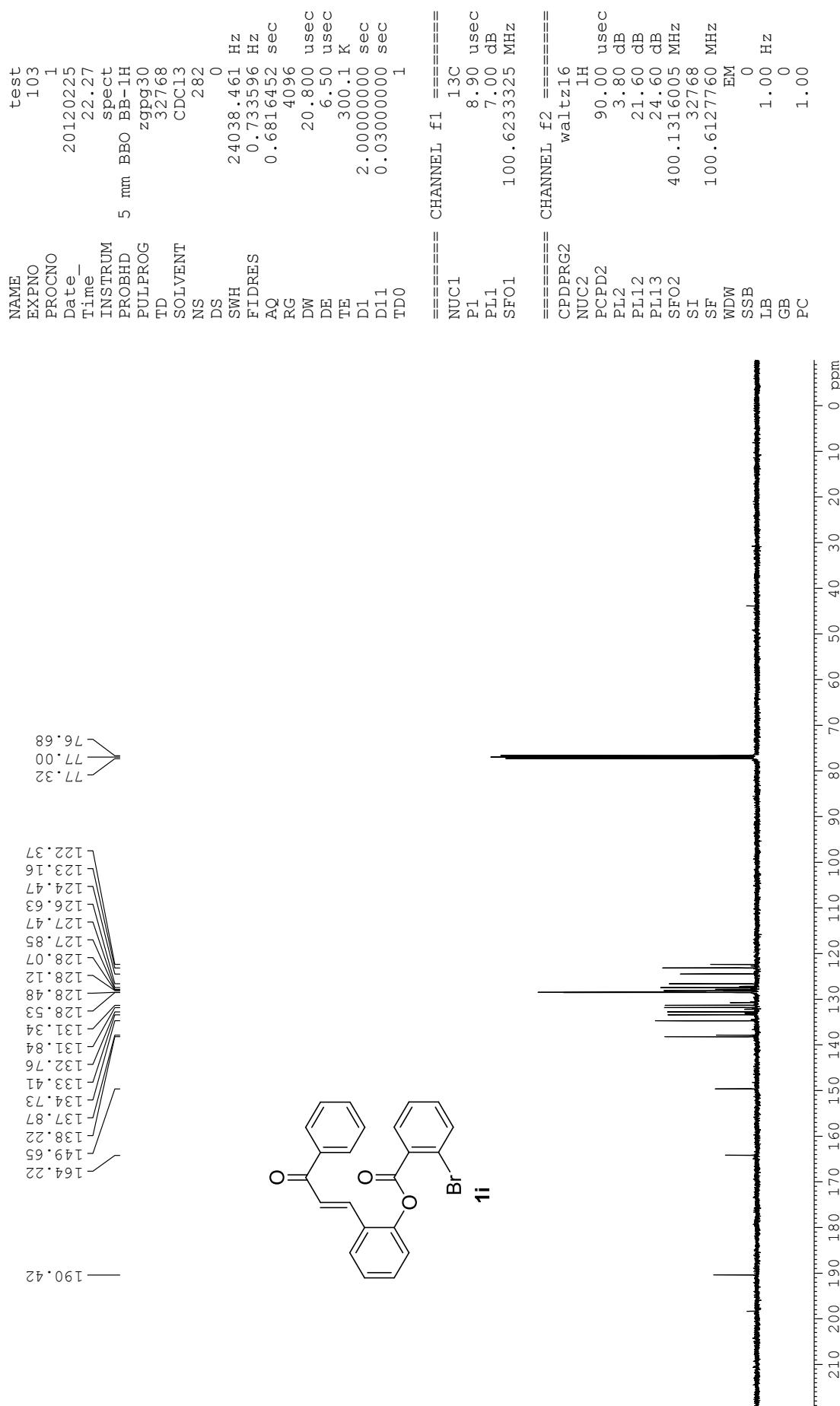


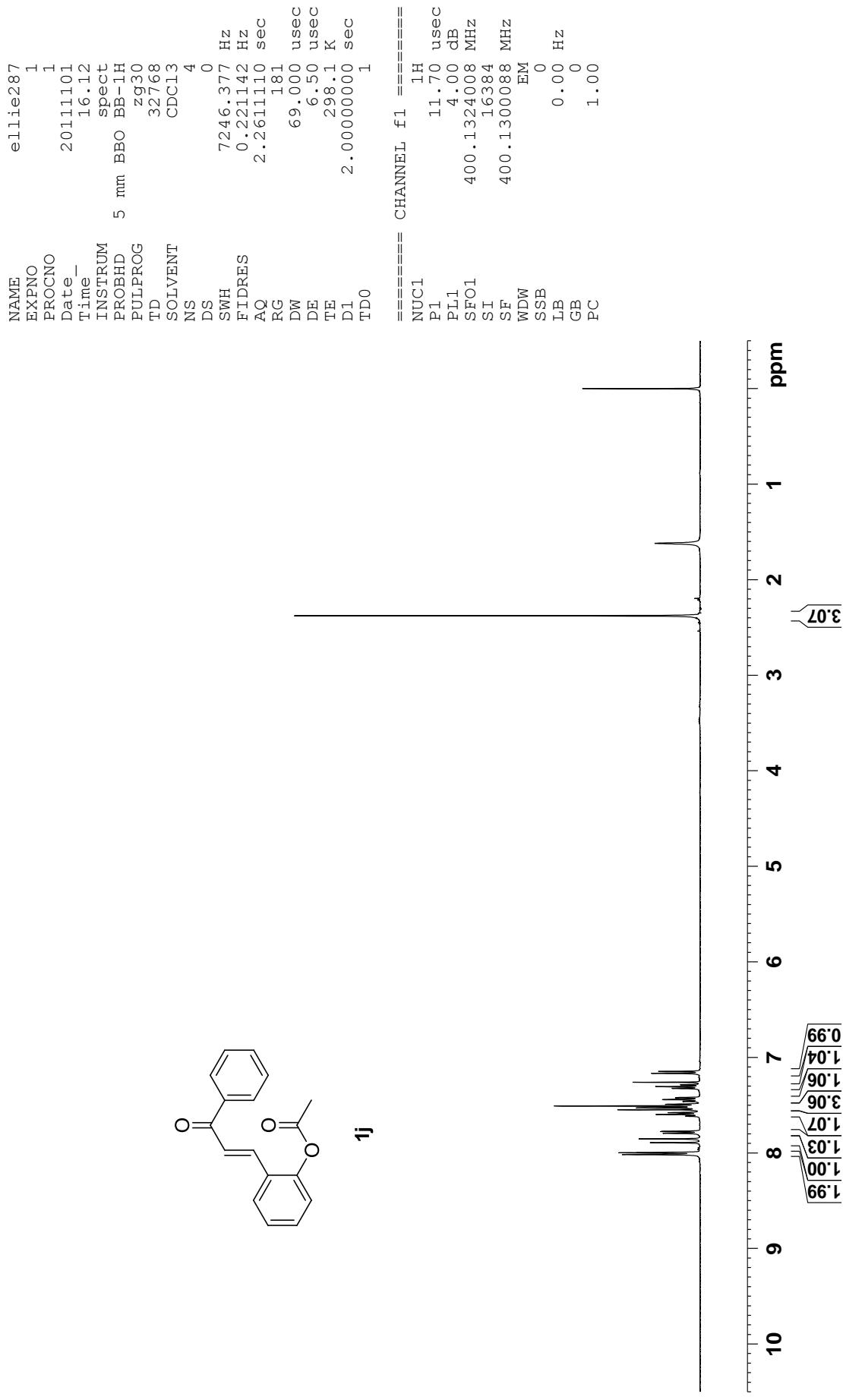


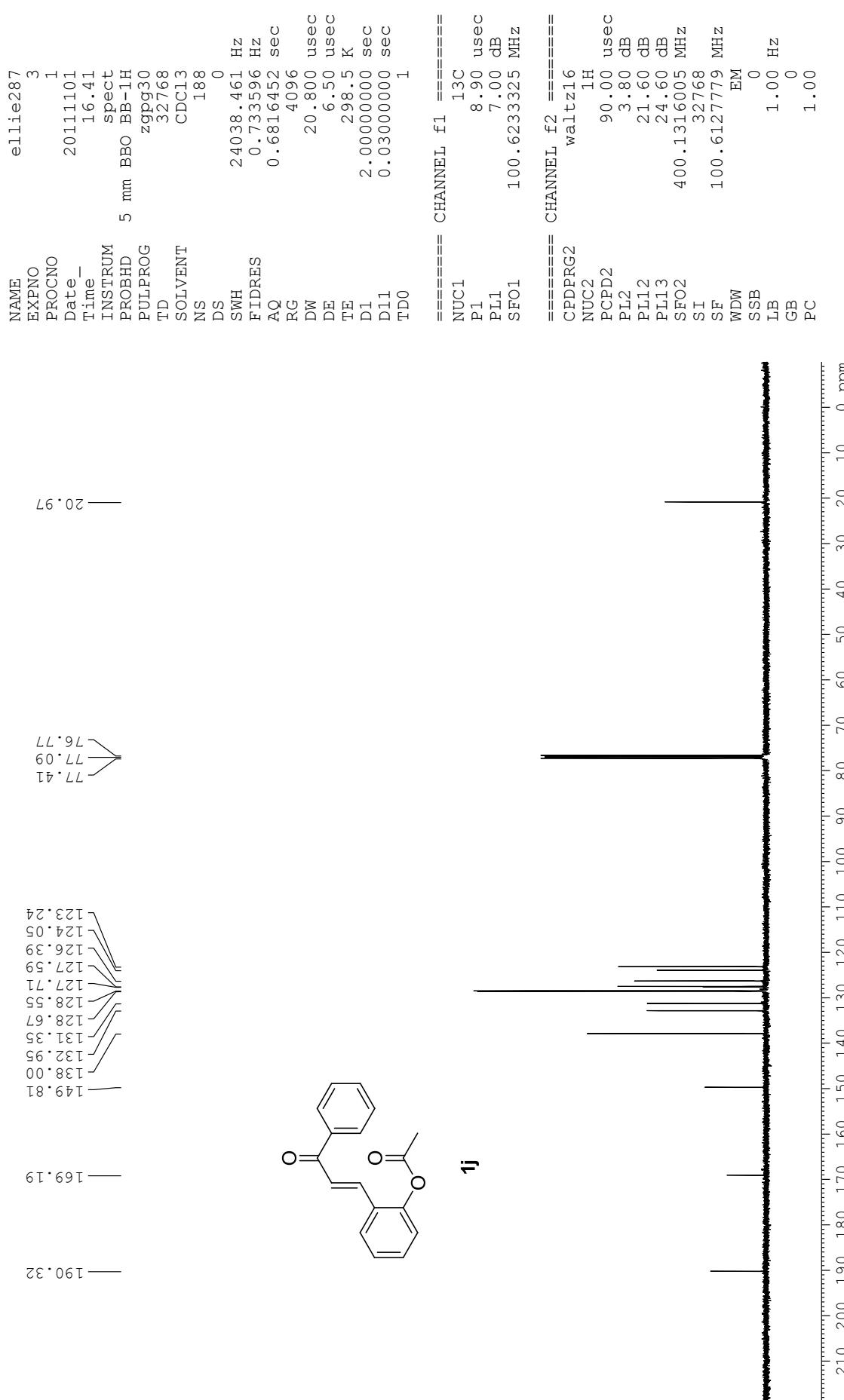


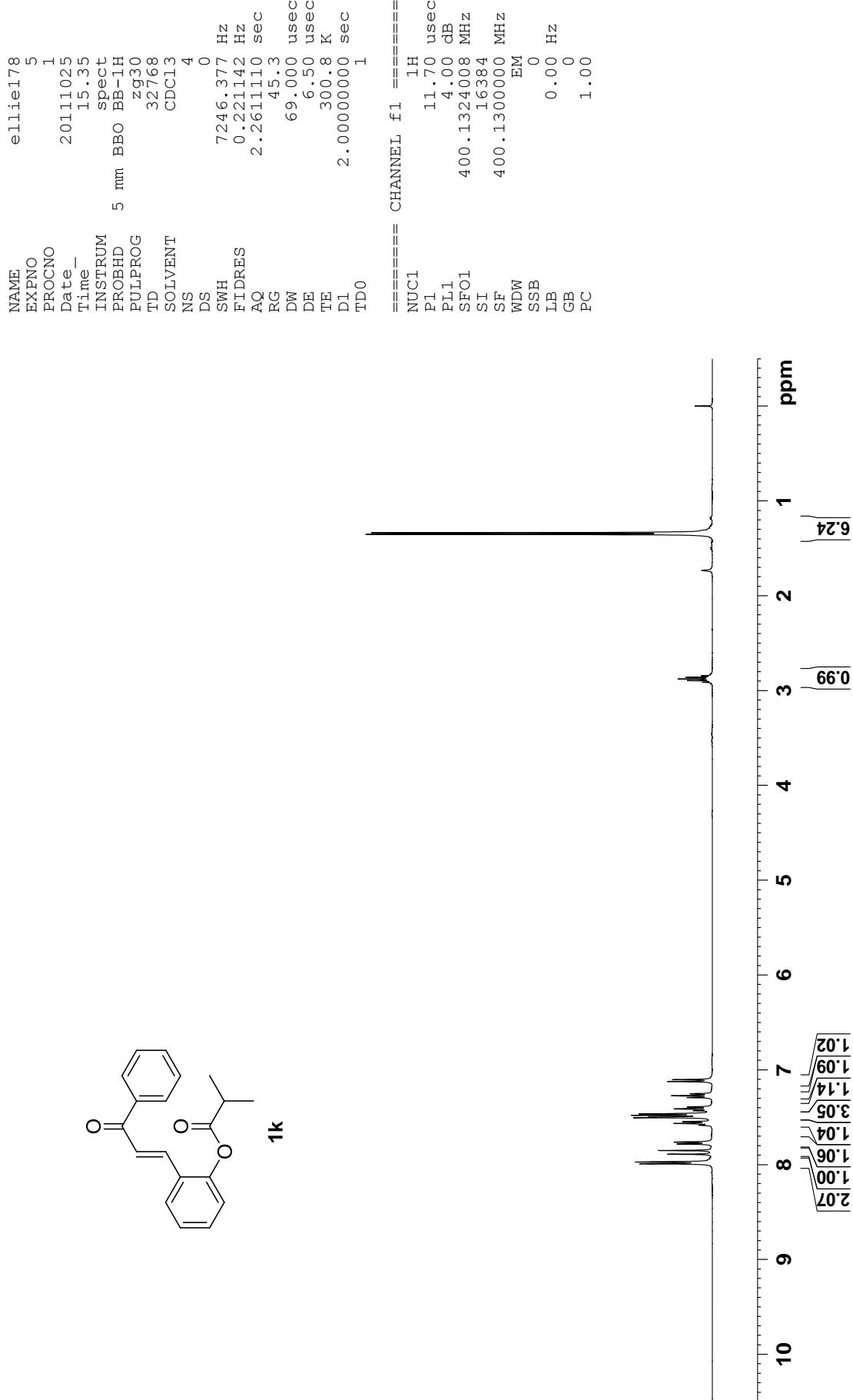


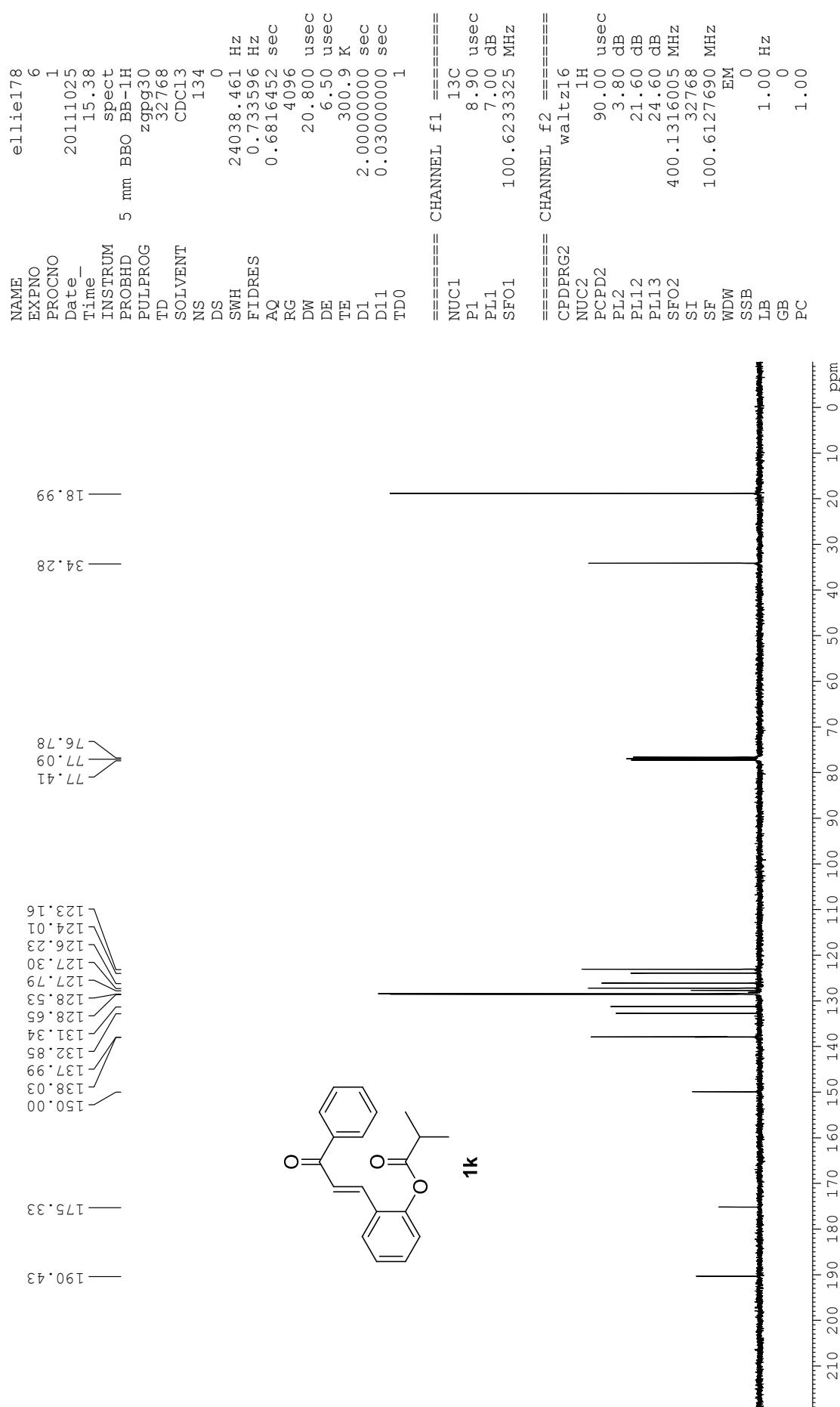


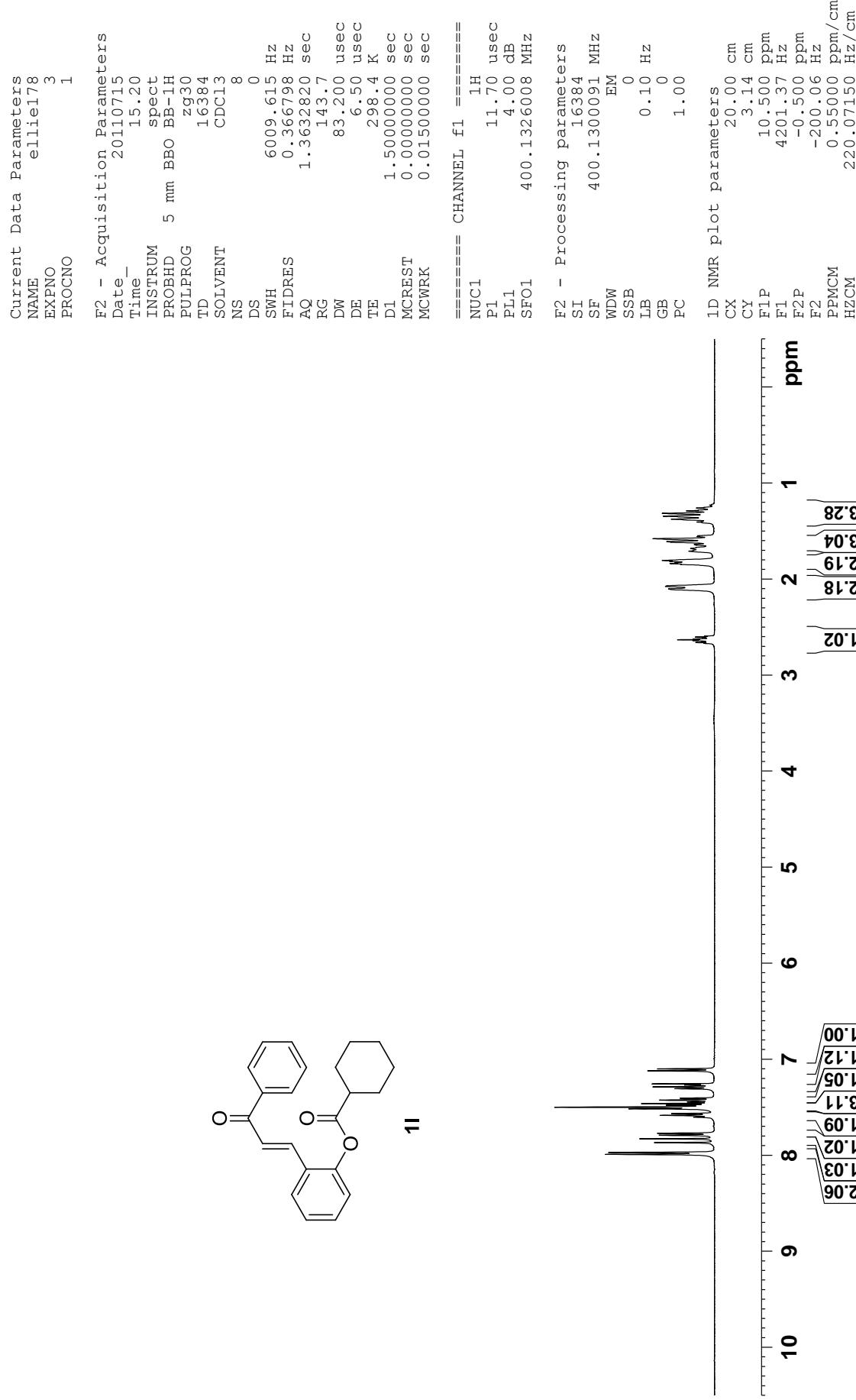


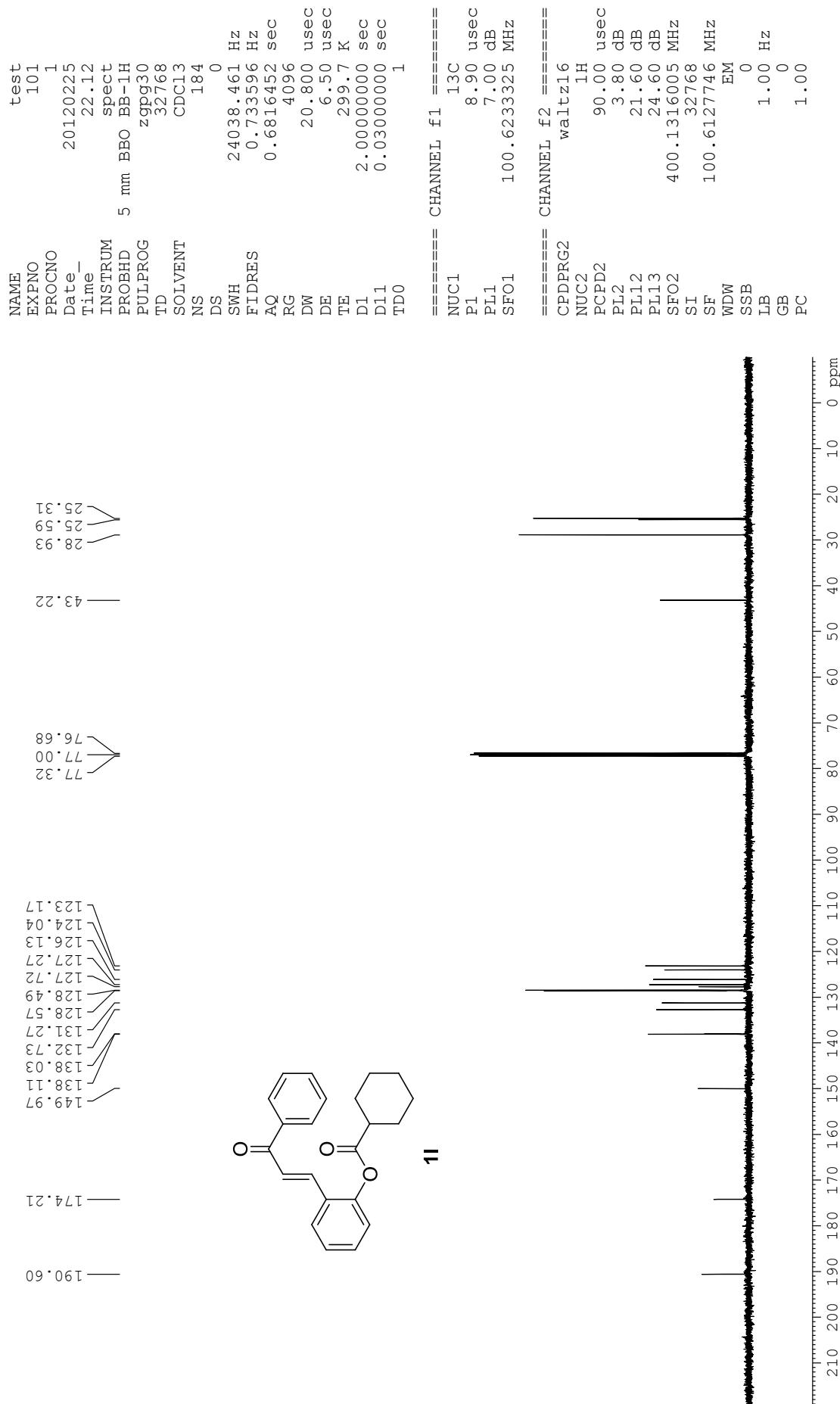


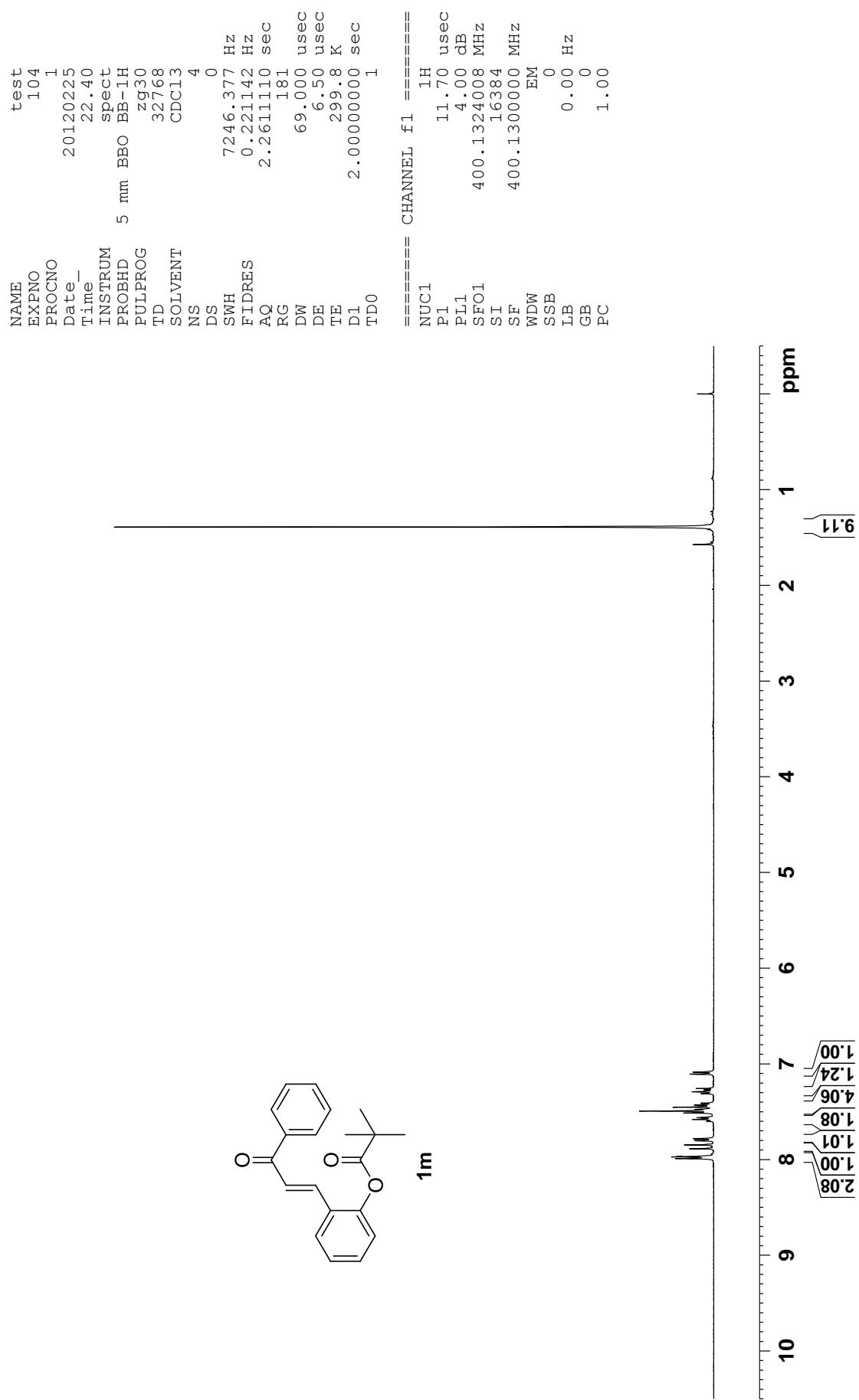


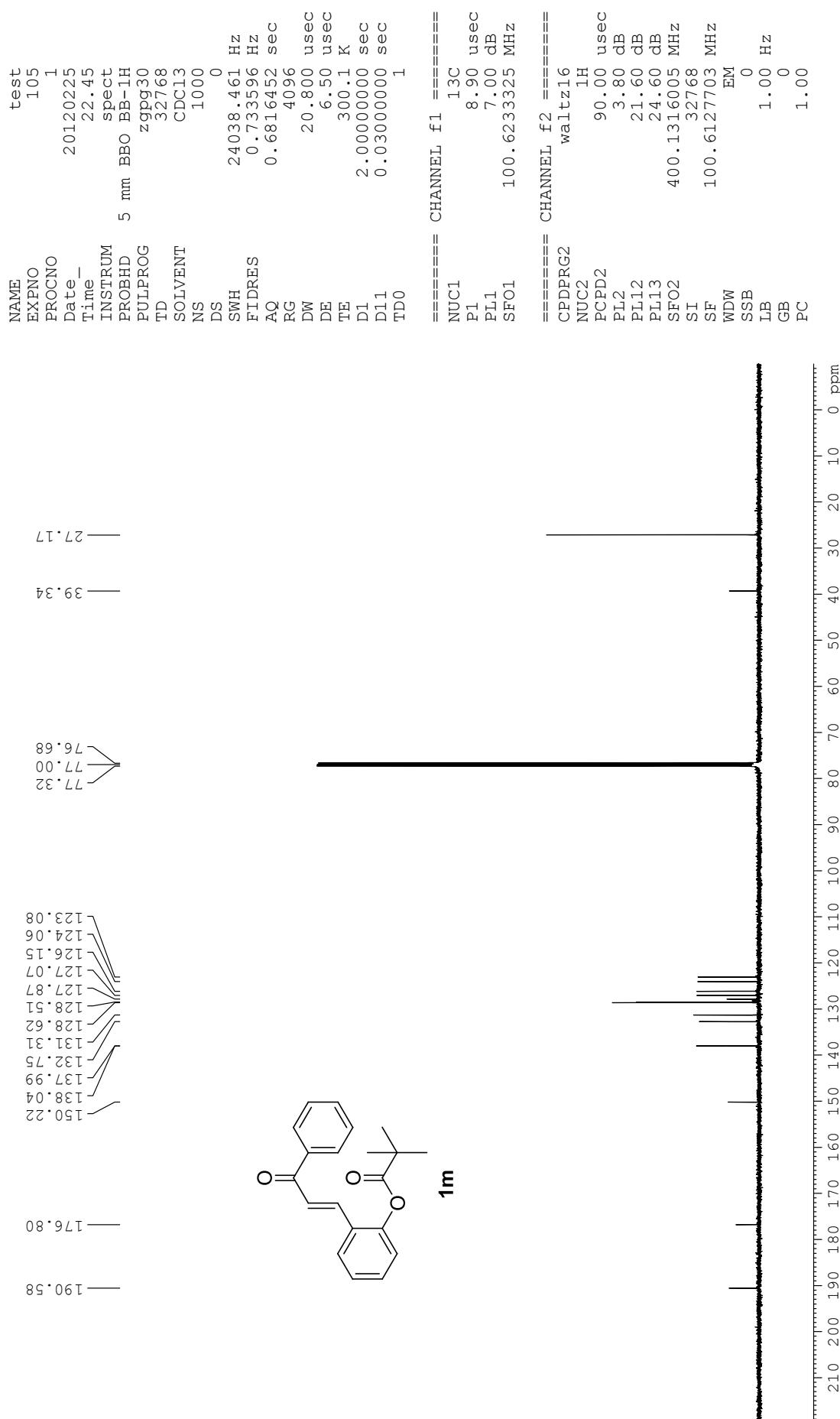


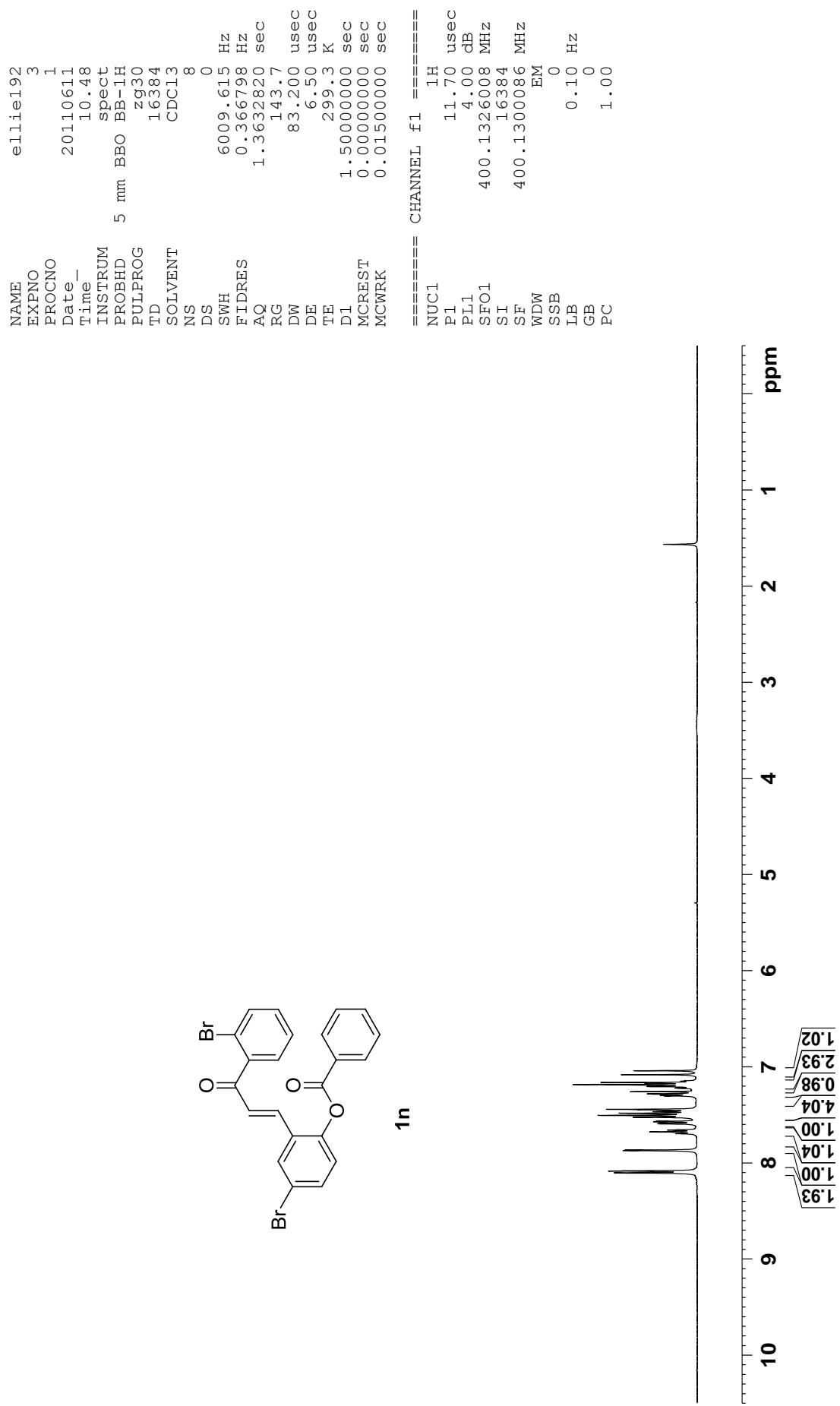


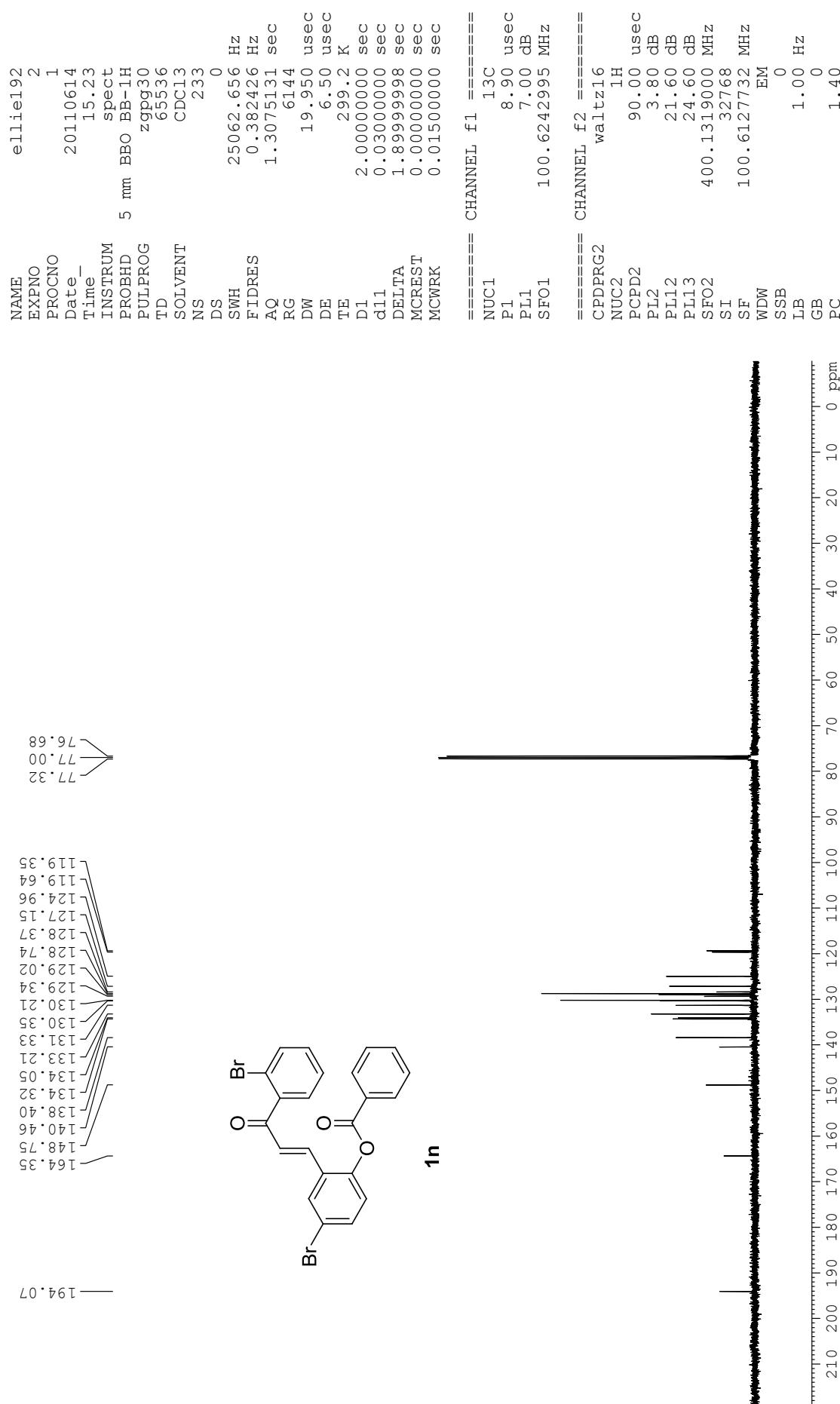


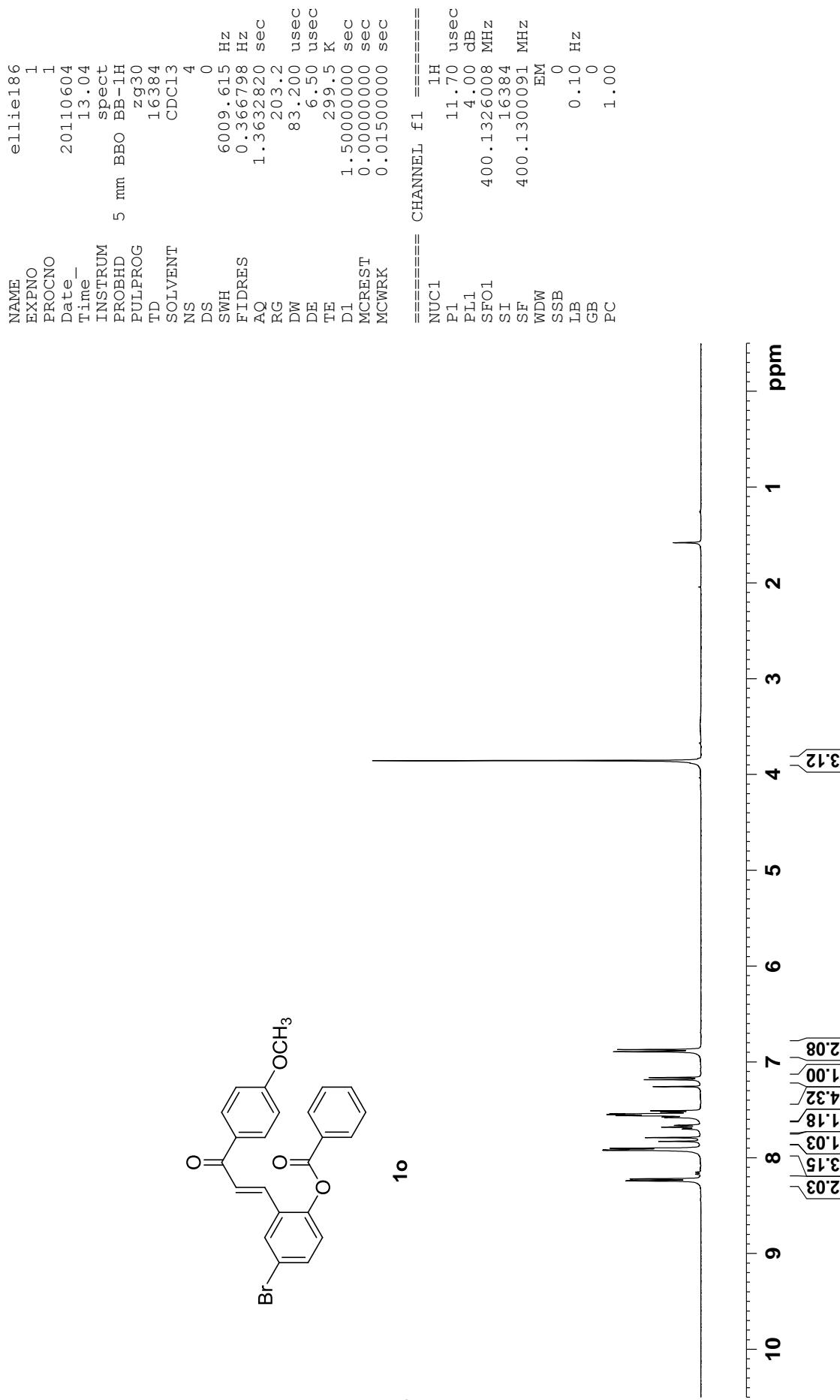


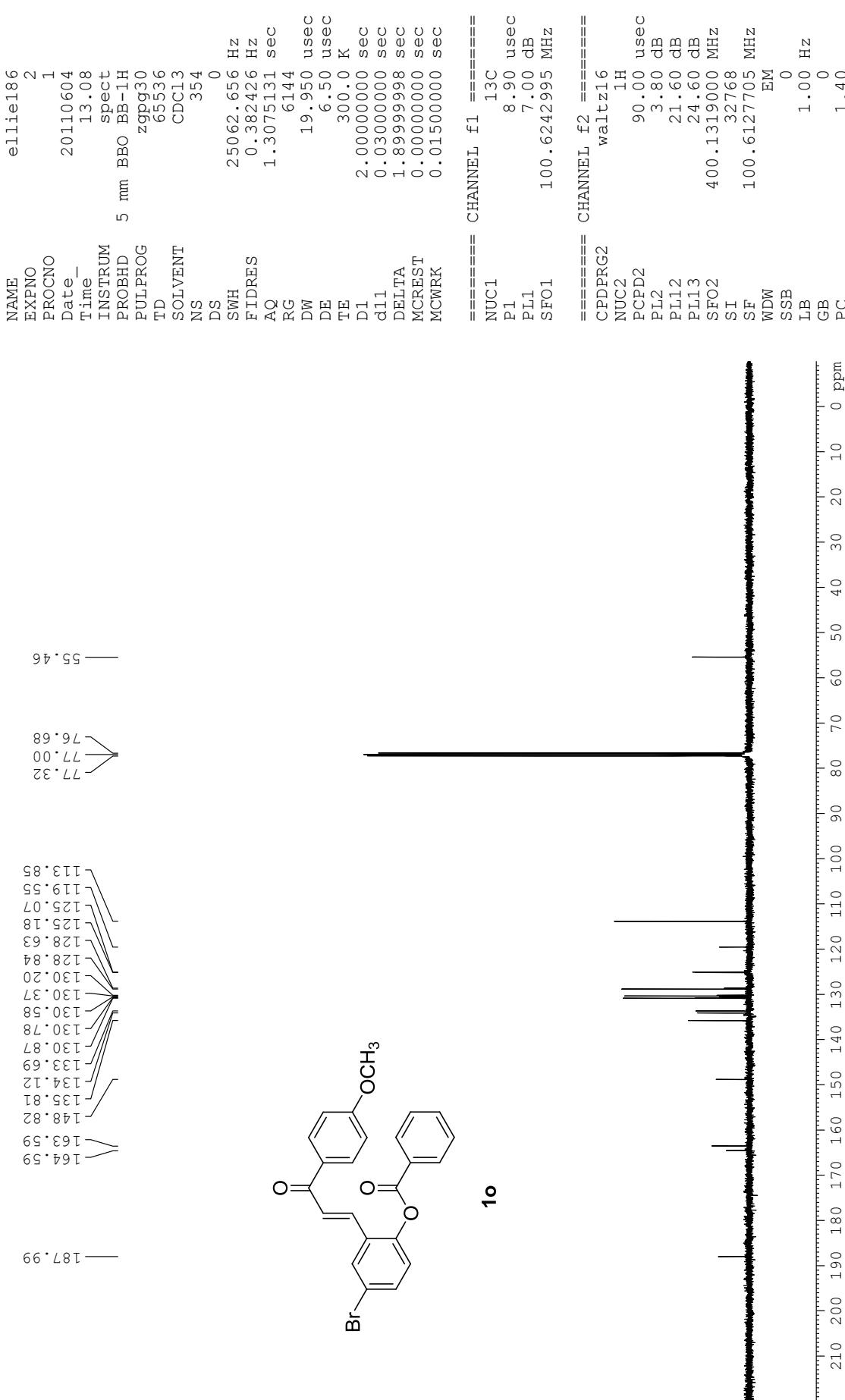


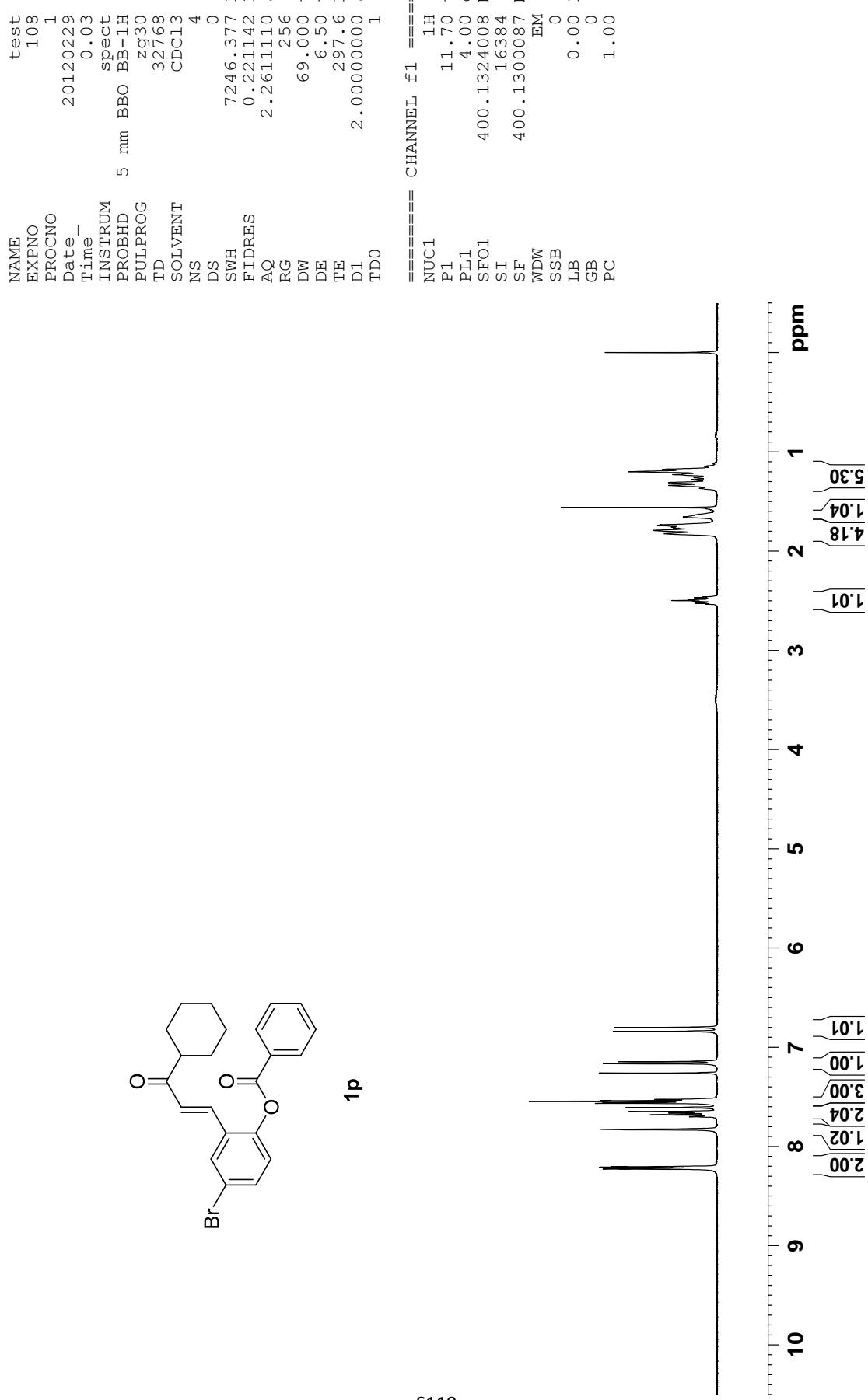


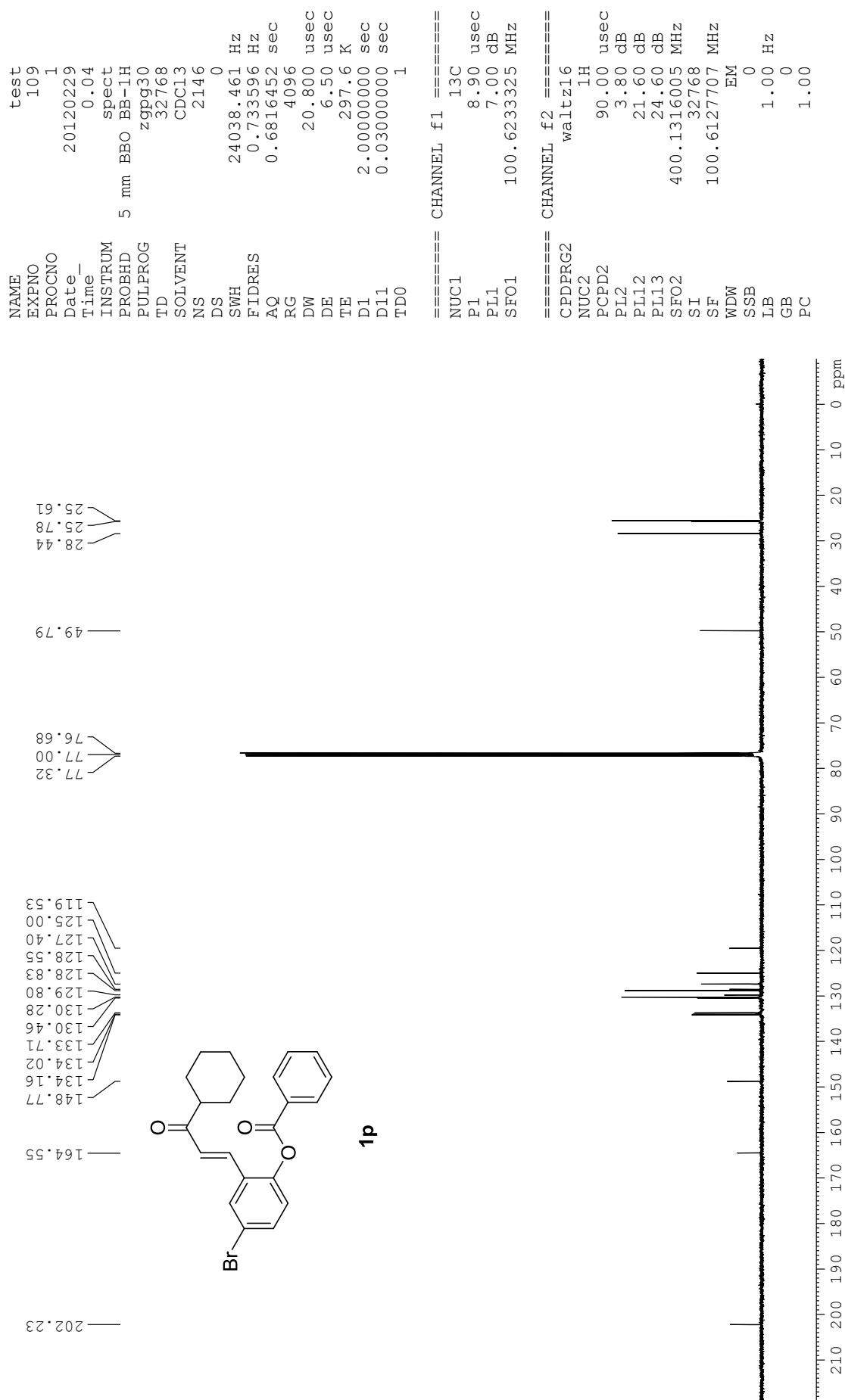










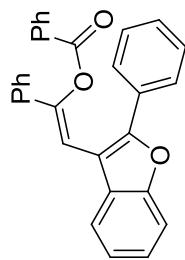


```

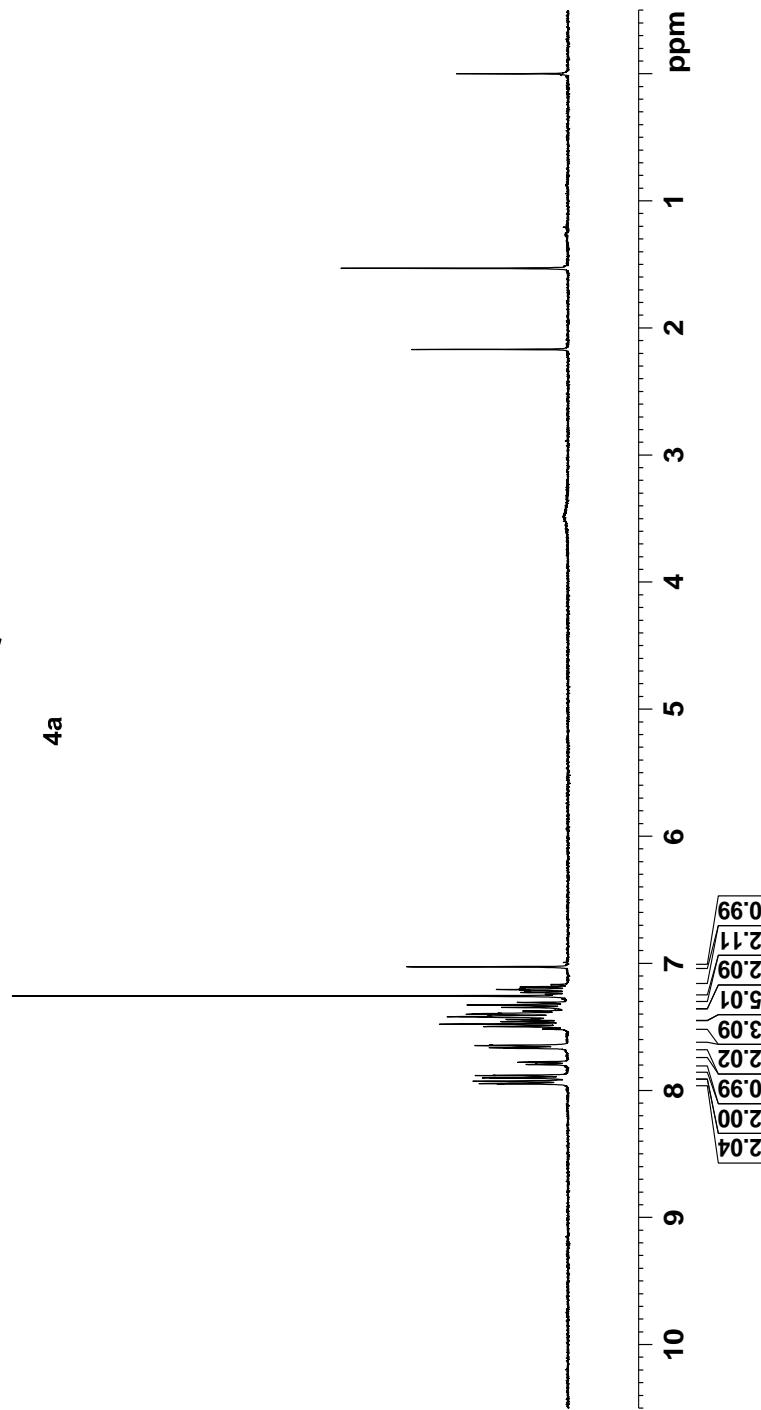
NAME ellie175
EXPNO 9
PROCNO 1
Date _ 20111125
Time _ 17.34
INSTRUM spect
PROBHD 5 mm
PULPROG BBO
TD 32768
SOLVENT CDC13
NS 4
DS 0
SWH 7246.377 Hz
FIDRES 0.221142 Hz
AQ 2.261110 sec
RG 362
DW 69.0000 usec
DE 6.50 usec
TE 299.7 K
D1 2.0000000 sec
TDO 1

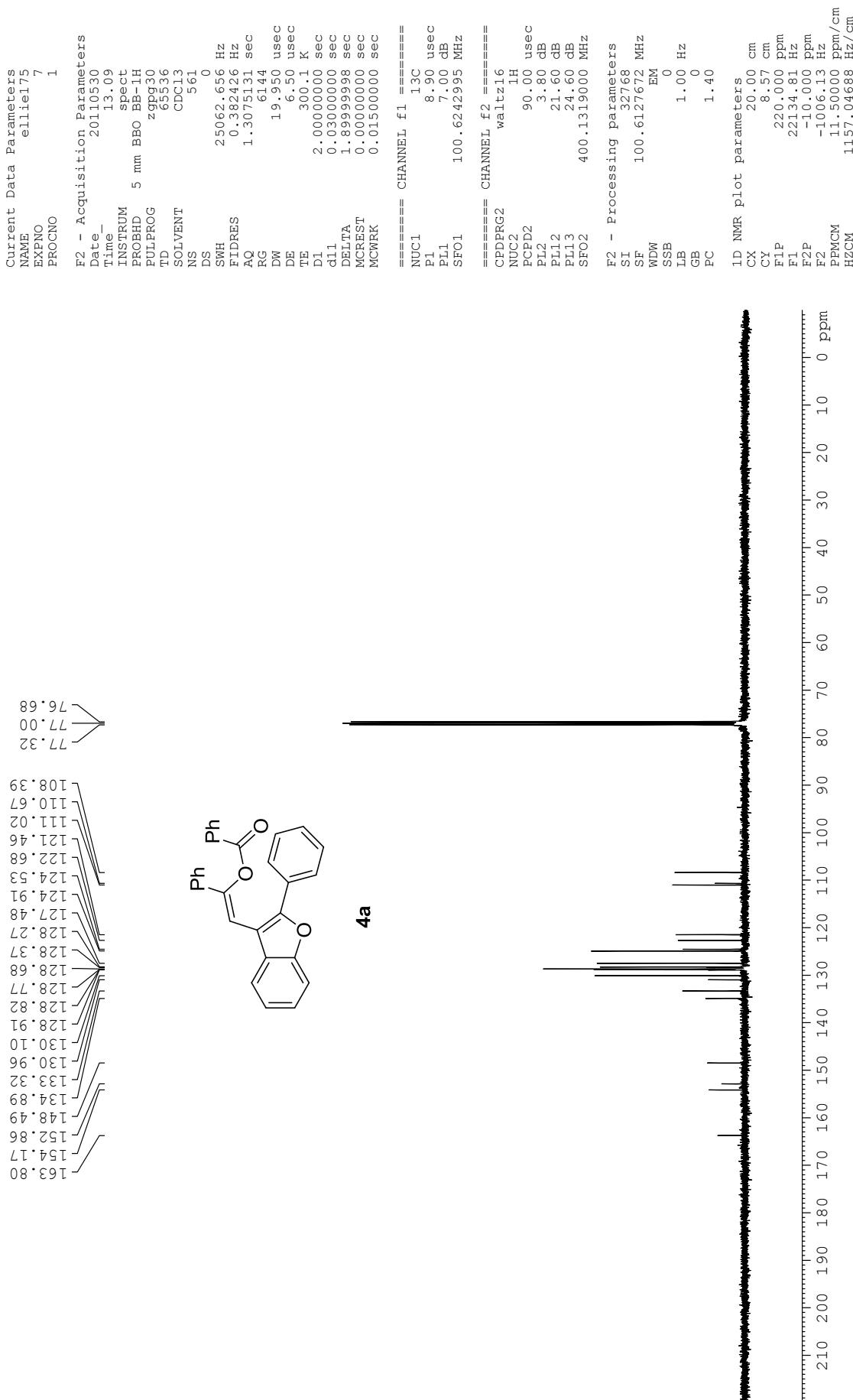
===== CHANNEL f1 =====
NUC1 1H
P1 11.70 usec
PL1 4.00 dB
SFO1 400.1324008 MHz
SI 16384
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

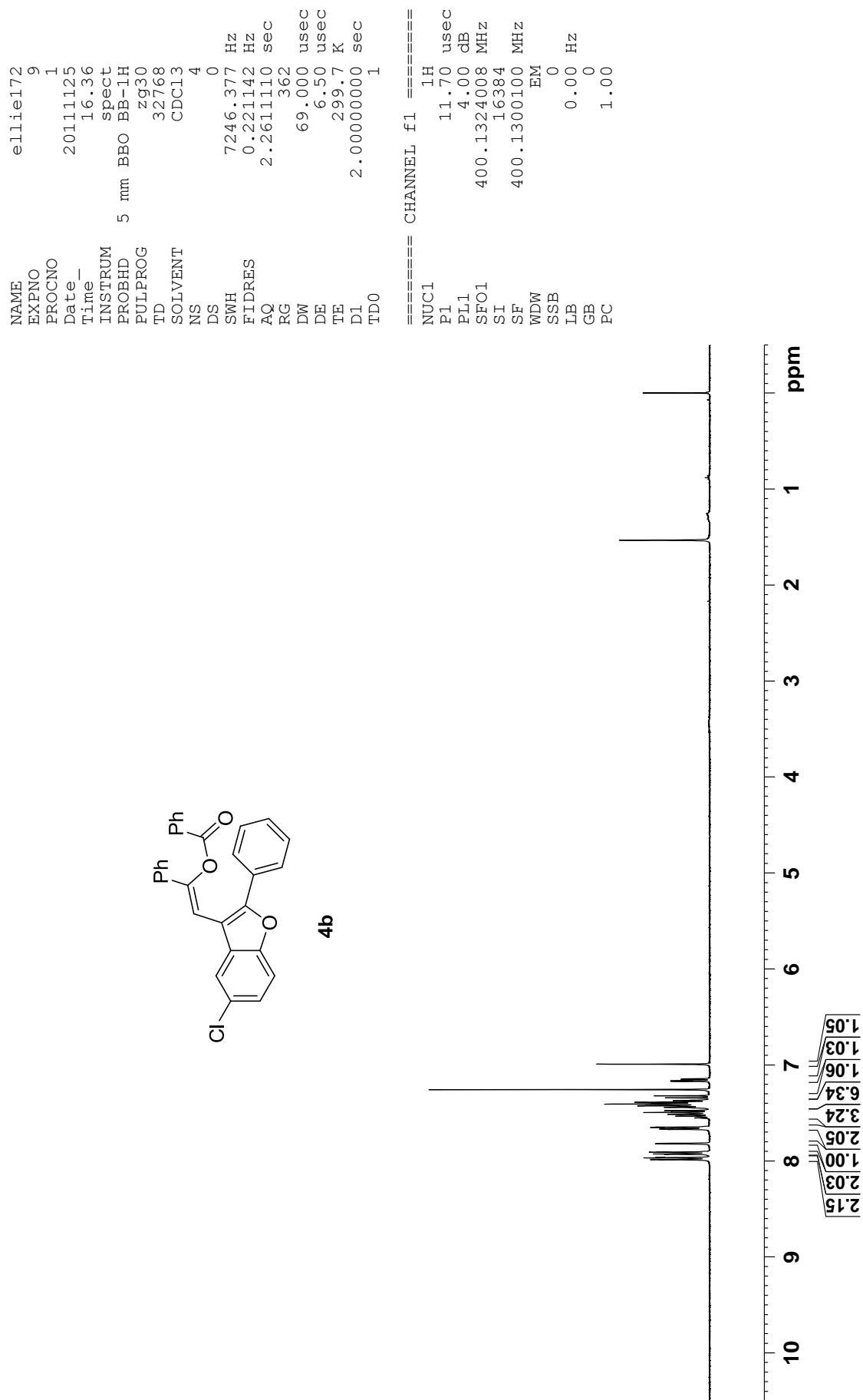
```

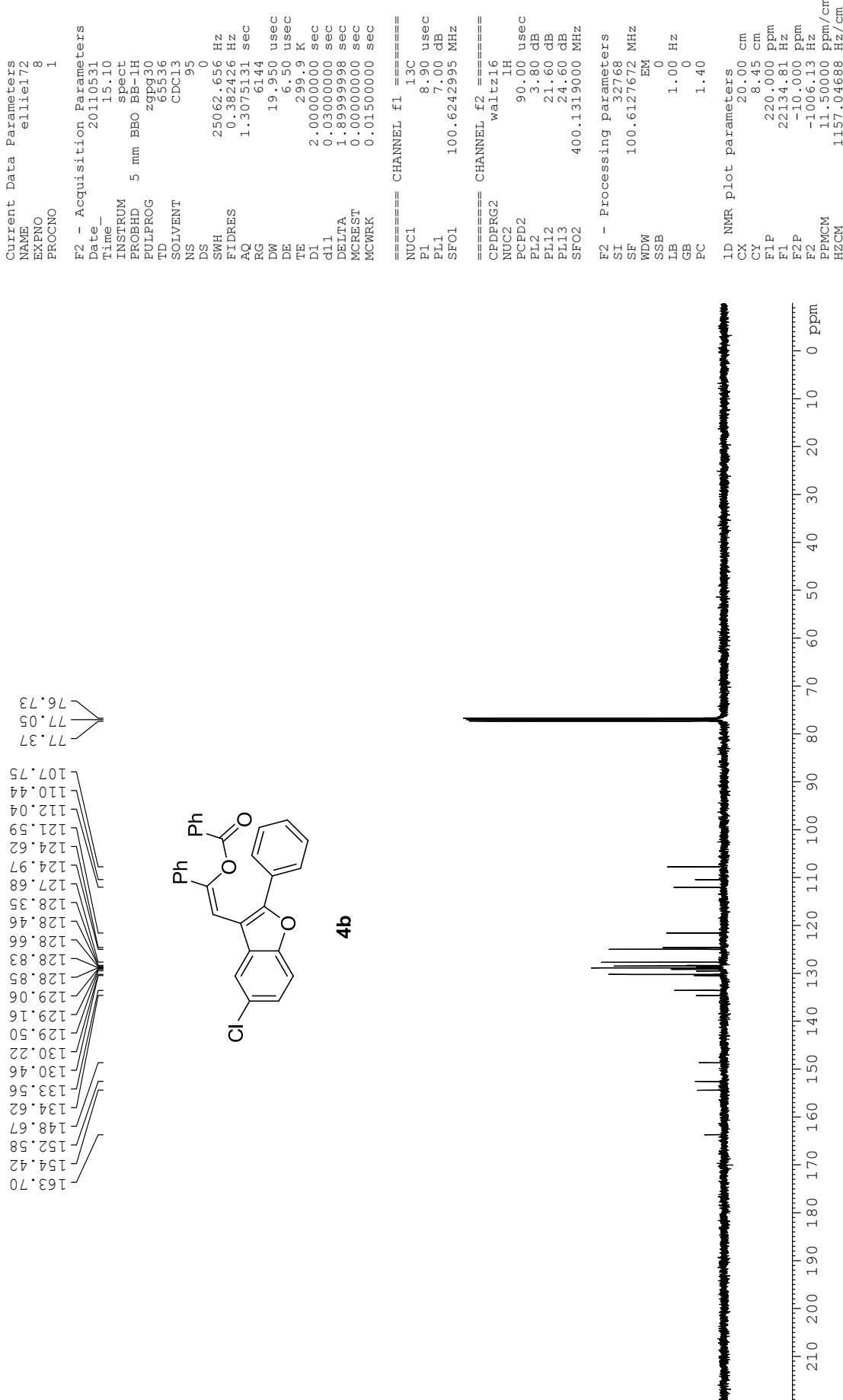


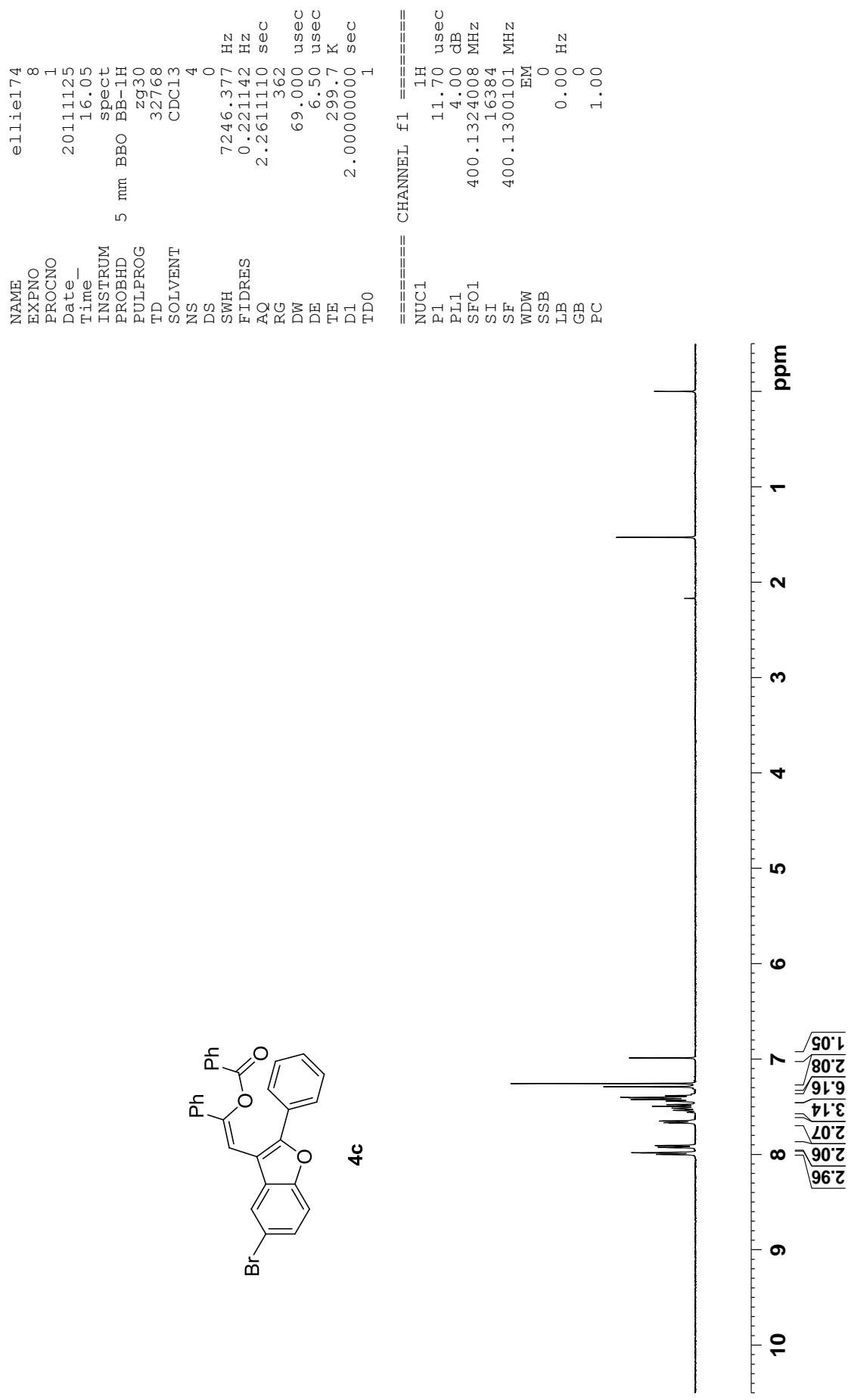
4a

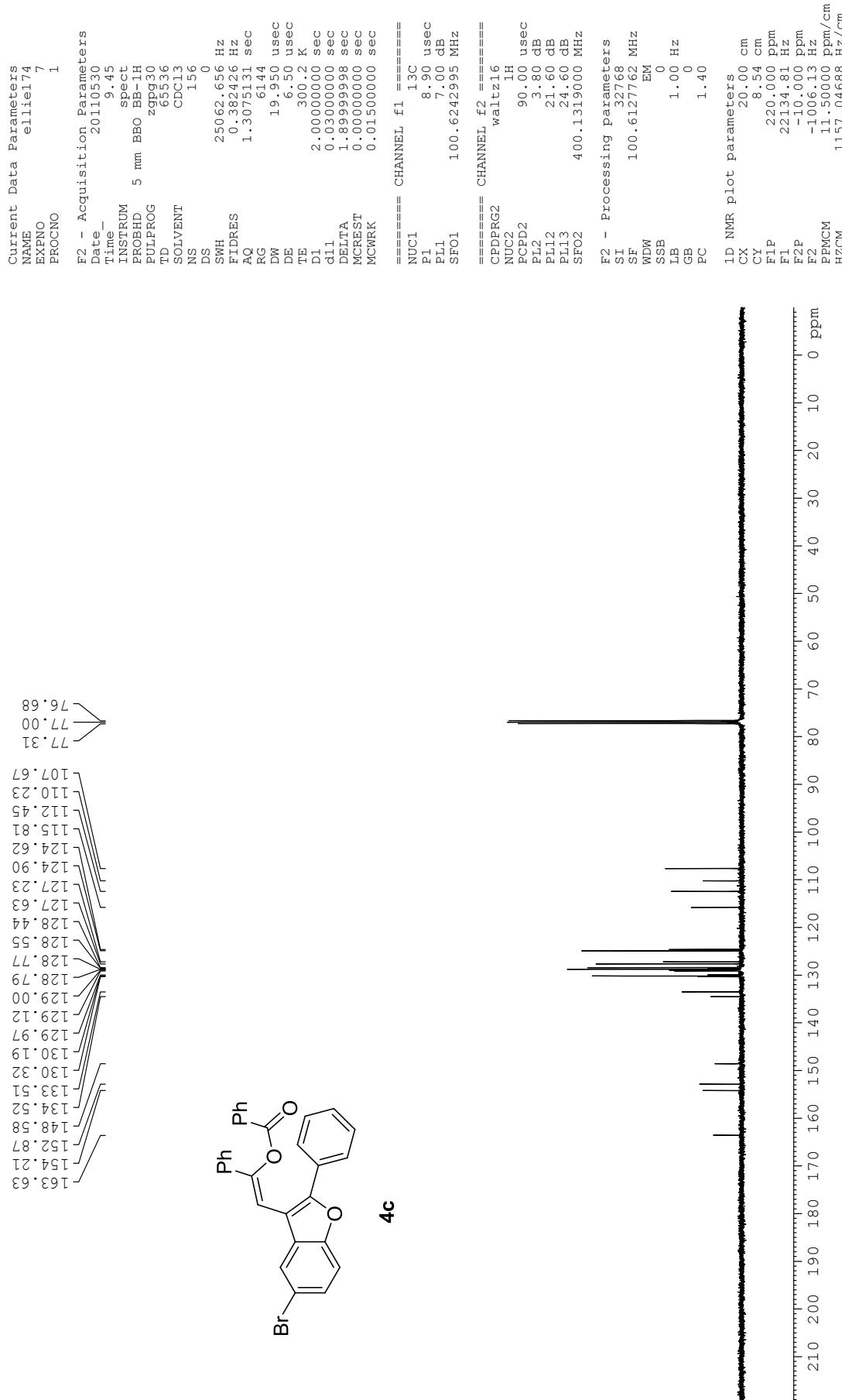


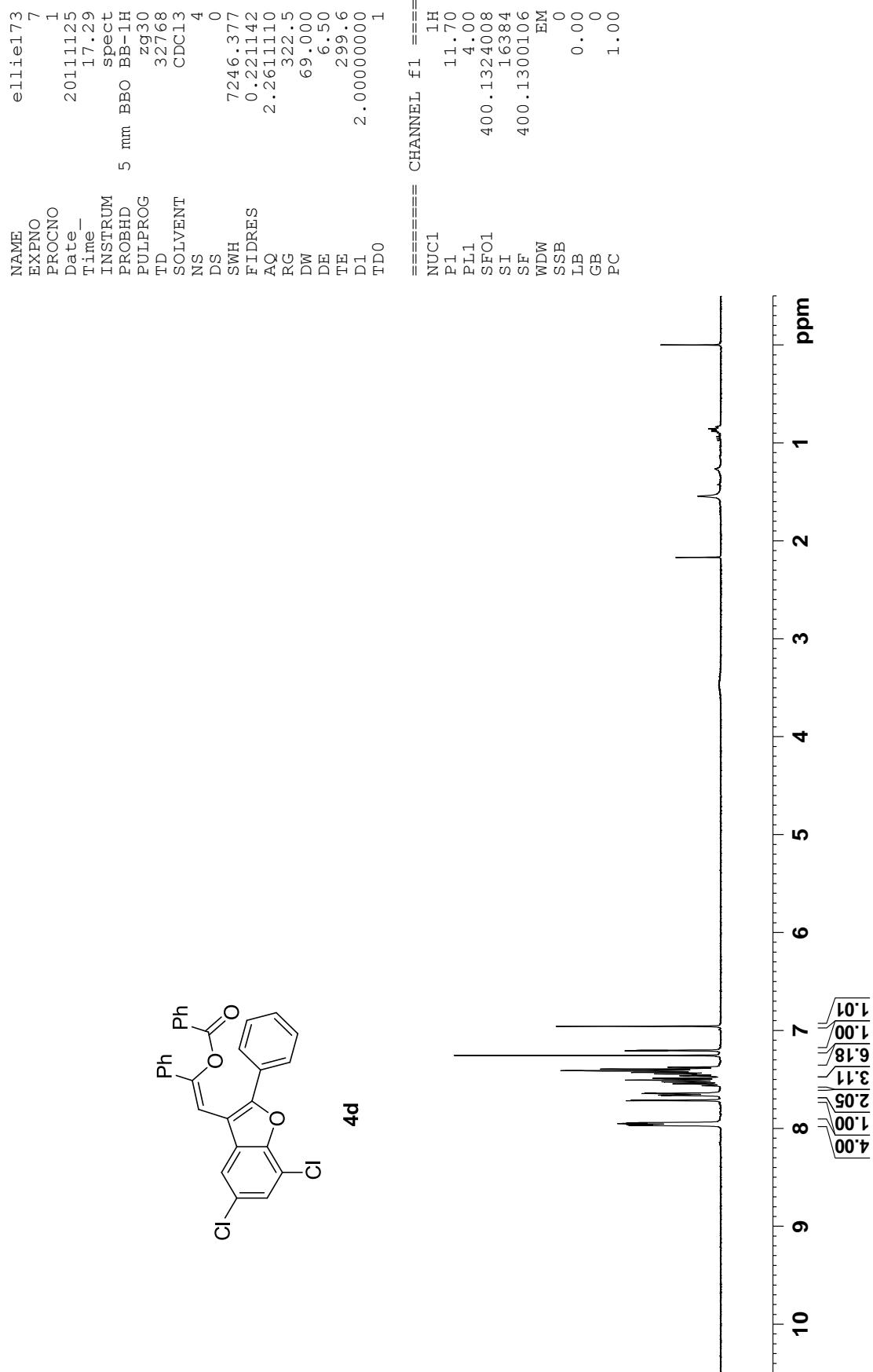


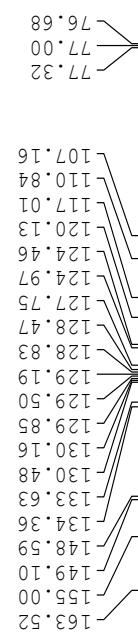












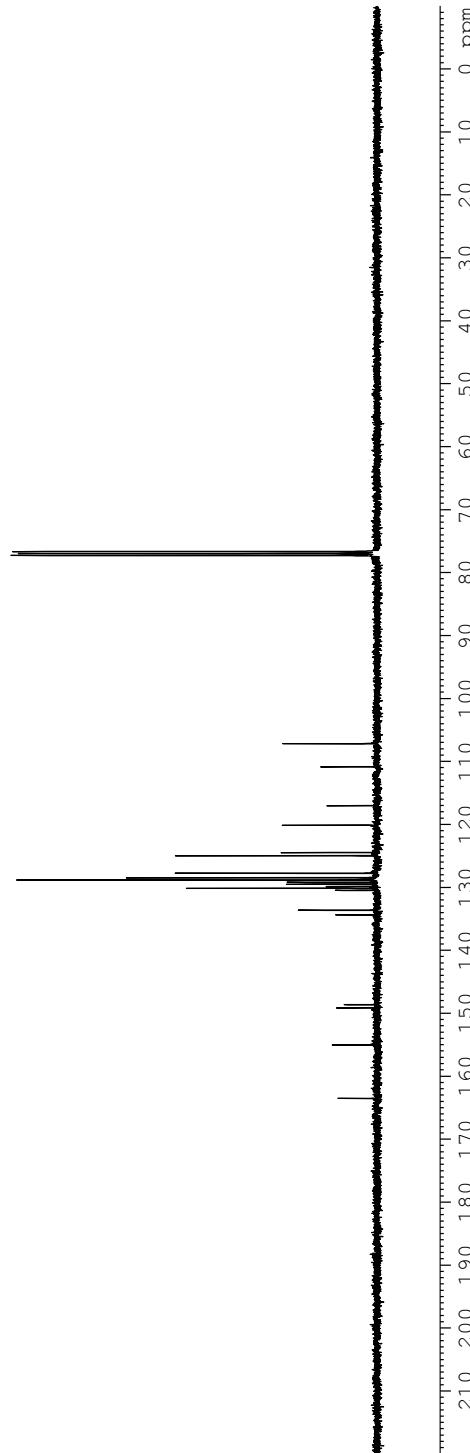
Current Data Parameters
NAME ellie173
EXPNO 6
PROCNO 1

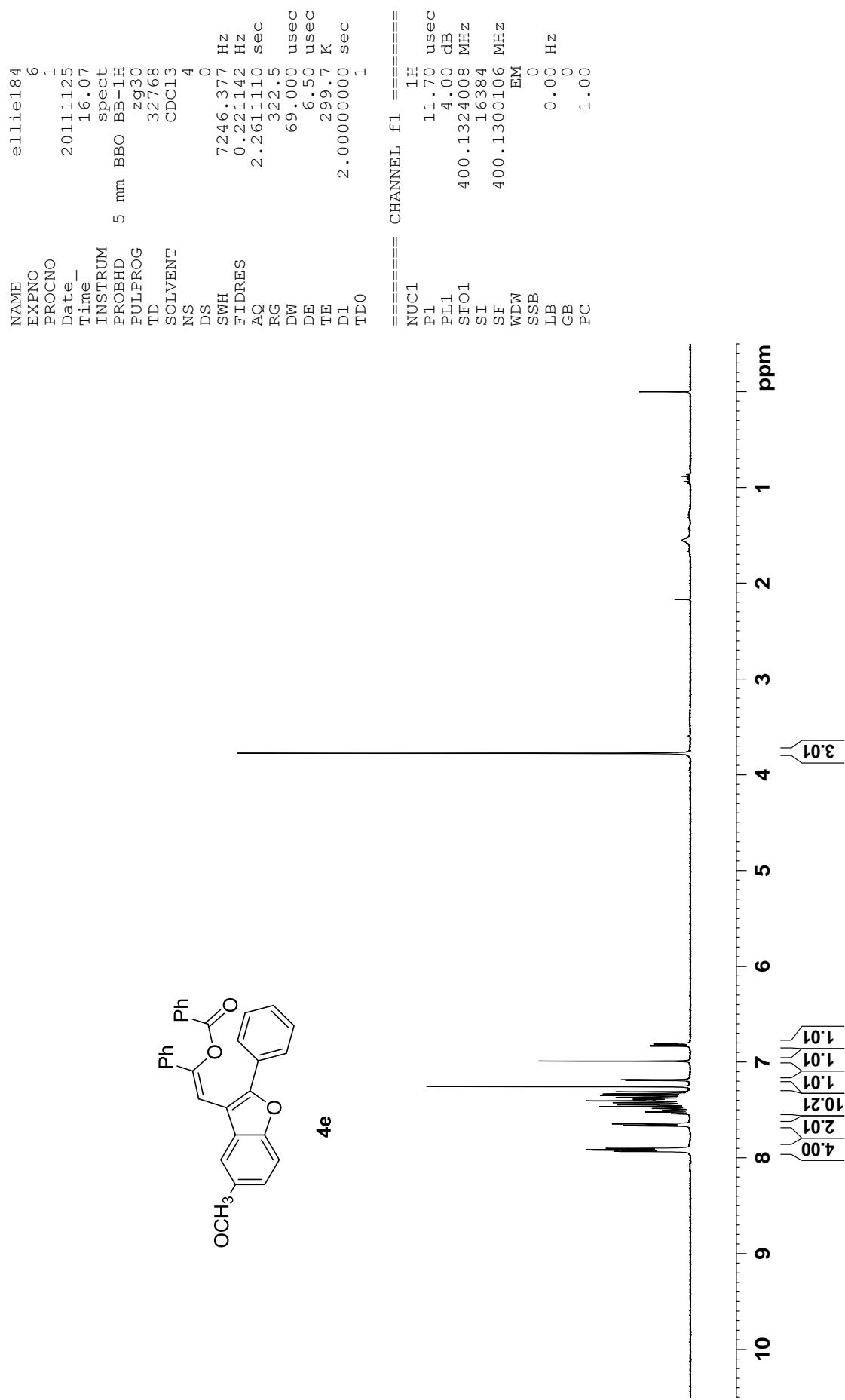
F2 - Acquisition Parameters
Date 20110528
Time 15.48
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG 20ppg30
TD 65536
SOLVENT CDCl₃
NS 231
DS 0
SWH 25062.656 Hz
FIDRES 0.382426 Hz
AQ 1.3075131 sec
RG 6144
DW 19.950 usec
DE 6.50 usec
TE 298.9 K
D1 2.000000 sec
d1 1 0.0300000 sec
DEUTA 1.8999998 sec
MCREST 0.0000000 sec
MCRK 0.0150000 sec

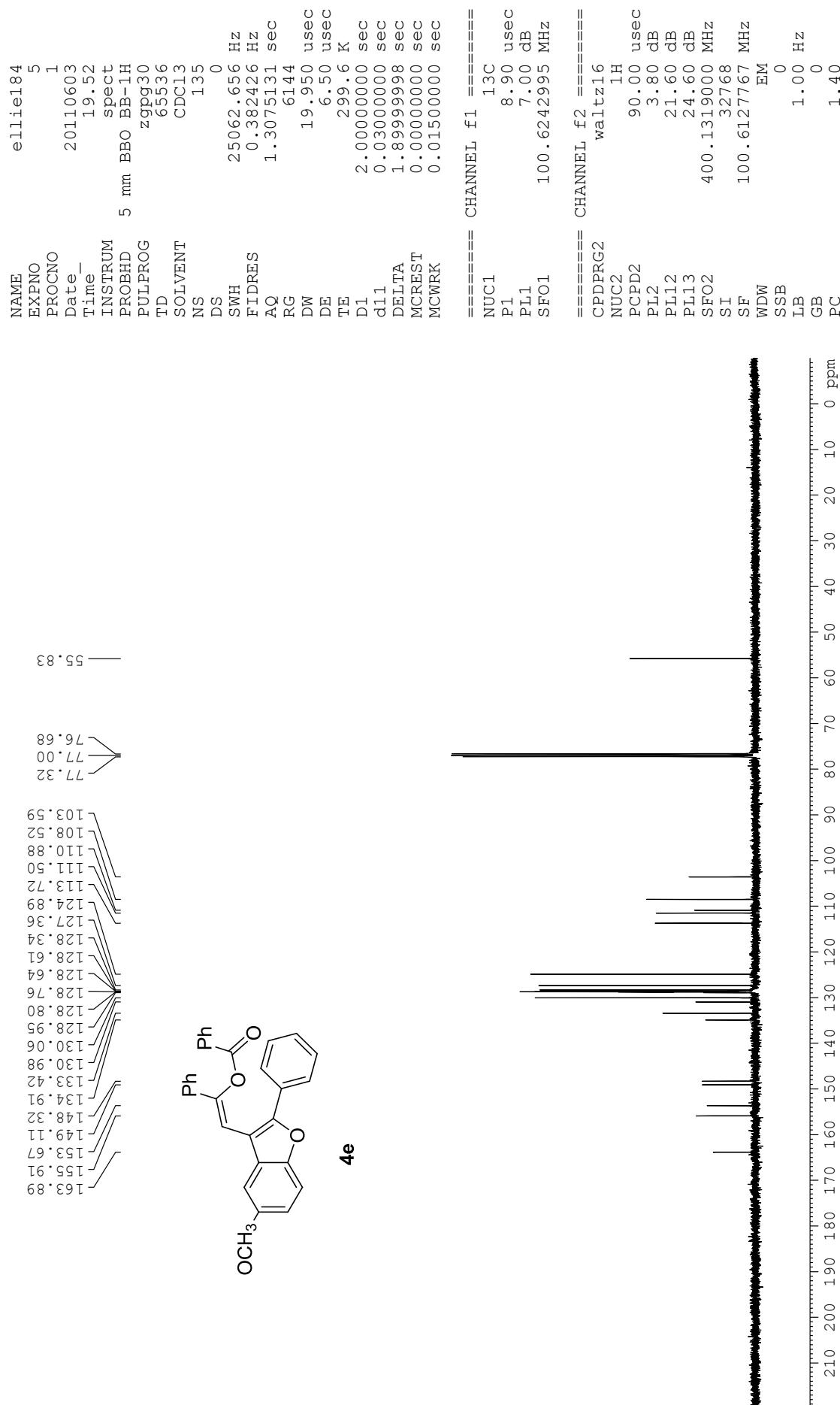
===== CHANNEL f1 =====
NUC1 13C
P1 8.90 usec
PL1 7.00 dB
SF01 100.6242995 MHz

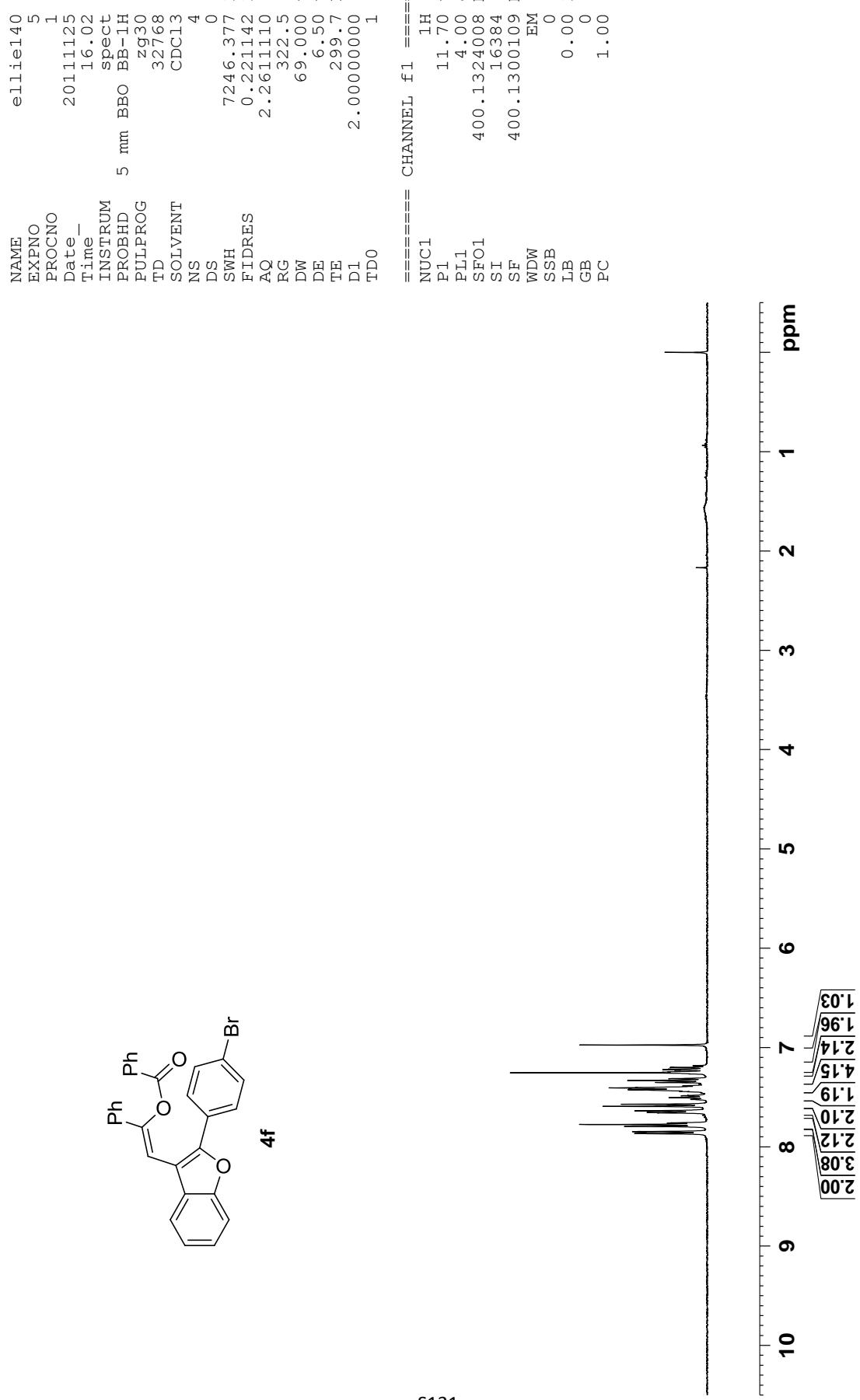
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 3.80 dB
PL12 21.60 dB
PL13 24.60 dB
SF02 400.139000 MHz

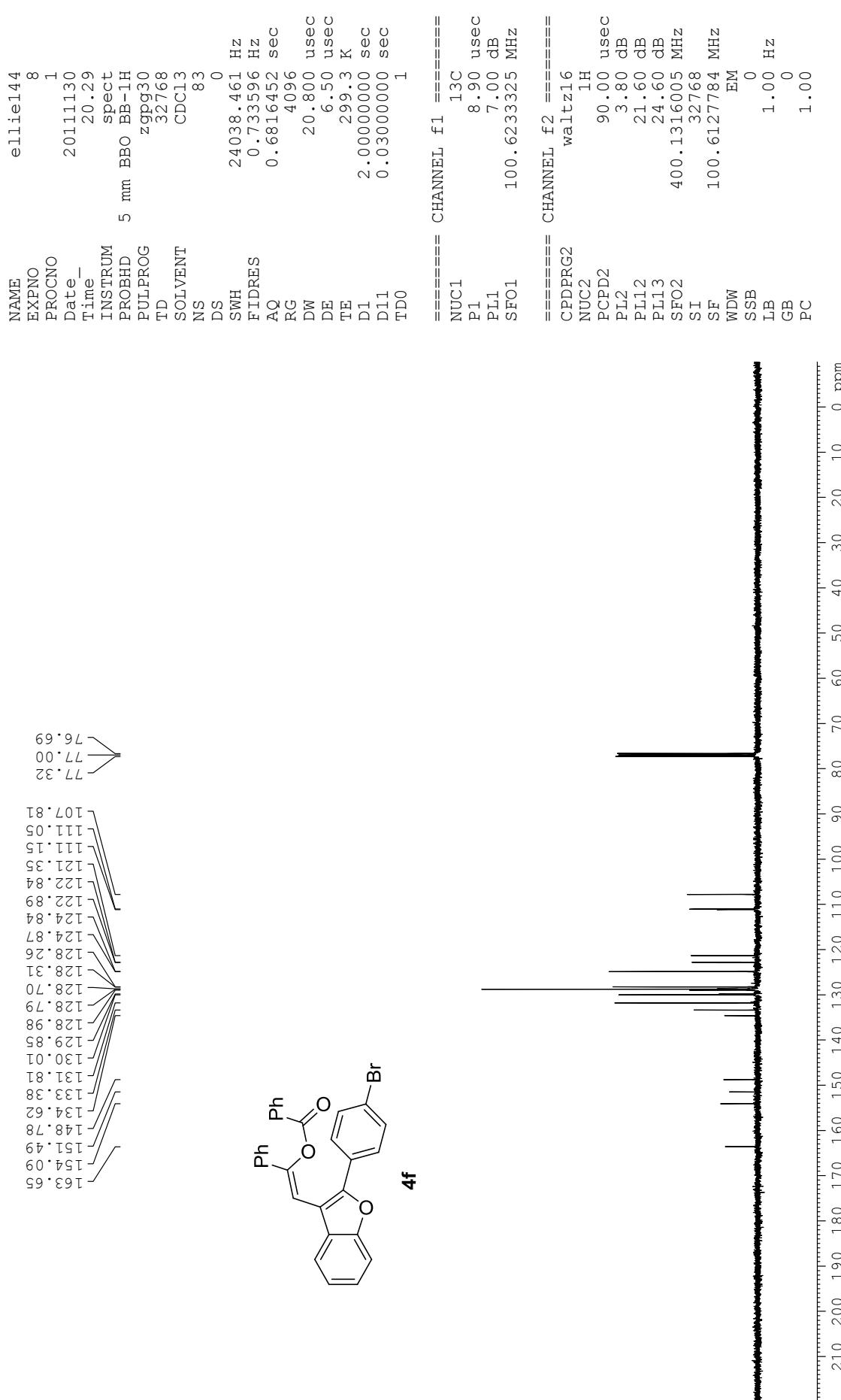
F2 - Processing parameters
SI 32768
SF 100.6127672 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

