SUPPLEMENTARY INFORMATION

doi:10.1038/nature24641

Site-Selective and Stereoselective Functionalization of Non-Activated Tertiary C–H Bonds

Kuangbiao Liao[1], Thomas C. Pickel[1], Vyacheslav Boyarskikh[1], John Bacsa[1], Djamaladdin G. Musaev[2] & Huw M. L. Davies*[1]

[1]Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, Georgia 30322.

[2]Cherry L. Emerson Center for Scientific Computation, Emory University, 1521 Dickey Drive, Atlanta, Georgia, 30322.

E-mail:hmdavie@emory.edu

Supporting Information

Contents

1 - General Considerations

1.1 Equipment and Methods

^{1}H and ^{13}C NMR spectra were recorded at either 500 MHz (^{13}C at 126 MHz) or 600 MHz (^{13}C at 151 MHz) on INOVA-500 or Bruker-600 spectrometer, as indicated. NMR spectra were run in solutions of deuterated chloroform ($CDCl_3$) with residual chloroform taken as an internal standard (7.26 ppm for ^{1}H, and 77.16 ppm for ^{13}C), and were reported in parts per million (ppm).

Abbreviations for signal multiplicity are as follow:s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. Coupling constants (*J* values) were calculated directly from the spectra. IR spectra were collected on a Nicolet iS10 FT-IR spectrometer. Mass spectra were taken on a Thermo Finnigan LTQ-FTMS spectrometer with APCI, ESI or NSI. Thin layer chromatographic (TLC) analysis was performed with glass-backed silica gel plates, visualizing with UV light (254 nm) and/or staining with aqueous $KMnO_4$ stain.

1.2 Solvents for Reaction

The dichloromethane(CH_2Cl_2) used for the carbenoid transformations was dried at reflux over calcium hydride in a 250-mL round bottom flask for 12 hours under argon, then distilled and stored under argon atmosphere and then used directly.

1.3 Substrates and Reagents

The substrates and reagents were purchased from the following suppliers and used without further purification:

Acros:2-Methylbutane (1 LT, 99+ % purity);

Sigma-Aldrich:3-Methylpentane (1 LT, ≥99 % purity); 2,5-Dimethylhexane (5 g, 99 % purity); 1-Bromo-3-methylbutane (100 g, 96 % purity); Cholesteryl acetate (100 g, 97 % purity); Cholesteryl pelargonate (100 g, 97 % purity); 2-Methylhexane (5g, 99% purity)

Alfa-Aesar:2-Methylpentane (100 mL, 99+ % purity); 2,3-Dimethylbutane (100 g, 99 % purity)

TCI:3-Ethyl-2-methylpentane (5 mL, >99 % purity); D-α-Tocopherol Acetate (Vitamin E) (25 g, >96 % purity)

The following substrates were prepared according to reported procedures[1]:

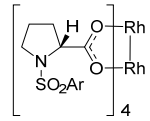
Butyl 5-methylhexanoate; pentyl 5-methylhexanoate; phytyl pivalate.

The following reagents were prepared according to reported procedures [2, 3, 4, 5]:

Methyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate.

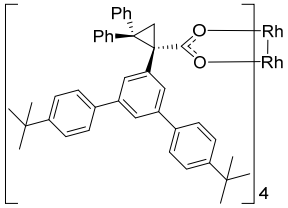
2 - C–H Functionalization Reactions

2.1 Catalysts Structures

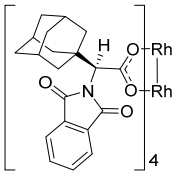


Ar = *p*-$C_{12}H_{25}C_6H_4$

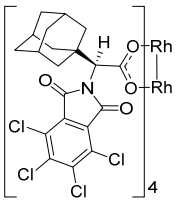
Rh_2(*R*-DOSP)$_4$



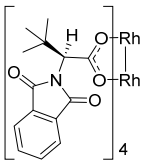
Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$



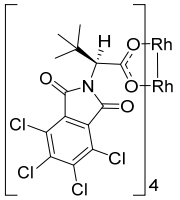
Rh_2(*S*-PTAD)$_4$



Rh_2(*S*-TCPTAD)$_4$

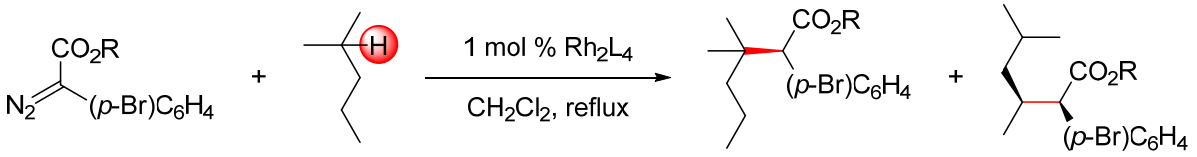


Rh_2(*S*-PTTL)$_4$



Rh_2(*S*-TCPTTL)$_4$

2.2 Data Summary for Catalyst and Diazo Screen

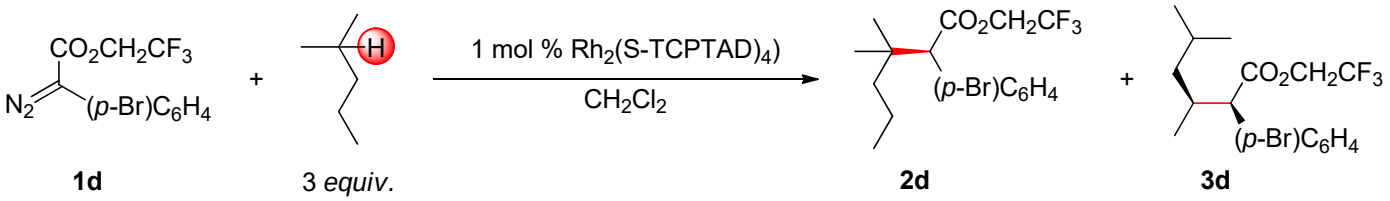


1a-e 3 *equiv.* **2a-e** **3a-e**

Catalyst	**1**	R	yield (%)[a]	r.r. (**2**:**3**)	e.e. (**2**, %)	d.r. (**3**)	e.e. (**3**, %)
Rh_2(*R*-DOSP)$_4$	**1a**	CH_3	83	85:15	-43	3: 1	-
Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$	**1a**	CH_3	23	35:65	-10	4: 1	-
Rh_2(*S*-PTAD)$_4$	**1a**	CH_3	50	74:26	-34	2: 1	-
Rh_2(*S*-PTTL)$_4$	**1a**	CH_3	80	74:26	-33	2: 1	-
Rh_2(*S*-TCPTTL)$_4$	**1a**	CH_3	86	86:14	77	2: 1	-
Rh_2(*S*-TCPTAD)$_4$	**1a**	CH_3	89	87:13	79	3: 1	-
Rh_2(*S*-TCPTAD)$_4$	**1b**	CH_2CCl_3	84 (74)[b]	89:11	84	2: 1	77
Rh_2(*S*-TCPTAD)$_4$	**1c**	CH_2CBr_3	88 (77)	87:13	77	2: 1	79
Rh_2(*S*-TCPTAD)$_4$	**1d**	CH_2CF_3	92 (83)	90:10	77	2: 1	79

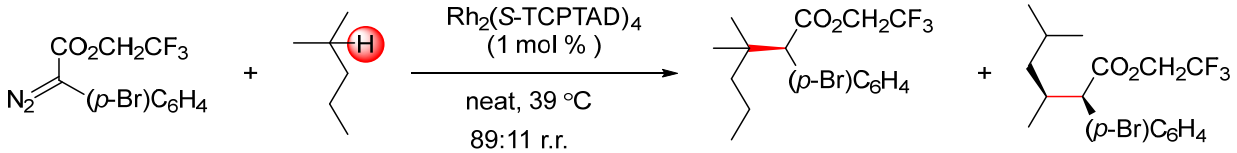
[a] Combined yield of **2** and **3**. [b] Isolated yield of **2** shown in parenthesis.

2.3 Reaction Condition Study



1d 3 *equiv.* **2d** **3d**

#	Temperature (°C)	r.r. (%)	e.e. (**2d**,%)	Yield (**2d**, %)	d.r. (**3d**,%)	Yield (**3d**, %)
1	39 (reflux)	90:10	77	83	2:1	9
2	*r.t.*	91:9	80	77	3:1	8
3	0	93:7	82	79	4:1	6
4	-10	95:5	84	78	5:1	4
5	-40	96:4	86	77	9:1	3
6	-78	96:4	80	65	7:1	0



1d **2d** (*R*) **3d** (*R,S*)

2.4 General Procedures for C–H Functionalization Reactions

A 5-mL flask was equipped with a reflux condenser and an octagonal magnetic stir bar. The flask was charged with Rh_2L_4 (0.002 mmol, 1 mol%) and treated by vacuum/argon to replace the air in the flask to argon. Substrate (0.6 mmol, 3 *equiv.*) and distilled CH_2Cl_2 (0.5 mL) were added, then the catalyst/substrate solution was heated to reflux (39 °C) under argon for 5 minutes [or the reaction was conducted at room temperature(24 °C), 0° C, -10 °C, -40 °C, -78 °C]. Diazo (0.2 mmol, 1.0 *equiv.*) was dissolved in 3 mL of distilled CH_2Cl_2 and then the diazo solution was added dropwise to the catalyst solution over 6h with a syringe pump under reflux condition [or the reaction was conducted at room temperature(24 °C), 0° C, -10 °C, -40 °C, -78 °C] and argon atmosphere. After addition, 0.5 mL distilled CH_2Cl_2 was used to dilute the left over diazo in the syringe needle and then the diazo solution was added dropwise to the reaction solution. Then the rest of the diazo solution in the syringe needle was further pushed into the reaction solution. Then the reaction mixture was allowed to stir for another 1 min, then the reaction mixture was transferred into a 25-mL round bottom flask with diethyl ether (5 mL x 3) and concentrated under vacuum, and crude ^1H NMR spectrum was obtained to analyze the reaction and measure the selectivity. Then the crude was purified by flash chromatography on silica gel to obtain the product.

3 - General Procedure of Data Analysis

3.1 General Procedure for the Regioisomeric Ratios (r.r.) and Diastereomeric Ratios (d.r.) Determination

To measure the regioisomeric ratios and diastereomeric ratios, the mixtures obtained as described in section 2.1 were analyzed by ^{1}H NMR using the following settings:

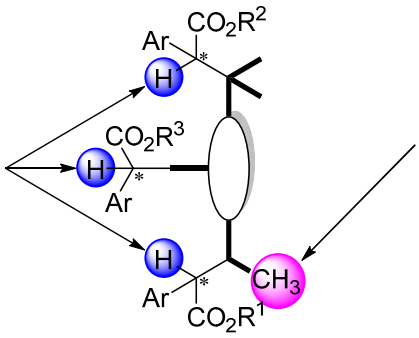
Instrument:600 MHz Bruker equipped with a prodigy probe with sensitivity over 1500:1

Number of scans:32

Relaxation time:5 seconds

The crude ^{1}H NMR spectra data was processed using MestReNova 11.0.2 (Mestrelab Research S.L.), applying an auto-phase correction as well as a Smooth Segment baseline correction. The baseline was manually inspected before integration. The ratios were measured by integrating the ^{1}H NMR peaks resulting from the indicated hydrogens below.

The regioisomeric ratios (*r.r.*) were measured by integrating the proton peaks of each regioisomers in the crude ^{1}H NMR spectra

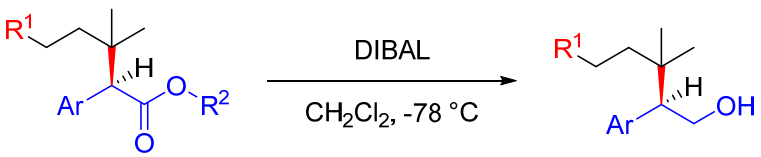


The diastereoisomeric ratios (*d.r.*) were measured by integrating the proton peaks of each diastereomers in the crude ^{1}H NMR spectra

In terms of the functionalization of cholesteryl acetate and Vitamin E, no other regioisomer was detected in the crude ^{1}H NMR spectra, LC-MS technique was used to confirm the results.

3.2 General Procedure for Enantiomeric Excess (e.e.) Determination on HPLC

As most of the enantiomers of the C–H functionalization products were difficult to be separated on the HPLC, they were reduced to the corresponding alcohol derivatives, which will have better separation on the HPLC, without changing the e.e. of the products. Therefore, the e.e. of the products were determined from the corresponding alcohol derivatives. [5]



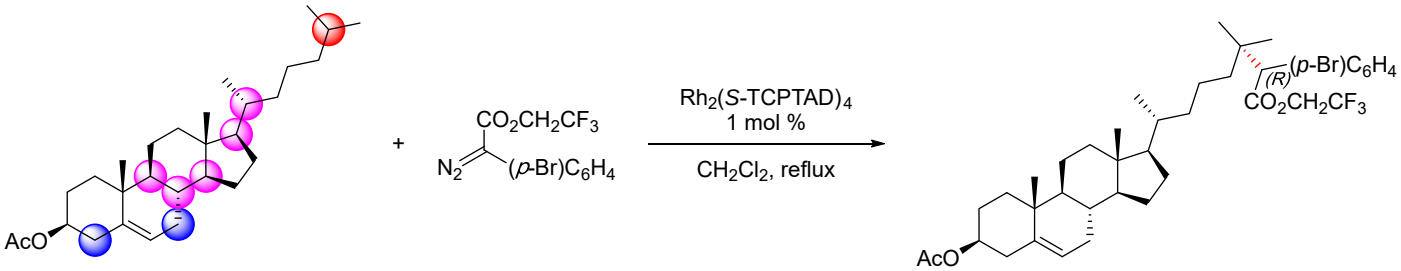
To a 25-mL round bottom flask with a stirred solution of the ester (0.1 mmol, 1.0 *equiv.*) in CH_2Cl_2 (3 mL) was added 1 M diisobutylaluminum hydride (DIBAL) in CH_2Cl_2 (0.5 mL, 0.5 mmol, 5 *equiv.*) slowly at -78 °C. The mixture was stirred overnight and allowed to warm up to room temperature. Once the starting material was fully consumed and confirmed by TLC, the solution was cooled down to 0 °C, then methanol (0.5 mL) was added dropwise to quench the reaction and then stirred for 20 min. The reaction mixture was concentrated to dry solid mixture, then 10 mL of ethyl acetate (EA) was added into the flask to extract the organic compound. Then

mixture in the flask was poured onto and filtered through a silica plug (3 *cm* height, 2 *cm* wide), and the solid residue was further extracted and washed by EA (10 mL x 4). Then the filtrate was concentrated and purified by flash column chromatography to afford the corresponding alcohol derivatives as white solid or colorless oil. The sample was dissolved in hexanes/isopropanol (5~30 mg/mL) and the e.e. value of the corresponding alcohol derivatives were determined on the HPLC.

The e.e. of the C–H functionalization products were then obtained from the e.e. of the corresponding alcohol derivatives, in which the e.e. values were considered equal to each other.

4 - Determination of the Absolute Stereochemistry

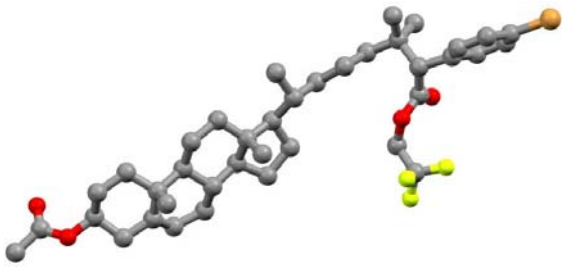
The absolute stereochemistry of Rh_2(*S*-TCPTAD)$_4$ catalyzed tertiary C-H insertion reaction of substrate **17** was determined by the X-Ray single crystal structure analysis of product **18*R*** (see section 10 for detail), the absolute stereochemistry of the secondary C-H insertion products were determined by the known asymmetric induction of Rh_2[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$.[5] Based on these data, the absolute stereochemistry of the rest of the reactions were tentatively assigned accordingly.



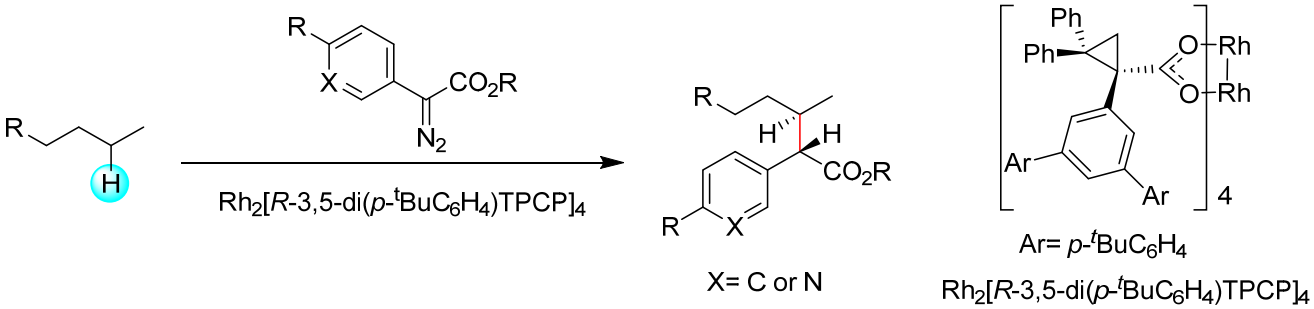
18
Cholesteryl acetate (1 *equiv.*)

1d
(1 *equiv.*)

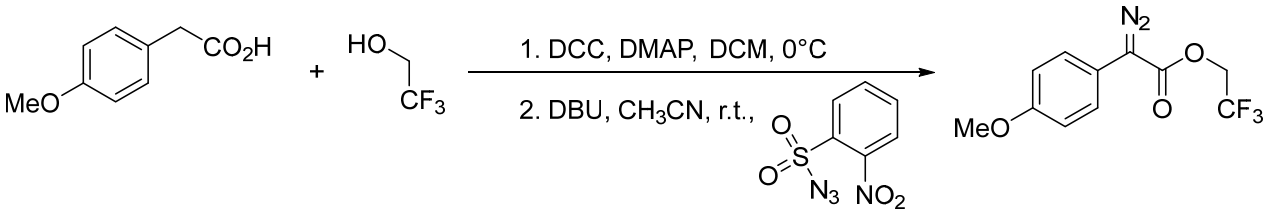
19*R*



The single crystal X-ray structure of **19*R***

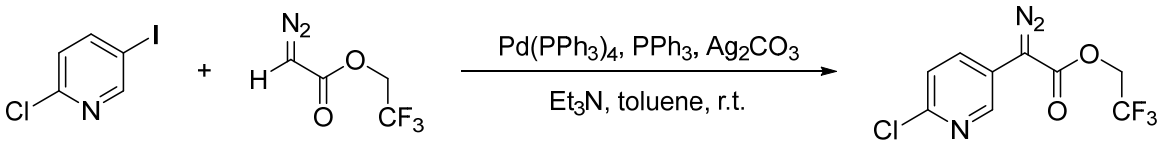


5 - Preparation of Diazo Compounds



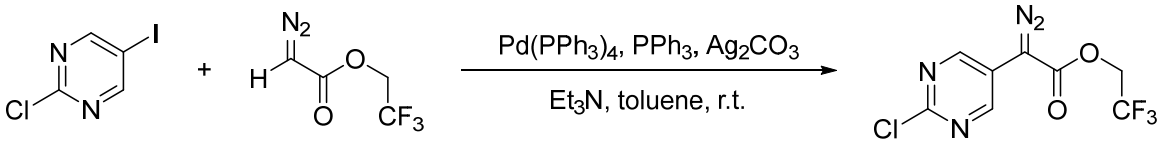
2,2,2-Trifluoroethyl 2-diazo-2-(4-methoxyphenyl)acetate. [3] A 250 mL flask was charged with 2-(4-methoxyphenyl)acetic acid (1.7 g, 10 mmol, 1.0 *equiv.*), N,N-dimethylpyridin-4-amine (DMAP) (0.1 g, 10 mmol, 0.1 *equiv.*), and 2,2,2-trifluoroethan-1-ol (1.2 g, 12 mmol, 1.2 *equiv.*) and CH_2Cl_2 (150 mL), then the solution was stirred and cooled to 0 °C. A solution of N,N'-Dicyclohexylcarbodiimide (DCC) (2.3 g, 11 mmol, 1.1 *equiv.*) in CH_2Cl_2 (50 mL) was poured slowly into the cold reaction mixture. The solution was allowed to stir overnight, at which point it had reached ambient temperature. The precipitate was removed by vacuum filtration on a silica plug (5 *cm* height, 5 *cm* wide), washing once with diethyl ether (50 mL). The filtrate was concentrated to give a crude oil. The crude was dissolved in acetonitrile (CH_3CN) (40 mL) in a 250 mL three-necked flask equipped with a 50-mL dropping funnel, a rubber septum fitted with argon inlet needle, an egg shaped in magnetic stir bar and 2-nitrobenzenesulfonyl azide (3.4 g, 15 mmol, 1.5 *equiv.*). Then 1,8-Diazabicycloundec-7-ene (DBU) (3.4 g, 22 mmol, 2.2 *equiv.*) in acetonitrile (20 mL) was transferred to the dropping funnel and added dropwise into reaction mixture at room temperature. The resulting mixture was stirred over 4 h, and reaction progress was monitored by TLC analysis. The reaction mixture was cooled with an ice bath, and saturated aqueous NH_4Cl (50 mL) was then added to quench the reaction. The mixture was extracted with diethyl ether (3 x 30 mL), and the combined organic layer was washed with saturated NaCl aqueous solution (50 mL), dried over sodium sulfate (10 g) and filtered. Then the filtrate was concentrated by rotary evaporation to afford the crude product. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 50/1) to give an orange solid in 47% overall yield (1.3 g).

TLC (diethyl ether:hexanes, 1:9 *v/v*); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 4.64 (q, J = 8.4 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.76, 158.50, 126.18, 122.94 (q, J = 277.5 Hz), 115.82, 114.76, 60.27 (q, J = 36.8 Hz), 55.36; HRMS (NSI) calcd for $C_{11}H_{10}O_3F_3$ ([M-N_2+H]$^+$):247.0577 found 247.0577; IR (neat):2976, 2089, 1709, 1610, 1514, 1281, 1255, 1138, 1076, 1032, 974, 828, 733.



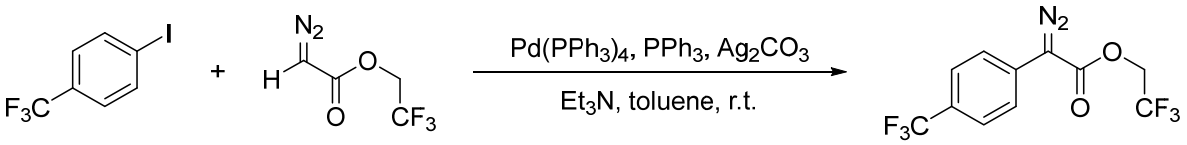
2,2,2-Trifluoroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate. [6] 2-Chloro-5-iodopyridine (718 mg, 0.3 mmol, 1.0 *equiv.*), tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (173 mg, 0.15 mmol, 0.05 *equiv.*), triphenylphosphine (PPh_3) (79 mg, 0.3 mmol, 0.1 *equiv.*), silver carbonate (Ag_2CO_3) (414 mg, 1.5 mmol, 0.5 *equiv.*) and triethylamine (Et_3N) (395 mg, 3.9 mmol, 1.3 *equiv.*) were suspended in toluene (20 mL) in a round-bottomed flask under nitrogen. Then 2,2,2-trichloroethyl 2-diazoacetate (504 mg, 3 mmol, 1.0 *equiv.*) was added. After stirring at r.t. for 12 h, the mixture was filtered through a short silica plug (3 *cm* height, 2 *cm* wide), eluting with ethyl acetate. The solvents were removed under reduced pressure and the crude residue was purified by column chromatography on silica gel eluting with gradient diethyl ether/hexanes (1% to 10%) to give the diazo as a yellow solid in 61 % yield (512 mg).

TLC (diethyl ether:hexanes, 1:7 *v/v*); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, J = 2.5 Hz, 1H), 7.83 (d, J = 6.7 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 4.67 (q, J = 8.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.40, 149.16, 144.50, 133.95, 124.47, 122.71 (q, J = 277.4 Hz), 120.85, 60.62 (q, J = 37.1 Hz); HRMS (NSI) calcd for $C_9H_6O_2N_3ClF_3$ ($[M+H]^+$):280.0106 found 280.0098; IR (neat):2976, 2099, 1685, 1482, 1418, 1274, 1248, 1225, 1166, 1115, 1071, 1020, 959, 841, 725.



2,2,2-Trifluoroethyl 2-(2-chloropyrimidin-5-yl)-2-diazoacetate. 2-Chloro-5-iodopyrimidine (721 mg, 0.3 mmol, 1.0 *equiv.*), tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (173 mg, 0.15 mmol, 0.05 *equiv.*), triphenylphosphine (PPh_3) (79 mg, 0.3 mmol, 0.1 *equiv.*), silver carbonate (Ag_2CO_3) (414 mg, 1.5 mmol, 0.5 *equiv.*) and triethylamine (Et_3N) (395 mg, 3.9 mmol, 1.3 *equiv.*) were suspended in toluene (20 mL) in a round-bottomed flask under nitrogen. Then 2,2,2-trichloroethyl 2-diazoacetate (504 mg, 3 mmol, 1.0 *equiv.*) was added. After stirring at r.t. for 12 h, the mixture was filtered through a short silica plug (3 *cm* height, 2 *cm* wide), eluting with ethyl acetate. The solvents were removed under reduced pressure and the crude residue was purified by column chromatography on silica gel eluting with gradient diethyl ether/hexanes (1% to 20%) to give the diazo as a yellow solid in 25 % yield (210 mg).

TLC (diethyl ether:hexanes, 1:3 *v/v*); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (s, 2H), 4.70 (q, J = 8.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.76, 158.80, 153.83, 121.67 (q, J = 277.6 Hz), 119.83, 60.87 (q, J = 37.3 Hz); HRMS (NSI) calcd for $C_8H_5O_2N_4ClF_3$ ($[M+H]^+$):281.0059 found 281.0048; IR (neat):2923, 2102, 1702, 1528, 1424, 1358, 1288, 1244, 1145, 1080, 972, 731.

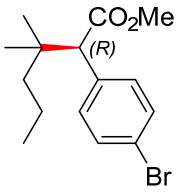


2,2,2-Trifluoroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate. 1-Iodo-4-(trifluoromethyl)benzene (816 mg, 0.3 mmol, 1.0 *equiv.*), tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (173 mg, 0.15 mmol, 0.05 *equiv.*), triphenylphosphine (PPh_3) (79 mg, 0.3 mmol, 0.1 *equiv.*), silver carbonate (Ag_2CO_3) (414 mg, 1.5 mmol, 0.5 *equiv.*) and triethylamine (Et_3N) (395 mg, 3.9 mmol, 1.3 *equiv.*) were suspended in toluene (20 mL) in a round-bottomed flask under nitrogen. Then 2,2,2-trichloroethyl 2-diazoacetate (504 mg, 3 mmol, 1.0 *equiv.*) was added. After stirring at r.t. for 12 h, the mixture was filtered through a short silica plug (3 *cm* height, 2 *cm* wide), eluting with ethyl acetate. The solvents were removed under reduced pressure and the crude residue was purified by column chromatography on silica gel eluting with gradient diethyl ether/hexanes (1% to 5%) to give the diazo as a yellow solid in 41 % yield (384 mg).

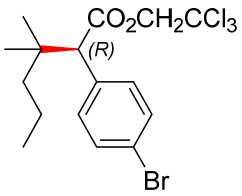
TLC (diethyl ether:hexanes, 1:9 *v/v*); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 4.67 (q, J = 8.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.55, 129.17, 128.26 (q, J = 32.9 Hz), 126.09 (q, J = 3.8 Hz), 124.07 (q, J = 272.0 Hz), 123.62, 122.92 (q, J = 277.5 Hz), 60.54 (q, J = 36.9 Hz); HRMS (NSI) calcd for $C_{11}H_6O_2N_2ClF_6$ ($[M+Cl]^-$):347.0028 found 347.0030; IR (neat):2979, 2098, 1717, 1618, 1411, 1356, 1325, 1280, 1240, 1115, 1074, 1016, 975, 840.

6 - Experimental Data for C–H Functionalization Products

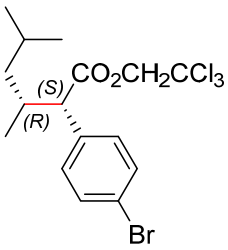
6.1 C–H Functionalization Products of 2-Methylpentane



Methyl *(R)*-2-(4-bromophenyl)-3,3-dimethylhexanoate (2a). $[\alpha]^{20}_{D}$ -12.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:20 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 3.64 (s, 3H), 3.48 (s, 1H), 1.29 (m, 3H), 1.14 (td, J = 9.9, 3.4 Hz, 1H), 0.98 (s, 3H), 0.88 (s, 3H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.27, 135.01, 131.80, 130.89, 121.29, 59.60, 51.47, 42.99, 37.15, 24.47, 24.18, 17.03, 14.83; HRMS (NSI) calcd for $C_{15}H_{22}BrO_2$ ($[M+H]^+$):313.0798 found 313.0797; IR (neat):2957, 2930, 2872, 1734, 1457, 1434, 1195, 1168, 1143, 1076, 1011, 825.

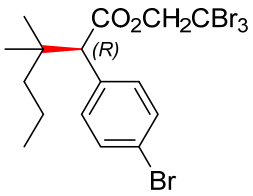


2,2,2-Trichloroethyl *(R)*-2-(4-bromophenyl)-3,3-dimethylhexanoate (2b). $[\alpha]^{20}_{D}$ -4.0° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 4.84 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 3.63 (s, 1H), 1.35 (tdd, J = 11.5, 8.9, 5.2 Hz, 3H), 1.25 – 1.16 (m, 1H), 1.04 (s, 3H), 0.92 (s, 3H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.21, 134.32, 131.95, 131.16, 121.76, 94.89, 74.26, 59.78, 43.19, 37.53, 24.70, 24.37, 17.16, 14.92; HRMS (NSI) calcd for $C_{16}H_{19}BrCl_3O_2$ ($[M-H]^-$):426.9629 found 426.9633; IR (neat):2959, 2872, 1748, 1489, 1370, 1118, 1076, 1011, 826, 761, 716.

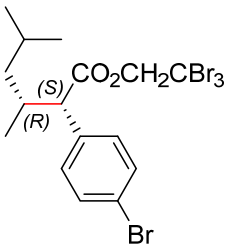


2,2,2-Trichloroethyl (2S,3R)-2-(4-bromophenyl)-3,5-dimethylhexanoate (3b). $[\alpha]^{20}_{D}$ +14° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.77 (d, J = 12.0 Hz, 1H), 4.63 (d, J = 12.0 Hz, 1H), 3.33 (d, J = 10.5 Hz, 1H), 2.29 (dddd, J = 16.8, 10.4, 6.5, 3.6 Hz, 1H), 1.03 (d, J = 6.5 Hz, 3H), 0.93 – 0.81 (m, 3H), 0.79 (d, J = 6.6 Hz, 3H), 0.74 (d, J = 6.5

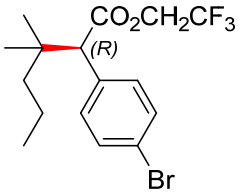
Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.97, 136.31, 131.83, 130.61, 121.70, 74.24, 58.79, 43.02, 34.25, 25.08, 24.18, 21.06, 18.04; HRMS (NSI) calcd for $C_{16}H_{21}BrCl_3O_2$ ($[M+H]^+$):428.9785 found 428.9793; IR (neat):2956, 2928, 2869, 1750, 1488, 1368, 1142, 1118, 1074, 1011, 825, 805, 759, 719.



2,2,2-Tribromoethyl *(R)*-2-(4-bromophenyl)-3,3-dimethylhexanoate (**2c**).$[\alpha]^{20}_D$ -8.3° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 4.98 (d, J = 12.3 Hz, 1H), 4.81 (d, J = 12.3 Hz, 1H), 3.64 (s, 1H), 1.44 – 1.30 (m, 3H), 1.25 – 1.17 (m, 1H), 1.06 (s, 3H), 0.93 (s, 3H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.05, 134.41, 132.04, 131.16, 121.74, 60.04, 43.24, 37.54, 24.76, 24.46, 17.19, 14.97; HRMS (NSI) calcd for $C_{16}H_{21}Br_4O_2$ ($[M+H]^+$):560.8270 found 560.8276; IR (neat):2963, 2935, 2874, 1752, 1489, 1414, 1278, 1164, 1122, 1076, 1012, 980, 825.

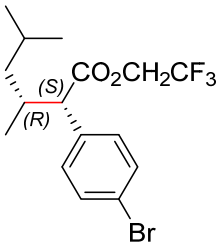


2,2,2-Tribromoethyl (2S,3R)-2-(4-bromophenyl)-3,5-dimethylhexanoate (**3c**).$[\alpha]^{20}_D$ +12.7° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.3 Hz, 3H), 4.92 (d, J = 12.3 Hz, 1H), 4.84 (d, J = 12.3 Hz, 1H), 3.35 (d, J = 10.6 Hz, 1H), 2.41 – 2.25 (m, 1H), 1.06 (d, J = 6.4 Hz, 3H), 0.94 – 0.82 (m, 3H), 0.79 (d, J = 6.6 Hz, 3H), 0.75 (d, J = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.69, 136.37, 131.81, 130.72, 121.68, 58.98, 43.04, 34.17, 25.10, 24.20, 21.08, 18.19; HRMS (NSI) calcd for $C_{16}H_{21}Br_4O_2$ ($[M+H]^+$):560.8270 found 560.8280; IR (neat):2954, 2926, 2868, 1747, 1488, 1385, 1366, 1142, 1116, 1074, 1011, 821, 715.



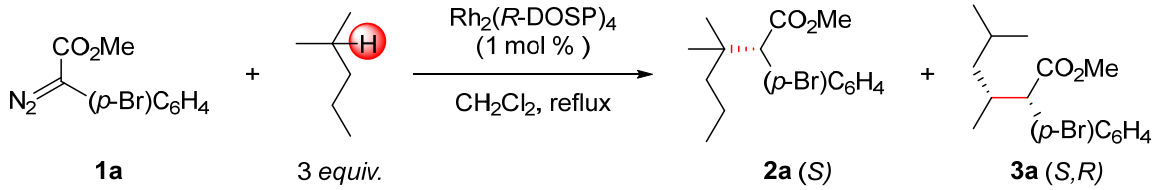
2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-3,3-dimethylhexanoate (**2d**).$[\alpha]^{20}_D$ -13.6° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.7

Hz, 2H), 4.62 (dq, J = 12.7, 8.5 Hz, 1H), 4.26 (dq, J = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 1.37 – 1.26 (m, 3H), 1.21 – 1.11 (m, 1H), 1.00 (s, 3H), 0.89 (s, 3H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.26, 134.13, 131.83, 131.20, 121.82, 60.16 (q, J = 36.5 Hz), 59.31, 43.07, 37.55, 24.54, 24.24, 17.13, 14.81; HRMS (NSI) calcd for $C_{16}H_{21}BrF_3O_2$ ($[M+H]^+$):381.0672 found 381.0673; IR (neat):2963, 2935, 2874, 1752, 1489, 1414, 1278, 1164, 1122, 1076, 1012, 980, 825.



2,2,2-Trifluoroethyl (*2S,3R*)-2-(4-bromophenyl)-3,5-dimethylhexanoate (3d).$[\alpha]^{20}_D$ +30.7° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 4.55 (dd, J = 12.7, 8.5 Hz, 1H), 4.33 (dd, J = 12.7, 8.4 Hz, 1H), 3.30 (d, J = 10.4 Hz, 1H), 2.23 (ddtd, J = 16.7, 10.2, 6.5, 3.9 Hz, 1H), 0.99 (d, J = 6.5 Hz, 3H), 0.93 – 0.81 (m, 3H), 0.79 (d, J = 6.6 Hz, 3H), 0.73 (d, J = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.11, 136.16, 131.89, 130.45, 121.77, 60.87, 60.58, 60.29, 60.00, 58.38, 43.00, 34.50, 25.07, 24.14, 21.02, 17.79; HRMS (NSI) calcd for $C_{16}H_{21}BrF_3O_2$ ($[M+H]^+$):381.0672 found 381.0676; IR (neat):2958, 2931, 2872, 1753, 1489, 1407, 1280, 1165, 1141, 1123, 1074, 1012, 979, 818, 758.

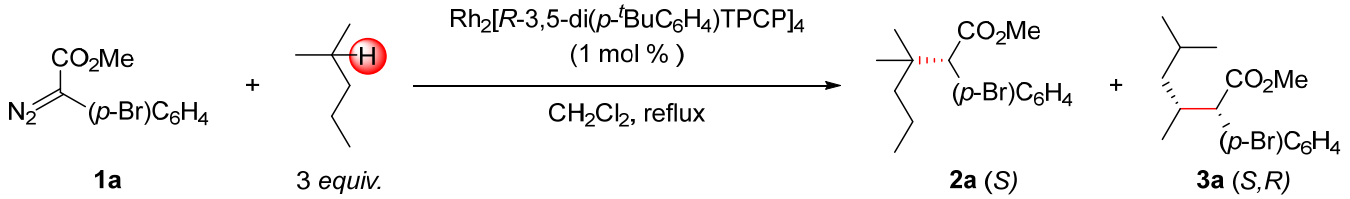
6.2 Catalyst and Diazo Screen for the Functionalization of 2-Methylpentane



1a 3 *equiv.* **2a** (*S*) **3a** (*S,R*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-DOSP)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (52 mg, 83% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a**:**3a**) of this reaction was 85:15 r.r. and the diastereoselectivity for **3a** was 3:1 d.r.. The enantioselectivity of this reaction for compound **2a** was -43 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 46.0 min (major) and 121.0 min (minor).

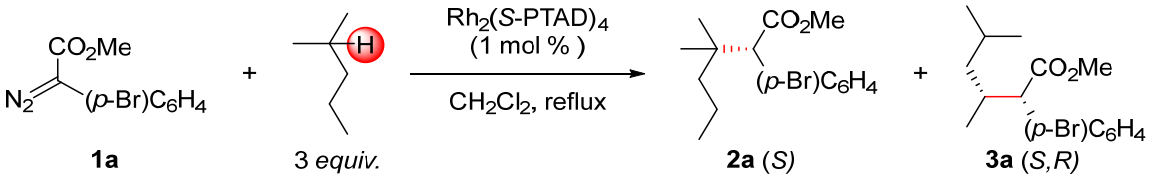


1a 3 *equiv.* **2a** (*S*) **3a** (*S,R*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (0.002 mmol, 5 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (14 mg, 23% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected, the major reason for the yield lost is the formation of carbene dimers. The regioselectivity (**2a**:**3a**) of this reaction was 35:65 r.r. and the diastereoselectivity for **3a** was 4:1 d.r.. The enantioselectivity of this reaction for compound **2a** was -10 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-

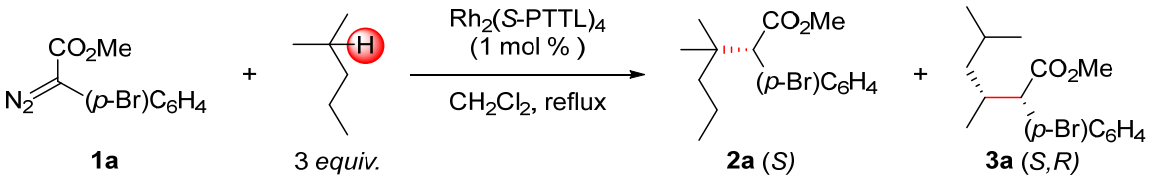
dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.9 min (major) and 125.5 min (minor).



1a 3 *equiv.* **2a** (*S*) **3a** (*S,R*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-PTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (31 mg, 50% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected, the major reason for the yield lost is the formation of carbene dimers. The regioselectivity (**2a**:**3a**) of this reaction was 74:26 r.r. and the diastereoselectivity for **3a** was 2:1 d.r.. The enantioselectivity of this reaction for compound **2a** was -34 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 46.9 min (major) and 122.4 min (minor).

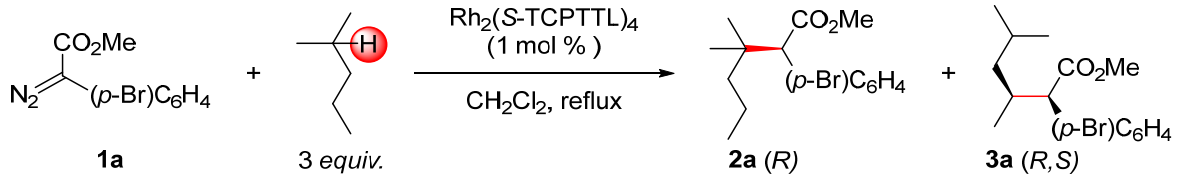


1a 3 *equiv.* **2a** (*S*) **3a** (*S,R*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-PTTL)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (50 mg, 80 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a**:**3a**) of this reaction was 74:26 r.r. and the diastereoselectivity for **3a** was 2:1 d.r.. The enantioselectivity of this reaction for

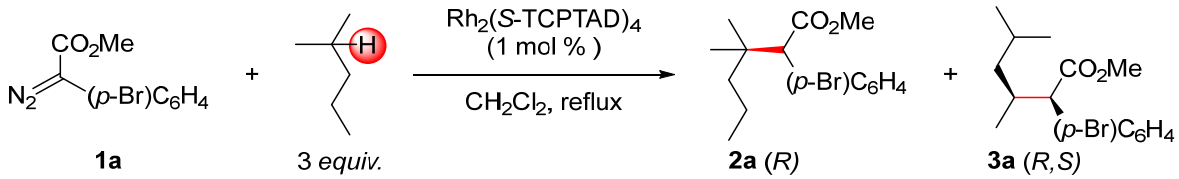
compound **2a** was -33 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 46.4 min (major) and 120.7 min (minor).



1a 3 *equiv.* **2a** (*R*) **3a** (*R,S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTTL)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (54 mg, 86 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a**:**3a**) of this reaction was 86:14 r.r. and the diastereoselectivity for **3a** was 2:1 d.r.. The enantioselectivity of this reaction for compound **2a** was 77 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.1 min (minor) and 117.1 min (major).

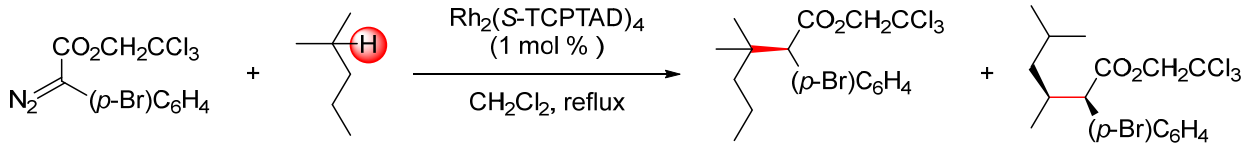


1a 3 *equiv.* **2a** (*R*) **3a** (*R,S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (56 mg, 89 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a**:**3a**) of this reaction was 87:13 r.r. and the diastereoselectivity for **3a** was 3:1 d.r.. The enantioselectivity of this reaction for

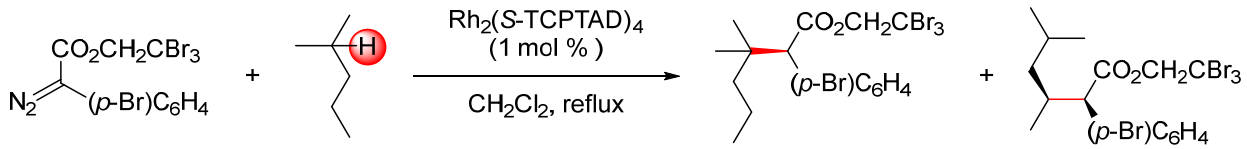
compound **2a** was 79 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.5 min (minor) and 119.8 min (major).



1b 3 *equiv.* **2b** (*R*) **3b** (*R,S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1b** (0.2 mmol, 74 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2b** as a colorless oil (64 mg, 74 % yield), and **3b** as a colorless oil (9 mg, 10 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2b** and **3b** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2b**:**3b**) of this reaction was 89:11 r.r. and the diastereoselectivity for **3b** was 2:1 d.r.. The enantioselectivity of this reaction for compound **2b** was 84 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.6 min (minor) and 91.9 min (major). The enantioselectivity of this reaction for compound **3b** was 77 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 210 nm, with the retention times at 93.4 min (major) and 113.0 min (minor).

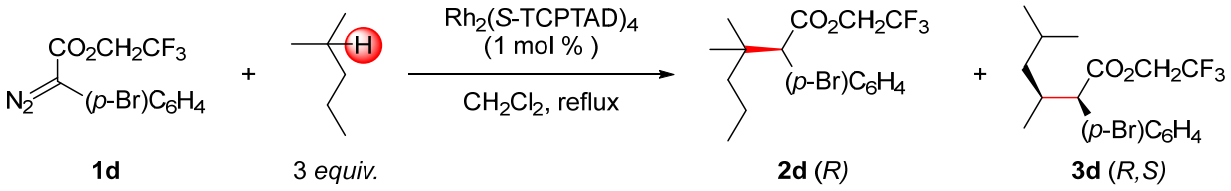


1c 3 *equiv.* **2c** (*R*) **3c** (*R,S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1c** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column

chromatography (hexanes/diethyl ether = 65/1) to afford compound **2c** as a colorless oil (87 mg, 77 % yield), and **3c** as a colorless oil (12 mg, 11 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2c** and **3c** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2c**:**3c**) of this reaction was 87:13 r.r. and the diastereoselectivity for **3c** was 2:1 d.r.. The enantioselectivity of this reaction for compound **2c** was 77 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.4 min (minor) and 122.6 min (major). The enantioselectivity of this reaction for compound **3c** was 79 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was ASH, 0.25 % isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 210 nm, with the retention times at 105.2 min (major) and 126.1 min (minor).

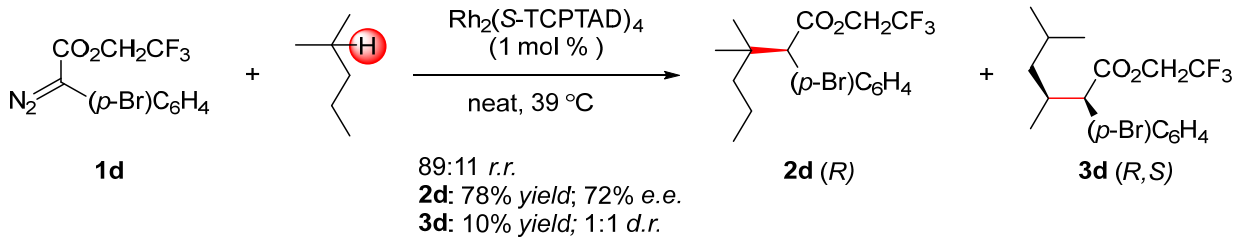


1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (63 mg, 83 % yield), and **3d** as a colorless oil (7 mg, 9 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d**:**3d**) of this reaction was 90:10 r.r. and the diastereoselectivity for **3d** was 2:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 77 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.3 min (minor) and 116.3 min (major). The enantioselectivity of this reaction for compound **3d** was 79 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was ASH, 0.25 % isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 210 nm, with the retention times at 104.8 min (major) and 126.9 min (minor).

6.3 Reaction Condition Screen for the Functionalization of 2-Methylpentane



1d

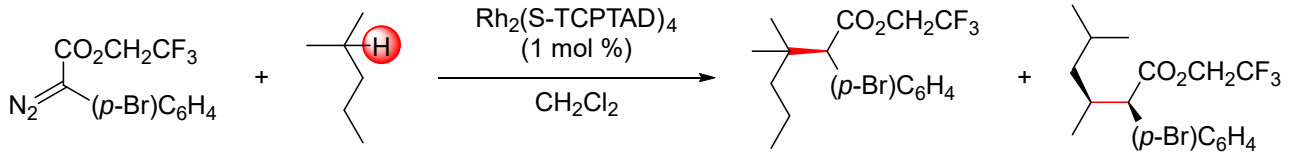
89:11 *r.r.*
2d: 78% *yield*; 72% *e.e.*
3d: 10% *yield;* 1:1 *d.r.*

2d (*R*)

3d (*R,S*)

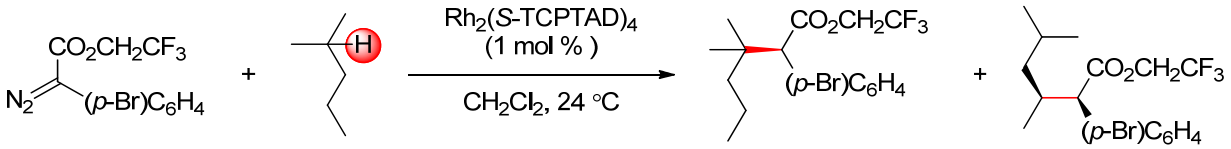
This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at 39 °C. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL 2-methylpentane, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (59 mg, 78 % yield) , and **3d** as a colorless oil (8 mg, 10 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected but **3d** wasn't idolated. The regioselectivity (**2d**:**3d**) of this reaction was 89:11 r.r. and the diastereoselectivity for **3d** was 1:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 72 % e.e.. The enantioselectivity analysis wer concudted in a different HPLC instrument with a different S,S-whelk chiral column, the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 25.8 min (minor) and 64.0 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.



1d 3 *equiv.* **2d** **3d**

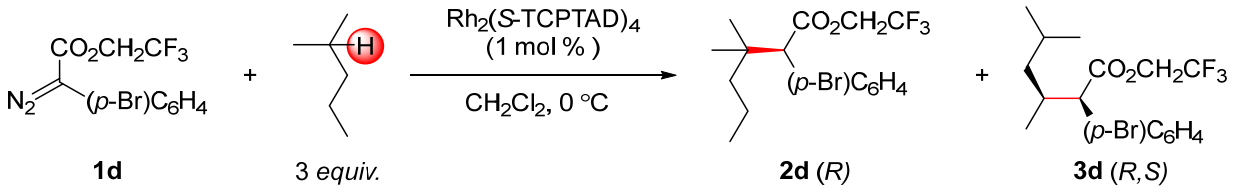
#	Temperature (°C)	r.r. (%)	e.e. (**2d**,%)	Yield (**2d**, %)	d.r. (**3d**,%)	Yield (**3d**, %)
1	39 (reflux)	90:10	77	83	2:1	9
2	r.t.	91:9	80	77	3:1	8
3	0	93:7	82	79	4:1	6
4	-10	95:5	84	78	5:1	4
5	-40	96:4	86	77	9:1	3
6	-78	96:4	80	65	7:1	0



1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at room temperature (24 °C). 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (59 mg, 77 % yield), and **3d** as a colorless oil (6 mg, 8 % yield).

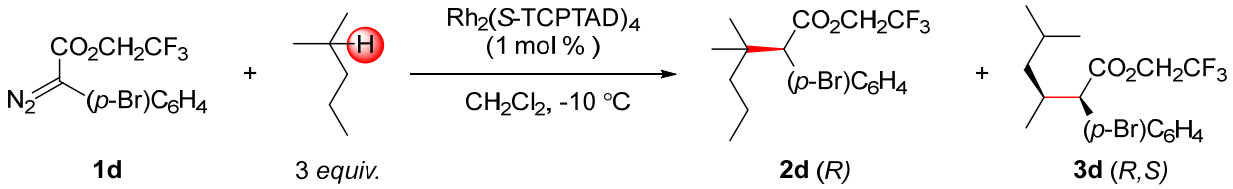
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d**:**3d**) of this reaction was 91:9 r.r. and the diastereoselectivity for **3d** was 3:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 80 % e.e.. The enantioselectivity analysis for the temperature study were concudted in a different HPLC instrument with a different S,S-whelk chiral column, both of the retention time of enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 25.8 min (minor) and 64.0 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.



1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at 0 °C. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (60 mg, 79 % yield), and **3d** as a colorless oil (5 mg, 6 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d**:**3d**) of this reaction was 91:9 r.r. and the diastereoselectivity for **3d** was 4:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 82 % e.e.. The enantioselectivity analysis wer concudted in a different HPLC instrument with a different S,S-whelk chiral column, the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 27.4 min (minor) and 68.5 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.

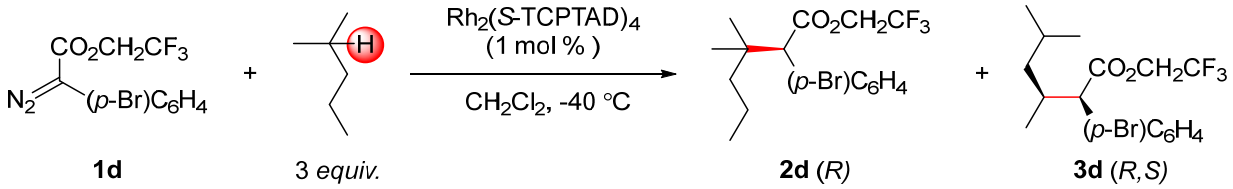


1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at -10 °C. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (59 mg, 78 % yield), and **3d** as a colorless oil (3 mg, 4 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d**:**3d**) of this reaction

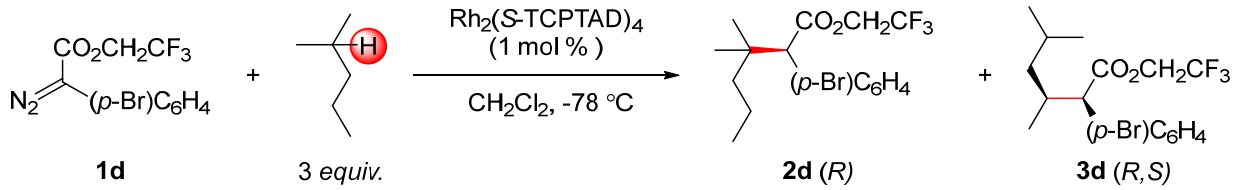
was 95:5 r.r. and the diastereoselectivity for **3d** was 5:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 84 % e.e.. The enantioselectivity analysis wer concudted in a different HPLC instrument with a different S,S-whelk chiral column, the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 27.5 min (minor) and 69.0 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.



1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at -40 °C. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (59 mg, 77 % yield), and **3d** as a colorless oil (2 mg, 3 % yield).

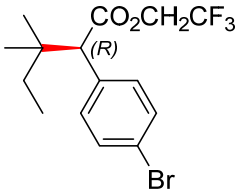
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d**:**3d**) of this reaction was 96:4 r.r. and the diastereoselectivity for **3d** was 9:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 86 % e.e.. The enantioselectivity analysis wer concudted in a different HPLC instrument with a different S,S-whelk chiral column, the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 27.6 min (minor) and 68.4 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.



This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at -78 °C. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (50 mg, 65 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected but **3d** wasn't idolated. The regioselectivity (**2d**:**3d**) of this reaction was 96:4 r.r. and the diastereoselectivity for **3d** was 7:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 80 % e.e.. The enantioselectivity analysis wer concudted in a different HPLC instrument with a different S,S-whelk chiral column, the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 28.8 min (minor) and 68.2 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.

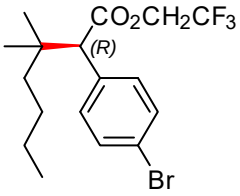
6.4 C–H Functionalization Products **4-27**



2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-3,3-dimethylpentanoate (**4**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **4** as a colorless oil (63 mg, 86% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **4** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_D$ -12.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 4.61 (dq, J = 12.7, 8.5 Hz, 1H), 4.27 (dq, J = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 1.42 – 1.34 (m, 1H), 1.25 (dq, J = 14.8, 7.5 Hz, 1H), 0.99 (s, 3H), 0.88 (s, 4H), 0.88 (t, J = 7.5 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.27, 134.13, 131.83, 131.20, 121.81, 60.18 (q, J = 36.7 Hz), 59.04, 37.58, 32.94, 23.88, 23.71, 8.27; HRMS (NSI) calcd for $C_{15}H_{19}BrF_3O_2$ ([M+H]$^+$):367.0515 found 367.0522; IR (neat):2969, 1752, 1489, 1414, 1276, 1164, 1122, 1076, 1012, 979, 822; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylpentan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 45.2 min (minor) and 119.0 min (major), 81 % e.e..

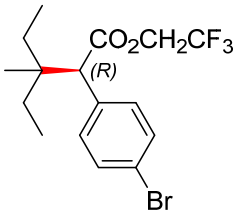


2,2,2-Trifluoroethyl (R)-2-(4-bromophenyl)-3,3-dimethylheptanoate (**5**). This compound was prepared according to the general procedure (at 39 °C and -40 °C) for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylhexane (0.6 mmol, 60 mg, 3.0 *equiv.*) in 0.5 mL

distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **5** as a colorless oil (39 °C: 60 mg, 76% yield; -40 °C: 51 mg, 65% yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **5** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 87:13 r.r. (39 °C) and 96:4 r.r. (-40 °C).

$[\alpha]^{20}_D$ -15.8° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 4.62 (dq, J = 12.7, 8.5 Hz, 1H), 4.25 (dq, J = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 1.36 – 1.14 (m, 6H), 1.00 (s, 3H), 0.89 (t, J = 7.1 Hz, 3H), 0.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.28, 134.15, 131.84, 131.21, 121.82, 60.18 (q, J = 36.5 Hz), 59.23, 40.49, 37.45, 26.14, 24.61, 24.23, 23.52, 14.23; HRMS (NSI) calcd for $C_{17}H_{23}BrF_3O_2$ ($[M+H]^+$):395.0828 found 395.0830; IR (neat):2961, 2933, 2872, 1753, 1489, 1414, 1278, 1165, 1122, 1076, 1012, 980, 827; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylheptan-1-ol prepared using DIBAL in DCM at -78 °C), at 39 °C, (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 45.5 min (minor) and 117.4 min (major), 77 % e.e.; at -40 °C, a different instrument was used, (S,S-Whelk, 1.5 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 130 min, UV 210 nm) retention times of 40.8 min (minor) and 102.7 min (major), 87 % e.e..

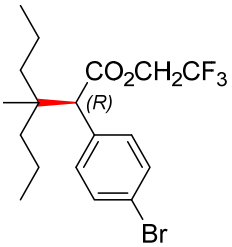


2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-3-ethyl-3-methylpentanoate (**6**). This compound was prepared according to the general procedure (at 39 °C and -40 °C) for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 3-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **6** as a colorless oil (39 °C: 56 mg, 73% yield; -40 °C: 49 mg, 64% yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **6** and the secondary C-H functionalization product, 2,2,2-trifluoroethyl (2R,3S)-2-(4-bromophenyl)-3,4-

dimethylhexanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 92:8 r.r. (39 °) and 98:2 r.r. (-40 °C).

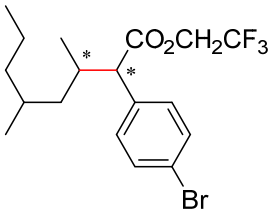
$[\alpha]^{20}_D$ -10.2° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 4.62 (dq, J = 12.7, 8.5 Hz, 1H), 4.24 (dq, J = 12.7, 8.5 Hz, 1H), 3.71 (s, 1H), 1.48 (dq, J = 14.8, 7.5 Hz, 1H), 1.34 (dq, J = 14.6, 7.4 Hz, 1H), 1.17 (ddt, J = 26.7, 14.1, 7.2 Hz, 2H), 0.95 (s, 3H), 0.87 (t, J = 7.5 Hz, 3H), 0.79 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.28, 134.04, 131.95, 131.17, 124.16, 121.78, 60.18 (q, J = 36.5 Hz), 56.82, 40.02, 28.65, 28.38, 20.49, 7.88, 7.71; HRMS (NSI) calcd for $C_{16}H_{21}BrF_3O_2$ ($[M+H]^+$):381.0672 found 381.0672; IR (neat):2969, 1752, 1489, 1414, 1383, 1275, 1161, 1121, 1077, 1012, 979, 828, 772, 717; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-ethyl-3-methylpentan-1-ol prepared using DIBAL in DCM at -78 °C), at 39 °C, (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 32.7 min (minor) and 119.9 min (major), 82 % e.e.; at -40 °C, a different instrument was used, (S,S-Whelk, 1.5 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 130 min, UV 210 nm) retention times of 29.7 min (minor) and 105.3 min (major), 92 % e.e..



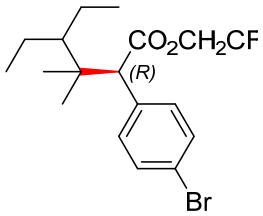
2,2,2-Trifluoroethyl (R)-2-(4-bromophenyl)-3-methyl-3-propylhexanoate (**7**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 4-methylheptane (0.6 mmol, 69 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **7** as a colorless oil (7 mg, 9% yield), however, the major product of this reaction was 2,2,2-trifluoroethyl 2-(4-bromophenyl)-3,5-dimethyloctanoate and the compound was also isolated as a colorless oil (64 mg, 79% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **7** and the secondary C-H functionalization product, 2,2,2-trifluoroethyl 2-(4-bromophenyl)-3,5-dimethyloctanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 11:89 r.r..

$[\alpha]^{20}_{D}$ -14.9° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 4.63 (dq, J = 12.7, 8.5 Hz, 1H), 4.23 (dq, J = 12.7, 8.5 Hz, 1H), 3.71 (s, 1H), 1.43 – 1.14 (m, 6H), 1.14 – 1.01 (m, 2H), 0.96 (s, 3H), 0.89 (t, J = 7.0 Hz, 3H), 0.83 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.31, 134.10, 131.96, 131.20, 125.67, 124.18, 121.81, 60.20 (*q, J* = 36.6 Hz), 57.53, 39.57, 39.24, 30.48, 21.49, 16.83, 16.62, 14.82, 14.79; HRMS (NSI) calcd for $C_{18}H_{23}BrF_3O_2$ ([M-H]$^-$):407.0839 found 407.0839; IR (neat): 2964, 1489, 1420, 1379, 1278, 1151, 1123, 1079, 1013, 979, 828, 772, 717; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3,6-trimethylheptan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 17.8 min (major) and 25.1 min (minor), 81 % e.e..



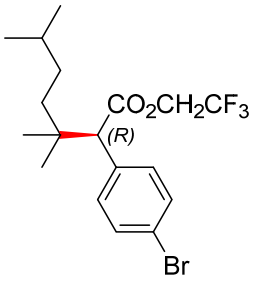
2,2,2-trifluoroethyl 2-(4-bromophenyl)-3,5-dimethyloctanoate. TLC (diethyl ether:hexanes, 1:10 v/v); the isolated material was a mixture of diastereomers, please see the 1H and 13C NMR spectra on Page 131-132 for detail; HRMS (NSI) calcd for C18H23BrF3O2 ([M-H]-):407.0839 found 407.0839; IR (neat): 2969, 1485, 1425, 1376, 1279, 1156, 1123, 1077, 1012, 978, 829, 770, 719.



2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-4-ethyl-3,3-dimethylhexanoate (**8**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 3-ethyl-2-methylpentane (0.6 mmol, 69 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **8** as a colorless oil (54 mg, 66% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **8** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_D$ -13.4° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 4.57 (dq, J = 12.7, 8.5 Hz, 1H), 4.27 (dq, J = 12.7, 8.5 Hz, 1H), 3.89 (s, 1H), 1.59 (dpt, J = 17.9, 7.5, 3.3 Hz, 3H), 1.15 (tp, J = 14.7, 7.4 Hz, 2H), 1.01 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H), 0.90 (t, J = 7.5 Hz, 4H), 0.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.42, 134.43, 132.14, 131.17, 121.79, 60.26 (q, J = 36.6 Hz), 57.07, 48.97, 41.43, 23.44, 23.17, 21.75, 21.56, 14.49, 14.03; HRMS (NSI) calcd for $C_{18}H_{23}BrF_3O_2$ ($[M-H]^-$):407.0828 found 407.0836; IR (neat):2967, 2932, 2878, 1752, 1489, 1414, 1277, 1165, 1138, 1115, 1076, 1012, 980, 823; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-4-ethyl-3,3-dimethylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 34.3 min (minor) and 109.6 min (major), 86 % e.e..

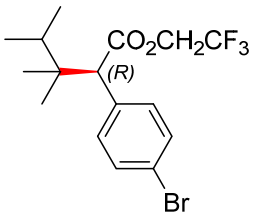


2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-3,3,6-trimethylheptanoate (**9**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2,5-dimethylhexane (0.6 mmol, 69 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **9** as a colorless oil (71 mg, 87% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **9** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_D$ -14.9° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 4.61 (dq, J = 12.7, 8.5 Hz, 1H), 4.26 (dq, J = 12.7, 8.5 Hz, 1H), 3.60 (s, 1H), 1.43 (dp, J = 12.8, 6.5 Hz, 1H), 1.36 – 1.27 (m, 1H), 1.24 – 1.13 (m, 3H), 1.00 (s, 3H), 0.88 (s, 4H), 0.86 (d, J = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.26, 134.15, 131.83, 131.20, 124.17, 121.96, 121.82, 60.18 (q, J = 36.5 Hz), 59.12, 38.52, 37.35, 32.87, 28.81, 24.66, 24.17, 22.76; HRMS (NSI) calcd for $C_{18}H_{23}BrF_3O_2$ ($[M-H]^-$):407.0828 found 407.0840; IR (neat):2960, 2871, 1753, 1489, 1469, 1414, 1369, 1278, 1165, 1124, 1077, 1012, 978, 825; HPLC (to improve the separation, the product was converted to 2-(4-

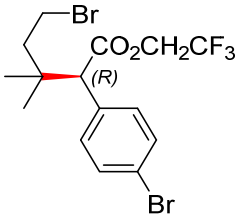
bromophenyl)-3,3,6-trimethylheptan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 44.1 min (minor) and 108.8 min (major), 78 % e.e..



2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-3,3,4-trimethylpentanoate (**10**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2,3-dimethylbutane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **10** as a colorless oil (71 mg, 93% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **10** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

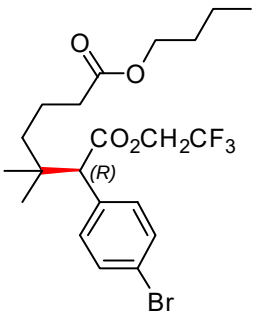
$[\alpha]^{20}_D$ -11.4° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 4.61 (dq, J = 12.7, 8.5 Hz, 1H), 4.24 (dq, J = 12.7, 8.5 Hz, 1H), 3.82 (s, 1H), 1.54 (hept, J = 6.7 Hz, 1H), 0.98 (s, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.89 (d, J = 6.8 Hz, 3H), 0.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.34, 134.32, 132.04, 131.19, 124.16, 121.81, 60.17 (q, J = 36.7 Hz), 57.06, 40.13, 34.30, 20.48, 20.45, 17.99, 17.26; HRMS (NSI) calcd for $C_{16}H_{21}BrF_3O_2$ ($[M+H]^+$):381.0672 found 381.0675; IR (neat):2970, 1752, 1489, 1277, 1166, 1146, 1117, 1076, 1012, 979, 834; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3,4-trimethylpentan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 33.0 min (minor) and 109.6 min (major), 83 % e.e..



2,2,2-Trifluoroethyl *(R)*-5-bromo-2-(4-bromophenyl)-3,3-dimethylpentanoate (**11**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 1-bromo-3-methylbutane (0.6 mmol, 91 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **11** as a colorless oil (62 mg, 70% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **11** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

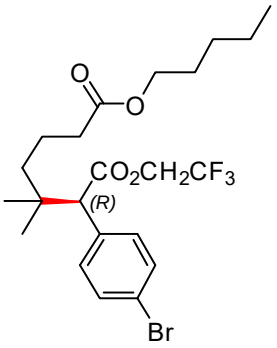
$[\alpha]^{20}_D$ -17.6° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 4.61 (dq, J = 12.6, 8.4 Hz, 1H), 4.30 (dq, J = 12.6, 8.4 Hz, 1H), 3.55 (s, 1H), 3.42 – 3.32 (m, 2H), 2.07 – 1.98 (m, 1H), 1.89 – 1.80 (m, 1H), 1.04 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.63, 133.10, 131.70, 131.51, 124.01, 122.30, 60.33 (q, J = 36.7 Hz), 59.58, 43.54, 38.51, 28.06, 24.24, 24.07; HRMS (NSI) calcd for $C_{15}H_{18}Br_2F_3O_2$ ($[M-H]^-$):444.9620 found 444.9622; IR (neat):2970, 1752, 1489, 1414, 1277, 1166, 1126, 1076, 1055, 1012, 977, 826; HPLC (to improve the separation, the product was converted to 5-bromo-2-(4-bromophenyl)-3,3-dimethylpentan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.3 % isopropanol in hexane, 0.3 mL/min, 10 mg/mL, 60 min, UV 210 nm) retention times of 30.5 min (minor) and 34.7 min (major), 84 % e.e..



7-Butyl 1-(2,2,2-trifluoroethyl) *(R)*-2-(4-bromophenyl)-3,3-dimethylheptanedioate (**12**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and butyl 5-methylhexanoate (0.6 mmol, 112 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **12** as a colorless oil (87 mg, 90% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **12** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_{D}$ -12.4° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 4.62 (dq, J = 12.7, 8.5 Hz, 1H), 4.27 (dq, J = 12.7, 8.5 Hz, 1H), 4.06 (t, J = 6.7 Hz, 2H), 3.59 (s, 1H), 2.35 – 2.19 (m, 2H), 1.68 – 1.62 (m, 2H), 1.62 – 1.56 (m, 2H), 1.41 – 1.31 (m, 3H), 1.24 – 1.16 (m, 1H), 1.02 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H), 0.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.62, 171.06, 133.82, 131.79, 131.25, 121.92, 121.90, 64.36, 60.17 (q, J = 36.5 Hz), 59.19, 39.85, 37.38, 34.73, 30.78, 29.82, 24.42, 24.15, 19.54, 19.25, 13.82; HRMS (NSI) calcd for $C_{21}H_{29}BrF_3O_4$ ($[M-H]^-$):481.1196 found 481.1201; IR (neat):2962, 2874, 1732, 1489, 1415, 1277, 1165, 1119, 1076, 1012, 978, 827; HPLC (ODH, 0.5 % isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 17.4 min (minor) and 22.4 min (major), 77 % e.e..

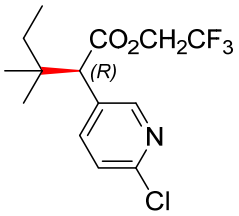


7-Pentyl 1-(2,2,2-trifluoroethyl) *(R)*-2-(4-bromophenyl)-3,3-dimethylheptanedioate (**13**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and pentyl 5-methylhexanoate (0.6 mmol, 120 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **13** as a colorless oil (72 mg, 73% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **13** and the most accessible secondary C-H insertion product, 2,2,2-trifluoroethyl 2-(4-bromophenyl)-3-methyl-6-((5-methylhexanoyl)oxy)hexanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_{D}$ -11.9° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 4.62 (dq, J = 12.7, 8.5 Hz, 1H), 4.26 (dq, J = 12.7, 8.5 Hz, 1H), 4.05 (t,

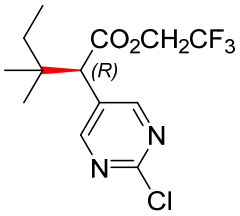
J = 6.8 Hz, 2H), 3.58 (s, 1H), 2.32 – 2.18 (m, 2H), 1.69 – 1.56 (m, 5H), 1.41 – 1.27 (m, 5H), 1.25 – 1.15 (m, 1H), 1.01 (s, 3H), 0.92 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.65, 171.08, 133.84, 131.80, 131.27, 121.95, 64.68, 60.19 (q, J = 36.7 Hz), 59.20, 39.88, 37.41, 34.76, 28.45, 28.20, 24.44, 24.18, 22.46, 19.57, 14.10; HRMS (NSI) calcd for $C_{22}H_{31}BrF_3O_4$ ($[M+H]^+$):495.1352 found 495.1354; IR (neat):2960, 2873, 1732, 1489, 1278, 1166, 1119, 1076, 1012, 978, 827; HPLC (ODH, 0.5 % isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 18.0 min (minor) and 22.7 min (major), 76 % e.e..



2,2,2-Trifluoroethyl *(R)*-2-(6-chloropyridin-3-yl)-3,3-dimethylpentanoate (**14**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (0.2 mmol, 56 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **14** as a colorless oil (39 mg, 60% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **14** the secondary C-H insertion product, 2,2,2-trifluoroethyl 2-(6-chloropyridin-3-yl)-3,4-dimethylpentanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 96:4 r.r.

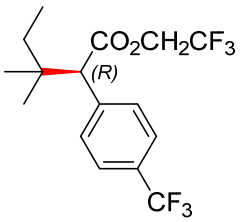
$[\alpha]^{20}_D$ +5.3° (c = 0.50, $CHCl_3$); TLC (diethyl ether:hexanes, 1:4 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 4.61 (p, *J* = 9.4, 8.7 Hz, 1H), 4.32 (p, *J* = 8.9 Hz, 1H), 3.63 (s, 1H), 1.37 (tt, *J* = 18.4, 8.7 Hz, 1H), 0.99 (s, 3H), 0.93 – 0.76 (m, 7H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.65, 150.86, 150.81, 139.71, 129.92, 123.61, 122.79 (q, *J* = 277.2 Hz), 60.29 (q, *J* = 36.7 Hz), 56.20, 37.75, 32.77, 23.67, 23.58, 8.10; HRMS (NSI) calcd for $C_{14}H_{18}ClF_3NO_2$ ($[M+H]^+$):324.0983 found 324.0977; IR (neat):2967, 2926, 2855, 1753, 1460, 1279, 1170, 1130, 1107, 1024, 980; HPLC (ODH, 0.5 % isopropanol in hexane, 0.5 mL/min, 5 mg/mL, 30 min, UV 210 nm) retention times of 18.3 min (major) and 25.6 min (minor), 68 % e.e..



2,2,2-Trifluoroethyl *(R)*-2-(2-chloropyrimidin-5-yl)-3,3-dimethylpentanoate (**15**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(2-chloropyrimidin-5-yl)-2-diazoacetate (0.2 mmol, 56 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **15** as a colorless oil (53 mg, 81 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **15** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

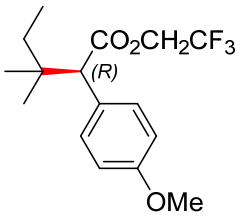
$[\alpha]^{20}_D$ +10.7° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:3 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (s, 2H), 4.65 (dq, *J* = 12.7, 8.3 Hz, 1H), 4.38 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.64 (s, 1H), 1.41 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.27 (dq, *J* = 7.5 Hz, 1H), 1.03 (s, 3H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.93 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.98, 160.82, 160.18, 127.72, 122.69 (q, J = 277.4 Hz), 60.60 (q, J = 36.8 Hz), 54.61, 38.00, 32.75, 29.71, 23.65, 23.61, 8.07; HRMS (NSI) calcd for $C_{13}H_{17}ClF_3N_2O_2$ ($[M+H]^+$):325.0936 found 325.0930; IR (neat):2969, 2926, 1752, 1576, 1546, 1401, 1278, 1162, 1130, 980; HPLC (ODH, 1 % isopropanol in hexane, 1 mL/min, 5 mg/mL, 20 min, UV 210 nm) retention times of 9.4 min (minor) and 10.5 min (major), 75 % e.e..



2,2,2-Trifluoroethyl *(R)*-3,3-dimethyl-2-(4-(trifluoromethyl)phenyl)pentanoate (**16**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (0.2 mmol, 62 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **16** as a colorless oil (63 mg, 89 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **16** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_{D}$ -2.0° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 4.62 (dq, J = 12.7, 8.5 Hz, 1H), 4.28 (dq, J = 12.7, 8.5 Hz, 1H), 3.70 (s, 1H), 1.45 – 1.35 (dq, J = 14.8, 7.5 Hz, 1H), 1.27 (dq, J = 14.8, 7.5 Hz, 1H), 1.01 (s, 3H), 0.90 (s, 3H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.94, 139.08, 130.40, 129.78 (q, J = 32.5 Hz), 124.84 (q, J = 3.7 Hz), 124.12 (q, J = 272.1 Hz), 122.90 (q, J = 277.4 Hz), 60.15 (q, J = 36.7 Hz), 59.33, 37.72, 32.88, 23.81, 23.65, 8.14; HRMS (NSI) calcd for $C_{16}H_{17}F_6O_2$ ($[M-H]^-$):355.1138 found 355.1137; IR (neat):2972, 1753, 1620, 1325, 1277, 1163, 1122, 1112, 1070, 1020, 980, 839; HPLC (to improve the separation, the product was converted to 3,3-dimethyl-2-(4-(trifluoromethyl)phenyl)pentan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 70 min, UV 210 nm) retention times of 23.5 min (minor) and 58.5 min (major), 74 % e.e..

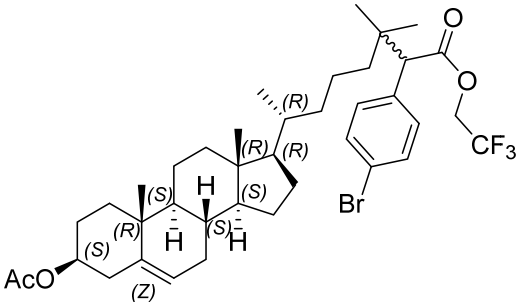


2,2,2-Trifluoroethyl *(R)*-2-(4-methoxyphenyl)-3,3-dimethylpentanoate (**17**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-diazo-2-(4-methoxyphenyl)acetate (0.2 mmol, 55 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **17** as a colorless oil (60 mg, 94 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **17** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_{D}$ -17.2° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 4.61 (dq, J = 12.7, 8.5 Hz, 1H), 4.24 (dq, J = 12.7, 8.5 Hz, 1H), 3.80 (s, 3H), 3.57 (s, 1H), 1.38 (dq, J = 15.0, 7.5 Hz, 1H), 1.26 (dq, J = 14.8, 7.5 Hz, 1H), 0.99 (s, 3H), 0.89 (s, 3H), 0.87 (t, J = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.71, 158.95, 131.09, 127.04, 123.04 (q, J = 277.4

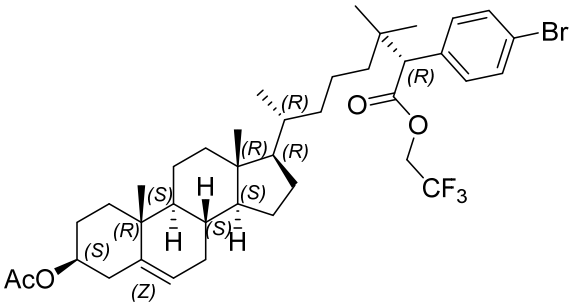
Hz), 113.31, 59.91 (q, J = 36.5 Hz), 58.74, 55.21, 37.36, 32.81, 23.79, 23.62, 8.18; HRMS (NSI) calcd for $C_{16}H_{20}F_3O_3$ ([M-H]$^-$):317.1370 found 317.1366; IR (neat):2969, 1752, 1611, 1512, 1277, 1249, 1166, 1123, 1037, 979, 832; HPLC (ODH, 0.3 % isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 50 min, UV 210 nm) retention times of 11.7 min (major) and 45.6 min (minor), 63 % e.e..



2,2,2-Trifluoroethyl (7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (**19**)

The diastereomers have no evident difference in the ^{1}H NMR and ^{13}C NMR spectra, presumably due to the fact that the newly generated chiral center is too far away from the existing chiral centers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 5.37 (d, J = 4.8 Hz, 1H), 4.66 – 4.56 (m, 2H), 4.26 (dq, J = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 2.32 (d, J = 6.8 Hz, 2H), 2.03 (s, 3H), 2.01 – 1.93 (m, 2H), 1.86 (d, J = 10.1 Hz, 2H), 1.80 (ddt, J = 13.2, 9.5, 4.9 Hz, 1H), 1.62 – 1.43 (m, 6H), 1.37 – 1.05 (m, 12H), 1.02 (s, 3H), 1.01 (s, 3H), 0.99 – 0.94 (m, 2H), 0.92 (d, J = 6.5 Hz, 3H), 0.89 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.25, 170.65, 139.76, 134.14, 131.80, 131.20, 124.15, 122.75, 121.94, 121.81, 74.09, 60.17 (q, J = 36.6 Hz), 59.21, 56.79, 56.14, 50.14, 42.45, 41.21, 39.85, 38.25, 37.56, 37.13, 36.71, 35.90, 32.01, 31.98, 28.32, 27.90, 24.64, 24.40, 24.30, 21.58, 21.15, 20.33, 19.44, 18.87, 11.96; HRMS (NSI) calcd for $C_{37}H_{51}BrF_3O_2$ ([M-$C_2H_3O_2$]$^+$):663.3019 found 663.3030.

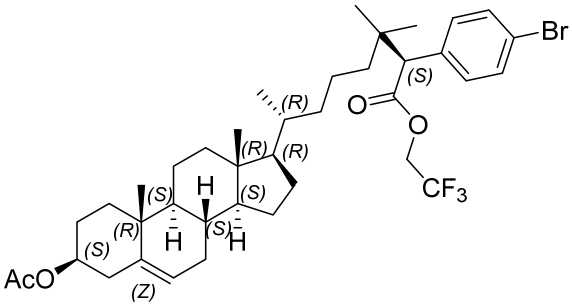


2,2,2-Trifluoroethyl (2*R*,7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (**19*R***). This compound was prepared according to the general procedure

for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (cholesteryl acetate) **18** (0.2 mmol, 86 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **19*R*** as a white solid (113 mg, 78 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **19*R*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

m.p.:143-145 °C; $[\alpha]^{20}_D$ -41.9° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2941, 2869, 1752, 1732, 1489, 1467, 1373, 1278, 1242, 1167, 1123, 1033, 1012, 979, 831; HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7S)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 10.0 min (minor) and 21.3 min (major), 11:1 d.r.

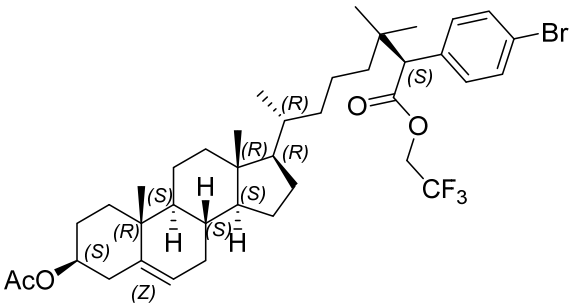


2,2,2-Trifluoroethyl (2*S*,7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (**19*S***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (cholesteryl acetate) **18** (0.2 mmol, 86 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed

by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **19*S*** as a white solid (124 mg, 86 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **19*S*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

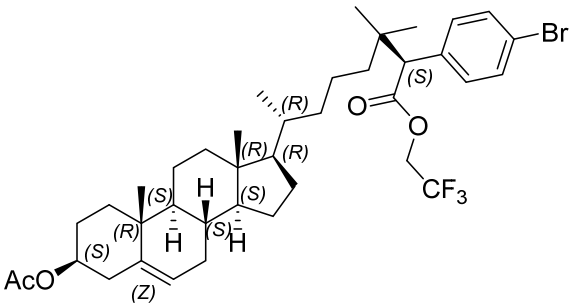
m.p.:144-146 °C; $[\alpha]^{20}_D$ -9.2° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2941, 2868, 1752, 1732, 1489, 1374, 1279, 1246, 1168, 1125, 1033, 1012, 979, 758; HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 9.9 min (major) and 21.5 min (minor), 11:1 d.r.



2,2,2-Trifluoroethyl (2*S*,7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (**19*S***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.0002 mmol, 0.4 mg, 0.1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (cholesteryl acetate) **18** (0.2 mmol, 86 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **19*S*** as a white solid (120 mg, 83 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **19*S*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

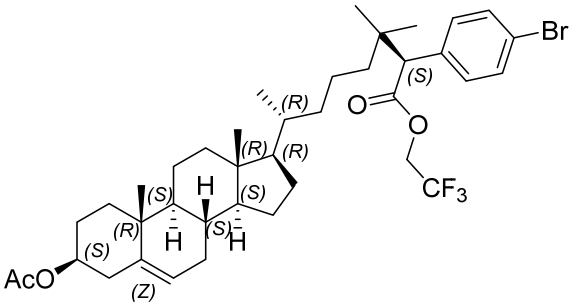
HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 9.9 min (major) and 21.5 min (minor), 9:1 d.r.



2,2,2-Trifluoroethyl (2*S*,7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (**19*S***). This compound was prepared according to the general procedure for C–H functionalization reactions at **room temperature (24 °C)**. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (cholesteryl acetate) **18** (0.2 mmol, 86 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **19*S*** as a white solid (117 mg, 80 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **19*S*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

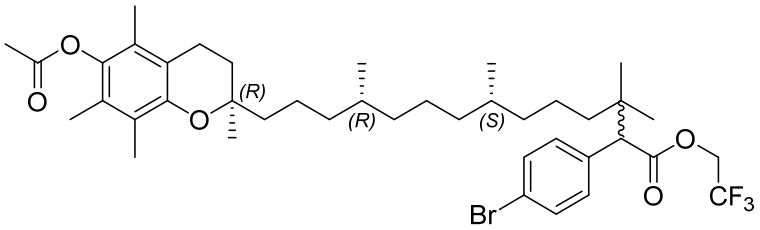
HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 10.9 min (major) and 24.2 min (minor), 13:1 d.r.



2,2,2-Trifluoroethyl (2*S*,7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (**19*S***). This compound was prepared according to the general procedure for C–H functionalization reactions at **0 °C**. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (cholesteryl acetate) **18**(0.2 mmol, 86 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **19*S*** as a white solid (88 mg, 60 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **19*S*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

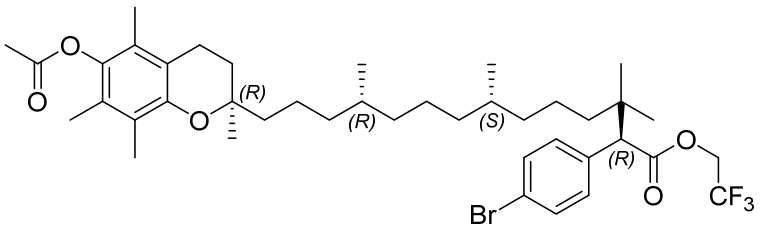
HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 10.9 min (major) and 24.1 min (minor), 16:1 d.r.



2,2,2-Trifluoroethyl (7*S*,11*R*)-14-((*R*)-6-acetoxy-2,5,7,8-tetramethylchroman-2-yl)-2-(4-bromophenyl)-3,3,7,11-tetramethyltetradecanoate (**21**)

The diastereomers have no evident difference in the ^{1}H NMR and ^{13}C NMR spectra, presumably due to the fact that the newly generated chiral center is too far away from the existing chiral centers.

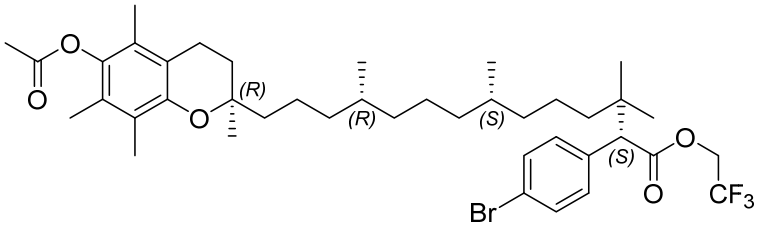
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.3 Hz, 3H), 4.60 (dq, J = 12.7, 8.5 Hz, 1H), 4.26 (dq, J = 12.8, 8.5 Hz, 1H), 3.59 (s, 1H), 2.59 (t, J = 6.7 Hz, 2H), 2.33 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.81 (dt, J = 13.9, 7.1 Hz, 1H), 1.78 – 1.70 (m, 1H), 1.55 (d, J = 11.4 Hz, 2H), 1.44 (ddt, J = 25.1, 13.6, 6.9 Hz, 1H), 1.40 – 1.35 (m, 2H), 1.35 – 1.26 (m, 7H), 1.23 (s, 5H), 1.15 – 1.02 (m, 4H), 1.00 (s, 3H), 0.90 (s, 3H), 0.86 (d, J = 5.7 Hz, 3H), 0.85 (d, J = 6.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.10, 168.74, 148.39, 139.49, 133.00, 130.66, 130.05, 125.63, 123.87, 122.00, 121.89 (q, J = 277.1 Hz), 120.66, 116.33, 74.02, 59.03 (q, J = 36.6 Hz), 58.14, 39.88, 36.67, 36.42, 36.39, 36.38, 31.78, 31.70, 30.91, 28.69, 28.35, 23.44, 23.14, 21.68, 20.18, 20.00, 19.57, 19.55, 18.70, 18.61, 13.11, 11.93, 11.08, 10.81, -1.02.; HRMS (NSI) calcd for $C_{37}H_{51}BrF_3O_2$ ($[M-C_4H_7O_3]^+$):663.3019 found 663.3019.



2,2,2-Trifluoroethyl (2*R*,7*S*,11*R*)-14-((*R*)-6-acetoxy-2,5,7,8-tetramethylchroman-2-yl)-2-(4-bromophenyl)-3,3,7,11-tetramethyltetradecanoate (**21*R***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and *(R)*-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl acetate (D-alpha-tocopheryl acetate or Vitamin E) **20** (0.2 mmol, 95 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **21*R*** as a colorless oil (98 mg, 64 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **21*R*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_D$ -7.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2927, 2868, 1754, 1489, 1459, 1414, 1368, 1278, 1208, 1166, 1127, 1076, 1011, 979; HPLC (OJH, 0.25 % isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 80 min, UV 254 nm) retention times of 25.7 min (major) and 37.9 min (minor), 11:1 d.r.

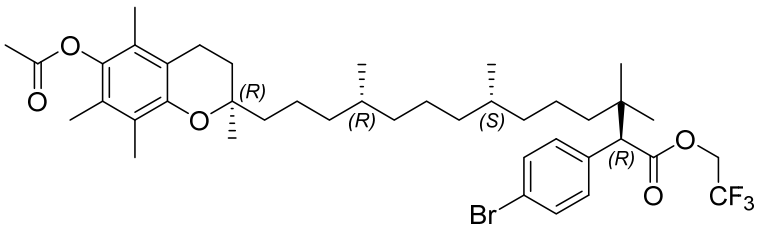


2,2,2-Trifluoroethyl (*2S,7S,11R*)-14-((*R*)-6-acetoxy-2,5,7,8-tetramethylchroman-2-yl)-2-(4-bromophenyl)-3,3,7,11-tetramethyltetradecanoate (**21*S***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and *(R)*-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl acetate (D-alpha-tocopheryl acetate or Vitamin E) **20** (0.2 mmol, 95 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **21*S*** as a colorless oil (126 mg, 82 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **21*S*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_D$ +5.3° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2927, 2867, 1755, 1489, 1457, 1417, 1368, 1279, 1208, 1167, 1128, 1076, 1012, 979; HPLC (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 80 min, UV 254 nm) retention times of 26.9 min (minor) and 39.9 min (major), 11:1 d.r.

In the functionalization of compound **20** (Vitamin E acetate), even though Rh_2(*S*-TCPTAD)$_4$ and Rh_2(*R*-TCPTAD)$_4$ gave the same calculated d.r. at 39 °C (reflux CH_2Cl_2), actually in the HPLC spectra Rh_2(*S*-TCPTAD)$_4$ gave slightly higher ratio, so we used Rh_2(*S*-TCPTAD)$_4$ to conduct the temperature study.

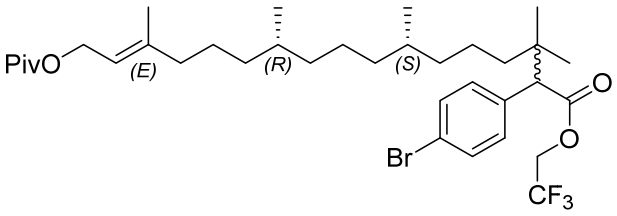


2,2,2-Trifluoroethyl (2*R*,7*S*,11*R*)-14-((*R*)-6-acetoxy-2,5,7,8-tetramethylchroman-2-yl)-2-(4-bromophenyl)-3,3,7,11-tetramethyltetradecanoate (**21*R***). This compound was prepared according to the general procedure for C–H functionalization reactions at **room temperature (24 °C)**. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and *(R)*-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl acetate (D-alpha-tocopheryl acetate or Vitamin E) **20** (0.2 mmol, 95 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The

crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **21*R*** as a colorless oil (92 mg, 60 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **21*R*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

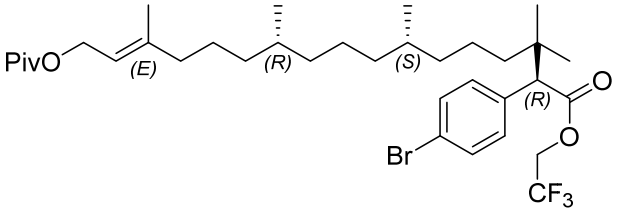
HPLC (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 80 min, UV 254 nm) retention times of 24.5 min (minor) and 39.3 min (major), >20:1 d.r.



2,2,2-Trifluoroethyl (7*S*,11*R*,*E*)-2-(4-bromophenyl)-3,3,7,11,15-pentamethyl-17-(pivaloyloxy)heptadec-15-enoate (23).

The diastereomers have no evident difference in the ^{1}H NMR and ^{13}C NMR spectra, presumably due to the fact that the newly generated chiral center is too far away from the existing chiral centers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 5.31 (tq, J = 6.9, 1.2 Hz, 1H), 4.61 (dq, J = 12.7, 8.5 Hz, 1H), 4.57 (d, J = 6.9 Hz, 2H), 4.26 (dq, J = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 2.00 (dp, J = 15.1, 7.7, 7.2 Hz, 2H), 1.68 (s, 3H), 1.40 – 1.21 (m, 12H), 1.19 (s, 9H), 1.15 – 1.01 (m, 4H), 1.00 (s, 3H), 0.89 (s, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H), 0.85 – 0.83 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.73, 171.26, 142.29, 134.13, 131.81, 131.20, 121.82, 118.62, 61.46, 60.17 (q, J = 36.7 Hz), 59.27, 41.02, 39.94, 38.87, 37.84, 37.53, 37.49, 36.68, 32.93, 32.82, 29.84, 27.35, 25.16, 24.62, 24.60, 24.28, 21.34, 19.86, 19.83, 16.48; HRMS (NSI) calcd for $C_{35}H_{58}O_4BrF_3N$ ($[M+NH_4]^+$):692.3496 found 692.3516.

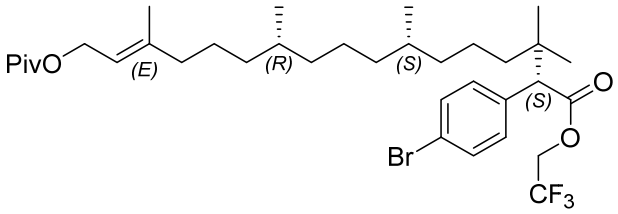


2,2,2-Trifluoroethyl (2*R*,7*S*,11*R*,*E*)-2-(4-bromophenyl)-3,3,7,11,15-pentamethyl-17-(pivaloyloxy)heptadec-15-enoate (**23*R***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL

distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22** (0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **23*R*** as a colorless oil (91 mg, 67 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **23*R* and compound 24** were observed, no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 77:23 r.r..

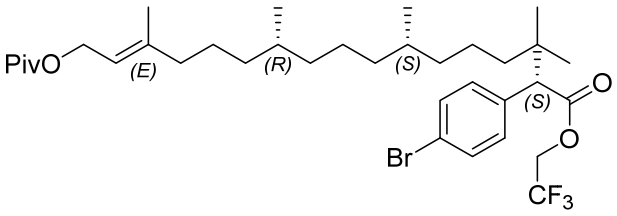
$[\alpha]^{20}_D$ -10.0° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2929, 2869, 1754, 1725, 1489, 1480, 1461, 1279, 1152, 1125, 1076, 1032, 1012, 979, 830, 770; HPLC (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 16.1 min (major) and 19.4 min (minor), 11:1 d.r.



2,2,2-Trifluoroethyl (2*S*,7*S*,11*R*,*E*)-2-(4-bromophenyl)-3,3,7,11,15-pentamethyl-17-(pivaloyloxy)heptadec-15-enoate (**23*S***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22** (0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **23*S*** as a colorless oil (93 mg, 69 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **23*S* and compound 24** were observed, no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 78:22 r.r..

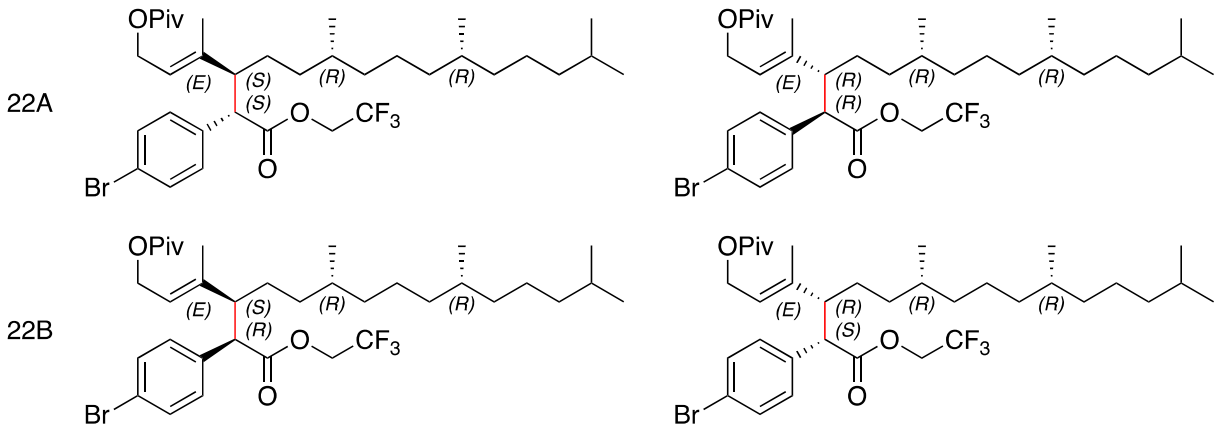
$[\alpha]^{20}_D$ +11.6° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2930, 2869, 1755, 1726, 1489, 1458, 1280, 1165, 1126, 1077, 1012, 980; HPLC (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 16.1 min (major) and 19.2 min (minor), 12:1 d.r.



2,2,2-Trifluoroethyl (2*S*,7*S*,11*R*,*E*)-2-(4-bromophenyl)-3,3,7,11,15-pentamethyl-17-(pivaloyloxy)heptadec-15-enoate (**23*S***). This compound was prepared according to the general procedure for C–H functionalization reactions at room temperature (24 °C). 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22** (0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **23*S*** as a colorless oil (70 mg, 52 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **23*S* and compound 24** were observed, no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 89:11 r.r..

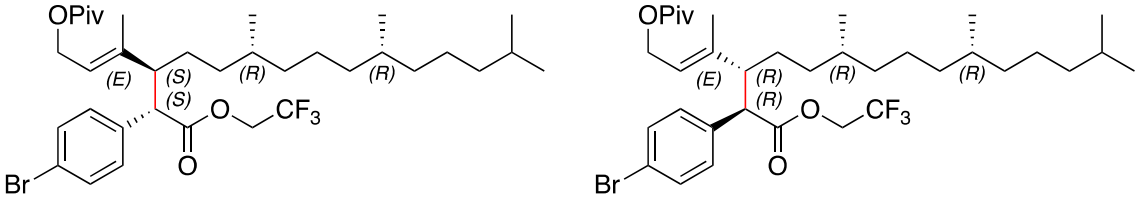
HPLC (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 16.1 min (major) and 19.2 min (minor), 12:1 d.r.



2,2,2-Trifluoroethyl (6*R*,10*R*)-2-(4-bromophenyl)-6,10,14-trimethyl-3-(4-(pivaloyloxy)but-2-en-2-yl)pentadecanoate (**24**). These compounds were prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ or Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22**(0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled

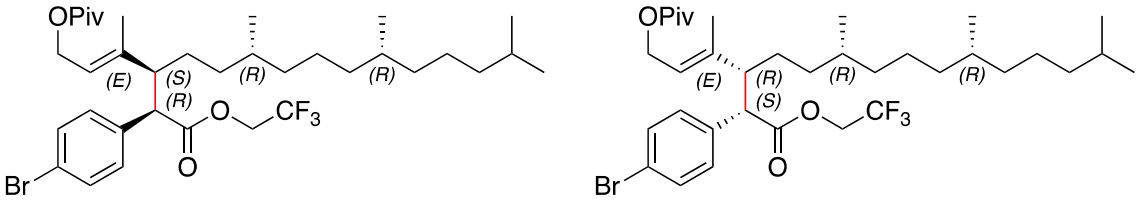
CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **24** as a colorless oil (27 mg, 20 % yield for Rh_2(*S*-TCPTAD)$_4$ and 28 mg, 21 % yield for Rh_2(*R*-TCPTAD)$_4$).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that the diastereomeric ratio (d.r.) between **(±) 24** (***S, S***) and **(±) 24** (***S, R***) was 2:1 for both Rh_2(*S*-TCPTAD)$_4$ and Rh_2(*R*-TCPTAD)$_4$.



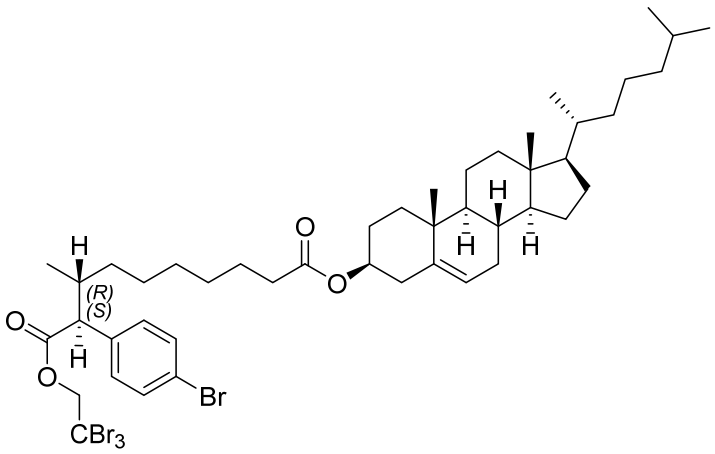
(±)2,2,2-Trifluoroethyl (2*S*,3*S*,6*R*,10*R*)-2-(4-bromophenyl)-6,10,14-trimethyl-3-((*E*)-4-(pivaloyloxy)but-2-en-2-yl)pentadecanoate [(±) 24 (*S, S*)]. These compounds were prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ or Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22** (0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **(±) 24** (***S, S***) as colorless oil (18 mg, 13 % yield for Rh_2(*S*-TCPTAD)$_4$ and 19 mg, 14 % yield for Rh_2(*R*-TCPTAD)$_4$).

TLC (diethyl ether:hexanes, 1:10 v/v); ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 5.25 (t, J = 7.1 Hz, 1H), 4.56 (dq, J = 12.7, 8.4 Hz, 1H), 4.39 – 4.26 (m, 3H), 3.60 (d, J = 11.6 Hz, 1H), 2.80 (td, J = 11.3, 3.3 Hz, 1H), 1.54 (s, 3H), 1.58 – 1.47 (m, 1H), 1.42 (s, 3H), 1.36 (ddt, J = 9.8, 6.6, 3.2 Hz, 2H), 1.34 – 1.26 (m, 2H), 1.26 – 1.20 (m, 3H), 1.22 – 1.17 (m, 3H), 1.15 (dddt, J = 12.0, 9.2, 6.4, 2.7 Hz, 2H), 1.10 (s, 9H), 1.09 – 1.00 (m, 2H), 1.02 – 0.93 (m, 1H), 0.87 (d, J = 6.6 Hz, 6H), 0.84 (d, J = 6.6 Hz, 3H), 0.82 (d, J = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.20, 171.71, 138.98, 135.29, 131.56, 130.25, 124.26, 122.79 (q, J = 277.6 Hz), 121.70, 60.49 (q, J = 36.5 Hz), 60.12, 54.92, 51.78, 39.37, 38.66, 37.64, 37.38, 37.31, 34.36, 32.78, 32.41, 29.71, 28.45, 27.98, 27.11, 24.80, 24.53, 22.72, 22.62, 19.72, 19.28, 12.25; HRMS (NSI) calcd for $C_{35}H_{53}BrO_4F_3$ ([M-H]$^-$):673.3085 found 673.3091; IR (neat):2954, 2925, 2854, 1756, 1727, 1489, 1462, 1281, 1168, 1147, 1075, 1012, 980.



(±)2,2,2-Trifluoroethyl (2*S*,3*R*,6*R*,10*R*)-2-(4-bromophenyl)-6,10,14-trimethyl-3-((*E*)-4-(pivaloyloxy)but-2-en-2-yl)pentadecanoate [**(±) 24 (*S*, *R*)**]. These compounds were prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ or Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22** (0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **(±) 24 (*S*, *R*)** as colorless oil (9 mg, 7 % yield for both Rh_2(*S*-TCPTAD)$_4$ and Rh_2(*R*-TCPTAD)$_4$).

TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 9.1 Hz, 5H), 5.49 (t, J = 6.7 Hz, 1H), 4.57 (qd, J = 12.7, 6.7 Hz, 2H), 4.44 (dq, J = 12.6, 8.5 Hz, 1H), 4.24 (dq, J = 12.7, 8.4 Hz, 1H), 3.63 (d, J = 11.6 Hz, 1H), 2.72 – 2.63 (m, 1H), 1.70 (s, 3H), 1.58 – 1.47 (m, 1H), 1.36 – 1.19 (m, 9H), 1.19 (s, 9H), 1.17 – 1.00 (m, 4H), 1.02 – 0.92 (m, 1H), 0.87 (d, J = 6.6 Hz, 6H), 0.91 – 0.82 (m, 4H), 0.81 (d, J = 6.6 Hz, 3H), 0.70 (d, J = 6.6 Hz, 3H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.34, 170.86, 139.93, 135.17, 131.89, 130.34, 123.63, 122.89 (q, J = 277.3 Hz), 121.94, 60.69, 60.53 (q, J = 36.7 Hz), 55.11, 52.22, 39.37, 38.73, 37.40, 37.29, 36.43, 33.97, 32.75, 32.39, 29.71, 27.98, 27.18, 26.72, 24.80, 24.18, 22.73, 22.63, 19.95, 19.71, 14.13, 12.56; HRMS (NSI) calcd for $C_{35}H_{53}BrO_4F_3$ ([M-H]$^-$):673.3085 found 673.3074; IR (neat):2954, 2924, 2854, 1756, 1730, 1488, 1461, 1281, 1168, 1149, 1075, 1012.

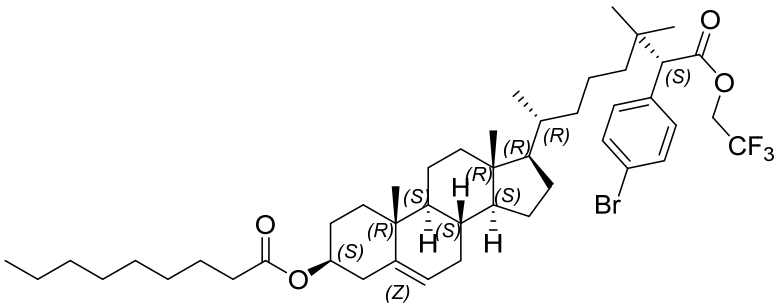


10-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) 1-(2,2,2-tribromoethyl) (2*S*,3*R*)-2-(4-bromophenyl)-3-methyldecanedioate (**26**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1c** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (cholesteryl

pelargonate) **25** (0.6 mmol, 105 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **26** as a colorless oil (137 mg, 68 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that the regioselectivity of this reaction was 3:87:10 r.r.. 3% of product was the C-H insertion at the most accessible primary position (the last primary carbon) of the *n*-alkyl chain, another 10% of the product was the C-H insertion at the most accessible tertiary position (the isopropyl tertiary carbon) of another alkyl chain. For this reaction, two new chiral centers will be generated, compound **26** is (*S*,*R*), other potential diastereomers are (*R*,*S*), (*S*,*S*) and (*R*,*R*), the ratio of [(*S*,*R*) + (*R*,*S*)] to [(*S*,*S*) + (*R*,*R*)] is 9.27:1.

$[\alpha]^{20}_D$ -4.6° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 5.37 (d, J = 4.7 Hz, 1H), 4.92 (d, J = 12.3 Hz, 1H), 4.84 (d, J = 12.3 Hz, 1H), 3.39 (d, J = 10.6 Hz, 1H), 2.33 – 2.24 (m, 3H), 2.22 (t, J = 7.5 Hz, 2H), 2.03 – 1.93 (m, 2H), 1.88 – 1.78 (m, 3H), 1.52 (dddd, J = 50.3, 26.9, 12.9, 5.1 Hz, 10H), 1.40 – 1.26 (m, 6H), 1.25 – 1.09 (m, 12H), 1.07 (d, J = 6.5 Hz, 3H), 1.02 (s, 3H), 1.01 – 0.93 (m, 3H), 0.91 (d, J = 6.5 Hz, 4H), 0.87 (d, J = 2.7 Hz, 3H), 0.86 (d, J = 2.7 Hz, 3H), 0.68 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.15, 171.45, 139.66, 136.20, 131.68, 130.52, 122.59, 121.54, 77.06, 73.68, 58.19, 56.67, 56.11, 50.00, 42.30, 39.71, 39.50, 38.15, 36.98, 36.58, 36.17, 36.00, 35.78, 35.18, 34.58, 33.19, 31.89, 31.85, 29.69, 29.19, 28.95, 28.22, 28.00, 27.80, 26.06, 24.88, 24.27, 23.82, 22.82, 22.56, 21.02, 19.33, 18.71, 17.93, 14.12, 11.85; HRMS (NSI) calcd for $C_{46}H_{69}Br_4O_4$ ($[M+H]^+$):1003.1903 found 1003.1937; IR (neat):2932, 2853, 2361, 1733, 1488, 1466, 1365, 1256, 1173, 1128, 1074, 1011, 756, 719; HPLC (to improve the separation, the product was converted to 3-methyl-2-(4-(trifluoromethyl)phenyl)decane-1,10-diol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 4 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 90 min, UV 210 nm) retention times of 47.5 min (major) and 78.8 min (minor), the ratio of (*S*,*R*) to (*R*,*S*) is 39:1. Combined with the ratio measured by crude ^{1}H NMR spectrum, the calculated d.r. of this reaction is 9:1.

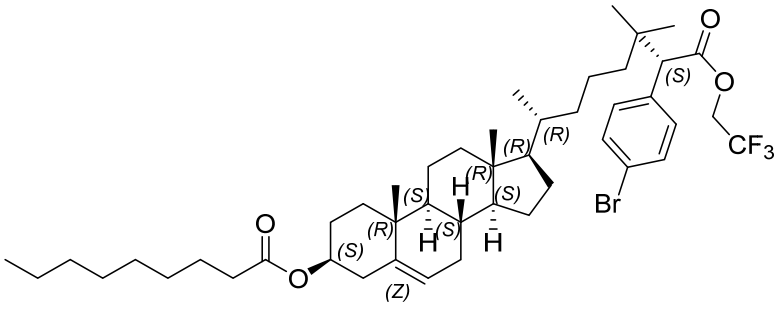


(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,7*S*)-7-(4-Bromophenyl)-6,6-dimethyl-8-oxo-8-(2,2,2-trifluoroethoxy)octan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-

cyclopenta[a]phenanthren-3-yl nonanoate (27). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (cholesteryl pelargonate) **25** (0.6 mmol, 105 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **27** as a white solid (122 mg, 74 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that the regioselectivity of this reaction was 87:13 r.r., and the minor regioisomer was the C-H insertion at the most accessible secondary position (the second last secondary carbon) of the *n*-alkyl chain.

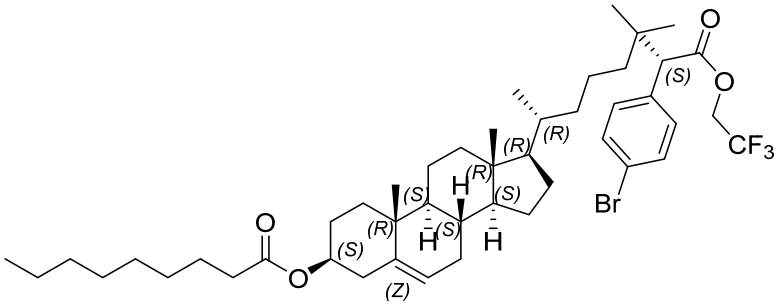
$[\alpha]^{20}_D$ -5.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 5.37 (d, J = 4.8 Hz, 1H), 4.66 – 4.55 (m, 2H), 4.27 (dq, J = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 2.36 – 2.29 (m, 2H), 2.27 (t, J = 7.5 Hz, 2H), 2.03 – 1.94 (m, 2H), 1.90 – 1.75 (m, 3H), 1.68 – 1.54 (m, 5H), 1.54 – 1.42 (m, 3H), 1.42 – 1.33 (m, 2H), 1.33 – 1.23 (m, 15H), 1.23 – 1.04 (m, 6H), 1.01 (d, J = 10.7 Hz, 6H), 0.98 – 0.95 (m, 1H), 0.92 (d, J = 6.5 Hz, 3H), 0.89 (s, 3H), 0.88 (t, J = 7.0 Hz, 3H), 0.67 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.31, 171.12, 139.72, 134.03, 131.68, 131.07, 122.92 (q, J = 277.3 Hz), 122.55, 121.69, 73.66, 60.06 (q, J = 36.6 Hz), 59.12, 56.66, 56.07, 50.02, 42.33, 41.10, 39.72, 38.16, 37.44, 37.01, 36.60, 35.82, 34.73, 31.89, 31.86, 31.81, 29.71, 29.23, 29.13, 28.23, 27.82, 25.07, 24.47, 24.27, 24.21, 22.65, 21.03, 20.30, 19.33, 18.74, 14.10, 11.84; HRMS (NSI) calcd for $C_{37}H_{51}BrF_3O_2$ ([M-$C_9H_{17}O_2$]$^-$):663.3019 found 663.3037; IR (neat):2930, 2853, 1751, 1734, 1489, 1457, 1279, 1168, 1124, 1012, 980; HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 9.9 min (major) and 21.3 min (minor), 6:1 d.r.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,7*S*)-7-(4-Bromophenyl)-6,6-dimethyl-8-oxo-8-(2,2,2-trifluoroethoxy)octan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (27). This compound was prepared according to the general procedure for C–H functionalization reactions at **room temperature (24 °C)**. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (cholesteryl pelargonate) **25** (0.6 mmol, 105 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **27** as a white solid (112 mg, 68 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that the regioselectivity of this reaction was 89:11 r.r., and the minor regioisomer was the C-H insertion at the most accessible secondary position (the second last secondary carbon) of the *n*-alkyl chain.

HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 11.8 min (major) and 24.06 min (minor), >20:1 d.r.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,7*S*)-7-(4-Bromophenyl)-6,6-dimethyl-8-oxo-8-(2,2,2-trifluoroethoxy)octan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (27). This compound was prepared according to the general procedure for C–H functionalization reactions at **0 °C**. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (cholesteryl pelargonate) **25** (0.6 mmol, 105 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was

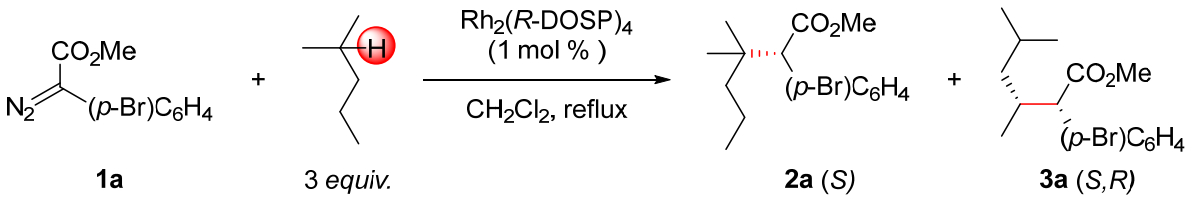
analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **27** as a white solid (107 mg, 65 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that the regioselectivity of this reaction was 92:8 r.r., and the minor regioisomer was the C-H insertion at the most accessible secondary position (the second last secondary carbon) of the *n*-alkyl chain.

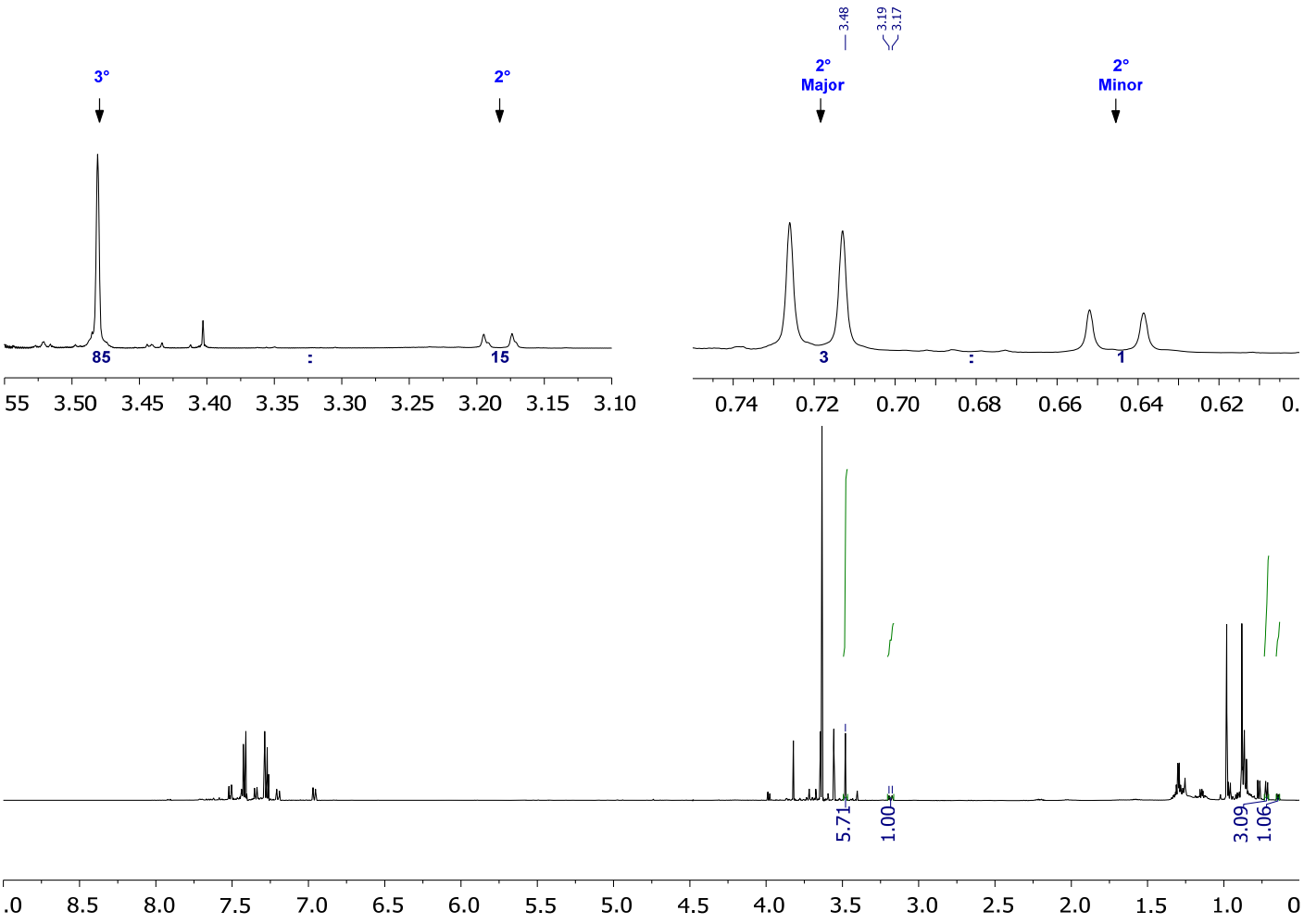
HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 11.9 min (major) and 24.5 min (minor), >20:1 d.r.

