Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Novel Ruthenium-Catalyst for Hydroesterification of Olefins with Formates

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Supporting Information

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I General Methods and Materials

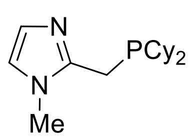
^{1}H NMR spectra were recorded on Bruker Avance 300 (300 MHz), Bruker Avance 400 (400 MHz) and Bruker Fourier 300 (300 MHz). ^{13}C NMR spectra as well as DEPT 135 spectra were acquired in a broad band decoupled mode on Bruker Avance 300 (75 MHz) and Bruker Avance 400 (101 MHz). ^{19}F (282 MHz) and ^{31}P (122 MHz) spectra were recorded on Bruker Avance 300. The measurements were carried out at ambient temperature in $CDCl_3$, toluene-d_8 or DMSO-d_6. Chemical shifts δ are given in ppm and related to the corresponding solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H NMR) and 77.16 ppm (^{13}C NMR), for toluene-d_8 2.09 ppm (^{1}H NMR) and 20.40 ppm (^{13}C NMR), and for DMSO-d_6 2.50 ppm (^{1}H NMR) and 39.52 ppm (^{13}C NMR). Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hexet), hept (heptet), , m (multiplet), br. s (broad singlet) and combinations of those.
For GC analyses, HP 6890 chromatograph with a 30 m HP5 column was used. IR spectra were obtained on Thermo Electron Nicolet FT-IR spectrometer (Thermo Electron, ATR) and the absorption bands λ^{-1} are given in cm^{-1}. The signals were assigned as w (weak), m (middle), m–s (middle to strong), s (strong) and vs (very strong). GC-MS was performed on an Agilent 6890 N/5973 chromatography mass selective detector system. Electron ionization (EI, 70 eV) mass spectra were recorded on a MAT 95XP instrument. The data are given as mass units per charge (m/z) and intensities of signals are given in parentheses. HRMS (ESI) was performed on Finnigan MAT 95XP (Thermo Electron).
X-Ray data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package.[1]
Column chromatography was performed on silica gel 60 (40–63 µm) with a suitable mixture of *n*-heptane and ethyl acetate as eluent. Thin layered chromatography was conducted on readily coated TLC plates (silica 60 F_{254}). Visualization was achieved by UV light (254 nm), coloration with cerium molybdate stain or with potassium permanganate and heating.
All reactions were carried out under argon atmosphere. Solvents, formates and aromatic alkenes used in hydroformylation reactions have been applied as purchased without further purification. Aliphatic alkenes have been purified by distillation under argon atmosphere. The solvents used in ligand and complex synthesis were purified, degased, or distilled under argon atmosphere.

II Experimental Section

A. Preparation and Characterization of Ligand 4a and Complex 6

Ligands **4b**,[2] **4c**,[2] **4f**[3] **and 5a-c**[4] have been prepared according to literature. Ligands **4d** and **4e** have been purchased and used without further purification.

2-((Dicyclohexylphosphino)methyl)-1-methyl-1H-imidazole (4a)



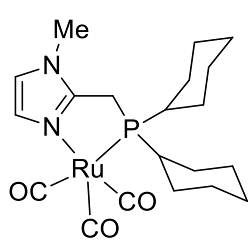
$C_{17}H_{29}N_2P$, 292.40 g mol^{-1}

Chlorodicyclohexylphosphine (1.35 ml, 6.1 mmol) was added dropwise to a solution of 1-methyl-2-((trimethylsilyl)methyl)-1*H*-imidazole (1.08 g, 6.4 mmol) in 20 ml abs. toluene at –70 °C. The reaction mixture was stirred at this temperature for 1 h. Then it was allowed to warm up slowly and was stirred at ambient temperature overnight. Afterwards the volatile components were removed under reduced pressure. The residue was dissolved in 15 ml abs. ether and washed with water (2 x 10 ml). The etheric layer was then dried over $MgSO_4$, filtrated and concentrated to a volume of ca. 5 ml, allowing the title compound to crystallize. After filtration and drying *in vacuo*, ligand **4a** was obtained as colorless solid in 76% yield. The spectral data are in agreement with the literature.[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (d, *J* = 1.3 Hz, 1H), 6.72 (dd, *J* = 1.3, 0.7 Hz, 1H), 3.61 (s, 3H), 2.87 (s, 2H), 1.82 – 1.65 (m, 8H), 1.65 – 1.46 (m, 4H), 1.36 – 1.15 (m, 8H), 1.15 – 0.93 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1 (d, *J* = 7.3 Hz, C), 126.9 (CH), 120.6 (CH), 33.5 (d, *J* = 14.3 Hz, CH), 33.4 (d, *J* = 9.5 Hz, CH_3), 29.6 (d, *J* = 13.2 Hz, CH_2), 28.7 (d, *J* = 8.7 Hz, CH_2), 27.4 (d, *J* = 10.9 Hz, CH_2), 27.2 (d, *J* = 8.1 Hz, CH_2), 26.5 (CH_2), 21.1 (d, *J* = 22.0 Hz, CH_2).
^{31}P NMR (122 MHz, $CDCl_3$) δ –6.93.

[Ru(CO)$_3$(4a)] (6)



$C_{20}H_{29}N_2O_3PRu$, 477.49 g mol^{-1}

Procedure A: Ruthenium dodecacarbonyl (0.0670 mmol, 42.6 mg) and ligand **4a** (0.200 mmol, 58.5 mg) were dissolved in 2 ml of abs. toluene. The resulting mixture was heated to 100 °C and stirred at this temperature for 45 min. After cooling to ambient temperature, the solution was first stored at –18 °C over night and afterwards at ambient temperature for several days allowing complex **6** to crystallize. Filtration followed by drying the dark orange compound *in vacuo* yielded suitable crystals for X-Ray analysis.

Procedure B: Ruthenium dodecacarbonyl (0.33 mmol, 213 mg) and ligand **4a** (1.0 mmol, 292 mg) were dissolved in 8 ml of abs. toluene. The resulting mixture was heated to 100 °C and stirred at this temperature for 45 min. After cooling to ambient temperature, the solvent was partially removed under reduced pressure allowing precipitation of complex **6**. The remaining solvent was decanted and the brown powder was dried *in vacuo* to give 40% yield (in 2:1 mixture with toluene).

