Electronic Supplementary Information for:

Azodicarboxylate-free esterification with triphenylphosphine mediated by flavin and visible light: method development and stereoselectivity control

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S1 Experimental – general comments

NMR spectra were recorded on a Varian Mercury Plus 300 (299.97 MHz for ^{1}H, 75.44 MHz for ^{13}C, and 282.23 MHz for ^{19}F) or Agilent 400-MR DDR2 (399.94 MHz for ^{1}H, 100.58 MHz for ^{13}C and 376.29 MHz for ^{19}F) at 298 K unless otherwise indicated. Chemical shifts δ are given in ppm, using residual solvent as an internal standard. ^{19}F NMR chemical shifts were measured relative to CCl_3F and ^{31}P NMR chemical shifts were measured relative to H_3PO_4. Coupling constants *J* are reported in Hz. High-resolution **mass spectra** were obtained on Q-Tof Micro (Waters), equipped with a quadrupole and TOF analyzers and MCP detector. TLC analyses were carried out on a DC Alufolien Kieselgel 60 F254 (Merck). Preparative column chromatography separations were performed on a silica gel Kieselgel 60 0.040-0.063 mm (Merck). **Melting points** were measured on a Boetius melting point apparatus and are uncorrected.

Starting materials, reagents and substrates were obtained from commercial suppliers and used without further purification. The solvents were purified and dried using standard procedures.[1] 3-methylriboflavin tetraacetate (**1**)[2] was prepared according to previously reported procedures. NMR spectra of the prepared compounds are in agreement with previously reported data.[2]

[1] D. D. Perrin, W. L. F. A. *Purification of Laboratory Chemicals, 4th Ed.*; Elsevier Science Ltd., Oxford, 1996.
[2] Schmaderer, H., et al., *Adv. Synth. Catal.* **2009**, 351, 163-174.

S2 Experimental – electrochemical and photophysical experiments

Electrochemical measurements Electrochemical measurements were carried out in a 15mL cell of Metrohm type, in acetonitrile (99.9 %, extra dry over molecular sieves). Tetrabutylammonium hexafluorophosphate (*puriss*. electrochemical grade, Fluka) was used as supporting electrolyte in concentration 0.1 mol L^{-1}. The sample solution was prepared directly in the cell, sample concentration was 0.1 mmol L^{-1}. The solution was deaerated by a stream of argon. Redox potential was studied by cyclic voltammetry (CV) on glassy carbon electrode (GC) with Ag/AgCl pseudo-reference electrode and Pt auxiliary electrode. Ferrocene was used as internal potential reference system in all measurements. For re-calculation, $Fc^{+/0}$ was taken to be 0.38 V vs. SCE.[3,4] Metrohm Autolab PGSTAT128N potentiostat was used for CV measurement, scan rate ranging from 50 to 500 mV/s. The accuracy of the potential measurement was ±5 mV. Redox potential of the catalysts $E(1/1^{\bullet-})$ were quantified as $E_{p,c}$ + ½($E_{p,a}$ - $E_{p,c}$) as the process was reversible. Redox potential $E(1^{\bullet-}/1^{2-})$ was taken as $E_{1/2}$(red) as the process was irreversible.

Spectral and photophysical measurements UV–Vis absorption spectra were recorded on JASCO V-650 spectrophotometer and on a Jobin Yvon-Spex Fluorolog 3-221 spectrofluorometer, using the option to measure absorption spectra; steady-state fluorescence excitation and emission spectra were also recorded on the same spectrofluorometer. The experiments were performed on 3mL of sample solutions contained in aquartz cell (1 cm x 1 cm) with sample absorbance not exceeding 0.1 at the excitation wavelength. Fluorescence spectra were collected with 1nm excitation and emission slits, using 0.2 s integration time. Fluorescence lifetime measurements were performed using the time-correlated single photon counting (TCSPC) method. Decays were measured using as excitation source a NanoLED diode N-360 (λ_{exc} = 368 nm) from Horiba Jobin–Yvon IBH Ltd. UK. Deconvolution of the fluorescence decay curves was performed using Version 4 of the IBH Consultants software. All the experiments were performed by using dry acetonitrile as asolvent and at RT (298 K). Maximum absorbance of all solutions was kept below 0.1 at the excitation wavelength.

Phosphorescence spectra and lifetime measurements were recorded on a Horiba Jobin-Yvon Spex Fluorolog 3–221 equipped in Dewar FL-1013 for liquid nitrogen, allowed measuring a sample at 77 K. The experiments were performed on 1mL of sample in acetonitrile solutions contained in cylindrical quartz test tube (diameter 4mm). The absorbance of asample did not exceed 0.2 at the excitation wavelength. Phosphorescence spectra were collected with 1 nm excitation and emission slits, using 0.5 s integration time. Phosphorescence lifetime measurements were performed by using Multi-Channel Scaling (MCS) technique. The excitation source was a Spectra LED diode S-390 (λ_{exc} = 394 nm, FWHM = 15 nm) from Horiba Jobin–Yvon IBH. Ltd. UK.

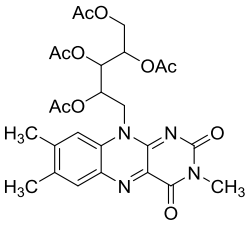
As our results demonstrate, the low–temperature measurements in the presence of KI enable observation of phosphorescence. In the presence of KI significant diminish of fluorescence is observed and intensify phosphorescence emission for 3Me-TARF at low-temeperature. As

[3] V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, 2000, **298**, 97.
[4] a) N. A. Romero and D. A. Nicewicz, *Chem Rev*, 2016, **116**, 10075-10166; b) M. Murakami, K. Ohkubo and S. Fukuzumi, *Chem. Eur. J.*, 2010, **16**, 7820-7832.

such, those experiments allow us to determine the triplet energy form direct spectral measurements.

Laser flash photolysis set-up Pump pulses (355 nm) with energies of about 1 mJ in the sample, 8 ns (FWHM), were generated at a repetition rate of 10 Hz by Q-switched Nd:YAGlaser (Continuum Surelite II). The probing light source was a 150 W xenon arc lamp (Applied Photophysics), used in the pulsed mode with a 1 Hz repetition rate. The transmitted probe light was dispersed by a monochromator (6 nm spectral resolution, Acton Research SpectraPro300i) and detected by a photomultiplier (R928 Hamamatsu) coupled to a digital oscilloscope (Tektronix TDS 680 C). A home-made program written in the LabView 4.1 environment was used for the ΔA calculations and the dialog between the PC and the oscilloscope. An input-output card (PCI-MIO-16XE-10) was used for time-control of TTL signals to trigger the laser, lamp pulser (1 Hz), and shutters (i.a. to reduce laser pulse repetition to 0.5 Hz). Experiments were performed on 4ml solution samples contained in a quartz cell (1 cm×1 cm cross-section). A sample absorbance of about 0.6 at the laser excitation wavelength (355 nm) was generally used. All solutions were deaerated for about 15 min prior to each experiment with an argon gas flow to remove traces of O_2. Control experiments by measuring the UV-vis absorption spectra before and laser experiments revealed practically no difference in data confirming a high flavin photostability. Multiexponential modeling of transient absorption kinetics was performed by the OriginPro 2017, global fitting was carried out with Asufit program.

S3 Experimental – Synthetic procedures



3-Methyl-2',3',4',5'-tetraacetylriboflavin (**1**): Prepared according to described procedure.[5] M.p. = 182 °C (ref.[6] 183 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.53 (s, 1H), 5.73 – 5.60 (m, 1H), 5.52 – 5.34 (m, 2H), 5.24 – 4.64 (m, 2H), 4.42 (dd, J = 12.4, 2.8 Hz, 1H), 4.24 (dd, J = 12.4, 5.8 Hz, 1H), 3.48 (s, 3H), 2.54 (s, 3H), 2.43 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H), 2.07 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 170.4, 170.0, 169.8, 160.0, 155.4, 149.2, 147.6, 136.7, 135.7, 134.8, 133.0, 131.3, 115.5, 70.6, 69.1, 62.0, 44.7, 28.8, 21.5, 21.2, 20.9, 20.8, 20.5, 19.6; HRMS (APCI) calcd for $C_{26}H_{30}N_4O_{10}$ ($[M+H]^+$) 559.20347, found 559.20329.

[5] März, M., et al., *Org. Biomol. Chem.*, **2017,**15, 1970-1975.
[6] Schmaderer, H., et al., *Adv.Synth. Catal.*, **2009**, 351(1-2), 163-174.

General procedure of preparation of chiral esters (standards)

Acid [3,5-bis(trifluoromethyl)benzoic acid, 3,5-bis(trifluoromethyl)benzoic acid, 2-methyl-2-phenylpropanoic acid, or 3-(trifluoromethyl)benzoic acid (1.2 mmol)], alcohol [(*R*) or (*S*)-1-phenylethanol or (*R*) or (*S*)- ethyl lactate (1 mmol)], DCC (1.5 mmol) and DMAP (0.1 mmol) were dissolved in dry DCM (10 mL) and the mixture was stirred for 24h at RT. After the reaction mixture was evaporated, the residue was purified by flash chromatography (silica gel, Hexane/EtOAc, 20:1) to give the product.

(*R*)- and (*S*)-1-Phenylethyl 2-methyl-2-phenylpropanoate (**17**): Colorless oil; Yield 37 % (0.100 g, 0.37 mmol) for (*R*)- and 40 % (0.107 g, 0.40 mmol) for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.12 (m, 10H), 5.86 (q, J = 6.6 Hz, 1H), 1.59 (d, J = 9.2 Hz, 6H), 1.43 (d, J = 6.6 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 144.6, 141.7, 128.3, 128.2, 127.5, 126.5, 125.7, 125.7, 72.5, 46.5, 26.4, 26.3, 22.1; Elemental analysis: calcd for $C_{18}H_{20}O_2$: C 80.56 %, H 7.51 %; found C 79.90 %, H 7.28 %.

(*R*)- and (*S*)-1-Phenylethyl 2-phenylacetate (**18**): Colorless oil; Yield 72 % (0.175 g, 0.72 mmol) for (*R*)- and 70 % (0.170 g, 0.70 mmol) for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.12 (m, 10H), 5.90 (q, *J* = 6.6 Hz, 1H), 3.75 – 3.55 (m, 2H), 1.52 (d, *J* = 6.6 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 141.7, 134.2, 129.4, 128.7, 128.6, 127.9, 127.2, 126.1, 72.9, 41.8, 22.4; HRMS (+EI) calcd for $C_{16}H_{16}O_2$ ($[M]^+$) 240.11448, found 240.11493.

(*R*)- and (*S*)-1-Phenylethyl 3-(trifluoromethyl)benzoate (**19**): Colorless oil; Yield 85 % (0.250 g, 0.85 mmol) for (*R*)- and 88 % (0.258 g, 0.88 mmol) for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.31 (m, 1H), 8.28 – 8.24 (m, 1H), 7.84 – 7.79 (m, 1H), 7.62 – 7.55 (m, 1H), 7.48 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.30 (m, 1H), 6.16 (q, *J* = 6.6 Hz, 1H), 1.70 (d, *J* = 6.6, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.22^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 141.4, 133.0, 131.5, 131.2 (q, *J* = 32.8 Hz), 129.6 (q, *J* = 3.6 Hz), 129.2, 128.8, 128.3, 126.7 (q, *J* = 4.0 Hz), 126.3, 123.8 (q, *J* = 272.8 Hz), 73.9, 22.4; HRMS (+EI) calcd for $C_{16}H_{13}F_3O_2$ ($[M]^+$) 294.08622, found 294.08640.

(*R*)- and (*S*)-1-Phenylethyl 3,5-bis(trifluoromethyl)benzoate (**20**): Colorless oil; Yield 75 % (0.270 g, 0.75 mmol) for (*R*)- and 73 % (0.265 g, 0.73 mmol) for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 2H), 8.06 (s, 1H), 7.49 – 7.31 (m, 5H), 6.19 (q, *J* = 6.6 Hz, 1H), 1.73 (d, *J* = 6.6 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.39; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 140.8, 132.8, 132.3 (q, *J* = 34.0 Hz), 129.9 (d, *J* = 3.8 Hz), 128.9, 128.6, 126.5 (q, *J* = 3.6 Hz), 126.4, 123.0 (q, *J* = 272.9 Hz), 74.7, 22.2; HRMS (+EI) calcd for $C_{17}H_{12}F_6O_2$ ($[M]^+$) 362.07360, found 362.07358.

Ethyl (*R*)- and (*S*)-2-((3-(trifluoromethyl)benzoyl)oxy) propionate (**21**): Colorless oil; Yield 69 % (0.200 g, 0.69 mmol) for (*R*)- and 67 % (0.195 g, 0.67 mmol) for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.33 (m, 1H), 8.30 – 8.25 (m, 1H), 7.87 – 7.81 (m, 1H), 7.64 – 7.57 (m, 1H), 5.34 (q, J = 7.1 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 1.66 (d, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.1, Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.26; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 164.8, 133.2, 131.3 (q, *J* = 32.9 Hz), 130.5, 129.9 (q, *J* = 3.7 Hz), 129.3, 126.9 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 272.4 Hz), 69.8, 61.7, 17.2, 14.3; HRMS (+EI) calcd for $C_{13}H_{13}F_3O_4$ ($[M]^+$) 290.07604, found 290.07586.

S4 Experimental – Photocatalytic esterification

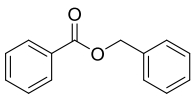
General procedure for photocatalytic esterification

Preliminary experiments on esterification

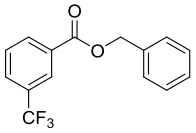
A mixture of benzylalcohol (0.150 mmol), benzoic acid (0.180 mmol), triphenylphosphine (0.30 mmol), nitrobenzene (0.15 mmol), catalyst **1** (0.0150 mmol) and activated MS 4 Å (150 mg) in BTF (2 mL) was degassed by freeze-pump-thaw procedure (3x) and then was stirred at 40 °C under irradiation with blue LEDs (448 nm, 1 W LED) for 24 hours. Then, the reaction mixture was filtered and the solvent was evaporated. The conversion was determined by ^{1}H NMR.

Esterification on preparative scale

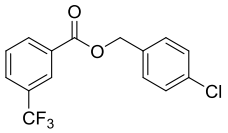
A mixture of alcohol (0.150 mmol), acid (0.180 mmol), triphenylphosphine (0.30 mmol), nitrobenzene (0.15 mmol) , catalyst (0.0150 mmol) and activated MS 4 Å (150 mg) in BTF (2 mL) was degassed by freeze-pump-thaw procedure (3x) and then was stirred at 40 °C under irradiation with blue LEDs (448 nm, 1 W LED) for 24 hours. Then, the reaction mixture was filtered and the solvent was evaporated. The residue was purified by flash chromatography (silica gel, *n*-hexane/EtOAc, 20:1 or 50:1) to give the product.



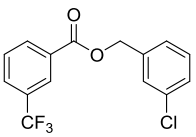
Benzyl benzoate (**2**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.32 (m, 7H), 5.38 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 136.2, 133.2, 130.3, 129.8, 128.7, 128.5, 128.4, 128.3, 66.8; HRMS (+EI) calcd for $C_{15}H_{11}F_3O_2$ ($[M]^+$) 212.08318, found 212.08239.



Benzyl 3-(trifluoromethyl)benzoate (**3**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.32 (m, 1H), 8.30 – 8.23 (m, 1H), 7.85 – 7.79 (m, 1H), 7.63 – 7.55 (m, 1H), 7.49 – 7.34 (m, 5H), 5.40 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.24; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 135.7, 133.1 (d, J = 1.5 Hz), 131.2 (q, J = 33.2 Hz), 131.2, 129.7 (q, J = 3.6 Hz), 129.2, 128.8, 128.7, 128.5, 126.8 (q, J = 3.9 Hz), 123.8 (q, J = 272.5 Hz), 67.4; HRMS (+EI) calcd for $C_{15}H_{11}F_3O_2$ ($[M]^+$) 280.07057, found 280.07160.



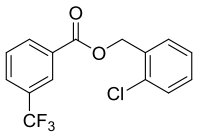
4-Chlorobenzyl 3-(trifluoromethyl)benzoate (**4**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.29 (m, 1H), 8.27 – 8.22 (m, 1H), 7.86 – 7.80 (m, 1H), 7.63 – 7.55 (m, 1H), 7.43 – 7.34 (m, 4H), 5.36 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.26; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 134.6, 134.2, 133.0, 131.3 (q, J = 33.1 Hz), 130.9, 129.9, 129.8 (q, J = 3.7 Hz), 129.3, 129.1, 126.8 (q, J = 3.9 Hz), 123.8 (q, J = 272.6 Hz), 66.6; HRMS (+EI) calcd for $C_{15}H_{10}ClF_3NO_2$ ($[M]^+$) 314.03159, found 314.03206.



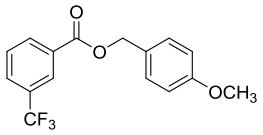
3-Chlorobenzyl 3-(trifluoromethyl)benzoate (**5**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.31 (m, 1H), 8.28 – 8.23 (m, 1H), 7.87 – 7.80 (m, 1H), 7.63 – 7.56 (m, 1H), 7.46 – 7.42 (m, 1H), 7.36 – 7.32 (m, 3H), 5.37 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.26; ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 137.5, 134.6, 132.9, 131.2 (q, J = 32.9 Hz), 130.7, 129.9, 129.7 (q, J = 3.6 Hz),

129.1, 128.7, 128.4, 126.6 (q, J = 3.9 Hz), 126.4, 123.6 (q, J = 272.7 Hz), 66.3; Elemental analysis: calcd for $C_{15}H_{10}ClF_3O_2$: C 57.25 %, H 3.20 %, F 18.11 %; found C 57.47 %, H 3.08 %, F 17.89 %.

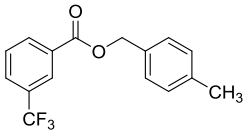
2-Chlorobenzyl 3-(trifluoromethyl)benzoate (**6**): White solid, m.p: 64–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.32 (m, 1H), 8.30 – 8.25 (m, 1H), 7.86 – 7.79 (m, 1H), 7.64 – 7.56 (m, 1H), 7.54 – 7.40 (m, 2H), 7.35 – 7.28 (m, 2H), 5.51 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.25; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 134.1, 133.4, 133.1, 131.3 (q, J = 33.1 Hz), 130.9, 130.3, 129.9, 129.9, 129.8 (q, J = 3.6 Hz), 129.3, 127.1, 126.8 (q, J = 3.8 Hz), 123.8 (q, J = 272.5 Hz), 64.8; Elemental analysis: calcd for $C_{15}H_{10}ClF_3O_2$: C 57.25 %, H 3.20 %, F 18.11 %; found C 57.35 %, H 3.04 %, F 18.15 %.



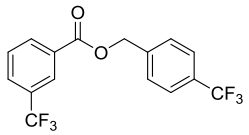
4-Methoxybenzyl 3-(trifluoromethyl)benzoate (**7**): Yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 – 8.29 (m, 1H), 8.26 – 8.21 (m, 1H), 7.83 – 7.78 (m, 1H), 7.61 – 7.53 (m, 1H), 7.44 – 7.36 (m, 2H), 6.97 – 6.89 (m, 2H), 5.33 (s, 2H), 3.82 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.23; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 160.0, 133.0, 131.3, 131.2 (q, J = 32.9 Hz), 130.5, 129.6 (q, J = 3.7 Hz), 129.2, 127.8, 126.7 (q, J = 3.9 Hz), 123.8 (q, J = 272.4 Hz), 114.2, 67.3, 55.5; HRMS (+EI) calcd for $C_{16}H_{13}F_3O_3$ ([M]$^+$) 310.08113, found 310.08211.



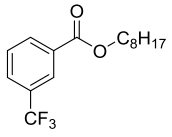
4-Methylbenzyl 3-(trifluoromethyl)benzoate (**8**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.30 (m, 1H), 8.28 – 8.20 (m, 1H), 7.85 – 7.76 (m, 1H), 7.61 – 7.53 (m, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.22 (d, 2H), 5.36 (s, 2H), 2.37 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.23; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 138.6, 133.0, 132.7, 131.2, 131.2 (q, J = 33.0 Hz), 129.6 (q, J = 3.7 Hz), 129.5, 129.2, 128.7, 126.8 (q, J = 3.9 Hz), 123.8 (q, J = 272.5 Hz), 67.4, 21.4; HRMS (+EI) calcd for $C_{16}H_{13}F_3O_2$ ([M]$^+$) 294.08622, found 294.08703.



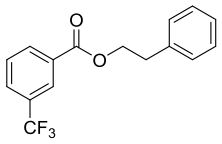
4-(Trifluormethyl)benzyl 3-(trifluoromethyl)benzoate (**9**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.31 (m, 1H), 8.29 – 8.24 (m, 1H), 7.87 - 7.82 (m, 1H), 7.67 (d, J = 8.1 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.58 (d, 2H), 5.45 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -55,88, -56.02; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 139.6, 133.1, 131.4 (q, J = 33.2 Hz), 130.9 (q, J = 32.5 Hz), 130.8, 129.9 (q, J = 3.7 Hz), 129.4, 128.5, 126.8 (q, J = 3.9 Hz), 125.8 (q, J = 3.8 Hz), 125.1 (q, J = 273.0 Hz), 122.7 (q, J = 272.1 Hz), 66.4; HRMS (+EI) calcd for $C_{16}H_{10}F_6O_2$ ([M]$^+$) 348.05799, found 348.05799.



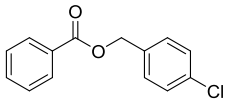
Octyl 3-(trifluoromethyl)benzoate (**10**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.27 (m, 1H), 8.26 – 8.19 (m, 1H), 7.86 – 7.76 (m, 1H), 7.63 – 7.53 (m, 1H), 4.35 (t, J = 6.8, 2.2 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.48 – 1.22 (m, 10H), 0.93 – 0.84 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.24; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 132.7, 131.4, 131.0 (q, J = 32.9 Hz), 129.3 (q, J = 3.6 Hz), 128.9, 126.4 (q, J = 3.8 Hz), 123.7 (q, J = 272.6 Hz), 65.7, 31.8, 29.2, 29.2, 28.6, 25.9, 22.6, 14.1; Elemental analysis: calcd for $C_{16}H_{21}F_3O_2$: C 63.56 %, H 7.00 %, F 18.85 %; found C 63.58 %, H 6.86 %, F 18.52 %.



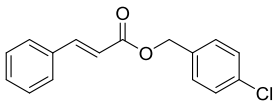
Phenethyl 3-(trifluoromethyl)benzoate (**11**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.25 (m, 1H), 8.22 – 8.16 (m, 1H), 7.84 – 7.79 (m, 1H), 7.61 – 7.54 (m, 1H), 7.39 – 7.22 (m, 5H), 4.57 (t, *J* = 7.0 Hz, 2H), 3.10 (t, *J* = 7.0 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.28; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 137.7, 132.9, 131.3, 131.2 (q, *J* = 32.9 Hz), 129.6 (q, *J* = 3.6 Hz), 129.2, 129.1, 128.8, 126.9, 126.7 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 272.4 Hz), 66.1, 35.3; Elemental analysis: calcd for $C_{16}H_{13}F_3O_2$: C 65.31 %, H 4.45 %, F 19.37 %; found C 65.25 %, H 4.23 %, F 19.12 %.



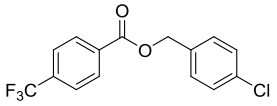
4-Chlorobenzyl benzoate (**12**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.61 – 7.52 (m, 3H), 7.49 – 7.33 (m, 4H), 5.32 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 134.5, 134.1, 133.1, 129.9, 129.7, 129.6, 128.8, 128.4, 65.9; HRMS (APCI) calcd for $C_{14}H_{11}ClO_2$ ($[M]^+$) 246.04421, found 246.04544.



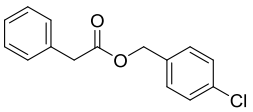
4-chlorobenzyl cinnamate (**13**): White solid, m.p: 49-51 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.41 – 7.37 (m, 3H), 7.37 – 7.34 (m, 4H), 6.48 (d, *J* = 16.0, 1H), 5.22 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 145.6, 134.7, 134.4, 134.3, 130.6, 129.8, 129.1, 128.9, 128.3, 117.7, 65.7; HRMS (+EI) calcd for $C_{16}H_{13}ClO_2$ ($[M]^+$) 272,05986, found 272.06060.



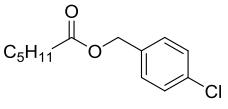
4-Chlorobenzyl 4-(trifluoromethyl)benzoate (**14**): White solid, m.p: 53-54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.14 (m, 1H), 7.75 – 7.67 (m, 1H), 7.42 – 7.34 (m, 2H), 5.35 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.59; 13C NMR (101 MHz, $CDCl_3$) δ 165.3, 134.8 (q, *J* = 32.6 Hz), 134.6, 134.2, 133.3, 130.2, 129.9, 129.1, 125.6 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 272.7 Hz), 66.6; HRMS (+EI) calcd for $C_{15}H_{10}ClF_3O_2$ ($[M]^+$) 314.03159, found 314.03244.



4-Chlorobenzyl 2-phenylacetate (**15**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 - 6.94 (m, 9H), 5.10 (s, 2H), 3.67 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 134.5, 134.2, 133.9, 129.6, 129.4, 128.9, 128.8, 127.3, 65.9, 41.5; HRMS (APCI) calcd for $C_{15}H_{13}ClO_2$ ($[M]^+$) 260.05986, found 260.06006.

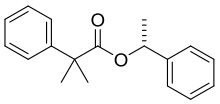


4-chlorobenzyl hexanoate (**16**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.31 – 7.26 (m, 2H), 5.07 (s, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.49 (m, 2H), 1.40 – 1.20 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 134.8, 134.2, 129.7, 128.9, 65.4, 34.4, 31.4, 24.8, 22.4, 14.0; HRMS (+EI) calcd for $C_{13}H_{17}ClO_2$ ($[M]^+$) 240.09171, found 240.09134.

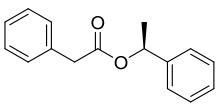


(*S*)-1-Phenylethyl 2-methyl-2-phenylpropanoate (**17**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.12 (m, 10H), 5.86 (q, J = 6.6 Hz, 1H), 1.59 (d, J = 9.2 Hz, 6H), 1.43 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 144.6, 141.7, 128.3, 128.2, 127.5, 126.5, 125.7, 125.7, 72.5, 46.5, 26.4, 26.3, 22.1; Elemental analysis: calcd for $C_{18}H_{20}O_2$: C 80.56 %, H 7.51 %; found C 79.90 %, H 7.28 %.

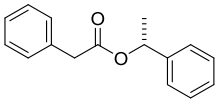
(*R*)-1-Phenylethyl 2-methyl-2-phenylpropanoate (**17**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.12 (m, 10H), 5.86 (q, J = 6.6 Hz, 1H), 1.59 (d, J = 9.2 Hz, 6H), 1.43 (d, J = 6.6 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 144.6, 141.7, 128.3, 128.2, 127.5, 126.5, 125.7, 125.7, 72.5, 46.5, 26.4, 26.3, 22.1; Elemental analysis: calcd for $C_{18}H_{20}O_2$: C 80.56 %, H 7.51 %; found C 79.89 %, H 7.35 %.



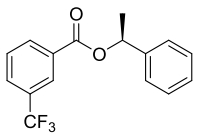
(*S*)-1-Phenylethyl 2-phenylacetate (**18**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.12 (m, 10H), 5.90 (q, *J* = 6.6 Hz, 1H), 3.75 – 3.55 (m, 2H), 1.52 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 141.7, 134.2, 129.4, 128.7, 128.6, 127.9, 127.2, 126.1, 72.9, 41.8, 22.4; HRMS (+EI) calcd for $C_{16}H_{16}O_2$ ($[M]^+$) 240.11448, found 240.11493.



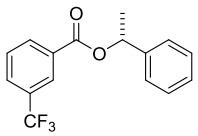
(*R*)-1-Phenylethyl 2-phenylacetate (**18**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.12 (m, 10H), 5.90 (q, *J* = 6.6 Hz, 1H), 3.75 – 3.55 (m, 2H), 1.52 (d, *J* = 6.6 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 141.7, 134.2, 129.4, 128.7, 128.6, 127.9, 127.2, 126.1, 72.9, 41.8, 22.4; HRMS (+EI) calcd for $C_{16}H_{16}O_2$ ($[M]^+$) 240.11448, found 240.11493.



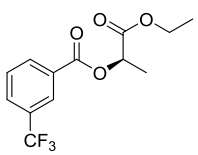
(*S*)-1-Phenylethyl 3-(trifluoromethyl)benzoate (**19**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.31 (m, 1H), 8.28 – 8.24 (m, 1H), 7.84 – 7.79 (m, 1H), 7.62 – 7.55 (m, 1H), 7.48 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.30 (m, 1H), 6.16 (q, *J* = 6.6 Hz, 1H), 1.70 (d, *J* = 6.6, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.22; ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 141.4, 133.0, 131.5, 131.2 (q, *J* = 32.8 Hz), 129.6 (q, *J* = 3.6 Hz), 129.2, 128.8, 128.3, 126.7 (q, *J* = 4.0 Hz), 126.3, 123.8 (q, *J* = 272.8 Hz), 73.9, 22.4; HRMS (+EI) calcd for $C_{16}H_{13}F_3O_2$ ($[M]^+$) 294.08622, found 294.08640.



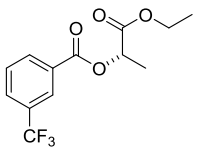
(*R*)-1-Phenylethyl 3-(trifluoromethyl)benzoate (**19**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.31 (m, 1H), 8.28 – 8.24 (m, 1H), 7.84 – 7.79 (m, 1H), 7.62 – 7.55 (m, 1H), 7.48 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.30 (m, 1H), 6.16 (q, *J* = 6.6 Hz, 1H), 1.70 (d, *J* = 6.6, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.22^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 141.4, 133.0, 131.5, 131.2 (q, *J* = 32.8 Hz), 129.6 (q, *J* = 3.6 Hz), 129.2, 128.8, 128.3, 126.7 (q, *J* = 4.0 Hz), 126.3, 123.8 (q, *J* = 272.8 Hz), 73.9, 22.4; HRMS (+EI) calcd for $C_{16}H_{13}F_3O_2$ ($[M]^+$) 294.08622, found 294.08640.



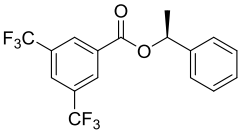
Ethyl (*R*)-2-((3-(trifluoromethyl)benzoyl)oxy) propionate (**21**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.33 (m, 1H), 8.30 – 8.25 (m, 1H), 7.87 – 7.81 (m, 1H), 7.64 – 7.57 (m, 1H), 5.34 (q, J = 7.1 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 1.66 (d, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.1, Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.26; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 164.8, 133.2, 131.3 (q, *J* = 32.9 Hz), 130.5, 129.9 (q, *J* = 3.7 Hz), 129.3, 126.9 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 272.4 Hz), 69.8, 61.7, 17.2, 14.3; HRMS (+EI) calcd for $C_{13}H_{13}F_3O_4$ ($[M]^+$) 290.07604, found 290.07586.



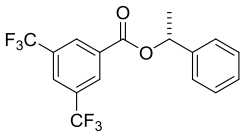
Ethyl (*S*)-2-((3-(trifluoromethyl)benzoyl)oxy) propionate (**21**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.33 (m, 1H), 8.30 – 8.25 (m, 1H), 7.87 – 7.81 (m, 1H), 7.64 – 7.57 (m, 1H), 5.34 (q, J = 7.1 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 1.66 (d, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.1, Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.26; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 164.8, 133.2, 131.3 (q, *J* = 32.9 Hz), 130.5, 129.9 (q, *J* = 3.7 Hz), 129.3, 126.9 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 272.4 Hz), 69.8, 61.7, 17.2, 14.3; HRMS (+EI) calcd for $C_{13}H_{13}F_3O_4$ ($[M]^+$) 290.07604, found 290.07586.



(*S*)-1-Phenylethyl 3,5-bis(trifluoromethyl)benzoate (**20**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 2H), 8.06 (s, 1H), 7.49 – 7.31 (m, 5H), 6.19 (q, *J* = 6.6 Hz, 1H), 1.73 (d, *J* = 6.6 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.39; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 140.8, 132.8, 132.3 (q, *J* = 34.0 Hz), 129.9 (d, *J* = 3.8 Hz), 128.9, 128.6, 126.5 (q, *J* = 3.6 Hz), 126.4, 123.0 (q, *J* = 272.9 Hz), 74.7, 22.2; HRMS (+EI) calcd for $C_{17}H_{12}F_6O_2$ ($[M]^+$) 362.07360, found 362.07358.



(*R*)-1-Phenylethyl 3,5-bis(trifluoromethyl)benzoate (**20**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 2H), 8.06 (s, 1H), 7.49 – 7.31 (m, 5H), 6.19 (q, *J* = 6.6 Hz, 1H), 1.73 (d, *J* = 6.6 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.39; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 140.8, 132.8, 132.3 (q, *J* = 34.0 Hz), 129.9 (d, *J* = 3.8 Hz), 128.9, 128.6, 126.5 (q, *J* = 3.6 Hz), 126.4, 123.0 (q, *J* = 272.9 Hz), 74.7, 22.2; HRMS (+EI) calcd for $C_{17}H_{12}F_6O_2$ ($[M]^+$) 362.07360, found 362.07358.



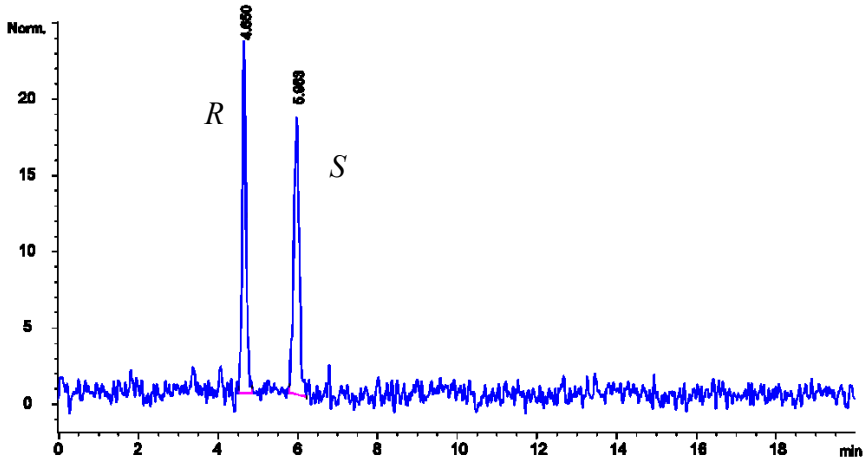
S5 HPLC or GC analysis of products (17-21) of stereoselective esterification

Data for Table 3

1-Phenylethyl 2-methyl-2-phenylpropanoate (17) /Table 3, Entry 1

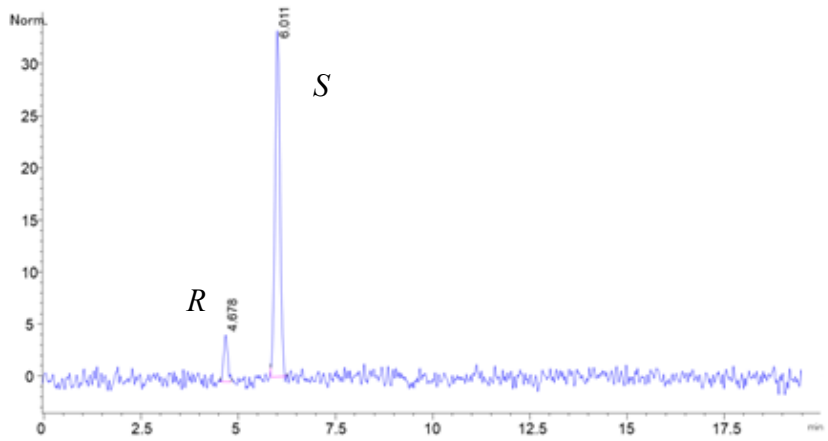
Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/isopropyl alcohol 97.5:2.5, flow 0.8 mL/min, temp. 15 °C, detection at 230 nm.

(*rac*)-1-Phenylethyl 2-methyl-2-phenylpropanoate (*rac*-**17**) - standard



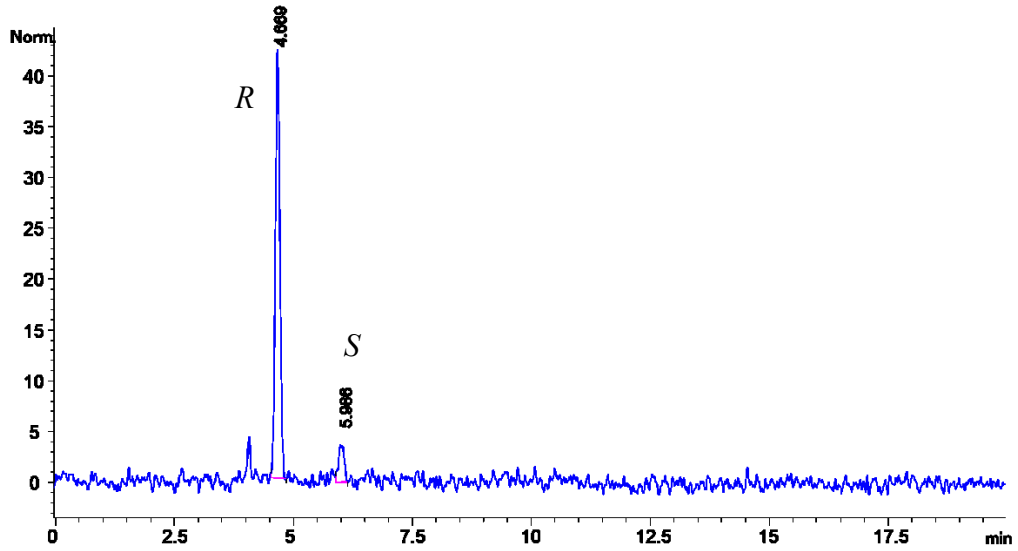
#	Time	Area	Height	Width	Area%	Symmetry
1	4.65	158.3	23.2	0.1038	47.379	0.901
2	5.963	175.9	18.1	.1432	52.621	0.899

(*S*)-1-Phenylethyl 2-methyl-2-phenylpropanoate (*S*-**17**) – standard



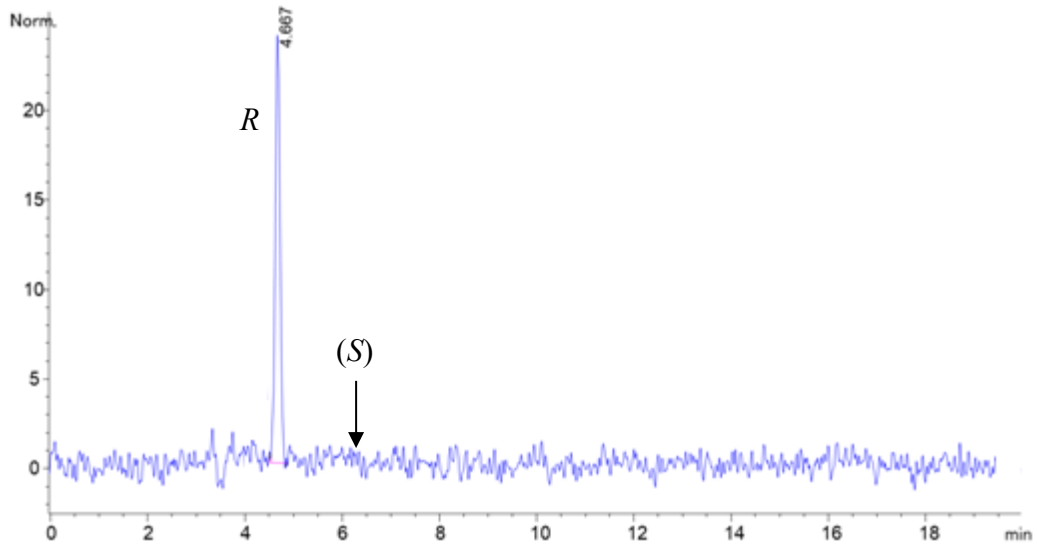
#	Time	Area	Height	Width	Area%	Symmetry
1	4.678	32.6	4.5	0.1019	9.85	0.91
2	6.011	298.1	33.3	0.1385	90.15	0.921

(*R*)-1-Phenylethyl 2-methyl-2-phenylpropanoate (*R*-**17**) – standard



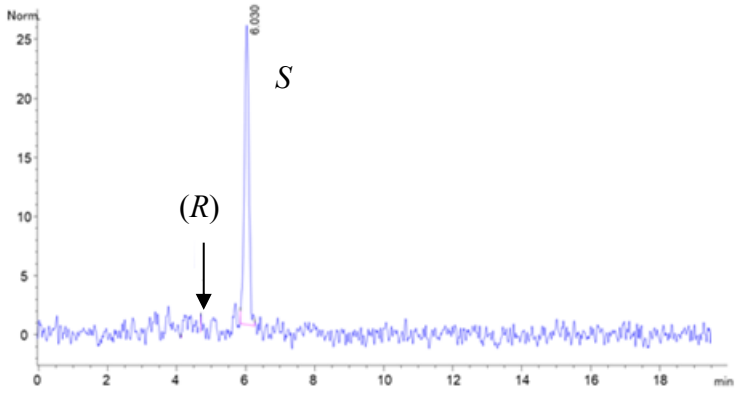
#	Time	Area	Height	Width	Area%	Symmetry
1	4.669	279.6	42.1	0.1034	90.116	0.968
2	5.986	30.7	3.6	0.1406	9.884	0.484

Table 3/ Entry 1 – Method **A** starting from (*S*)-1-phenylethanol



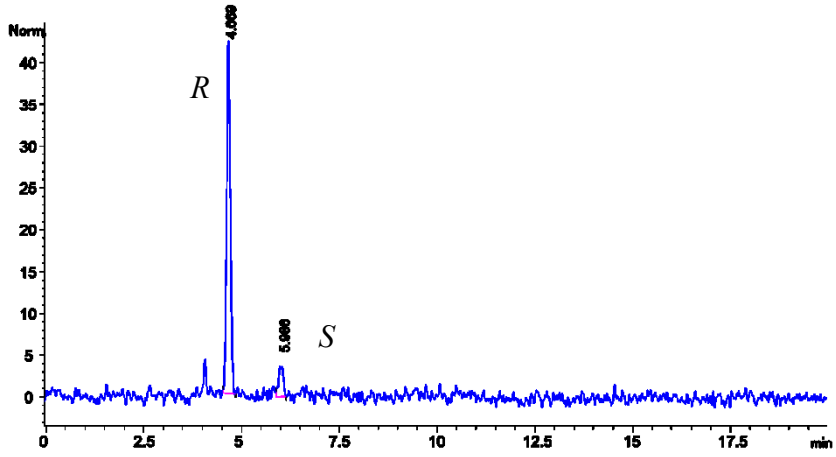
#	Time	Area	Height	Width	Area%	Symmetry
1	4.667	166.7	23.9	0.1093	100.00	0.953

Table 3/ Entry 1 – Method **A** starting from (*R*)-1-phenylethanol



#	Time	Area	Height	Width	Area%	Symmetry
1	6.03	231.7	25.3	0.1407	100.00	1.01

Table 3/ Entry 1 – Method **C** starting from (*R*)-1-phenylethanol

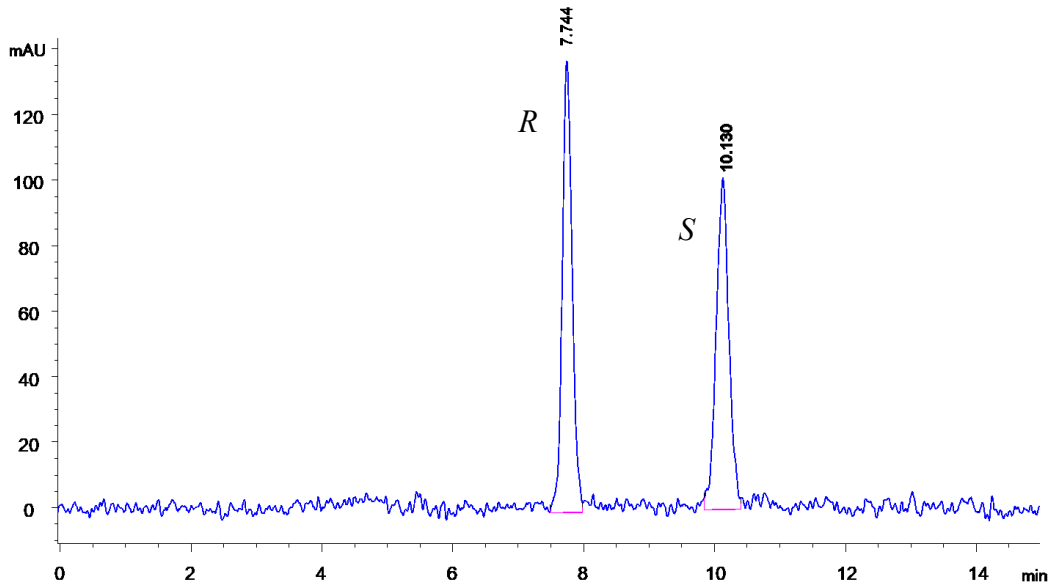


#	Time	Area	Height	Width	Area%	Symmetry
1	4.669	279.6	42.1	0.1034	90.116	0.968
2	5.986	30.7	3.6	0.1406	9.884	0.484

1-Phenylethyl 2-phenylacetate /Table 3, Entry 2

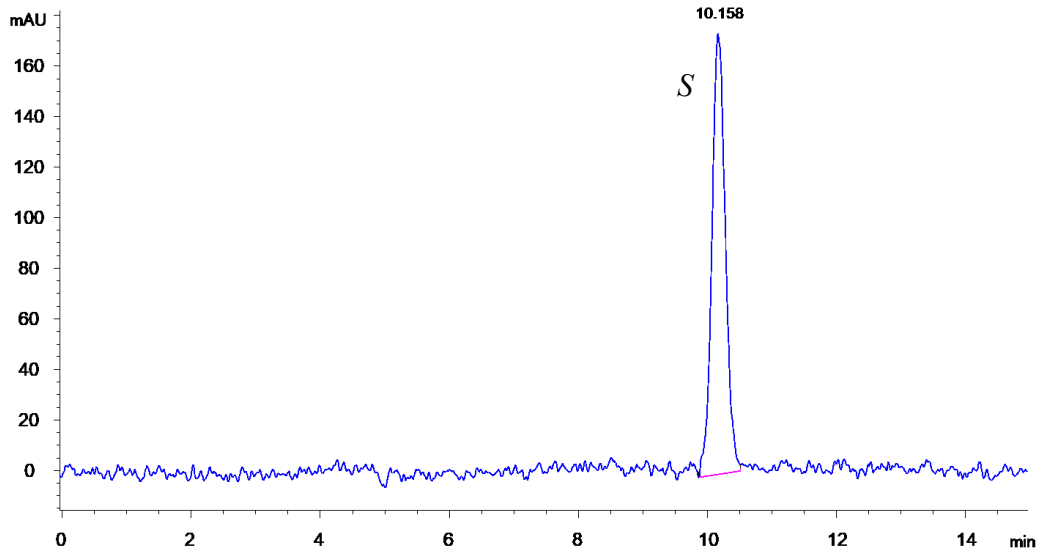
Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/isopropyl alcohol 97.5:2.5, flow 0.8 mL/min, temp. 15 °C, detection at 230 nm.