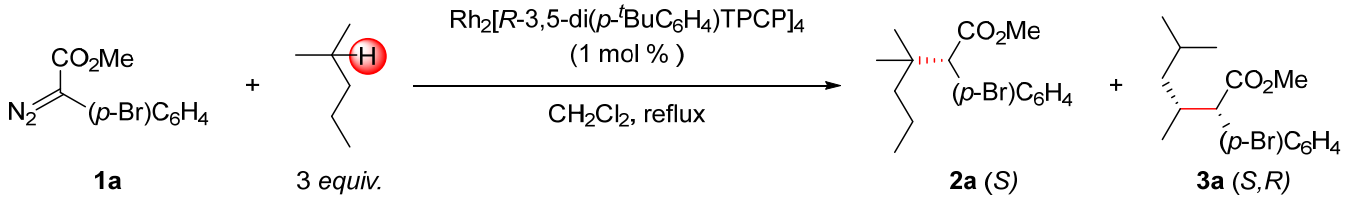
7 - Crude ^{1}H NMR Spectra for the Ratio Determination

7.1 Catalyst and Diazo Screen of 2-Methylpentane

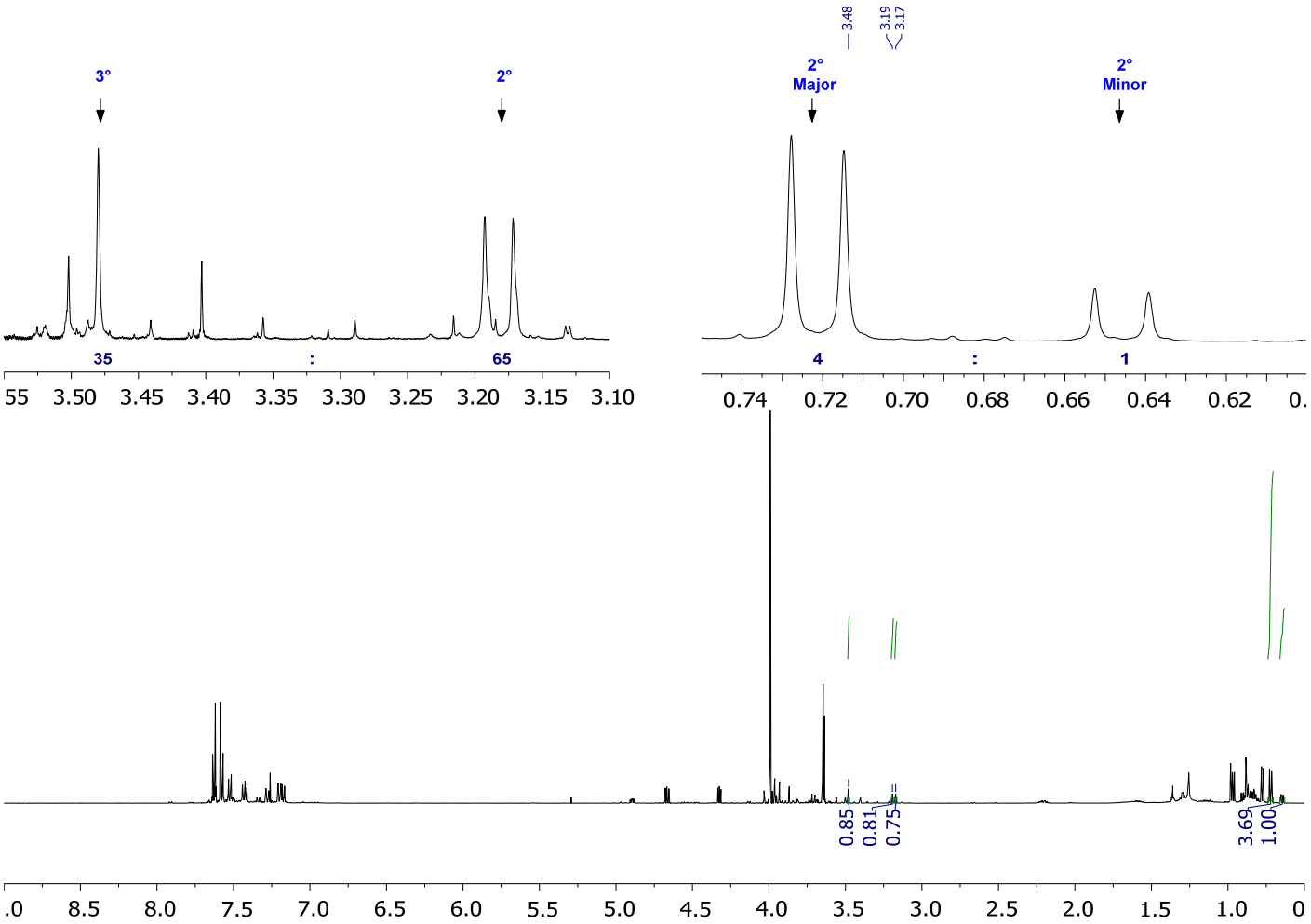


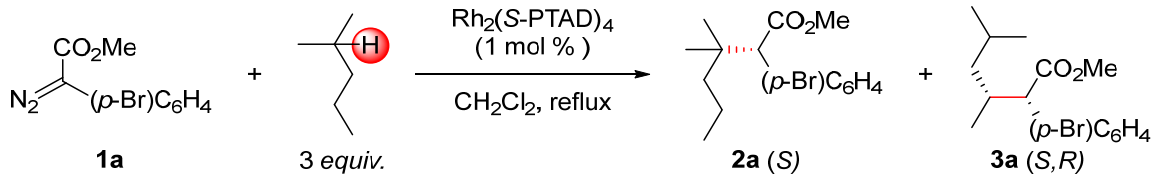
1a 3 *equiv.* **2a** (*S*) **3a** (*S,R*)

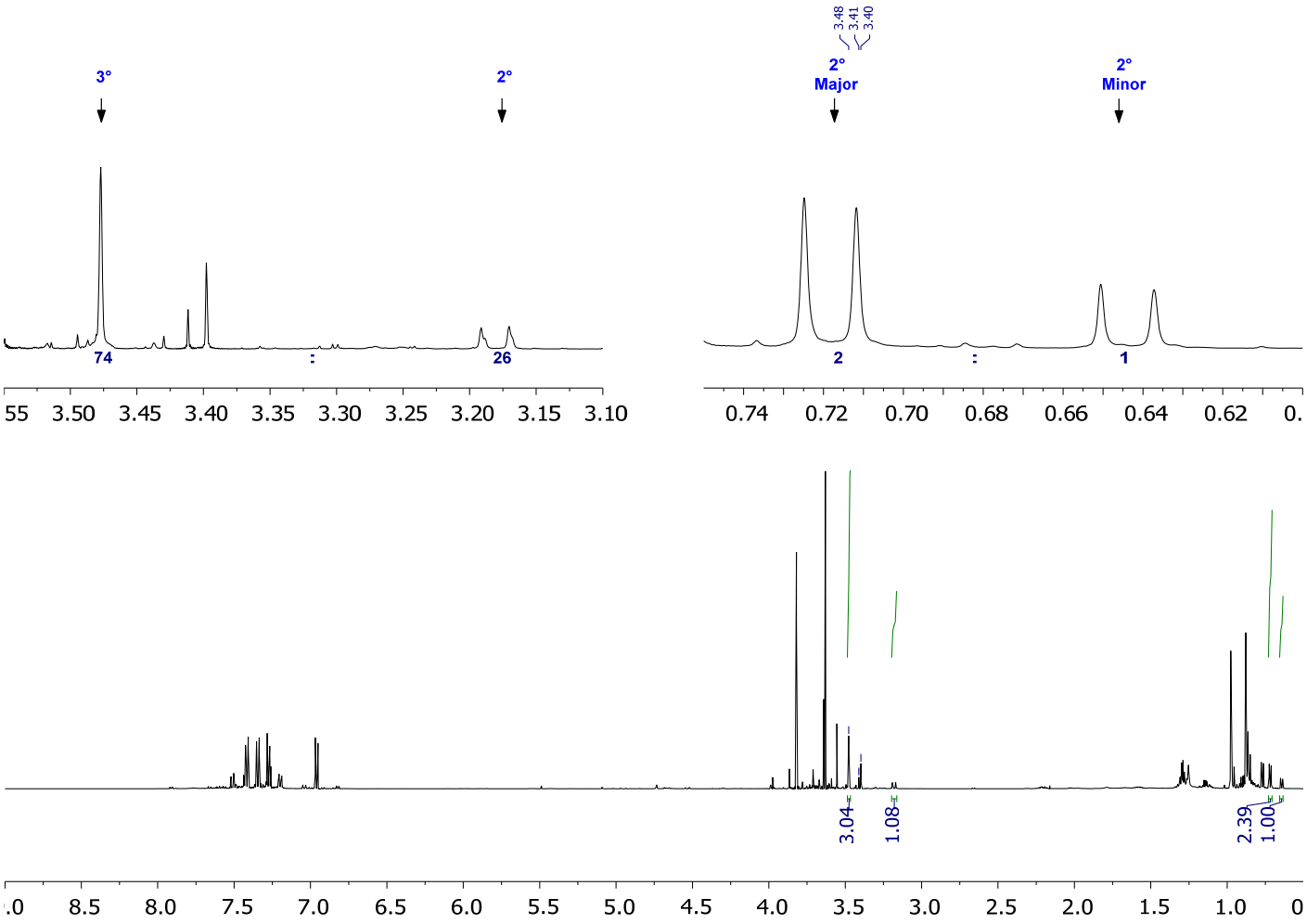


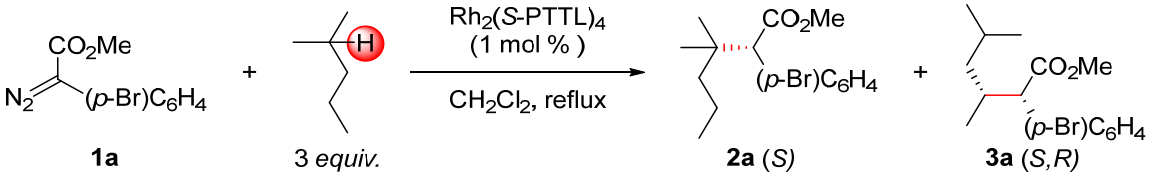


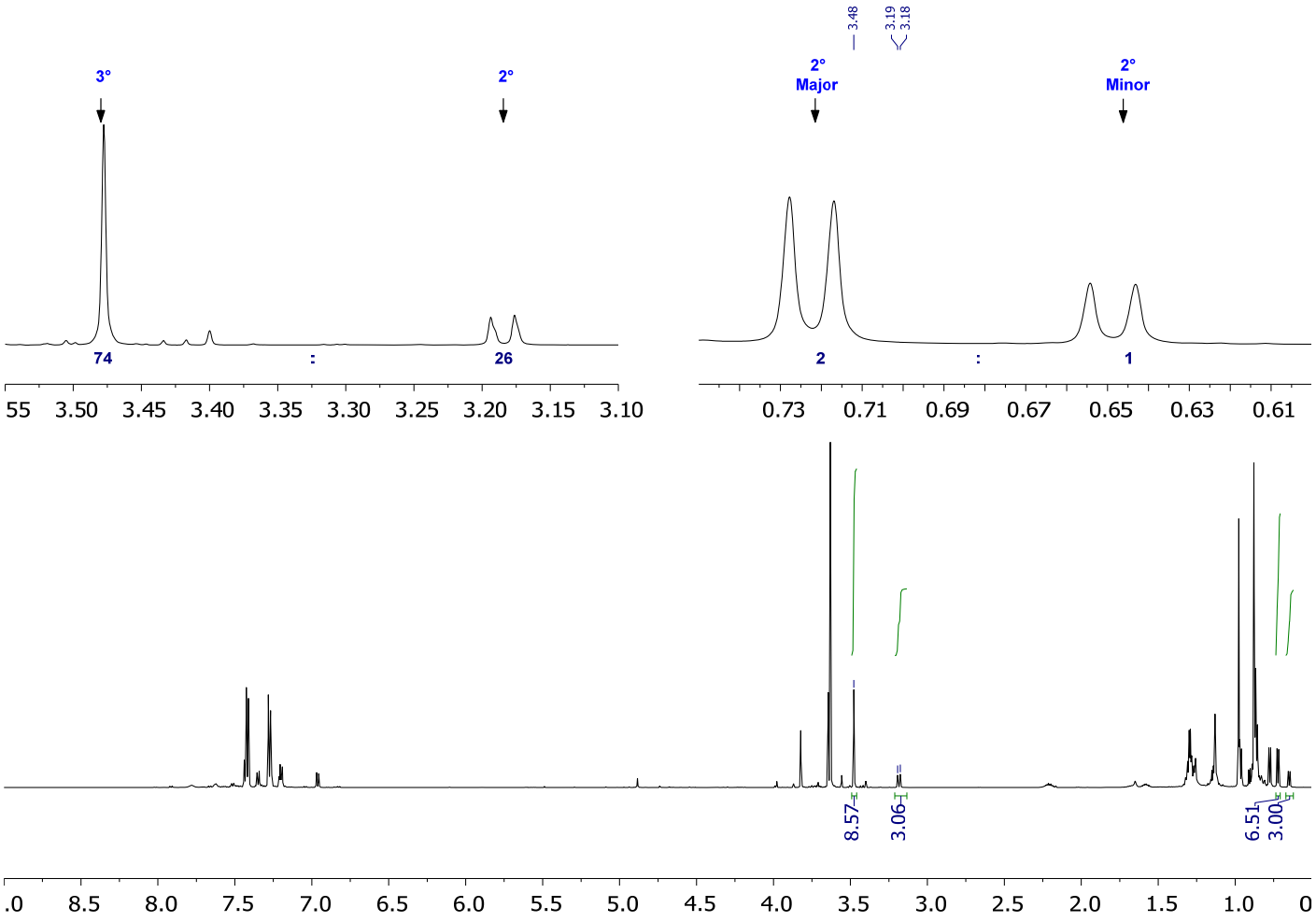
1a 3 *equiv.* **2a** (*S*) **3a** (*S,R*)

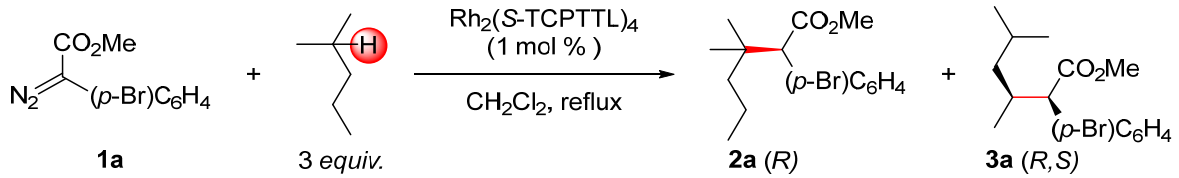


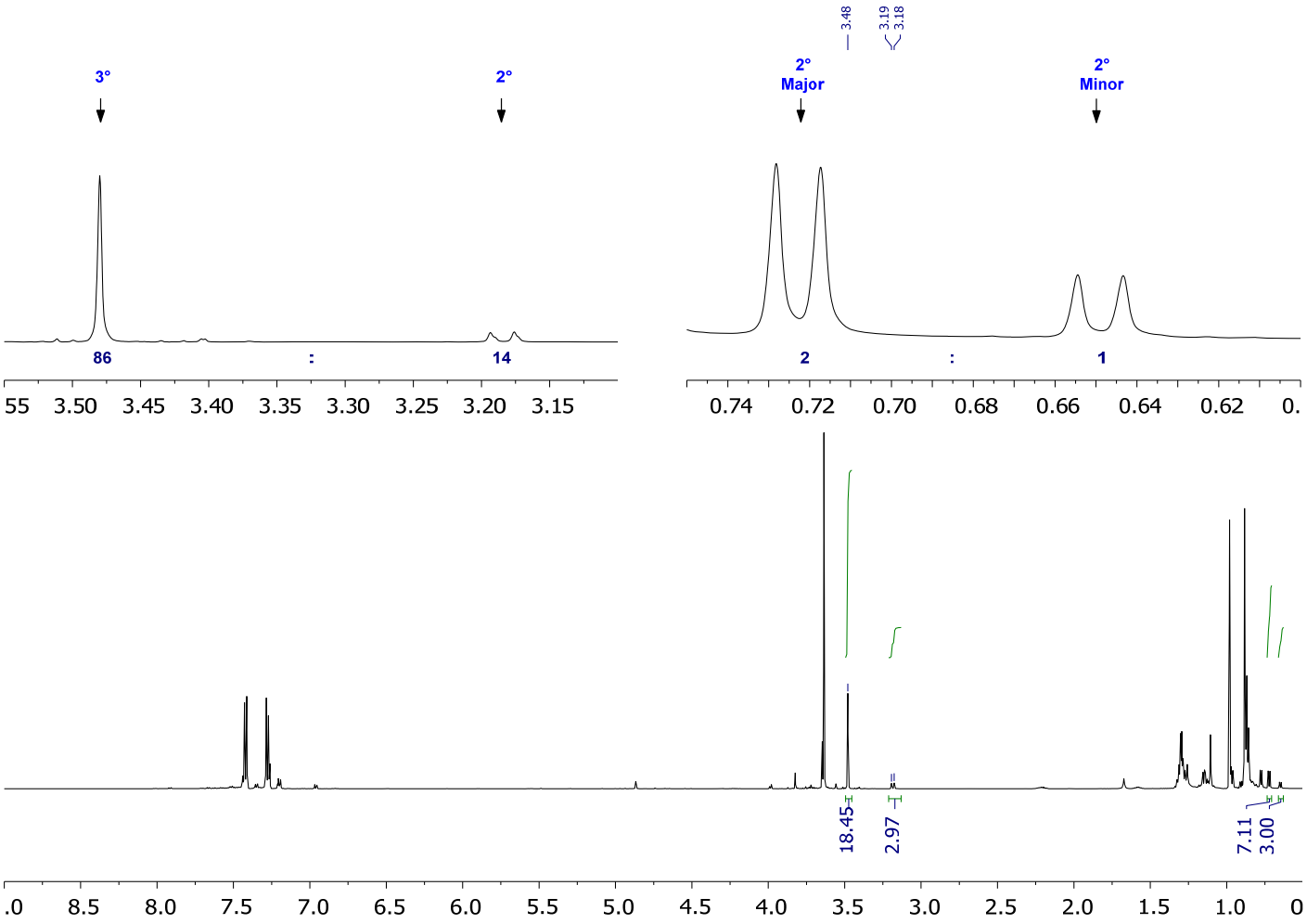

CO2Me
N2
(p-Br)C6H4
1a
+
H
3 equiv.
Rh2(S-PTAD)4
(1 mol %)
CH2Cl2, reflux
CO2Me
(p-Br)C6H4
2a (S)
+
CO2Me
(p-Br)C6H4
3a (S,R)

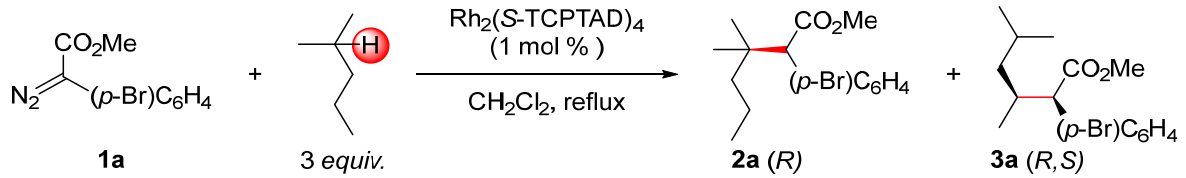

3°
2°
74
:
26
3.48
3.41
3.40
2°
Major
2°
Minor
2
:
1
55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10
0.74 0.72 0.70 0.68 0.66 0.64 0.62 0.
3.04
1.08
2.39
1.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

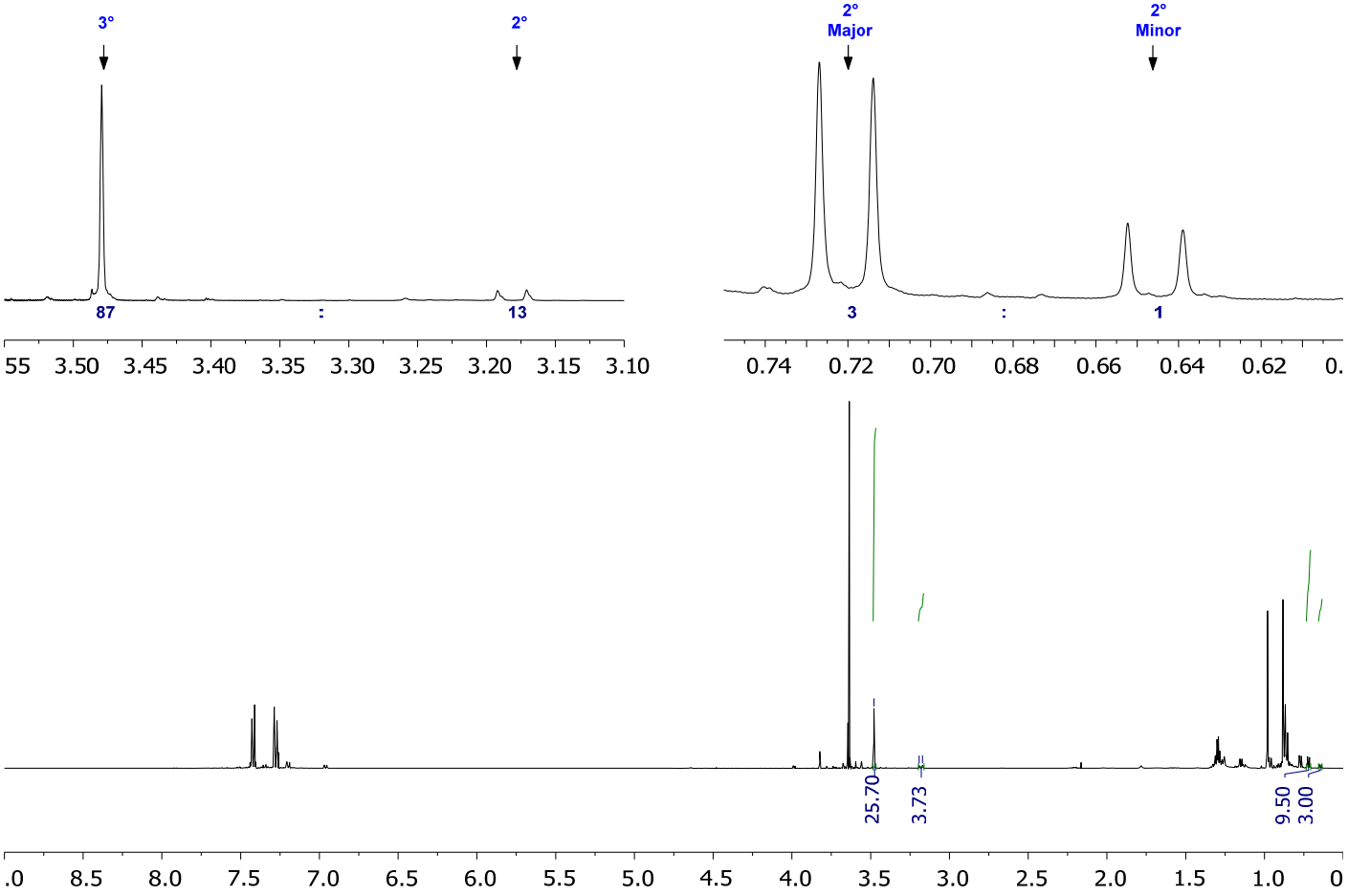

CO2Me
N2
(p-Br)C6H4
1a
+
H
3 equiv.
Rh2(S-PTTL)4
(1 mol %)
CH2Cl2, reflux
CO2Me
(p-Br)C6H4
2a (S)
+
CO2Me
(p-Br)C6H4
3a (S,R)


3°
2°
74
:
26
55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10
3.48
3.19
3.18
2° Major
2° Minor
2
:
1
0.73 0.71 0.69 0.67 0.65 0.63 0.61
8.57
3.06
6.51
3.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

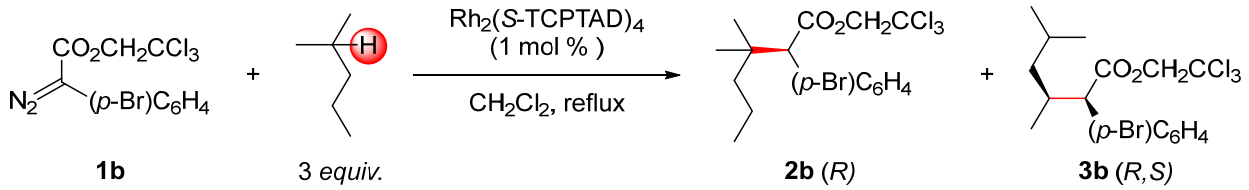

CO2Me
N2
(p-Br)C6H4
1a
+
H
3 equiv.
Rh2(S-TCPTTL)4
(1 mol %)
CH2Cl2, reflux
CO2Me
(p-Br)C6H4
2a (R)
+
CO2Me
(p-Br)C6H4
3a (R,S)


3°
2°
86
:
14
3.48
3.19
3.18
2°
Major
2°
Minor
2
:
1
55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15
0.74 0.72 0.70 0.68 0.66 0.64 0.62 0.
18.45
2.97
7.11
3.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

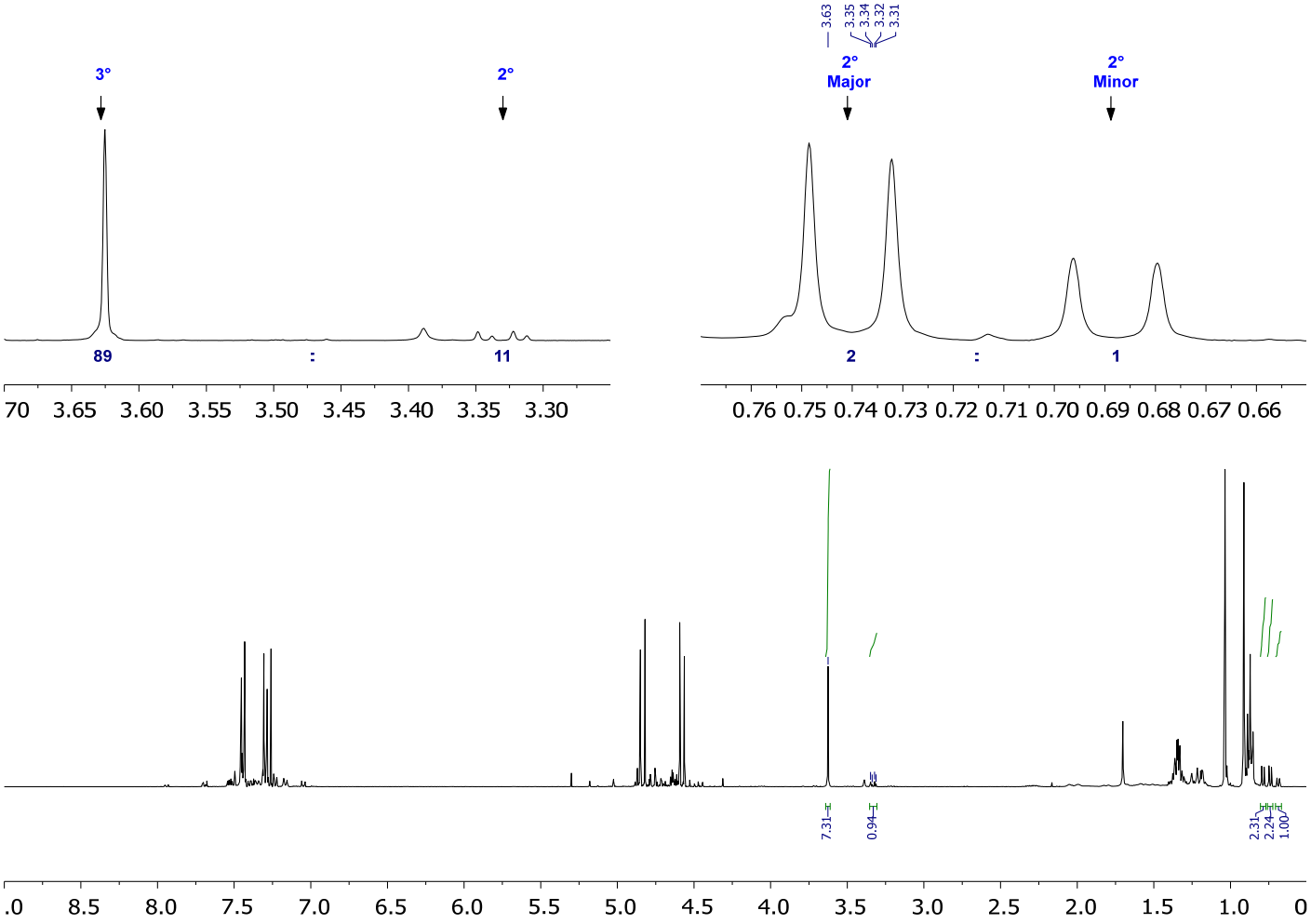

CO2Me
N2
(p-Br)C6H4
1a
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2Me
(p-Br)C6H4
2a (R)
+
CO2Me
(p-Br)C6H4
3a (R,S)

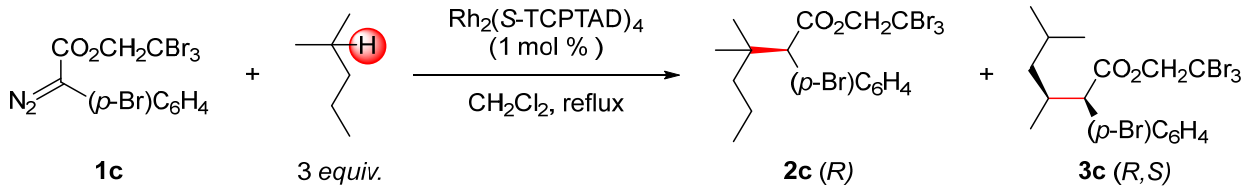

3°
2°
87
:
13
3.48
3.19
3.17
2° Major
2° Minor
3
:
1
55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10
0.74 0.72 0.70 0.68 0.66 0.64 0.62 0.

25.70
3.73
9.50
3.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

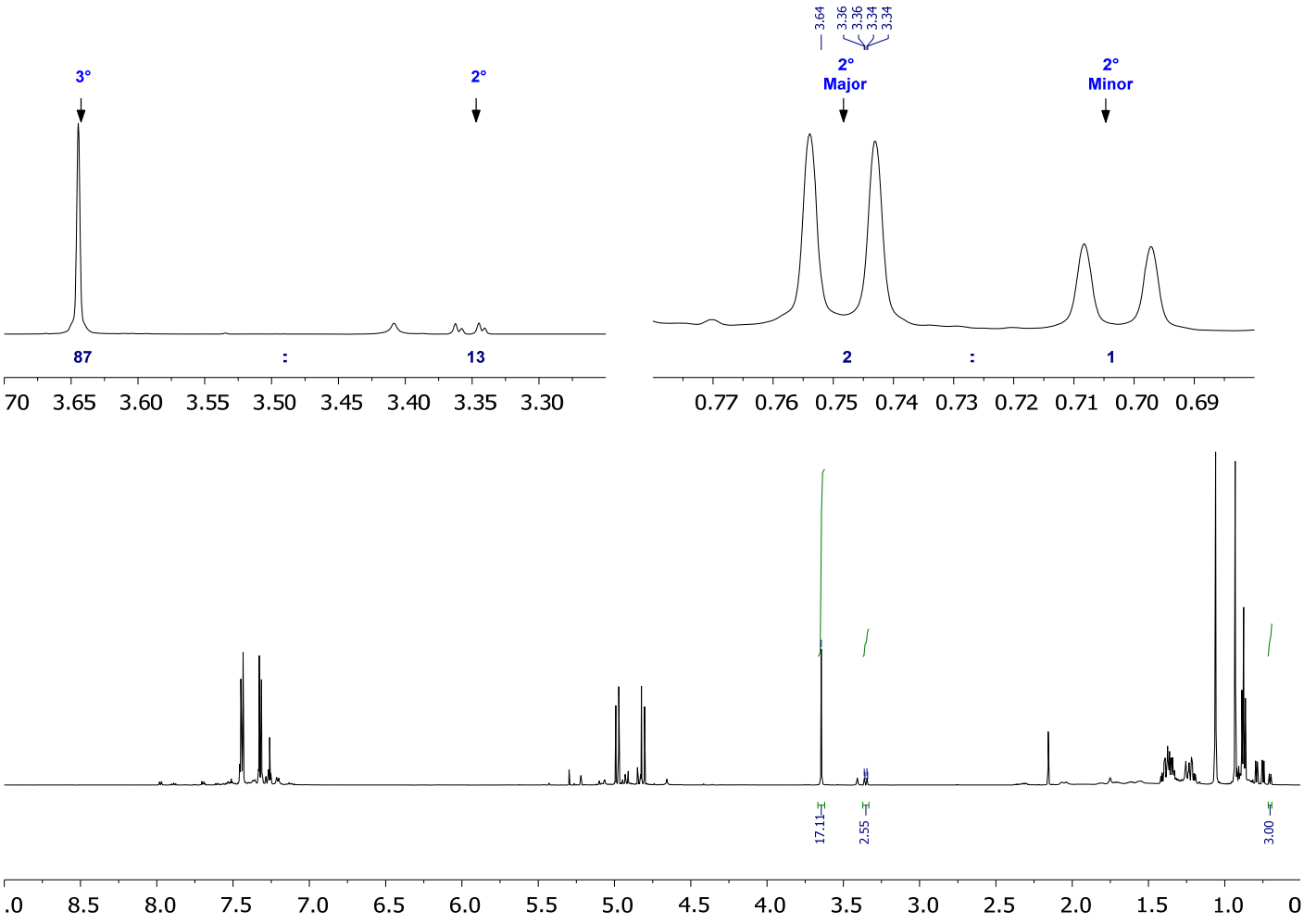


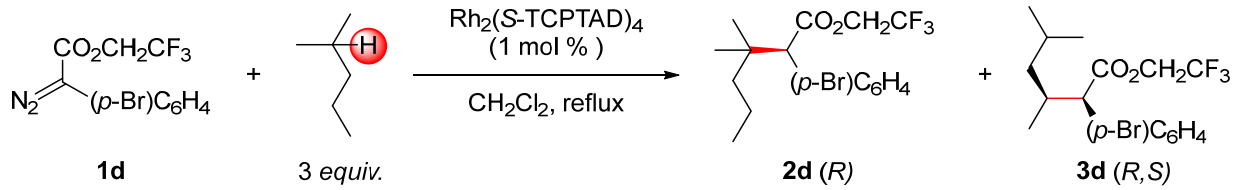
1b 3 *equiv.* **2b** (*R*) **3b** (*R,S*)

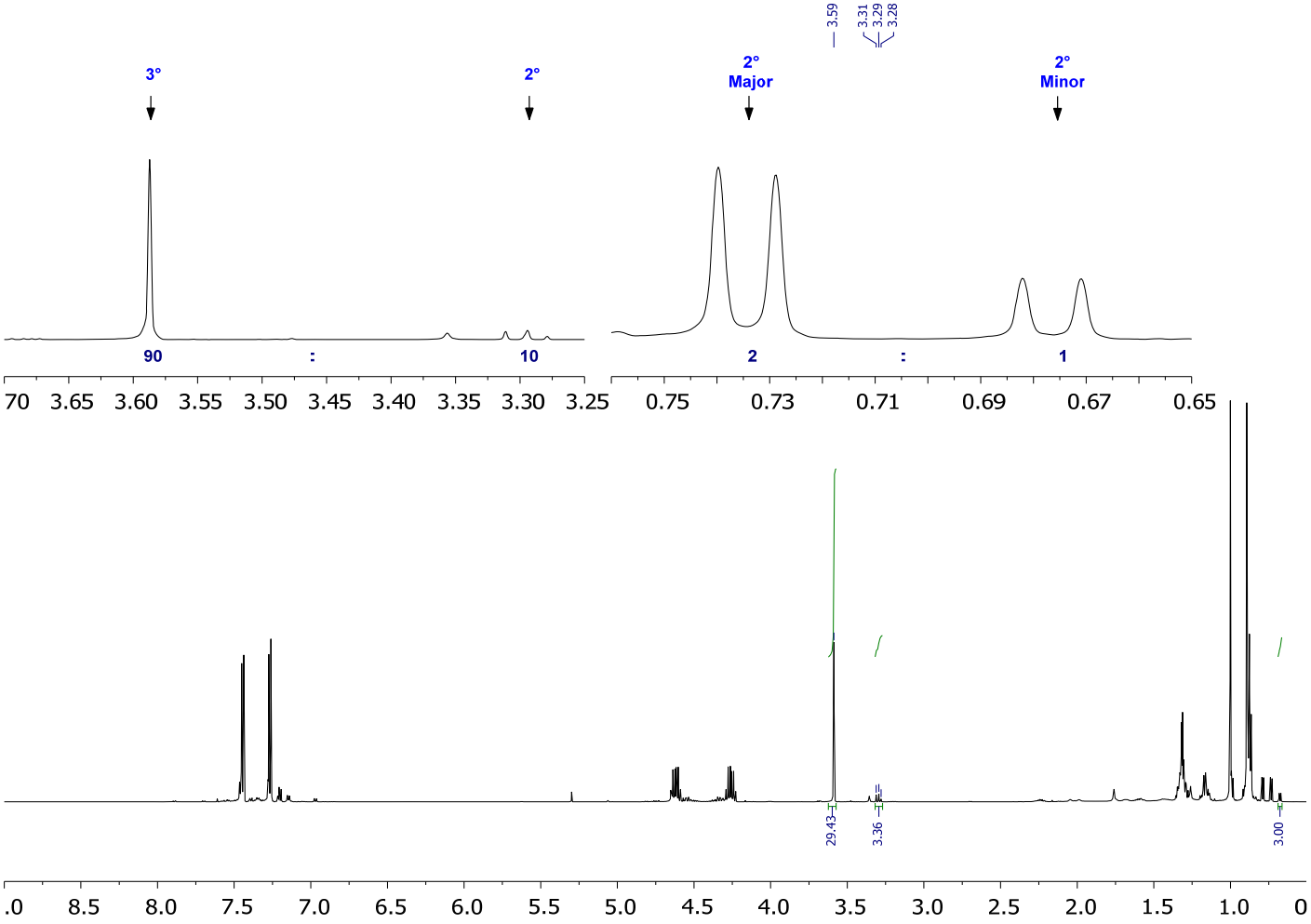




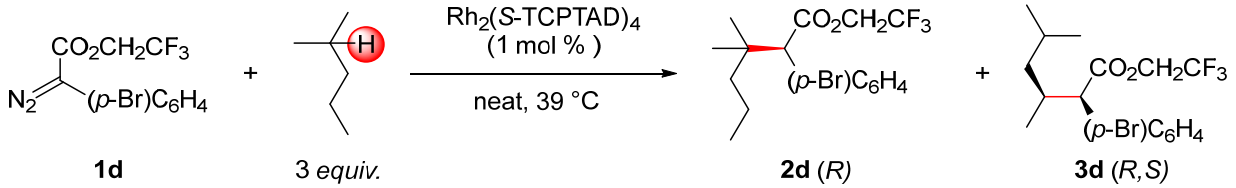
1c 3 *equiv.* **2c** (*R*) **3c** (*R,S*)



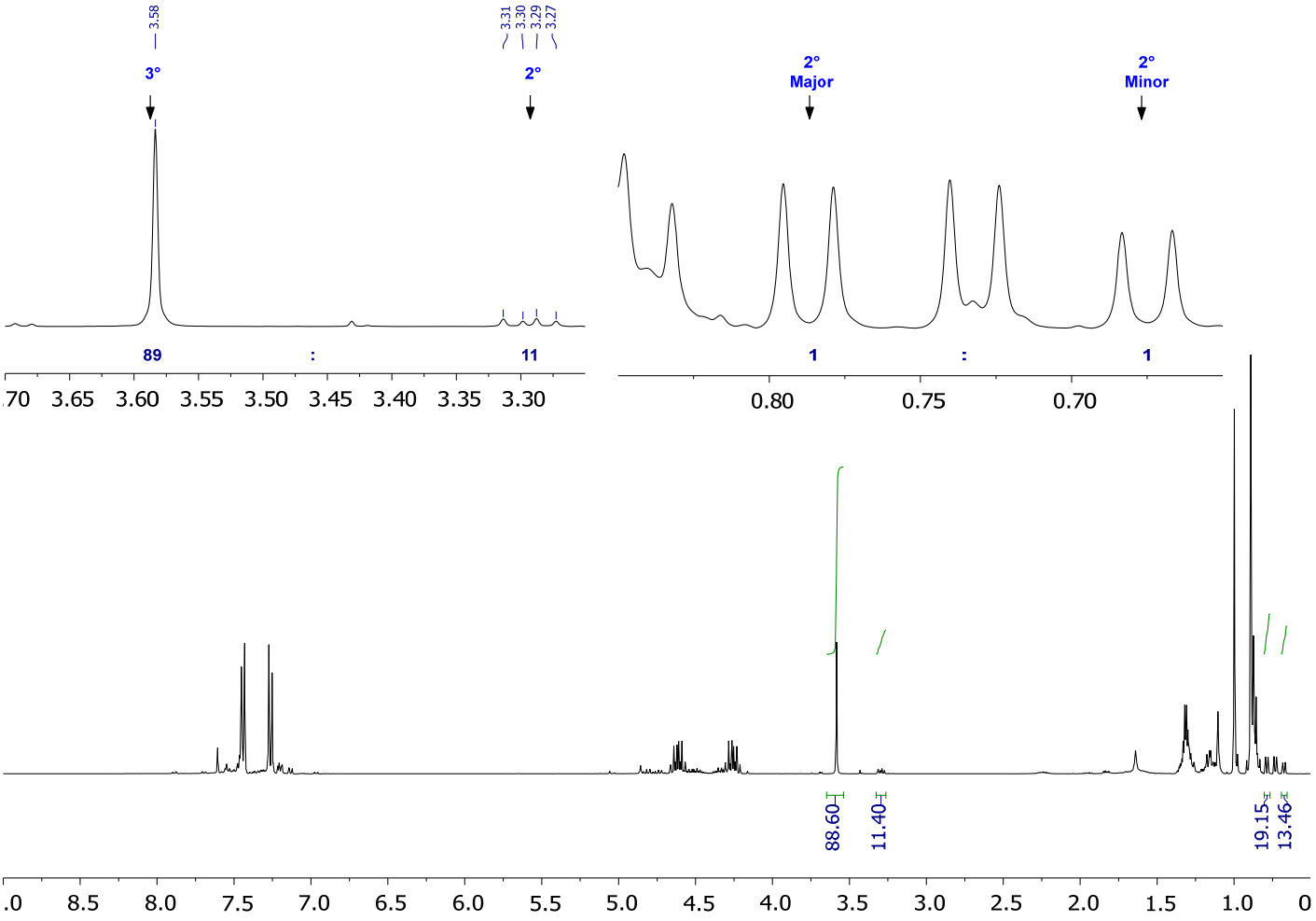

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(p-Br)C6H4
2d (R)
+
CO2CH2CF3
(p-Br)C6H4
3d (R,S)

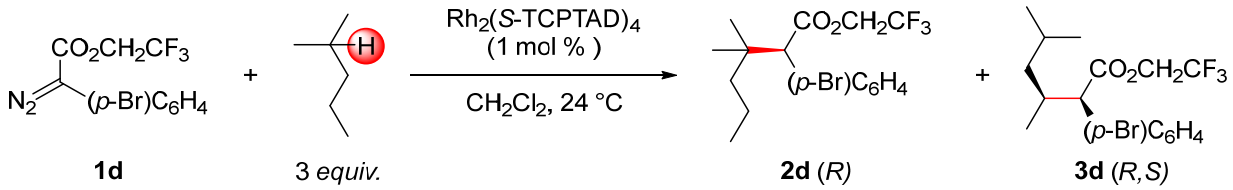

3°
2°
2°
Major
2°
Minor
3.59
3.31
3.29
3.28
90 : 10
2 : 1
70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25
0.75 0.73 0.71 0.69 0.67 0.65
29.43
3.36
3.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

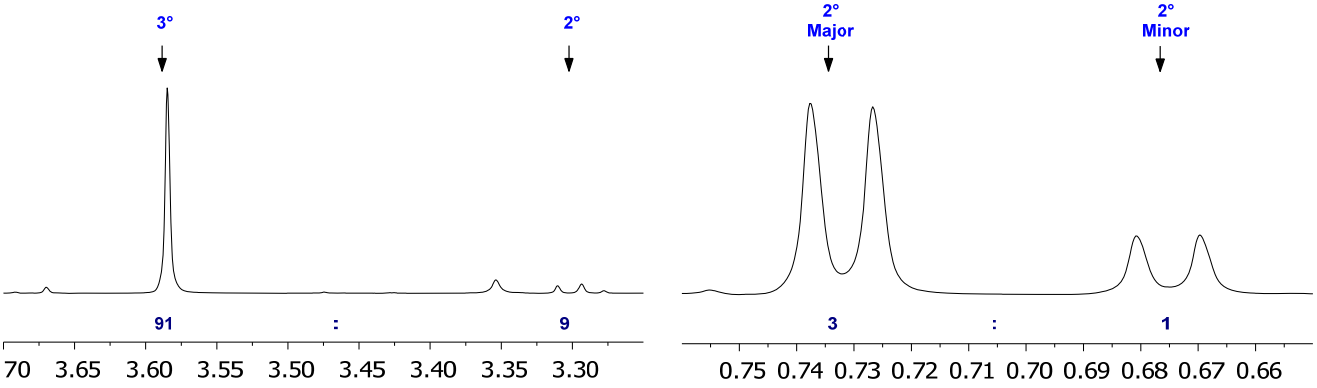
7.2 Reaction Condition Screen of 2-Methylpentane

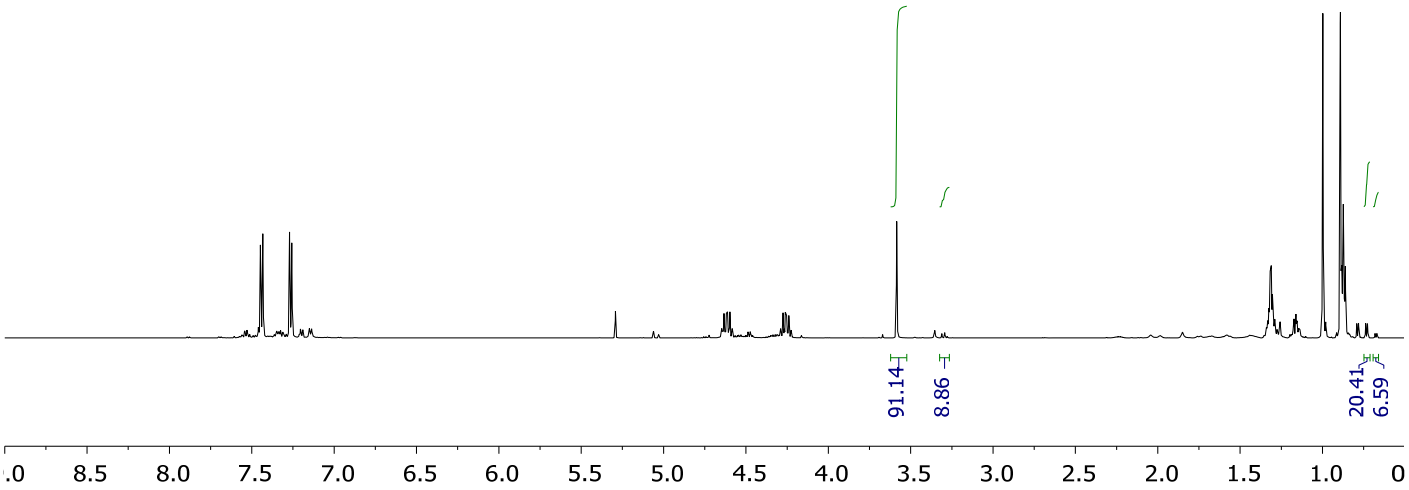


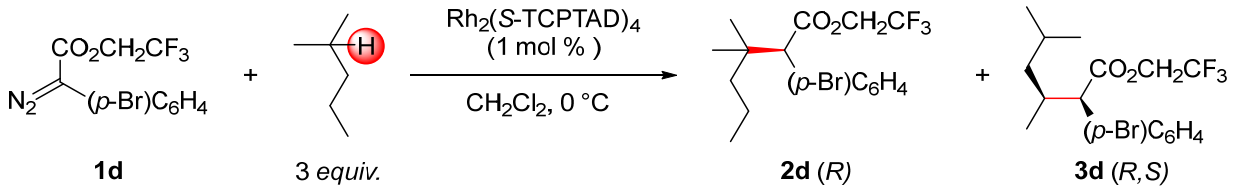
1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)

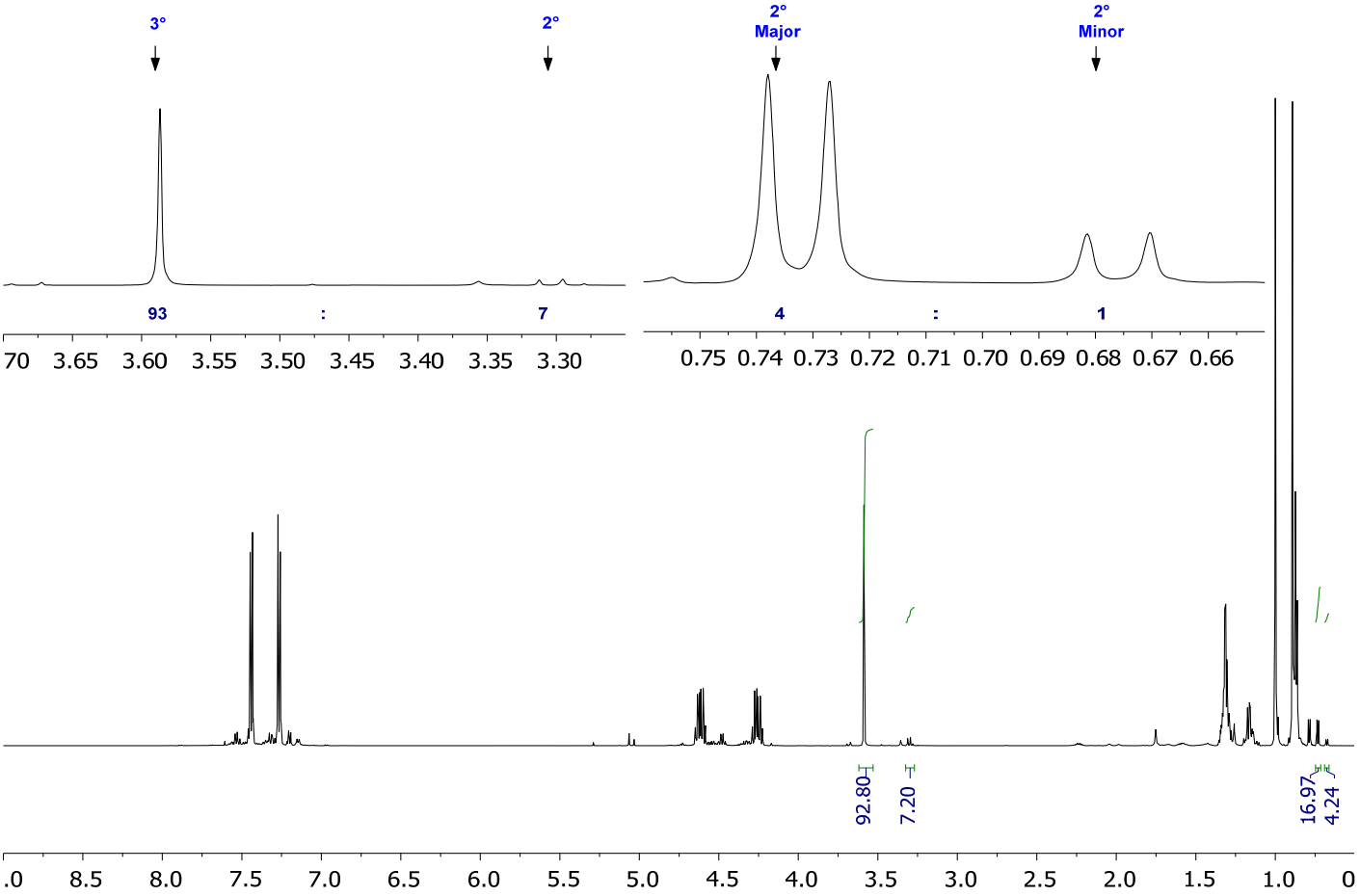


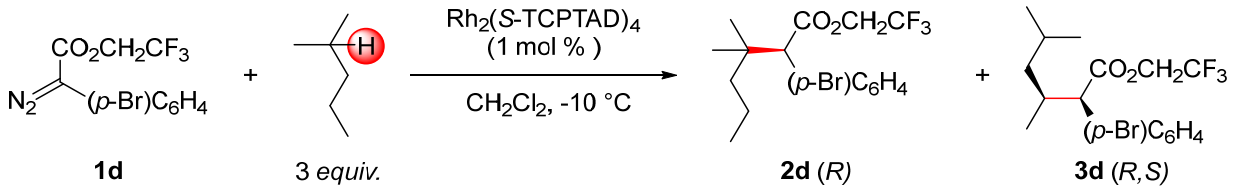

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, 24 °C
CO2CH2CF3
(p-Br)C6H4
2d (R)
+
CO2CH2CF3
(p-Br)C6H4
3d (R,S)


3°
2°
91
:
9
70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
2°
Major
2°
Minor
3
:
1
0.75 0.74 0.73 0.72 0.71 0.70 0.69 0.68 0.67 0.66

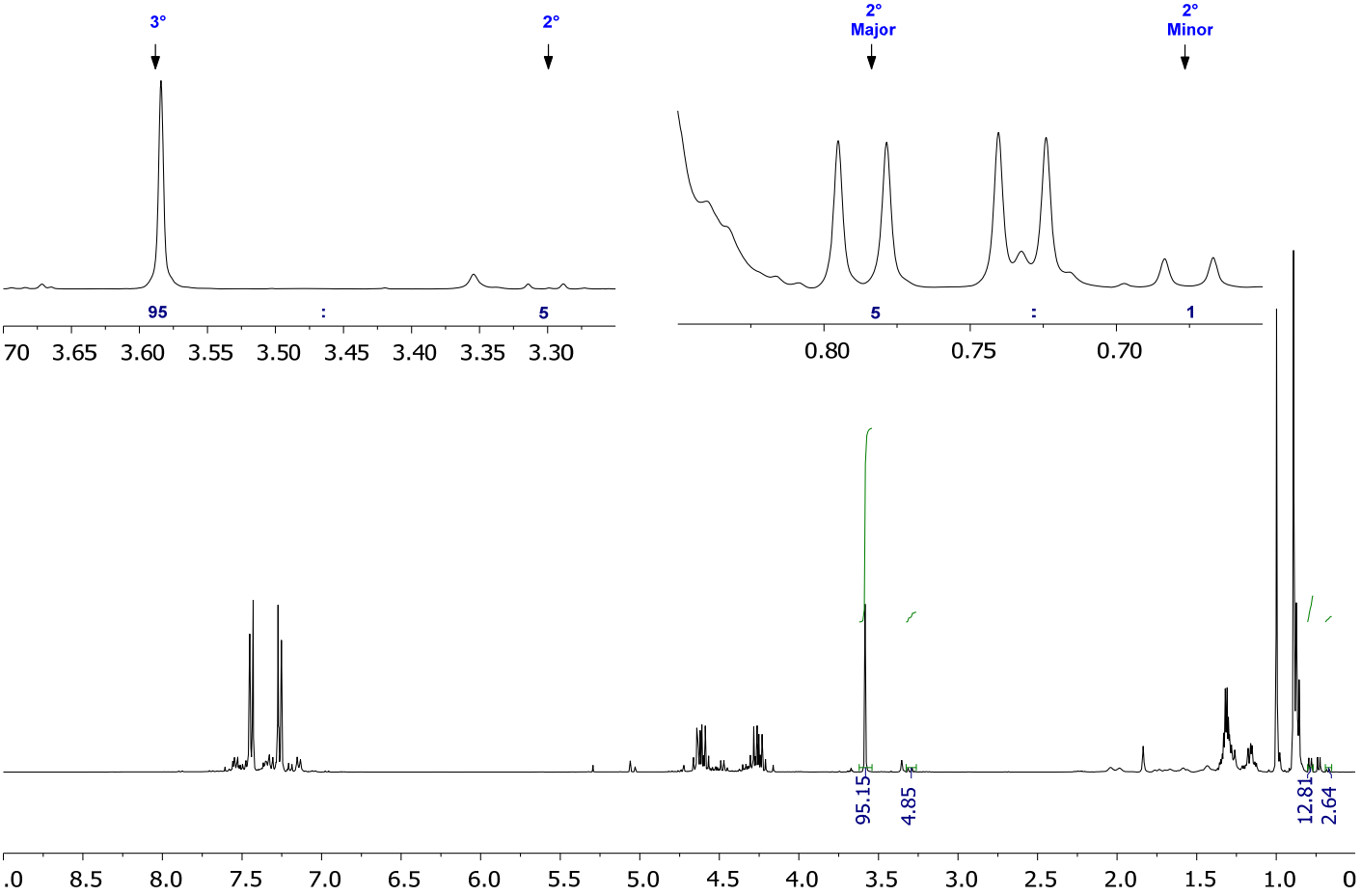

91.14
8.86
20.41
6.59
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

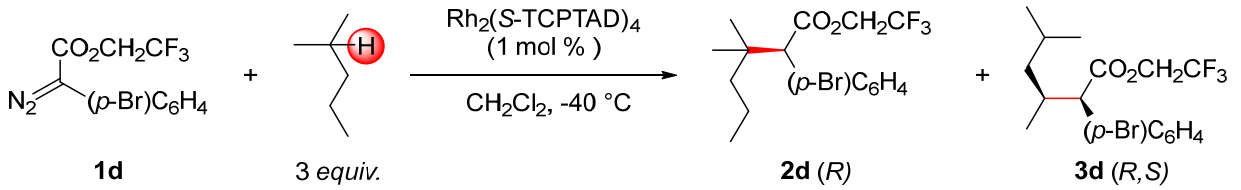

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, 0 °C
CO2CH2CF3
(p-Br)C6H4
2d (R)
+
CO2CH2CF3
(p-Br)C6H4
3d (R,S)


3°
2°
93
:
7
2°
Major
2°
Minor
4
:
1
70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
0.75 0.74 0.73 0.72 0.71 0.70 0.69 0.68 0.67 0.66
92.80
7.20
16.97
4.24
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

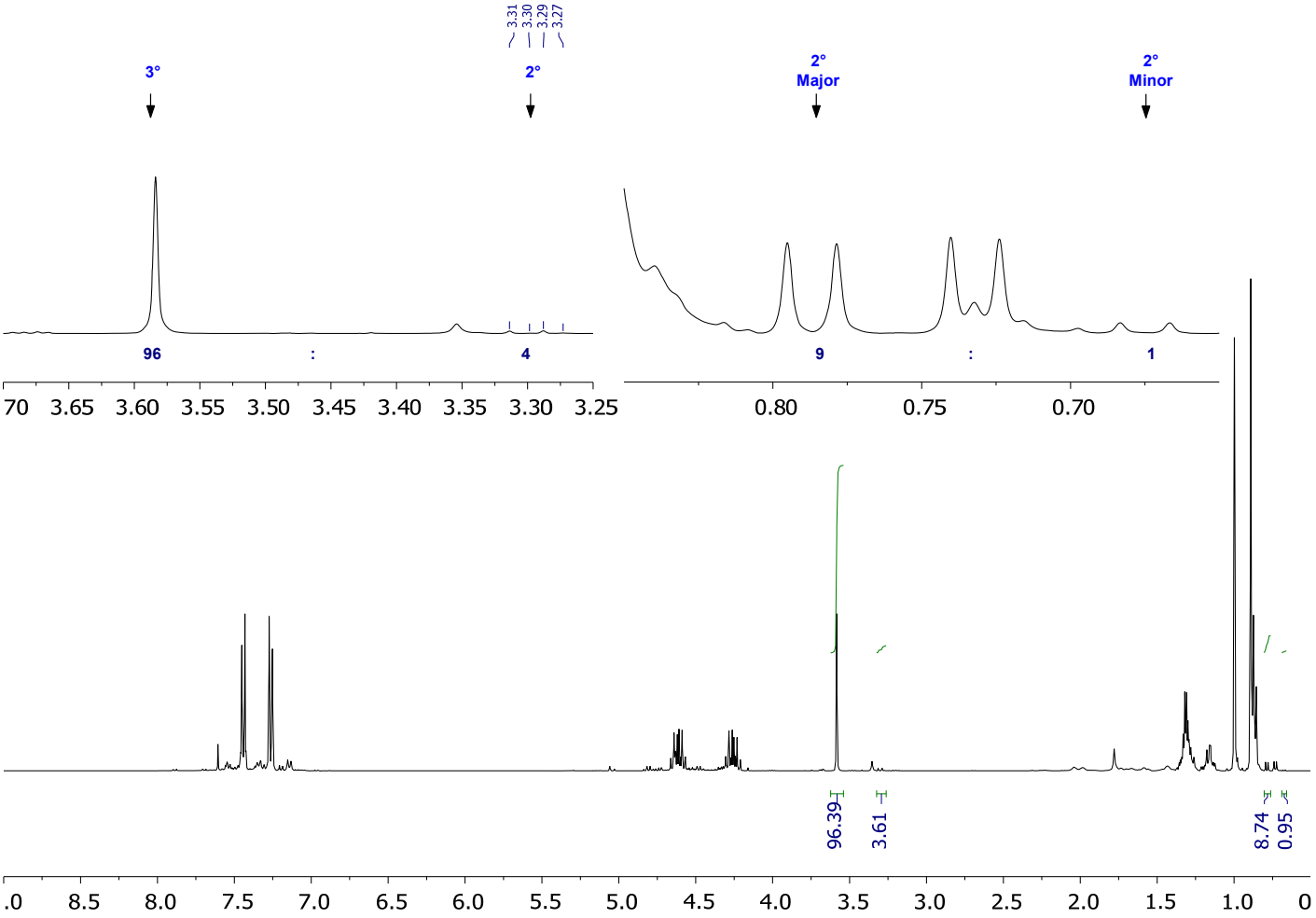


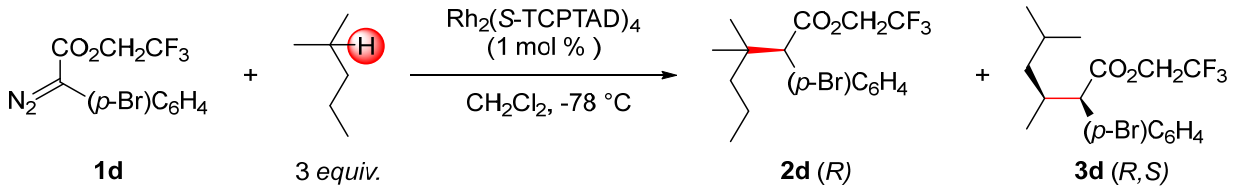
1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)



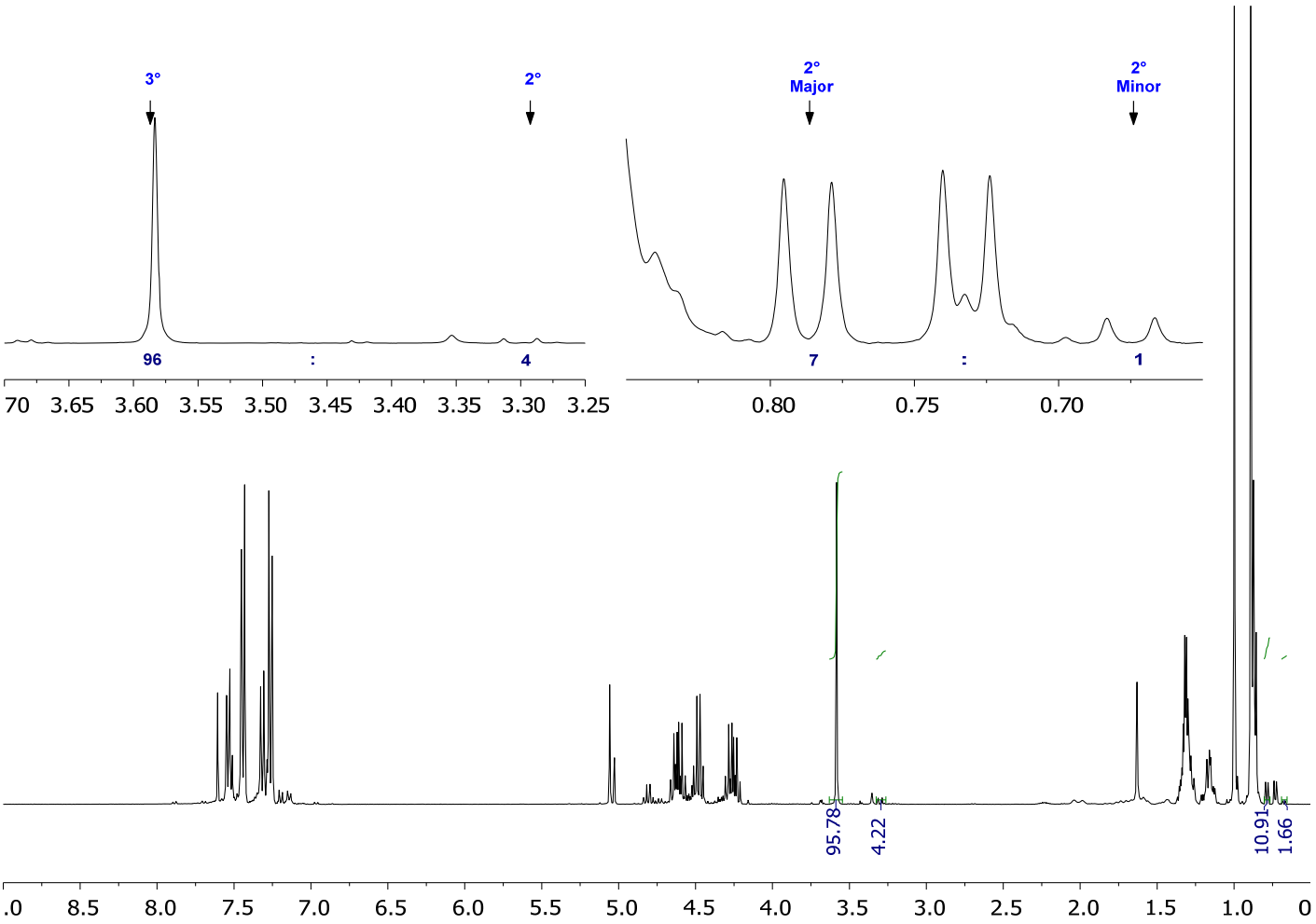


1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)

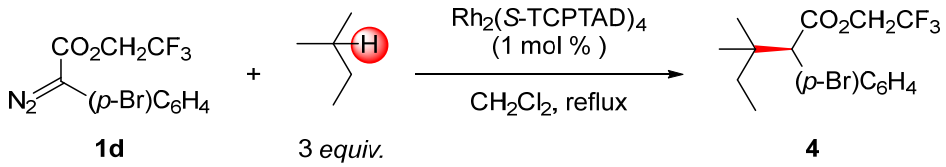


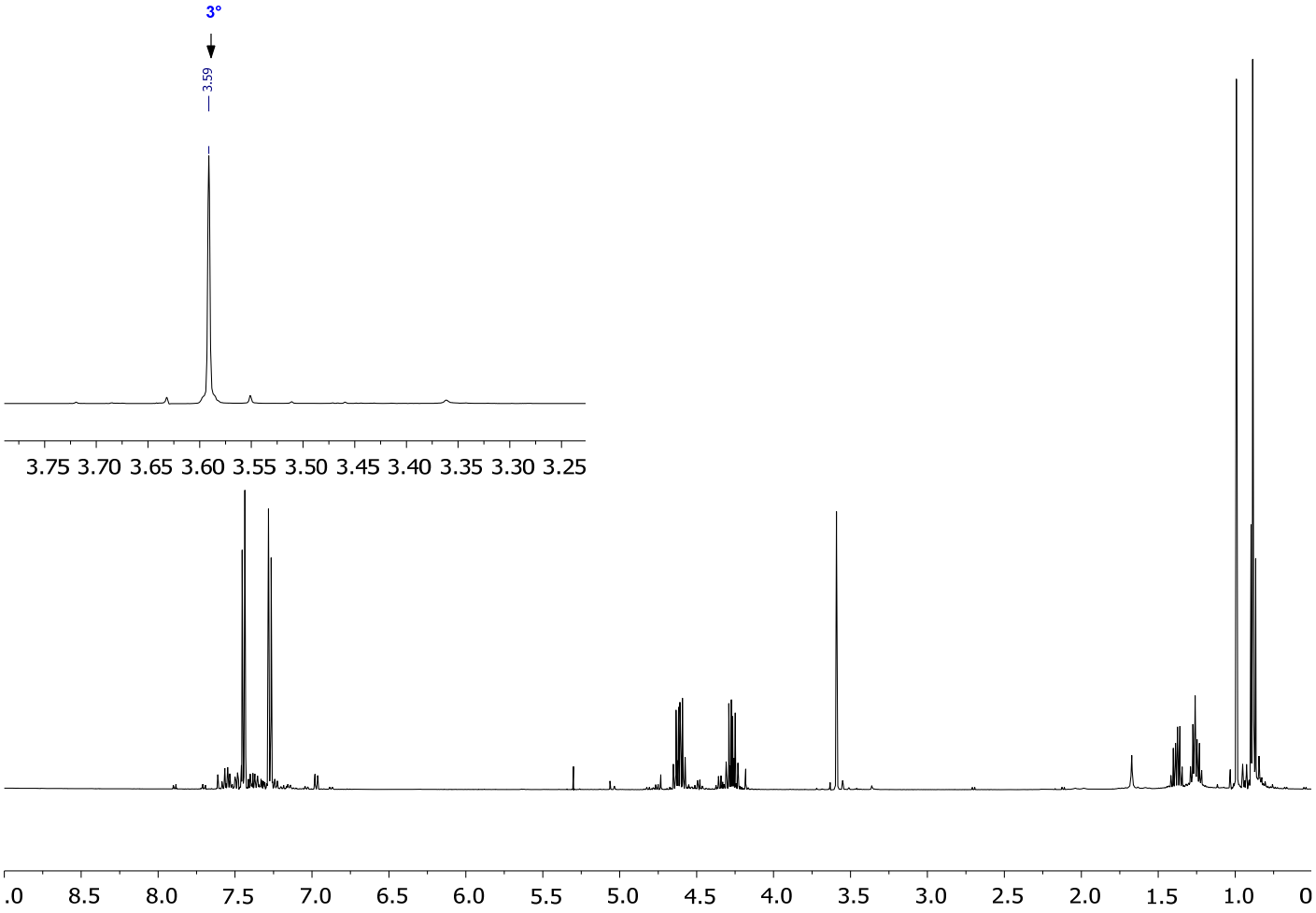


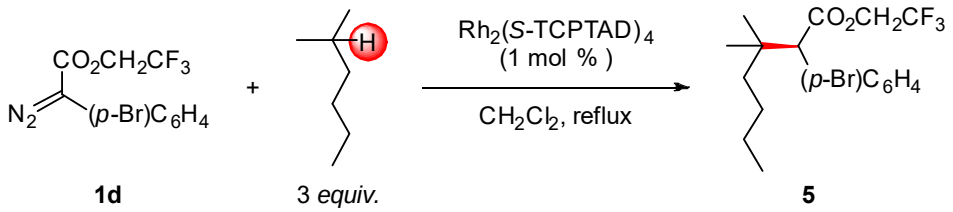
1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)



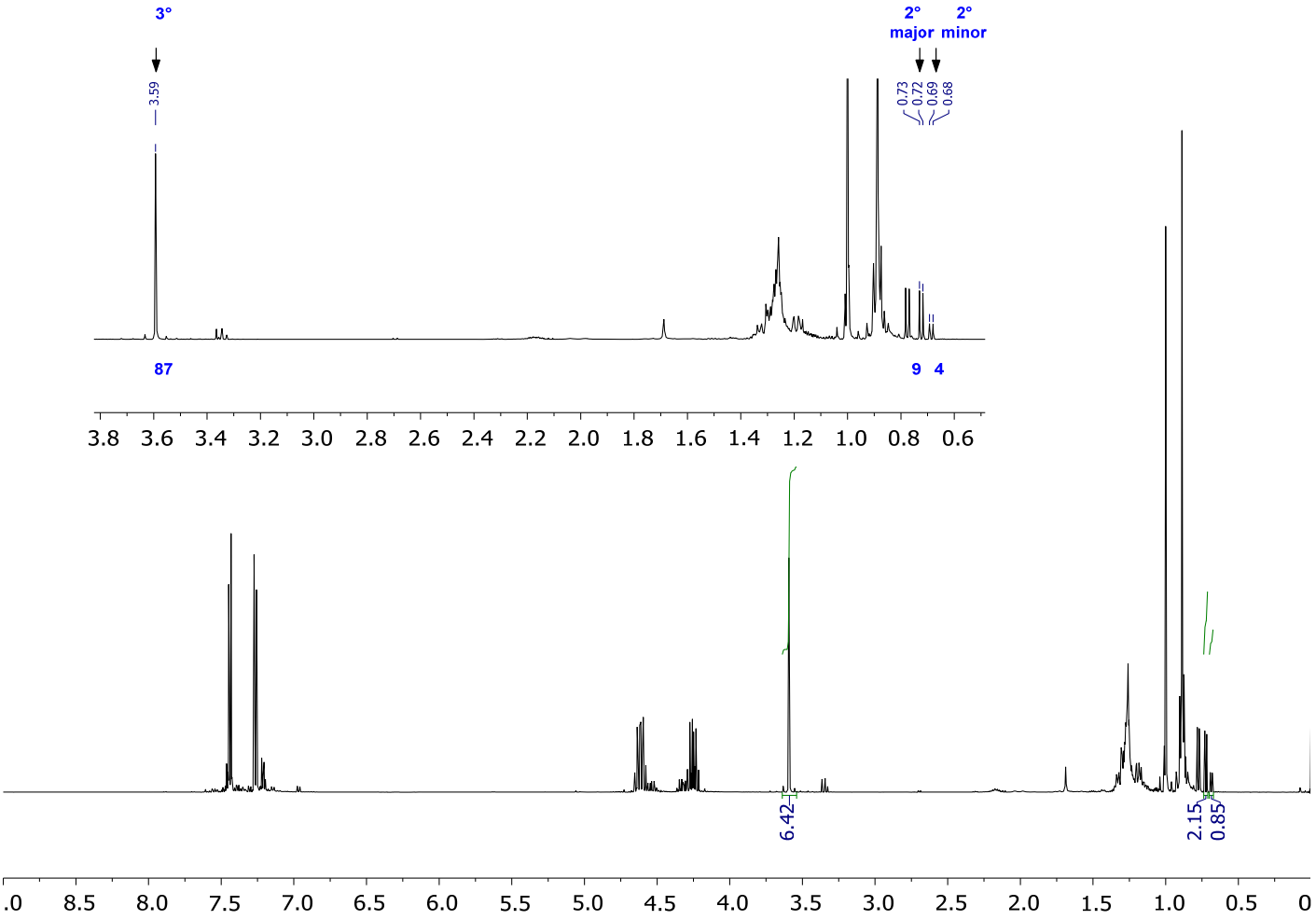
7.3 C–H Functionalization Products **4-26**

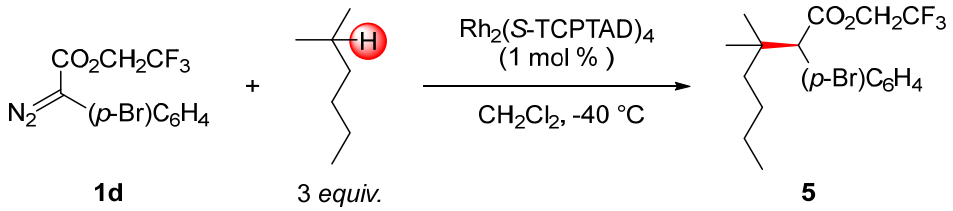




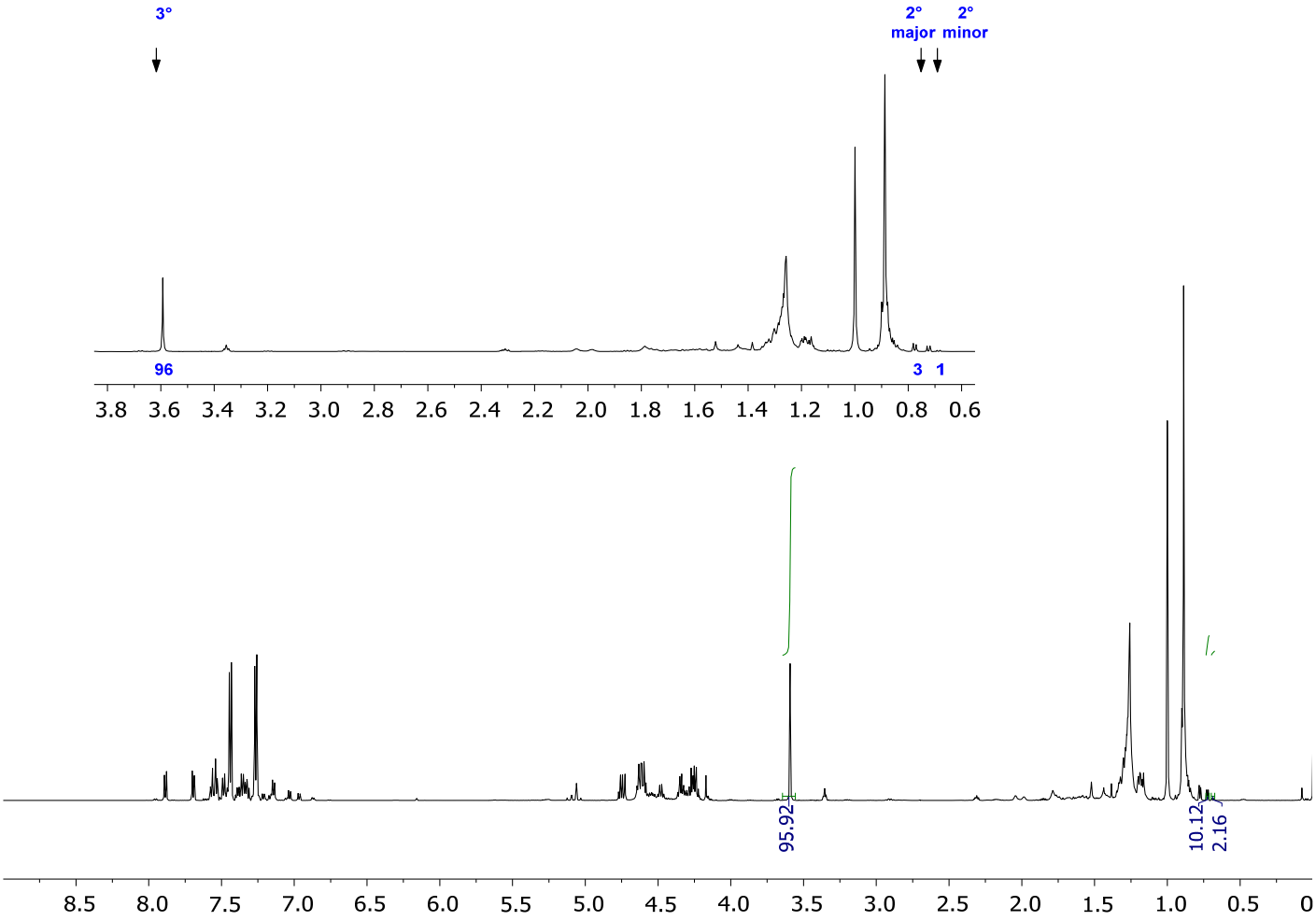

CO2CH2CF3
N2
(p-Br)C6H4
+
H
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(p-Br)C6H4

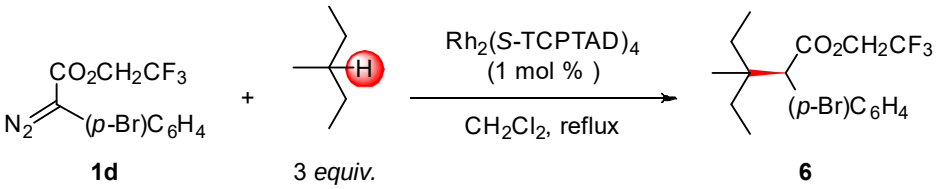
1d 3 *equiv.* **5**


3°
2°
major
2°
minor
3.59
0.73
0.72
0.69
0.68
87
9
4
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
6.42
2.15
0.85
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

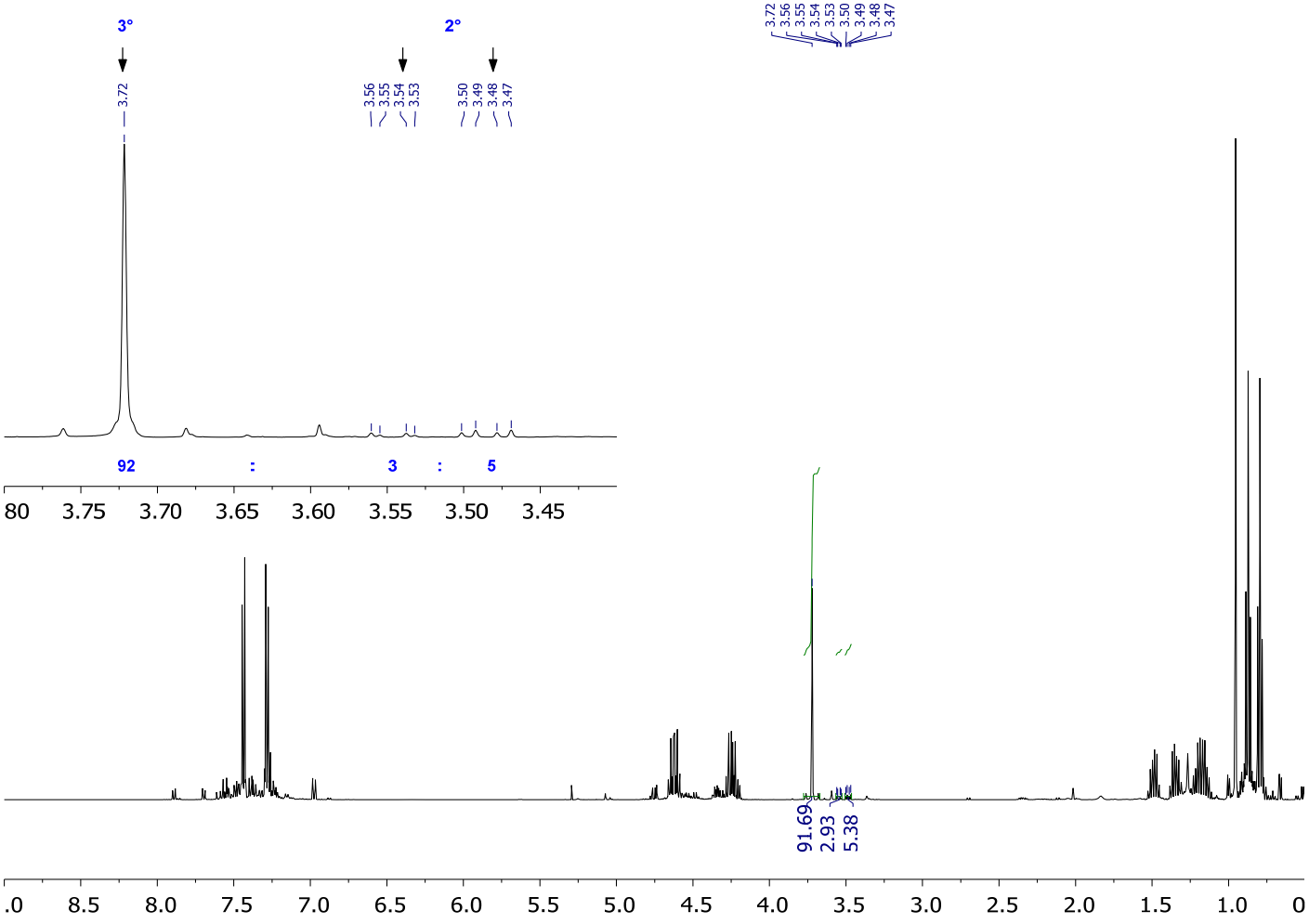

CO2CH2CF3
N2
(p-Br)C6H4
+
H
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, -40 °C
CO2CH2CF3
(p-Br)C6H4

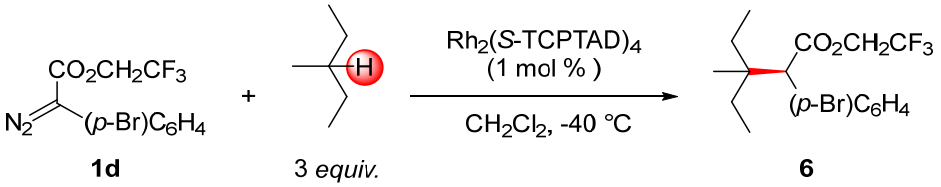
1d 3 *equiv.* **5**

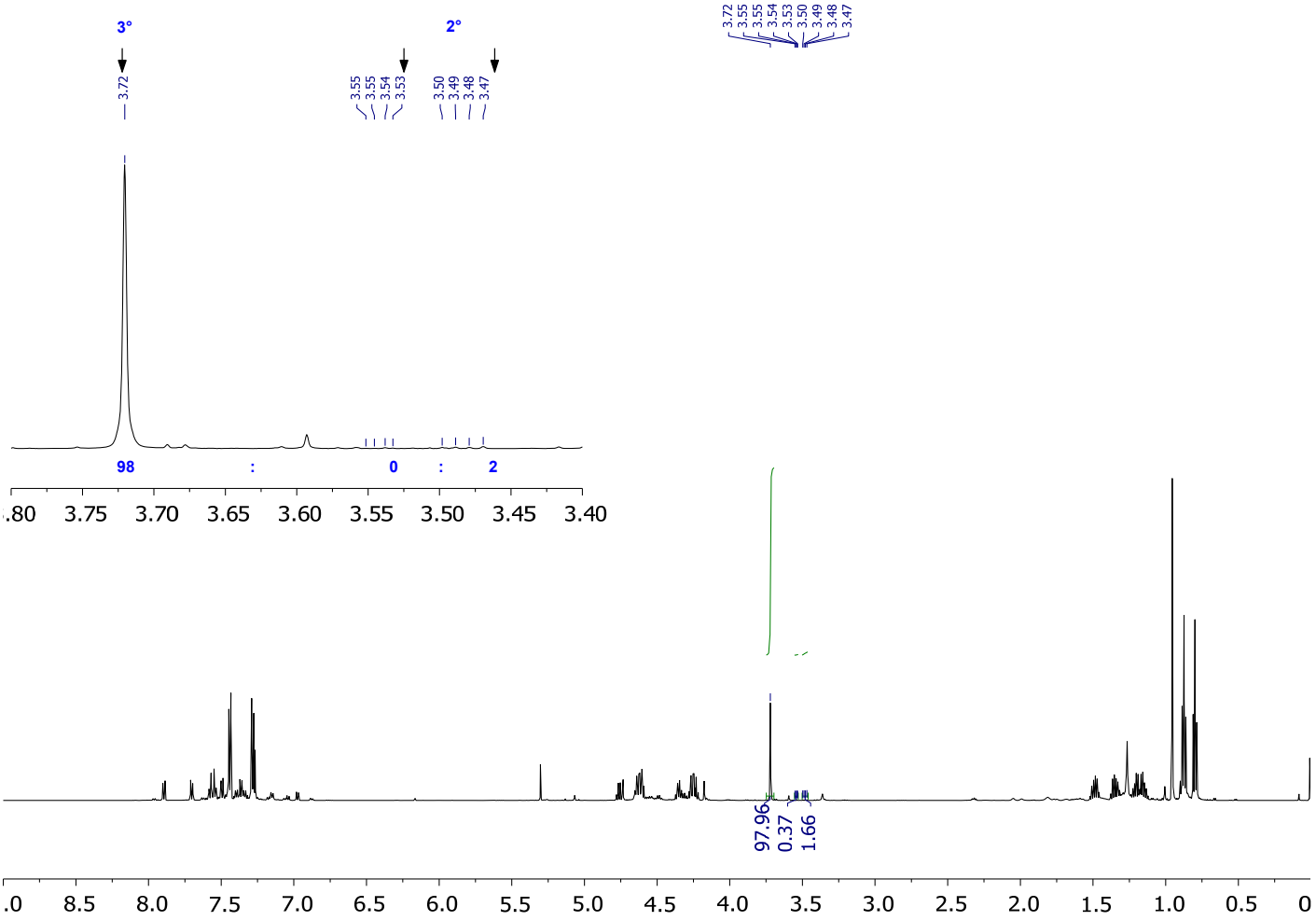

3°
2° major
2° minor
96
3
1
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
95.92
10.12
2.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

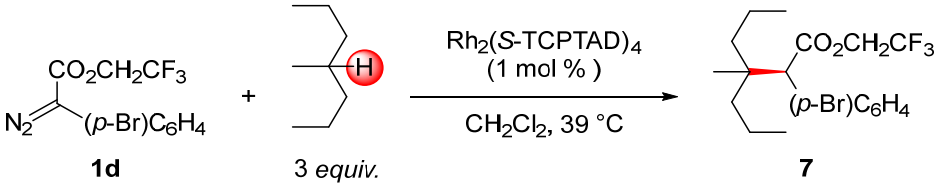

CO2CH2CF3
N2
(p-Br)C6H4
+
H
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(p-Br)C6H4

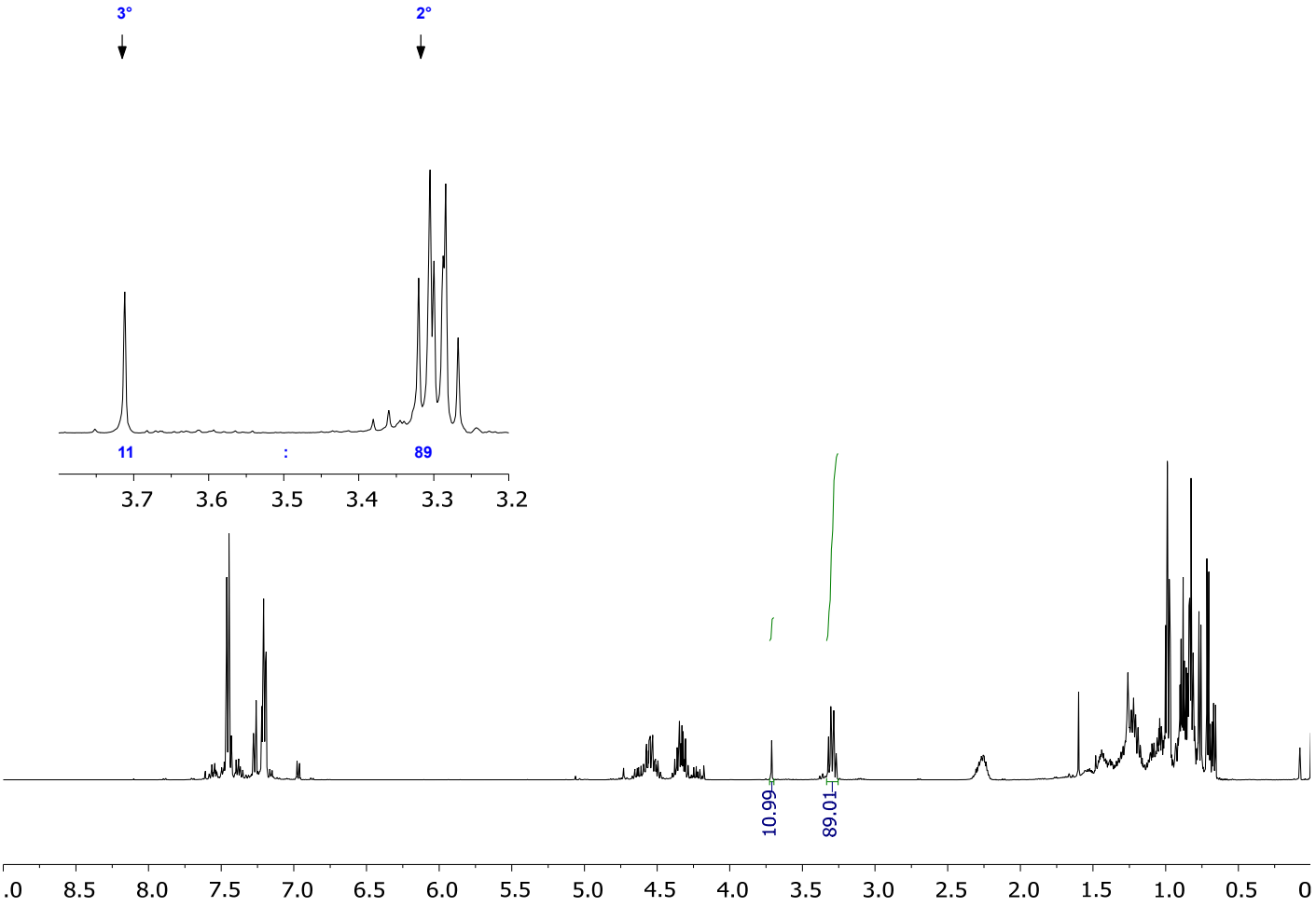
1d 3 *equiv.* **6**

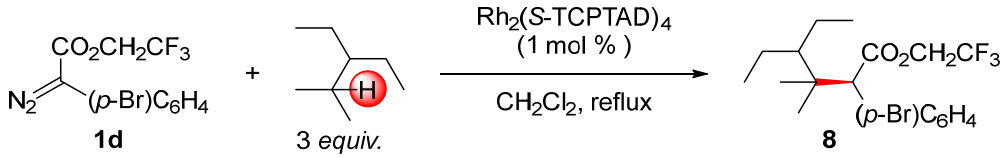

3°
2°
3.72
3.56
3.55
3.54
3.53
3.50
3.49
3.48
3.47
92 : 3 : 5
91.69
2.93
5.38

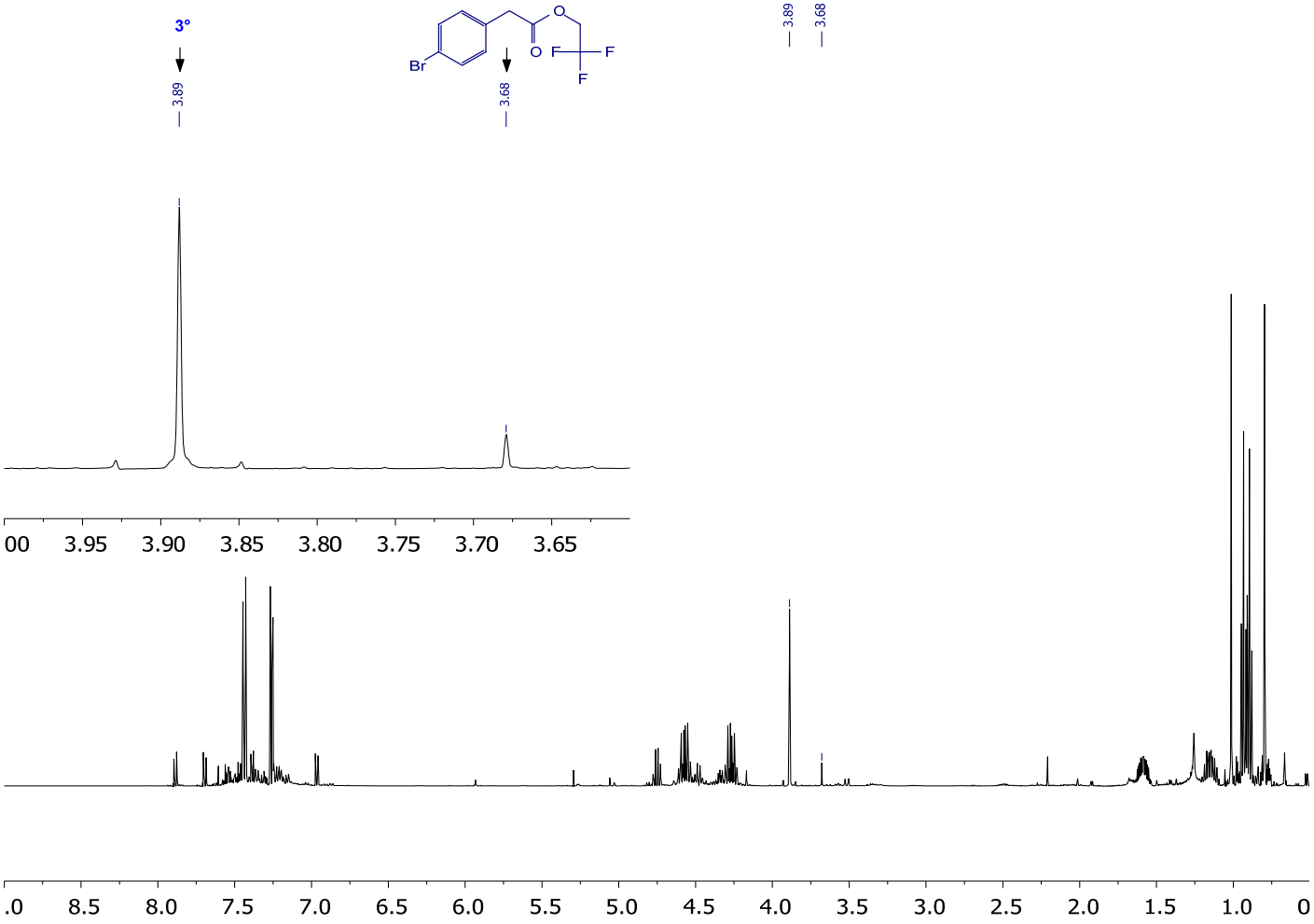

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, -40 °C
CO2CH2CF3
(p-Br)C6H4
6

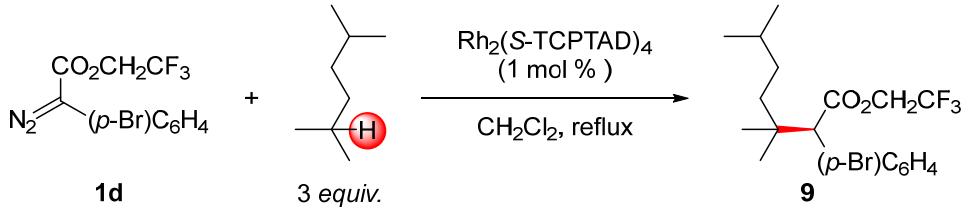

3°
2°
3.72
3.55
3.55
3.54
3.53
3.50
3.49
3.48
3.47
98 : 0 : 2
.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40
97.96
0.37
1.66
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0


CO2CH2CF3
N2
(p-Br)C6H4
1d
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, 39 °C
CO2CH2CF3
(p-Br)C6H4
7

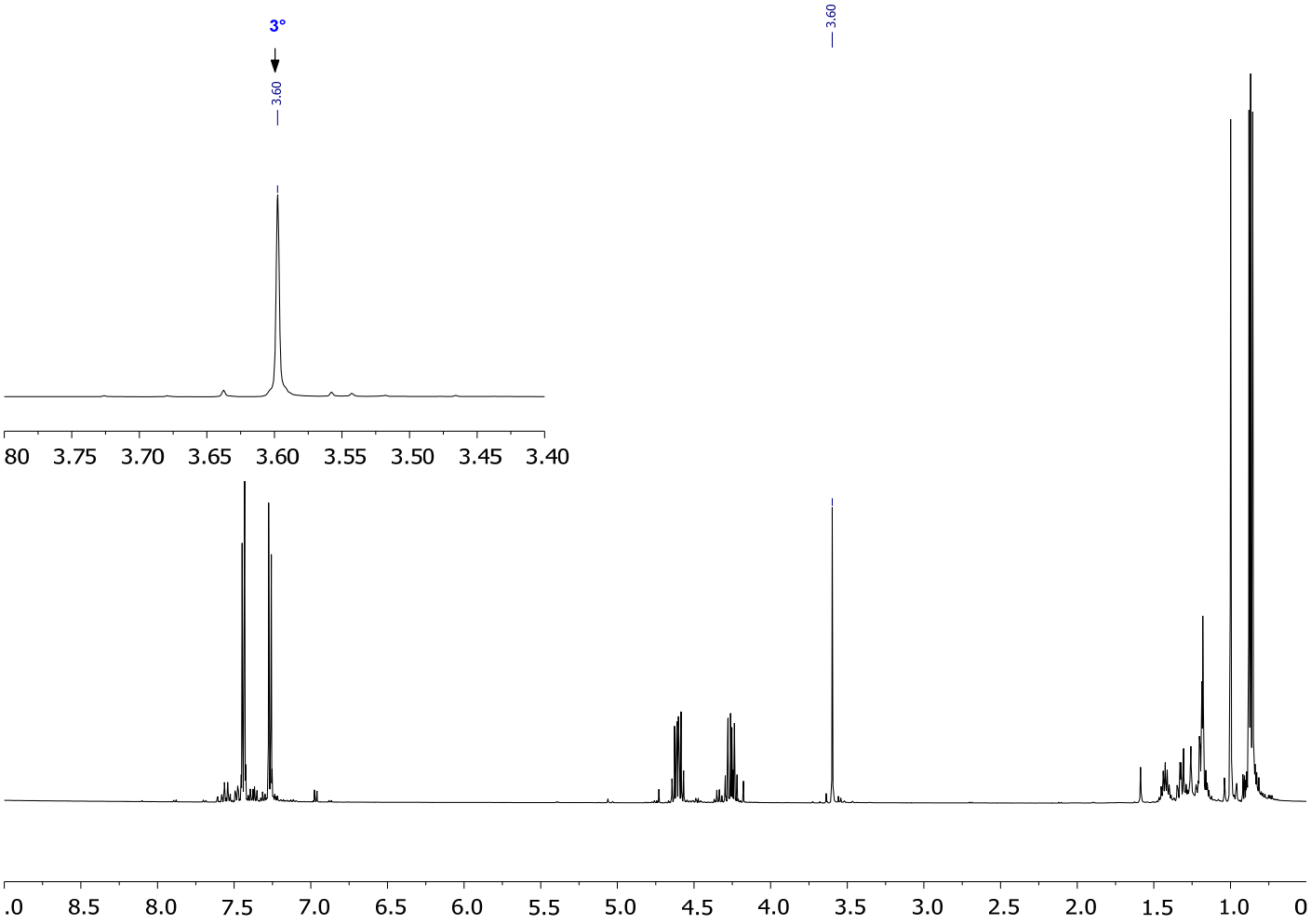

3°
2°
11
:
89
3.7
3.6
3.5
3.4
3.3
3.2
10.99
89.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

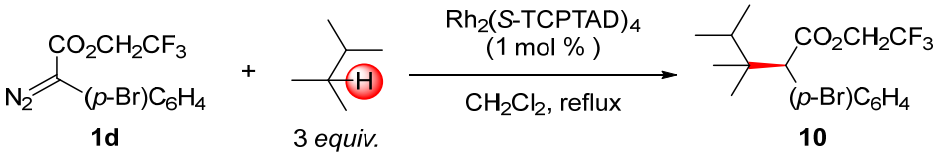

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(p-Br)C6H4
8

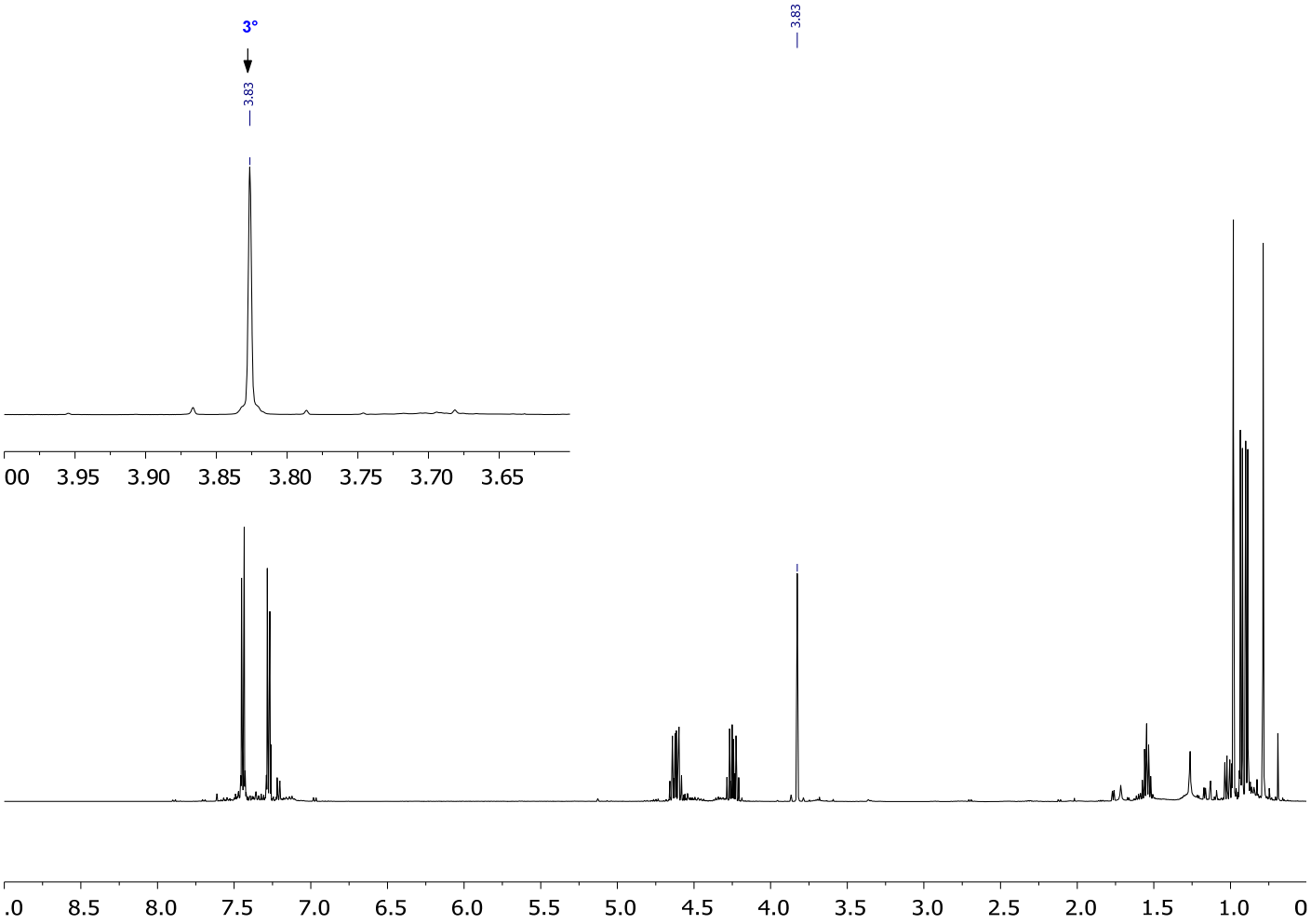

3°
3.89
Br
O
O F F
F
3.68
3.89
3.68
00 3.95 3.90 3.85 3.80 3.75 3.70 3.65
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

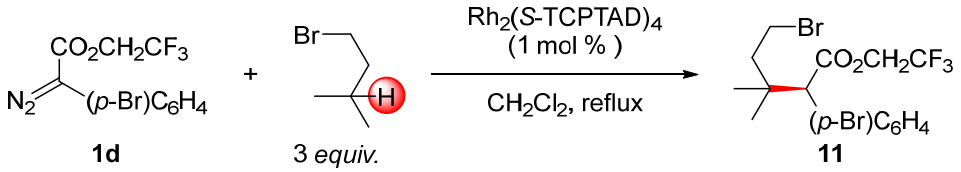

CO2CH2CF3
N2
(p-Br)C6H4
+
H
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(p-Br)C6H4

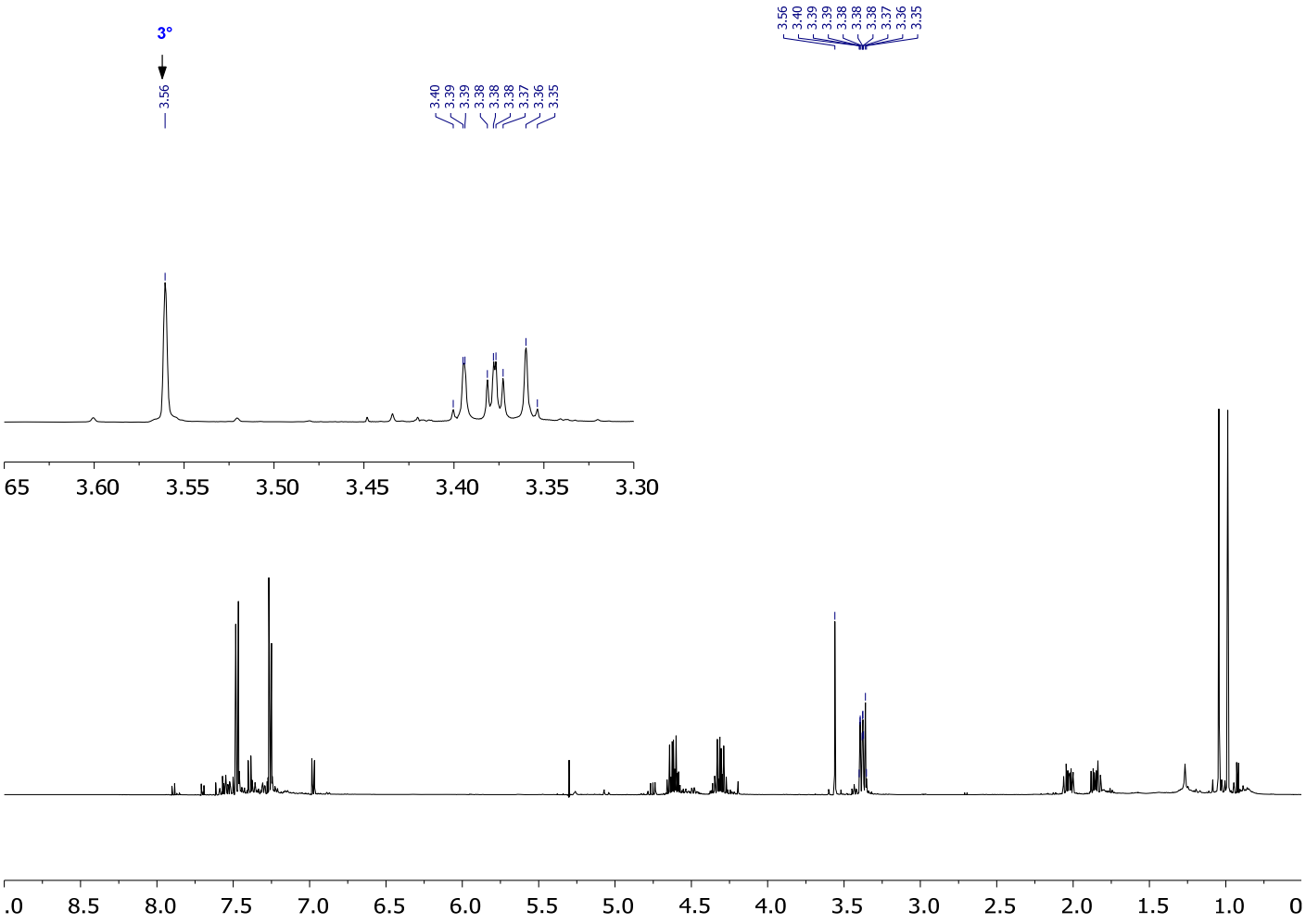
1d 3 *equiv.* **9**

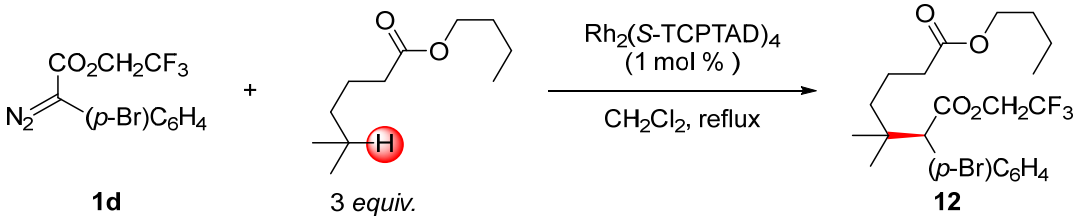

3°
3.60
3.60
80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

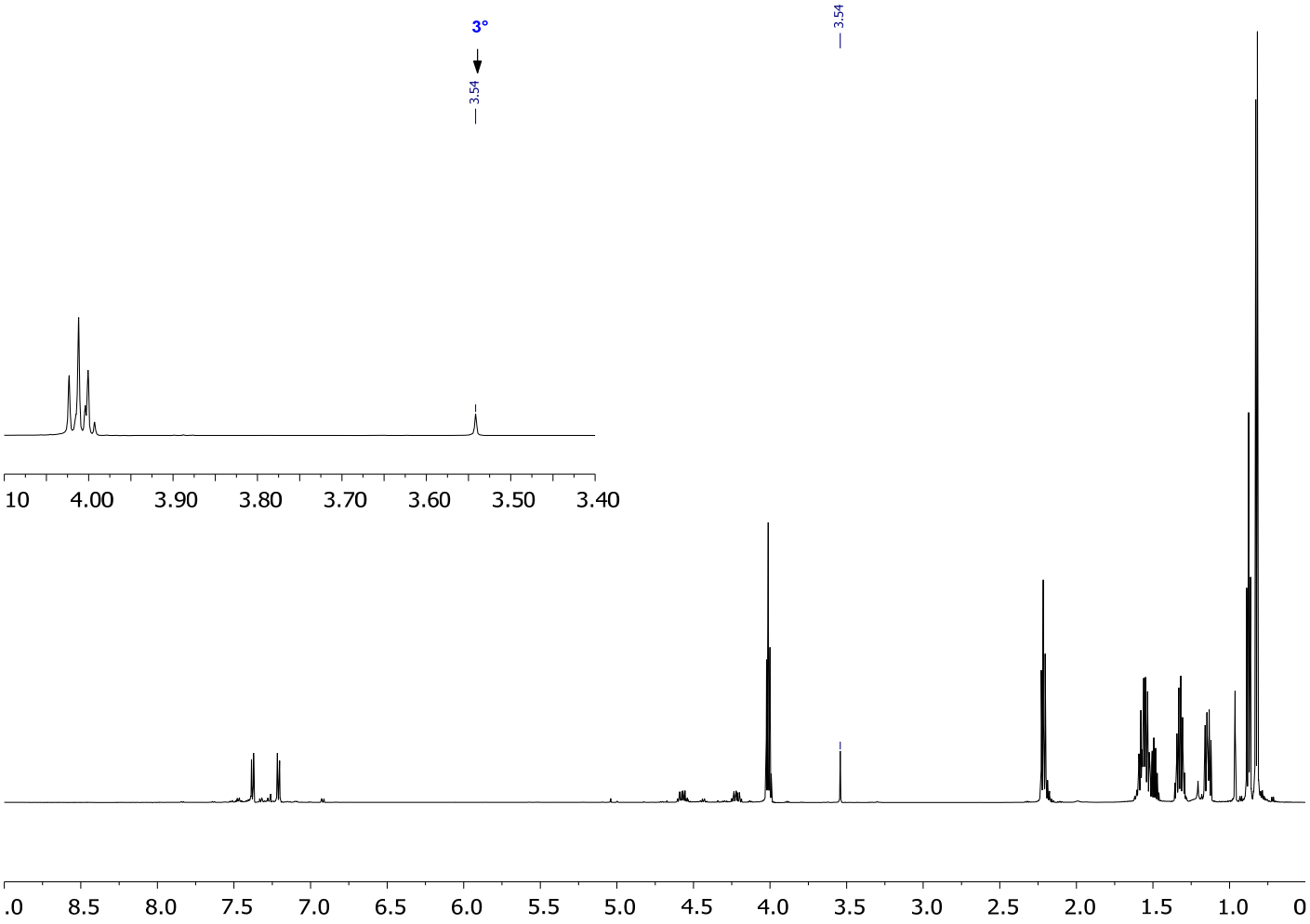

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(p-Br)C6H4
10

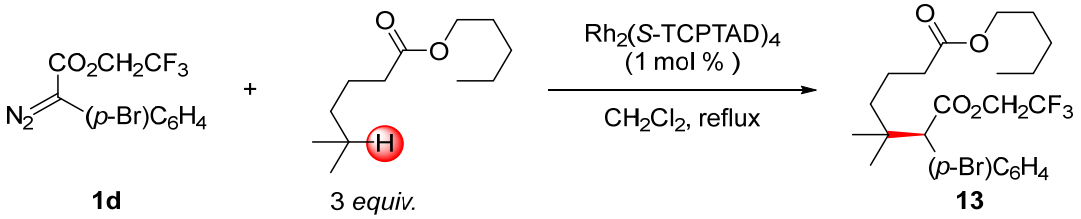

3°
3.83
3.83
00 3.95 3.90 3.85 3.80 3.75 3.70 3.65
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

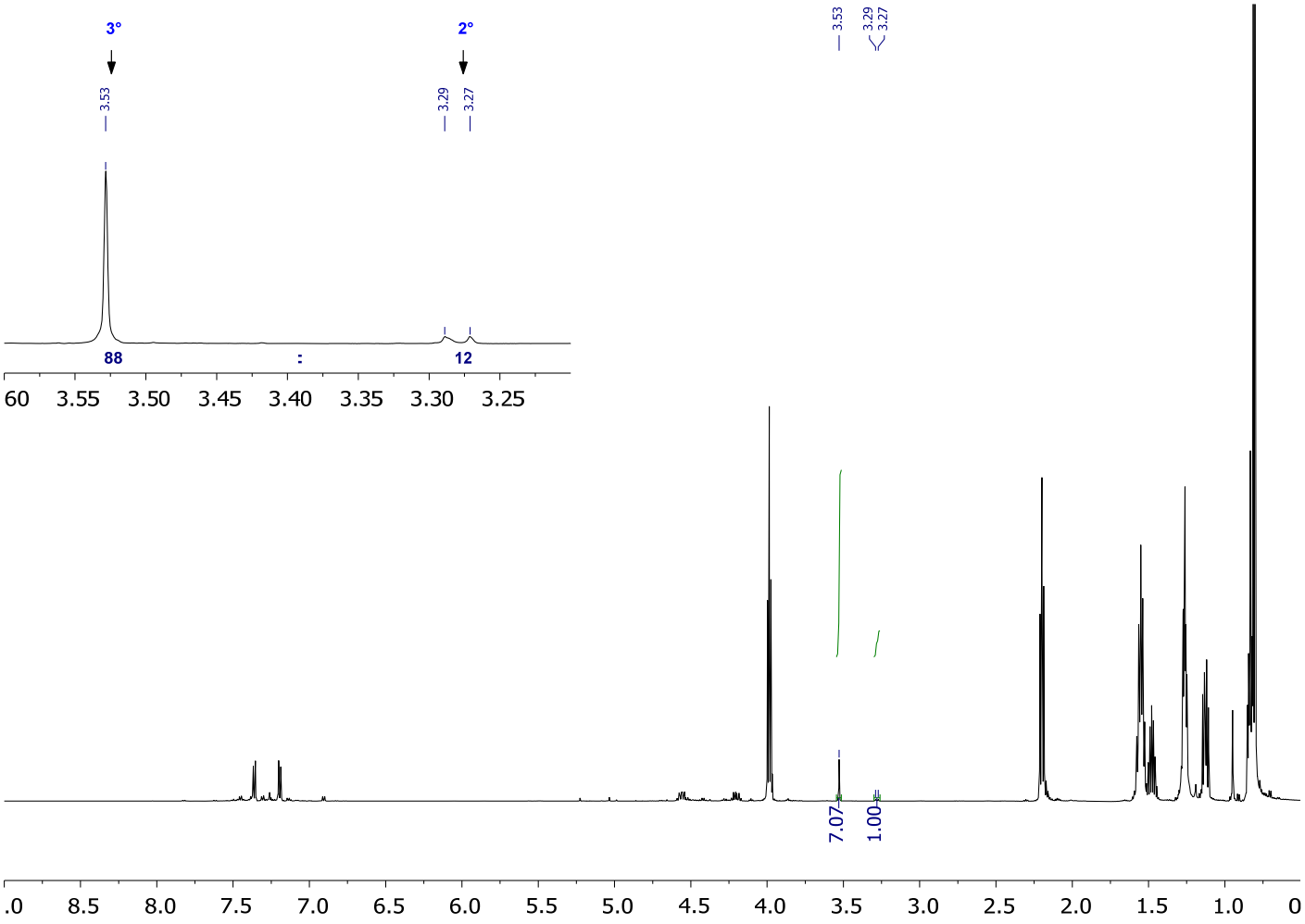

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
Br
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
Br
CO2CH2CF3
(p-Br)C6H4
11

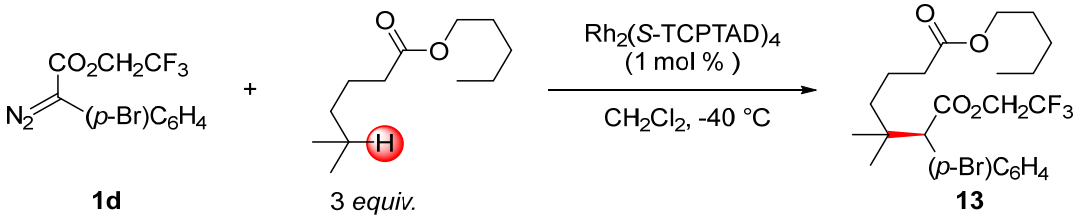

3°
3.56
3.40
3.39
3.39
3.38
3.38
3.38
3.37
3.36
3.35
65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

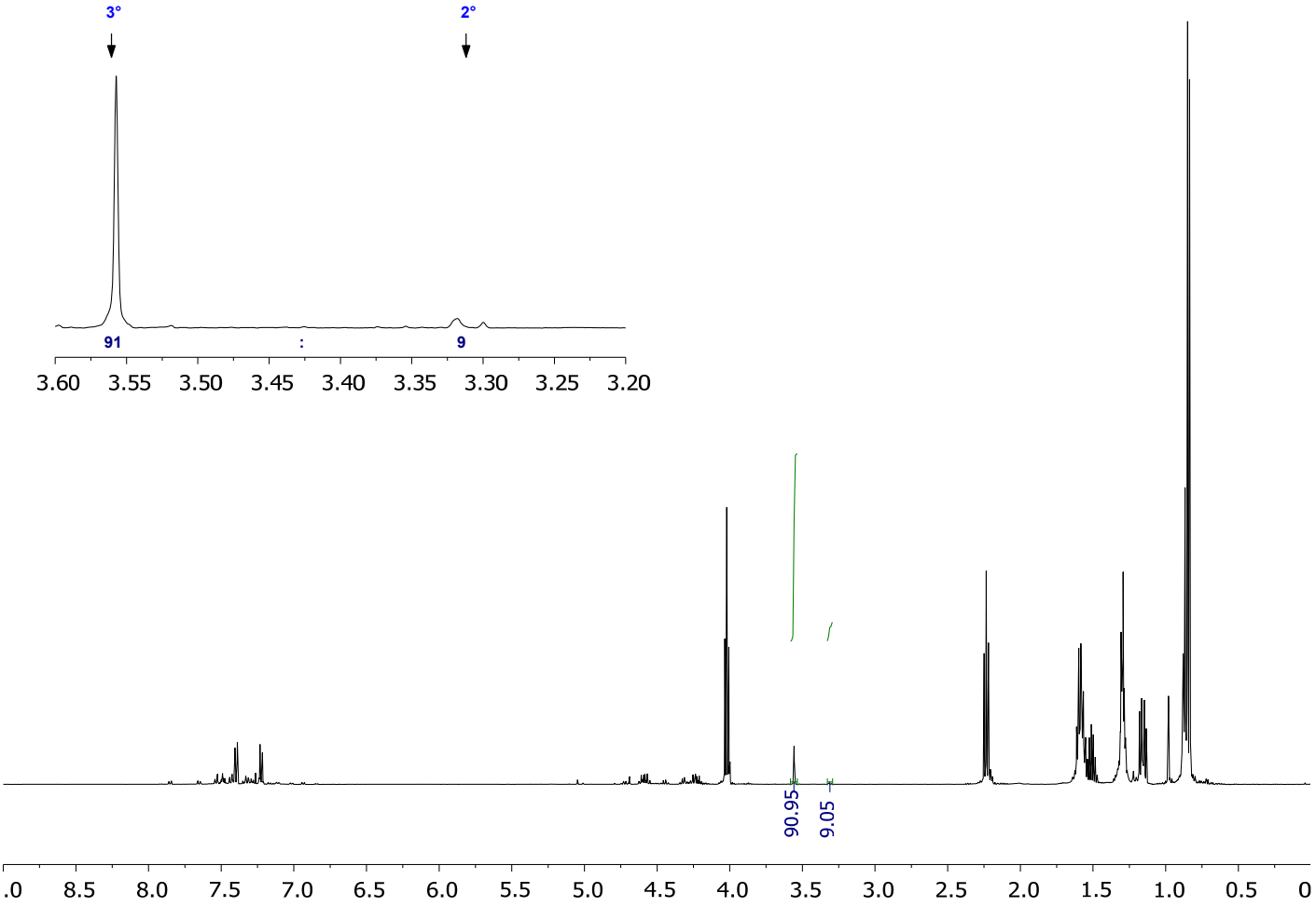

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
O
O
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
O
O
CO2CH2CF3
(p-Br)C6H4
12

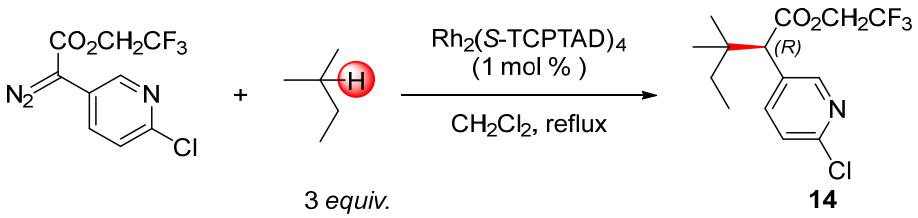

3°
3.54
3.54
10
4.00
3.90
3.80
3.70
3.60
3.50
3.40
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0


CO2CH2CF3
N2
(p-Br)C6H4
1d
+
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(p-Br)C6H4
13


3°
2°
3.53
3.29
3.27
88 : 12
7.07
1.00

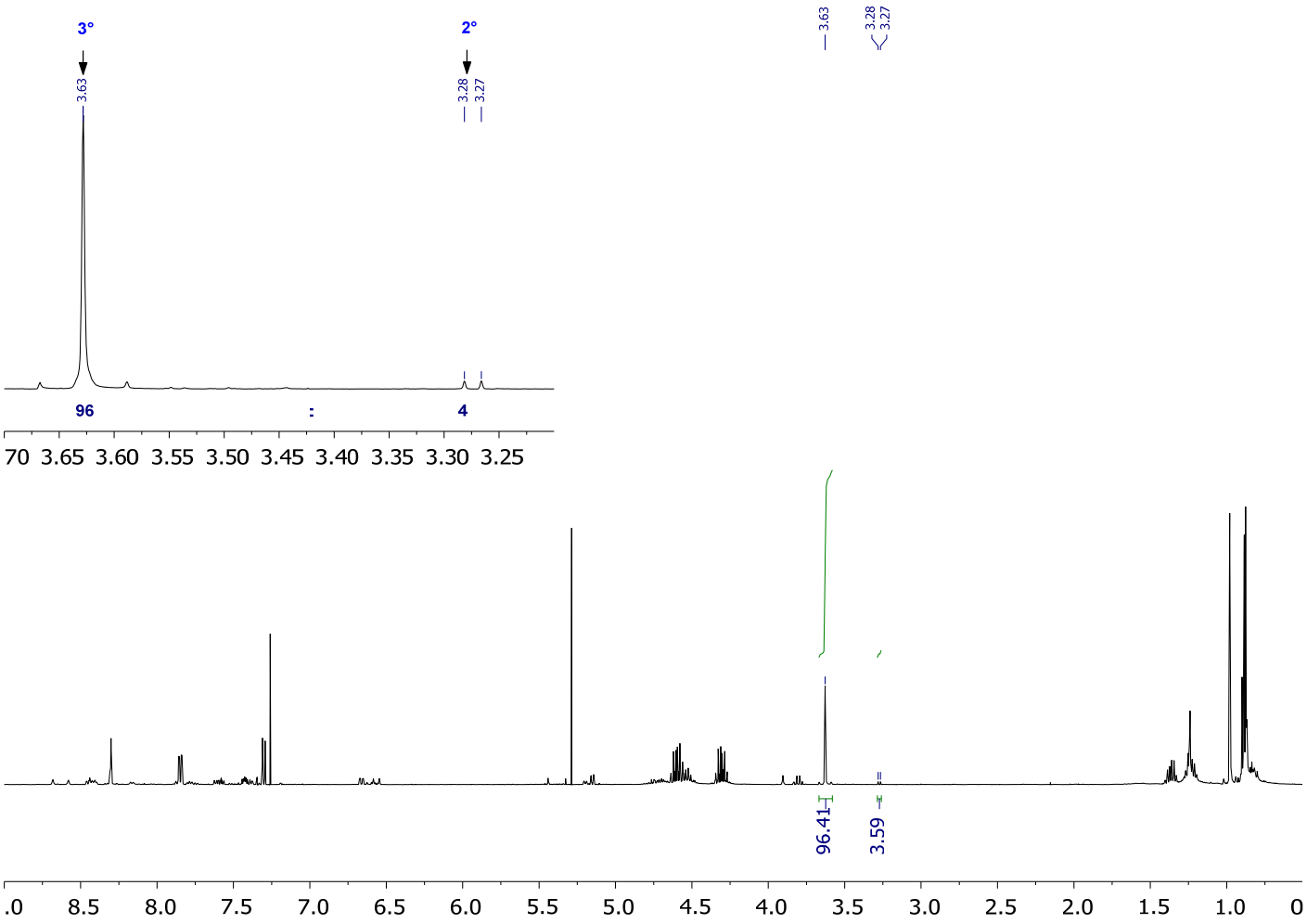

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
O
O
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, -40 °C
O
O
CO2CH2CF3
(p-Br)C6H4
13

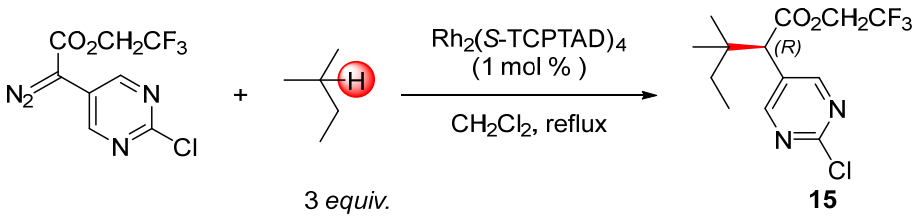

3°
2°
91
:
9
3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20
90.95
9.05
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