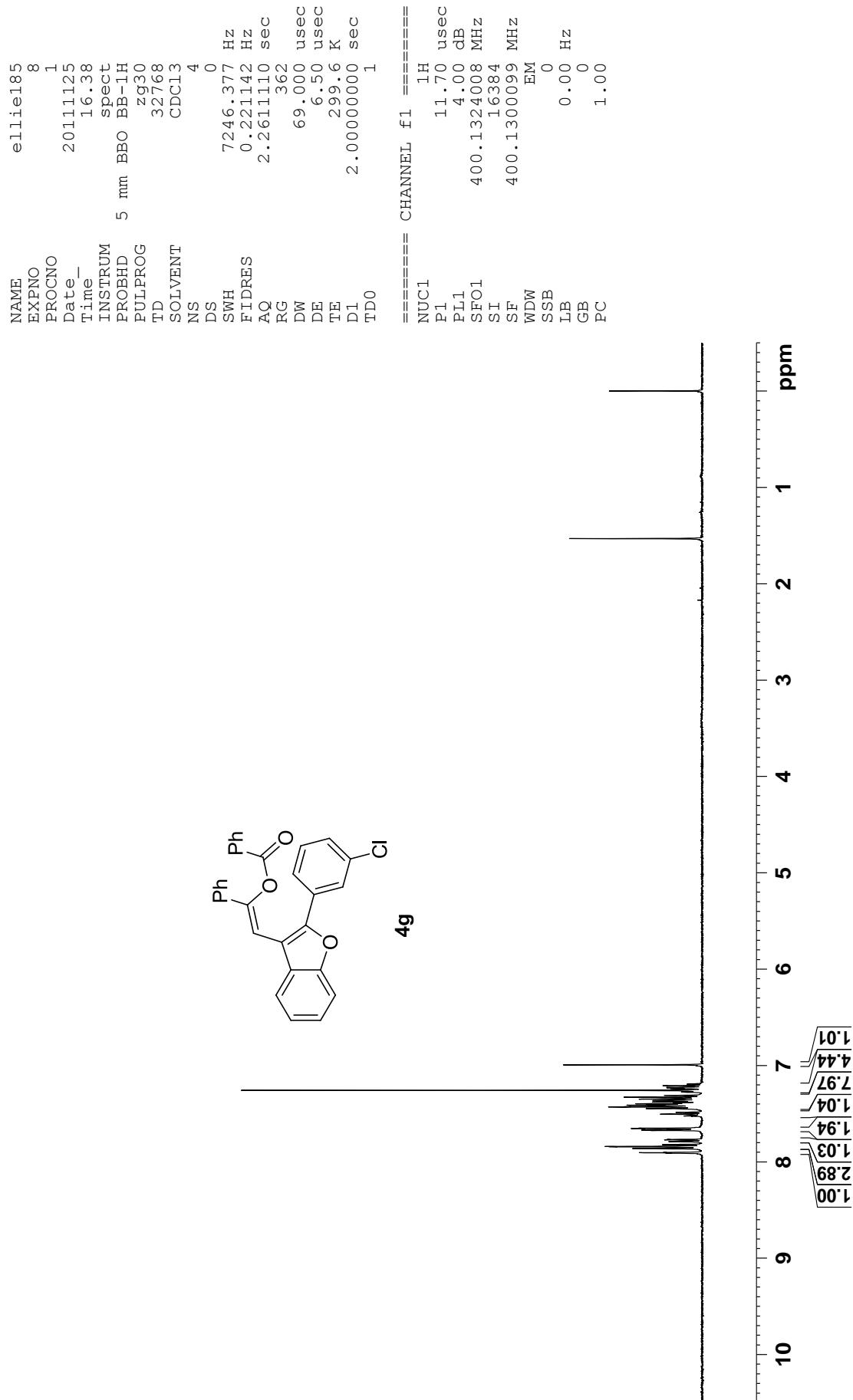


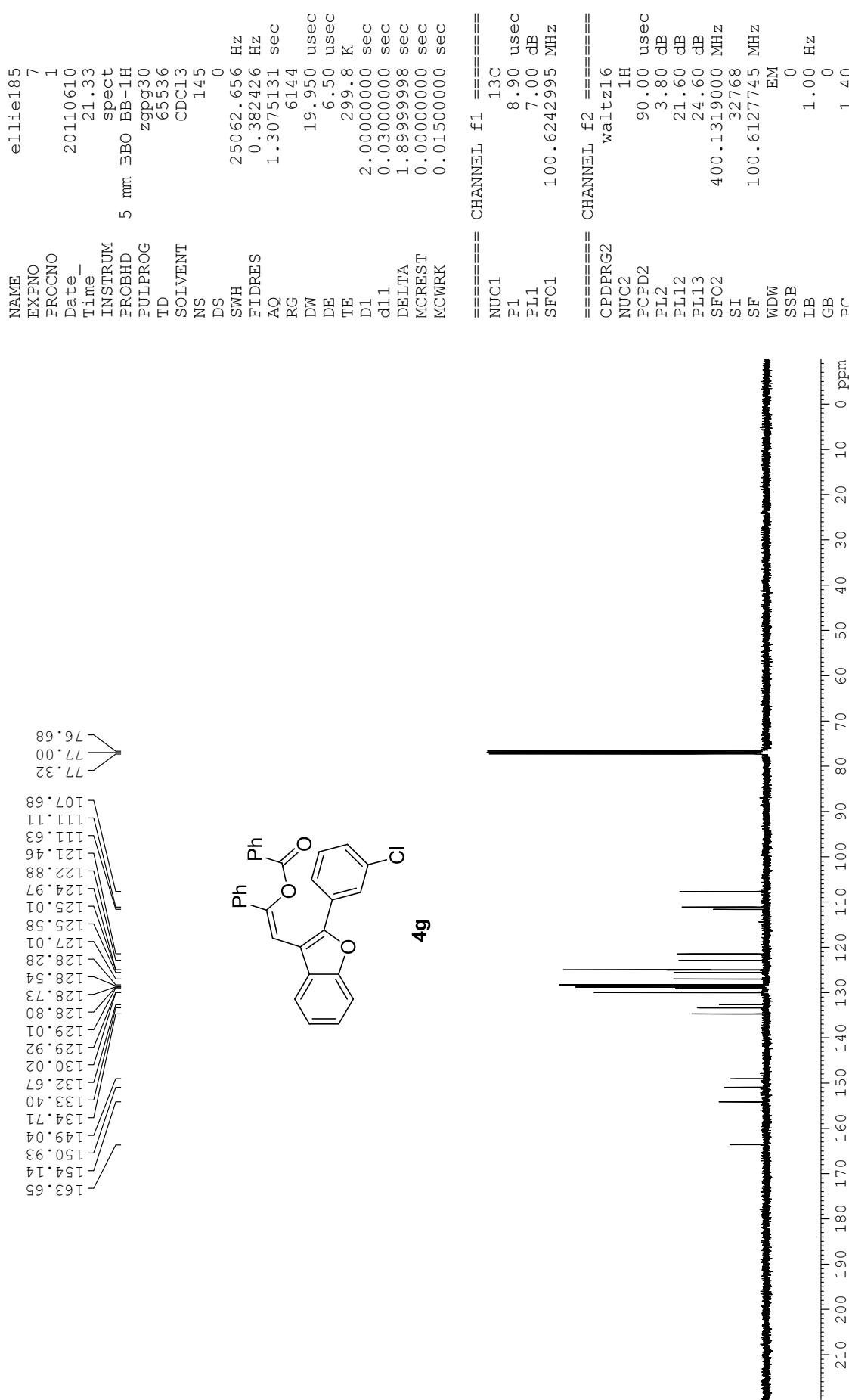


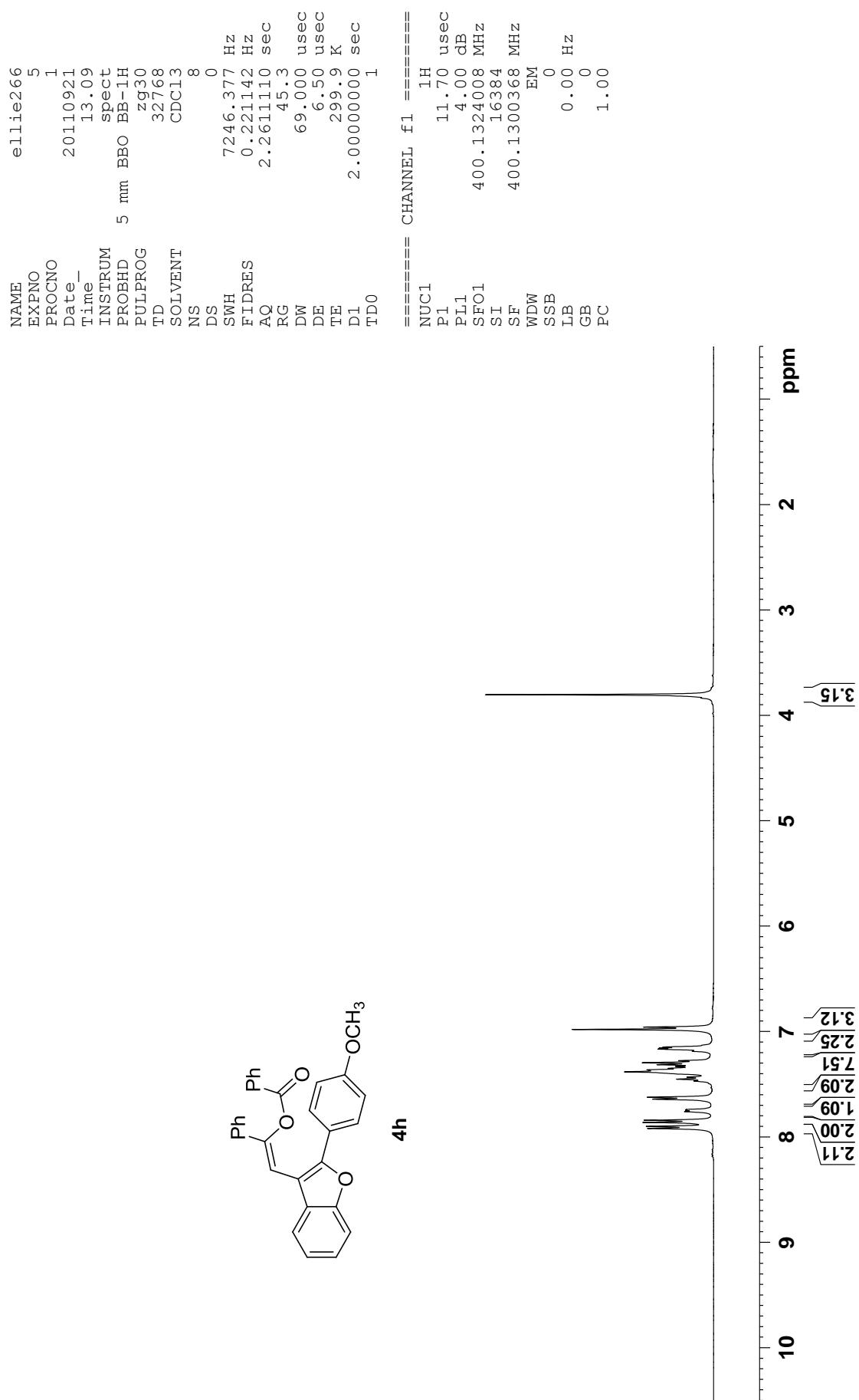


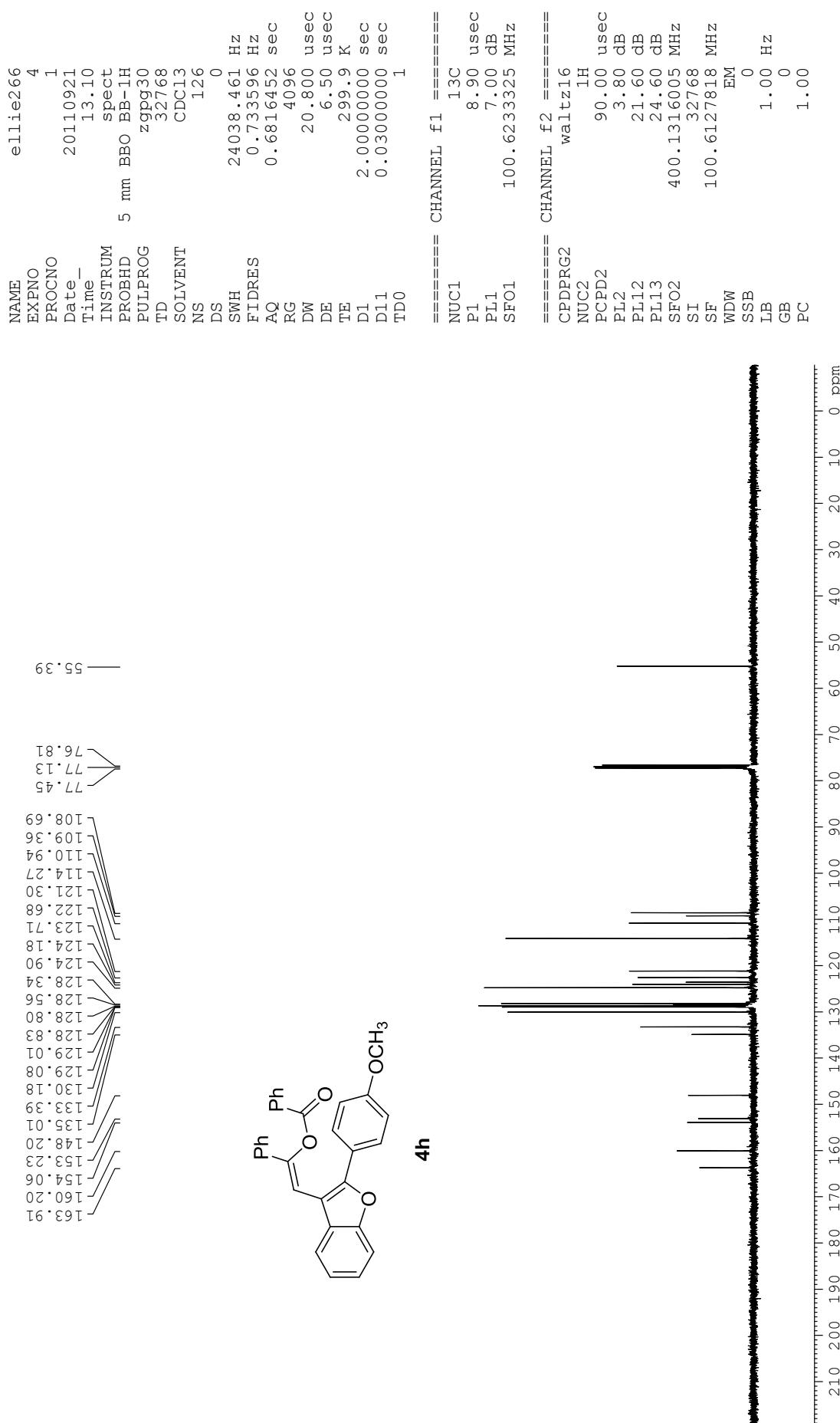


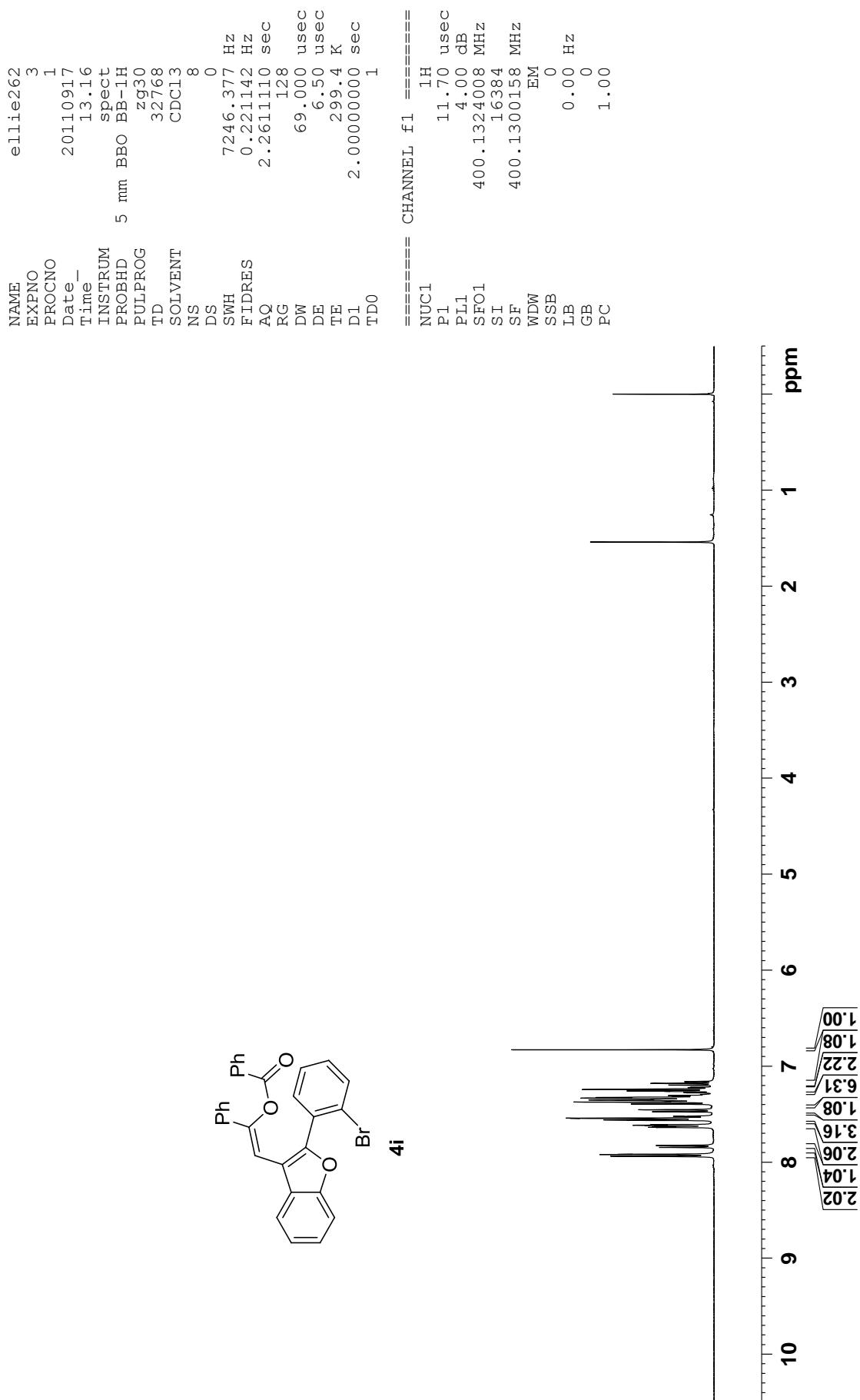


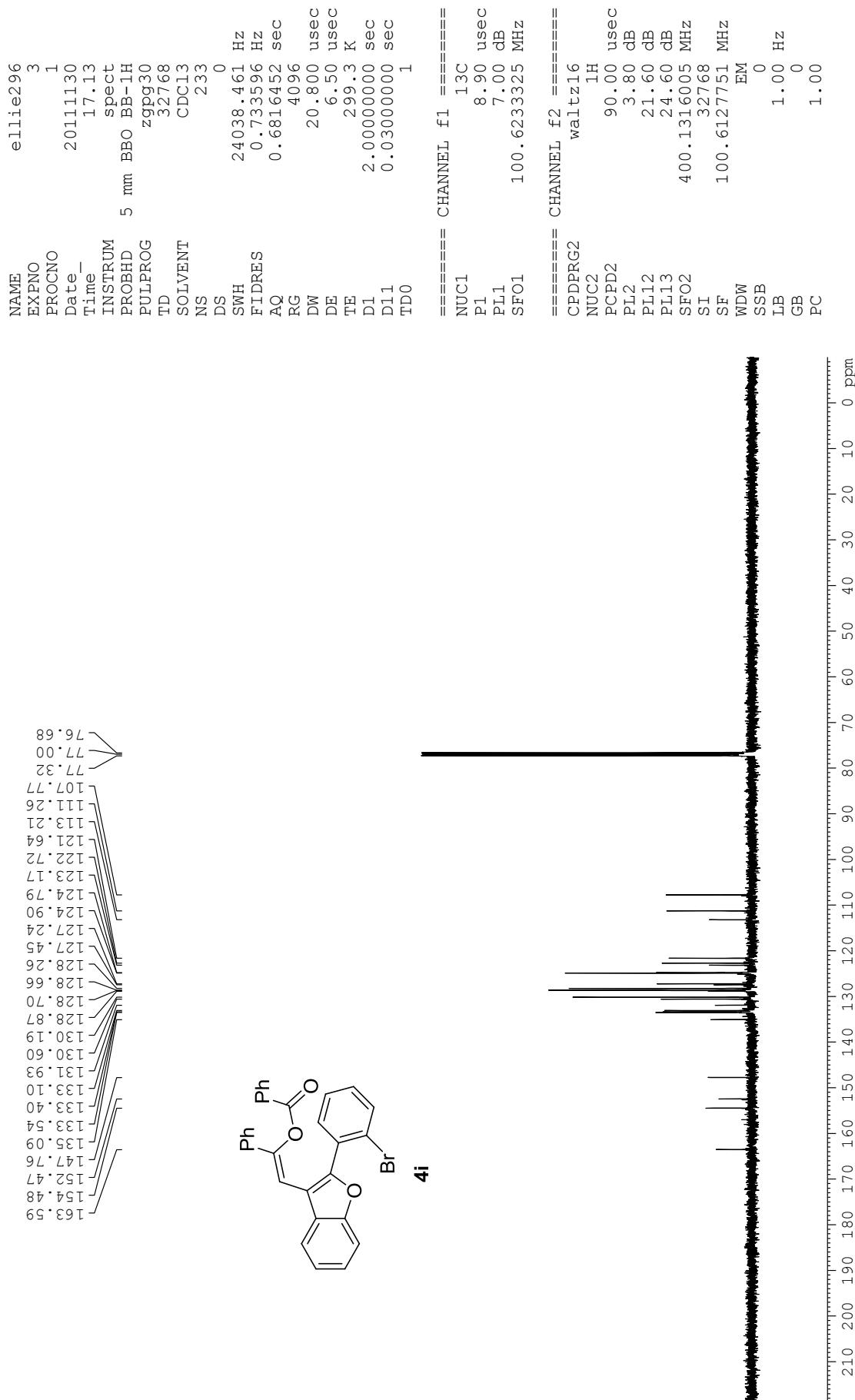


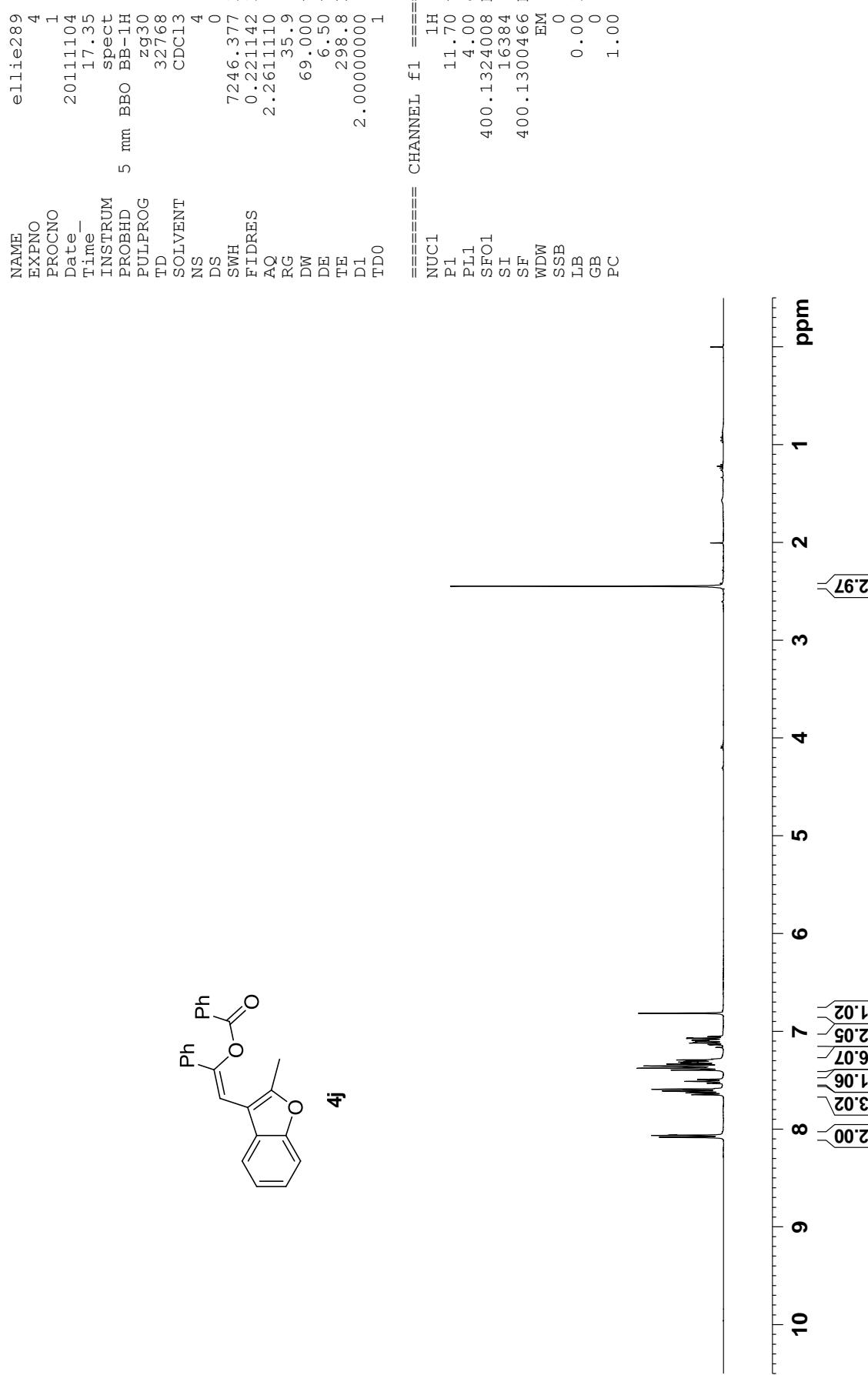


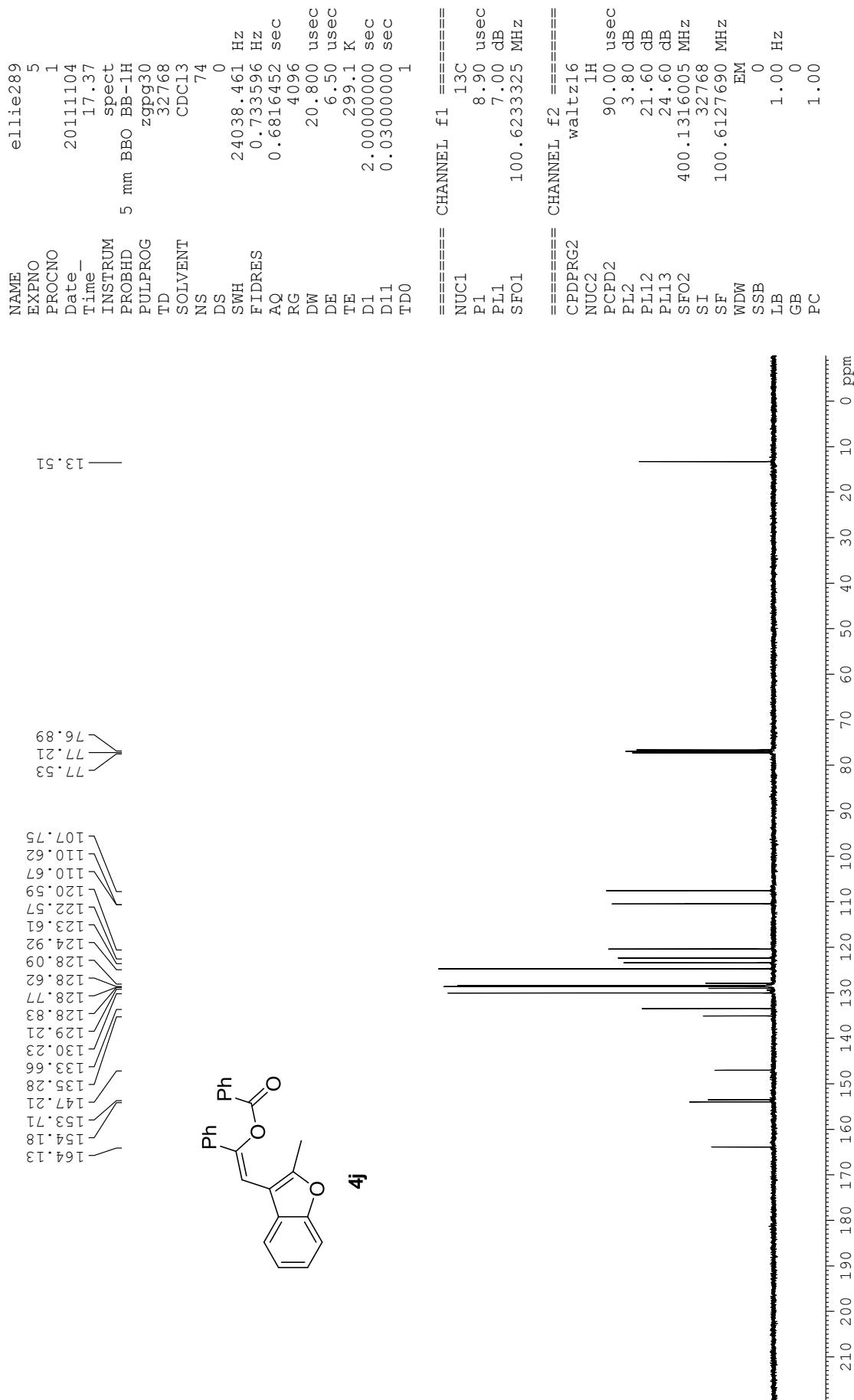


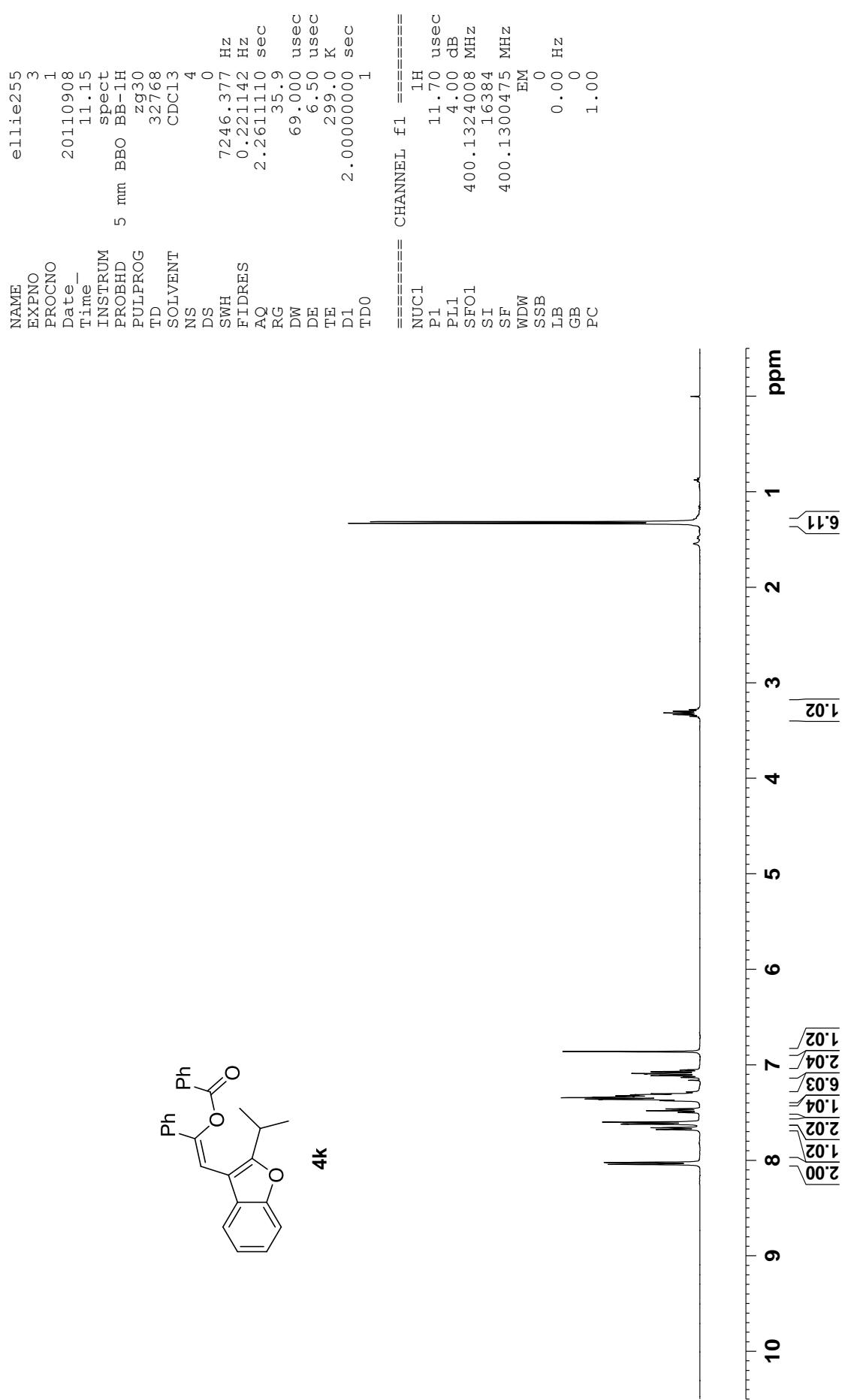


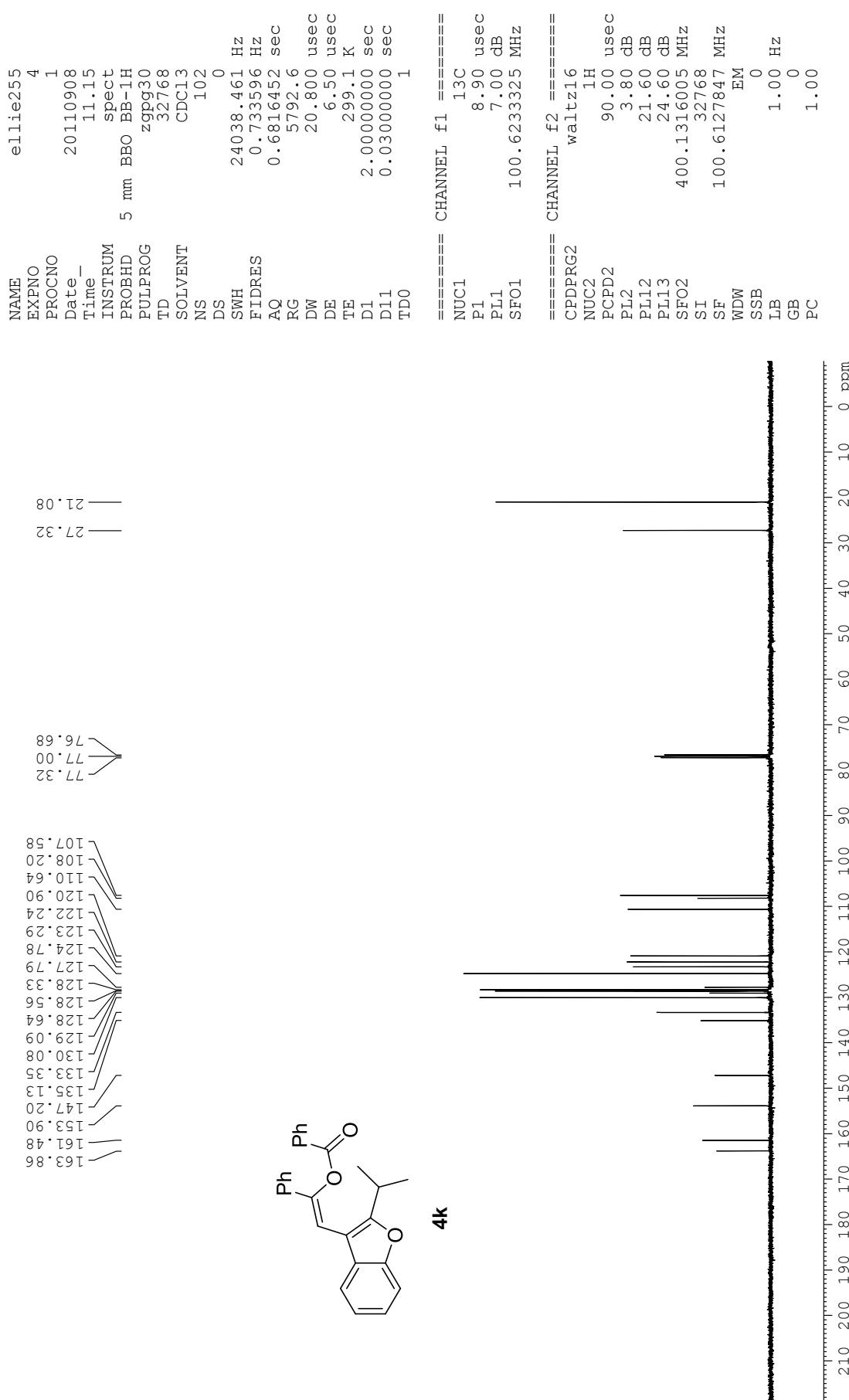


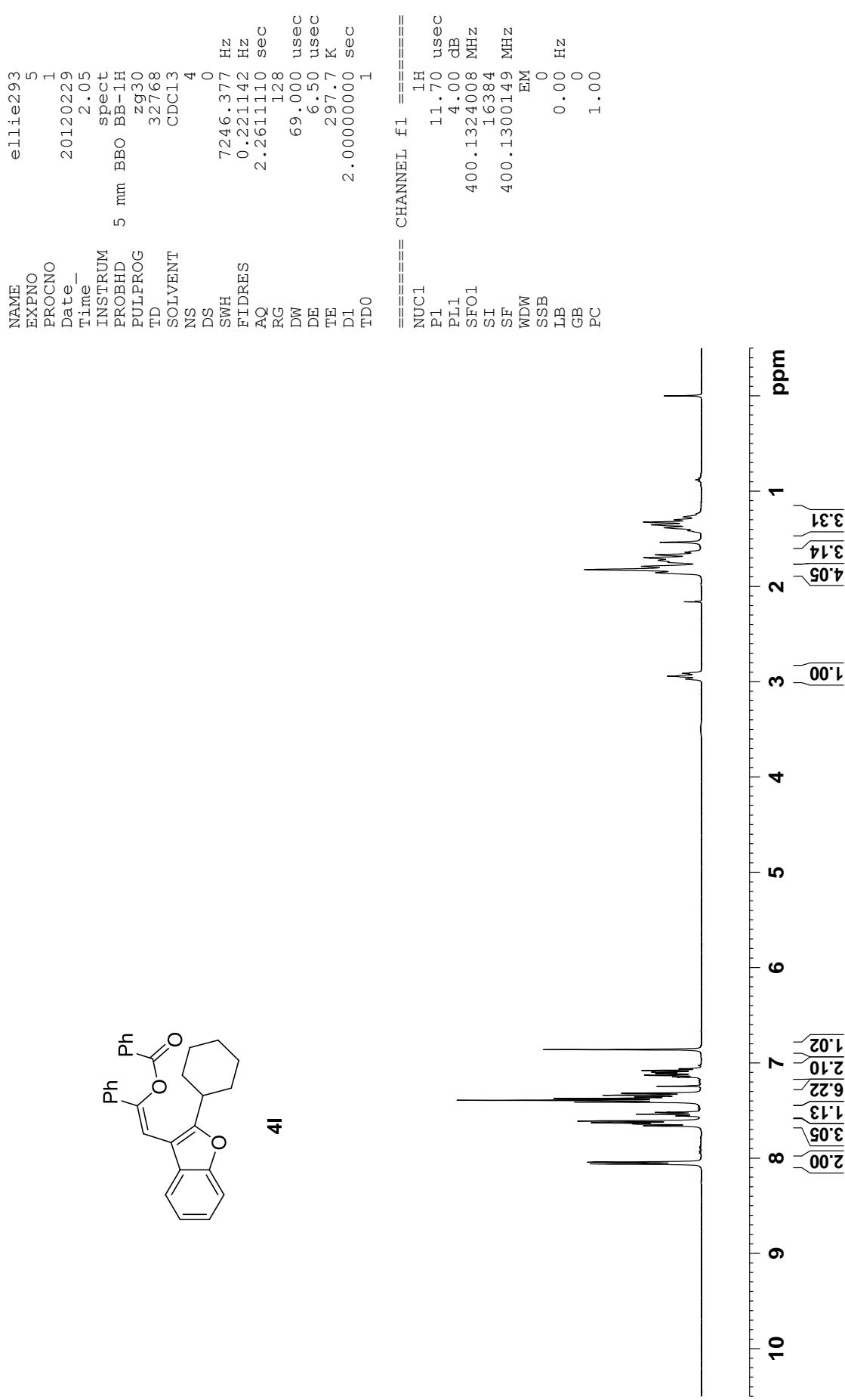


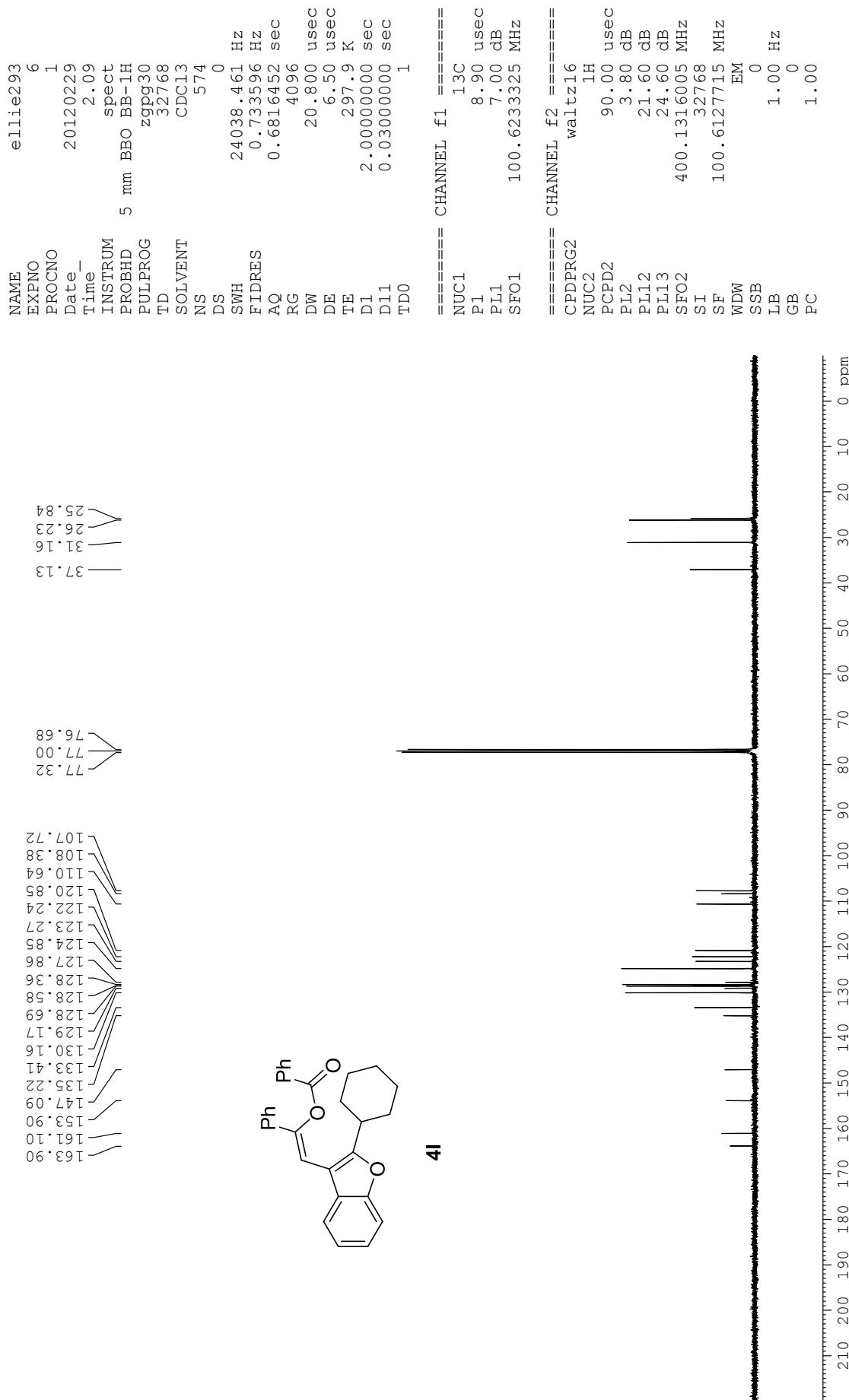


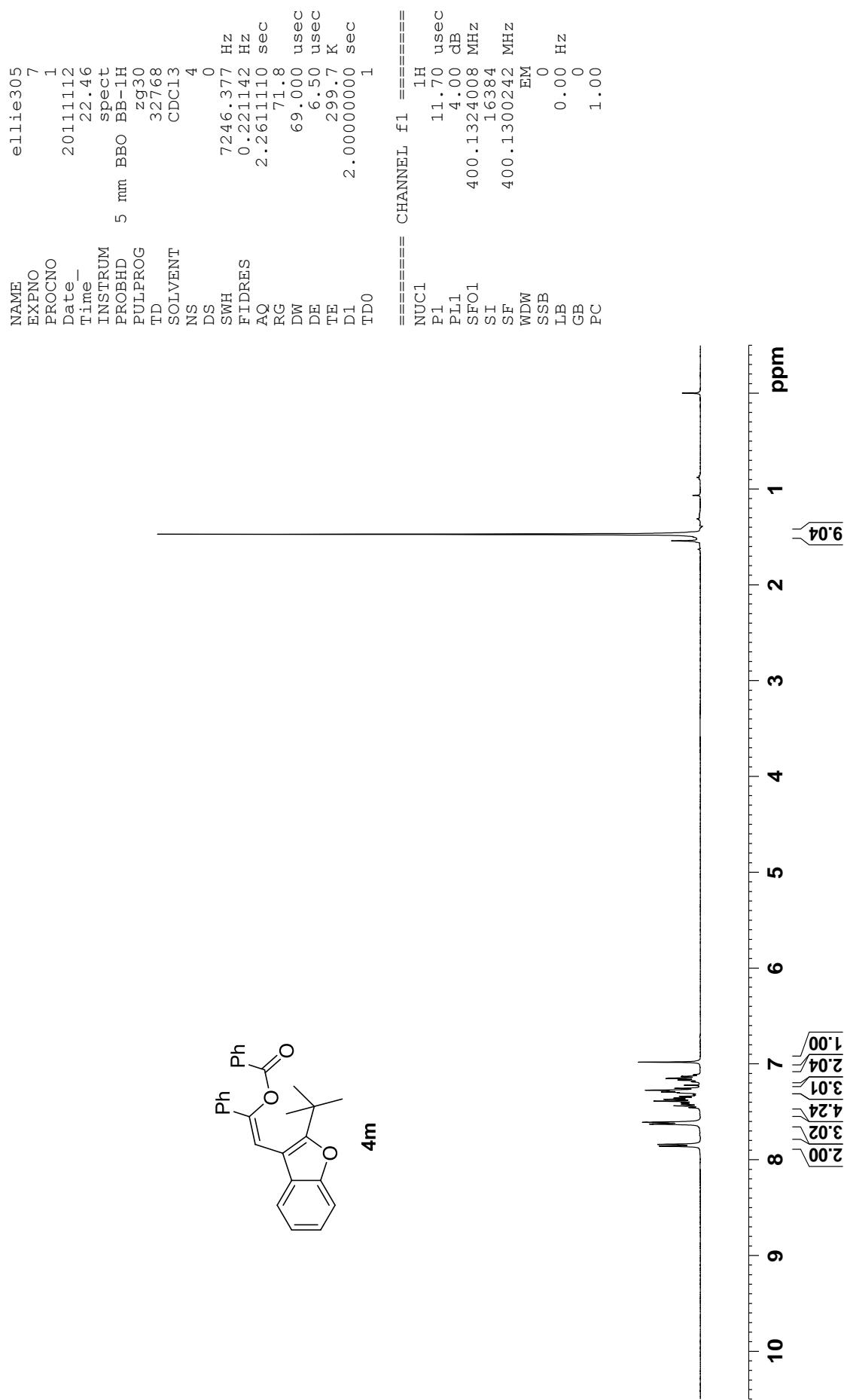


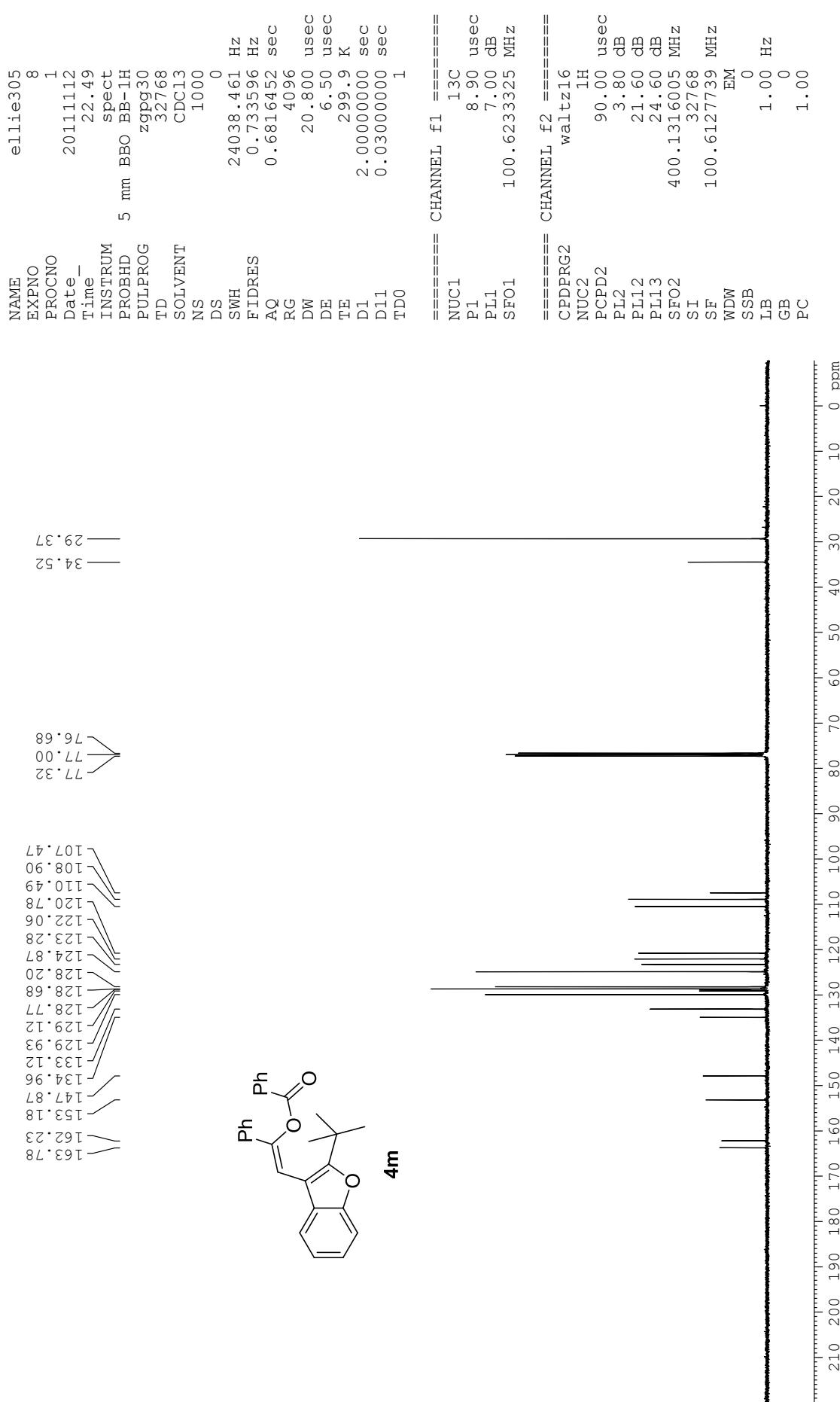


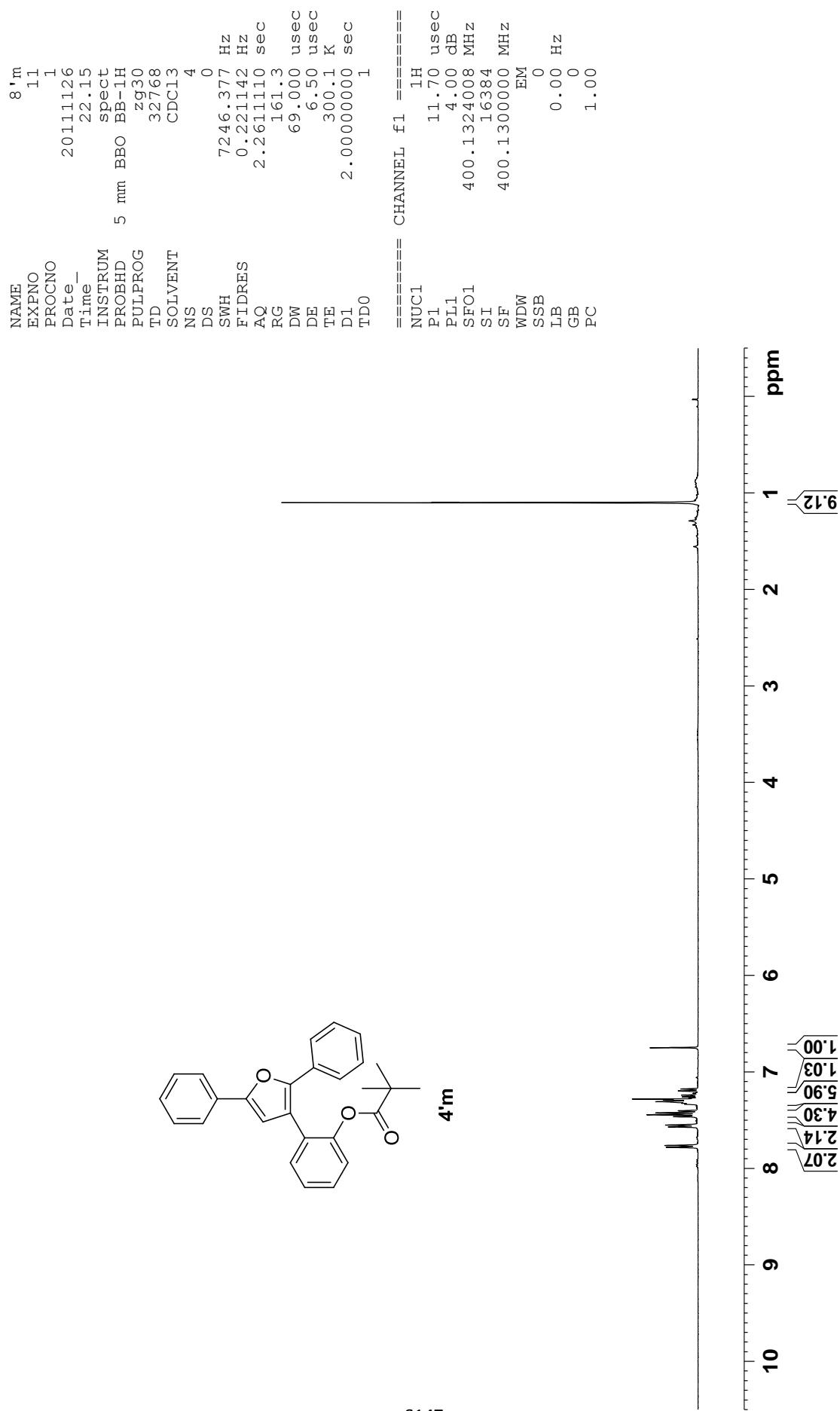


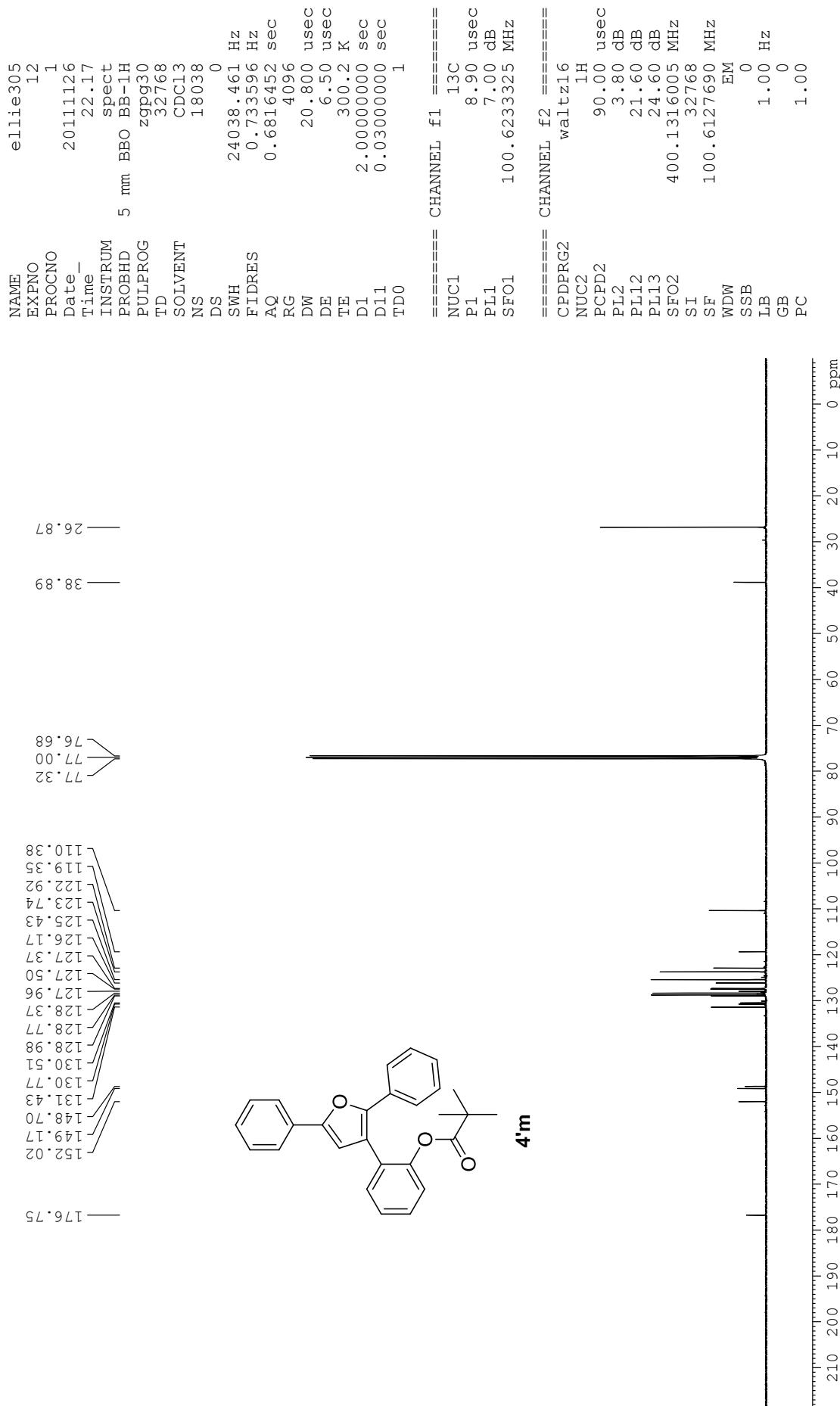


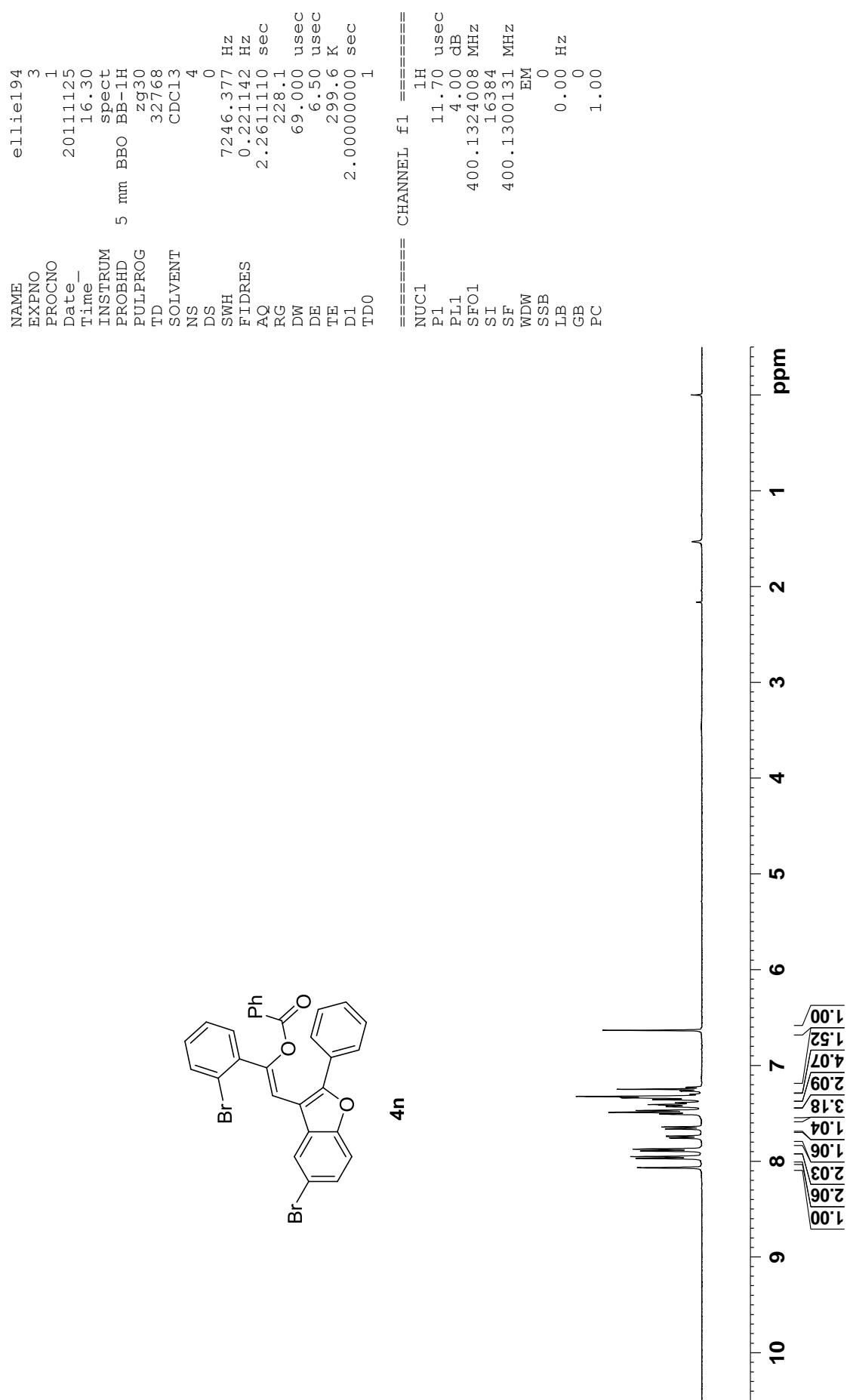


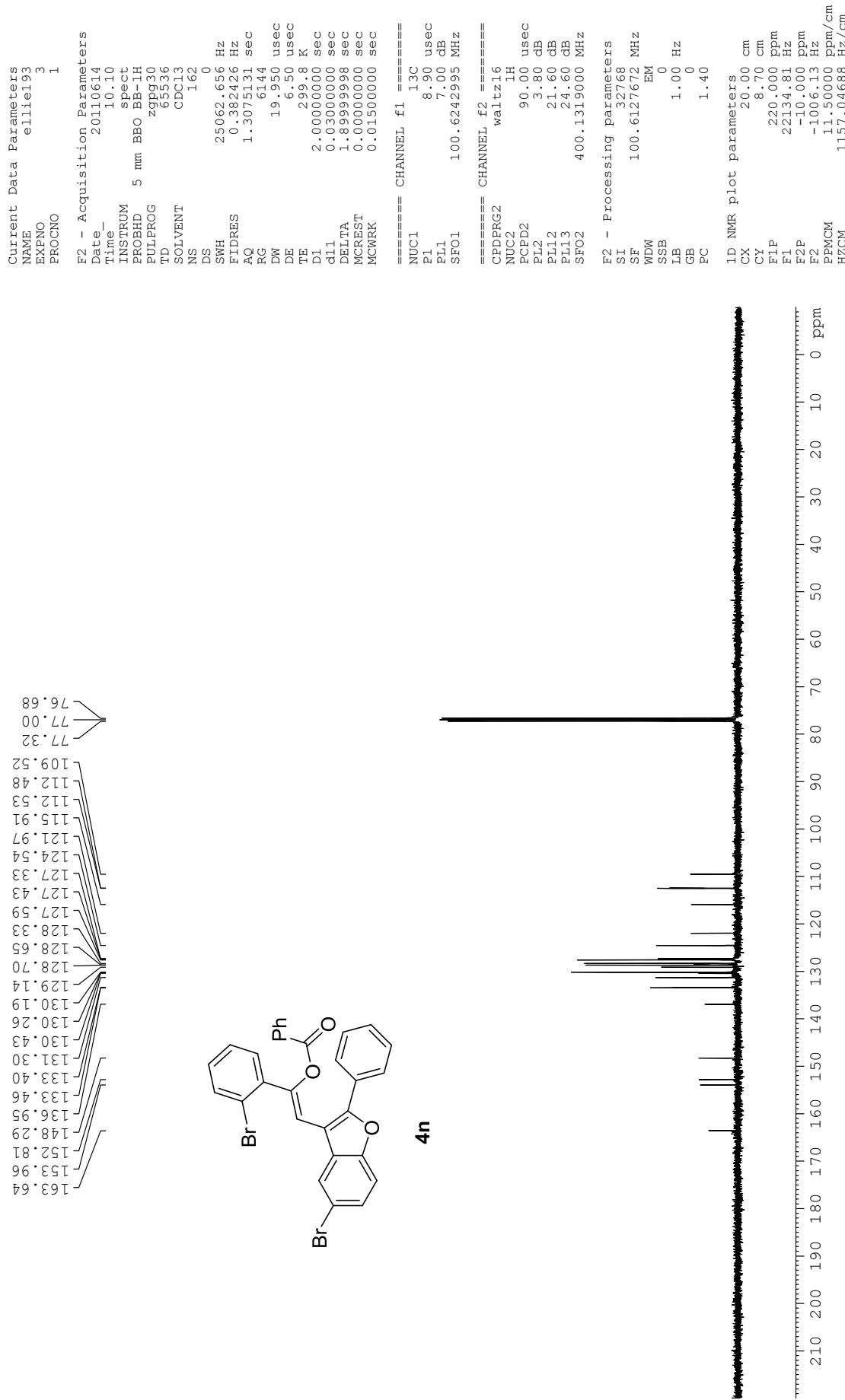


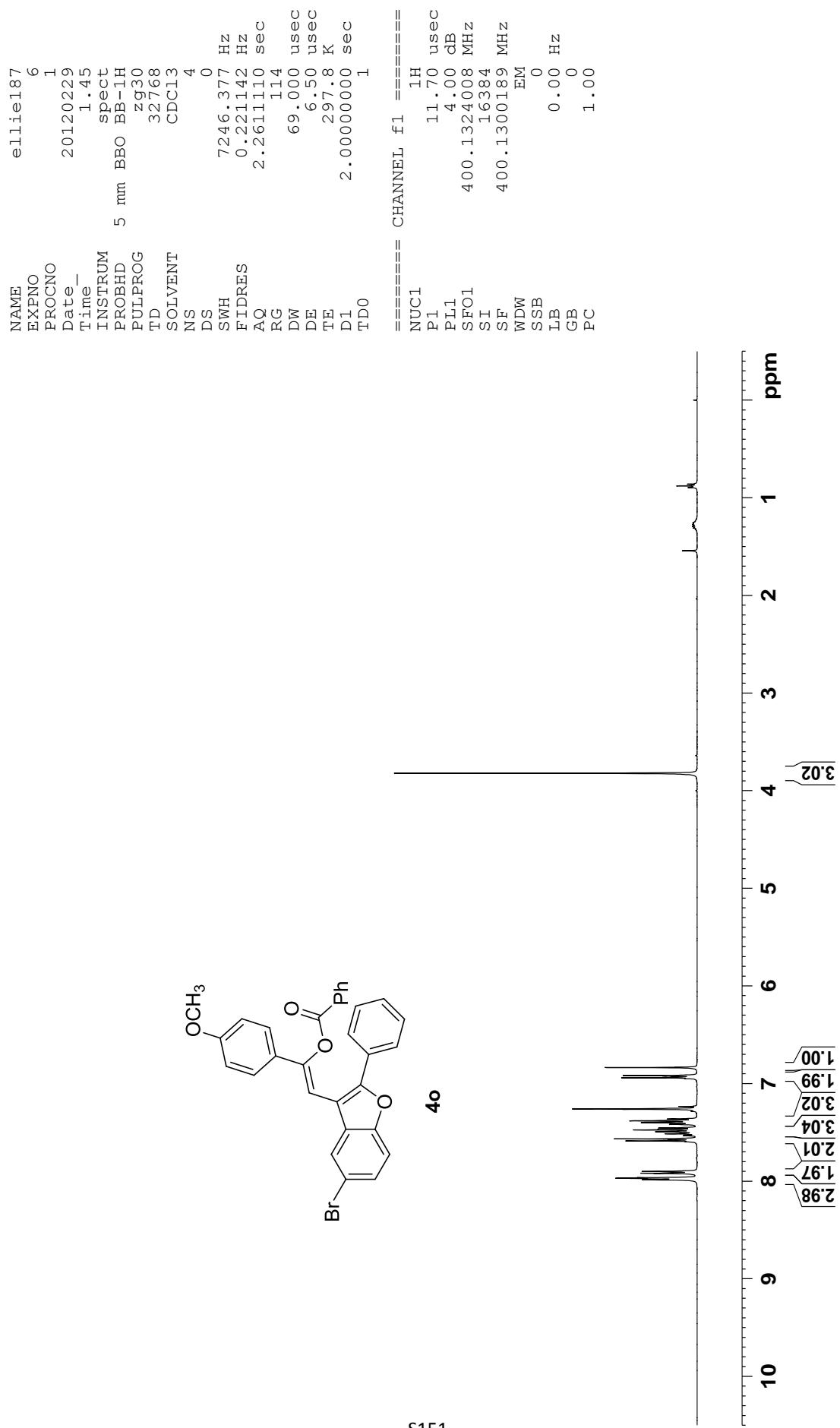


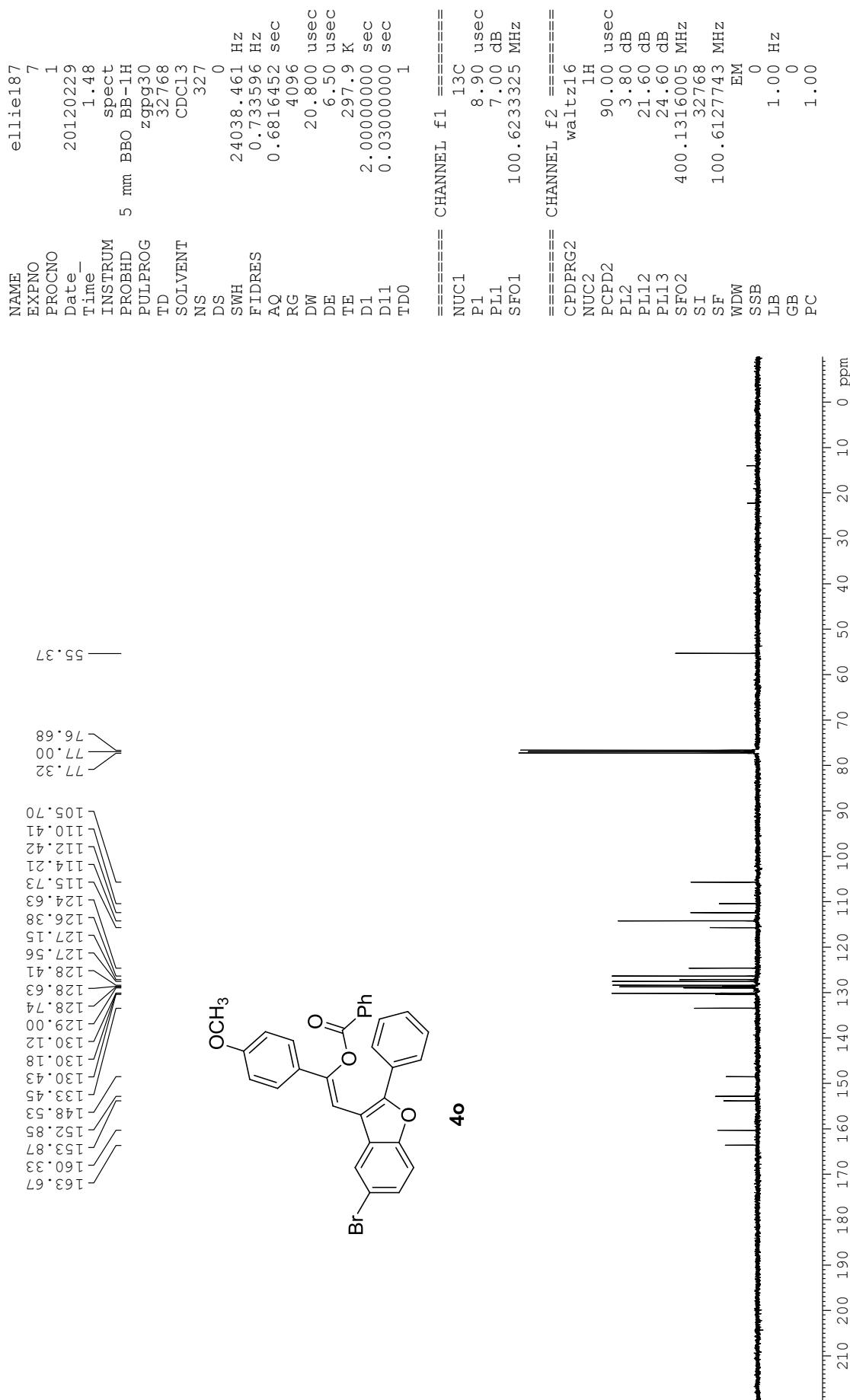


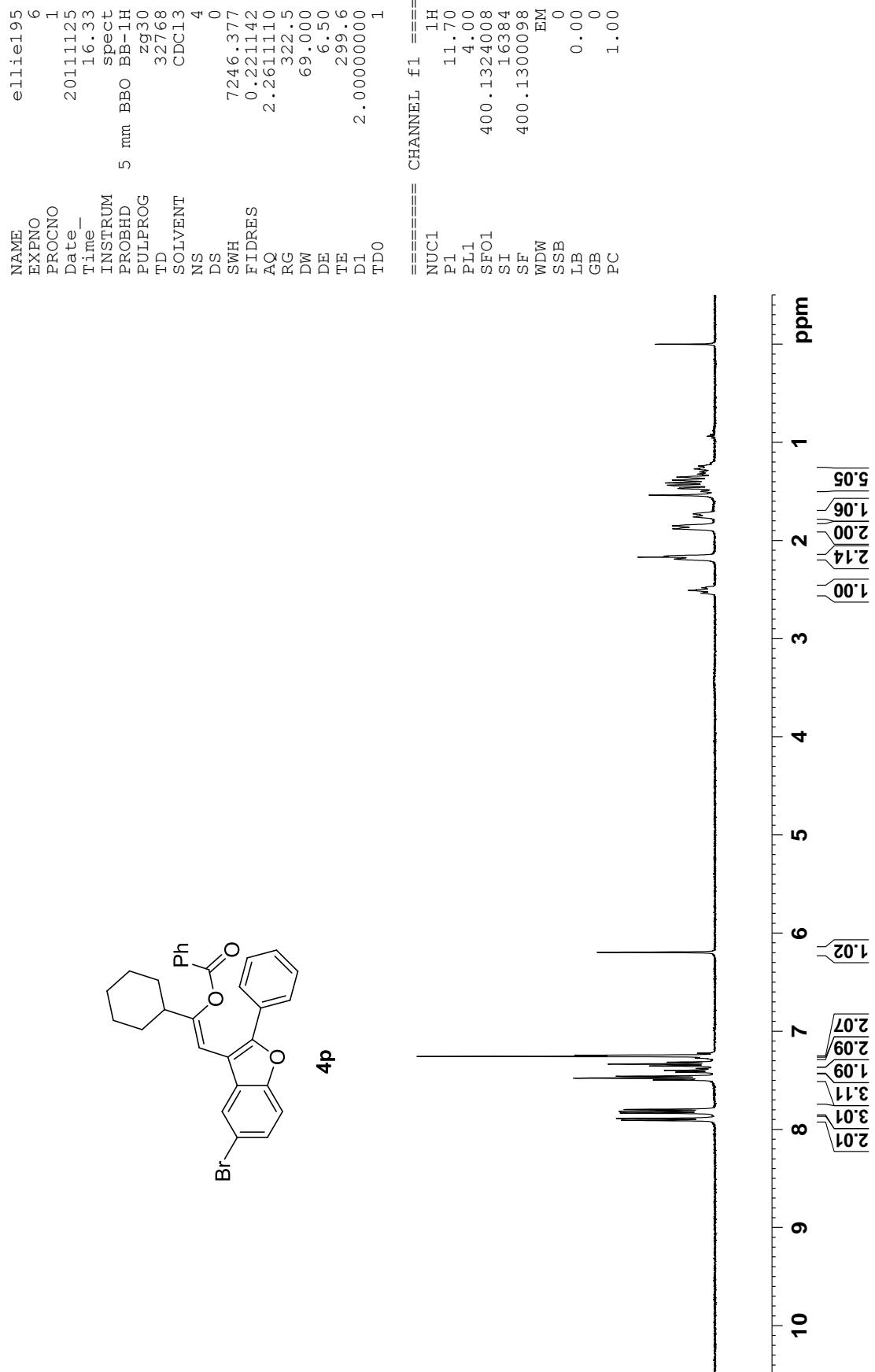


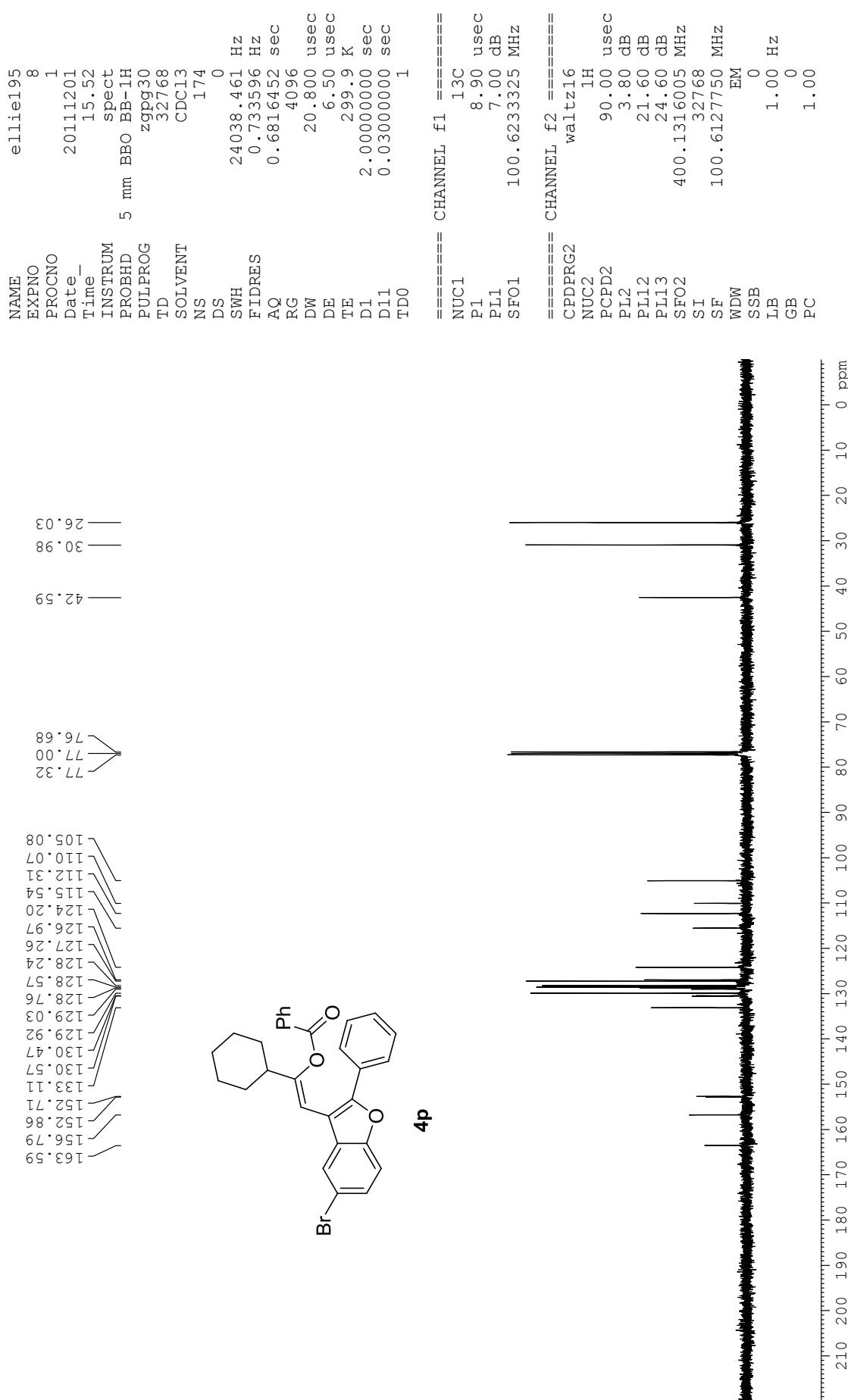


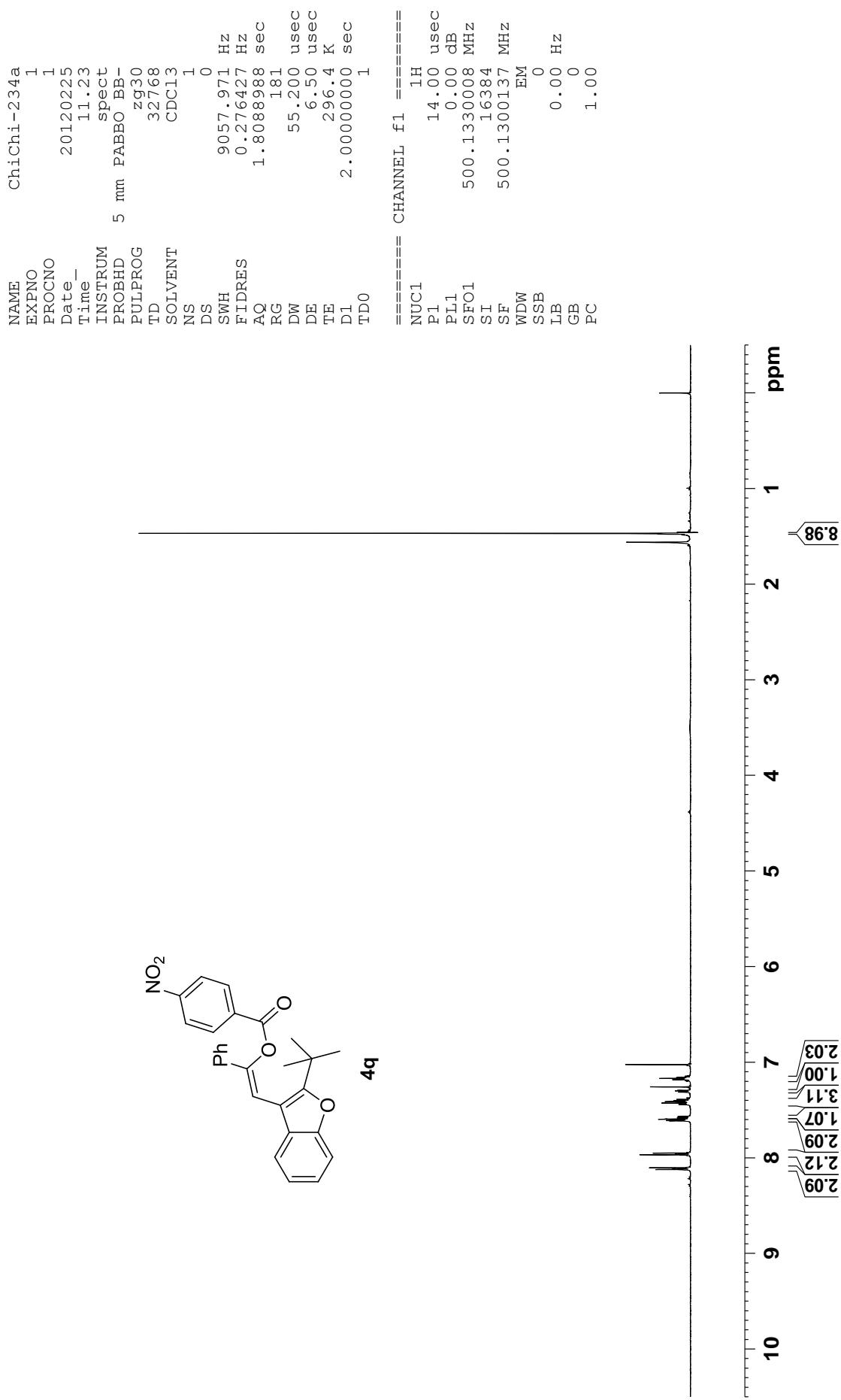


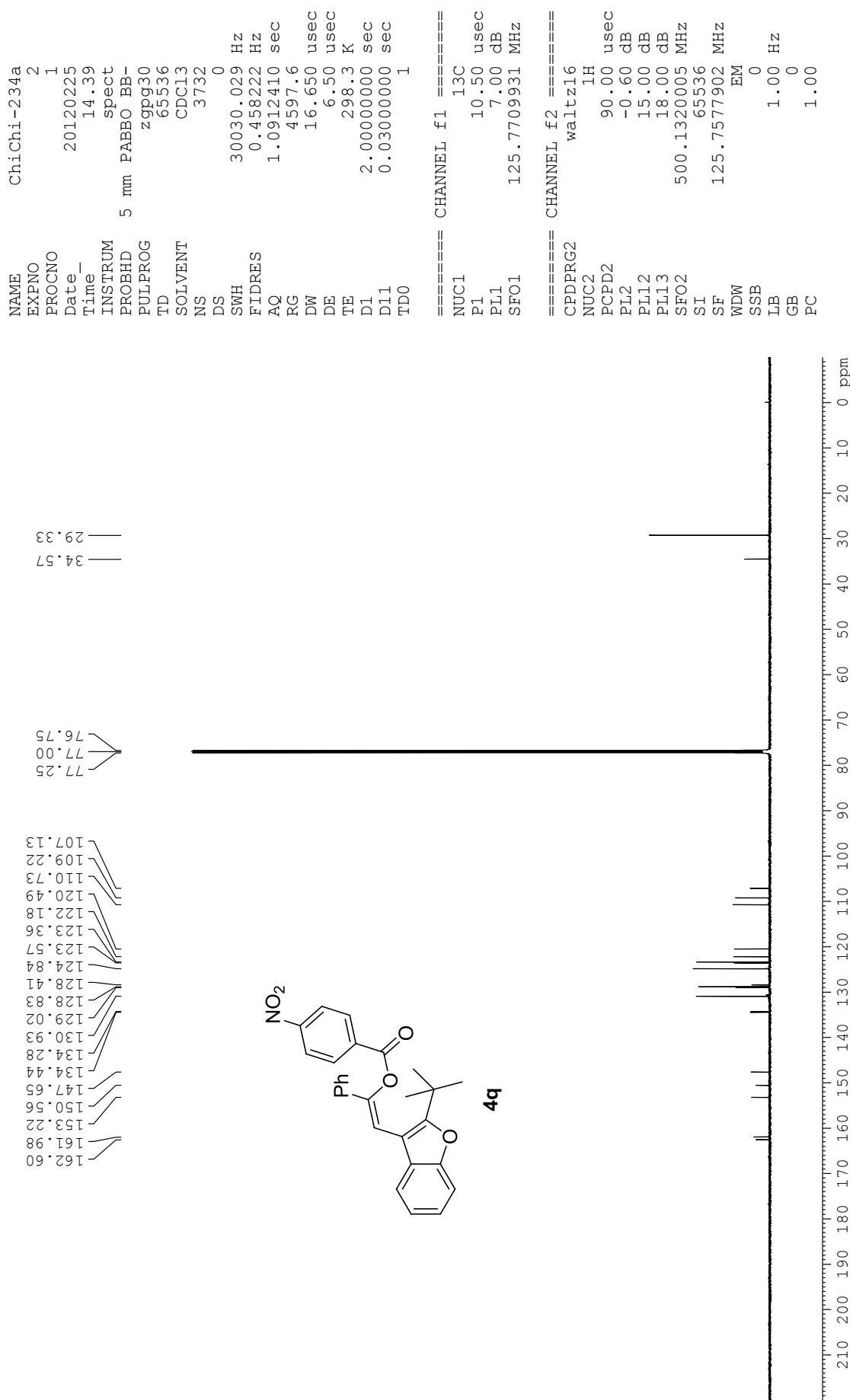


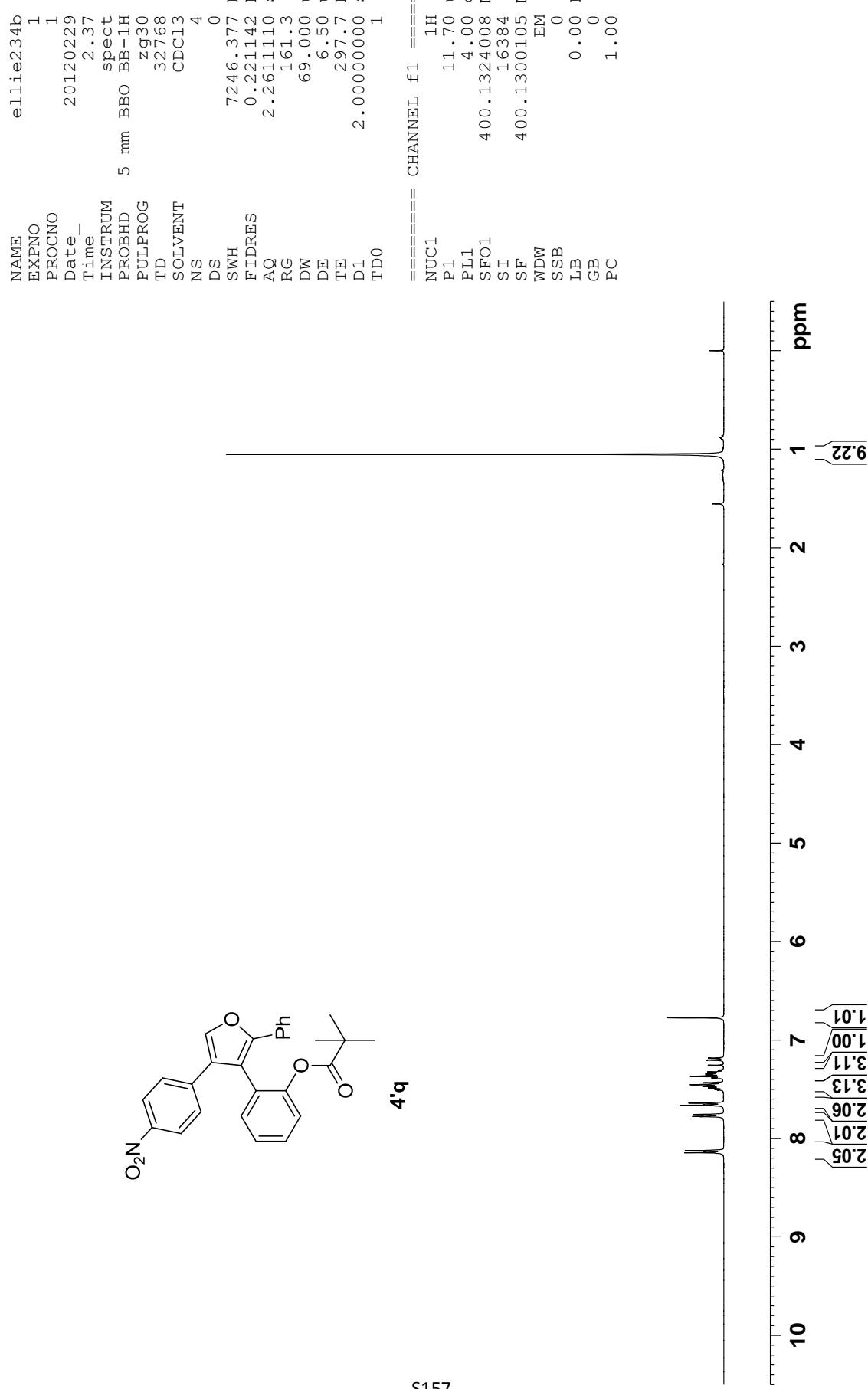


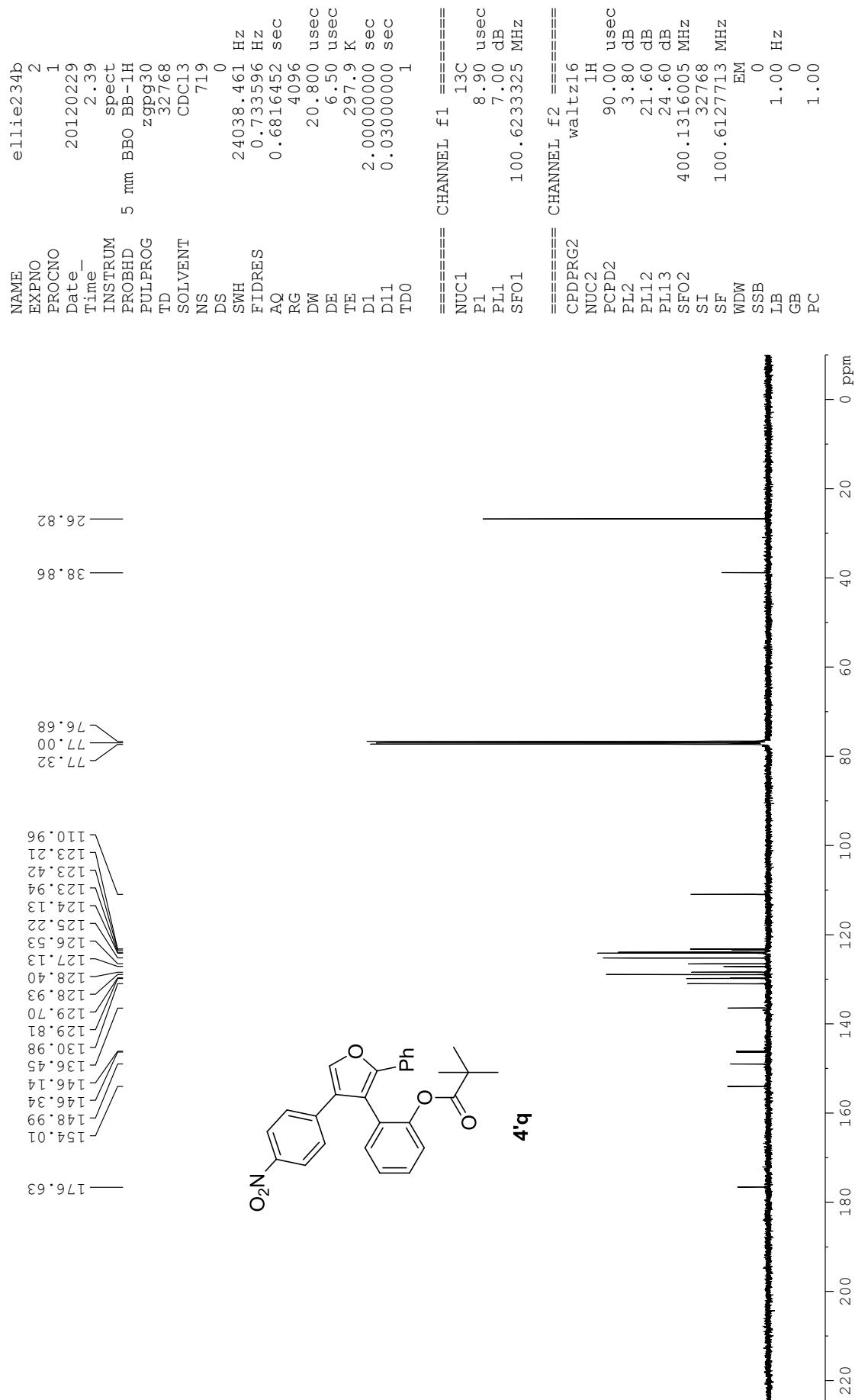






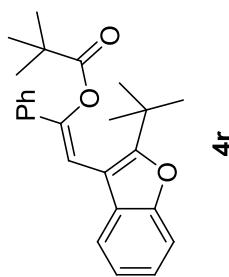
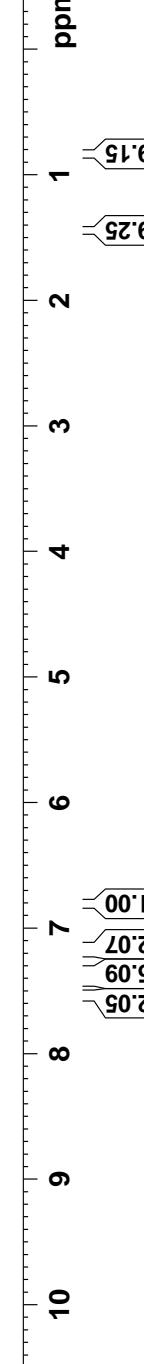


