Supporting Information

Catalytic enantioselective oxa-hetero-Diels-Alder reactions of enones with aryl trifluoromethyl ketones

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1. General

For thin layer chromatography (TLC), Merck silica gel 60 F254 aluminum sheets were used. Flash column chromatography was performed using Merck silica gel 60 (230-400 mesh) or Yamazen flash column (60 Å, 40 μm). ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance 400. Proton chemical shifts are reported in ppm downfield from tetramethylsilane or from the residual solvent as internal standard in $CDCl_3$ (δ 7.26 ppm) and in CD_3OD (δ 3.31 ppm). Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.0 ppm) and in CD_3OD (δ 49.0 ppm). High-resolution mass spectra were recorded on a Thermo Scientific LTQ Orbitrap ESI ion trap mass spectrometer. Enantiomeric excesses were determined by chiral-phase HPLC using a Hitachi instrument. Optical rotations were measured on a Jasco P2200 polarimeter.

2. Synthesis of catalysts and enones

Amine catalysts **A**[1,2] and **E**[3] were synthesized by reported procedures.[1-3] Enones were purchased or synthesized by reported procedures[1] or by modified methods of the reported procedures.[4]

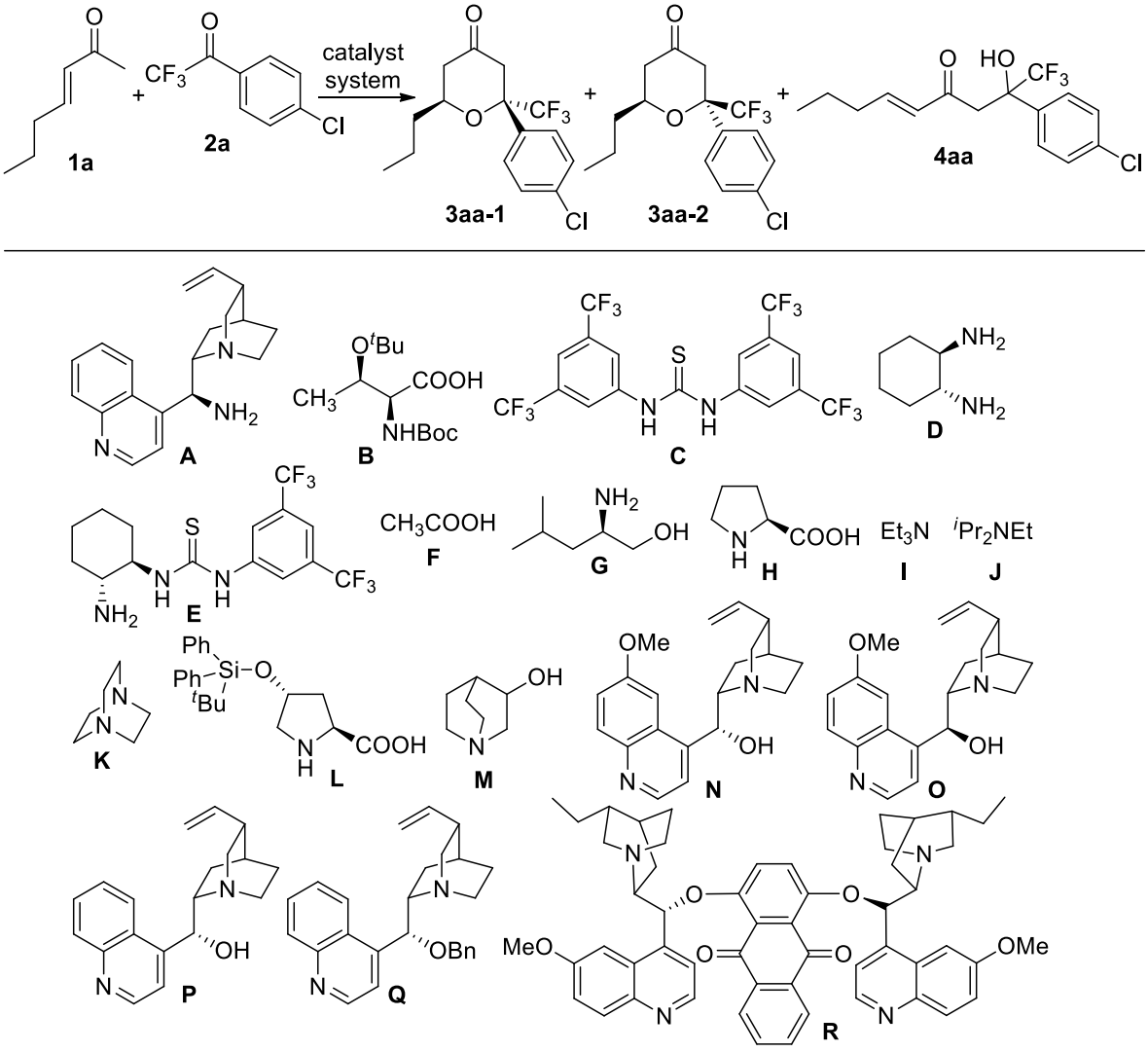
4-(4-Bromophenyl)but-3-en-2-one

To a mixture of water (10.0 mL), acetone (8.0 mL), and 4-bromobenzaldehyde (3.7 g, 20 mmol), NaOH solution (10% in water, 5 mL) was added at room temperature (25 ^{o}C), and the mixture was stirred at the same temperature for 1 h.[4] Generated precipitate was collected by filtration, washed with hexane, dried under vacuum to give 4-(4-bromophenyl)but-3-en-2-one (4.3g, 95%). The ^{1}H and ^{13}C NMR of this product matched to the reported data.[5]

3. Screening of catalyst systems

Additional screening results to Table 1 of the main text are shown in Table S1 (entries 13-19).

Table S1. Screening of catalyst systems for the hetero-Dield-Alder reaction of **1a** and **2a**.[a]

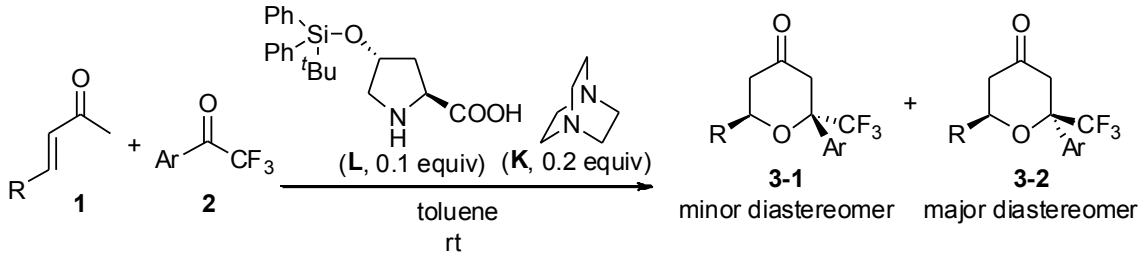


entry	catalyst system	time (h)	**3aa**:**4aa**	dr **3aa-1**:**3aa-2**	er **3aa-1**/**3aa-2**
13	**A** (0.2 equiv)-**F** (0.4 equiv)	24	70:30	8:1	ND/ND
14	**H** (0.2 equiv)-**M** (0.2 equiv)	24	>95:5	1:1	ND/94:6
15	**H** (0.2 equiv)-**N** (0.2 equiv)	24	>95:5	1:1.3	82:18/88:12
16	**H** (0.2 equiv)-**O** (0.2 equiv)	27	95:5	1:2.2	81:19/90:10
17	**H** (0.2 equiv)-**P** (0.2 equiv)	36	95:5	1:1.5	85:15/91:9
18	**H** (0.2 equiv)-**Q** (0.2 equiv)	48	>95:5	1:1.3	ND/94:6
19	**H** (0.2 equiv)-**R** (0.2 equiv)	36	>95:5	1.3:1	ND/80:20

[a] To a solution of enone **1a** (0.5 mmol) and 4-chlorophenyl trifluoromethyl ketone (**2a**) (0.1 mmol) in toluene (super dehydrated, 0.2 mL), catalyst system components were added at room temperature (25 ^{o}C), and the reaction mixture was stirred at the same temperature until **2a** was consumed (monitored by TLC and crude ^{1}H NMR). The ratio of **3aa**/**4aa** and the dr of **3aa** were determined by ^{1}H NMR analysis before purification. The ee was determined by chiral-phase HPLC analysis after purification.

4. Oxa-hetero-Diels-Alder reactions

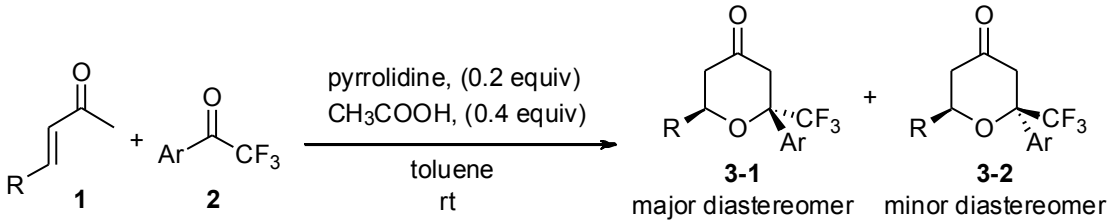
General procedure for the catalytic enantioselective oxa-hetero-Diels-Alder reactions (Table 2)



To a solution of enone **1** (1.0 mmol) and aryl trifluomethyl ketone **2** (0.2 mmol) in toluene (super dehydrated, 0.4 mL), (2*S*,4*R*)-4-(*tert*-butyldiphenylsilyloxy)pyrrolidine-2-carboxylic acid (**L**) (7.4 mg, 0.02 mmol) and DABCO (**K**) (4.49 mg, 0.04 mmol) were added at room temperature (25 ^{o}C), and the mixture was stirred at the same temperature until **2** was consumed (monitored by TLC and crude ^{1}H NMR). The mixture was purified by flash column chromatography (hexane/CH_2Cl_2 = 3:1 to 2:1) to give product **3** (**3-1** and **3-2**). For all the cases using catalyst system **L**-**K**, isomer **3-2** was the major diastereomer and **3-1** was the minor diastereomer. R_f values of **3-1** and **3-2** were the same or similar. The dr was determined by ^{1}H NMR analysis before purification, and the value was retained after purification except a large-scale reaction (i.e., a 1.0 mmol-scale reaction to afford **3bb-2**). The ee was determined by chiral-phase HPLC analysis after purification. The ratio of **3**/**4** (**3** = **3-1** and **3-2**, **4** = aldol product) was determined by ^{1}H NMR analysis before purification.

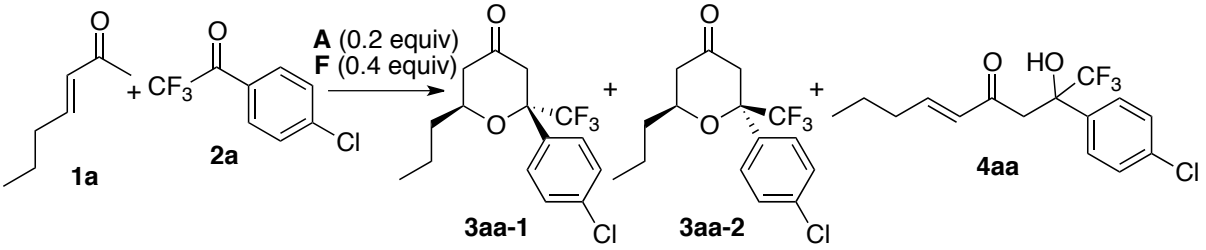
Relative stereochemistries of **3aa** (**3aa-1** and **3aa-2**) were deduced from the relative stereochemistries of **6-1** and **6-2**, which were determined by ^{1}H NMR *J* values and NOESY experiments (see pp S13-S15 for compounds **6-1** and **6-2**). Relative stereochemistries of **3ag** (**3ag-1** and **3ag-2**) were determined by ^{1}H NMR *J* values and NOESY experiments (see pp S8-S9 for compound **3ag**). Relative stereochemistries of compound **3** other than **3aa** and **3ag** were determined by analogy. The absolute stereochemistry of **3** was tentatively assigned by the deduction from the previously suggested transition states[6] and the product[1] of the [4+2] cycloaddition of the in situ-formed enamine of **1a** with isatin under catalyst system **A**-**B**.

General procedure for the syntheisis of racemic standards of 3



To a solution of enone **1** (1.0 mmol) and aryl trifluomethyl ketone **2** (0.2 mmol) in toluene (super dehydrated, 0.4 mL), pyrrolidine (3.2 μL, 0. 04 mmol) and acetic acid (**F**) (4.6 μL, 0.08 mmol) were added at room temperature (25 ^{o}C), and the reaction mixture was stirred at the same temperature until **2** was consumed (monitored by TLC and crude ^{1}H NMR). The mixture was purified by flash column chromatography (hexane/CH_2Cl_2 = 3:1 to 2:1) to give racemic product **3-1** and **3-2** as a diastereomer mixture. Among all the products except **3ba** and **3bb**, isomer **3-1** was the major diastereomer and **3-2** was the minor diastereomer. **3**:**4** > 95:5.

Synthesis of compound 4aa with 3aa

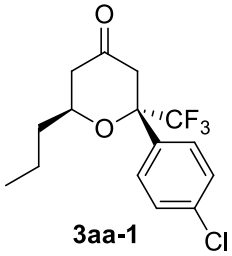


To a solution of enone **1a** (56.0 μL, 0.5 mmol) and 4-chlorophenyl trifluoromethyl ketone (**2a**) (15.0 μL, 0.1 mmol) in toluene (super dehydrated, 0.2 mL), amine catalyst **A** (5.87 mg, 0.02 mmol) and acetic acid (**F**) (2.3 μL, 0.04 mmol) were added at room temperature (25 ^{o}C), and the mixture was stirred at the same temperature until **2a** was consumed (monitored by TLC and crude ^{1}H NMR). The mixture was purified by flash column chromatography (hexane/CH_2Cl_2 = 3:1 to 2:1) to give **3aa** and **4aa** (21.0 mg, **3aa-1**:**3aa-2**:**4aa** = 62:8:30). Compound **4aa** was eluted with **3aa** in usual silica gel flash column chromatography. The ratio of **3aa**/**4aa** and the dr of **3aa** were determined by ^{1}H NMR analysis.

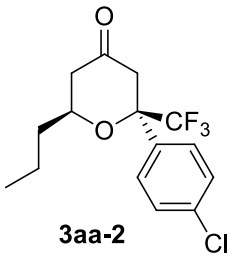
A 2 mmol-scale reaction to afford 3aa

To a solution of **1a** (1.3 mL, 10.0 mmol) and **2a** (417.0 mg, 2.0 mmol) in toluene (super dehydrated, 2.0 mL), (2*S*,4*R*)-4-(*tert*-butyldiphenylsilyloxy)pyrrolidine-2-carboxylic acid (**L**) (74.0 mg, 0.2 mmol,) and DABCO (**K**) (44.8 mg, 0.4 mmol) were added at room temperature (25 ^{o}C) and the reaction mixture was stirred at the same temperature for 24 h. The reaction mixture was purified by flash column chromatography (hexane/CH_2Cl_2 = 3:1 to 2:1) to give product **3aa-1** and **3aa-2** as a diastereomer mixture (320.0 mg, 50%, **3aa-1**:**3aa-2** =1:1.9, **3aa-2** er 96:4).

2-(4-Chlorophenyl)-6-propyl-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one (3aa)



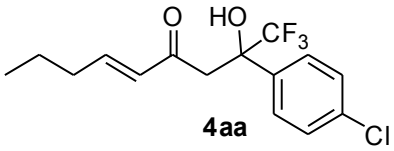
3aa-1



3aa-2

Synthesized by the general procedure; 24 h, 37.6 mg (59%), dr **3aa-1**:**3aa-2** = 1:1.9, **3aa-2** er 97:3. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, J = 7.2 Hz, 3H × 1.9/2.9, C$\underline{H}_3$), 1.01 (t, J = 7.2 Hz, 3H × 1/2.9, C$\underline{H}_3$), 1.35-1.81 (m, 4H, C$\underline{H}_2$C$\underline{H}_2$CH$_3$), 2.21 (dd, J = 11.6 Hz, 16.0 Hz, 1H × 1/2.9, CHC$\underline{H}$HC=O), 2.26 (ddd, J = 1.6 Hz, 2.4 Hz, 14.7 Hz, 1H × 1.9/2.9, CHC$\underline{H}$HC=O), 2.39 (dd, J = 11.6 Hz, 14.7 Hz, 1H × 1.9/2.9, CHC$\underline{H}$HC=O), 2.49 (dd, J = 2.4 Hz, 16.0 Hz, 1H × 1/2.9, CHC$\underline{H}$HC=O), 2.85 (d, J = 15.6 Hz, 1H × 1/2.9, CF$_3$CC$\underline{H}$HC=O), 3.01 (d, J = 14.3 Hz, 1H × 1.9/2.9, CF$_3$CC$\underline{H}$HC=O), 3.19 (d, J = 14.3 Hz, 1H × 1.9/2.9, CF$_3$CC$\underline{H}$HC=O), 3.29 (d, J = 15.6 Hz, 1H × 1/2.9, CF$_3$CC$\underline{H}$HC=O), 3.65-3.71 (m, 1H × 1.9/2.9, OC$\underline{H}$), 4.39-4.44 (m, 1H × 1/2.9, OC$\underline{H}$), 7.35-7.49 (m, 4H, Ar$\underline{H}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 13.9, 18.4, 38.1, 38.4, 42.7, 43.8, 45.7, 46.8, 72.1, 73.2, 78.5 (q, $J_{C,F}$ = 28 Hz), 80.5 (q, $J_{C,F}$ = 30 Hz), 123.6 (q, $J_{C,F}$ = 282 Hz), 124.9 (q, $J_{C,F}$ = 287 Hz), 127.8, 128.6, 129.1, 129.8, 132.0, 135.3, 135.9, 136.2, 202.9, 203.1. HRMS (ESI): calcd for $C_{15}H_{15}O_2ClF_3$ ([M - H]$^-$) 319.0707, found 319.0713. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, major enantiomer) = 11.6 min, t_R (major diastereomer, minor enantiomer) = 13.5 min. t_R (minor diastereomer) = 19.4 min and 20.3 min.

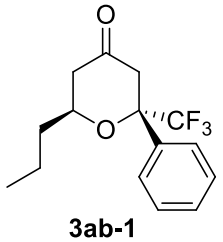
Compound 4aa



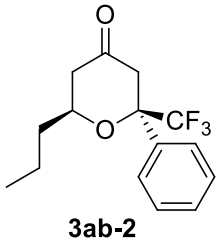
4aa

Data of **4aa** extracted from the data of a mixture of **4aa** with **3aa** (**3aa-1**:**3aa-2**:**4aa** = 62:8:30 and 64:18:18): ^{1}H NMR (400 MHz, $CDCl_3$): peaks separated from **3aa**: δ 3.23 (d, J = 16.8 Hz, 1H, CF$_3$CC$\underline{H}$HC=O), 3.46 (d, J = 16.8 Hz, 1H, CF$_3$CC$\underline{H}$HC=O), 6.08 (dd, J = 4.0 Hz, 16.0 Hz, 1H, C$\underline{H}$=CHCH$_2$), 6.95 (dt, J = 6.8 Hz, 16.0 Hz, 1H, CH=C$\underline{H}$CH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 21.1, 34.6, 41.3, 76.1 (q, $J_{C,F}$ = 29 Hz), 124.4 (q, $J_{C,F}$ = 283 Hz), 127.9, 128.7, 130.4, 134.9, 136.3, 151.4, 199.3.

2-Phenyl-6-propyl-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one (3ab)



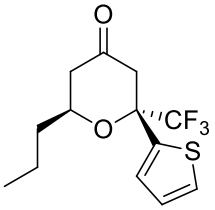
3ab-1



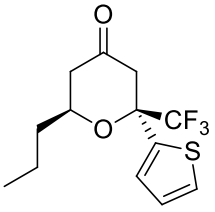
3ab-2

Synthesized by the general procedure; 48 h, 31.4 mg (55%), dr **3ab-1**:**3ab-2** = 1:1.3, **3ab-2** er 96:4. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, J = 7.2 Hz, 3H × 1.3/2.3, C$\underline{H}_3$), 1.02 (t, J = 7.2 Hz, 3H × 1/2.3, C$\underline{H}_3$), 1.34-1.82 (m, 4H, C$\underline{H}_2$C$\underline{H}_2$CH$_3$), 2.22 (dd, J = 12.0 Hz, 16.4 Hz, 1H × 1/2.3, CHC$\underline{H}$HC=O), 2.25 (ddd, J = 1.6 Hz, 2.8 Hz, 14.9 Hz, 1H × 1.3/2.3, CHC$\underline{H}$HC=O), 2.38 (ddd, J = 0.8 Hz, 11.5 Hz, 14.9 Hz, 1H × 1.3/2.3, CHC$\underline{H}$HC=O), 2.48 (ddd, J = 0.8 Hz, 2.8 Hz, 16.4 Hz, 1H × 1/2.3, CHC$\underline{H}$HC=O), 2.90 (d, J = 15.6 Hz, 1H × 1/2.3, CF$_3$CC$\underline{H}$HC=O), 3.01 (dd, J = 0.8 Hz, 14.8 Hz, 1H × 1.3/2.3, CF$_3$CC$\underline{H}$HC=O), 3.26 (dd, J = 0.8 Hz, 14.8 Hz, 1H × 1.3/2.3, CF$_3$CC$\underline{H}$HC=O), 3.31 (dd, J = 0.8 Hz, 15.6 Hz, 1H × 1/2.3, CF$_3$CC$\underline{H}$HC=O), 3.68-3.75 (m, 1H × 1.3/2.3, OC$\underline{H}$), 4.39-4.44 (m, 1H × 1/2.3, OC$\underline{H}$), 7.36-7.56 (m, 5H, Ar$\underline{H}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 13.9, 18.4, 18.5, 38.2, 38.5, 42.8, 44.0, 45.8, 46.8, 71.9, 73.1, 78.7 (q, $J_{C,F}$ = 28 Hz), 80.8 (q, $J_{C,F}$ = 29 Hz), 123.9 (q, $J_{C,F}$ = 282 Hz), 125.1 (q, $J_{C,F}$ = 287 Hz), 126.3, 128.3, 128.8, 129.0, 129.5, 133.4, 137.7, 203.4, 203.6 ppm; HRMS (ESI): calcd for $C_{15}H_{18}O_2F_3$ ([M + H]$^+$) 287.1253, found 287.1258. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, major enantiomer) = 11.7 min, t_R (major diastereomer, minor enantiomer) = 18.9 min. t_R (minor diastereomer) = 20.6 min and 21.4 min.

6-Propyl-2-(thiophen-2-yl)-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one (3ac)



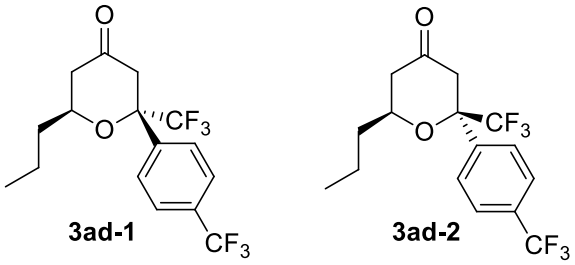
3ac-1



3ac-2

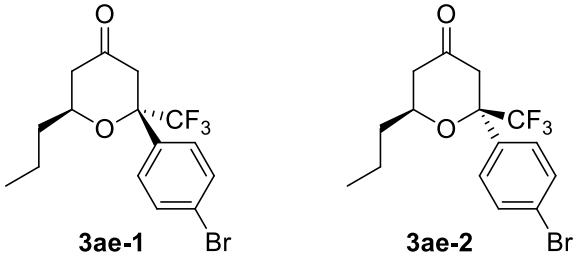
Synthesized by the general procedure; 28 h, 30.1 mg (52%), dr **3ac-1**:**3ac-2** = 1:1.4, **3ac-2** er 91:9. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, J = 7.2 Hz, 3H × 1.4/2.4, C$\underline{H}_3$), 0.99 (t, J = 7.2 Hz, 3H × 1/2.4, C$\underline{H}_3$), 1.34-1.80 (m, 4H, C$\underline{H}_2$C$\underline{H}_2$CH$_3$), 2.27-2.40 (m, 1H × 1/2.4, CHC$\underline{H}$HC=O, 2H × 1.4/2.4, CHC$\underline{HH}$C=O), 2.48 (dd, J = 2.7 Hz, 17.3 Hz, 1H × 1/2.4, CHC$\underline{H}$HC=O), 2.96 (d, J = 15.6 Hz, 1H × 1/2.4, CF$_3$CC$\underline{H}$HC=O), 2.99 (d, J = 14.7 Hz, 1H × 1.4/2.4, CF$_3$CC$\underline{H}$HC=O), 3.14 (dd, J = 0.7 Hz, 14.7 Hz, 1H × 1.4/2.4, CF$_3$CC$\underline{H}$HC=O), 3.29 (d, J = 15.6 Hz, 1H × 1/2.4, CF$_3$CC$\underline{H}$HC=O), 3.76-3.82 (m, 1H × 1.4/2.4, OC$\underline{H}$), 4.39-4.44 (m, 1H × 1/2.4, OC$\underline{H}$), 6.99-7.05 (m, 1H × 1.4/2.4, 2H × 1/2.4, Ar$\underline{H}$), 7.13 (dd, J = 1.2 Hz, 3.7 Hz, 1H × 1.4/2.4, Ar$\underline{H}$), 7.34 (dd, J = 1.2 Hz, 5.2 Hz, 1H × 1/2.4, Ar$\underline{H}$), 7.44 (dd, J = 1.2 Hz, 5.2 Hz, 1H × 1.4/2.4, Ar$\underline{H}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 13.9, 18.2, 18.3, 38.0, 43.9, 44.6, 45.4, 46.9, 72.2, 73.5, 78.1 (q, $J_{C,F}$ = 30 Hz), 79.4 (q, $J_{C,F}$ = 31 Hz), 123.4 (q, $J_{C,F}$ = 282 Hz), 124.5 (q, $J_{C,F}$ = 286 Hz), 125.5, 126.8, 127.0, 127.2, 128.7, 130.0, 137.1, 141.8, 202.9, 203.0. HRMS (ESI): calcd for $C_{13}H_{14}O_2F_3S$ ([M - H]$^-$) 291.0661, found 291.0663. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, major enantiomer) = 13.49 min, t_R (major diastereomer, minor enantiomer) = 20.6 min. t_R (minor diastereomer) = 23.1 min and 25.4 min.

6-Propyl-2-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)dihydro-2*H*-pyran-4(3*H*)-one (3ad)



Synthesized by the general procedure; 18 h, 30.2 mg (43%), dr **3ad-1**:**3ad-2** = 1:1.7, **3ad-2** er 97:3. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, J = 7.2 Hz, 3H × 1.7/2.7, C$\underline{H}_3$), 1.02 (t, J = 7.1 Hz, 3H × 1/2.7, C$\underline{H}_3$), 1.37-1.83 (m, 4H, C$\underline{H}_2$C$\underline{H}_2$CH$_3$), 2.17-2.31 (m, 1H, CHC$\underline{H}$HC=O), 2.42 (dd, J = 11.5 Hz, 15.0 Hz, 1H × 1.7/2.7, CHC$\underline{H}$HC=O), 2.52 (dd, J = 2.1 Hz, 16.6 Hz, 1H × 1/2.7, CHC$\underline{H}$HC=O), 2.88 (d, J = 15.6 Hz, 1H × 1/2.7, CF$_3$CC$\underline{H}$HC=O), 3.08 (dd, J = 0.7 Hz, 14.7 Hz, 1H × 1.7/2.7, CF$_3$CC$\underline{H}$HC=O), 3.24 (d, J = 14.7 Hz, 1H × 1.7/2.7, CF$_3$CC$\underline{H}$HC=O), 3.34 (dd, J = 0.6 Hz, 15.6 Hz, 1H × 1/2.7, CF$_3$CC$\underline{H}$HC=O), 3.65-3.72 (m, 1H × 1.7/2.7, OC$\underline{H}$), 4.42-4.47 (m, 1H × 1/2.7, OC$\underline{H}$), 7.63-7.71 (m, 4H, Ar$\underline{H}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 13.9, 18.4, 38.1, 38.4, 42.8, 43.9, 45.8, 46.7, 72.4, 73.4, 78.6 (q, $J_{C,F}$ = 28 Hz), 80.6 (q, $J_{C,F}$ = 30 Hz), 123.57 (q, $J_{C,F}$ = 282 Hz), 123.66 (q, $J_{C,F}$ = 271 Hz), 123.8 (q, $J_{C,F}$ = 271 Hz), 124.8 (q, $J_{C,F}$ = 287 Hz), 125.4 (q, $J_{C,F}$ = 4 Hz), 125.8 (q, $J_{C,F}$ = 4 Hz), 126.9, 128.8, 131.3 (q, $J_{C,F}$ = 33 Hz), 131.8 (q, $J_{C,F}$ = 32 Hz), 137.6, 141.5, 202.6, 202.8. HRMS (ESI): calcd for $C_{16}H_{15}O_2F_6$ ([M - H]$^-$) 353.0971, found 353.0990. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, minor enantiomer) = 13.4 min, t_R (major diastereomer, major enantiomer) = 14.1 min. t_R (minor diastereomer) = 15.8 min and 20.4 min.

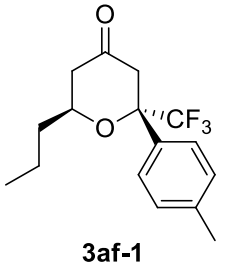
2-(4-Bromophenyl)-6-propyl-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one (3ae)



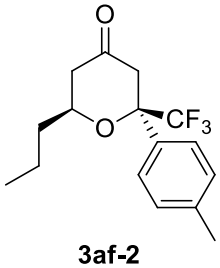
Synthesized by the general procedure; 24 h, 44.0 mg (59%), dr **3ae-1**:**3ae-2** = 1:2.4, er of **3ae-2** 97:3. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, J = 7.2 Hz, 3H × 2.4/3.4, C$\underline{H}_3$), 1.01 (t, J = 7.1 Hz, 3H × 1/3.4, C$\underline{H}_3$), 1.35-1.81 (m, 4H × 3.4/3.4, C$\underline{H}_2$C$\underline{H}_2$CH$_3$), 2.17-2.29 (m, 1H, CHC$\underline{H}$HC=O), 2.39 (dd, J = 11.5 Hz, 14.8 Hz, 1H × 2.4/3.4, CHC$\underline{H}$HC=O), 2.49 (dd, J = 2.3 Hz, 16.4 Hz, 1H × 1/3.4, CHC$\underline{H}$HC=O), 2.85 (d, J = 15.6 Hz, 1H × 1/3.4, CF$_3$CC$\underline{H}$HC=O), 3.01 (d, J = 14.8 Hz, 1H × 2.4/3.4, CF$_3$CC$\underline{H}$HC=O), 3.19 (d, J = 14.8 Hz, 1H × 2.4/3.4, CF$_3$CC$\underline{H}$HC=O), 3.28 (d, J = 15.6 Hz, 1H × 1/3.4, CF$_3$CC$\underline{H}$HC=O), 3.65-3.71 (m, 1H × 2.4/3.4, OC$\underline{H}$), 4.39-4.43 (m, 1H × 1/3.4, OC$\underline{H}$), 7.35-7.58 (m, 4H, Ar$\underline{H}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 13.9, 18.4, 38.1, 38.4, 42.7, 43.8, 45.7, 46.8, 72.1, 73.3, 78.5 (q, $J_{C,F}$ = 28 Hz), 80.6 (q, $J_{C,F}$ = 30 Hz), 123.5, 123.6 (q, $J_{C,F}$ = 282 Hz), 124.2, 124.8 (q, $J_{C,F}$ = 287 Hz), 128.1, 130.1, 131.6, 132.1, 132.5, 136.8, 202.9, 203.1. HRMS (ESI): calcd for

$C_{15}H_{15}O_2BrF_3$ ([M - H]$^-$) 363.0202, found 363.0208. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, major enantiomer) = 11.5 min, t_R (major diastereomer, minor enantiomer) = 12.6 min. t_R (minor diastereomer) = 18.2 min and 19.7 min.

6-Propyl-2-(p-tolyl)-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one (3af)



3af-1

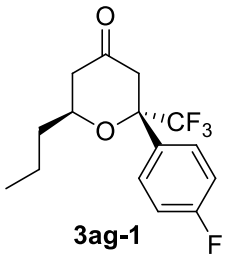


3af-2

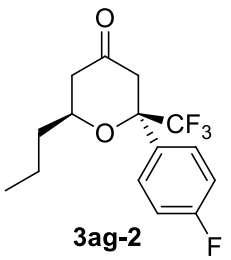
Synthesized by the general procedure; 72 h (**2** was not consumed), 17.6 mg (29%), dr **3af-1**:**3af-2** = 1:1.3, **3af-2** er 94:6.

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, *J* = 7.2 Hz, 3H × 1.3/2.3, C$\underline{H}_3$), 1.01 (t, *J* = 7.2 Hz, 3H × 1/2.3, C$\underline{H}_3$), 1.36-1.82 (m, 4H, C$\underline{H}_2$C$\underline{H}_2$CH$_3$), 2.18-2.26 (m, 1H, CHC$\underline{H}$HC=O), 2.32-2.39 (m, 1H×1.3/2.3, CHC$\underline{H}$HC=O), 2.36 (s, 3H, ArC$\underline{H}_3$), 2.47 (ddd, *J* = 0.8 Hz, 2.4 Hz, 16.4 Hz, 1H × 1/2.3, CHC$\underline{H}$HC=O), 2.89 (d, *J* = 15.6 Hz, 1H × 1/2.3, CF$_3$CC$\underline{H}$HC=O), 2.98 (dd, *J* = 0.8 Hz, 14.6 Hz, 1H × 1.3/2.3, CF$_3$CC$\underline{H}$HC=O), 3.25 (dd, *J* = 0.8 Hz, 14.6 Hz, 1H × 1.3/2.3, CF$_3$CC$\underline{H}$HC=O), 3.29 (dd, *J* = 0.8 Hz, 15.6 Hz, 1H × 1/2.3, CF$_3$CC$\underline{H}$HC=O), 3.67-3.74 (m, 1H × 1.3/2.3, OC$\underline{H}$), 4.37-4.42 (m, 1H × 1/2.3, OC$\underline{H}$), 7.18-7.23 (m, 2H, Ar$\underline{H}$), 7.36-7.44 (m, 2H, Ar$\underline{H}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 13.9, 18.4, 18.5, 21.0, 21.1, 38.2, 38.5, 42.9, 44.0, 45.8, 46.9, 71.7, 73.0, 78.7 (q, $J_{C,F}$ = 28 Hz), 80.7 (q, $J_{C,F}$ = 29 Hz), 123.9 (q, $J_{C,F}$ = 282 Hz), 125.2 (q, $J_{C,F}$ = 287 Hz), 126.2, 128.3, 129.0, 129.5, 130.2, 134.8, 139.0, 139.6, 203.65, 203.73. HRMS (ESI): calcd for $C_{16}H_{20}O_2F_3$ ([M + H]$^+$) 301.1410, found 301.1408. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 99.5:0.5, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, minor enantiomer) = 13.3 min, t_R (major diastereomer, major enantiomer) = 13.9 min. t_R (minor diastereomer) = 15.3 min and 18.5 min.

2-(4-Fluorophenyl)-6-propyl-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one (3ag)



3ag-1

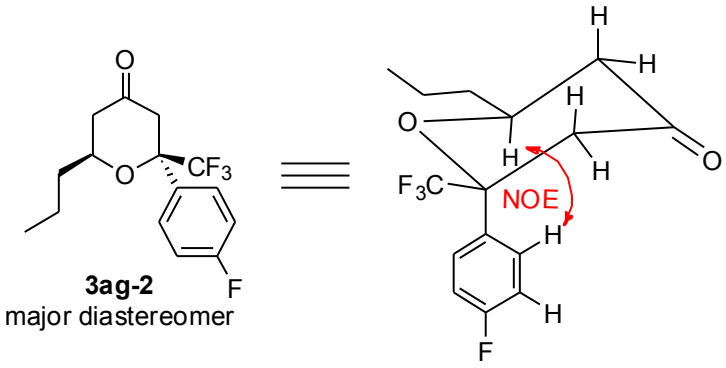


3ag-2

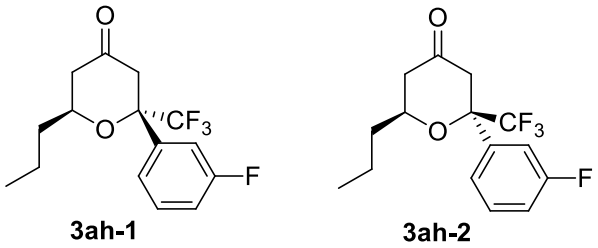
Synthesized by the general procedure; 26 h, 33.4 mg (55%), dr **3ag-1**:**3ag-2** = 1:2.2, **3ag-2** er 96:4.

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, *J* = 7.2 Hz, 3H × 2.2/3.2, C$\underline{H}_3$), 1.01 (t, *J* = 7.2 Hz, 3H × 1/3.2, C$\underline{H}_3$), 1.35-1.81 (m, 4H, C$\underline{H}_2$C$\underline{H}_2$CH$_3$), 2.22 (dd, *J* = 11.6 Hz, 16.6 Hz, 1H × 1/3.2, CHC$\underline{H}$HC=O), 2.27 (ddd, *J* = 1.6 Hz, 2.8 Hz, 14.8 Hz, 1H × 2.2/3.2, CHC$\underline{H}$HC=O), 2.39 (ddd, *J* = 0.7 Hz, 11.4 Hz, 14.8 Hz, 1H × 2.2/3.2, CHC$\underline{H}$HC=O), 2.49 (ddd, *J* = 0.6 Hz, 2.8 Hz, 16.6 Hz, 1H × 1/3.2, CHC$\underline{H}$HC=O), 2.86 (d, *J* = 15.6 Hz, 1H × 1/3.2, CF$_3$CC$\underline{H}$HC=O), 3.02 (dd, *J* = 0.8 Hz, 14.6 Hz, 1H ×

2.2/3.2, $CF_3CC\underline{H}HC=O$), 3.21 (dd, J = 0.7 Hz, 14.6 Hz, 1H × 2.2/3.2, $CF_3CC\underline{H}HC=O$), 3.30 (dd, J = 0.6 Hz, 15.6 Hz, 1H × 1/3.2, $CF_3CC\underline{H}HC=O$), 3.65-3.71 (m, 1H × 2.2/3.2, OC<u>H</u>), 4.38-4.44 (m, 1H × 1/3.2, OC<u>H</u>), 7.05-7.14 (m, 2H, Ar<u>H</u>), 7.46-7.54 (m, 2H, Ar<u>H</u>). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 13.9, 18.4, 38.1, 38.5, 42.9, 44.0, 45.8, 46.8, 72.0, 73.2, 78.5 (q, $J_{C,F}$ = 28 Hz), 80.5 (q, $J_{C,F}$ = 30 Hz), 115.3 (d, $J_{C,F}$ = 21 Hz), 115.9 (d, $J_{C,F}$ = 22 Hz), 123.7 (q, $J_{C,F}$ = 282 Hz), 125.0 (q, $J_{C,F}$ = 287 Hz), 128.3 (d, $J_{C,F}$ = 8 Hz), 129.2 (d, $J_{C,F}$ = 3 Hz), 130.4 (d, $J_{C,F}$ = 9 Hz), 133.5, 163.0 (d, $J_{C,F}$ = 247 Hz), 163.3 (d, $J_{C,F}$ = 248 Hz), 203.1, 203.3. HRMS (ESI): calcd for $C_{15}H_{15}O_2F_4$ ([M - H]$^-$) 303.1003, found 303.1013. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, major enantiomer) = 10.6 min, t_R (major diastereomer, minor enantiomer) = 13.4 min. t_R (minor diastereomer) = 19.3 min and 20.9 min. The relative stereochemistry was determined by the NOESY experiment.



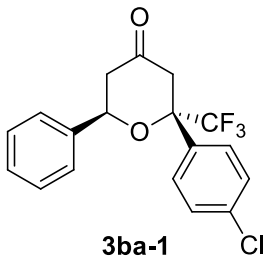
2-(3-Fluorophenyl)-6-propyl-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one (3ah)



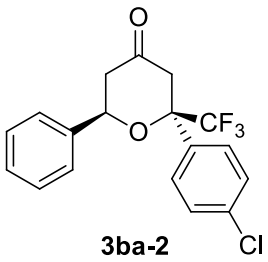
Synthesized by the general procedure; 24 h, 33.0 mg (54%), dr **3ah-1**:**3ah-2** = 1:2.2, **3ah-2** er 95:5. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, J = 7.2 Hz, 3H × 2.2/3.2, C<u>H</u>$_3$), 1.02 (t, J = 7.0 Hz, 3H × 1/3.2, C<u>H</u>$_3$), 1.36-1.82 (m, 4H, C<u>H</u>$_2$C<u>H</u>$_2$CH$_3$), 2.23 (dd, J = 11.6 Hz, 16.6 Hz, 1H × 1/3.2, CHC<u>H</u>HC=O), 2.28 (ddd, J = 1.6 Hz, 2.7 Hz, 15.0 Hz, 1H × 2.2/3.2, CHC<u>H</u>HC=O), 2.40 (ddd, J = 0.6 Hz, 11.5 Hz, 15.0 Hz, 1H × 2.2/3.2, CHC<u>H</u>HC=O), 2.50 (ddd, J = 0.7 Hz, 2.7 Hz, 16.6 Hz, 1H × 1/3.2, CHC<u>H</u>HC=O), 2.86 (d, J = 15.6 Hz, 1H × 1/3.2, $CF_3CC\underline{H}HC=O$), 3.02 (dd, J = 0.8 Hz, 14.8 Hz, 1H × 2.2/3.2, $CF_3CC\underline{H}HC=O$), 3.10 (dd, J = 0.6 Hz, 14.8 Hz, 1H × 2.2/3.2, $CF_3CC\underline{H}HC=O$), 3.29 (dd, J = 0.7 Hz, 15.6 Hz, 1H × 1/3.2, $CF_3CC\underline{H}HC=O$), 3.69-3.75 (m, 1H × 2.2/3.2, OC<u>H</u>), 4.39-4.45 (m, 1H × 1/3.2, OC<u>H</u>), 7.05-7.42 (m, 4H, Ar<u>H</u>). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 13.9, 18.38, 18.44, 38.1, 38.4, 42.8, 44.0, 45.8, 46.7, 72.2, 73.3, 78.4 (q, $J_{C,F}$ = 28 Hz), 80.4 (q, $J_{C,F}$ = 30 Hz), 114.0 (d, $J_{C,F}$ = 24 Hz), 115.6 (d, $J_{C,F}$ = 23 Hz), 116.1 (d, $J_{C,F}$ = 21 Hz), 116.7 (d, $J_{C,F}$ = 21 Hz), 121.9, 123.6 (q, $J_{C,F}$ = 282 Hz), 124.0 (d, $J_{C,F}$ = 3 Hz), 124.9 (q, $J_{C,F}$ = 287 Hz), 129.9 (d, $J_{C,F}$ = 8 Hz), 130.4 (d, $J_{C,F}$ = 8 Hz), 136.2 (d, $J_{C,F}$ = 7 Hz), 140.2 (d, $J_{C,F}$ = 7 Hz), 162.6 (d, $J_{C,F}$ = 245 Hz), 163.0 (d, $J_{C,F}$ = 246 Hz), 202.9, 203.1. HRMS (ESI): calcd for $C_{15}H_{17}O_2F_4$ ([M + H]$^+$) 305.1159, found 305.1158. HPLC (Daicel

Chiralpak AS, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, major enantiomer) = 14.3 min, t_R (major diastereomer, minor enantiomer) = 16.7 min. t_R (minor diastereomer) = 19.3 min and 25.2 min.

2-(4-Chlorophenyl)-6-phenyl-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one (3ba)



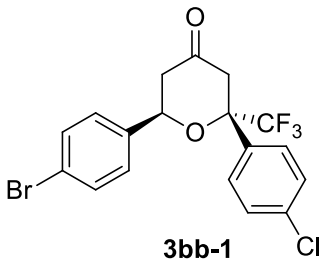
3ba-1



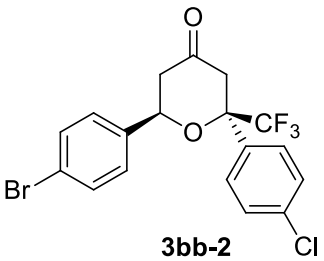
3ba-2

Synthesized by the general procedure; 24 h, 58.1 mg (82%), dr **3ba-1**:**3ba-2** = 1:4.2, **3ba-2** er 91:9. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.56 (ddd, *J* = 1.6 Hz, 3.2 Hz, 15.2 Hz, 1H × 4.2/5.2, CHC<u>H</u>HC=O), 2.59 (dd, *J* = 11.6 Hz, 16.8 Hz, 1H × 1/5.2, CHC<u>H</u>HC=O), 2.72 (ddd, *J* = 0.7 Hz, 11.6 Hz, 15.2 Hz, 1H × 4.2/5.2, CHC<u>H</u>HC=O), 2.76 (ddd, *J* = 0.6 Hz, 2.8 Hz, 16.8 Hz, 1H × 1/5.2, CHC<u>H</u>HC=O), 3.02 (d, *J* = 15.6 Hz, 1H × 1/5.2, CF_3CC<u>H</u>HC=O), 3.18 (dd, *J* = 0.7 Hz, 14.7 Hz, 1H × 4.2/5.2, CF_3CC<u>H</u>HC=O), 3.32 (dd, *J* = 0.6 Hz, 14.7 Hz, 1H × 4.2/5.2, CF_3CC<u>H</u>HC=O), 3.44 (dd, *J* = 0.6 Hz, 15.6 Hz, 1H × 1/5.2, CF_3CC<u>H</u>HC=O), 4.74 (dd, *J* = 3.2 Hz, 11.6 Hz, 1H × 4.2/5.2, OC<u>H</u>), 5.46 (dm, *J* = 11.6 Hz, 1H × 1/5.2, OC<u>H</u>), 7.35-7.57 (m, 9H, Ar<u>H</u>). ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.7, 43.7, 47.3, 48.6, 73.9, 75.5, 79.0 (q, $J_{C,F}$ = 29 Hz), 80.9 (q, $J_{C,F}$ = 30 Hz), 123.6 (q, $J_{C,F}$ = 282 Hz), 124.9 (q, $J_{C,F}$ = 287 Hz), 125.7, 126.0, 127.9, 128.6, 128.7, 128.8, 128.9, 129.1, 129.3, 129.8, 131.47, 131.55, 135.5, 136.2, 139.1, 139.5, 202.0, 202.2. HRMS (ESI): calcd for $C_{18}H_{15}O_2ClF_3$ ($[M + H]^+$) 355.0707, found 355.0700. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, major enantiomer) = 22.0 min, t_R (major diastereomer, minor enantiomer) = 25.9 min. t_R (minor diastereomer) = 35.6 min and 47.2 min.