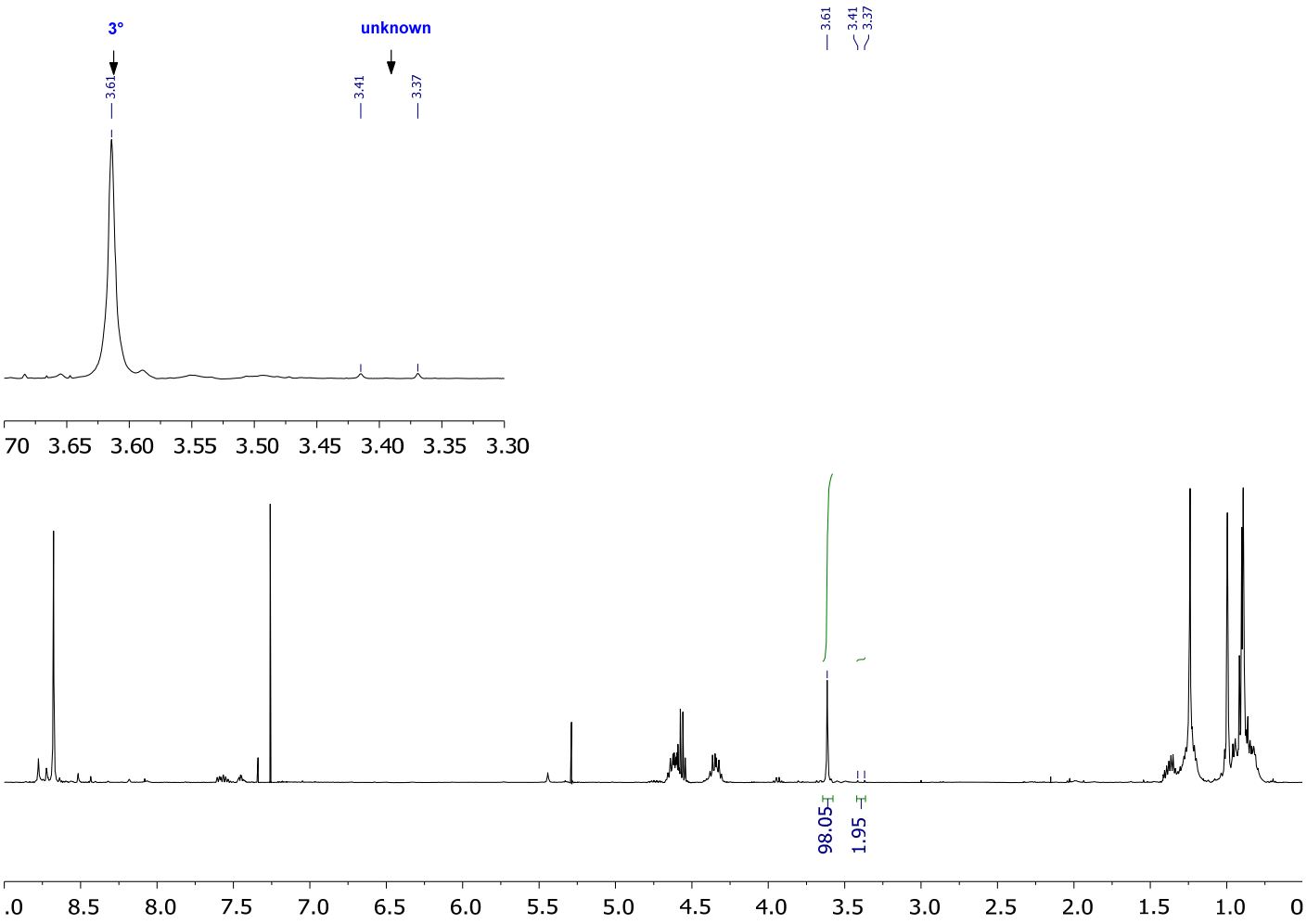

CO2CH2CF3
N2
N
Cl
+
H
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(R)
N
Cl

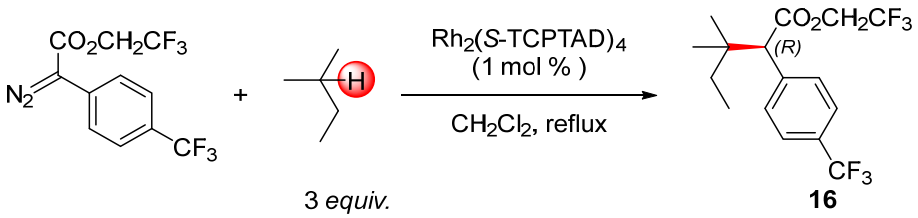
3 *equiv.*

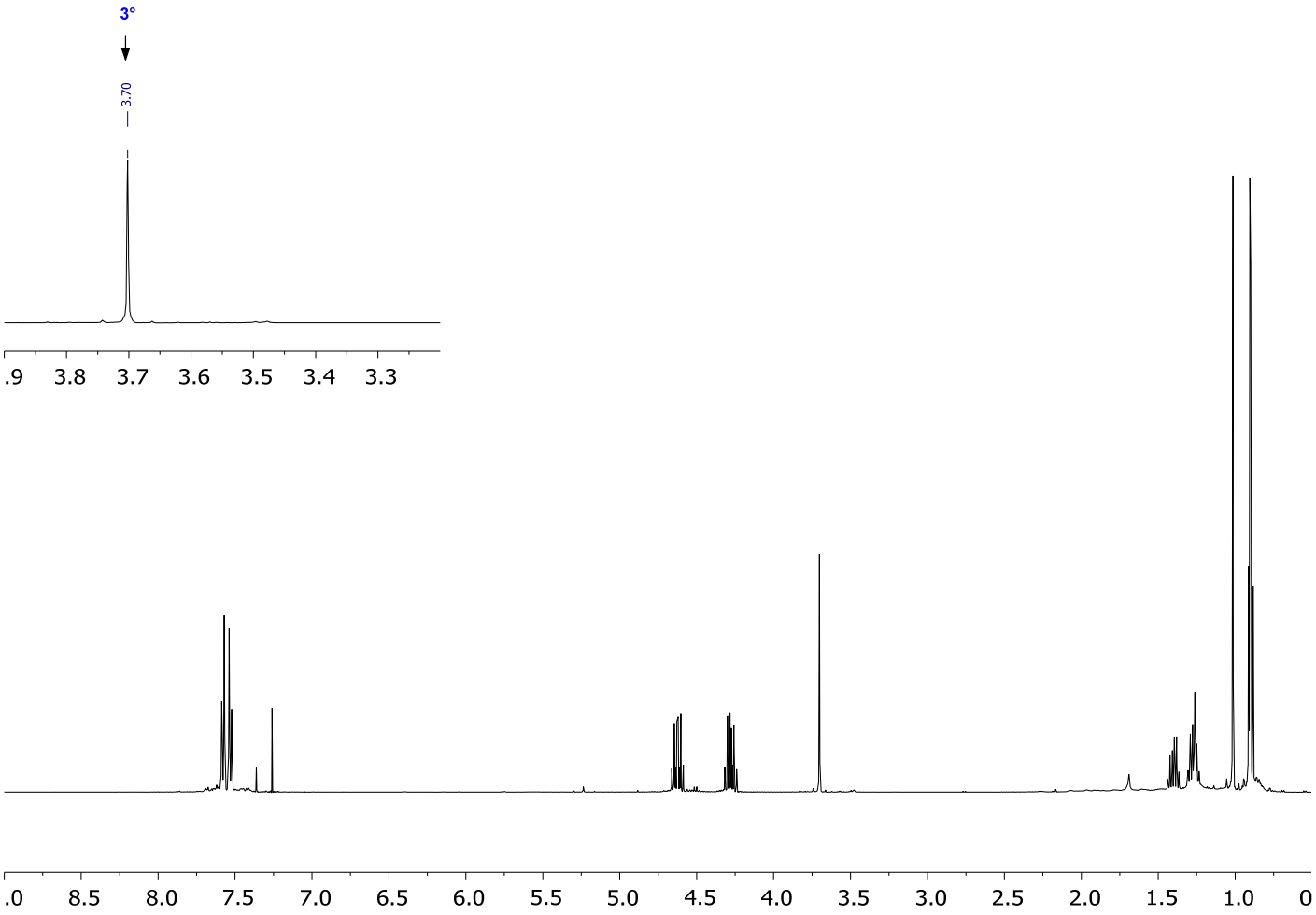
14

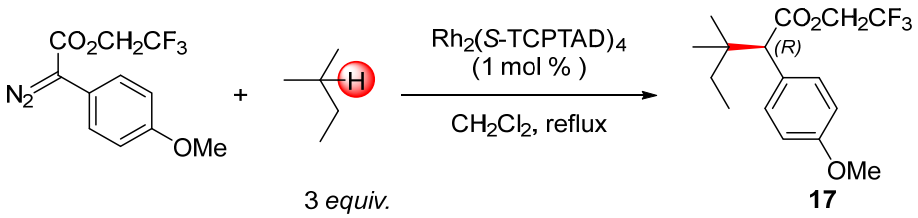

3°
2°
3.63
3.28
3.27
96
:
4
70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25
96.41
3.59
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

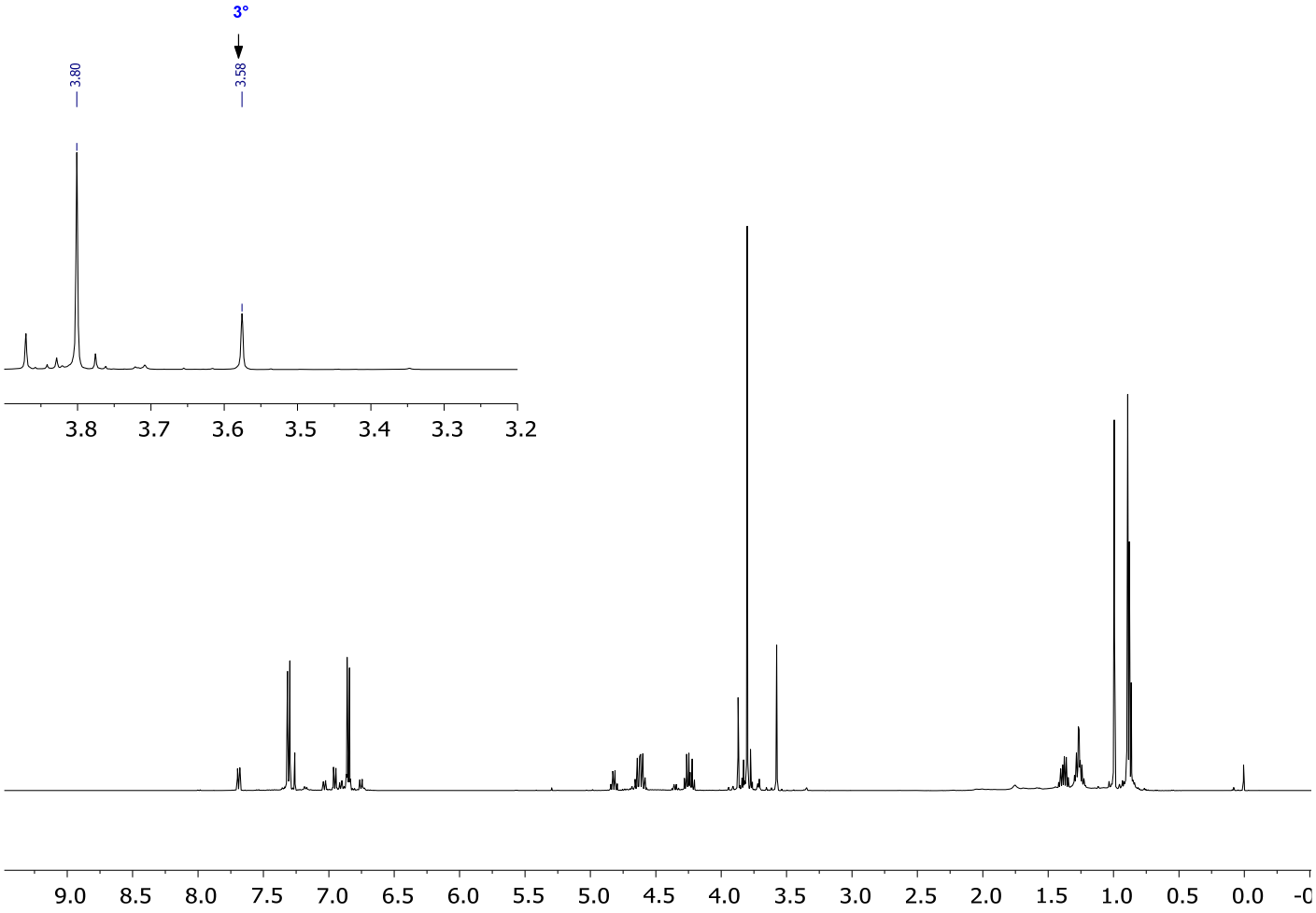

CO2CH2CF3
N2
N
N
Cl
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(R)
N
N
Cl
15

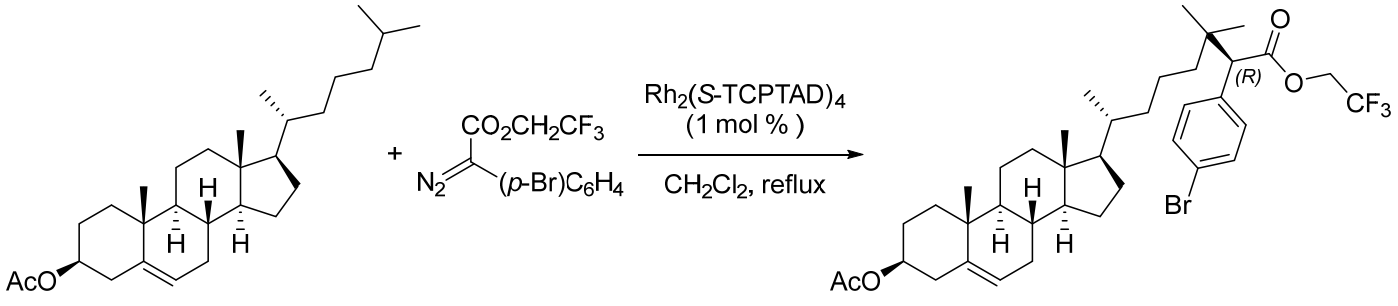

3°
unknown
3.61
3.41
3.37
70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
98.05
1.95
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0


CO2CH2CF3
N2
CF3
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(R)
CF3
16


3°
3.70
.9 3.8 3.7 3.6 3.5 3.4 3.3
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0


CO2CH2CF3
N2
OMe
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(R)
OMe
17

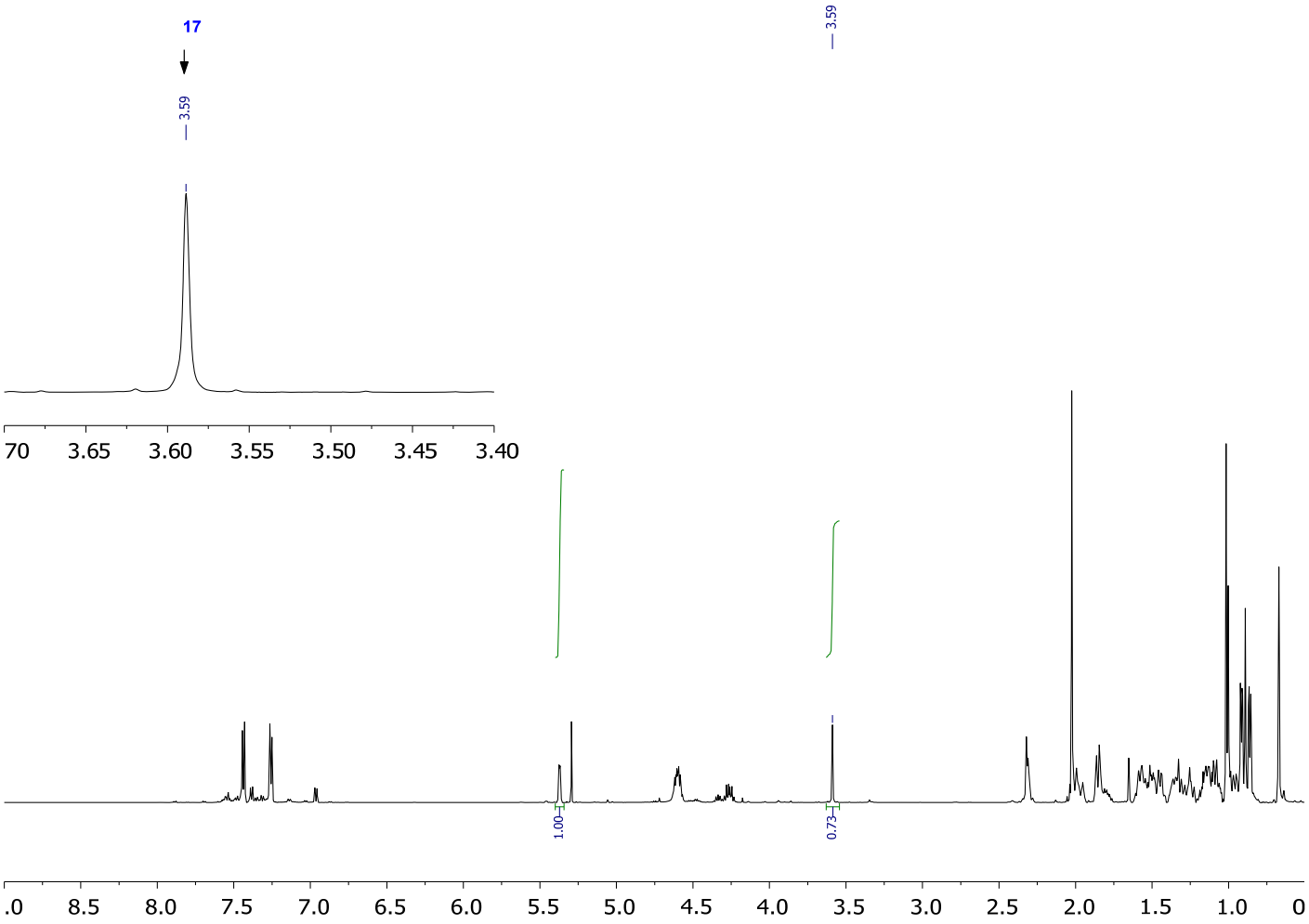

3°
3.80
3.58
3.8
3.7
3.6
3.5
3.4
3.3
3.2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

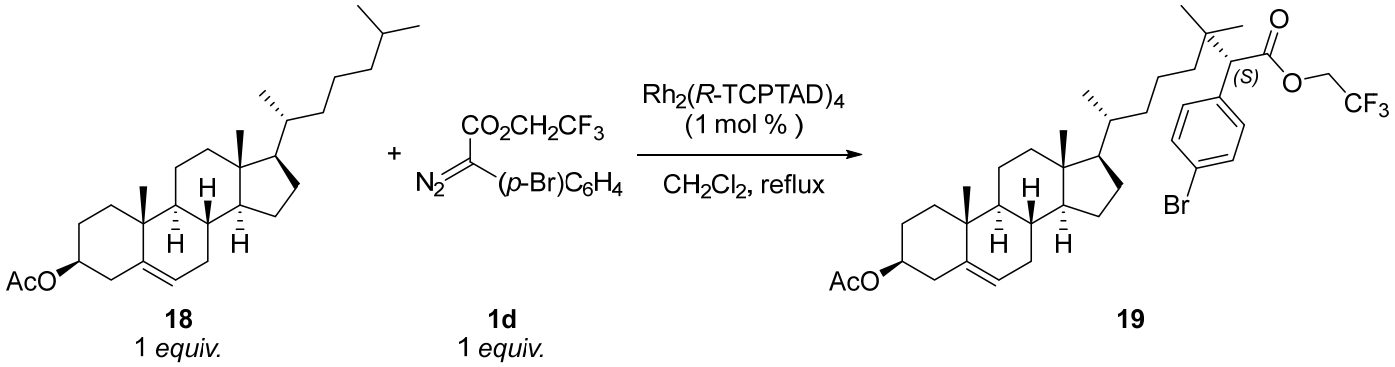


18
1 *equiv.*

1d
1 *equiv.*

19

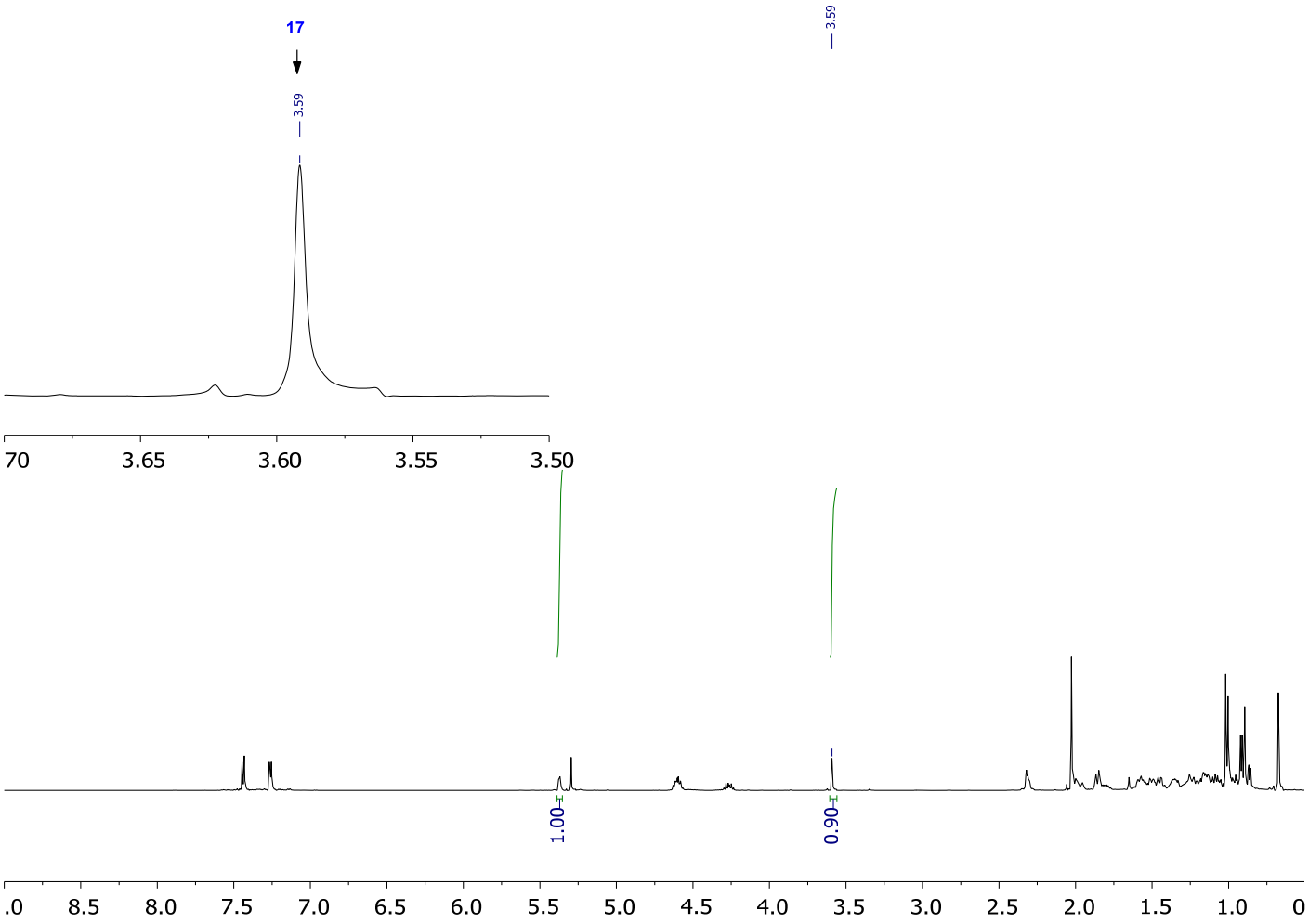


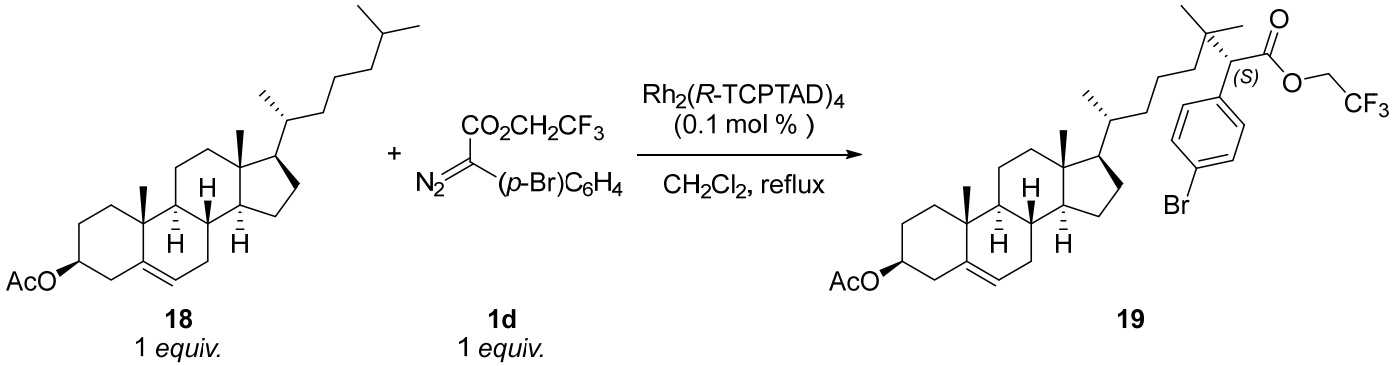


18
1 *equiv.*

1d
1 *equiv.*

19

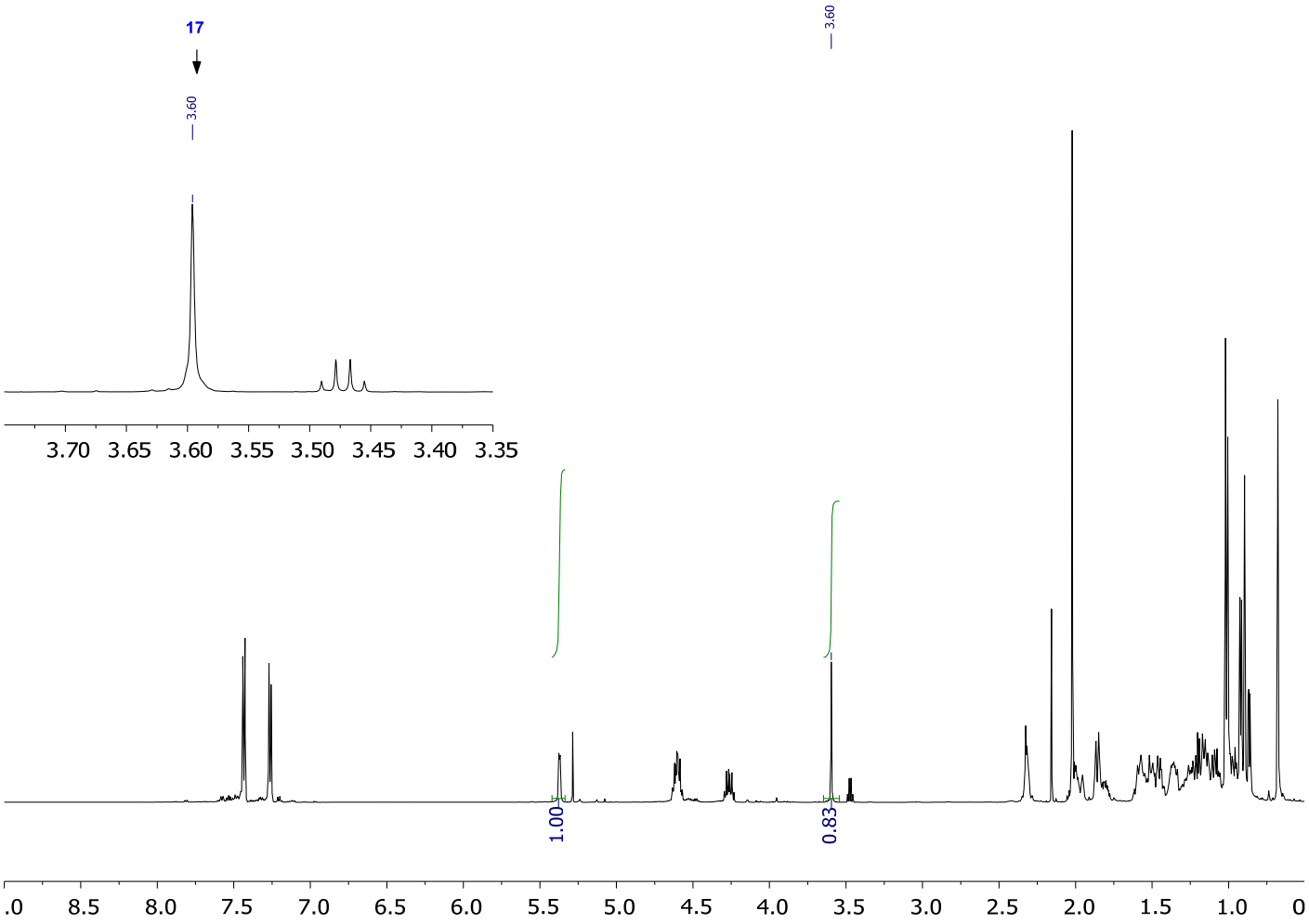


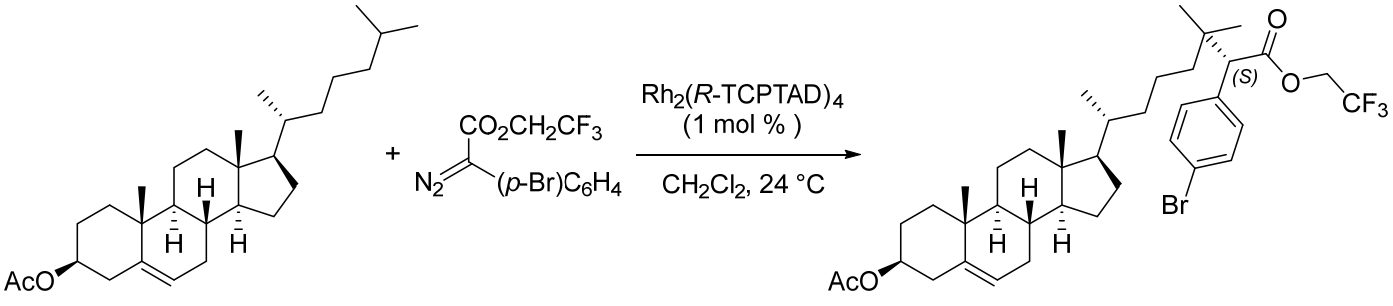


18
1 *equiv.*

1d
1 *equiv.*

19

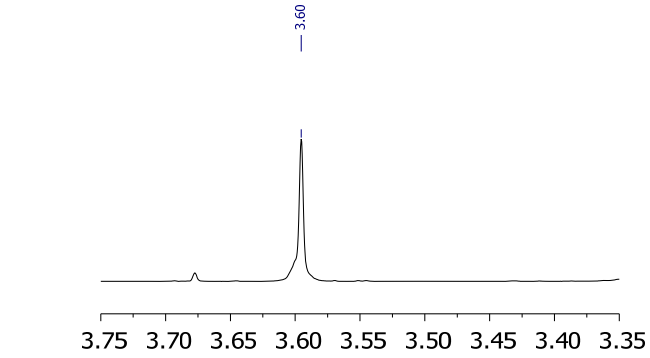


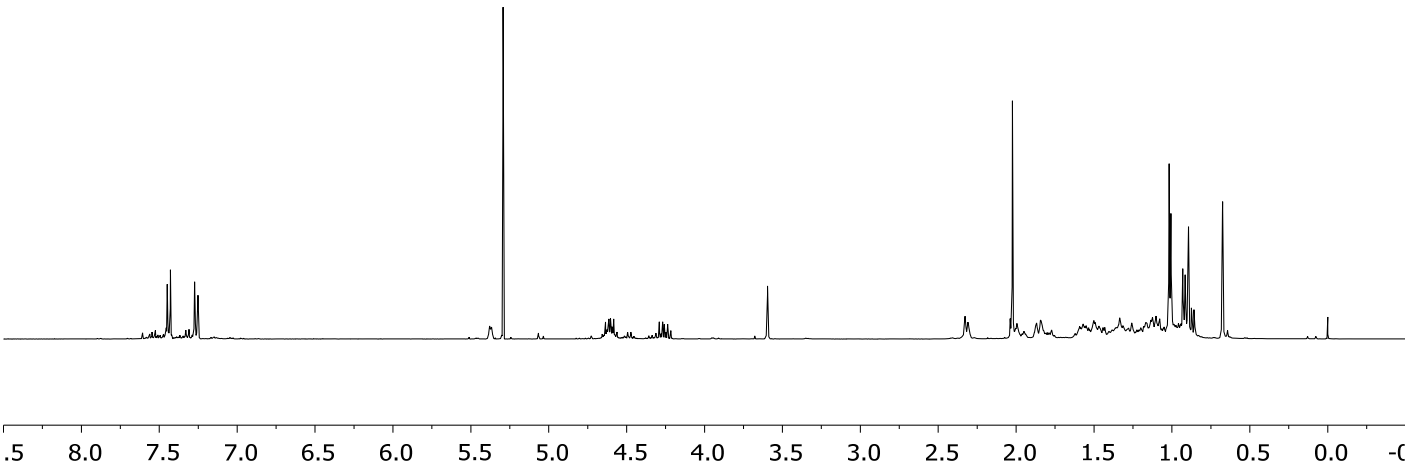


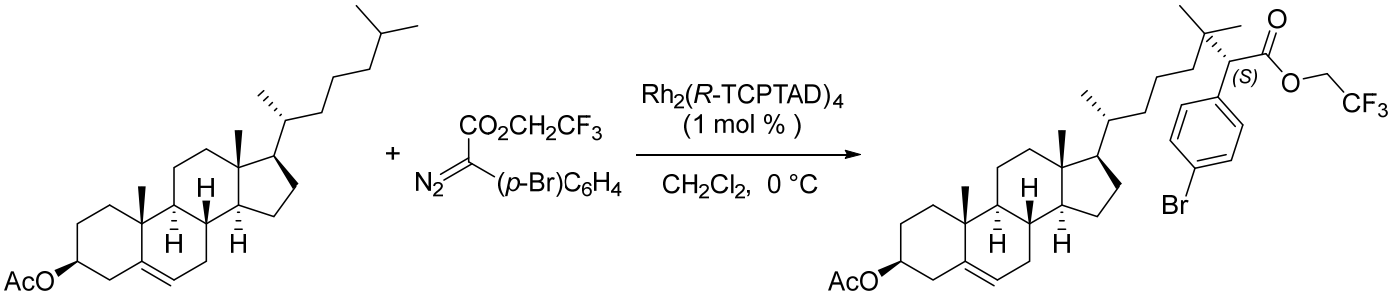
18
1 *equiv.*

1d
1 *equiv.*

19



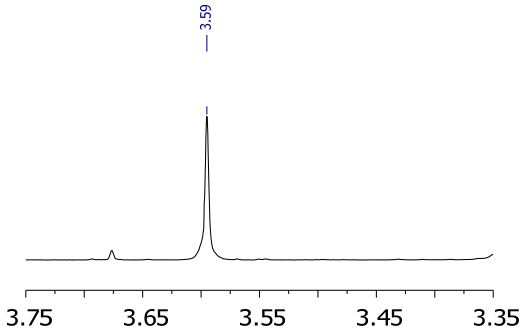


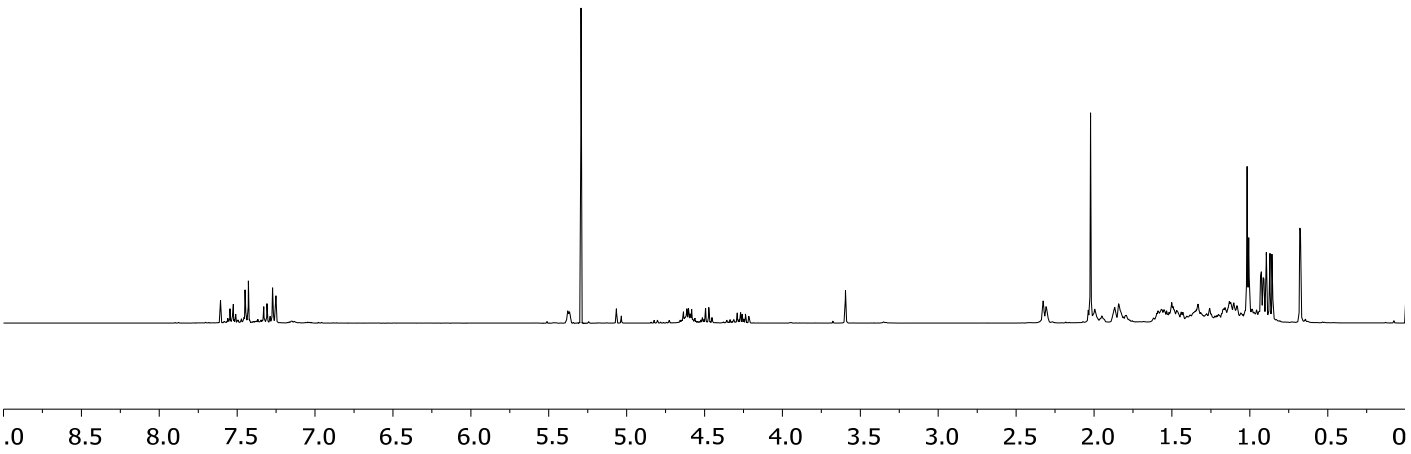


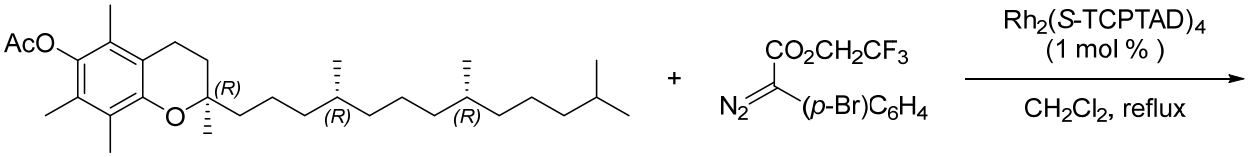
18
1 *equiv.*

1d
1 *equiv.*

19

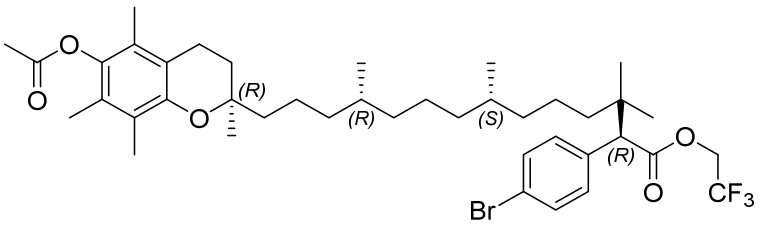




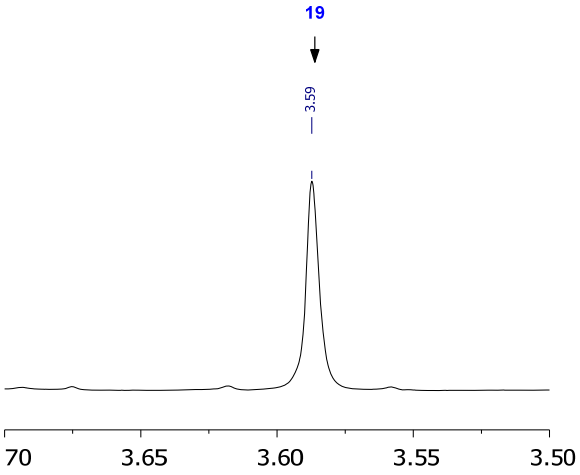


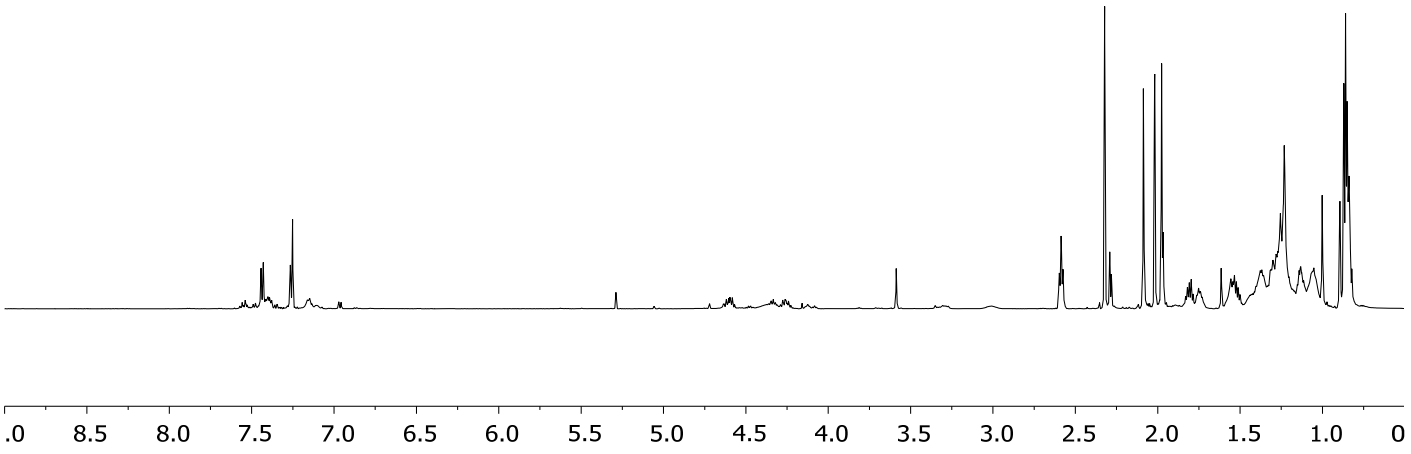
20
1 *equiv.*

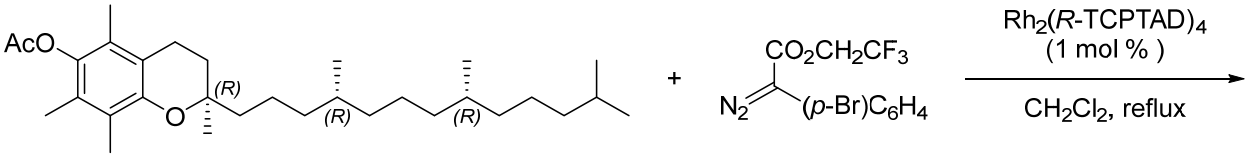
1d
1 *equiv.*



21

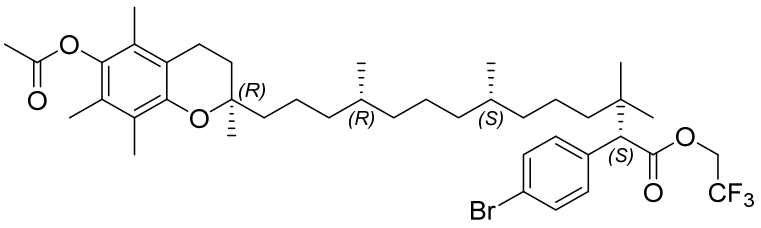




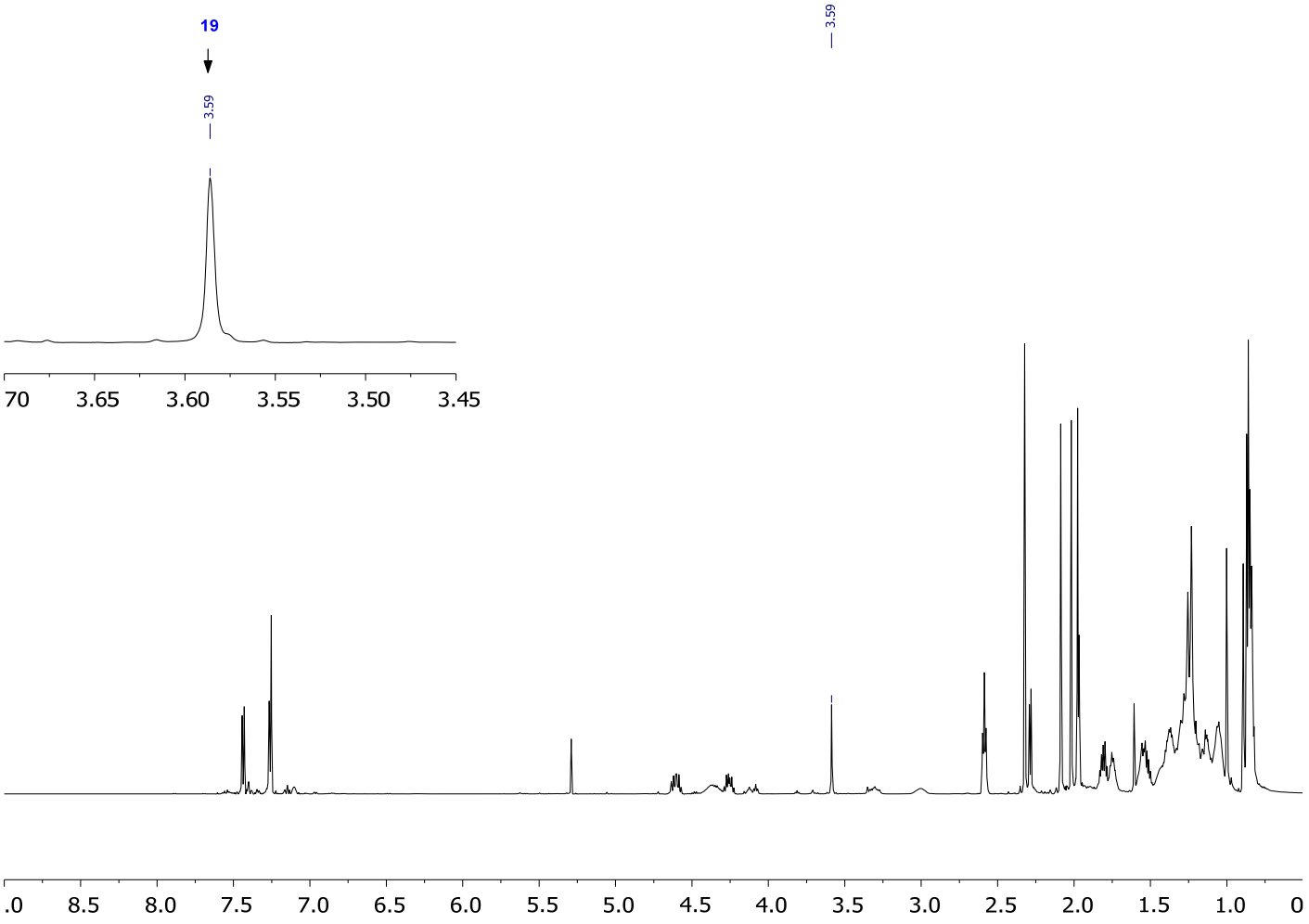


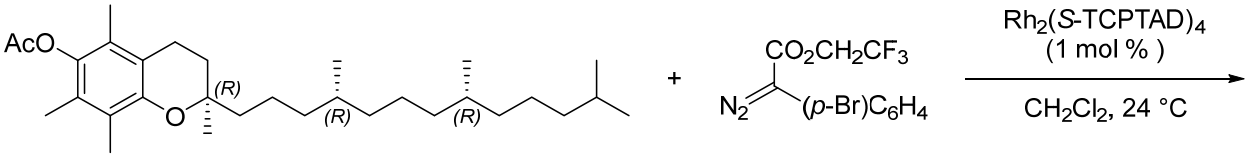
20
1 *equiv.*

1d
1 *equiv.*



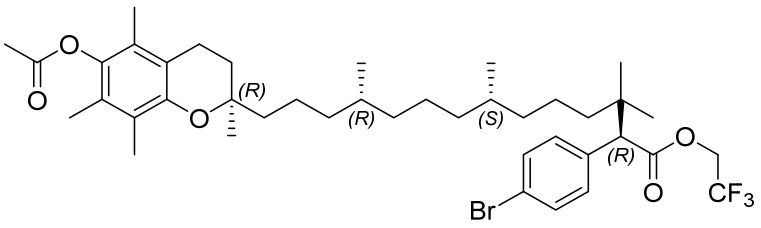
21



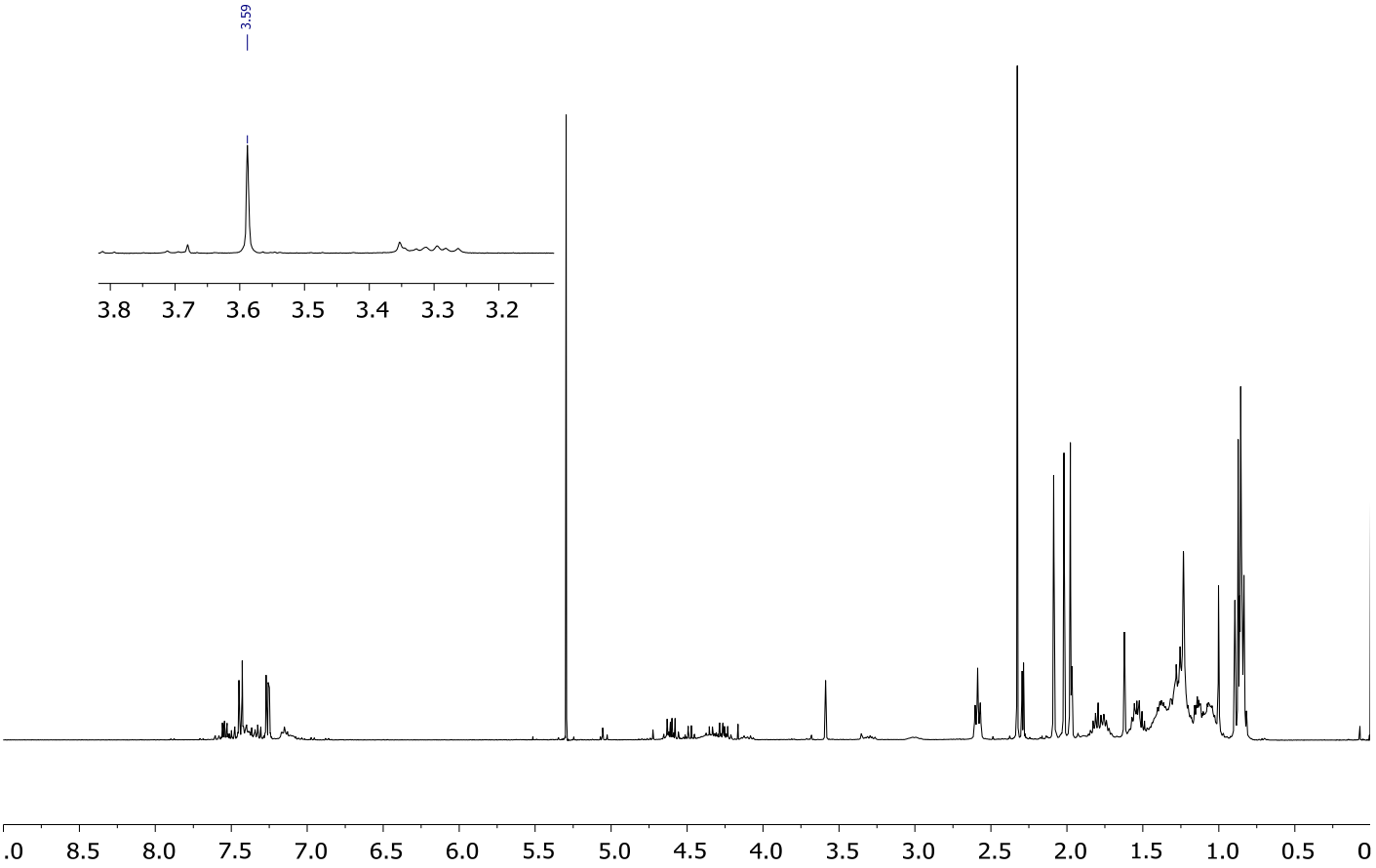


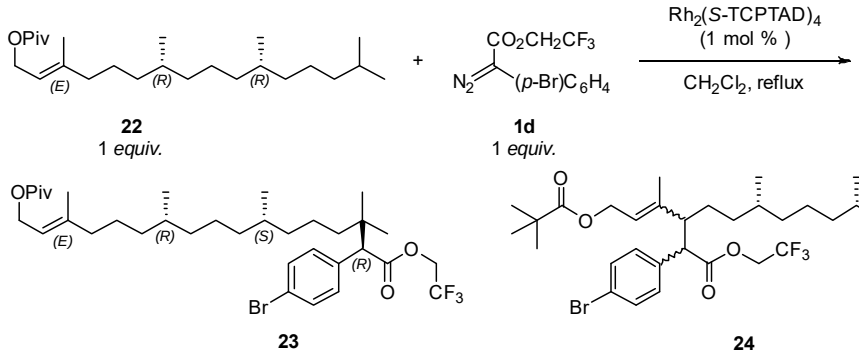
20
1 *equiv.*

1d
1 *equiv.*



21



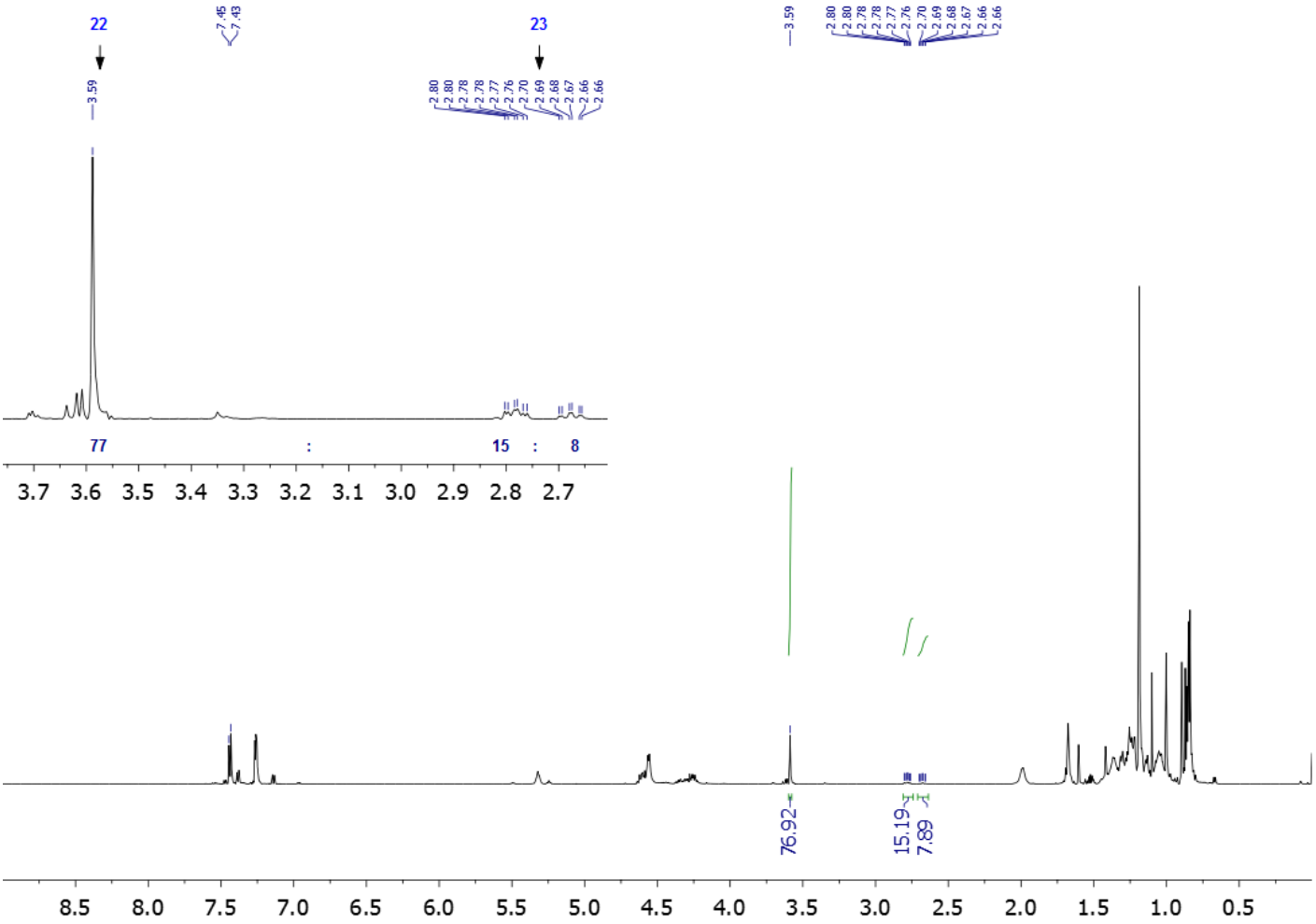


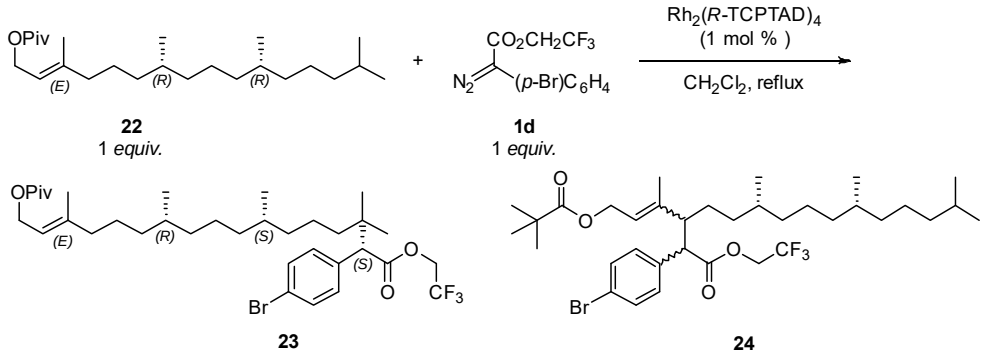
22
1 *equiv.*

1d
1 *equiv.*

23

24



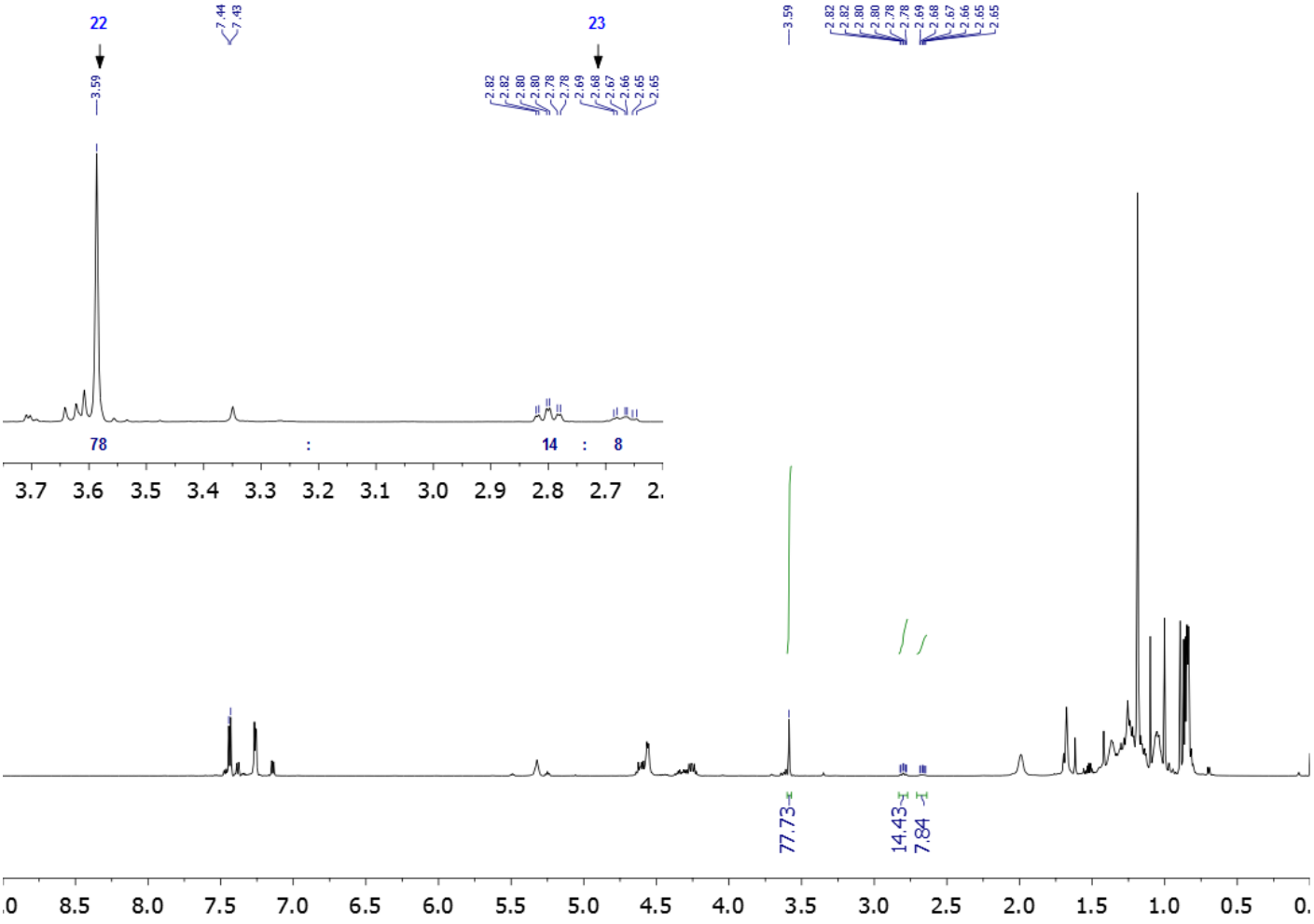


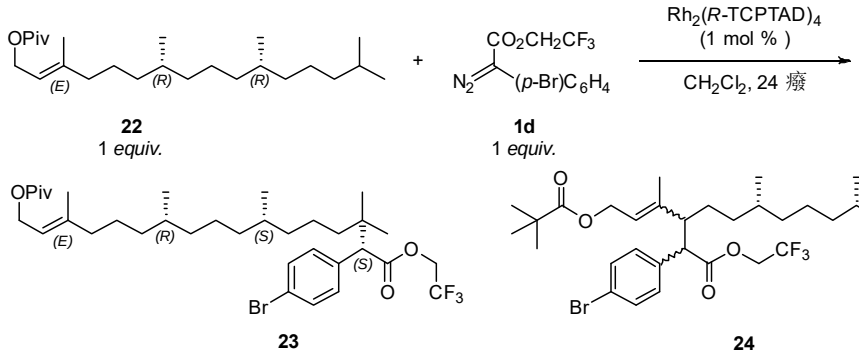
22
1 *equiv.*

1d
1 *equiv.*

23

24



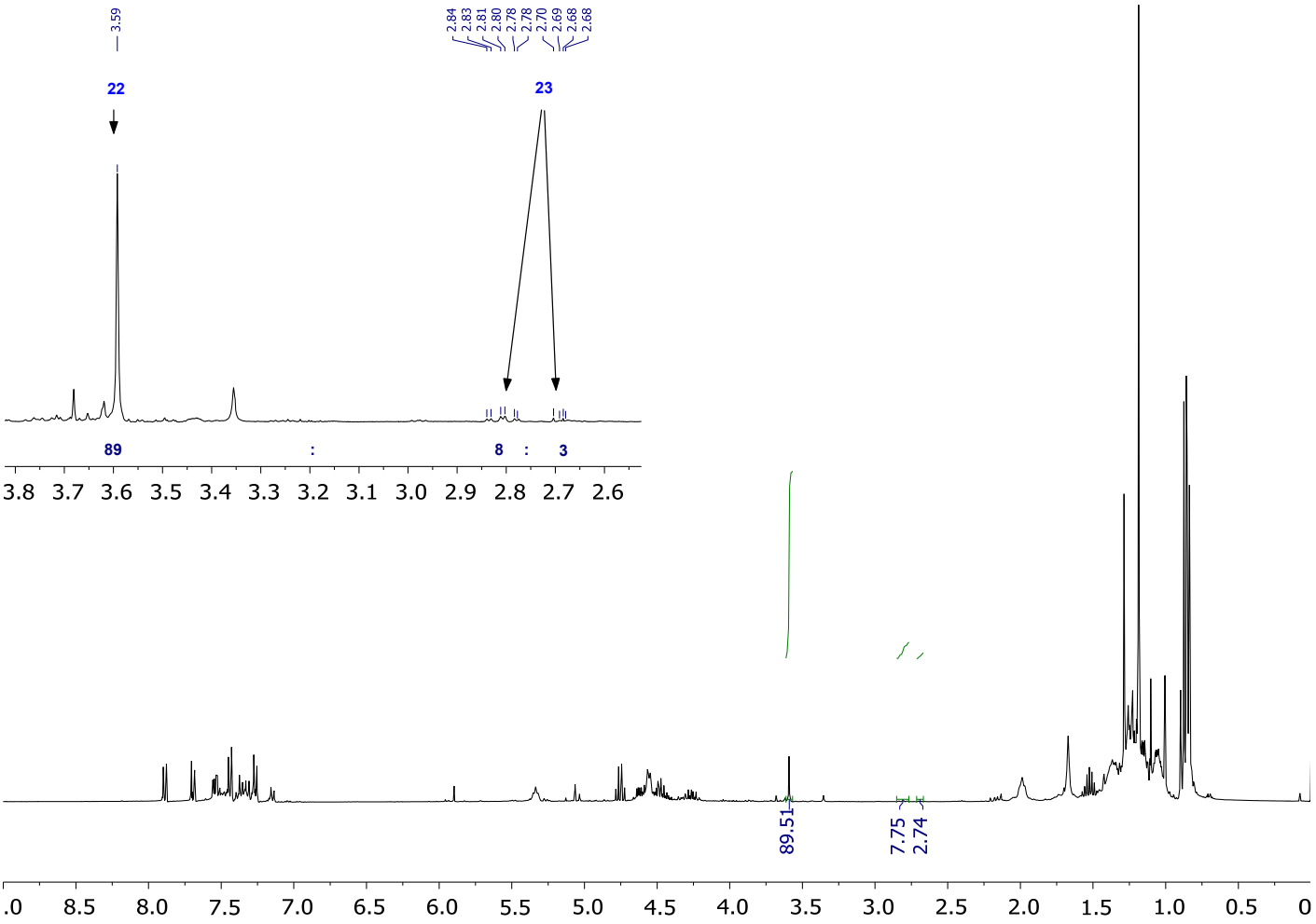


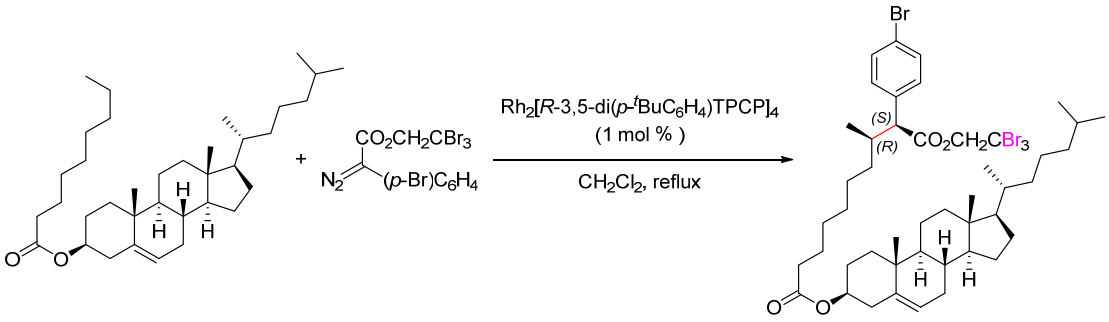
22
1 *equiv.*

1d
1 *equiv.*

23

24

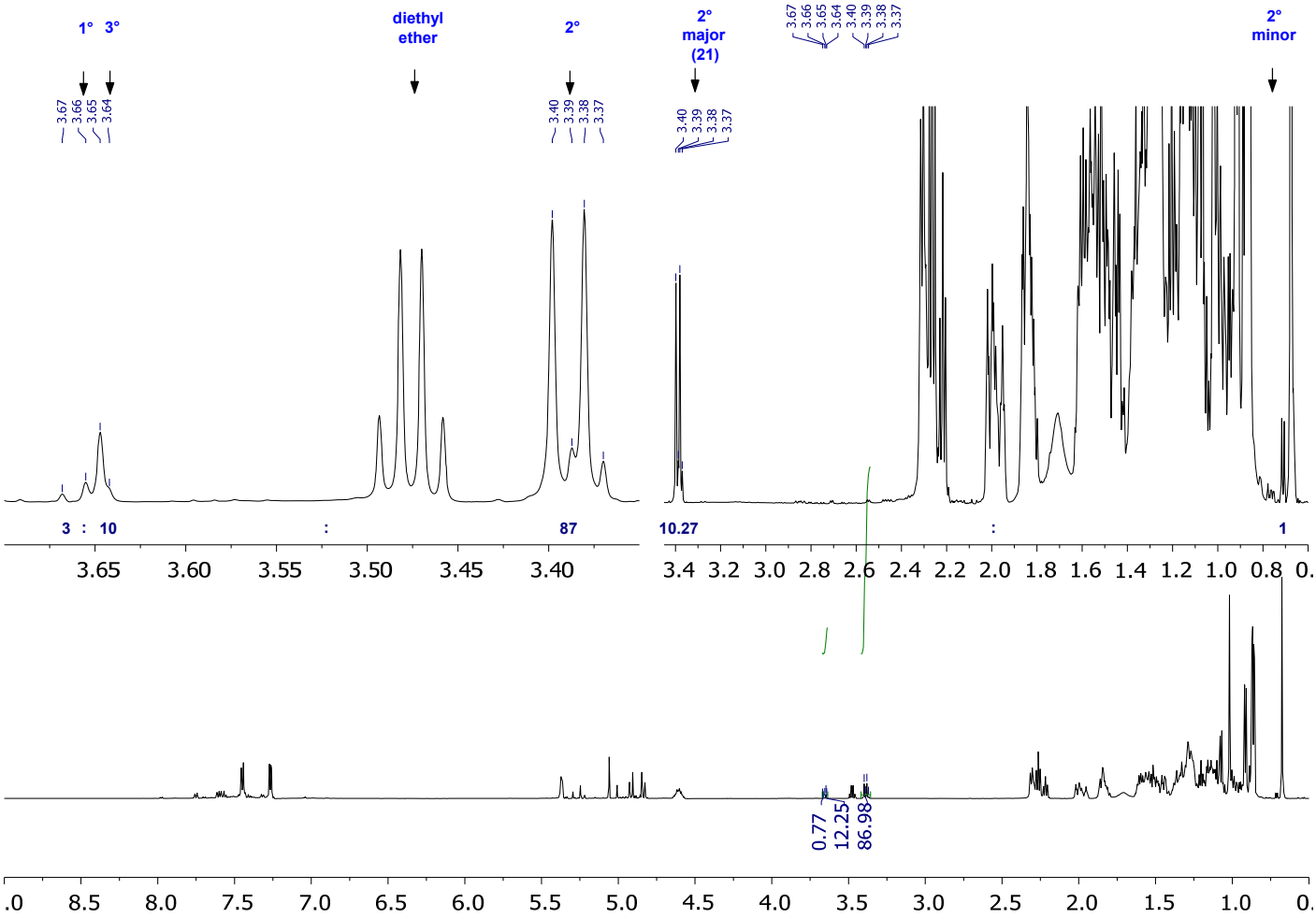


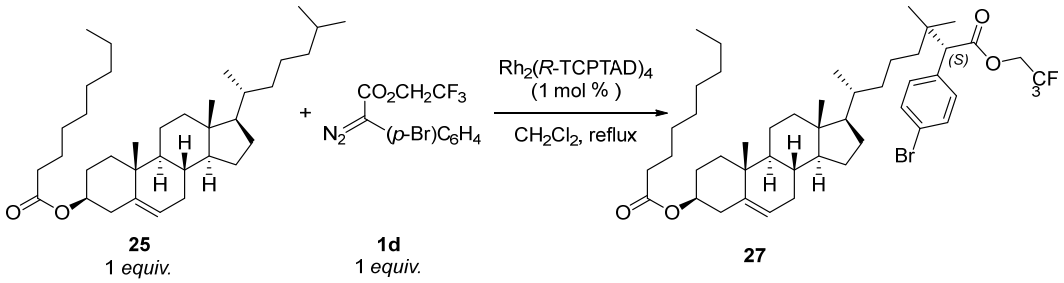


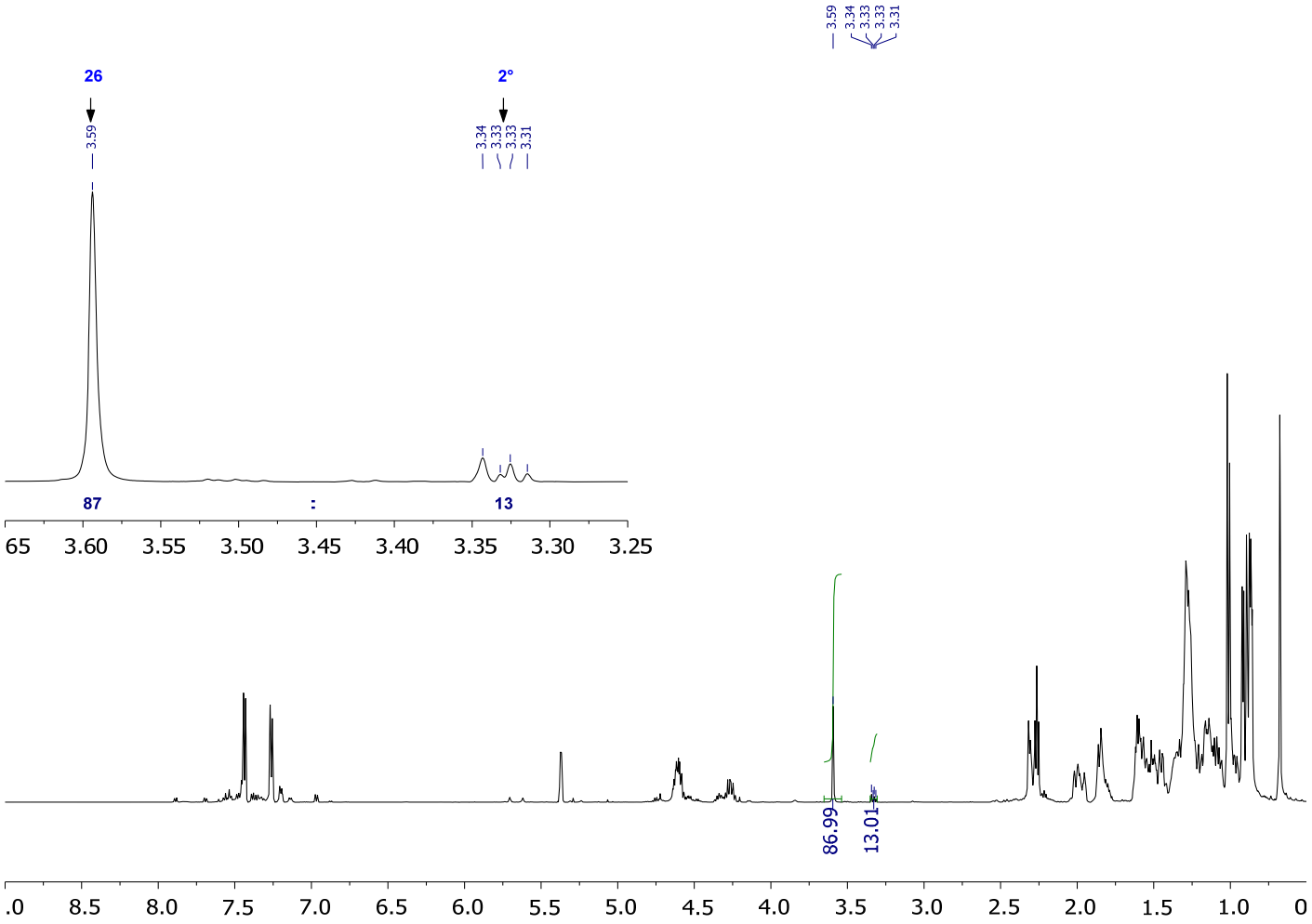
25
1 *equiv.*

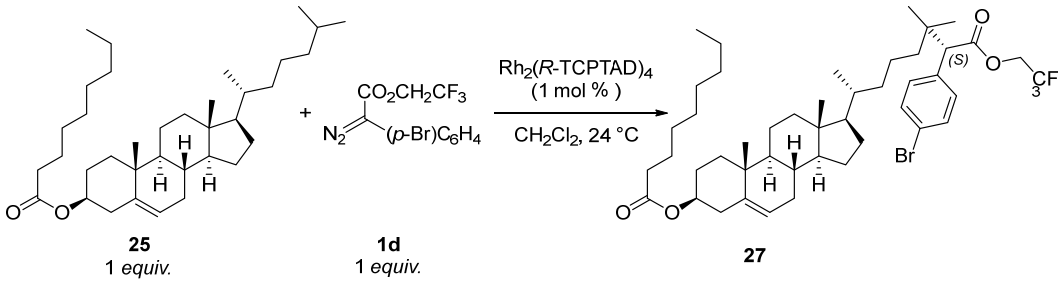
1c
1 *equiv.*

26




Rh2(R-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
N2
(p-Br)C6H4
Br
(S)
CF3
25
1 equiv.
1d
1 equiv.
27

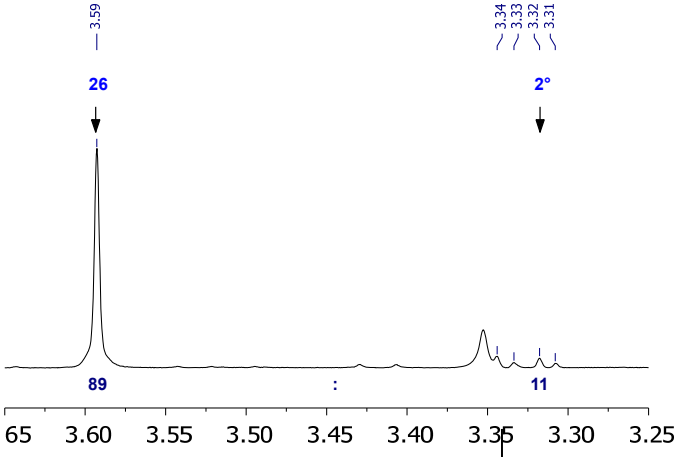

26
2°
3.59
3.34
3.33
3.33
3.31
87
:
13
86.99
13.01

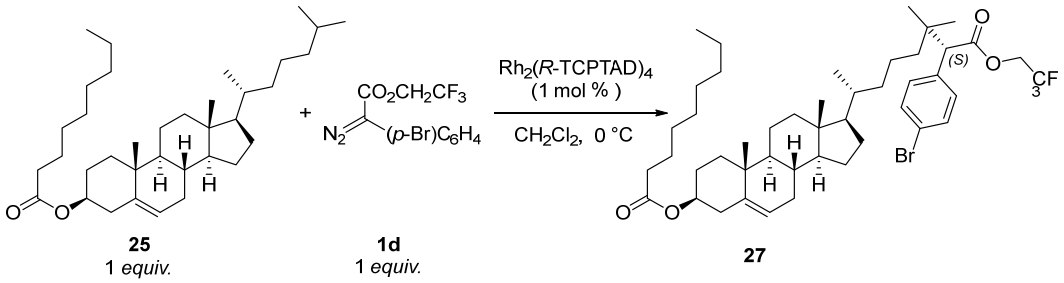


25
1 *equiv.*

1d
1 *equiv.*

27

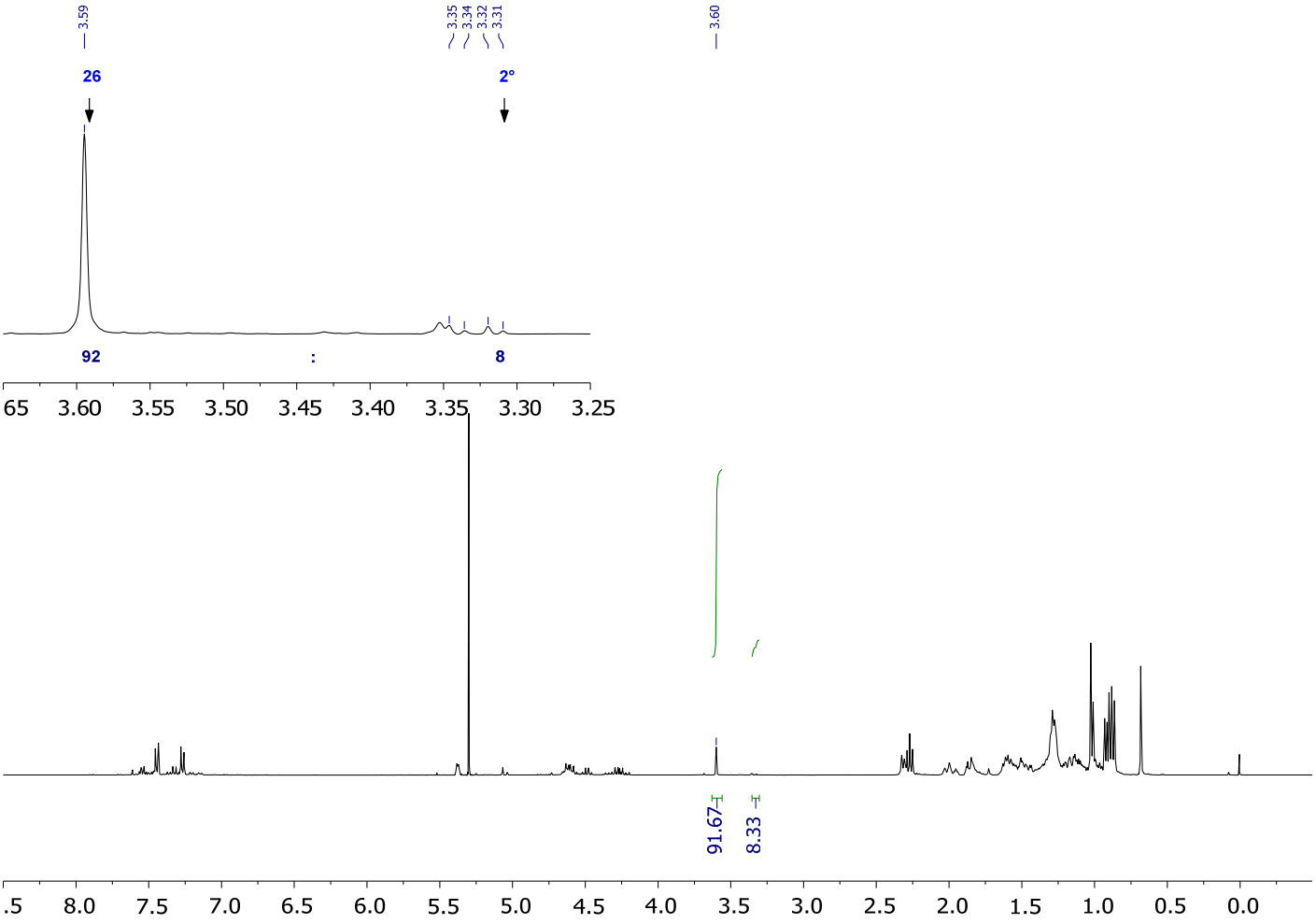




25
1 *equiv.*

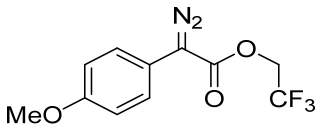
1d
1 *equiv.*

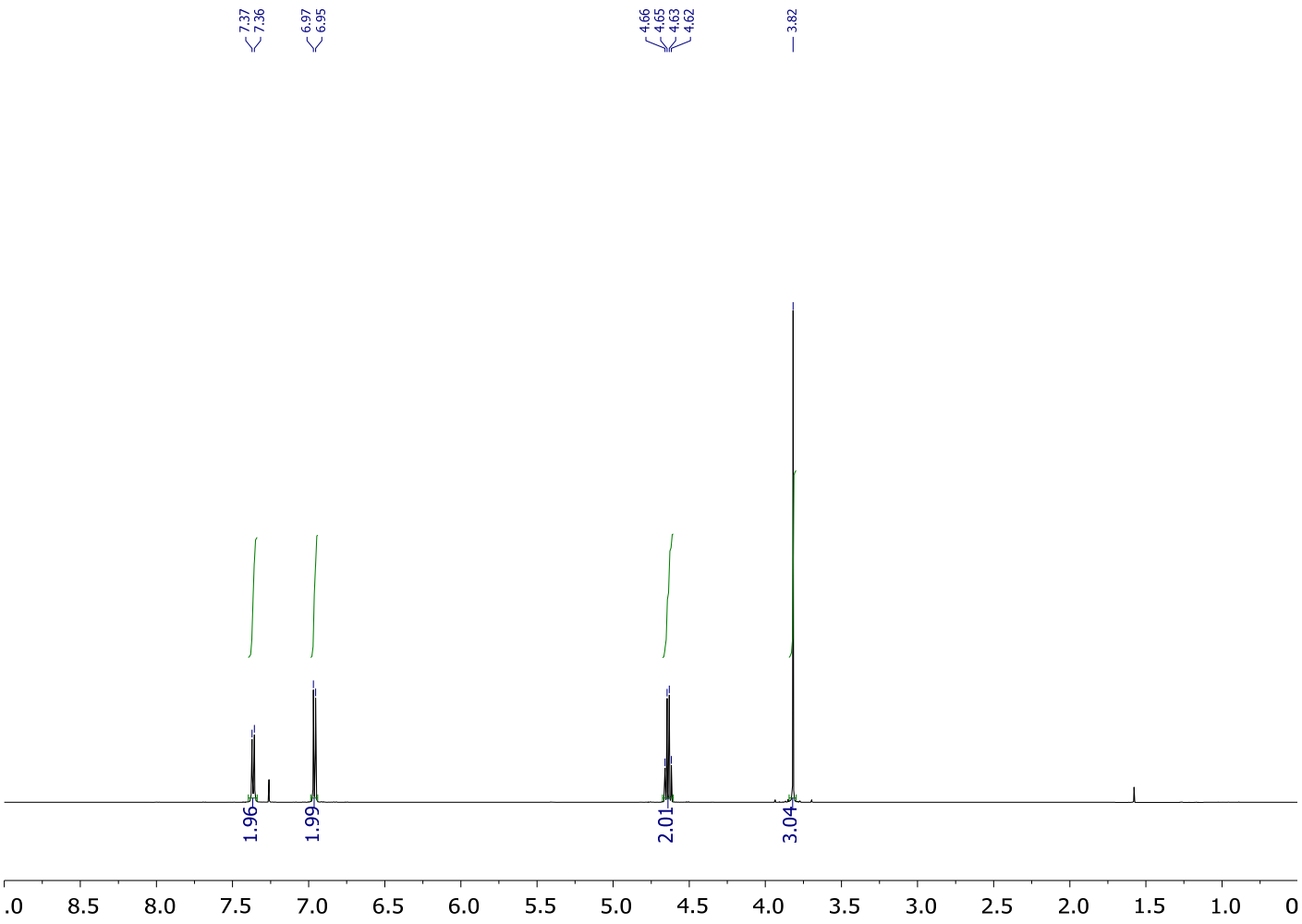
27

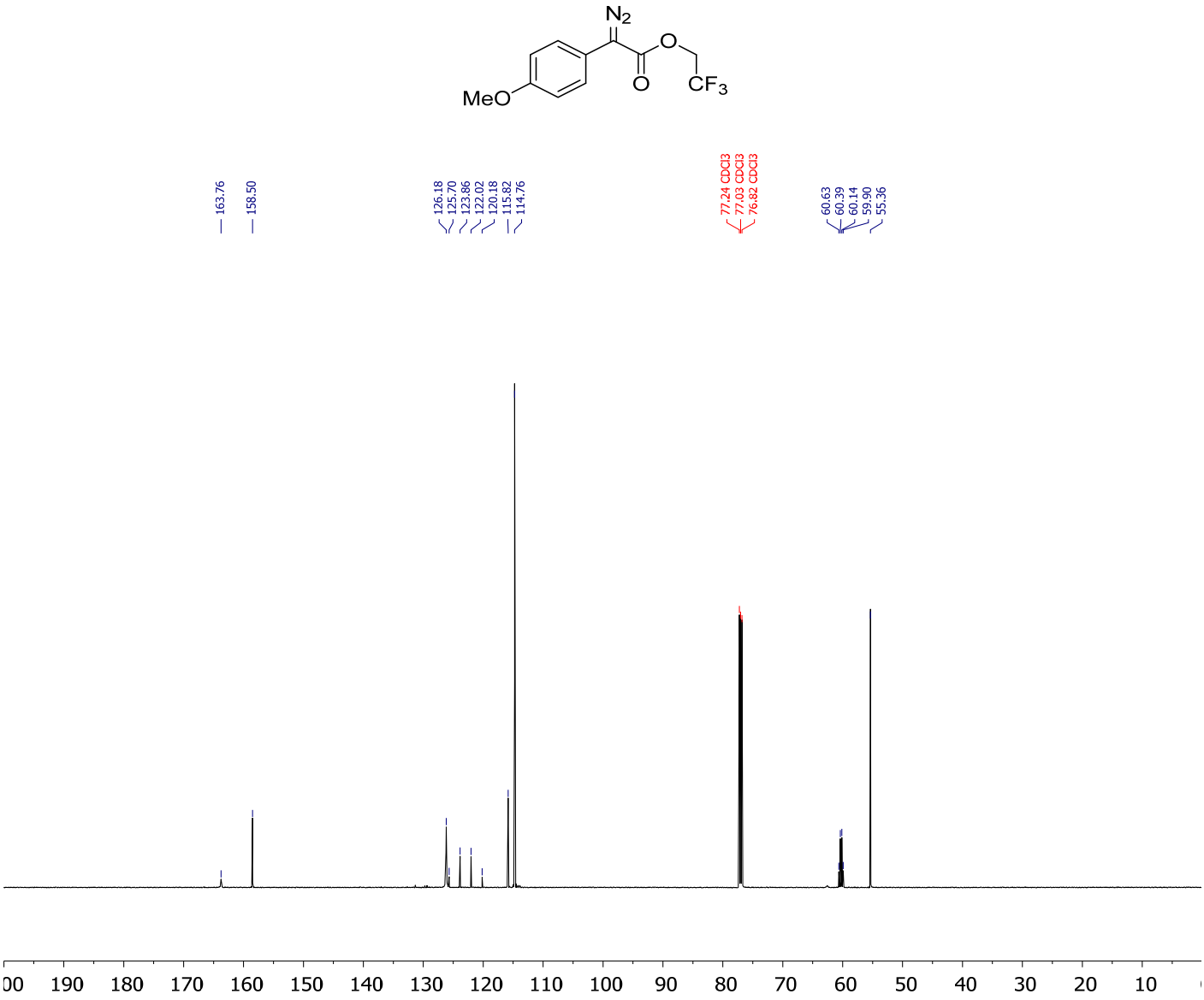


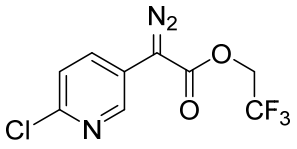
8 - NMR Spectra for Product Characterization

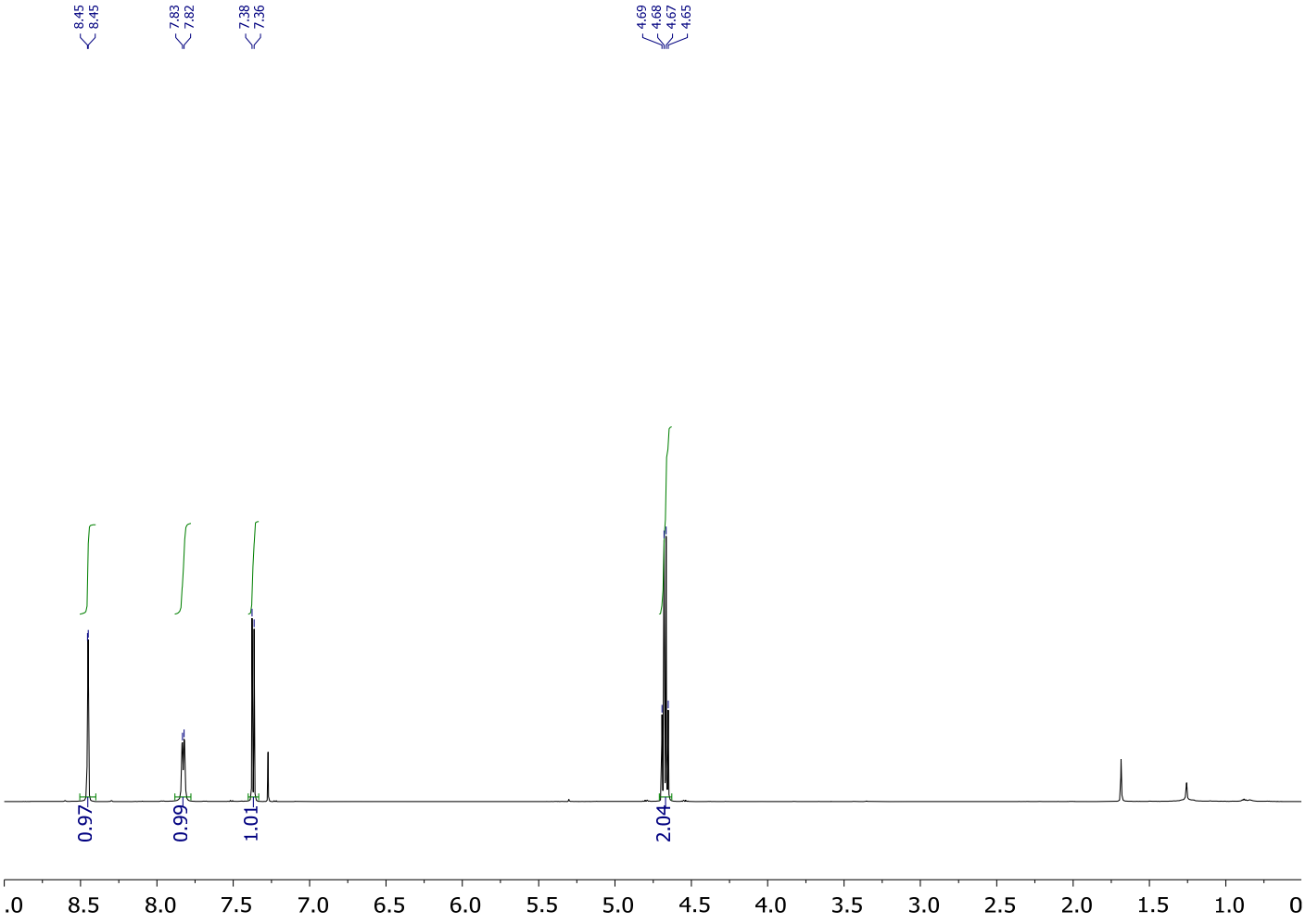
8.1 Preparation of Diazo Compounds

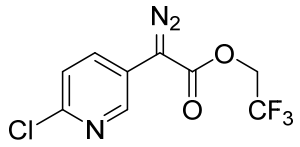


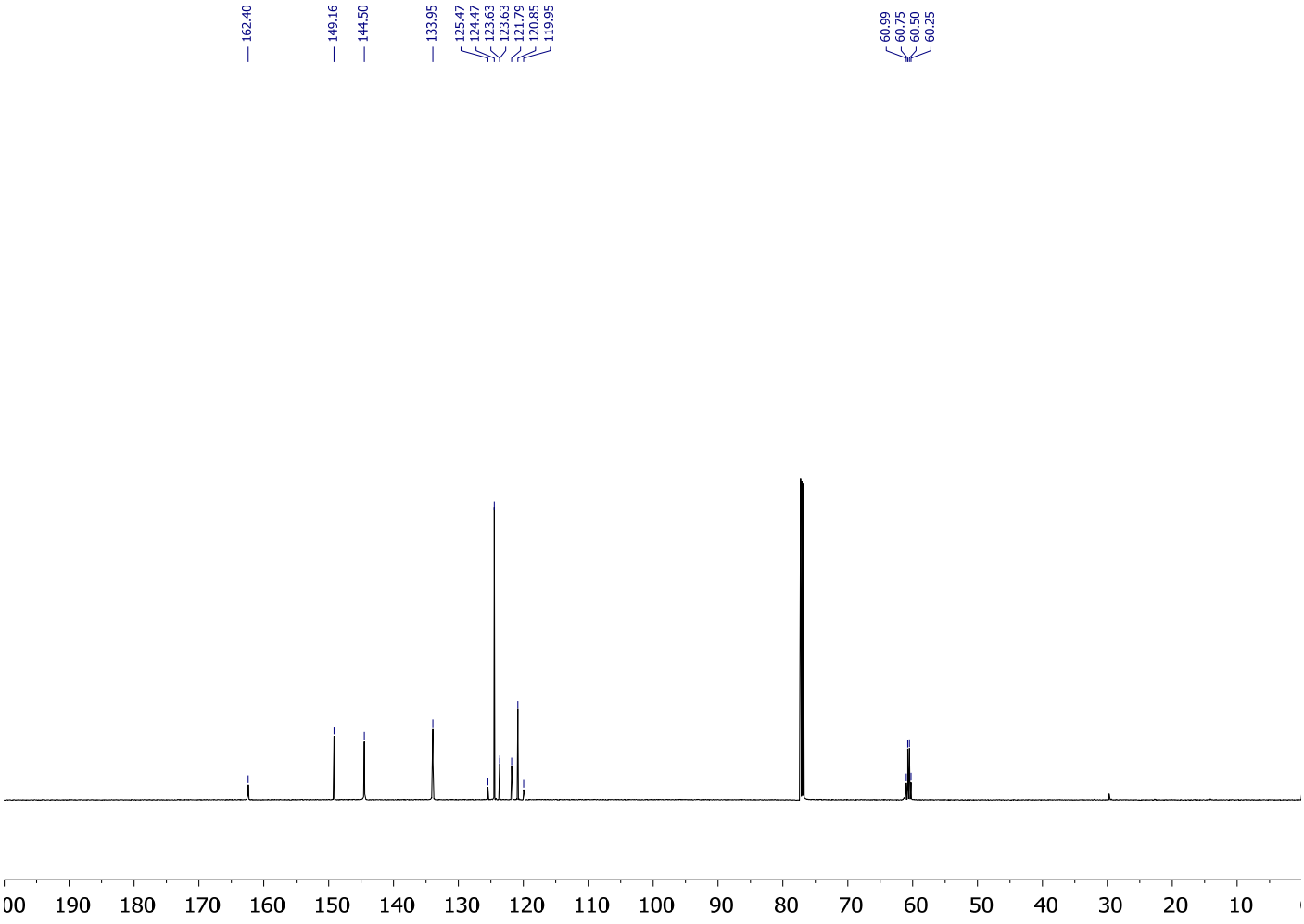


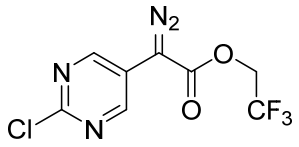

N2
O
O
CF3
MeO
163.76
158.50
126.18
125.70
123.86
122.02
120.18
115.82
114.76
77.24 CDCl3
77.03 CDCl3
76.82 CDCl3
60.63
60.39
60.14
59.90
55.36
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

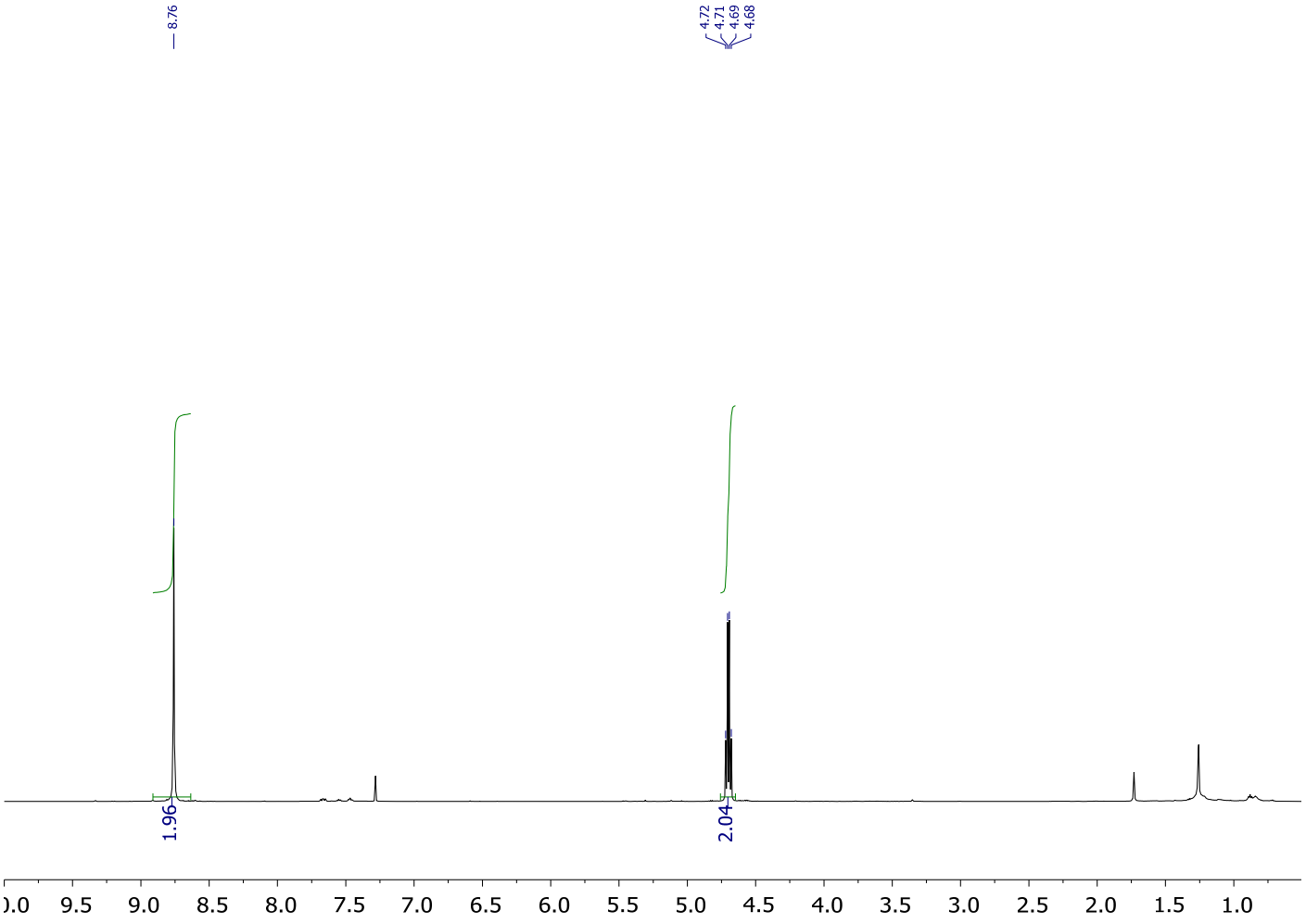

N2
O
O
CF3
Cl
N

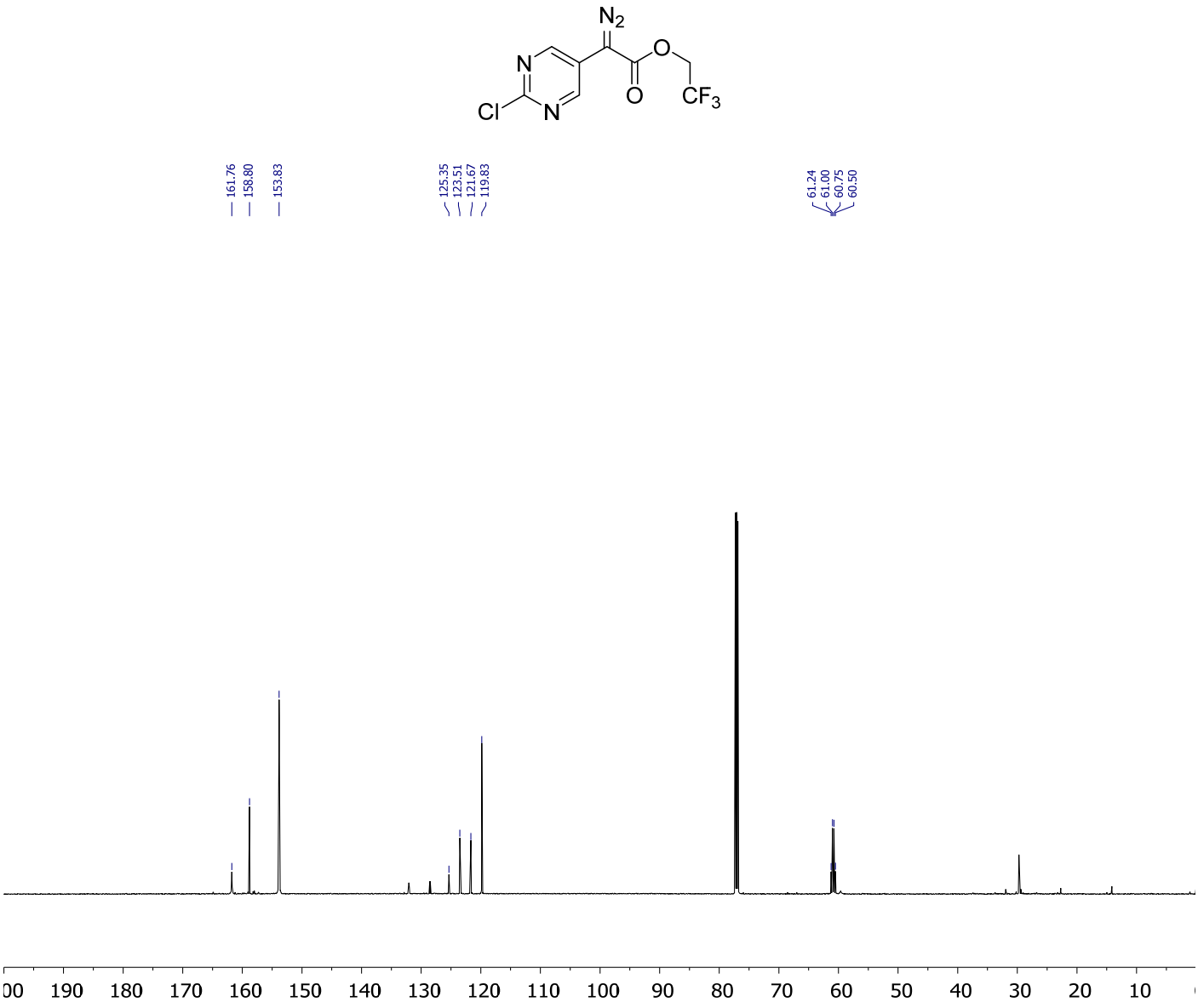

8.45
8.45
7.83
7.82
7.38
7.36
4.69
4.68
4.67
4.65
0.97
0.99
1.01
2.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

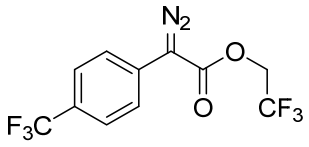

N2
O
O
CF3
Cl
N

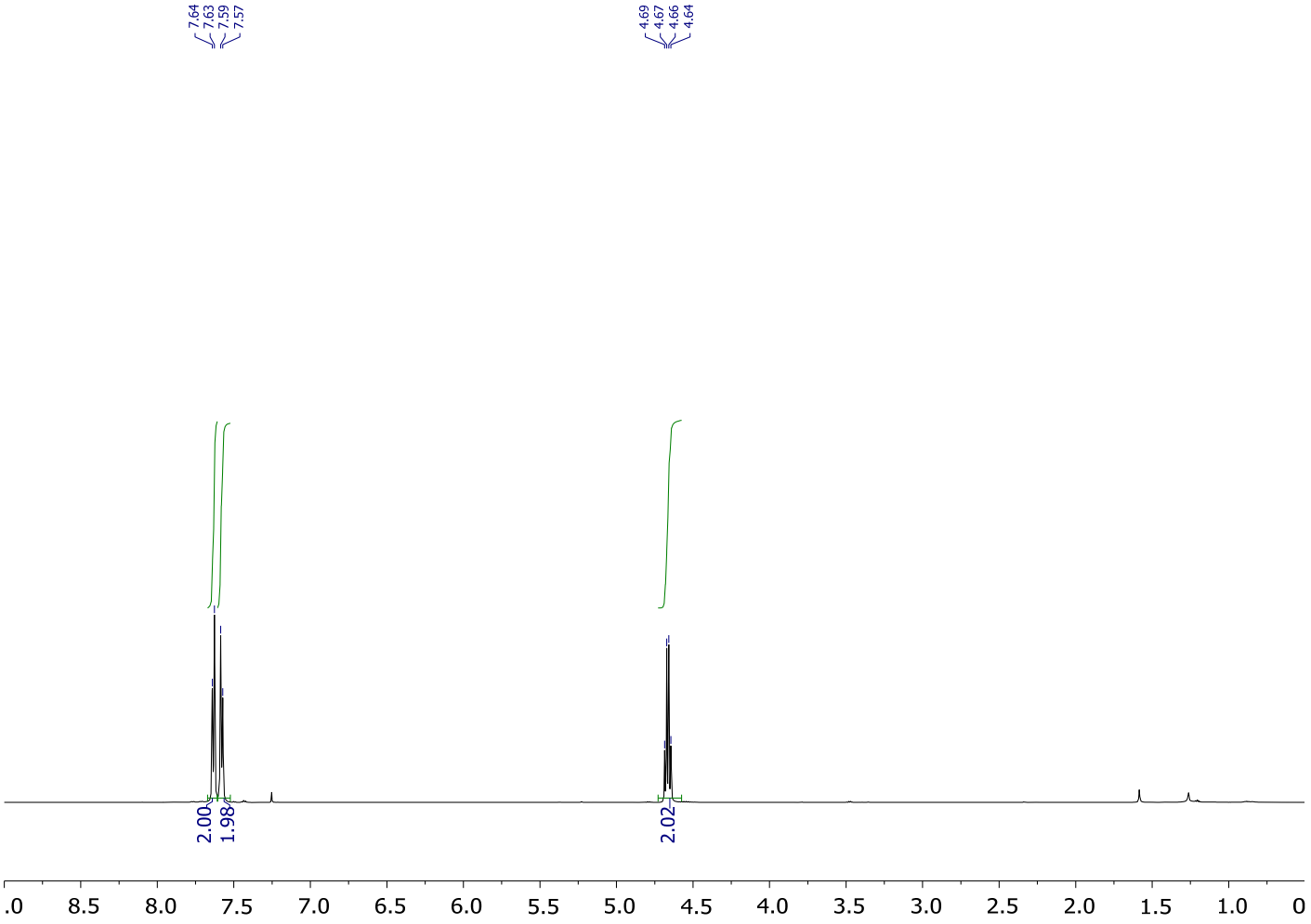

162.40
149.16
144.50
133.95
125.47
124.47
123.63
123.63
121.79
120.85
119.95
60.99
60.75
60.50
60.25
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

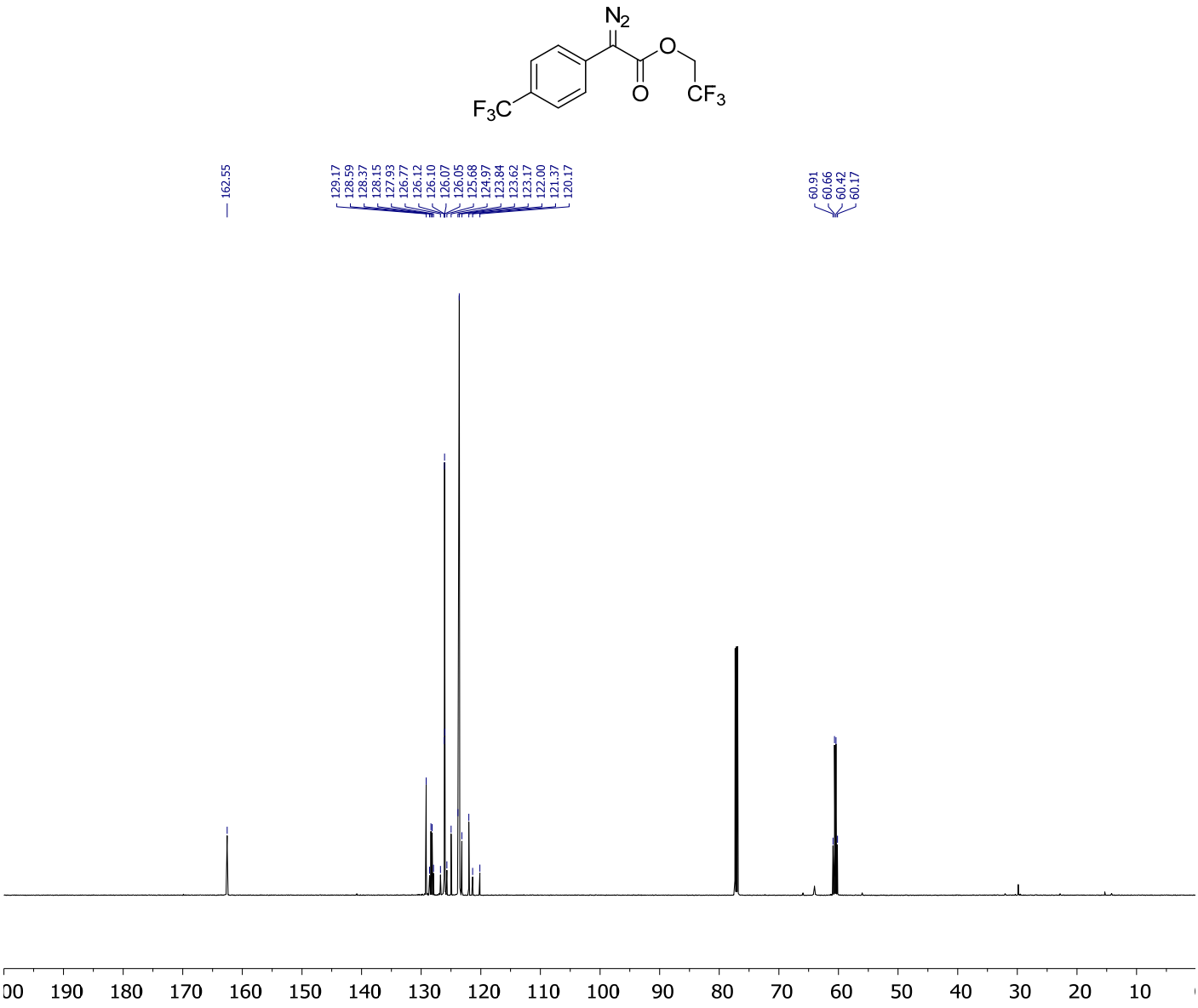

N2
N
O
Cl
N
O
CF3


8.76
4.72
4.71
4.69
4.68
1.96
2.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

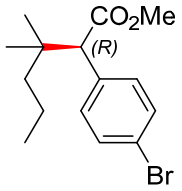

N2
N
O
Cl
N
O
CF3
161.76
158.80
153.83
125.35
123.51
121.67
119.83
61.24
61.00
60.75
60.50
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

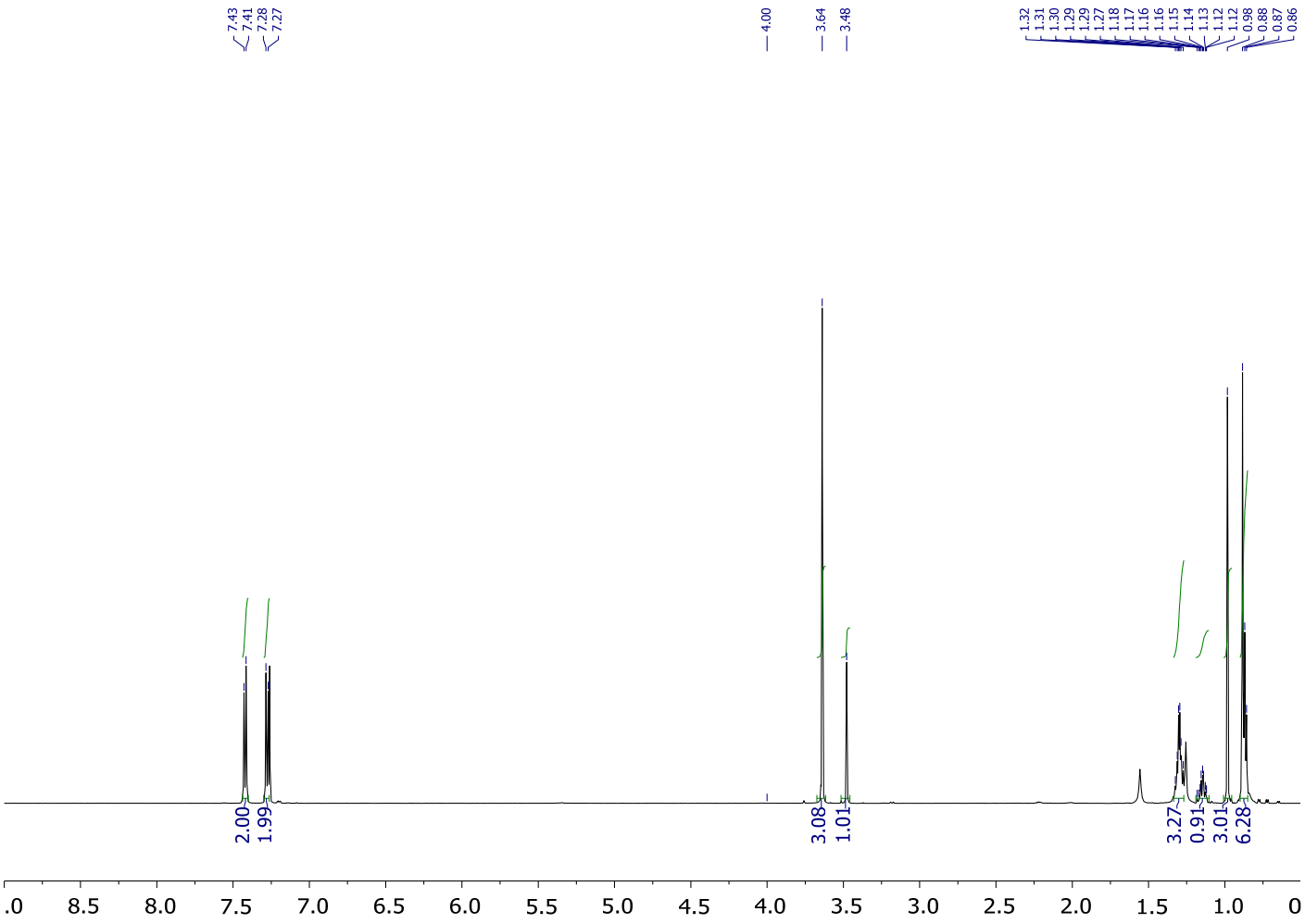

N2
O
O
F3C
CF3

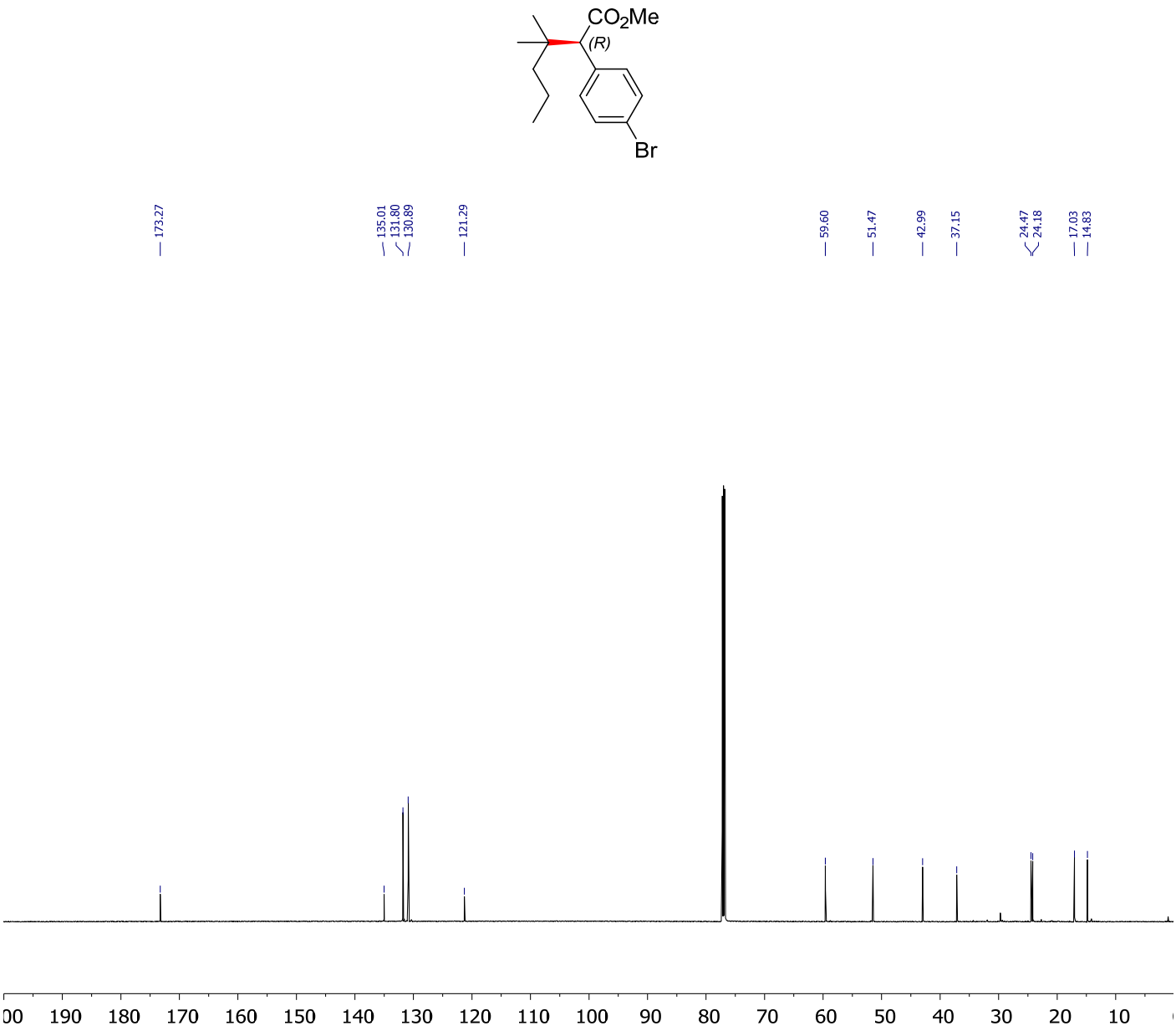

7.64
7.63
7.59
7.57
4.69
4.67
4.66
4.64
2.00
1.98
2.02
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

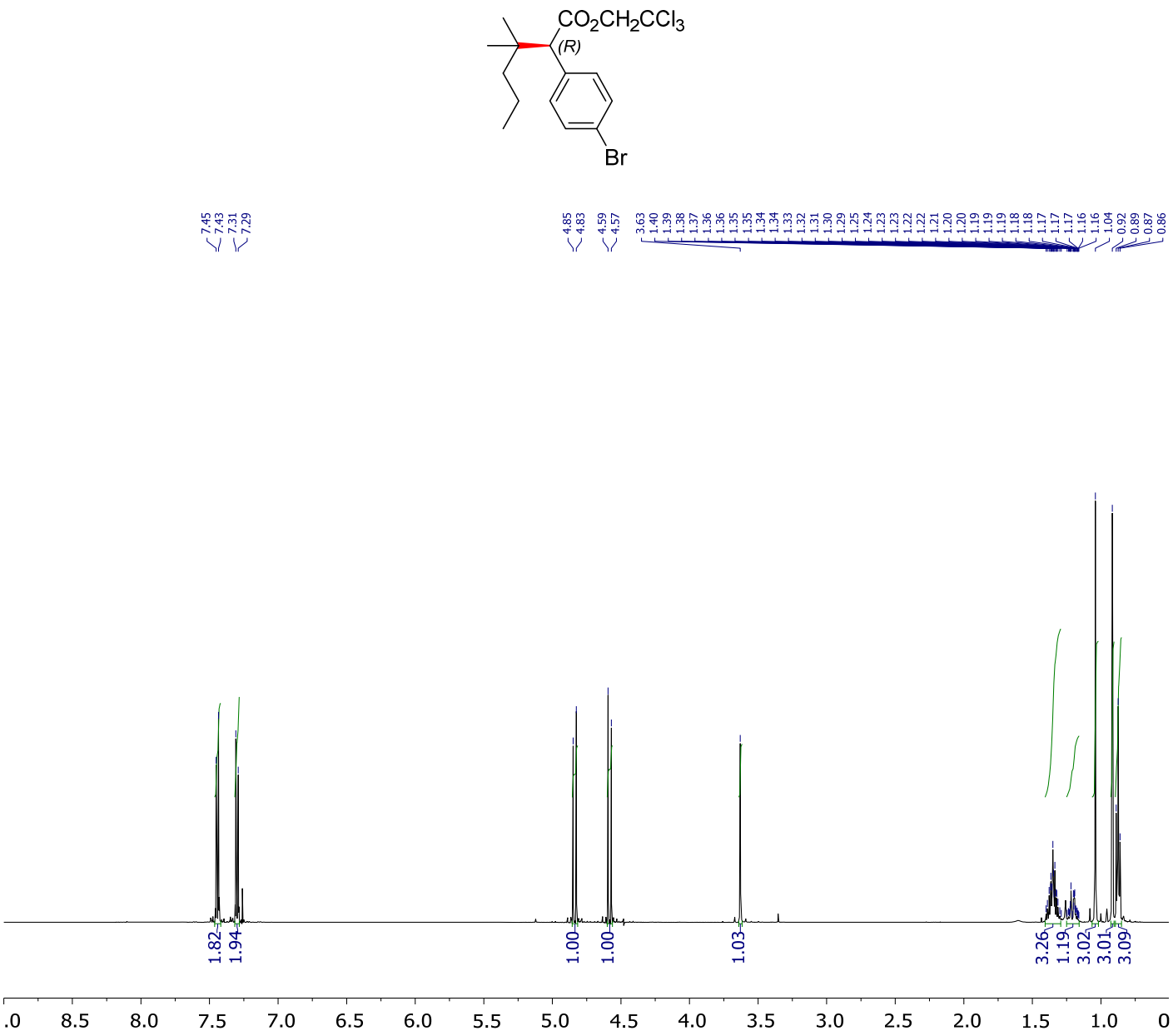

N2
O
O
F3C
CF3
162.55
129.17
128.59
128.37
128.15
127.93
126.77
126.12
126.10
126.07
126.05
125.68
124.97
123.84
123.62
123.17
122.00
121.37
120.17
60.91
60.66
60.42
60.17
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

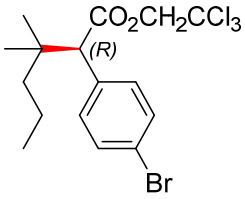
8.2 C–H Functionalization Products of 2-Methylpentane

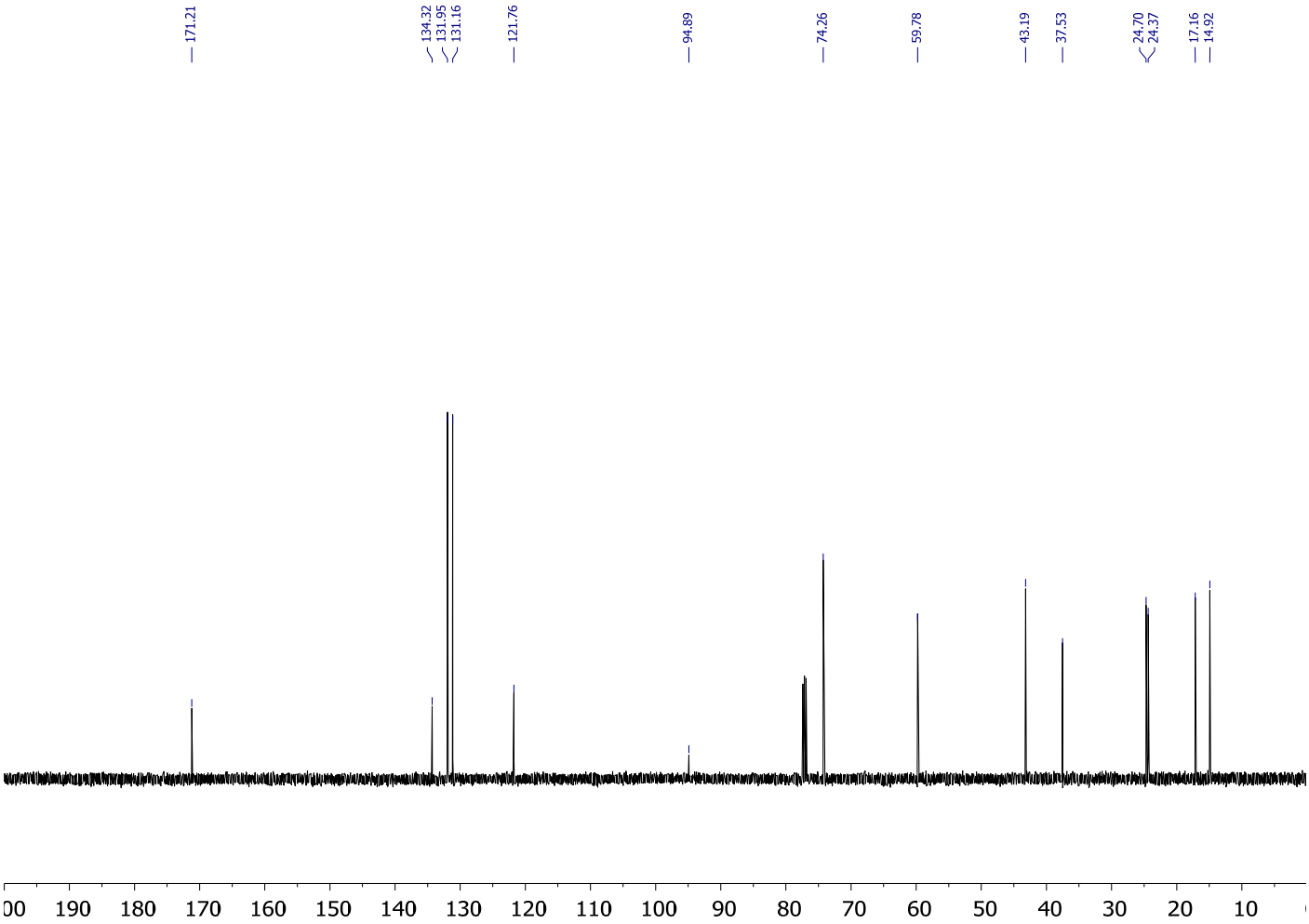


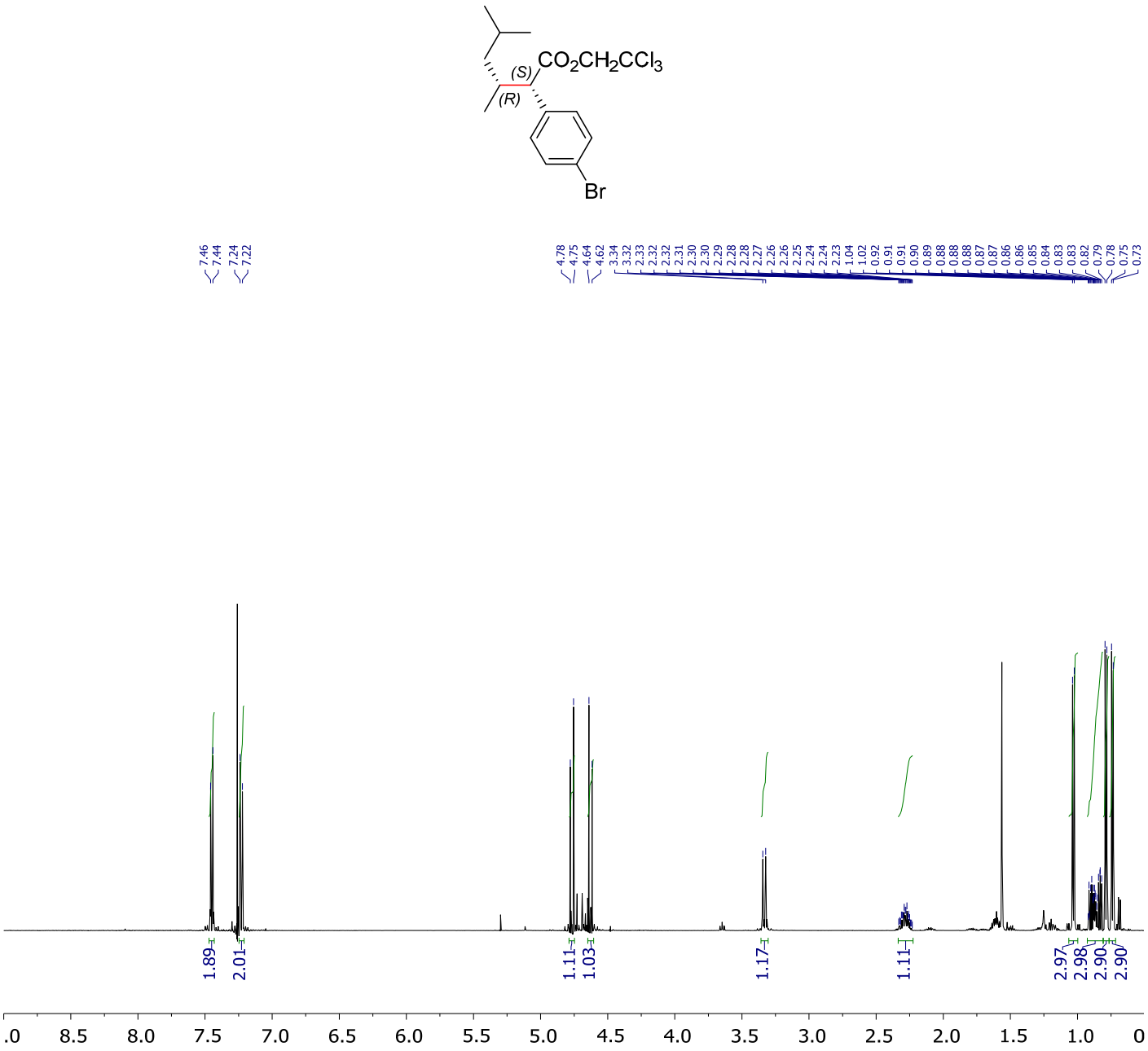


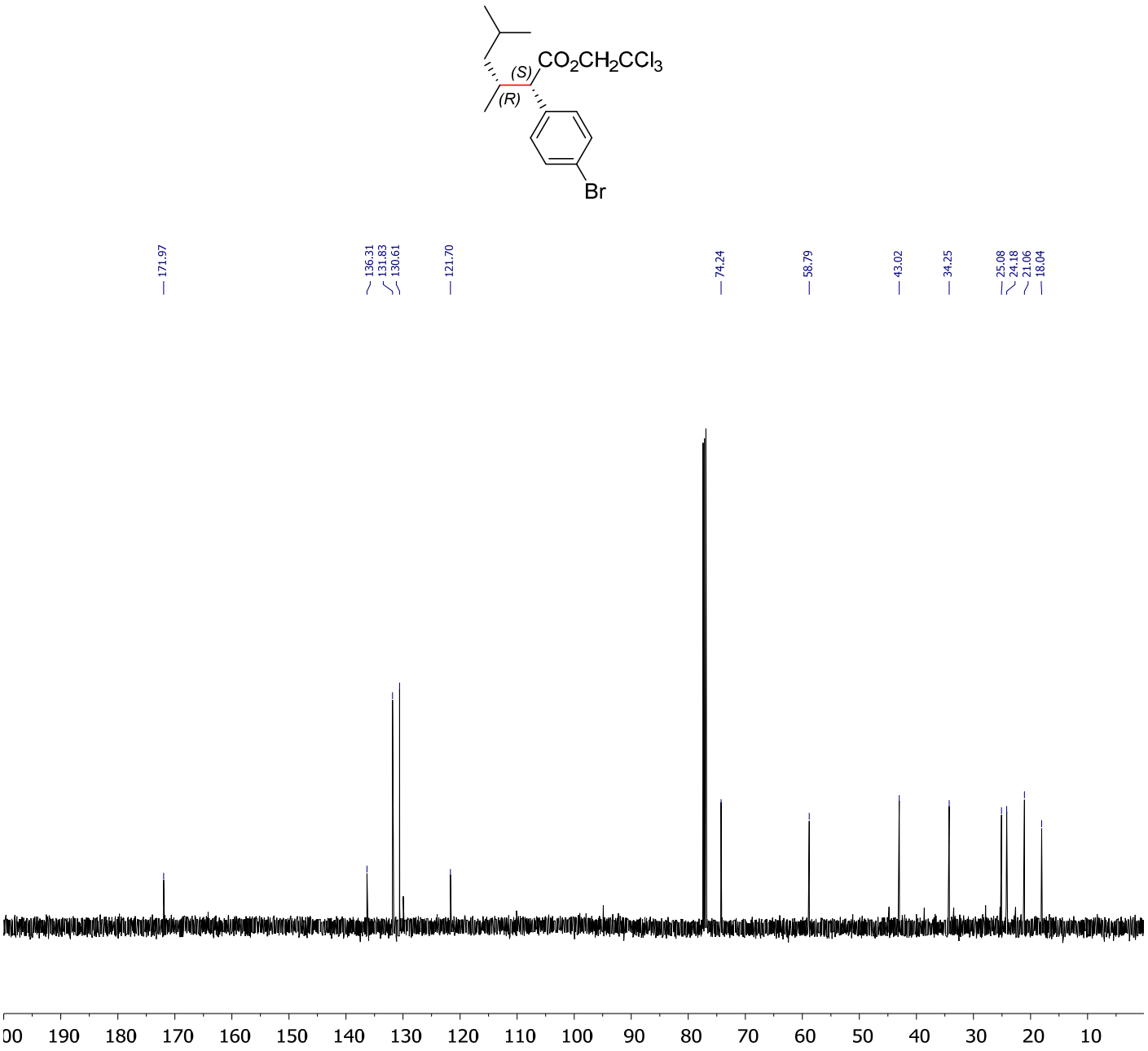

CO2Me
(R)
Br
173.27
135.01
131.80
130.89
121.29
59.60
51.47
42.99
37.15
24.47
24.18
17.03
14.83
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

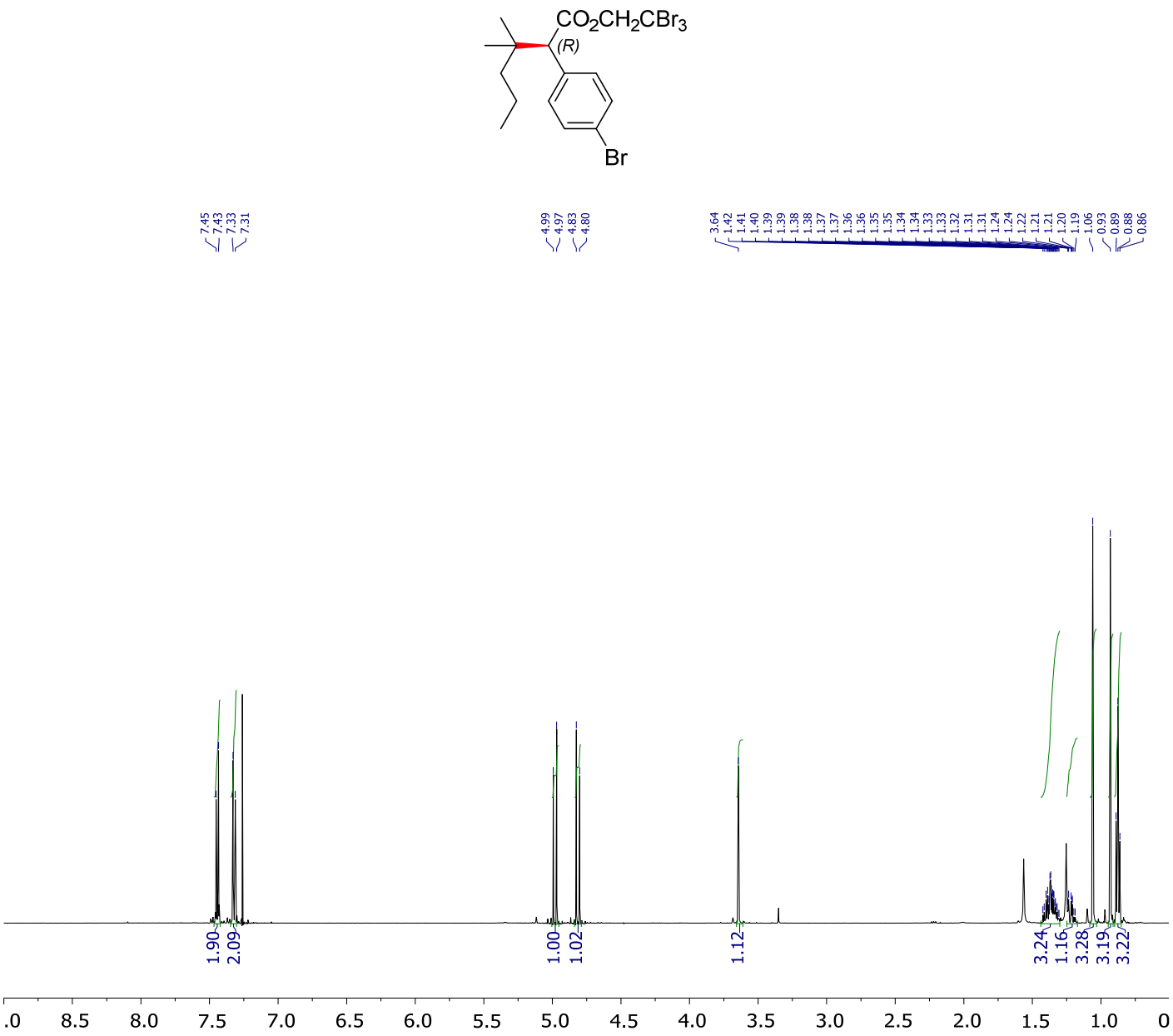

CO2CH2CCl3
(R)
Br
7.45
7.43
7.31
7.29
4.85
4.83
4.59
4.57
3.63
1.40
1.39
1.38
1.37
1.36
1.36
1.35
1.35
1.34
1.34
1.33
1.32
1.31
1.30
1.29
1.25
1.24
1.23
1.23
1.22
1.22
1.21
1.20
1.20
1.19
1.19
1.19
1.18
1.18
1.17
1.17
1.17
1.16
1.16
1.04
0.92
0.89
0.87
0.86
1.82
1.94
1.00
1.00
1.03
3.26
1.19
3.02
3.01
3.09
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

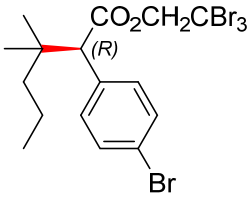

$CO_2CH_2CCl_3$
(R)
Br

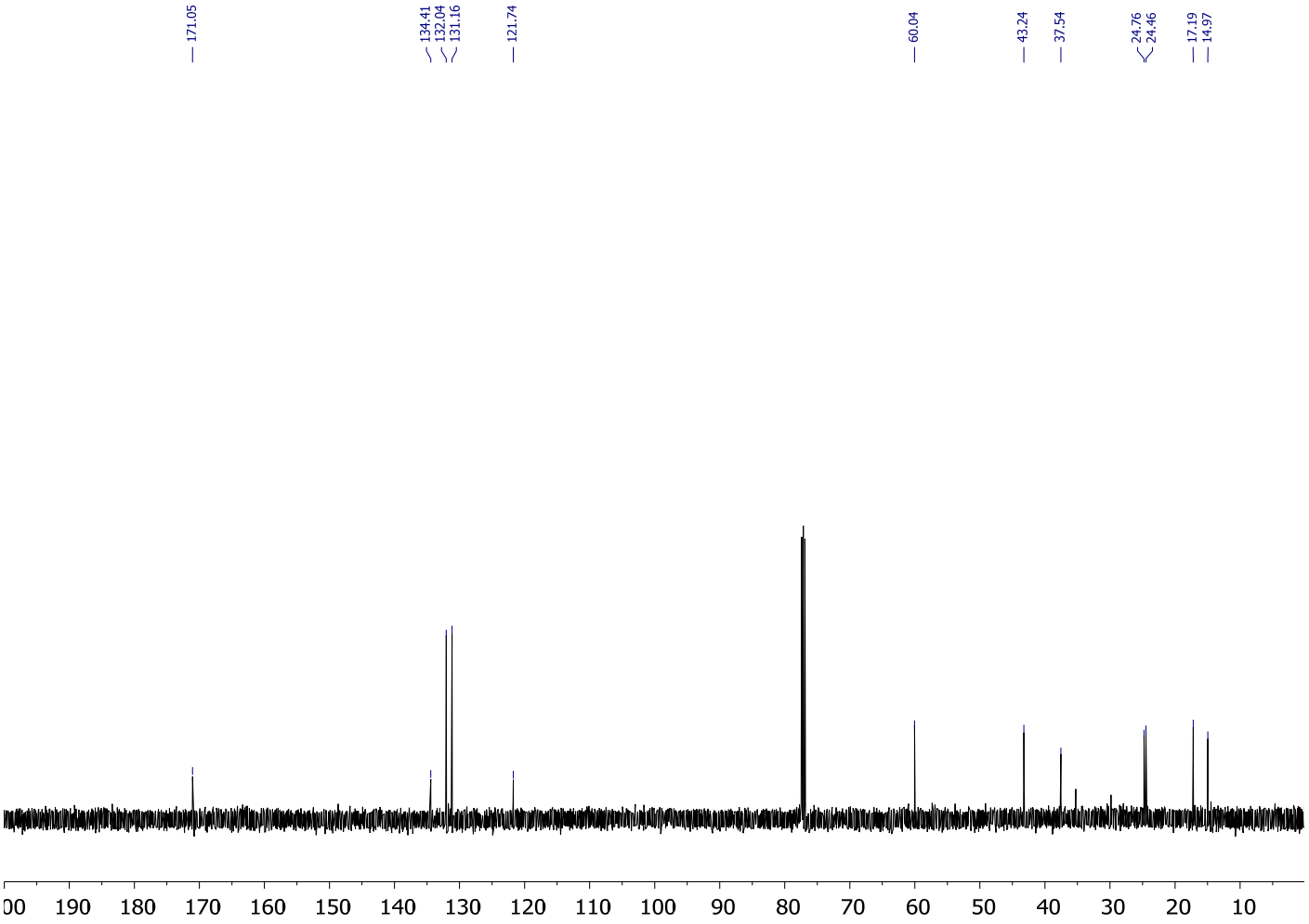

171.21
134.32
131.95
131.16
121.76
94.89
74.26
59.78
43.19
37.53
24.70
24.37
17.16
14.92
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

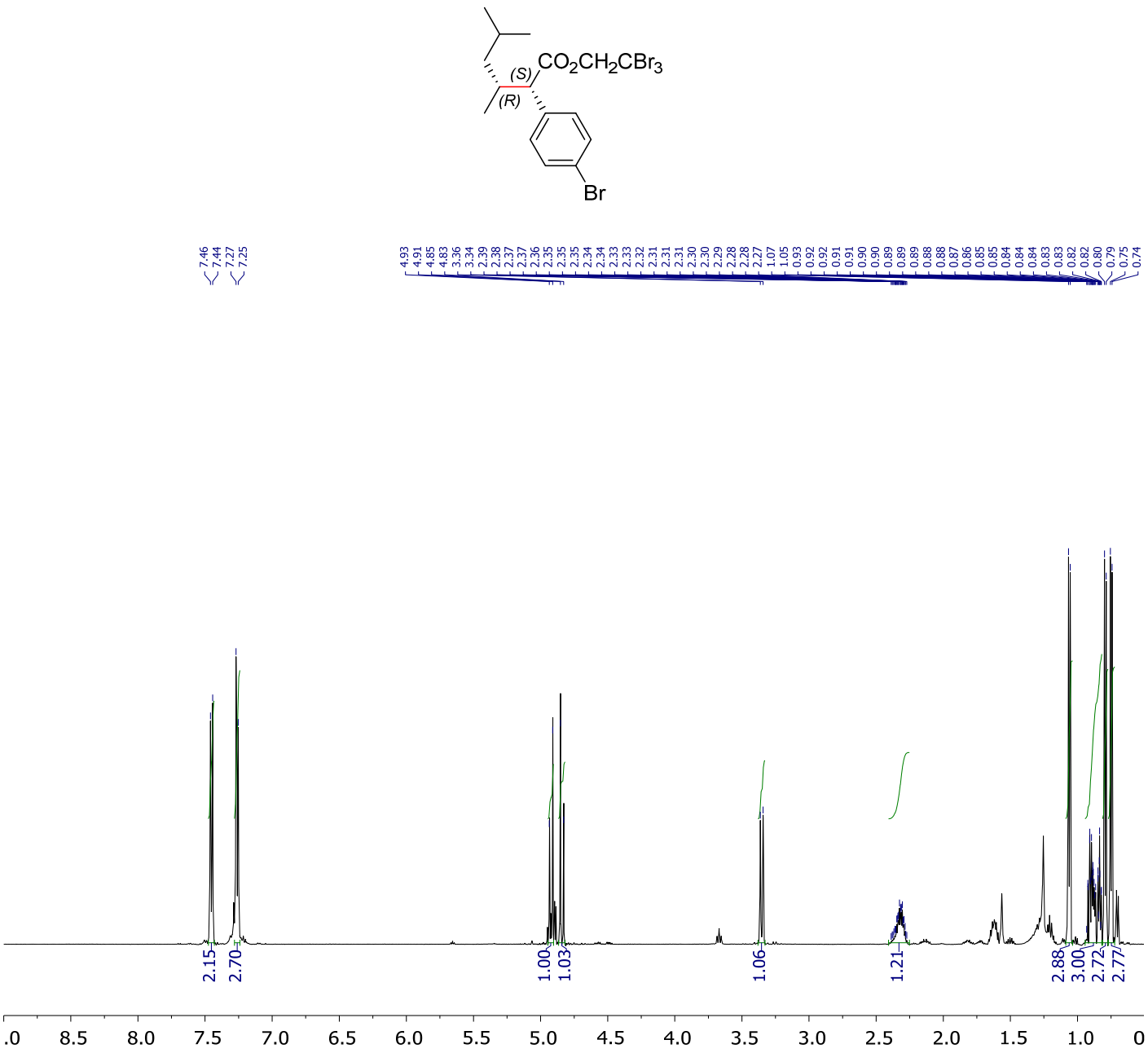

CO2CH2CCl3
(S)
(R)
Br
7.46
7.44
7.24
7.22
4.78
4.75
4.64
4.62
3.34
3.32
2.33
2.32
2.32
2.31
2.30
2.30
2.29
2.28
2.28
2.27
2.26
2.26
2.25
2.24
2.24
2.23
1.04
1.02
0.92
0.91
0.91
0.90
0.89
0.88
0.88
0.88
0.87
0.87
0.86
0.86
0.85
0.84
0.83
0.82
0.79
0.78
0.75
0.73
1.89
2.01
1.11
1.03
1.17
1.11
2.97
2.98
2.90
2.90
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

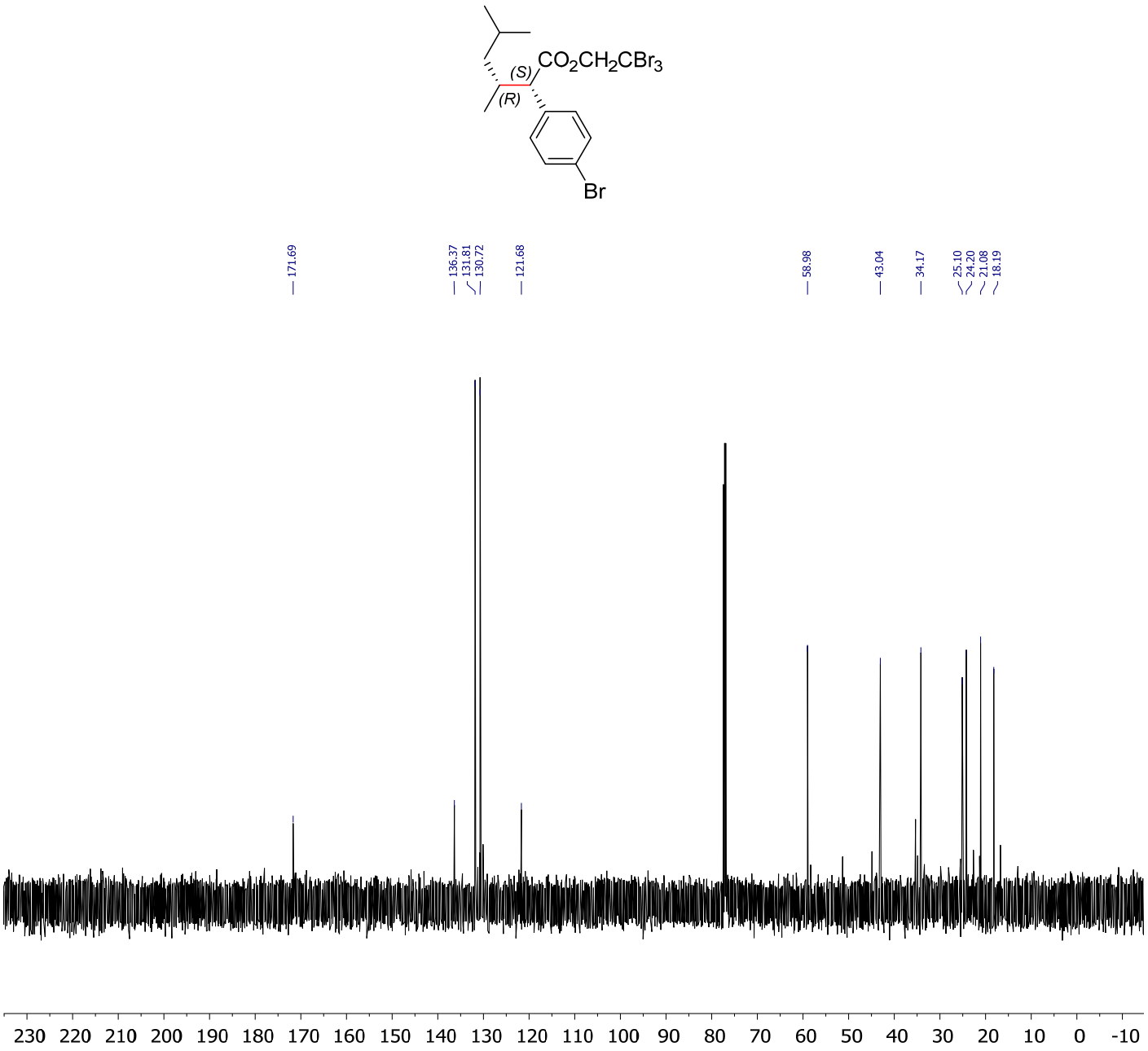

CO2CH2CCl3
(S)
(R)
Br
171.97
136.31
131.83
130.61
121.70
74.24
58.79
43.02
34.25
25.08
24.18
21.06
18.04
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

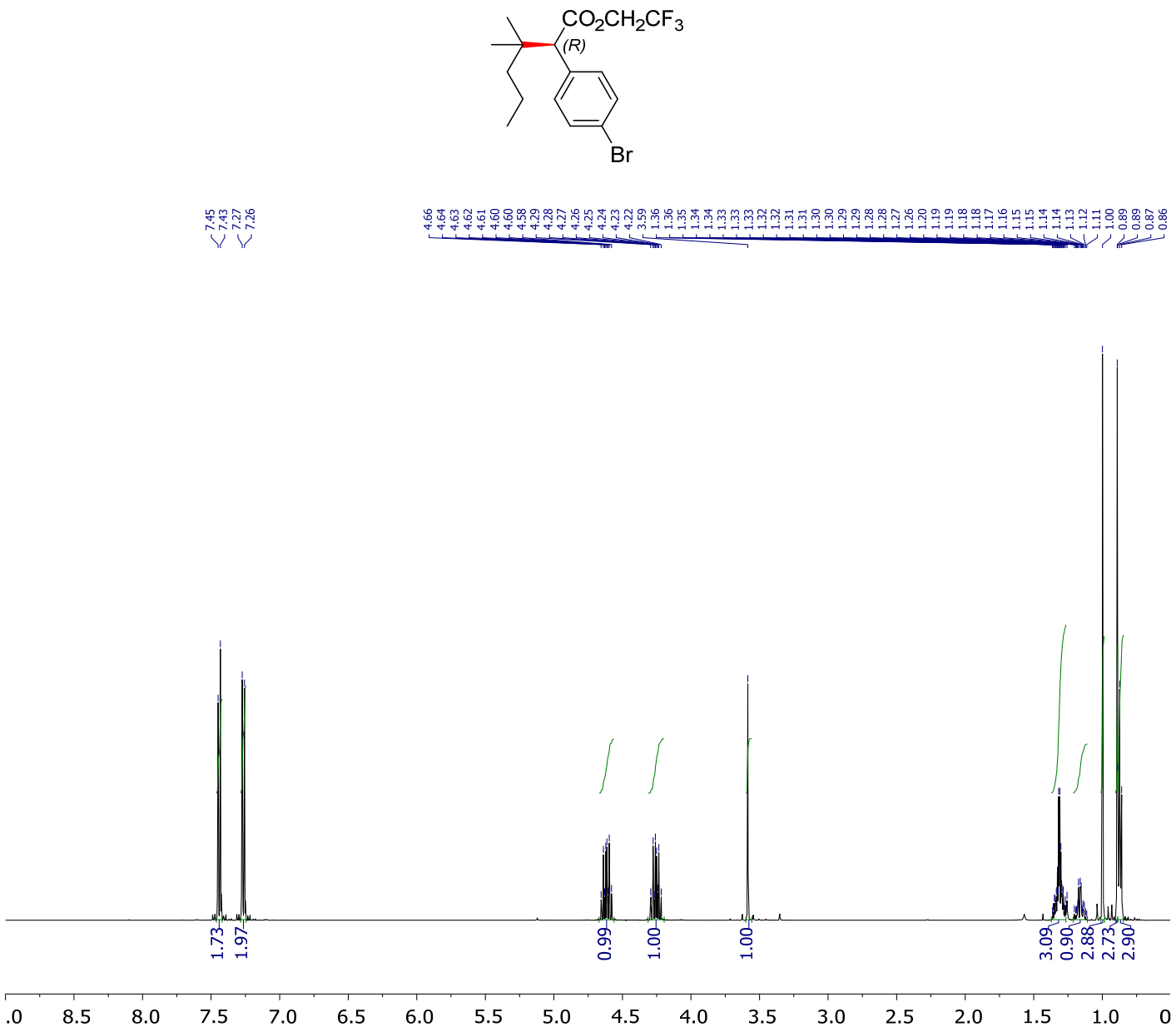

CO2CH2CBr3
(R)
Br
7.45
7.43
7.33
7.31
4.99
4.97
4.83
4.80
3.64
1.42
1.41
1.40
1.39
1.39
1.38
1.38
1.37
1.37
1.36
1.36
1.35
1.35
1.34
1.34
1.33
1.33
1.32
1.31
1.31
1.24
1.24
1.22
1.21
1.21
1.20
1.19
1.06
0.93
0.89
0.88
0.86
1.90
2.09
1.00
1.02
1.12
3.24
1.16
3.28
3.19
3.22
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

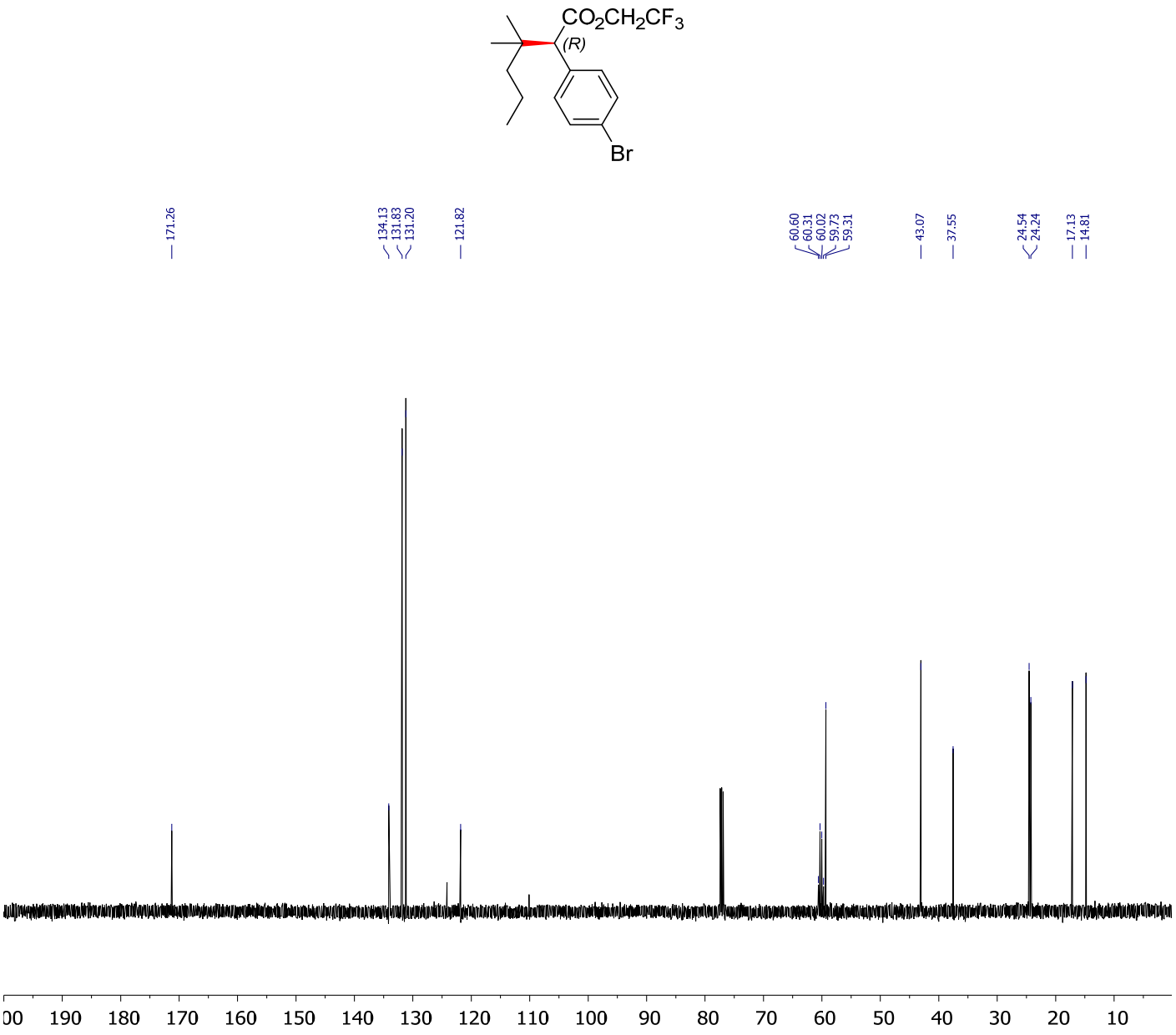

CO2CH2CBr3
(R)
Br

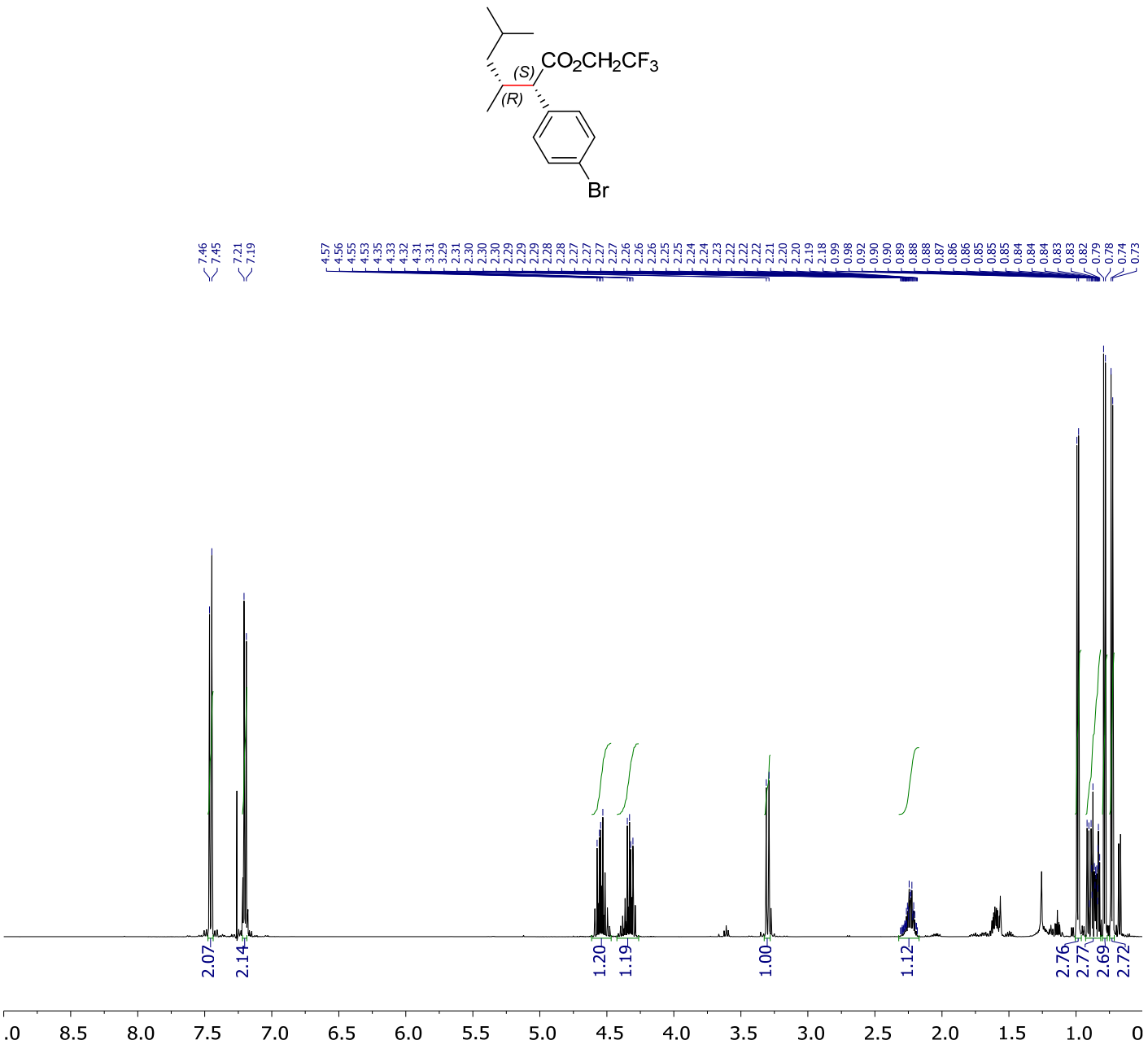

171.05
134.41
132.04
131.16
121.74
60.04
43.24
37.54
24.76
24.46
17.19
14.97
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

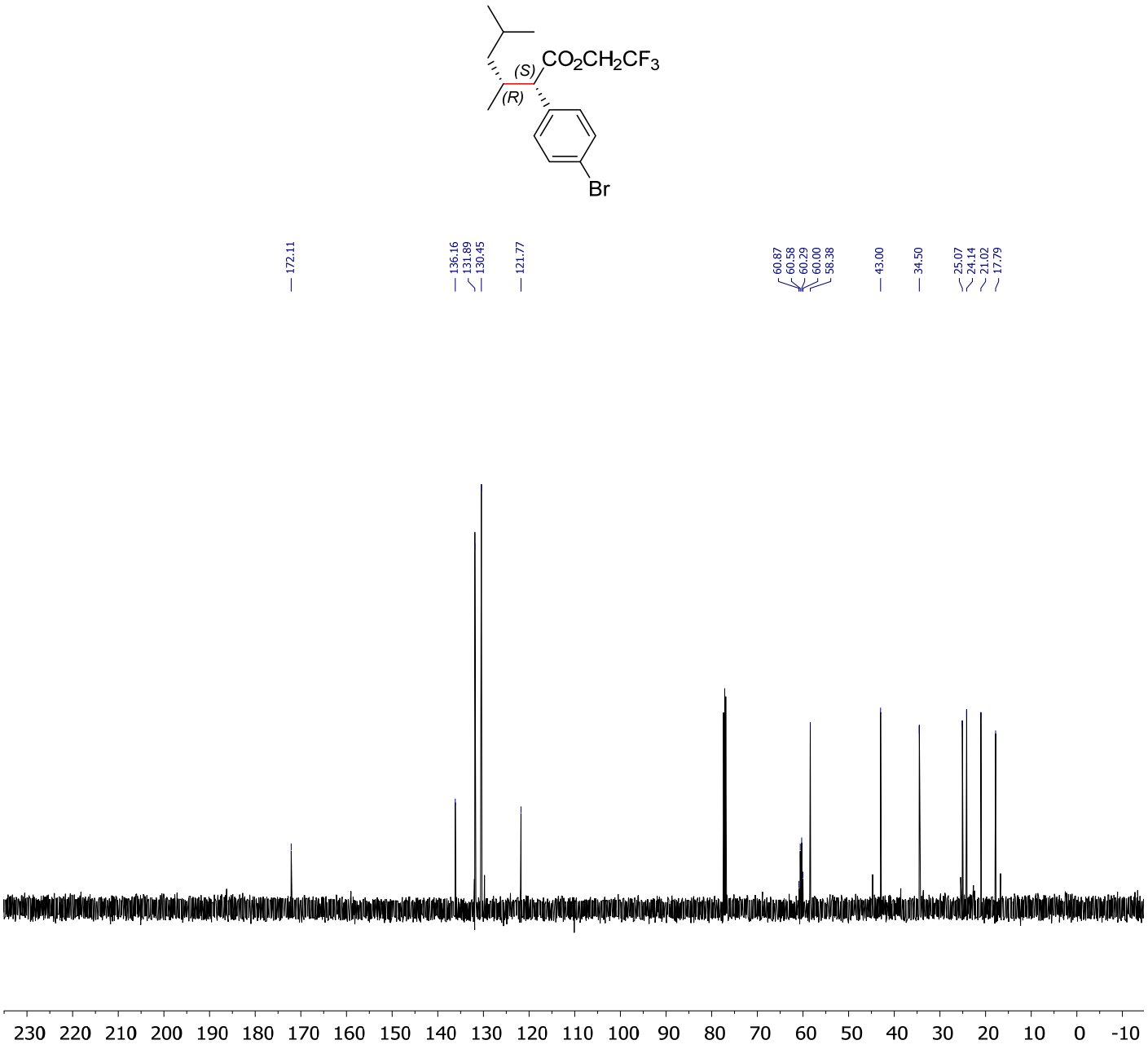

CO2CH2CBr3
(S)
(R)
Br
7.46
7.44
7.27
7.25
4.93
4.91
4.85
4.83
3.36
3.34
2.39
2.38
2.37
2.37
2.36
2.35
2.35
2.35
2.34
2.34
2.33
2.33
2.32
2.31
2.31
2.31
2.30
2.30
2.29
2.28
2.28
2.27
1.07
1.05
0.93
0.92
0.92
0.91
0.91
0.90
0.90
0.89
0.89
0.89
0.88
0.88
0.87
0.86
0.85
0.85
0.84
0.84
0.84
0.83
0.83
0.82
0.82
0.80
0.79
0.75
0.74
2.15
2.70
1.00
1.03
1.06
1.21
2.88
3.00
2.72
2.77
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0


CO2CH2CBr3
(S)
(R)
Br
171.69
136.37
131.81
130.72
121.68
58.98
43.04
34.17
25.10
24.20
21.08
18.19
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

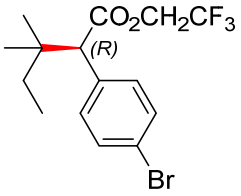

CO2CH2CF3
(R)
Br
7.45
7.43
7.27
7.26
4.66
4.64
4.63
4.62
4.61
4.60
4.60
4.60
4.58
4.29
4.28
4.27
4.26
4.25
4.24
4.23
4.22
3.59
1.36
1.36
1.35
1.34
1.34
1.33
1.33
1.33
1.32
1.32
1.31
1.31
1.30
1.30
1.29
1.29
1.28
1.28
1.27
1.26
1.20
1.19
1.19
1.18
1.18
1.17
1.16
1.15
1.15
1.14
1.14
1.13
1.12
1.11
1.00
0.89
0.89
0.87
0.86
1.73
1.97
0.99
1.00
1.00
3.09
0.90
2.88
2.73
2.90
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

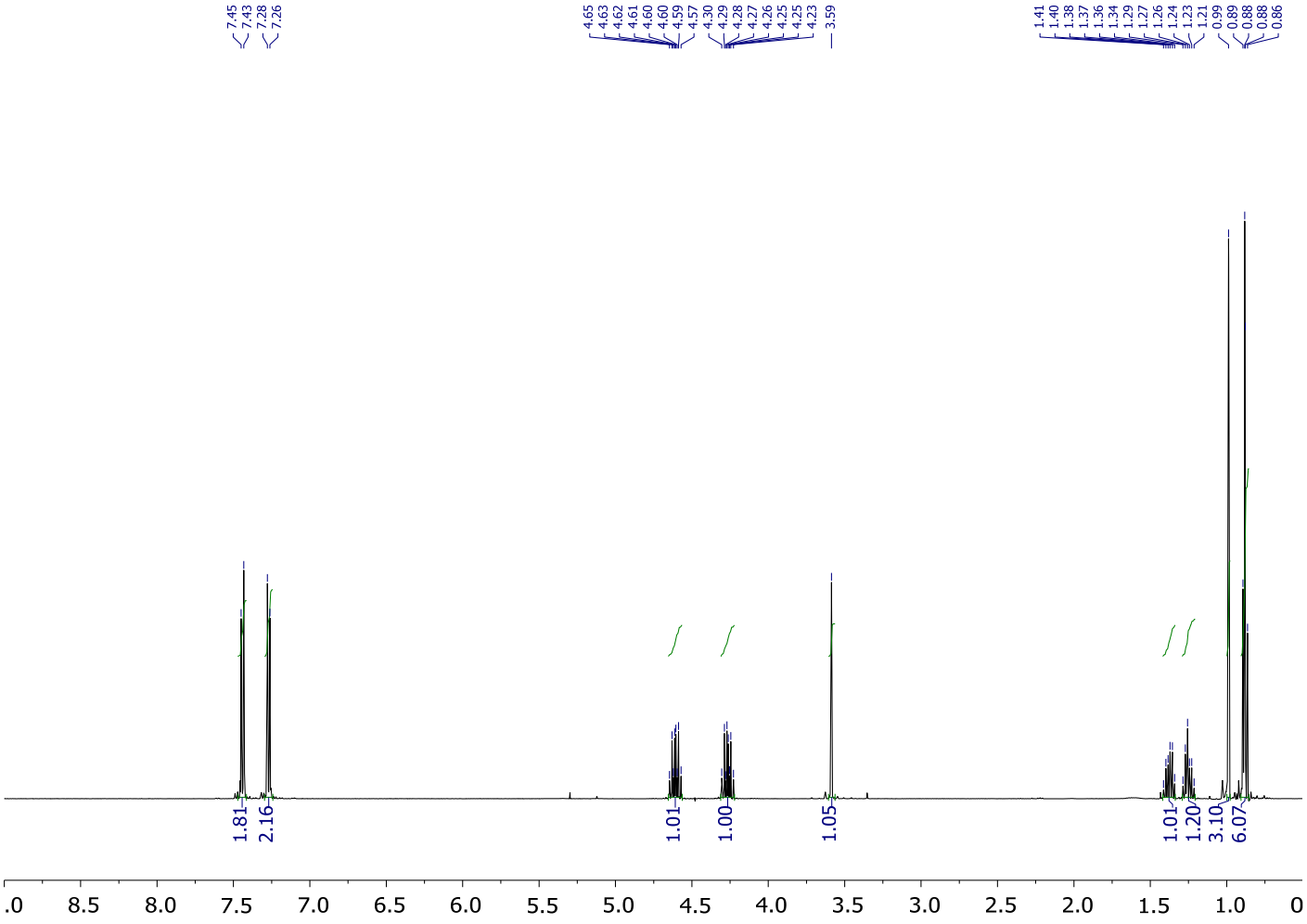

CO2CH2CF3
(R)
Br
171.26
134.13
131.83
131.20
121.82
60.60
60.31
60.02
59.73
59.31
43.07
37.55
24.54
24.24
17.13
14.81
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

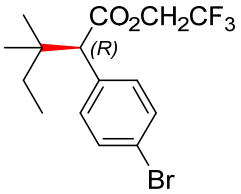

CO2CH2CF3
(S)
(R)
Br
7.46
7.45
7.21
7.19
2.07
2.14
1.20
1.19
1.00
1.12
2.76
2.77
2.69
2.72
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

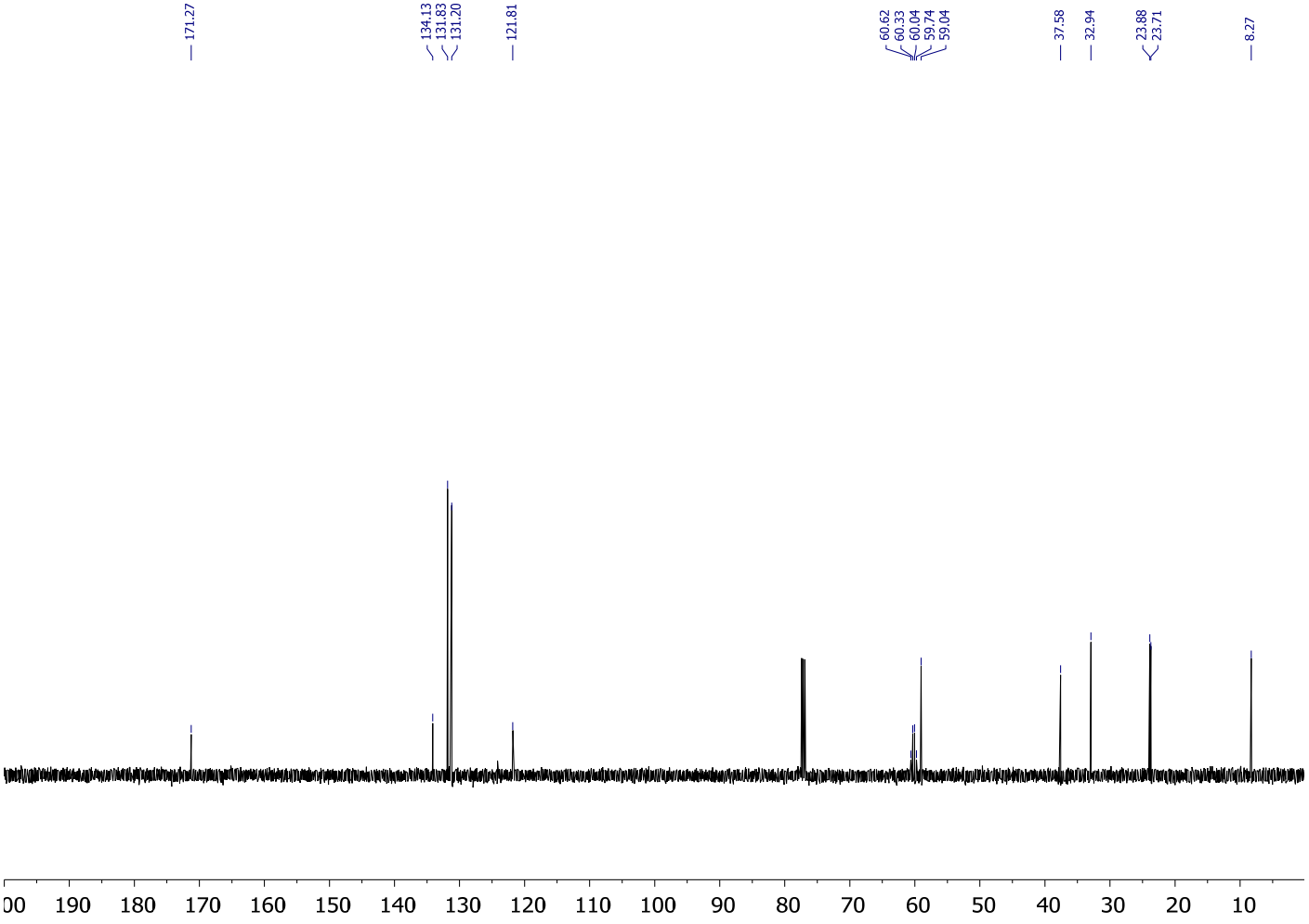

CO2CH2CF3
(S)
(R)
Br
172.11
136.16
131.89
130.45
121.77
60.87
60.58
60.29
60.00
58.38
43.00
34.50
25.07
24.14
21.02
17.79
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

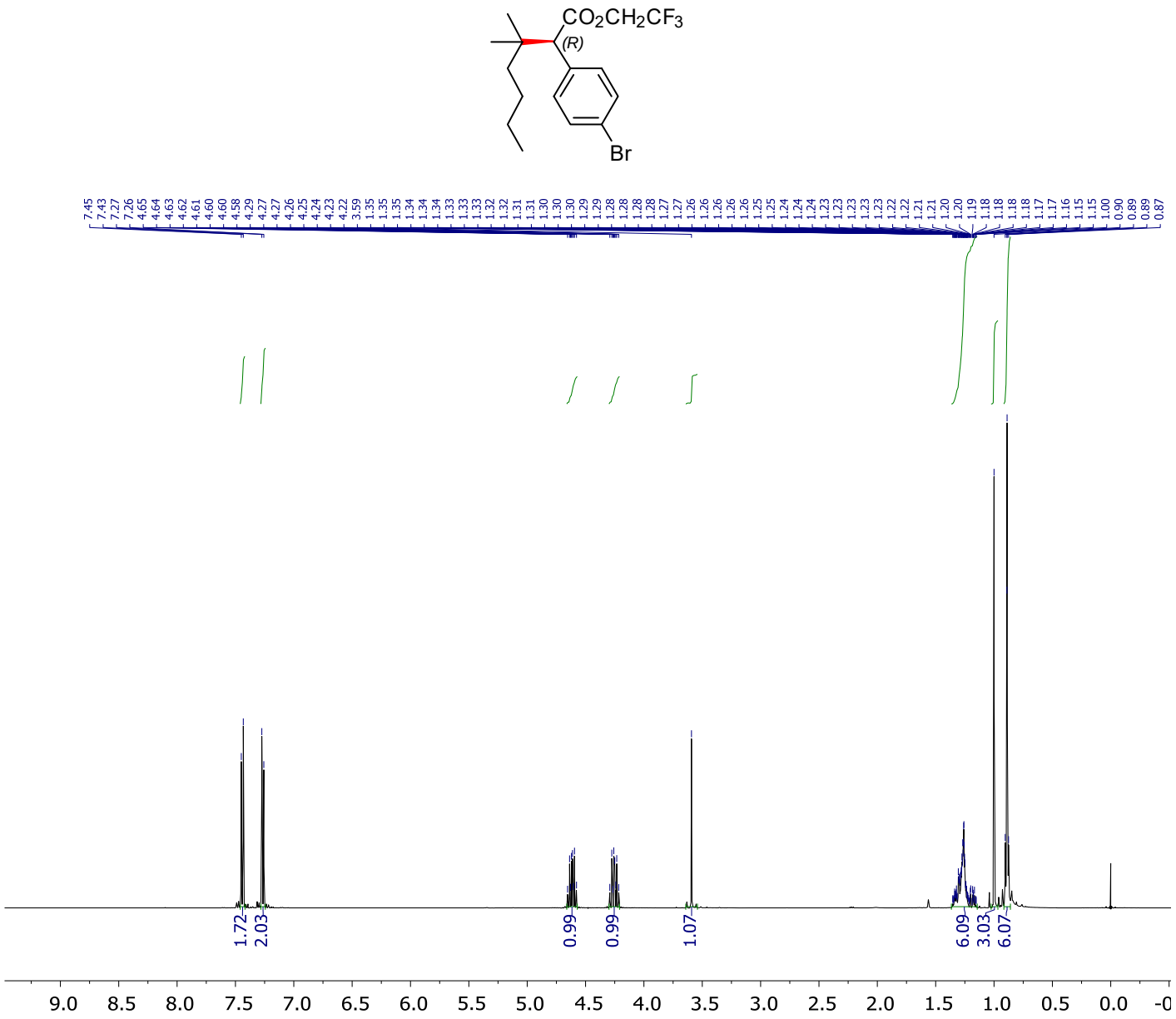
8.3 C–H Functionalization Products **4-26**

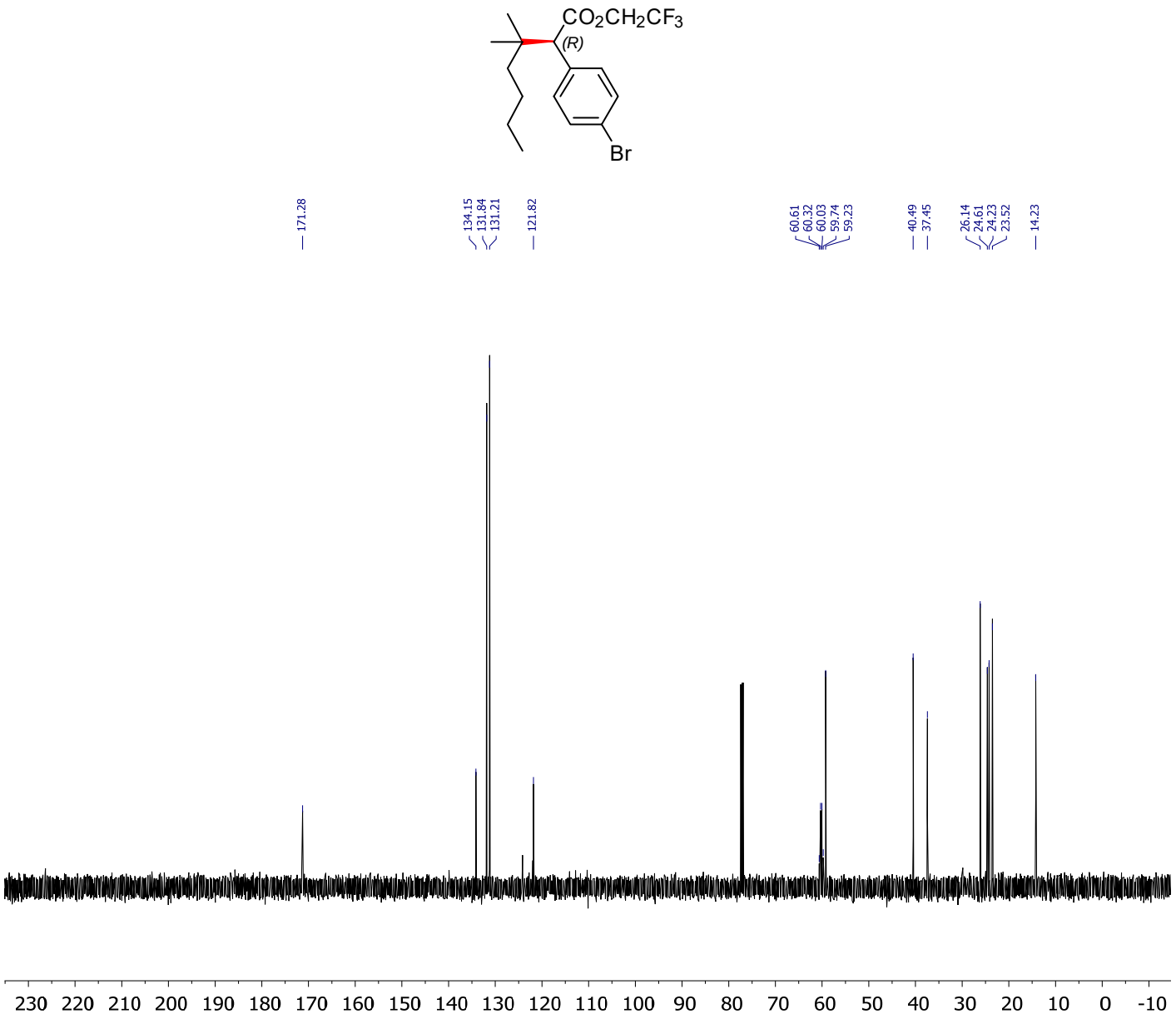


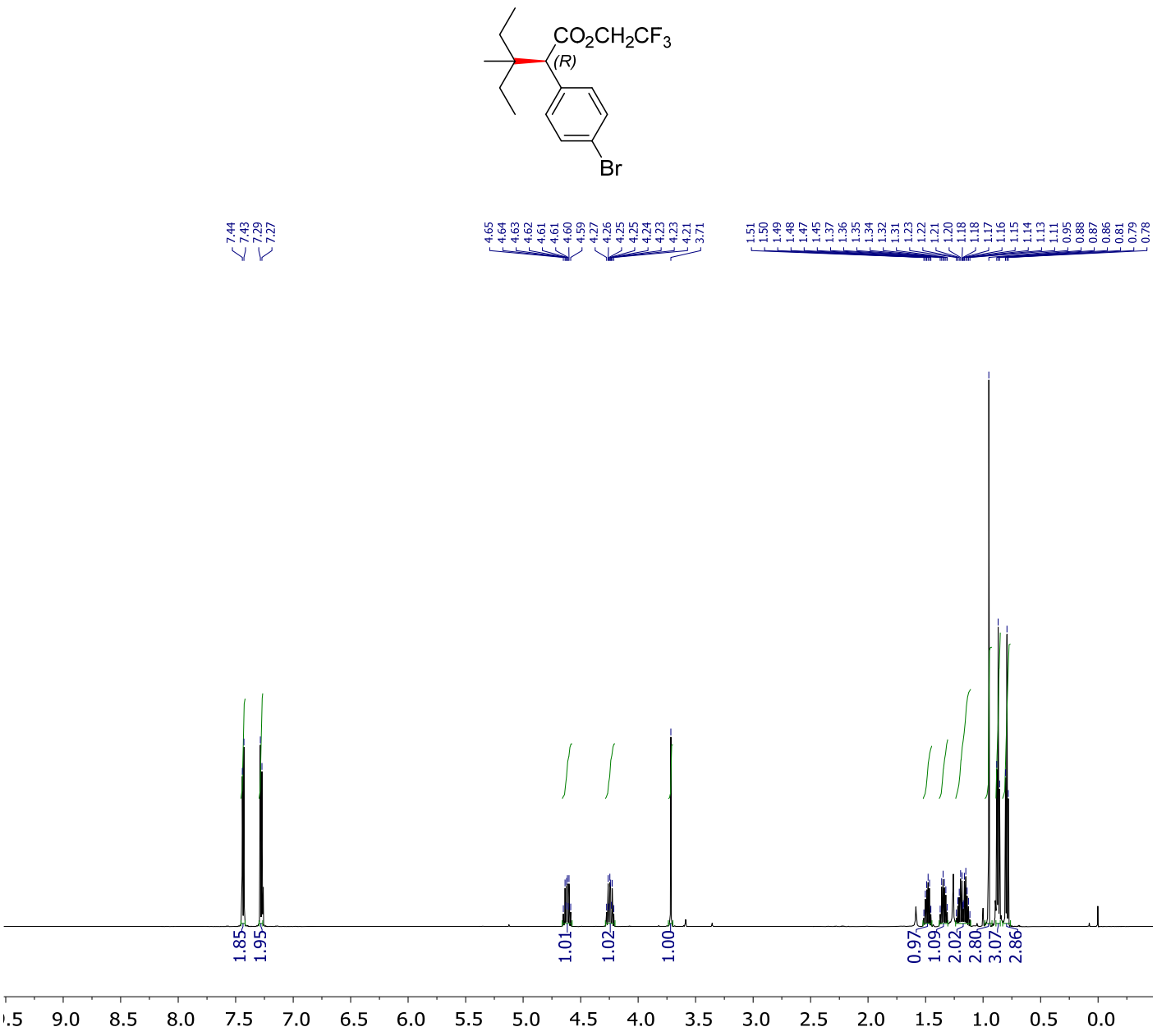


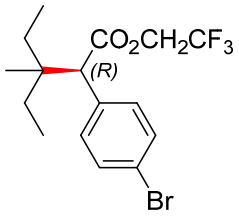

CO2CH2CF3
(R)
Br

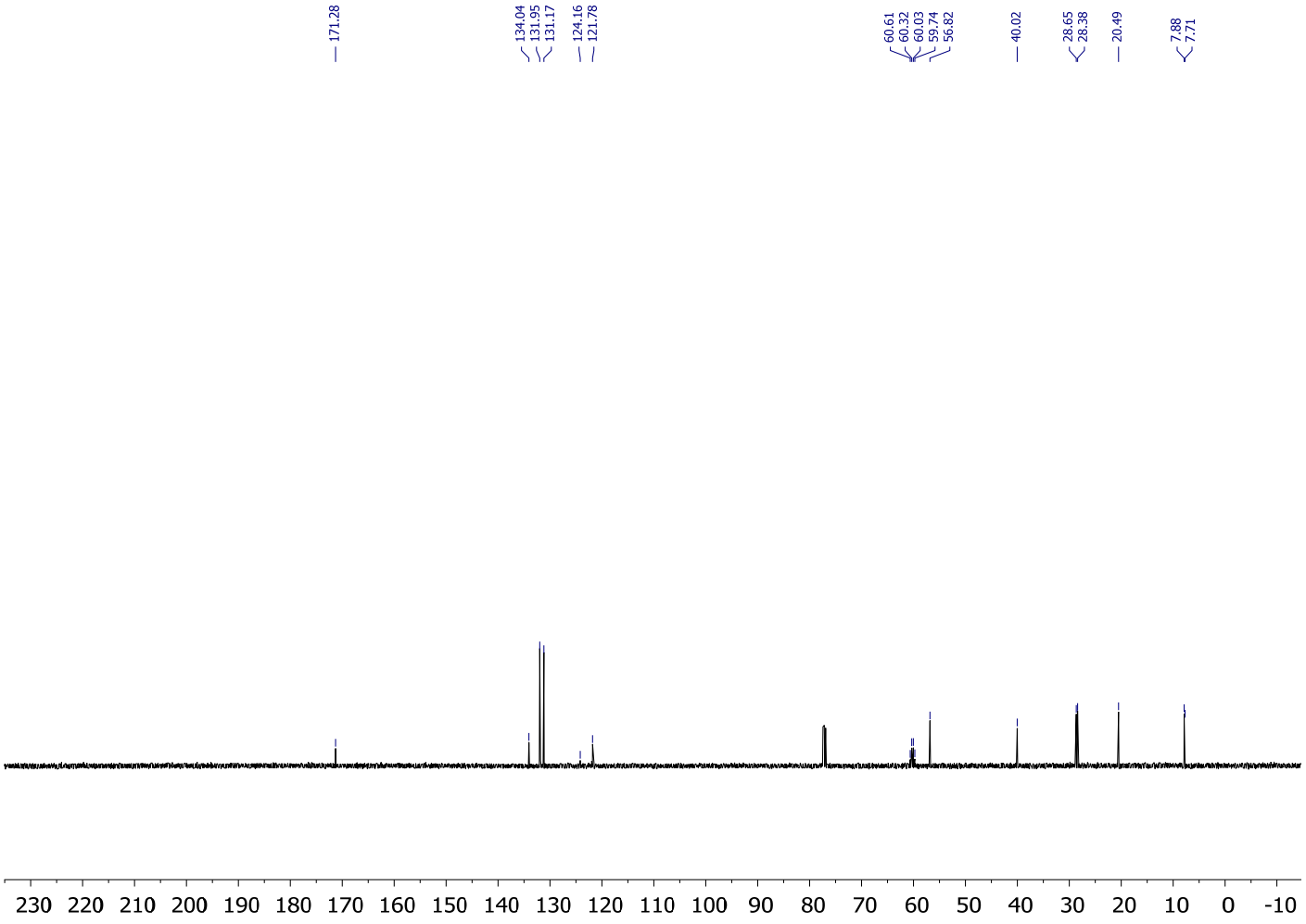

171.27
134.13
131.83
131.20
121.81
60.62
60.33
60.04
59.74
59.04
37.58
32.94
23.88
23.71
8.27
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

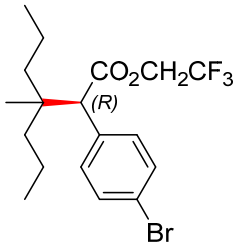

CO2CH2CF3
(R)
Br
1.72
2.03
0.99
0.99
1.07
6.09
3.03
6.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

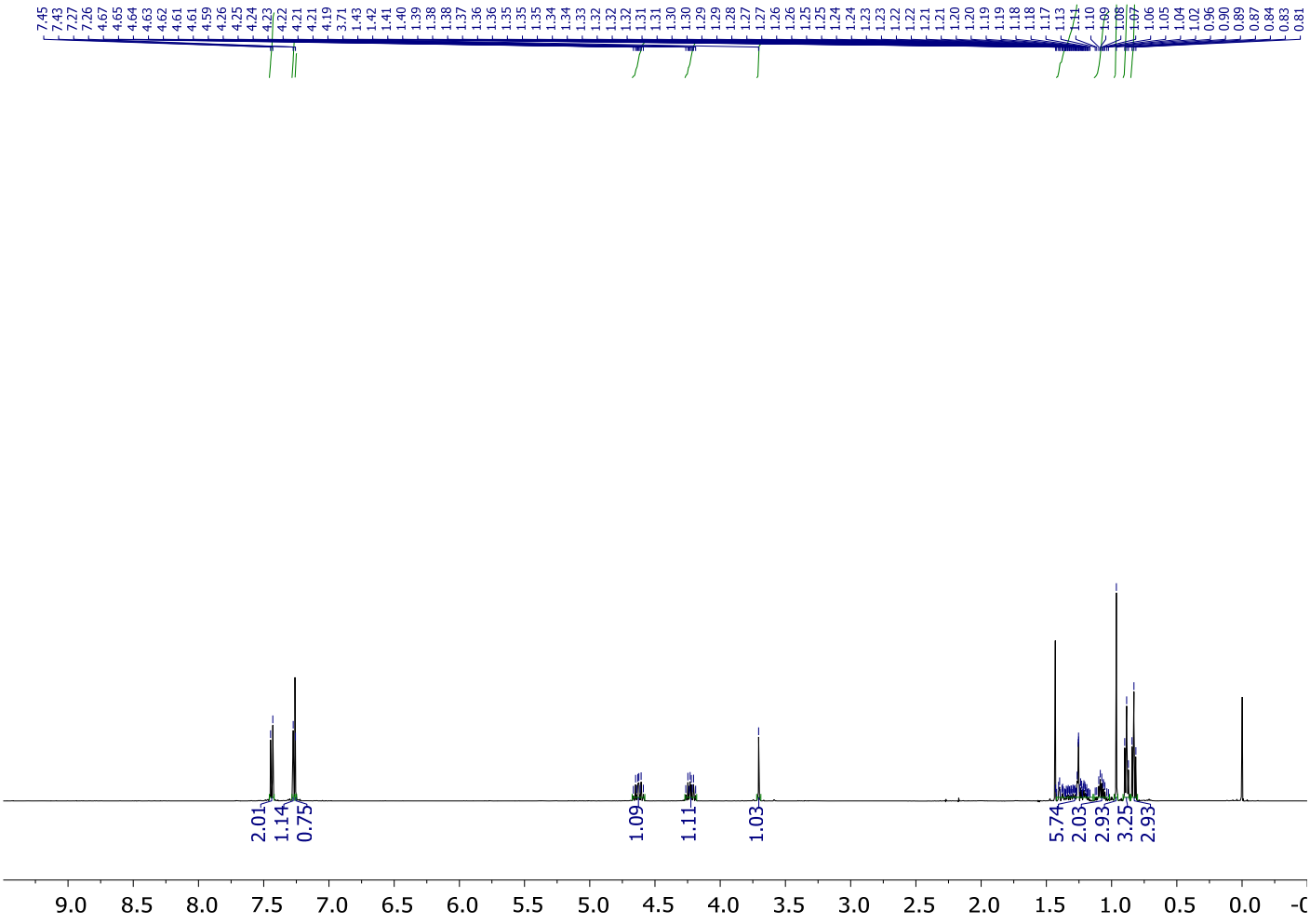

CO2CH2CF3
(R)
Br
171.28
134.15
131.84
131.21
121.82
60.61
60.32
60.03
59.74
59.23
40.49
37.45
26.14
24.61
24.23
23.52
14.23
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

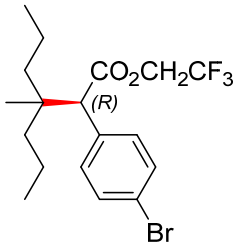

CO2CH2CF3
(R)
Br
7.44
7.43
7.29
7.27
4.65
4.64
4.63
4.62
4.61
4.61
4.60
4.59
4.27
4.26
4.25
4.25
4.24
4.23
4.23
4.21
3.71
1.51
1.50
1.49
1.48
1.47
1.45
1.37
1.36
1.35
1.34
1.32
1.31
1.23
1.22
1.21
1.20
1.18
1.18
1.17
1.16
1.15
1.14
1.13
1.11
0.95
0.88
0.87
0.86
0.81
0.79
0.78
1.85
1.95
1.01
1.02
1.00
0.97
1.09
2.02
2.80
3.07
2.86
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

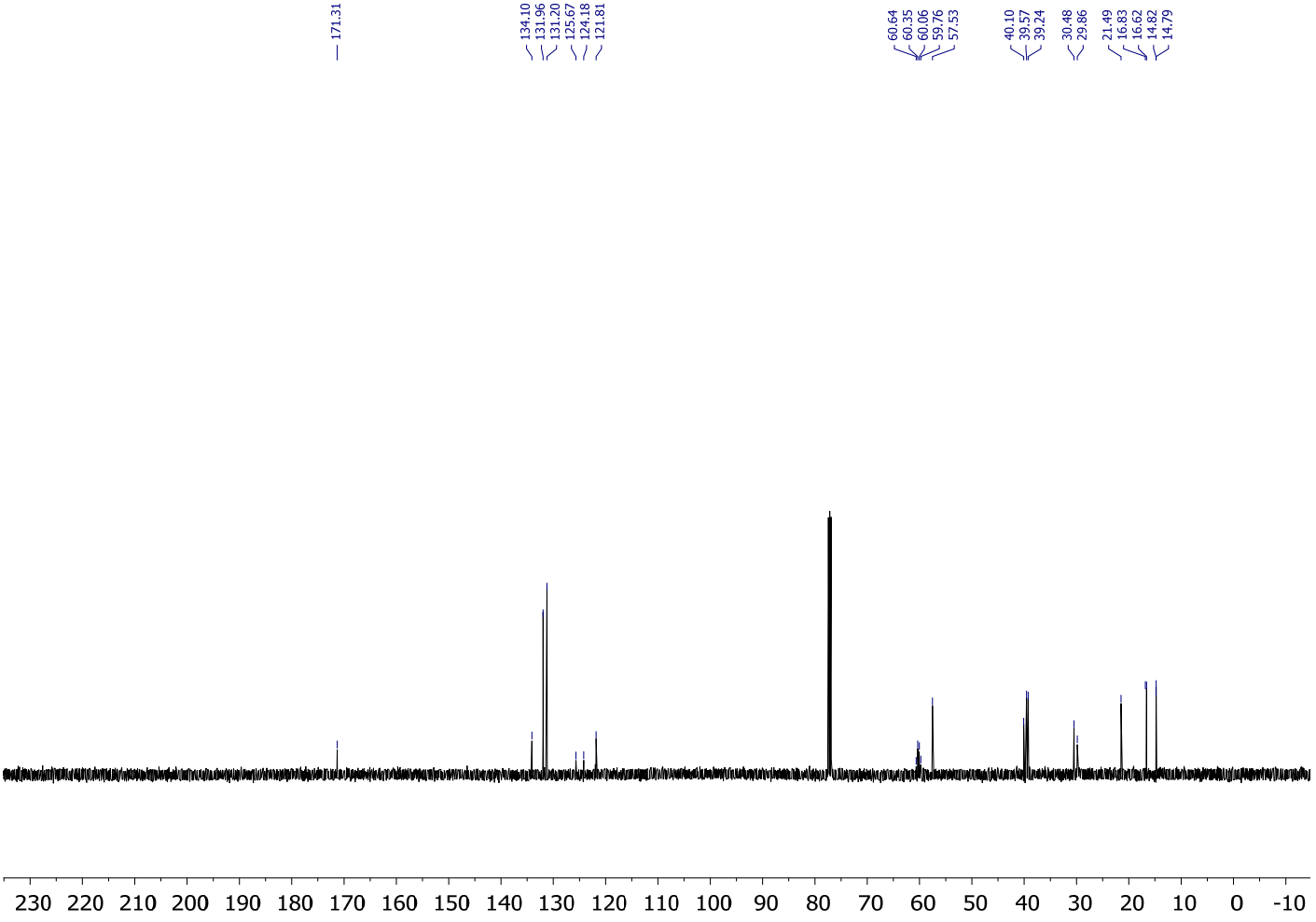

CO2CH2CF3
(R)
Br

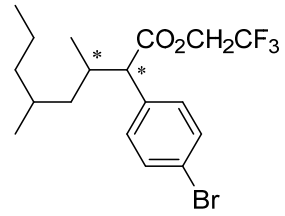

171.28
134.04
131.95
131.17
124.16
121.78
60.61
60.32
60.03
59.74
56.82
40.02
28.65
28.38
20.49
7.88
7.71
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


CO2CH2CF3
(R)
Br

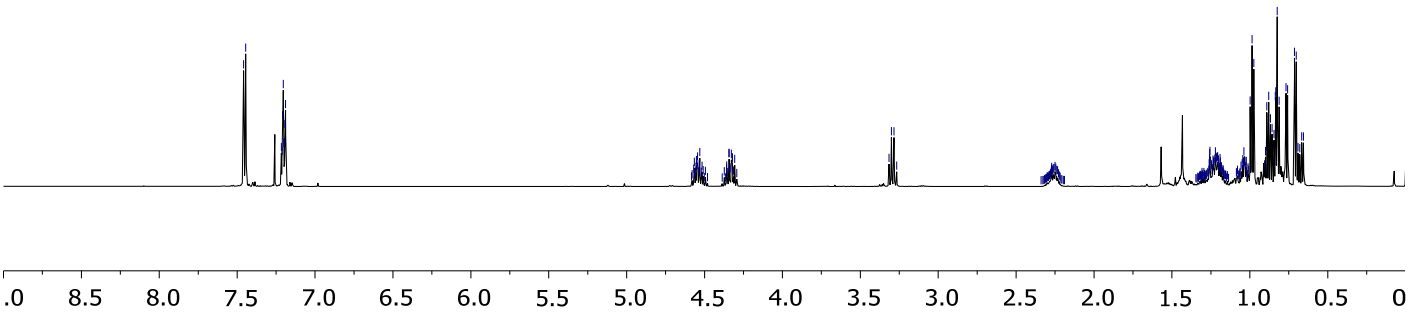

7.45 7.43 7.27 7.26 4.67 4.65 4.64 4.63 4.62 4.61 4.61 4.59 4.26 4.25 4.24 4.23 4.22 4.21 4.21 4.19 3.71 1.43 1.42 1.41 1.40 1.39 1.38 1.38 1.37 1.36 1.36 1.35 1.35 1.35 1.34 1.34 1.33 1.32 1.32 1.32 1.31 1.31 1.30 1.30 1.29 1.29 1.28 1.27 1.27 1.26 1.26 1.25 1.25 1.24 1.24 1.23 1.22 1.22 1.21 1.21 1.20 1.20 1.19 1.19 1.18 1.18 1.17 1.13 1.11 1.10 1.09 1.08 1.07 1.06 1.05 1.04 1.02 0.96 0.90 0.89 0.87 0.84 0.83 0.81
2.01
1.14
0.75
1.09
1.11
1.03
5.74
2.03
2.93
3.25
2.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

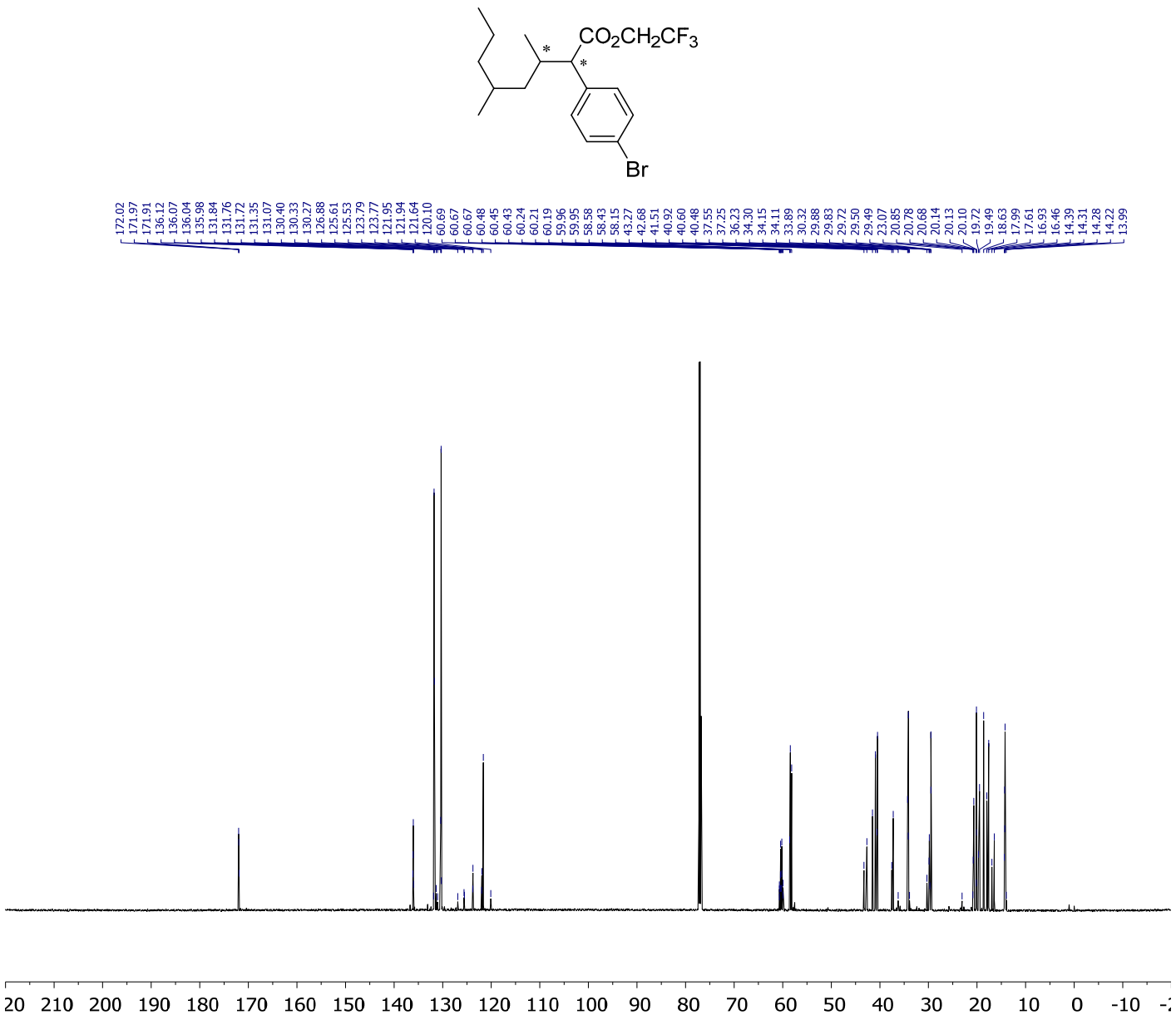

CO2CH2CF3
(R)
Br

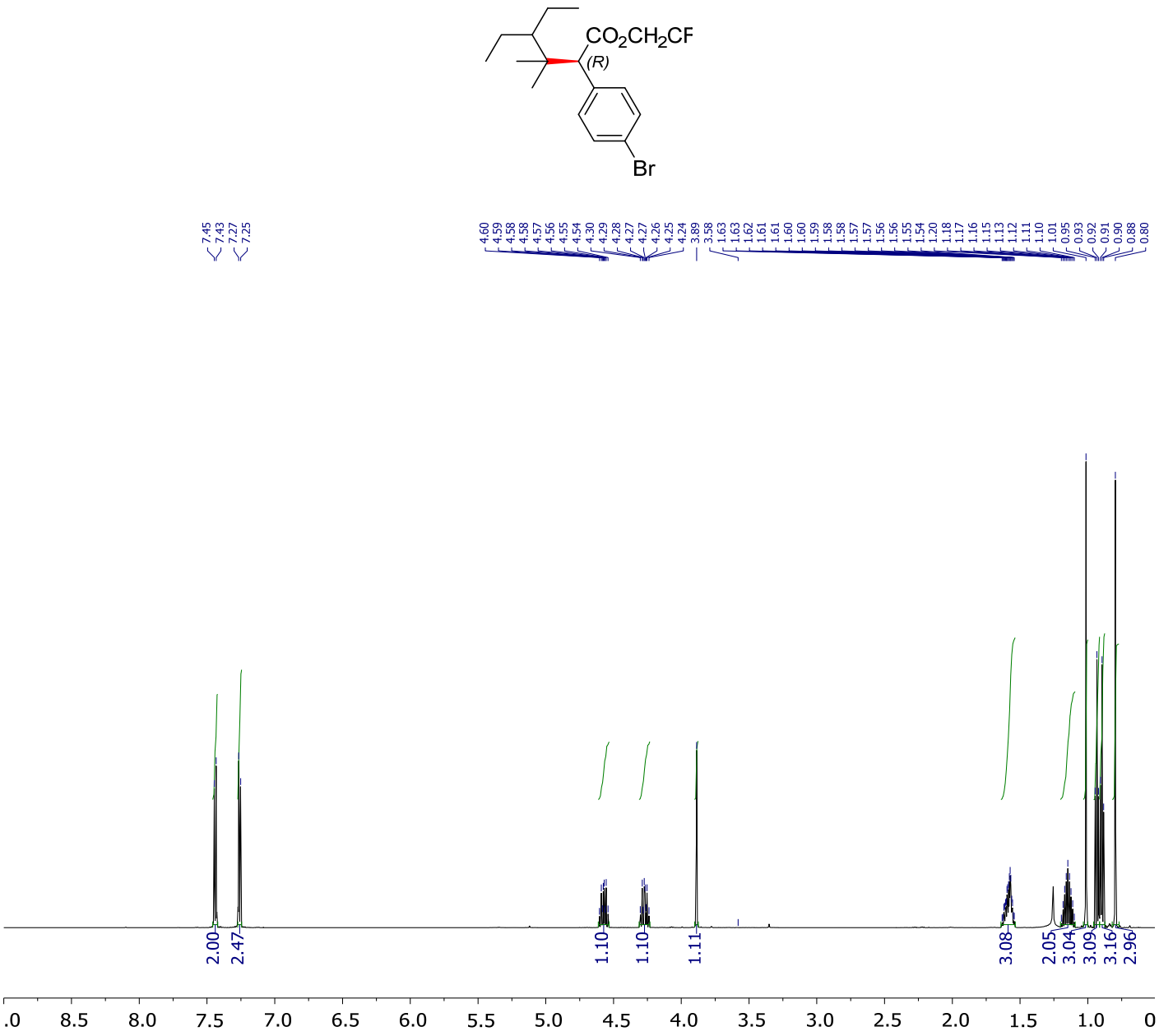

171.31
134.10
131.96
131.20
125.67
124.18
121.81
60.64
60.35
60.06
59.76
57.53
40.10
39.57
39.24
30.48
29.86
21.49
16.83
16.62
14.82
14.79
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

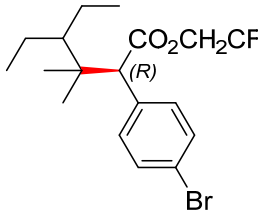

CO2CH2CF3
*
*
Br

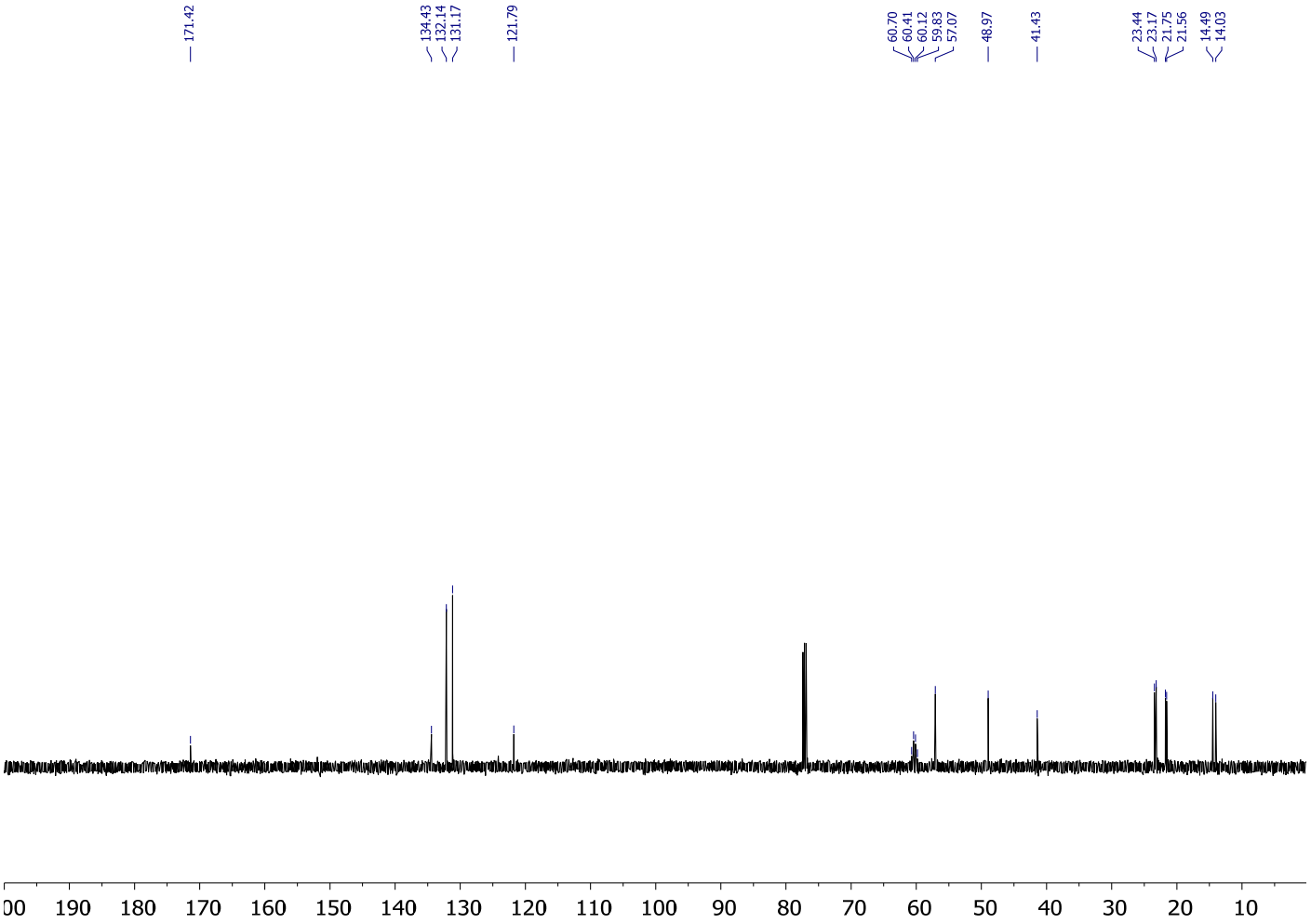

7.46 7.45 7.22 7.21 7.21 7.20 7.20 7.20 7.19 7.19 4.57 4.56 4.55 4.55 4.54 4.53 4.53 4.52 4.36 4.34 4.34 4.33 4.32 4.32 4.31 3.32 3.30 3.28 3.27 2.27 2.25 1.26 1.26 1.26 1.25 1.25 1.24 1.23 1.22 1.22 1.22 1.22 1.21 1.21 1.21 1.20 1.20 1.20 1.19 1.19 1.19 1.19 1.18 1.18 1.06 1.05 1.05 1.04 1.04 1.03 1.03 1.03 1.02 1.00 0.99 0.97 0.90 0.90 0.89 0.88 0.87 0.86 0.84 0.84 0.83 0.82 0.81 0.77 0.76 0.71 0.70 0.69 0.68 0.67 0.66

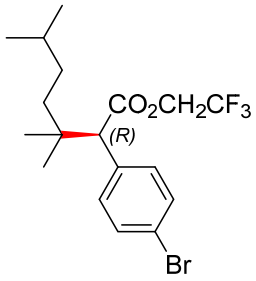

.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

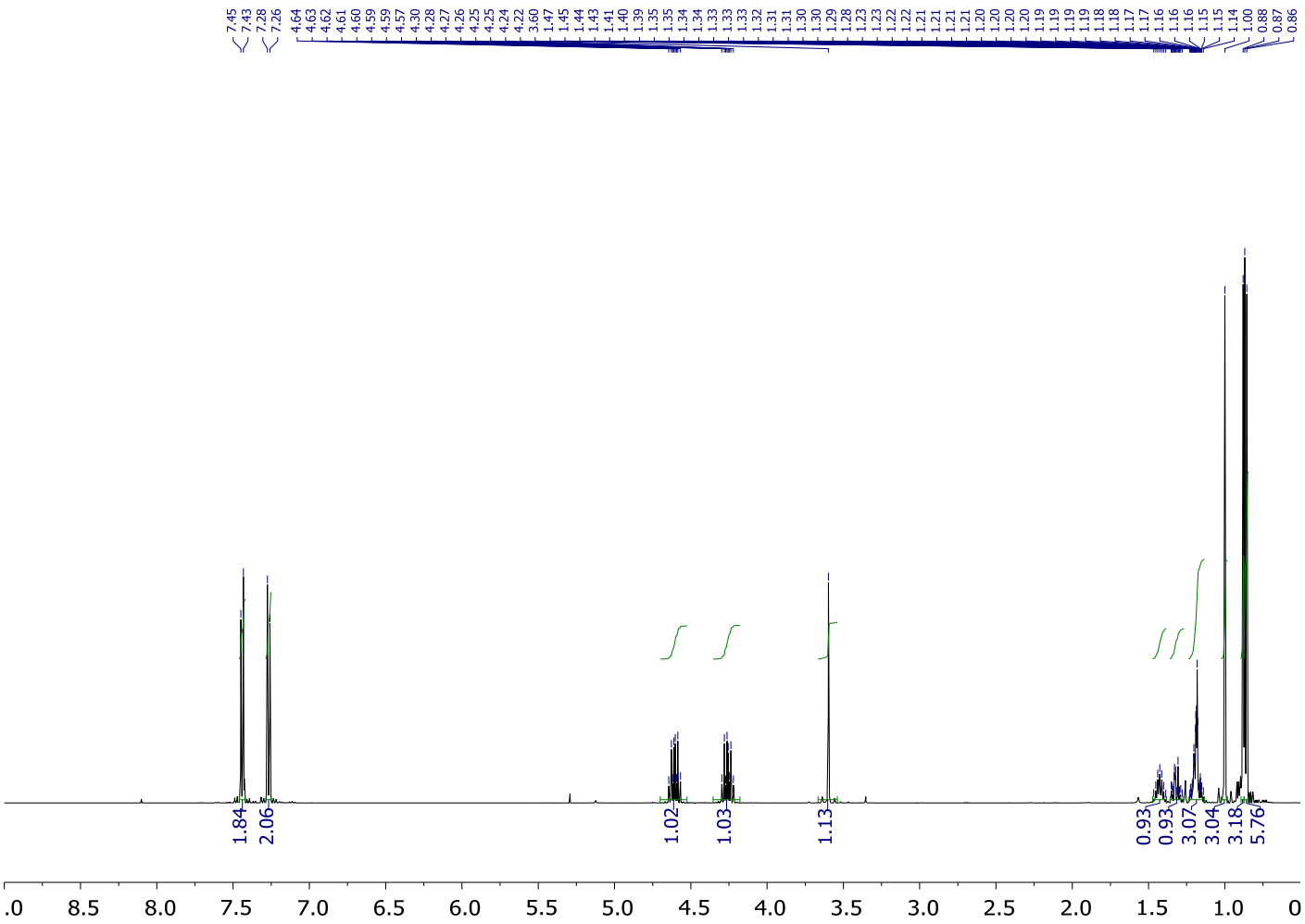

CO2CH2CF3
Br
172.02
171.97
171.91
136.12
136.07
136.04
135.98
131.84
131.76
131.72
131.35
131.07
130.40
130.33
130.27
126.88
125.61
125.53
123.79
123.77
121.95
121.94
121.64
120.10
60.69
60.67
60.67
60.48
60.45
60.43
60.24
60.21
60.19
59.96
59.95
58.58
58.43
58.15
43.27
42.68
41.51
40.92
40.60
40.48
37.55
37.25
36.23
34.30
34.15
34.11
33.89
30.32
29.88
29.83
29.72
29.50
29.49
23.07
20.85
20.78
20.68
20.14
20.13
20.10
19.72
19.49
18.63
17.99
17.61
16.93
16.46
14.39
14.31
14.28
14.22
13.99
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

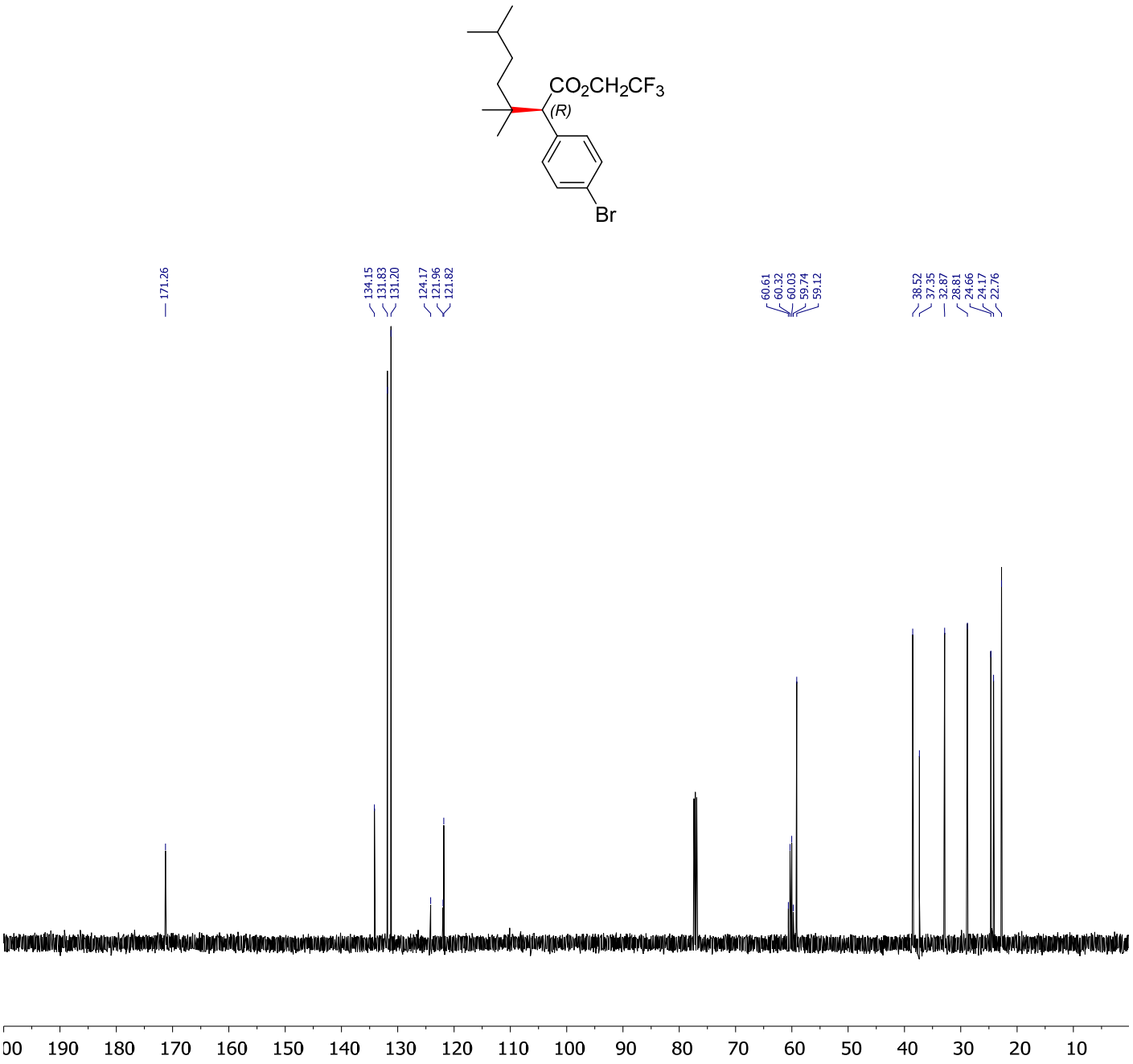

CO2CH2CF
(R)
Br
7.45
7.43
7.27
7.25
4.60
4.59
4.58
4.58
4.58
4.57
4.56
4.55
4.54
4.30
4.29
4.28
4.27
4.27
4.26
4.25
4.24
3.89
3.58
1.63
1.63
1.62
1.61
1.61
1.60
1.60
1.59
1.58
1.58
1.57
1.57
1.56
1.56
1.55
1.54
1.20
1.18
1.17
1.16
1.15
1.13
1.12
1.11
1.10
1.01
0.95
0.93
0.92
0.91
0.90
0.88
0.80
2.00
2.47
1.10
1.10
1.11
3.08
2.05
3.04
3.09
3.16
2.96
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

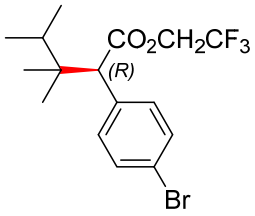

CO2CH2CF
(R)
Br

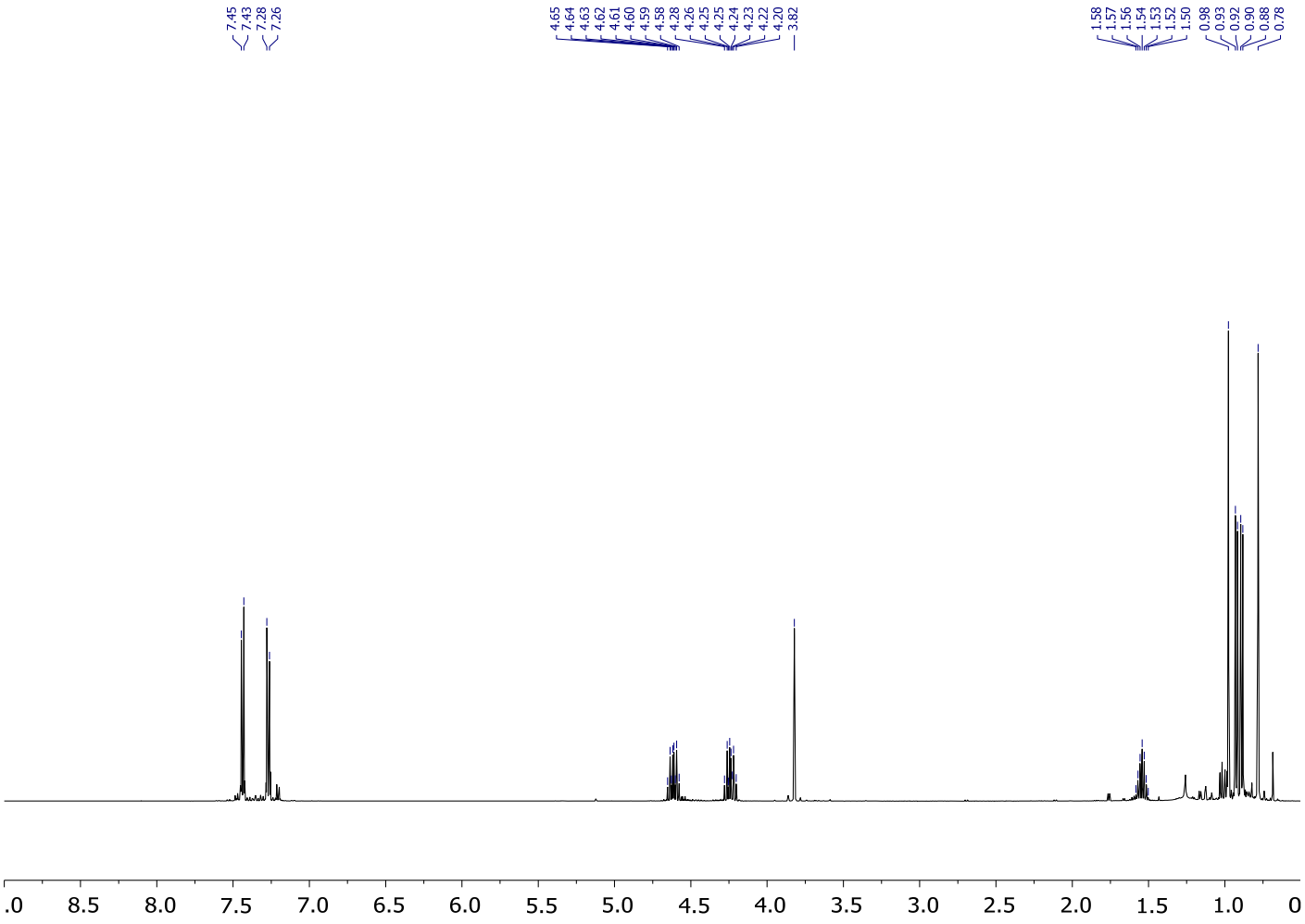

171.42
134.43
132.14
131.17
121.79
60.70
60.41
60.12
59.83
57.07
48.97
41.43
23.44
23.17
21.75
21.56
14.49
14.03
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

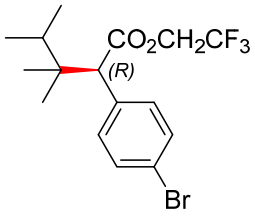

CO2CH2CF3
(R)
Br

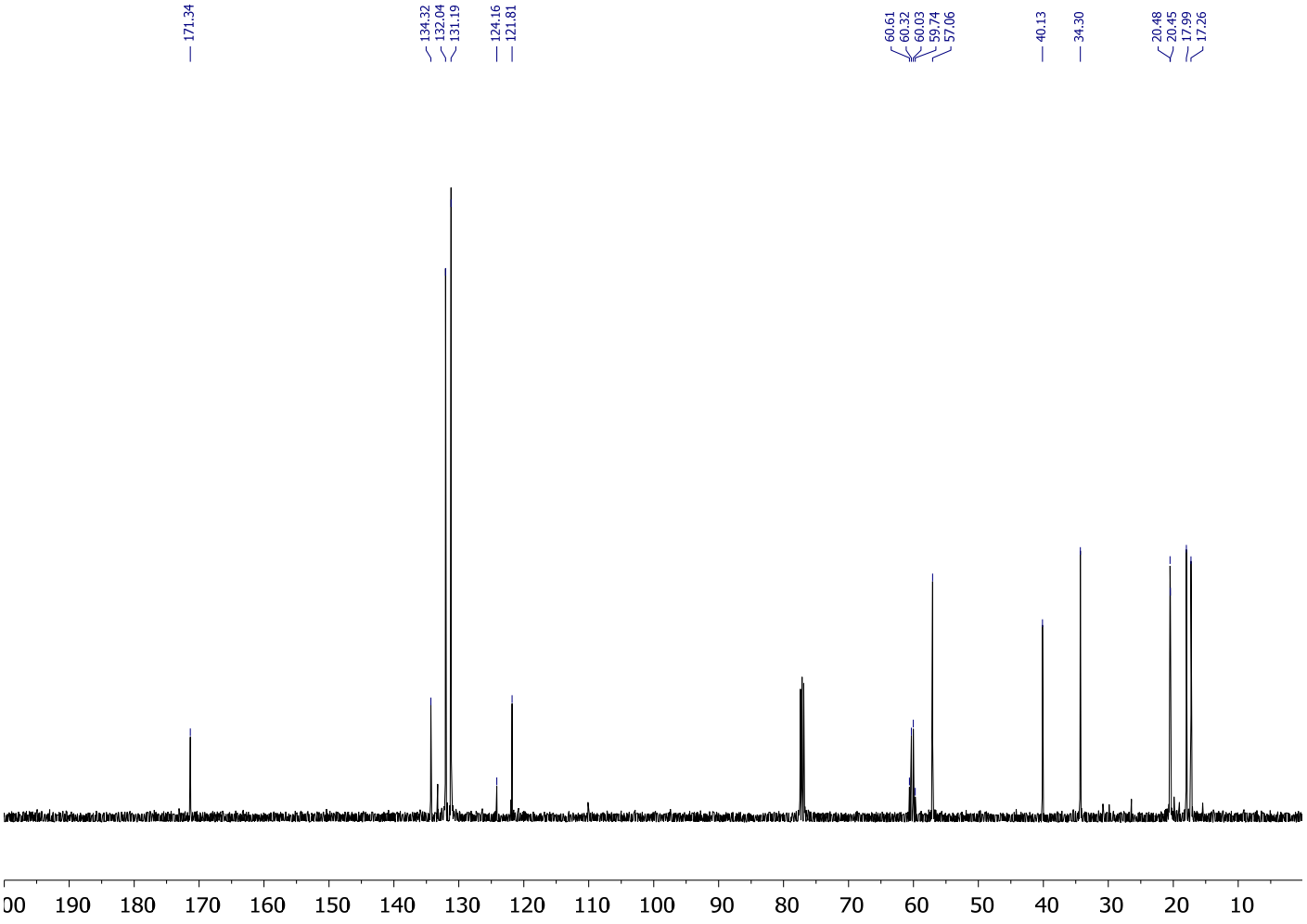

7.45 7.43 7.28 7.26
4.64 4.63 4.62 4.61 4.60 4.59 4.59 4.57 4.30 4.28 4.27 4.26 4.25 4.25 4.24 4.22 3.60 1.47 1.45 1.44 1.43 1.41 1.40 1.39 1.35 1.35 1.34 1.34 1.33 1.33 1.32 1.31 1.31 1.30 1.30 1.29 1.28 1.23 1.22 1.22 1.21 1.21 1.21 1.20 1.20 1.20 1.19 1.19 1.19 1.19 1.18 1.18 1.17 1.17 1.16 1.16 1.15 1.15 1.14 1.00 0.88 0.87 0.86
1.84 2.06 1.02 1.03 1.13 0.93 0.93 3.07 3.04 3.18 5.76
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

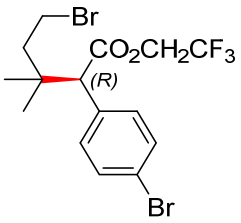

CO2CH2CF3
(R)
Br
171.26
134.15
131.83
131.20
124.17
121.96
121.82
60.61
60.32
60.03
59.74
59.12
38.52
37.35
32.87
28.81
24.66
24.17
22.76
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

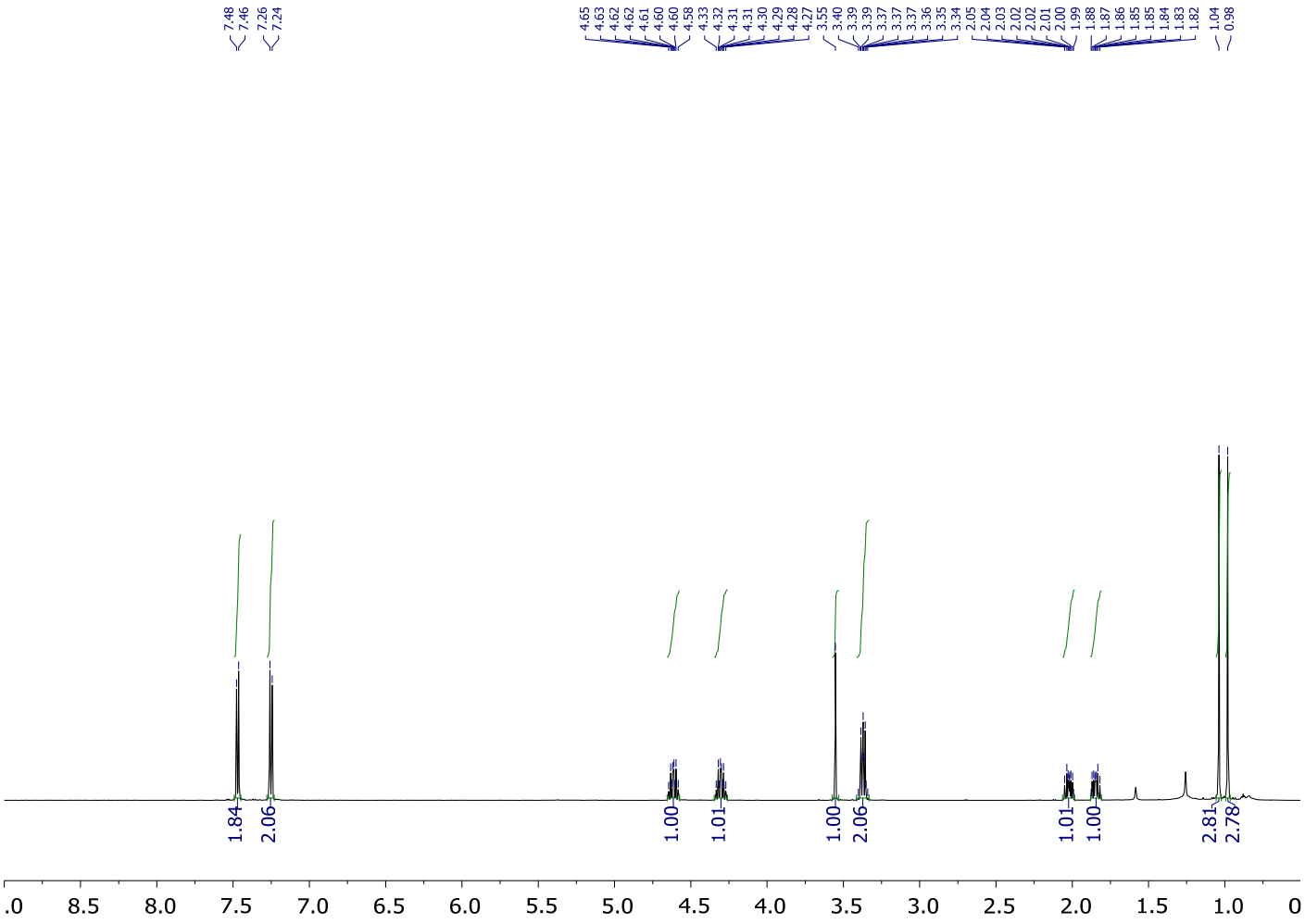

CO2CH2CF3
(R)
Br

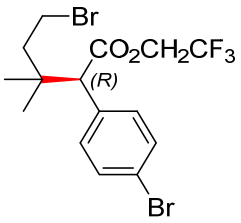

7.45
7.43
7.28
7.26
4.65
4.64
4.63
4.62
4.61
4.60
4.59
4.58
4.28
4.26
4.25
4.25
4.24
4.23
4.22
4.20
3.82
1.58
1.57
1.56
1.54
1.53
1.52
1.50
0.98
0.93
0.92
0.90
0.88
0.78
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

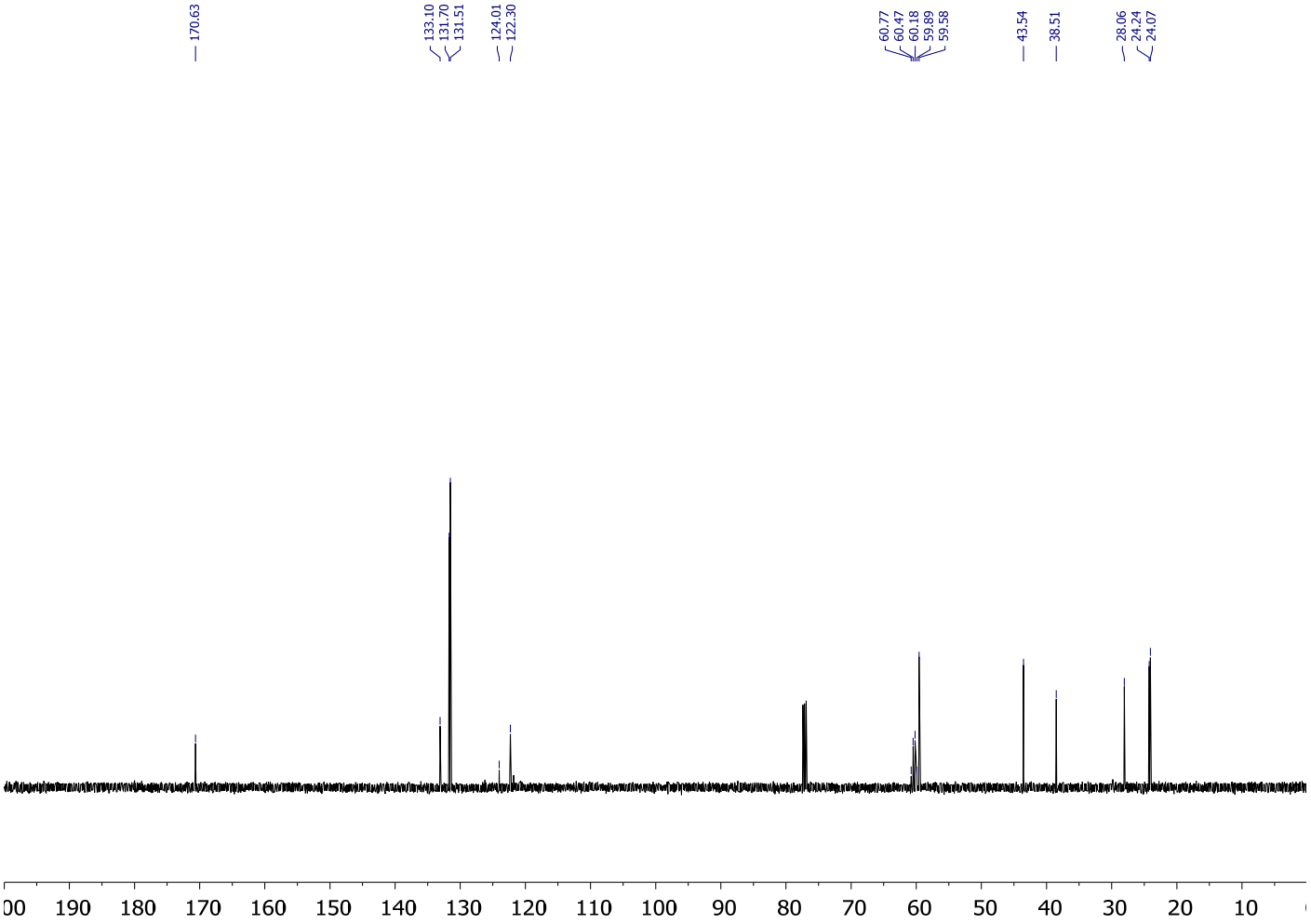

CO2CH2CF3
(R)
Br

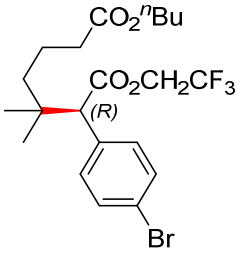

171.34
134.32
132.04
131.19
124.16
121.81
60.61
60.32
60.03
59.74
57.06
40.13
34.30
20.48
20.45
17.99
17.26
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

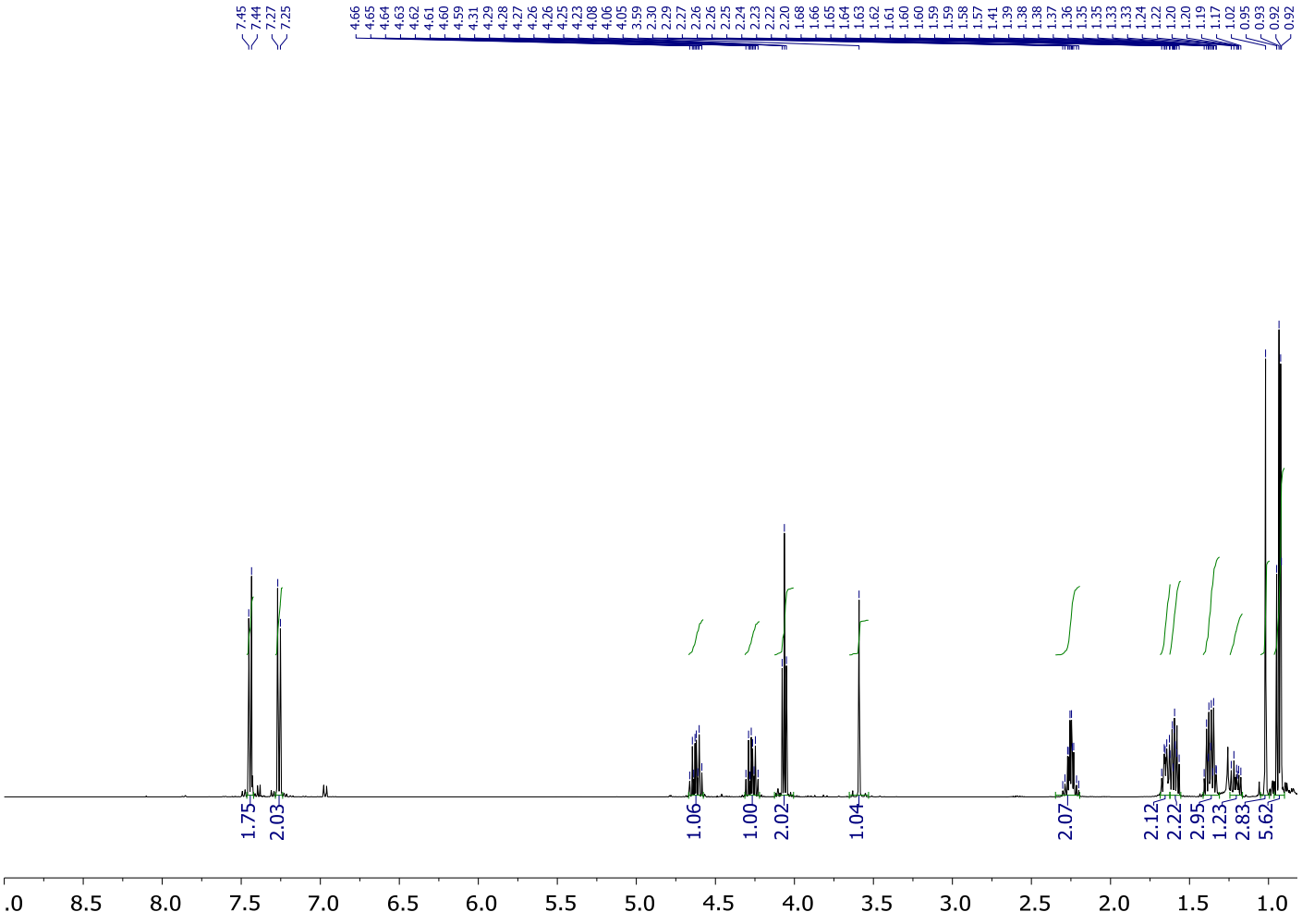

Br
CO2CH2CF3
(R)
Br

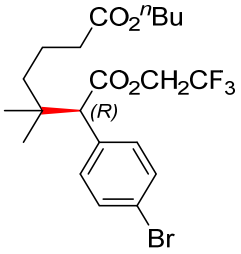

7.48
7.46
7.26
7.24
4.65
4.63
4.62
4.62
4.61
4.60
4.60
4.58
4.33
4.32
4.31
4.31
4.30
4.29
4.28
4.27
3.55
3.40
3.39
3.39
3.37
3.37
3.37
3.36
3.35
3.34
2.05
2.04
2.03
2.02
2.02
2.01
2.00
1.99
1.88
1.87
1.86
1.85
1.85
1.84
1.83
1.82
1.04
0.98
1.84
2.06
1.00
1.01
1.00
2.06
1.01
1.00
2.81
2.78
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

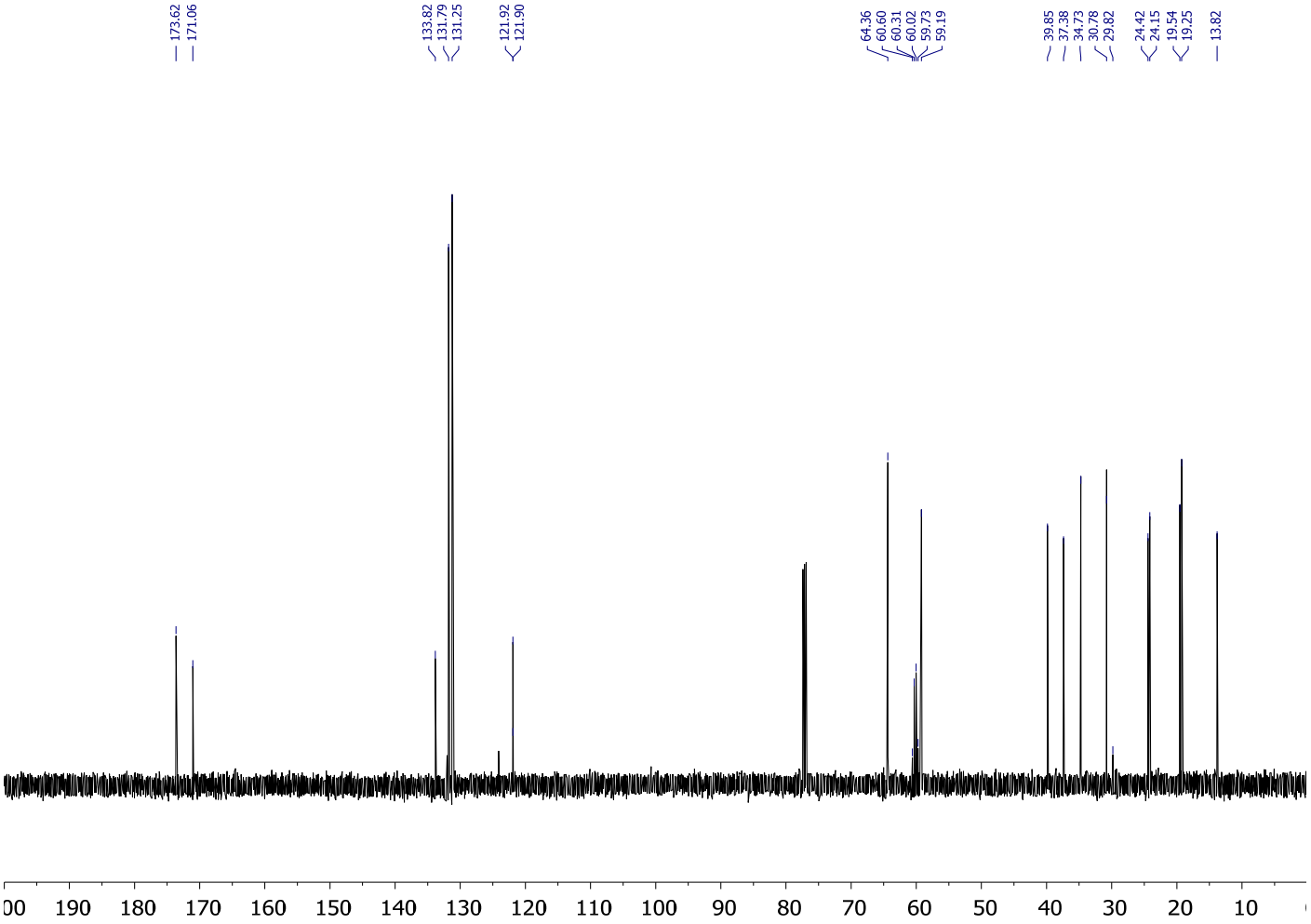

Br
CO2CH2CF3
(R)
Br

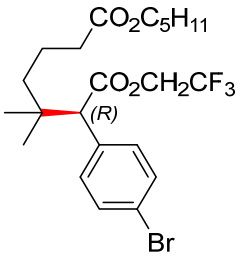

170.63
133.10
131.70
131.51
124.01
122.30
60.77
60.47
60.18
59.89
59.58
43.54
38.51
28.06
24.24
24.07
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

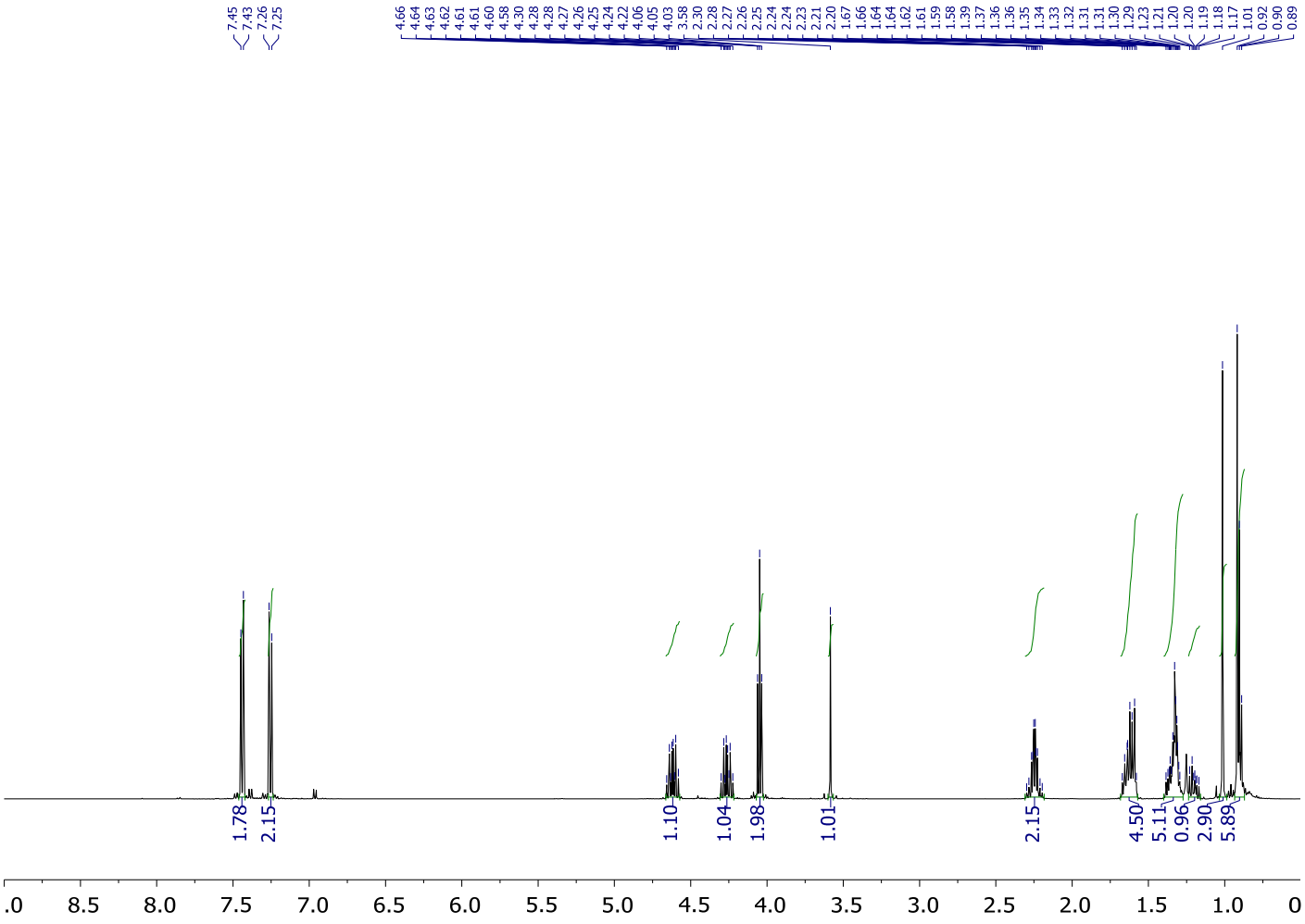

CO2nBu
CO2CH2CF3
(R)
Br

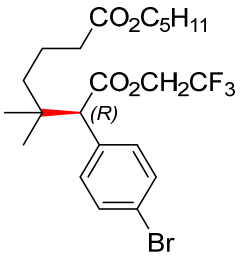

7.45
7.44
7.27
7.25
4.66
4.65
4.64
4.63
4.62
4.61
4.60
4.59
4.31
4.29
4.28
4.27
4.26
4.26
4.25
4.23
4.08
4.06
4.05
3.59
2.30
2.29
2.27
2.26
2.26
2.25
2.24
2.23
2.22
2.20
1.68
1.66
1.65
1.64
1.63
1.62
1.61
1.60
1.60
1.59
1.59
1.58
1.57
1.41
1.39
1.38
1.38
1.37
1.36
1.35
1.35
1.33
1.33
1.24
1.22
1.20
1.20
1.19
1.17
1.02
0.95
0.93
0.92
0.92
1.75
2.03
1.06
1.00
2.02
1.04
2.07
2.12
2.22
2.95
1.23
2.83
5.62
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

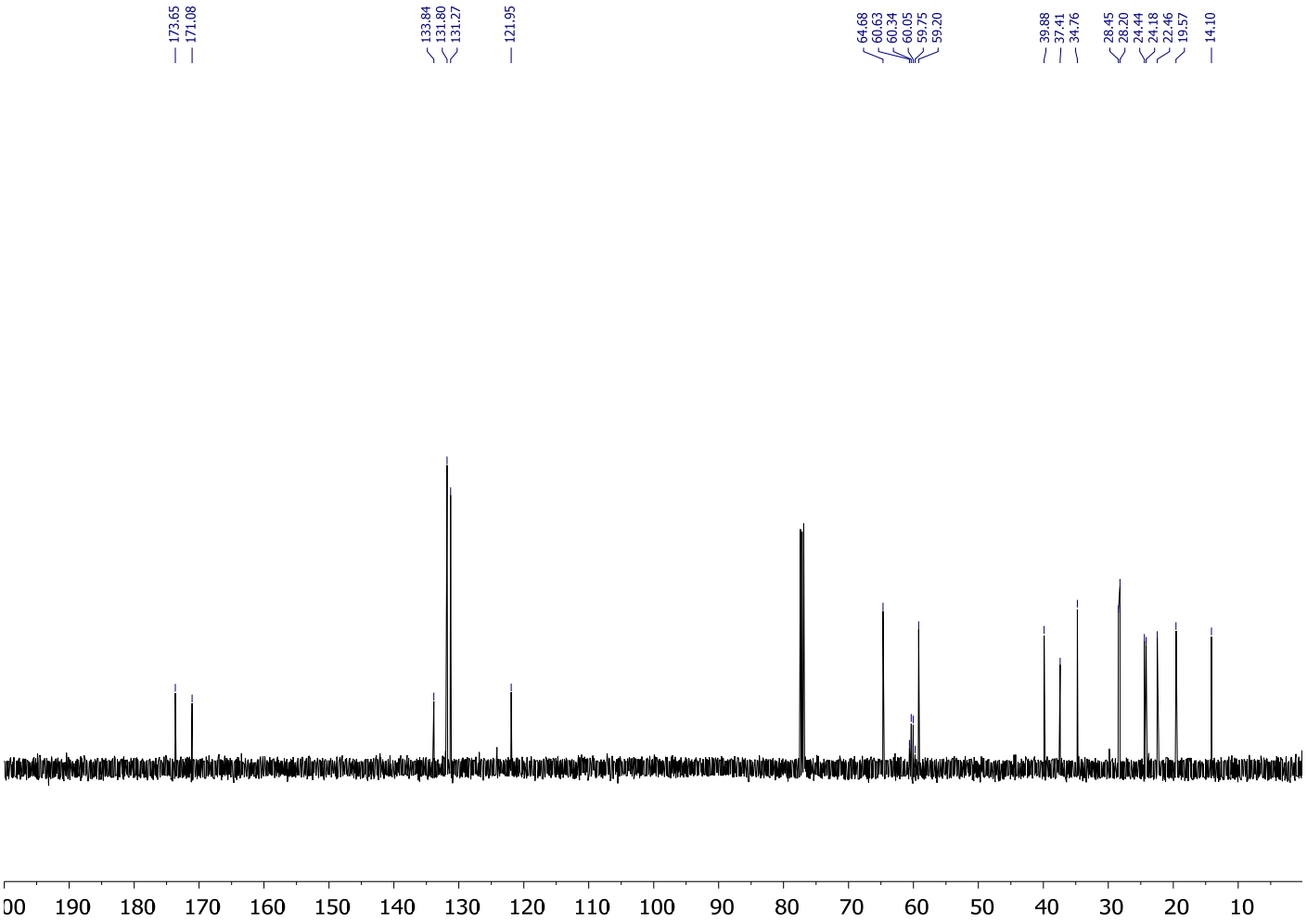

CO2nBu
CO2CH2CF3
(R)
Br

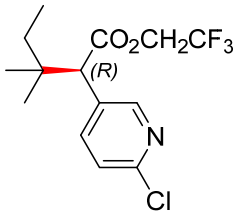

173.62
171.06
133.82
131.79
131.25
121.92
121.90
64.36
60.60
60.31
60.02
59.73
59.19
39.85
37.38
34.73
30.78
29.82
24.42
24.15
19.54
19.25
13.82
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

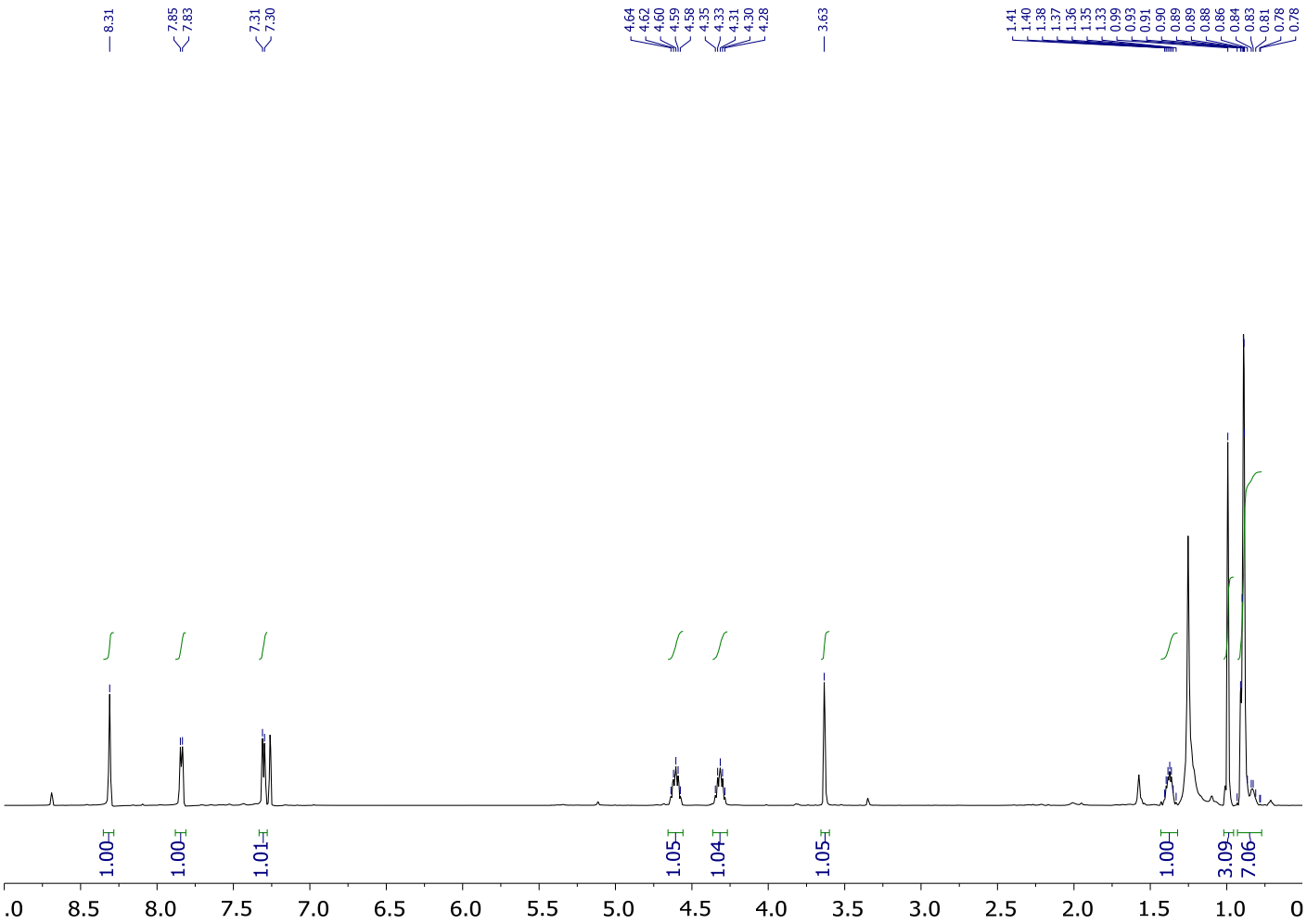

CO2C5H11
CO2CH2CF3
(R)
Br

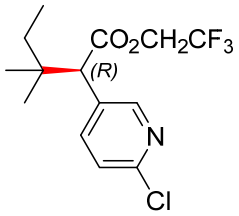

7.45
7.43
7.26
7.25
4.66
4.64
4.63
4.62
4.61
4.61
4.60
4.58
4.30
4.28
4.28
4.27
4.26
4.25
4.24
4.22
4.06
4.05
4.03
3.58
2.30
2.28
2.27
2.26
2.25
2.24
2.24
2.23
2.21
2.20
1.67
1.66
1.64
1.64
1.62
1.61
1.59
1.58
1.39
1.37
1.36
1.36
1.35
1.34
1.33
1.32
1.31
1.31
1.30
1.29
1.23
1.21
1.20
1.20
1.19
1.18
1.17
1.01
0.92
0.90
0.89
1.78
2.15
1.10
1.04
1.98
1.01
2.15
4.50
5.11
0.96
2.90
5.89
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

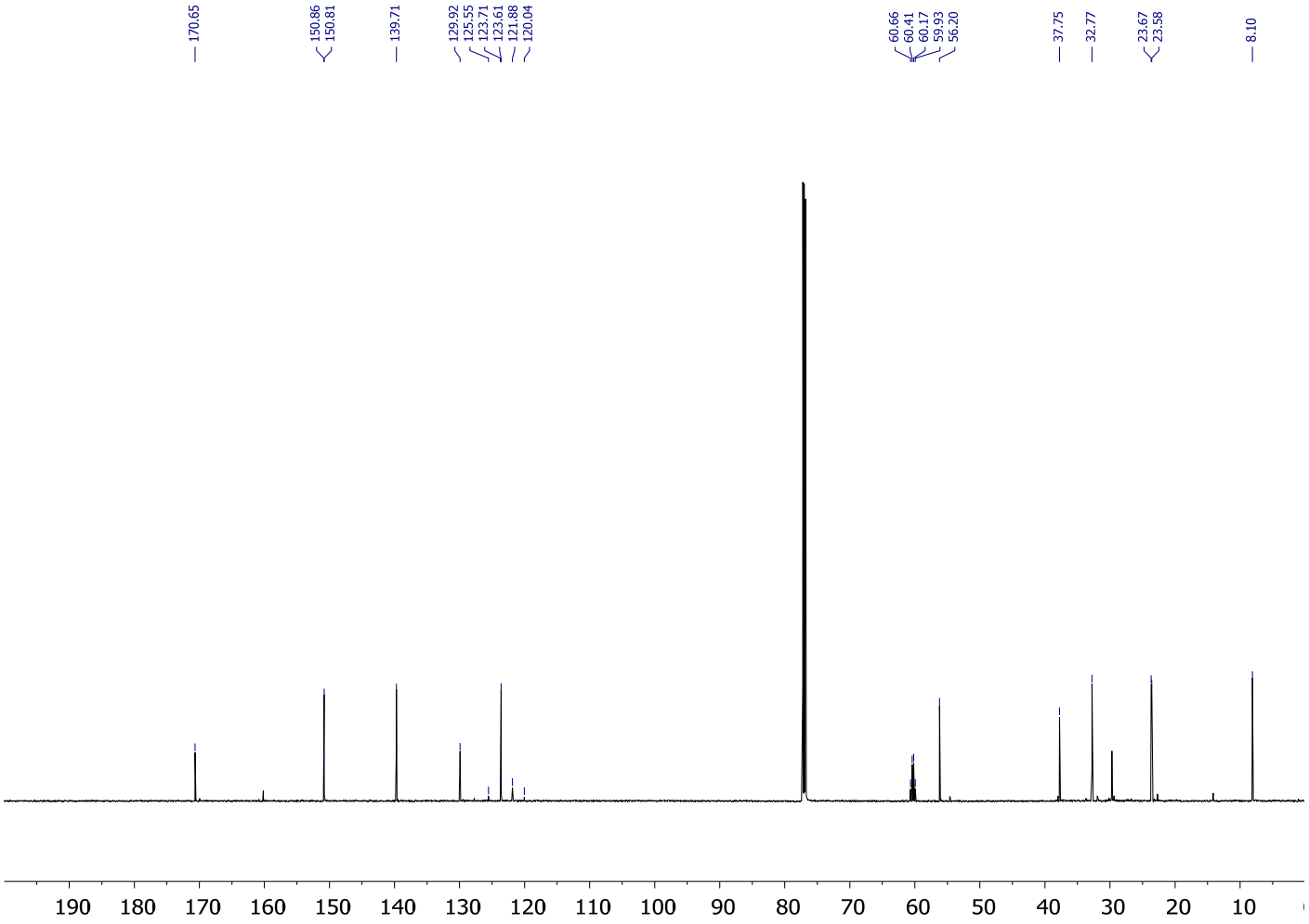

CO2C5H11
CO2CH2CF3
(R)
Br

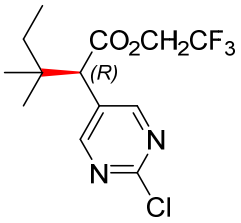

173.65
171.08
133.84
131.80
131.27
121.95
64.68
60.63
60.34
60.05
59.75
59.20
39.88
37.41
34.76
28.45
28.20
24.44
24.18
22.46
19.57
14.10
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

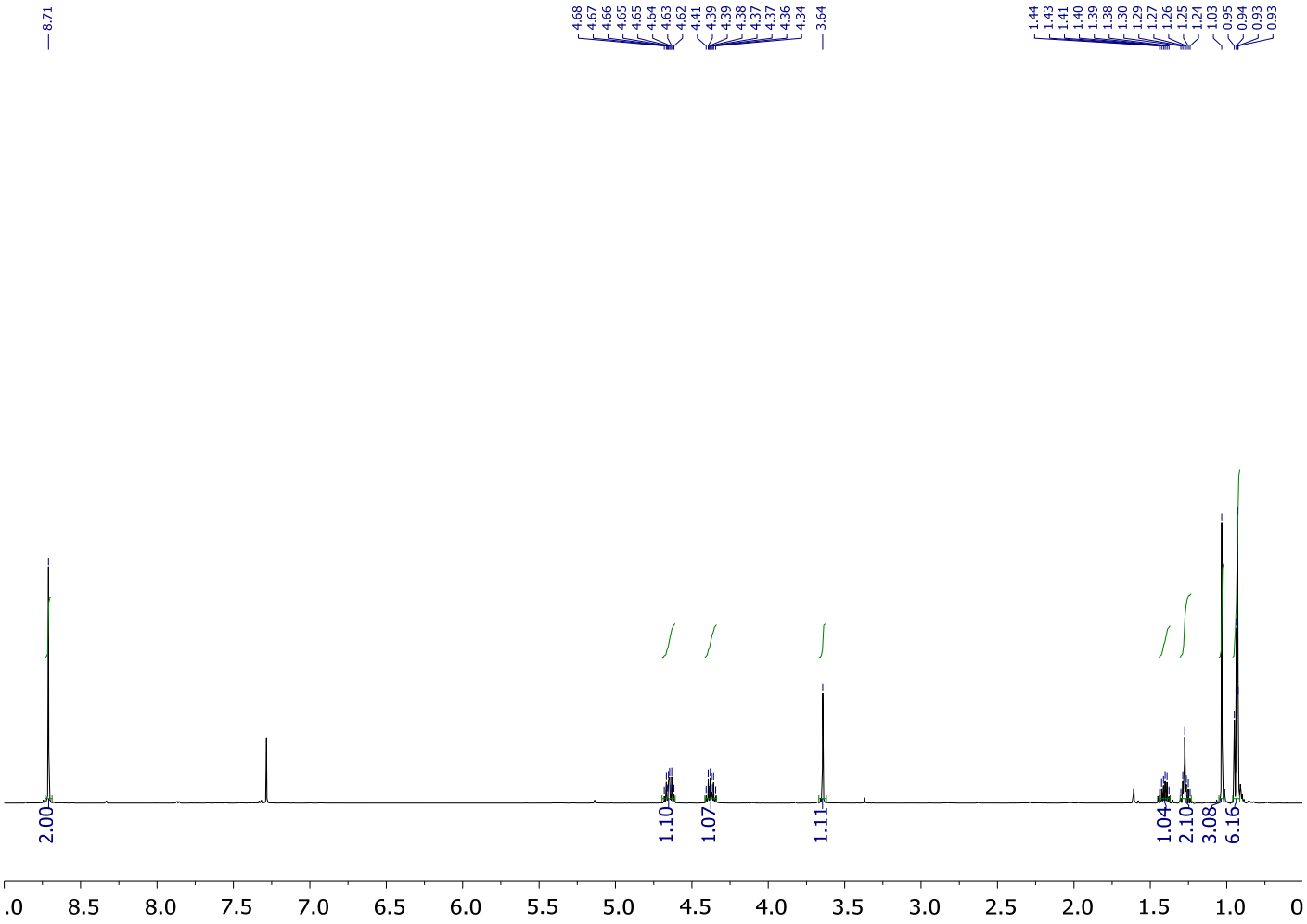

CO2CH2CF3
(R)
N
Cl

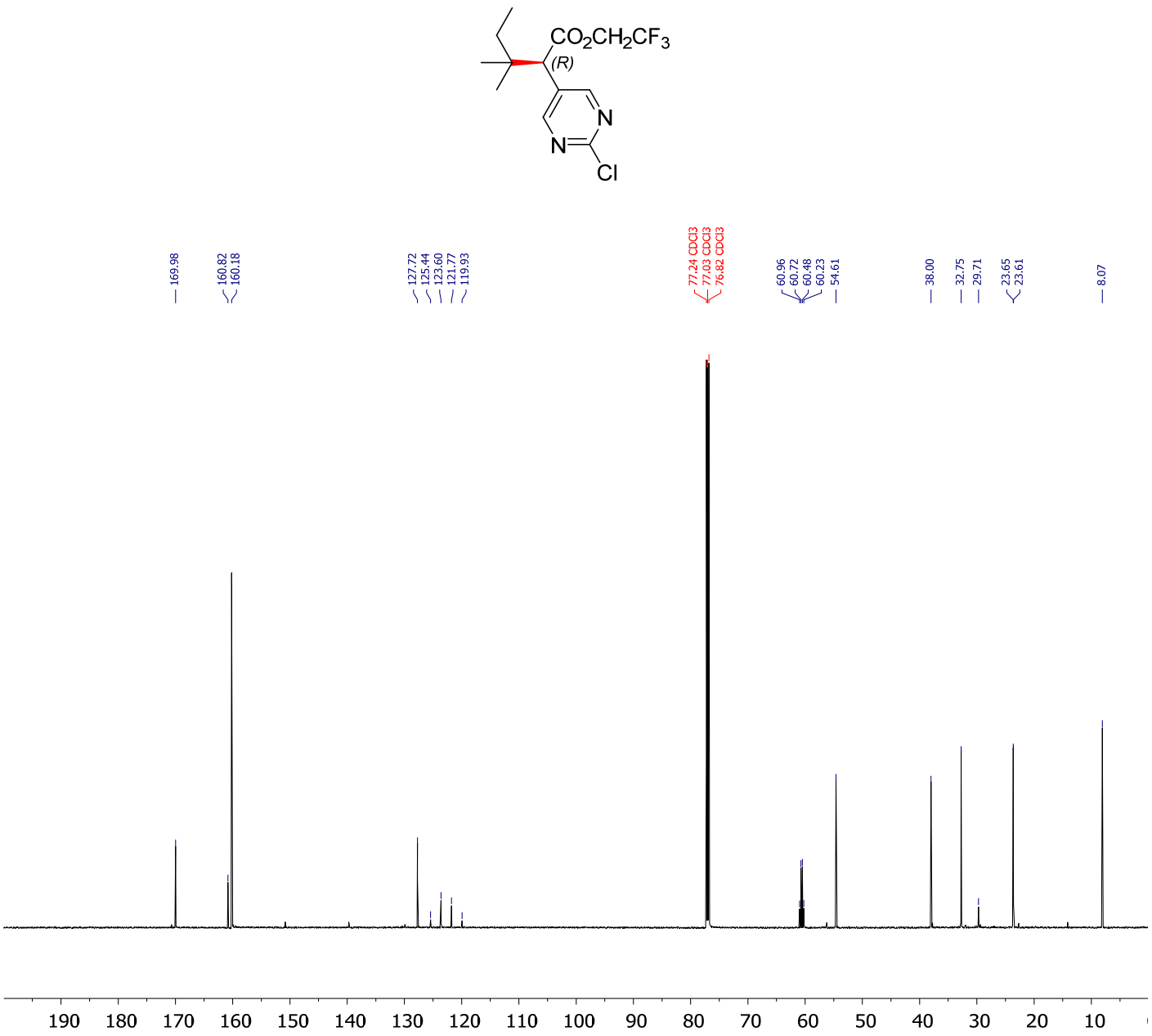

8.31
7.85
7.83
7.31
7.30
4.64
4.62
4.60
4.59
4.58
4.35
4.33
4.31
4.30
4.28
3.63
1.41
1.40
1.38
1.37
1.36
1.35
1.33
0.99
0.93
0.91
0.90
0.89
0.89
0.88
0.86
0.84
0.83
0.81
0.78
0.78
1.00
1.00
1.01
1.05
1.04
1.05
1.00
3.09
7.06
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

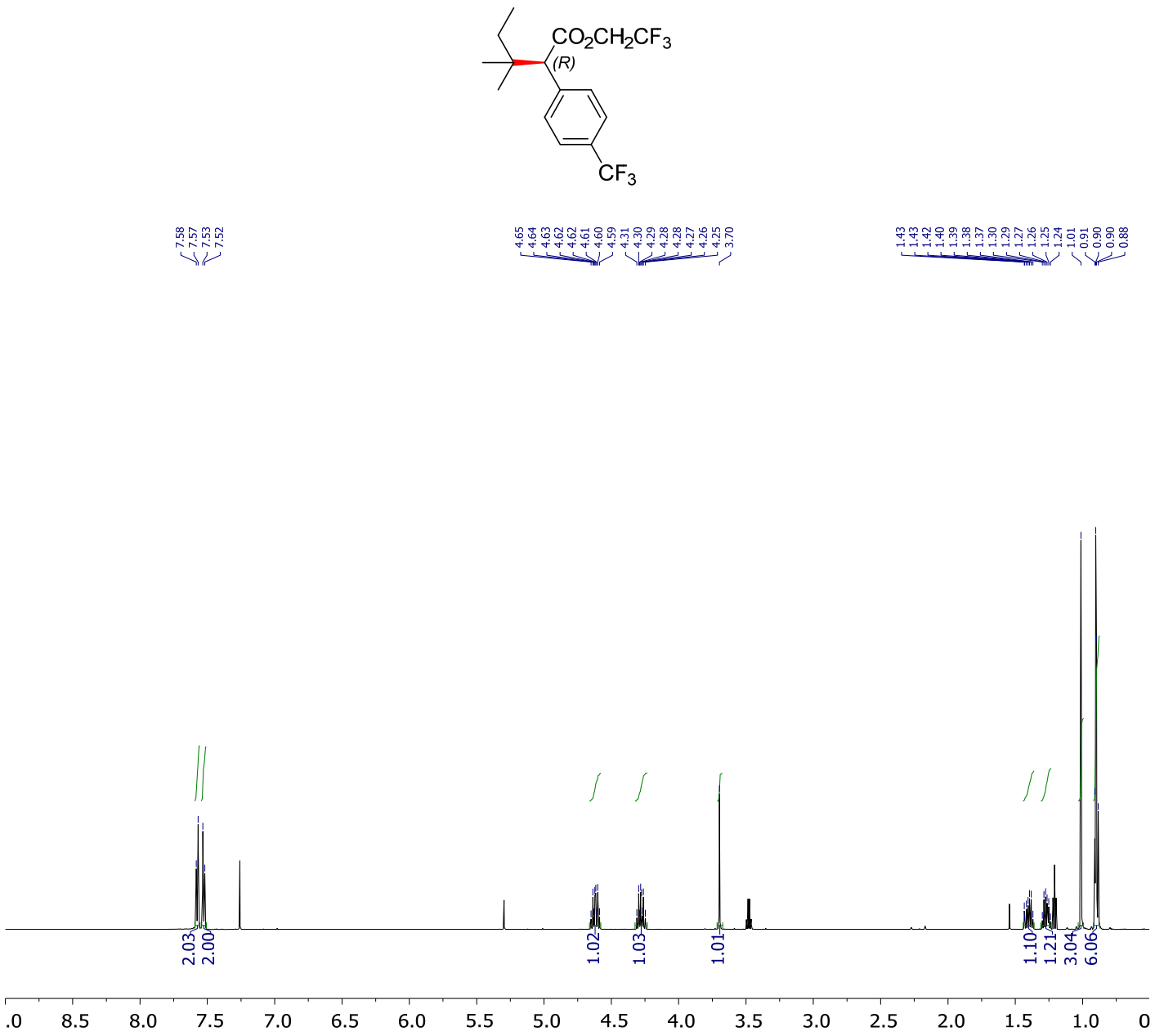

CO2CH2CF3
(R)
N
Cl

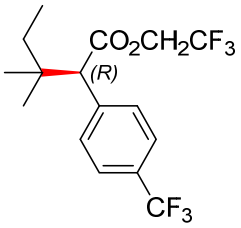

170.65
150.86
150.81
139.71
129.92
125.55
123.71
123.61
121.88
120.04
60.66
60.41
60.17
59.93
56.20
37.75
32.77
23.67
23.58
8.10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

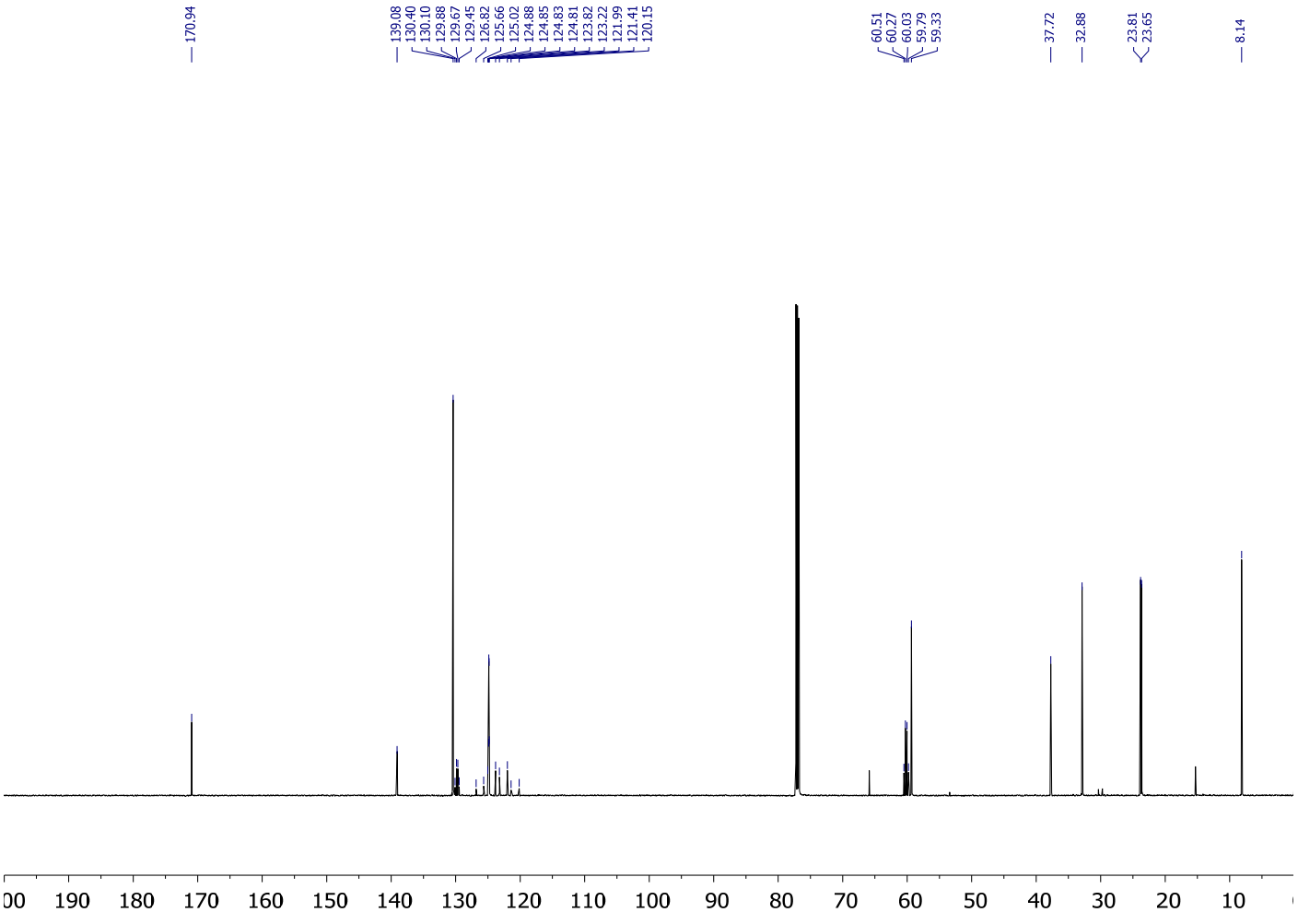

CO2CH2CF3
(R)
N
N
Cl

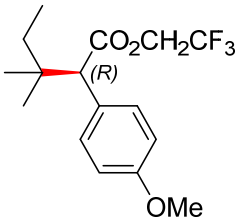

8.71
4.68
4.67
4.66
4.65
4.65
4.64
4.63
4.62
4.41
4.39
4.39
4.38
4.37
4.37
4.36
4.34
3.64
1.44
1.43
1.41
1.40
1.39
1.38
1.30
1.29
1.27
1.26
1.25
1.24
1.03
0.95
0.94
0.93
0.93
2.00
1.10
1.07
1.11
1.04
2.10
3.08
6.16
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

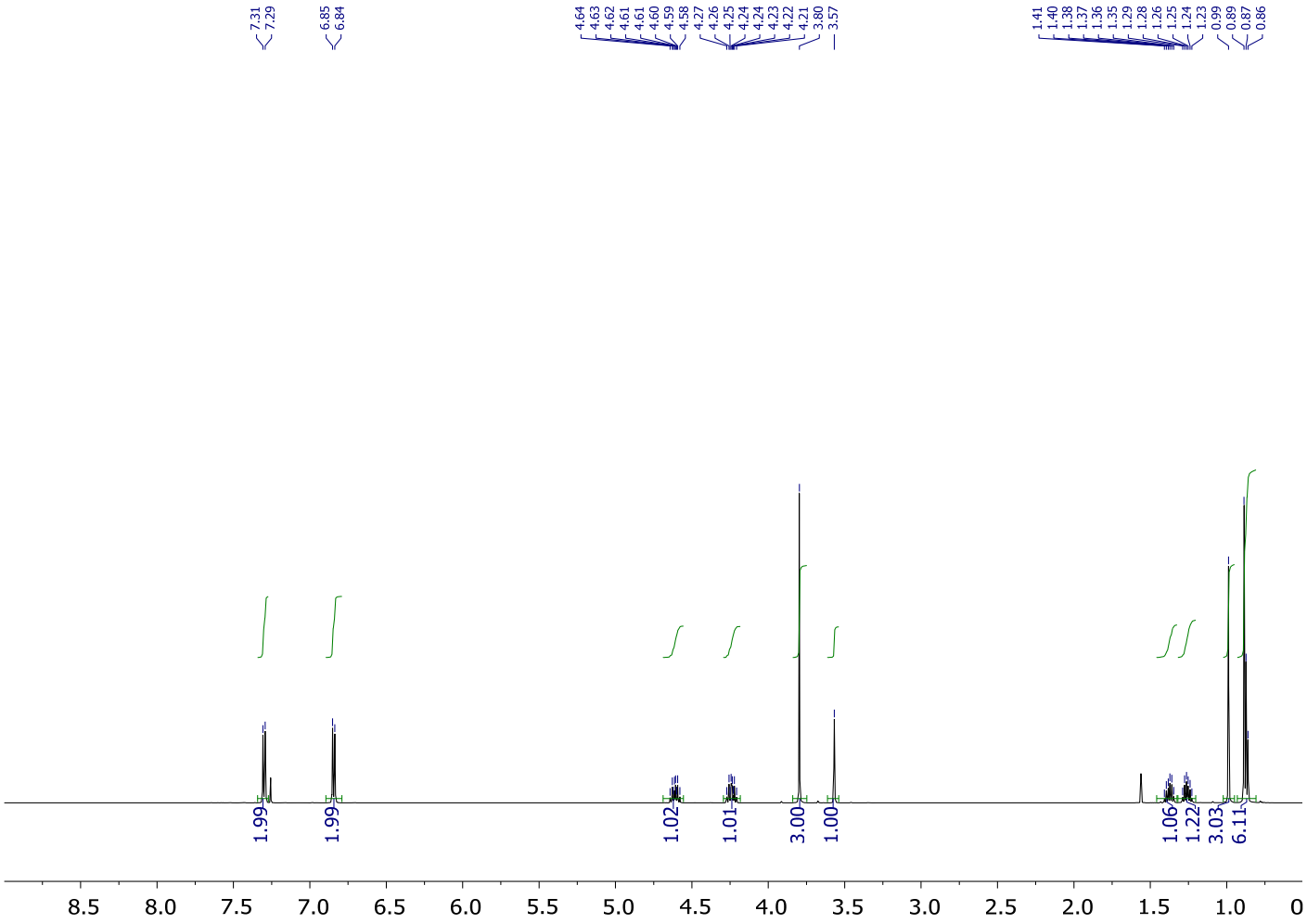

CO2CH2CF3
(R)
N
N
Cl
169.98
160.82
160.18
127.72
125.44
123.60
121.77
119.93
77.24 CDCl3
77.03 CDCl3
76.82 CDCl3
60.96
60.72
60.48
60.23
54.61
38.00
32.75
29.71
23.65
23.61
8.07
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

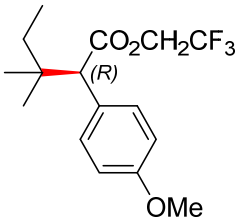

CO2CH2CF3
(R)
CF3
7.58
7.57
7.53
7.52
4.65
4.64
4.63
4.62
4.62
4.61
4.60
4.59
4.31
4.30
4.29
4.28
4.28
4.27
4.26
4.25
3.70
1.43
1.43
1.42
1.40
1.39
1.38
1.37
1.30
1.29
1.27
1.26
1.25
1.24
1.01
0.91
0.90
0.90
0.88
2.03
2.00
1.02
1.03
1.01
1.10
1.21
3.04
6.06
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

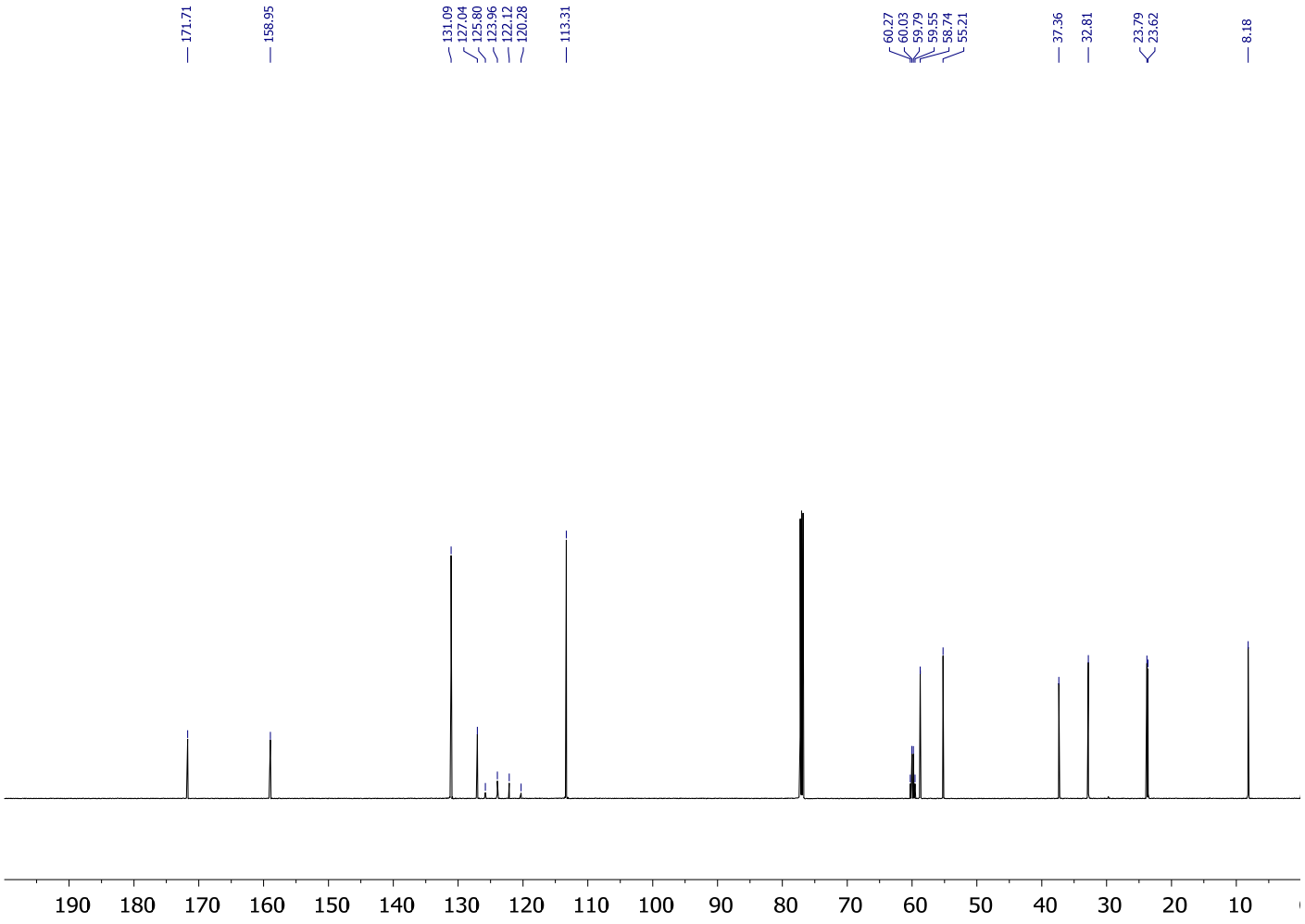

CO2CH2CF3
(R)
CF3

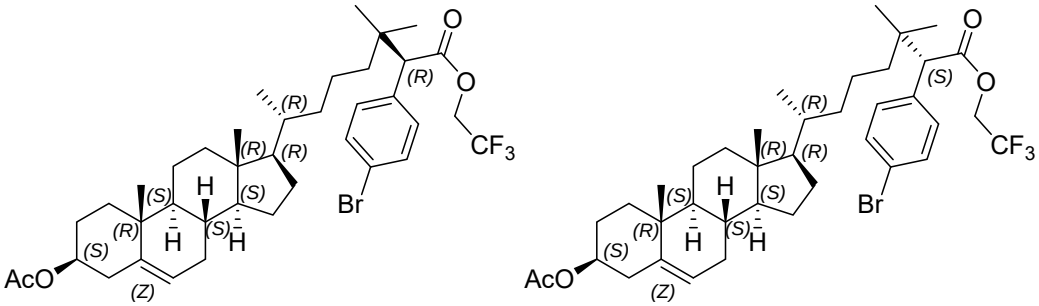

170.94
139.08
130.40
130.10
129.88
129.67
129.45
126.82
125.66
125.02
124.88
124.85
124.83
124.81
123.82
123.22
121.99
121.41
120.15
60.51
60.27
60.03
59.79
59.33
37.72
32.88
23.81
23.65
8.14
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

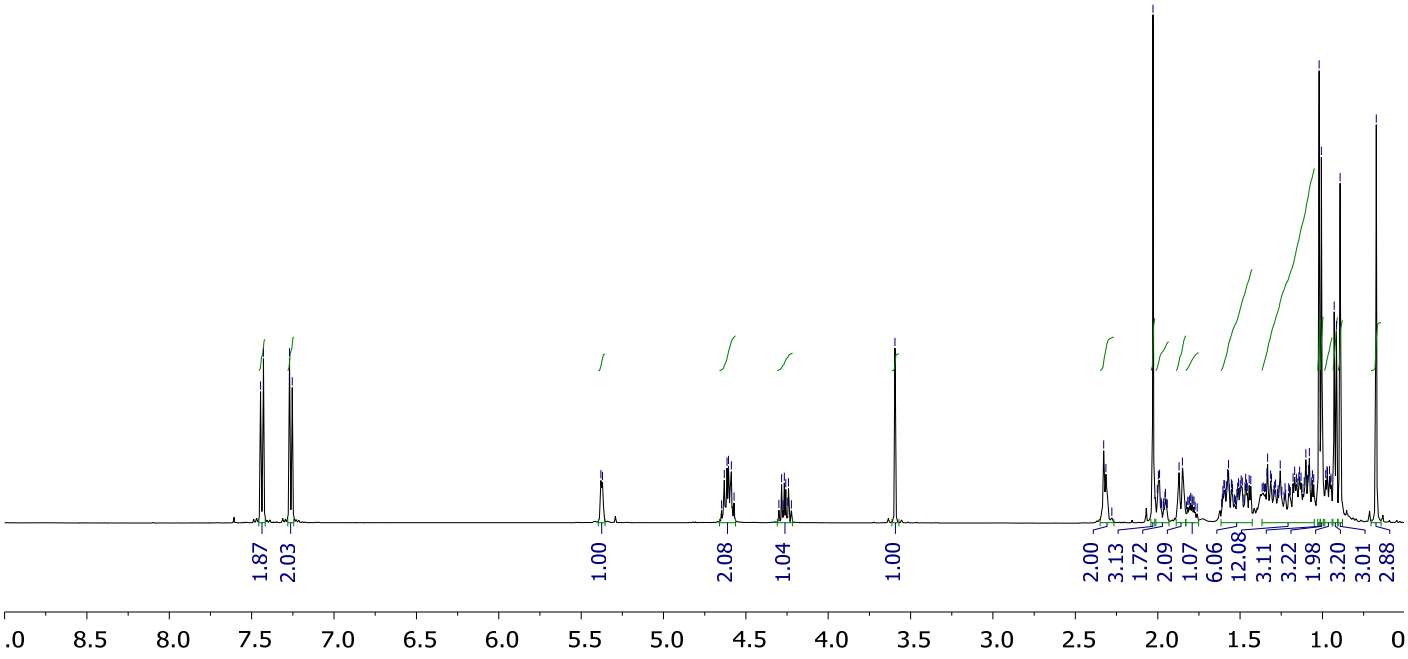

CO2CH2CF3
(R)
OMe

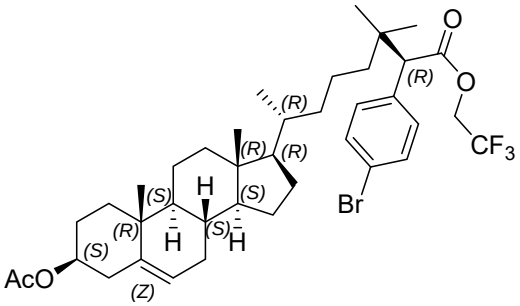

7.31
7.29
6.85
6.84
4.64
4.63
4.62
4.61
4.61
4.60
4.59
4.58
4.27
4.26
4.25
4.24
4.24
4.23
4.22
4.21
3.80
3.57
1.41
1.40
1.38
1.37
1.36
1.35
1.29
1.28
1.26
1.25
1.24
1.23
0.99
0.89
0.87
0.86
1.99
1.99
1.02
1.01
3.00
1.00
1.06
1.22
3.03
6.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

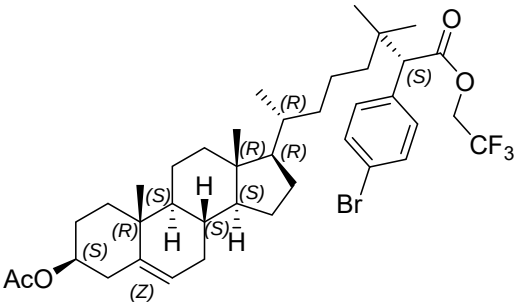

CO2CH2CF3
(R)
OMe


171.71
158.95
131.09
127.04
125.80
123.96
122.12
120.28
113.31
60.27
60.03
59.79
59.55
58.74
55.21
37.36
32.81
23.79
23.62
8.18
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

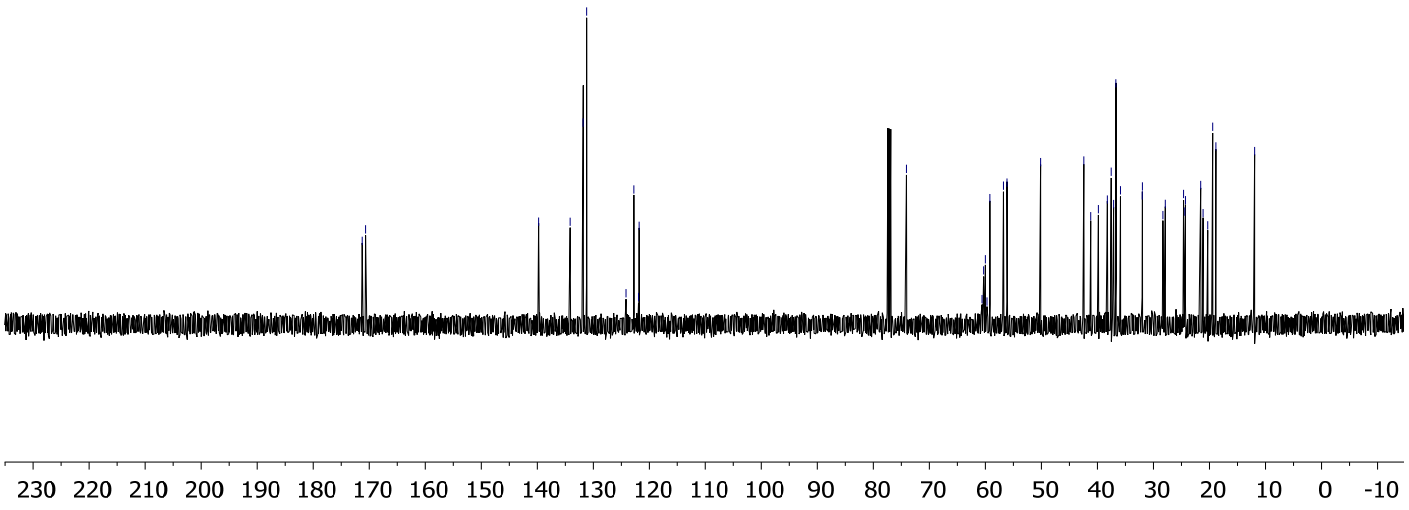

O
O
CF3
Br
AcO
(R)
(S)
H
(Z)

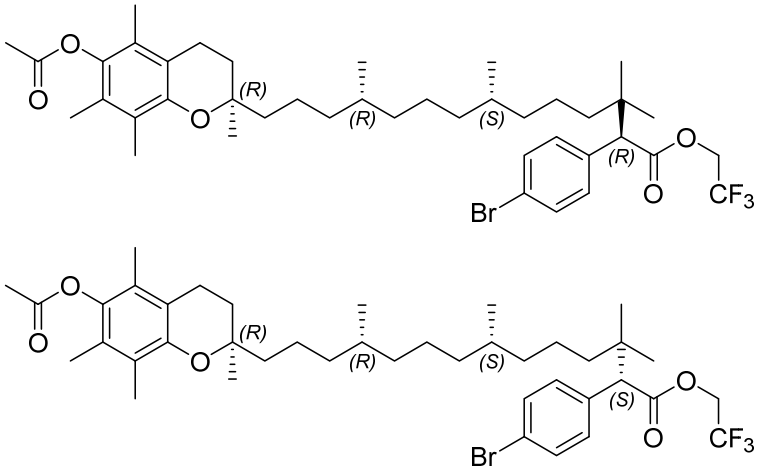

1.87
2.03
1.00
2.08
1.04
1.00
2.00
3.13
1.72
2.09
1.07
6.06
12.08
3.11
3.22
1.98
3.20
3.01
2.88
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0



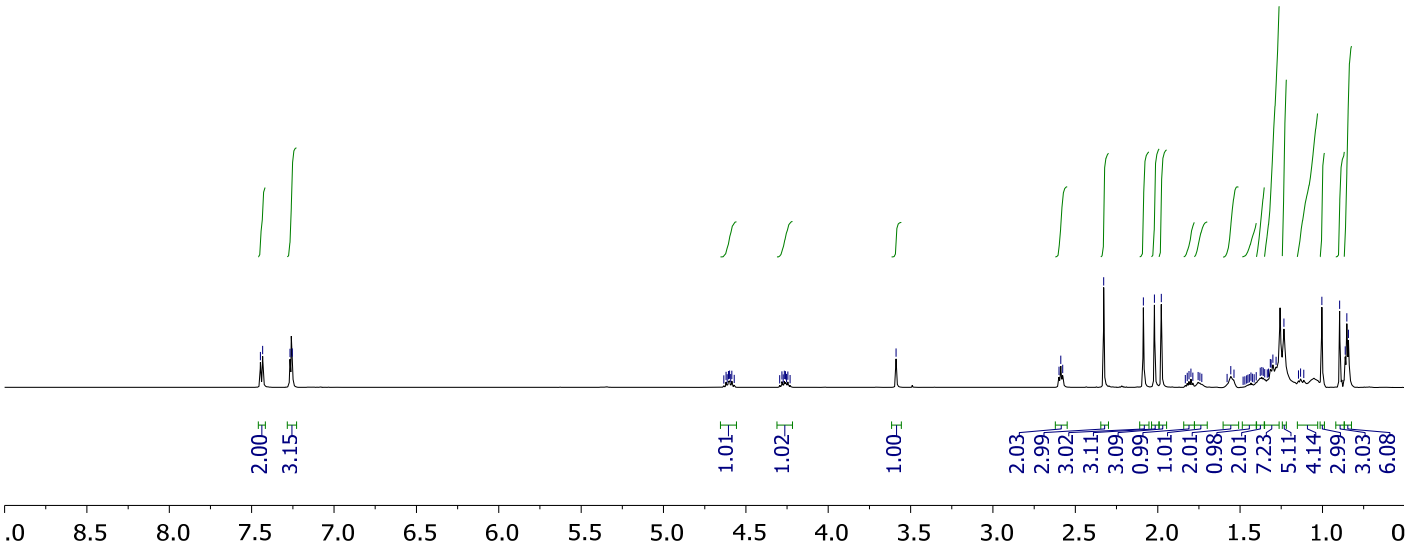


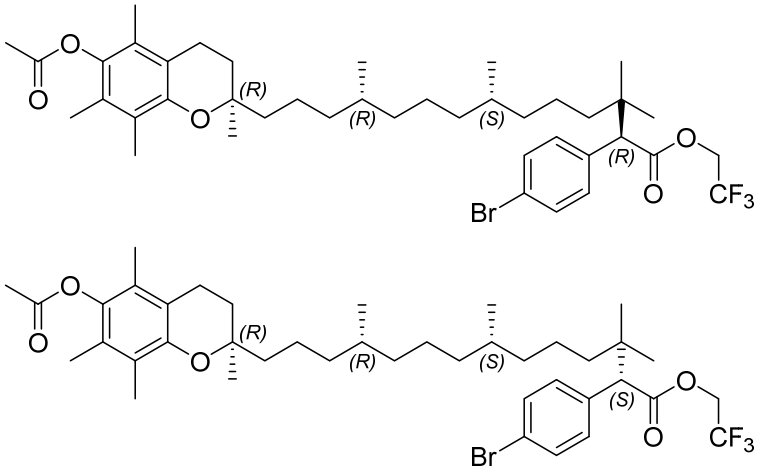
171.25
170.65
139.76
134.14
131.80
131.20
124.15
122.75
121.94
121.81
74.09
60.60
60.31
60.02
59.73
59.21
56.79
56.14
50.14
42.45
41.21
39.85
38.25
37.56
37.13
36.71
35.90
32.01
31.98
28.32
27.90
24.64
24.40
24.30
21.58
21.15
20.33
19.44
18.87
11.96

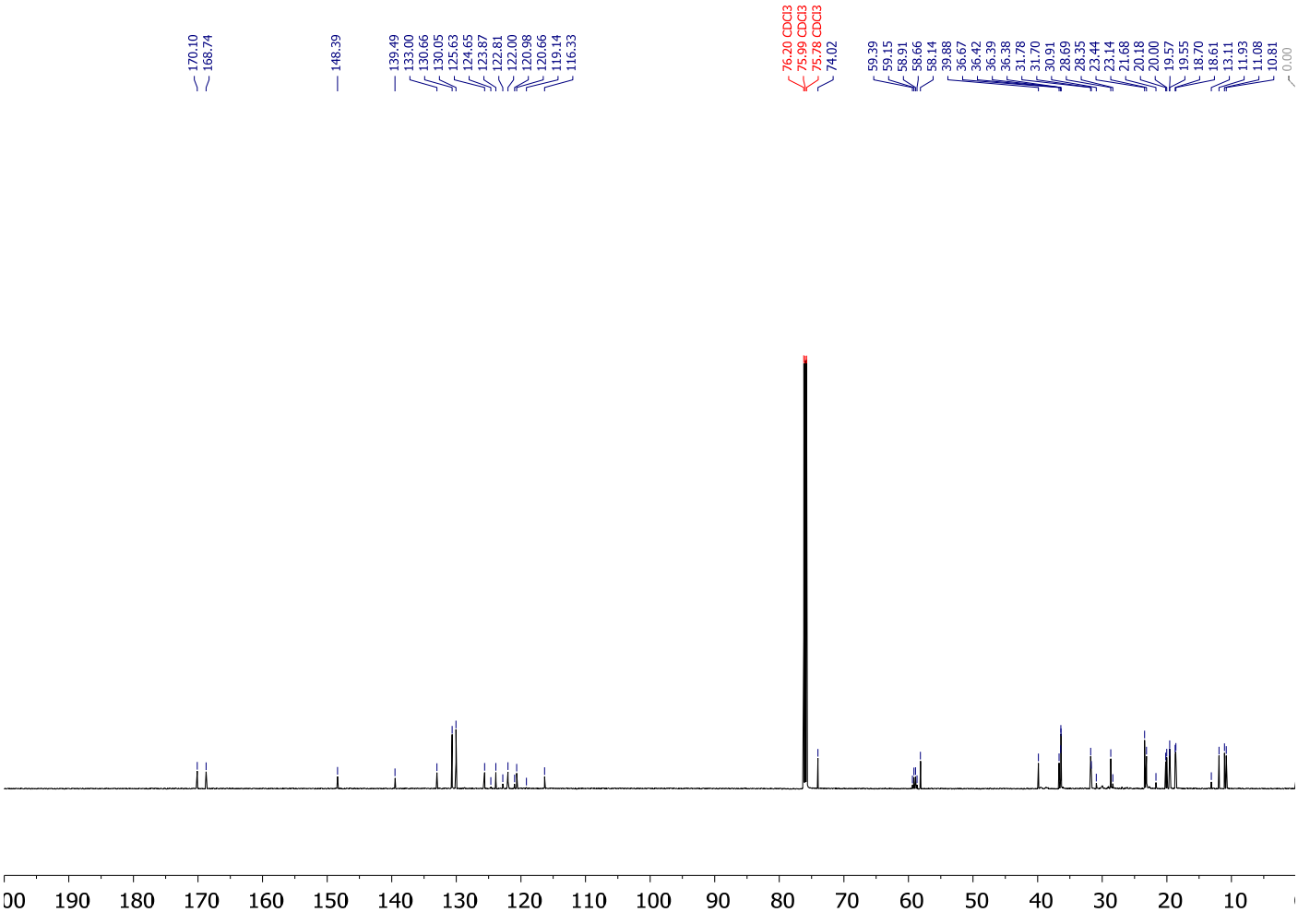


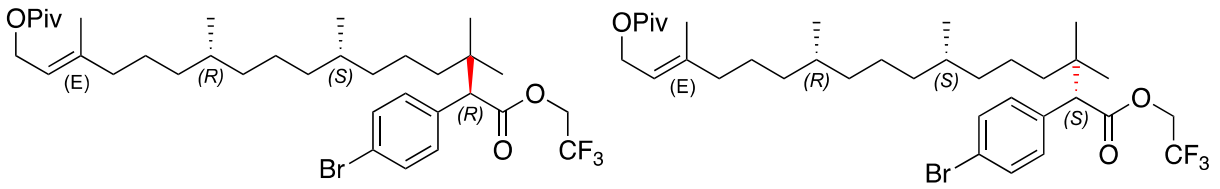

O
O
(R)
O
(R)
(S)
(R)
O
O
CF3
Br
O
O
(R)
O
(R)
(S)
(S)
O
O
CF3
Br

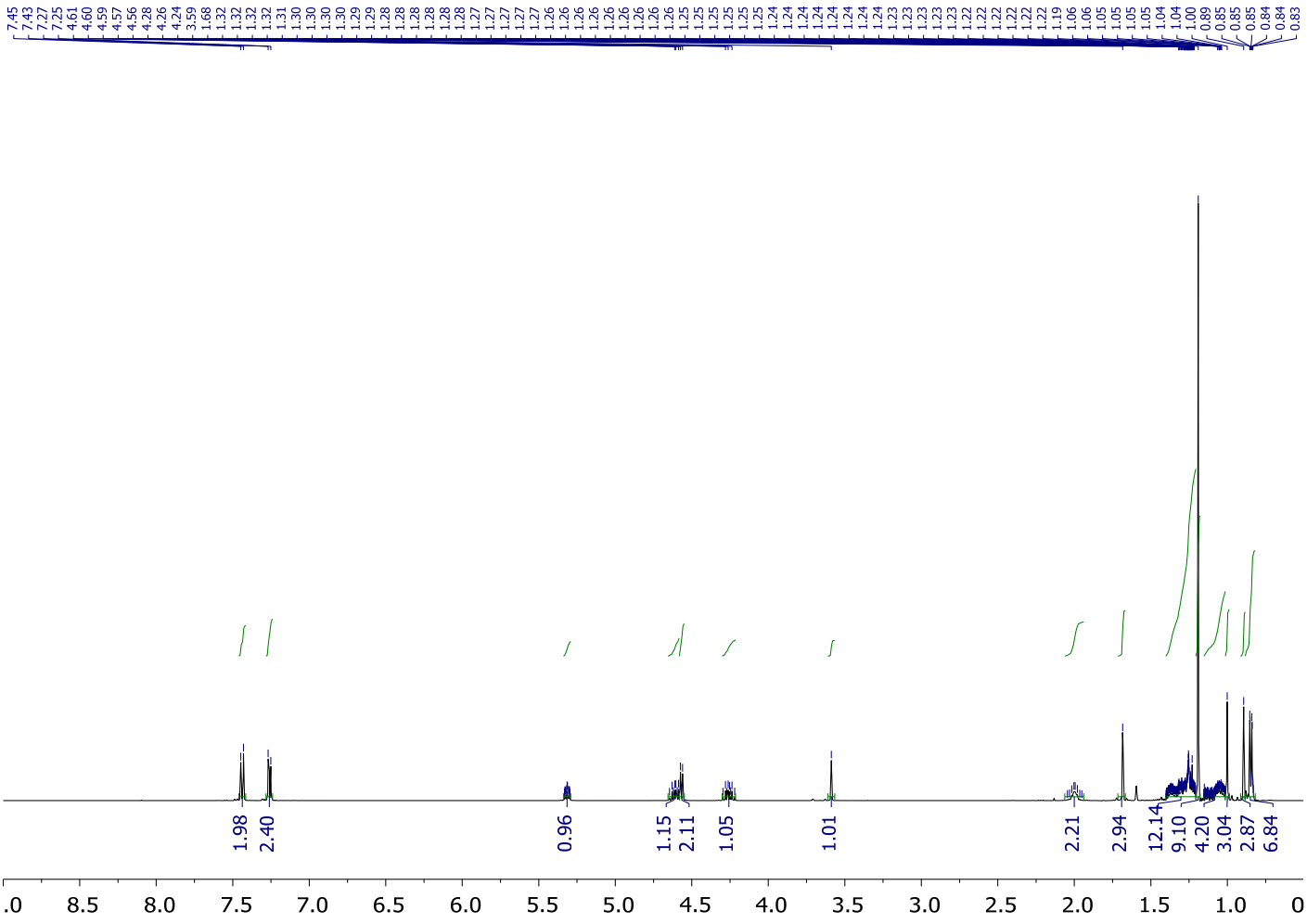

7.45
7.43
7.27
7.25
4.63
4.62
4.61
4.61
4.60
4.59
4.58
4.57
4.29
4.28
4.27
4.27
4.26
4.25
4.25
4.23
3.59
2.60
2.59
2.58
2.33
2.09
2.02
1.98
1.83
1.82
1.81
1.80
1.79
1.75
1.74
1.73
1.58
1.56
1.54
1.48
1.47
1.46
1.45
1.44
1.43
1.42
1.41
1.40
1.38
1.37
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.28
1.23
1.15
1.13
1.11
1.00
0.90
0.86
0.85
0.84

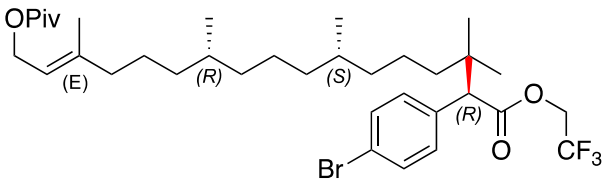

2.00
3.15
1.01
1.02
1.00
2.03
2.99
3.02
3.11
3.09
0.99
1.01
2.01
0.98
2.01
7.23
5.11
4.14
2.99
3.03
6.08
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

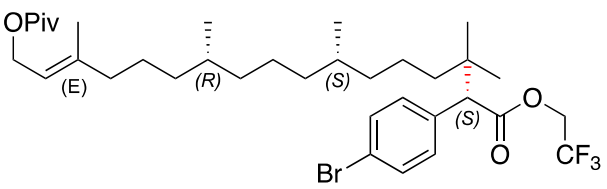

O
O
(R)
O
(R)
(S)
(R)
O
O
CF3
Br
O
O
(R)
O
(R)
(S)
(S)
O
O
CF3
Br


170.10
168.74
148.39
139.49
133.00
130.66
130.05
125.63
124.65
123.87
122.81
122.00
120.98
120.66
119.14
116.33
76.20 CDCl3
75.99 CDCl3
75.78 CDCl3
74.02
59.39
59.15
58.91
58.66
58.14
39.88
36.67
36.42
36.39
36.38
31.78
31.70
30.91
28.69
28.35
23.44
23.14
21.68
20.18
20.00
19.57
19.55
18.70
18.61
13.11
11.93
11.08
10.81
0.00
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

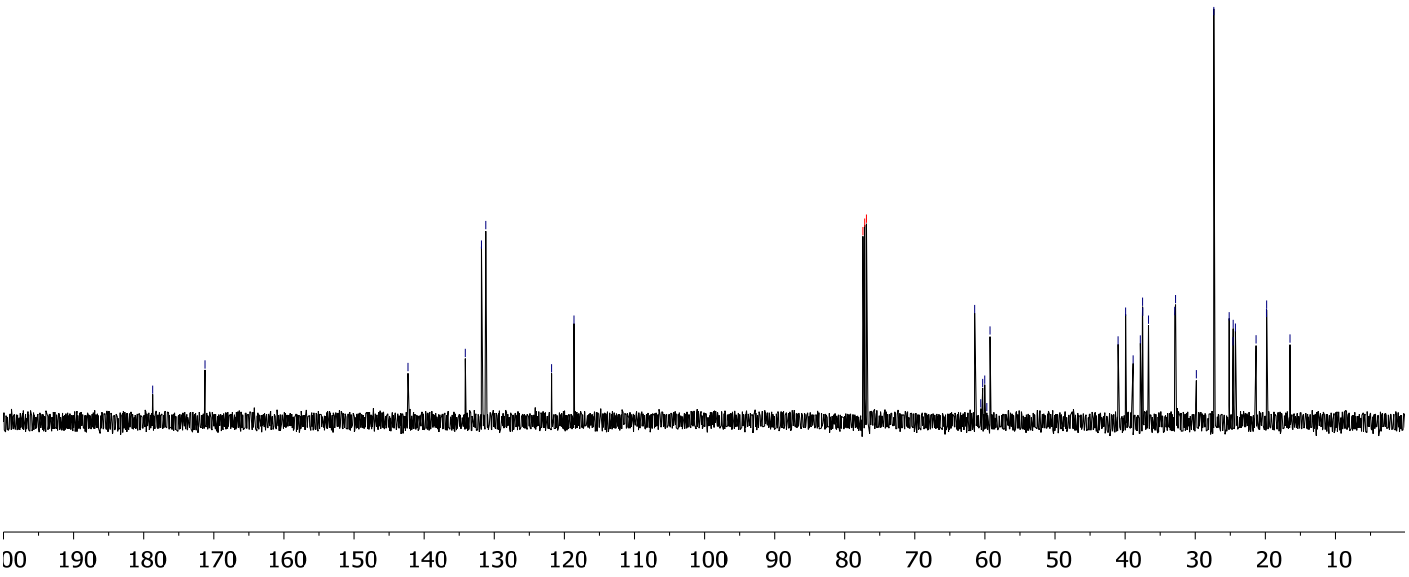

OPiv
(E)
(R)
(S)
(R)
O
O
CF3
Br
OPiv
(E)
(R)
(S)
(S)
O
O
CF3
Br


1.98
2.40
0.96
1.15
2.11
1.05
1.01
2.21
2.94
12.14
9.10
4.20
3.04
2.87
6.84
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

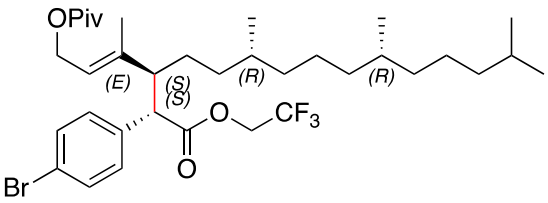


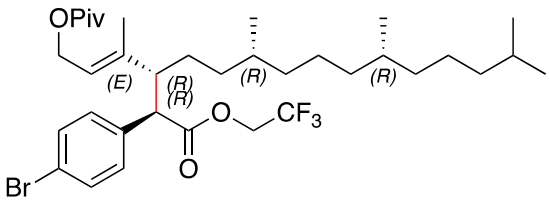


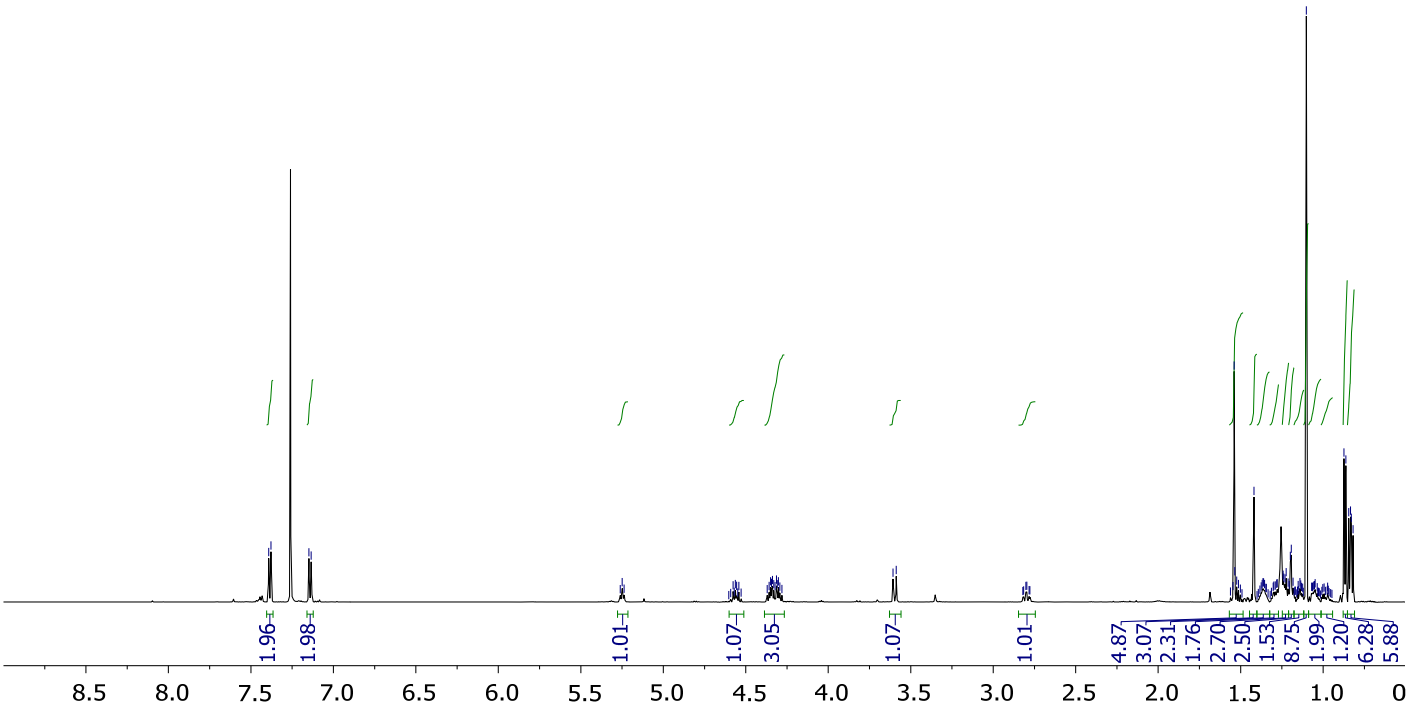
178.73
171.26
142.29
134.13
131.81
131.20
121.82
118.62
77.40 cdcl3
77.15 cdcl3
76.90 cdcl3
61.46
60.61
60.32
60.03
59.73
59.27
41.02
39.94
38.87
37.84
37.53
37.49
36.68
32.93
32.82
29.84
27.35
25.16
24.62
24.60
24.28
21.34
19.86
19.83
16.48

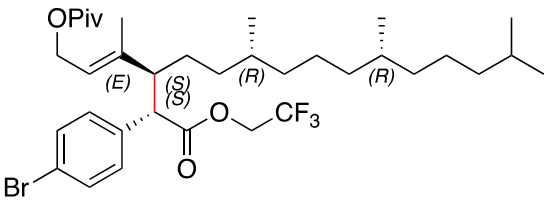


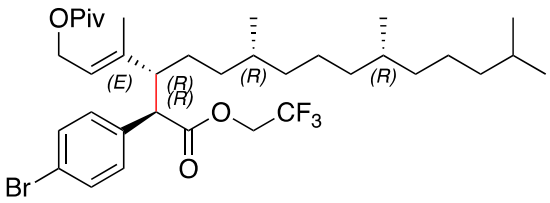
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

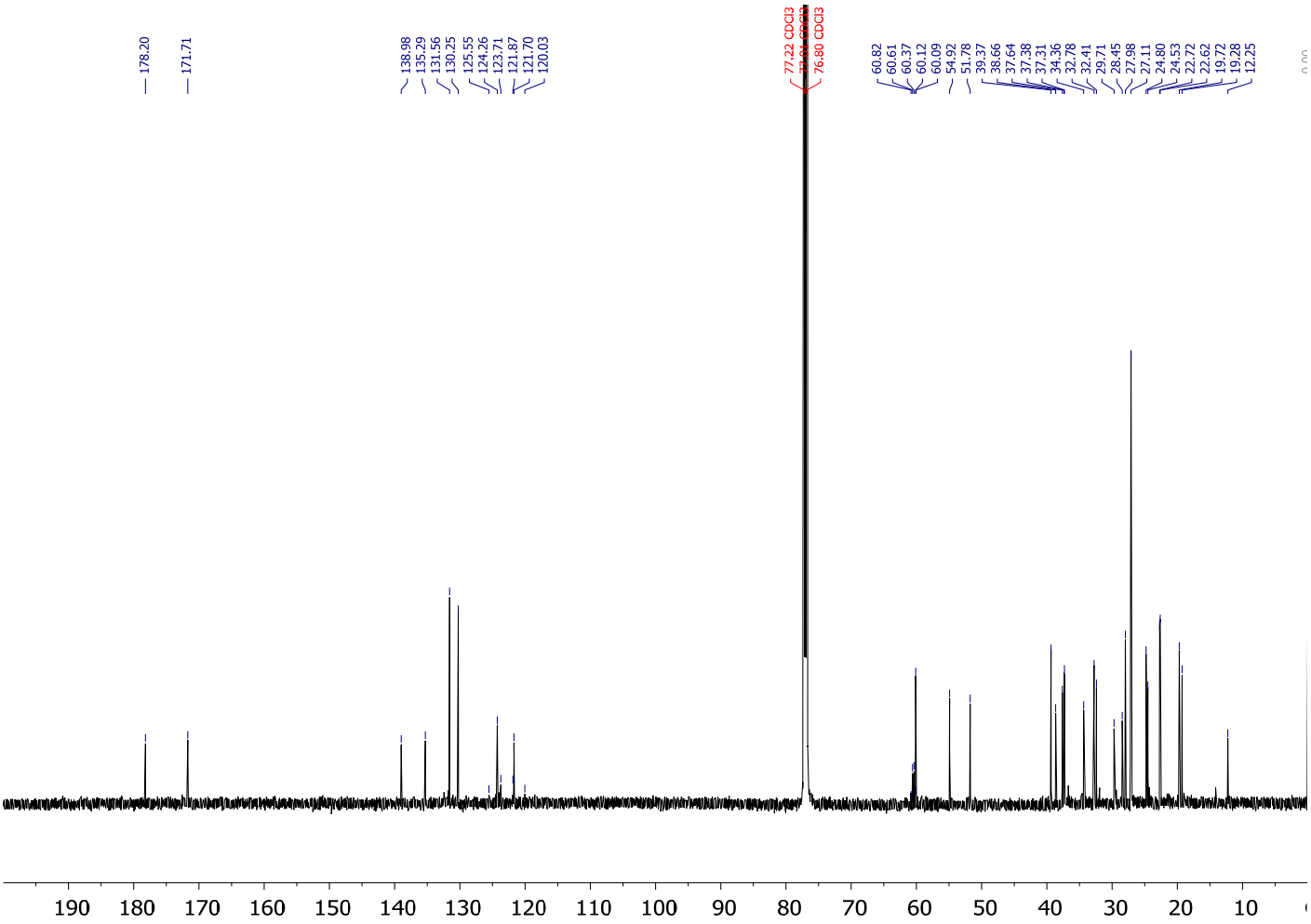

OPiv
(E)
(S)
(S)
(R)
(R)
O
CF3
O
Br

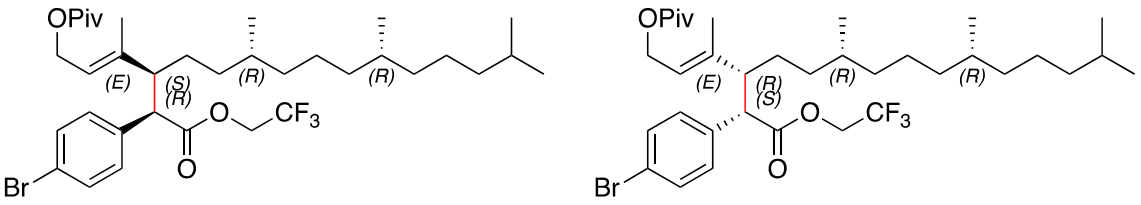

OPiv
(E)
(R)
(R)
(R)
(R)
O
CF3
O
Br

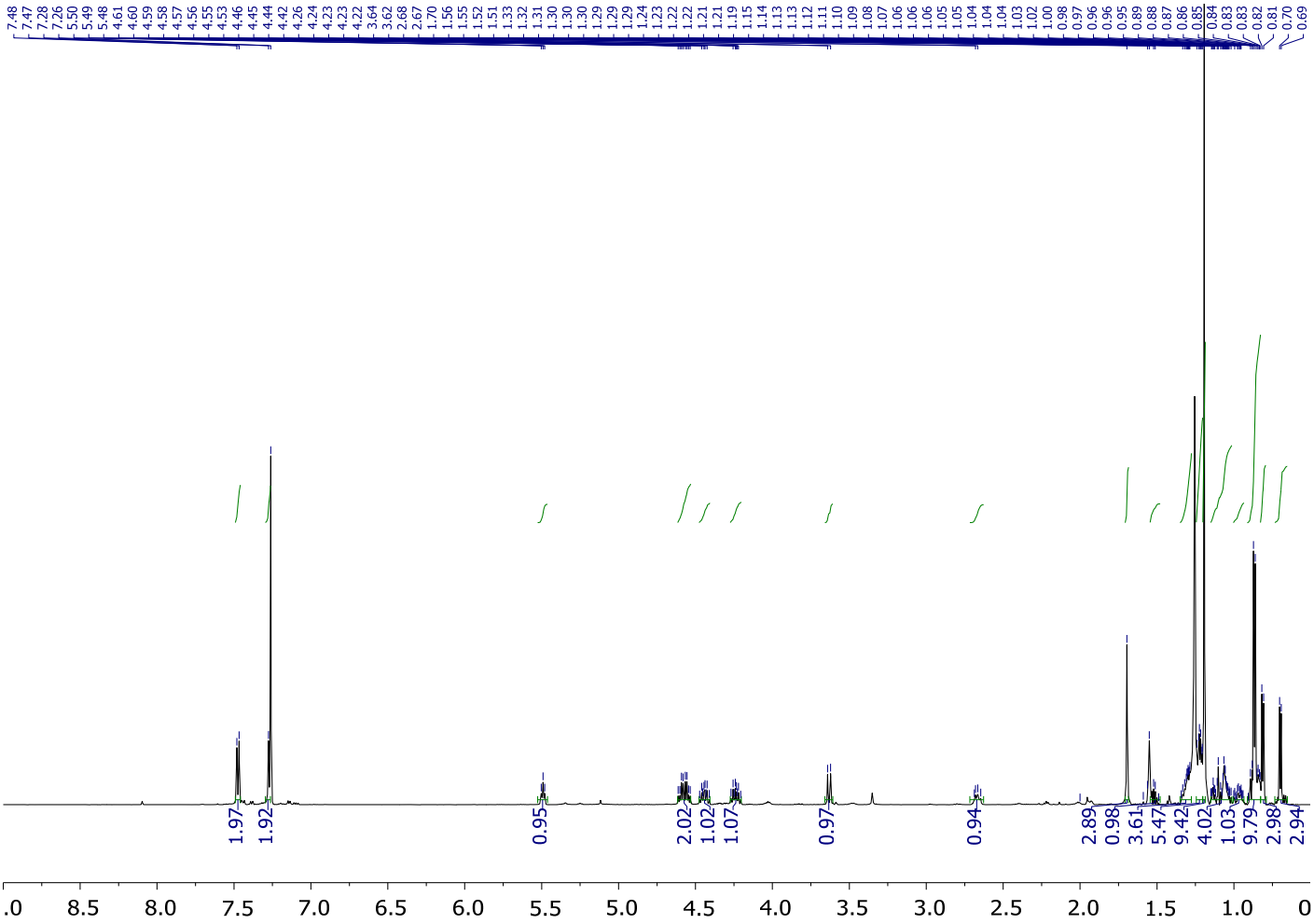

1.96
1.98
1.01
1.07
3.05
1.07
1.01
4.87
3.07
2.31
1.76
2.70
2.50
1.53
8.75
1.99
1.20
6.28
5.88
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

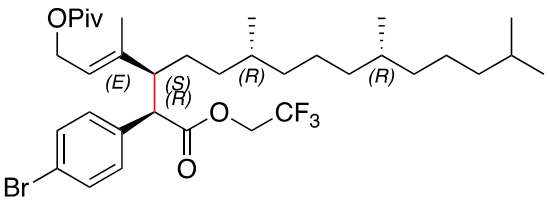

OPiv
(E)
(S)
(S)
(R)
(R)
O
CF3
O
Br

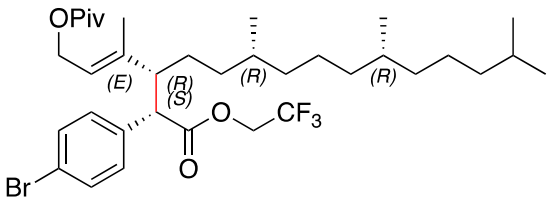

OPiv
(E)
(R)
(R)
(R)
(R)
O
CF3
O
Br

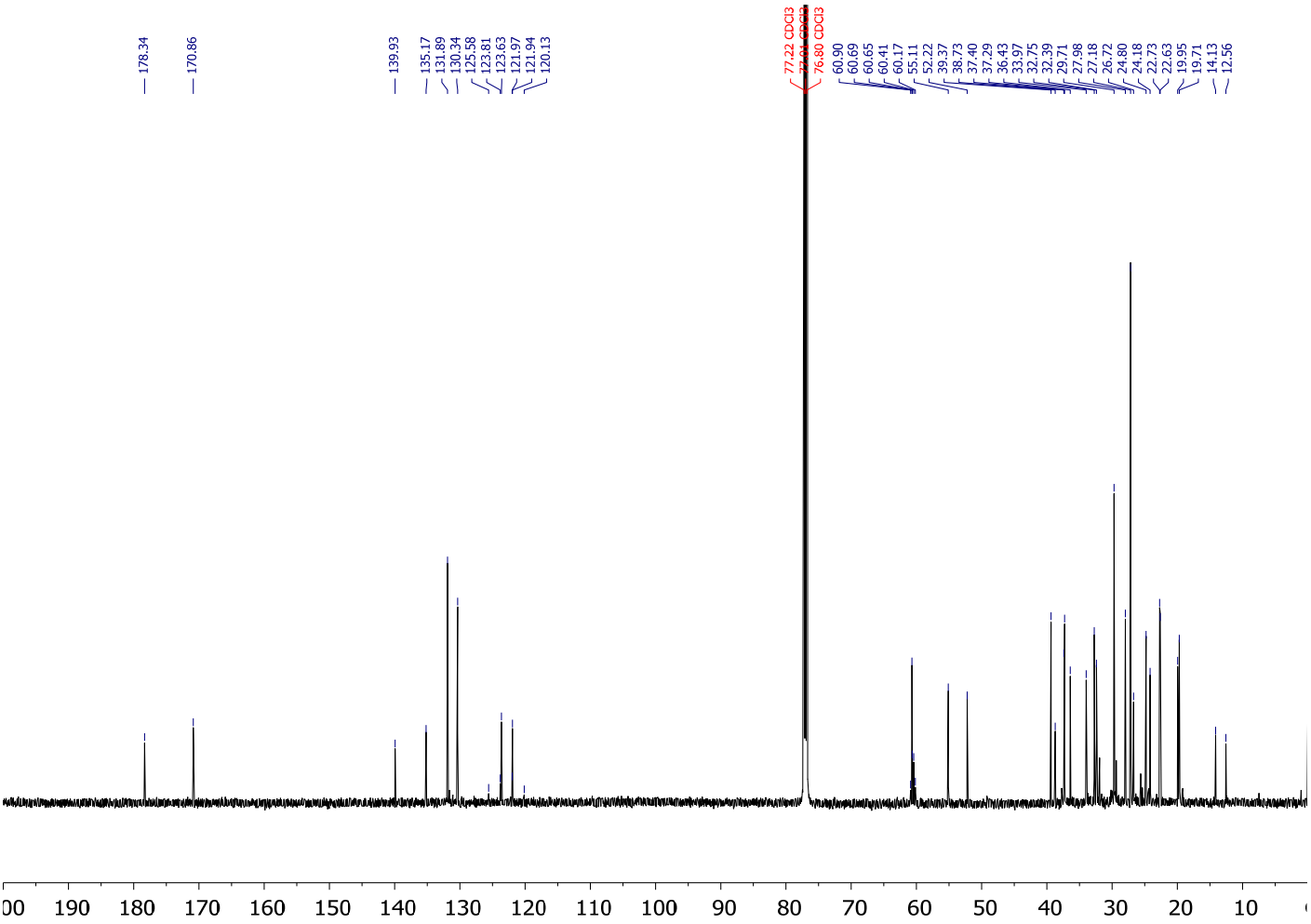

178.20
171.71
138.98
135.29
131.56
130.25
125.55
124.26
123.71
121.87
121.70
120.03
77.22 CDCl3
76.80 CDCl3
60.82
60.61
60.37
60.12
60.09
54.92
51.78
39.37
38.66
37.64
37.38
37.31
34.36
32.78
32.41
29.71
28.45
27.98
27.11
24.80
24.53
22.72
22.62
19.72
19.28
12.25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

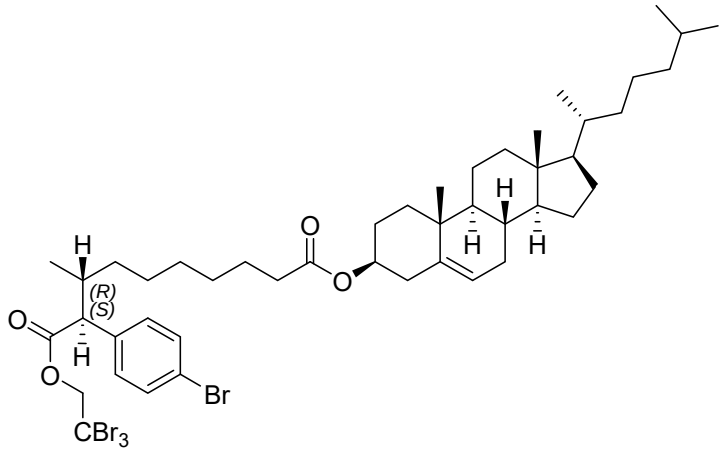

OPiv
(E)
(S)
(R)
(R)
(R)
O
CF3
O
Br
OPiv
(E)
(R)
(S)
(R)
(R)
(R)
O
CF3
O
Br


7.48 7.47 7.28 7.26 5.50 5.49 5.48 4.61 4.60 4.59 4.58 4.57 4.56 4.55 4.53 4.46 4.45 4.44 4.42 4.26 4.24 4.23 4.23 4.22 3.64 3.62 2.68 2.67 1.70 1.56 1.55 1.52 1.51 1.33 1.32 1.31 1.30 1.30 1.30 1.29 1.29 1.29 1.24 1.23 1.22 1.22 1.21 1.21 1.19 1.15 1.14 1.13 1.13 1.12 1.11 1.10 1.09 1.08 1.07 1.06 1.06 1.06 1.05 1.05 1.04 1.04 1.04 1.03 1.02 1.00 0.98 0.97 0.96 0.96 0.95 0.89 0.88 0.87 0.86 0.85 0.84 0.83 0.83 0.82 0.81 0.70 0.69
1.97 1.92 0.95 2.02 1.02 1.07 0.97 0.94 2.89 0.98 3.61 5.47 9.42 4.02 1.03 9.79 2.98 2.94
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

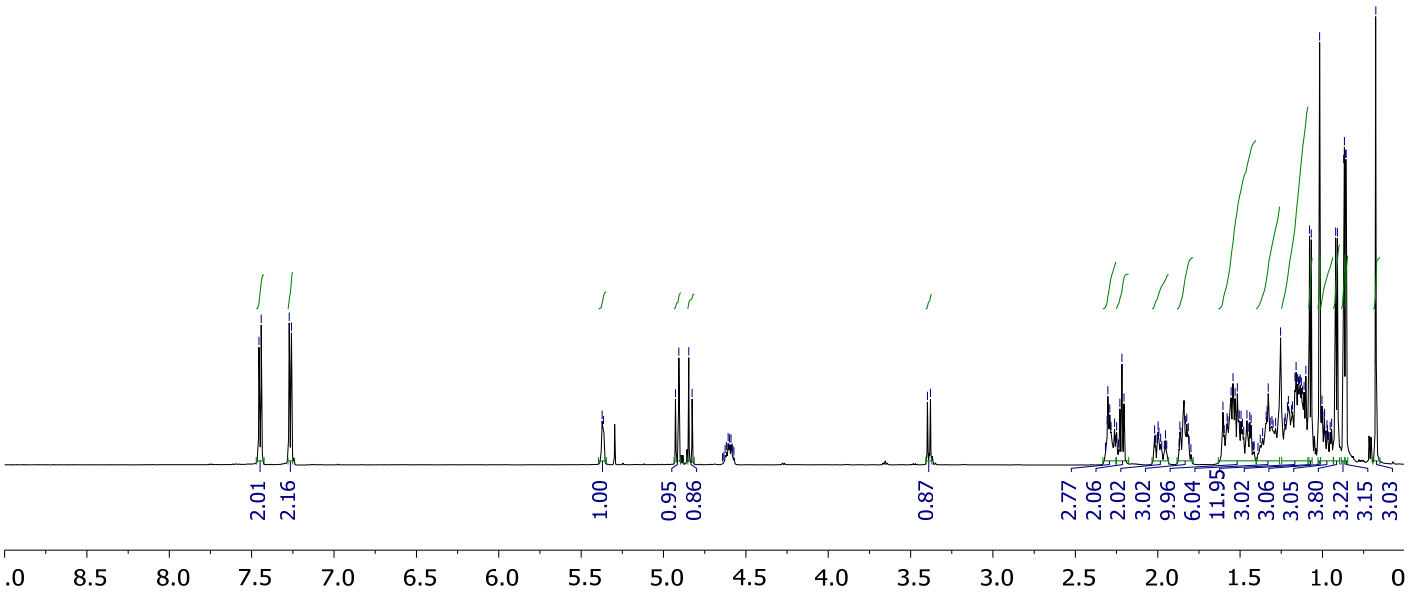

OPiv
(E)
(S)
(R)
(R)
(R)
O
CF3
O
Br

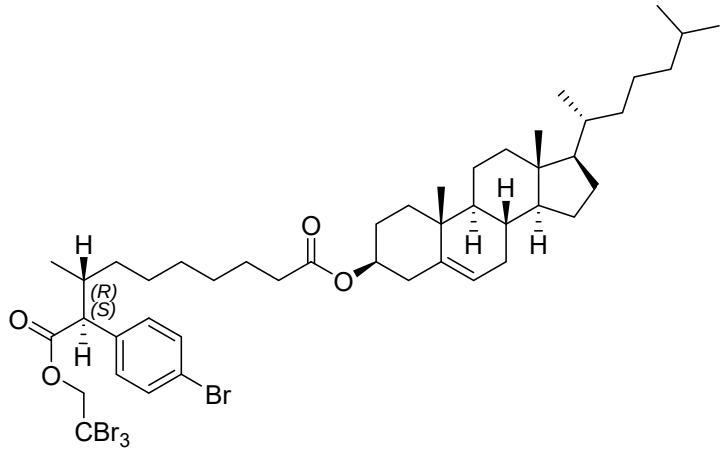

OPiv
(E)
(R)
(S)
(R)
(R)
O
CF3
O
Br


178.34
170.86
139.93
135.17
131.89
130.34
125.58
123.81
123.63
121.97
121.94
120.13
77.22 CDCl3
76.80 CDCl3
60.90
60.69
60.65
60.41
60.17
55.11
52.22
39.37
38.73
37.40
37.29
36.43
33.97
32.75
32.39
29.71
27.98
27.18
26.72
24.80
24.18
22.73
22.63
19.95
19.71
14.13
12.56
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

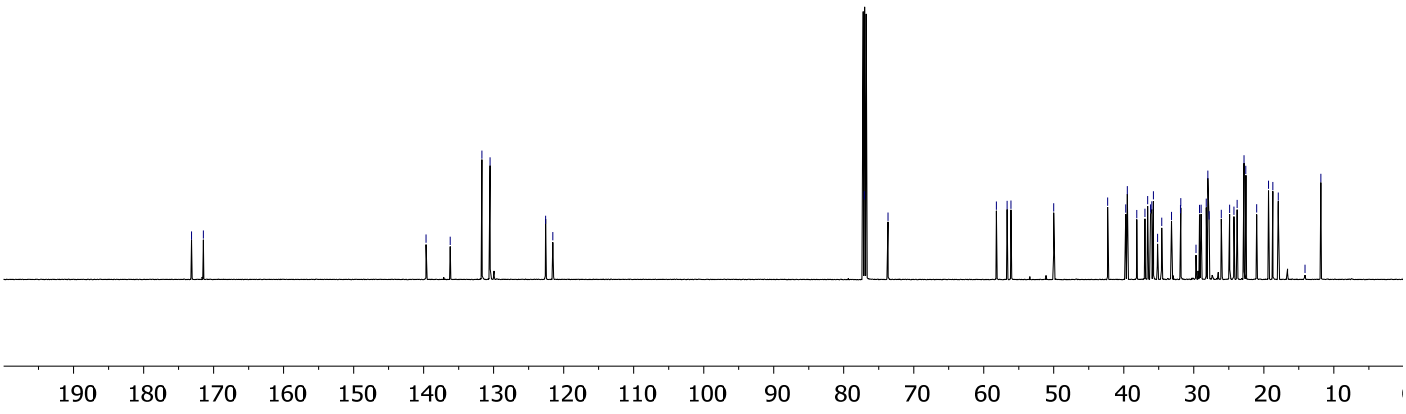

H
O
O
H
H
H
(R)
(S)
O
H
O
Br
CBr3

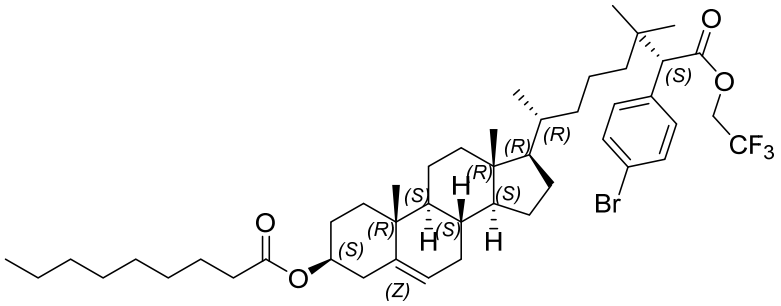

7.46 7.44 7.27 7.26 5.37 5.36 4.93 4.91 4.85 4.83 3.40 3.38 2.31 2.30 2.29 2.28 2.26 2.25 2.23 2.22 2.20 2.02 2.00 1.99 1.87 1.86 1.83 1.82 1.81 1.60 1.60 1.58 1.57 1.55 1.54 1.53 1.52 1.51 1.49 1.49 1.48 1.46 1.45 1.44 1.43 1.34 1.34 1.33 1.32 1.31 1.30 1.28 1.25 1.23 1.23 1.21 1.21 1.19 1.18 1.17 1.16 1.15 1.15 1.14 1.14 1.13 1.12 1.11 1.10 1.08 1.07 1.02 1.01 1.00 0.99 0.99 0.97 0.97 0.95 0.94 0.92 0.91 0.87 0.87 0.86 0.86 0.68

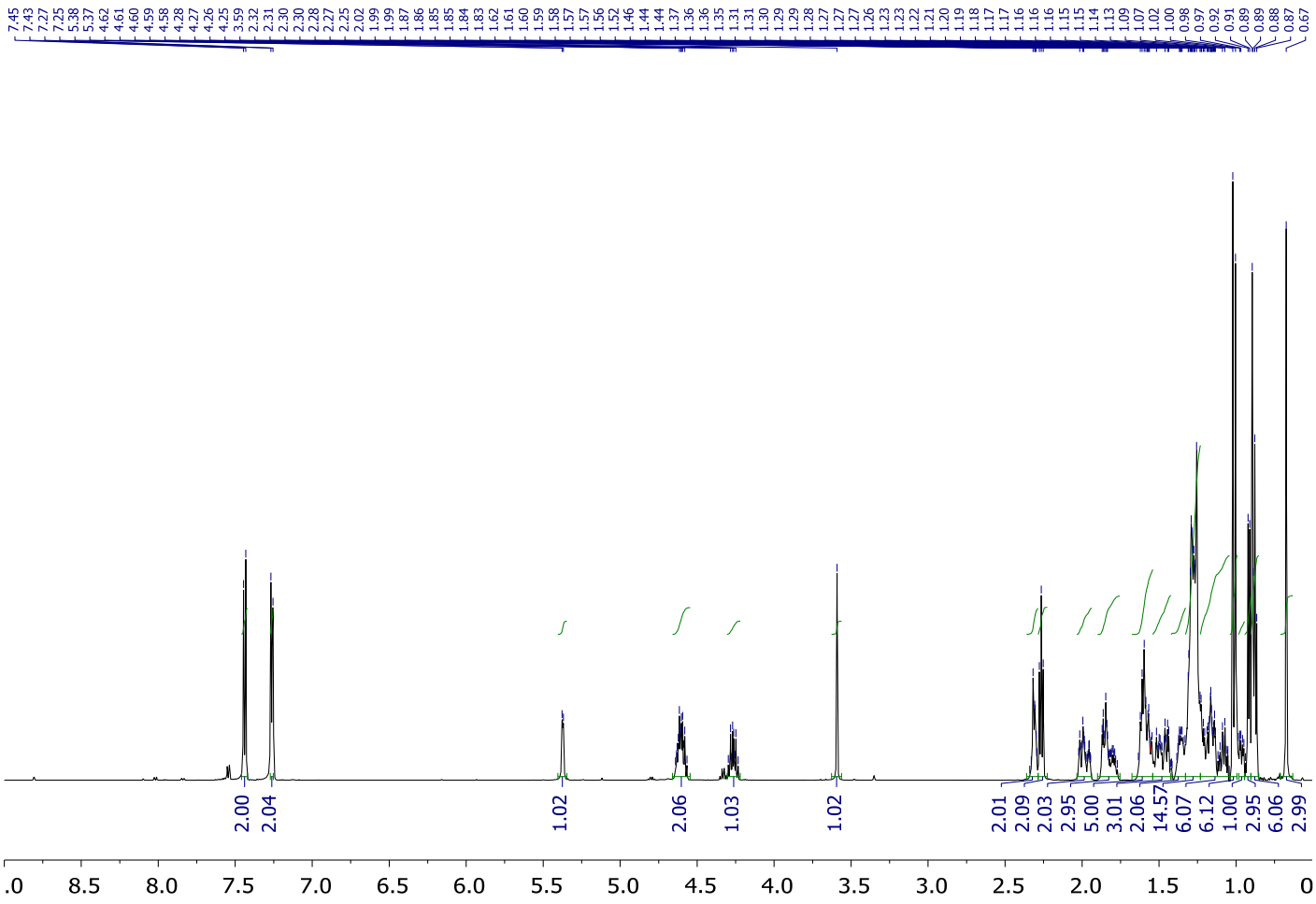

2.01 2.16 1.00 0.95 0.86 0.87 2.77 2.06 2.02 3.02 9.96 6.04 11.95 3.02 3.06 3.05 3.80 3.22 3.15 3.03
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

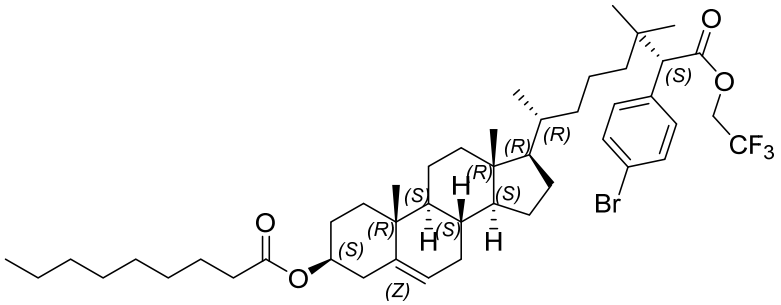

H
O
O
H
H
H
(R)
(S)
O
H
O
Br
CBr3

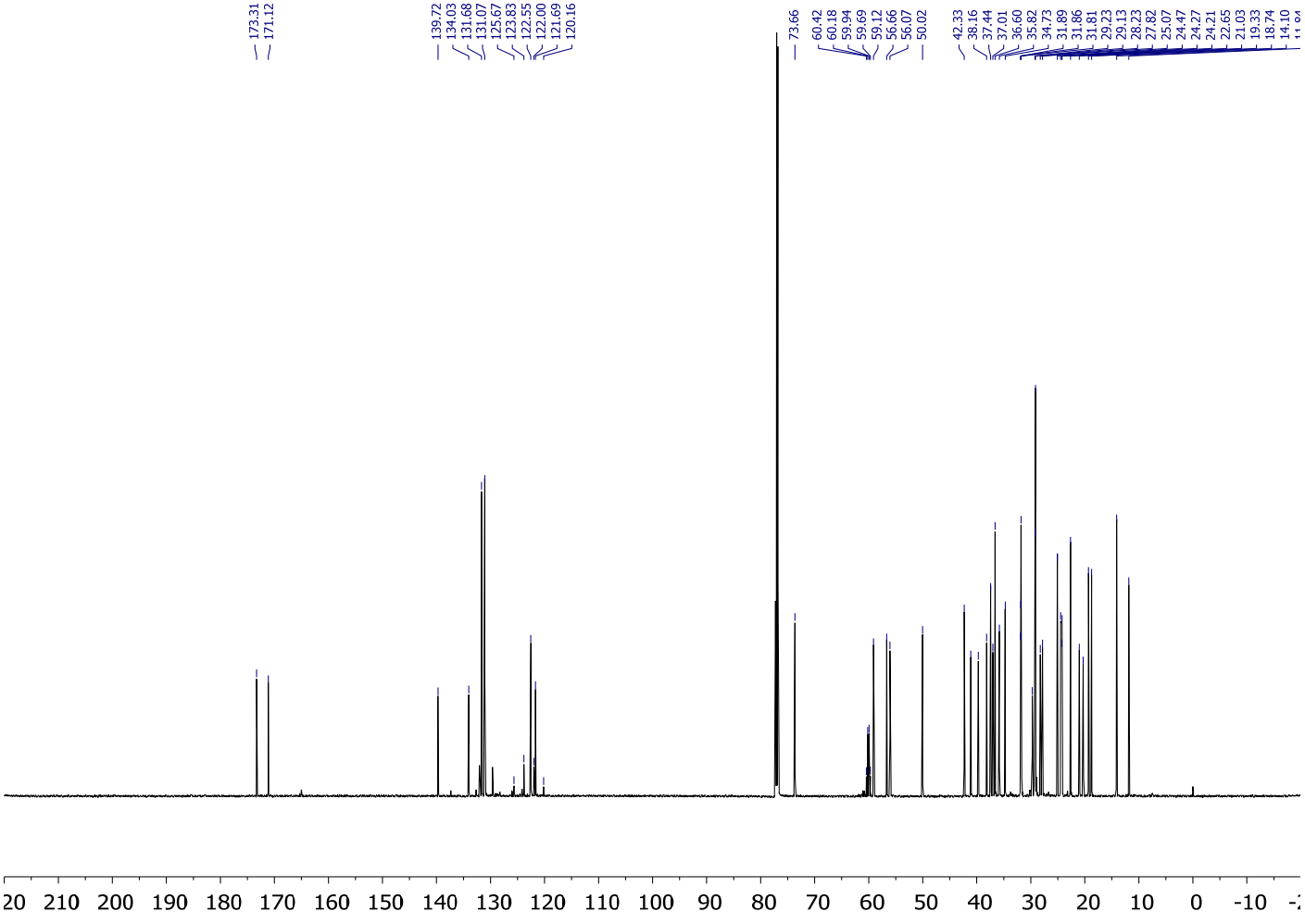

173.15
171.45
139.66
136.20
131.68
130.52
122.59
121.54
77.06
73.68
58.19
56.67
56.11
50.00
42.30
39.71
39.50
38.15
36.98
36.58
36.17
36.00
35.78
35.18
34.58
33.19
31.89
31.85
29.69
29.19
28.95
28.22
28.00
27.80
26.06
24.88
24.27
23.82
22.82
22.56
21.02
19.33
18.71
17.93
14.12
11.85


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


O
O
(S)
O
CF3
(R)
(R)
(R)
H
(S)
(S)
(S)
(R)
(S)
H
H
Br
O
(Z)

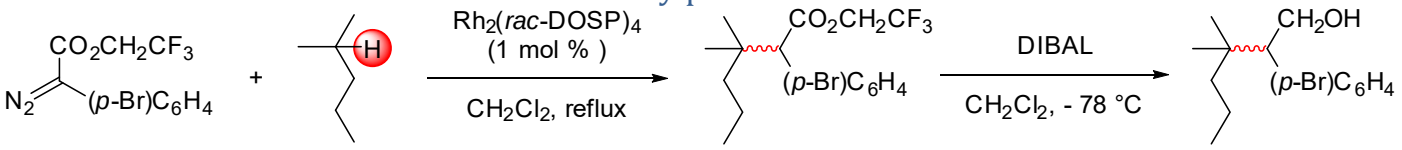

7.45 7.43 7.27 7.25 5.38 5.37 4.62 4.61 4.60 4.59 4.58 4.28 4.27 4.26 4.25 3.59 2.32 2.31 2.30 2.30 2.28 2.27 2.25 2.02 1.99 1.99 1.87 1.86 1.85 1.85 1.84 1.83 1.62 1.61 1.60 1.59 1.58 1.57 1.57 1.56 1.52 1.46 1.44 1.44 1.37 1.36 1.36 1.35 1.31 1.31 1.30 1.29 1.29 1.28 1.27 1.27 1.27 1.26 1.23 1.23 1.22 1.21 1.20 1.19 1.18 1.17 1.17 1.16 1.16 1.16 1.15 1.15 1.14 1.13 1.09 1.07 1.02 1.00 1.00 0.98 0.97 0.92 0.91 0.89 0.89 0.88 0.87 0.67
2.00 2.04 1.02 2.06 1.03 1.02 2.01 2.09 2.03 2.95 5.00 3.01 2.06 14.57 6.07 6.12 1.00 2.95 6.06 2.99
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

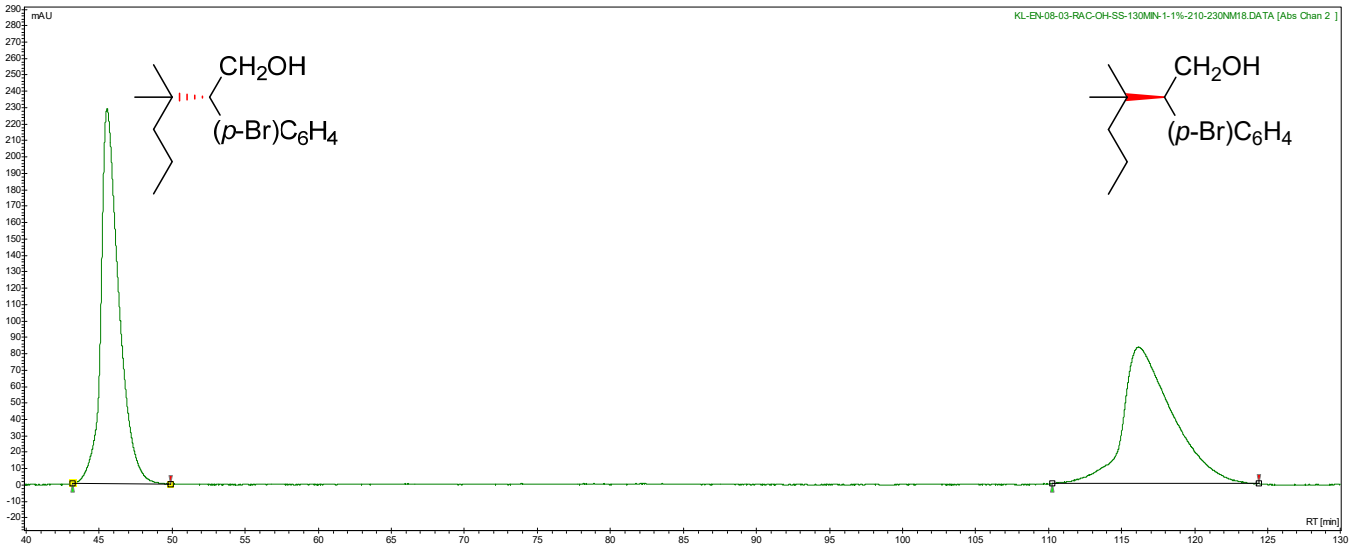

O
O
(S)
O
CF3
(R)
(R)
(R)
H
(S)
(S)
(S)
(R)
(S)
H
H
Br
O
O
(Z)


173.31
171.12
139.72
134.03
131.68
131.07
125.67
123.83
122.55
122.00
121.69
120.16
73.66
60.42
60.18
59.94
59.69
59.12
56.66
56.07
50.02
42.33
38.16
37.44
37.01
36.60
35.82
34.73
31.89
31.86
31.81
29.23
29.13
28.23
27.82
25.07
24.47
24.27
24.21
22.65
21.03
19.33
18.74
14.10
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

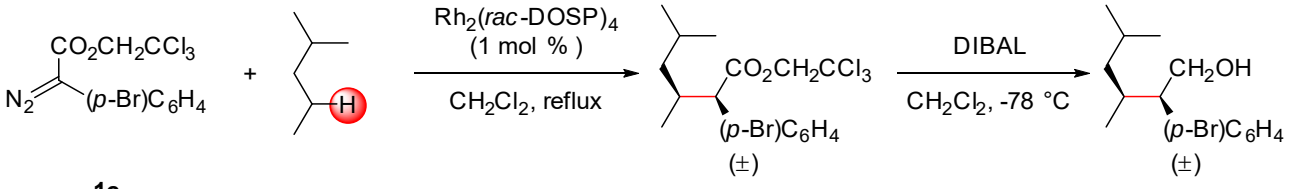
9 - HPLC

9.1 C–H Functionalization Products of 2-Methylpentane

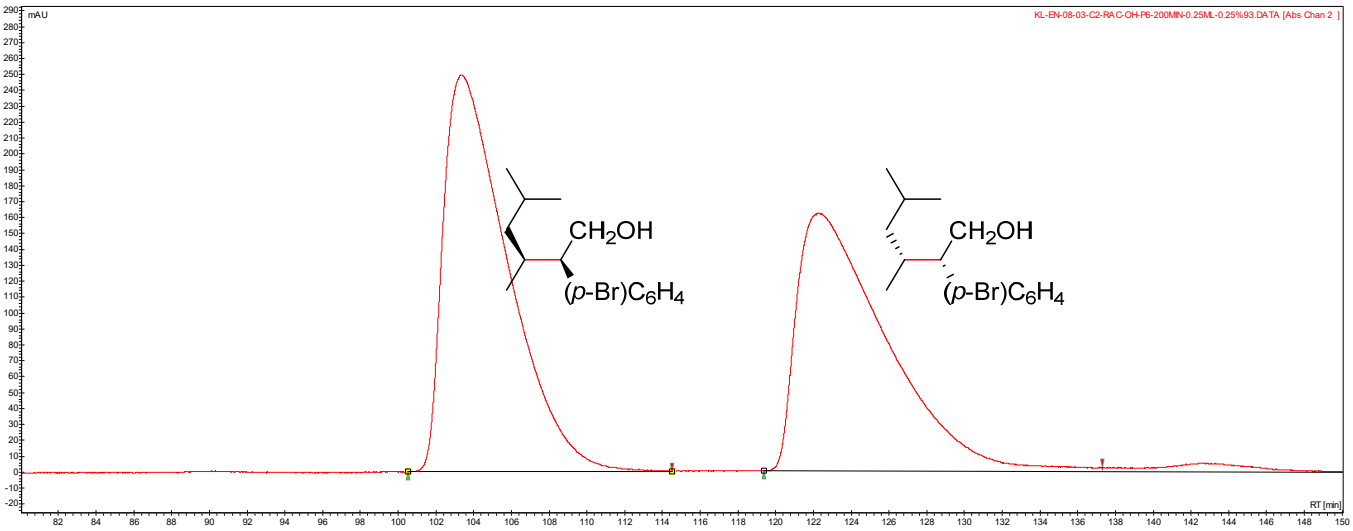




#	Time [Min]	Area % [%]
1	45.54	49.859
2	116.15	50.141

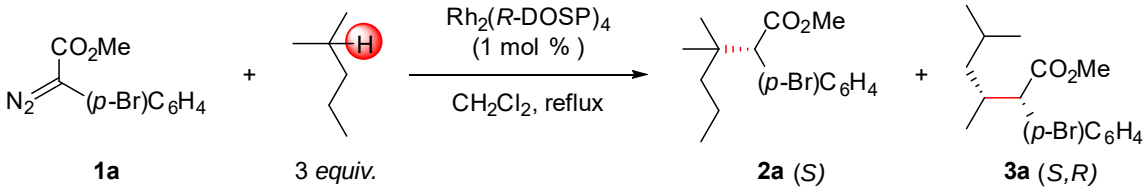


1c 3 *equiv.* **3b**

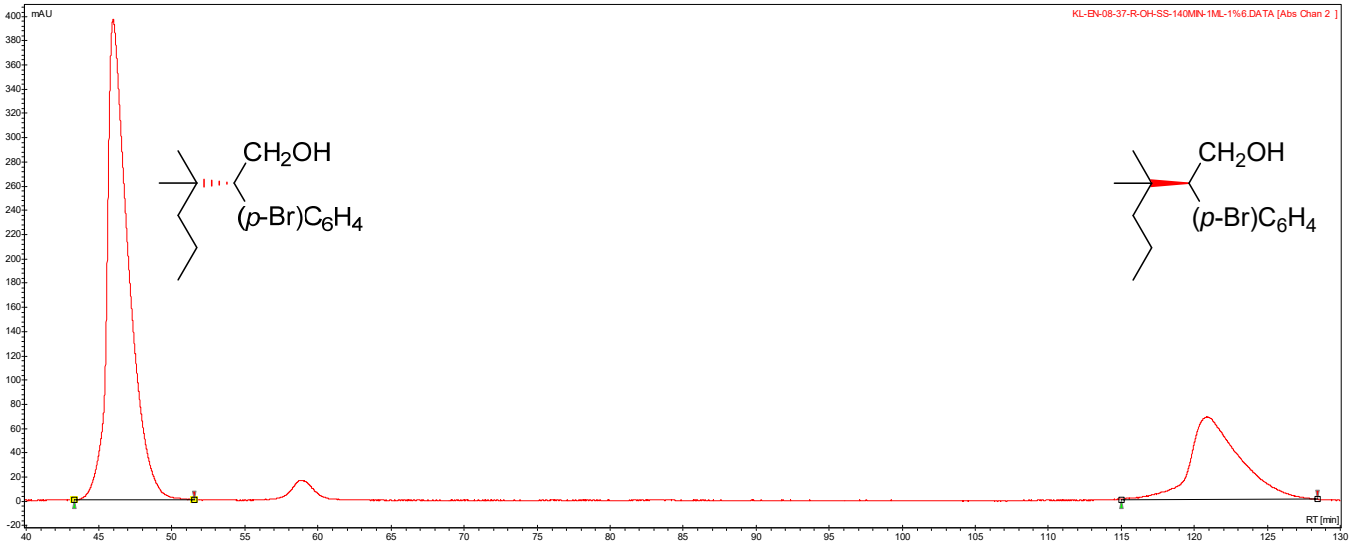


#	Time [Min]	Area % [%]
1	103.34	52.556
2	122.27	47.444

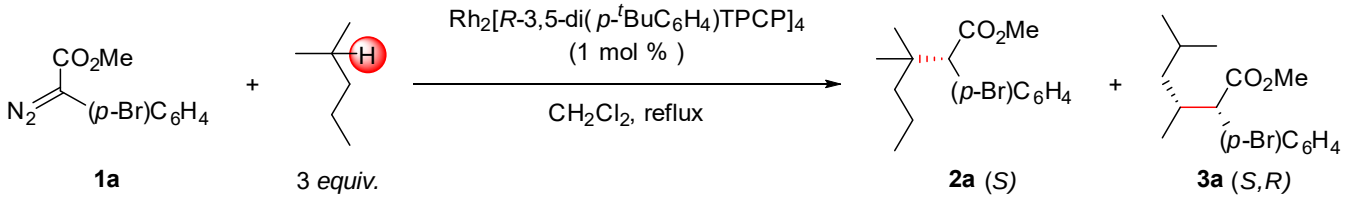
9.2 Catalyst and Diazo Screen for the Functionalization of 2-Methylpentane



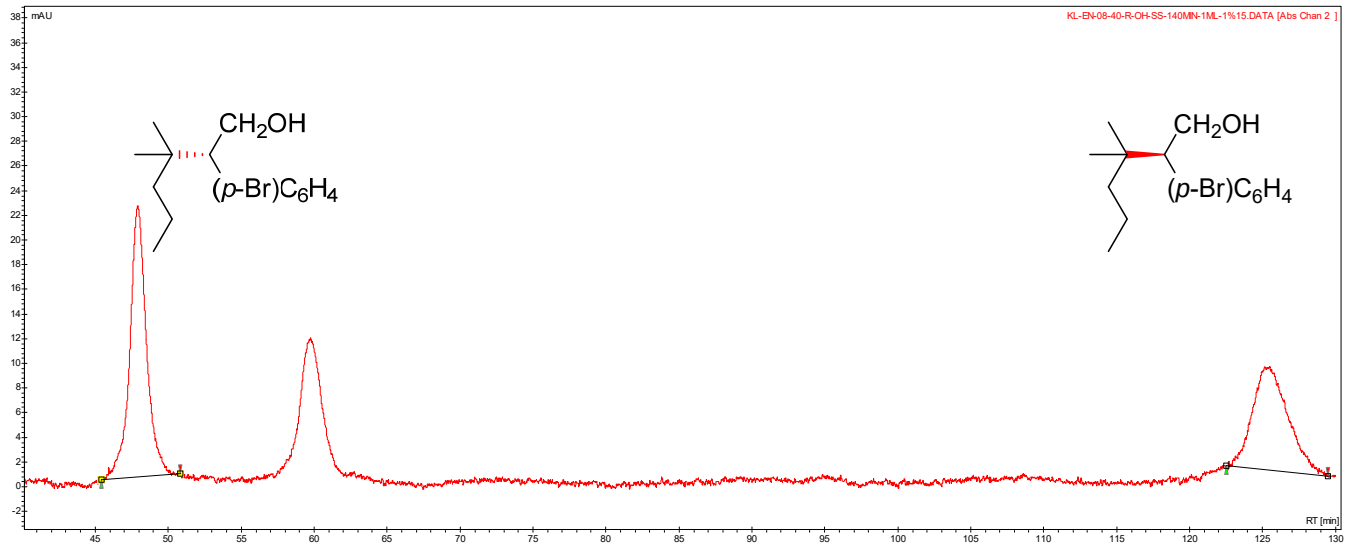
1a 3 *equiv.* **2a** (*S*) **3a** (*S,R*)



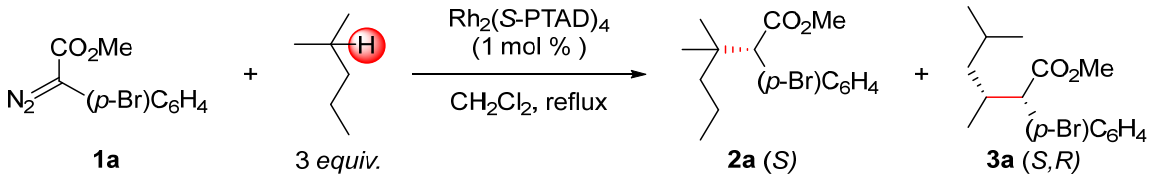
#	Time [Min]	Area % [%]
1	45.98	71.449
2	120.82	28.551
		-43 % e.e.



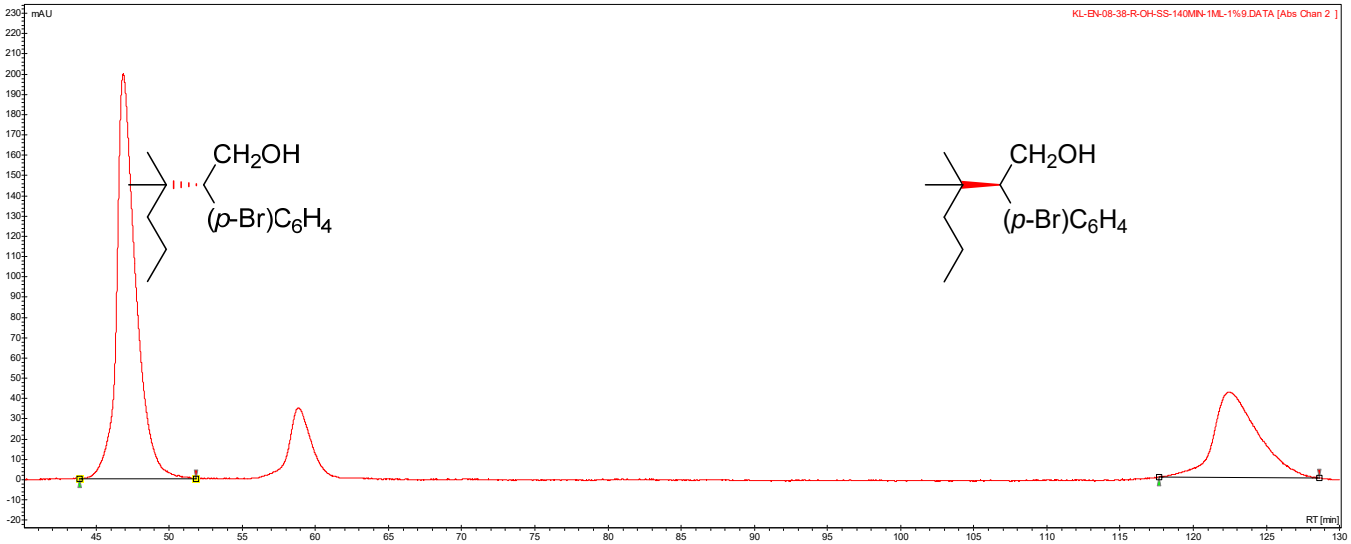
1a 3 *equiv.* **2a** (*S*) **3a** (*S,R*)



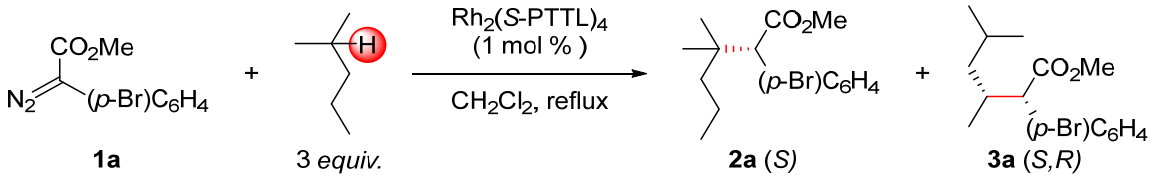
#	Time [Min]	Area % [%]
1	47.91	54.986
2	125.47	45.014
		-10 % e.e.



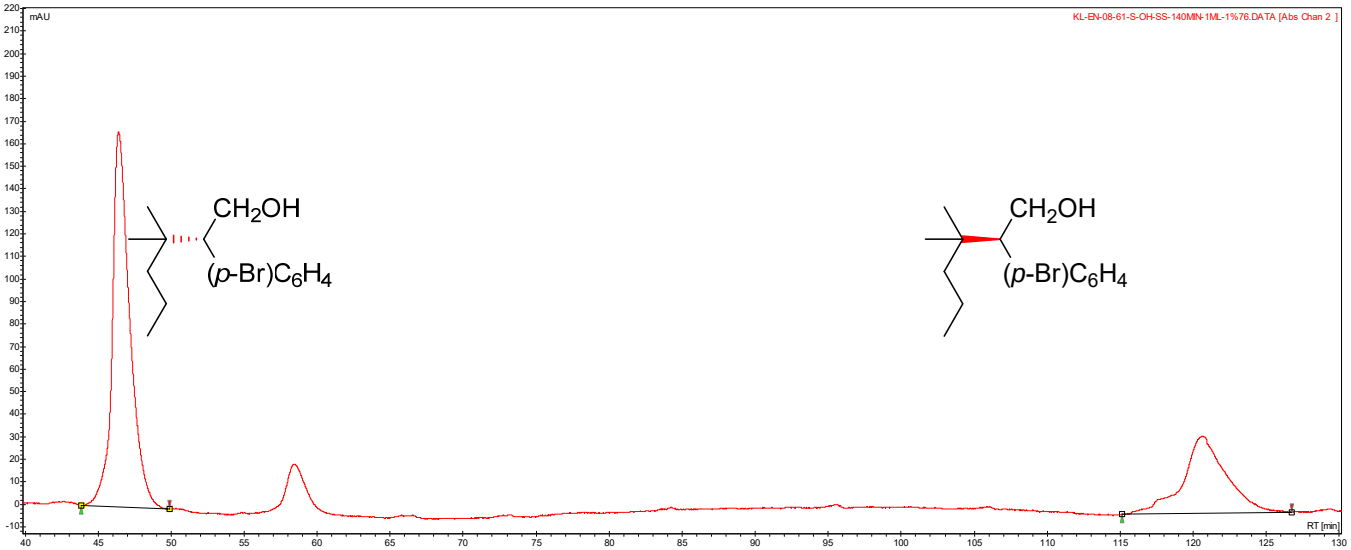
1a 3 *equiv.* **2a** (*S*) **3a** (*S,R*)



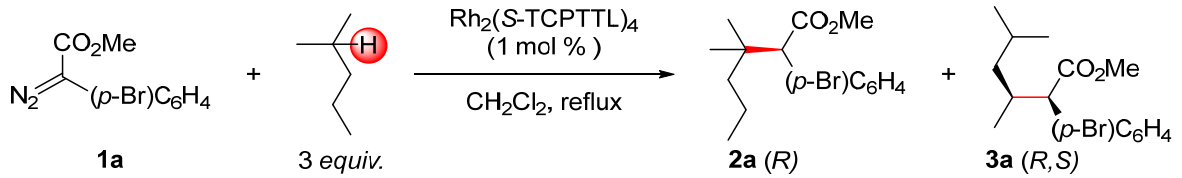
#	Time [Min]	Area % [%]
1	46.86	66.765
2	122.38	33.235
		-34 % e.e.

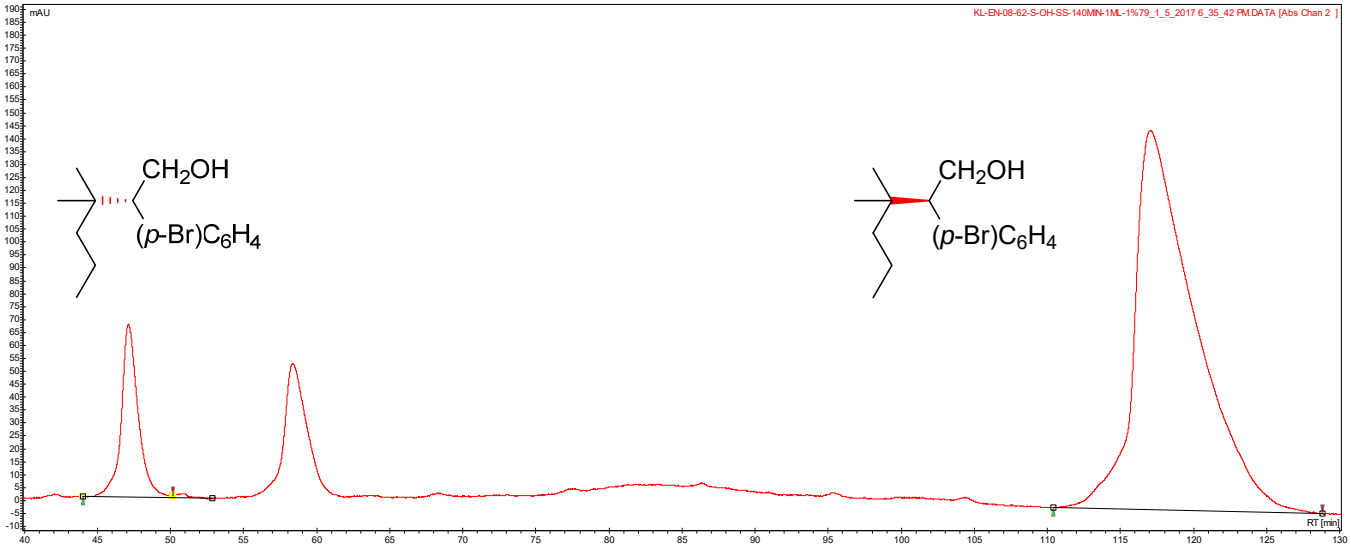


1a 3 *equiv.* **2a** (*S*) **3a** (*S,R*)

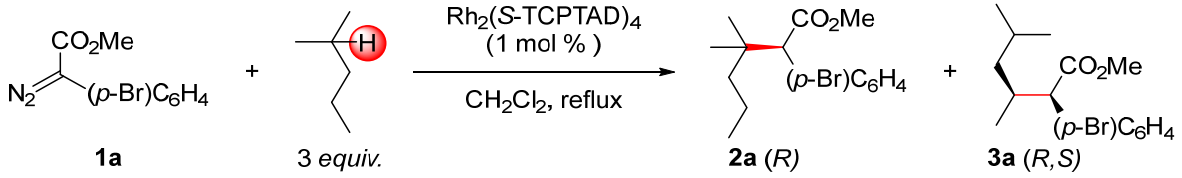


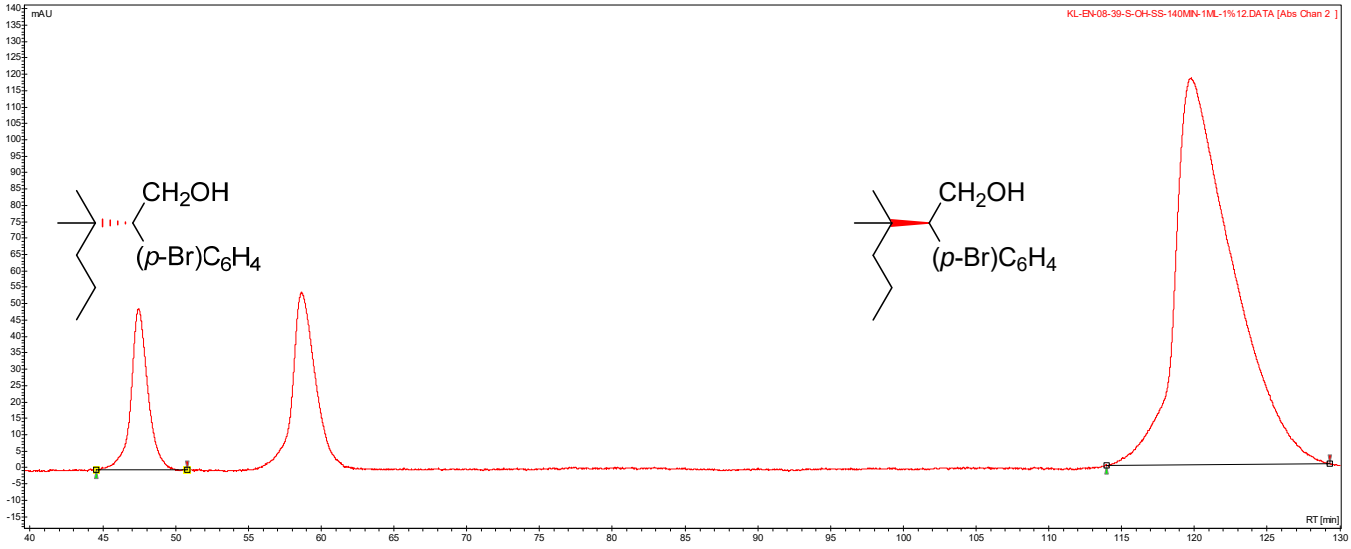
#	Time [Min]	Area % [%]
1	46.40	66.565
2	120.66	33.435
		-33 % e.e.



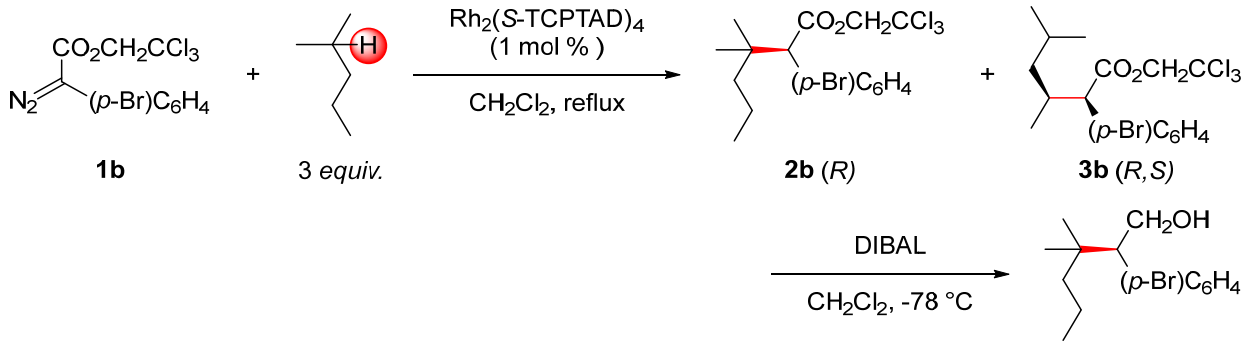


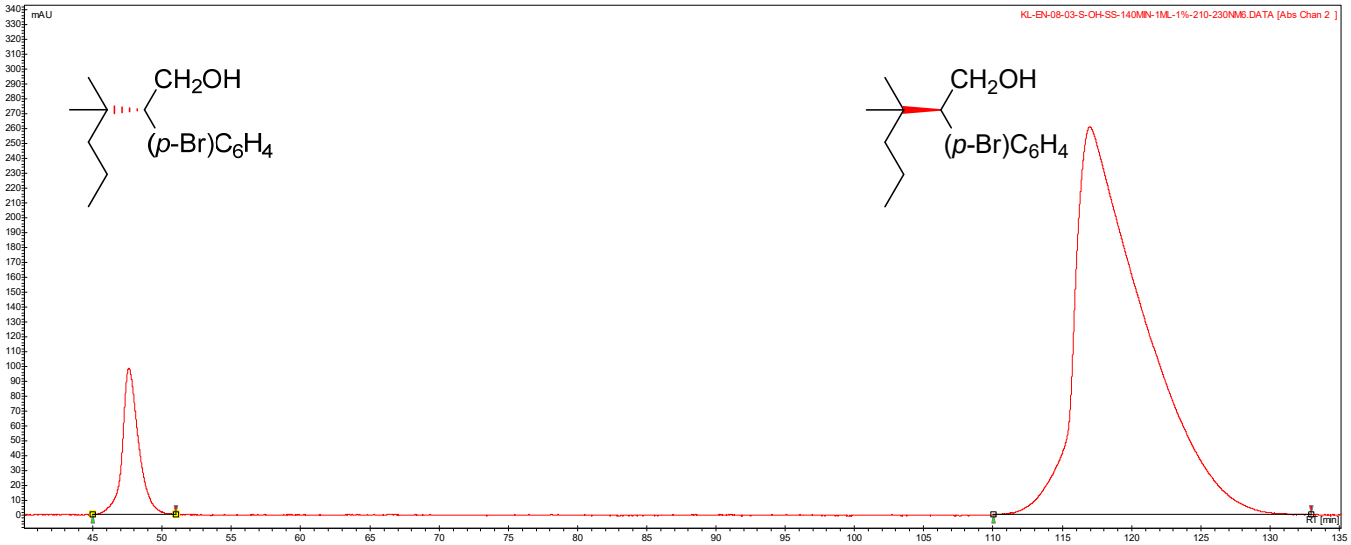
#	Time [Min]	Area % [%]
1	47.13	11.286
2	117.05	88.714
		77 % e.e.



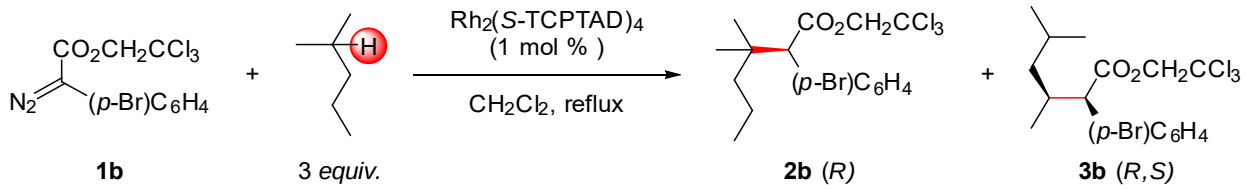


#	Time [Min]	Area % [%]
1	47.46	10.742
2	119.78	89.258
		79 % e.e.

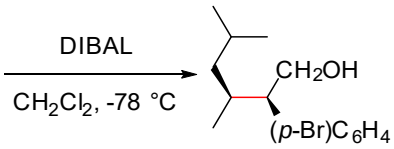


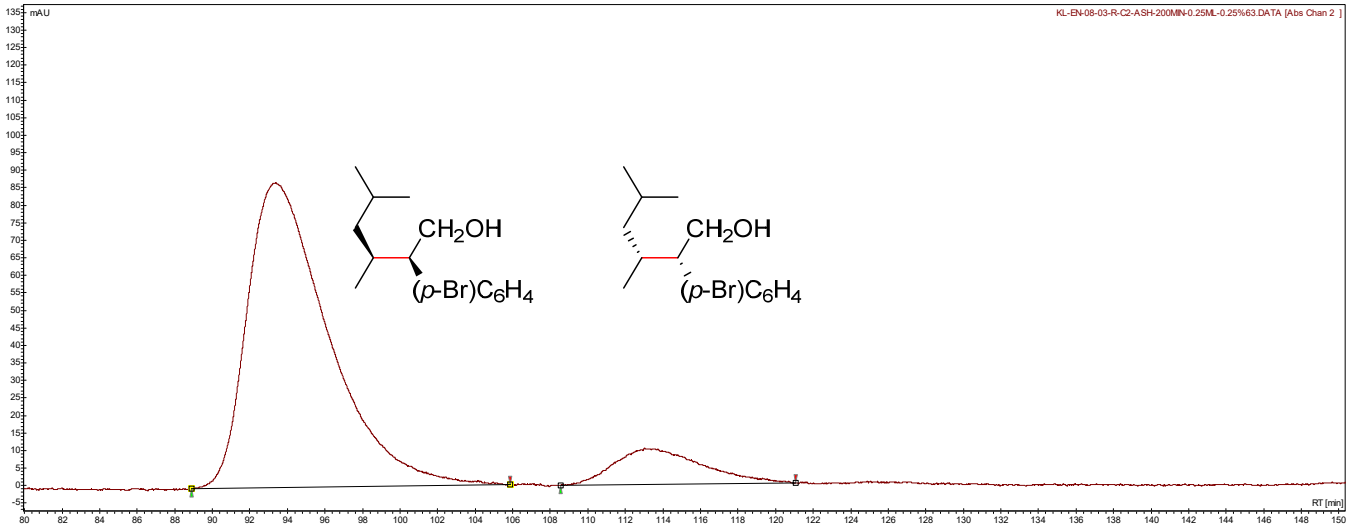


#	Time [Min]	Area % [%]
1	47.61	8.069
2	91.93	91.931
		84 % e.e.

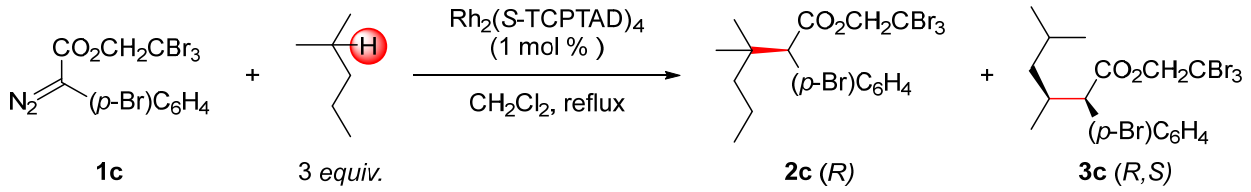


1b 3 *equiv.* **2b** (*R*) **3b** (*R,S*)

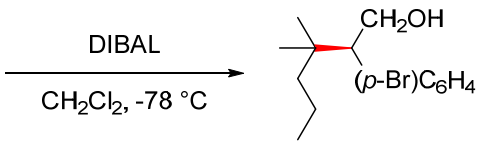


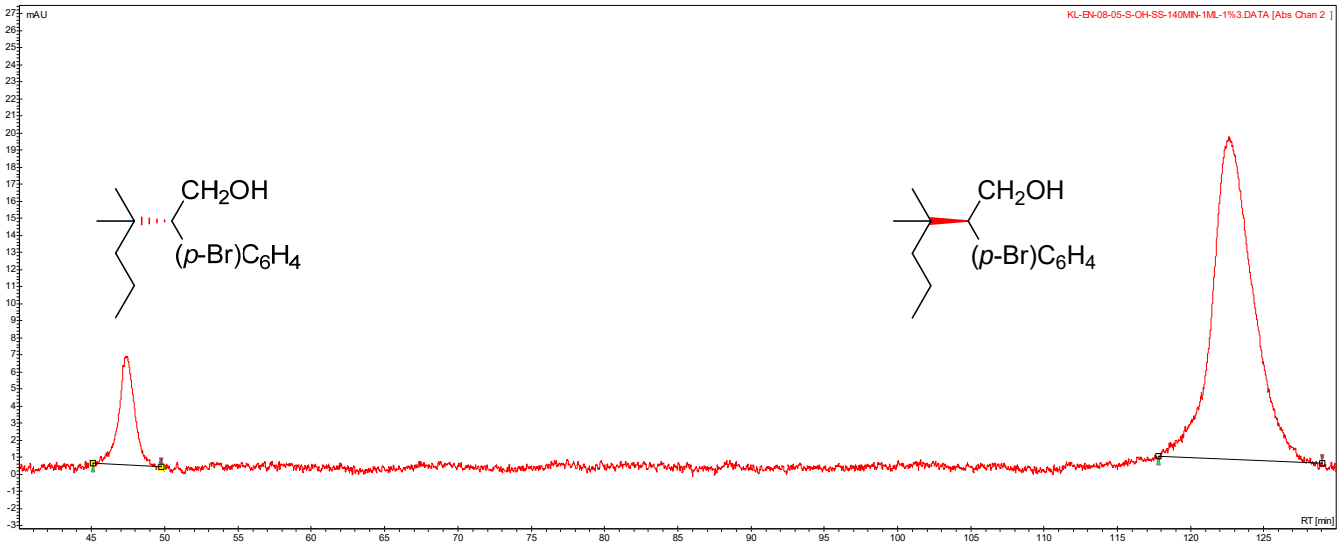


#	Time [Min]	Area % [%]
1	93.38	88.720
2	113.03	11.280
		77 % e.e.

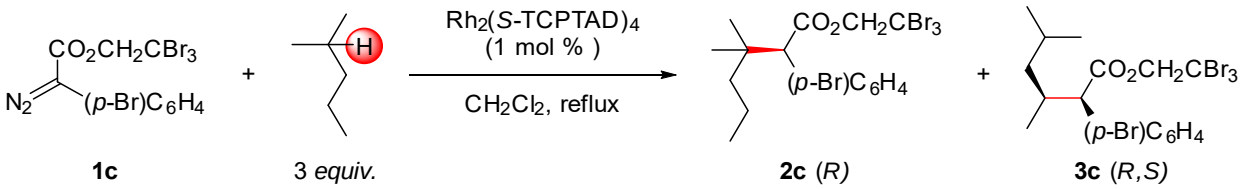


1c 3 *equiv.* **2c** (*R*) **3c** (*R,S*)

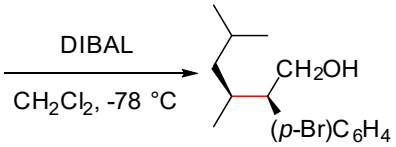


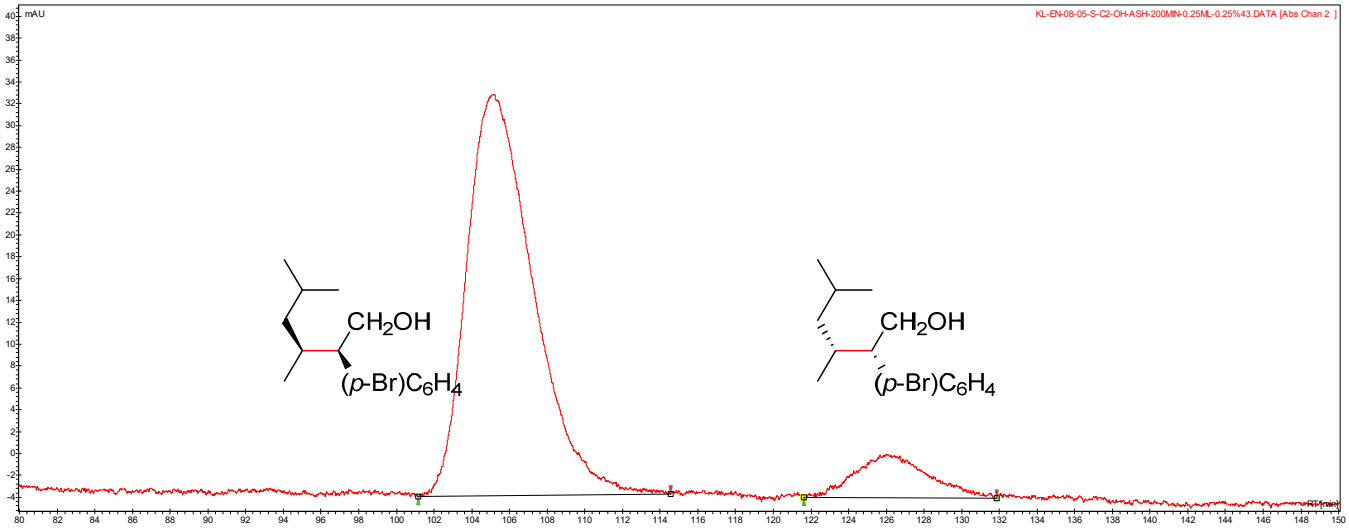


#	Time [Min]	Area % [%]
1	47.39	11.589
2	122.62	88.411
		77 % e.e.



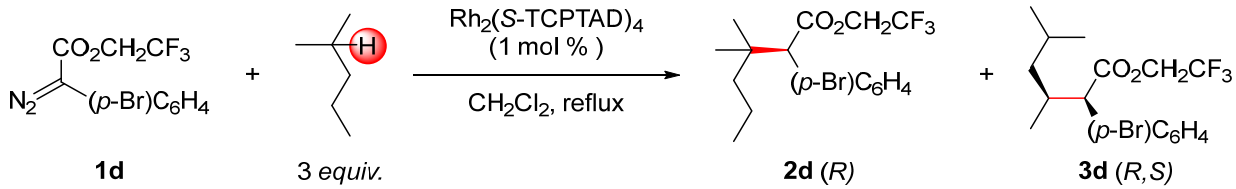
1c **2c** (*R*) **3c** (*R,S*)

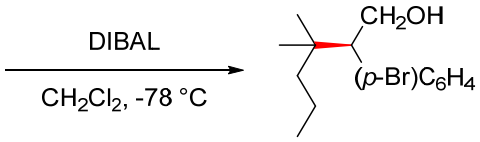


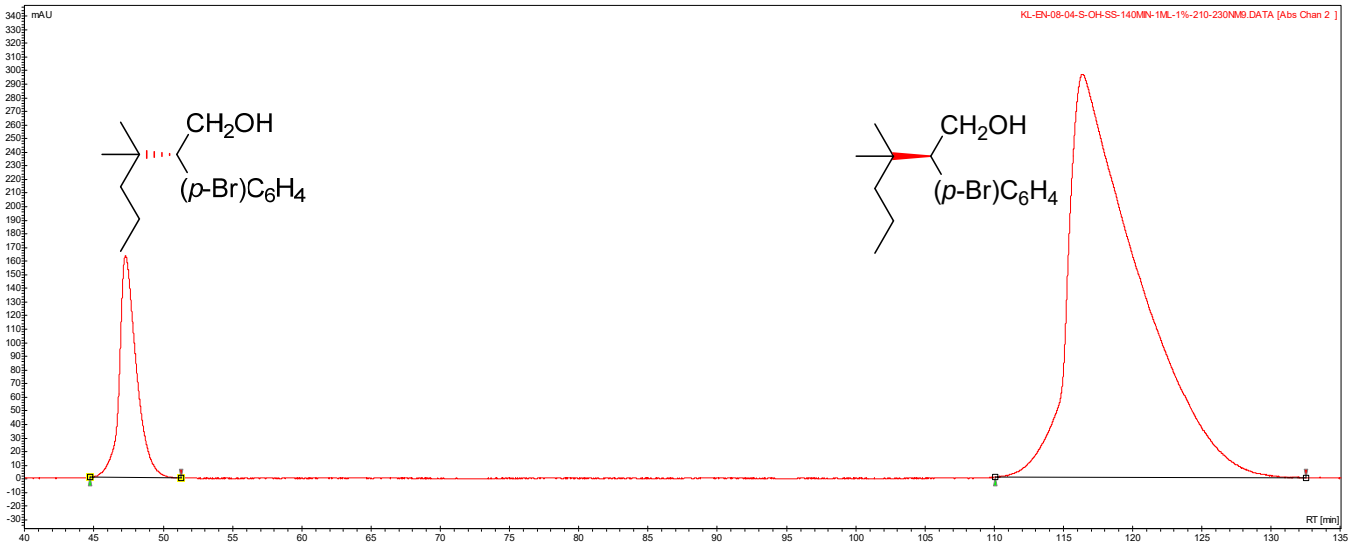


#	Time [Min]	Area % [%]
1	105.17	89.476
2	126.09	10.524

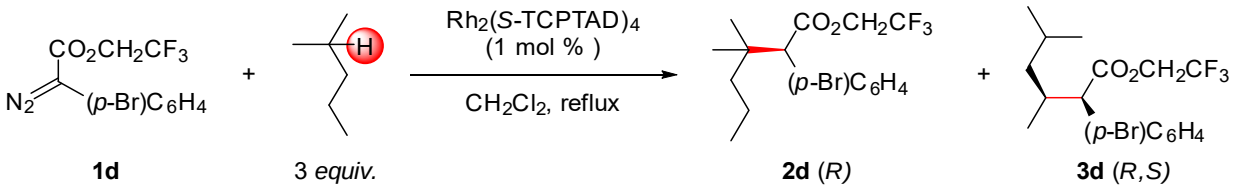
79 % e.e.



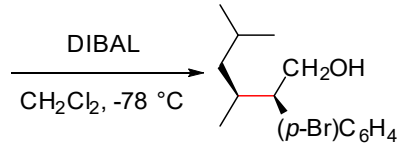


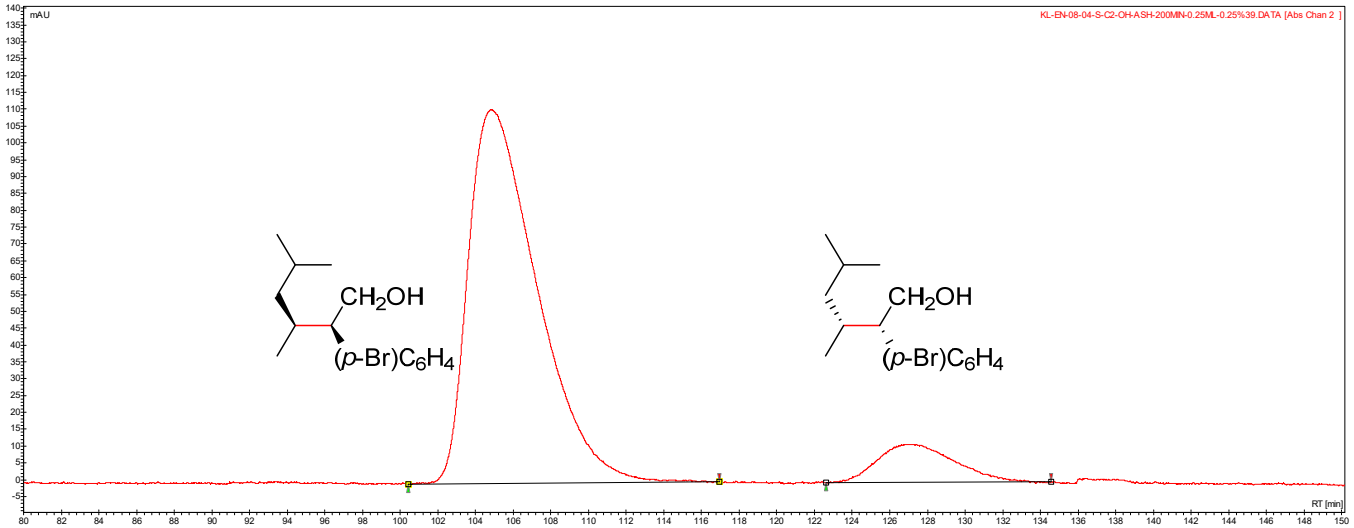


#	Time [Min]	Area % [%]
1	47.28	11.694
2	116.33	88.306
		77 % e.e.



1d 3 *equiv.* **2d** (*R*) **3d** (*R*,*S*)

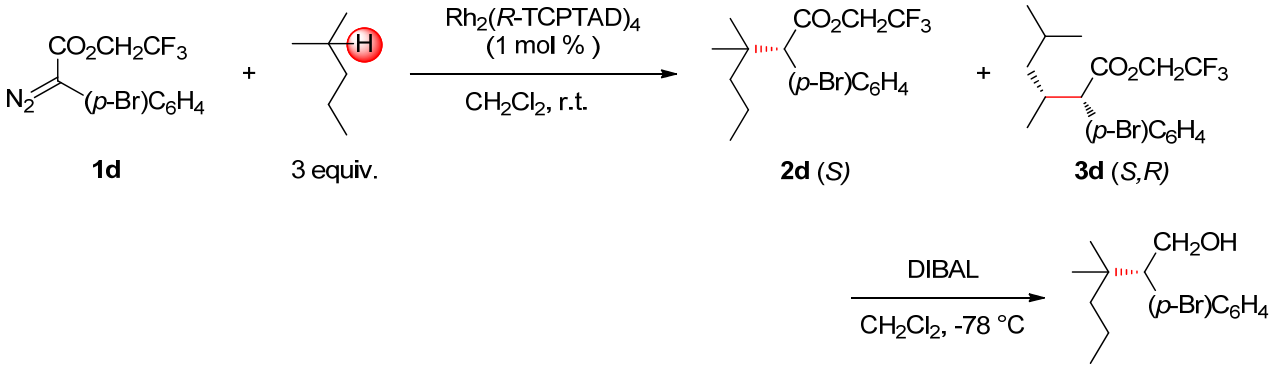


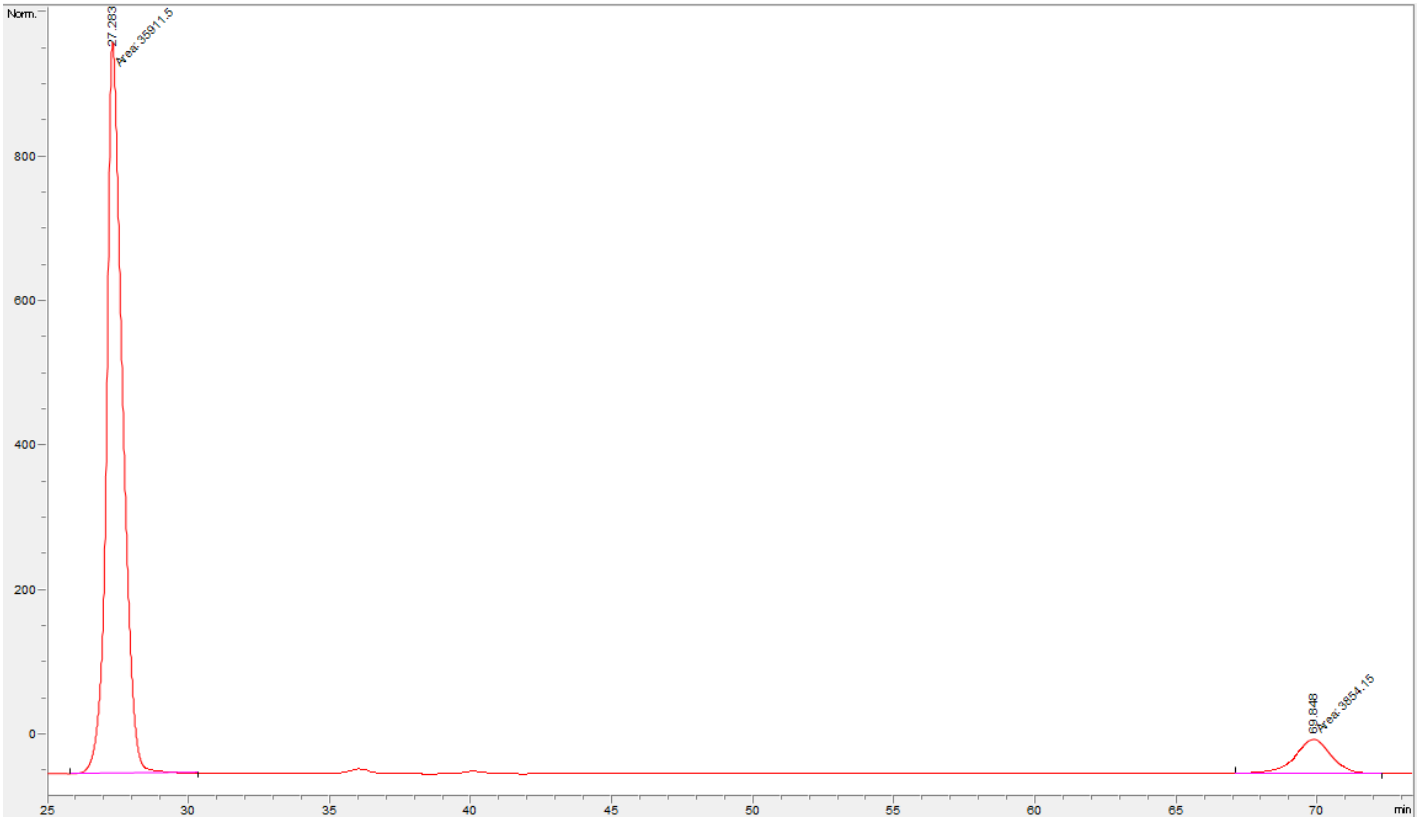


#	Time [Min]	Area % [%]
1	104.83	89.640
2	126.85	10.360
		79 % e.e.

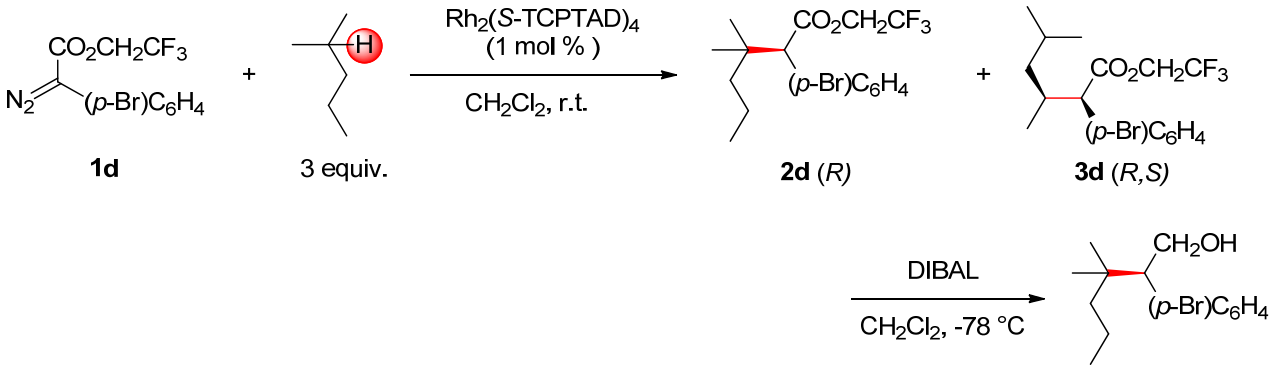
9.3 Reaction Condition Screen for the Functionalization of 2-Methylpentane

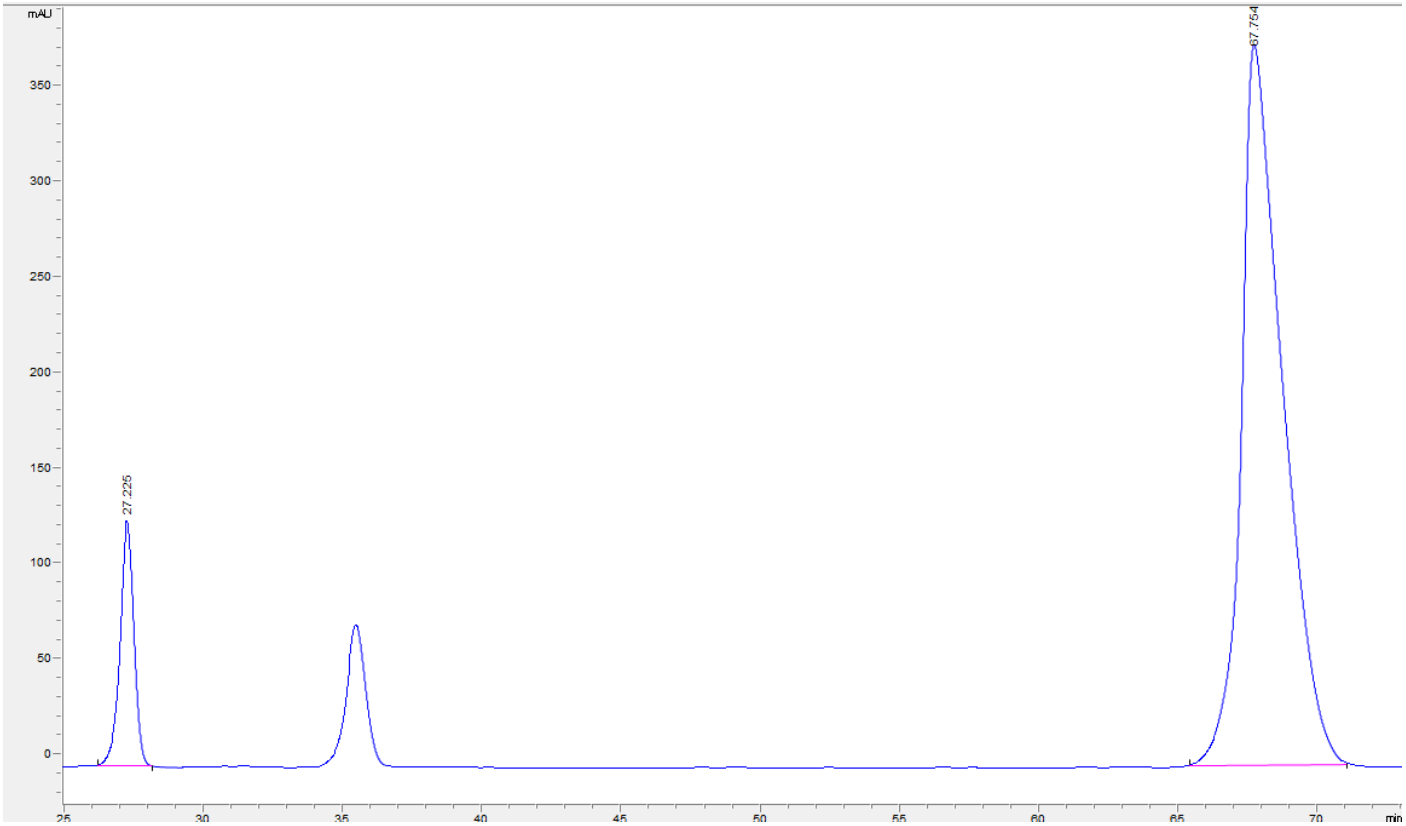
A different HPLC machine with a different S,S-whelk chiral column was used, so the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$.





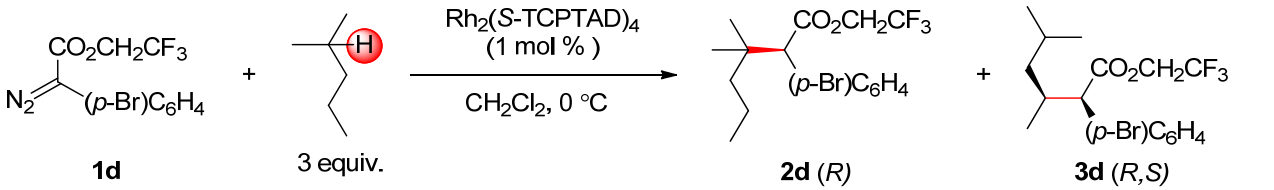
#	Time [Min]	Area% [%]
1	27.283	90.308
2	69.848	9.692 n
		-80% e.e.

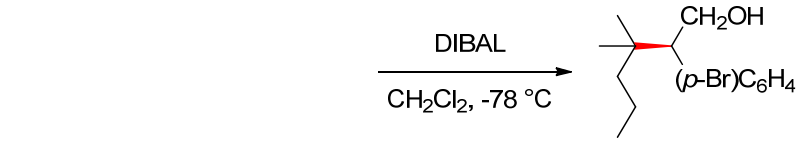


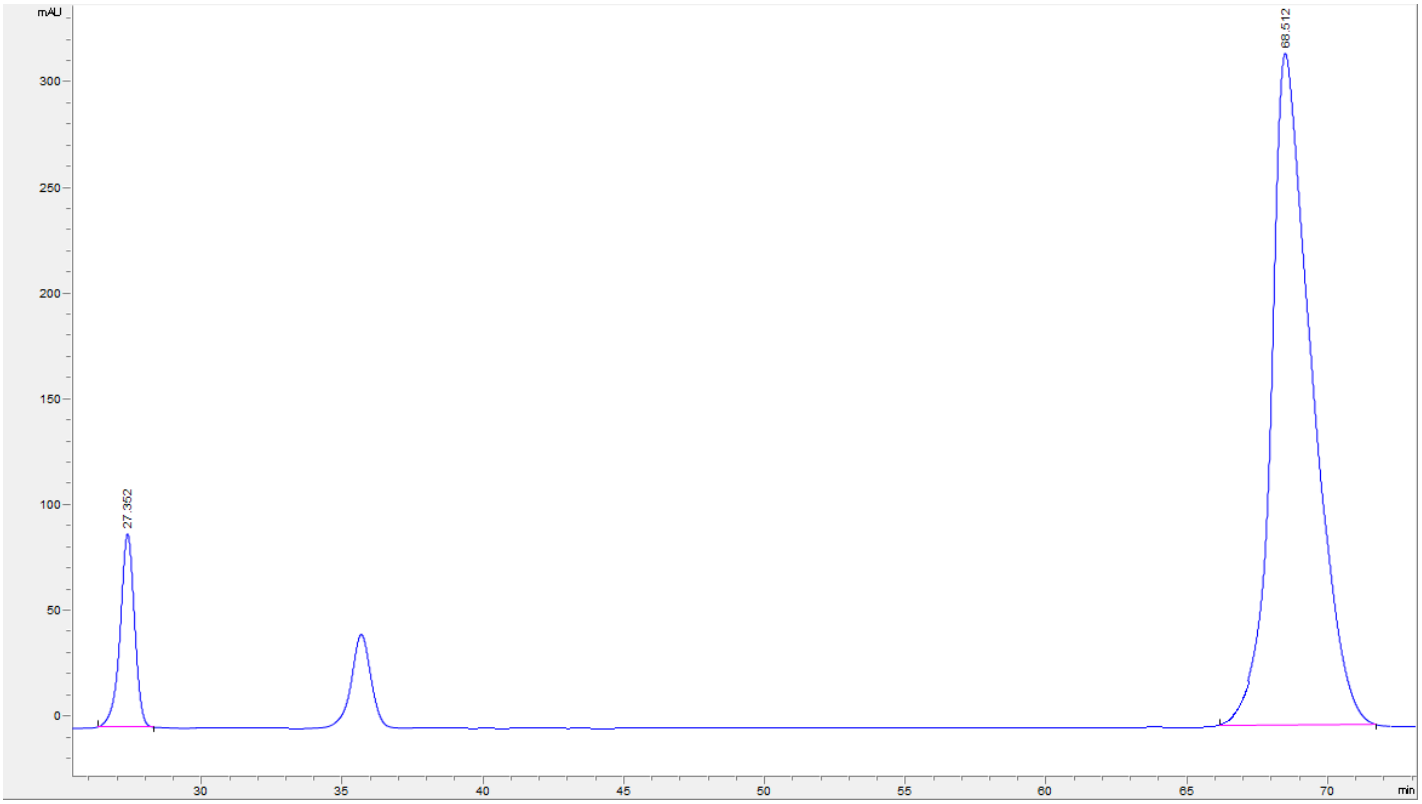


#	Time [Min]	Area% [%]
1	25.830	10.208
2	63.988	89.794

80% e.e.

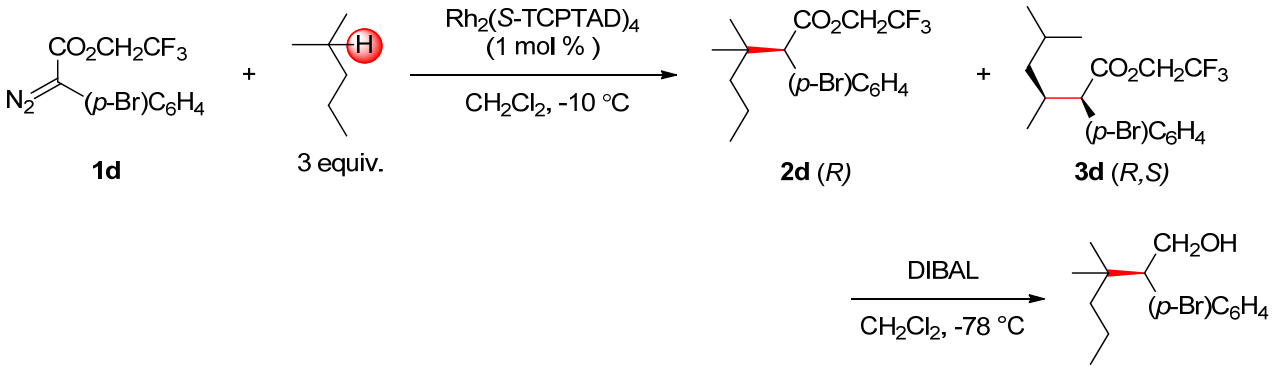


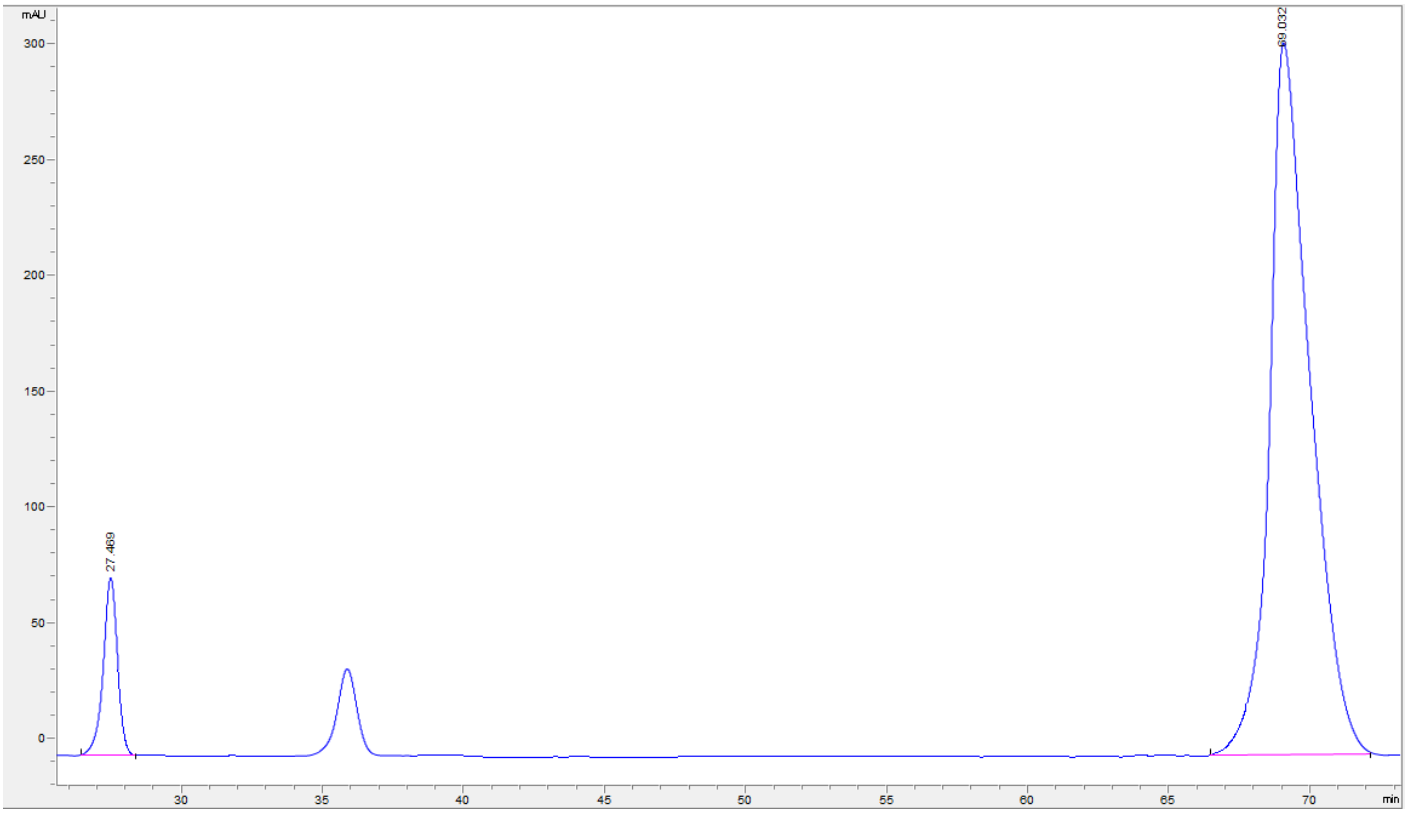




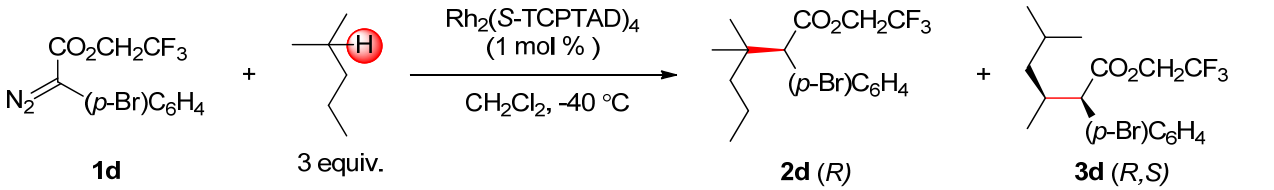
#	Time [Min]	Area% [%]
1	27.352	9.261
2	68.512	90.739

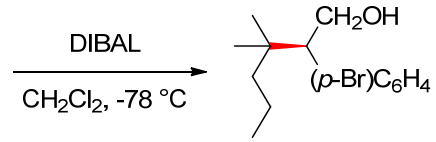
82% e.e.

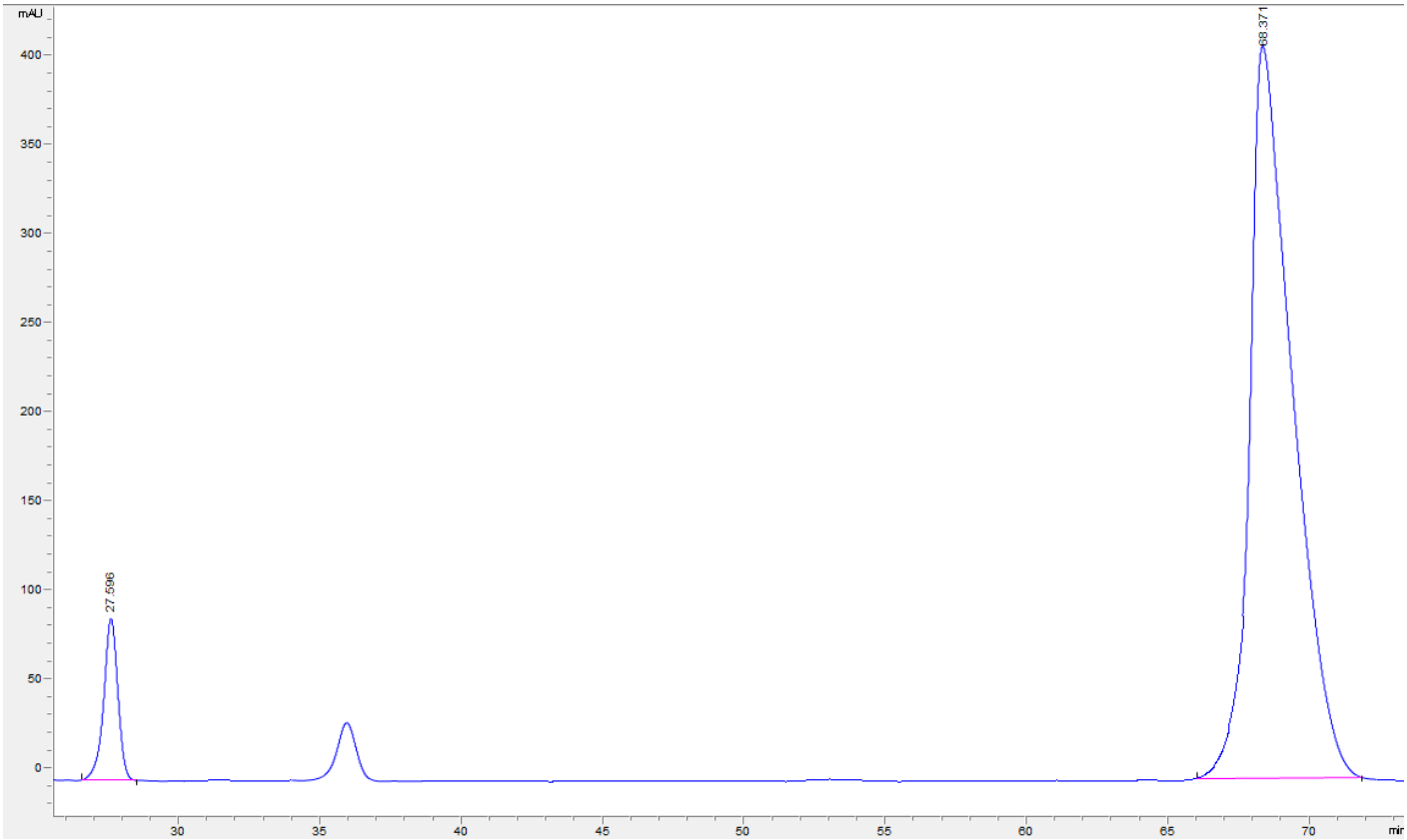




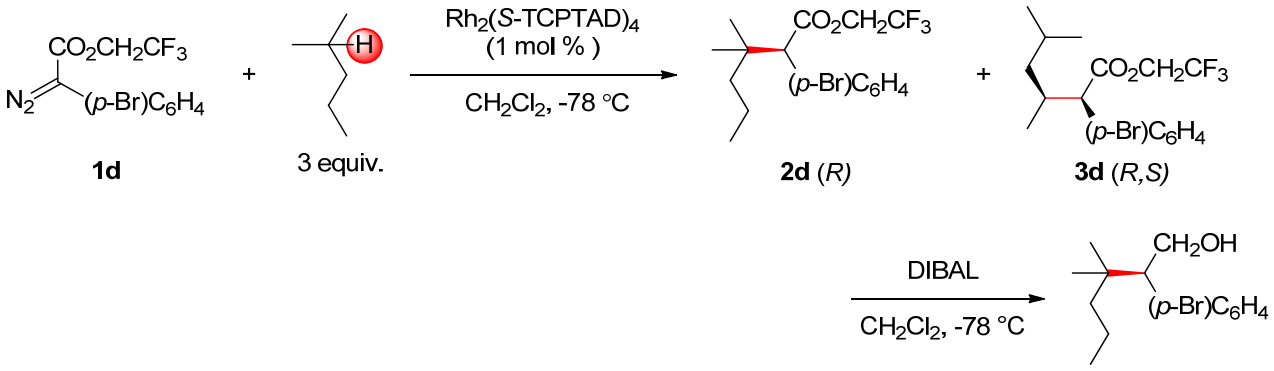
#	Time [Min]	Area% [%]
1	27.469	8.071
2	69.032	91.929
		84% e.e.

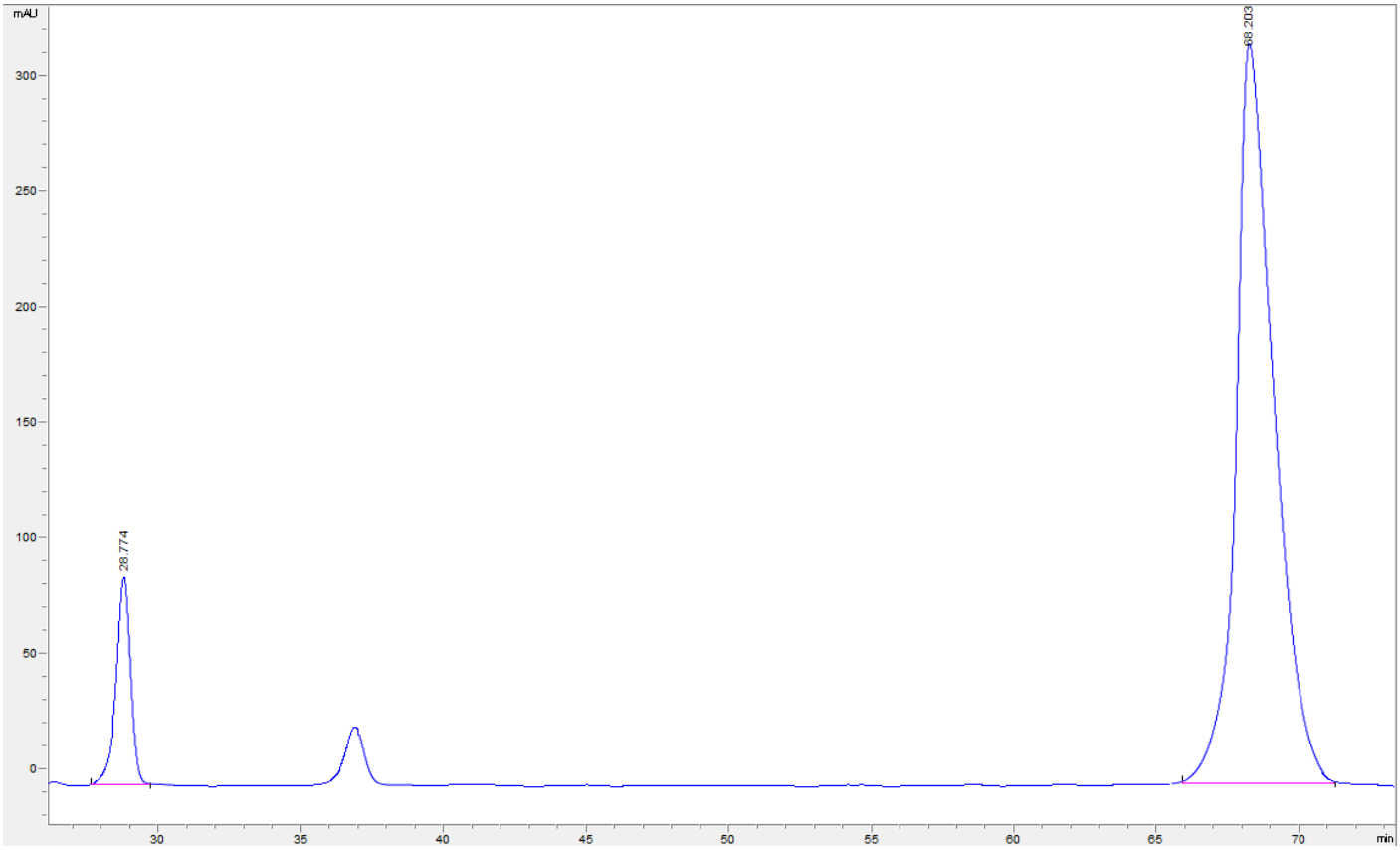






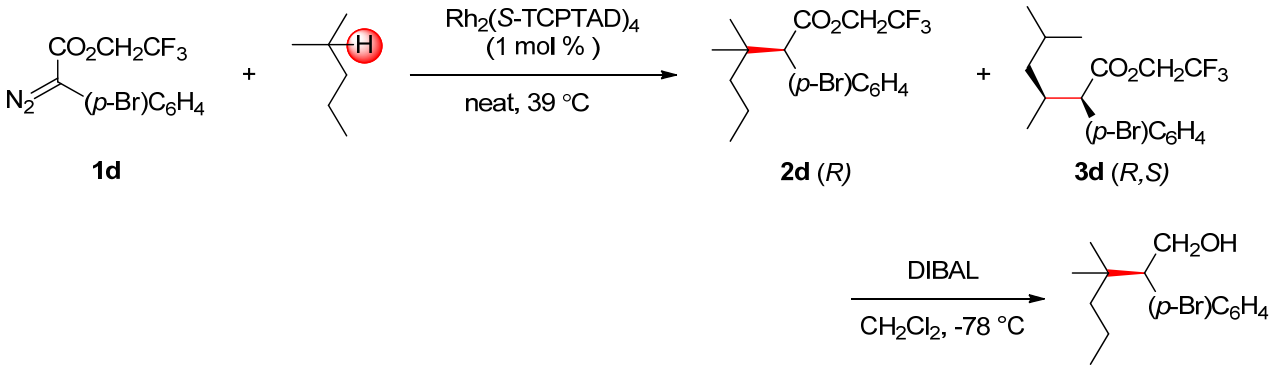
#	Time [Min]	Area% [%]
1	27.596	6.745
2	68.371	93.255
		86% e.e.

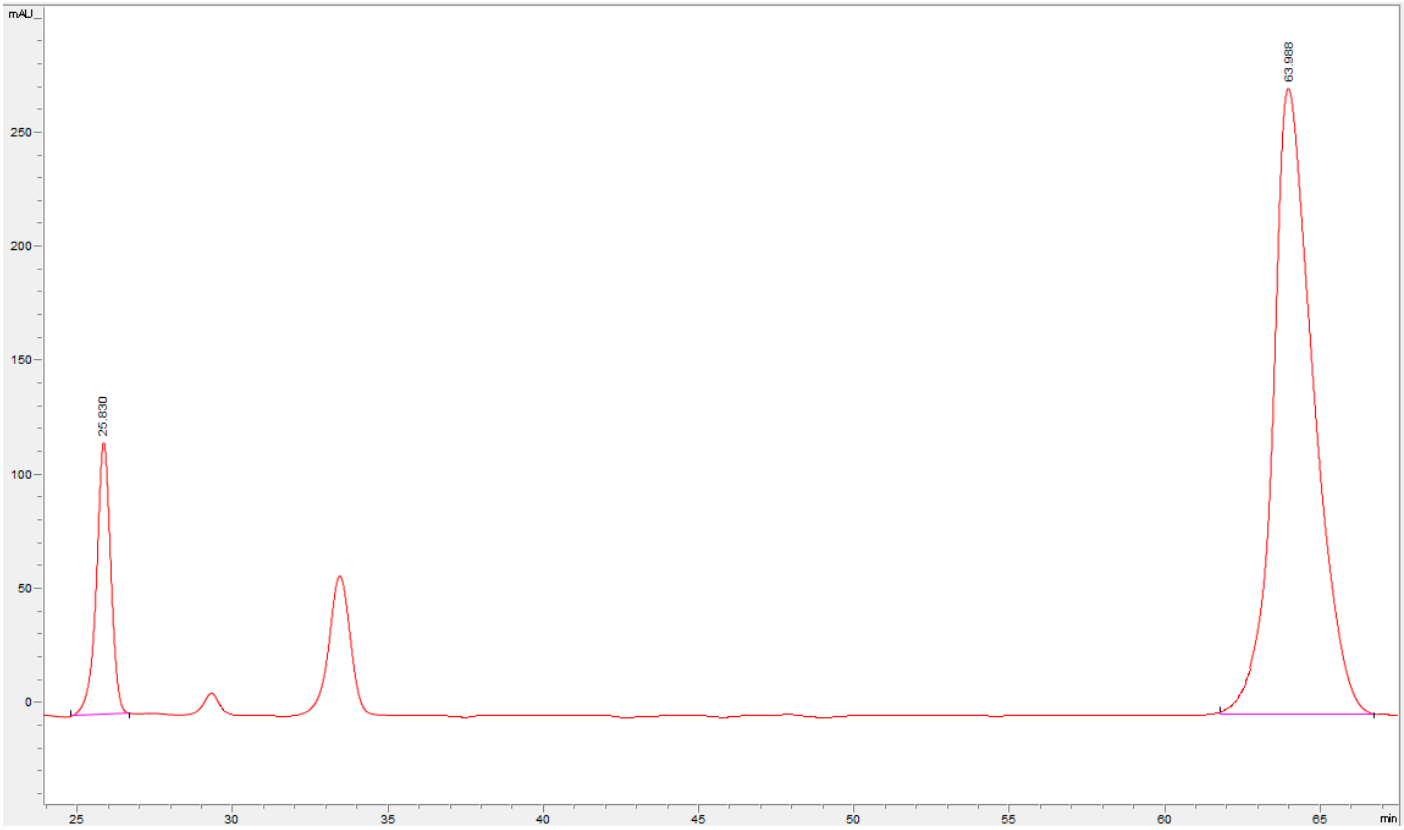




#	Time [Min]	Area% [%]
1	28.774	9.729
2	68.203	90.271

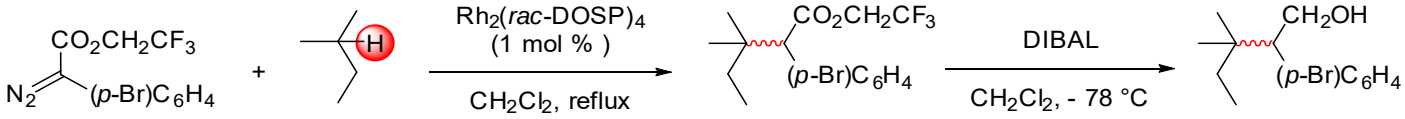
80% e.e.

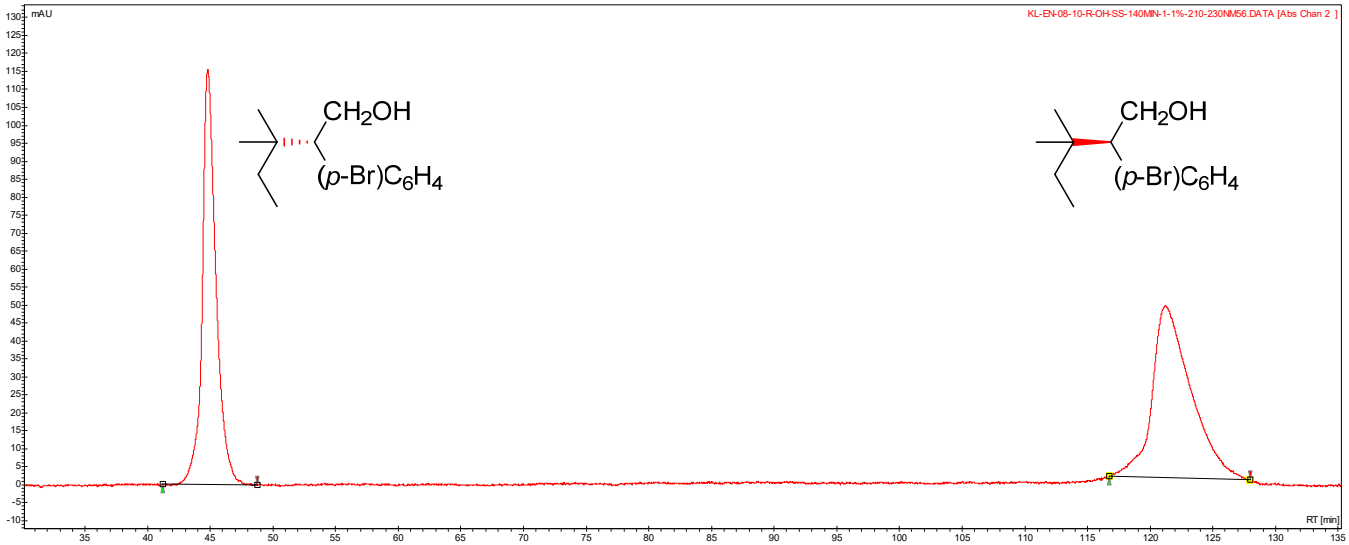




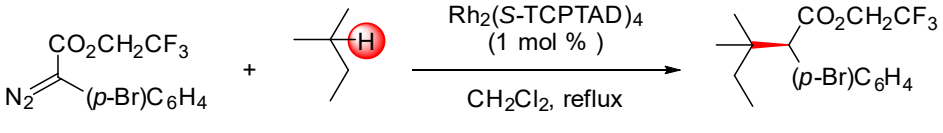
#	Time [Min]	Area% [%]
1	25.830	13.436
2	63.988	86.564
		73% e.e.

9.3 C–H Functionalization Products **4-26**

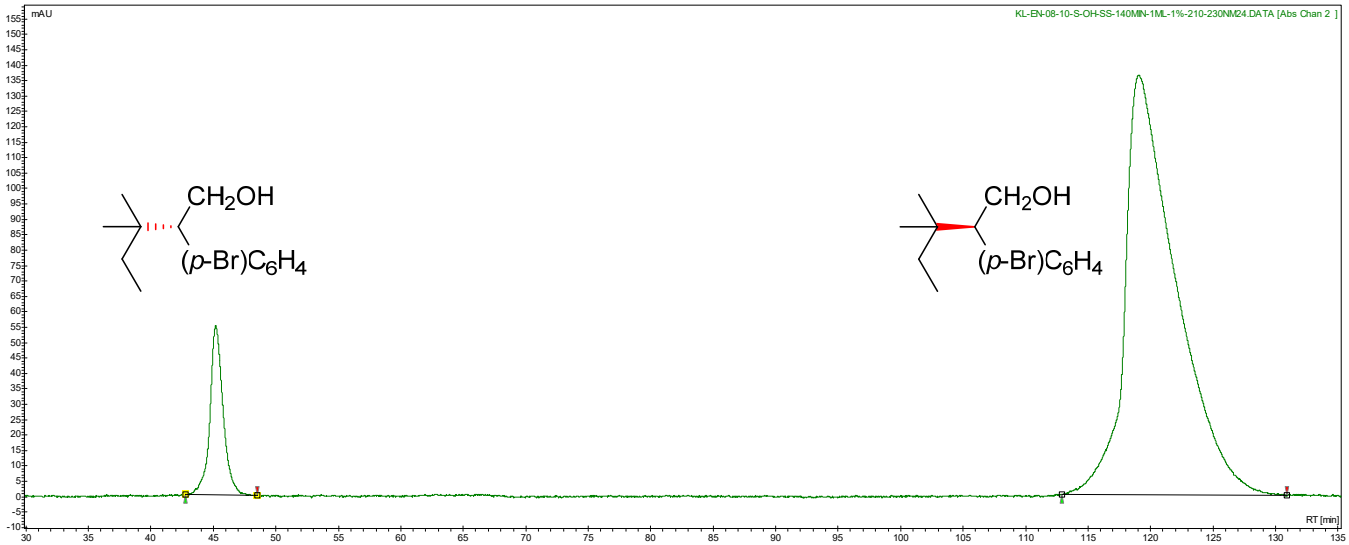




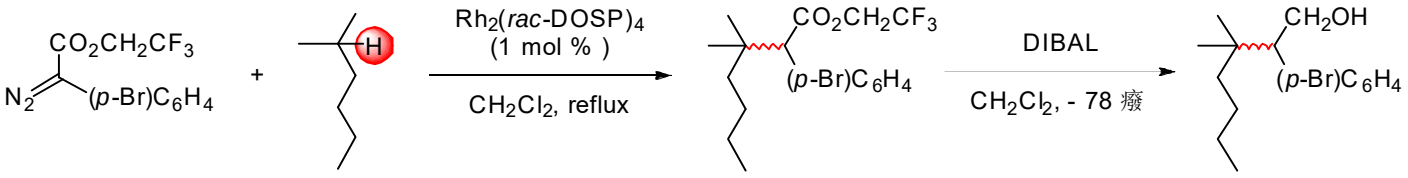
#	Time [Min]	Area % [%]
1	44.81	46.077
2	121.22	53.92

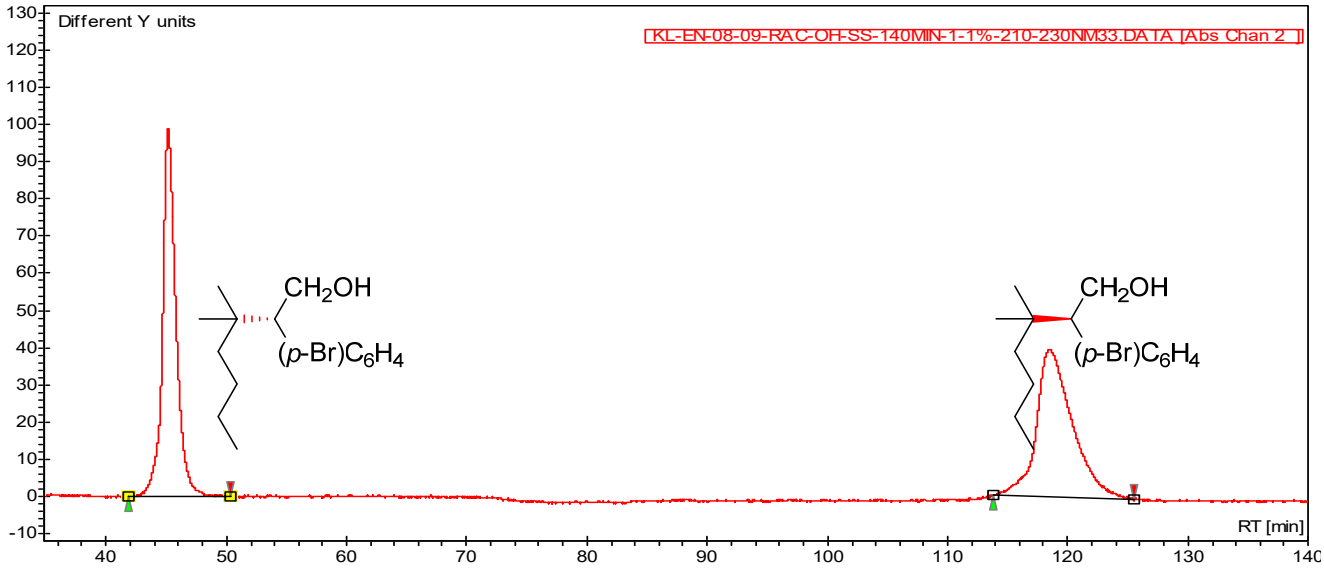


1d 3 *equiv.* **4**

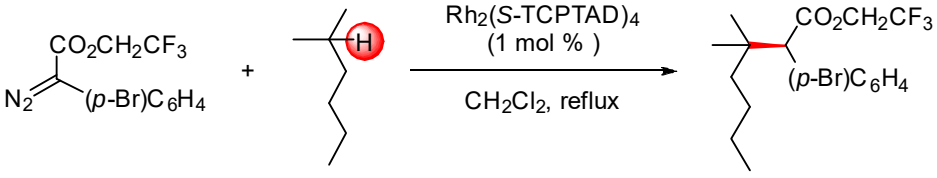


#	Time [Min]	Area % [%]
1	45.20	9.435
2	119.00	90.565
		81 % e.e.

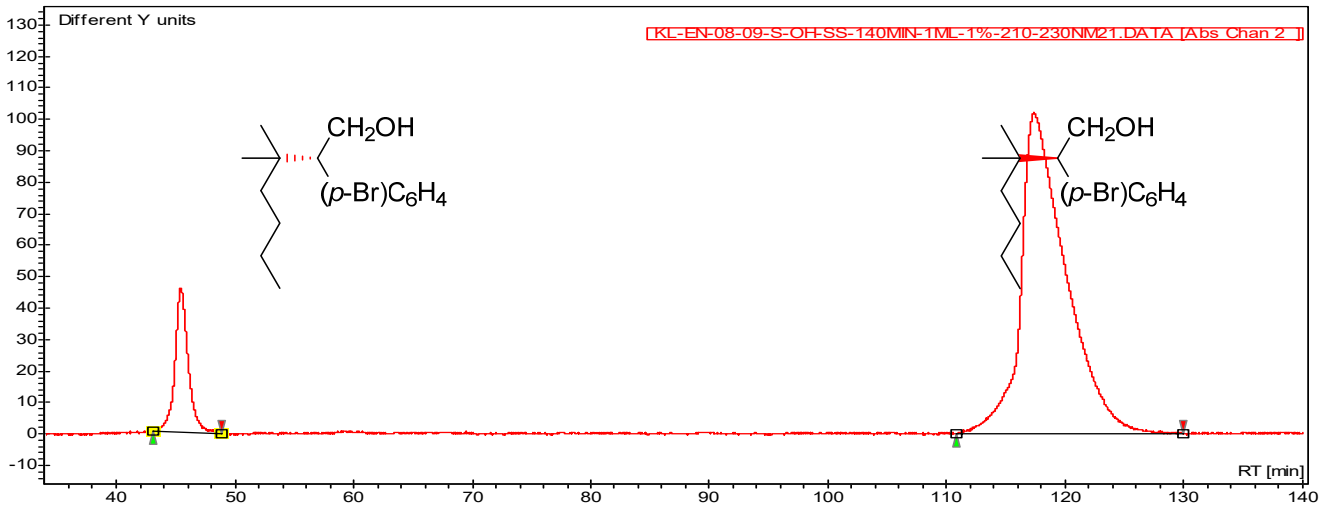




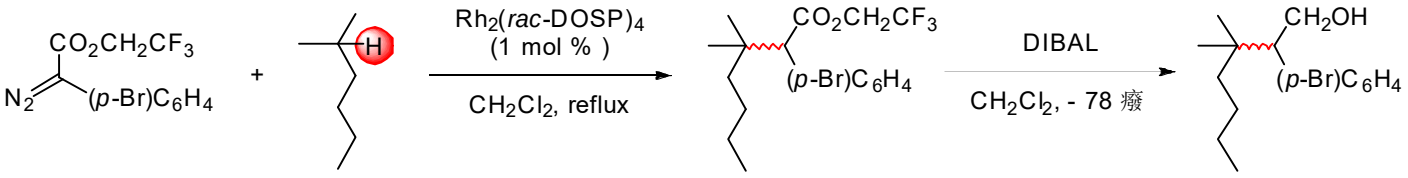
#	Time [Min]	Area % [%]
1	45.15	48.468
2	118.51	51.532

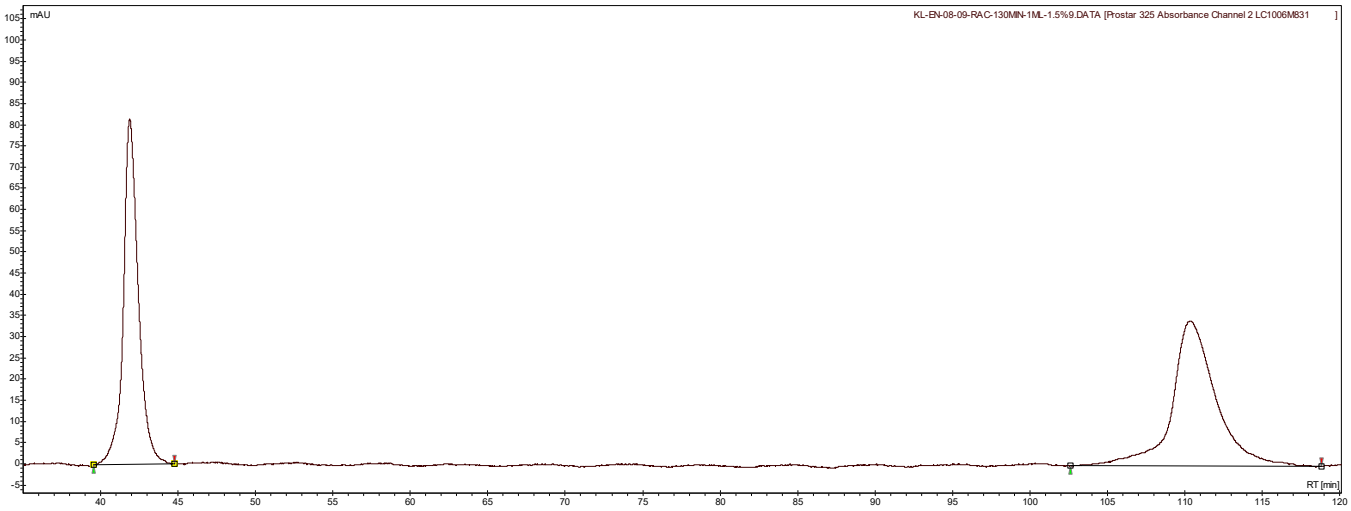


1d 3 *equiv.* **5**

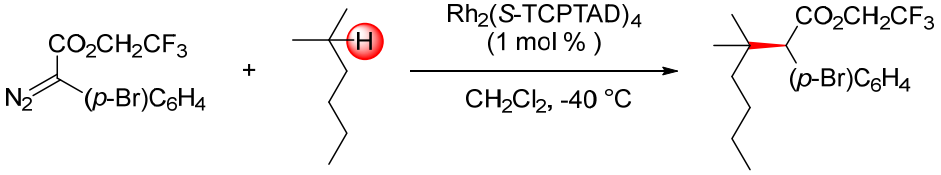


#	Time [Min]	Area % [%]
1	45.48	11.597
2	117.39	88.403
		77 % e.e.

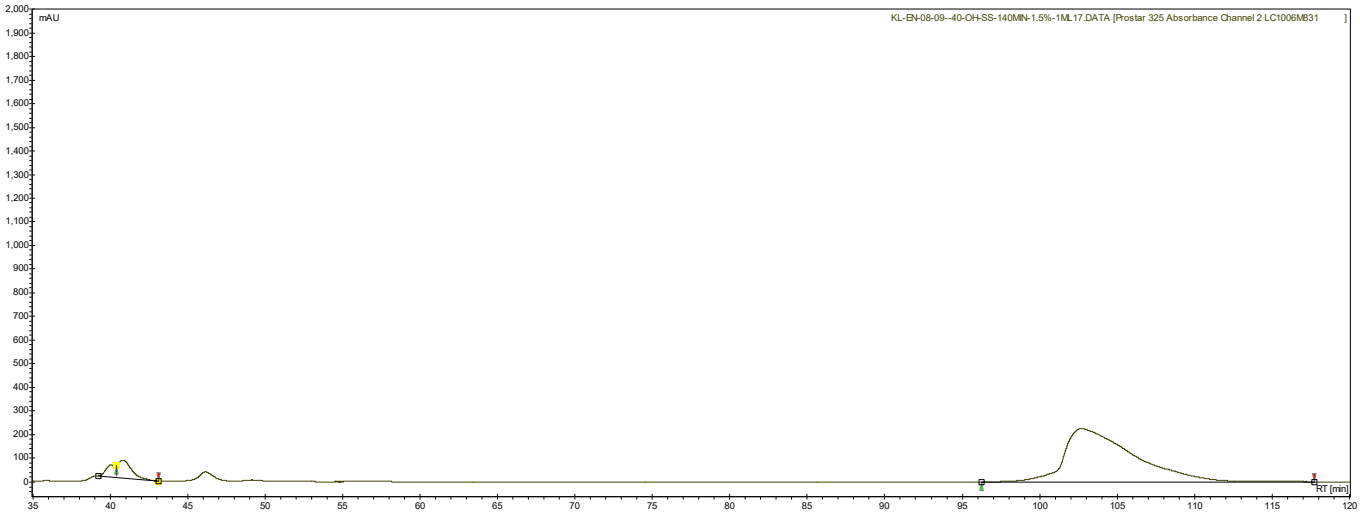




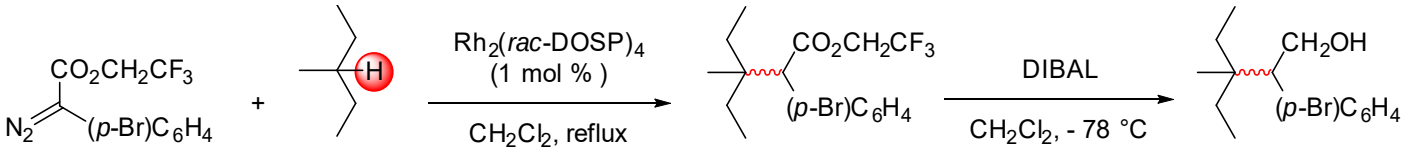
#	Time [Min]	Area % [%]
1	41.88	44.963
2	110.38	55.037

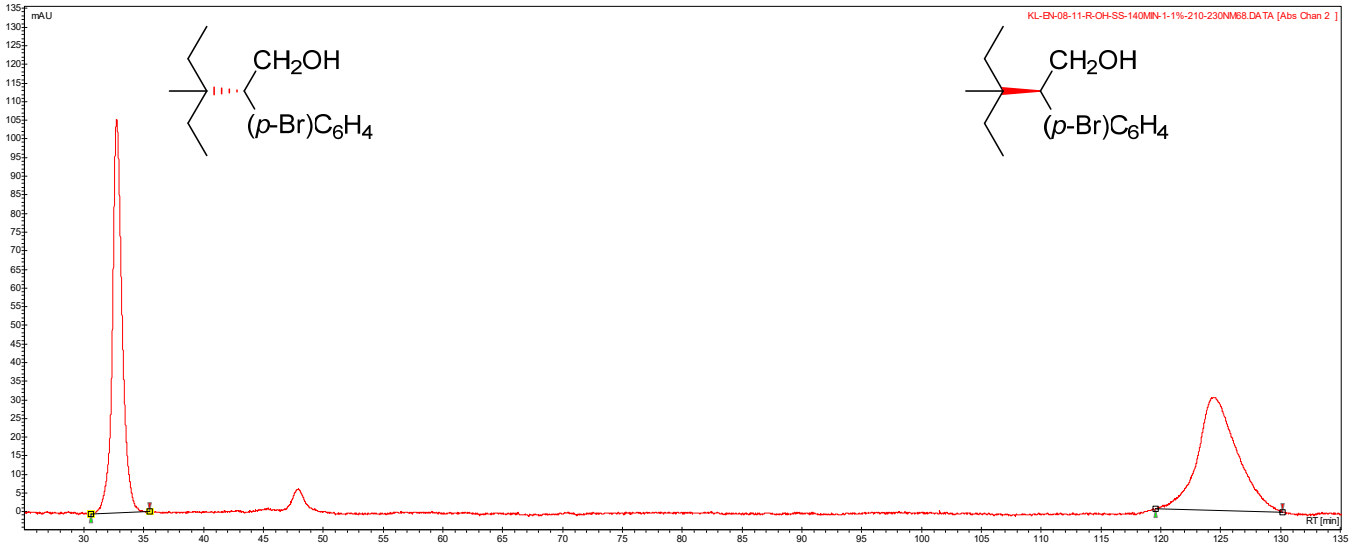


1d 3 *equiv.* **5**

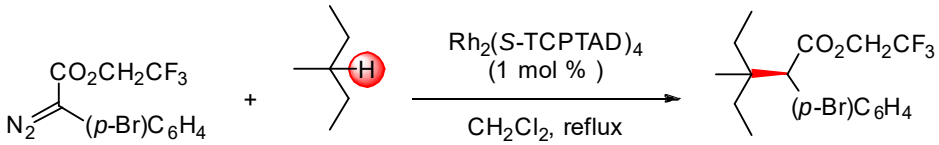


#	Time [Min]	Area % [%]
1	40.81	6.286
2	102.67	93.714
		87 % e.e.

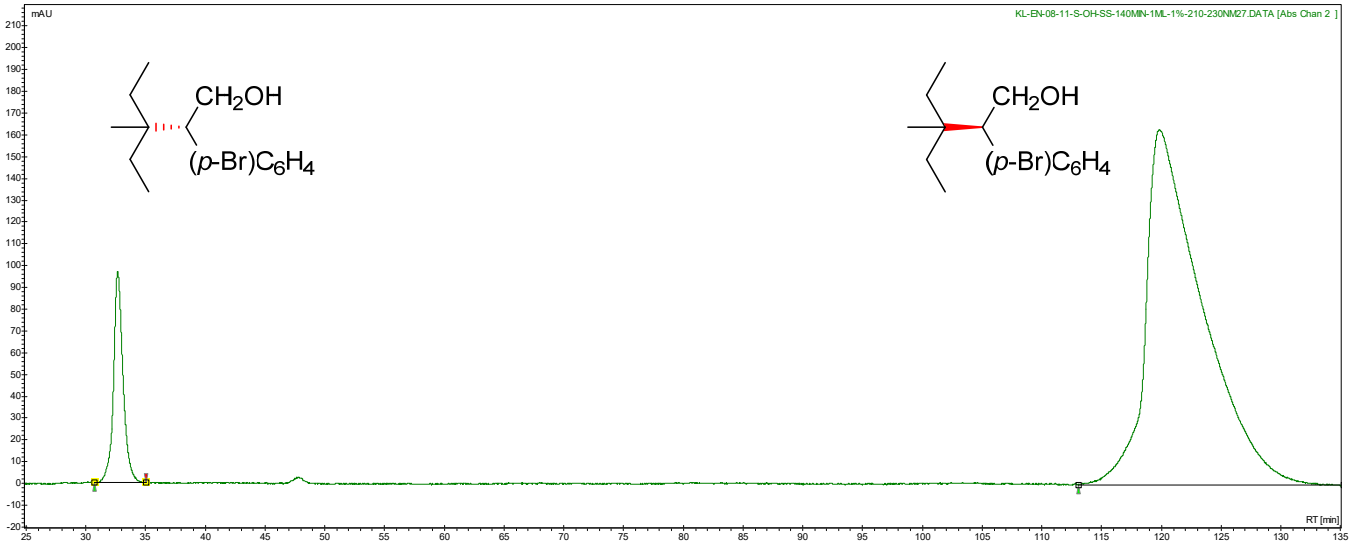




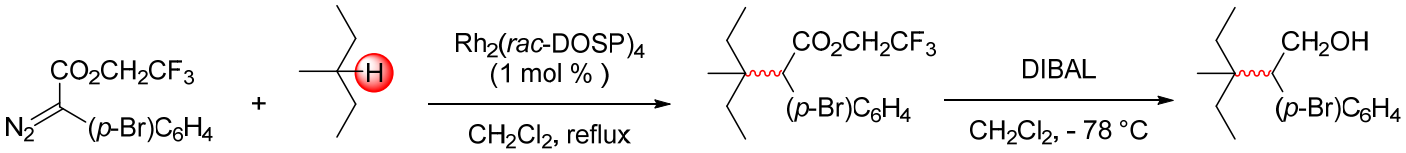
#	Time [Min]	Area % [%]
1	32.73	46.258
2	124.52	53.742

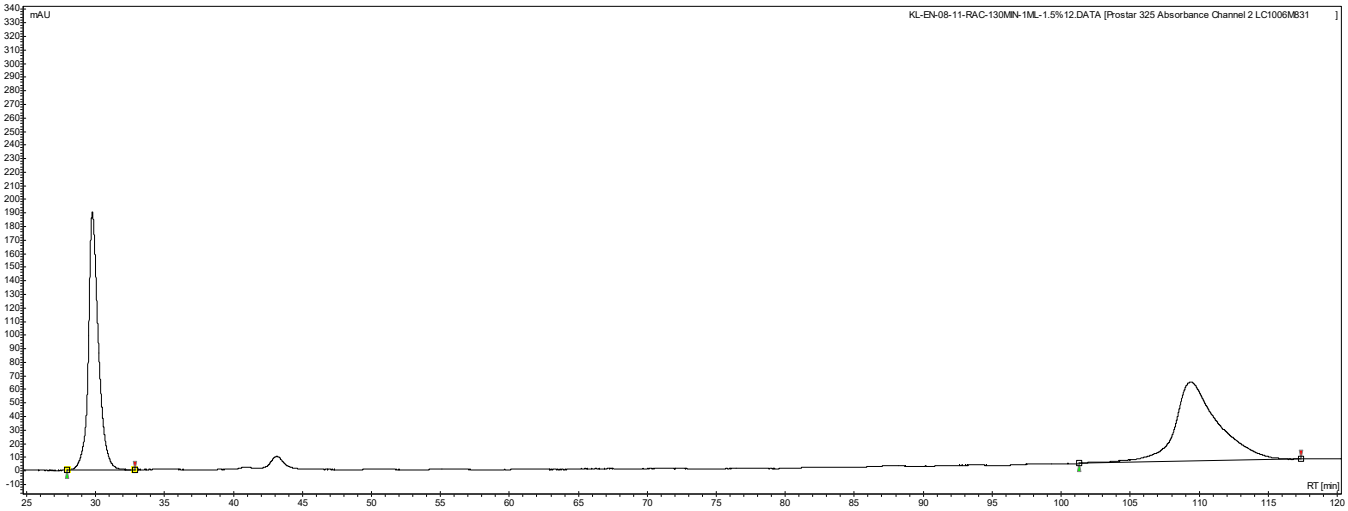


1d 3 *equiv.* **6**

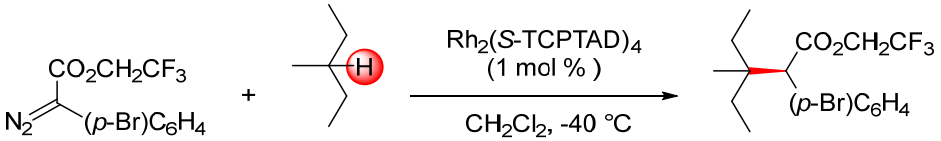


#	Time [Min]	Area % [%]
1	32.67	9.096
2	119.86	90.904
		82 % e.e.

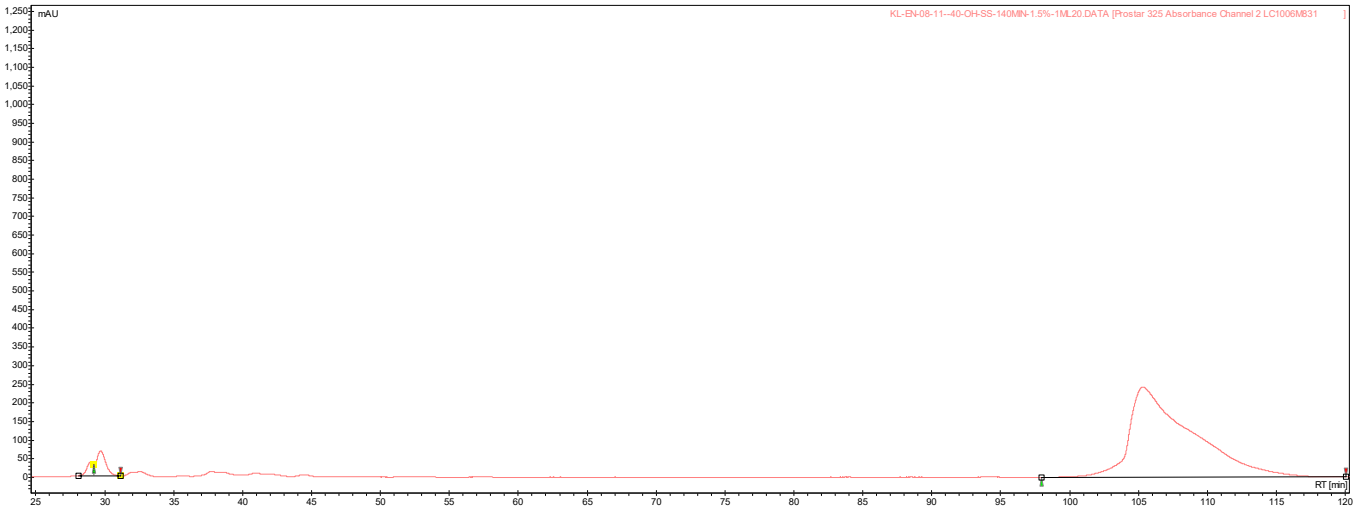




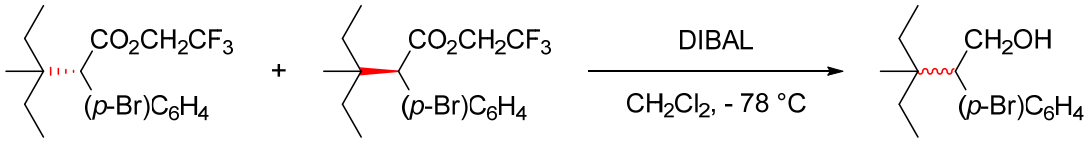
#	Time [Min]	Area % [%]
1	29.77	43.020
2	109.43	56.980



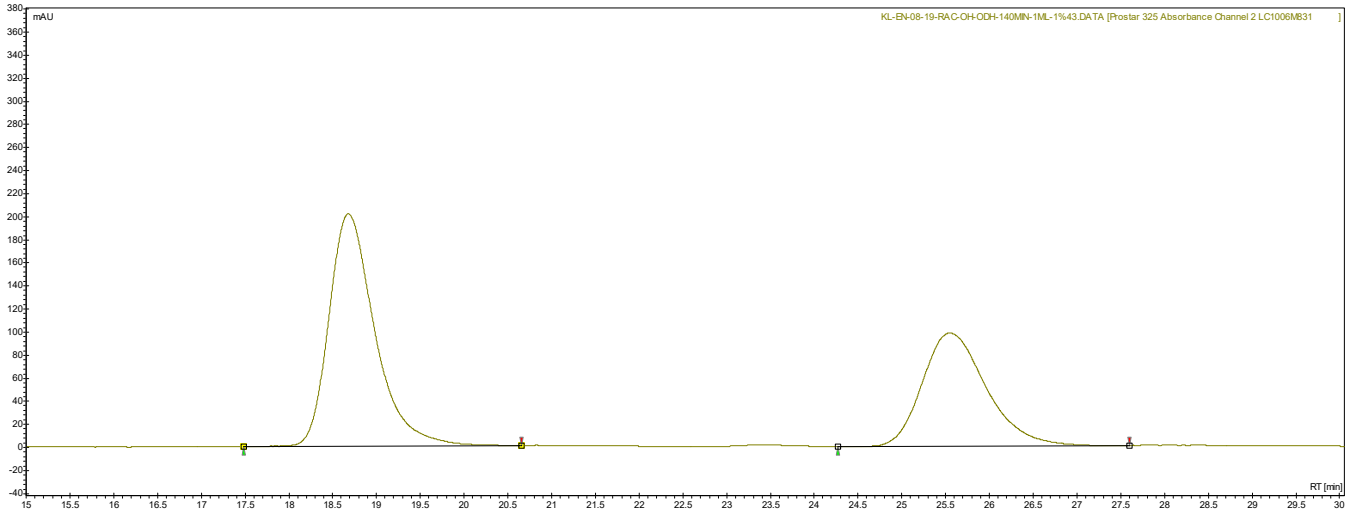
1d 3 *equiv.* **6**



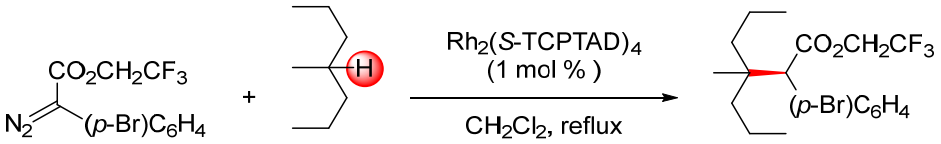
#	Time [Min]	Area % [%]
1	29.70	3.977
2	105.31	96.023
		92 % e.e.



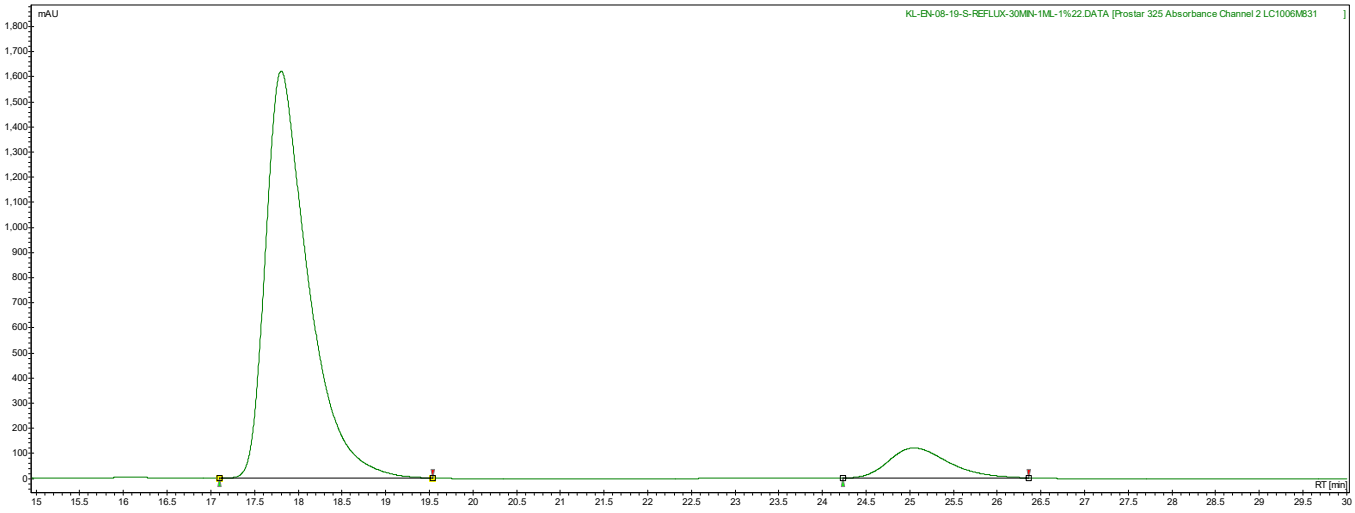
(S:R=3:2)



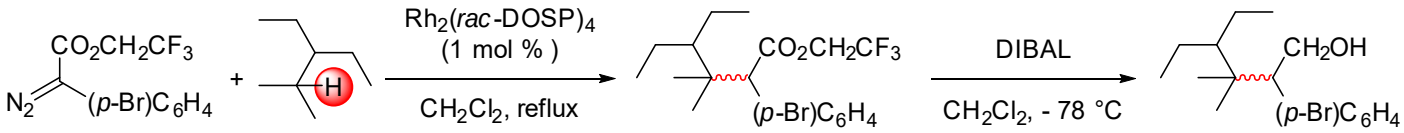
#	Time [Min]	Area % [%]
1	18.68	59.566
2	25.55	40.434

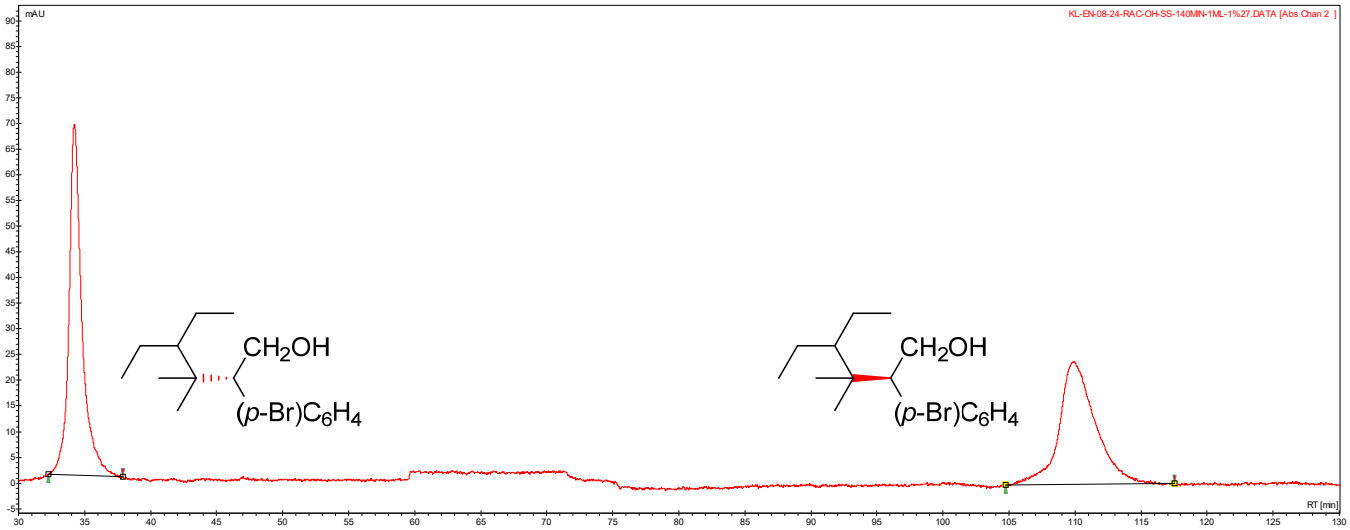


1d 3 *equiv.* **7**

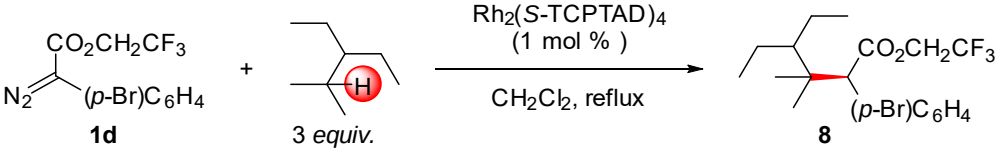


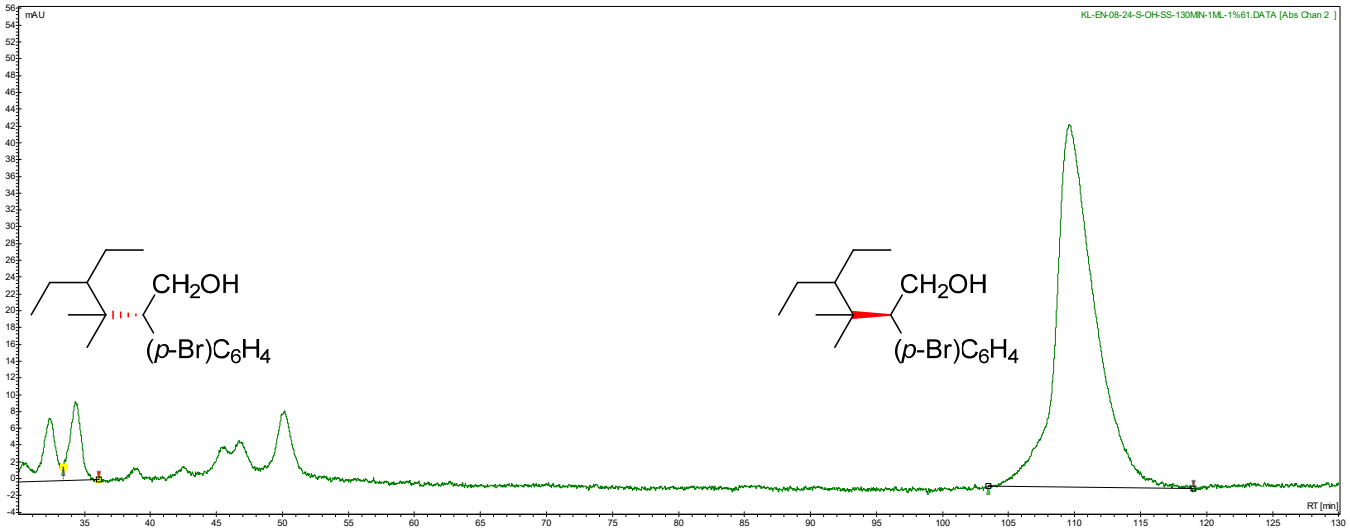
#	Time [Min]	Area % [%]
1	17.81	90.547
2	25.05	9.453
		81% e.e.



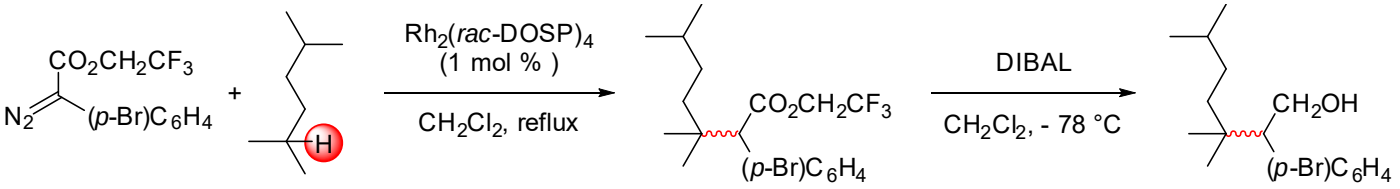


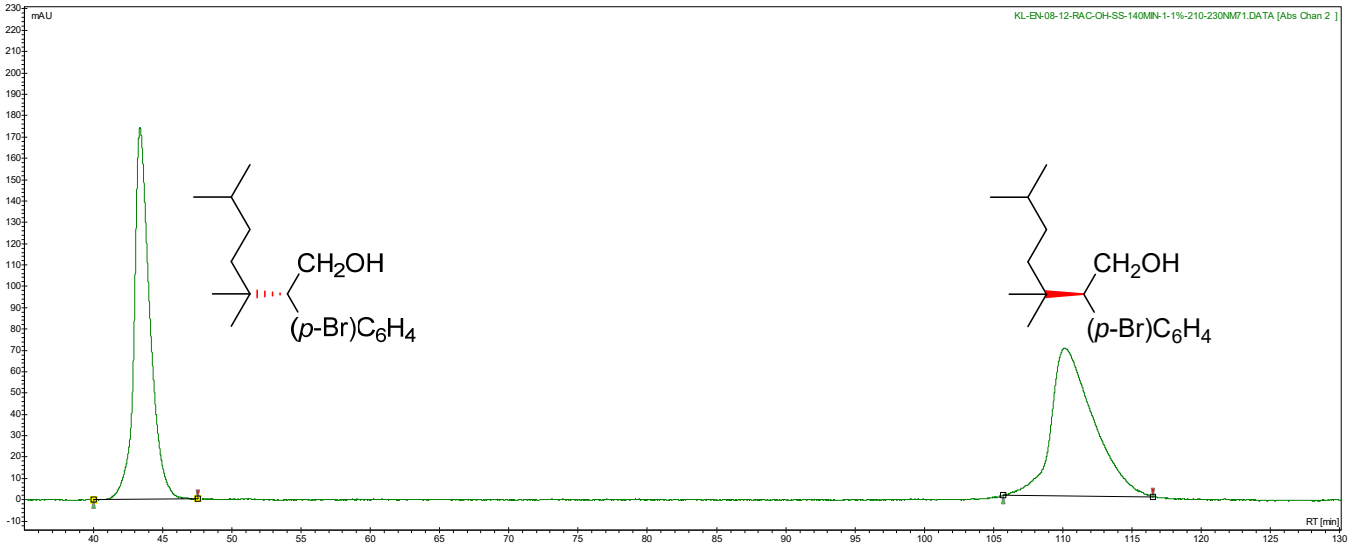
#	Time [Min]	Area % [%]
1	34.21	50.646
2	109.84	49.354



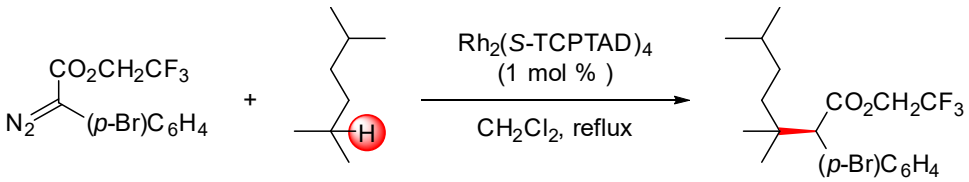


#	Time [Min]	Area % [%]
1	34.32	5.859
2	109.62	94.141
		86 % e.e.

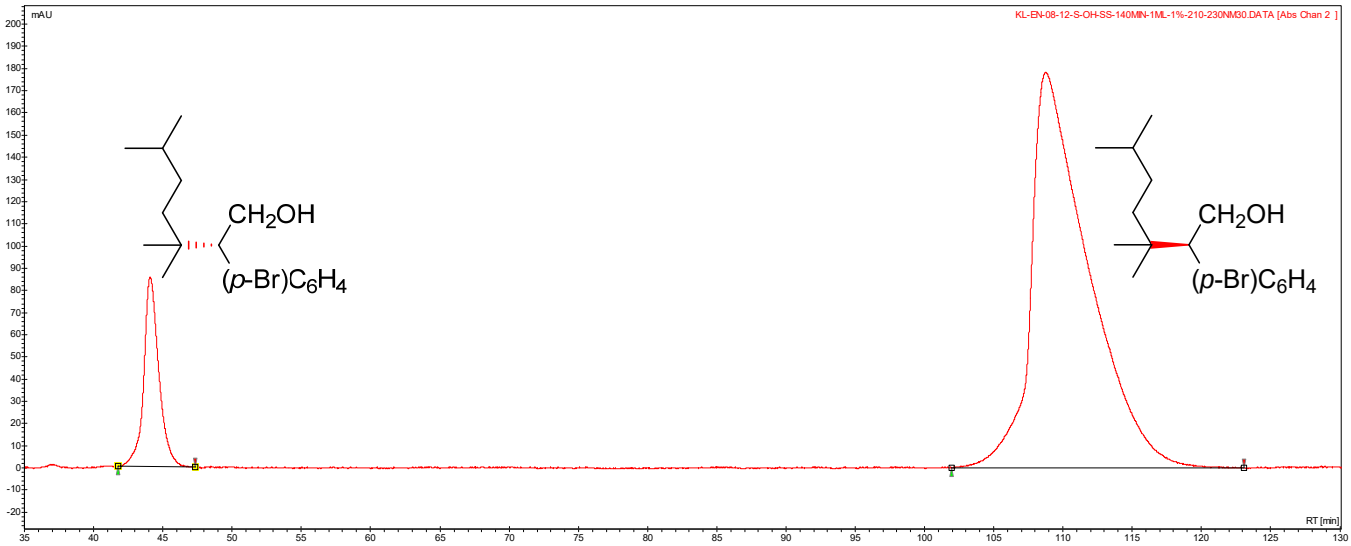




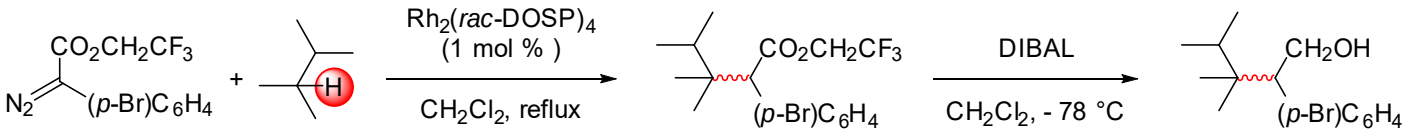
#	Time [Min]	Area % [%]
1	43.35	48.322
2	110.12	51.678

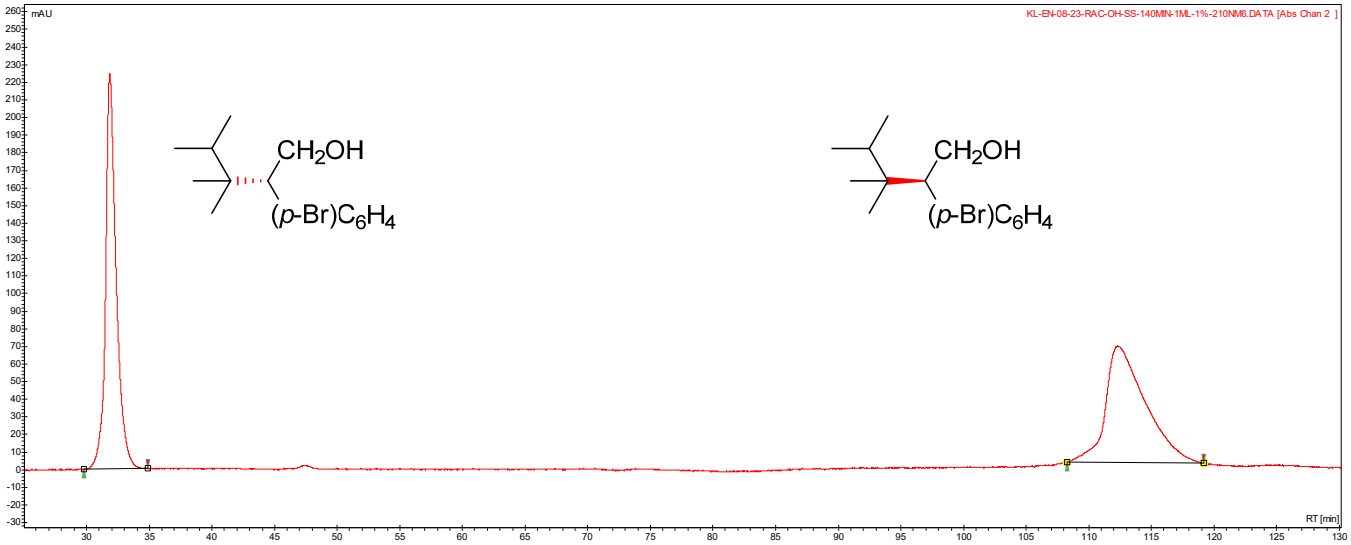


1d 3 *equiv.* **9**

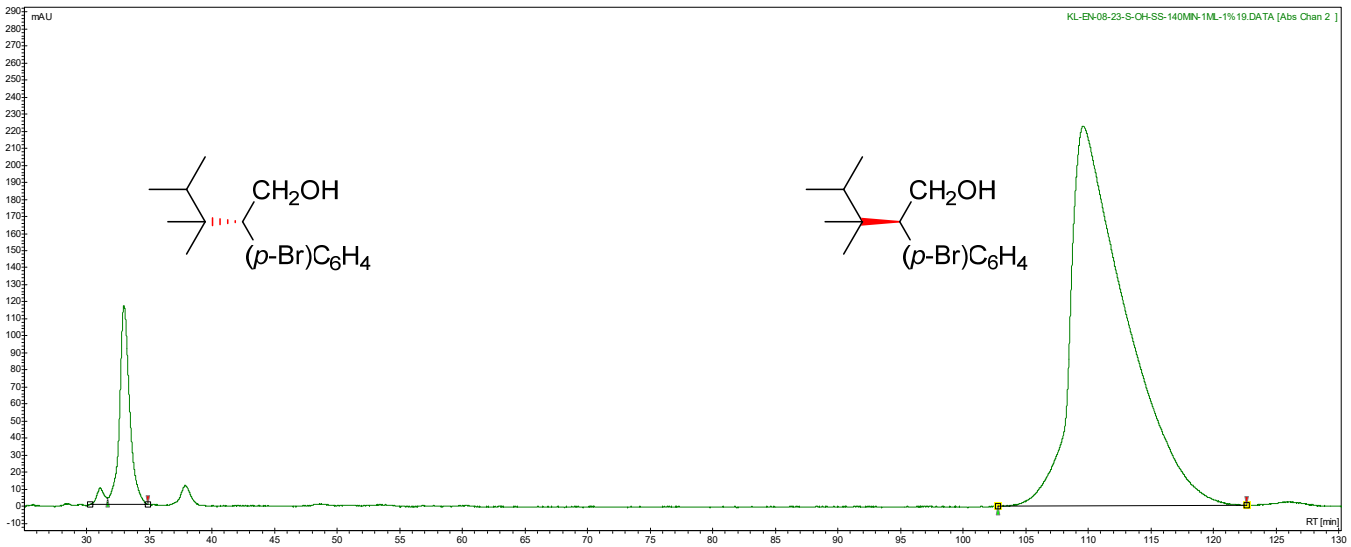


#	Time [Min]	Area % [%]
1	44.08	11.204
2	108.78	88.796
		78 % e.e.

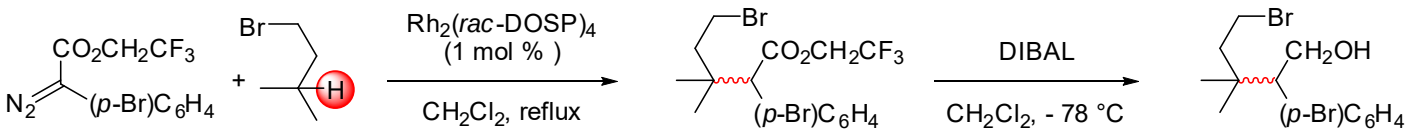


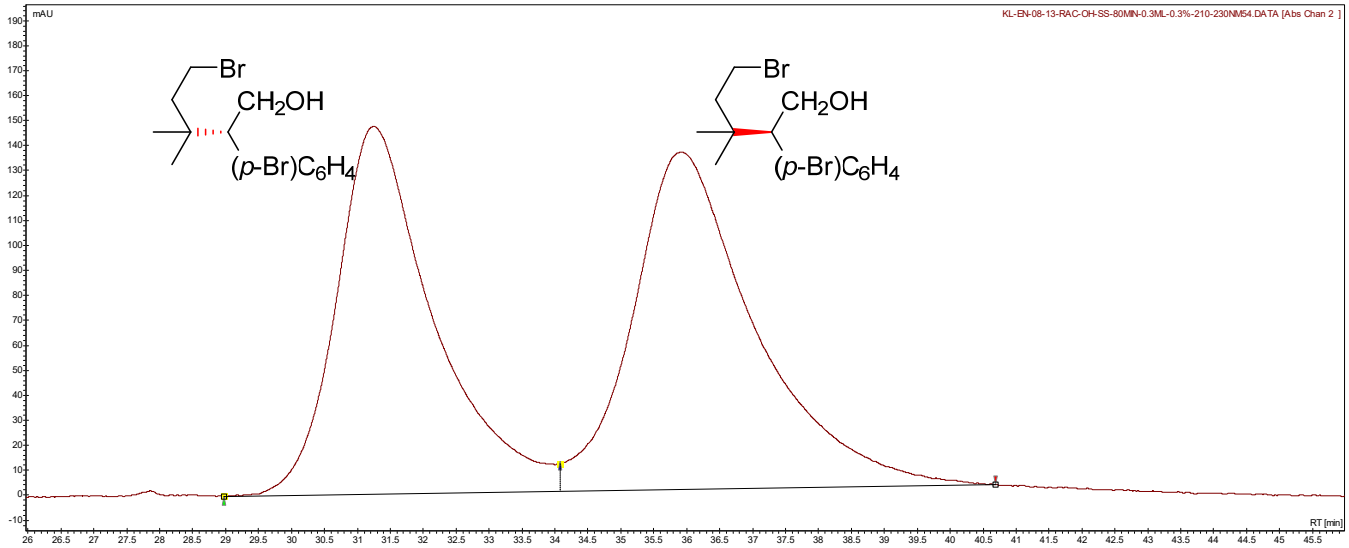


#	Time [Min]	Area % [%]
1	31.84	47.542
2	112.29	52.458

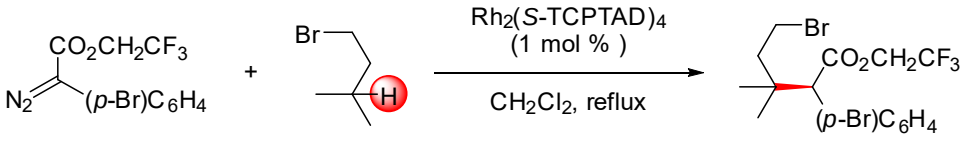


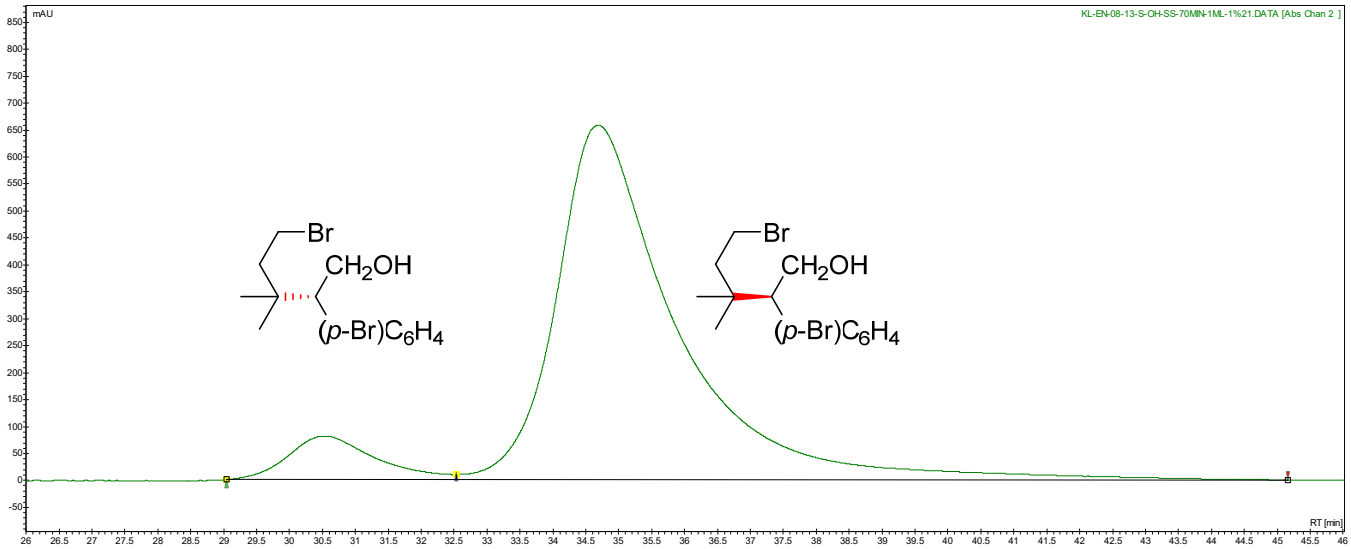
#	Time [Min]	Area % [%]
1	32.97	8.688
2	109.63	91.312
		83 % e.e.



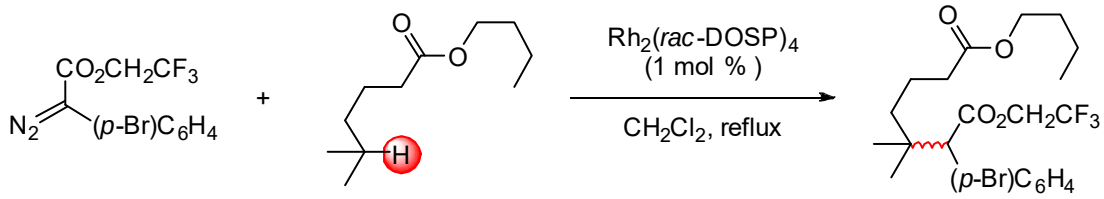


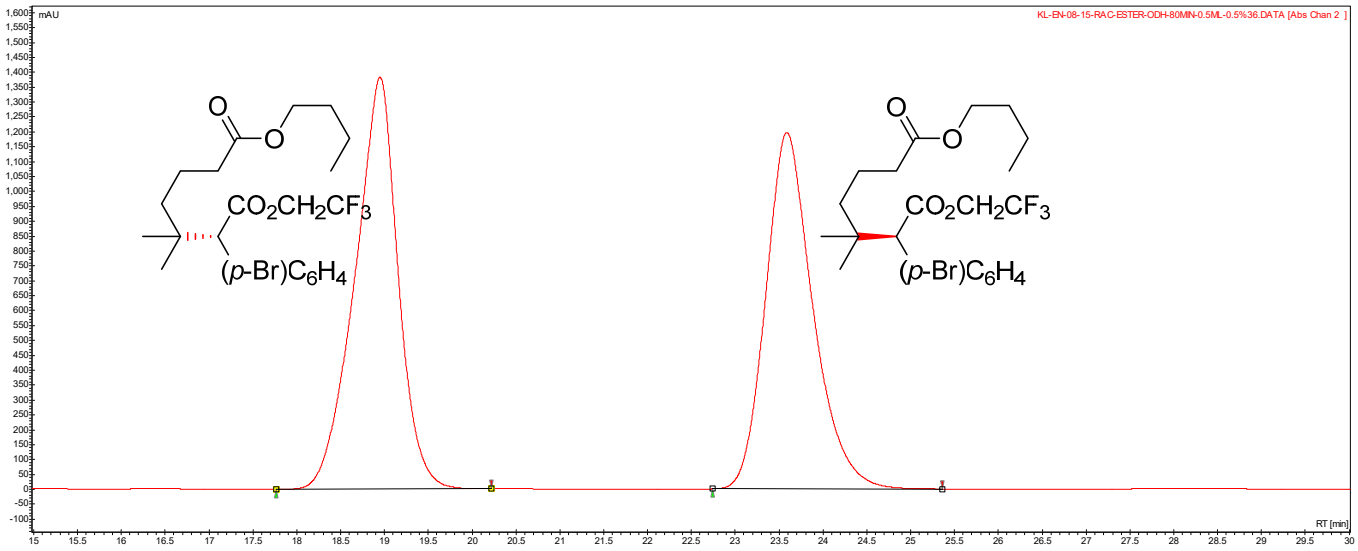
#	Time [Min]	Area % [%]
1	31.25	46.375
2	35.92	53.625



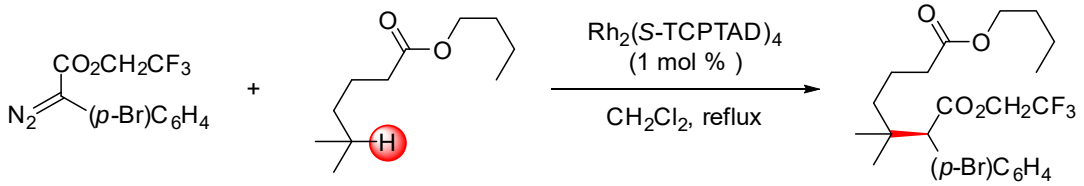


#	Time [Min]	Area % [%]
1	30.53	8.153
2	34.69	91.847
		84 % e.e.

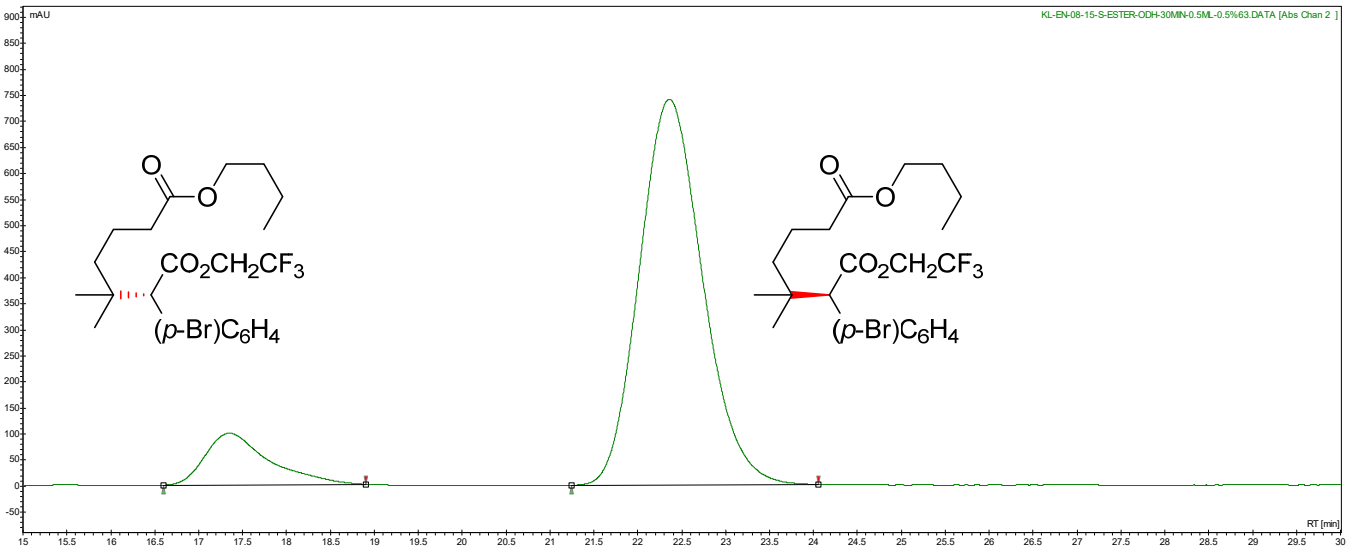




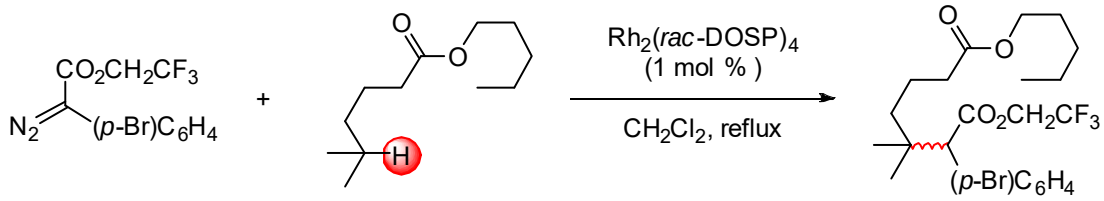
#	Time [Min]	Area % [%]
1	18.95	51.328
2	23.59	48.672

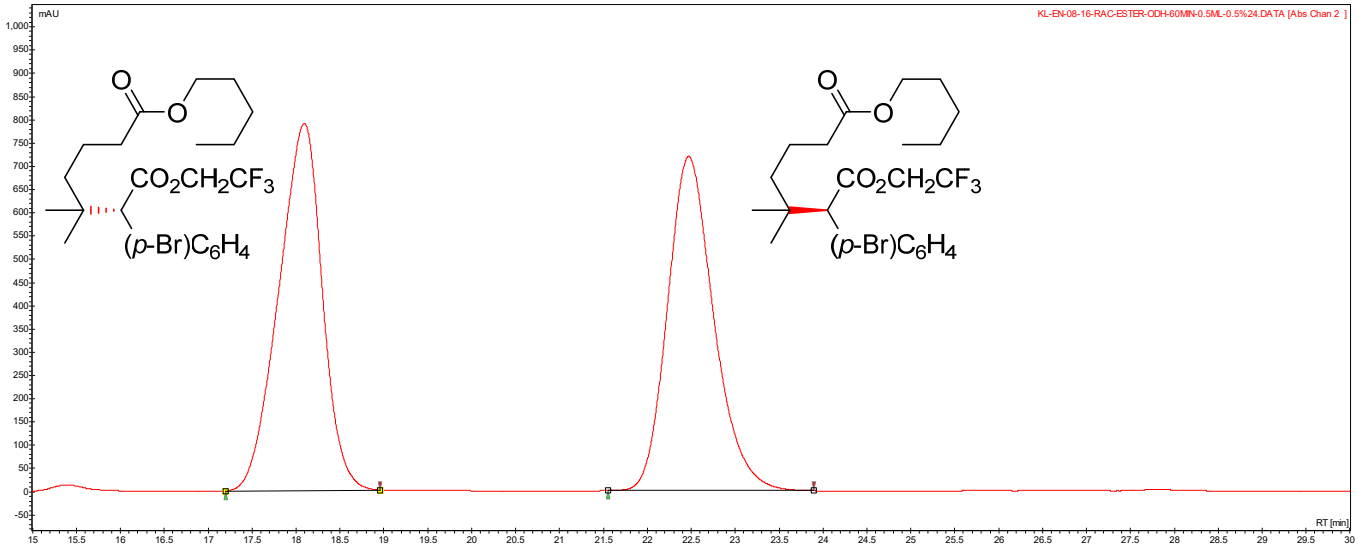


1d 3 *equiv.* **12**

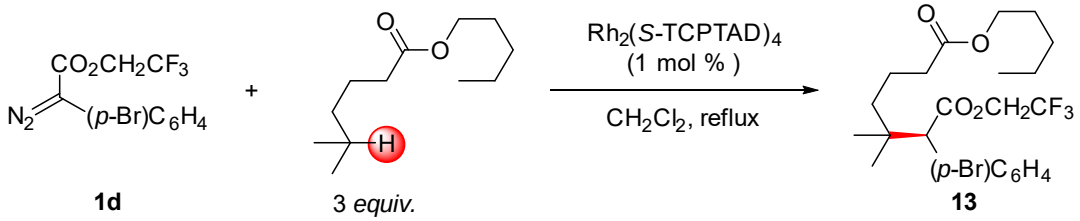


#	Time [Min]	Area % [%]
1	17.35	11.928
2	22.36	88.072
		77 % e.e.

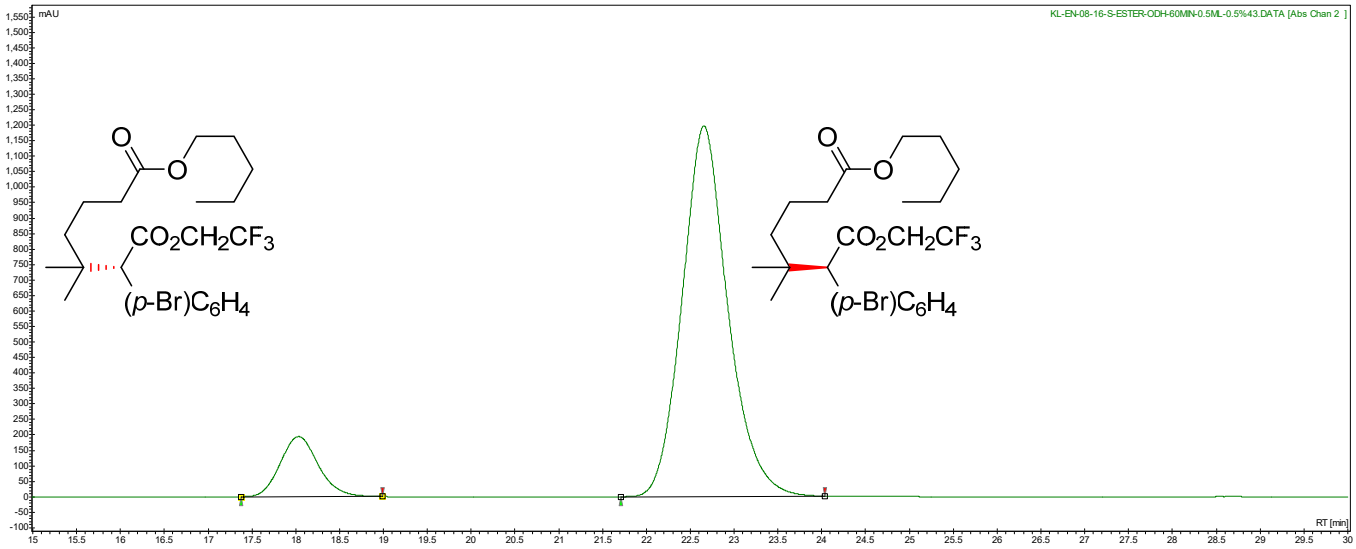




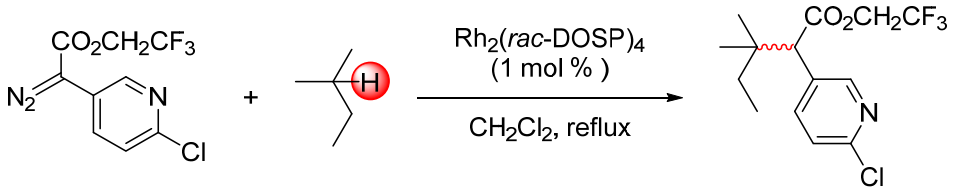
#	Time [Min]	Area % [%]
1	18.09	50.801
2	22.47	49.199

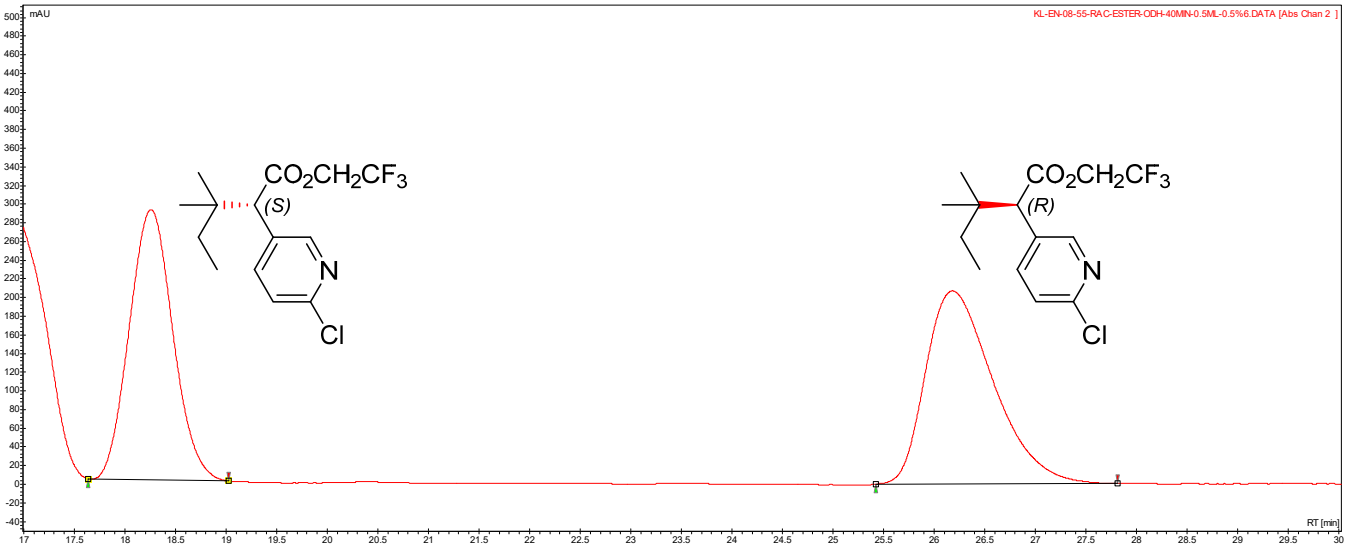


1d 3 *equiv.* **13**

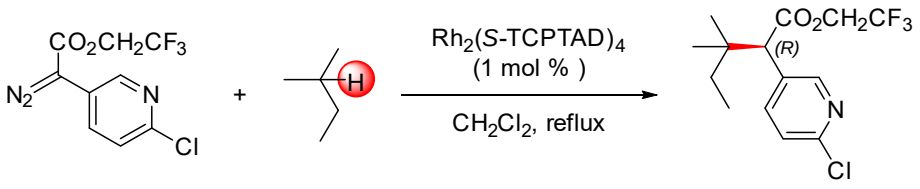


#	Time [Min]	Area % [%]
1	18.03	11.871
2	22.66	88.129
		76 % e.e.



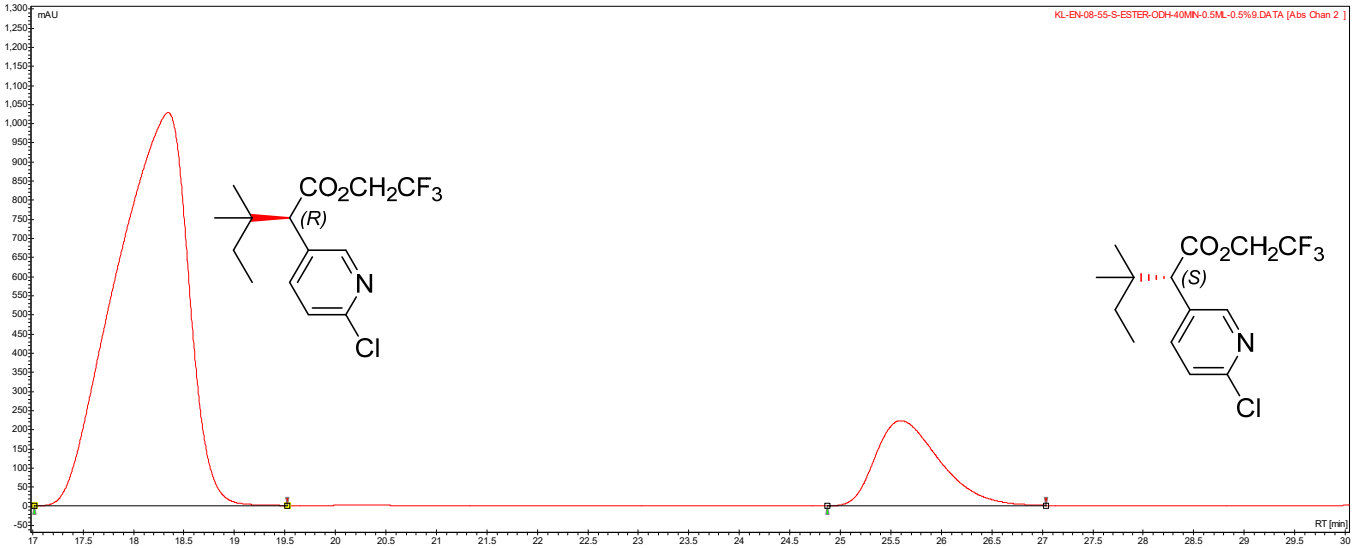


#	Time [Min]	Area % [%]
1	18.26	47.418
2	26.18	52.582

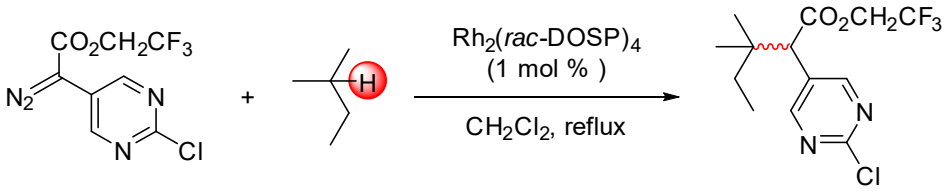


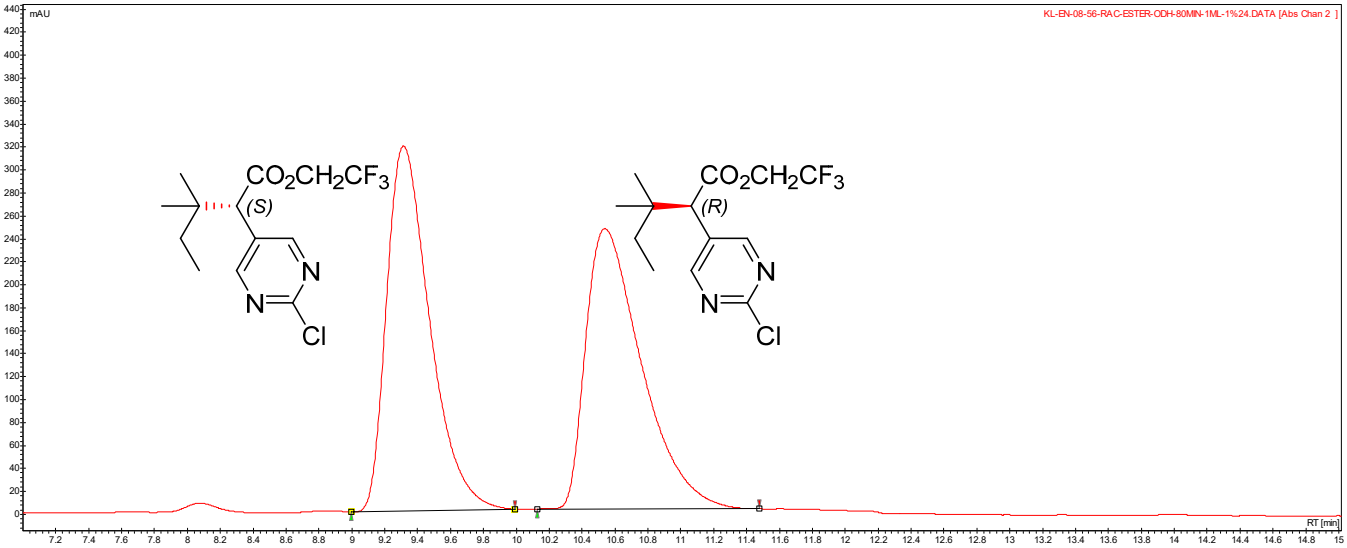
3 *equiv.*

14

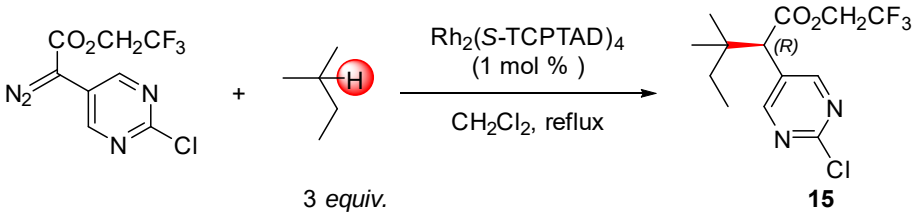


#	Time [Min]	Area % [%]
1	18.34	83.806
2	25.60	16.194
		68 % e.e.



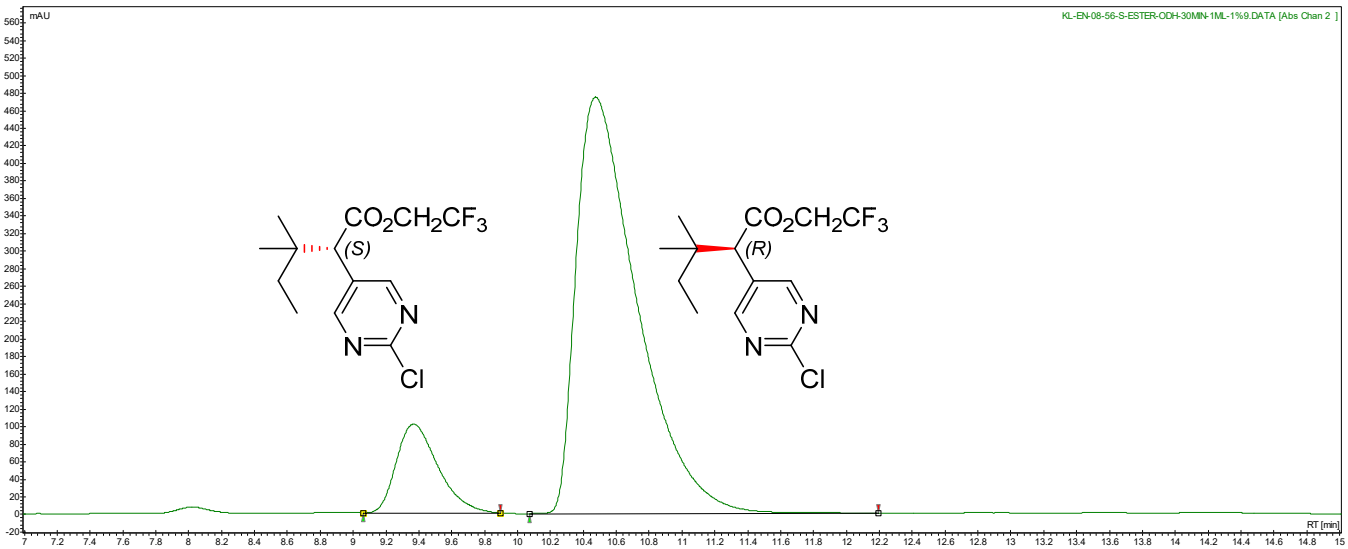


#	Time [Min]	Area % [%]
1	9.31	50.138
2	10.54	49.862

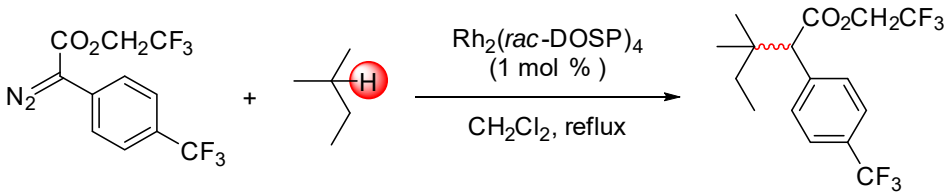


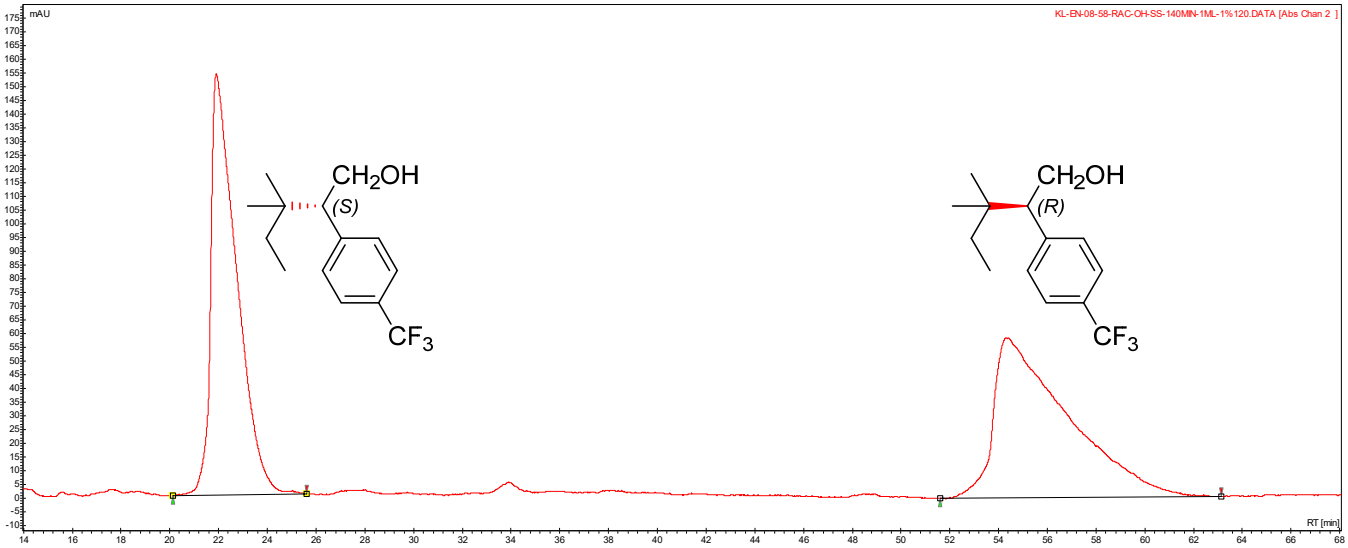
3 *equiv.*

15

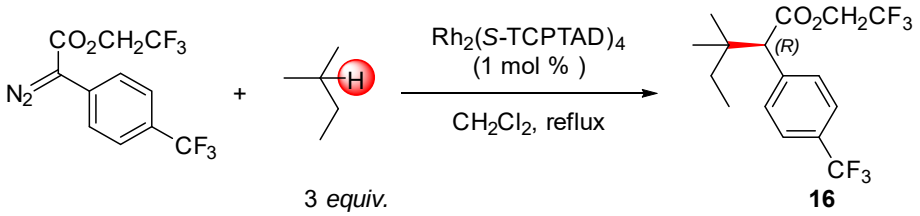


#	Time [Min]	Area % [%]
1	9.37	12.701
2	10.47	87.299
		75 % e.e.



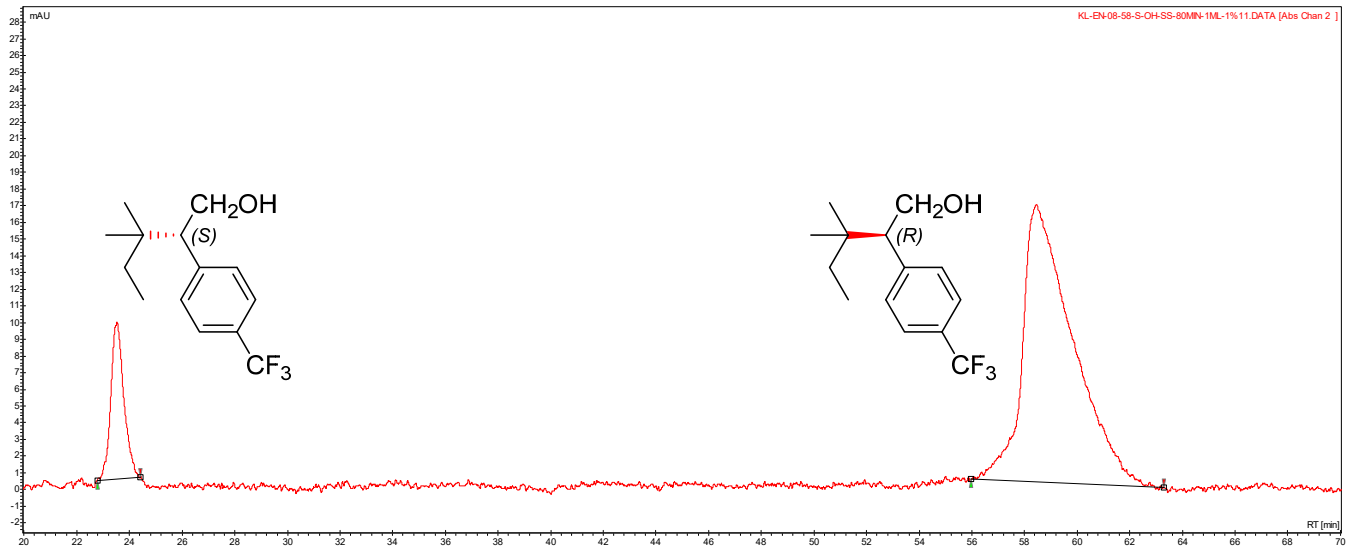


#	Time [Min]	Area % [%]
1	21.91	47.862
2	54.41	52.138

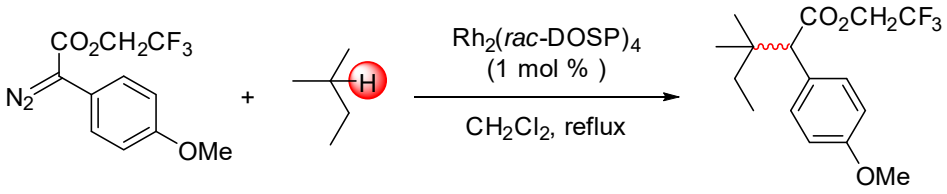


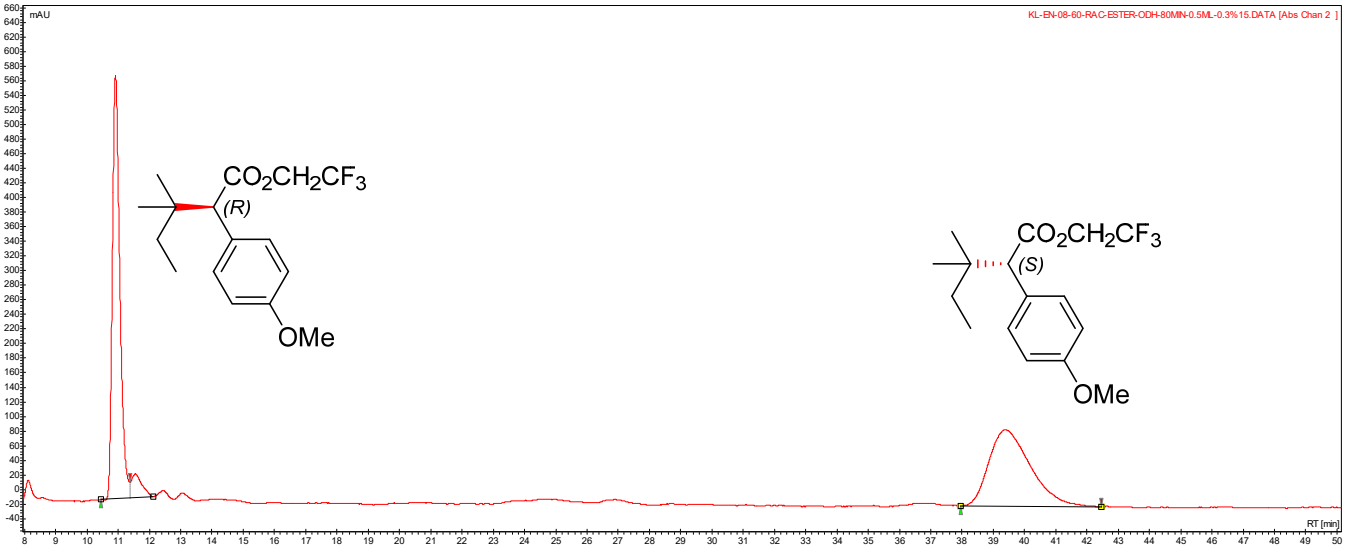
3 *equiv.*

16

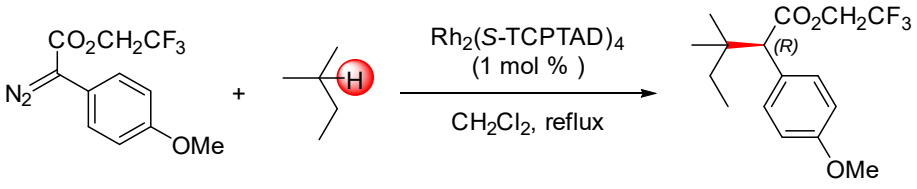


#	Time [Min]	Area % [%]
2	23.53	12.822
1	58.45	87.178
		74 % e.e.



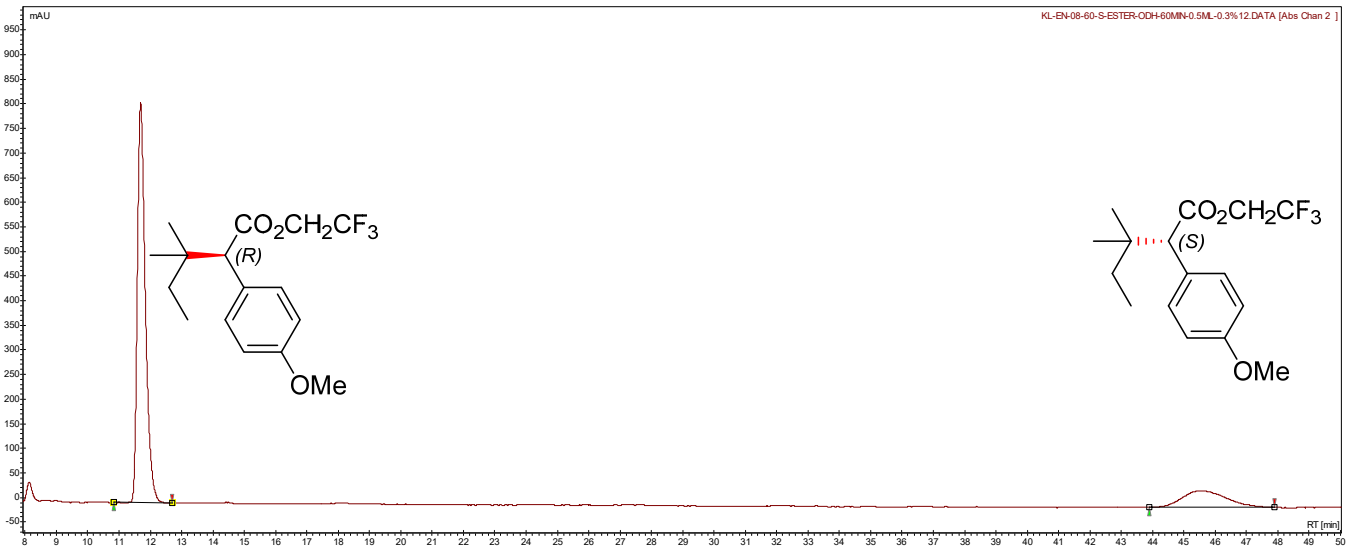


#	Time [Min]	Area % [%]
1	21.91	47.862
2	54.41	52.138

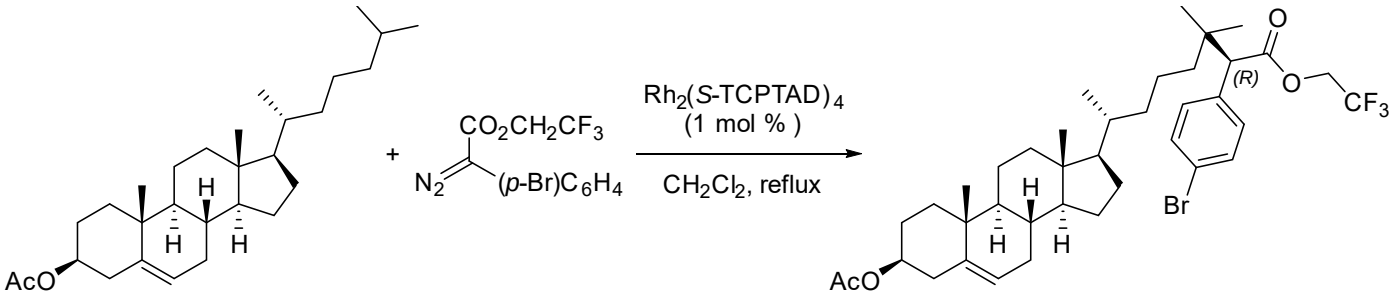


3 *equiv.*

17



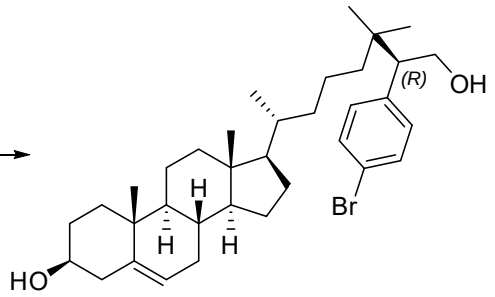
#	Time [Min]	Area % [%]
1	11.69	81.477
2	45.61	18.523
		63 % e.e.

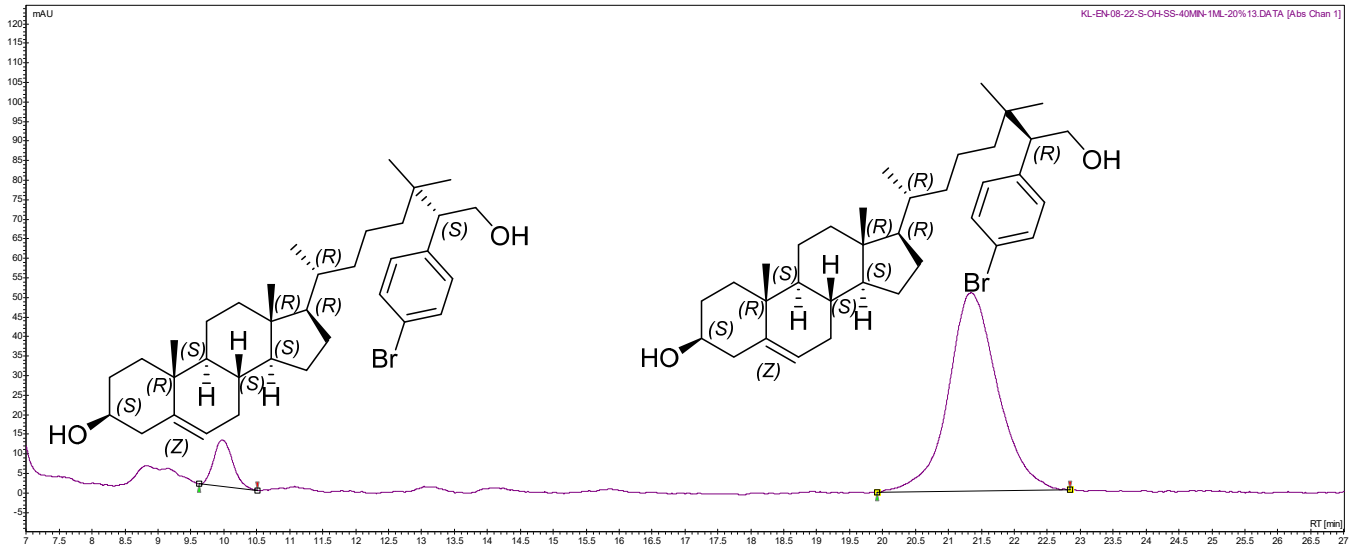


18
1 *equiv.*

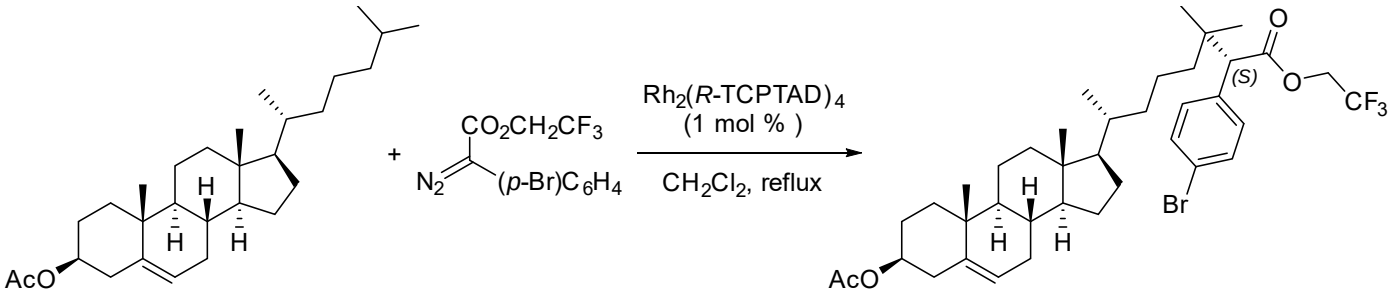
1d
1 *equiv.*

19





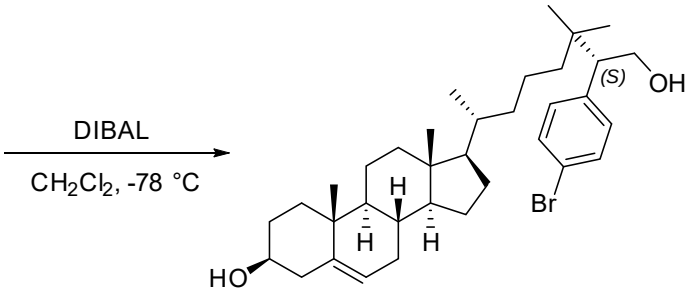
#	Time [Min]	Area % [%]
1	9.97	8.250
2	21.34	91.750
		11:1 d.r.

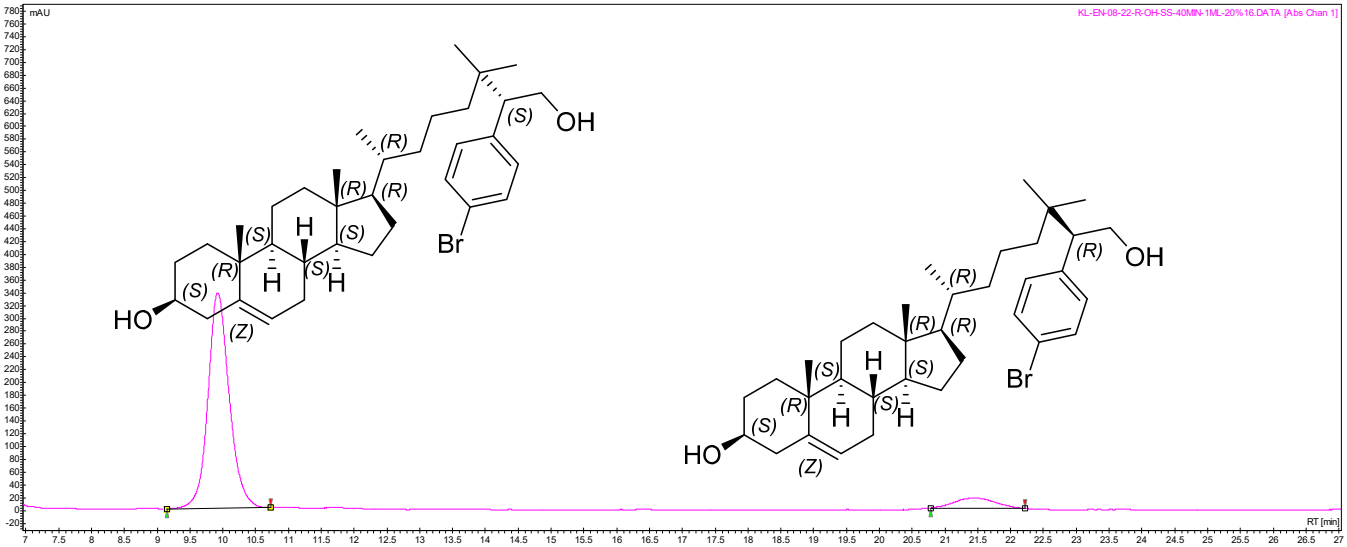


18
1 *equiv.*

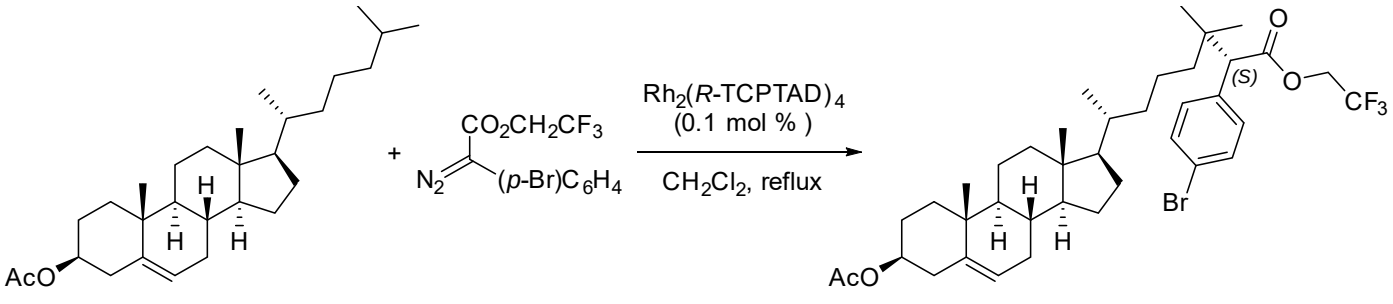
1d
1 *equiv.*

19





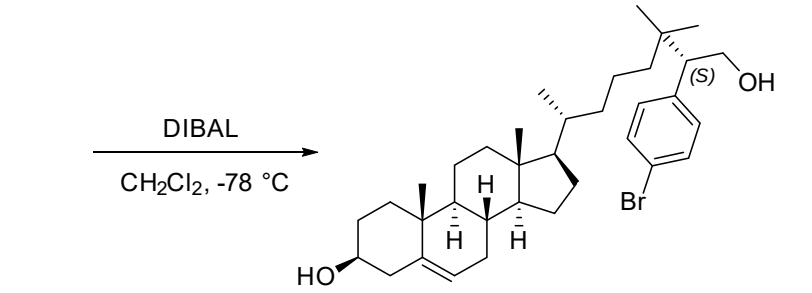
#	Time [Min]	Area % [%]
1	9.92	91.762
2	21.46	8.238
		11:1 d.r.

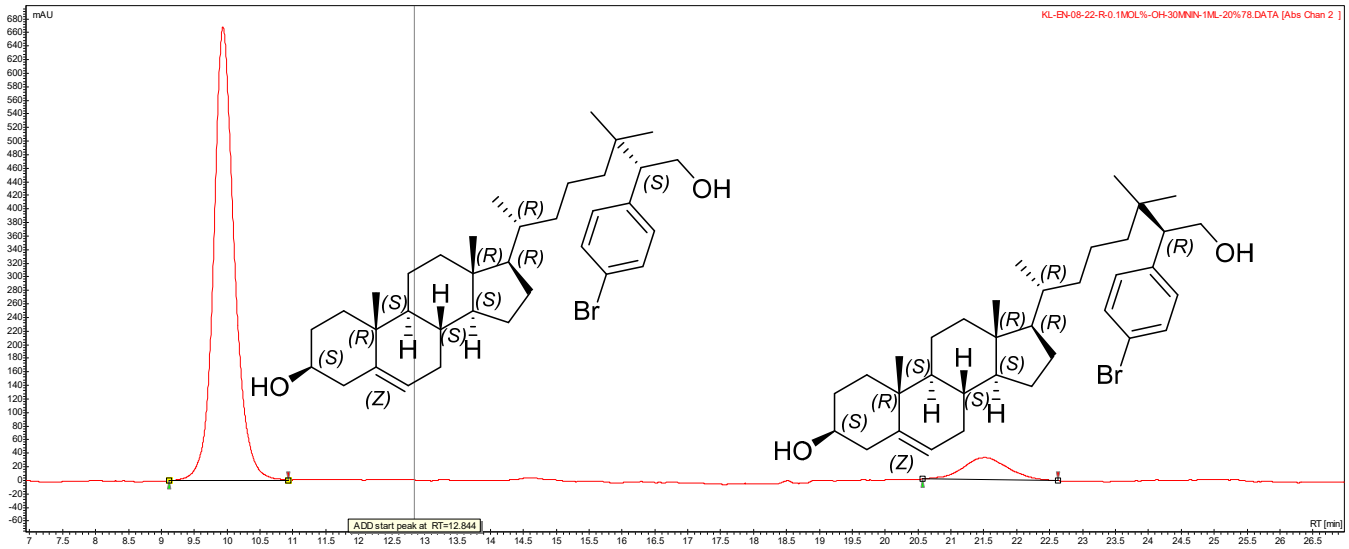


18
1 *equiv.*

1d
1 *equiv.*

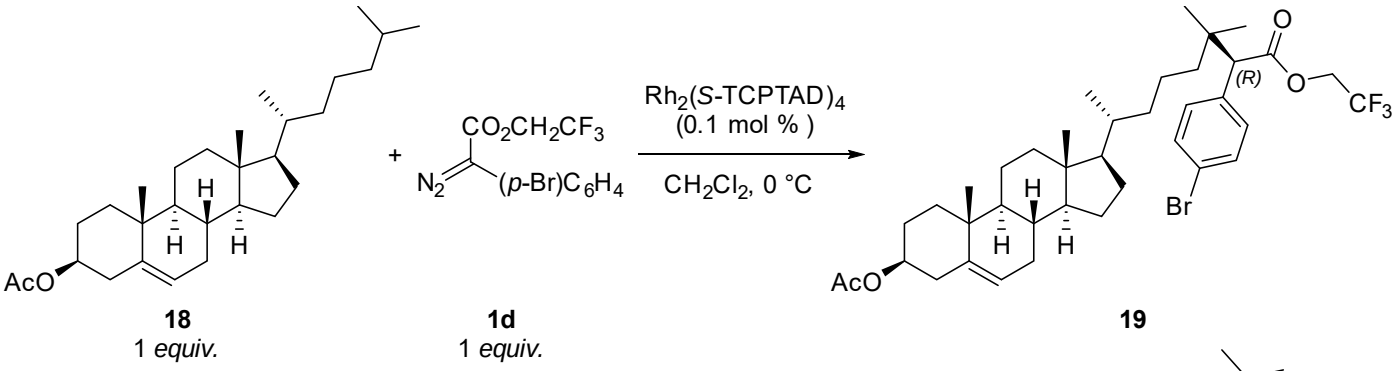
19





#	Time [Min]	Area % [%]
1	9.94	90.311
2	21.51	9.689
		9:1 d.r.

A different HPLC machine with a different S,S-whelk chiral column was used, so the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$.

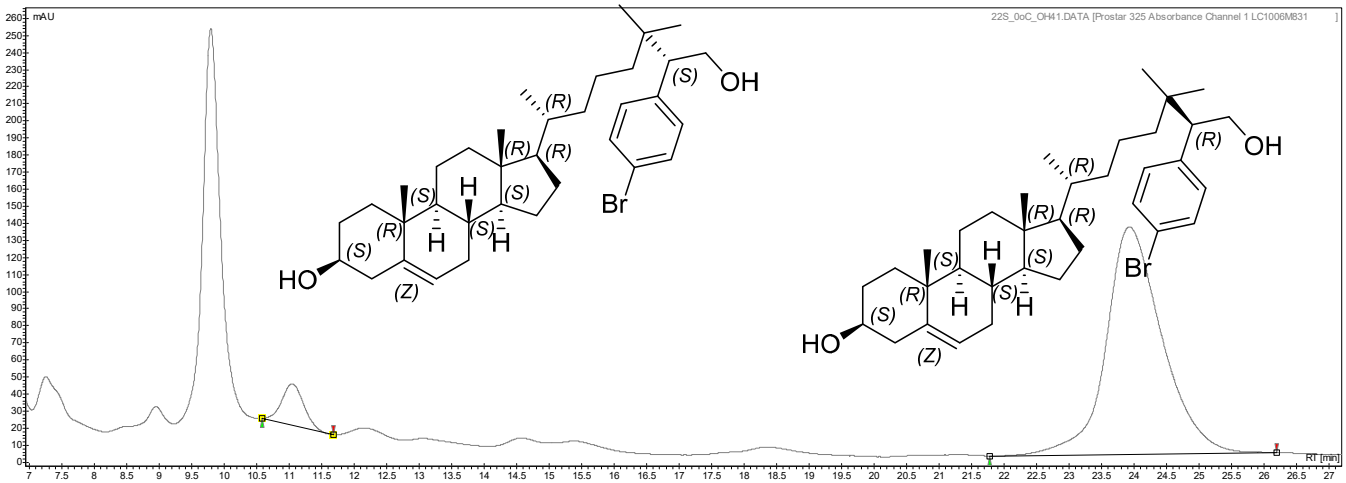


18
1 *equiv.*

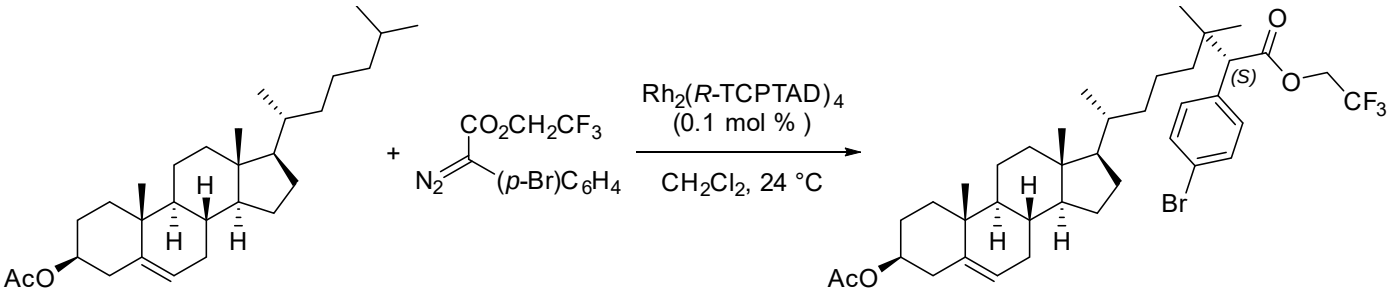
1d
1 *equiv.*

19

DIBAL
CH_2Cl_2, -78 °C



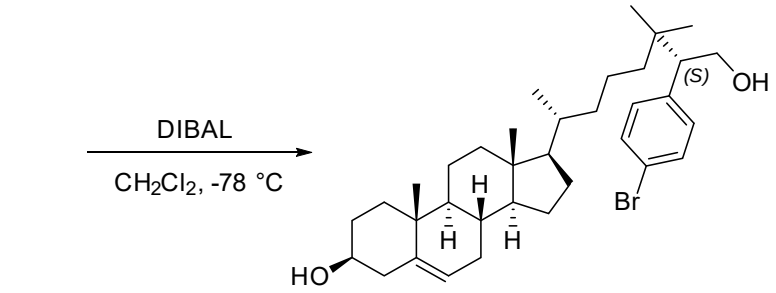
#	Time [Min]	Area % [%]
1	11.05	6.709
2	23.92	93.291
		14:1 d.r.

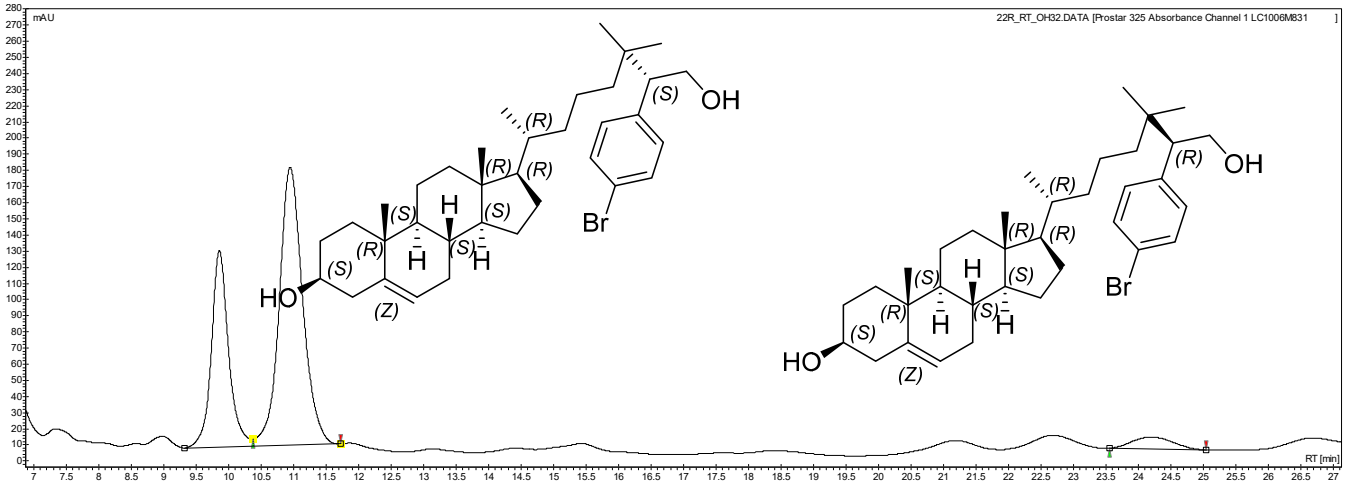


18
1 *equiv.*

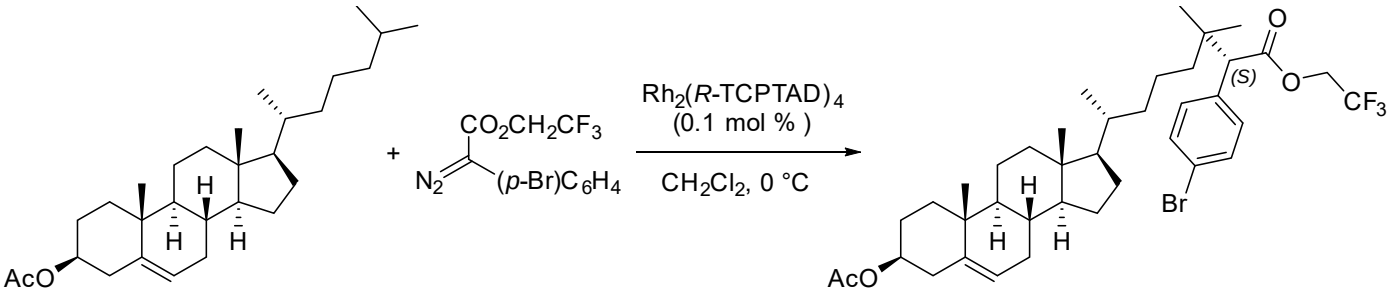
1d
1 *equiv.*

19





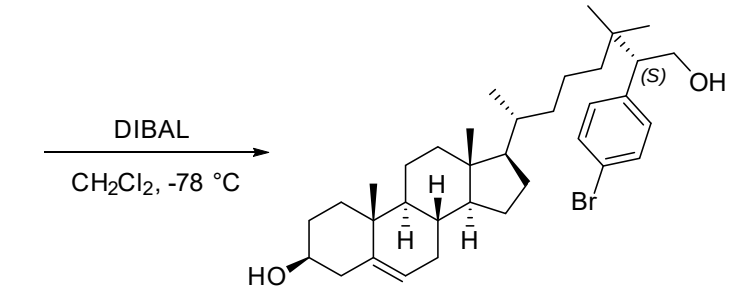
#	Time [Min]	Area % [%]
1	10.94	92.926
2	24.19	7.074
		13:1 d.r.

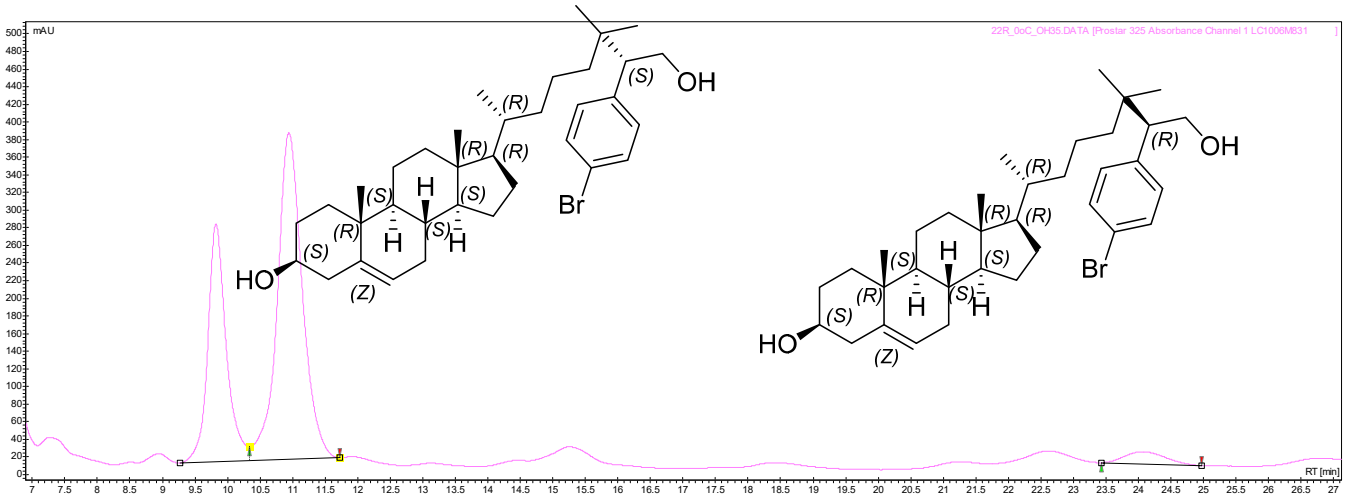


18
1 *equiv.*

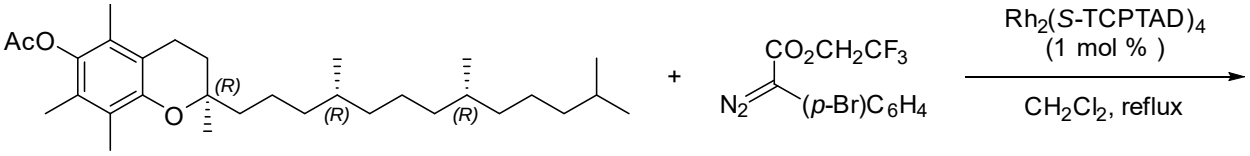
1d
1 *equiv.*

19



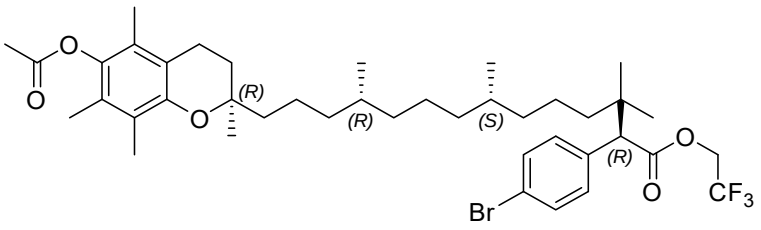


#	Time [Min]	Area % [%]
1	10.94	94.267
2	24.08	5.733
		16:1 d.r.

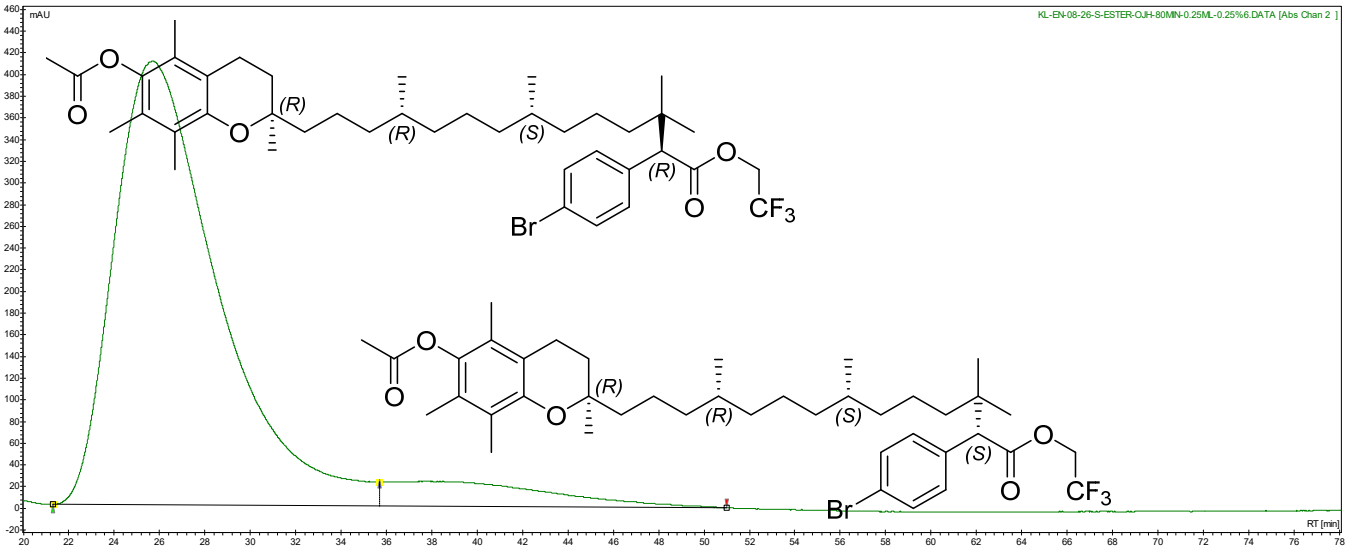


20
1 *equiv.*

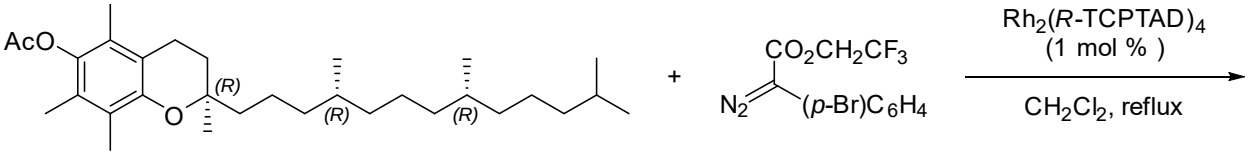
1d
1 *equiv.*



21

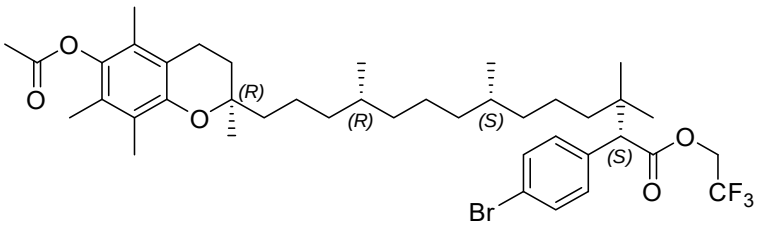


#	Time [Min]	Area % [%]
1	25.74	91.846
2	37.89	8.154
		11:1 d.r.

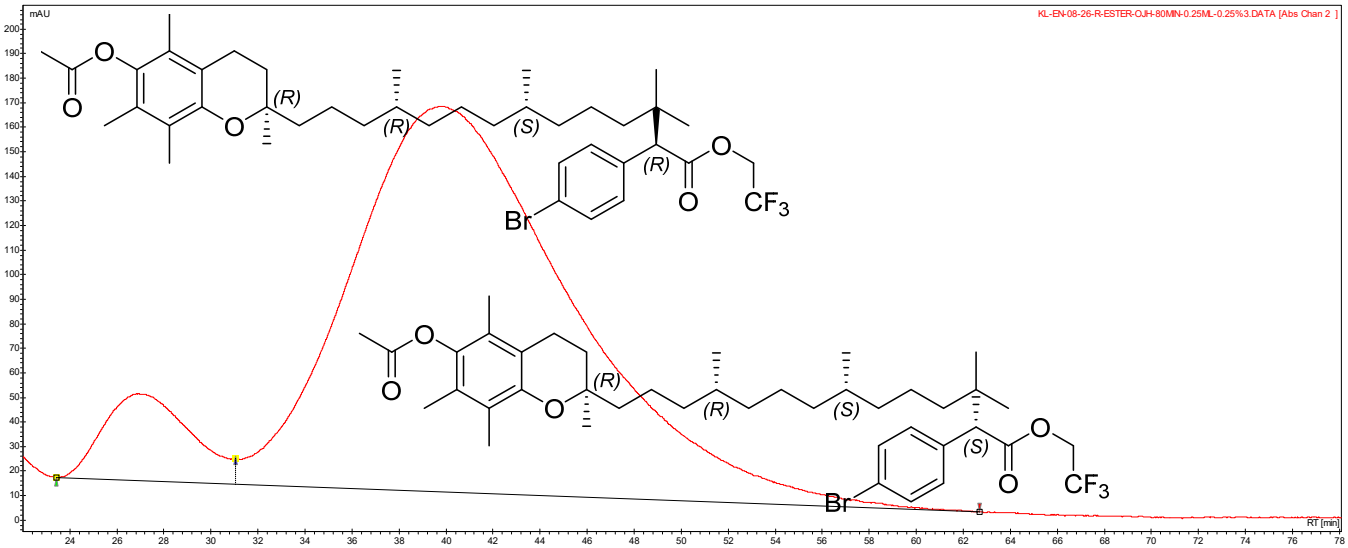


20
1 *equiv.*

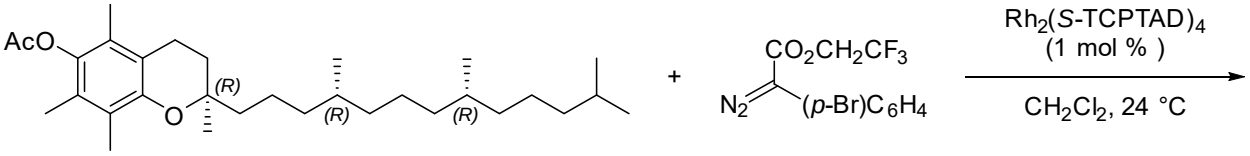
1d
1 *equiv.*



21

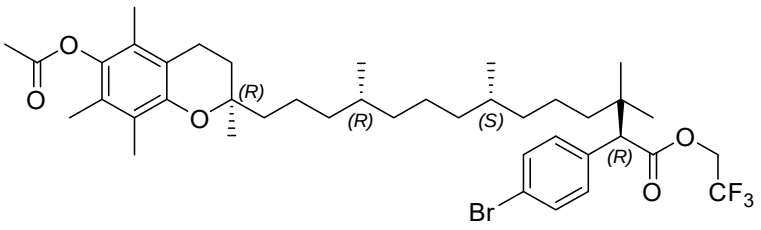


#	Time [Min]	Area % [%]
1	26.94	8.220
2	39.92	91.780
		11:1 d.r.

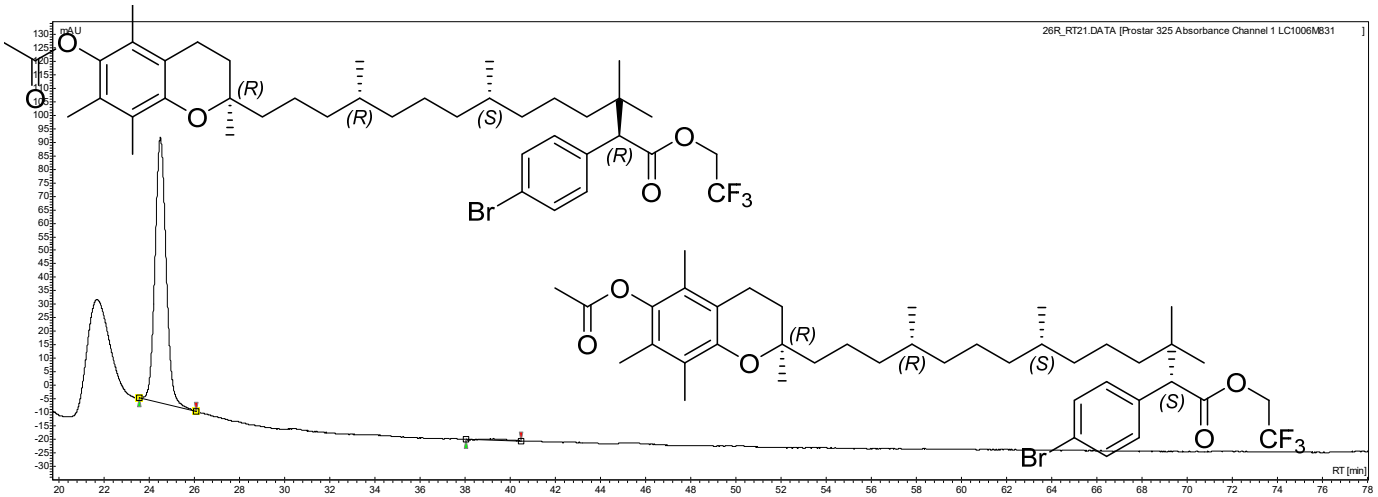


20
1 *equiv.*

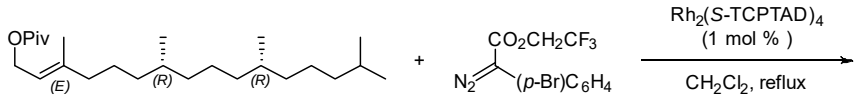
1d
1 *equiv.*



21

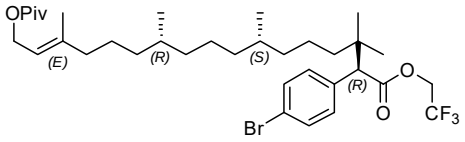


#	Time [Min]	Area % [%]
1	24.49	99.363
2	39.25	0.637
		>20:1 d.r.

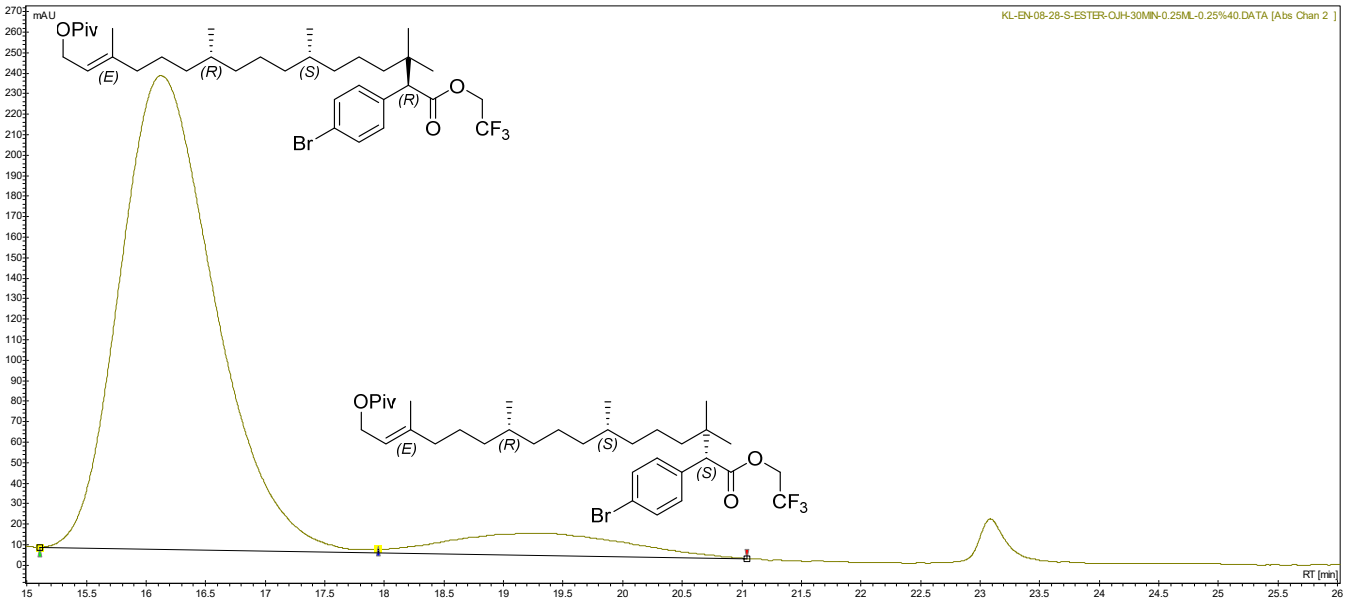


22
1 *equiv.*

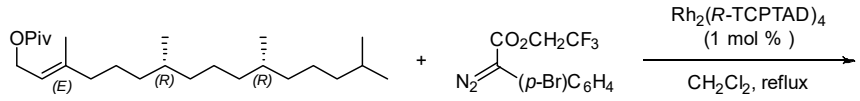
1d
1 *equiv.*



23

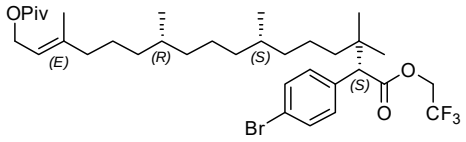


#	Time [Min]	Area % [%]
1	16.12	91.930
2	19.36	8.070
		11:1 d.r.

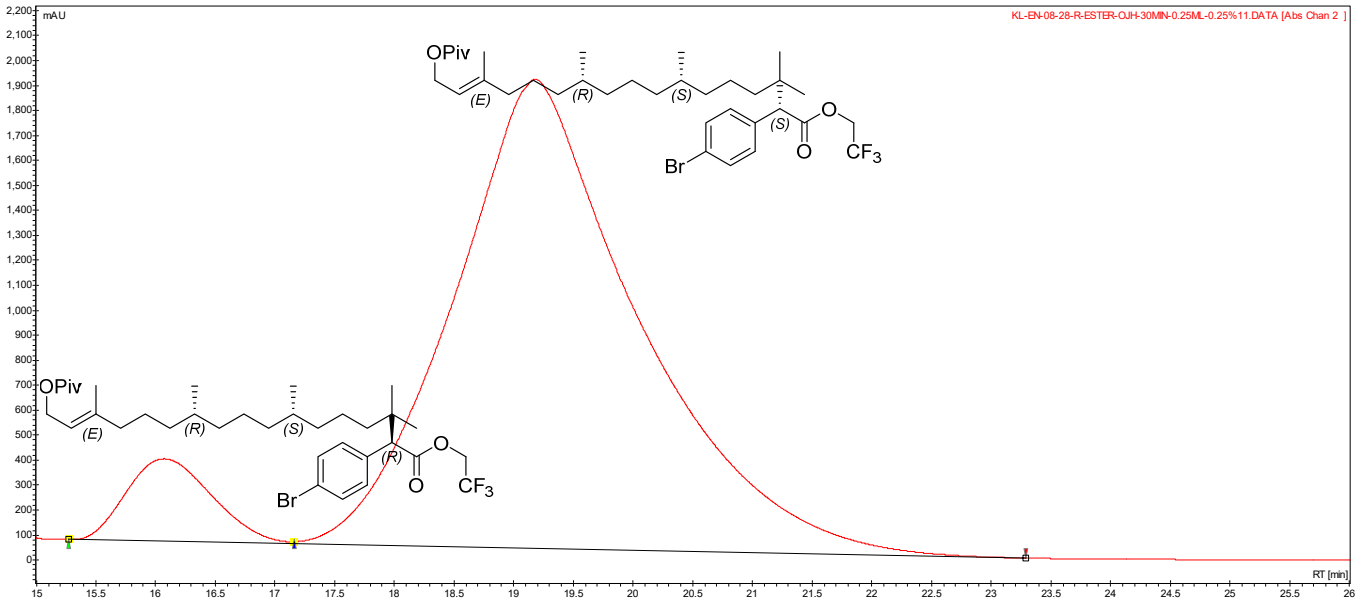


22
1 *equiv.*

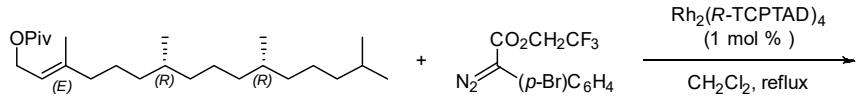
1d
1 *equiv.*



23

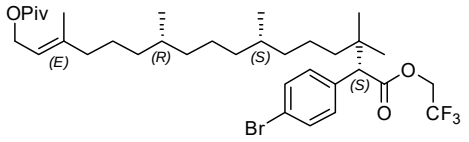


#	Time [Min]	Area % [%]
1	16.07	7.550
2	19.18	92.450
		12:1 d.r.

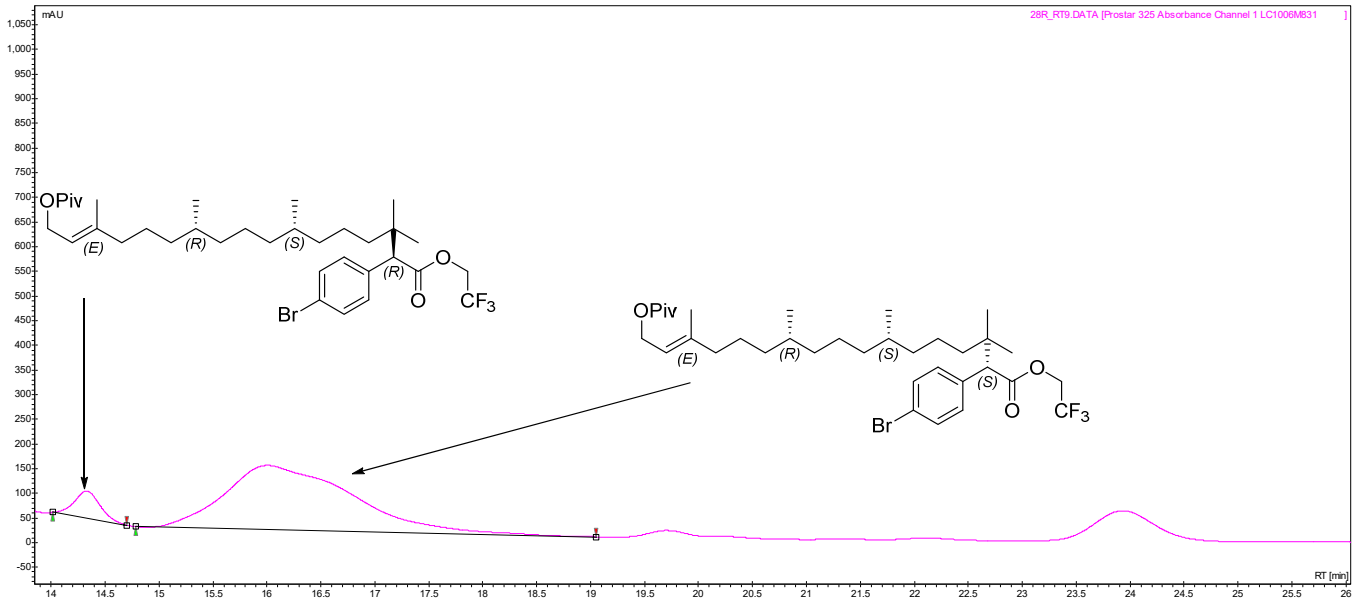


22
1 *equiv.*

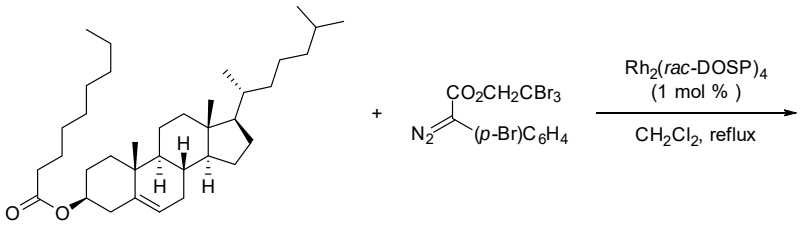
1d
1 *equiv.*



23

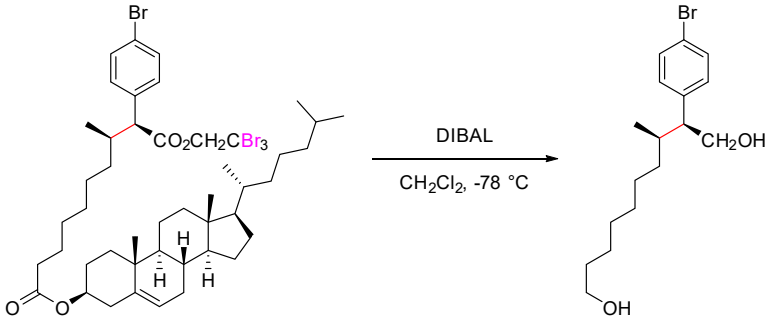


#	Time [Min]	Area % [%]
1	14.34	7.905
2	16.01	92.096
		12:1 d.r.

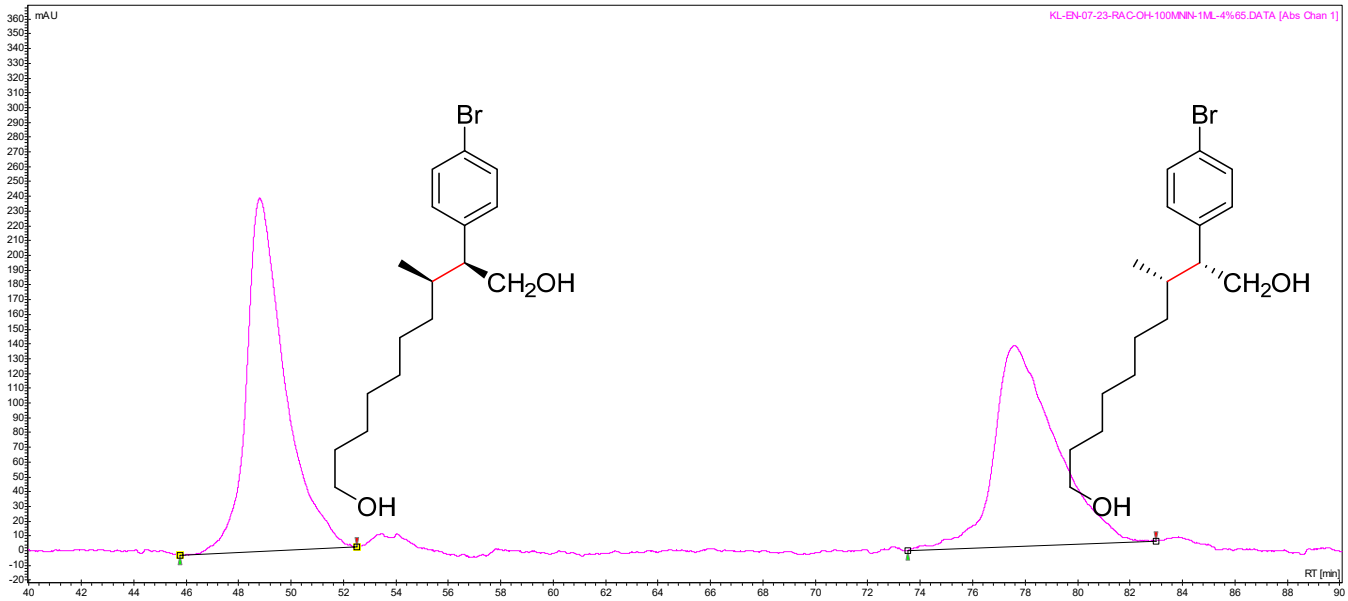


25
1 *equiv.*

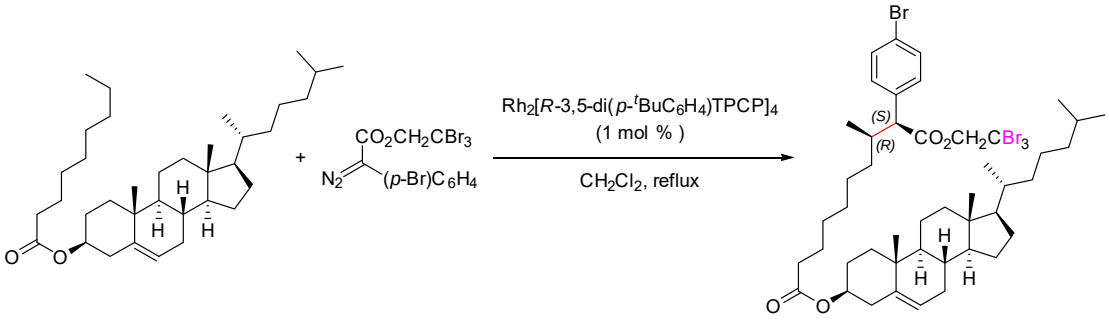
1c
1 *equiv.*



(±)26



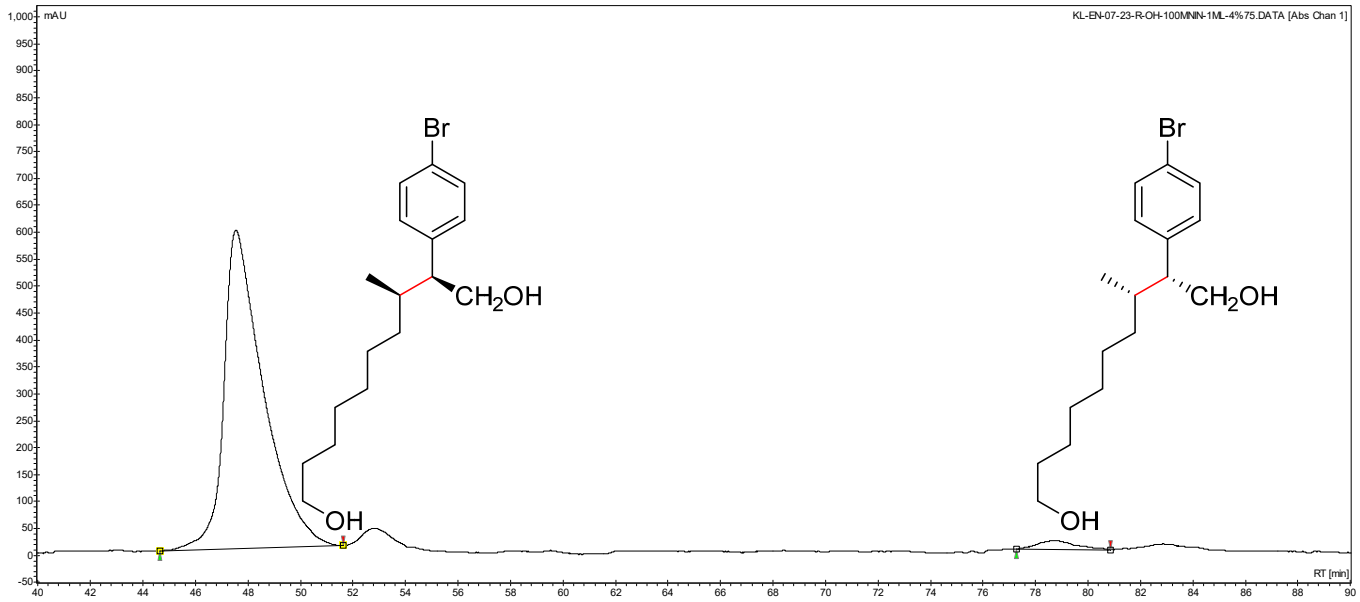
#	Time [Min]	Area % [%]
1	48.80	52.343
2	77.61	47.657



25
1 *equiv.*

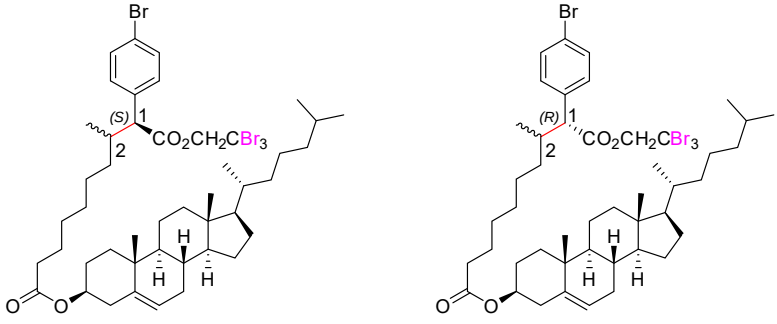
1c
1 *equiv.*

26

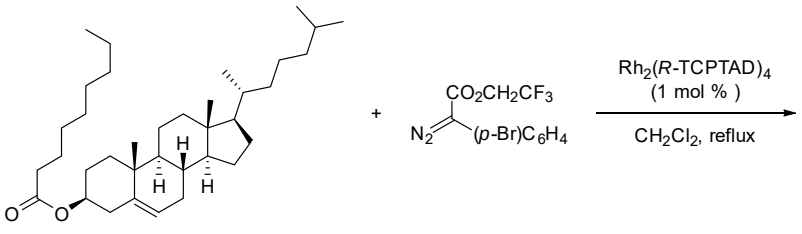


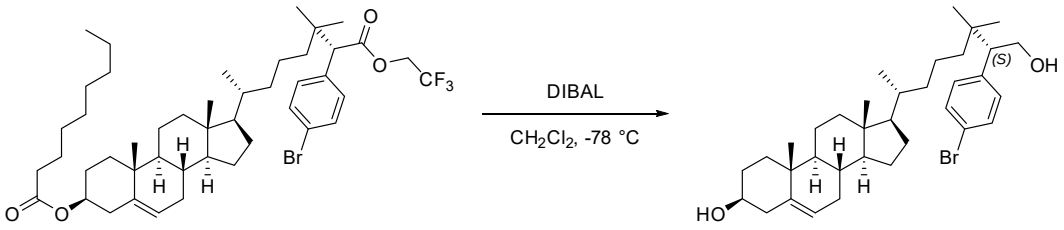
#	Time [Min]	Area % [%]
1	47.53	97.512
2	78.83	2.488
		39:1 d.r.

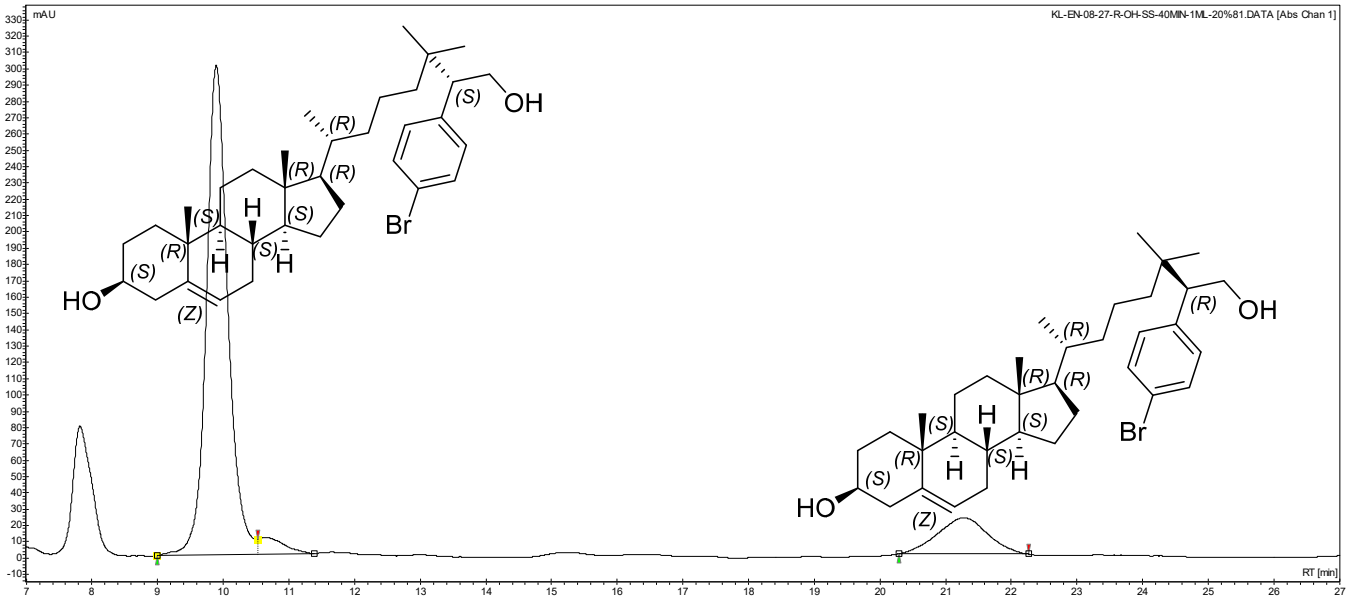
The 39:1 d.r. represents the ratio of C1 chiral center to the steroid, as shown below:



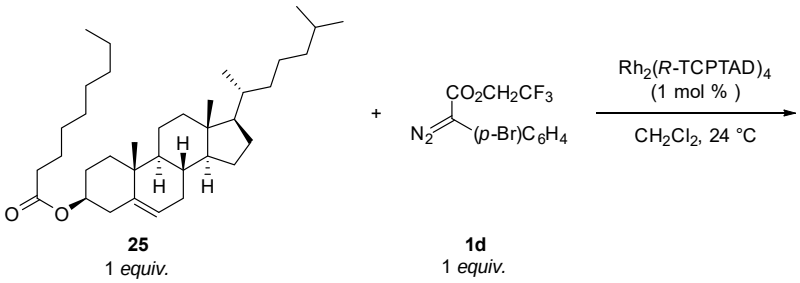
39 : 1

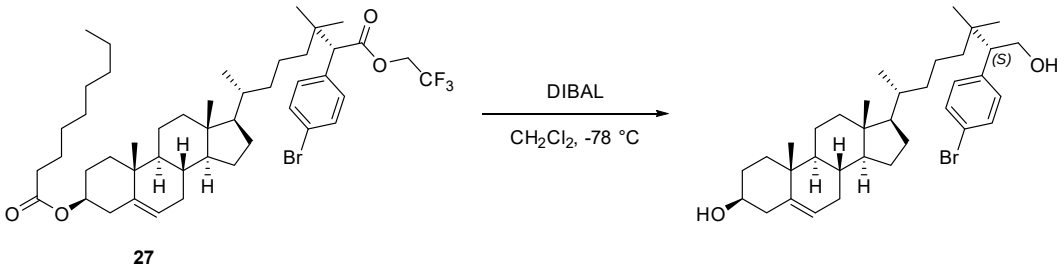


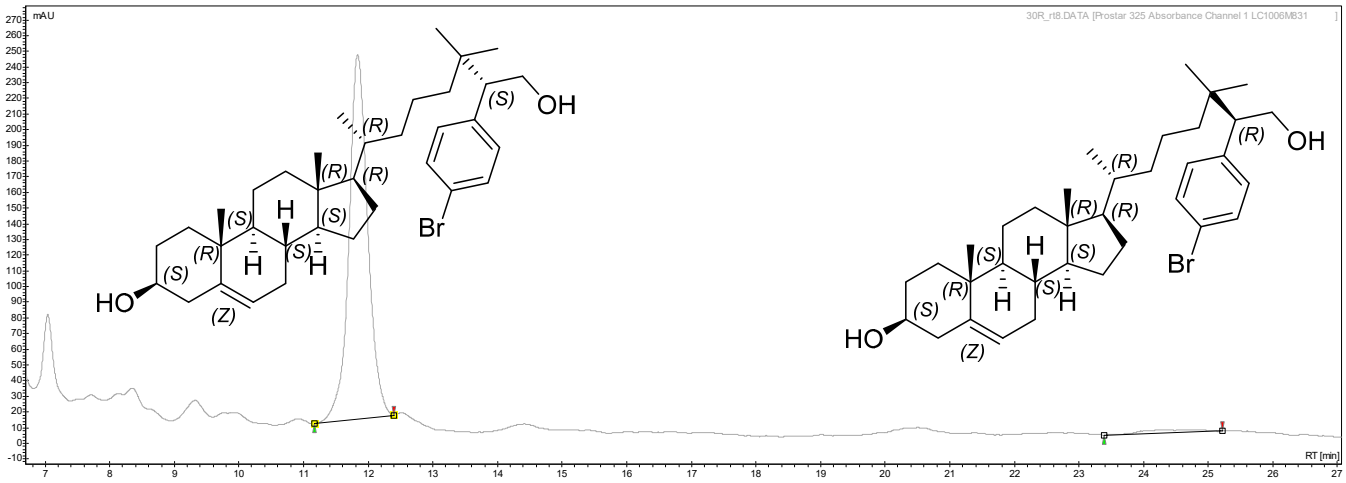




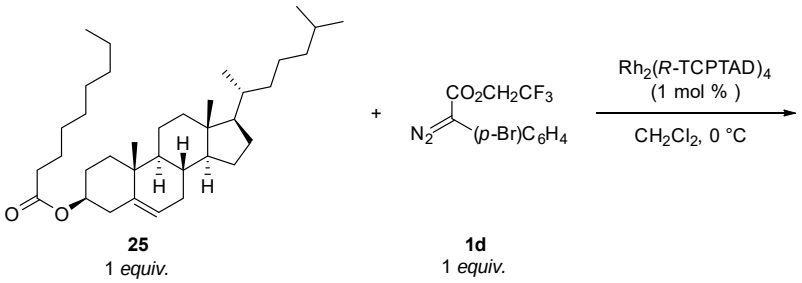
#	Time [Min]	Area % [%]
1	9.89	85.363
2	21.30	14.637
		6:1 d.r.





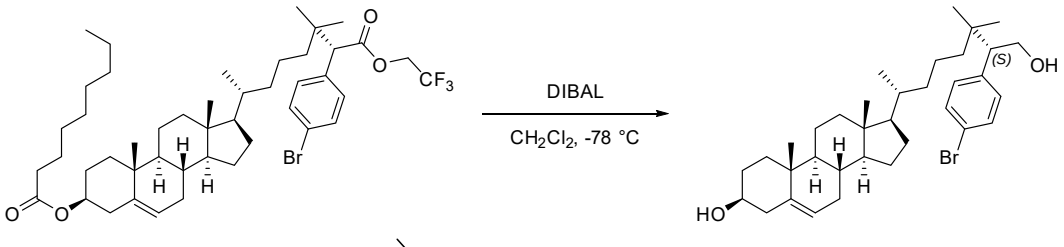


#	Time [Min]	Area % [%]
1	11.84	97.333
2	24.06	2.667
		>20:1 d.r.

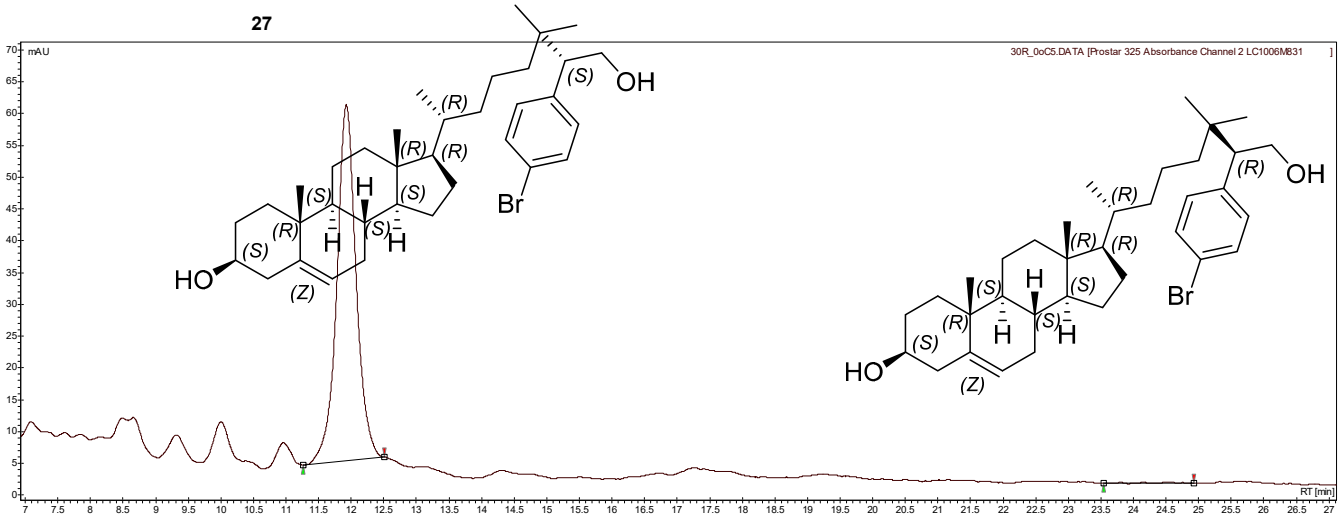


25
1 *equiv.*

1d
1 *equiv.*



27



#	Time [Min]	Area % [%]
1	11.92	99.457
2	24.47	0.543
		>20:1 d.r.

10 - X-Ray Crystallographic Data for **19*R***

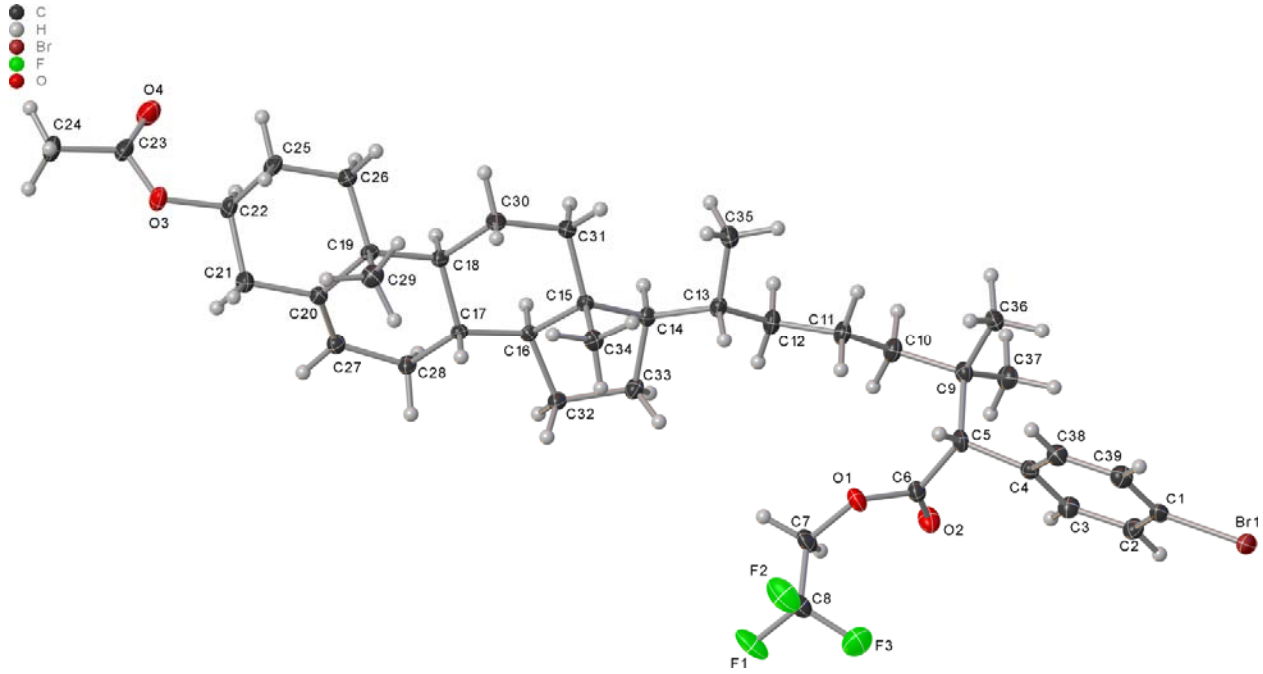


Table 1 Crystal data and structure refinement for 19*R*.

Identification code	19*R*
Empirical formula	$C_{39}H_{54}BrF_3O_4$
Formula weight	723.72
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.8637(16)
b/Å	15.308(4)
c/Å	30.278(7)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	3644.8(15)
Z	4
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	1.182
F(000)	1528.0
Crystal size/mm^3	1.165 × 0.591 × 0.296
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.69 to 61.016
Index ranges	-11 ≤ h ≤ 11, -21 ≤ k ≤ 21, -43 ≤ l ≤ 38
Reflections collected	48851
Independent reflections	11132 [R_{int} = 0.0465, R_{sigma} = 0.0280]
Data/restraints/parameters	11132/2/440
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0377, wR_2 = 0.0903
Final R indexes [all data]	R_1 = 0.0442, wR_2 = 0.0941
Largest diff. peak/hole / e Å^{-3}	0.74/-0.22
Flack parameter	-0.013(3)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 19*R*. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	7538.3(3)	1662.9(2)	10528.5(2)	23.74(7)

F1	1005(2)	3514.1(13)	7763.3(7)	40.8(5)
F2	3364(3)	4127.9(12)	7955.9(8)	42.1(5)
F3	2072(3)	3277.1(14)	8410.0(6)	43.5(5)
O3	7622(3)	5249.5(11)	3254.1(5)	21.2(3)
O1	4985(2)	2514.2(12)	8024.4(6)	21.4(4)
O2	3982(2)	1302.8(13)	8366.9(7)	25.2(4)
O4	8464(3)	4073.4(13)	2861.8(7)	29.3(4)
C6	5133(3)	1802.9(16)	8299.4(8)	18.0(4)
C27	4866(3)	4318.7(16)	4574.3(8)	16.8(4)
C28	4698(3)	3896.7(16)	5020.3(8)	15.8(4)
C1	7333(3)	1684.8(15)	9902.6(7)	17.5(4)
C2	6065(3)	1193.9(17)	9699.7(8)	19.6(5)
C20	6310(3)	4647.4(14)	4407.8(8)	15.2(4)
C32	4783(3)	3220.2(16)	5975.7(8)	16.1(4)
C23	8036(3)	4829.5(17)	2879.0(8)	20.3(5)
C15	7878(3)	3351.5(15)	5979.7(7)	13.0(4)
C18	7928(3)	3901.1(15)	5021.4(7)	14.0(4)
C19	8022(3)	4605.0(14)	4649.0(8)	14.3(4)
C22	7694(3)	4747.0(15)	3662.8(7)	17.8(4)
C39	8423(3)	2206.0(17)	9656.9(9)	20.3(5)
C14	7437(3)	2600.1(13)	6307.3(6)	14.2(3)
C34	7949(3)	4228.6(15)	6227.4(8)	16.6(4)
C13	8458(3)	2525.9(16)	6741.1(7)	16.4(4)

C17	6306(3)	3985.8(14)	5305.1(7)	12.4(4)
C25	9428(3)	4846.8(18)	3880.4(8)	19.9(5)
C10	7672(4)	973.7(15)	7750.4(7)	19.2(4)
C11	8398(3)	1757.0(17)	7494.2(8)	19.4(4)
C16	6332(3)	3294.1(14)	5666.5(7)	12.4(4)
C35	10392(3)	2465.4(19)	6663.5(9)	23.7(5)
C9	7936(3)	972.1(15)	8257.4(8)	16.7(4)
C4	6995(3)	1735.4(15)	8982.4(7)	15.6(4)
C33	5487(3)	2723.8(16)	6384.4(8)	18.0(4)
C36	9836(3)	1092.7(17)	8367.2(9)	20.2(5)
C38	8243(3)	2224.0(16)	9199.2(8)	18.7(4)
C26	9433(3)	4331.8(17)	4316.5(8)	18.8(4)
C31	9490(3)	3228.2(17)	5697.3(8)	18.3(4)
C12	7830(3)	1737.0(16)	7010.0(8)	19.8(5)
C21	6292(3)	5100.5(17)	3961.8(8)	19.7(5)
C7	3409(3)	2613.3(18)	7794.4(9)	22.1(5)
C3	5893(3)	1224.7(16)	9241.1(8)	19.0(5)
C8	2464(4)	3388.3(16)	7983.2(9)	24.4(5)
C37	7337(4)	82.4(15)	8429.8(8)	20.9(4)
C24	7861(4)	5426(2)	2487.1(9)	27.5(6)
C30	9553(3)	3874.5(17)	5307.6(8)	19.4(5)
C29	8438(3)	5522.3(16)	4837.7(9)	20.5(5)
C5	6942(3)	1753.8(15)	8477.5(8)	15.5(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 19*R*. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	22.33(11)	33.72(13)	15.17(10)	-1.42(9)	-0.75(10)	7.24(12)
F1	25.0(9)	37.5(10)	59.8(13)	-1.1(9)	-17.8(9)	10.1(7)
F2	37.9(10)	21.5(8)	67.0(14)	5.7(8)	-14.3(10)	-2.4(7)
F3	50.1(12)	49.9(11)	30.4(9)	-4.9(8)	5.9(8)	9.7(10)
O3	29.7(9)	19.5(7)	14.3(7)	3.6(6)	1.2(8)	1.7(8)
O1	17.9(8)	22.0(8)	24.4(9)	6.7(7)	-5.4(7)	1.3(7)
O2	16.8(8)	30.4(10)	28.4(10)	8.9(8)	-3.6(7)	-5.8(7)
O4	40.0(12)	26.9(10)	20.9(9)	-0.1(7)	7.1(8)	5.3(9)
C6	16.7(10)	21.1(11)	16.2(10)	2.8(8)	-1.8(8)	0.4(8)
C27	15.9(10)	19.5(10)	15(1)	0.4(8)	-1.7(8)	-0.2(8)
C28	12.4(9)	19.7(10)	15.1(10)	2.1(8)	0.7(8)	-2.4(8)
C1	17.6(10)	18.7(9)	16.1(9)	-1.4(8)	-0.3(8)	4.9(10)
C2	18.4(11)	22.0(11)	18.4(11)	2.0(9)	2.1(9)	-2.0(9)
C20	15.6(10)	15.3(9)	14.5(11)	0.4(8)	0.3(8)	1.5(8)
C32	13.5(9)	20.1(11)	14.8(10)	1.3(8)	1.3(8)	0.1(8)
C23	21.0(11)	26.2(12)	13.8(10)	1.8(9)	2.0(8)	-0.5(9)
C15	13.8(9)	12.4(8)	12.8(9)	0.0(7)	0.5(7)	1.0(7)
C18	12.4(9)	15.8(9)	13.8(9)	0.2(7)	0.6(7)	-0.2(7)
C19	13.5(9)	15.4(9)	14.1(10)	0.1(8)	2.0(8)	0.0(8)

C22	23.1(12)	17.2(9)	13.0(9)	3.5(7)	1.8(9)	-0.4(9)
C39	18.1(11)	20.7(11)	22.2(12)	-1.6(9)	-2.2(9)	-2.6(9)
C14	15.7(8)	14.2(8)	12.6(8)	0.0(7)	-1.1(9)	-0.3(9)
C34	17.8(10)	15.0(9)	16.8(10)	-2.4(8)	-3.1(8)	-2.1(8)
C13	19.4(10)	17.2(10)	12.5(10)	1.0(8)	0.0(8)	0.9(8)
C17	11.8(9)	13.2(9)	12.1(9)	-0.7(7)	0.3(7)	-0.1(8)
C25	19.4(11)	25.7(12)	14.5(11)	4.2(9)	4.1(9)	-2.0(9)
C10	24.3(12)	17.4(10)	15.8(9)	2.7(7)	-0.6(10)	-3.5(10)
C11	23.8(11)	19.9(11)	14.5(10)	4.3(8)	-1.3(8)	-4.6(10)
C16	13.4(9)	12.1(9)	11.9(9)	-1.2(7)	0.8(7)	-0.7(8)
C35	19.0(11)	32.2(13)	19.8(12)	7.8(10)	-0.4(9)	3.5(10)
C9	17.2(10)	15.6(10)	17.2(10)	4.2(8)	-1.0(8)	-1.3(8)
C4	15.8(9)	14.6(10)	16.5(10)	1.7(8)	0.1(7)	0.6(8)
C33	17.9(10)	21.3(11)	14.9(10)	2.1(8)	0.4(8)	-3.0(9)
C36	17.6(11)	23.7(12)	19.2(11)	4.9(9)	-1.2(9)	2.4(9)
C38	17.7(10)	17.2(10)	21.1(11)	1.6(8)	-0.4(9)	-1.9(9)
C26	16.3(10)	23.4(11)	16.9(11)	3.4(9)	3.2(9)	2.8(9)
C31	15.1(9)	24.0(12)	15.7(10)	1.7(9)	0.9(8)	4.4(9)
C12	25.8(12)	19(1)	14.6(9)	3.3(8)	-1.8(8)	-2.1(9)
C21	20.2(11)	21.8(11)	17.2(11)	4.9(9)	0.9(9)	2.6(9)
C7	18.3(11)	25.9(12)	22.1(12)	1.6(10)	-6.9(9)	3.9(9)
C3	17.1(10)	19.3(11)	20.7(12)	1.2(9)	0.4(9)	-4.4(9)
C8	20.3(10)	23.5(11)	29.3(12)	0.3(9)	-6.4(11)	2.5(13)

C37	24.8(12)	16.0(9)	21.8(10)	5.3(8)	1.1(10)	-2.8(10)
C24	32.1(16)	34.9(14)	15.5(11)	8.1(10)	1.1(10)	3.6(11)
C30	11.5(10)	27.2(12)	19.5(12)	4.6(9)	1.7(9)	0.5(9)
C29	20.5(11)	18.8(11)	22.1(12)	-0.1(9)	1.1(9)	-5.1(9)
C5	15.4(8)	15.2(10)	16(1)	4.6(8)	-4.0(7)	-3.5(8)

Table 4 Bond Lengths for 19*R*.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C1	1.902(2)	C18	C19	1.562(3)
F1	C8	1.340(3)	C18	C17	1.544(3)
F2	C8	1.338(3)	C18	C30	1.544(3)
F3	C8	1.339(3)	C19	C26	1.556(3)
O3	C23	1.345(3)	C19	C29	1.551(3)
O3	C22	1.458(3)	C22	C25	1.522(4)
O1	C6	1.376(3)	C22	C21	1.526(3)
O1	C7	1.429(3)	C39	C38	1.393(4)
O2	C6	1.203(3)	C14	C13	1.543(3)
O4	C23	1.206(3)	C14	C33	1.563(4)
C6	C5	1.523(3)	C13	C35	1.542(4)
C27	C28	1.503(3)	C13	C12	1.538(3)
C27	C20	1.340(3)	C17	C16	1.523(3)
C28	C17	1.536(3)	C25	C26	1.538(3)
C1	C2	1.391(3)	C10	C11	1.538(3)

C1	C39	1.387(3)	C10	C9	1.549(3)
C2	C3	1.396(4)	C11	C12	1.533(3)
C20	C19	1.533(3)	C9	C36	1.542(3)
C20	C21	1.518(3)	C9	C37	1.533(3)
C32	C16	1.540(3)	C9	C5	1.577(3)
C32	C33	1.554(3)	C4	C38	1.398(3)
C23	C24	1.503(4)	C4	C3	1.405(3)
C15	C14	1.558(3)	C4	C5	1.530(3)
C15	C34	1.539(3)	C31	C30	1.541(3)
C15	C16	1.544(3)	C7	C8	1.512(4)
C15	C31	1.541(3)			

Table 5 Bond Angles for 19*R*.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C23	O3	C22	117.06(19)	C35	C13	C14	112.8(2)
C6	O1	C7	116.9(2)	C12	C13	C14	109.97(19)
O1	C6	C5	109.4(2)	C12	C13	C35	110.5(2)
O2	C6	O1	122.9(2)	C28	C17	C18	111.13(18)
O2	C6	C5	127.7(2)	C16	C17	C28	110.66(18)
C20	C27	C28	125.0(2)	C16	C17	C18	109.27(18)
C27	C28	C17	113.19(19)	C22	C25	C26	108.8(2)
C2	C1	Br1	119.42(18)	C11	C10	C9	116.8(2)
C39	C1	Br1	119.47(18)	C12	C11	C10	111.0(2)

C39	C1	C2	121.1(2)	C32	C16	C15	104.69(17)
C1	C2	C3	119.4(2)	C17	C16	C32	118.49(18)
C27	C20	C19	123.3(2)	C17	C16	C15	114.36(18)
C27	C20	C21	119.9(2)	C10	C9	C5	110.55(19)
C21	C20	C19	116.8(2)	C36	C9	C10	110.1(2)
C16	C32	C33	103.78(18)	C36	C9	C5	107.35(19)
O3	C23	C24	110.7(2)	C37	C9	C10	107.31(19)
O4	C23	O3	124.2(2)	C37	C9	C36	109.3(2)
O4	C23	C24	125.0(2)	C37	C9	C5	112.22(19)
C34	C15	C14	110.00(18)	C38	C4	C3	118.0(2)
C34	C15	C16	112.20(18)	C38	C4	C5	118.6(2)
C34	C15	C31	110.30(19)	C3	C4	C5	123.4(2)
C16	C15	C14	100.02(17)	C32	C33	C14	106.85(18)
C31	C15	C14	116.47(19)	C39	C38	C4	121.9(2)
C31	C15	C16	107.47(18)	C25	C26	C19	114.6(2)
C17	C18	C19	112.51(18)	C30	C31	C15	111.88(19)
C17	C18	C30	111.96(18)	C11	C12	C13	113.4(2)
C30	C18	C19	112.60(18)	C20	C21	C22	111.0(2)
C20	C19	C18	109.37(18)	O1	C7	C8	109.0(2)
C20	C19	C26	109.26(19)	C2	C3	C4	120.9(2)
C20	C19	C29	108.81(19)	F1	C8	C7	110.2(2)
C26	C19	C18	108.39(18)	F2	C8	F1	107.5(2)
C29	C19	C18	111.63(19)	F2	C8	F3	106.8(2)

C29	C19	C26	109.3(2)	F2	C8	C7	112.4(2)
O3	C22	C25	110.5(2)	F3	C8	F1	107.5(2)
O3	C22	C21	106.74(19)	F3	C8	C7	112.2(2)
C25	C22	C21	110.8(2)	C31	C30	C18	114.8(2)
C1	C39	C38	118.8(2)	C6	C5	C9	110.52(19)
C15	C14	C33	102.92(18)	C6	C5	C4	112.3(2)
C13	C14	C15	118.73(19)	C4	C5	C9	113.26(19)
C13	C14	C33	113.07(18)				

Table 6 Torsion Angles for 19*R*.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C1	C2	C3	178.68(19)	C34	C15	C31	C30	-68.6(2)
Br1	C1	C39	C38	-179.19(19)	C13	C14	C33	C32	153.10(19)
O3	C22	C25	C26	178.24(19)	C17	C18	C19	C20	-47.2(2)
O3	C22	C21	C20	-177.34(19)	C17	C18	C19	C26	-166.28(19)
O1	C6	C5	C9	-107.8(2)	C17	C18	C19	C29	73.2(2)
O1	C6	C5	C4	124.6(2)	C17	C18	C30	C31	48.7(3)
O1	C7	C8	F1	177.9(2)	C25	C22	C21	C20	-57.0(3)
O1	C7	C8	F2	58.1(3)	C10	C11	C12	C13	177.6(2)
O1	C7	C8	F3	-62.3(3)	C10	C9	C5	C6	46.9(3)
O2	C6	C5	C9	70.1(3)	C10	C9	C5	C4	173.94(19)
O2	C6	C5	C4	-57.5(4)	C11	C10	C9	C36	-53.4(3)
C6	O1	C7	C8	109.9(2)	C11	C10	C9	C37	-172.3(2)

C27 C28 C17 C18	-37.7(3)	C11 C10 C9 C5	65.0(3)
C27 C28 C17 C16	-159.28(19)	C16 C32 C33 C14	4.3(2)
C27 C20 C19 C18	17.3(3)	C16 C15 C14 C13	-167.80(19)
C27 C20 C19 C26	135.8(2)	C16 C15 C14 C33	-42.0(2)
C27 C20 C19 C29	-104.9(3)	C16 C15 C31 C30	54.0(3)
C27 C20 C21 C22	-130.3(2)	C35 C13 C12 C11	71.0(3)
C28 C27 C20 C19	2.3(4)	C9 C10 C11 C12	-172.0(2)
C28 C27 C20 C21	-176.8(2)	C33 C32 C16 C15	-31.4(2)
C28 C17 C16 C32	-53.9(3)	C33 C32 C16 C17	-160.26(19)
C28 C17 C16 C15	-178.12(18)	C33 C14 C13 C35	-176.2(2)
C1 C2 C3 C4	0.8(4)	C33 C14 C13 C12	60.0(2)
C1 C39 C38 C4	0.3(4)	C36 C9 C5 C6	166.98(19)
C2 C1 C39 C38	-0.8(4)	C36 C9 C5 C4	-66.0(2)
C20 C27 C28 C17	8.1(3)	C38 C4 C3 C2	-1.2(4)
C20 C19 C26 C25	48.4(3)	C38 C4 C5 C6	-139.1(2)
C23 O3 C22 C25	92.6(3)	C38 C4 C5 C9	94.8(3)
C23 O3 C22 C21	-146.9(2)	C31 C15 C14 C13	76.8(3)
C15 C14 C13 C35	-55.5(3)	C31 C15 C14 C33	-157.42(19)
C15 C14 C13 C12	-179.30(19)	C31 C15 C16 C32	168.07(19)
C15 C14 C33 C32	23.8(2)	C31 C15 C16 C17	-60.6(2)
C15 C31 C30 C18	-51.0(3)	C21 C20 C19 C18	-163.58(19)
C18 C19 C26 C25	167.5(2)	C21 C20 C19 C26	-45.1(3)
C18 C17 C16 C32	-176.59(19)	C21 C20 C19 C29	74.2(2)

C18 C17 C16 C15	59.2(2)	C21 C22 C25 C26	60.2(3)		
C19 C20 C21 C22	50.6(3)	C7 O1 C6 O2	-3.8(4)		
C19 C18 C17 C28	59.0(2)	C7 O1 C6 C5	174.3(2)		
C19 C18 C17 C16	-178.55(18)	C3 C4 C38 C39	0.7(4)		
C19 C18 C30 C31	176.6(2)	C3 C4 C5 C6	43.5(3)		
C22 O3 C23 O4	-0.2(4)	C3 C4 C5 C9	-82.6(3)		
C22 O3 C23 C24	178.7(2)	C37 C9 C5 C6	-72.9(2)		
C22 C25 C26 C19	-57.2(3)	C37 C9 C5 C4	54.2(3)		
C39 C1 C2 C3	0.2(4)	C30 C18 C19 C20	-174.91(19)		
C14 C15 C16 C32	46.1(2)	C30 C18 C19 C26	66.0(2)		
C14 C15 C16 C17	177.35(17)	C30 C18 C19 C29	-54.4(3)		
C14 C15 C31 C30	165.1(2)	C30 C18 C17 C28	-172.96(19)		
C14 C13 C12 C11	-163.8(2)	C30 C18 C17 C16	-50.6(2)		
C34 C15 C14 C13	-49.6(3)	C29 C19 C26 C25	-70.6(3)		
C34 C15 C14 C33	76.2(2)	C5 C4 C38 C39	-176.8(2)		
C34 C15 C16 C32	-70.5(2)	C5 C4 C3 C2	176.2(2)		
C34 C15 C16 C17	60.8(2)				

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 19*R*.