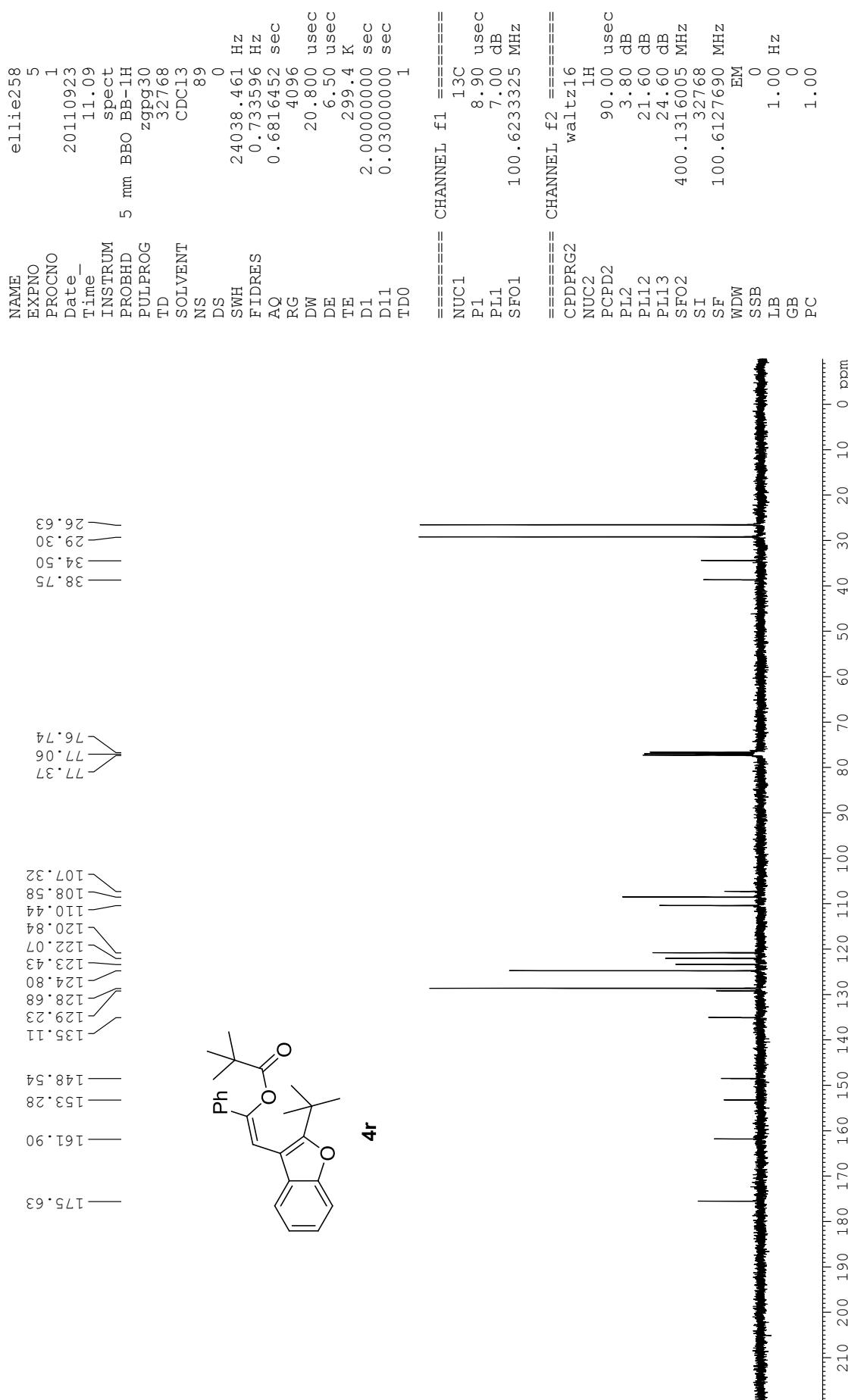


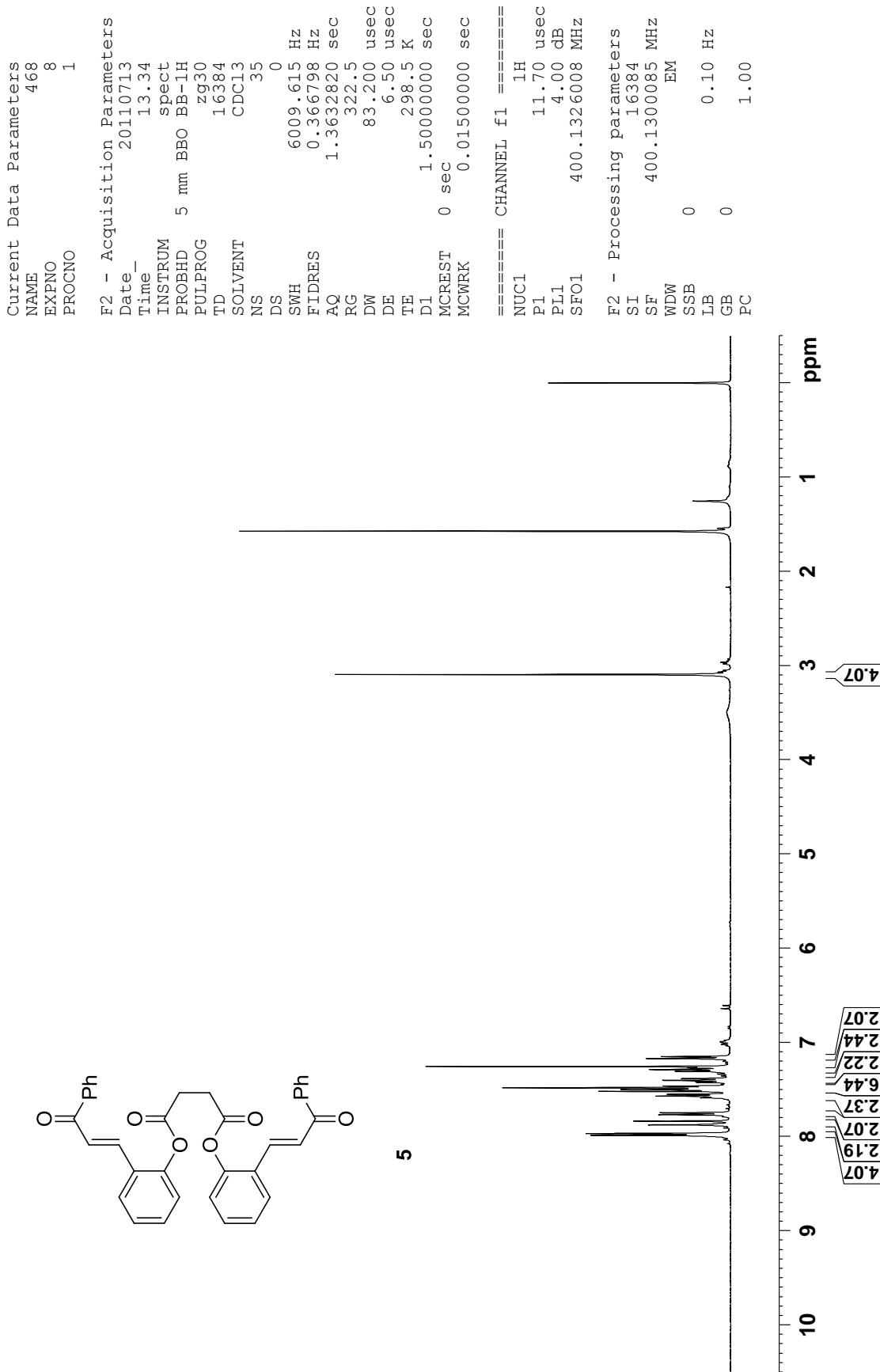


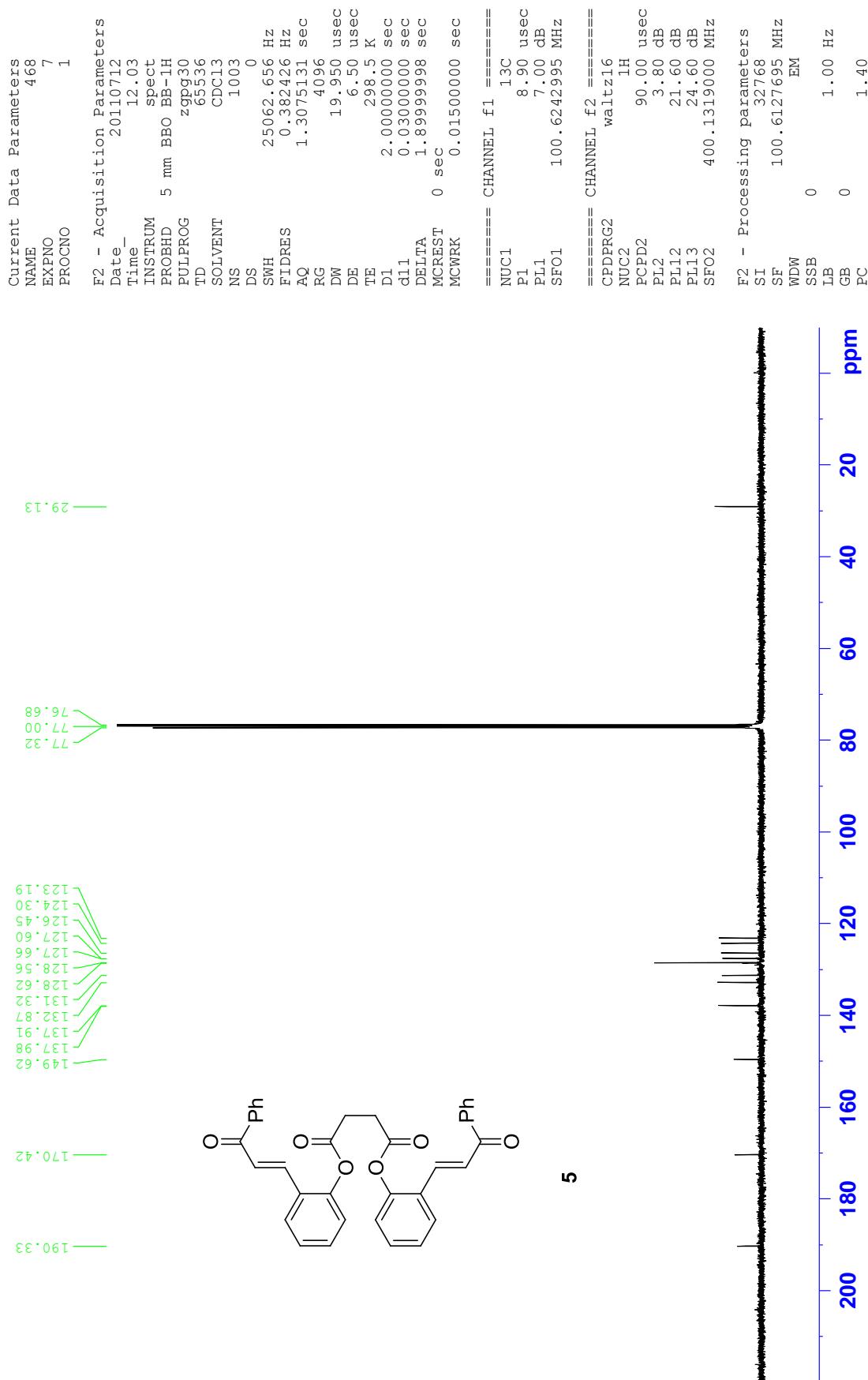
Current Data Parameters
NAME ellie254
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110903
Time_ 10.00
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 19
DS 0
SWH 6009.615 Hz
FIDRES 0.3666798 Hz
AQ 1.3632820 sec
RG 203.2
DW 83.200 usec
DE 6.50 usec
TE 299.5 K
D1 1.5000000 sec
MCREST 0.0000000 sec
MCWRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 11.70 usec
PL1 4.00 dB
SFO1 400.1326008 MHz
F2 - Processing parameters
SI 16384
SF 400.1300135 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00









Current Data Parameters
NAME 472
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters

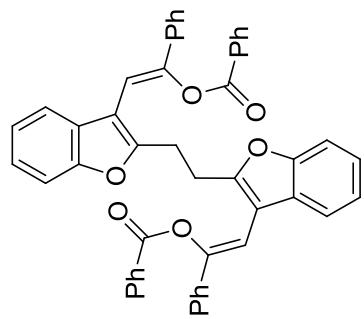
Date 20110714
Time 23.15
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 16384
SOLVENT CDCl₃
NS 8
DS 0
SWH 6009.615 Hz
FIDRES 0.366798 Hz
AQ 1.3632820 sec
RG 203.2
DW 83.200 usec
DE 6.50 usec
TE 300.2 K
D1 1.5000000 sec
MCREST 0 sec
MCWRK 0.01500000 sec

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

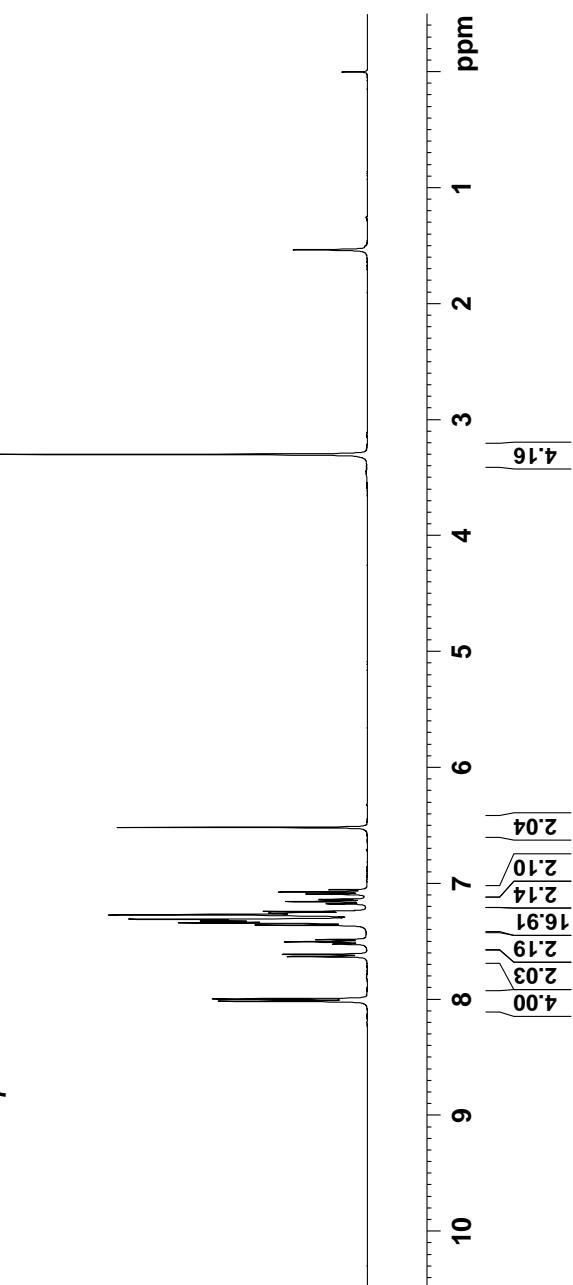
NUC1 ¹H
P1 11.70 usec
PL1 4.00 dB
SFO1 400.1326008 MHz

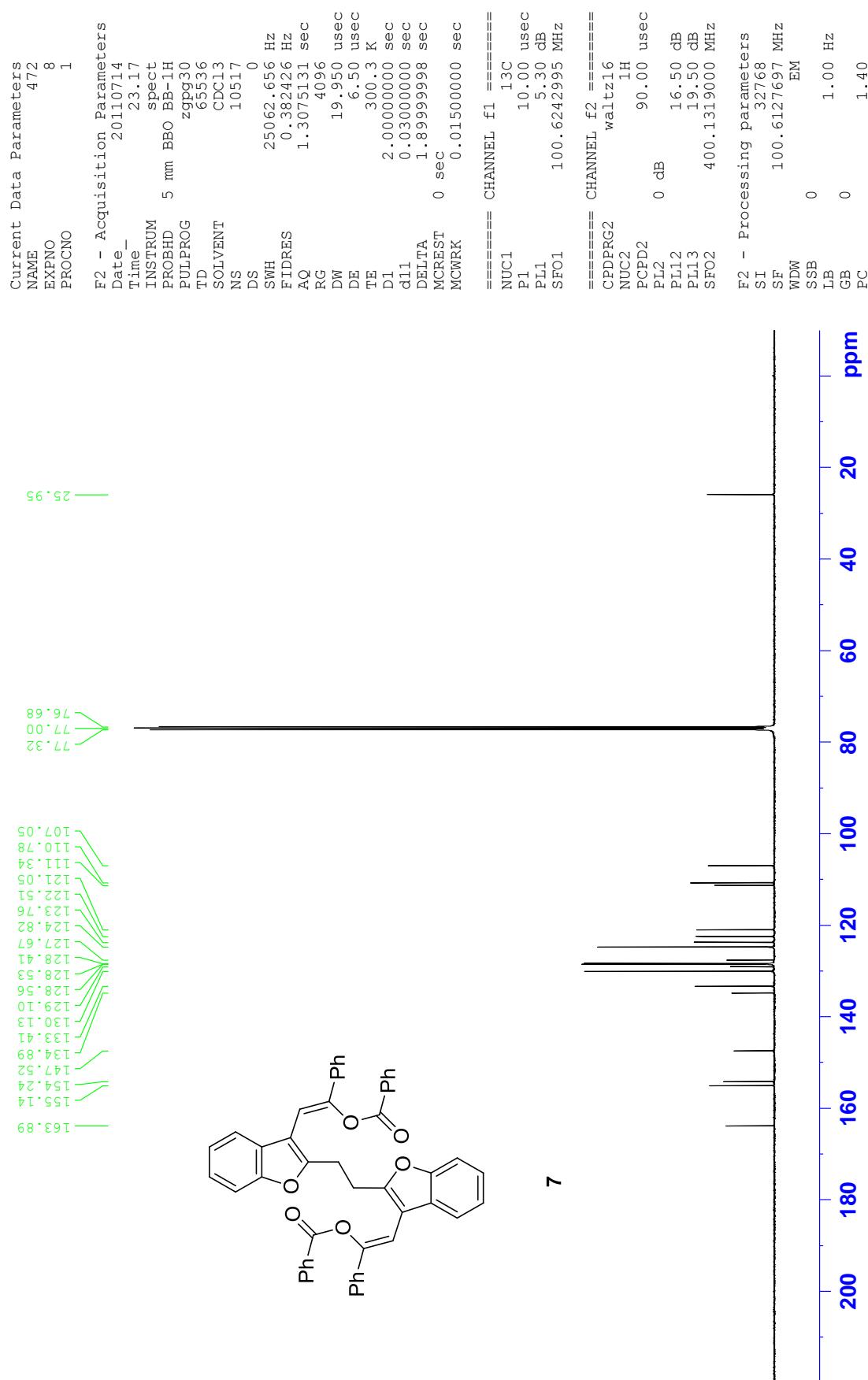
F2 - Processing parameters

SI 16384
SF 400.1300147 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00



7

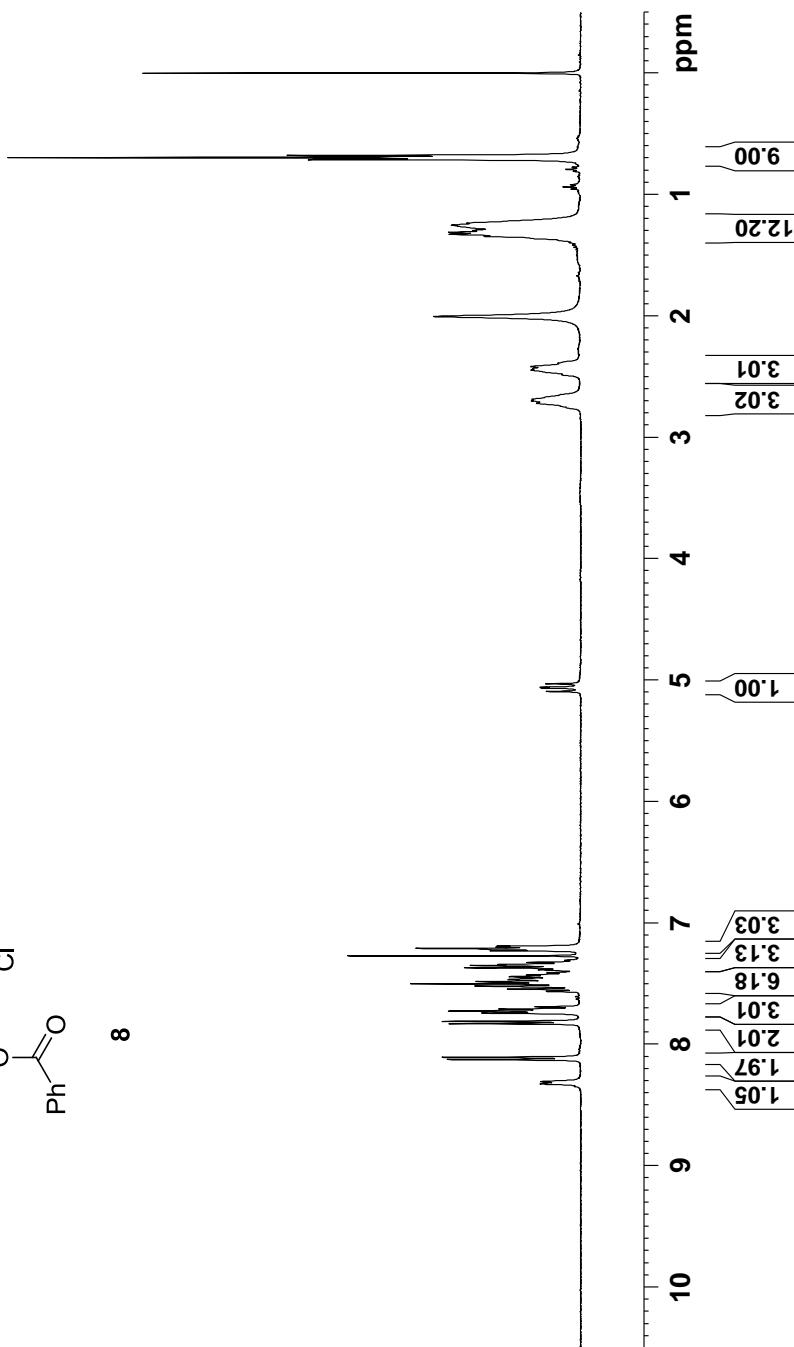
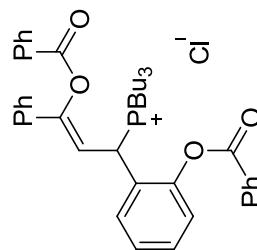


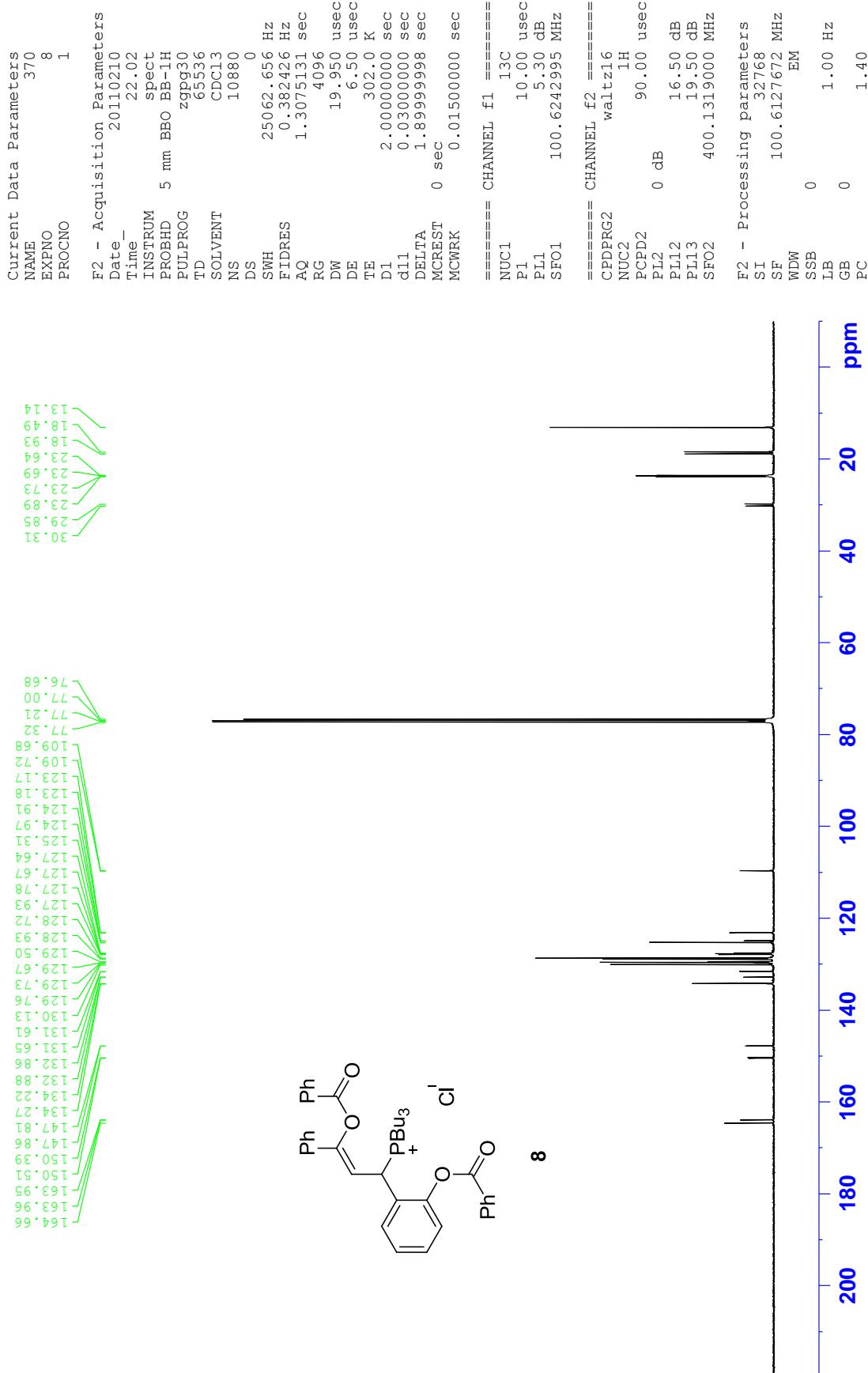


Current NAME	Data EXPNO	Parameters PROCNO
try	128	1

F2 - Acquisition Parameters

Date	20110921
Time	18.01
INSTRUM	
PROBHD	5 mm
PULPROG	BBO
TD	BB-1H
SOLVENT	Z930
NS	32768
DS	CDC13
SWH	CDC13
FIDRES	16
AQ	0
RG	7246.377
DW	Hz
DE	0.221142
TE	Hz
TD	2.261110
D1	sec
TDO	128
	69.000
	usec
	6.50
	usec
	299.4
	K
	2.000000000
	sec





Current Data Parameters
NAME Regina-p
EXPNO 3
PROCNO 1

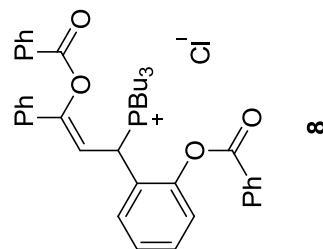
F2 - Acquisition Parameters
Date_ 20120203
Time 20.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 80
DS 0
SWH 80645.164 Hz
FIDRES 1.230548 Hz
AQ 0.4063794 sec
RG 20642.5
DW 6.200 usec
DE 6.50 usec
TE 293.9 K
D1 2.0000000 sec
D11 0.0300000 sec
TDO 1

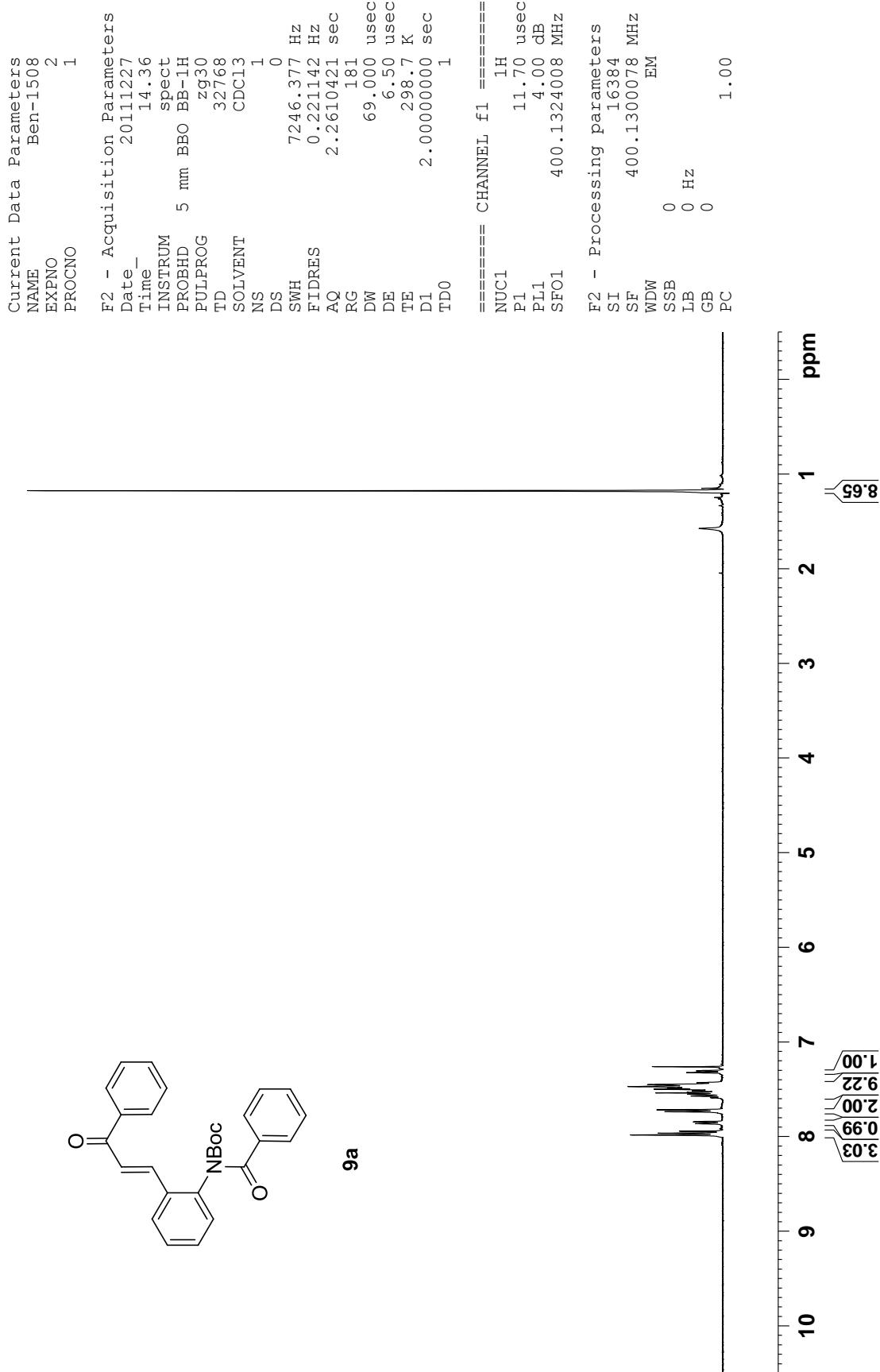
===== CHANNEL f1 =====
NUC1 31P
P1 12.00 usec
PL1 6.00 dB
SFO1 202.4462122 MHz

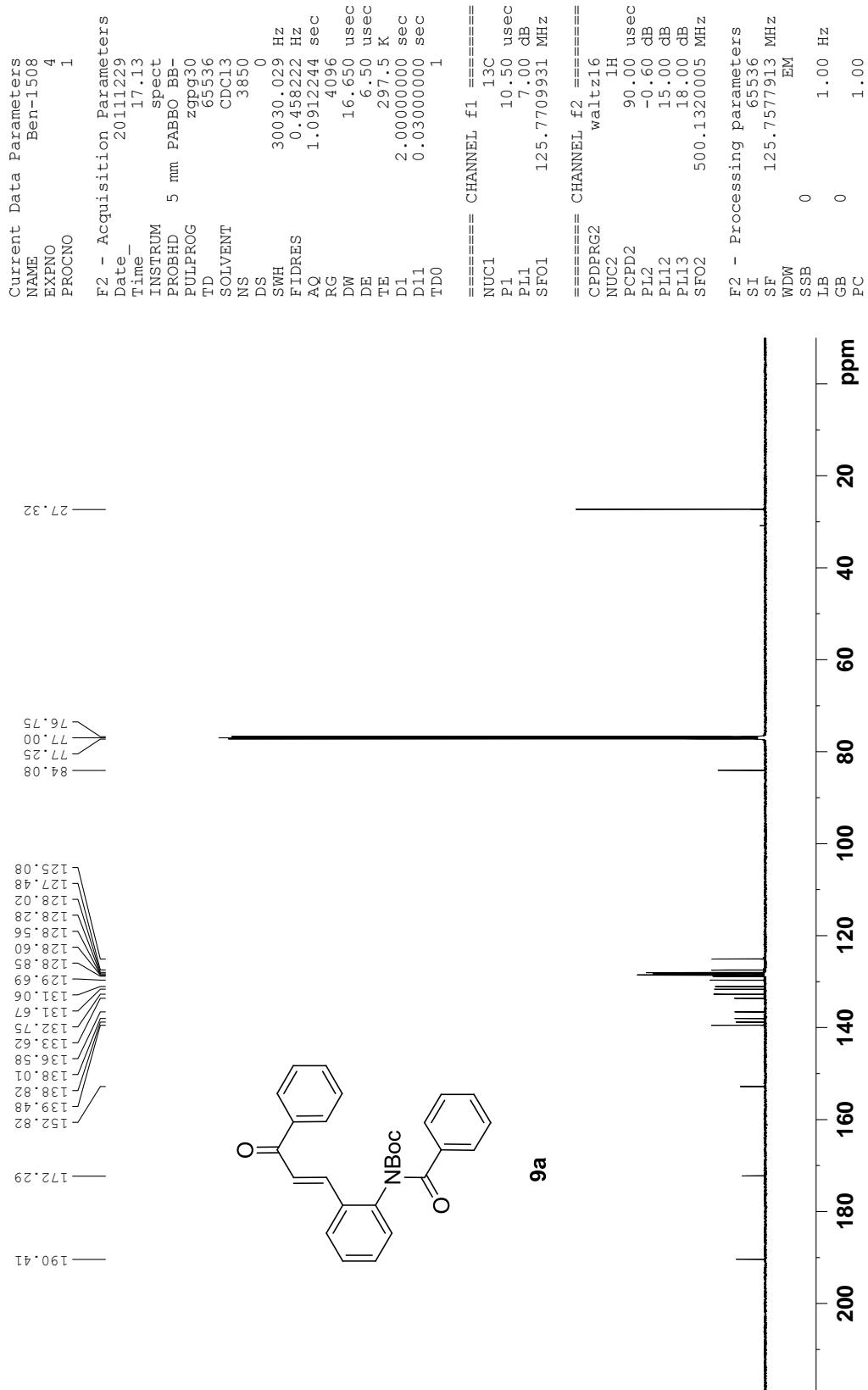
===== CHANNEL f2 =====
CPDRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.60 dB
PL12 15.00 dB
PL13 18.00 dB
SFO2 500.1320005 MHz

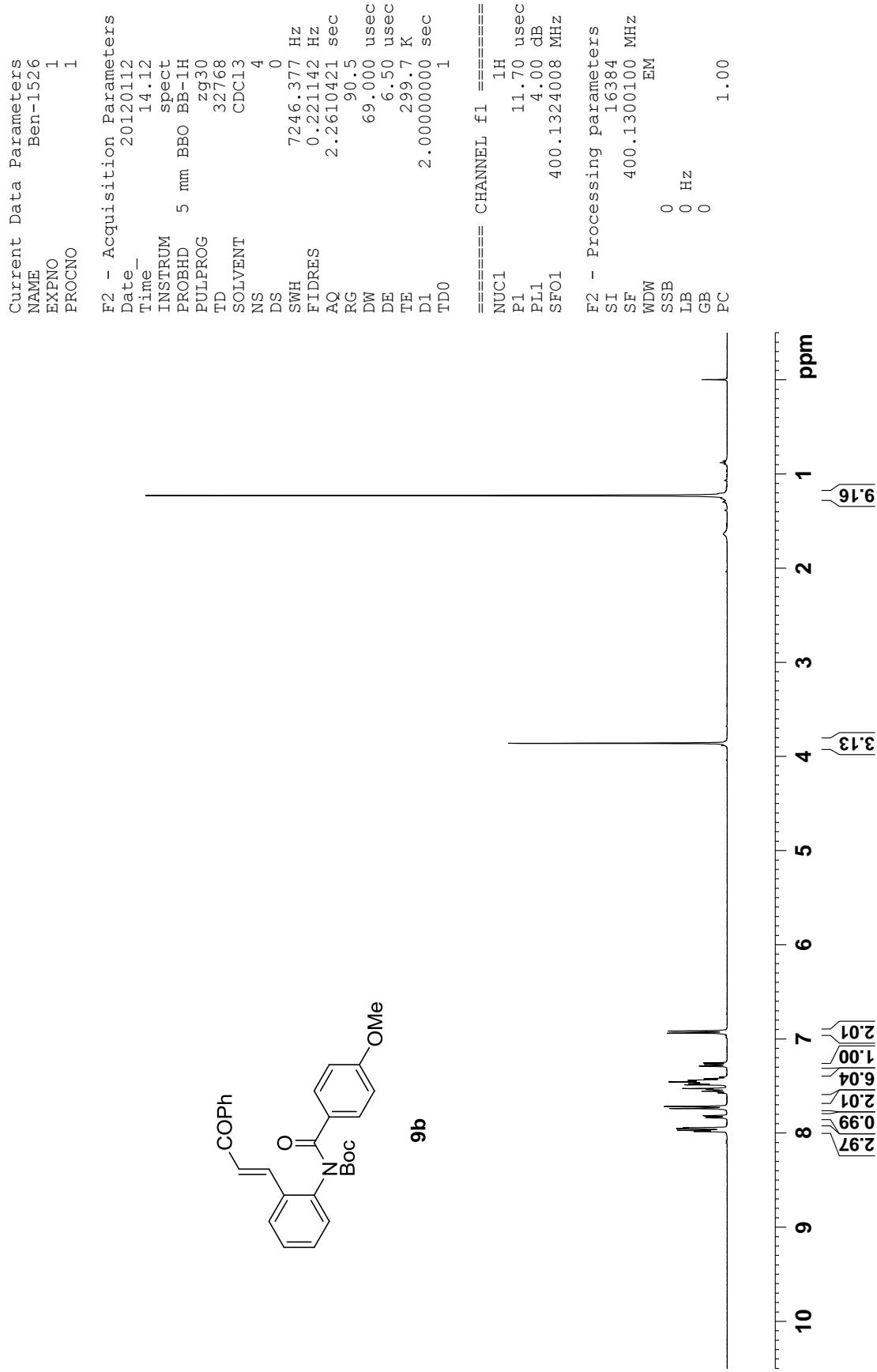
F2 - Processing parameters
SI 32768
SF 202.4564874 MHz
WDW EM
SSB 0
LB 1.00 Hz
SF 0
PC 1.00

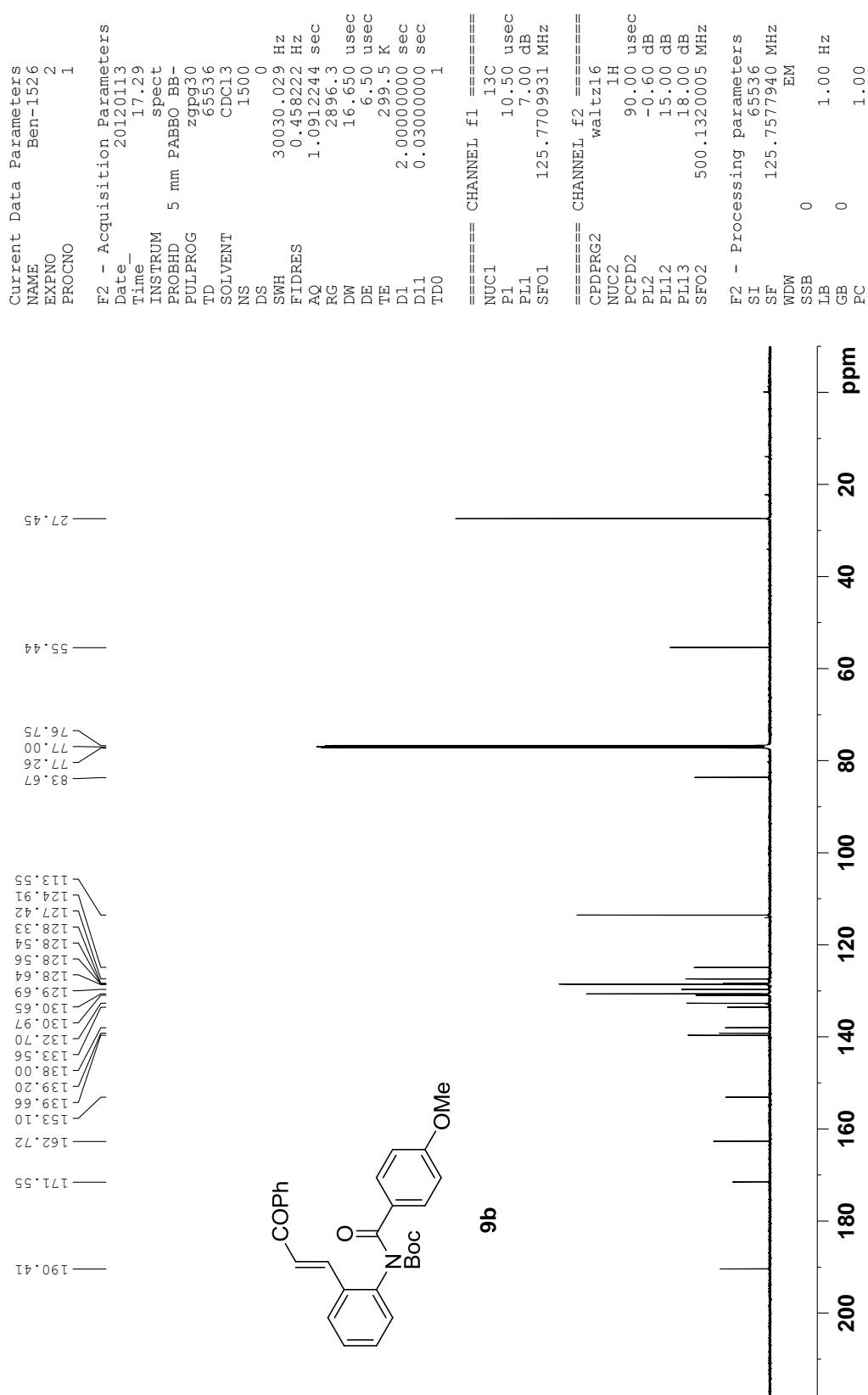
68.96 —

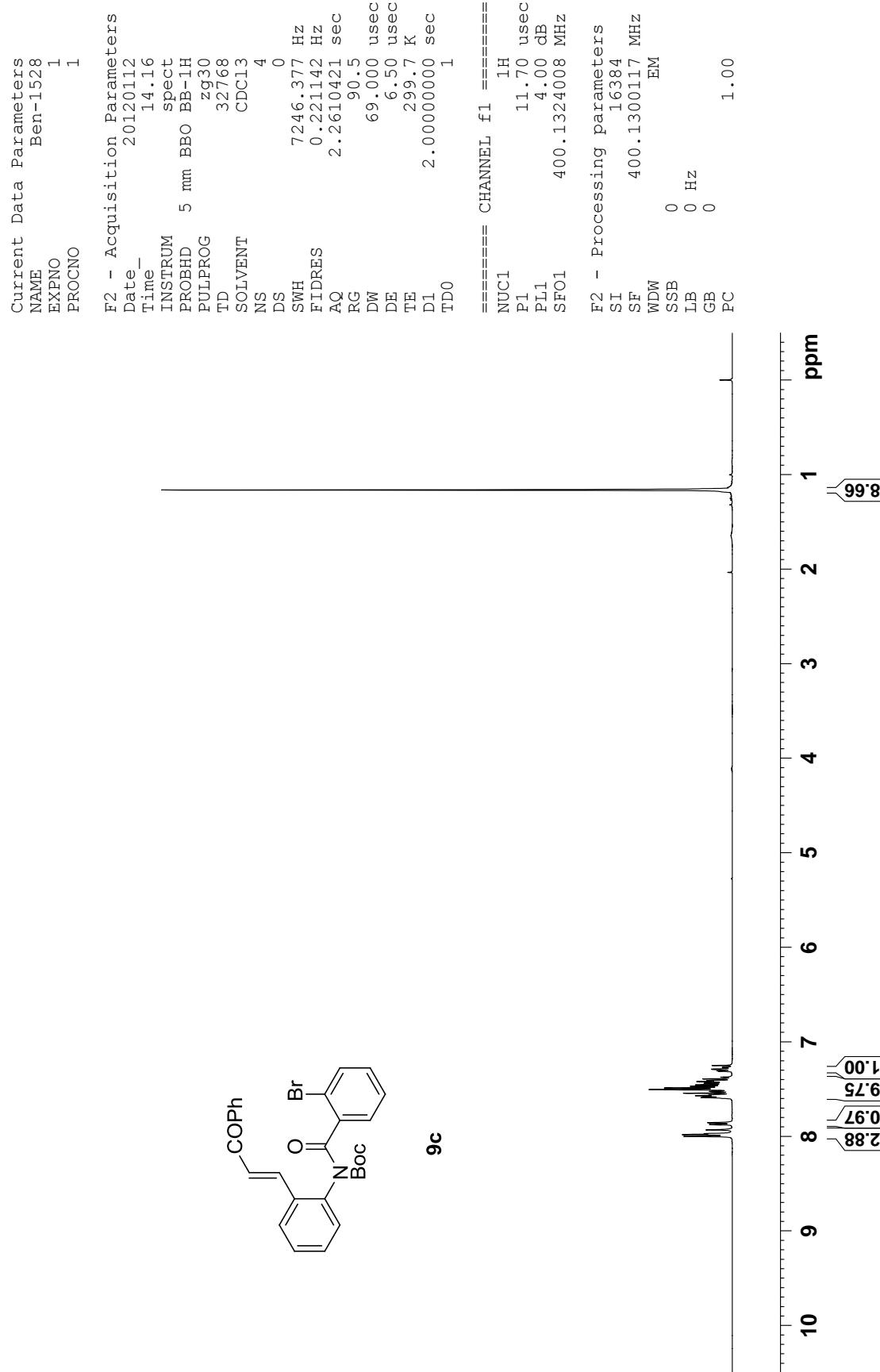


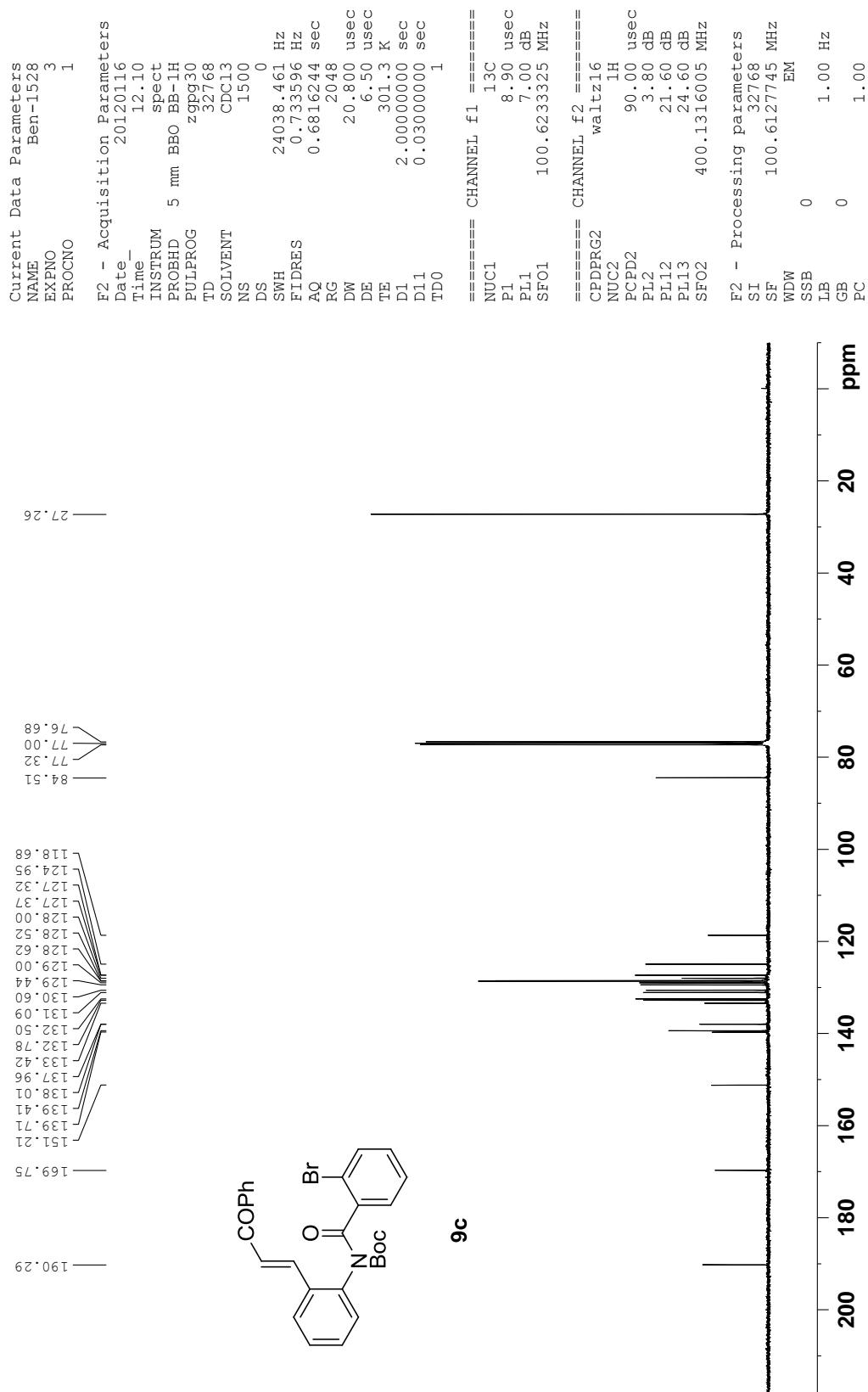








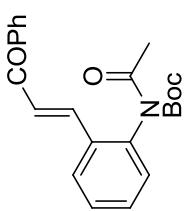




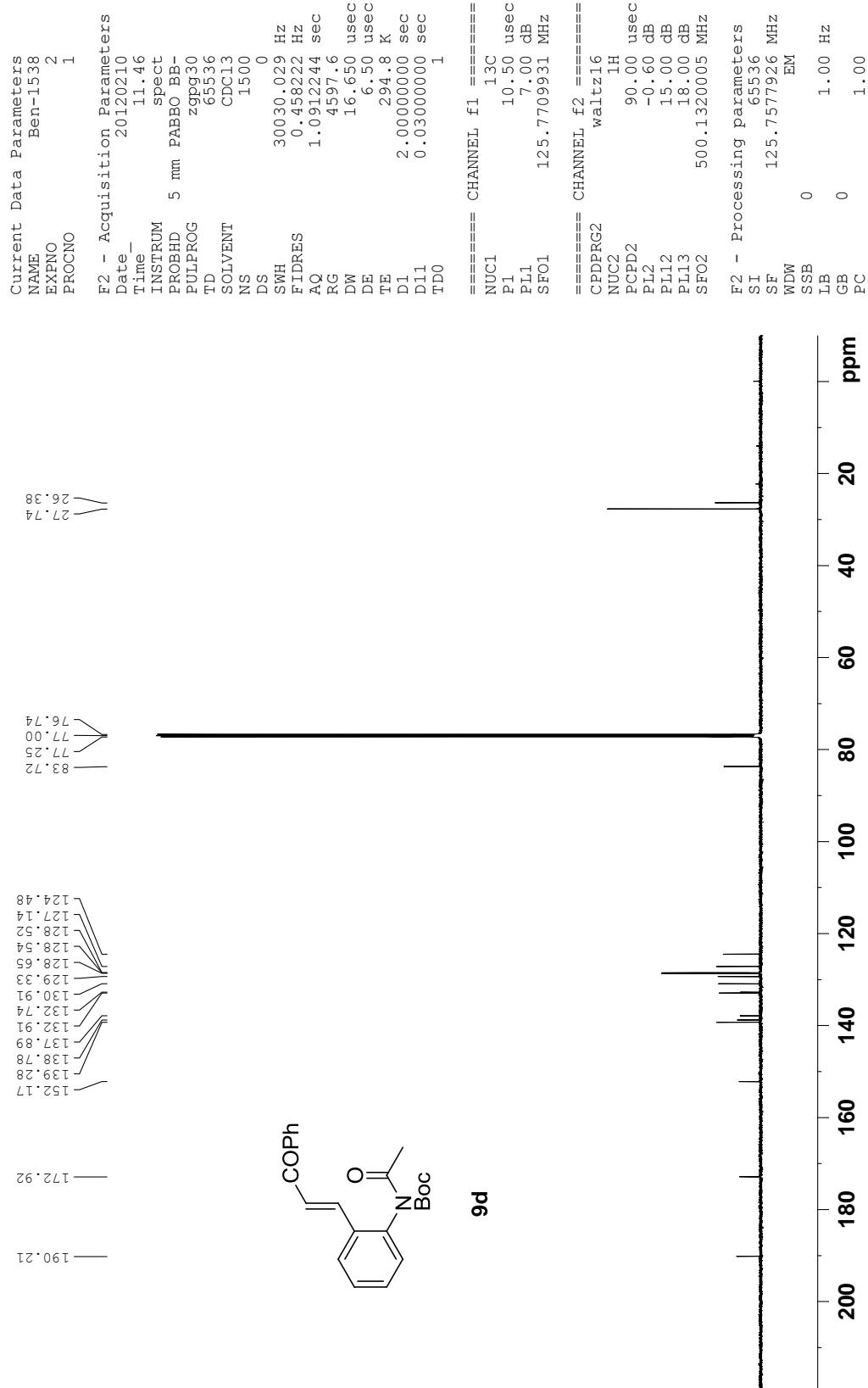
Current Data Parameters
NAME Ben-1538
EXPNO 1
PROCNO 1

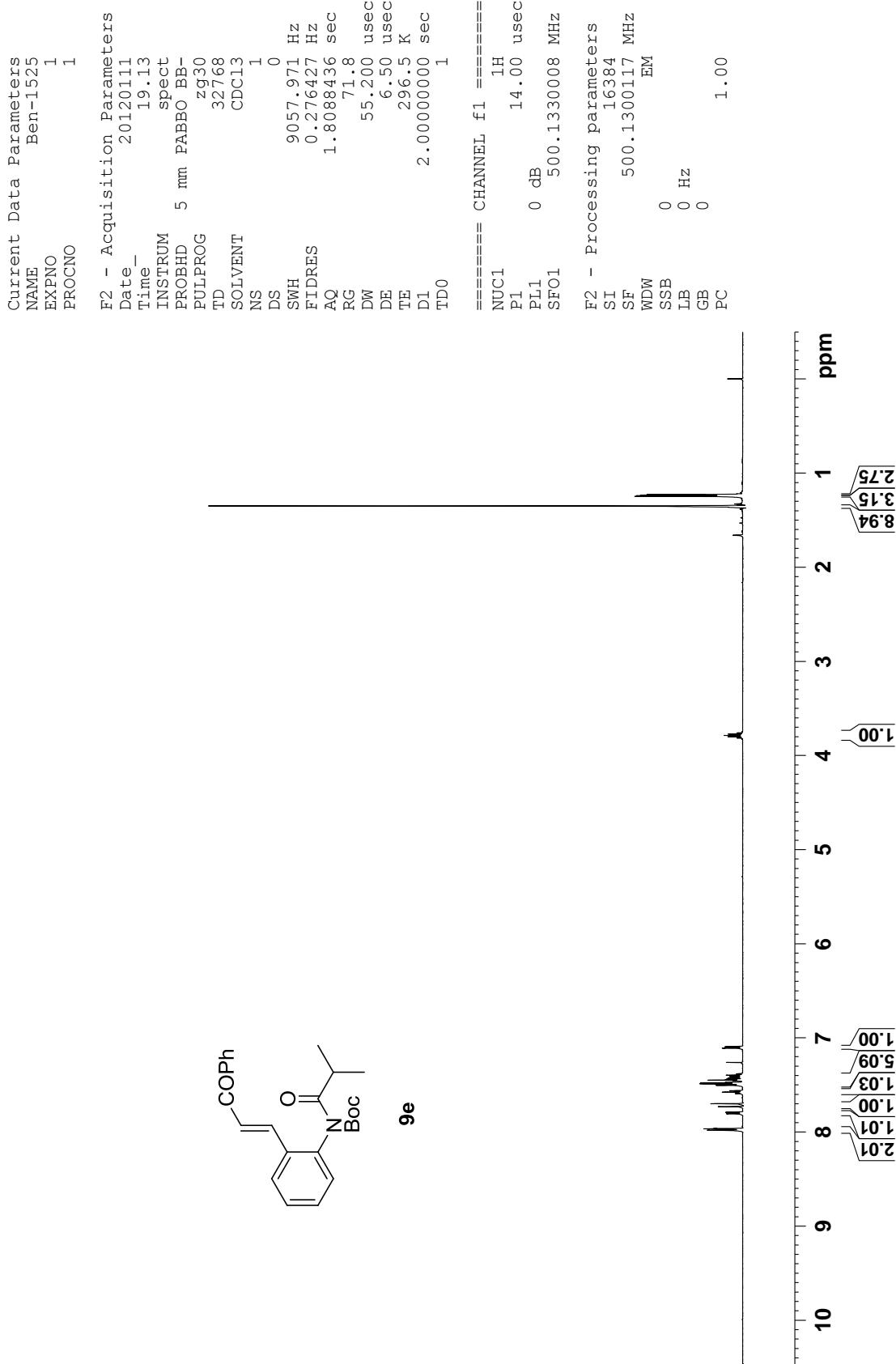
F2 - Acquisition Parameters
Date 20120210
Time 10.26
INSTRUM spect
PROBHD 5 mm BABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 1
DS 0
SWH 9057.971 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 181
DW 55.200 usec
DE 6.50 usec
TE 292.6 K
D1 2.0000000 sec
TDO 1

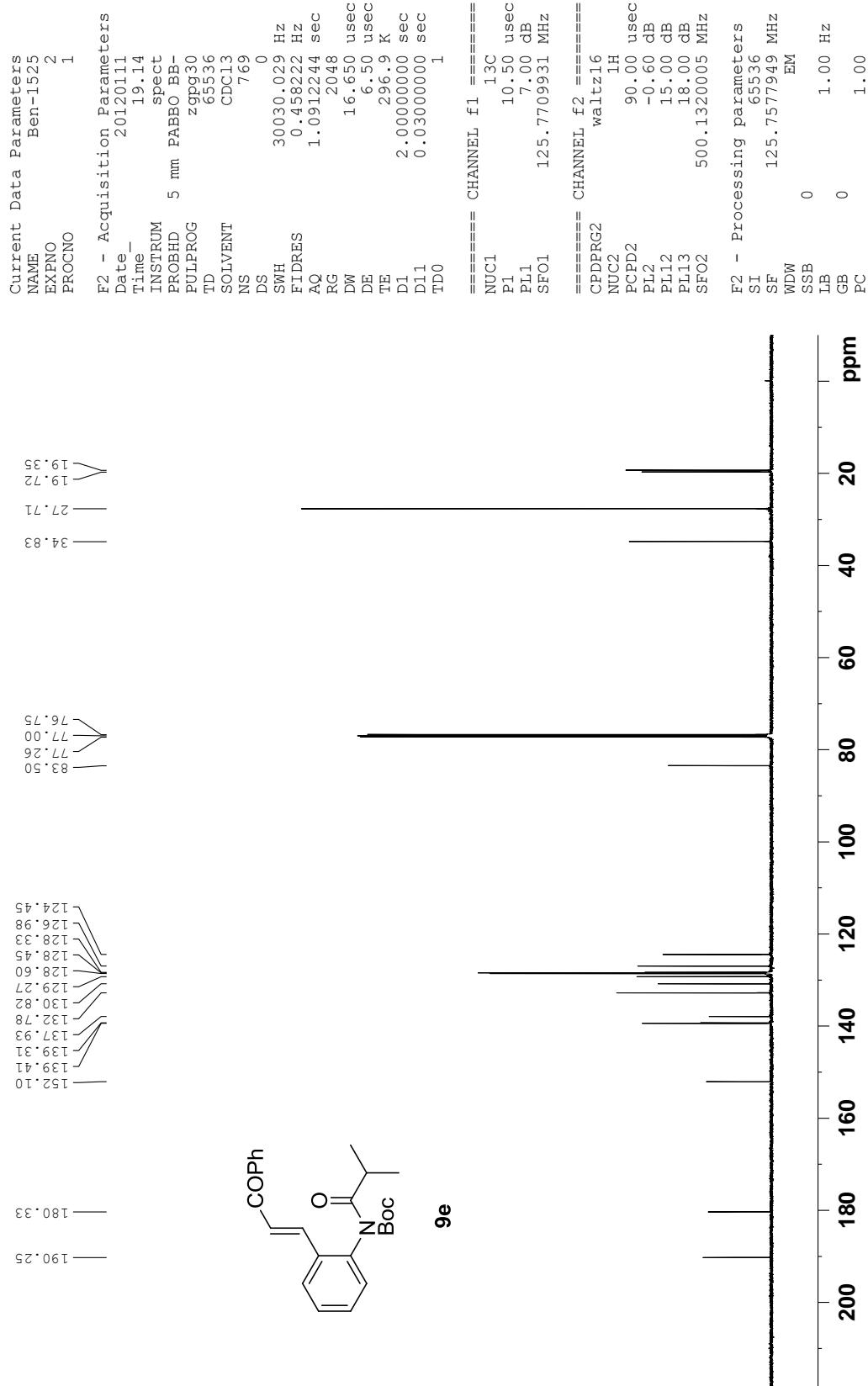
===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0 dB
SFO1 500.1330008 MHz
F2 - Processing parameters
SI 16384
SF 500.1300112 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