(*rac*)-1-Phenylethyl 2-phenylacetate (*rac*-**18**) - standard



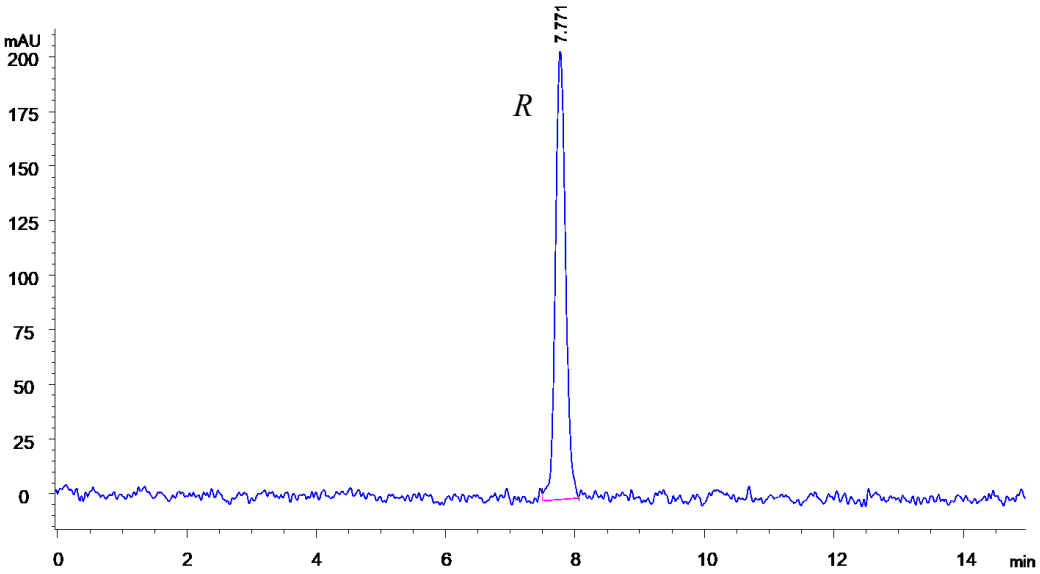
#	Time	Area	Height	Width	Area%	Symmetry
1	7.744	1451.1	138.1	0.1751	51.431	0.826
2	10.13	1370.3	101.4	0.2253	48.569	1.079

(*S*)-1-Phenylethyl 2-phenylacetate (*S*-**18**) - standard



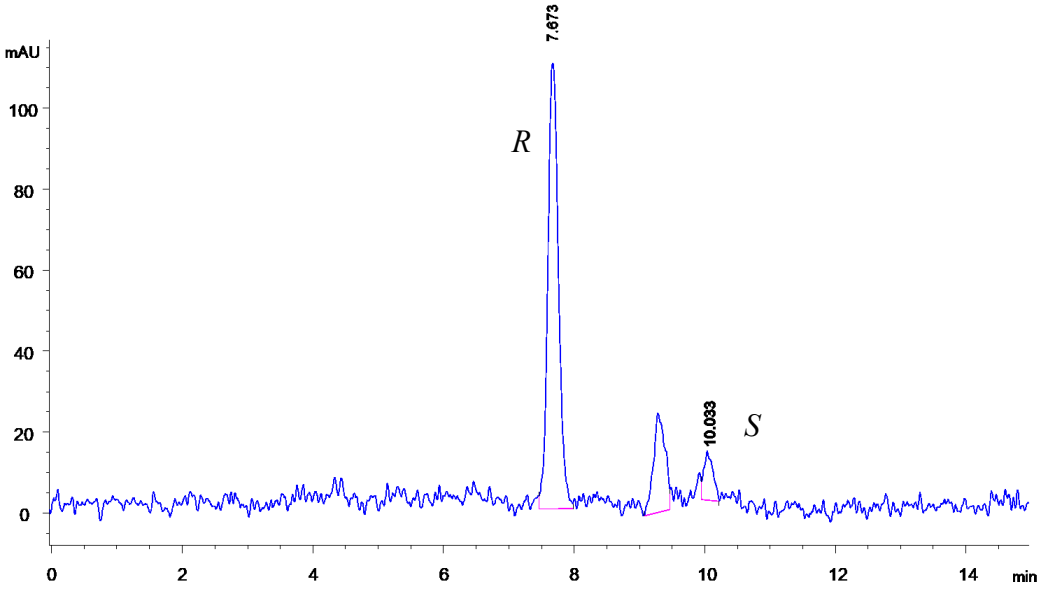
#	Time	Area	Height	Width	Area%	Symmetry
1	10.158	2530.9	174.3	0.1834	100.000	0.786

(*R*)-1-Phenylethyl 2-phenylacetate (*R*-**18**) - standard



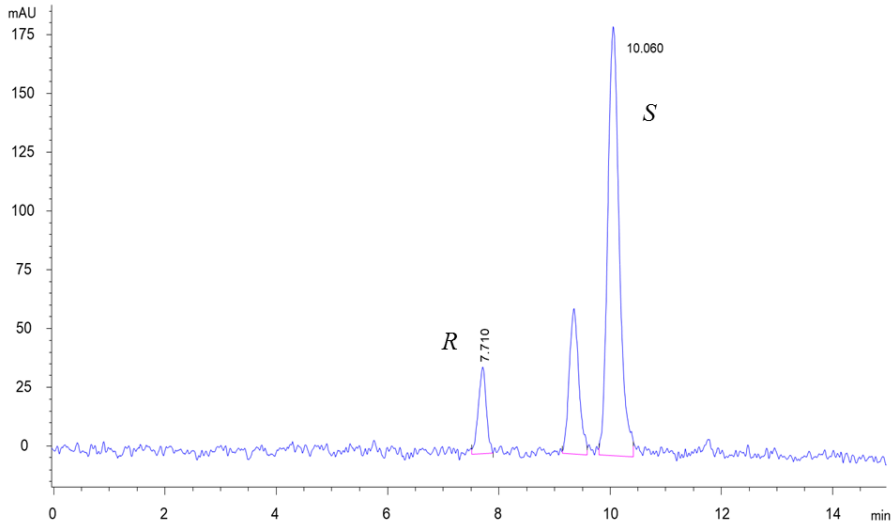
#	Time	Area	Height	Width	Area%	Symmetry
1	7.771	2244	205.3	0.1575	100.000	0.857

Table 3/ Entry 2 – Method **A** starting from (*S*)-1-phenylethanol



#	Time	Area	Height	Width	Area%	Symmetry
1	7.673	1247.2	110.1	0.1701	91.63	0.813
2	10.033	113.9	11.9	0.1174	8.37	0.569

Table 3/ Entry 2 – Method **A** starting from (*R*)-1-phenylethanol

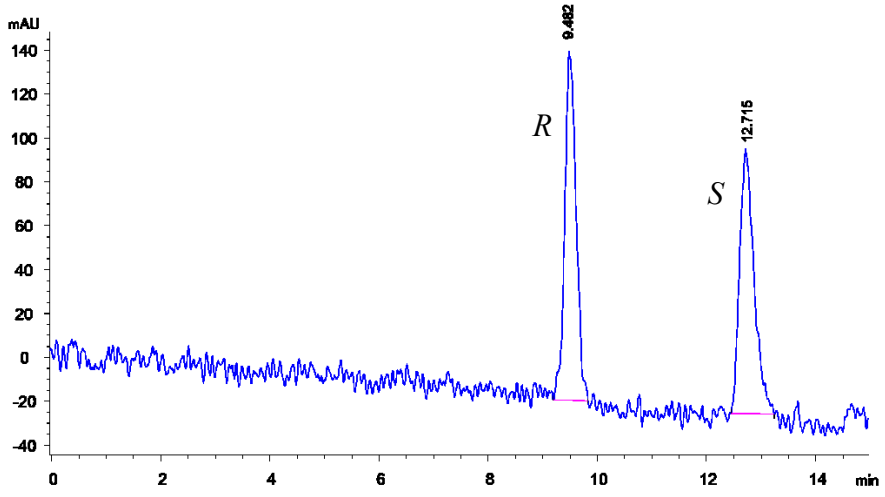


#	Time	Area	Height	Width	Area%	Symmetry
1	7.71	368.2	36.9	0.1365	12.27	1.217
2	10.06	2632.7	182.7	0.2402	87.73	0.867

Change of conditions of analysis:

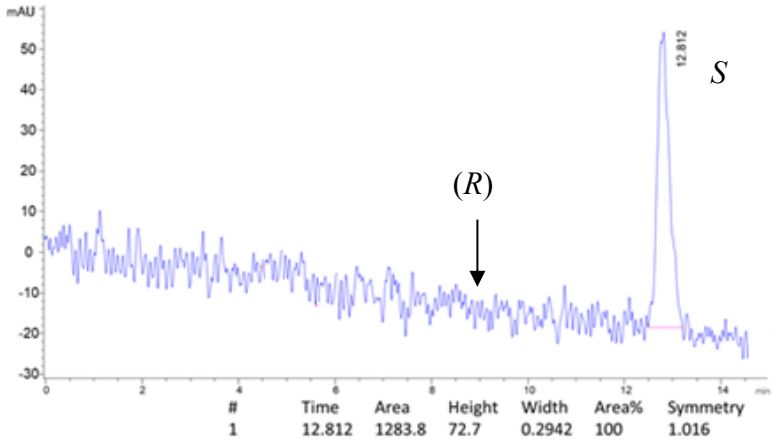
Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/ethanol 97.5:2.5, flow 0.8 mL/min, temp. 10 °C, detection at 230 nm.

(*rac*)-ester (**18**) - standard



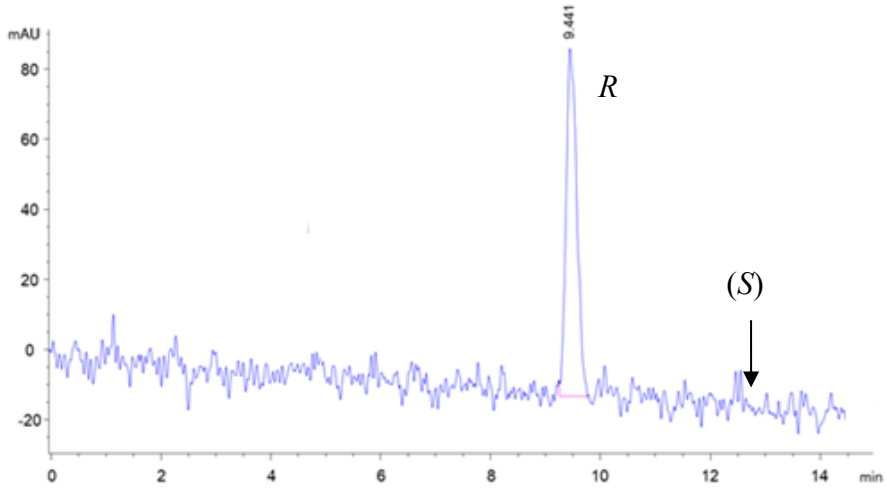
#	Time	Area	Height	Width	Area%	Symmetry
1	9.482	2294.7	159.2	0.2403	50.690	0.66
2	12.715	2232.2	121.2	0.307	49.310	0.676

Table 3/ Entry 2 – Method **B** starting from (*S*)-1-phenylethanol



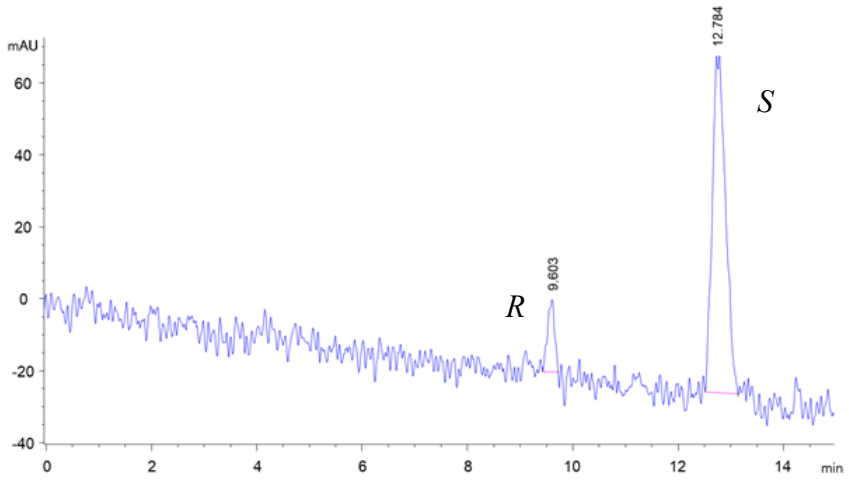
#	Time	Area	Height	Width	Area%	Symmetry
1	12.812	1283.8	72.7	0.2942	100	1.016

Table 3/ Entry 2 – Method **B** starting from (*R*)-1-phenylethanol



#	Time	Area	Height	Width	Area%	Symmetry
1	9.441	1343.6	99.1	0.226	100.0	0.573

Table 3/ Entry 2 – Method **C** starting from (*R*)-1-phenylethanol

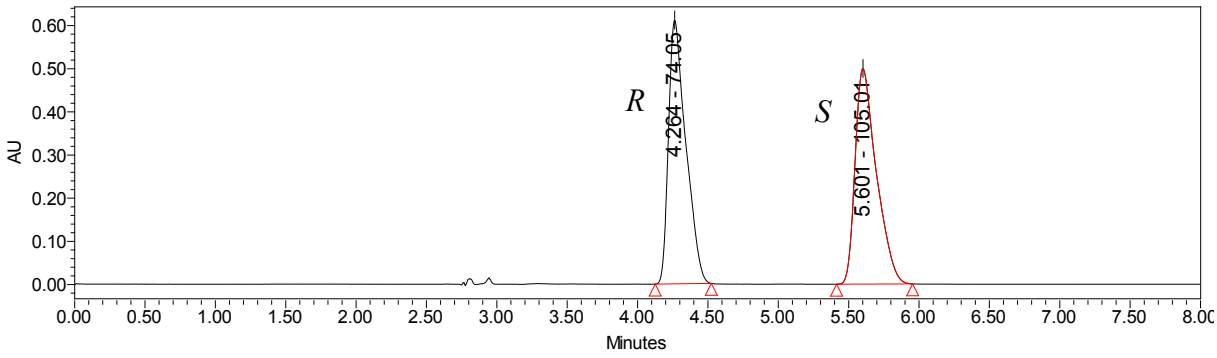


#	Time	Area	Height	Width	Area%	Symmetry
1	9.603	187.4	20.2	0.155	10.222	1.587
2	12.784	1645.6	93.8	0.2925	89.778	1.041

1-Phenylethyl 3-(trifluoromethyl)benzoate/Table 3, Entry 3

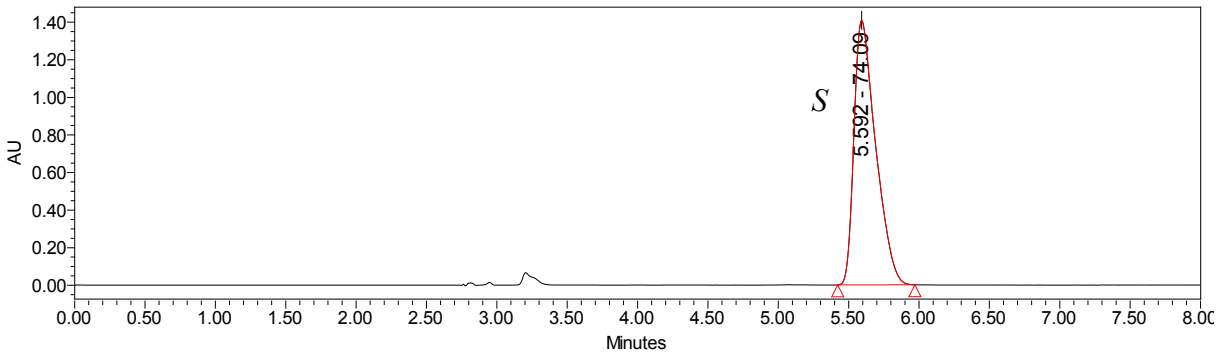
Analysis were performed on Acquity UPC^2 (Waters, USA) using Chiralpak AD-H column (250x3 mm i.d., 5 µm), supercritical CO_2/propan-2-ol 95:5, flow 1.0 mL/min, temp. 35 °C, detection at 220 nm.

rac-1-phenylethyl 3-(trifluoromethyl)benzoate (*rac*-**19**) - standard



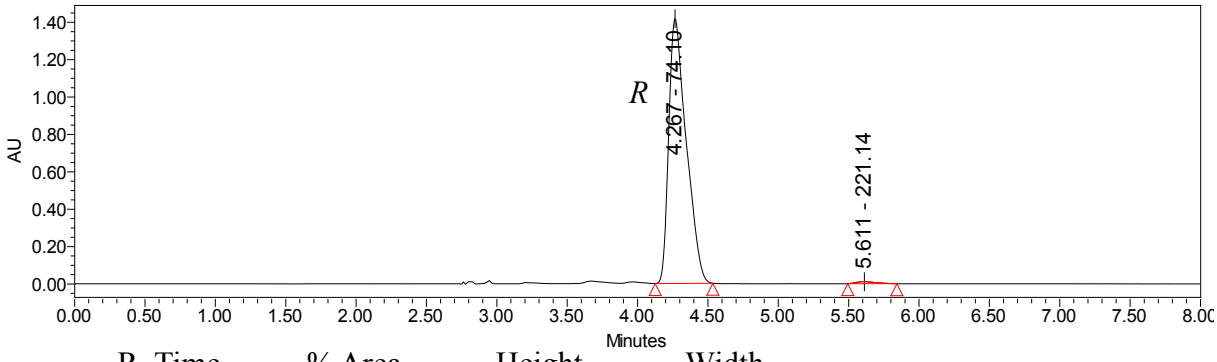
	R.Time	% Area	Height	Width
2	5.601	50.03	499348	32.407
1	4.264	49.97	610882	23.905

(*S*)-1-phenylethyl 3-(trifluoromethyl)benzoate ((*S*)-**19**) - standard



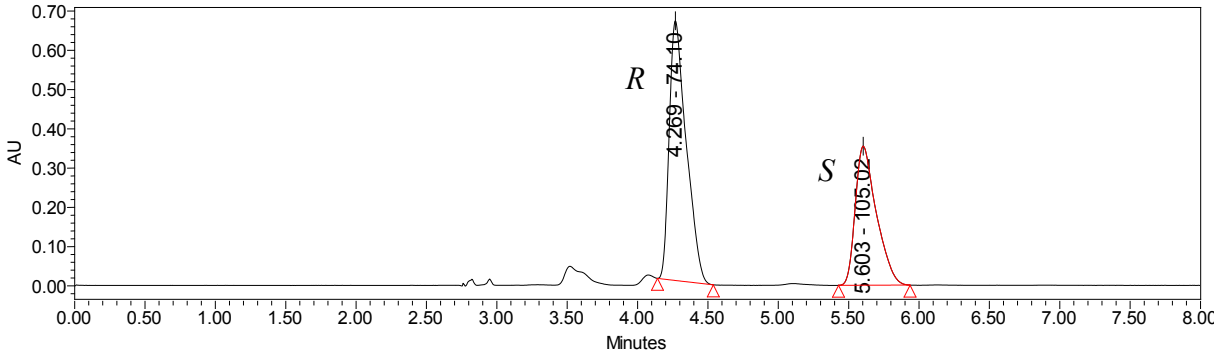
	R. Time	% Area	Height	Width
1	5.592	100.00	1406862	32.907

(*R*)-1-phenylethyl 3-(trifluoromethyl)benzoate ((*R*)-**19**) - standard



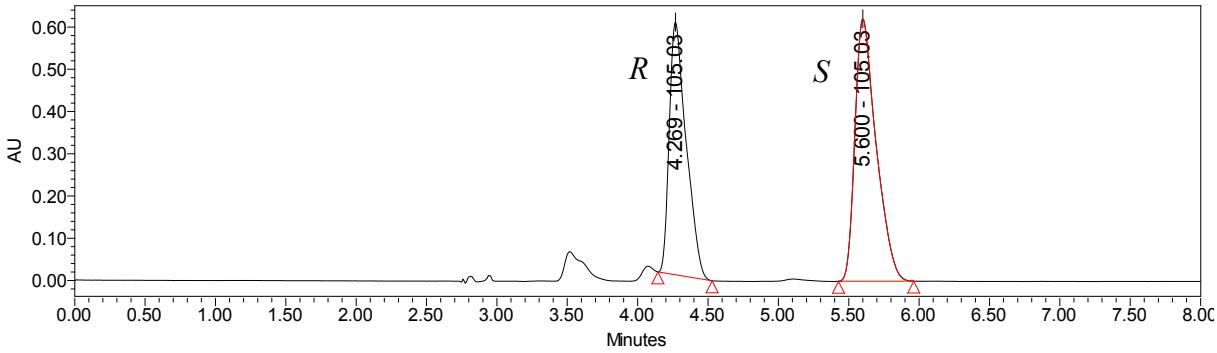
	R. Time	% Area	Height	Width
1	4.267	99.13	1415714	24.605
2	5.611	0.87	11078	20.904

Table 3/ Entry 3 – Method **A** starting from (*S*)-1-phenylethanol



	R. Time	% Area	Height	Width
1	4.269	60.21	661508	23.805
2	5.603	39.79	354137	30.507

Table 3/ Entry 3 – Method **A** starting from (*R*)-1-phenylethanol

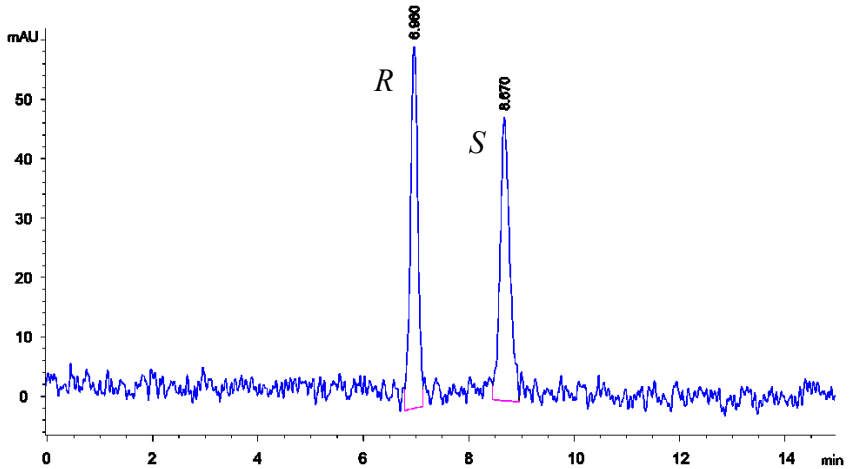


	R. Time	% Area	Height	Width
1	4.269	43.44	598188	23.155
2	5.600	56.56	620768	32.107

Change of conditions of analysis:

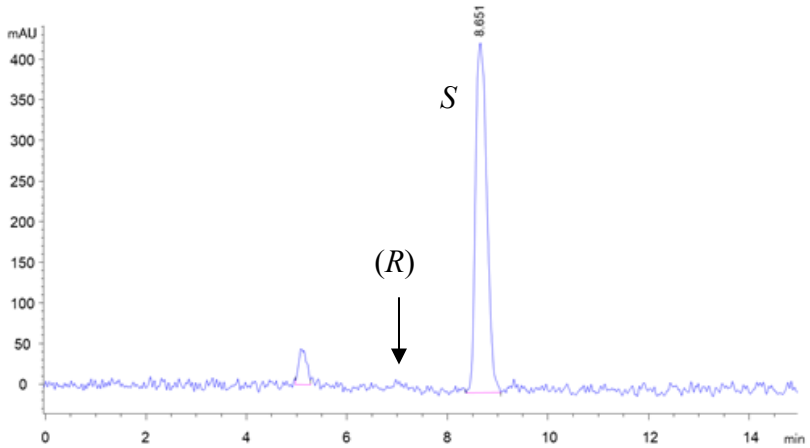
Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/ethanol 97.5:2.5, flow 0.7 mL/min, temp. 15 °C, detection at 254 nm.

(*rac*)-ester **19** - standard



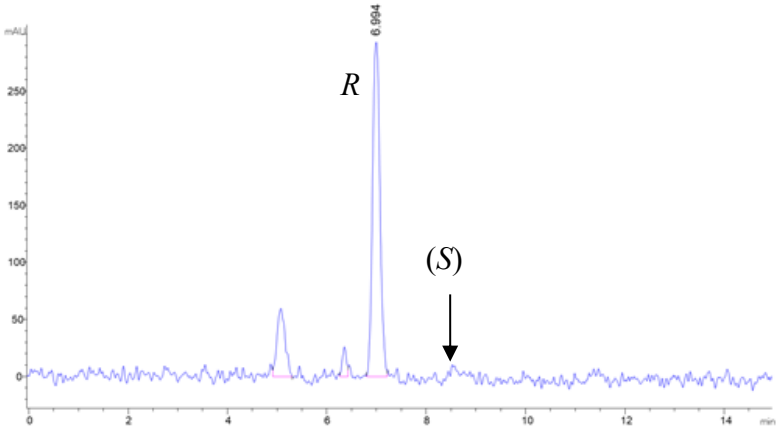
#	Time	Area	Height	Width	Area%	Symmetry
1	6.96	596.5	60.9	0.1463	49.584	0.96
2	8.67	606.5	47.7	0.1682	50.416	0.745

Table 3/ Entry 3 – Method **B** starting from (*S*)-1-phenylethanol



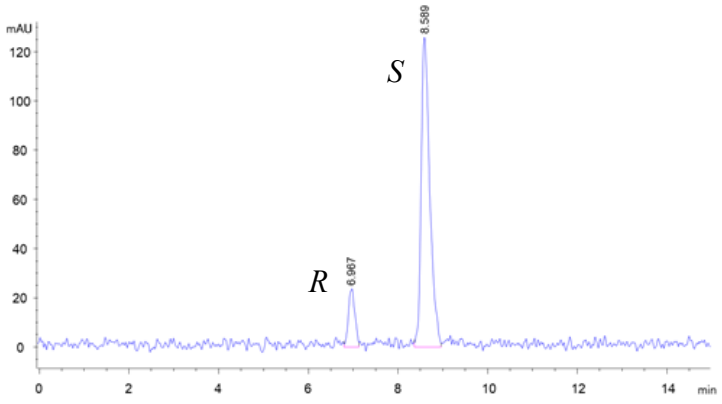
#	Time	Area	Height	Width	Area%	Symmetry
1	8.651	6727.7	431	0.1941	100	0.707

Table 3/ Entry 3 – Method **B** starting from (*R*)-1-phenylethanol



#	Time	Area	Height	Width	Area%	Symmetry
1	6.994	3043.1	293.1	0.173	100.0	0.966

Table 3/ Entry 3 – Method **C** starting from (*R*)-1-phenylethanol

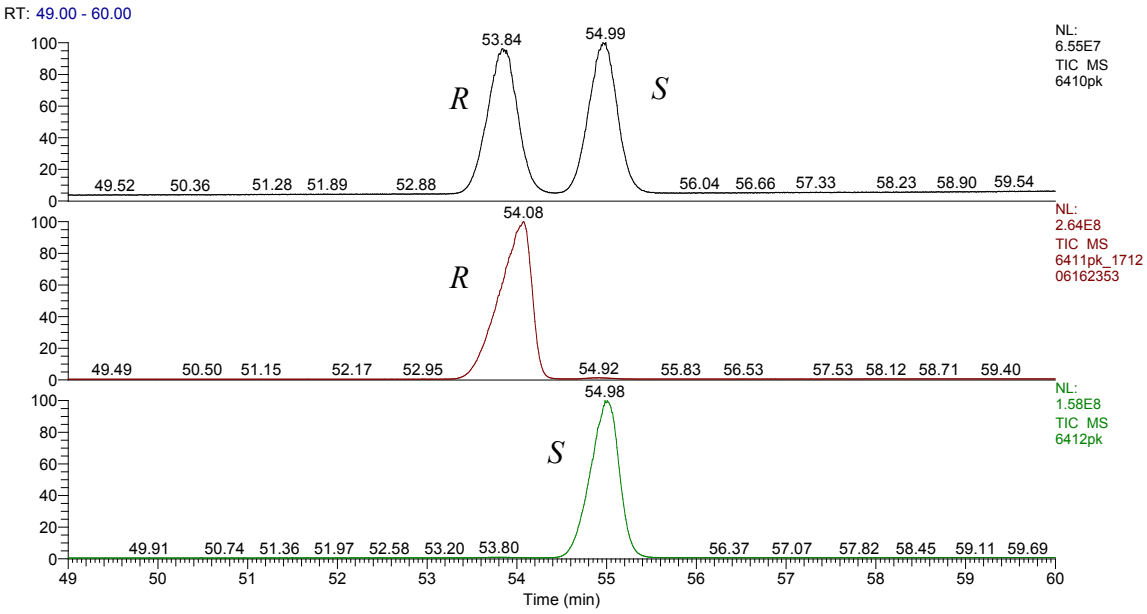


#	Time	Area	Height	Width	Area%	Symmetry
1	6.967	243.1	23.8	0.1701	12.595	1.074
2	8.589	1687.3	126.1	0.223	87.405	0.593

1-Phenylethyl 3,5-bis(trifluoromethyl)benzoate/ Table 3, Entry 4

Chemical analysis was carried out using coupled gas chromatography with mass spectrometric detector (electron ionization 70 eV) DSQ II (Thermo-Scientific, Waltham, MA, USA) equipped with chiral stationary phase column (30 m, id 0.25 mm, 0.25 µm film thickness) with octakis-(6-O-methyl-2,3-di-O-pentyl-γ-cyclodextrin phase (custom made) enabling separation of chiral compounds. The gas chromatograph inlet was heated to 200 °C, MS transferline 200 °C, ion source 200 °C, helium was used as a carrier gas at flow 1.0 mL min^{-1}. Temperature program of the oven was 70 °C (2 min) to 150 °C (10 min) at 1 °C.min^{-1} and then to 200 °C (15 min) at 10 °C.min^{-1}.

1-Phenylethyl 3,5-bis(trifluoromethyl)benzoate (*rac*-**20**) - standard



(*rac*-**20**)

Apex RT	Start RT	End RT	Area	**%Area**	Height	%Height
53,84	53,26	54,41	1408830457	**50,5**	59859884	49,05
54,99	54,46	55,55	1381194228	**49,5**	62180107	50,95

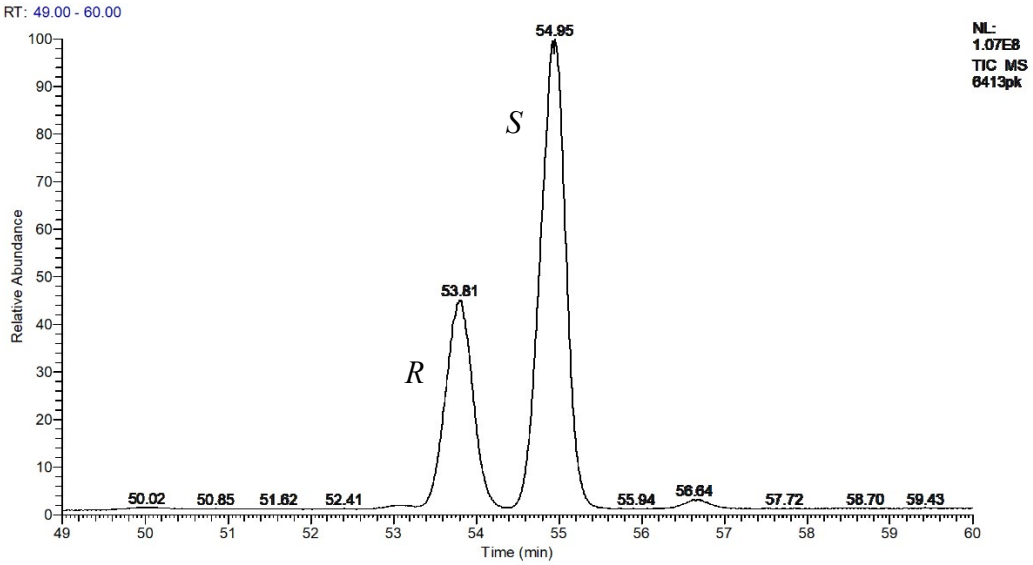
(*S*-**20**)

Apex RT	Start RT	End RT	Area	**%Area**	Height	%Height
53,8	53,5	54,09	10177733,28	**0,29**	536885,5	0,34
54,98	54,38	55,53	3508928703	**99,71**	1,56E+08	99,66

(*R*-**20**)

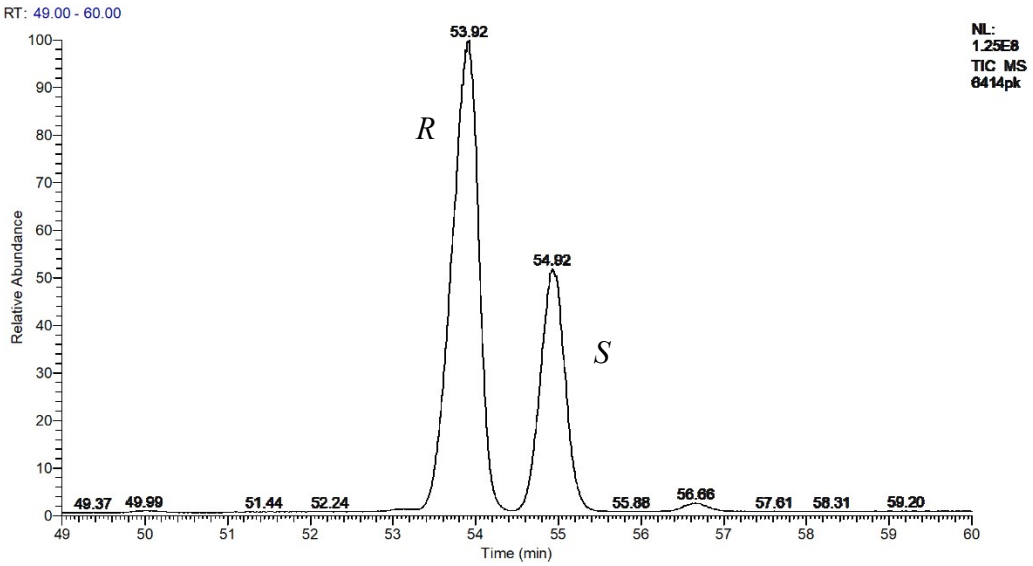
Apex RT	Start RT	End RT	Area	**%Area**	Height	%Height
54,08	53,26	54,48	6583458543	**99,48**	2,63E+08	99,27
54,92	54,65	55,18	34127602,37	**0,52**	1941772	0,73

Table 3/ Entry 4 – Method **A** starting from (*S*)-1-phenylethanol



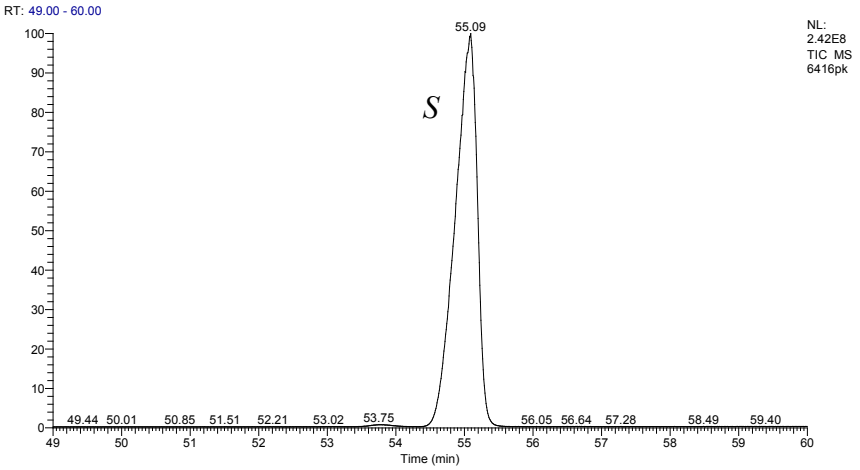
Apex RT	Start RT	End RT	Area	**%Area**	Height	%Height
53,81	53,32	54,32	1053853742	**31,95**	46519840	30,7
54,95	54,43	55,47	2244687075	**68,05**	1,05E+08	69,3

Table 3/ Entry 4 – Method **A** starting from (*R*)-1-phenylethanol



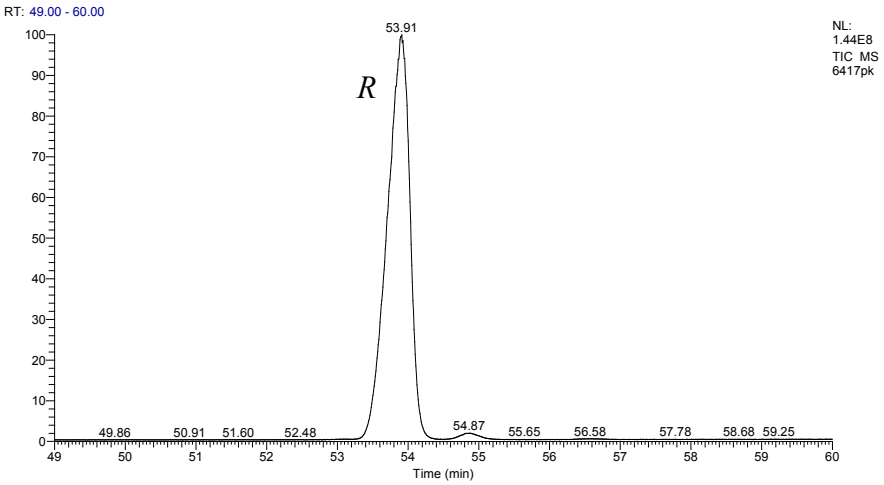
Apex RT	Start RT	End RT	Area	**%Area**	Height	%Height
53,92	53,31	54,39	2808752405	**68,11**	1,24E+08	66,05
54,92	54,48	55,45	1315037524	**31,89**	63531254	33,95

Table 3/ Entry 4 – Method **B** starting from (*S*)-1-phenylethanol



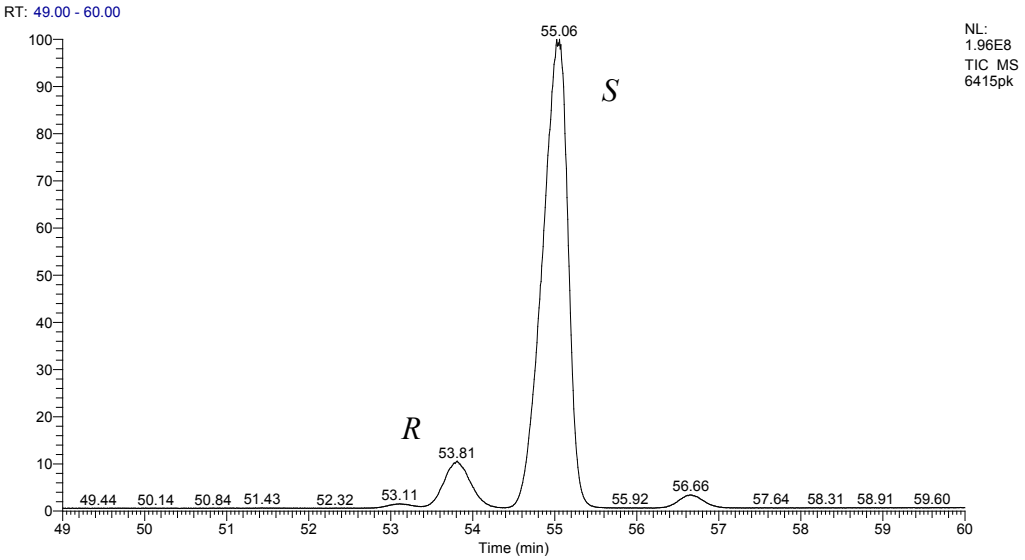
Apex RT	Start RT	End RT	Area	**%Area**	Height	%Height
53,79	53,48	54,14	27950608,42	**0,52**	1261307	0,52
55,09	54,42	55,56	5378712630	**99,48**	2,41E+08	99,48

Table 3/ Entry 4 – Method **B** starting from (*R*)-1-phenylethanol



Apex RT	Start RT	End RT	Area	**%Area**	Height	%Height
53,91	53,27	54,38	3189049241	**98,72**	1,43E+08	98,49
54,87	54,55	55,17	41189344,21	**1,28**	2203723	1,51

Table 3/ Entry 4 – Method **C** starting from (*R*)-1-phenylethanol

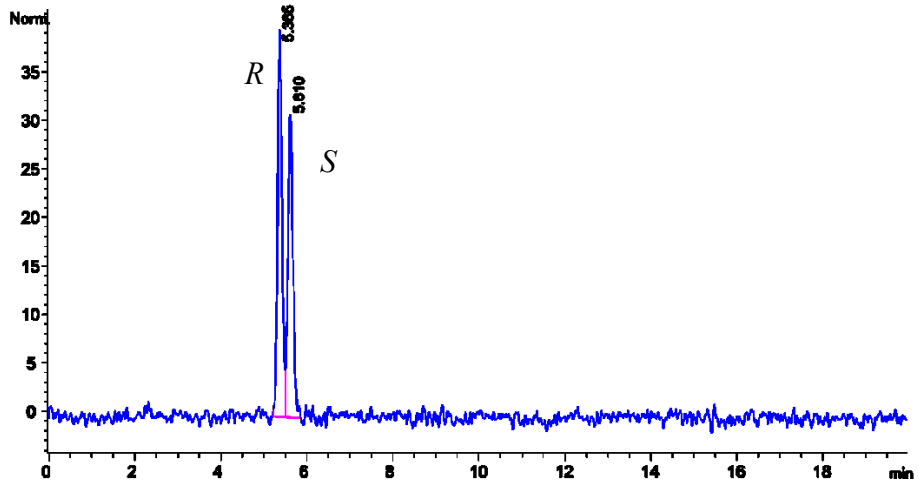


Apex RT	Start RT	End RT	Area	**%Area**	Height	%Height
53,81	53,42	54,25	421714012,4	**9,08**	19193942	8,97
55,06	54,46	55,49	4224317747	**90,92**	1,95E+08	91,03

Ethyl 2-((3-(trifluoromethyl)benzoyl)oxy) propionate/ Table 3, Entry 5

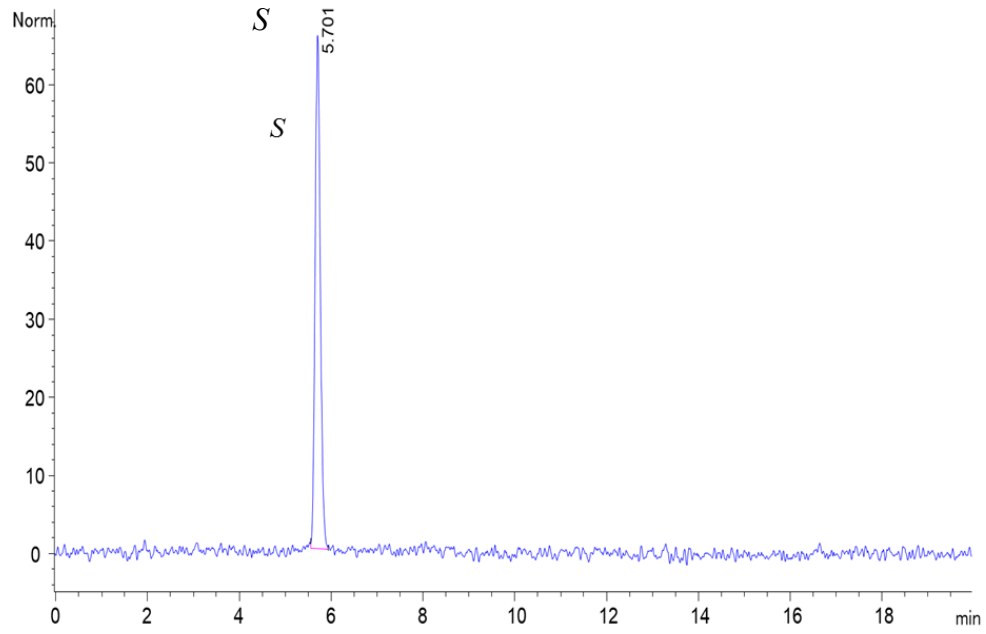
Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/isopropyl alcohol 97.5:2.5, flow 0.8 mL/min, temp. 15 °C, detection at 230 nm.

