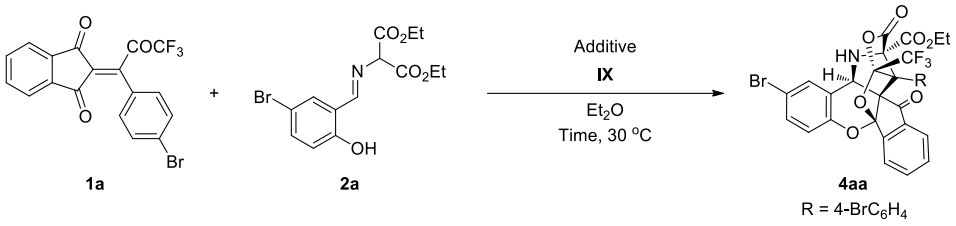
Table of contents

General aspects and materials:

All reactions were carried out in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were used as purchased from commercial suppliers without further purification. Analytical thin layer chromatography (TLC) was performed on pre-coated, alumina-backed silica gel plates (Merck 60 F_{254}, 0.2 mm thickness) which were developed using UV irradiation at 254 nm. Flash column chromatography was performed using silica gel (SiliCycle SiliaFlash P60, 230-400 mesh). Melting points were measured on a Fargo melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 500 spectrometer and only selected peaks are mentioned. ^{1}H NMR spectra were recorded on either a Bruker AV-400 spectrometer or a Bruker AV-III HD-400 spectrometer. ^{19}F NMR has been recorded only for selected cases where the C-F couplings were very weak and could not be identified in ^{13}C NMR. Chemical shifts are reported in δ ppm referenced to an internal TMS standard (δ = 0.0 ppm) for ^{1}H NMR, chloroform-d (δ = 77.16 ppm) for ^{13}C NMR, H_3PO_4 (δ = 0.0 ppm) for ^{31}P NMR and fluorobenzene (δ = -113.15 ppm) for ^{19}F NMR. The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, td = triplet of doublet, qd = quartet of doublet, br = broad, p = pseudo. High resolution mass spectra were recorded on JEOL MStation JMS-700 (2) using EI (Magnetic sector analyzer) or on Waters Xevo G2-S Tof using ESI (TOF analyzer). The X-ray diffraction measurements were carried out at 200 K on a Bruker KAPPA APEX II CCD area detector system equipped with a graphite monochromator and either a Mo-Kα or a Cu-Kα fine-focus sealed tube (k = 0.71073 Å). Optical rotations were measured in $CHCl_3$ on a polarimeter with a 50 mm cell (c given in g/100mL) operating at λ = 589 nm, corresponding to the sodium D line, at the indicated temperatures. The known 2-arylidene indandione substrates were synthesized following the procedure reported earlier by our group[1]. Likewise, the known imine substrates were synthesized following the procedure reported by our group[2] and Xu et. al.[3] The new indandione substrates **S1g**-**S1h**, **1g**-**1k**, new phosphine salt **S2j**, new imine substrates **2c**, **2e**, **2g**, **2h** were synthesized following the procedure mentioned in this supporting information.

Optimization of the reaction conditions:

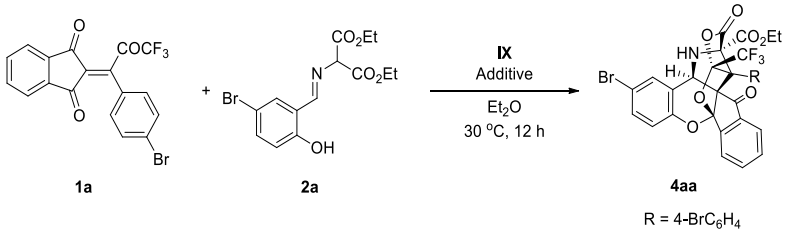
Table S1| Screening of different acidic additives for the synthesis of cascade reaction product **4aa**.[a]



Entry	Additive	pKa	Time (h)[b]	Yield **4aa** (%)[c]	ee (%)[d]
1	*o*-Nitrobenzoic acid	2.19	211	9	n.d.[e]
2	*p*-Nitrobenzoic acid	3.40	67	19	99
3	*m*-Nitrobenzoic acid	3.48	108	14	n.d.[e]
4	Benzoic acid	4.19	42	45	99
5	*p*-Hydroxybenzoic acid	4.57	67	39	98
6	CH_3COOH	4.76	108	35	98
7	*p*-Nitrophenol	7.15	73	41	99
8	α-Naphthol	9.34	71	70	90
9	4-Hydroxyanisole	10.26	61	51	98

[a]Unless otherwise specified, all the reactions were carried out using **1a** (0.1 mmol) and **2a** (1.0 equiv) with 20 mol % of **IX** and 15 mol % additive in diethyl ether (0.5 mL) and were stirred at 30 °C. [b]Indicates the time after which no further improvement in the yield of **4aa** was observed. [c]Determined by ^{1}H NMR analysis of the crude reaction mixture using Ph_3CH as an internal standard. [d]Determined by HPLC analysis on a chiral stationary phase. [e]n.d. = Not determined.

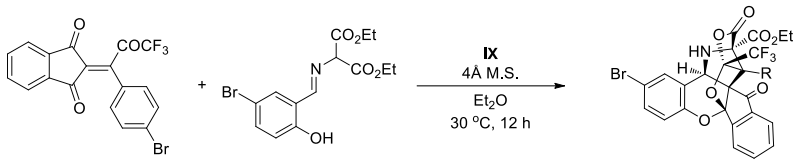
Table S2| Screening of molecular sieves for the synthesis of cascade reaction product **4aa**.[a]



Entry	Additive	Yield **4aa** (%)[b]	ee (%)[c]
1[d]	None	70	92
2	3Å M.S.	82	91
3	4Å M.S.	86	95

[a]Unless otherwise specified, all the reactions were carried out using **1a** (0.1 mmol) and **2a** (1.0 equiv.) with 20 mol % of **IX** and additive (~40 mg) in diethyl ether (0.5 mL) and were stirred at 30 °C. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture using Ph_3CH as an internal standard. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Anhydrous diethyl ether was used.

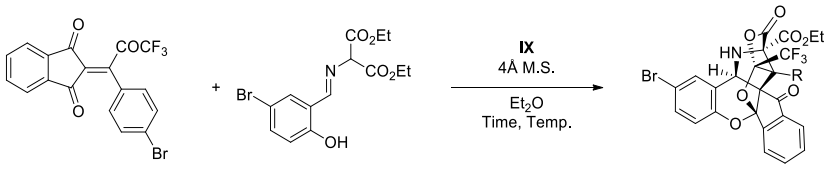
Table S3| Screening of equivalent ratio of starting materials for the synthesis of cascade reaction product **4aa**.[a]



Entry	Equiv. (**1a**:**2a**)	Yield **4aa** (%)[b]	ee (%)[c]
1	1 : 1	86	95
2	1 : 1.1	87	95
3	1 : 1.2	88	95

[a]Unless otherwise specified, all the reactions were carried out with 20 mol % of **IX** and 4 Å molecular sieves (~40 mg) in diethyl ether (0.5 mL) and were stirred at 30 °C. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture using Ph_3CH as an internal standard. [c]Determined by HPLC analysis on a chiral stationary phase.

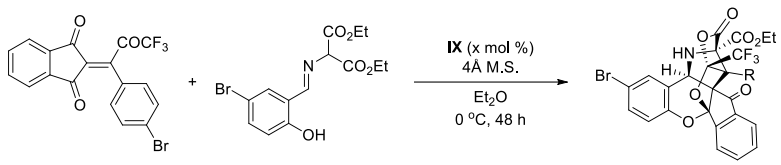
Table S4| Temperature screening for the synthesis of cascade reaction product **4aa**.[a]



Entry	Temp. (°C)	Time (h)	Yield **4aa** (%)[b]	ee (%)[c]
1	30	12	87	95
2	20	48	90	96
3	10	48	90	97
4	0	48	91	99

[a]Unless otherwise specified, all the reactions were carried out using **1a** (0.1 mmol) and **2a** (1.1equiv.) with 20 mol % of **IX** and 4 Å molecular sieves (~40 mg) in diethyl ether (0.5 mL). [b]Determined by ^{1}H NMR analysis of the crude reaction mixture using Ph_3CH as an internal standard. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S5| Screening of catalyst loading for the synthesis of cascade reaction product **4aa**.[a]



1a **2a** **4aa**

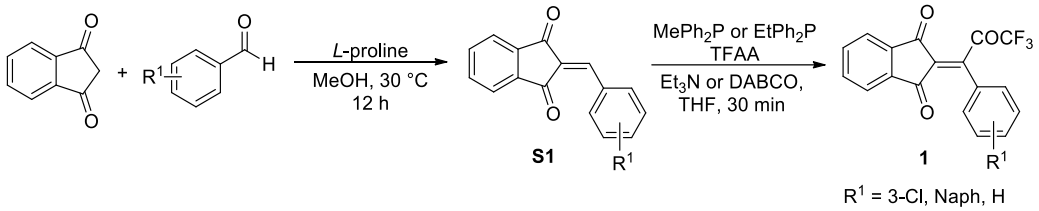
R = 4-BrC_6H_4

Entry	x (mol %)	Yield **4aa** (%)[b]	ee (%)[c]
1	20	91	99
2	10	92	99
3	5	80	99

[a]Unless otherwise specified, all the reactions were carried out using **1a** (0.1 mmol) and **2a** (1.1equiv.) with 20 mol % of **IX** and 4 Å molecular sieves (~40 mg) in diethyl ether (0.5 mL) and were stirred at 0 °C. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture using Ph_3CH as an internal standard. [c]Determined by HPLC analysis on a chiral stationary phase.

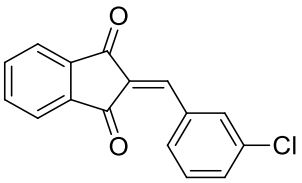
General experimental procedures and characterization data for new compounds:

General procedure A for the preparation of starting materials S1g and S1h



A dry and argon-flushed 50 mL round-bottomed flask equipped with a magnetic stir bar was sequentially charged with 1,3-indanedione (1.506 g, 10.0 mmol), *L*-proline (0.349 g, 0.3 equiv.), appropriately substituted benzaldehyde (1.1 equiv.) and methanol (20 mL). The reaction mixture was stirred for 12 hours at 30 ºC. Thereafter, the resulting slurry was filtered and the residue was washed with methanol until it was free from any residual starting materials to get the pure product **S1**.

2-(3-chlorobenzylidene)-1*H*-indene-1,3(2*H*)-dione (S1g)



Following the general procedure A, **S1g** was obtained using 3-chlorobenzaldehyde (1.546 g, 1.1 equiv.) as a yellow solid (85% yield, 2.280 g); R_f 0.83 (EtOAc/Hex = 1/1); mp.: 167.1-167.7 °C;

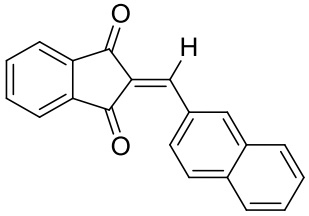
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.52 (s, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 7.94-8.05 (m, 2H), 7.78-7.86 (m, 2H), 7.76 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42 (pt, *J* = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 189.7, 188.8, 144.9, 142.6, 140.1, 135.7, 135.5, 134.8, 134.6, 133.3, 132.9, 132.2, 130.3, 130.0, 123.6, 123.5.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3093, 3060, 1687, 1613, 1590, 738;

HRMS (ESI) calcd for $C_{16}H_{10}O_2Cl$, $[M+H]^+$ 269.0369, found: 269.0372.

2-(naphthalen-2-ylmethylene)-1*H*-indene-1,3(2*H*)-dione (S1h)



Following the general procedure A, **S1h** was obtained using 2-naphthaldehyde (1.718 g, 1.1 equiv.) as a greenish solid (88% yield, 2.501 g); R_f 0.83 (EtOAc/Hex = 1/1); mp.: 232.9-233.8 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.94 (s, 1H), 8.61 (dd, *J* = 8.7 Hz, 1H), 8.08-7.99 (m, 4H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.86-7.79 (m, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H).

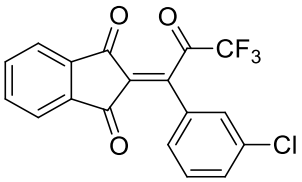
^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 190.5, 189.3, 147.2, 142.8, 140.3, 136.9, 135.6, 135.5, 135.3, 133.1, 131.0, 129.9, 129.4, 129.3, 129.1, 128.6, 127.9, 126.9, 123.49, 123.48.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3080, 3053, 1721, 1682, 1584, 729;

HRMS (ESI) calcd for $C_{20}H_{13}O_2$, $[M+H]^+$ 285.0916, found: 285.0917.

Typical procedure for the synthesis of 1g:

2-(1-(3-chlorophenyl)-3,3,3-trifluoro-2-oxopropylidene)-1*H*-indene-1,3(2*H*)-dione (1g)



A dry and nitrogen-flushed 25 mL round-bottomed flask, equipped with a magnetic stirring bar and a septum, was sequentially charged with a solution of **S1g** (403 mg, 1.5 mmol), $MePh_2P$ (29 μL, 10 mol %), TFAA (252.7 μL, 1.2 equiv.) and Et_3N (274.3 μL, 1.3 equiv.) in THF (7.5 mL). The reaction mixture was stirred for 30 minutes at 30 °C. Thereafter, the solvent was removed by evaporation *in vacuo*. Purification by flash chromatography furnished **1g** as a pale yellow solid (95% yield, 519.7 mg).

R_f 0.50 (EtOAc/Hex = 1/8); mp.: 124.6-125.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.08-7.99 (m, 2H), 7.95-7.88 (m, 2H), 7.67-7.64 (m, 1H), 7.56 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.52-7.42 (m, 2H).

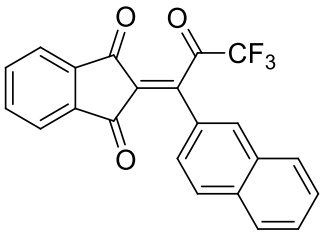
^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 189.2, 187.2 (q, *J* = 39.0 Hz), 185.5, 149.3, 143.5, 139.6, 137.0, 136.6, 135.1, 132.6, 131.6, 130.13, 130.10, 129.2, 128.3, 124.3, 115.2 (q, *J* = 291.5 Hz).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3072, 1746, 1697, 1588, 1217;

HRMS (EI) calcd for $C_{18}H_8ClF_3O_3$, [M] 364.0114, found: 364.0114.

Typical procedure for the synthesis of 1h:

2-(3,3,3-trifluoro-1-(naphthalen-2-yl)-2-oxopropylidene)-1*H*-indene-1,3(2*H*)-dione (1h)



A dry and nitrogen-flushed 25 mL round-bottomed flask, equipped with a magnetic stirring bar and a septum, was sequentially charged with a solution of **S1h** (426.5 mg, 1.5 mmol), $EtPh_2P$ (31 μL, 10 mol %), TFAA (253 μL, 1.2 equiv.) and Et_3N (274.3 μL, 1.3 equiv.) in THF (7.5 mL). The reaction mixture was stirred for 30 minutes at 30 °C. Thereafter, the solvent was removed by evaporation *in vacuo*. Purification by flash chromatography furnished **1h** as a pale yellow solid (35% yield, 199.7 mg).

R_f 0.80 (EtOAc /Hex = 1/1); mp.: 158.9-159.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.19 (s, 1H), 8.06-7.98 (m, 2H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.91-7.84 (m, 3H), 7.72 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.63 (td, *J* = 7.9, 1.3 Hz, 1H), 7.57 (td, *J* = 7.9, 1.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 189.8, 187.6 (q, *J* = 38.6 Hz), 186.0, 151.7, 143.5, 139.5, 136.7, 136.3, 135.3, 132.7, 132.3, 130.5, 129.6, 129.2, 128.6, 128.0, 127.3, 126.4, 125.0, 124.1,

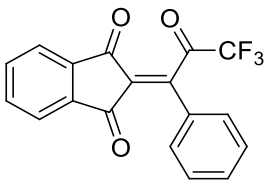
115.4 (q, J = 291.7 Hz).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 1744, 1733, 1696, 1618, 1214, 1152, 1069;

HRMS (ESI) calcd for $C_{22}H_{12}O_3F_3$, $[M+H]^+$ 381.0739, found: 381.0737.

Typical procedure for the synthesis of 1i:

2-(3,3,3-trifluoro-2-oxo-1-phenylpropylidene)-1*H*-indene-1,3(2*H*)-dione (1i)



A dry and nitrogen-flushed 25 mL round-bottomed flask, equipped with a magnetic stirring bar and a septum, was sequentially charged with a solution of **S1i** (70.3 mg, 1.5 mmol), $EtPh_2P$ (47 μL, 15 mol %), TFAA (271 μL, 1.3 equiv.) and DABCO (524 mg, 1.4 equiv.) in THF (7.5 mL) The reaction mixture was stirred for 30 minutes at 30 ºC. Thereafter, the solvent was removed by evaporation *in vacuo*. Purification by flash chromatography furnished **1i** as a pale yellow solid (5% yield, 24.8 mg).

R_f 0.50 (EtOAc/Hex = 1/8); mp.: 130.1-130.6 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.98-8.06 (m, 2H), 7.86-7.93 (m, 2H), 7.65 (dd, J = 8.0, 1.3 Hz, 2H), 7.56-7.63 (m, 1H), 7.48-7.56 (m, 2H).

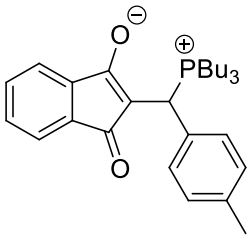
^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 189.6, 187.6 (q, J = 38.7 Hz), 185.9, 151.6, 143.5, 139.5, 136.8, 136.3, 132.9, 130.6, 128.9, 127.5, 124.13, 124.10, 115.3 (q, J = 291.7 Hz).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3070, 1745, 1693, 1618, 1219.

HRMS (EI) calcd for $C_{18}H_9F_3O_3$, [M] 330.0504, found: 330.0506.

Typical procedure for the preparation of S2j

1-oxo-2-(*p*-tolyl(tributylphosphonio)methyl)-1*H*-inden-3-olate (S2j)



A dry and argon-flushed 10 mL Schlenk flask equipped with a magnetic stir bar and a septum was sequentially charged with 2-(4-methylbenzylidene)-1*H*-indene-1,3(2*H*)-dione (124.1 mg, 0.5 mmol), THF (2.0 mL) and PBu_3 (1.1 equiv.). The reaction mixture was stirred for 10 min at 30 °C. Thereafter, solvent was removed by *in vacuo* and the residue was washed sequentially with pentane and diethyl ether until all the residual phosphine was removed to obtain pure **S2j** as a pale yellow solid (85% yield, 191.5 mg).

R_f 0.13 (EtOAc/Hex = 1/1); mp.: 151.0-151.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.49 (dd, J = 8.1, 2.0 Hz, 2H), 7.31-7.37 (m, 2H), 7.24-7.31 (m, 2H), 7.10 (d, J = 7.8 Hz, 2H), 4.83 (d, J = 17.5 Hz, 1H), 2.10-2.36 (m, 9H), 2.30 (s, 3H), 1.24-1.47 (m, 12H), 0.87 (t, J = 7.0 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 190.6 (d, J = 5.3 Hz), 139.6 (d, J = 5.2 Hz), 137.9 (d, J = 2.9 Hz), 132.5, 130.0 (d, J = 2.9 Hz), 129.9 (d, J = 4.7 Hz), 129.7 (d, J = 2.9 Hz, 118.1 (d, J = 2.9 Hz), 99.1, 35.3 (d, J = 44.1 Hz), 24.2 (d, J = 14.7 Hz), 24.1 (d, J = 5.1 Hz), 21.2, 19.9 (d, J = 44.4 Hz), 13.4.

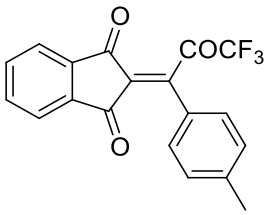
^{31}P NMR (200 MHz, $CDCl_3$) δ/ppm: 34.6.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3028, 2957, 2928, 2871, 1609, 1537, 1452, 1406, 1310, 719;

HRMS (ESI) calcd for $C_{29}H_{40}O_2P$, $[M+H]^+$ 451.2766, found: 451.2763.

Typical procedure for the synthesis of 1j:

2-(3,3,3-trifluoro-2-oxo-1-(*p*-tolyl)propylidene)-1*H*-indene-1,3(2*H*)-dione (1j)



A dry and nitrogen-flushed 10 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was sequentially charged with a solution of **S2j** (90.1 mg, 0.2 mmol), TFAA (66.7 μL, 2.4 equiv.) and Et_3N (72.4 μL, 2.6 equiv.) in THF (1 mL). The reaction mixture was stirred for 10 min at 30 ºC. Thereafter, the solvent was removed by evaporation *in vacuo*. Purification by flash chromatography (hexanes/dichloromethane: 1/1) furnished as yellow solid (25% yield, 17.2 mg).

R_f 0.45 (EtOAc/Hex = 1/5); mp.: 133.9-134.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.04-7.98 (m, 2H), 7.92-7.84 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H).

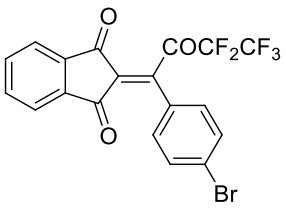
^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 189.9, 187.7 (q, *J* = 38.5 Hz), 186.1, 152.0, 144.5, 143.4, 139.3, 136.6, 136.2, 131.0, 129.75, 129.71, 124.6, 124.0, 115.2 (q, *J* = 291.7 Hz), 22.0.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 1742, 1687, 1600, 1585, 1220, 1136, 1061;

HRMS (ESI) calcd for $C_{19}H_{12}F_3O_3$, $[M+H]^+$ 345.0739, found: 345.0738.

Typical procedure for the synthesis of 1k:

2-(1-(4-bromophenyl)-3,3,4,4,4-pentafluoro-2-oxobutylidene)-1*H*-indene-1,3(2*H*)-dione (1k)



A dry and argon-flushed 10 mL Schlenk flask equipped with a magnetic stir bar and a septum was sequentially charged with 2-(4-bromobenzylidene)-1*H*-indene-1,3(2*H*)-dione (93.9 mg,

0.3 mmol), THF (1.5 mL), $EtPh_2P$ (6.3 μL, 10 mol %), pentafluoropropionic anhydride (72.5 μL, 1.2 equiv.) and Et_3N (55.4 μL, 1.3 equiv.). The reaction mixture was stirred for 10 minutes at 30 °C. Thereafter, the solvent was removed *in vacuo* and the residue was subjected to flash chromatography over silica gel to furnish **1k** as a yellow solid (70% yield, 96.4 mg); R_f 0.60 (EtOAc/Hex = 1/3);

mp.: 104.6-105.3 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.96-8.08 (m, 2H), 7.86-7.95 (m, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 189.4 (t, J = 30.2 Hz), 188.9, 185.7, 149.7, 143.3, 139.6, 136.9, 136.5, 132.1, 131.5, 131.3, 127.7, 126.0, 124.2, 124.1, 117.8 (qt, J = 288.0 Hz, 34.6 Hz), 107.0 (tq, J = 268.5 Hz, 38.3 Hz).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3070, 1736, 1697, 1586, 1488, 1218;

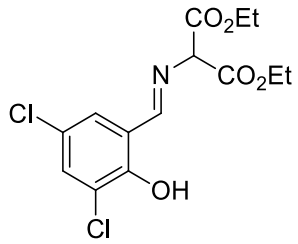
HRMS (EI) calcd for $C_{19}H_8BrF_5O_3$, [M] 457.9577, found: 457.9580.

General procedure B for the synthesis of 2c, 2e, 2g and 2h:

To a stirred solution of diethyl aminomalonate hydrochloride (3.000 g, 14.2 mmol) and H_2O (30 mL) in 50ml round-bottomed flask was added $NaHCO_3$ (1.310 g, 15.6 mmol) and stirred for 15 min. Then the reaction mixture was extracted with EtOAc (3x50 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under *in vacuo* to afford crude diethyl aminomalonate (2.302 g, 13.1 mmol) which was used without further purification.

Substituted salicylaldehyde was added to a solution of diethyl aminomalonate (2.302 g, 13.1 mmol) and $MgSO_4$ (7.86 g, 65.5 mmol) in CH_2Cl_2 (30 mL) and stirred for 48 hours. After completion of the reaction, $MgSO_4$ was removed by filtration and the filtrate was concentrated under reduced pressure to obtain crude **2**. If the product was solid, it was recrystallized from DCM/Hexanes to afford pure **2**. In case of liquids, the crude product was directly used without further purification.

(*E*)-diethyl 2-((3,5-dichloro-2-hydroxybenzylidene)amino)malonate (2c)



Following the general procedure B, **2c** was obtained from 3,5-dichloro-2-hydroxybenzaldehyde (2.50 g, 1.0 equiv.) and was recrystallized from DCM/Hexanes to afford **2c** as yellow solid (82% yield, 3.740 g); R_f 0.33 (DCM/Hex = 1/1); mp.: 105.0-105.3 °C.

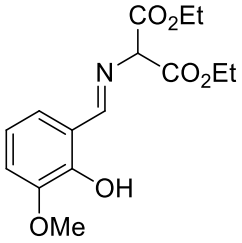
^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 13.5 (brs, 1H), 8.35 (s, 1H), 7.31 (d, J = 2.6 Hz, 1H), 7.13 (d, J = 2.6 Hz, 1H), 4.85 (s, 1H), 4.20 (qd, J = 7.0, 0.8 Hz, 4H), 1.22 (t, J = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 168.2, 165.5, 155.7, 132.8, 129.9, 123.1, 122.7, 119.6, 71.9, 62.6, 13.9.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 2988, 2919, 1746, 1637, 1452, 1239, 1180, 1121;

HRMS (ESI) calcd for $C_{14}H_{16}Cl_2NO_5$, $[M+H]^+$ 348.0406, found: 348.0407.

(*E*)-diethyl 2-((2-hydroxy-3-methoxybenzylidene)amino)malonate (2e)



Following the general procedure B, **2e** was obtained from 2-hydroxy-3-methoxybenzaldehyde (1.59 g, 0.8 equiv.) as yellow oil (85% yield, 3.441 g); R_f 0.20 (DCM/Hex = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 13.0 (brs, 1H), 8.41 (s, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.88 (dd, J = 8.0, 1.3 Hz, 1H), 6.79 (pt, J = 8.0 Hz, 1H), 4.79 (s, 1H), 4.22 (q, J = 7.1 Hz, 4H), 3.84 (s, 3H), 1.24 (t, J = 7.1 Hz, 6H).

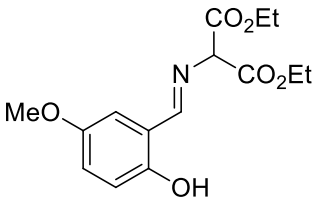
^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 169.9, 166.2, 151.4, 148.6, 123.9, 118.7, 118.6, 115.2,

72.9, 62.6, 56.3, 14.1.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 2984, 1742, 1629, 1466, 1254;

HRMS (EI) calcd for $C_{15}H_{19}NO_6$, [M] 309.1212, found: 309.1212.

(*E*)-diethyl 2-((2-hydroxy-5-methoxybenzylidene)amino)malonate (2g)



Following the general procedure B, **2g** was obtained from 2-hydroxy-5-methoxybenzaldehyde (1.59 g, 0.8 equiv.) as a yellow oil (88% yield, 3.562 g); R_f 0.20 (DCM/Hex = 1/1).

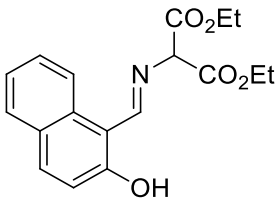
^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 12.2 (brs, 1H), 8.44 (s, 1H), 6.98 (dd, *J* = 9.2, 3.0 Hz, 1H), 6.96 (d, *J* = 9.2 Hz, 1H), 6.82 (d, *J* = 3.0 Hz, 1H), 4.86 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 4H), 3.78 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 169.7, 166.3, 155.5, 152.3, 121.0, 118.3, 118.2, 115.4, 72.9, 62.6, 56.1, 14.1.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 2985, 1741, 1636, 1590, 1492, 1273;

HRMS (EI) calcd for $C_{15}H_{19}NO_6$, [M] 309.1212, found: 309.1212.

(*E*)-diethyl 2-(((2-hydroxynaphthalen-1-yl)methylene)amino)malonate (2h)



Following the general procedure B, **2h** was obtained from 2-hydroxy-1-naphthaldehyde (1.69 g, 0.75 equiv.) as yellow oil (79% yield, 3.41 g); R_f 0.13 (DCM/Hex = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 14.57 (brs, 1H), 9.23 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.50 (pt, *J* = 7.8 Hz, 1H), 7.33 (pt, *J* = 7.4

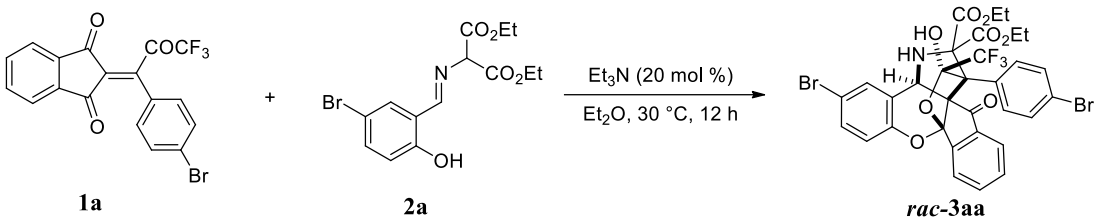
Hz, 1H), 7.11 (d, *J* = 9.2 Hz, 1H), 4.96 (s, 1H), 4.32 (q, *J* = 7.2 Hz, 4H), 1.33 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 166.9, 166.2, 164.0, 136.1, 133.1, 129.3, 128.1, 127.5, 123.6, 121.2, 119.1, 108.7, 71.4, 62.7, 14.1.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 2984, 1743, 1625, 1474, 1227.

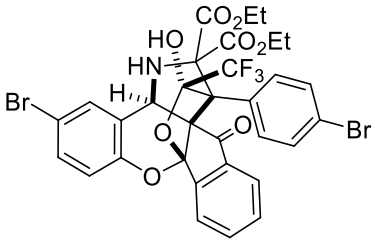
HRMS (EI) calcd for $C_{18}H_{19}NO_5$, [M] 329.1263, found: 329.1265.

Typical procedure for the synthesis of intermediate *rac*-3aa:



A screw-capped glass vial equipped with a magnetic stirring bar was sequentially charged with **1a** (40.9 mg, 0.1 mmol), **2a** (39.4 mg, 1.1 equiv.), diethyl ether (0.5 mL) and Et_3N (2.7 μL, 20 mol %) and stirred at 30 °C for 12 hours. The progress of the reaction was monitored by using TLC and ^{1}H NMR data analysis. After the completion of reaction, solvent was removed in vacuo and the residue was subjected to flash column chromatography on silica gel (EtOAc/ hexanes = 1:10) to obtain the adduct *rac*-**3aa**.

(1*R*,3a*R*,8a*R*,13a*R*,15*R*)-diethyl 5-bromo-1-(4-bromophenyl)-15-hydroxy-13-oxo-15-(trifluoromethyl)-3,3a-dihydro-1*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[4,3-b]pyrrole-2,2(13*H*)-dicarboxylate (*rac*-3aa)



rac-**3aa** was obtained as white solid (15% yield, 11.9 mg); R_f 0.50 (EtOAc/Hex = 1/3); mp.: 200.3-201.2 °C.

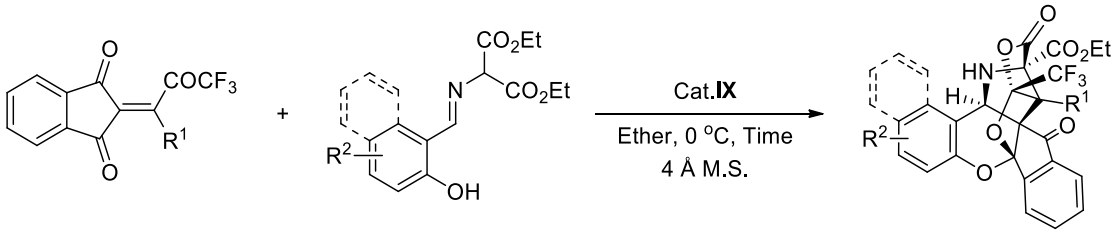
^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.99 (d, J = 7.6 Hz, 2H), 7.82 (td, J = 7.6, 1.3 Hz, 1H), 7.57-7.72 (m, 3H), 7.39 (brs, 1H), 7.32 (dd, J = 8.4, 2.3 Hz, 1H), 7.29-7.22 (m, 1H), 7.07 (brs, 1H), 6.89 (d, J = 8.6 Hz, 1H), 6.44 (brs, 1H), 4.73 (brs, 1H), 4.50-4.22 (m, 4H), 3.53 (brs, 1H), 1.36 (t, J = 7.1 Hz, 3H), 1.25 (t, J =7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 195.2, 166.8, 166.7, 151.2, 144.1, 137.8, 137.3, 134.2, 132.5, 132.3, 132.0, 130.6, 129.5, 125.2, 124.1, 123.4, 122.4, 121.1, 120.5 (q, J = 287.2 Hz), 115.9, 114.8, 112.1 (q, J = 31.5 Hz), 78.7, 75.8, 63.2, 63.1, 57.2, 14.0, 13.8.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3453, 3297, 2993, 1724, 1603, 1486, 1298, 1215, 1174, 1137.

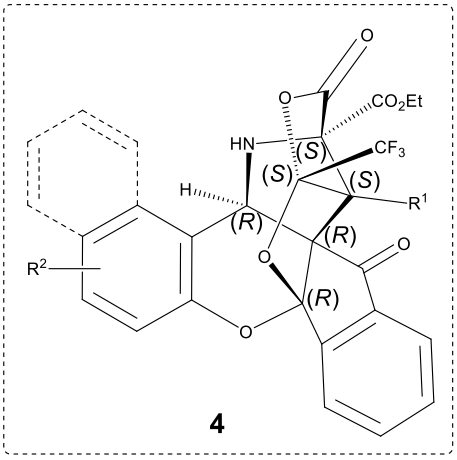
HRMS (ESI) calcd for $C_{32}H_{25}Br_2F_3NO_8$, $[M+H]^+$ 765.9899, found: 765.9899.

General procedure C for the synthesis of cascade reaction product 4:



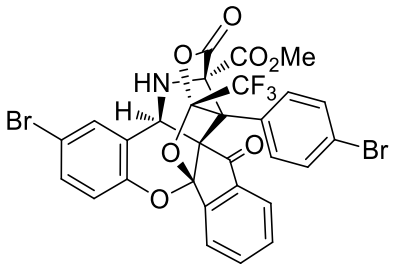
1 2 4

A capped glass vial equipped with magnetic stir bar was charged with **1** (0.1 mmol), **2** (1.1 equiv.), 4 Å molecular sieves (~40 mg) and catalyst **IX** (6.3 mg, 10 mol %). Diethyl ether (0.5 mL) was then added and the reaction mixture was stirred at 0 °C. The progress of the reaction was monitored by TLC and ^{1}H NMR analysis. After the completion of reaction, the reaction mixture was quenched with 2N HCl (0.5 mL) and extracted with either ethyl acetate or dichloromethane (3 x 0.5 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and then concentrated *in vacuo*. The residue thus obtained was purified by flash column chromatography on silica gel (hexanes/ethyl acetate) to afford pure product **4**.



4

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-methyl 6-bromo-14b-(4-bromophenyl)-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4aa')



Following the general procedure C, using **1a** (40.9 mg, 0.1 mmol) and **2a'** (36.3 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 96 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4aa'** as white solid (88% yield, 62.2 mg); R_f 0.88 (EtOAc/Hex = 1/1); mp.: 152.0-152.9 °C; $[\alpha]_D^{23}$ = 46.49 (c = 0.5 in CH_2Cl_2); **HPLC**: 98% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 248 nm, t_{major} = 12.12 min, t_{minor} = 20.13 min;

^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.11 (d, *J* = 7.7 Hz, 1H), 7.93 (td, *J* = 7.5, 0.9 Hz, 1H), 7.86 (dd, *J* = 2.2, 0.9 Hz, 1H), 7.63 (pt, *J* = 7.5 Hz, 1H), 7.40-7.46 (m, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 2H), 4.76 (d, *J* = 5.7 Hz, 1H), 4.58 (d, *J* = 5.7 Hz, 1H), 3.69 (s, 3H).

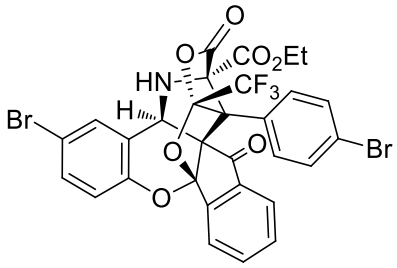
^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.2, 168.0, 166.2, 149.4, 147.8, 137.5, 135.7, 133.6, 132.3, 131.8, 131.5, 129.0, 128.7 (q, *J* = 2.9 Hz), 124.7, 123.7, 123.6, 122.9, 120.6 (q, *J* = 286.5

Hz), 119.9, 116.9, 111.2, 109.9 (q, *J* = 35.8 Hz), 81.1, 79.7, 74.3, 56.5, 54.1.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3339, 2956, 1816, 1754, 1604, 1475, 1210, 1050.

HRMS (ESI) calcd for $C_{29}H_{17}Br_2F_3NO_7$, $[M+H]^+$ 705.9324, found: 705.9323.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 6-bromo-14b-(4-bromophenyl)-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4aa)



Following the general procedure C, using **1a** (40.9 mg, 0.1 mmol) and **2a** (39.4 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 48 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4aa** as white solid (92% yield, 66.4 mg); R_f 0.38 (EtOAc/Hex = 1/8); mp.: 119.4-120.4 °C; $[\alpha]_D^{30}$ = 235.96 (c = 0.5 in CH_2Cl_2); **HPLC**: 99% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 278 nm, t_{major} = 12.37 min, t_{minor} = 16.78 min.

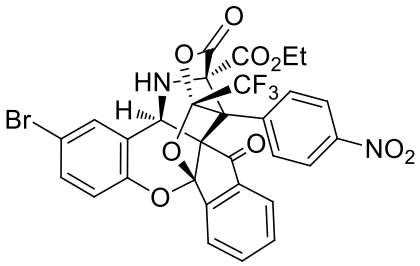
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.11 (d, *J* = 7.8 Hz, 1H), 7.92 (pt, *J* = 7.8 Hz, 1H), 7.86 (dd, *J* = 2.2, 1.3 Hz, 1H), 7.63 (pt,, *J* = 7.8 Hz, 1H), 7.40-7.46 (m, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 4.76 (d, *J* = 5.7 Hz, 1H), 4.58 (d, *J* = 5.7 Hz, 1H), 4.22 (dq, *J* = 10.7 Hz, 7.2 Hz, 1H), 4.13 (dq, *J* = 10.7 Hz, 7.2 Hz, 1H), 1.03 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.3, 168.1, 165.7, 149.4, 147.8, 137.5, 135.7, 133.6, 132.3, 131.8, 131.4, 129.0, 128.8 (q, *J* = 2.9 Hz), 124.7, 123.7, 123.6, 123.0, 120.6 (q, *J* = 286.6 Hz), 119.9, 116.9, 111.2, 109.9 (q, *J* = 35.7 Hz), 81.2, 79.8, 74.5, 63.9, 56.5, 13.4.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3358, 1816, 1748, 1473, 1210, 1050.

HRMS (ESI) calcd for $C_{30}H_{19}Br_2F_3NO_7$, $[M+H]^+$ 719.9480, found: 719.9477.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 6-bromo-14b-(4-nitrophenyl)-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4ba)



Following the general procedure C, using **1b** (37.5 mg, 0.1 mmol) and **2a** (39.4 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 72 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ba** as white solid (79% yield, 54.3 mg); R_f 0.24 (EtOAc/Hex = 1/8); mp.: 246.9-247.6 °C; $[\alpha]_D^{30}$ = 95.288 (c = 0.5 in CH_2Cl_2);.

HPLC: 99% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 278 nm, t_{major} = 18.25 min, t_{minor} = 24.20 min.

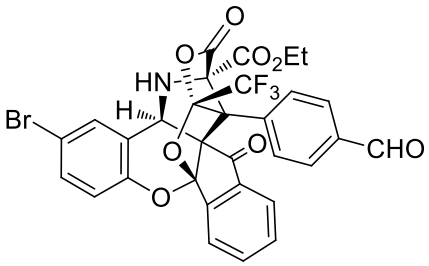
^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.14 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.96 (pt, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 2H), 7.83-7.87 (m, 1H), 7.65 (pt, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 1H), 4.78 (d, *J* = 5.3 Hz, 1H), 4.60 (d, *J* = 5.3 Hz, 1H), 4.24 (dq, *J* = 10.7 Hz, 7.2 Hz, 1H), 4.14 (dq, *J* = 10.7 Hz, 7.2 Hz, 1H), 1.03 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.2, 167.8, 165.5, 149.3, 147.9, 147.7, 137.9, 137.1, 135.4, 133.7, 132.6, 131.7, 128.5 (q, *J* = 3.1 Hz), 124.8, 123.7, 123.2, 122.7, 120.5 (q, *J* = 286.8 Hz), 120.0, 117.1, 111.3, 109.8 (q, *J* = 36.0 Hz), 80.9, 79.6, 74.5, 64.1, 56.5, 13.4.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3341, 1816, 1748, 1603, 1527, 1474, 1352, 1210, 1051.

HRMS (ESI) calcd for $C_{30}H_{19}BrF_3N_2O_9$, $[M+H]^+$ 687.0226, found: 687.0228.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 6-bromo-14b-(4-formylphenyl)-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4ca)



Following the general procedure C, using **1c** (35.8 mg, 0.1 mmol) and **2a** (39.4 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 78 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:8) to obtain **4ca** as white solid (78% yield, 52.3 mg); R_f 0.25 (EtOAc/Hex = 1/4); mp.: 153.5-154.9 °C; $[\alpha]_D^{30}$ = 74.928 (c = 0.5 in CH_2Cl_2); **HPLC**: 99% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.00 mL/min, λ= 278 nm, t_{minor} = 36.85 min, t_{major} = 49.82 min.

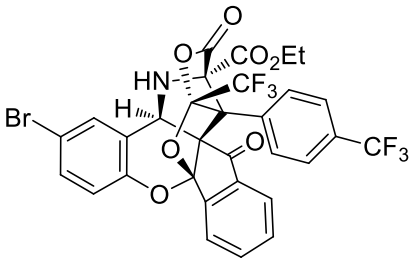
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 9.93 (s, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.94 (td, *J* = 7.6 Hz, 1.3 Hz, 1H), 7.86 (dd, *J* = 2.2, 1.3 Hz, 1H), 7.62 (td, *J* = 8.0, 0.9 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.44 (ddd, *J* = 8.4, 2.2, 0.9 Hz, 1H), 7.35 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 1H), 4.78 (d, *J* = 5.7 Hz, 1H), 4.62 (d, *J* = 5.7 Hz, 1H), 4.23 (dq, *J* = 10.6 Hz, 7.1 Hz, 1H), 4.13 (dq, *J* = 10.6 Hz, 7.1 Hz, 1H), 1.01 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.2, 191.1, 168.0, 165.6, 149.4, 147.8, 137.7, 136.3, 136.1, 135.6, 133.7, 132.4, 131.8, 129.1, 128.0 (q, *J* = 3.3 Hz), 124.8, 123.6, 122.9, 120.6 (q, *J* = 286.8 Hz), 120.0, 117.0, 111.3, 110.0 (q, *J* = 35.9 Hz), 81.4, 79.7, 74.7, 64.0, 56.6, 13.4.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3453, 2993, 1815, 1749, 1610, 1475, 1213, 1051.

HRMS (ESI) calcd for $C_{31}H_{20}BrF_3NO_8$, $[M+H]^+$ 670.0324, found: 670.0323.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 6-bromo-3,14-dioxo-1-(trifluoromethyl)-14b-(4-(trifluoromethyl)phenyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4da)



Following the general procedure C, using **1d** (39.8 mg, 0.1 mmol) and **2a** (39.4 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 24 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:8) to obtain **4da** was as white solid (94% yield, 66.8 mg); R_f 0.42 (EtOAc/Hex = 1/8); mp.: 127.9-128.9 °C; $[\alpha]_D^{30}$ = 50.368 (c = 0.5 in CH_2Cl_2);

HPLC: 96% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.00 mL/min, λ= 278 nm, t_{minor} = 8.75 min, t_{major} = 19.20 min.

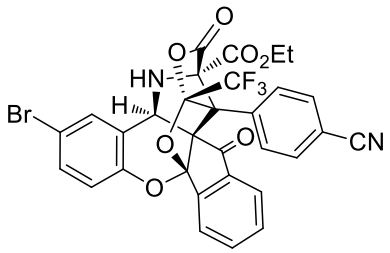
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.13 (d, *J* = 7.5 Hz, 1H), 7.94 (td, *J* = 7.5, 0.9 Hz, 1H), 7.87 (dd, *J* = 2.2, 0.9 Hz, 1H), 7.63 (td, *J* = 7.5, 0.9 Hz, 1H), 7.44 (dd, *J* = 8.8 Hz, 2.6 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 1H), 4.78 (d, *J* = 5.7 Hz, 1H), 4.61 (dd, *J* = 5.7 Hz, 2.2 Hz, 1H), 4.23 (dq, *J* = 10.6 Hz, 7.1 Hz, 1H), 4.13 (dq, *J* = 10.6 Hz, 7.1 Hz, 1H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.2, 168.0, 165.6, 149.4, 147.8, 137.6, 135.6, 134.1, 133.6, 132.4, 131.8, 131.2 (q, *J* = 33.0 Hz), 127.8 (q, *J* = 3.2 Hz), 125.1 (q, *J* = 3.7 Hz), 124.7, 123.5, 123.46 (q, *J* = 272.4 Hz), 122.9, 120.6 (q, *J* = 286.3 Hz), 120.0, 117.0, 111.3, 109.9 (q, *J* = 35.8 Hz), 81.2, 79.8, 74.5, 63.9, 56.5, 13.3.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3350, 1817, 1749, 1607, 1474, 1331, 1212, 1172, 1133, 1051.

HRMS (ESI) calcd for $C_{31}H_{19}BrF_6NO_7$, $[M+H]^+$ 710.0249, found: 710.0253.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 6-bromo-14b-(4-cyanophenyl)-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4ea)



Following the general procedure C, using **1e** (35.5 mg, 0.1 mmol) and **2a** (39.4 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 78 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ea** as white solid (70% yield, 46.7 mg); R_f 0.36 (EtOAc/Hex = 1/4); mp.: 290.2-291.3 °C; $[\alpha]_D^{30}$ = 112.528 (c = 0.5 in CH_2Cl_2).

HPLC: 99% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 278 nm, t_{minor} = 44.65 min, t_{major} = 89.58 min.

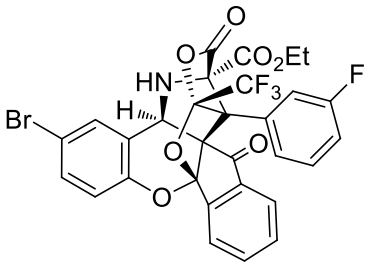
^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.13 (d, *J* = 7.5 Hz, 1H), 7.95 (pt, *J* = 7.5 Hz, 1H), 7.85 (s, 1H), 7.65 (pt, *J* = 7.5 Hz, 1H), 7.44 (dd, *J* = 8.8 Hz, 2.2 Hz, 1H), 7.42-7.34 (m, 3H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 1H), 4.78 (d, *J* = 5.3 Hz, 1H), 4.61 (d, *J* = 5.3 Hz, 1H), 4.23 (dq, *J* = 10.8 Hz, 7.2 Hz, 1H), 4.13 (dq, *J* = 10.8 Hz, 7.2 Hz, 1H), 1.02 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.1, 167.9, 165.5, 149.3, 147.8, 137.8, 135.4, 135.2, 133.6, 132.5, 131.8, 131.7, 128.0 (q, *J* = 3.2 Hz), 124.8, 123.6, 122.8, 120.5 (q, *J* = 285.6 Hz), 120.0, 117.6, 117.0, 113.2, 111.3, 109.8 (q, *J* = 35.7 Hz), 81.0, 79.6, 74.4, 64.0, 56.4, 13.3.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3342, 2234, 1814, 1750, 1734, 1609, 1474, 1212, 1051.

HRMS (ESI) calcd for $C_{31}H_{19}BrF_3N_2O_7$, $[M+H]^+$ 667.0328, found: 667.0330.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 6-bromo-14b-(3-fluorophenyl)-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4fa)



Following the general procedure C, using **1f** (34.8 mg, 0.1 mmol) and **2a** (39.4 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 48 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4fa** as white solid (94% yield, 62.1 mg); R_f 0.28 (EtOAc/Hex = 1/8); mp.: 192.2-193.3 °C; $[\alpha]_D^{30}$ = 82.048 (c = 0.5 in CH_2Cl_2);.

HPLC: 96% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 278 nm, t_{major} = 12.52 min, t_{minor} = 15.00 min.

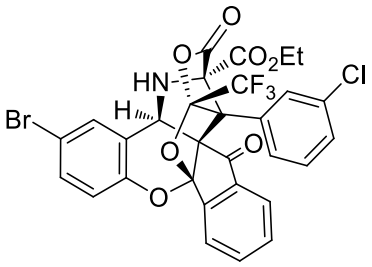
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.12 (d, *J* = 8.0 Hz, 1H), 7.93 (td, *J* = 7.6, 1.2 Hz, 1H), 7.87 (dd, *J* = 2.2, 0.9 Hz, 1H), 7.62 (pt, *J* = 7.6 Hz, 1H), 7.36-7.45 (m, 2H), 7.12-7.04 (m, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.93 (td, *J* = 8.0, 2.2 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.54-6.61 (m, 1H), 4.76 (d, *J* = 5.7 Hz, 1H), 4.60 (d, *J* = 5.7 Hz, 1H), 4.27-4.12 (m, 2H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.0, 168.1, 165.6, 162.1 (d, *J* = 248.0 Hz), 149.4, 147.6, 137.5, 135.8, 133.5, 132.2, 132.1 (d, *J* = 7.3 Hz), 131.9, 129.9 (d, *J* = 8.2 Hz), 124.7, 123.4, 123.0, 122.96 (q, *J* = 2.9 Hz), 120.6 (q, *J* = 286.6 Hz), 119.9, 116.9, 116.1 (d, *J* = 20.6 Hz), 115.1 (dq, *J* = 24.8 Hz, 3.4 Hz), 111.3, 109.9 (q, *J* = 35.8 Hz), 81.3, 79.8, 74.6, 63.9, 56.5, 13.3;

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3342, 1815, 1749, 1593, 1474, 1210, 1050.

HRMS (ESI) calcd for $C_{30}H_{19}BrF_4NO_7$, $[M+H]^+$ 660.0281, found: 660.0286.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 6-bromo-14b-(3-chlorophenyl)-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4ga)



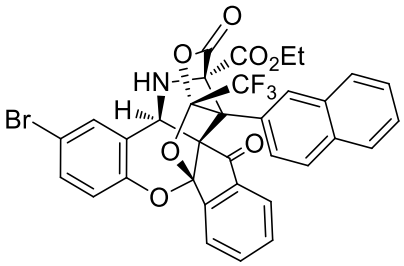
Following the general procedure C, using **1g** (36.5 mg, 0.1 mmol) and **2a** (39.4 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 48 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ga** as white solid (97% yield, 65.6 mg); R_f 0.30 (EtOAc/Hex = 1/8); mp.: 178.4-179.0 °C; $[\alpha]_D^{30}$ = 142.16 (c = 0.5 in CH_2Cl_2). **HPLC**: 99% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 278 nm, t_{major} = 12.14 min, t_{minor} = 14.05 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.13 (d, *J* = 7.6 Hz, 1H), 7.94 (pt, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 1.5 Hz, 1H), 7.65 (pt, *J* = 8.0 Hz, 1H), 7.42 (d, *J*= 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.05 (pt, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 4.75 (s, 1H), 4.57 (brs, 1H), 4.27-4.15 (m, 2H), 1.05 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.1, 168.1, 165.7, 149.4, 147.6, 137.5, 135.9, 134.5, 133.5, 132.3, 131.9, 131.7, 129.5, 129.2, 128.1 (q, *J* = 3.4 Hz), 125.1, 124.7, 123.5, 123.0, 120.6 (q, *J* = 286.7 Hz), 119.9, 116.9, 111.3, 109.9 (q, *J* = 35.9 Hz), 81.2, 79.6, 74.6, 63.9, 56.5, 13.4; **IR** (KBr) $\tilde{\nu}$ (cm^{-1}): 3327, 2982, 1818, 1733, 1475, 1221, 1055.

HRMS (ESI) calcd for $C_{30}H_{19}BrClF_3NO_7$, $[M+H]^+$ 675.9986, found: 675.9986.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 6-bromo-14b-(naphthalen-2-yl)-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4ha)



Following the general procedure C, using **1h** (38.0 mg, 0.1 mmol) and **2a** (39.4 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 72 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ha** as white solid (73% yield, 50.5 mg); R_f 0.13 (EtOAc/Hex = 1/9); mp.: 151.8-152.6 °C; $[\alpha]_D^{23}$ = 36.08 (c = 0.5 in CH_2Cl_2). **HPLC**: 98% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 248 nm, t_{major} = 14.12 min, t_{minor} = 19.02 min.

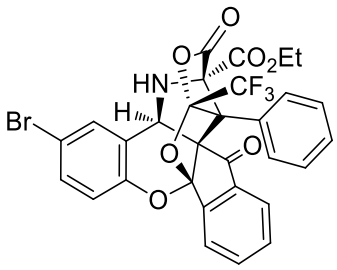
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.17 (d, *J* = 7.9 Hz, 1H), 7.97-7.90 (m, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.32-7.58 (m, 6H), 7.30 (s, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.02-6.95 (m, 2H), 4.78 (d, *J* = 6.2 Hz, 1H), 4.70 (d, *J* = 6.2 Hz, 1H), 4.23 (dq, *J* = 10.6 Hz, 7.1 Hz, 1H), 4.13 (dq, *J* = 10.6 Hz, 7.1 Hz, 1H), 0.96 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.1, 168.4, 166.1, 149.5, 147.8, 137.2, 136.1, 133.5, 132.6, 132.3, 132.0, 128.2, 127.9, 127.5, 127.46, 127.1, 127.0, 124.7, 124.0 (q, *J* = 2.4 Hz), 123.5, 123.2, 120.8 (q, *J* = 286.1 Hz), 119.9, 116.9, 111.4, 110.2 (q, *J* = 35.7 Hz), 81.9, 79.9, 75.0, 63.8, 56.5, 13.3.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3340, 1815, 1748, 1602, 1474, 1208, 1049.

HRMS (ESI) calcd for $C_{34}H_{22}BrF_3NO_7$, $[M+H]^+$ 692.0532, found: 692.0540.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 6-bromo-3,14-dioxo-14b-phenyl-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4ia)



Following the general procedure C, using **1i** (33.0 mg, 0.1 mmol) and **2a** (39.4 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 140 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ia** as white solid (88% yield, 56.5 mg); R_f 0.25 (EtOAc/Hex = 1/8); mp.: 225.4-226.8 °C; $[\alpha]_D^{30}$ = 63.728 (c = 0.5 in CH_2Cl_2).

HPLC: 94% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 278 nm, t_{minor} = 42.30 min, t_{major} = 72.99 min.

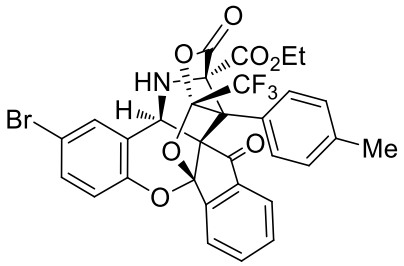
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.11 (d, *J* = 7.9 Hz, 1H), 7.91 (td, *J* = 7.5, 0.9 Hz, 1H), 7.90 (dd, *J* = 2.2, 0.9 Hz, 1H), 7.59 (td, *J* = 7.9 Hz, 0.9 Hz 1H), 7.43 (ddd, *J* = 8.8 Hz, 2.2, 0.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.20 (pt, *J* = 7.4 Hz, 1H), 7.02-7.09 (m, 2H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.76 (d, *J* = 6.0 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 1H), 4.24-4.09 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.3, 168.4, 165.9, 149.5, 147.8, 137.2, 136.0, 133.4, 132.0, 131.9, 129.9, 129.0, 128.3, 127.2 (q, *J* = 2.9 Hz), 124.6, 123.4, 123.2, 120.8 (q, *J* = 286.9 Hz), 119.9, 116.9, 111.3, 110.2 (q, *J* = 35.7 Hz), 81.8, 79.9, 74.7, 63.7, 56.5, 13.3.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3336, 1814, 1749, 1604, 1474, 1211, 1050.

HRMS (ESI) calcd for $C_{30}H_{20}BrF_3NO_7$, $[M+H]^+$ 642.0375, found: 642.0372.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 6-bromo-3,14-dioxo-14b-(p-tolyl)-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4ja)



Following the general procedure C, using **1j** (34.4 mg, 0.1 mmol) and **2a** (39.4 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 72 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:8) to obtain **4ja** as white solid (66% yield, 43.3 mg); R_f 0.32 (EtOAc/Hex = 1/5); mp.: 264.2-264.9 °C; $[\alpha]_D^{23}$ = 33.31 (c = 0.5 in CH_2Cl_2); **HPLC**: 96% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 248 nm, t_{major} = 17.45 min, t_{minor} = 20.88 min.

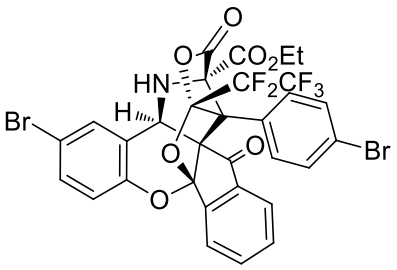
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.10 (d, *J* = 8.0 Hz, 1H), 7.94-7.88 (m, 2H), 7.60 (td, *J* = 8.0, 0.9 Hz 1H), 7.42 (ddd, *J* = 8.8, 2.7, 0.9 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 4.75 (d, *J* = 6.1 Hz, 1H), 4.60 (d, *J* = 6.1 Hz, 1H), 4.21 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.13 (dq, *J* = 10.6, 7.1 Hz, 1H), 2.23 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.4, 168.5, 166.0, 149.5, 147.8, 139.0, 137.2, 136.0, 133.4, 132.0, 128.9, 127.1 (q, *J* = 3.0 Hz), 126.7, 124.6, 123.5, 123.2, 120.7 (q, *J* = 286.6 Hz), 119.9, 116.8, 111.2, 110.2 (q, *J* = 35.5 Hz), 81.7, 79.9, 74.7, 63.7, 56.5, 21.0, 13.3.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3325, 2972, 1820, 1747, 1606, 1474, 1206, 1051.

HRMS (ESI) calcd for $C_{31}H_{22}BrF_3NO_7$, $[M+H]^+$ 656.0532, found: 656.0532.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 6-bromo-14b-(4-bromophenyl)-3,14-dioxo-1-(perfluoroethyl)-3,3a,4,4a,14,14b-hexahydro-1H-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4ka)



Following the general procedure C, using **1k** (45.9 mg, 0.1 mmol) and **2a** (39.4 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 144 hours, and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ka** as white solid (27% yield, 20.8 mg); R_f 0.60 (EtOAc/Hex = 1/3) mp.: 140.5-141.4 °C; $[\alpha]_D^{20}$ = 36.67 (c = 0.5 in CH_2Cl_2).

HPLC: 94% ee, Chiralpak IA column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 248 nm, t_{minor} = 22.99 min, t_{major} = 44.60 min.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.10 (d, *J* = 8.0 Hz, 1H), 7.92 (td, *J* = 7.6, 0.7 Hz, 1H), 7.86 (dd, *J* = 2.2, 1.3 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.38-7.46 (m, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.75 (d, *J* = 5.7 Hz, 1H), 4.60 (d, *J* = 5.7 Hz, 1H), 4.23 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.11 (dq, *J* = 10.6, 7.1 Hz, 1H), 1.02 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.2, 167.9, 165.6, 149.4, 147.8, 137.5, 135.6, 133.6, 132.2, 131.8, 131.4, 129.6, 128.7, 128.6, 124.6, 123.6, 123.3, 122.9, 119.9, 118.1 (qt, *J* = 288.8, 35.7 Hz), 116.9, 111.9 (tq, *J* = 269.3, 38.0 Hz), 111.5, 110.5, 110.3, 110.2, 109.9, 109.2 (q, *J* = 37.7 Hz), 82.7, 79.5, 74.0, 63.9, 56.4, 13.3.

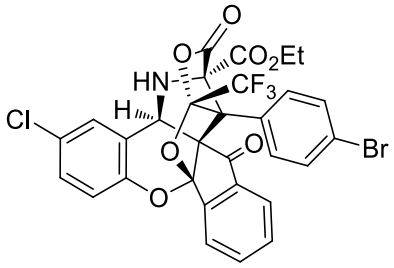
^{19}F NMR (376 MHz, C_6H_5F) *δ*/ppm: -80.1, -106.7 (d, *J* = 275.4 Hz), -121.0 (d, *J* = 275.2 Hz).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3337, 2986, 1819, 1750, 1734, 1603, 1475, 1232;

HRMS (ESI) calcd for $C_{31}H_{19}Br_2F_5NO_7$, $[M+H]^+$ 769.9448, found: 769.9449.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 14b-(4-bromophenyl)-6-chloro-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-

***b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4ab)**



Following the general procedure C, using **1a** (40.9 mg, 0.1 mmol) and **2b** (34.5 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 44 hours, and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ab** as white solid (88% yield, 59.6 mg); R_f 0.38 (EtOAc/Hex = 1/8); mp.: 213.7-214.9 °C; $[\alpha]_D^{30}$ = 111.488 (c = 0.5 in CH_2Cl_2);

HPLC: 99% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 278 nm, t_{major} = 11.24 min, t_{minor} = 15.60 min.

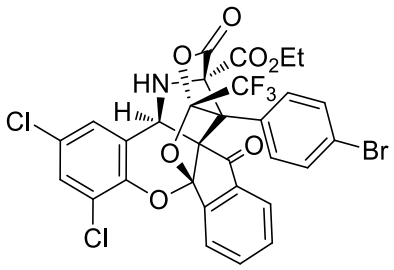
^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.11 (d, *J* = 7.7 Hz, 1H), 7.92 (td, *J* = 7.5, 0.8 Hz, 1H), 7.72 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.63 (td, *J* = 7.5, 0.9 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.28 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 2H), 4.75 (d, *J* = 5.8 Hz, 1H), 4.58 (d, *J* = 5.8 Hz, 1H), 4.22 (dq, *J* = 10.7, 7.2 Hz, 1H), 4.13 (dq, *J* = 10.7, 7.2 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.3, 168.2, 165.7, 148.9, 147.8, 137.5, 135.7, 132.3, 131.4, 130.6, 129.6, 129.0, 128.9, 128.8 (q, *J* = 2.9 Hz), 124.7, 123.6, 123.55, 122.6, 120.6 (q, *J* = 278.0 Hz), 119.6, 111.3, 109.9 (q, *J* = 35.9 Hz), 81.2, 79.8, 74.4, 63.9, 56.6, 13.4.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3348, 1815, 1749, 1734, 1602, 1475, 1211, 1050.

HRMS (ESI) calcd for $C_{30}H_{19}BrClF_3NO_7$, $[M+H]^+$ 675.9986, found: 675.9993.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 14b-(4-bromophenyl)-6,8-dichloro-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4ac)



Following the general procedure C, using **1a** (40.9 mg, 0.1 mmol) and **2c** (38.3 mg, 1.1 equiv.) as the substrates and either DCM or diethyl ether as solvent, the reaction mixture was stirred for 72 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ac** as a white solid (83% yield, 59.0 mg for reaction in DCM; 70% yield, 49.8 mg for reaction in Et_2O); R_f 0.20 (EtOAc/Hex = 1/9); mp.: 114.7-115.4 °C; $[\alpha]_D^{23}$ = 30.88 (c = 0.5 in CH_2Cl_2).

HPLC: 98% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 278 nm, t_{major} = 12.24 min, t_{minor} = 18.73 min (for product obtained using diethyl ether as reaction solvent); 92% ee, t_{major} = 11.96 min, t_{minor} = 18.33 min (product obtained using CH_2Cl_2 as reaction solvent).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.18 (d, J = 7.8 Hz, 1H), 7.95 (t, J = 7.5 Hz, 1H), 7.69-7.62 (m, 2H), 7.43 (d, J = 7.8 Hz, 1H), 7.40 (d, J = 1.9 Hz, 1H), 7.20 (d, J= 8.7 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 4.76 (d, J = 6.0 Hz, 1H), 4.61 (d, J = 6.0 Hz, 1H), 4.23 (dq, J = 10.7 Hz, 7.1 Hz, 1H), 4.14 (dq, J = 10.7 Hz, 7.1 Hz, 1H), 1.03 (t, J = 7.2 Hz, 3H).

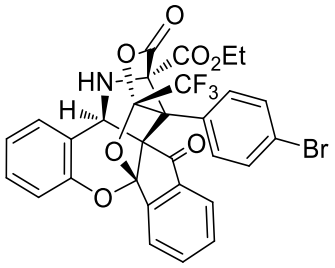
^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 195.8, 167.8, 165.4, 147.2, 144.9, 137.6, 135.6, 132.3, 131.3, 130.7, 129.2, 128.7 (q, J = 3.4 Hz), 127.3, 124.7, 124.2, 124.0, 123.5, 120.3 (q, J = 286.5 Hz), 111.2, 109.9 (q, J = 36.2 Hz), 81.1, 79.7, 74.5, 63.9, 56.8, 13.2.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3344, 2925, 1816, 1748, 1603, 1455, 1212, 1049.