6-(4-Bromophenyl)-2-(4-chlorophenyl)-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one (3bb)



3bb-1



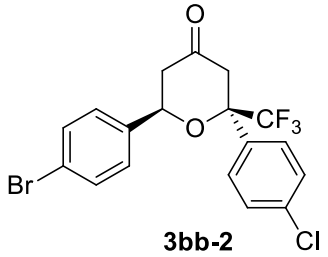
3bb-2

Synthesized by the general procedure; 24 h, 54.2 mg (63%), dr **3bb-1**:**3bb-2** = 1:4.1, **3bb-2** er 94:6. Colorless gum. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (ddd, *J* = 1.6 Hz, 3.2 Hz, 15.0 Hz, 1H × 4.1/5.1, CHC<u>H</u>HC=O), 2.46 (dd, *J* = 11.6 Hz, 16.4 Hz, 1H × 1/5.1, CHC<u>H</u>HC=O), 2.58 (ddd, *J* = 0.8 Hz, 11.6 Hz, 15.0 Hz, 1H × 4.1/5.1, CHC<u>H</u>HC=O), 2.66 (ddd, *J* = 0.8 Hz, 2.8 Hz, 16.4 Hz, 1H × 1/5.1, CHC<u>H</u>HC=O), 2.93 (d, *J* = 15.6 Hz, 1H × 1/5.1, CF_3CC<u>H</u>HC=O), 3.09 (dd, *J* = 0.8 Hz, 14.8 Hz, 1H × 4.1/5.1, CF_3CC<u>H</u>HC=O), 3.24 (dd, *J* = 0.8 Hz, 14.8 Hz, 1H × 4.1/5.1, CF_3CC<u>H</u>HC=O), 3.35 (dd, *J* = 0.8 Hz, 15.6 Hz, 1H × 1/5.1, CF_3CC<u>H</u>HC=O), 4.61 (dd, *J* = 3.2 Hz, 11.6 Hz, 1H × 4.1/5.1, OC<u>H</u>), 5.34

(dd, J = 2.8 Hz, 11.6 Hz, 1H × 1/5.1, OC<u>H</u>), 7.17-7.52 (m, 8H, Ar<u>H</u>). ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.7, 43.6, 47.1, 48.4, 73.3, 74.9, 79.1 (q, $J_{C,F}$ = 29 Hz), 81.0 (q, $J_{C,F}$ = 30 Hz), 122.55, 122.64, 123.5 (q, $J_{C,F}$ = 282 Hz), 124.8 (q, $J_{C,F}$ = 287 Hz), 127.3, 127.6, 127.8, 128.8, 129.4, 129.7, 131.2, 132.0, 132.1, 135.6, 136.3, 138.1, 138.5, 201.4, 201.7. HRMS (ESI): calcd for $C_{18}H_{14}O_2BrClF_3$ ($[M + H]^+$) 432.9812, found 432.9797. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, minor enantiomer) = 30.3 min, t_R (major diastereomer, major enantiomer) = 34.1 min.

A 1 mmol-scale reaction to afford 3bb-2

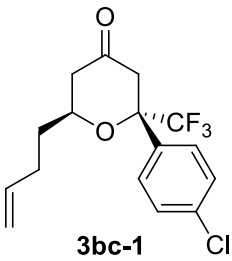
To a solution of 4-(4-bromophenyl)but-3-en-2-one (**1j**) (1.05g, 5.0 mmol) and 4-chlorophenyl trifluomethyl ketone (**2a**) (208.6 mg, 1.0 mmol) in toluene (super dehydrated, 2.0 mL), (2*S*,4*R*)-4-(*tert*-butyldiphenylsilyloxy)pyrrolidine-2-carboxylic acid (**L**) (37.0 mg, 0.1 mmol,) and DABCO (**K**) (22.4 mg, 0.2 mmol) were added at room temperature (25 °C), and the mixture was stirred at the same temperature for 24 h. The dr was determined by ^{1}H NMR analysis before purification to be 1:4.1 (**3bb-1**:**3bb-2**). The mixture was purified by flash column chromatography (hexane/CH_2Cl_2 = 3:1 to 2:1) to give **3bb-2** (255.0 mg, 61%, er 92:8).



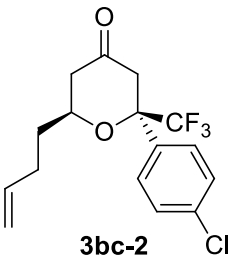
3bb-2

Colorless gum; er 92:8. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (ddd, J = 1.6 Hz, 3.2 Hz, 15.0 Hz, 1H, CHC<u>H</u>HC=O), 2.58 (ddd, J = 0.8 Hz, 11.6 Hz, 15.0 Hz, 1H, CHC<u>H</u>HC=O), 3.08 (dd, J = 0.8 Hz, 14.6 Hz, 1H, CF_3CC<u>H</u>HC=O), 3.24 (dd, J = 0.8 Hz, 14.6 Hz, 1H, CF_3CC<u>H</u>HC=O), 4.61 (dd, J = 3.2 Hz, 11.6 Hz, 1H, OC<u>H</u>), 7.17-7.20 (m, 2H, Ar<u>H</u>), 7.33-7.39 (m, 4H, Ar<u>H</u>), 7.45-7.48 (m, 2H, Ar<u>H</u>). ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.7, 48.4, 73.3, 81.0 (q, $J_{C,F}$ = 30 Hz), 122.6, 123.6 (q, $J_{C,F}$ = 282 Hz), 127.3, 129.4, 129.7, 131.3, 132.0, 136.3, 138.2, 201.5.

6-(But-3-en-1-yl)-2-(4-chlorophenyl)-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one (3bc)



3bc-1



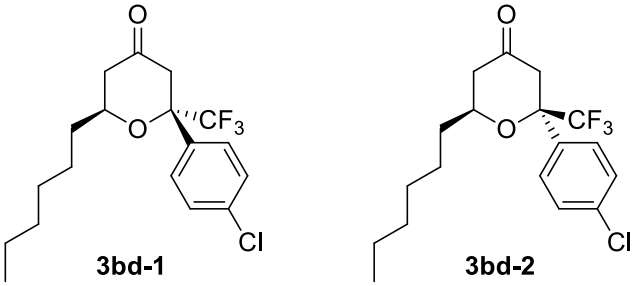
3bc-2

Synthesized by the general procedure; 29 h, 31.2 mg (47%), dr **3bc-1**:**3bc-2** = 1:1.7, **3bc-2** er 96:4.

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60-1.94 (m, 2H, C<u>H</u>$_2$CH_2CH=CH_2), 2.11-2.52 (m, 4H, CH_2C<u>H</u>$_2$CH=CH_2, CHC<u>H</u>$_2$C=O), 2.86 (d, J = 15.6 Hz, 1H × 1/2.7, CF_3CC<u>H</u>HC=O), 3.02 (dd, J = 0.5 Hz, 14.6 Hz, 1H × 1.7/2.7, CF_3CC<u>H</u>HC=O), 3.20 (d, J = 14.6 Hz, 1H × 1.7/2.7, CF_3CC<u>H</u>HC=O), 3.29

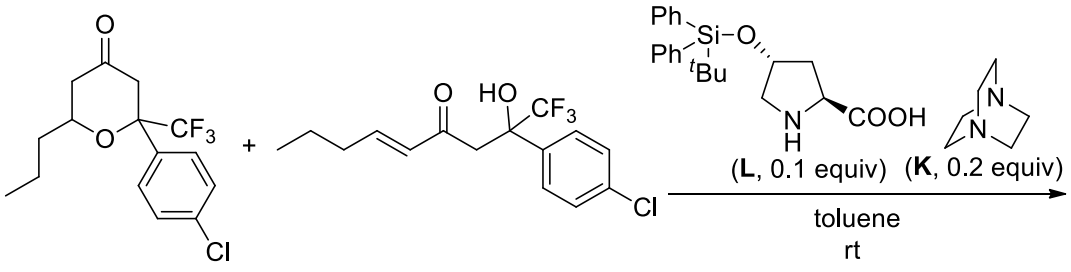
(d, J = 15.6 Hz, 1H × 1/2.7, $CF_3CC\underline{H}HC{=}O$), 3.67-3.37 (m, 1H × 1.7/2.7, $OC\underline{H}$), 4.40-4.46 (m, 1H × 1/2.7, $OC\underline{H}$), 4.95-5.14 (m, 2H, $CH_2CH{=}C\underline{H_2}$), 5.74-5.91 (m, 1H, $CH_2C\underline{H}{=}CH_2$), 7.36-7.51 (m, 4H, $Ar\underline{H}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.2, 29.3, 35.2, 35.5, 42.7, 43.8, 45.7, 46.7, 71.7, 72.8, 78.5 (q, $J_{C,F}$ = 28 Hz), 80.6 (q, $J_{C,F}$ = 30 Hz), 115.5, 115.7, 123.6 (q, $J_{C,F}$ = 282 Hz), 124.9 (q, $J_{C,F}$ = 287 Hz), 127.8, 128.6, 129.1, 129.8, 131.8, 135.3, 136.0, 137.2, 137.3, 202.6, 202.8. HRMS (ESI): calcd for $C_{16}H_{17}O_2ClF_3$ ($[M + H]^+$) 333.0864, found 333.0858. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, major enantiomer) = 16.6 min, t_R (major diastereomer, minor enantiomer) = 19.9 min. t_R (minor diastereomer) = 29.5 min and 55.9 min.

2-(4-Chlorophenyl)-6-hexyl-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one (3bd)



Synthesized by the general procedure; 26 h, 39.3 (51%), dr **3bd-1**:**3bd-2** = 1:2.3, **3bd-2** er 95:5.
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-1.80 (m, 13H, $(C\underline{H_2})_5C\underline{H_3}$), 2.17-2.29 (m, 1H, $CHC\underline{H}HC{=}O$), 2.38 (dd, J = 11.6 Hz, 14.9 Hz, 1H × 2.3/3.3, $CHC\underline{H}HC{=}O$), 2.49 (dd, J = 2.8 Hz, 16.6 Hz, 1H × 1/3.3, $CHC\underline{H}HC{=}O$), 2.85 (d, J = 15.6 Hz, 1H × 1/3.3, $CF_3CC\underline{H}HC{=}O$), 3.01 (dd, J = 0.6 Hz, 14.6 Hz, 1H × 2.3/3.3, $CF_3CC\underline{H}HC{=}O$), 3.19 (d, J = 14.6 Hz, 1H × 2.3/3.3, $CF_3CC\underline{H}HC{=}O$), 3.29 (d, J = 15.6 Hz, 1H × 1/3.3, $CF_3CC\underline{H}HC{=}O$), 3.63-3.70 (m, 1H × 2.3/3.3, $OC\underline{H}$), 4.37-4.41 (m, 1H × 1/3.3, $OC\underline{H}$), 7.33-7.51 (m, 4H, $Ar\underline{H}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ =14.0, 22.6, 25.05, 25.06, 29.0, 29.1, 31.66, 31.68, 36.0, 36.3, 42.7, 43.8, 45.7, 46.8, 72.3, 73.6, 78.5 (q, $J_{C,F}$ = 28 Hz), 80.5 (q, $J_{C,F}$ = 30 Hz), 123.6 (q, $J_{C,F}$ = 282 Hz), 124.9 (q, $J_{C,F}$ = 287 Hz), 127.8, 128.6, 129.1, 129.8, 132.0, 135.9, 202.9, 203.1. HRMS (ESI): calcd for $C_{18}H_{23}O_2ClF_3$ ($[M + H]^+$) 363.1333, found 363.1326. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major diastereomer, minor enantiomer) = 10.8 min, t_R (major diastereomer, major enantiomer) = 11.5 min. t_R (minor diastereomer) = 12.9 min and 17.1 min.

5. Analysis of the stability of the products under the catalytic conditions

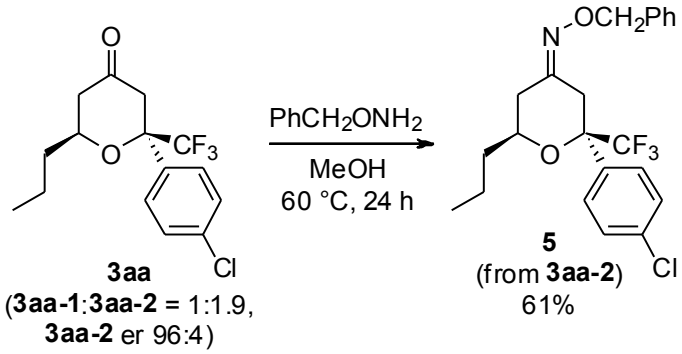


3aa-1:**3aa-2**:**4aa** = 3:1:1.6

To a mixture of racemic **3aa** and racemic **4aa** (**3aa-1**:**3aa-2**:**4aa** = 3:1:1.6, 44.8 mg, **3aa** 0.10 mmol, **4aa** 0.04 mmol) in toluene (super dehydrated, 0.2 mL), proline derivative **L** (0.01 mmol, 3.7 mg) and DABCO (**K**) (0.02 mmol, 2.3 mg) were added at room temperature (25 °C). At 30 min, 20 h, 44 h, and 115 h, an aliquot was taken from the mixture, diluted with $CDCl_3$, and analyzed by ^1H NMR. No decomposition of the compounds and no changes in the ratios were detected.

6. Transformations of the oxa-hetero-Diels-Alder reaction products

Transformation of 3aa to 5

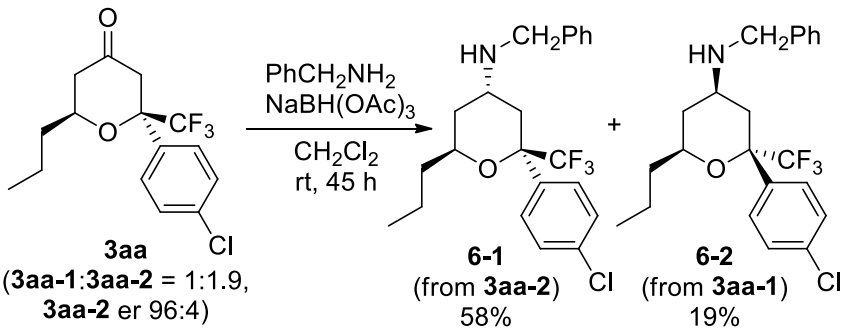


To a solution of **3aa** (**3aa-1**:**3aa-2** = 1:1.9, **3aa-2** er 96:4, 32.1 mg, 0.10 mmol) in MeOH (1.0 mL), $PhCH_2ONH_2$ (12.3 mg, 0.10 mmol) was added at room temperature (25 °C). The mixture was stirred at 60 °C for 24 h (consumption of **3aa** was analyzed by TLC). After being cooled to room temperature, the mixture was purified by flash column chromatography (hexane/EtOAc = 15:1 to 10:1) to give **5** (major diastereomer from **3aa-2**, 25.9 mg, 61%).

2-(4-Chlorophenyl)-6-propyl-2-(trifluoromethyl)dihydro-2*H*-pyran-4(3*H*)-one *O*-benzyl oxime (5)

Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J = 7.2 Hz, 3H, C<u>H</u>$_3$), 1.34-1.73 (m, 4H, C<u>H</u>$_2$C<u>H</u>$_2$CH$_3$), 1.93 (dd, J = 11.6 Hz, 15.2 Hz, 1H, CHC<u>H</u>HC=N), 2.87 (d, J = 14.8 Hz, 1H, CF$_3$CC<u>H</u>HC=N), 3.00 (ddd, J = 0.4 Hz, 2.8 Hz, 15.2 Hz, 1H, CHC<u>H</u>HC=N), 3.11 (d, J = 14.8 Hz, 1H, CF$_3$CC<u>H</u>HC=N), 3.38-3.45 (m, 1H, OC<u>H</u>), 5.05 (s, 2H, C<u>H</u>$_2$Ph), 7.21-7.41 (m, 9H, Ar<u>H</u>). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 18.6, 31.5, 32.6, 38.1, 70.6, 75.6, 79.4 (q, $J_{C,F}$ = 29 Hz), 123.9 (q, $J_{C,F}$ = 282 Hz), 127.71, 127.73, 128.3, 128.7, 130.1, 132.4, 135.2, 137.8, 152.2. HRMS (ESI): calcd for $C_{22}H_{24}O_2NClF_3$ ($[M + H]^+$) 426.1430, found 426.1442.

Transformation of 3aa to 6



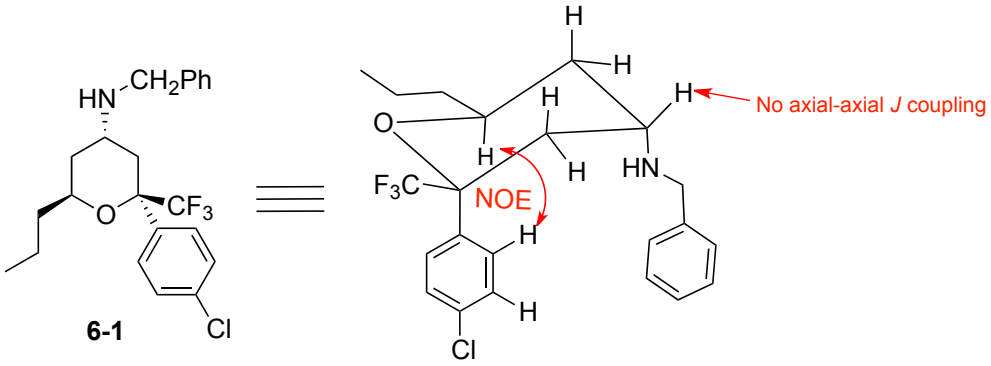
To a solution of **3aa** (**3aa-1**:**3aa-2** = 1:1.9, **3aa-2** er 96:4, 32.1 mg, 0.10 mmol) in CH_2Cl_2 (1.5 mL), benzylamine (32.7 μL, 0.30 mmol) and $NaBH(OAc)_3$ (64 mg, 0.30 mmol) were added at room temperature (25 °C), and the mixture was stirred at the same temperature for 45 h (consumption of **3aa** was analyzed by TLC). After addition of aqueous NaOH (1 N, 0.6 mL), the mixture was extracted with CH_2Cl_2 (x 3). Organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, concentrated, and purified by flash column chromatography (hexane/EtOAc = 20:1 to 6:1) gave **6-1** (from **3aa-2**, 23.9 mg, 58%, single diastereomer, er 95:5) and **6-2** (from **3aa-1**, 7.8 mg, 19%, single diastereomer).

Compound 6-1

R_f = 0.29 (hexane/ EtOAc = 10:1).

Colorless oil. $[\alpha]_D^{24}$ +31.7 (c = 1.93, $CHCl_3$, er 95:5 determined by the HPLC analysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.2 Hz, 3H, C<u>H</u>$_3$), 1.31-1.72 (m, 6H, $CH_2C\underline{H}_2CH_3$, $C\underline{H}_2CH_2CH_3$, $CHC\underline{H}_2CHNH$), 2.33-2.36 (m, 1H, $CCF_3C\underline{H}HCH$), 2.45 (dd, *J* = 5.2 Hz, 14.4 Hz, 1H, $CCF_3C\underline{H}HCH$), 3.23-3.26 (m, 1H, $C\underline{H}NHCH_2Ph$), 3.67 (s, 2H, $C\underline{H}_2Ph$), 3.74-3.81 (m, 1H, OC<u>H</u>), 7.06-7.07 (m, 2H, Ar<u>H</u>), 7.22-7.38 (m, 5H, Ar<u>H</u>), 7.49 (d, *J* = 8.8 Hz, 2H, Ar<u>H</u>). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 18.6, 30.6, 35.1, 38.4, 48.8, 50.9, 67.2, 77.6 (q, $J_{C,F}$ = 28 Hz), 124.6 (q, $J_{C,F}$ = 282 Hz), 127.2, 127.8, 128.4, 128.9, 134.6 ,135.4. HRMS (ESI) calcd for $C_{22}H_{26}ONClF_3$ ($[M + H]^+$) 412.1650, found 412.1644. HPLC (Daicel Chiralpak IA, hexane/*i*-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major enantiomer) = 8.0 min, t_R (minor enantiomer) = 12.1 min.

Relative stereochemistry of **6-1** was determined by ^{1}H NMR and NOESY analyses.

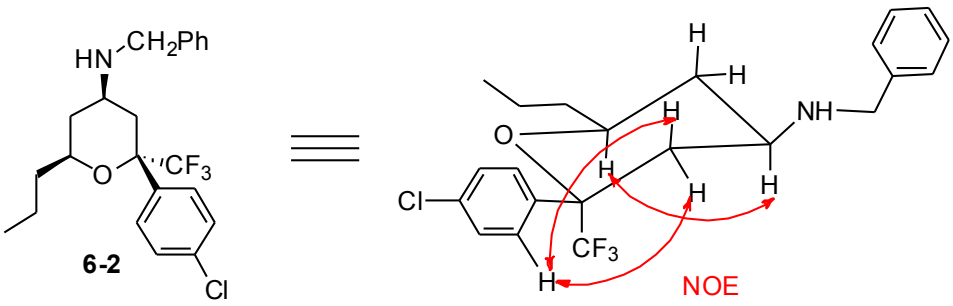


Compound 6-2

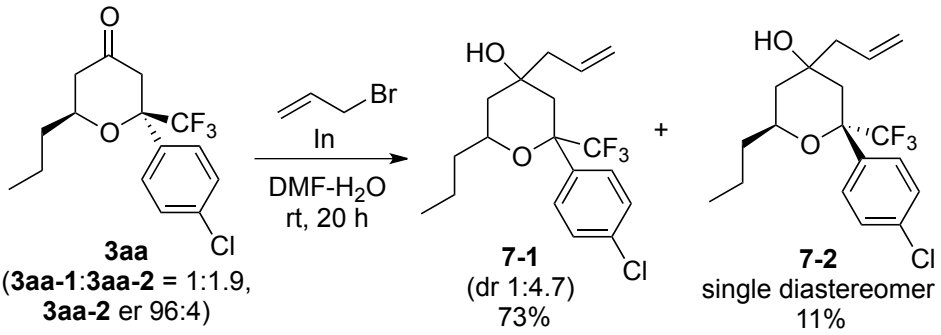
R_f = 0.24 (hexane/ EtOAc = 10:1).

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, *J* = 7.2 Hz, 3H, C<u>H</u>$_3$), 1.06 (dt, *J* = 12.8 Hz, 11.6 Hz, 1H, CHC<u>H</u>HCHNHBn), 1.43-1.69 (m, 5H, $C\underline{H}_2C\underline{H}_2CH_3$, $CF_3C\underline{H}HCHNH$), 2.01-2.06 (m, 1H, CHC<u>H</u>HCH), 2.87 (ddd, *J* = 1.6 Hz, 4.4 Hz, 13.8 Hz, 1H, $CCF_3C\underline{H}HCH$), 3.19-3.24 (m, 1H, C<u>H</u>NH), 3.86 (d, *J* = 15.5 Hz, 1H, C<u>H</u>HPh), 3.89 (d, *J* = 15.5 Hz, 1H, C<u>H</u>HPh), 4.00-4.05 (m, 1H, OC<u>H</u>), 7.27-7.35 (m, 7H, Ar<u>H</u>), 7.49 (m, 2H, Ar<u>H</u>). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 18.6, 37.4, 37.6, 38.8, 50.0, 50.6, 73.0, 76.7 (q, $J_{C,F}$ = 27 Hz), 125.9 (q, $J_{C,F}$ = 290 Hz), 127.3, 127.6, 128.0, 128.2, 128.6, 134.3, 139.0. HRMS (ESI) calcd for $C_{22}H_{26}ONClF_3$ ($[M + H]^+$) 412.1650, found 412.1637.

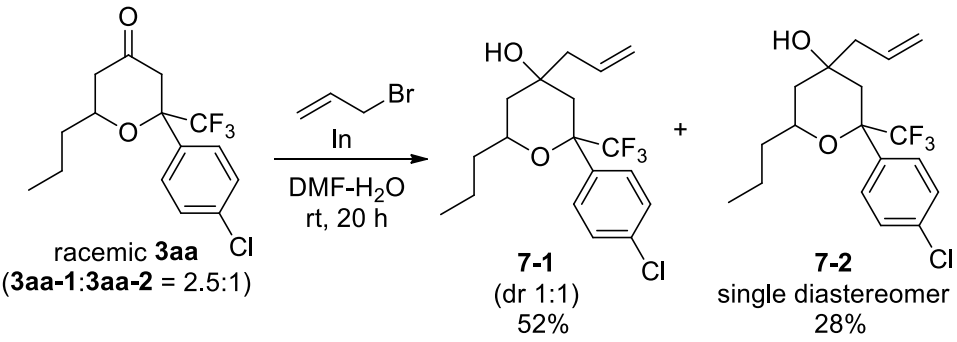
Relative stereochemistry of **6-2** was determined by ^{1}H NMR and NOESY analyses.



Transformation of 3aa to 7



A mixture of **3aa** (**3aa-1**:**3aa-2** = 1:1.9, **3aa-2** er 96:4, 32.1 mg, 0.10 mmol), allylbromide (86 μL, 1.0 mmol), and In (15.3 mg, 0.13 mmol) in DMF (0.8 mL)-H_2O (0.1 mL) was stirred at room temperature (25 ^oC) for 20 h. The mixture was added to aqueous saturated NH_4Cl and extracted with CH_2Cl_2 (x 3). Organic layers were combined, washed with brine, dried with $MgSO_4$, concentrated, and purified by flash column chromatography (hexane/EtOAc = 20:1 to 10:1) to give **7-1** (26.4 mg, 73%, a mixture of two diastereomers, **7-1a** from **3aa-1**, **7-1b** from **3aa-2**, **7-1a**:**7-1b** = 1:4.7) and **7-2** (from **3aa-1**, 4.1 mg, 11%, single diastereomer).



A mixture of racemic **3aa** (**3aa-1**:**3aa-2** = 2.5:1, 32.1 mg, 0.10 mmol), allylbromide (86 μL, 1.0 mmol), and In (15.3 mg, 0.13 mmol) in DMF (0.8 mL)-H_2O (0.1 mL) was stirred at room temperature (25 ^oC) for 20 h. The mixture was added to aqueous saturated NH_4Cl and extracted with CH_2Cl_2 (x 3). Organic layers were combined, washed with brine, dried with $MgSO_4$, concentrated, and purified by flash column chromatography (hexane/EtOAc = 20:1 to 10:1) to give **7-1** (18.8 mg, 52%, a mixture of two diastereomers, **7-1a** from **3aa-1**, **7-1b** from **3aa-2**, **7-1a**:**7-1b** = 1:1) and **7-2** (from **3aa-1**, 10.1 mg, 28%, single diastereomer).

Compound 7-1

R_f = 0.38 (hexane/ EtOAc = 10:1).

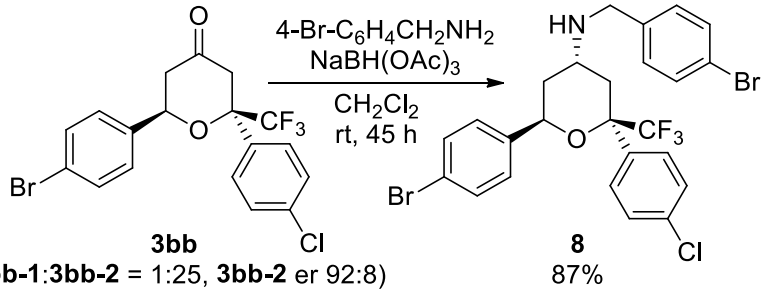
Colorless oil. **7-1a**:**7-1b** = 1:4.7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95-1.00 (m, 3H, C$\underline{H}_3$), 1.39-1.72 {m, (4H, C$\underline{H}_2$C$\underline{H}_2$CH$_3$), (2H × 4.7/5.7, OCHC$\underline{H}_2$COH), (1H × 1/5.7, OCHC$\underline{H}$HCOH)}, 1.90 (dd, *J* = 3.4 Hz, 14.5 Hz, 1H × 1/5.7, OCHC$\underline{H}$HCOH), 1.99 (d, *J* = 14.4 Hz, 1H × 4.7/5.7, CCF$_3$C$\underline{H}$HCOH), 2.22-2.32 (m, 2H, C$\underline{H}_2$CH=CH$_2$), 2.37 (s, 2H × 1/5.7, CCF$_3$C$\underline{H}_2$COH), 2.49 (d, *J* = 14.4 Hz, 1H × 4.7/5.7, CCF$_3$C$\underline{H}$HCOH), 3.75-3.81 (m, 1H × 4.7/5.7, OC$\underline{H}$), 3.92-3.99 (m, 1H × 1/5.7, OC$\underline{H}$), 5.13-5.26 (m, 2H, CH=C$\underline{H}_2$), 5.78-5.92 (m, 1H, C$\underline{H}$=CH$_2$), 7.34-7.39 (m, 2H, Ar$\underline{H}$), 7.48 (d, *J* = 8.6 Hz, 2H × 4.7/5.7, Ar$\underline{H}$), 7.57 (d, *J* = 8.4 Hz, 2H × 1/5.7, Ar$\underline{H}$). ^{13}C NMR (100 MHz, $CDCl_3$): * donates **7-1b**, δ 13.8, *14.2, 18.5, *18.7, *35.6, 37.3, *38.0, 38.4, *41.9, 43.2, 47.9, *48.6, *67.7, *69.2, 69.5, 71.3, 77.0 (q, $J_{C,F}$ = 28 Hz), *78.1 (q, $J_{C,F}$ = 28 Hz), 119.8, *120.4, *124.4 (q, $J_{C,F}$ = 282 Hz), 125.3 (q, $J_{C,F}$ = 286 Hz), 128.2, *128.3, 128.4, *129.7, *131.8, 132.3, *133.8, 134.5, *134.7, 137.9.

Compound 7-2

R_f = 0.31 (hexane/ EtOAc = 10:1).

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, *J* = 7.2 Hz, 3H, C$\underline{H}_3$), 1.35 (dd, *J* = 11.8 Hz, 14.1 Hz, 1H, OCHC$\underline{H}$HCOH), 1.46-1.74 (m, 5H, C$\underline{H}_2$C$\underline{H}_2$CH$_3$, OCHC$\underline{H}$HCOH), 1.93-2.04 (m, 2H, C$\underline{H}_2$CH=CH$_2$), 2.08 (dd, *J* = 0.6 Hz, 14.5 Hz, 1H, CCF$_3$C$\underline{H}$HCOH), 2.54 (dd, *J* = 0.9 Hz, 14.5 Hz, 1H, CCF$_3$C$\underline{H}$HCOH), 4.29-4.33 (m, 1H, OC$\underline{H}$), 5.05-5.11 (m, 1H, CH=C$\underline{H}$H), 5.19-5.22 (m, 1H, CH=C$\underline{H}$H), 5.72-5.83 (m, 1H, C$\underline{H}$=CH$_2$), 7.32-7.35 (m, 2H, Ar$\underline{H}$), 7.50 (d, *J* = 8.4 Hz, 2H, Ar$\underline{H}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 18.6, 38.2, 39.4, 42.5, 48.3, 68.4, 70.0, 76.2 (q, $J_{C,F}$ = 28 Hz), 120.6, 125.5 (q, $J_{C,F}$ = 287 Hz), 127.7, 128.2, 132.0, 134.3 ,139.1.

Transformation of 3bb to 8



3bb (**3bb-1**:**3bb-2** = 1:25, **3bb-2** er 92:8)

8 87%

To a solution of **3bb** (**3bb-1:3bb-2** = 1:25, **3bb-2** er 92:8, 70.0 mg, 0.161 mmol) in CH_2Cl_2 (2.5 mL), 4-bromobenzylamine (93.0 mg, 0.50 mmol) and $NaBH(OAc)_3$ (106.8 mg, 0.50 mmol) were added at room temperature (25 ^{o}C) and the mixture was stirred at the same temperature for 45 h (consumption of **3bb** was analyzed by TLC). After addition of aqueous NaOH (1 N, 1.5 mL), the mixture was extracted with CH_2Cl_2 (x 3). Organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, concentrated, and purified by flash column chromatography (hexane/EtOAc = 10:1) to give **8** (97.1 mg, 87%, er 92:8, single diastereomer).

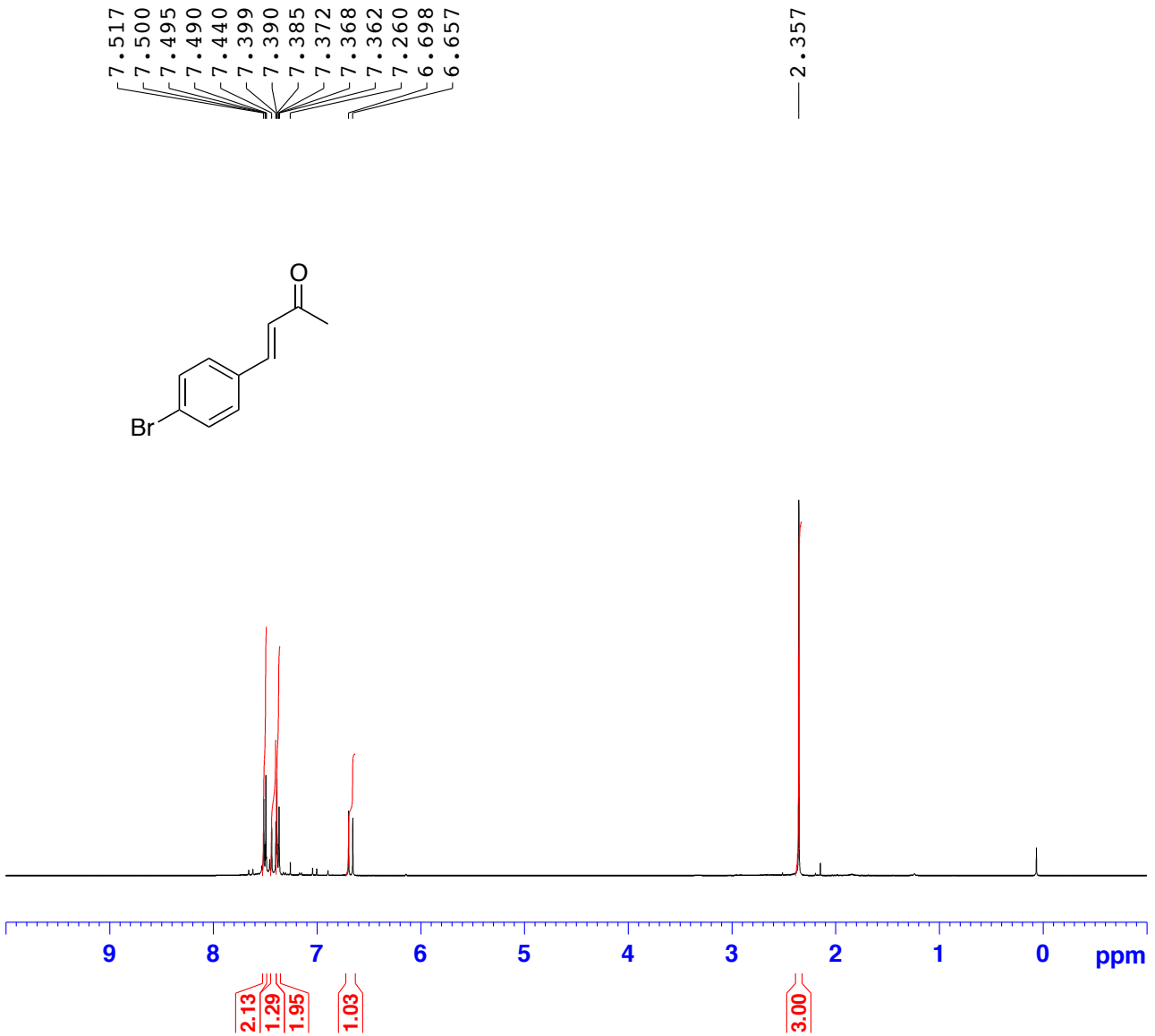
_N_-(4-Bromobenzyl)-6-(4-bromophenyl)-2-(4-chlorophenyl)-2-(trifluoromethyl)tetrahydro-2_H_-pyran-4-amine (8)

Colorless oil. $[\alpha]_D^{25}$ –23.4 (c = 2.70, $CHCl_3$, er 92:8 determined by the HPLC analysis).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.78-1.88 (m, 2H, CHC$\underline{H_2}$CHNH), 2.39 (dd, J = 4.0 Hz, 14.4 Hz, 1H, CF_3CC$\underline{H}$HC=O), 2.57 (dd, J = 3.2 Hz, 14.4 Hz, 1H, CF_3CC$\underline{H}$HC=O), 3.34 (m 1H, C$\underline{H}$NH), 3.60 (d, J = 14.0 Hz, 1H, C$\underline{H}$HPh), 3.66 (d, J = 14.0 Hz, 1H, C$\underline{H}$HPh), 4.87 (dd, J = 3.6 Hz, 10.6 Hz, 1H, OC$\underline{H}$), 6.86 (d, J = 8.0 Hz, 2H Ar$\underline{H}$), 7.23 (d, J = 8.4 Hz, 2H Ar$\underline{H}$), 7.36-7.40 (m, 4H, Ar$\underline{H}$), 7.47-7.52 (m, 4H, Ar$\underline{H}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.5, 37.5, 49.4, 50.6, 68.5, 78.3 (q, $J_{C,F}$ = 28 Hz), 120.8, 121.6, 124.5 (q, $J_{C,F}$ = 282 Hz), 127.4, 128.6, 129.3, 131.4, 131.6, 134.79, 134.80, 138.9, 140.6. HRMS (ESI) calcd for $C_{25}H_{22}ONBr_2ClF_3$ ($[M + H]^+$) 601.9678, found 601.9703. HPLC (Daicel Chiralpak IA, hexane/_i_-PrOH = 99:1, 0.6 mL/min, λ = 220 nm): t_R (major enantiomer) = 18.6 min, t_R (minor enantiomer) = 23.0 min.

7. References

1. H.-L. Cui, F. Tanaka, *Chem. Eur. J.*, 2013, **19**, 6213.
2. Y. Lu, F. Zhong, X. Han, *Adv. Synth. Catal*., 2010, **352**, 2778..
3. X.-J. Zhang, S.-P. Liu, J.-H. Lao, G.-J. Du, M. Yan, A. S. C. Chan, *Tetrahedron: Asymmetry*, 2009, **20**, 1451..
4. H. Sun, X. Wang, G. Li, L. Zhang, J. Liu, L. Zhao, *RSC Adv.* 2015, **5**, 29456.
5. T. Stern, S. Rückbrod, C. Czekelius, C. Donner, H. Brunner, *Adv. Synth. Catal.*, 2010, **352**,1983.
6. H.-L. Cui, P. V. Chouthaiwale, F. Yin, F. Tanaka, *Asian J. Org. Chem.*, 2016, **5**, 153.

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EXPNO                     20
PROCNO                     1

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PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    31.13
DW                   62.400 usec
DE                    6.50 usec
TE                   300.2 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300094 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
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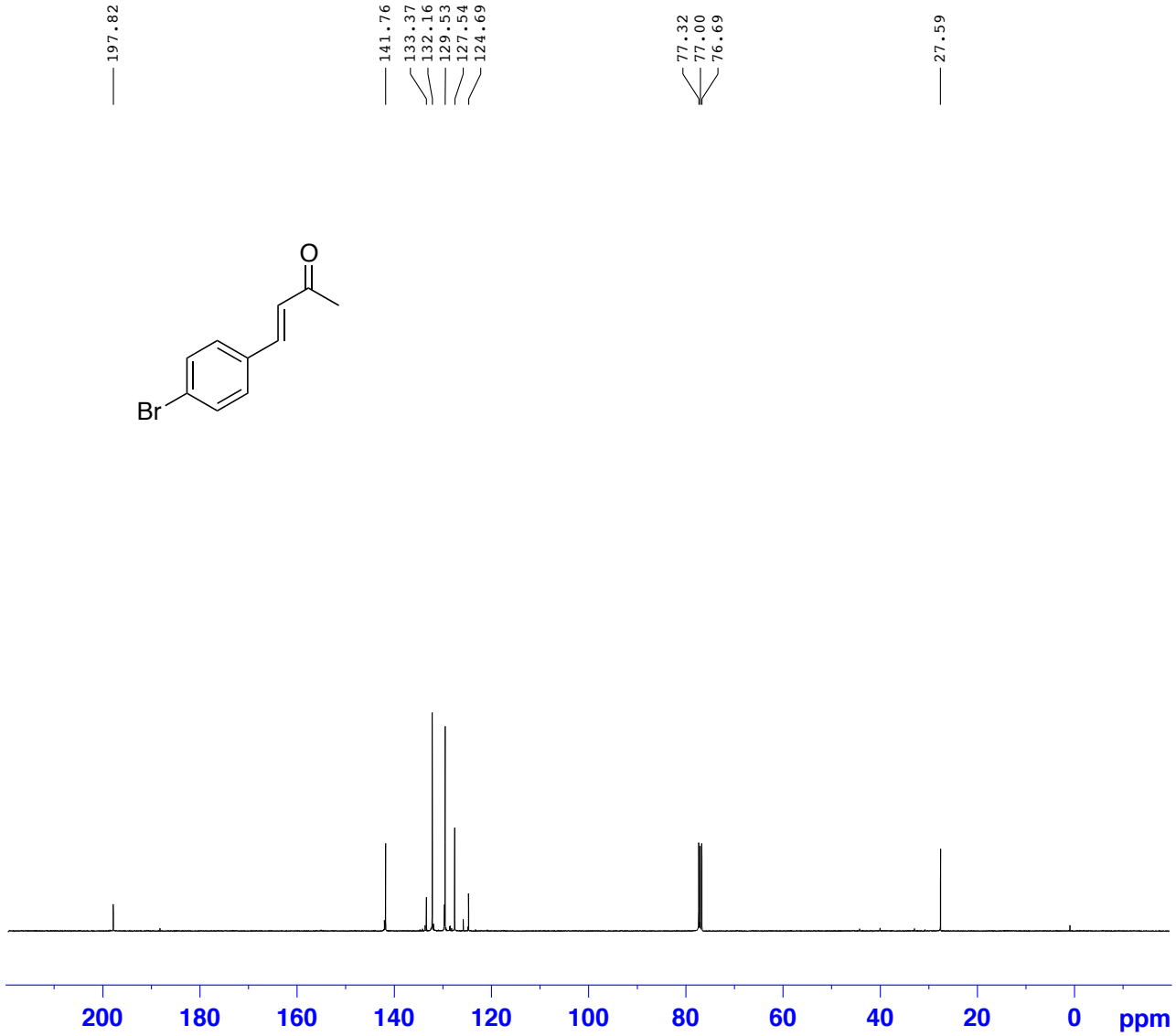


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EXPNO                    21
PROCNO                    1

F2 - Acquisition Parameters
Date_              20160412
Time                  11.40
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1500
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                   20.800 usec
DE                    6.50 usec
TE                   301.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                   13C
P1                   10.00 usec
PLW1          70.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           8.00000000 W
PLW12          0.28125000 W
PLW13          0.28125000 W

F2 - Processing parameters
SI                    32768
SF            100.6127739 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
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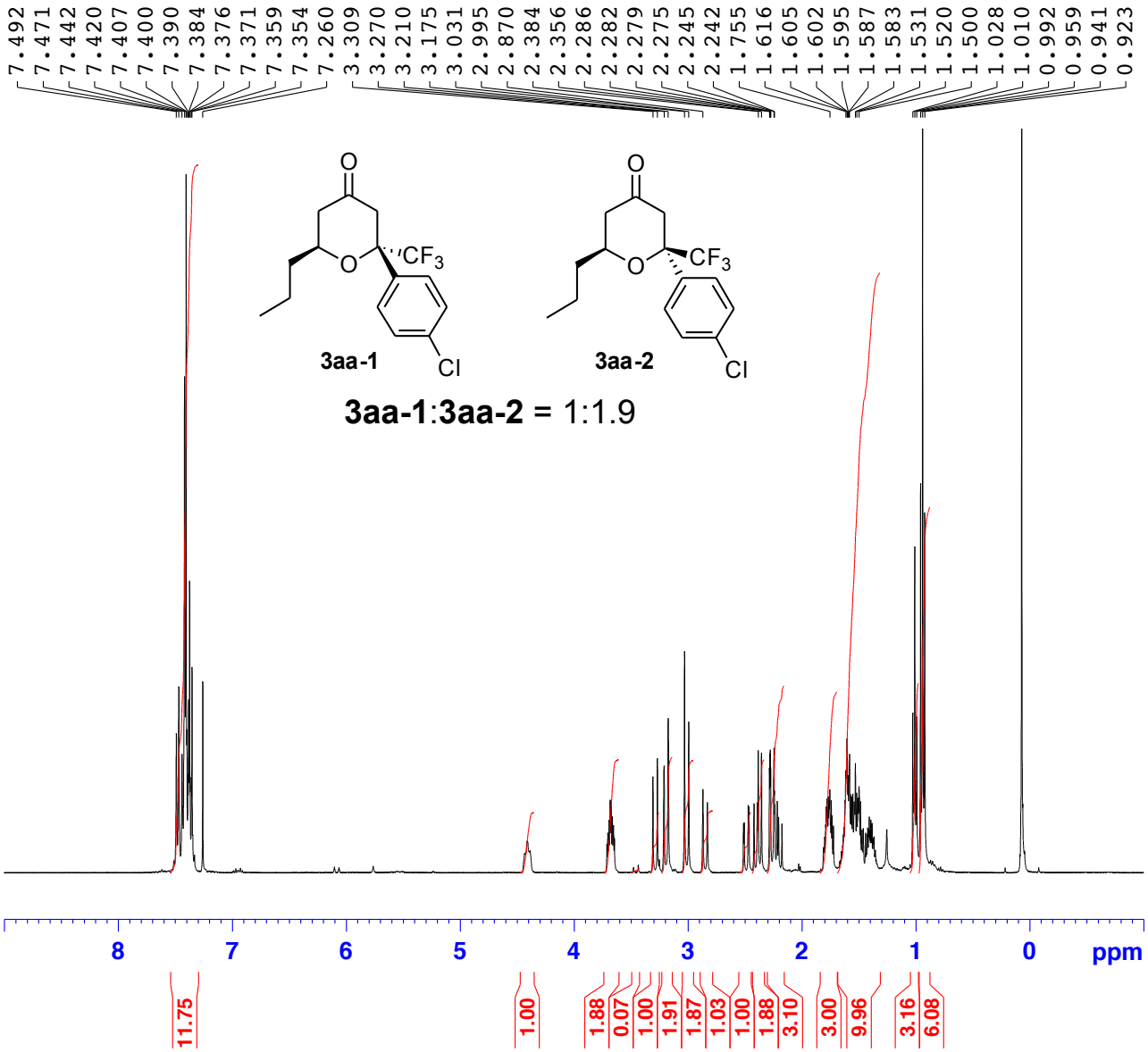


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EXPNO                    40
PROCNO                    1