Ethyl (*rac*)-2-((3-(trifluoromethyl)benzoyl)oxy) propionate (*rac*-**21**) - standard



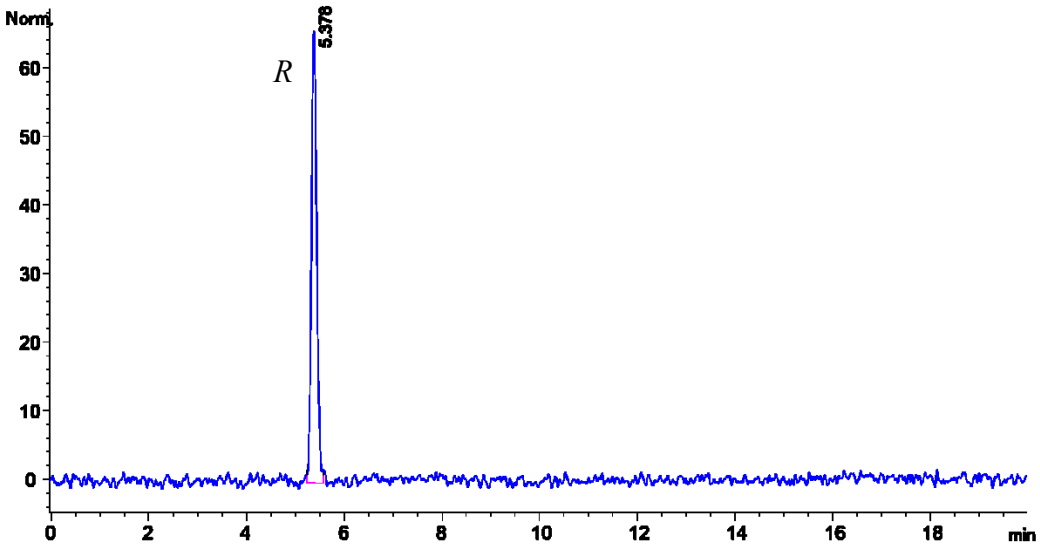
#	Time	Area	Height	Width	Area%	Symmetry
1	5.365	293.4	39.9	0.1137	53.698	0.847
2	5.61	253	31.2	0.1246	46.302	0.833

Ethyl (*S*)-2-((3-(trifluoromethyl)benzoyl)oxy) propionate (**21**) - standard



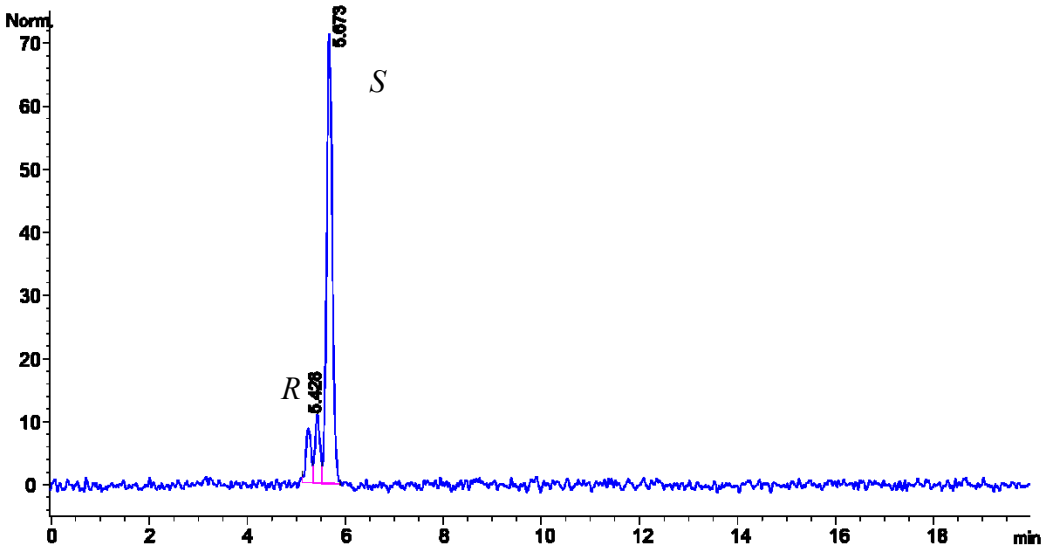
#	Time	Area	Height	Width	Area%	Symmetry
1	5.701	520.3	65.9	0.1222	100.000	0.848

Ethyl (*R*)-2-((3-(trifluoromethyl)benzoyl)oxy) propionate (**21**) - standard



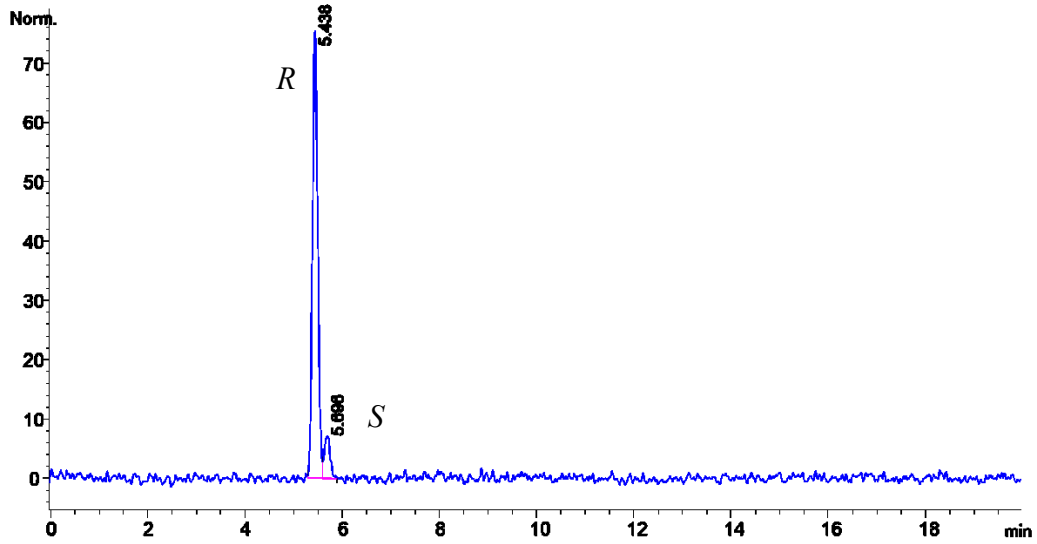
#	Time	Area	Height	Width	Area%	Symmetry
1	5.378	505.5	65.8	0.1177	100.000	0.817

Table 3/ Entry 5 – Method **A** starting from (*S*)-ethyl lactate



#	Time	Area	Height	Width	Area%	Symmetry
1	5.428	76.6	10.8	0.1047	11.76	0.874
2	5.673	574.7	71.3	0.1241	88.24	0.88

Table 3/ Entry 5 – Method **A** starting from (*R*)-ethyl lactate

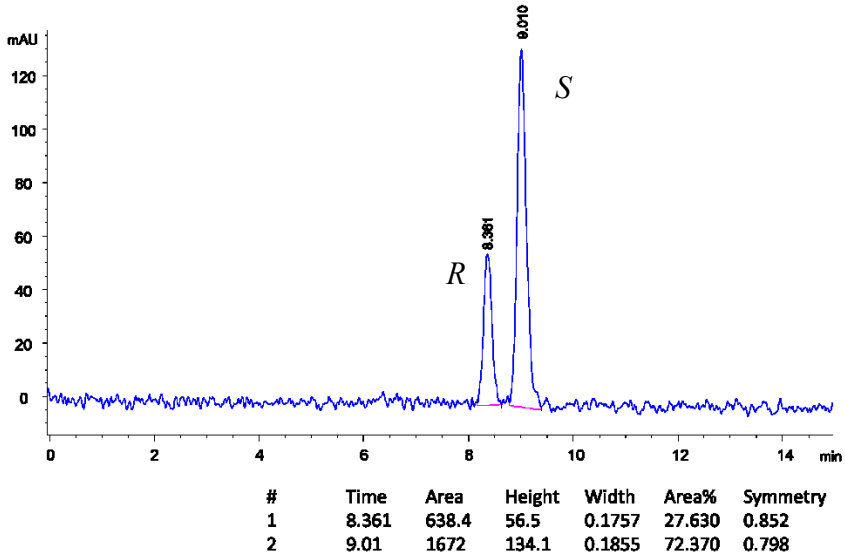


#	Time	Area	Height	Width	Area%	Symmetry
1	5.438	576.5	75.5	0.1191	90.287	0.887
2	5.696	62	7.2	0.1169	9.713	1.041

Change of conditions of analysis:

Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/ethanol 97.5:2.5, flow 0.7 mL/min, temp. 15 °C, detection at 254 nm.

30:70 - (*R:S*)-ester **21**



#	Time	Area	Height	Width	Area%	Symmetry
1	8.361	638.4	56.5	0.1757	27.630	0.852
2	9.01	1672	134.1	0.1855	72.370	0.798

Table 3/ Entry 5 – Method **B** starting from (*S*)-ethyl lactate

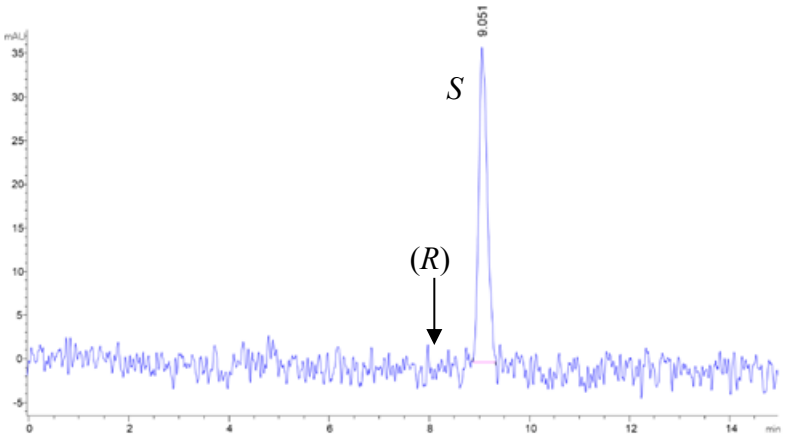


Table 3/ Entry 5 – Method **B** starting from (*R*)-ethyl lactate

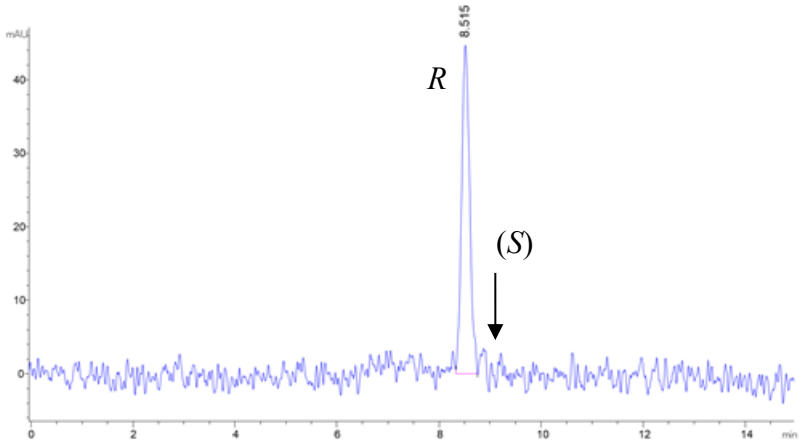
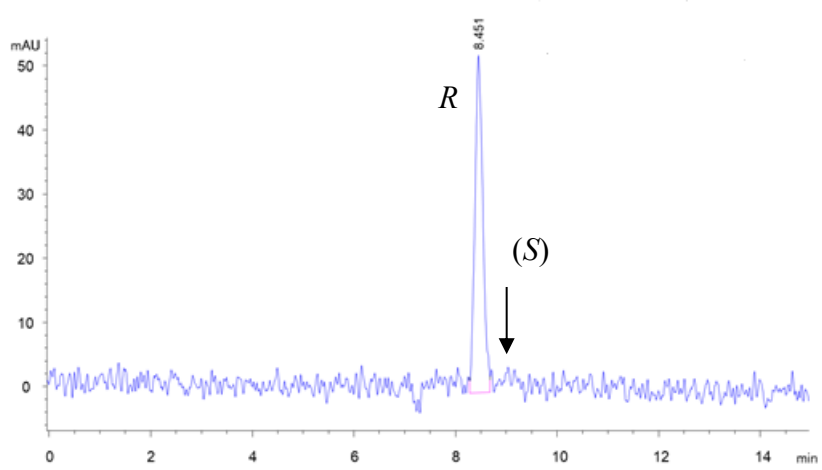


Table 3/ Entry 5 – Method **C** starting from (*S*)-ethyl lactate

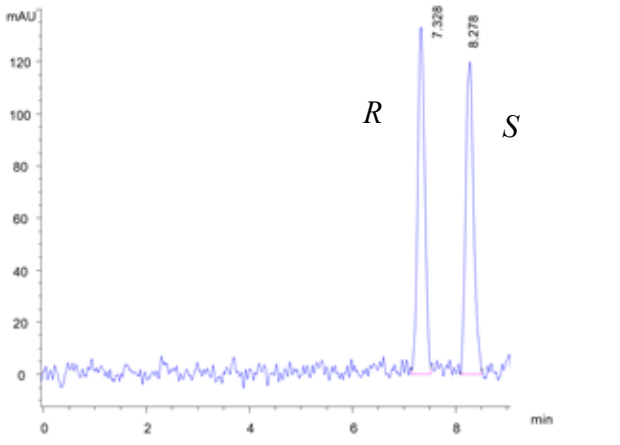


Data for Table 4 (Method A)

1-Phenylethyl 2-phenylacetate

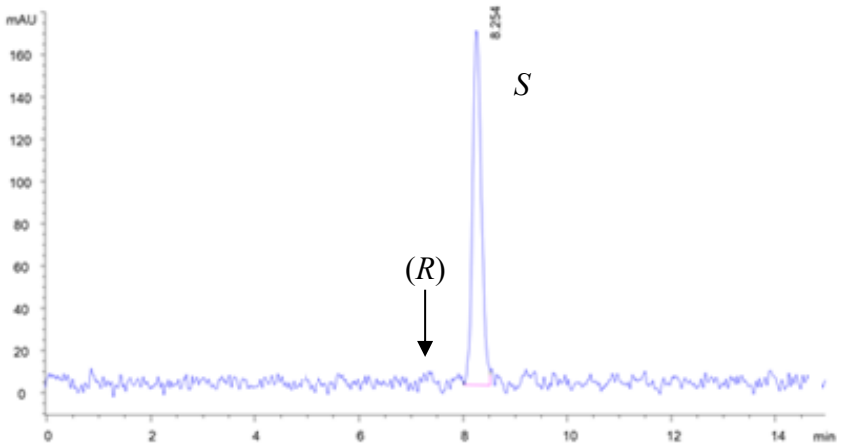
Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/ethanol 97.5:2.5, flow 0.8 mL/min, temp. 25 °C, detection at 254 nm.

(*rac*)-ester **18 -** standard



#	Time	Area	Height	Width	Area%	Symmetry
1	7.328	1269.4	133.6	0.1584	49.622	0.832
2	8.278	1288.7	120.1	0.1788	50.378	1.059

Table 4/ CH_3CN – Method **A** starting from (*S*)-1-phenylethanol

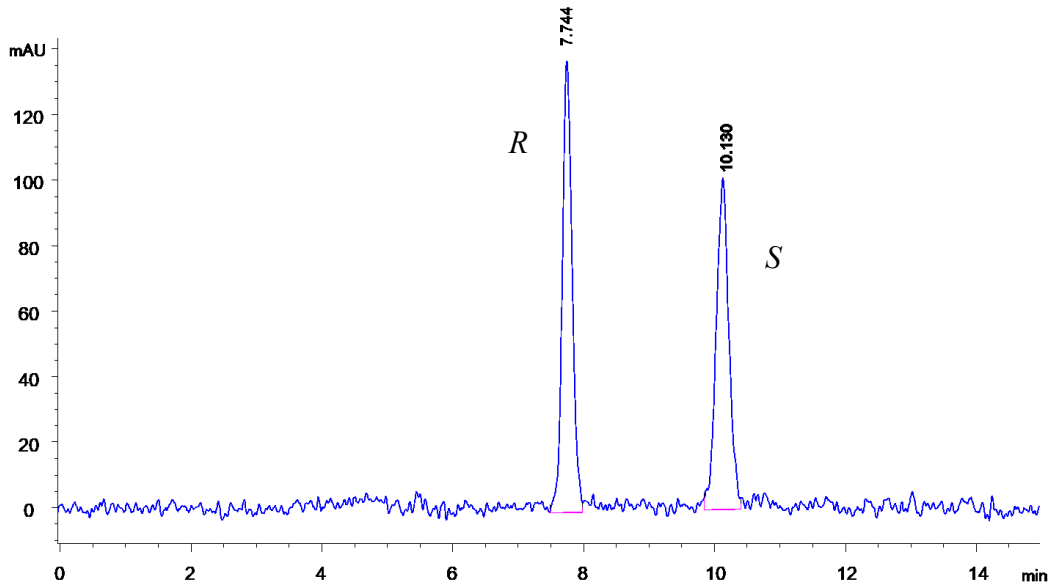


#	Time	Area	Height	Width	Area%	Symmetry
1	8.254	1976.3	167.9	0.1753	100.000	0.737

Change of conditions of analysis:

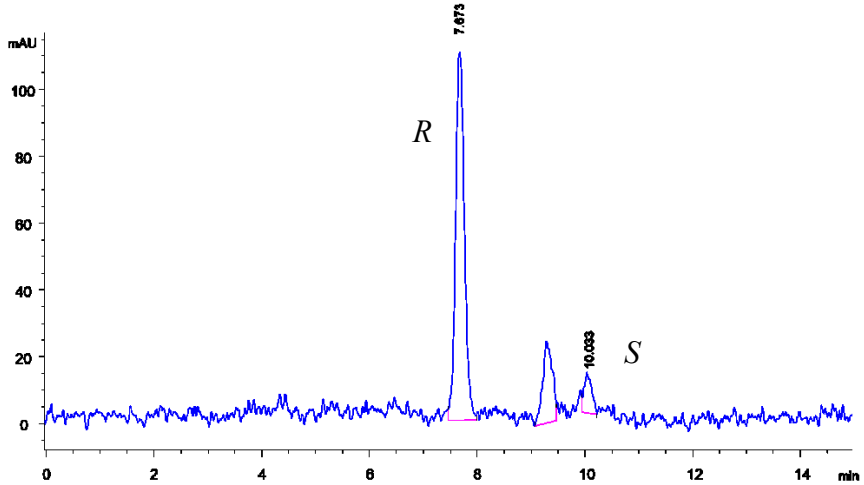
Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/isopropyl alcohol 97.5:2.5, flow 0.8 mL/min, temp. 15 °C, detection at 230 nm.

(*rac*)- ester **18** - standard



#	Time	Area	Height	Width	Area%	Symmetry
1	7.744	1451.1	138.1	0.1751	51.431	0.826
2	10.13	1370.3	101.4	0.2253	48.569	1.079

Table 4/ BTF – Method **A** starting from (*S*)-1-phenylethanol

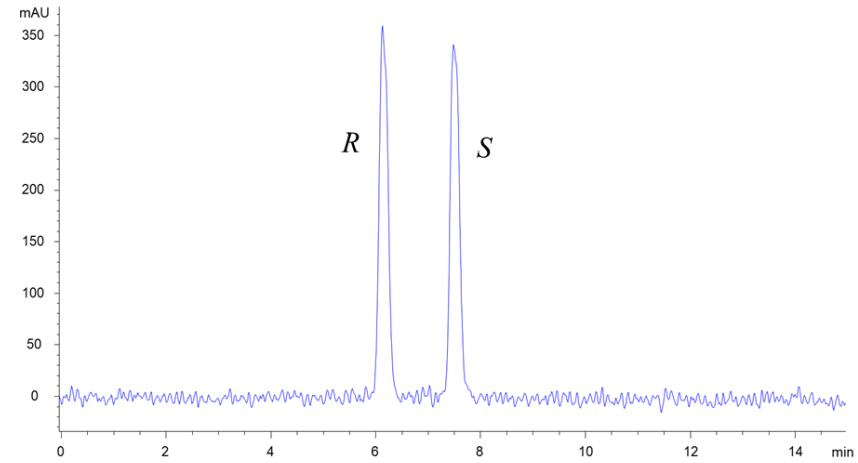


#	Time	Area	Height	Width	Area%	Symmetry
1	7.673	1247.2	110.1	0.1701	91.63	0.813
2	10.033	113.9	11.9	0.1174	8.37	0.569

1-Phenylethyl 3-(trifluoromethyl)benzoate

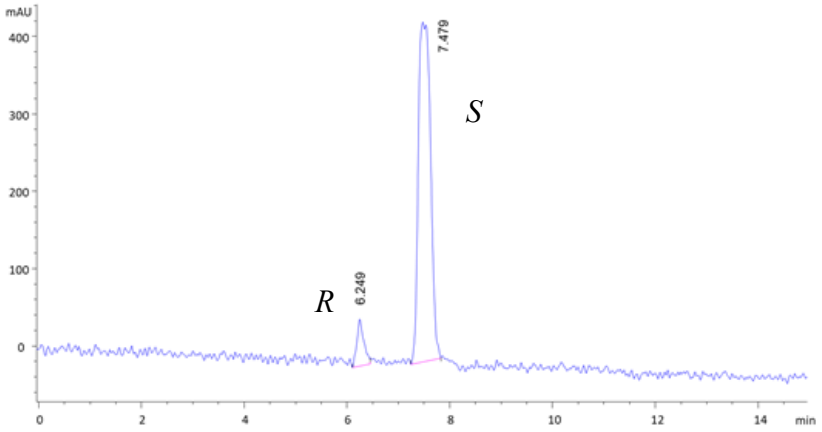
Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/ethanol 97.5:2.5, flow 0.7 mL/min, temp. RT, detection at 230 nm.

(*rac*)-ester **19** - standard



#	Time	Area	Height	Width	Area%	Symmetry
1	6.129	4320.5	363.5	0.1667	49.632	0.612
2	7.482	4384.5	347.6	0.1691	50.368	0.55

Table 4/ CH_3CN – Method **A** starting from (*S*)-1-phenylethanol

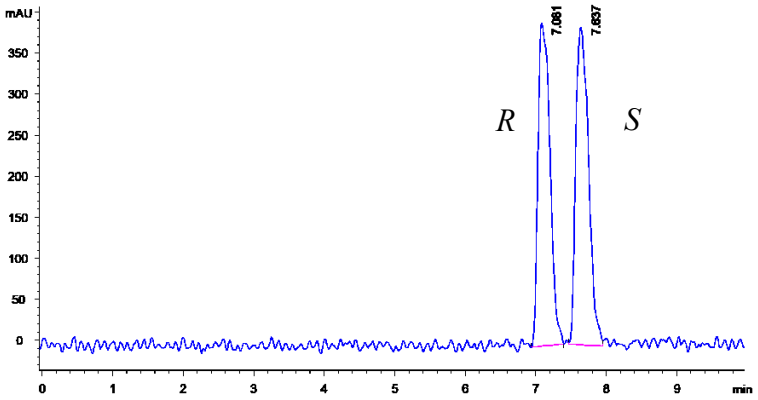


#	Time	Area	Height	Width	Area%	Symmetry
1	6.249	569.3	60.7	0.1254	7.292	0.665
2	7.479	7237.4	439	0.2748	92.708	0.605

Change of conditions of analysis:

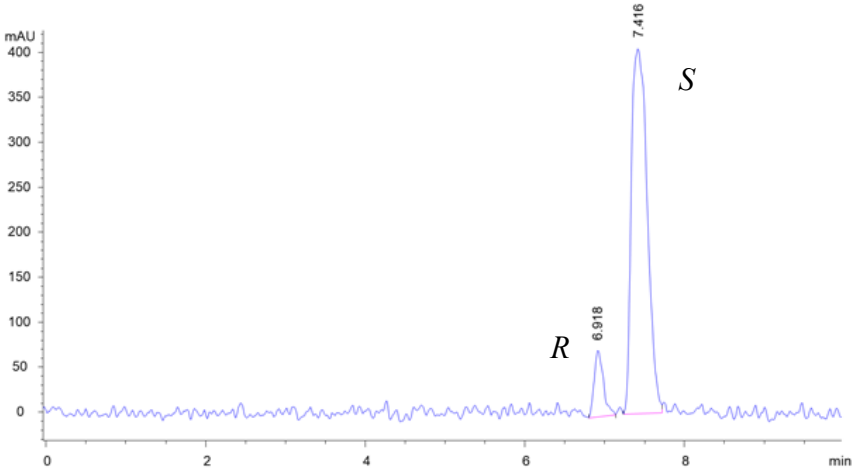
Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/ethanol 97.5:2.5, flow 0.7 mL/min, temp. RT, detection at 230 nm.

(*rac*)-ester **19**



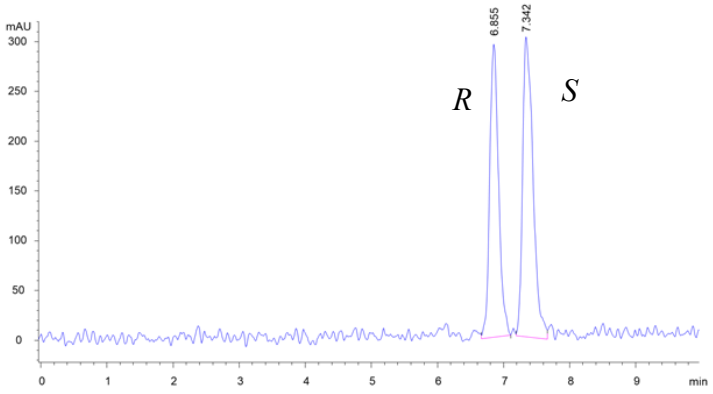
#	Time	Area	Height	Width	Area%	Symmetry
1	7.081	4678.7	393.3	0.1628	48.721	0.444
2	7.637	4924.3	387	0.1824	51.279	0.622

Table 4/ acetone – Method **A** starting from (*S*)-1-phenylethanol



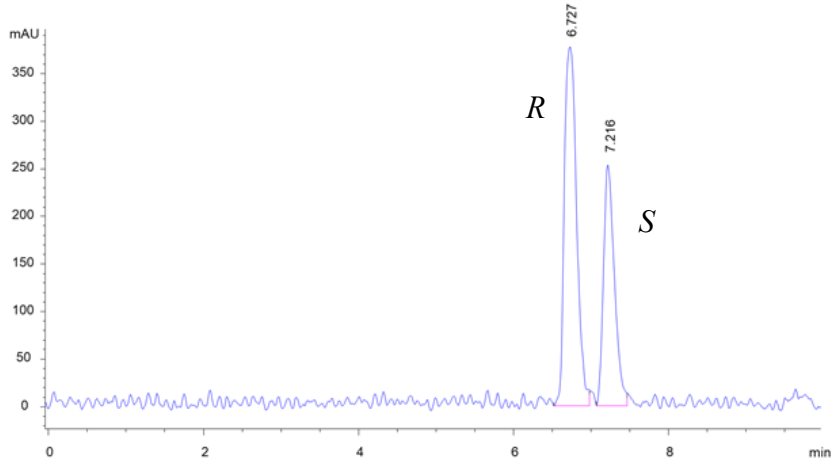
#	Time	Area	Height	Width	Area%	Symmetry
1	6.918	588.1	73.6	0.1112	9.511	0.697
2	7.416	5595.3	405.5	0.175	90.489	0.674

Table 4/ THF – Method **A** starting from (*S*)-1-phenylethanol



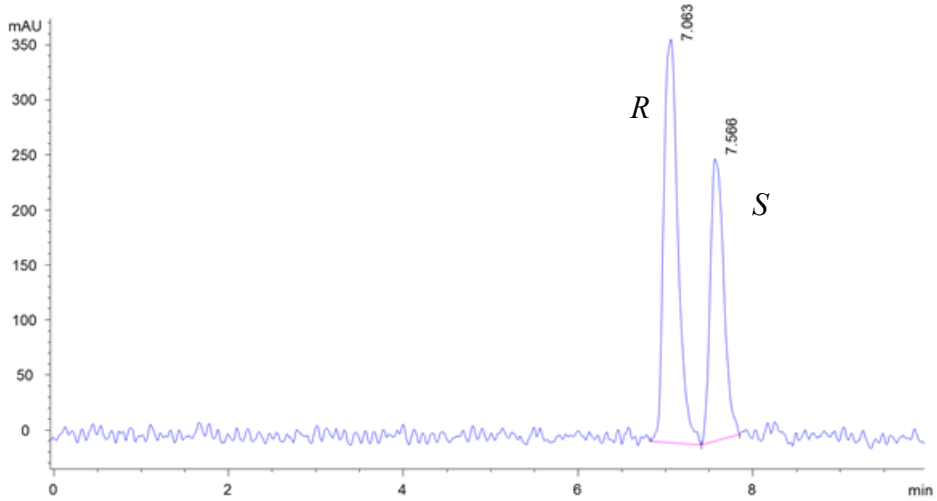
#	Time	Area	Height	Width	Area%	Symmetry
1	6.855	2752.6	294.3	0.1411	45.514	0.83
2	7.342	3295.1	301.2	0.1516	54.486	0.486

Table 4/ PhCl – Method **A** starting from (*S*)-1-phenylethanol



#	Time	Area	Height	Width	Area%	Symmetry
1	6.727	4178.2	377.7	0.1844	62.492	0.801
2	7.216	2507.8	253.8	0.1647	37.508	0.637

Table 4/ toluene – Method **A** starting from (*S*)-1-phenylethanol

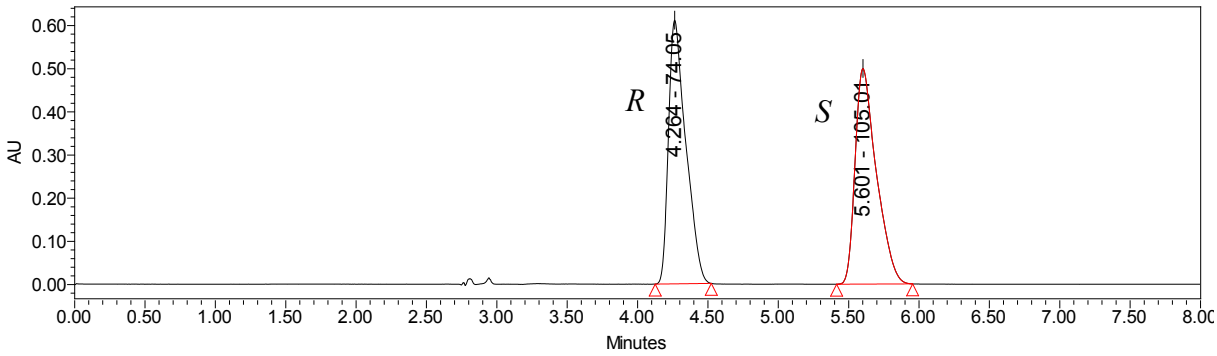


#	Time	Area	Height	Width	Area%	Symmetry
1	7.063	4172	366.9	0.1567	60.083	0.923
2	7.566	2771.7	256.7	0.164	39.917	0.563

Change of conditions of analysis:

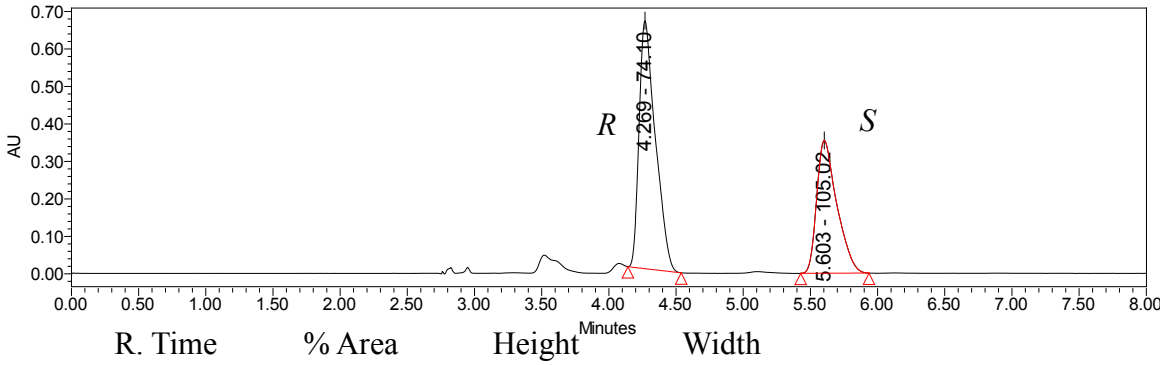
Analysis were performed on Acquity UPC^2 (Waters, USA) using Chiralpak AD-H column (250x3 mm i.d., 5 µm), supercritical CO_2/propan-2-ol 95:5, flow 1.0 mL/min, temp. 35 °C, detection at 220 nm.

(*rac*-**19**) - standard



	R.Time	% Area	Height	Width
2	5.601	50.03	499348	32.407
1	4.264	49.97	610882	23.905

Table 4/ BTF – Method **A** starting from (*S*)-1-phenylethanol



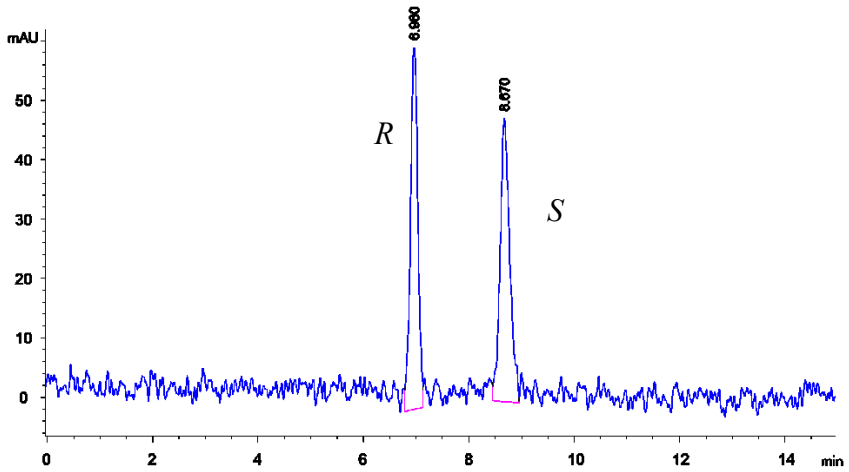
	R. Time	% Area	Height	Width
1	4.269	60.21	661508	23.805
2	5.603	39.79	354137	30.507

Other data (Method A)

1-Phenylethyl 3-(trifluoromethyl)benzoate

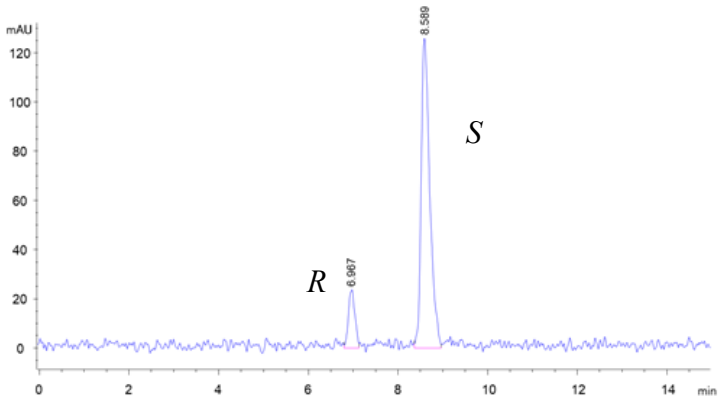
(*rac*)-ester **19**

Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/ethanol 97.5:2.5, flow 0.7 mL/min, temp. 15 °C, detection at 254 nm.