^{1}H NMR (300 MHz, DMSO) δ 7.14 (t, *J* = 1.2 Hz, 1H), 6.76 (d, *J* = 1.4 Hz, 1H), 3.63 (s, 3H), 3.05 (d, *J* = 8.3 Hz, 2H), 2.02 – 1.82 (m, 4H), 1.82 – 1.53 (m, 8H), 1.41 – 1.25 (m, 6H), 1.25 – 1.03 (m, 4H).
^{13}C NMR (75 MHz, DMSO) δ 218.1 (CO), 218.0 (CO), 151.5 (d, *J* = 24.2 Hz, C), 130.9 (d, *J* = 3.6 Hz, CH), 122.8 (CH), 34.9 (CH_3), 34.7 (d, *J* = 15.7 Hz, CH), 28.1 (d, *J* = 7.0 Hz, CH_2), 26.9 (CH_2), 26.3 (d, *J* = 25.0 Hz, CH_2), 26.3 (CH_2), 25.8 (CH_2), 21.5 (d, *J* = 14.8 Hz, CH_2).
^{31}P NMR (122 MHz, DMSO) δ 64.99.

IR (ATR) λ^{-1} 2921 (m), 2853 (m), 1970 (s), 1879 (s), 1856 (vs), 1539 (w), 1495 (m), 1447 (m), 1396 (m), 1343 (w), 1283 (w), 1267 (w), 1238 (w), 1190 (w), 1170 (w), 1136 (w), 1104 (w), 1089 (w), 1038 (w), 1001 (w), 914 (w), 887 (w), 849 (m), 827 (w), 777 (w), 760 (w), 736 (s), 726 (s), 719 (m), 671 (w), 648 (m), 608 (s), 590 (s), 545 (s), 520 (m), 512 (m), 489 (m), 456 (m), 423 (s).

HRMS (ESI) calculated $C_{19}H_{30}N_2O_3PRu$ $[M+H-CO]^+$ 451.10881; found 451.10951.

Crystal data for complex **6**:

$C_{20}H_{29}N_2O_3PRu$, M = 477.49 g mol^{-1}, monoclinic, space group $P2_1/n$, a = 12.1519(4), b = 13.1631(4), c = 13.3186(4) Å, β = 99.585(1)°, V = 2100.66(11) Å^3, T = 150(2) K, Z = 4, 37175 reflections measured, 5075 independent reflections (R_{int} = 0.0216), final R values ($I > 2\sigma(I)$): R_1 = 0.0172, wR_2 = 0.0439, final R values (all data): R_1 = 0.0195, wR_2 = 0.0457, 245 parameters.

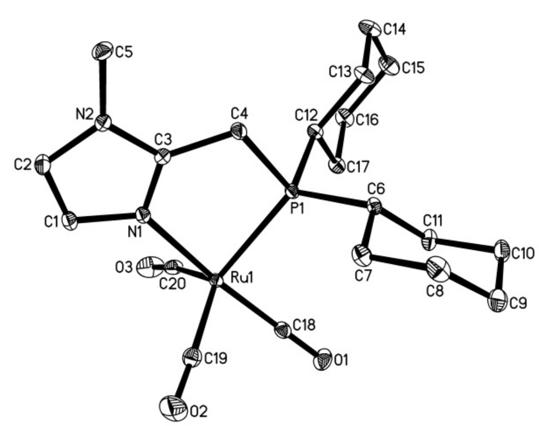
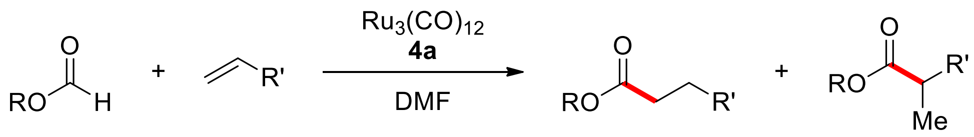


Figure S1. Crystal structure of [Ru(CO)$_3$(**4a**)] (**6**).

B. General Procedure for Hydroesterification Reaction

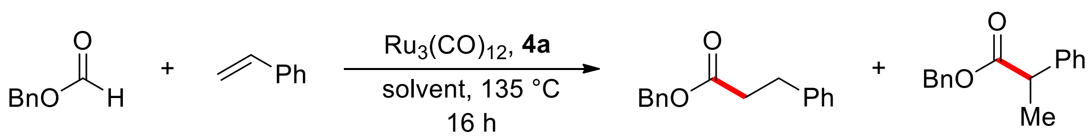


1 **2** **3** **3'**

Scheme S1. Model reaction.

Formate **1** (3.0 mmol), alkene **2** (4.5 mmol) and DMF (1.5 ml) were added to $Ru_3(CO)_{12}$ (16.0 mg, 25.0 µmol, 0.83 mol%) and 2-(dicyclohexylphosphino)methyl)-1-methyl-1*H*-imidazole (**4a**, 21.9 mg, 75.0 µmol, 2.5mol%) at ambient temperature. The reaction mixture was heated to 135 °C and stirred at this temperature for 24 h. After cooling down, it was diluted with EtOAc, washed with water and brine and dried over $MgSO_4$. The volatile components were then removed under reduced pressure and the crude product was subjected to column chromatography (eluent *n*-heptane/EtOAc) to obtain the purified product **3**. The linear to branched ratio was determined by ^{1}H NMR.
Alterations of the described conditions are marked in the table and specified in the footnotes.

Table S1. Variation of the solvents in model reaction.

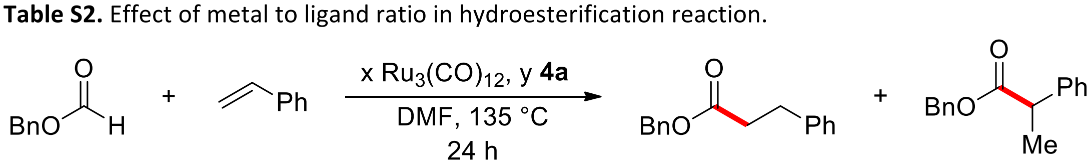


1a **2a** **3aa** **3'aa**

entry	solvent	yield^a (%)	**3aa**:**3'aa**
1	neat	90^b	50:50
2	mesitylene	82^b	48:52
3	PC	15	64:36
4	NMP	65	56:44
5	DMF	72	66:34
6	DMSO	61	69:31

a isolated yield; *b* isolating a clean product with methods described in general procedure was not possible.

Table S2. Effect of metal to ligand ratio in hydroesterification reaction.