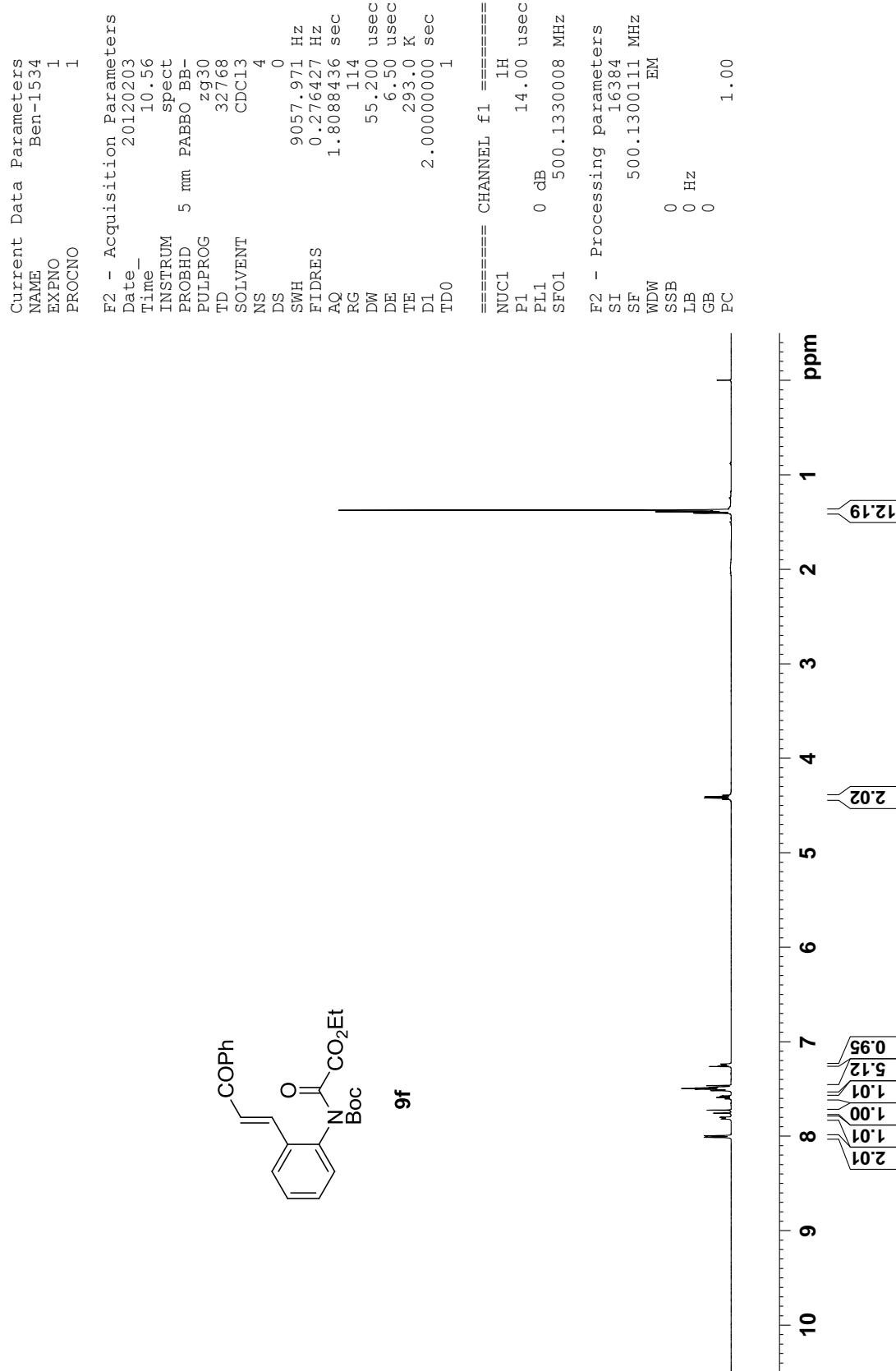


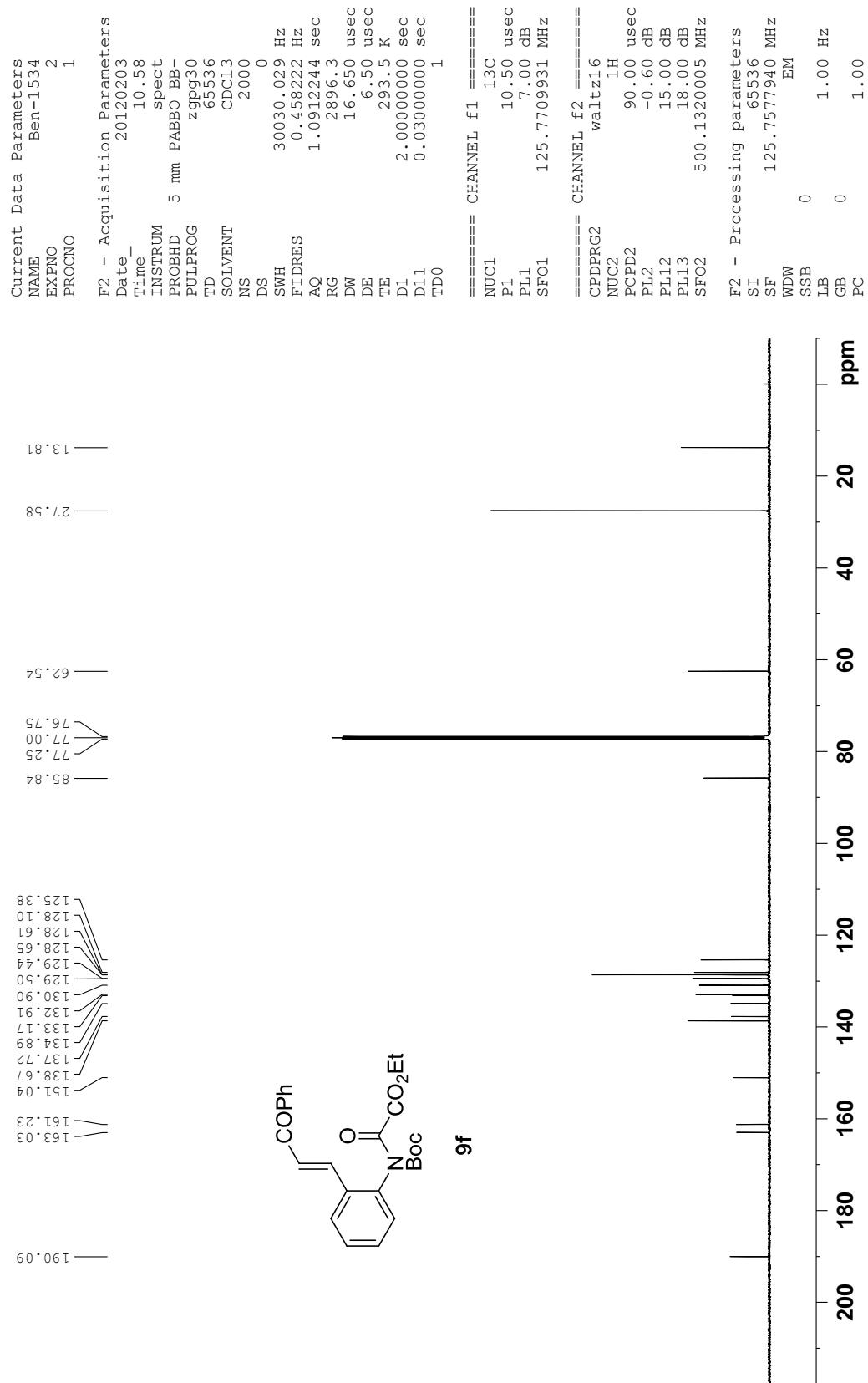
9d

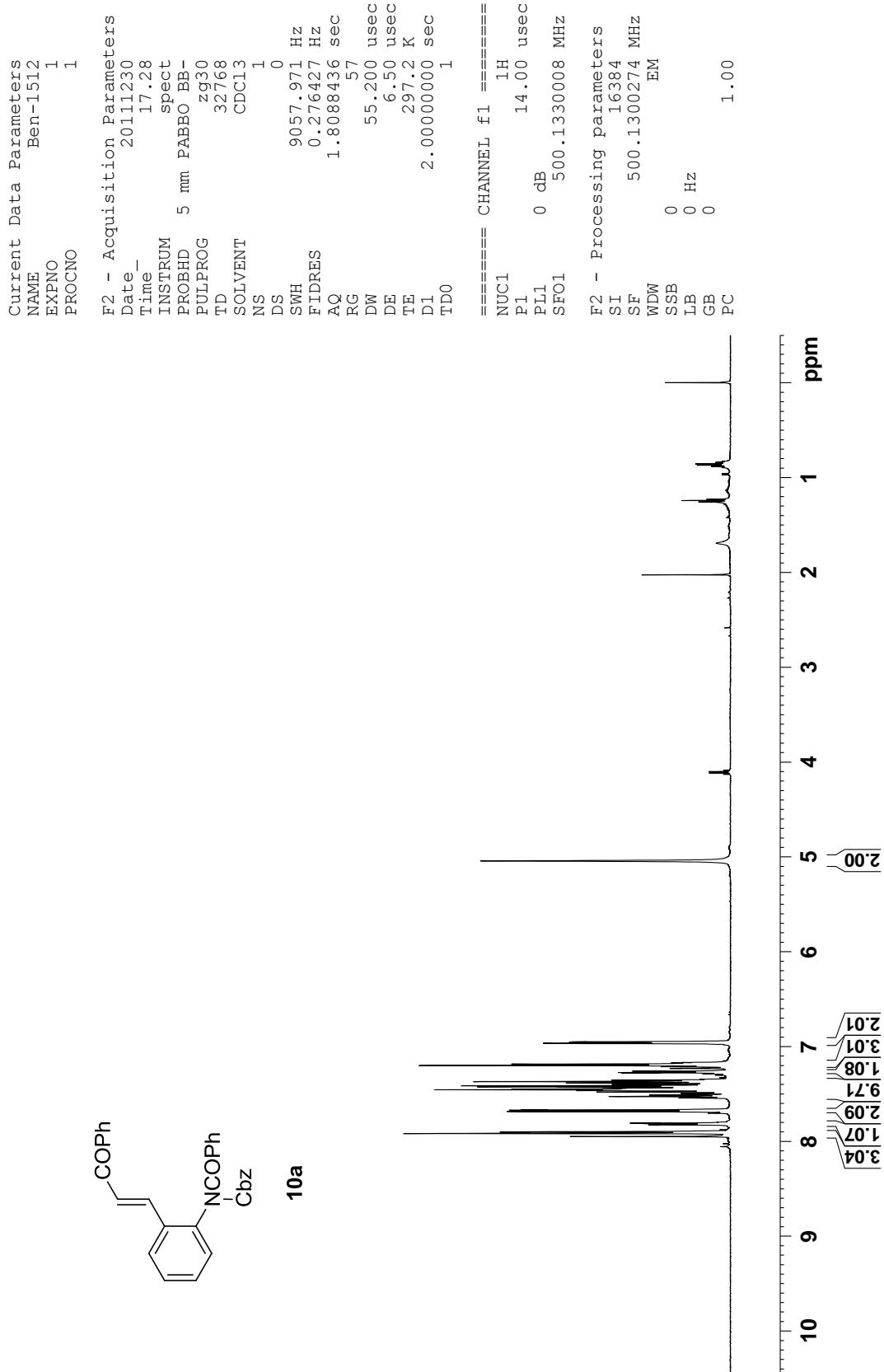


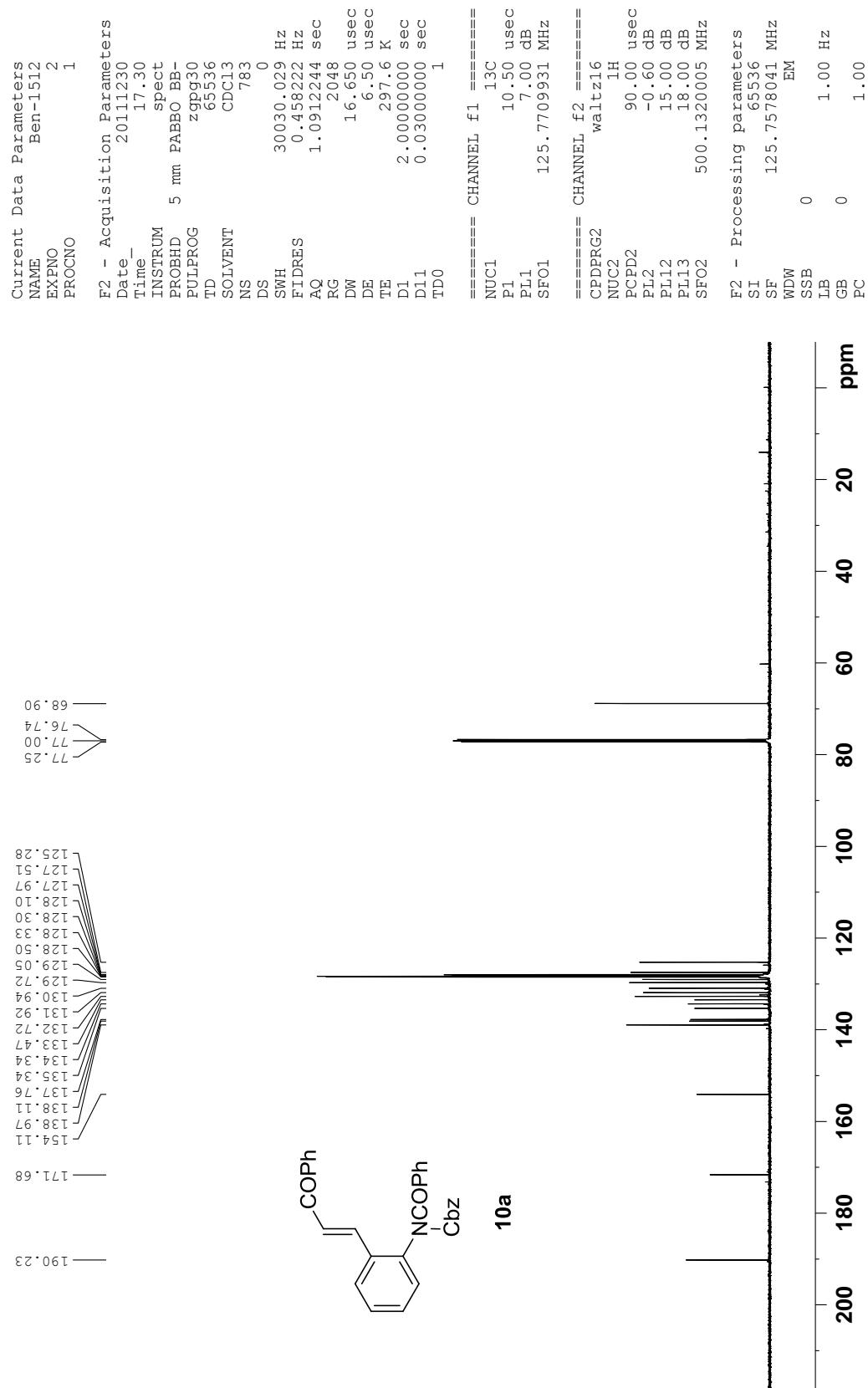


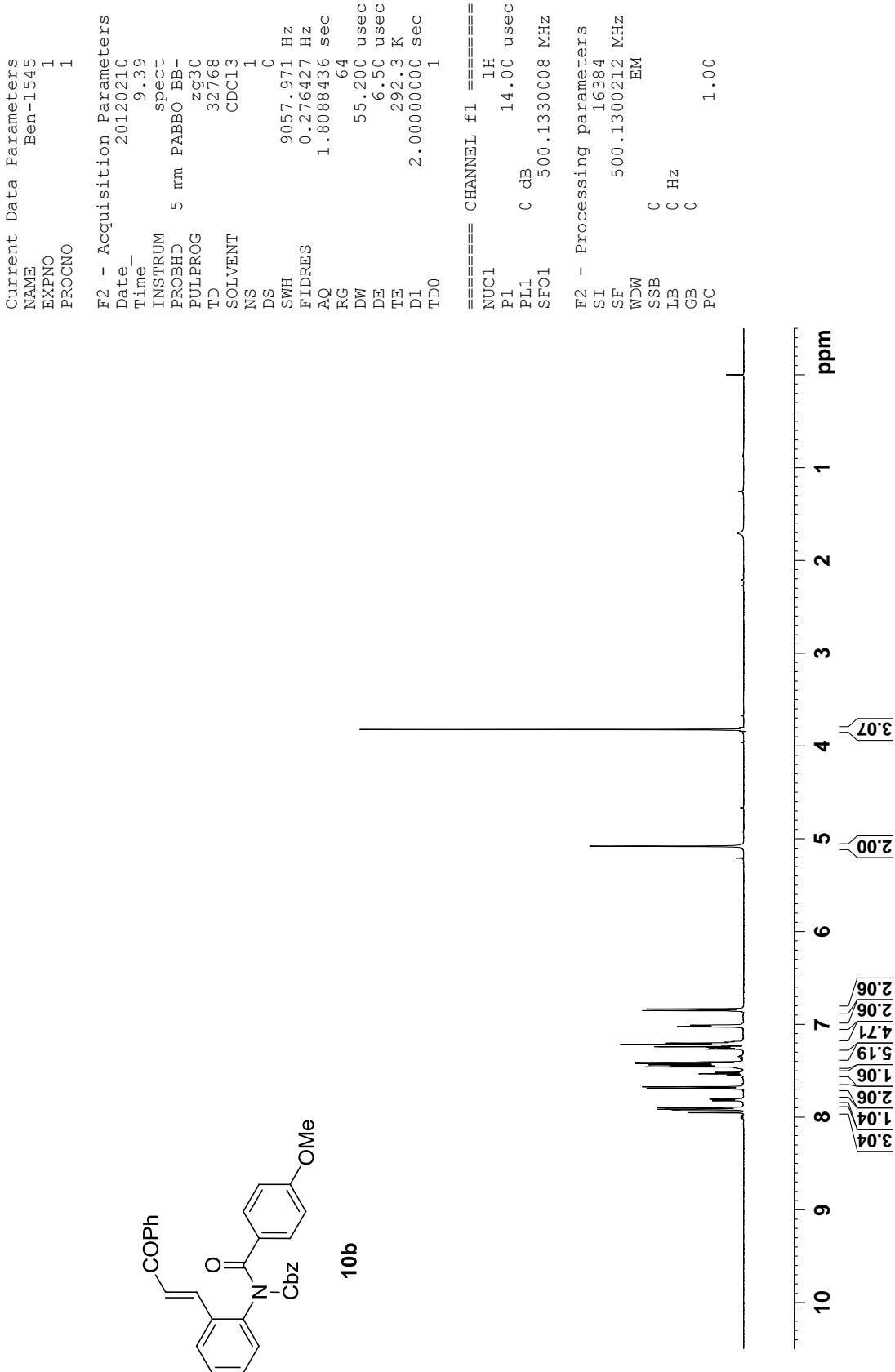


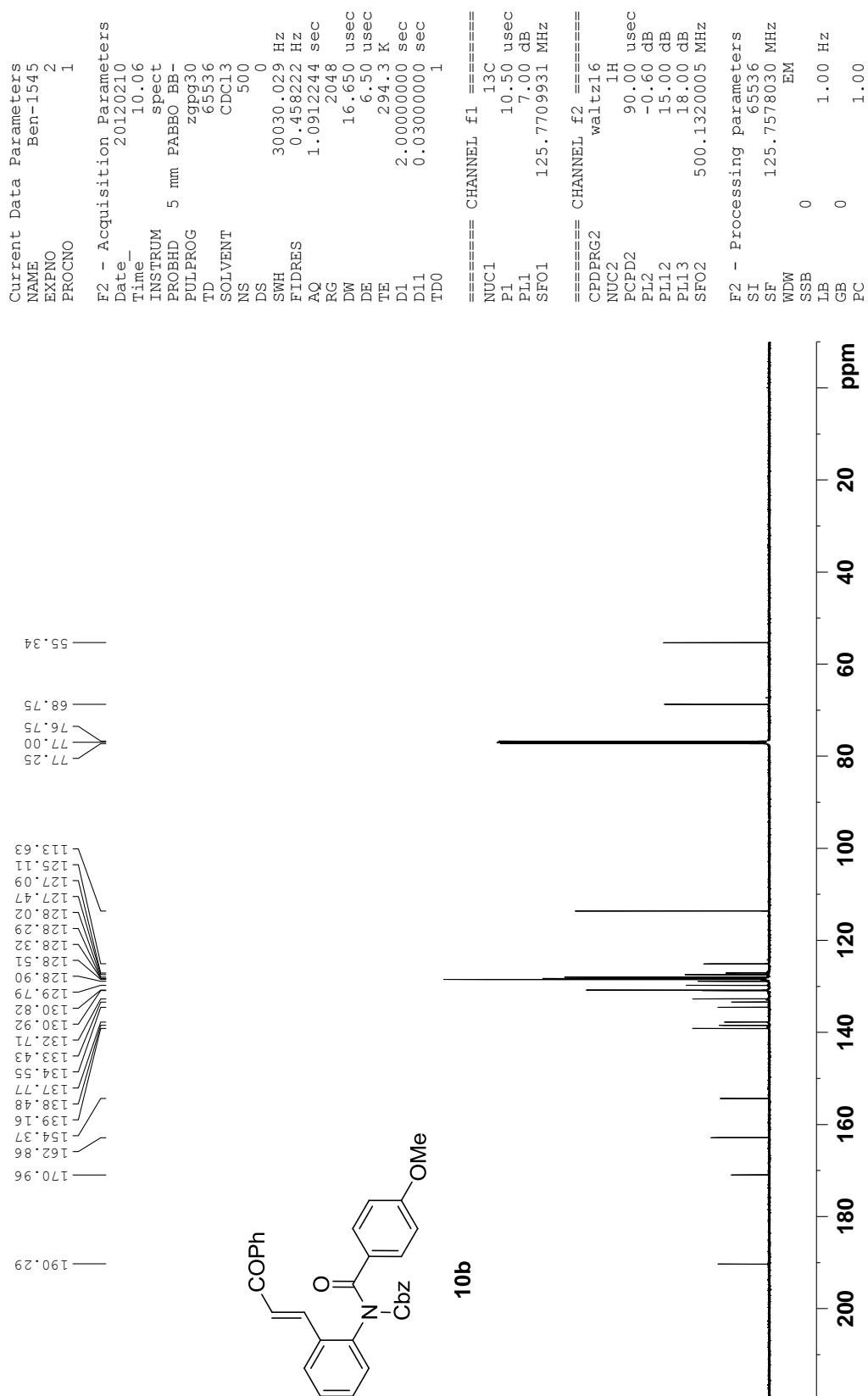


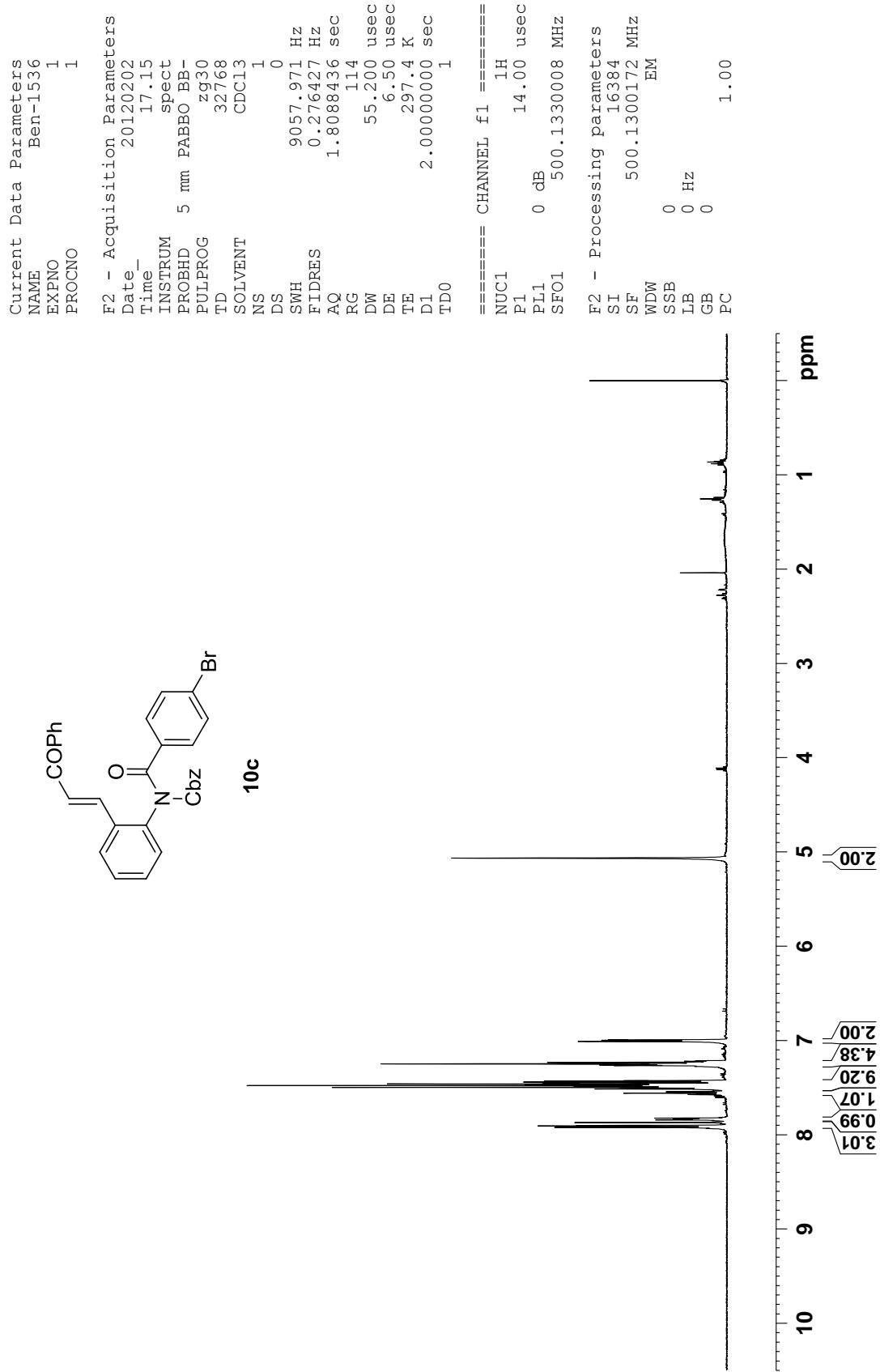


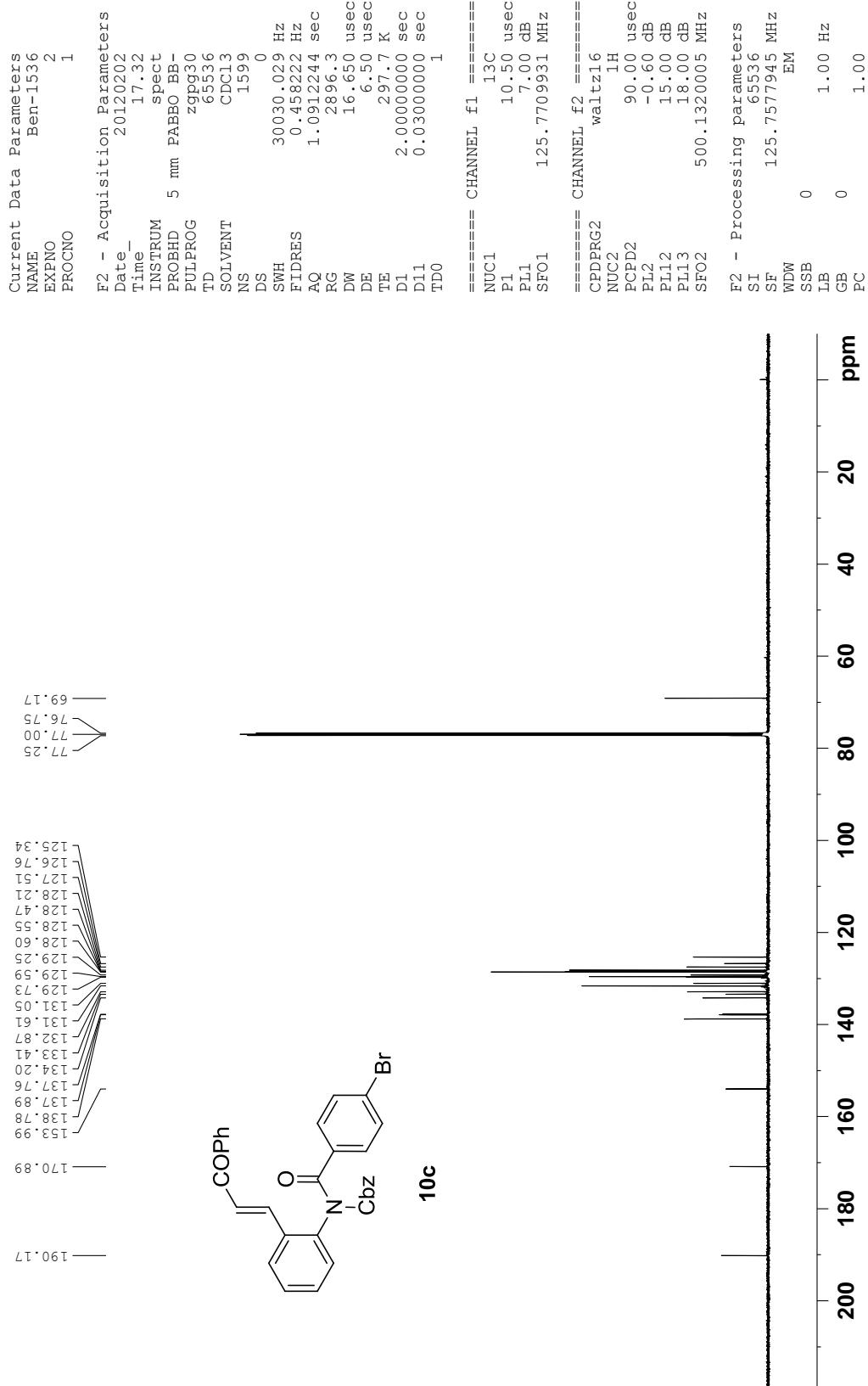


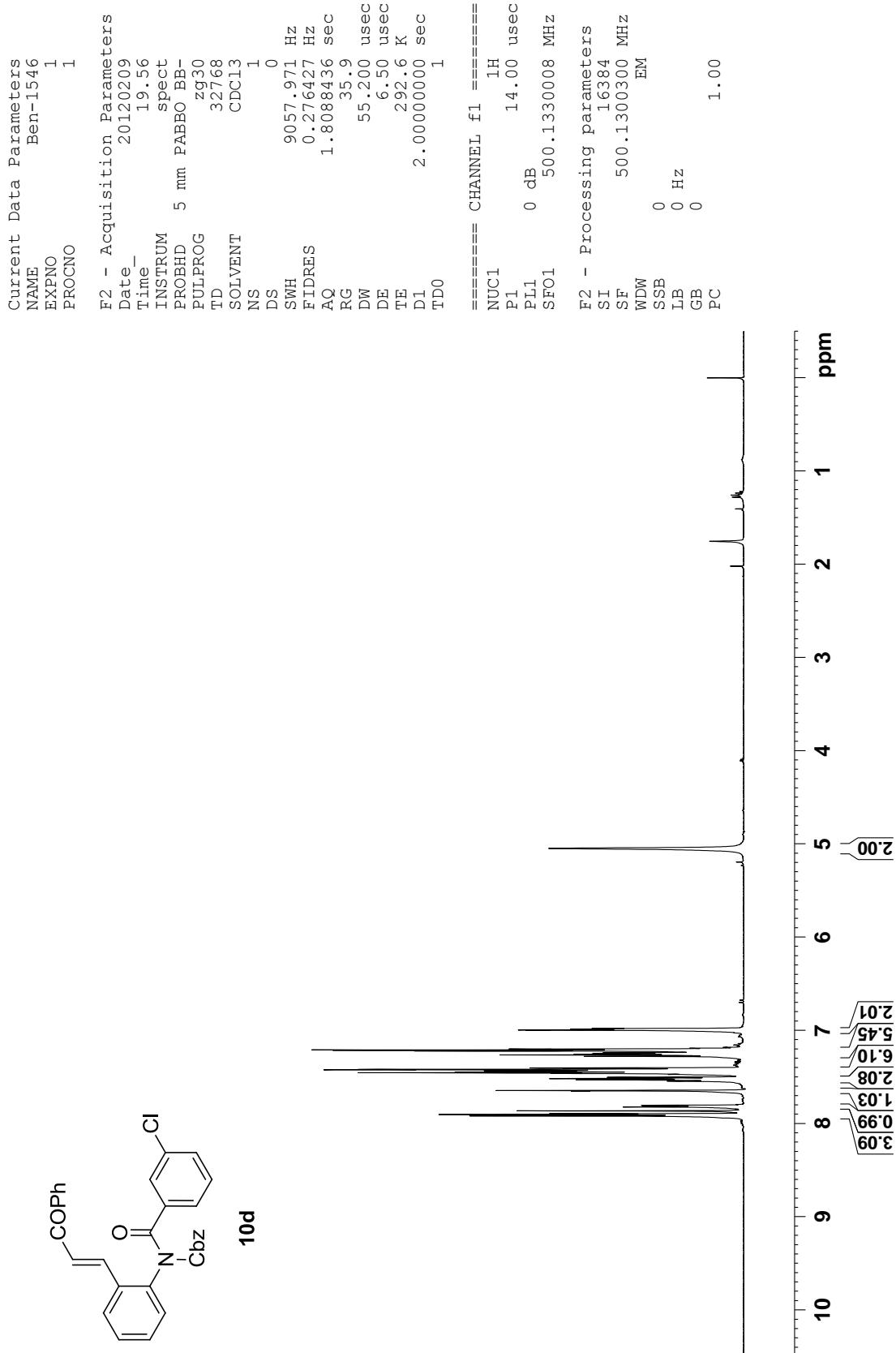


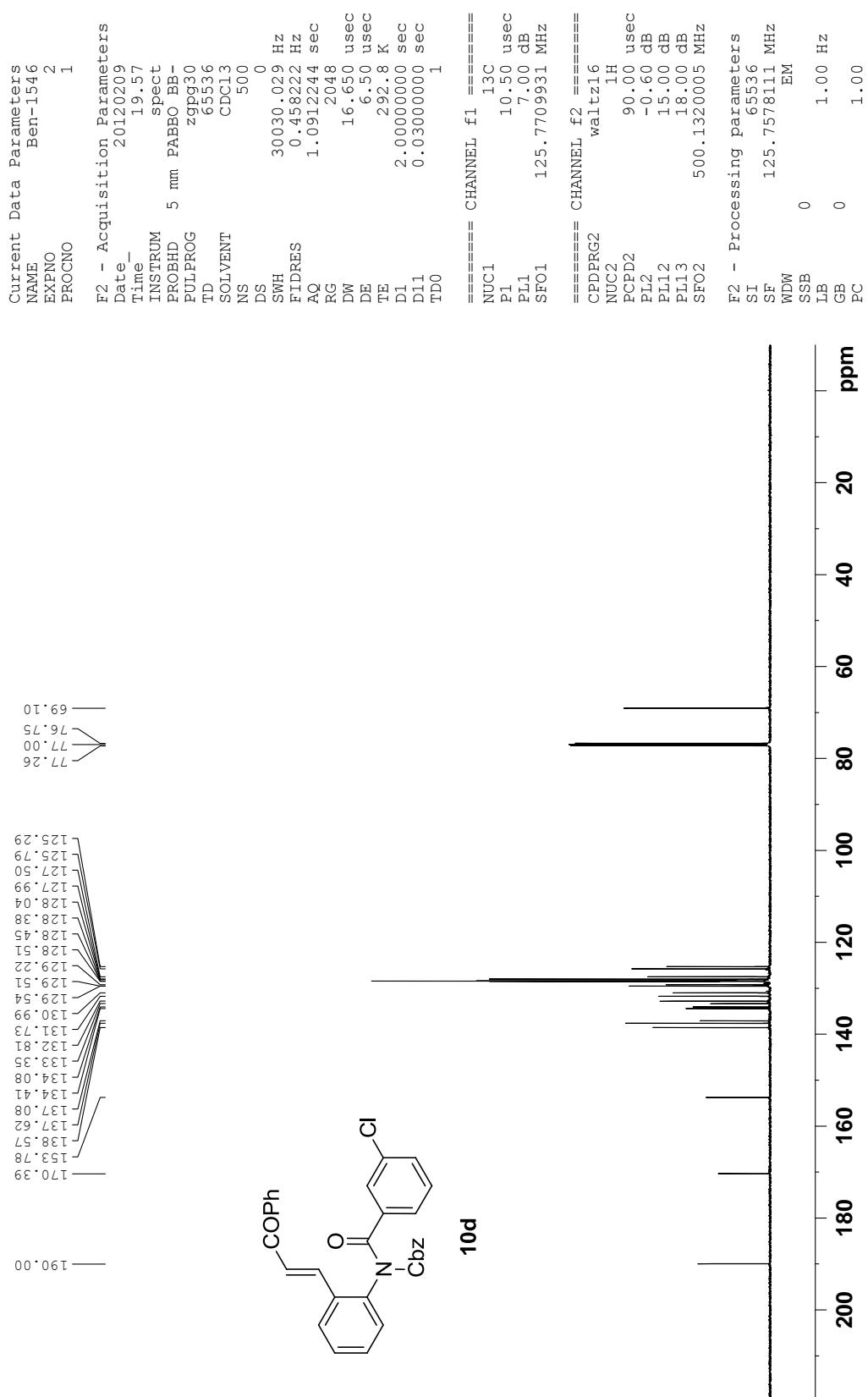


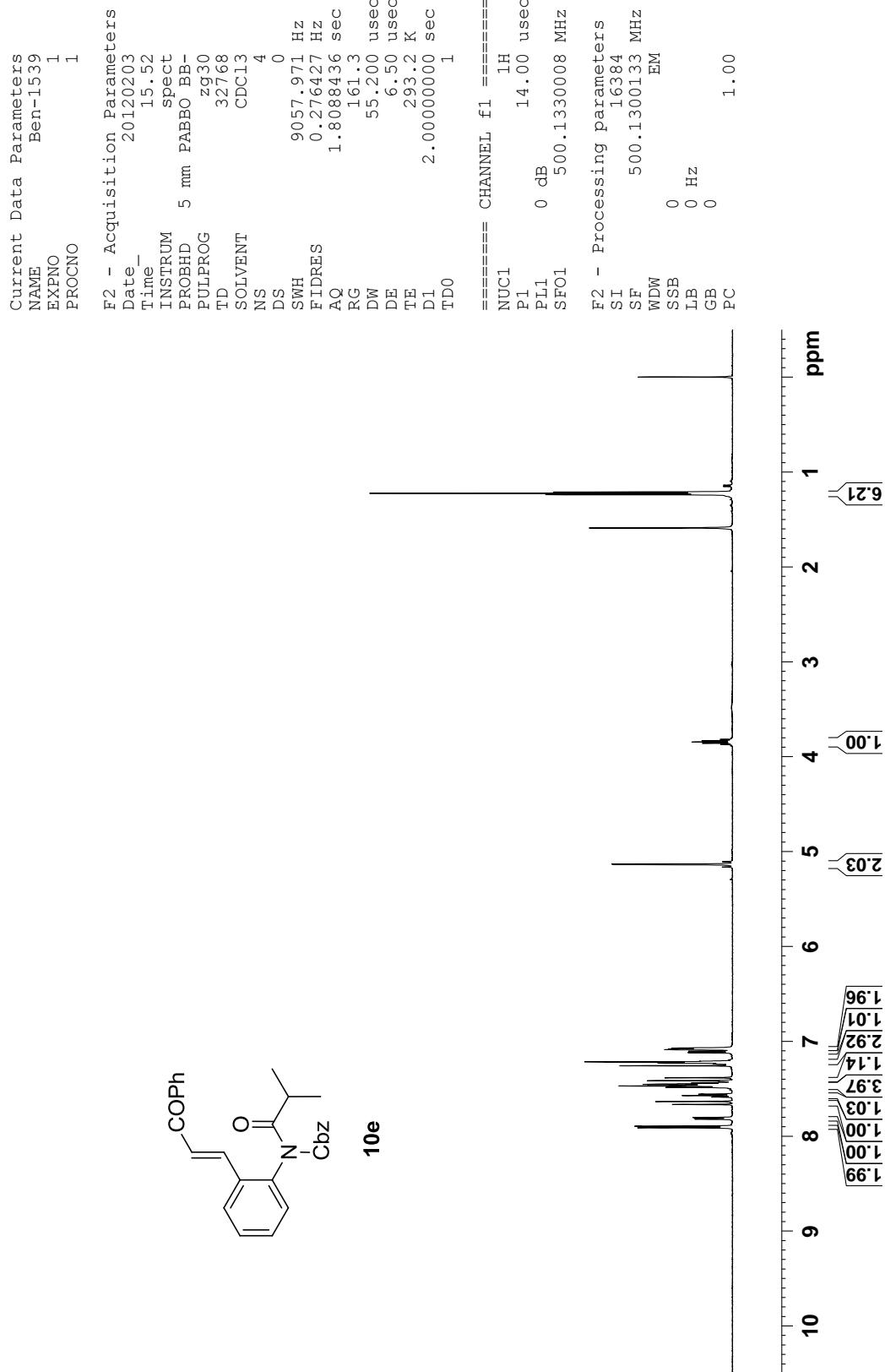


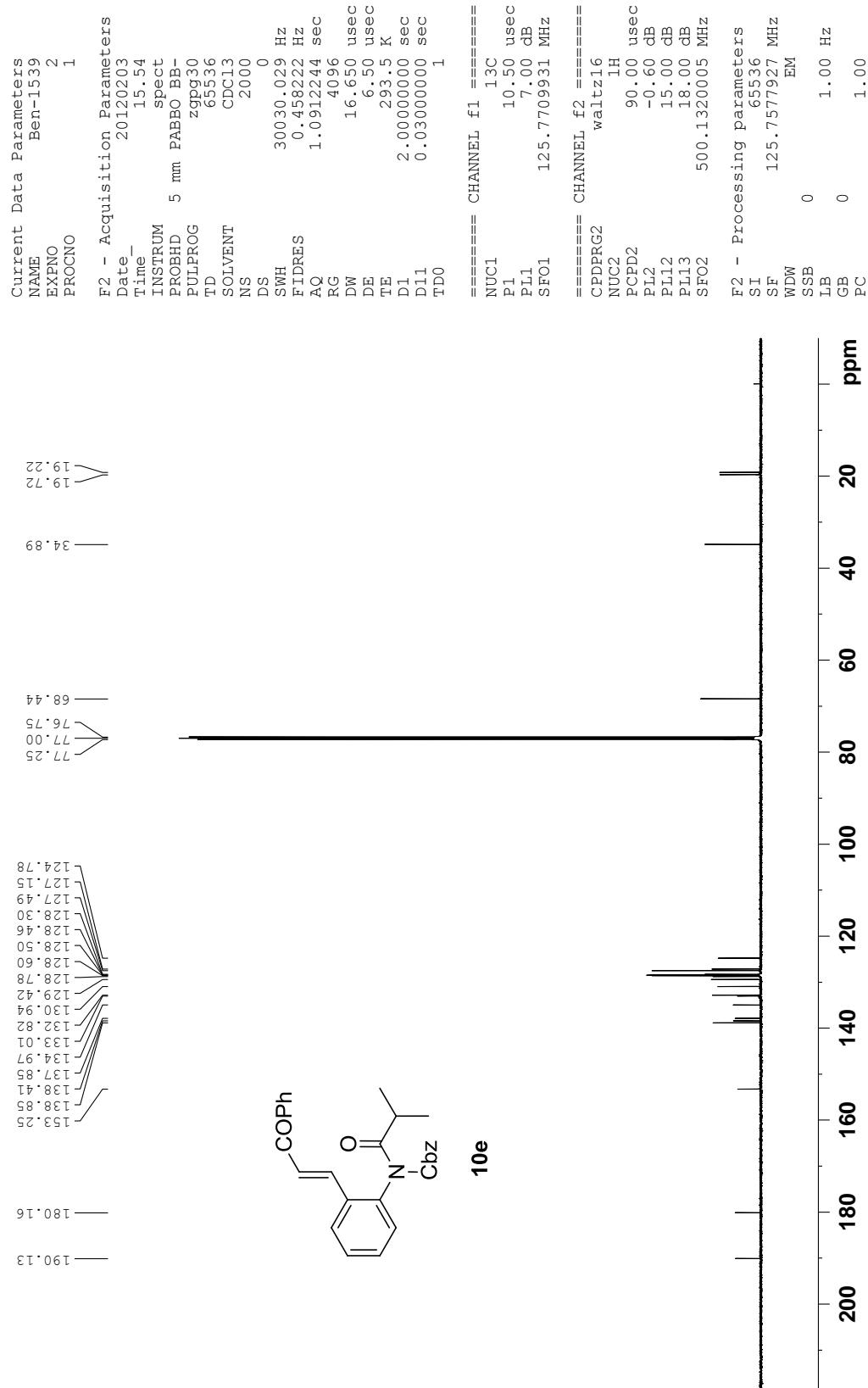


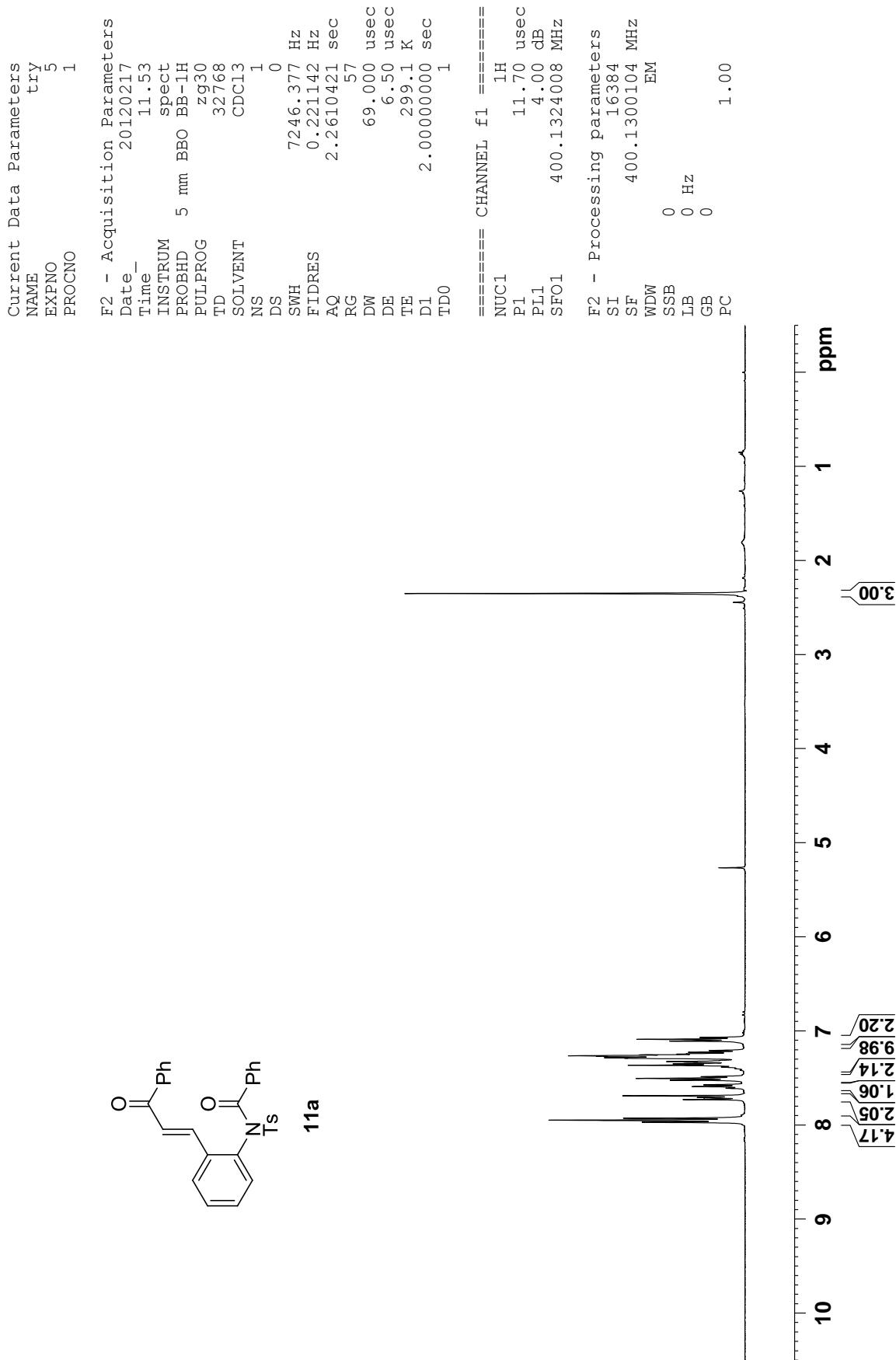


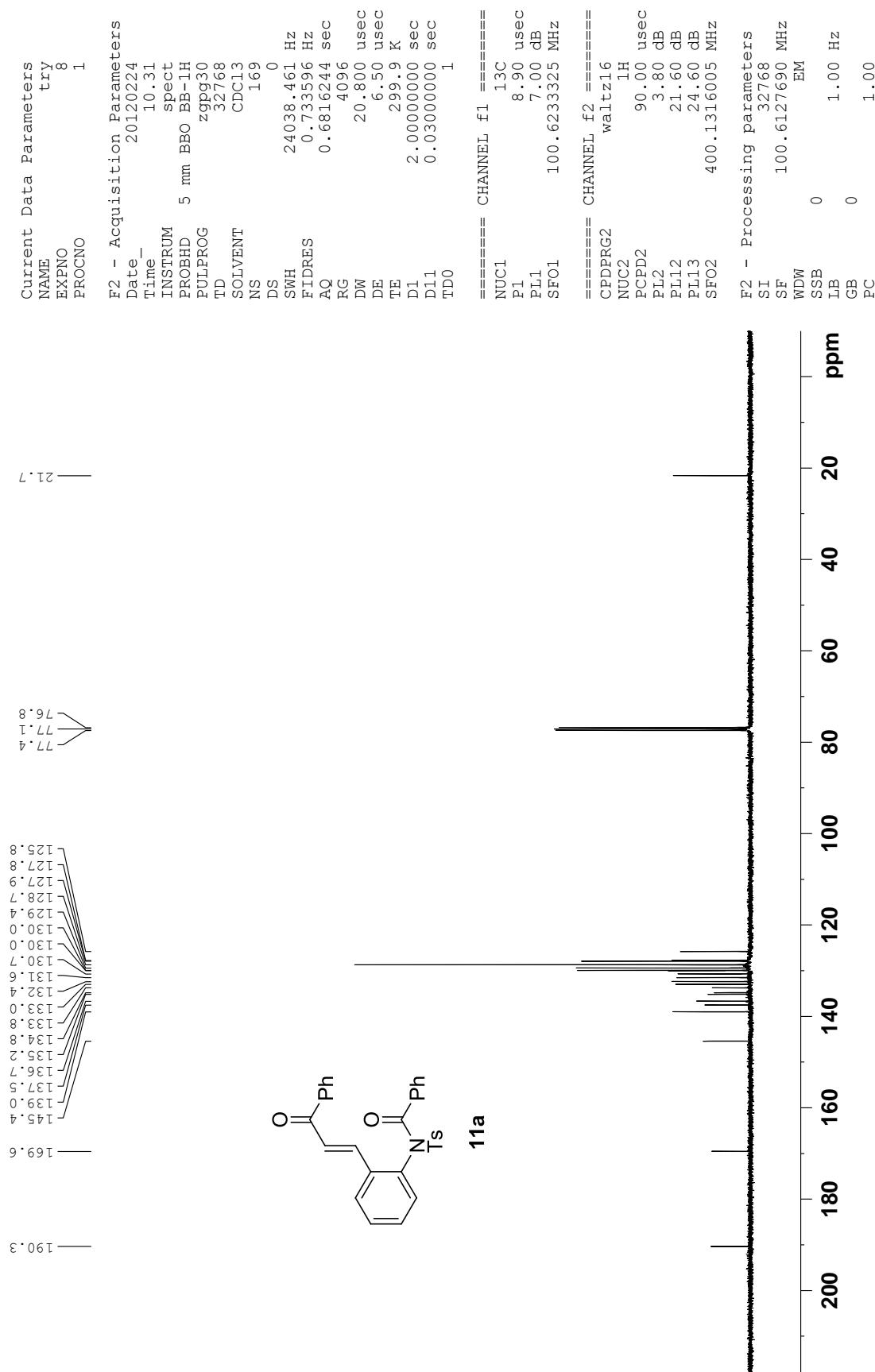


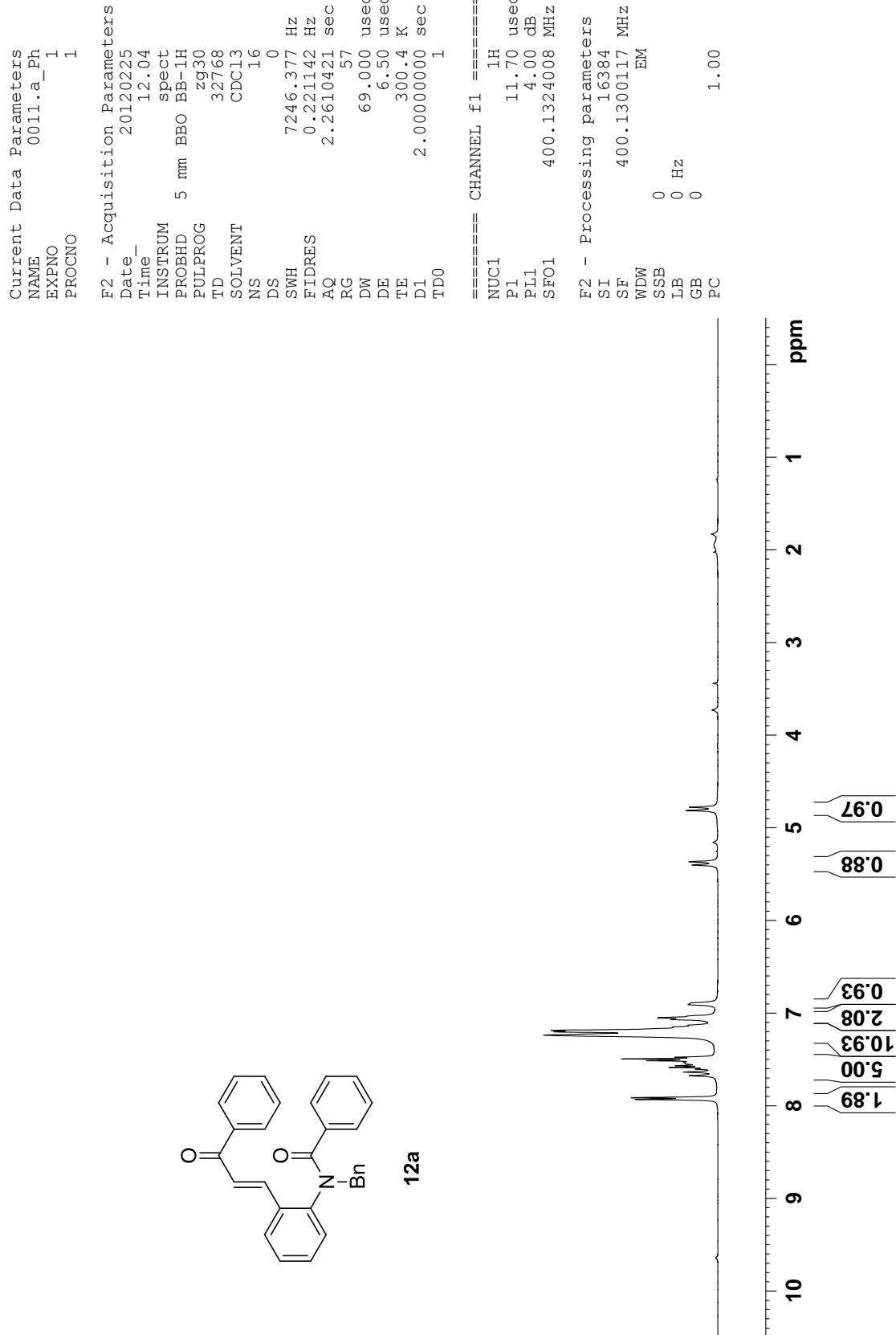


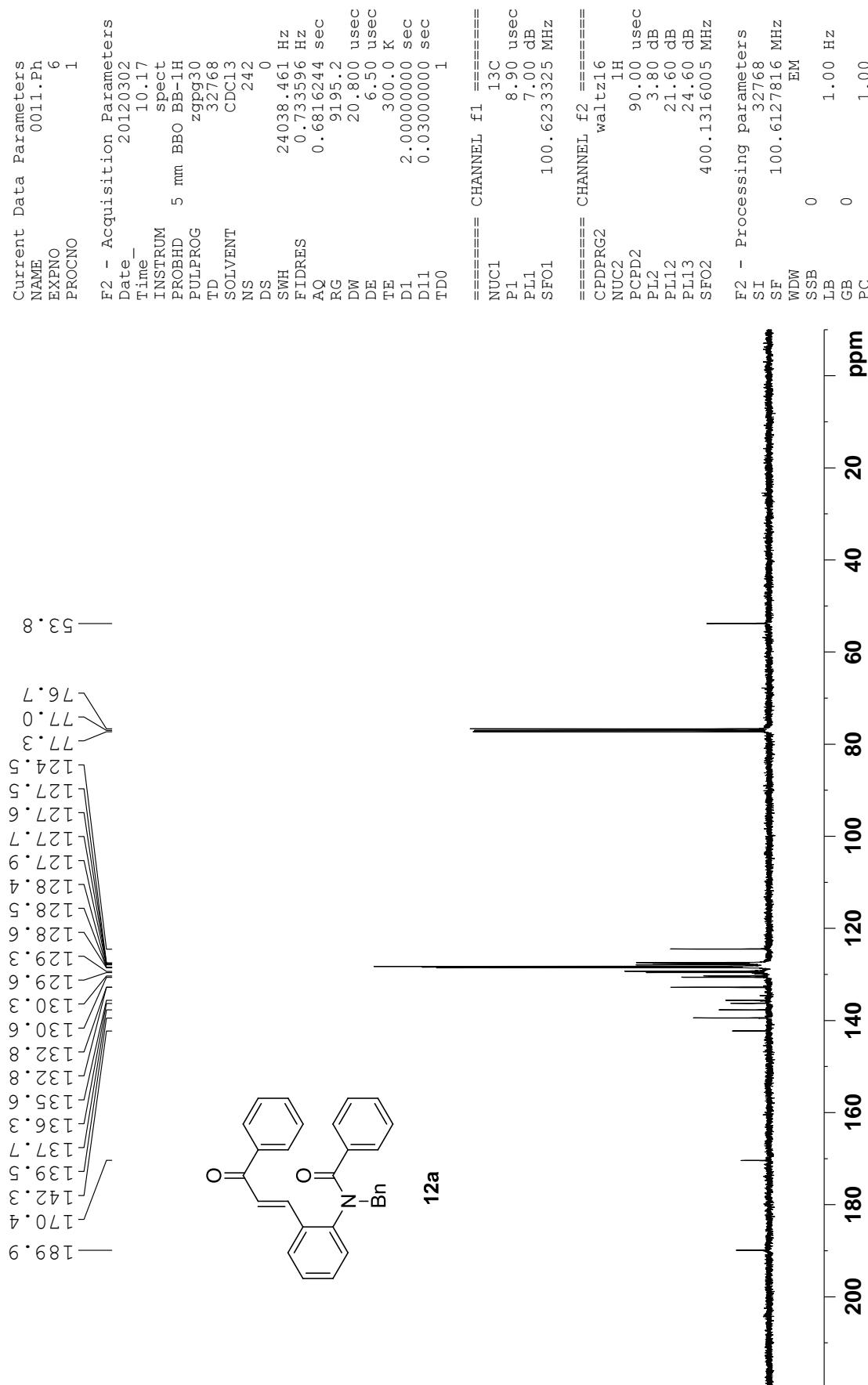


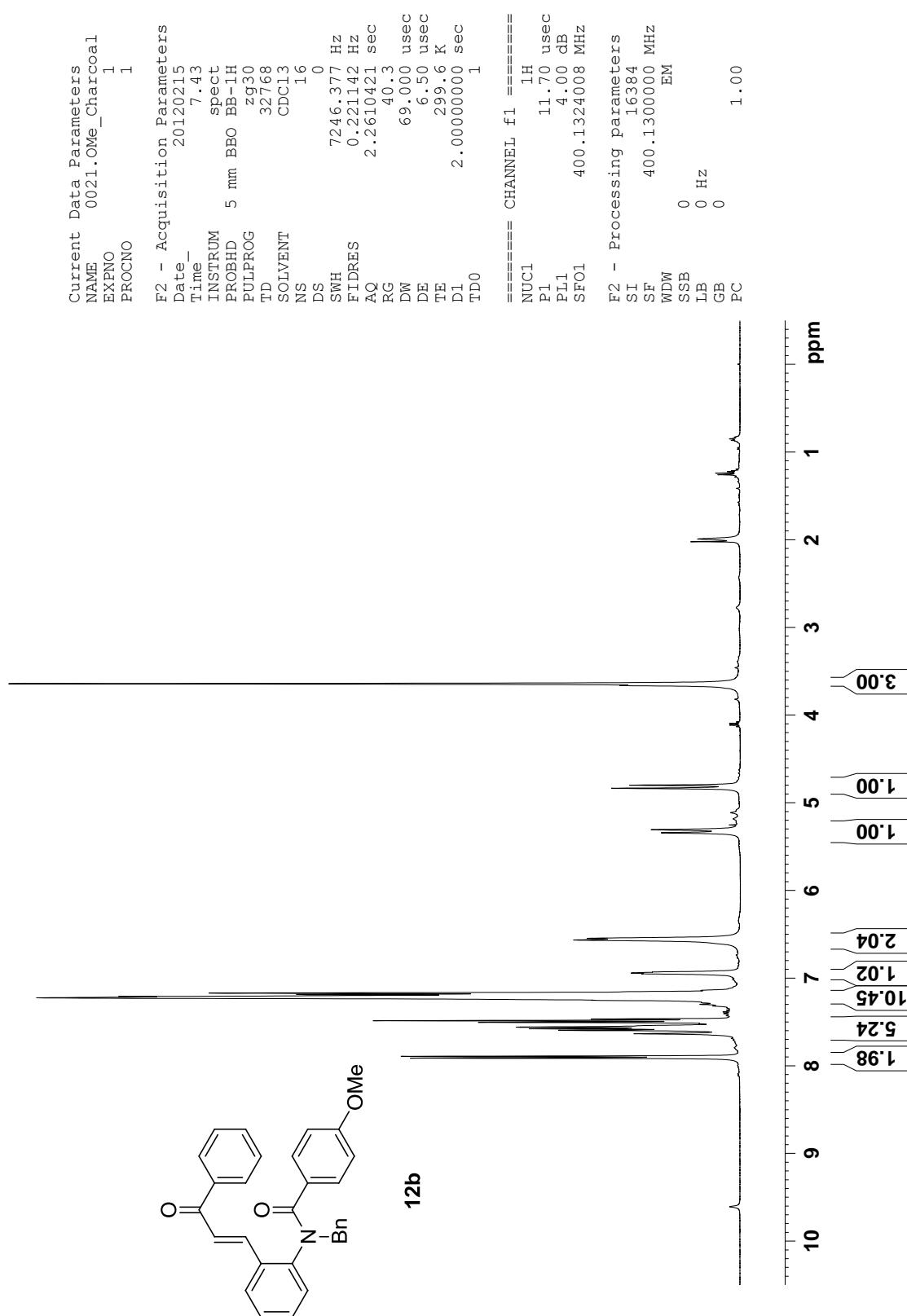


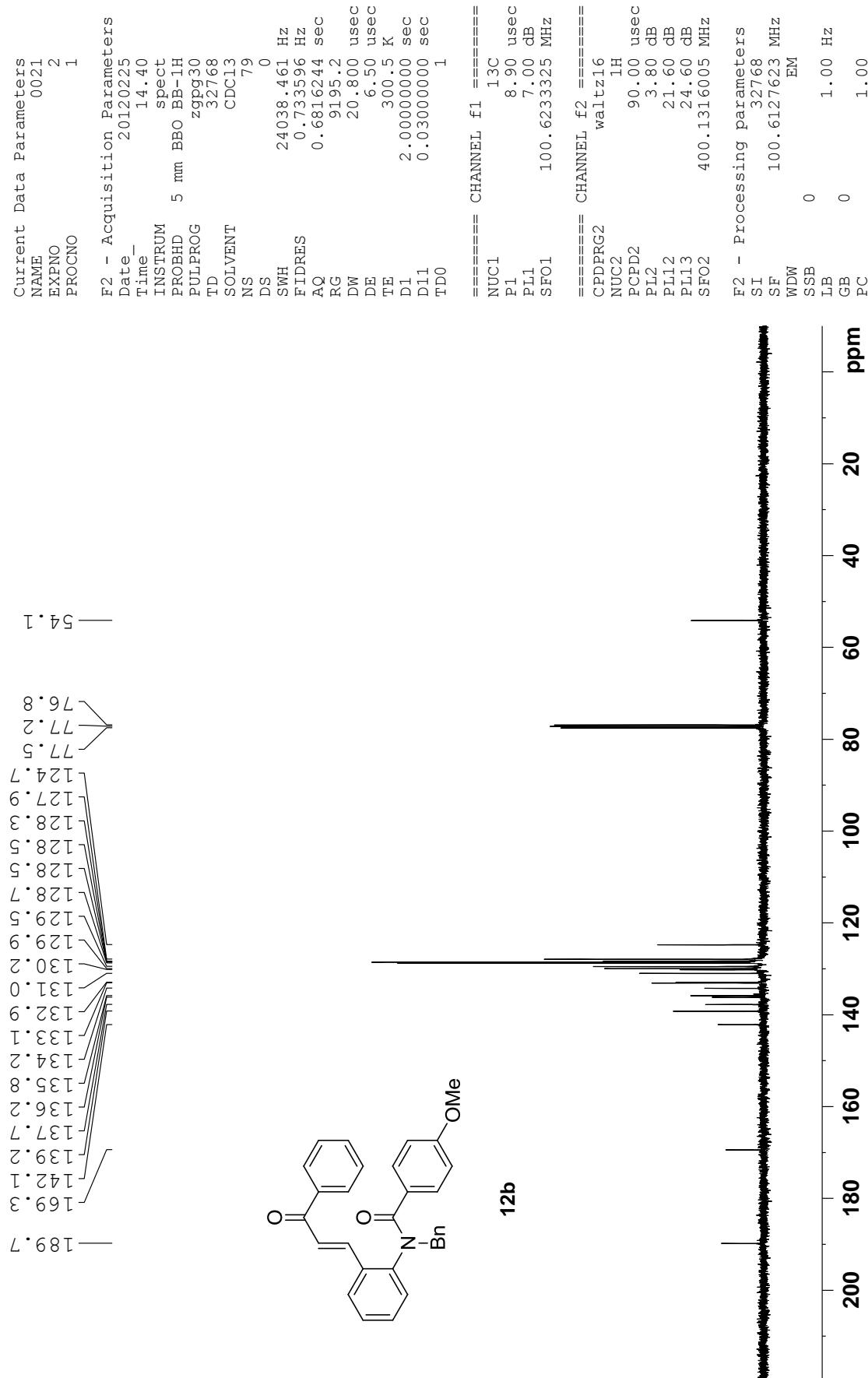


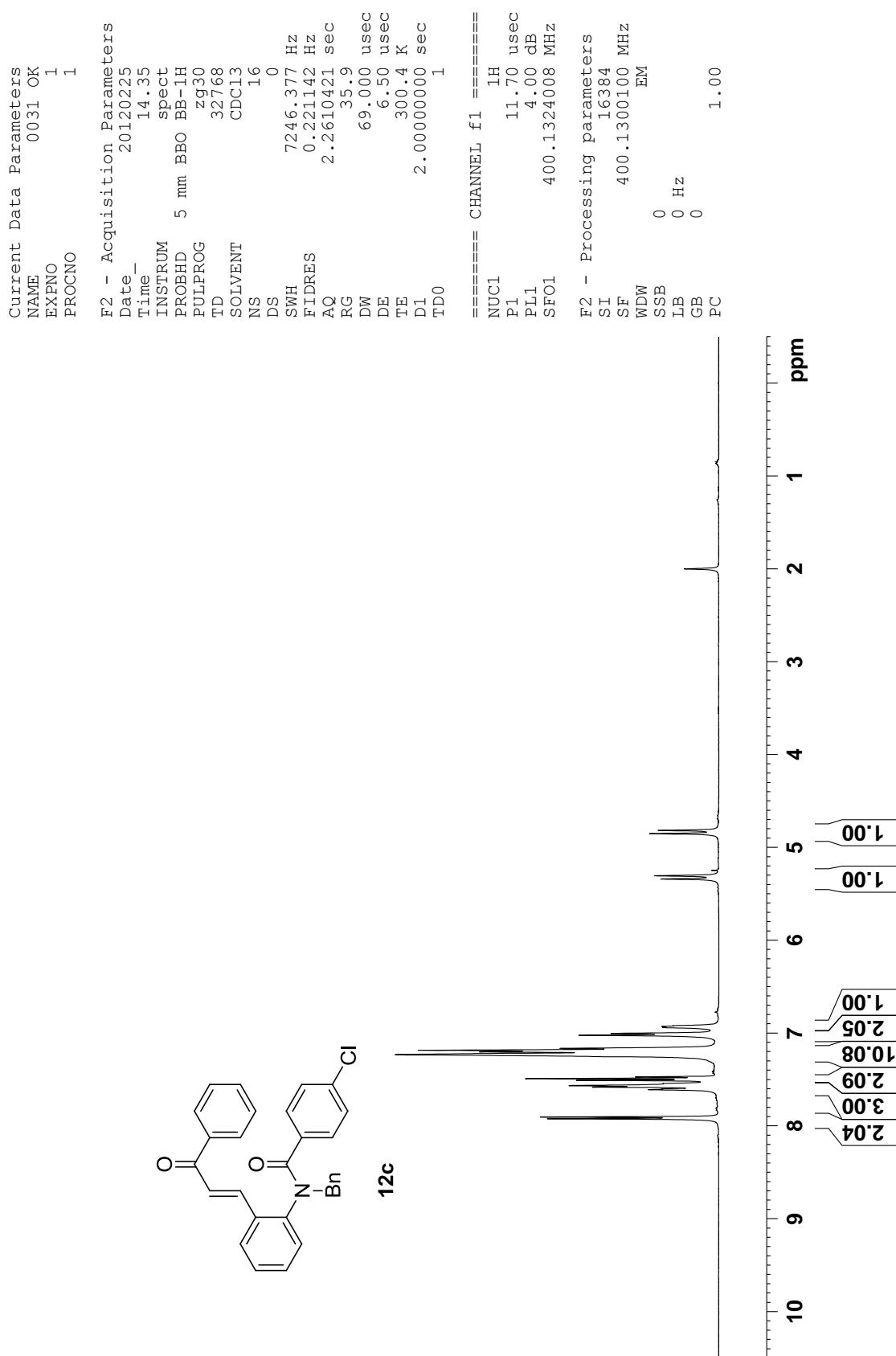


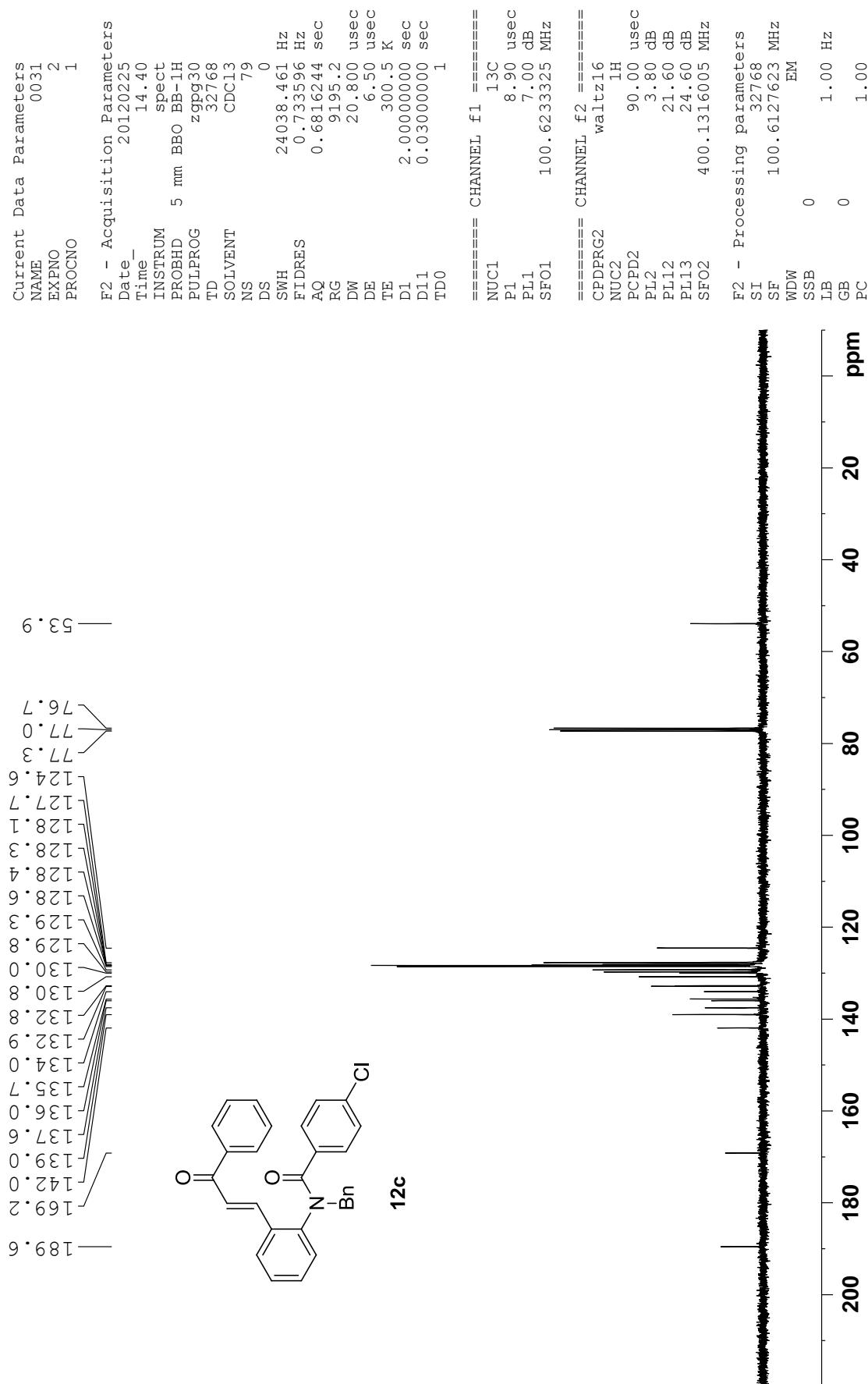








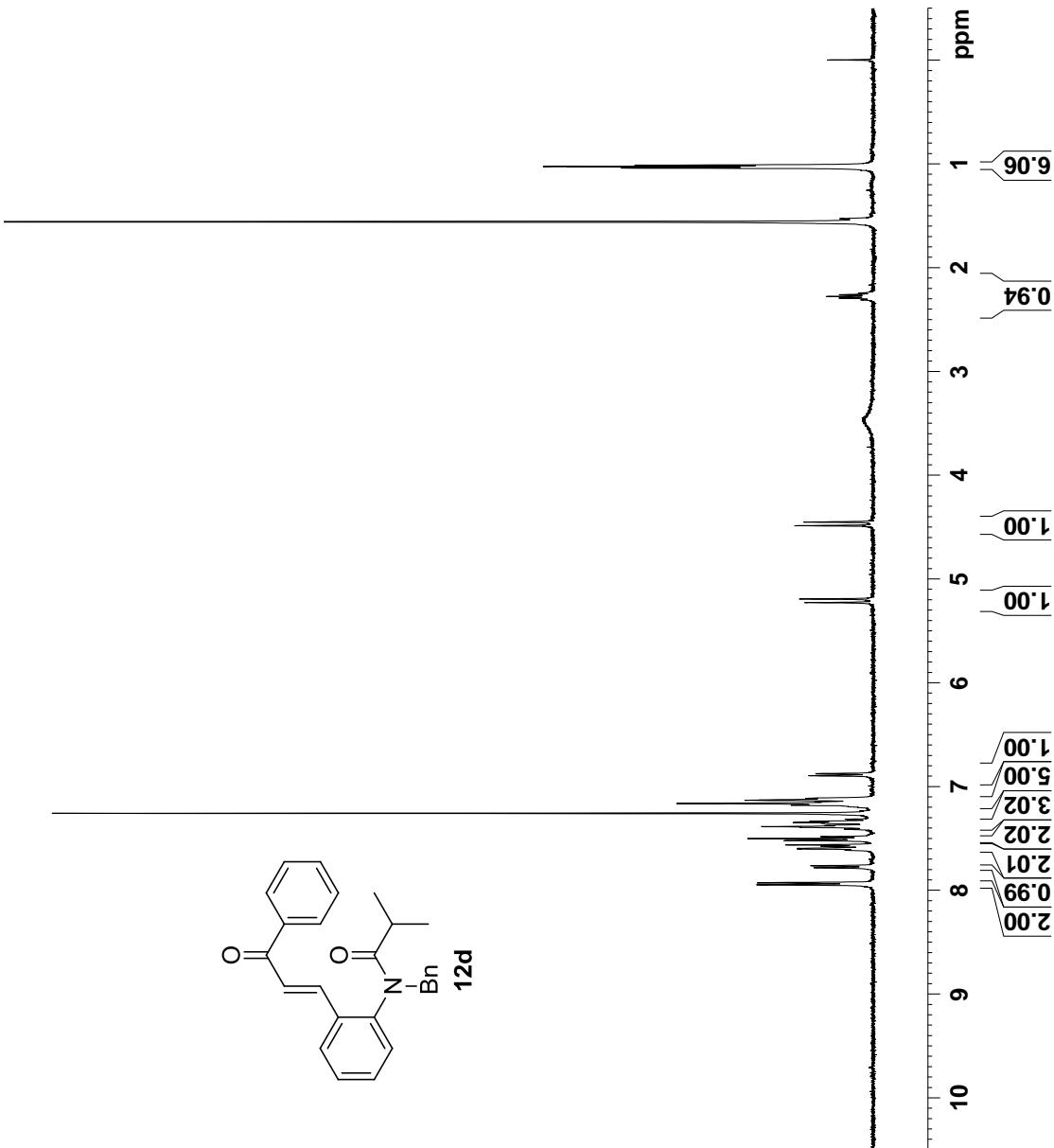


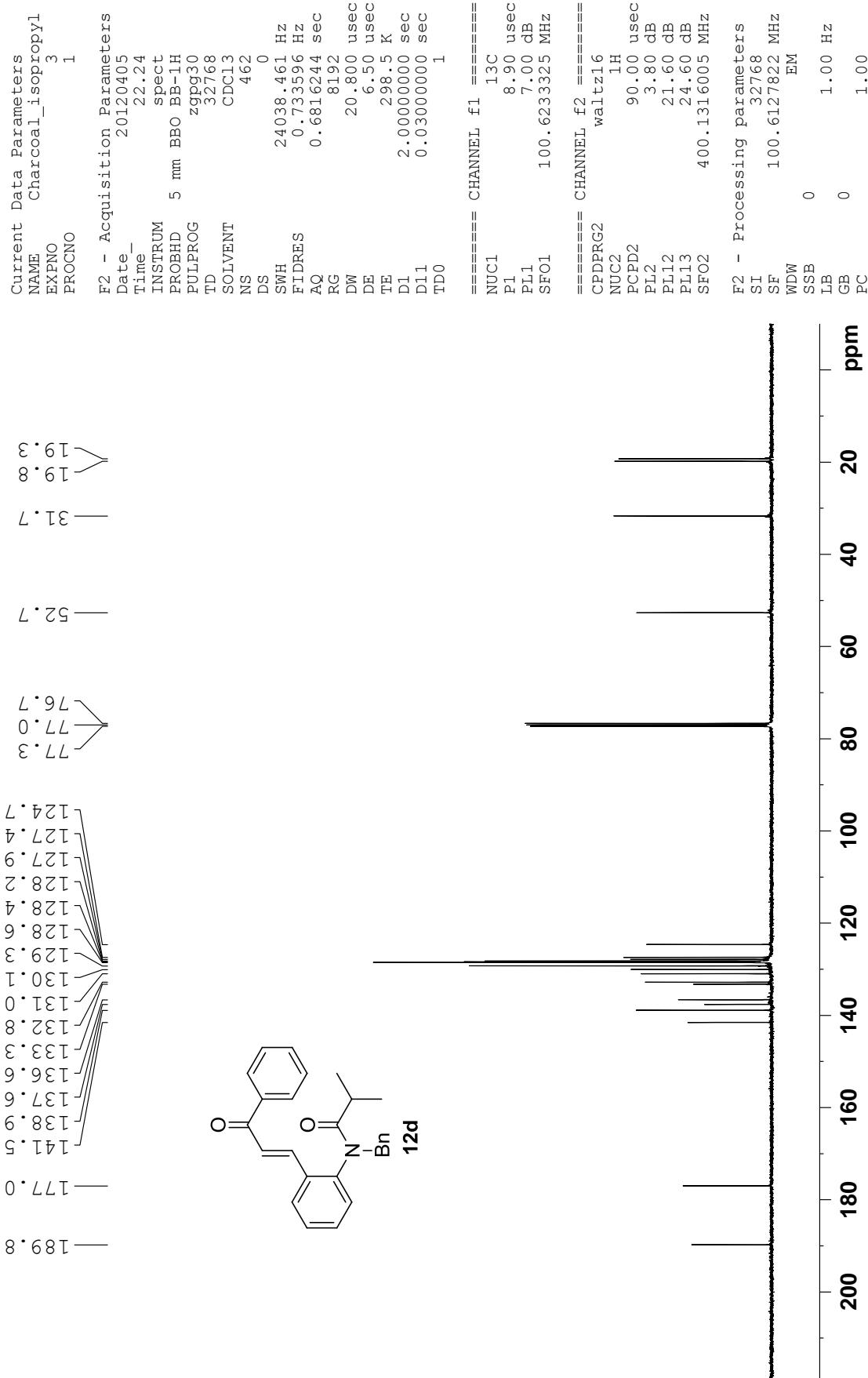


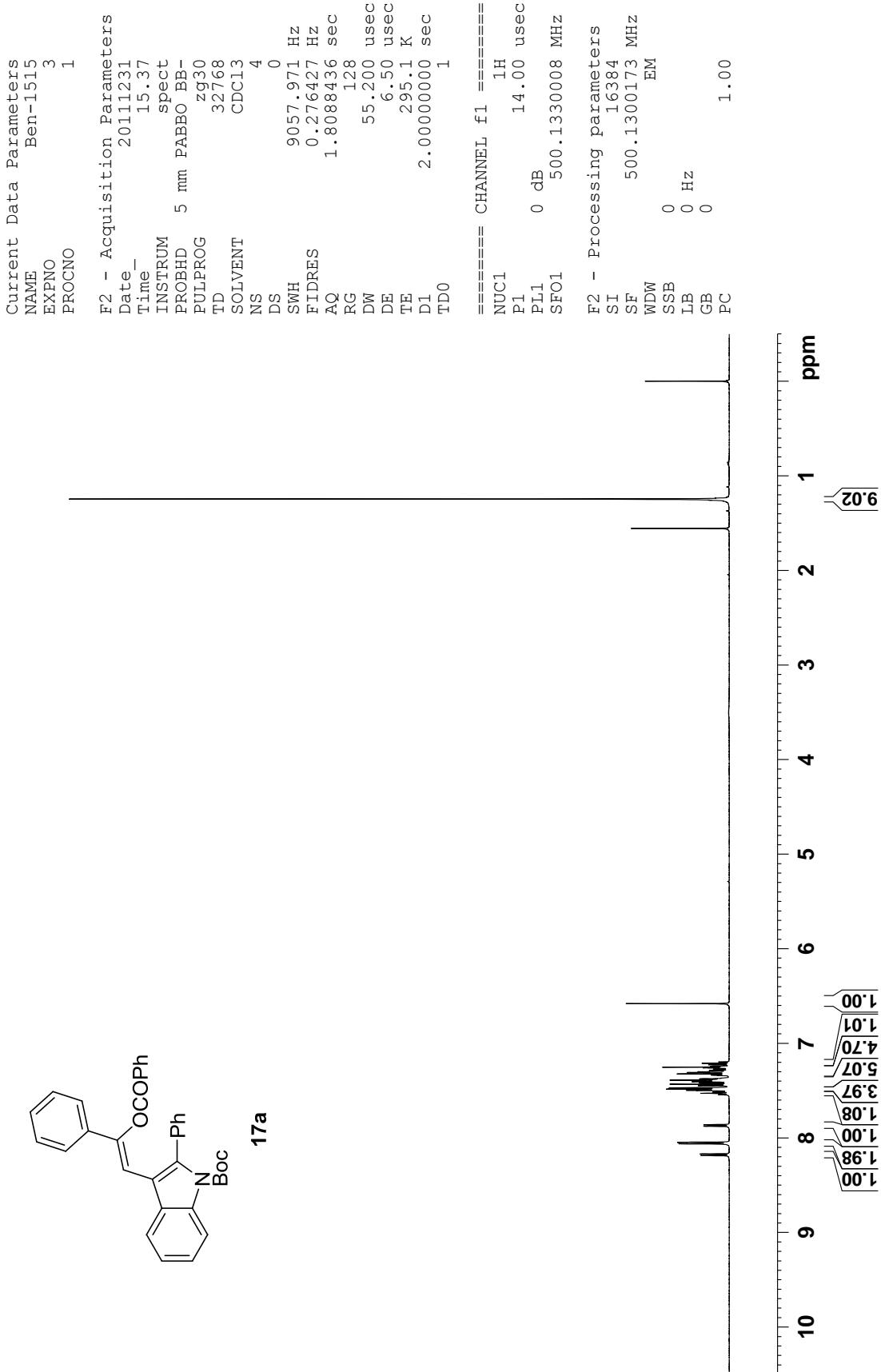
Current Data Parameters
NAME 0041_Isopropyl_Charcoal
EXPNO 1
PROCNO 1

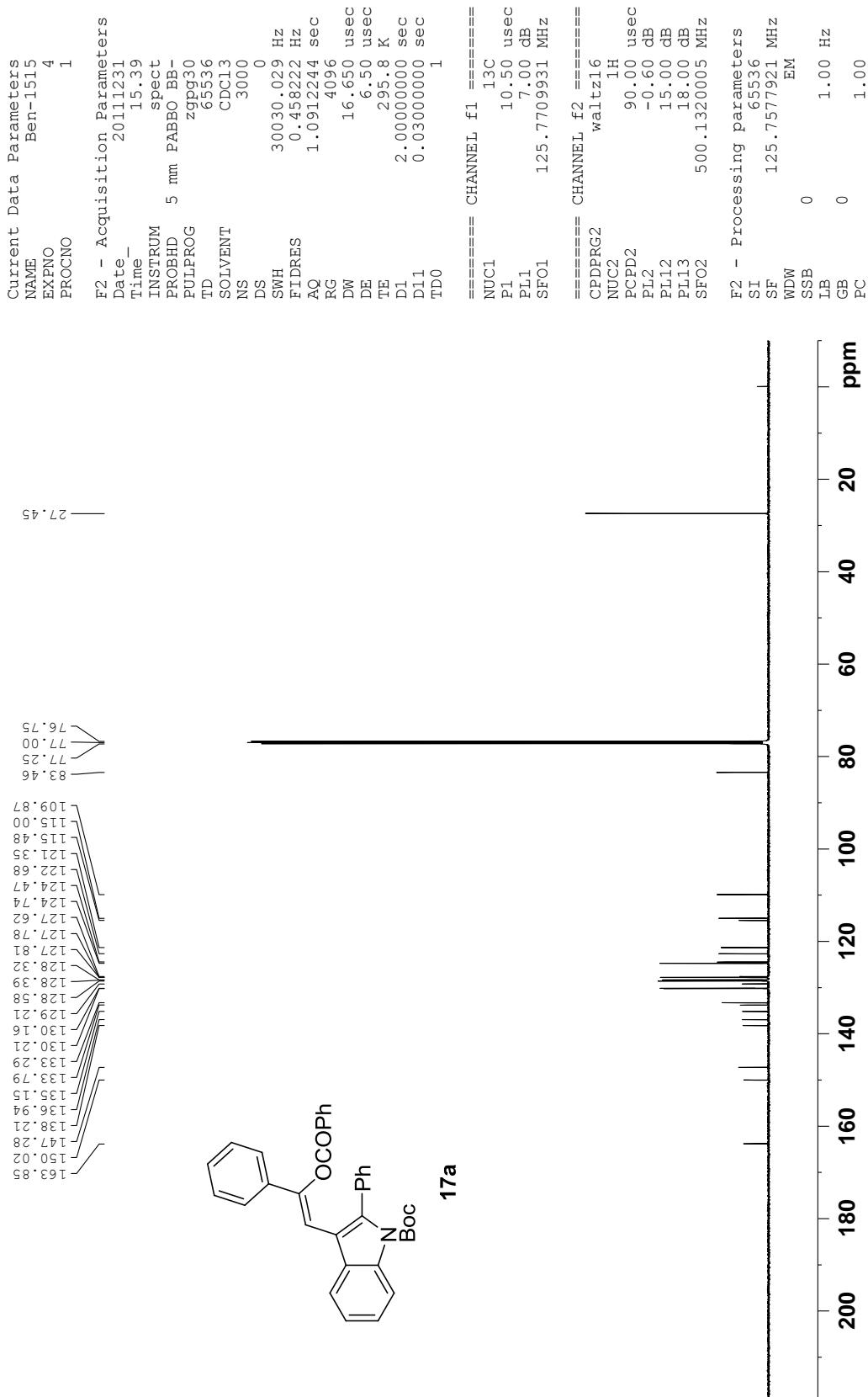
F2 - Acquisition Parameters
Date 20120119
Time 17.58
INSTRUM spect
PROBID 5 mm BBO BB-1H
PULPROG PULPROG
TD 32768
SOLVENT CDCl₃
NS 16
DS 0
SWH 7246.377 Hz
FIDRES 0.221142 Hz
AQ 2.2610421 sec
RG 362
DW 69.000 usec
DE 6.500 usec
TE 300.5 K
D1 2.000000001 sec
TDO

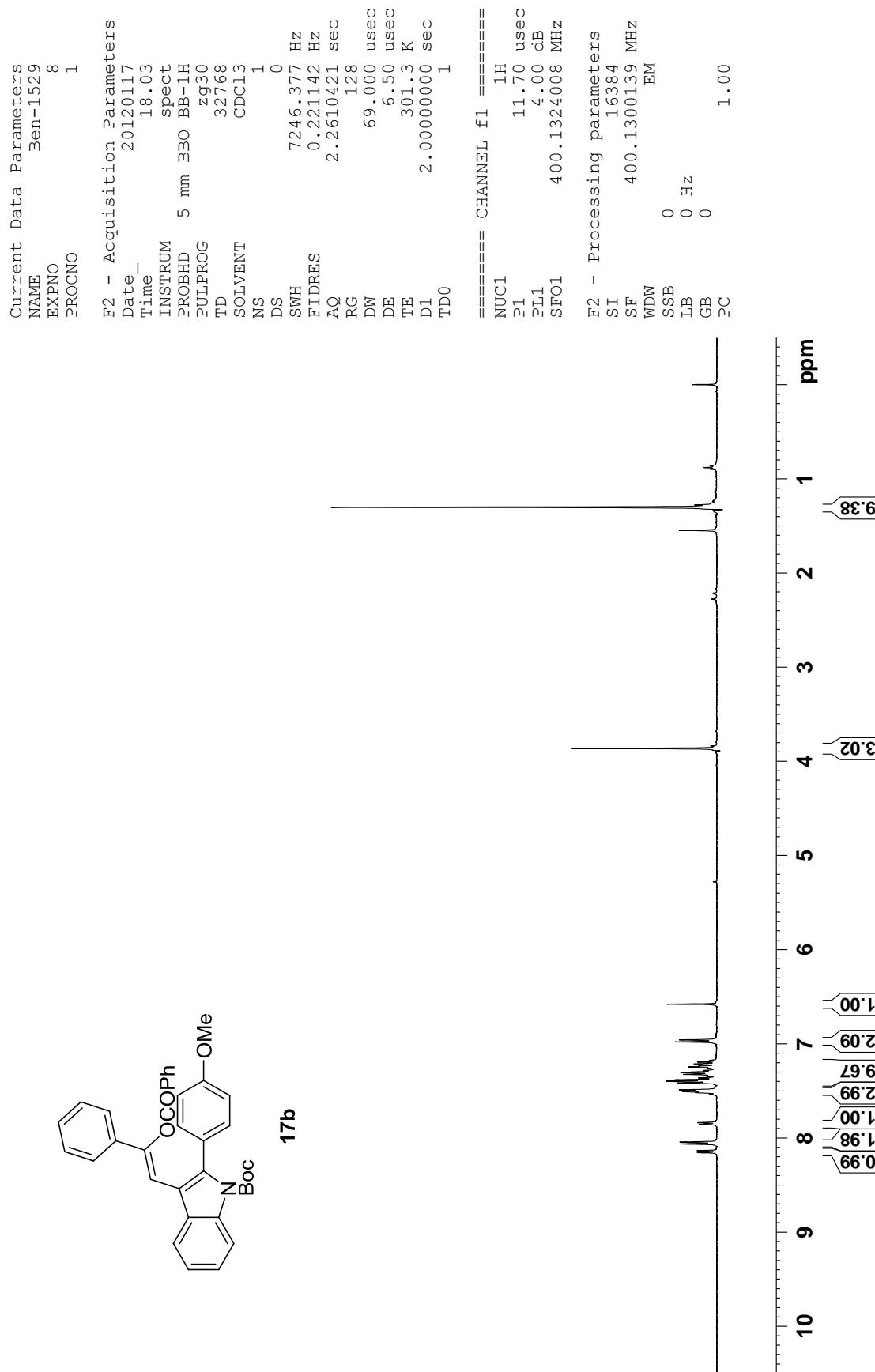
===== CHANNEL f1 ======
NUC1 1H
P1 11.70 usec
PL1 4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 16384
SF 400.1300086 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

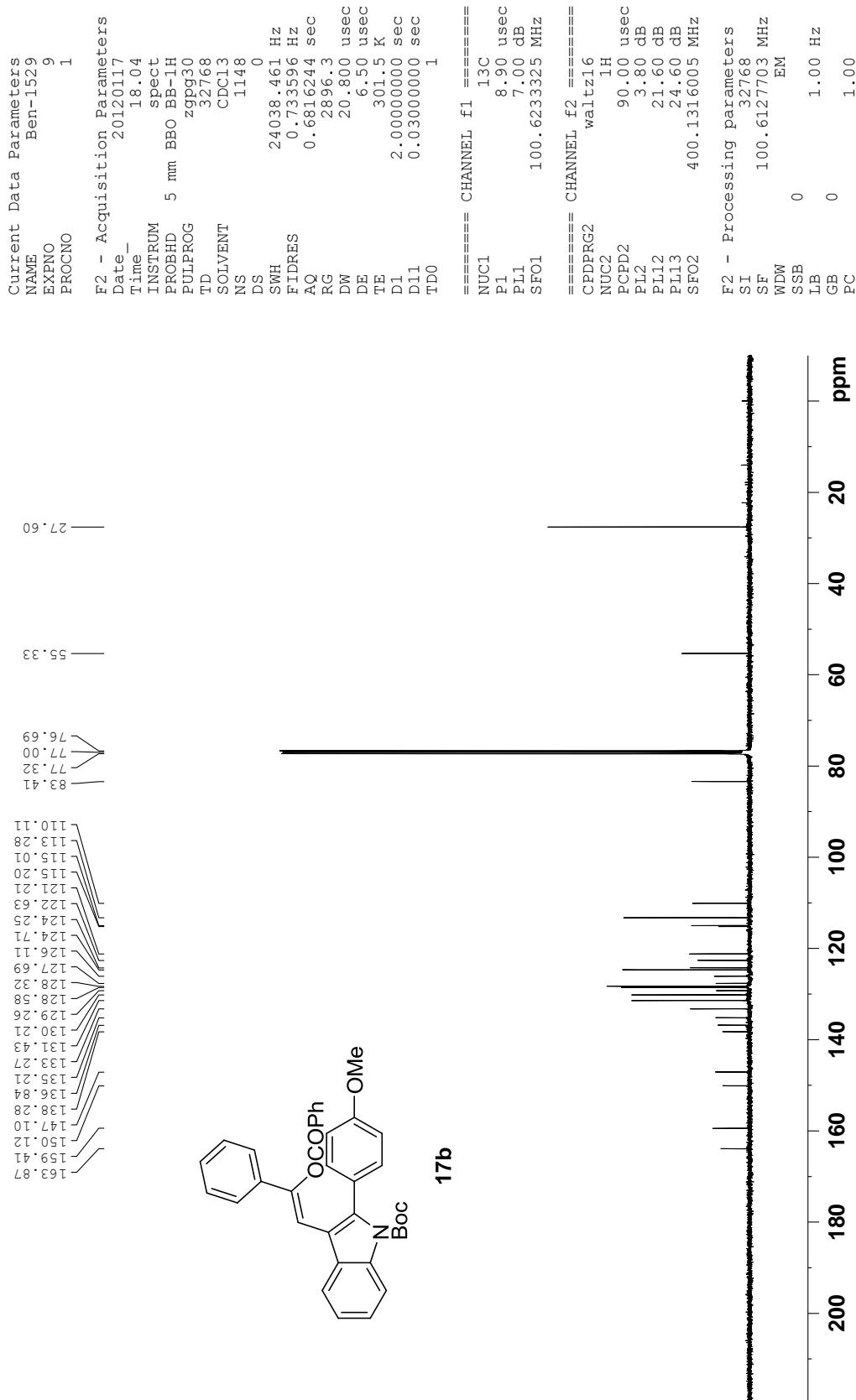


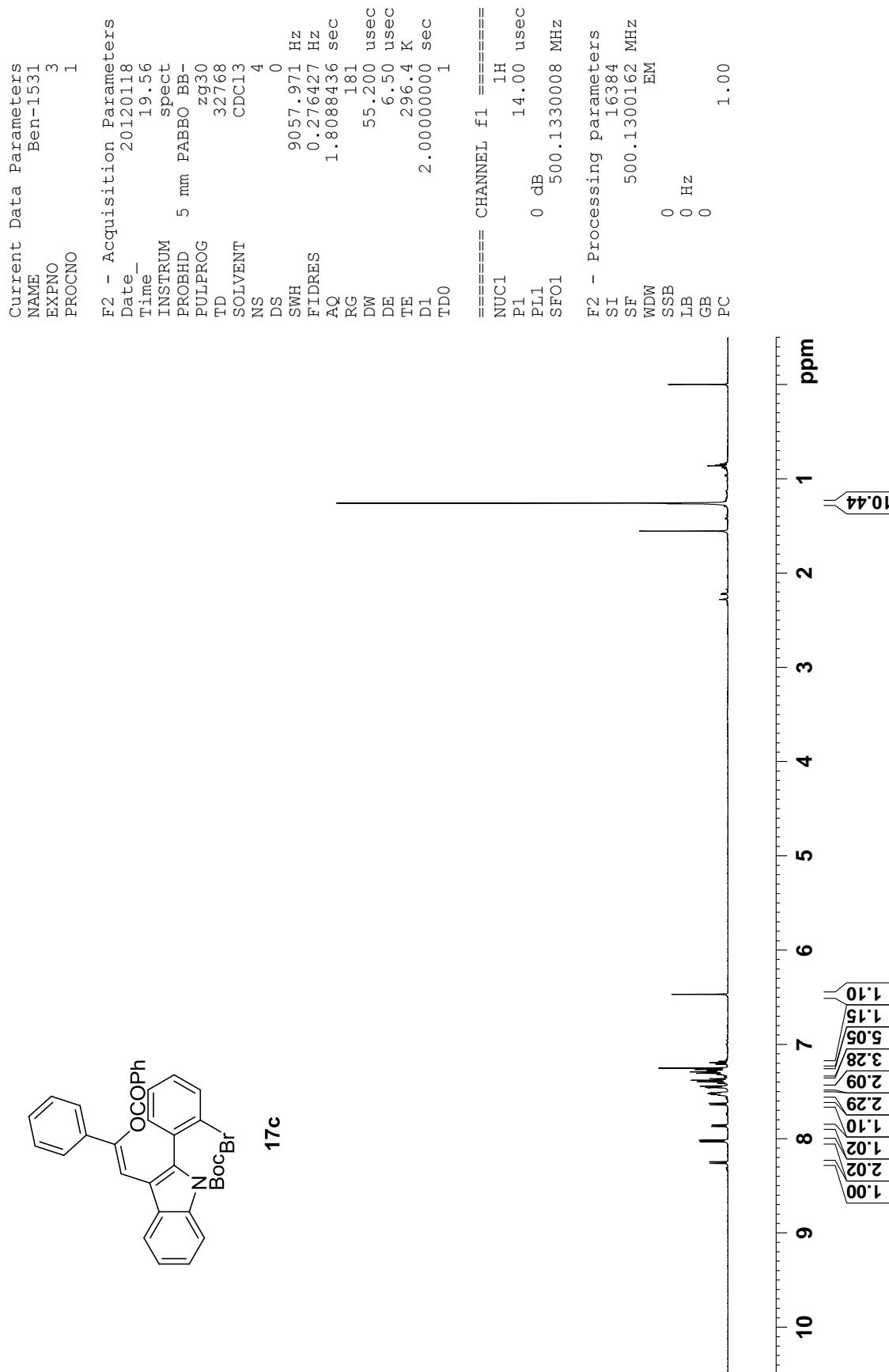


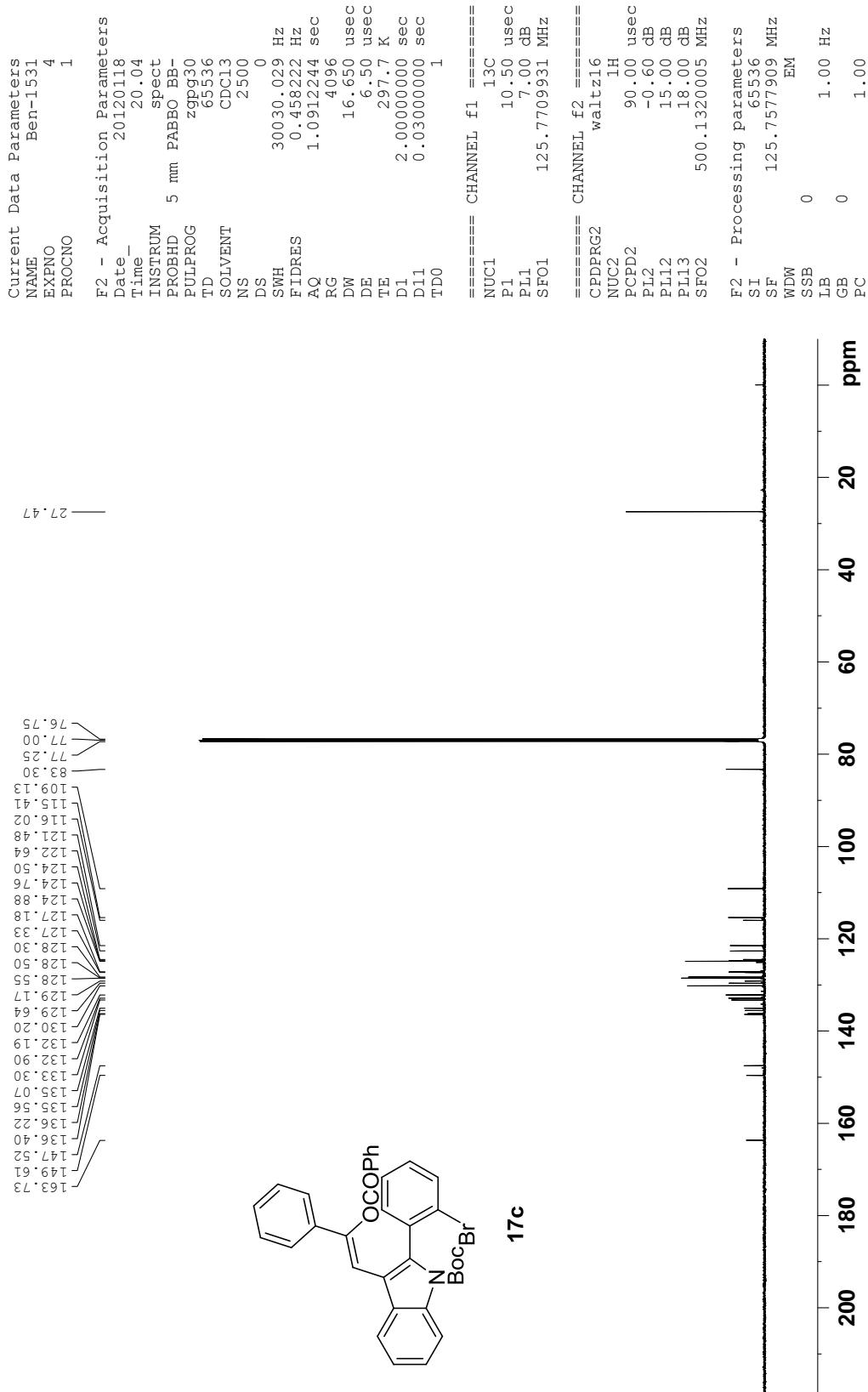


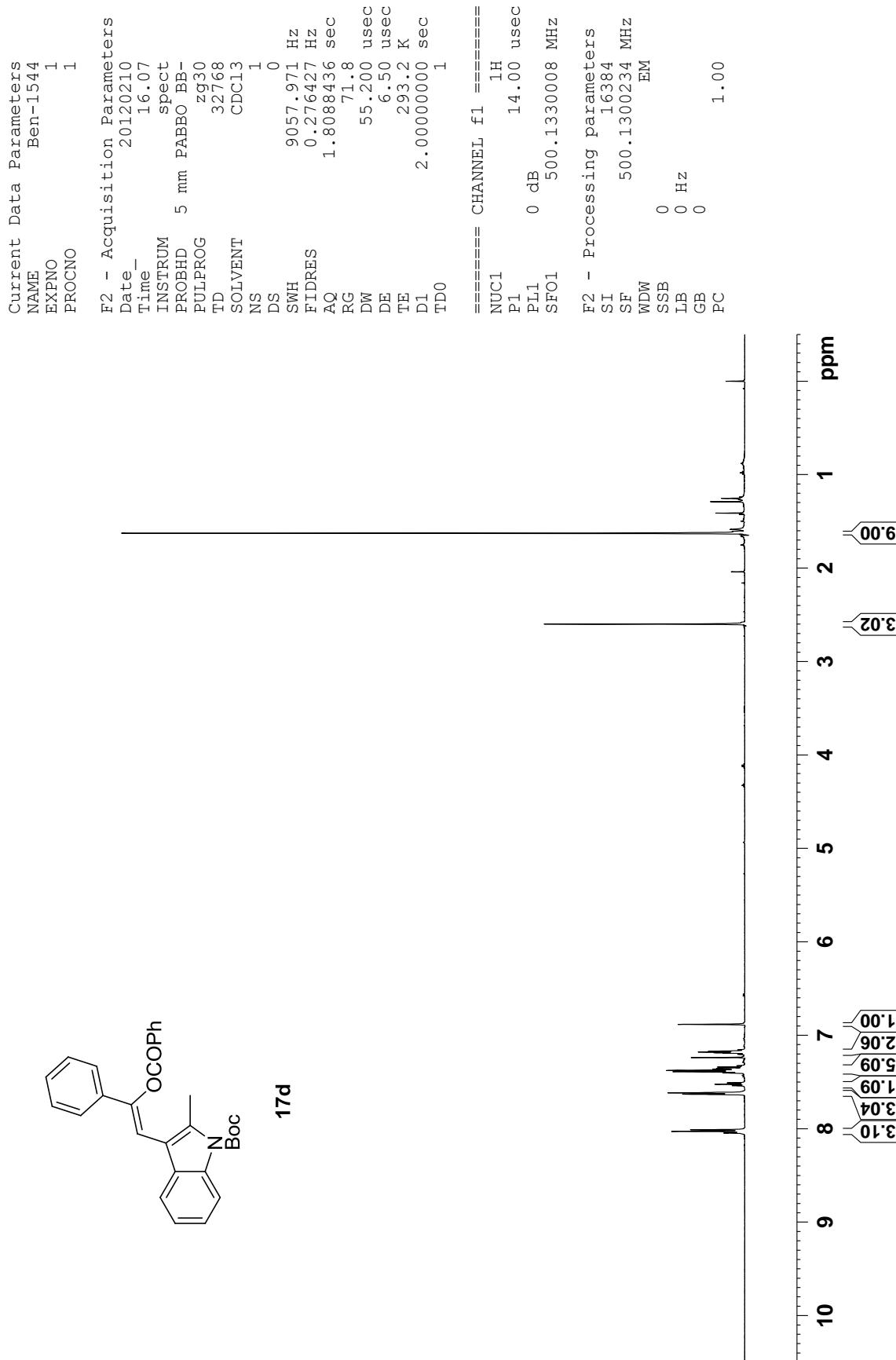


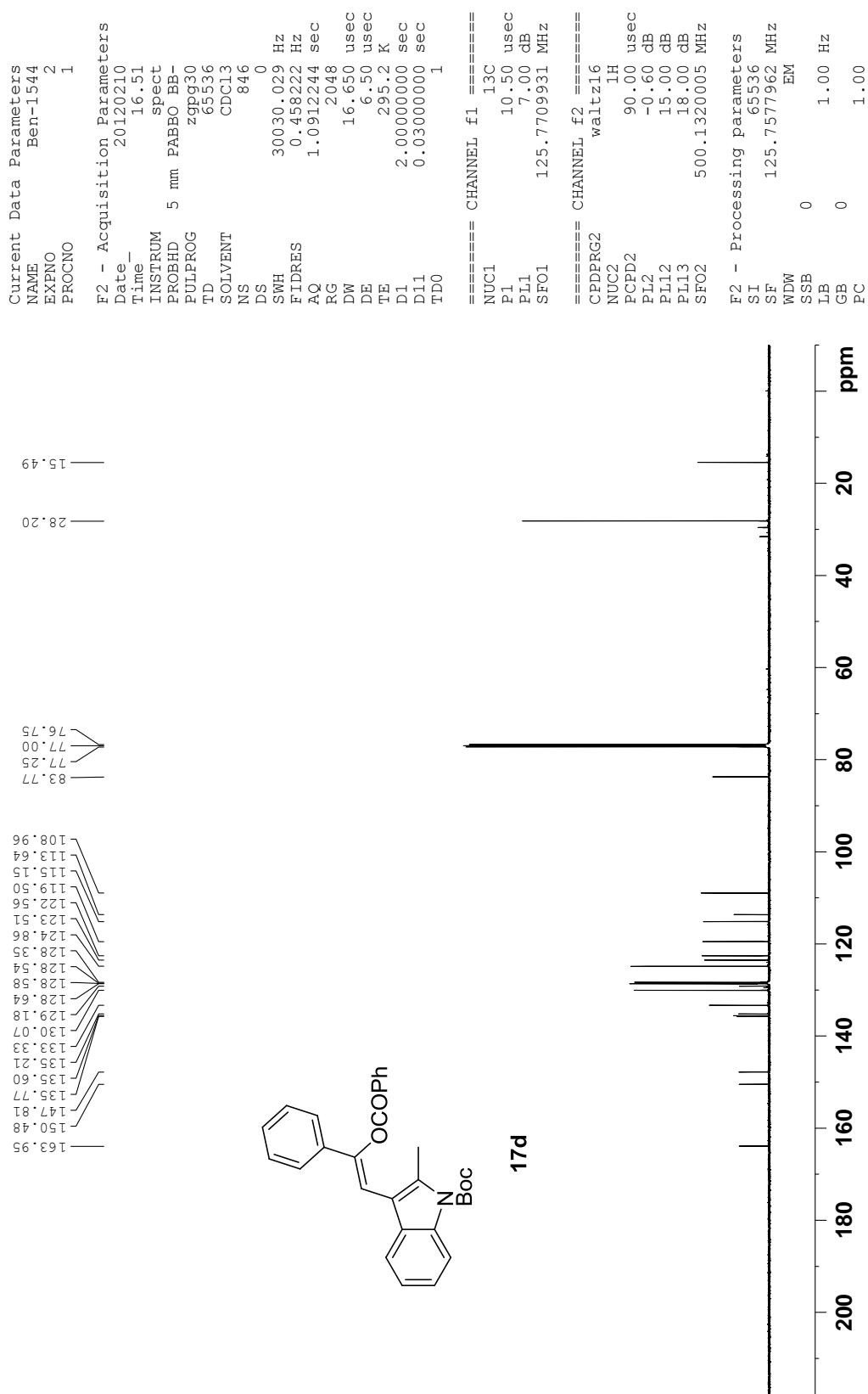


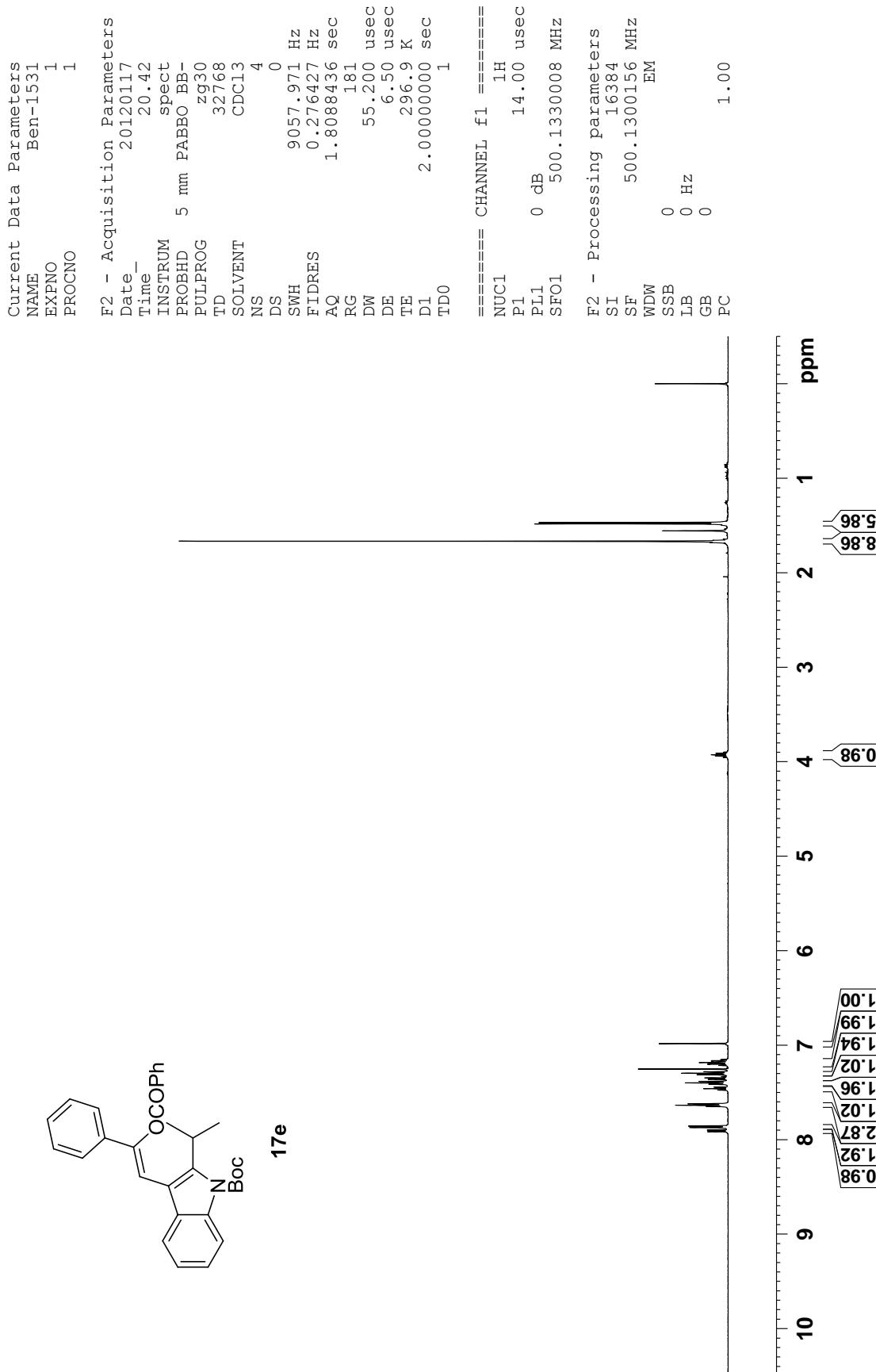


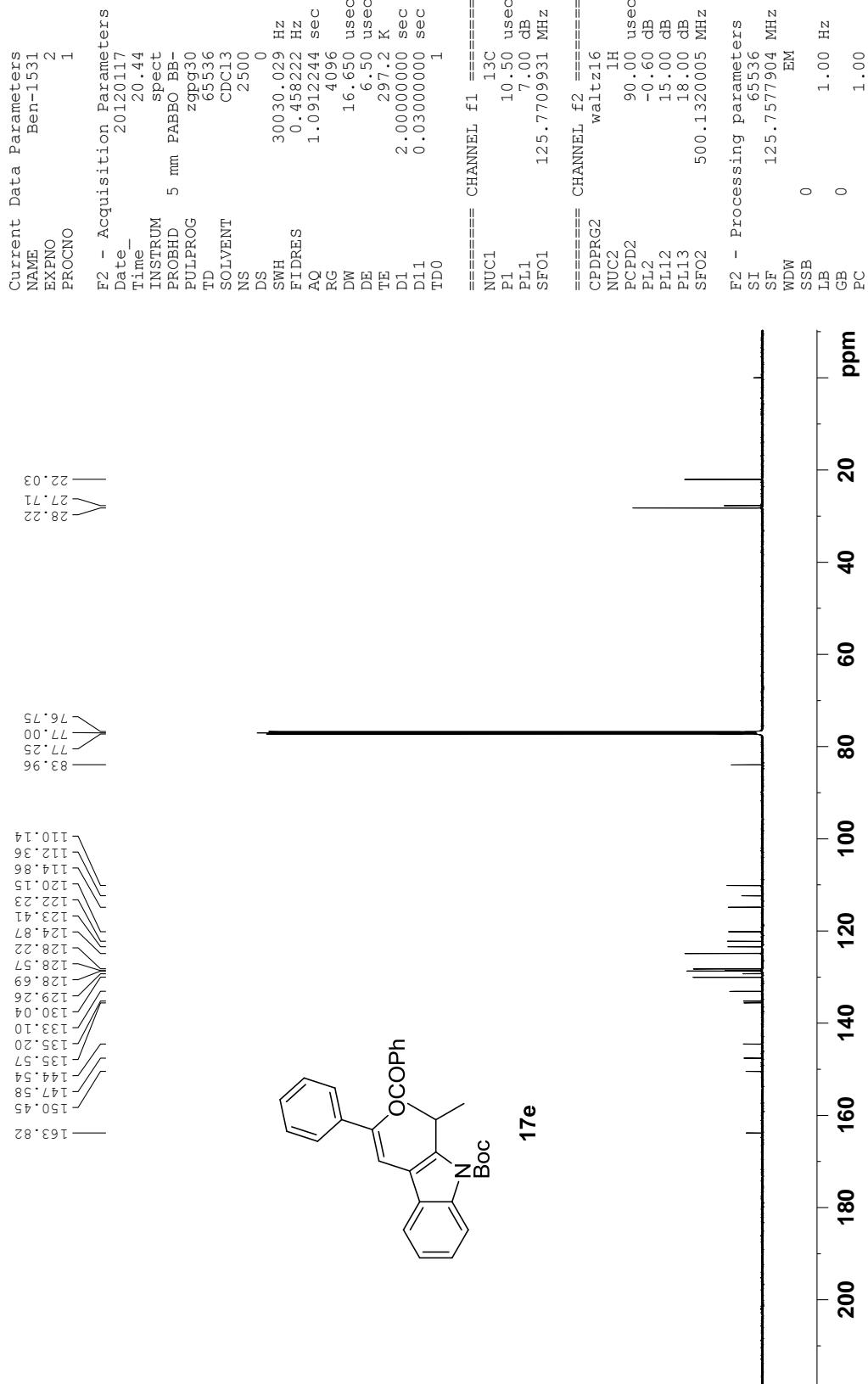


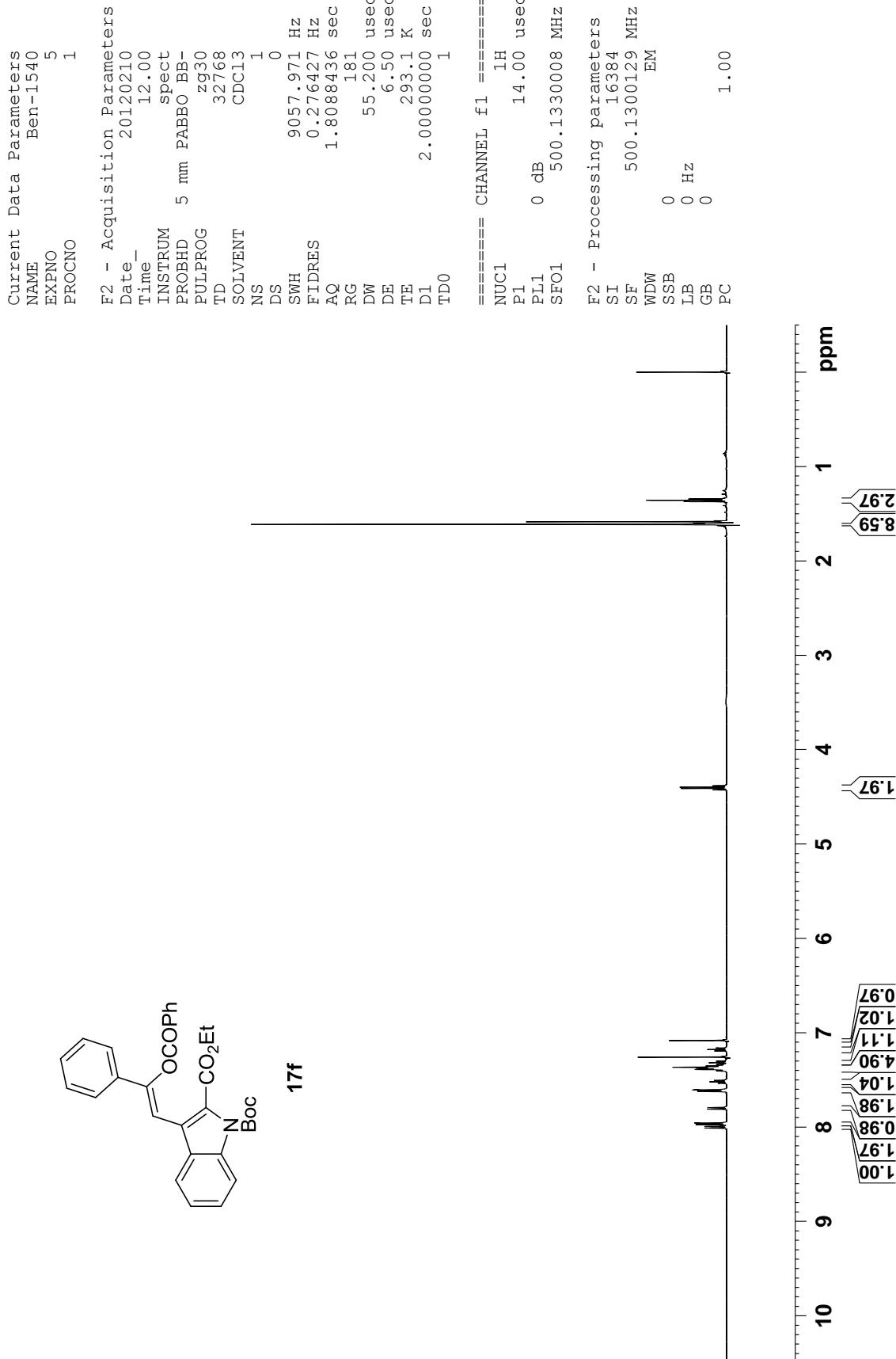


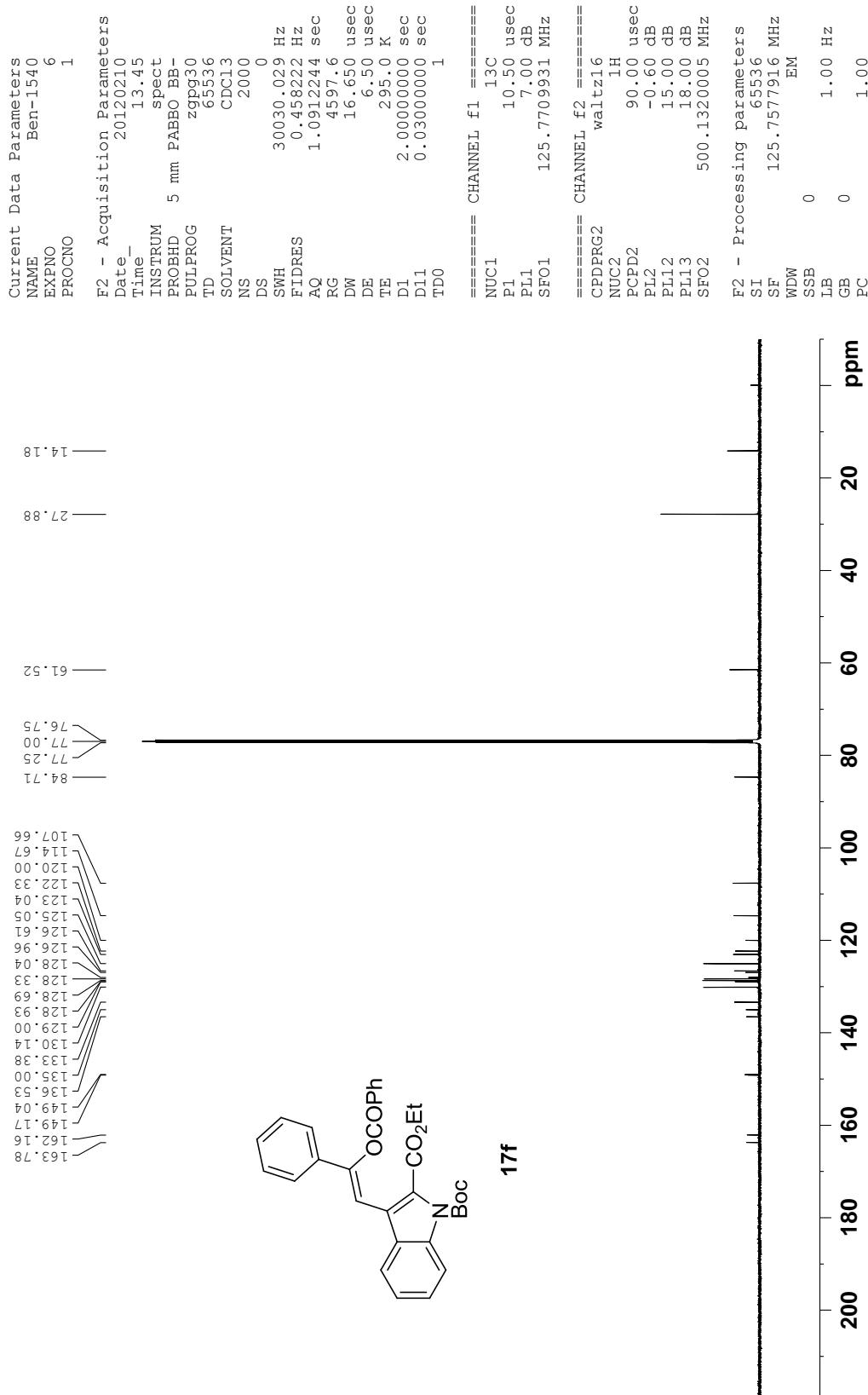


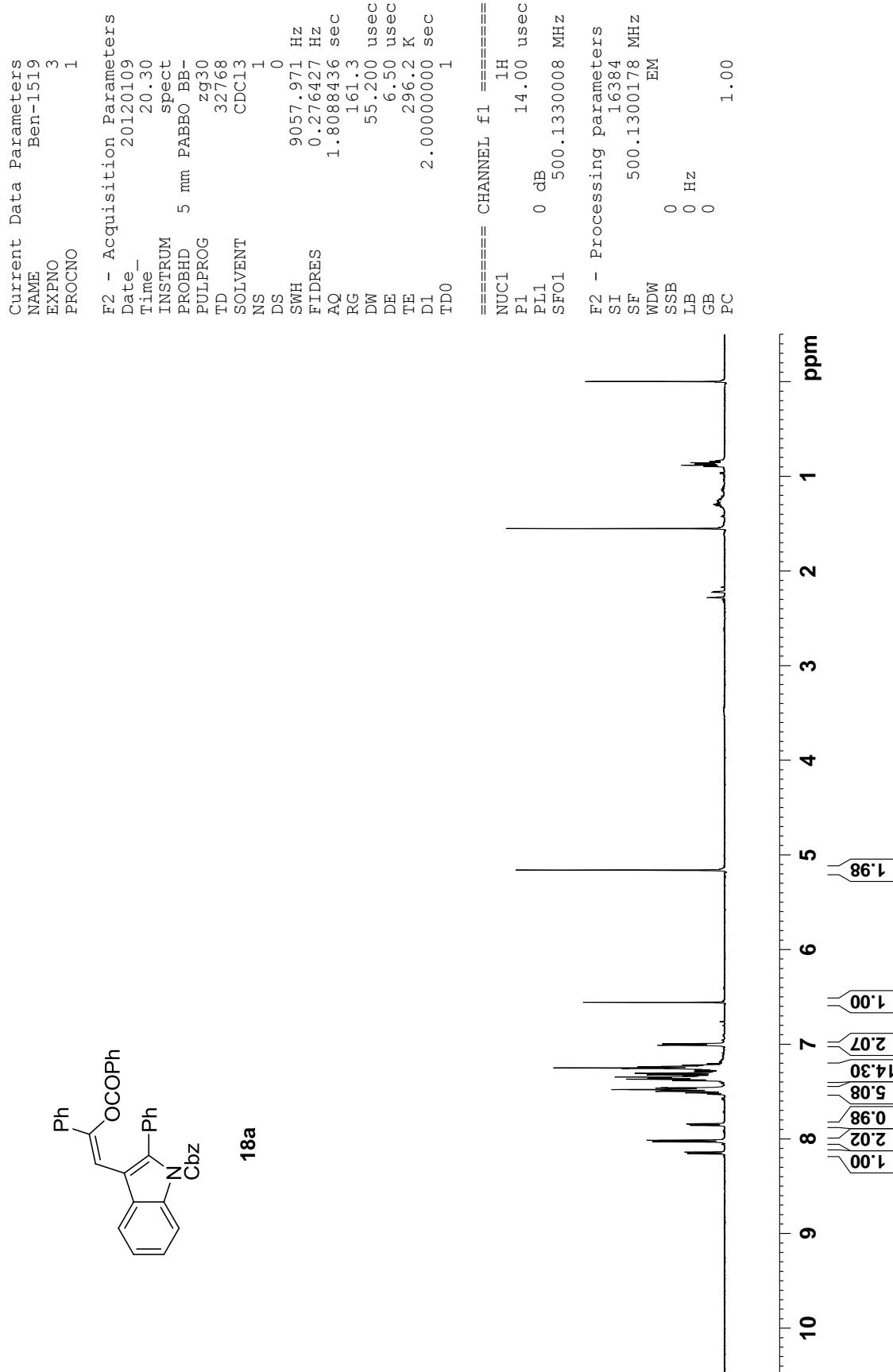


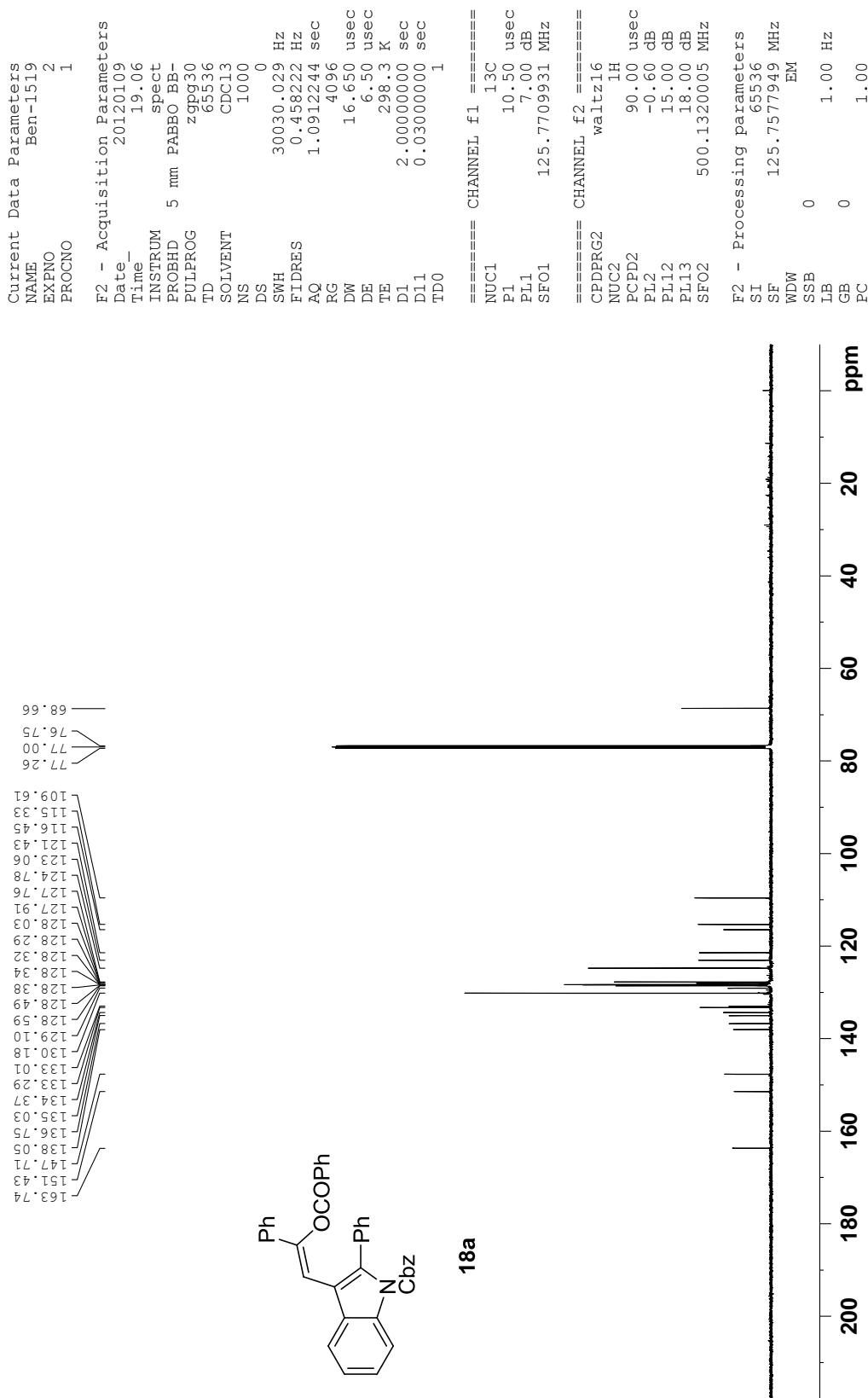


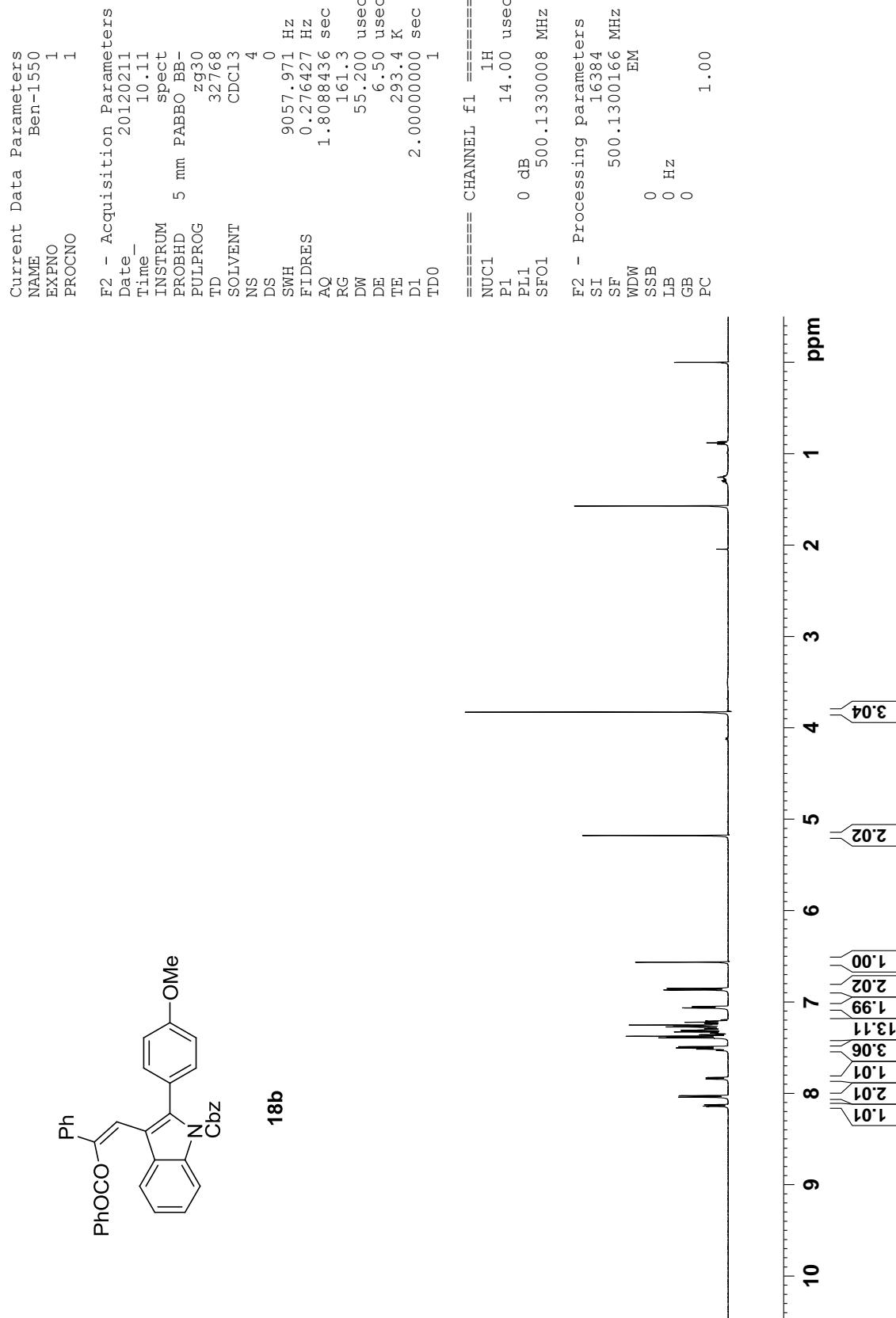


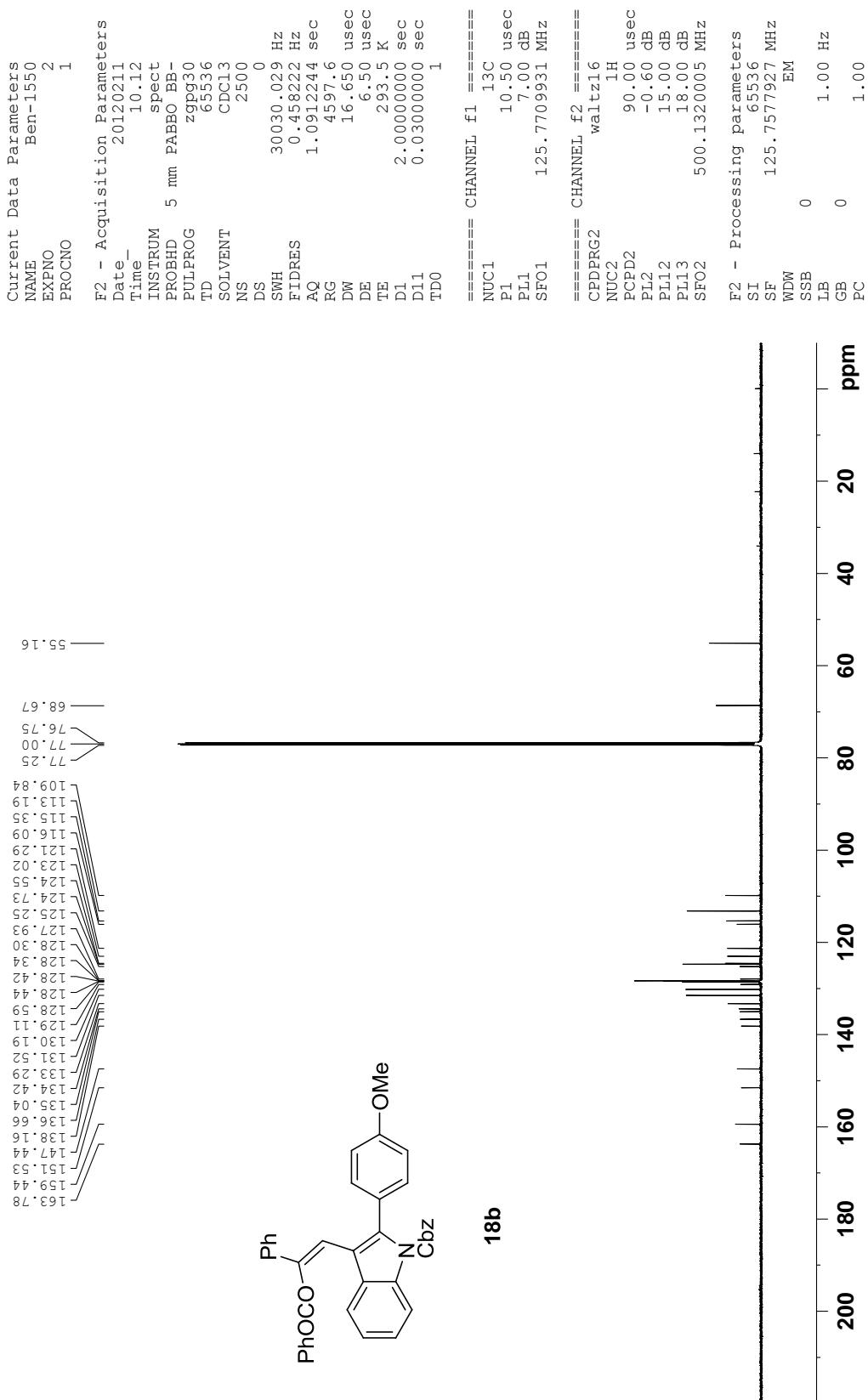


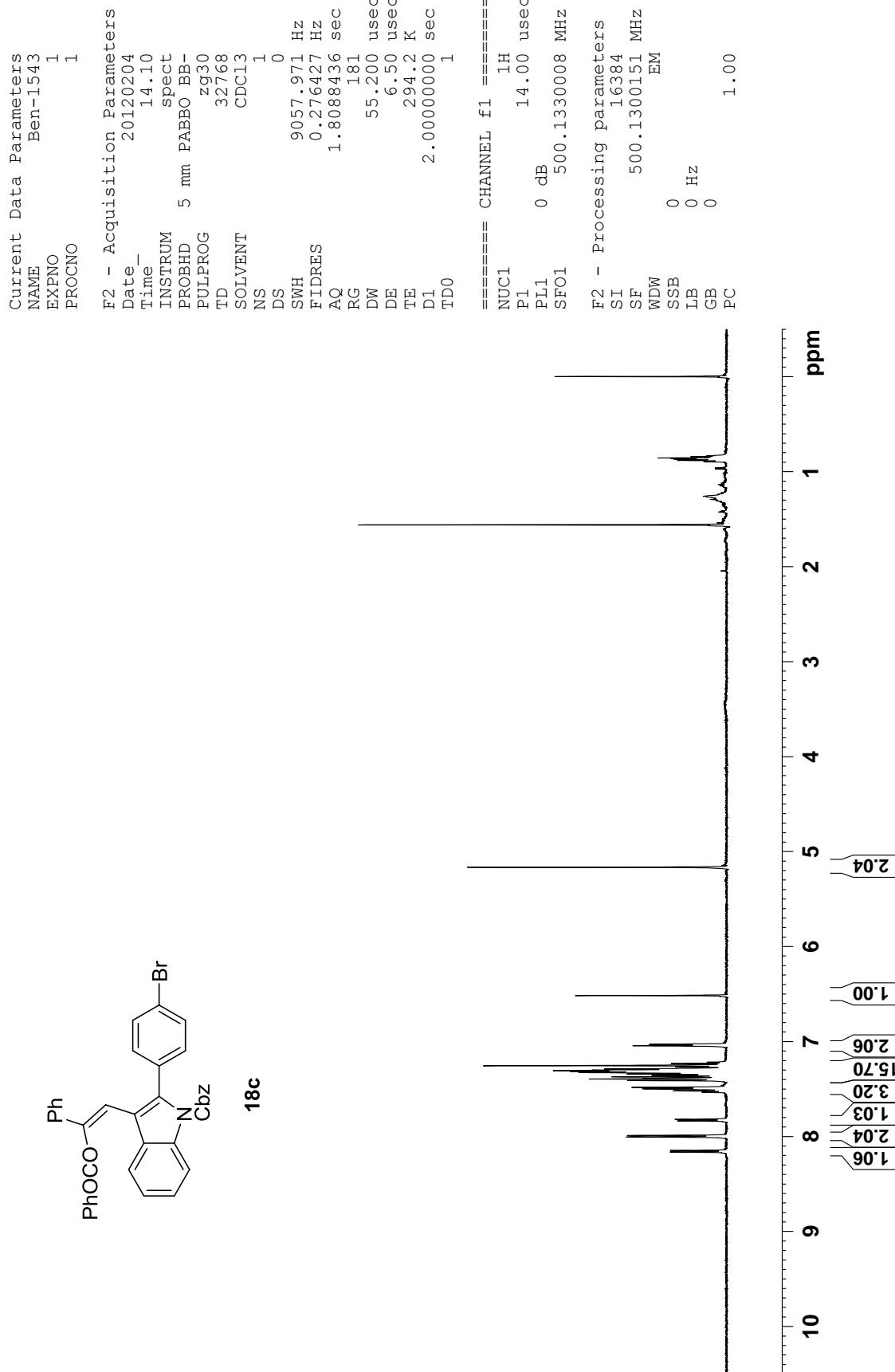
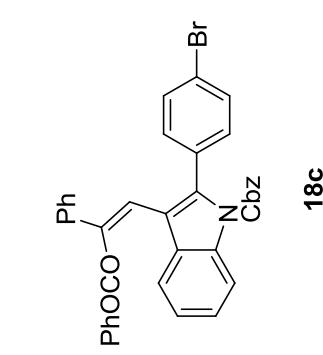