Atom	*x*	*y*	*z*	U(eq)
H28A	4439	3269	4980	19
H28B	3729	4165	5179	19
H2	5324	841	9872	24

H32A	3852	2888	5834	19
H32B	4356	3805	6060	19
H18	7855	3322	4870	17
H39	9276	2545	9798	24
H14	7589	2037	6144	17
H34A	6871	4326	6382	25
H34B	8141	4703	6016	25
H34C	8882	4216	6442	25
H13	8233	3064	6919	20
H17	6301	4575	5447	15
H25A	9661	5472	3939	24
H25B	10326	4621	3682	24
H10A	8188	435	7629	23
H10B	6435	943	7691	23
H11A	8007	2307	7633	23
H11B	9656	1744	7509	23
H16	6427	2718	5512	15
H35A	10620	2061	6420	36
H35B	10947	2252	6932	36
H35C	10837	3045	6589	36
H33A	4921	2149	6415	22
H33B	5283	3065	6657	22
H36A	10511	671	8198	30

H36B	10017	997	8684	30
H36C	10188	1687	8289	30
H38	8990	2578	9030	22
H26A	10555	4408	4460	23
H26B	9298	3703	4248	23
H31A	10507	3314	5885	22
H31B	9520	2623	5582	22
H12A	6573	1720	6999	24
H12B	8260	1195	6871	24
H21A	6454	5736	4004	24
H21B	5174	5009	3819	24
H7A	2715	2078	7828	27
H7B	3626	2706	7476	27
H3	5020	896	9102	23
H37A	6108	25	8383	31
H37B	7589	37	8746	31
H37C	7930	-384	8270	31
H24A	6654	5534	2429	41
H24B	8382	5151	2228	41
H24C	8434	5981	2549	41
H30A	10528	3718	5116	23
H30B	9766	4468	5426	23
H29A	8285	5963	4606	31

H29B	9619	5533	4941	31
H29C	7674	5650	5085	31
H22	7490(40)	4123(7)	3590(9)	19
H5	7460(50)	2290(20)	8398(10)	19
H27	3770(20)	4370(20)	4420(10)	26(8)

Experimental

Single crystals of $C_{39}H_{54}BrF_3O_4$ **[18*R*]** were **[The material was recrystallised from --- by as supplied]**. A suitable crystal was selected and **[The crystal was mounted on a loop with paratone oil]** on a **Saxi-CrysAlisPro-abstract goniometer imported SAXI images** diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of [19*R*]

Crystal Data for $C_{39}H_{54}BrF_3O_4$ (M =723.72 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 7.8637(16) Å, b = 15.308(4) Å, c = 30.278(7) Å, V = 3644.8(15) Å^3, Z = 4, T = 100(2) K, μ(MoKα) = 1.182 mm^{-1}, *Dcalc* = 1.319 g/cm^3, 48851 reflections measured (2.69° ≤ 2Θ ≤ 61.016°), 11132 unique (R_{int} = 0.0465, R_{sigma} = 0.0280) which were used in all calculations. The final R_1 was 0.0377 (I > 2σ(I)) and wR_2 was 0.0941 (all data).

Refinement model description

Number of restraints - 2, number of constraints - unknown.

Details:

1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Restrained distances
 C27-H27
 0.99 with sigma of 0.005
 C22-H22
 0.995 with sigma of 0.005
3.a Ternary CH refined with riding coordinates:
 C18(H18), C14(H14), C13(H13), C17(H17), C16(H16)
3.b Secondary CH2 refined with riding coordinates:
 C28(H28A,H28B), C32(H32A,H32B), C25(H25A,H25B), C10(H10A,H10B), C11(H11A,
 H11B), C33(H33A,H33B), C26(H26A,H26B), C31(H31A,H31B), C12(H12A,H12B),

C21(H21A,H21B), C7(H7A,H7B), C30(H30A,H30B)

3.c Aromatic/amide H refined with riding coordinates:

C2(H2), C39(H39), C38(H38), C3(H3)

3.d Idealised Me refined as rotating group:

C34(H34A,H34B,H34C), C35(H35A,H35B,H35C), C36(H36A,H36B,H36C), C37(H37A,H37B, H37C), C24(H24A,H24B,H24C), C29(H29A,H29B,H29C)

This report has been created with Olex2, compiled on 2016.08.25 svn.r3337 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

11 - X-Ray Crystallographic Data for **Rh$_2$(*R*-TCPTAD)$_4$**

Rh$_2$(*R*-TCPTAD)$_4$

EMORY UNIVERSITY | X-ray Crystallography Center

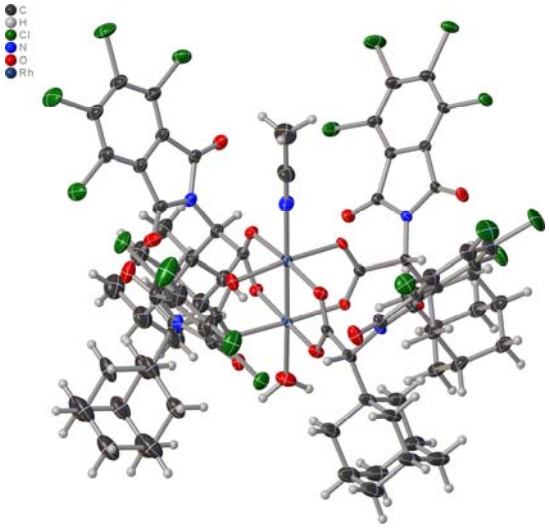
Submitted by: **Kuangbiao Liao**

Emory University

Solved by: **Thomas C. Pickel**

Sample ID: **Rh$_2$(*R*-TCPTAD)$_4$**

Crystal Data and Experimental



Experimental. Single violet needle-shaped crystals of [**Rh$_2$(*R*-TCPTAD)$_4$**] were crystallised by vapour diffusion. The major component was MeCN and ethyl ether; the minor methylene chloride and MeOH. A suitable crystal (0.70×0.50×0.40 mm^3) was selected and mounted on a loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was cooled to T = 100(2) K during data collection. The structure was solved with the **XT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{86}H_{77}Cl_{24}N_5O_{17}Rh_2$, M_r = 2509.14, monoclinic, $P2_1$ (No. 4), a = 13.9309(2) Å, b = 23.4777(4) Å, c = 19.4295(4) Å, = 90.0°, = 97.9250(17)°, = 90.0°, V = 6294.0(2) Å^3, T = 100(2) K, Z = 2, Z' = 1, (MoK) = 0.824 mm^{-1}, 157466 reflections measured, 38220 unique (R_{int} = 0.0523) which were used in all calculations. The final wR_2 was 0.1590 (all data) and R_1 was 0.0641 (I > 2σ(I)).

Compound	**Rh_2(*R*-TCPTAD)$_4$**
Formula	$C_{86}H_{77}Cl_{24}N_5O_{17}Rh_2$
$D_{calc.}$/ g cm^{-3}	1.324
/mm^{-1}	0.824
Formula Weight	2509.14
Colour	violet
Shape	needle
Size/mm^3	0.70×0.50×0.40
T/K	100(2)
Crystal System	monoclinic
Flack Parameter	-0.007(8)
Hooft Parameter	-0.005(5)
Space Group	$P2_1$
a/Å	13.9309(2)
b/Å	23.4777(4)
c/Å	19.4295(4)
/°	90.0
/°	97.9250(17)
/°	90.0
V/Å^3	6294.0(2)
Z	2
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK
$_{min}$/°	1.693
$_{max}$/°	30.508
Measured Refl.	157466
Independent Refl.	38220
Reflections with I > 2σ(I)	32915
R_{int}	0.0523
Parameters	1203
Restraints	1130
Largest Peak	1.919
Deepest Hole	-1.069
GooF	1.043
wR_2 (all data)	0.1590
wR_2	0.1513
R_1 (all data)	0.0770

R_1	0.0641

Structure Quality Indicators

Reflections: d min (Mo) 0.70 | I/σ 22.9 | Rint 5.23% | complete 100%

Refinement: Shift 0.000 | Max Peak 1.9 | Min Peak -1.1 | GooF 1.043 | -0.007(8)

A violet needle-shaped crystal with dimensions 0.70×0.50×0.40 mm^3 was mounted on a loop with paratone oil. Data were collected using a APEX2 Mo source diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 100(2) K.

Data were measured using scans of 0.5° per frame for 20.0 s using MoK radiation (fine-focus sealed tube, 45 kV, 35 mA).The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent). The maximum resolution that was achieved was = 30.508°.

The diffraction patterns were indexed using CrysAlisPro (Agilent) and the unit cells were refined using CrysAlisPro (Agilent) on 65720 reflections, 42 % of the observed reflections. Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Agilent) and CrysAlisPro 1.171.39.9g (Rigaku Oxford Diffraction, 2015). An empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm was used. The final completeness is 99.8% out to 30.508° in . The absorption coefficient of this material is 0.824 mm^{-1} at this wavelength (= 0.71073 Å) and the minimum and maximum transmissions are 0.72898 and 1.00.

The structure was solved and the space group $P2_1$ (# 4) determined by the **XT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2014/7 of **XL** (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

The structure contains regions of diffuse and disordered solvent. These volumes were treated using Platon SQUEEZE (Spek, 2015).

The Flack parameter was refined to -0.007(8). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in -0.005(5). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

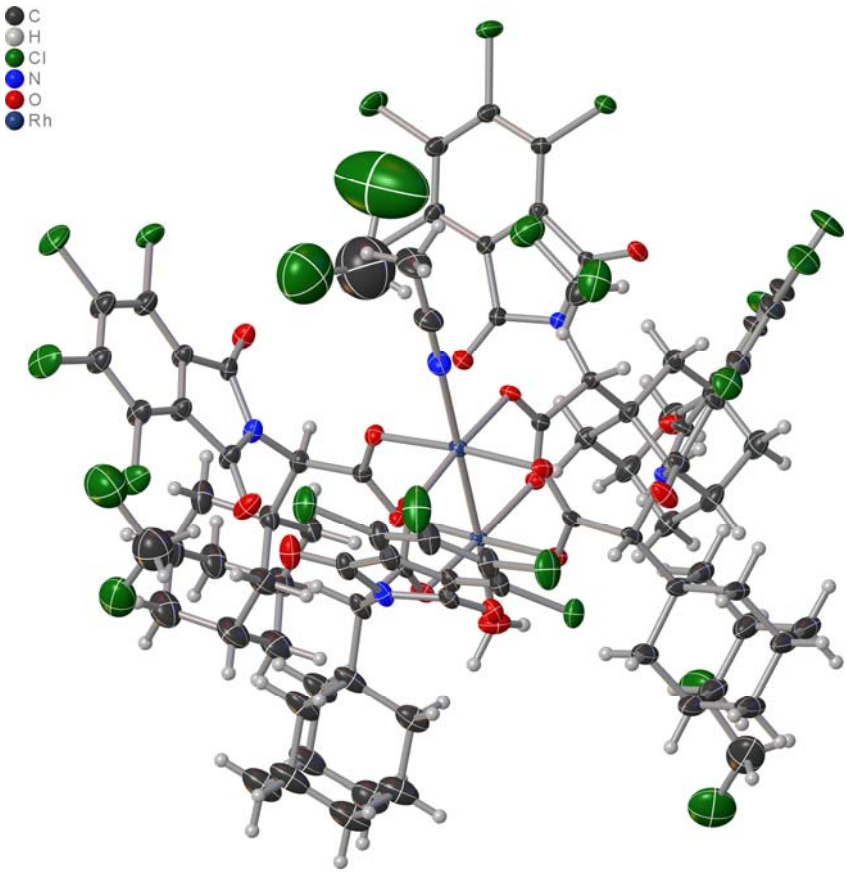


Figure 1:

Plot of the asymmetric unit with solvent molecules.

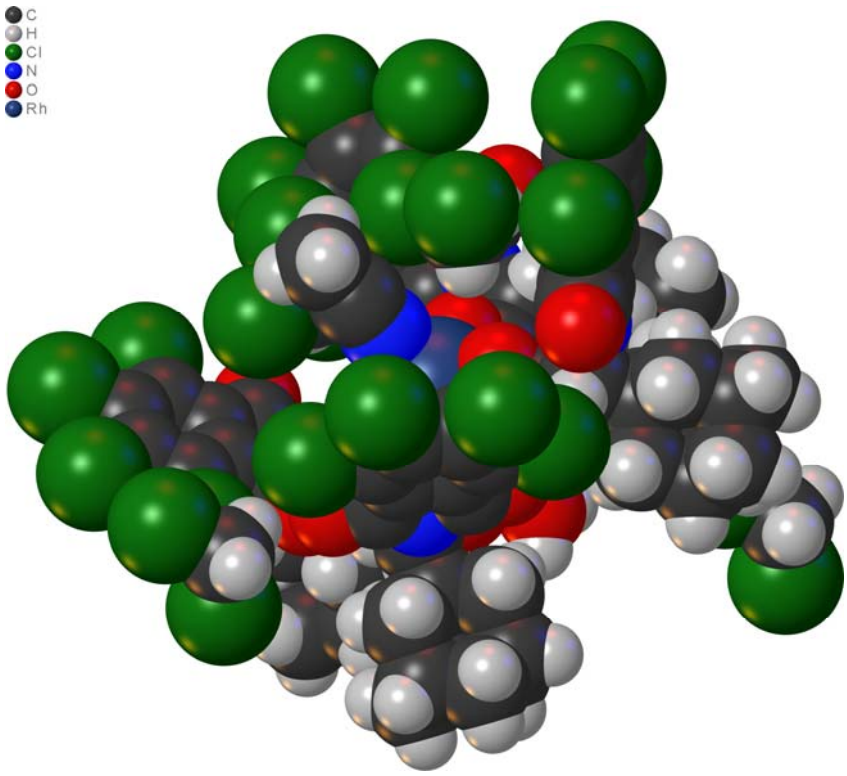


Figure 2:

Space filling plot of the asymmetric unit with solvent molecules.

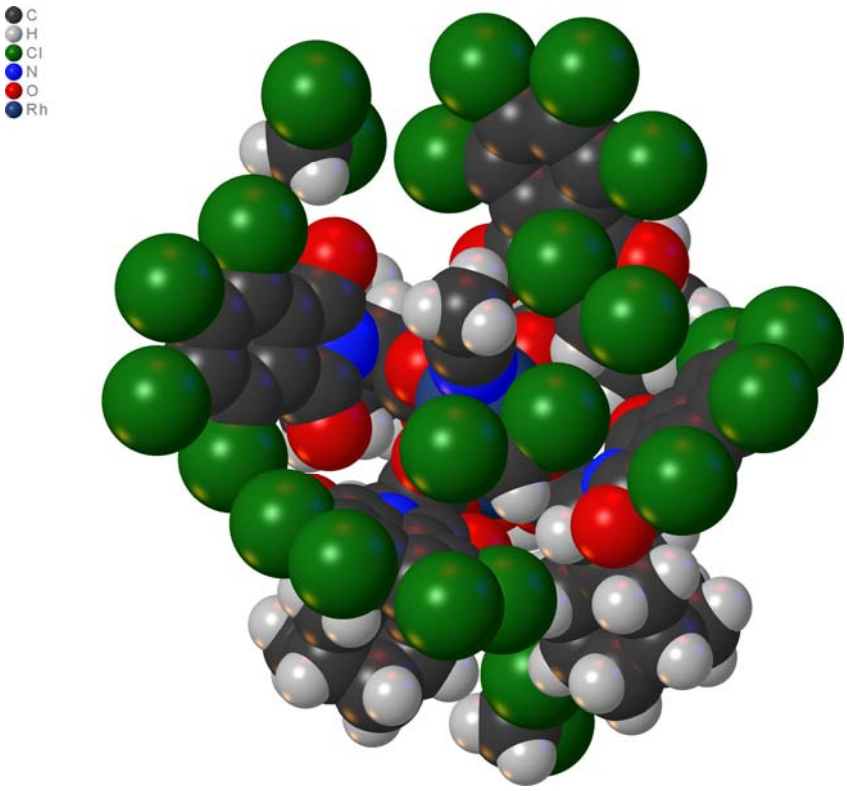


Figure 3:

Space filling plot of the asymmetric unit showing how the cup shaped cavity encapsulates solvent molecules.

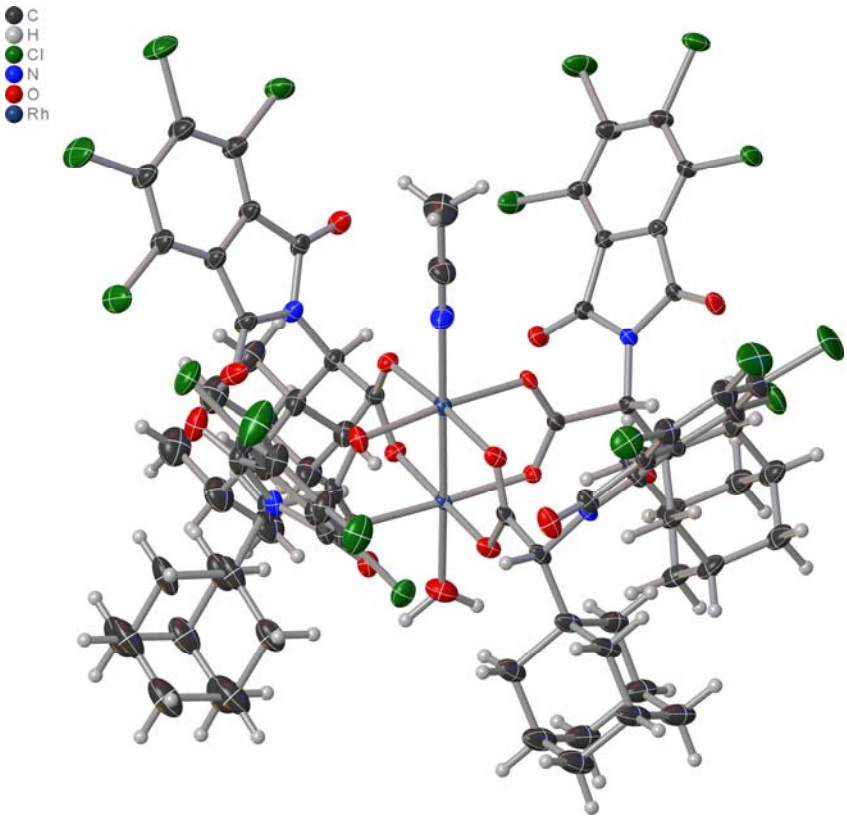


Figure 4:

Thermal ellipsoid plot of the asymmetric unit without solvent molecules for clarity.

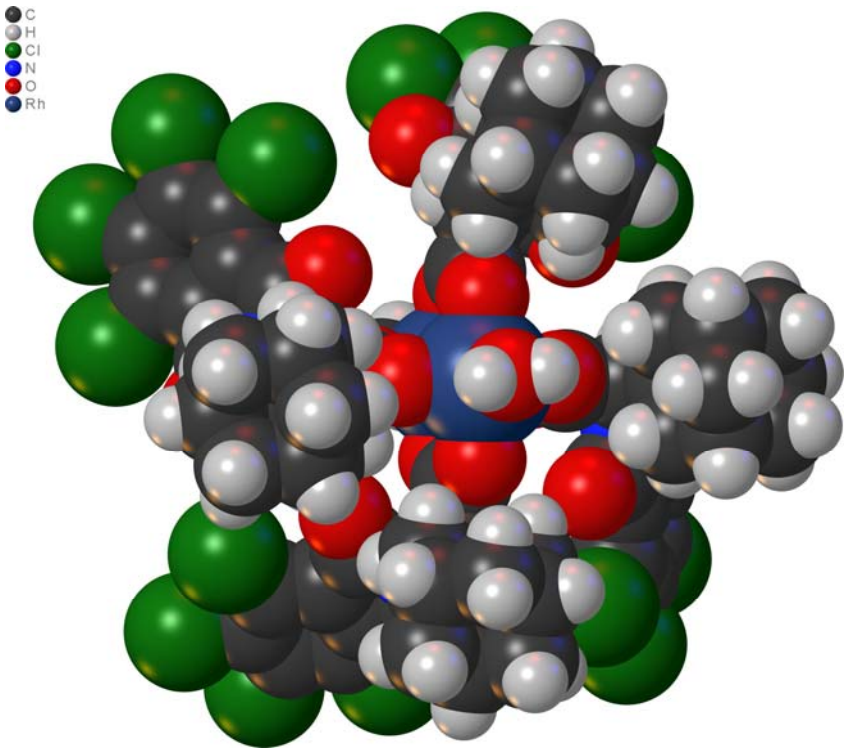


Figure 5:

Space filling plot of the asymmetric unit without solvent molecules for clarity.

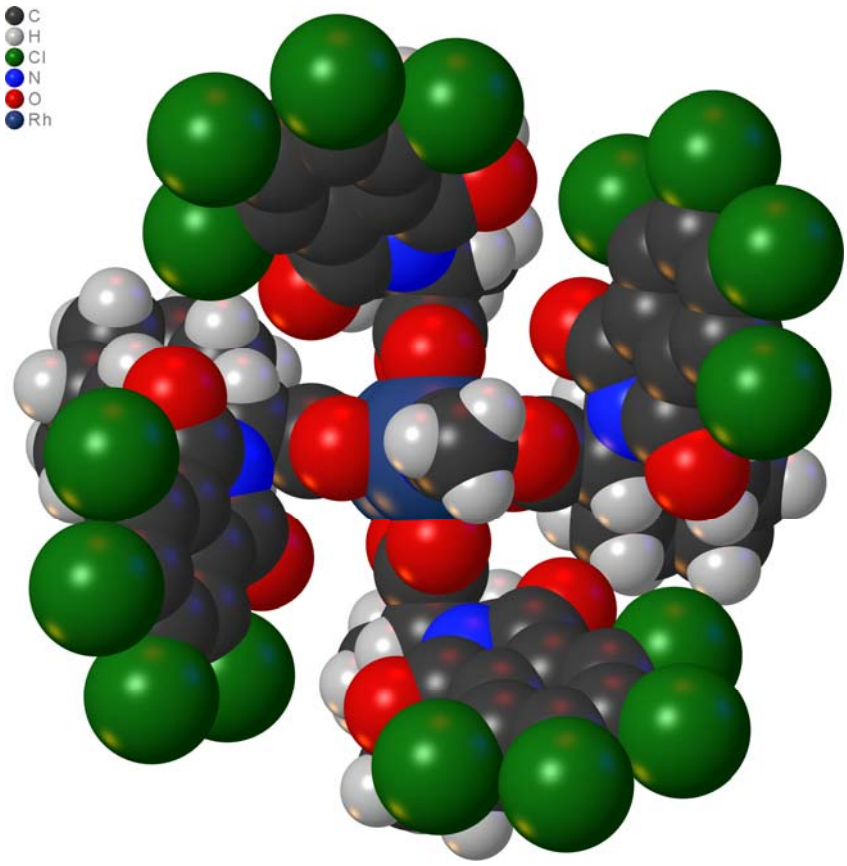
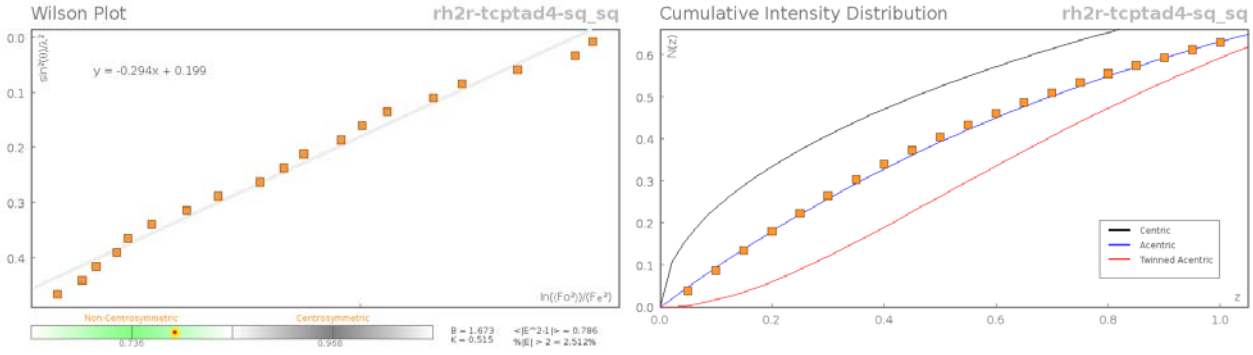
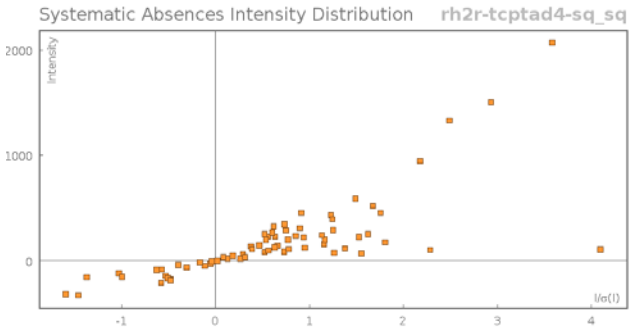


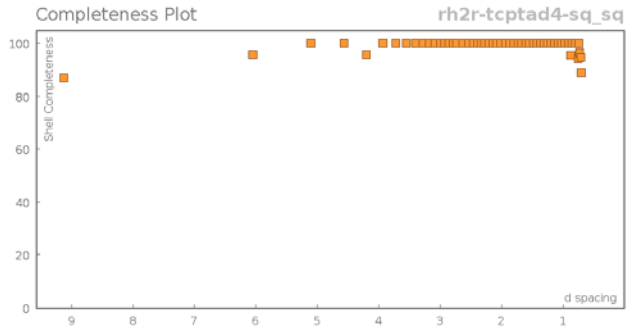
Figure 6:

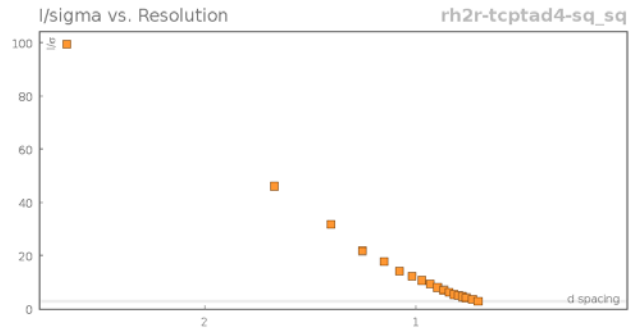
Space filling plot of the asymmetric unit showing the large cup shaped cavity.

Data Plots: Diffraction Data

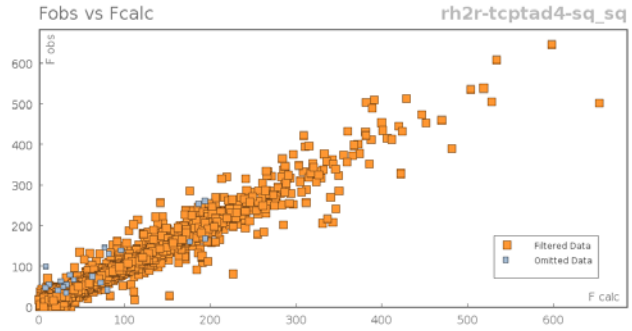


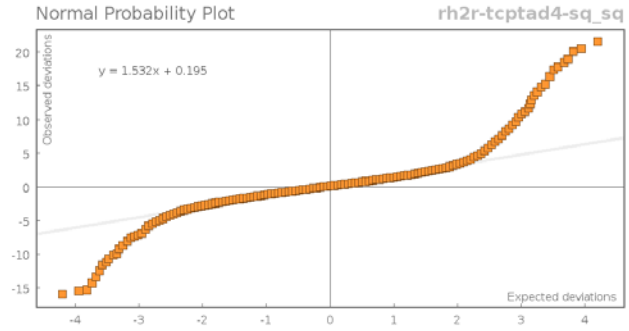






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	157727	Unique reflections	38220
Completeness	0.996	Mean I/	22.86
hkl_{max} collected	(19, 33, 27)	hkl_{min} collected	(-19, -33, -27)
hkl_{max} used	(19, 33, 27)	hkl_{min} used	(-19, -33, 0)
Lim d_{max} collected	20.0	Lim d_{min} collected	0.7
d_{max} used	12.03	d_{min} used	0.7
Friedel pairs	35805	Friedel pairs merged	0
Inconsistent equivalents	308	R_{int}	0.0523
R_{sigma}	0.0449	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	189

Multiplicity	(16366, 38122, 14845, 3422, 438, 784)	Maximum multiplicity	10
Removed systematic absences	72	Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer

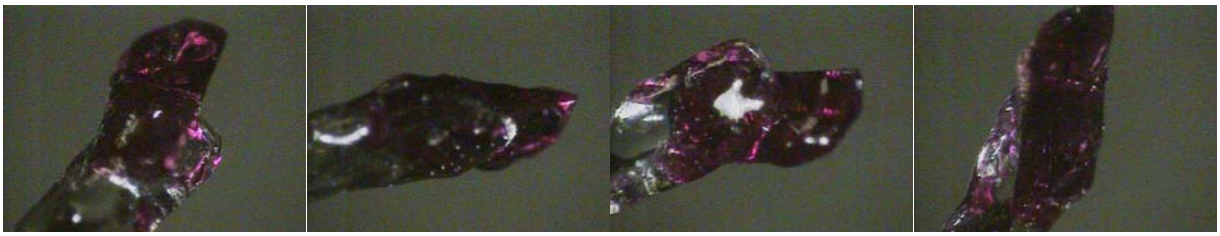


Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Rh_2(*R*-TCPTAD)$_4$**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Rh1	4977	5309	3544	13.18(8)
Rh2	6309	5341	2883	14.90(8)
Cl1	7410.8(18)	9029.2(9)	2023.6(12)	45.3(5)
Cl1B	12155.2(15)	6127.1(14)	5584.3(15)	62.5(7)
Cl1C	8754.6(14)	1748.9(9)	2735.7(12)	41.0(5)
Cl1D	5147(2)	4648.7(12)	-1780.8(11)	53.3(6)
Cl3	6342.1(13)	8281.6(8)	3010.9(9)	30.9(3)
Cl3B	10161.4(15)	5515.1(10)	5626.6(13)	45.2(5)
Cl3C	6871.5(12)	2441.4(8)	2885.4(10)	31.1(4)
Cl3D	4152.6(17)	5232.9(9)	-617.2(10)	42.9(5)
Cl4	7453(2)	8657.0(12)	499.4(12)	57.7(7)
Cl4B	12251.6(13)	7245.7(12)	4741.7(15)	55.2(6)
Cl4C	10751.8(12)	2153.2(8)	3466(1)	30.7(3)
Cl4D	6304.0(18)	3527.6(10)	-1479.1(11)	43.8(5)
Cl7	6245.2(17)	7596.8(10)	-110.9(10)	39.9(5)
Cl7B	10348.5(14)	7829.6(9)	4039.1(12)	40.1(4)
Cl7C	10911.4(10)	3235.8(7)	4415.5(9)	25.4(3)
Cl7D	6439.3(15)	2947.0(8)	-20.7(10)	34.2(4)
O1	5515(3)	5896(2)	2231(3)	23.4(9)
O1B	6863(3)	6003.3(19)	3500(3)	19.9(8)
O1C	7027(3)	4789.6(19)	3599(2)	17.1(8)
O1D	5644(3)	4690(2)	2295(2)	19.0(8)
O1W	3695(4)	5247(3)	4141(3)	38.1(13)
O2	4219(3)	5821.2(19)	2807(3)	21.4(9)

Atom	x	y	z	U_{eq}
O2B	5547(3)	6004.6(19)	4057(3)	21.5(9)
O2C	5817(3)	4817.4(19)	4253(2)	16.8(8)
O2D	4452(3)	4631.3(19)	2973(2)	18.6(8)
O3	5180(3)	7130(2)	2824(3)	25.9(9)
O3B	8020(3)	5782(2)	4943(3)	24.4(9)
O3C	6447(3)	3542(2)	3725(2)	22.9(9)
O3D	4106(4)	4960(2)	977(3)	31.6(11)
O4	4831(4)	6734(2)	506(3)	35.4(11)
O4B	8131(3)	7556(2)	3992(3)	30.3(11)
O4C	9388(3)	4105(2)	4871(3)	22.6(9)
O4D	5515(4)	3206(2)	1331(2)	26.1(9)
N1	4732(4)	6877(2)	1670(3)	22.9(9)
N1B	7817(4)	6686(2)	4479(3)	17.6(8)
N1C	7779(4)	3903(2)	4413(3)	17.0(8)
N1D	4675(4)	4059(2)	1299(3)	20.3(8)
N2	7545(4)	5366(4)	2271(3)	29.6(12)
C1	5215(4)	7202(3)	2221(3)	20.6(9)
C1B	8342(4)	6227(3)	4793(3)	19.5(10)
C1C	7292(4)	3530(3)	3940(3)	17.7(9)
C1D	4482(5)	4519(3)	847(3)	22.7(11)
C2	5796(4)	7629(3)	1878(3)	21.4(9)
C2B	9376(4)	6420(3)	4868(4)	21(1)
C2C	8055(4)	3119(3)	3750(3)	16.8(9)
C2D	4852(5)	4342(3)	194(3)	23.5(11)
C3	6309(5)	8099(3)	2150(3)	23.7(10)
C3B	10224(5)	6151(3)	5204(4)	30.3(12)
C3C	7973(4)	2646(3)	3329(3)	20.9(10)
C3D	4777(6)	4607(3)	-445(4)	28.7(13)
C4	6802(5)	8425(3)	1712(4)	30.5(13)
C4B	11109(5)	6428(4)	5166(4)	35.7(13)
C4C	8820(5)	2352(3)	3249(4)	24.2(11)
C4D	5218(6)	4341(3)	-967(4)	31.7(13)
C5	6788(6)	8273(3)	1024(4)	32.1(13)
C5B	11149(5)	6937(4)	4798(5)	36.6(14)
C5C	9716(4)	2530(3)	3580(4)	22.4(11)
C5D	5748(6)	3833(3)	-835(4)	33.0(14)
C6	6263(5)	7794(3)	751(4)	28.3(12)
C6B	10293(5)	7204(3)	4483(4)	29.9(12)
C6C	9800(4)	3011(2)	4010(3)	17.8(9)

Atom	x	y	z	U_{eq}
C6D	5803(5)	3574(3)	-182(4)	27.6(12)
C7	5755(5)	7485(3)	1179(3)	23.5(10)
C7B	9423(4)	6937(3)	4547(4)	22.2(10)
C7C	8954(4)	3294(2)	4092(3)	16.2(9)
C7D	5330(5)	3821(3)	315(3)	23.1(11)
C8	5067(5)	6992(3)	1045(4)	26.0(11)
C8B	8405(4)	7126(3)	4293(4)	21.6(11)
C8C	8805(4)	3817(2)	4516(3)	15.3(9)
C8D	5219(5)	3631(3)	1028(3)	19.5(10)
C9	4095(5)	6396(3)	1775(4)	24.5(9)
C9B	6745(4)	6721(3)	4355(4)	20.5(9)
C9C	7337(4)	4390(2)	4724(3)	16.5(8)
C9D	4393(5)	4005(3)	2002(3)	20.5(9)
C10	4658(4)	6007(3)	2338(4)	21.3(10)
C10B	6361(4)	6192(3)	3940(3)	17.6(9)
C10C	6658(4)	4693(2)	4138(3)	15.3(9)
C10D	4858(4)	4491(3)	2455(3)	16.8(9)
C11	3039(5)	6592(3)	1862(5)	34.5(11)
C11B	6290(4)	6880(3)	5009(4)	26.3(10)
C11C	6927(5)	4230(3)	5405(3)	19.9(9)
C11D	3288(5)	3894(3)	1984(4)	25.8(10)
C12	2982(6)	6957(3)	2508(5)	37.9(13)
C12B	6286(5)	6392(3)	5529(4)	30.9(11)
C12C	6039(5)	3833(3)	5291(3)	22.3(10)
C12D	2636(5)	4417(4)	1855(5)	36.8(13)
C13	1921(6)	7142(4)	2551(6)	50.9(15)
C13B	5819(6)	6588(4)	6164(5)	41.8(13)
C13C	5681(6)	3704(3)	5994(4)	28.8(11)
C13D	1580(6)	4256(5)	1845(5)	47.5(14)
C14	1527(7)	7477(4)	1886(6)	54.2(16)
C14B	6418(6)	7089(4)	6520(5)	44.4(14)
C14C	6482(6)	3398(3)	6473(4)	34.4(12)
C14D	1291(7)	3799(5)	1264(6)	53.4(16)
C15	1570(6)	7123(4)	1263(6)	52.1(15)
C15B	6432(5)	7579(4)	6010(5)	40.7(13)
C15C	7363(6)	3788(3)	6593(4)	33.3(12)
C15D	1896(7)	3284(5)	1397(5)	46.8(14)
C16	2622(6)	6926(4)	1211(5)	42.3(14)
C16B	6863(5)	7382(3)	5368(4)	31.8(12)

Atom	x	y	z	U_{eq}
C16C	7718(5)	3921(3)	5899(3)	25.8(11)
C16D	2977(6)	3446(4)	1418(4)	37.4(13)
C17	2389(6)	6055(4)	1905(5)	41.1(14)
C17B	5238(5)	7100(3)	4783(4)	33.0(12)
C17C	6672(5)	4784(3)	5767(3)	22.6(10)
C17D	3119(5)	3621(3)	2692(4)	27.4(11)
C18	1324(6)	6251(4)	1962(5)	47.7(14)
C18B	4800(5)	7285(4)	5439(5)	42.2(13)
C18C	6297(6)	4649(3)	6465(4)	29.2(11)
C18D	2050(5)	3464(4)	2683(4)	36.4(13)
C19	957(7)	6583(5)	1328(6)	54.8(17)
C19B	5394(6)	7790(4)	5769(6)	46.6(15)
C19C	7120(6)	4338(3)	6939(4)	33.3(12)
C19D	1739(7)	3029(4)	2108(5)	44.1(15)
C20	1321(8)	6620(4)	2598(6)	53.2(16)
C20B	4782(6)	6787(4)	5930(5)	44.5(14)
C20C	5408(6)	4266(3)	6324(4)	30.6(12)
C20D	1422(6)	4006(5)	2560(6)	46.5(15)
C21	8180(5)	5364(4)	1951(4)	34.9(15)
C22	8970(5)	5344(6)	1538(5)	55(2)
Cl1S	1944(3)	5333.5(16)	7402(2)	85.7(9)
Cl2S	3702(3)	5287(2)	6749.3(18)	94.7(12)
C1S	3111(10)	5606(5)	7374(7)	71(2)
Cl3S	4878(3)	6611(2)	-1818(2)	98.4(12)
Cl4S	3146(3)	6530.0(14)	-1132.4(17)	71.7(8)
C2S	4275(11)	6832(7)	-1143(8)	83(3)
Cl5S	7457(6)	4169(3)	1120(4)	157(2)
Cl6S	8720(8)	3456(7)	2070(7)	291(7)
C3S	7605(13)	3833(12)	2004(12)	174(5)
Cl7S	9462(2)	4546.6(11)	3228.9(14)	53.3(6)
Cl8S	9864(2)	5753.3(13)	3424.6(14)	60.5(7)
C4S	9245(7)	5166(4)	3694(5)	43(2)

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) **Rh_2(*R*-TCPTAD)$_4$**. The anisotropic displacement factor exponent takes the form: $-2\ ^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	9.56(14)	12.57(16)	17.47(18)	-0.52(18)	2.04(12)	-0.41(16)
Rh2	11.81(15)	16.48(18)	16.62(18)	2.20(19)	2.70(13)	-0.96(18)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	56.0(12)	37.3(10)	40.1(11)	0.2(8)	-2.1(9)	-25.8(9)
Cl1B	21.9(8)	89.4(19)	69.1(16)	-7.0(14)	-18.2(9)	18.6(10)
Cl1C	36.4(9)	31.2(9)	56.1(12)	-26.4(9)	9.1(8)	-1.8(7)
Cl1D	78.0(16)	62.3(14)	22.4(9)	15.2(9)	17.4(9)	17.4(12)
Cl3	36.8(9)	29.2(8)	25.4(8)	-5.5(6)	-0.4(6)	-6.7(7)
Cl3B	35.4(9)	45.9(10)	51.7(12)	14.0(9)	-3.0(8)	17.3(8)
Cl3C	22.9(7)	33.8(8)	36.5(9)	-16.8(7)	4.3(6)	-7.7(6)
Cl3D	63.1(12)	38.0(11)	29.4(8)	15.1(7)	12.6(8)	18.1(9)
Cl4	72.7(16)	66.7(15)	34(1)	7.4(10)	8.1(10)	-43.5(13)
Cl4B	15.4(7)	76.6(16)	73.3(16)	-19.7(13)	5.1(8)	-17.4(8)
Cl4C	24.4(7)	29.4(8)	39.2(9)	-8.6(7)	7.4(6)	8.9(6)
Cl4D	61.5(13)	45.6(11)	29.4(9)	-3.7(8)	24.4(9)	4.4(9)
Cl7	54.6(12)	45.8(11)	18.8(8)	3.4(7)	3.5(7)	-14.1(9)
Cl7B	34.2(9)	37.8(9)	49.4(11)	-1.8(8)	9.7(8)	-18.6(7)
Cl7C	14.8(6)	30.7(8)	29.6(8)	-6.4(6)	-0.6(5)	3.8(5)
Cl7D	45.1(10)	26.6(8)	32.8(9)	-3.3(7)	12.7(8)	9.5(7)
O1	18.3(15)	24(2)	26(2)	8.2(18)	-2.0(14)	-1.5(14)
O1B	14.4(17)	17.3(19)	28(2)	-3.3(15)	2.0(14)	-3.5(14)
O1C	12.5(16)	21(2)	18.0(16)	5.1(14)	3.0(13)	4.8(14)
O1D	19.9(16)	22(2)	16.2(19)	-1.1(15)	5.1(14)	-2.4(14)
O1W	30(2)	37(3)	50(3)	-1(3)	14(2)	6(2)
O2	17.4(17)	17(2)	28.4(19)	7.4(15)	-0.4(14)	2.5(14)
O2B	15.2(15)	17.1(19)	32(2)	-6.6(17)	2.8(14)	-3.5(13)
O2C	15.3(14)	19.8(19)	15.7(19)	2.5(15)	3.2(12)	2.1(13)
O2D	16.8(17)	21(2)	18.9(17)	-3.1(14)	4.5(14)	-5.4(15)
O3	24(2)	27(2)	24.8(16)	2.3(14)	-0.3(13)	-0.4(17)
O3B	20.1(18)	18.7(15)	35(2)	1.7(15)	6.3(17)	2.6(13)
O3C	16.9(14)	27(2)	24(2)	-2.9(17)	0.6(13)	0.9(13)
O3D	53(3)	20.6(17)	24(2)	4.7(15)	13(2)	9.9(17)
O4	49(3)	31(2)	24.0(18)	2.3(16)	-5.5(17)	-10(2)
O4B	22(2)	21.6(17)	44(3)	6.3(17)	-5.7(19)	-4.5(14)
O4C	17.1(16)	20.9(18)	28(2)	-3.7(16)	-4.2(15)	1.7(14)
O4D	38(2)	19.6(17)	21(2)	2.4(14)	3.9(17)	3.7(16)
N1	22.5(17)	19.6(17)	24.1(16)	4.6(12)	-4.9(13)	-2.7(14)
N1B	12.5(12)	15.0(14)	24.6(19)	-1.5(12)	-0.5(11)	0.2(10)
N1C	15.0(14)	17.9(16)	17.5(18)	-1.7(14)	0.1(12)	2.6(11)
N1D	29(2)	15.2(15)	16.5(15)	0.8(11)	2.4(13)	-0.6(14)
N2	22(2)	44(4)	23(3)	1(3)	6.1(19)	-3(3)
C1	17(2)	19.4(19)	23.8(15)	3.4(13)	-3.4(13)	0.4(16)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1B	13.0(15)	19.1(15)	26(3)	0.3(15)	0.0(14)	2.2(11)
C1C	16.6(14)	18.7(18)	18(2)	-2.3(16)	1.5(12)	0.4(12)
C1D	34(3)	17.8(16)	17.0(17)	1.5(13)	5.7(16)	2.3(16)
C2	19(2)	21.2(17)	22.0(16)	3.0(12)	-3.4(13)	-1.0(15)
C2B	14.3(13)	24.1(16)	24(2)	-2.3(14)	0.8(12)	1.1(11)
C2C	17.1(15)	17.5(16)	16(2)	-0.6(15)	2.7(13)	0.2(11)
C2D	32(3)	21.3(18)	17.1(15)	1.6(12)	4.9(15)	3.7(17)
C3	25(2)	22.2(19)	22.1(17)	1.4(13)	-3.7(14)	-3.6(17)
C3B	17.2(16)	38(2)	34(3)	-2(2)	-4.9(15)	8.1(13)
C3C	20.3(16)	19.6(18)	24(2)	-6.6(17)	5.9(14)	-2.5(13)
C3D	40(3)	28(2)	18.3(17)	6.2(14)	6.3(17)	5(2)
C4	33(3)	31(2)	26.3(17)	3.4(14)	-2.4(16)	-12(2)
C4B	15.5(16)	50(2)	40(3)	-9(2)	-2.8(16)	1.7(14)
C4C	21.9(15)	20.7(19)	31(3)	-8.1(19)	6.1(14)	-0.3(13)
C4D	44(3)	34(2)	19.4(18)	2.8(15)	9.2(18)	4(2)
C5	38(3)	31(2)	25.5(18)	5.1(15)	-1.6(16)	-12(2)
C5B	15.5(16)	50(2)	43(3)	-10(2)	-1.8(16)	-3.6(14)
C5C	20.1(16)	18.6(18)	29(2)	-6.3(18)	5.4(14)	2.0(13)
C5D	46(3)	34(2)	21.1(18)	1.0(15)	10.5(18)	6(2)
C6	33(3)	31(2)	19.8(17)	4.6(14)	-0.7(15)	-10(2)
C6B	15.9(16)	36(2)	38(3)	-6.4(19)	3.2(15)	-9.7(13)
C6C	16.8(15)	16.8(17)	20(2)	-0.2(16)	2.8(13)	3.2(12)
C6D	37(3)	25(2)	21.7(17)	-1.0(14)	7.9(17)	3.5(19)
C7	26(2)	22.5(19)	20.1(16)	3.8(13)	-2.8(13)	-3.6(17)
C7B	13.7(14)	24.4(17)	27(3)	-2.5(16)	-1.0(13)	-2.5(11)
C7C	16.4(14)	14.7(16)	17(2)	0.5(15)	1.8(12)	0.9(11)
C7D	32(3)	20.5(18)	16.9(16)	1.4(13)	4.3(15)	3.4(17)
C8	28(2)	24(2)	23.8(16)	5.1(13)	-4.2(14)	-5.4(19)
C8B	14.6(15)	18.9(16)	30(3)	-0.1(16)	-0.9(14)	-4.0(12)
C8C	13.5(14)	15.4(17)	16(2)	0.1(15)	0.2(12)	2.0(11)
C8D	25(2)	16.5(16)	15.9(16)	-1.1(12)	0.4(15)	-2.0(15)
C9	22.0(14)	21.0(16)	27.7(18)	6.9(13)	-6.8(12)	-3.5(11)
C9B	12.9(13)	16.8(16)	30.6(17)	-4.4(13)	-0.5(11)	0.3(11)
C9C	17.9(17)	16.7(17)	14.8(15)	0.4(12)	2.3(12)	3.7(13)
C9D	24.9(17)	19.5(19)	17.2(16)	0.9(13)	2.4(12)	-1.9(14)
C10	16.4(16)	21(2)	25(2)	4.6(17)	-4.7(14)	-3.9(14)
C10B	11.9(15)	15.1(18)	25(2)	-1.0(16)	-1.5(14)	0.4(13)
C10C	14.8(16)	15(2)	15.8(17)	0.9(14)	2.5(12)	0.5(14)
C10D	17.5(17)	16(2)	17.0(18)	2.1(15)	2.6(14)	0.9(15)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	19.7(16)	27(2)	54(3)	16.3(18)	-3.1(15)	-1.1(14)
C11B	15.6(17)	24(2)	39.7(19)	-12.5(15)	5.0(14)	-2.1(14)
C11C	27.7(19)	17.9(18)	14.8(15)	0.5(12)	5.8(13)	2.5(14)
C11D	23.7(17)	34(2)	19(2)	2.3(16)	1.2(13)	-6.8(14)
C12	29(2)	29(3)	55(3)	14(2)	1.6(18)	-0.5(17)
C12B	27(2)	28(2)	39(2)	-11.1(17)	9.1(18)	-1.0(17)
C12C	30(2)	19(2)	19.5(19)	0.5(15)	8.3(15)	1.0(16)
C12D	25(2)	40(2)	45(3)	5(2)	0.9(18)	-3.0(16)
C13	30(2)	44(3)	78(3)	16(2)	6(2)	4.4(19)
C13B	34(2)	48(3)	47(3)	-20.3(19)	15.5(19)	-5.1(19)
C13C	43(2)	25(2)	22(2)	-0.1(16)	14.9(17)	-1.5(17)
C13D	26(2)	61(3)	55(3)	7(2)	0.6(19)	-7.8(19)
C14	30(3)	48(3)	82(3)	22(2)	2(2)	1(2)
C14B	31(3)	47(3)	57(3)	-26(2)	14(2)	-1(2)
C14C	50(3)	30(2)	25(2)	3.5(18)	12.2(19)	3.1(18)
C14D	41(3)	66(3)	53(3)	6(2)	4(2)	-17(2)
C15	27(2)	47(3)	79(3)	24(2)	-4(2)	2.7(19)
C15B	22(2)	44(3)	58(3)	-28(2)	9.8(18)	-3.5(18)
C15C	49(3)	33(2)	20(2)	4.1(16)	9.7(17)	3.7(18)
C15D	40(3)	61(3)	37(3)	1(2)	1.5(19)	-20(2)
C16	27(2)	37(3)	58(3)	21(2)	-8.7(18)	-0.5(19)
C16B	17(2)	27(2)	51(3)	-19.2(19)	4.1(17)	-1.2(16)
C16C	35(2)	25(2)	16.8(18)	2.6(16)	2.8(15)	5.6(17)
C16D	40(2)	45(3)	27(2)	-4(2)	3.7(17)	-16.0(19)
C17	26(2)	32(2)	62(4)	15(2)	-3.8(19)	-6.8(16)
C17B	20.8(16)	31(2)	47(2)	-11.0(16)	3.6(14)	1.1(14)
C17C	32(2)	20.1(18)	16.4(19)	-0.2(14)	6.7(16)	3.0(16)
C17D	24(2)	35(3)	23(2)	3.0(18)	4.2(15)	-4.8(17)
C18	25(2)	44(3)	71(3)	17(2)	-1.1(19)	-3.6(18)
C18B	21(2)	48(3)	59(3)	-23(2)	9.6(18)	-4.0(18)
C18C	45(2)	27(2)	18(2)	0.3(16)	11.7(17)	-0.6(17)
C18D	23(2)	53(3)	34(3)	2(2)	3.8(17)	-10.6(18)
C19	34(3)	51(3)	76(3)	21(2)	-4(2)	-1(2)
C19B	23(2)	46(3)	71(4)	-28(2)	8(2)	-0.7(18)
C19C	49(3)	34(2)	19(2)	2.4(17)	10.4(18)	2.8(19)
C19D	38(3)	57(3)	37(3)	0(2)	3(2)	-16(2)
C20	42(2)	49(2)	67(3)	13.4(18)	4.4(18)	-2.3(18)
C20B	32(2)	48(3)	56(3)	-24(2)	14(2)	-4.8(19)
C20C	45(2)	26(2)	24(3)	-2.0(18)	15.1(19)	-0.7(17)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C20D	26(3)	57(3)	56(3)	4(2)	4(2)	-7(2)
C21	21(3)	44(4)	40(4)	5(4)	8(2)	-1(3)
C22	25(3)	91(7)	53(5)	6(6)	19(3)	-7(5)
Cl1S	98(2)	52.6(14)	105(2)	13.9(18)	9.8(17)	23.1(17)
Cl2S	105(2)	111(3)	64.6(18)	4(2)	0.4(16)	50(2)
C1S	92(4)	57(5)	61(4)	10(4)	0(3)	26(3)
Cl3S	88(2)	122(3)	83(2)	5(2)	2.2(18)	15(2)
Cl4S	84.3(19)	61.1(16)	65.1(18)	5.6(13)	-5.5(14)	14.1(14)
C2S	87(3)	80(4)	80(3)	3(2)	4(2)	0(2)
Cl5S	165(6)	137(5)	167(5)	-16(4)	19(4)	-19(4)
Cl6S	237(7)	368(15)	284(11)	155(11)	94(7)	82(10)
C3S	174(6)	174(6)	172(5)	3(3)	18(3)	-10(3)
Cl7S	61.6(14)	48.2(13)	51.7(14)	-3.6(10)	13.4(11)	9.9(11)
Cl8S	71.9(17)	60.9(15)	50.4(14)	-2.2(12)	14.7(12)	-24.8(13)
C4S	47(5)	46(5)	39(5)	-5(3)	18(4)	-7(3)

Table 3: Bond Lengths in Å for **Rh_2(*R*-TCPTAD)$_4$**.

Atom	Atom	Length/Å
Rh1	Rh2	2.39913(4)
Rh1	O1W	2.265(5)
Rh1	O2	2.048(4)
Rh1	O2B	2.018(4)
Rh1	O2C	2.038(4)
Rh1	O2D	2.018(4)
Rh2	O1	2.036(5)
Rh2	O1B	2.049(4)
Rh2	O1C	2.055(4)
Rh2	O1D	2.051(5)
Rh2	N2	2.224(5)
Cl1	C4	1.720(7)
Cl1B	C4B	1.719(8)
Cl1C	C4C	1.728(7)
Cl1D	C4D	1.729(7)
Cl3	C3	1.721(7)
Cl3B	C3B	1.711(8)
Cl3C	C3C	1.721(6)
Cl3D	C3D	1.716(7)
Cl4	C5	1.723(8)

Atom	Atom	Length/Å
Cl4B	C5B	1.716(8)
Cl4C	C5C	1.733(6)
Cl4D	C5D	1.716(8)
Cl7	C6	1.734(7)
Cl7B	C6B	1.710(8)
Cl7C	C6C	1.720(6)
Cl7D	C6D	1.724(7)
O1	C10	1.268(8)
O1B	C10B	1.256(8)
O1C	C10C	1.250(7)
O1D	C10D	1.268(7)
O2	C10	1.243(8)
O2B	C10B	1.266(7)
O2C	C10C	1.258(7)
O2D	C10D	1.265(7)
O3	C1	1.192(8)
O3B	C1B	1.188(8)
O3C	C1C	1.193(7)
O3D	C1D	1.203(8)
O4	C8	1.214(9)
O4B	C8B	1.202(8)
O4C	C8C	1.199(7)
O4D	C8D	1.201(8)
N1	C1	1.408(8)
N1	C8	1.385(10)
N1	C9	1.469(8)
N1B	C1B	1.395(8)
N1B	C8B	1.397(8)
N1B	C9B	1.483(7)
N1C	C1C	1.379(8)
N1C	C8C	1.430(7)
N1C	C9C	1.468(8)
N1D	C1D	1.395(8)
N1D	C8D	1.403(8)
N1D	C9D	1.479(8)
N2	C21	1.150(9)
C1	C2	1.501(9)
C1B	C2B	1.499(8)
C1C	C2C	1.519(8)

Atom	Atom	Length/Å
C1D	C2D	1.493(9)
C2	C3	1.380(9)
C2	C7	1.393(9)
C2B	C3B	1.418(9)
C2B	C7B	1.369(9)
C2C	C3C	1.374(8)
C2C	C7C	1.396(8)
C2D	C3D	1.380(9)
C2D	C7D	1.396(9)
C3	C4	1.393(10)
C3B	C4B	1.405(10)
C3C	C4C	1.394(9)
C3D	C4D	1.404(10)
C4	C5	1.382(11)
C4B	C5B	1.397(13)
C4C	C5C	1.388(9)
C4D	C5D	1.407(11)
C5	C6	1.405(10)
C5B	C6B	1.410(10)
C5C	C6C	1.400(8)
C5D	C6D	1.400(10)
C6	C7	1.371(10)
C6B	C7B	1.386(9)
C6C	C7C	1.380(8)
C6D	C7D	1.371(9)
C7	C8	1.503(9)
C7B	C8B	1.504(8)
C7C	C8C	1.509(8)
C7D	C8D	1.485(9)
C9	C10	1.552(9)
C9	C11	1.573(10)
C9B	C10B	1.536(8)
C9B	C11B	1.542(10)
C9C	C10C	1.548(8)
C9C	C11C	1.558(8)
C9D	C10D	1.530(9)
C9D	C11D	1.557(9)
C11	C12	1.531(13)
C11	C16	1.532(11)

Atom	Atom	Length/Å
C11	C17	1.562(10)
C11B	C12B	1.528(11)
C11B	C16B	1.536(9)
C11B	C17B	1.559(9)
C11C	C12C	1.540(9)
C11C	C16C	1.539(9)
C11C	C17C	1.543(9)
C11D	C12D	1.527(11)
C11D	C16D	1.539(10)
C11D	C17D	1.563(10)
C12	C13	1.555(12)
C12B	C13B	1.544(11)
C12C	C13C	1.546(9)
C12D	C13D	1.517(11)
C13	C14	1.548(14)
C13	C20	1.494(14)
C13B	C14B	1.548(12)
C13B	C20B	1.527(12)
C13C	C14C	1.530(11)
C13C	C20C	1.539(10)
C13D	C14D	1.569(15)
C13D	C20D	1.550(14)
C14	C15	1.476(17)
C14B	C15B	1.520(15)
C14C	C15C	1.522(12)
C14D	C15D	1.476(16)
C15	C16	1.553(12)
C15	C19	1.542(14)
C15B	C16B	1.529(11)
C15B	C19B	1.539(11)
C15C	C16C	1.531(10)
C15C	C19C	1.516(11)
C15D	C16D	1.548(12)
C15D	C19D	1.549(13)
C17	C18	1.572(12)
C17B	C18B	1.549(12)
C17C	C18C	1.553(9)
C17D	C18D	1.531(10)
C18	C19	1.489(14)

Atom	Atom	Length/Å
C18	C20	1.510(11)
C18B	C19B	1.534(11)
C18B	C20B	1.513(10)
C18C	C19C	1.551(11)
C18C	C20C	1.523(11)
C18D	C19D	1.533(12)
C18D	C20D	1.543(14)
C21	C22	1.449(10)
Cl1S	C1S	1.755(16)
Cl2S	C1S	1.729(14)
Cl3S	C2S	1.731(16)
Cl4S	C2S	1.728(16)
Cl5S	C3S	1.88(2)
Cl6S	C3S	1.778(3)
Cl7S	C4S	1.761(9)
Cl8S	C4S	1.744(9)

Table 4: Bond Angles in ° for **Rh_2(*R*-TCPTAD)$_4$**.

Atom	Atom	Atom	Angle/°
O1W	Rh1	Rh2	177.58(16)
O2	Rh1	Rh2	88.25(13)
O2	Rh1	O1W	91.7(2)
O2B	Rh1	Rh2	87.60(13)
O2B	Rh1	O1W	94.8(2)
O2B	Rh1	O2	90.01(19)
O2B	Rh1	O2C	88.5(2)
O2C	Rh1	Rh2	87.99(12)
O2C	Rh1	O1W	92.1(2)
O2C	Rh1	O2	176.01(18)
O2D	Rh1	Rh2	88.79(12)
O2D	Rh1	O1W	88.8(2)
O2D	Rh1	O2	88.0(2)
O2D	Rh1	O2B	175.95(19)
O2D	Rh1	O2C	93.21(18)
O1	Rh2	Rh1	87.66(15)
O1	Rh2	O1B	90.4(2)

Atom	Atom	Atom	Angle/°
O1	Rh2	O1C	175.2(2)
O1	Rh2	O1D	87.97(18)
O1	Rh2	N2	92.5(2)
O1B	Rh2	Rh1	88.11(13)
O1B	Rh2	O1C	88.49(19)
O1B	Rh2	O1D	175.12(19)
O1B	Rh2	N2	92.1(2)
O1C	Rh2	Rh1	87.64(12)
O1C	Rh2	N2	92.2(2)
O1D	Rh2	Rh1	87.24(13)
O1D	Rh2	O1C	92.80(18)
O1D	Rh2	N2	92.6(2)
N2	Rh2	Rh1	179.7(2)
C10	O1	Rh2	118.2(4)
C10B	O1B	Rh2	117.7(4)
C10C	O1C	Rh2	117.6(4)
C10D	O1D	Rh2	118.5(4)
C10	O2	Rh1	117.4(4)
C10B	O2B	Rh1	119.6(4)
C10C	O2C	Rh1	118.3(4)
C10D	O2D	Rh1	118.3(4)
C1	N1	C9	123.1(6)
C8	N1	C1	112.2(5)
C8	N1	C9	123.7(6)
C1B	N1B	C8B	113.3(5)
C1B	N1B	C9B	124.7(5)
C8B	N1B	C9B	122.0(5)
C1C	N1C	C8C	113.2(5)
C1C	N1C	C9C	125.0(5)
C8C	N1C	C9C	121.4(5)
C1D	N1D	C8D	112.7(5)
C1D	N1D	C9D	126.5(5)
C8D	N1D	C9D	120.8(5)
C21	N2	Rh2	178.2(8)
O3	C1	N1	126.3(6)
O3	C1	C2	129.0(6)
N1	C1	C2	104.7(5)
O3B	C1B	N1B	126.4(5)
O3B	C1B	C2B	129.3(6)

Atom	Atom	Atom	Angle/°
N1B	C1B	C2B	104.2(5)
O3C	C1C	N1C	126.2(6)
O3C	C1C	C2C	128.2(6)
N1C	C1C	C2C	105.6(5)
O3D	C1D	N1D	125.9(6)
O3D	C1D	C2D	129.1(6)
N1D	C1D	C2D	105.1(5)
C3	C2	C1	130.3(6)
C3	C2	C7	121.1(6)
C7	C2	C1	108.7(5)
C3B	C2B	C1B	129.6(6)
C7B	C2B	C1B	109.3(5)
C7B	C2B	C3B	121.1(6)
C3C	C2C	C1C	130.8(5)
C3C	C2C	C7C	121.1(5)
C7C	C2C	C1C	108.0(5)
C3D	C2D	C1D	130.2(6)
C3D	C2D	C7D	121.5(6)
C7D	C2D	C1D	108.3(6)
C2	C3	Cl3	121.0(5)
C2	C3	C4	118.6(6)
C4	C3	Cl3	120.5(5)
C2B	C3B	Cl3B	121.1(6)
C4B	C3B	Cl3B	122.2(5)
C4B	C3B	C2B	116.8(7)
C2C	C3C	Cl3C	121.3(5)
C2C	C3C	C4C	117.6(6)
C4C	C3C	Cl3C	121.0(5)
C2D	C3D	Cl3D	122.4(6)
C2D	C3D	C4D	117.5(6)
C4D	C3D	Cl3D	120.1(5)
C3	C4	Cl1	119.9(6)
C5	C4	Cl1	119.6(6)
C5	C4	C3	120.5(6)
C3B	C4B	Cl1B	118.5(7)
C5B	C4B	Cl1B	120.2(6)
C5B	C4B	C3B	121.3(7)
C3C	C4C	Cl1C	119.5(5)
C5C	C4C	Cl1C	119.1(5)

Atom	Atom	Atom	Angle/°
C5C	C4C	C3C	121.4(6)
C3D	C4D	Cl1D	119.9(6)
C3D	C4D	C5D	121.2(7)
C5D	C4D	Cl1D	118.9(6)
C4	C5	Cl4	120.0(6)
C4	C5	C6	120.6(7)
C6	C5	Cl4	119.4(6)
C4B	C5B	Cl4B	119.5(6)
C4B	C5B	C6B	120.8(7)
C6B	C5B	Cl4B	119.7(7)
C4C	C5C	Cl4C	119.9(5)
C4C	C5C	C6C	121.0(6)
C6C	C5C	Cl4C	119.1(5)
C4D	C5D	Cl4D	119.9(6)
C6D	C5D	Cl4D	120.4(6)
C6D	C5D	C4D	119.7(7)
C5	C6	Cl7	121.0(6)
C7	C6	Cl7	120.3(5)
C7	C6	C5	118.7(7)
C5B	C6B	Cl7B	120.4(6)
C7B	C6B	Cl7B	122.3(6)
C7B	C6B	C5B	117.2(7)
C5C	C6C	Cl7C	121.1(4)
C7C	C6C	Cl7C	121.9(5)
C7C	C6C	C5C	117.0(5)
C5D	C6D	Cl7D	119.9(6)
C7D	C6D	Cl7D	121.3(5)
C7D	C6D	C5D	118.8(7)
C2	C7	C8	107.1(6)
C6	C7	C2	120.6(6)
C6	C7	C8	132.2(6)
C2B	C7B	C6B	122.6(6)
C2B	C7B	C8B	108.0(5)
C6B	C7B	C8B	129.3(6)
C2C	C7C	C8C	108.5(5)
C6C	C7C	C2C	121.9(5)
C6C	C7C	C8C	129.6(5)
C2D	C7D	C8D	108.2(6)
C6D	C7D	C2D	121.1(6)

Atom	Atom	Atom	Angle/°
C6D	C7D	C8D	130.7(6)
O4	C8	N1	125.0(6)
O4	C8	C7	128.6(7)
N1	C8	C7	106.4(6)
O4B	C8B	N1B	126.2(6)
O4B	C8B	C7B	129.0(6)
N1B	C8B	C7B	104.8(5)
O4C	C8C	N1C	125.8(5)
O4C	C8C	C7C	129.8(5)
N1C	C8C	C7C	104.4(5)
O4D	C8D	N1D	125.3(6)
O4D	C8D	C7D	129.3(6)
N1D	C8D	C7D	105.4(5)
N1	C9	C10	107.1(5)
N1	C9	C11	112.4(5)
C10	C9	C11	119.0(6)
N1B	C9B	C10B	108.1(5)
N1B	C9B	C11B	113.4(5)
C10B	C9B	C11B	118.4(5)
N1C	C9C	C10C	107.6(5)
N1C	C9C	C11C	112.6(5)
C10C	C9C	C11C	118.5(5)
N1D	C9D	C10D	108.8(5)
N1D	C9D	C11D	112.5(5)
C10D	C9D	C11D	118.5(5)
O1	C10	C9	113.6(6)
O2	C10	O1	128.2(6)
O2	C10	C9	118.2(6)
O1B	C10B	O2B	126.6(6)
O1B	C10B	C9B	117.1(5)
O2B	C10B	C9B	116.2(5)
O1C	C10C	O2C	127.4(5)
O1C	C10C	C9C	114.9(5)
O2C	C10C	C9C	117.7(5)
O1D	C10D	C9D	116.5(5)
O2D	C10D	O1D	126.6(6)
O2D	C10D	C9D	116.8(5)
C12	C11	C9	114.0(6)
C12	C11	C16	109.6(7)

Atom	Atom	Atom	Angle/°
C12	C11	C17	108.2(7)
C16	C11	C9	108.4(7)
C16	C11	C17	107.5(6)
C17	C11	C9	109.1(6)
C9B	C11B	C17B	109.0(6)
C12B	C11B	C9B	113.7(5)
C12B	C11B	C16B	108.9(6)
C12B	C11B	C17B	110.2(6)
C16B	C11B	C9B	108.3(5)
C16B	C11B	C17B	106.4(5)
C12C	C11C	C9C	113.9(5)
C12C	C11C	C17C	110.1(5)
C16C	C11C	C9C	109.2(5)
C16C	C11C	C12C	107.2(5)
C16C	C11C	C17C	107.7(5)
C17C	C11C	C9C	108.5(5)
C9D	C11D	C17D	108.5(5)
C12D	C11D	C9D	115.6(6)
C12D	C11D	C16D	109.2(6)
C12D	C11D	C17D	108.4(6)
C16D	C11D	C9D	108.0(6)
C16D	C11D	C17D	106.7(6)
C11	C12	C13	111.0(7)
C11B	C12B	C13B	110.2(6)
C11C	C12C	C13C	110.0(5)
C13D	C12D	C11D	110.9(7)
C14	C13	C12	109.1(9)
C20	C13	C12	108.5(8)
C20	C13	C14	109.3(9)
C12B	C13B	C14B	108.9(7)
C20B	C13B	C12B	109.8(7)
C20B	C13B	C14B	109.3(7)
C14C	C13C	C12C	109.4(6)
C14C	C13C	C20C	110.5(6)
C20C	C13C	C12C	109.2(6)
C12D	C13D	C14D	109.3(8)
C12D	C13D	C20D	109.9(7)
C20D	C13D	C14D	109.3(8)
C15	C14	C13	110.4(9)

Atom	Atom	Atom	Angle/°
C15B	C14B	C13B	109.8(8)
C15C	C14C	C13C	108.4(6)
C15D	C14D	C13D	110.6(8)
C14	C15	C16	111.5(8)
C14	C15	C19	108.1(9)
C19	C15	C16	107.4(8)
C14B	C15B	C16B	110.2(7)
C14B	C15B	C19B	110.2(7)
C16B	C15B	C19B	107.9(7)
C14C	C15C	C16C	109.8(6)
C19C	C15C	C14C	110.8(7)
C19C	C15C	C16C	109.6(6)
C14D	C15D	C16D	109.5(8)
C14D	C15D	C19D	108.9(9)
C16D	C15D	C19D	109.1(7)
C11	C16	C15	110.6(8)
C15B	C16B	C11B	111.4(6)
C15C	C16C	C11C	110.8(6)
C11D	C16D	C15D	111.3(7)
C11	C17	C18	109.2(7)
C18B	C17B	C11B	108.9(6)
C11C	C17C	C18C	110.7(5)
C18D	C17D	C11D	110.6(6)
C19	C18	C17	108.3(8)
C19	C18	C20	109.7(9)
C20	C18	C17	109.5(8)
C19B	C18B	C17B	108.1(7)
C20B	C18B	C17B	110.2(7)
C20B	C18B	C19B	112.9(8)
C19C	C18C	C17C	107.6(6)
C20C	C18C	C17C	109.0(6)
C20C	C18C	C19C	110.2(6)
C17D	C18D	C19D	110.2(7)
C17D	C18D	C20D	109.5(7)
C19D	C18D	C20D	109.8(7)
C18	C19	C15	111.6(8)
C18B	C19B	C15B	108.0(7)
C15C	C19C	C18C	109.3(6)
C18D	C19D	C15D	109.4(8)

Atom	Atom	Atom	Angle/°
C13	C20	C18	111.0(9)
C18B	C20B	C13B	109.0(7)
C18C	C20C	C13C	109.9(6)
C18D	C20D	C13D	107.7(8)
N2	C21	C22	178.2(12)
Cl2S	C1S	Cl1S	113.4(8)
Cl4S	C2S	Cl3S	115.0(9)
Cl6S	C3S	Cl5S	105.0(9)
Cl8S	C4S	Cl7S	111.8(5)

Table 5: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Rh_2(*R*-TCPTAD)$_4$**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H1WA	3689	5075	4594	57
H1WB	3056	5399	3990	57
H9	4030	6171	1333	29
H9B	6596	7049	4028	25
H9C	7878	4664	4867	20
H9D	4719	3650	2201	25
H12A	3394	7299	2492	45
H12B	3234	6736	2929	45
H12C	6959	6264	5682	37
H12D	5917	6066	5303	37
H12E	6214	3473	5075	27
H12F	5513	4017	4973	27
H12G	2822	4701	2225	44
H12H	2727	4591	1404	44
H13	1899	7387	2970	61
H13B	5816	6265	6500	50
H13C	5096	3453	5912	35
H13D	1166	4603	1745	57
H14A	848	7593	1907	65
H14B	1917	7827	1856	65
H14C	6129	7218	6931	53
H14D	7089	6961	6679	53
H14E	6255	3308	6922	41
H14F	6653	3037	6257	41
H14G	600	3696	1253	64
H14H	1376	3960	806	64
H15	1305	7340	836	62
H15B	6830	7899	6239	49
H15C	7892	3589	6902	40
H15D	1710	2998	1020	56
H16A	2624	6682	795	51
H16B	3034	7262	1158	51
H16C	7545	7266	5506	38
H16D	6857	7703	5036	38

Atom	x	y	z	U_{eq}
H16E	7895	3562	5681	31
H16F	8304	4163	5982	31
H16G	3383	3101	1511	45
H16H	3085	3600	960	45
H17A	2643	5824	2316	49
H17B	2396	5817	1484	49
H17C	5247	7427	4463	40
H17D	4837	6795	4538	40
H17E	6168	4994	5459	27
H17F	7255	5029	5855	27
H17G	3523	3274	2778	33
H17H	3317	3893	3074	33
H18	903	5909	1996	57
H18B	4119	7416	5293	51
H18C	6124	5011	6691	35
H18D	1959	3295	3142	44
H19A	276	6695	1346	66
H19B	972	6341	912	66
H19C	5102	7938	6170	56
H19D	5403	8101	5426	56
H19E	7702	4585	7017	40
H19F	6911	4255	7395	40
H19G	1046	2931	2103	53
H19H	2125	2676	2197	53
H20A	648	6732	2642	64
H20B	1581	6401	3017	64
H20C	4397	6471	5693	53
H20D	4475	6902	6339	53
H20E	4895	4462	6007	37
H20F	5153	4186	6765	37
H20G	1616	4288	2933	56
H20H	730	3911	2560	56
H22A	8756	5147	1099	82
H22B	9520	5140	1795	82
H22C	9169	5733	1440	82
H1SA	3063	6021	7281	85
H1SB	3504	5554	7835	85
H2SA	4684	6743	-698	99
H2SB	4199	7251	-1170	99

Atom	x	y	z	U_{eq}
H3SA	7629	4127	2371	209
H3SB	7062	3570	2049	209
H4SA	8541	5248	3628	51
H4SB	9452	5101	4196	51

Table 6: Solvent masking (PLATON/SQUEEZE) information for **Rh_2(*R*-TCPTAD)$_4$**.

No	x	y	z	V	e	Content
1	0.000	-0.008	0.000	1738	410	

Citations

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Rigaku Oxford Diffraction, (2015), CrysAlisPro Software system, version 1.171.39.9g,

Rigaku Corporation, Oxford, UK.

Sheldrick, G.M., A short history of ShelX, *Acta Cryst.*, (2008), **A64**, 339-341.

Spek, A. L. (1980-2014). PLATON. Version 191114. Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands.

```
#==============================================================================
# PLATON/CHECK-( 70414) versus check.def version of 310314   for Entry: rh2r-tcp
# Data: rh2r-tcptad4-sq_sq.cif - Type: CIF       Bond Precision   C-C = 0.0109 A
# Refl: rh2r-tcptad4-sq_sq.fcf - Type: LIST4                    Temp = 100 K
#                                    X-Ray        Nref/Npar =  16.3
# Cell  13.9309(2)  23.4777(4)  19.4295(4)          90  97.9250(17)         90
# Wavelength 0.71073    Volume Reported     6294.0(2)   Calculated   6294.03(19)
# SpaceGroup from Symmetry P 21       Hall: P 2yb              monoclinic
#              Reported P 1 21 1        P 2yb              monoclinic
# MoietyFormula C82 H69 Cl16 N5 O17 Rh2, 4(C H2 Cl2)
#      Reported C82 H69 Cl16 N5 O17 Rh2, 4(C H2 Cl2)
#    SumFormula C86 H77 Cl24 N5 O17 Rh2
#      Reported C86 H77 Cl24 N5 O17 Rh2
# Mr       =   2509.15[Calc],   2509.14[Rep]
# Dx,gcm-3  =     1.324[Calc],     1.324[Rep]
# Z        =         2[Calc],         2[Rep]
# Mu (mm-1) =     0.824[Calc],     0.824[Rep]
# F000     =    2524.0[Calc],    2524.0[Rep]  or F000' =   2527.46[Calc]
# Reported   T Limits: Tmin=0.729              Tmax=1.000  AbsCorr=MULTI-SCAN
# Calculated T Limits: Tmin=0.616 Tmin'=0.556  Tmax=0.719
# Reported   Hmax= 19, Kmax= 33, Lmax= 27, Nref=  38220        , Th(max)= 30.508
# Obs in FCF Hmax= 19, Kmax= 33, Lmax= 27, Nref=  38220[ 19594], Th(max)= 30.508
# Calculated Hmax= 19, Kmax= 33, Lmax= 27, Nref=  38391[ 19624], Ratio=1.95/1.00
# PLATON/Squeeze:      1738.0 Ang**3, Total El.Count =   410.0 e-
# Reported   Rho(min) = -1.07, Rho(max) =  1.92 e/Ang**3 (From CIF)
# w=1/[sigma**2(Fo**2)+(0.0808P)**2+ 14.7866P], P=(Fo**2+2*Fc**2)/3
# R= 0.0641( 32914), wR2= 0.1590( 38220), S = 1.040      (From FCF data only)
# R= 0.0641( 32915), wR2= 0.1590( 38220), S = 1.043, Npar= 1203, Flack -0.007(8)
# Number Bijvoet Pairs =18626 ( 99%)     (13732 Selected for:  Parsons  0.040(4)
# P2(tr) 1.000, P3(tr) 1.000, P3(tw) 0.000,  Student-T Nu  9.28, Hooft -0.013(6)
#==============================================================================
For Documentation: http://http://www.platonsoft.nl/CIF-VALIDATION.pdf
#==============================================================================

#==============================================================================
>>> The Following Improvement and Query ALERTS were generated - (Acta-Mode) <<<
#==============================================================================
Format: alert-number_ALERT_alert-type_alert-level text

420_ALERT_2_B D-H Without Acceptor       O1W    -   H1WA   ...     Please Check
420_ALERT_2_B D-H Without Acceptor       O1W    -   H1WB   ...     Please Check
#==============================================================================
161_ALERT_4_C Missing or Zero su (esd) on x-coordinate for ...        RH1
```

161_ALERT_4_C Missing or Zero su (esd) on x-coordinate for ... RH2
162_ALERT_4_C Missing or Zero su (esd) on y-coordinate for ... RH1
162_ALERT_4_C Missing or Zero su (esd) on y-coordinate for ... RH2
163_ALERT_4_C Missing or Zero su (esd) on z-coordinate for ... RH1
163_ALERT_4_C Missing or Zero su (esd) on z-coordinate for ... RH2
220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 3.6 Ratio
222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.1 Ratio
244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C1S Check
244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C3S Check
342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0109 Ang.
411_ALERT_2_C Short Inter H...H Contact H15B .. H18D .. 2.14 Ang.
731_ALERT_1_C Bond Calc 2.39910(10), Rep 2.39913(4) ..... 3 su-Rat
RH1 -RH2 1.555 1.555 # 1
911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 19 Why ?
913_ALERT_3_C Missing # of Very Strong Reflections in FCF .... 1 Note
#==========

002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 7 Note
003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 125 Why ?
007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 2 Why ?
008_ALERT_5_G No _iucr_refine_reflections_details in the CIF Please Do !
063_ALERT_4_G Crystal Size Likely too Large for Beam Size .... 0.70 mm
083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 14.79 Why ?
232_ALERT_2_G Hirshfeld Test Diff (M-X) Rh1 -- O1W .. 5.3 su
434_ALERT_2_G Short Inter HL..HL Contact Cl1 .. Cl1S . 3.34 Ang.
606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure ! Info
720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 10 Note
760_ALERT_1_G CIF Contains no Torsion Angles ..... ? Info
790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 3 Note
C H2 Cl2
791_ALERT_4_G The Model has Chirality at C9 ..... R Verify
791_ALERT_4_G The Model has Chirality at C9B ..... R Verify
791_ALERT_4_G The Model has Chirality at C9C ..... R Verify
791_ALERT_4_G The Model has Chirality at C9D ..... R Verify
791_ALERT_4_G The Model has Chirality at C18 ..... R Verify
791_ALERT_4_G The Model has Chirality at C18B ..... R Verify
791_ALERT_4_G The Model has Chirality at C18C ..... R Verify
791_ALERT_4_G The Model has Chirality at C18D ..... R Verify
802_ALERT_4_G CIF Input Record(s) with more than 80 Characters ! Info
860_ALERT_3_G Number of Least-Squares Restraints ..... 1130 Note
869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed ! Info
910_ALERT_3_G Missing # of FCF Reflections Below Th(Min) ..... 3 Why ?
912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 9 Note
#==========

ALERT_Level and ALERT_Type Summary

==========

2 ALERT_Level_B = A Potentially Serious Problem - Consider Carefully

15 ALERT_Level_C = Check. Ensure it is Not caused by an Omission or Oversight

25 ALERT_Level_G = General Info/Check that it is not Something Unexpected

2 ALERT_Type_1 CIF Construction/Syntax Error, Inconsistent or Missing Data.

9 ALERT_Type_2 Indicator that the Structure Model may be Wrong or Deficient.

6 ALERT_Type_3 Indicator that the Structure Quality may be Low.

23 ALERT_Type_4 Improvement, Methodology, Query or Suggestion.

2 ALERT_Type_5 Informative Message, Check.

#==========

1 Missing Experimental Info Issue(s) (Out of 54 Tests) - 98 % Satisfied

0 Experimental Data Related Issue(s) (Out of 28 Tests) - 100 % Satisfied

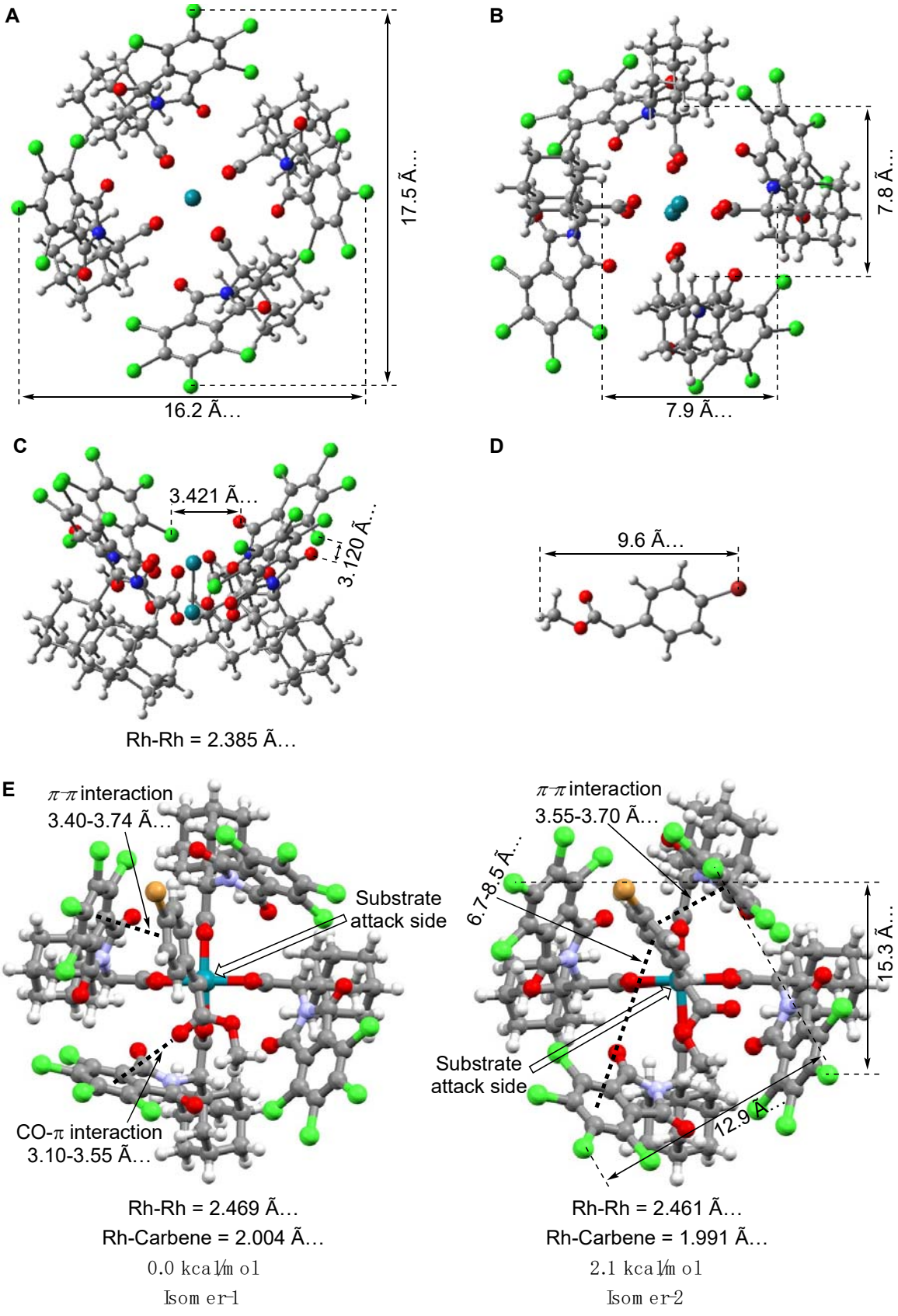
11 Structural Model Related Issue(s) (Out of 117 Tests) - 91 % Satisfied

30 Unresolved or to be Checked Issue(s) (Out of 223 Tests) - 87 % Satisfied

#==========

12 - Computational study of Rh_2(*S*-TCPTAD)$_4$

Computational Procedure. Geometry of the Rh_2(*S*-TCPTAD)$_4$, and their carbenes, [(*p*-Br-C_6H_4)C(COOMe)], complexes were optimized in the gas phase with no geometry constraints. Vibrational analyses were performed to ensure that all reported structures are true minima. In these calculations we used the Density Functional Theory with M06L-functional[7] in conjunction with the 6-31G(d) basis sets for all atoms, except Rh: For Rh we used the lanl2dz basis set with the associated Hay-Wadt ECPs.[8-9] Previously,[10] we have shown that this approach describes both geometries and relative energies of the transition metal systems with reasonable accuracy. All calculations were carried out with the Gaussian 09 software package.[11]


A
17.5 Å…
16.2 Å…
B
7.8 Å…
7.9 Å…
C
3.421 Å…
3.120 Å…
Rh-Rh = 2.385 Å…
D
9.6 Å…
E
π-π interaction
3.40-3.74 Å…
Substrate
attack side
CO-π interaction
3.10-3.55 Å…
Rh-Rh = 2.469 Å…
Rh-Carbene = 2.004 Å…
0.0 kcal/mol
Isomer-1
π-π interaction
3.55-3.70 Å…
6.7-8.5 Å…
15.3 Å…
Substrate
attack side
12.9 Å…
Rh-Rh = 2.461 Å…
Rh-Carbene = 1.991 Å…
2.1 kcal/mol
Isomer-2

Triplet Carbene: CCOOMe_PhBr

C	0.09888200	1.59108200	0.48702400
C	-1.19936900	1.11870200	0.25213300
C	-2.29189900	1.70156200	0.94602600
C	-1.47617100	0.06568200	-0.66399700
C	-3.58585900	1.26158200	0.74345100
H	-2.09693800	2.50878400	1.64957200
C	-2.77210200	-0.37149600	-0.86425100
H	-0.64815200	-0.38867000	-1.20114600
C	-3.82315300	0.22366400	-0.16140200
H	-4.41566900	1.71479500	1.27919500
H	-2.97837400	-1.17571600	-1.56598600
Br	-5.58917700	-0.38613200	-0.43193800
C	1.38810300	1.23879100	-0.03553700
O	1.58247300	0.36261300	-0.86955900
O	2.37263700	1.99203000	0.50272800
C	3.67899900	1.67808100	0.01910700
H	3.73035000	1.80478500	-1.06682100
H	4.35239800	2.37384000	0.52056500
H	3.94297500	0.64370800	0.26246000

Rh_2(*S*-TCPTAD)$_4$

Rh	0.06610900	0.31393900	-1.87950400
O	-2.00557500	0.31054000	-1.93610000
O	2.12384900	0.31139600	-1.71101900
O	-2.12498200	0.20319800	0.32587200
O	2.01489300	0.02460400	0.53587700
O	0.09178300	2.36133600	-1.64949700
O	0.02944400	-1.74718600	-2.00870200
O	-0.11778800	-1.95914600	0.24301300
O	-0.01359000	2.18256000	0.60785500
C	-0.10541600	-2.41456500	-0.94346000
C	0.09578600	2.83497600	-0.47667700
C	-2.62970700	0.29434400	-0.83656700
C	2.63519600	0.13721400	-0.56644700
Rh	-0.06461500	0.10326000	0.49244900
C	0.21350500	4.35193000	-0.30570200
C	0.42735200	5.20811800	-1.57356600
N	1.21455800	4.59256400	0.73416800
C	-0.79459200	5.06423200	-2.50328100
C	0.51823300	6.69290700	-1.16195000
C	1.71503700	4.84494100	-2.33091900
C	2.39740500	3.86380900	0.87478000
C	0.98571200	5.45468500	1.81398400
H	-0.92817500	4.01936400	-2.80292000

H	-1.70462300	5.35011700	-1.95112800
C	-0.62474800	5.94733100	-3.74232100
C	0.68081300	7.58865400	-2.39349500
H	-0.38154800	6.97778500	-0.59430200
H	1.37472000	6.84462300	-0.48685000
C	1.86492100	5.73123400	-3.57147900
H	2.58556500	4.98317800	-1.67071900
H	1.70040200	3.78651400	-2.61669400
O	2.79420600	3.01737500	0.09791600
C	3.01822900	4.34843300	2.13675300
O	-0.00432800	6.13757100	1.96477000
C	2.18248200	5.32177700	2.68552100
C	-0.52547200	7.41325300	-3.31779700
C	0.65131000	5.54053800	-4.48562600
H	-1.49526600	5.80920800	-4.39967800
H	0.74848100	8.63577800	-2.06465200
C	1.95630400	7.19771000	-3.14330500
H	2.78107900	5.44306900	-4.10777200
C	4.20089200	3.97896300	2.75727500
C	2.50297100	5.97656700	3.86215400
H	-0.42168600	8.06190400	-4.20088100
H	-1.44731600	7.72062000	-2.80075900
H	0.58260000	4.49011500	-4.80672400
H	0.76603600	6.14711600	-5.39684600

H	2.08894600	7.84512400	-4.02333300
H	2.83670400	7.34941600	-2.49992200
Cl	5.19999600	2.73675700	2.12042800
C	4.54803800	4.63559100	3.95859000
C	3.71030600	5.62740900	4.50331200
Cl	1.47232100	7.18034300	4.51970500
Cl	6.00596400	4.21660800	4.76097400
Cl	4.15606500	6.41623200	5.96154500
C	-4.15763700	0.36122900	-0.85176500
C	-4.87427300	0.33514400	-2.21771900
N	-4.55896600	1.47796700	0.00668100
C	-4.51709100	-0.97853800	-2.94063100
C	-6.39714000	0.32627900	-1.97139200
C	-4.54444800	1.53816300	-3.11684700
C	-3.90204900	2.71046900	0.07975900
C	-5.54376200	1.34067200	0.99324300
H	-3.43726700	-1.03665100	-3.11538500
H	-4.77628600	-1.82925400	-2.29101900
C	-5.26846300	-1.07899200	-4.26890600
C	-7.16249100	0.21743200	-3.29294500
H	-6.66011200	-0.50901900	-1.30387400
H	-6.69861600	1.24912900	-1.45145800
C	-5.30171900	1.41981700	-4.44491400
H	-4.83339200	2.47138900	-2.60750800

H	-3.46375000	1.59546800	-3.29428400
O	-2.94873600	3.04129600	-0.59718400
C	-4.60552700	3.47337200	1.14785000
O	-6.19246600	0.33749000	1.20085100
C	-5.59274000	2.65112100	1.69185000
C	-6.77516700	-1.07968100	-4.00633700
C	-4.90216300	0.11967300	-5.14964800
H	-4.97594100	-2.01260500	-4.77260000
H	-8.24137600	0.21718800	-3.08029900
C	-6.80919200	1.41270000	-4.18109400
H	-5.04156900	2.27845400	-5.08069700
C	-4.40885300	4.76473400	1.60990900
C	-6.42026400	3.08439000	2.71438200
H	-7.32908300	-1.16876700	-4.95329100
H	-7.05113900	-1.94823300	-3.38951400
H	-3.82103100	0.11937700	-5.35579200
H	-5.41330200	0.04589000	-6.12165100
H	-7.36157900	1.35499800	-5.13135000
H	-7.11274500	2.35150800	-3.69258400
Cl	-3.18224500	5.77579900	0.96356000
C	-5.24651700	5.23058700	2.64755300
C	-6.24225400	4.39917500	3.19396100
Cl	-7.62679700	2.06134400	3.37814800
Cl	-7.24859700	4.98736800	4.45375900

C	-0.23770800	-3.93601700	-1.05435500
C	-0.28760000	-4.55329500	-2.46991900
N	-1.34395000	-4.34516300	-0.18987400
C	1.05235300	-4.27277600	-3.17989900
C	-0.42780200	-6.08553400	-2.34109100
C	-1.45864000	-4.04182400	-3.32744800
C	-2.53457800	-3.63271400	-0.03467800
C	-1.21919800	-5.38702500	0.73839700
H	1.21677000	-3.19493700	-3.27635000
H	1.87760600	-4.66175400	-2.56213900
C	1.07164700	-4.92581400	-4.56210200
C	-0.40282900	-6.75097000	-3.71966100
H	0.38107600	-6.48173600	-1.70754600
H	-1.37329000	-6.33493000	-1.83411900
C	-1.41820100	-4.69571200	-4.71271900
H	-2.41370500	-4.28045300	-2.83260900
H	-1.41449500	-2.95032900	-3.41907700
O	-2.85281100	-2.65267900	-0.67906900
C	-3.27560400	-4.32525900	1.05442800
O	-0.24348100	-6.09500200	0.86470500
C	-2.49729500	-5.39542300	1.49758500
C	0.92333800	-6.44089600	-4.41562400
C	-0.08675400	-4.37156500	-5.39695500
H	2.02692200	-4.69173600	-5.05393300

H	-0.51089600	-7.83771500	-3.59144000
C	-1.55859700	-6.21297700	-4.56686800
H	-2.24990900	-4.30229000	-5.31578400
C	-4.50983600	-4.04736400	1.61972600
C	-2.92924200	-6.24091400	2.50566600
H	0.95505900	-6.92751800	-5.40234300
H	1.76293200	-6.84729800	-3.83102900
H	0.02163700	-3.28277600	-5.51508700
H	-0.06745600	-4.80685700	-6.40774800
H	-1.55581200	-6.69353700	-5.55709500
H	-2.52246400	-6.46000000	-4.09561900
Cl	-5.43645500	-2.68884800	1.13144800
C	-4.97184300	-4.90022200	2.64659800
C	-4.19260000	-5.98940400	3.08113500
Cl	-1.96262800	-7.55326900	3.04160800
Cl	-6.49580200	-4.59791000	3.37437500
Cl	-4.77766900	-7.01214300	4.32900500
C	4.15959800	0.06929400	-0.44383200
C	5.00394900	0.30744800	-1.71373800
N	4.48625700	-1.17969800	0.24756900
C	4.71806900	1.72396700	-2.25328100
C	6.49786700	0.25835000	-1.32945900
C	4.76300300	-0.73621400	-2.81789100
C	3.84243600	-2.40081000	0.02983000

C	5.37894200	-1.23193700	1.32543300
H	3.66028400	1.82577500	-2.51820100
H	4.91490400	2.45984800	-1.45761200
C	5.59097700	2.01691300	-3.47444600
C	7.38330600	0.55718300	-2.54171300
H	6.69693100	0.97855800	-0.52086000
H	6.75122500	-0.73725700	-0.93304500
C	5.63750700	-0.42280200	-4.03582500
H	5.01116600	-1.73968400	-2.43735500
H	3.70355300	-0.75711900	-3.09881400
O	2.96308400	-2.59510400	-0.78570700
C	4.45432100	-3.35195100	0.99719500
O	5.99634300	-0.28815100	1.77087300
C	5.38114300	-2.65152900	1.77008800
C	7.06689500	1.95463100	-3.07836000
C	5.30613300	0.97711400	-4.56244400
H	5.34791100	3.02218600	-3.84983800
H	8.43749500	0.50711500	-2.23305300
C	7.11360500	-0.47914700	-3.63523200
H	5.43871000	-1.16847700	-4.81919800
C	4.23228100	-4.70642100	1.18534900
C	6.12226400	-3.27761600	2.75851400
H	7.70685800	2.18132400	-3.94462200
H	7.28445500	2.71370400	-2.31174000

H	4.24862800	1.02615700	-4.86339600
H	5.90496400	1.19411300	-5.46008700
H	7.75328100	-0.28145400	-4.50885300
H	7.36910600	-1.48769300	-3.27510000
Cl	3.08124100	-5.57057800	0.25102700
C	4.98074400	-5.36591300	2.18466000
C	5.91777600	-4.65894700	2.96222500
Cl	7.26143800	-2.40822800	3.70257800
Cl	4.74660800	-7.04453800	2.44974300
Cl	6.81960100	-5.48369000	4.16709300
H	4.42091400	0.85785800	0.27808200
H	0.65755800	-4.34134200	-0.55607600
H	-4.48065400	-0.53486500	-0.30027400
H	-0.73949600	4.66583700	0.14939500
Cl	-5.04558100	6.82649100	3.24476200

{Rh_2(S-TCPTAD)$_4$}-Carbene: Isomer-1

E_{tot} = -15160.3365089 a. u.

Rh	0.21143400	0.29777500	-2.00790200
O	-1.88258100	0.30667300	-2.08571400
O	2.29015900	0.29034500	-1.81030400
O	-2.03511500	0.11470000	0.17389900
O	2.09592000	-0.00360500	0.42933300
O	0.23931800	2.37356800	-1.76836600
O	0.20022900	-1.78238300	-2.08582000
O	0.00548700	-2.00923800	0.16508600
O	0.00723200	2.12461300	0.47809700
C	0.04647700	-2.44942800	-1.02909000
C	0.16310000	2.80397300	-0.58989700
C	-2.51298700	0.26409100	-1.00029500
C	2.75233100	0.10150700	-0.65764500
Rh	0.01424700	0.05699500	0.44097700
C	0.20986200	4.30140700	-0.28651900
C	0.55779500	5.29779200	-1.40588800
C	-0.51806800	5.21965200	-2.50894800
C	0.51544800	6.71685300	-0.80088100
C	1.94700600	5.08352900	-2.02825000
C	2.26824400	3.83073300	1.09076900
C	0.46087000	4.81779400	2.15021300

H	-0.52791400	4.21722000	-2.95225600
H	-1.51224400	5.37132500	-2.06042100
C	-0.25222300	6.27226900	-3.58628800
C	0.77423900	7.77226400	-1.87630100
H	-0.46165300	6.88535400	-0.31980000
H	1.27479600	6.80498000	-0.00862600
C	2.20094100	6.13312600	-3.11480400
H	2.72132000	5.16923600	-1.25271900
H	2.02677700	4.06722100	-2.43784500
O	2.85773700	3.18500200	0.24599200
C	2.64517700	4.08188600	2.50772500
O	-0.67567100	5.20680600	2.30905600
C	1.53645100	4.62148900	3.15810600
C	-0.29777700	7.66916500	-2.96362900
C	1.12851000	6.02781000	-4.20230800
H	-1.02465800	6.18768100	-4.36412200
H	0.74170800	8.77005400	-1.41467800
C	2.15478800	7.53247400	-2.49404900
H	3.19318500	5.95797300	-3.55524700
C	3.83664800	3.85547200	3.17393600
C	1.55995400	4.90628800	4.51316400
H	-0.13216500	8.43804400	-3.73350800
H	-1.29362800	7.85743900	-2.53214900
H	1.16106800	5.03237900	-4.66993000

H	1.32373100	6.76291400	-4.99803700
H	2.36314500	8.29512400	-3.25972900
H	2.93535200	7.63149600	-1.72403700
Cl	5.18844800	3.17404500	2.37003500
C	3.90150800	4.19060700	4.54366800
C	2.76739100	4.69128100	5.21252600
Cl	0.16603300	5.50619900	5.31656000
Cl	5.37888100	3.98046500	5.39213500
Cl	2.85366600	5.06088600	6.88588700
C	-4.03736800	0.40308800	-0.95461400
C	-4.83991000	0.39725800	-2.26441300
N	-4.32031600	1.53588800	-0.06524500
C	-4.51840600	-0.90185000	-3.02791800
C	-6.33820100	0.37549300	-1.89732900
C	-4.59044000	1.60705000	-3.17937900
C	-3.65832700	2.76633900	-0.14030300
C	-4.90685400	1.34259400	1.19782800
H	-3.45448900	-0.92931000	-3.29113900
H	-4.69966500	-1.76522900	-2.37061100
C	-5.37621300	-1.00765600	-4.28879600
C	-7.20196000	0.26275100	-3.15512900
H	-6.54181600	-0.46807500	-1.21716500
H	-6.59865300	1.29081200	-1.34290200
C	-5.44587800	1.48778900	-4.44644200

H	-4.85067800	2.53470500	-2.64801100
H	-3.52459900	1.67883100	-3.43070100
O	-2.87999300	3.09553700	-1.01442500
C	-4.04056400	3.50533500	1.08903800
O	-5.45299500	0.32124300	1.55699800
C	-4.71722300	2.62246900	1.92933800
C	-6.85559500	-1.02859700	-3.89946300
C	-5.09624100	0.19707300	-5.19151100
H	-5.11890400	-1.93617000	-4.81928100
H	-8.26206900	0.25126800	-2.86272700
C	-6.92861500	1.46454000	-4.06433700
H	-5.24503200	2.35385600	-5.09333300
C	-3.77830800	4.81147300	1.46779500
C	-5.07621600	2.98816700	3.21524500
H	-7.48732600	-1.12824300	-4.79519400
H	-7.06508200	-1.90122800	-3.26066900
H	-4.03689300	0.20683800	-5.48829600
H	-5.68835700	0.12527900	-6.11673700
H	-7.55310100	1.40297500	-4.96854000
H	-7.20251000	2.39822800	-3.54952300
Cl	-3.13651600	5.95025300	0.35164500
C	-4.11072600	5.19758900	2.78149800
C	-4.73832400	4.28580400	3.65247200
Cl	-5.88510900	1.88870900	4.25762200

Cl	-5.11681400	4.76296600	5.25814900
C	-0.07952700	-3.97505200	-1.12499800
C	-0.02067200	-4.61177000	-2.52920200
N	-1.26286600	-4.36862700	-0.35559700
C	1.35511800	-4.31735100	-3.16226800
C	-0.13955200	-6.14433400	-2.38664000
C	-1.14847800	-4.13306800	-3.45911300
C	-2.47144600	-3.67001700	-0.34797600
C	-1.24093300	-5.40325300	0.58627800
H	1.51068900	-3.23752400	-3.25696500
H	2.14697500	-4.69081200	-2.49208700
C	1.46277600	-4.98604200	-4.53417600
C	-0.02594700	-6.82735000	-3.75158600
H	0.64076200	-6.51602300	-1.70376500
H	-1.10694200	-6.40626300	-1.93001300
C	-1.01808900	-4.80323900	-4.82928400
H	-2.12429400	-4.39016900	-3.01719800
H	-1.12374500	-3.04197600	-3.55851600
O	-2.70920100	-2.66929800	-0.99366500
C	-3.34857800	-4.39636400	0.61048900
O	-0.29362200	-6.12306900	0.81829900
C	-2.59882000	-5.41726600	1.19422200
C	1.33138300	-6.50213500	-4.37813900
C	0.34431600	-4.46346000	-5.44160100

H	2.44052300	-4.74075300	-4.97353900
H	-0.12208100	-7.91423100	-3.61469000
C	-1.14121000	-6.32036100	-4.66933300
H	-1.81970500	-4.43412400	-5.48537800
C	-4.67548100	-4.19007200	0.95067400
C	-3.13779700	-6.25463500	2.15694400
H	1.42417400	-6.99754000	-5.35665700
H	2.14435700	-6.88874700	-3.74494200
H	0.43988400	-3.37467800	-5.56901100
H	0.42997800	-4.91195900	-6.44313900
H	-1.07567300	-6.81442400	-5.65071300
H	-2.12571300	-6.57685600	-4.24824300
Cl	-5.60773200	-2.94499700	0.22022700
C	-5.24710000	-5.03255400	1.92770100
C	-4.48409400	-6.05173300	2.52900100
Cl	-2.20382900	-7.49730300	2.88248200
Cl	-6.88254200	-4.80422600	2.39341400
Cl	-5.19427500	-7.06161000	3.72113700
C	4.26301000	0.00607500	-0.42406500
C	5.20608000	0.00047900	-1.63604200
N	4.46885100	-1.11038600	0.50579300
C	5.08154200	1.34654600	-2.37991400
C	6.65343900	-0.11160200	-1.11681500
C	4.94928600	-1.15917800	-2.61189500

C	3.76281400	-2.31854700	0.42905900
C	5.03547000	-0.91500200	1.76937700
H	4.05814100	1.48182900	-2.74896500
H	5.27707600	2.17061900	-1.67335100
C	6.07333100	1.40046900	-3.54419500
C	7.65057800	-0.05772700	-2.27502900
H	6.85324800	0.70049600	-0.39886600
H	6.77896100	-1.05679500	-0.56652500
C	5.93991000	-1.08927100	-3.77858200
H	5.06326200	-2.11935300	-2.08635600
H	3.91446900	-1.12240500	-2.97631500
O	3.07836300	-2.66593600	-0.51181300
C	4.01651000	-3.01256700	1.72087800
O	5.59312900	0.09901900	2.13684000
C	4.77741300	-2.16522700	2.52724900
C	7.50237400	1.27494900	-3.01302200
C	5.78235700	0.24741900	-4.50943000
H	5.95517200	2.35999100	-4.06799600
H	8.67037100	-0.14968600	-1.87377900
C	7.36911300	-1.21021800	-3.24302500
H	5.73328000	-1.91645800	-4.47297400
C	3.60534900	-4.25678500	2.16984700
C	5.14459600	-2.52090500	3.81433100
H	8.22420300	1.33164400	-3.84204400

H	7.72856100	2.11098800	-2.33385900
H	4.76209500	0.34014300	-4.91113200
H	6.46920700	0.29159500	-5.36854300
H	8.09065400	-1.18919400	-4.07391000
H	7.49996600	-2.17572600	-2.73074400
Cl	2.63628000	-5.28503300	1.20183400
C	3.98717300	-4.64897000	3.47201000
C	4.74699600	-3.78894600	4.28714000
Cl	6.04420300	-1.45032700	4.81252700
Cl	3.51110900	-6.18656700	4.06491200
Cl	5.19317600	-4.27848100	5.86990100
H	4.51127000	0.89754500	0.17483000
H	0.76660100	-4.37541400	-0.54647700
H	-4.37197800	-0.47287200	-0.37802900
H	-0.80984400	4.54357700	0.05228900
Cl	-3.75025300	6.78679600	3.31422000
C	-0.25624200	0.06220400	2.42619100
C	-1.67485600	-0.16354200	2.76715900
C	0.60830500	0.47388100	3.48871300
C	2.00914200	0.62283200	3.30527200
C	0.09830900	0.67735000	4.80160500
C	2.85461000	0.86977000	4.37267200
H	2.42584200	0.52155300	2.30674000
C	0.93251300	0.95818900	5.86470800

H	-0.97448700	0.62189200	4.97144000
C	2.31336300	1.02264800	5.65258000
H	3.93149400	0.93644600	4.21491900
H	0.53003000	1.10902400	6.86288800
Br	3.44867300	1.31665900	7.12150200
O	-2.43823700	0.76478600	2.97686200
O	-2.01342200	-1.45764900	2.77188600
C	-3.40363100	-1.71574700	3.02547300
H	-3.99550300	-1.47853100	2.13570400
H	-3.46204600	-2.77870800	3.26692600
H	-3.76756600	-1.10713600	3.85823100
N	1.02844200	4.45387600	0.91910600

{Rh_2(S-TCPTAD)$_4$}-Carbene: Isomer-2

E_{tot} = -15160.3331428 a. u.

Rh	0.21297200	0.14964000	-2.08776600
O	-1.86082800	0.07241500	-2.27686900
O	2.25502800	0.23796500	-1.75551700
O	-2.09173900	-0.03503100	-0.02247400
O	2.03585900	-0.10592900	0.47729600
O	0.11306500	2.19298700	-1.77615100
O	0.23245400	-1.92635100	-2.27051500
O	-0.05078600	-2.16208300	-0.03379700
O	-0.09557000	1.99114200	0.47372900
C	-0.02469000	-2.59127500	-1.23601000
C	0.04522000	2.65158300	-0.60722900
C	-2.53292100	0.07027800	-1.21059300
C	2.70643100	0.06525800	-0.59356500
Rh	-0.05910900	-0.09890600	0.34581300
C	0.10358200	4.17178600	-0.40665400
C	0.35201100	5.04145000	-1.65823800
N	1.03399700	4.43698000	0.69366800
C	-0.83738500	4.87530500	-2.62657100
C	0.39745800	6.52577500	-1.23961700
C	1.67380600	4.70953300	-2.37072300
C	2.22770000	3.74254800	0.90540700

C	0.72445700	5.29830200	1.75060900
H	-0.94244300	3.82812300	-2.93001700
H	-1.76864100	5.14432200	-2.10096800
C	-0.64537600	5.76455400	-3.85706700
C	0.58343300	7.42828300	-2.46372300
H	-0.52736200	6.78998900	-0.70329100
H	1.22706900	6.69192200	-0.53459200
C	1.84280700	5.59941900	-3.60623400
H	2.51643400	4.87060900	-1.67984000
H	1.69700800	3.65209500	-2.65652800
O	2.70550200	2.92676300	0.14265300
C	2.74453200	4.22506900	2.21596800
O	-0.27997900	5.97339600	1.83522600
C	1.85471800	5.17939100	2.70924100
C	-0.58866000	7.23118300	-3.42705200
C	0.66239800	5.38386000	-4.55817900
H	-1.49065600	5.61089800	-4.54349700
H	0.61875100	8.47553500	-2.13014400
C	1.88988300	7.06644900	-3.17409400
H	2.78120500	5.33047900	-4.11354400
C	3.88145500	3.86588100	2.92121000
C	2.07217800	5.82027400	3.91732300
H	-0.46815600	7.88332800	-4.30543600
H	-1.53268200	7.51987700	-2.94032900

H	0.62518600	4.33227600	-4.88011300
H	0.79437200	5.99250700	-5.46569500
H	2.03523100	7.71894300	-4.04842400
H	2.74672600	7.23578700	-2.50376500
Cl	4.93684700	2.64195500	2.35170300
C	4.12703100	4.51380400	4.15208300
C	3.23403600	5.48405800	4.64417300
Cl	0.96393200	6.98590300	4.51928900
Cl	5.52819600	4.10756800	5.05436000
Cl	3.55281200	6.26124700	6.14100000
C	-4.06006700	0.16399300	-1.27267200
C	-4.72379500	0.38612900	-2.64639100
N	-4.48038900	1.12460100	-0.25031900
C	-4.42606100	-0.82187000	-3.55709800
C	-6.25047500	0.44787200	-2.43693300
C	-4.28138400	1.68186700	-3.34747200
C	-3.84395700	2.33817300	0.01903700
C	-5.40724500	0.78288400	0.74041200
H	-3.34709300	-0.90802400	-3.72654500
H	-4.74686800	-1.74756000	-3.05061700
C	-5.15020200	-0.66934300	-4.89741000
C	-6.97854700	0.59844800	-3.77382700
H	-6.59049600	-0.45726300	-1.91097300
H	-6.50101700	1.30071200	-1.78748000

C	-5.00209700	1.82206700	-4.69238800
H	-4.51623800	2.54852300	-2.71088200
H	-3.19306400	1.68060400	-3.49049400
O	-2.92476400	2.80921200	-0.62281000
C	-4.50084800	2.86843800	1.24403600
O	-6.07039600	-0.23334700	0.75081600
C	-5.39587300	1.90646400	1.70939600
C	-6.66032700	-0.60162800	-4.66767600
C	-4.67580700	0.61746800	-5.58027600
H	-4.90886600	-1.53451000	-5.53224400
H	-8.06121200	0.64689000	-3.58702000
C	-6.51405500	1.88516300	-4.46211100
H	-4.66319400	2.74562200	-5.18382600
C	-4.29530200	4.05211800	1.92995500
C	-6.07714400	2.06513800	2.90370800
H	-7.18891900	-0.50967400	-5.62876700
H	-7.01395300	-1.53064900	-4.19533800
H	-3.59227600	0.56805200	-5.76649100
H	-5.16450600	0.72814300	-6.56035100
H	-7.03932400	2.01192100	-5.42110600
H	-6.76598400	2.75854600	-3.84128600
Cl	-3.23180100	5.26277900	1.33702900
C	-4.97637600	4.23576300	3.15227300
C	-5.85099700	3.24751300	3.63970400

Cl	-7.14268600	0.85466000	3.49230400
Cl	-6.65840200	3.48047900	5.13762900
C	-0.31543800	-4.09330400	-1.38020700
C	-0.73194100	-4.61452200	-2.77270800
N	-1.20719700	-4.46126800	-0.27715700
C	0.50110600	-4.57611100	-3.69852500
C	-1.16393800	-6.08668000	-2.62732100
C	-1.88987000	-3.83600500	-3.42022600
C	-2.28059000	-3.65640400	0.13766700
C	-0.74533200	-5.28702800	0.75308100
H	0.85776300	-3.54547500	-3.80842500
H	1.31888700	-5.15079200	-3.23251300
C	0.16159900	-5.16755100	-5.06796900
C	-1.50276000	-6.68564800	-3.99505200
H	-0.36124700	-6.66412100	-2.14095200
H	-2.04323300	-6.15105600	-1.96901900
C	-2.21307900	-4.42692300	-4.79664300
H	-2.77715600	-3.88845000	-2.77457900
H	-1.63042600	-2.77249700	-3.50940500
O	-2.86624100	-2.86173500	-0.56763100
C	-2.49235700	-3.97940200	1.57348600
O	0.17656500	-6.07041800	0.65448900
C	-1.57847800	-4.96725300	1.93830700
C	-0.27229400	-6.62499700	-4.90175400

C	-0.97656000	-4.35849500	-5.69662800
H	1.05230800	-5.11591100	-5.71074300
H	-1.81300300	-7.73202000	-3.85928900
C	-2.64305200	-5.88699100	-4.63343000
H	-3.03267800	-3.84783000	-5.24845000
C	-3.33746100	-3.39324000	2.50330100
C	-1.47072800	-5.41110600	3.24555100
H	-0.50291200	-7.06891000	-5.88220000
H	0.54834700	-7.21668700	-4.46817700
H	-0.66488500	-3.31173300	-5.83168600
H	-1.21397200	-4.75431200	-6.69596900
H	-2.90356400	-6.31983300	-5.61129700
H	-3.54569500	-5.94703100	-4.00650800
Cl	-4.45927400	-2.18787900	2.04553100
C	-3.22352400	-3.81282000	3.84641800
C	-2.30504800	-4.81420600	4.21365500
Cl	-0.31898300	-6.60678200	3.68576900
Cl	-4.19787300	-3.06513300	5.04783600
Cl	-2.17410400	-5.29736800	5.85705900
C	4.22664000	0.09544100	-0.37962400
C	5.12269600	0.32407000	-1.61374400
N	4.58356400	-1.08853400	0.40761900
C	4.80982100	1.71167900	-2.21108300
C	6.59662900	0.34658100	-1.15771200

C	4.97389900	-0.76276700	-2.69044600
C	3.96060600	-2.33376500	0.27916000
C	5.38905100	-1.01276000	1.54963100
H	3.76279000	1.76575400	-2.52652400
H	4.94489100	2.47781500	-1.43022400
C	5.72781500	2.00021300	-3.39991300
C	7.52765600	0.64244500	-2.33757000
H	6.72830500	1.09856900	-0.36444700
H	6.86680400	-0.62533800	-0.71618500
C	5.89490300	-0.45430300	-3.87547300
H	5.23607300	-1.74291300	-2.26107900
H	3.93132900	-0.83143000	-3.02182400
O	3.16332400	-2.63463200	-0.58683100
C	4.45464500	-3.14605900	1.42463200
O	5.99079500	-0.02792600	1.92251100
C	5.31750300	-2.35568100	2.18302800
C	7.18416600	2.00904200	-2.93442100
C	5.53551100	0.91469500	-4.46333700
H	5.46400000	2.98210800	-3.82056400
H	8.56686300	0.64437000	-1.97772300
C	7.35120100	-0.43830400	-3.40648100
H	5.76162300	-1.23071000	-4.64269000
C	4.12875800	-4.43552600	1.81011100
C	5.89787700	-2.82761000	3.34898500

H	7.85545200	2.23247500	-3.77759700
H	7.33730600	2.79989800	-2.18449000
H	4.49253700	0.91188100	-4.81433500
H	6.16820600	1.12658000	-5.33865700
H	8.02283800	-0.24223400	-4.25621700
H	7.62957800	-1.42320000	-3.00075200
Cl	2.99052500	-5.36672200	0.93205000
C	4.69742400	-4.93244000	3.00367200
C	5.57733500	-4.13870800	3.76302100
Cl	6.96347300	-1.85051000	4.27298200
Cl	4.27705600	-6.50591900	3.54637700
Cl	6.25654500	-4.76088900	5.21015500
H	4.39963000	0.93933400	0.30522900
H	0.62921200	-4.60304300	-1.12650400
H	-4.41892800	-0.80462900	-0.88768000
H	-0.88390600	4.44772700	-0.00494300
Cl	-4.71615300	5.67008900	4.06056900
C	-0.39361700	-0.26563800	2.30086500
C	-1.21414600	0.85107800	2.80494500
C	-0.01625000	-1.31454000	3.18455400
C	0.90945000	-2.31450900	2.78521600
C	-0.51391300	-1.36473500	4.51526500
C	1.33969300	-3.27782200	3.67846200
H	1.29283900	-2.30385300	1.76797300

C	-0.08514000	-2.32642500	5.40985700
H	-1.25254000	-0.62974700	4.83376400
C	0.86159600	-3.26803000	4.99199300
H	2.04381800	-4.04709200	3.37260700
H	-0.46491400	-2.35132700	6.42832000
Br	1.53193700	-4.52266900	6.21942000
O	-0.45587100	1.83262100	3.32647300
O	-2.42760200	0.89291500	2.70681500
C	-1.16665300	3.04959800	3.58969100
H	-2.05793300	2.85833600	4.19578500
H	-0.47062600	3.69437800	4.12813500
H	-1.46176600	3.51373200	2.64104600

13 - References:

1. Wu, Z.Q., Ono, R.J., Chen, Z., & Bielawski, C.W. Synthesis of poly(3-alkylthiophene)-block-poly(arylisocyanide): two sequential, mechanistically distinct polymerizations using a single catalyst. *J. Am. Chem. Soc.* **132**, 14000-14001 (2010).
2. Zhou, J., Xu, X. & Hu, W. Enantioselective three-component reaction for the preparation of *β*-amino-*α*-hydroxy esters. *Org. Synth.* **88**, 418-426 (2011).
3. Guptill, D.M. & Davies, H.M.L. 2,2,2-Trichloroethyl aryldiazoacetates as robust reagents for the enantioselective C−H functionalization of methyl ethers. *J. Am. Chem. Soc.* **136**, 17718-17721 (2014).
4. Brodsky, B. H.; Du Bois, J. Deacylative oxidation strategy for the preparation of *α*-functionalized carbonyls. *Org. Lett.* **15**, 2619-2621 (2004).
5. Liao, K. B., Negretti, S., Musaev, D. G., Bacsa, J. & Davies, H. M. L. Site-selective and stereoselective functionalization of unactivated C-H bonds. *Nature* **533**, 230-234 (2016).
6. Davies, H.; Fu, L.; Mighion, J.; Voight, E. Synthesis of 2,2,2,-Trichloroethyl Aryl- and Vinyldiazoacetates byPalladium-Catalyzed Cross-Coupling. *Chem. Eur. J.* 10.1002/chem.201700101, (2017).
7. Zhao, Y.; Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions, *J. Chem. Phys.* **125,** 194101 (2006).
8. Hay, P. J.; Wadt, W. R. *Ab Initio* effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys.*, **82**, 270-283 (1985).
9. Hay, P. J.; Wadt, W. R. *Ab Initio* effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **82**, 299-310 (1985).
10. Xu, H.; Muto, K.; Yamaguchi, J.; Zhao, C.; Itami, K.; Musaev, D. G. Key Mechanistic Features of Ni-catalyzed C–H/C–O Biaryl Coupling of Azoles and Naphthalen-2-yl Pivalates. *J. Am. Chem. Soc.* **136**, 14834-14844 (2014).
11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; J. A. Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; N. Rega, J. M. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; K. Morokuma, V. G. Z.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Ö. Farkas, J. B. F.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Revision D.01 ed.; Gaussian, I., Ed. Wallingford CT., 2009.