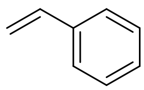
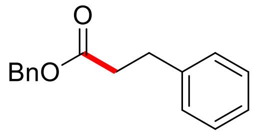
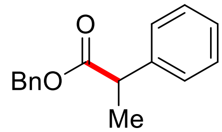
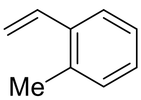
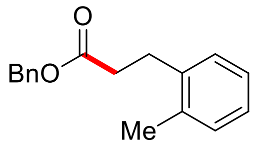
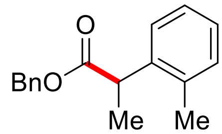
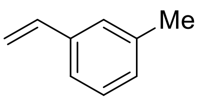
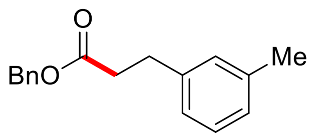
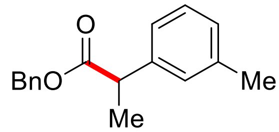
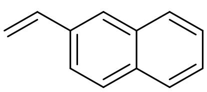
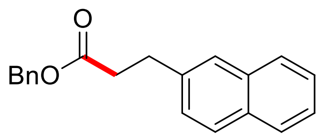
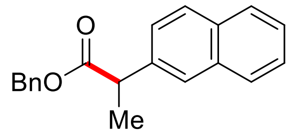
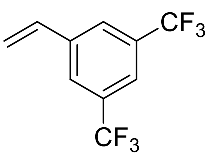
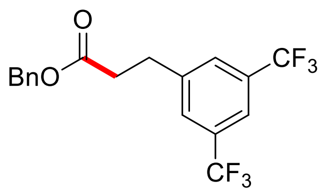
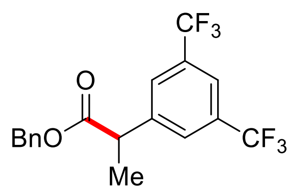
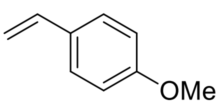
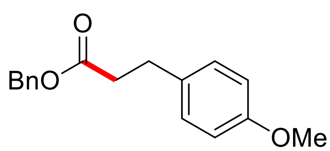
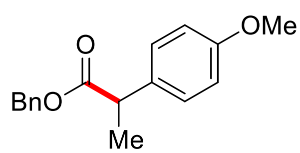
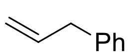
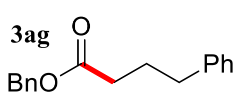
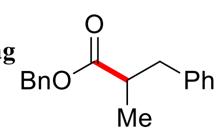
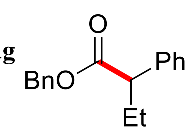
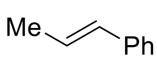
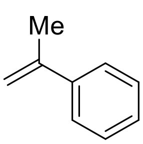
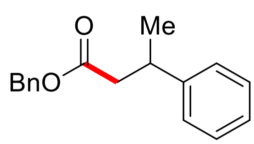
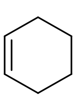
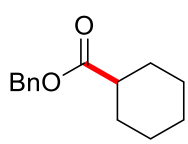
1a **2a** **3aa** **3'aa**

entry	[Ru] (mol%)	**4a** (mol%)	yield^a (%)	**3aa**:**3'aa**
1	2.5	0	2	65:35
2	2.5	1.25	20	79:21
3	5.0	2.5	42	79:21
4	2.5	2.5	89	67:33
5	2.5	5.0	traces	n.d.^{b}
6	0	2.5	n.c.^{c}	-

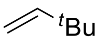
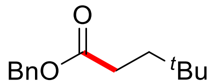
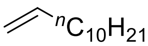
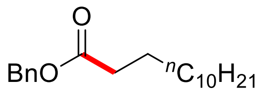
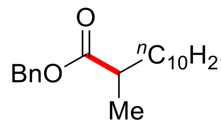
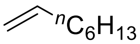
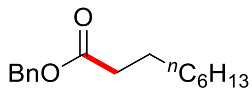
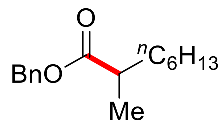
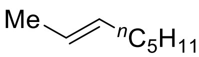
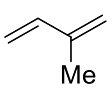
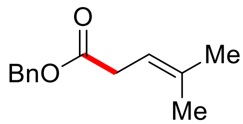
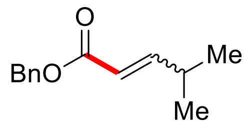
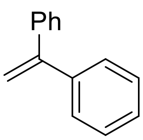
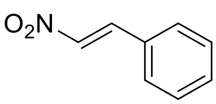
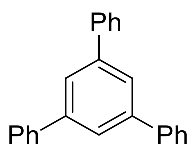
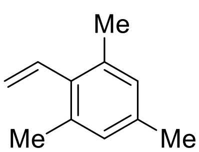
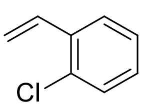
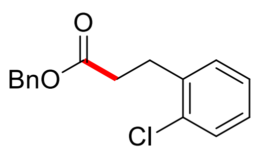
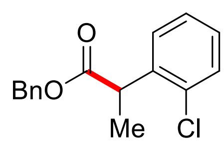
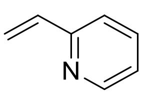
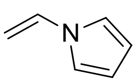
a isolated yield; *b* not definable; *c* no conversion.

C. Extended List of Tested Alkenes

Table S3. Complete list of tested alkenes **2**.

entry	alkene	products[a]			yield (%)[b] (**3ay**:**3'ay**)[c]
1	**2a** 	**3aa** 	**3'aa** 		89 (67:33)
2	**2b** 	**3ab** 	**3'ab** 		88 (76:24)
3	**2c** 	**3ac** 	**3'ac** 		85 (51:49)
4	**2d** 	**3ad** 	**3'ad** 		72 (64:36)
5	**2e** 	**3ae** 	**3'ae** 		86 (56:44)
6	**2f** 	**3af** 	**3'af** 		57 (51:49)
7[d,e]	**2g** 	**3ag** 	**3'ag** 	**3''ag** 	42 (59:22:18)
8[d,e]	**2'g** 				31 (51:29:20)
9[d,e]	**2h** 	**3ah** 			10
10[d]	**2i** 	**3ai** 			35

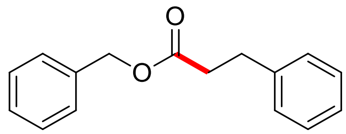
a obtained products; *b* isolated yield of hydroesterification product; *c* linear to branched ratio determined by ^{1}H NMR; *d* reaction was carried out at 150 °C; *e* 1.7mol% $Ru_3(CO)_{12}$, 5.0mol% ligand **4a**; *f* extended reaction time of 65 h; *g* high polymerization rate of alkene.