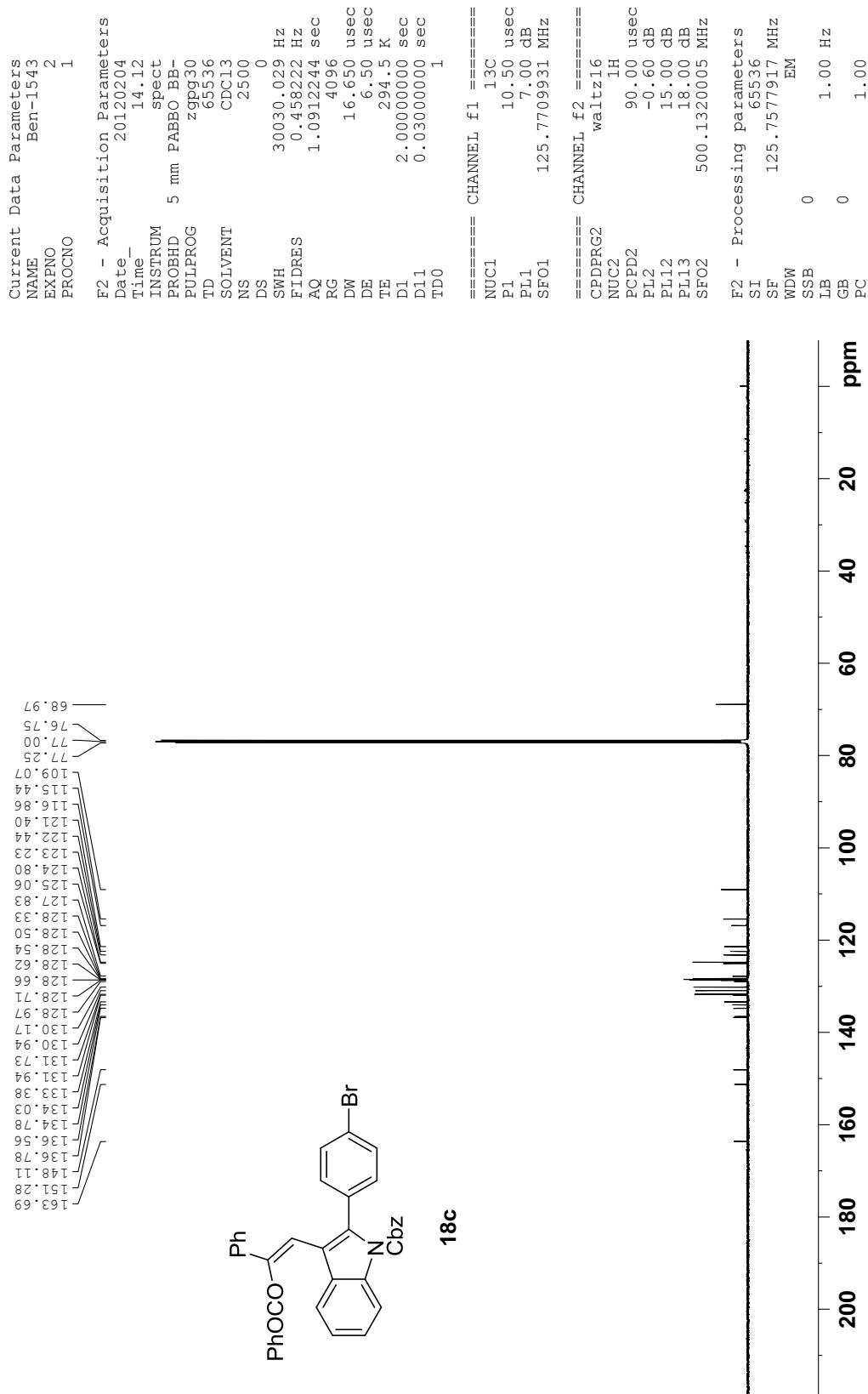


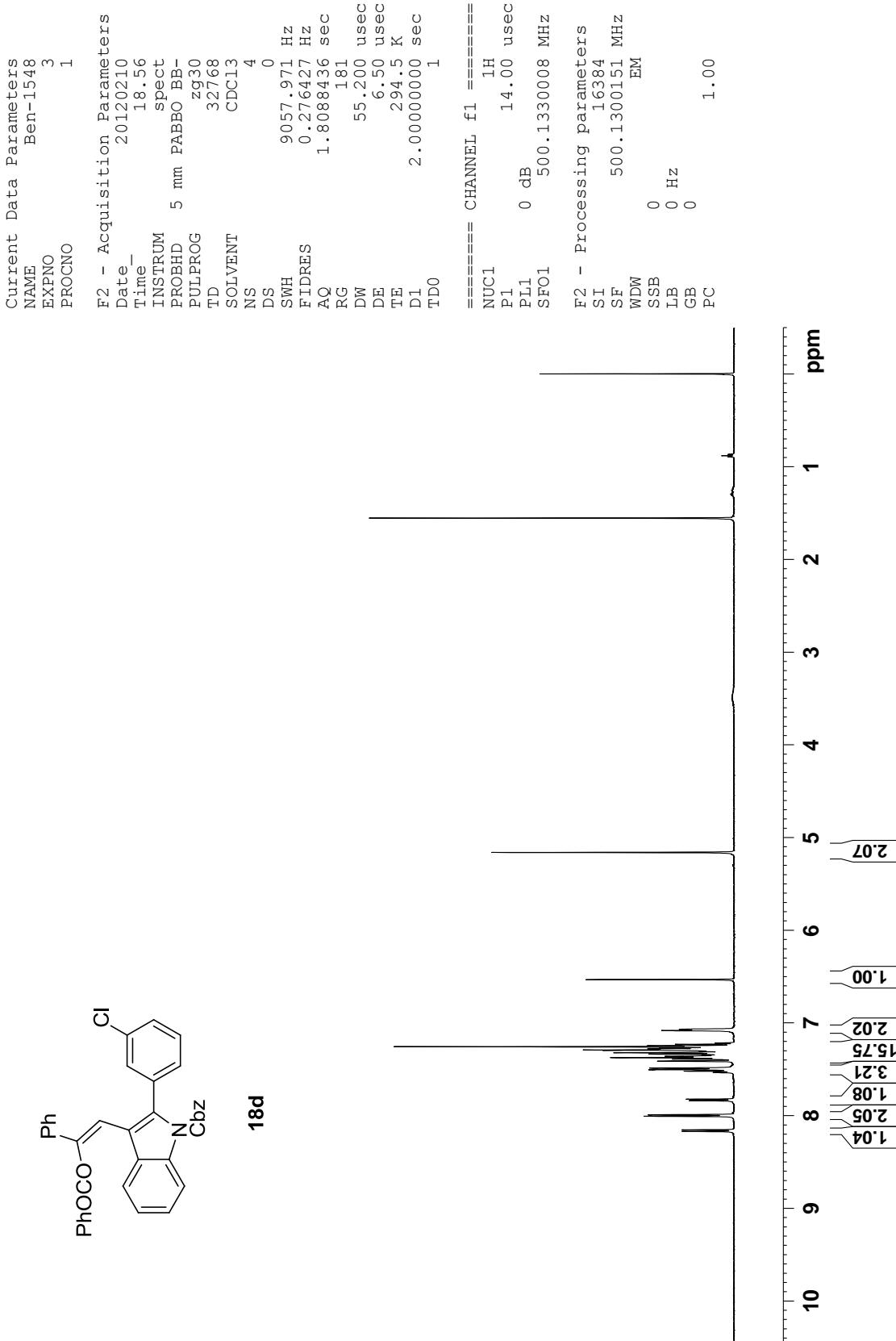


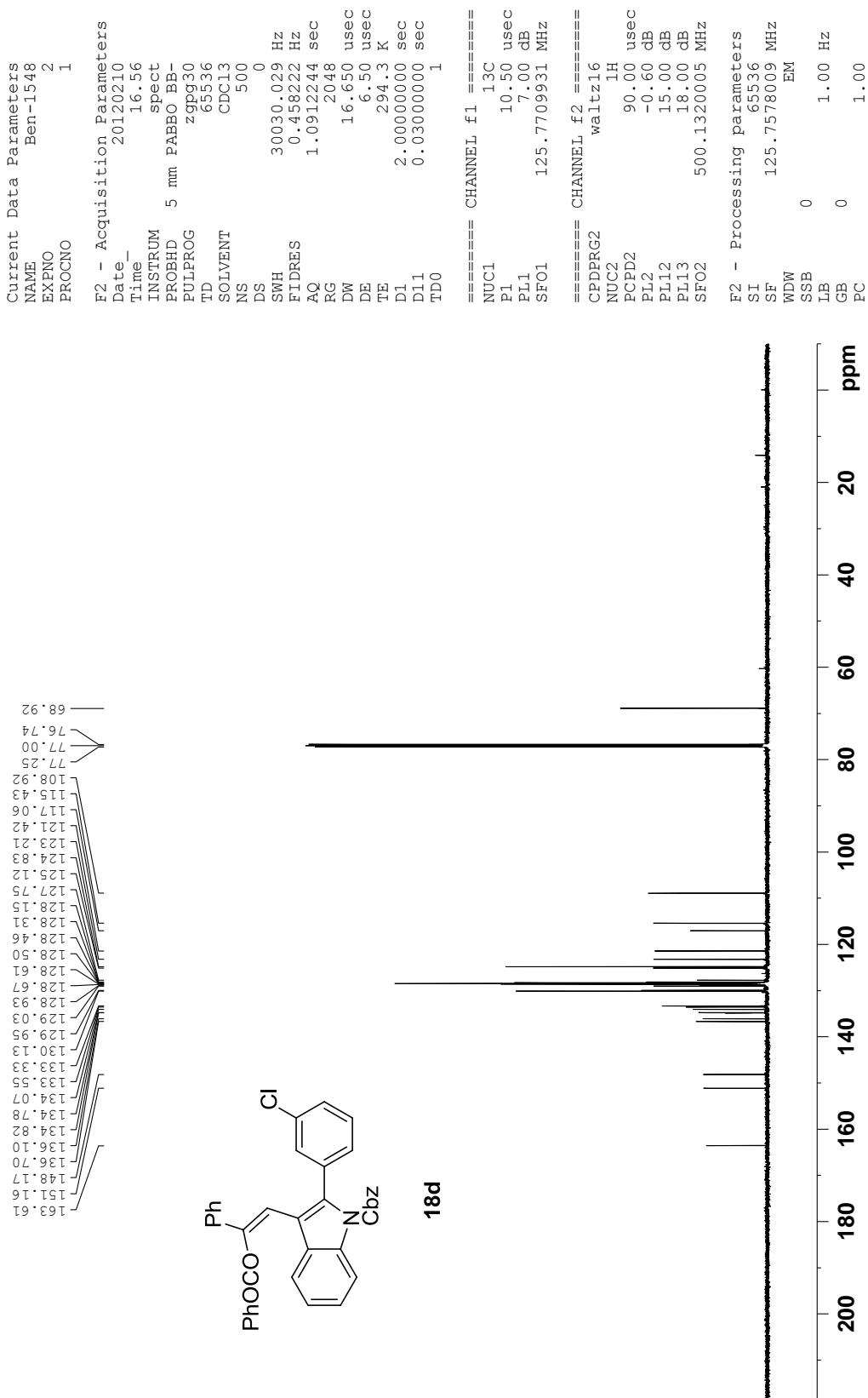


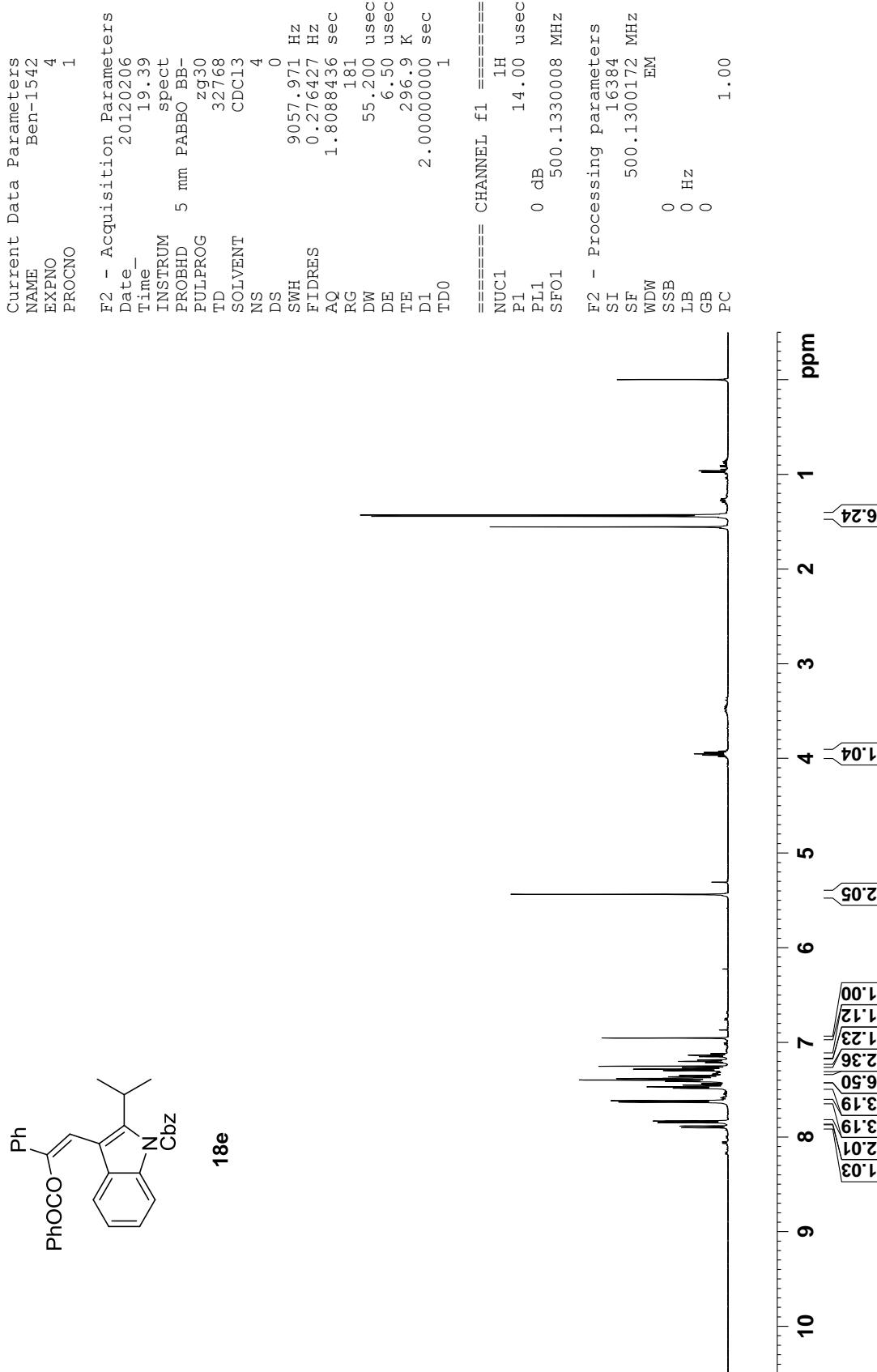
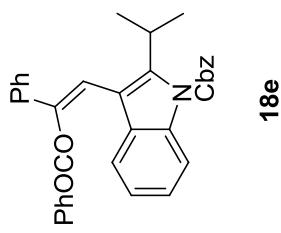


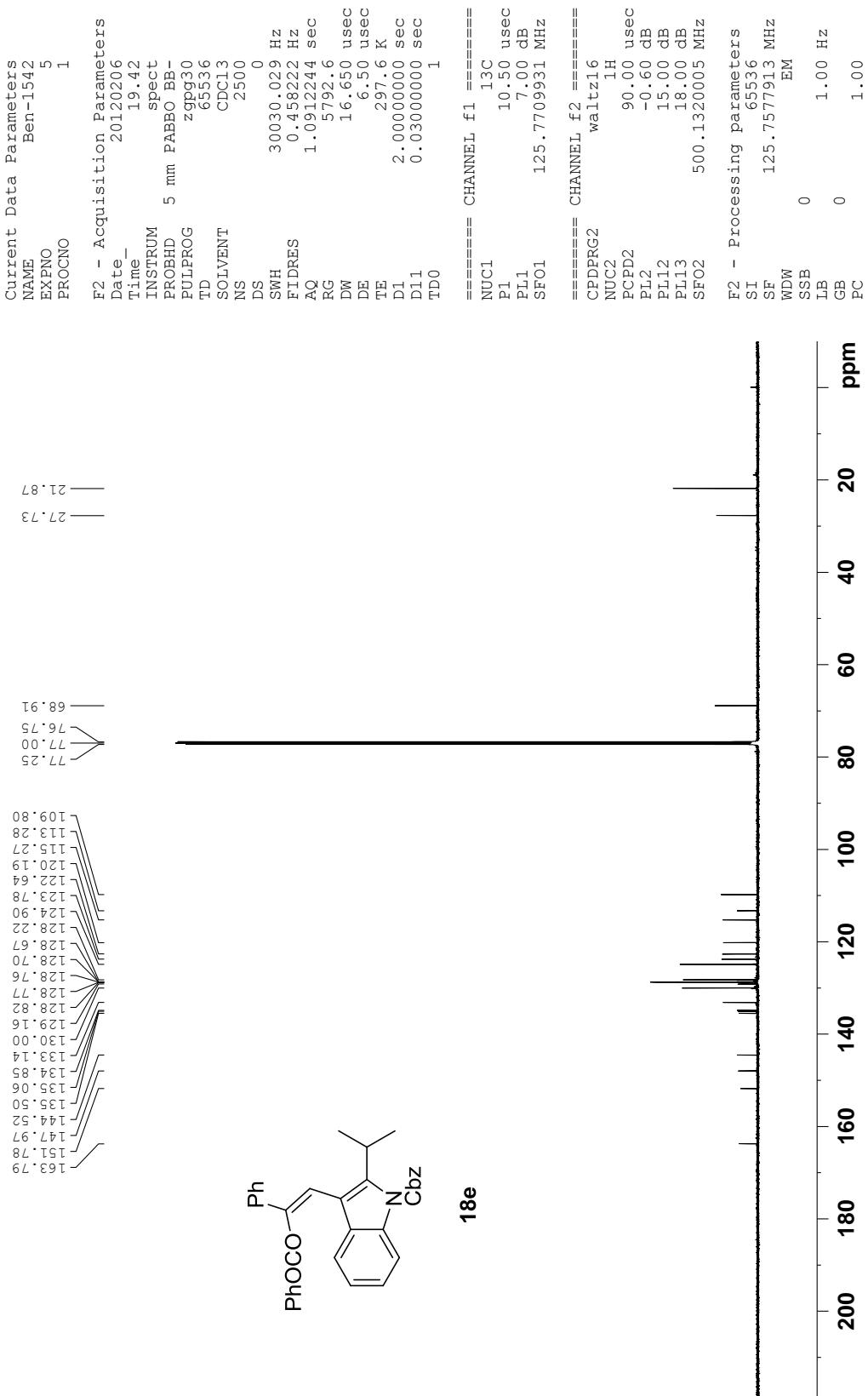


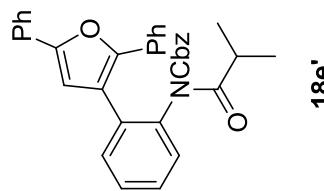
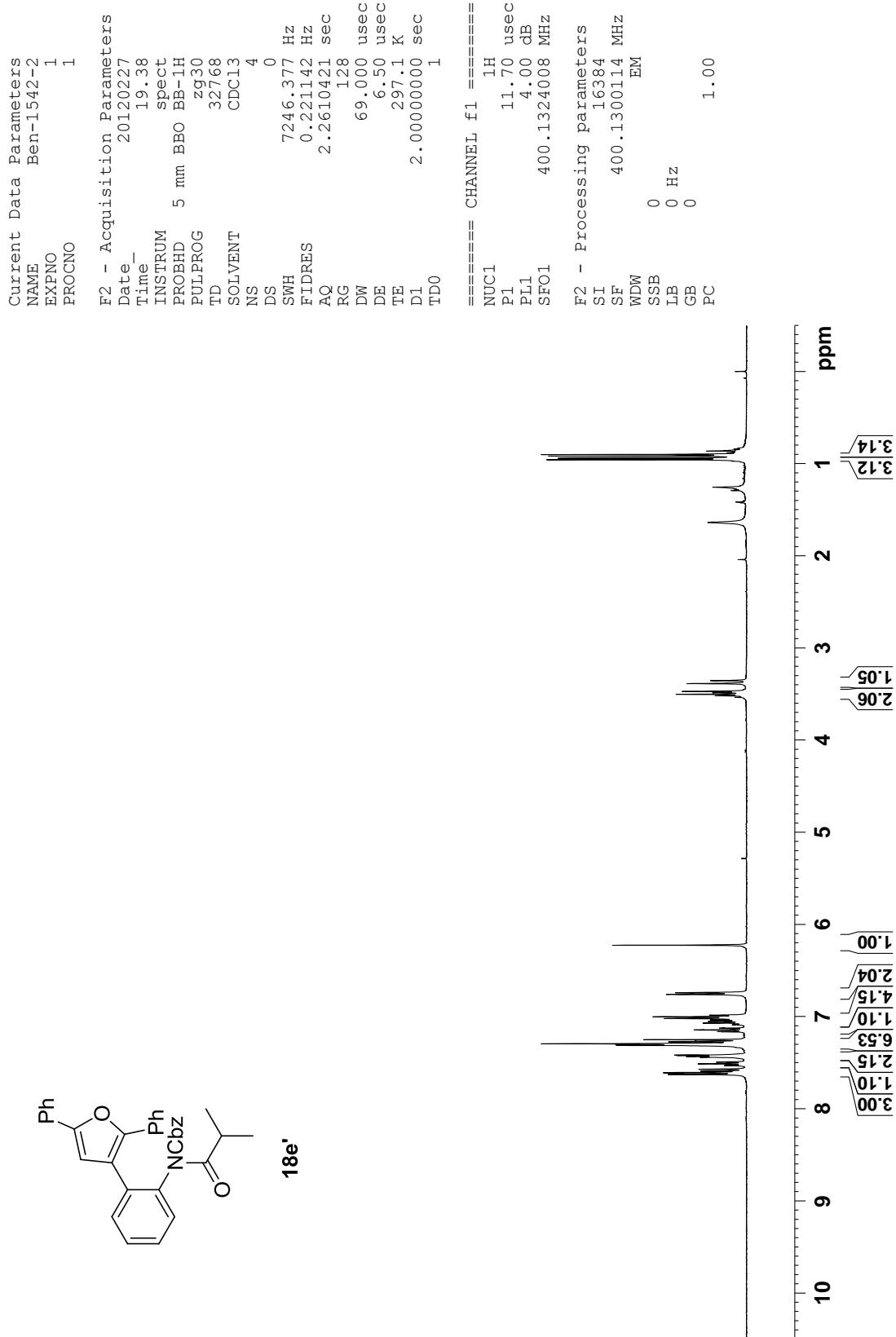