F2 - Acquisition Parameters
Date_             20150122
Time                 13.50
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    31.13
DW                  62.400 usec
DE                   6.50 usec
TE                  298.5 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                    1H
P1                   15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                      65536
SF            400.1300097 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
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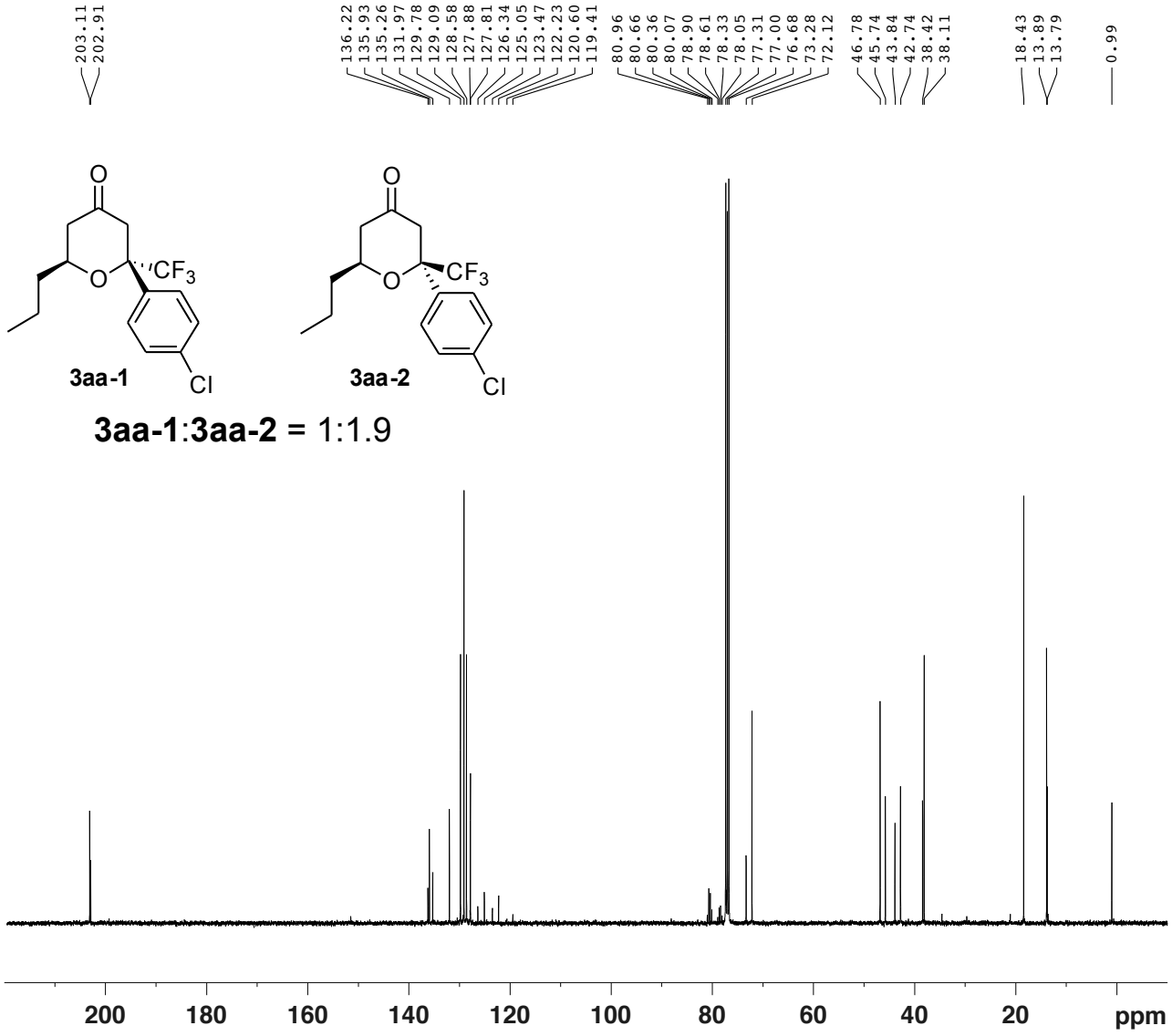


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EXPNO                     60
PROCNO                     1

F2 - Acquisition Parameters
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Time                  16.04
INSTRUM               spect
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PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                   20.800 usec
DE                    6.50 usec
TE                   299.5 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                   1H
CPDPRG[2            waltz16
PCPD2                80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                    32768
SF             100.6127711 MHz
WDW                    EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
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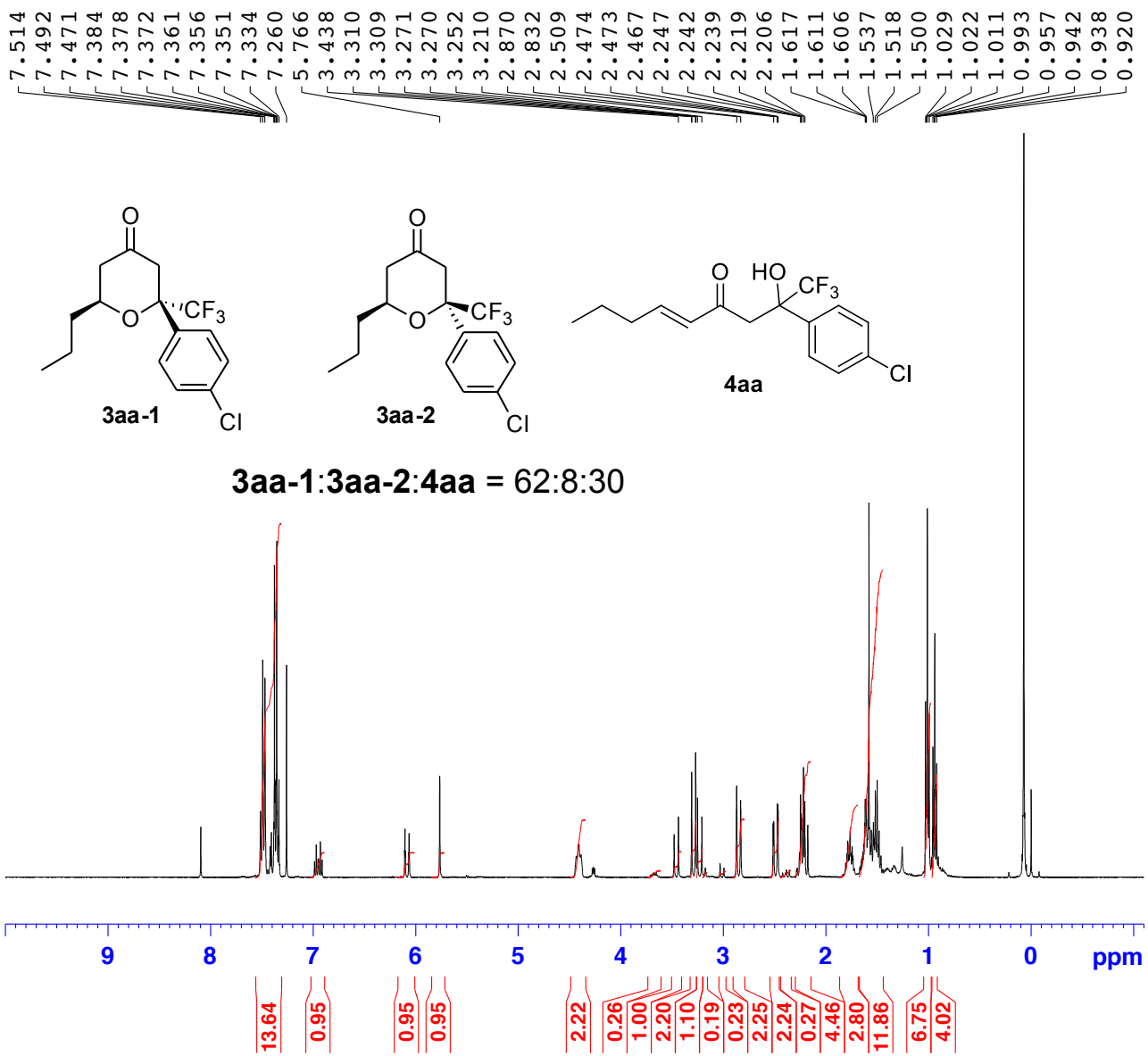


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EXPNO                     40
PROCNO                     1

F2 - Acquisition Parameters
Date_              20140910
Time                  10.23
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    31.13
DW                   62.400 usec
DE                    6.50 usec
TE                   298.3 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300098 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
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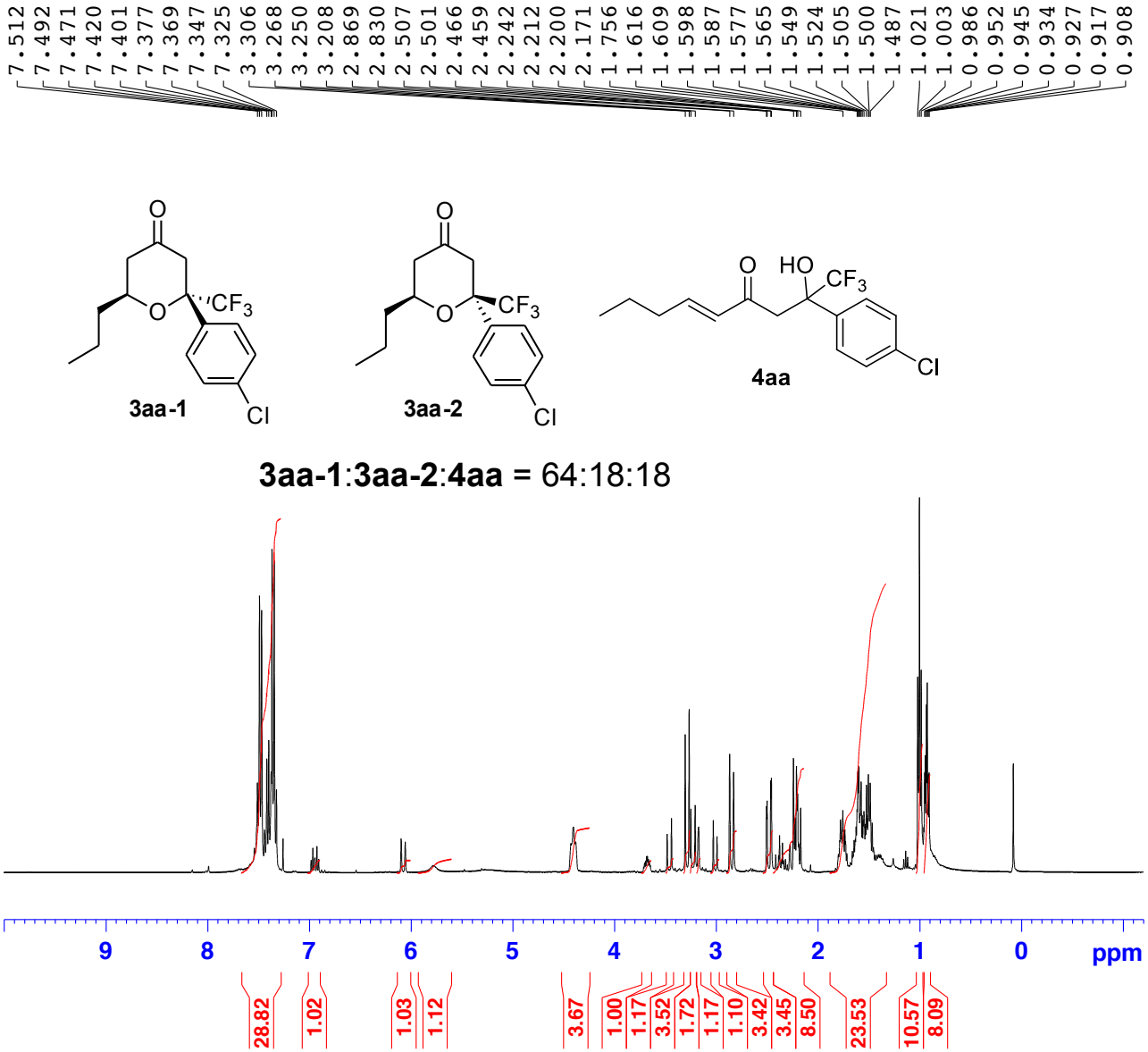


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EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20160405
Time                  12.09
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    19.65
DW                   62.400 usec
DE                    6.50 usec
TE                   300.3 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                      1H
P1                   15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF              400.1300091 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
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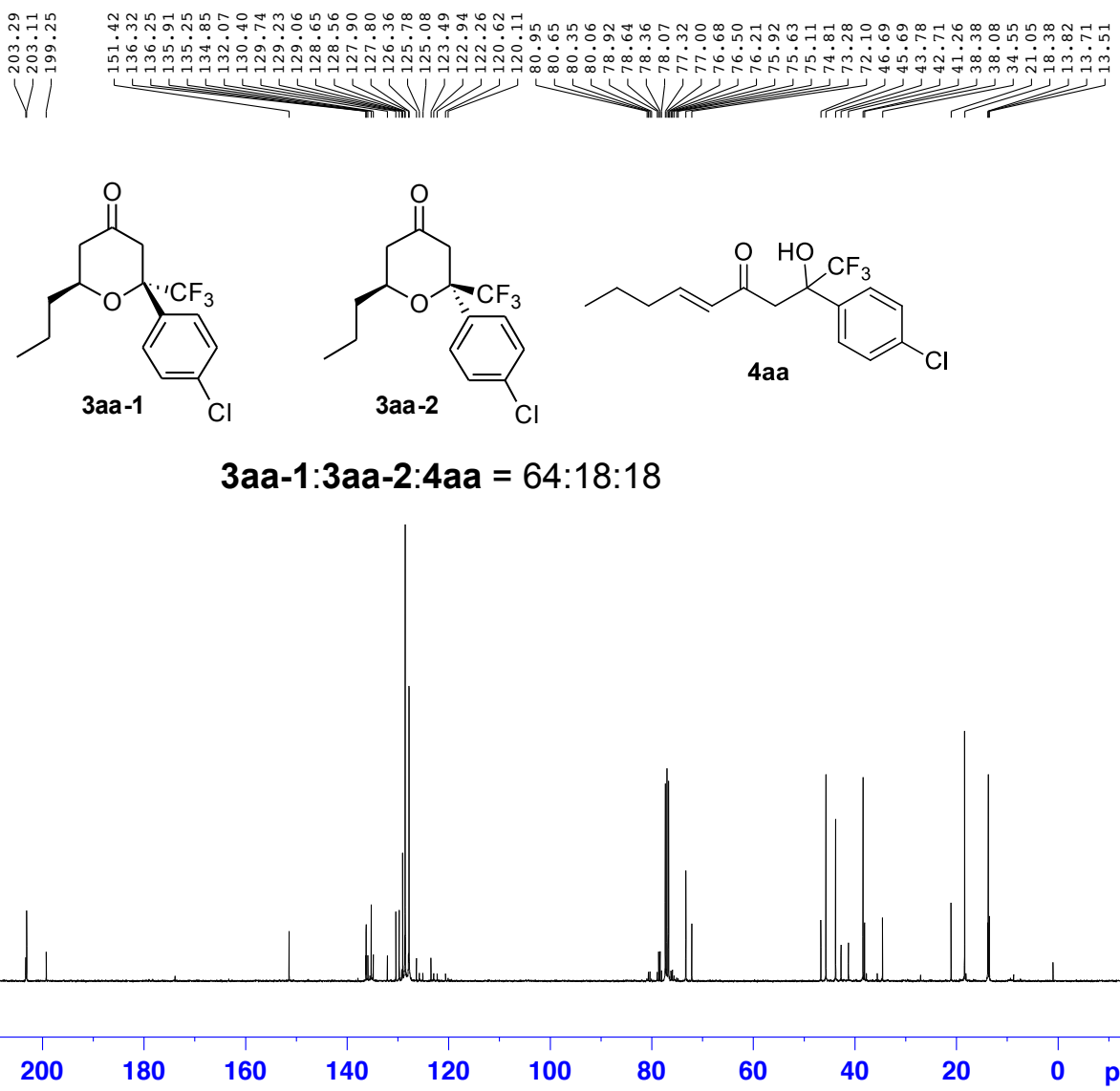


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Current Data Parameters
NAME                 DZ-829
EXPNO                    21
PROCNO                    1

F2 - Acquisition Parameters
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Time                 13.45
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1685
DS                      4
SWH             24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631488 sec
RG                 195.88
DW                 20.800 usec
DE                  6.50 usec
TE                 302.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          70.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                  1H
CPDPRG[2           waltz16
PCPD2               80.00 usec
PLW2           8.00000000 W
PLW12          0.28125000 W
PLW13          0.28125000 W

F2 - Processing parameters
SI                   32768
SF            100.6127710 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
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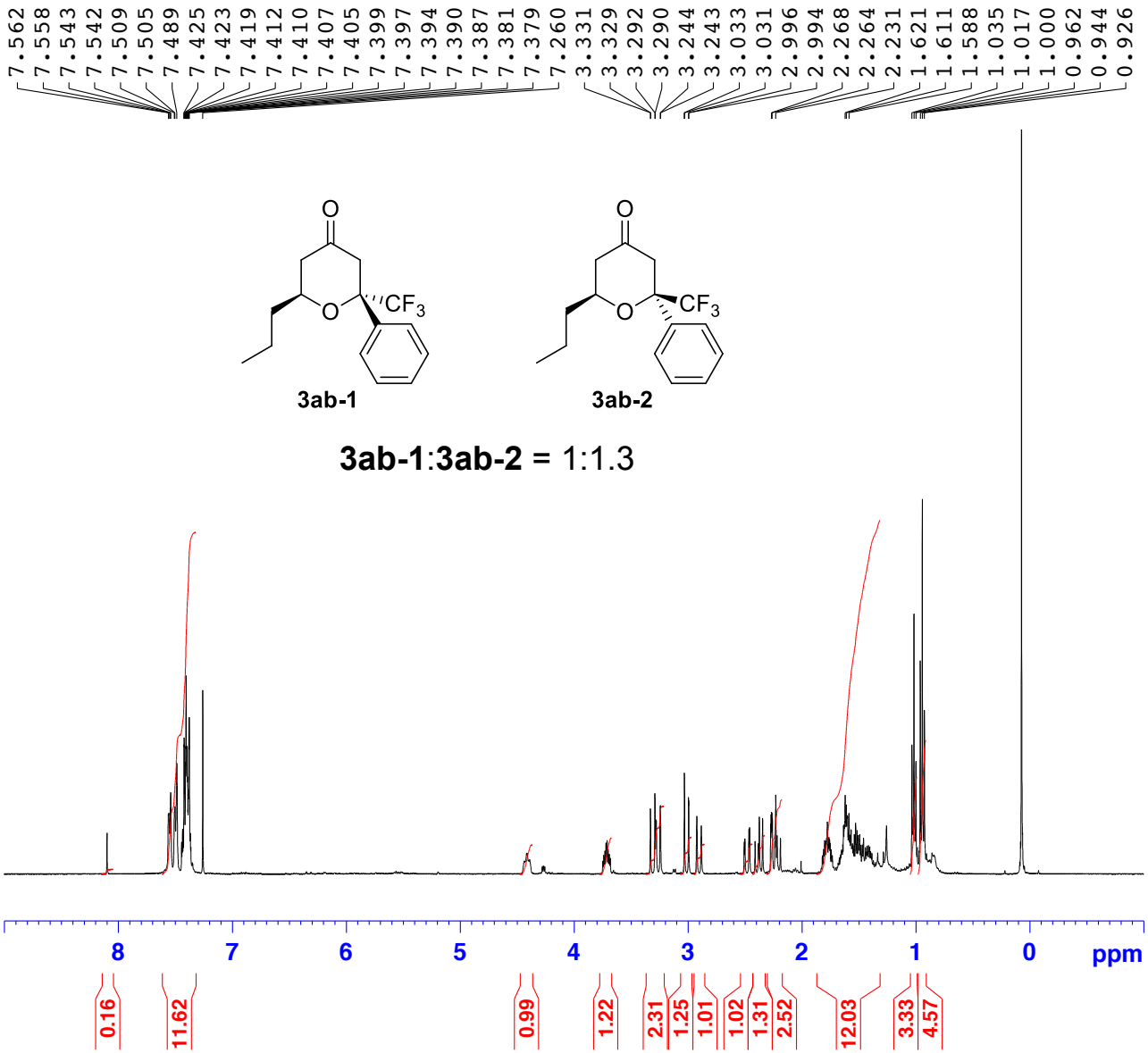


```
Current Data Parameters
NAME                  DZ-616
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_               20150126
Time                   13.05
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                     31.13
DW                   62.400 usec
DE                    6.50 usec
TE                   298.4 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300097 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
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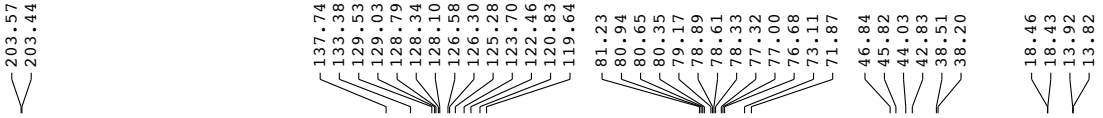
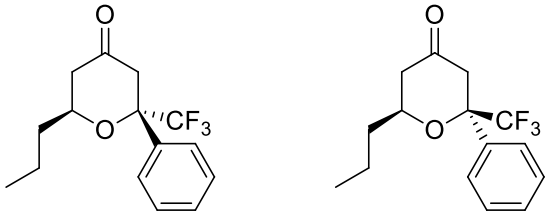
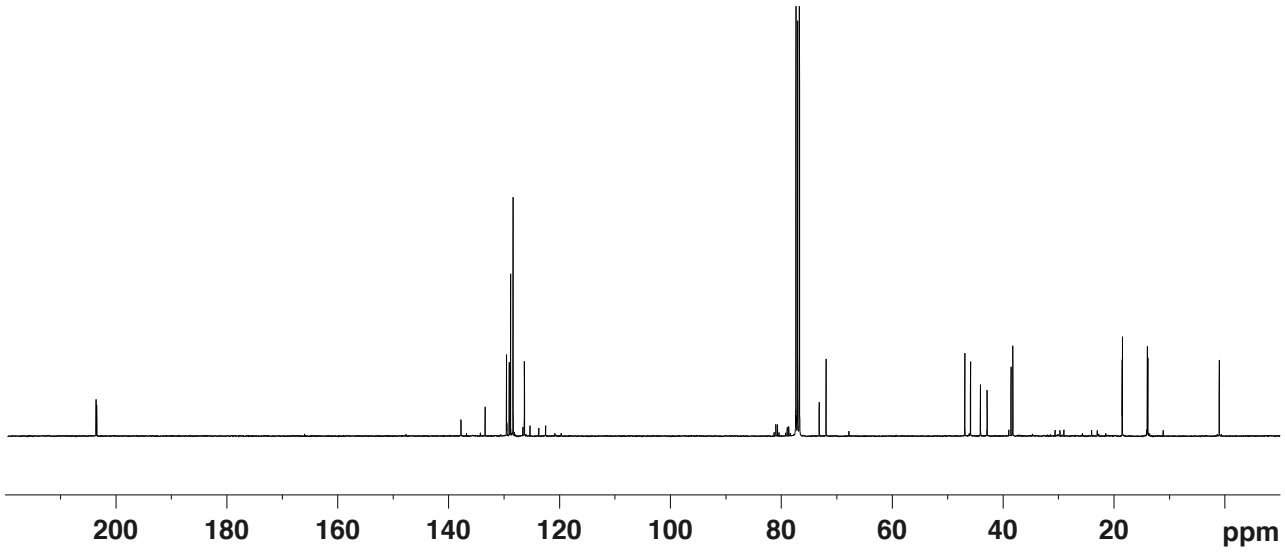




3ab-1

3ab-2

3ab-1:**3ab-2** = 1:1.3

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Current Data Parameters
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EXPNO                   40
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150127
Time                  8.38
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                  15000
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631488 sec
RG                 195.88
DW                20.800 usec
DE                 6.50 usec
TE                299.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                  13C
P1                 10.00 usec
PLW1          70.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                  1H
CPDPRG[2           waltz16
PCPD2              80.00 usec
PLW2           8.00000000 W
PLW12          0.28125000 W
PLW13          0.28125000 W

F2 - Processing parameters
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SF            100.6127706 MHz
WDW                  EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
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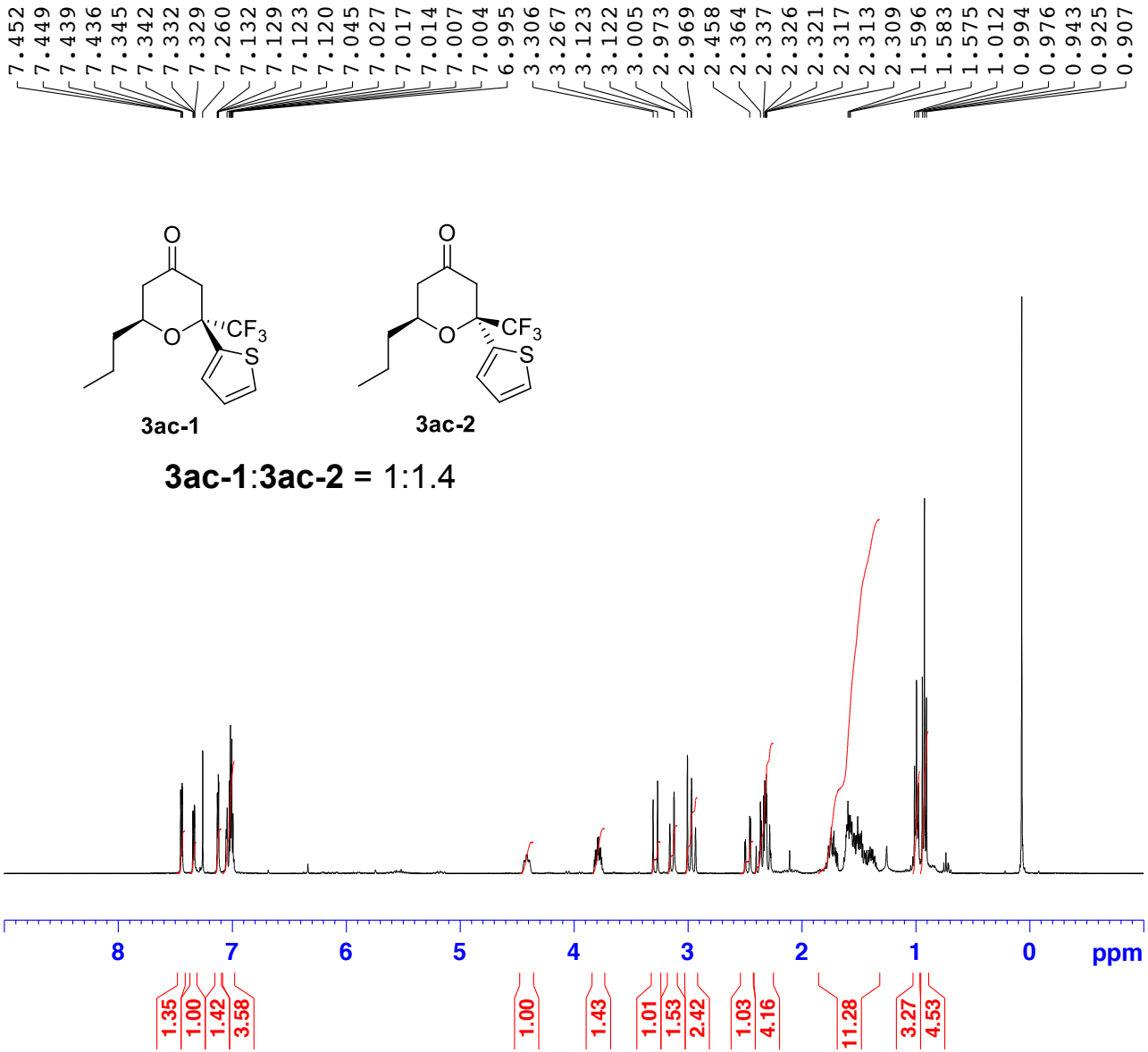


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Current Data Parameters
NAME                  DZ-625
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150130
Time                  15.44
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894465 sec
RG                    31.13
DW                   62.400 usec
DE                    6.50 usec
TE                   298.3 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                      1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300098 MHz
WDW                      EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
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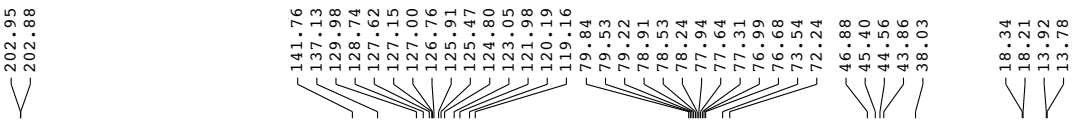
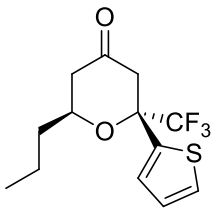
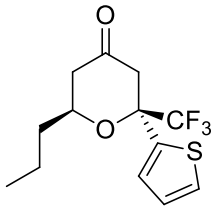




3ac-1



3ac-2

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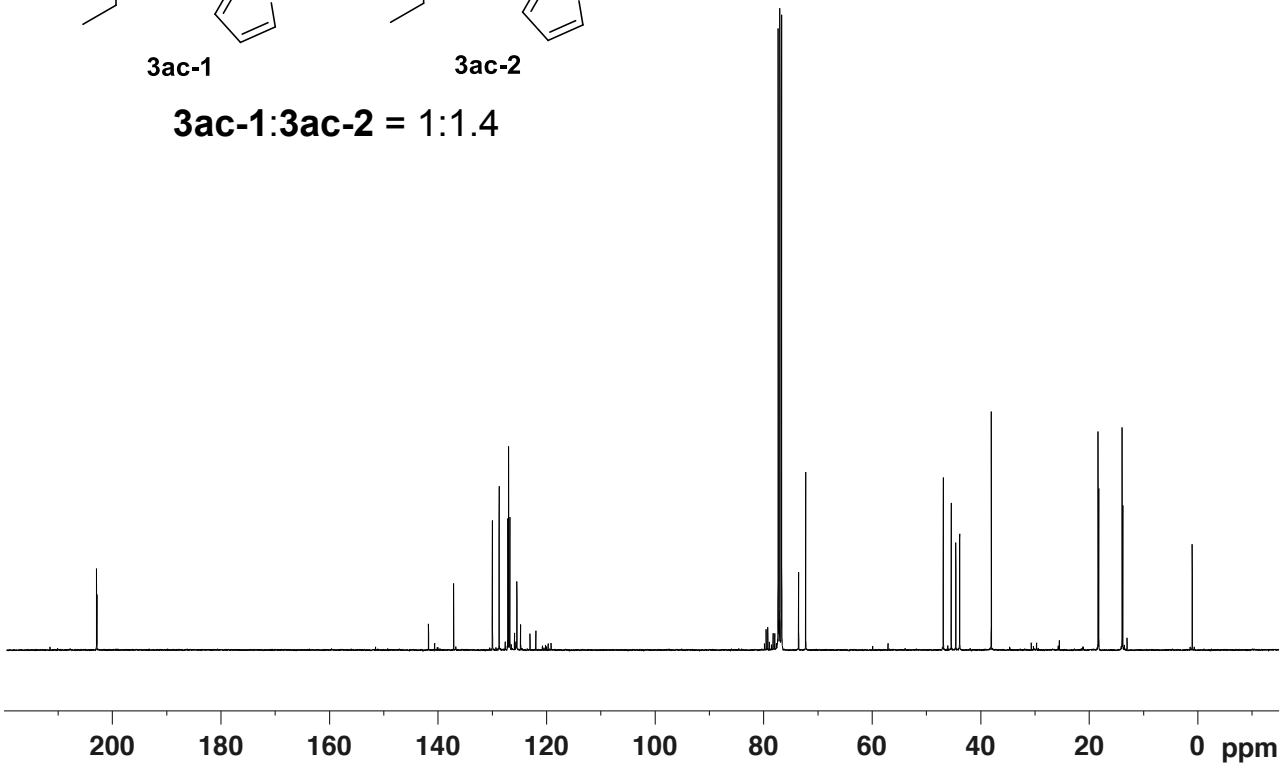


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Current Data Parameters
NAME                  DZ-625
EXPNO                     40
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150131
Time                   8.55
INSTRUM               spect
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PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    15000
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                  20.800 usec
DE                   6.50 usec
TE                   299.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                   1H
CPDPRG[2            waltz16
PCPD2                80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                    32768
SF             100.6127713 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
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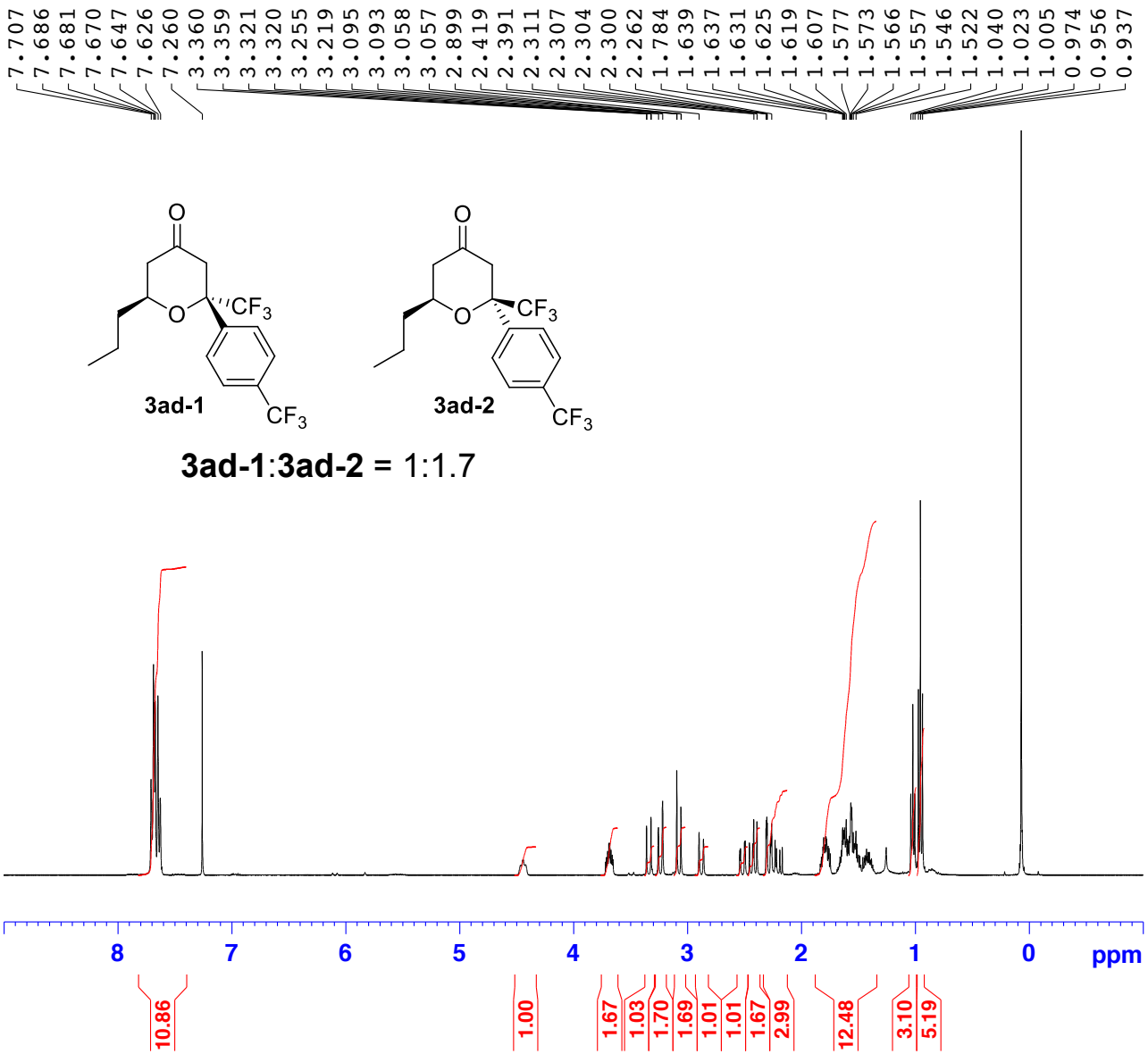


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Current Data Parameters
NAME                  DZ-634
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150205
Time                  18.27
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    54.59
DW                   62.400 usec
DE                    6.50 usec
TE                   298.2 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                    15.00 usec
PLW1            8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300099 MHz
WDW                      EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```
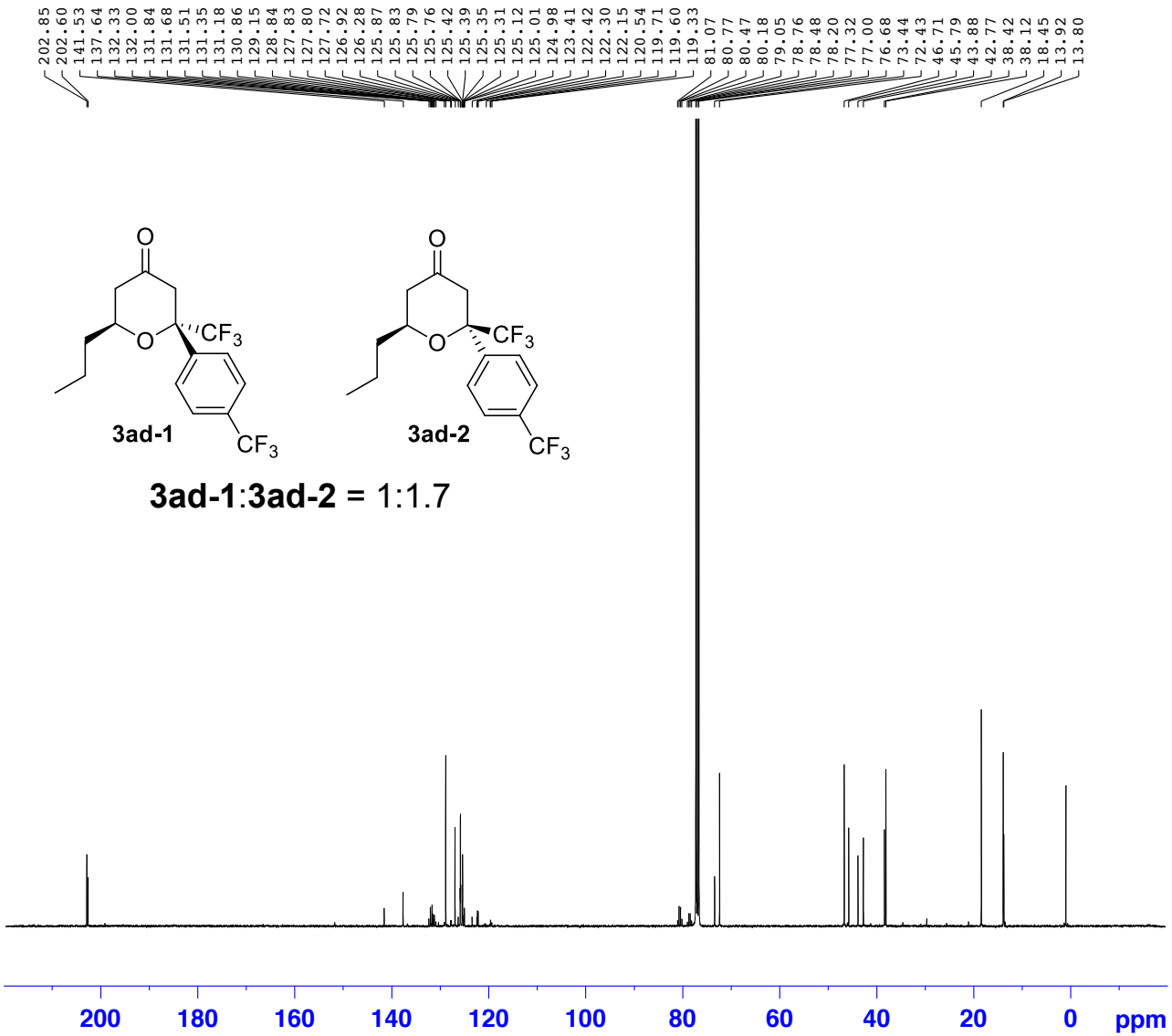
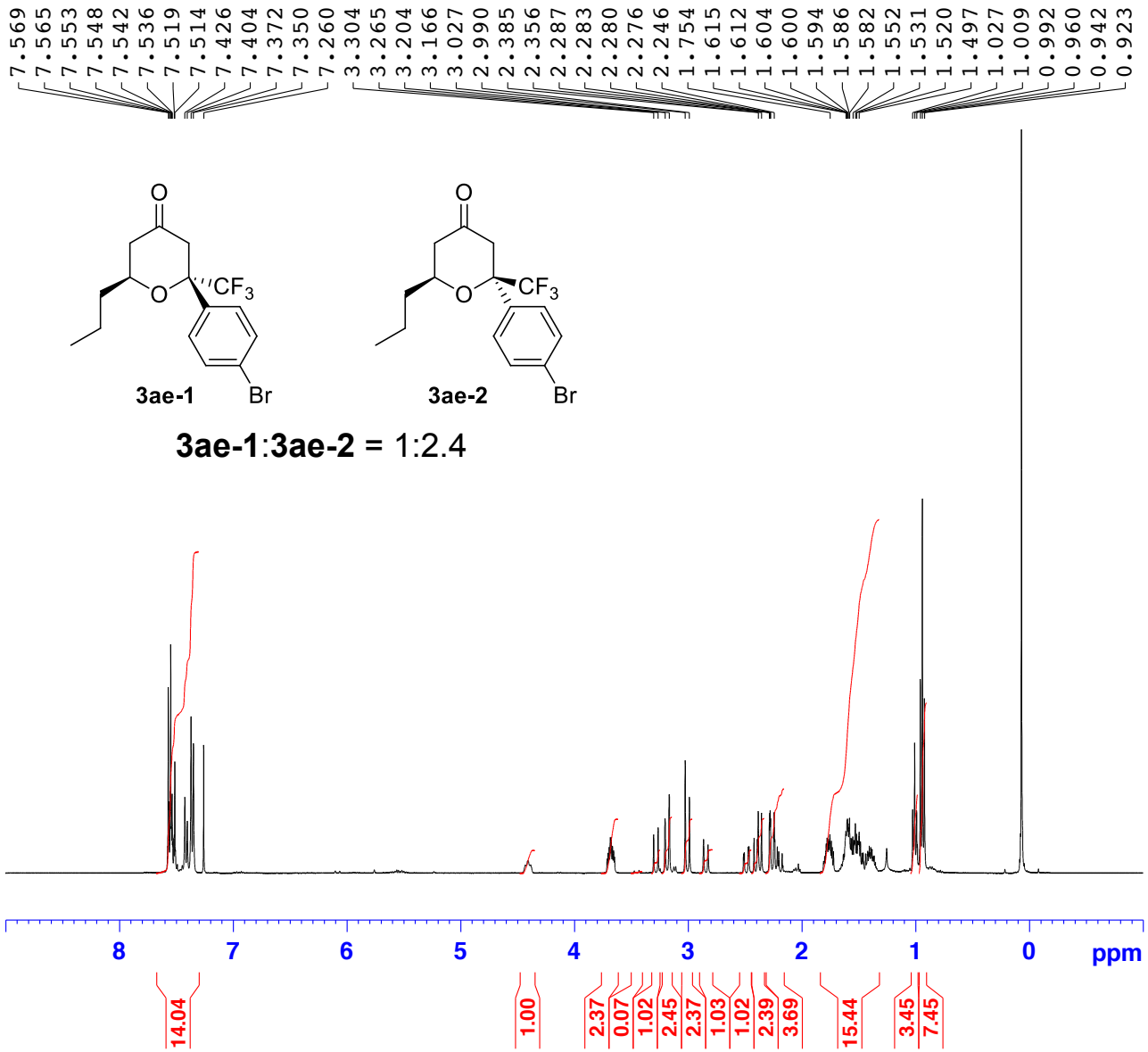
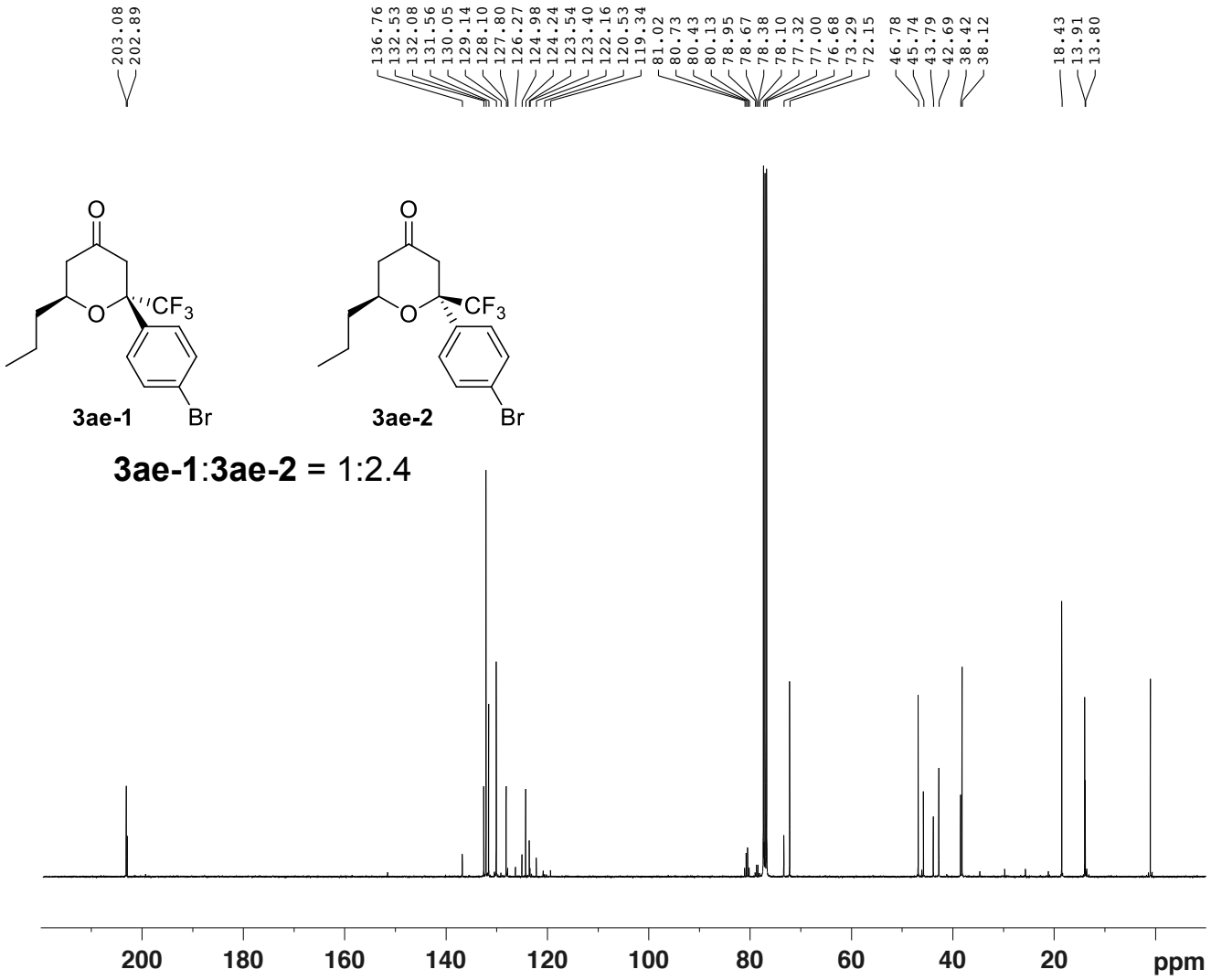



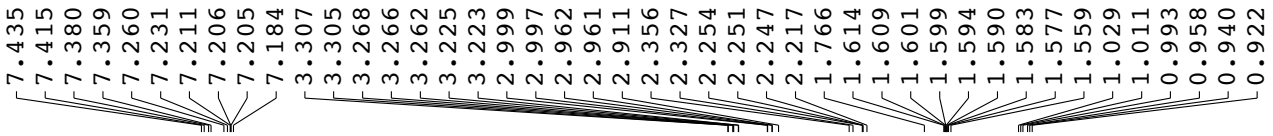

```
Current Data Parameters
NAME                 DZ-634
EXPNO                    30
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150207
Time                   9.03
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    15000
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                   20.800 usec
DE                    6.50 usec
TE                   299.4 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                    32768
SF             100.6127695 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