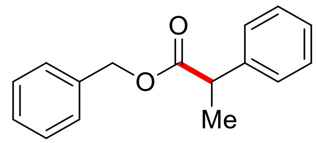
entry	alkene		products[a]				yield (%)[b] (**3ay**:**3'ay**)[c]
11[d]	**2j**		**3aj**				11 72[f]
12[d]	**2k**		**3ak**		**3'ak**		17 (76:24)
13[d,e]	**2l**		**3al**		**3'al**		21 (76:24) 44[f] (70:30)
14[d]	**2'l**						40[f] (67:33)
15	**2m**		**3am**		**3'am**		73 (82:18)
16	**2n**		no conversion				-
17[d,e]	**2o**			**7**, 15%			-
18	**2p**		no conversion				-
19	**2q**[g]		**3aq**		**3'aq**		17 (91:9)
20	**2s**		no conversion				-
21	**2t**		no conversion				-

a obtained products; *b* isolated yield of hydroesterification product; *c* linear to branched ratio determined by ^{1}H NMR; *d* reaction was carried out at 150 °C; *e* 1.7mol% $Ru_3(CO)_{12}$, 5.0mol% ligand **4a**; *f* extended reaction time of 65 h; *g* high polymerization rate of alkene.

D. Spectroscopic Data of Isolated Hydroesterification Products

Benzyl 3-phenylpropanoate (3aa) and benzyl 2-phenylpropanoate (3'aa)





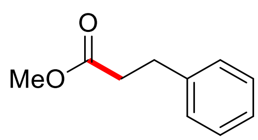
$C_{16}H_{16}O_2$, 240.30 g mol^{-1}

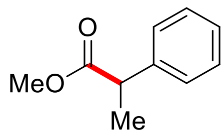
Compounds **3aa** and **3'aa** were prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and styrene (**2a**, 0.52 ml, 4.5 mmol) following the general procedure. The mixture was purified by column chromatography and obtained as colorless oil (2.66 mmol, **89%**, 67:33). The spectral data are in agreement with the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) **3aa** δ 7.50 – 7.10 (m, 10H), 5.18 (s, 2H), 3.04 (t, *J* = 7.8 Hz, 2H), 2.75 (t, *J* = 7.8 Hz, 2H); **3'aa** δ 7.50 – 7.10 (m, 10H), 5.22 (d, *J* = 13.0 Hz, 1H), 5.14 (d, *J* = 12.5 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 1H), 1.59 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) **3aa** δ 172.6 (C), 140.4 (C), 136.0 (C), 128.5 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 126.3 (CH), 66.2 (CH_2), 35.9 (CH_2), 31.0 (CH_2); **3'aa** δ 174.2 (C), 140.4 (C), 136.0 (C), 128.6 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.6 (CH), 127.2 (CH), 66.4 (CH_2), 45.5 (CH), 18.5 (CH_3).

R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.37 – 0.38.

Methyl 3-phenylpropanoate (3ba) and methyl 2-phenylpropanoate (3'ba)





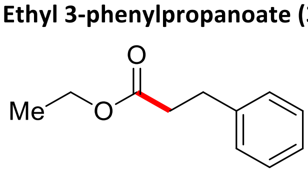
$C_{10}H_{12}O_2$, 164.20 g mol^{-1}

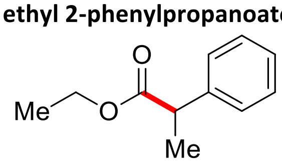
Compounds **3ba** and **3'ba** were prepared from methyl formate (**1b**, 0.19 ml, 3.0 mmol) and styrene (**2a**, 0.52 ml, 4.5 mmol) following the general procedure. The mixture was purified by column chromatography and obtained as colorless oil (2.13 mmol, **71%**, 52:48). The spectral data are in agreement with the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) **3ba** δ 7.59 – 7.14 (m, 5H), 3.74 (s, 3H), 3.01 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H); **3'ba** δ 7.59 – 7.14 (m, 5H), 3.80 (q, *J* = 7.2 Hz, 1H), 3.73 (s, 3H), 1.58 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) **3ba** δ 173.3 (C), 140.6 (C), 128.6 (CH), 128.3 (CH), 126.3 (CH), 51.6 (CH_3), 35.8 (CH_2), 31.0 (CH_2); **3'ba** δ 175.0 (C), 140.6 (C), 128.7 (CH), 127.5 (CH), 127.2 (CH), 52.0 (CH_3), 45.5 (CH), 18.7 (CH_3).

R_f (SiO_2, *n*-heptane/EtOAc 19:1) 0.21 – 0.22.

Ethyl 3-phenylpropanoate (3ca) and ethyl 2-phenylpropanoate (3'ca)





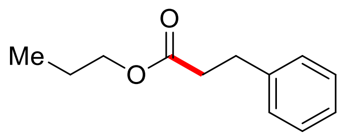
$C_{11}H_{14}O_2$, 178.23 g mol^{-1}

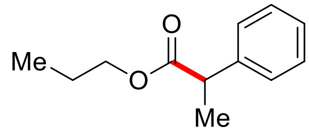
Compounds **3ca** and **3'ca** were prepared from ethyl formate (**1c**, 0.24 ml, 3.0 mmol) and styrene (**2a**, 0.52 ml, 4.5 mmol) following the general procedure. The mixture was purified by column chromatography and obtained as colorless oil (2.86 mmol, **95%**, 66:34). The spectral data are in agreement with the literature.[7,8]

^{1}H NMR (300 MHz, $CDCl_3$) **3ca** δ 7.43 – 7.20 (m, 5H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.03 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); **3'ca** δ 7.43 – 7.22 (m, 5H), 4.30 – 4.05 (m, 2H), 3.78 (q, *J* = 7.2 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) **3ca** δ 172.9 (C), 140.6 (C), 128.5 (CH), 128.4 (CH), 126.3 (CH), 60.4 (CH_2), 36.0 (CH_2), 31.1 (CH_2), 14.3 (CH_3); **3'ca** δ 174.6 (C), 140.8 (C), 128.6 (CH), 127.5 (CH), 127.1 (CH), 60.8 (CH_2), 45.6 (CH), 18.7 (CH), 14.2 (CH_3).

R_f (SiO_2, *n*-heptane/EtOAc 19:1) 0.27 – 0.28.