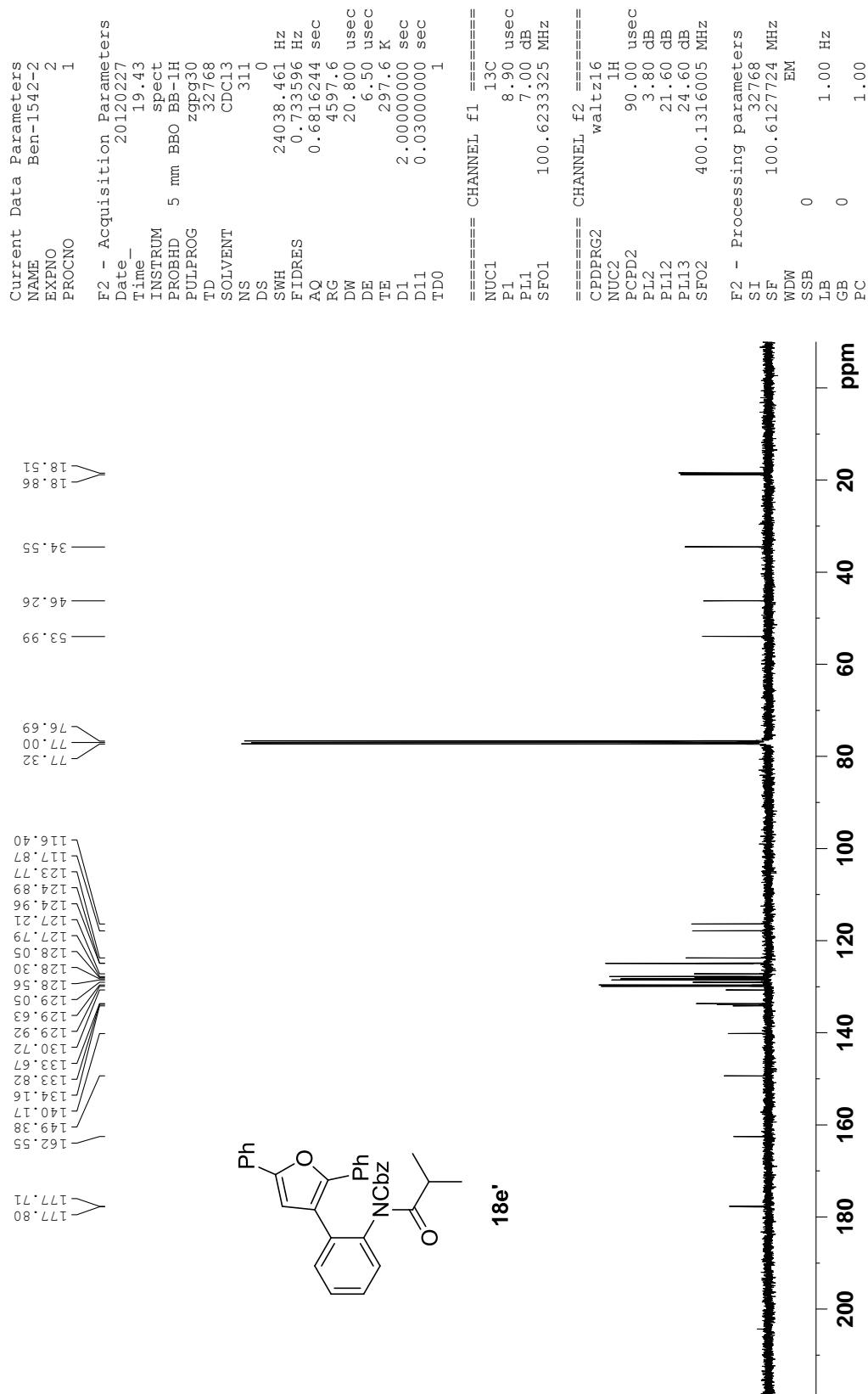


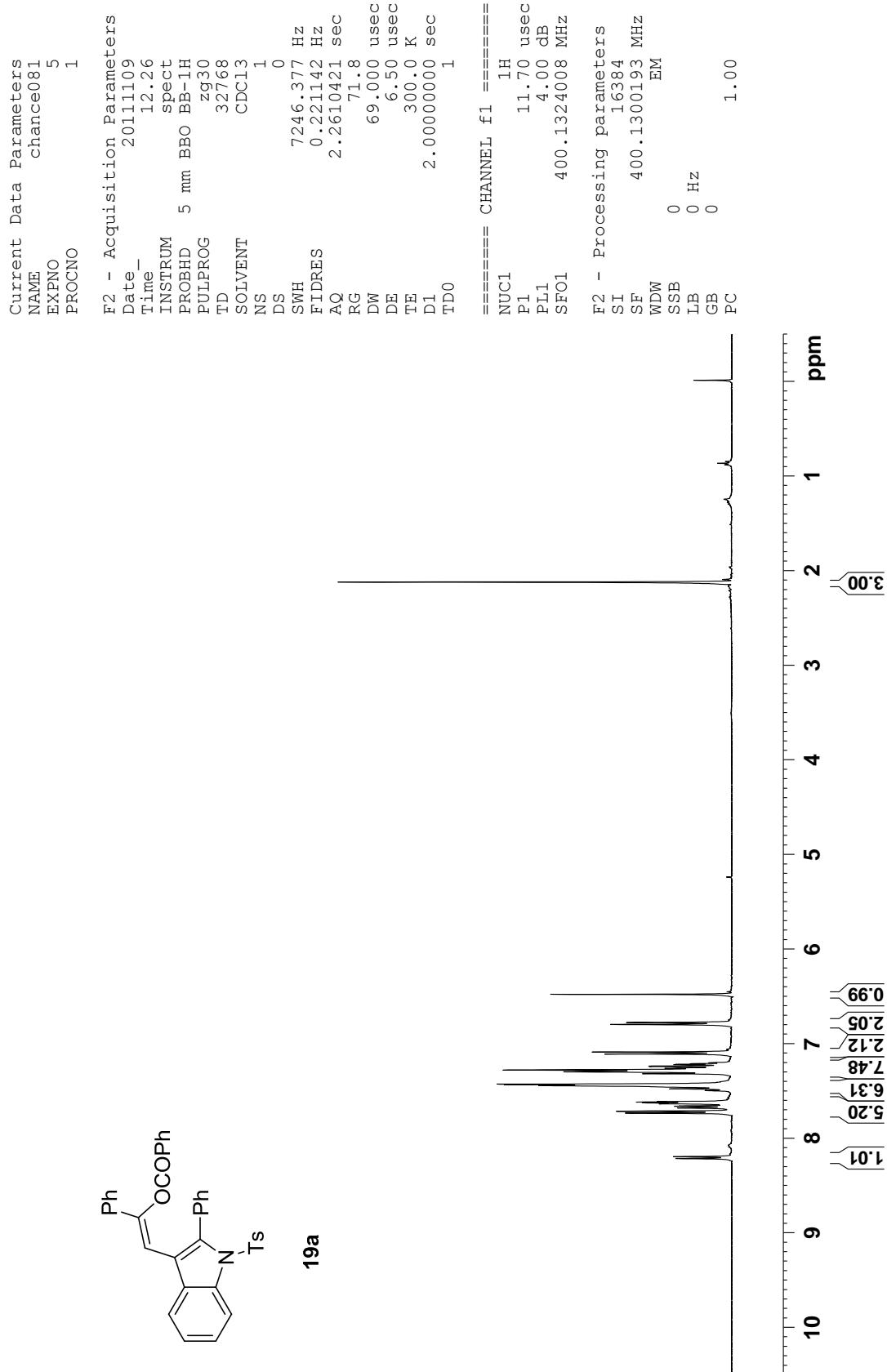


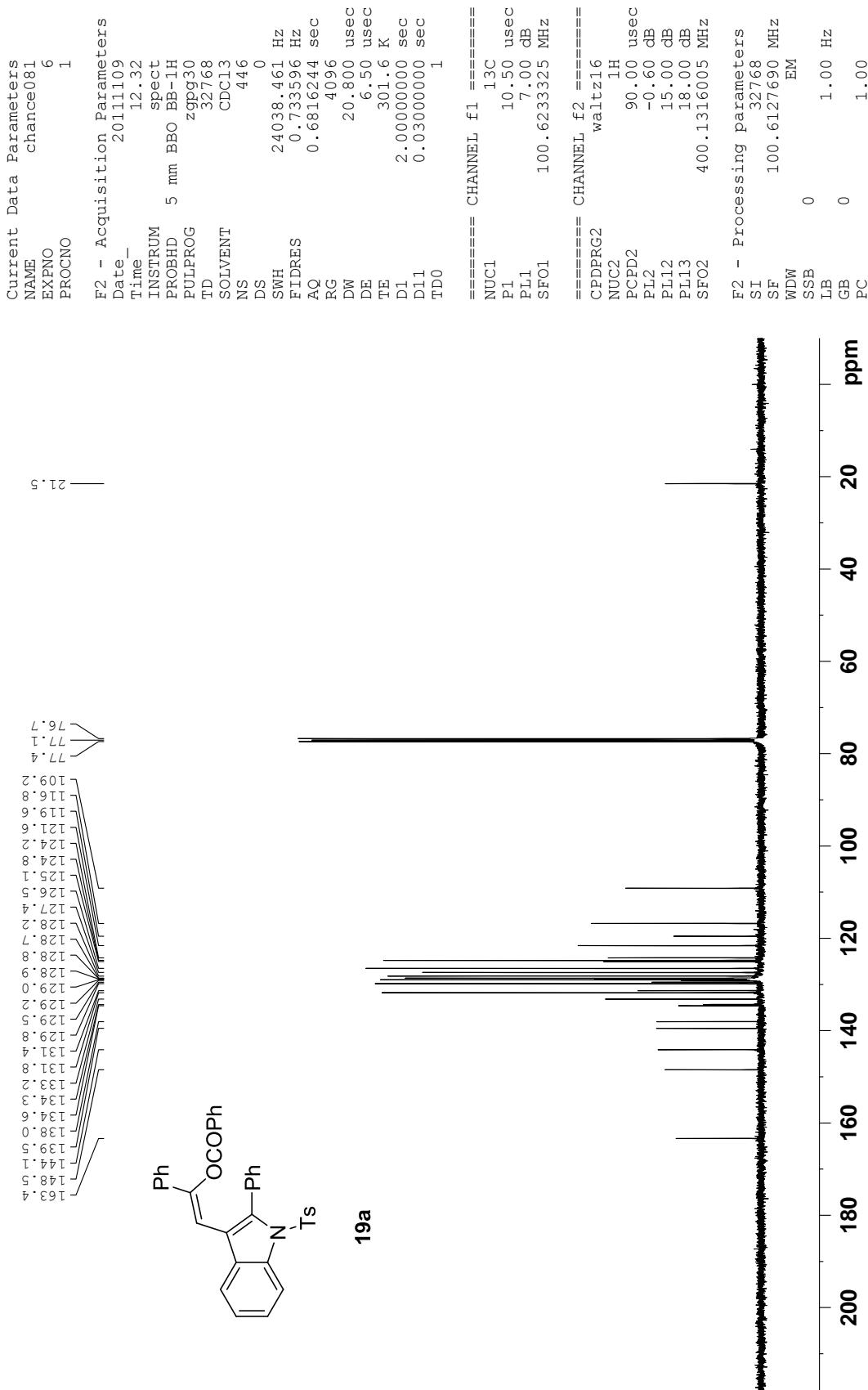


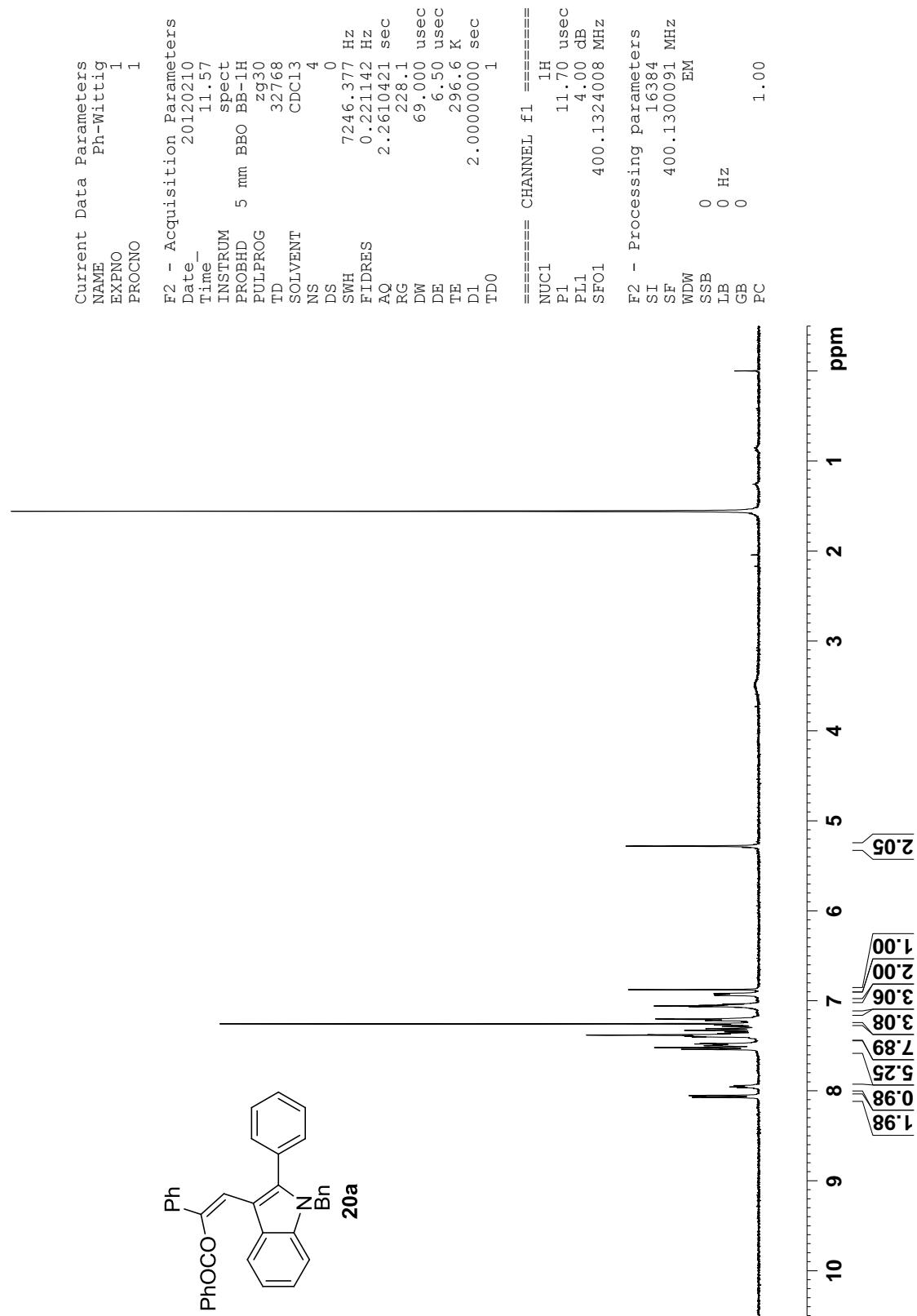


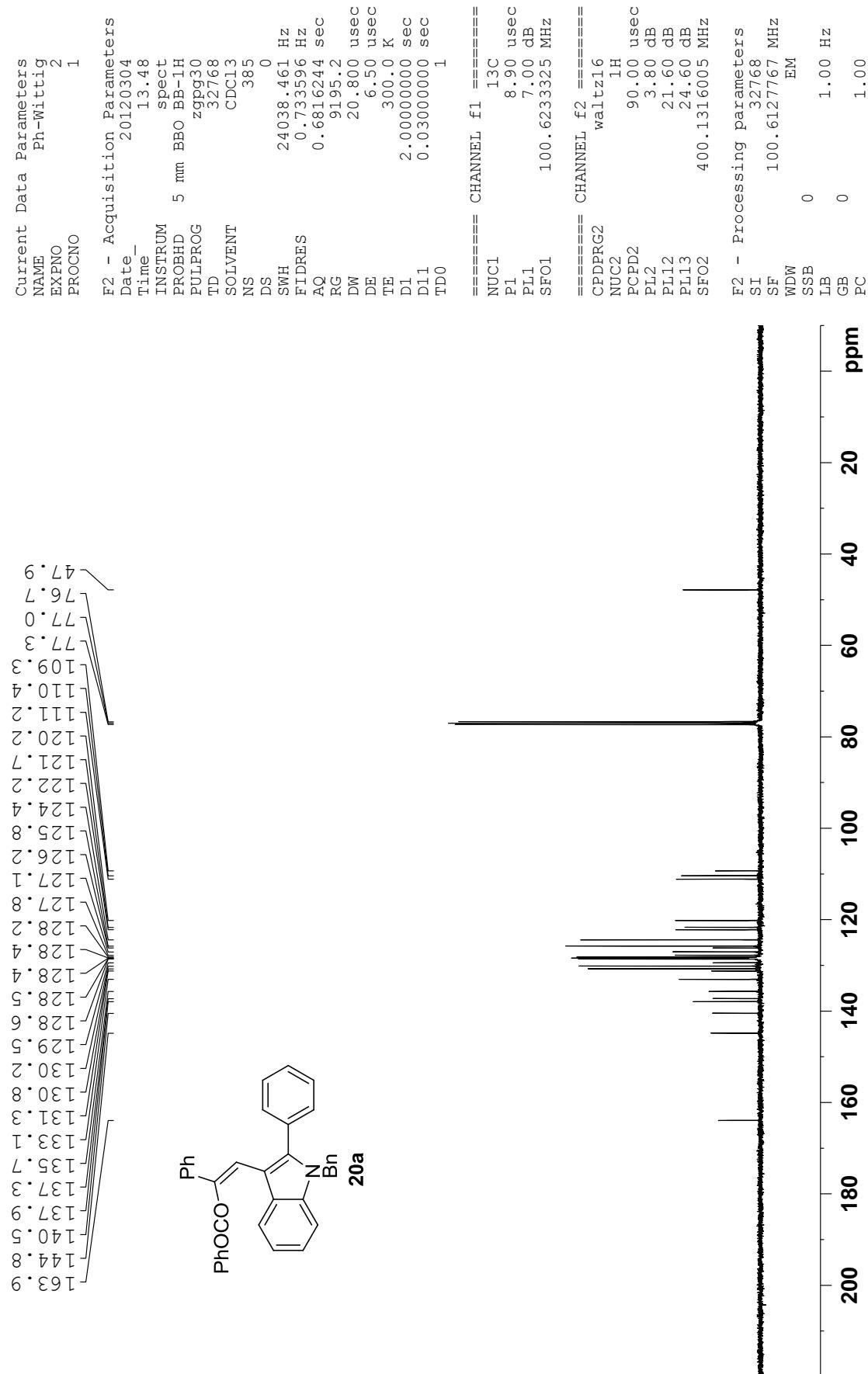


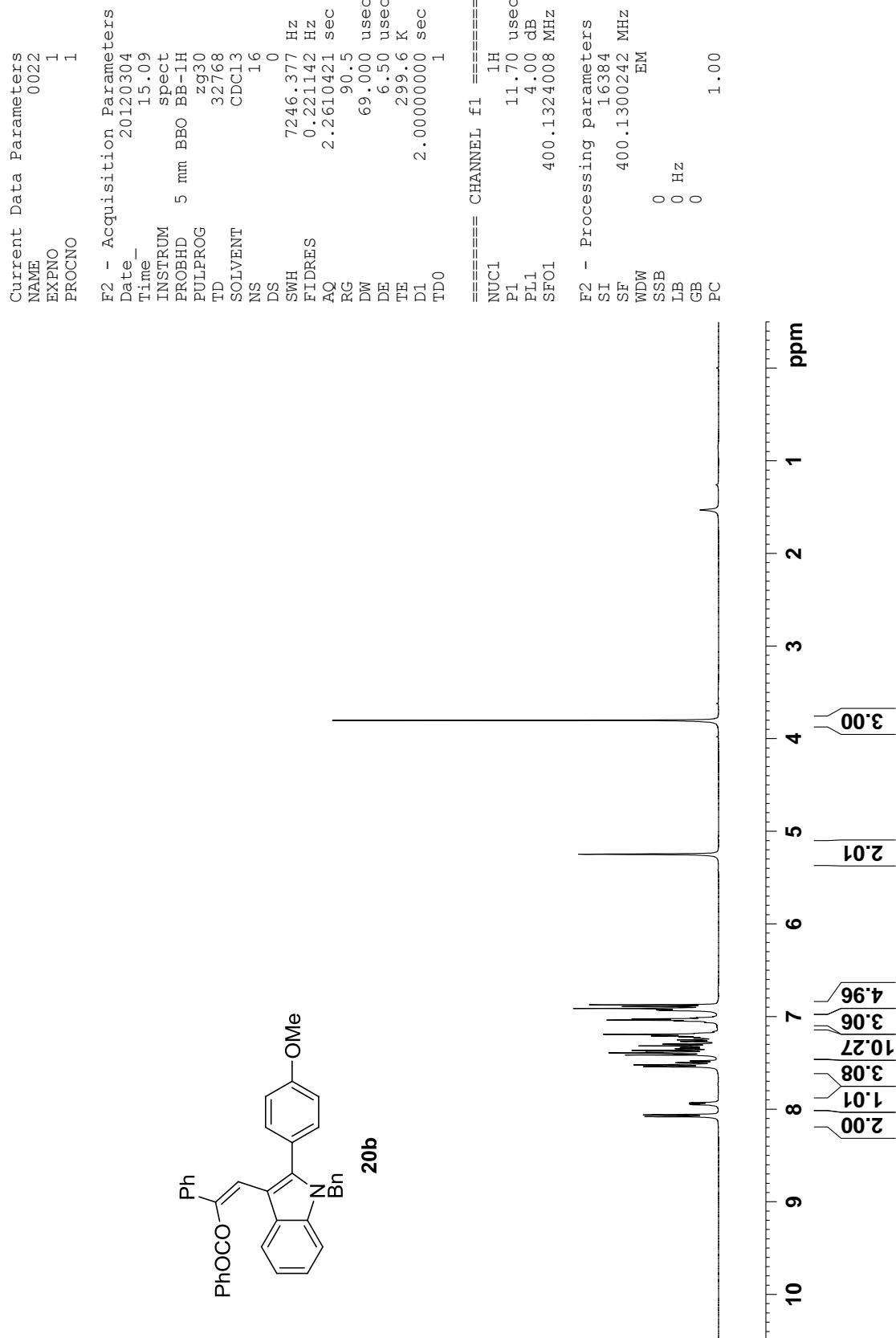


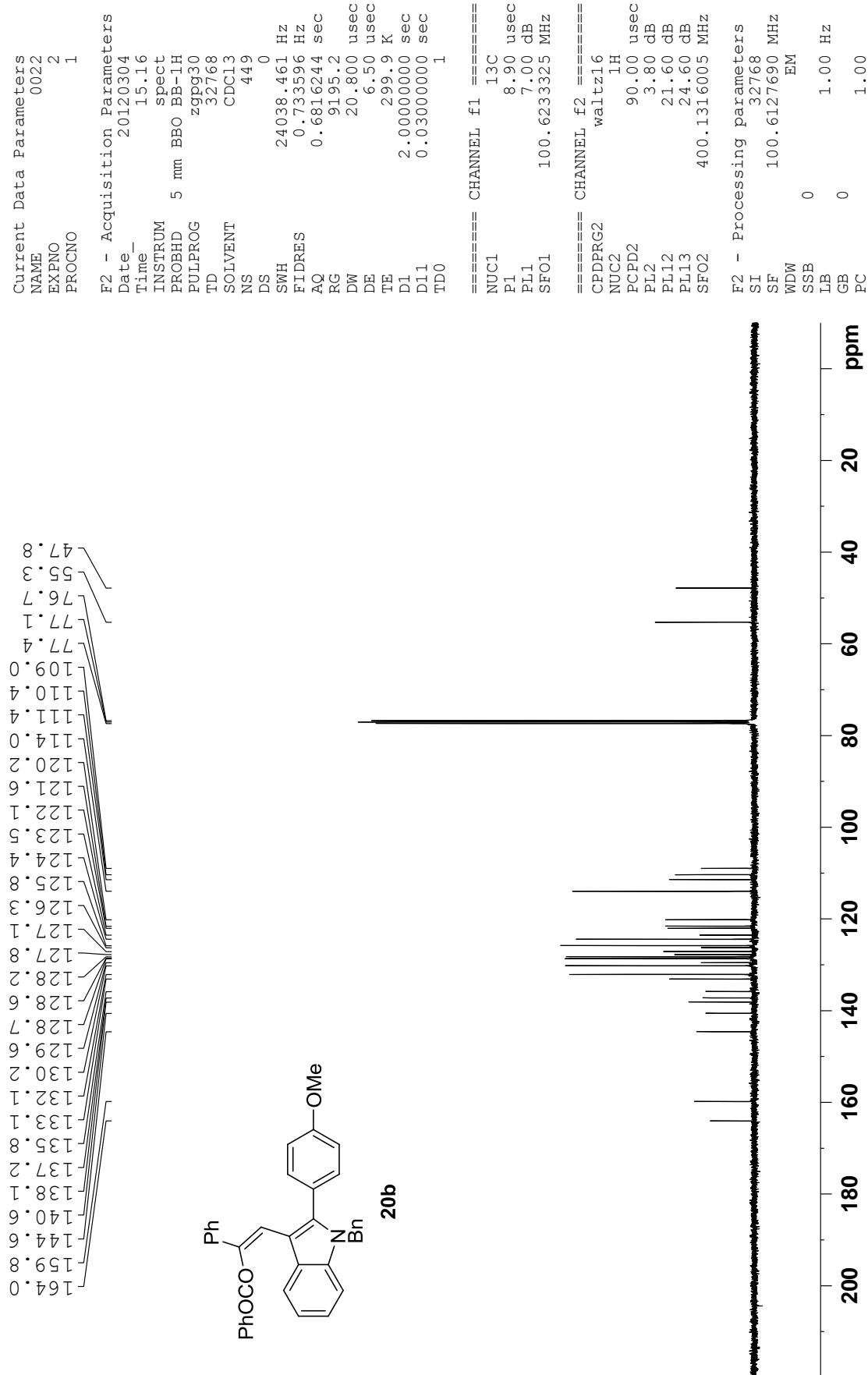


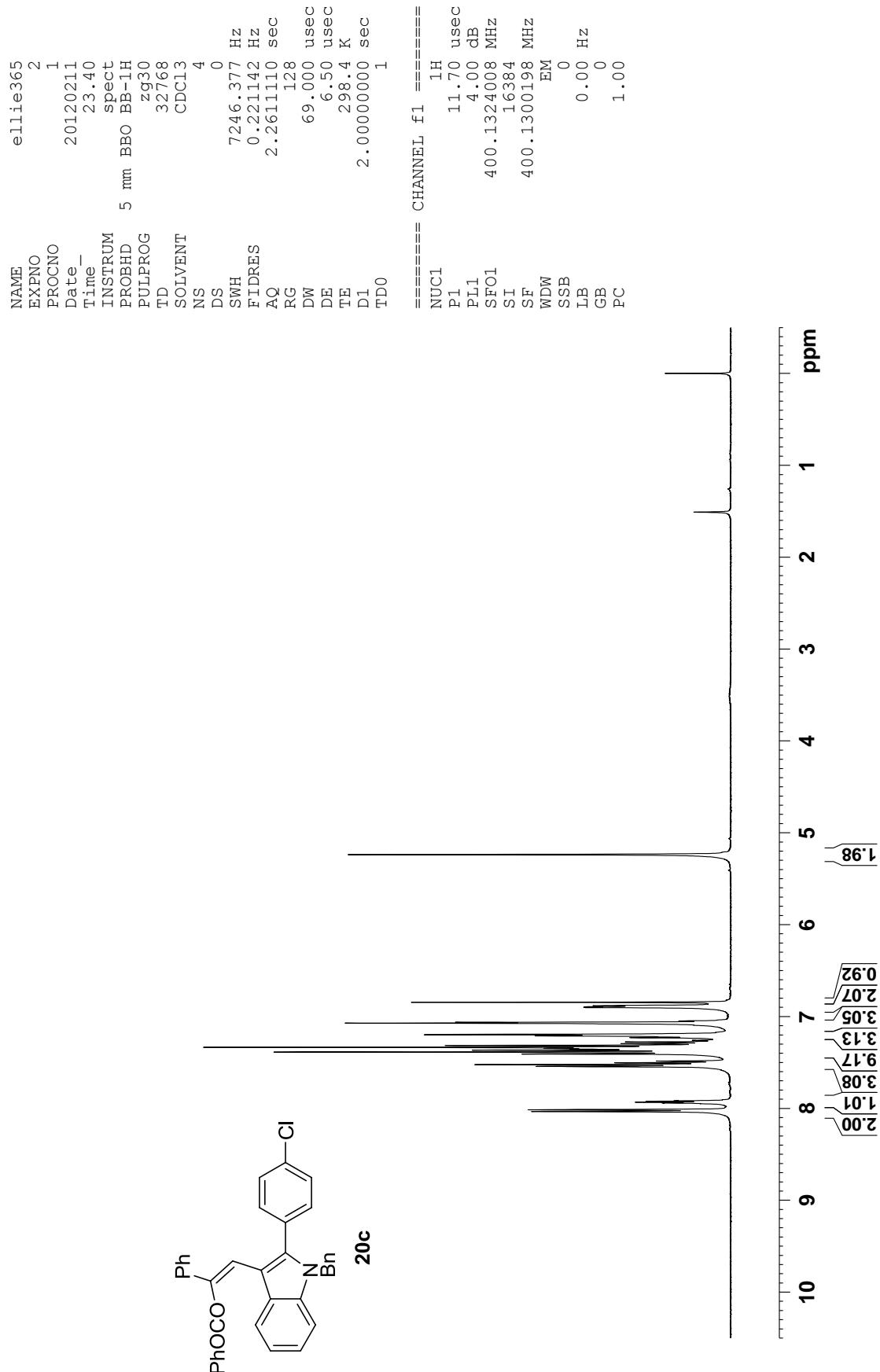


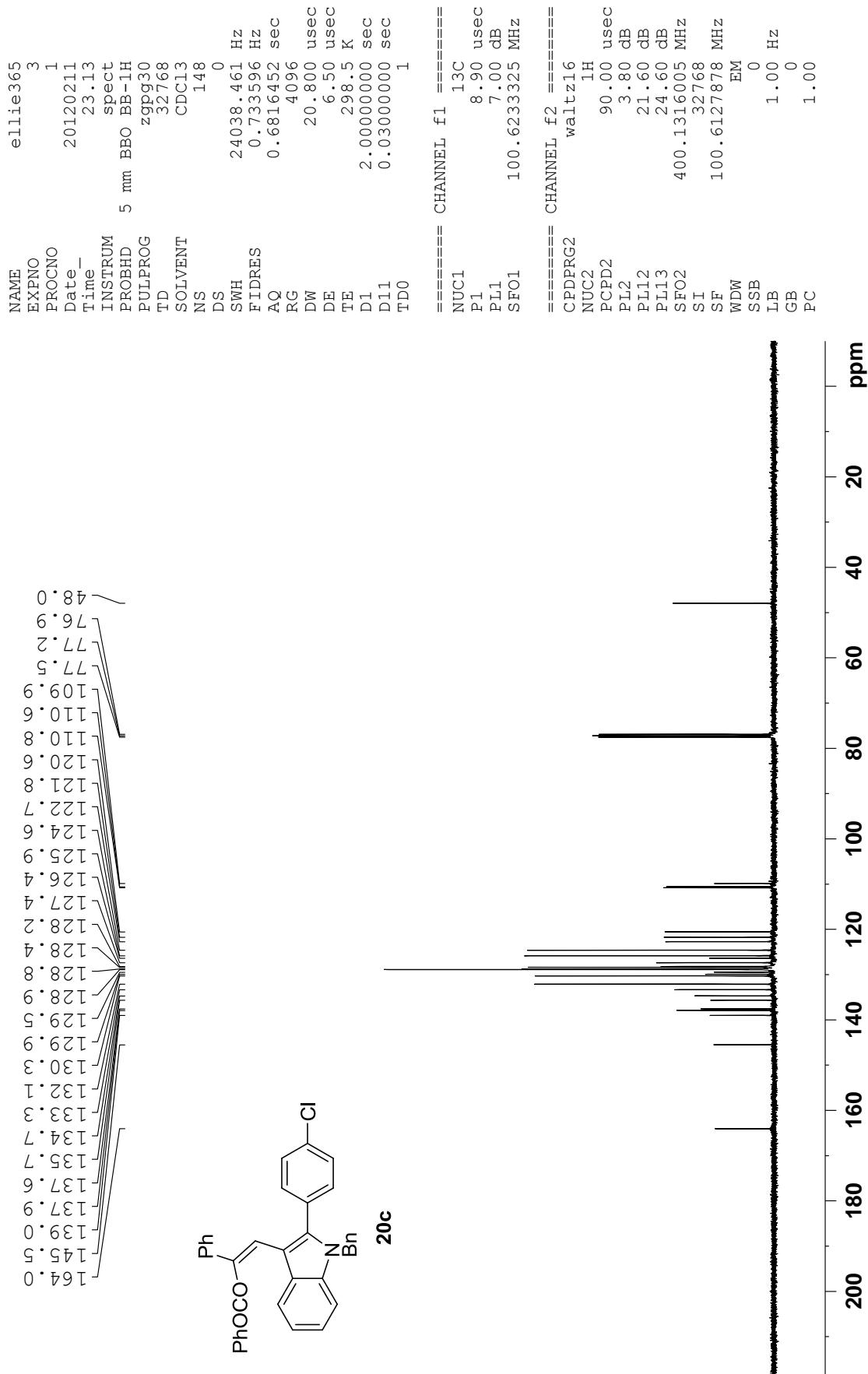


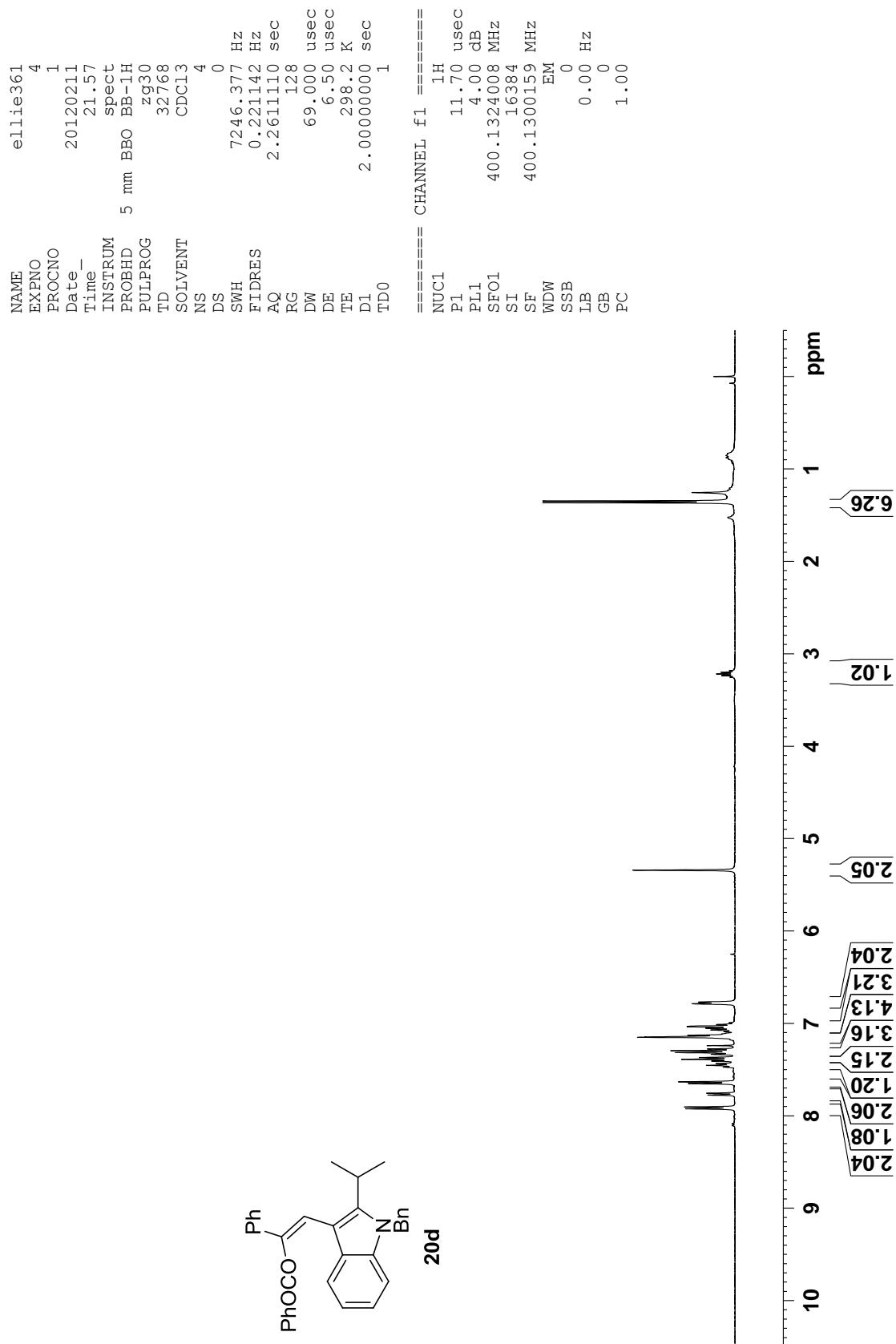


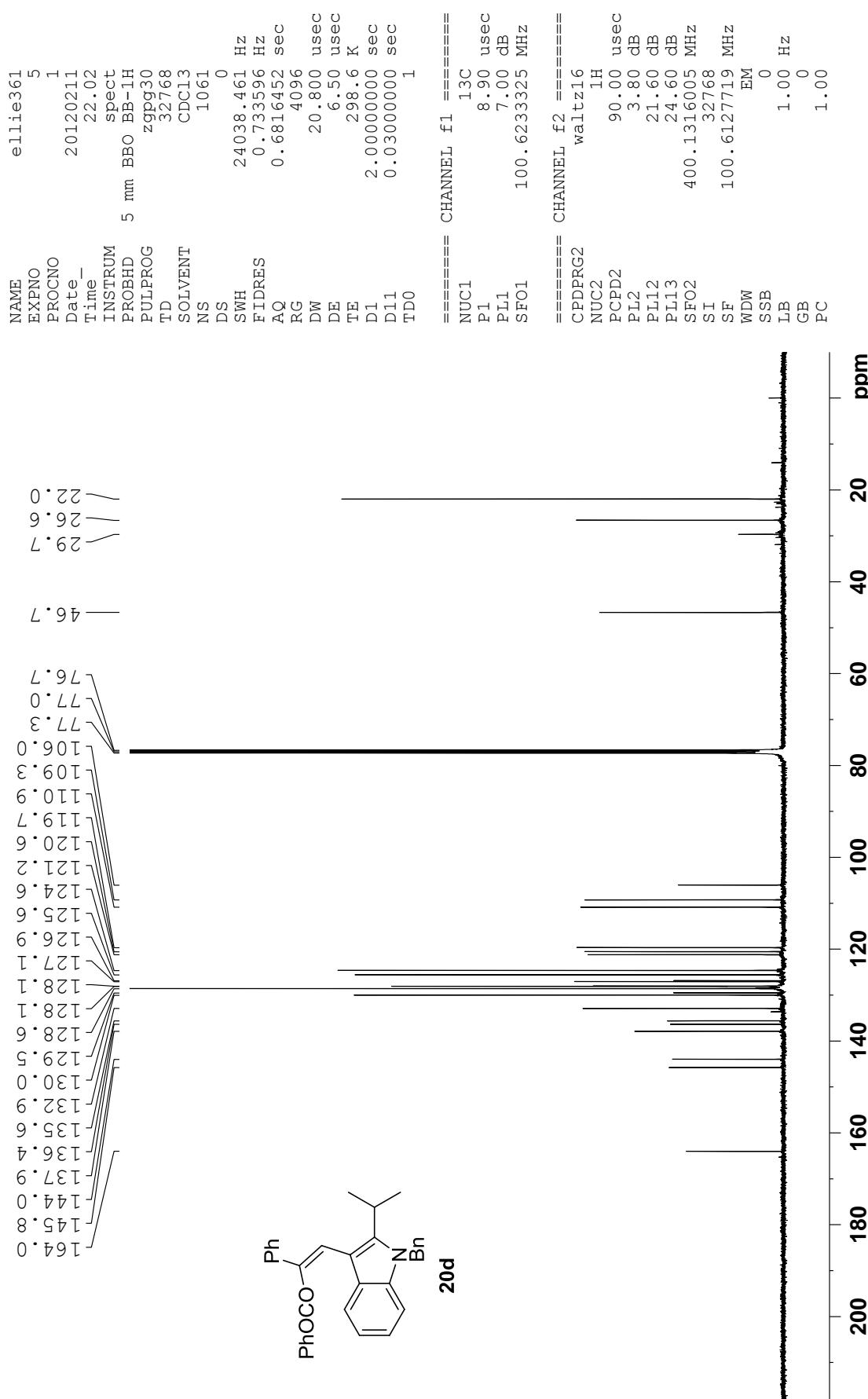


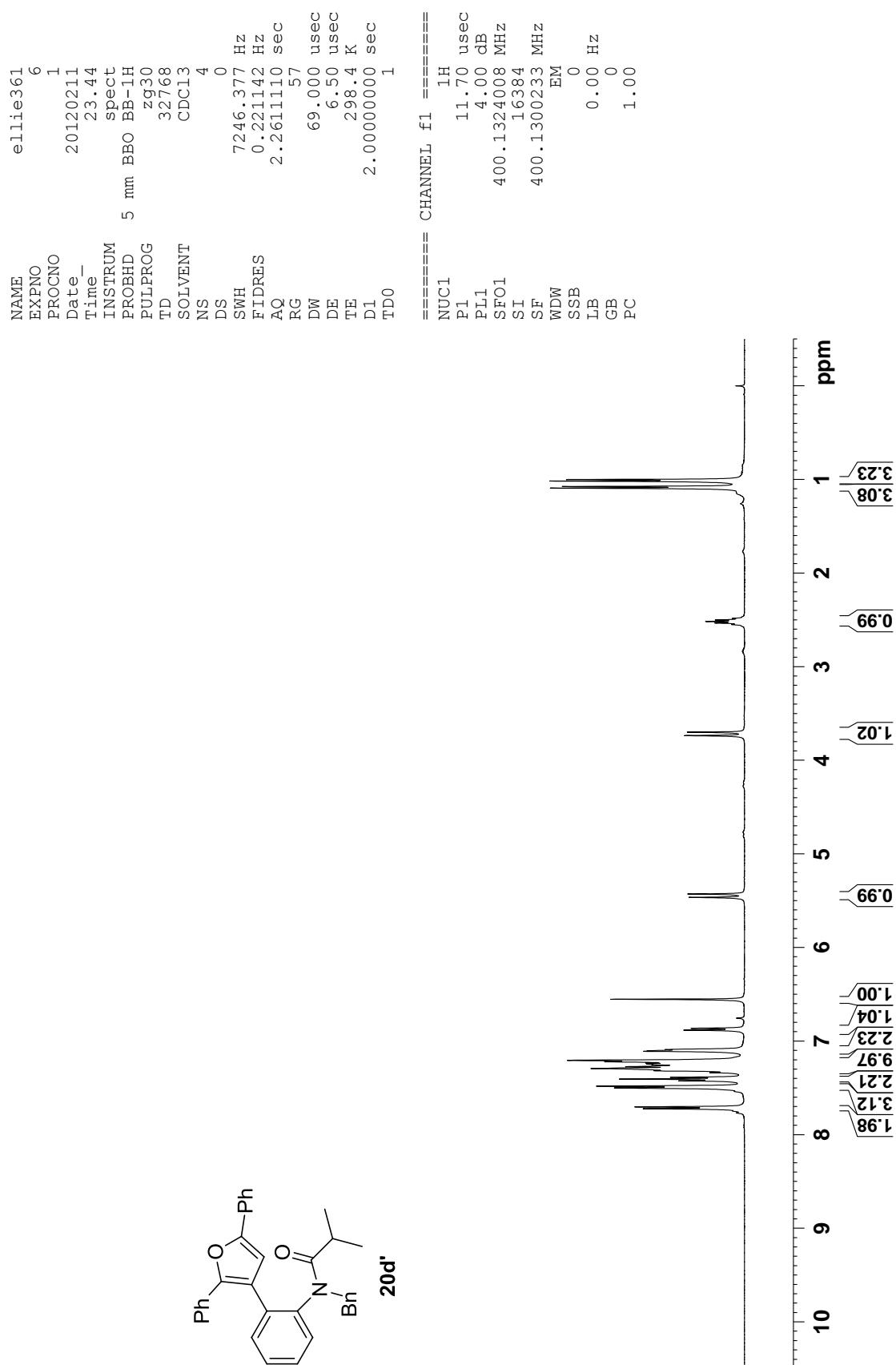


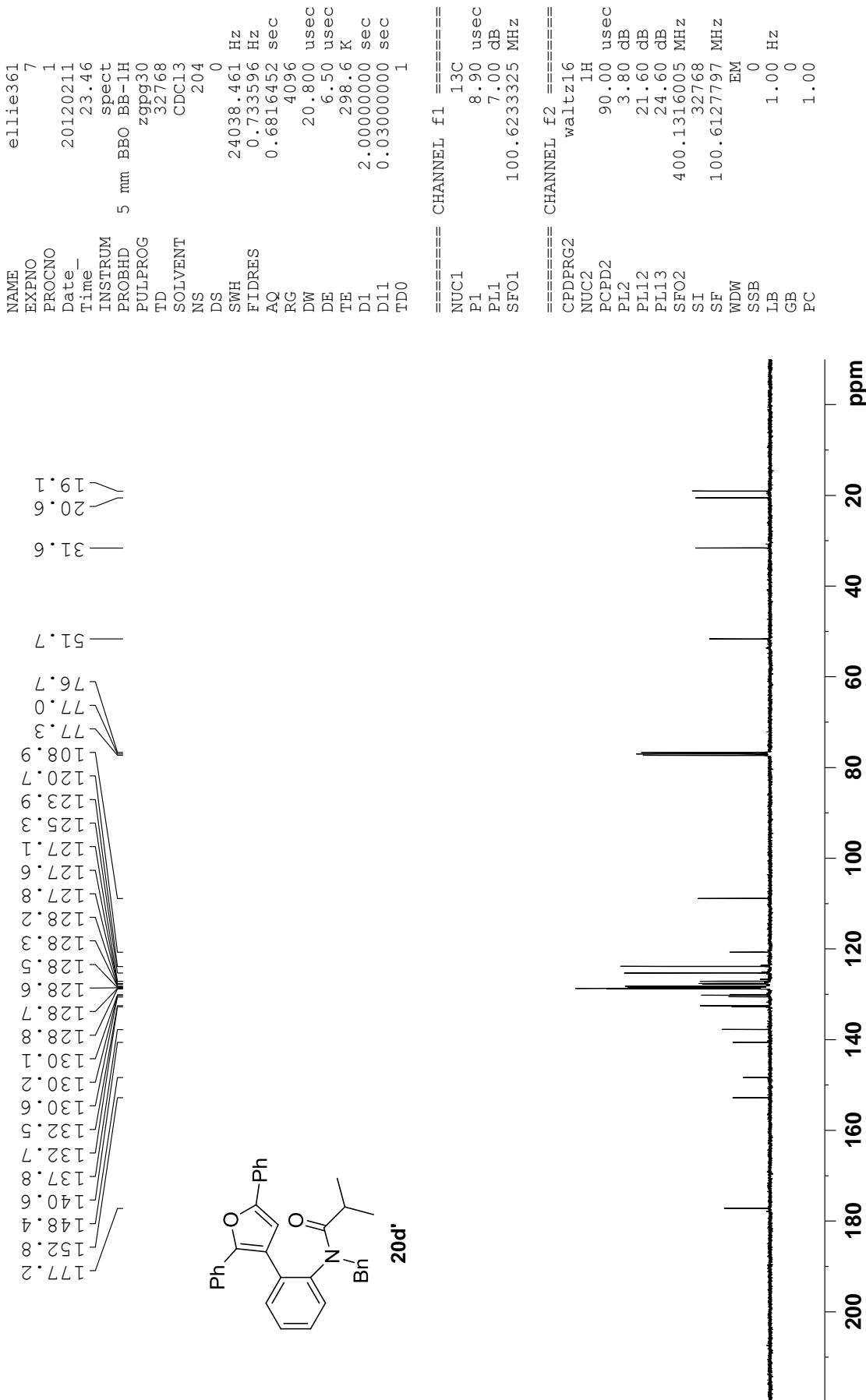


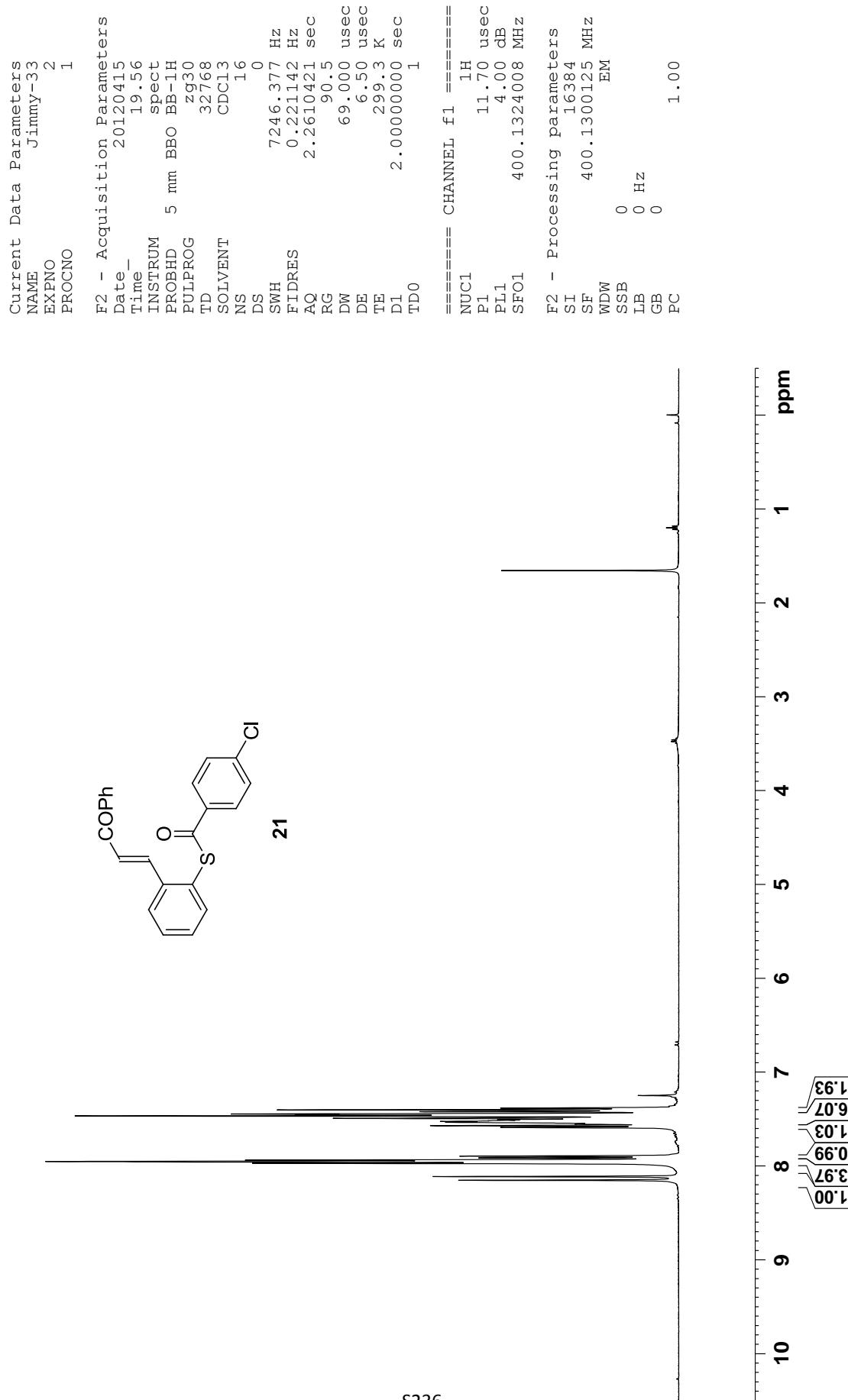


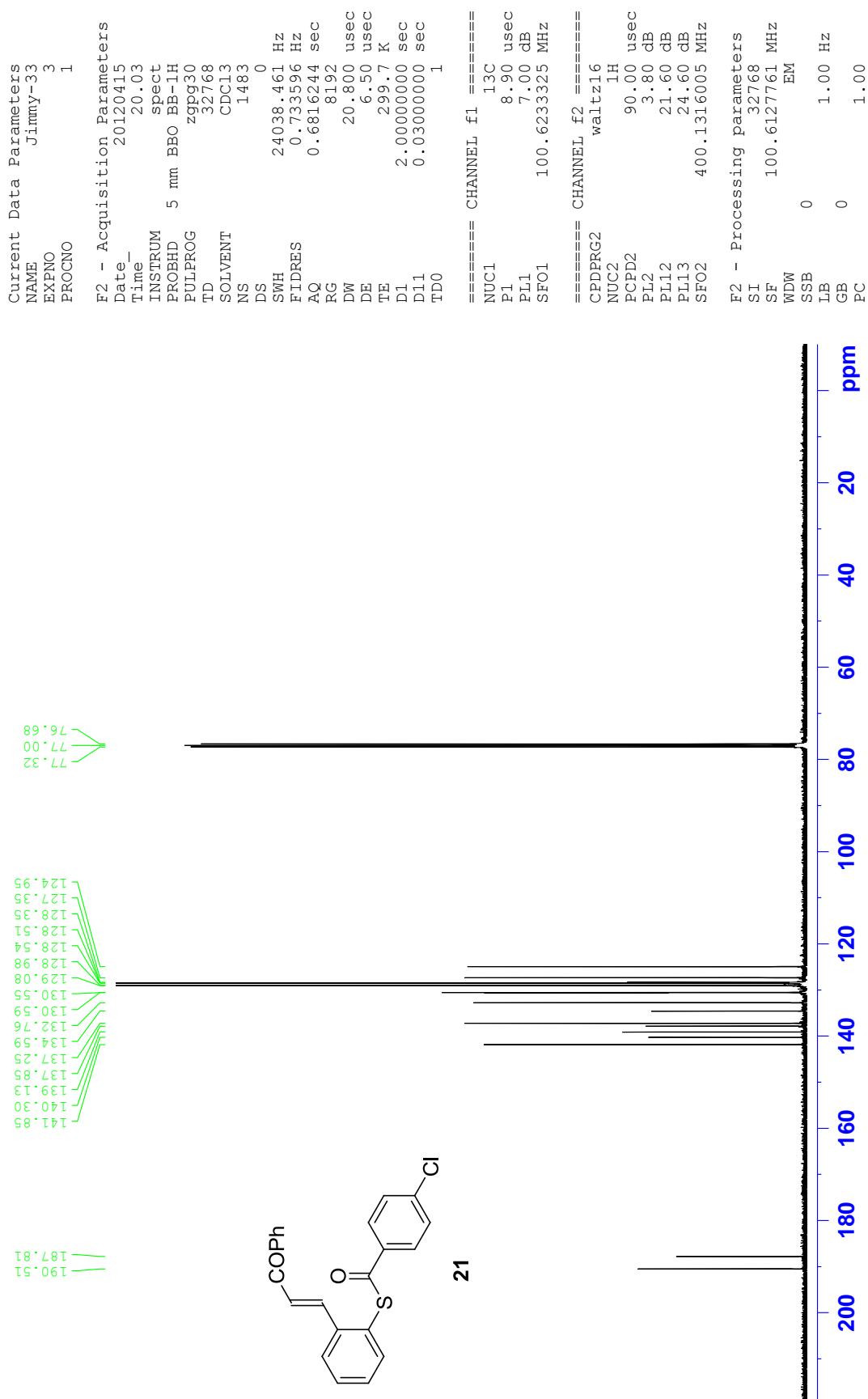


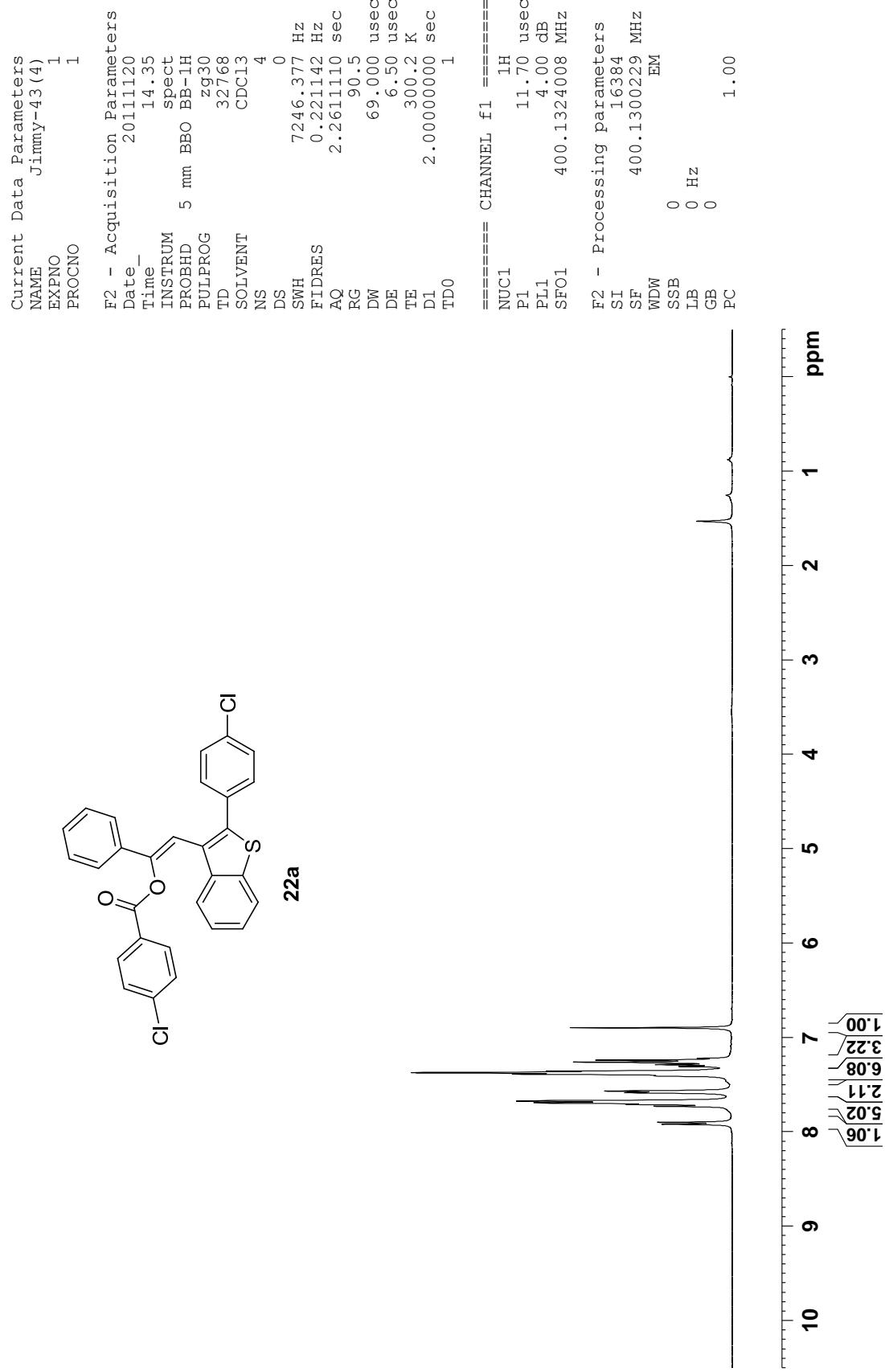


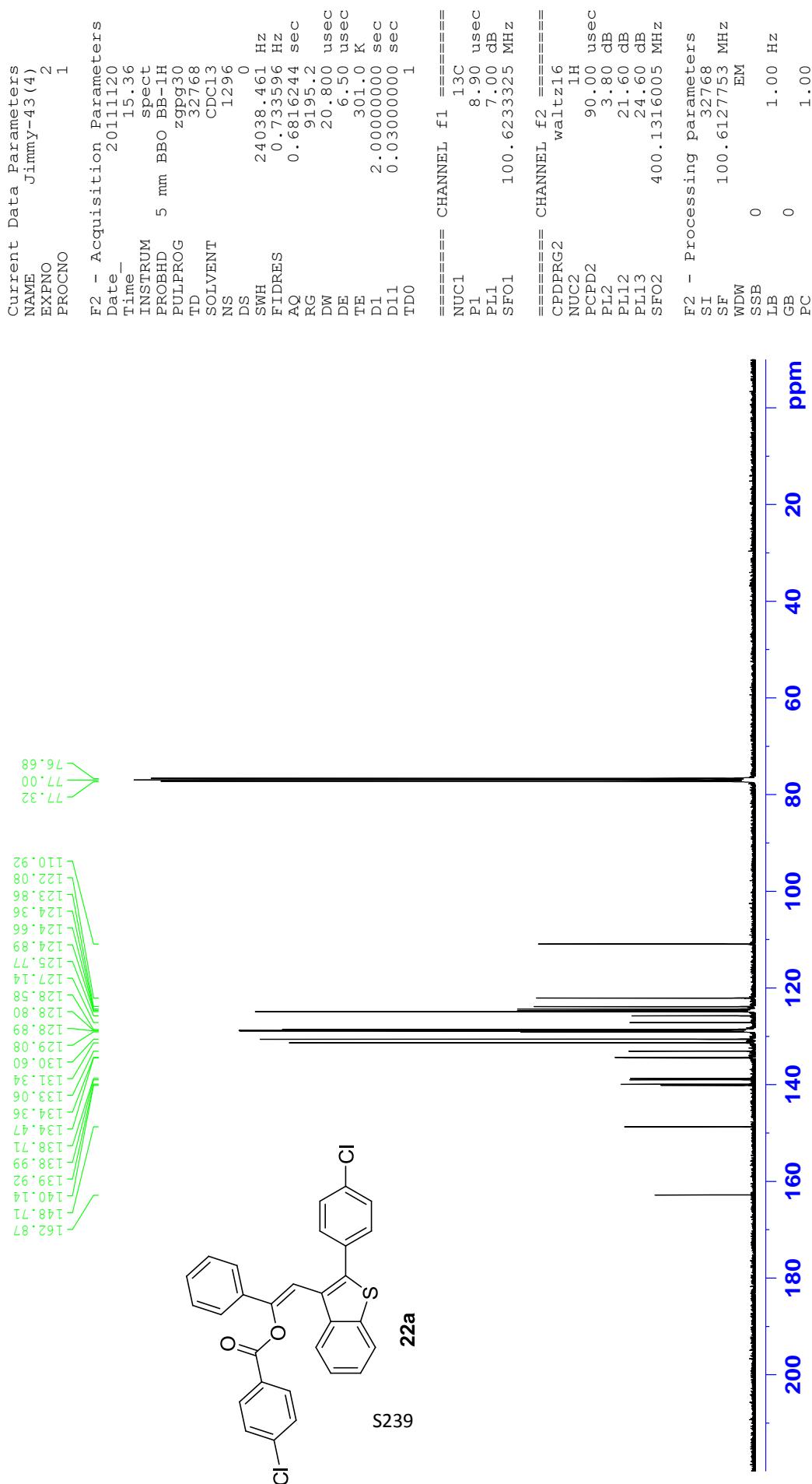


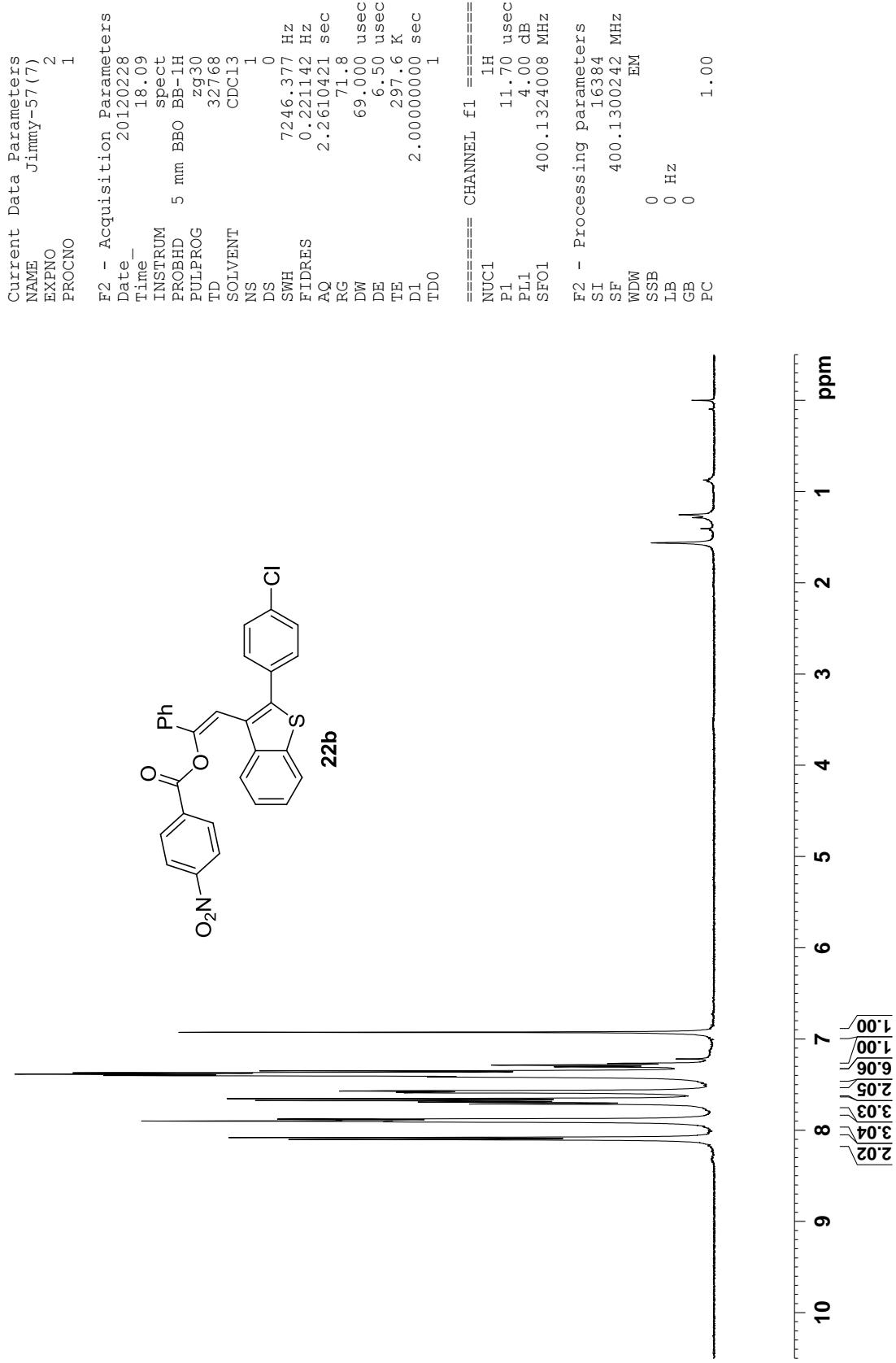


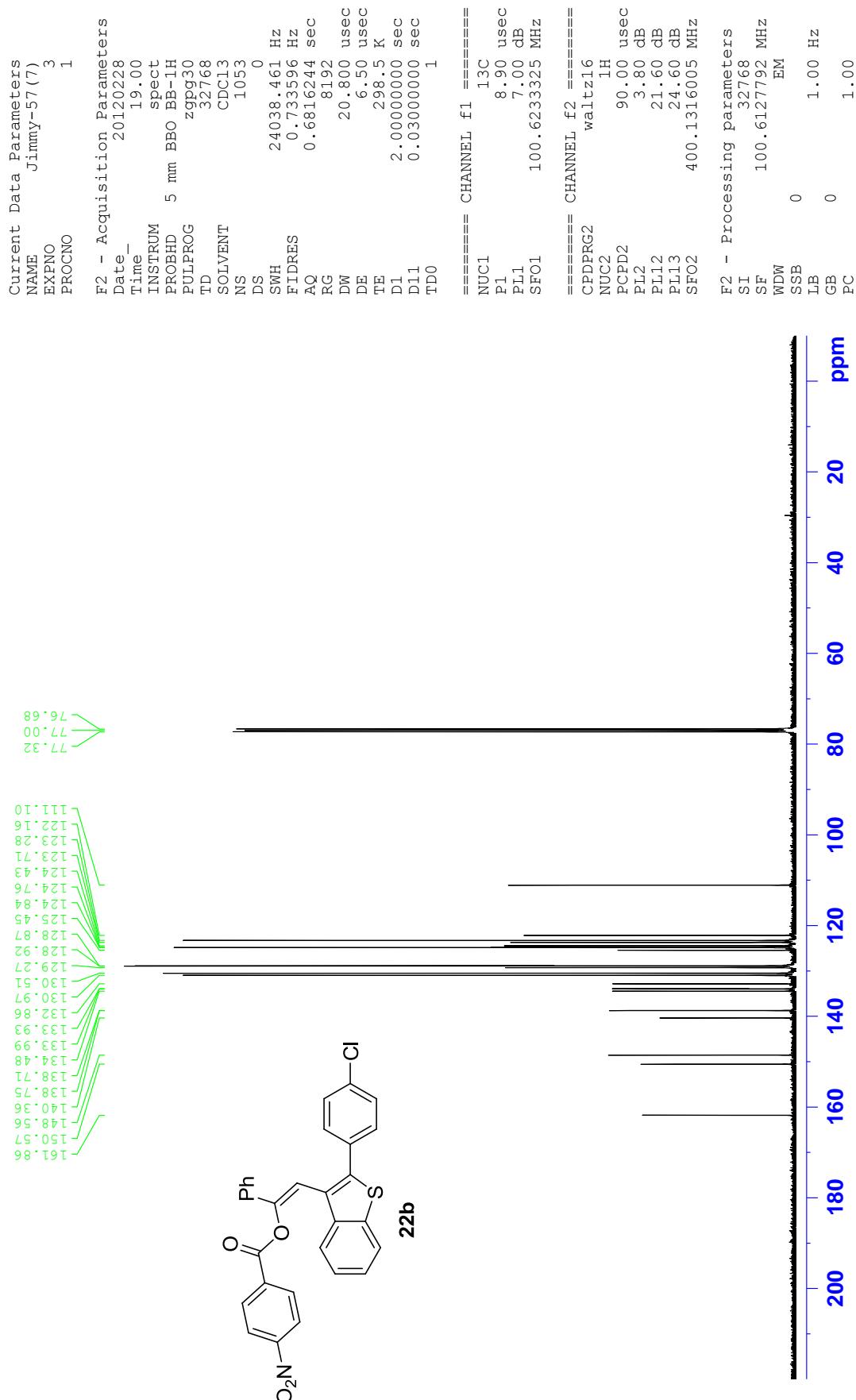


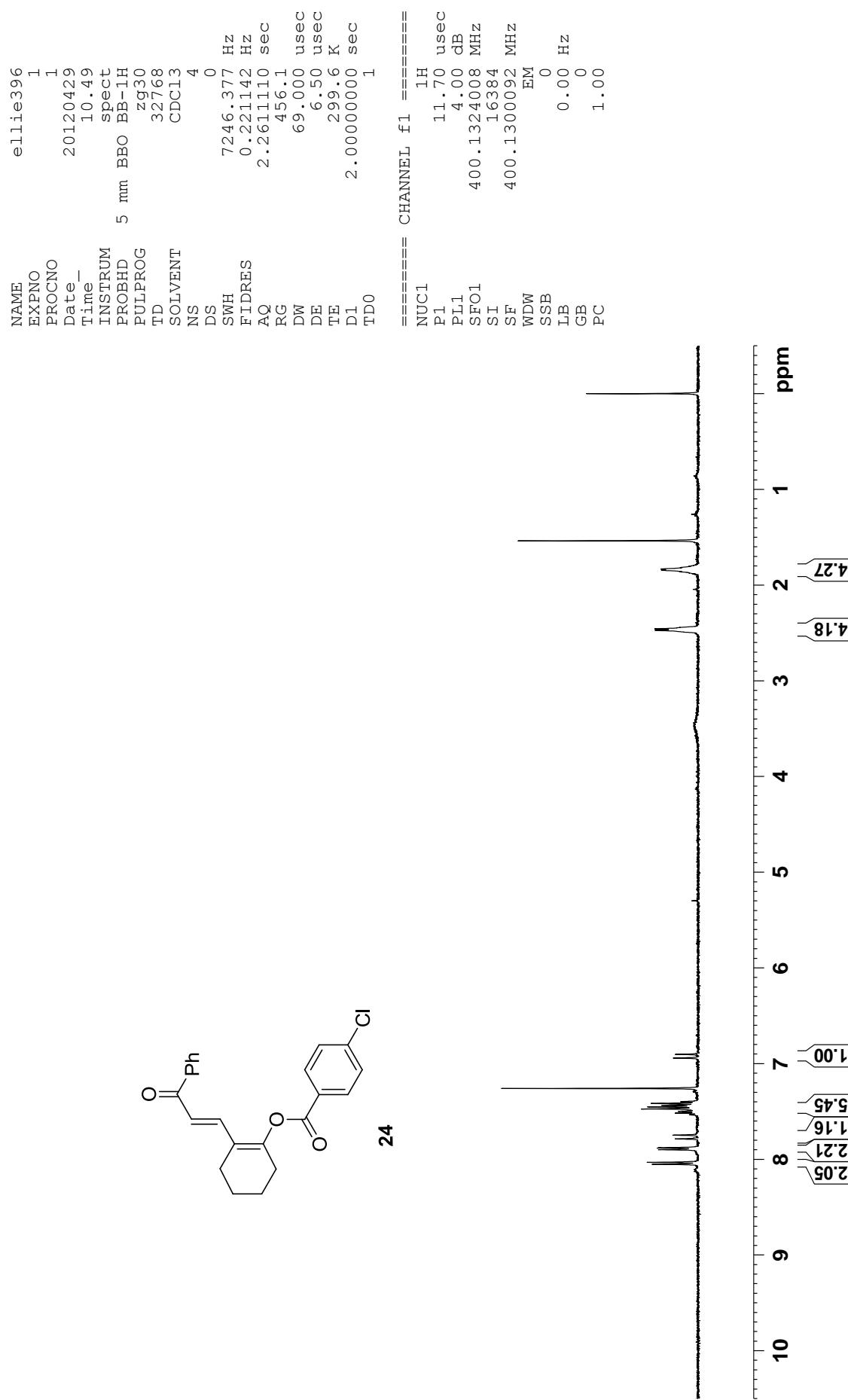




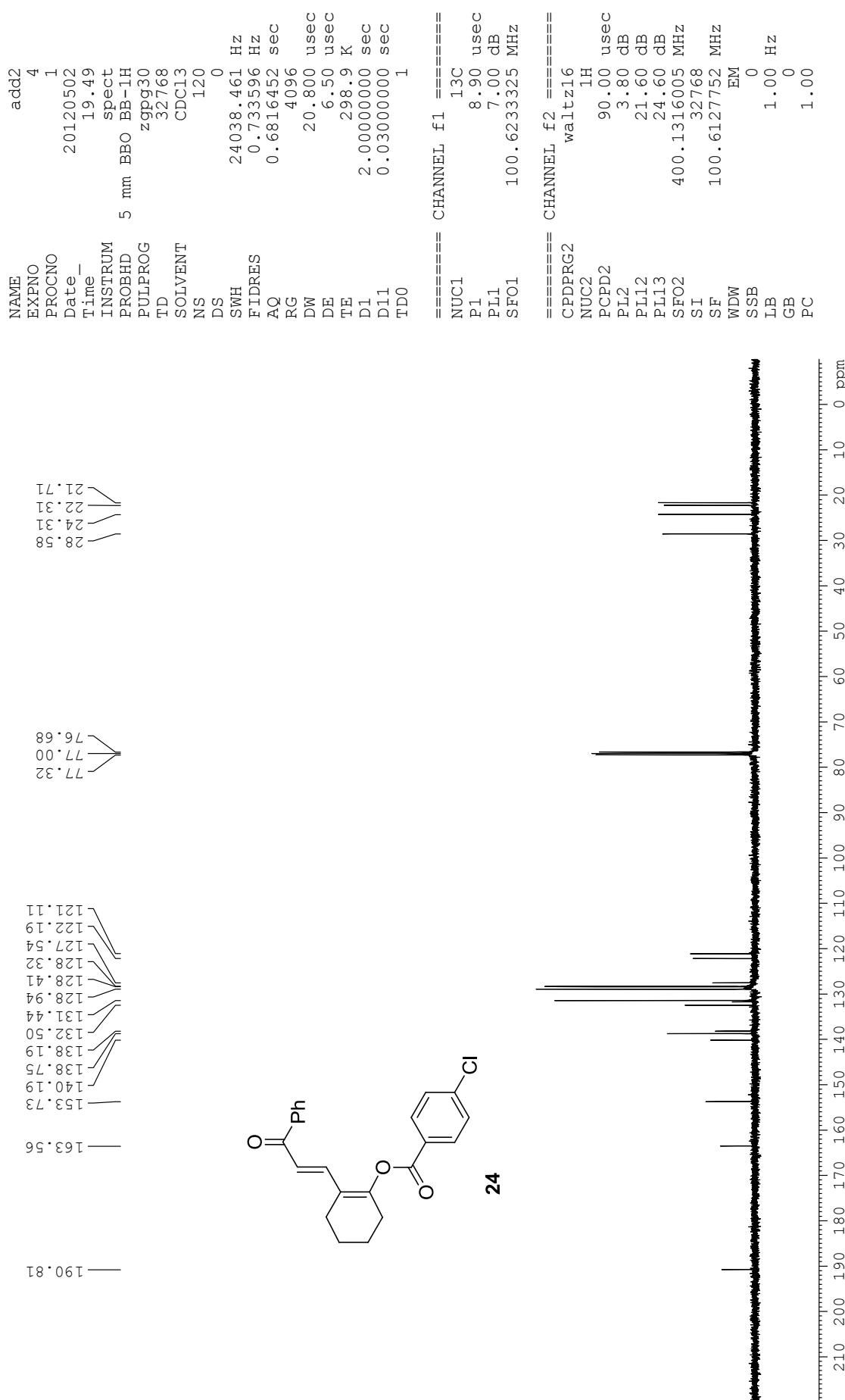


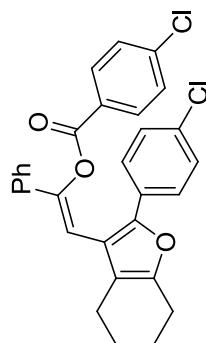
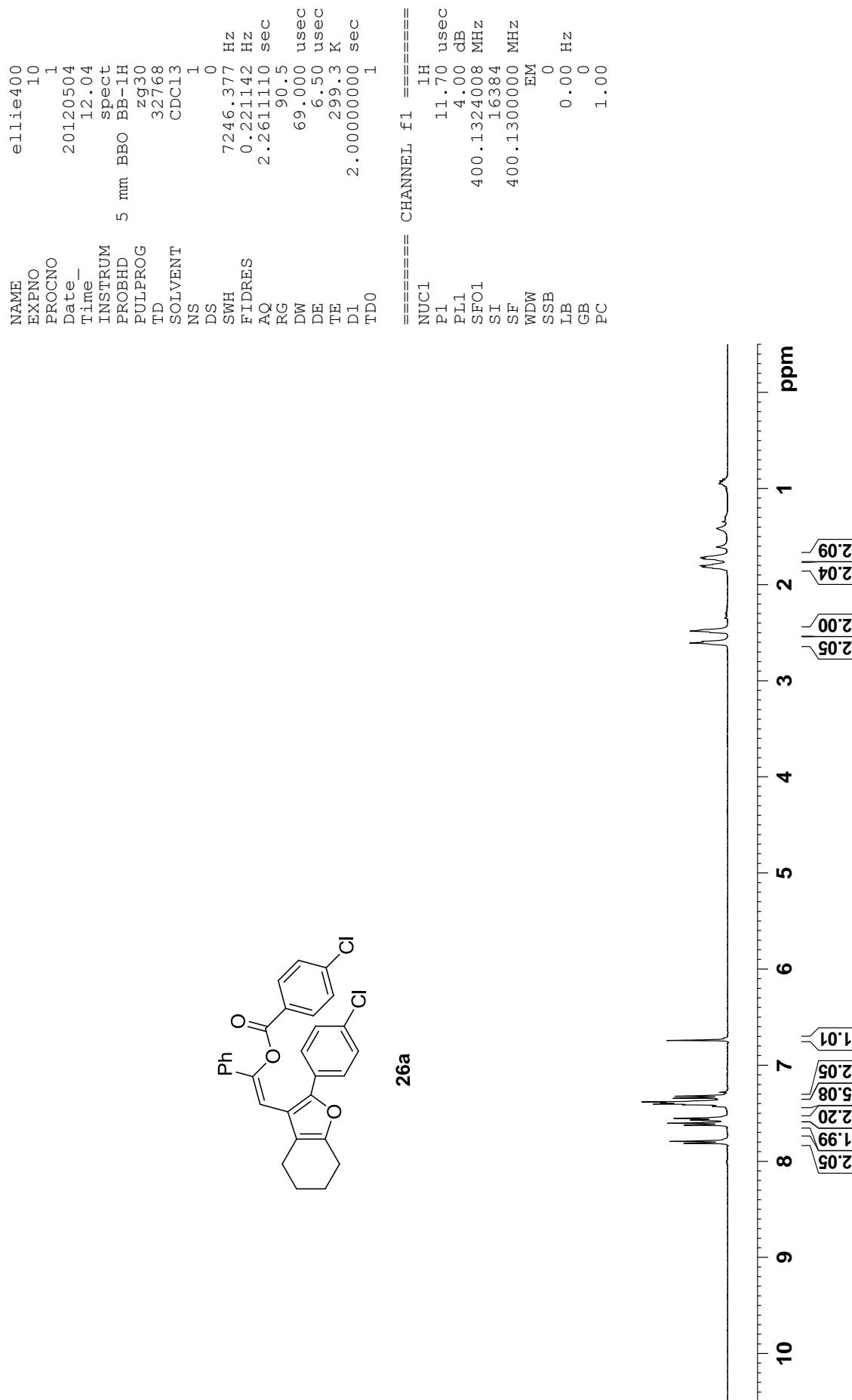




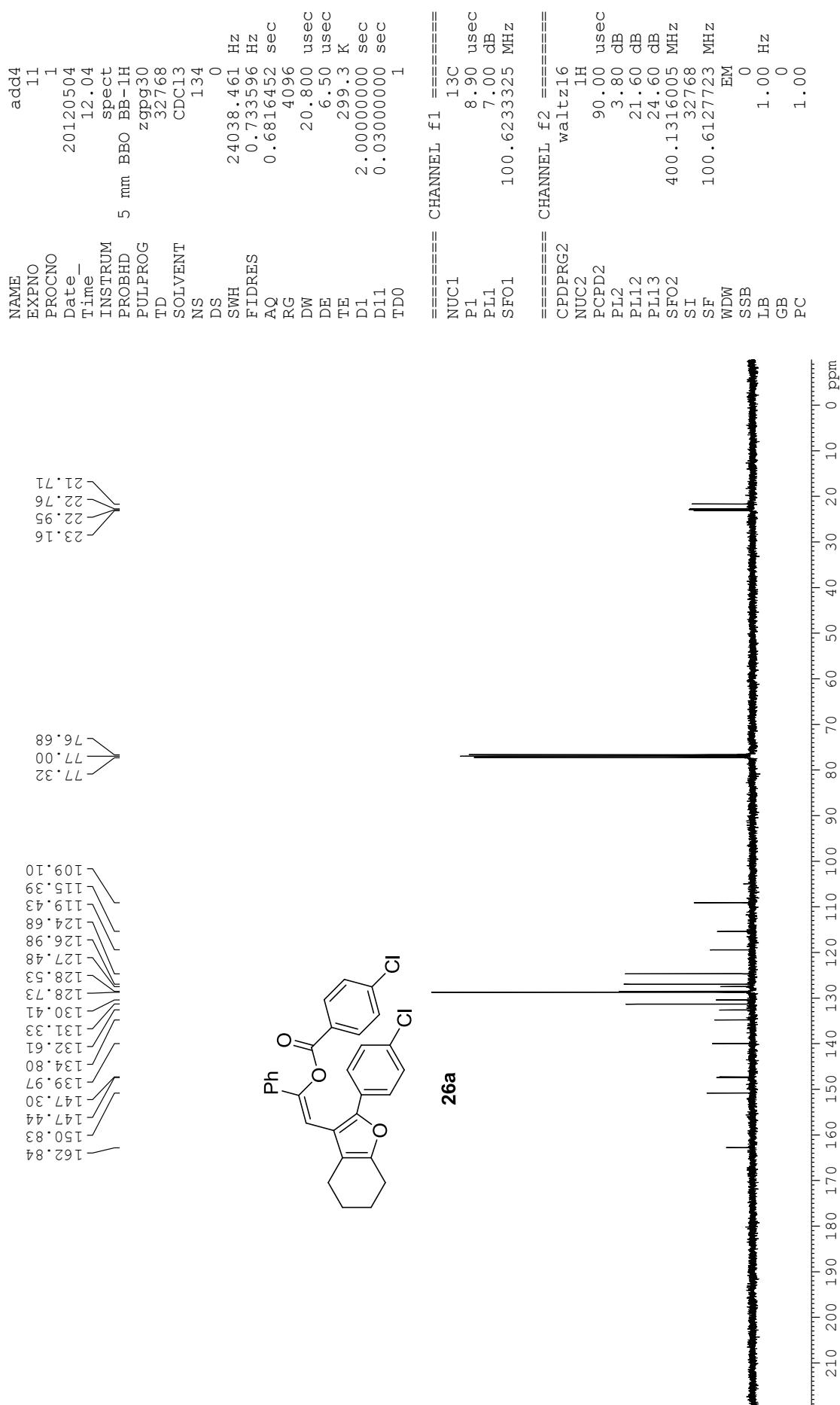


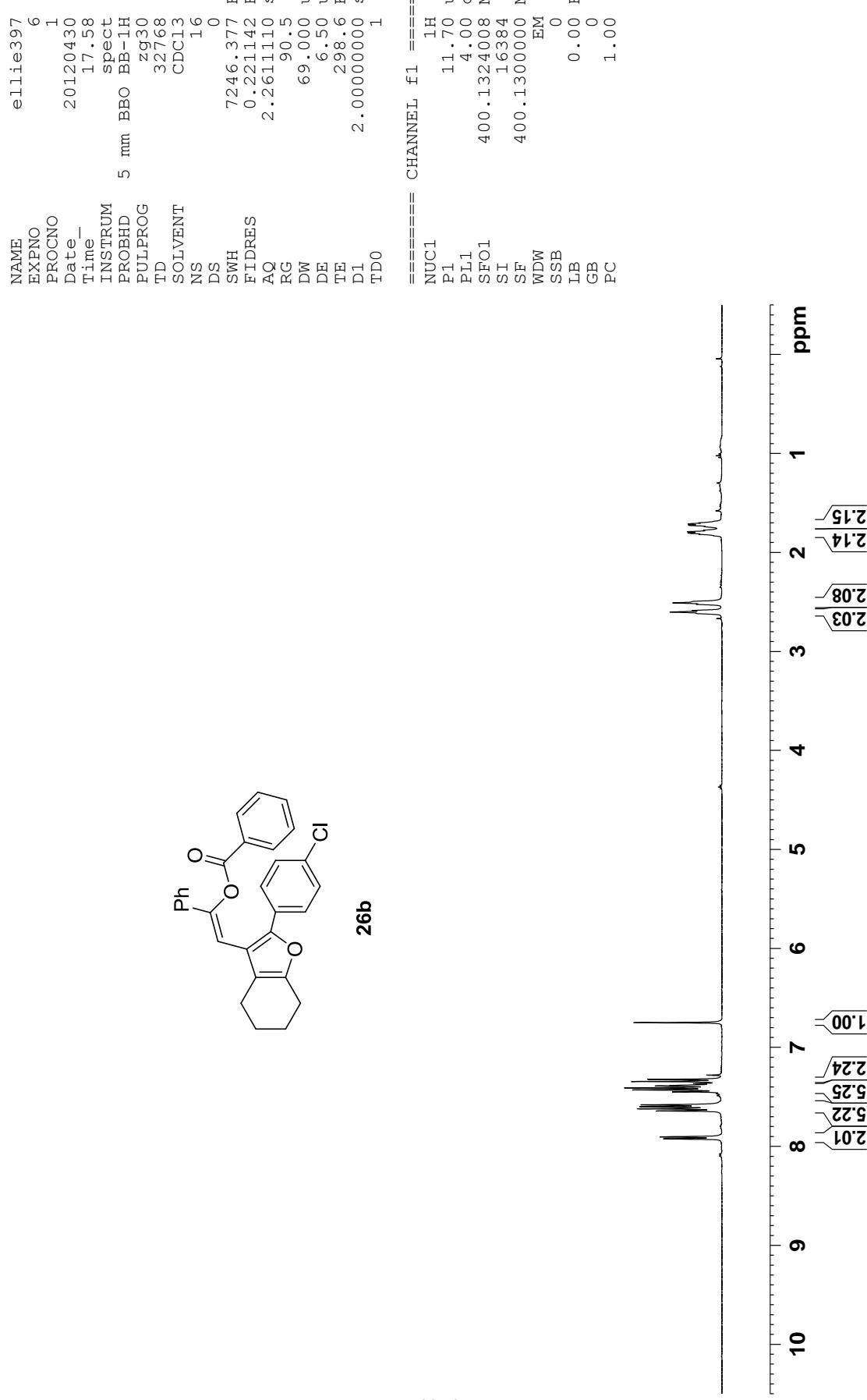
24

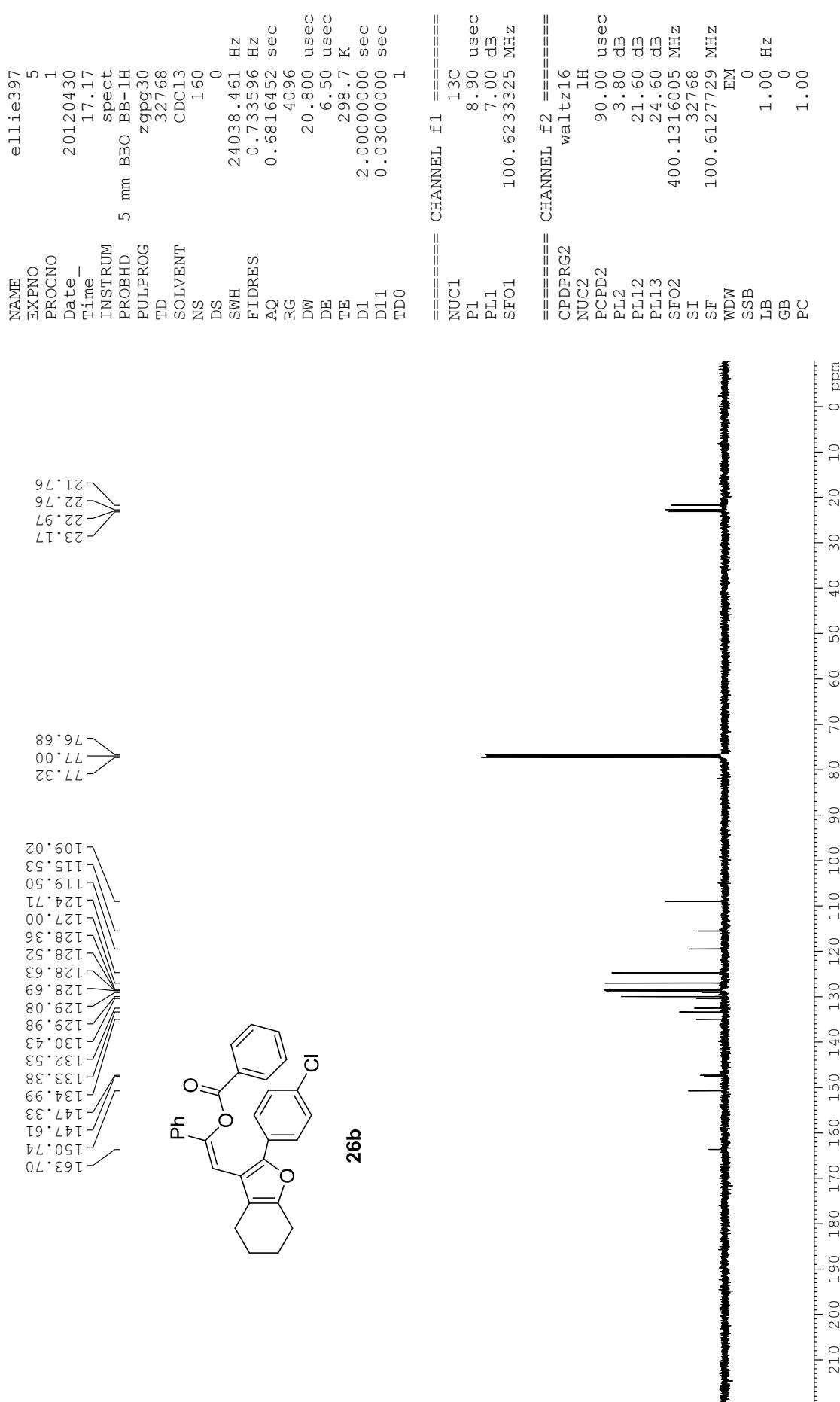


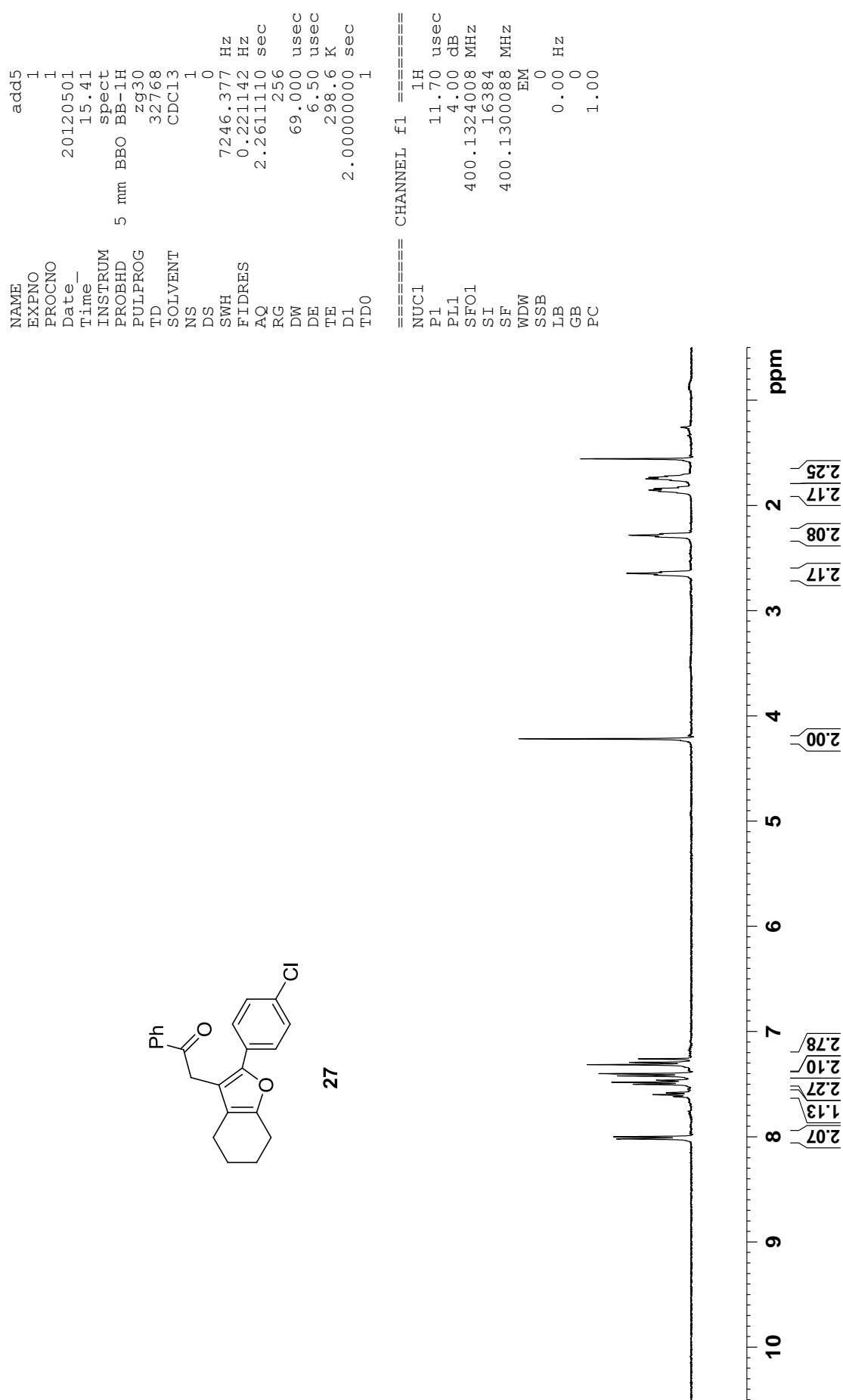


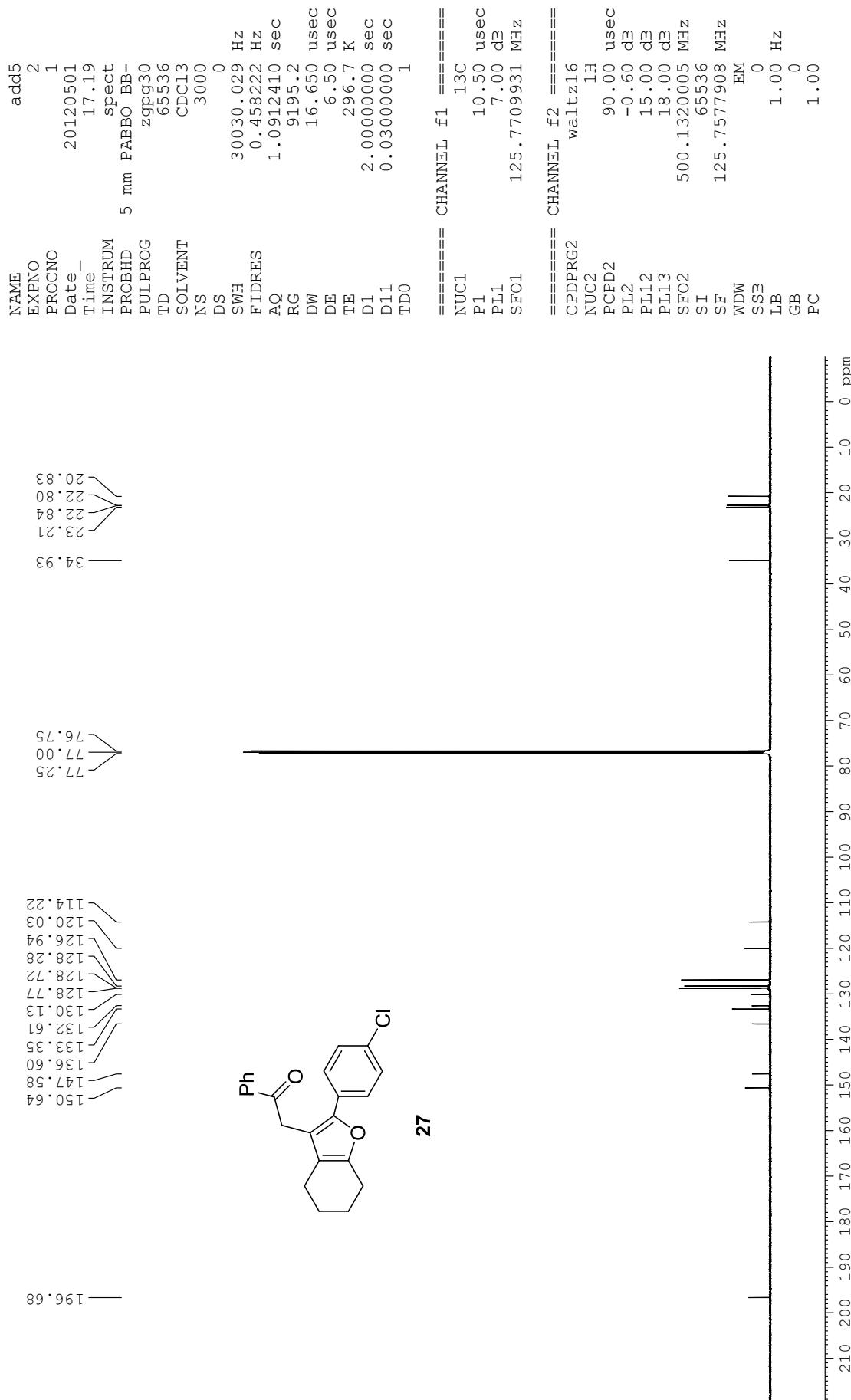
26a

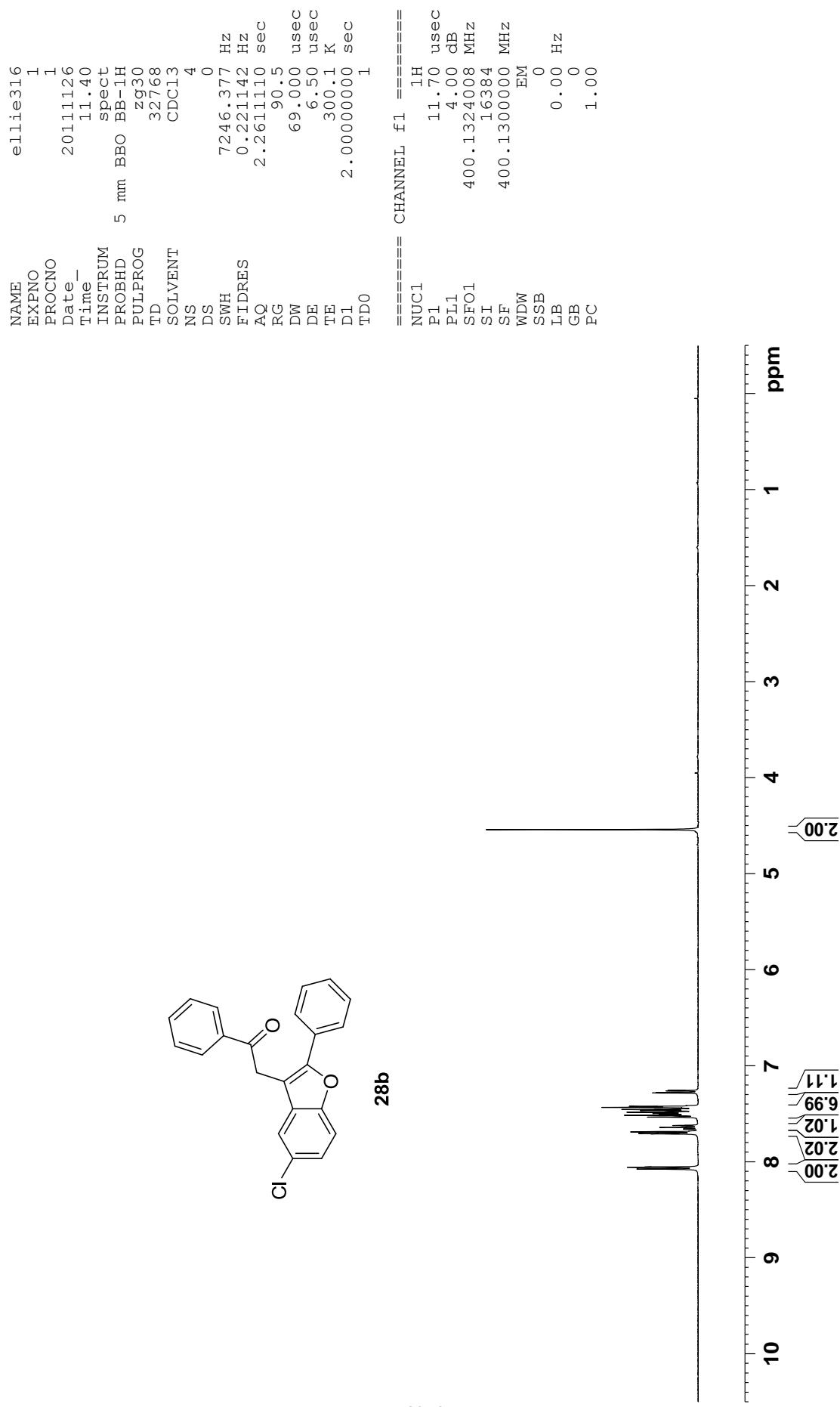


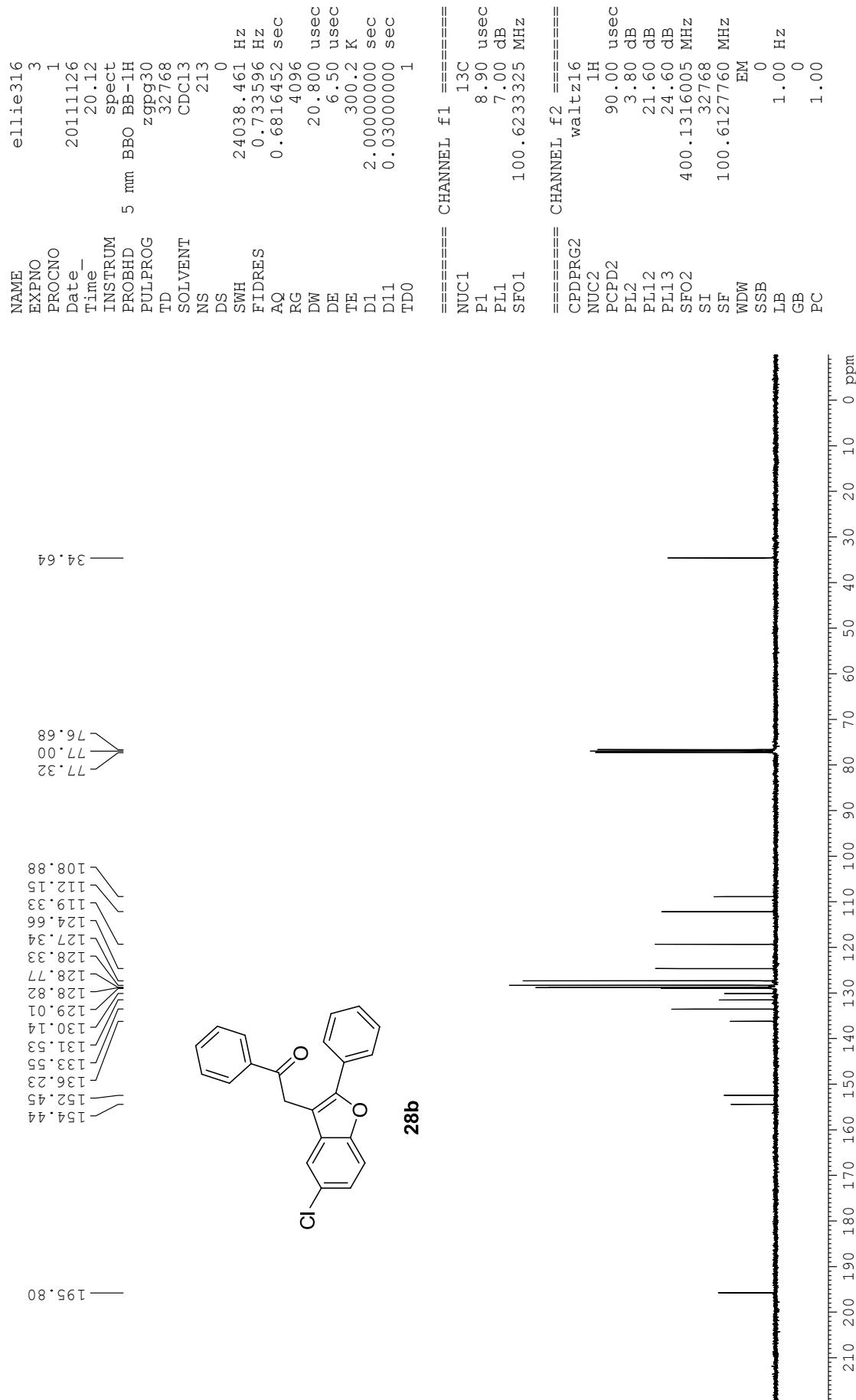


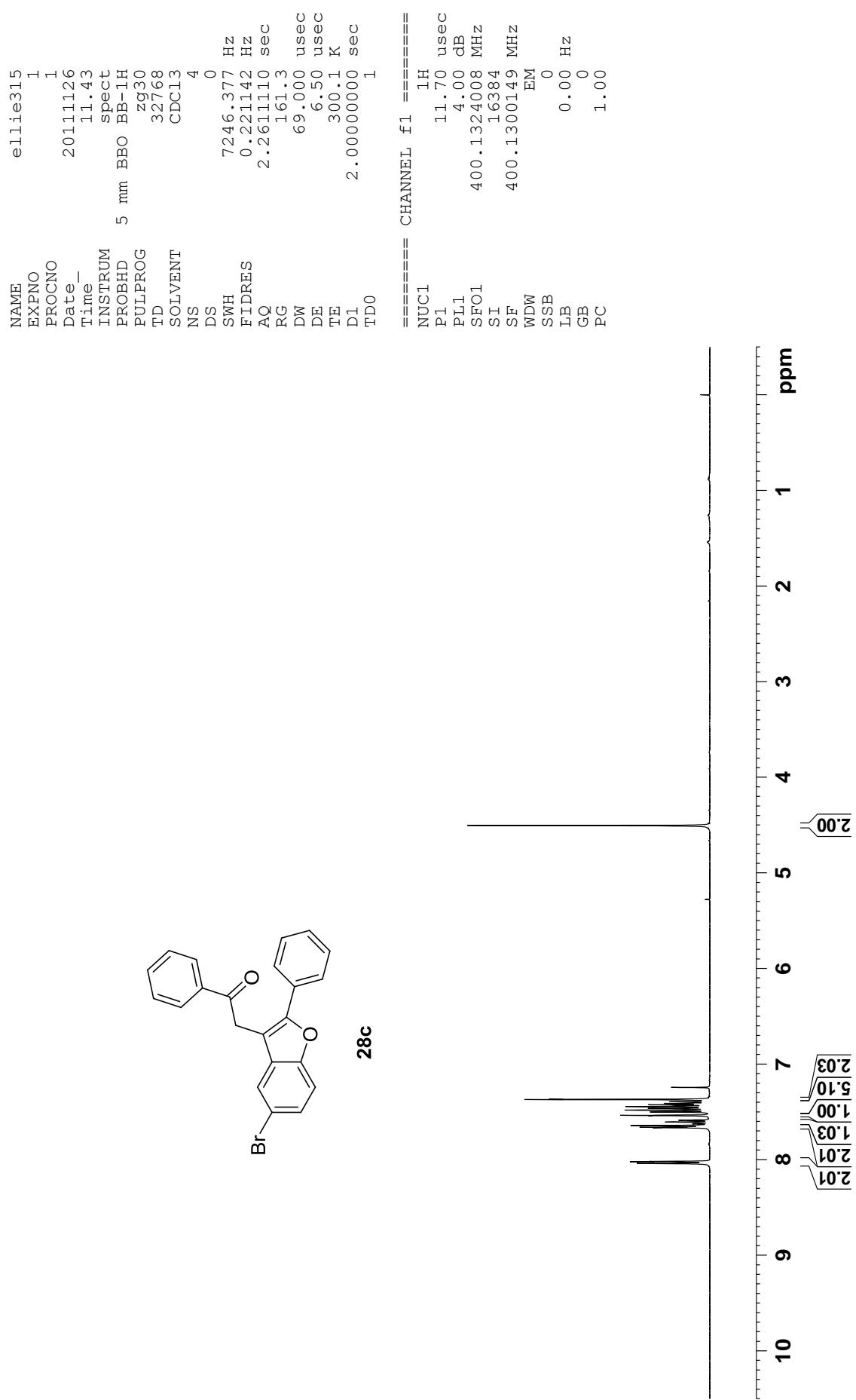


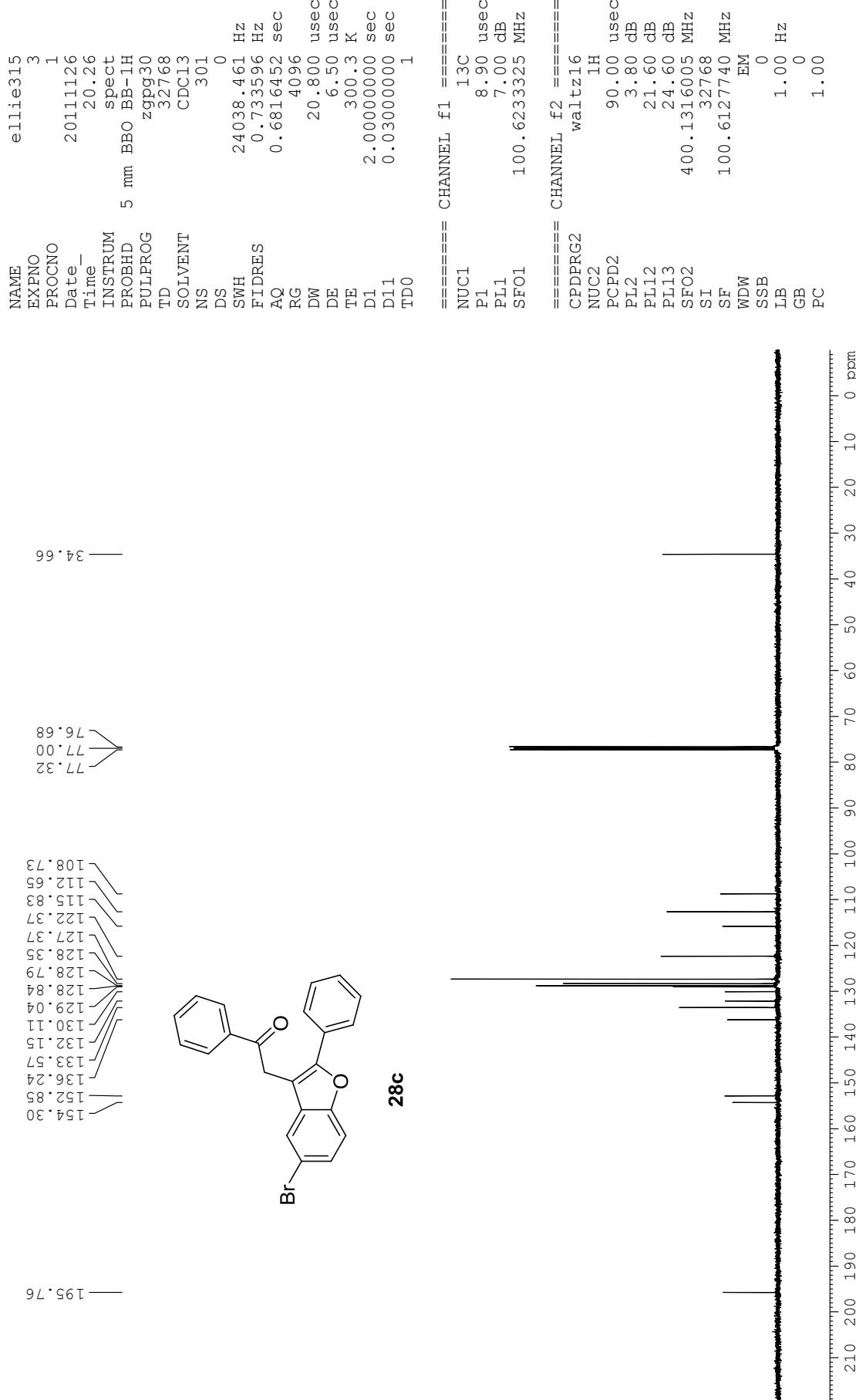








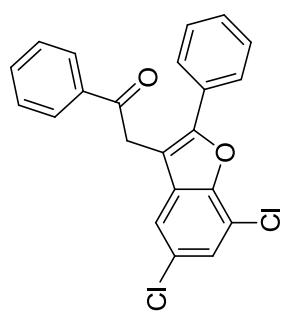




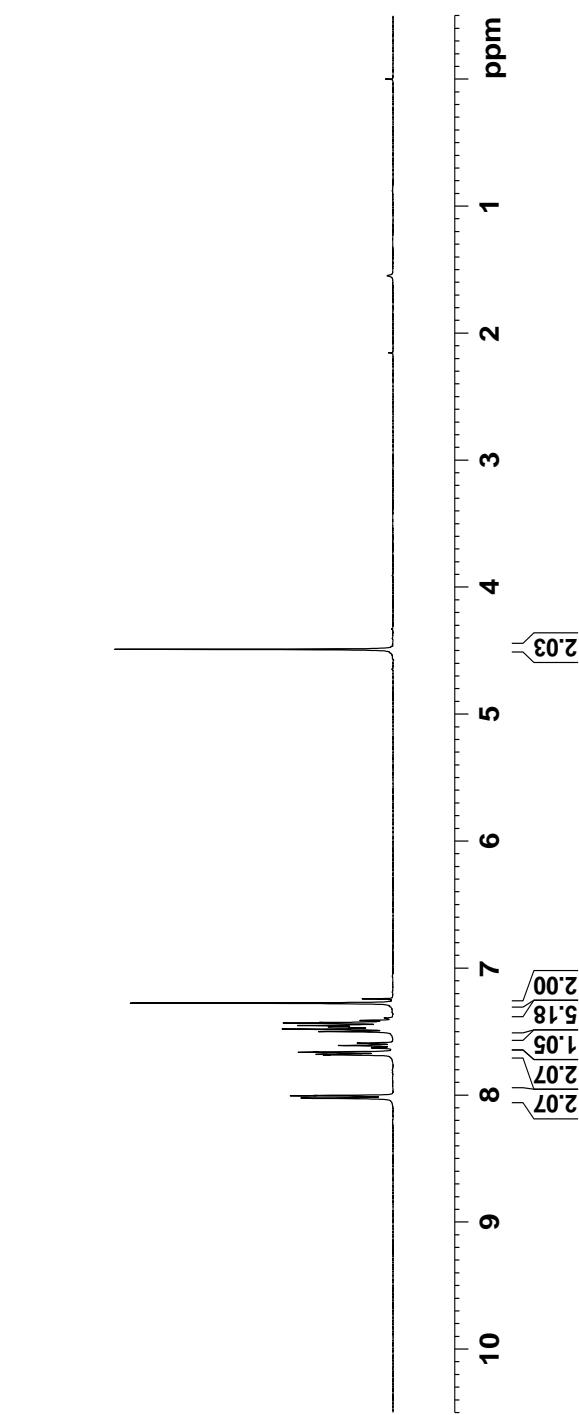
NAME ellie317
EXPNO 1
PROCNO 1
Date 2011126
Time 13.19
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl₃
NS 4
DS 0
SWH 7246.377 Hz
FIDRES 0.221142 Hz
AQ 2.261110 sec
RG 128
DW 69.000 usec
DE 6.50 usec
TE 299.9 K
D1 2.0000000 sec
TDO 1

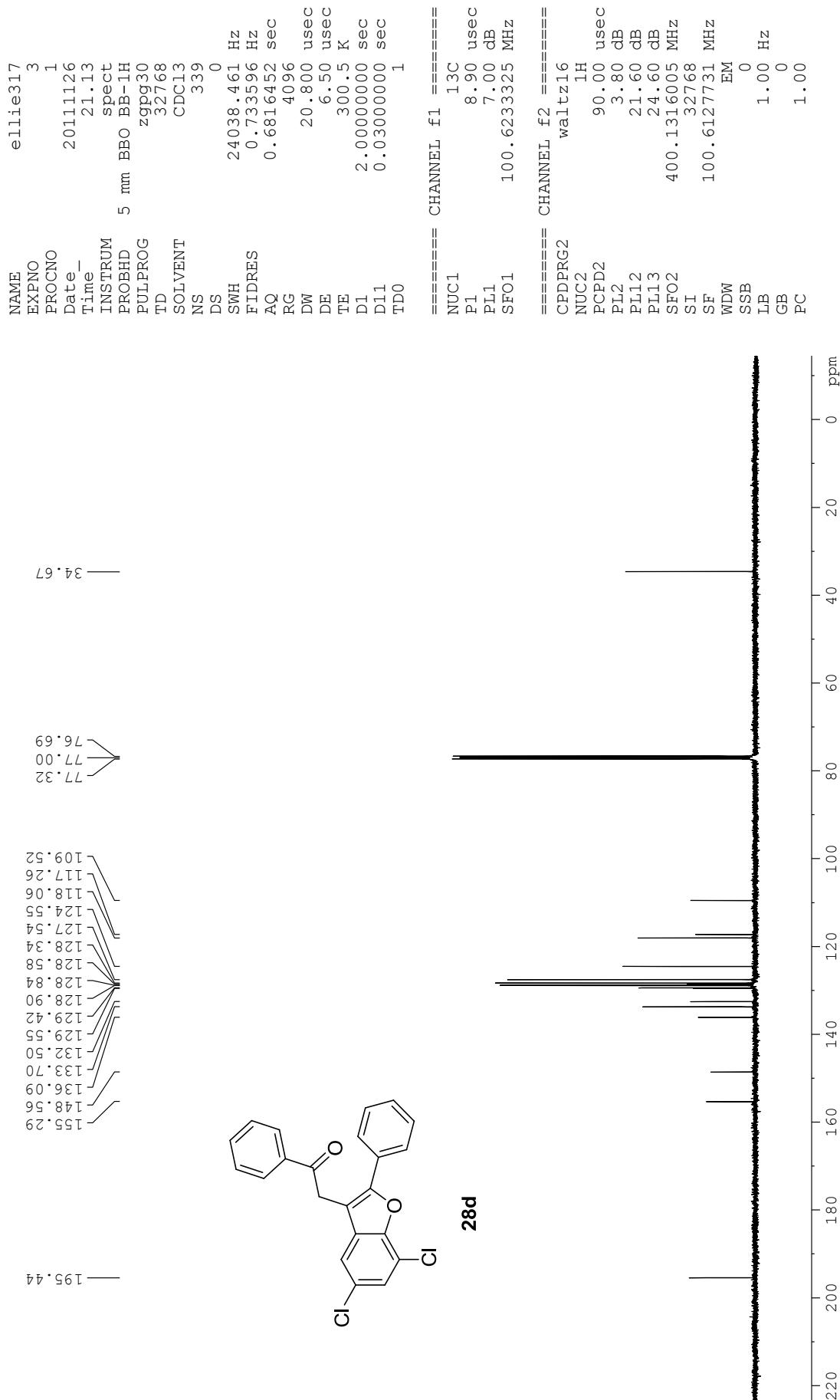
===== CHANNEL f1 =====

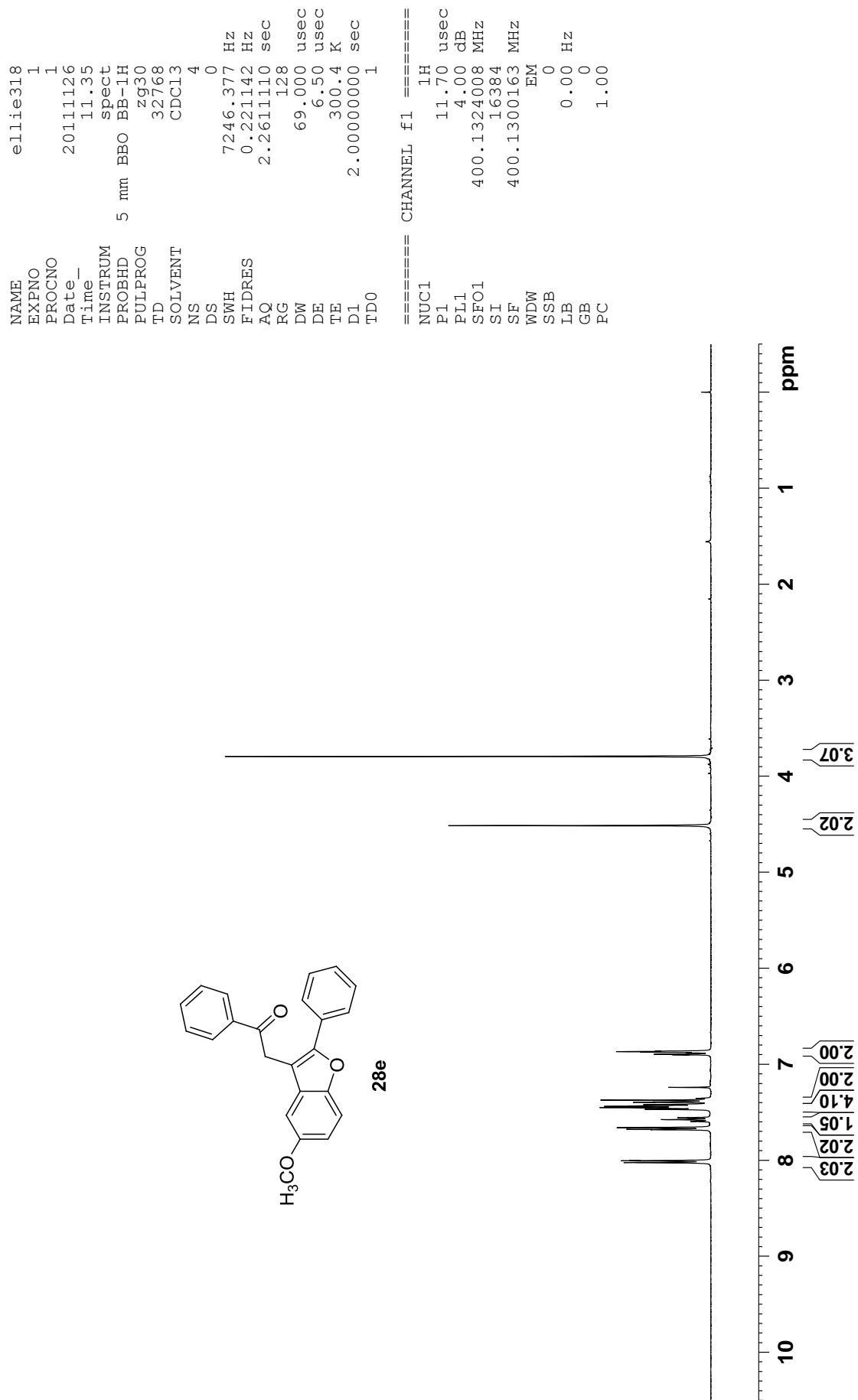
NUC1 1H
P1 11.70 usec
PL1 4.00 dB
SFO1 400.1324008 MHz
SI 16384
SF 400.1300158 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

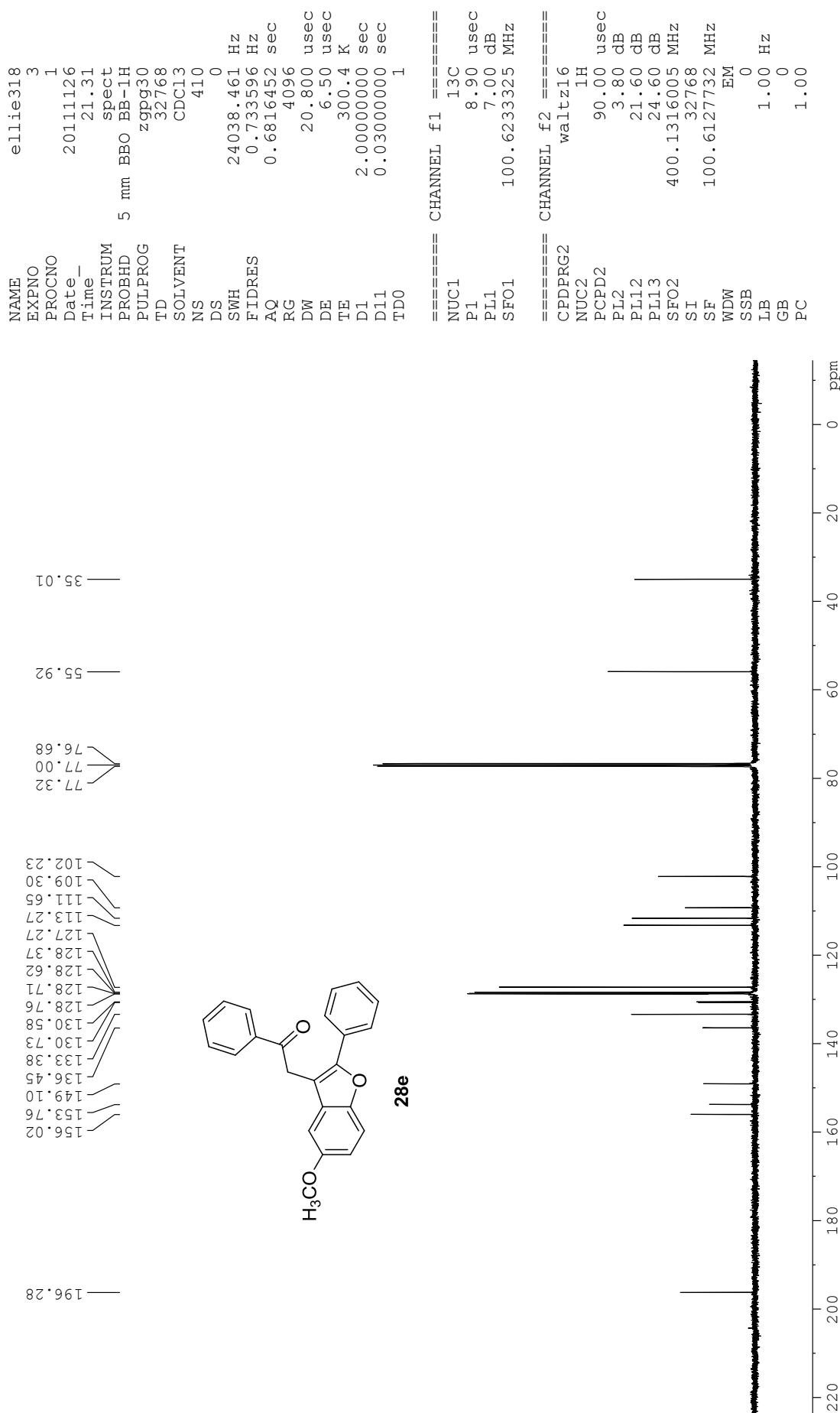


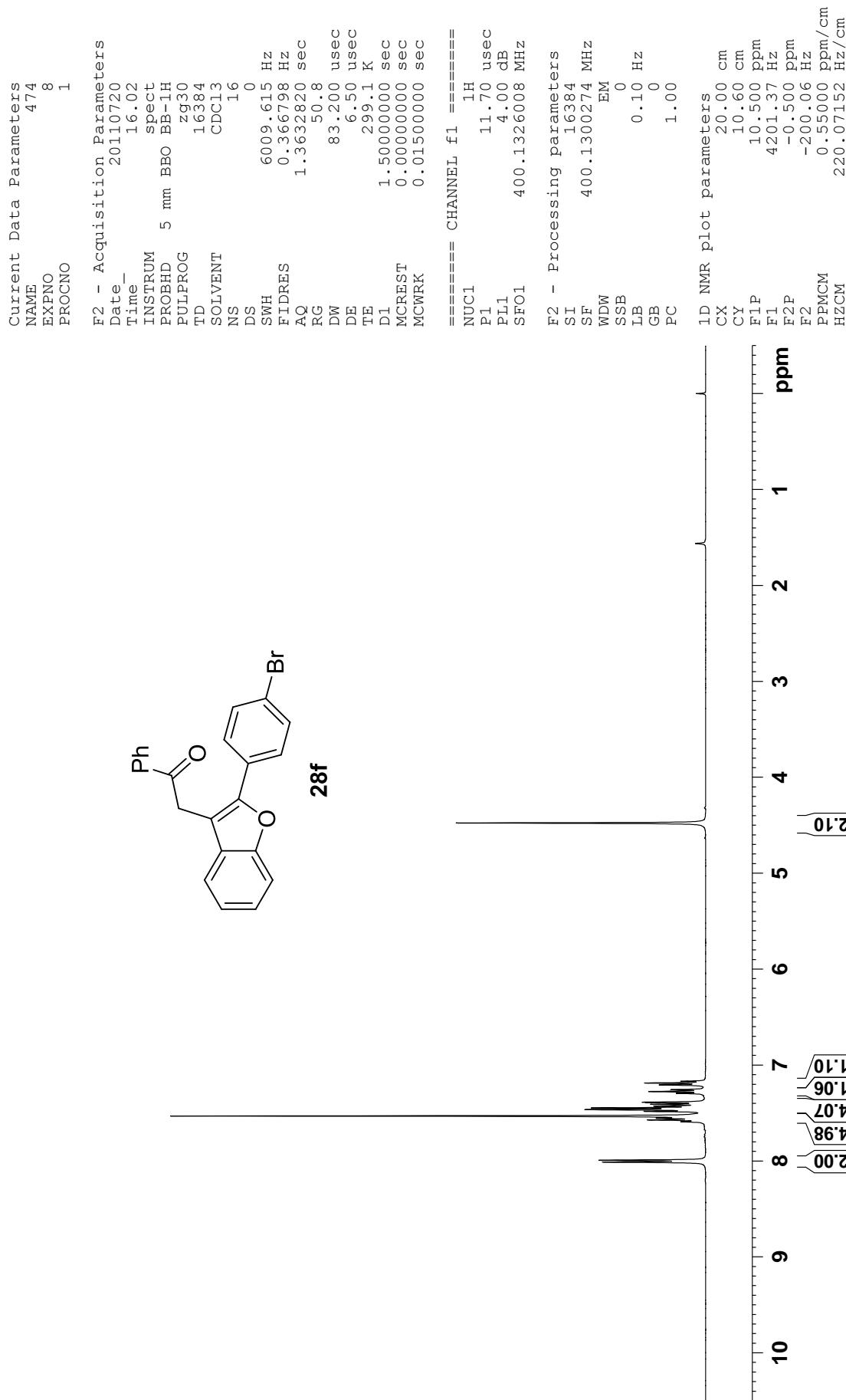
28d

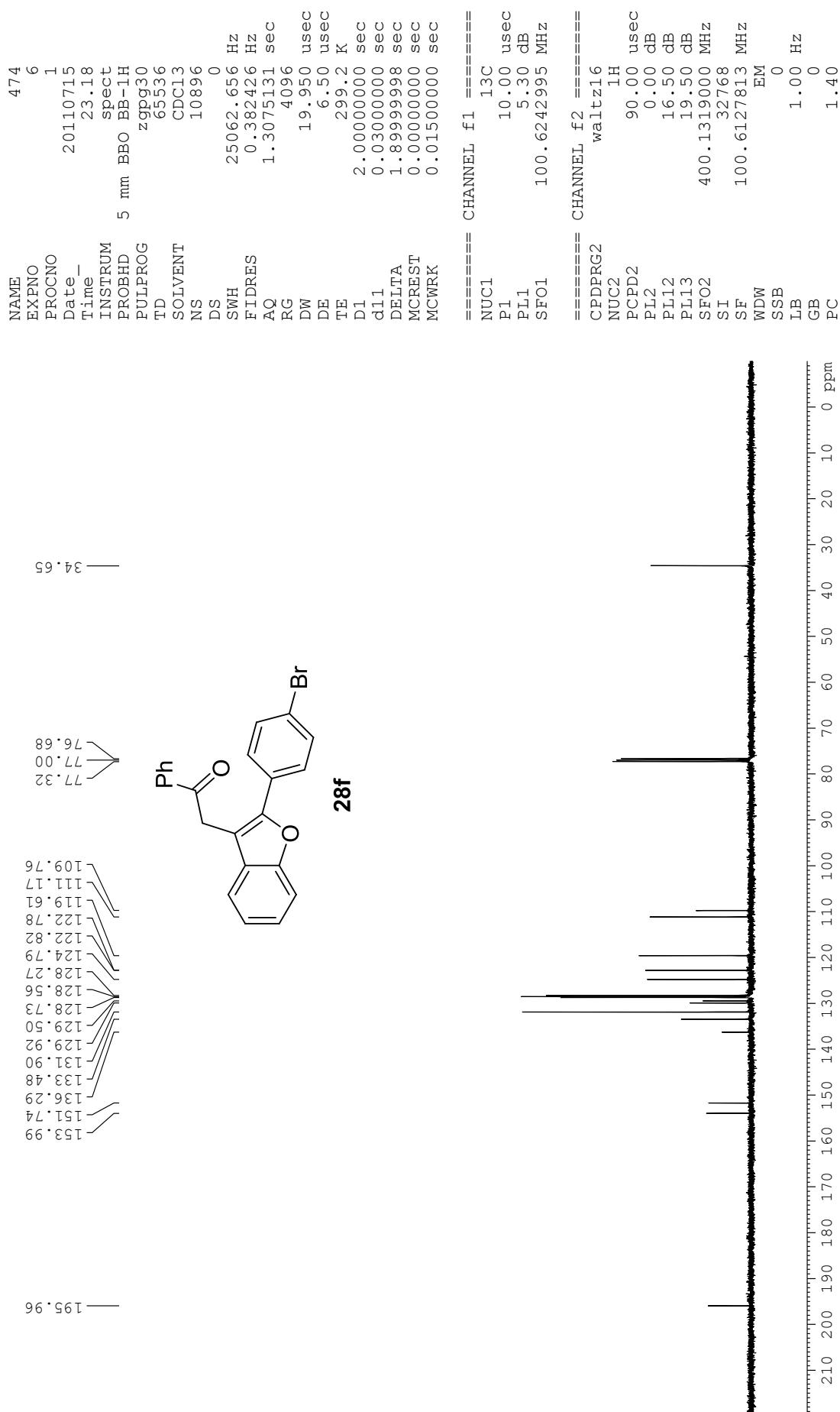


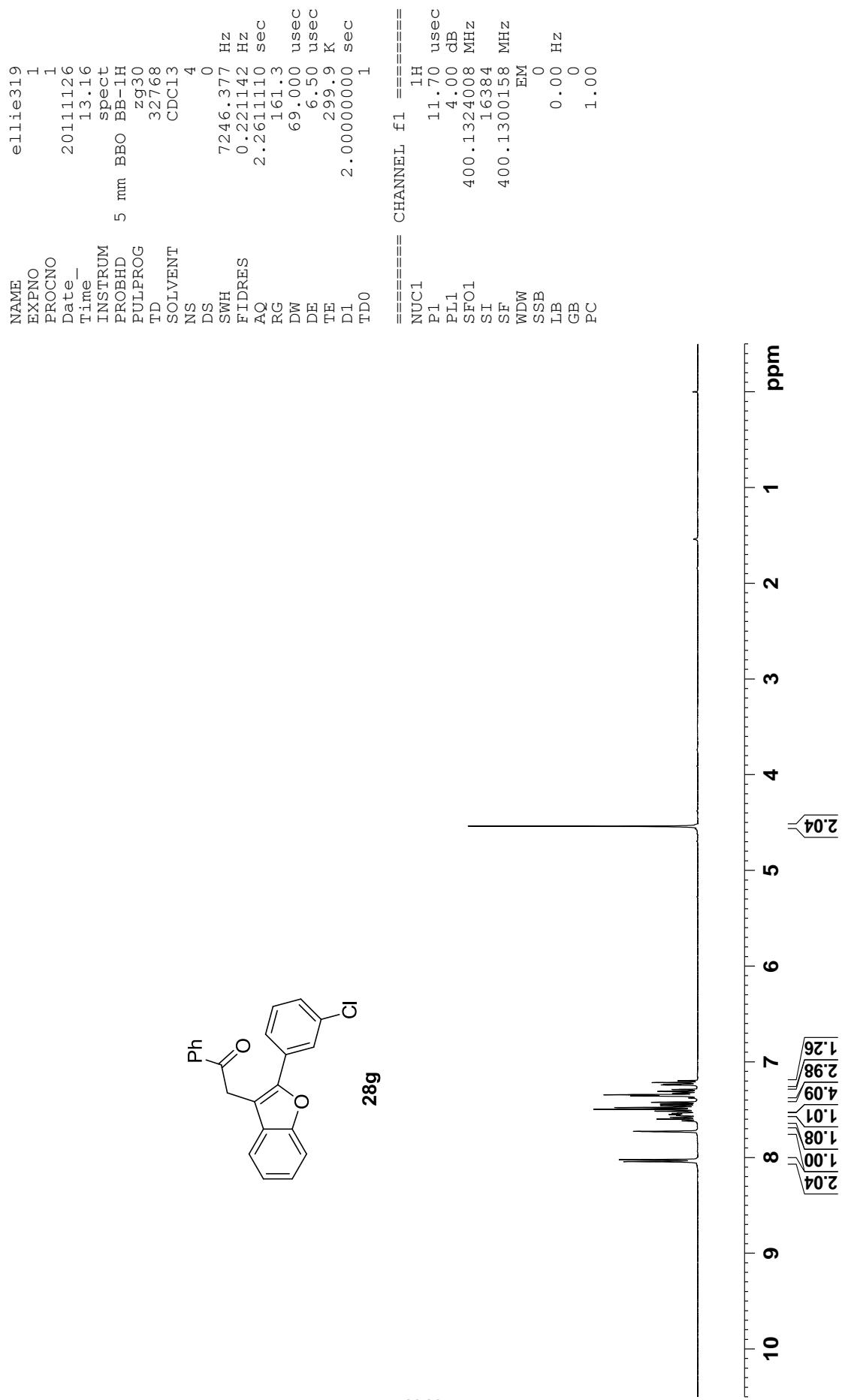


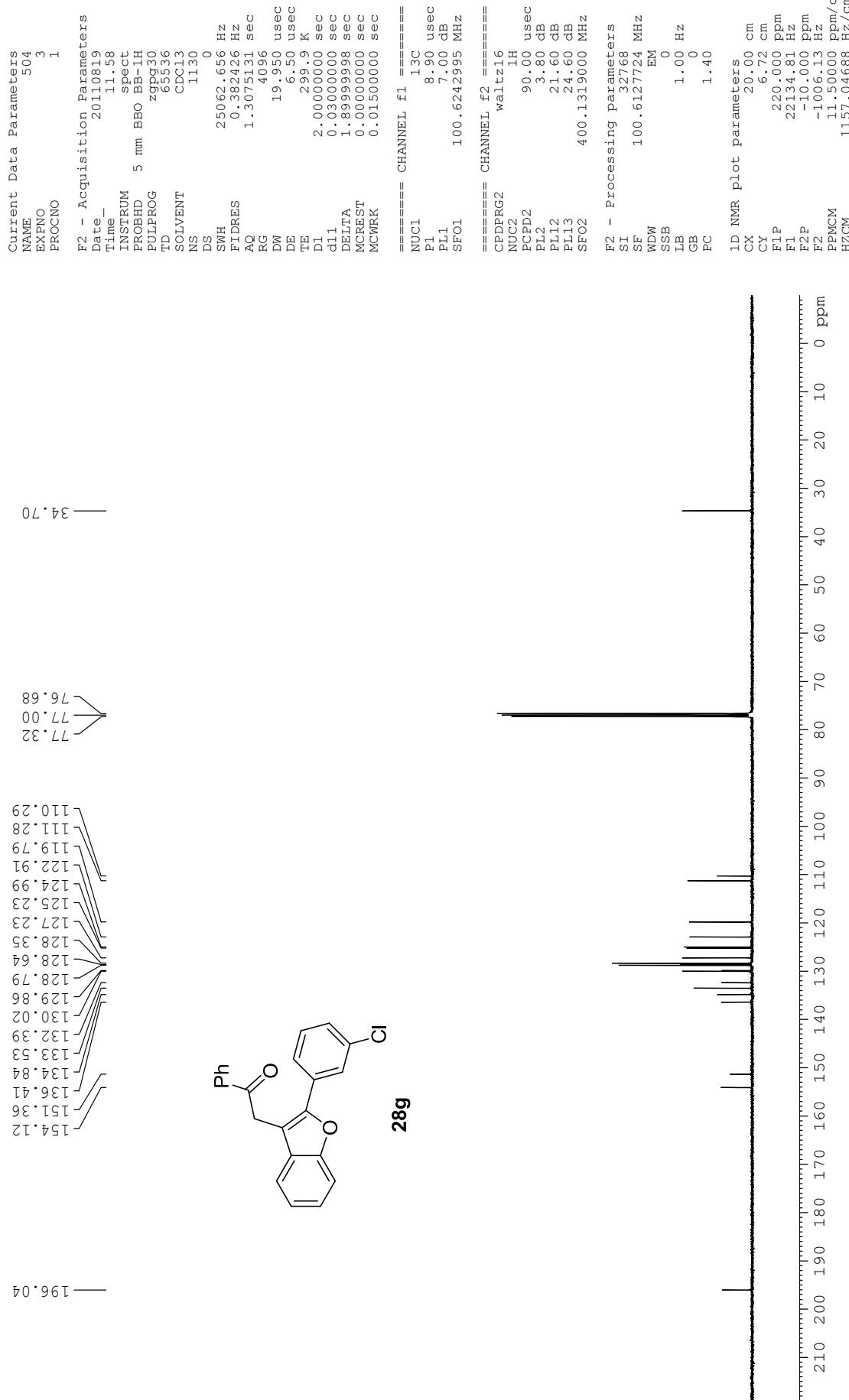
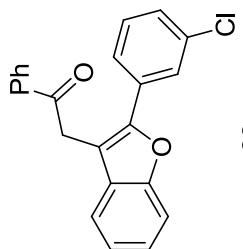
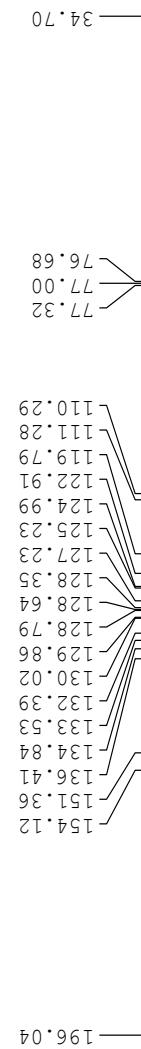