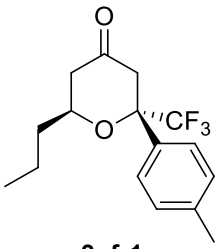



```
Current Data Parameters
NAME                  DZ-642
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150213
Time                  13.42
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    31.13
DW                   62.400 usec
DE                    6.50 usec
TE                   298.3 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300097 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

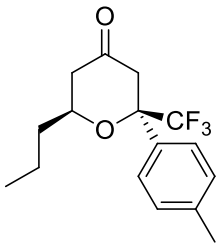



```
Current Data Parameters
NAME                  DZ-642
EXPNO                     50
PROCNO                     1

F2 - Acquisition Parameters
Date_               20150214
Time                    7.50
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT                CDCl3
NS                     15000
DS                         4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                  20.800 usec
DE                   6.50 usec
TE                  299.4 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                     32768
SF             100.6127706 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



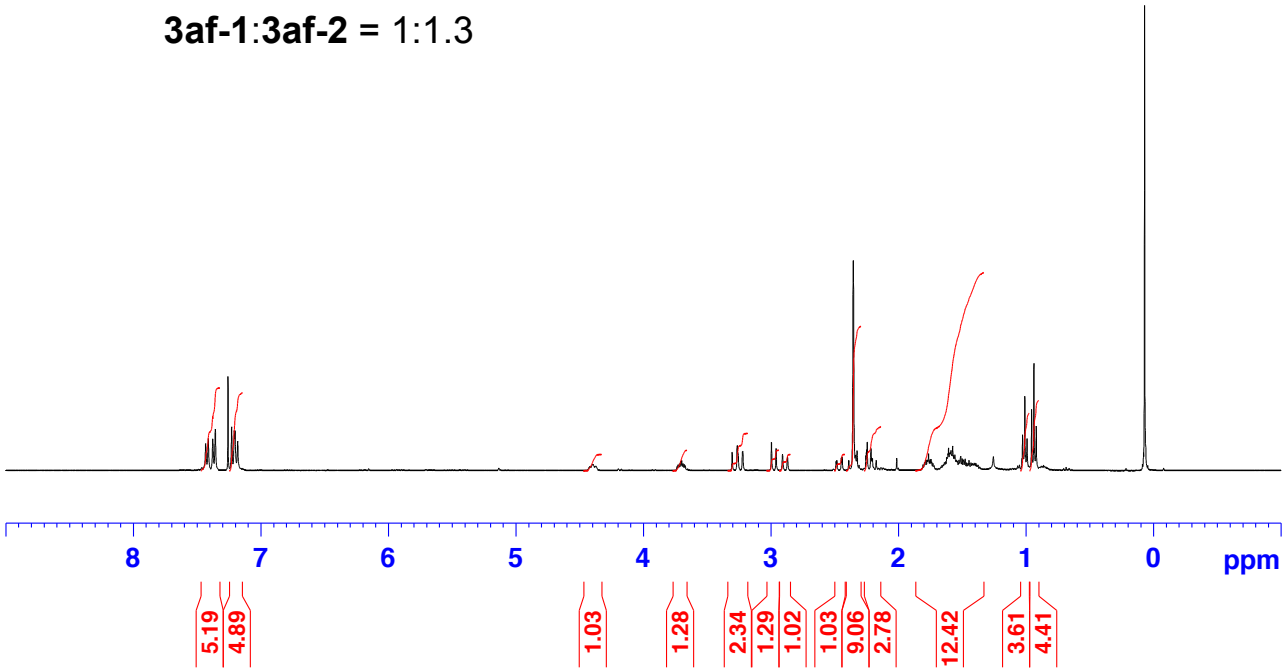


3af-1

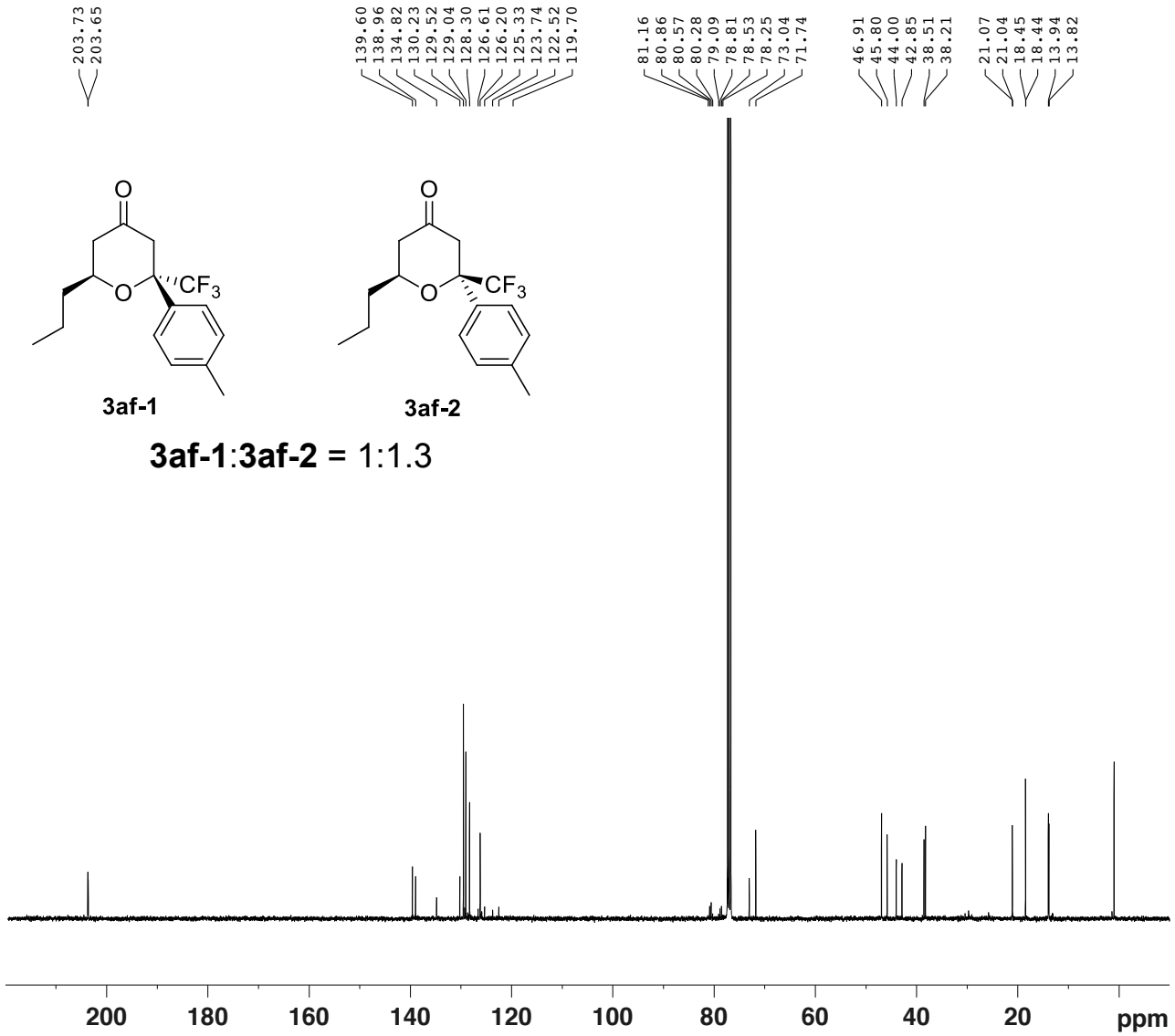


3af-2

3af-1:**3af-2** = 1:1.3

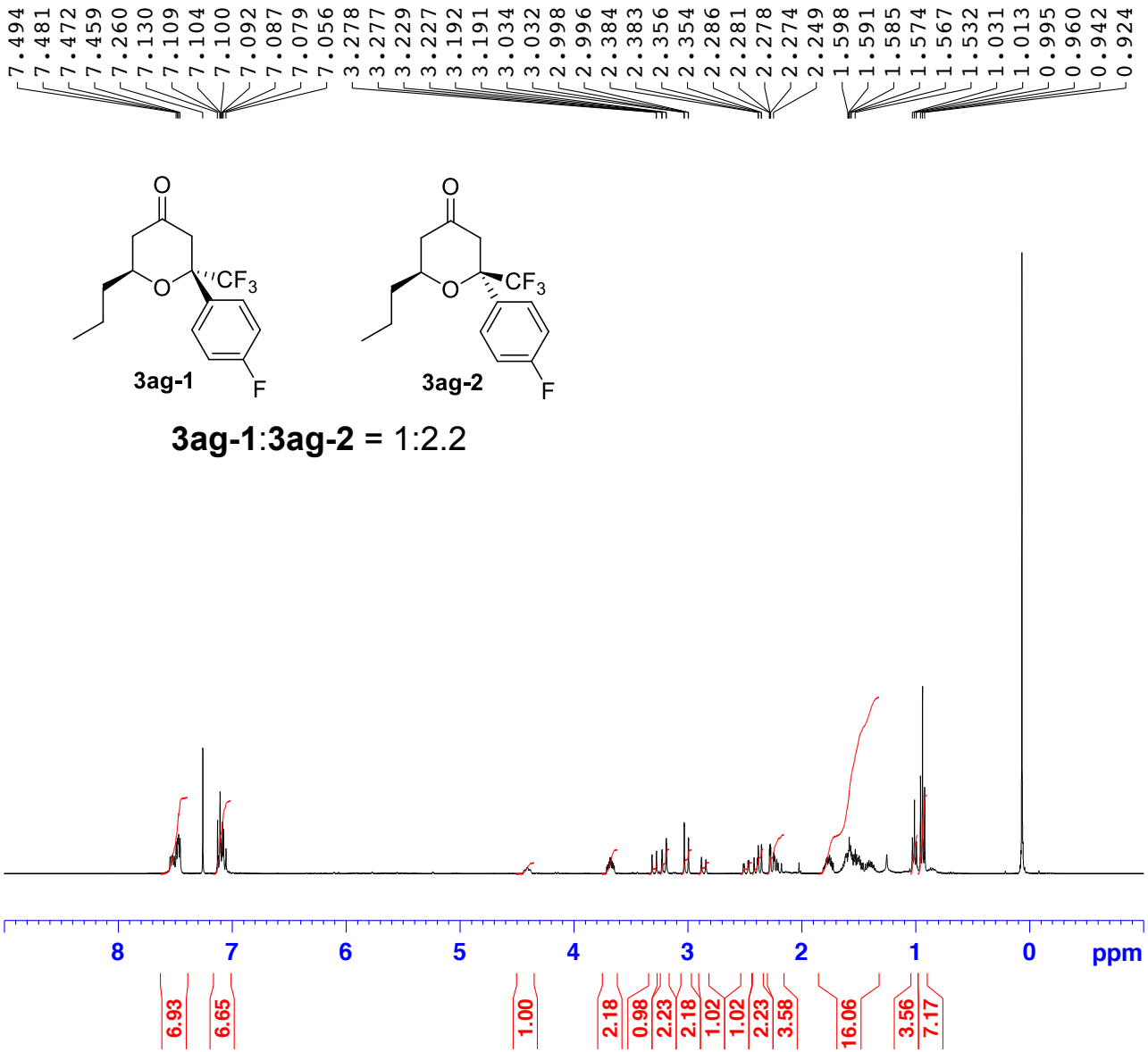



```
Current Data Parameters
NAME                  DZ-717
EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150616
Time                  18.36
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894465 sec
RG                    54.59
DW                   62.400 usec
DE                    6.50 usec
TE          0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                   15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300098 MHz
WDW                     EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.00
```

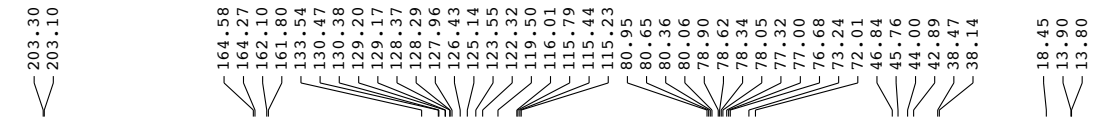


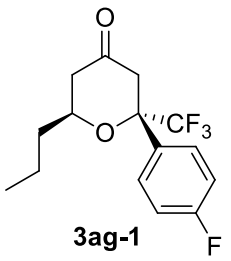
3af-1:**3af-2** = 1:1.3

```
Current Data Parameters
NAME                  DZ-717
EXPNO                     40
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150617
Time                  12.23
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     3000
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                   20.800 usec
DE                    6.50 usec
TE          0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                     32768
SF             100.6127706 MHz
WDW                       EM
SSB         0
LB                     1.00 Hz
GB          0
PC                     1.40
```

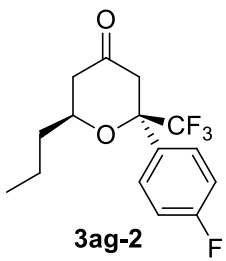



```
Current Data Parameters
NAME                  DZ-632
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150204
Time                  21.26
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    54.59
DW                   62.400 usec
DE                    6.50 usec
TE                   298.6 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300098 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```



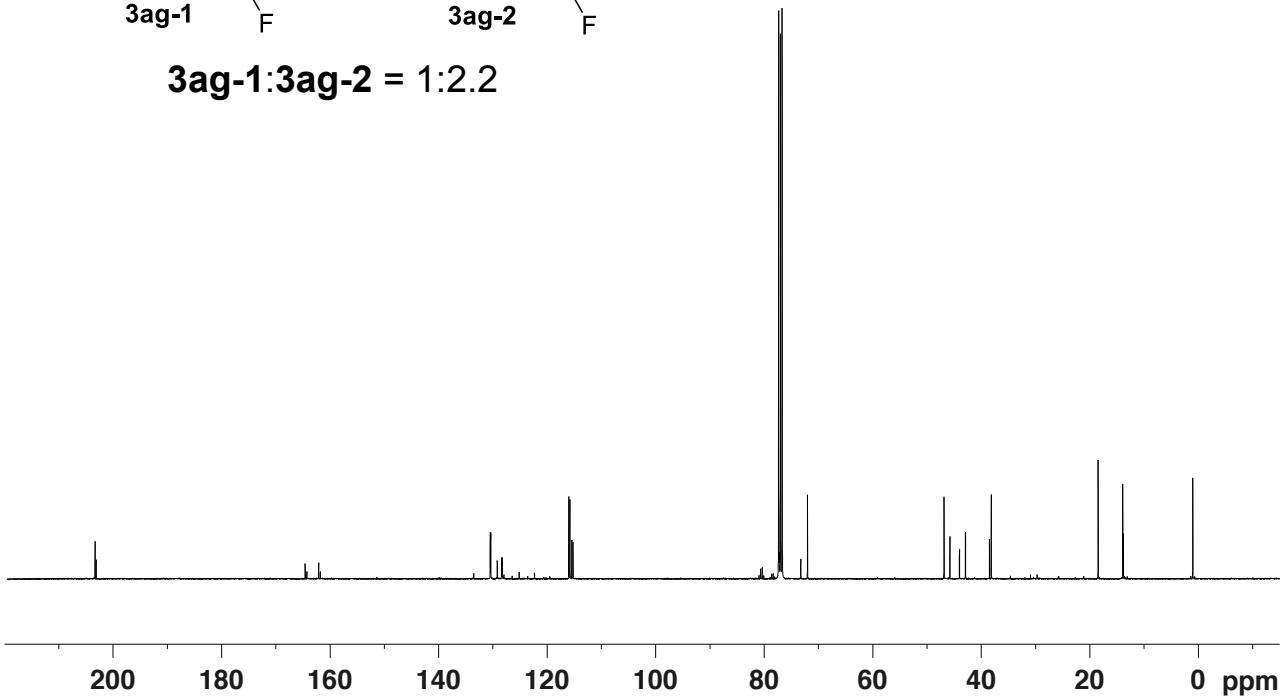


3ag-1

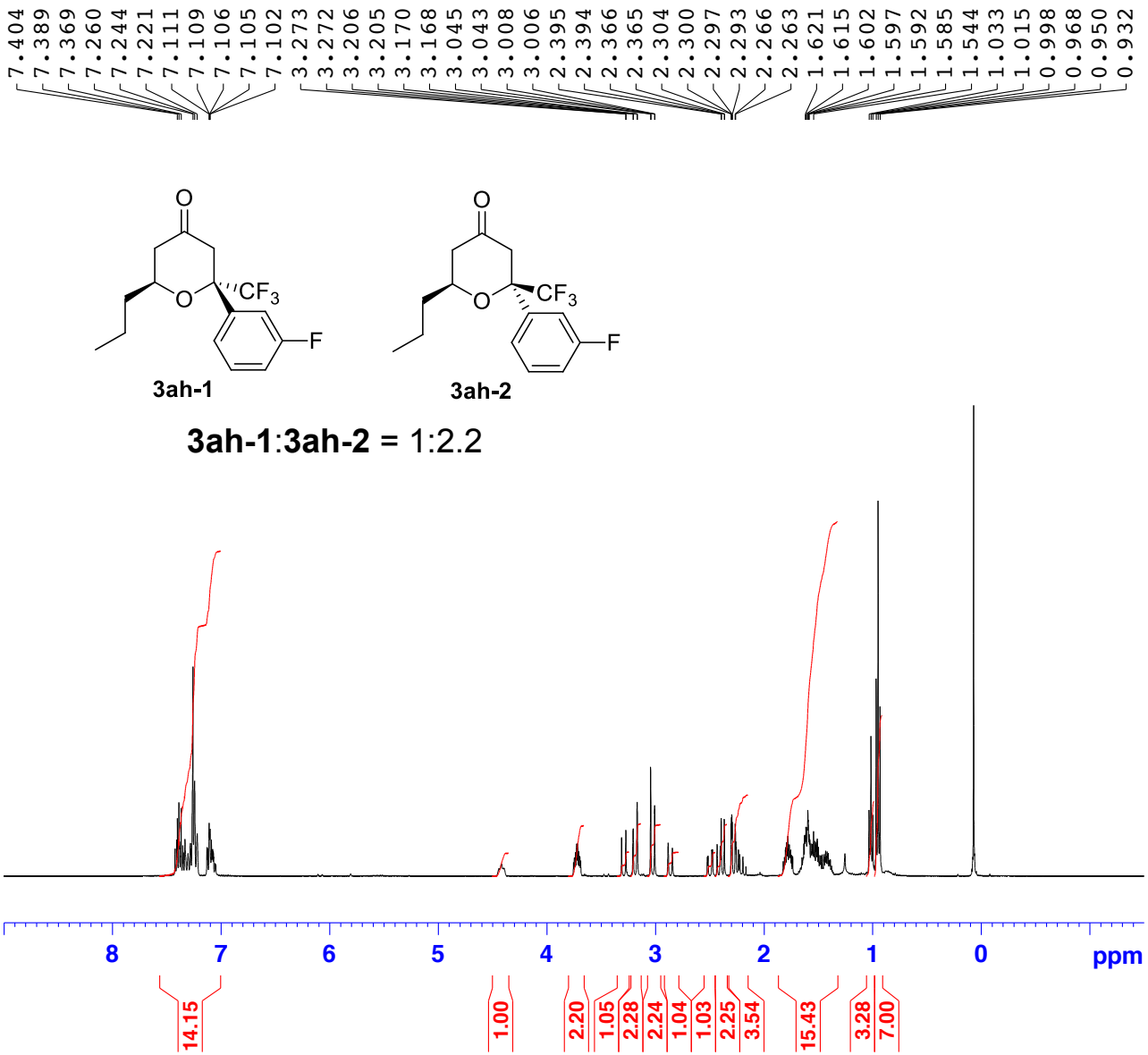


3ag-2

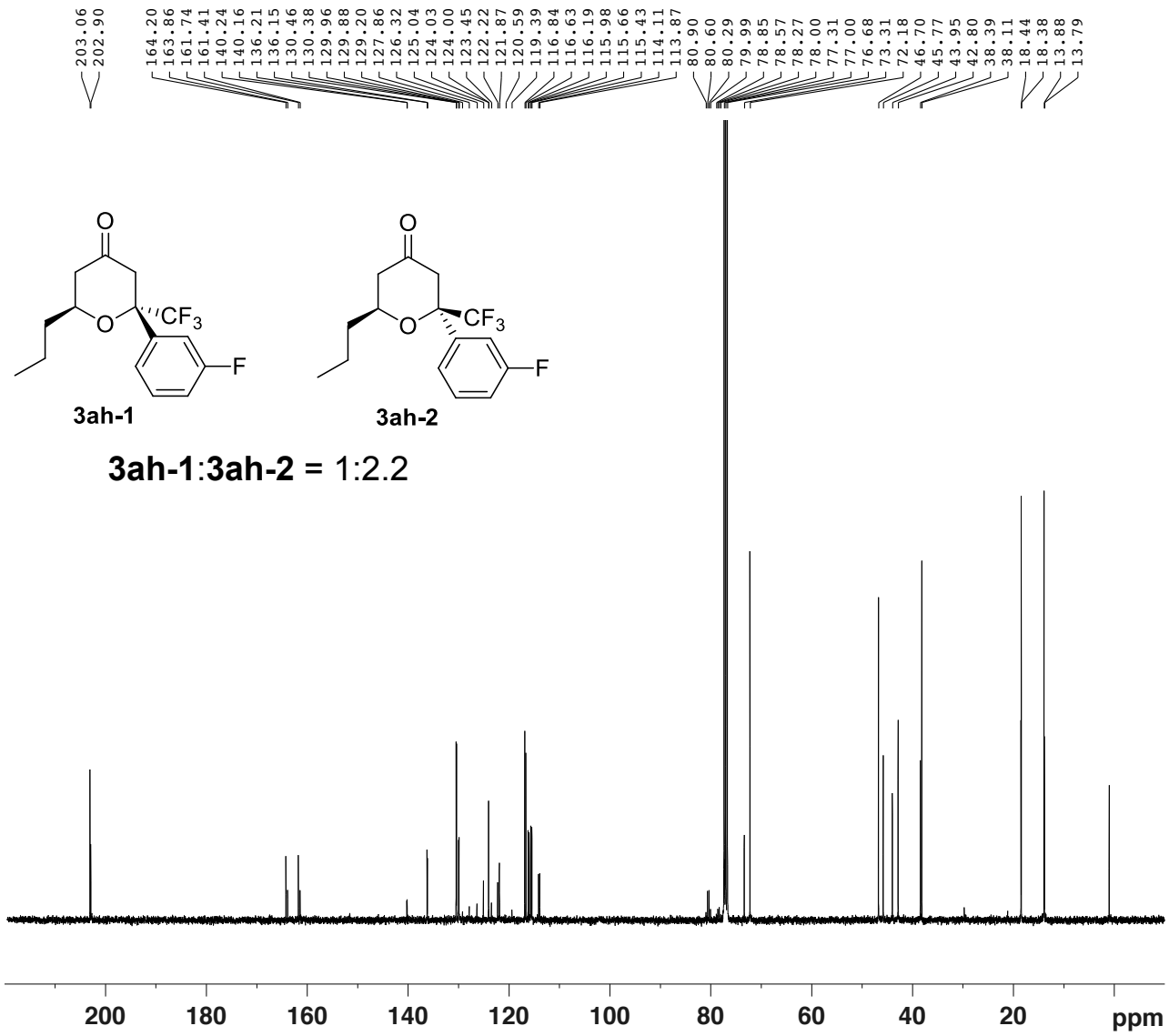
3ag-1:**3ag-2** = 1:2.2



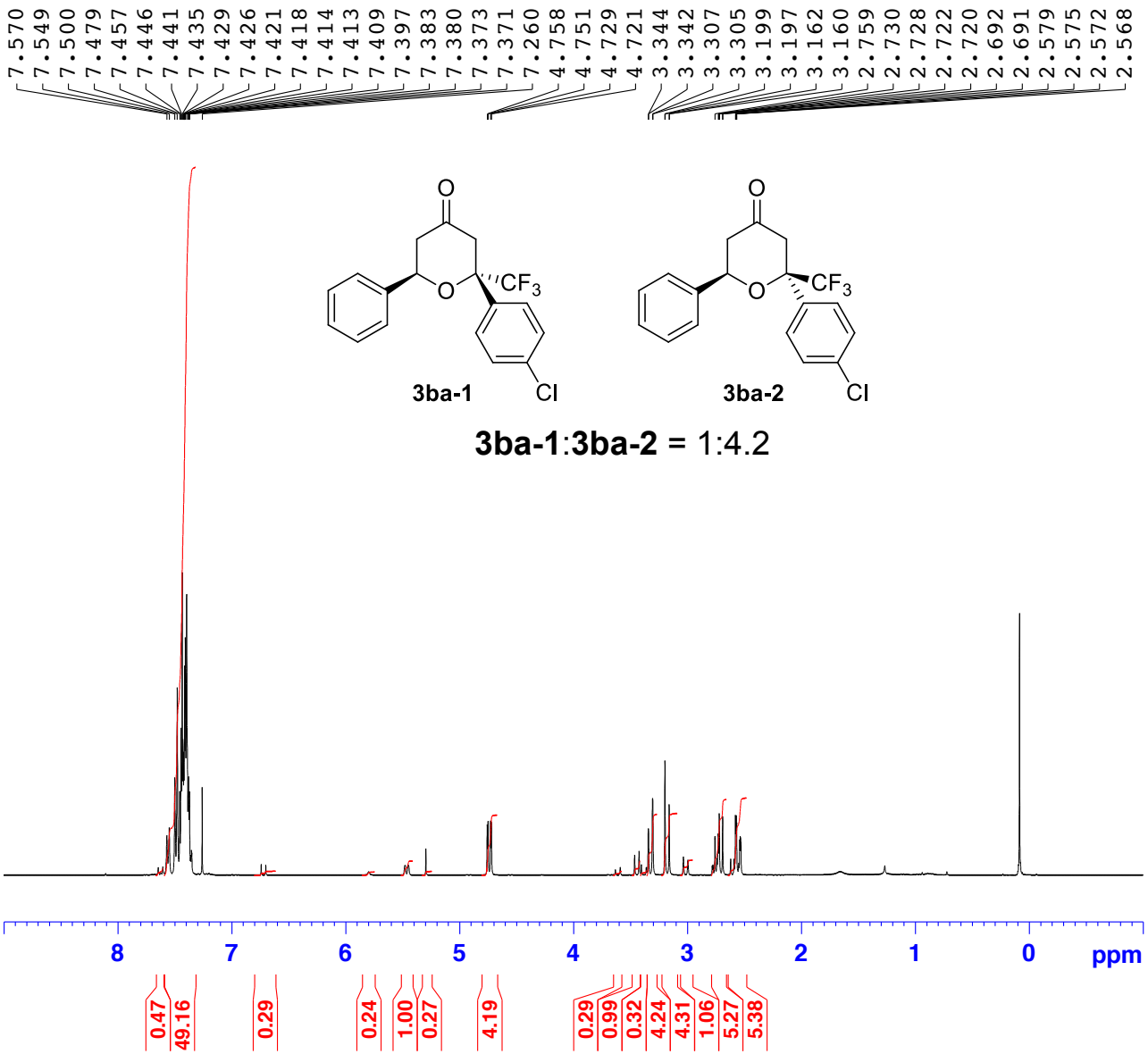

```
Current Data Parameters
NAME                 DZ-632
EXPNO                    40
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150206
Time                   8.51
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT                CDCl3
NS                    15000
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                  20.800 usec
DE                   6.50 usec
TE                  299.4 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                    32768
SF             100.6127699 MHz
WDW                     EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



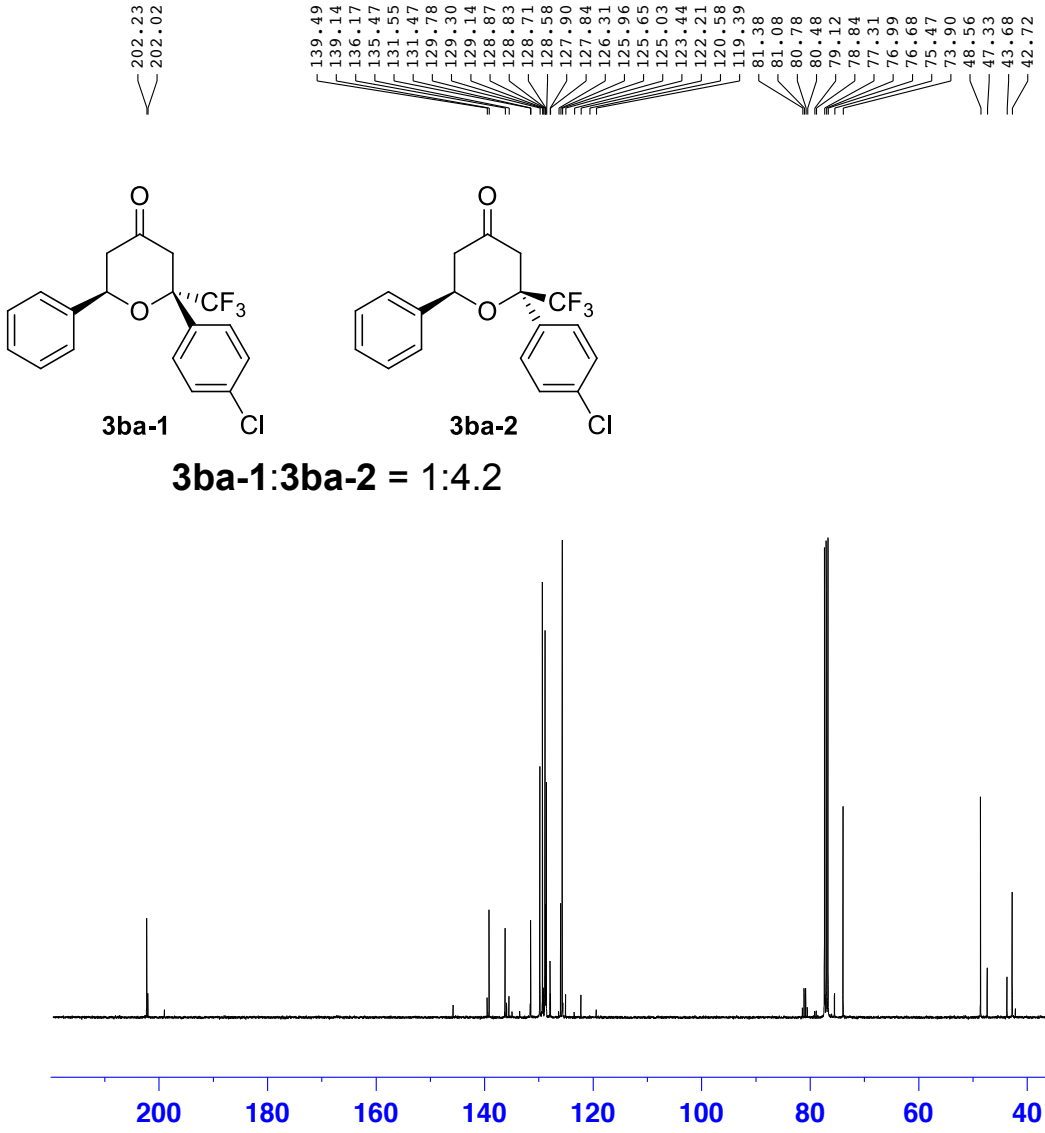

```
Current Data Parameters
NAME                  DZ-725
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150618
Time                  12.47
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    31.13
DW                   62.400 usec
DE                    6.50 usec
TE          0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                   15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI                    65536
SF           400.1300098 MHz
WDW                     EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.00
```



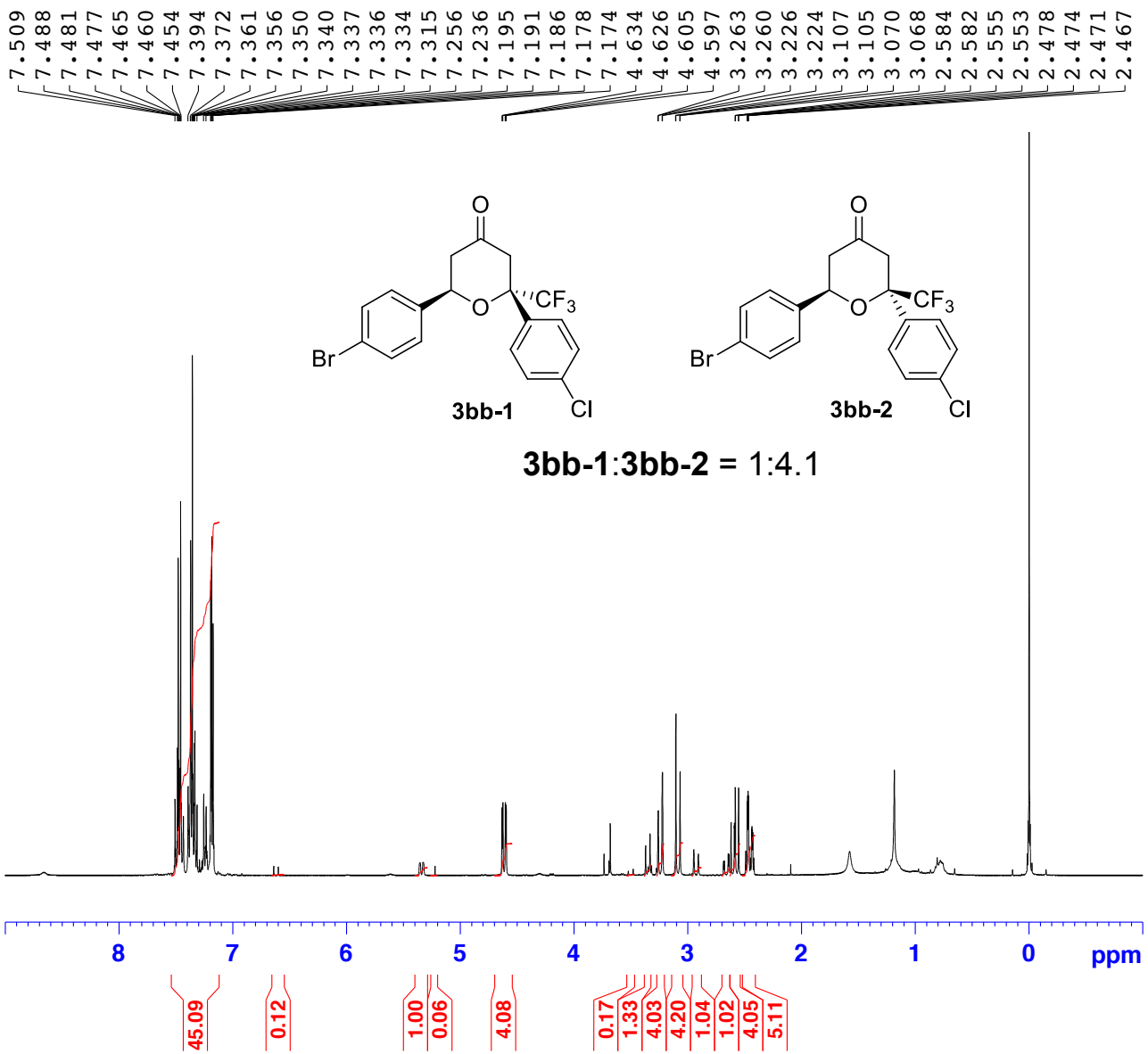

```
Current Data Parameters
NAME                  DZ-725
EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150623
Time                  12.03
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2500
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                   20.800 usec
DE                    6.50 usec
TE          0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                 80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                     32768
SF             100.6127706 MHz
WDW                       EM
SSB         0
LB                     1.00 Hz
GB          0
PC                     1.40
```



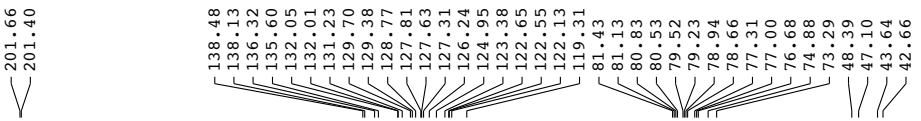

```
Current Data Parameters
NAME                  DZ-733
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150624
Time                  16.44
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894465 sec
RG                    31.13
DW                   62.400 usec
DE                    6.50 usec
TE          0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                   15.00 usec
PLW1            8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300097 MHz
WDW                     EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.00
```

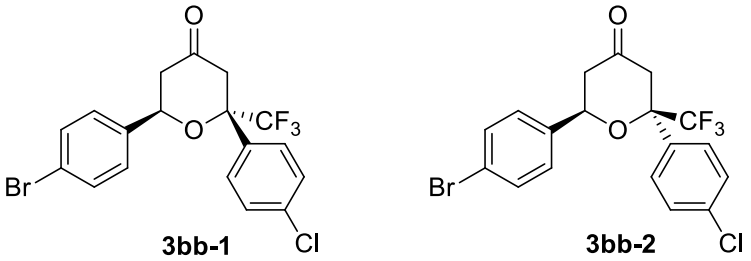



```
Current Data Parameters
NAME                  DZ-733
EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150625
Time                  13.52
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     3000
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                   20.800 usec
DE                    6.50 usec
TE          0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                    32768
SF             100.6127728 MHz
WDW                     EM
SSB         0
LB                     1.00 Hz
GB          0
PC                     1.40
```

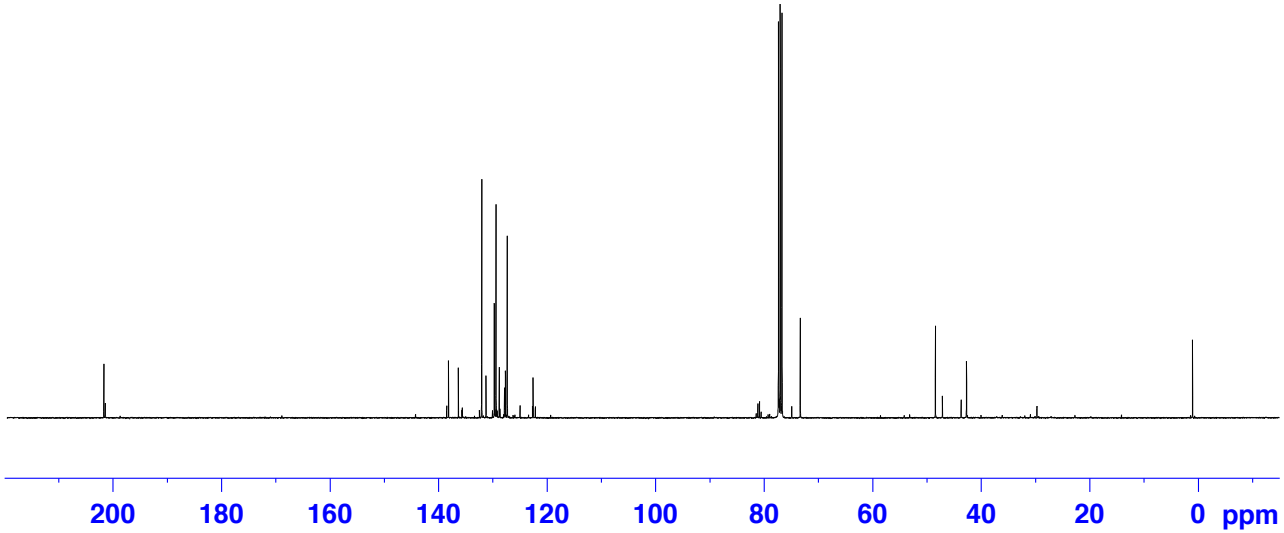



```
Current Data Parameters
NAME                  DZ-766
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150807
Time                  17.28
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    54.59
DW                   62.400 usec
DE                    6.50 usec
TE                   298.8 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300391 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

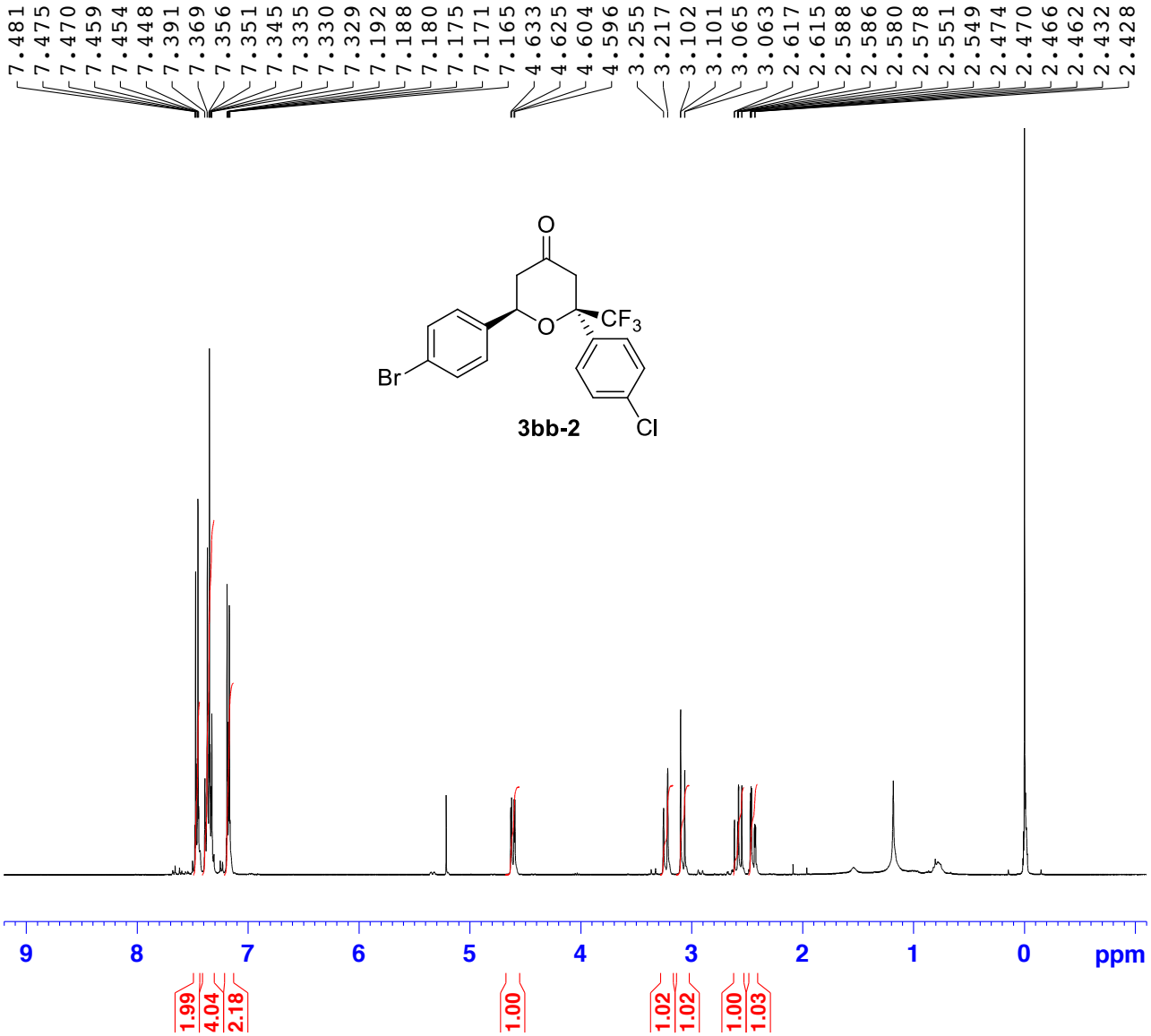




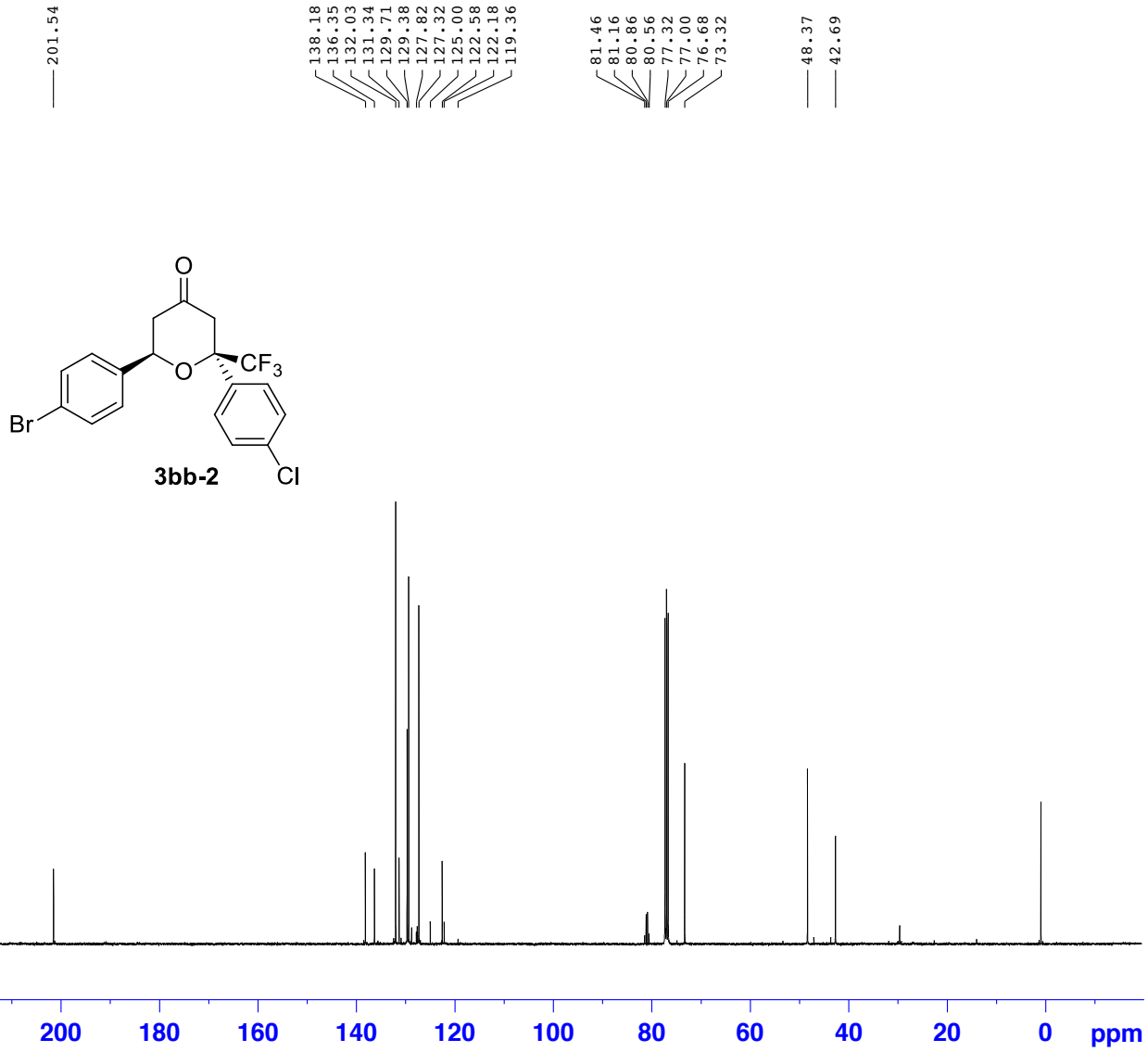
3bb-1:**3bb-2** = 1:4.1



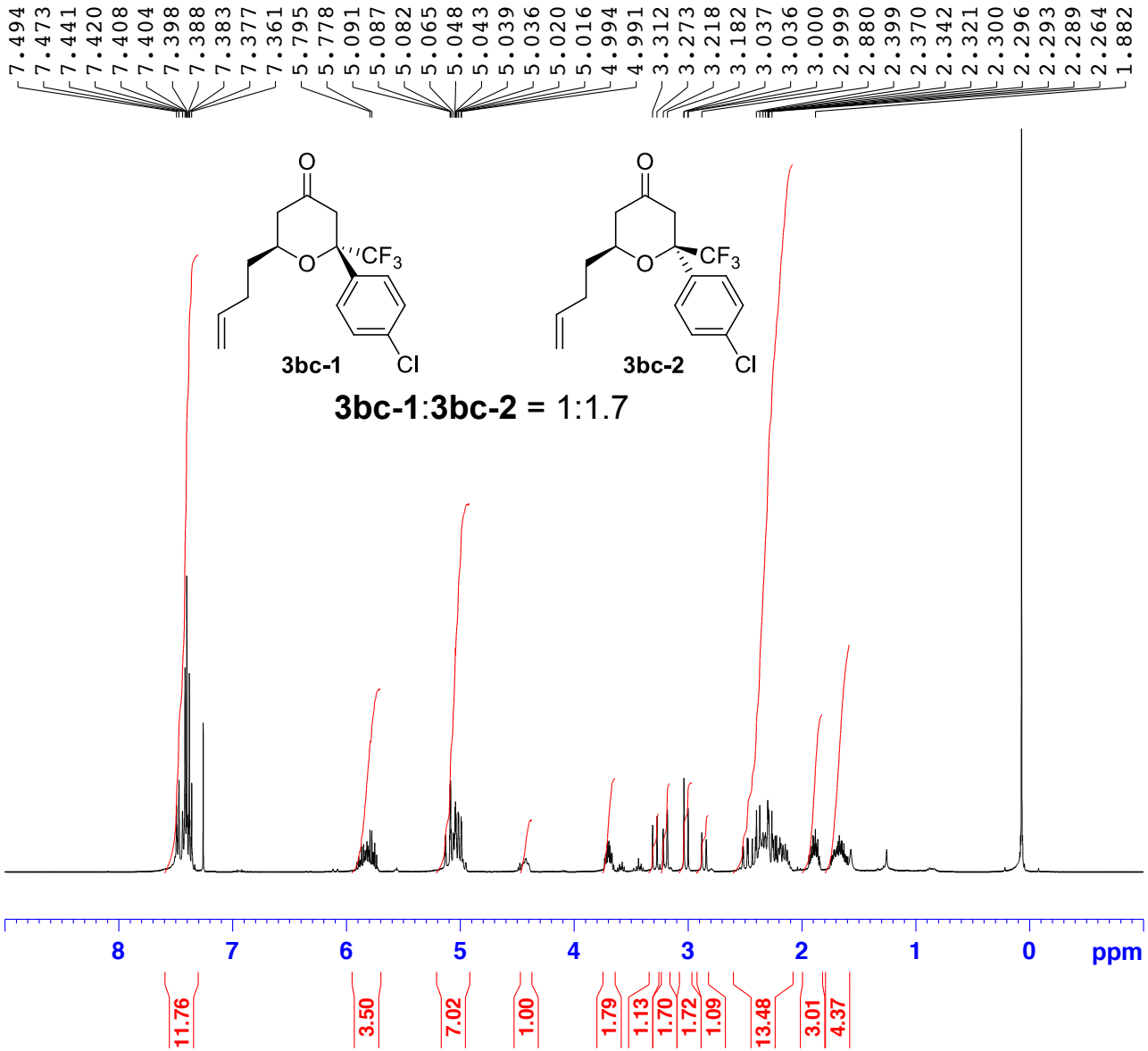

```
Current Data Parameters
NAME                 DZ-766
EXPNO                    40
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150812
Time                   1.59
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     9000
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                    195.88
DW                    20.800 usec
DE                     6.50 usec
TE                    299.9 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                     32768
SF             100.6127713 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```




```
Current Data Parameters
NAME                  DZ-894
EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_              20160217
Time                  21.13
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    31.13
DW                   62.400 usec
DE                    6.50 usec
TE                   301.1 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                   15.00 usec
PLW1            8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300414 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```



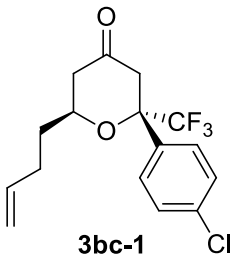

```
Current Data Parameters
NAME                  DZ-894
EXPNO                     60
PROCNO                     1

F2 - Acquisition Parameters
Date_              20160218
Time                  12.46
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2100
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                   20.800 usec
DE                    6.50 usec
TE                   301.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                    32768
SF             100.6127688 MHz
WDW                    EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```



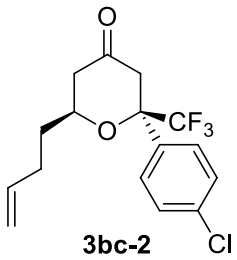

```
Current Data Parameters
NAME                  DZ-735
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150625
Time                  16.53
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894465 sec
RG                    31.13
DW                   62.400 usec
DE                    6.50 usec
TE          0 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                   15.00 usec
PLW1            8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300097 MHz
WDW                      EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.00
```

202.83
202.64

137.29
137.18
135.99
135.33
131.78
129.81
129.11
128.62
127.80
126.29
125.02
123.42
122.20
120.55
119.38
115.70
115.51
81.01
80.71
80.42
80.12
78.94
78.66
78.37
78.09
77.32
77.00
76.68
72.78
71.71
46.70
45.65
43.81
42.73
35.49
35.18
29.35
29.23

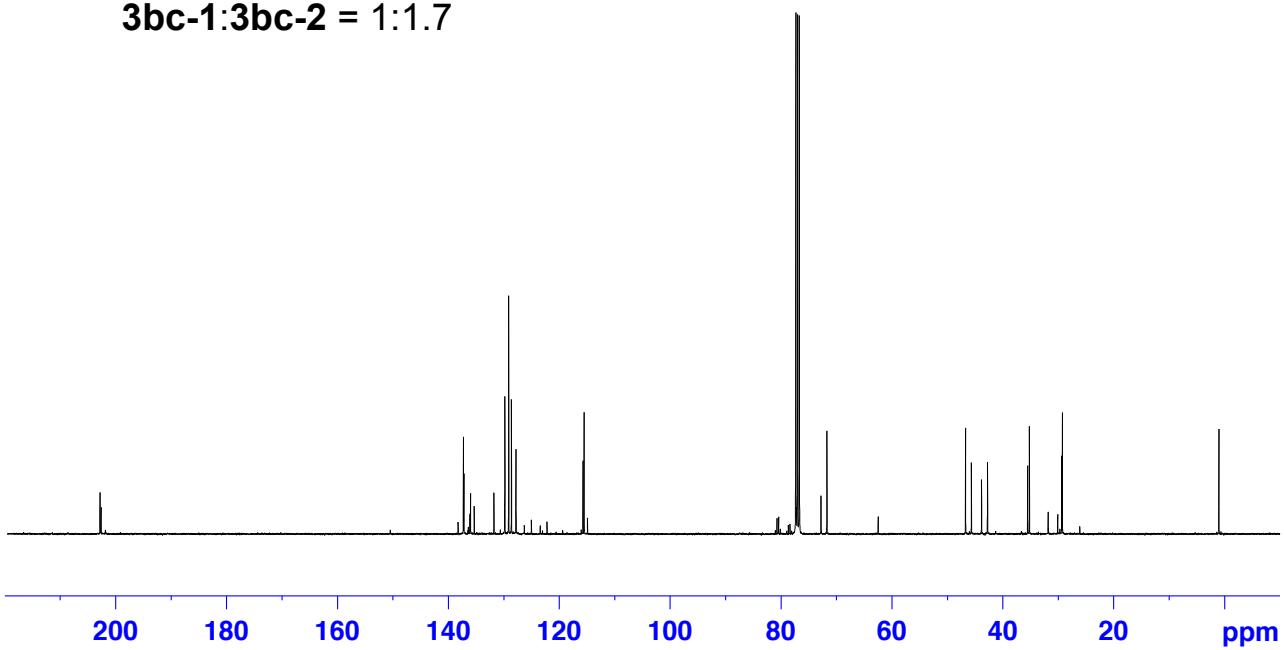


3bc-1

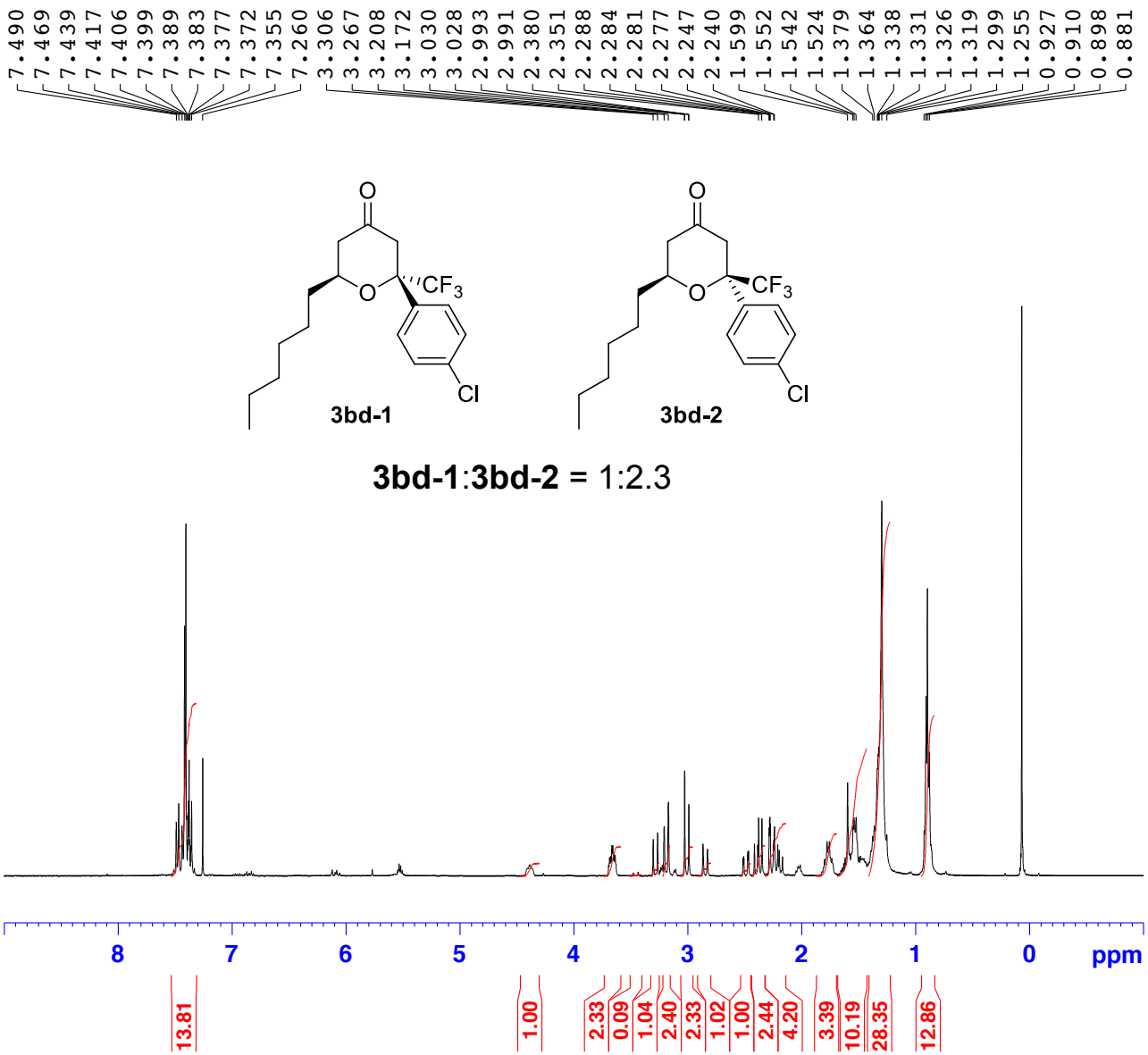


3bc-2

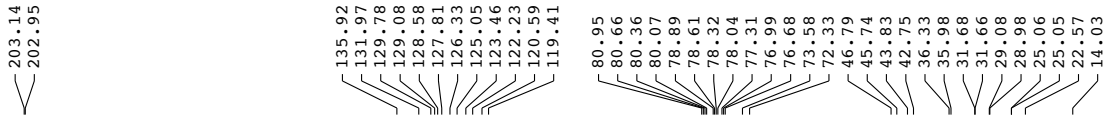
3bc-1:**3bc-2** = 1:1.7

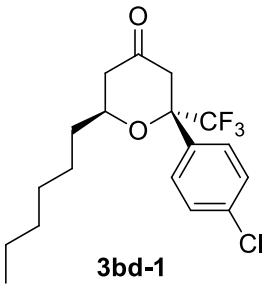



```
Current Data Parameters
NAME                  DZ-735C
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20150626
Time                   7.16
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    10240
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                   20.800 usec
DE                    6.50 usec
TE          0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                    32768
SF             100.6127706 MHz
WDW                     EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```

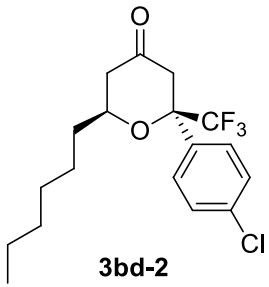



```
Current Data Parameters
NAME                  DZ-731
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150623
Time                  18.00
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    31.13
DW                   62.400 usec
DE                    6.50 usec
TE          0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                   1H
P1                   15.00 usec
PLW1            8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300098 MHz
WDW                      EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.00
```



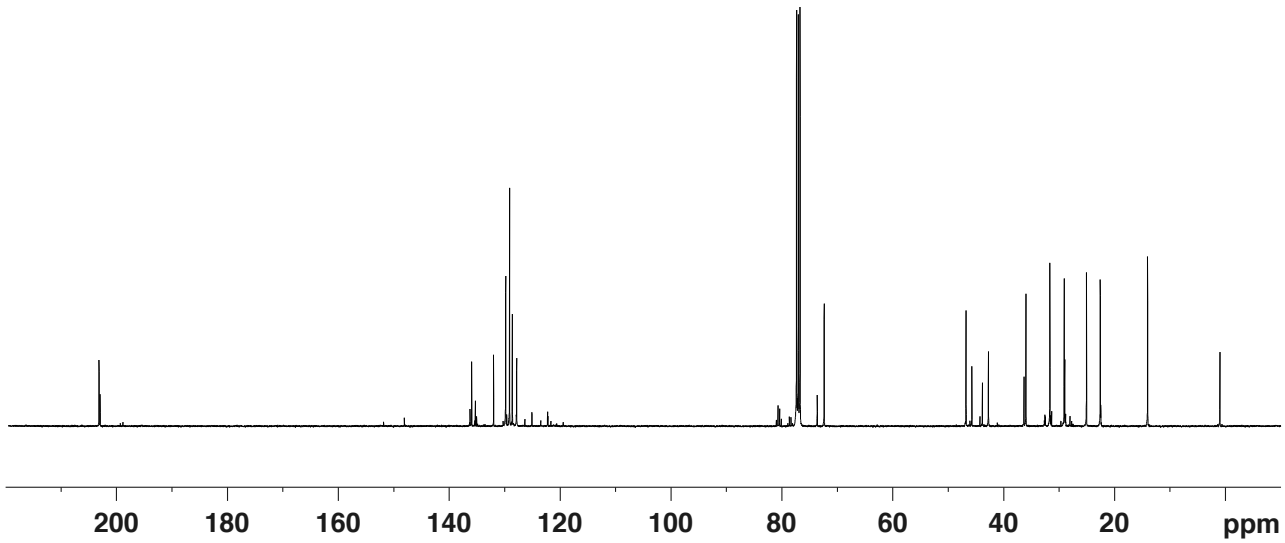


3bd-1

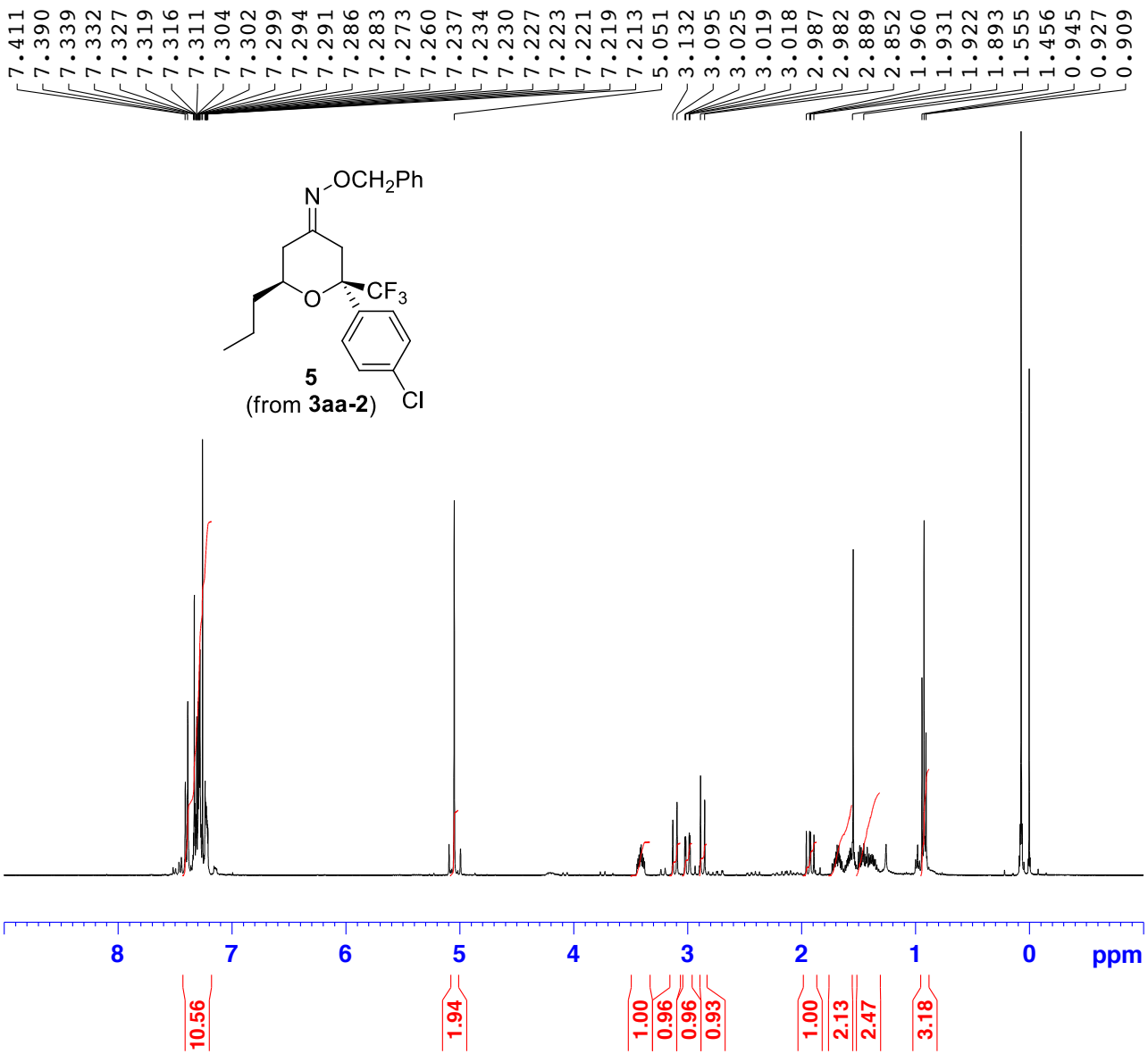


3bd-2

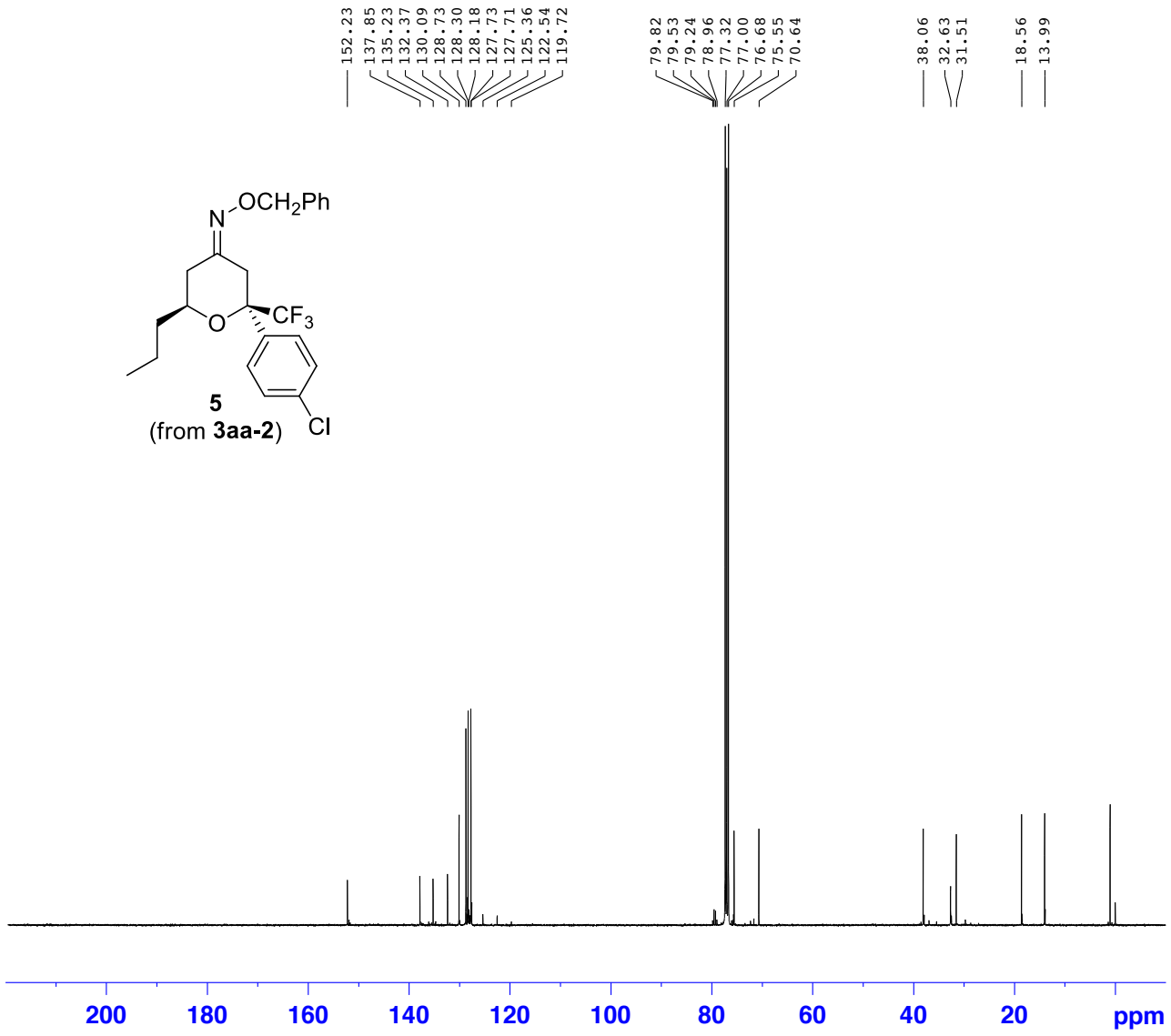
3bd-1:**3bd-2** = 1:2.3




```
Current Data Parameters
NAME                  DZ-731
EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150624
Time                   2.13
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     8000
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                  20.800 usec
DE                   6.50 usec
TE          0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                    32768
SF             100.6127713 MHz
WDW                      EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```

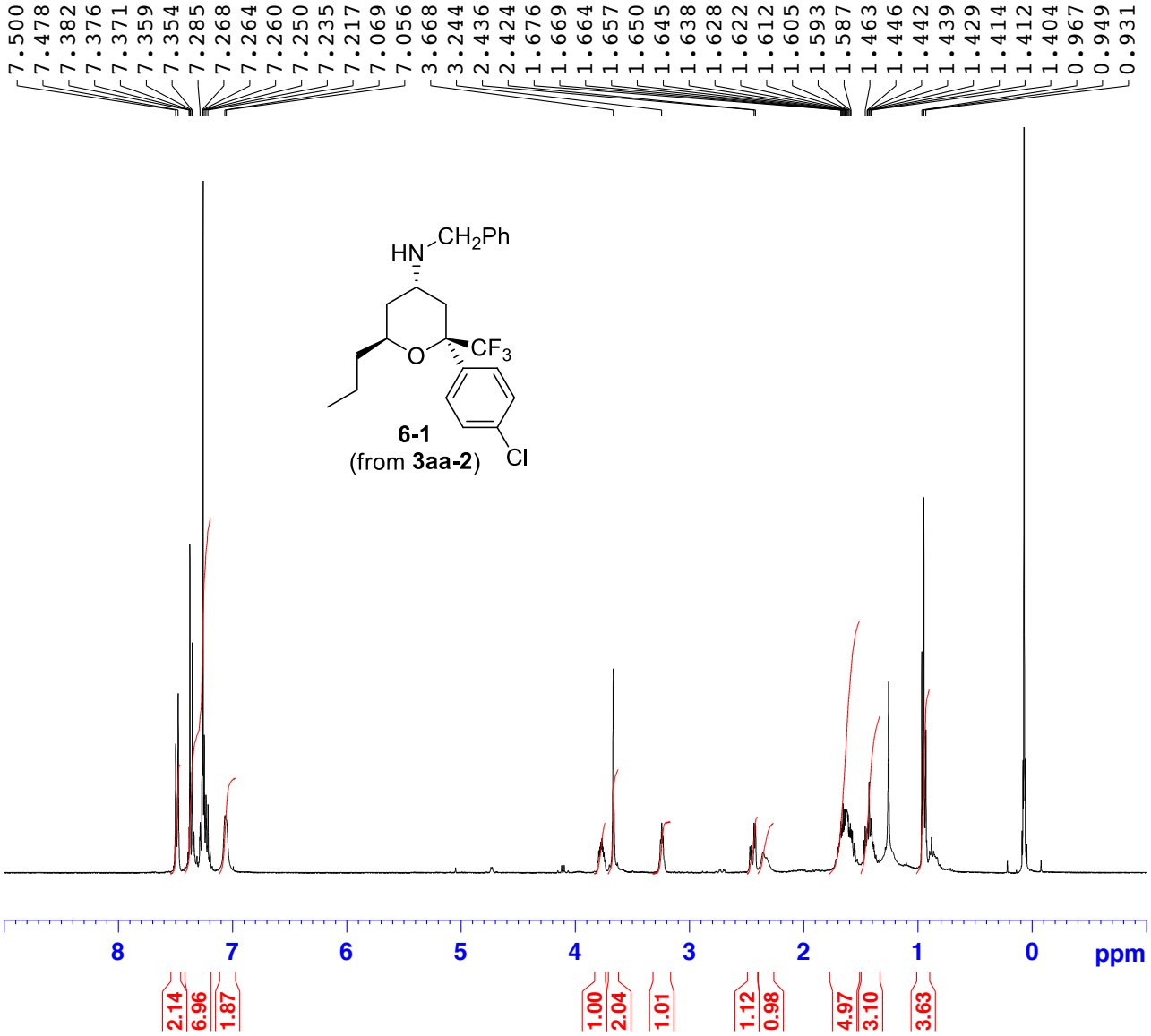



```
Current Data Parameters
NAME                  DZ-784-2
EXPNO                       20
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20151020
Time                      9.27
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894465 sec
RG                       62.88
DW                      62.400 usec
DE                       6.50 usec
TE                      298.5 K
D1                   1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               400.1324710 MHz
NUC1                        1H
P1                       15.00 usec
PLW1                8.00000000 W

F2 - Processing parameters
SI                      65536
SF                 400.1300095 MHz
WDW                        EM
SSB                 0
LB                       0.30 Hz
GB                  0
PC                       1.00
```

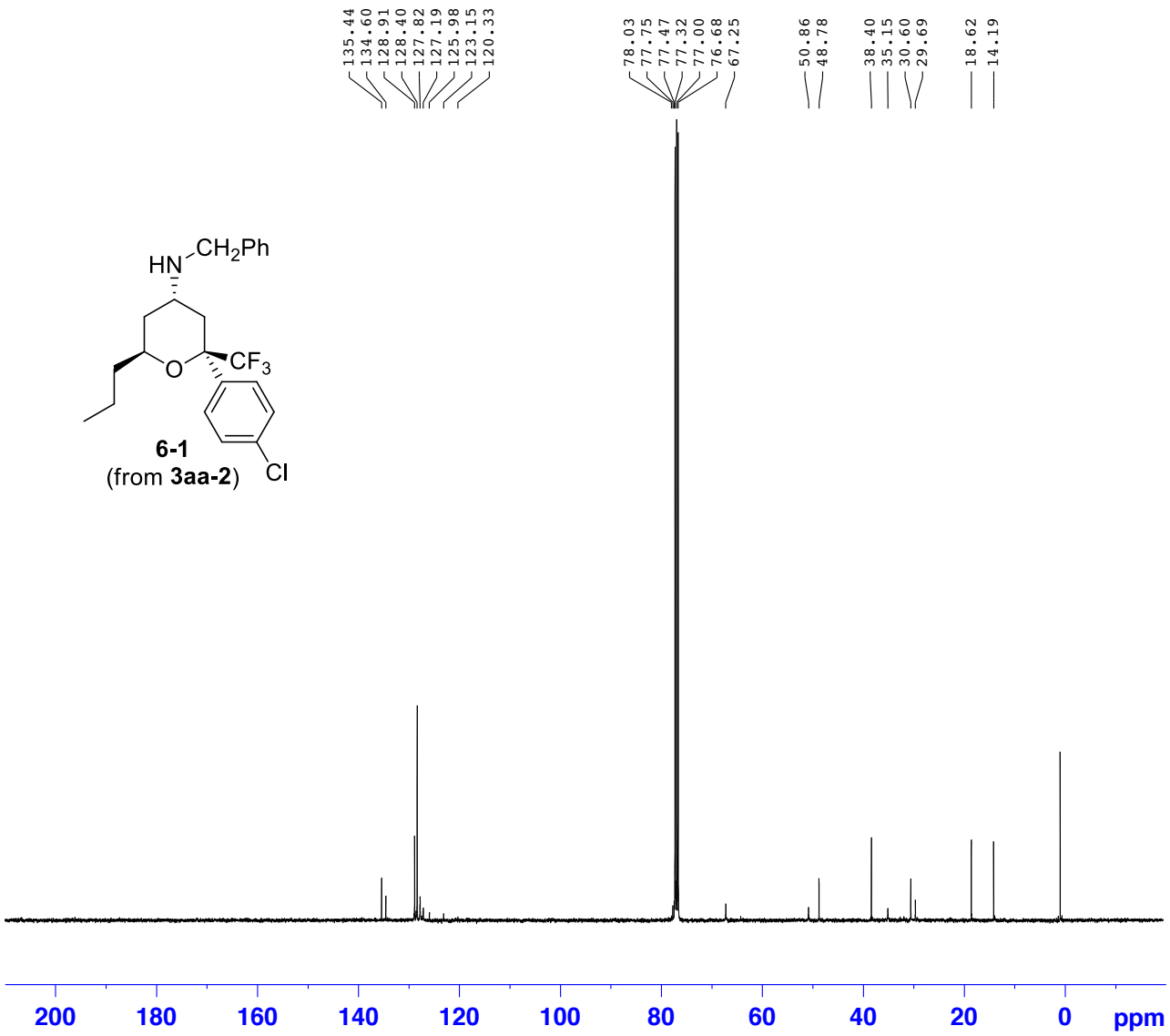


5
(from **3aa-2**)

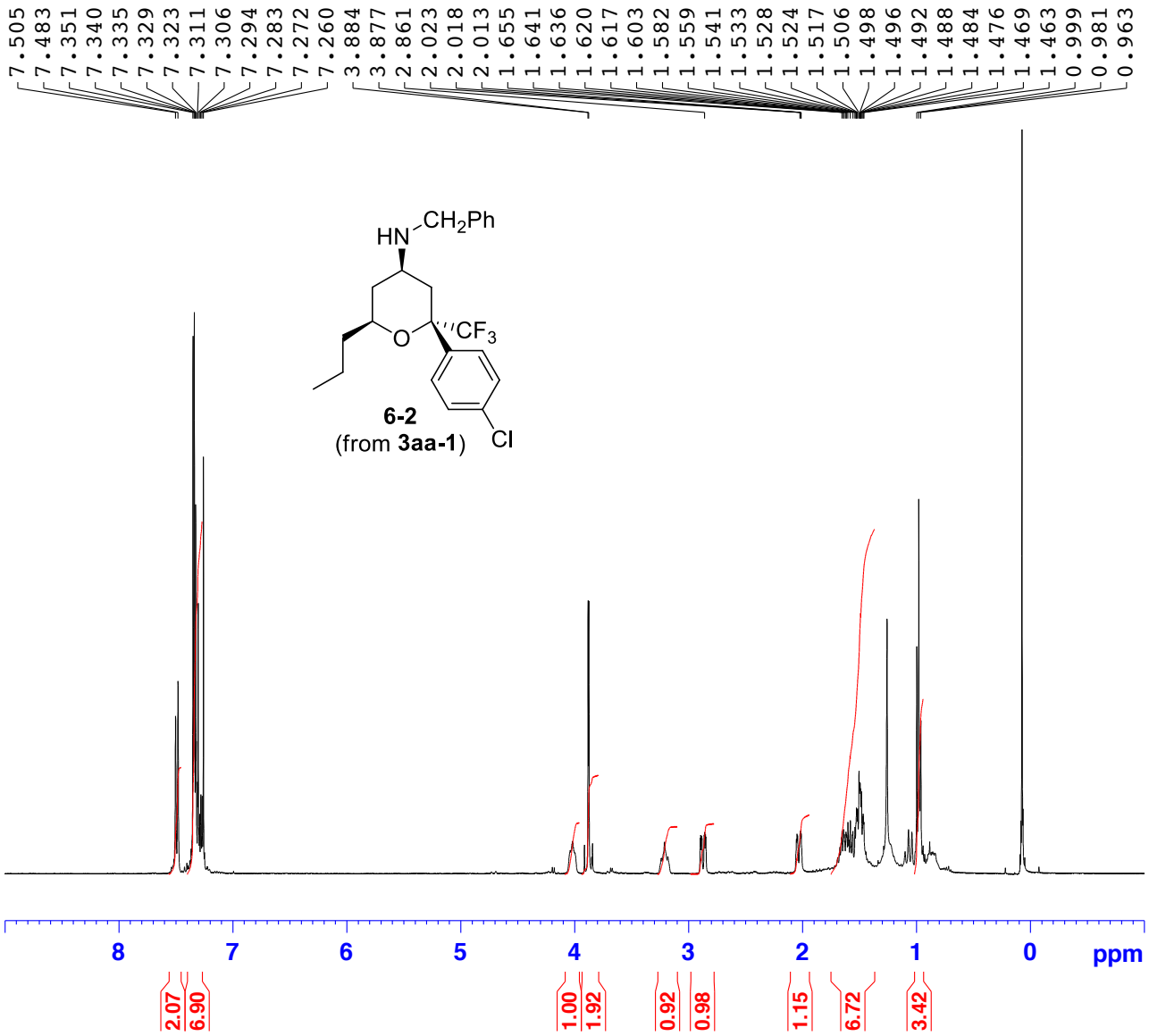
```
Current Data Parameters
NAME            DZ-784-3
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151021
Time                8.26
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                15000
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                195.88
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        100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1        70.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         8.00000000 W
PLW12        0.28125000 W
PLW13        0.28125000 W

F2 - Processing parameters
SI                32768
SF          100.6127699 MHz
WDW                EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



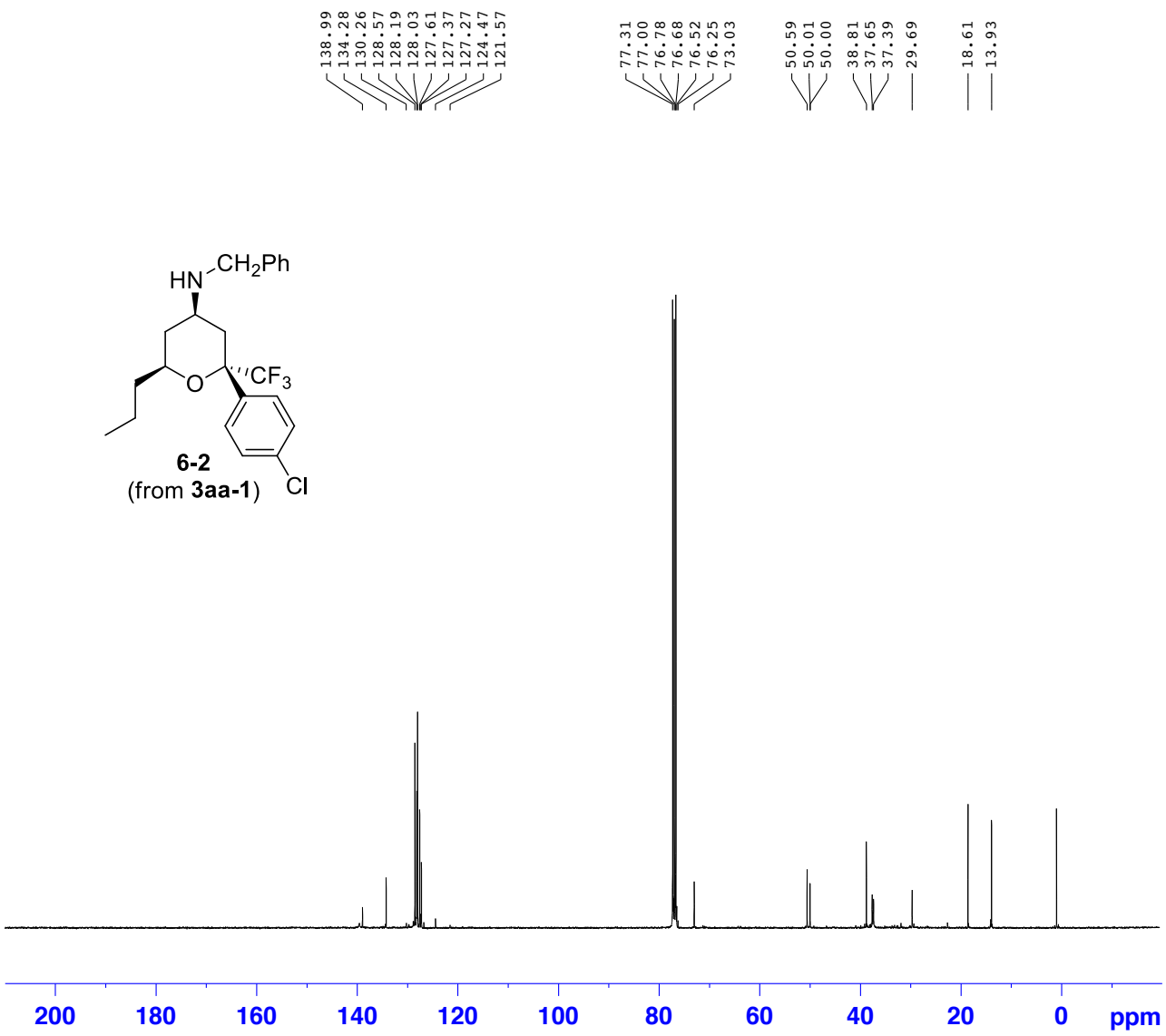

```
Current Data Parameters
NAME                  DZ-808
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20151026
Time                   15.22
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                     62.88
DW                    62.400 usec
DE                     6.50 usec
TE                    298.5 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                      1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF               400.1300097 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



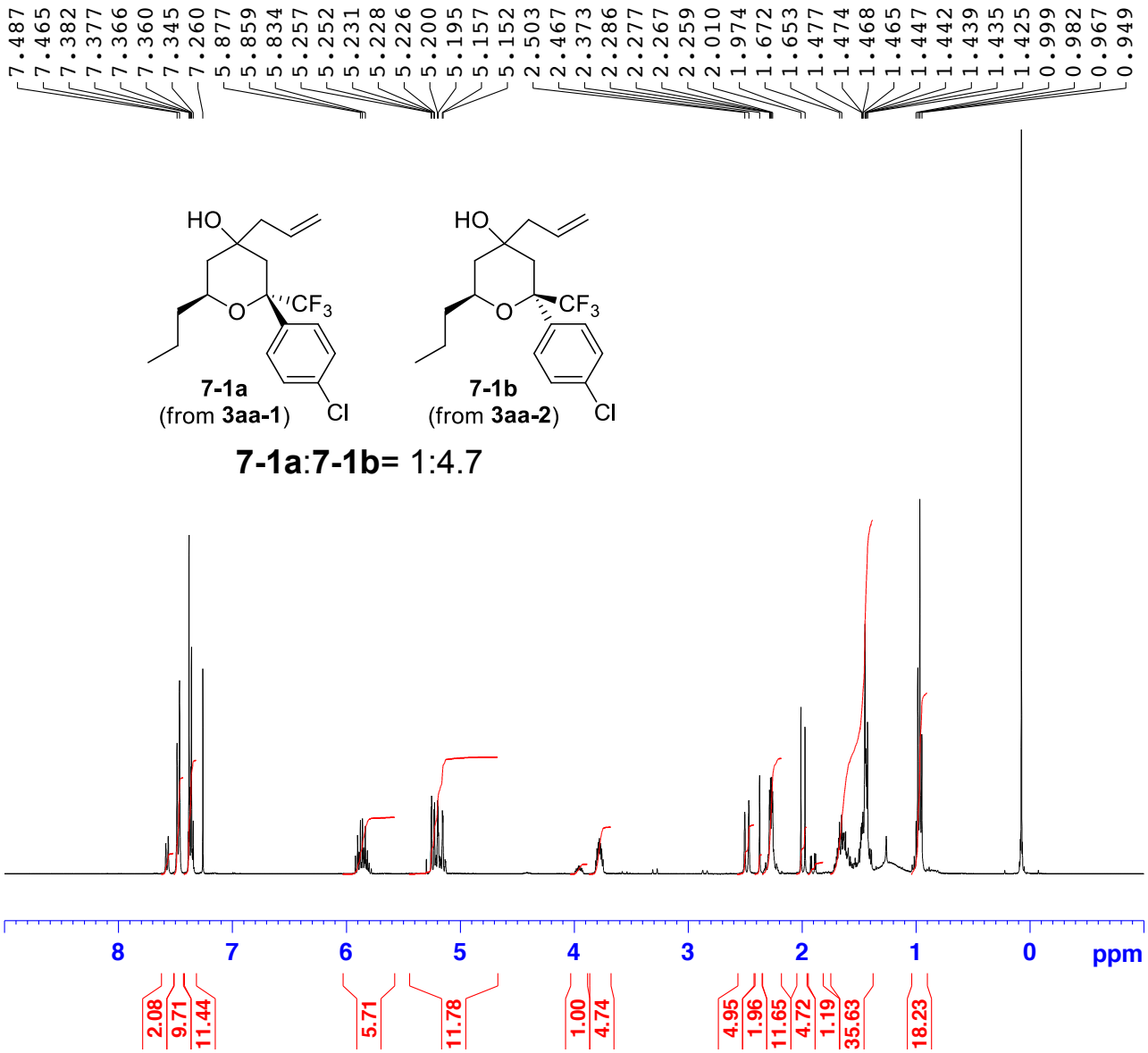

```
Current Data Parameters
NAME                 DZ-808
EXPNO                    40
PROCNO                    1

F2 - Acquisition Parameters
Date_              20151028
Time                 21.55
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                   13000
DS                       4
SWH             24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631488 sec
RG                  195.88
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          100.6228293 MHz
NUC1                   13C
P1                  10.00 usec
PLW1          70.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2               80.00 usec
PLW2           8.00000000 W
PLW12          0.28125000 W
PLW13          0.28125000 W

F2 - Processing parameters
SI                    32768
SF            100.6127702 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```



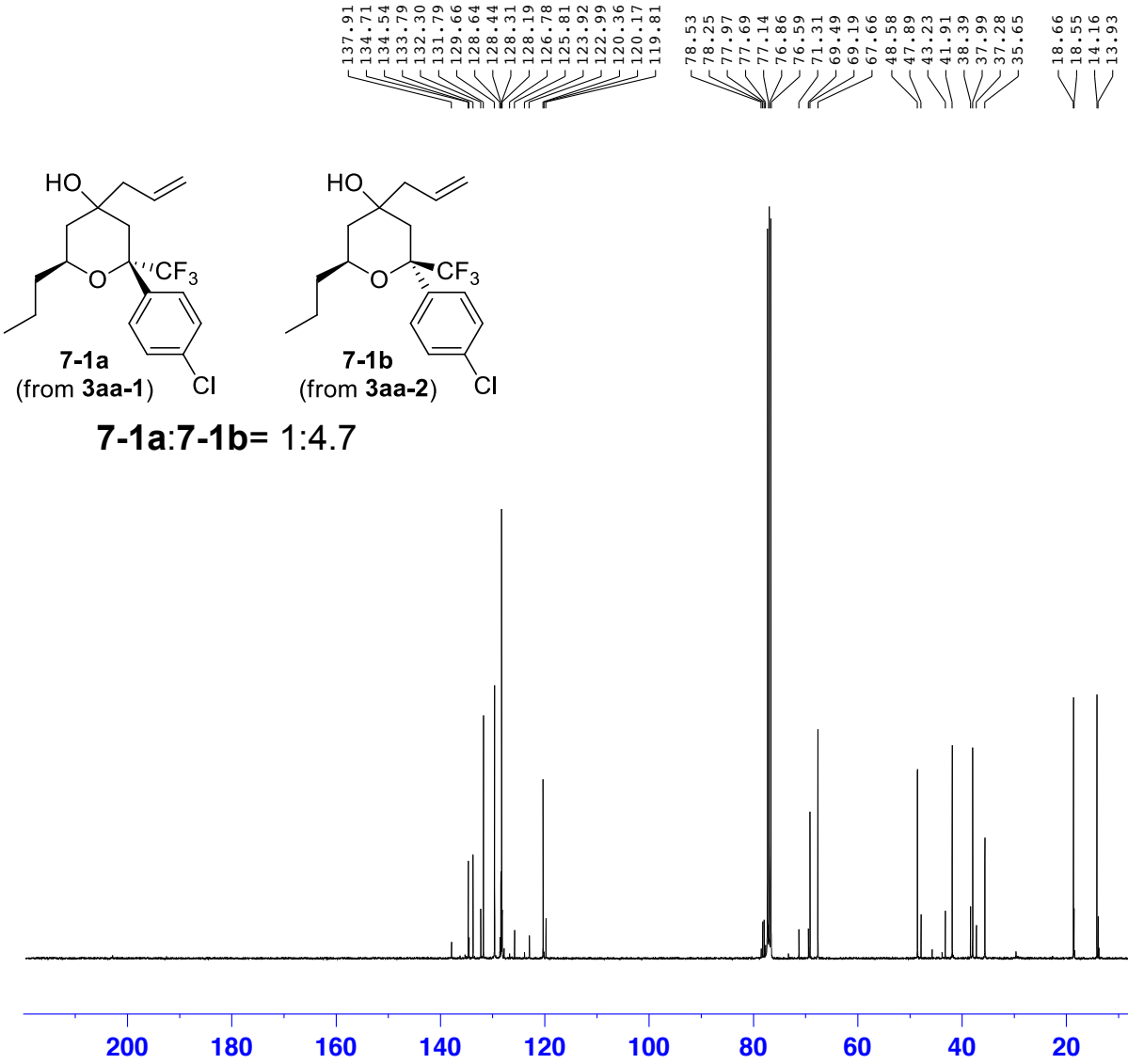

```
Current Data Parameters
NAME                  DZ-808
EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_              20151026
Time                  18.18
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    49.09
DW                   62.400 usec
DE                    6.50 usec
TE                   298.5 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                   15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300095 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```



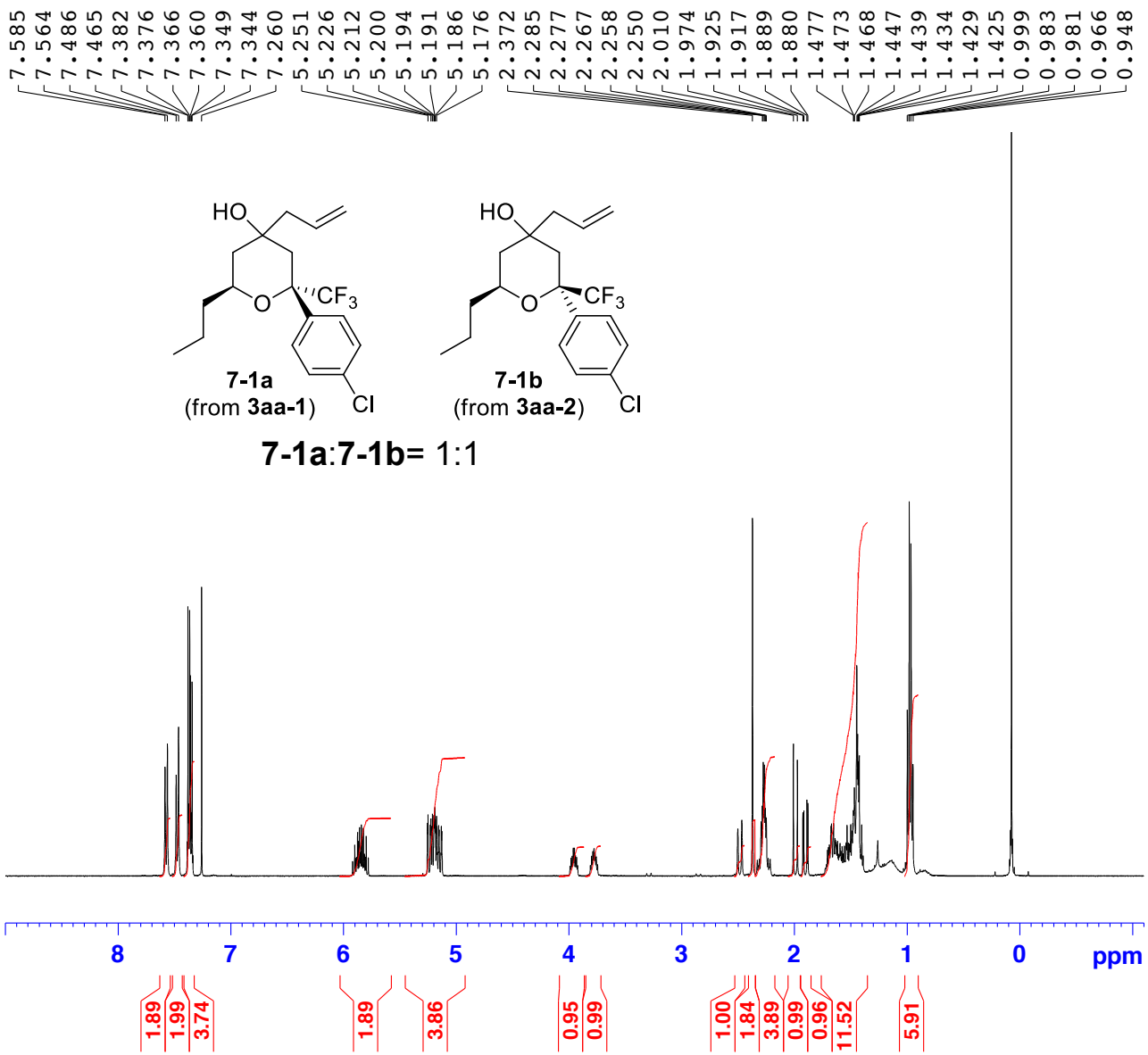

```
Current Data Parameters
NAME                 DZ-808
EXPNO                    60
PROCNO                    1

F2 - Acquisition Parameters
Date_              20151031
Time                   5.52
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    12000
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
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          100.6228293 MHz
NUC1                   13C
P1                   10.00 usec
PLW1          70.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           8.00000000 W
PLW12          0.28125000 W
PLW13          0.28125000 W

F2 - Processing parameters
SI                    32768
SF            100.6127709 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```



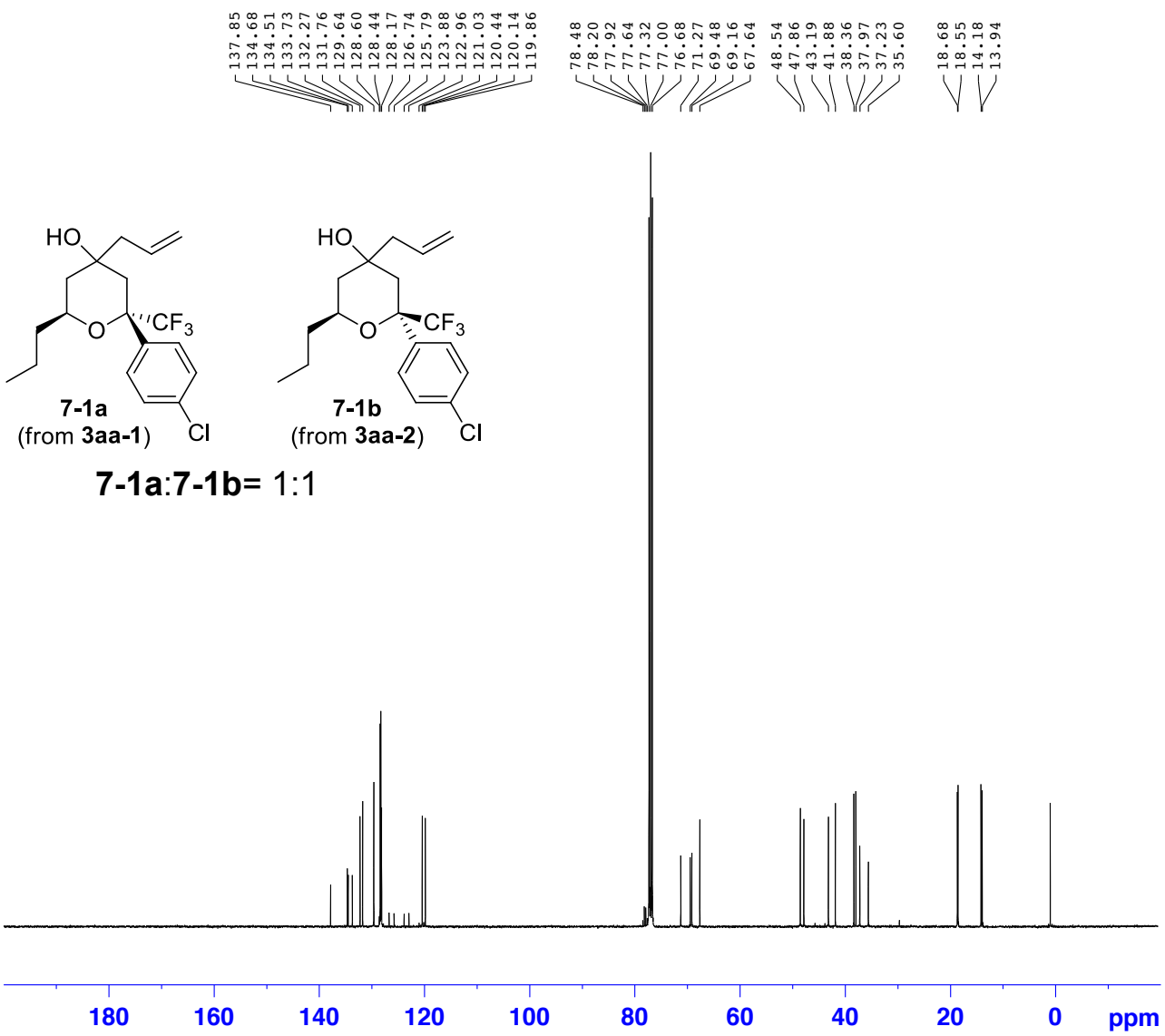

```
Current Data Parameters
NAME                  DZ-811
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20151027
Time                  16.59
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    31.13
DW                   62.400 usec
DE                    6.50 usec
TE                   298.6 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                      1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300095 MHz
WDW                      EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```



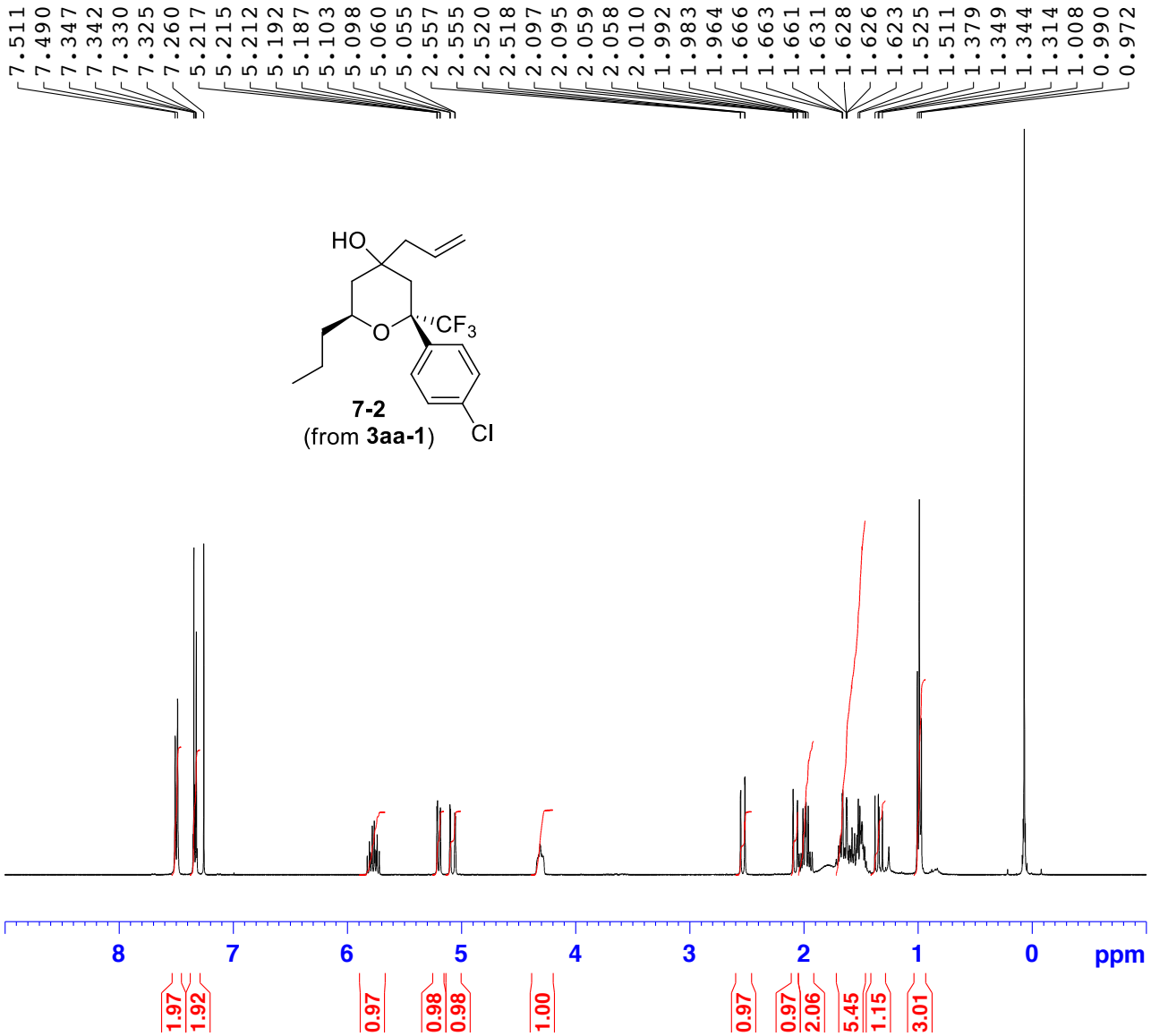

```
Current Data Parameters
NAME                  DZ-811
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20151125
Time                   7.09
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    11000
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                   20.800 usec
DE                    6.50 usec
TE                   300.8 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            100.6228293 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2            400.1316005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                     32768
SF              100.6127680 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



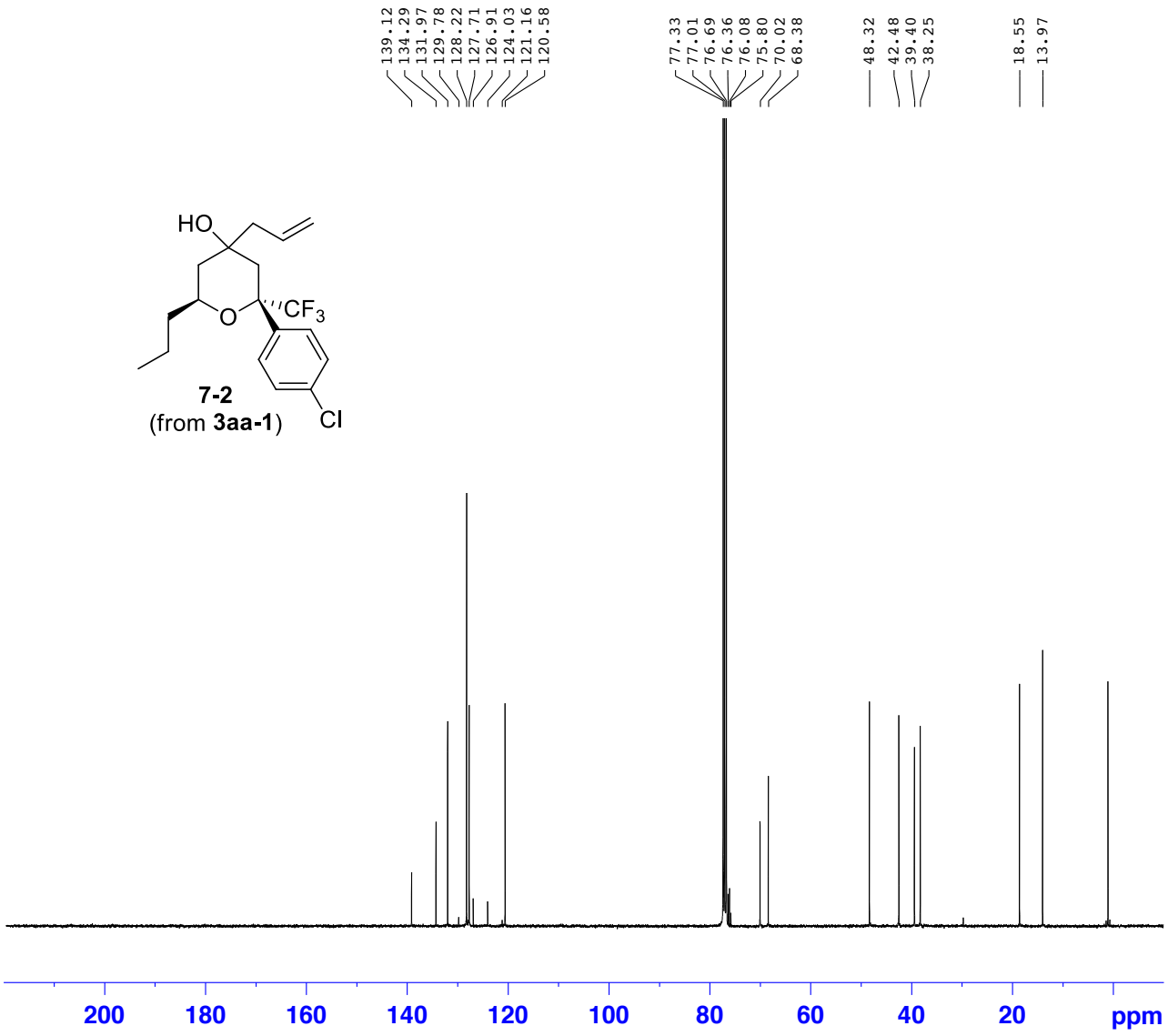

```
Current Data Parameters
NAME                  DZ-809
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20151026
Time                  15.26
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894465 sec
RG                    31.13
DW                    62.400 usec
DE                     6.50 usec
TE                    298.5 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                      1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                        65536
SF             400.1300095 MHz
WDW                       EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```



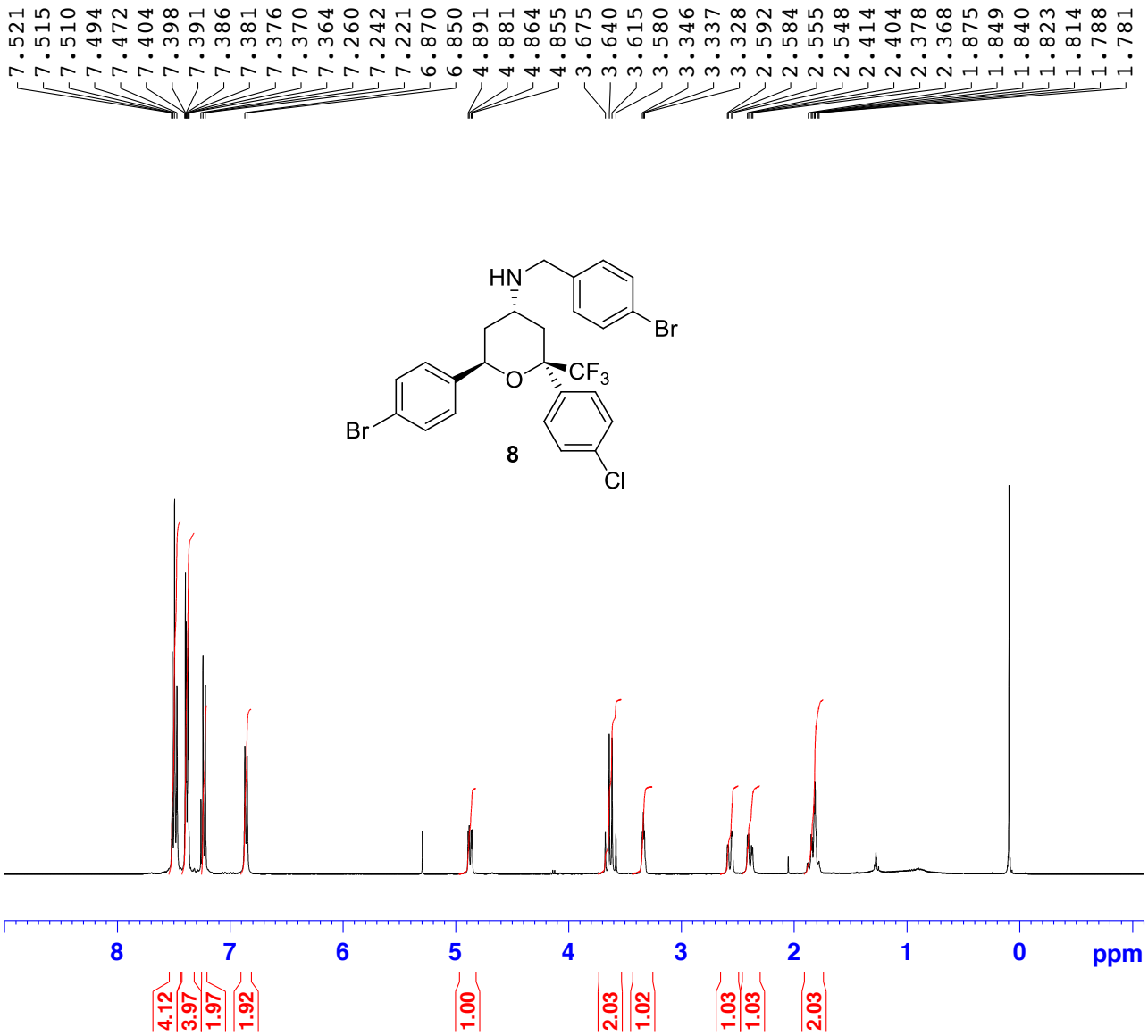

```
Current Data Parameters
NAME                  DZ-809
EXPNO                     40
PROCNO                     1

F2 - Acquisition Parameters
Date_              20151027
Time                   7.14
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    10000
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   195.88
DW                  20.800 usec
DE                   6.50 usec
TE                  299.5 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                 80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                     32768
SF             100.6127702 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```



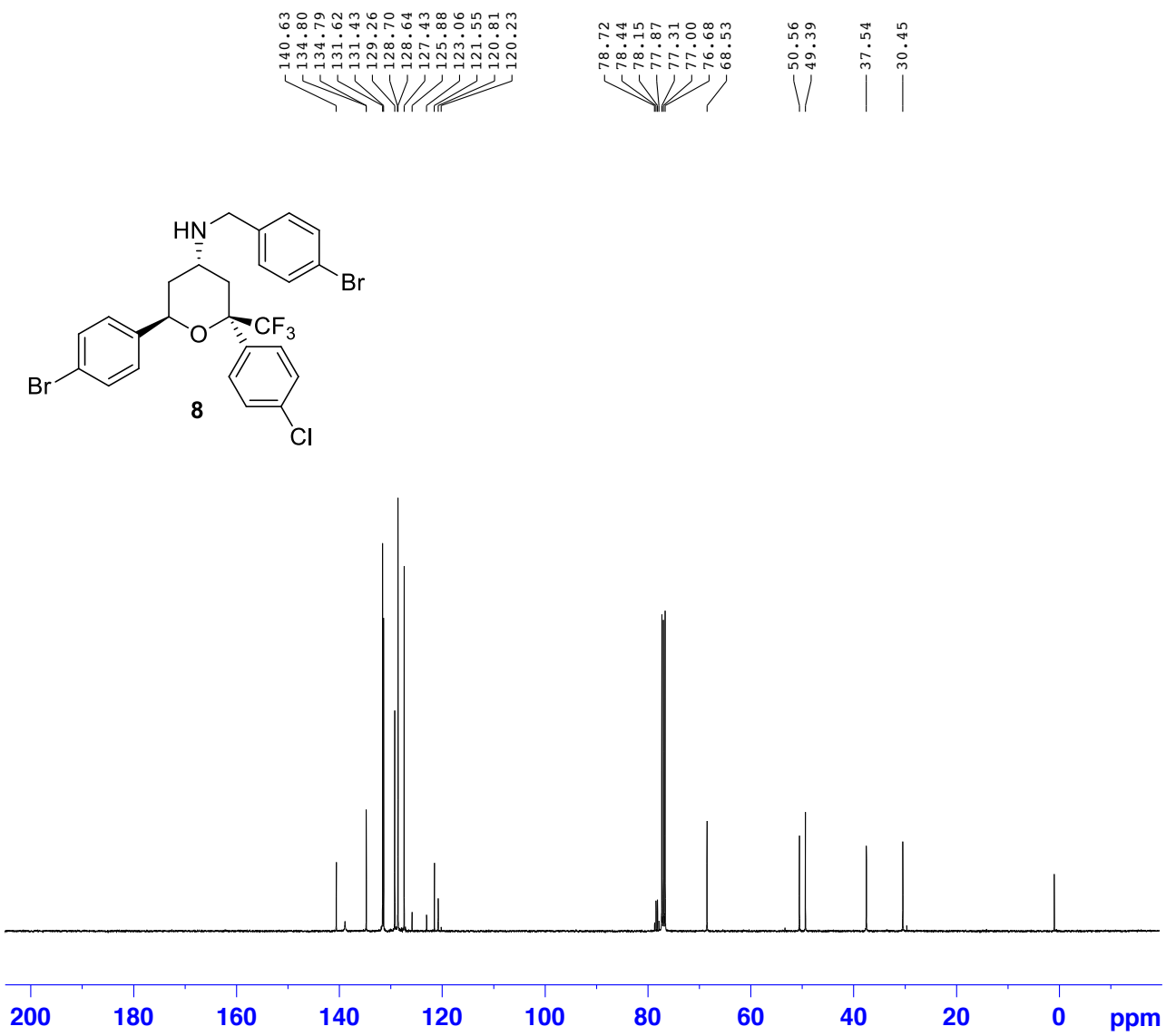

```
Current Data Parameters
NAME                  DZ-809
EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_              20151026
Time                  15.36
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894465 sec
RG                    54.59
DW                   62.400 usec
DE                    6.50 usec
TE                   298.5 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300095 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```



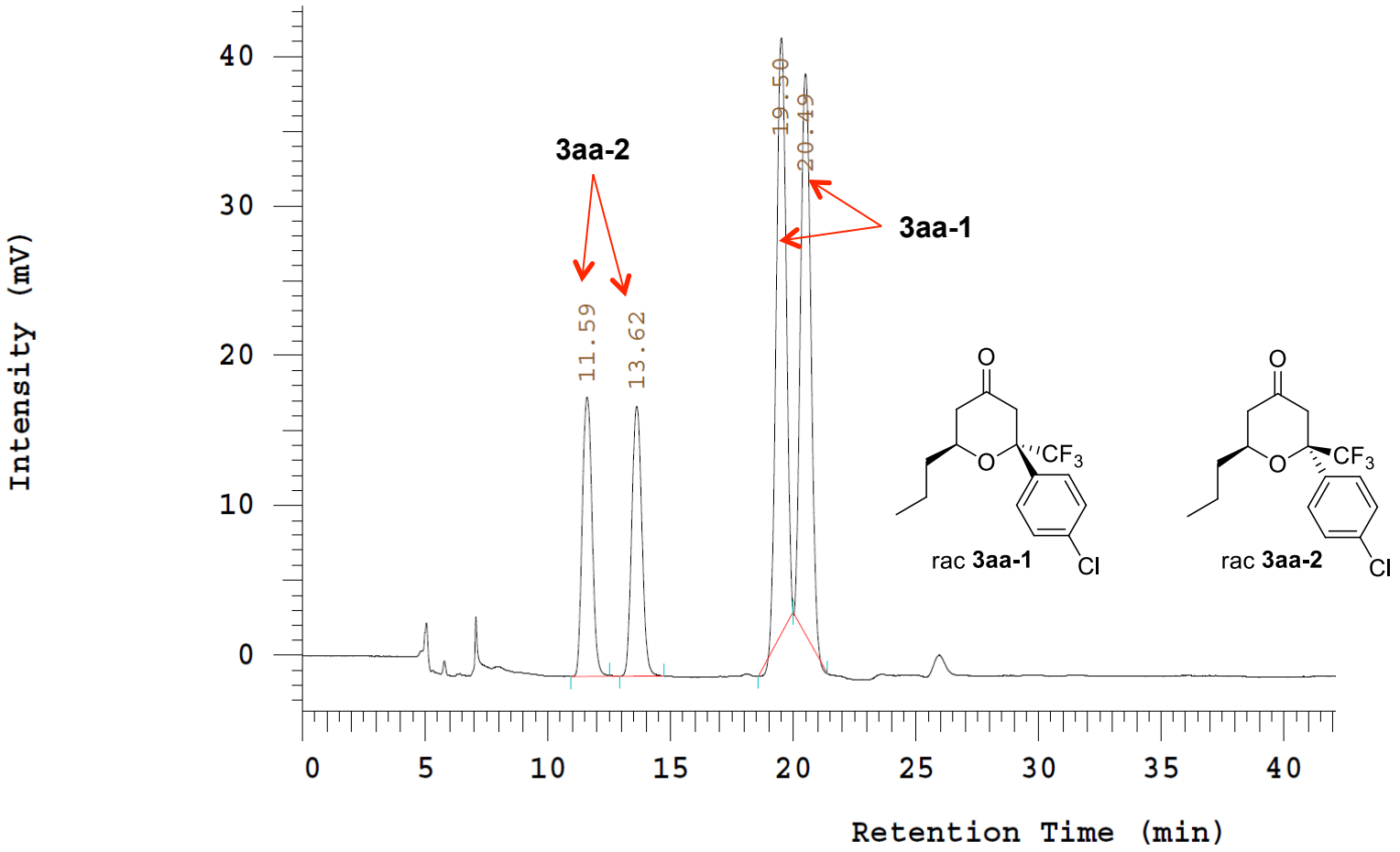

```
Current Data Parameters
NAME                  DZ-809
EXPNO                     70
PROCNO                     1

F2 - Acquisition Parameters
Date_              20151101
Time                   6.30
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    12000
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                    195.88
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           100.6228293 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                 80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                     32768
SF             100.6127690 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```



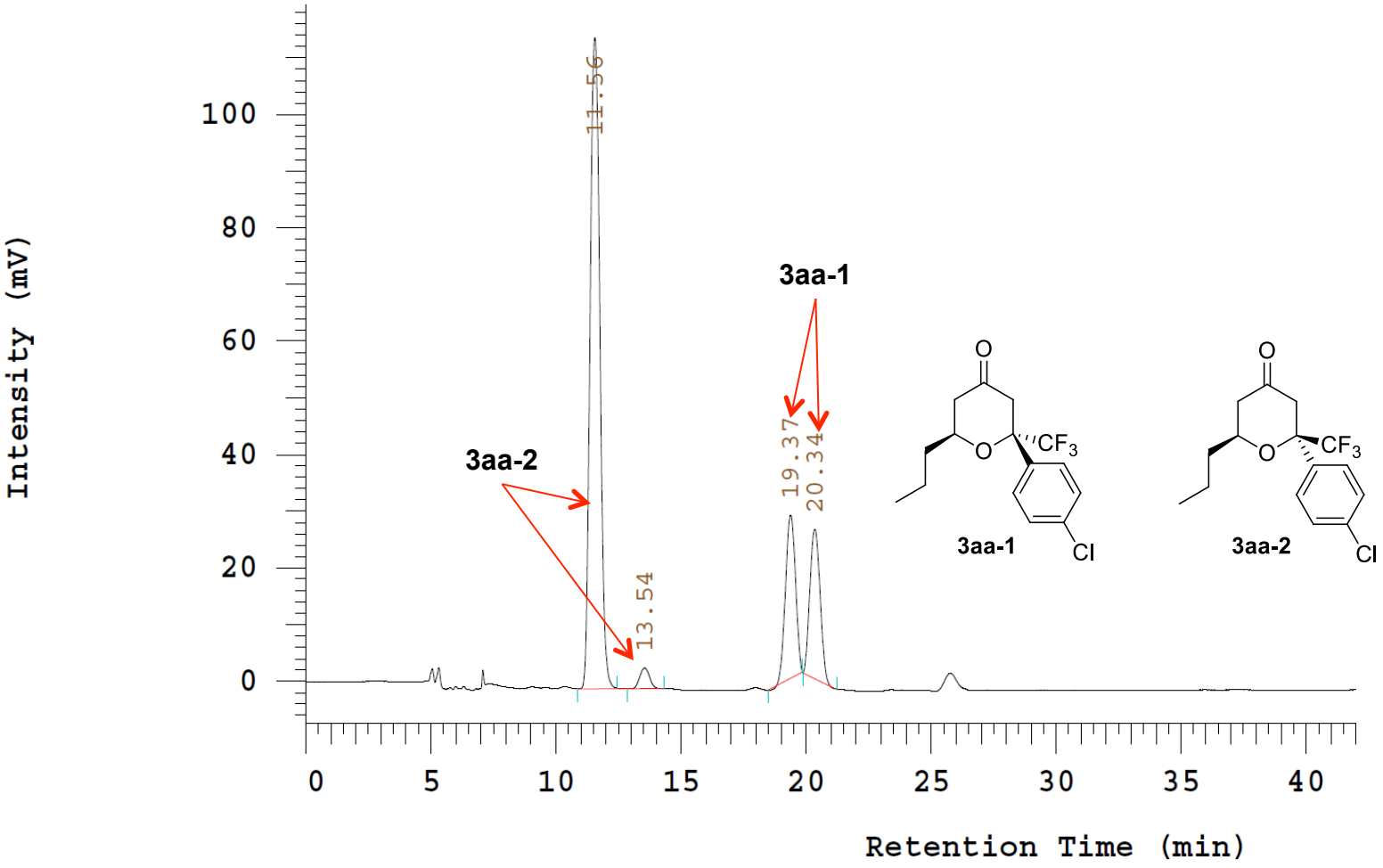

```
Current Data Parameters
NAME                  DZ-914
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20160212
Time                  11.45
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894465 sec
RG                    31.13
DW                    62.400 usec
DE                     6.50 usec
TE                    300.6 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                      1H
P1                    15.00 usec
PLW1           8.00000000 W

F2 - Processing parameters
SI                        65536
SF             400.1300095 MHz
WDW                       EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```