Propyl 3-phenylpropanoate (3da) and propyl 2-phenylpropanoate (3'da)





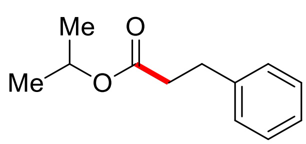
$C_{12}H_{16}O_2$, 192.25 g mol^{-1}

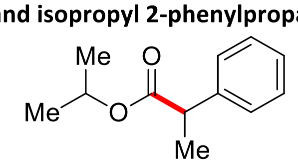
Compounds **3da** and **3'da** were prepared from *n*-propyl formate (**1d**, 0.29 ml, 3.0 mmol) and styrene (**2a**, 0.52 ml, 4.5 mmol) following the general procedure. The mixture was purified by column chromatography and obtained as colorless oil (2.83 mmol, **94%**, 64:36). The spectral data are in agreement with the literature.[6]

^{1}H NMR (300 MHz, $CDCl_3$) **3da** δ 7.40 – 7.29 (m, 3H), 7.29 – 7.20 (m, 2H), 4.07 (t, *J* = 6.7 Hz, 2H), 3.00 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 1.73 – 1.57 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); **3'da** δ 7.40 – 7.29 (m, 3H), 7.29 – 7.20 (m, 2H), 4.07 (t, *J* = 6.7 Hz, 2H), 3.76 (q, *J* = 7.2 Hz, 1H), 1.73 – 1.57 (m, 2H), 1.55 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) **3da** δ 172.9 (C), 140.6 (C), 128.5 (CH), 128.3 (CH), 126.2 (CH), 66.1 (CH_2), 35.9 (CH_2), 31.0 (CH_2), 22.0 (CH_2), 10.4 (CH_3); **3'da** δ 174.6 (C), 140.8 (C), 128.6 (CH), 127.5 (CH), 127.1 (CH), 66.3 (CH_2), 45.6 (CH_3), 22.0 (CH_2), 18.5 (CH), 10.3 (CH_3).

R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.43 – 0.44.

Isopropyl 3-phenylpropanoate (3ea) and isopropyl 2-phenylpropanoate (3'ea)





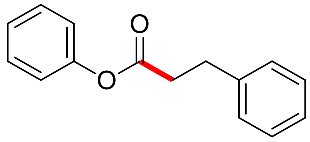
$C_{12}H_{16}O_2$, 192.25 g mol^{-1}

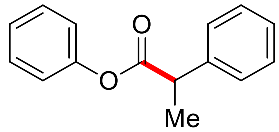
Compounds **3ea** and **3'ea** were prepared from isopropyl formate (**1e**, 0.30 ml, 3.0 mmol) and styrene (**2a**, 0.52 ml, 4.5 mmol) following the general procedure. The mixture was purified by column chromatography and obtained as colorless oil (1.04 mmol, **35%**, 83:17). The spectral data are in agreement with the literature.[6]

^{1}H NMR (300 MHz, $CDCl_3$) **3ea** δ 7.37 – 7.21 (m, 5H), 5.05 (hept, *J* = 6.3 Hz, 1H), 2.98 (t, *J* = 7.8 Hz, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.24 (d, *J* = 6.3 Hz, 6H); **3'ea** δ 7.37 – 7.21 (m, 5H), 5.04 (hept, *J* = 6.2 Hz, 1H), 3.71 (q, *J* = 7.2 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) **3ea** δ 172.4 (C), 140.6 (C), 128.5 (CH), 128.4 (CH), 126.2 (CH), 67.7 (CH), 36.3 (CH_2), 31.1 (CH_2), 21.8 (CH_3); **3'ea** δ 174.0 (C), 140.9 (C), 128.5 (CH), 127.5 (CH), 127.0 (CH), 67.9 (CH), 45.8 (CH), 21.8 (CH_3), 21.6 (CH_3), 18.6 (CH_3).
R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.37 – 0.38.

Phenyl 3-phenylpropanoate (3ga) and phenyl 2-phenylpropanoate (3'ga)





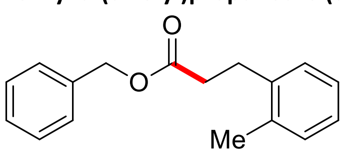
$C_{15}H_{14}O_2$, 226.27 g mol^{-1}

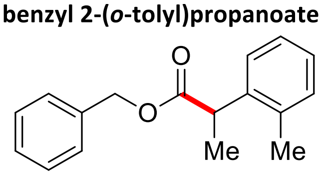
Compounds **3ga** and **3'ga** were prepared from phenyl formate (**1g**, 0.33 ml, 3.0 mmol) and styrene (**2a**, 0.52 ml, 4.5 mmol) following the general procedure. The mixture was purified by column chromatography and obtained as colorless oil (1.68 mmol, **56%**, 96:4). The spectral data are in agreement with the literature.[9,10]

^{1}H NMR (300 MHz, $CDCl_3$) **3ga** δ 7.53 – 7.25 (m, 8H), 7.16 – 7.09 (m, 2H), 3.17 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H); **3'ga** δ 7.53 – 7.25 (m, 8H), 7.16 – 7.09 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 1H), 1.72 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) **3ga** δ 171.4 (C), 150.7 (C), 140.2 (C), 129.4 (CH), 128.6 (CH), 128.4 (CH), 126.5 (CH), 125.8 (CH), 121.6 (CH), 36.0 (CH_2), 31.0 (CH_2); **3'ga** δ 173.0 (C), 150.9 (C), 140.9 (C), 129.4 (CH), 128.8 (CH), 127.6 (CH), 127.4 (CH), 121.4 (CH), 45.7 (CH), 18.6 (CH_3).

R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.37.

Benzyl 3-(*o*-tolyl)propanoate (3ab) and benzyl 2-(*o*-tolyl)propanoate (3'ab)





$C_{17}H_{18}O_2$, 254.32 g mol^{-1}

Compounds **3ab** and **3'ab** were prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and 2-methylstyrene (**2b**, 0.58 ml, 4.5 mmol) following the general procedure. The mixture was purified by column chromatography and obtained as colorless oil (2.64 mmol, **88%**, 76:24).

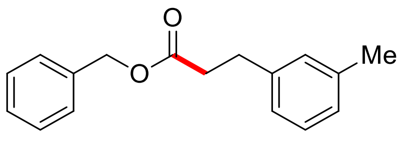
^{1}H NMR (300 MHz, $CDCl_3$) **3ab** δ 7.54 – 7.33 (m, 5H), 7.35 – 7.17 (m, 4H), 5.26 (s, 2H), 3.11 (t, *J* = 7.8 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.45 (s, 3H); **3'ab** δ 7.54 – 7.33 (m, 5H), 7.35 – 7.17 (m, 4H), 5.30 (d, *J* = 12.7 Hz, 1H), 5.19 (d, *J* = 12.5 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 2.49 (s, 3H), 1.64 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) **3ab** δ 172.8 (C), 138.6 (C), 136.0 (C), 130.3 (CH), 128.6 (CH), 128.6 (CH), 128.3 (CH), 126.5 (CH), 126.2 (CH), 66.3 (CH_2), 34.6 (CH_2), 28.3 (CH_2), 19.3 (CH_3); **3'ab** δ 174.6 (C), 139.0 (C), 136.1 (C), 135.7 (C), 130.5 (CH), 128.5 (CH), 128.1 (CH), 127.9 (CH), 127.0 (CH), 126.6 (CH), 126.4 (CH), 66.4 (CH_2), 41.4 (CH), 19.7 (CH_3), 17.9 (CH_3).