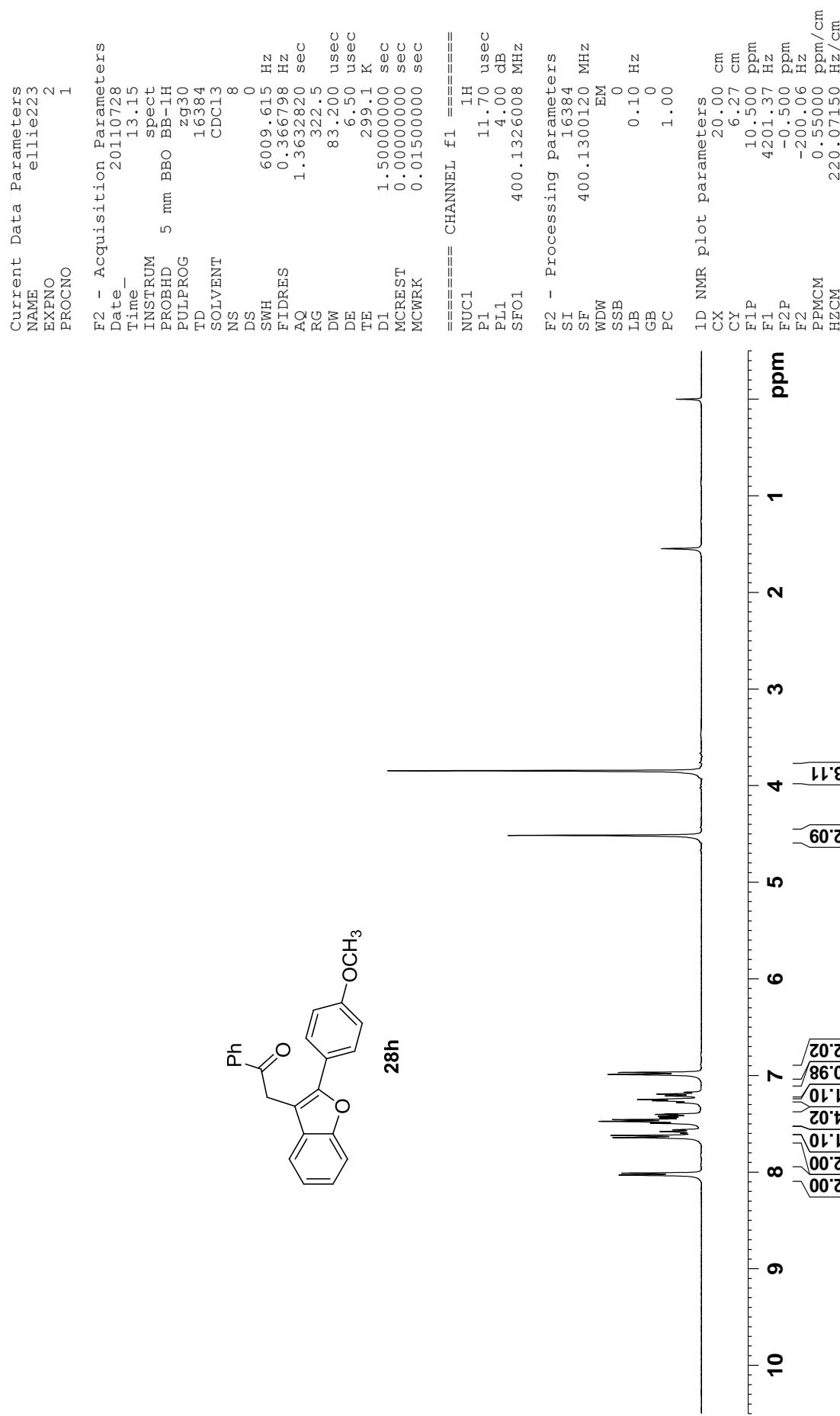


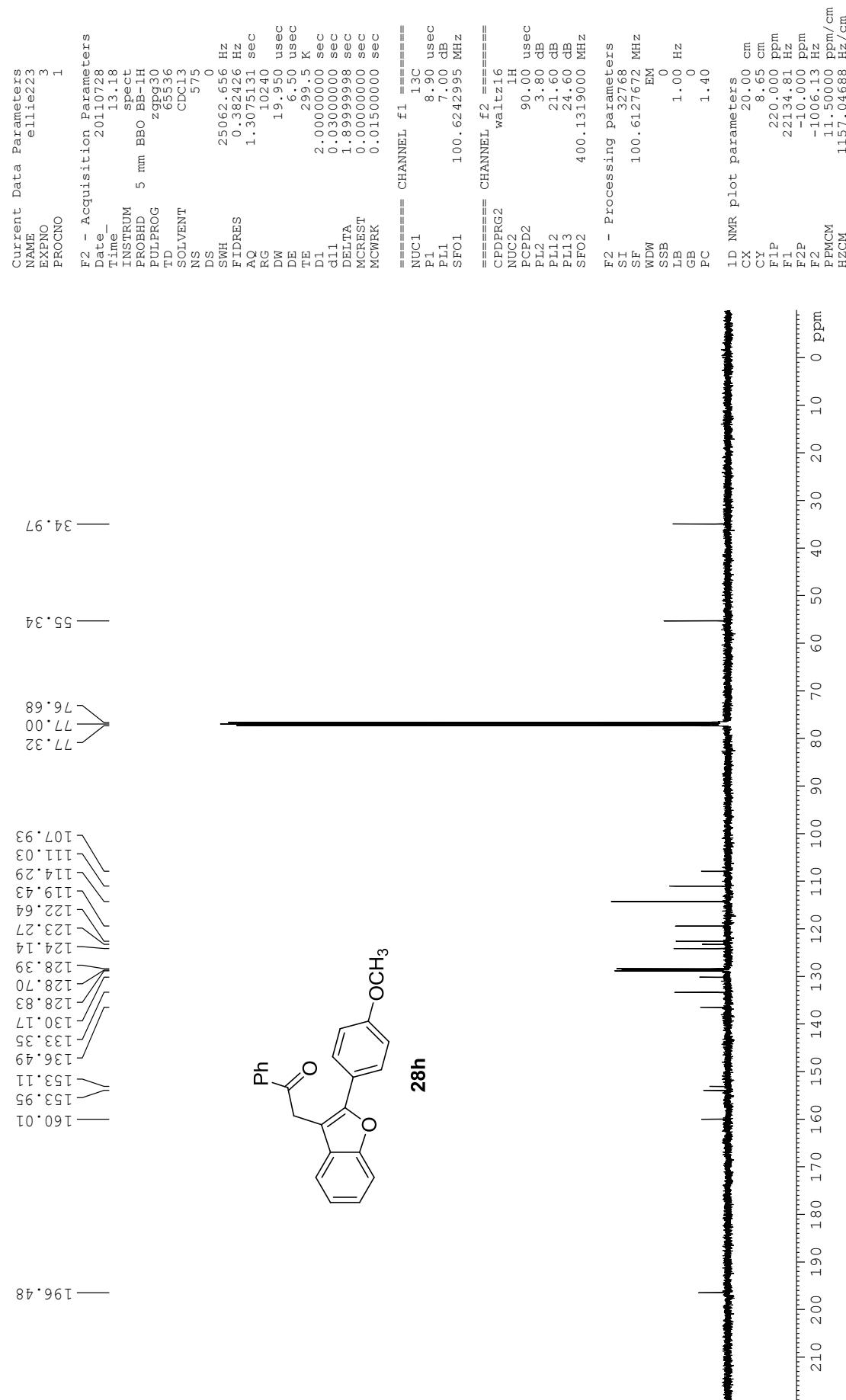


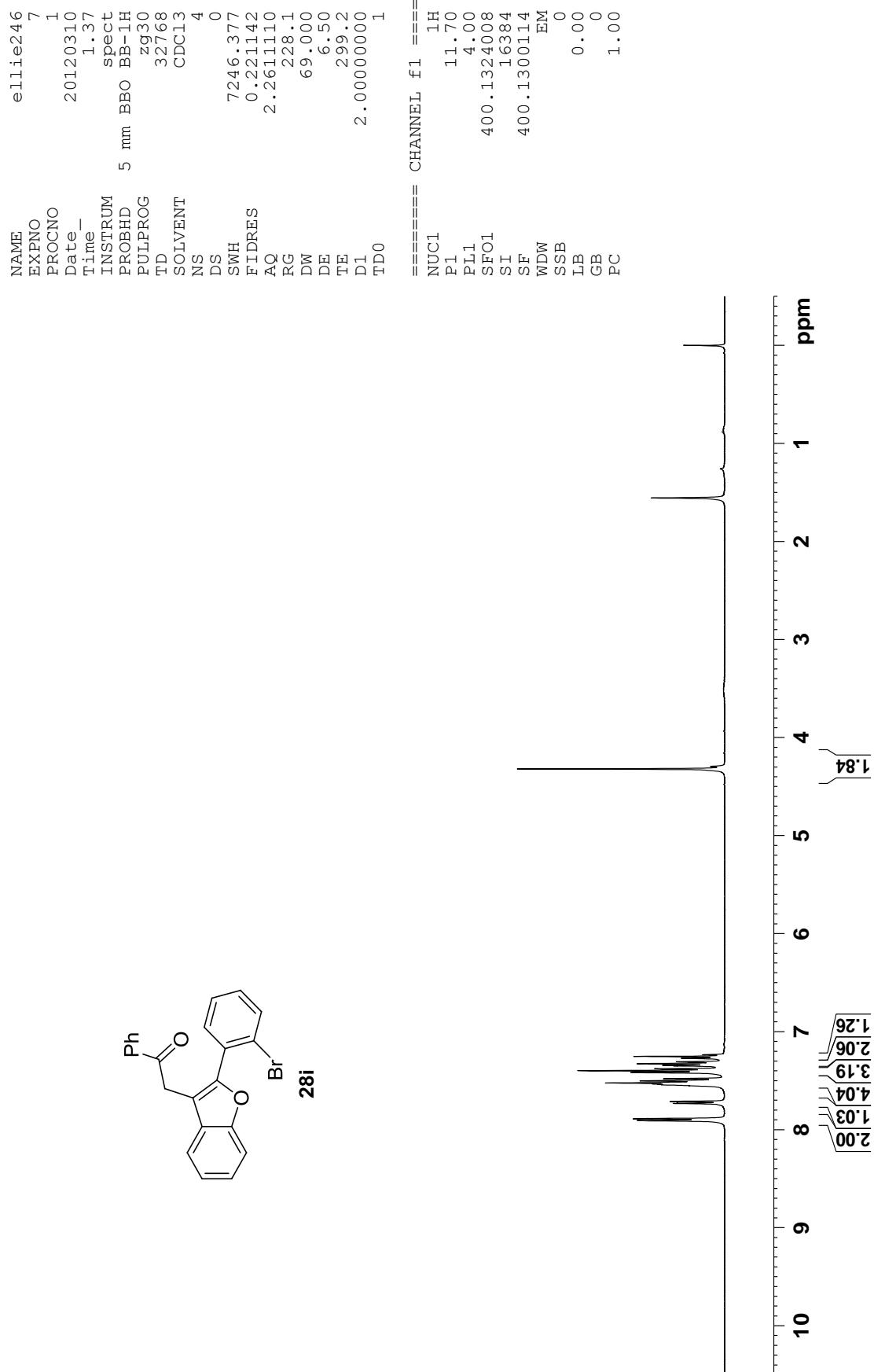


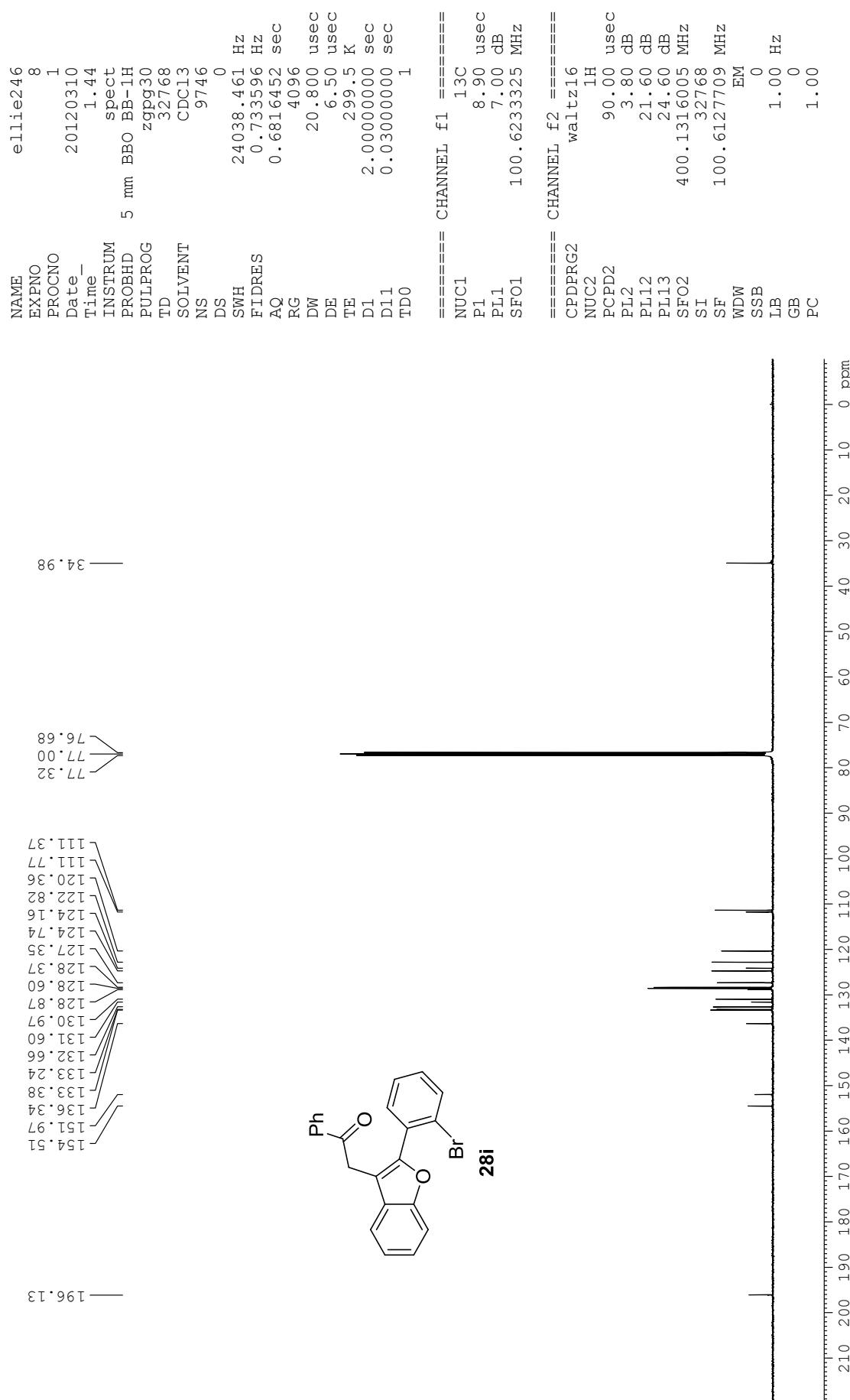


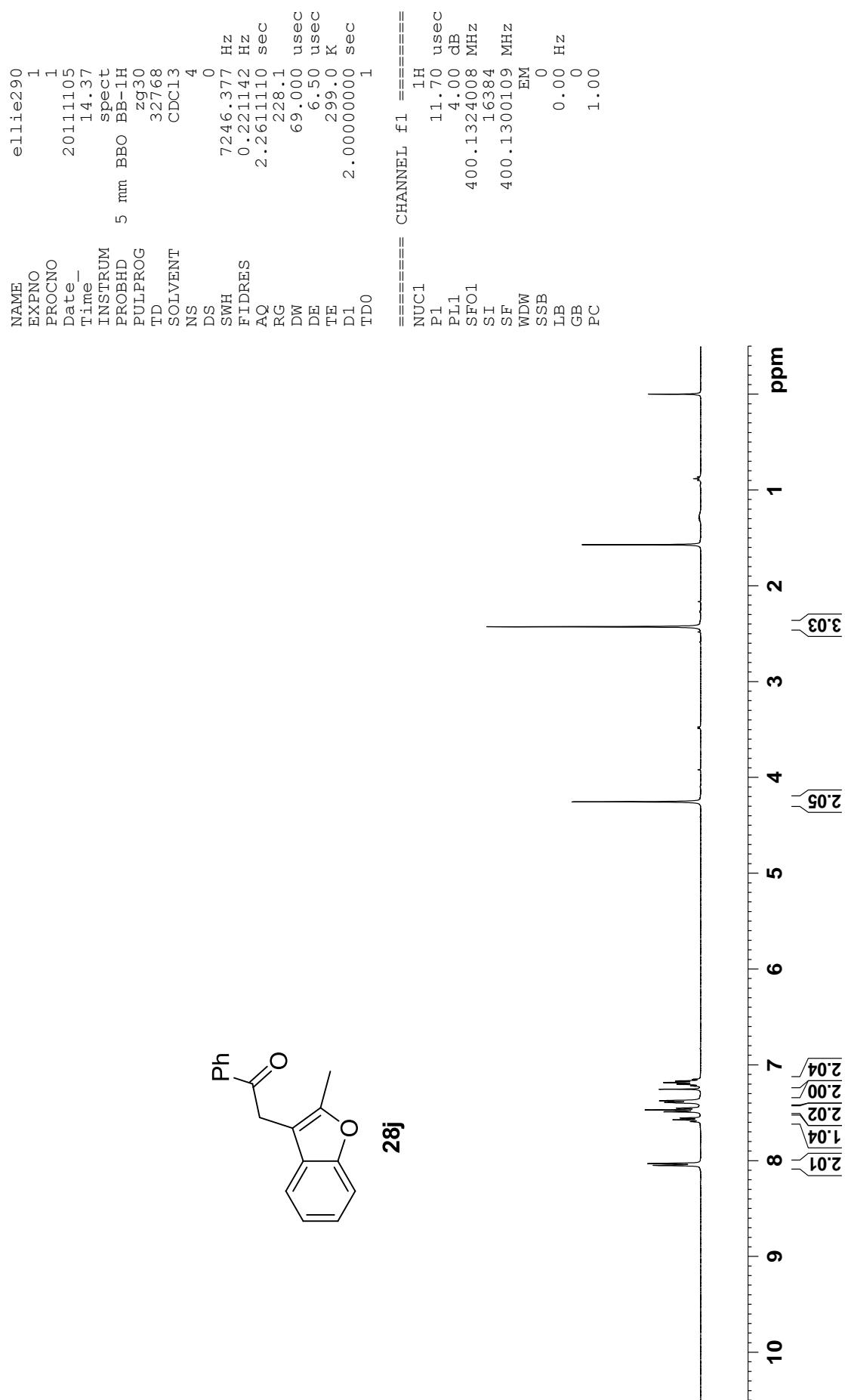


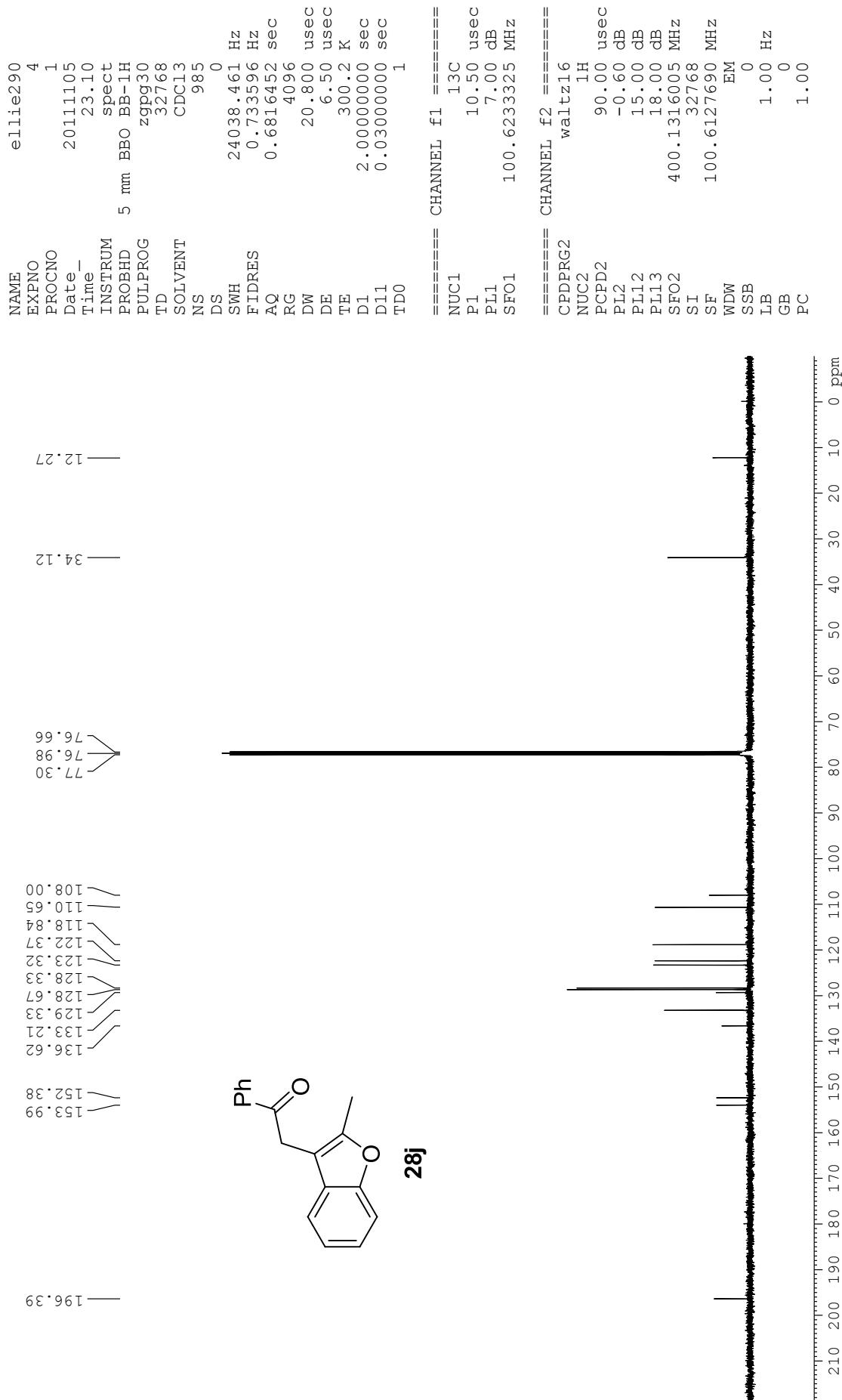


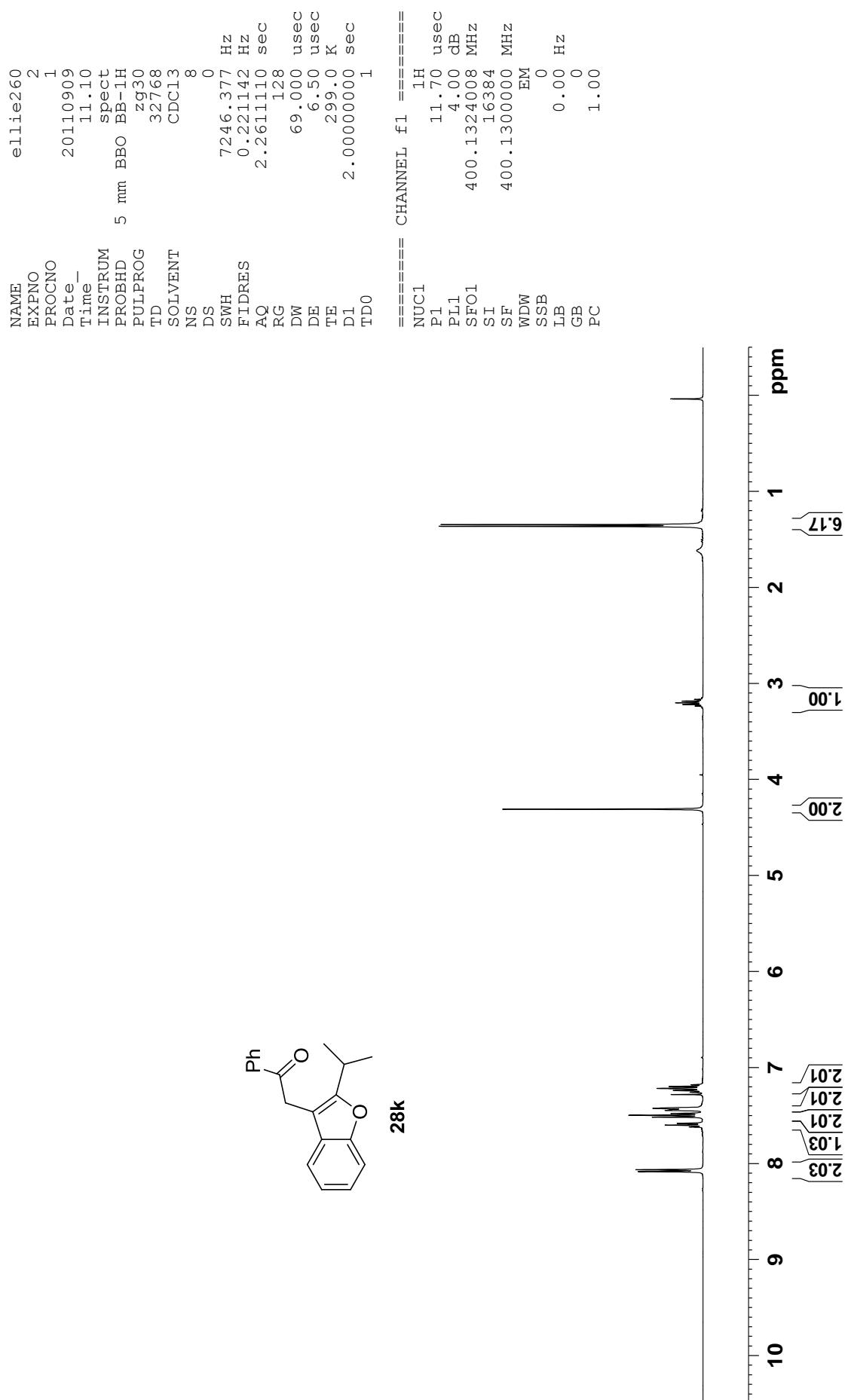


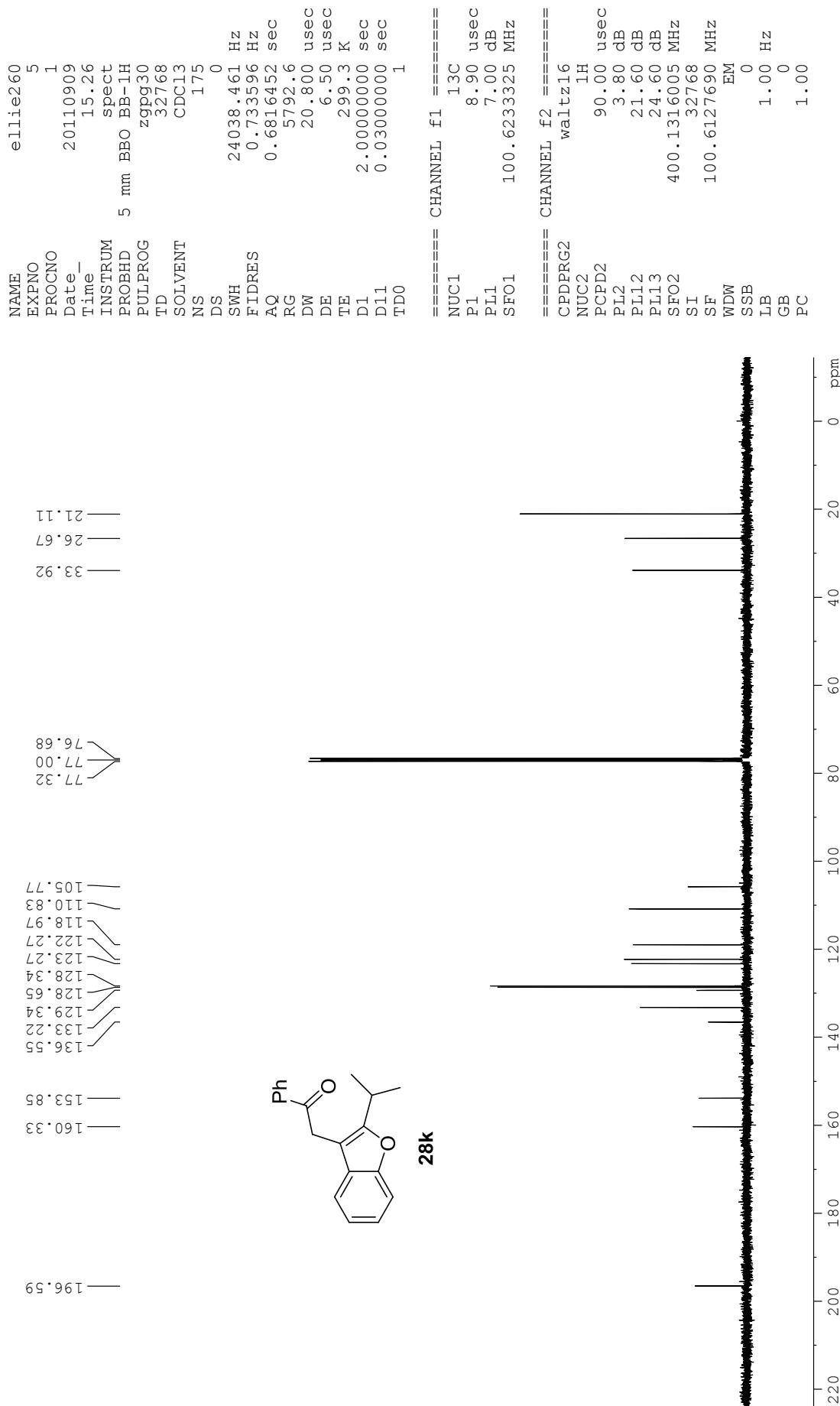


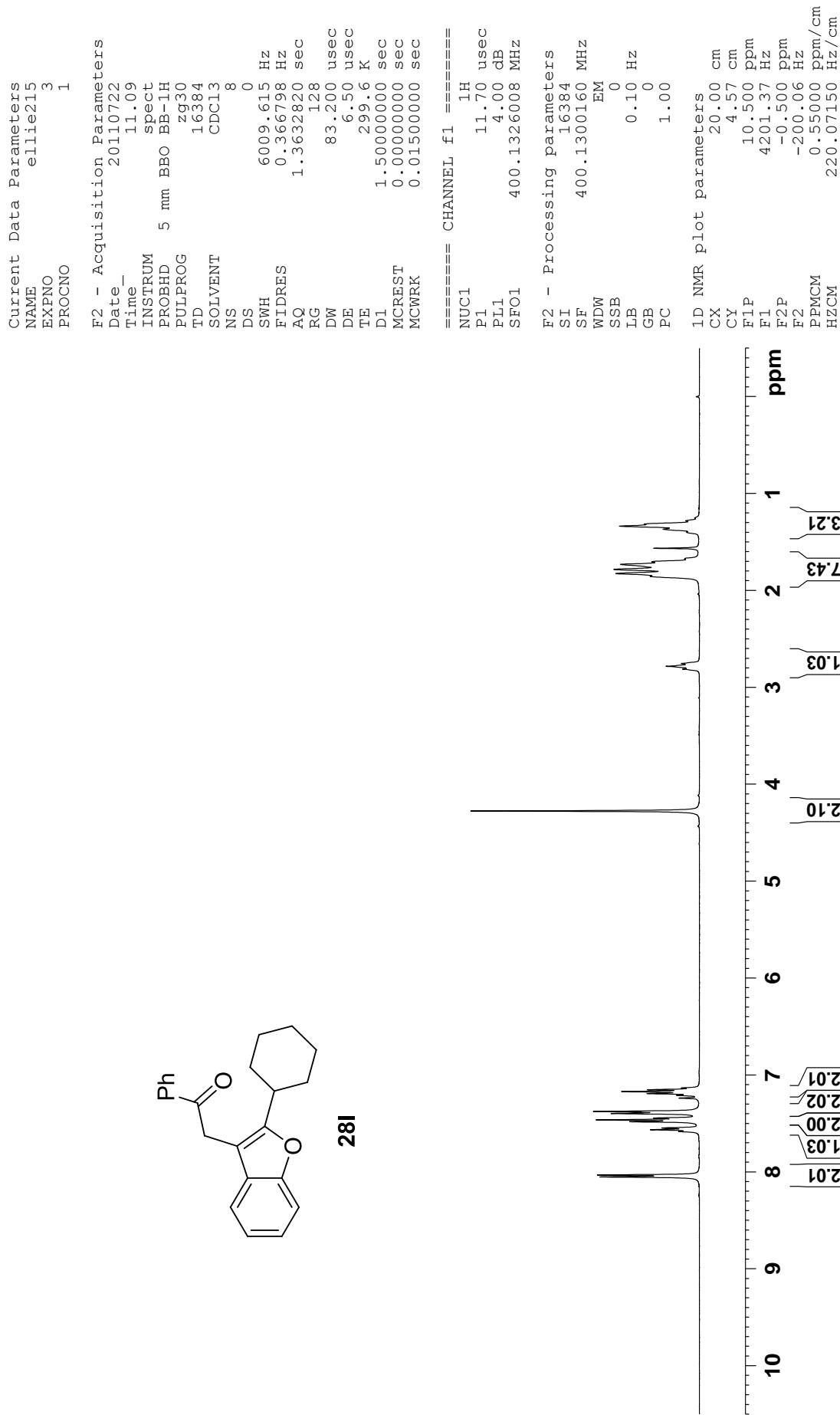




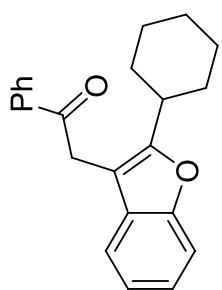




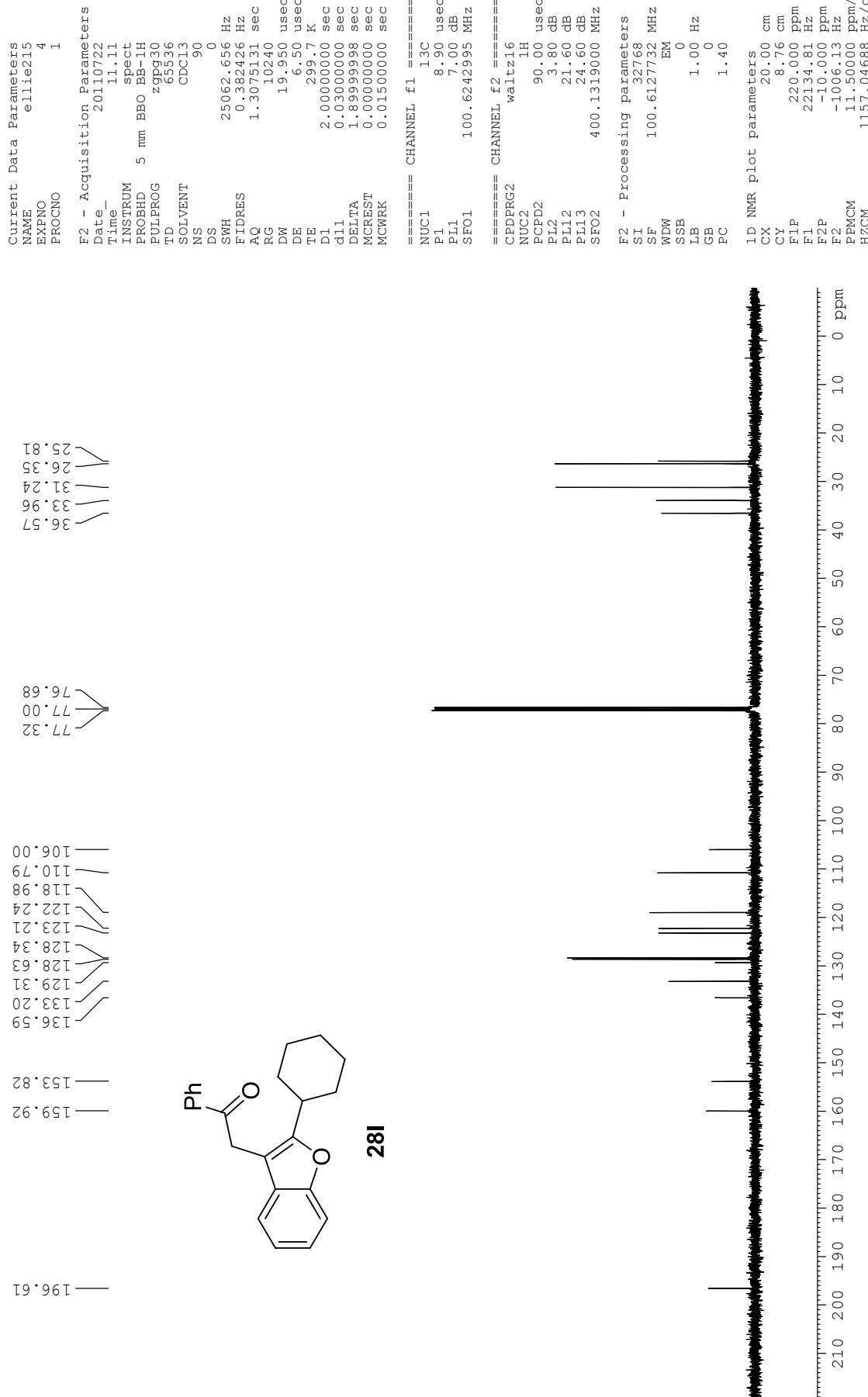


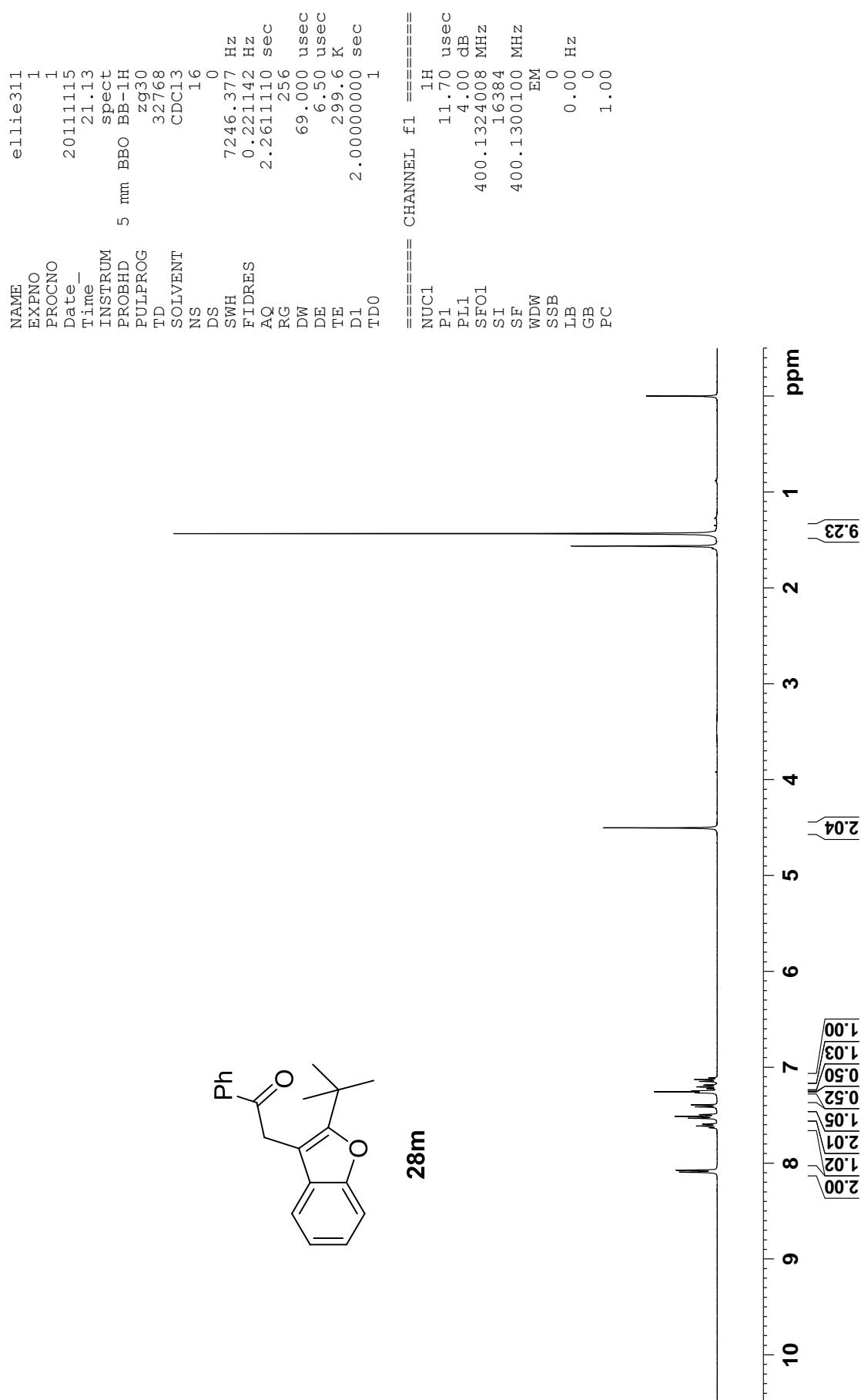


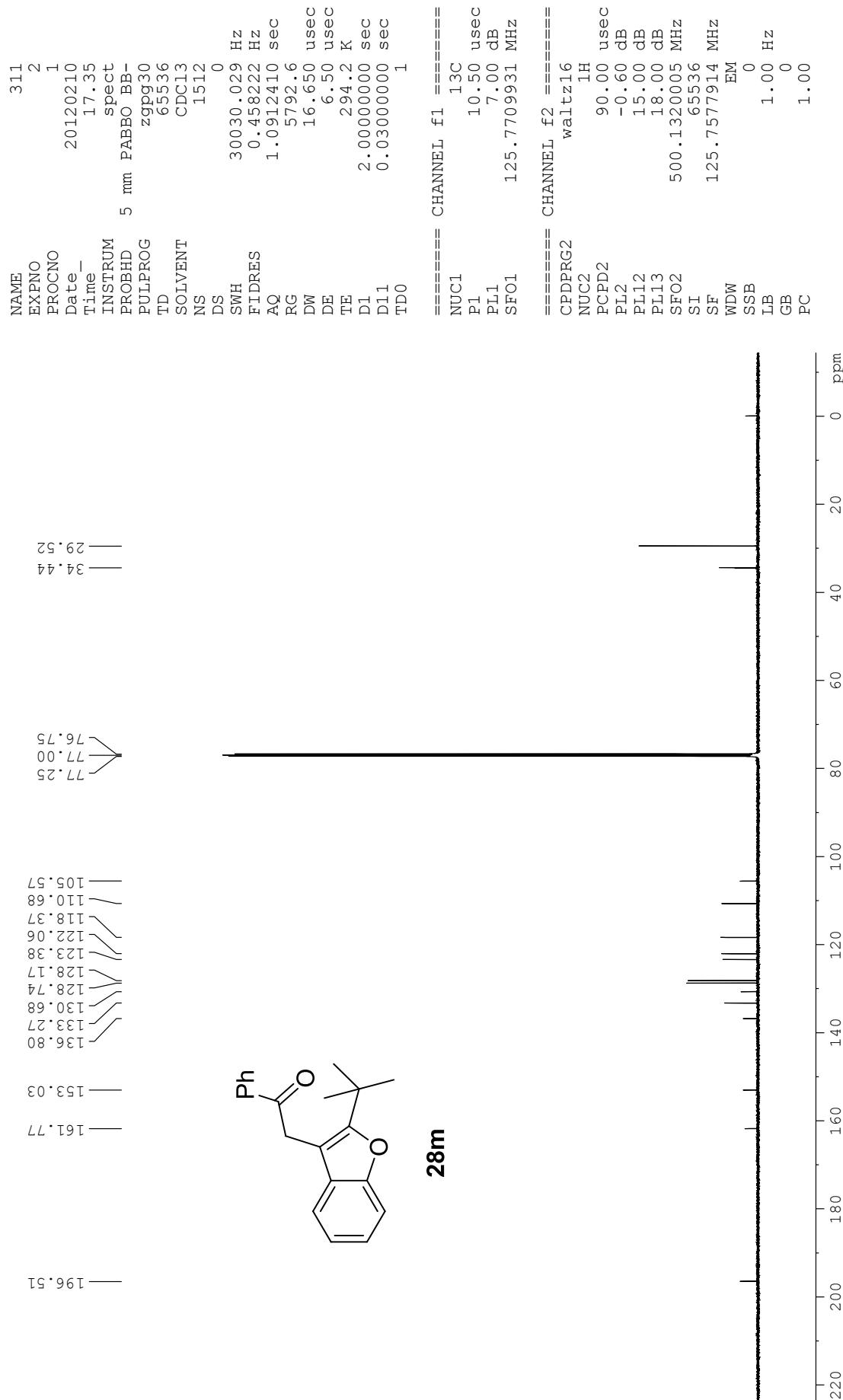
196.61
 153.82
 159.92
 133.20
 129.31
 128.63
 128.34
 123.21
 122.24
 118.98
 110.79
 106.00
 77.32
 77.00
 76.68
 36.57
 33.96
 31.24
 26.35
 25.81

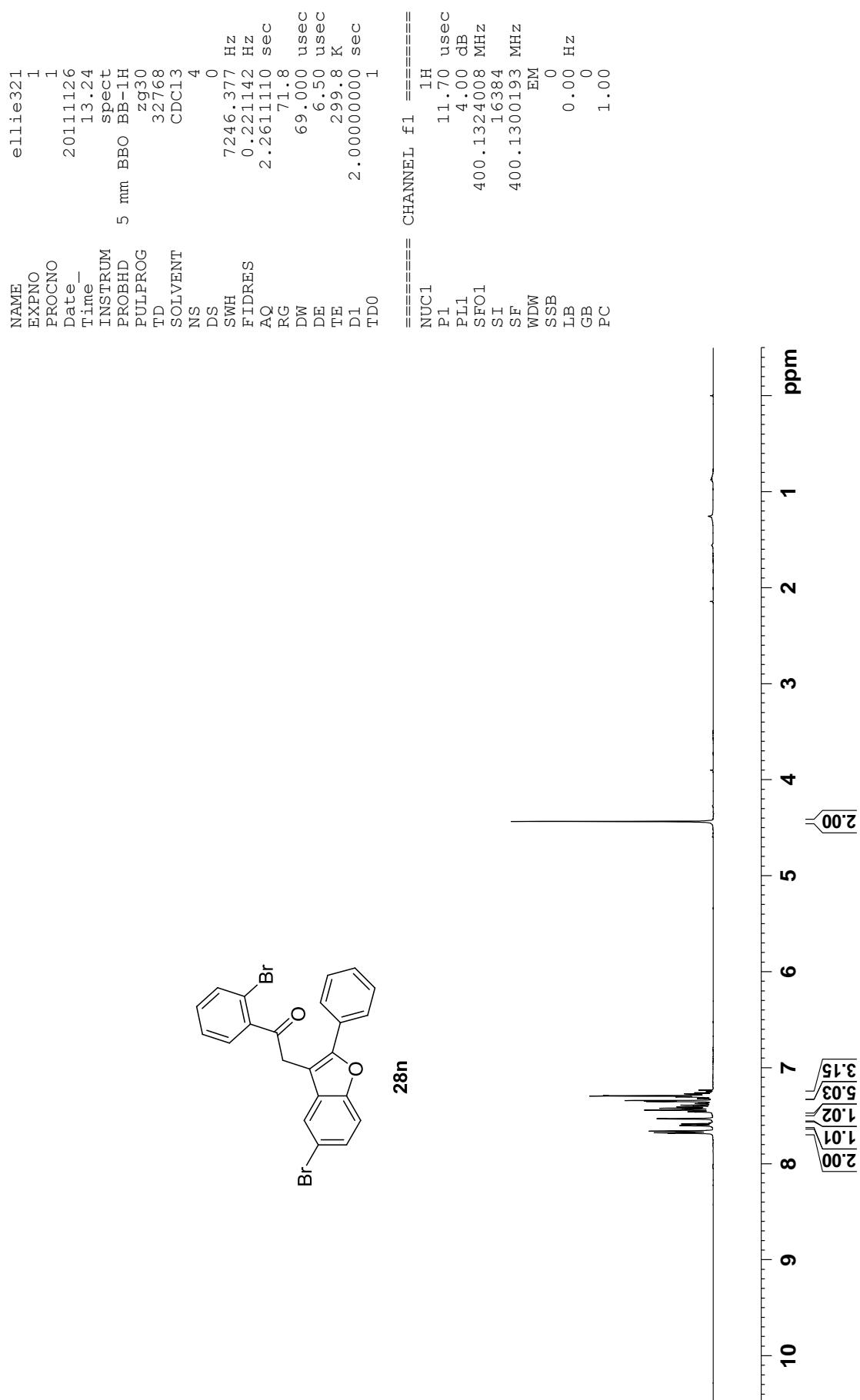


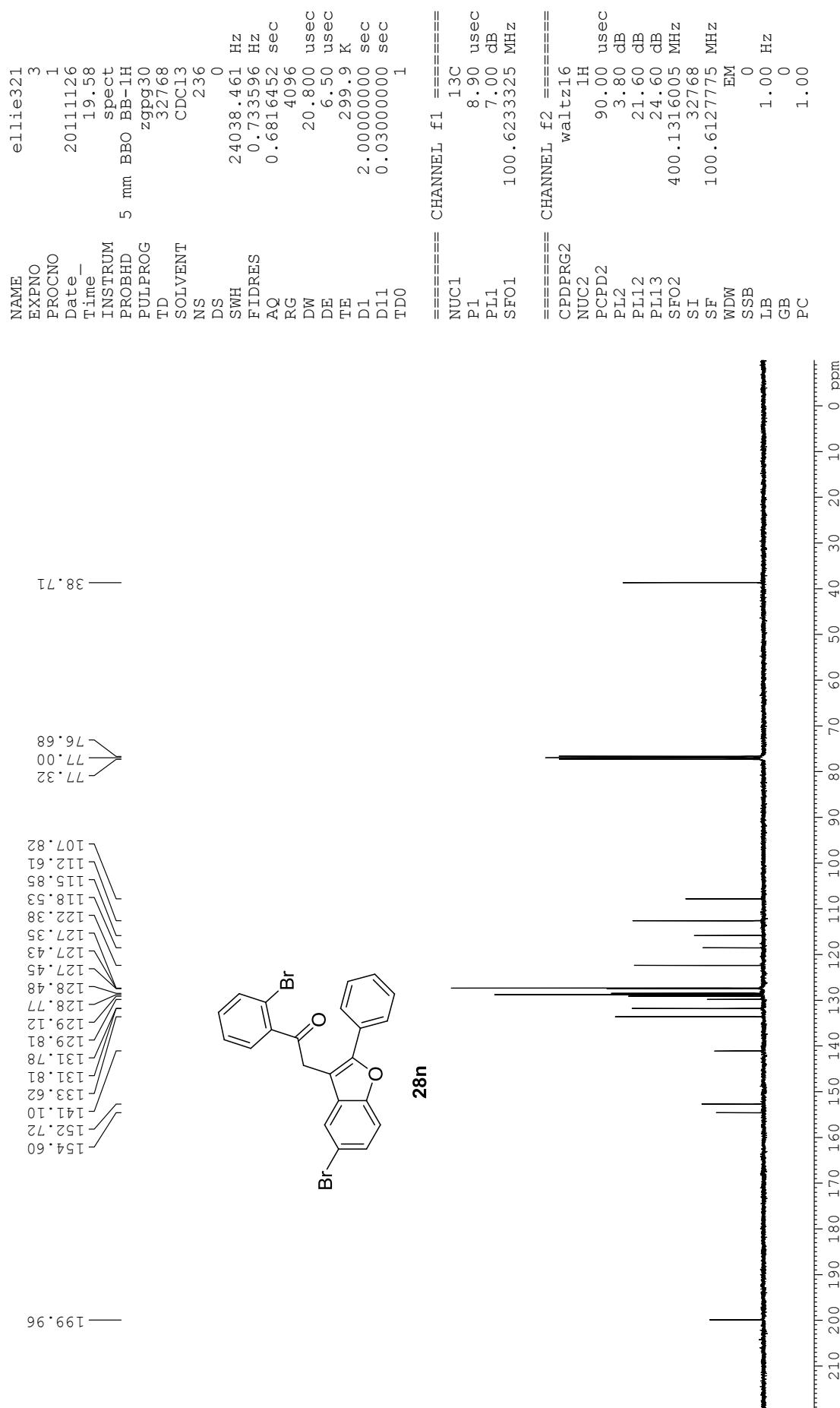
28l

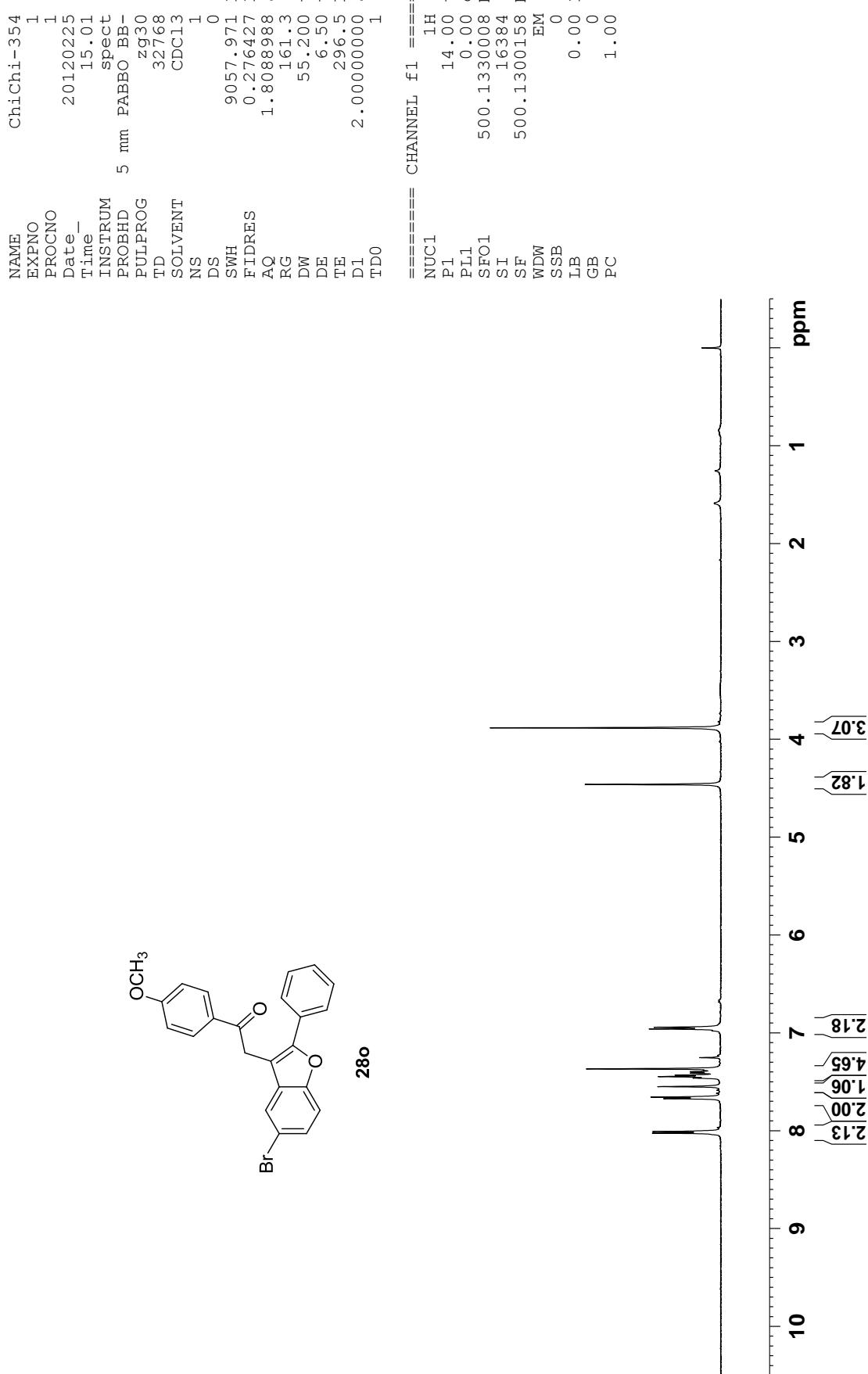


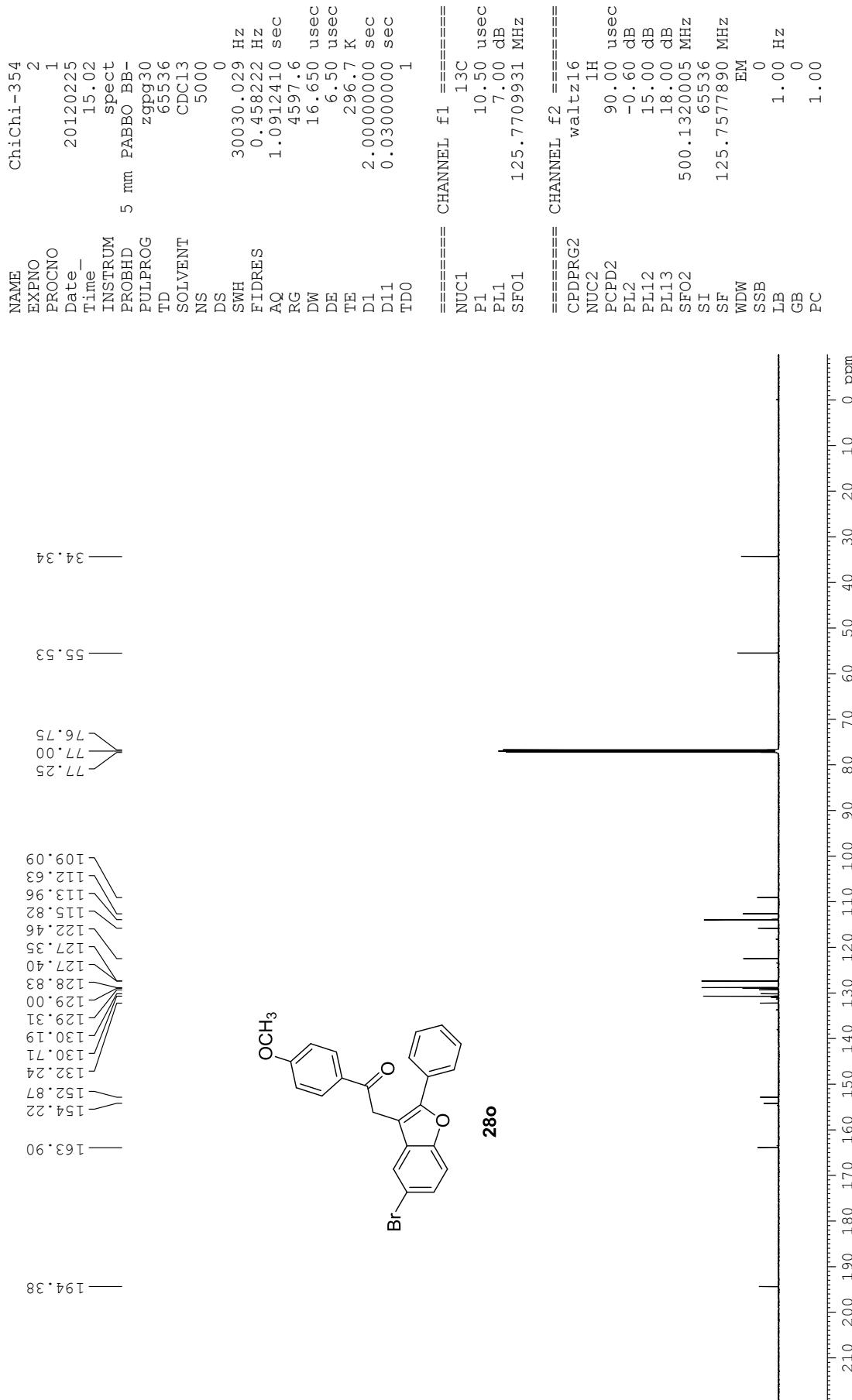


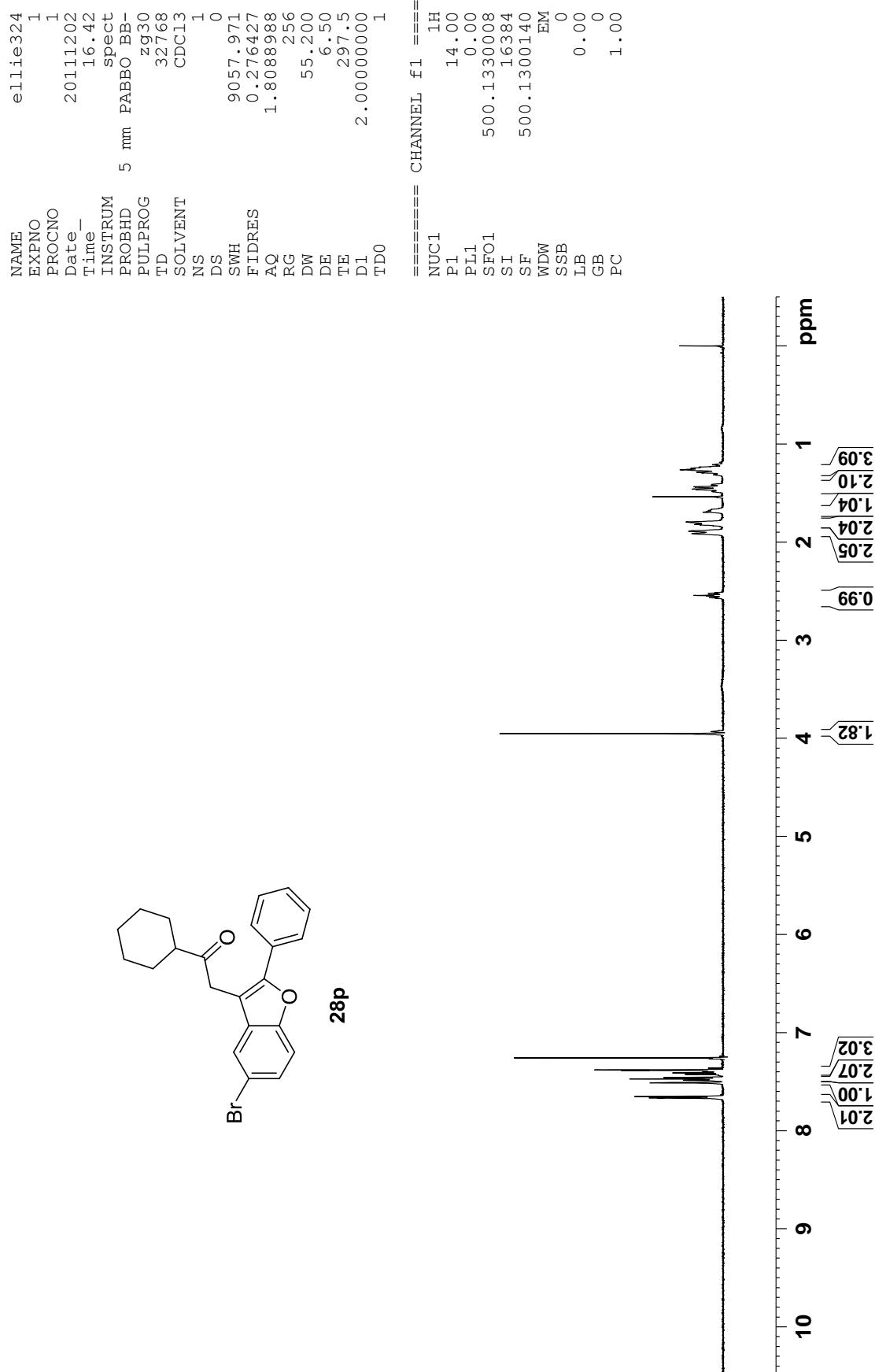


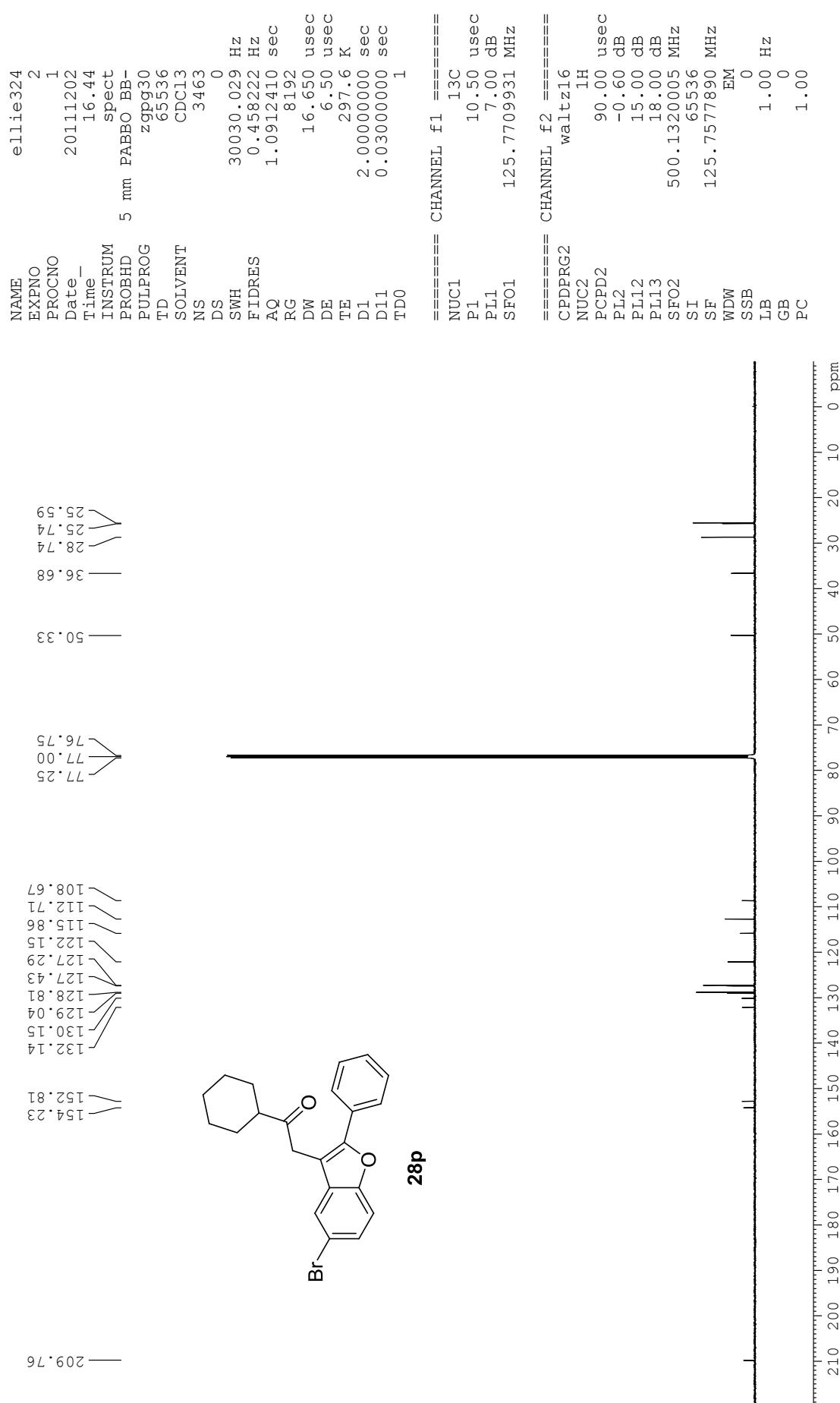


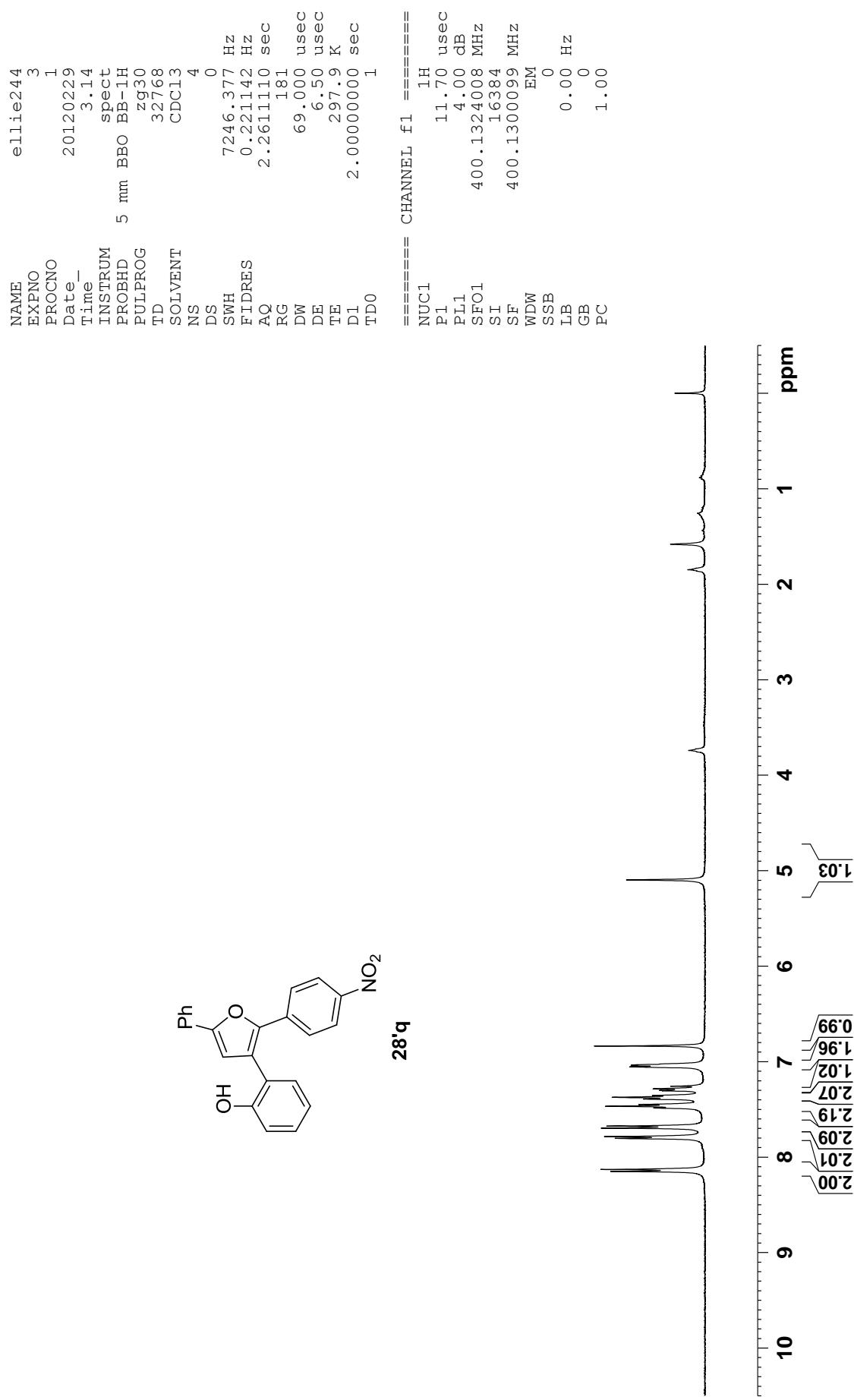


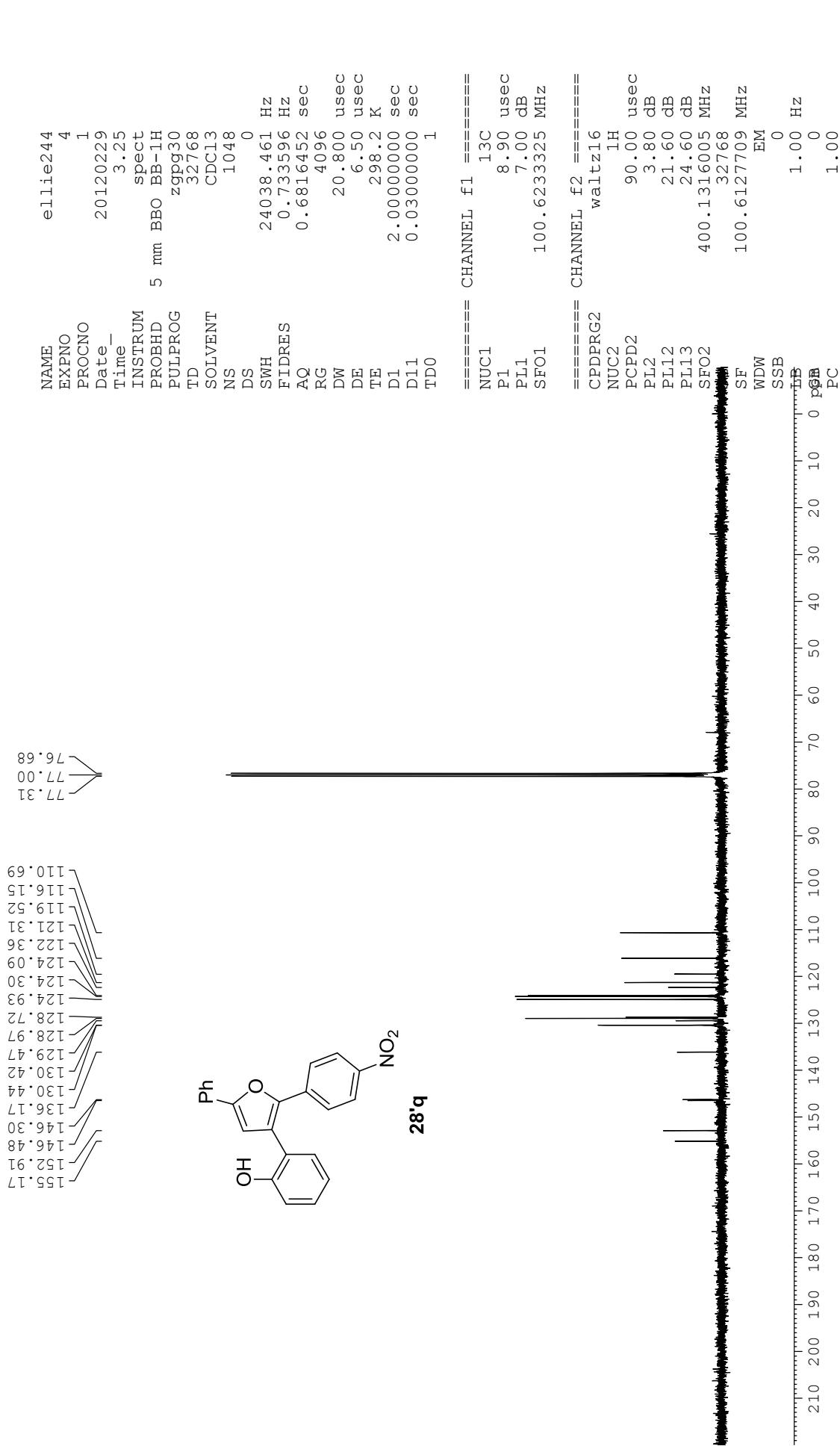


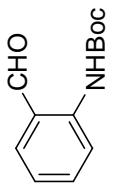




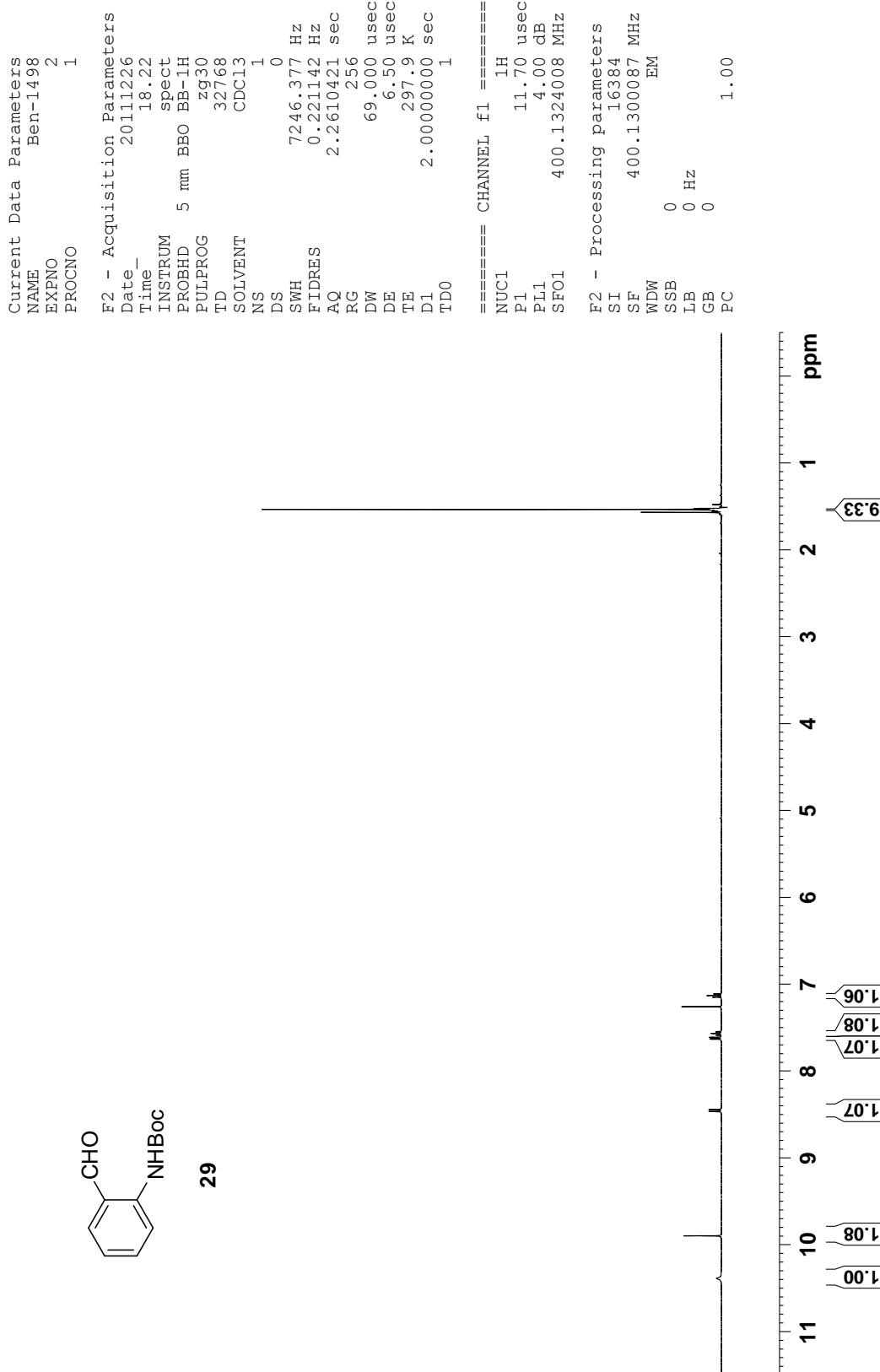


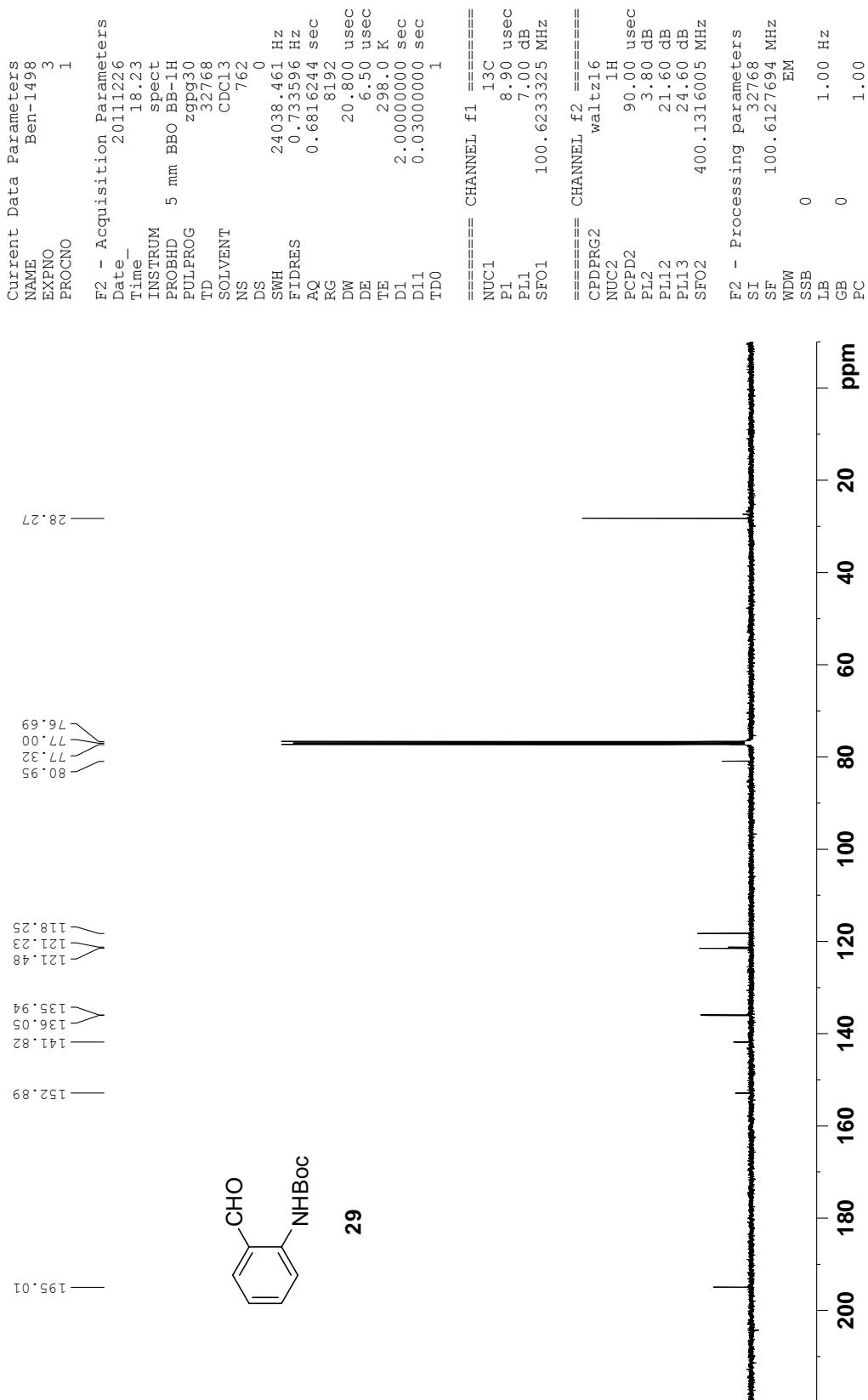


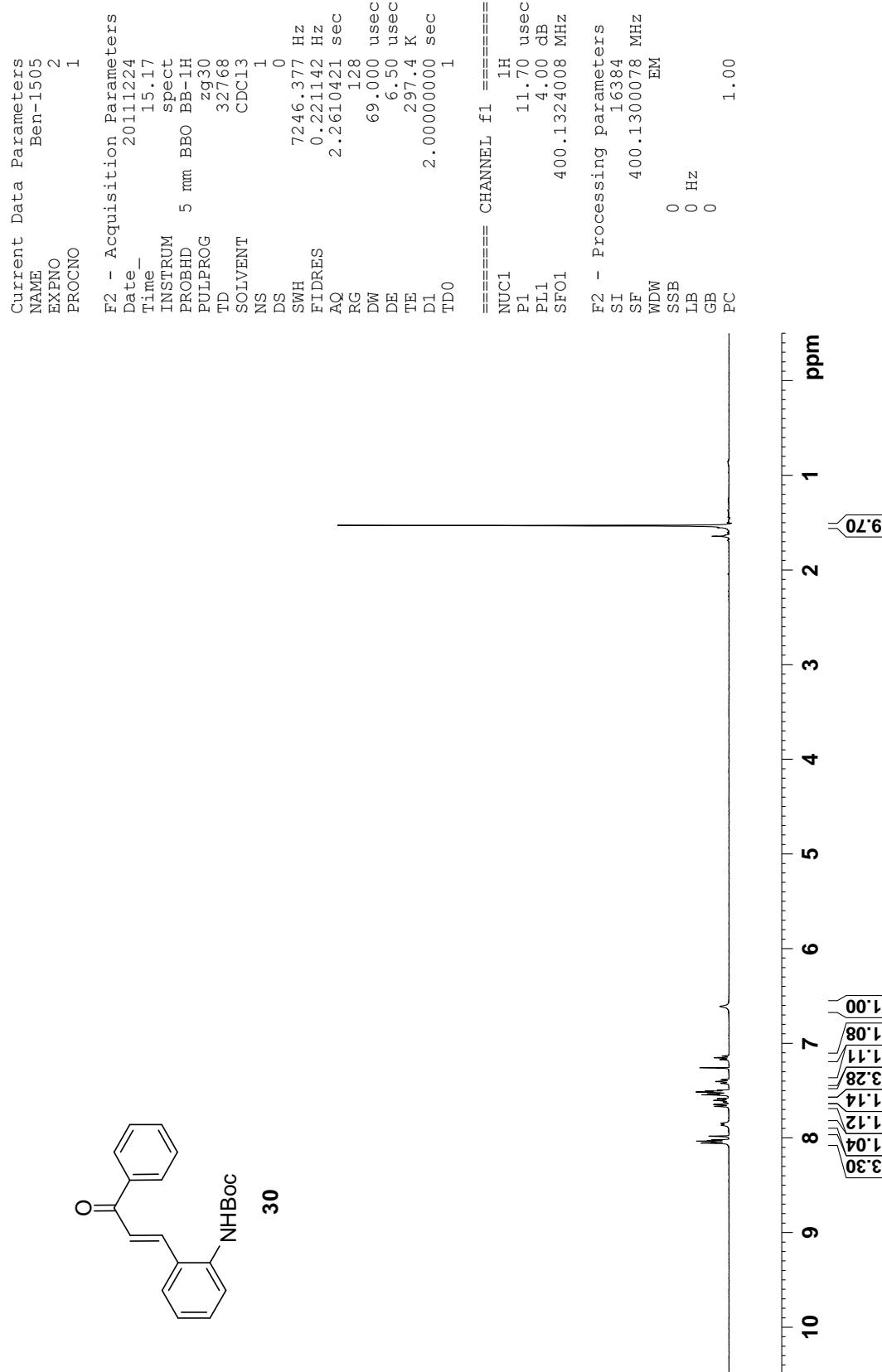


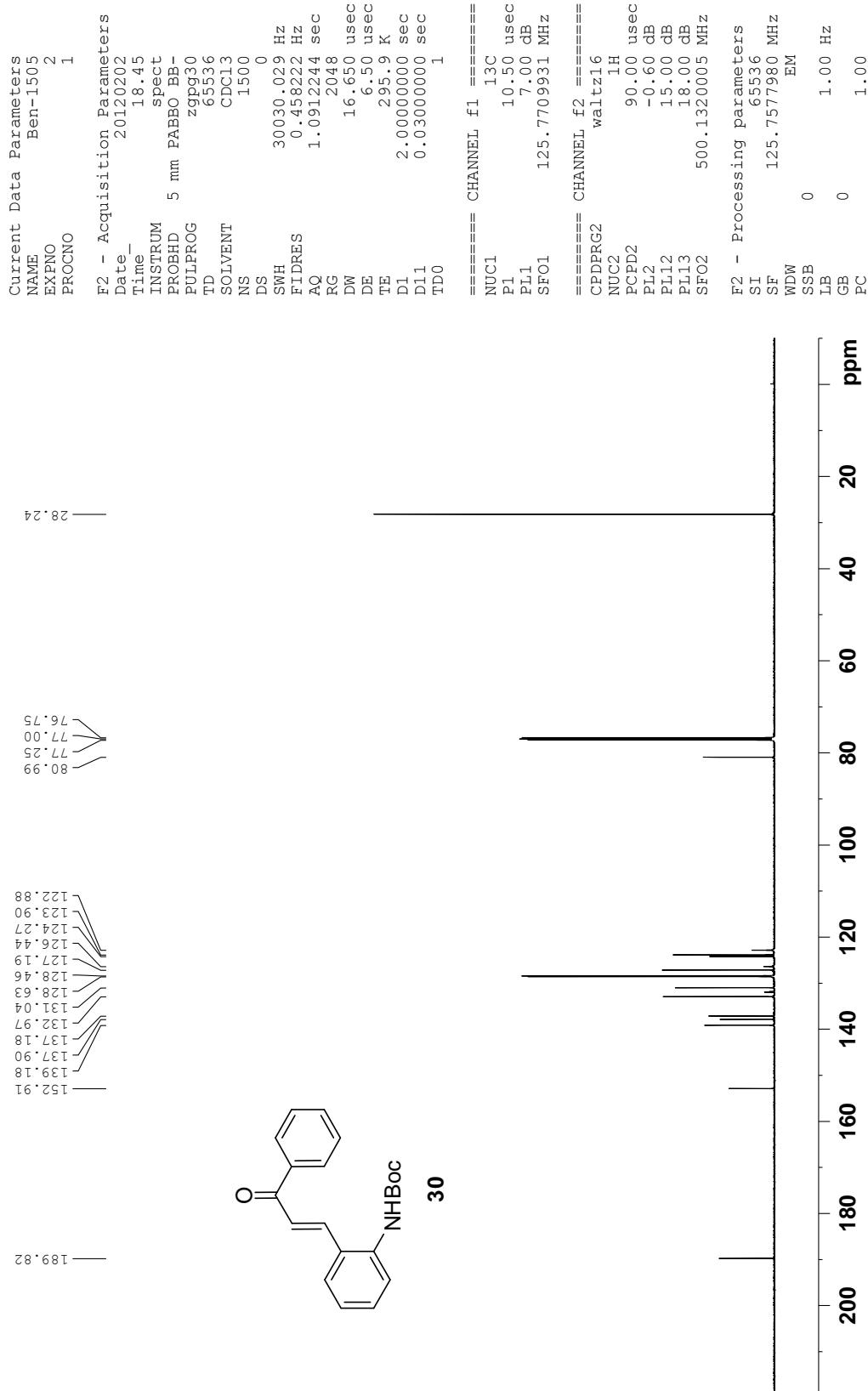


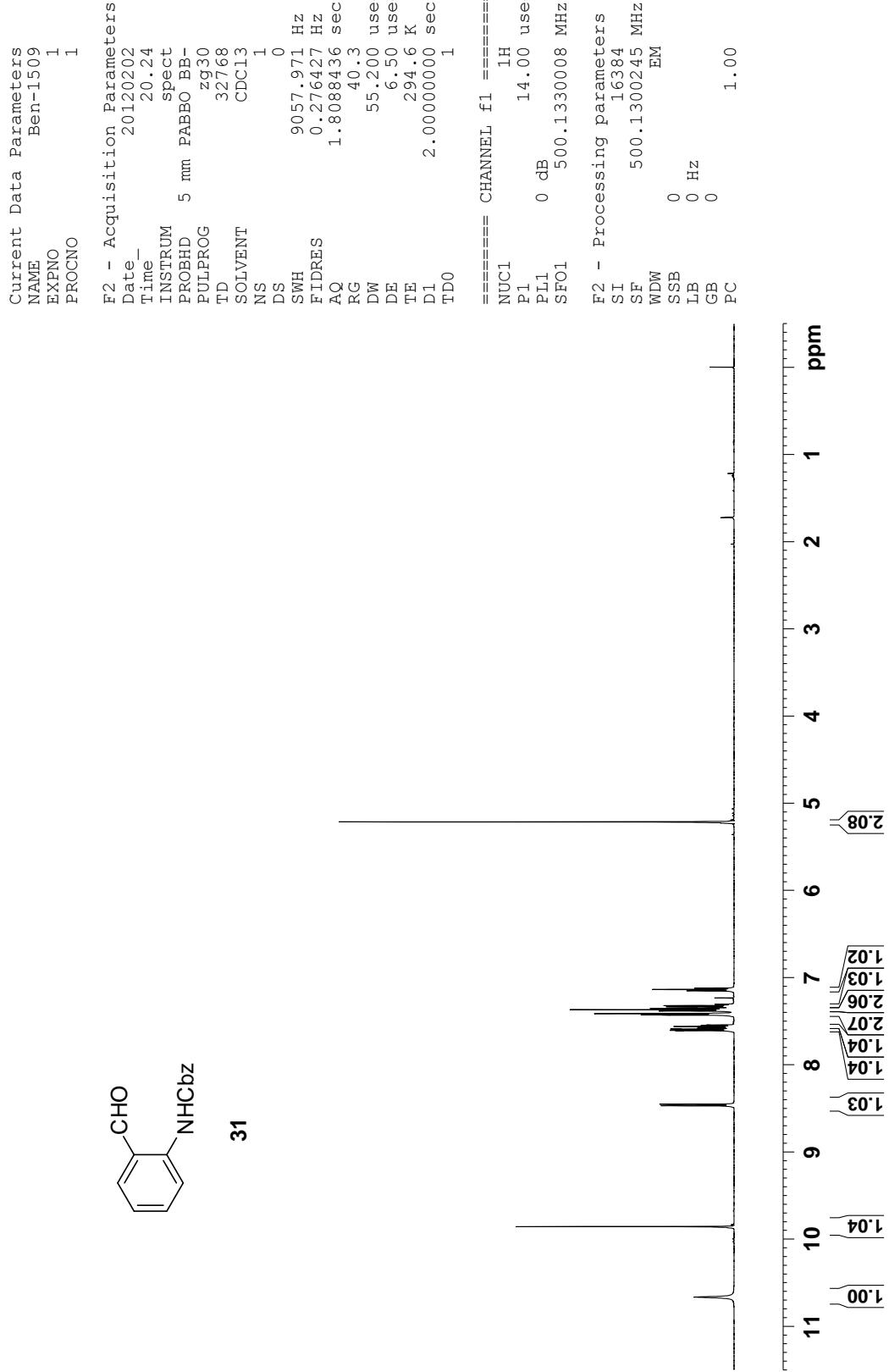
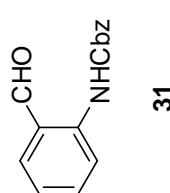
29