#	Time	Area	Height	Width	Area%	Symmetry
1	6.96	596.5	60.9	0.1463	49.584	0.96
2	8.67	606.5	47.7	0.1682	50.416	0.745

Method **C** – **CH_3CN** starting from (*R*)-1-phenylethanol

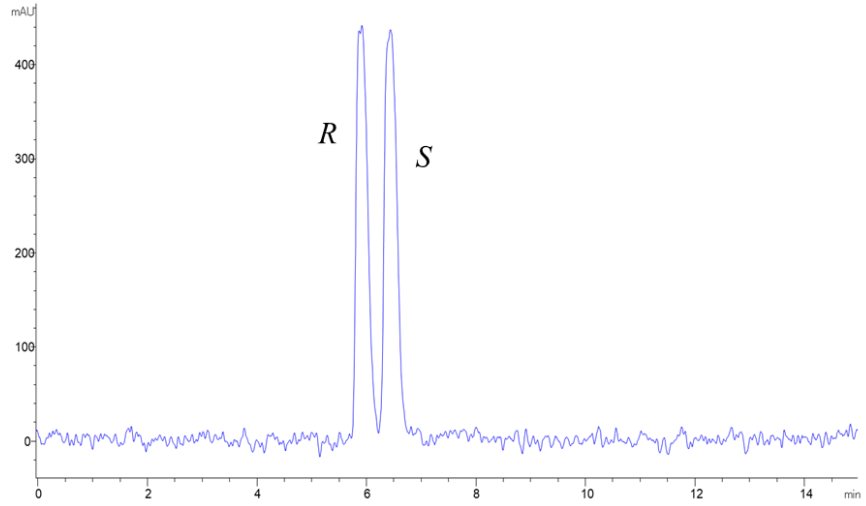


#	Time	Area	Height	Width	Area%	Symmetry
1	6.967	243.1	23.8	0.1701	12.595	1.074
2	8.589	1687.3	126.1	0.223	87.405	0.593

Change of conditions of analysis:

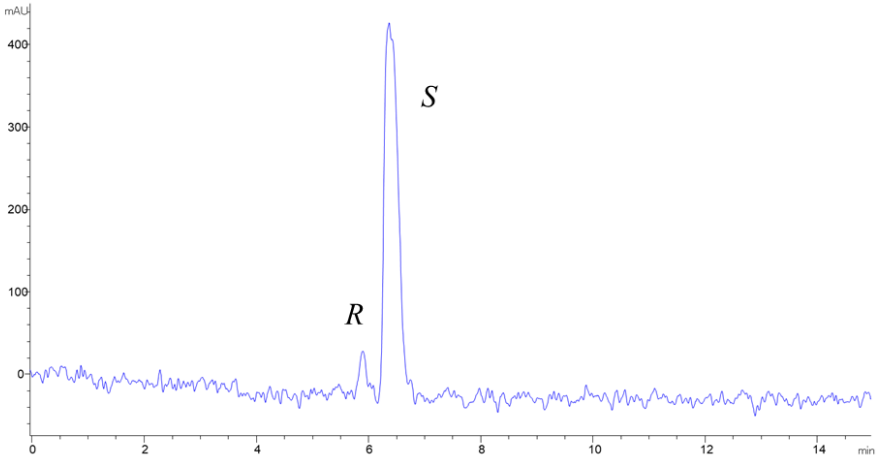
Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/ethanol 97.5:2.5, flow 0.7 mL/min, temp. RT, detection at 254 nm.

(*rac*)-ester **19**



#	Time	Area	Height	Width	Area%	Symmetry
1	5.914	6280.1	436.5	0.2398	48.392	0.913
2	6.433	6697.4	433.5	0.2575	51.608	0.862

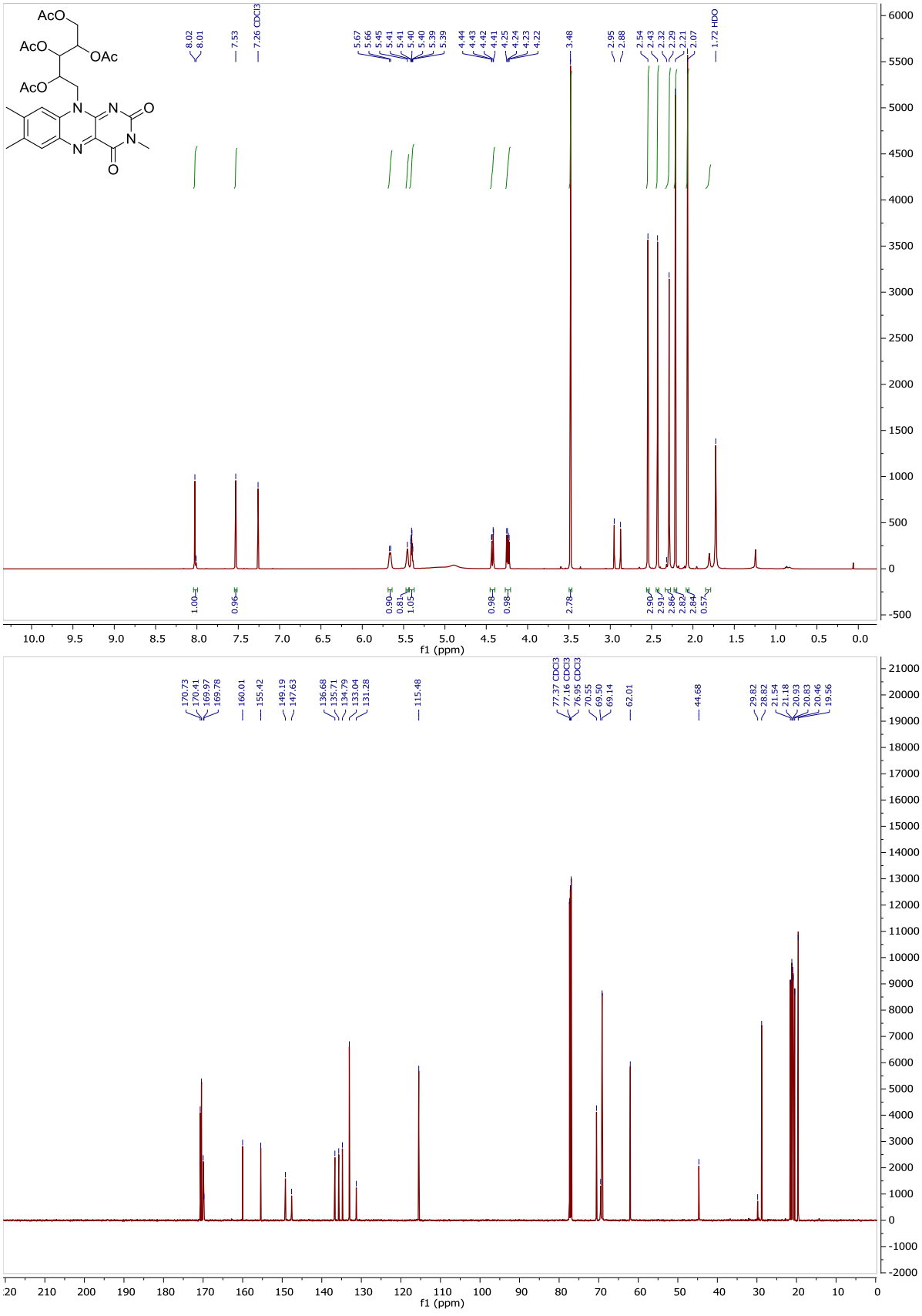
Method **C** - **BTF** starting from (*R*)-1-phenylethanol



#	Time	Area	Height	Width	Area%	Symmetry
1	5.903	598.3	57.2	0.1743	7.283	0.878
2	6.367	7616.5	455.6	0.2786	92.717	0.548

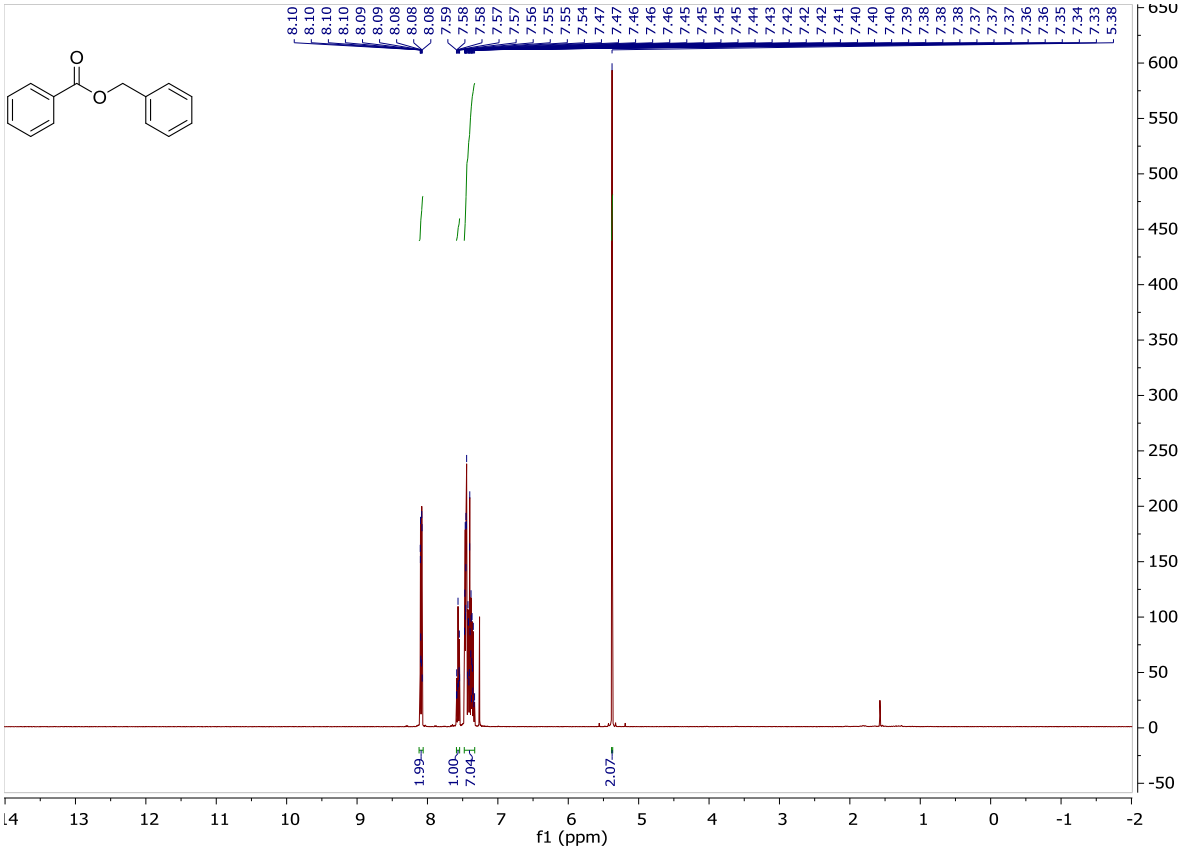
S6 ^{1}H and ^{13}C NMR spectra of 1

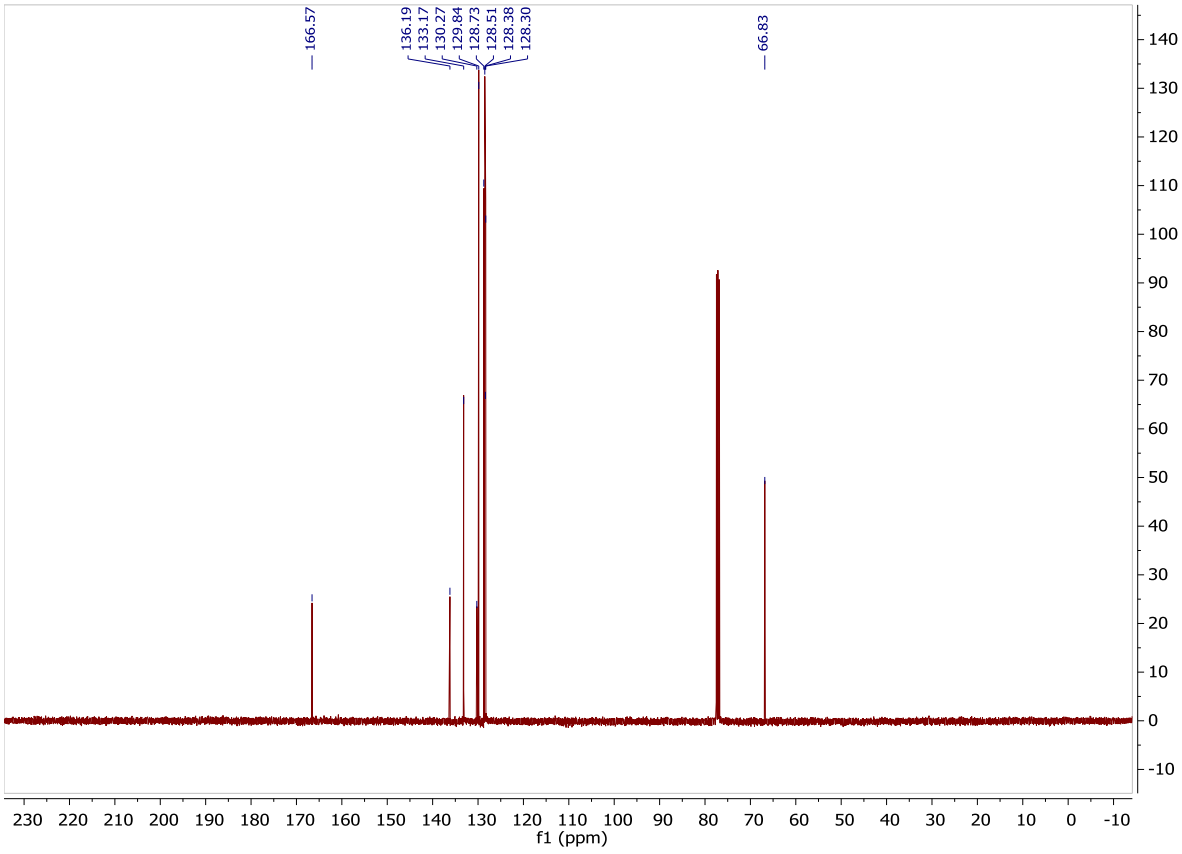
3-Methyl-2',3',4',5'-tetraacetylriboflavin (1)



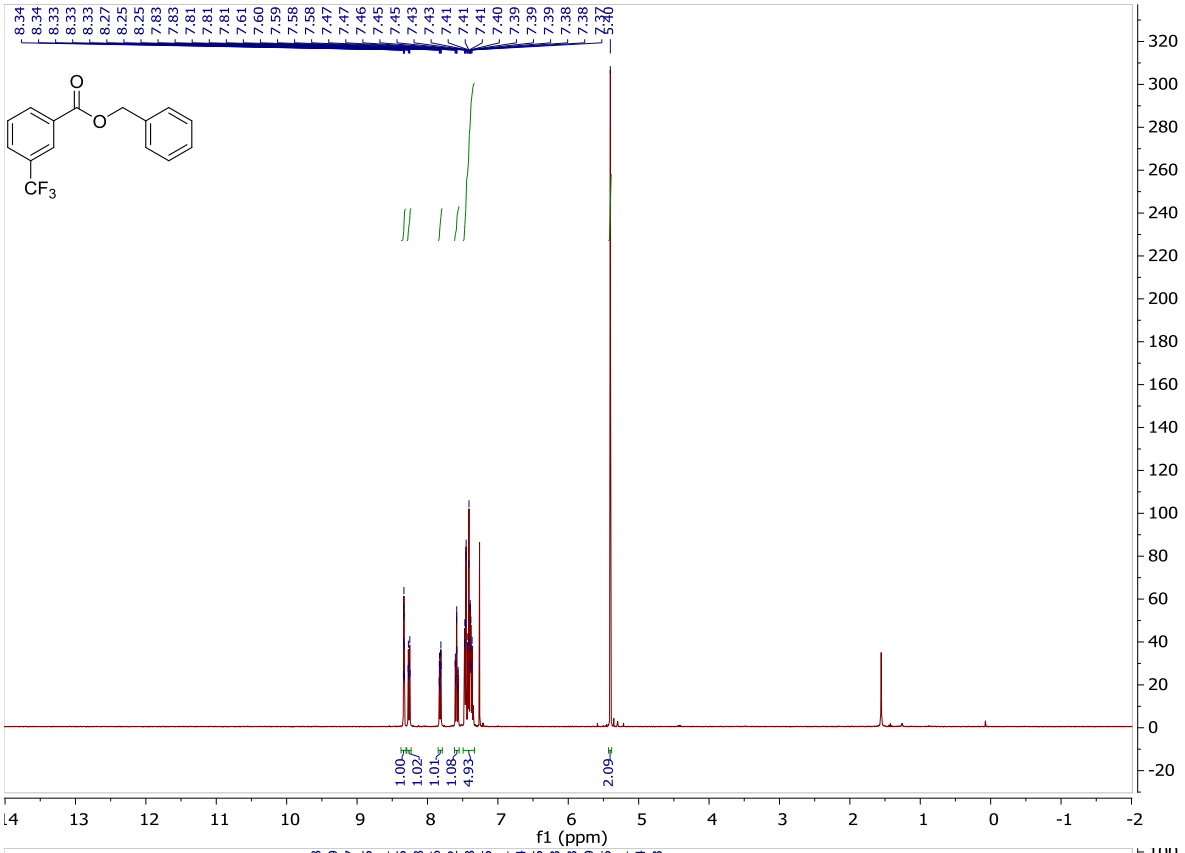
S7 ^{1}H, ^{13}C and ^{19}F NMR spectra of esters

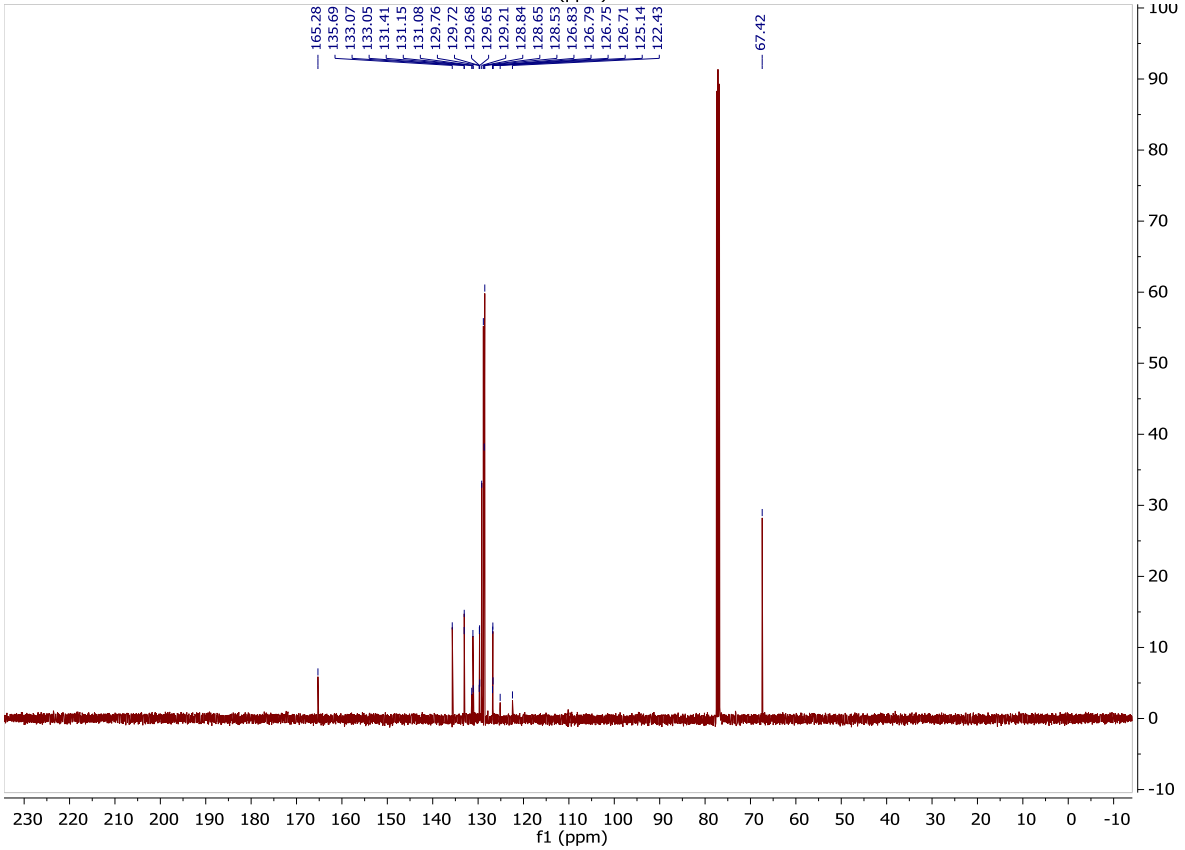
Benzyl benzoate (2)

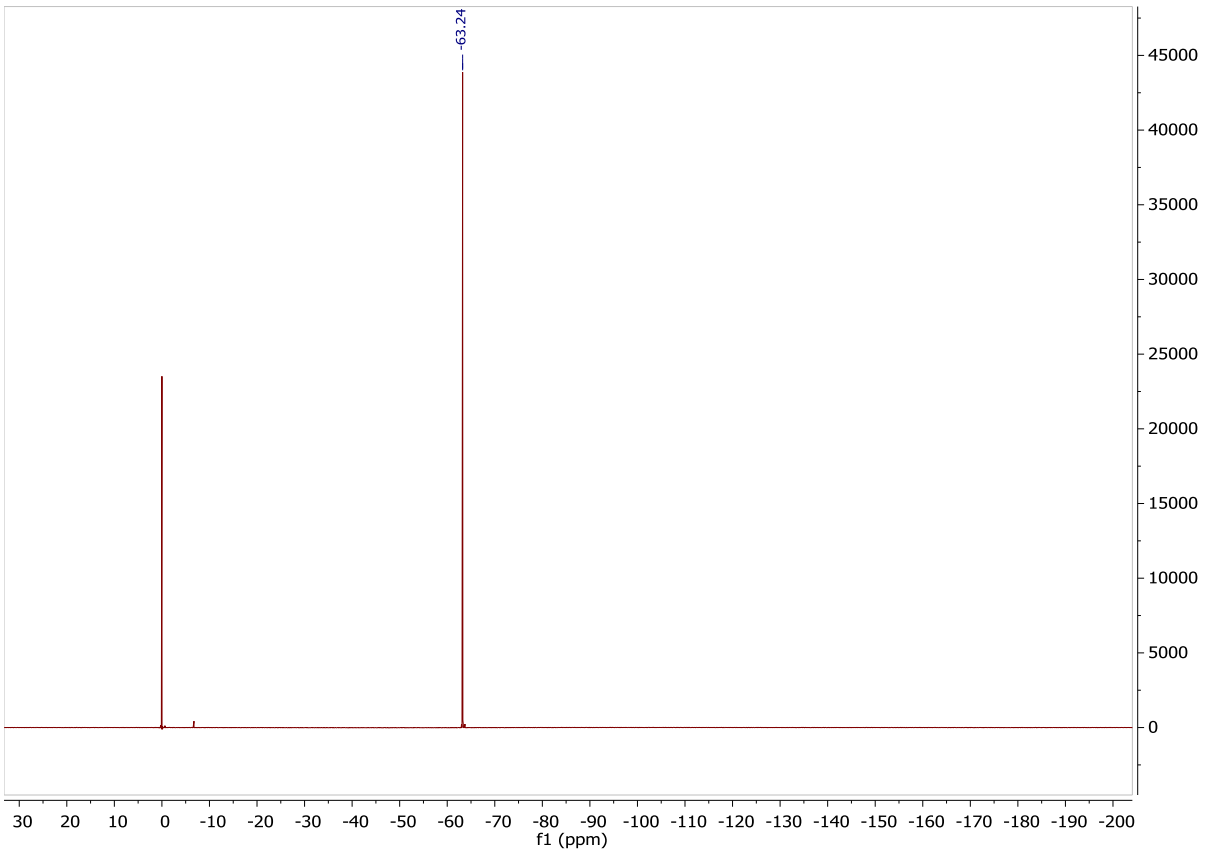




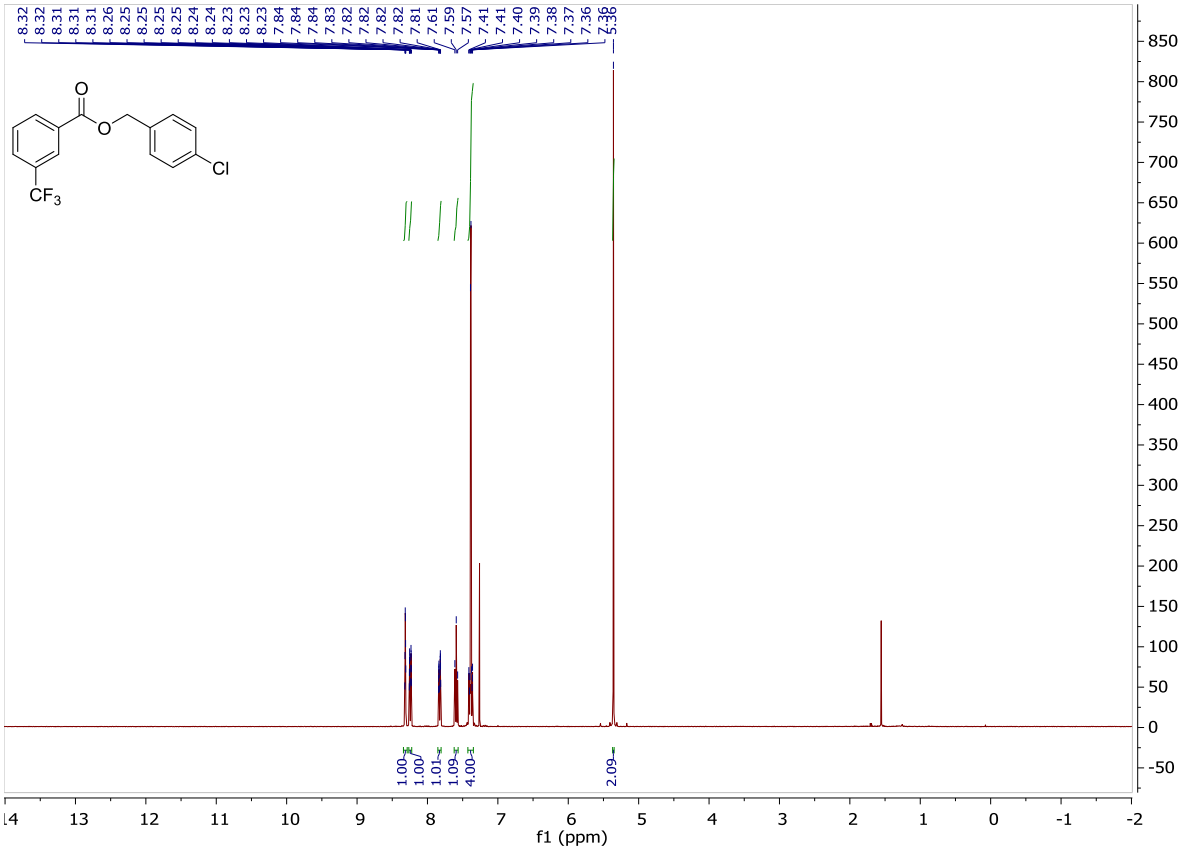
Benzyl 3-(trifluoromethyl)benzoate (3)

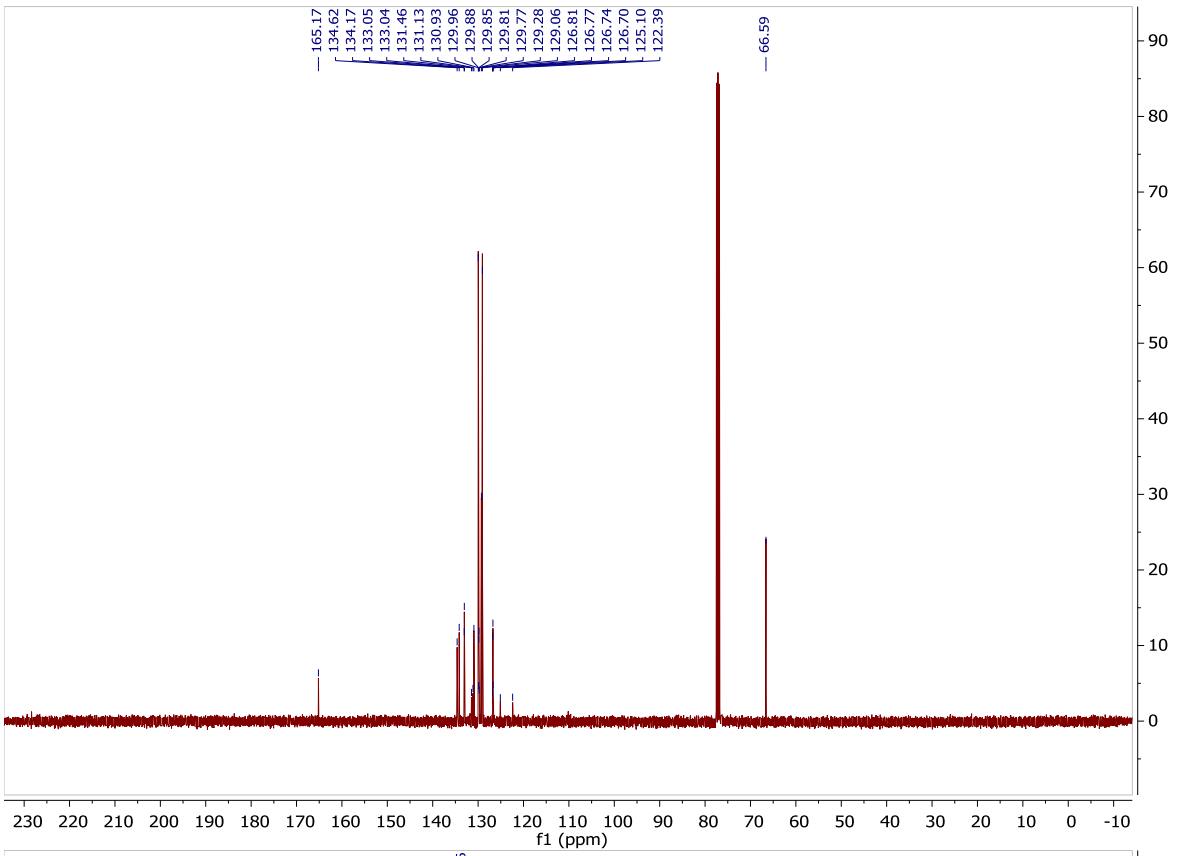


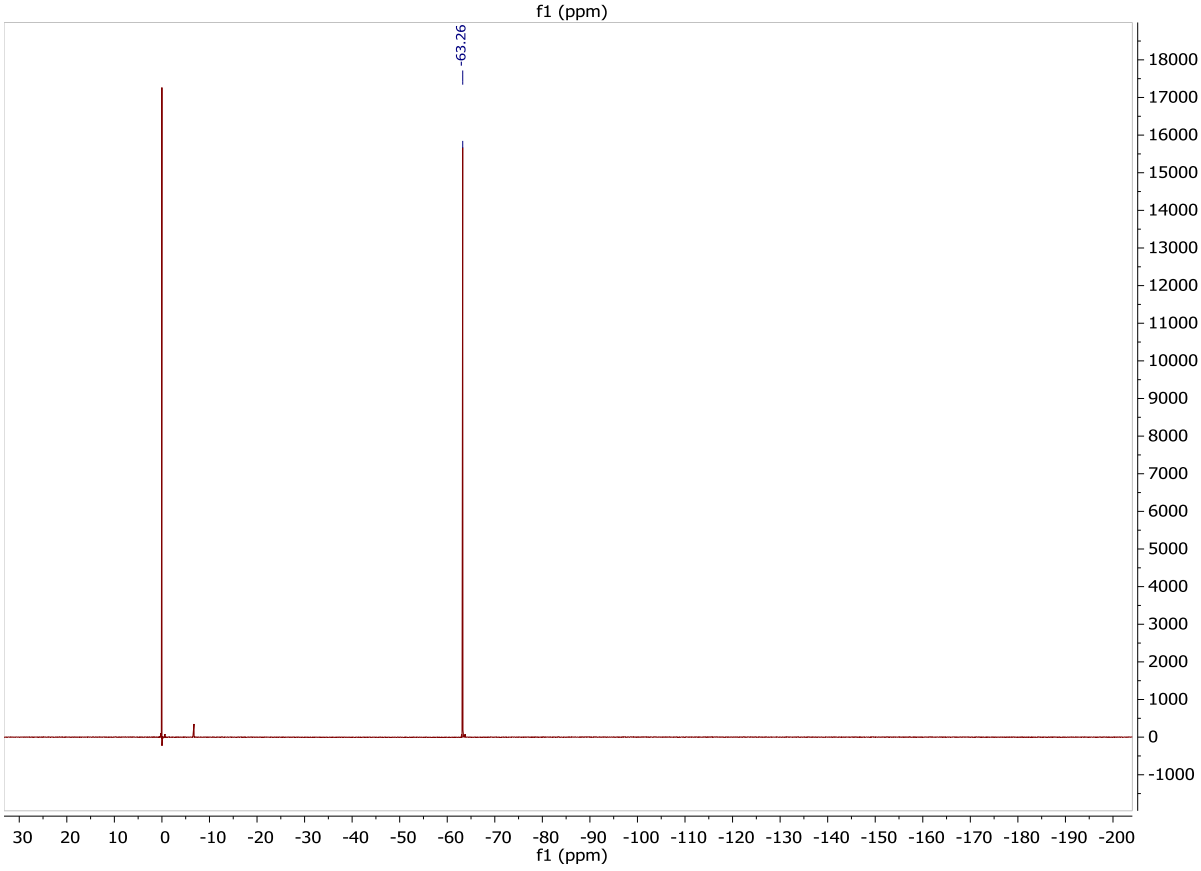




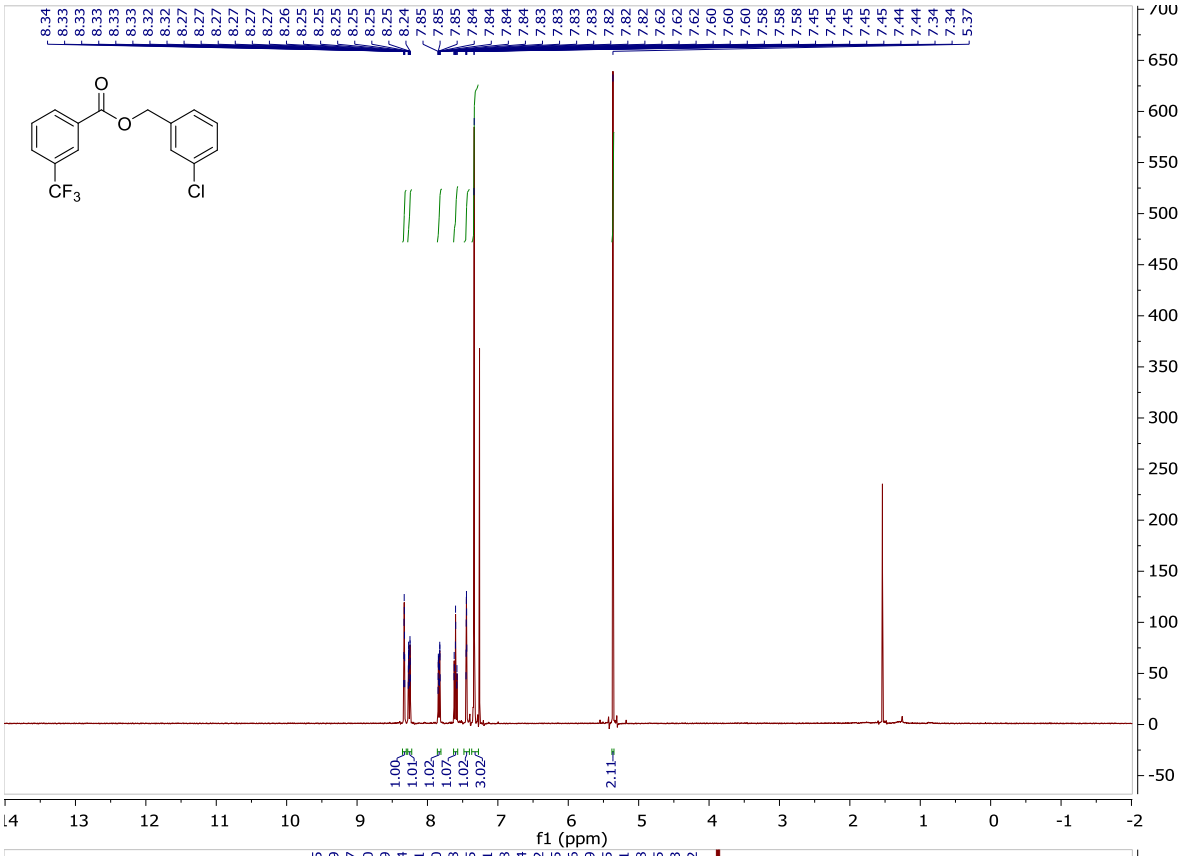
4-Chlorobenzyl 3-(trifluoromethyl)benzoate (4)

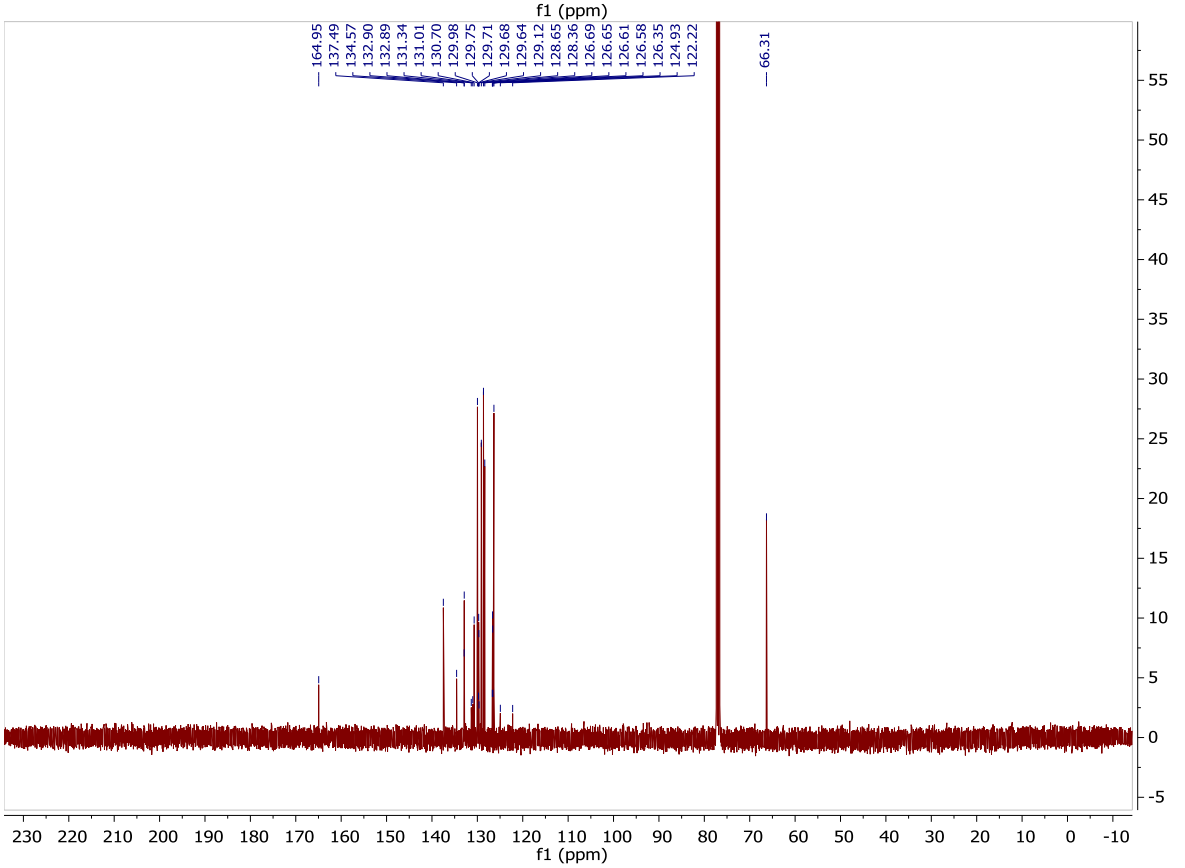


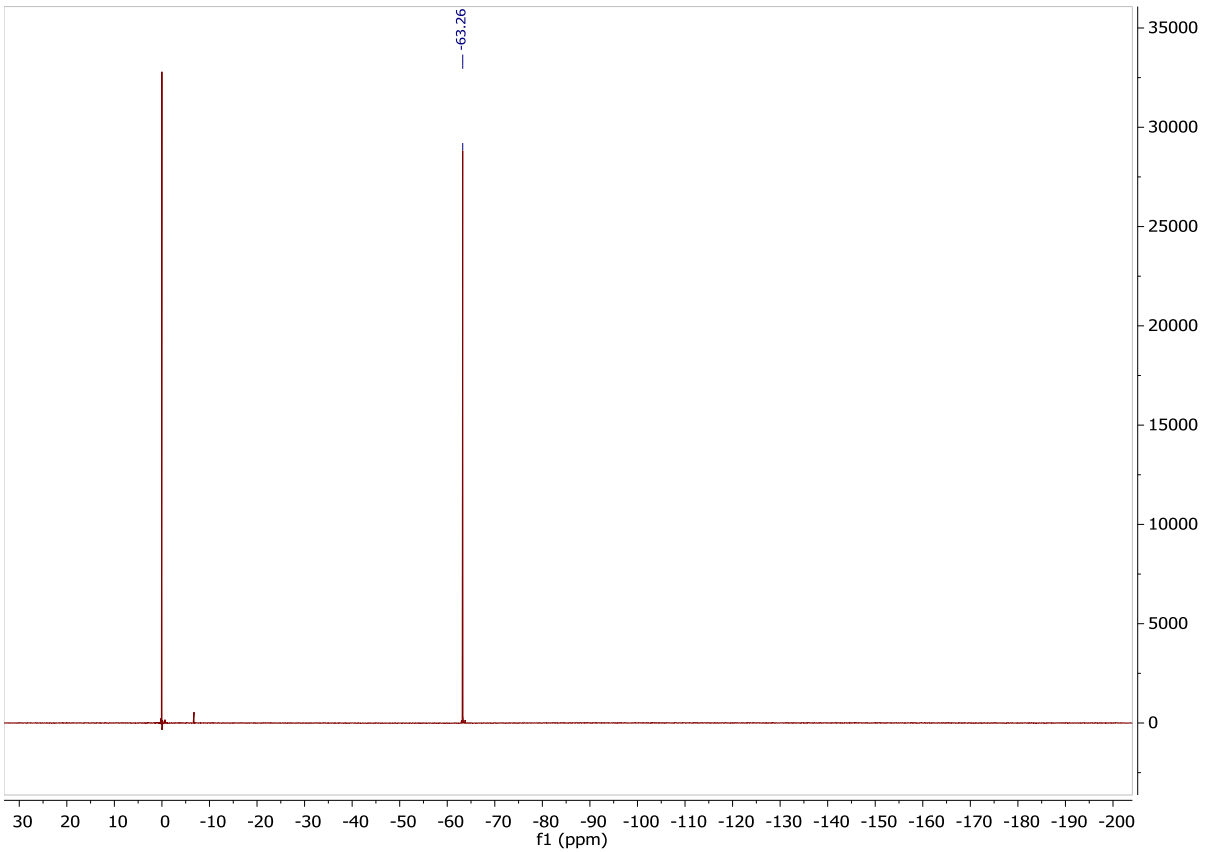

165.17
134.62
134.17
133.05
133.04
131.46
131.13
130.93
129.96
129.88
129.85
129.81
129.77
129.28
129.06
126.81
126.77
126.74
126.70
125.10
122.39
66.59
f1 (ppm)