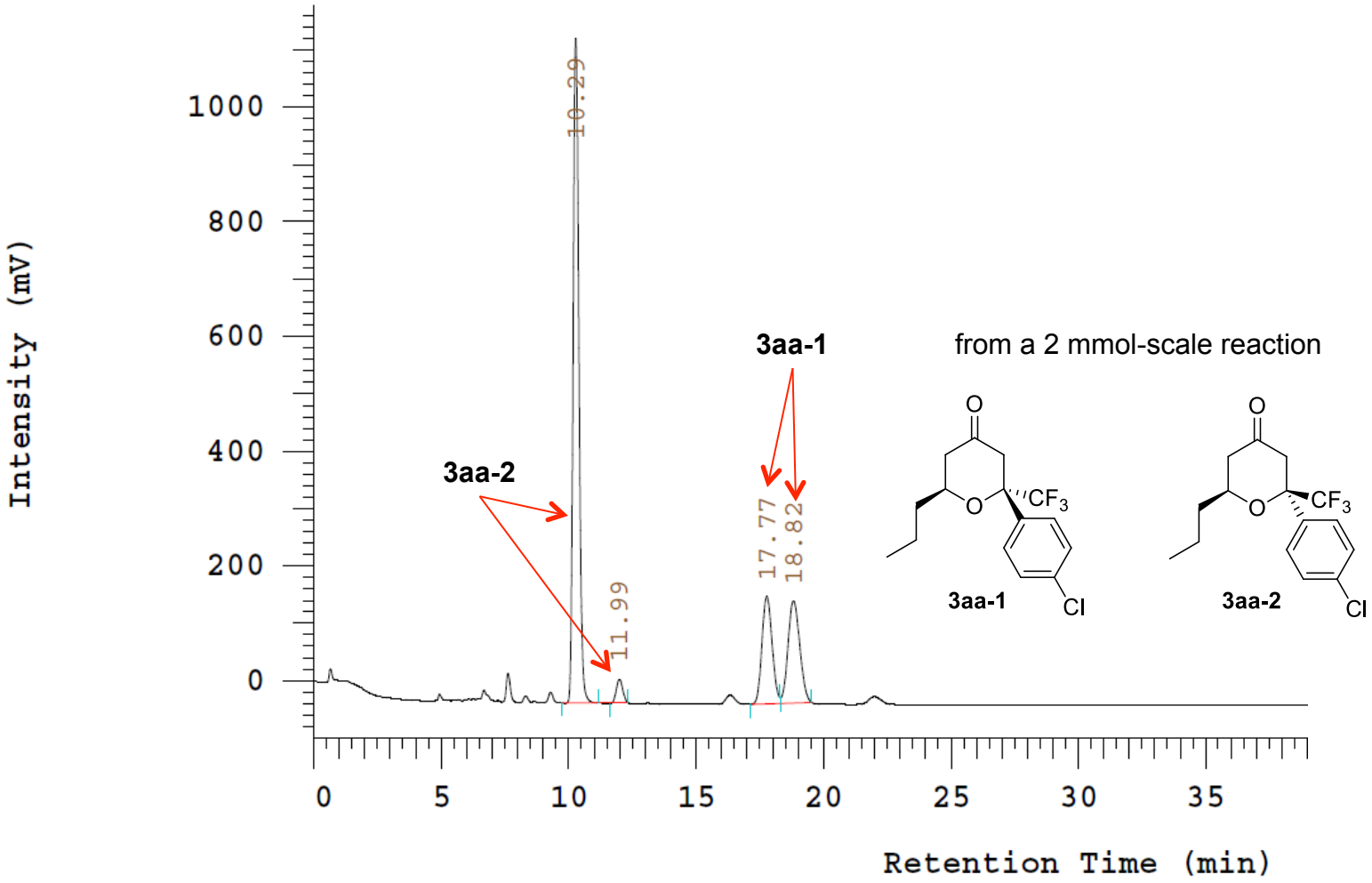

```
Current Data Parameters
NAME                  DZ-914
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20160212
Time                  14.06
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      2400
DS                         4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631488 sec
RG                    195.88
DW                   20.800 usec
DE                    6.50 usec
TE                   302.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2            8.00000000 W
PLW12           0.28125000 W
PLW13           0.28125000 W

F2 - Processing parameters
SI                     32768
SF             100.6127710 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```



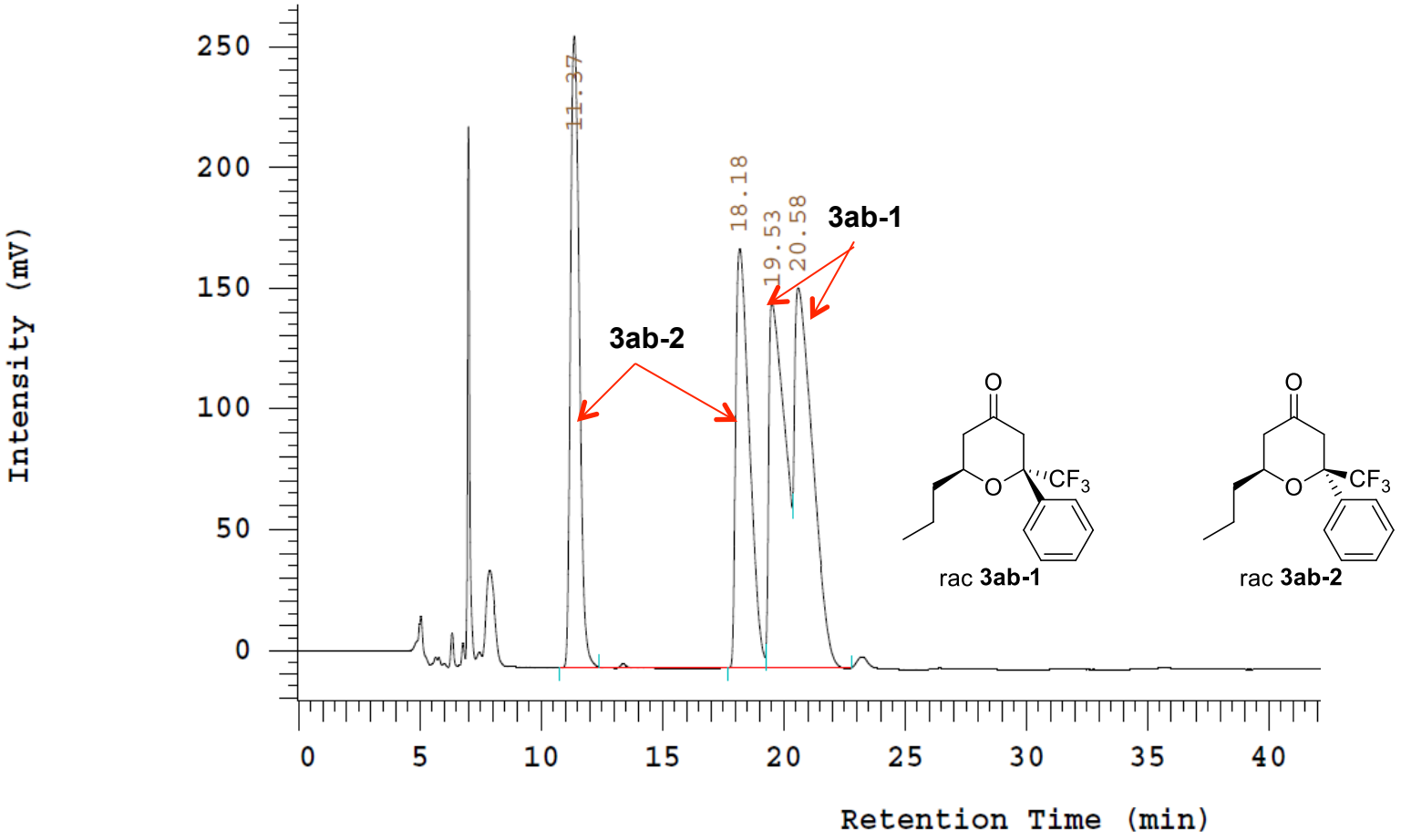
No.	RT	Area	Area %
1	11.59	503817	16.087
2	13.62	503801	16.086
3	19.50	1069127	34.137
4	20.49	1055095	33.689
		3131840	100.000



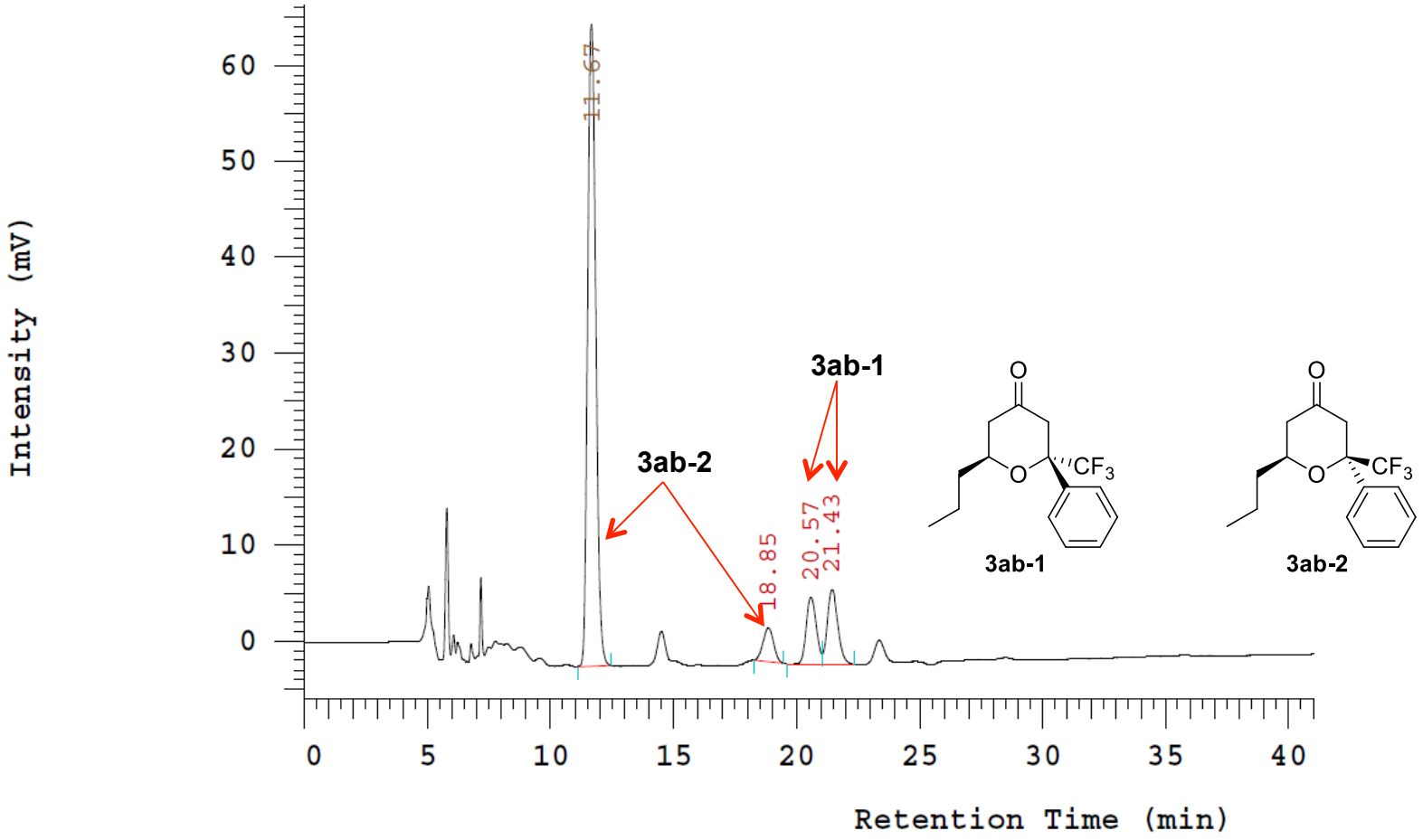
No.	RT	Area	Area %
1	11.56	3015575	65.291
2	13.54	95596	2.070
3	19.37	777583	16.836
4	20.34	729890	15.803
		4618644	100.000



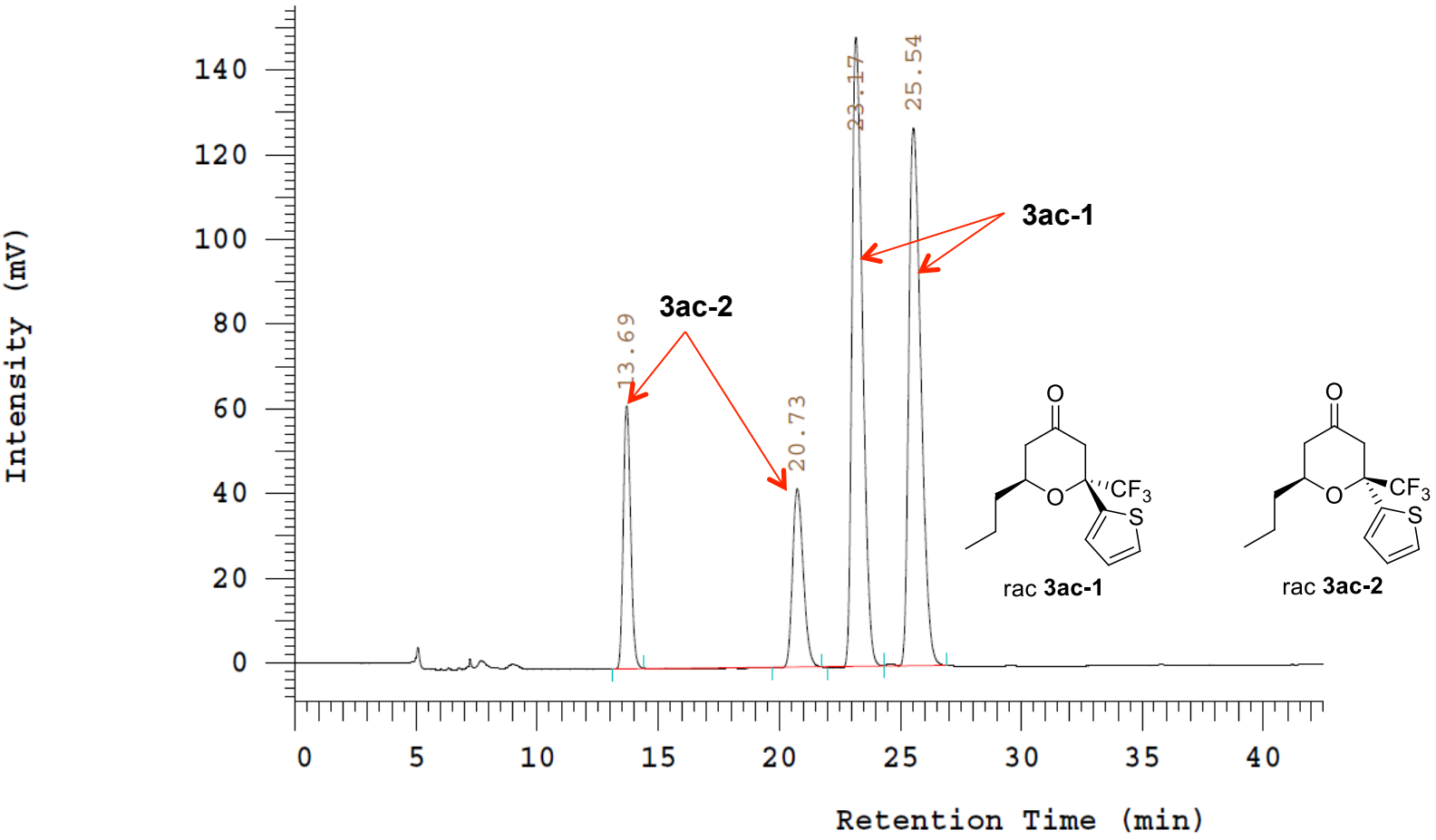
No.	RT	Area	Area %
1	10.29	17144163	60.303
2	11.99	653609	2.299
3	17.77	5047852	17.755
4	18.82	5584416	19.643
		28430040	100.000



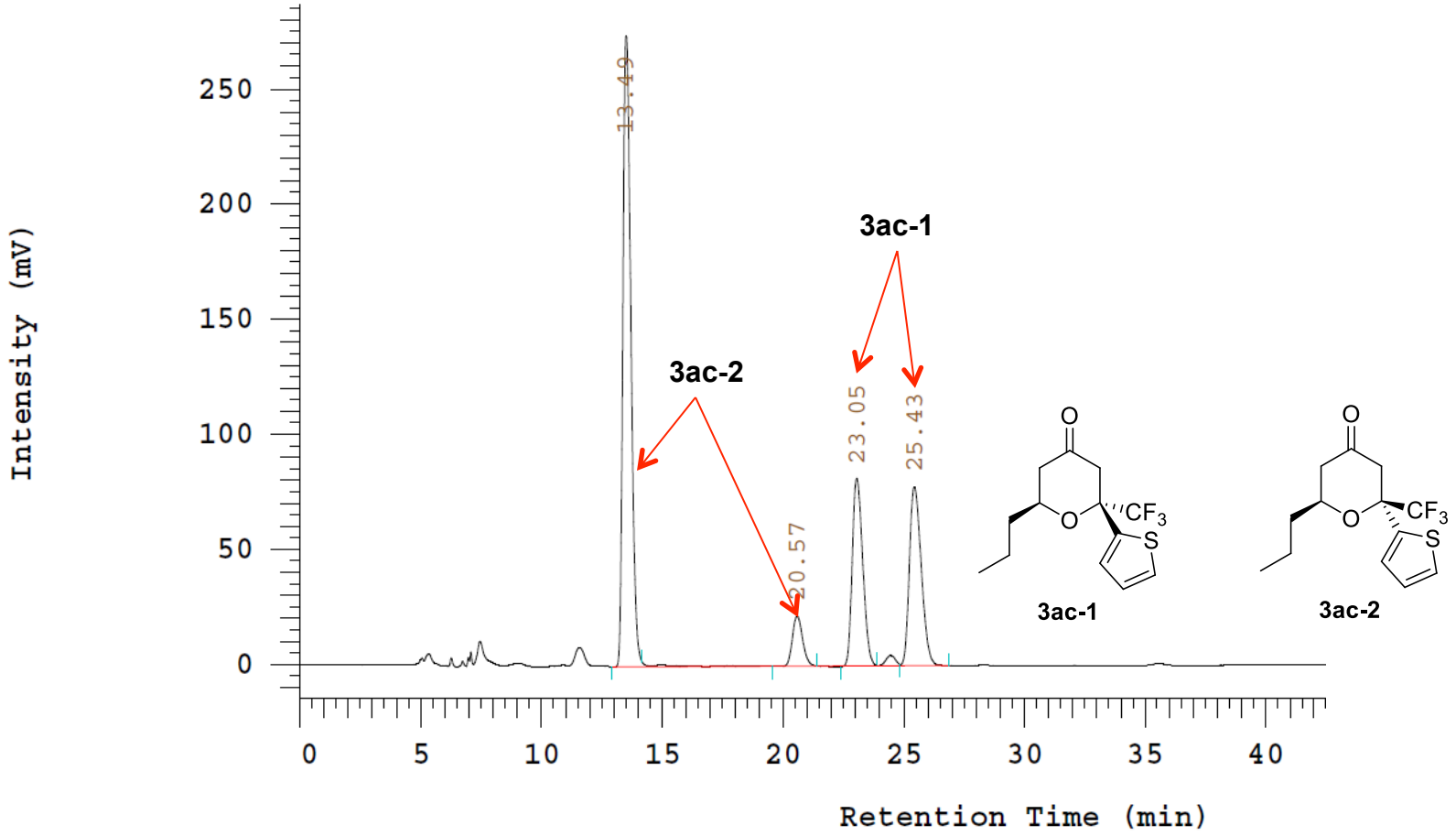
No.	RT	Area	Area %
1	11.37	6433349	22.767
2	18.18	6642505	23.507
3	19.53	6937656	24.552
4	20.58	8243635	29.174
		28257145	100.000



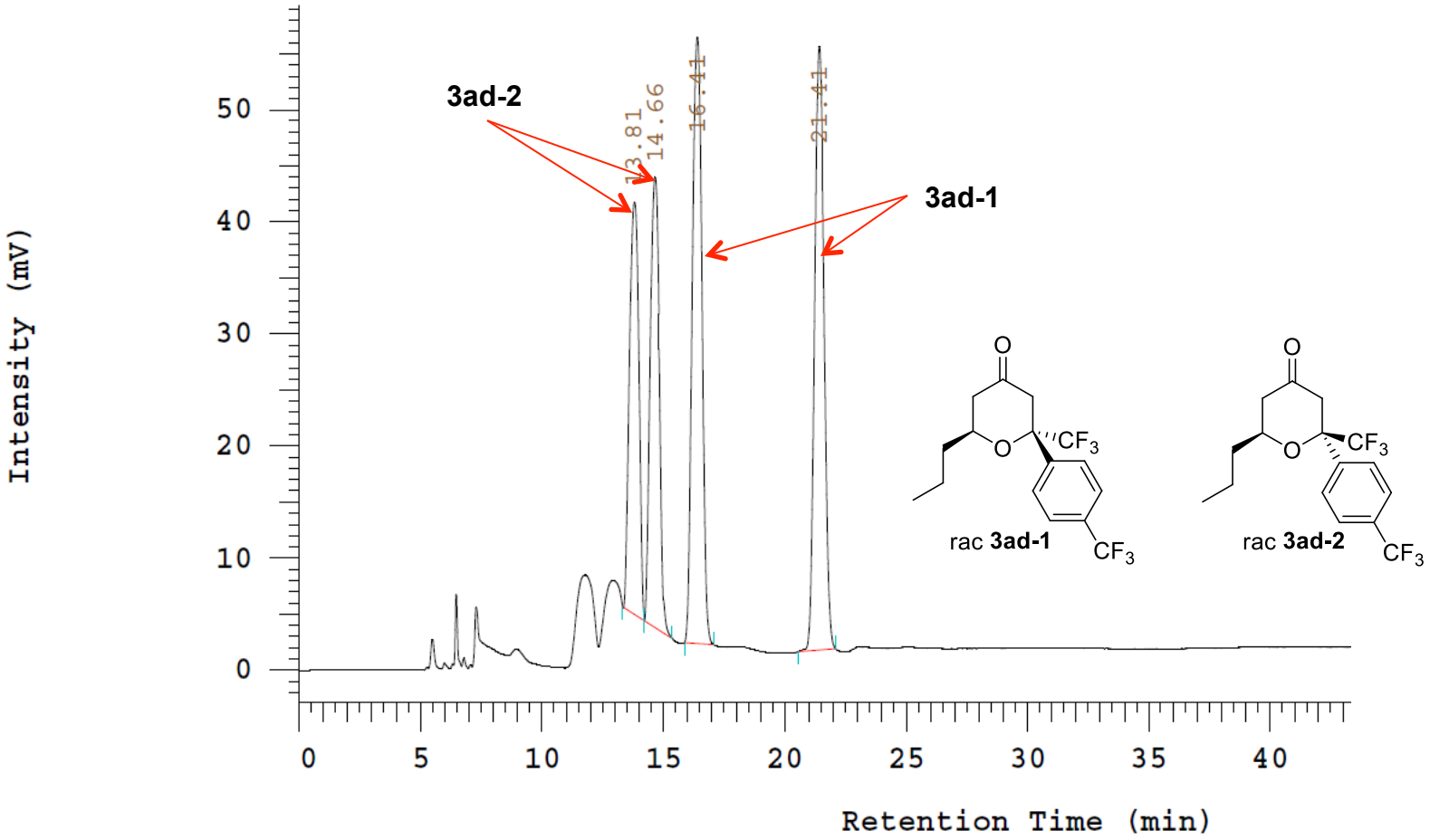
No.	RT	Area	Area %
1	11.67	1484328	73.847
2	18.85	101339	5.042
3	20.57	192331	9.569
4	21.43	232004	11.543
		2010002	100.000



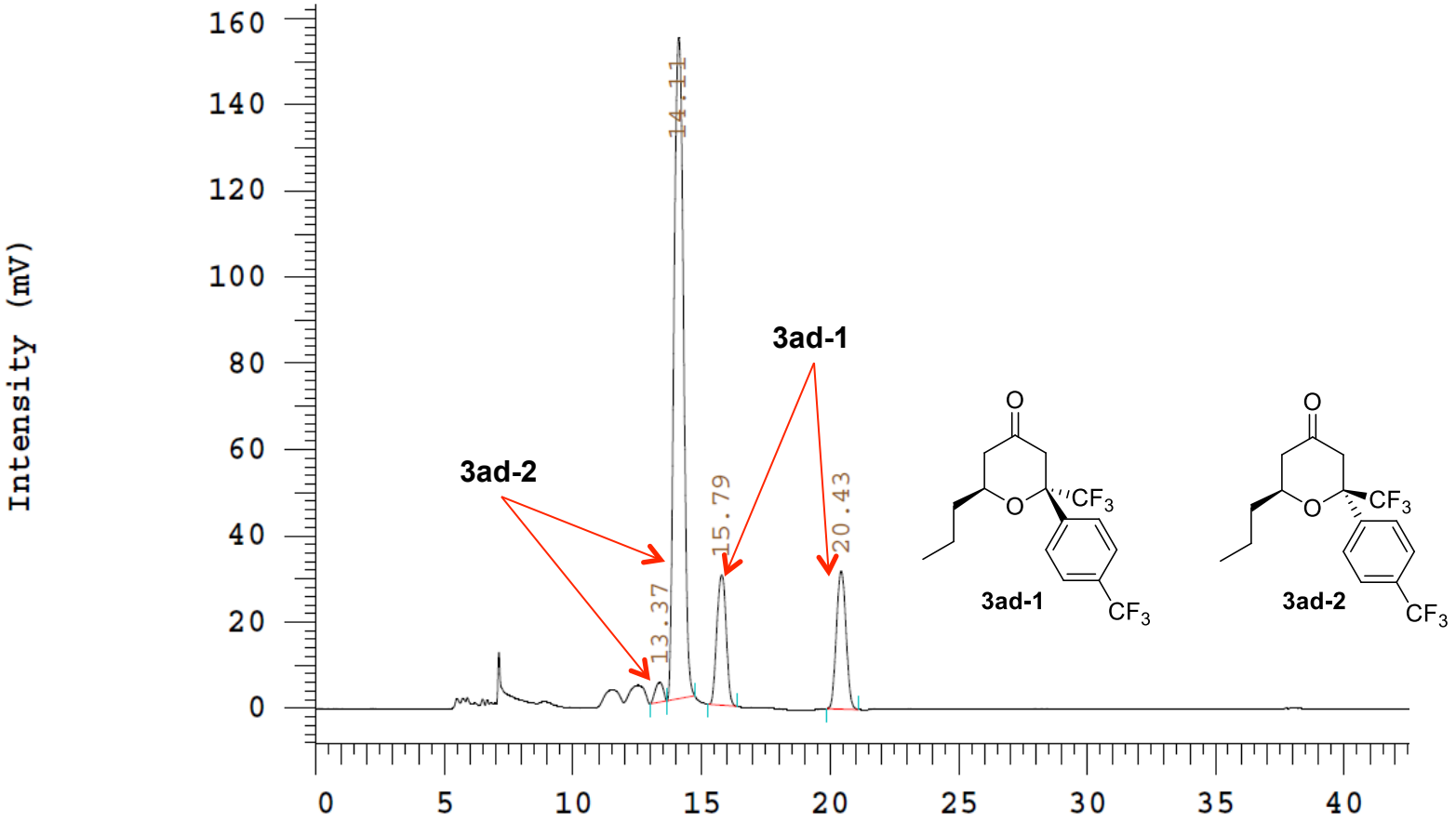
No.	RT	Area	Area %
1	13.69	1265023	11.292
2	20.73	1254587	11.199
3	23.17	4342462	38.763
4	25.54	4340574	38.746
		11202646	100.000



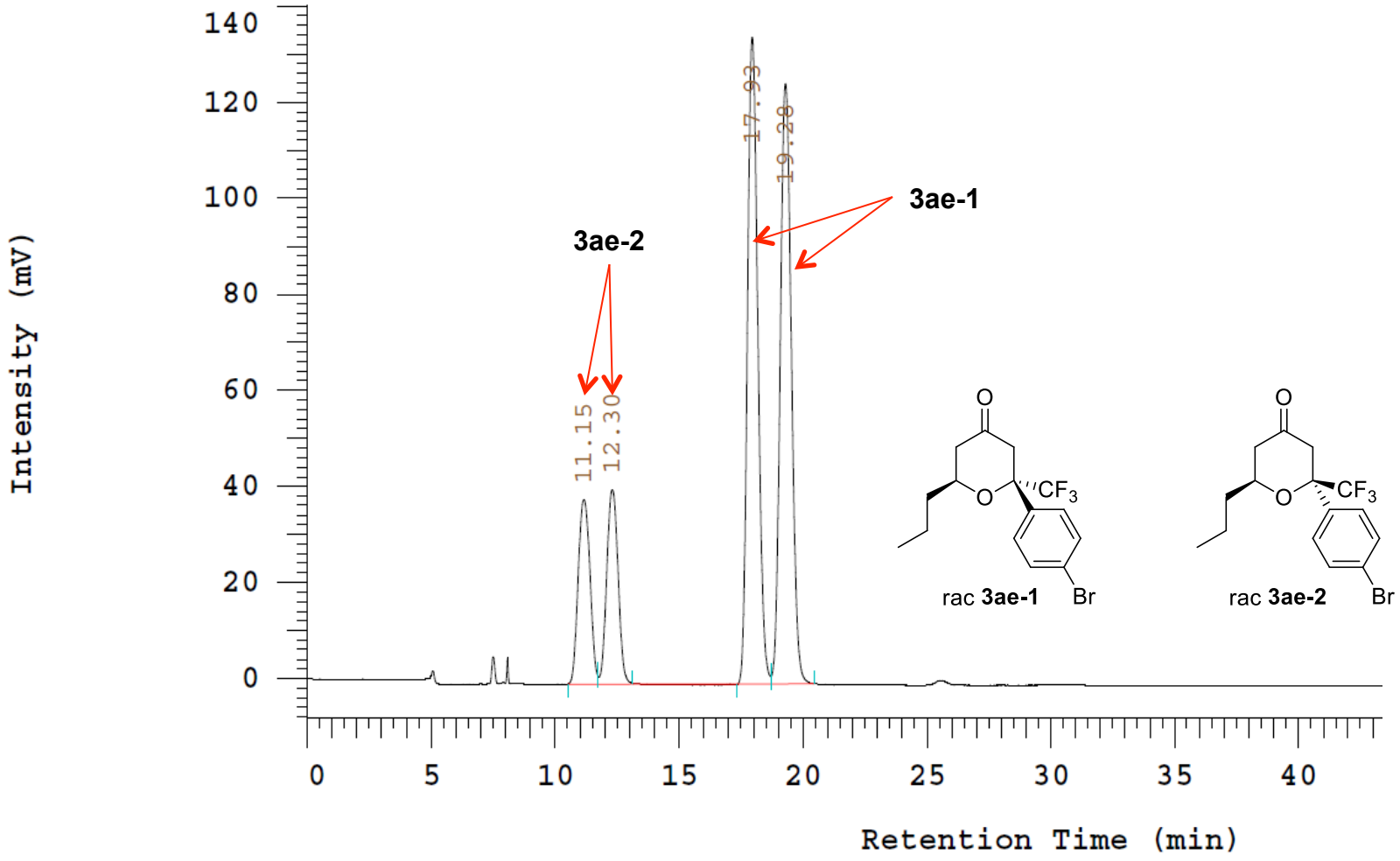
No.	RT	Area	Area %
1	13.49	6030618	51.760
2	20.57	621496	5.334
3	23.05	2395646	20.562
4	25.43	2603278	22.344
		11651038	100.000



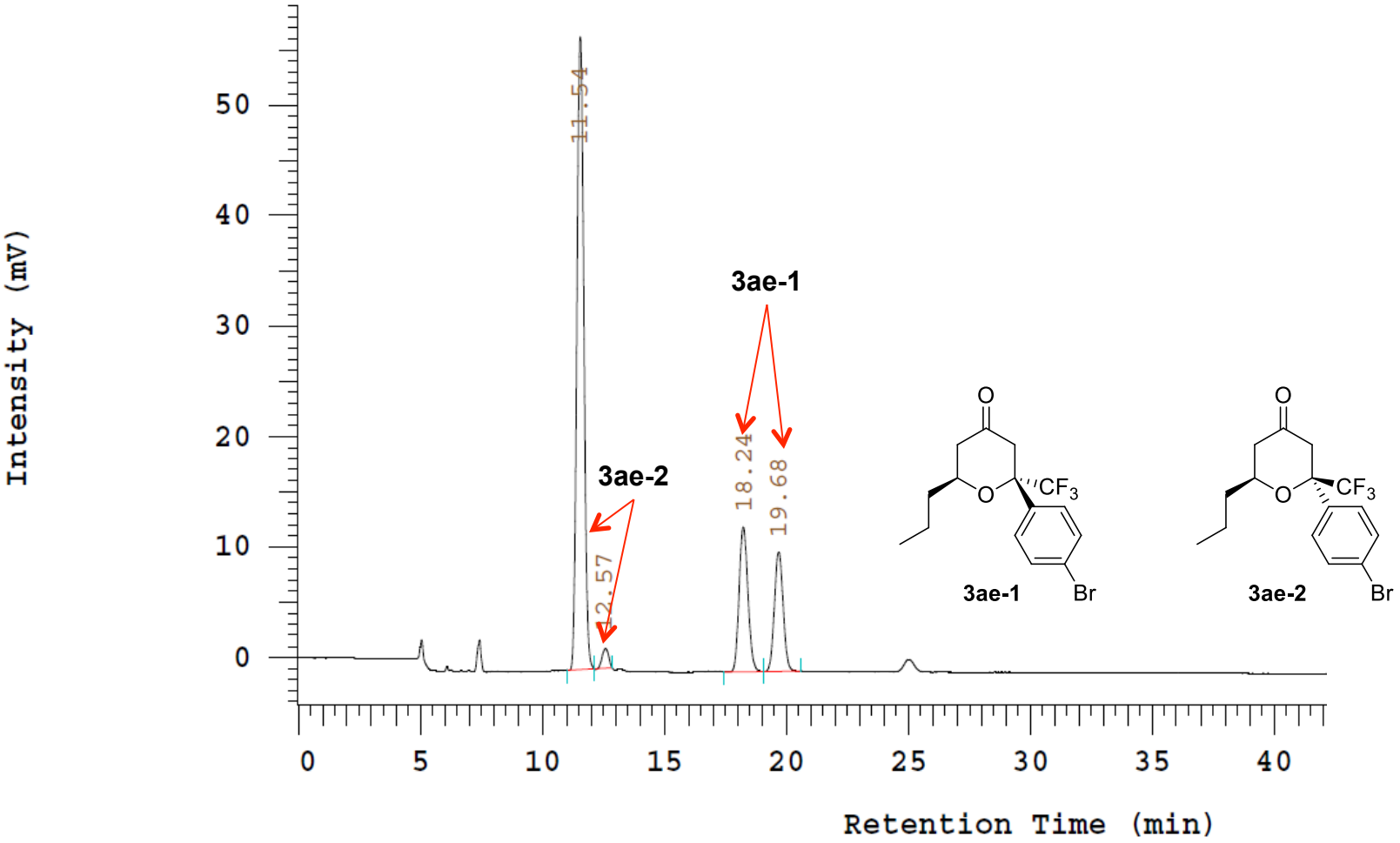
No.	RT	Area	Area %
1	13.81	960292	19.542
2	14.66	1044785	21.261
3	16.41	1450508	29.517
4	21.41	1458511	29.680
		4914096	100.000



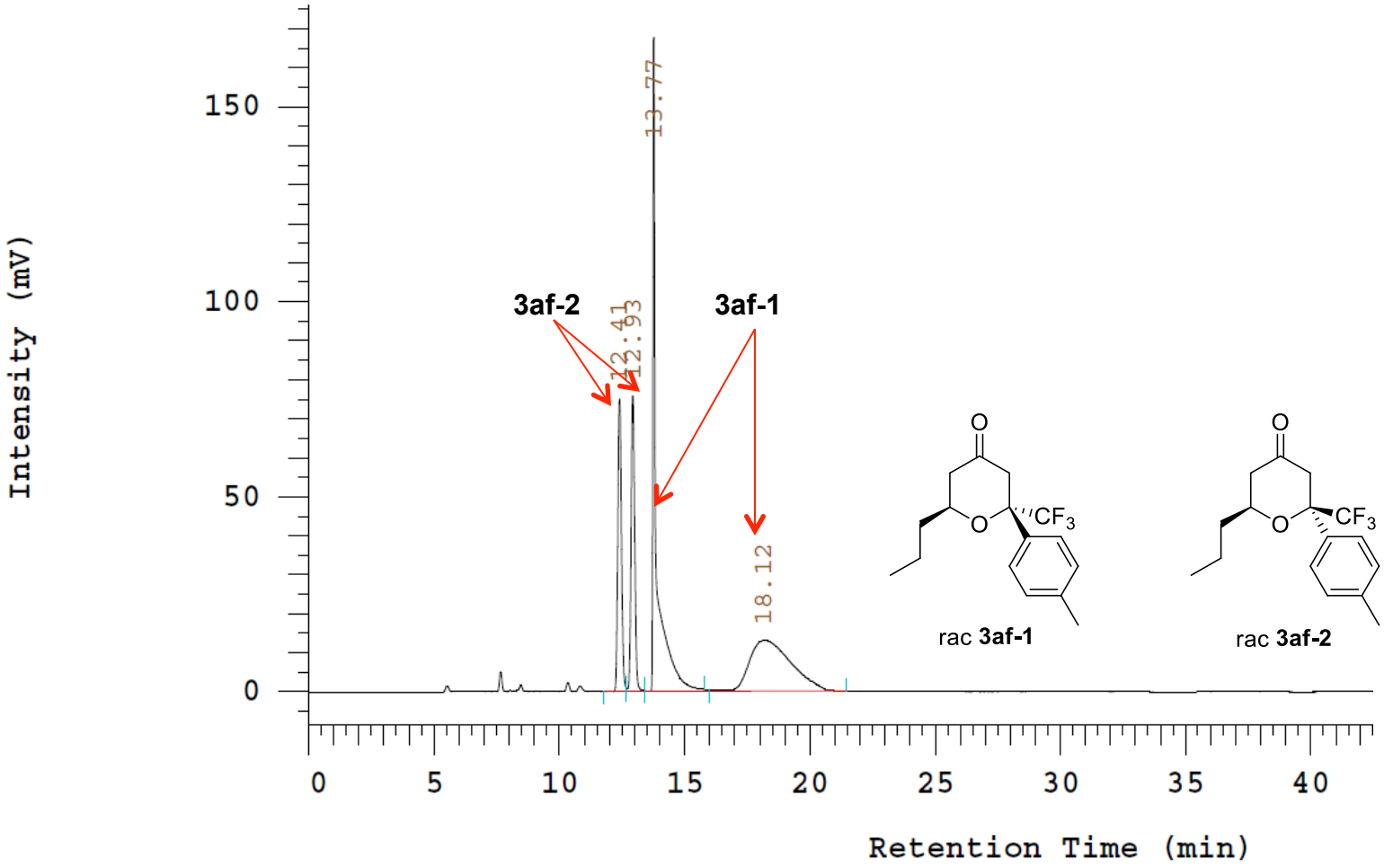
No.	RT	Area	Area %
1	13.37	96413	1.785
2	14.11	3762408	69.670
3	15.79	734451	13.600
4	20.43	807031	14.944
		5400303	100.000



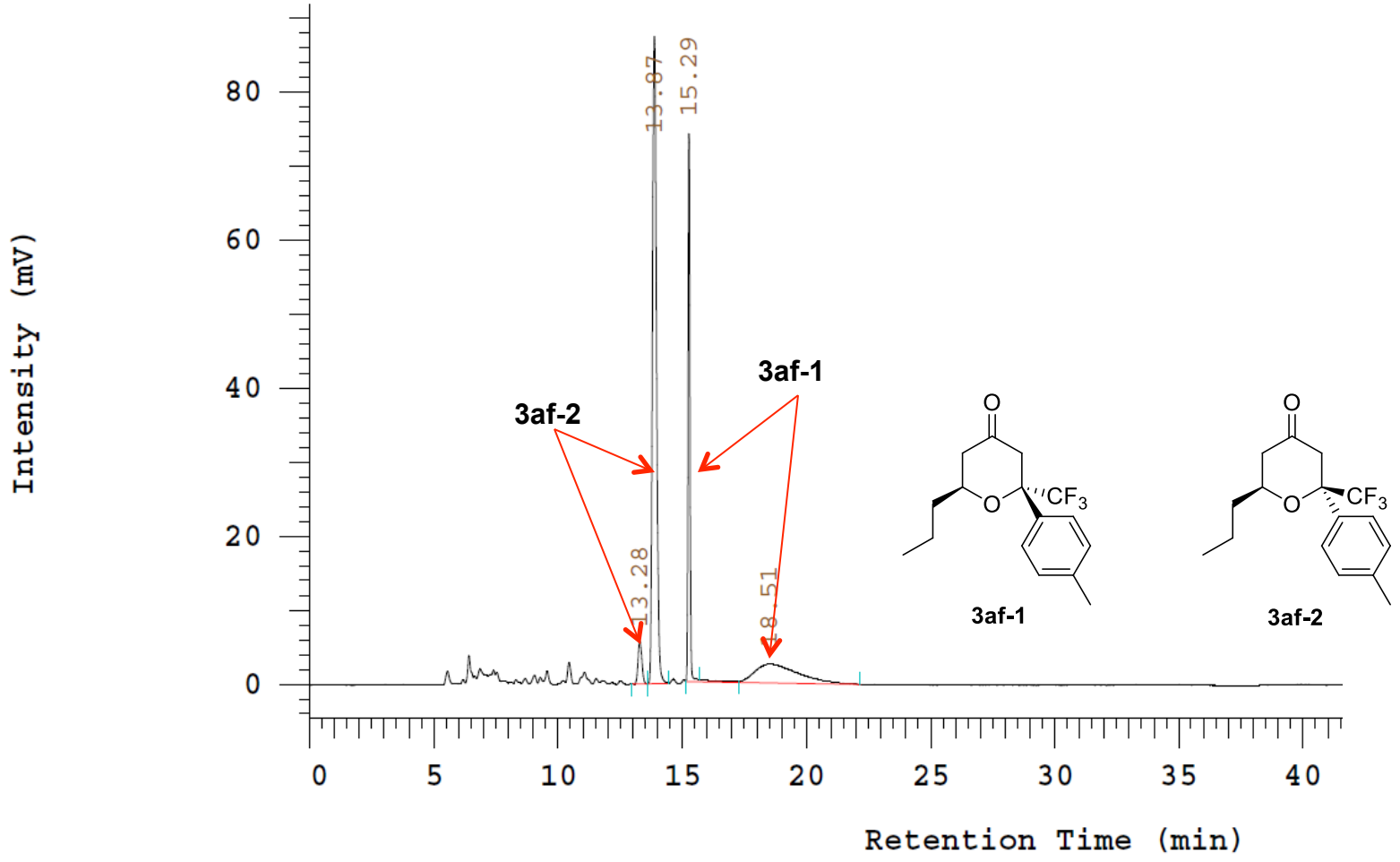
No.	RT	Area	Area %
1	11.15	1242195	12.318
2	12.30	1264434	12.538
3	17.93	3793265	37.615
4	19.28	3784672	37.529



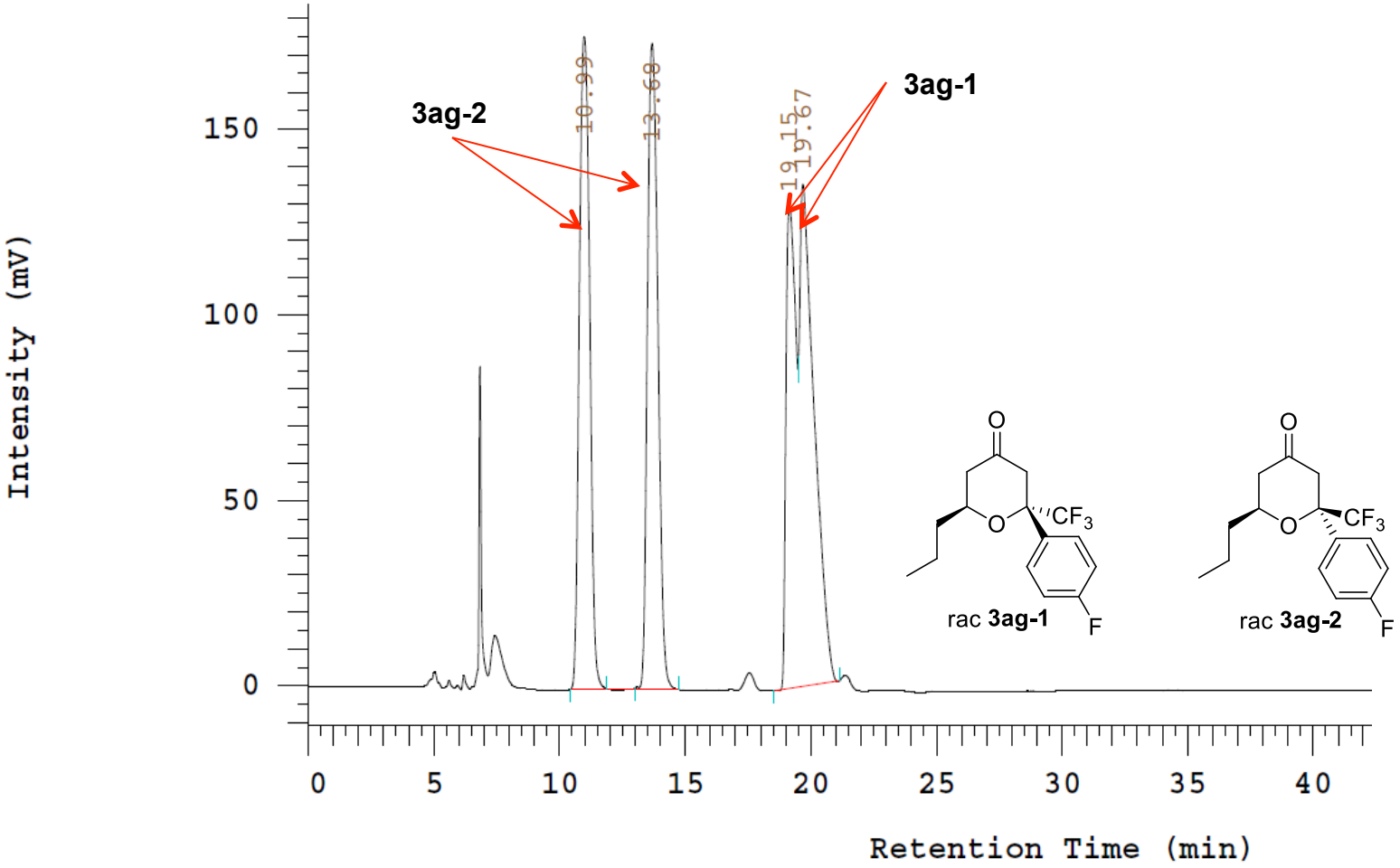
No.	RT	Area	Area %
1	11.54	1085188	63.852
2	12.57	30654	1.804
3	18.24	320555	18.861
4	19.68	263130	15.483
		1699527	100.000



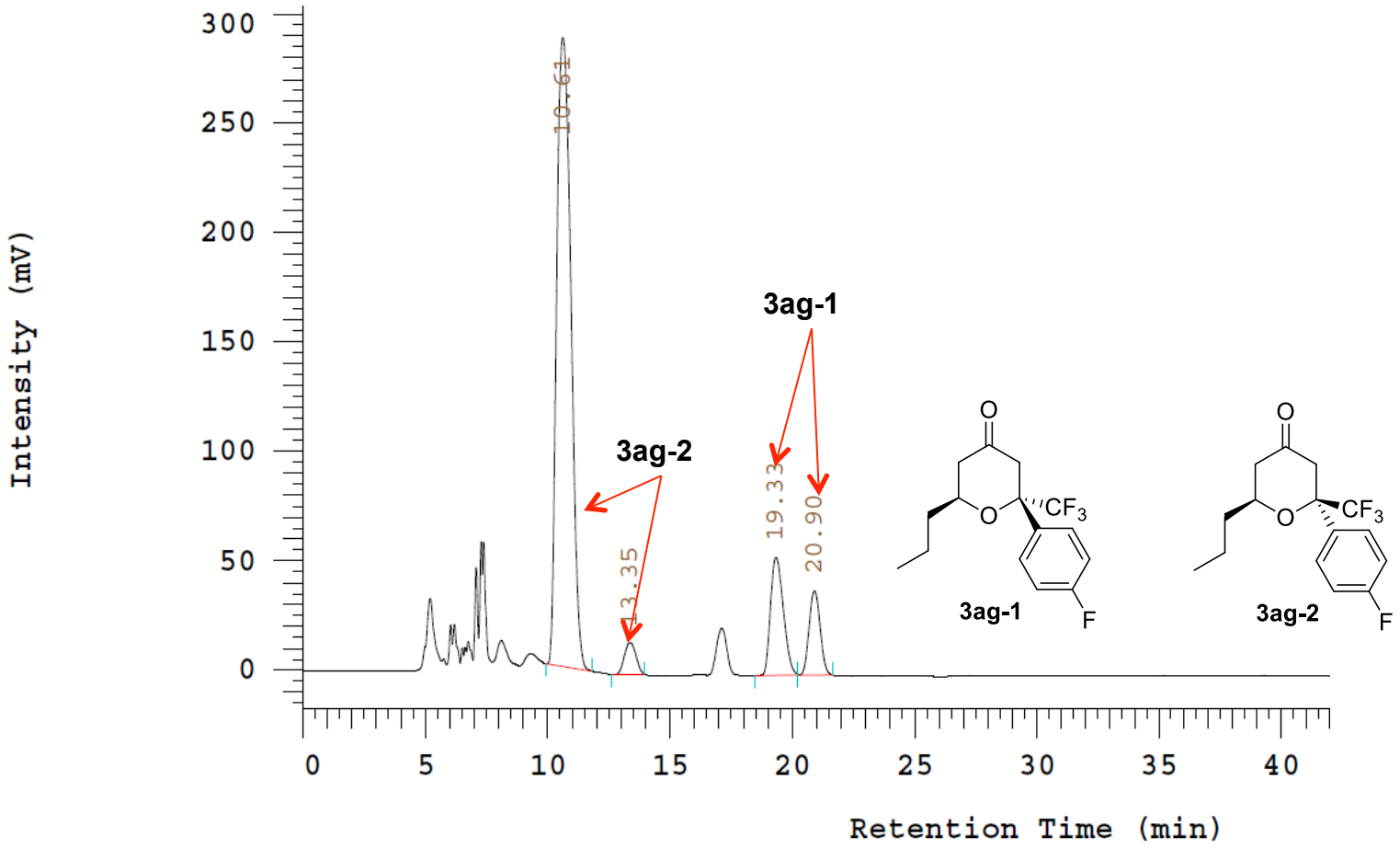
No.	RT	Area	Area %
1	12.41	698414	15.770
2	12.93	712910	16.098
3	13.77	1524449	34.422
4	18.12	1492892	33.710
		4428665	100.000



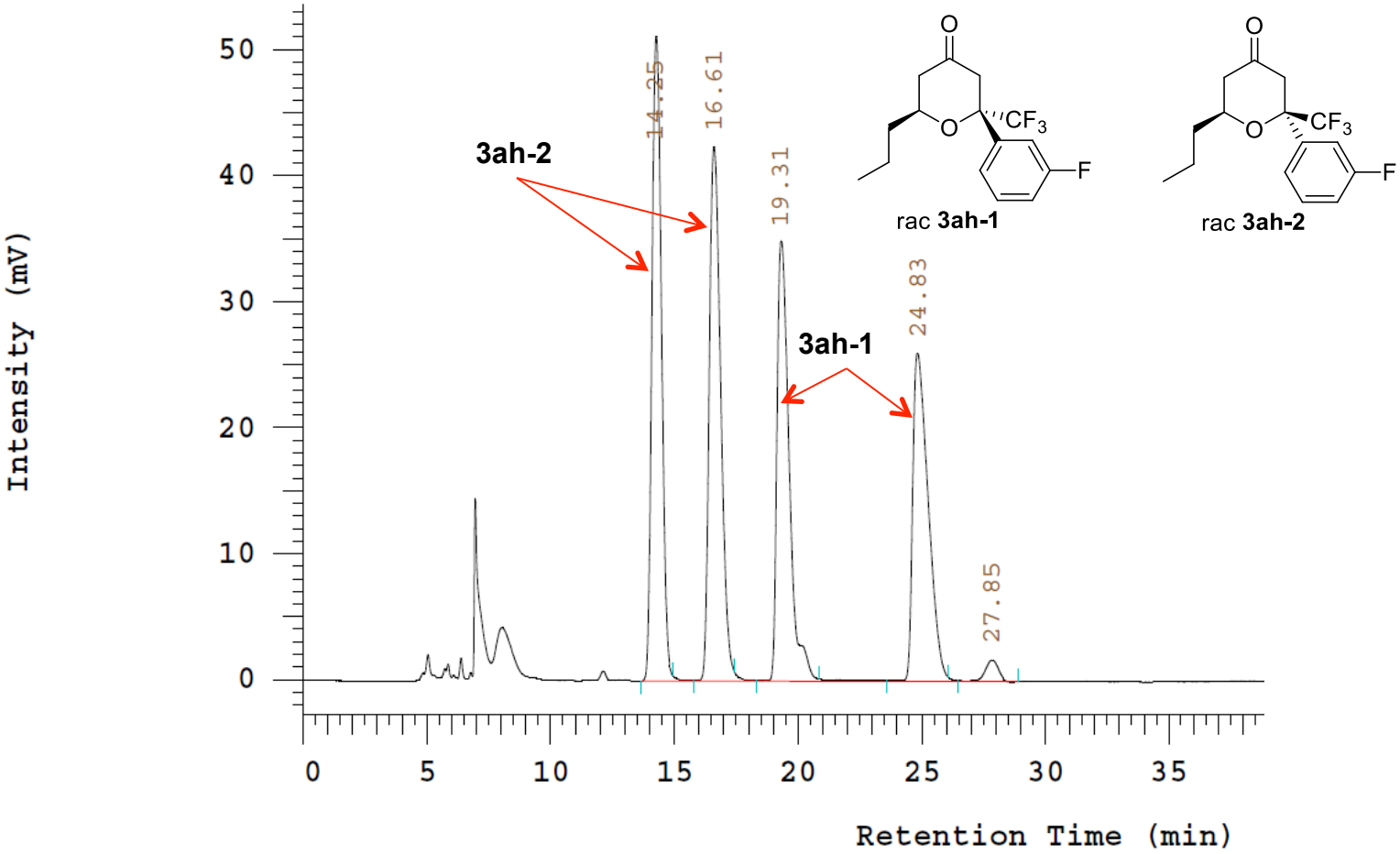
No.	RT	Area	Area %
1	13.28	56335	3.460
2	13.87	920917	56.553
3	15.29	342674	21.043
4	18.51	308487	18.944
		1628413	100.000



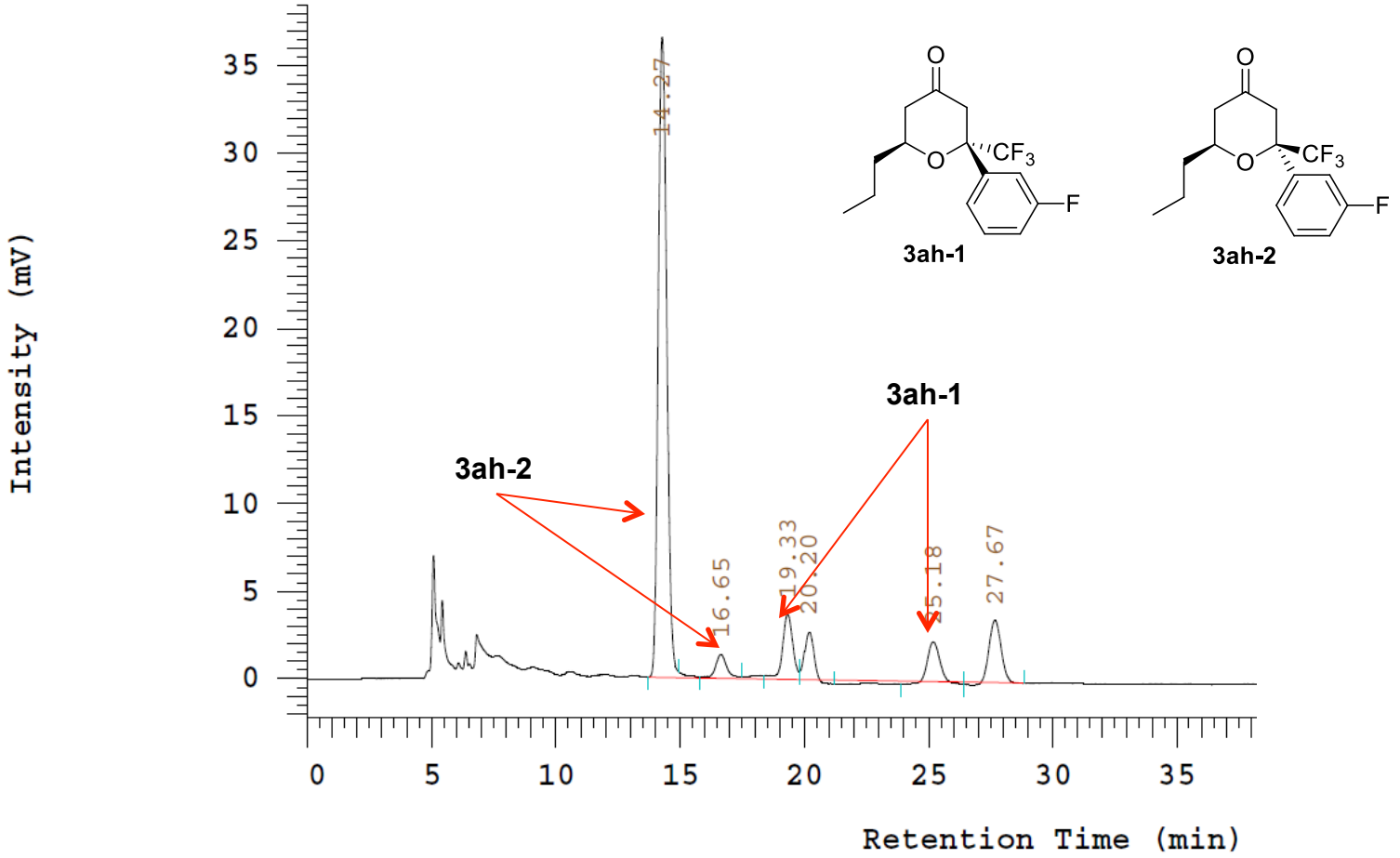
No.	RT	Area	Area %
1	10.99	4915310	26.179
2	13.68	4911664	26.159
3	19.15	3421640	18.223
4	19.67	5527464	29.439
		18776078	100.000



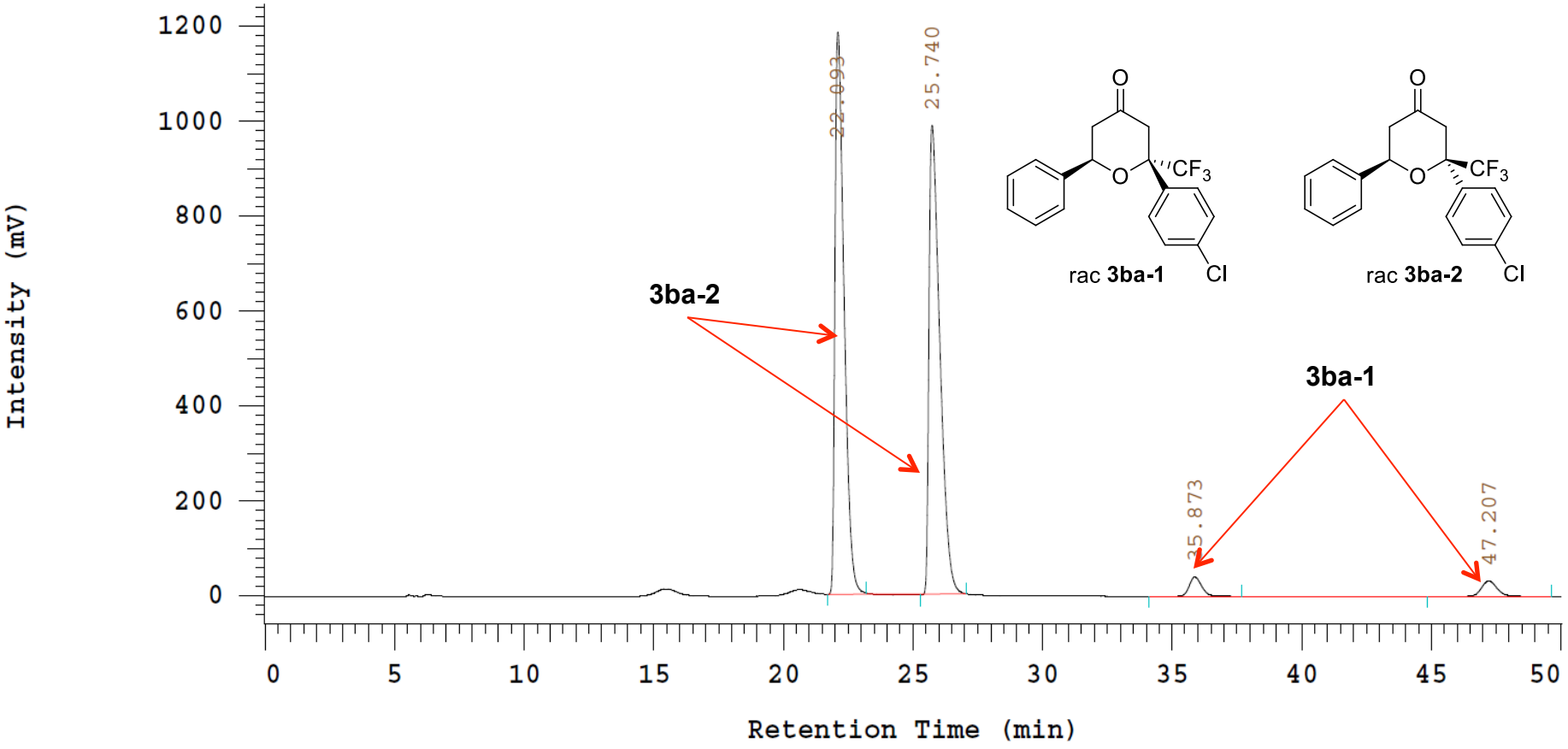
No.	RT	Area	Area %
1	10.61	11373350	76.036
2	13.35	469406	3.138
3	19.33	1927100	12.883
4	20.90	1188055	7.943
		14957911	100.000



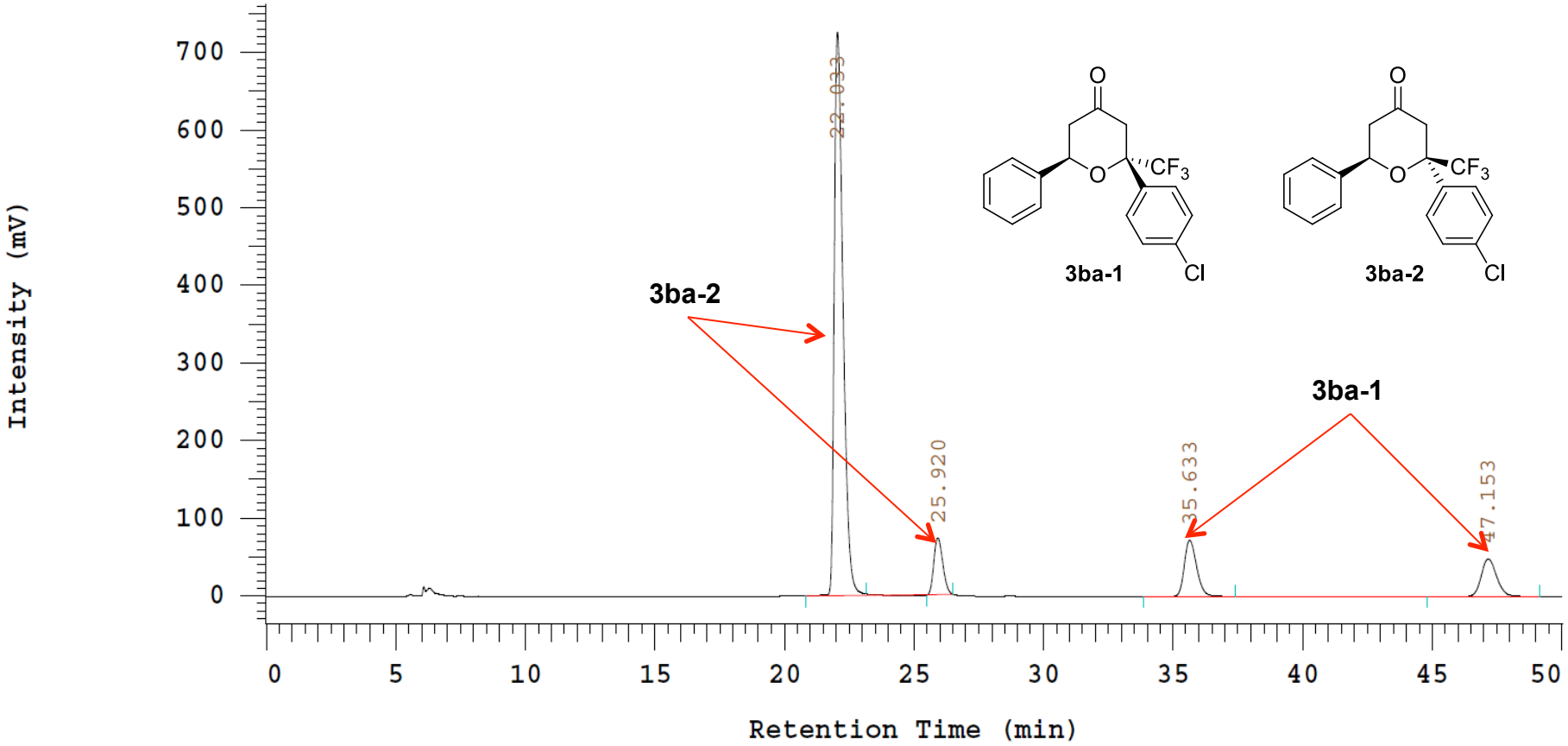
No.	RT	Area	Area %
1	14.25	1332513	26.623
2	16.61	1330192	26.577
3	19.31	1168360	23.344
4	24.83	1111458	22.207
5	27.85	62540	1.250
		5005063	100.000



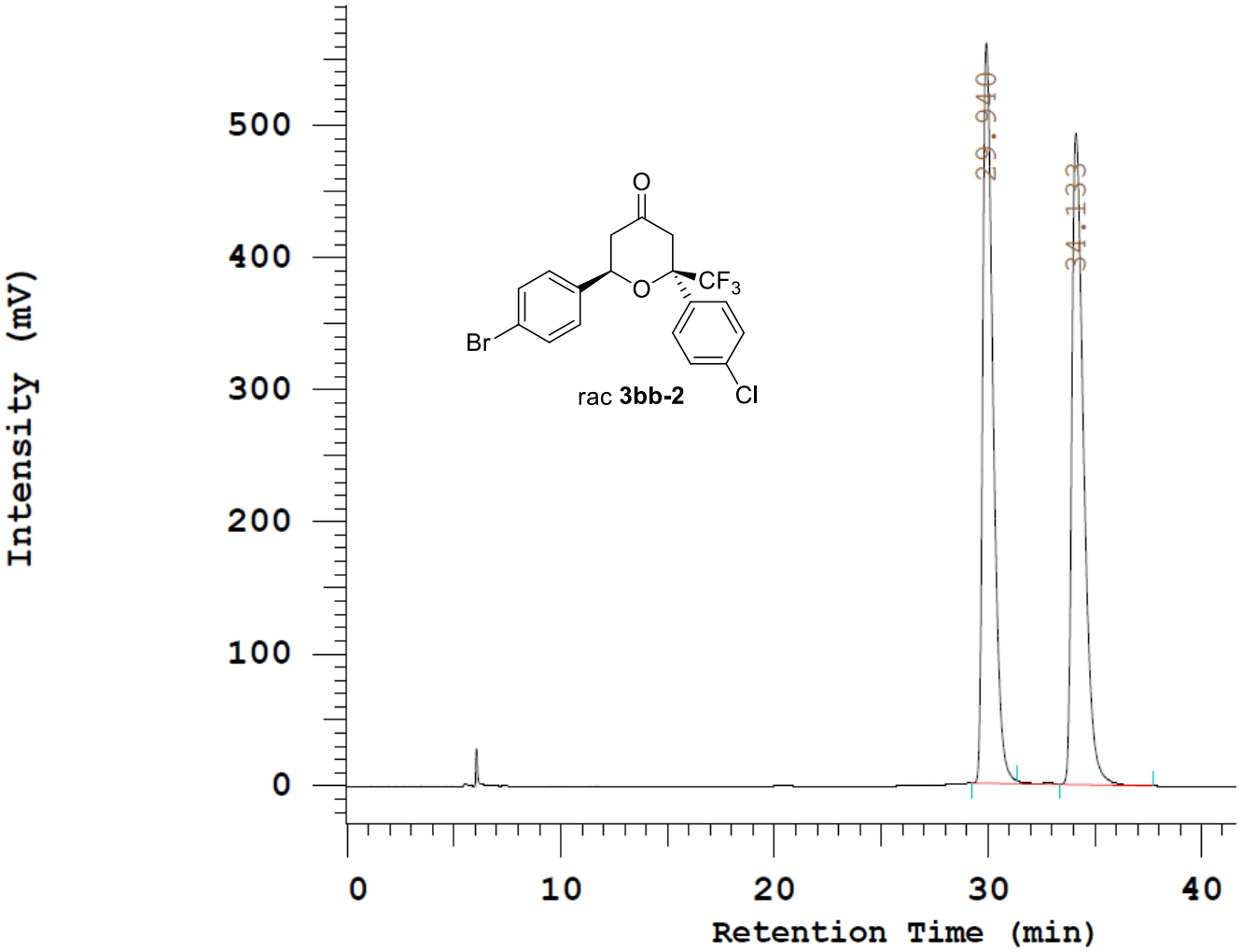
No.	RT	Area	Area %
1	14.27	848554	68.735
2	16.65	43828	3.550
3	19.33	105562	8.551
4	20.20	62079	5.029
5	25.18	64065	5.189
6	27.67	110440	8.946
		1234528	100.000



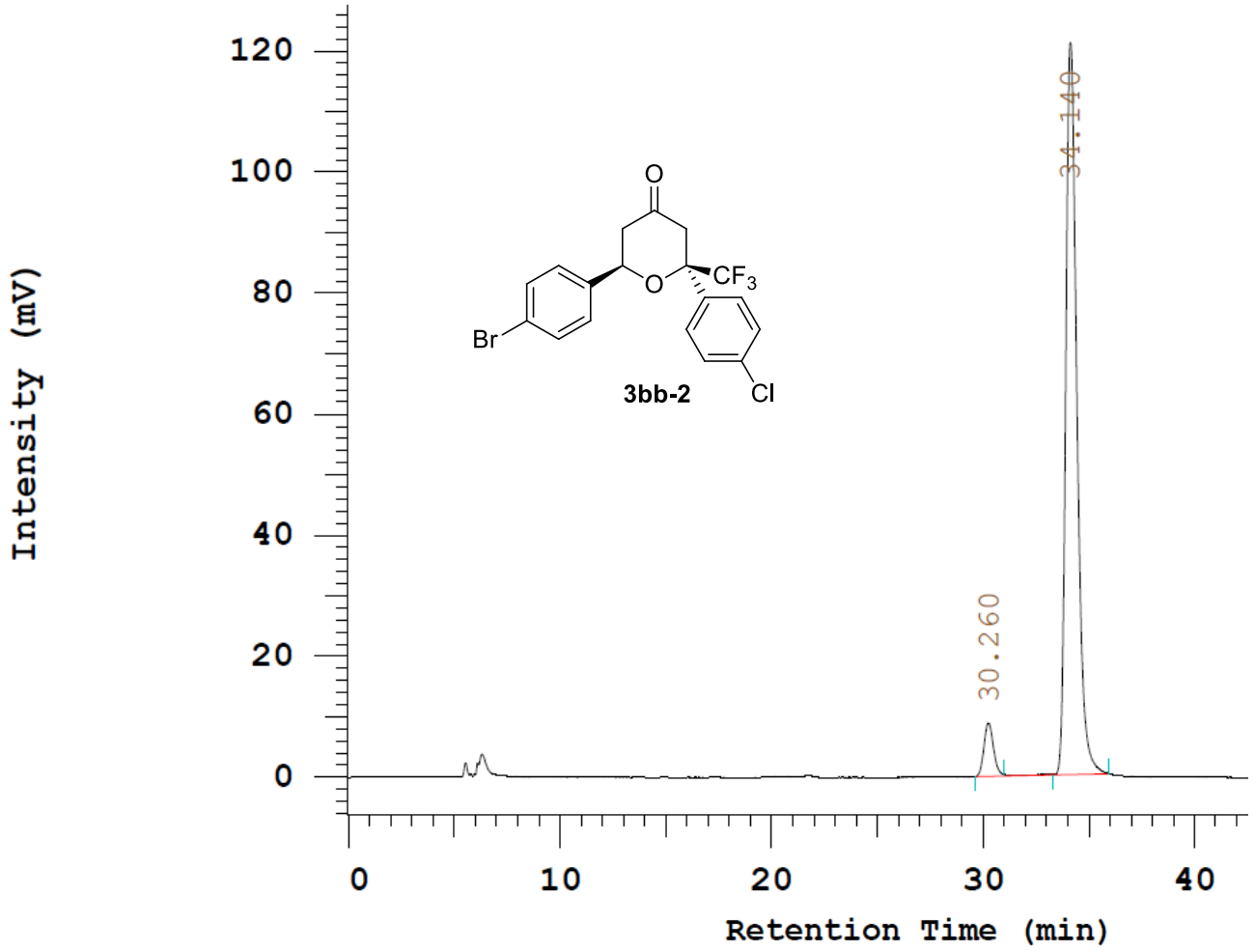
No.	RT	Area	Conc 1
1	22.093	28224985	47.778
2	25.740	28212567	47.757
3	35.873	1312888	2.222
4	47.207	1324804	2.243
		59075244	100.000



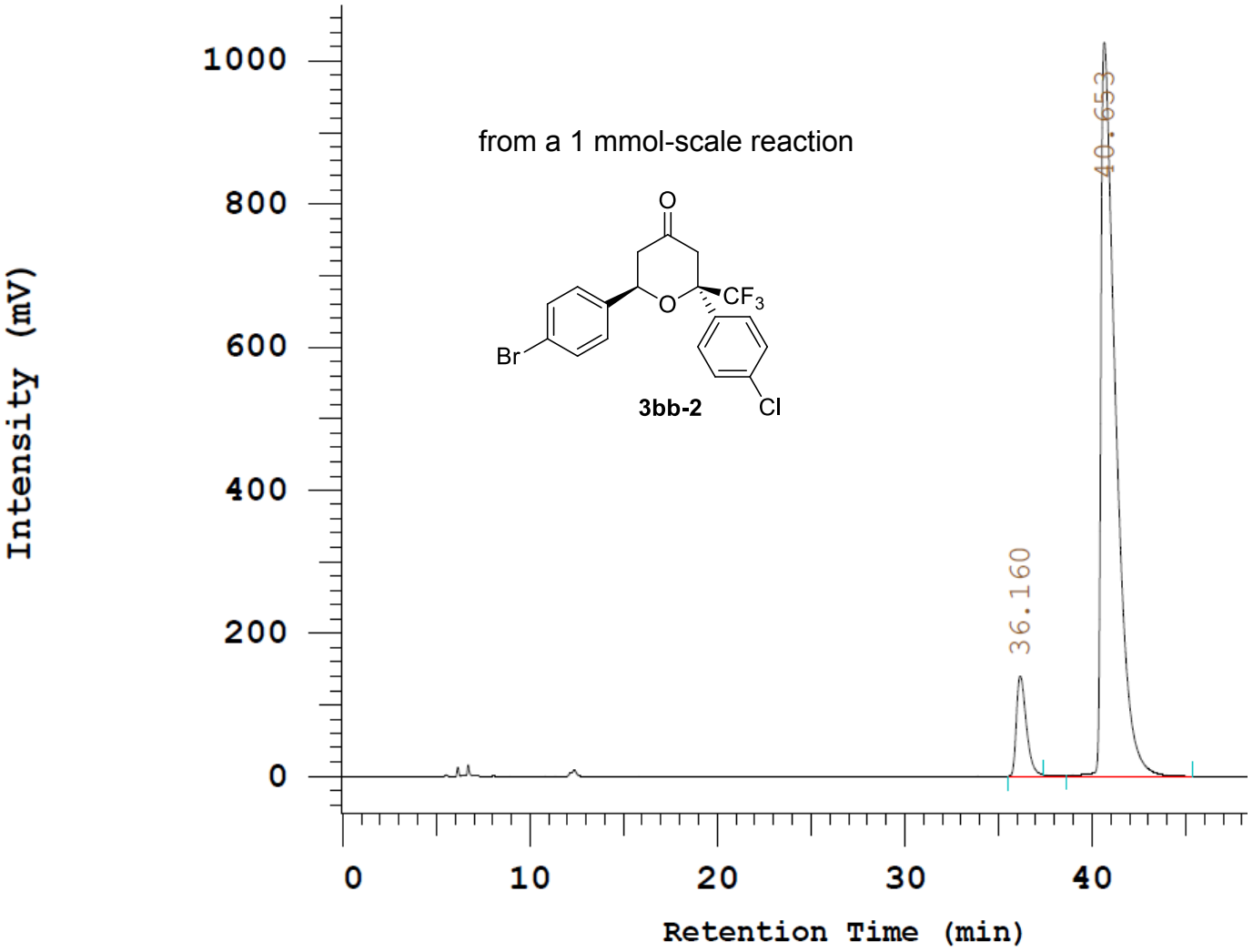
No.	RT	Area	Conc 1
1	22.033	16535875	73.372
2	25.920	1716693	7.617
3	35.633	2344778	10.404
4	47.153	1939725	8.607
		22537071	100.000



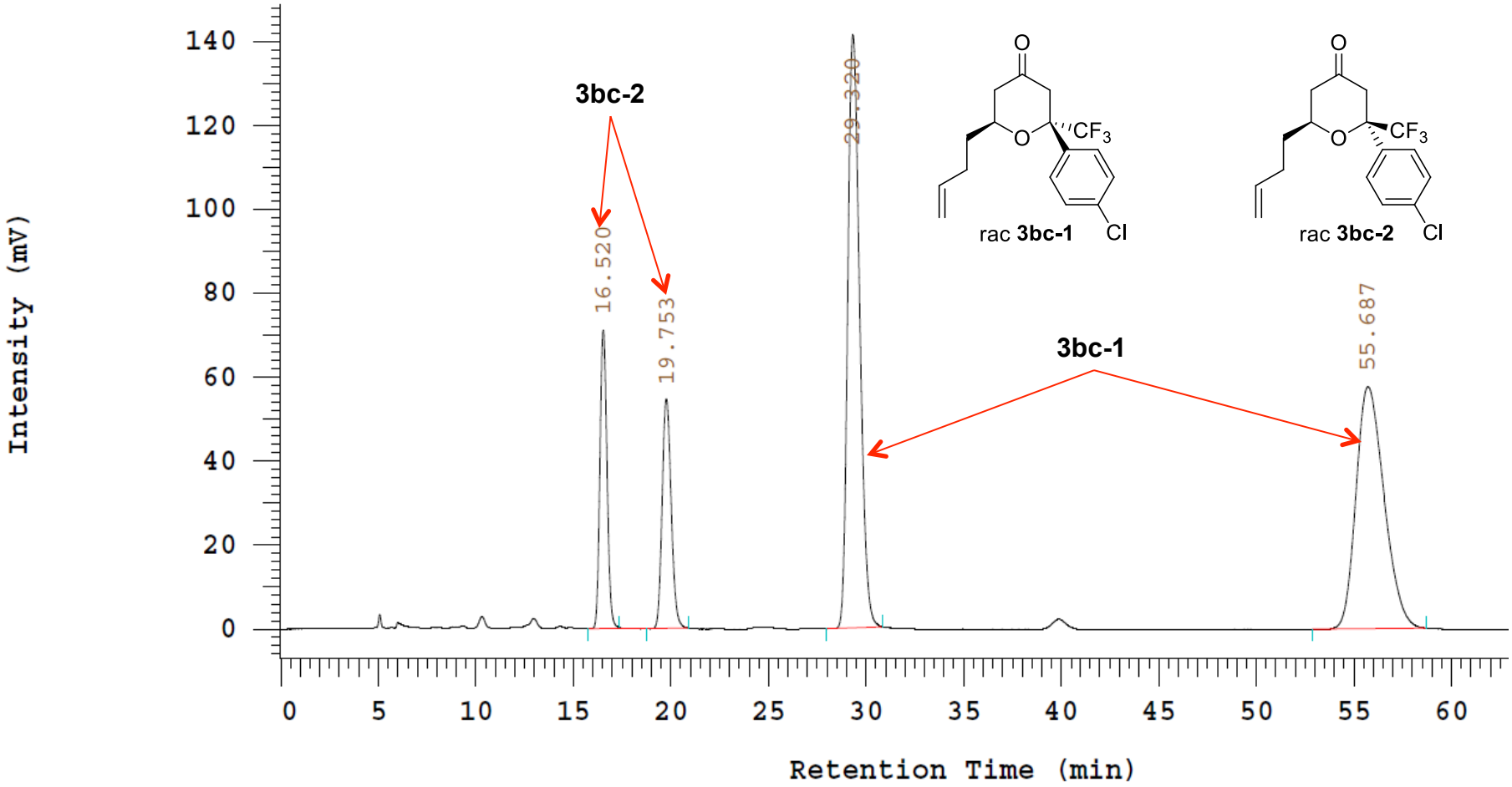
No.	RT	Area	Conc 1
1	29.940	18368354	49.832
2	34.133	18492405	50.168
		36860759	100.000



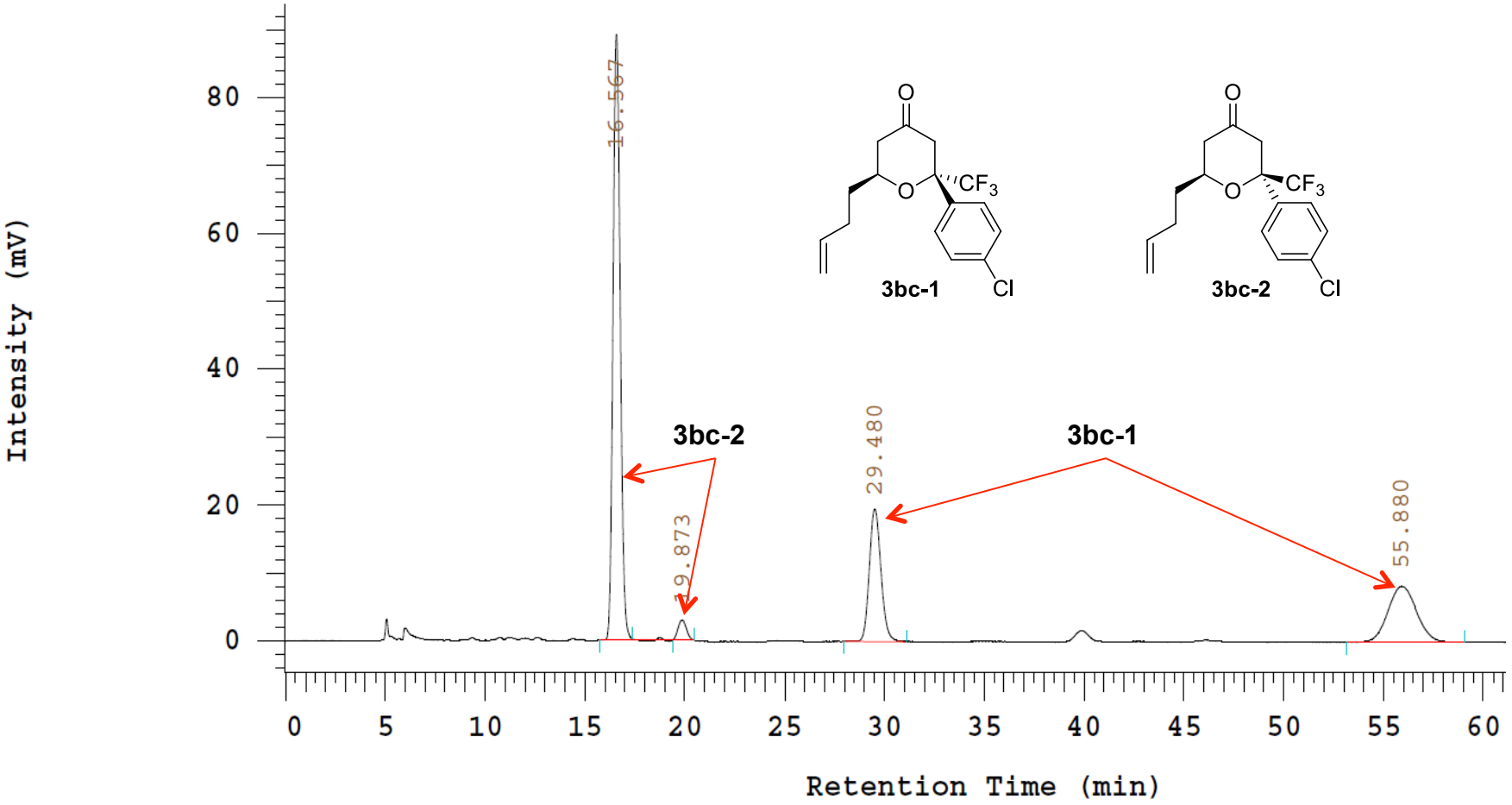
No.	RT	Area	Conc 1
1	30.260	267661	5.916
2	34.140	4256400	94.084
		4524061	100.000



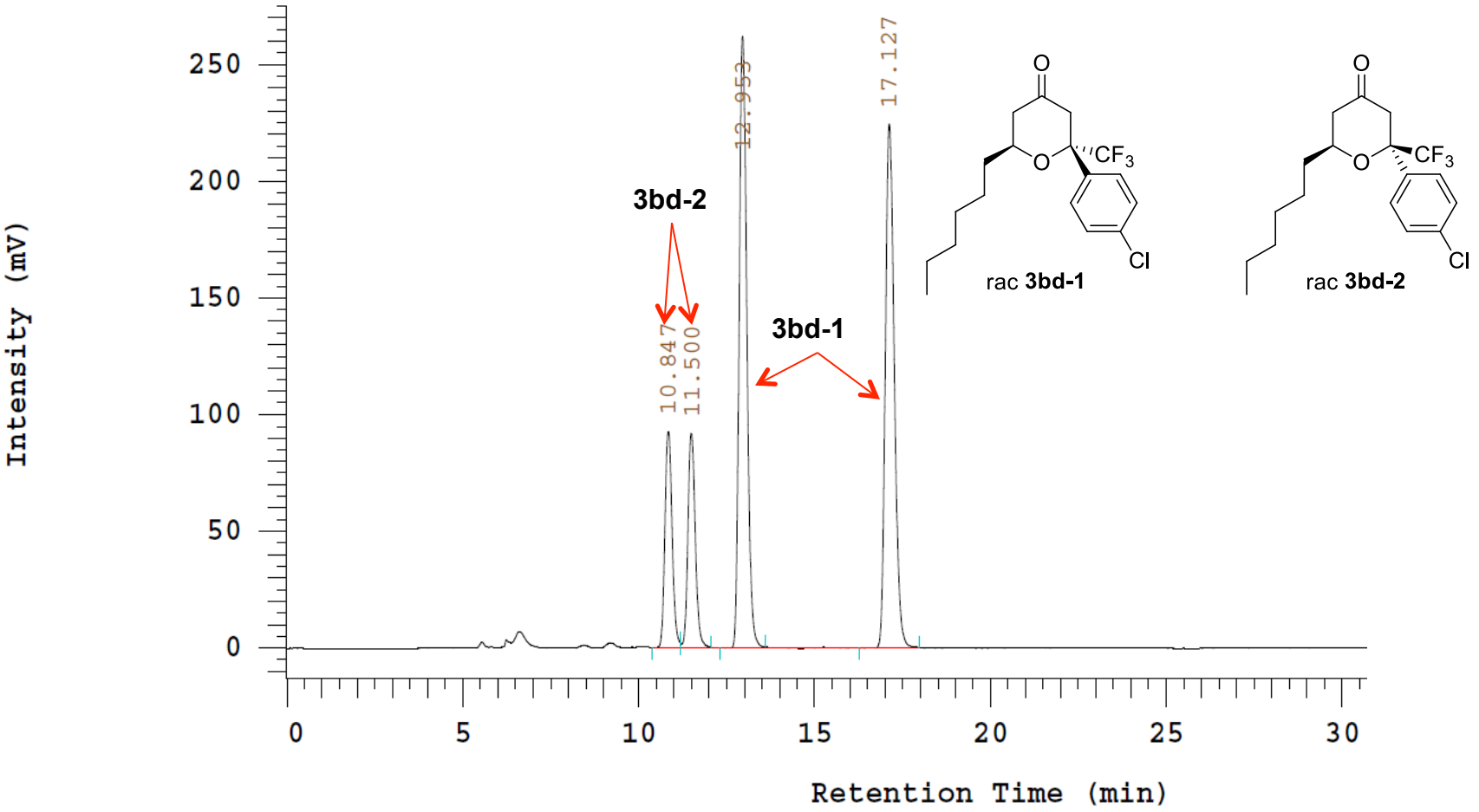
No.	RT	Area	Conc 1
1	36.160	5012473	8.376
2	40.653	54827345	91.624
		59839818	100.000



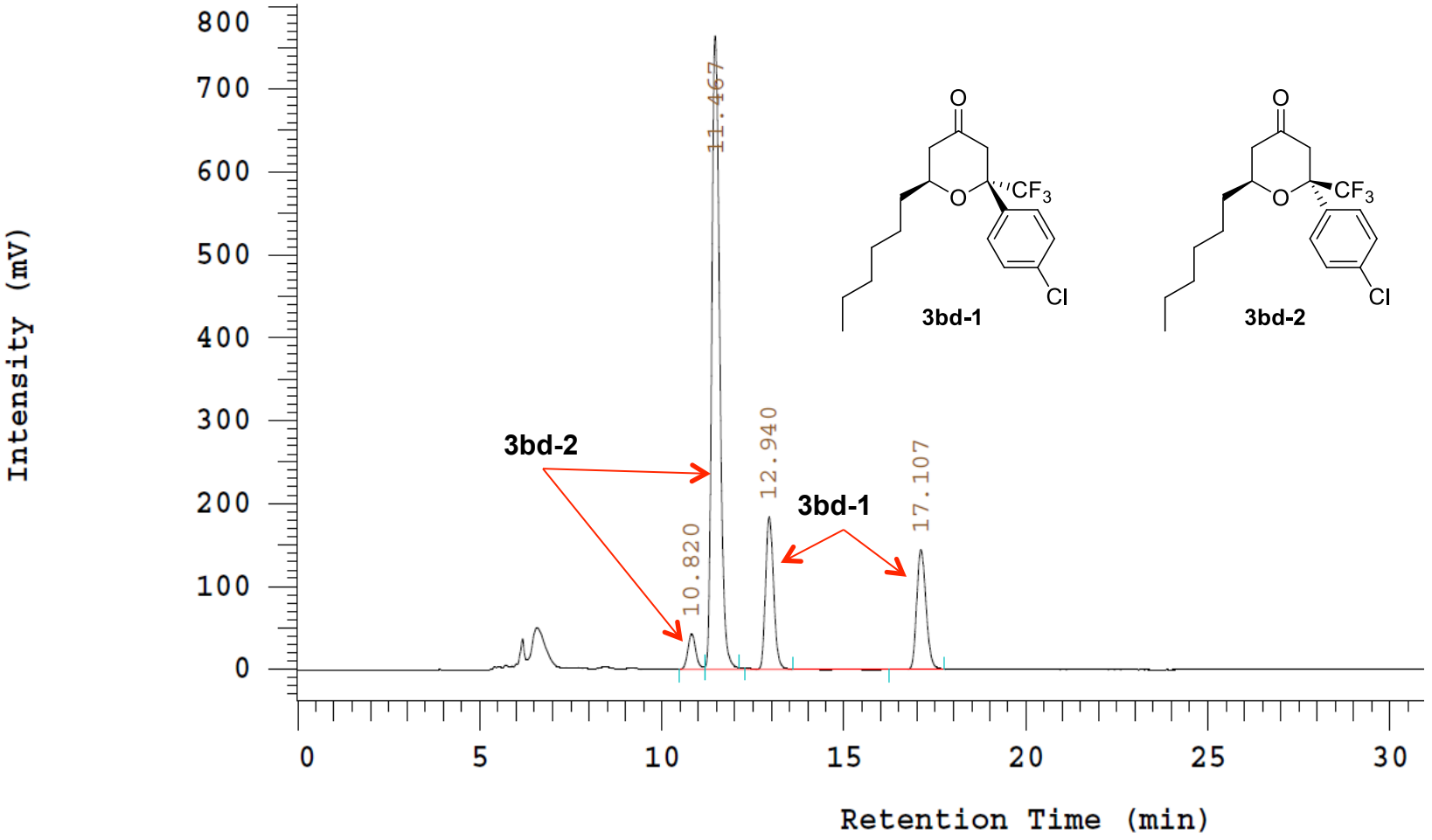
No.	RT	Area	Conc 1
1	16.520	1713931	11.423
2	19.753	1699463	11.326
3	29.320	5847567	38.972
4	55.687	5743486	38.279
		15004447	100.000



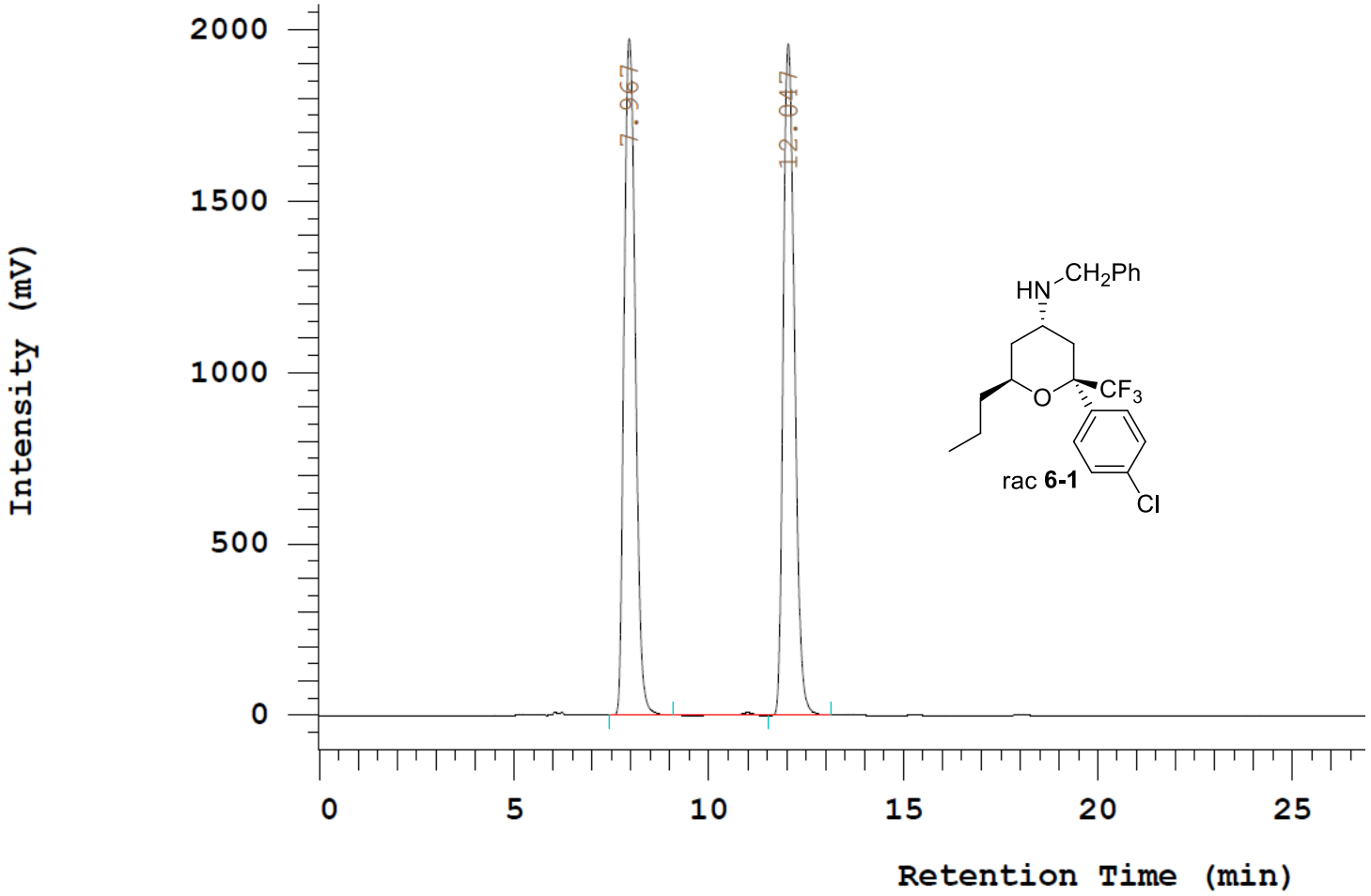
No.	RT	Area	Conc 1
1	16.567	2144523	56.102
2	19.873	82972	2.171
3	29.480	777514	20.340
4	55.880	817564	21.388
		3822573	100.000



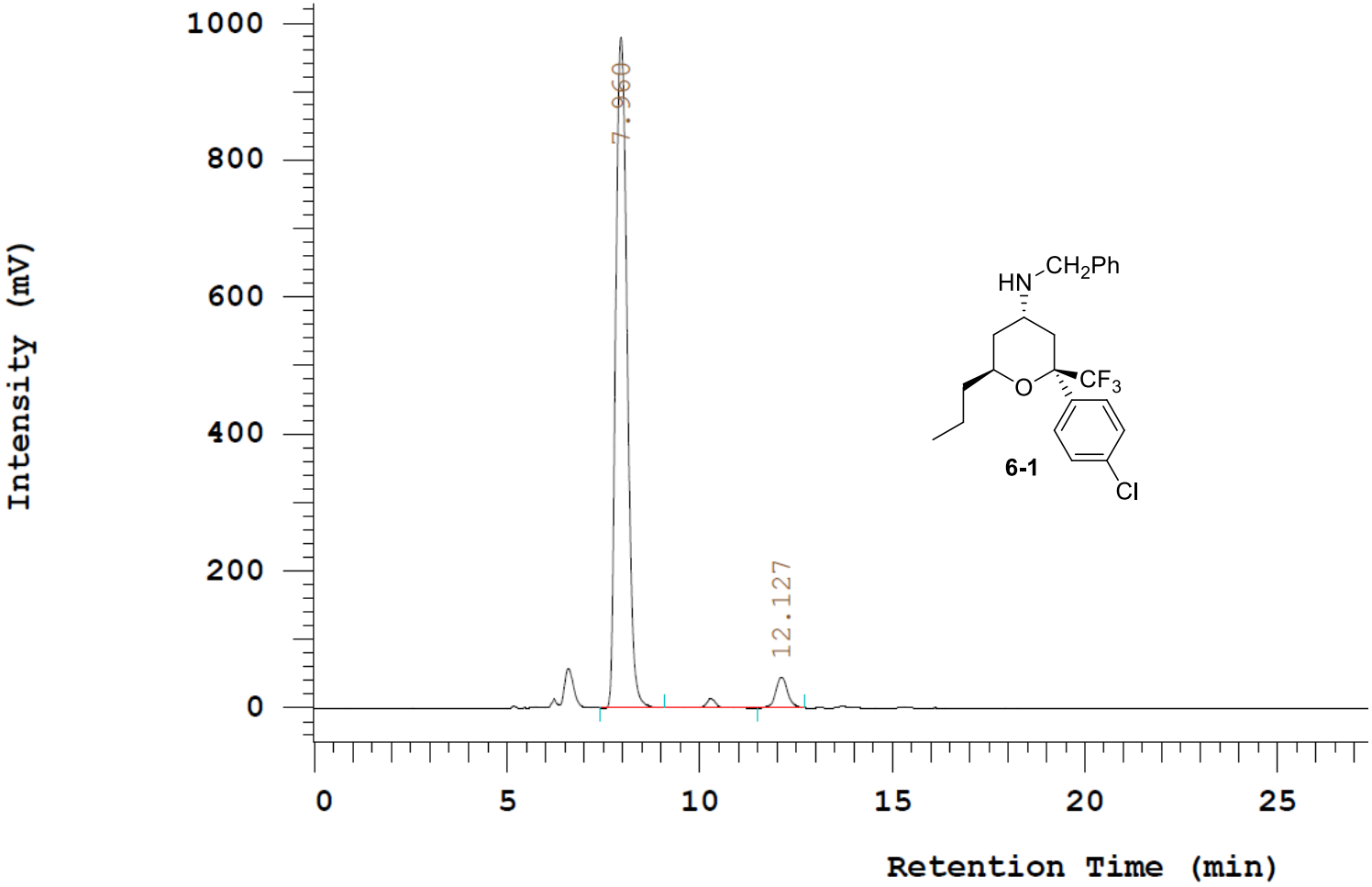
No.	RT	Area	Conc 1
1	10.847	1277823	12.428
2	11.500	1296542	12.610
3	12.953	3855338	37.495
4	17.127	3852505	37.468
		10282208	100.000



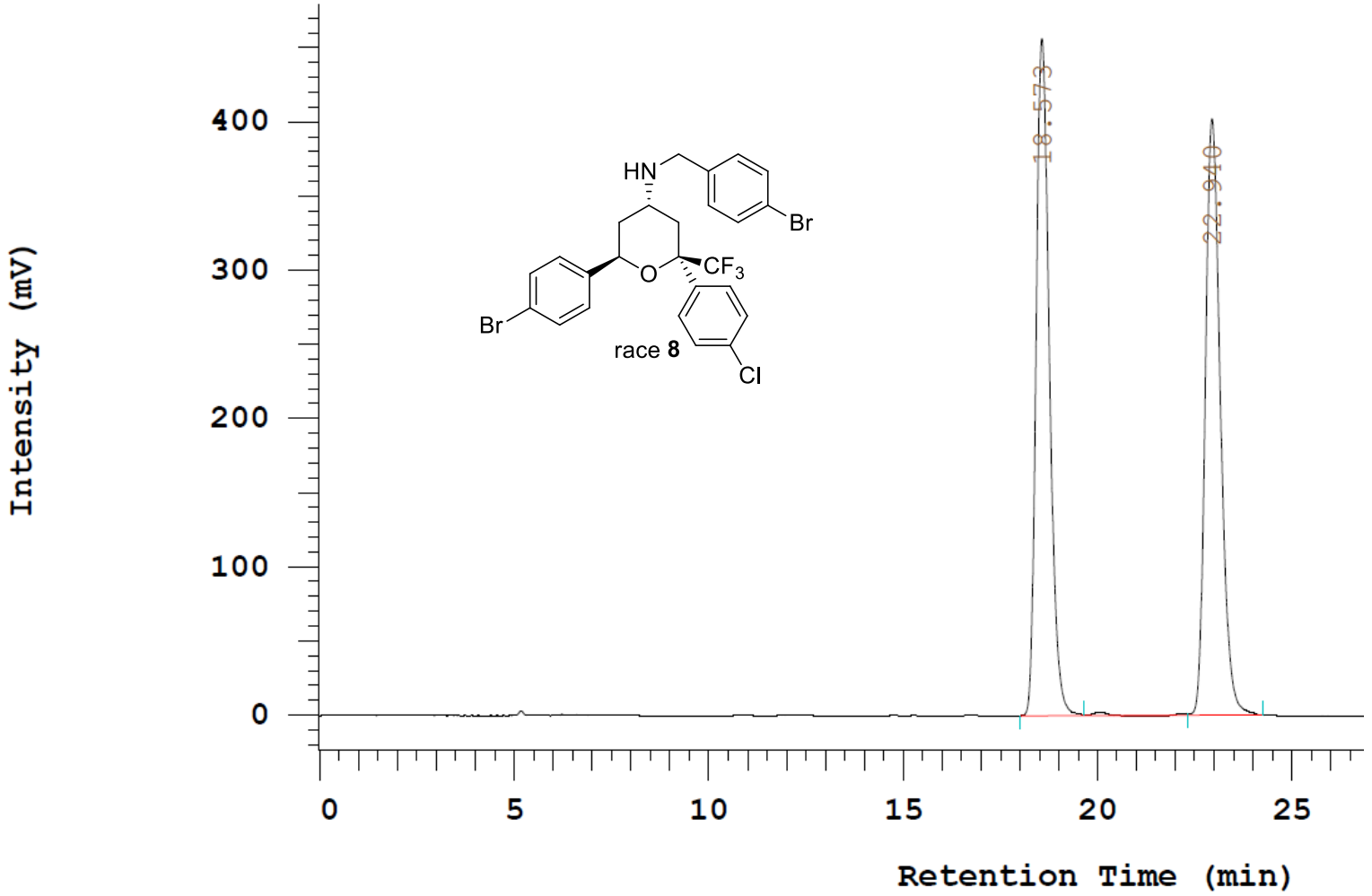
No.	RT	Area	Conc 1
1	10.820	631439	3.687
2	11.467	11251041	65.689
3	12.940	2768360	16.163
4	17.107	2476996	14.462
		17127836	100.000



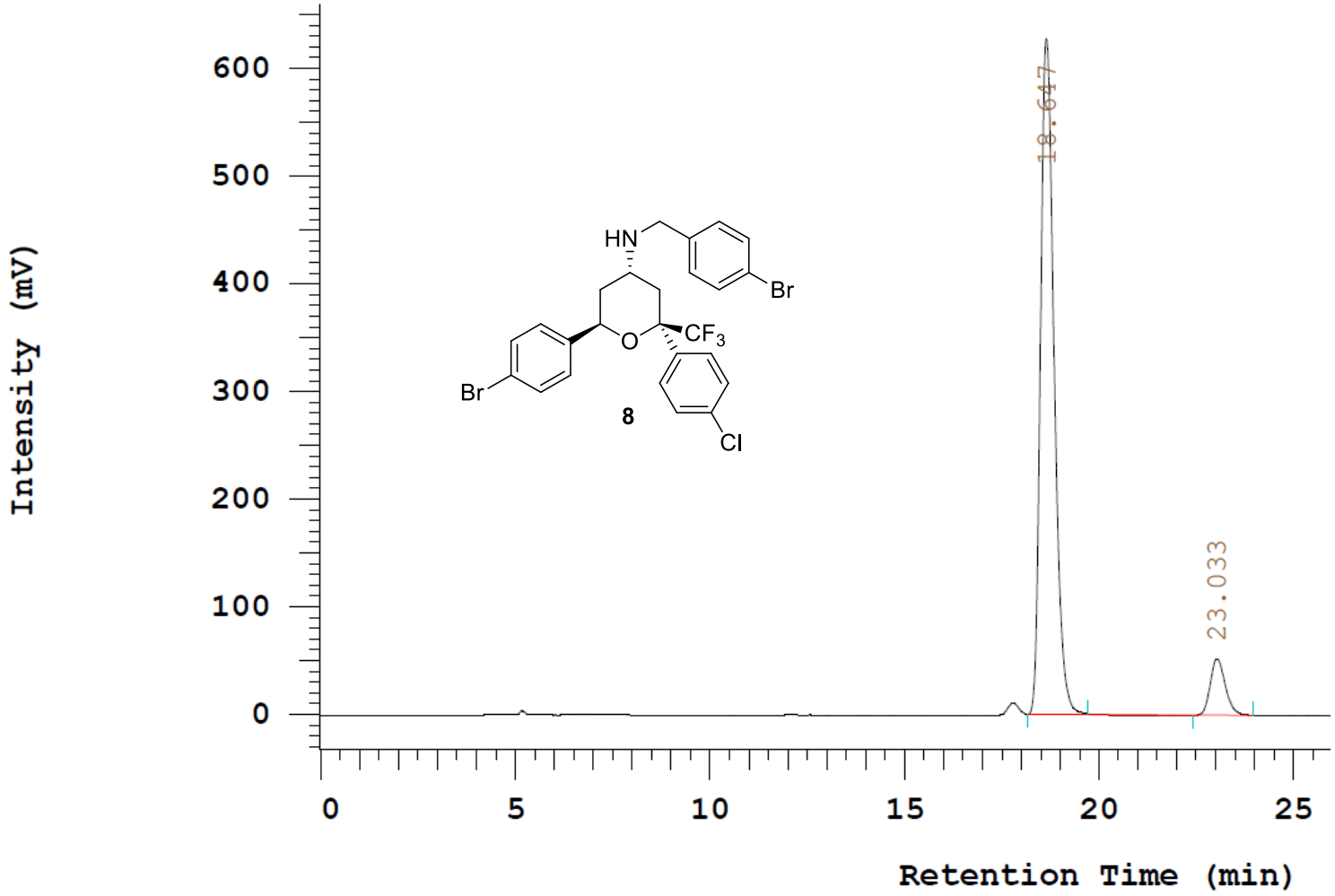
No.	RT	Area	Conc 1
1	7.967	39021959	50.026
2	12.047	38981143	49.974
		78003102	100.000



No.	RT	Area	Conc 1
1	7.960	19812140	95.449
2	12.127	944641	4.551
		20756781	100.000



No.	RT	Area	Conc 1
1	18.573	10690778	49.960
2	22.940	10707749	50.040
		21398527	100.000



No.	RT	Area	Conc 1
1	18.647	14925739	91.546
2	23.033	1378362	8.454
		16304101	100.000