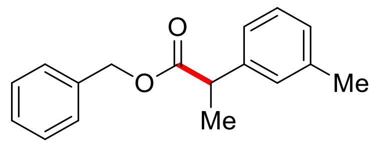
R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.38.

IR (ATR) λ^{-1} 3065 (w), 3031 (w), 2948 (w), 1731 (vs), 1604 (w), 1494 (m), 1455 (m), 1380 (m), 1354 (w), 1283 (w), 1231 (w), 1212 (m), 1149 (vs), 1106 (m), 1082 (w), 1053 (w), 1029 (w), 1002 (w), 909 (w), 825 (w), 731 (s), 696 (vs), 578 (w), 493 (w), 454 (m).

MS (GC-MS, EI) **3ab** m/z (%) 254 (5) [M^+], 194 (19), 181 (2), 163 (58), 133 (25), 121 (87), 105 (27), 91 (100), 77 (20), 65 (21); **3'ab** m/z 254 (4) [M^+], 181 (4), 163 (6), 119 (100), 104 (6), 91 (61), 77 (9), 65 (12).
HR-MS (EI) m/z calcd. for $C_{17}H_{18}O_2$ 254.13013, found 254.12997.

Benzyl 3-(*m*-tolyl)propanoate (3ac) and benzyl 2-(*m*-tolyl)propanoate (3'ac)





$C_{17}H_{18}O_2$, 256.32 g mol^{-1}

Compounds **3ac** and **3'ac** were prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and 3-methylstyrene (**2c**, 0.60 ml, 4.5 mmol) following the general procedure. The mixture was purified by column chromatography and obtained as colorless oil (2.55 mmol, **85%**, 67:33).

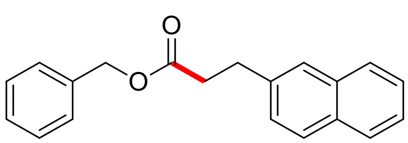
^{1}H NMR (300 MHz, $CDCl_3$) **3ac** δ 7.68 – 7.52 (m, 4H), 7.52 – 7.39 (m, 2H), 7.39 – 7.21 (m, 3H), 5.37 (s, 2H), 3.20 (t, *J* = 7.8 Hz, 2H), 2.94 (t, *J* = 7.8 Hz, 2H), 2.57 (s, 3H); **3'ac** 7.68 – 7.52 (m, 4H), 7.52 – 7.39 (m, 2H), 7.39 – 7.21 (m, 3H), 5.42 (d, *J* = 12.5 Hz, 1H), 5.32 (d, *J* = 12.5 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 1H), 2.58 (s, 3H), 1.77 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) **3ac** δ 174.5 (C), 140.4 (C), 138.1 (C), 136.0 (C), 128.5 (CH), 128.3 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 66.4 (CH_2), 36.0 (CH_2), 31.0 (CH_2), 21.5 (CH_3); **3'ac** δ 172.8 (C), 140.4 (C), 138.3 (C), 136.1 (C), 129.2 (CH), 128.6 (CH), 128.6 (CH), 128.5 (CH), 127.1 (CH), 125.4 (CH), 124.7 (CH), 66.3 (CH_2), 45.5 (CH), 21.5 (CH_3), 18.6 (CH_3).

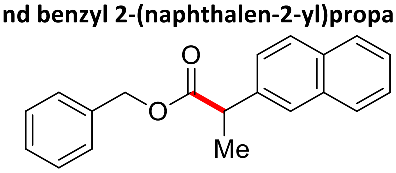
R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.42.

IR (ATR) λ^{-1} 3062 (w), 3032 (w), 2976 (w), 2935 (w), 2875 (w), 1731 (vs), 1608 (w), 1589 (w), 1497 (w), 1455 (m), 1378 (w), 1330 (w), 1293 (w), 1232 (m), 1166 (s), 1148 (vs), 1082 (m), 1056 (w), 1028 (w), 1001 (w), 904 (w), 882 (w), 780 (m), 735 (s), 695 (vs), 579 (w), 497 (w), 443 (m).

MS (GC-MS, EI) m/z (%) 254 (4) [M^+], 119 (100), 103 (4), 91 (53), 77 (8), 65 (10).
HR-MS (EI) m/z calcd. for $C_{17}H_{18}O_2$ 254.13013, found 254.12956.

Benzyl 3-(naphthalen-2-yl)propanoate (3ad) and benzyl 2-(naphthalen-2-yl)propanoate (3'ad)





$C_{20}H_{18}O_2$, 290.36 g mol^{-1}

Compounds **3ad** and **3'ad** were prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and 2-vinylnaphthalene (**2d**, 0.69 g, 4.5 mmol) following the general procedure. The mixture was purified by column chromatography and obtained as yellowish oil (2.16 mmol, **72%**, 67:33).

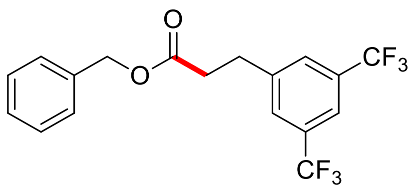
^{1}H NMR (300 MHz, $CDCl_3$) **3ad** δ 7.88 – 7.72 (m, 3H), 7.65 (s, 1H), 7.52 – 7.41 (m, 2H), 7.38 – 7.27 (m, 6H), 5.14 (s, 2H), 3.17 (t, *J* = 7.8 Hz, 2H), 2.81 (t, *J* = 7.8 Hz, 2H); **3'ad** δ 7.88 – 7.72 (m, 3H), 7.65 (s, 1H), 7.52 – 7.41 (m, 2H), 7.38 – 7.27 (m, 6H), 5.22 (d, *J* = 12.5 Hz, 1H), 5.10 (d, *J* = 12.5 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) **3ad** δ 172.8 (C), 138.0 (C), 136.00 (C), 133.7 (C), 132.3 (C), 128.6 (CH), 128.3 (CH), 128.2 (CH), 127.7 (CH), 127.7 (CH), 127.1 (CH), 126.6 (CH), 126.1 (CH), 125.5 (CH), 66.4 (CH_2), 35.9 (CH_2), 31.2 (CH_2); **3'ad** δ 174.4 (C), 138.0 (C), 136.1 (C), 133.6 (C), 132.7 (C), 128.6 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 126.3 (CH), 126.2 (CH), 125.9 (CH), 66.6 (CH_2), 45.8 (CH), 18.7 (CH_3).

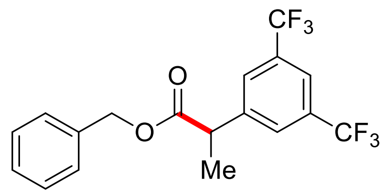
R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.32 – 0.35.

IR (ATR) λ^{-1} 3053 (w), 2936 (w), 1730 (vs), 1632 (w), 1600 (w), 1508 (w), 1498 (w), 1455 (m), 1380 (w), 1349 (w), 1290 (m), 1212 (m), 1153 (s), 1145 (s), 1081 (w), 1019 (w), 962 (m), 892 (w), 855 (m), 816 (s), 741 (vs), 695 (vs), 651 (w), 620 (w), 578 (w), 474 (vs).

MS (GC-MS, EI) **3ad** m/z (%) 290 (29) [M^+], 199 (46), 157 (100), 141 (27), 129 (24), 115 (17), 91 (50), 77 (10), 65 (11); **3'ad** m/z (%)290 (20) [M^+], 155 (100), 128 (9), 91 (28), 77 (5), 65 (5).
HR-MS (EI) m/z calcd. for $C_{20}H_{18}O_2$ 290.13013, found 290.12990.

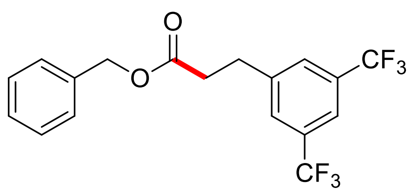
Benzyl 3-(3,5-bis(trifluoromethyl)phenyl)propanoate (3ae) and enzyl 2-(3,5-bis(trifluoromethyl)phenyl)propanoate (3'ae)





$C_{18}H_{14}F_6O_2$, 376.29 g mol^{-1}

Compounds **3ae**and **3'ae** were prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and styrene (**2e**, 0.50 ml, 2.7 mmol) following the general procedure. The esters were isolated by column chromatography as colorless oils giving **3ae** in 48% (1.29 mmol) and **3'ae** in 38% (1.02 mmol) yield.



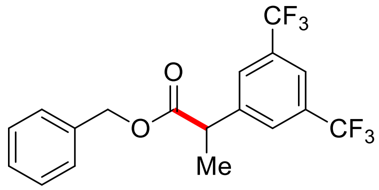
3ae

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (br. s, 1H), 7.66 (br. s, 2H), 7.47 – 7.27 (m, 5H), 5.11 (s, 2H), 3.10 (t, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9 (C), 142.9 (C), 135.7 (C), 131.9 (q, *J* = 33.1 Hz, C), 128.7 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 123.5 (q, *J* = 272.5 Hz, C), 120.6 (hept, *J* = 3.7 Hz, CH), 66.8 (CH_2), 35.2 (CH_2), 30.6 (CH_2).
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.46.

R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.32.

IR (ATR) λ^{-1} 3037 (w), 2952 (w), 1735 (m–s), 1622 (w), 1499 (w), 1456 (w), 1378 (m–s), 1358 (m), 1275 (vs), 1166 (s), 1125 (vs), 1107 (s), 1051 (w), 1029 (w), 1002 (w), 892 (m–s), 867 (w), 844 (m), 744 (m), 736 (m), 725 (m), 703 (m–s), 697 (s), 682 (s), 577 (w), 501 (w), 461 (w).

MS (GC-MS, EI) m/z (%) 376 (8) [M^+], 357 (5), 316 (5), 241 (12), 201 (10), 151 (5), 108 (60), 91 (100), 65 (10).
HR-MS (EI) m/z calcd. for $C_{18}H_{14}F_6O_2$ 376.08925; found 376.08840.



3'ae

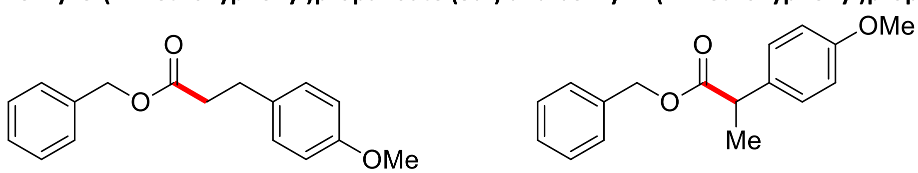
^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.79 (br. s, 1H), 7.75 (br. s, 2H), 7.42 – 7.28 (m, 3H), 7.28 – 7.16 (m, 2H), 5.14 (s, 2H), 3.91 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H).
^{13}**C NMR** (75 MHz, $CDCl_3$) δ 172.9 (C), 142.8 (C), 135.5 (C), 132.0 (q, *J* = 33.3 Hz, C), 128.7 (CH), 128.6 (CH), 128.2 (CH), 128.2 (CH), 128.1 (CH), 123.4 (q, *J* = 272.8 Hz, C), 121.5 (hept, *J* = 3.7 Hz, CH), 67.3 (CH_2), 45.4 (CH), 18.5 (CH_3).
^{19}**F NMR** (282 MHz, $CDCl_3$) δ –62.44.

$\mathbf{R}_f$ (SiO_2, *n*-heptane/EtOAc 9:1) 0.40.

IR (ATR) λ^{-1} 3070 (w), 3037 (w), 2985 (w), 2943 (w), 1736 (m–s), 1623 (w), 1499 (w), 1462 (w), 1457 (w), 1372 (m–s), 1275 (vs), 1166 (vs), 1125 (vs), 1086 (m–s), 1063 (m), 1016 (w), 953 (w), 898 (s), 846 (m), 786 (w), 751 (m), 726 (m), 697 (s), 681 (s), 602 (w), 495 (w), 456 (w).

MS (GC-MS, EI) m/z (%) 376 (2) [M^+], 357 (1), 303 (15), 241 (7), 221 (5), 201 (9), 151 (3), 108 (2), 91 (100), 65 (7).
HR-MS (EI) m/z calcd. for $C_{18}H_{14}F_6O_2$ 376.08925; found 376.08838.