-63.26
f1 (ppm)

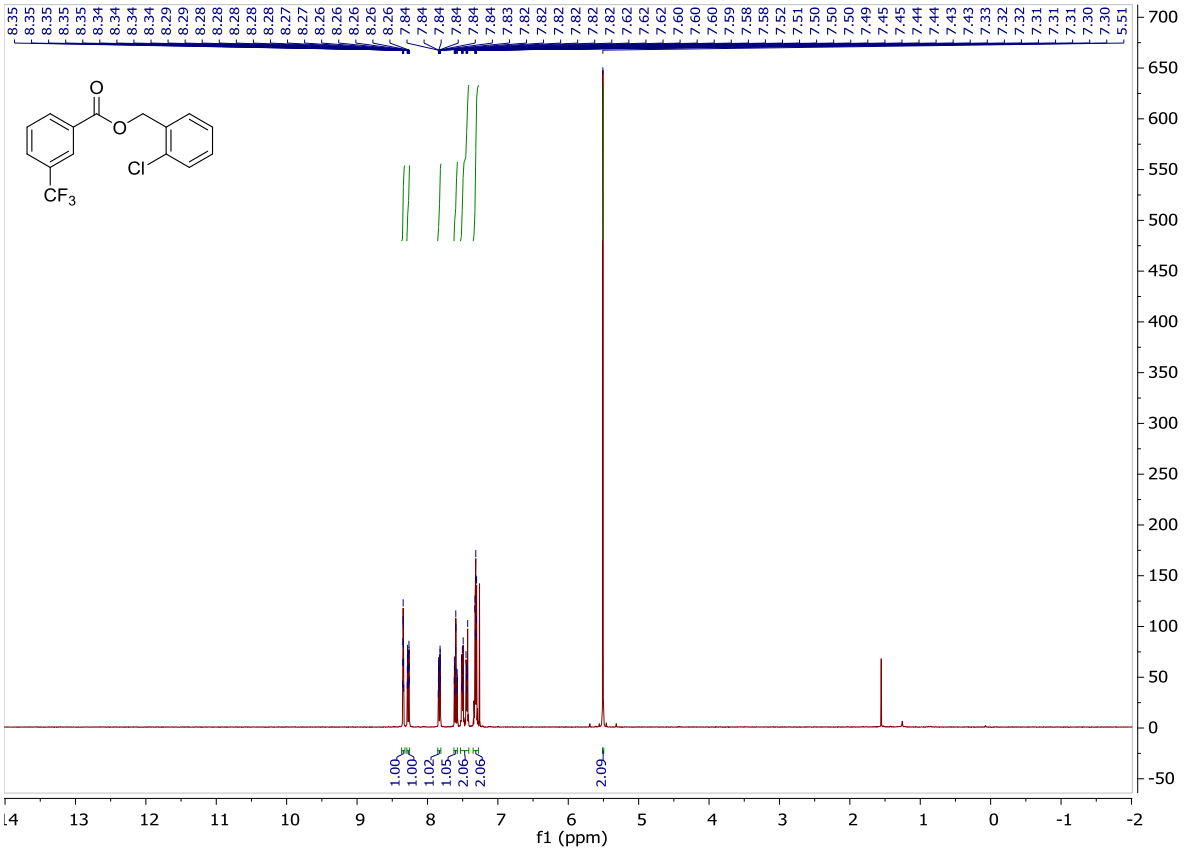
3-chlorobenzyl 3-(trifluoromethyl)benzoate (5)

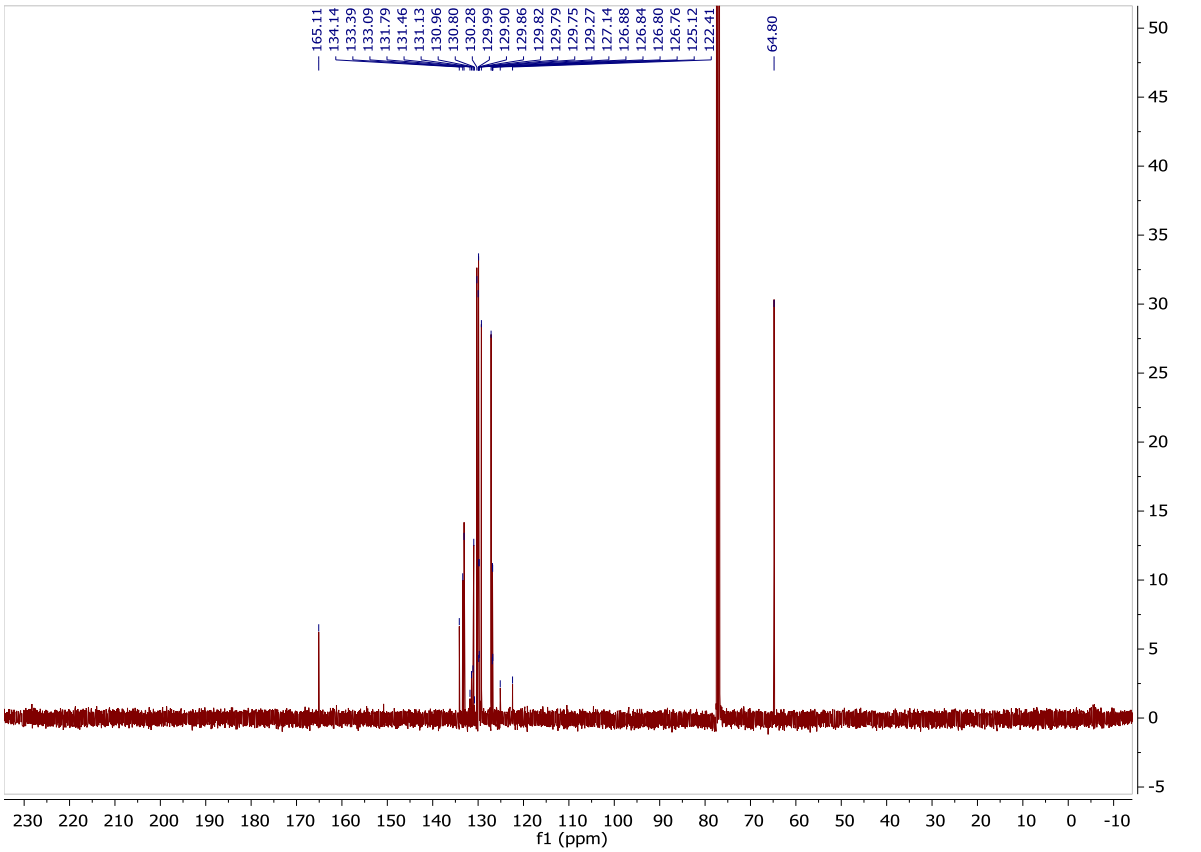


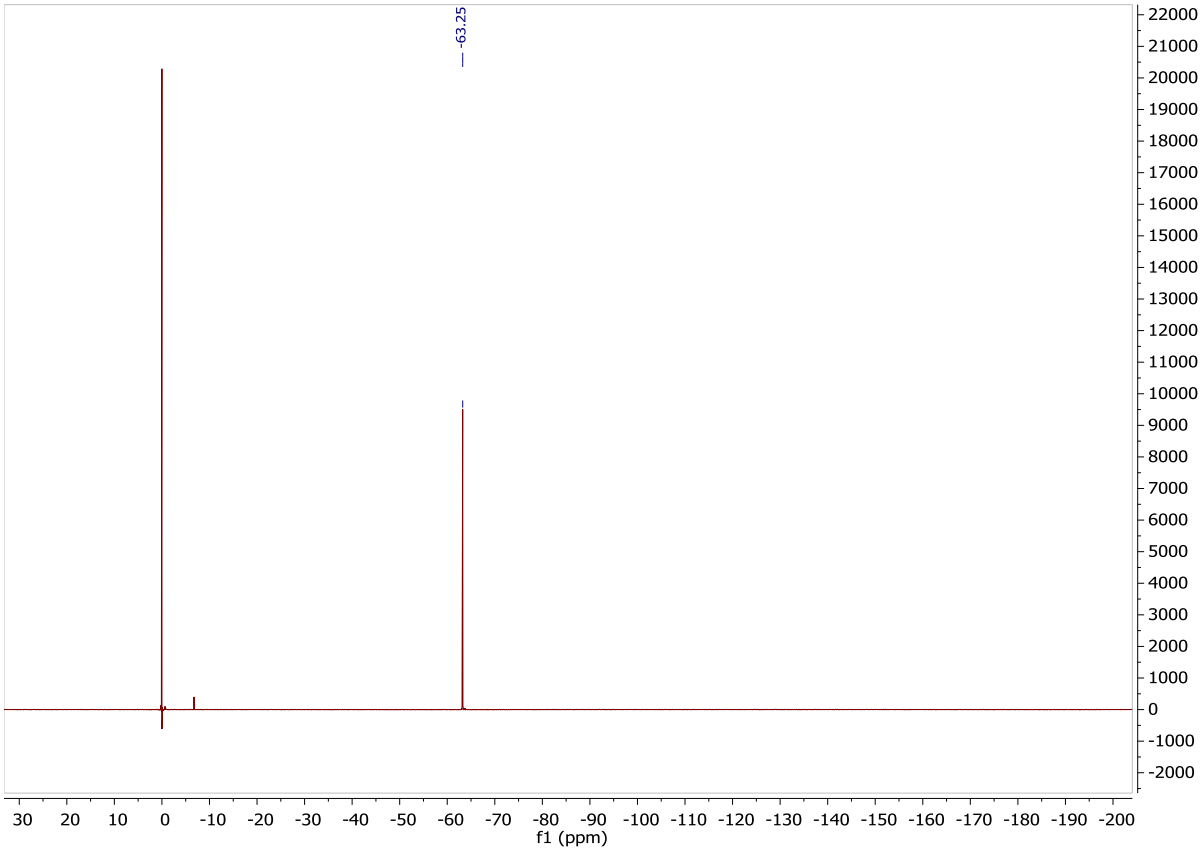




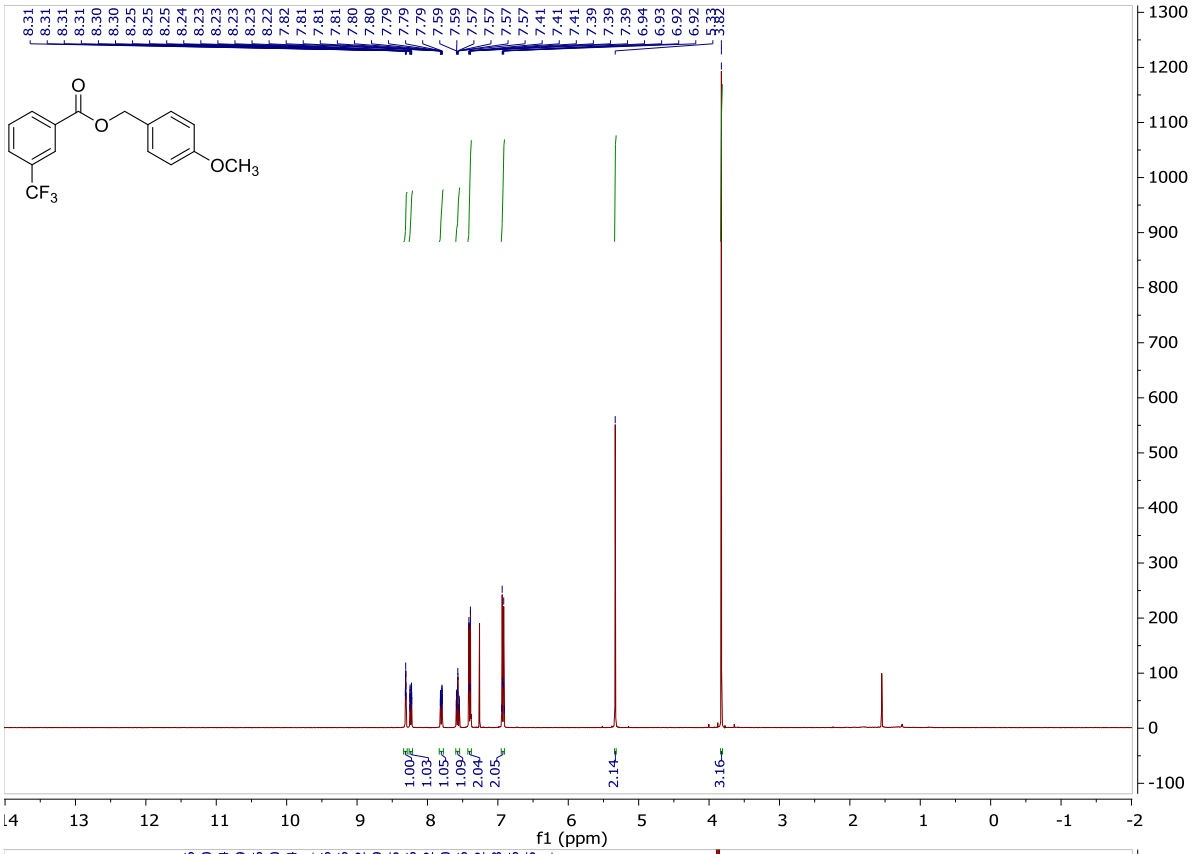
2-chlorobenzyl 3-(trifluoromethyl)benzoate (6)

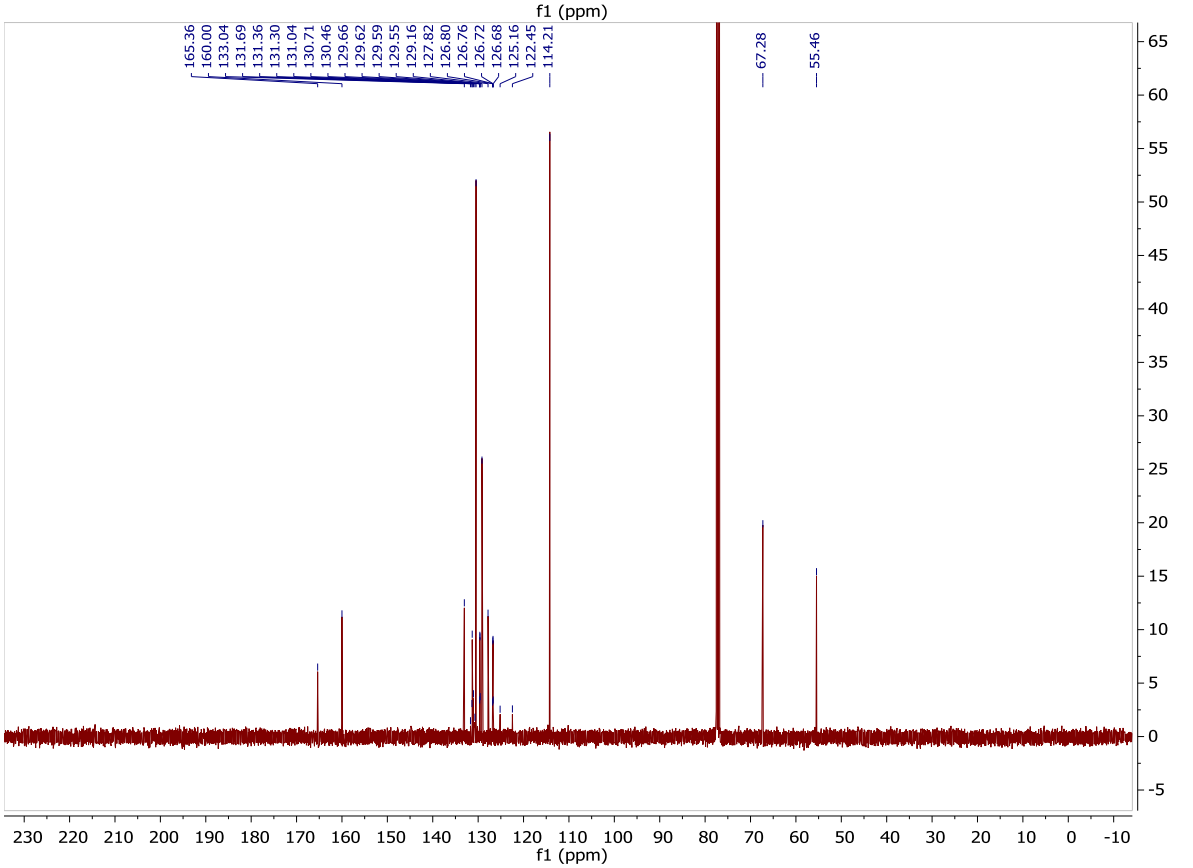


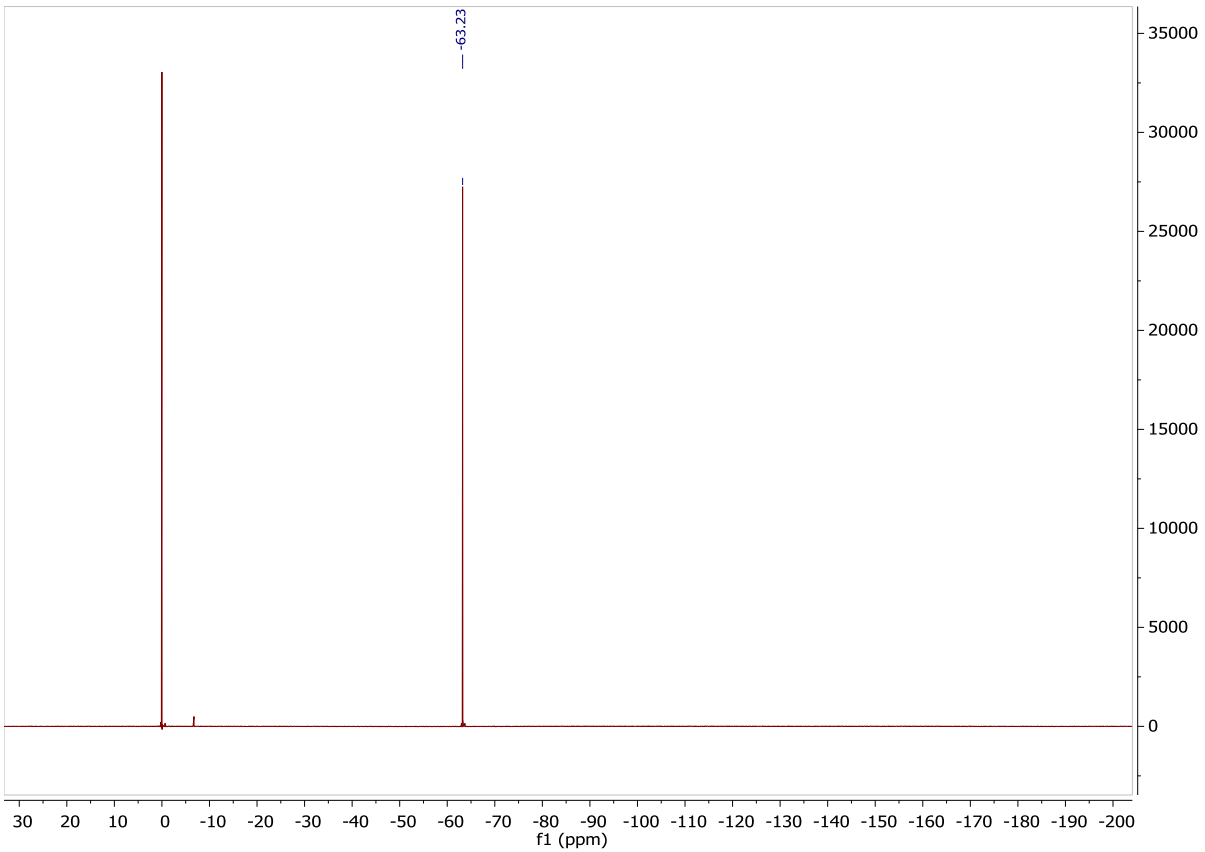

165.11
134.14
133.39
133.09
131.79
131.46
131.13
130.96
130.80
130.28
129.99
129.90
129.86
129.82
129.79
129.75
129.27
127.14
126.88
126.84
126.80
126.76
125.12
122.41
64.80
f1 (ppm)


-63.25
f1 (ppm)

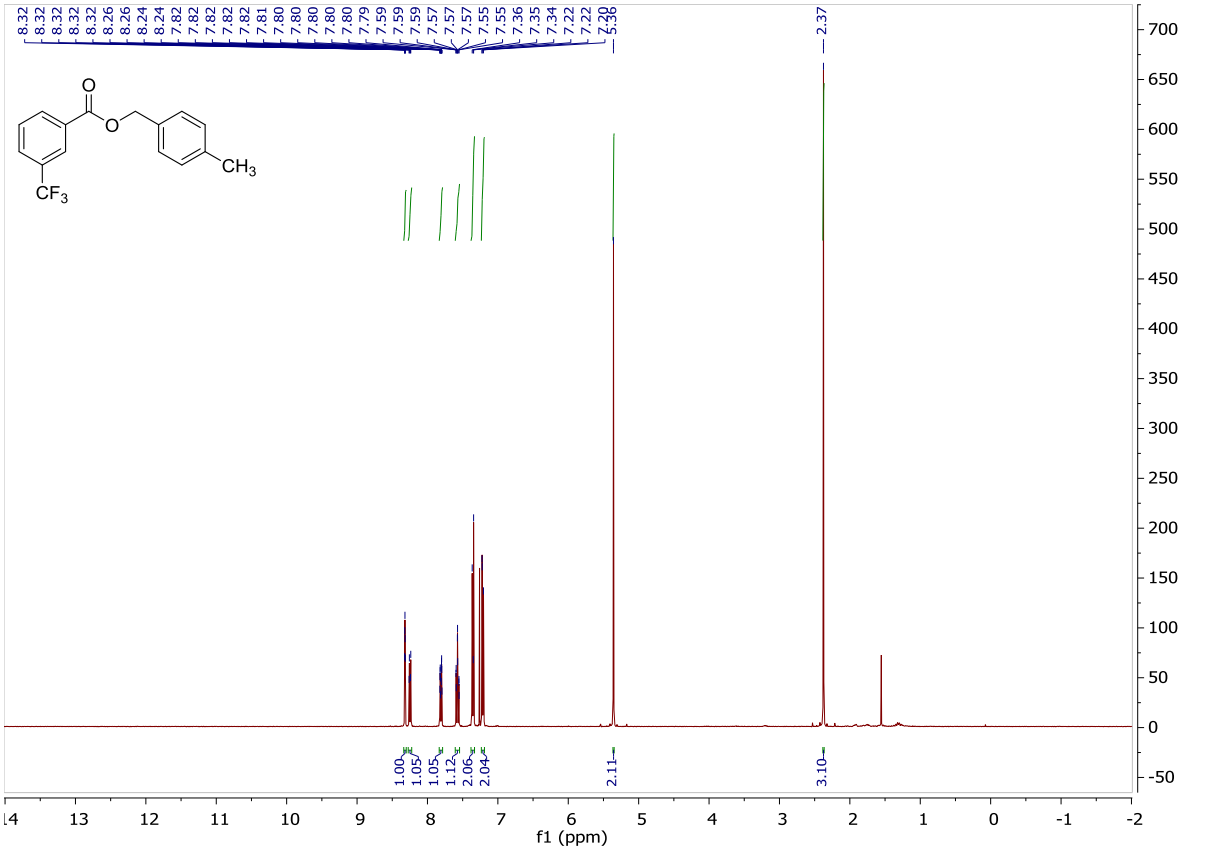
4-(Methoxy)benzyl 3-(trifluoromethyl)benzoate (7)

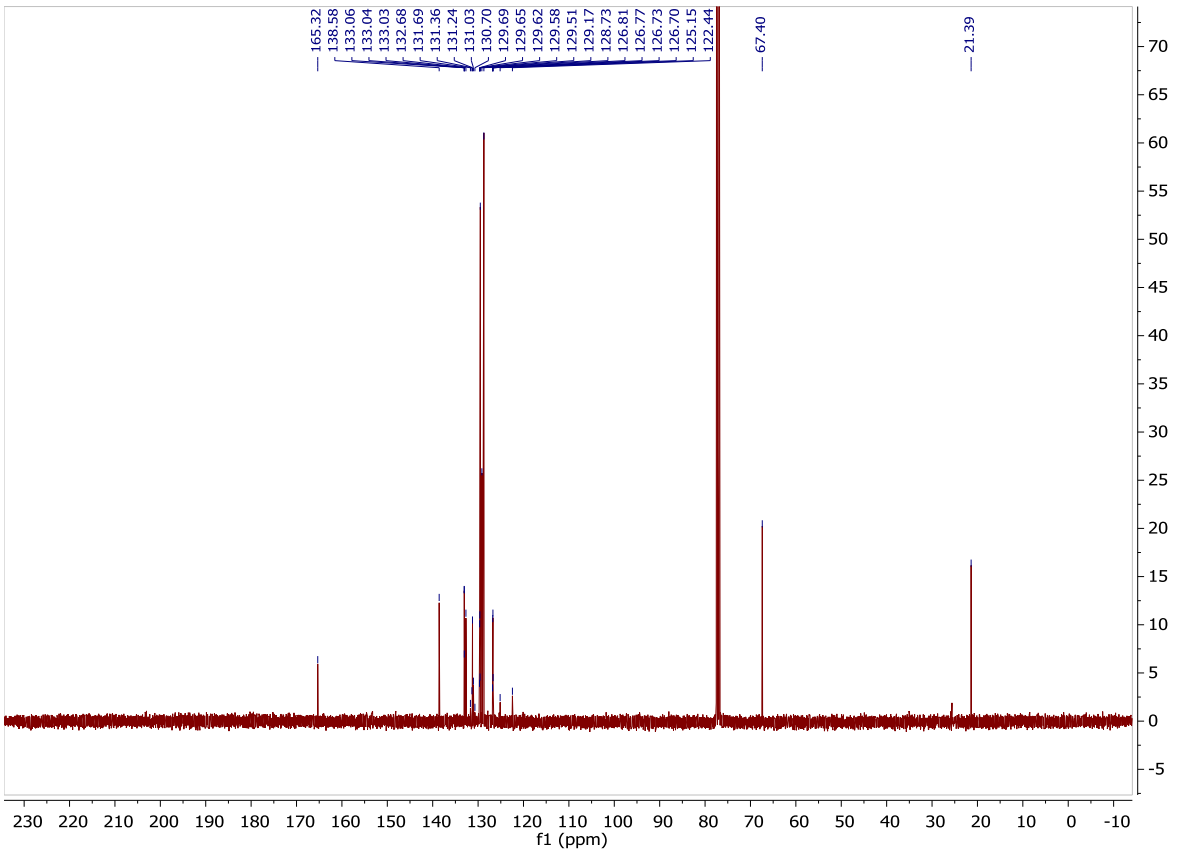


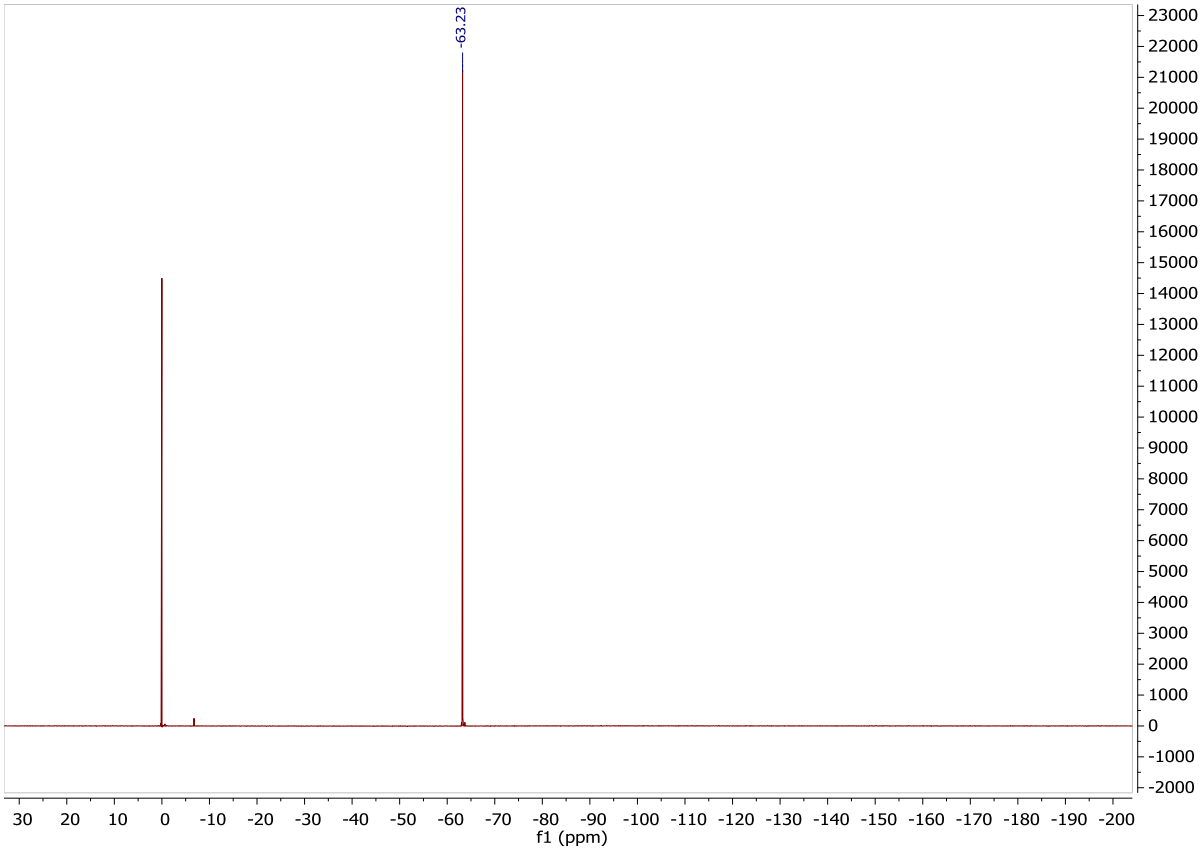




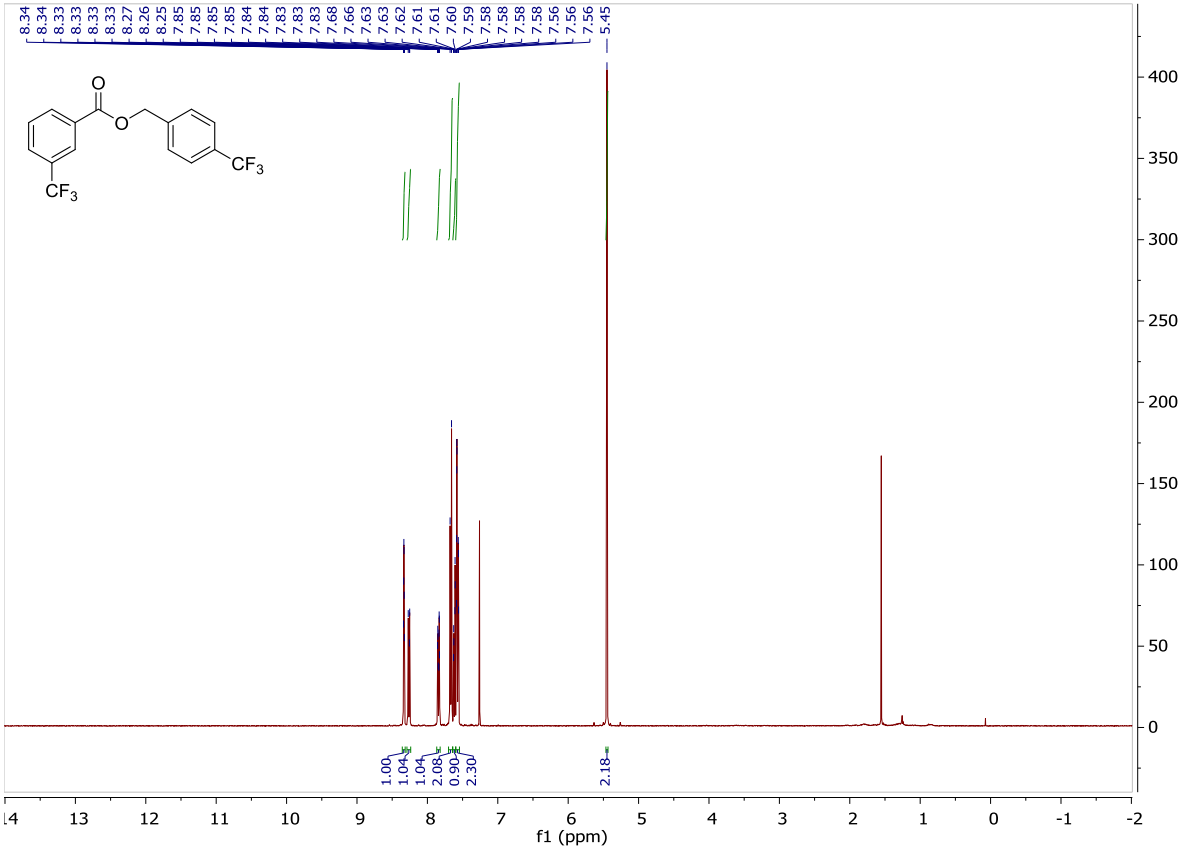
4-Methylbenzyl 3-(trifluoromethyl)benzoate (8)

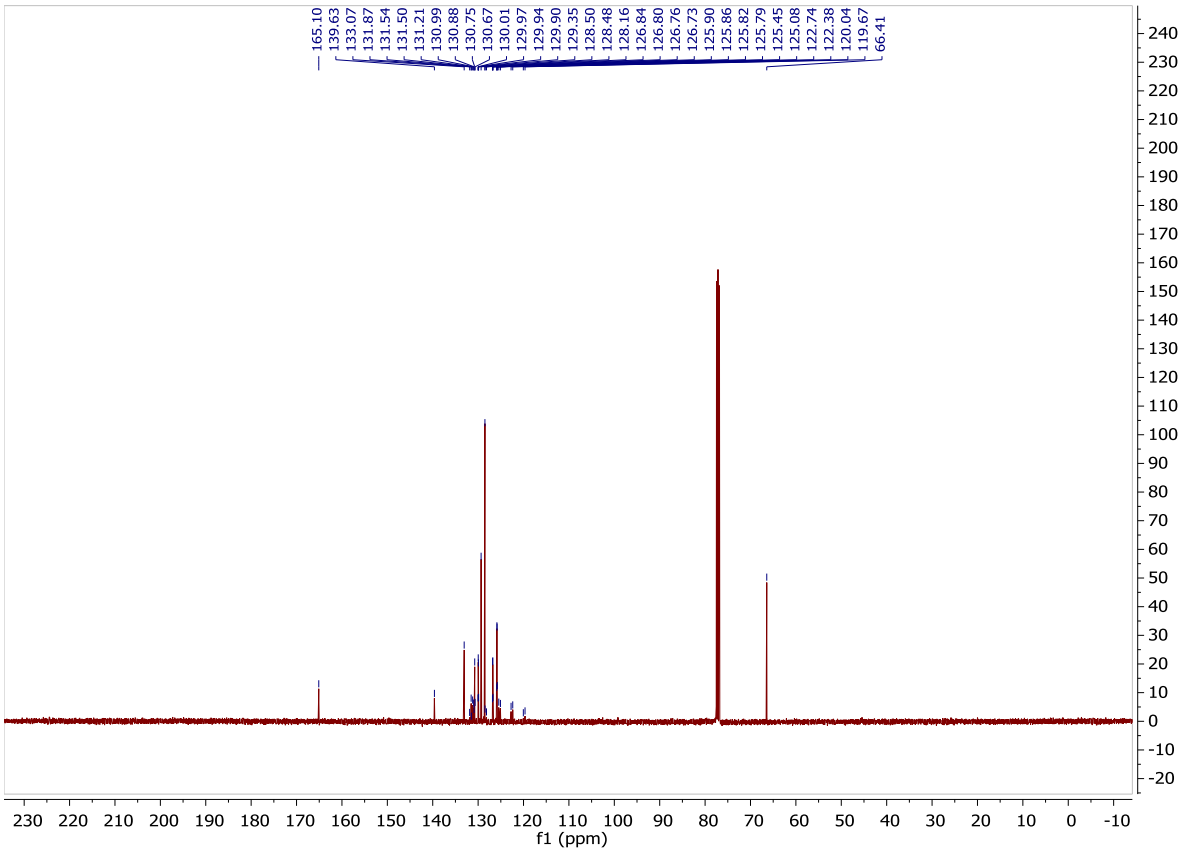


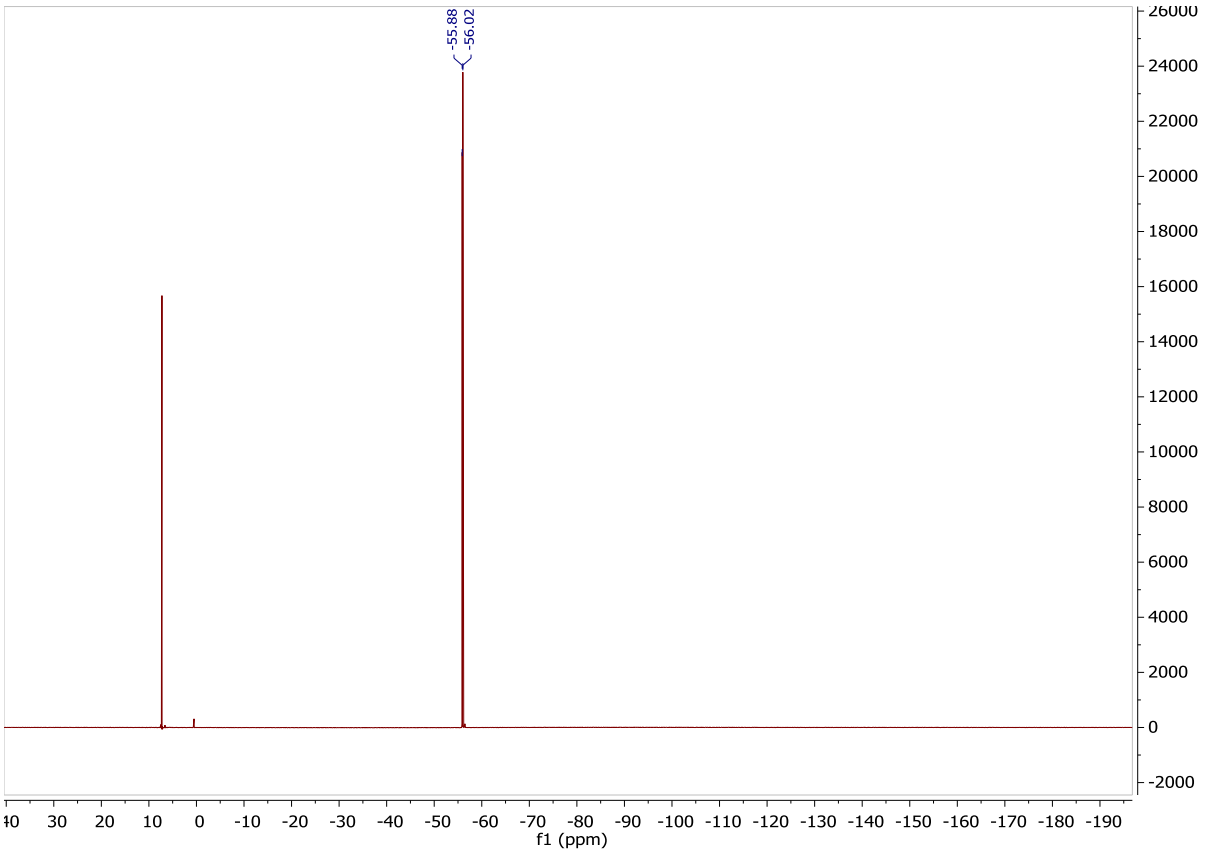

165.32
138.58
133.06
133.04
133.03
132.68
131.69
131.36
131.24
131.03
130.70
129.69
129.65
129.62
129.58
129.51
129.17
128.73
126.81
126.77
126.73
126.70
125.15
122.44
67.40
21.39
f1 (ppm)


-63.23
f1 (ppm)

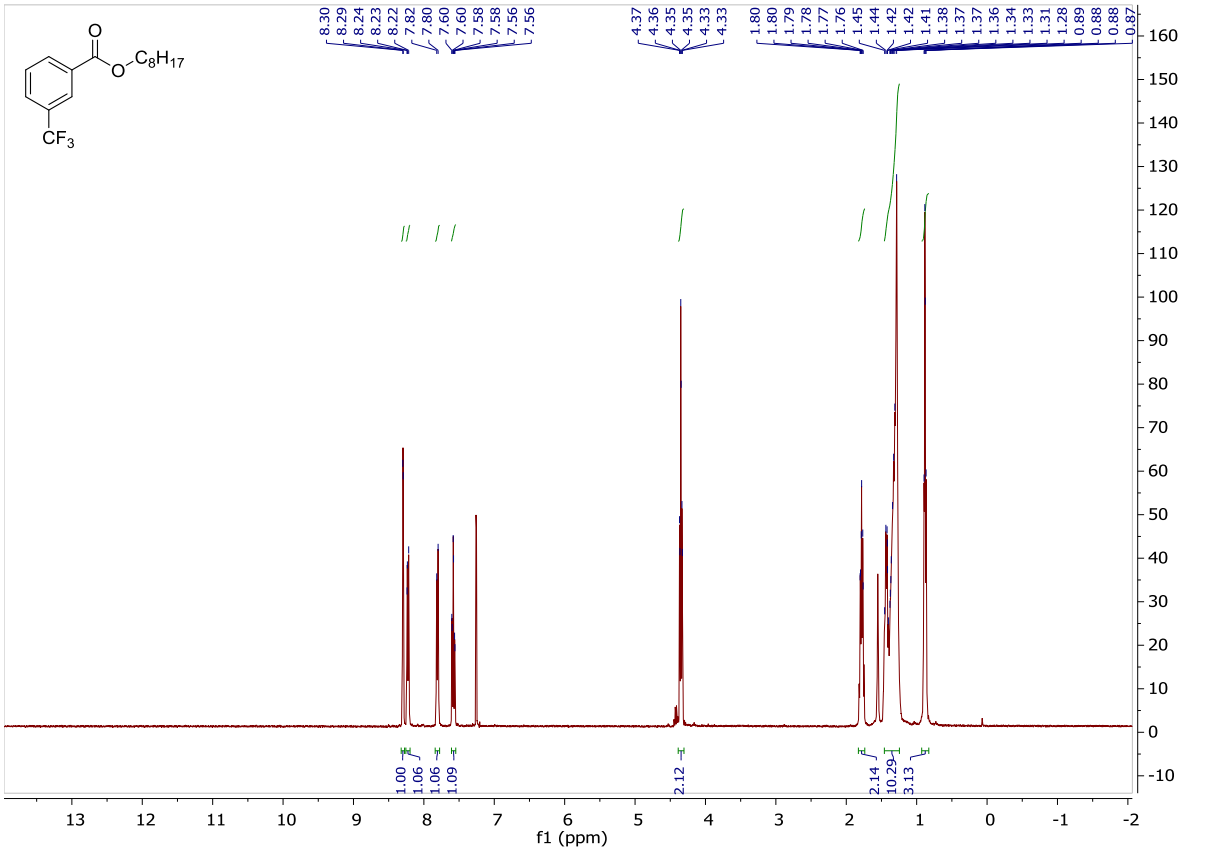
4-(Trifluoromethyl)benzyl 3-(trifluoromethyl)benzoate (9)

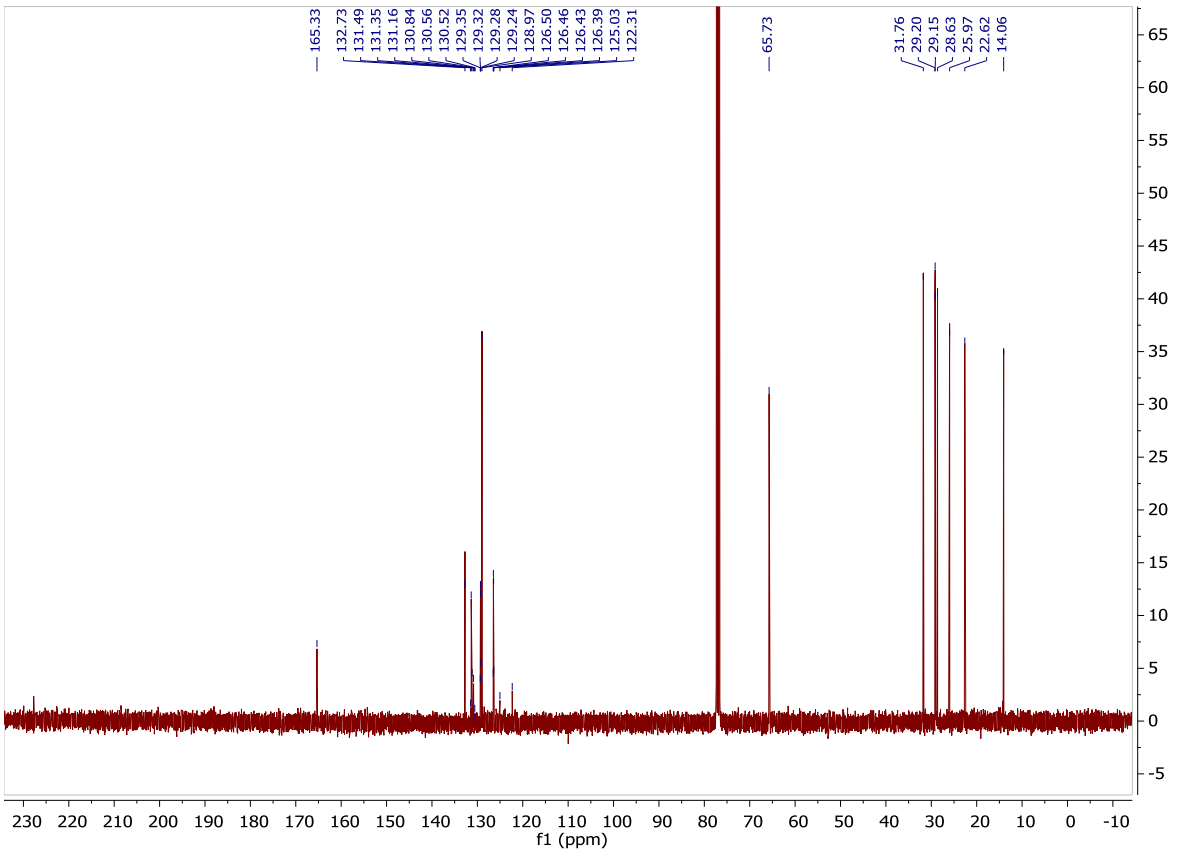


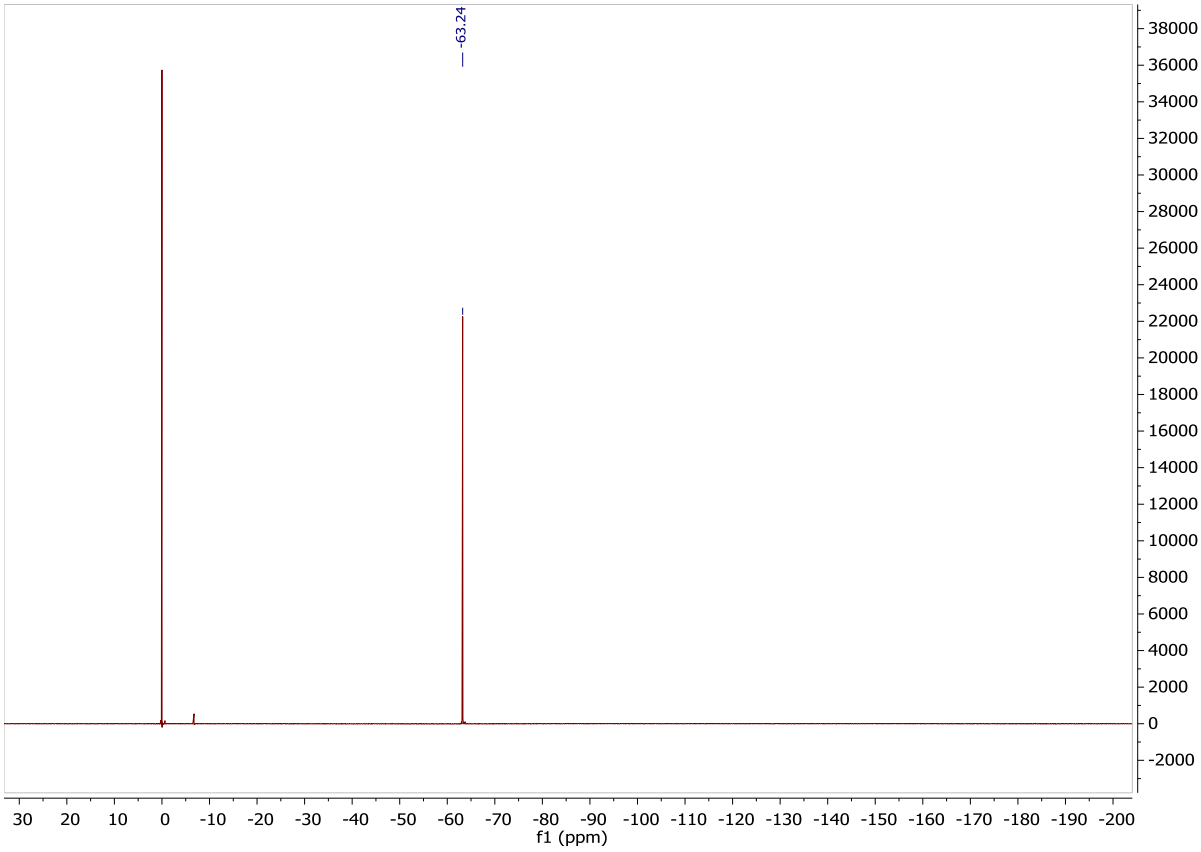




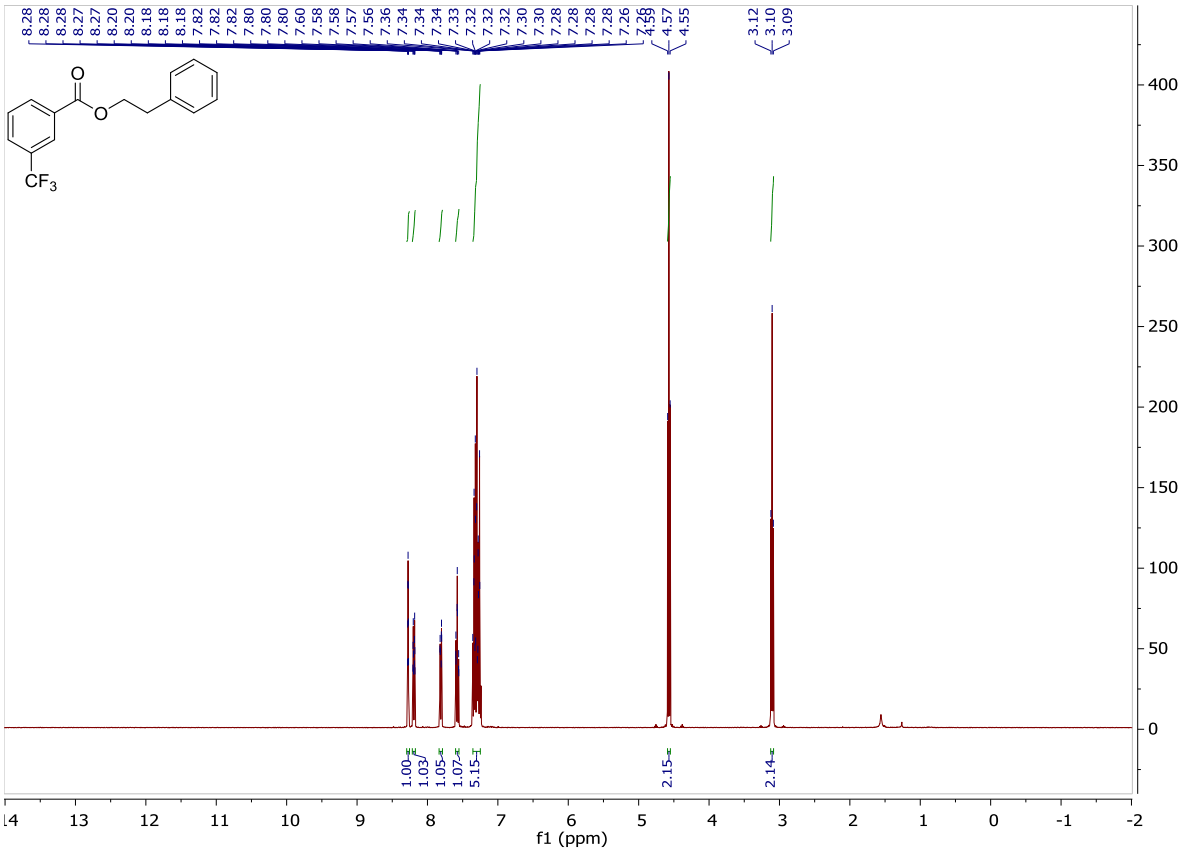
Octyl 3-(trifluoromethyl)benzoate (10)

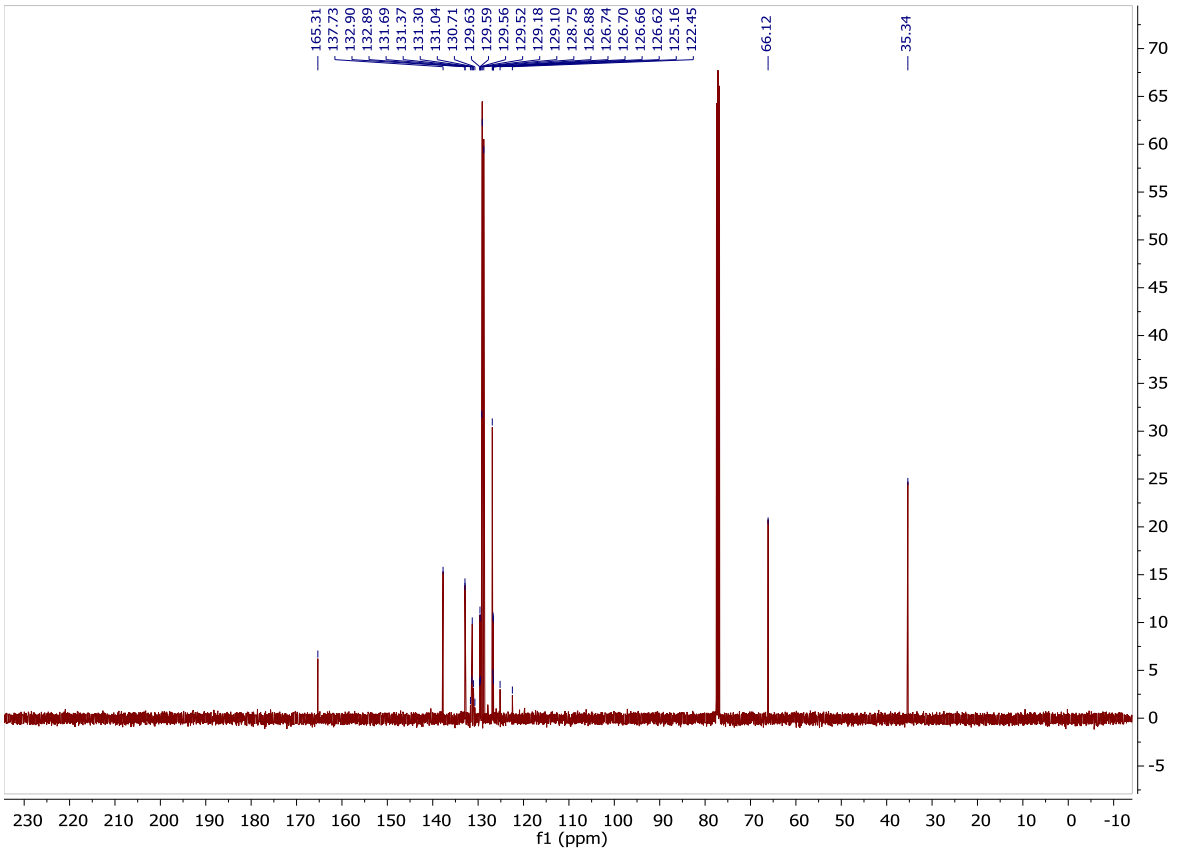


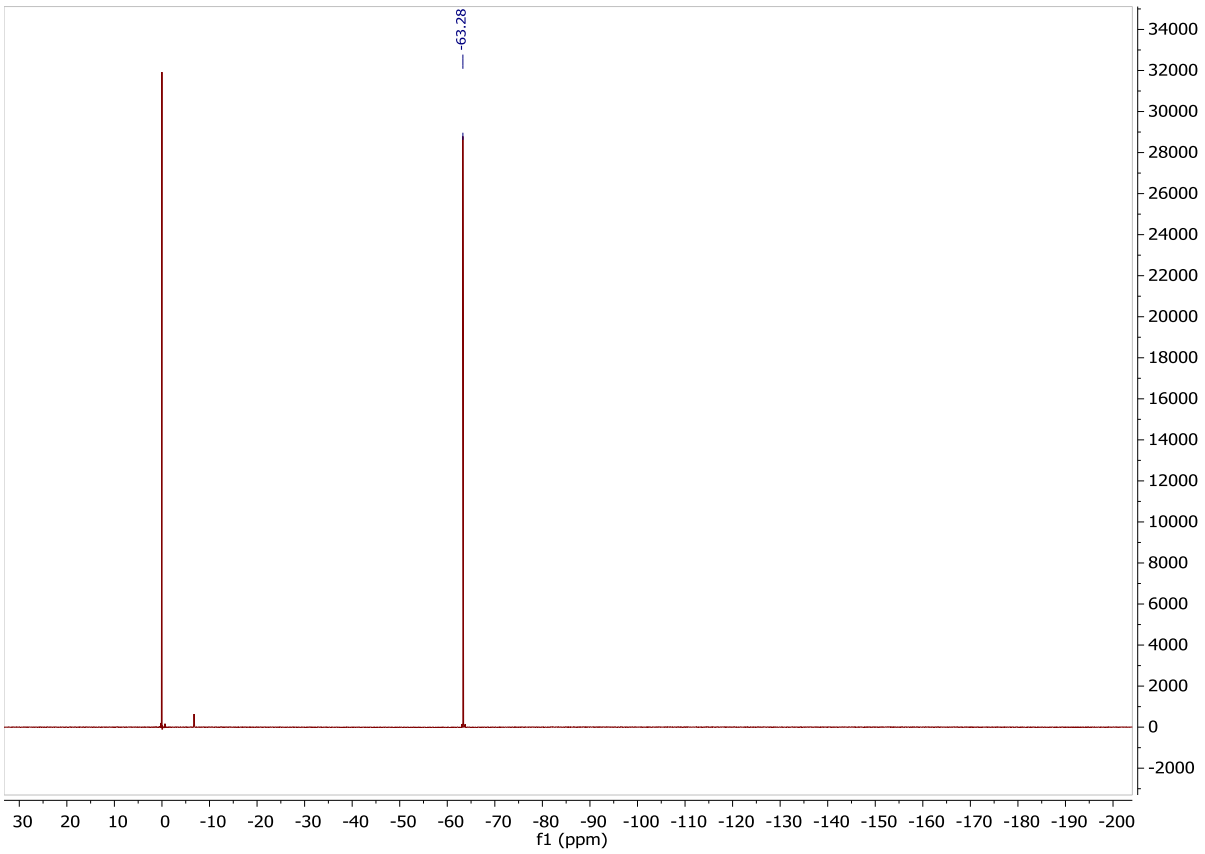

165.33
132.73
131.49
131.35
131.16
130.84
130.56
130.52
129.35
129.32
129.28
129.24
128.97
126.50
126.46
126.43
126.39
125.03
122.31
65.73
31.76
29.20
29.15
28.63
25.97
22.62
14.06
f1 (ppm)


-63.24
f1 (ppm)

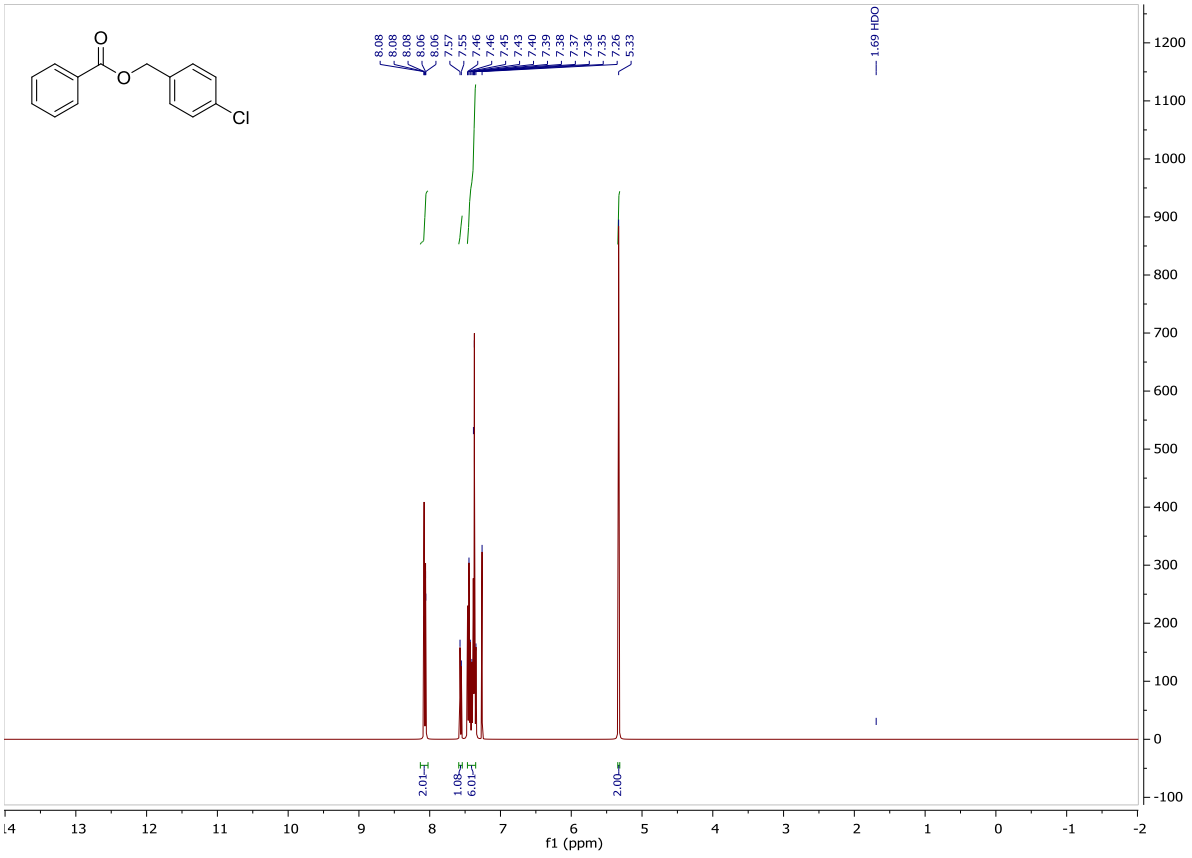
Phenethyl 3-(trifluoromethyl)benzoate (11)

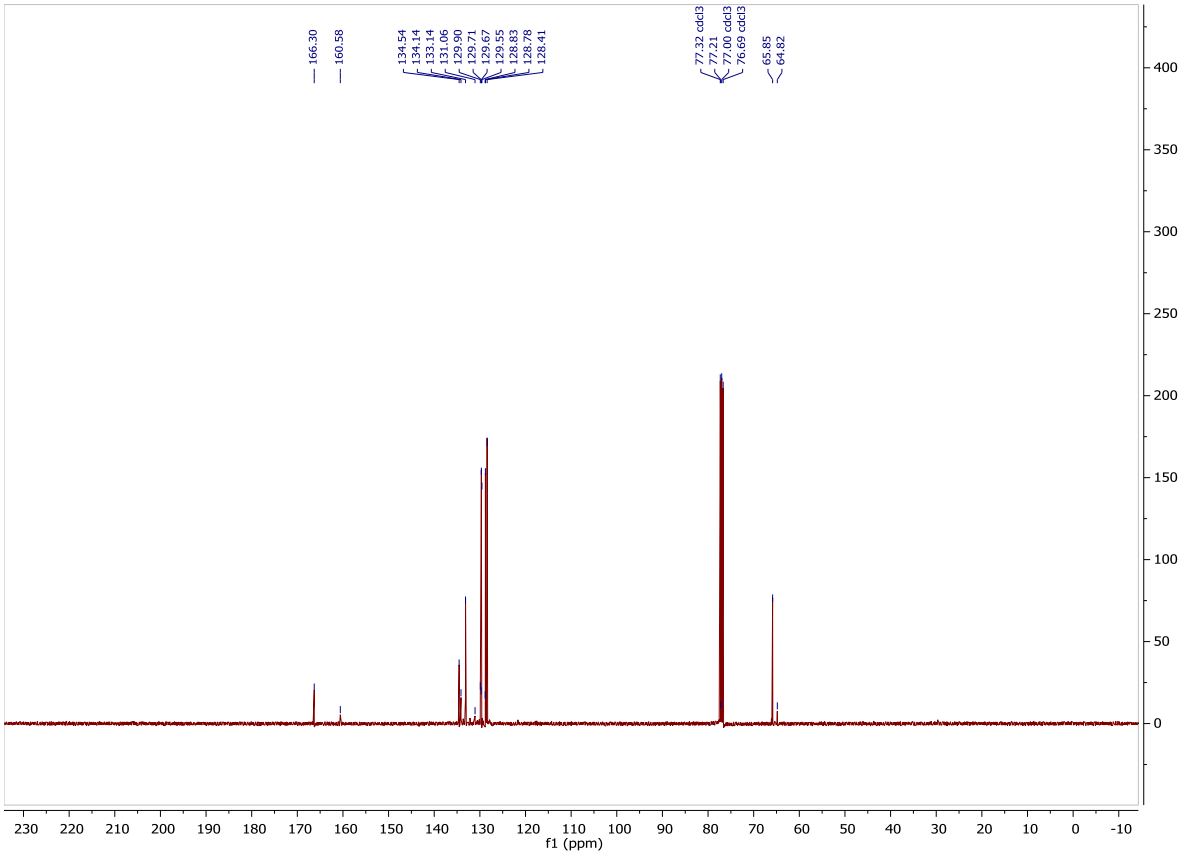




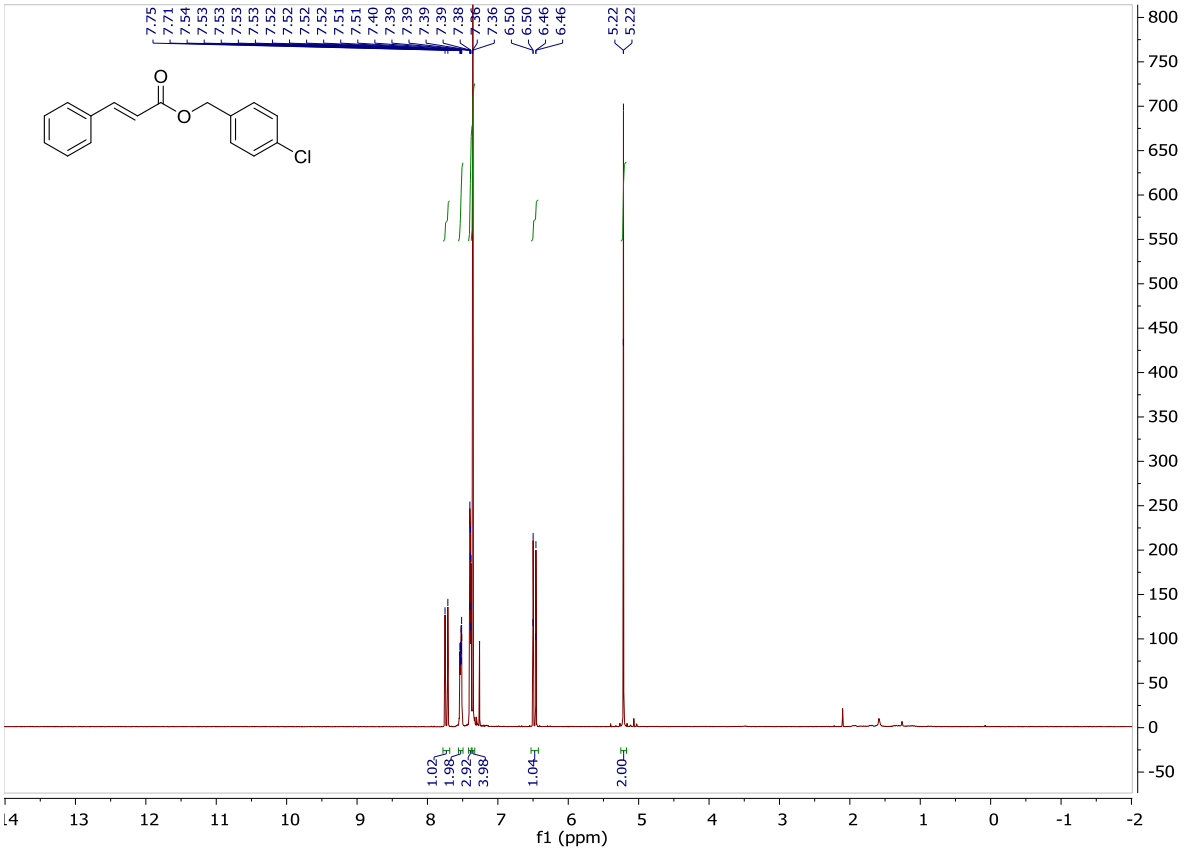


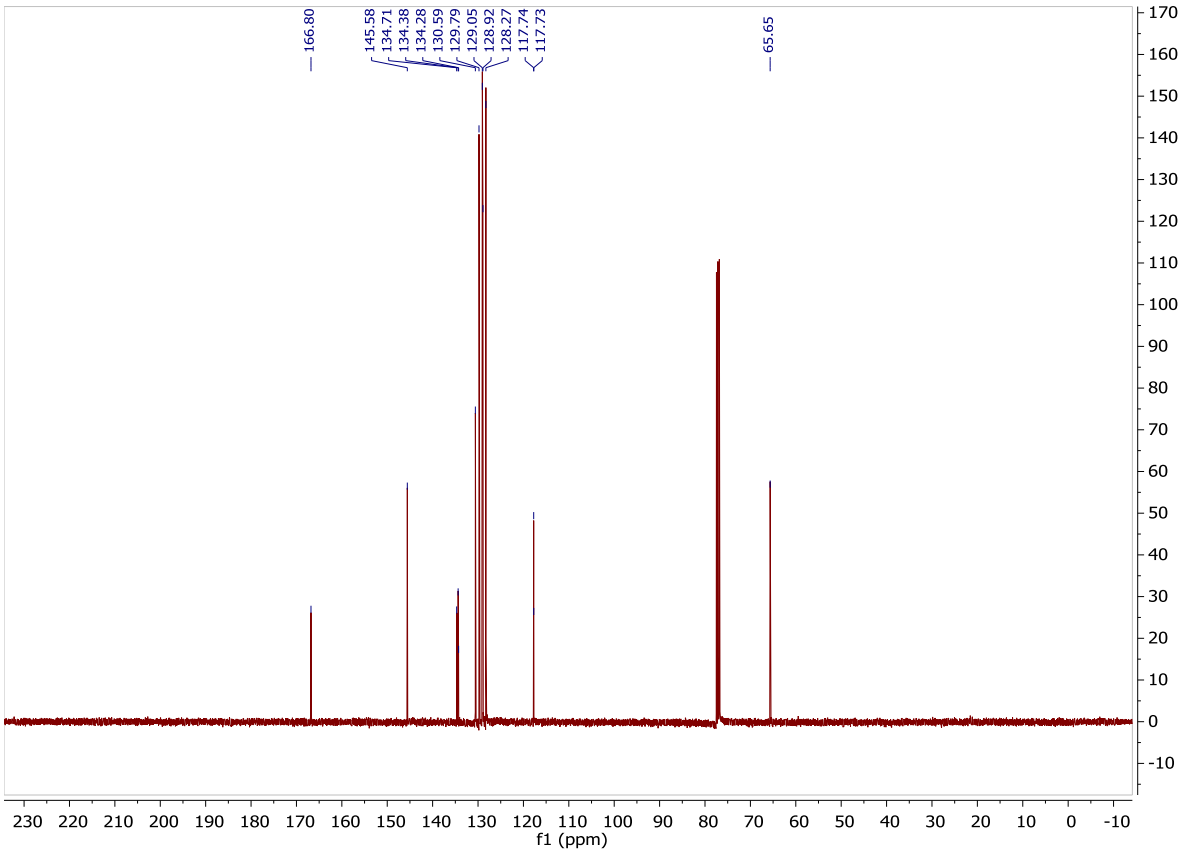
4-Chlorobenzyl benzoate (12)



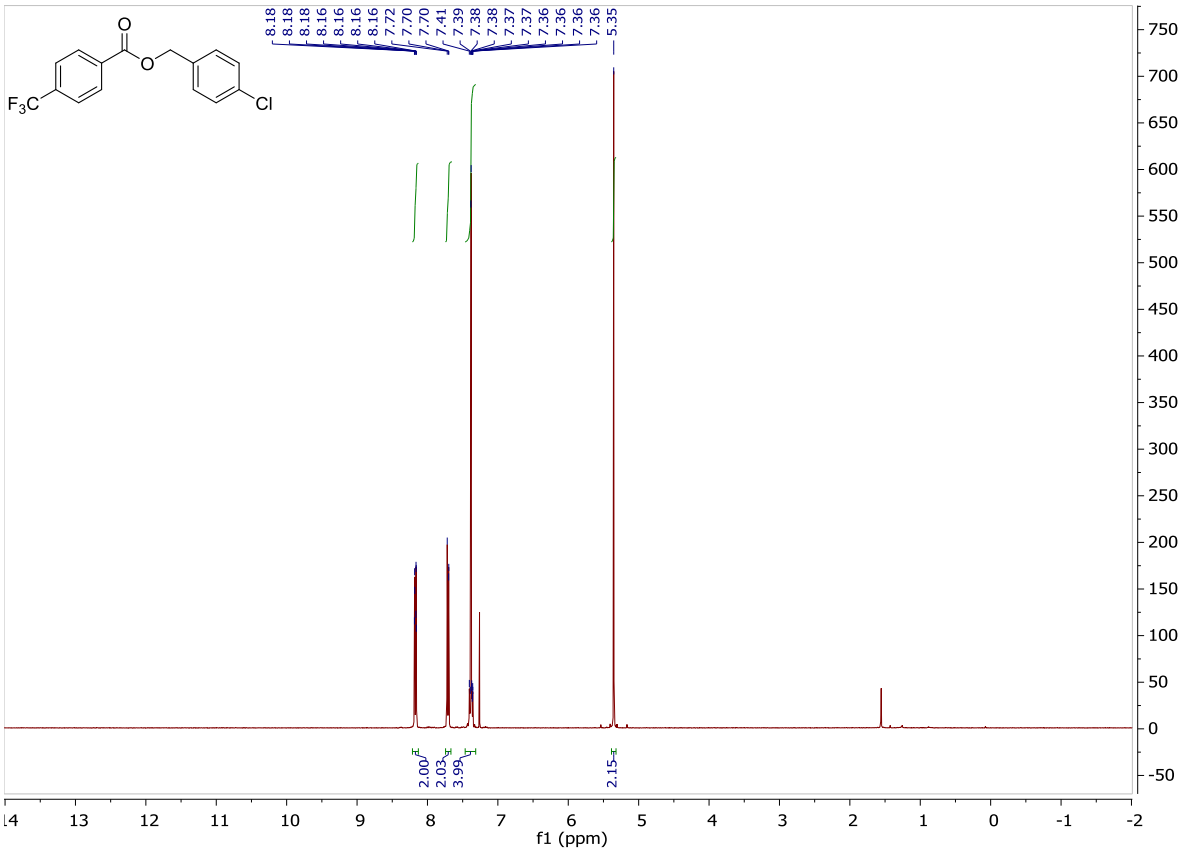


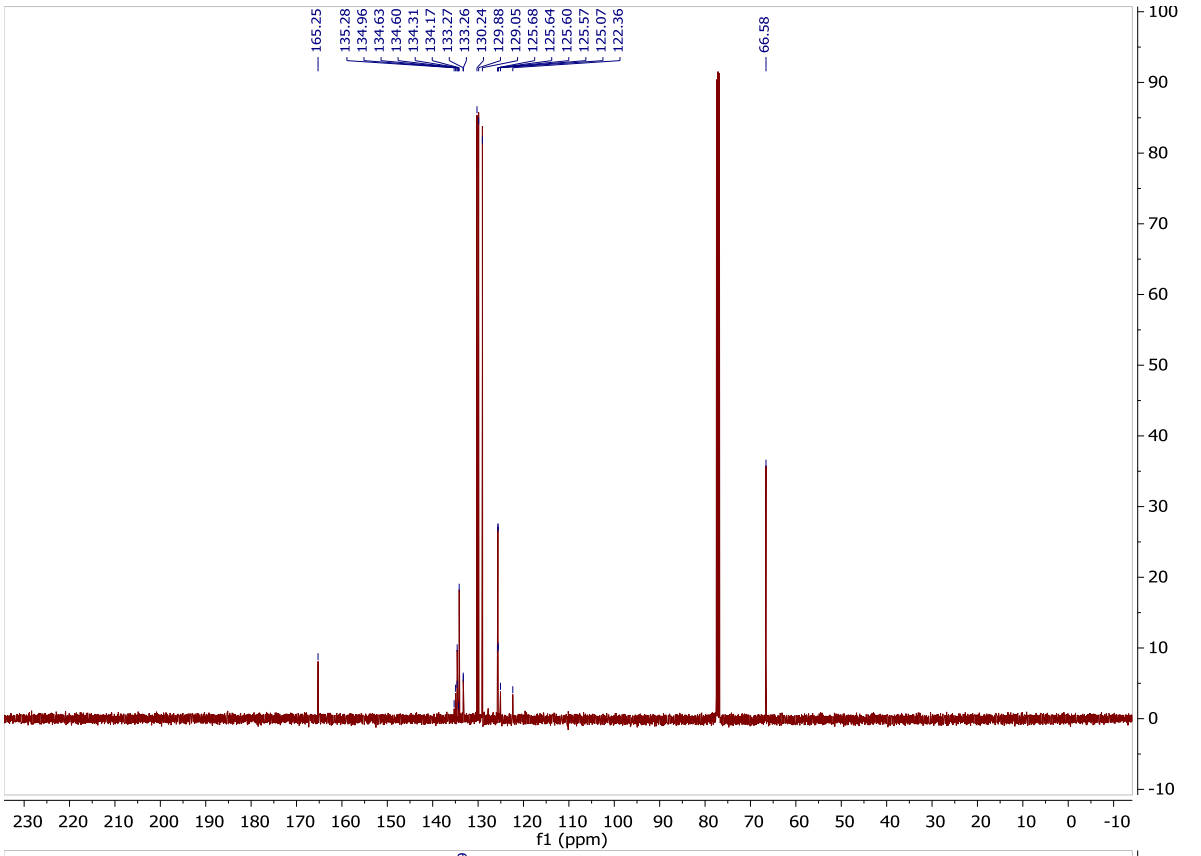
4-chlorobenzyl cinnamate (13)

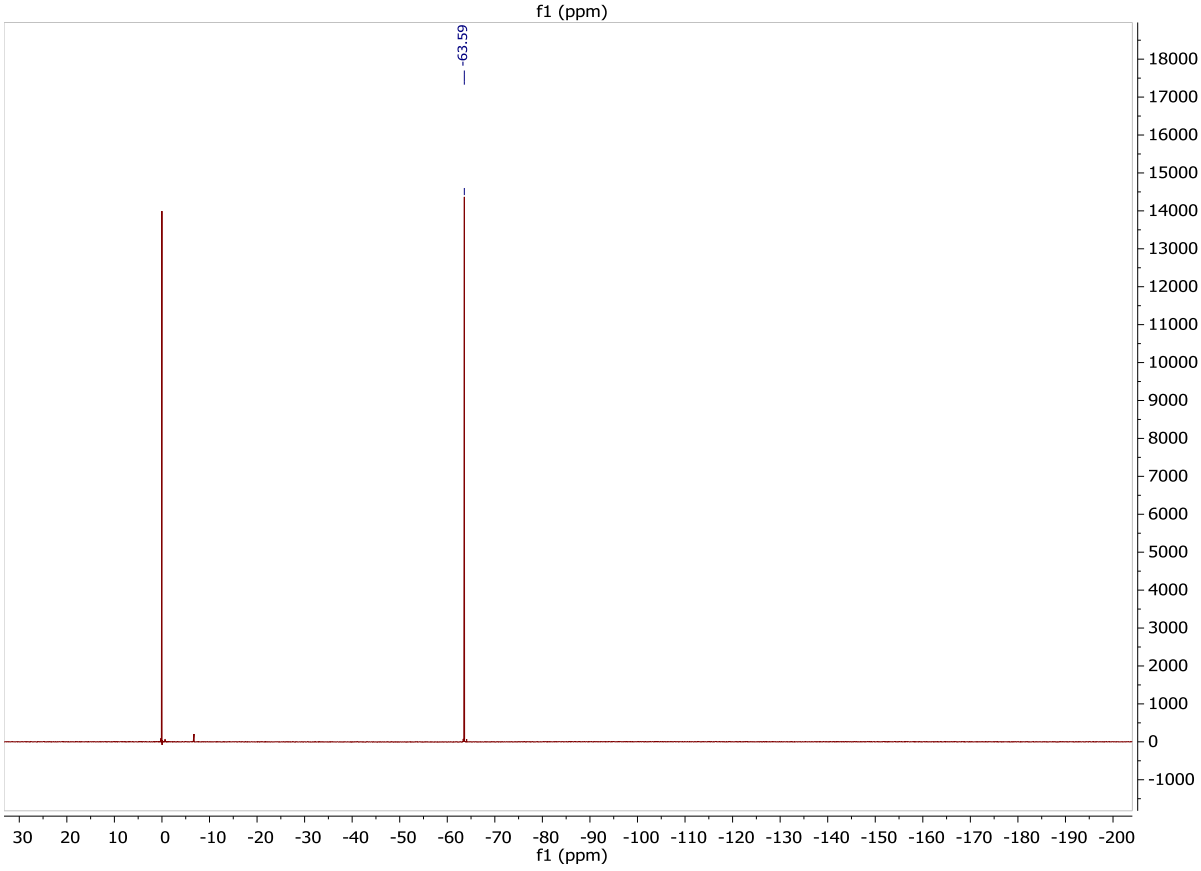




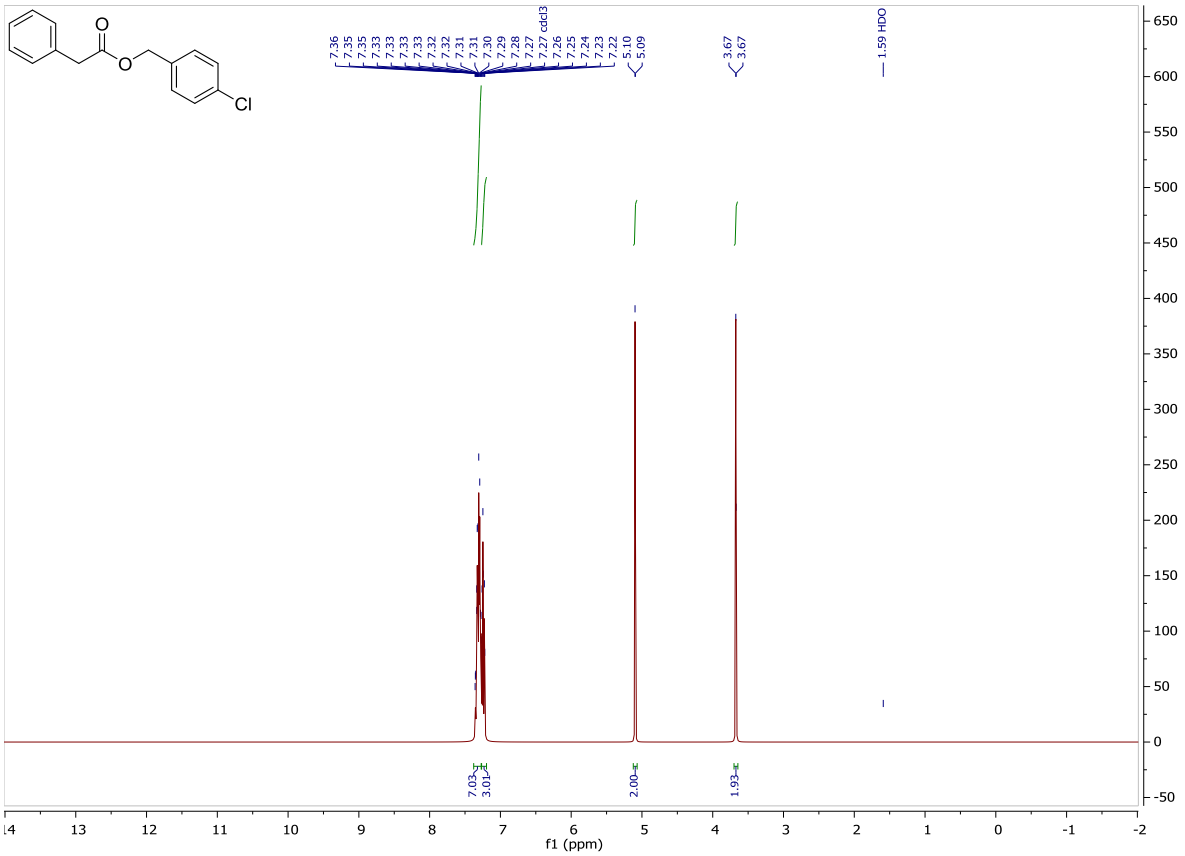
4-Chlorobenzyl 4-(trifluoromethyl)benzoate (14)