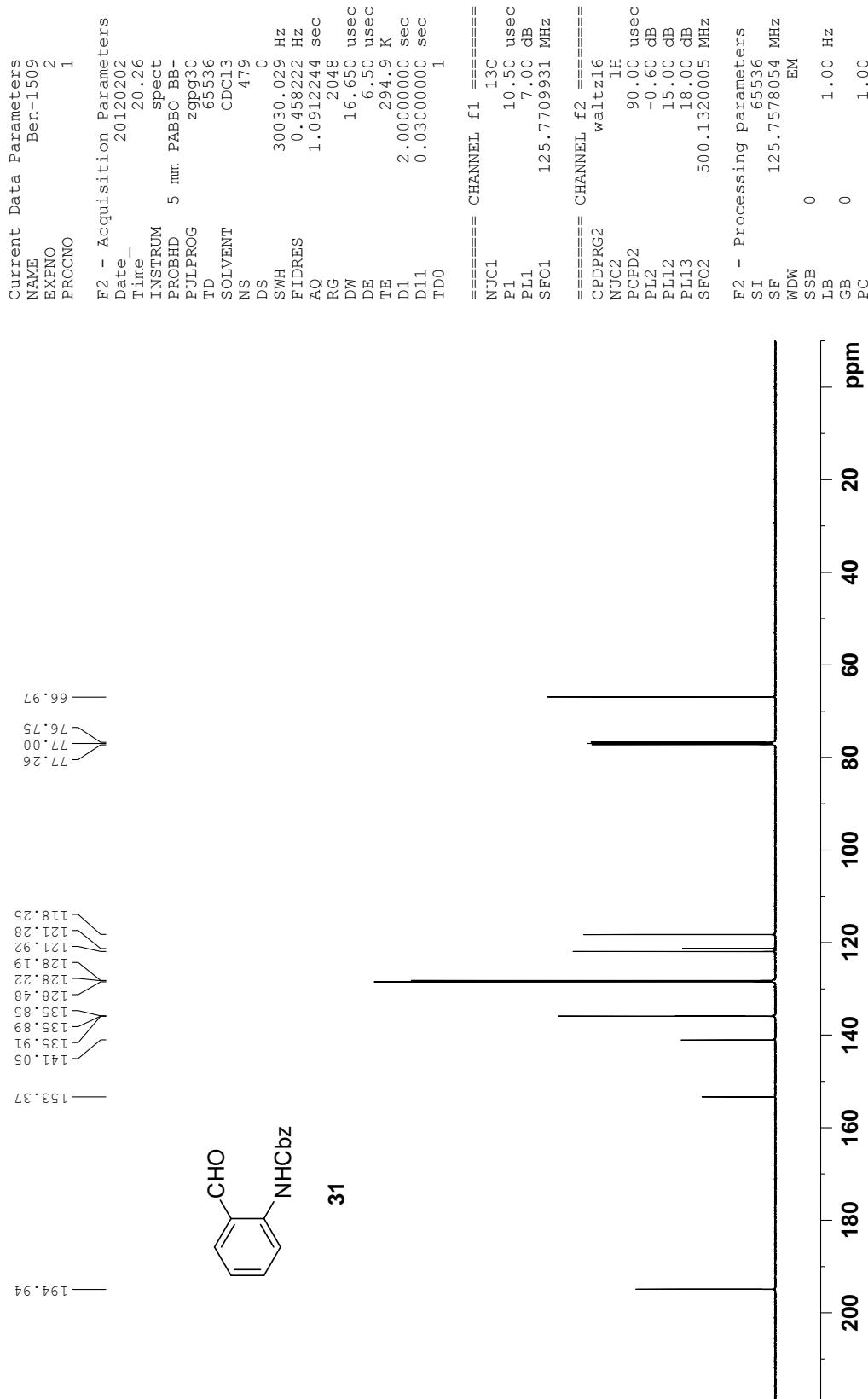


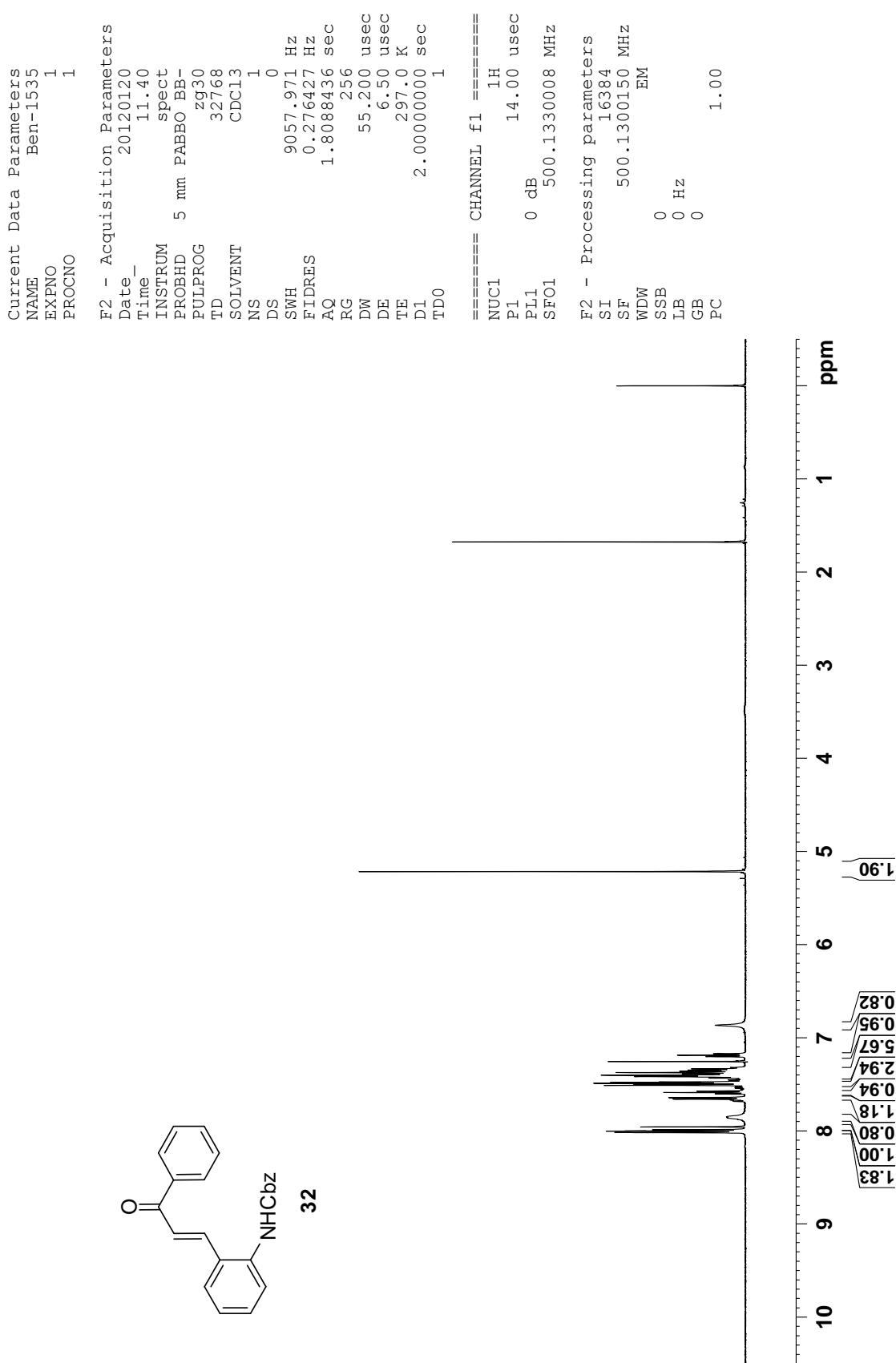


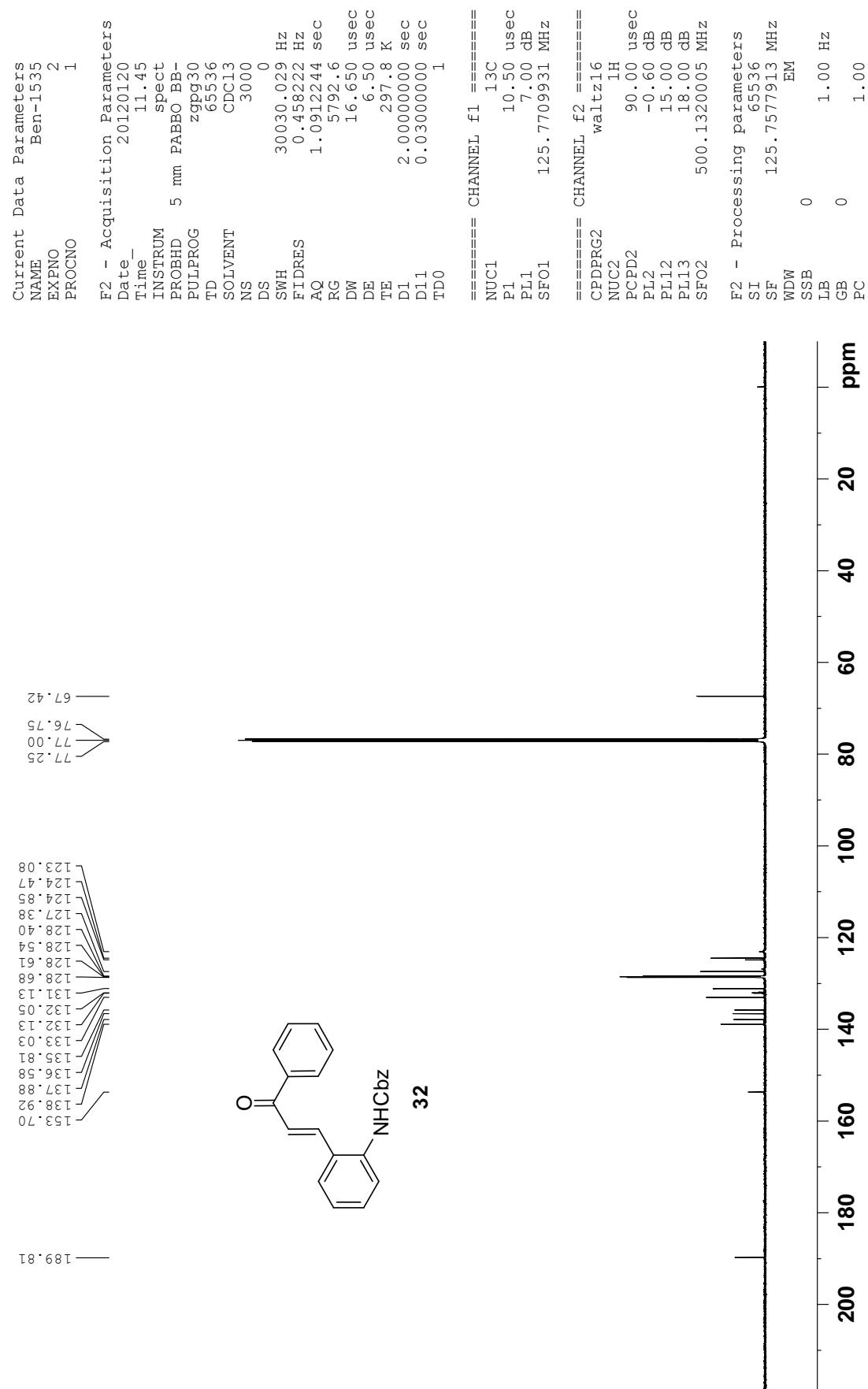


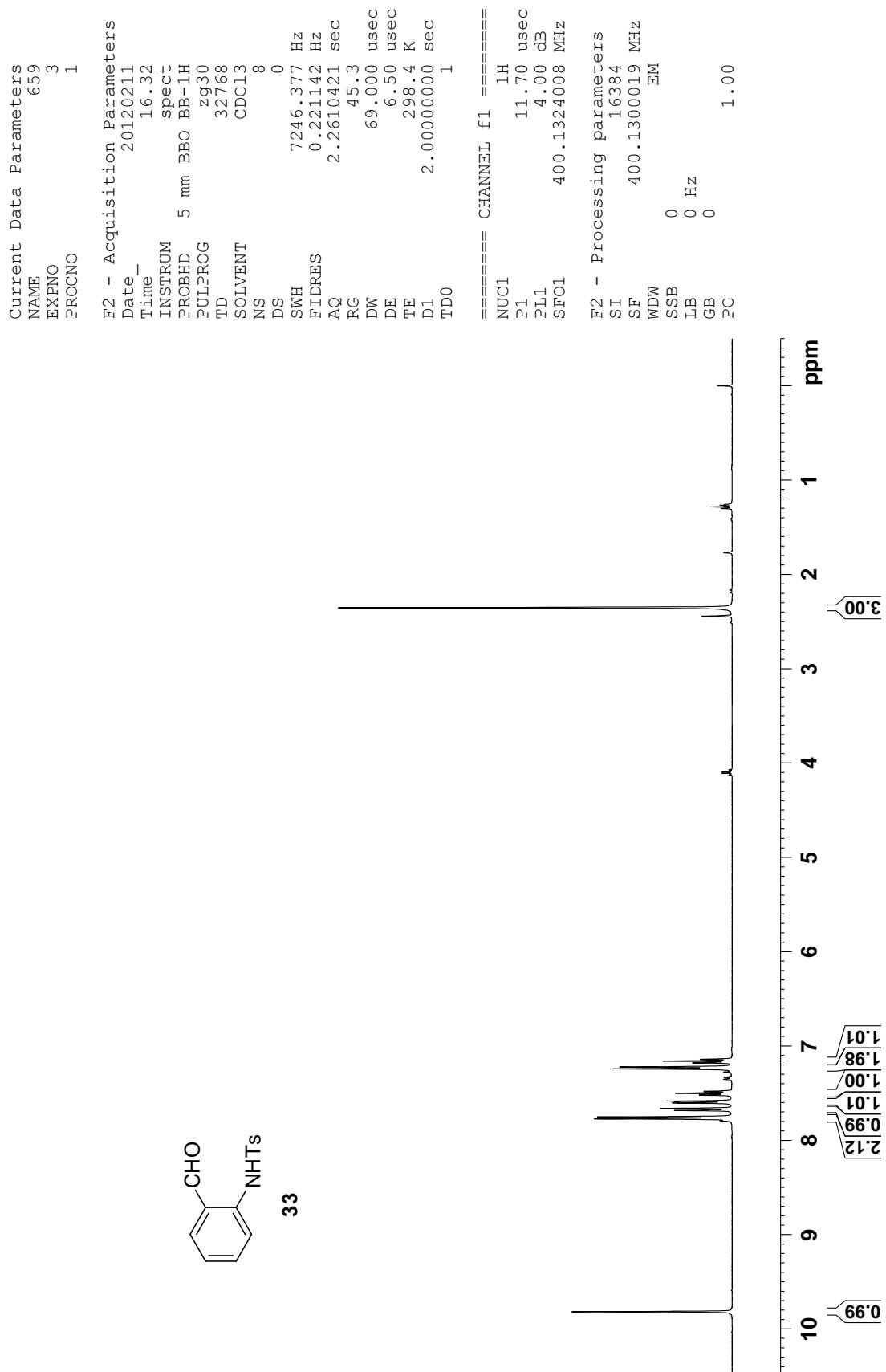


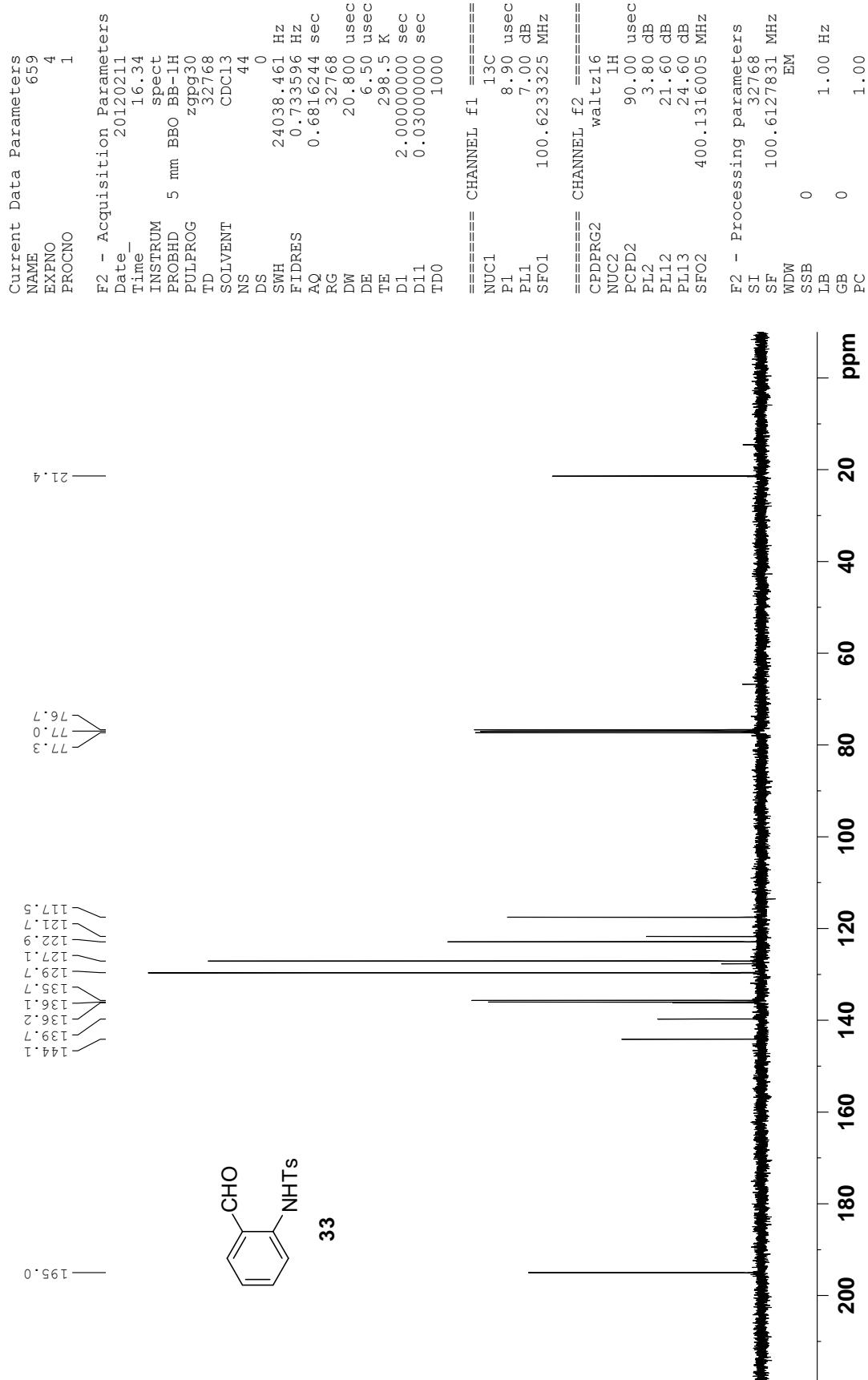


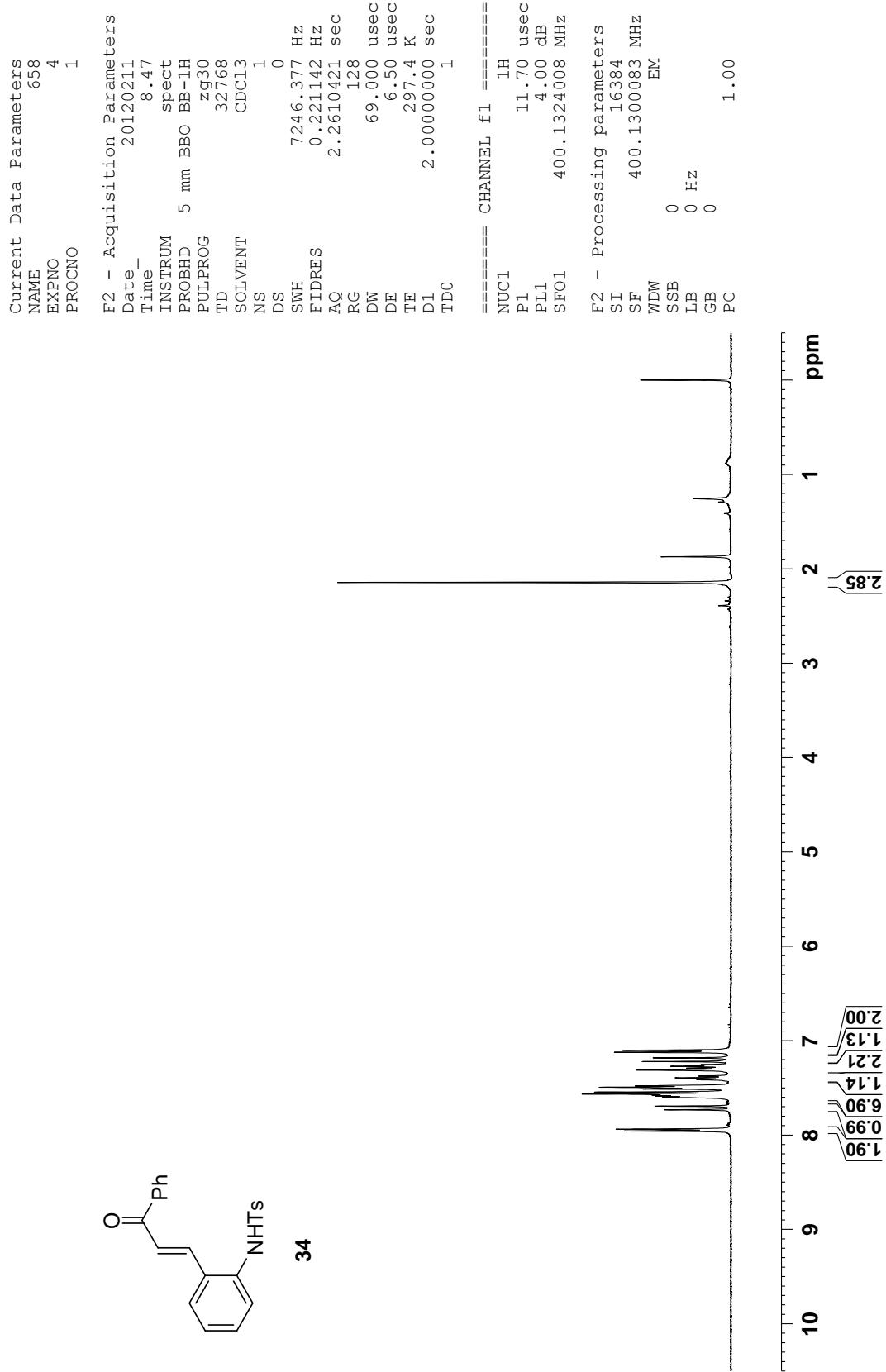


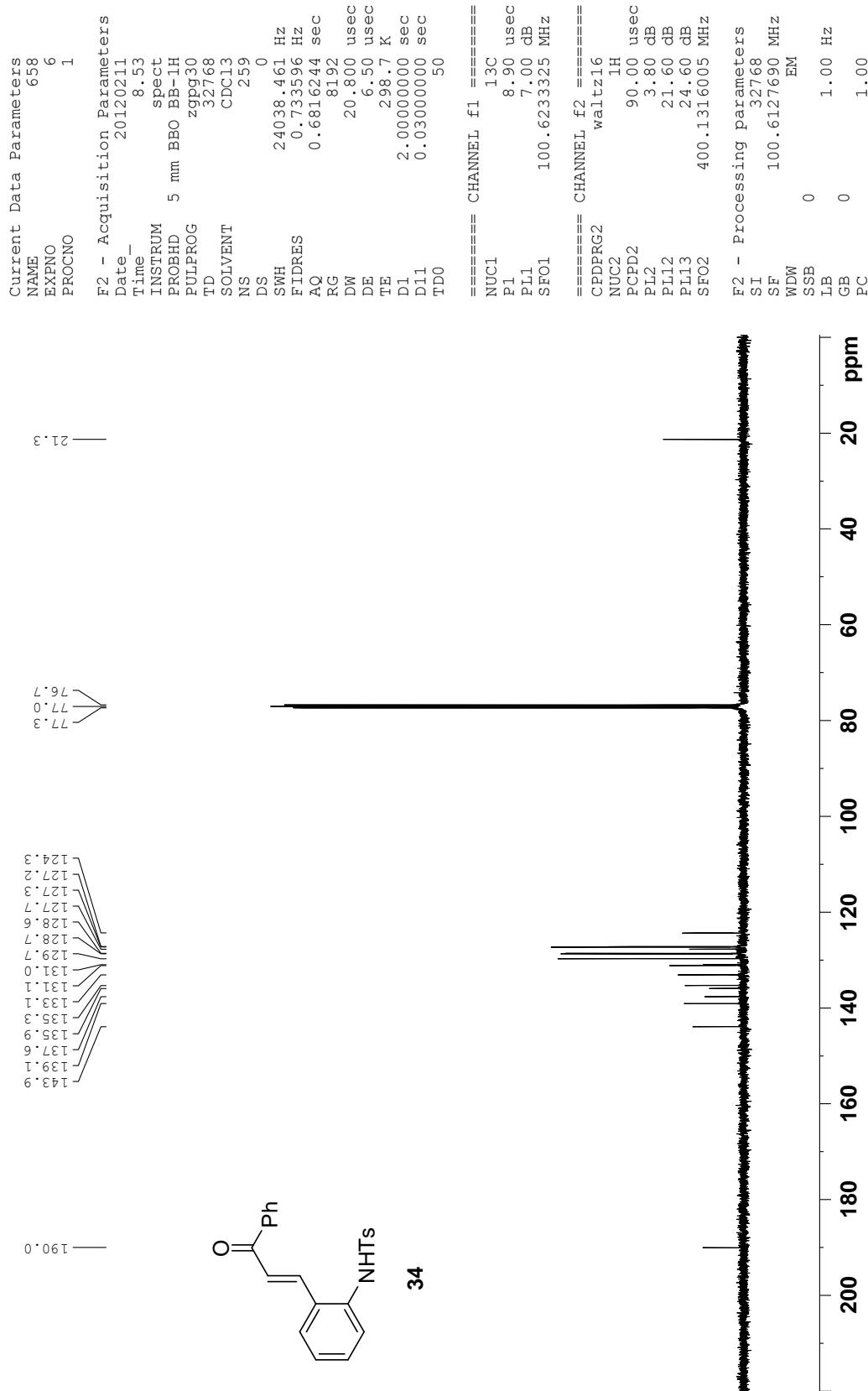


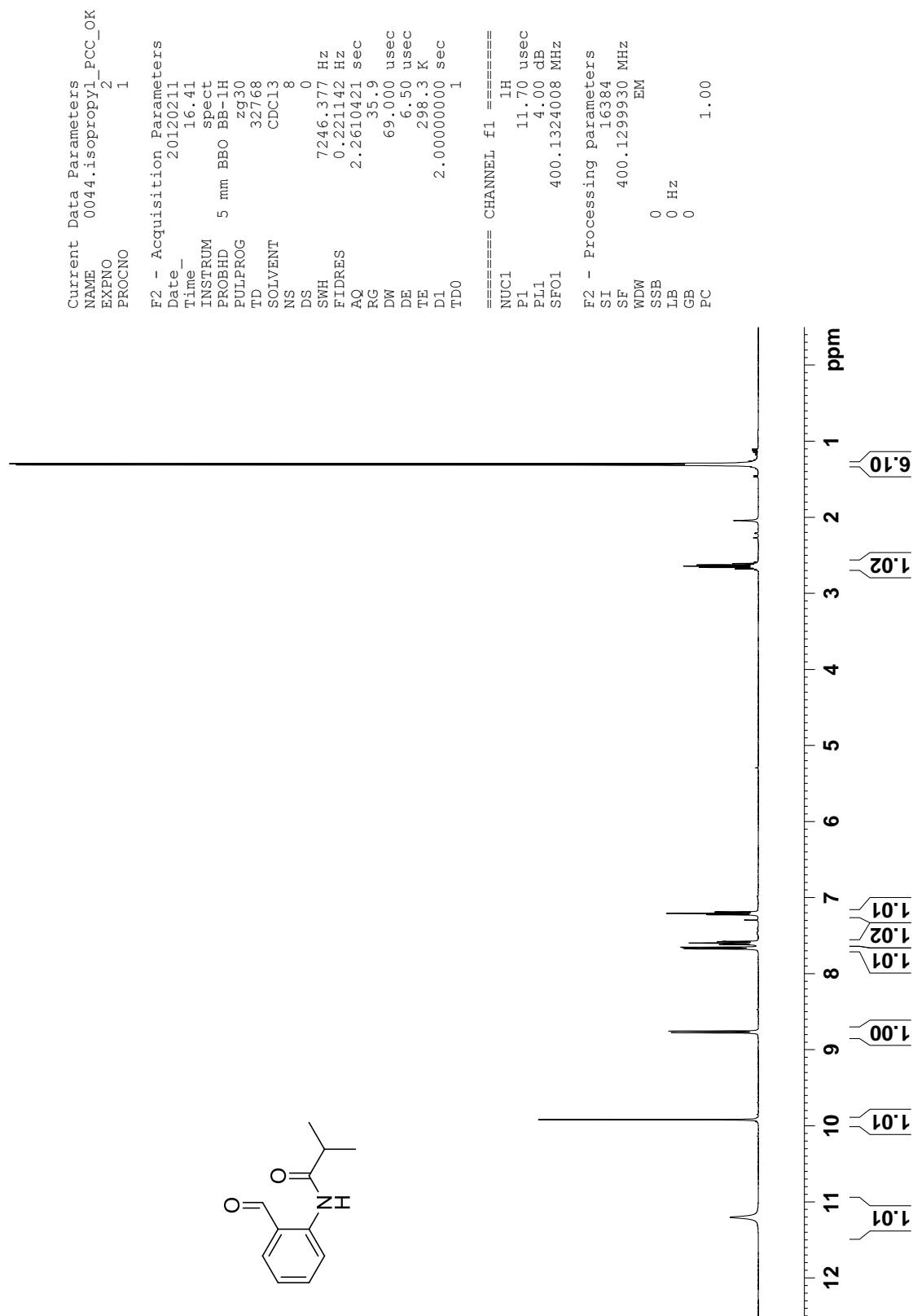


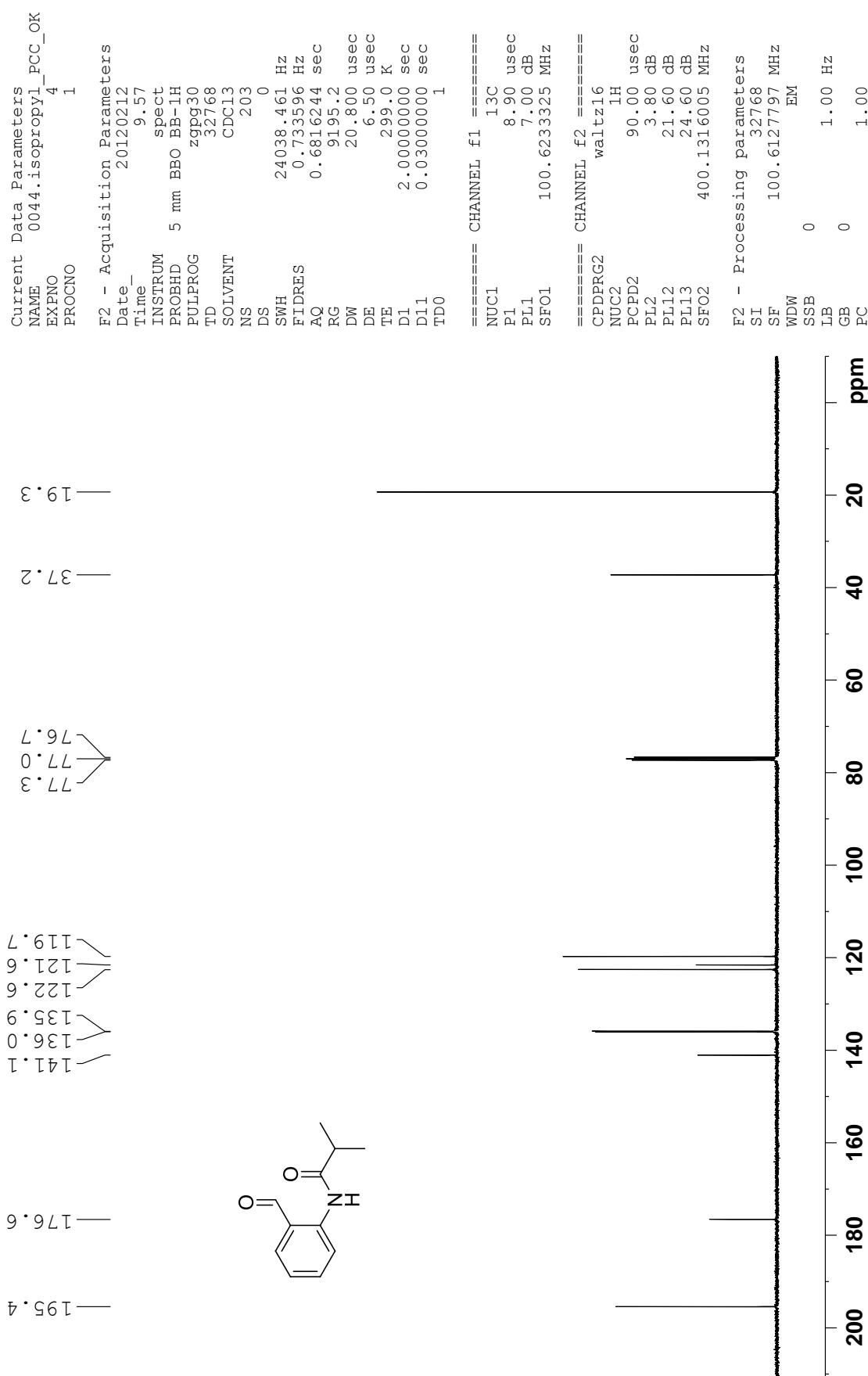


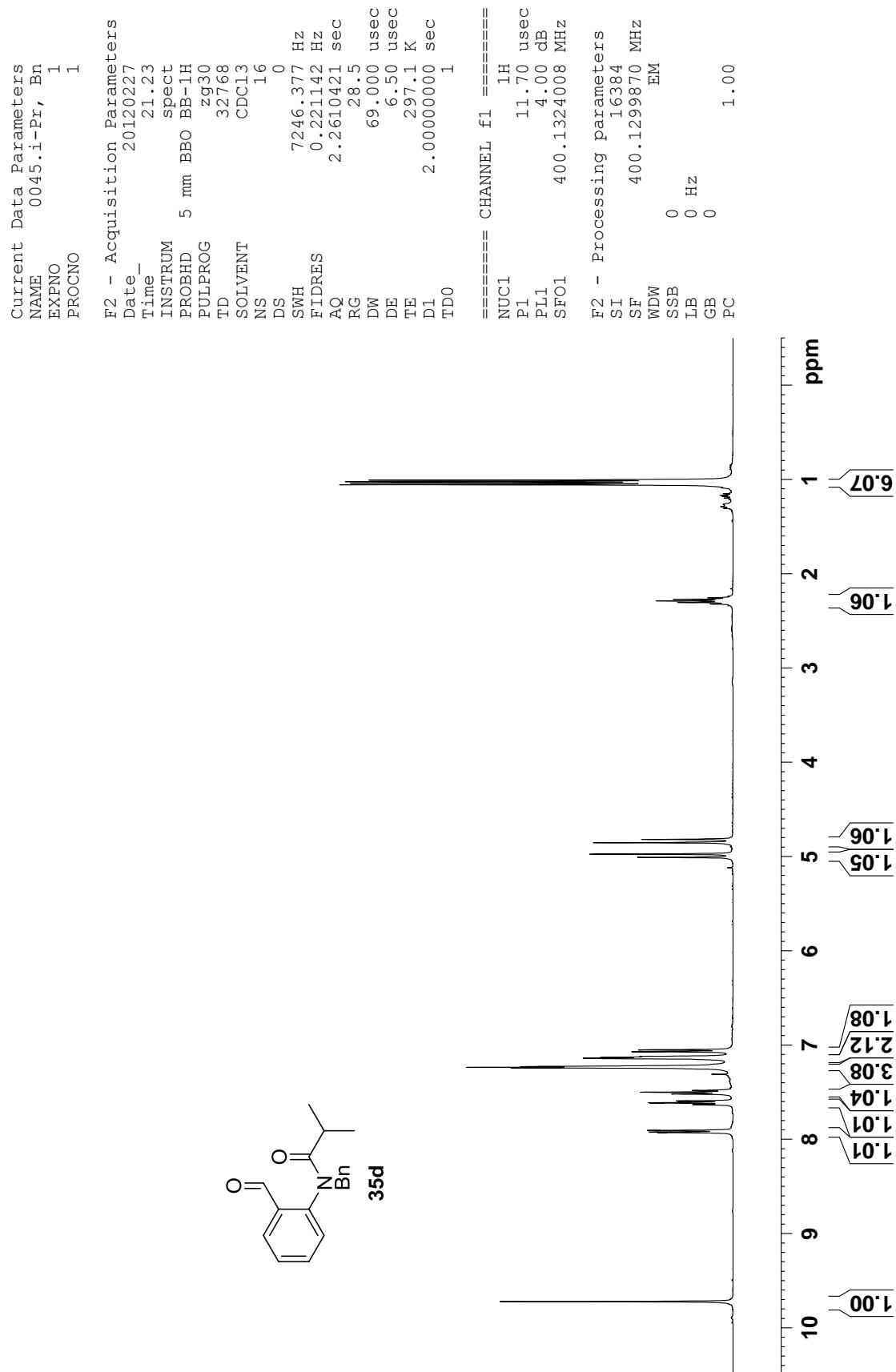


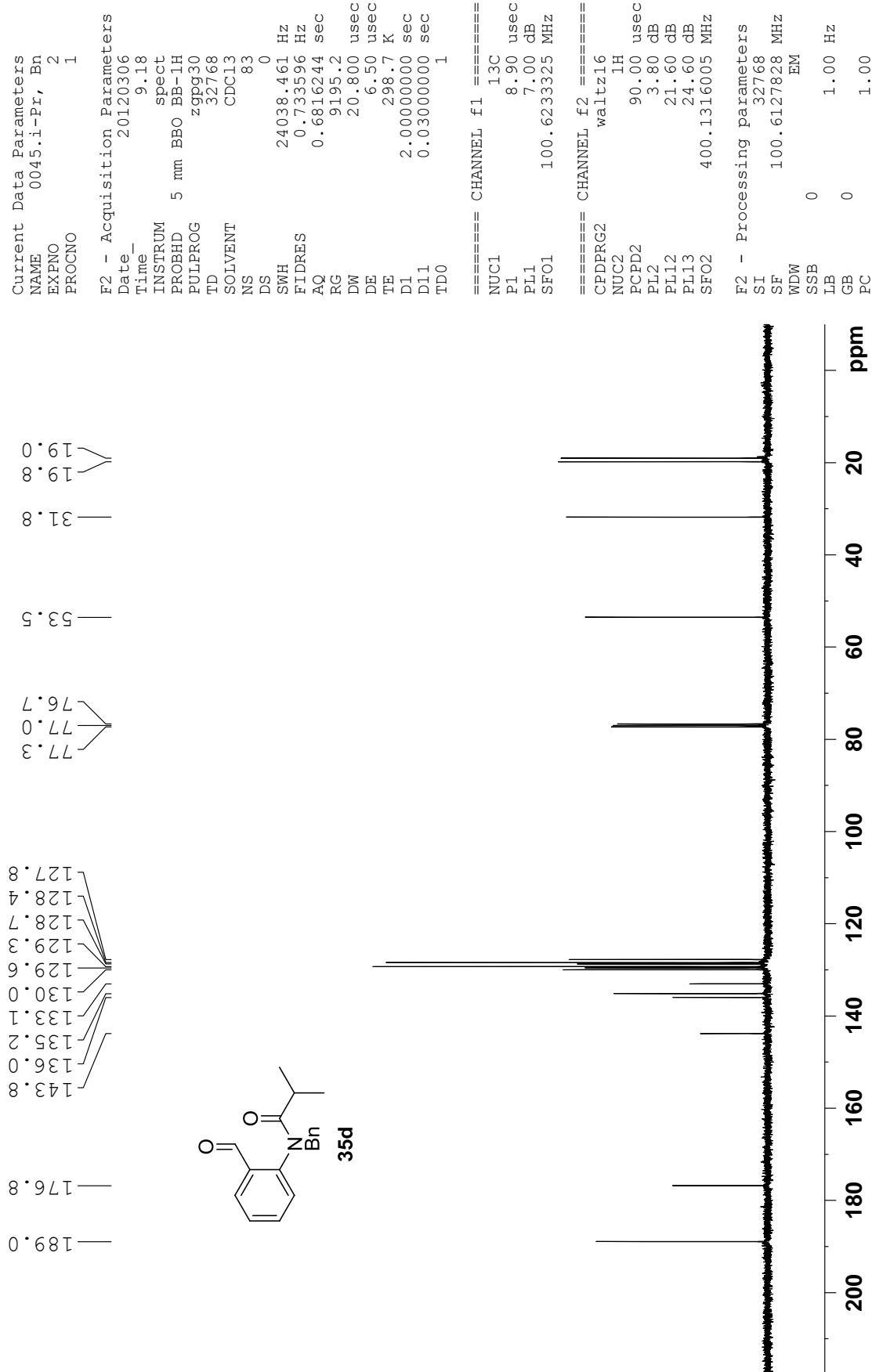


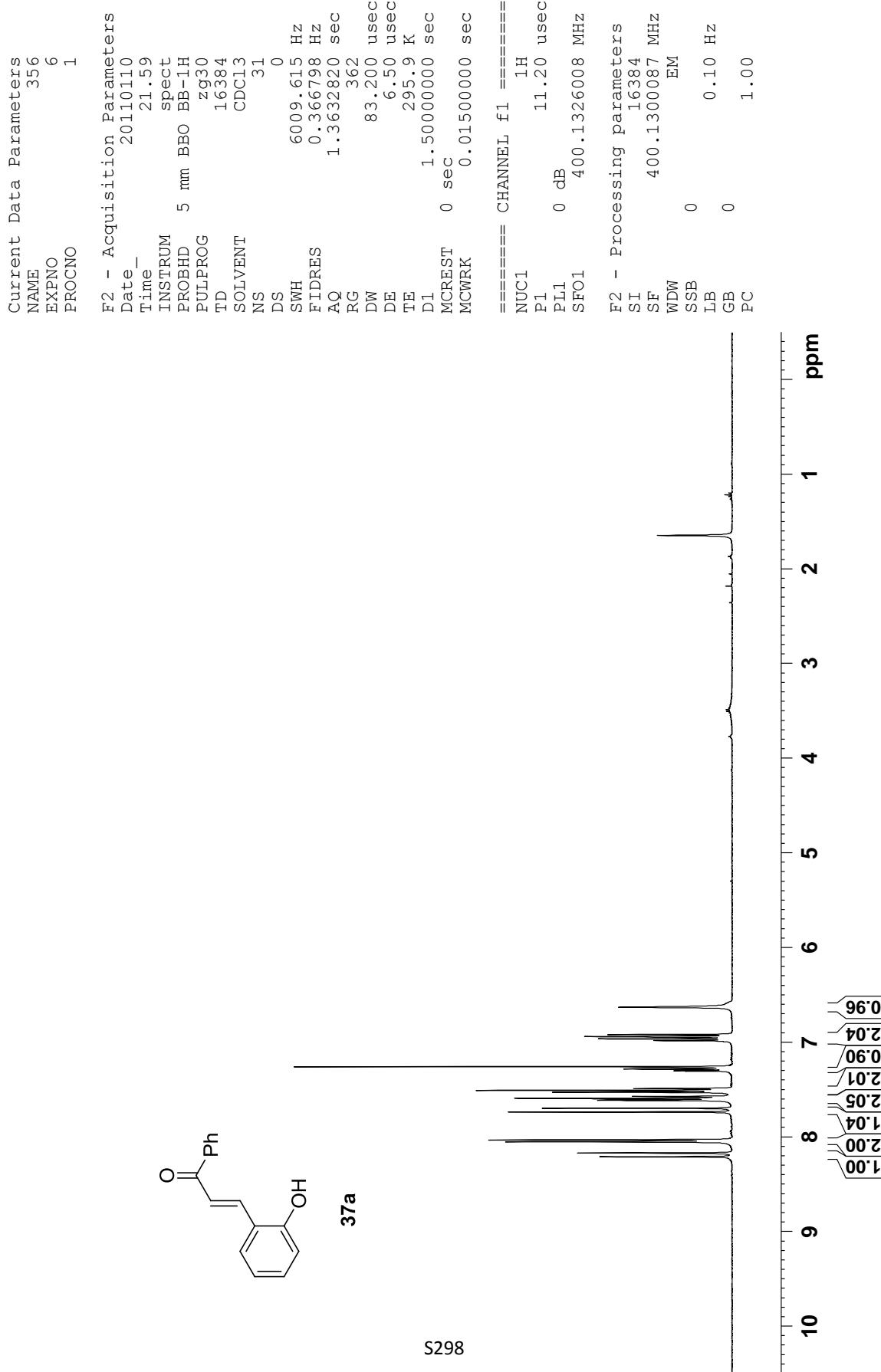


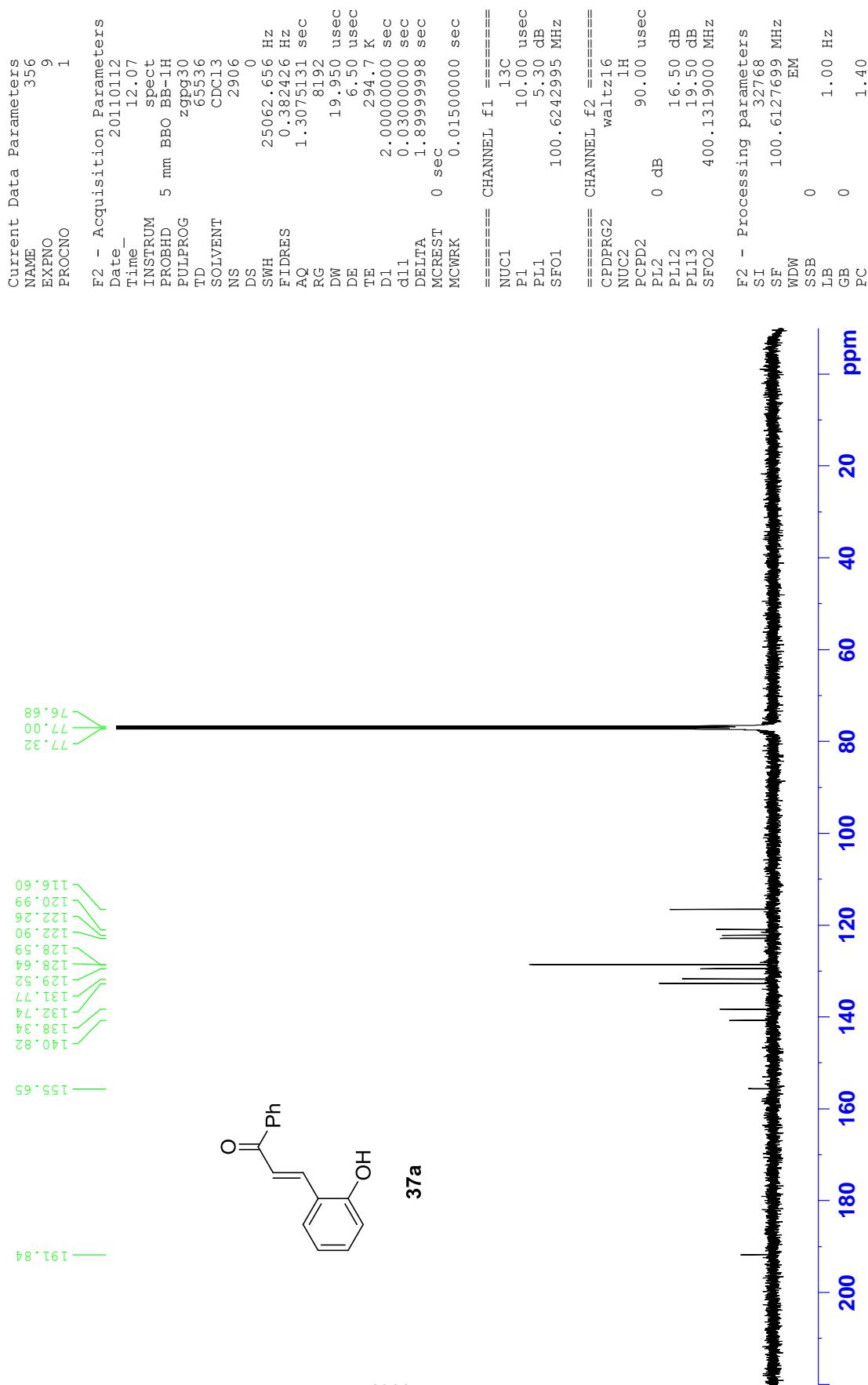


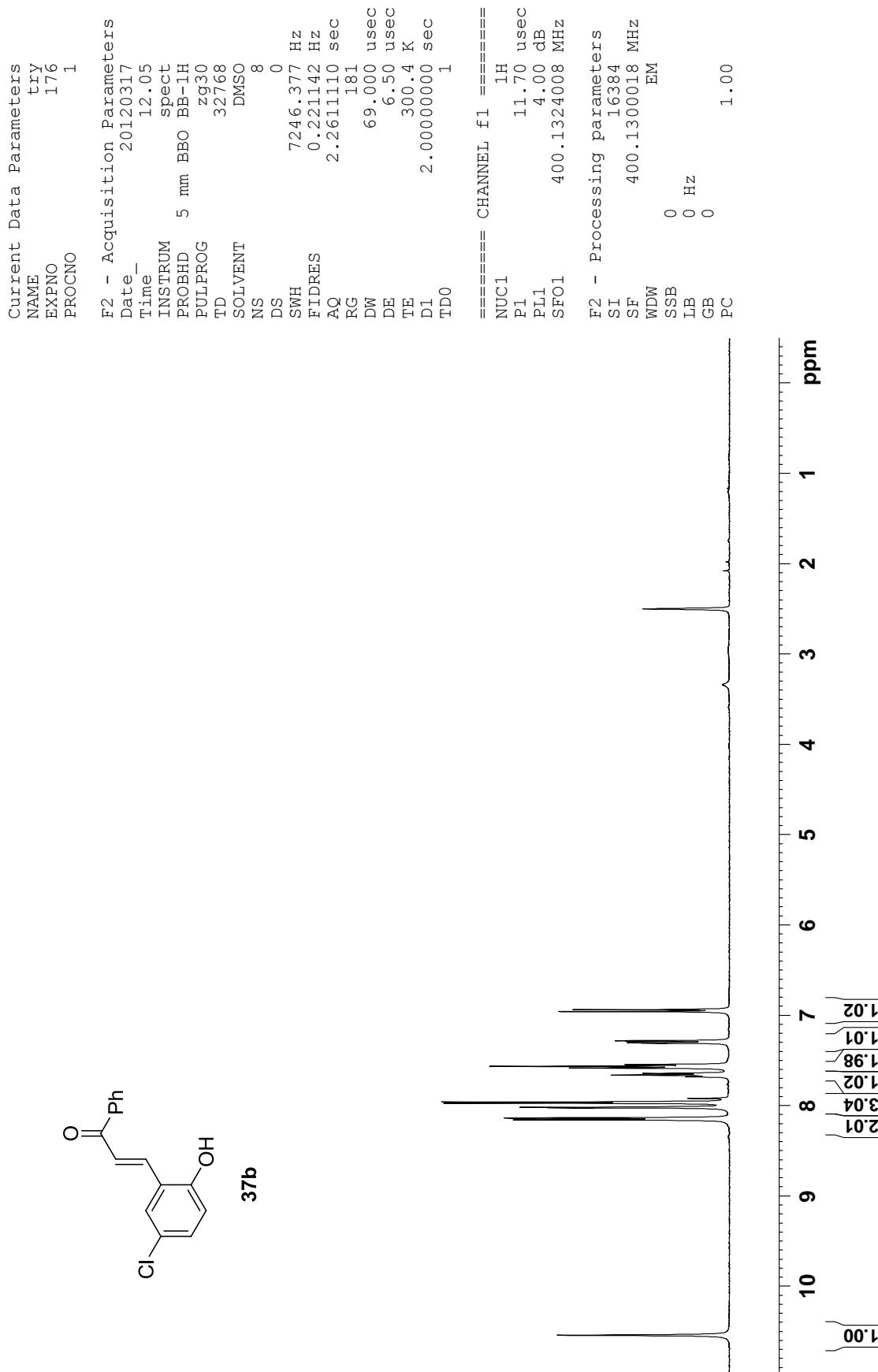


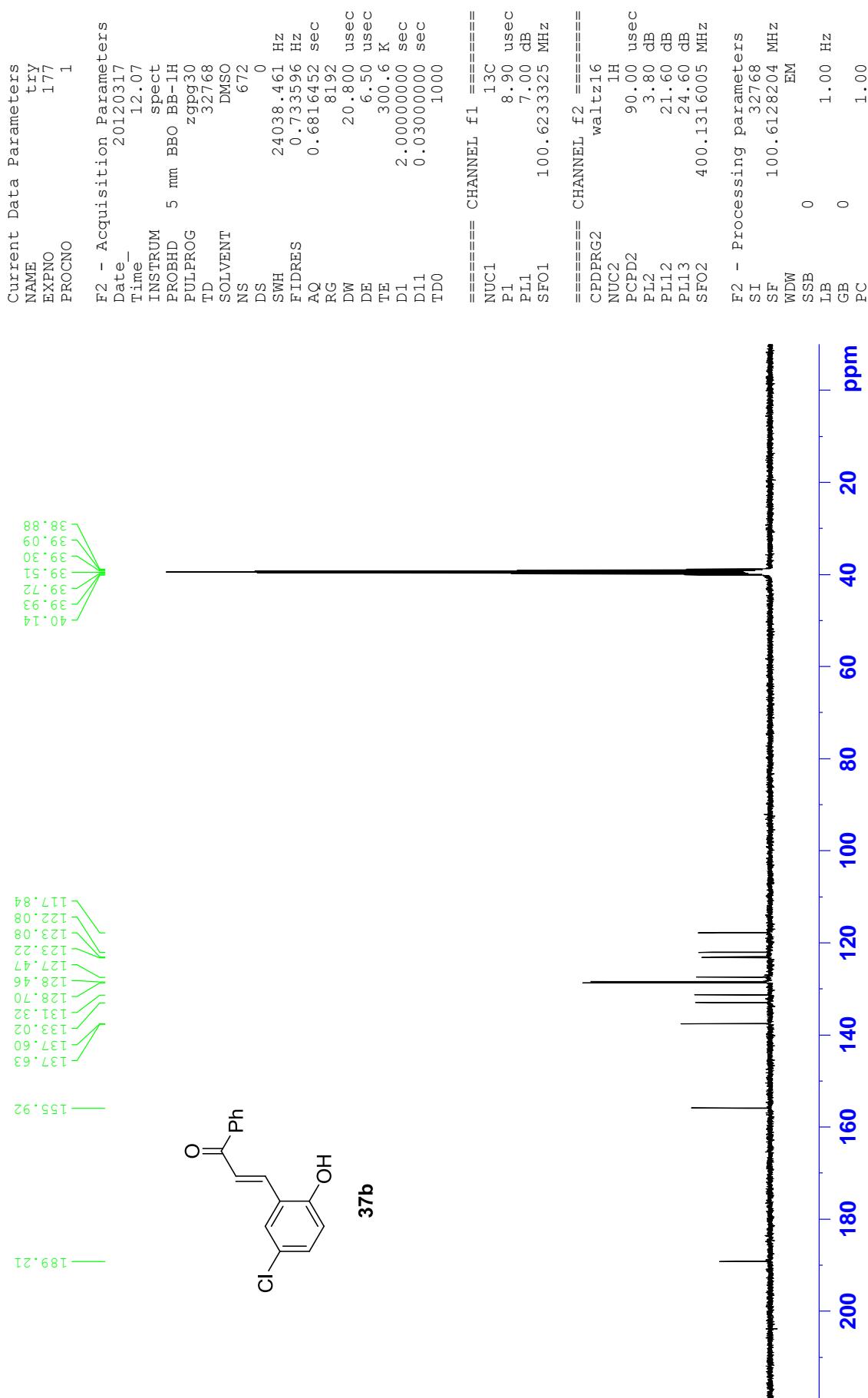










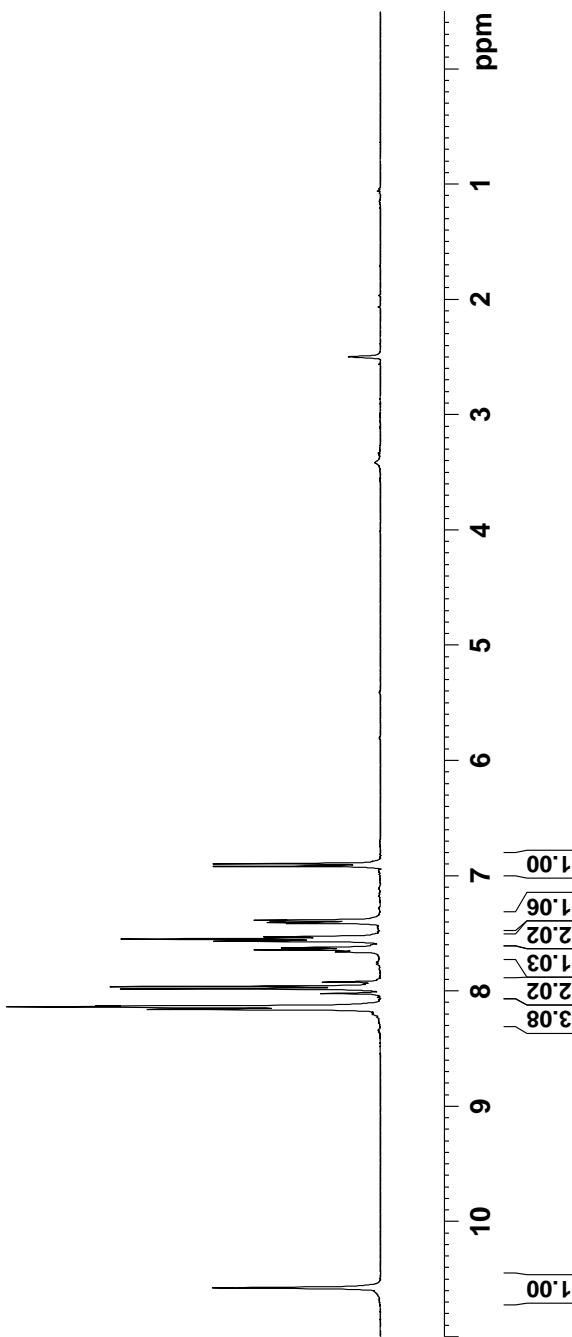
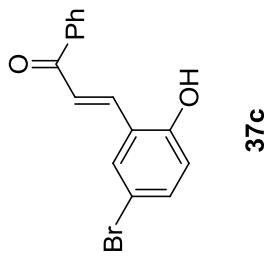


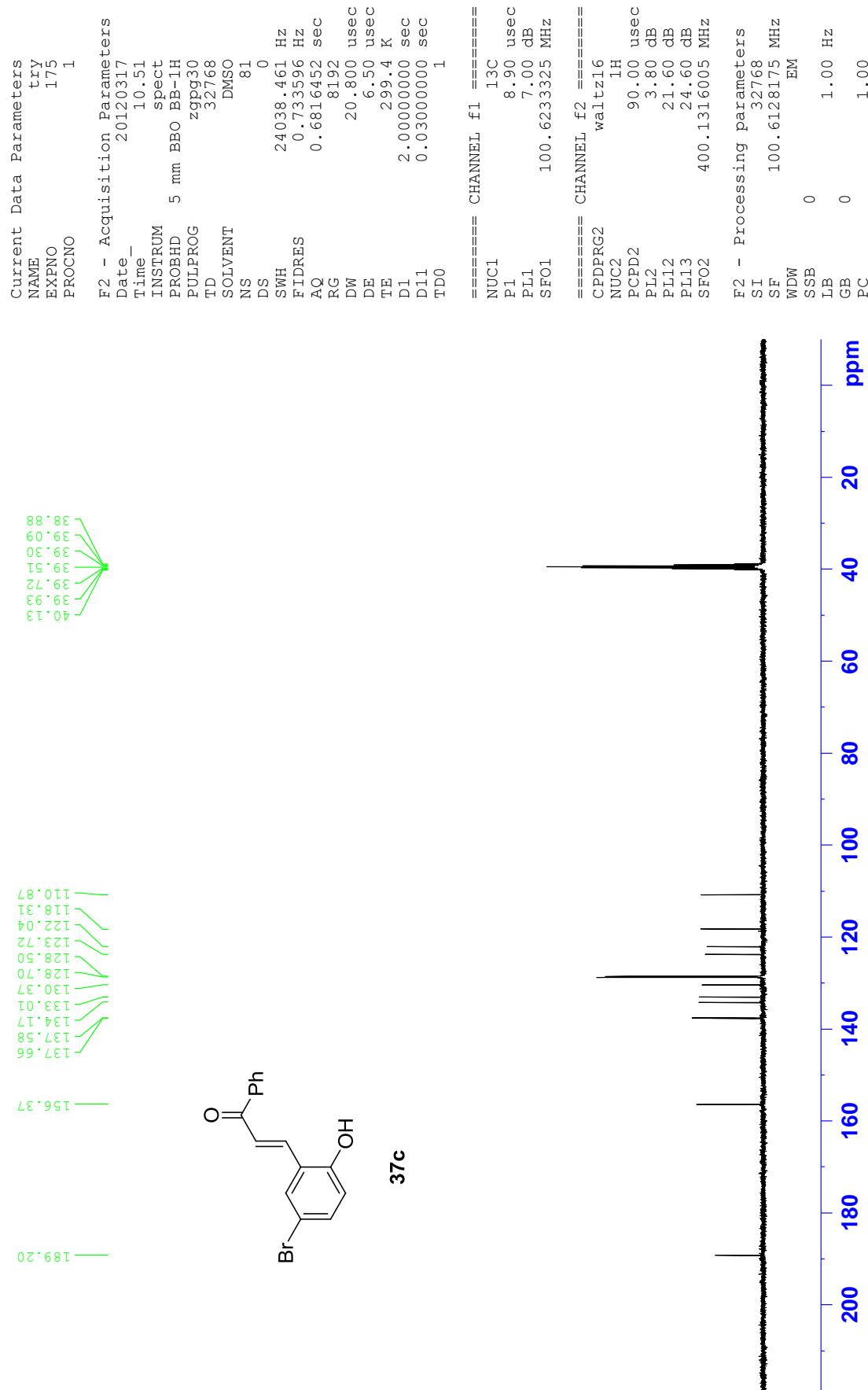
Current Data Parameters
NAME try
EXPNO 174
PROCNO 1

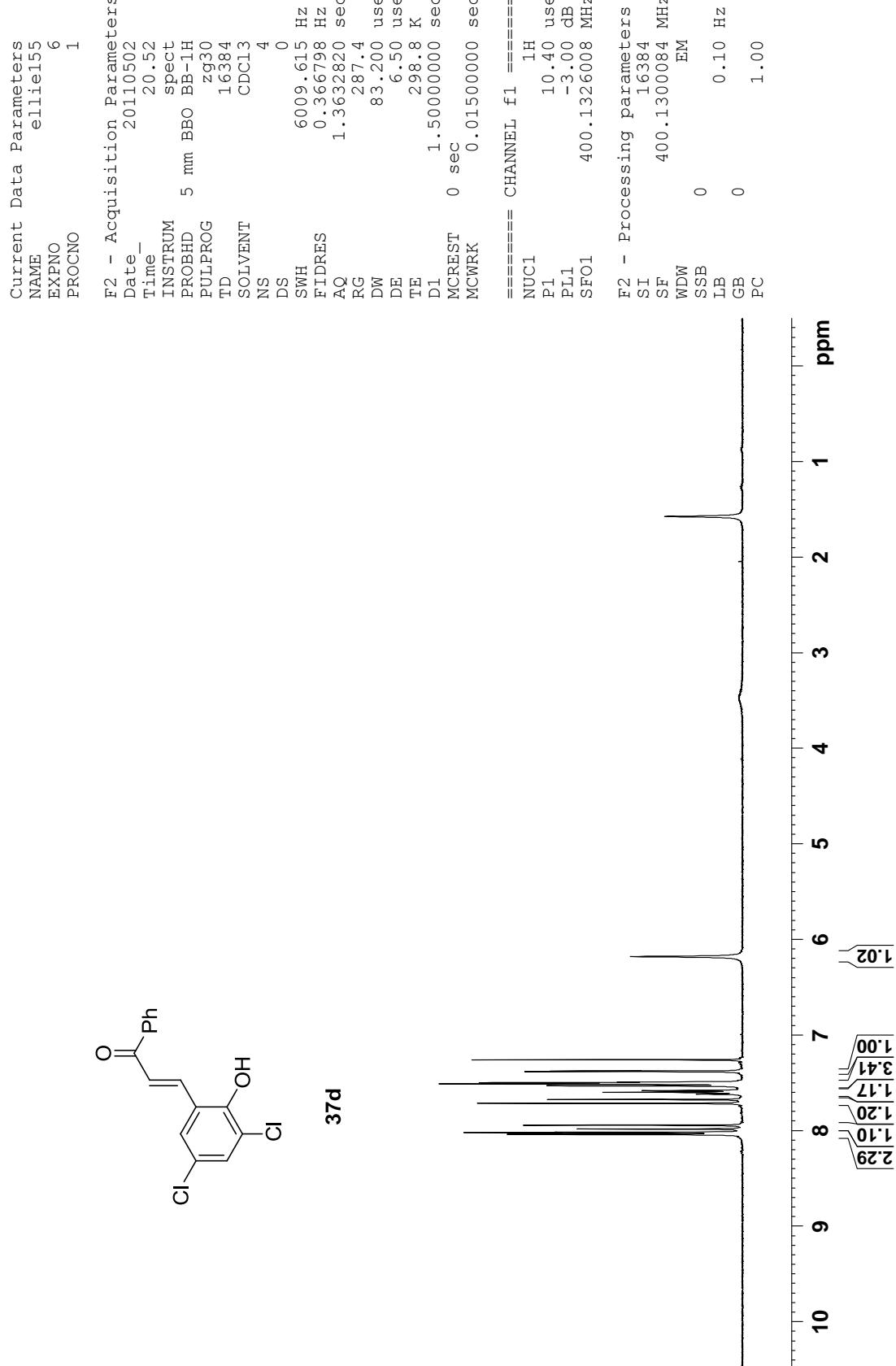
F2 - Acquisition Parameters
Date 20120317
Time 10.50
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG PULFROG
TD 32768
SOLVENT DMSO
NS 1
DS 0
SWH 7246.377 Hz
FIDRES 0.221142 Hz
AQ 2.261110 sec
RG 71.8
DW 69.000 usec
DE 6.50 usec
TE 299.4 K
D1 2.0000000 sec
TD0 1

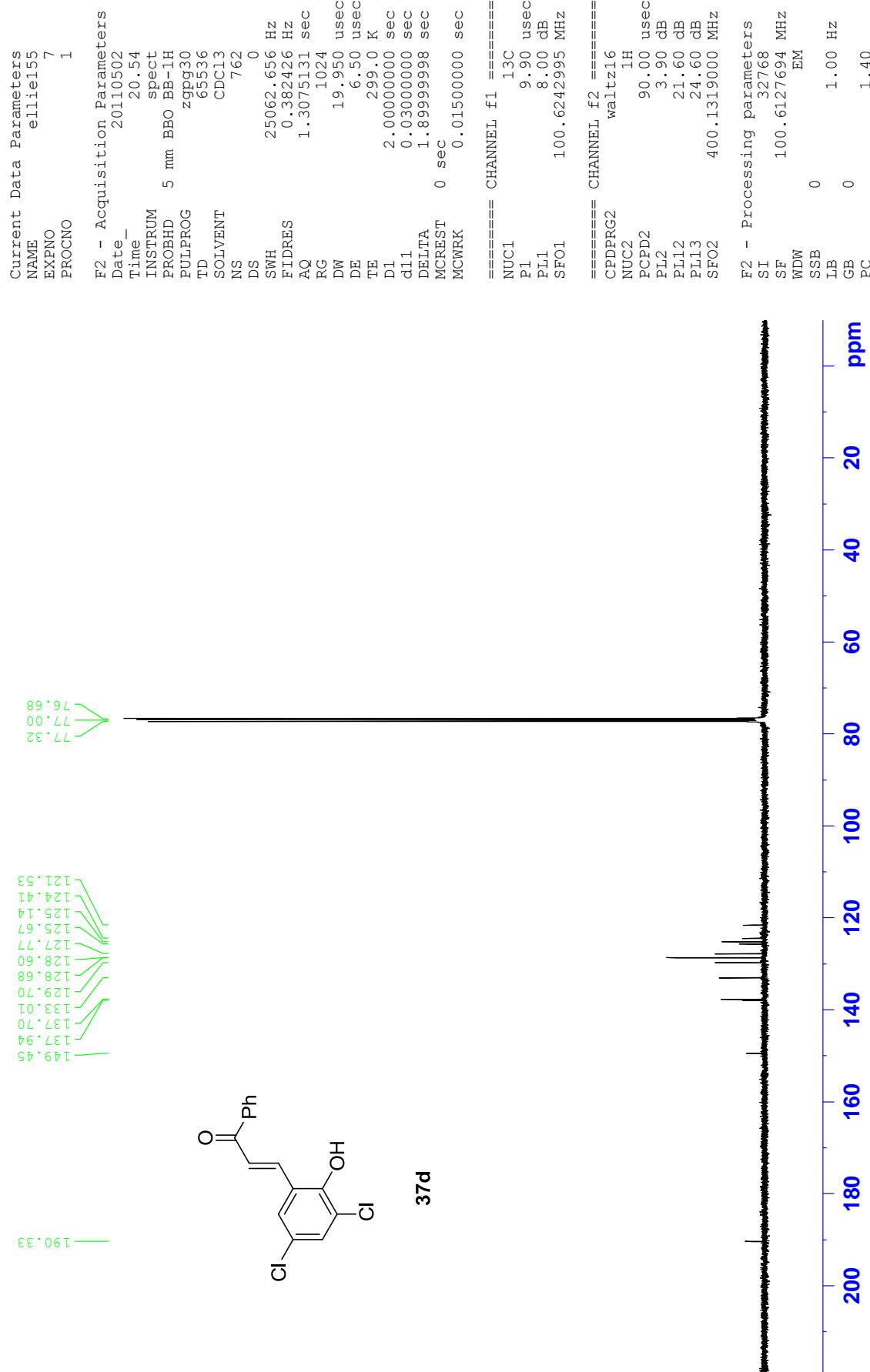
===== CHANNEL f1 =====
NUC1 1H
P1 11.70 usec
PL1 4.00 dB
SFO1 400.1324008 MHz

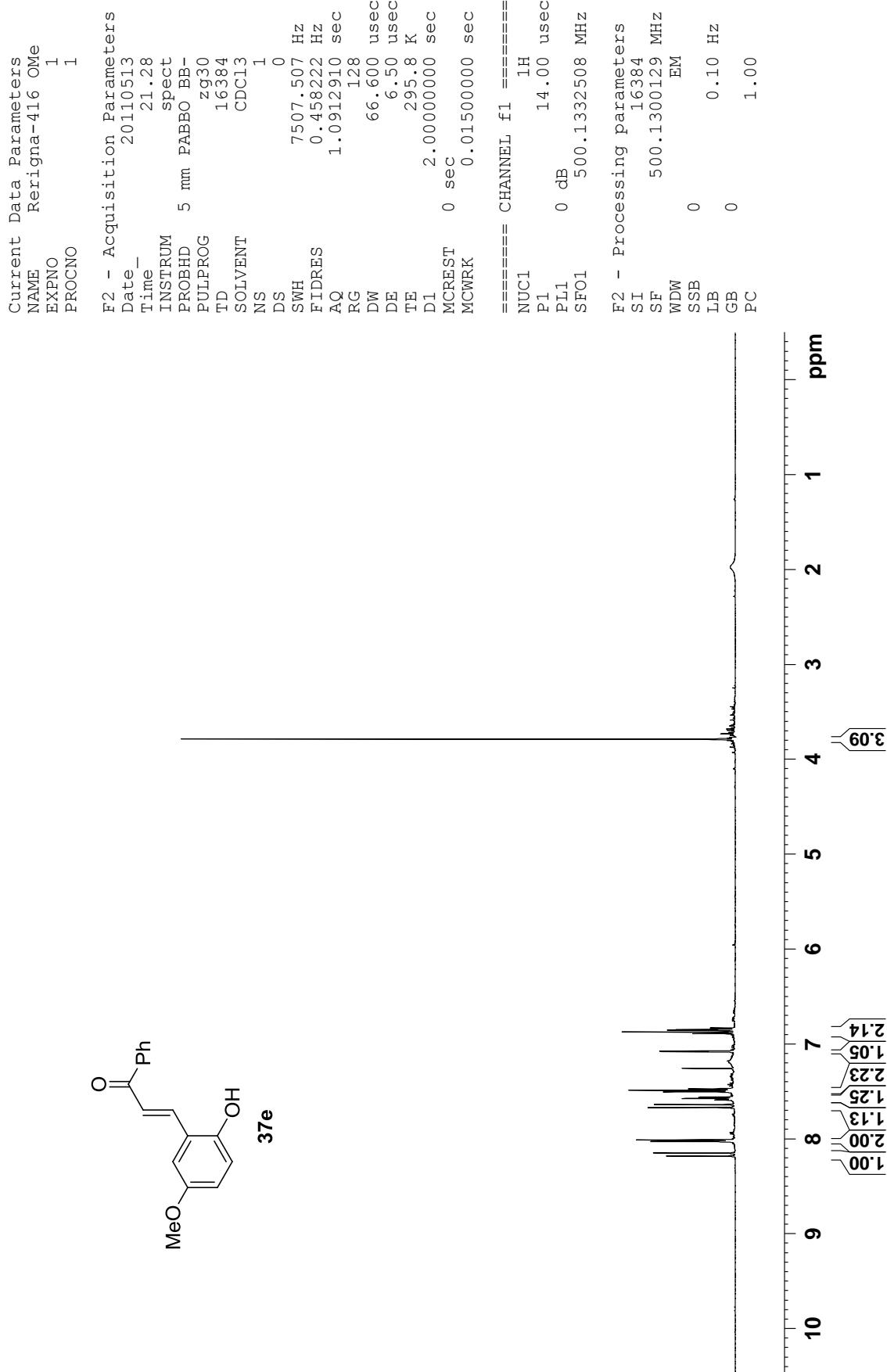
F2 - Processing parameters
SI 16384
SF 400.1300019 MHz
WDW EM
SSB 0 Hz
LB 0 Hz
GB 0
PC 1.00

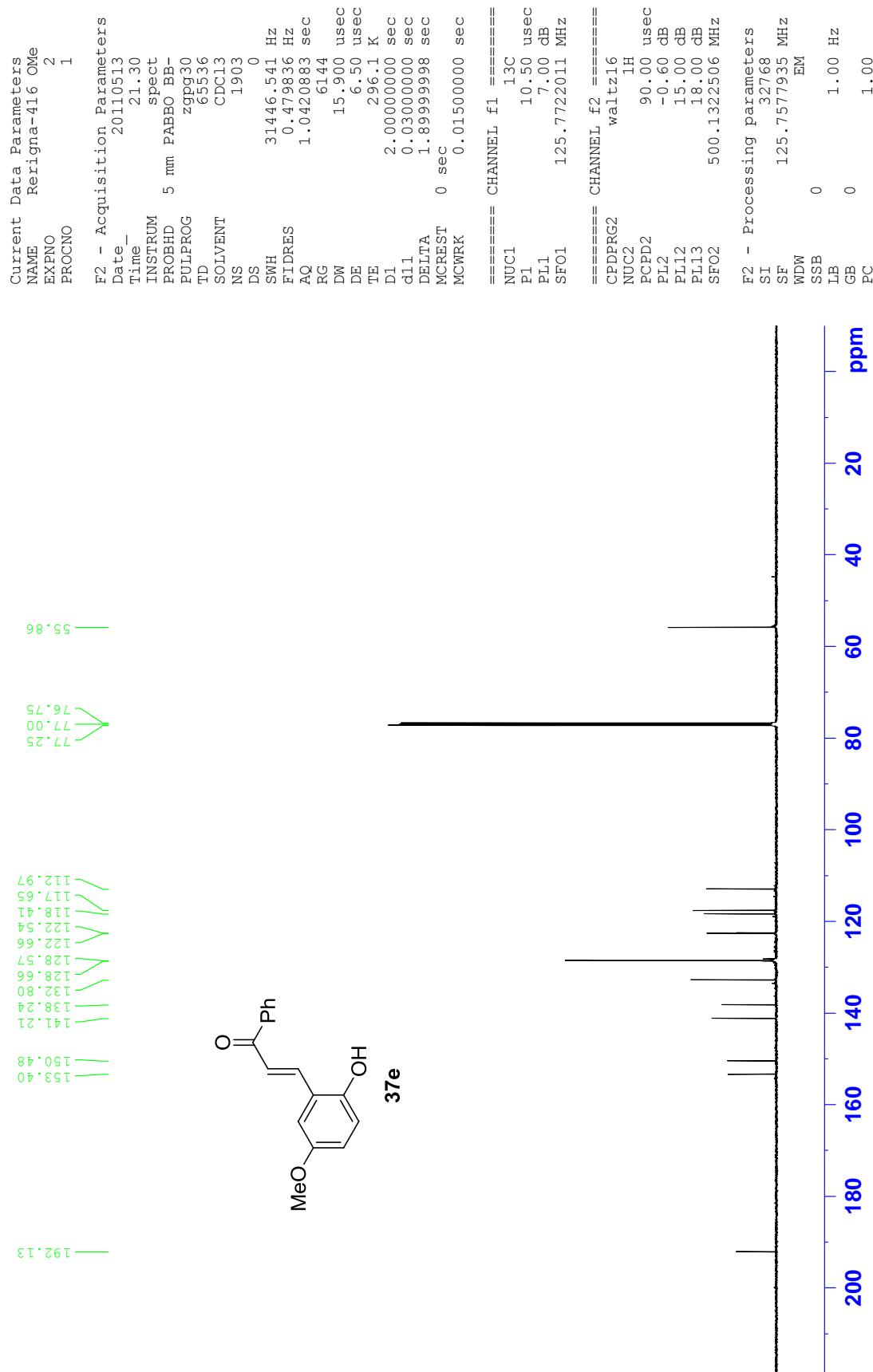


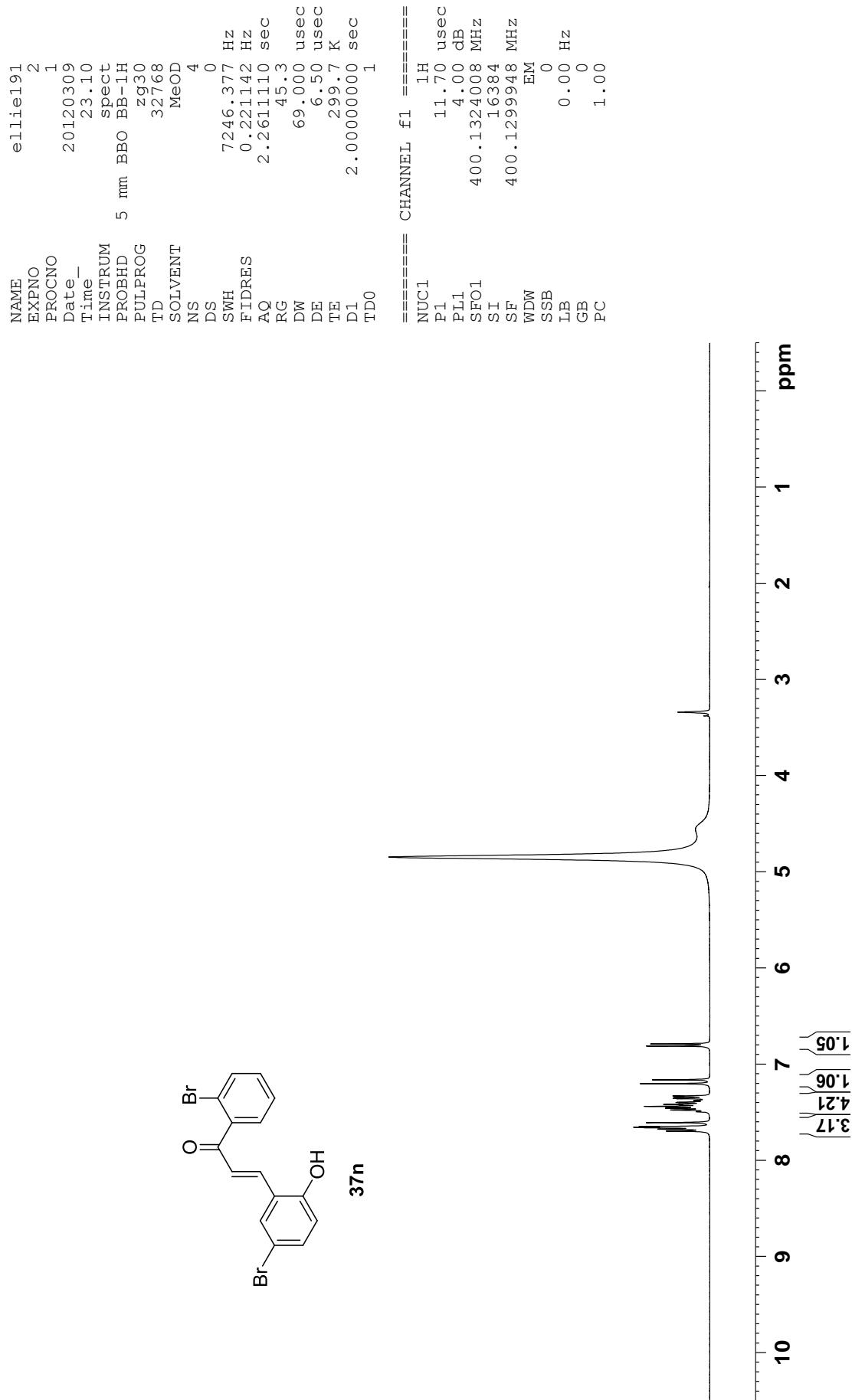


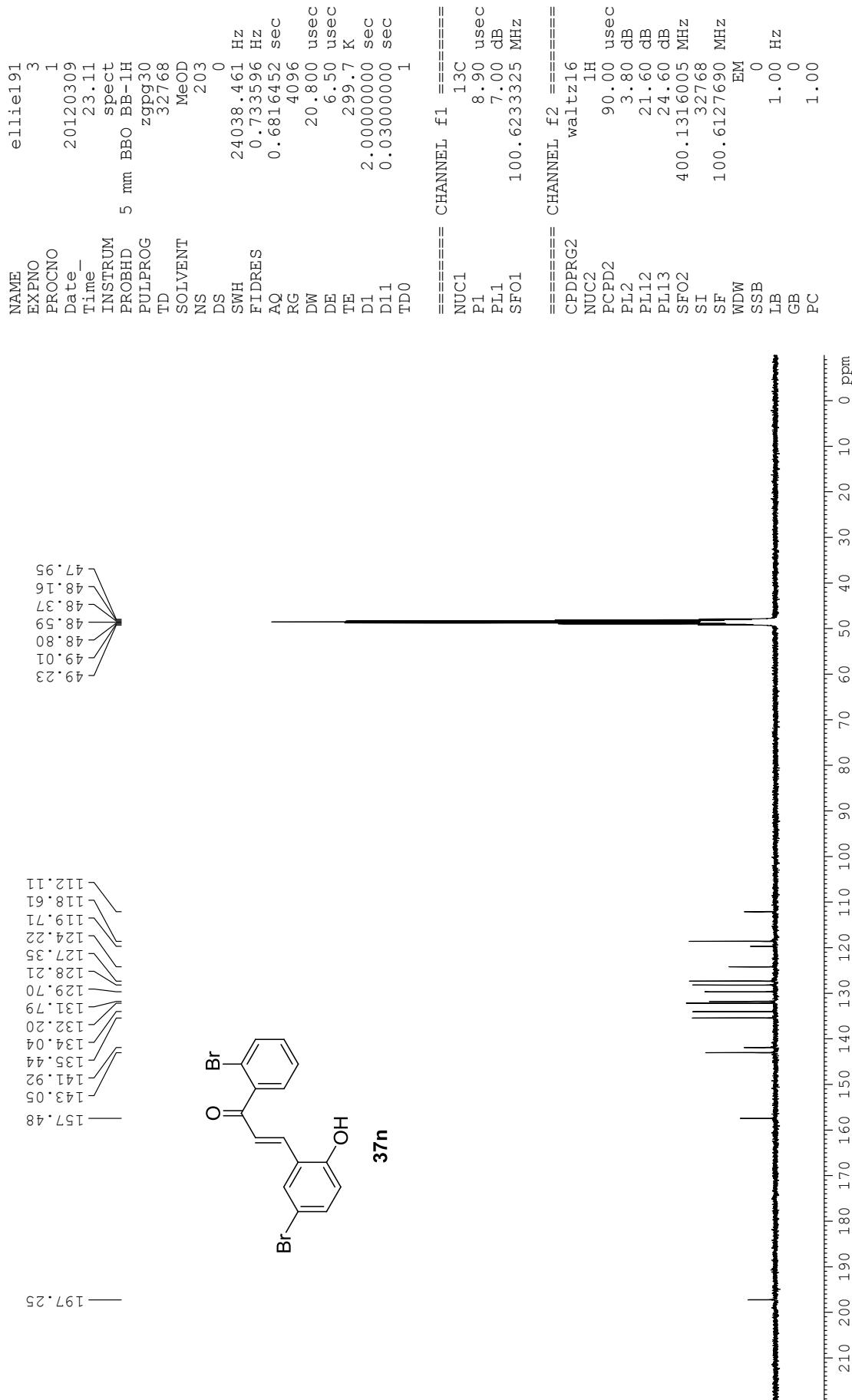


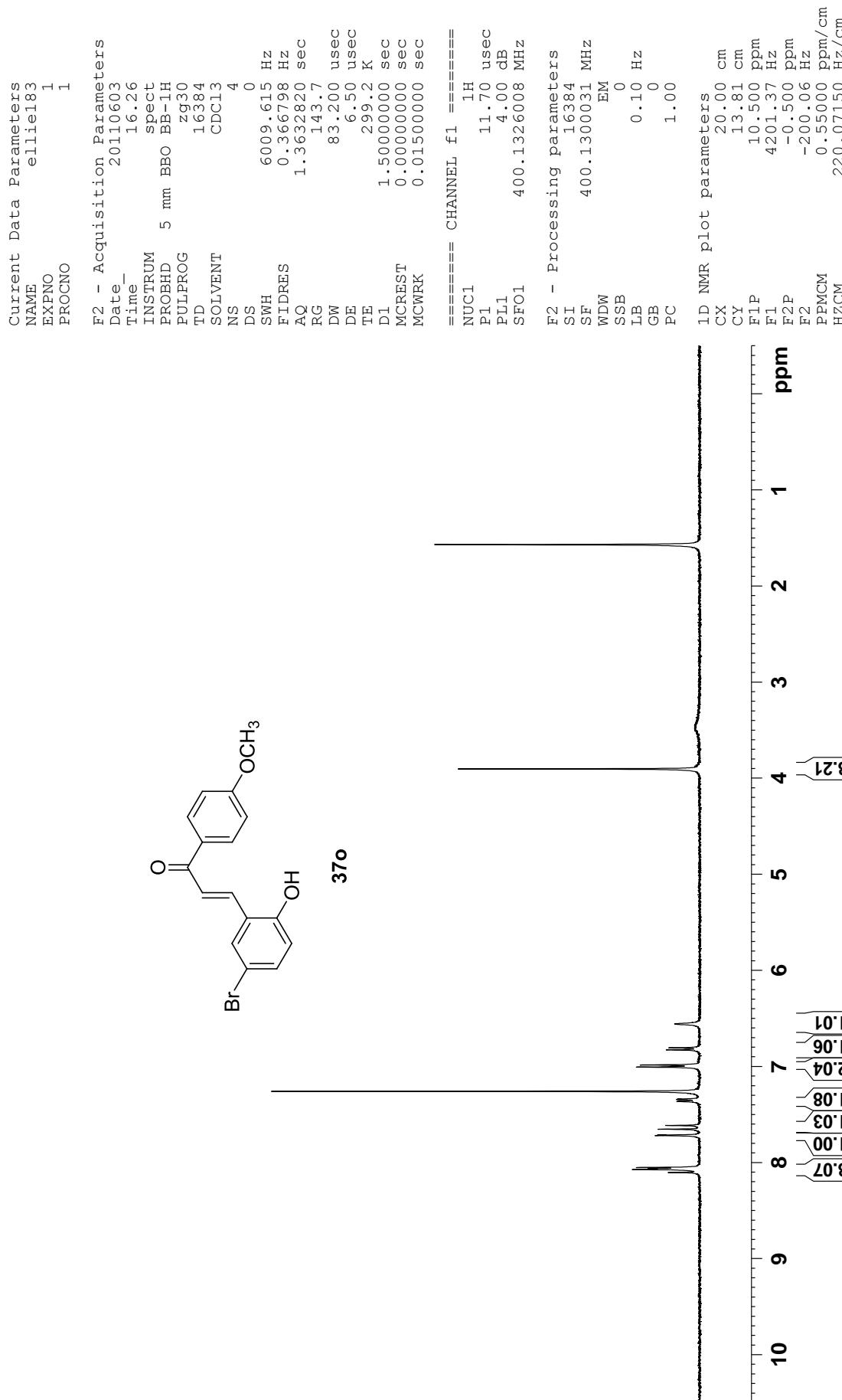


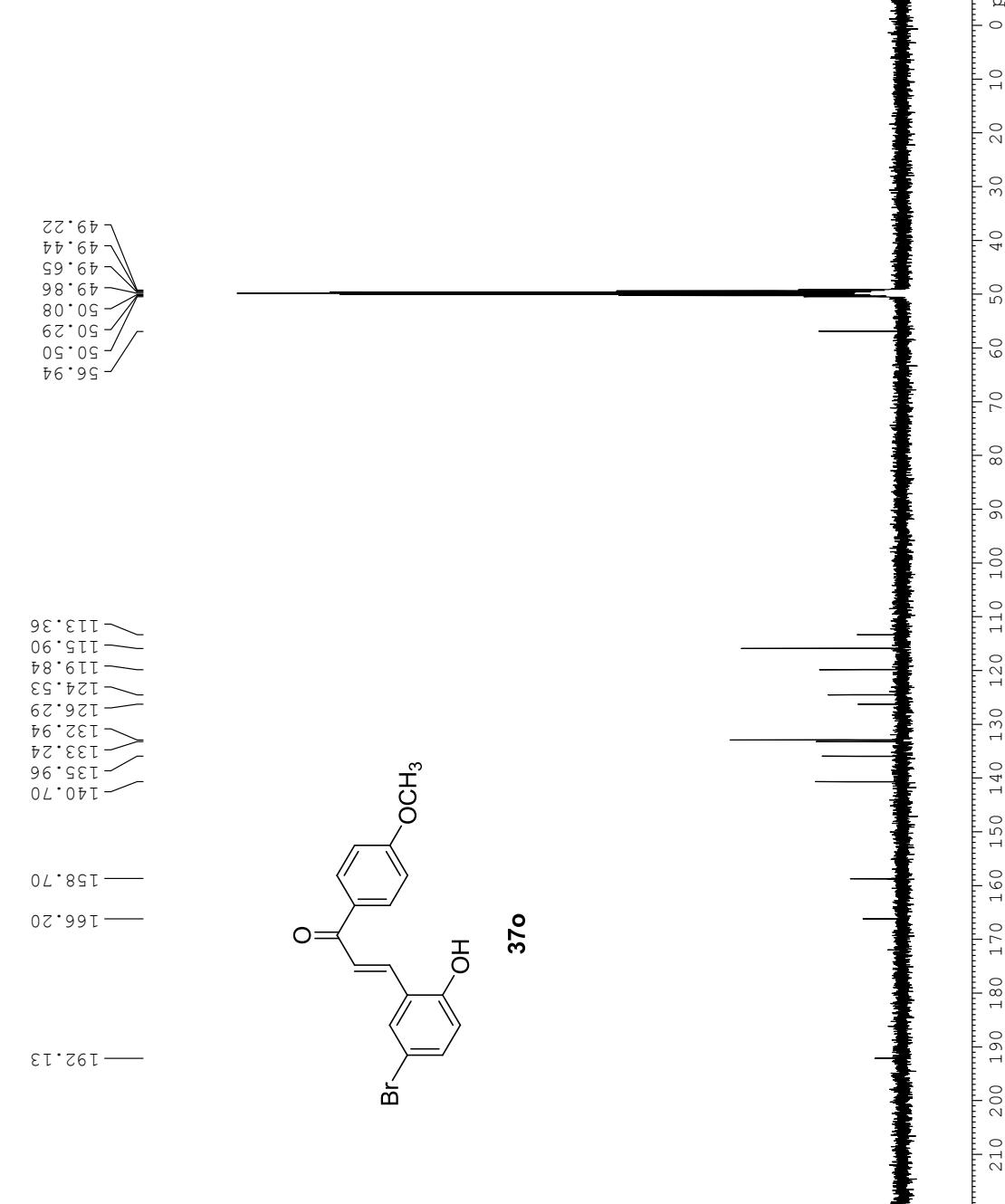


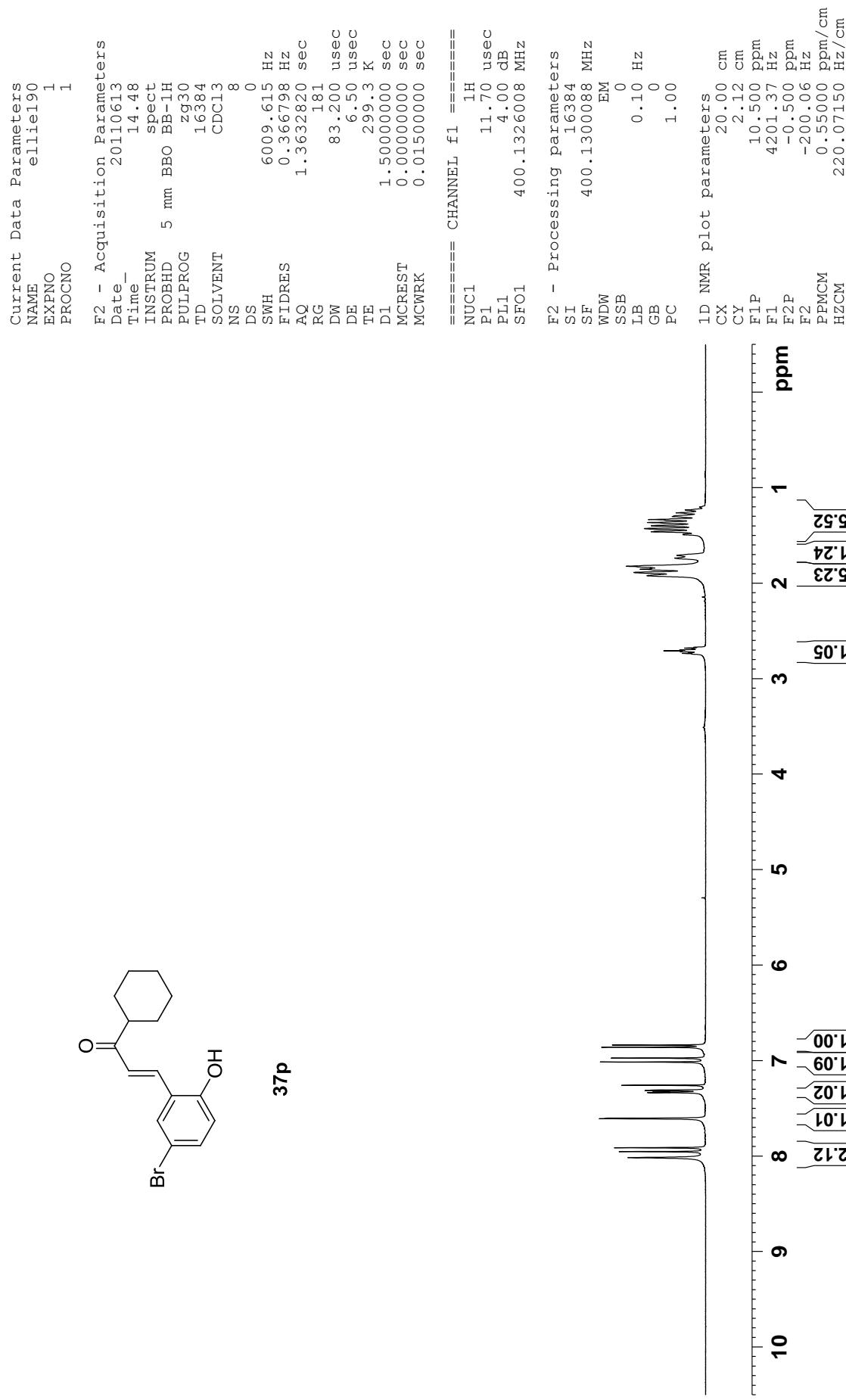




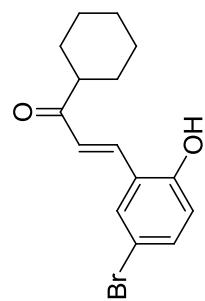




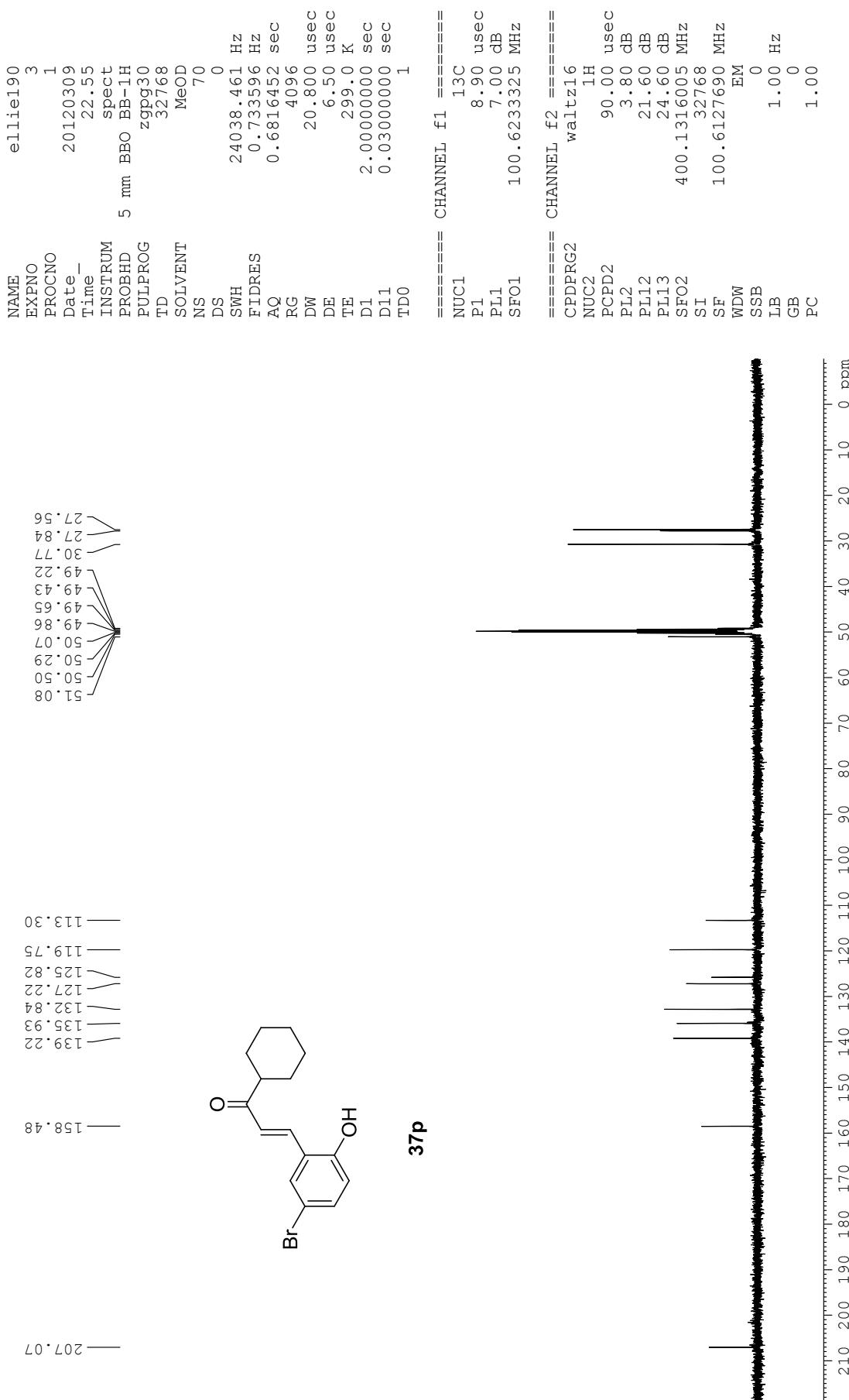




27.56
27.84
30.77
49.22
49.43
49.65
49.86
50.07
50.29
50.50
51.08
113.30
119.75
125.82
127.22
132.84
135.93
139.22
158.48
207.07

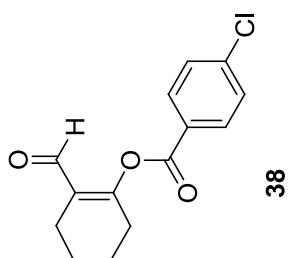
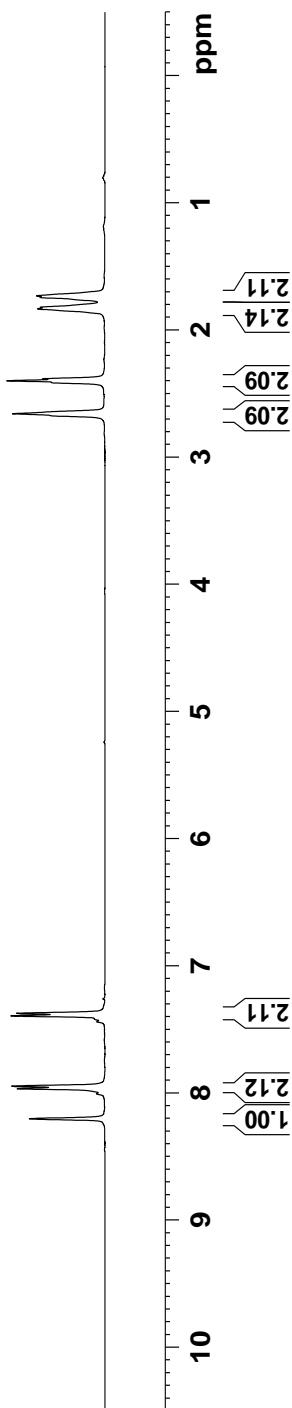


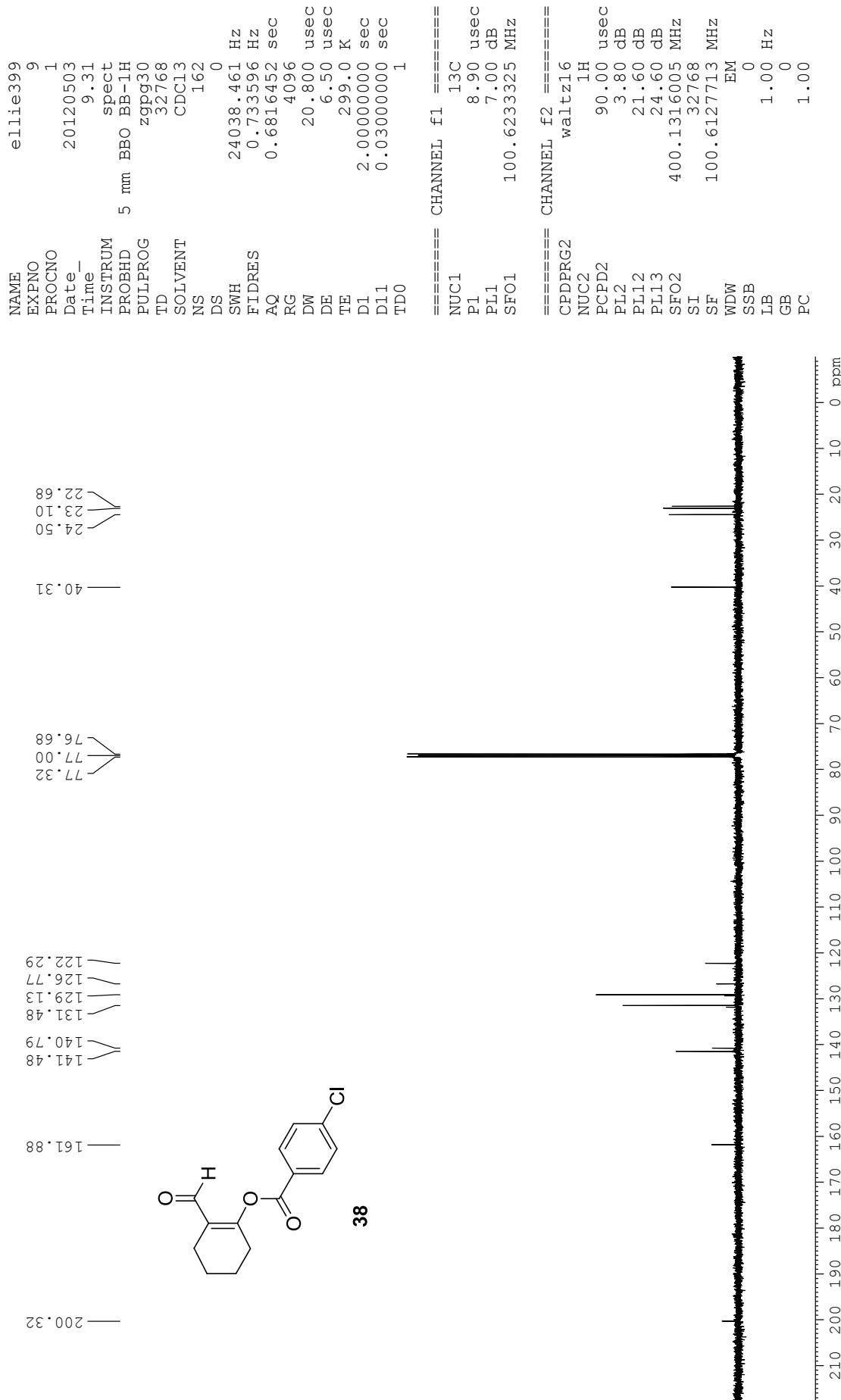
37p



```
NAME          add1
EXPNO         8
PROCNO        1
Date         20120503
Time        19.41
INSTRUM      spect
PROBHD      5 mm BBO BB-1H
PULPROG      zg30
TD           32768
SOLVENT      CDCl3
NS            4
DS            0
SWH          7246.377 Hz
FIDRES      0.221142 Hz
AQ           2.261110 sec
RG            32
DW           69.000 usec
DE           6.500 usec
TE           298.8 K
D1          2.0000000 sec
TD0           1

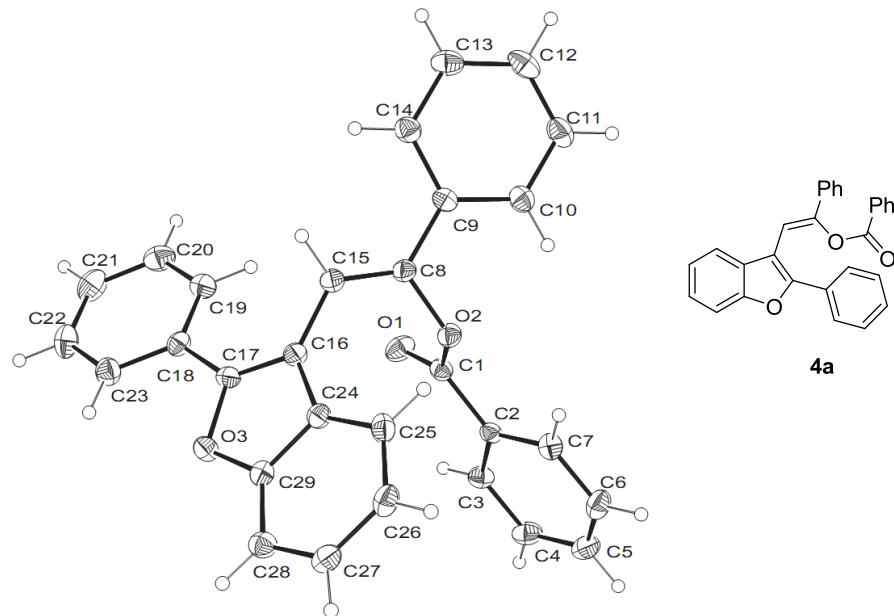
===== CHANNEL f1 =====
NUC1          1H
P1           11.70 usec
PL1          4.00 dB
SFO1      400.11324008 MHz
SI           16384
SF          400.1300078 MHz
WDW         EM
SSB          0
LB           0.00 Hz
GB           0
PC          1.00
```



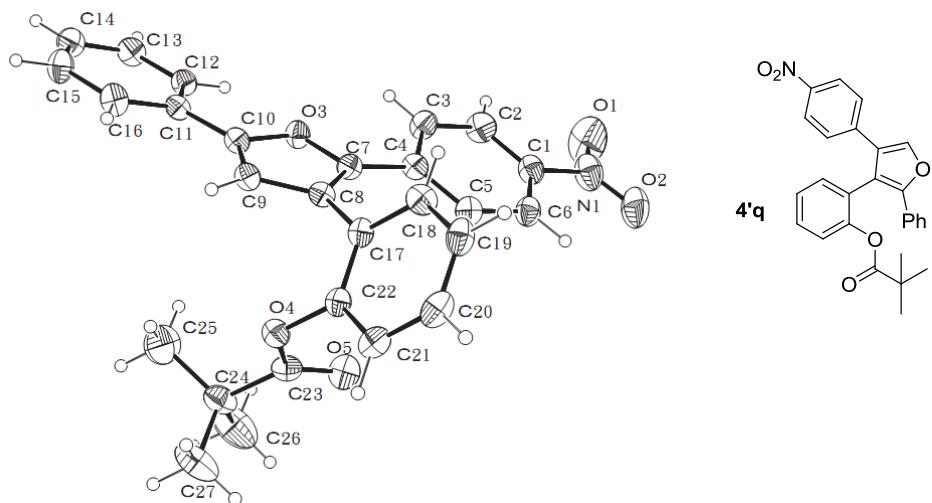


VIII. Spectra of X-ray crystallography 4a, 4'q, 8, 17e, 18d, 19a, 20a, 20b, and 22b

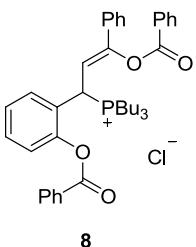
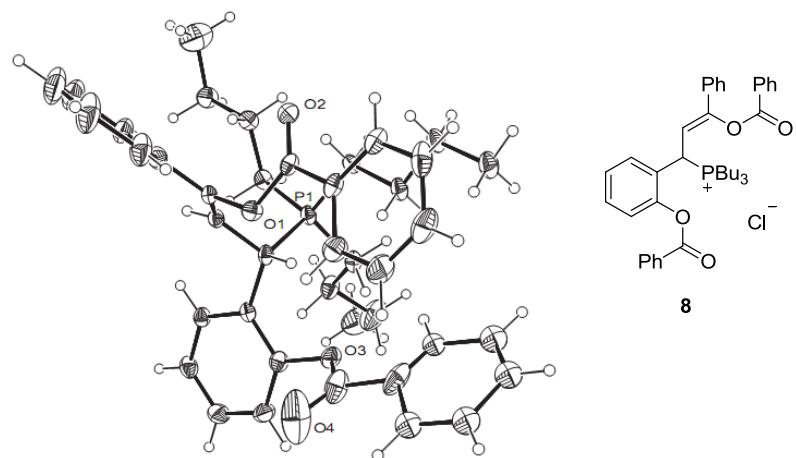
4a:



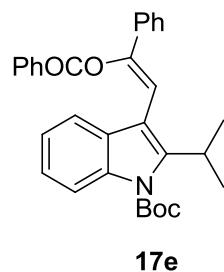
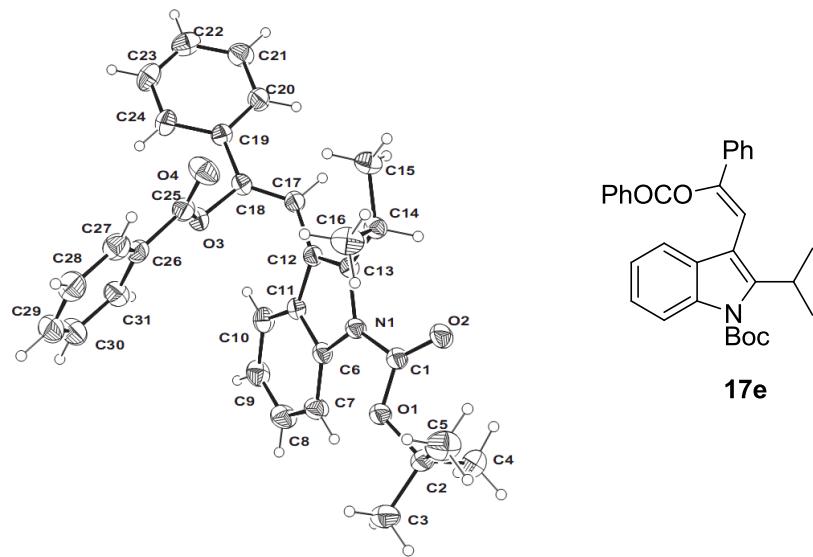
4'q:



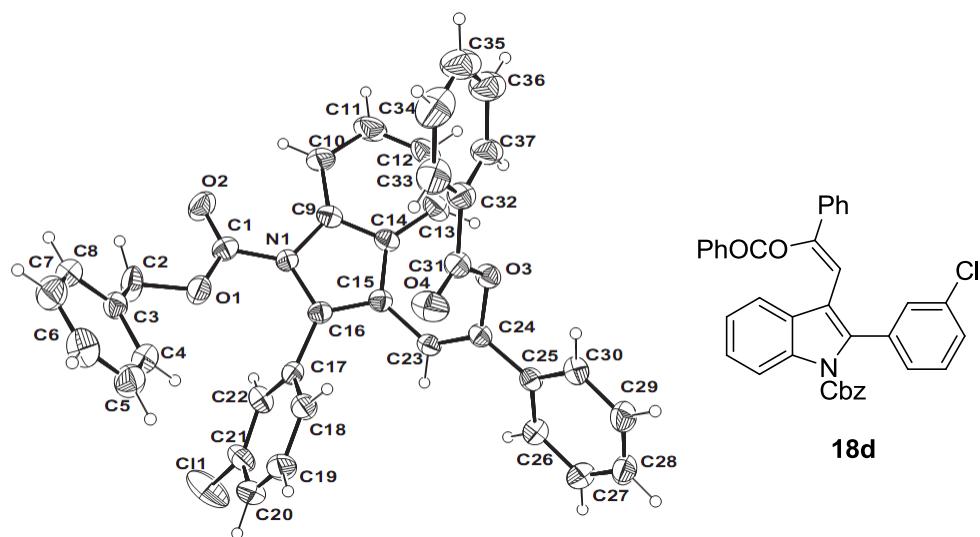
8:



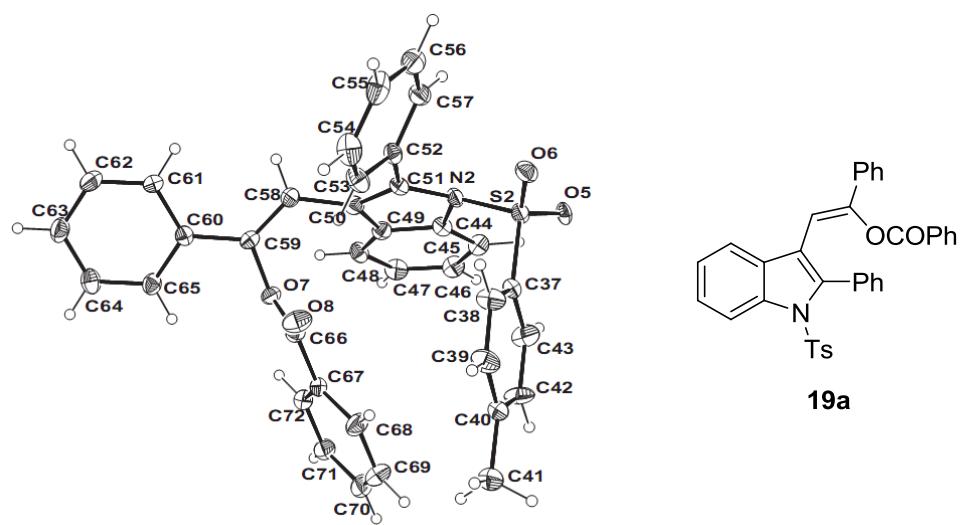
17e:



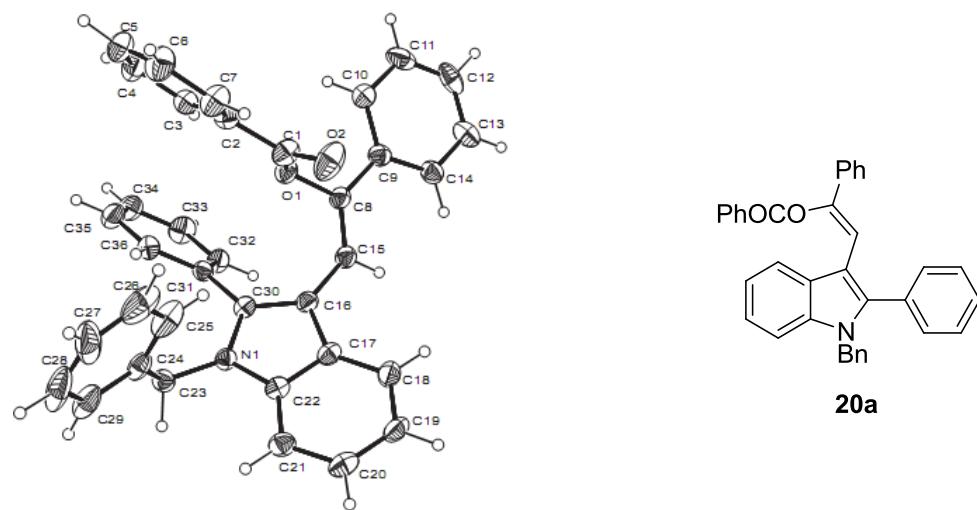
18d:



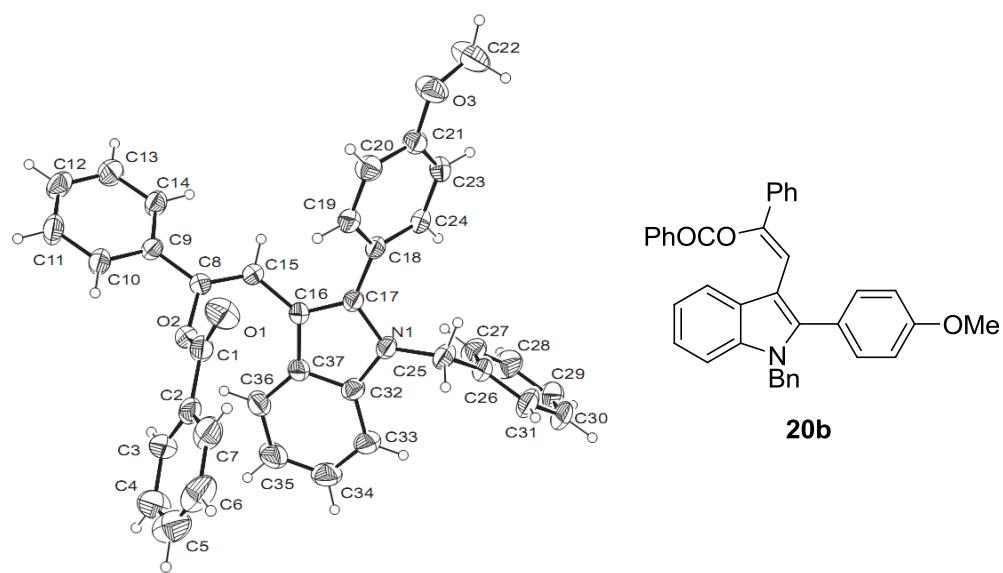
19a:



20a:



20b:



22b:

