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Electronic Supporting Information

Sequential Asymmetric Hydrogenation and Photoredox Chemistry with a Single Catalyst

Xiao Zhang, Jie Qin, Xiaoqiang Huang, and Eric Meggers*

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35043 Marburg, Germany

*E-mail: meggers@chemie.uni-marburg.de

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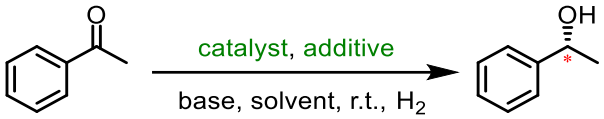
1. General information

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. Catalytic reactions were performed in a Schlenk tube (10 mL). A 21 W compact fluorescent lamp (CFL), 6 W and 24 W blue LEDs served as the ight sources. The catalyst Λ-**IrS**[1] was synthesized according to our published procedure. HPLC grade of solvents and deionized water were used without further purification. Reagents that were purchased from commercial suppliers were used without further purification. Flash column chromatography was performed with silica gel 60 M from Macherey-Nagel (irregular shaped, 230-400 mesh, pH 6.8, pore volume: 0.81 mL × g^{-1}, mean pore size: 66 Å, specific surface: 492 m^2 × g^{-1}, particle size distribution: 0.5% < 25 μm and 1.7% > 71 μm, water content: 1.6%). ^{1}H NMR, ^{19}F NMR and proton decoupled ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz), or Bruker AM (500 MHz) spectrometers at ambient temperature. NMR standards were used as follows: ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$). ^{19}F NMR spectroscopy: δ = 0 ppm ($CFCl_3$). ^{13}C NMR spectroscopy: δ = 77.0 ppm ($CDCl_3$). IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 TFT-MS instrument using ESI/EI/APCI/FD technique. Chiral HPLC chromatography was performed with an Agilent 1200, Agilent 1260 HPLC system or Shimadzu Lc-2030c HPLC system. Optical rotations were measured on a Krüss P8000-T polarimeter with $[\alpha]_D^{22}$ values reported in degrees with concentrations reported in g/100 mL.

2. Asymmetric hydrogenation of acetophenone with Λ-IrS

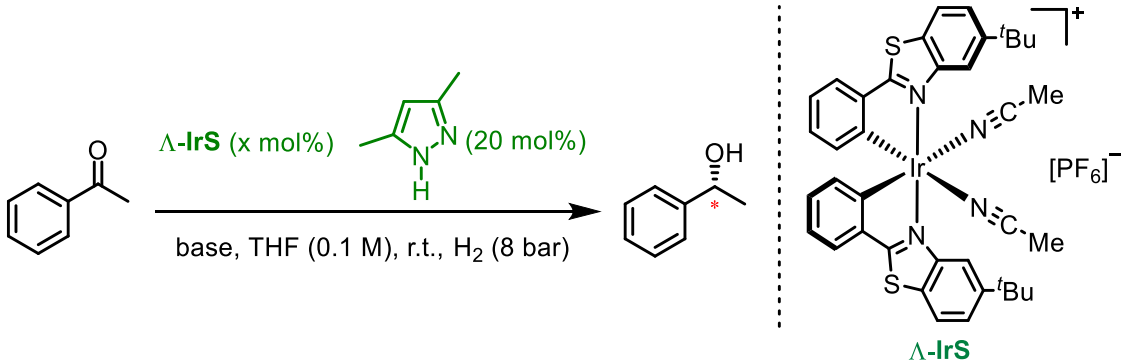
2.1 General procedure



A dried 5 mL tube was charged with acetophenone (0.10 mmol), catalyst, additive, base and solvent, and placed into a stainless steel pressure reactor. The reactor was refilled with H_2 and degassed for 5 cycles, and then hydrogen pressure subsequently increased to indicated pressure. The reaction mixture in the reactor was stirred at room temperature for certain time. After release of H_2, the crude reaction mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 4:1) to afford the desired chiral 1-phenylethan-1-ol as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralcel OJ column (HPLC: OJ, 220 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_1 = 12.44 min, t_2 = 14.21 min).

2.2 Screening of reaction conditions

2.2.1 Effect of bases and catalyst loading[a]

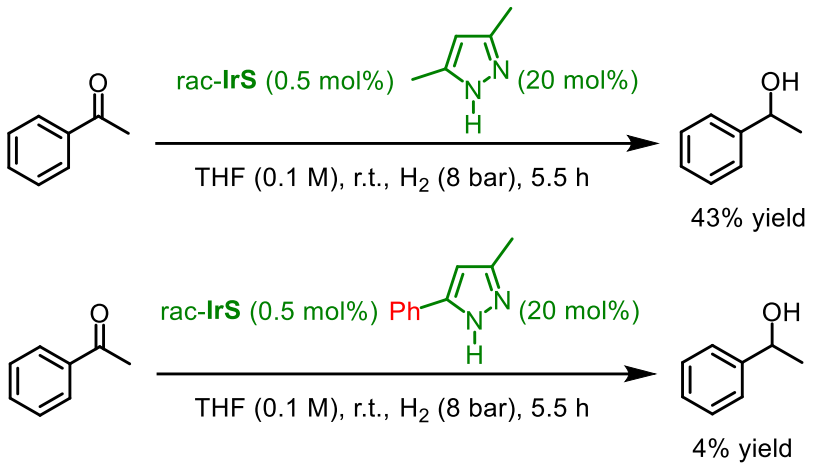


entry	base	3,5-dimethyl pyrazole	x	conv. (%)[b]	yield (%)	ee (%)
1	NaO^{t}Bu (2 eq.)	yes	1	100	39	90
2	NaO^{t}Bu (20 mol%)	yes	1	100	80	92
3	-	yes	1	100	100	94
4	-	yes	0.5	100	100	94
5	-	-	0.5	<5	n.d.	n.d.

[a]Reaction conditions: acetophenone (0.10 mmol), Λ-**IrS** (1.0 or 0.5 mol%), 3,5-dimethyl pyrazole (20 mol%), THF

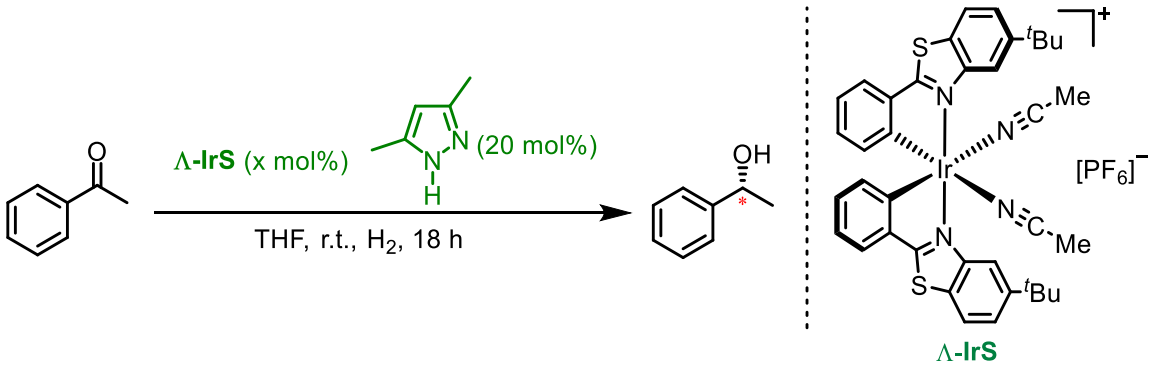
(1.0 mL, 0.1 M), r.t., H_2 (8 bar), 18 h. n.d. = not determined. [b]Determined by ^{1}H-NMR.

2.2.2 Effect of different pyrazoles[a]



[a]Reaction conditions: acetophenone (0.10 mmol), rac-**IrS** (0.5 mol%), pyrazole (20 mol%), THF (1.0 mL, 0.1 M), r.t., H_2 (8 bar), 5.5 h.

2.2.3 Effect of pressure and concentration[a]



entry	x	pressure of H_2	concentration	conv. (%)[b]	ee (%)
1	0.5%	8 bar	0.1 M	100	94
2	0.5%	20 bar	0.1 M	100	96
3	0.25%	20 bar	0.2 M	100	95
4	0.1%	20 bar	0.2 M	95	94
5	0.1%	20 bar	0.5 M	88	92
6	0.1%	20 bar	1.0 M	74	92
7	0.1%	50 bar	0.2 M	100	96

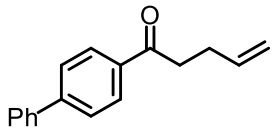
[a]Reaction conditions: acetophenone, Λ-**IrS**, 3,5-dimethyl pyrazole (20 mol%), THF, r.t., H_2, 18 h. [b]Determined by ^{1}H-NMR.

3. Sequential asymmetric hydrogenation and photoredox catalysis with Λ-IrS

3.1 Iridium-catalyzed asymmetric hydrogenation and sequential photocatalytic radical trifluoromethylation/cyclization cascade

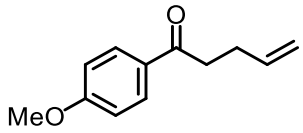
3.1.1 Synthesis of substrates

Substrates **1** were synthesized according to reported procedures.[2] The experimental data are shown below.



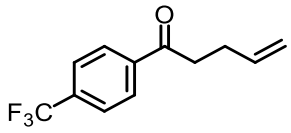
1-([1,1'-biphenyl]-4-yl)pent-4-en-1-one (1a)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.58-7.50 (m, 4H), 7.35 (t, J = 6.9 Hz, 2H), 7.28 (t, J = 6.9 Hz, 1H), 5.89-5.76 (m, 1H), 5.00 (dd, J = 17.4, 1.5 Hz, 1H), 4.93 (d, J = 10.2 Hz, 1H), 2.99 (t, J = 7.5 Hz, 2H), 2.42 (q, J = 6.6 Hz, 2H).



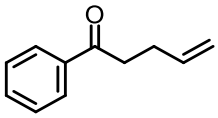
1-(4-methoxyphenyl)pent-4-en-1-one (1b)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.89-5.75 (m, 1H), 5.00 (dd, J = 16.8, 1.5 Hz, 1H), 4.92 (d, J = 10.2, 1.2 Hz, 1H), 3.78 (s, 3H), 2.93 (t, J = 6.9 Hz, 2H), 2.40 (q, J = 6.6 Hz, 2H).



1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (1c)

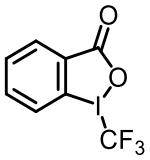
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H), 5.89-5.75 (m, 1H), 5.05-4.93 (m, 2H), 3.02 (t, J = 7.2 Hz, 2H), 2.43 (q, J = 6.6 Hz, 2H).



1-phenylpent-4-en-1-one (1d)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 5.98-5.84 (m, 1H), 5.09 (dd, J = 17.4, 1.5 Hz, 1H), 5.02 (d, J = 9.9 Hz, 1H), 3.08 (t, J = 7.2 Hz, 2H), 2.51 (q, J = 7.5 Hz, 2H).

Togni's reagent **2** was synthesized according to reported procedures.[3] The analytical data are shown below.

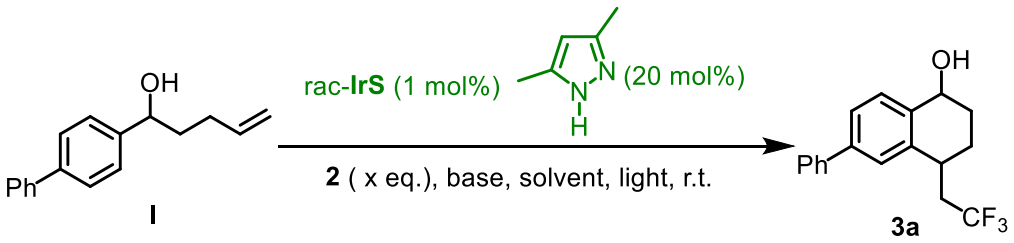


1-(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (2)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39-8.37 (m, 1H), 7.72 (br s, 3H).

3.1.2 General procedure

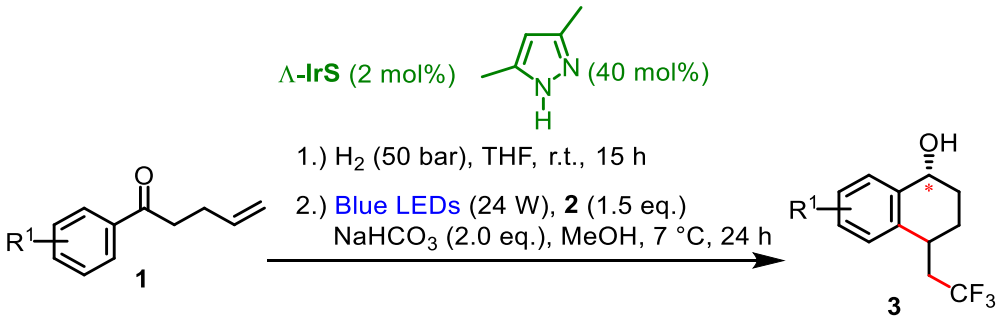
3.1.2.1 General procedure for optimizing the reaction conditions for photoredox chemistry



A dried 10 mL Schlenk tube was charged with Togni's reagent **2**, base, rac-**IrS** (1.9 mg, 1 mol%) and 3,5-dimethyl pyrazole (3.8 mg, 20 mol%). The tube was purged with nitrogen, then solvent was added via syringe, followed by 1-([1,1'-biphenyl]-4-yl)pent-4-en-1-ol (47.6 mg, 0.20 mmol). The reaction mixture was degassed via freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from visible light. The reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under

nitrogen atmosphere. Afterwards, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 8:1) to afford the product **3a**.

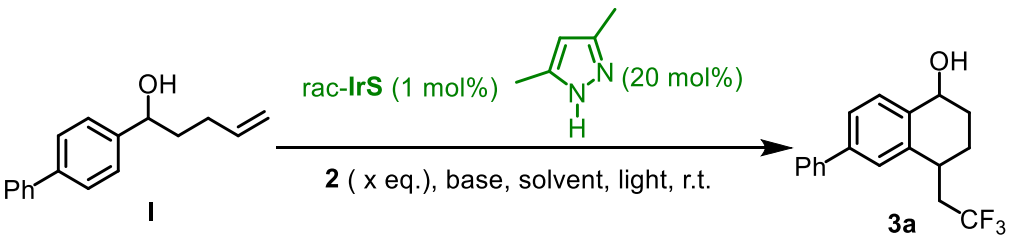
3.1.2.2 General procedure for the sequential reactions with **Λ-IrS** using a single purification



A dried 5 mL tube was charged with substrates **1** (0.20 mmol), Λ-**IrS** (3.8 mg, 2 mol%), 3,5-dimethyl pyrazole (7.7 mg, 40 mol%) and THF (2.0 mL, 0.1 M), and placed into a stainless steel pressure reactor. The reactor was refilled with H_2 and degassed for 5 cycles, and then hydrogen pressure subsequently increased to 50 bar. The reaction mixture in the reactor was stirred at room temperature for 15 h. After release of H_2, the solvent was removed under reduced pressure. Togni's reagent **2** (94.8 mg, 0.30 mmol), $NaHCO_3$ (33.6 mg, 0.40 mmol) and MeOH (2.0 mL, 0.1 M) were added to the residual crude material. The reaction mixture was degassed via freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from Blue LEDs (24 W). The reaction mixture was stirred at 7 ^{o}C under nitrogen atmosphere until complete disappearance of the starting material (monitored by TLC), then concentrated under reduced pressure and purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 8:1) to afford the products **3**.

3.1.3 Screening of reaction conditions

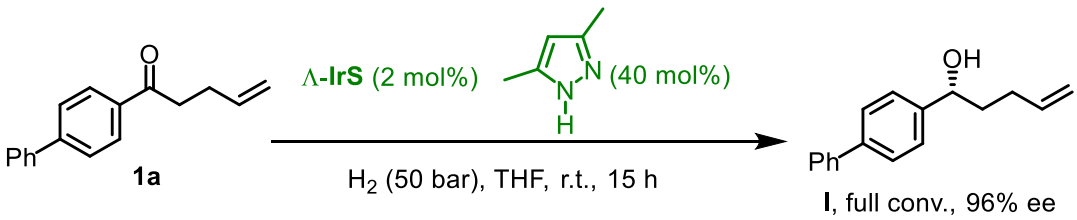
3.1.3.1 Optimization of the reaction conditions for photoredox chemistry[a]



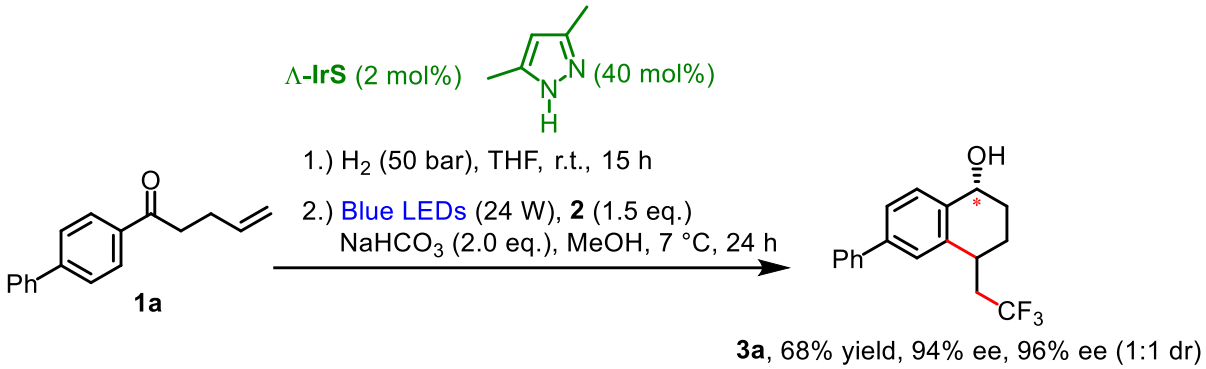
entry	photocatalyst	light	base	solvent	x	conv. (%)[b]	yield (%)[b]
1	-	Blue LEDs (24 W)	$NaHCO_3$	MeOH	1.2	n.d.	0
2	yes	-	$NaHCO_3$	MeOH	1.2	n.d.	0
3	yes	Blue LEDs (24 W)	$NaHCO_3$	MeOH	1.2	93	72
4	yes	Blue LEDs (24 W)	Na_2HPO_4	MeOH	1.2	91	70
5	yes	Blue LEDs (24 W)	2,6-lutidine	MeOH	1.2	89	60
6	yes	Blue LEDs (24 W)	$^{i}Pr_2NEt$	MeOH	1.2	30	15
7	yes	Blue LEDs (24 W)	-	MeOH	1.2	72	49
8	yes	Blue LEDs (24 W)	$NaHCO_3$	MeOH	1.5	100	74
9	yes	Blue LEDs (24 W)	$NaHCO_3$	CH_3CN	1.5	100	70
10	yes	Blue LEDs (24 W)	$NaHCO_3$	acetone	1.5	75	40
11	yes	Blue LEDs (24 W)	$NaHCO_3$	CH_2Cl_2	1.5	80	44
12	yes	Blue LEDs (24 W)	$NaHCO_3$	$CHCl_3$	1.5	77	44
13	yes	Blue LEDs (24 W)	$NaHCO_3$	THF	1.5	15	<10
14	yes	CFL (21 W)	$NaHCO_3$	MeOH	1.5	100	70
15[c]	yes	Blue LEDs (24 W)	$NaHCO_3$	MeOH	1.5	100	80

[a]Reaction conditions: 1-([1,1'-biphenyl]-4-yl)pent-4-en-1-ol (0.20 mmol), Togni's reagent **2**, rac-**IrS** (1.0 mol%), 3,5-dimethyl pyrazole (20 mol%), base (0.40 mmol), solvent (2.0 mL, 0.1 M), r.t., visible light, 15 h. [b]Determined by the crude ^{1}H NMR of the reaction mixtures (using $ClCH_2CH_2Cl$ as the internal standard). [c]1-([1,1'-biphenyl]-4-yl)pent-4-en-1-ol (0.20 mmol), Togni's reagent **2** (0.30 mmol), rac-**IrS** (1.0 mol%), 3,5-dimethyl pyrazole (20 mol%), $NaHCO_3$ (0.40 mmol), MeOH (2.0 mL, 0.1 M), 7 °C, Blue LEDs (24 W), 24 h. n.d. = not determined.

3.1.3.2 Evaluation of the sequential reactions with **Λ-IrS** using a single purification[a]

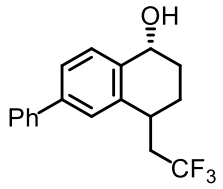


[a]Reaction conditions: Λ-**IrS** (2.0 mol%), 3,5-dimethyl pyrazole (40 mol%), **1a** (0.20 mmol), THF (2.0 mL, 0.1 M), H_2 (50 bar), r.t., 15 h.



[a]Reaction conditions: Λ-**IrS** (2.0 mol%), 3,5-dimethyl pyrazole (40 mol%), **1a** (0.20 mmol), THF (2.0 mL, 0.1 M), H_2 (50 bar), r.t., 15 h; then **2** (0.30 mmol), $NaHCO_3$ (0.4 mmol), MeOH (2.0 mL, 0.1 M), 7 °C, Blue LEDs (24 W), 24 h.

3.1.4 Experimental and characterization data of products



(1*R*)-6-phenyl-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (3a)

According to the general procedure, the reaction using 1-([1,1'-biphenyl]-4-yl)pent-4-en-1-one **1a** (47.2 mg, 0.20 mmol) as the starting material gave 41.6 mg (68%) of **3a** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak AS-H column (250 x 4.6 mm), 94% ee, 96% ee (HPLC: AS-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 40 °C, t_r (major) = 14.80 min, t_r (minor) = 15.71 min; another isomer: t_r (minor) = 16.73 min, t_r (major) = 19.18 min). $[\alpha]_D^{22}$ = -28.8° (*c* 1.0, CH_2Cl_2). The product was present as a 1:1 mixture of diastereoisomers.

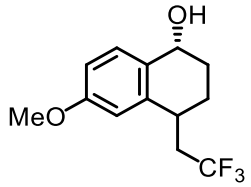
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.45 (m, 6H), 7.42-7.37 (m, 2H), 4.82-4.79 (m, 1H), 3.38-3.25 (m, 1H), 2.73-2.25 (m, 3H), 2.16-1.84 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 141.1, 140.6, 140.5, 138.9, 138.8, 138.1, 137.5, 129.6, 128.8, 127.50, 127.46, 127.2, 127.02, 126.9 (q, *J* = 276 Hz), 126.8 (q, *J* = 276 Hz), 126.7, 126.0, 125.8, 68.1, 67.0, 40.6 (q, *J* = 27 Hz), 40.1 (q, *J* = 27 Hz), 32.3 (q, *J* = 3 Hz), 32.2 (q, *J* = 3 Hz), 29.0, 28.1, 24.4, 22.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.72, -63.75.

IR (film): ν (cm^{-1}) 3308, 3072, 3025, 2947, 2878, 1667, 1603, 1564, 1480, 1436, 1373, 1308, 1251, 1190, 1116, 1085, 1046, 984, 931, 887, 839, 756, 697, 671, 631, 601, 563, 509, 438.

HRMS (APCI, *m*/*z*) calcd for $C_{18}H_{17}F_3ONa$ $[M+Na]^+$: 329.1124, found: 329.1146.



(1*R*)-6-methoxy-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (3b)

According to the general procedure, the reaction using 1-(4-methoxyphenyl)pent-4-en-1-one **1b** (38.0 mg, 0.20 mmol) as the starting material gave 28.2 mg (54%) of **3b** as a yellow solid. Enantiomeric

excess was established by HPLC analysis using a Chiralcel OJ-H column (250 x 4.6 mm), 94% ee, 95% ee (HPLC: OJ-H, 220 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 12.61 min, t_r (minor) = 15.78 min; another isomer: t_r (minor) = 36.70 min, t_r (major) = 46.65 min). $[\alpha]_D^{22}$ = -24.4° (*c* 1.0, CH_2Cl_2). The product was present as a 1:1 mixture of diastereoisomers.

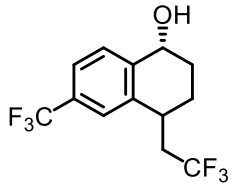
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.31 (m, 1H), 6.84-6.80 (m, 1H), 6.70-6.66 (m, 1H), 4.76-4.72 (m, 1H), 3.81 and 3.80 (s, 3H), 3.25-3.10 (m, 1H), 2.62-1.71 (m, 7H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 159.3, 140.0, 139.9, 131.5, 130.8, 130.6, 129.9, 126.9 (q, *J* = 276 Hz), 126.7 (q, *J* = 276 Hz), 113.3, 112.94, 112.86, 67.9, 66.7, 55.3, 40.6 (q, *J* = 26 Hz), 39.9 (q, *J* = 27 Hz), 32.5 (q, *J* = 3 Hz), 32.3 (q, *J* = 2 Hz), 29.3, 27.8, 24.3, 22.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.92, -63.98.

IR (film): *v* (cm^{-1}) 3310, 2942, 2846, 1612, 1574, 1498, 1463, 1437, 1376, 1306, 1274, 1246, 1115, 1082, 1037, 931, 877, 819, 697, 668, 573, 556, 457.

HRMS (APCI, *m*/*z*) calcd for $C_{13}H_{14}F_3O$ $[M+H-H_2O]^+$: 243.0991, found: 243.0987.



(1*R*)-4-(2,2,2-trifluoroethyl)-6-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (3c)

According to the general procedure, the reaction using 1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one **1c** (45.6 mg, 0.20 mmol) as the starting material gave 45.8 mg (76%) of **3c** as a yellow solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column (250 x 4.6 mm), 96% ee, 97% ee (HPLC: AD-H, 220 nm, *n*-hexane/isopropanol = 98:2, flow rate 0.5 mL/min, 25 °C, t_r (major) = 30.57 min, t_r (minor) = 37.33 min; another isomer: t_r (minor) = 34.48 min, t_r (major) = 44.84 min). $[\alpha]_D^{22}$ = -33.3° (*c* 1.0, CH_2Cl_2). The product was present as a 1:1 mixture of diastereoisomers.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.58 (m, 1H), 7.52-7.49 (m, 1H), 7.43 (s, 1H), 4.81-4.93 (m, 1H), 3.35-3.19 (m, 1H), 2.58-1.59 (m, 7H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.93, 142.92, 142.49, 142.47, 139.2, 139.1, 130.5 (q, *J* = 32 Hz), 130.3 (q, *J* = 33 Hz), 129.6, 128.8, 126.6 (q, *J* = 276 Hz), 126.5 (q, *J* = 276 Hz), 125.3 (q, *J* = 4 Hz), 125.0 (q, *J* = 4 Hz), 123.93 (q, *J* = 271 Hz), 123.89 (q, *J* = 271 Hz), 68.1, 67.0, 40.5 (q, *J* = 28 Hz),

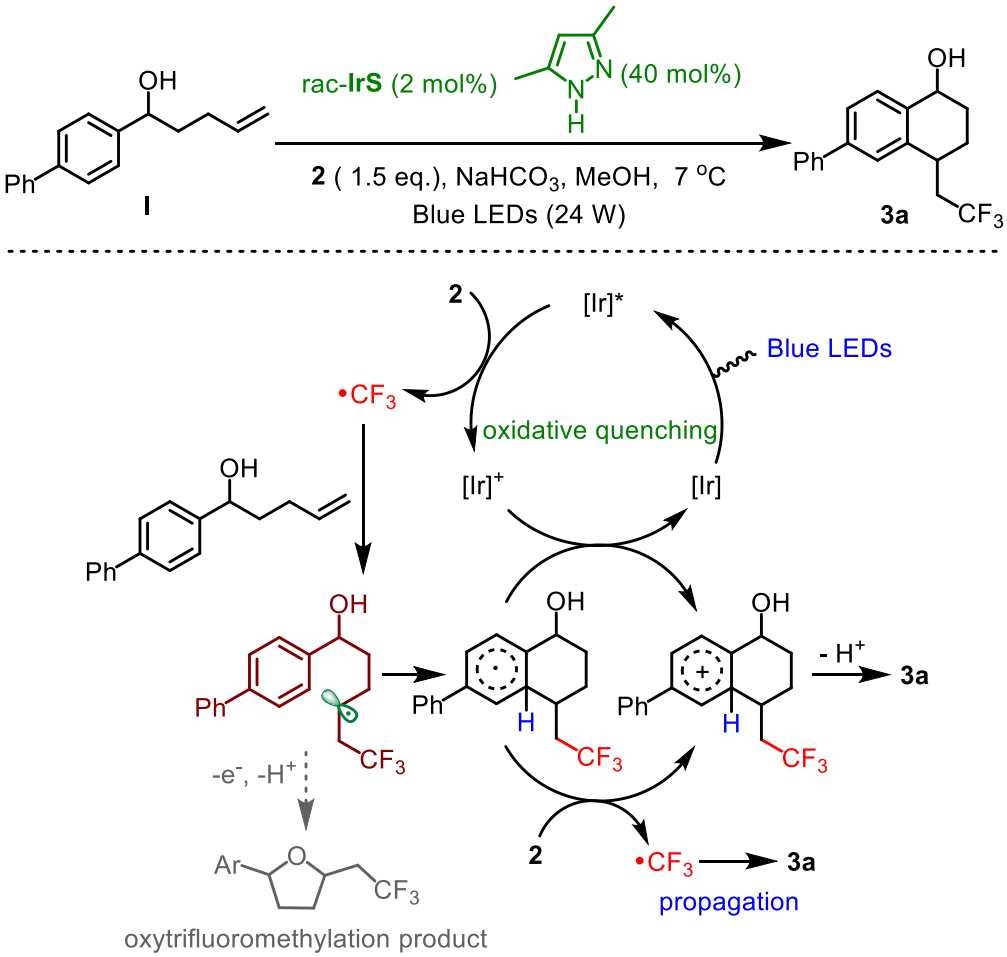
40.0 (q, J = 27 Hz), 32.19, 32.17, 28.7, 28.4, 24.14, 24.12, 22.89, 22.87.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.77, -62.81, -63.81, -63.95.

IR (film): ν (cm^{-1}) 3305, 2942, 1600, 1431, 1378, 1329, 1251, 1116, 1068, 985, 933, 907, 839, 730, 673, 643, 612, 567, 497, 409.

HRMS (FD, m/z) calcd for $C_{13}H_{12}F_6O$ $[M]^+$: 298.0792, found: 298.0785.

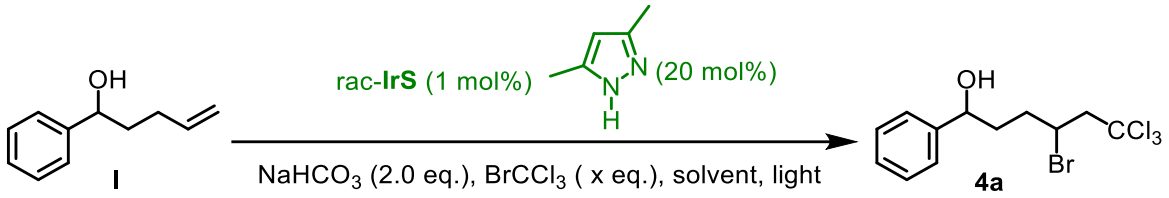
3.1.5 Proposed mechanism for the photoredox chemistry



3.2 Iridium-catalyzed asymmetric hydrogenation and sequential photocatalytic atom transfer radical addition (ATRA)

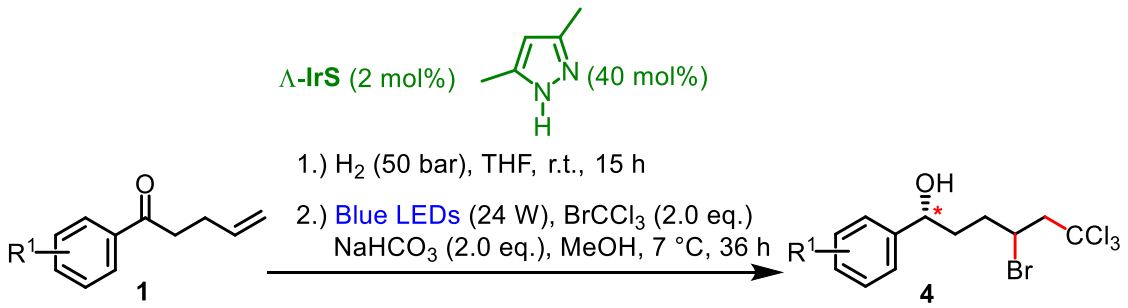
3.2.1 General procedure

3.2.1.1 General procedure for optimizing the reaction conditions for photoredox chemistry



A dried 10 mL Schlenk tube was charged with $NaHCO_3$, rac-**IrS** (1.9 mg, 1 mol%) and 3,5-dimethyl pyrazole (3.8 mg, 20 mol%). The tube was purged with nitrogen, then solvent was added via syringe, followed by 1-phenylpent-4-en-1-ol (32.4 mg, 0.20 mmol) and $BrCCl_3$. The reaction mixture was degassed via freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from visible light. The reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 15:1) to afford the product **4a**.

3.2.1.2 General procedure for the sequential reactions with **Λ-IrS** using a single purification

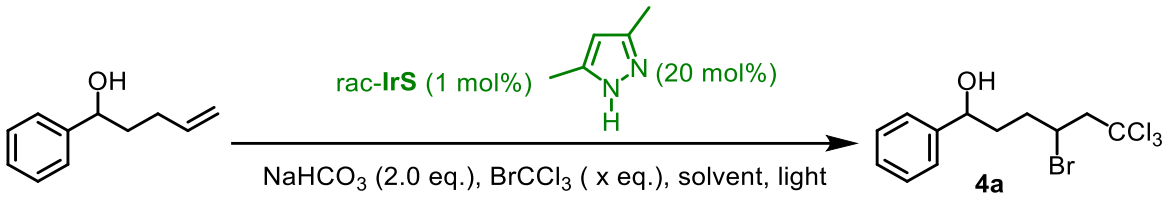


A dried 5 mL tube was charged with substrates **1** (0.20 mmol), Λ-**IrS** (3.8 mg, 2 mol%), 3,5-dimethyl pyrazole (7.7 mg, 40 mol%) and THF (2.0 mL, 0.1 M), and placed into a stainless steel pressure reactor. The reactor was refilled with H_2 and degassed for 5 cycles, and then hydrogen pressure subsequently increased to 50 bar. The reaction mixture in the reactor was stirred at room

temperature for 15 h. After release of H_2, the solvent was removed under reduced pressure. $BrCCl_3$ (79.2 mg, 0.40 mmol), $NaHCO_3$ (33.6 mg, 0.40 mmol) and MeOH (2.0 mL, 0.1 M) were added to the residual crude material. The reaction mixture was degassed via freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from Blue LEDs (24 W). The reaction mixture was stirred at 7 °C for 36 h, then concentrated under reduced pressure and purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 15:1) to afford the products **4**.

3.2.2 Screening of reaction conditions

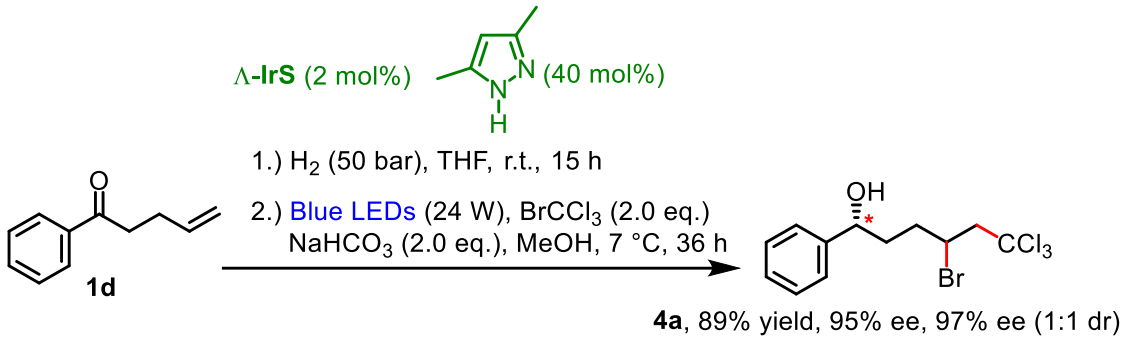
3.2.2.1 Optimization of the reaction conditions for photoredox chemistry[a]



entry	photocatalyst	light	x	solvent	temp.	yield (%)
1	-	Blue LEDs (24 W)	1.1	CH_3CN	r.t.	5
2	yes	-	1.1	CH_3CN	r.t.	0
3	yes	Blue LEDs (24 W)	1.1	CH_3CN	r.t.	58
4	yes	Blue LEDs (24 W)	1.1	THF	r.t.	9
5	yes	Blue LEDs (24 W)	1.1	DCM	r.t.	47
6	yes	Blue LEDs (24 W)	1.1	$CHCl_3$	r.t.	42
7	yes	Blue LEDs (24 W)	1.1	toluene	r.t.	47
8	yes	Blue LEDs (24 W)	1.1	acetone	r.t.	5
9	yes	Blue LEDs (24 W)	1.1	MeOH	r.t.	60
10	yes	Blue LEDs (24 W)	1.5	MeOH	r.t.	67
11	yes	Blue LEDs (24 W)	2	MeOH	r.t.	73
12[b]	yes	Blue LEDs (24 W)	2	MeOH	7 °C	90

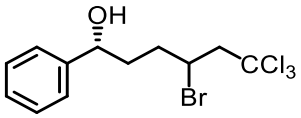
[a]Reaction conditions: 1-phenylpent-4-en-1-ol (0.20 mmol), $BrCCl_3$, rac-**IrS** (1.0 mol%), 3,5-dimethyl pyrazole (20 mol%), $NaHCO_3$ (0.40 mmol), solvent (2.0 mL, 0.1 M), r.t., Blue LEDs (24 W), 15 h. [b]Reaction conditions: 1-phenylpent-4-en-1-ol (0.20 mmol), $BrCCl_3$ (0.40 mmol), rac-**IrS** (1.0 mol%), 3,5-dimethyl pyrazole (20 mol%), $NaHCO_3$ (0.40 mmol), MeOH (2.0 mL, 0.1 M), 7 °C, Blue LEDs (24 W), 36 h.

3.2.2.2 Evaluation of the sequential reactions with **Λ-IrS** using a single purification[a]



[a]Reaction conditions: Λ-**IrS** (2.0 mol%), 3,5-dimethyl pyrazole (40 mol%), **1d** (0.20 mmol), THF (2.0 mL, 0.1 M), H_2 (50 bar), r.t., 15 h; then $BrCCl_3$ (0.40 mmol), $NaHCO_3$ (0.40 mmol), MeOH (2.0 mL, 0.1 M), 7 °C, Blue LEDs (24 W), 36 h.

3.2.3 Experimental and characterization data of products



(1*R*)-4-bromo-6,6,6-trichloro-1-phenylhexan-1-ol (4a)

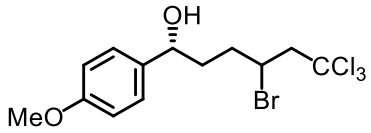
According to the general procedure, the reaction using 1-phenylpent-4-en-1-one **1d** (32.0 mg, 0.20 mmol) as the starting material gave 64.0 mg (89%) of **4a** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, 95% ee, 97% ee (HPLC: IG, 220 nm, *n*-hexane/isopropanol = 98:2, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 41.73 min, t_r (major) = 52.61 min; another isomer: t_r (major) = 55.51 min, t_r (minor) = 64.33 min). $[\alpha]_D^{22}$ = +14.2° (*c* 1.0, CH_2Cl_2). The product was present as a 1:1 mixture of diastereoisomers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.35 (m, 4H), 7.32-7.28 (m, 1H), 4.78-4.72 (m, 1H), 4.40-4.34 (m, 1H), 3.47-3.42 (m, 1H), 3.23-3.18 (m, 1H), 2.29-1.87 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 144.0, 128.7, 128.6, 127.9, 127.8, 125.8, 125.7, 97.04, 97.00, 74.01, 73.4, 62.60, 62.55, 48.9, 48.7, 36.6, 36.4, 35.9, 35.5.

IR (film): ν (cm^{-1}) 3363, 3063, 3030, 2925, 2861, 1493, 1449, 1422, 1287, 1195, 1052, 1018, 948, 768, 701, 633, 553.

HRMS (APCI, *m*/*z*) calcd for $C_{12}H_{13}Cl_3Br$ $[M+H-H_2O]^+$: 340.9261, found: 340.9261.



(1*R*)-4-bromo-6,6,6-trichloro-1-(4-methoxyphenyl)hexan-1-ol (4b)

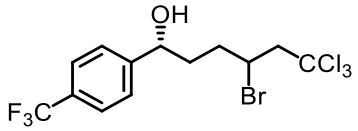
According to the general procedure, the reaction using 1-(4-methoxyphenyl)pent-4-en-1-one **1b** (38.0 mg, 0.20 mmol) as the starting material gave 54.2 mg (70%) of **4b** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, 98% ee, 99% ee (HPLC: IG, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 22.38 min, t_r (major) = 24.16 min; another isomer: t_r (major) = 27.54 min, t_r (minor) = 34.42 min). $[\alpha]_D^{22}$ = +20.5° (*c* 1.0, CH_2Cl_2). The product was present as a 1:1 mixture of diastereoisomers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22-7.19 (m, 2H), 6.83-6.81 (m, 2H), 4.64-4.58 (m, 1H), 4.31-4.26 (m, 1H), 3.73 (s, 3H), 3.39-3.34 (m, 1H), 3.15-3.10 (m, 1H), 2.18-1.78 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.29, 159.24, 136.3, 136.1, 127.1, 127.0, 114.00, 113.98, 97.05, 97.01, 73.6, 73.1, 62.6, 62.5, 55.3, 48.9, 48.7, 36.5, 36.3, 36.0, 35.6.

IR (film): ν (cm^{-1}) 3404, 3002, 2930, 2838, 1610, 1510, 1452, 1298, 1244, 1175, 1032, 947, 831, 779, 700, 632, 548, 420.

HRMS (APCI, *m*/*z*) calcd for $C_{13}H_{15}BrCl_3O$ $[M+H-H_2O]^+$: 370.9366, found: 370.9360.



(1*R*)-4-bromo-6,6,6-trichloro-1-(4-(trifluoromethyl)phenyl)hexan-1-ol (4c)

According to the general procedure, the reaction using 1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one **1c** (45.6 mg, 0.20 mmol) as the starting material gave 76.5 mg (90%) of **4c** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralcel OJ-H column, 97% ee, 97% ee (HPLC: OJ-H, 220 nm, *n*-hexane/isopropanol = 98:2, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 53.50 min, t_r (major) = 71.28 min; another isomer: t_r (major) = 57.85 min, t_r (minor) = 87.12 min). $[\alpha]_D^{22}$ = +10.3° (*c* 1.0, CH_2Cl_2). The product was present as a 1:1 mixture of diastereoisomers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.62 (m, 2H), 7.50-7.47 (m, 2H), 4.86-4.81 (m, 1H), 4.41-4.33 (m, 1H), 3.48-3.43 (m, 1H), 3.23-3.18 (m, 1H), 2.33-1.91 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.07, 147.98, 130.08 (q, *J* = 32 Hz), 130.00 (q, *J* = 32 Hz), 126.1,

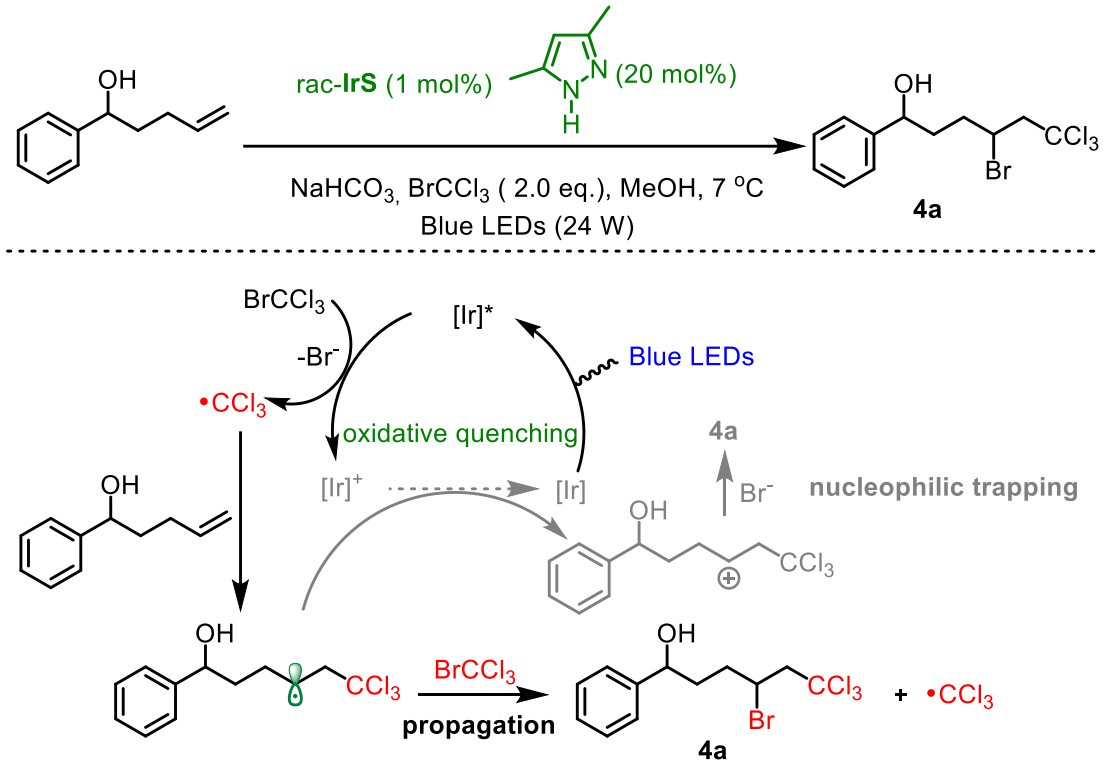
126.0, 125.61, 125.58, 125.56, 124.1 (q, J = 270 Hz), 96.95, 96.92, 73.3, 72.6, 62.6, 62.5, 48.7, 48.5, 36.8, 36.5, 35.7, 35.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.51, -62.52.

IR (film): ν (cm^{-1}) 3360, 2928, 1620, 1419, 1322, 1164, 1119, 1064, 1013, 950, 841, 795, 702, 604, 537, 480, 438, 405.

HRMS (FD, m/z) calcd for $C_{13}H_{13}BrCl_3F_3O$ $[M]^+$: 425.9168, found: 425.9153.

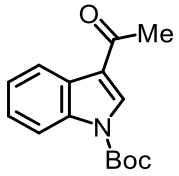
3.2.4 Proposed mechanism for the photoredox chemistry



3.3 Iridium-catalyzed asymmetric hydrogenation and sequential CF_3 radical addition to indoles

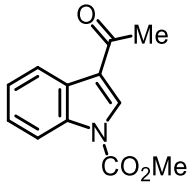
3.3.1 Synthesis of substrates

Substituted indoles **5a-d** were synthesized according to reported procedures.[4] The experimental data are shown below.



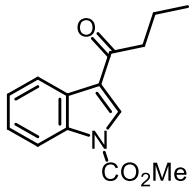
***tert*-butyl 3-acetyl-1*H*-indole-1-carboxylate (5a)**

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, J = 7.5 Hz, 1H), 8.19 (s, 1H), 8.10 (d, J = 7.5 Hz, 1H), 7.39-7.31 (m, 2H), 2.55 (s, 3H), 1.72 (s, 9H).



methyl 3-acetyl-1*H*-indole-1-carboxylate (5b)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39-8.36 (m, 1H), 8.25 (s, 1H), 8.18-8.15 (m, 1H), 7.44-7.34 (m, 2H), 4.12 (s, 3H), 2.57 (s, 3H).



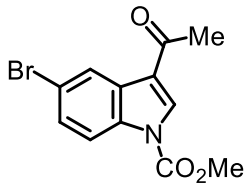
methyl 3-butyryl-1*H*-indole-1-carboxylate (5c)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28-8.22 (m, 1H), 8.02-7.97 (m, 2H), 7.28-7.20 (m, 2H), 3.95 (s, 3H), 2.70 (d, J = 7.5 Hz, 2H), 1.74-1.62 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 150.8, 135.3, 131.1, 127.2, 125.5, 124.4, 122.6, 120.7, 114.6, 54.2, 41.7, 17.9, 13.8.

IR (film): ν (cm^{-1}) 3128, 2963, 2874, 1750, 1665, 1604, 1542, 1440, 1389, 1357, 1289, 1229, 1197, 1139, 1090, 1047, 1015, 956, 925, 885, 831, 762, 676, 613, 574, 532, 423.

HRMS (APCI, m/z) calcd for $C_{14}H_{15}NO_3H$ $[M+H]^+$: 246.1125, found: 246.1124.



methyl 3-acetyl-5-bromo-1*H*-indole-1-carboxylate (5d)

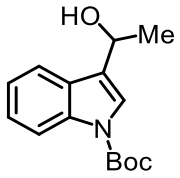
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.13 (s, 1H), 7.94 (d, J = 8.7 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 4.11 (s, 3H), 2.52 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 150.4, 134.0, 132.4, 128.6, 128.5, 125.2, 120.2, 118.1, 116.1, 54.6, 27.4.

IR (film): ν (cm^{-1}) 3125, 2957, 1738, 1657, 1544, 1436, 1365, 1258, 1223, 1186, 1160, 1050, 947, 891, 800, 758, 622, 560, 479, 422.

HRMS (APCI, m/z) calcd for $C_{12}H_{10}BrNO_3H$ $[M+H]^+$: 295.9917, found: 295.9912.

Substituted indole **5e** was synthesized according to reported procedures.[5] The experimental data are shown below.

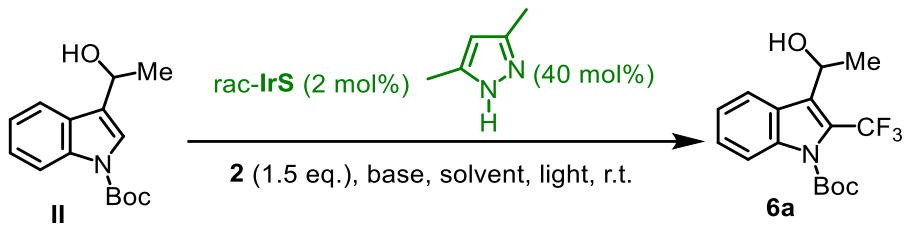


***tert*-butyl 3-(1-hydroxyethyl)-1*H*-indole-1-carboxylate (II)**

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.57 (s, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 5.20 (q, J = 6.3 Hz, 1H), 1.78 (br s, 1H), 1.69 (s, 9H), 1.68 (d, J = 7.2 Hz, 3H).

3.3.2 General procedure

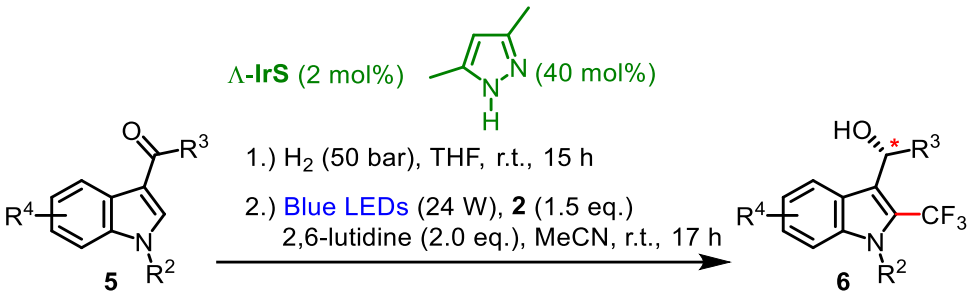
3.3.2.1 General procedure for optimizing the reaction conditions for photoredox chemistry



A dried 10 mL Schlenk tube was charged with Togni's reagent **2** (94.8 mg, 0.30 mmol), base (0.40 mmol), rac-**IrS** (3.8 mg, 2 mol%) and 3,5-dimethyl pyrazole (7.7 mg, 40 mol%). The tube was purged with nitrogen, then solvent was added via syringe, followed by *tert*-butyl 3-(1-hydroxyethyl)-1*H*-indole-1-carboxylate **II** (52.2 mg, 0.20 mmol). The reaction mixture was degassed via freeze-

pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from visible light. The reaction was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the solvent was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 15:1) to afford the product **6a**.

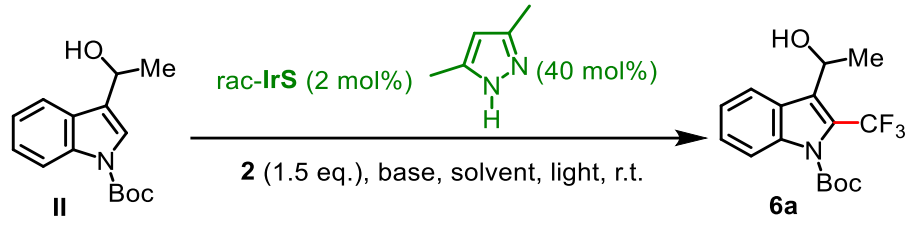
3.3.2.2 General procedure for the sequential reactions with **Λ-IrS** using a single purification



A dried 5 mL tube was charged with substituted indoles **5** (0.20 mmol), Λ-**IrS** (3.8 mg, 2 mol%), 3,5-dimethyl pyrazole (7.7 mg, 40 mol%) and THF (2.0 mL, 0.1 M), and placed into a stainless steel pressure reactor. The reactor was refilled with H_2 and degassed for 5 cycles, and then hydrogen pressure subsequently increased to 50 bar. The reaction mixture in the reactor was stirred at room temperature for 15 h. After release of H_2, the solvent was removed under reduced pressure. Togni's reagent **2** (94.8 mg, 0.30 mmol), 2,6-lutidine (42.8 mg, 0.40 mmol) and CH_3CN (2.0 mL, 0.1 M) were added to the residual crude material. The reaction mixture was degassed via freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from Blue LEDs (24 W). The reaction mixture was stirred at room temperature under nitrogen atmosphere until complete disappearance of the starting material (monitored by TLC), concentrated under reduced pressure and purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20:1) to afford the products **6**.

3.3.3 Screening of reaction conditions

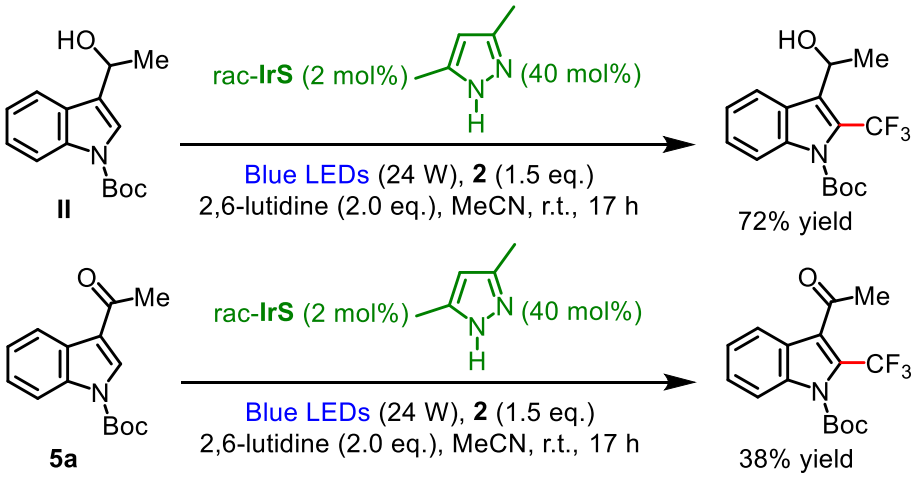
3.3.3.1 Optimization of the reaction conditions for photoredox chemistry[a]



entry	photocatalyst	light	base	solvent	concentration	yield (%)
1	-	Blue LEDs (24 W)	-	CH_3CN	0.2 M	0
2	yes	-	-	CH_3CN	0.2 M	0
3	yes	Blue LEDs (24 W)	-	CH_3CN	0.2 M	40
4	yes	Blue LEDs (24 W)	$NaHCO_3$	CH_3CN	0.2 M	43
5	yes	Blue LEDs (24 W)	2,6-lutidine	CH_3CN	0.2 M	46
6	yes	Blue LEDs (24 W)	$^{i}Pr_2NEt$	CH_3CN	0.2 M	<10
7	yes	CFL (21 W)	2,6-lutidine	CH_3CN	0.2 M	36
8	yes	Blue LEDs (24 W)	2,6-lutidine	MeOH	0.2 M	26
9	yes	Blue LEDs (24 W)	2,6-lutidine	DCM	0.2 M	36
10	yes	Blue LEDs (24 W)	2,6-lutidine	$CHCl_3$	0.2 M	45
11	yes	Blue LEDs (24 W)	2,6-lutidine	CH_3CN	0.1 M	72

[a]Reaction conditions: *tert*-butyl 3-(1-hydroxyethyl)-1*H*-indole-1-carboxylate (0.20 mmol), Togni's reagent **2** (0.30 mmol), rac-**IrS** (2.0 mol%), 3,5-dimethyl pyrazole (40 mol%), base (0.40 mmol), solvent (1.0 mL or 2.0 mL), r.t., visible light.

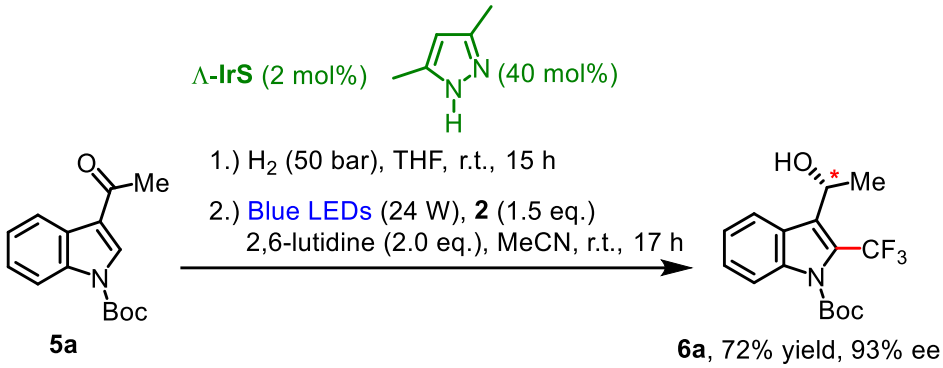
3.3.3.2 Comparison of the reactivities between 3-acyl substituted indole and the corresponding alcohol [a]



[a]Reaction conditions: *tert*-butyl 3-(1-hydroxyethyl)-1*H*-indole-1-carboxylate or 3-acyl substituted indole (0.20 mmol), Togni's reagent **2** (0.30 mmol), rac-**IrS** (2.0 mol%), 3,5-dimethyl pyrazole (40 mol%), 2,6-lutidine (0.40

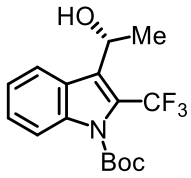
mmol), MeCN (2.0 mL, 0.1 M), r.t., Blue LEDs (24 W), 17 h.

3.3.3.3 Evaluation of the sequential reactions with **Λ-IrS** using a single purification[a]



[a]Reaction conditions: Λ-**IrS** (2.0 mol%), 3,5-dimethyl pyrazole (40 mol%), **5a** (0.20 mmol), THF (2.0 mL, 0.1 M), H_2 (50 bar), r.t., 15 h; then **2** (0.30 mmol), 2,6-lutidine (0.40 mmol), MeCN (2.0 mL, 0.1 M), r.t., Blue LEDs (24 W), 17 h.

3.3.4 Experimental and characterization data of products



***tert*-butyl (*R*)-3-(1-hydroxyethyl)-2-(trifluoromethyl)-1*H*-indole-1-carboxylate (6a)**

According to the general procedure, the reaction using *tert*-butyl 3-acetyl-1*H*-indole-1-carboxylate **5a** (51.8 mg, 0.20 mmol) as the starting material gave 47.4 mg (72%) of **6a** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralcel OD-H column, ee = 93% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 98:2, flow rate 1 mL/min, 25 °C, t_r (major) = 9.04 min, t_r (minor) = 9.87 min). $[\alpha]_D^{22}$ = -7.7° (*c* 1.0, CH_2Cl_2).

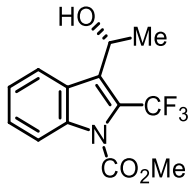
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.062 (d, *J* = 9.0 Hz, 1H), 8.055 (d, *J* = 8.0 Hz, 1H), 7.35 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 5.48-5.44 (m, 1H), 2.08 (br s, 1H), 1.58 (s, 9H), 1.57 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 137.4, 130.3, 127.1, 125.6, 123.2, 123.0, 121.5 (q, *J* = 267 Hz), 120.8 (q, *J* = 38 Hz), 115.0, 85.5, 64.2 (q, *J* = 4 Hz), 27.7, 23.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -53.16.

IR (film): ν (cm^{-1}) 2984, 2937, 1743, 1568, 1452, 1394, 1367, 1325, 1277, 1239, 1205, 1128, 1093, 1033, 980, 900, 870, 833, 751, 698, 610, 555, 468, 437.

HRMS (FD, *m*/*z*) calcd for $C_{16}H_{18}F_3NO_3$ [M]$^+$: 329.1239, found: 329.1226.



methyl (*R*)-3-(1-hydroxyethyl)-2-(trifluoromethyl)-1*H*-indole-1-carboxylate (6b)

According to the general procedure, the reaction using methyl 3-acetyl-1*H*-indole-1-carboxylate **5b** (43.4 mg, 0.20 mmol) as the starting material gave 37.8 mg (66%) of **6b** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak AS-H column, ee = 96% (HPLC: AS-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (minor) = 6.72 min, t_r (major) = 7.32 min). $[\alpha]_D^{22}$ = +18.8° (*c* 1.0, CH_2Cl_2).

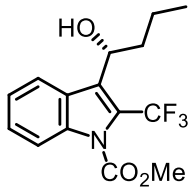
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 8.10 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.44 (dt, *J* = 7.0, 1.0 Hz, 1H), 7.30 (dt, *J* = 7.5, 1.0 Hz, 1H), 5.58-5.54 (m, 1H), 4.05 (s, 3H), 2.17 (br s, 1H), 1.65 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 137.1, 131.2, 127.4, 125.8, 124.6, 123.4, 121.4 (q, *J* = 269 Hz), 120.7 (q, *J* = 38 Hz), 115.2, 64.2 (q, *J* = 4 Hz), 54.3, 23.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -55.05.

IR (film): *v* (cm^{-1}) 3426, 2983, 1750, 1594, 1569, 1444, 1393, 1333, 1272, 1234, 1209, 1128, 1094, 1041, 988, 940, 893, 754, 702, 635, 556, 436, 399.

HRMS (APCI, *m*/*z*) calcd for $C_{13}H_{11}F_3NO_2$ [M+H-H_2O]$^+$: 270.0736, found: 270.0729.



methyl (*R*)-3-(1-hydroxybutyl)-2-(trifluoromethyl)-1*H*-indole-1-carboxylate (6c)

According to the general procedure, the reaction using methyl 3-butyryl-1*H*-indole-1-carboxylate **5c** (49.0 mg, 0.20 mmol) as the starting material gave 39.3 mg (62%) of **6c** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak AS-H column, ee = 96% (HPLC: AS-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (minor) = 8.27 min, t_r (major) = 9.55 min). $[\alpha]_D^{22}$ = +14.9° (*c* 1.0, CH_2Cl_2).

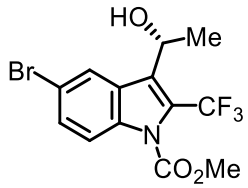
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.37 (t, J = 8.5 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 5.30-5.27 (m, 1H), 3.98 (s, 3H), 2.03-1.96 (m, 2H), 1.77-1.70 (m, 1H), 1.52-1.42 (m, 1H), 1.34-1.25 (m, 1H), 0.87 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 137.1, 130.5, 127.3, 126.1, 123.6, 123.4, 121.4 (q, J = 268 Hz), 121.2 (q, J = 38 Hz), 115.2, 67.7 (q, J = 3 Hz), 54.3, 39.5, 19.2, 13.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ -54.18.

IR (film): ν (cm^{-1}) 3528, 2961, 2872, 1751, 1568, 1445, 1390, 1333, 1270, 1234, 1209, 1130, 1090, 1024, 966, 913, 857, 805, 752, 637, 580, 554, 439, 402.

HRMS (APCI, m/z) calcd for $C_{15}H_{15}F_3NO_2$ $[M+H-H_2O]^+$: 298.1049, found: 298.1047.



methyl (*R*)-5-bromo-3-(1-hydroxyethyl)-2-(trifluoromethyl)-1*H*-indole-1-carboxylate (6d)

According to the general procedure, the reaction using methyl 3-acetyl-5-bromo-1*H*-indole-1-carboxylate **5d** (59.0 mg, 0.20 mmol) as the starting material gave 38.0 mg (52%) of **6d** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak AS-H column, ee = 99% (HPLC: AS-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (minor) = 11.07 min, t_r (major) = 15.20 min). $[\alpha]_D^{22}$ = +9.19° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 2.0 Hz, 1H), 7.97 (dd, J = 9.0, 0.5 Hz, 1H), 7.52 (dd, J = 9.0, 2.0 Hz, 1H), 5.55-5.50 (m, 1H), 4.05 (s, 3H), 2.18 (br s, 1H), 1.62 (d, J = 6.5 Hz, 3H).

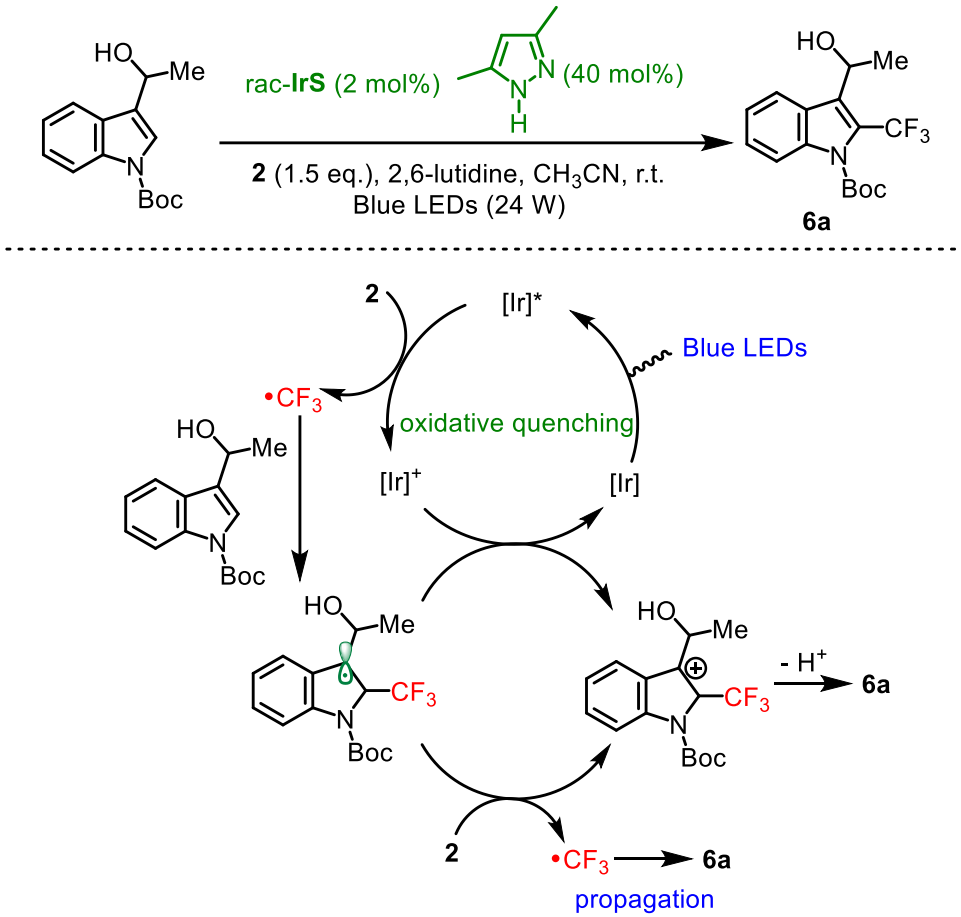
^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 135.8, 130.5, 130.3, 127.5, 126.1, 121.5 (q, J = 38 Hz), 121.1 (q, J = 270 Hz), 116.7, 64.1 (q, J = 4 Hz), 54.6, 23.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ -54.56.

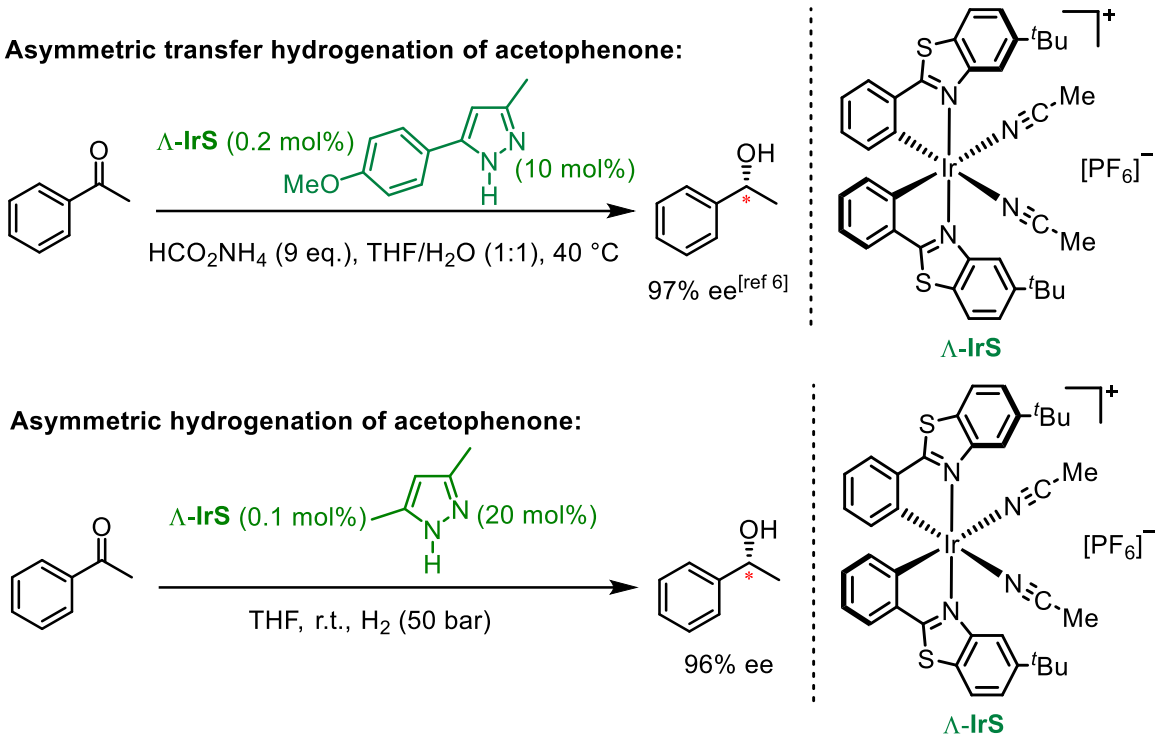
IR (film): ν (cm^{-1}) 3433, 3393, 3098, 2992, 2960, 2926, 2857, 1741, 1560, 1448, 1380, 1358, 1322, 1269, 1235, 1207, 1182, 1147, 1117, 1071, 1039, 941, 896, 856, 805, 760, 724, 712, 602, 564, 467, 437.

HRMS (APCI, m/z) calcd for $C_{13}H_{10}BrF_3NO_2$ $[M+H-H_2O]^+$: 347.9842, found: 347.9835.

3.3.5 Proposed mechanism for the photoredox chemistry



4. Assignment of absolute configurations of final products



Using acetophenone as the model substrate, the Λ-**IrS** together with 3,5-disubstituted pyrazole catalyzed asymmetric transfer hydrogenation or asymmetric hydrogenation reaction gave the desired chiral 1-phenylethan-1-ol. The absolute configuration of the product was assigned as (*R*)-configuration by comparing the sign of the optical rotation and chiral HPLC retention time data synthesized here with that reported in the literature.[6] All other products (**3**, **4**, **6**) were assigned by analogy.

Optical rotation of (*R*)-1-phenylethan-1-ol:

$[\alpha]_D^{20}$ = +40.4 (*c* 1.0, $CHCl_3$, 96% ee)

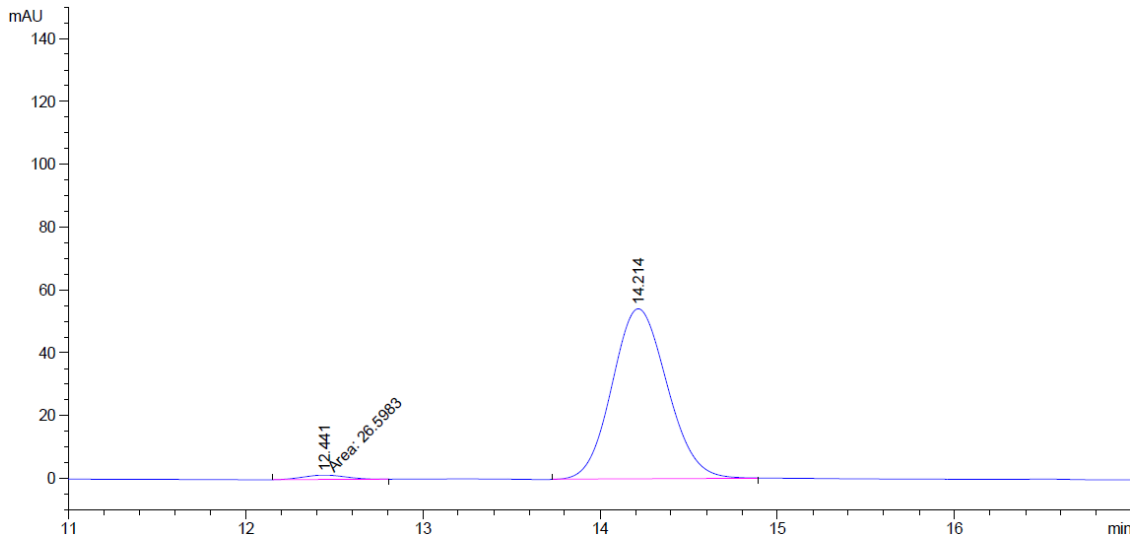
Lit.[6]: $[\alpha]_D^{20}$ = +36.0 (*c* 1.0, $CHCl_3$, 97% ee for *R*-configuration)

Chiral HPLC with (*R*)-1-phenylethan-1-ol:

(Daicel Chiralcel OJ column, 220 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C)

t_r (minor) = 12.4 min, t_r (major) = 14.2 min

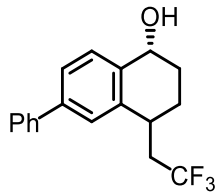
Lit.[6]: t_r (minor) = 11.6 min, t_r (major) = 13.4 min



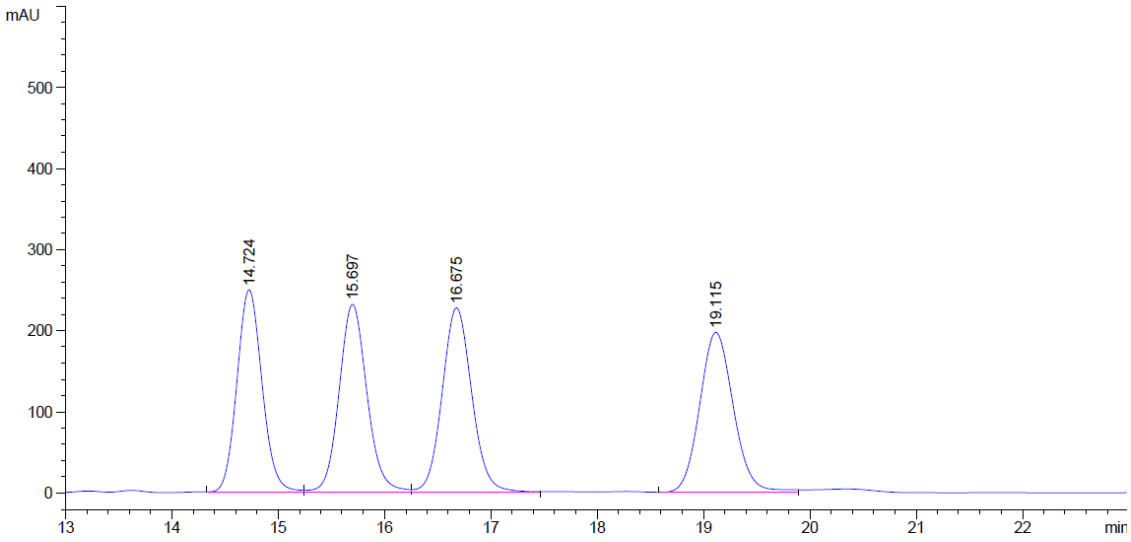
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.441	MM	0.2997	26.59829	1.47924	2.2215
2	14.214	BB	0.3382	1170.72791	54.14713	97.7785

5. Enantioselectivities as determined by chiral HPLC

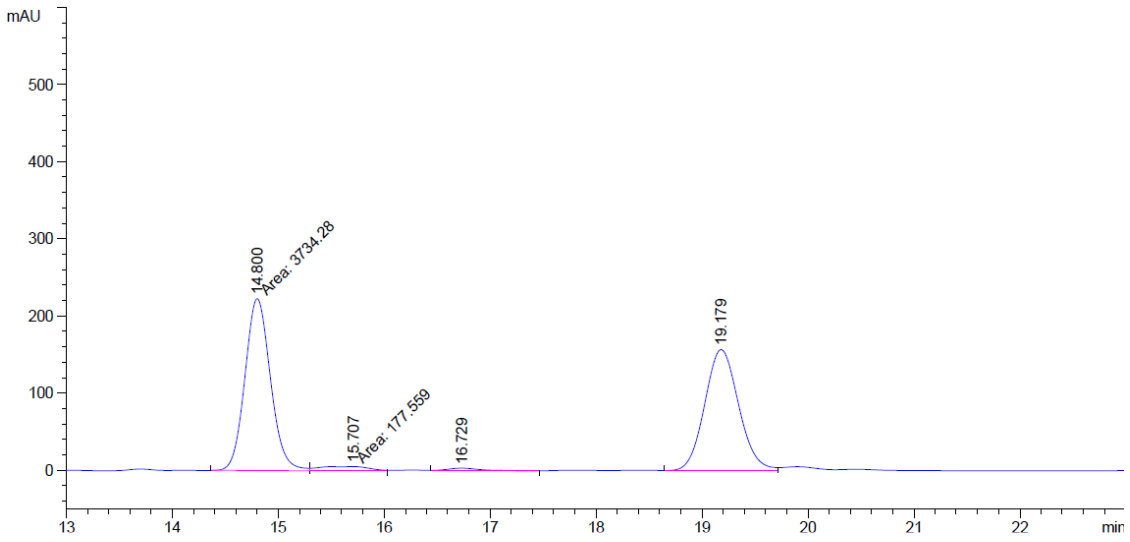
Enantiomeric purities of the reaction products were determined with a Daicel Chiralpak AD-H, AS-H, IC, IG (250 × 4.6 mm) or Daicel Chiralcel OD-H, OJ-H (250 × 4.6 mm) HPLC column on an Agilent 1200 or 1260 Series or Shimadzu Lc-2030c HPLC System using *n*-hexane/isopropanol as a mobile phase.



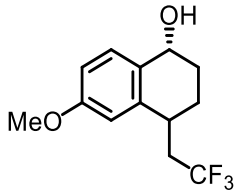
3a, 94% ee, 96% ee



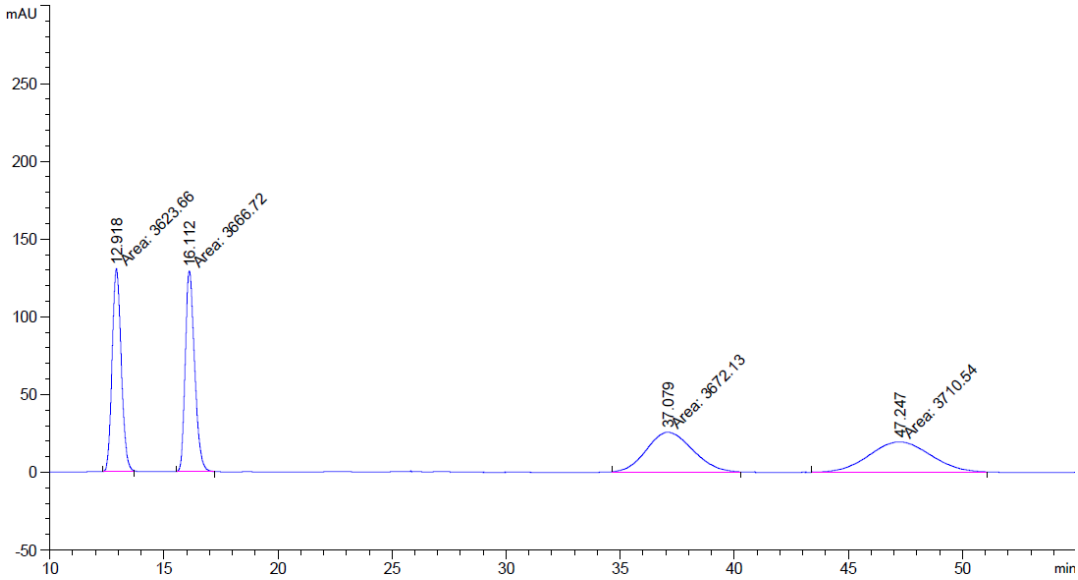
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.724	VV	0.2556	4140.11768	250.27568	24.0127
2	15.697	VV	0.2827	4264.01367	232.20432	24.7313
3	16.675	VB	0.3020	4450.57031	228.03238	25.8133
4	19.115	VB	0.3448	4386.69336	197.65157	25.4428



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.800	MM	0.2794	3734.28076	222.74991	49.8733
2	15.707	MM	0.5393	177.55867	5.48681	2.3714
3	16.729	VB	0.3225	73.28159	3.40351	0.9787
4	19.179	VV	0.3478	3502.41577	156.86580	46.7766

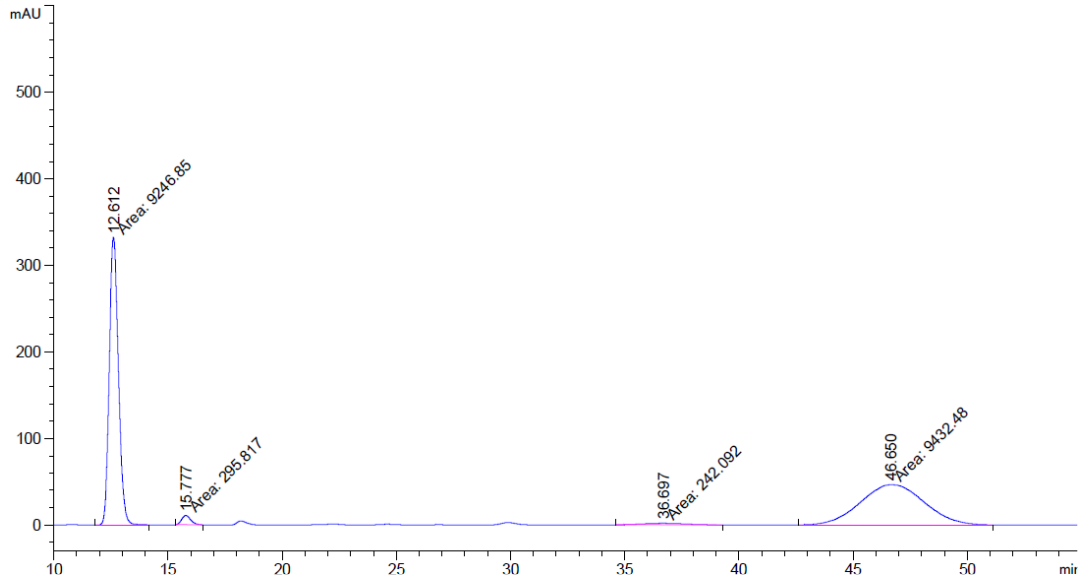


3b, 94% ee, 95% ee



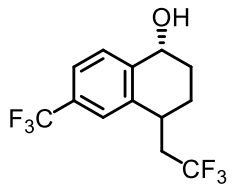
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.918	MM	0.4631	3623.65723	130.42186	24.6960
2	16.112	MM	0.4746	3666.71802	128.76506	24.9895
3	37.079	MM	2.3612	3672.13135	25.92041	25.0264

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	47.247	MM	3.1469	3710.53809	19.65166	25.2881

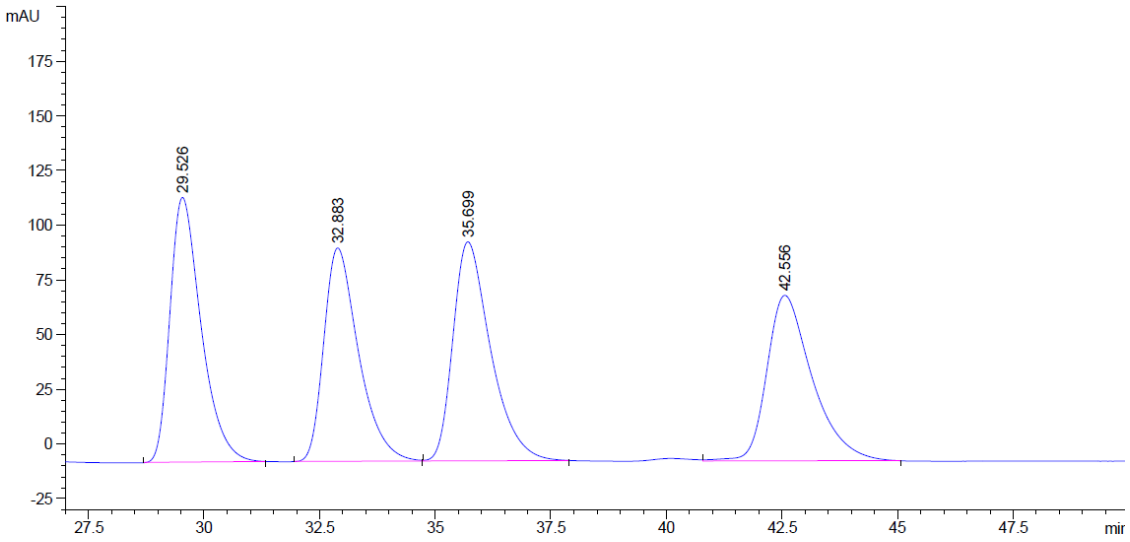


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.612	MM	0.4636	9246.84668	332.43628	48.1175
2	15.777	MM	0.4593	295.81696	10.73395	1.5393
3	36.697	MM	2.1929	242.09215	1.83997	1.2598

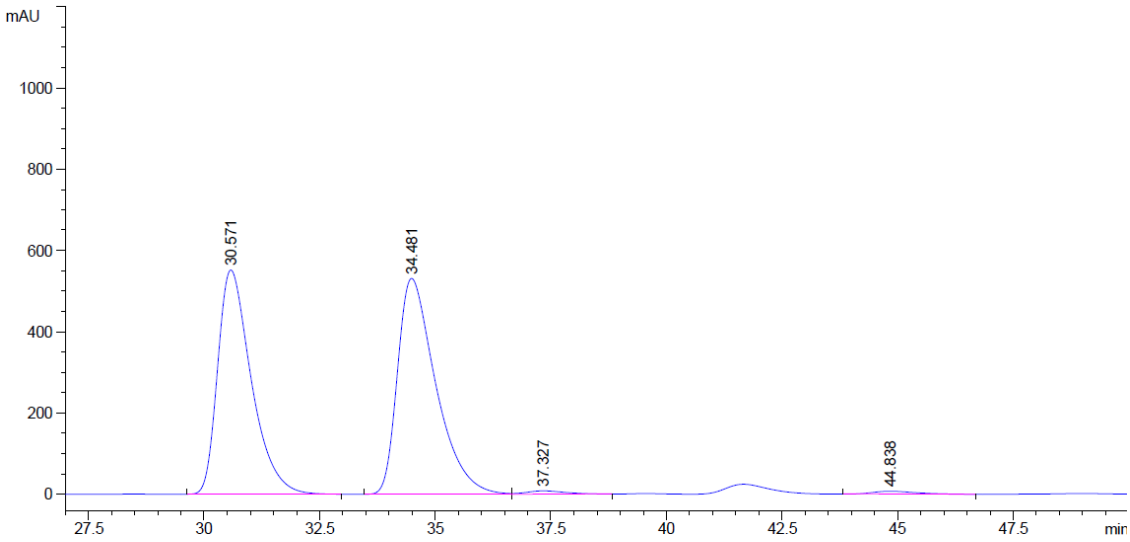
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	46.650	MM	3.3294	9432.47852	47.21767	49.0834



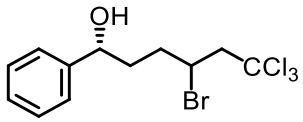
3c, 96% ee, 97% ee



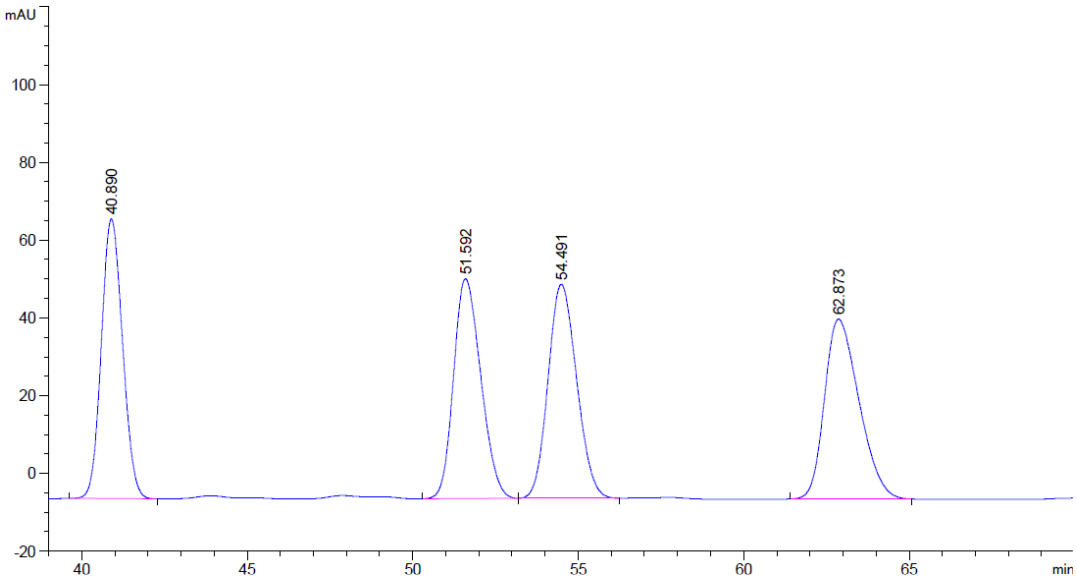
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.526	BB	0.7172	5695.35254	121.18583	26.2725
2	32.883	BB	0.7899	5112.63232	97.65367	23.5844
3	35.699	BB	0.8565	5682.09473	100.23214	26.2113
4	42.556	VB	1.0186	5187.95508	75.77689	23.9319



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.571	BB	0.7716	2.78860e4	551.80463	46.9389
2	34.481	BB	0.8699	3.05293e4	531.27917	51.3881
3	37.327	BV	0.8670	509.21671	8.40498	0.8571
4	44.838	BB	0.9483	484.74518	7.28291	0.8159

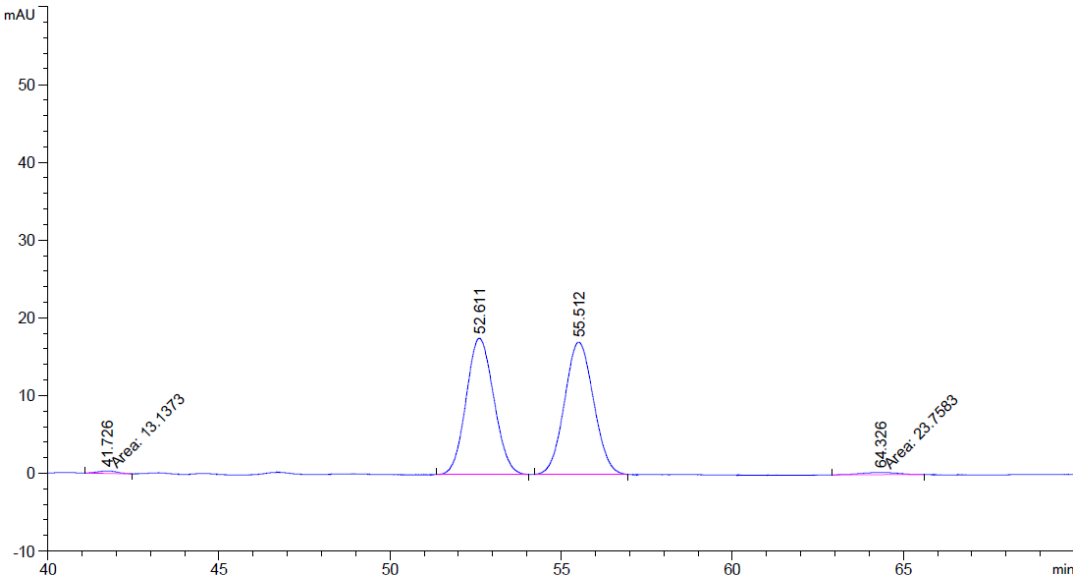


4a, 95% ee, 97% ee



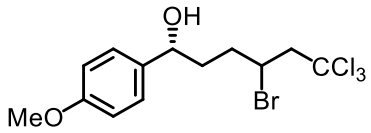
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.890	VB R	0.5267	3205.89648	71.97402	24.4815
2	51.592	BB	0.6703	3234.04980	56.58580	24.6964
3	54.491	BB	0.7027	3305.42456	55.03412	25.2415

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	62.873	BB	0.8463	3349.83521	46.26208	25.5806

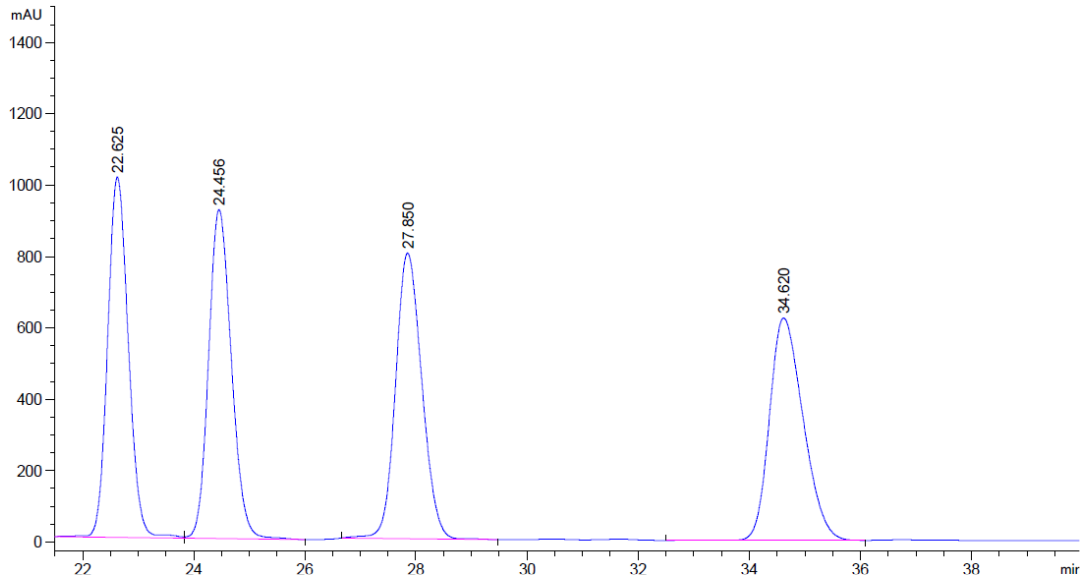


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.726	MM	0.6685	13.13733	3.27555e-1	0.6486
2	52.611	BB	0.6580	985.99542	17.53559	48.6795
3	55.512	BB	0.6885	1002.59277	17.02623	49.4989

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	64.326	MM	1.2585	23.75828	3.14650e-1	1.1730

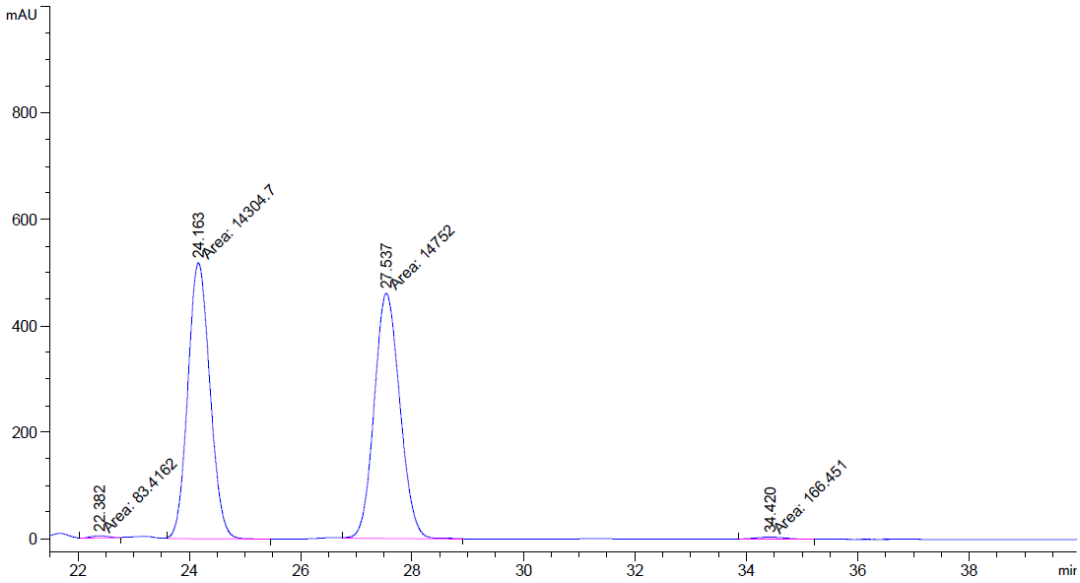


4b, 98% ee, 99% ee



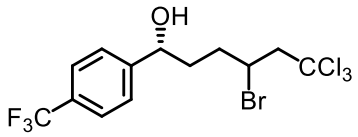
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.625	VV R	0.3966	2.61753e4	1009.82379	24.9352
2	24.456	VB	0.4361	2.62567e4	921.08984	25.0127
3	27.850	BV R	0.4943	2.63429e4	800.48657	25.0948

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	34.620	VB R	0.6196	2.61986e4	622.98700	24.9573

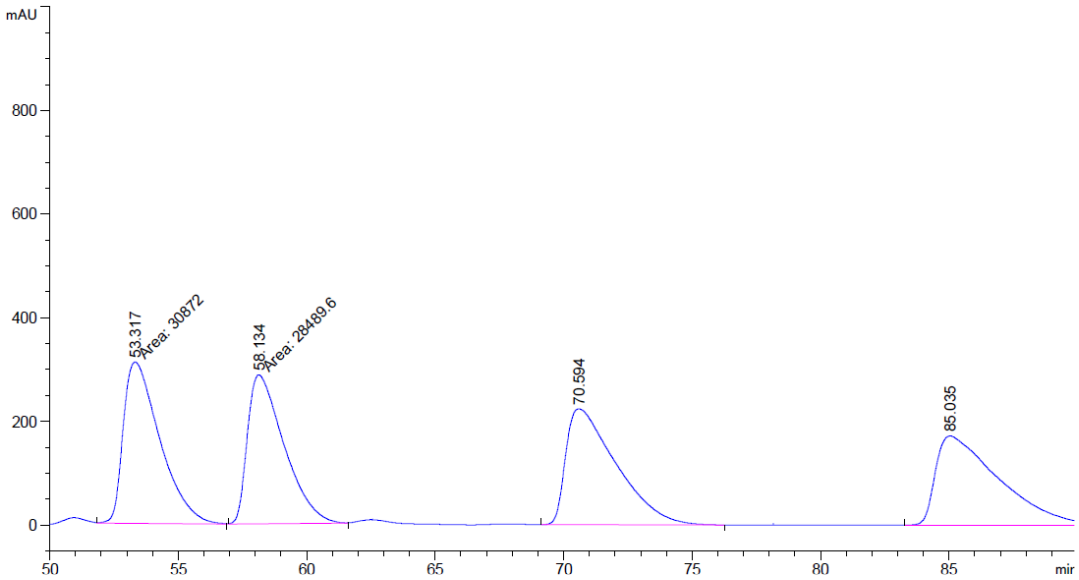


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.382	MM	0.3261	83.41624	4.26332	0.2846
2	24.163	MM	0.4595	1.43047e4	518.85132	48.8105
3	27.537	MM	0.5339	1.47520e4	460.52557	50.3369

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	34.420	MM	0.6838	166.45055	4.05698	0.5680

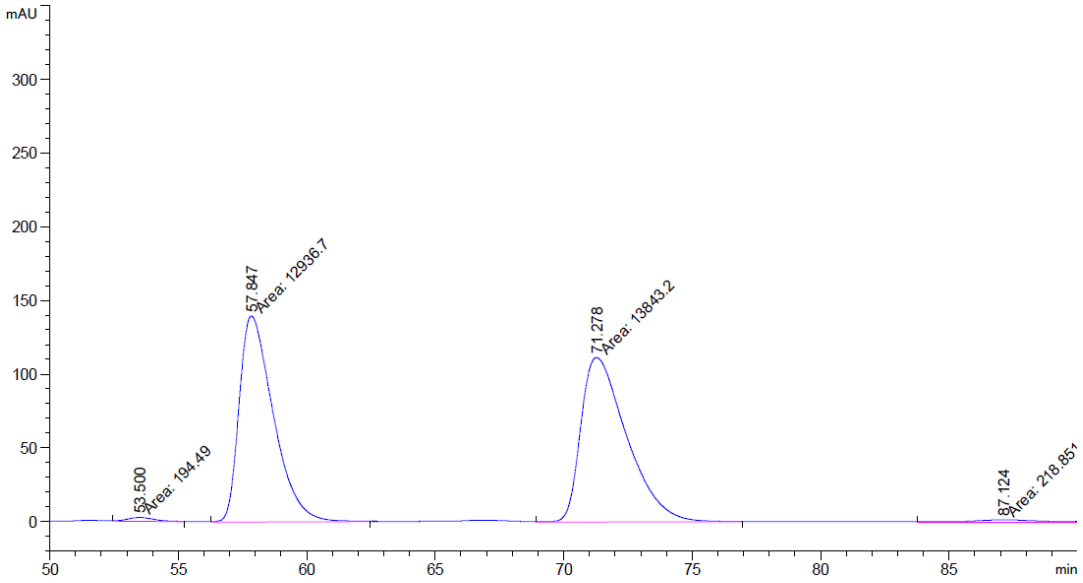


4c, 97% ee, 97% ee



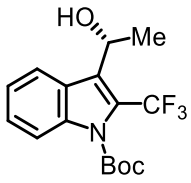
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	53.317	MM	1.6530	3.08720e4	311.28061	25.9465
2	58.134	MM	1.6523	2.84896e4	287.36447	23.9442
3	70.594	BB	1.5836	3.03206e4	223.58723	25.4831

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	85.035	BB	1.9947	2.93012e4	171.50902	24.6263

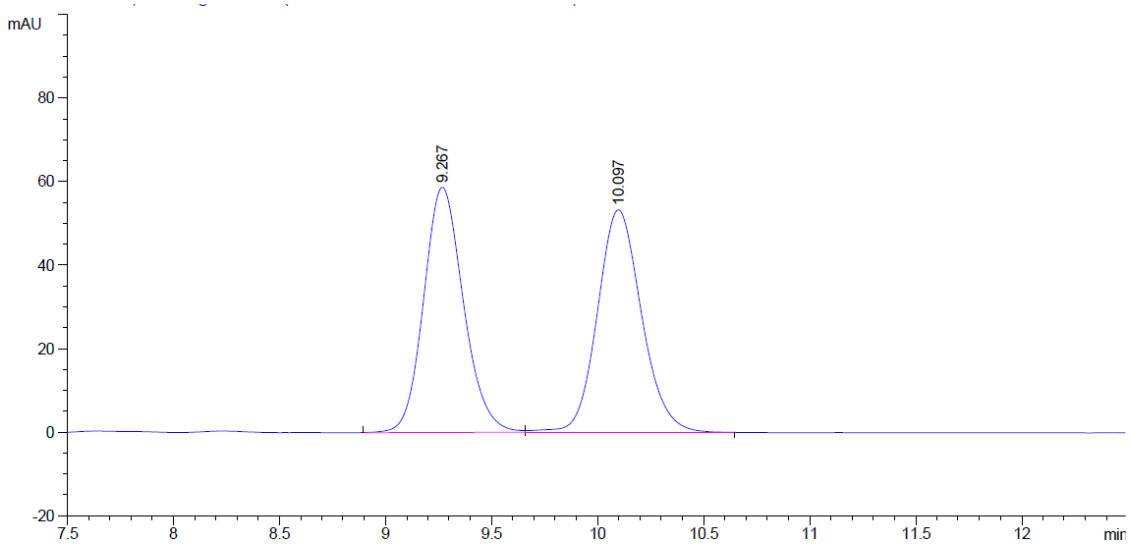


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	53.500	MM	1.2562	194.48984	2.58030	0.7152
2	57.847	MM	1.5429	1.29367e4	139.74194	47.5732
3	71.278	MM	2.0690	1.38432e4	111.51137	50.9068

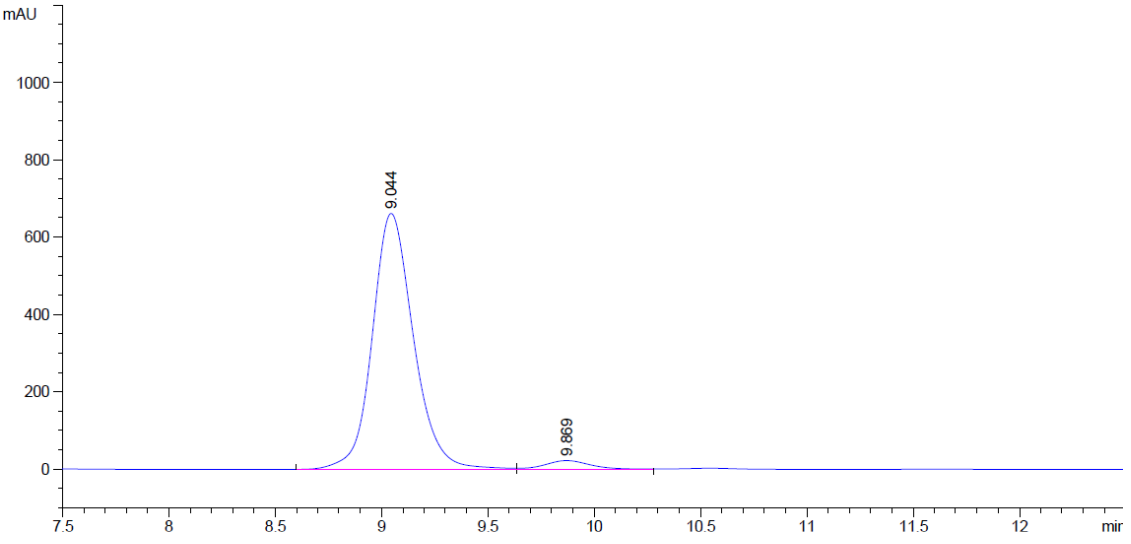
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	87.124	MM	2.3152	218.85069	1.57548	0.8048



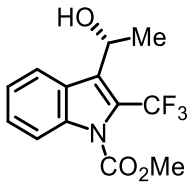
6a, 93% ee



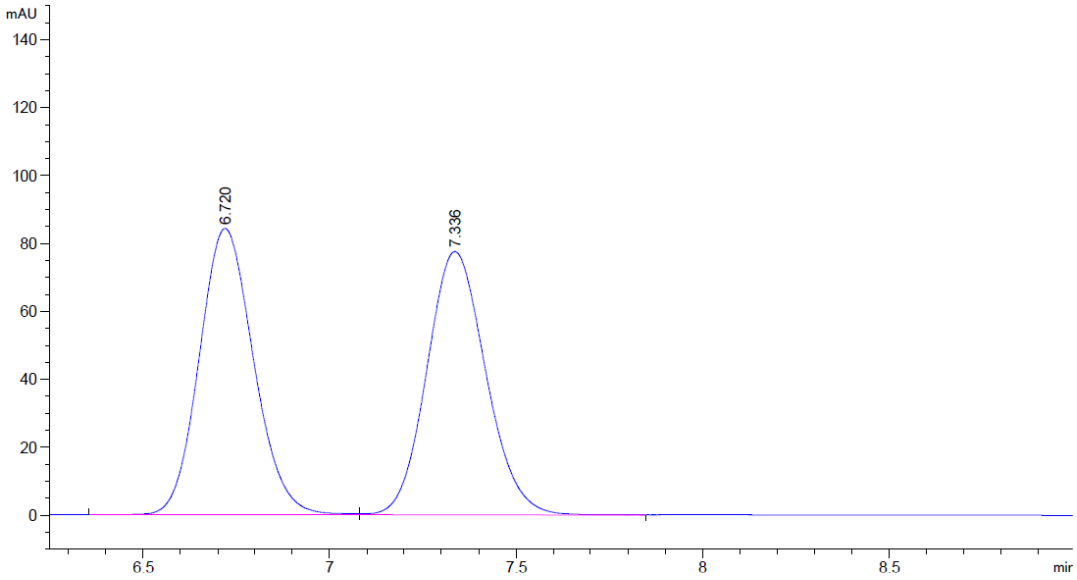
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.267	BV	0.2004	767.74628	58.79488	49.7460
2	10.097	VB	0.2235	775.58789	53.35481	50.2540



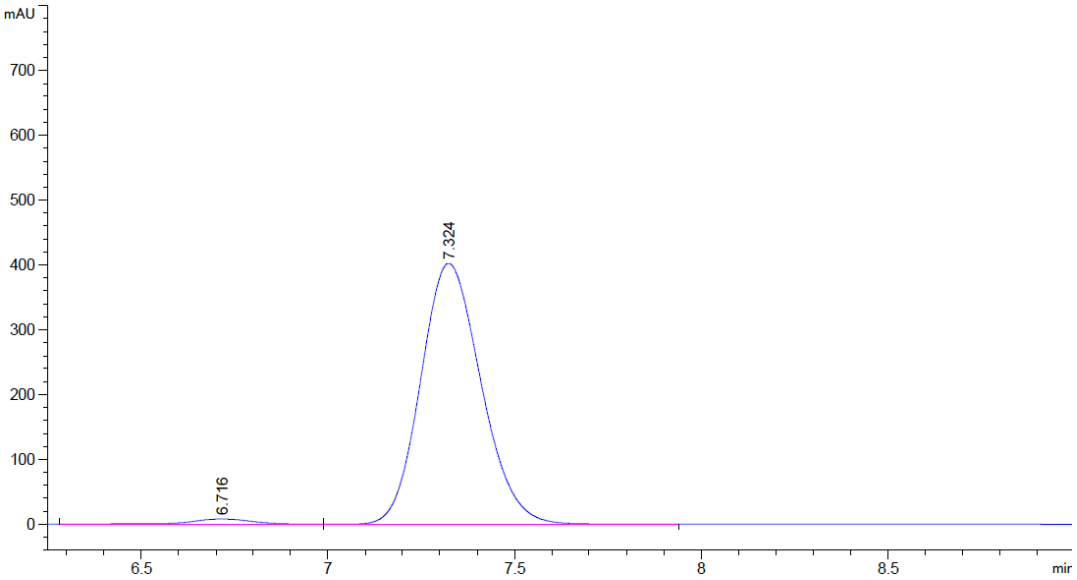
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.044	BV	0.2051	8911.38184	661.84729	96.2915
2	9.869	VB	0.2287	343.20734	22.71309	3.7085



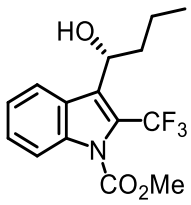
6b, 96% ee



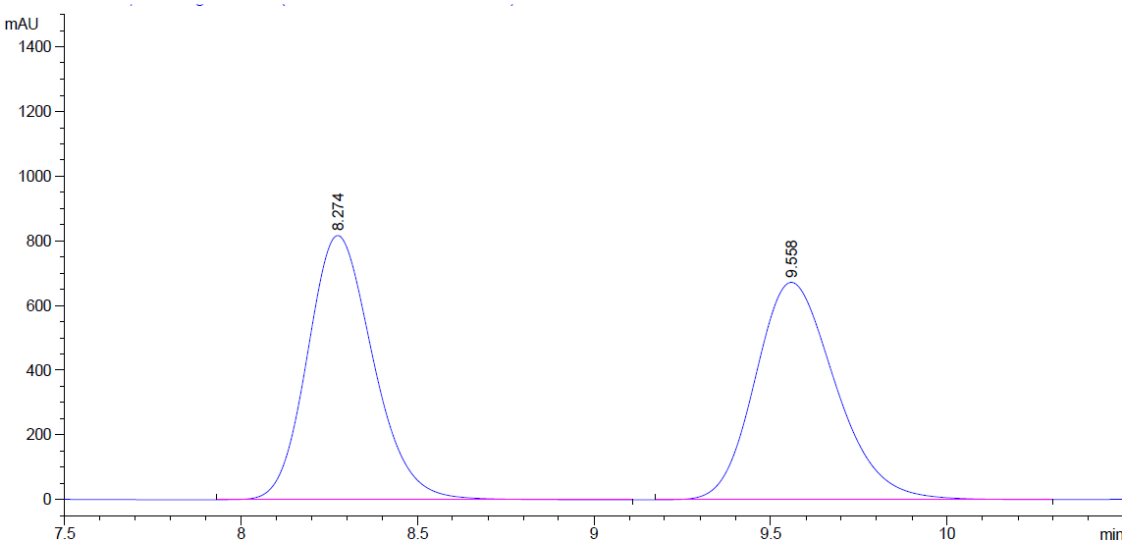
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.720	BV	0.1544	855.21863	84.29634	50.0796
2	7.336	VB	0.1678	852.49878	77.52527	49.9204



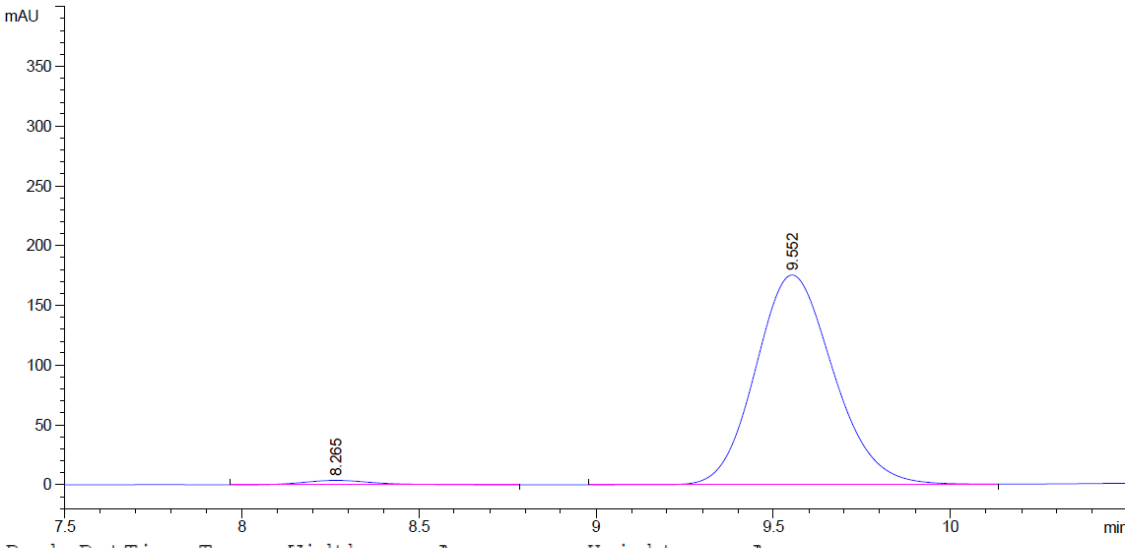
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.716	VV R	0.1615	92.41404	8.01603	2.0069
2	7.324	VB	0.1743	4512.45215	402.36688	97.9931



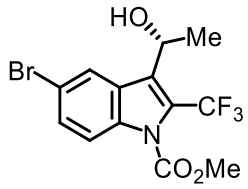
6c, 96% ee



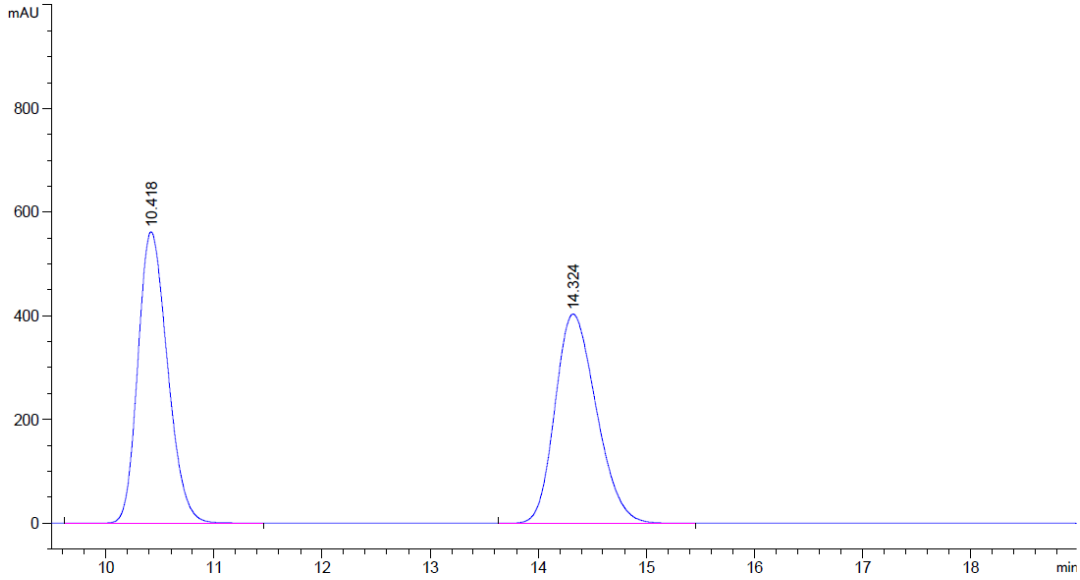
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.274	BB	0.2001	1.05530e4	817.68060	49.7954
2	9.558	BB	0.2457	1.06397e4	672.72894	50.2046



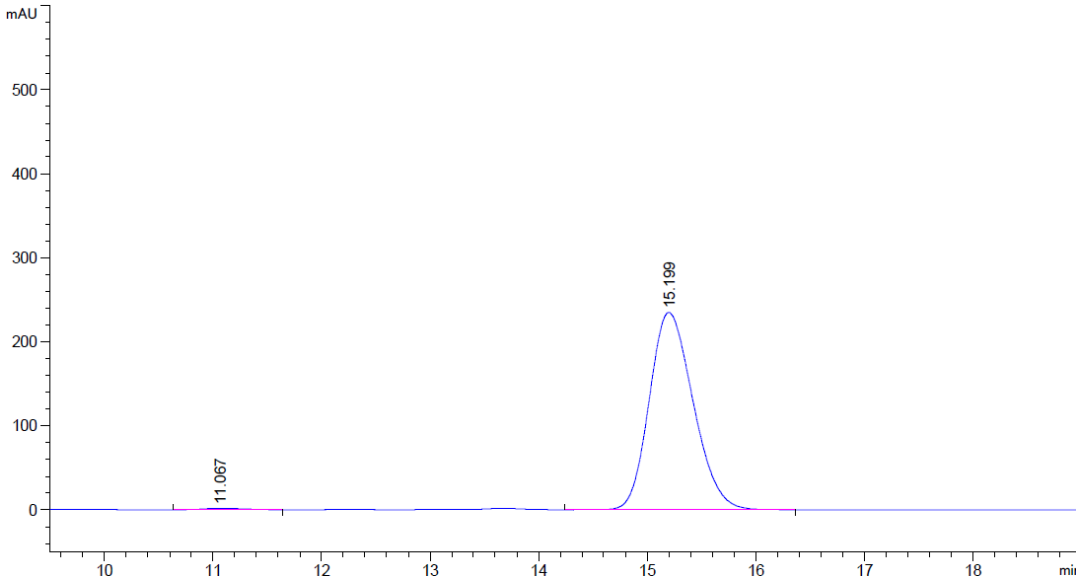
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.265	VB	0.2189	53.56618	3.72229	1.9497
2	9.552	BB	0.2372	2693.77612	175.61642	98.0503



6d, 99% ee

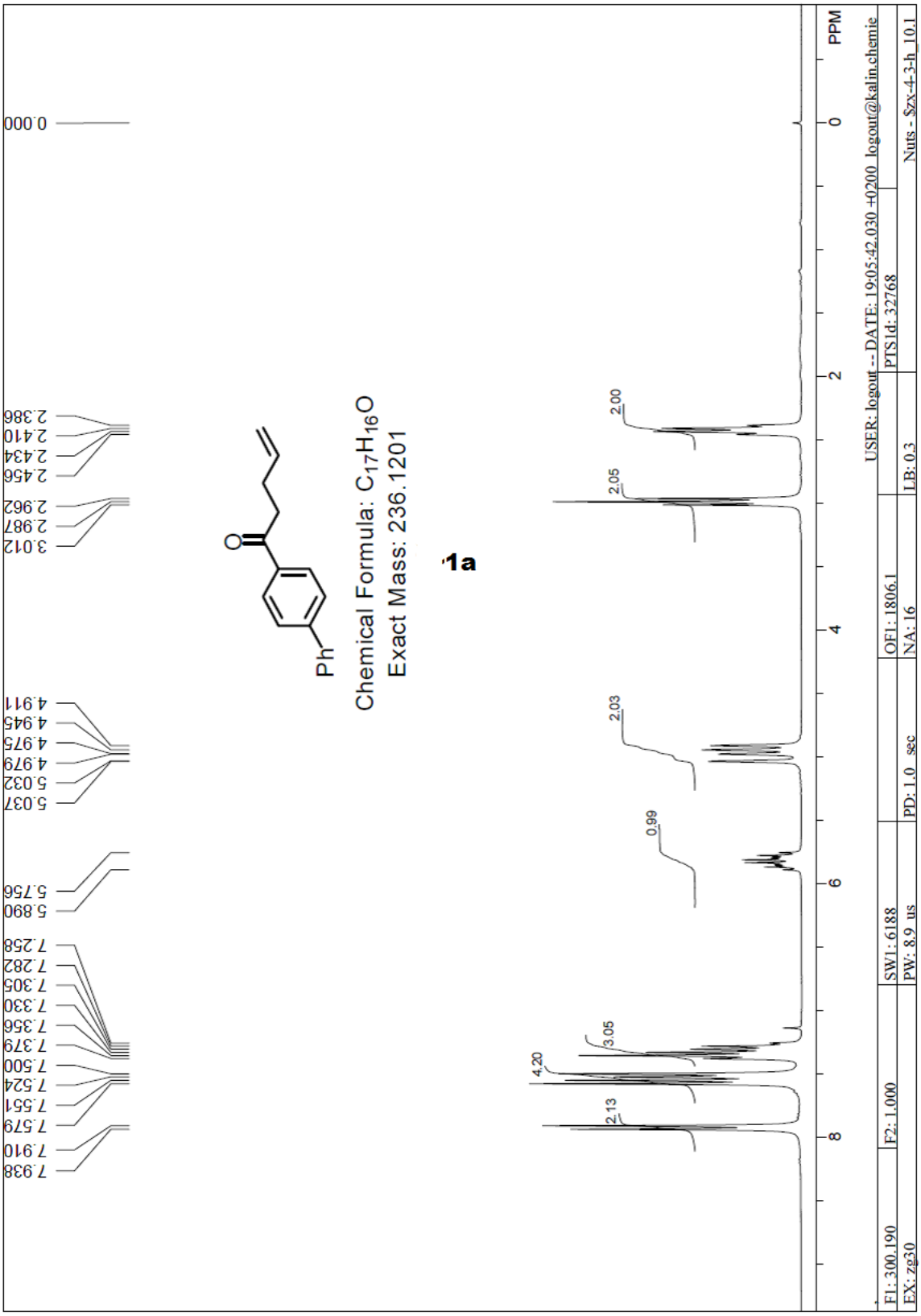


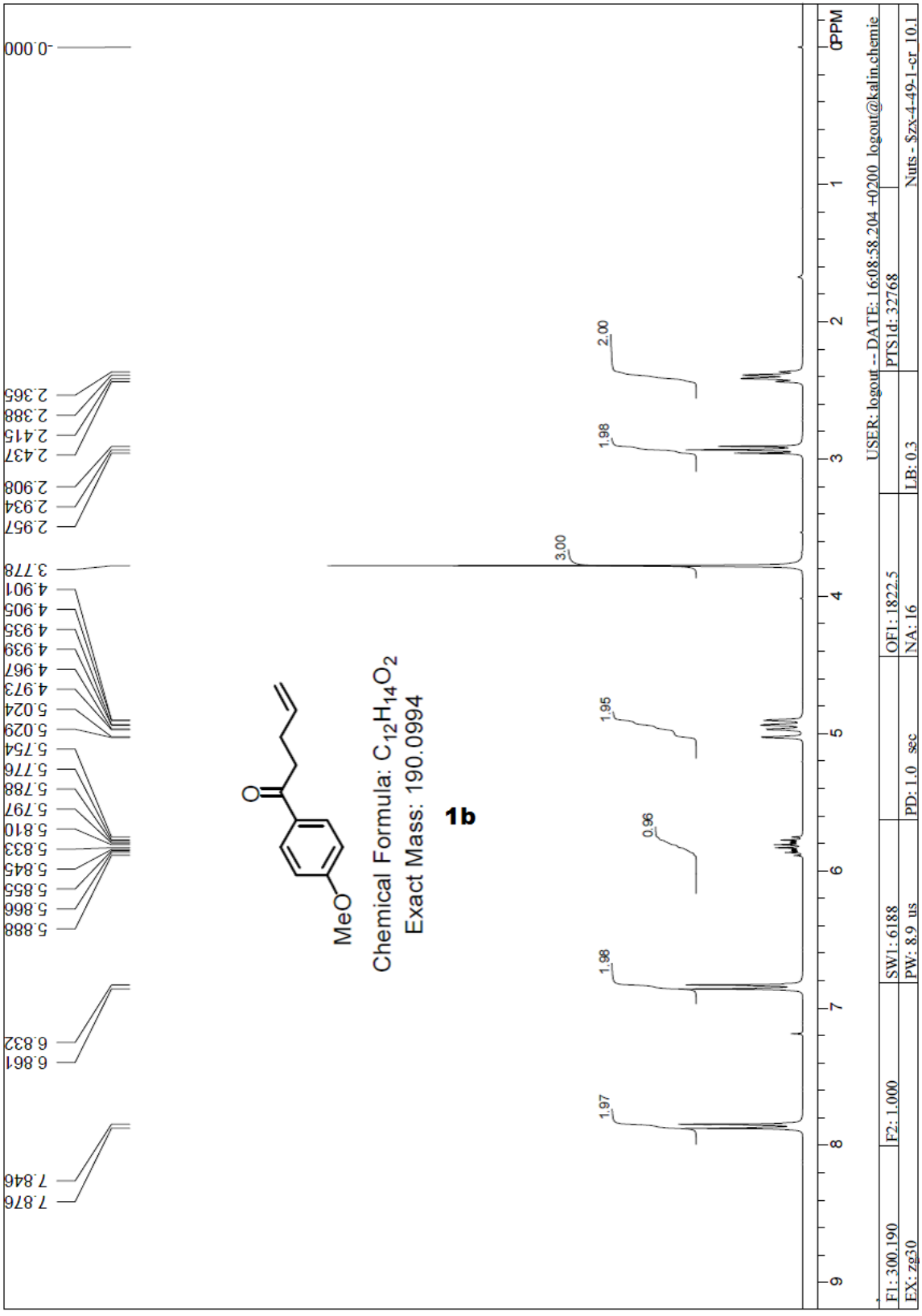
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.418	BB	0.2944	1.06830e4	561.74139	49.9710
2	14.324	BB	0.4071	1.06954e4	403.04877	50.0290

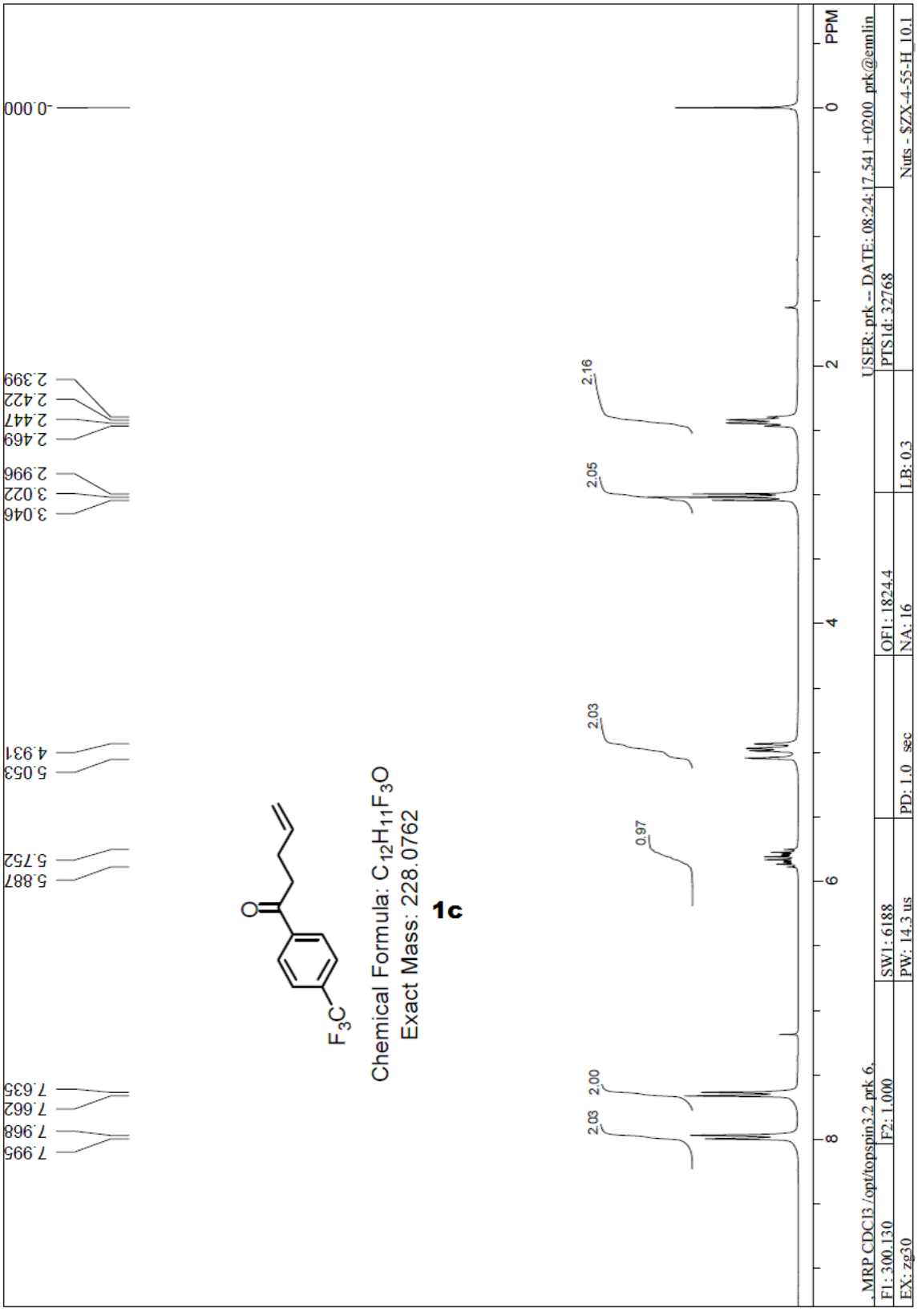


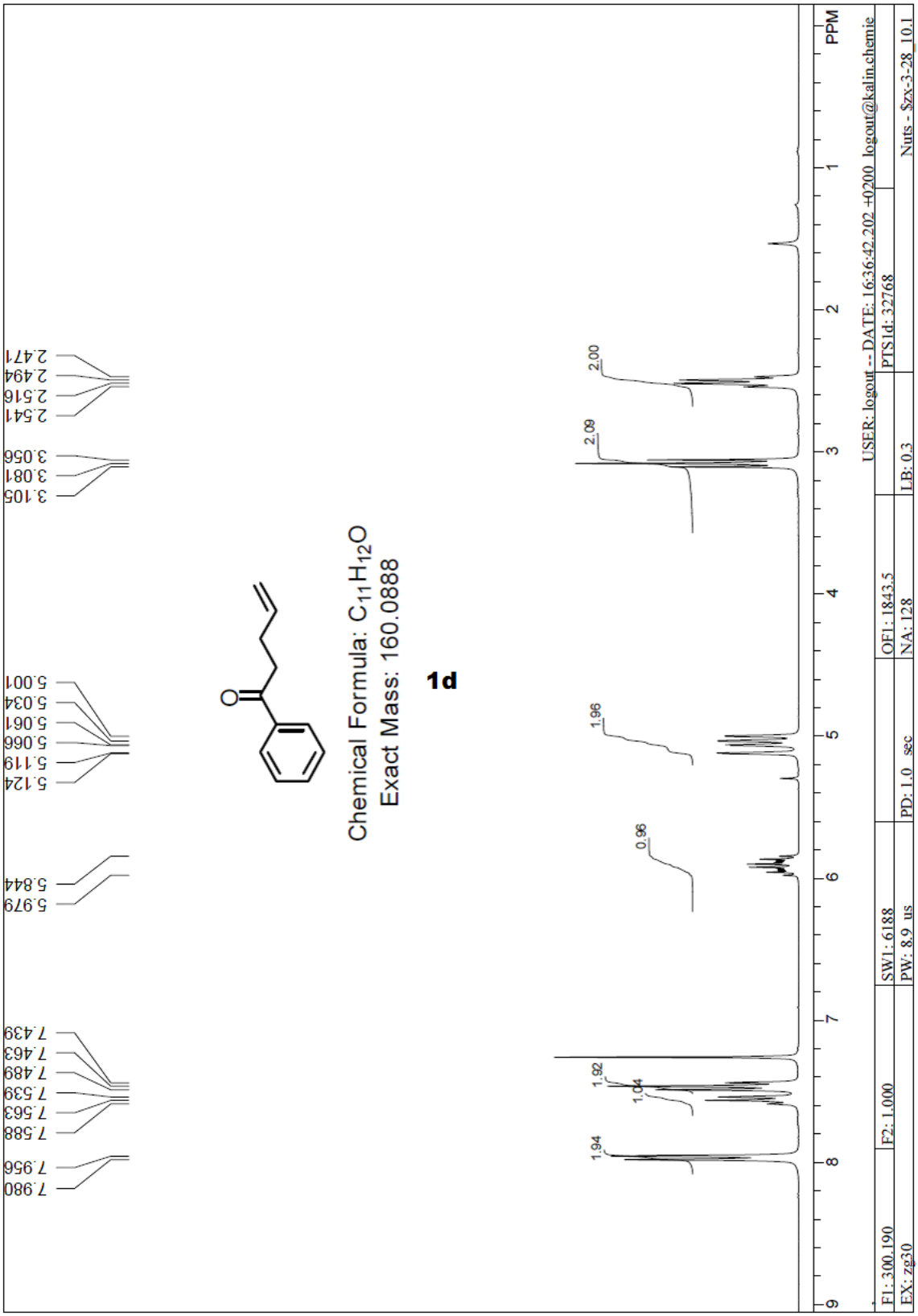
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.067	BB	0.2868	42.23516	1.72380	0.6372
2	15.199	BB	0.4258	6586.14697	234.76961	99.3628

6. NMR spectra of new compounds




0.000
2.365
2.388
2.415
2.437
2.908
2.934
2.957
3.778
4.901
4.905
4.935
4.939
4.967
4.973
5.024
5.029
5.754
5.776
5.788
5.797
5.810
5.833
5.845
5.855
5.866
5.888
6.832
6.861
7.846
7.876
MeO
Chemical Formula: C12H14O2
Exact Mass: 190.0994
1b
1.97
1.98
0.96
1.95
3.00
1.98
2.00
PPM
USER: logout -- DATE: 16:08:58.204 +0200 logout@kalin.chemie
F1: 300.190
F2: 1.000
SW1: 6188
PW: 8.9 us
PD: 1.0 sec
OF1: 1822.5
NA: 16
PTS1d: 32768
LB: 0.3
EX: zg30
Nuts - $zx-4-49-1-cr_10.1


0.000
2.399
2.422
2.447
2.469
2.996
3.022
3.046
4.931
5.053
5.752
5.887
7.635
7.662
7.968
7.995
Chemical Formula: C12H11F3O
Exact Mass: 228.0762
1c
F3C
2.03
2.00
2.03
0.97
2.05
2.16
8
6
4
2
0
PPM
. MRP CDCl3 /opt/topspin3.2 prk 6.
USER: prk -- DATE: 08:24:17.541 +0200 prk@emnlin
F1: 300.130
F2: 1.000
SW1: 6188
OF1: 1824.4
PTS1d: 32768
EX: zg30
PW: 14.3 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $ZX-4-55-H_10.1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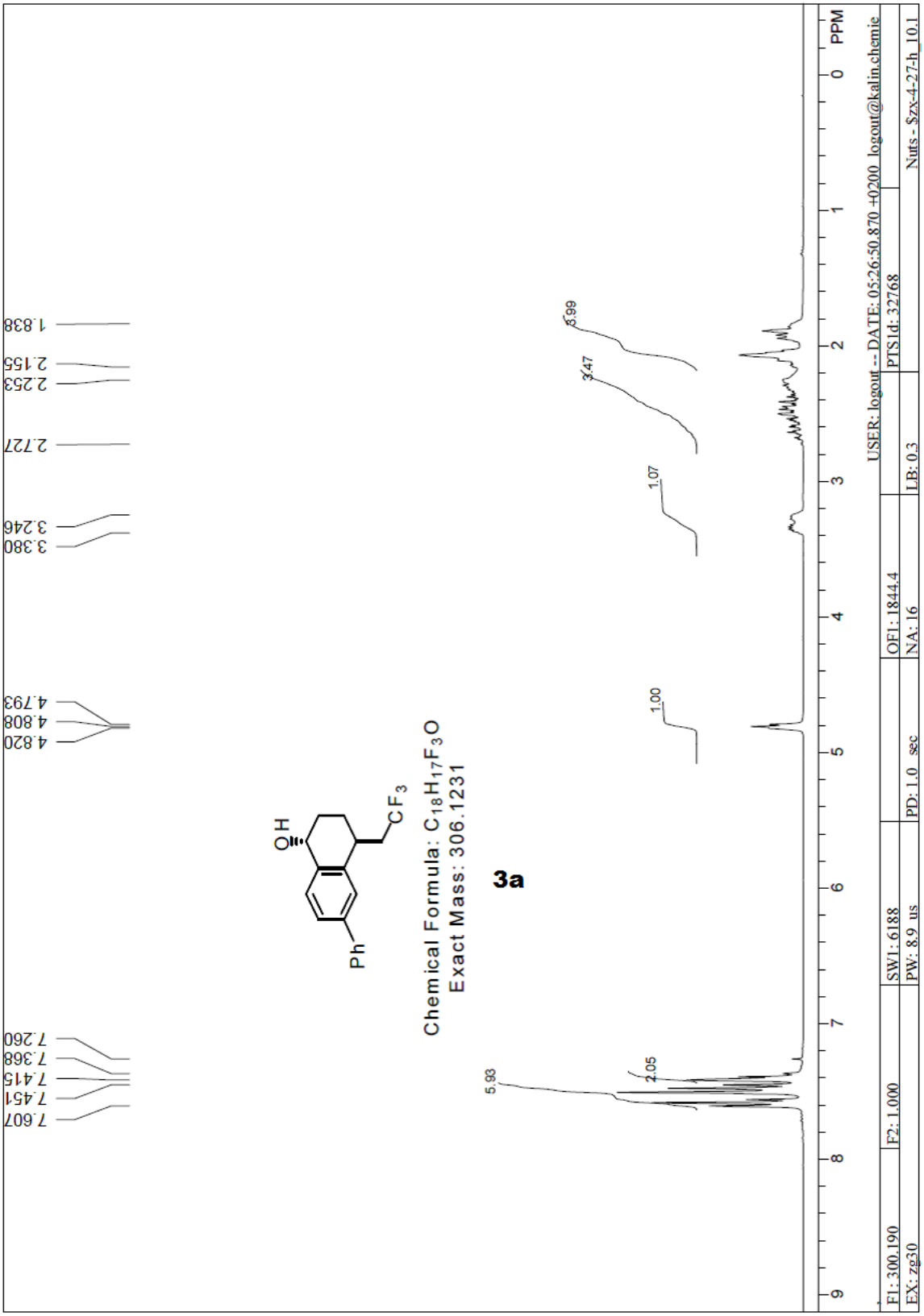
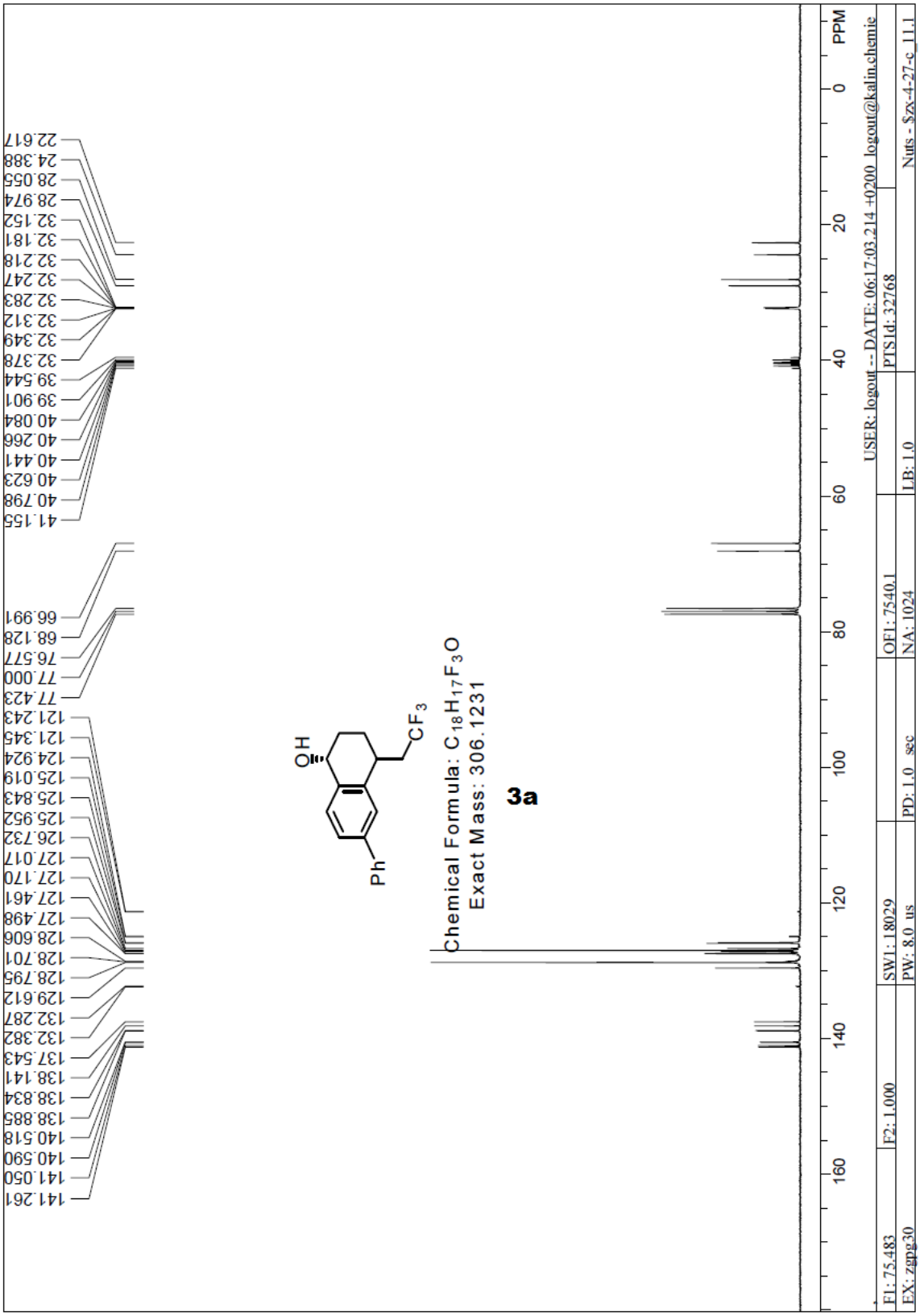
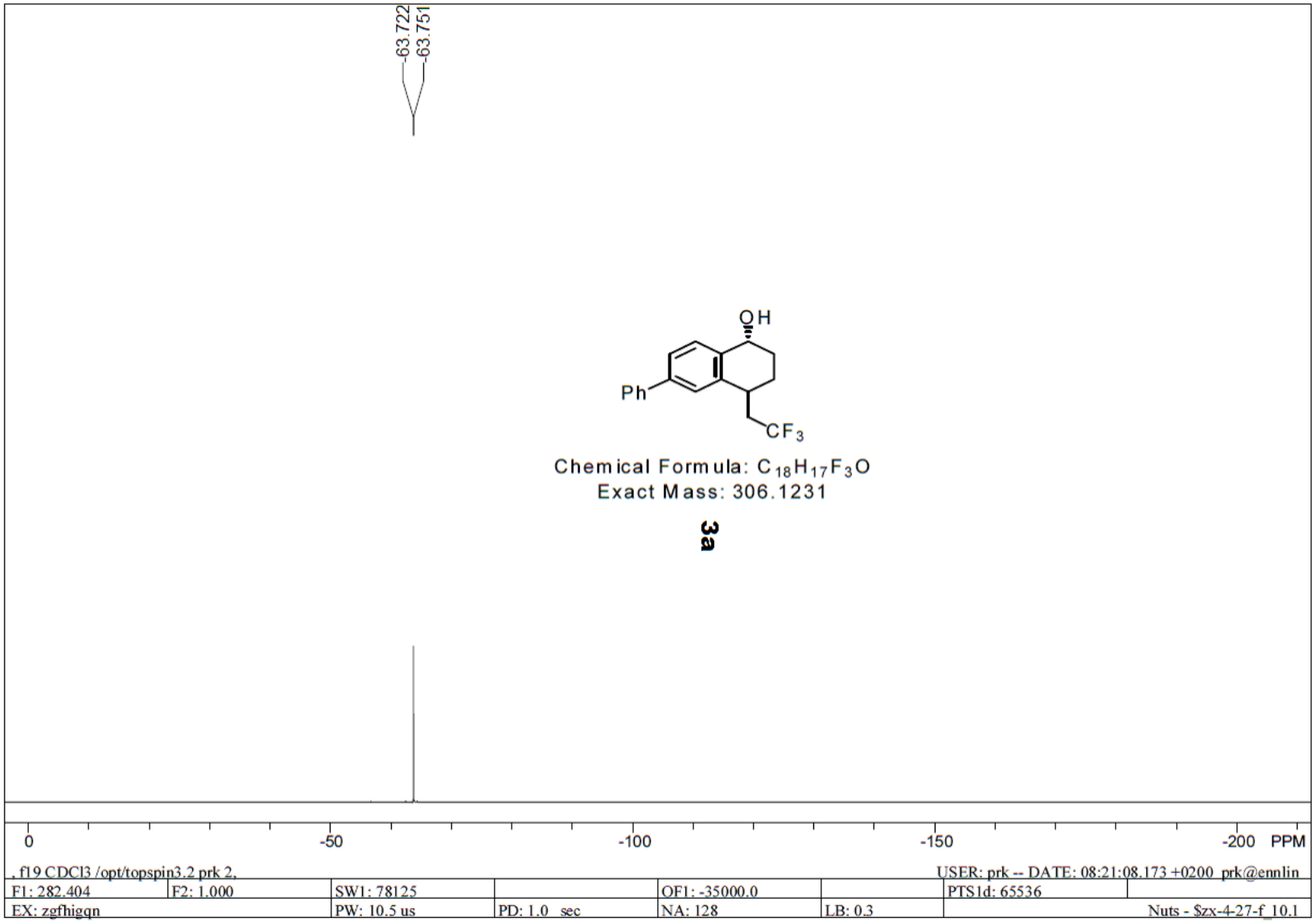
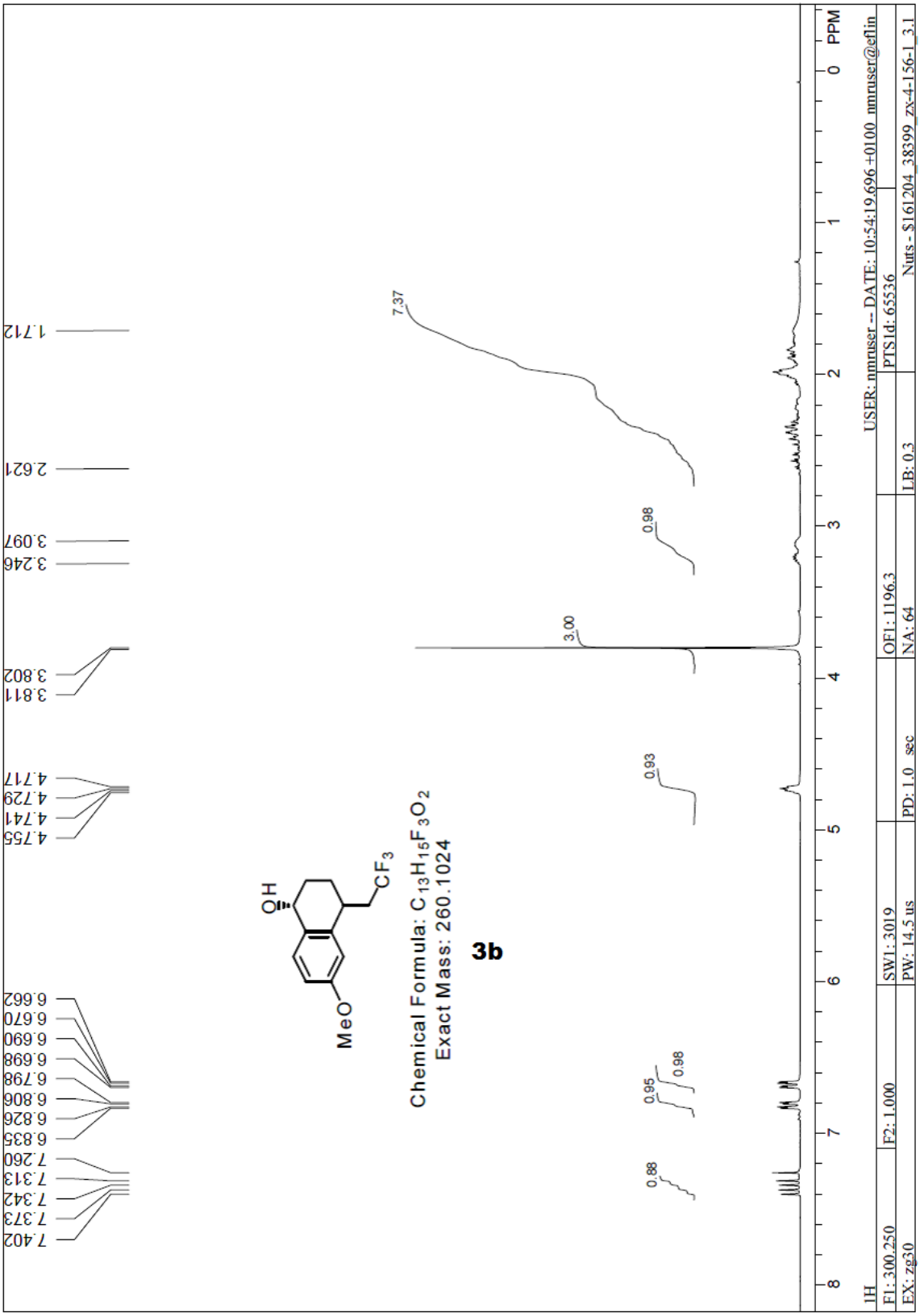
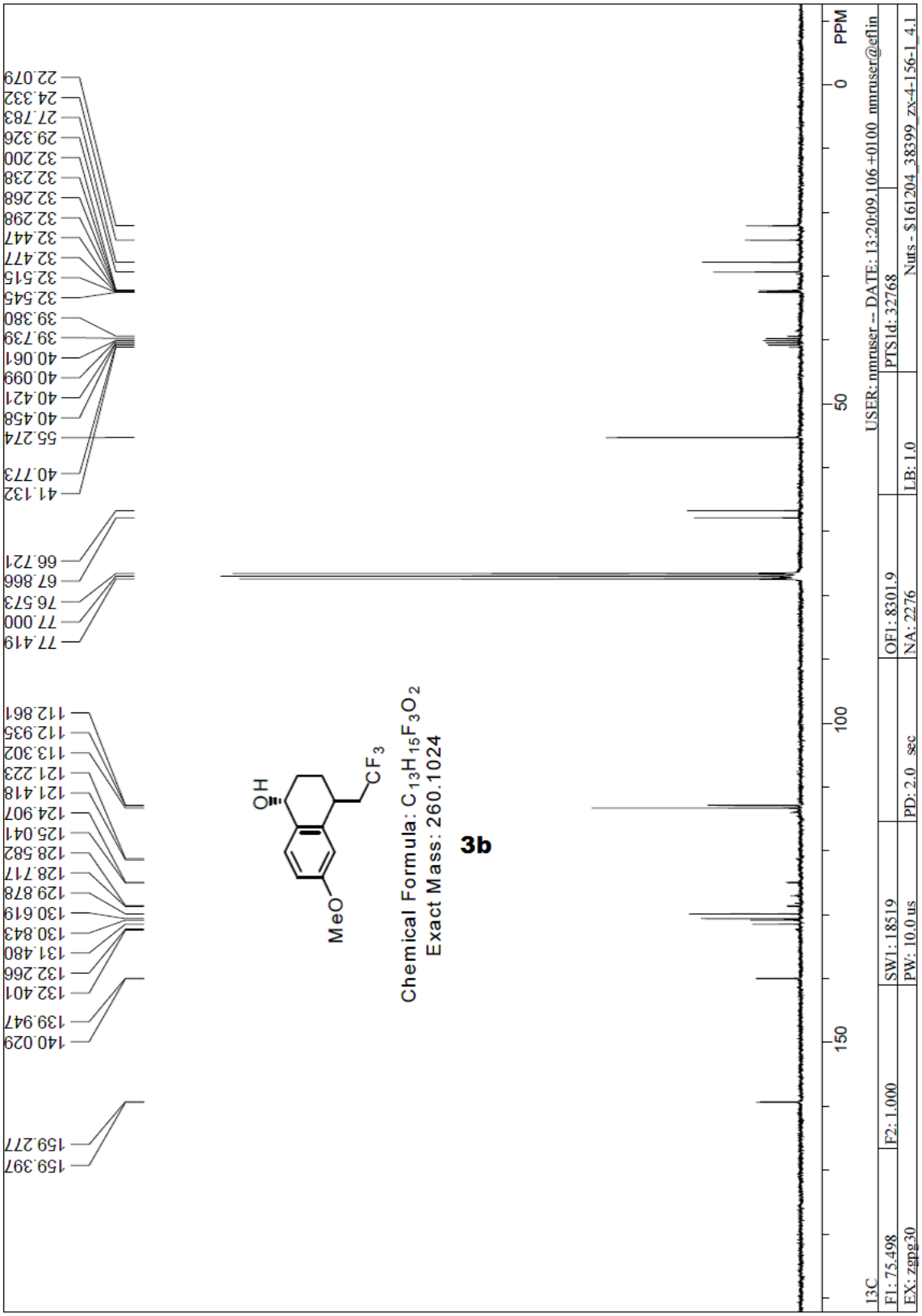
7.956
7.588
7.563
7.539
7.489
7.463
7.439
5.979
5.844
5.124
5.119
5.066
5.061
5.034
5.001
3.105
3.081
3.056
2.541
2.516
2.494
2.471
Chemical Formula: C11H12O
Exact Mass: 160.0888
1d
1.94
1.92
1.04
0.96
1.96
2.09
2.00
PPM
USER: logout -- DATE: 16:36:42.202 +0200 logout@kalin.chemie
F1: 300.190
F2: 1.000
SW1: 6188
PW: 8.9 us
PD: 1.0 sec
OF1: 1843.5
NA: 128
PTS1d: 32768
LB: 0.3
EX: zg30
Nuts - $zx-3-28_10.1


7.607
7.451
7.415
7.368
7.260
4.820
4.808
4.793
3.380
3.246
2.727
2.253
2.155
1.838
Chemical Formula: C18H17F3O
Exact Mass: 306.1231
3a
OH
CF3
Ph
5.93
2.05
1.00
1.07
3.47
3.99
PPM
USER: logout -- DATE: 05:26:50.870 +0200 logout@kalin.chemie
F1: 300.190
F2: 1.000
SW1: 6188
PW: 8.9 us
OF1: 1844.4
NA: 16
PD: 1.0 sec
PTS1d: 32768
LB: 0.3
EX: zg30
Nuts - $zx-4-27-h_10.1


22.617
24.388
28.055
28.974
32.152
32.181
32.218
32.247
32.283
32.312
32.349
32.378
39.544
39.901
40.084
40.266
40.441
40.623
40.798
41.155
66.991
68.128
76.577
77.000
77.423
121.243
121.345
124.924
125.019
125.843
125.952
126.732
127.017
127.170
127.461
127.498
128.606
128.701
128.795
129.612
132.287
132.382
137.543
138.141
138.834
138.885
140.518
140.590
141.050
141.261
OH
CF3
Ph
Chemical Formula: C18H17F3O
Exact Mass: 306.1231
3a
PPM
0
20
40
60
80
100
120
140
160
USER: logout -- DATE: 06:17:03.214 +0200 logout@kalin.chemie
F1: 75.483
F2: 1.000
SW1: 18029
OF1: 7540.1
PTS1d: 32768
EX: zgpg30
PW: 8.0 us
PD: 1.0 sec
NA: 1024
LB: 1.0
Nuts - $zx-4-27-c_11.1


63.722
63.751
OH
Ph
CF3
Chemical Formula: C18H17F3O
Exact Mass: 306.1231
3a
0
-50
-100
-150
-200
PPM
, f19 CDCl3 /opt/topspin3.2 prk 2,
USER: prk -- DATE: 08:21:08.173 +0200 prk@ennlin
F1: 282.404
F2: 1.000
SW1: 78125
OF1: -35000.0
PTS1d: 65536
EX: zgfhigqn
PW: 10.5 us
PD: 1.0 sec
NA: 128
LB: 0.3
Nuts - $zx-4-27-f_10.1


7.402
7.373
7.342
7.313
7.260
6.835
6.826
6.806
6.798
6.698
6.690
6.670
6.662
4.755
4.741
4.729
4.717
3.811
3.802
3.246
3.097
2.621
1.712
OH
MeO
CF3
Chemical Formula: C13H15F3O2
Exact Mass: 260.1024
3b
7.37
3.00
0.98
0.93
0.95
0.98
0.88
PPM
1H
F1: 300.250
F2: 1.000
EX: zg30
SW1: 3019
PW: 14.5 us
PD: 1.0 sec
OF1: 1196.3
NA: 64
LB: 0.3
USER: nmruser -- DATE: 10:54:19.696 +0100 nmruser@eflin
PTS1d: 65536
Nuts - $161204_38399_zx-4-156-1_3.1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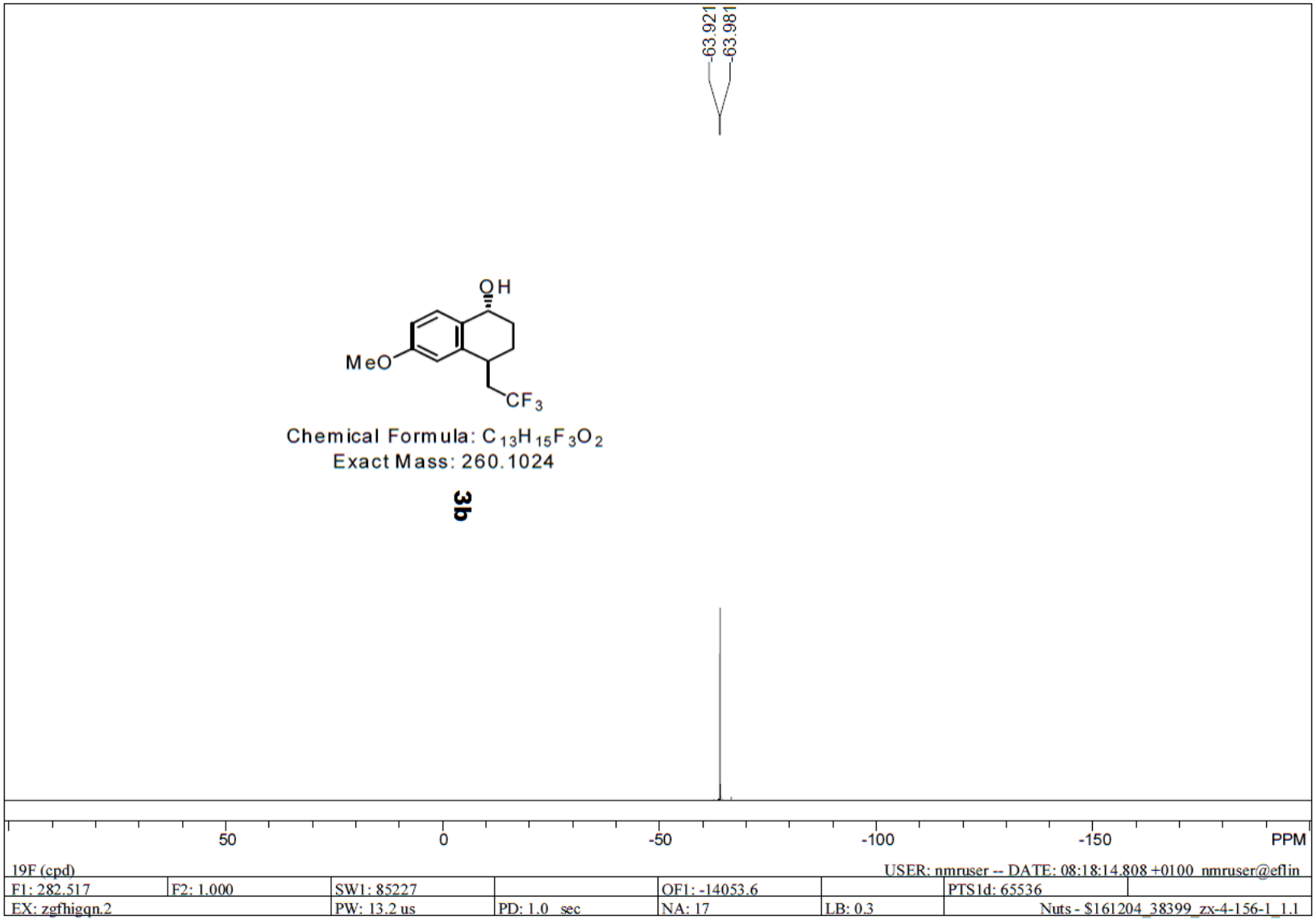
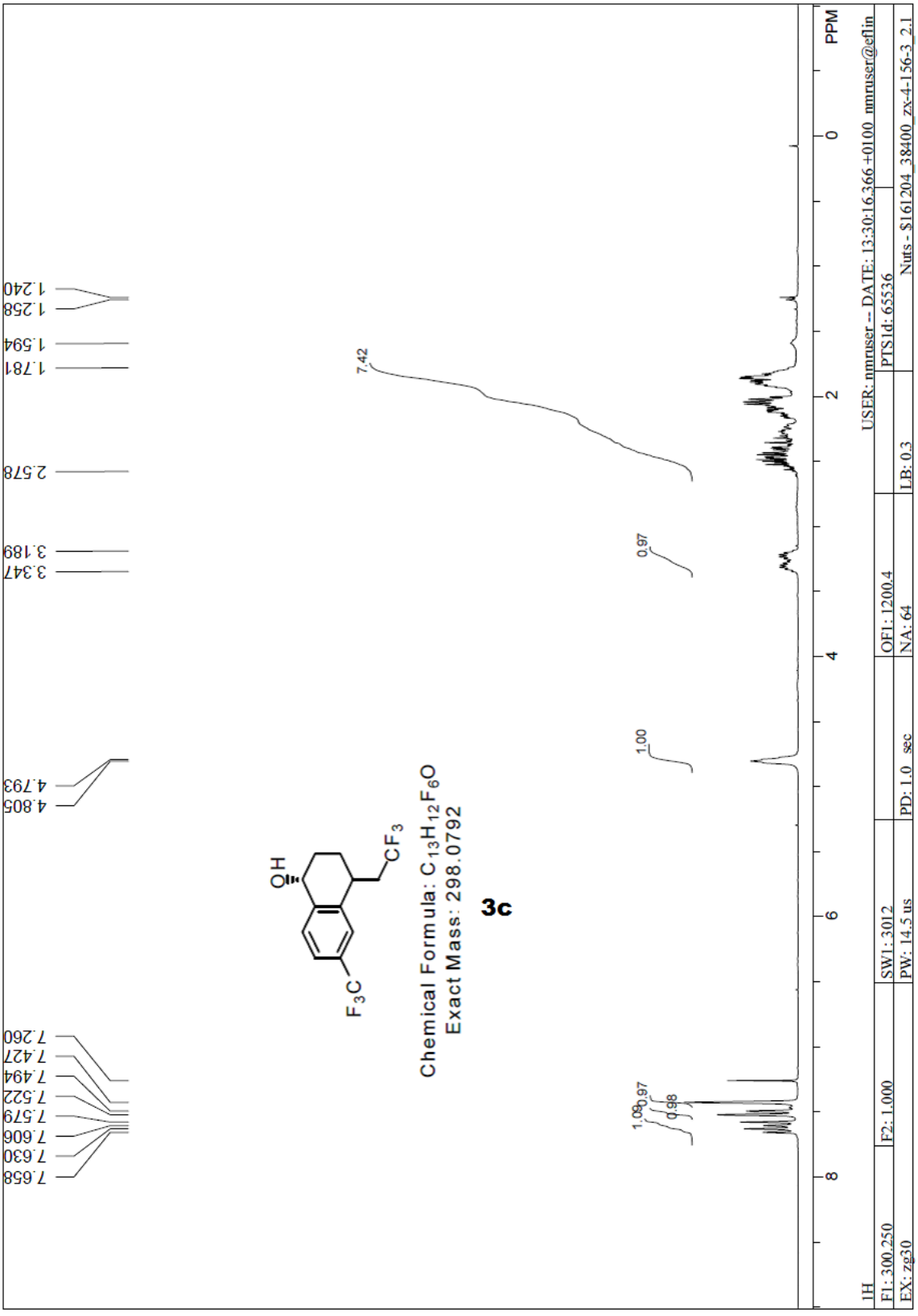
24.332
27.783
29.326
32.200
32.238
32.268
32.298
32.447
32.477
32.515
32.545
39.380
39.739
40.061
40.099
40.421
40.458
55.274
40.773
41.132
66.721
67.866
76.573
77.000
77.419
112.861
112.935
113.302
121.223
121.418
124.907
125.041
128.582
128.717
129.878
130.619
130.843
131.480
132.266
132.401
139.947
140.029
159.277
159.397
OH
CF3
MeO
Chemical Formula: C13H15F3O2
Exact Mass: 260.1024
3b
PPM
150
100
50
0
13C
F1: 75.498
F2: 1.000
SW1: 18519
OF1: 8301.9
PTS1d: 32768
EX: zgpg30
PW: 10.0 us
PD: 2.0 sec
NA: 2276
LB: 1.0
USER: nmruser -- DATE: 13:20:09.106 +0100 nmruser@efiin
Nuts - $161204_38399_zx-4-156-1_4.1


-63.921
-63.981
OH
MeO
CF3
Chemical Formula: C13H15F3O2
Exact Mass: 260.1024
3b
50
0
-50
-100
-150
PPM
19F (cpd)
USER: nmruser -- DATE: 08:18:14.808 +0100 nmruser@eflin
F1: 282.517
F2: 1.000
SW1: 85227
OF1: -14053.6
PTS1d: 65536
EX: zgfhigqn.2
PW: 13.2 us
PD: 1.0 sec
NA: 17
LB: 0.3
Nuts - $161204_38399_zx-4-156-1_1.1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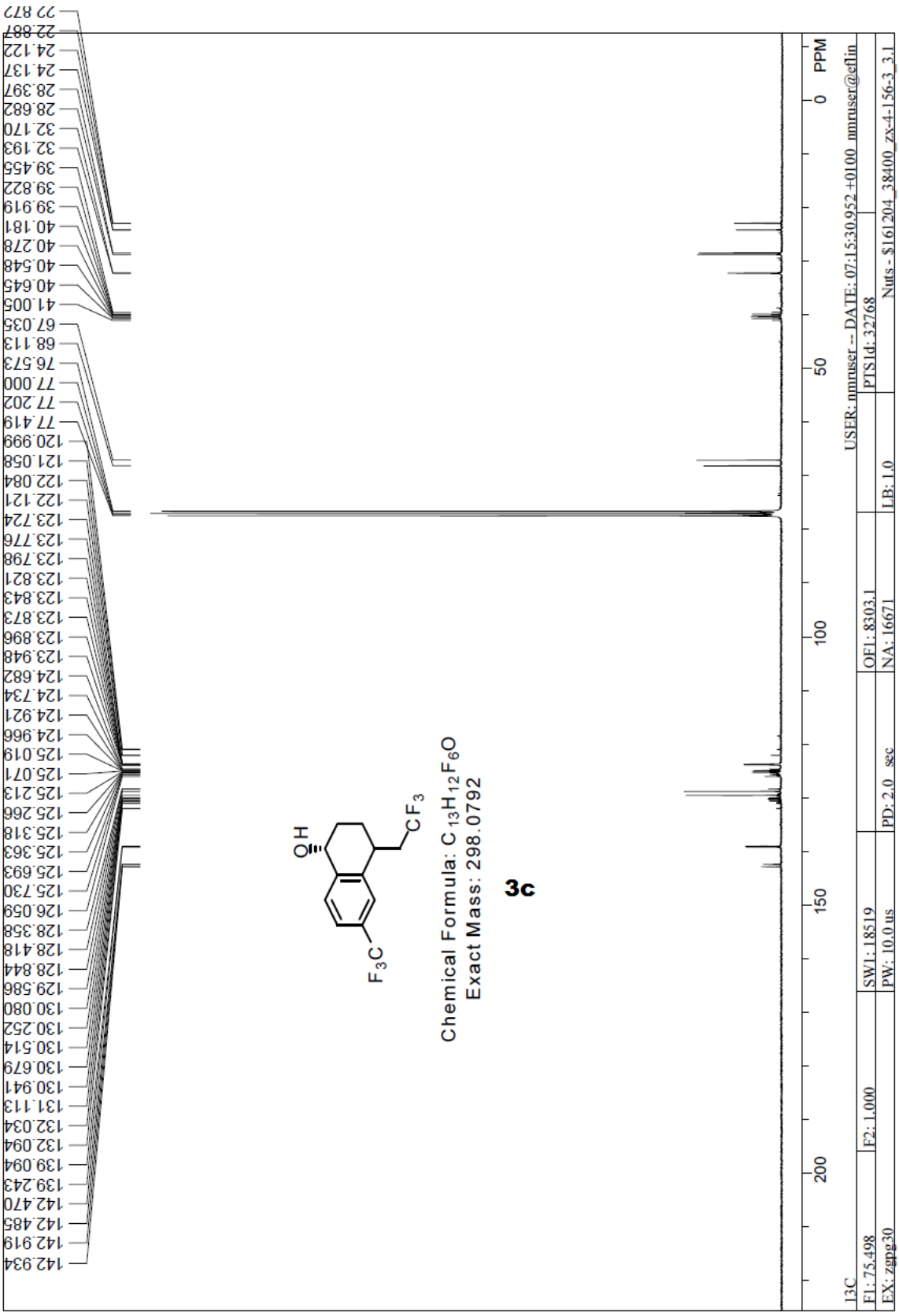
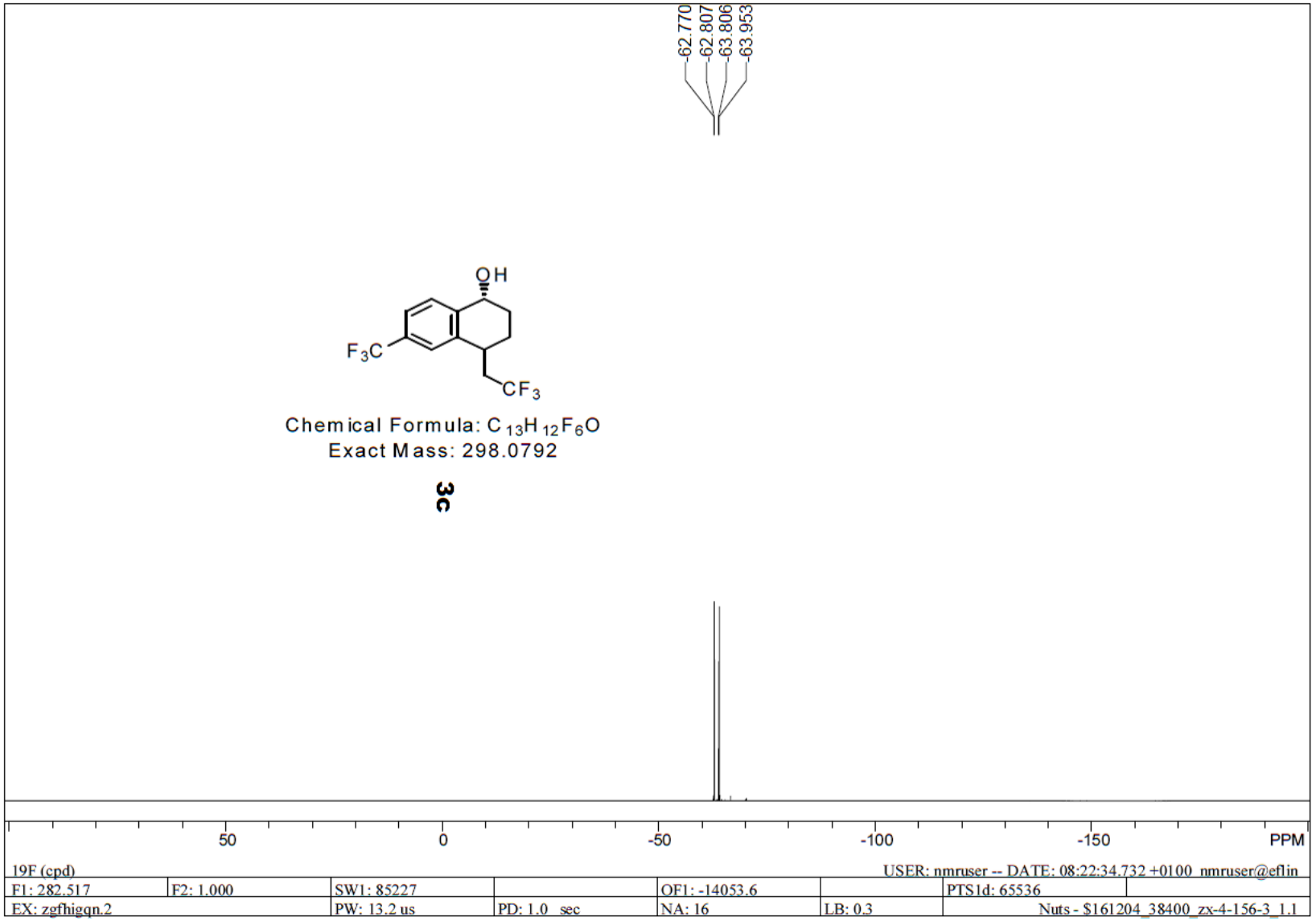
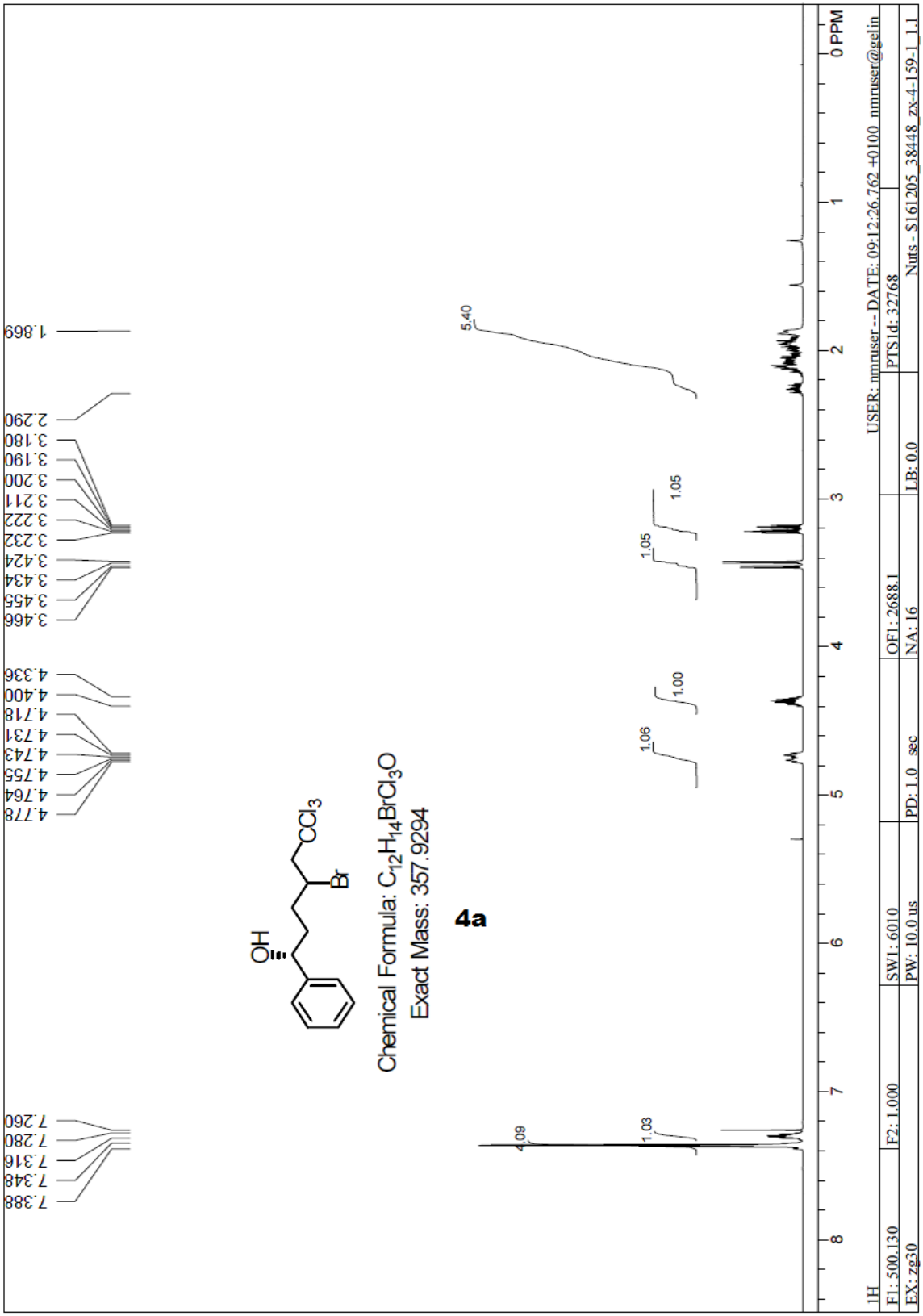
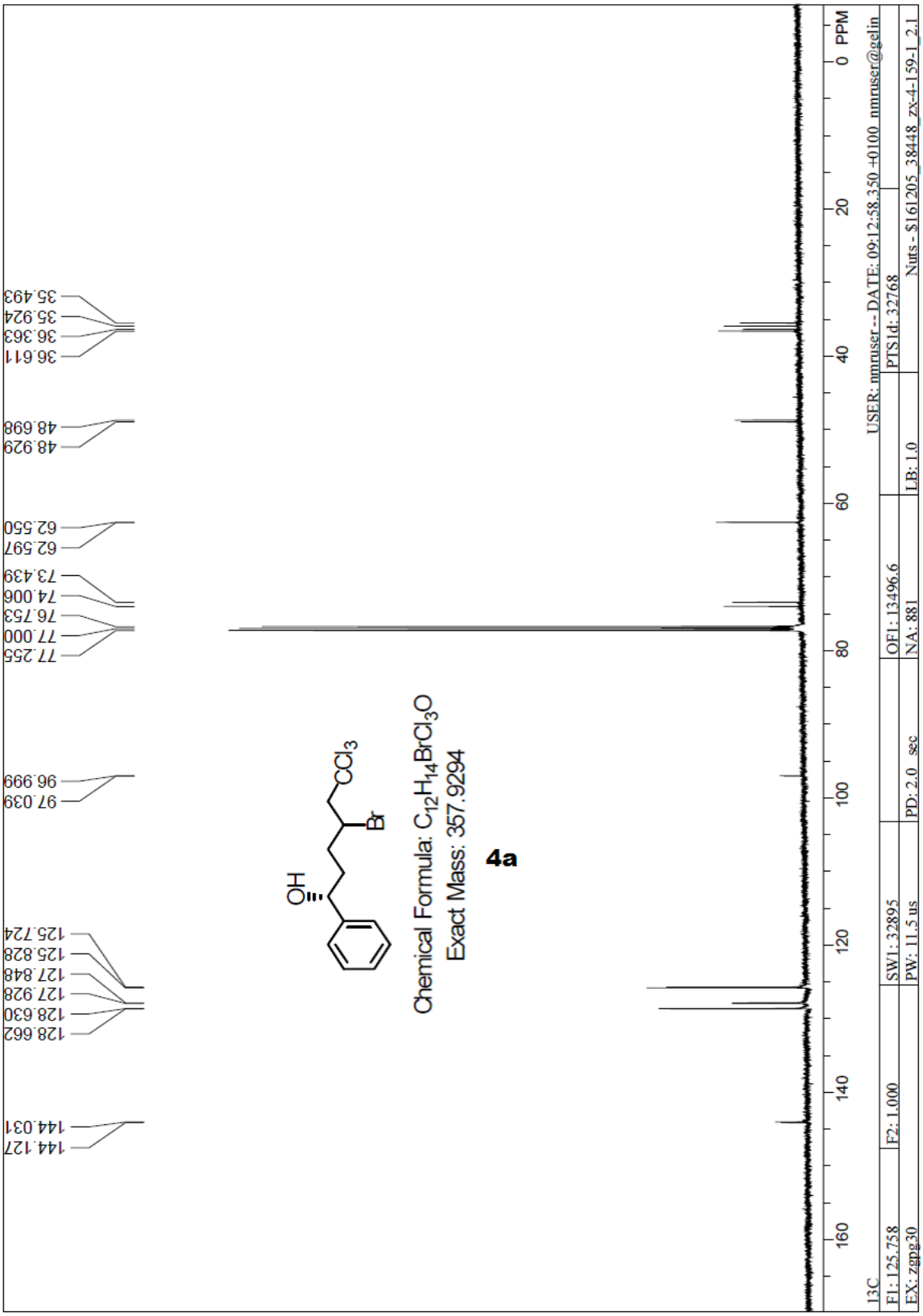
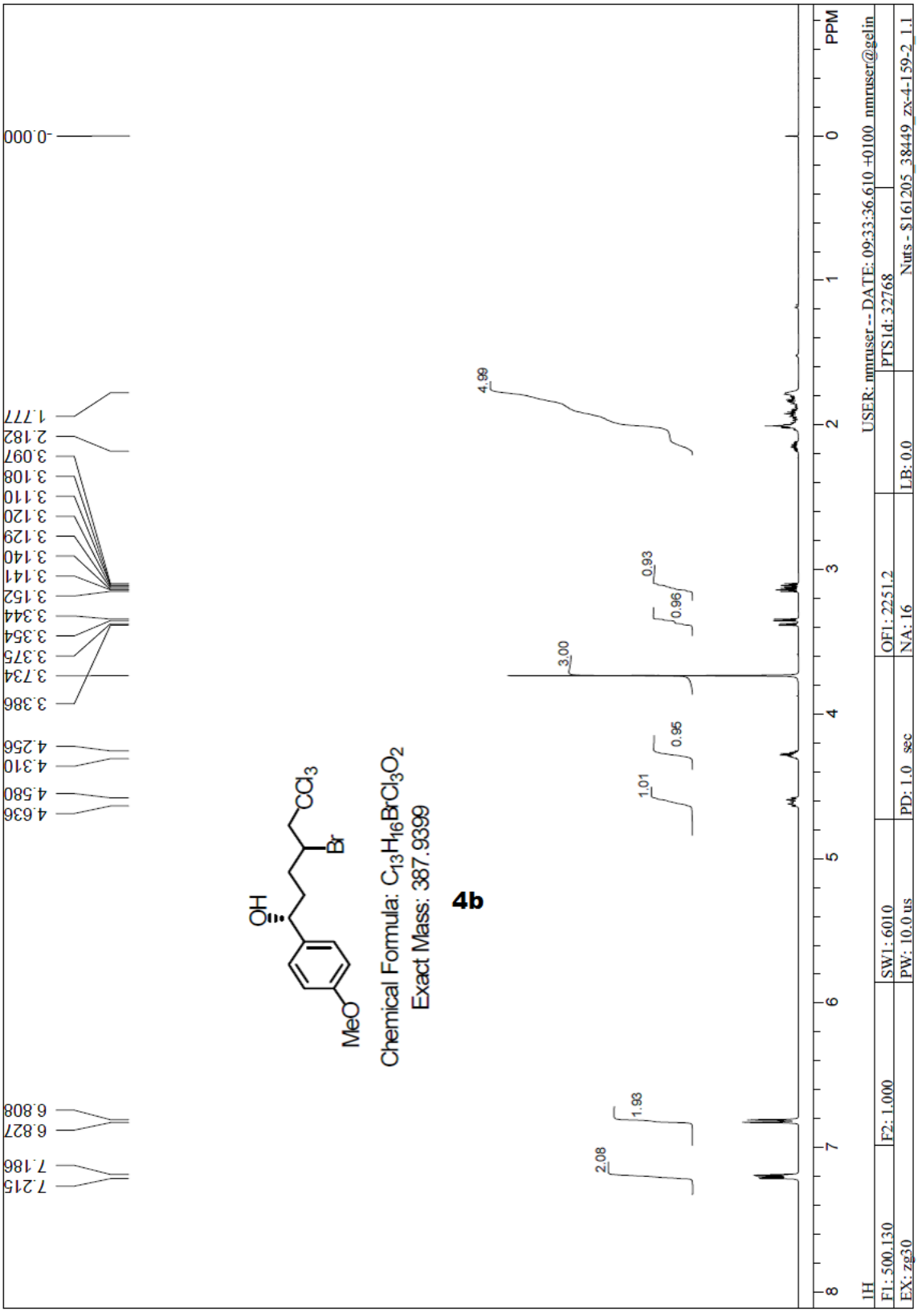
7.630
7.606
7.579
7.522
7.494
7.427
7.260
4.805
4.793
3.347
3.189
2.578
1.781
1.594
1.258
1.240
7.42
0.97
1.00
1.09
0.97
0.98
OH
CF3
F3C
Chemical Formula: C13H12F6O
Exact Mass: 298.0792
3c
PPM
0
2
4
6
8
1H
F1: 300.250
F2: 1.000
SW1: 3012
PW: 14.5 us
PD: 1.0 sec
OF1: 1200.4
NA: 64
LB: 0.3
PTS1d: 65536
Nuts - $161204_38400_zx-4-156-3_2.1
EX: zg30
USER: nmruser -- DATE: 13:30:16.366 +0100 nmruser@efiin

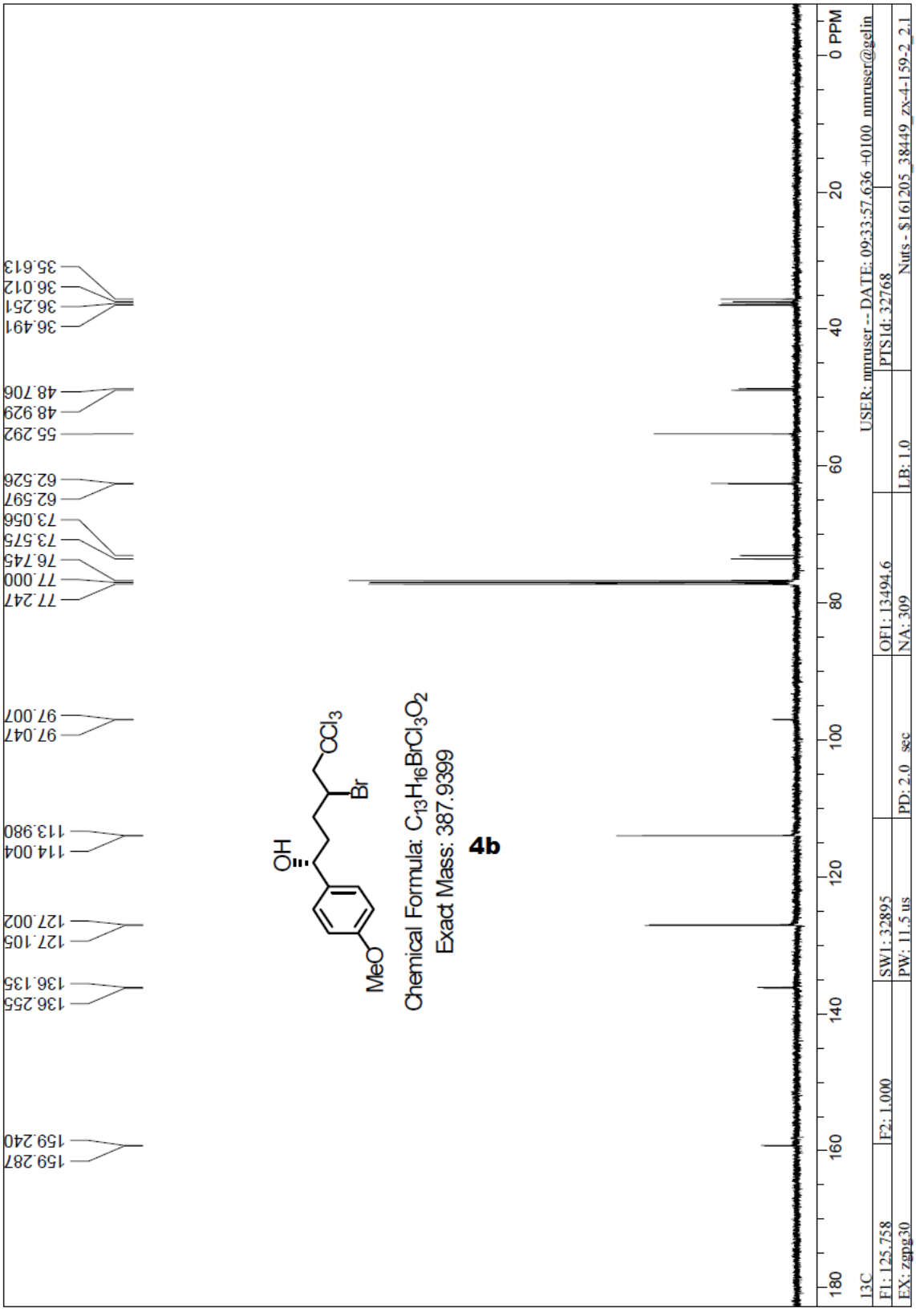

Chemical Formula: C13H12F6O
Exact Mass: 298.0792
3c
13C
F1: 75.498
F2: 1.000
SW1: 18519
PW: 10.0 us
PD: 2.0 sec
OF1: 8303.1
NA: 16671
LB: 1.0
PTS1d: 32768
Nuts - $161204_38400_zx-4-156-3_3.1
EX: zgpg30
USER: nmruser -- DATE: 07:15:30.952 +0100 nmruser@efiin
PPM

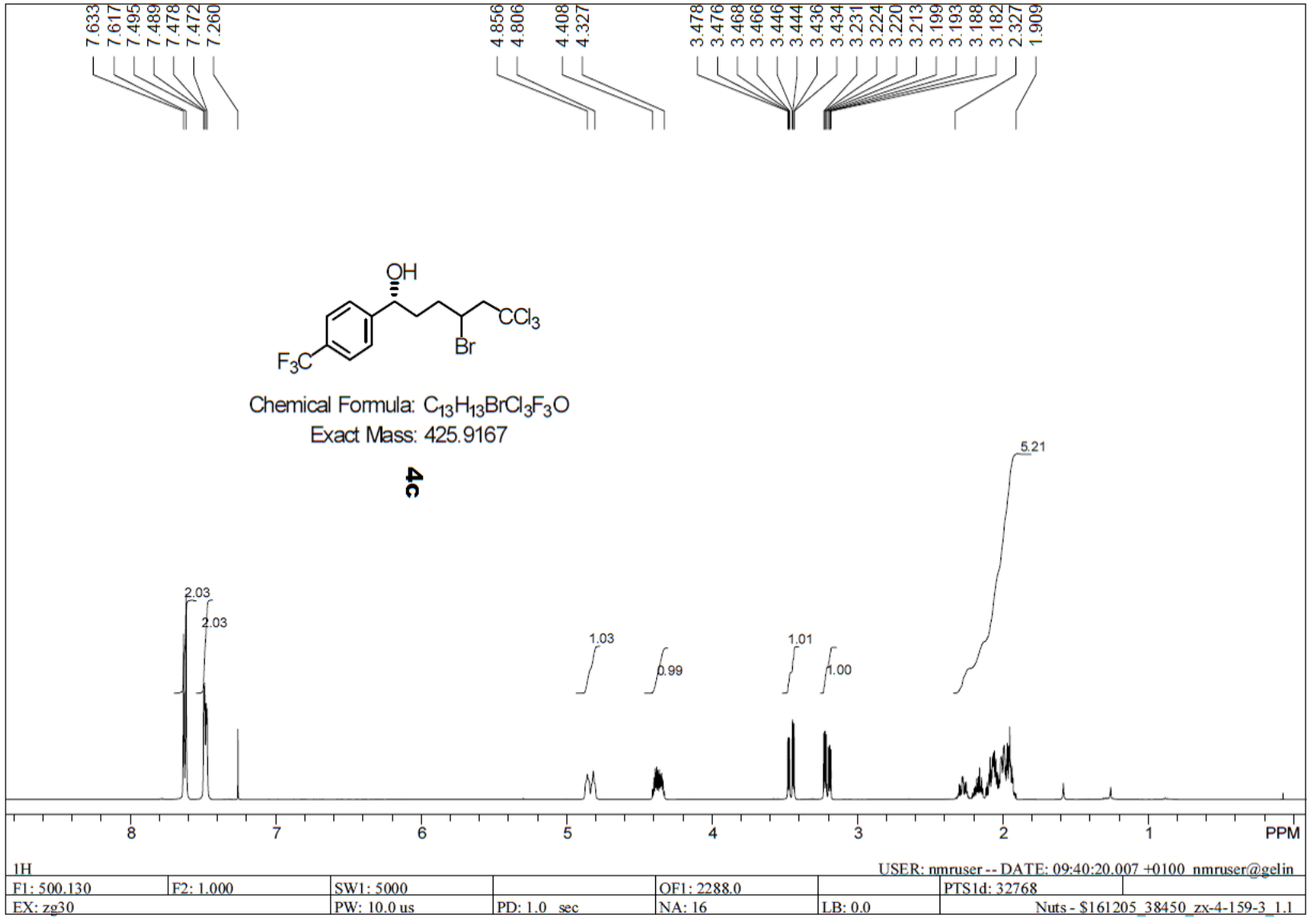

-62.770
-62.807
-63.806
-63.953
OH
F3C
CF3
Chemical Formula: C13H12F6O
Exact Mass: 298.0792
3c
50
0
-50
-100
-150
PPM
19F (cpd)
USER: nmruser -- DATE: 08:22:34.732 +0100 nmruser@eflin
F1: 282.517
F2: 1.000
SW1: 85227
OF1: -14053.6
PTS1d: 65536
EX: zgfhigqn.2
PW: 13.2 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $161204_38400_zx-4-156-3_1.1

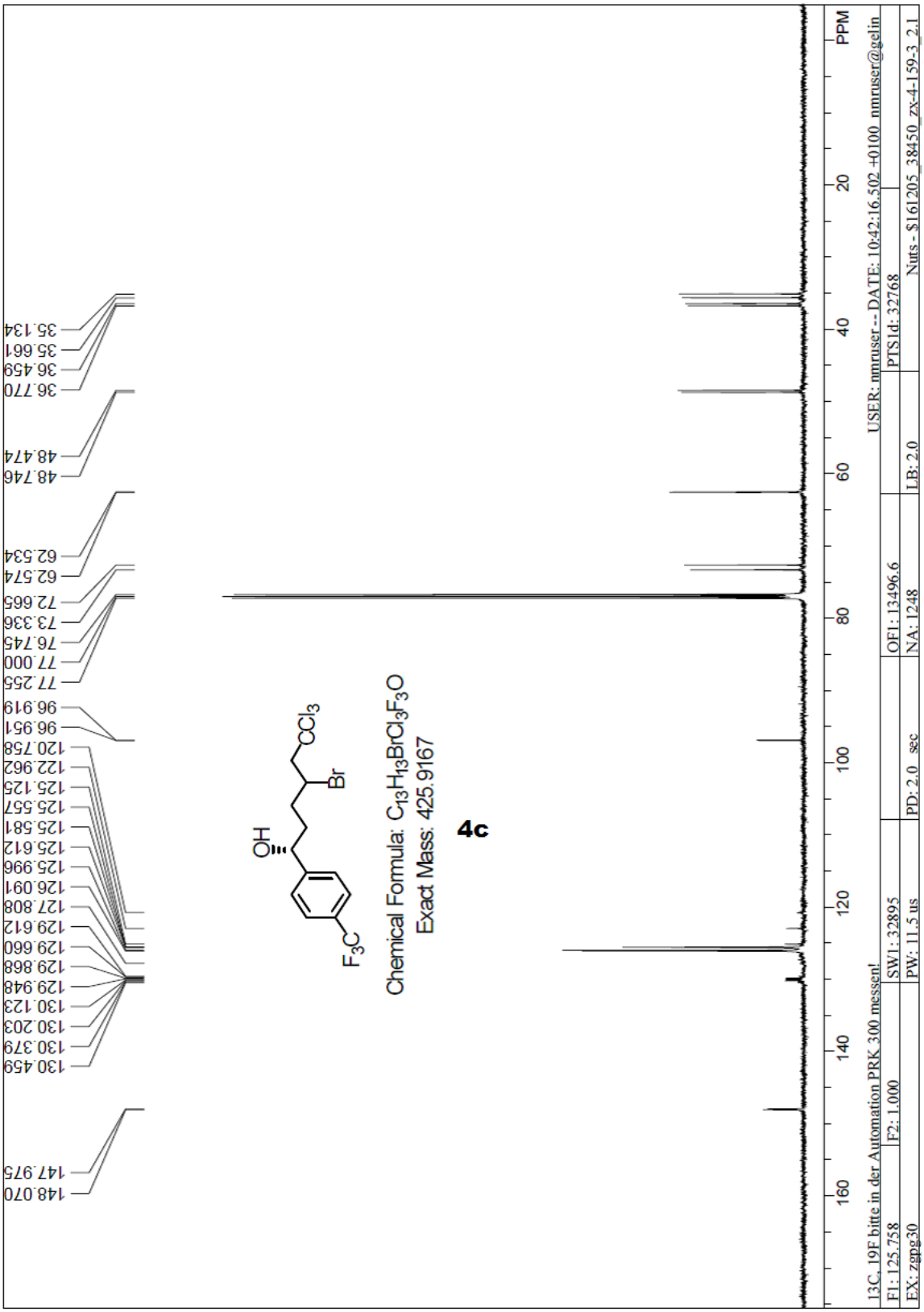

1.869
2.290
3.180
3.190
3.200
3.211
3.222
3.232
3.424
3.434
3.455
3.466
4.336
4.400
4.718
4.731
4.743
4.755
4.764
4.778
7.260
7.280
7.316
7.348
7.388
OH
CCl3
Br
Chemical Formula: C12H14BrCl3O
Exact Mass: 357.9294
4a
5.40
4.09
1.03
1.06
1.00
1.05
1.05
1.05
0 PPM
1H
F1: 500.130
F2: 1.000
SW1: 6010
OF1: 2688.1
PTS1d: 32768
EX: zg30
PW: 10.0 us
PD: 1.0 sec
NA: 16
LB: 0.0
USER: nmruser -- DATE: 09:12:26.762 +0100 nmruser@gelin
Nuts - $161205_38448_zx-4-159-1_1.1

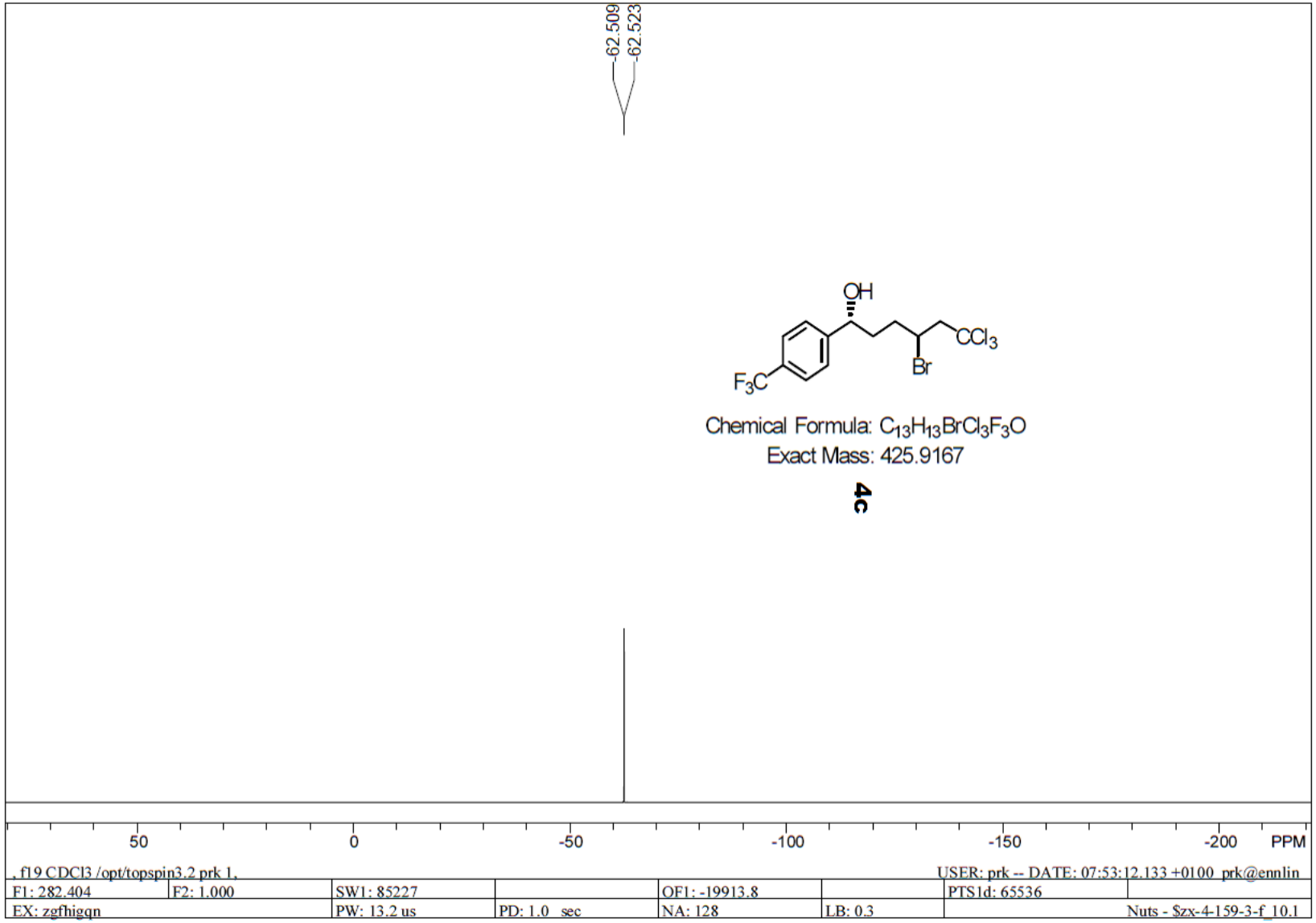

35.493
35.924
36.363
36.611
48.698
48.929
62.550
62.597
73.439
74.006
76.753
77.000
77.255
96.999
97.039
125.724
125.828
127.848
127.928
128.630
128.662
144.127
144.031
OH
CCl3
Br
Chemical Formula: C12H14BrCl3O
Exact Mass: 357.9294
4a
160
140
120
100
80
60
40
20
0 PPM
13C
F1: 125.758
F2: 1.000
SW1: 32895
PW: 11.5 us
PD: 2.0 sec
OF1: 13496.6
NA: 881
LB: 1.0
PTS1d: 32768
EX: zgpg30
USER: nmruser -- DATE: 09:12:58.350 +0100 nmruser@gelin
Nuts - $161205_38448_zx-4-159-1_2.1

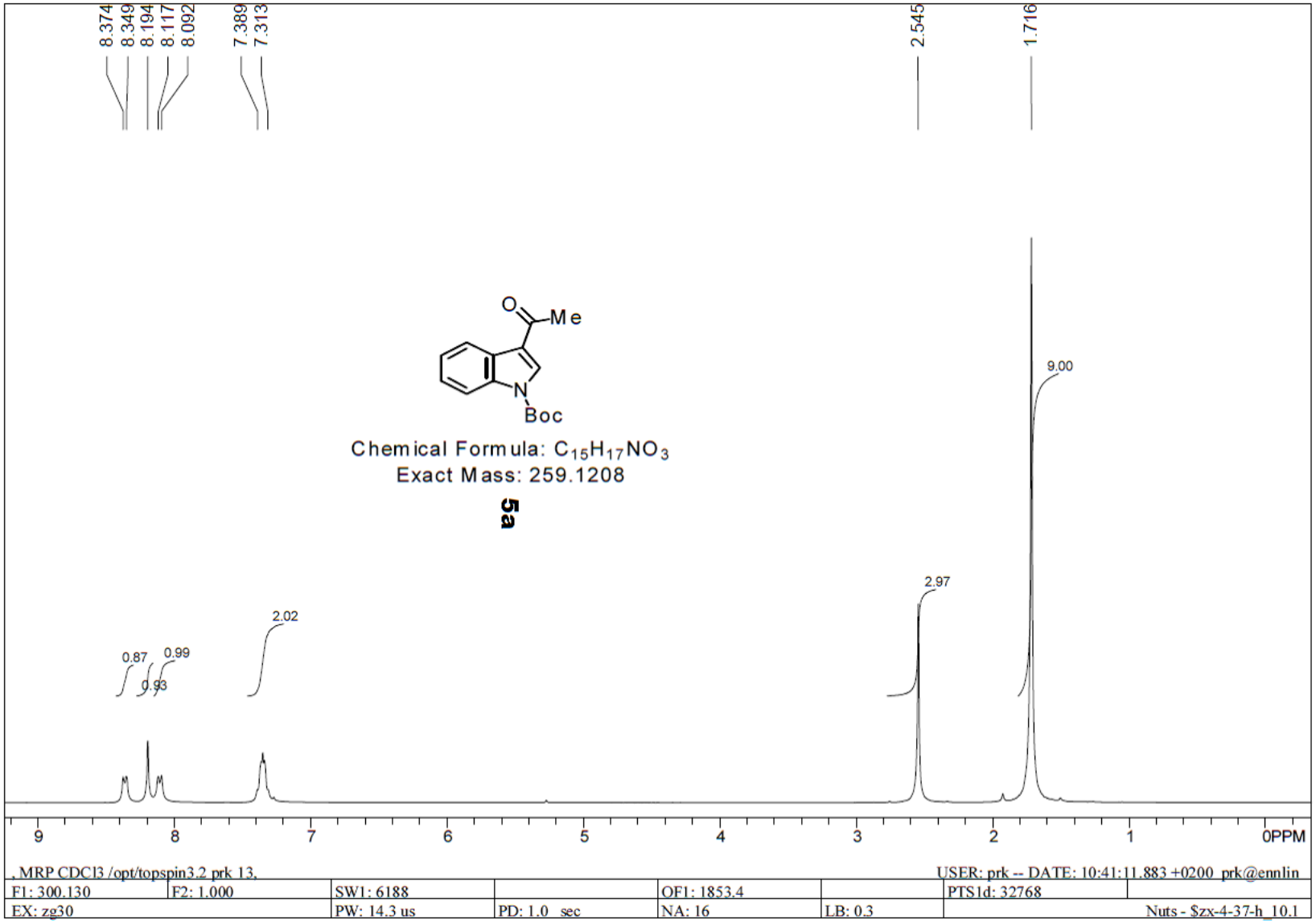

4b
Chemical Formula: C13H16BrCl3O2
Exact Mass: 387.9399
OH
CCl3
Br
MeO
7.215
7.186
6.827
6.808
4.636
4.580
4.310
4.256
3.734
3.386
3.375
3.354
3.344
3.152
3.141
3.140
3.129
3.120
3.110
3.108
3.097
2.182
1.777
0.000
2.08
1.93
1.01
0.95
3.00
0.96
0.93
4.99
PPM
1H
F1: 500.130
F2: 1.000
SW1: 6010
PW: 10.0 us
PD: 1.0 sec
OF1: 2251.2
NA: 16
LB: 0.0
PTS1d: 32768
USER: nmruser -- DATE: 09:33:36.610 +0100 nmruser@gelin
EX: zg30
Nuts - $161205_38449_zx-4-159-2_1.1

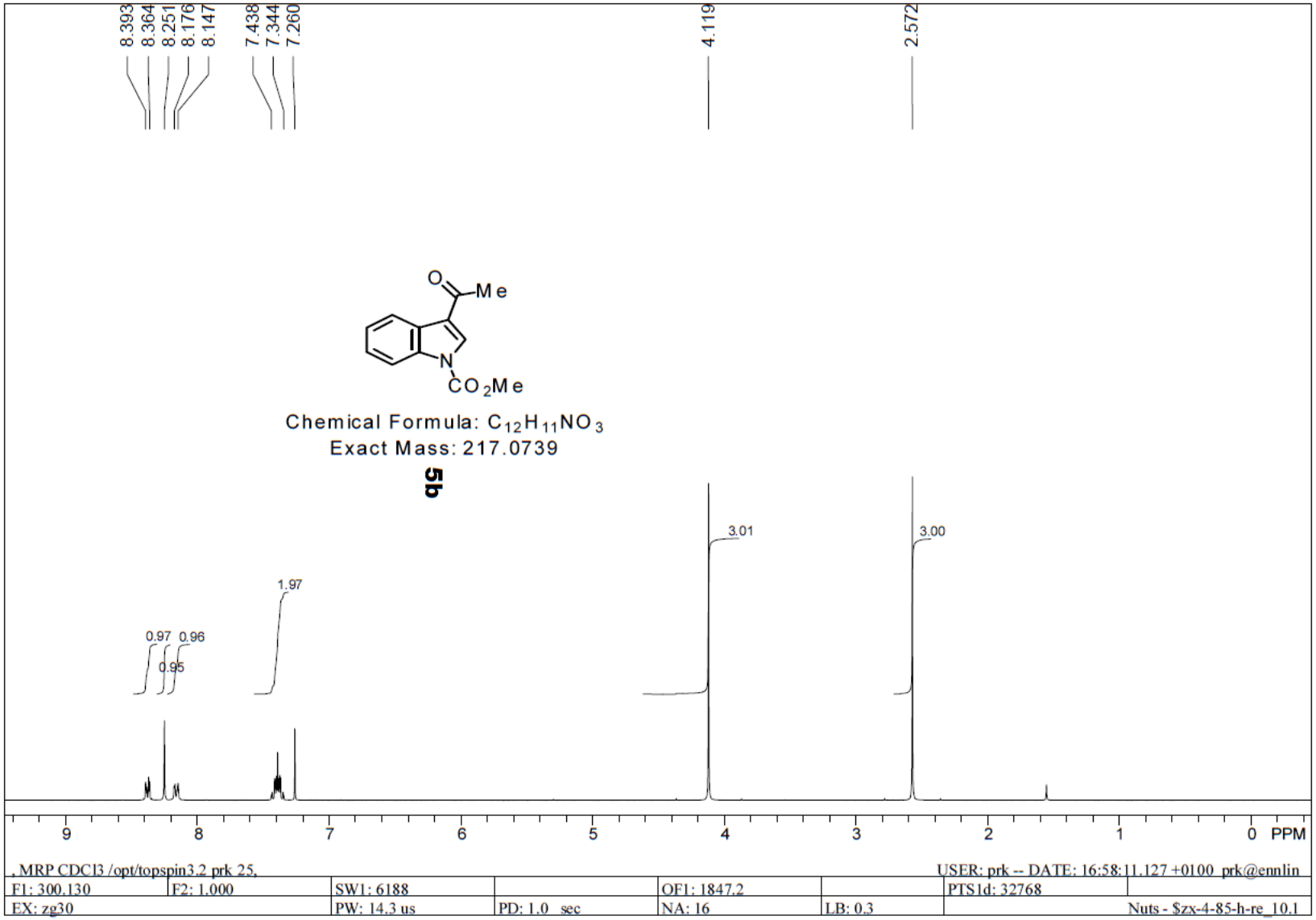

35.613
36.012
36.251
36.491
48.706
48.929
55.292
62.526
62.597
73.056
73.575
76.745
77.000
77.247
97.007
97.047
113.980
114.004
127.002
127.105
136.135
136.255
159.240
159.287
OH
Br
CCl3
MeO
Chemical Formula: C13H16BrCl3O2
Exact Mass: 387.9399
4b
0 PPM
13C
USER: nmruser -- DATE: 09:33:57.636 +0100 nmruser@gelin
F1: 125.758
F2: 1.000
SW1: 32895
OF1: 13494.6
PTS1d: 32768
EX: zgpg30
PW: 11.5 us
PD: 2.0 sec
NA: 309
LB: 1.0
Nuts - $161205_38449_zx-4-159-2_2.1

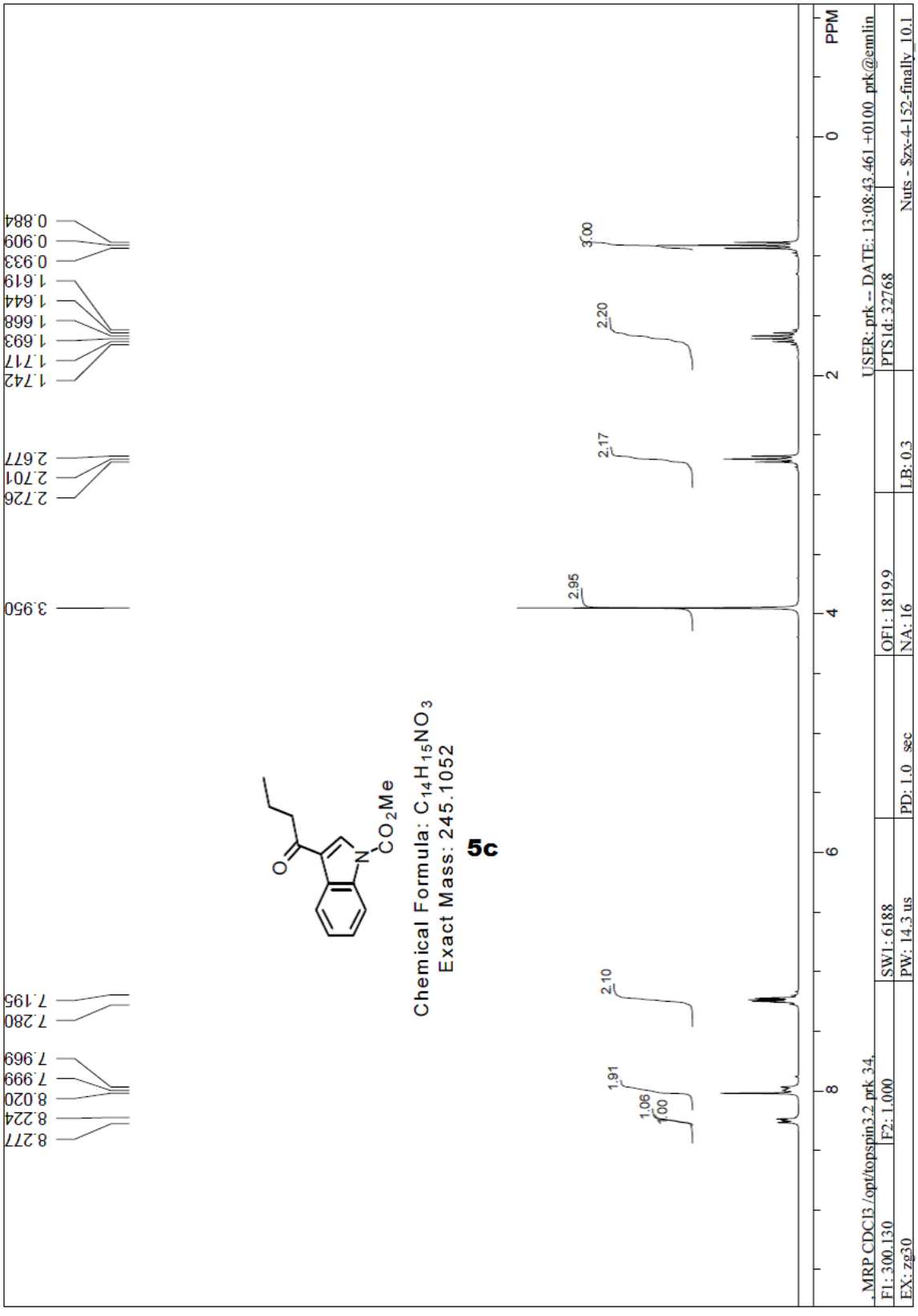

7.633
7.617
7.495
7.489
7.478
7.472
7.260
4.856
4.806
4.408
4.327
3.478
3.476
3.468
3.466
3.446
3.444
3.436
3.434
3.231
3.224
3.220
3.213
3.199
3.193
3.188
3.182
2.327
1.909
OH
CCl3
Br
F3C
Chemical Formula: C13H13BrCl3F3O
Exact Mass: 425.9167
4c
5.21
2.03
2.03
1.03
0.99
1.01
1.00
8
7
6
5
4
3
2
1
PPM
1H
USER: nmruser -- DATE: 09:40:20.007 +0100 nmruser@gelin
F1: 500.130
F2: 1.000
SW1: 5000
OF1: 2288.0
PTS1d: 32768
EX: zg30
PW: 10.0 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $161205_38450_zx-4-159-3_1.1

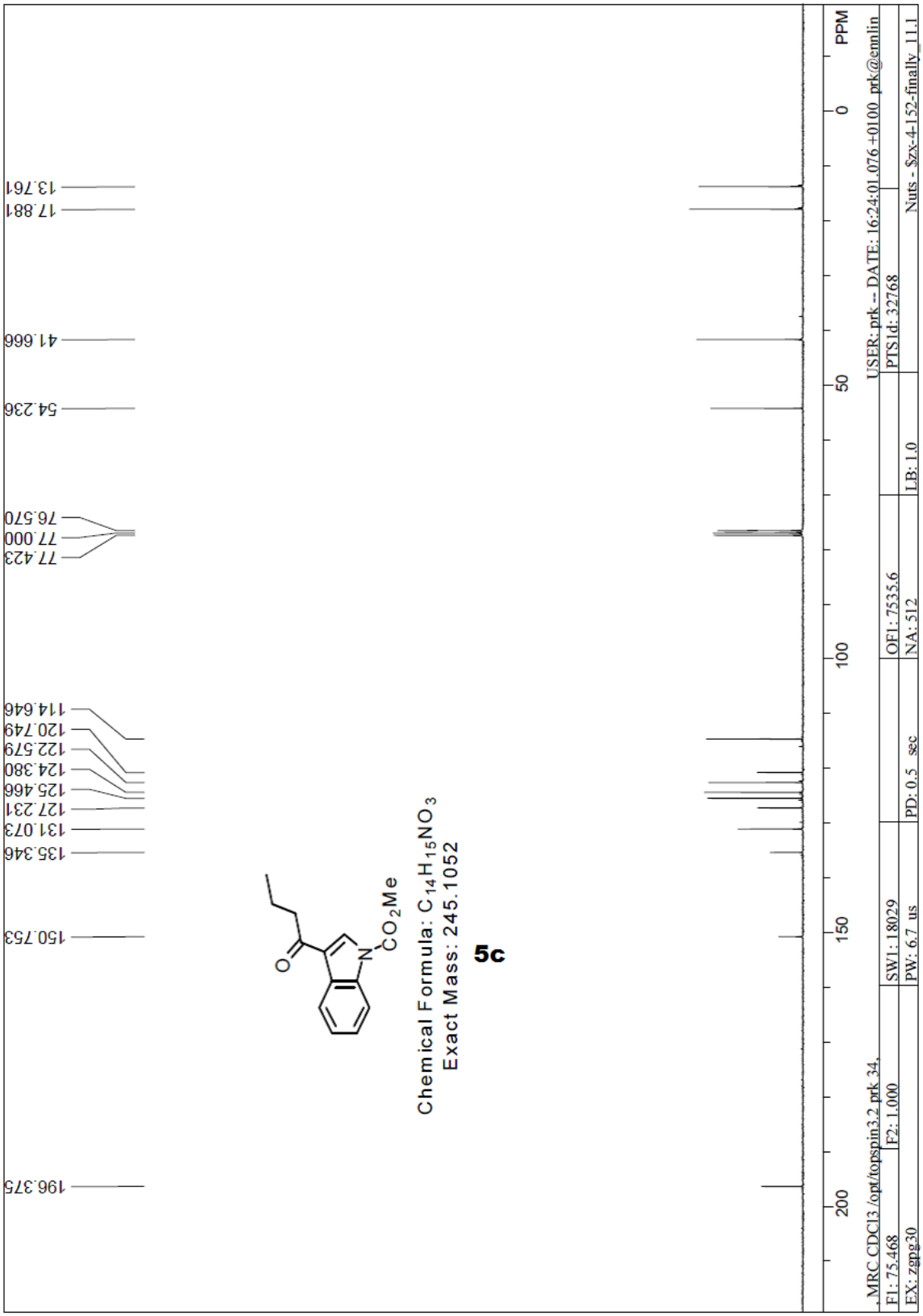

35.134
35.661
36.459
36.770
48.474
48.746
62.534
62.574
72.665
73.336
76.745
77.000
77.255
96.919
96.951
120.758
122.962
125.125
125.557
125.581
125.612
125.996
126.091
127.808
129.612
129.660
129.868
129.948
130.123
130.203
130.379
130.459
147.975
148.070
OH
Br
CCl3
F3C
Chemical Formula: C13H13BrCl3F3O
Exact Mass: 425.9167
4c
PPM
13C, 19F bitte in der Automation PRK 300 messen!
USER: nmruser -- DATE: 10:42:16.502 +0100 nmruser@gelin
F1: 125.758
F2: 1.000
SW1: 32895
OF1: 13496.6
PTS1d: 32768
EX: zgpg30
PW: 11.5 us
PD: 2.0 sec
NA: 1248
LB: 2.0
Nuts - $161205_38450_zx-4-159-3_2.1

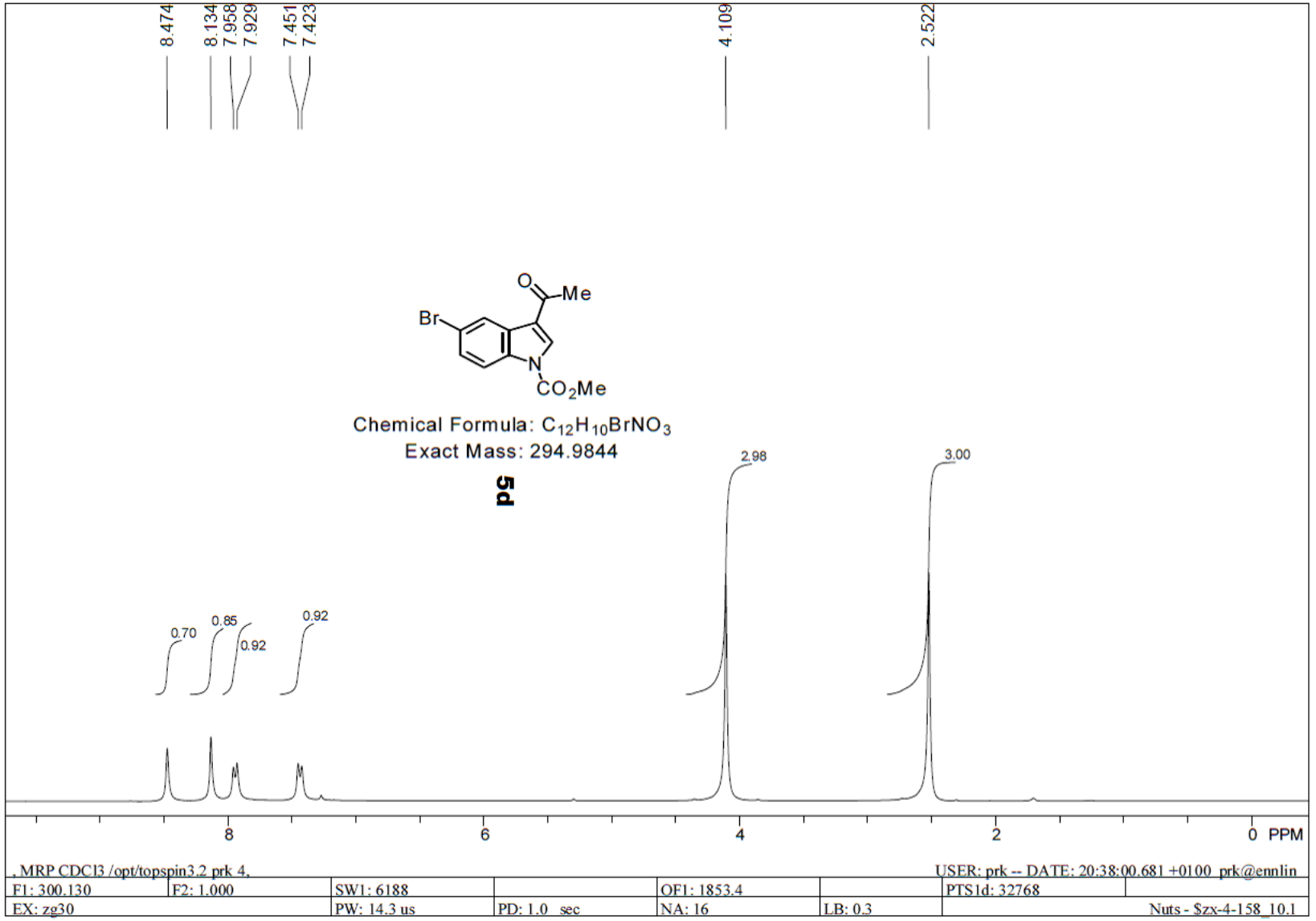

-62.509
-62.523
OH
CCl3
Br
F3C
Chemical Formula: C13H13BrCl3F3O
Exact Mass: 425.9167
4c
50
0
-50
-100
-150
-200
PPM
, f19 CDCl3 /opt/topspin3.2 prk 1,
USER: prk -- DATE: 07:53:12.133 +0100 prk@ennlin
F1: 282.404
F2: 1.000
SW1: 85227
OF1: -19913.8
PTS1d: 65536
EX: zgfhigqn
PW: 13.2 us
PD: 1.0 sec
NA: 128
LB: 0.3
Nuts - $zx-4-159-3-f_10.1

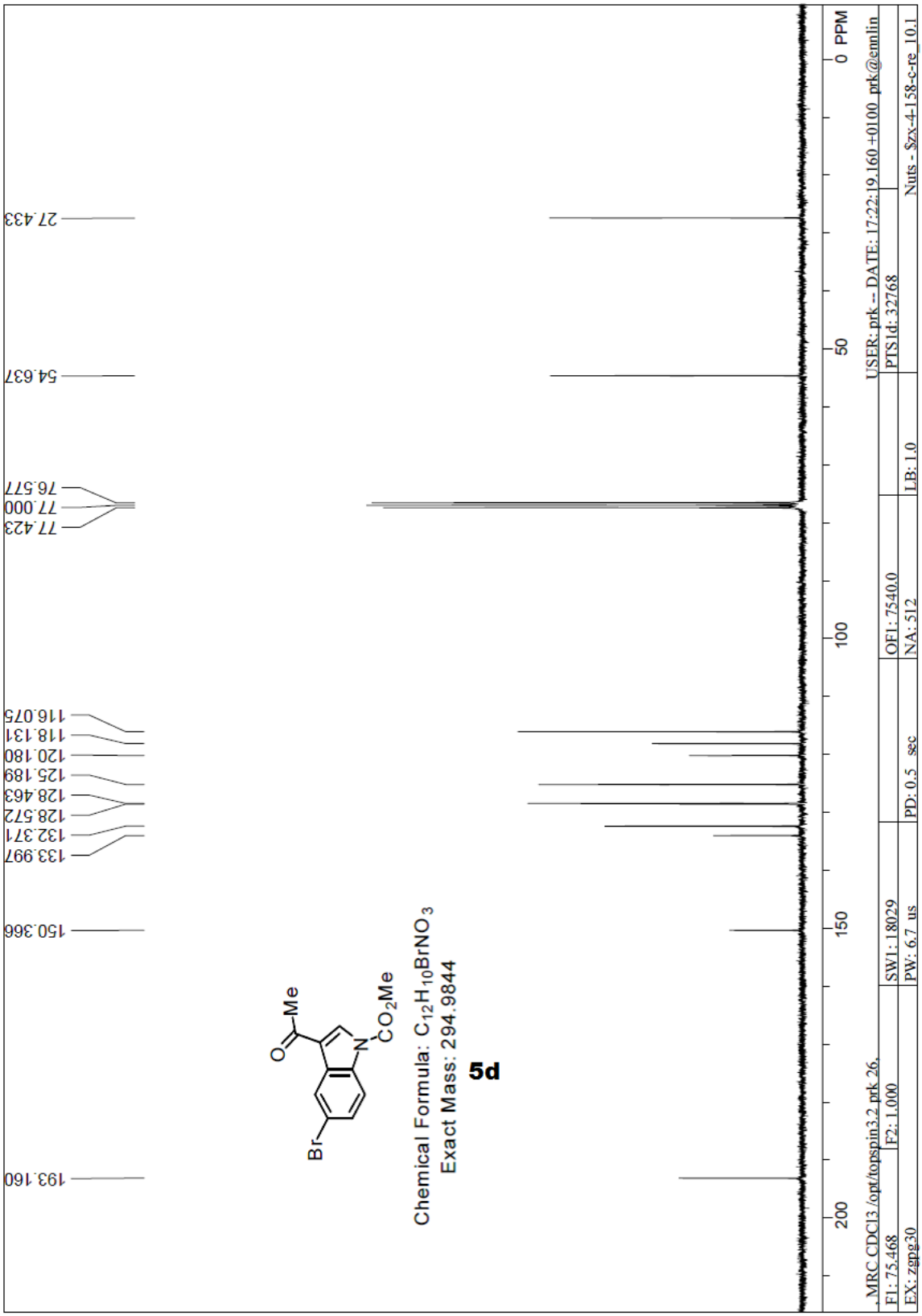

8.374
8.349
8.194
8.117
8.092
7.389
7.313
2.545
1.716
O
Me
N
Boc
Chemical Formula: C15H17NO3
Exact Mass: 259.1208
5a
9.00
2.97
2.02
0.87
0.99
0.93
9
8
7
6
5
4
3
2
1
0PPM
, MRP CDCl3 /opt/topspin3.2 prk 13,
USER: prk -- DATE: 10:41:11.883 +0200 prk@ennlin
F1: 300.130
F2: 1.000
SW1: 6188
OF1: 1853.4
PTS1d: 32768
EX: zg30
PW: 14.3 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $zx-4-37-h_10.1

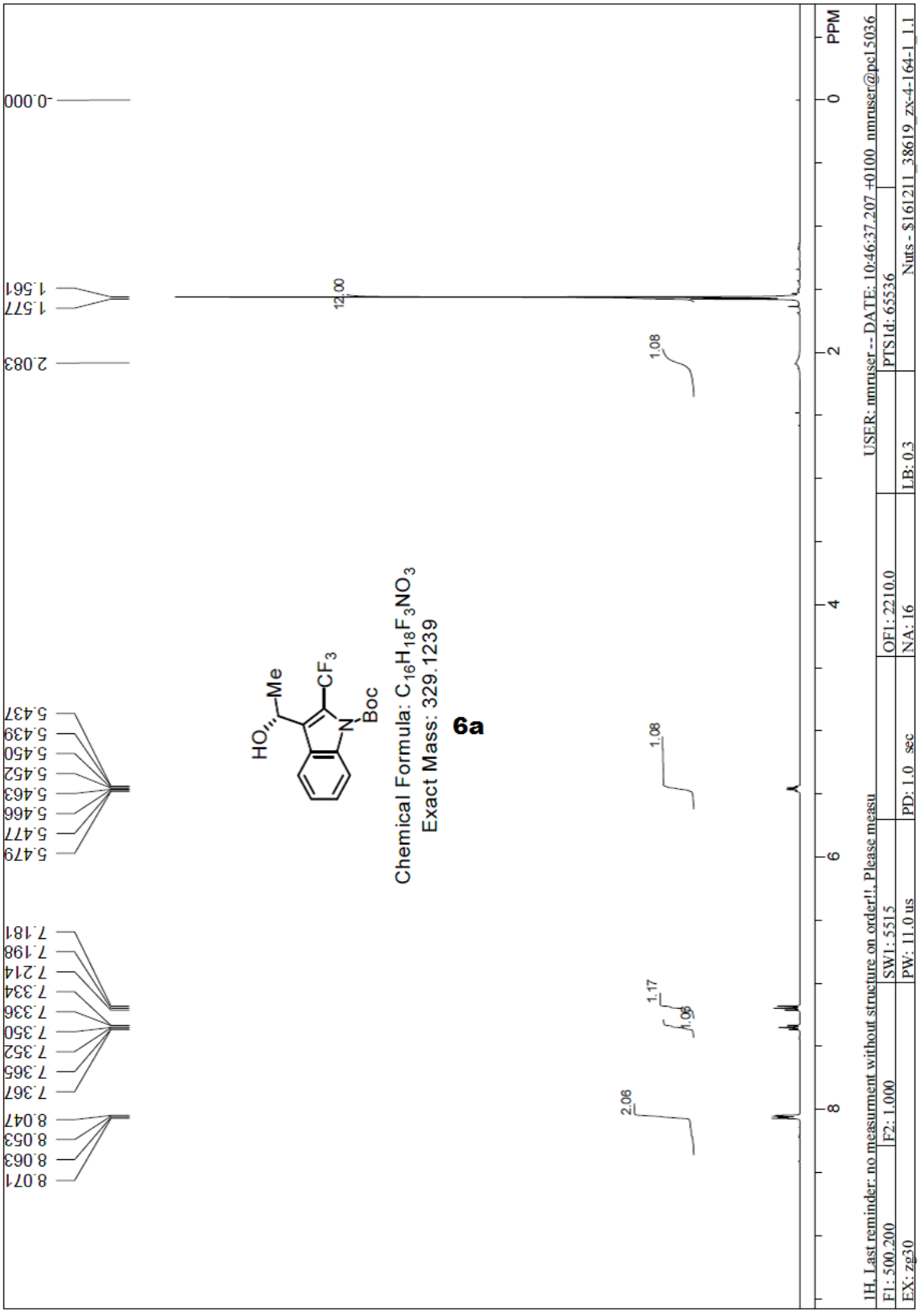

8.393
8.364
8.251
8.176
8.147
7.438
7.344
7.260
4.119
2.572
O
Me
N
CO2Me
Chemical Formula: C12H11NO3
Exact Mass: 217.0739
5b
0.97
0.96
0.95
1.97
3.01
3.00
9
8
7
6
5
4
3
2
1
0 PPM
, MRP CDCl3 /opt/topspin3.2 prk 25,
USER: prk -- DATE: 16:58:11.127 +0100 prk@ennlin
F1: 300.130
F2: 1.000
SW1: 6188
OF1: 1847.2
PTS1d: 32768
EX: zg30
PW: 14.3 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $zx-4-85-h-re_10.1

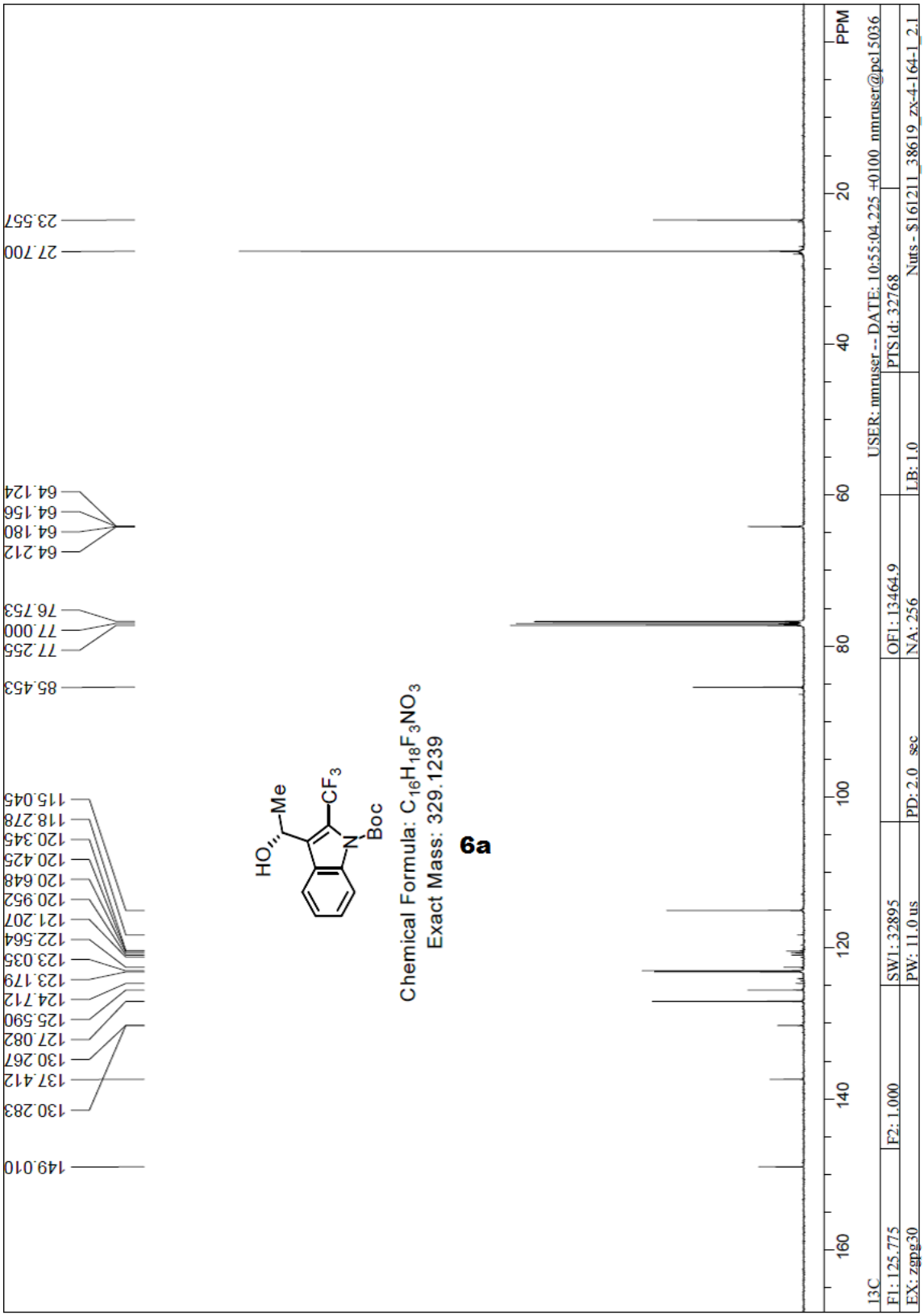

8.277
8.224
8.020
7.999
7.969
7.280
7.195
3.950
2.726
2.701
2.677
1.742
1.717
1.693
1.668
1.644
1.619
0.933
0.909
0.884
O
N
CO2Me
Chemical Formula: C14H15NO3
Exact Mass: 245.1052
5c
1.91
1.06
1.00
2.10
2.95
2.17
2.20
3.00
8
6
4
2
0
PPM
.MRP CDCl3 /opt/topspin3.2 prk 34.
USER: prk -- DATE: 13:08:43.461 +0100 prk@emnlin
F1: 300.130
F2: 1.000
SW1: 6188
OF1: 1819.9
PTS1d: 32768
EX: zg30
PW: 14.3 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $zx-4-152-finally_10.1

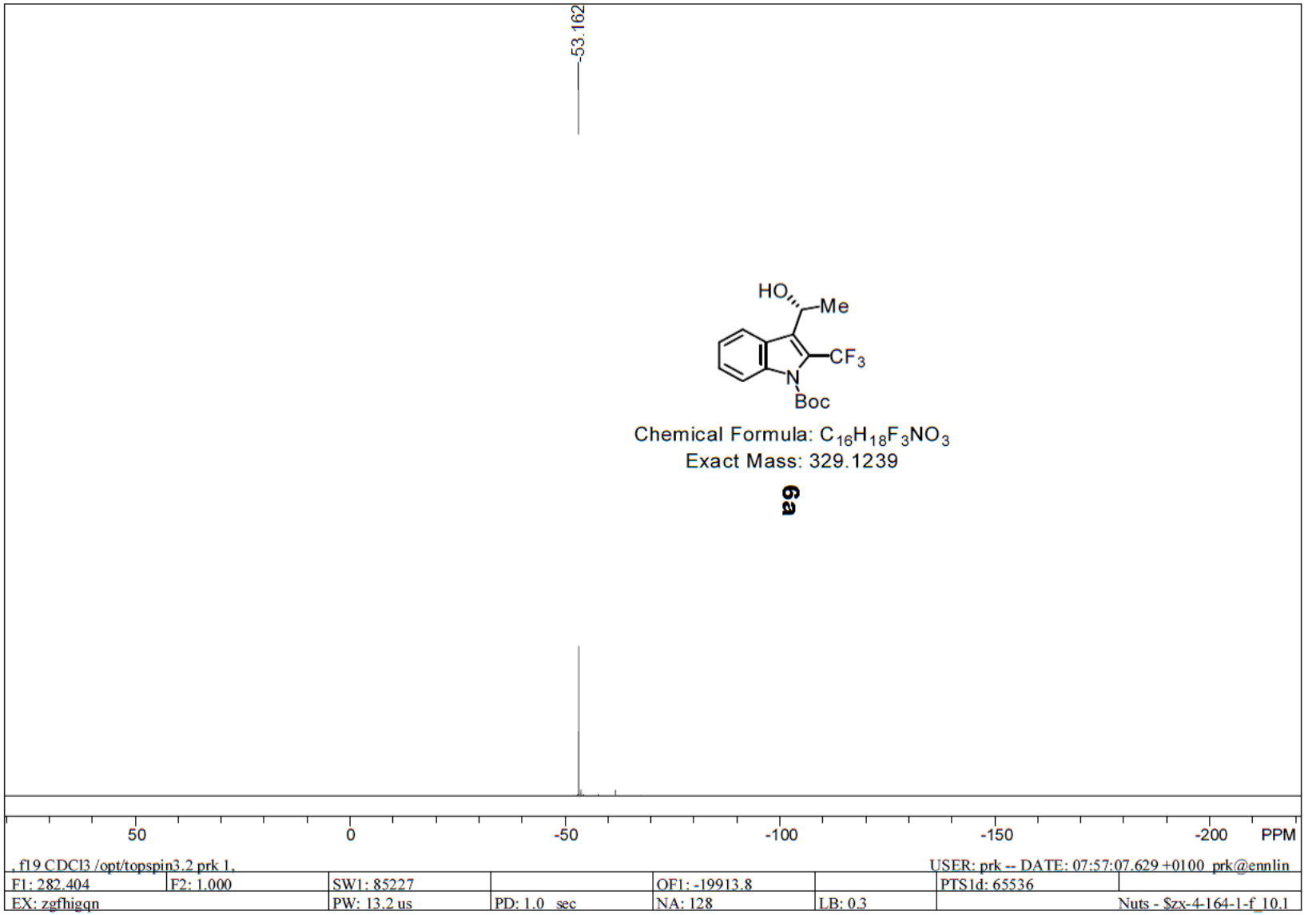

13.761
17.881
41.666
54.236
76.570
77.000
77.423
114.646
120.749
122.579
124.380
125.466
127.231
131.073
135.346
150.753
196.375
PPM
0
50
100
150
200
Chemical Formula: C14H15NO3
Exact Mass: 245.1052
5c
CO2Me
N
O
. MRC CDCl3 /opt/topspin3.2 prk 34,
USER: prk -- DATE: 16:24:01.076 +0100 prk@emnlin
F1: 75.468
F2: 1.000
SW1: 18029
OF1: 7535.6
PTS1d: 32768
EX: zgpg30
PW: 6.7 us
PD: 0.5 sec
NA: 512
LB: 1.0
Nuts - $zx-4-152-finally_11.1

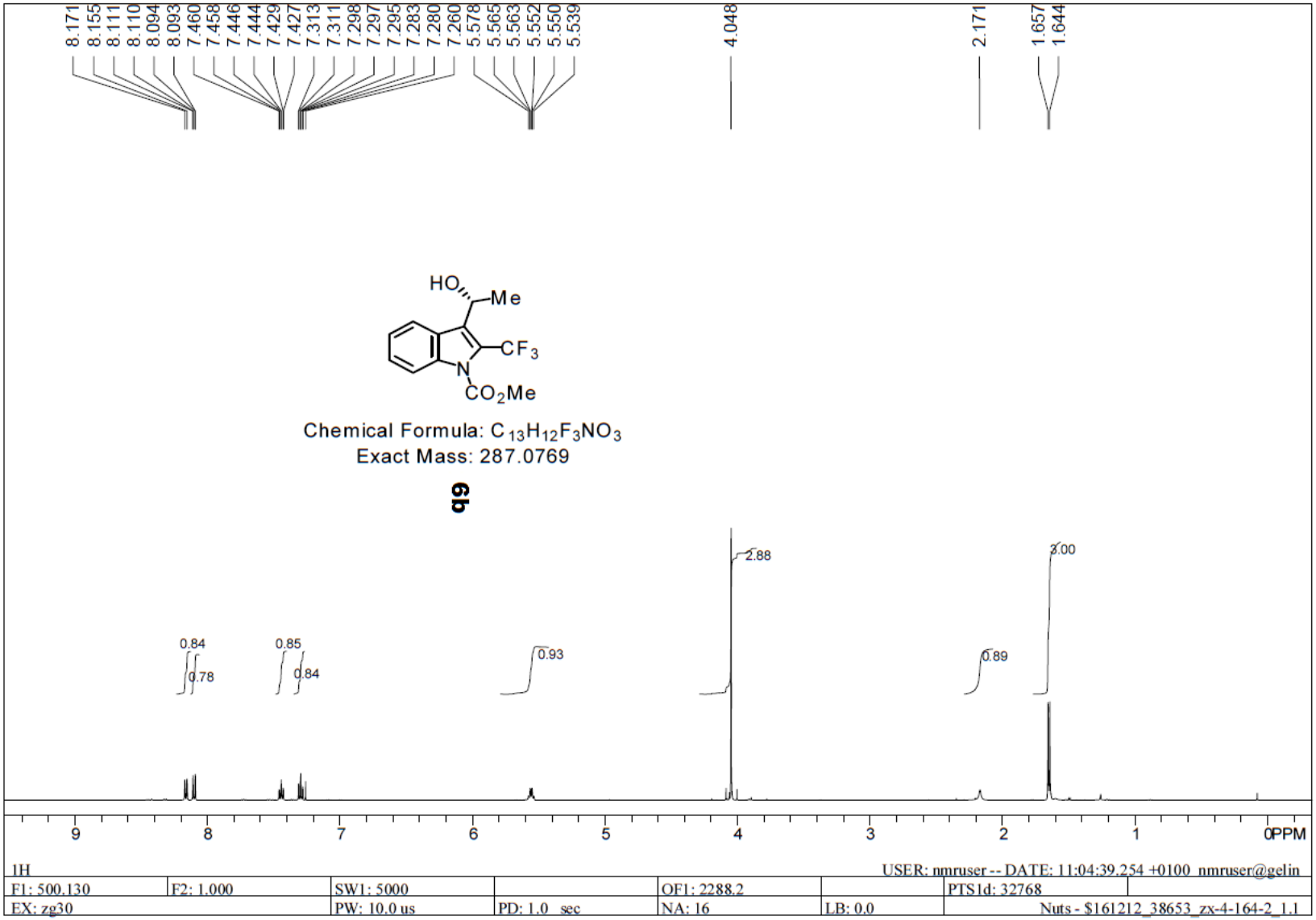

8.474
8.134
7.958
7.929
7.451
7.423
4.109
2.522
O
Me
Br
N
CO2Me
Chemical Formula: C12H10BrNO3
Exact Mass: 294.9844
5d
2.98
3.00
0.70
0.85
0.92
0.92
8
6
4
2
0 PPM
, MRP CDCl3 /opt/topspin3.2 prk 4,
USER: prk -- DATE: 20:38:00.681 +0100 prk@ennlin
F1: 300.130
F2: 1.000
SW1: 6188
OF1: 1853.4
PTS1d: 32768
EX: zg30
PW: 14.3 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $zx-4-158_10.1

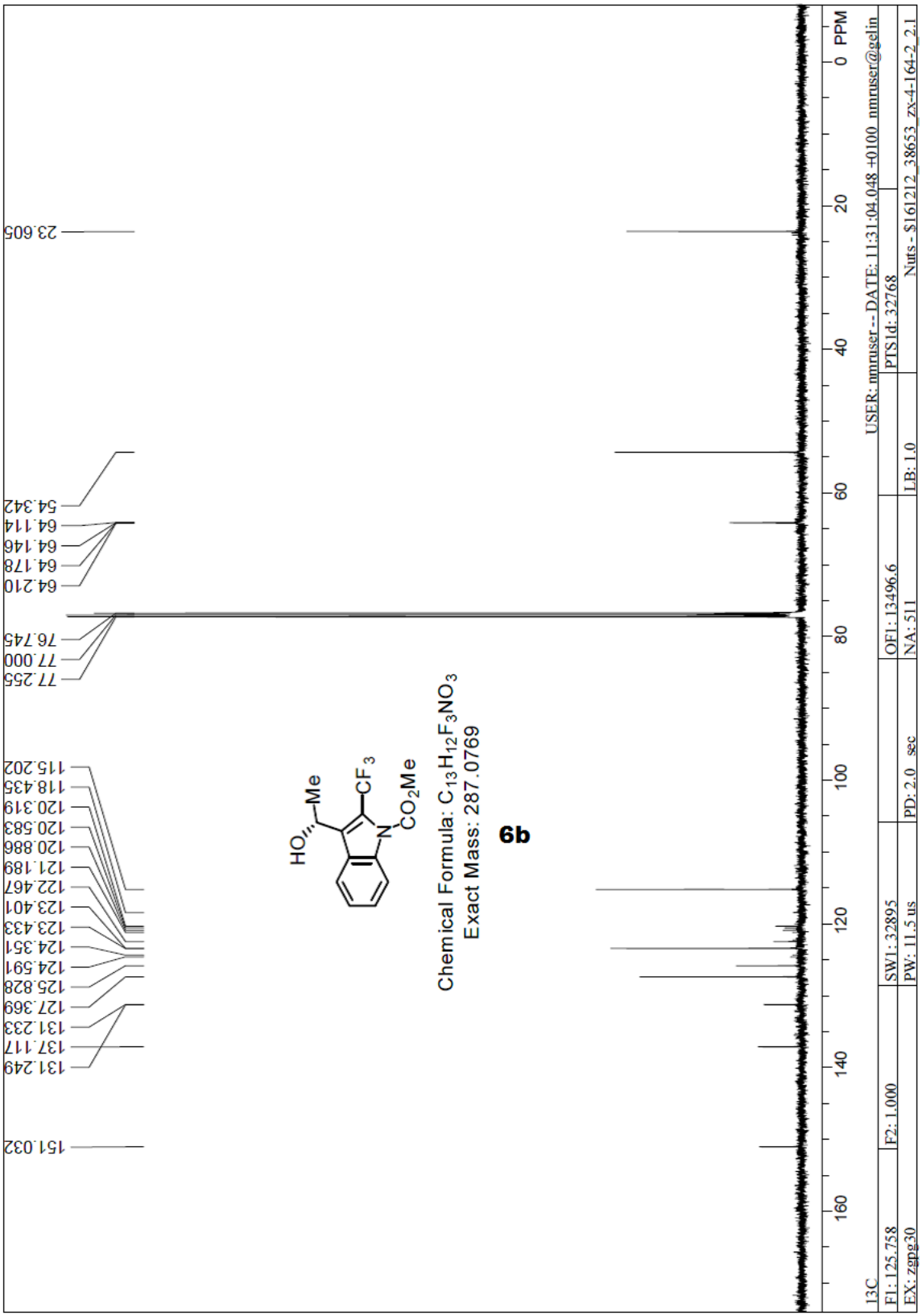

27.433
54.637
76.577
77.000
77.423
116.075
118.131
120.180
125.189
128.463
128.572
132.371
133.997
150.366
193.160
Me
O
N
CO2Me
Br
Chemical Formula: C12H10BrNO3
Exact Mass: 294.9844
5d
200
150
100
50
0 PPM
MRC CDCl3 /opt/topspin3.2 prk 26.
USER: prk -- DATE: 17:22:19 160 +0100 prk@emnlin
F1: 75.468
F2: 1.000
SW1: 18029
OF1: 7540.0
PTS1d: 32768
EX: zgpg30
PW: 6.7 us
PD: 0.5 sec
NA: 512
LB: 1.0
Nuts - $zx-4-158-c-re_10.1

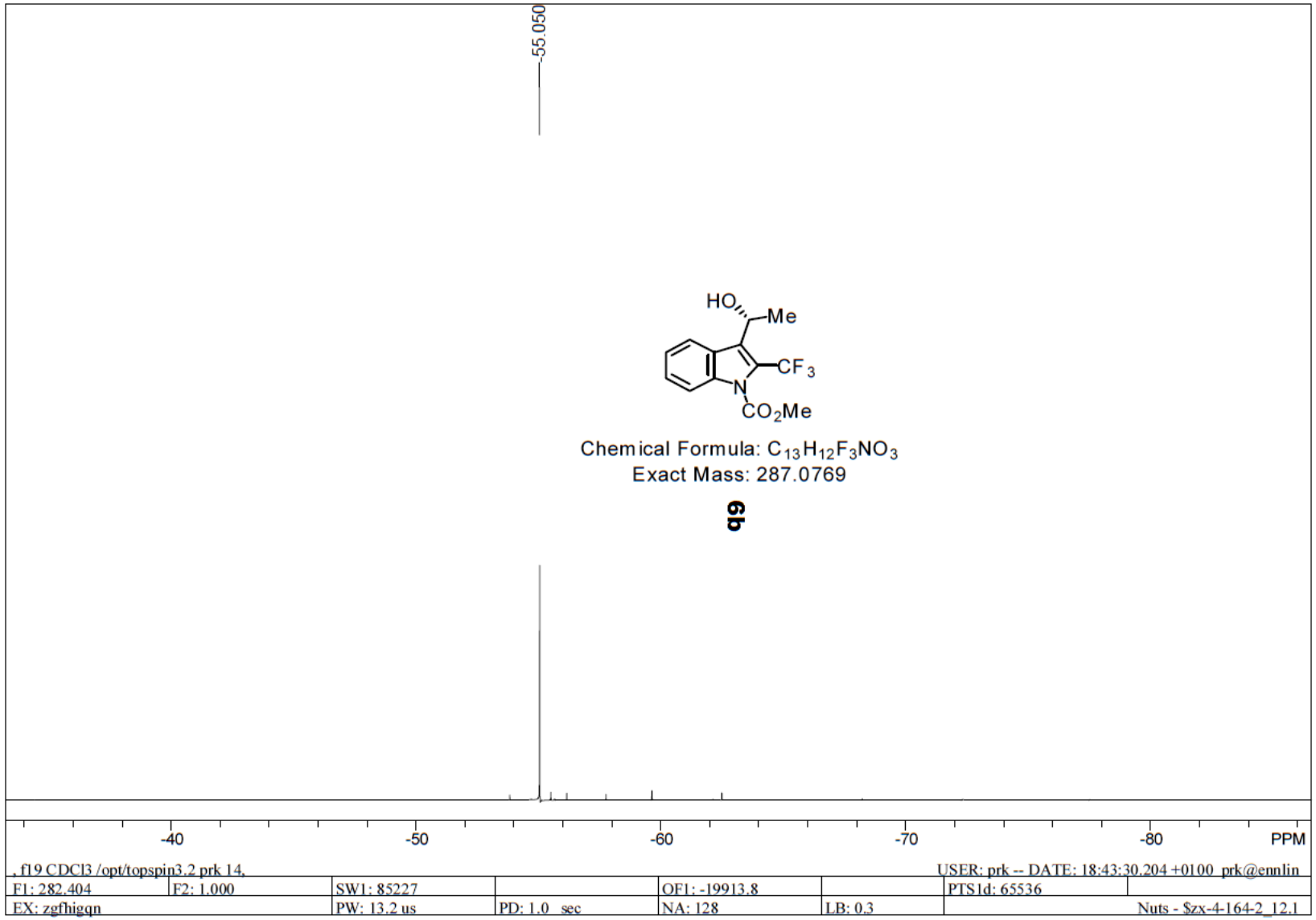

0.000
1.561
1.577
2.083
5.437
5.439
5.450
5.452
5.463
5.466
5.477
5.479
7.181
7.198
7.214
7.334
7.336
7.350
7.352
7.365
7.367
8.047
8.053
8.063
8.071
12.00
1.08
1.08
1.17
1.06
2.06
Me
HO
CF3
N
Boc
Chemical Formula: C16H18F3NO3
Exact Mass: 329.1239
6a
PPM
0
2
4
6
8
1H, Last reminder: no measurment without structure on order!!, Please measu
USER: nmruser -- DATE: 10:46:37 207 +0100 nmruser@pc15036
F1: 500.200
F2: 1.000
SW1: 5515
OF1: 2210.0
PTS1d: 65536
EX: zg30
PW: 11.0 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $161211_38619_zx-4-164-1_1.1

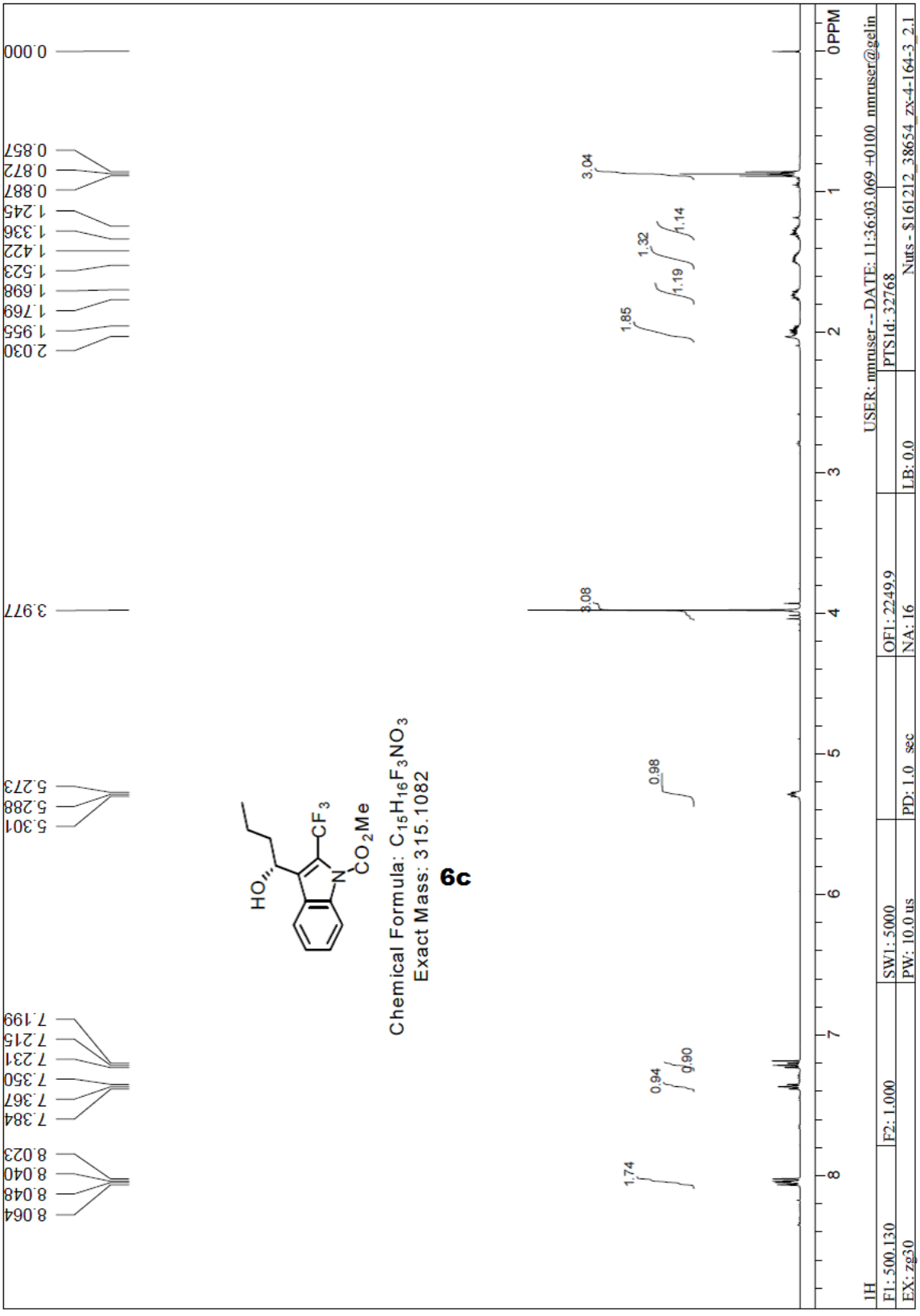

23.557
27.700
64.124
64.156
64.180
64.212
76.753
77.000
77.255
85.453
115.045
118.278
120.345
120.425
120.648
120.952
121.207
122.564
123.035
123.179
124.712
125.590
127.082
130.267
137.412
130.283
149.010
HO
Me
CF3
N
Boc
Chemical Formula: C16H18F3NO3
Exact Mass: 329.1239
6a
PPM
13C
F1: 125.775
F2: 1.000
SW1: 32895
OF1: 13464.9
EX: zgpg30
PW: 11.0 us
PD: 2.0 sec
NA: 256
LB: 1.0
USER: nmruser -- DATE: 10:55:04.225 +0100 nmruser@pc15036
PTS1d: 32768
Nuts - $161211_38619_zx-4-164-1_2.1

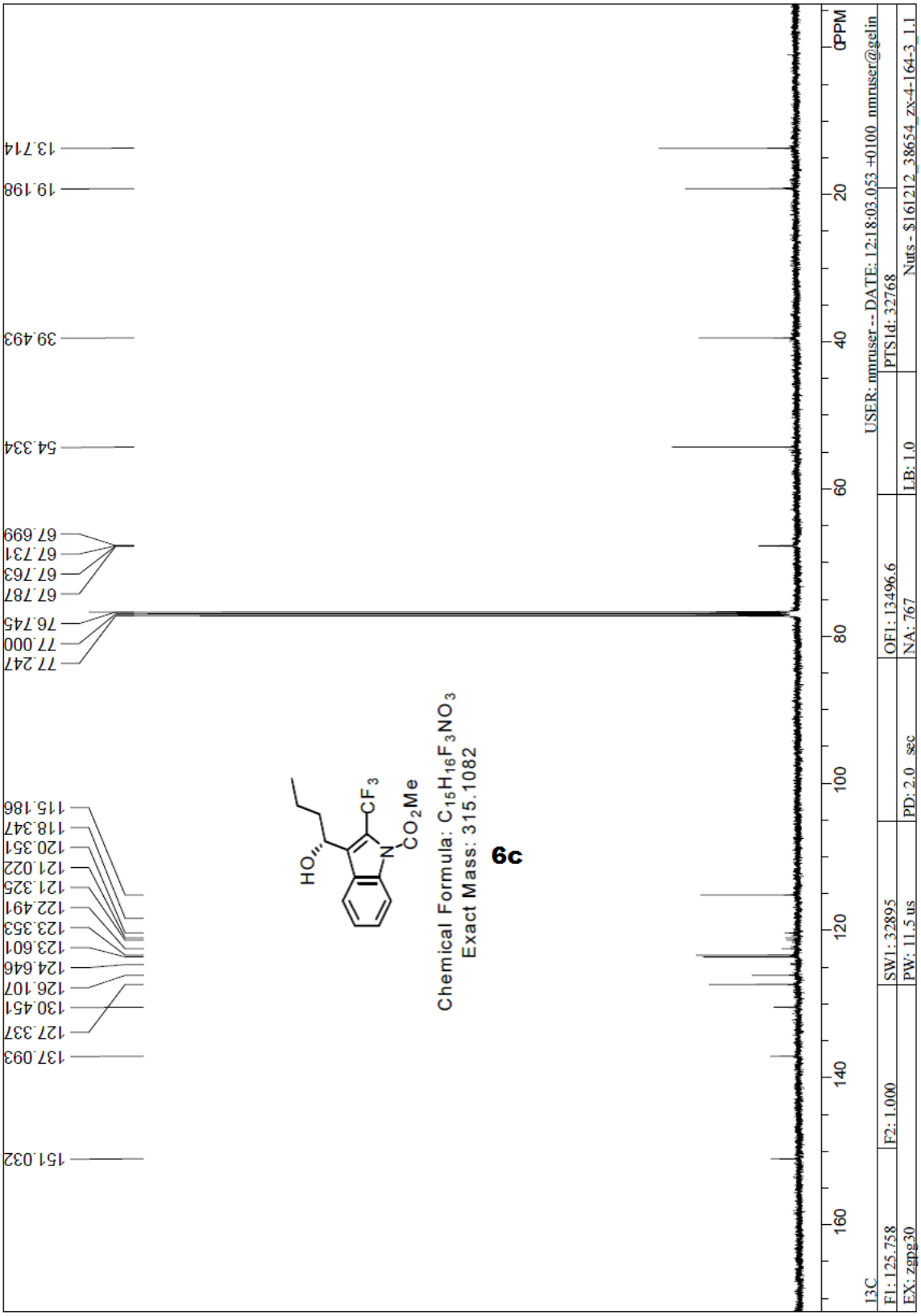

-53.162
HO
Me
CF3
N
Boc
Chemical Formula: C16H18F3NO3
Exact Mass: 329.1239
6a
50
0
-50
-100
-150
-200
PPM
, f19 CDCl3 /opt/topspin3.2 prk 1,
USER: prk -- DATE: 07:57:07.629 +0100 prk@ennlin
F1: 282.404
F2: 1.000
SW1: 85227
OF1: -19913.8
PTS1d: 65536
EX: zgfhigqn
PW: 13.2 us
PD: 1.0 sec
NA: 128
LB: 0.3
Nuts - $zx-4-164-1-f_10.1

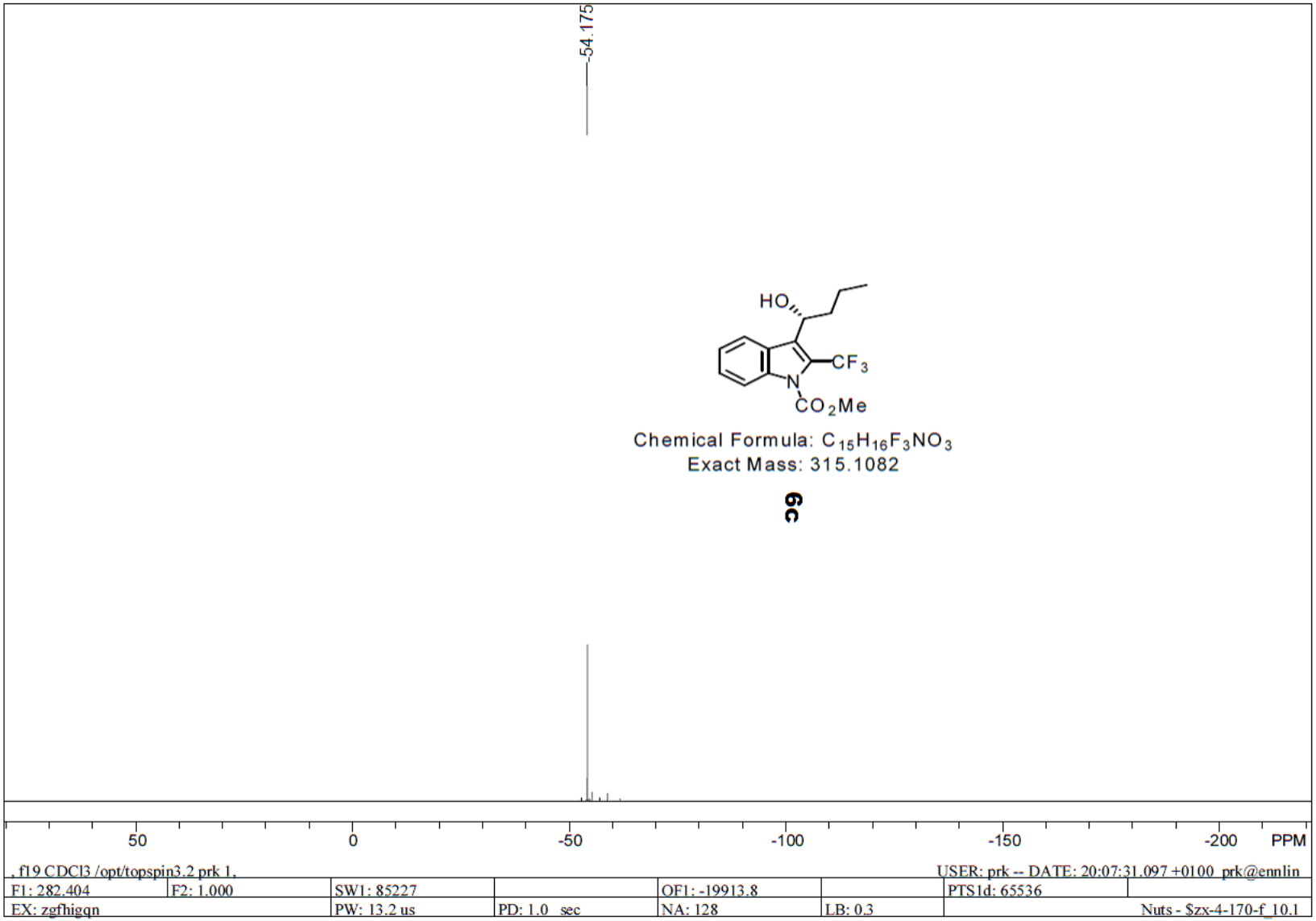

8.171
8.155
8.111
8.110
8.094
8.093
7.460
7.458
7.446
7.444
7.429
7.427
7.313
7.311
7.298
7.297
7.295
7.283
7.280
7.260
5.578
5.565
5.563
5.552
5.550
5.539
4.048
2.171
1.657
1.644
HO
Me
CF3
N
CO2Me
Chemical Formula: C13H12F3NO3
Exact Mass: 287.0769
6b
0.84
0.78
0.85
0.84
0.93
2.88
0.89
3.00
9
8
7
6
5
4
3
2
1
0PPM
1H
USER: nmruser -- DATE: 11:04:39.254 +0100 nmruser@gelin
F1: 500.130
F2: 1.000
SW1: 5000
OF1: 2288.2
PTS1d: 32768
EX: zg30
PW: 10.0 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $161212_38653_zx-4-164-2_1.1

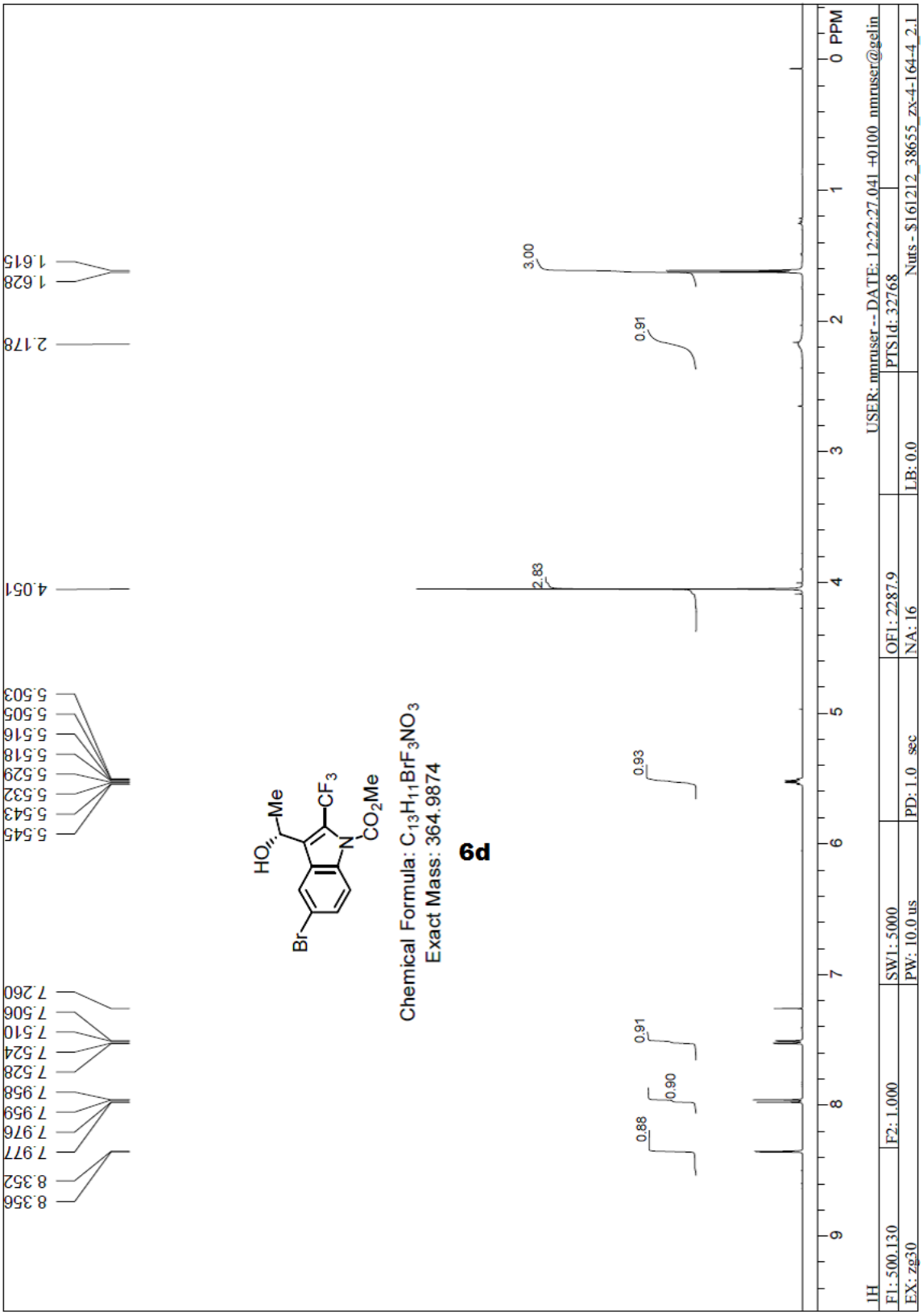

23.605
54.342
64.114
64.146
64.178
64.210
76.745
77.000
77.255
115.202
118.435
120.319
120.583
120.886
121.189
122.467
123.401
123.433
124.351
124.591
125.828
127.369
131.233
137.117
131.249
151.032
HO
Me
CF3
N
CO2Me
Chemical Formula: C13H12F3NO3
Exact Mass: 287.0769
6b
13C
F1: 125.758
F2: 1.000
SW1: 32895
PW: 11.5 us
PD: 2.0 sec
OF1: 13496.6
NA: 511
LB: 1.0
PTS1d: 32768
EX: zgpg30
USER: nmruser -- DATE: 11:31:04.048 +0100 nmruser@gelin
Nuts - $161212_38653_zx-4-164-2_2.1
160
140
120
100
80
60
40
20
0 PPM

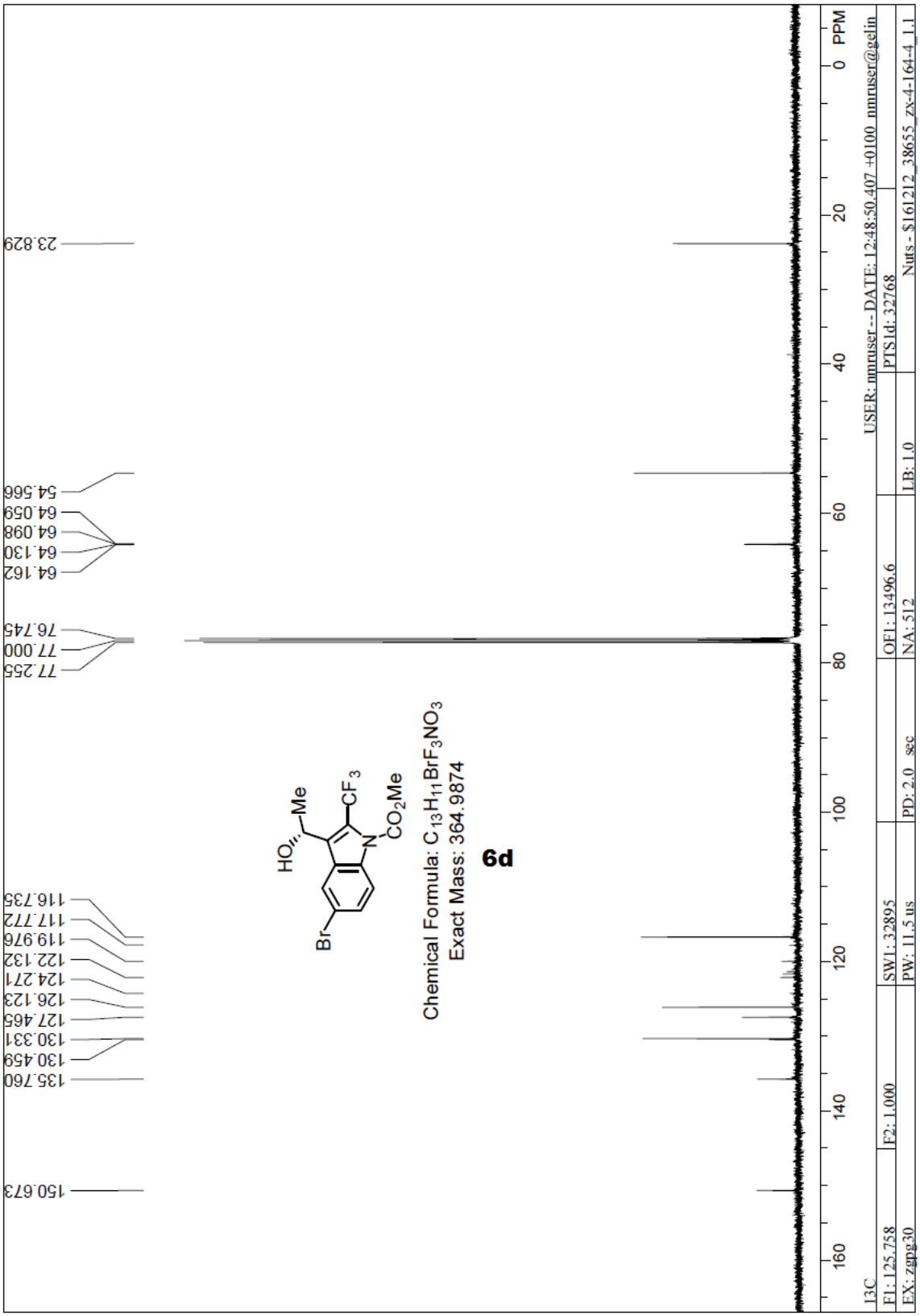

-55.050
HO
Me
CF3
N
CO2Me
Chemical Formula: C13H12F3NO3
Exact Mass: 287.0769
6b
-40
-50
-60
-70
-80
PPM
, f19 CDCl3 /opt/topspin3.2 prk 14,
USER: prk -- DATE: 18:43:30.204 +0100 prk@ennlin
F1: 282.404
F2: 1.000
SW1: 85227
OF1: -19913.8
PTS1d: 65536
EX: zgfhigqn
PW: 13.2 us
PD: 1.0 sec
NA: 128
LB: 0.3
Nuts - $zx-4-164-2_12.1

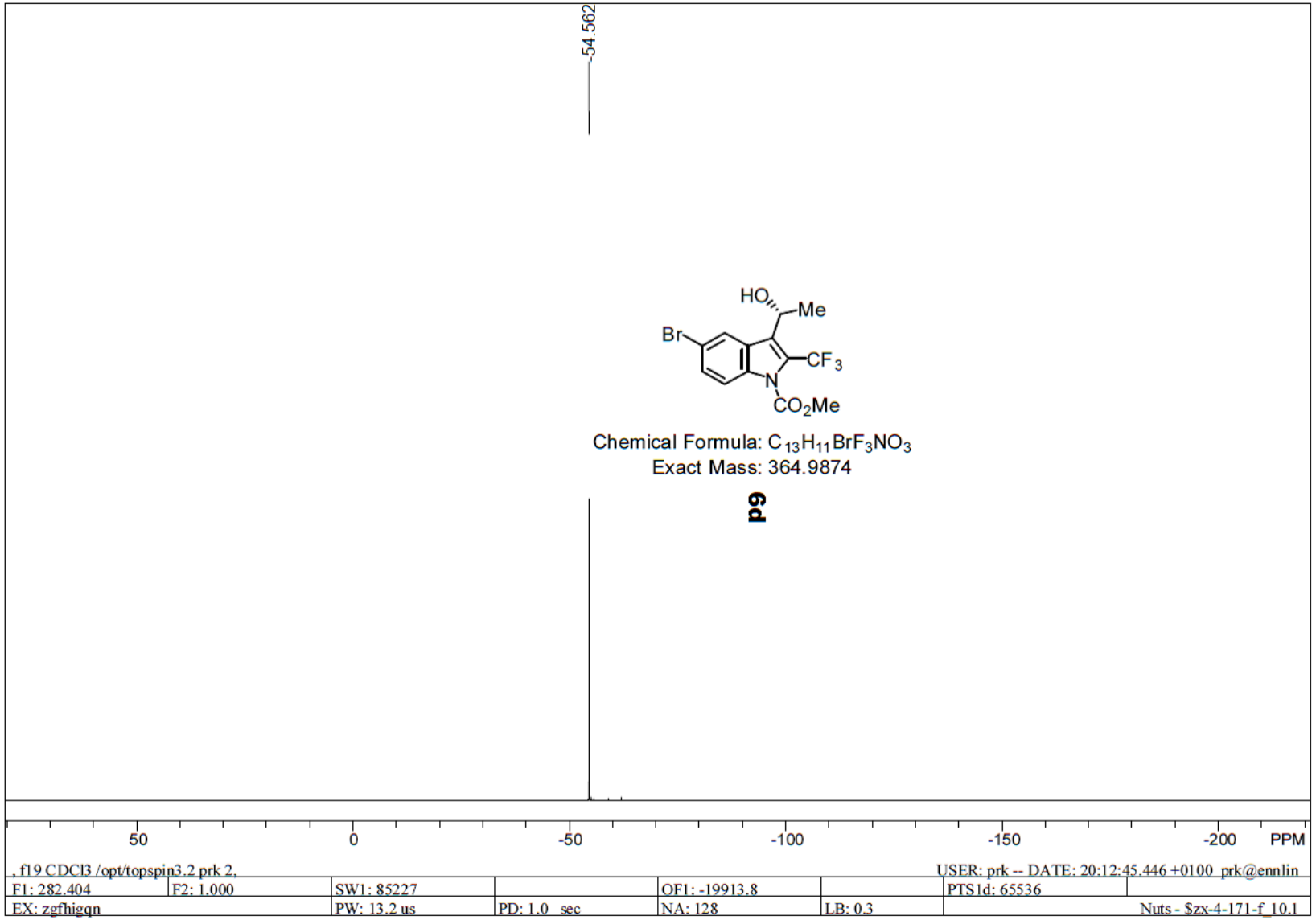

Chemical Formula: $C_{15}H_{16}F_3NO_3$
Exact Mass: 315.1082
6c
1H
F1: 500.130
F2: 1.000
SW1: 5000
OF1: 2249.9
EX: zg30
PW: 10.0 us
PD: 1.0 sec
NA: 16
LB: 0.0
USER: nmruser -- DATE: 11:36:03.069 +0100 nmruser@gelin
PTS1d: 32768
Nufs - $161212_38654_zx-4-164-3_2.1
0PPM


13.714
19.198
39.493
54.334
67.699
67.731
67.763
67.787
76.745
77.000
77.247
115.186
118.347
120.351
121.022
121.325
122.491
123.353
123.601
124.646
126.107
130.451
127.337
137.093
151.032
HO
CF3
N
CO2Me
Chemical Formula: C15H16F3NO3
Exact Mass: 315.1082
6c
160
140
120
100
80
60
40
20
0
PPM
13C
F1: 125.758
F2: 1.000
SW1: 32895
EX: zgpg30
PW: 11.5 us
PD: 2.0 sec
OF1: 13496.6
NA: 767
LB: 1.0
USER: nmruser -- DATE: 12:18:03.053 +0100 nmruser@gelin
PTS1d: 32768
Nuts - $161212_38654_zx-4-164-3_1.1


-54.175
HO
CF3
N
CO2Me
Chemical Formula: C15H16F3NO3
Exact Mass: 315.1082
6c
50
0
-50
-100
-150
-200
PPM
, f19 CDCl3 /opt/topspin3.2 prk 1,
USER: prk -- DATE: 20:07:31.097 +0100 prk@ennlin
F1: 282.404
F2: 1.000
SW1: 85227
OF1: -19913.8
PTS1d: 65536
EX: zgfhigqn
PW: 13.2 us
PD: 1.0 sec
NA: 128
LB: 0.3
Nuts - $zx-4-170-f_10.1


6d
Chemical Formula: C13H11BrF3NO3
Exact Mass: 364.9874
1H
F1: 500.130
F2: 1.000
SW1: 5000
PW: 10.0 us
PD: 1.0 sec
OF1: 2287.9
NA: 16
LB: 0.0
PTS1d: 32768
USER: nmruser -- DATE: 12:22:27.041 +0100 nmruser@gelin
Nufs - $161212_38655_zx-4-164-4_2.1
PPM


23.829
54.566
64.059
64.098
64.130
64.162
76.745
77.000
77.255
116.735
117.772
119.976
122.132
124.271
126.123
127.465
130.331
130.459
135.760
150.673
Me
HO
CF3
CO2Me
Br
N
Chemical Formula: C13H11BrF3NO3
Exact Mass: 364.9874
6d
13C
F1: 125.758
F2: 1.000
SW1: 32895
OF1: 13496.6
EX: zgpg30
PW: 11.5 us
PD: 2.0 sec
NA: 512
LB: 1.0
PTS1d: 32768
USER: nmruser -- DATE: 12:48:50.407 +0100 nmruser@gelin
Nuts - $161212_38655_zx-4-164-4_1.1
PPM
0
20
40
60
80
100
120
140
160


-54.562
HO
Me
Br
CF3
N
CO2Me
Chemical Formula: C13H11BrF3NO3
Exact Mass: 364.9874
6d
50
0
-50
-100
-150
-200
PPM
, f19 CDCl3 /opt/topspin3.2 prk 2,
USER: prk -- DATE: 20:12:45.446 +0100 prk@ennlin
F1: 282.404
F2: 1.000
SW1: 85227
OF1: -19913.8
PTS1d: 65536
EX: zgfhigqn
PW: 13.2 us
PD: 1.0 sec
NA: 128
LB: 0.3
Nuts - $zx-4-171-f_10.1

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