HRMS (ESI) calcd for $C_{30}H_{18}BrCl_2F_3NO_7$, $[M+H]^+$ 709.9596, found: 709.9604.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 14b-(4-bromophenyl)-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-

***d*]pyrrole-3a-carboxylate (4ad)**



Following the general procedure C, using **1a** (40.9 mg, 0.1 mmol) and **2d** (30.7 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 48 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ad** as white solid (83% yield, 53.3 mg); R_f 0.15 (EtOAc/Hex = 1/9); mp.: 162.2-162.9 °C; $[\alpha]_D^{23}$ = 54.19 (c = 0.5 in CH_2Cl_2). **HPLC**: 99% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 278 nm, t_{major} = 13.14 min, t_{minor} = 25.84 min.

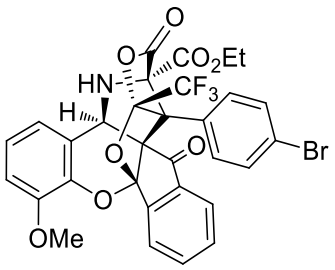
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.12 (d, *J* = 7.7 Hz, 1H), 7.91 (pt, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.61 (pt, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.32 (pt, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.15 (pt, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 4.79 (d, *J* = 4.8 Hz, 1H), 4.56 (d, *J* = 4.8 Hz, 1H), 4.20 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.12 (dq, *J* = 10.8, 7.1 Hz, 1H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.4, 168.4, 165.8, 150.1, 148.0, 137.2, 135.6, 132.0, 131.2, 130.4, 129.2, 128.8, 124.5, 124.1, 123.4, 123.3, 120.6, 120.5 (q, *J* = 286.7 Hz), 118.0, 111.1, 109.8 (q, *J* = 35.9 Hz), 80.7, 79.6, 74.2, 63.6, 56.4, 13.2.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3335, 2989, 1815, 1750, 1602, 1488, 1211, 1050.

HRMS (ESI) calcd for $C_{30}H_{20}BrF_3NO_7$, $[M+H]^+$ 642.0375, found: 642.0380.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 14b-(4-bromophenyl)-8-methoxy-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylat (4ae)



Following the general procedure C, using **1a** (40.9 mg, 0.1 mmol) and **2e** (34.0 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 60 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ae** as white solid (82% yield, 55.1 mg); R_f 0.05 (EtOAc/Hex = 1/9); mp.: 209.8-210.3 °C; $[\alpha]_D^{23}$ = 54.85 (c = 0.5 in CH_2Cl_2). **HPLC**: 98% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 248 nm, t_{major} = 17.74 min, t_{minor} = 37.01 min.

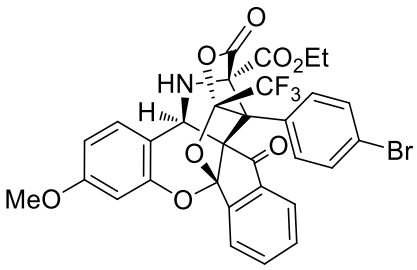
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.21 (d, *J* = 7.8 Hz, 1H), 7.91 (pt, *J* = 7.6 Hz, 1H), 7.60 (pt, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.08 (pt, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.80 (d, *J* = 4.9 Hz, 1H), 4.50 (d, *J* = 4.9 Hz, 1H), 4.20 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.12 (dq, *J* = 10.6, 7.1 Hz, 1H), 3.90 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.5, 168.6, 165.9, 149.1, 148.0, 139.8, 137.4, 135.8, 132.1, 131.3, 129.4, 128.9 (q, *J* = 3.2 Hz), 124.9, 123.9, 123.5, 123.4, 122.0, 120.8 (q, *J* = 286.7 Hz), 120.0, 113.0, 111.3, 110.1 (q, *J* = 35.9 Hz), 80.6, 79.7, 74.1, 63.7, 56.5, 56.46, 13.3.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3336, 2986, 1818, 1750, 1603, 1486, 1215, 1050.

HRMS (ESI) calcd for $C_{31}H_{22}BrF_3NO_8$, $[M+H]^+$ 672.0481, found: 672.0487.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 14b-(4-bromophenyl)-7-methoxy-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4af)



Following the general procedure C, using **1a** (40.9 mg, 0.1 mmol) and **2f** (34.0 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 97 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4af** as white solid (76% yield, 51.1 mg); R_f 0.08 (EtOAc/Hex = 1/9); mp.: 214.2-214.9 °C; $[\alpha]_D^{23}$ = 60.32 (c = 0.5 in CH_2Cl_2). **HPLC**: 99% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 248 nm, t_{major} = 20.18 min, t_{minor} = 31.96 min.

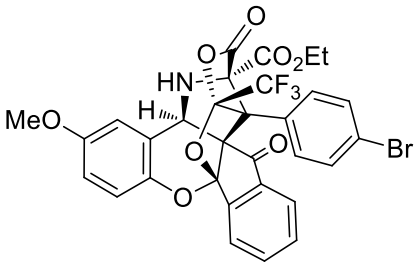
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.11 (d, *J* = 7.7 Hz, 1H), 7.91 (td, *J* = 7.6, 0.9 Hz, 1H), 7.61 (pt, *J* = 8.0 Hz, 1H), 7.55 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.42 (d,, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.71 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.60 (d, *J* = 2.7 Hz, 1H), 4.75 (d, *J* = 4.8 Hz, 1H), 4.49 (d, *J* = 4.8 Hz, 1H), 4.21 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.13 (dq, *J* = 10.6, 7.1 Hz, 1H), 3.81 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.6, 168.6, 166.0, 161.4, 151.3, 148.1, 137.3, 135.7, 132.1, 131.3, 129.7, 129.4, 128.9 (q, *J* = 3.2 Hz), 124.6, 123.5, 123.4, 120.7 (q, *J* = 286.7 Hz), 112.4, 111.4, 111.1, 109.9 (q, *J* = 35.6 Hz), 103.0, 80.9, 79.7, 74.5, 63.7, 56.4, 55.6, 13.4.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3314, 2980, 1810, 1740, 1626, 1589, 1502, 1183, 1047.

HRMS (ESI) calcd for $C_{31}H_{22}BrF_3NO_8$, $[M+H]^+$ 672.0481, found: 672.0486.

(1*S*,3a*S*,4a*R*,9a*R*,14a*R*,14b*S*)-ethyl 14b-(4-bromophenyl)-6-methoxy-3,14-dioxo-1-(trifluoromethyl)-3,3a,4,4a,14,14b-hexahydro-1*H*-1,9a-epoxyfuro[3,4-*b*]indeno[1',2':2,3]chromeno[3,4-*d*]pyrrole-3a-carboxylate (4ag)



Following the general procedure C, using **1a** (40.9 mg, 0.1 mmol) and **2g** (34.0 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 48 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ag** as white solid (88% yield, 59.2 mg); R_f 0.08 (EtOAc/Hex = 1/9); mp.: 188.6-188.9 °C; $[\alpha]_D^{23}$ = 55.53 (c = 0.5 in CH_2Cl_2). **HPLC**: 97% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 248 nm, t_{major} = 14.45 min, t_{minor} = 18.68 min.

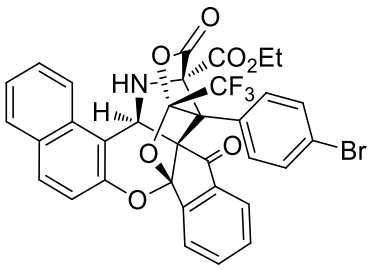
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.10 (d, *J* = 7.5 Hz, 1H), 7.90 (td, *J* = 7.5, 0.8 Hz, 1H), 7.60 (td,, *J* = 7.9, 0.8 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 2.6 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.87 (ddd, *J* = 8.8, 3.0, 0.9 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 4.77 (d, *J* = 5.3 Hz, 1H), 4.51 (d, *J* = 5.3 Hz, 1H), 4.20 (dq, *J* = 10.6, 7.2 Hz, 1H), 4.12 (dq, *J* = 10.6, 7.2 Hz, 1H), 3.82 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.7, 168.2, 166.0, 156.2, 148.2, 144.0, 137.3, 135.9, 132.0, 131.3, 129.3, 128.9 (q, *J* = 3.2 Hz), 124.6, 123.5, 123.4, 121.6, 120.7 (q, *J* = 286.7 Hz), 119.1, 117.4, 112.6, 111.7, 110.0 (q, *J* = 35.6 Hz), 80.9, 79.9, 74.6, 63.7, 57.0, 56.1, 13.3.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3320, 2973, 1814, 1750, 1602, 1490, 1205, 1048.

HRMS (ESI) calcd for $C_{31}H_{22}BrF_3NO_8$, $[M+H]^+$ 672.0481, found: 672.0488.

(1*S*,3a*S*,4a*R*,11a*R*,16a*R*,16b*S*)-ethyl 16b-(4-bromophenyl)-3,16-dioxo-1-(trifluoromethyl)-3,3a,4,4a,16,16b-hexahydro-1*H*-1,11a-epoxybenzo[5,6]indeno[1',2':2,3]chromeno[4,3-*b*]furo[3,4-*d*]pyrrole-3a-carboxylate (4ah)



Following the general procedure C, using **1a** (40.9 mg, 0.1 mmol) and **2h** (36.2 mg, 1.1 equiv.) as the substrates, the reaction mixture was stirred for 96 hours and purified by flash column chromatography on silica gel (EtOAc/ hexanes = 1:9) to obtain **4ah** as white solid (83% yield, 57.5 mg); R_f 0.15 (EtOAc/Hex = 1/9); mp.: 145.4-146.3 °C; $[\alpha]_D^{20}$ = 71.3 (c = 0.5 in CH_2Cl_2); **HPLC**: 99% ee, Chiralpak IB column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.00 mL/min, λ= 248 nm, t_{major} = 12.27 min, t_{minor} = 14.89 min.

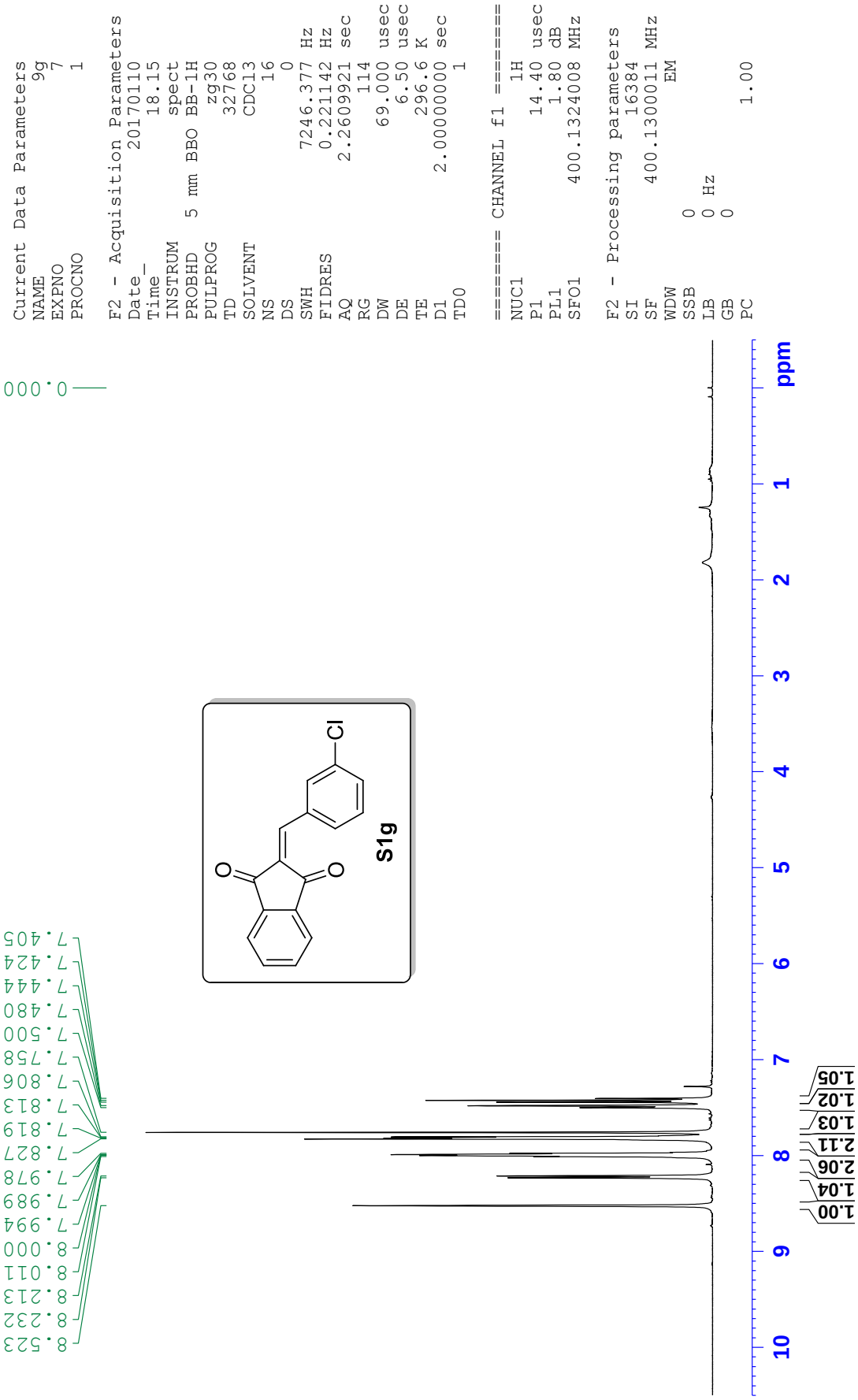
^{1}H NMR (400 MHz, $CDCl_3$) *δ*/ppm: 8.09 (d, *J* = 7.9 Hz, 1H), 8.04 (t, *J* = 8.4 Hz, 1H), 7.85 (td, *J* = 7.6, 1.3 Hz, 1H), 7.76 (t, *J* = 8.9 Hz, 1H), 7.56-7.64 (m, 2H), 7.54 (pt, *J* = 7.4 Hz, 1H), 7.36-7.46 (m, 2H), 7.21 (d, *J* = 8.9 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 5.37 (d, *J* = 2.7 Hz, 1H), 4.11-4.26 (m, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

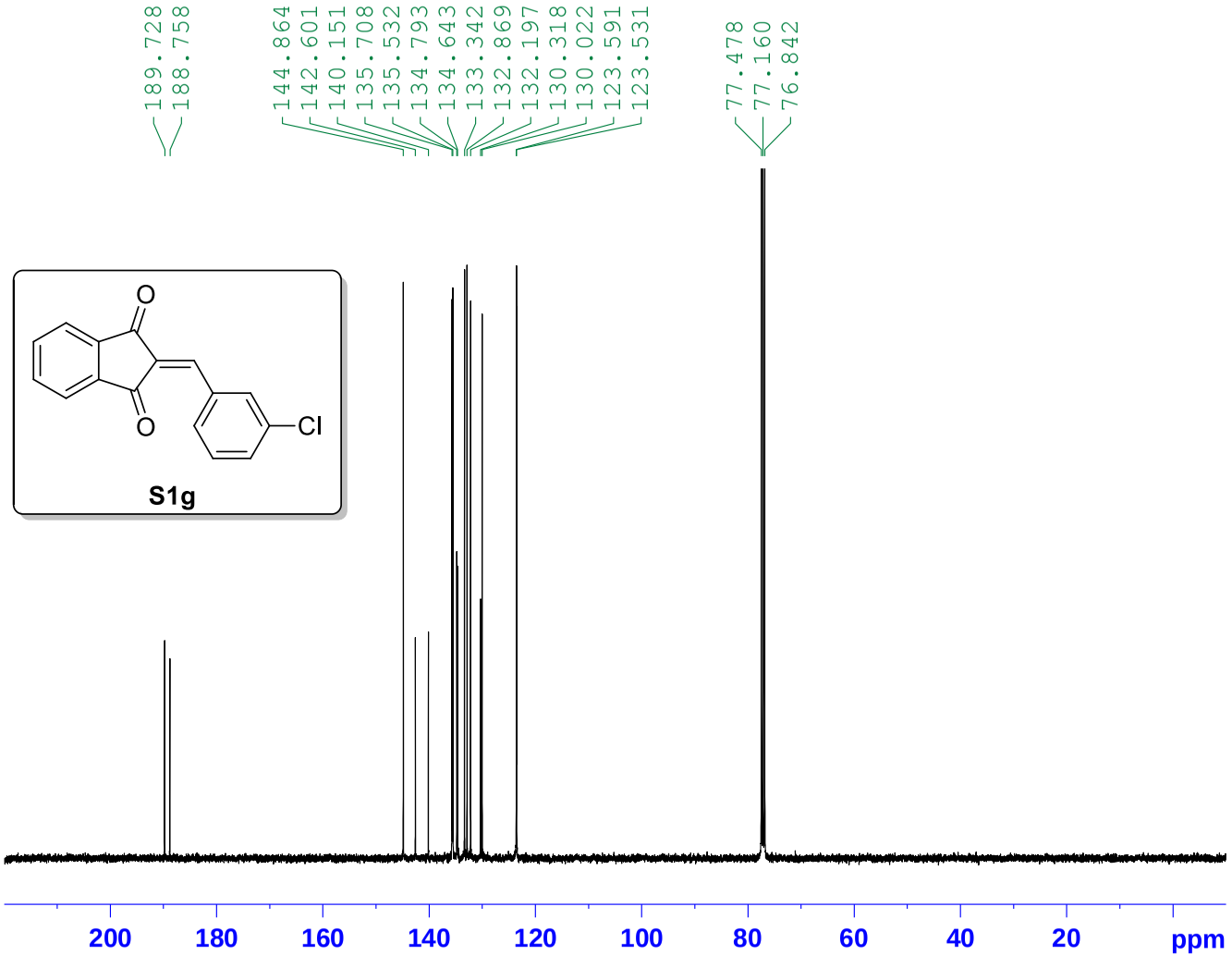
^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 196.5, 169.6, 165.8, 147.5, 147.0, 137.5, 134.9, 132.4, 131.8, 131.7, 131.4, 130.7, 129.9, 129.2, 128.9 (q, *J* = 2.9 Hz), 128.0, 125.0, 124.6, 123.9, 123.5, 122.6, 120.4 (q, *J* = 286.2 Hz), 118.2, 112.6, 111.5 (q, *J* = 35.3 Hz), 110.6, 78.9, 78.4, 72.9, 63.7, 55.7, 13.4.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3414, 2927, 1812, 1748, 1731, 1602, 1467, 1214, 1055.

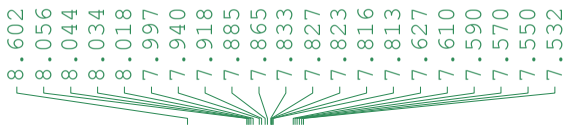
HRMS (ESI) calcd for $C_{34}H_{22}BrF_3NO_7$, $[M+H]^+$ 692.0532, found: 692.0528.

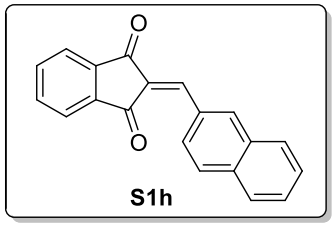
^{1}H and ^{13}C NMR Spectra of all new compounds:

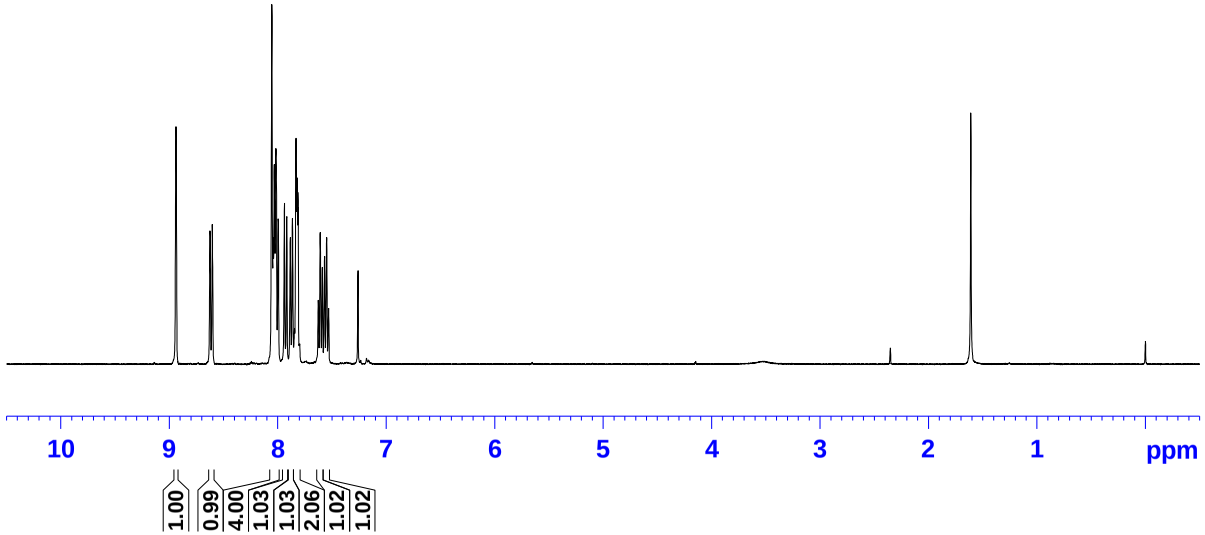




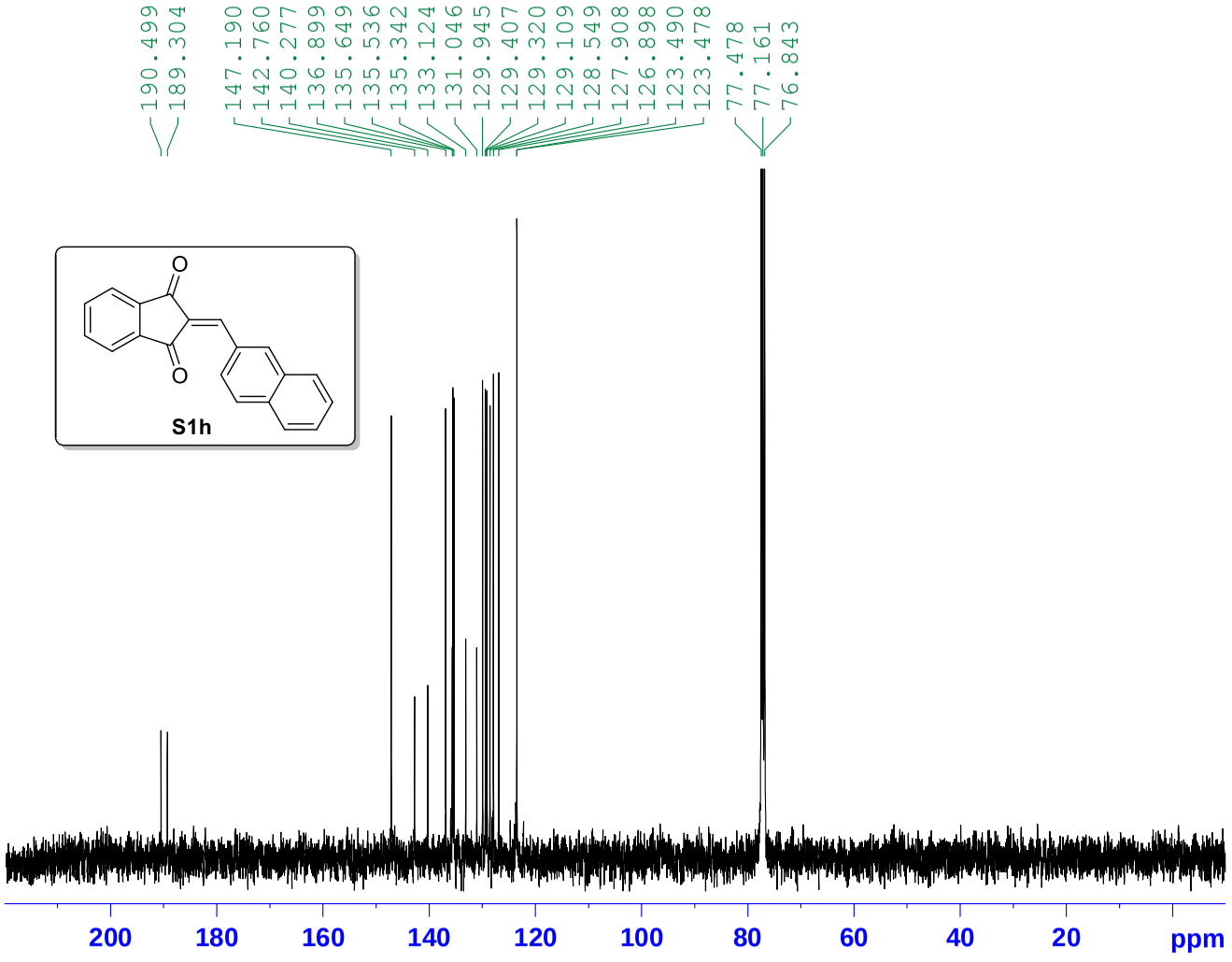

```
Current Data Parameters
NAME                   9g
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170110
Time               18.21
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                 1385
DS                    0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             0.6815744 sec
RG                 4096
DW                20.800 usec
DE                 6.50 usec
TE                296.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2               90.00 usec
PL2                  1.80 dB
PL12                17.00 dB
PL13                20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF          100.6127603 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```



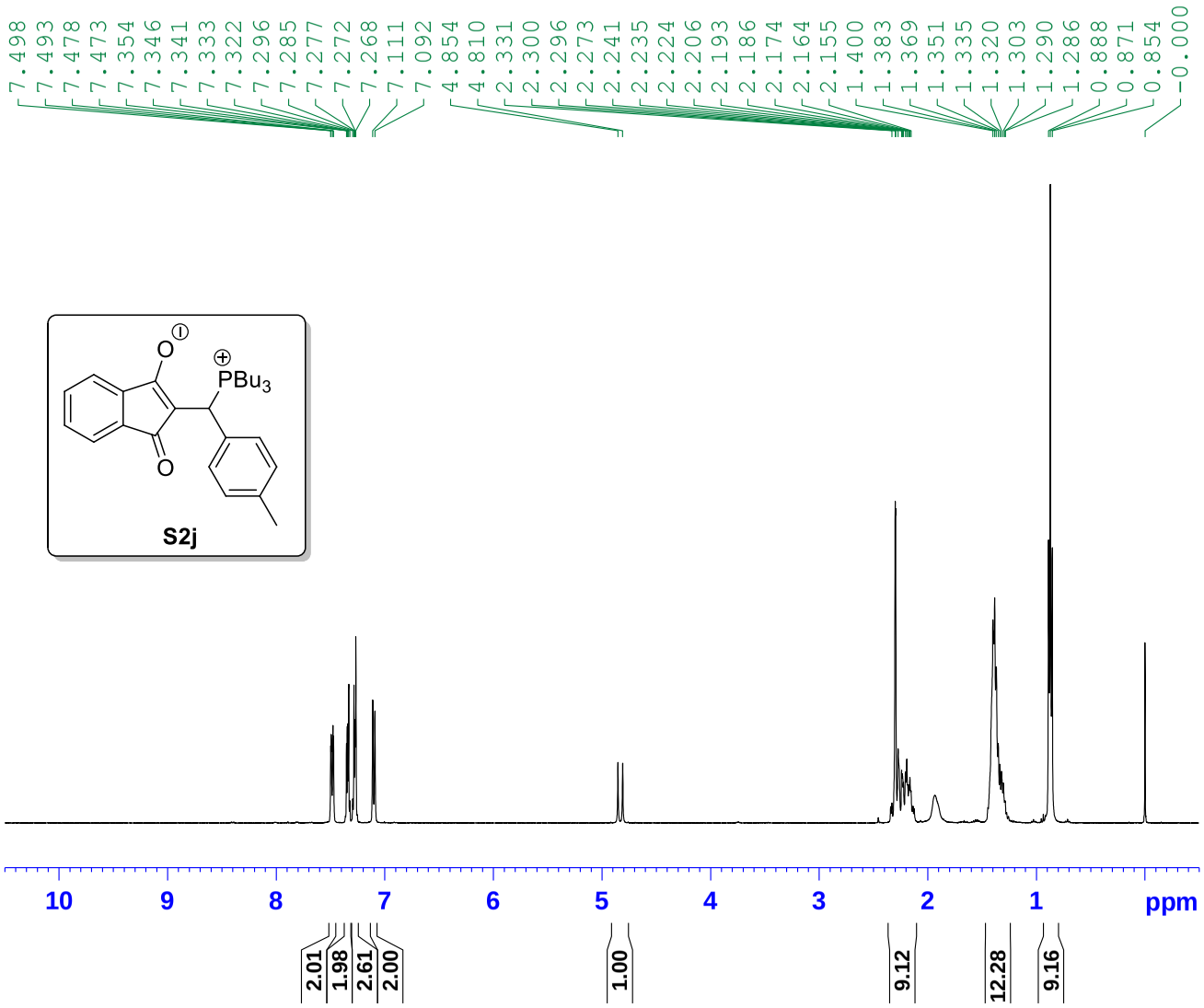




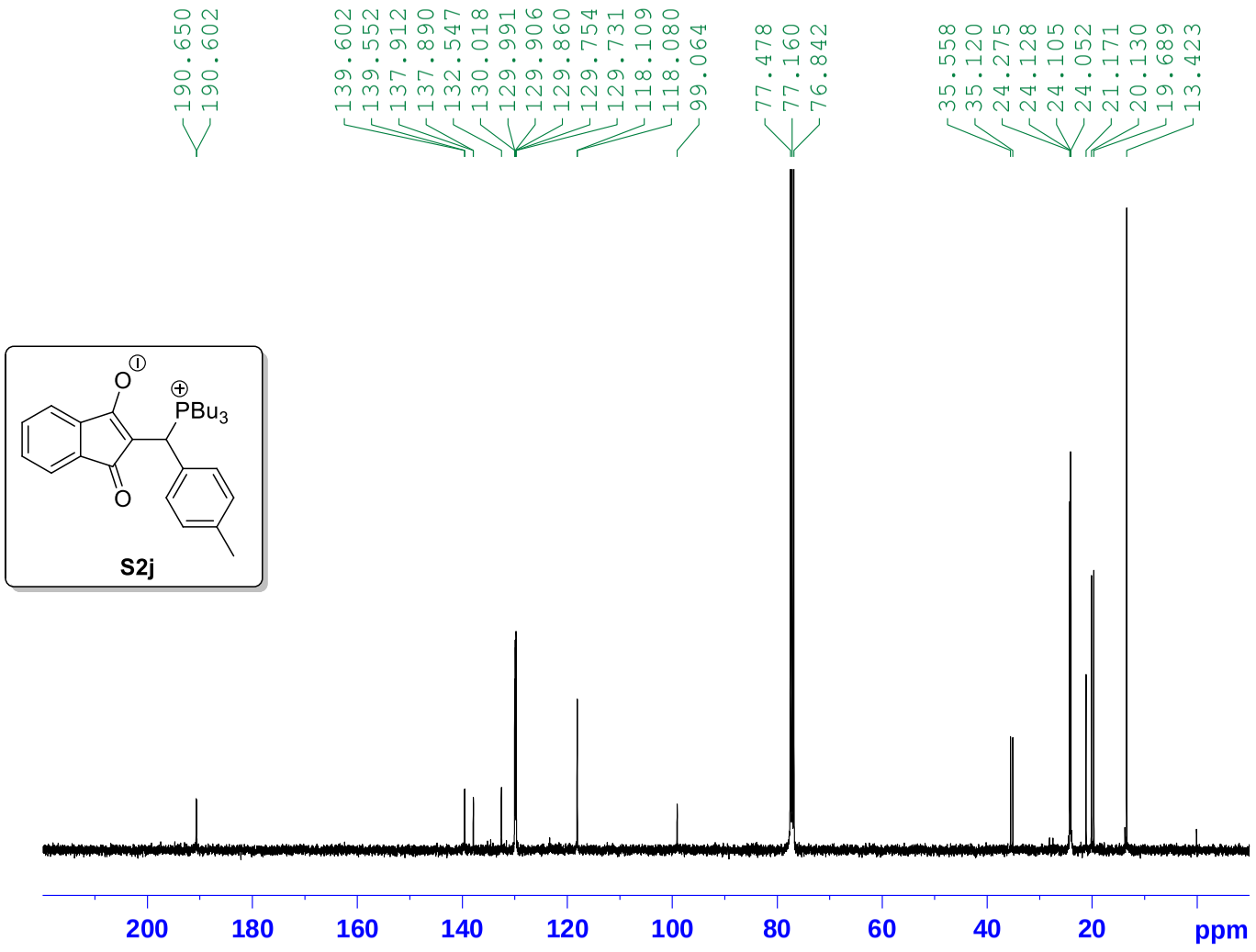

```
Current Data Parameters
NAME                  Mei-S1h
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_                20170414
Time                    13.39
INSTRUM                 spect
PROBHD   5 mm BBO BB-1H
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                         16
DS                          0
SWH                  7246.377 Hz
FIDRES               0.221142 Hz
AQ                   2.2609921 sec
RG                        256
DW                     69.000 usec
DE                      6.50 usec
TE                      295.4 K
D1                2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     14.40 usec
PL1                     1.80 dB
SFO1             400.1324008 MHz

F2 - Processing parameters
SI                      16384
SF               400.1300087 MHz
WDW                        EM
SSB          0
LB           0 Hz
GB           0
PC                      1.00
```



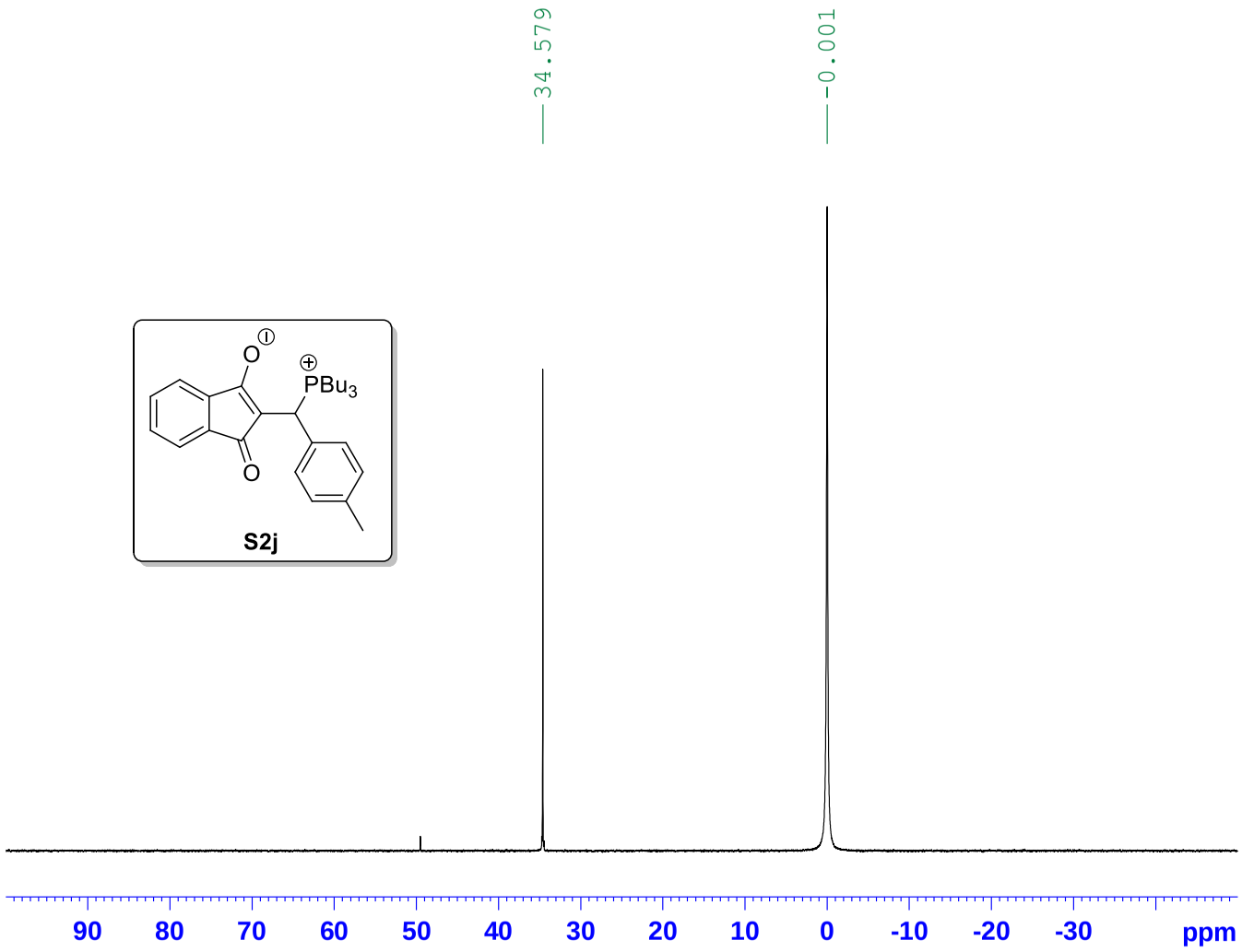

```
Current Data Parameters
NAME                   9h
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170210
Time               17.17
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  918
DS                    0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            0.6815744 sec
RG               198.09
DW               20.800 usec
DE                6.50 usec
TE               297.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                10.00 usec
PLW1        47.50000000 W

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

F2 - Processing parameters
SI                32768
SF          100.6127543 MHz
WDW                EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.00
```



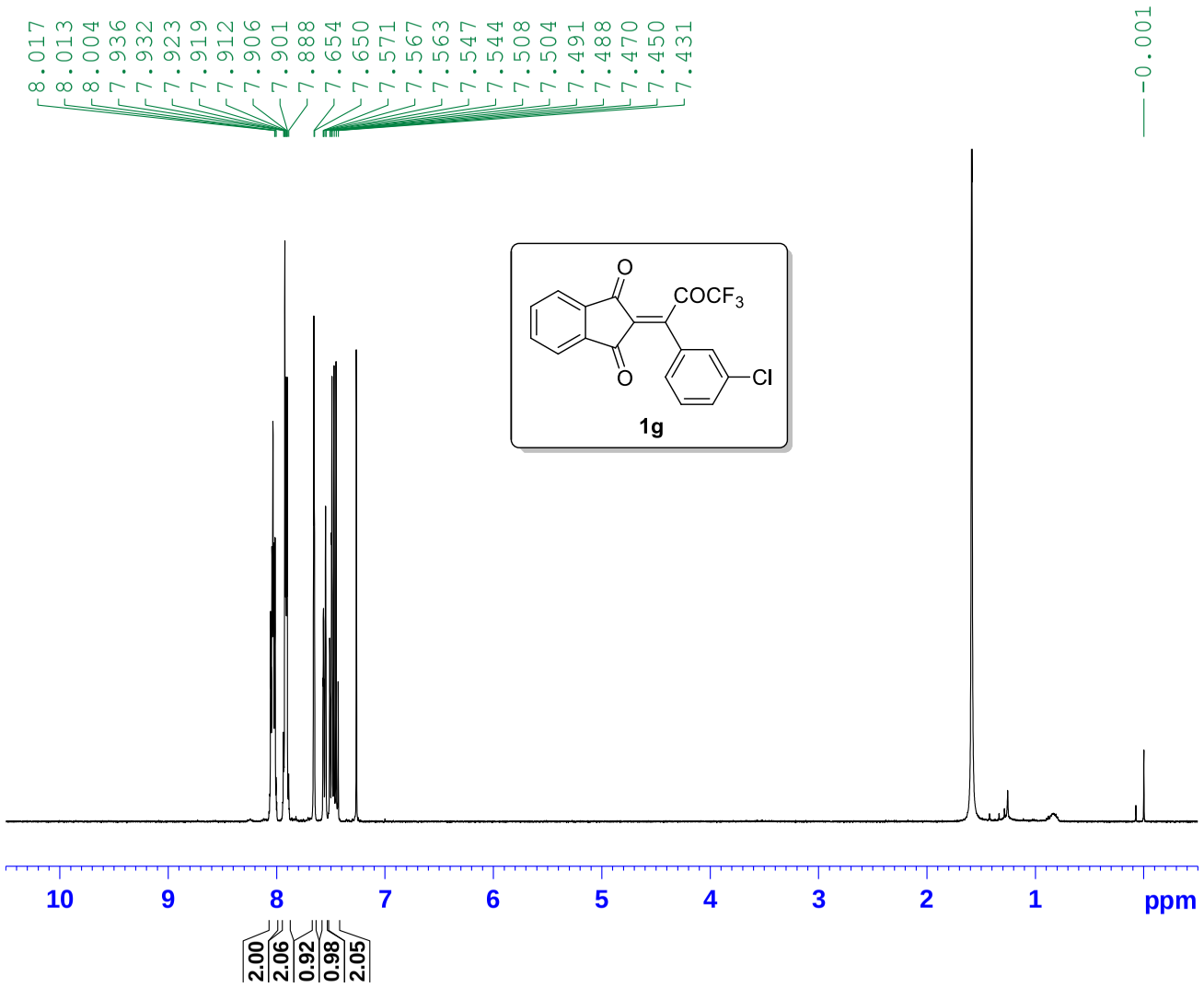

```
Current Data Parameters
NAME                  10j
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160908
Time                14.52
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              7211.539 Hz
FIDRES           0.220079 Hz
AQ               2.2719147 sec
RG                  99.72
DW                 69.333 usec
DE                 10.50 usec
TE                 298.1 K
D1              2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324008 MHz
NUC1                   1H
P1                  12.90 usec
PLW1          15.00000000 W

F2 - Processing parameters
SI                  16384
SF            400.1300070 MHz
WDW                    EM
SSB       0
LB        0 Hz
GB        0
PC                   1.00
```



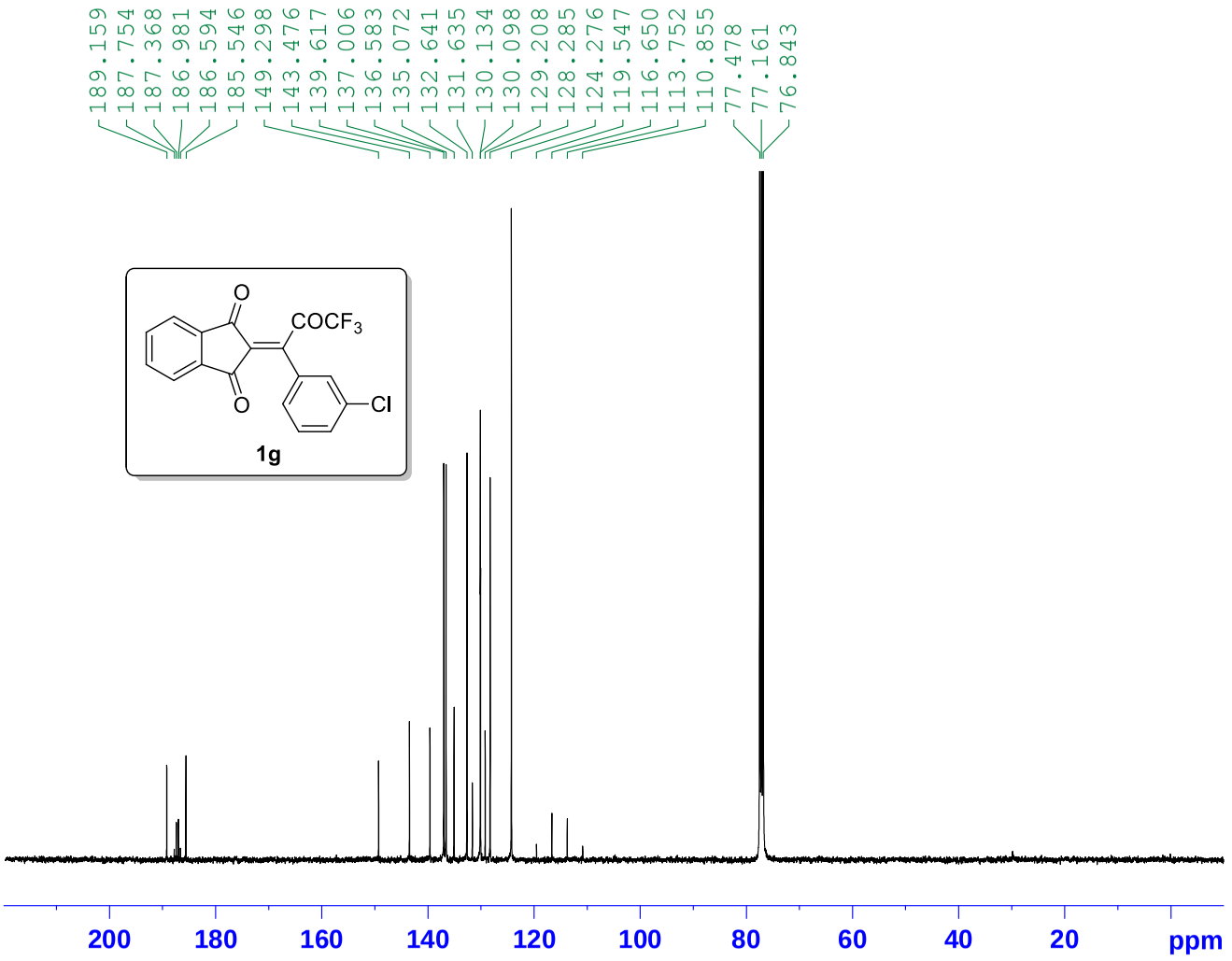

```
Current Data Parameters
NAME                  10j
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160909
Time               12.06
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                  3600
DS                     0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            0.6815744 sec
RG                  8192
DW                20.800 usec
DE                 6.50 usec
TE                296.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2              90.00 usec
PL2                1.80 dB
PL12               17.00 dB
PL13               20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127562 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.00
```



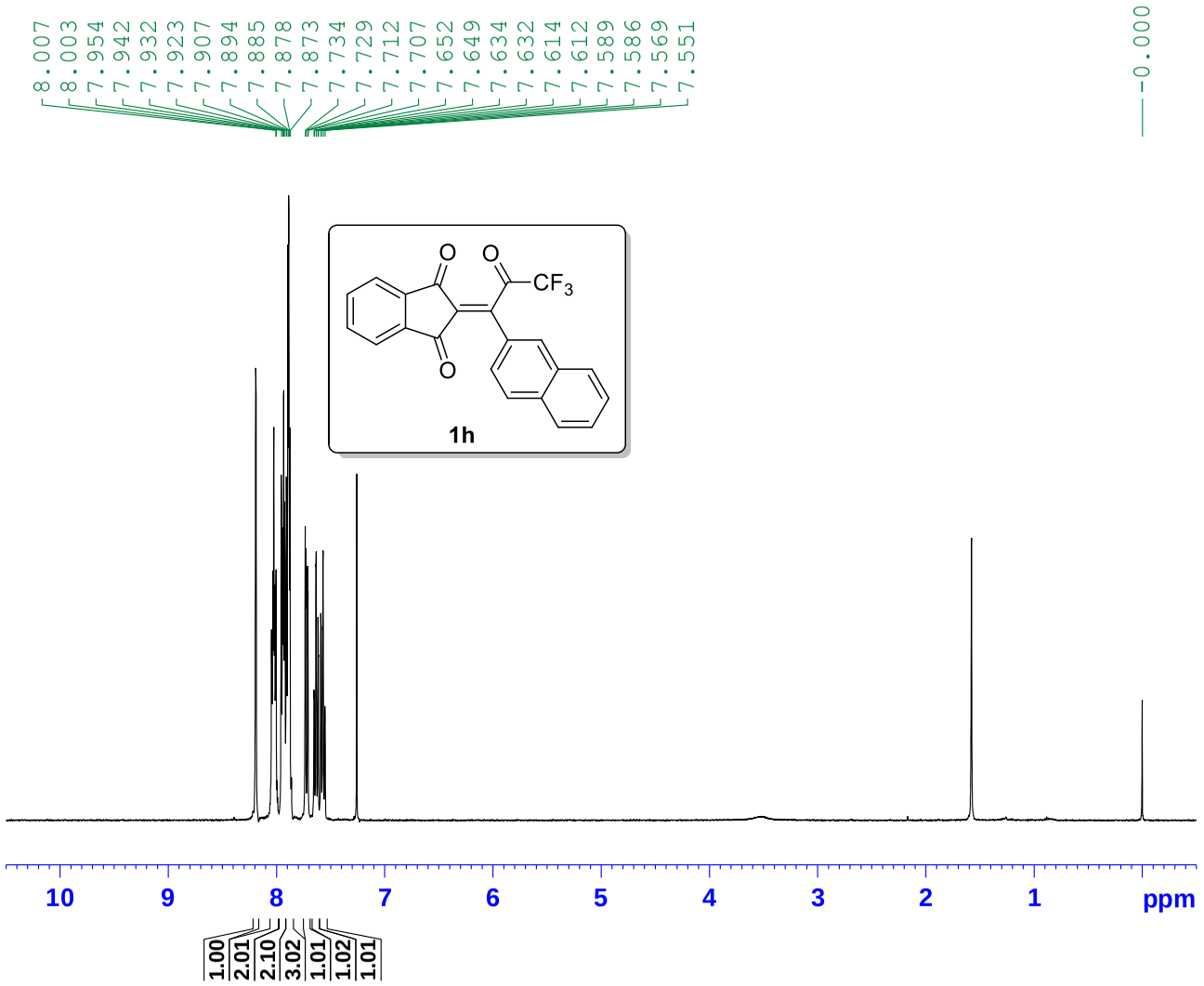

```
Current Data Parameters
NAME           10j-P NMR
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160915
Time               15.46
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                    7
DS                    4
SWH           49019.609 Hz
FIDRES         0.747980 Hz
AQ             0.6684672 sec
RG               198.09
DW               10.200 usec
DE                6.50 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        161.9836917 MHz
NUC1                31P
P1                15.00 usec
PLW1        12.69999981 W

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

F2 - Processing parameters
SI                32768
SF          161.9754935 MHz
WDW                EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.40
```



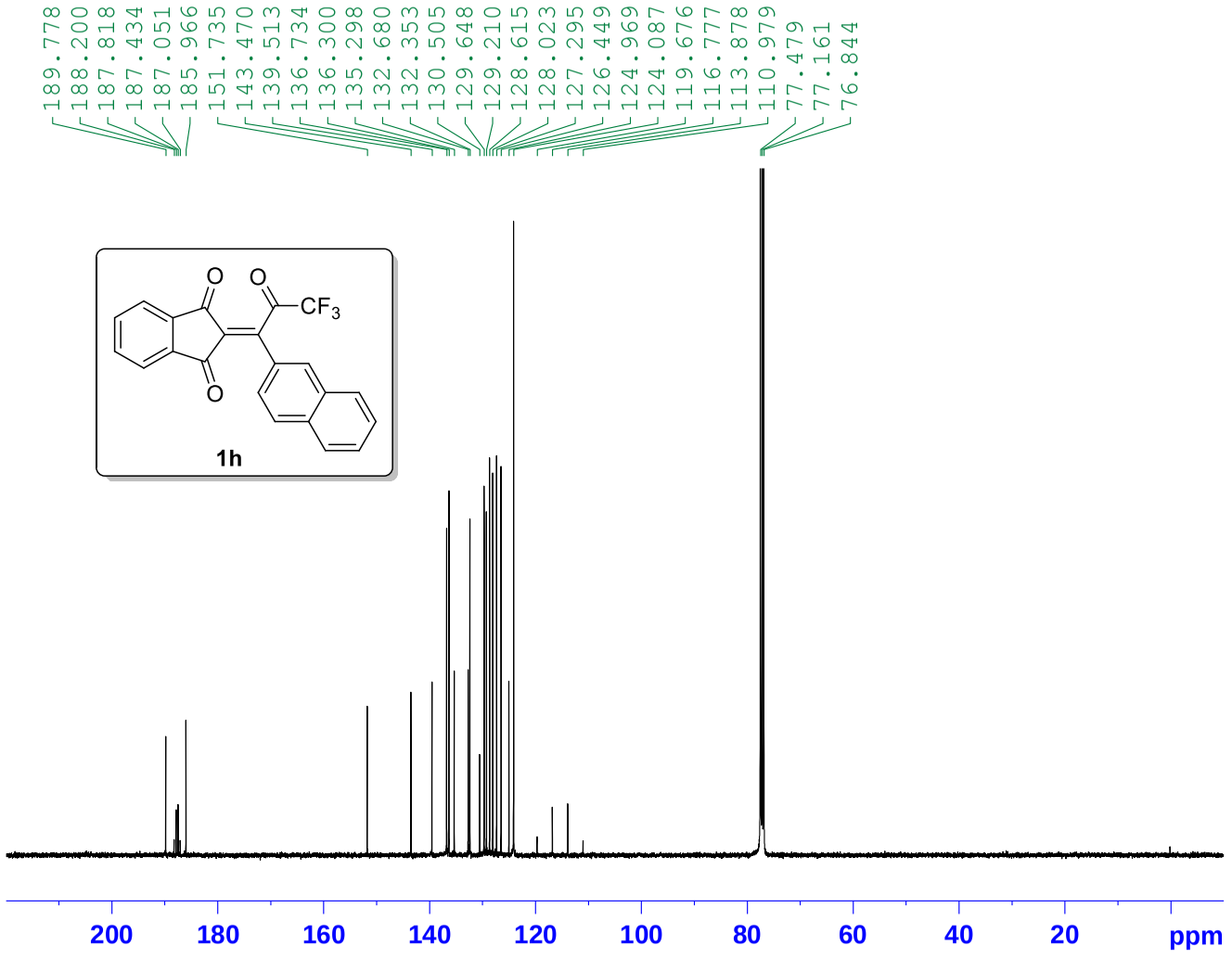

```
Current Data Parameters
NAME                   1g
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160701
Time               22.17
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             7211.539 Hz
FIDRES          0.220079 Hz
AQ             2.2719147 sec
RG                198.09
DW                69.333 usec
DE                10.50 usec
TE                298.5 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                 12.90 usec
PLW1         15.00000000 W

F2 - Processing parameters
SI                 16384
SF           400.1300090 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```



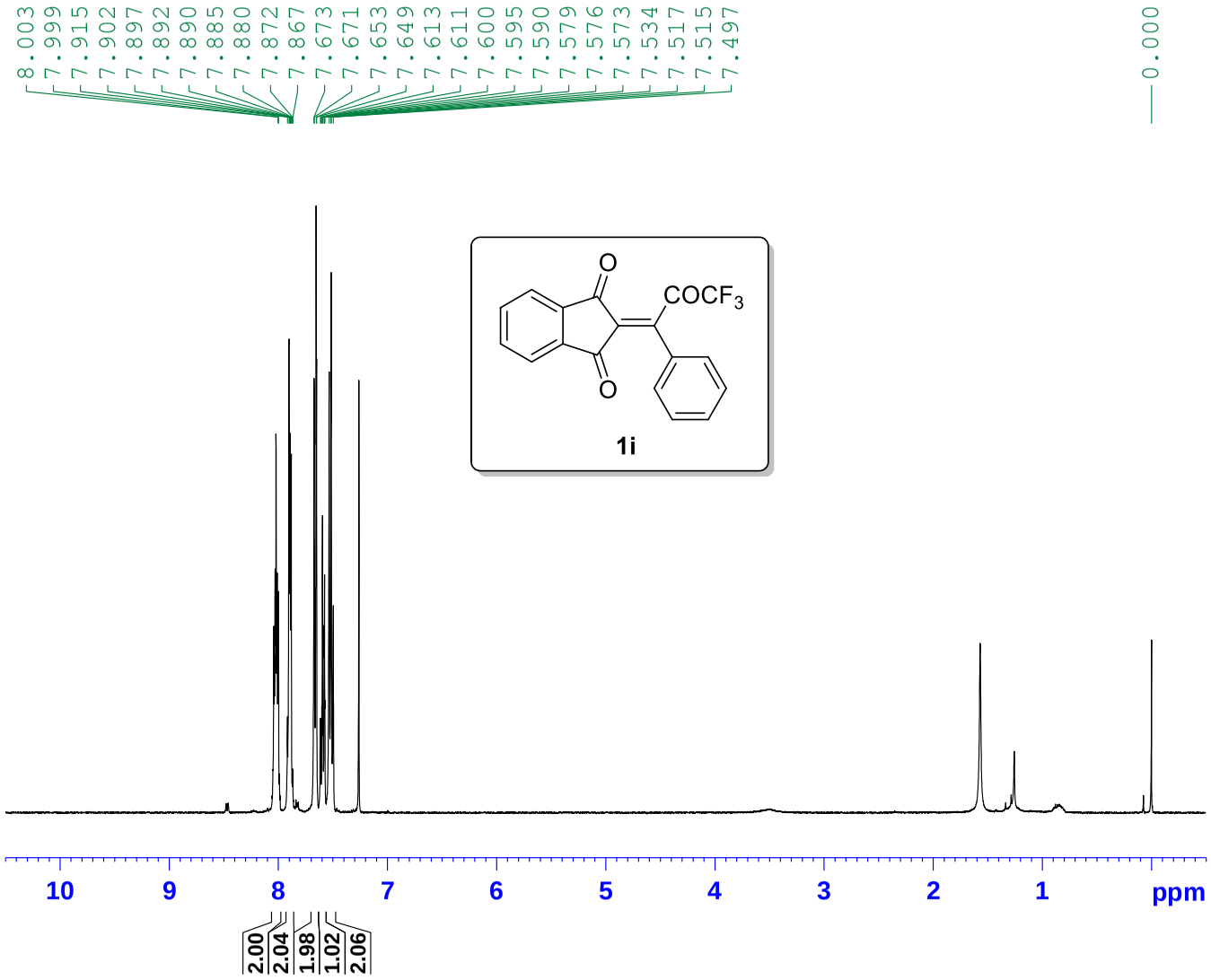

```
Current Data Parameters
NAME                  1g
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160702
Time               9.42
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                14931
DS                    0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             0.6815744 sec
RG                198.09
DW                20.800 usec
DE                 6.50 usec
TE                299.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                13C
P1                10.00 usec
PLW1         47.50000000 W

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

F2 - Processing parameters
SI                32768
SF           100.6127538 MHz
WDW                EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.00
```



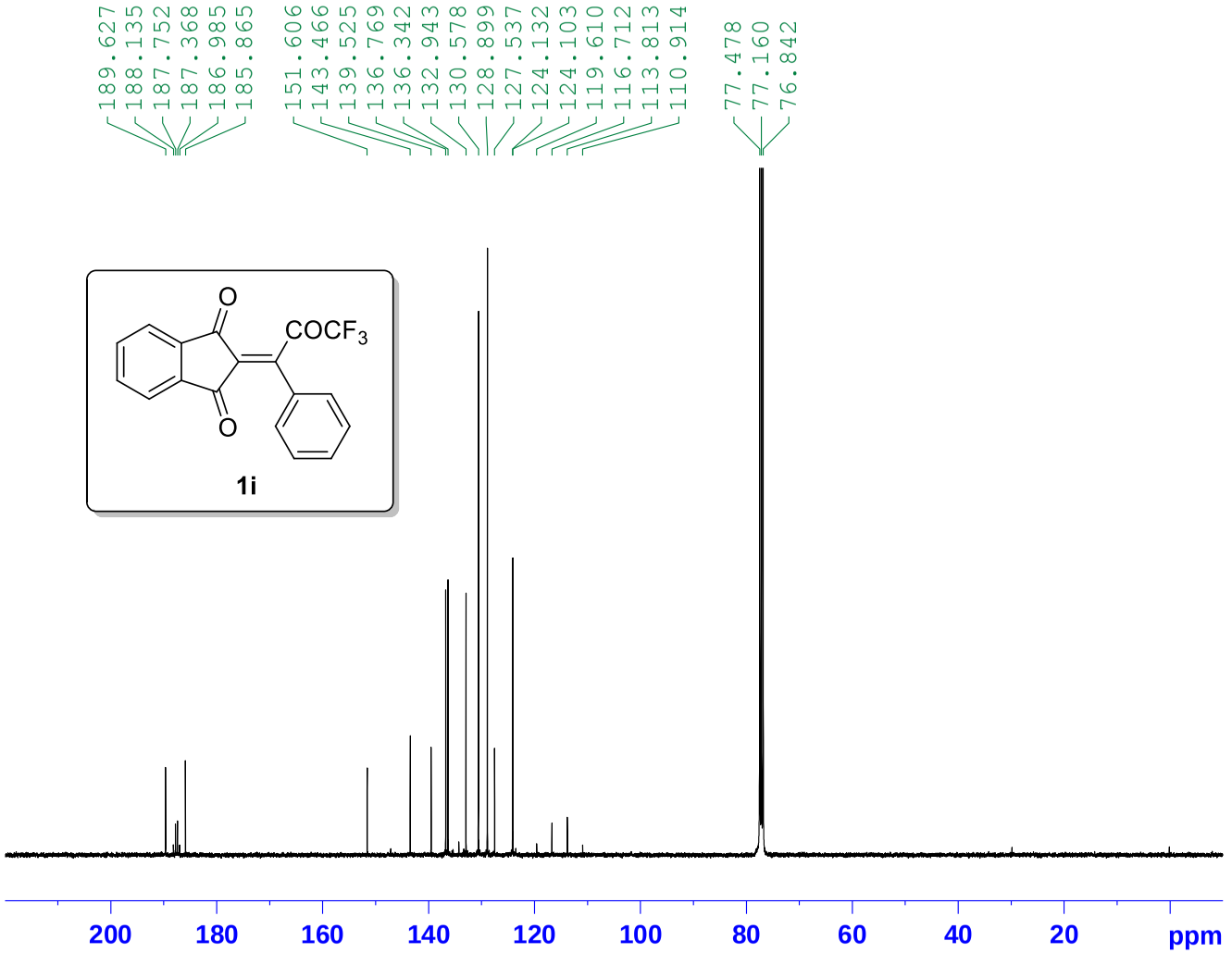

```
Current Data Parameters
NAME                   1h
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20161123
Time               22.34
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             7246.377 Hz
FIDRES          0.221142 Hz
AQ              2.2609921 sec
RG                   181
DW                69.000 usec
DE                 6.50 usec
TE                296.8 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.40 usec
PL1                 1.80 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300105 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```



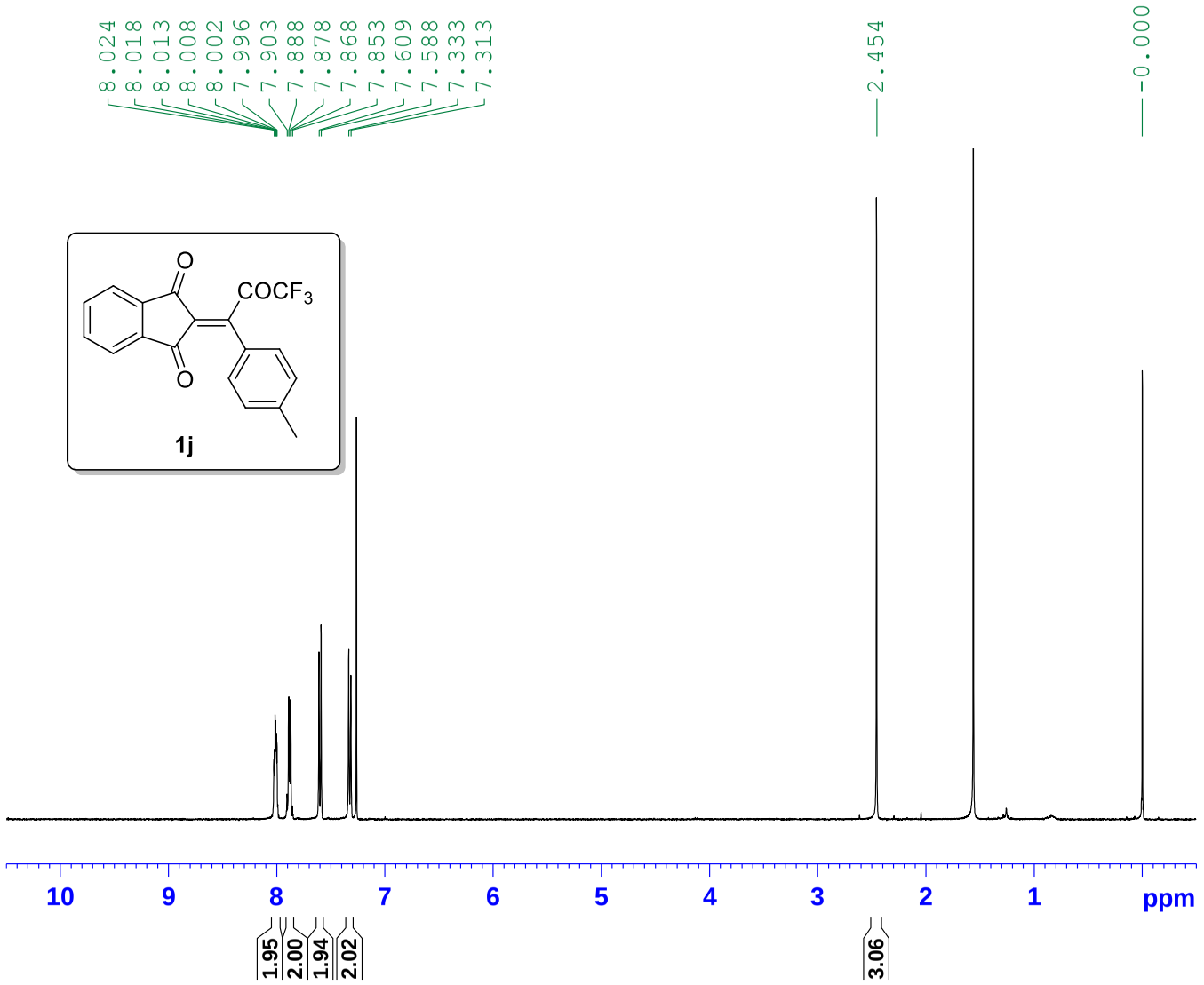

```
Current Data Parameters
NAME                      1h
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20161123
Time                  22.36
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG              zgpg30
TD                    32768
SOLVENT               CDCl3
NS                    14172
DS                        0
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                0.6815744 sec
RG                   3649.1
DW                  20.800 usec
DE                   6.50 usec
TE                  296.8 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

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

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                   1.80 dB
PL12                 17.00 dB
PL13                 20.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127547 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.00
```



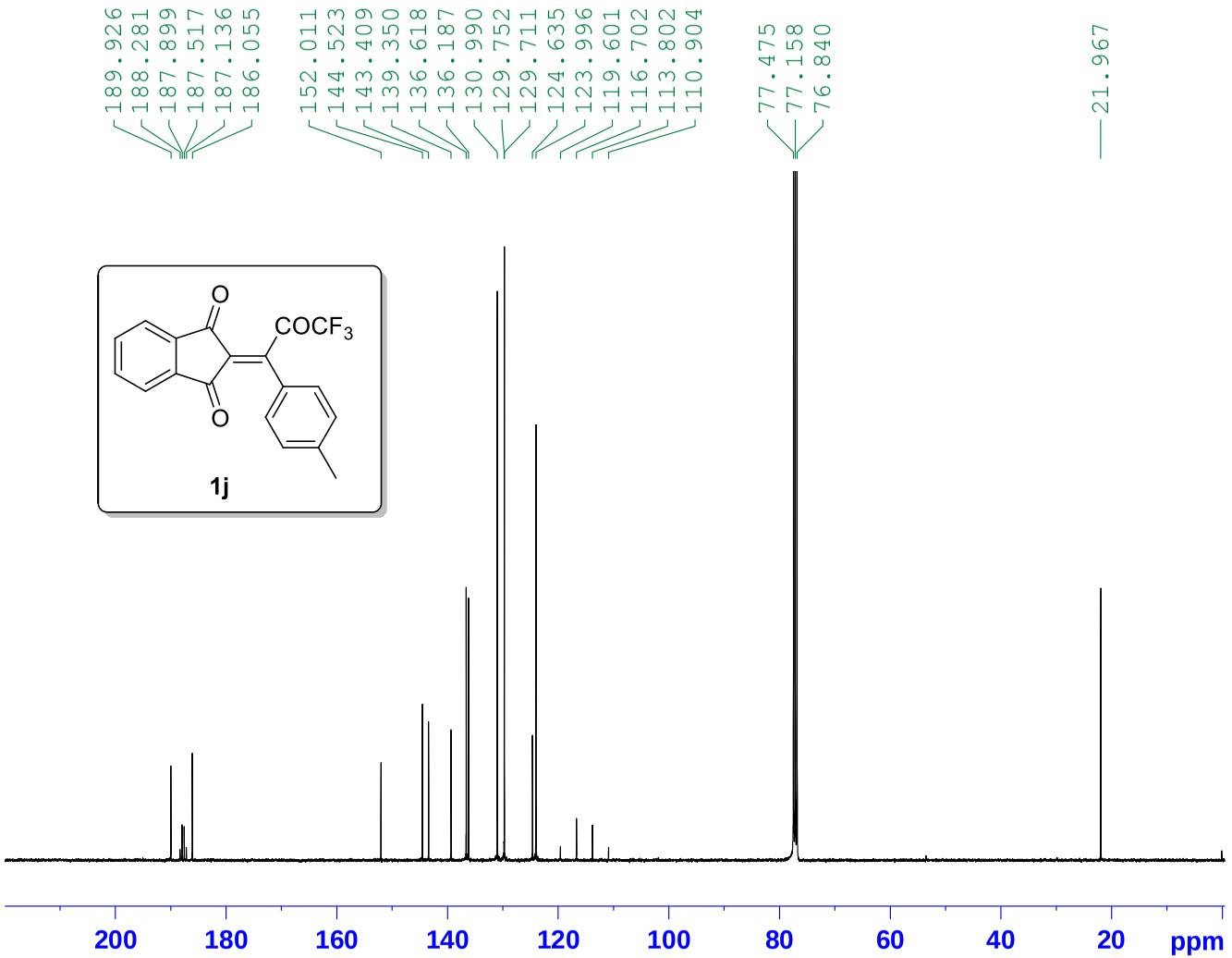

```
Current Data Parameters
NAME                  1i
EXPNO                128
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160702
Time              21.55
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            7246.377 Hz
FIDRES          0.221142 Hz
AQ             2.2609921 sec
RG                  256
DW               69.000 usec
DE                6.50 usec
TE                298.4 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.40 usec
PL1                1.80 dB
SFO1        400.1324008 MHz

F2 - Processing parameters
SI                16384
SF          400.1300087 MHz
WDW                  EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```



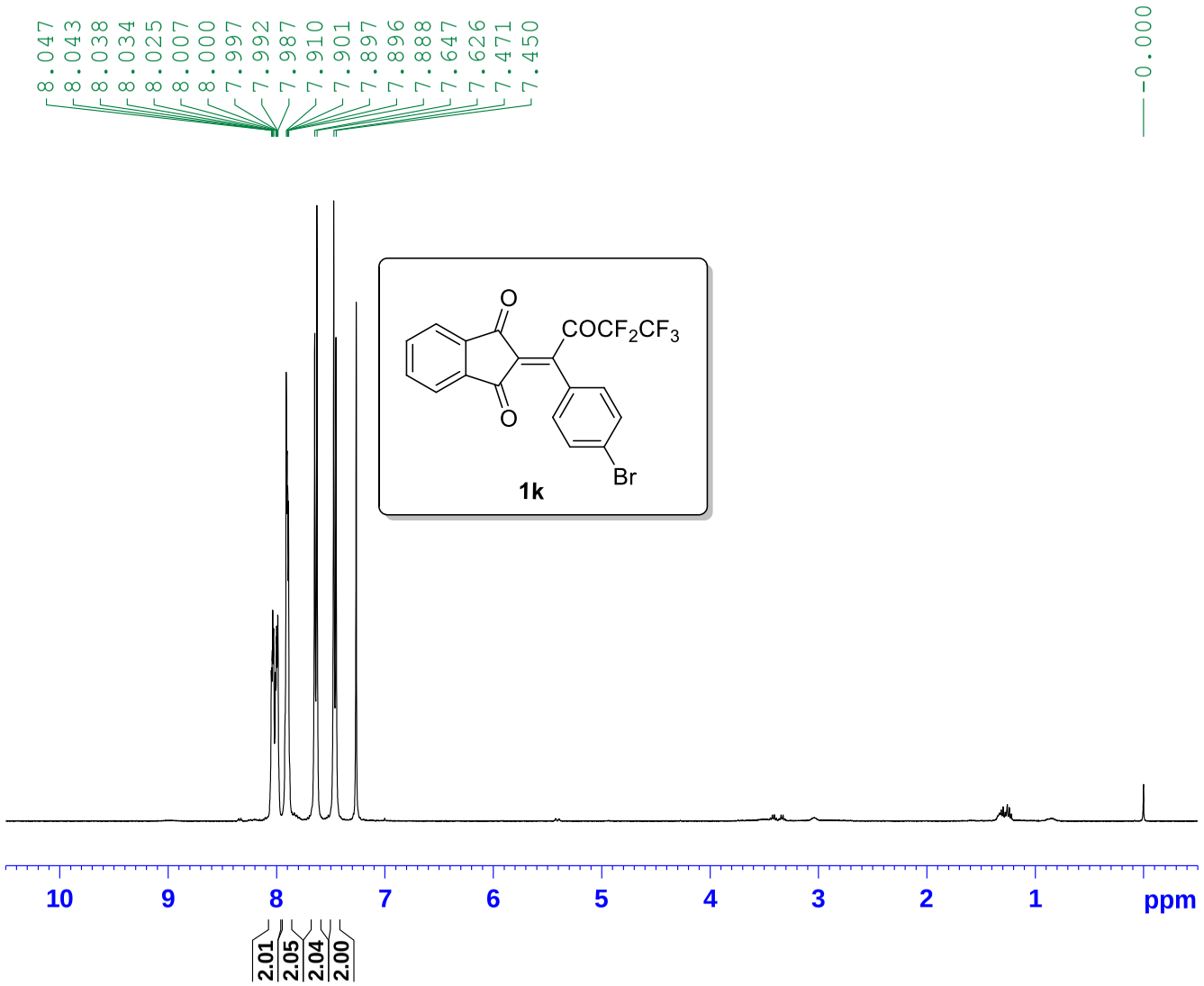

```
Current Data Parameters
NAME                  1i
EXPNO                129
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160702
Time               21.59
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                 20000
DS                     0
SWH          24038.461 Hz
FIDRES        0.733596 Hz
AQ            0.6815744 sec
RG                9195.2
DW               20.800 usec
DE                6.50 usec
TE                298.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 1.80 dB
PL12               17.00 dB
PL13               20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127533 MHz
WDW                  EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```



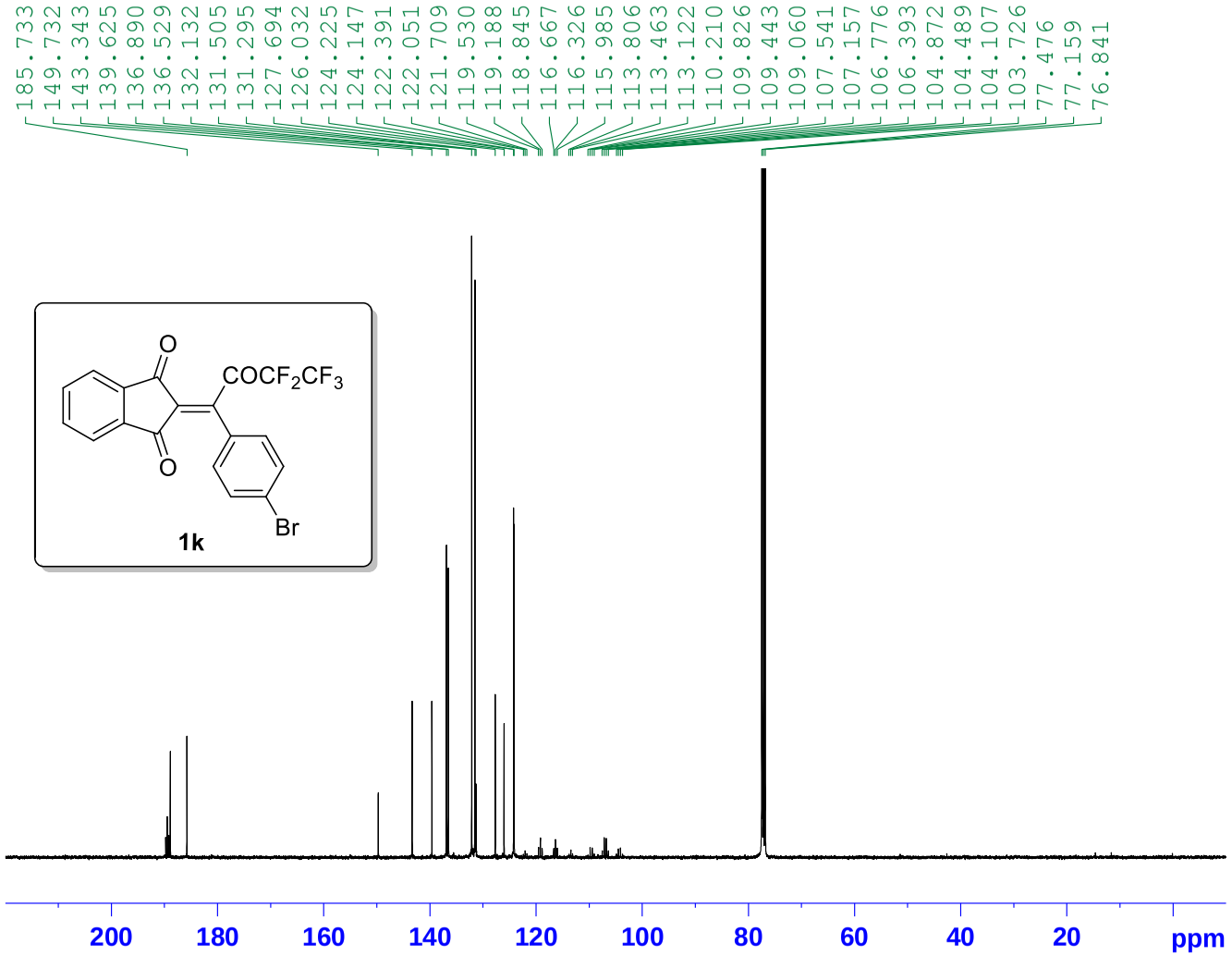

```
Current Data Parameters
NAME                  1j
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160908
Time                11.37
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             7211.539 Hz
FIDRES          0.220079 Hz
AQ              2.2719147 sec
RG                198.09
DW                69.333 usec
DE                10.50 usec
TE                298.4 K
D1           2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                 12.90 usec
PLW1         15.00000000 W

F2 - Processing parameters
SI                 16384
SF           400.1300095 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```



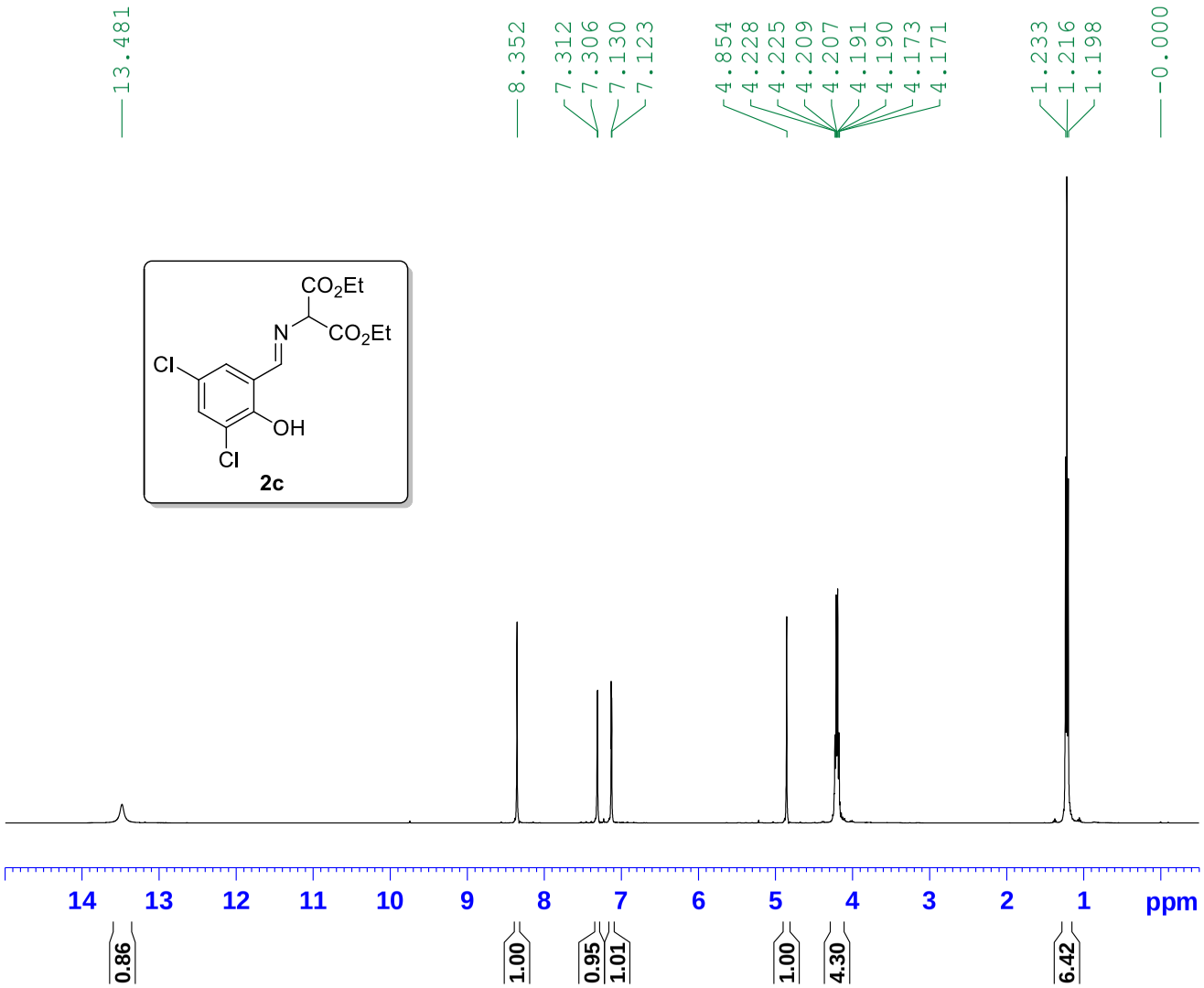

```
Current Data Parameters
NAME                  1j
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160908
Time               22.25
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                 32768
SOLVENT            CDCl3
NS                 13300
DS                     0
SWH          24038.461 Hz
FIDRES        0.733596 Hz
AQ            0.6815744 sec
RG                9195.2
DW               20.800 usec
DE                6.50 usec
TE                296.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             90.00 usec
PL2                1.80 dB
PL12              17.00 dB
PL13              20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127562 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.00
```



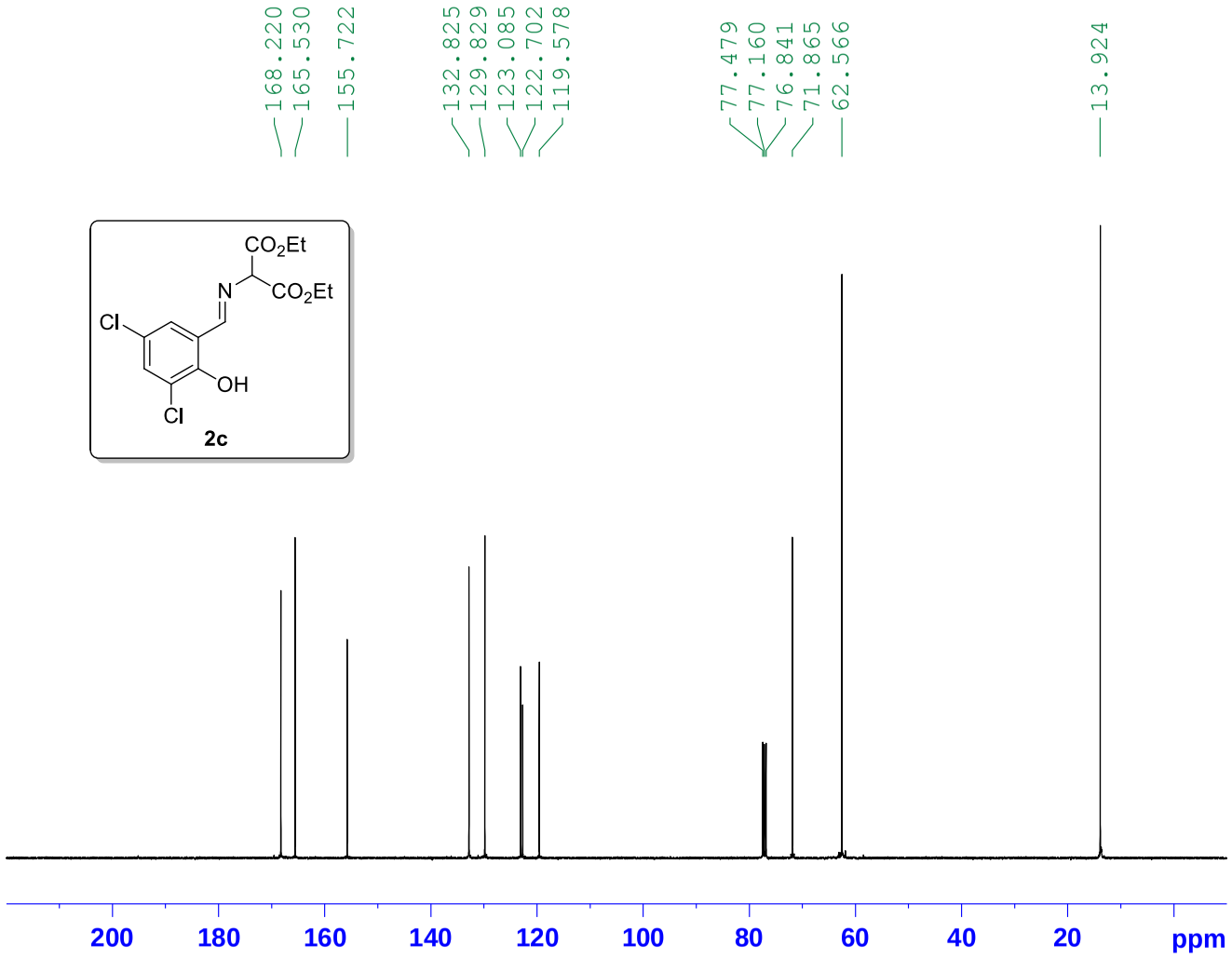

```
Current Data Parameters
NAME                   11
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170215
Time               22.15
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             7246.377 Hz
FIDRES          0.221142 Hz
AQ              2.2609921 sec
RG                 161.3
DW                69.000 usec
DE                 6.50 usec
TE                298.6 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.40 usec
PL1                 1.80 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300078 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```



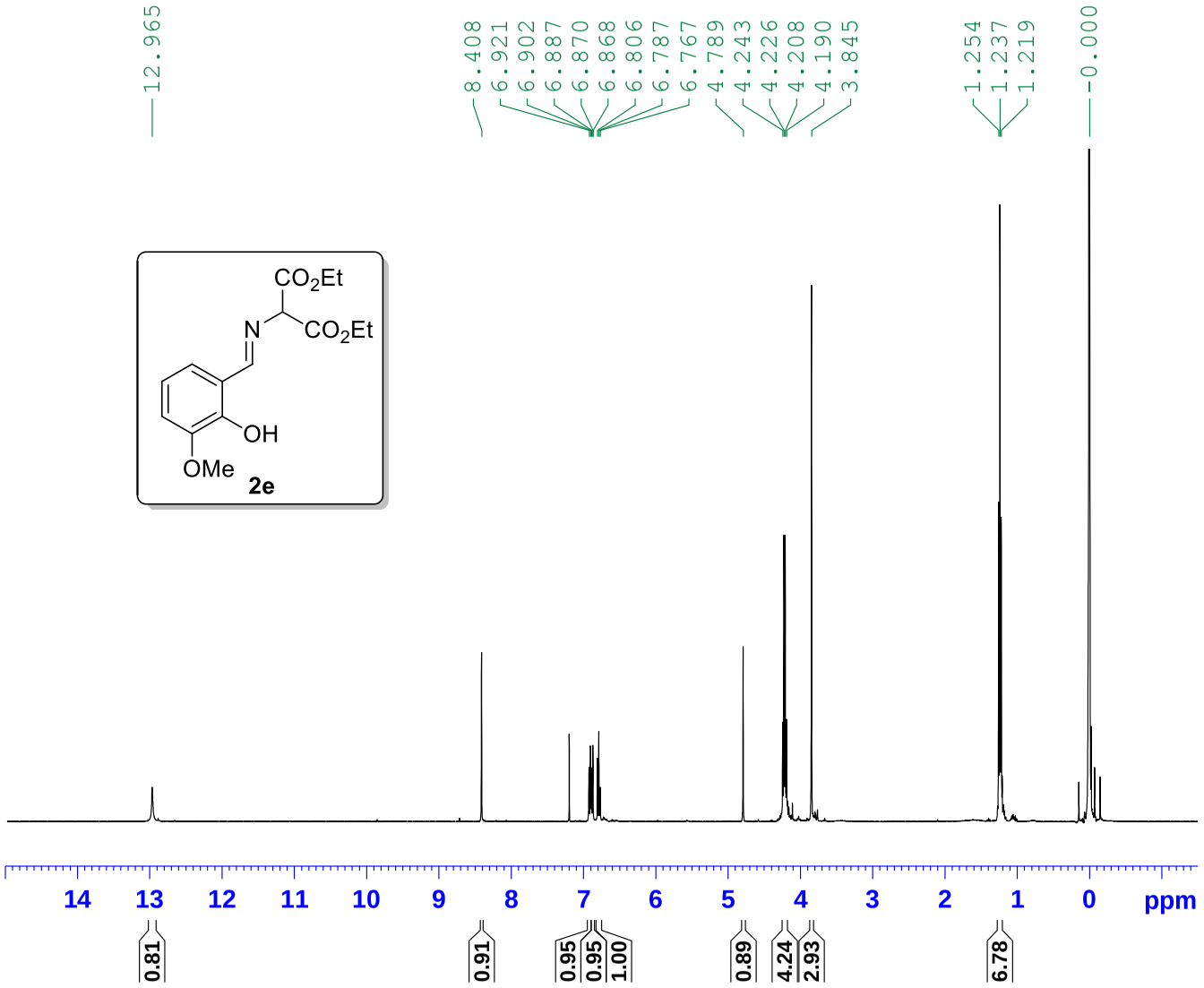

```
Current Data Parameters
NAME                   11
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170215
Time               22.17
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                13998
DS                    0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            0.6815744 sec
RG               5792.6
DW                20.800 usec
DE                 6.50 usec
TE                298.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 1.80 dB
PL12               17.00 dB
PL13               20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127541 MHz
WDW                  EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```



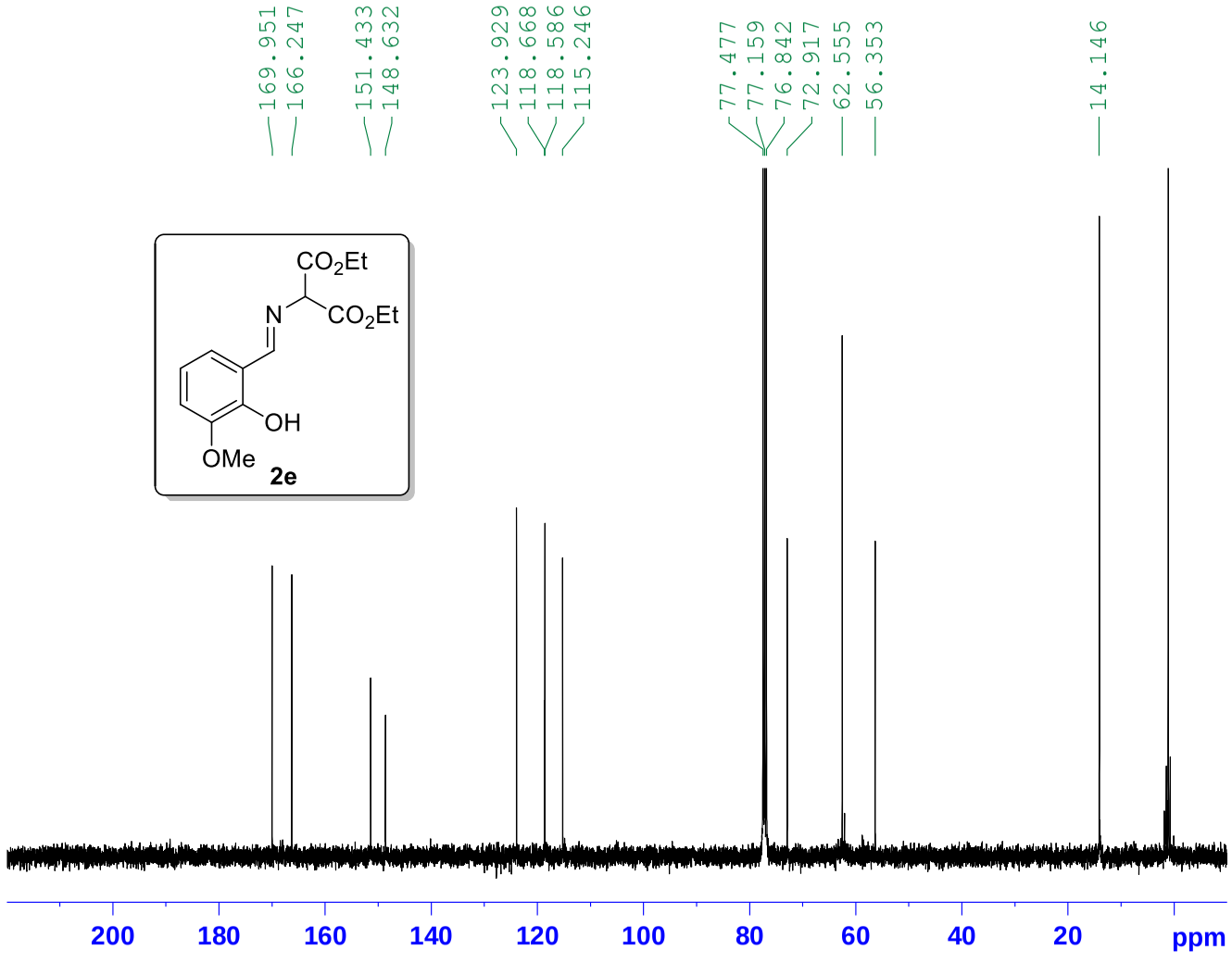

```
Current Data Parameters
NAME                  2c
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170111
Time              12.21
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   0
SWH           7246.377 Hz
FIDRES        0.221142 Hz
AQ            2.2609921 sec
RG                25.4
DW              69.000 usec
DE               6.50 usec
TE              296.5 K
D1           2.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.40 usec
PL1                1.80 dB
SFO1        400.1324008 MHz

F2 - Processing parameters
SI                16384
SF          400.1300220 MHz
WDW                  EM
SSB       0
LB        0 Hz
GB        0
PC                1.00
```



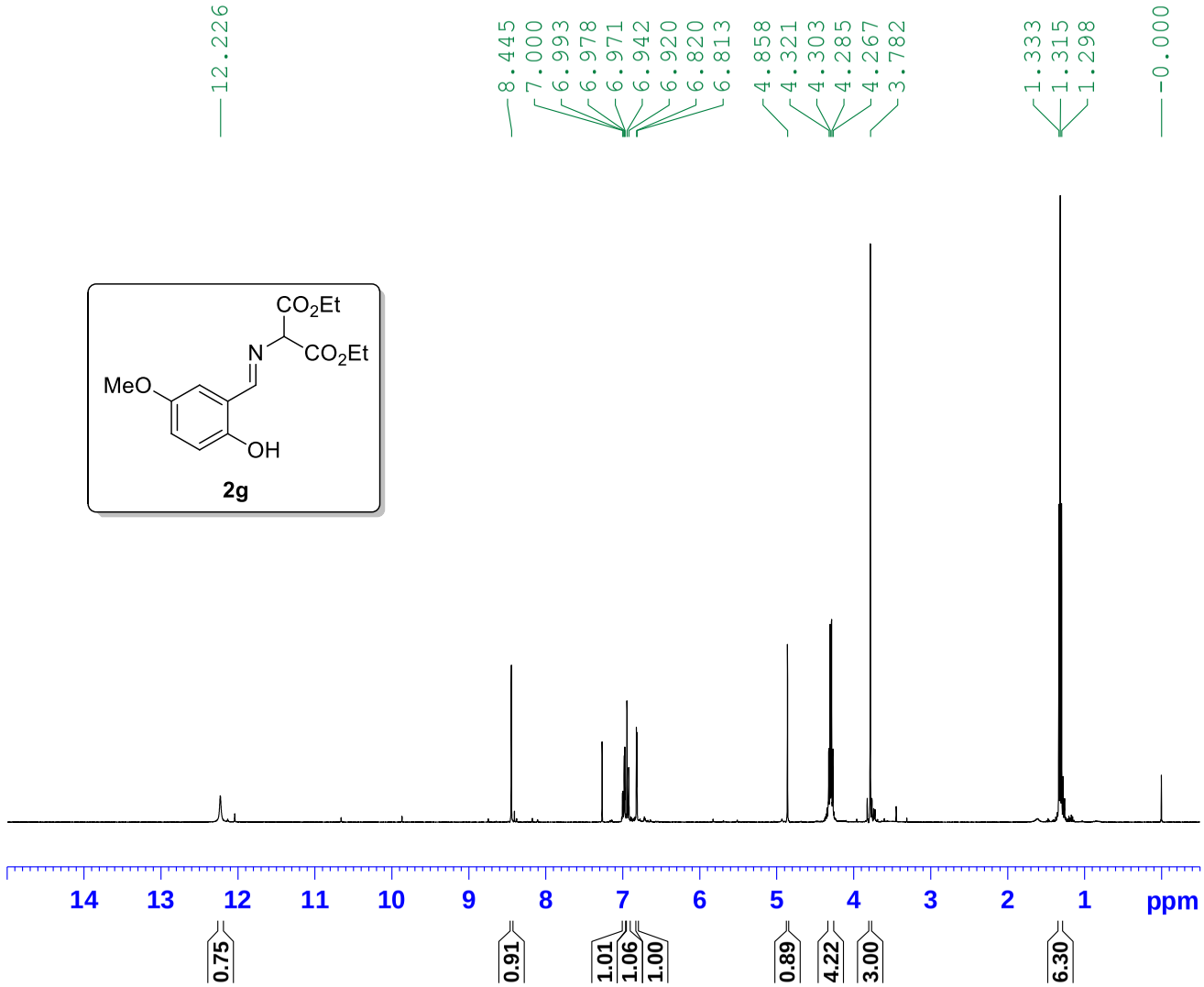

```
Current Data Parameters
NAME                  2c
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170111
Time               12.23
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   903
DS                     0
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ              0.6815744 sec
RG                1625.5
DW                20.800 usec
DE                 6.50 usec
TE                296.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

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

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                 1.80 dB
PL12               17.00 dB
PL13               20.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127720 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```



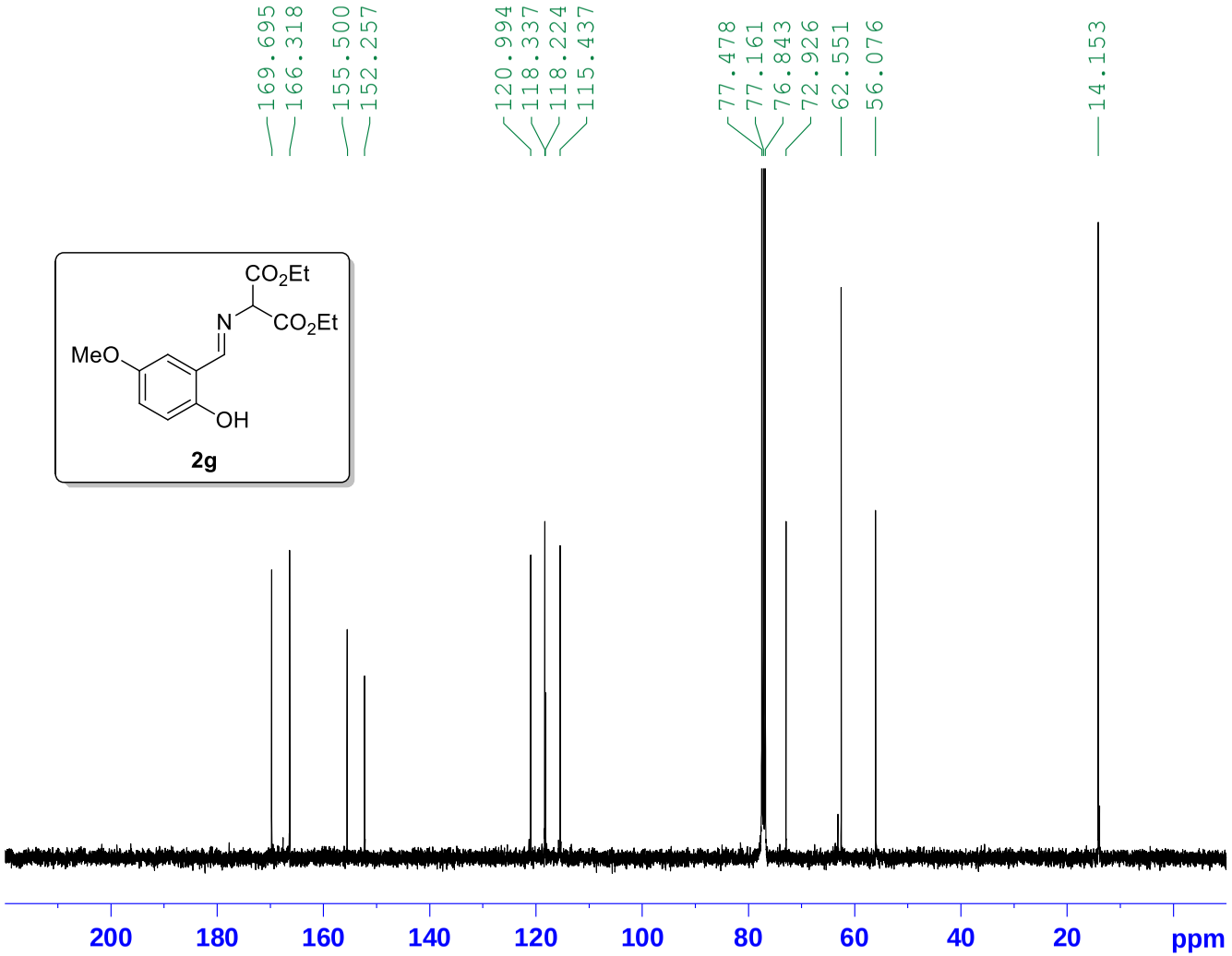

```
Current Data Parameters
NAME                      2e
EXPNO                      5
PROCNO                     1

F2 - Acquisition Parameters
Date_              20161113
Time                  16.04
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                7246.377 Hz
FIDRES            0.221142 Hz
AQ                2.2609921 sec
RG                     71.8
DW                   69.000 usec
DE                    6.50 usec
TE                   295.5 K
D1              2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                   14.40 usec
PL1                   1.80 dB
SFO1          400.1324008 MHz

F2 - Processing parameters
SI                    16384
SF            400.1300357 MHz
WDW                      EM
SSB          0
LB           0 Hz
GB           0
PC                     1.00
```



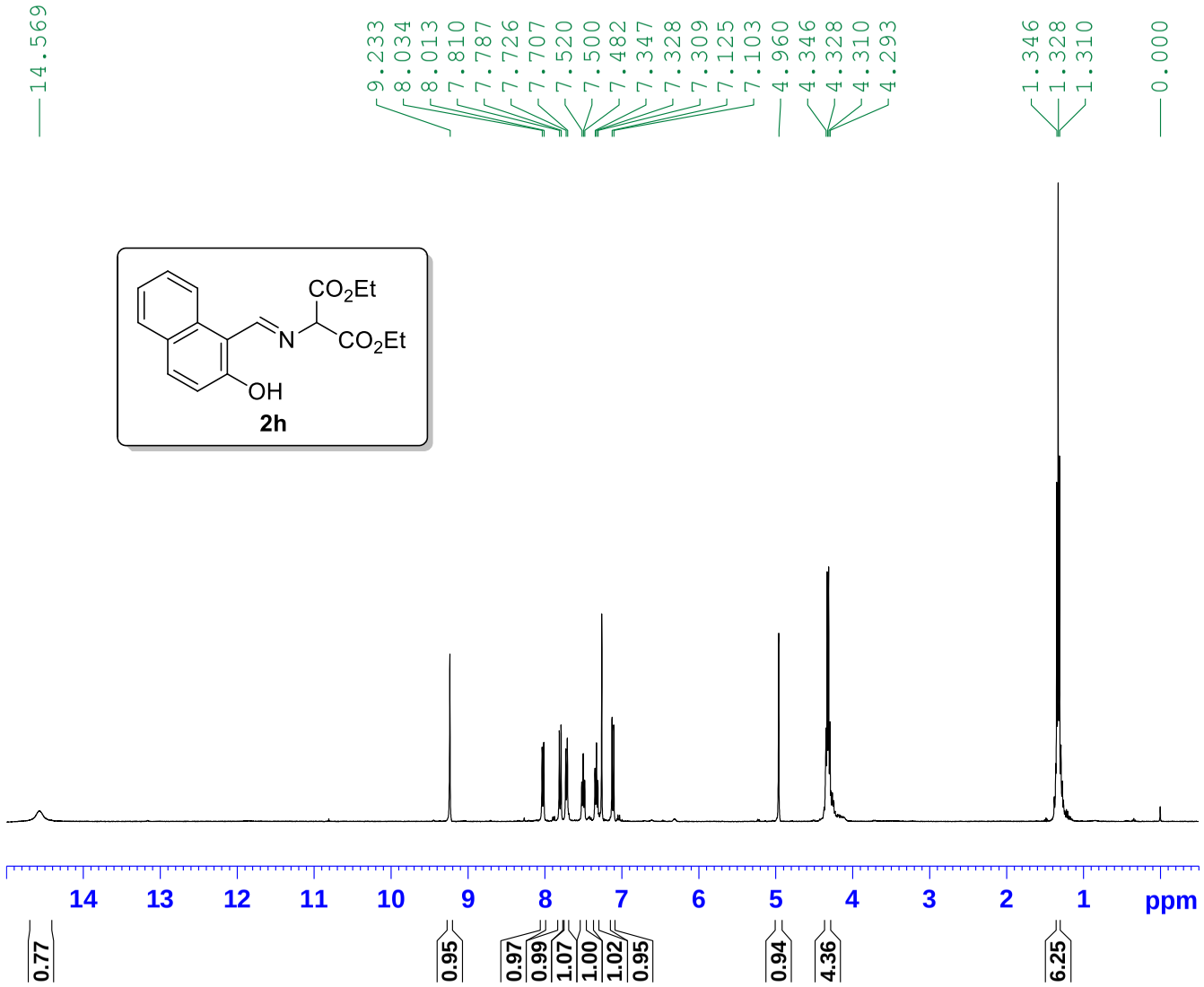

```
Current Data Parameters
NAME                  2e
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161113
Time               16.06
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                  1540
DS                     0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             0.6815744 sec
RG                3649.1
DW                20.800 usec
DE                 6.50 usec
TE                295.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 1.80 dB
PL12                17.00 dB
PL13                20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127551 MHz
WDW                  EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```



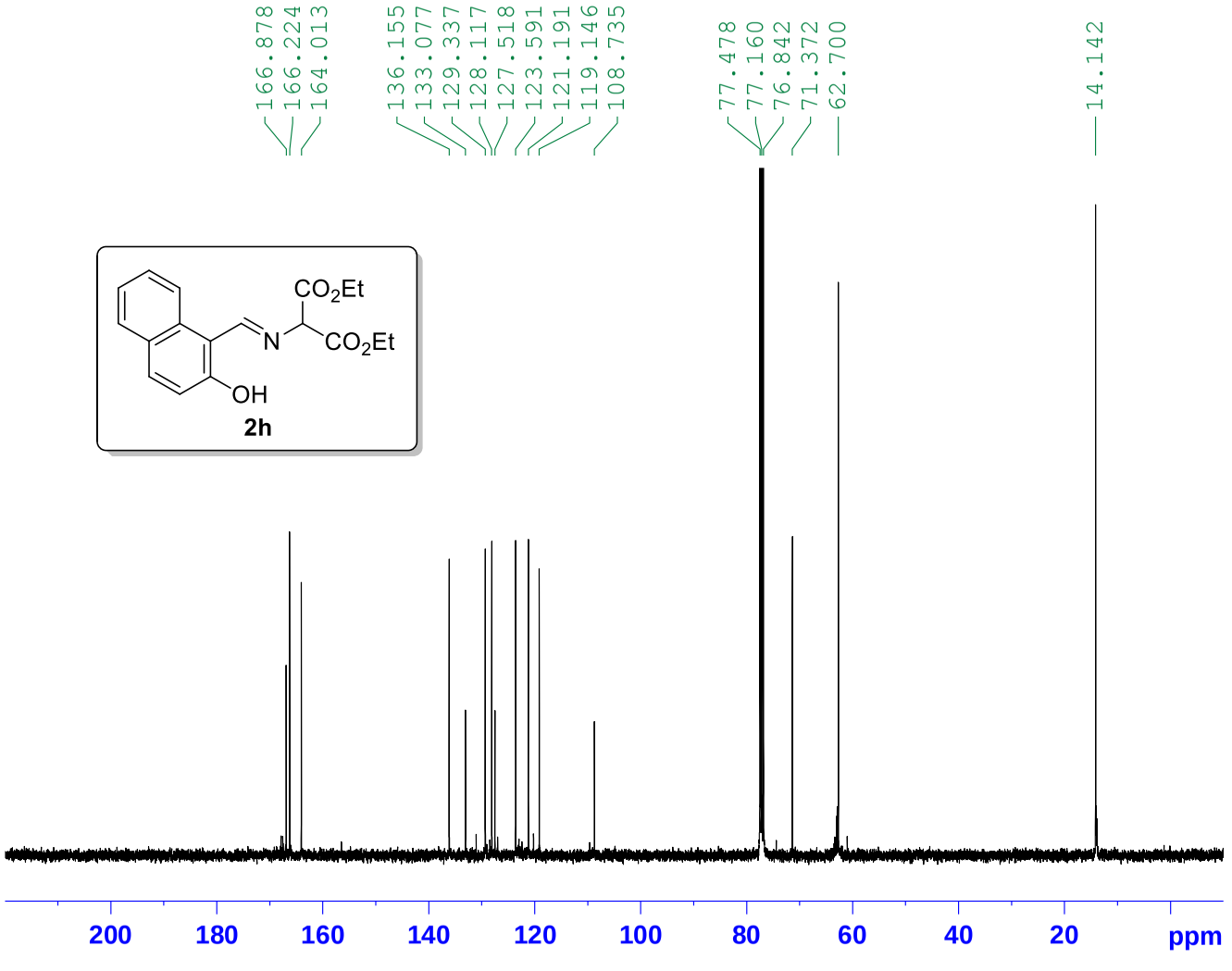

```
Current Data Parameters
NAME                  2g
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161112
Time              18.09
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            7246.377 Hz
FIDRES        0.221142 Hz
AQ            2.2609921 sec
RG                  114
DW               69.000 usec
DE                6.50 usec
TE                295.6 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.40 usec
PL1                1.80 dB
SFO1        400.1324008 MHz

F2 - Processing parameters
SI                16384
SF          400.1300074 MHz
WDW                  EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```



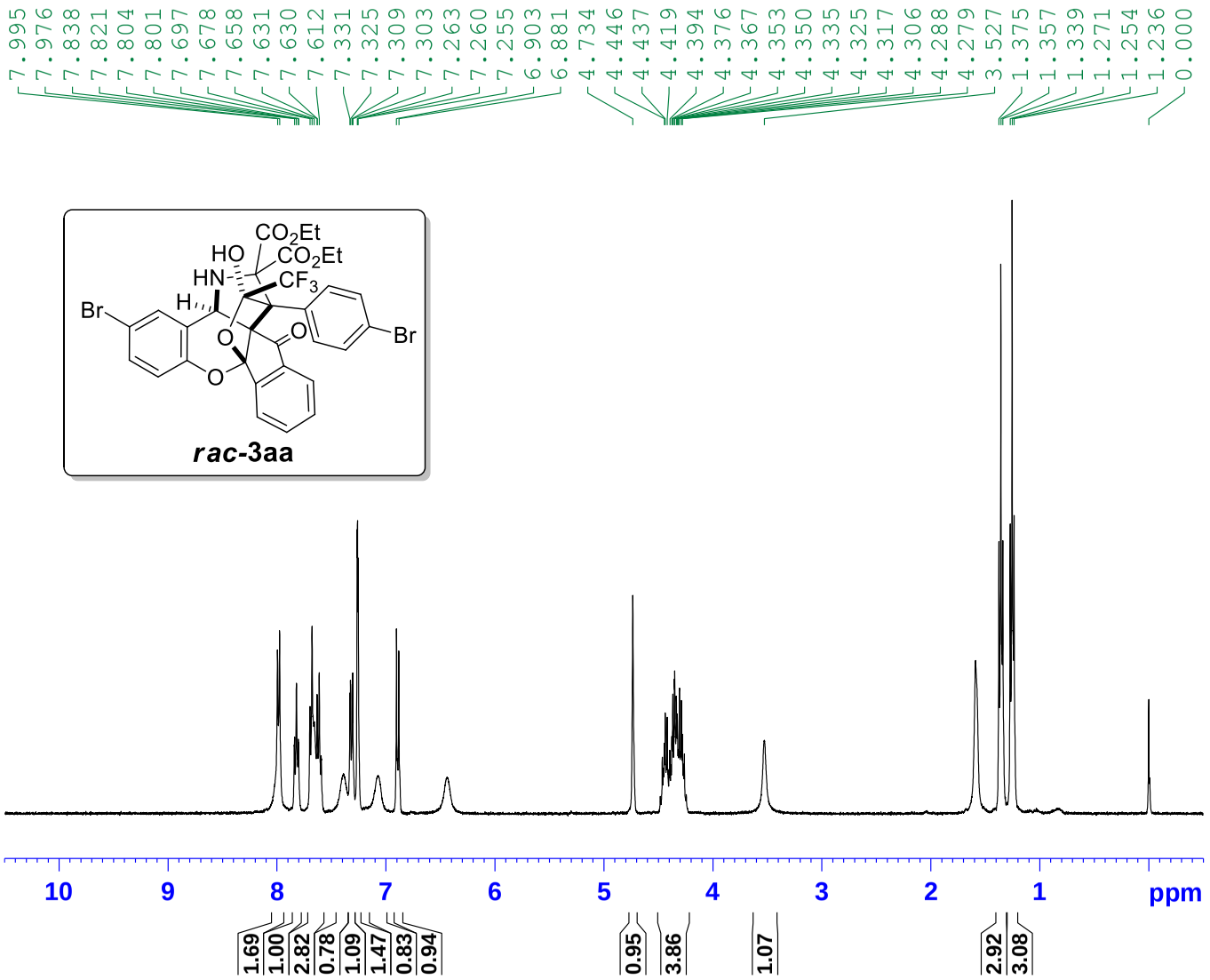

```
Current Data Parameters
NAME                      2g
EXPNO                      4
PROCNO                     1

F2 - Acquisition Parameters
Date_               20161112
Time                   18.12
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg30
TD                     32768
SOLVENT                CDC13
NS                      1810
DS                         0
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                0.6815744 sec
RG                    4597.6
DW                   20.800 usec
DE                    6.50 usec
TE                   295.6 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                        1

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

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                     1H
PCPD2                90.00 usec
PL2                   1.80 dB
PL12                 17.00 dB
PL13                 20.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF            100.6127551 MHz
WDW                       EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.00
```



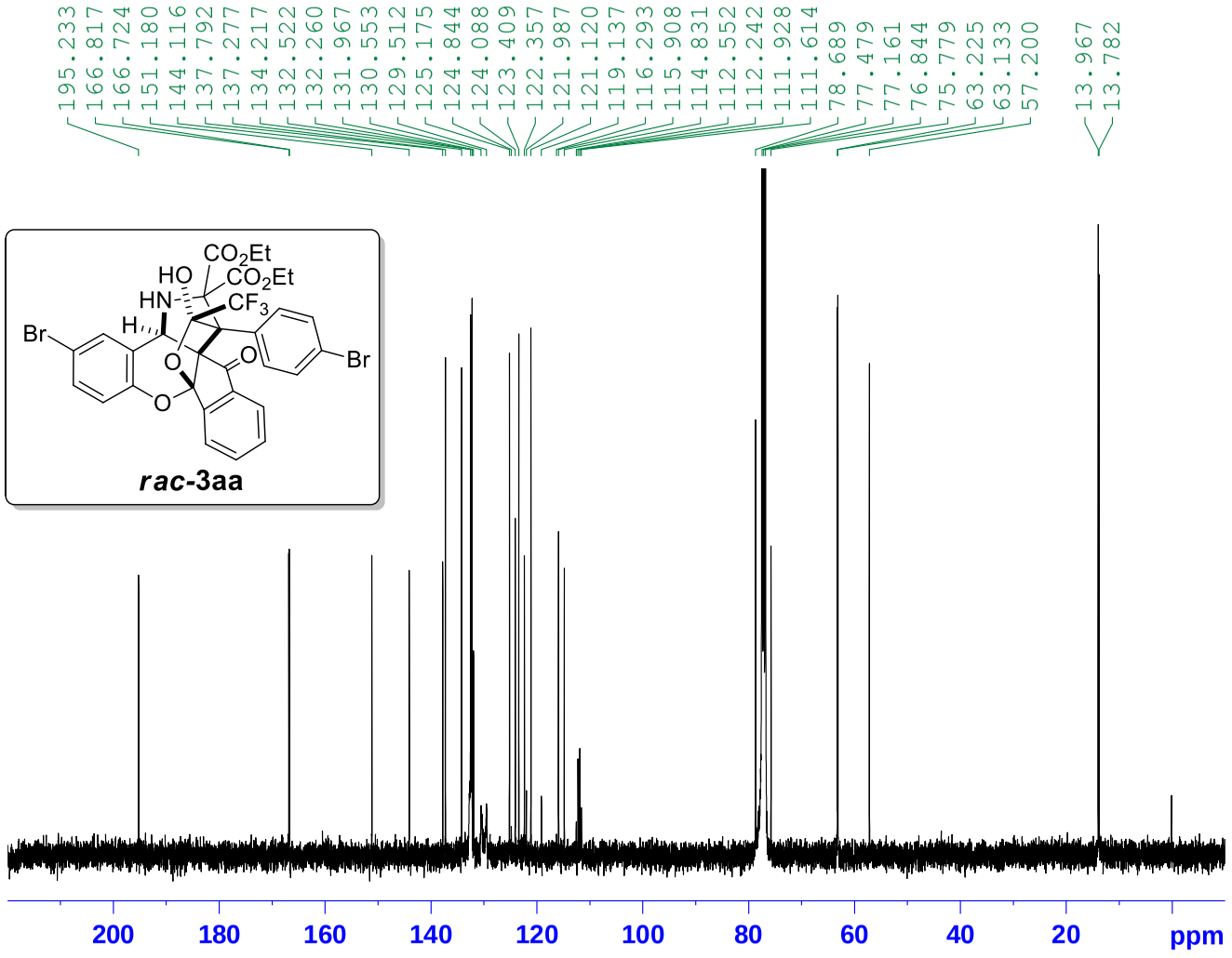

```
Current Data Parameters
NAME                      2h
EXPNO                      9
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170209
Time                  12.04
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                        8
DS                        0
SWH               7246.377 Hz
FIDRES           0.221142 Hz
AQ               2.2609921 sec
RG                      114
DW                 69.000 usec
DE                  6.50 usec
TE                  296.8 K
D1              2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                 14.40 usec
PL1                 1.80 dB
SFO1          400.1324008 MHz

F2 - Processing parameters
SI                    16384
SF            400.1300096 MHz
WDW                      EM
SSB       0
LB        0 Hz
GB        0
PC                    1.00
```



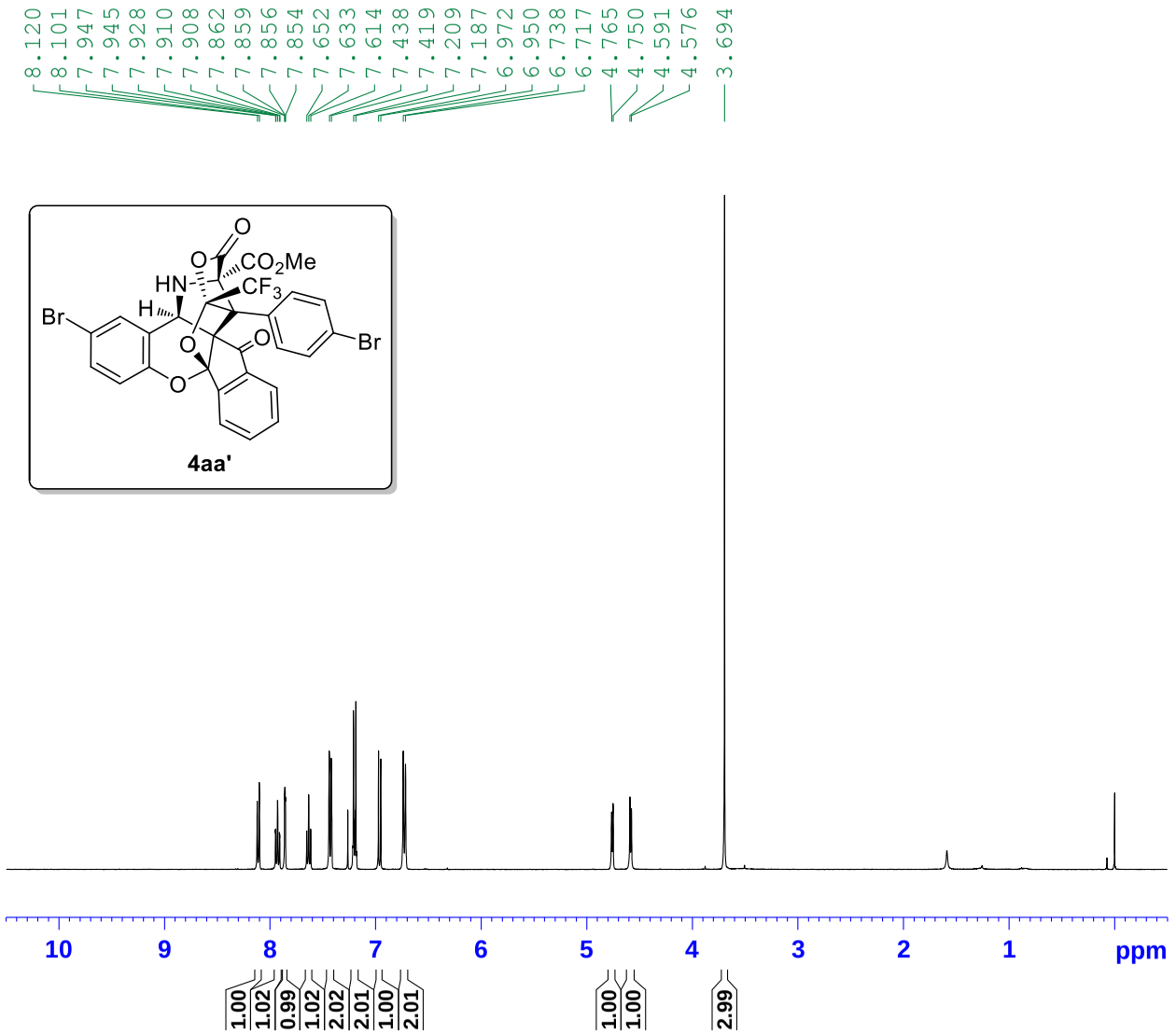

```
Current Data Parameters
NAME                      2h
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20170209
Time                   12.05
INSTRUM                spect
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                     32768
SOLVENT                CDCl3
NS                      1227
DS                         0
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                0.6815744 sec
RG                      4096
DW                   20.800 usec
DE                    6.50 usec
TE                   296.8 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                        1

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

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                     1H
PCPD2                90.00 usec
PL2                   1.80 dB
PL12                 17.00 dB
PL13                 20.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF            100.6127584 MHz
WDW                       EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.00
```



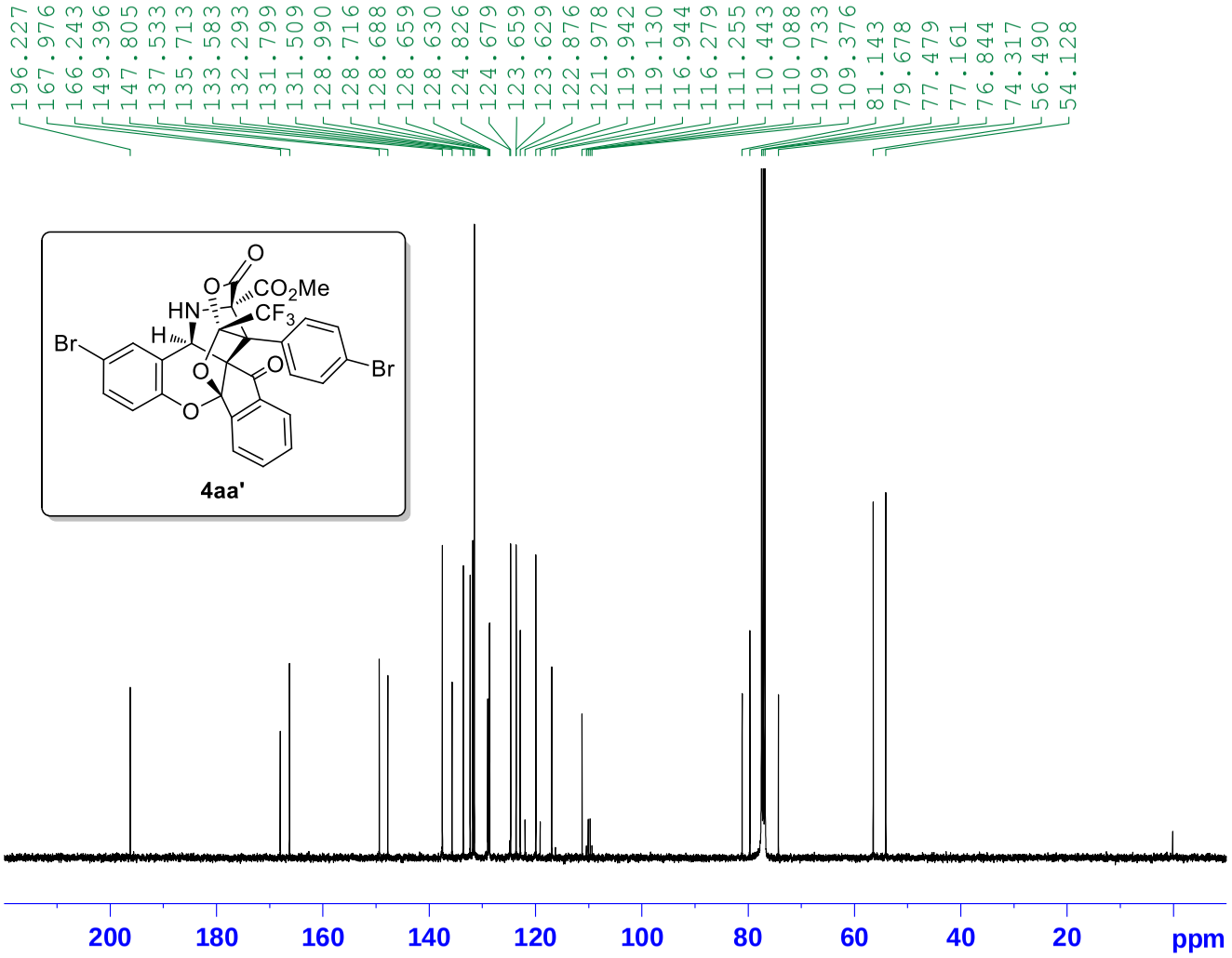

```
Current Data Parameters
NAME                  rac-3aa
EXPNO                      18
PROCNO                      1

F2 - Acquisition Parameters
Date_               20170207
Time                   21.53
INSTRUM                spect
PROBHD    5 mm BBO BB-1H
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         0
SWH                 7246.377 Hz
FIDRES              0.221142 Hz
AQ                  2.2609921 sec
RG                     322.5
DW                    69.000 usec
DE                     6.50 usec
TE                    296.6 K
D1                 2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                       1H
P1                     11.90 usec
PL1                     3.00 dB
SFO1            400.1324008 MHz

F2 - Processing parameters
SI                     16384
SF              400.1300082 MHz
WDW                       EM
SSB          0
LB           0 Hz
GB           0
PC                      1.00
```



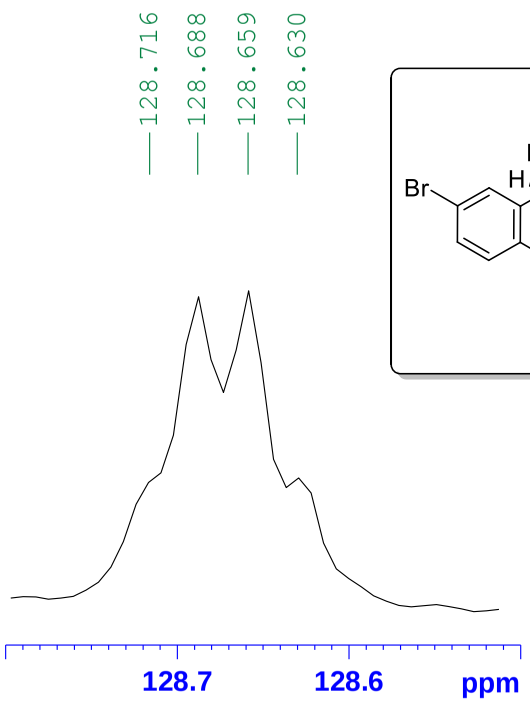

```
Current Data Parameters
NAME                  rac-3aa
EXPNO                      19
PROCNO                      1

F2 - Acquisition Parameters
Date_                20170207
Time                    22.17
INSTRUM                 spect
PROBHD   5 mm BBO BB-1H
PULPROG                zgpg30
TD                      32768
SOLVENT                 CDCl3
NS                      15346
DS                          0
SWH                 24038.461 Hz
FIDRES               0.733596 Hz
AQ                   0.6815744 sec
RG                      9195.2
DW                      20.800 usec
DE                       6.50 usec
TE                      296.7 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

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

======== CHANNEL f2 ========
CPDPRG[2                waltz16
NUC2                       1H
PCPD2                    90.00 usec
PL2                       1.80 dB
PL12                     17.00 dB
PL13                     20.00 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                 100.6127547 MHz
WDW                           EM
SSB          0
LB                        1.00 Hz
GB           0
PC                        1.00
```

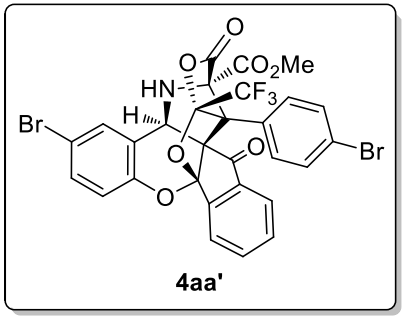


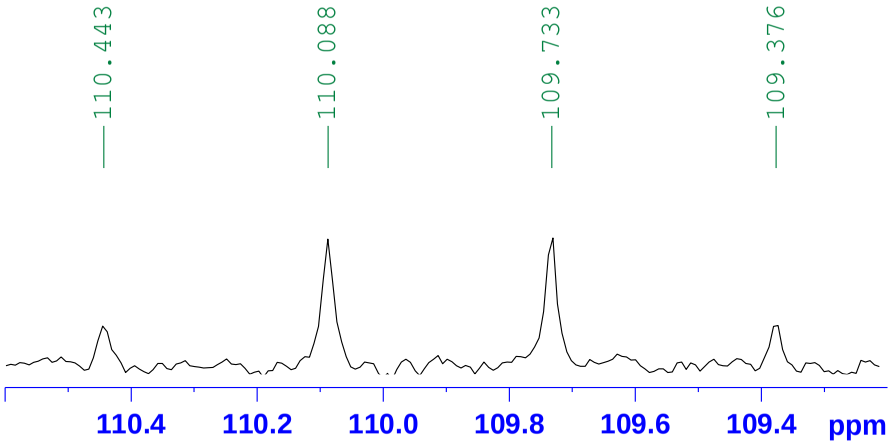

```
Current Data Parameters
NAME                  4aa'
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_              20161104
Time                 23.06
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      18
DS                       0
SWH               7246.377 Hz
FIDRES           0.221142 Hz
AQ               2.2609921 sec
RG                     181
DW                69.000 usec
DE                 6.50 usec
TE                 295.8 K
D1             2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.40 usec
PL1                 1.80 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                   16384
SF           400.1300083 MHz
WDW                     EM
SSB       0
LB        0 Hz
GB        0
PC                   1.00
```

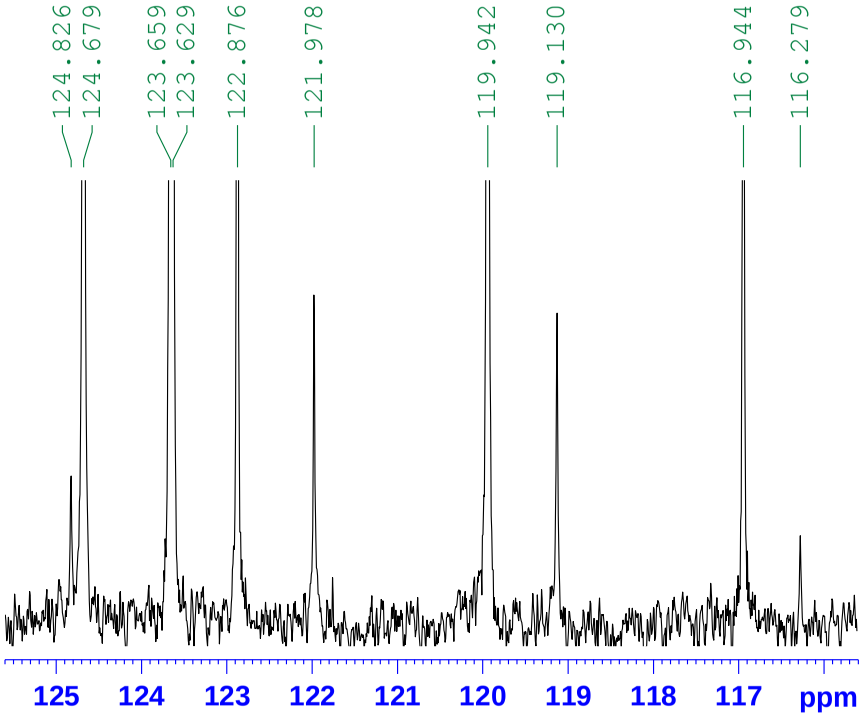


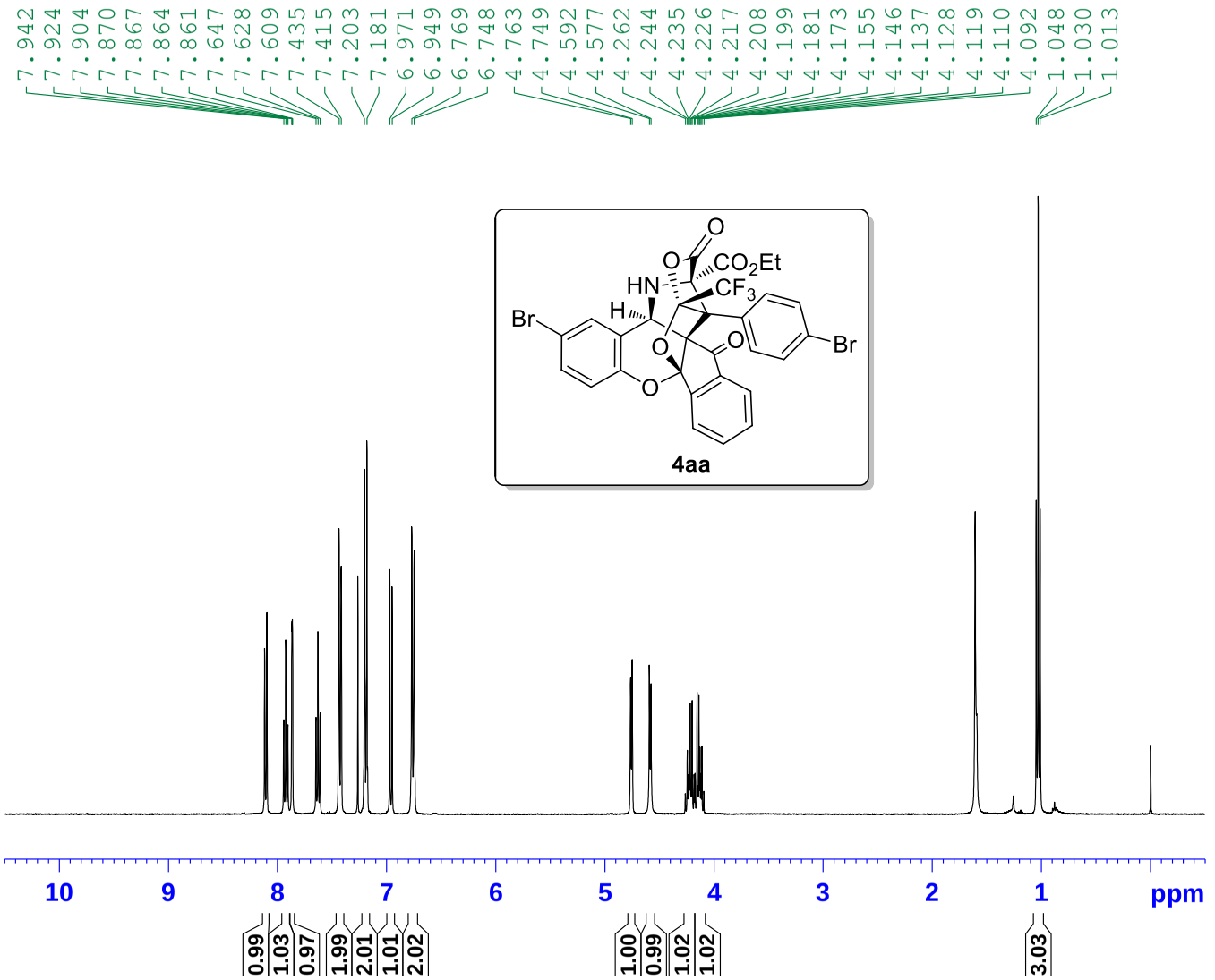

```
Current Data Parameters
NAME                  4aa'
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_              20161104
Time                 23.09
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                   12172
DS                       0
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                0.6815744 sec
RG                  5792.6
DW                  20.800 usec
DE                   6.50 usec
TE                  295.8 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1

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

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                   1H
PCPD2                90.00 usec
PL2                   1.80 dB
PL12                 17.00 dB
PL13                 20.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127555 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.00
```


128.716
128.688
128.659
128.630
128.7
128.6
ppm

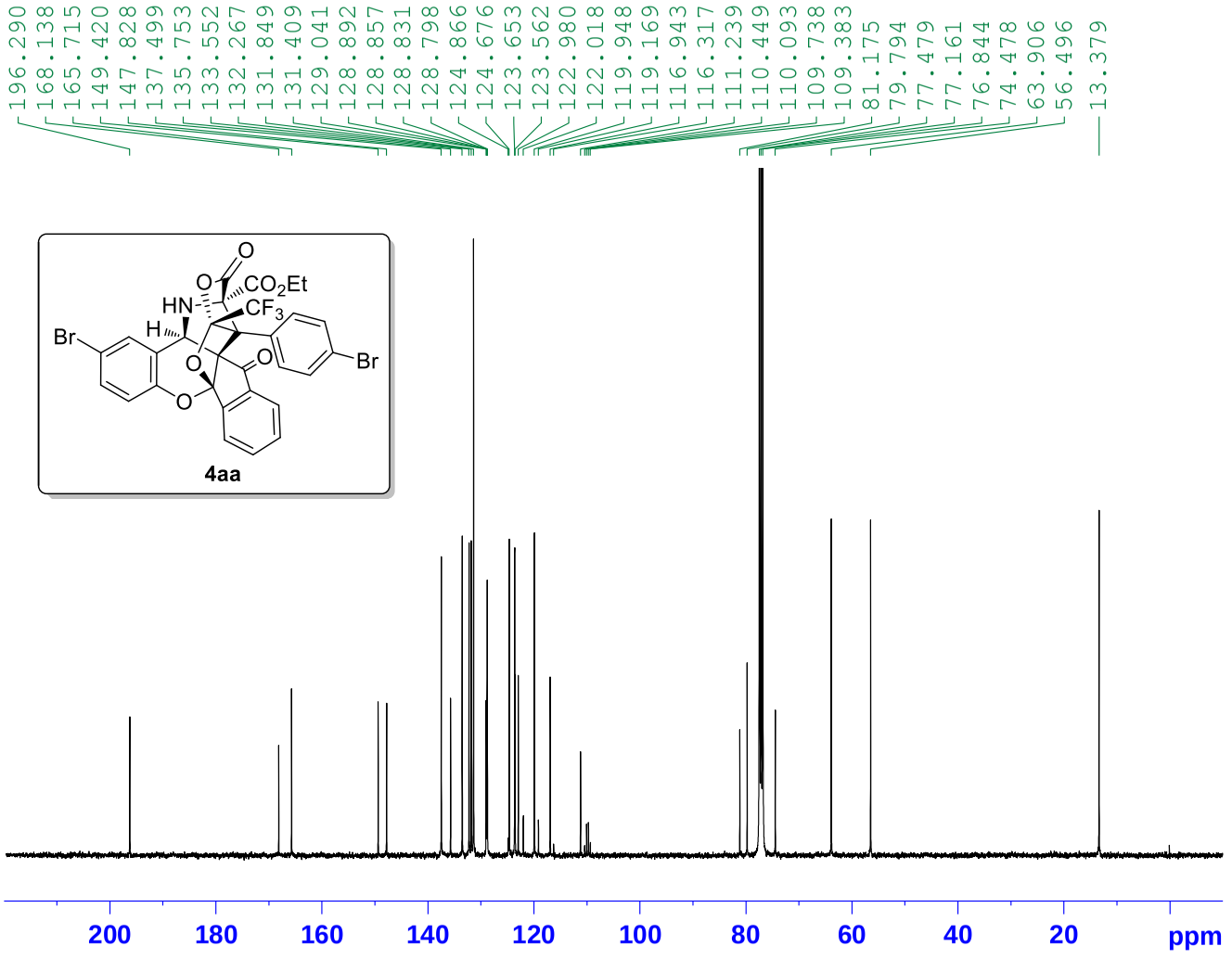

O
O
CO2Me
HN
CF3
H
Br
Br
O
O
O
4aa'


110.443
110.088
109.733
109.376
110.4
110.2
110.0
109.8
109.6
109.4
ppm

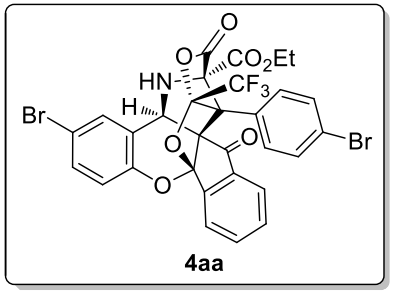

124.826
124.679
123.659
123.629
122.876
121.978
119.942
119.130
116.944
116.279
125
124
123
122
121
120
119
118
117
ppm



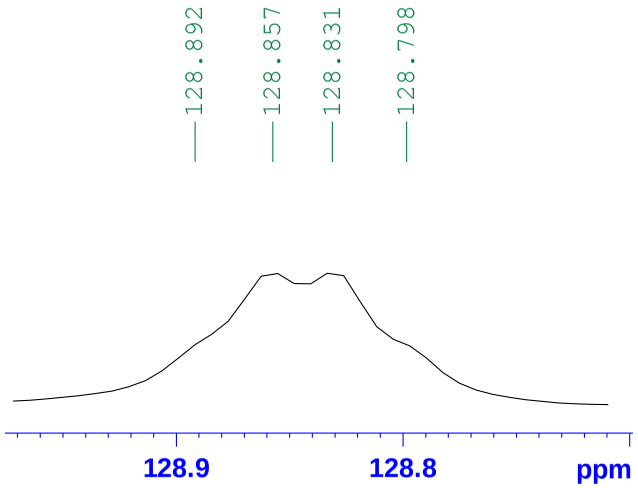

```
Current Data Parameters
NAME                  4aa
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160709
Time              21.13
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH             7211.539 Hz
FIDRES          0.220079 Hz
AQ              2.2719147 sec
RG                113.31
DW                69.333 usec
DE                10.50 usec
TE                297.8 K
D1             2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                1H
P1                12.90 usec
PLW1         15.00000000 W

F2 - Processing parameters
SI                16384
SF           400.1300087 MHz
WDW                 EM
SSB       0
LB        0 Hz
GB        0
PC                1.00
```

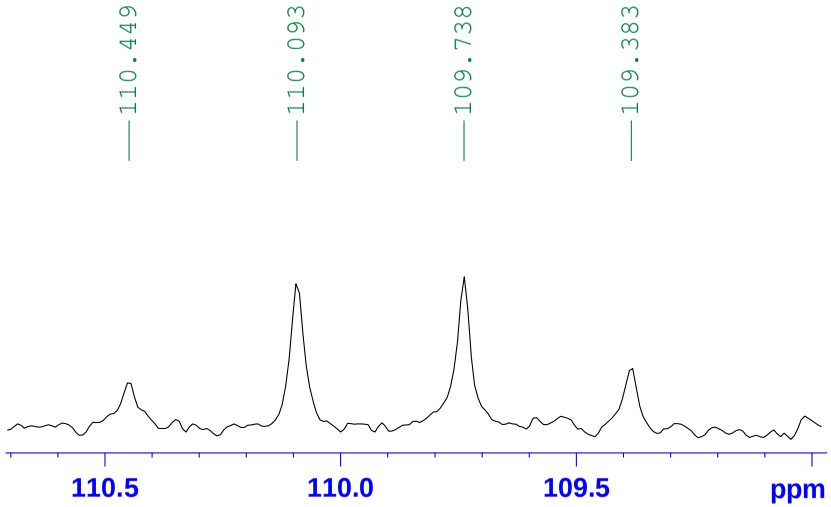


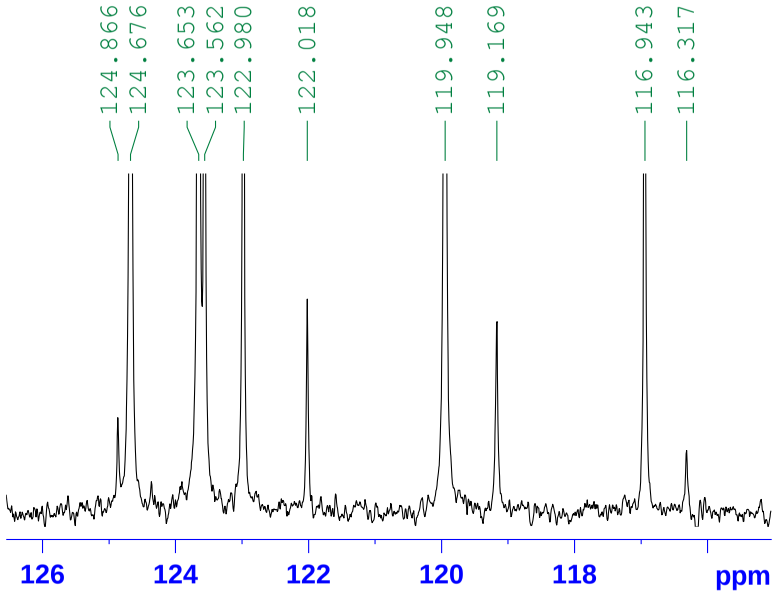

```
Current Data Parameters
NAME                  4aa
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160709
Time              21.16
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                20000
DS                    0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             0.6815744 sec
RG                198.09
DW                20.800 usec
DE                 6.50 usec
TE                298.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                13C
P1                10.00 usec
PLW1         47.50000000 W

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

F2 - Processing parameters
SI                32768
SF           100.6127546 MHz
WDW                 EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

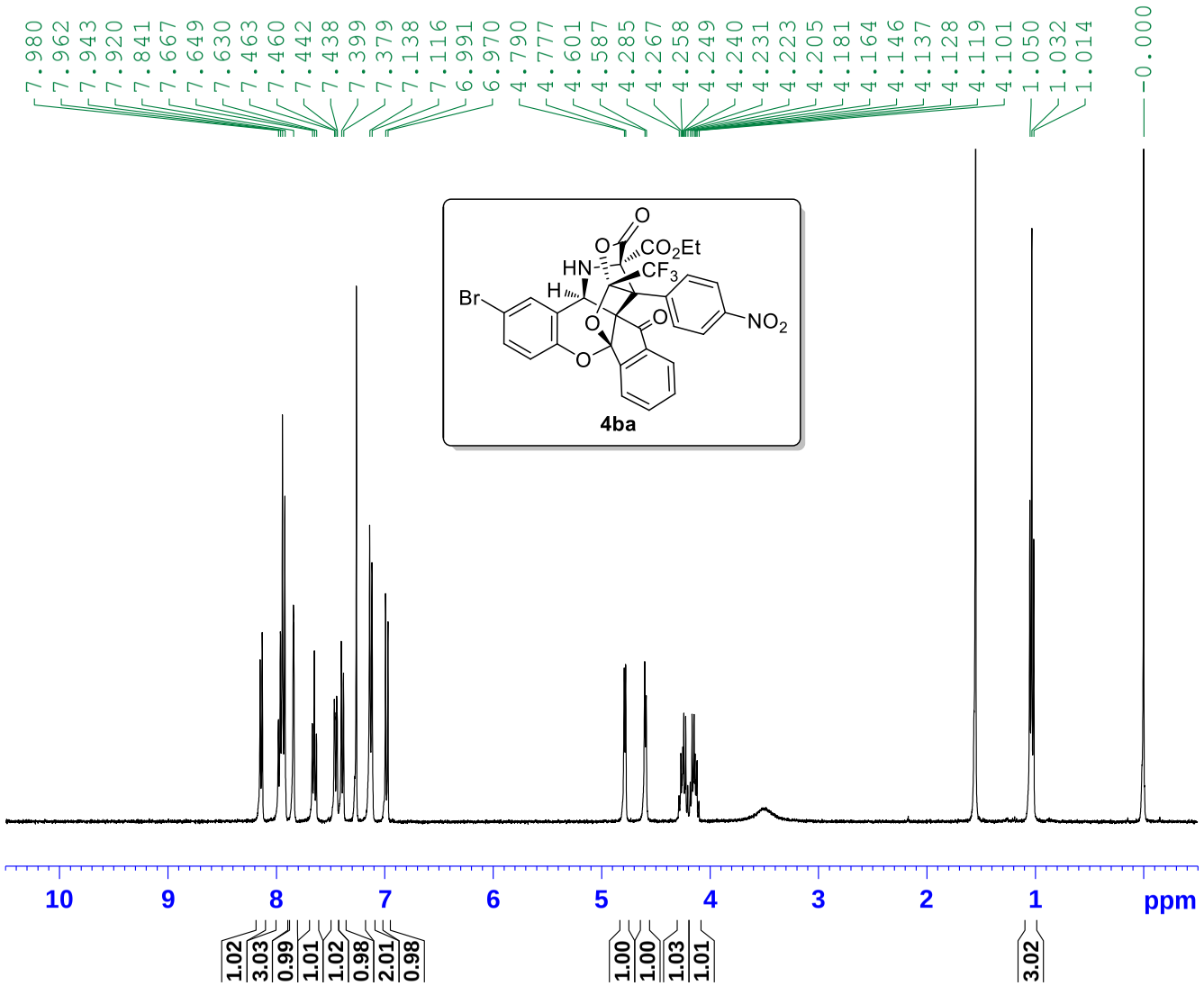

O
O
CO2Et
HN
CF3
H
Br
Br
O
O
O

4aa

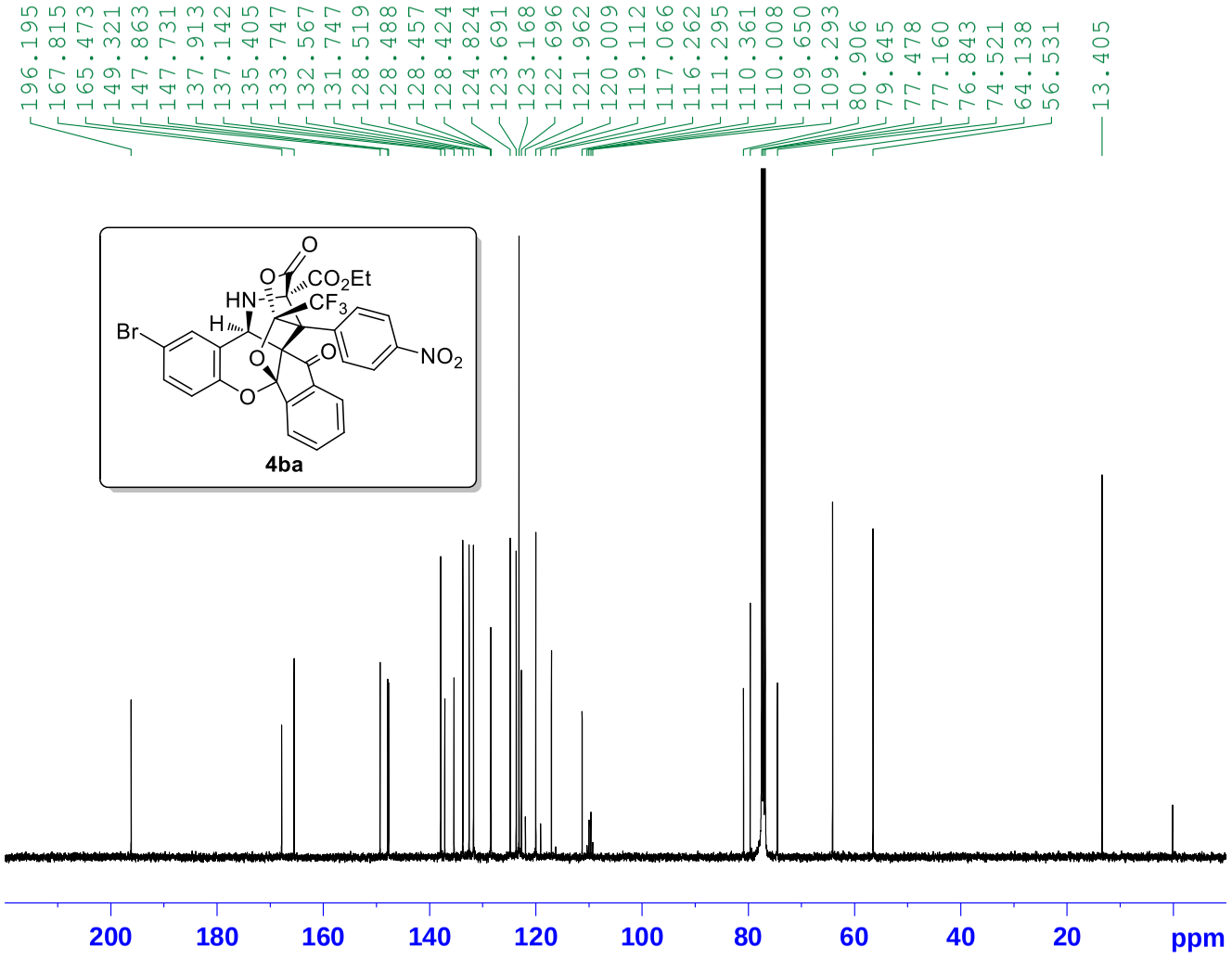

128.892
128.857
128.831
128.798
128.9
128.8
ppm


110.449
110.093
109.738
109.383
110.5
110.0
109.5
ppm

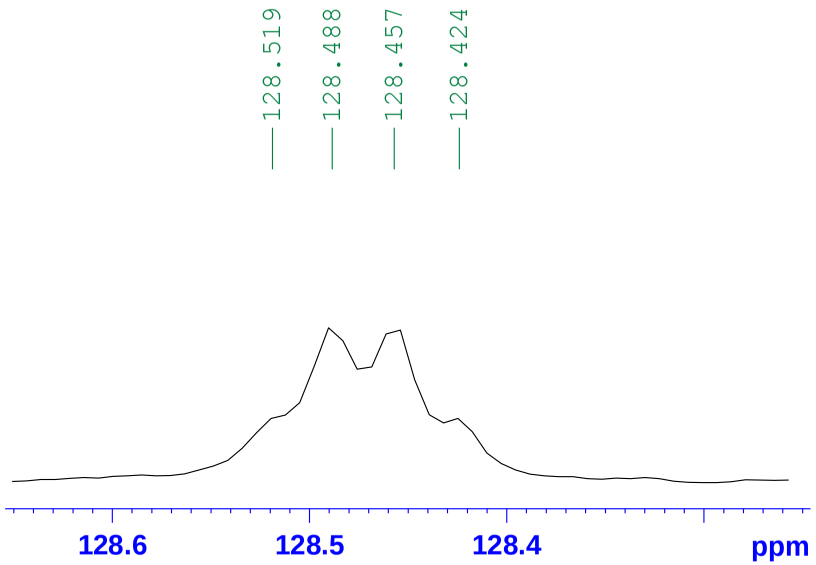

124.866
124.676
123.653
123.562
122.980
122.018
119.948
119.169
116.943
116.317
126
124
122
120
118
ppm

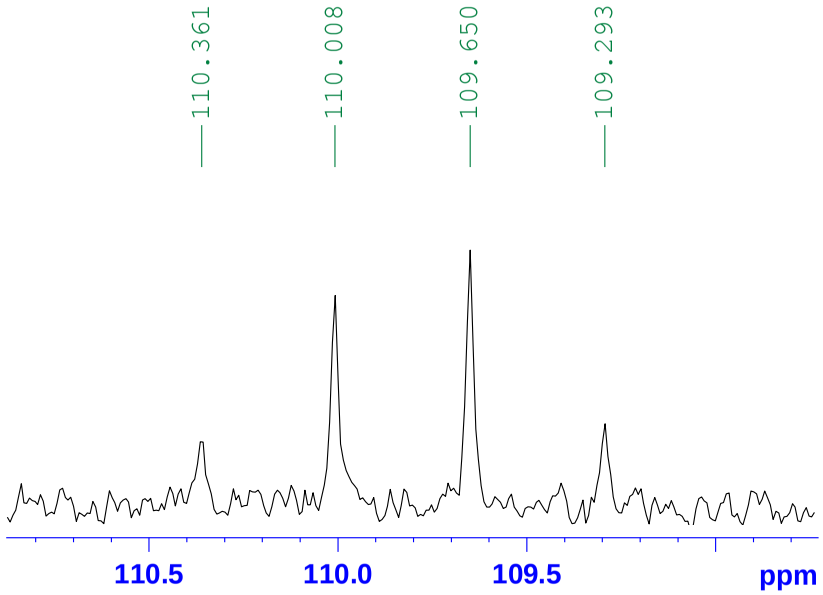


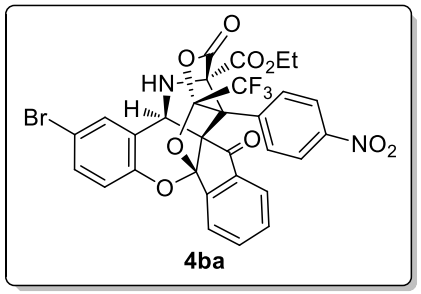

```
Current Data Parameters
NAME                  Mei-4ba
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_                20170325
Time                    17.07
INSTRUM                 spect
PROBHD   5 mm BBO BB-1H
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                         50
DS                          0
SWH                 7246.377 Hz
FIDRES              0.221142 Hz
AQ                  2.2609921 sec
RG                        362
DW                     69.000 usec
DE                      6.50 usec
TE                     298.5 K
D1                  2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     14.40 usec
PL1                     1.80 dB
SFO1             400.1324008 MHz

F2 - Processing parameters
SI                      16384
SF                 400.1300091 MHz
WDW                        EM
SSB          0
LB           0 Hz
GB           0
PC                      1.00
```

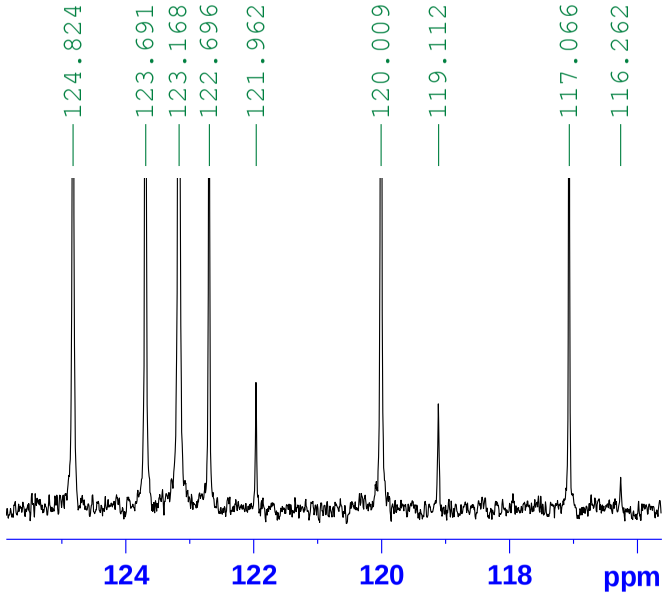


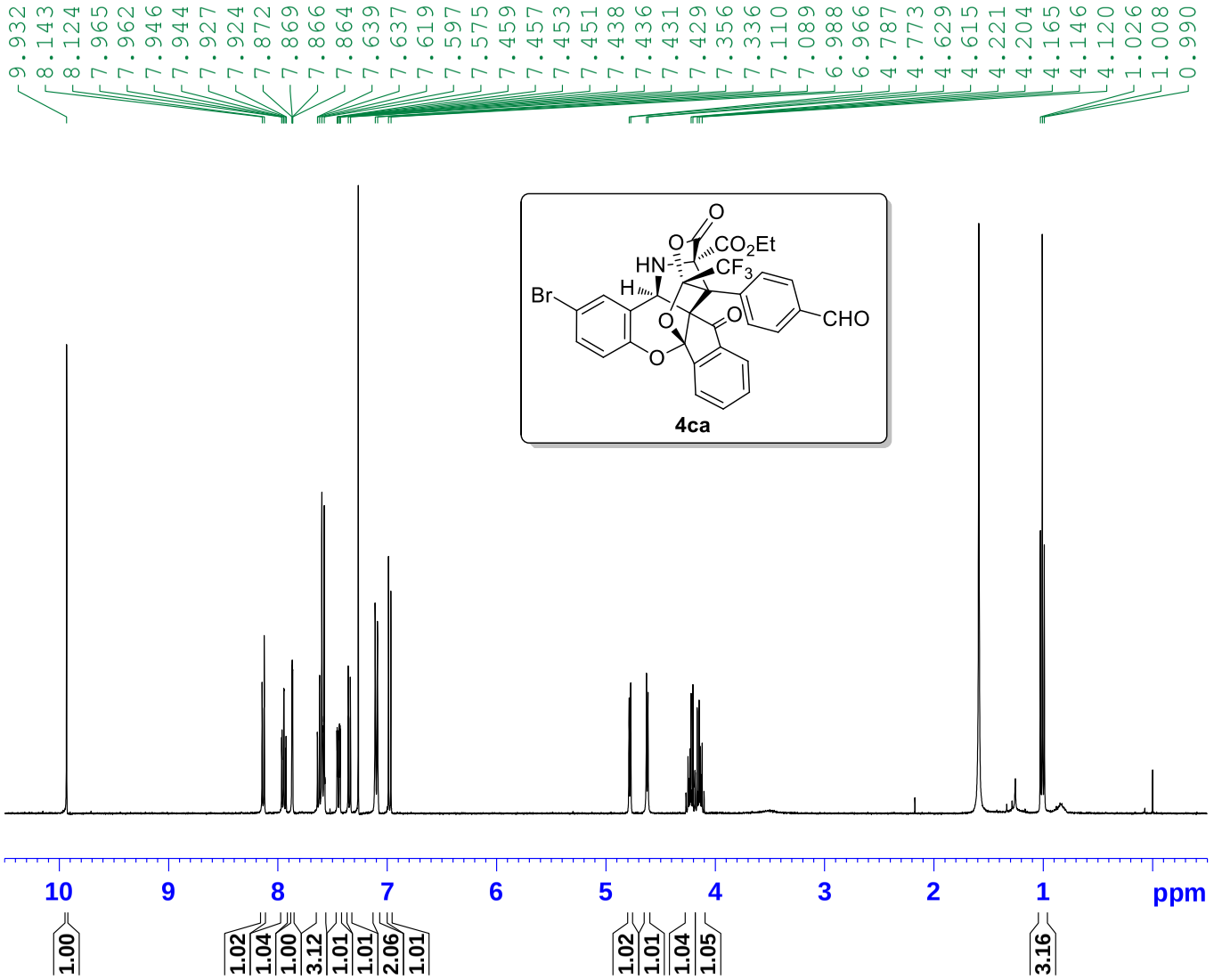

```
Current Data Parameters
NAME                  4ba
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160521
Time              22.02
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                17626
DS                    0
SWH          24038.461 Hz
FIDRES        0.733596 Hz
AQ            0.6815744 sec
RG               9195.2
DW               20.800 usec
DE                6.50 usec
TE               297.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                1.80 dB
PL12              17.00 dB
PL13              20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127541 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.00
```


128.519
128.488
128.457
128.424
128.6
128.5
128.4
ppm

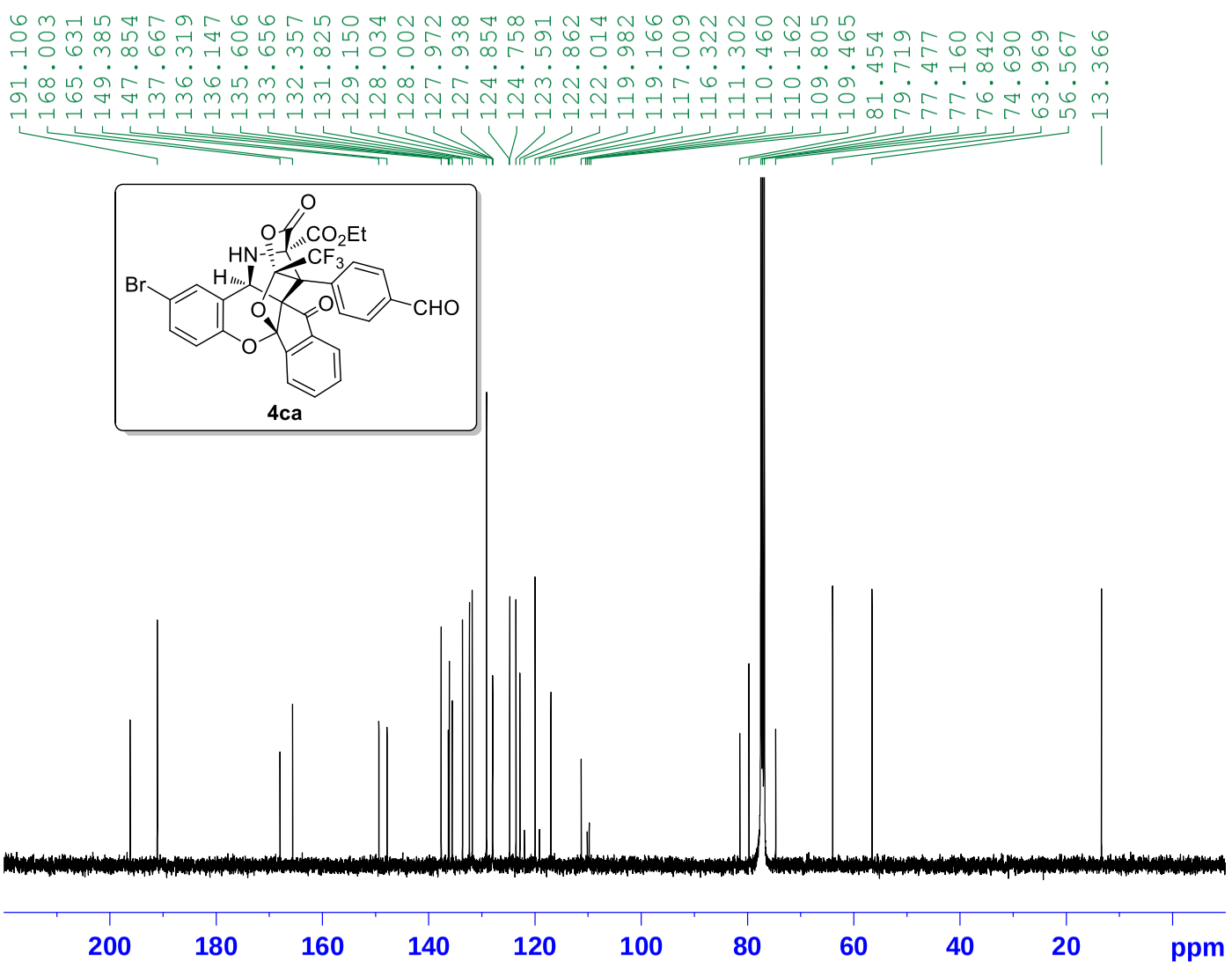

110.361
110.008
109.650
109.293
110.5
110.0
109.5
ppm


O
O
CO2Et
HN
CF3
H
Br
O
O
NO2
O
4ba

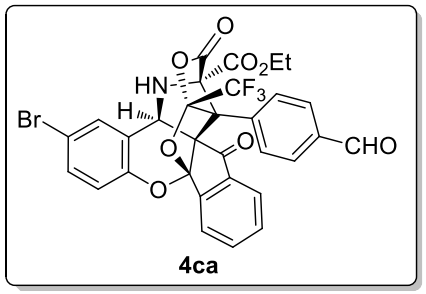

124.824
123.691
123.168
122.696
121.962
120.009
119.112
117.066
116.262
124
122
120
118
ppm

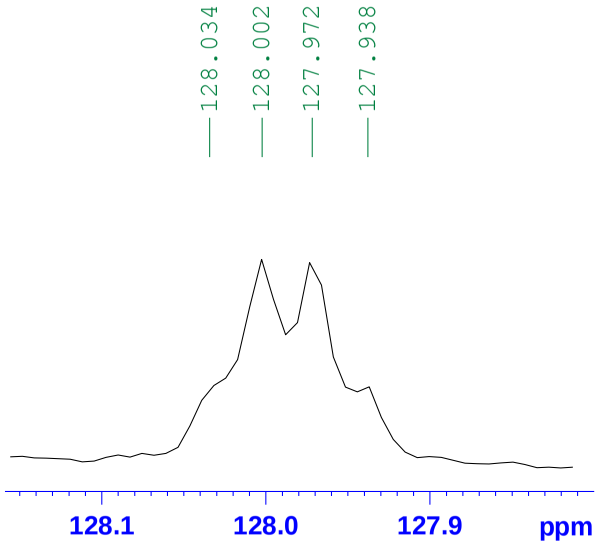


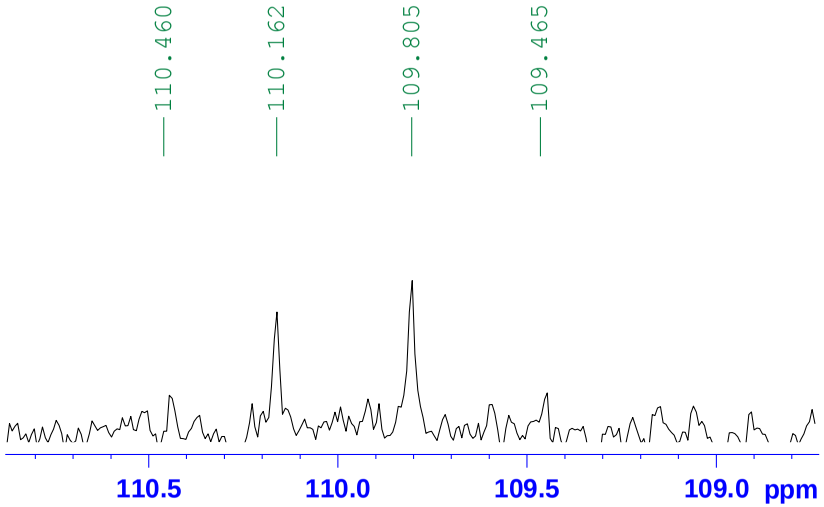

```
Current Data Parameters
NAME                  4ca
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160801
Time                22.30
INSTRUM             spect
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              7246.377 Hz
FIDRES           0.221142 Hz
AQ               2.2609921 sec
RG                    362
DW                 69.000 usec
DE                  6.50 usec
TE                 297.0 K
D1              2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.40 usec
PL1                 1.80 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                  16384
SF           400.1300078 MHz
WDW                    EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

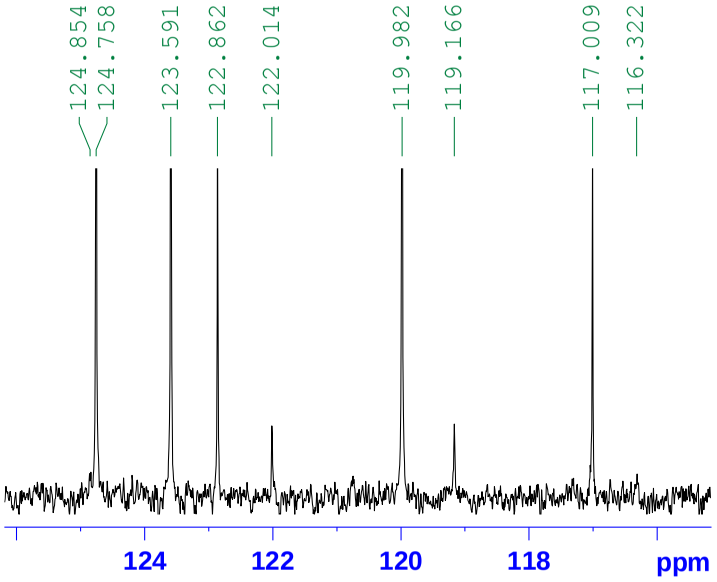


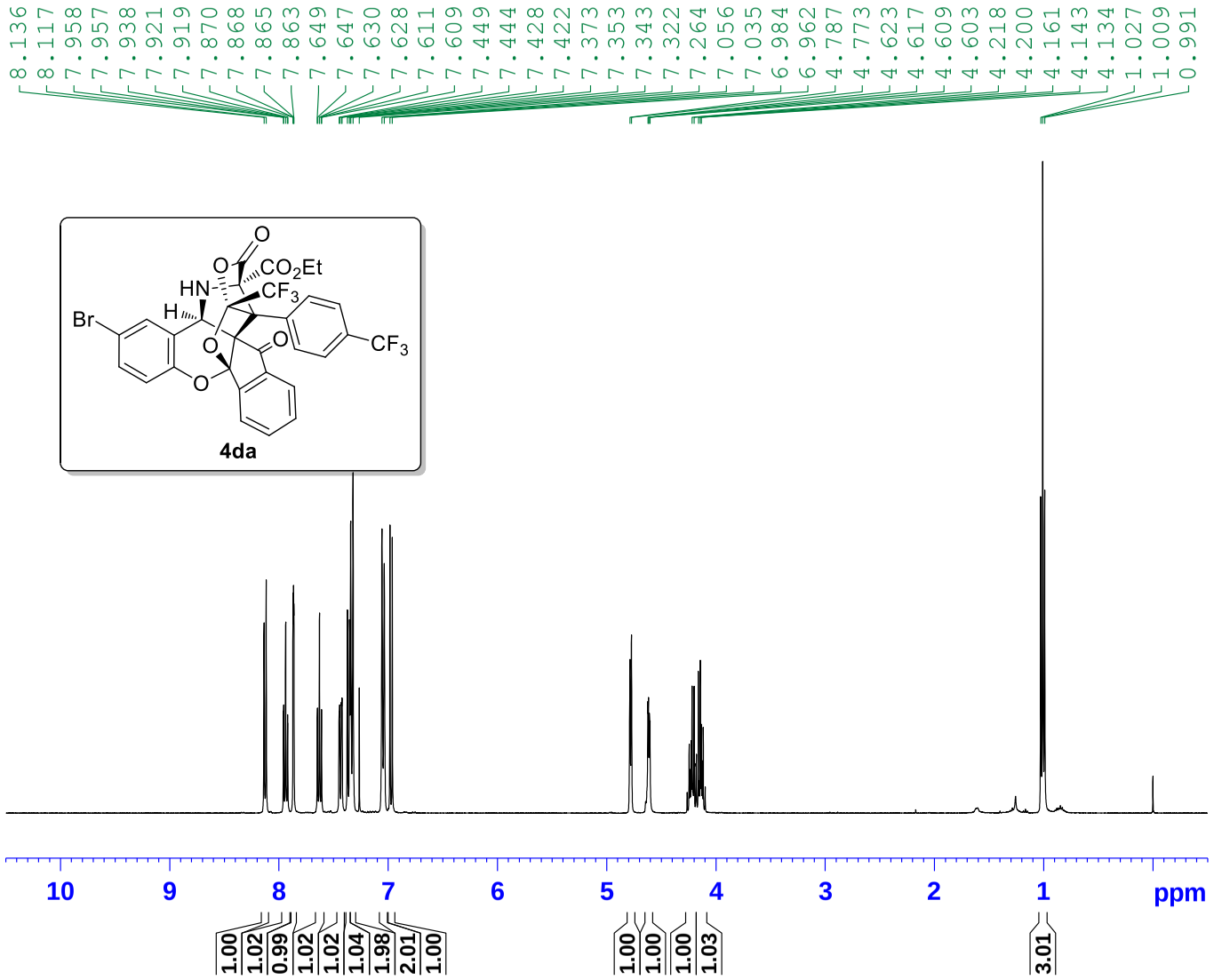

```
Current Data Parameters
NAME                   4ca
EXPNO                    7
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160801
Time                 22.32
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                   14470
DS                       0
SWH              24038.461 Hz
FIDRES           0.733596 Hz
AQ               0.6815744 sec
RG                  9195.2
DW                  20.800 usec
DE                   6.50 usec
TE                  297.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

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

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                  1.80 dB
PL12                17.00 dB
PL13                20.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF           100.6127540 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.00
```


O
O
CO2Et
HN
CF3
H
Br
O
O
O
CHO
4ca

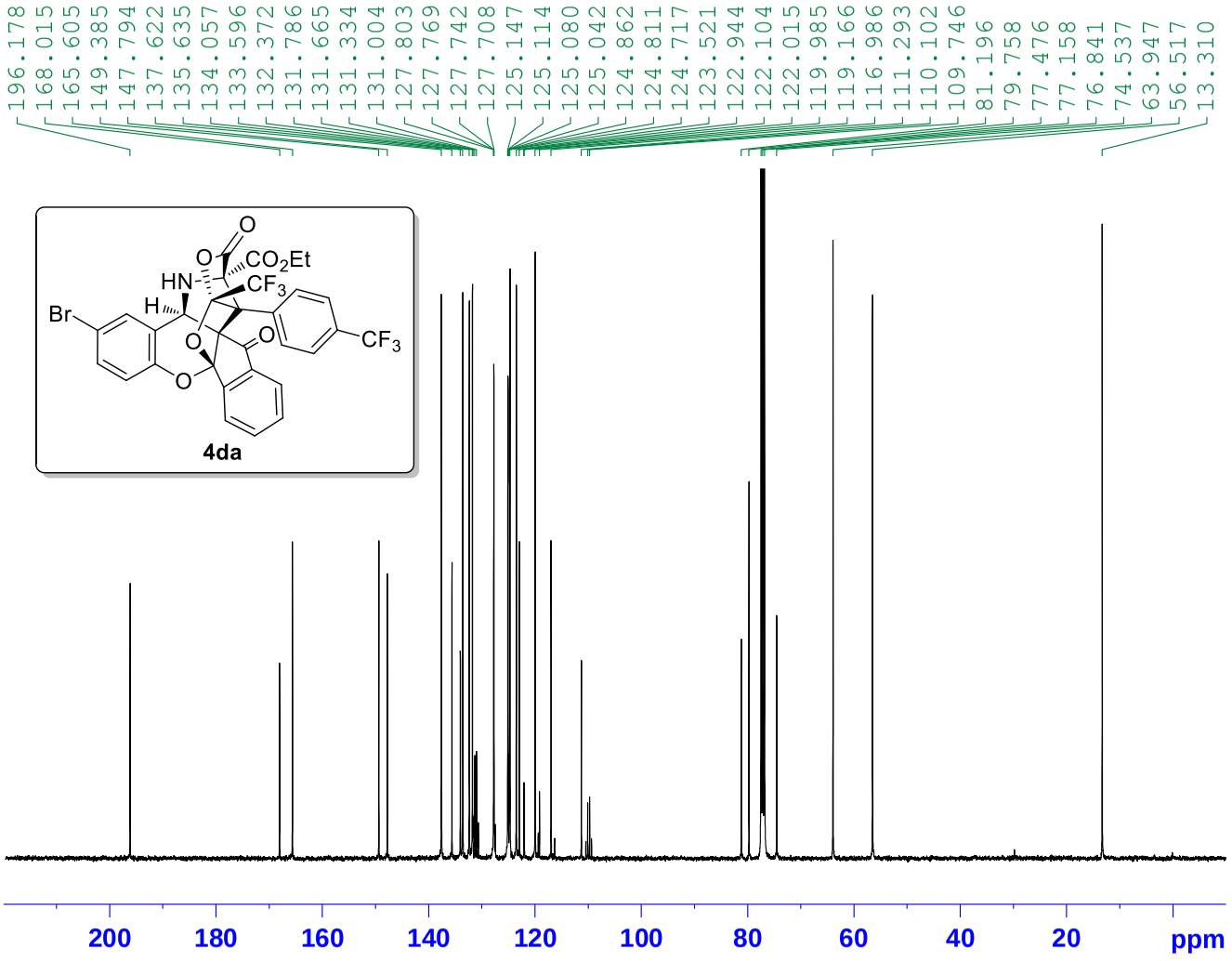

128.034
128.002
127.972
127.938
128.1
128.0
127.9
ppm


110.460
110.162
109.805
109.465
110.5
110.0
109.5
109.0
ppm

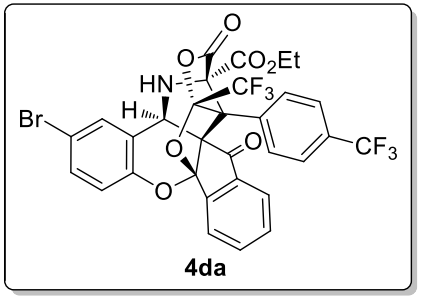

124.854
124.758
123.591
122.862
122.014
119.982
119.166
117.009
116.322
124
122
120
118
ppm

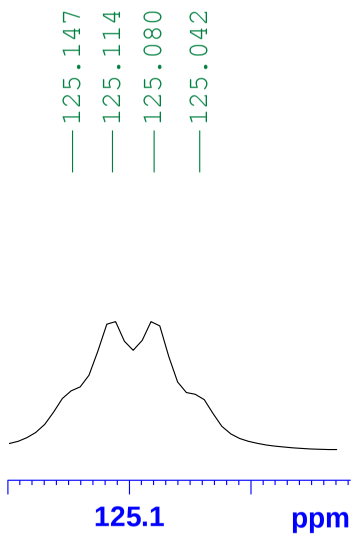


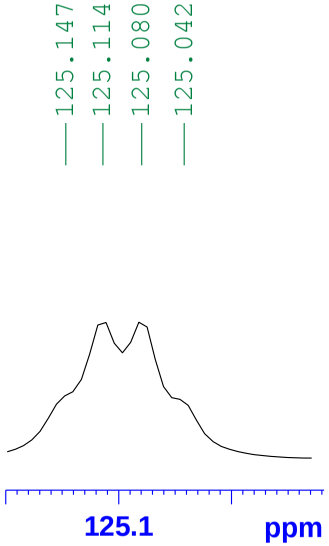

```
Current Data Parameters
NAME                  4da
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170117
Time                22.07
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              7211.539 Hz
FIDRES           0.220079 Hz
AQ               2.2719147 sec
RG                  89.08
DW                 69.333 usec
DE                 10.50 usec
TE                 297.5 K
D1            2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324008 MHz
NUC1                   1H
P1                  12.90 usec
PLW1         15.00000000 W

F2 - Processing parameters
SI                  16384
SF            400.1300084 MHz
WDW                    EM
SSB       0
LB        0 Hz
GB        0
PC                   1.00
```

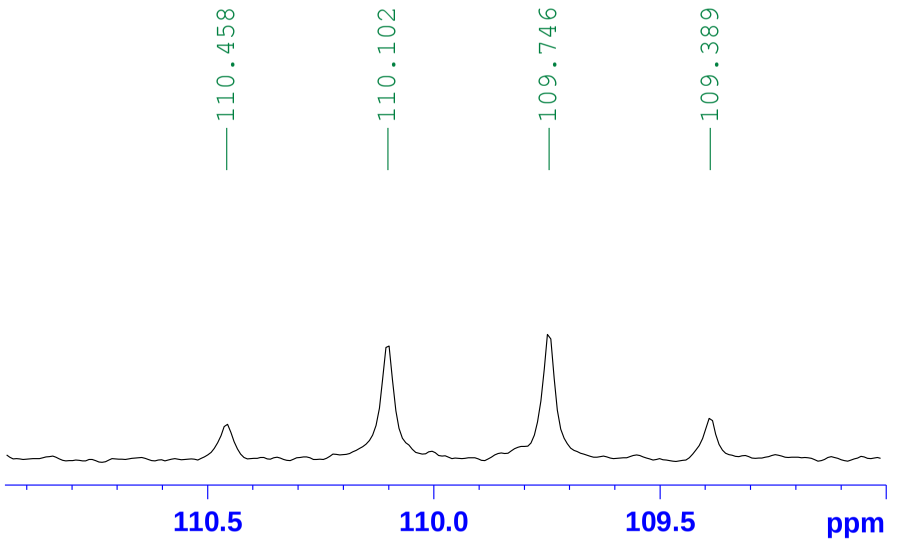


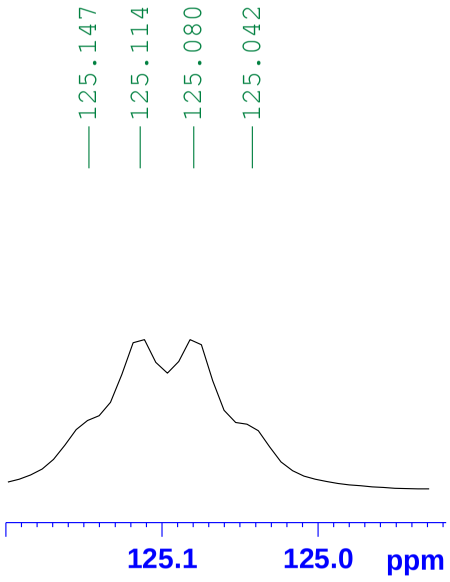

```
Current Data Parameters
NAME                   4da
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170117
Time                 22.40
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG            zgpg30
TD                   32768
SOLVENT              CDCl3
NS                   13780
DS                       0
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ              0.6815744 sec
RG                  198.09
DW                20.800 usec
DE                 6.50 usec
TE                 297.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                    13C
P1                  10.00 usec
PLW1          47.50000000 W

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

F2 - Processing parameters
SI                   32768
SF            100.6127557 MHz
WDW                     EM
SSB       0
LB                  2.00 Hz
GB        0
PC                  1.00
```

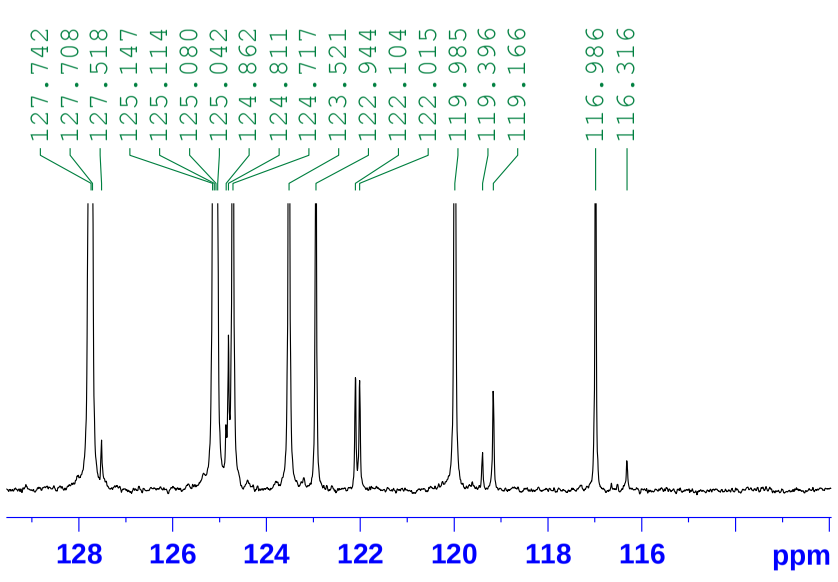

O
O
CO2Et
HN
CF3
H
Br
O
O
CF3
O
4da

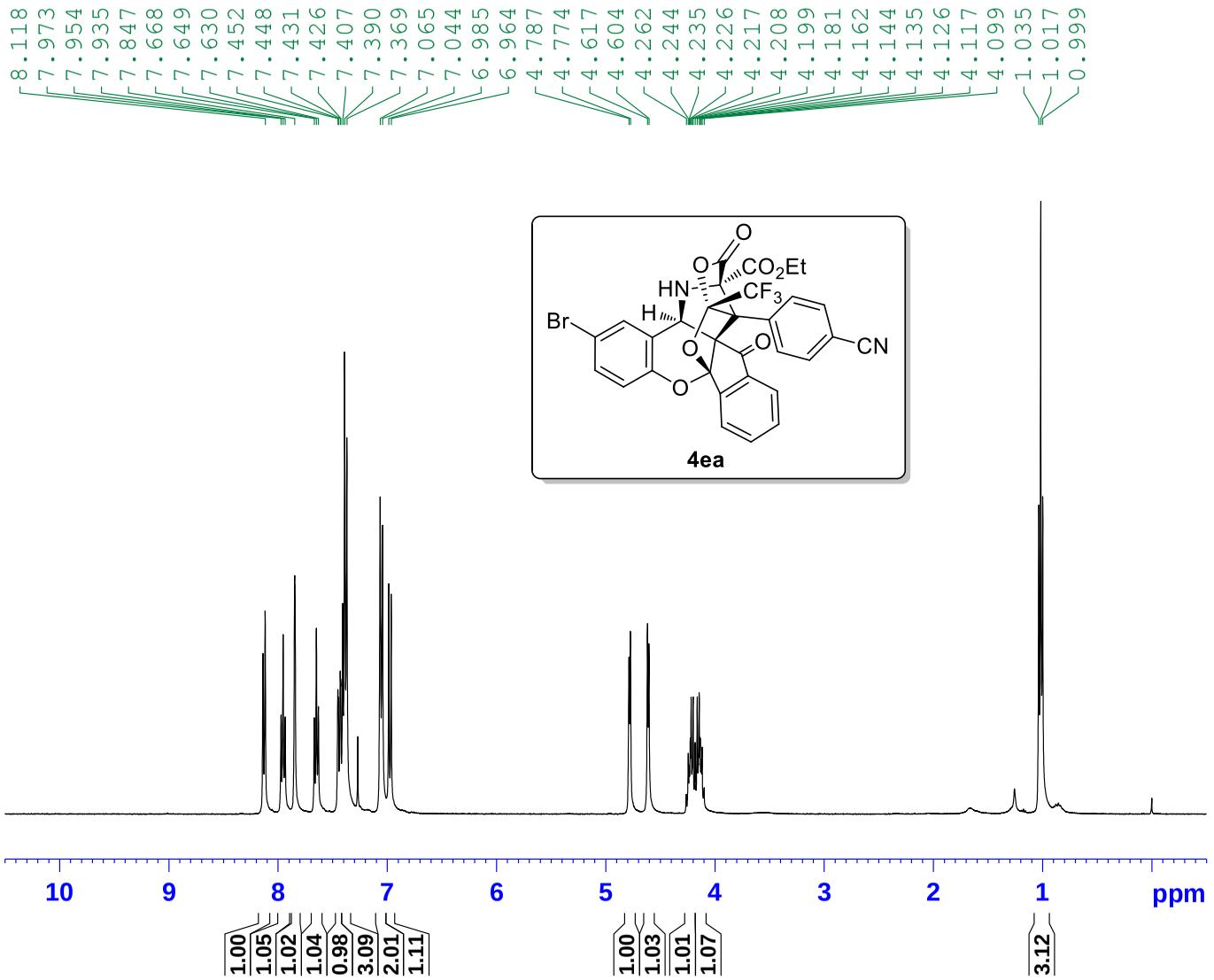

125.147
125.114
125.080
125.042
125.1
ppm


125.147
125.114
125.080
125.042
125.1
ppm

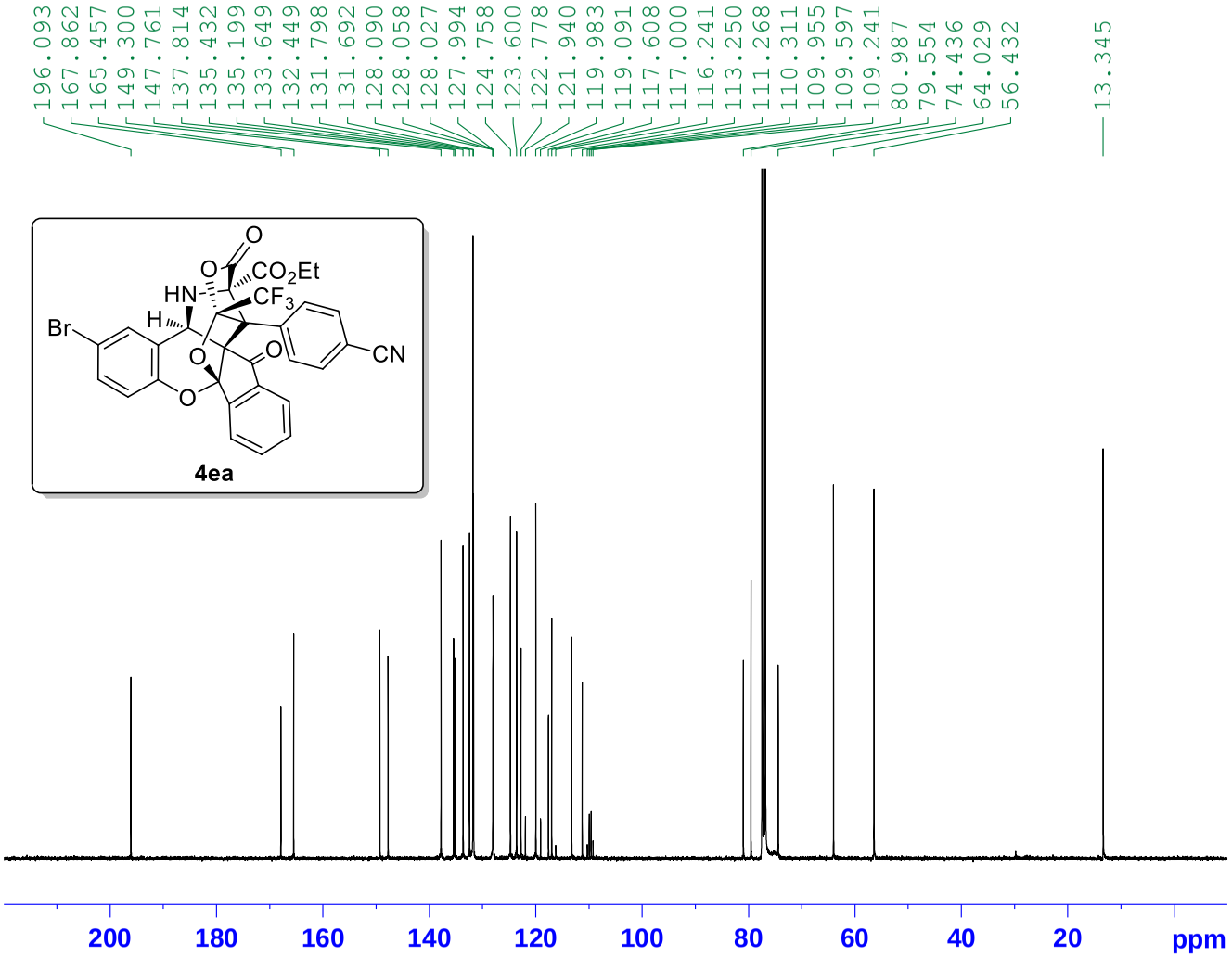

110.458
110.102
109.746
109.389
110.5
110.0
109.5
ppm


125.147
125.114
125.080
125.042
125.1
125.0
ppm

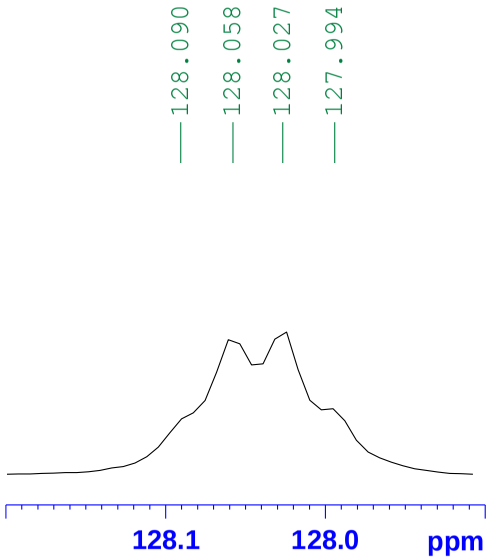

127.742
127.708
127.518
125.147
125.114
125.080
125.042
124.862
124.811
124.717
123.521
122.944
122.104
122.015
119.985
119.396
119.166
116.986
116.316
128
126
124
122
120
118
116
ppm

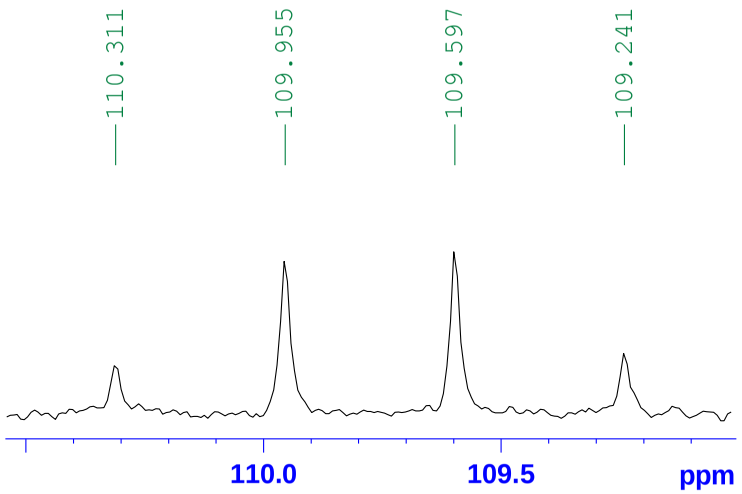


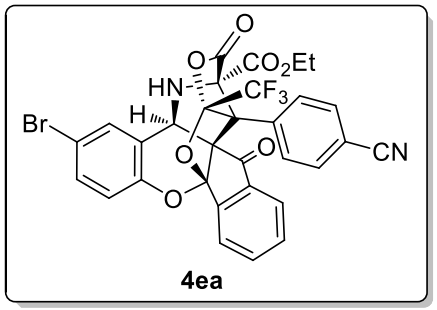

```
Current Data Parameters
NAME                  4ea
EXPNO                  18
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170203
Time                22.10
INSTRUM             spect
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              7246.377 Hz
FIDRES           0.221142 Hz
AQ              2.2609921 sec
RG                    114
DW                 69.000 usec
DE                  6.50 usec
TE                 297.4 K
D1            2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.40 usec
PL1                 1.80 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                  16384
SF           400.1300056 MHz
WDW                    EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

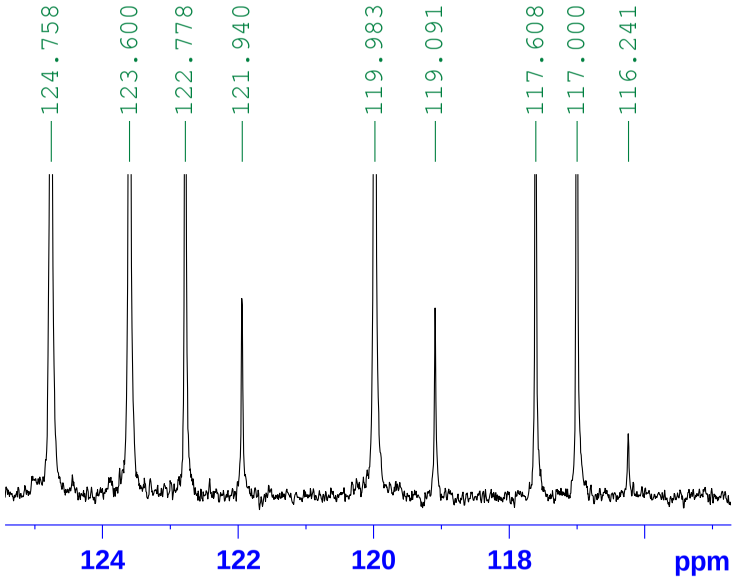


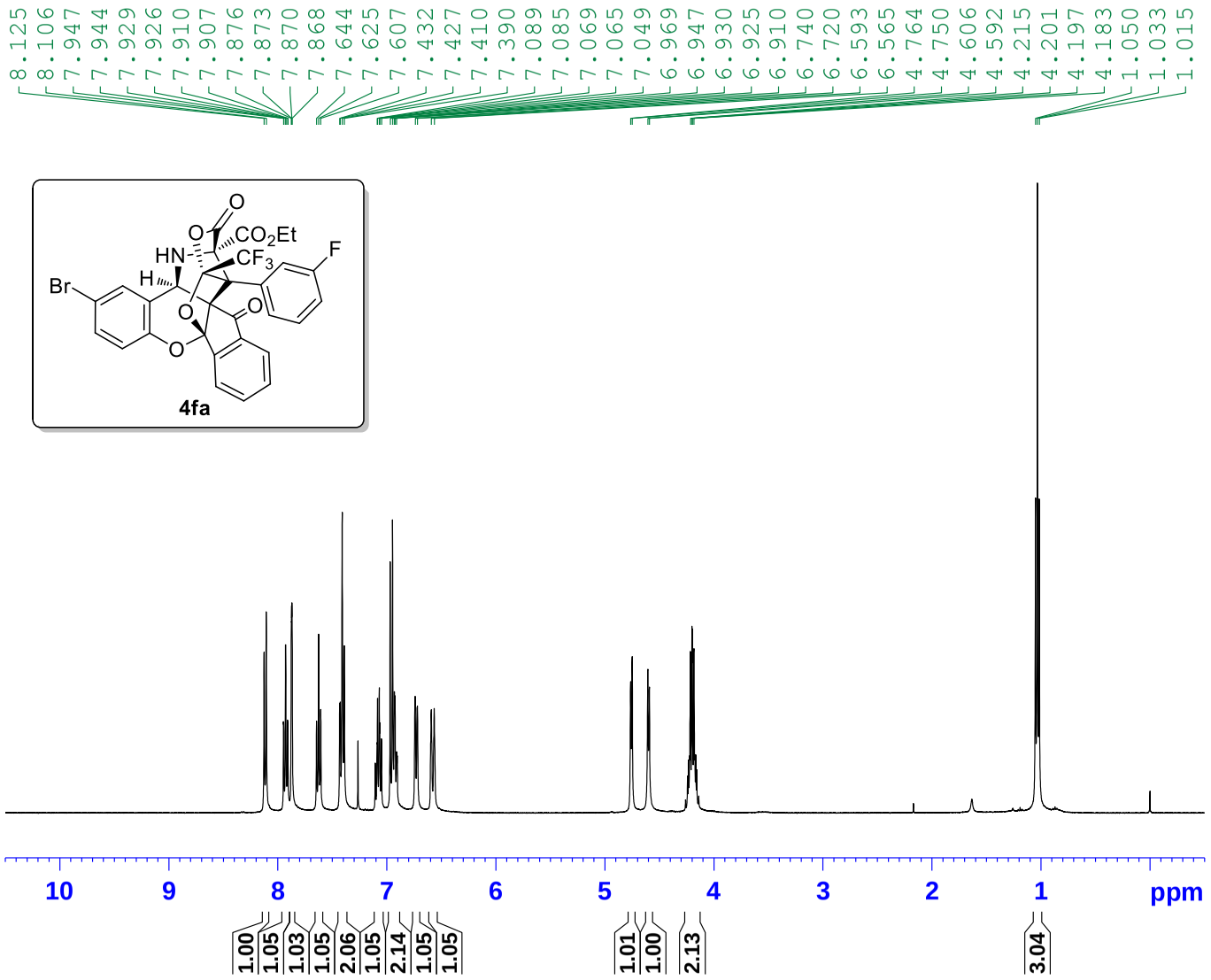

```
Current Data Parameters
NAME                  4ea
EXPNO                  19
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170203
Time                22.13
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  32768
SOLVENT             CDCl3
NS                  15566
DS                      0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             0.6815744 sec
RG                 4597.6
DW                20.800 usec
DE                 6.50 usec
TE                297.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

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

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2               90.00 usec
PL2                  1.80 dB
PL12                17.00 dB
PL13                20.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF           100.6127577 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.00
```


128.090
128.058
128.027
127.994
128.1
128.0
ppm

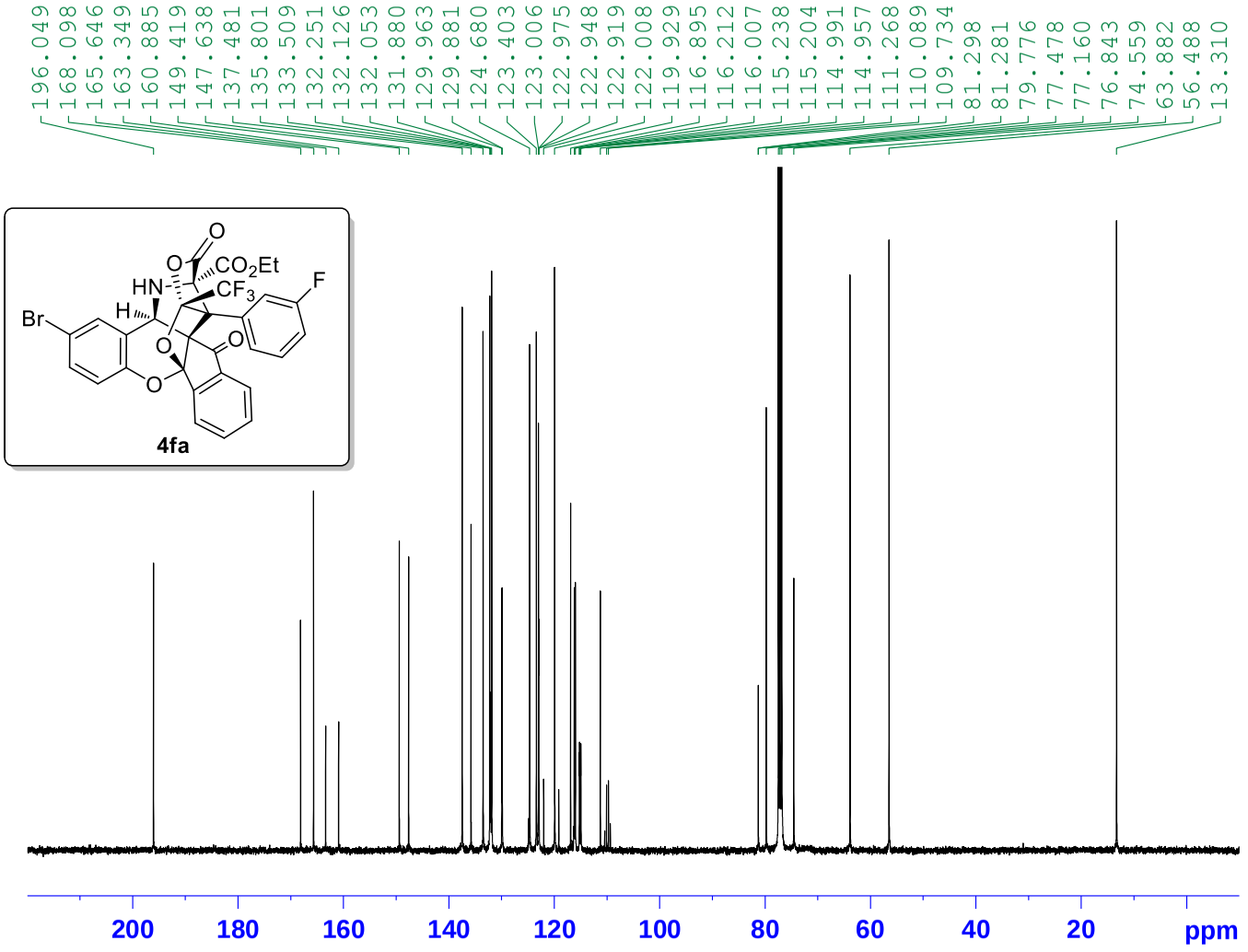

110.311
109.955
109.597
109.241
110.0
109.5
ppm


O
O
CO2Et
HN
CF3
H
Br
O
O
CN
O
4ea

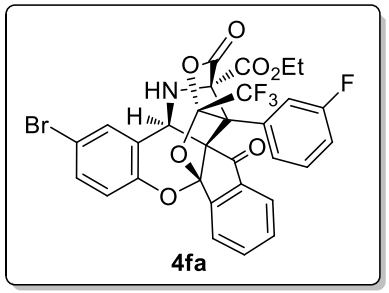

124.758
123.600
122.778
121.940
119.983
119.091
117.608
117.000
116.241
124
122
120
118
ppm

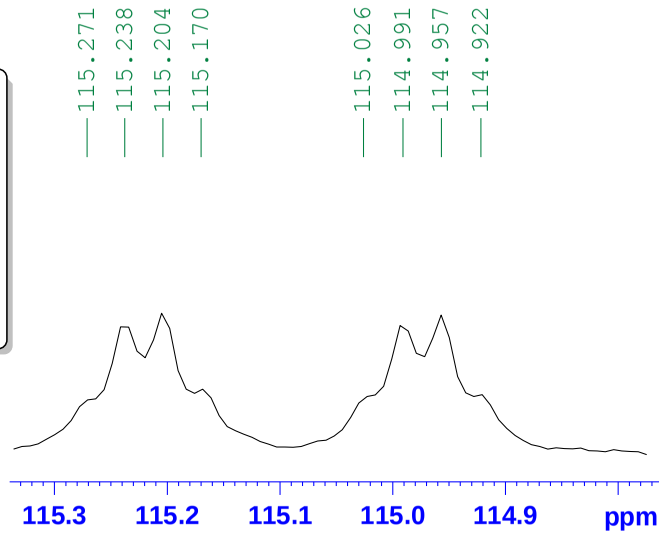


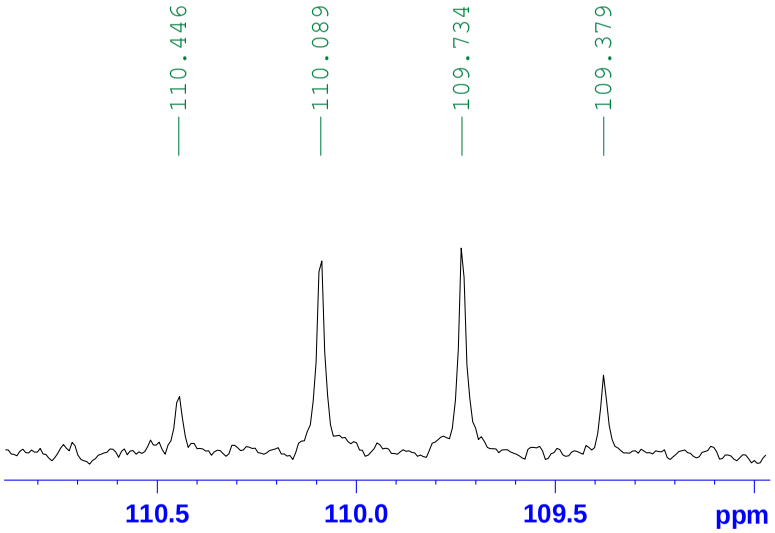

```
Current Data Parameters
NAME                  4fa
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170113
Time                1.23
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             7246.377 Hz
FIDRES          0.221142 Hz
AQ              2.2609921 sec
RG                   114
DW                69.000 usec
DE                 6.50 usec
TE                298.3 K
D1           2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.40 usec
PL1                1.80 dB
SFO1        400.1324008 MHz

F2 - Processing parameters
SI                 16384
SF          400.1300078 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

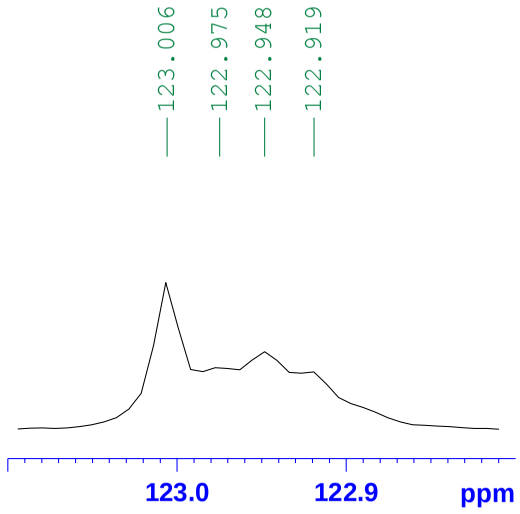


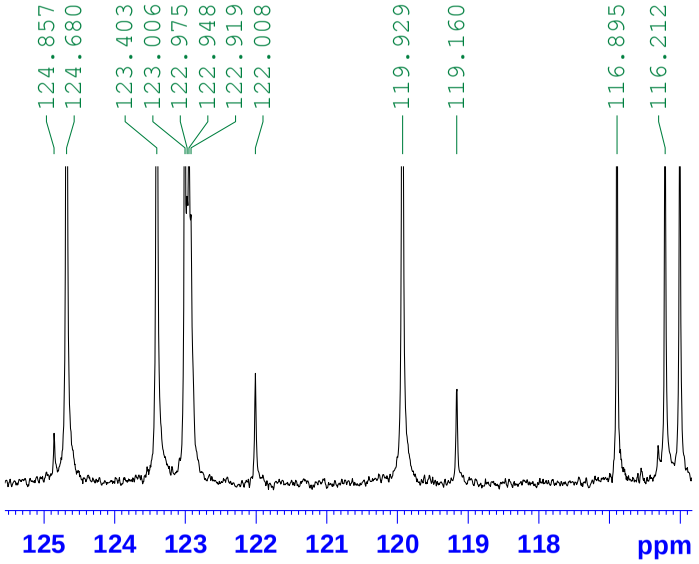

```
Current Data Parameters
NAME                  4fa
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170113
Time                1.26
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                 11360
DS                     0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             0.6815744 sec
RG                  8192
DW                20.800 usec
DE                 6.50 usec
TE                298.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2              90.00 usec
PL2                1.80 dB
PL12               17.00 dB
PL13               20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127563 MHz
WDW                 EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.00
```

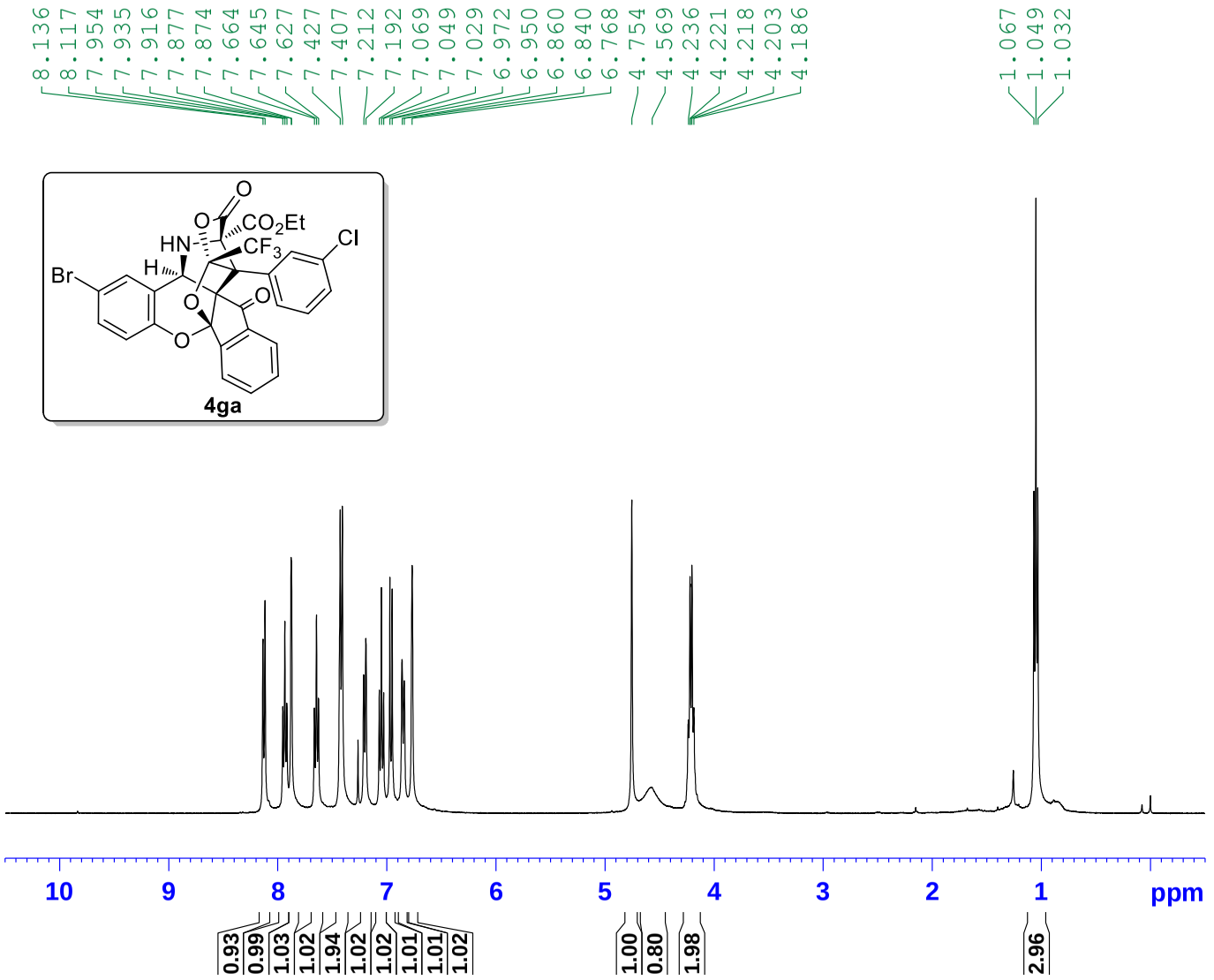

O
O
CO2Et
HN
CF3
F
H
Br
O
O
O
4fa


115.271
115.238
115.204
115.170
115.026
114.991
114.957
114.922
115.3
115.2
115.1
115.0
114.9
ppm

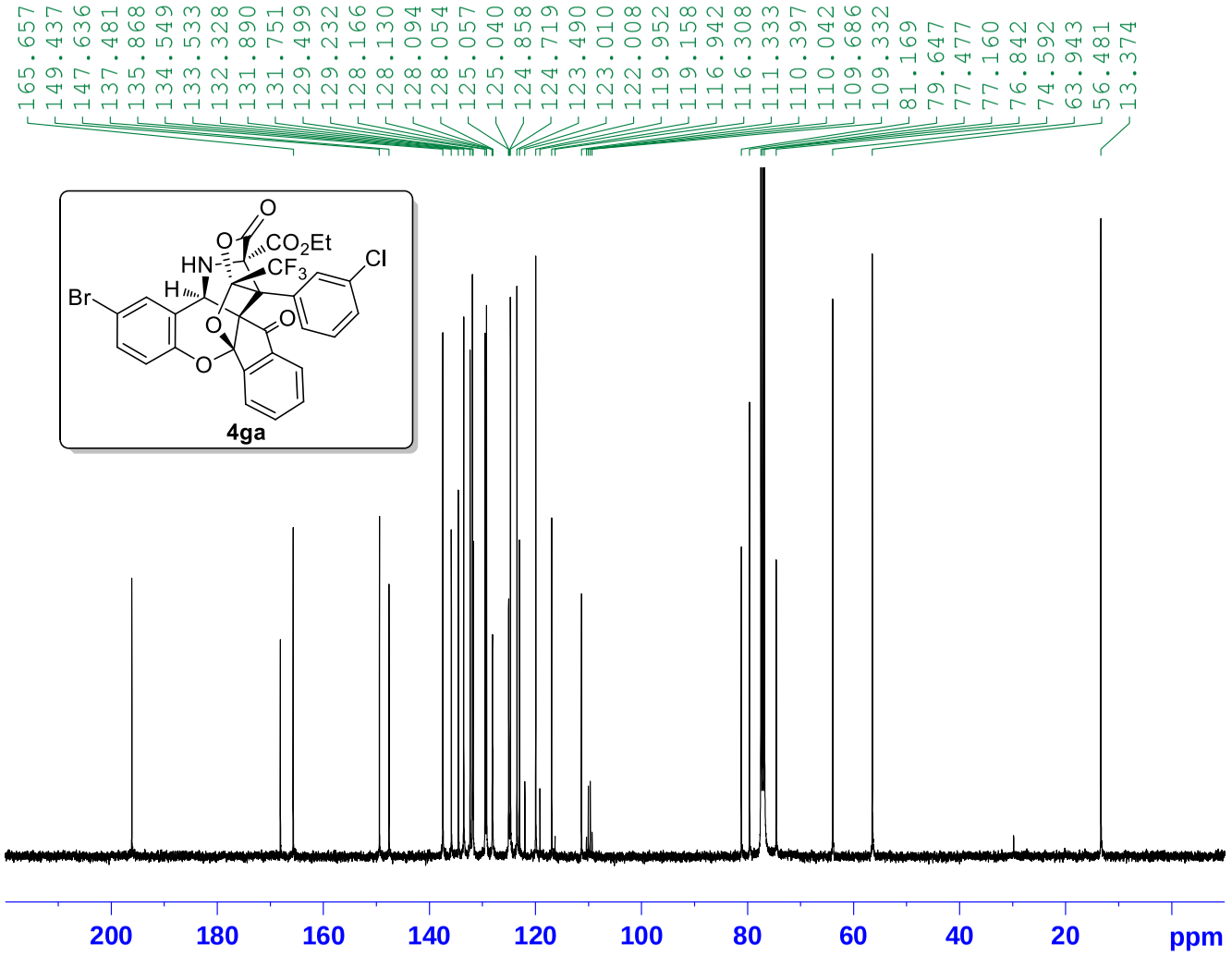

110.446
110.089
109.734
109.379
110.5
110.0
109.5
ppm


123.006
122.975
122.948
122.919
123.0
122.9
ppm

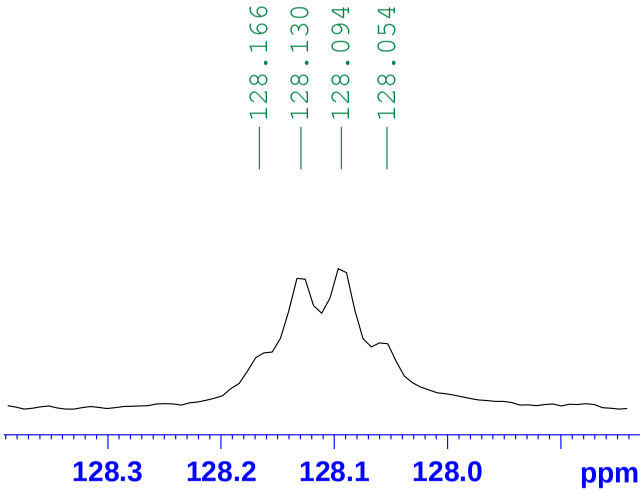

124.857
124.680
123.403
123.006
122.975
122.948
122.919
122.008
119.929
119.160
116.895
116.212
125
124
123
122
121
120
119
118
ppm

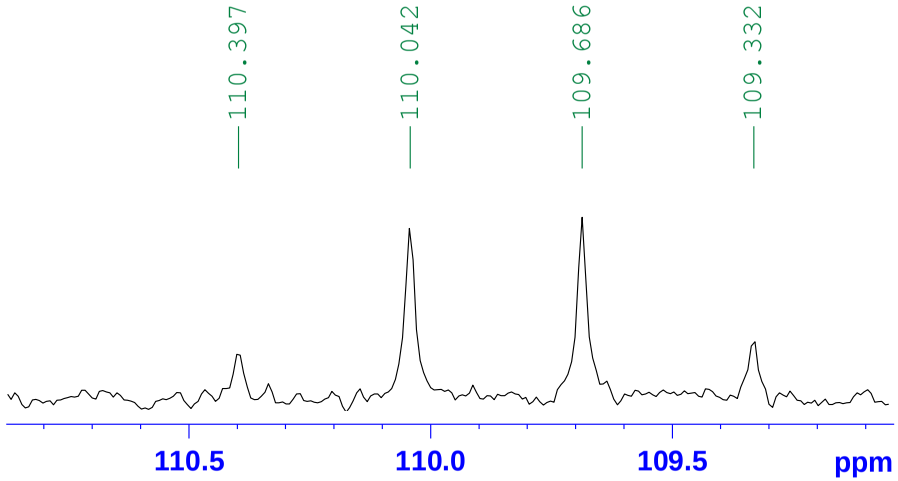


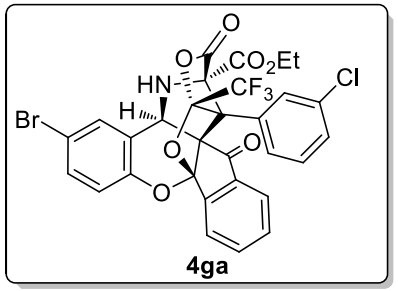

```
Current Data Parameters
NAME                  4ga
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170202
Time              22.00
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            7246.377 Hz
FIDRES         0.221142 Hz
AQ            2.2609921 sec
RG                  114
DW               69.000 usec
DE                6.50 usec
TE                298.9 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.40 usec
PL1                1.80 dB
SFO1        400.1324008 MHz

F2 - Processing parameters
SI                16384
SF          400.1300078 MHz
WDW                  EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

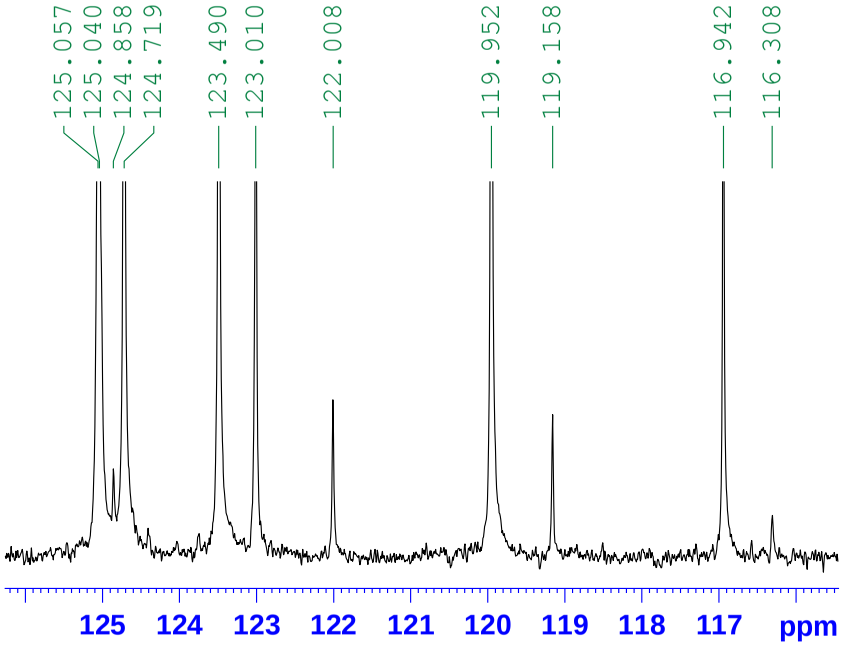


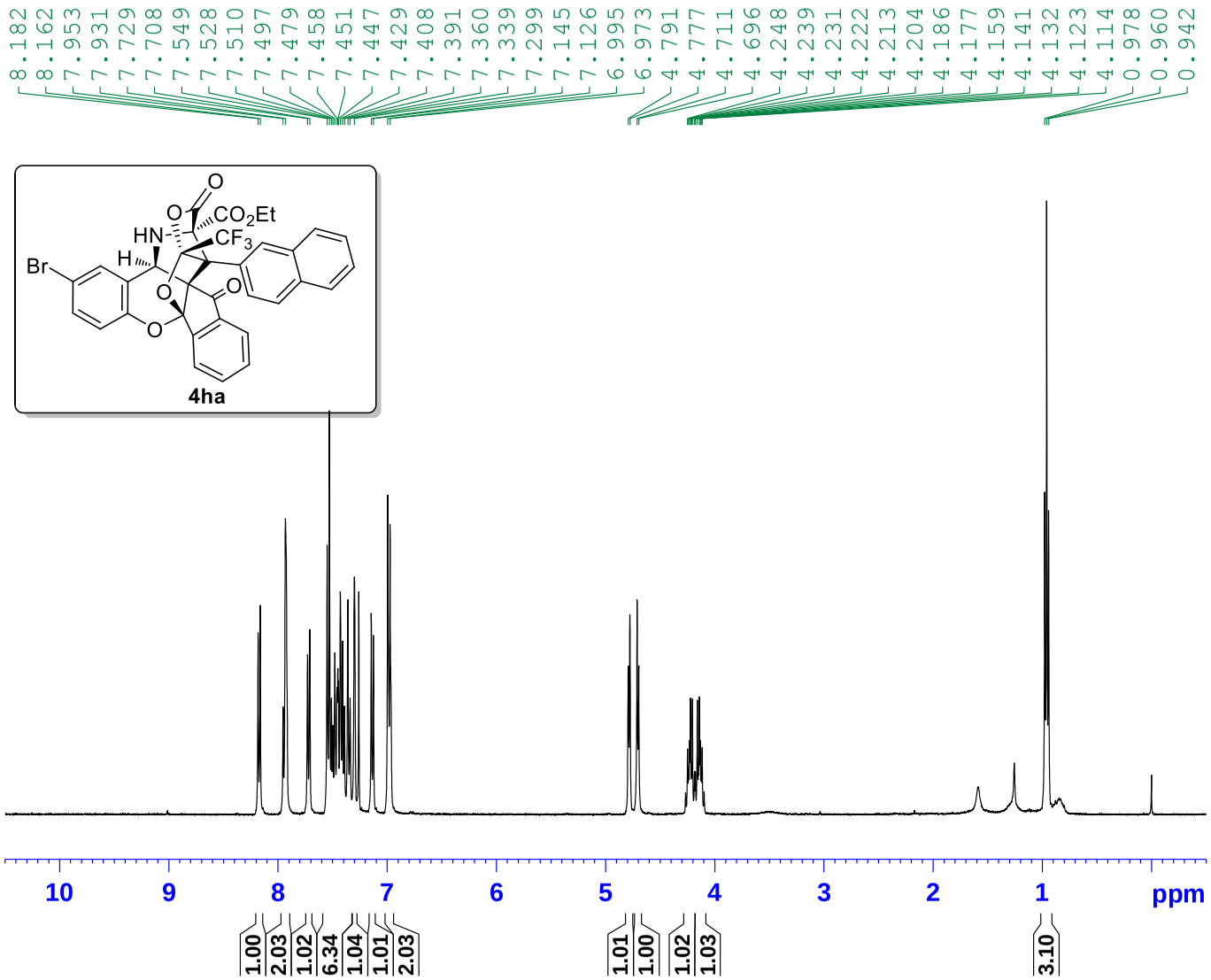

```
Current Data Parameters
NAME                  4ga
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170202
Time              22.03
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                13063
DS                    0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            0.6815744 sec
RG               4597.6
DW                20.800 usec
DE                 6.50 usec
TE                299.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 1.80 dB
PL12               17.00 dB
PL13               20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127548 MHz
WDW                  EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```


128.166
128.130
128.094
128.054
128.3
128.2
128.1
128.0
ppm

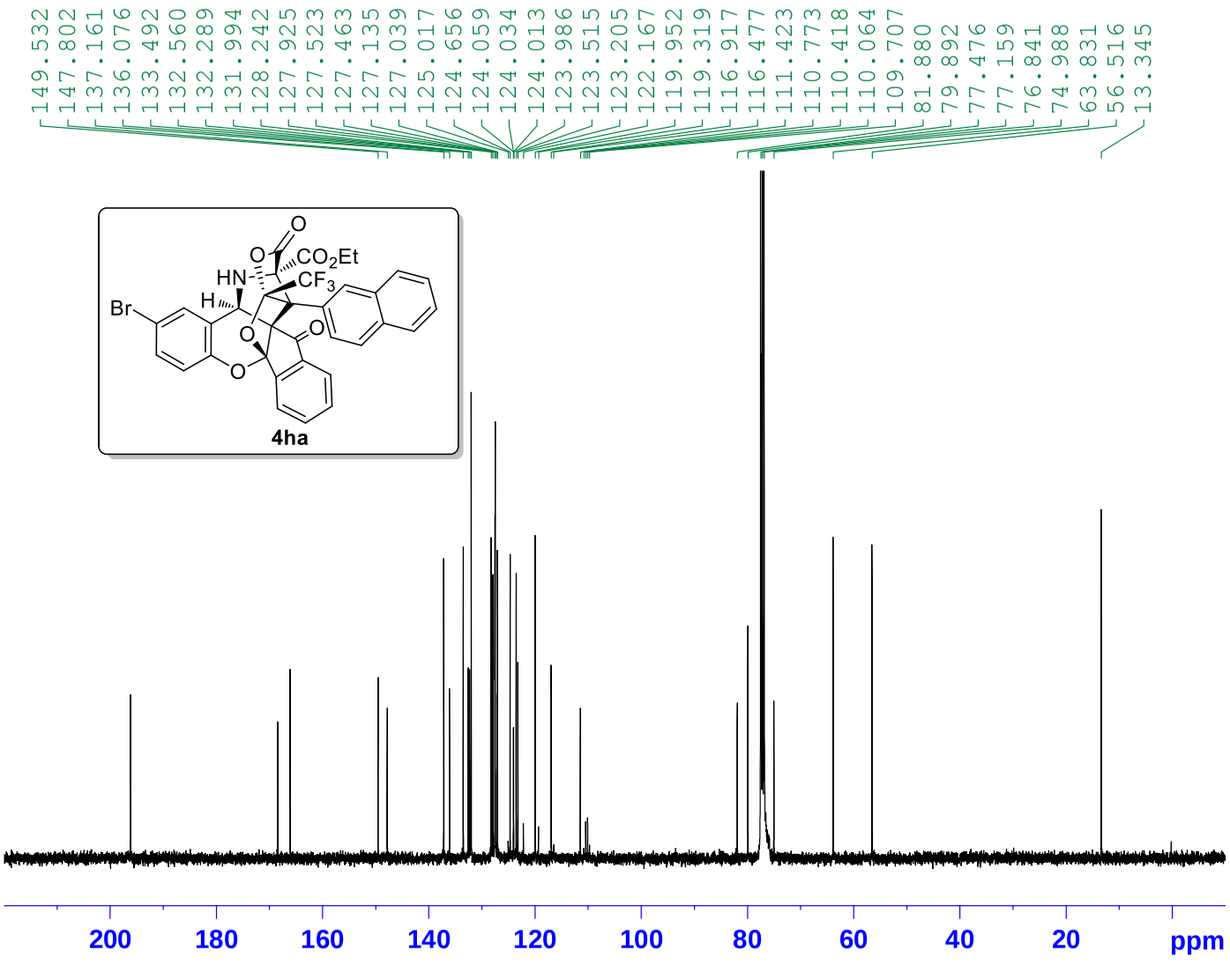

110.397
110.042
109.686
109.332
110.5
110.0
109.5
ppm


O
O
CO2Et
HN
CF3
H
Br
Cl
O
O
O
4ga

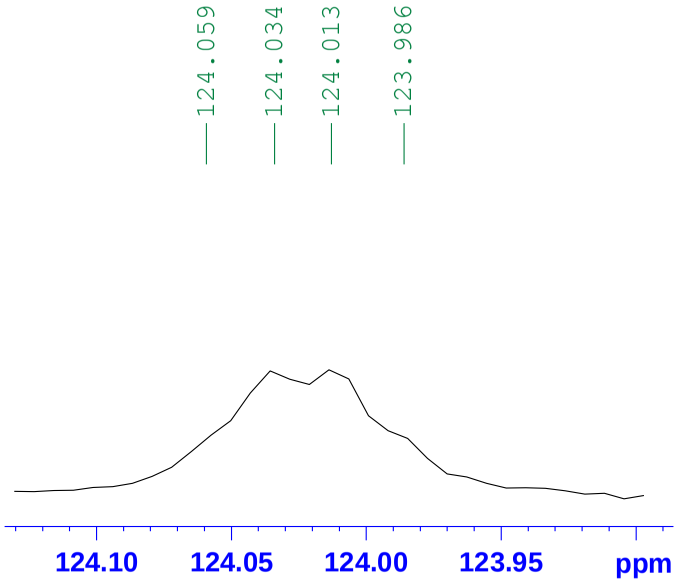

125.057
125.040
124.858
124.719
123.490
123.010
122.008
119.952
119.158
116.942
116.308
125
124
123
122
121
120
119
118
117
ppm

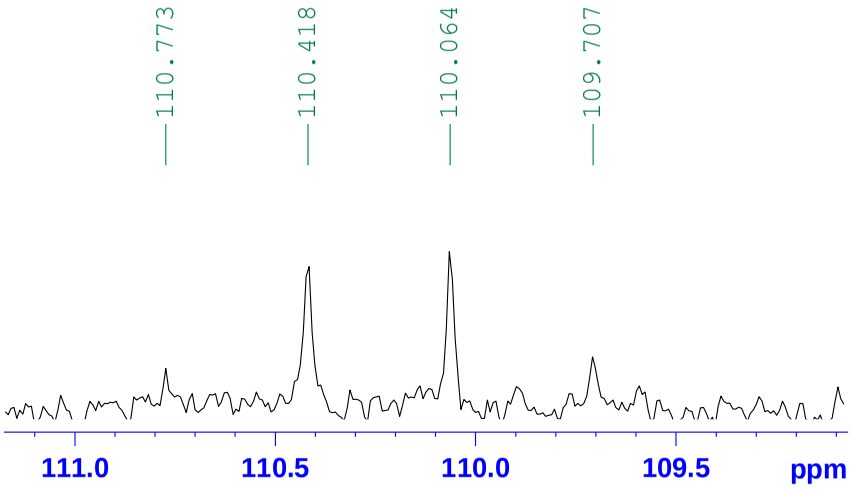


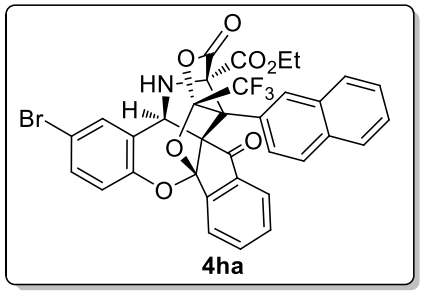

```
Current Data Parameters
NAME                  4ha
EXPNO                  15
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170208
Time                11.08
INSTRUM             spect
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              7246.377 Hz
FIDRES           0.221142 Hz
AQ               2.2609921 sec
RG                    181
DW                 69.000 usec
DE                  6.50 usec
TE                 296.5 K
D1            2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.40 usec
PL1                 1.80 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                  16384
SF           400.1300096 MHz
WDW                    EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

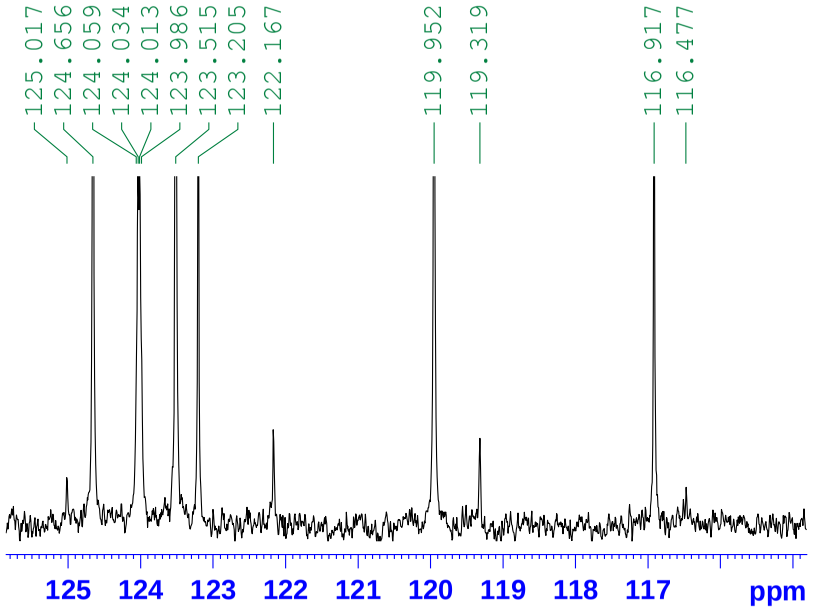


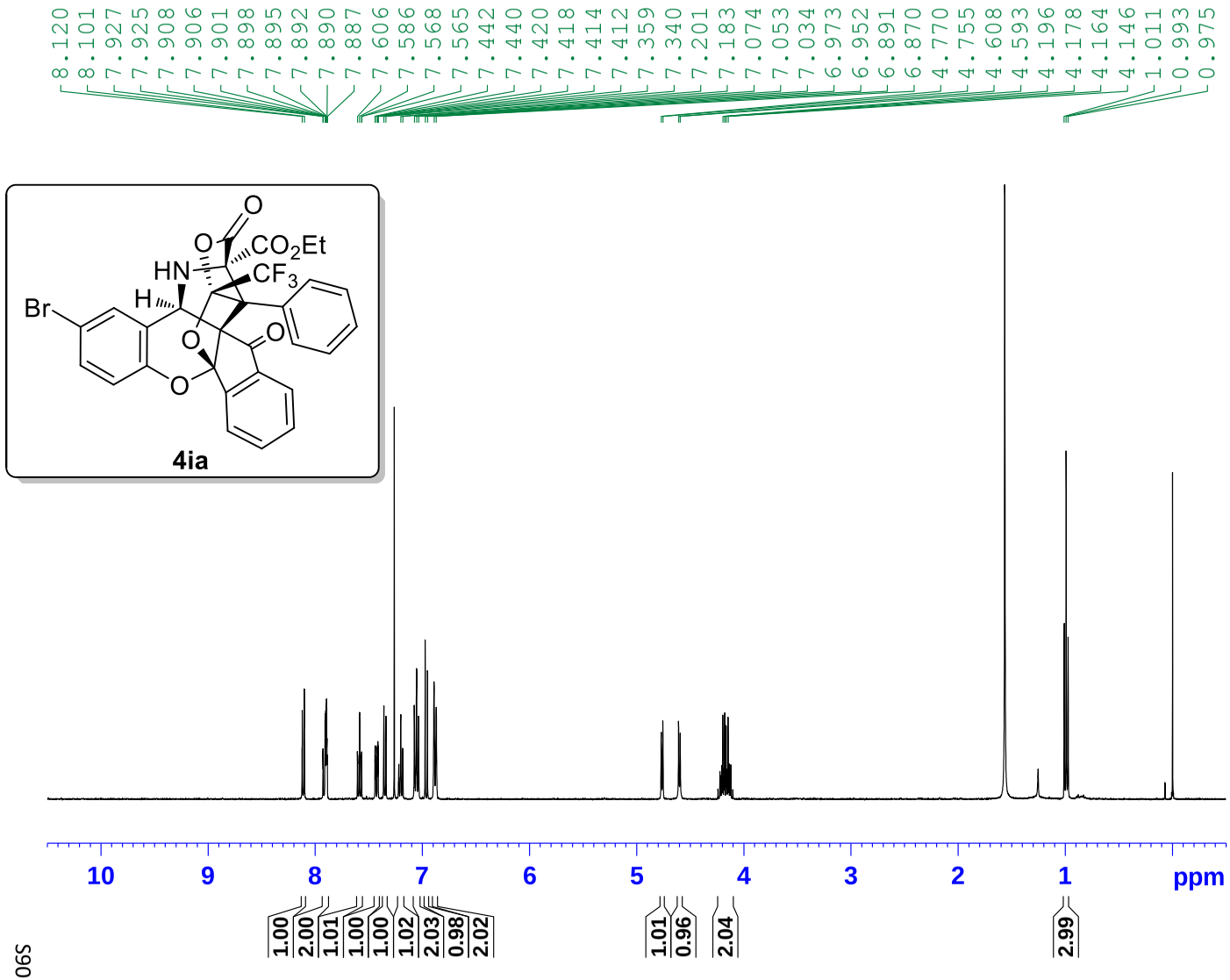

```
Current Data Parameters
NAME                   4ha
EXPNO                   17
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170209
Time                 22.14
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                   14572
DS                       0
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                0.6815744 sec
RG                   5792.6
DW                   20.800 usec
DE                    6.50 usec
TE                   297.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

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

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                   1H
PCPD2                90.00 usec
PL2                   1.80 dB
PL12                 17.00 dB
PL13                 20.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127540 MHz
WDW                    EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.00
```


124.059
124.034
124.013
123.986
124.10
124.05
124.00
123.95
ppm

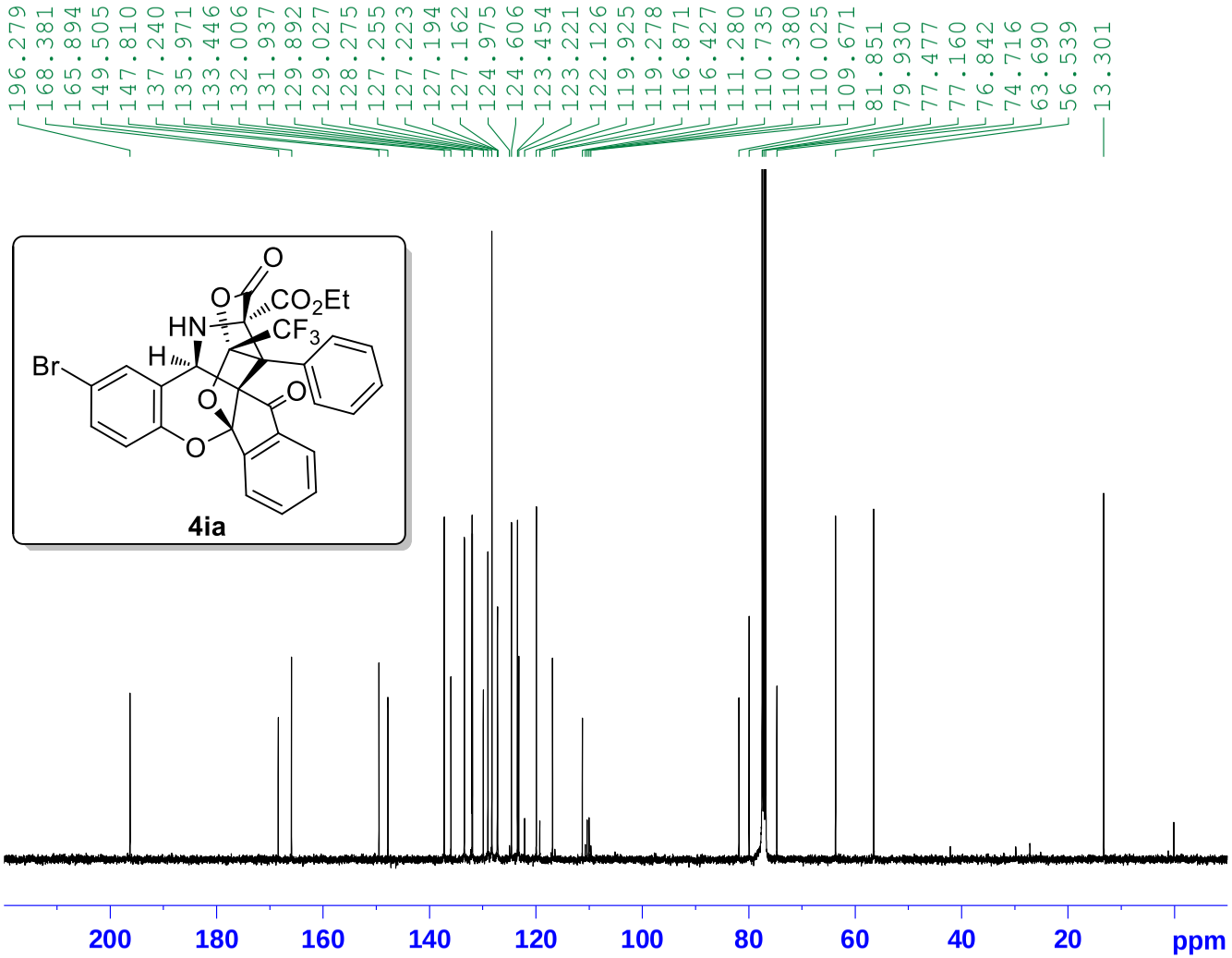

110.773
110.418
110.064
109.707
111.0
110.5
110.0
109.5
ppm


O
O
CO2Et
HN
CF3
H
Br
O
O
O
4ha

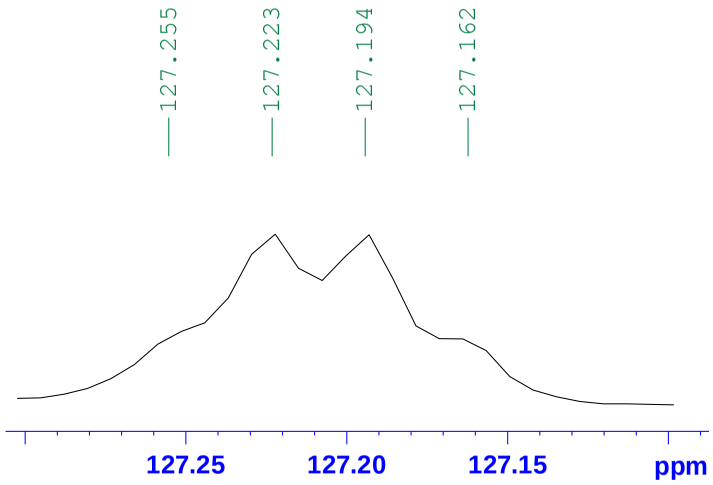

125.017
124.656
124.059
124.034
124.013
123.986
123.515
123.205
122.167
119.952
119.319
116.917
116.477
125
124
123
122
121
120
119
118
117
ppm

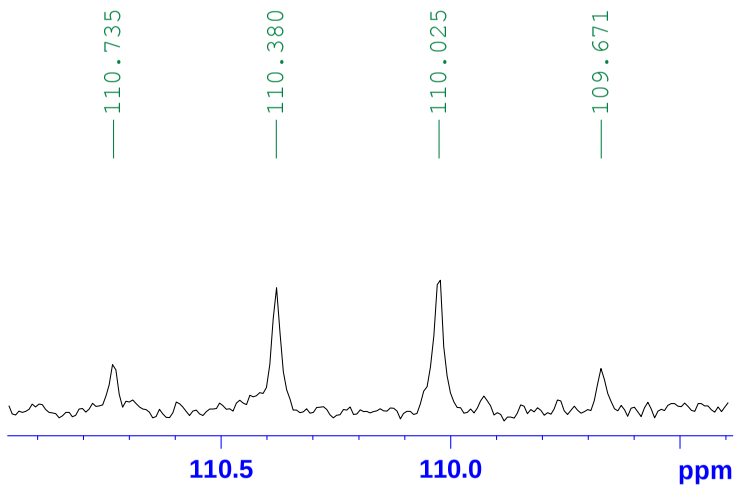


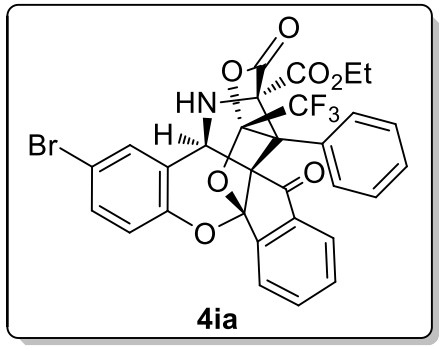

```
Current Data Parameters
NAME                  4ia
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170106
Time                9.24
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             7211.539 Hz
FIDRES          0.220079 Hz
AQ              2.2719147 sec
RG                198.09
DW                69.333 usec
DE                10.50 usec
TE                297.8 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                 12.90 usec
PLW1         15.00000000 W

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

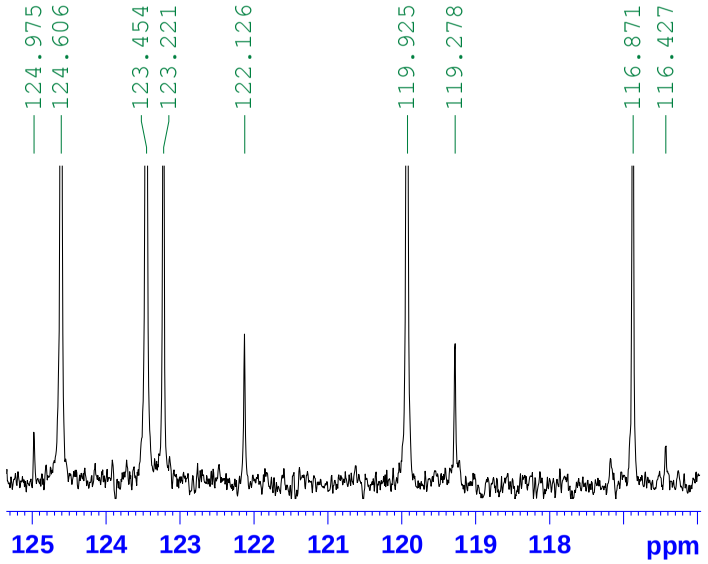


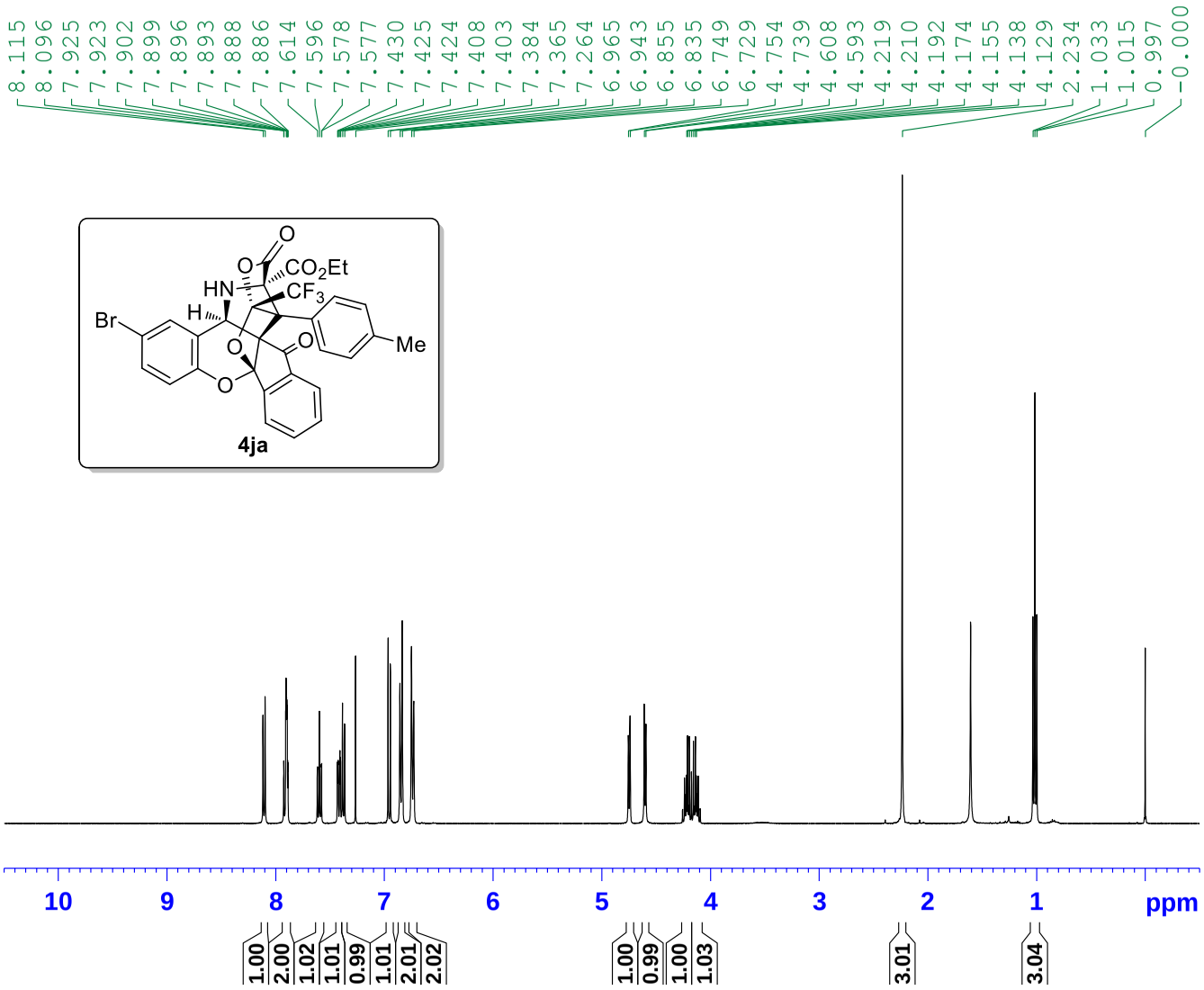

```
Current Data Parameters
NAME                  4ia
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160529
Time              20.59
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                12000
DS                    0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            0.6815744 sec
RG                 8192
DW               20.800 usec
DE                6.50 usec
TE                300.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 1.80 dB
PL12               17.00 dB
PL13               20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127540 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.00
```


127.255
127.223
127.194
127.162
127.25
127.20
127.15
ppm

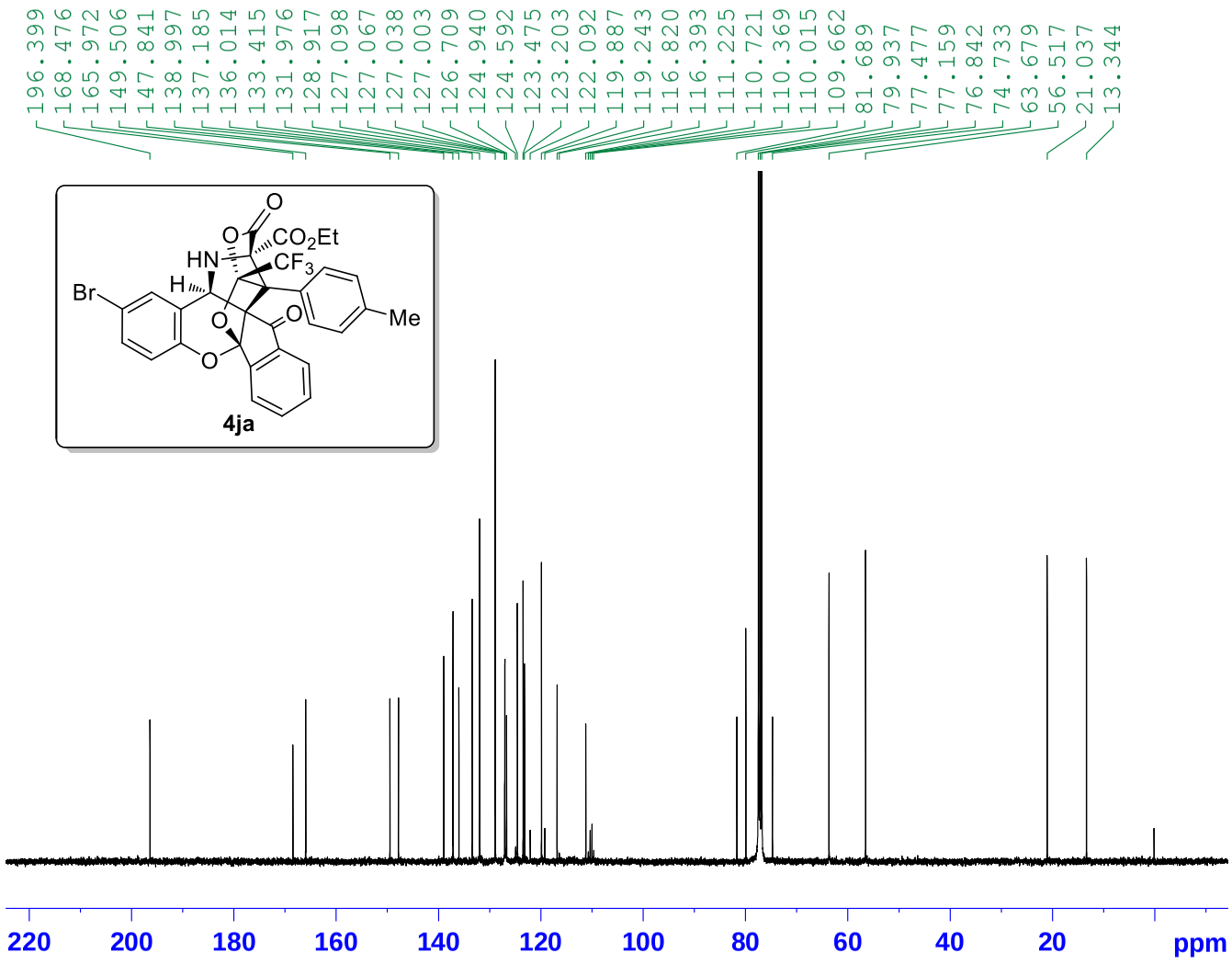

110.735
110.380
110.025
109.671
110.5
110.0
ppm


O
O
CO2Et
HN
CF3
H
Br
O
O
O
4ia

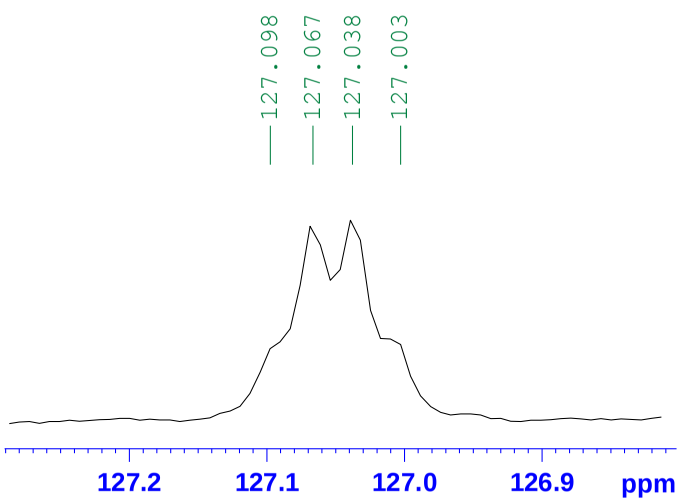

124.975
124.606
123.454
123.221
122.126
119.925
119.278
116.871
116.427
125
124
123
122
121
120
119
118
ppm

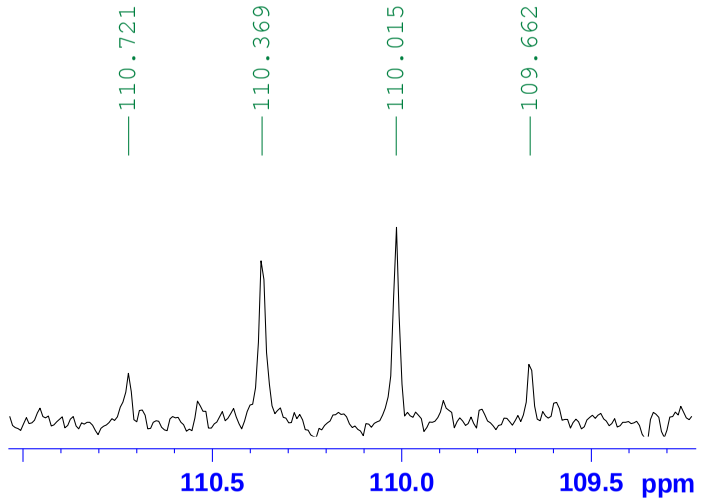


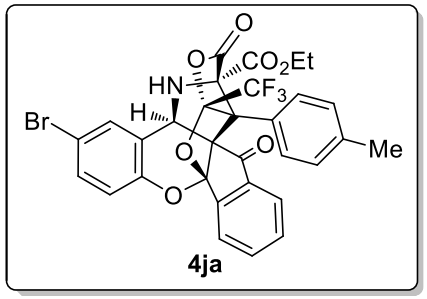

```
Current Data Parameters
NAME                  4ja
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160918
Time                22.01
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             7246.377 Hz
FIDRES          0.221142 Hz
AQ              2.2609921 sec
RG                   181
DW                69.000 usec
DE                 6.50 usec
TE                295.6 K
D1           2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.40 usec
PL1                 1.80 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                 16384
SF          400.1300078 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

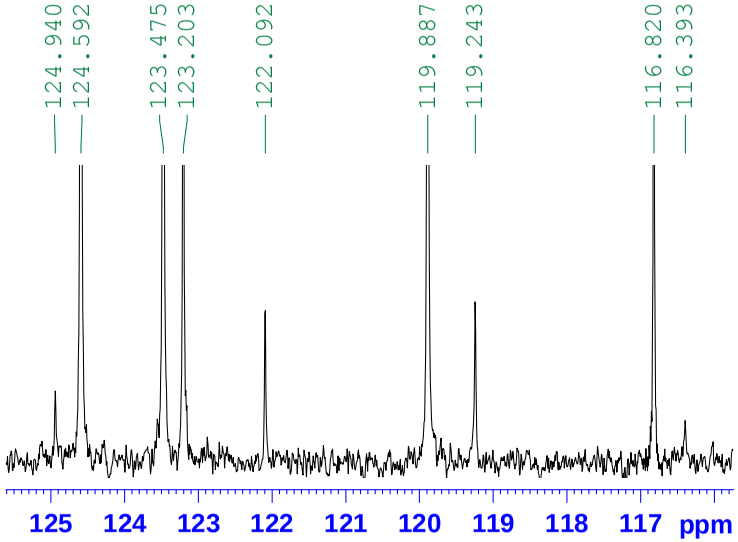


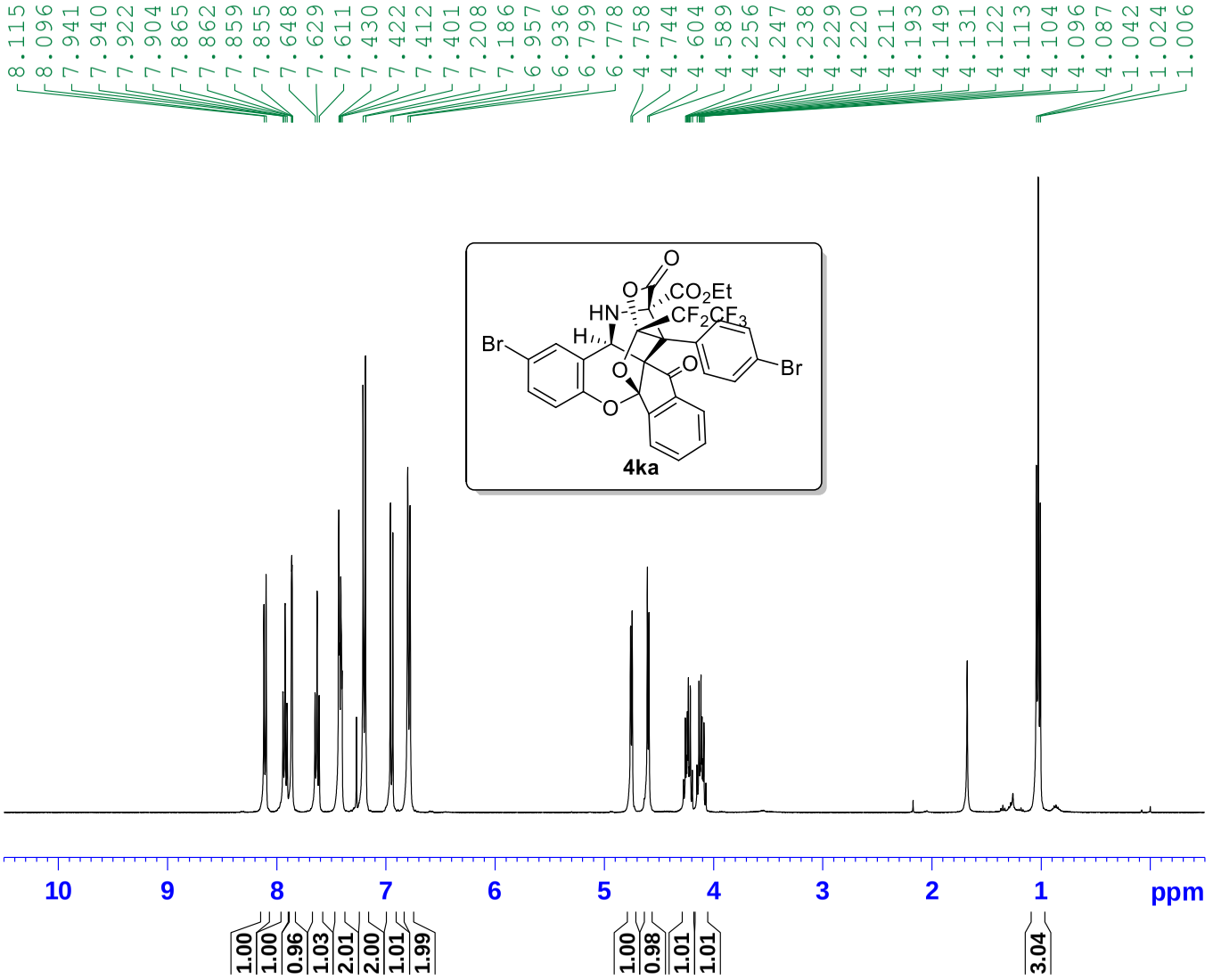

```
Current Data Parameters
NAME                   4ja
EXPNO                    7
PROCNO                   1

F2 - Acquisition Parameters
Date_           20160918
Time               22.03
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                 32768
SOLVENT            CDCl3
NS                 13446
DS                     0
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ              0.6815744 sec
RG                 9195.2
DW                20.800 usec
DE                 6.50 usec
TE                295.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

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

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                 1.80 dB
PL12               17.00 dB
PL13               20.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127548 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.00
```


127.098
127.067
127.038
127.003
127.2
127.1
127.0
126.9
ppm

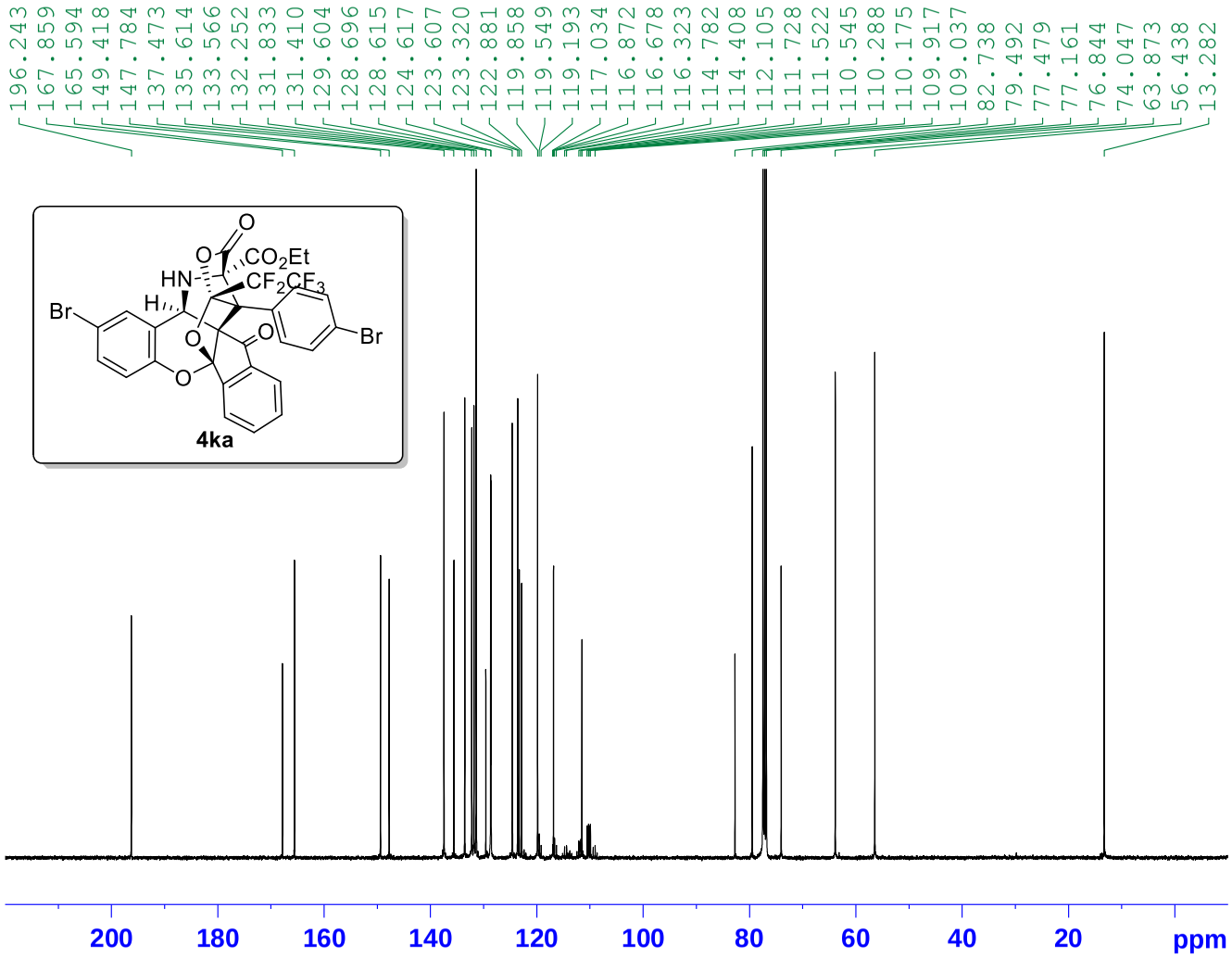

110.721
110.369
110.015
109.662
110.5
110.0
109.5
ppm


O
O
CO2Et
HN
CF3
H
Br
O
O
Me
O
4ja

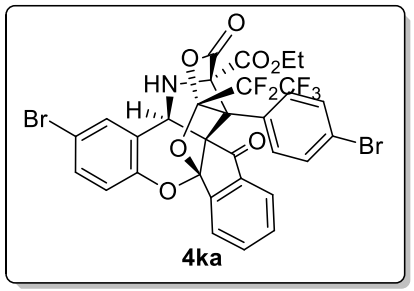

124.940
124.592
123.475
123.203
122.092
119.887
119.243
116.820
116.393
125
124
123
122
121
120
119
118
117
ppm

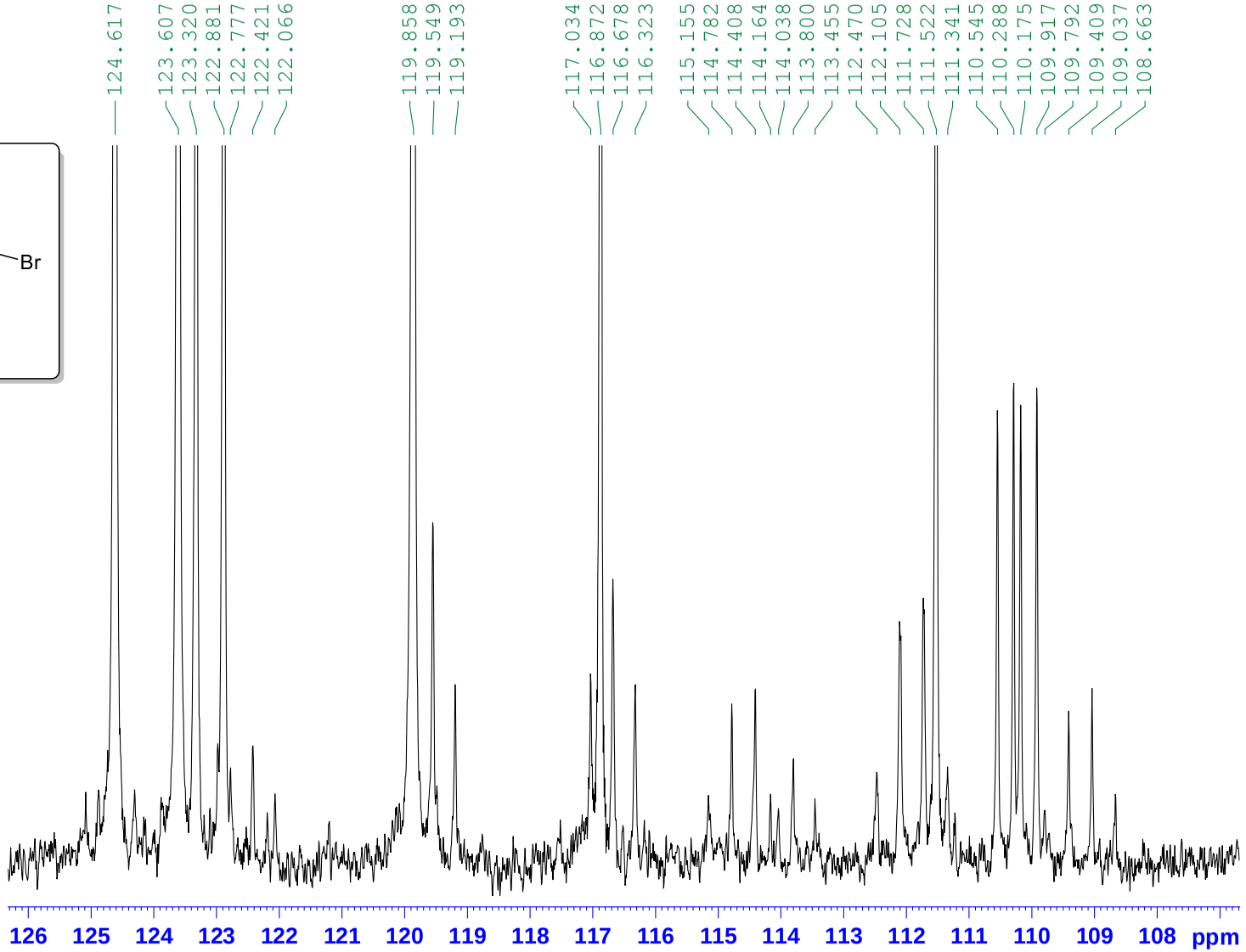


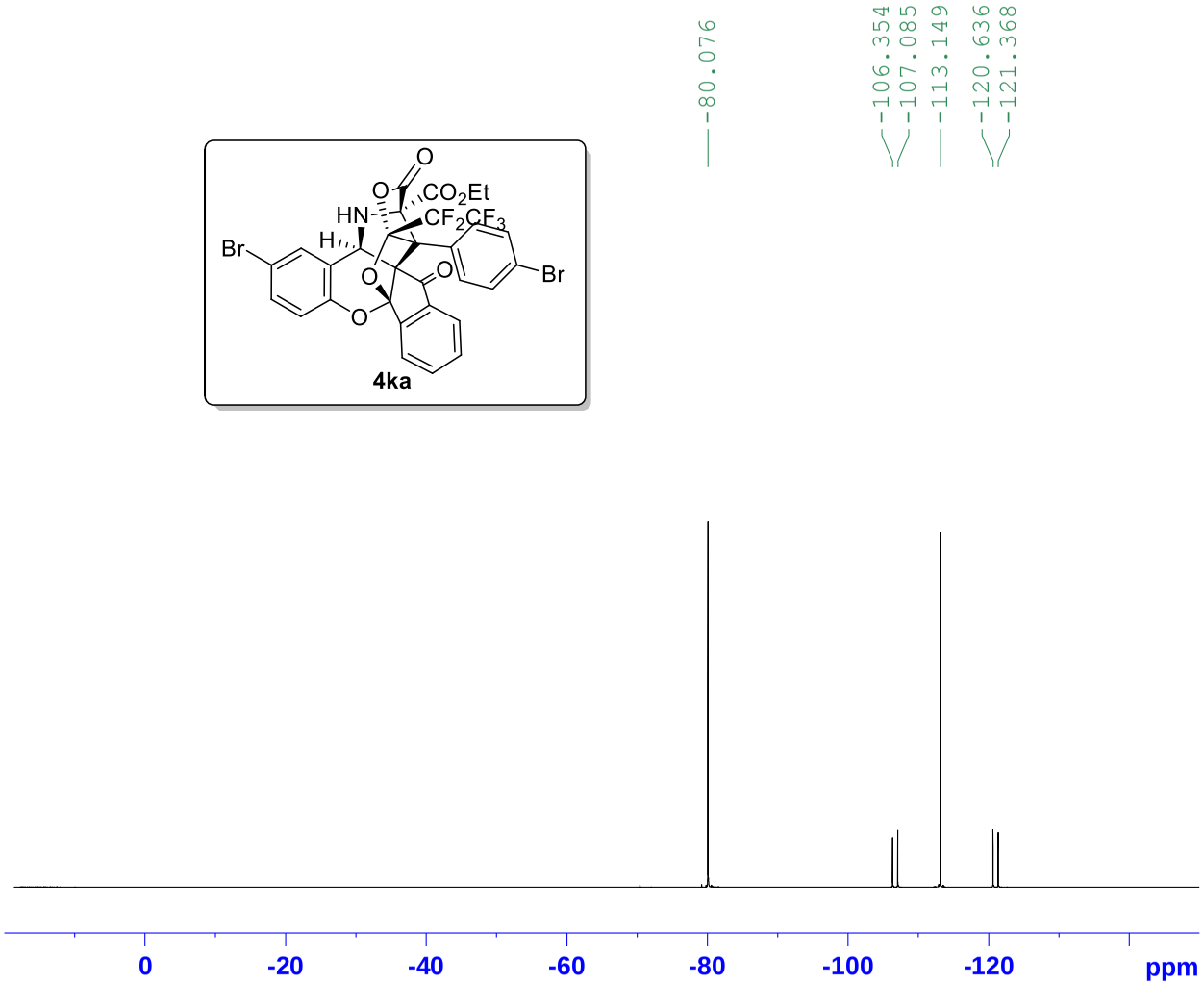

```
Current Data Parameters
NAME                  4la
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20170309
Time               23.17
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             7246.377 Hz
FIDRES          0.221142 Hz
AQ              2.2609921 sec
RG                   114
DW                69.000 usec
DE                 6.50 usec
TE                295.3 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.40 usec
PL1                1.80 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                 16384
SF          400.1300060 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```



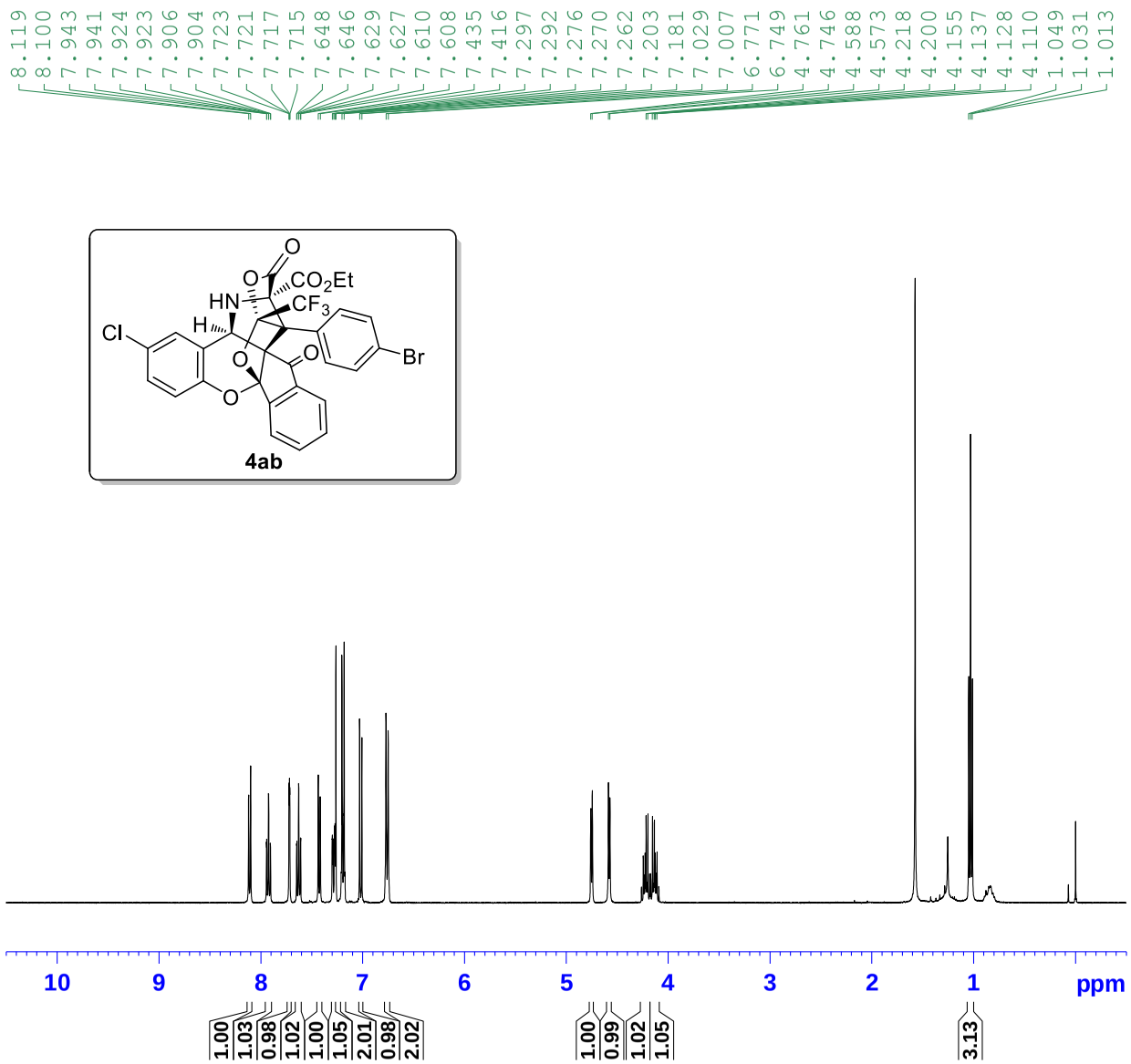

```
Current Data Parameters
NAME                  4la
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170309
Time               23.18
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                 29461
DS                     0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             0.6815744 sec
RG               11585.2
DW                20.800 usec
DE                 6.50 usec
TE                295.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2              90.00 usec
PL2                1.80 dB
PL12               17.00 dB
PL13               20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127577 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.00
```


O
O
CO2Et
HN
CF2CF3
H
Br
O
O
Br
O
4ka

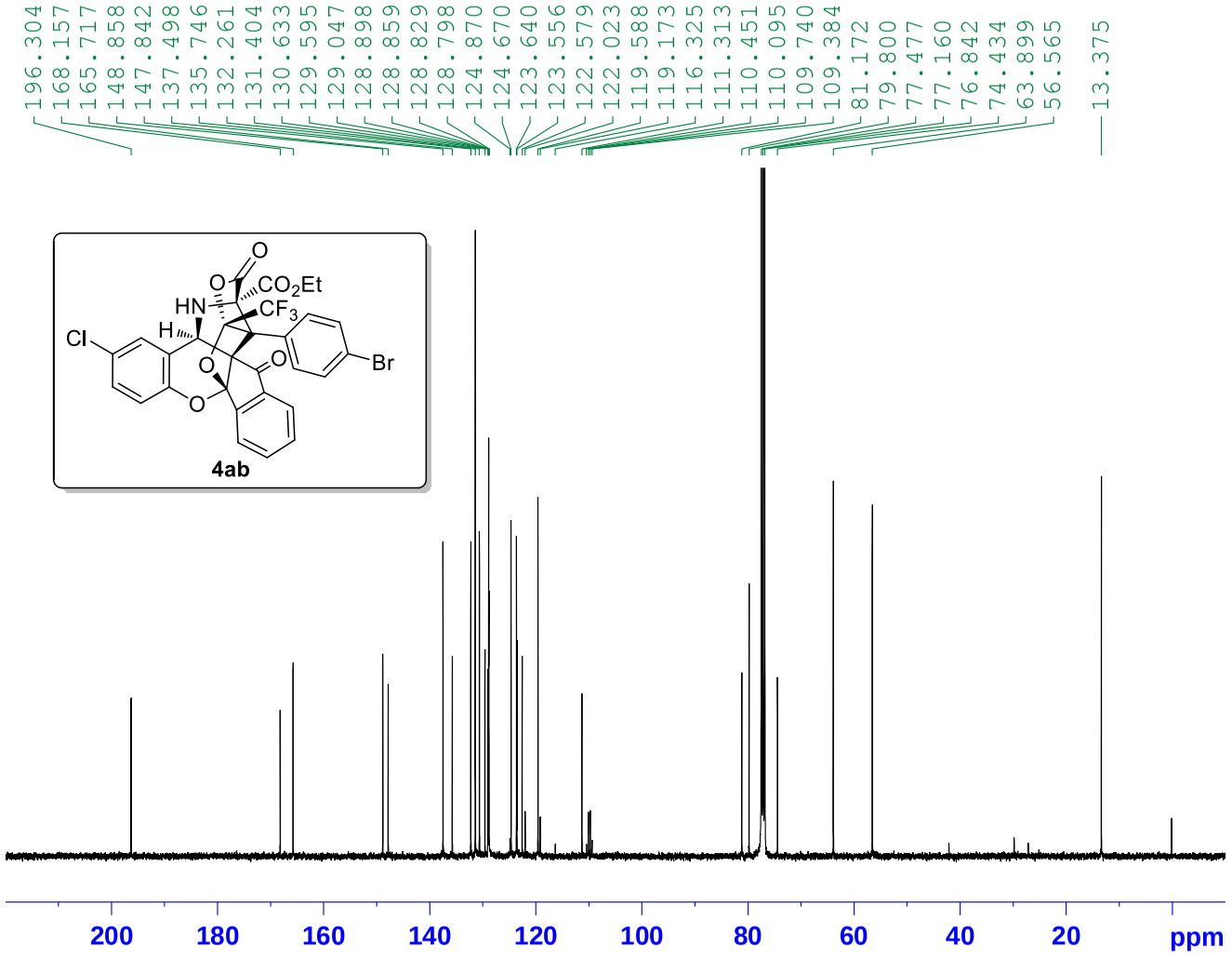

124.617
123.607
123.320
122.881
122.777
122.421
122.066
119.858
119.549
119.193
117.034
116.872
116.678
116.323
115.155
114.782
114.408
114.164
114.038
113.800
113.455
112.470
112.105
111.728
111.522
111.341
110.545
110.288
110.175
109.917
109.792
109.409
109.037
108.663
126
125
124
123
122
121
120
119
118
117
116
115
114
113
112
111
110
109
108
ppm



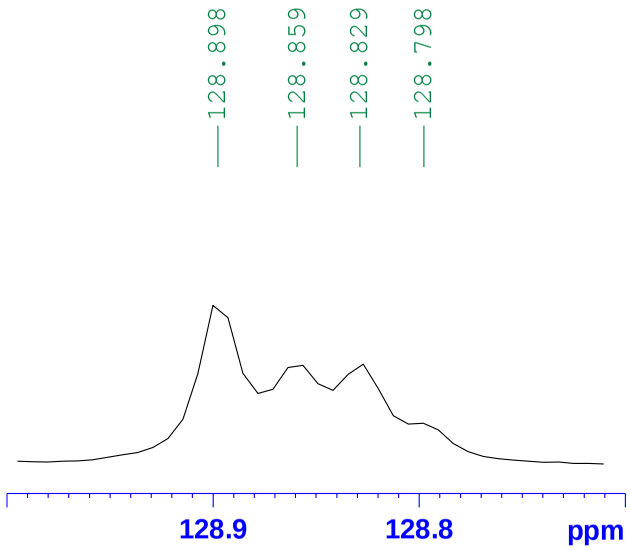

```
Current Data Parameters
NAME      3F NMR Kain-256
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170317
Time                21.17
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zgig
TD                131072
SOLVENT             CDCl3
NS                     16
DS                      0
SWH             89285.711 Hz
FIDRES          0.681196 Hz
AQ              0.7340032 sec
RG                 198.09
DW                  5.600 usec
DE                  6.50 usec
TE                 297.5 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         376.4607168 MHz
NUC1                19F
P1                14.00 usec
PLW1         19.79999924 W

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

F2 - Processing parameters
SI                  65536
SF           376.4983428 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```

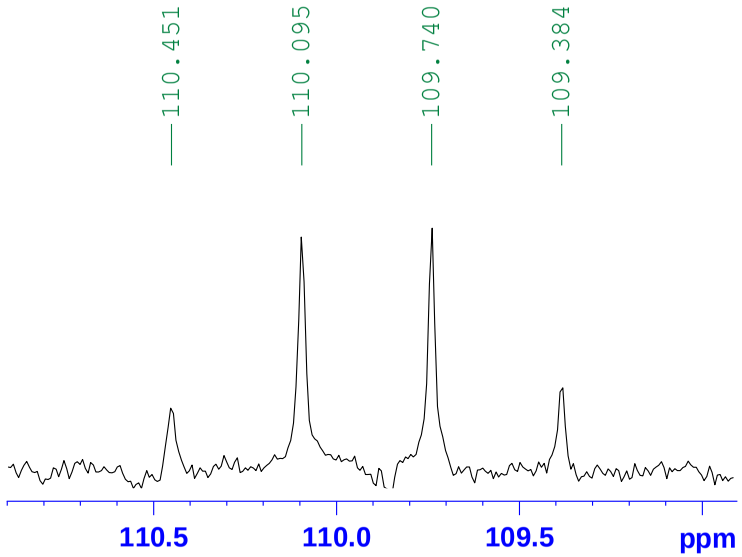


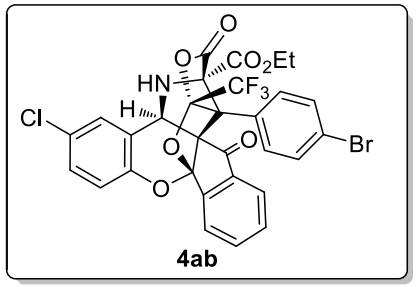

```
Current Data Parameters
NAME      5-Cl imine product
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_            20170411
Time                17.01
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              7211.539 Hz
FIDRES           0.220079 Hz
AQ              2.2719147 sec
RG                 144.49
DW                 69.333 usec
DE                 10.50 usec
TE                 298.5 K
D1            2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                  12.90 usec
PLW1         15.00000000 W

F2 - Processing parameters
SI                  16384
SF           400.1300091 MHz
WDW                    EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

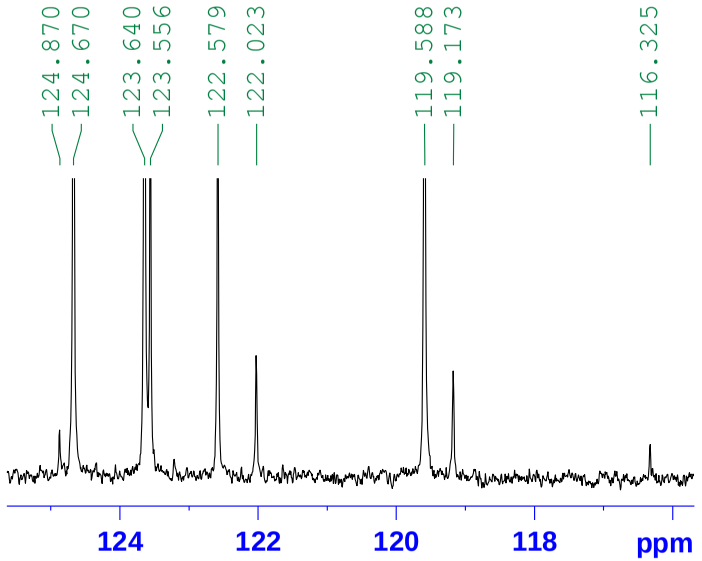


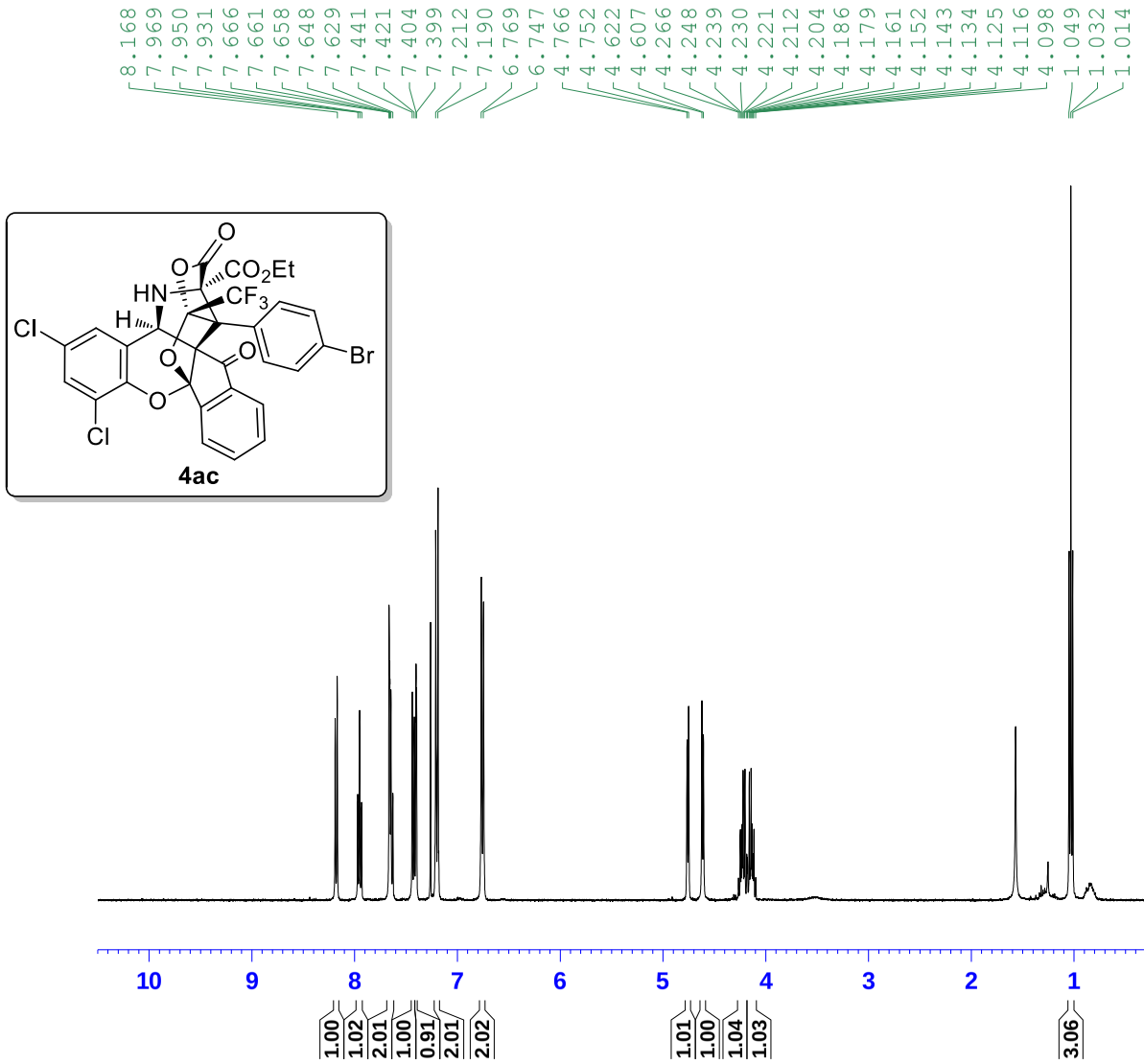

```
Current Data Parameters
NAME                  4ab
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160523
Time               22.17
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                15000
DS                    0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             0.6815744 sec
RG                9195.2
DW                20.800 usec
DE                 6.50 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2               90.00 usec
PL2                  1.80 dB
PL12                17.00 dB
PL13                20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127546 MHz
WDW                  EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```


128.898
128.859
128.829
128.798
128.9
128.8
ppm

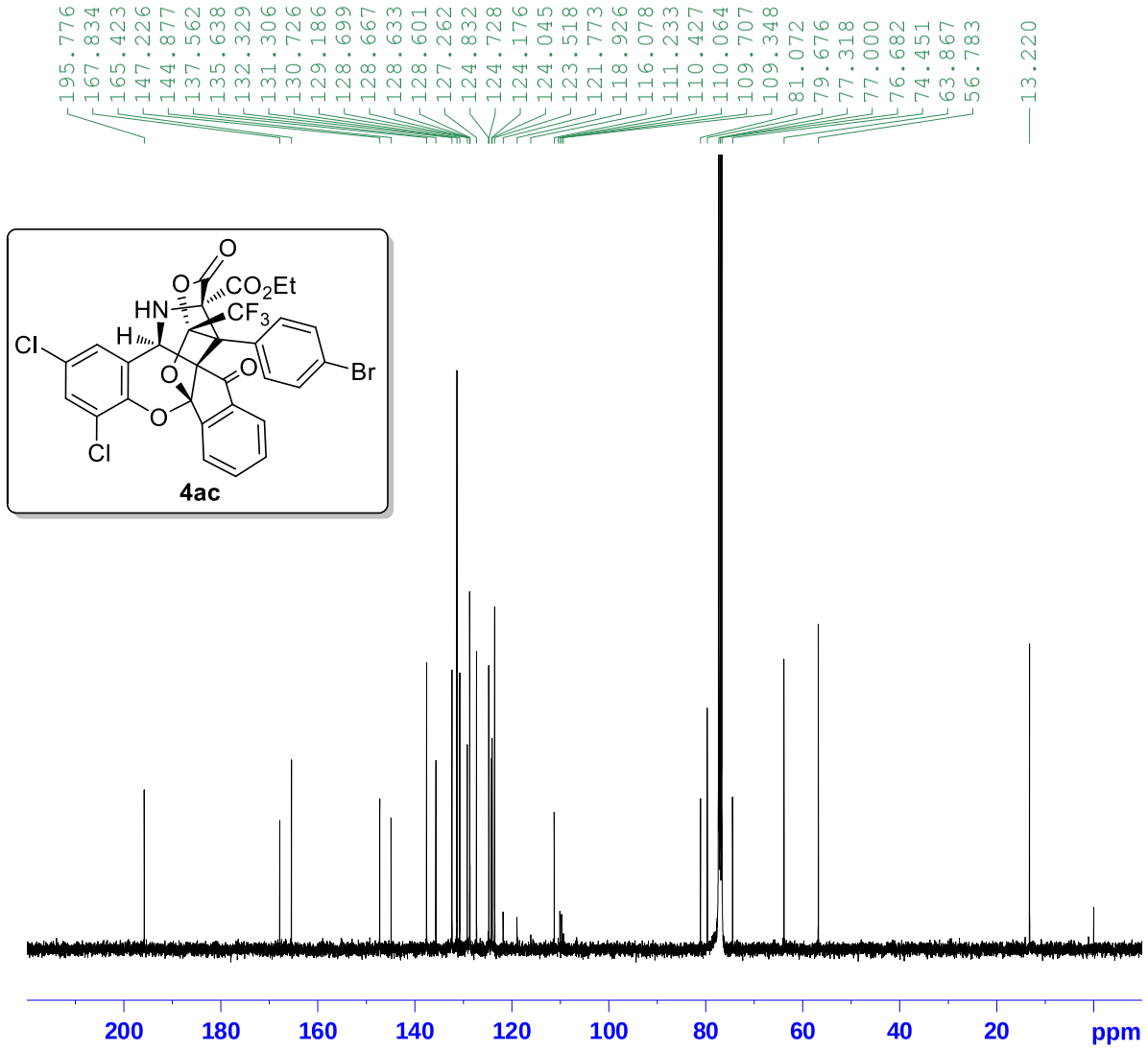

110.451
110.095
109.740
109.384
110.5
110.0
109.5
ppm


O
O
CO2Et
HN
CF3
H
Cl
Br
O
O
O
4ab

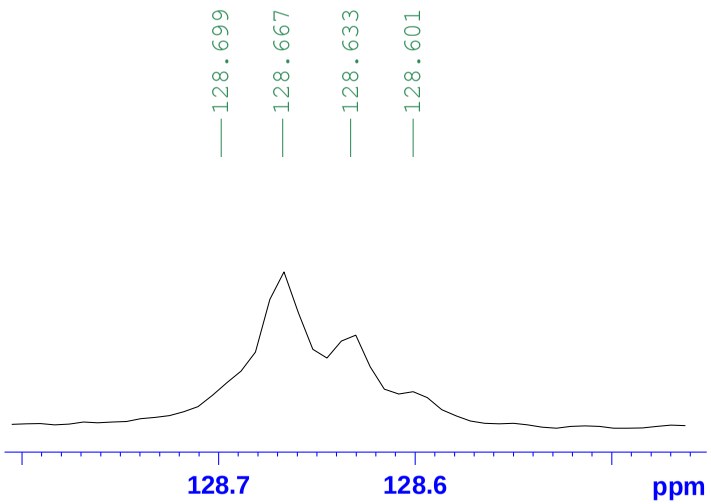

124.870
124.670
123.640
123.556
122.579
122.023
119.588
119.173
116.325
124
122
120
118
ppm

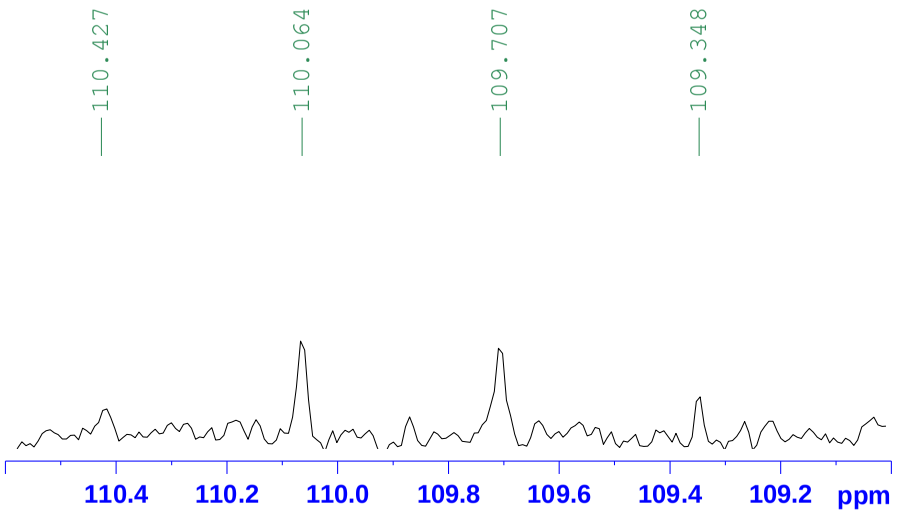


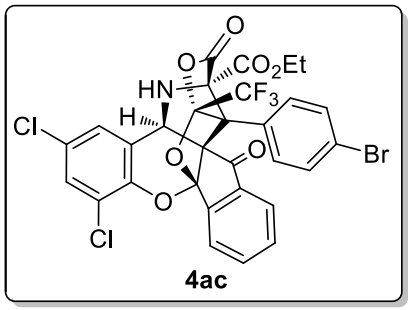

```
Current Data Parameters
NAME      3, 5-imine product
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20170417
Time                 22.07
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               7246.377 Hz
FIDRES            0.221142 Hz
AQ               2.2609921 sec
RG                     256
DW                69.000 usec
DE                 6.50 usec
TE                 295.5 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  14.40 usec
PL1                  1.80 dB
SFO1          400.1324008 MHz

F2 - Processing parameters
SI                   16384
SF            400.1300083 MHz
WDW                     EM
SSB       0
LB        0 Hz
GB        0
PC                   1.00
```

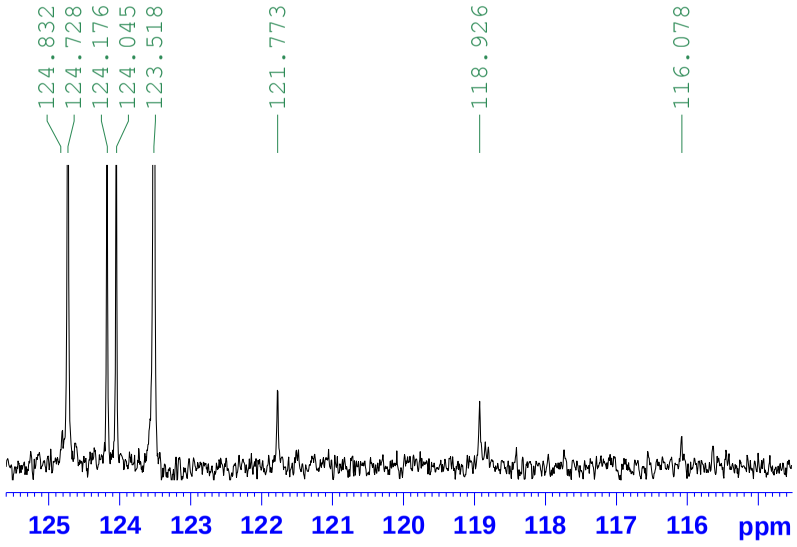


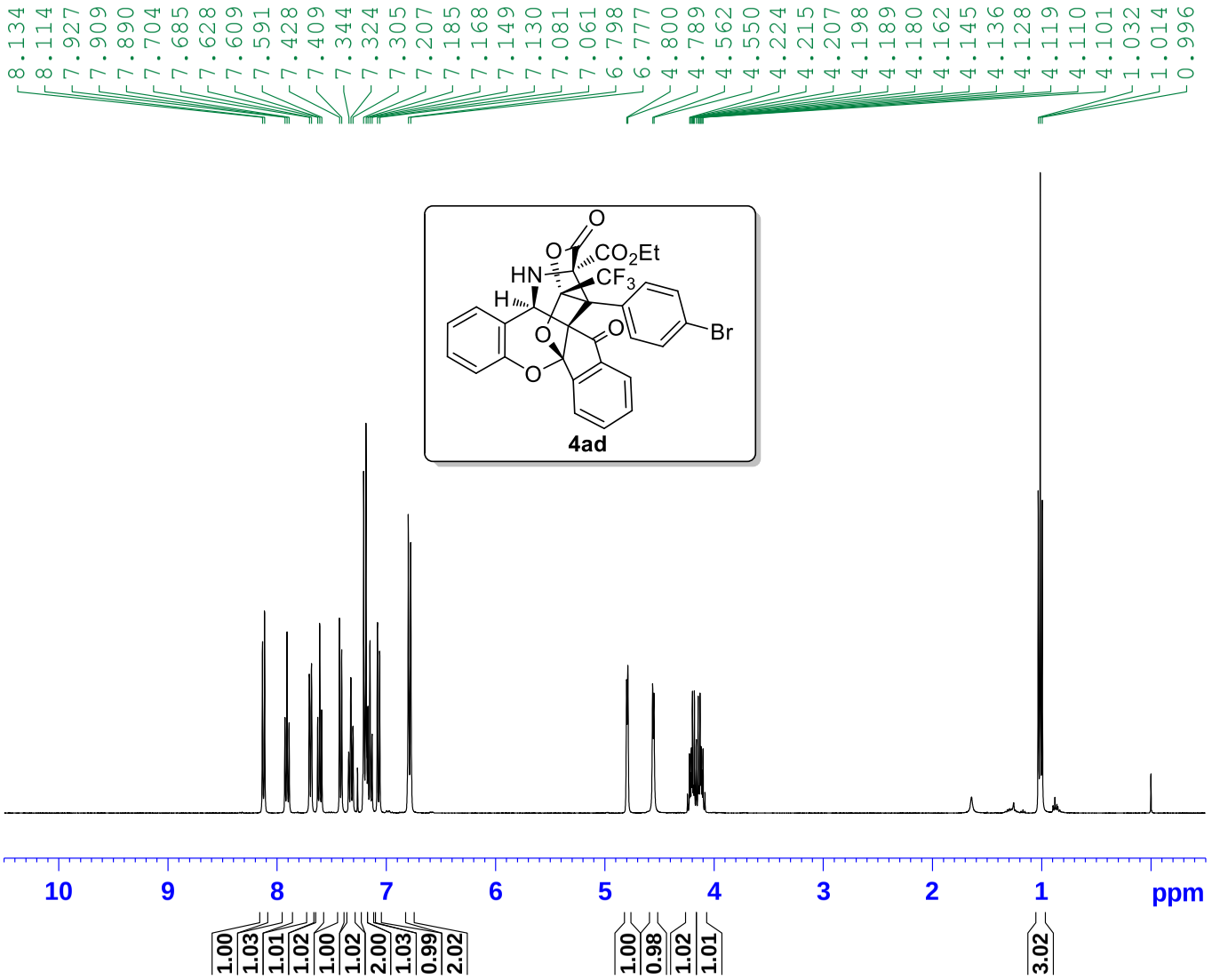

```
Current Data Parameters
NAME      3, 5-imine product
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170417
Time                 22.09
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG            zgpg30
TD                   32768
SOLVENT              CDCl3
NS                   14124
DS                       0
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               0.6815744 sec
RG                  9195.2
DW                  20.800 usec
DE                   6.50 usec
TE                  295.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                      1

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

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                   1H
PCPD2                90.00 usec
PL2                   1.80 dB
PL12                 17.00 dB
PL13                 20.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF           100.6127708 MHz
WDW                    EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.00
```


128.699
128.667
128.633
128.601
128.7
128.6
ppm

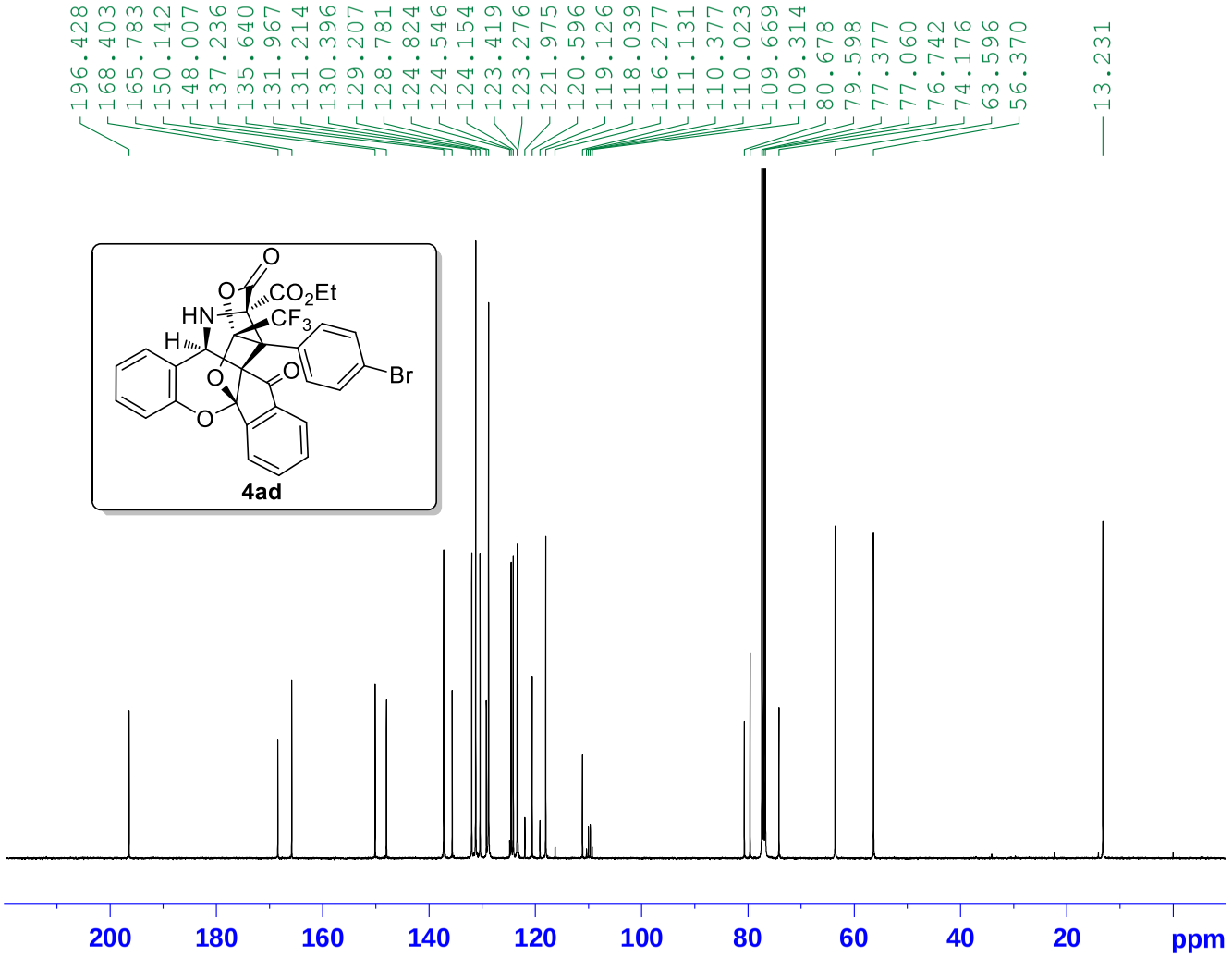

110.427
110.064
109.707
109.348
110.4
110.2
110.0
109.8
109.6
109.4
109.2
ppm


O
O
CO2Et
HN
CF3
H
Cl
Br
O
O
O
Cl
4ac

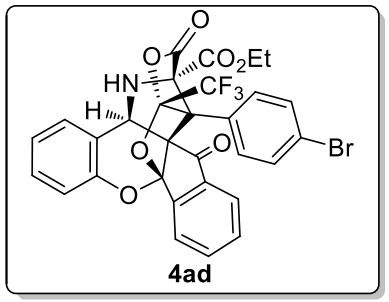

124.832
124.728
124.176
124.045
123.518
121.773
118.926
116.078
125
124
123
122
121
120
119
118
117
116
ppm

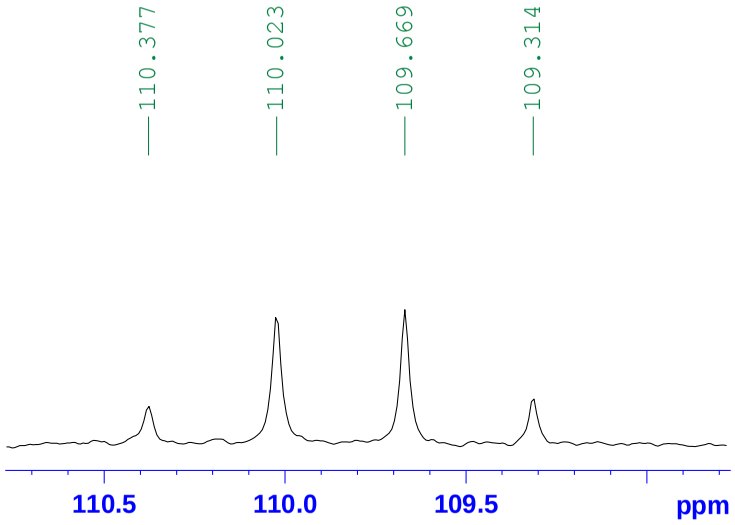


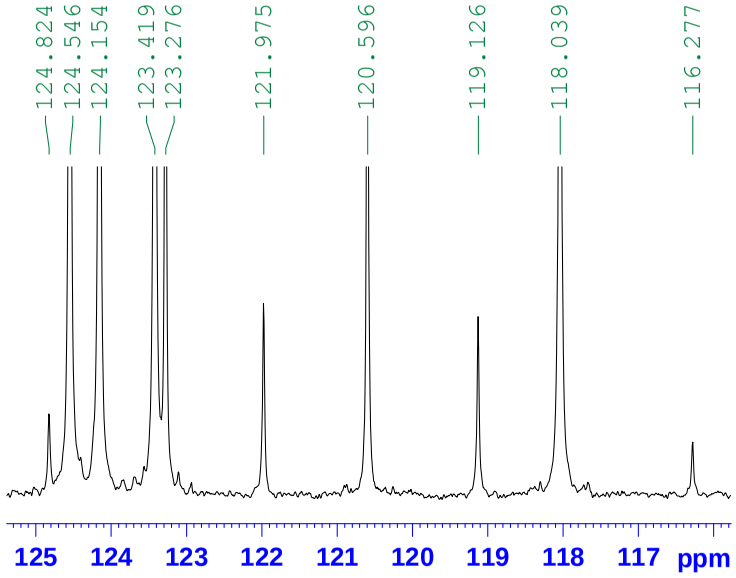

```
Current Data Parameters
NAME                  4ad
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20161031
Time               22.05
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             7211.539 Hz
FIDRES          0.220079 Hz
AQ              2.2719147 sec
RG                 63.58
DW                69.333 usec
DE                10.50 usec
TE                298.2 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                 12.90 usec
PLW1         15.00000000 W

F2 - Processing parameters
SI                 16384
SF          400.1300088 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

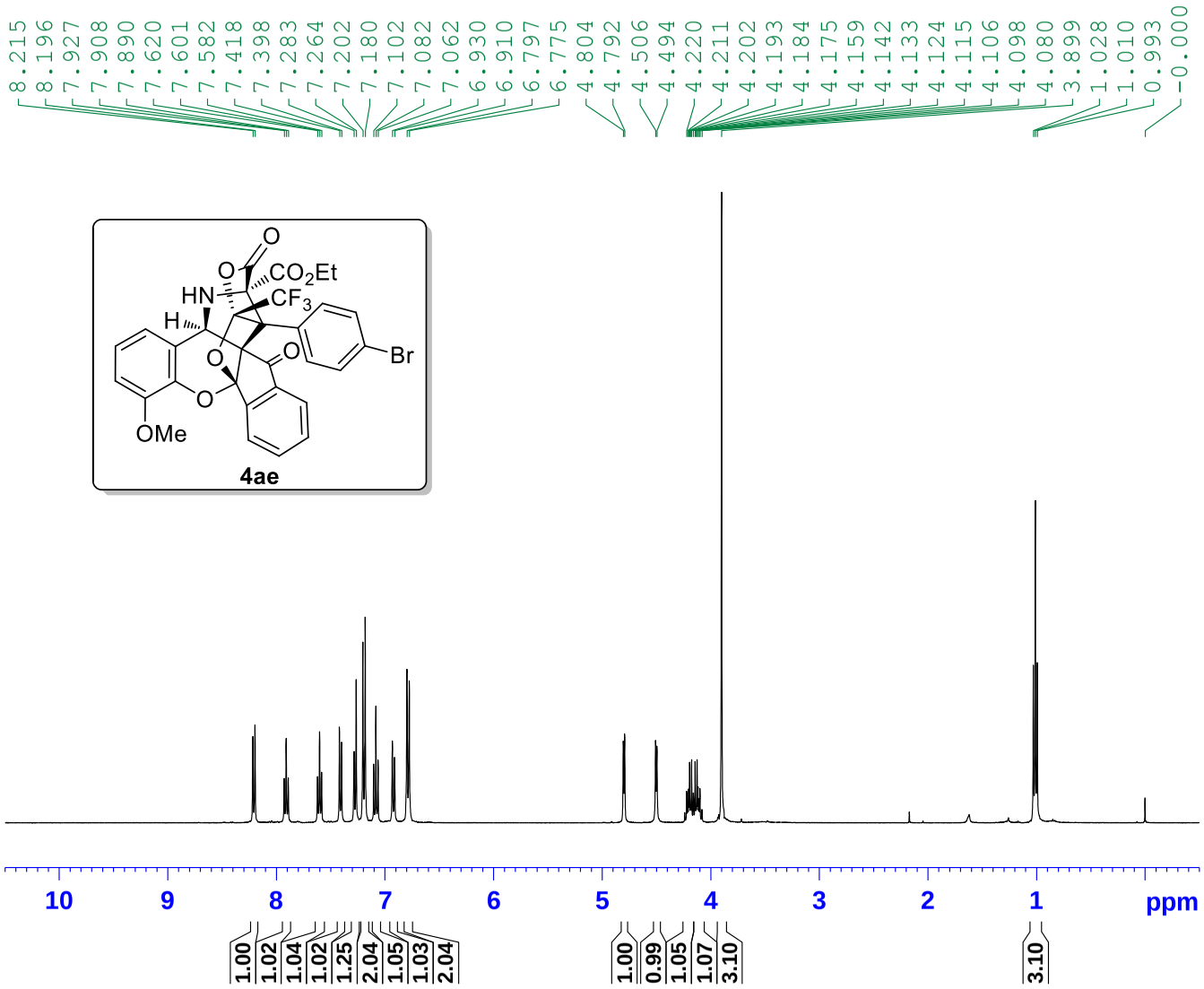



```
Current Data Parameters
NAME                   4ad
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_           20161031
Time               22.07
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 32768
SOLVENT            CDCl3
NS                 12818
DS                     0
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ              0.6815744 sec
RG                198.09
DW                20.800 usec
DE                 6.50 usec
TE                298.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                10.00 usec
PLW1         47.50000000 W

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

F2 - Processing parameters
SI                 32768
SF           100.6127681 MHz
WDW                  EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.00
```

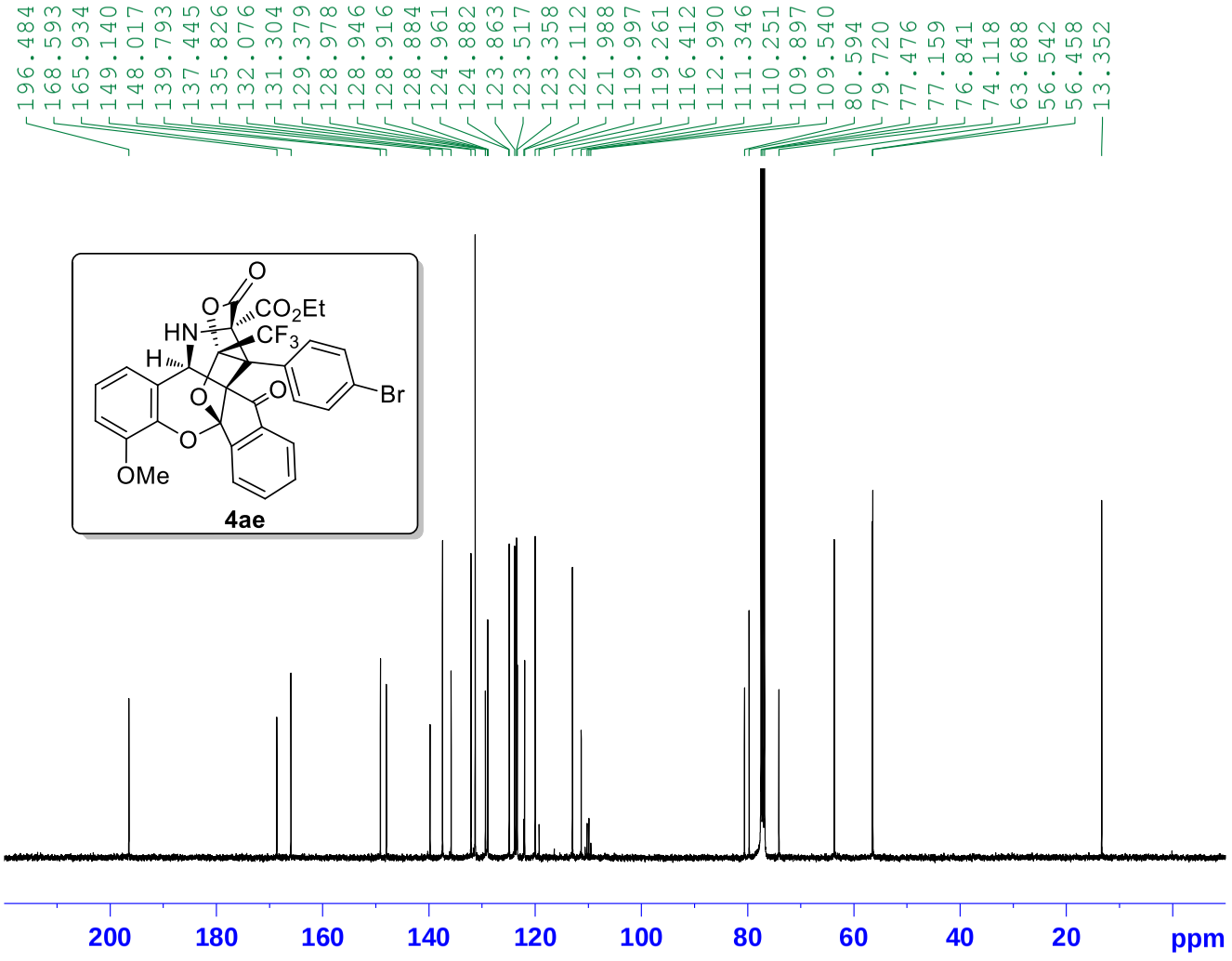

O
O
CO2Et
HN
CF3
H
O
O
O
Br
4ad


110.377
110.023
109.669
109.314
110.5
110.0
109.5
ppm

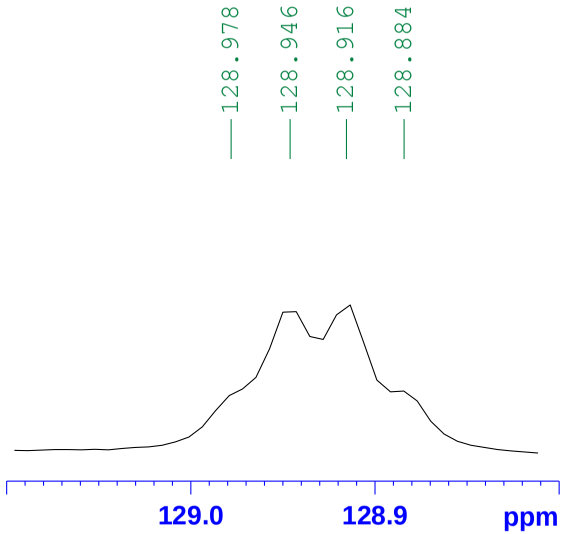

124.824
124.546
124.154
123.419
123.276
121.975
120.596
119.126
118.039
116.277
125
124
123
122
121
120
119
118
117
ppm

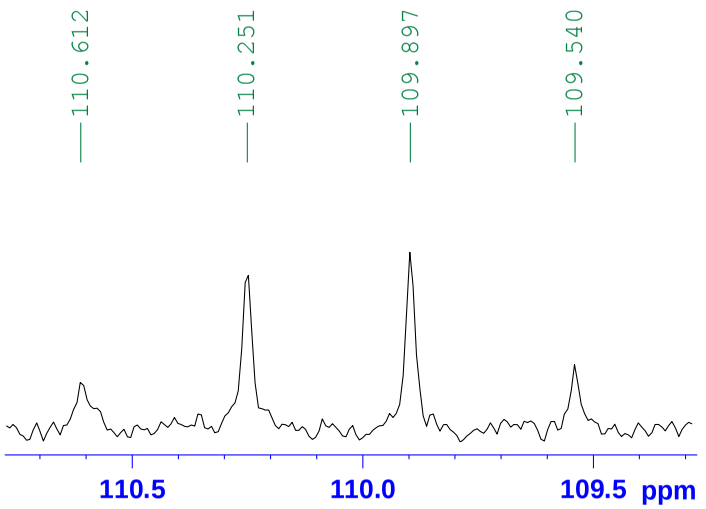


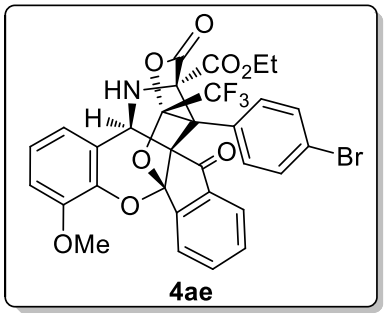

```
Current Data Parameters
NAME                   4ae
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20161201
Time                 22.08
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               7246.377 Hz
FIDRES           0.221142 Hz
AQ               2.2609921 sec
RG                     114
DW                69.000 usec
DE                 6.50 usec
TE                 296.8 K
D1             2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  14.40 usec
PL1                  1.80 dB
SFO1          400.1324008 MHz

F2 - Processing parameters
SI                   16384
SF            400.1300078 MHz
WDW                     EM
SSB       0
LB        0 Hz
GB        0
PC                    1.00
```



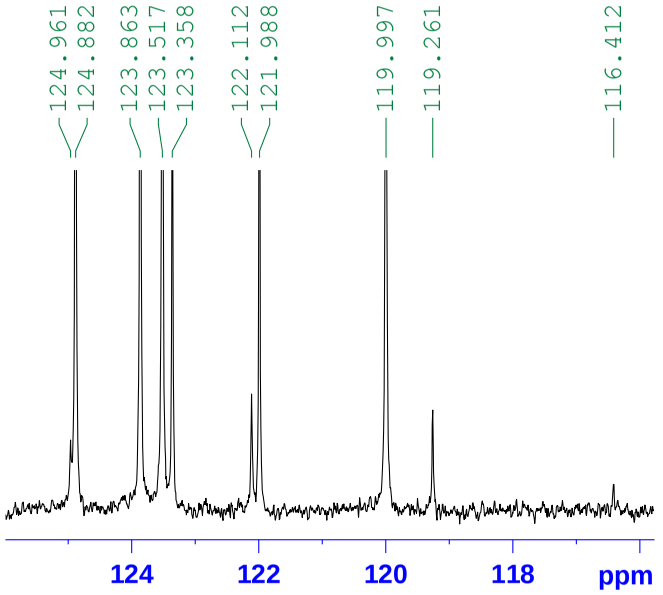

```
Current Data Parameters
NAME                  4ae
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_           20161201
Time               22.23
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                12963
DS                    0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             0.6815744 sec
RG                4597.6
DW                20.800 usec
DE                 6.50 usec
TE                296.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2               90.00 usec
PL2                  1.80 dB
PL12                17.00 dB
PL13                20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127555 MHz
WDW                  EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```

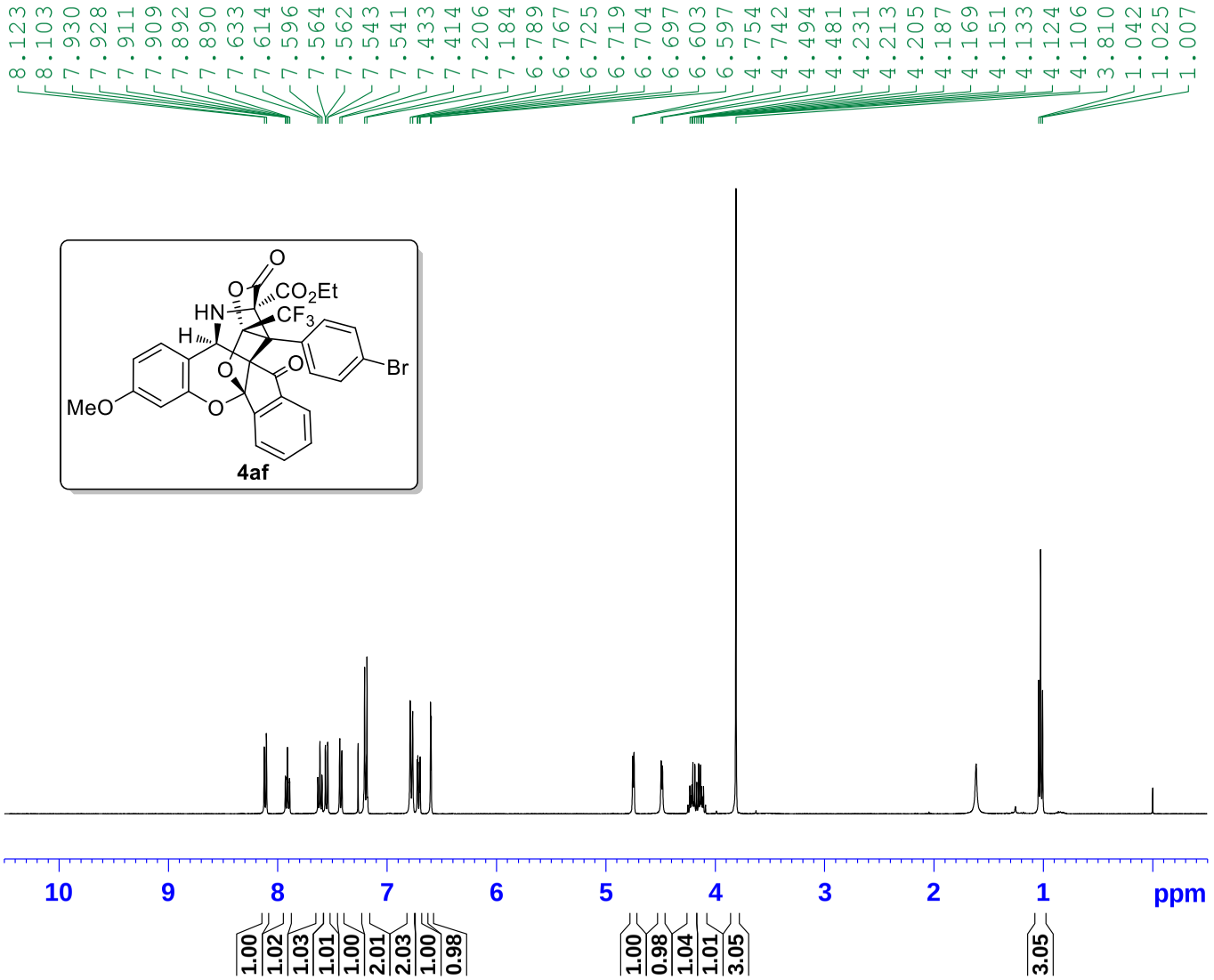

128.978
128.946
128.916
128.884
129.0
128.9
ppm


110.612
110.251
109.897
109.540
110.5
110.0
109.5
ppm

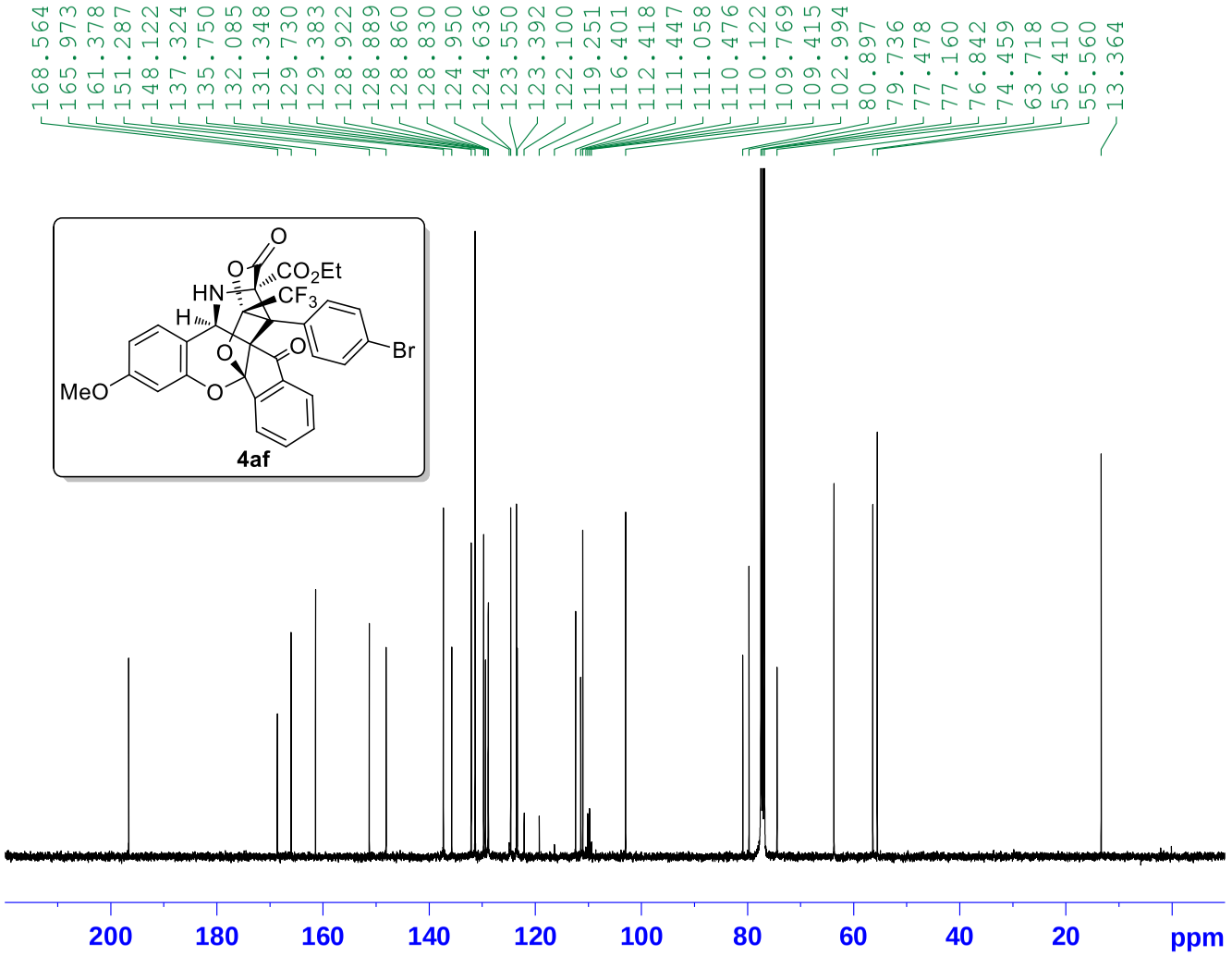

O
O
CO2Et
HN
CF3
H
O
O
O
Br
OMe

4ae

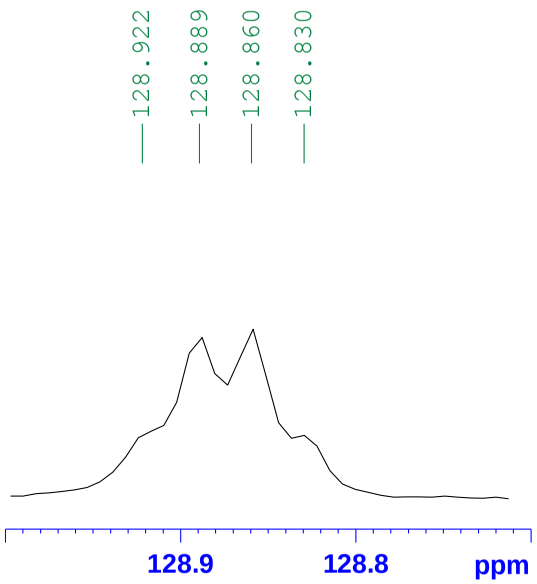

124.961
124.882
123.863
123.517
123.358
122.112
121.988
119.997
119.261
116.412
124
122
120
118
ppm

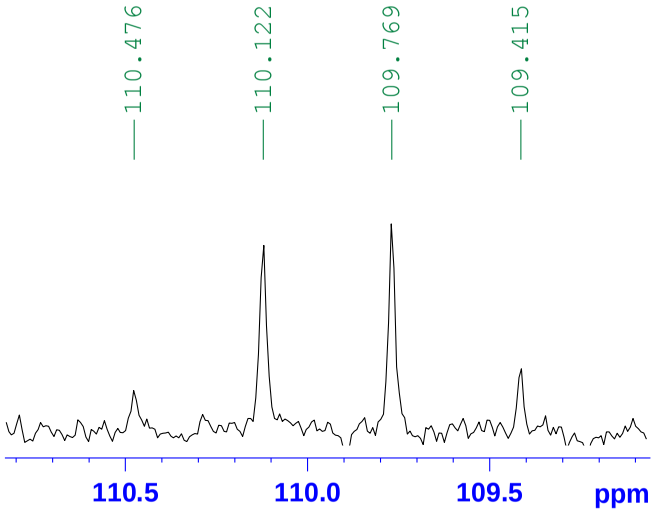


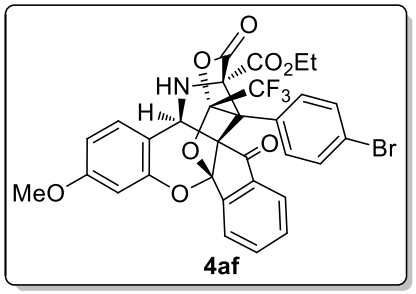

```
Current Data Parameters
NAME                   4af
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20161019
Time                 22.23
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              7246.377 Hz
FIDRES           0.221142 Hz
AQ               2.2609921 sec
RG                    181
DW                 69.000 usec
DE                  6.50 usec
TE                 297.2 K
D1              2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.40 usec
PL1                 1.80 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                  16384
SF           400.1300074 MHz
WDW                    EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

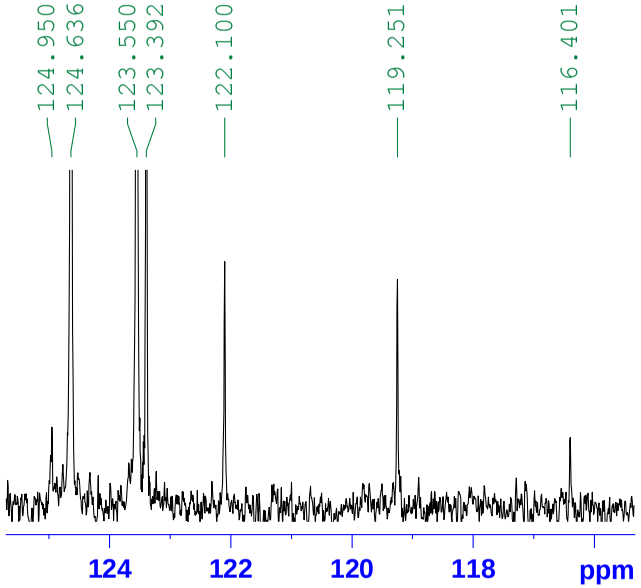


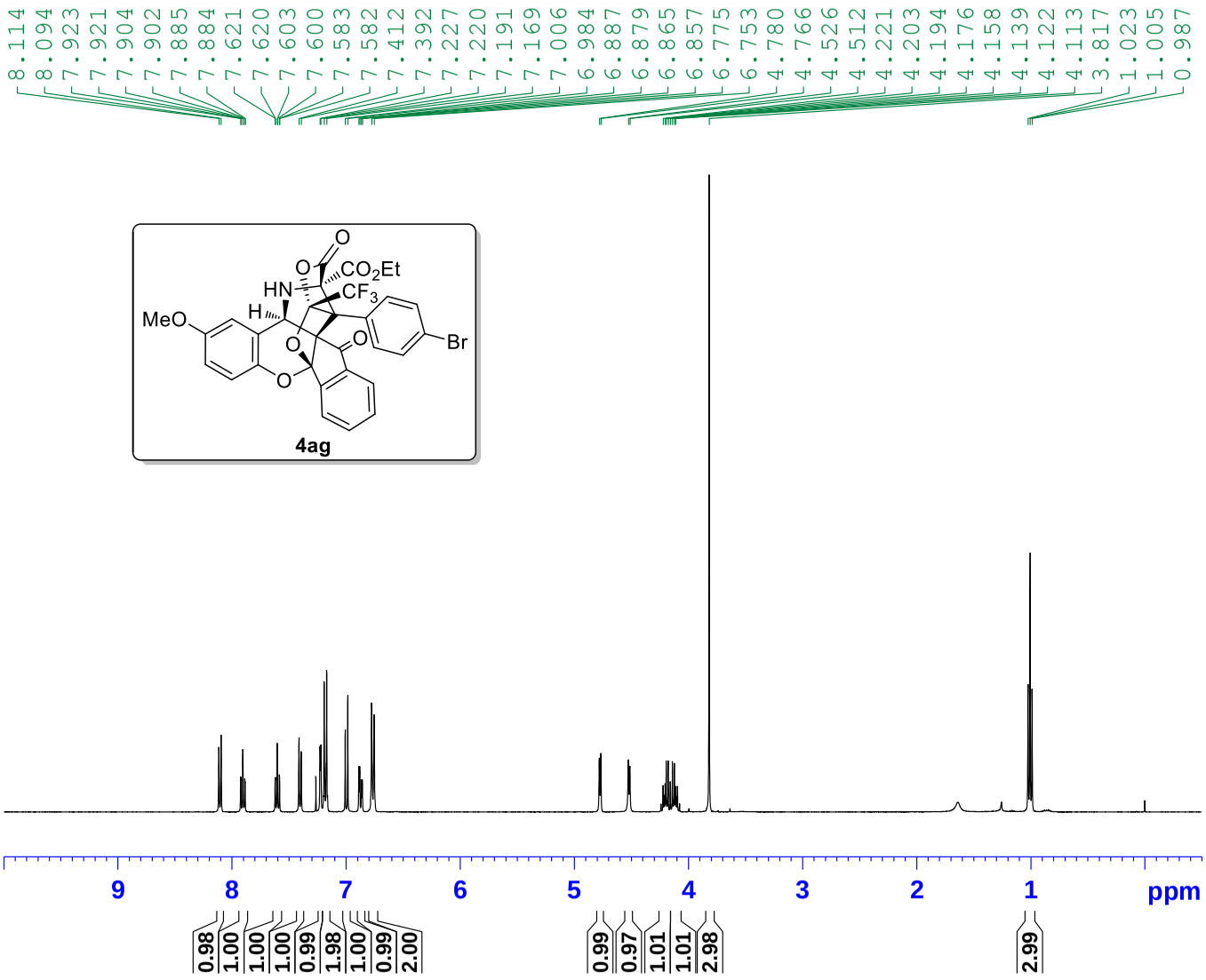

```
Current Data Parameters
NAME                  4af
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20161019
Time                22.25
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  32768
SOLVENT             CDCl3
NS                  12281
DS                      0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             0.6815744 sec
RG                 5792.6
DW                20.800 usec
DE                 6.50 usec
TE                297.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

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

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                 1.80 dB
PL12               17.00 dB
PL13               20.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF           100.6127552 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```


128.922
128.889
128.860
128.830
128.9
128.8
ppm

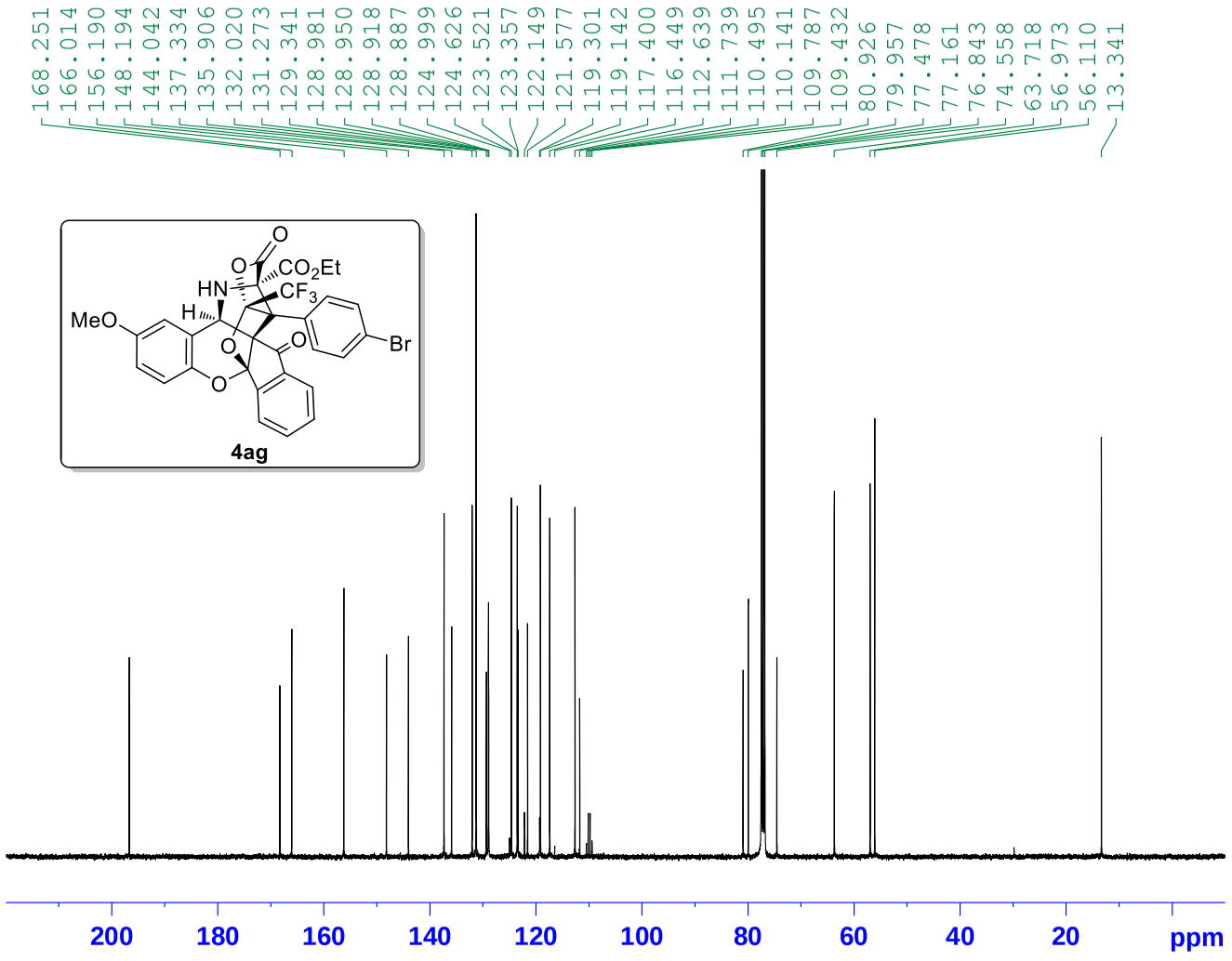

110.476
110.122
109.769
109.415
110.5
110.0
109.5
ppm


O
O
CO2Et
HN
CF3
H
O
O
Br
MeO
O
4af

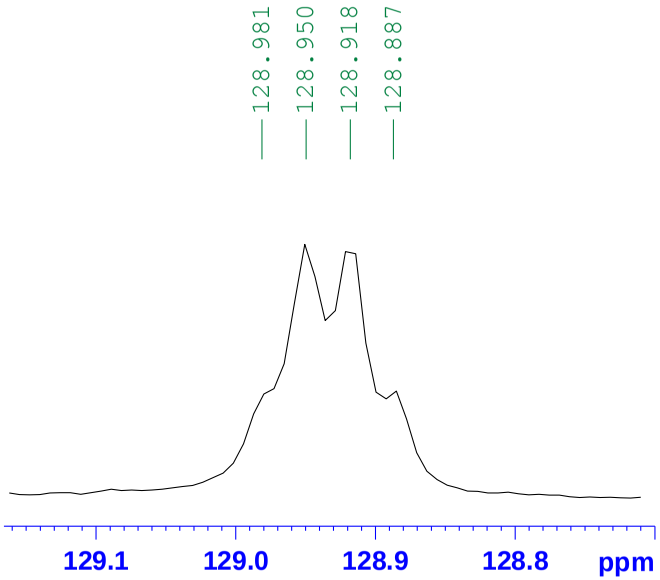

124.950
124.636
123.550
123.392
122.100
119.251
116.401
124
122
120
118
ppm

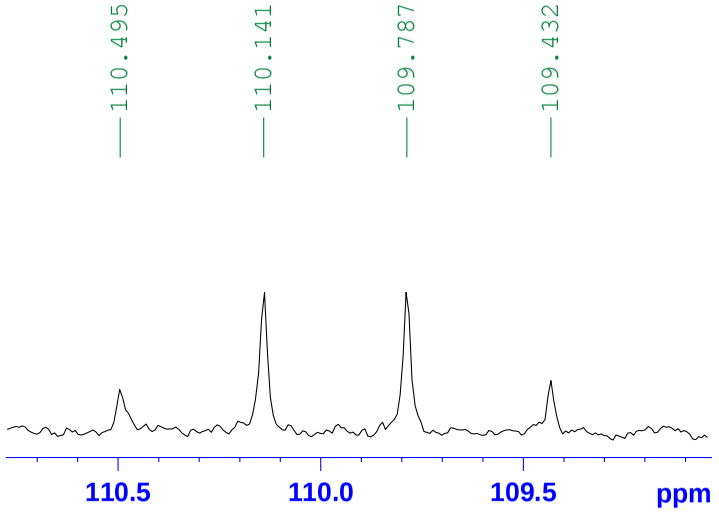


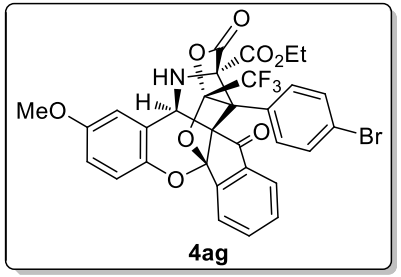

```
Current Data Parameters
NAME                  4ag
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_           20161027
Time              22.07
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            7246.377 Hz
FIDRES        0.221142 Hz
AQ            2.2609921 sec
RG                  114
DW               69.000 usec
DE                6.50 usec
TE                297.2 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.40 usec
PL1                1.80 dB
SFO1        400.1324008 MHz

F2 - Processing parameters
SI                16384
SF          400.1300078 MHz
WDW                  EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

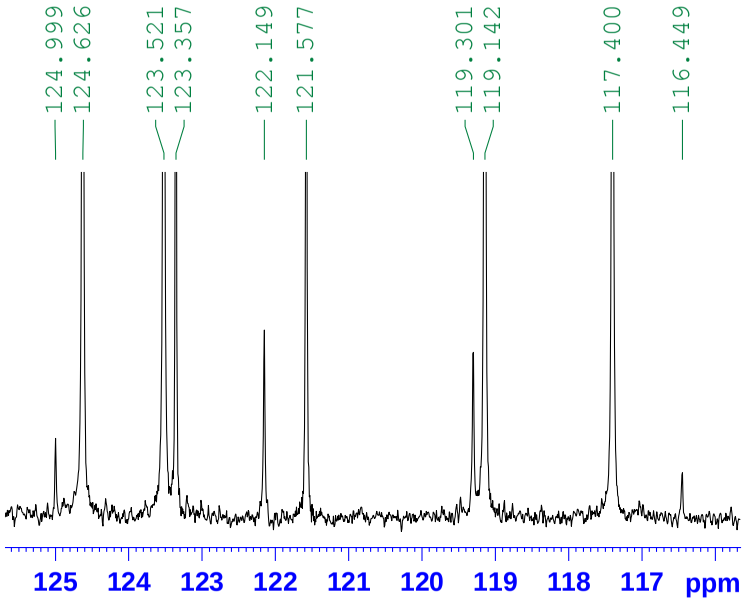


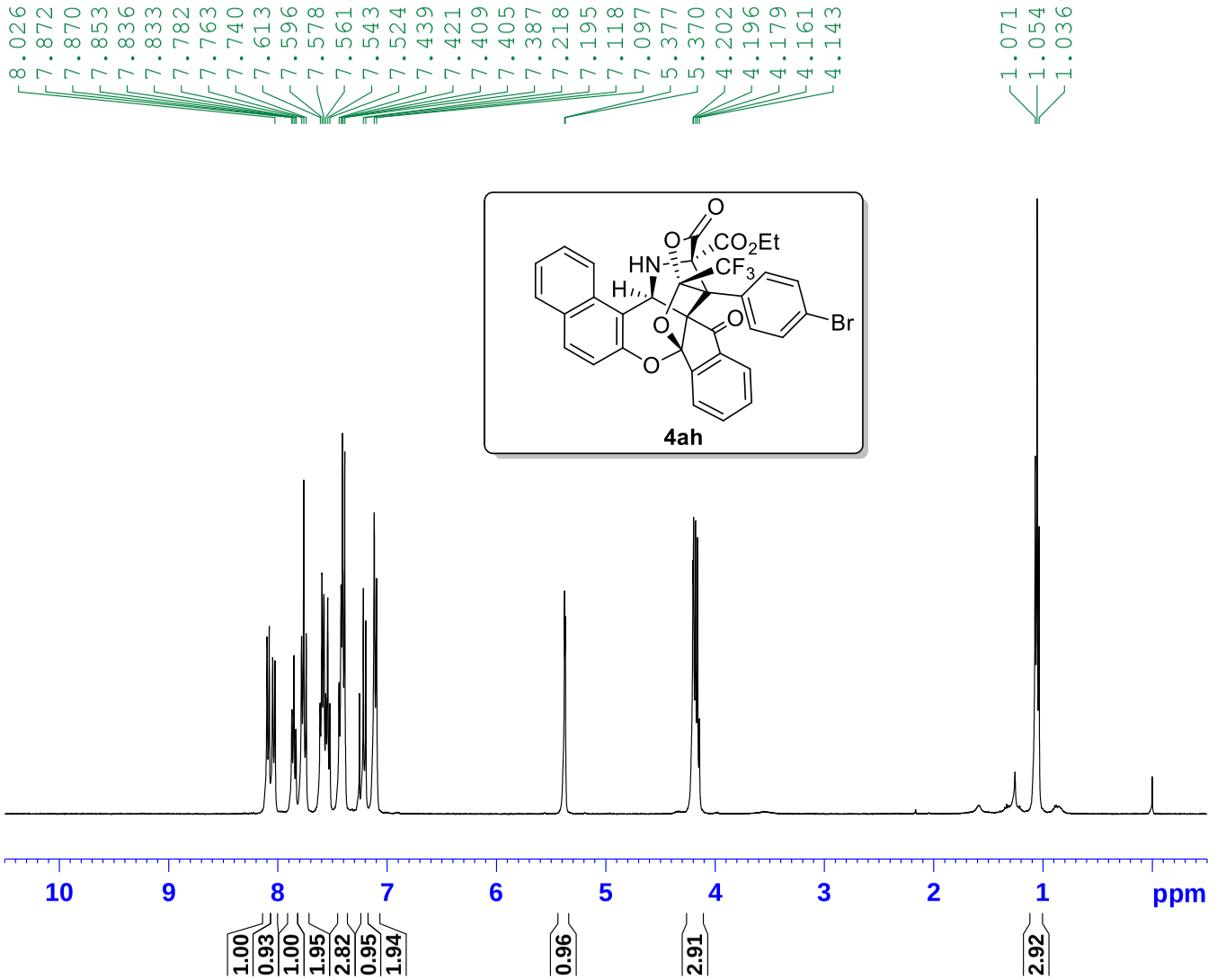

```
Current Data Parameters
NAME                  4ag
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_           20161027
Time               22.09
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                14550
DS                    0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             0.6815744 sec
RG                4597.6
DW                20.800 usec
DE                 6.50 usec
TE                297.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2               90.00 usec
PL2                  1.80 dB
PL12                17.00 dB
PL13                20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127554 MHz
WDW                  EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```


128.981
128.950
128.918
128.887
129.1
129.0
128.9
128.8
ppm

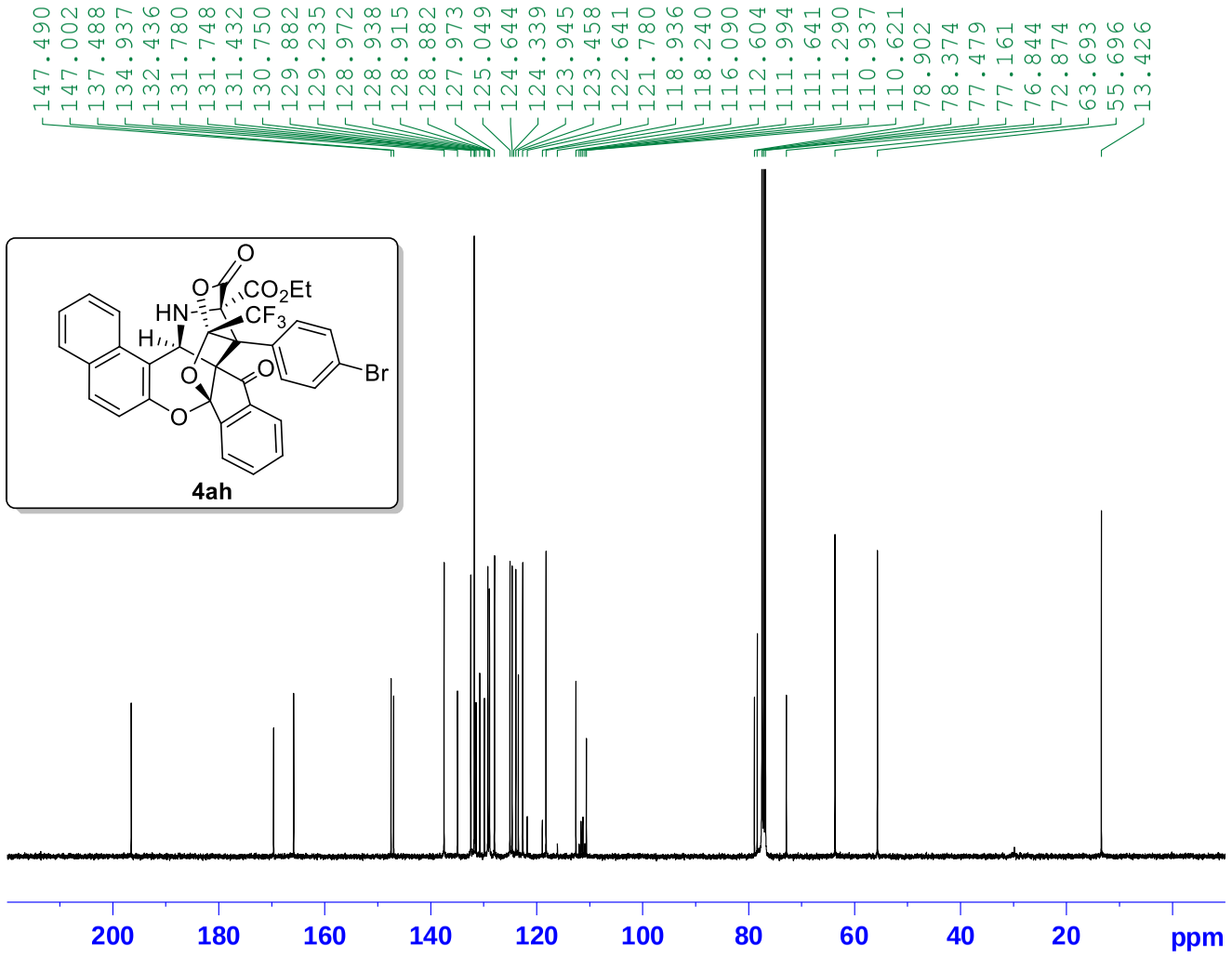

110.495
110.141
109.787
109.432
110.5
110.0
109.5
ppm


O
O
CO2Et
HN
CF3
H
MeO
O
O
Br
O
4ag

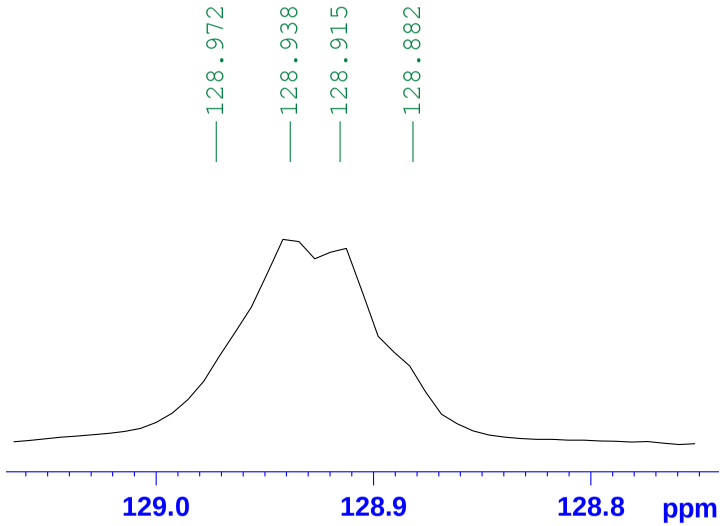

124.999
124.626
123.521
123.357
122.149
121.577
119.301
119.142
117.400
116.449
125
124
123
122
121
120
119
118
117
ppm

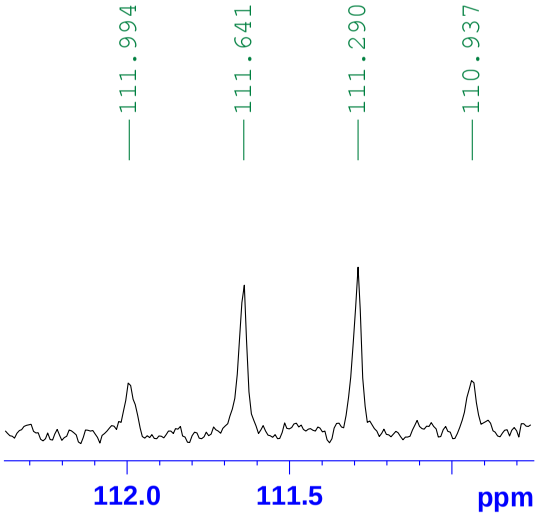


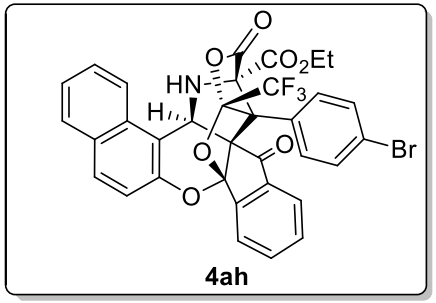

```
Current Data Parameters
NAME                  4ah
EXPNO                  15
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170301
Time               22.18
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             7246.377 Hz
FIDRES          0.221142 Hz
AQ              2.2609921 sec
RG                   114
DW                69.000 usec
DE                 6.50 usec
TE                295.5 K
D1           2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.40 usec
PL1                1.80 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300118 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

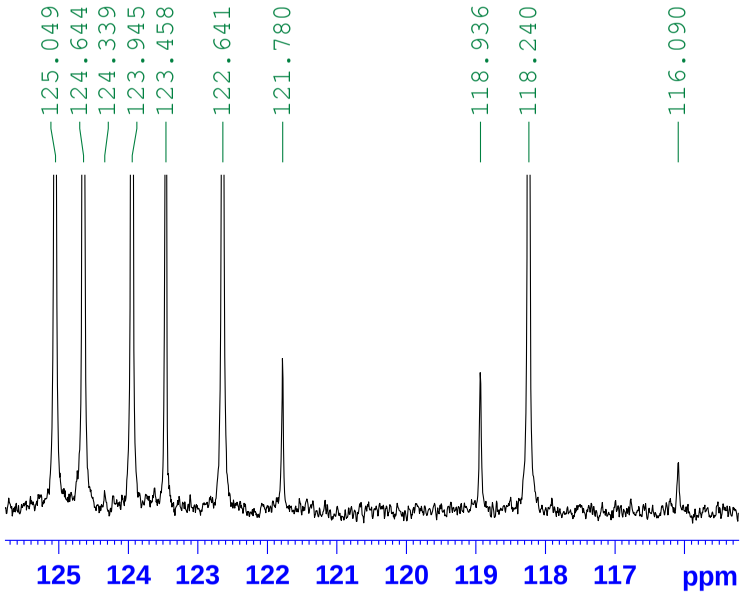



```
Current Data Parameters
NAME                  4ah
EXPNO                  16
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170301
Time               22.20
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                 15071
DS                     0
SWH          24038.461 Hz
FIDRES        0.733596 Hz
AQ            0.6815744 sec
RG               4597.6
DW                20.800 usec
DE                 6.50 usec
TE                295.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

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

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2               90.00 usec
PL2                  1.80 dB
PL12                17.00 dB
PL13                20.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127571 MHz
WDW                  EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```


128.972
128.938
128.915
128.882
129.0
128.9
128.8
ppm

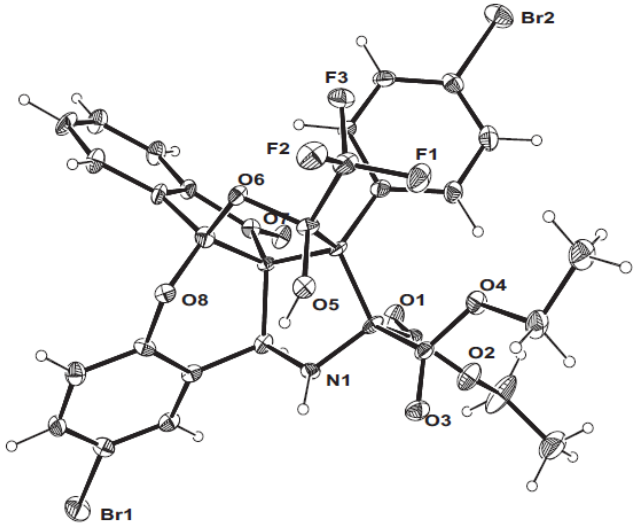

111.994
111.641
111.290
110.937
112.0
111.5
ppm


O
O
CO2Et
HN
CF3
H
O
O
O
Br
4ah


125.049
124.644
124.339
123.945
123.458
122.641
121.780
118.936
118.240
116.090
125
124
123
122
121
120
119
118
117
ppm

X-ray structures of *rac*-3aa and 4ab:

a) *rac*-**3aa** (CCDC no. 1473859): The thermal ellipsoid drawn at 30% probability level.

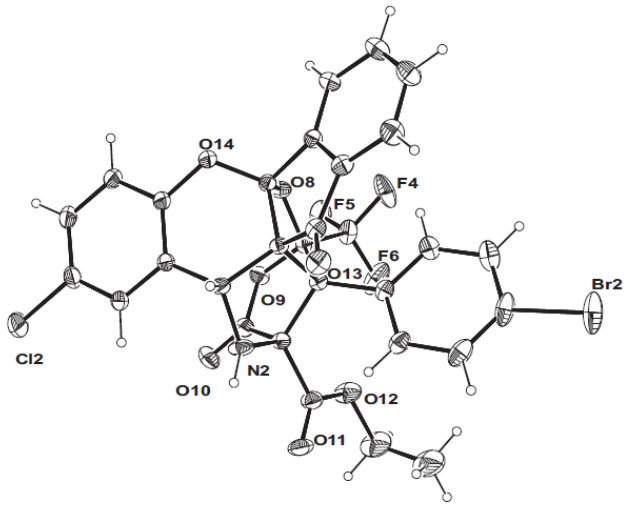


Crystal data and structure refinement for *rac*-3aa:

Empirical formula	C32 H24 Br2 F3 N O8	
Formula weight	767.34	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.7847(11) Å	□= 113.199(8)°.
	b = 13.1195(16) Å	□= 98.631(9)°.
	c = 13.9270(15) Å	□ = 105.657(9)°.
Volume	1514.4(3) Å^3	
Z	2	
Density (calculated)	1.683 Mg/m^3	
Absorption coefficient	2.749 mm^{-1}	
F(000)	768	
Crystal size	0.36 x 0.05 x 0.01 mm^3	
Theta range for data collection	2.26 to 25.15°.	
Index ranges	-11<=h<=11, -14<=k<=15, -16<=l<=16	
Reflections collected	13614	
Independent reflections	5345 [R(int) = 0.1156]	
Completeness to theta = 25.15°	98.4 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9730 and 0.4377	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5345 / 8 / 415
Goodness-of-fit on F^2	0.842
Final R indices [I>2sigma(I)]	R1 = 0.0633, wR2 = 0.1449
R indices (all data)	R1 = 0.2017, wR2 = 0.2121
Largest diff. peak and hole	0.641 and -0.828 e.Å^{-3}

b) **4ab** (Absolute Configuration, CCDC no. 1526049): The thermal ellipsoid drawn at 30% probability level.



Crystal data and structure refinement for 4ab:

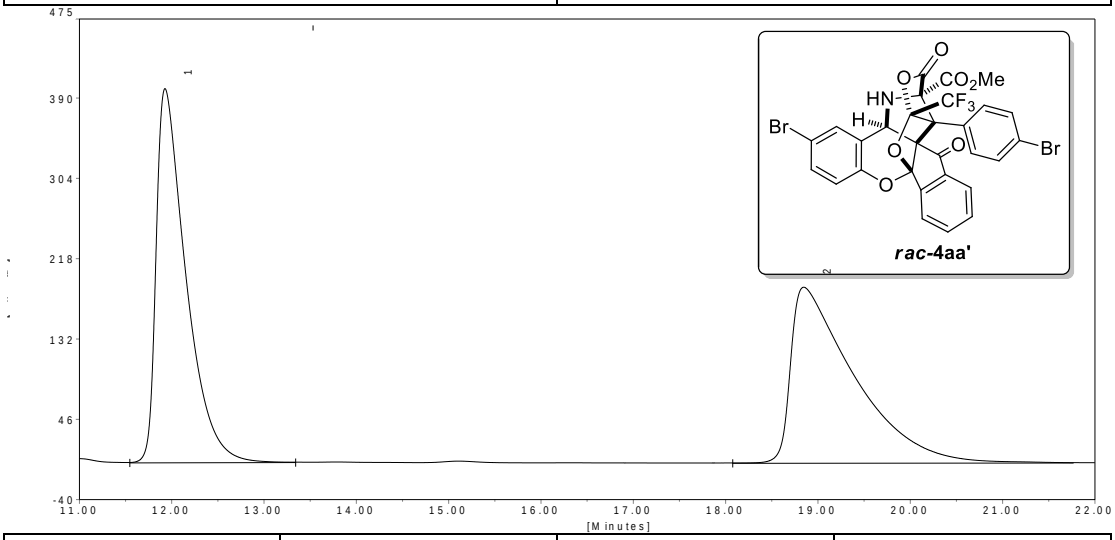
Empirical formula	C30 H18 Br Cl F3 N O7	
Formula weight	676.81	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Trigonal	
Space group	P 31 2 1	
Unit cell dimensions	a = 11.2302(2) Å	□= 90°.
	b = 11.2302(2) Å	□= 90°.
	c = 76.8595(16) Å	□ = 120°.
Volume	8394.7(3) Å^3	
Z	12	
Density (calculated)	1.607 Mg/m^3	
Absorption coefficient	3.508 mm^{-1}	
F(000)	4080	
Crystal size	0.55 x 0.40 x 0.35 mm^3	

Theta range for data collection	1.72 to 66.89°.
Index ranges	-13<=h<=13, -13<=k<=13, -91<=l<=90
Reflections collected	75593
Independent reflections	9949 [R(int) = 0.0353]
Completeness to theta = 66.89°	99.5 %
Absorption correction	multi-scan
Max. and min. transmission	0.3731 and 0.2485
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9949 / 0 / 779
Goodness-of-fit on F^2	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.1065
R indices (all data)	R1 = 0.0413, wR2 = 0.1066
Absolute structure parameter	0.037(13)
Largest diff. peak and hole	0.469 and -0.538 e.$Å^{-3}$

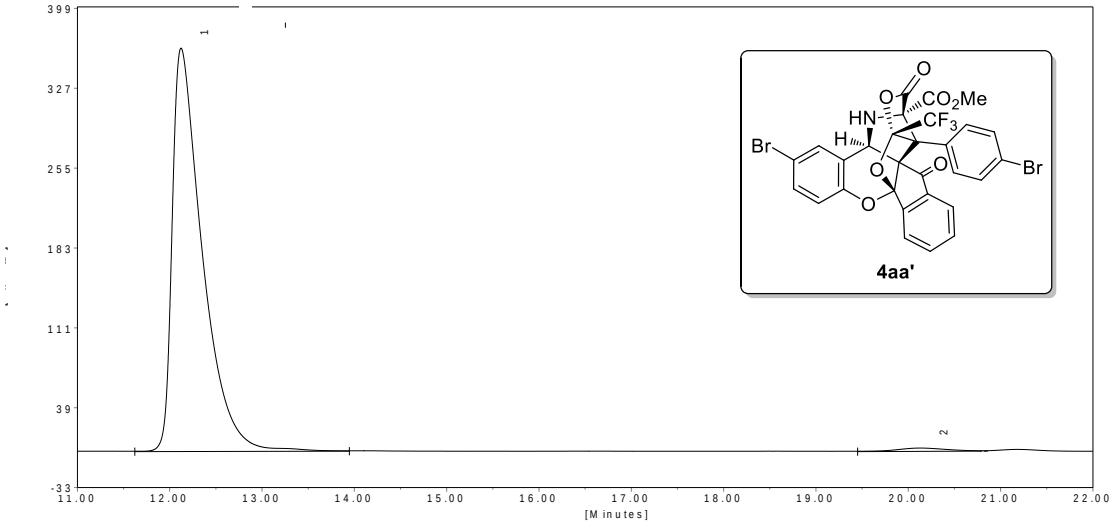
HPLC Chromatograms for the cascade products:

HPLC Chromatogram for **4aa'**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 90: 10	Detector: UV 248 nm



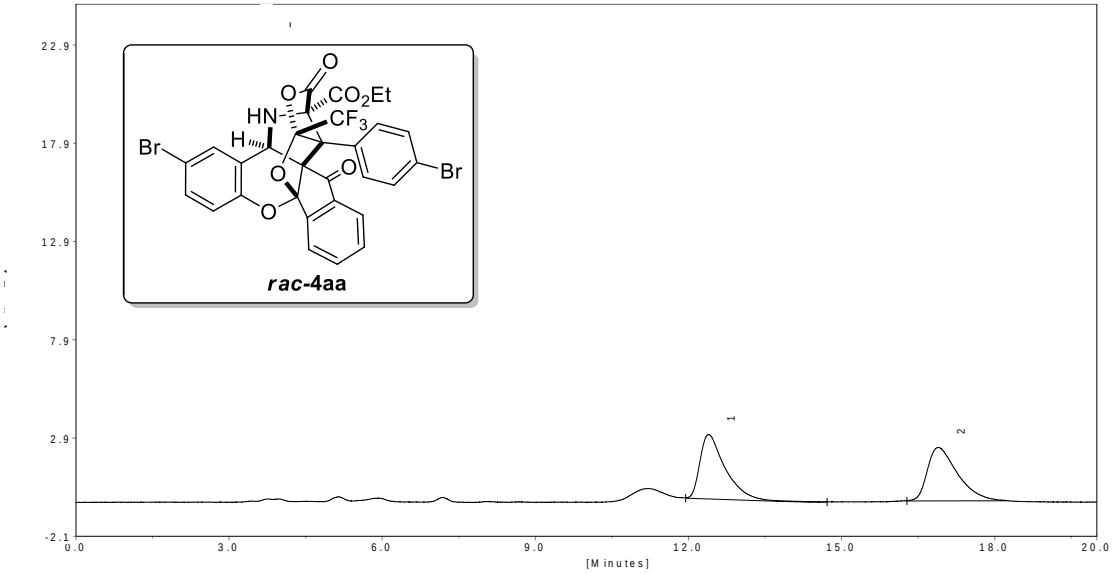
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
11.93	400.26	8948.02	49.9785
18.85	188.10	8955.73	50.0215



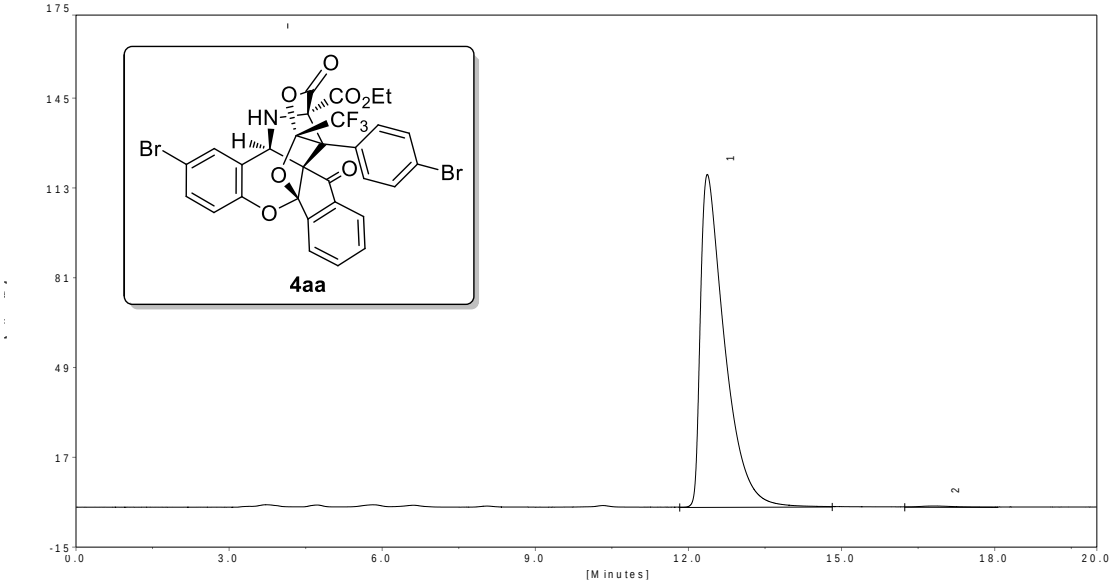
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.12	363.38	8208.10	98.9638
20.13	2.64	85.95	1.0362

HPLC Chromatogram for **4aa**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=90:10	Detector: UV 278 nm



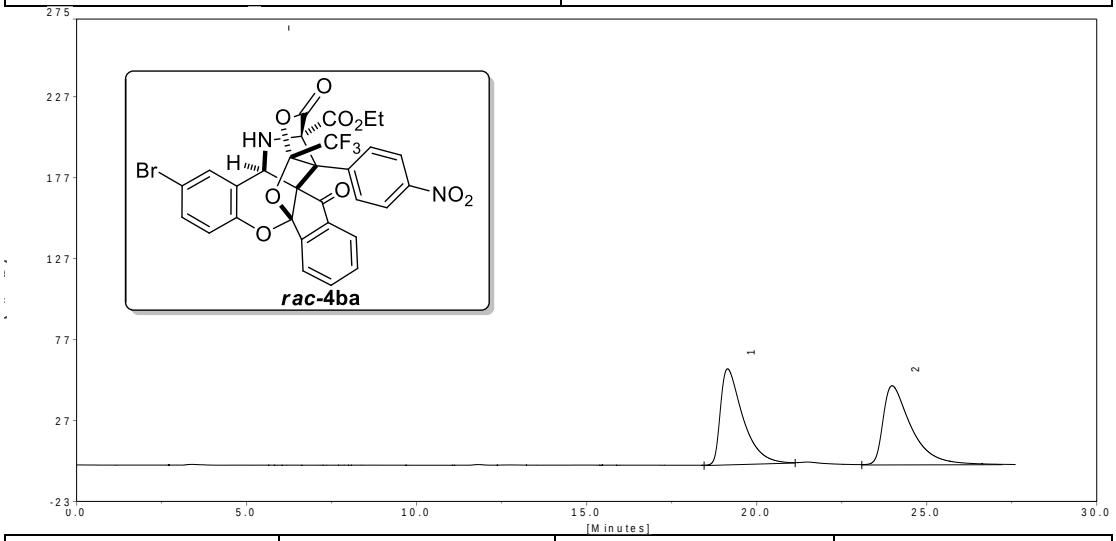
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.38	3.25	107.99	49.7151
16.89	2.69	109.23	50.2849



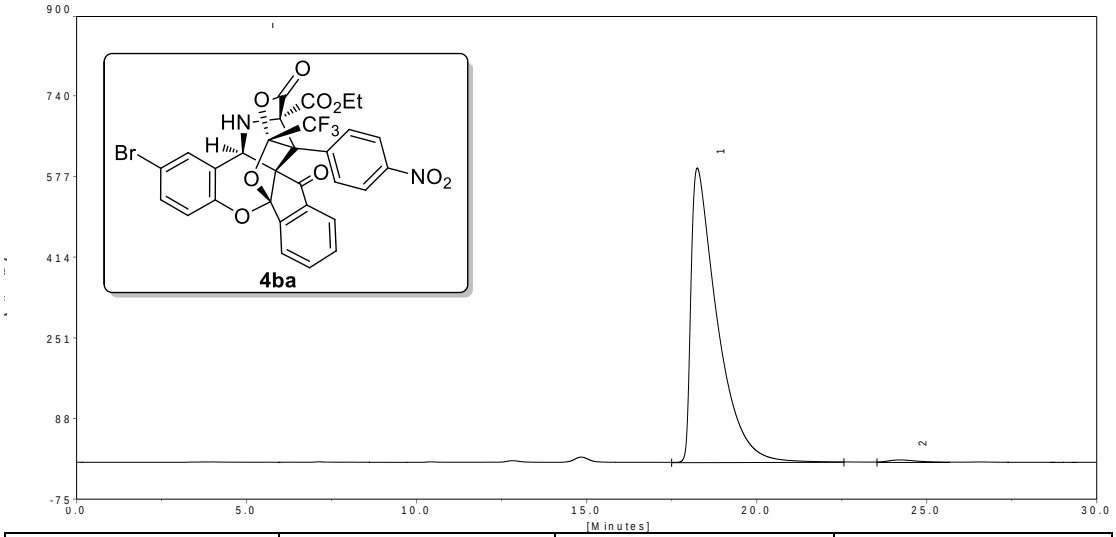
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.37	118.53	3894.75	99.6905
16.78	0.32	12.09	0.3095

HPLC Chromatogram for **4ba**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=90:10	Detector: UV 278 nm



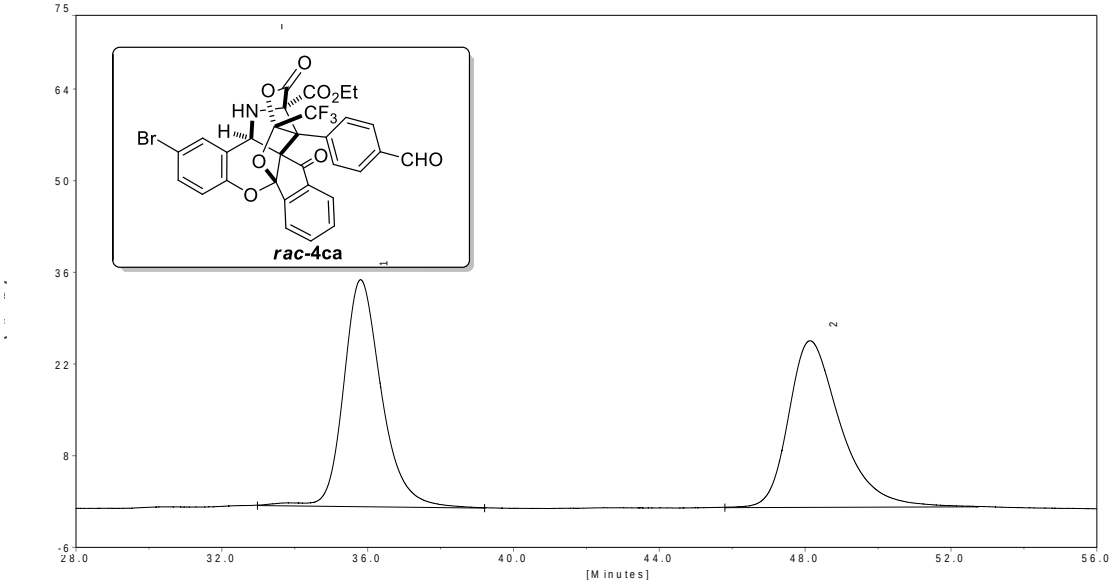
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
19.15	59.15	2694.44	49.2074
23.98	48.69	2781.24	50.7926



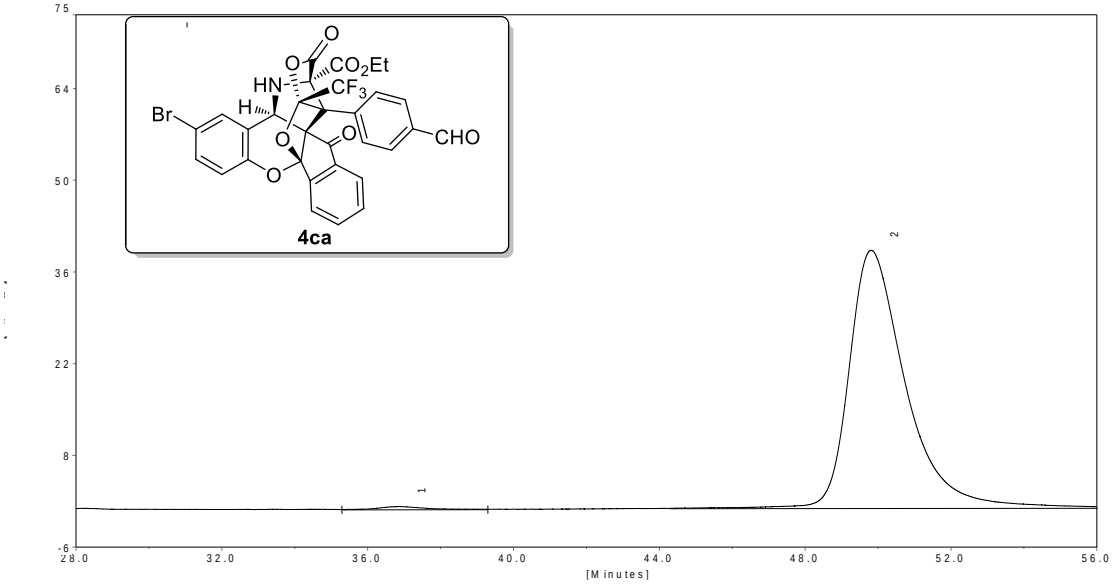
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
18.25	594.72	31761.97	99.2991
24.20	4.27	224.19	0.7009

HPLC Chromatogram for **4ca**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=80:20	Detector: UV 278 nm



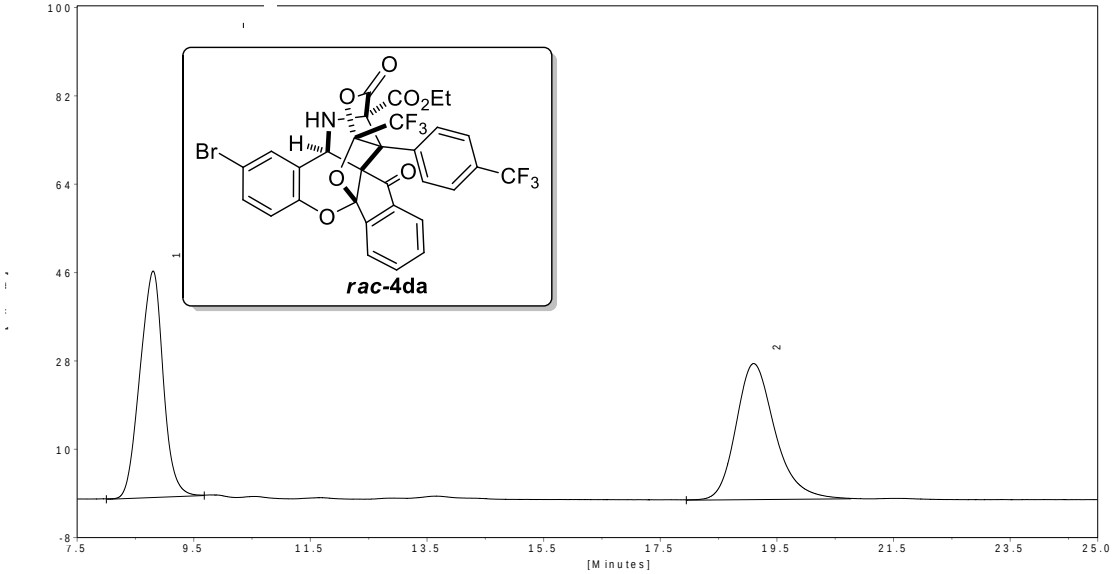
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
35.81	34.61	2492.75	49.9182
48.14	25.38	2500.92	50.0818



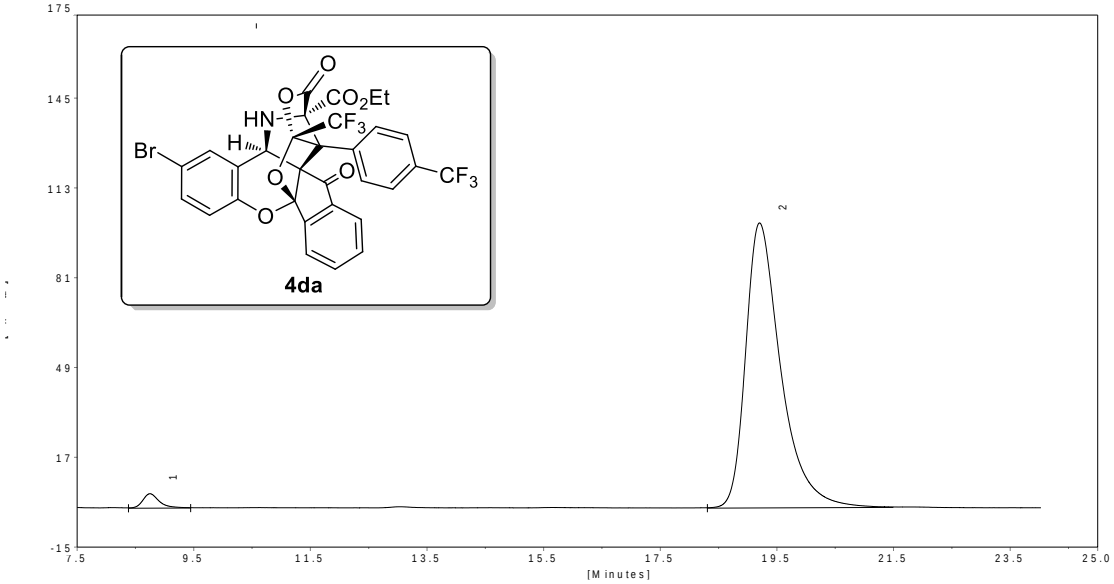
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
36.85	0.42	31.82	0.7409
49.82	39.36	4262.96	99.2591

HPLC Chromatogram for **4da**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=80:20	Detector: UV 278 nm



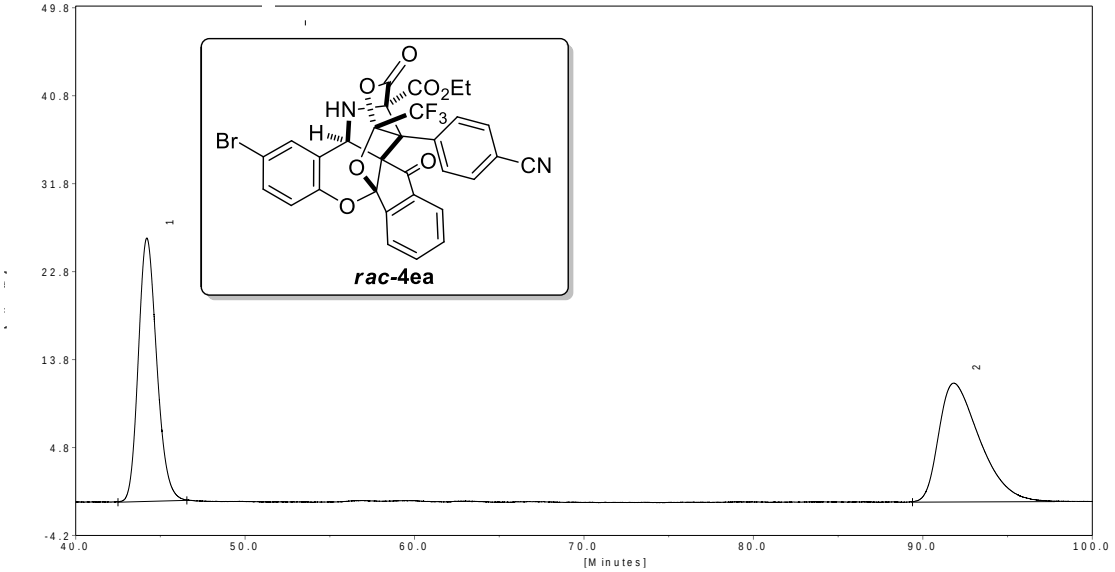
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
8.80	46.05	1268.12	49.8508
19.10	27.64	1275.71	50.1492



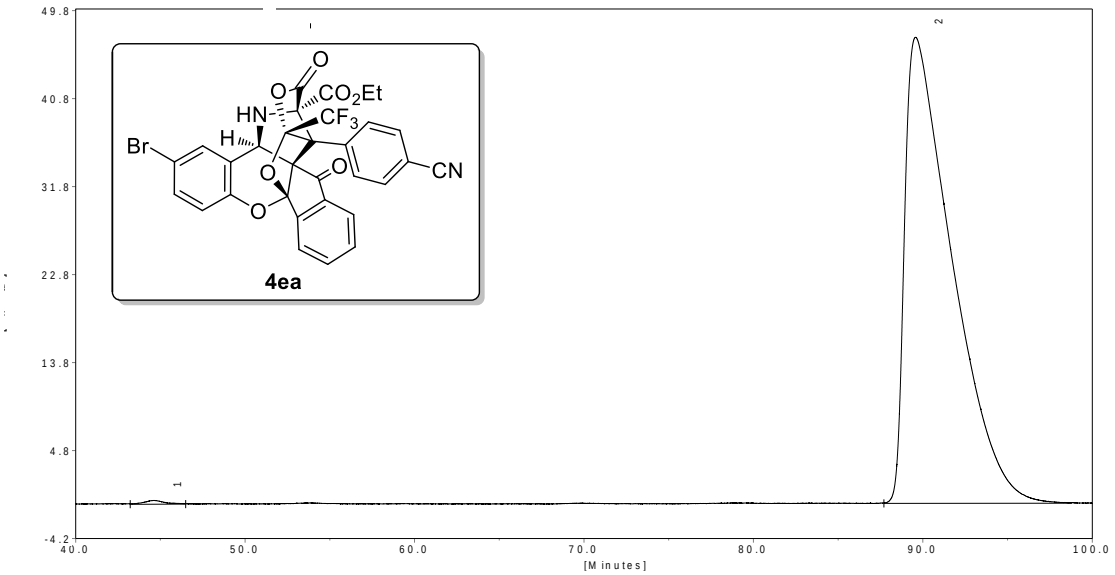
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
8.75	5.01	94.57	2.1893
19.20	101.41	4225.03	97.8107

HPLC Chromatogram for **4ea**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=90:10	Detector: UV 278 nm



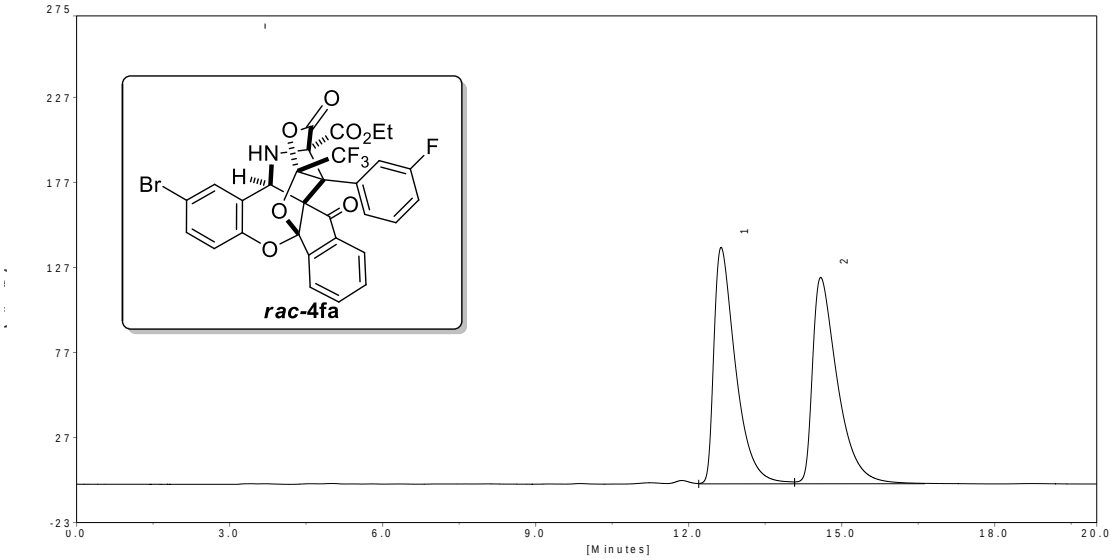
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
44.20	26.91	2022.68	49.9509
91.81	12.12	2026.65	50.0491



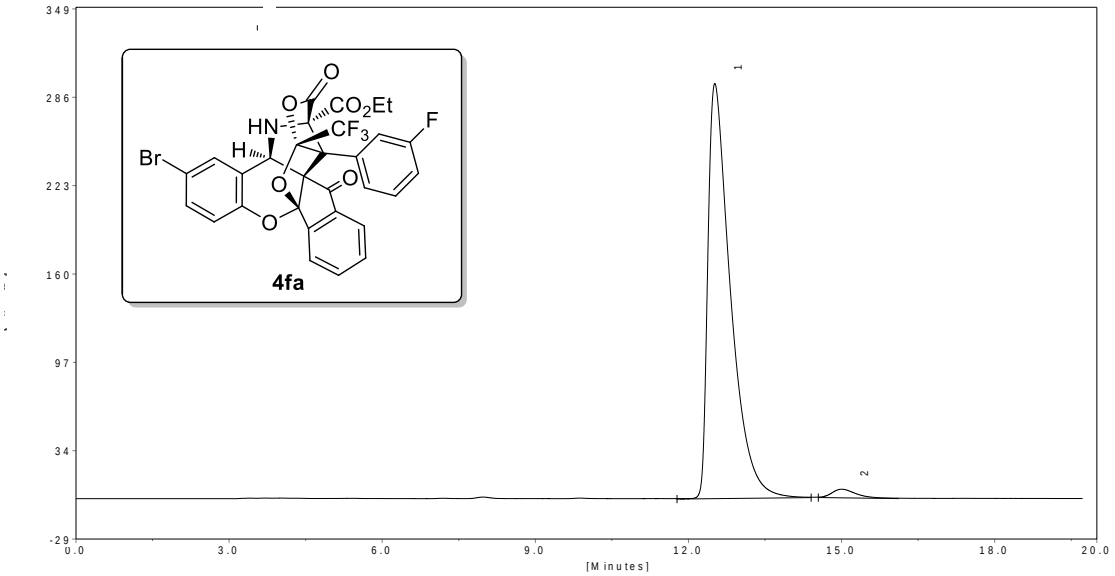
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
44.65	0.34	24.13	0.2610
89.58	47.64	9220.50	99.7390

HPLC Chromatogram for **4fa**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=90:10	Detector: UV 278 nm



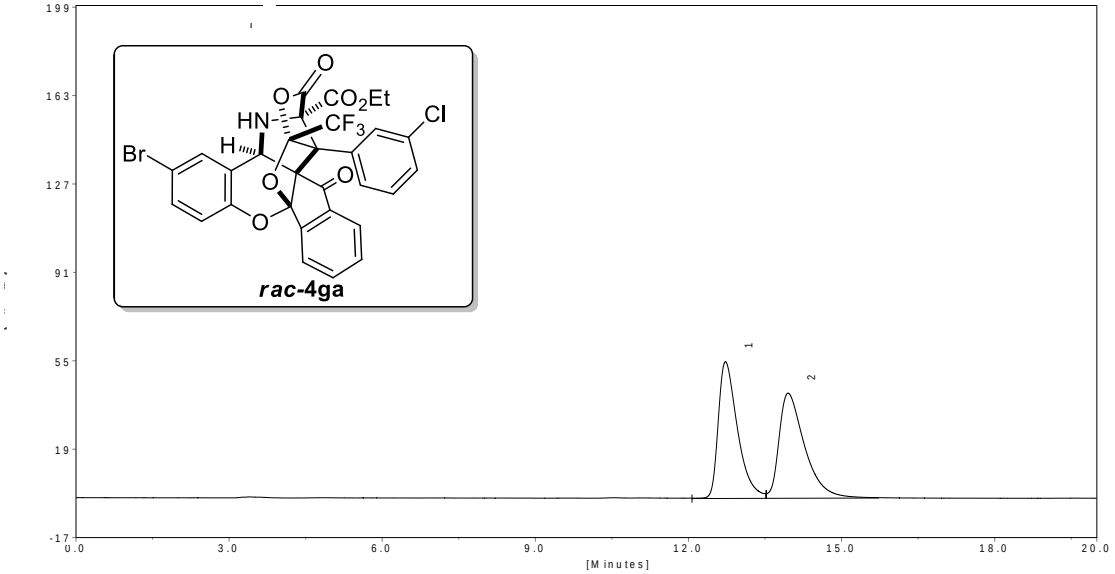
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.64	138.88	4088.13	49.9326
14.59	121.18	4099.17	50.0674



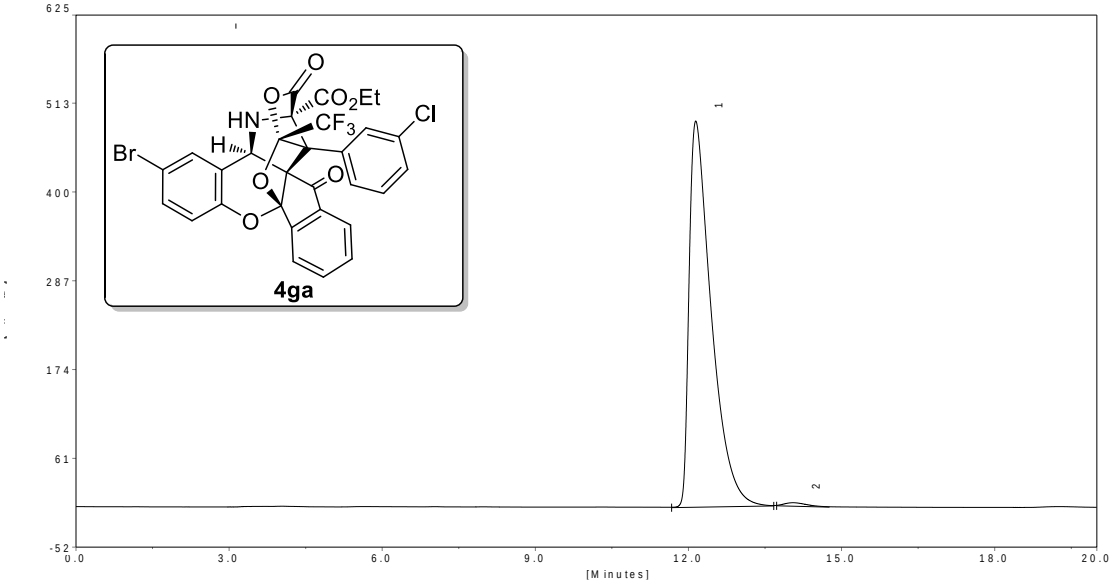
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.52	295.80	9069.80	98.0382
15.00	5.87	181.49	1.9618

HPLC Chromatogram for **4ga**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=90:10	Detector: UV 278 nm



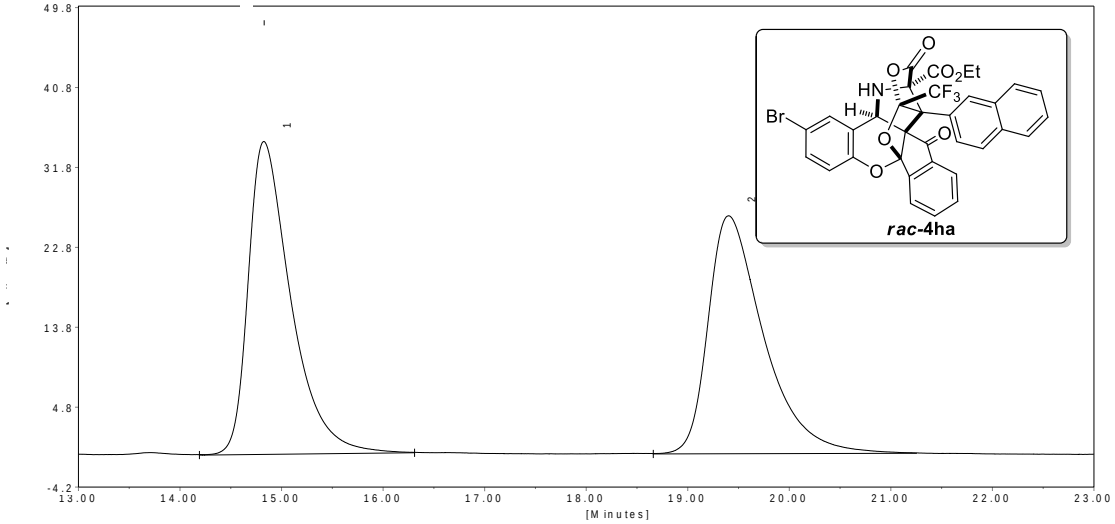
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.73	55.56	1447.84	49.5208
13.95	42.68	1475.86	50.4792



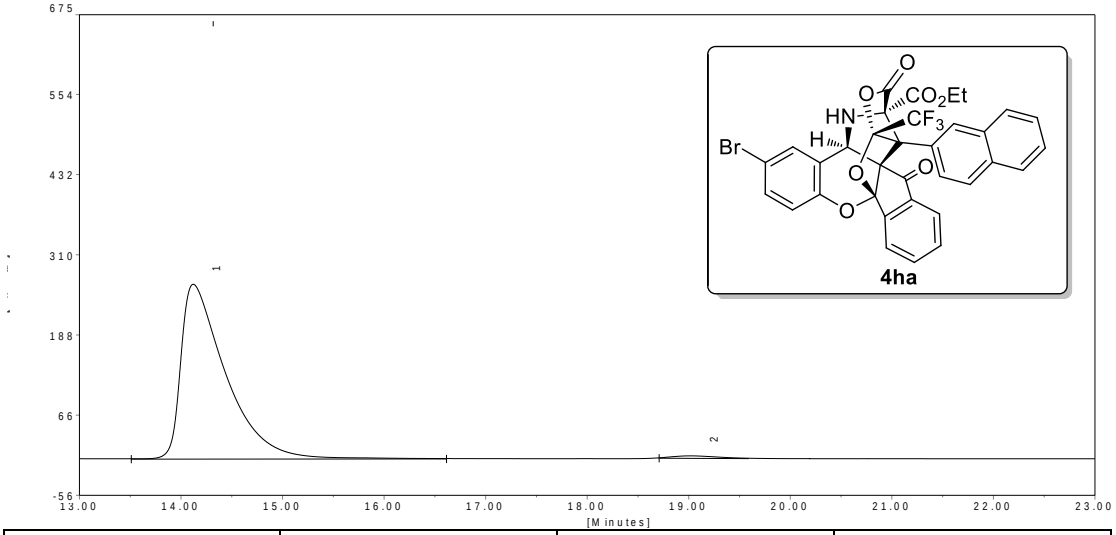
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.14	491.01	14790.53	99.2511
14.05	3.97	111.60	0.7489

HPLC Chromatogram for **4ha**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 90: 10	Detector: UV 248 nm



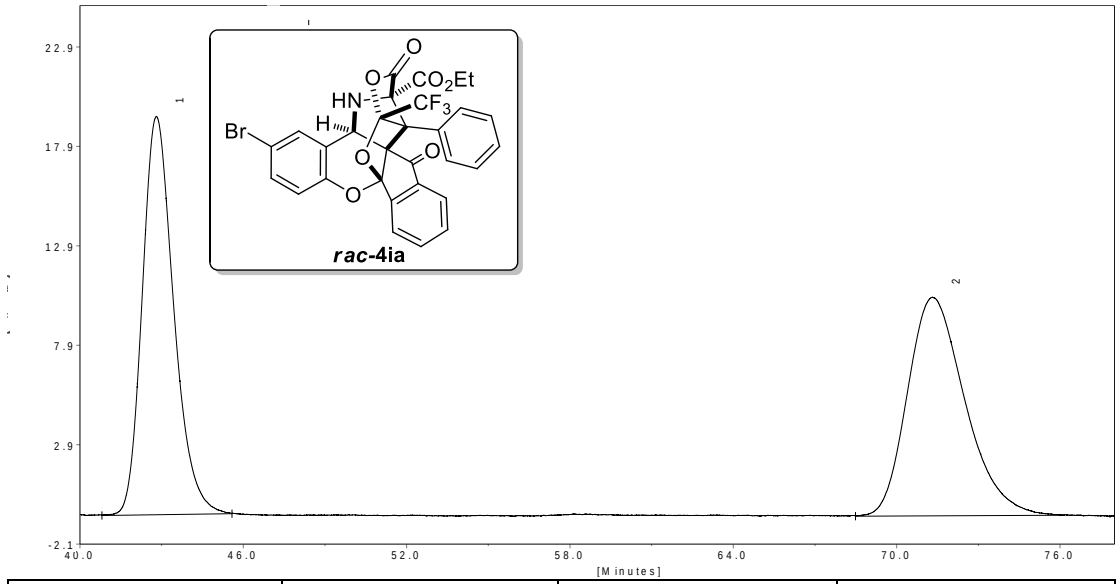
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
14.83	35.19	1024.08	50.2418
19.40	26.76	1014.23	49.7582



Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
14.12	265.46	8081.29	98.9055
19.02	3.21	89.43	1.0945

HPLC Chromatogram for **4ia**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=90:10	Detector: UV 278 nm

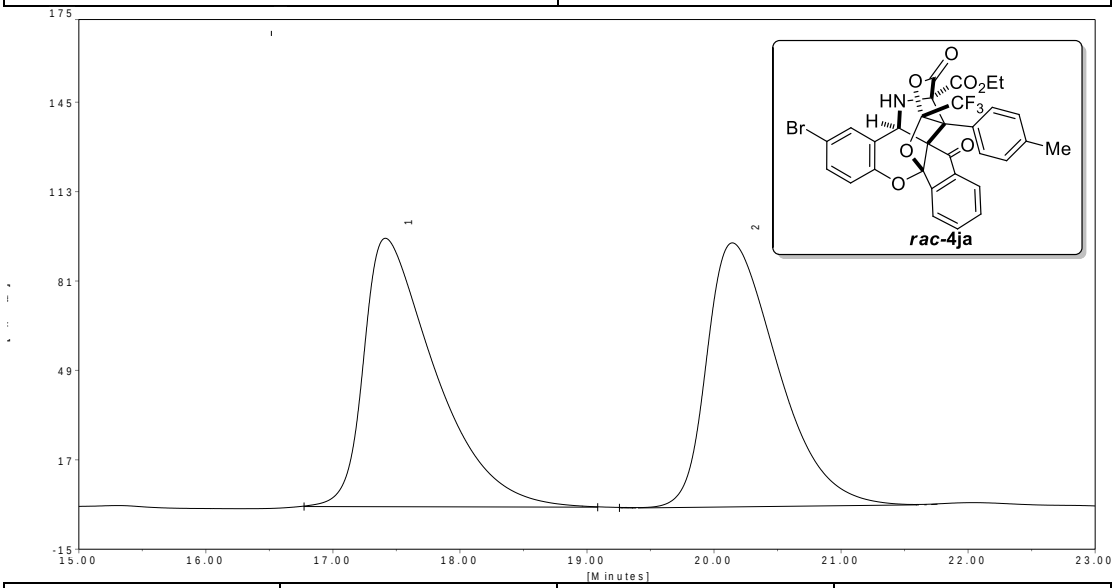


Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
42.81	20.01	1601.34	49.9976
71.31	10.97	1601.50	50.0024

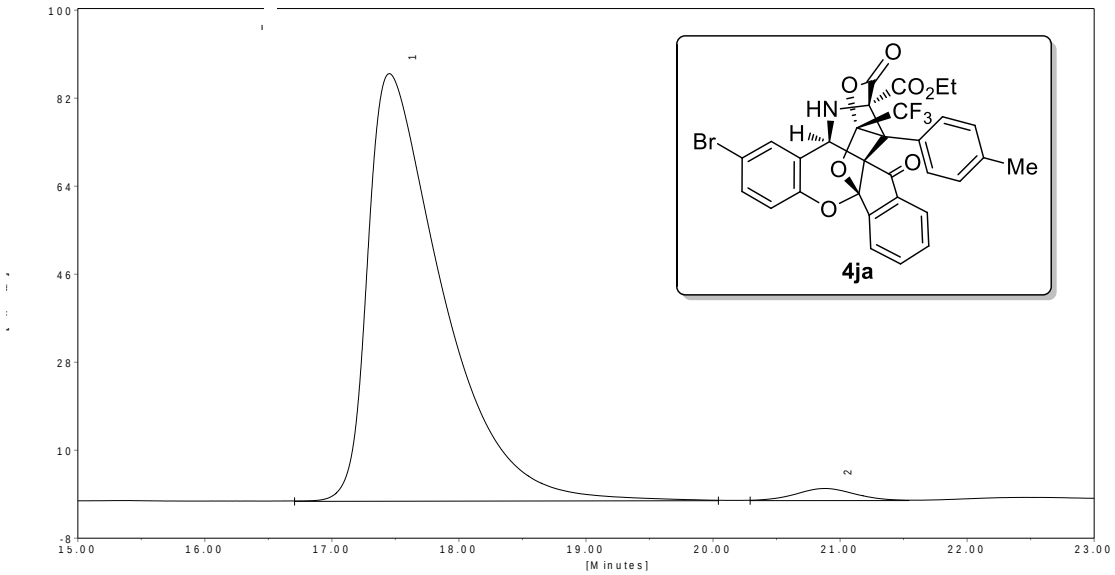
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
42.30	3.55	273.94	2.9274
72.99	56.60	9083.68	97.0726

HPLC Chromatogram for **4ja**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=90:10	Detector: UV 248 nm



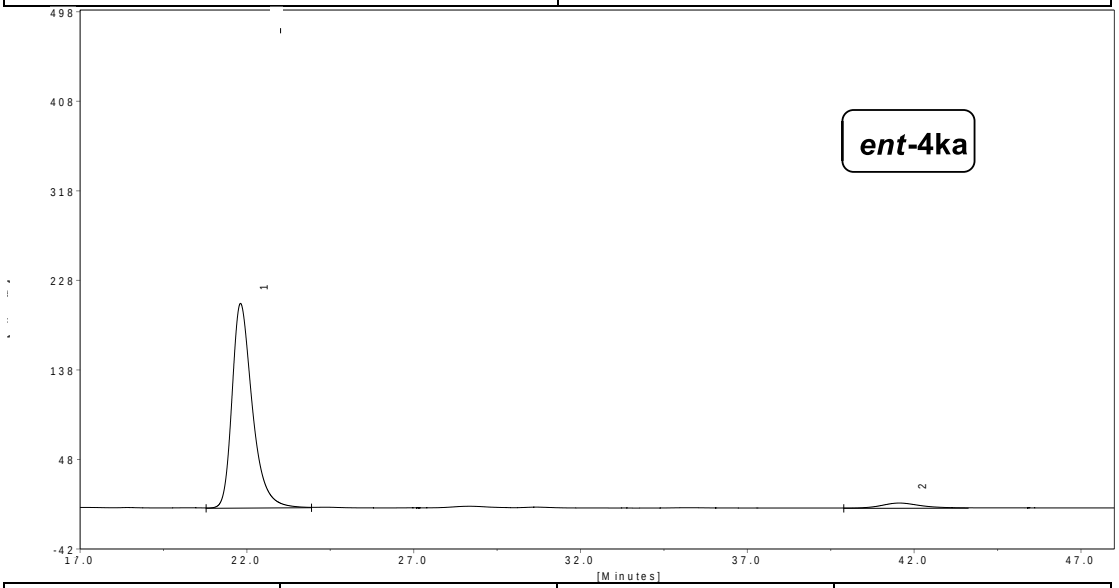
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
17.41	95.94	3750.02	50.7332
20.14	94.23	3641.63	49.2668



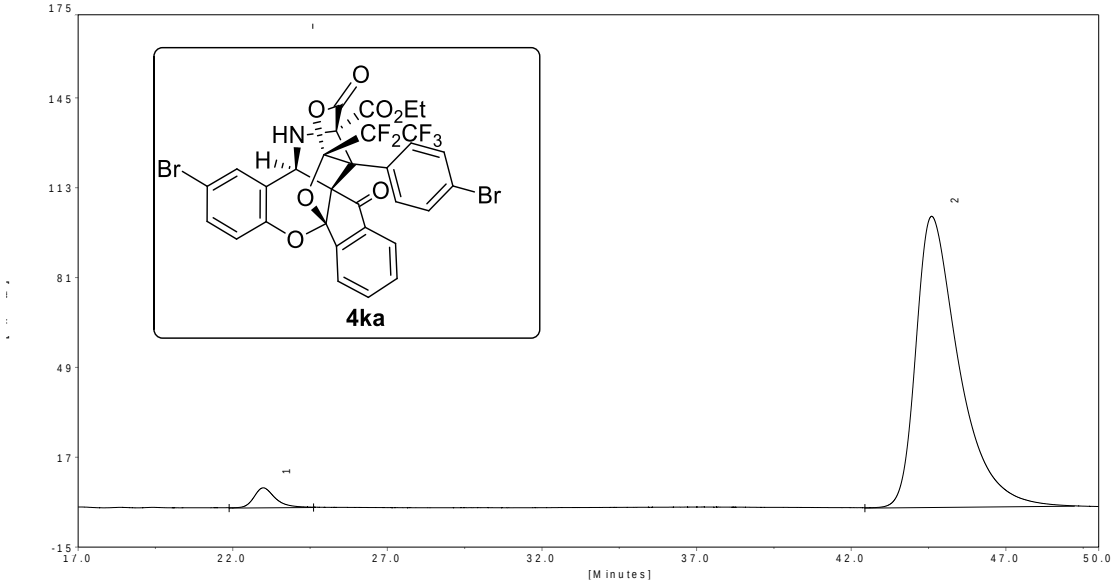
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
17.45	87.38	3570.69	97.9546
20.88	2.39	74.56	2.0454

HPLC Chromatogram for **4ka**

Column: chiralpak IA	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=90:10	Detector: UV 248 nm



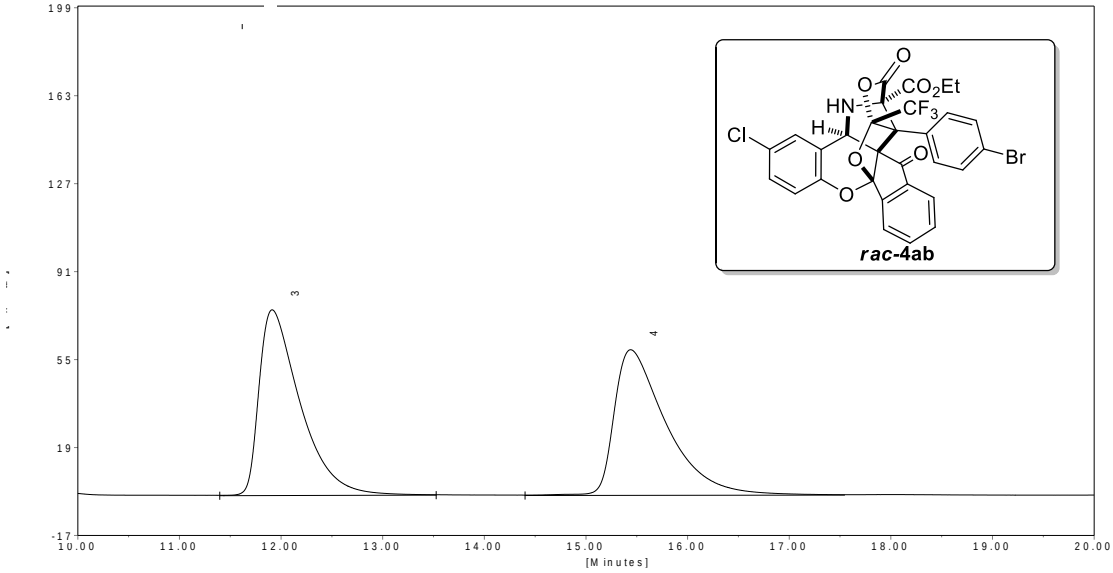
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
21.81	205.42	8618.21	95.8642
41.54	4.89	371.81	4.1358



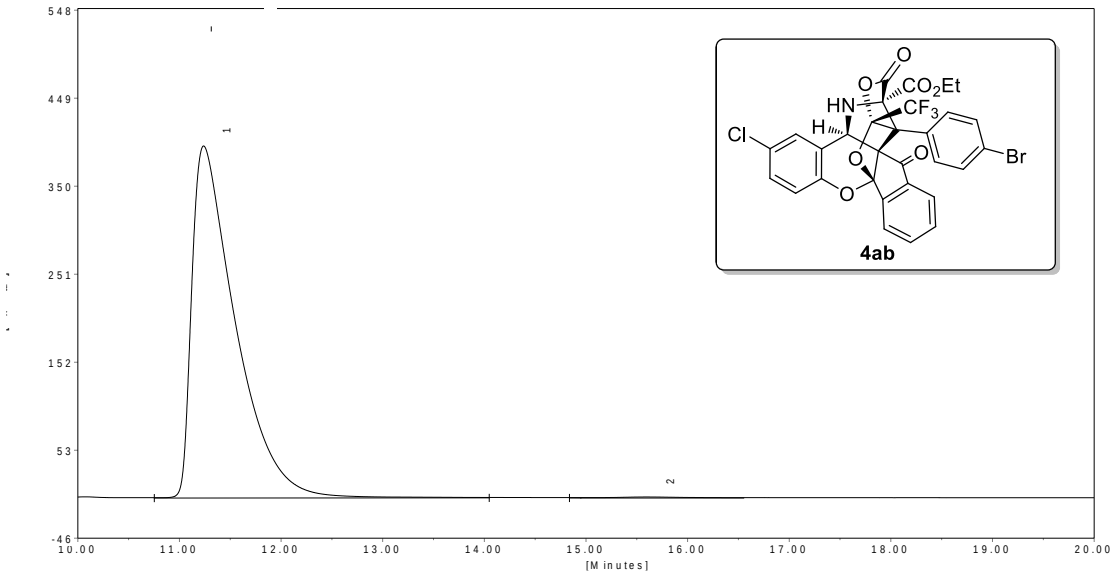
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
22.99	6.99	324.32	3.1445
44.60	103.58	9989.56	96.8555

HPLC Chromatogram for **4ab**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 90: 10	Detector: UV 278 nm



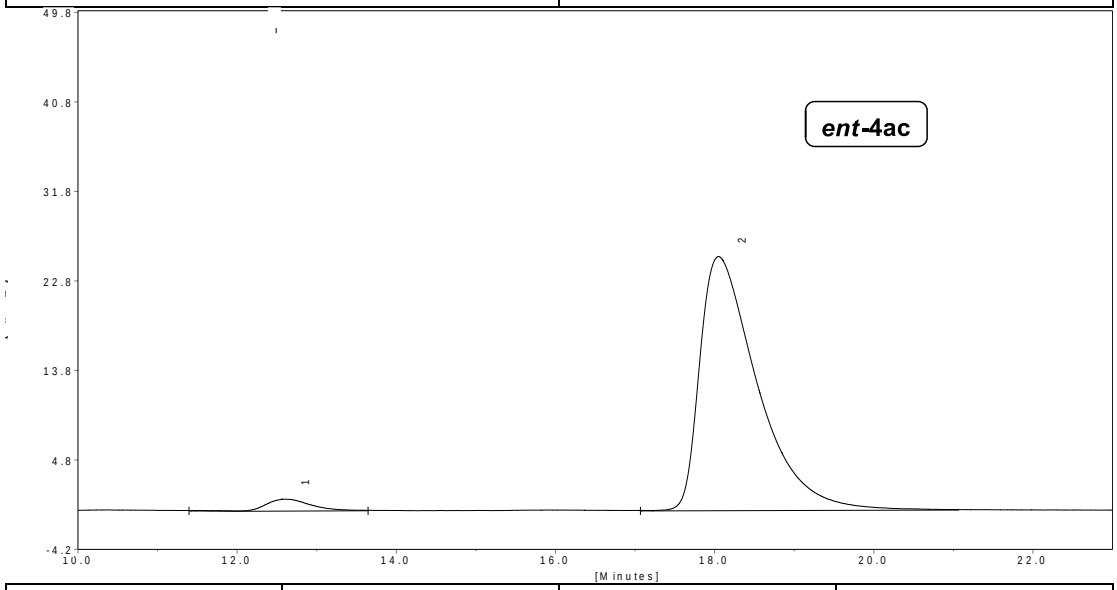
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
11.91	75.80	2108.33	50.0357
15.44	59.43	2105.32	49.9643



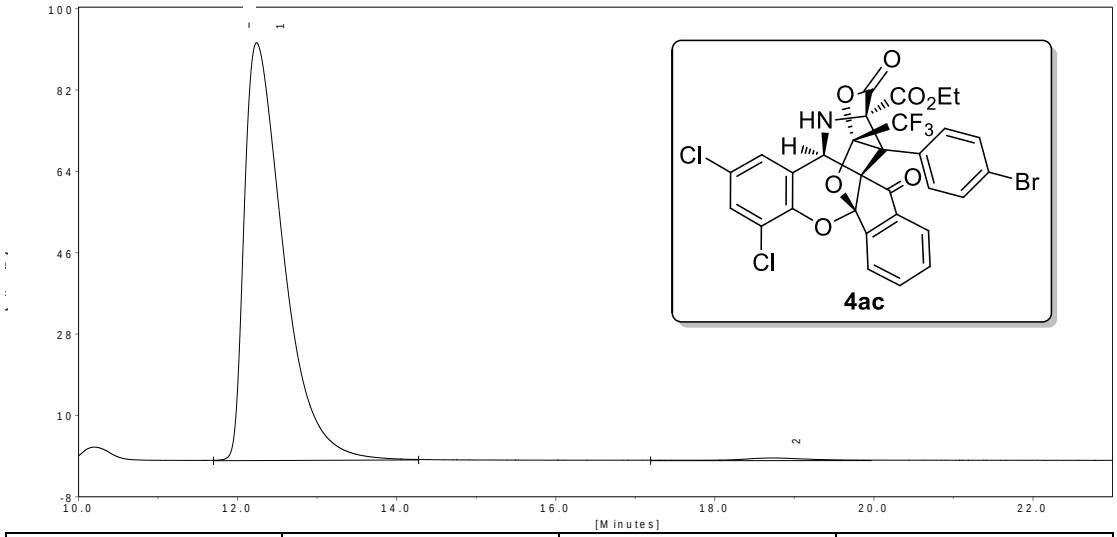
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
11.24	395.64	11755.14	99.8064
15.60	0.70	22.80	0.1936

HPLC Chromatogram for **4ac**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 90: 10	Detector: UV 278 nm



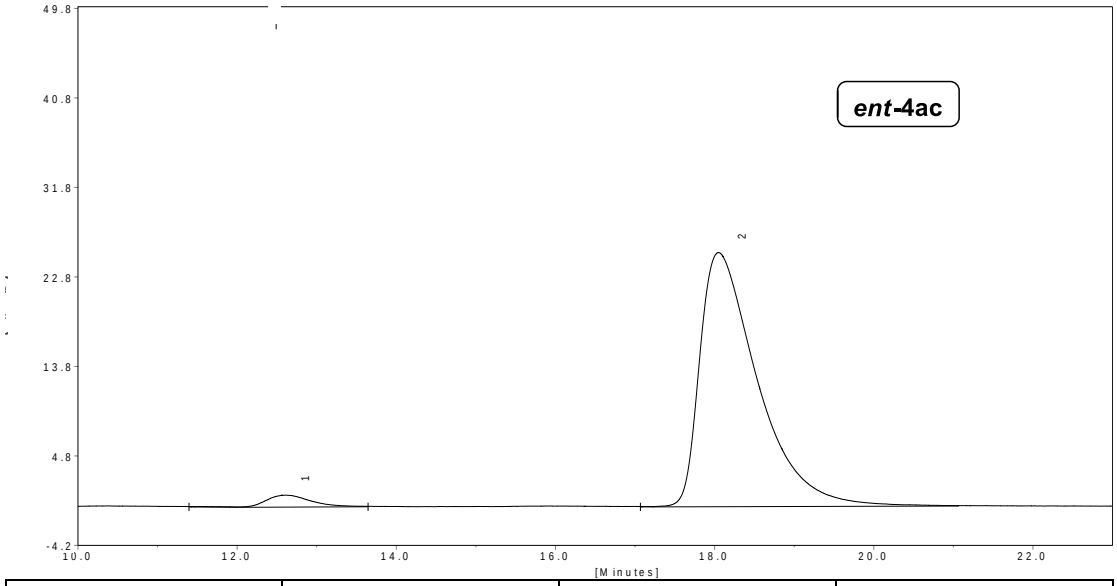
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.56	1.16	40.07	3.0371
18.05	25.51	1279.36	96.9629



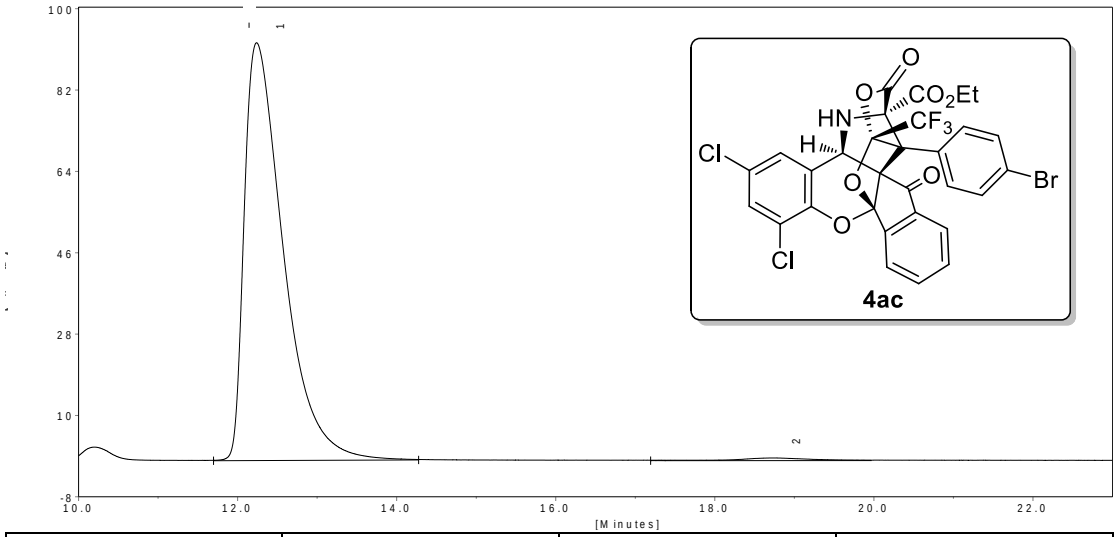
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.24	92.36	3141.17	99.2549
18.73	0.48	23.58	0.7451

HPLC Chromatogram for **4ac**†

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 90: 10	Detector: UV 278 nm



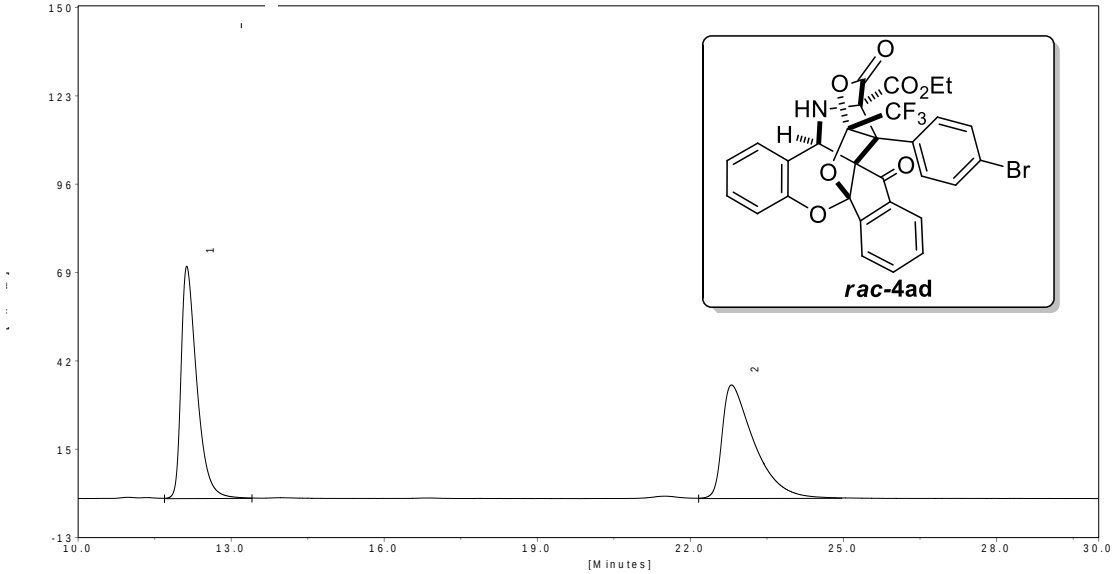
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.56	1.16	40.07	3.0371
18.05	25.51	1279.36	96.9629



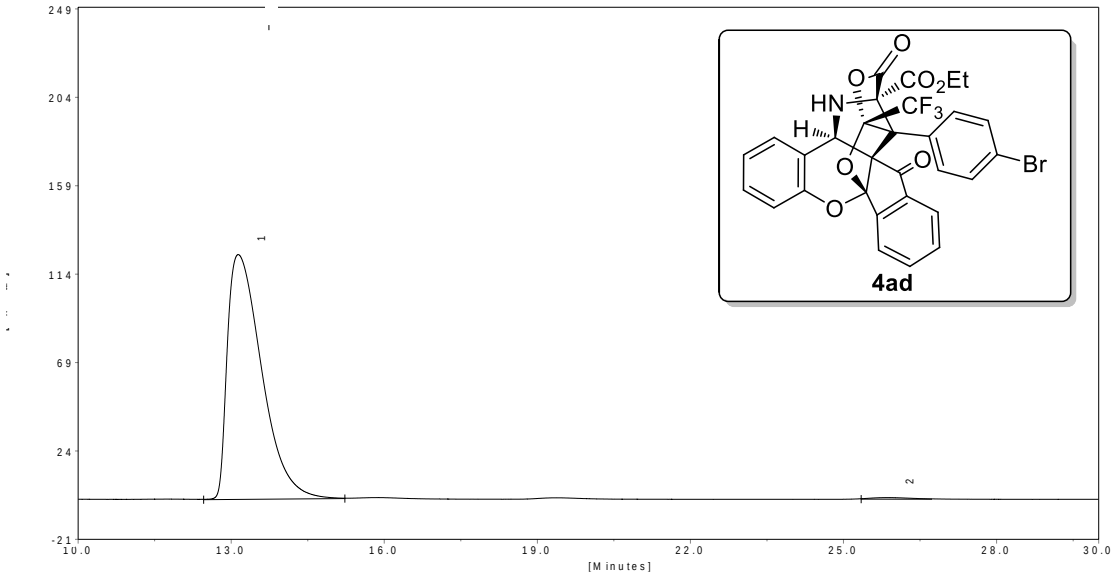
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
11.96	182.09	6522.63	95.9896
18.33	5.62	272.51	4.0104

HPLC Chromatogram for **4ad**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex:IPA=90:10	Detector: UV 278 nm



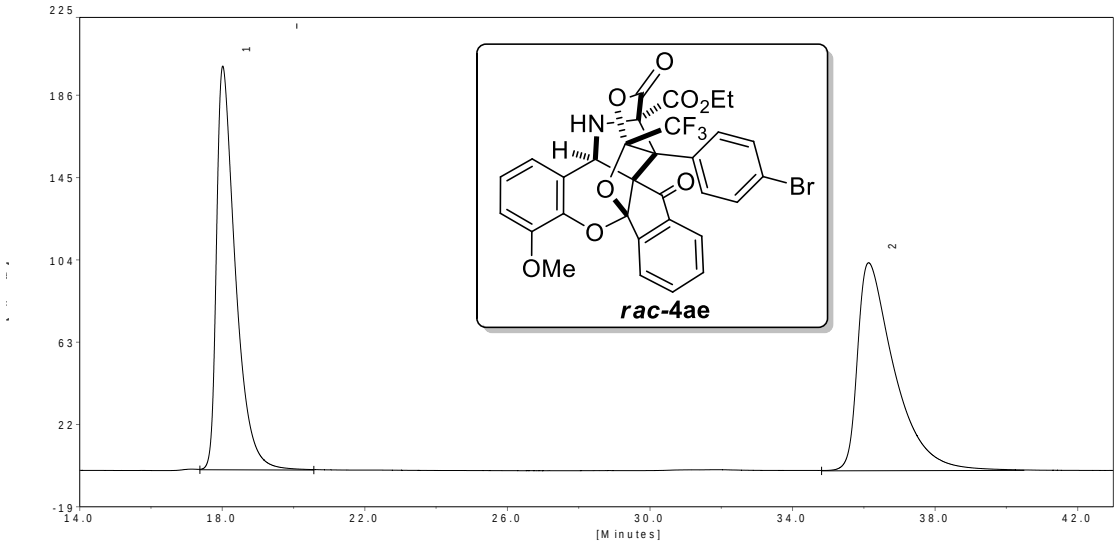
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.13	70.93	1513.07	50.2770
22.81	34.60	1496.40	49.7230



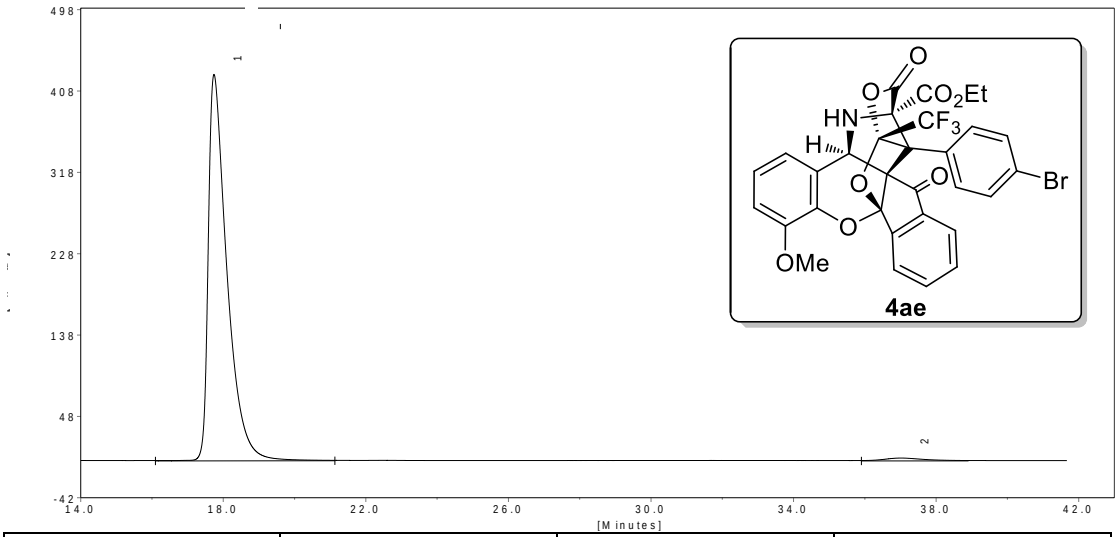
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
13.14	124.45	5791.49	99.5242
25.84	0.60	27.68	0.4758

HPLC Chromatogram for **4ae**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 90: 10	Detector: UV 248 nm



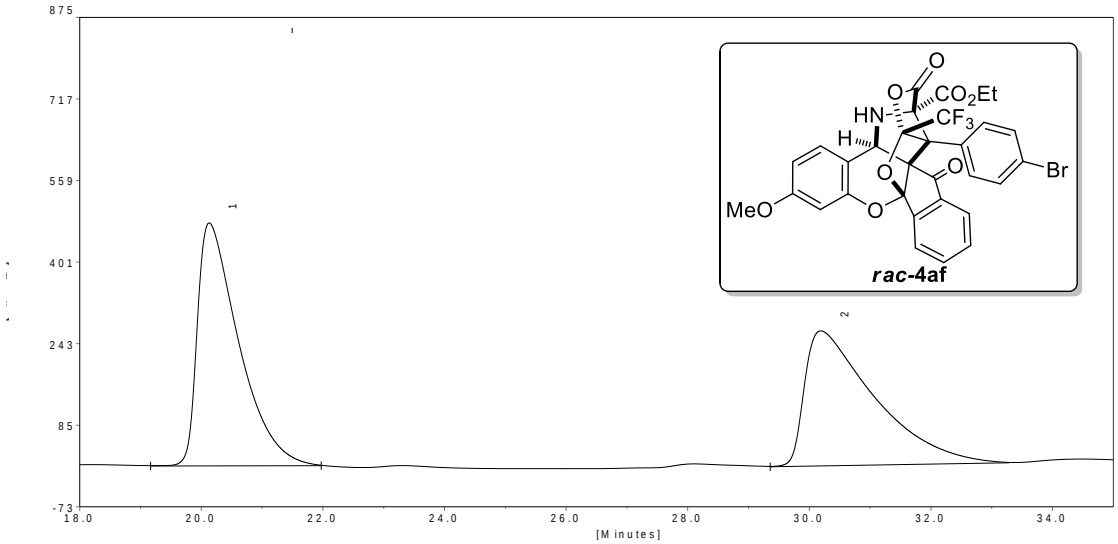
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
18.01	200.92	7365.68	49.9345
36.14	103.43	7384.99	50.0655



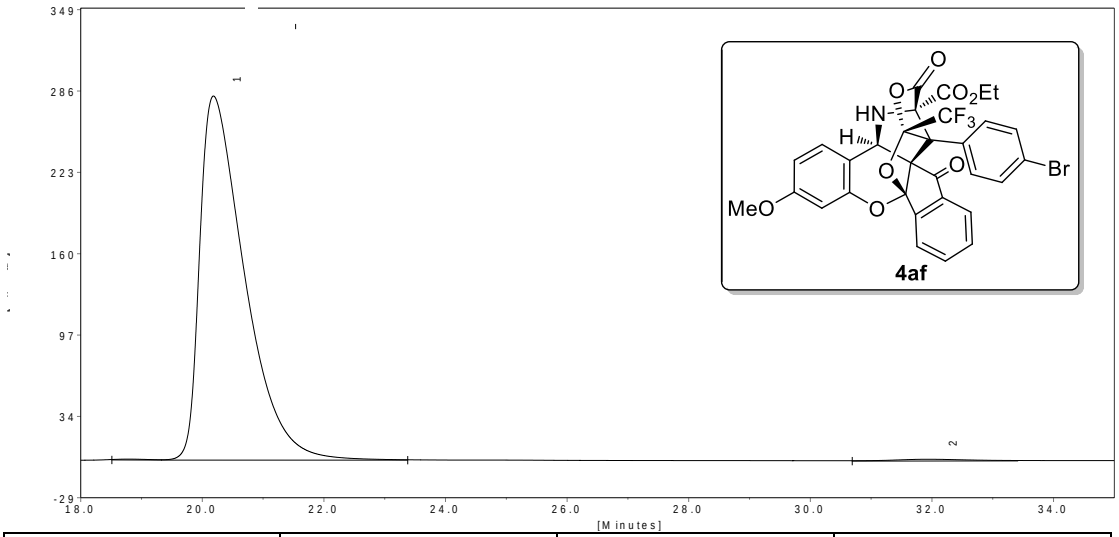
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
17.74	427.13	15463.12	98.7890
37.01	2.74	189.55	1.2110

HPLC Chromatogram for **4af**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 90: 10	Detector: UV 248 nm



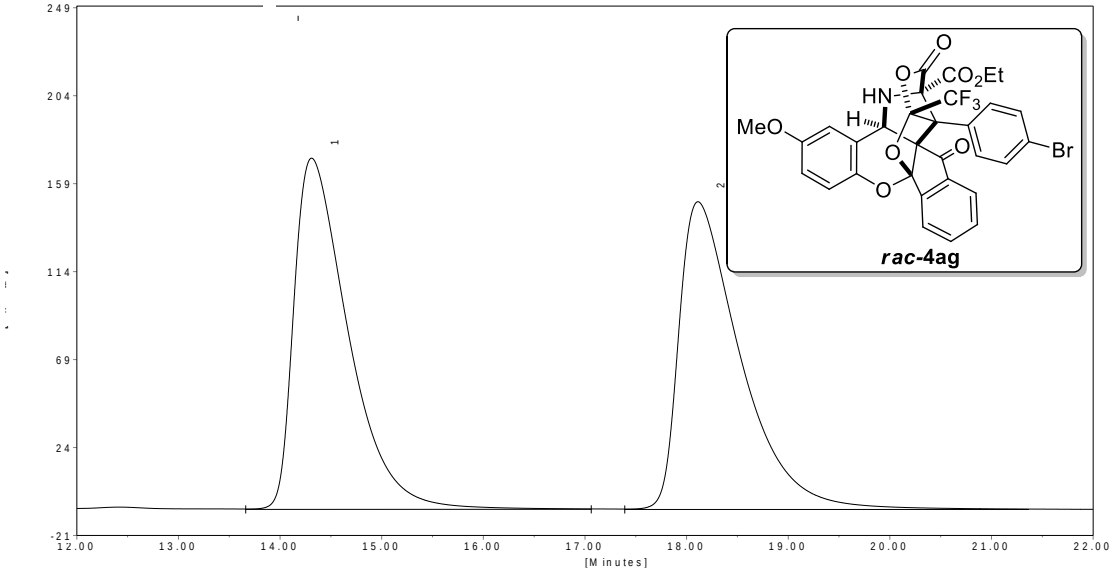
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
20.13	469.87	22075.47	51.6402
30.19	260.82	20673.12	48.3598



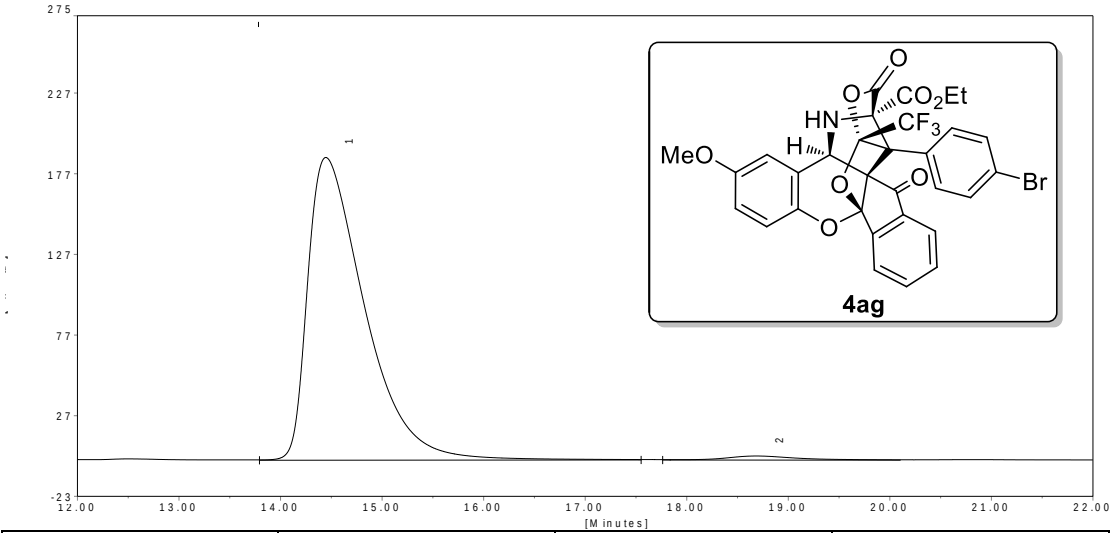
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
20.18	281.58	14352.87	99.4918
31.96	1.04	73.32	0.5082

HPLC Chromatogram for **4ag**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 90: 10	Detector: UV 248 nm



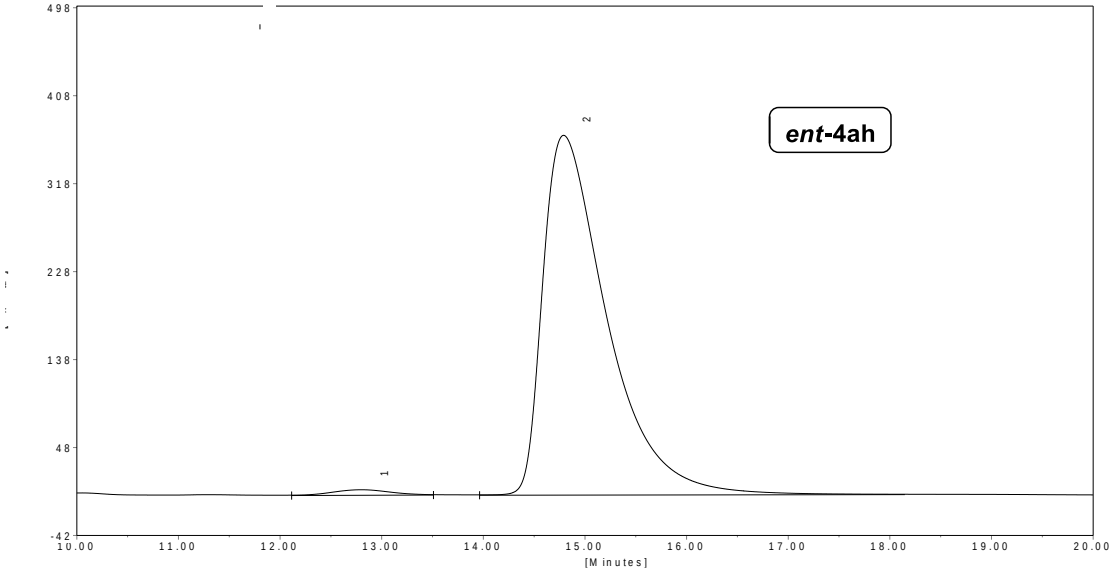
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
14.31	179.50	6628.83	50.0594
18.11	157.24	6613.10	49.9406



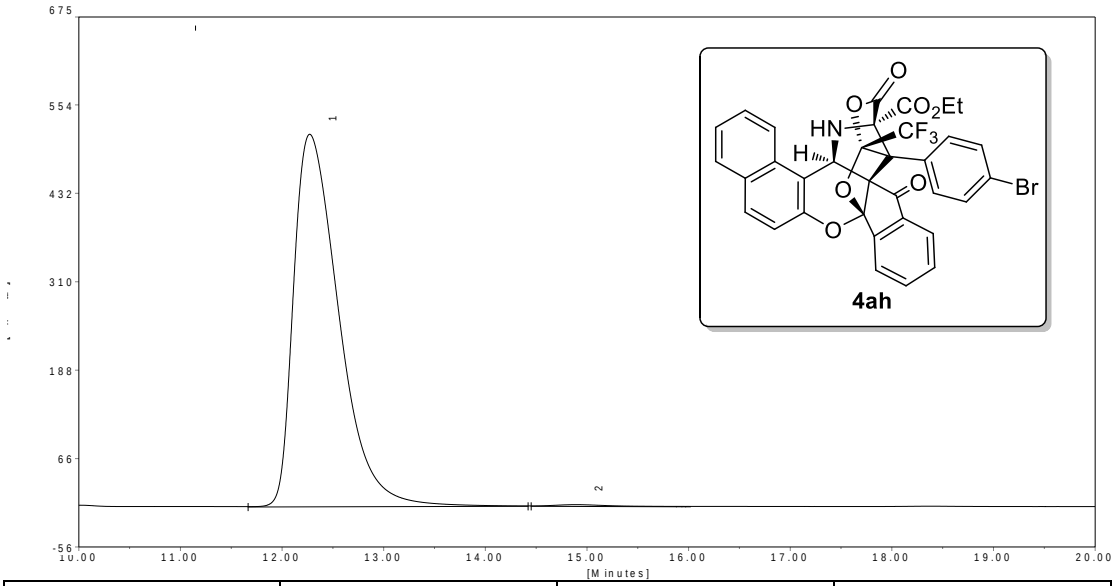
Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
14.45	187.43	7277.09	98.6869
18.68	2.28	96.83	1.3131

HPLC Chromatogram for **4ah**

Column: chiralpak IB	Flow rate: 1.0 ml/min
Solvent: Hex: IPA = 90: 10	Detector: UV 248 nm



Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.80	5.29	196.81	1.2064
14.79	367.75	16117.49	98.7936



Ret. time (min)	Height (mv)	Area (mv.sec)	Rel. area (%)
12.27	513.57	15823.31	99.6381
14.89	1.92	57.47	0.3619

References

S1. C.-J. Lee, C.-N. Sheu, C.-C. Tsai,; Z.-Z. Wu and W. Lin, *Chem. Commun*. **2014**, *50*, 5304.

S2. G.-H. Chang, C.-Y. Wang, G. M. Reddy, Y.-L. Tsai and W. Lin, *J. Org. Chem*. **2016**, *81*, 10071.

S3. L. Tian, G.-Q. Xu, Y.-H. Li, Y.-M. Liang and P.-F. Xu, *Chem. Commun*. **2014**, *50*, 2428.