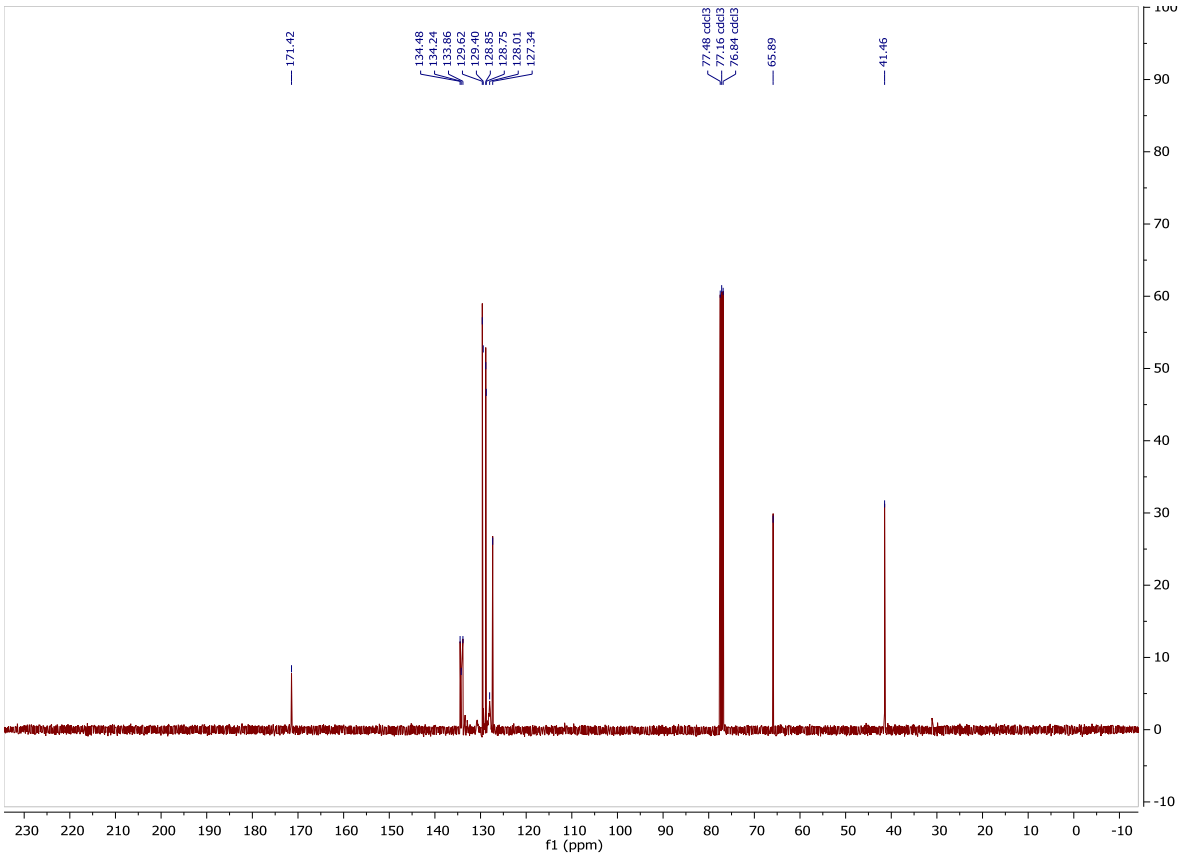



165.25
135.28
134.96
134.63
134.60
134.31
134.17
133.27
133.26
130.24
129.88
129.05
125.68
125.64
125.60
125.57
125.07
122.36
66.58
f1 (ppm)

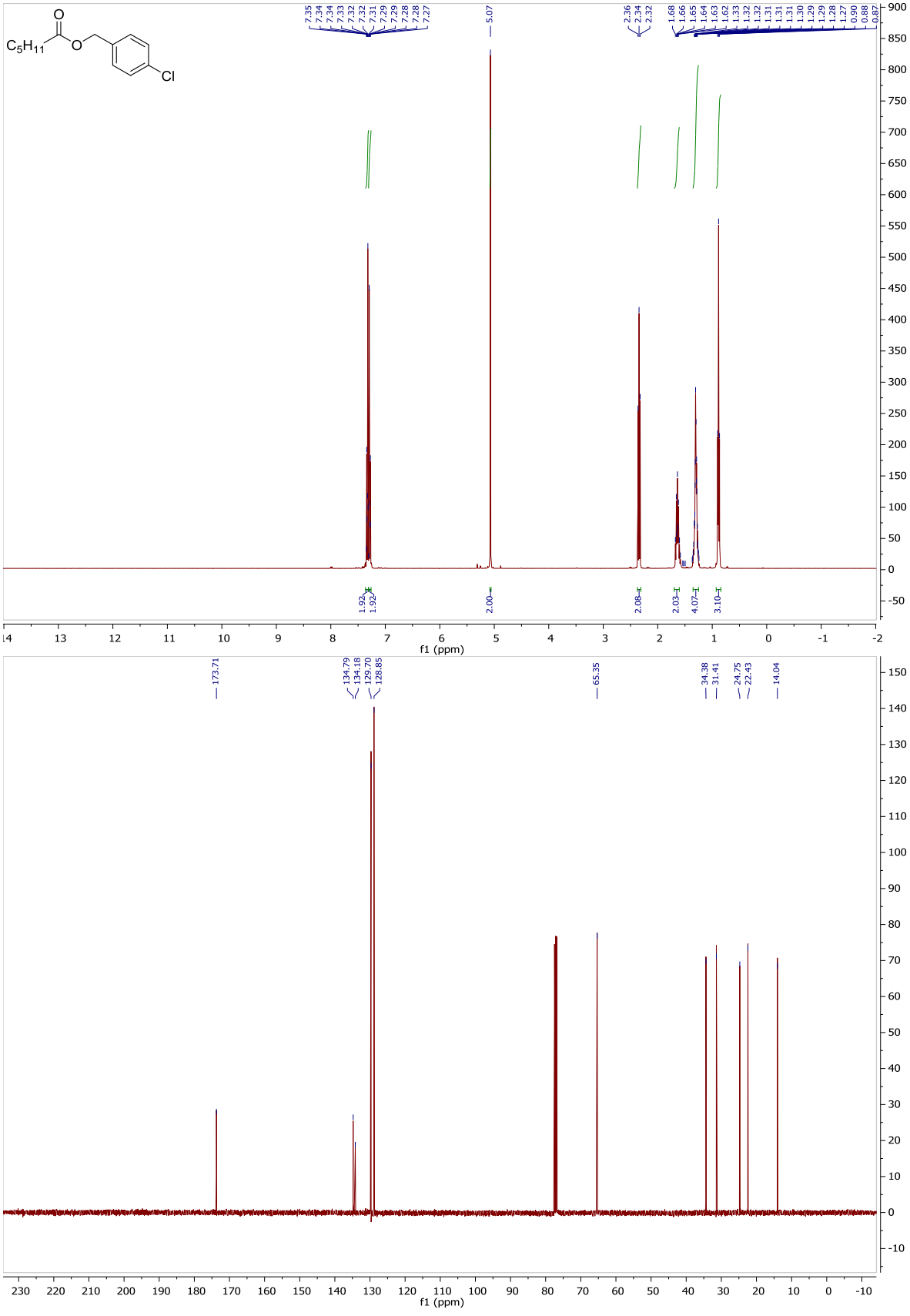

-63.59
f1 (ppm)

4-Chlorobenzyl 2-phenylacetate (15)

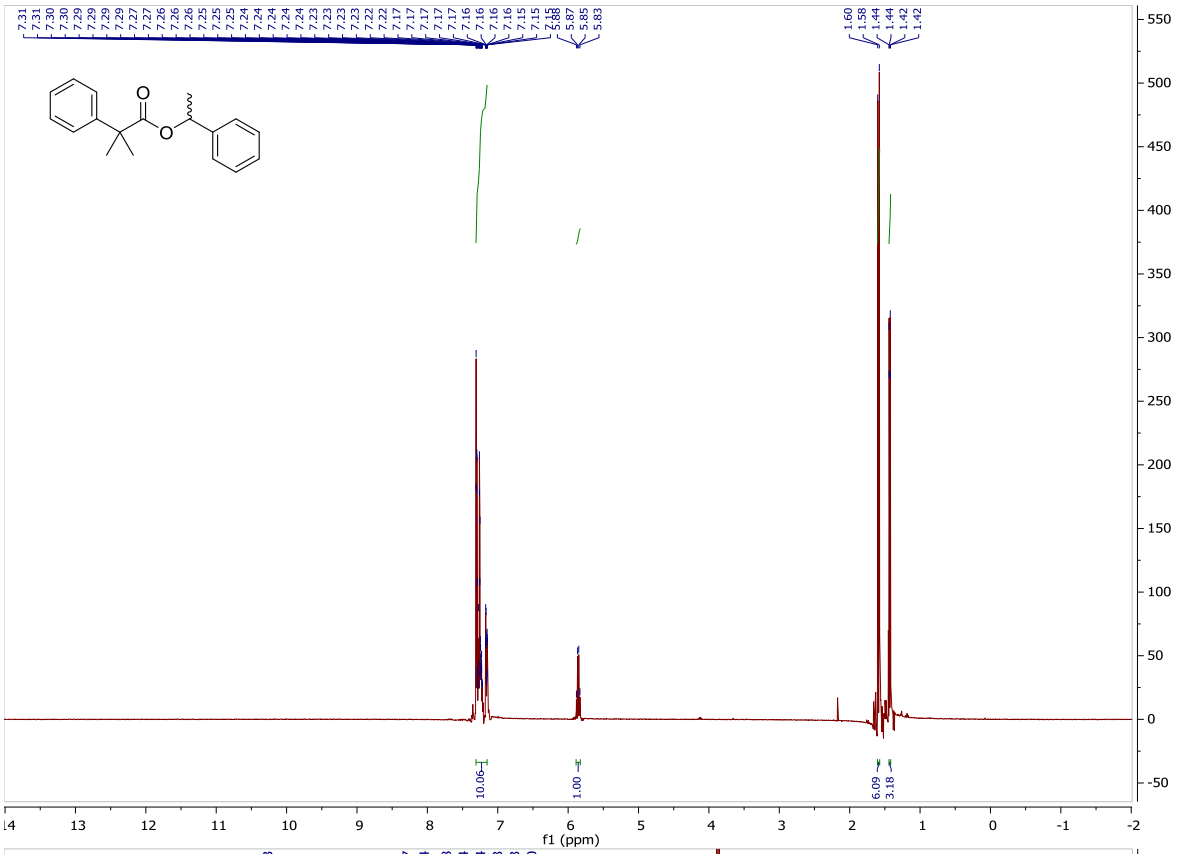


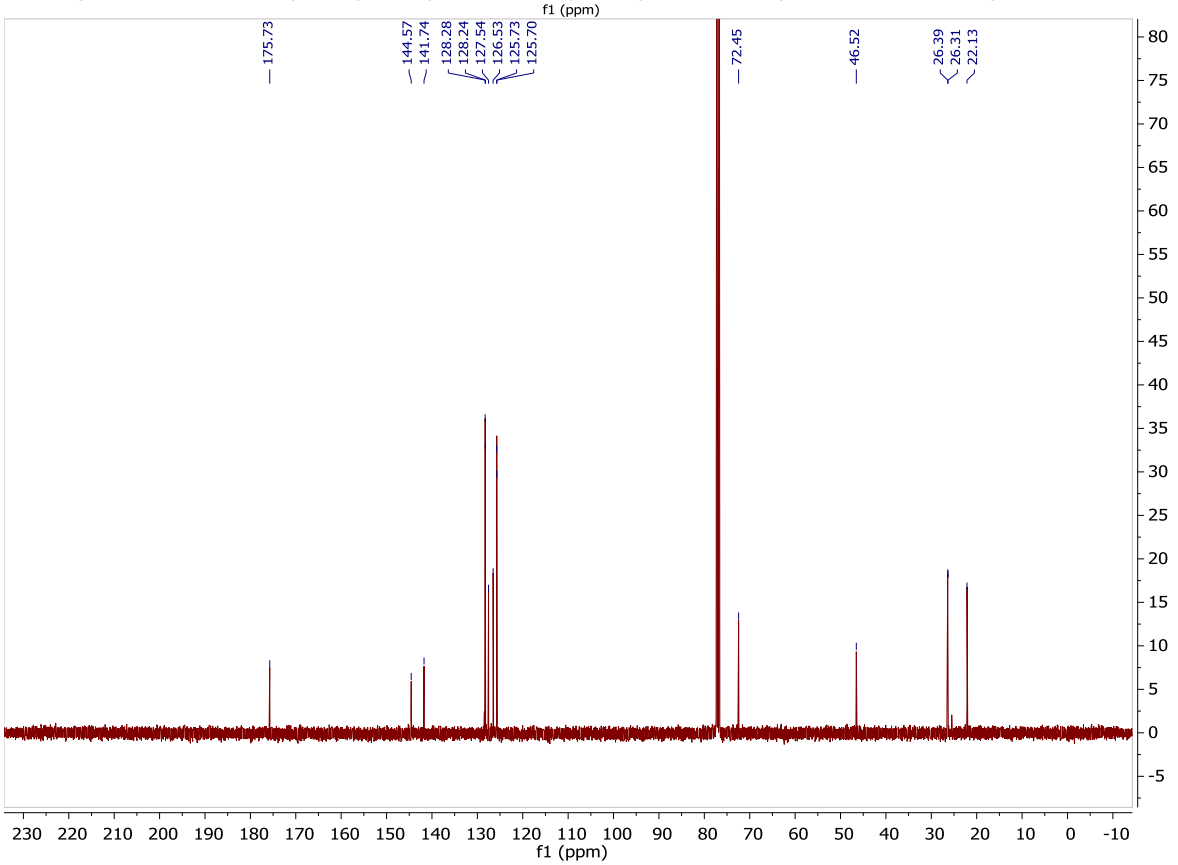


4-chlorobenzyl hexanoate (16)

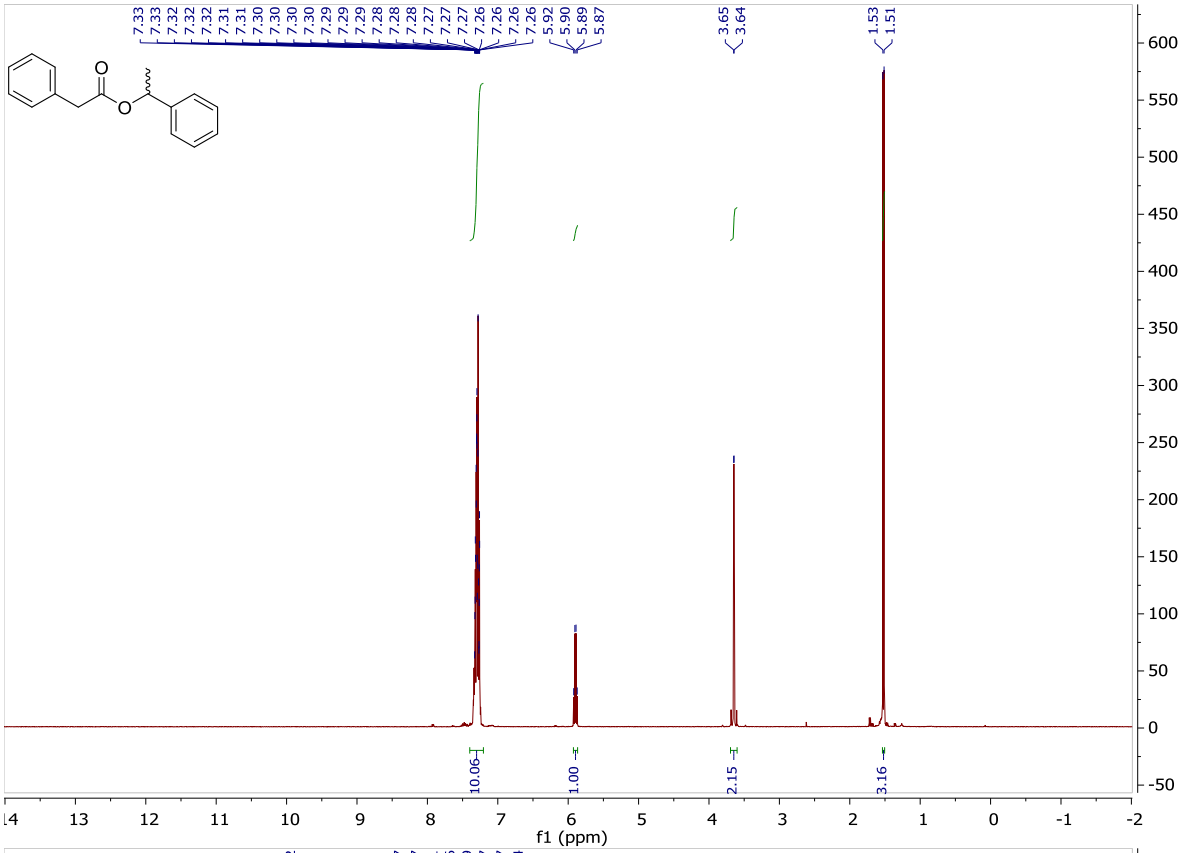


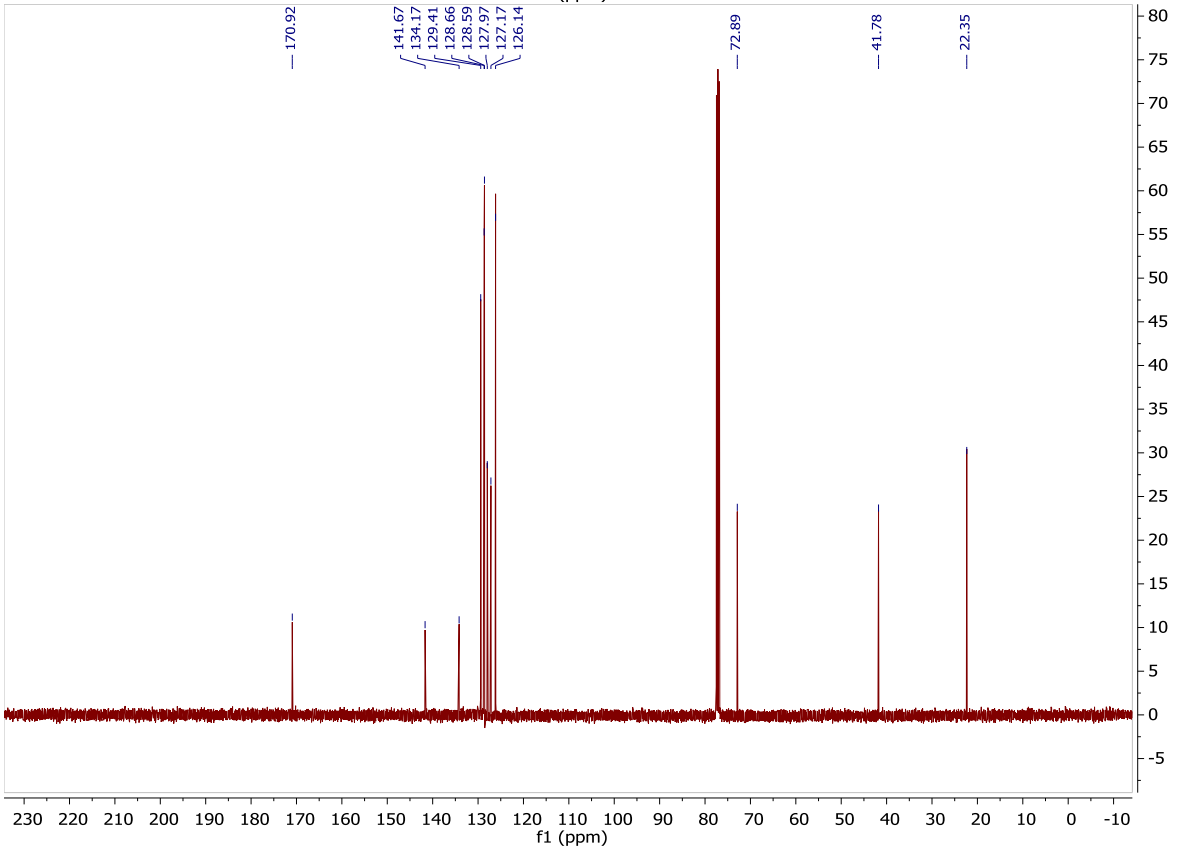
(*S*)- and (*R*)-1-Phenylethyl 2-methyl-2-phenylpropanoate (17)



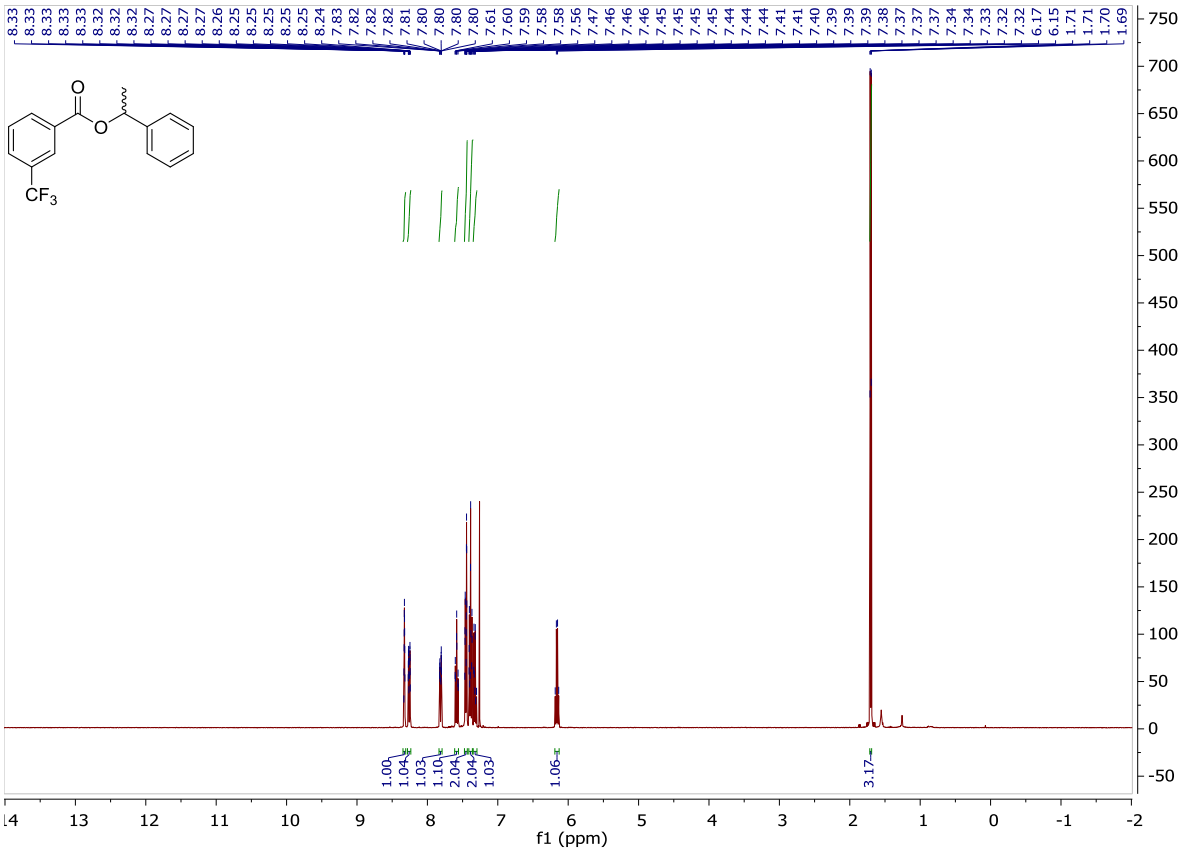


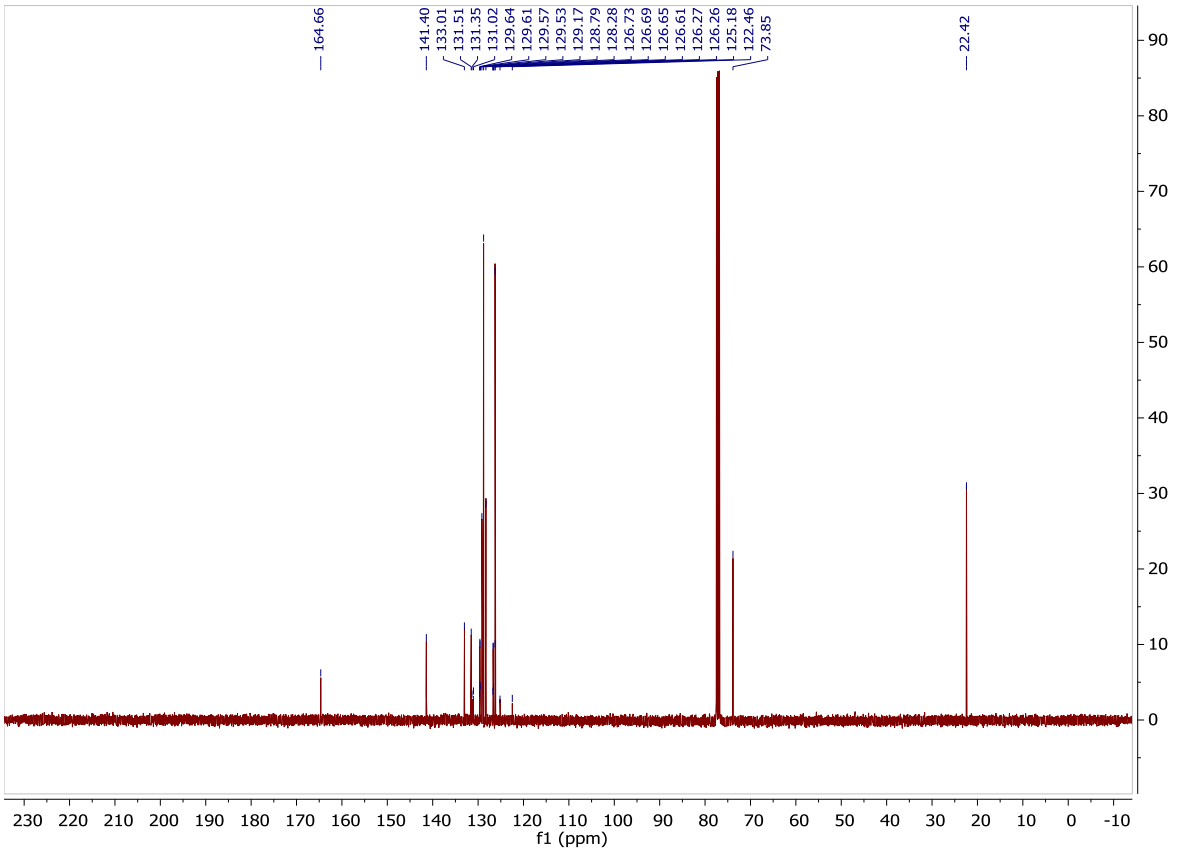
(*S*)- and (*R*)-1-Phenylethyl 2-phenylacetate (18)

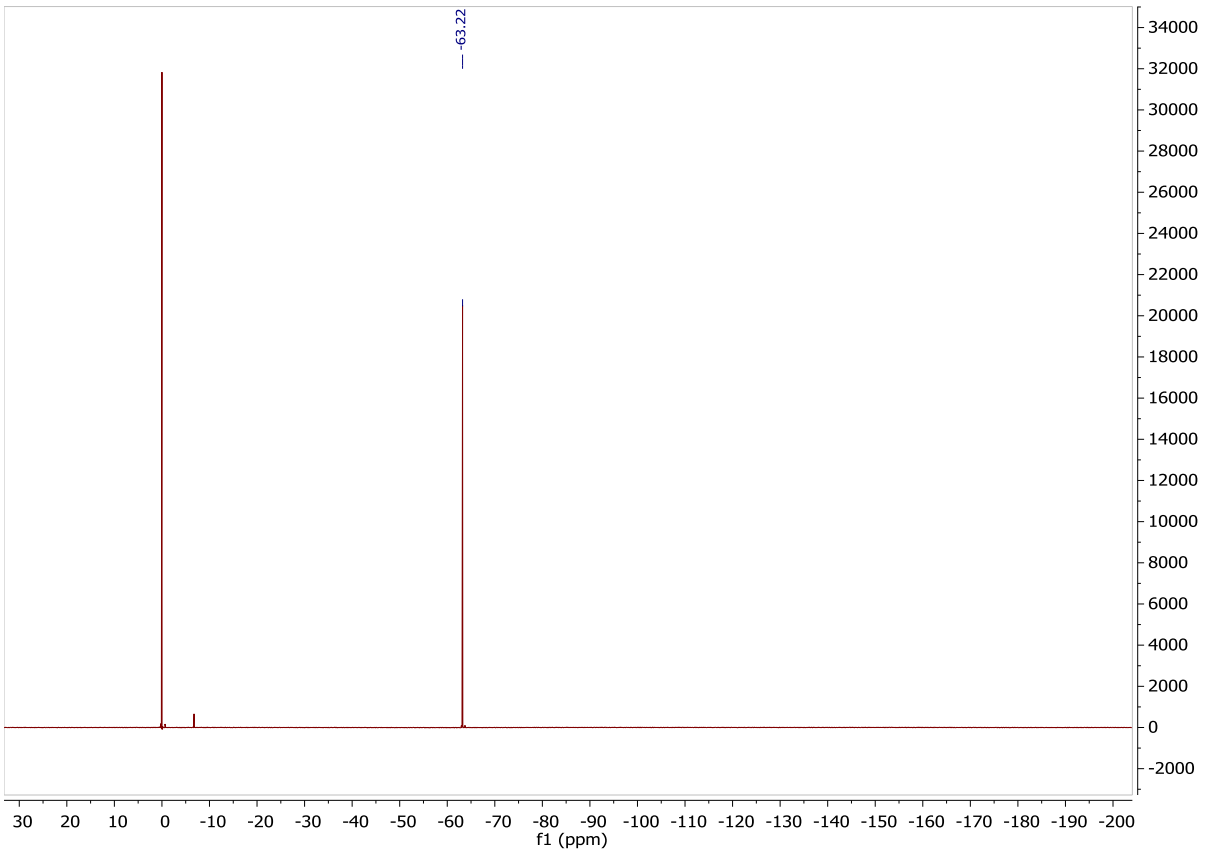




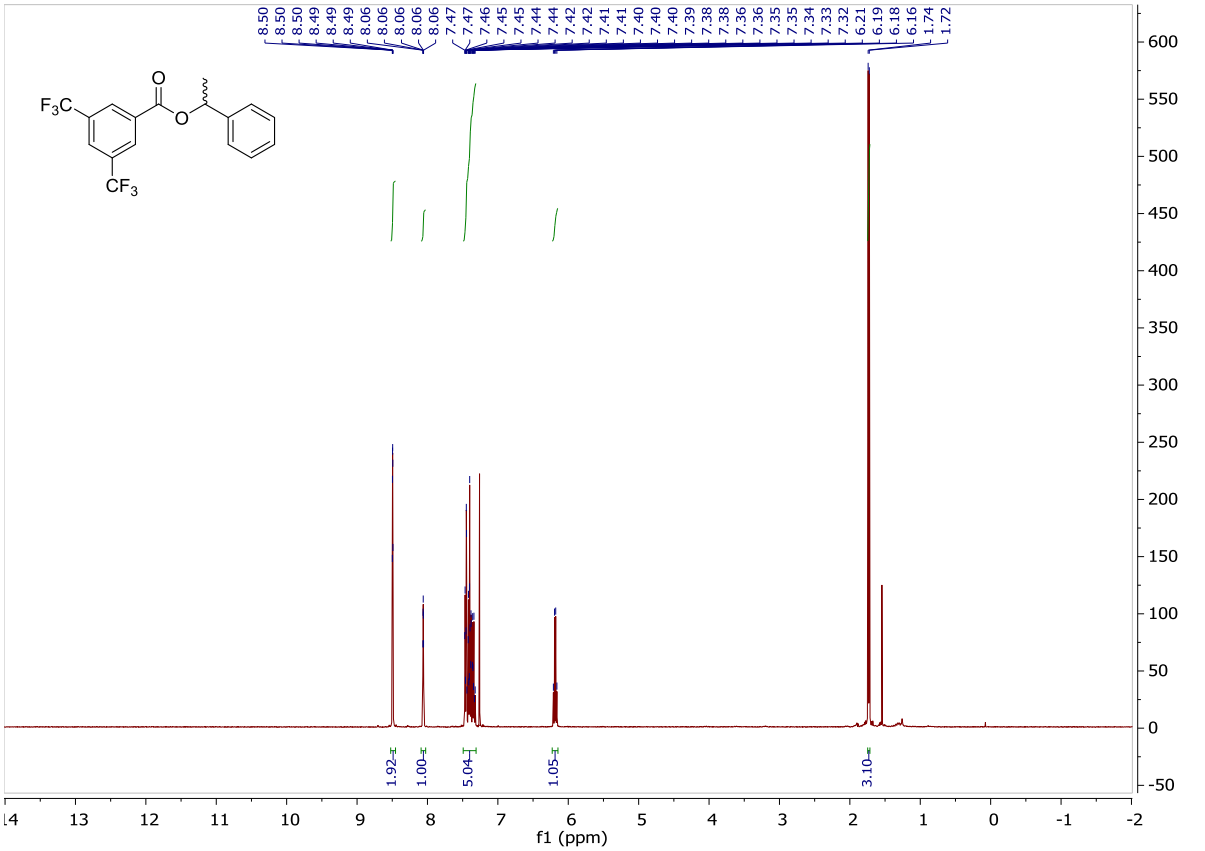
(*S*)- and (*R*)-1-Phenylethyl 3-(trifluoromethyl)benzoate (19)

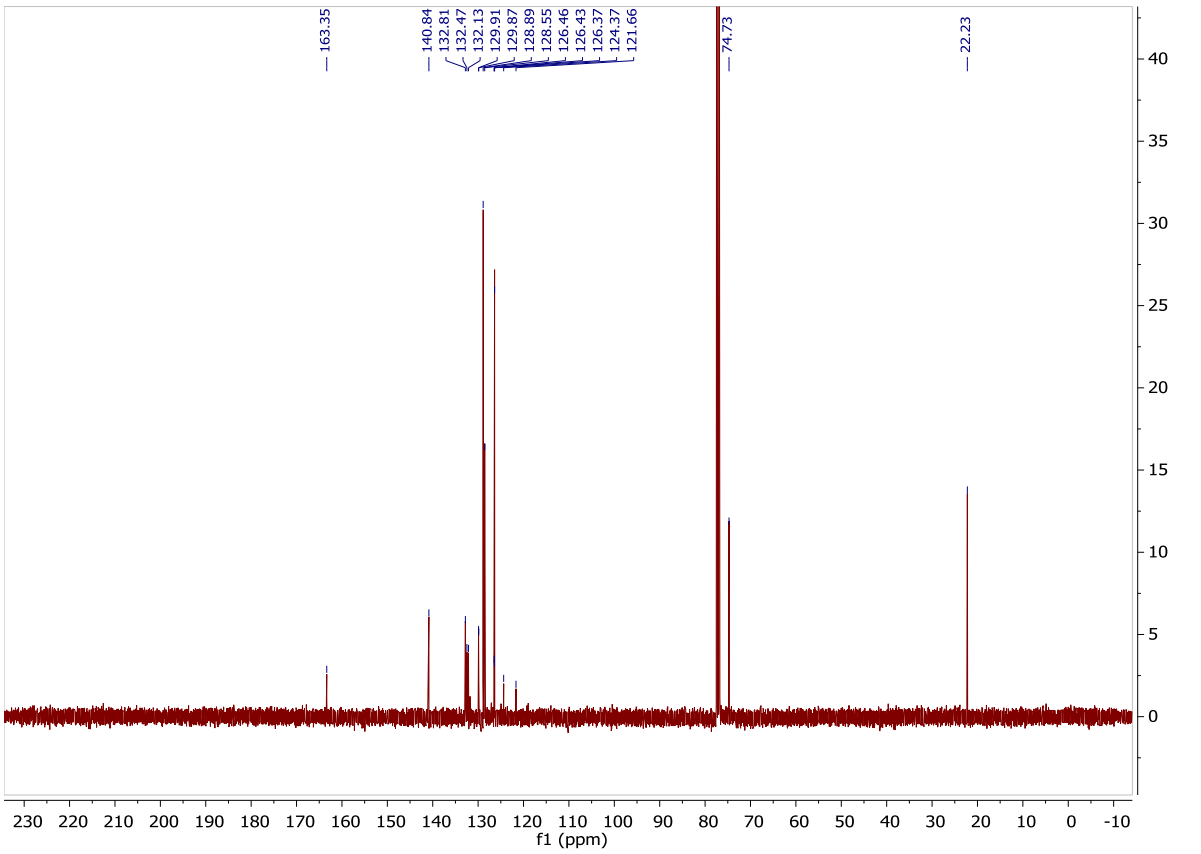


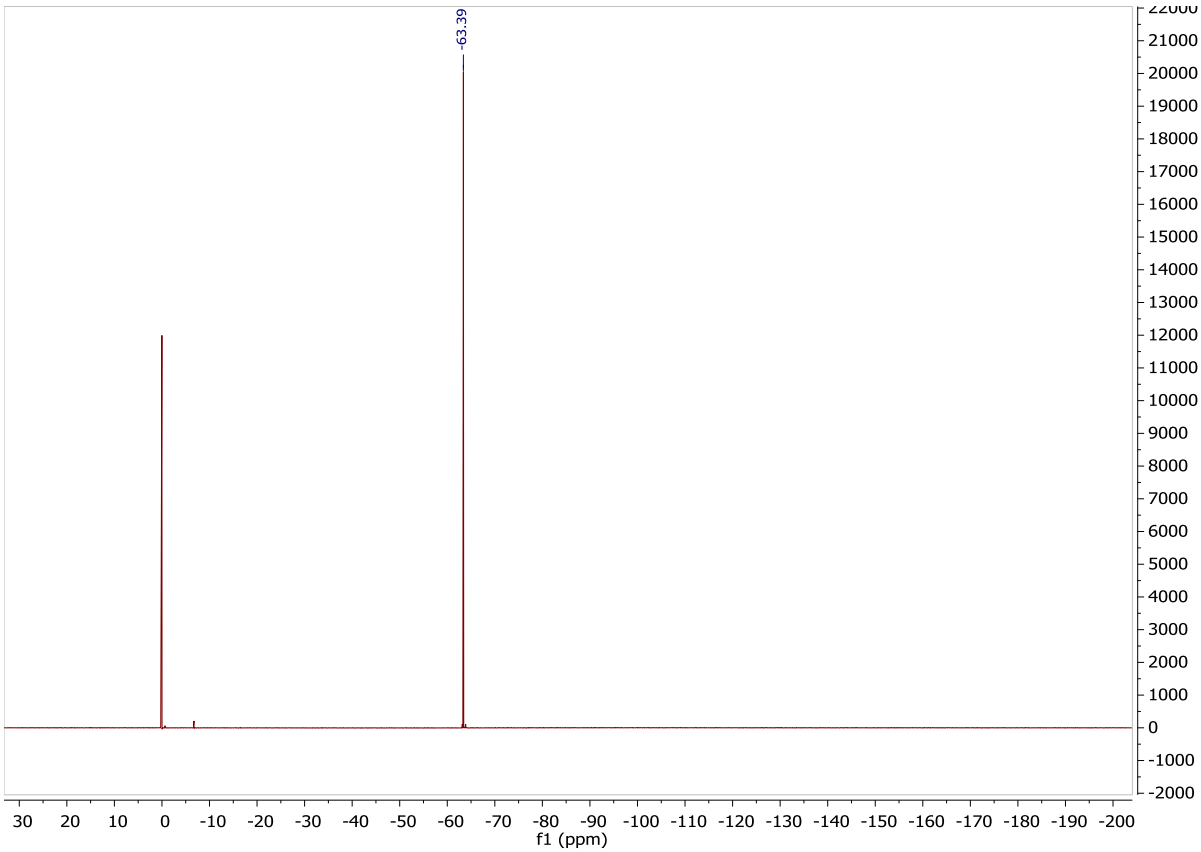




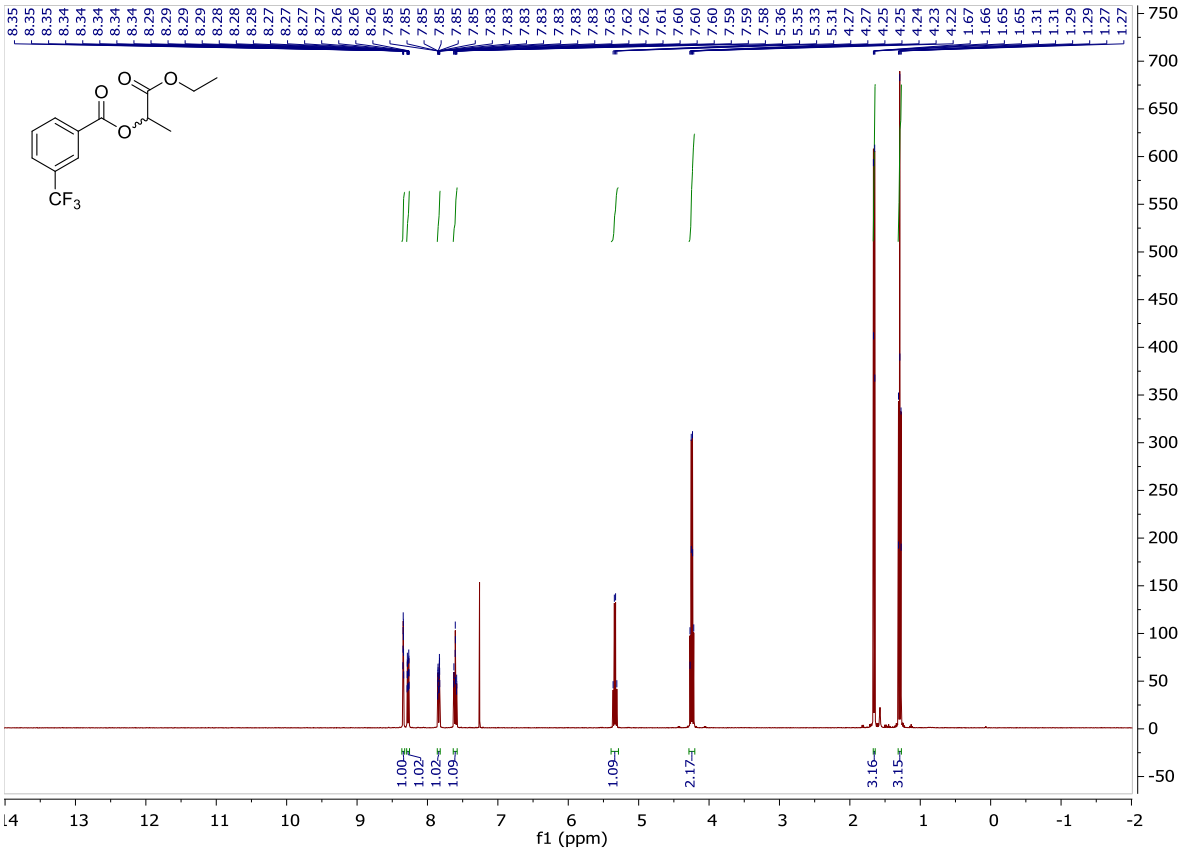
(*S*)- and (*R*)-1-Phenylethyl 3,5-bis(trifluoromethyl)benzoate (20)

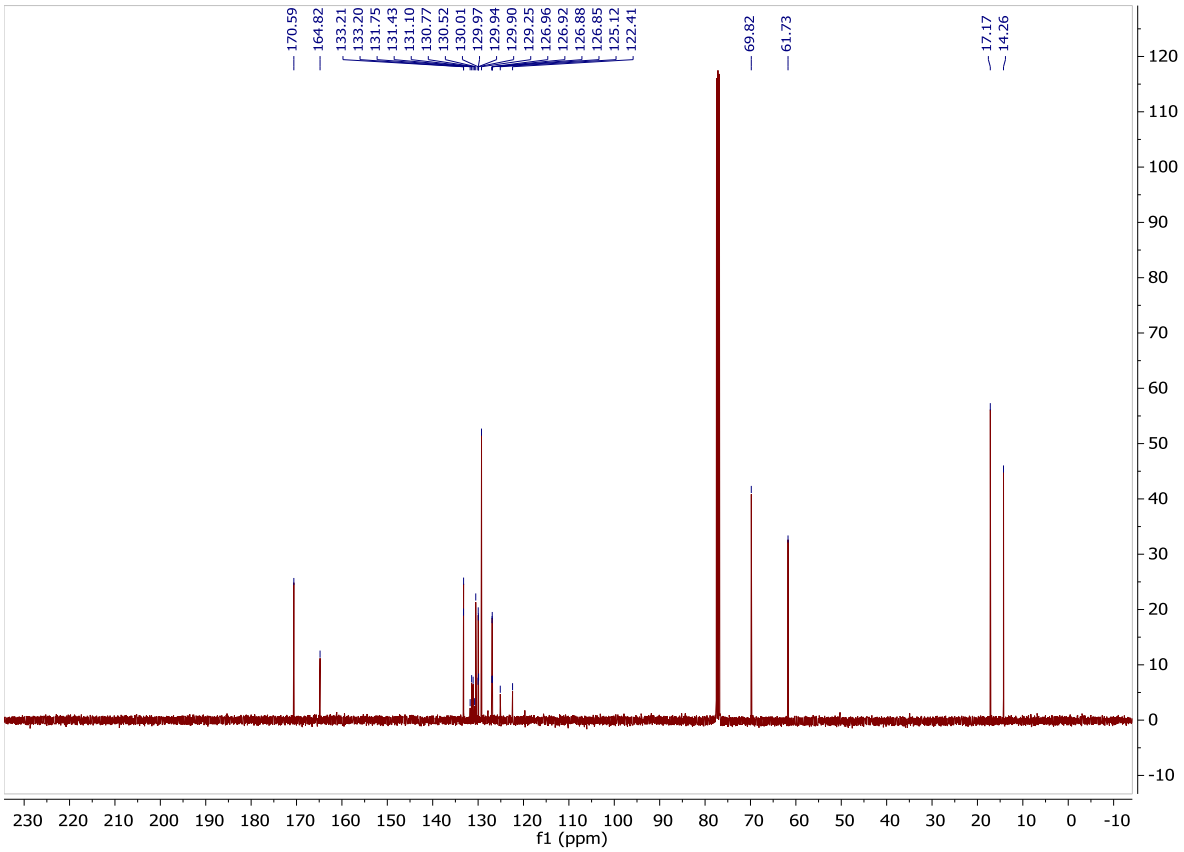


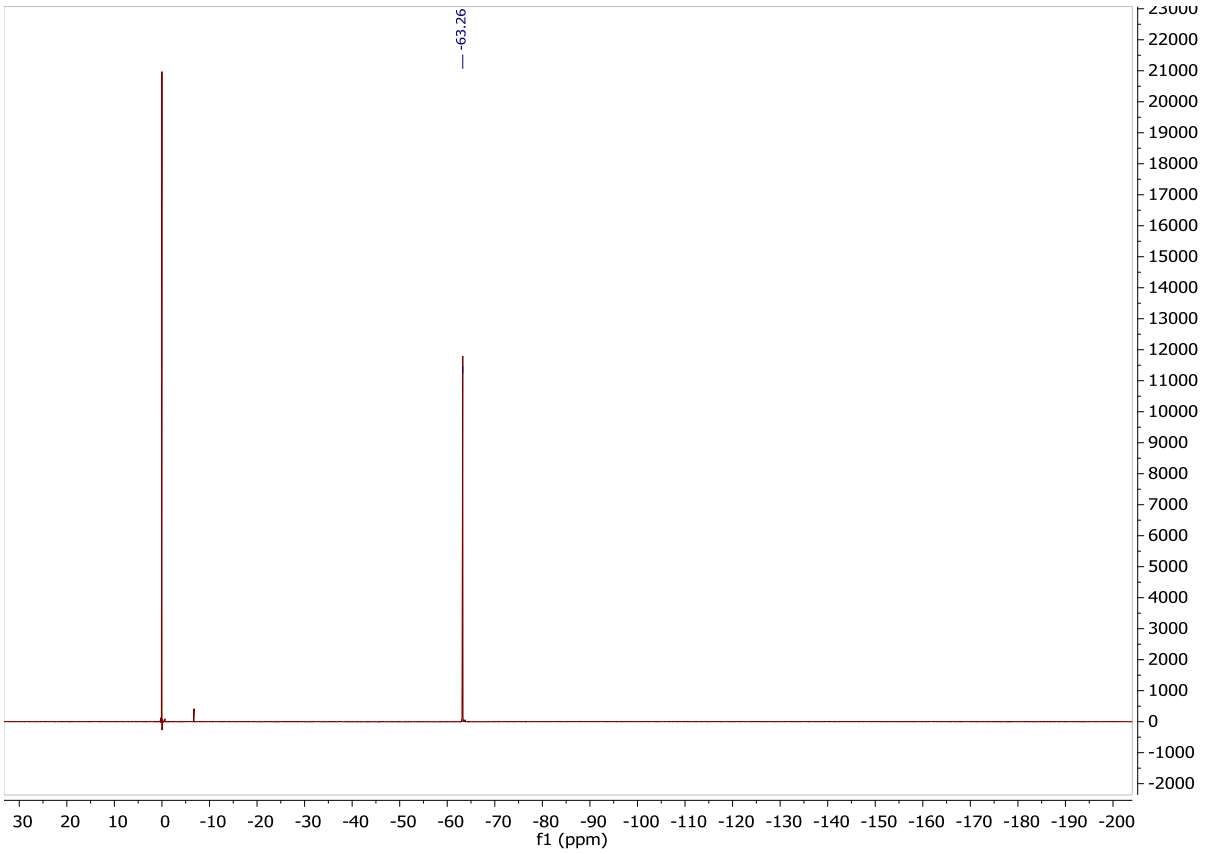

163.35
140.84
132.81
132.47
132.13
129.91
129.87
128.89
128.55
126.46
126.43
126.37
124.37
121.66
74.73
22.23
f1 (ppm)


-63.39
f1 (ppm)

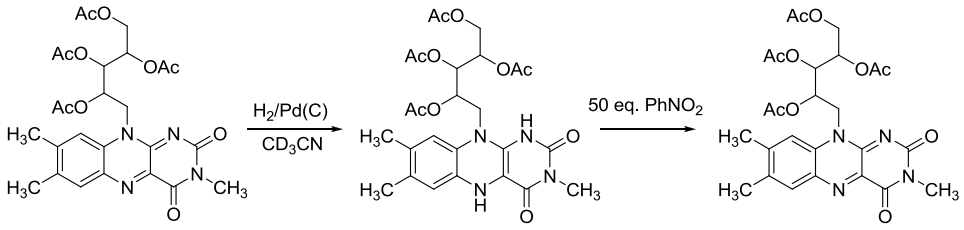
Ethyl (*S*)- and (*R*)-2-((3-(trifluoromethyl)benzoyl)oxy) propionate (21)

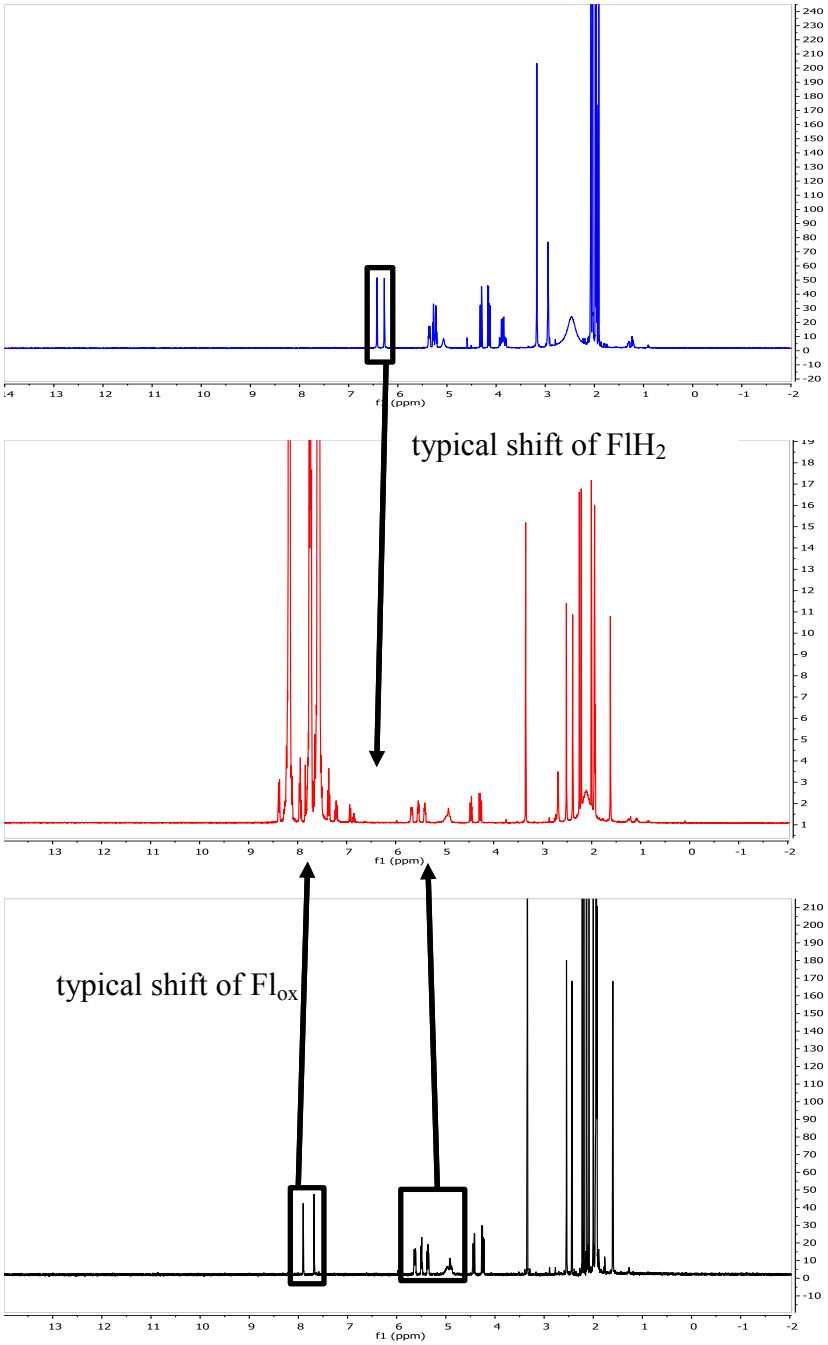





-63.26
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

S8 ^{1}H NMR spectrum of regeneration of Fl



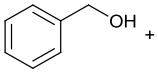
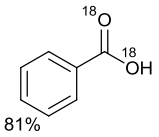
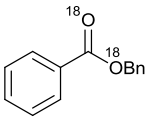
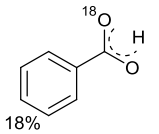
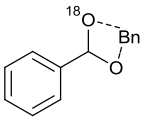
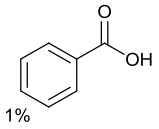
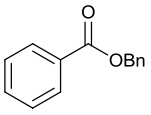


Blue: FlH_2

Red: FlH_2 + 50 eq. $PhNO_2$

Black: Fl_{ox}

S9 ^{18}O-Labeling experiments

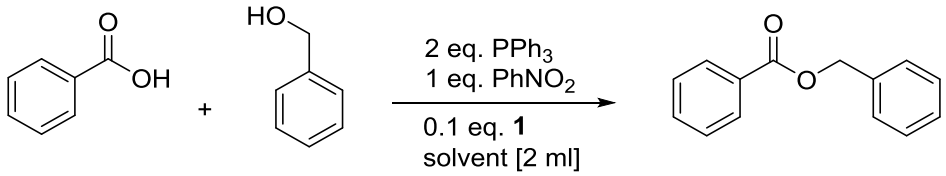
				Theoretical amount for 100% alkyl substitution (%)	Theoretical amount for 100 % acyl substitution (%)	Measured amount in BFT (%)	Measured amount in CH_3CN (%)
				**81**	**0**	**62**	**28**
				**18**	**90**	**33**	**59**
				**1**	**10**	**5**	**13**

Ratio retention:inversion in BFT = 25:75

Ration retention :inversion = 66:34

S10 Preliminary screening of the reaction conditions

Preliminary screening of solvents[a] and temperature



Entry	Solvents	T [°C]	Conv. [%][b]
1	BTF	10	44
2	BTF	25	47
3	BTF	40	66
4	BTF	50	54
5	CH_3CN	10	37
6	CH_3CN	25	32
7	CH_3CN	40	35
8	CH_3CN	50	38
9	THF	25	15
10	$CHCl_3$	25	21
11	DCM	25	32
12	toluen	25	38

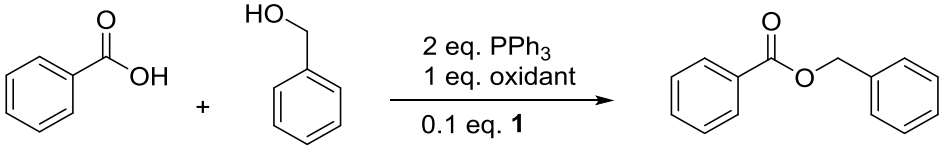
[a] n(**alcohol**) = 0.15 mmol; n(**acid**) = 0.18 mmol; $n(PhNO_2)$ = 0.15 mmol; n(**1**) = 0.015 mmol; $n(PPh_3)$ = 0.3 mmol; 4 Å MS (150 mg); 40 °C; Ar; 448 nm; [b] Determined by ^{1}H NMR.

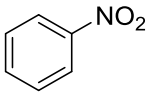
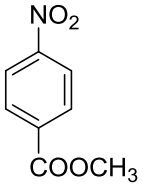
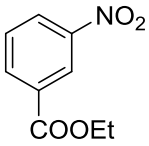
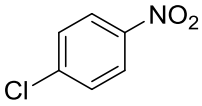
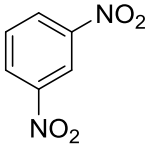
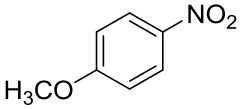
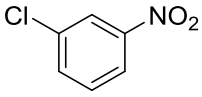
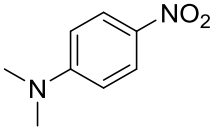
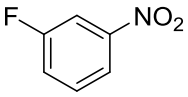
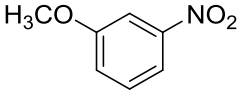
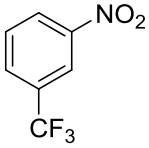
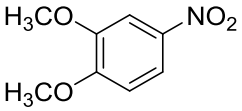
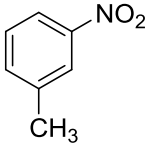
Preliminary screening of amounts of reagents[a]

Entry	Equivalents of reagents					Conv. [%][b]
	Acid	Alcohol	PPh_3	$PhNO_2$	Cat.	
1	1.2	1	1	1	0.1	39
2	1.2	1	2	1	0.1	66
3	1.2	1	3	1	0.1	71
4	1.2	1	2	0.2	0.1	36
5	1.2	1	2	0.3	0.1	50
6	1.2	1	2	0.5	0.1	57
7	1.2	1	2	-	0.1	5
8	1.2	1	2	-	0.2	7

[a] n(**alcohol**) = 0.15 mmol; n(**acid**) = 0.18 mmol; $n(PhNO_2)$ = 0.15 mmol; n(**1**) = 0.015 mmol; $n(PPh_3)$ = 0.3 mmol; 4 Å MS (150 mg); 40 °C; 2 ml BTF, Ar; 448 nm; [b] Determined by ^{1}H NMR.

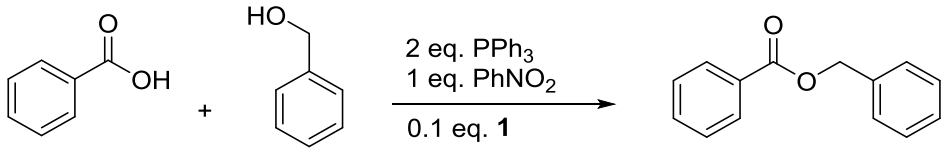
Preliminary screening of different of nitro-compounds



Entry	Oxidant	Conv. [%][b] Solvents CH_3CN	BTF	Entry	Oxidant	Conv. [%][b] Solvents CH_3CN	BTF
1		35	66	8		27	58
2		44	64	9		39	44
3		11	46	10		39	75
4		42	60	11		3	5
5		27	63	12		59	59
6		15	53	13		1	42
7		31	70				

[a] *n*(**alcohol**) = 0.15 mmol; *n*(**acid**) = 0.18 mmol; *n*(**oxidant**) = 0.15 mmol; *n*(**1**) = 0.015 mmol; *n*(PPh_3) = 0.3 mmol; 4 Å MS (150 mg); 40 °C; 2 ml BTF; Ar; 448 nm; [b] Determined by ^{1}H NMR.

S11 Blank experiments



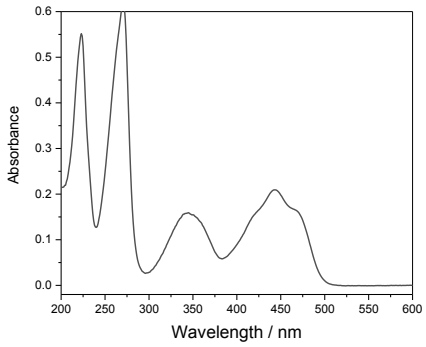
Blank experiments for photocatalytic esterification in the presence (✓) or absence (-) of catalyst **1**, PPh_3, $PhNO_2$, light or molecular sieves.[a]

Entry	Cat. (**3d**)	PPh_3	$PhNO_2$	Light[b]	MS 4 Å	Conversion[c] 24 h [%]
1	-	✓	✓	✓	✓	0
2	✓	-	✓	✓	✓	0
3	✓	✓	-	✓	✓	5
4	✓	✓	✓	-	✓	0
5	✓	✓	✓	✓	-	10
6	✓	✓	✓	✓	✓	66

[a] n(**alcohol**) = 0.15 mmol; n(**acid**) = 0.18 mmol; $n(PhNO_2)$ = 0.15 mmol; n(**1**) = 0.015 mmol; $n(PPh_3)$ = 0.3 mmol; 4 Å MS (150 mg); 2 ml BTF; 40 °C; Ar; [b] 448 nm; [c] Determined by ^{1}H NMR.

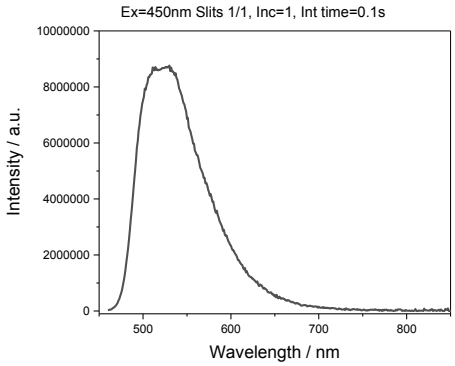
S12 Spectral and electrochemical data of 1

Absorption spectrum of **1** in acetonitrile (298 K)
$c(\mathbf{1}) = 1.76 \times 10^{-5}$ M

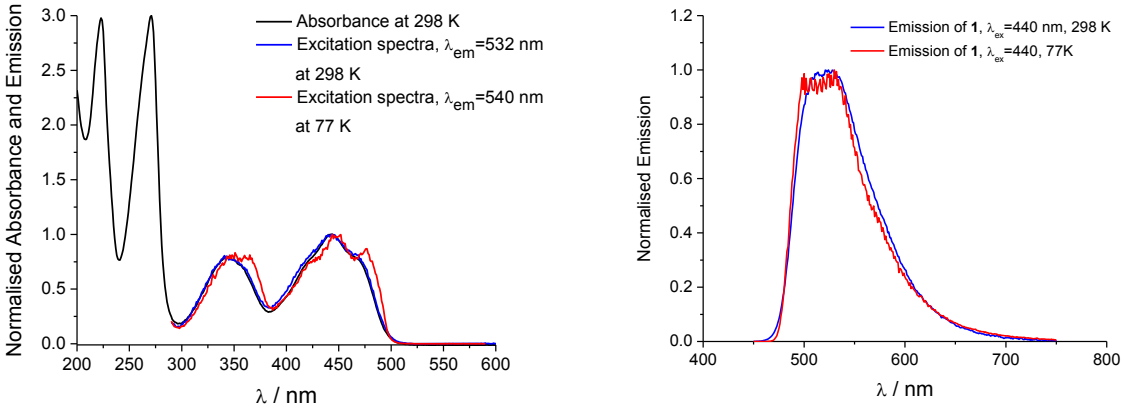


Fluorescence spectrum of **1** in acetonitrile (298 K)

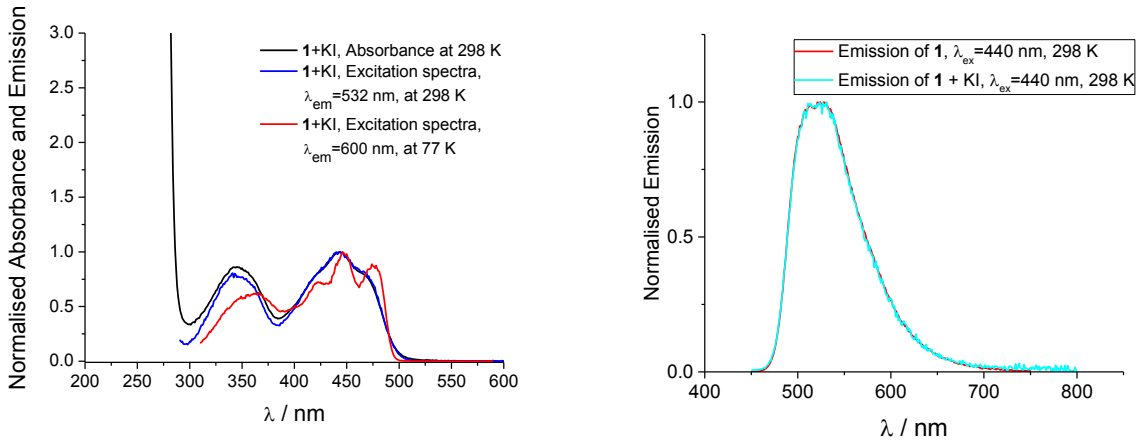
$c(\mathbf{1}) = 1.76 \times 10^{-5}$ M, $\tau_F = 5.7$ ns



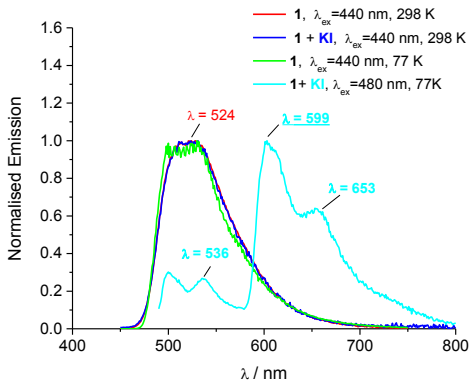
Absorption spectrum of **1** in acetonitrile (298 K) c(**1**) = 1.76 x 10^{-5} M, together with excitation (left panel) and emission (right panel) spectra of **1** in acetonitrile at 298 K and 77 K.



Absorption spectrum of **1** + KI (c_{KI} = 0.083 M) in acetonitrile (298 K), together with excitation spectra at 298 and 77 K (left panel) and emission spectra of **1** in acetonitrile with and without KI (right panel) at 298.



Fluorescence and phosphorescence spectra of **1** in acetonitrile at **298 K** and **77 K**



Emission lifetimes at 77 K:

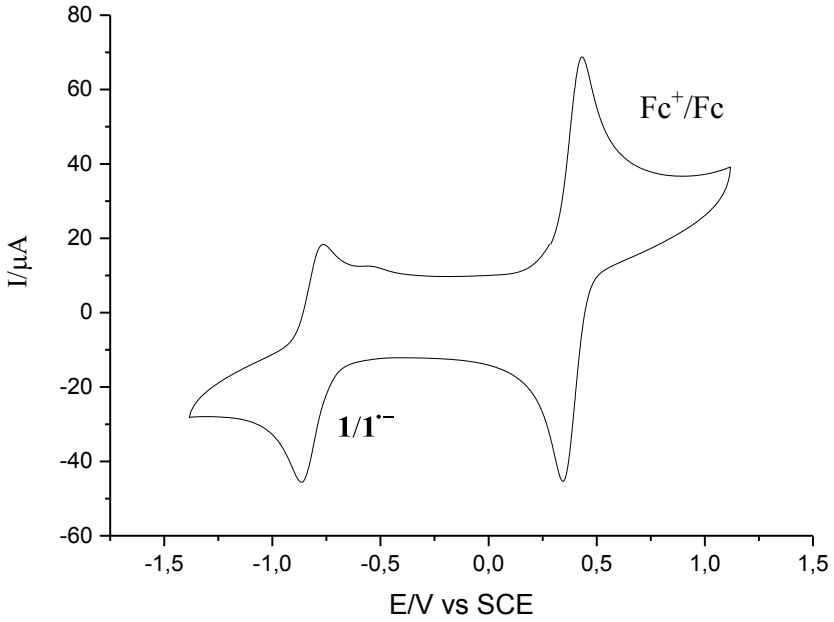
3MeTARF in ACN, λ_{em} = 680 (SpectraLED λ_{ex} = 394 nm), $\tau_{Phosporescence}$ = 0.25 s

3MeTARF in ACN, λ_{em} = 500 (NanoLED λ_{ex} = 368 nm), $\tau_{Fluorescence}$ = 8.9 ns

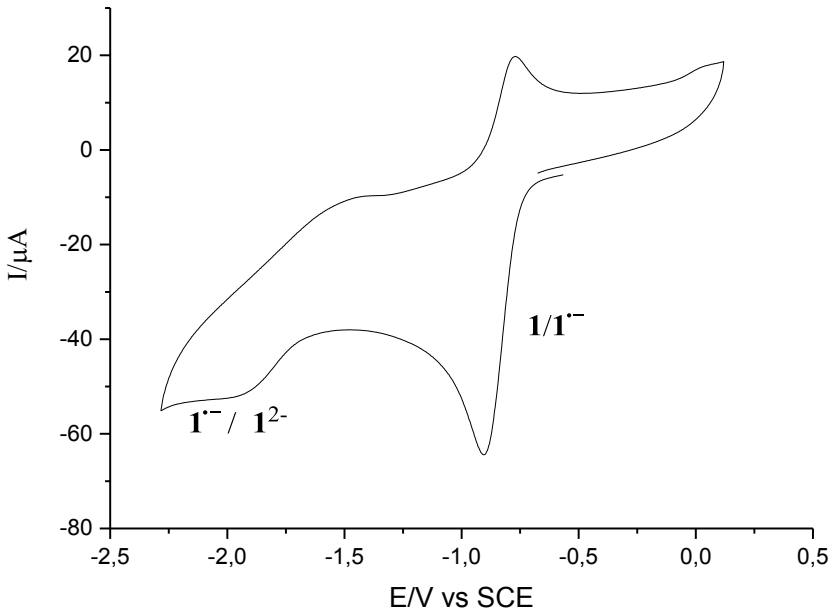
3MeTARF + KI in ACN, λ_{em} = 680 (SpectraLED λ_{ex} = 394 nm), $\tau_{Phosporescence}$ = 0.17 s

3MeTARF + KI in ACN, λ_{em} = 540 (NanoLED λ_{ex} = 368 nm), $\tau_{Fluorescence}$ = 1.5 ns

Cyclic voltametry of **1** (c = $1.0 \cdot 10^{-4}$ mol/l), Fc (c = $1.0 \cdot 10^{-4}$ mol/l) in CH_3CN/0.1 TBAHFP, ν = 500 mV/s



Cyclic voltametry of **1** (c = $1.0 \cdot 10^{-4}$ mol/l) in CH_3CN/0.1 TBAHFP, ν = 500 mV/s



Electrochemical potentials in ground and excited states

$E(1/1^{\bullet-})$ = -0.82V vs SCE from cyclic voltammetry measured using Fc+/Fc standard (0.380 V vs SCE, ref.[7]
$E(1^{\bullet-}/1^{2-})$ = -1.81V vs SCE from cyclic voltammetry measured using Fc+/Fc standard (0.380 V vs SCE, ref.[8]

Redox properties in an excited state estimated based on S1 and T1 energies (E(S) and E(T), respectively) calculated from fluorescence and phosphorescence data according to equations recommended by the literature.[8]

$\boldsymbol{E^*_{red}}$ (S) = E(S) + $\boldsymbol{E(1/1^{\bullet-})}$ = 2.58 + (-0.82) = 1.76 eV
$\boldsymbol{E^*_{red}}$ (T) = E(T) + $\boldsymbol{E(1/1^{\bullet-})}$ = 2.07 + (-0.82) = 1.25 eV

[7] V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, 2000, **298**, 97.
[8] a) N. A. Romero and D. A. Nicewicz, *Chem Rev*, 2016, **116**, 10075-10166; b) M. Murakami, K. Ohkubo and S. Fukuzumi, *Chem. Eur. J.*, 2010, **16**, 7820-7832.

S13 Fluorescence of 1 quenching with Ph_3P in acetonitrile

Absorption spectrum of **1** upon addition of Ph_3P
c(**1**) = 1.76 x 10^{-5} M

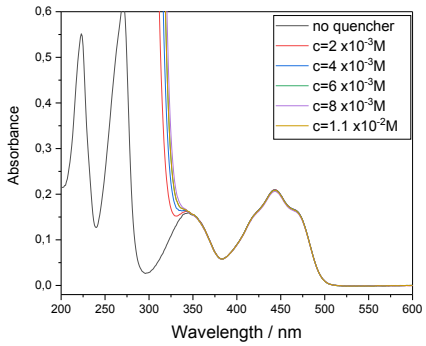


Figure 1. Changes in absorption spectrum of 3MeTARF in ACN upon addition of triphenylphosphine (Ph_3P) as a quencher.

Fluorescence quenching experiment
c(**1**) = 1.76 x 10^{-5} M

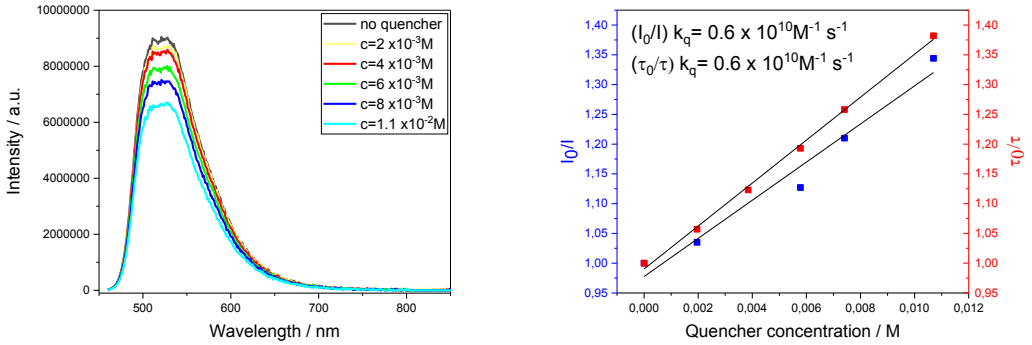
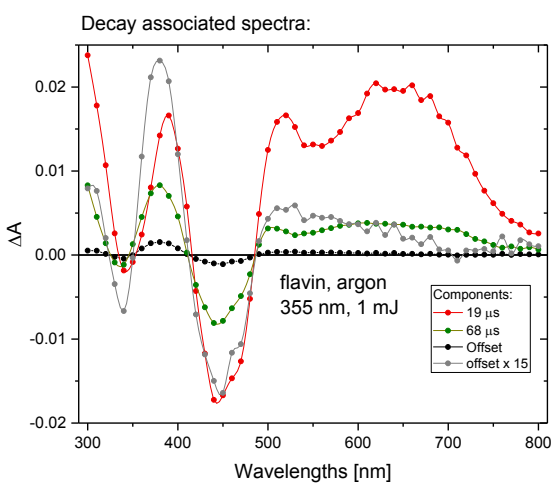


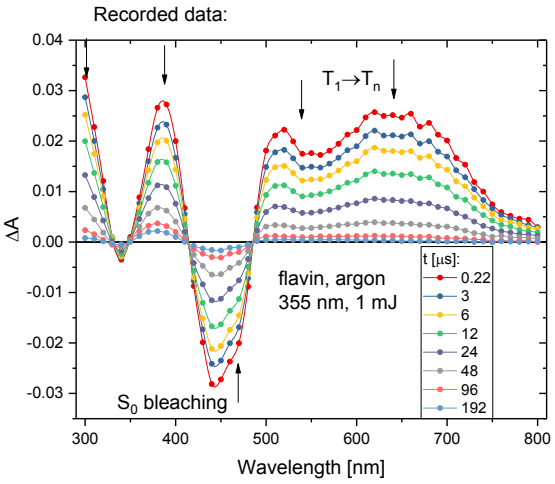
Figure 2. Changes in fluorescence spectrum of **1** in ACN (left panel) and Stern-Volmer plot (right panel) upon quenching by Ph_3P.
Conditions: quencher (Ph_3P) concentration (0 - 1.1×10^{-2} M); A(450 nm)=0.2; excitation wavelength 450 nm; excitation slit 1nm, emission slit 1nm, increment=1 nm, integration time=0.1 s.

S14 Laser flash photolysis experiments

Conditions: 355 nm as excitation wavelength, argon saturated pure flavin acetonitrile solution, 1cm×1cm cuvette, 4 mL solution

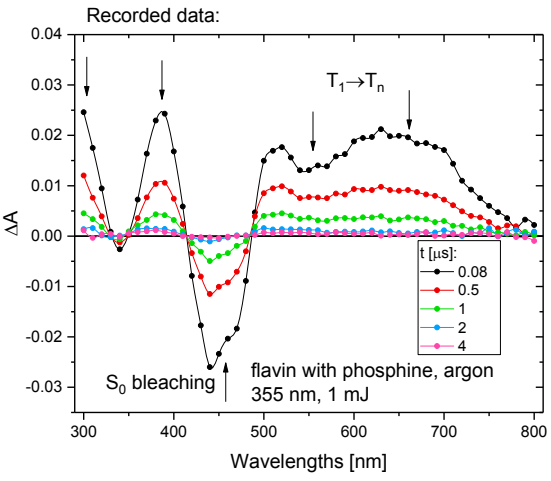
Experiment 1: flavin in the triplet excited state in water-free acetonitrile

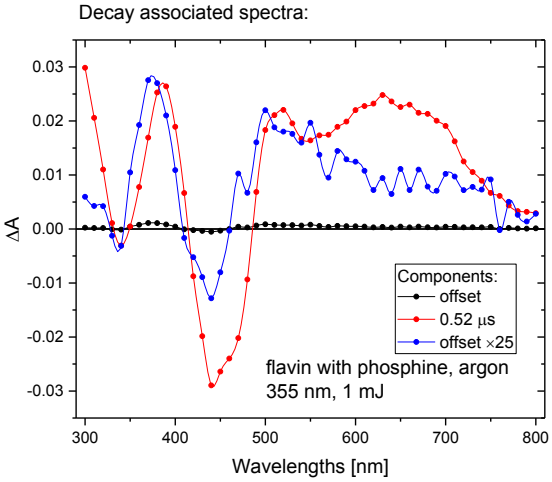




Comment: The initial transient absorption spectrum at 0.22 μs (left graph) corresponds to flavin in the excited triplet state and flavin ground state S_0 bleaching. At longer delays the decay of T_1-flavin population is observed in parallel to S_0-flavin repopulation. At 192 μs a remaining spectrum is revealed due to flavin anion absorption (formed presumably upon triplet self-quenching process involving T_1-flavin and S_0-flavin). Global analysis reveals 3 components: 19 μs due to triplet-triplet annihilation process, 68 μs represents T_1 –flavin lifetime, and the offset shows flavin anion absorption and S_0-flavin bleaching.

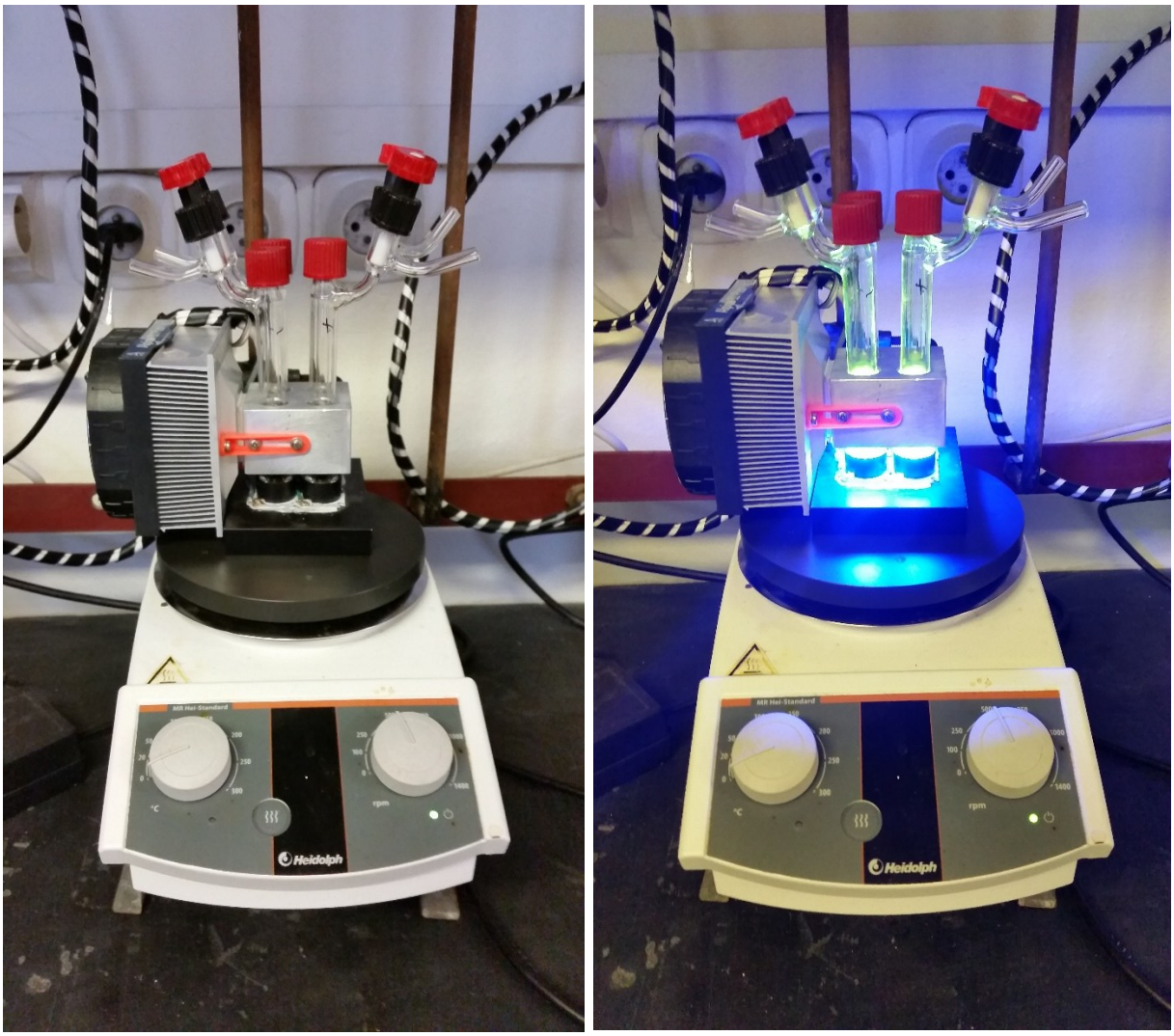
Experiment 2: quenching of flavin 1 in the T_1 state by triphenylphospine [0.7×10^{-3} M]





Comment: The initial transient absorption spectrum at. 0.08 μs (left graph) corresponds to flavin in the T_1-state and S_0 bleaching. The retrieved lifetime of T_1-flavin is drastically short (0.52 μs) due to efficient quenching by phosphine. The remaining offset is mostly due to flavin anion absorption and S_0-flavin bleaching.

S15 Experimental setup



Reactions were performed in Schlenk flask irradiated at a distance 10 mm from the bottom by blue LED (Luxeon STAR/0, 1W; 220 mW@350 mA, 2.8-4 V, 440-460 nm, $\Delta\lambda_{1/2}$= 20 nm). Schlenk flask were located in aluminium block which was tempered (±0.2 °C) by Peltier unit. Reaction mixtures were stirred (500 min^{-1}) with magnetic stirrer.