Benzyl 3-(4-methoxyphenyl)propanoate (3af) and benzyl 2-(4-methoxyphenyl)propanoate (3'af)

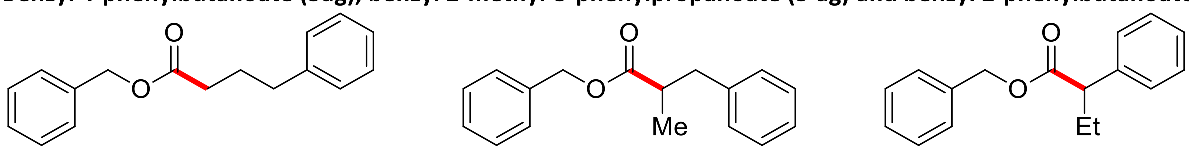


$C_{17}H_{18}O_3$, 270.32 g mol^{-1}
Compounds **3af** and **3'af** were prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and 4-vinylanisole (**2f**, 0.60 ml, 4.5 mmol) following the general procedure. The mixture was purified by column chromatography and obtained as colorless oil (1.70 mmol, **57%**, 51:49). The spectral data are in agreement with the literature.[5]

^{1}**H NMR** (300 MHz, $CDCl_3$) **3af** δ 7.45 – 7.33 (m, 4H), 7.33 – 7.25 (m, 2H), 7.20 – 7.11 (m, 1H), 6.89 (dd, *J* = 11.8, 8.7 Hz, 2H), 5.16 (s, 2H), 3.82 (s, 3H), 2.97 (t, *J* = 7.7 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H); **3'af** δ 7.45 – 7.33 (m, 4H), 7.33 – 7.25 (m, 2H), 7.20 – 7.11 (m, 1H), 6.89 (dd, *J* = 11.8, 8.7 Hz, 2H), 5.21 (d, *J* = 13.2 Hz, 1H), 5.11 (d, *J* = 12.6 Hz, 1H), 3.83 (s, 3H), 3.79 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H).
^{13}**C NMR** (75 MHz, $CDCl_3$) **3af** δ 172.8 (C), 158.1 (C), 136.0 (C), 132.5 (C), 129.3 (CH), 128.6 (CH), 128.2 (CH), 128.2 (CH), 113.9 (CH), 66.2 (CH_2), 55.2 (CH_3), 36.2 (CH_2), 30.2 (CH_2); **3'af** δ 174.6 (C), 158.8 (C), 136.1 (C), 132.6 (C), 128.6 (CH), 128.5 (CH), 128.1 (C), 127.9 (C), 114.0 (CH), 66.4 (CH_2), 55.3 (CH_3), 44.7 (CH), 18.6 (CH_3).

$\mathbf{R}_f$ (SiO_2, *n*-heptane/EtOAc 4:1) 0.41.

Benzyl 4-phenylbutanoate (3ag), benzyl 2-methyl-3-phenylpropanoate (3'ag) and benzyl 2-phenylbutanoate (3''ag)



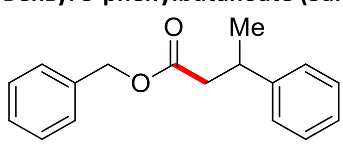
$C_{17}H_{18}O_2$, 254.32 g mol^{-1}

Compounds **3ag**, **3'ag** and **3''ag** were prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and either allylbenzene (**2g**, 0.60 ml, 4.5 mmol; Table S3, entry 7) or β-methyl styrene (**2'g**, 0.58 ml, 4.5 mmol; Table S3, entry 8). The reactions were carried out at 150 °C applying 5mol% of the catalyst composed of $Ru_3(CO)_{12}$ (0.05 mmol, 31.96 mg) and ligand **4a** (0.15 mmol, 43.86 mg) under otherwise standard conditions. The mixture was purified by column chromatography and obtained as colorless oil in **42%** (1.26 mmol, 59:22:18) yield from **2g** and **31%** (0.93 mmol, 51:29:20) from **2'g**, respectively. The spectral data are in agreement with the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) **3ag** δ 7.33 – 6.97 (m, 10H), 5.00 (s, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.26 (t, *J* = 7.6 Hz, 2H), 1.87 (p, *J* = 7.6 Hz, 2H); **3'ag** δ 7.33 – 6.97 (m, 10H), 4.97 (s, 2H), 2.94 (dd, *J* = 13.0, 6.8 Hz, 1H), 2.70 (h, *J* = 6.8 Hz, 1H), 2.63 – 2.55 (m, 1H), 1.08 (d, *J* = 6.8 Hz, 3H); **3''ag** δ 7.33 – 6.97 (m, 10H), 5.07 (d, *J* = 12.5 Hz, 1H), 4.92 (d, *J* = 12.4 Hz, 1H), 3.41 (t, *J* = 7.7 Hz, 1H), 2.11 – 1.94 (m, 1H), 1.80 – 1.64 (m, 1H), 0.78 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) **3ag** δ 173.2 (C), 141.3 (C), 136.1 (C), 129.0 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 126.0 (CH), 66.2 (CH_2), 35.2 (CH_2), 33.7 (CH_2), 26.6 (CH_2); **3'ag** δ 175.8 (C), 39.3 (C), 136.1 (C), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 126.3 (CH), 66.1 (CH_2), 41.6 (CH), 39.8 (CH_2), 16.9 (CH_3); **3''ag** δ 173.8 (C), 139.0 (C), 136.1 (C), 128.6 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 66.3 (CH_2), 53.6 (CH), 26.8 (CH_2), 12.2 (CH_3).

R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.34 – 0.39.

Benzyl 3-phenylbutanoate (3ah)



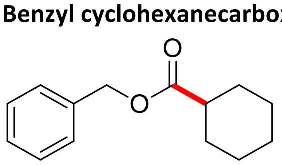
$C_{17}H_{18}O_2$, 254.32 g mol^{-1}

Compound **3ah** was prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and α-methyl styrene (**2h**, 0.58 ml, 4.5 mmol). The reaction was carried out at 150 °C applying 5mol% of the catalyst composed of $Ru_3(CO)_{12}$ (0.05 mmol, 31.96 mg) and ligand **4a** (0.15 mmol, 43.86 mg) under otherwise standard conditions. The product was purified by column chromatography and obtained as colorless oil (0.29 mmol, **10%**). The spectral data are in agreement with the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.02 (m, 10H), 4.96 (s, 2H), 3.21 (h, *J* = 7.1 Hz, 1H), 2.58 (dd, *J* = 15.1, 7.2 Hz, 1H), 2.50 (dd, *J* = 15.1, 8.0 Hz, 1H), 1.20 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3 (C), 145.7 (C), 136.0 (C), 128.6 (CH), 128.6 (CH), 128.3 (CH), 126.9 (CH), 126.5 (CH), 66.3 (CH_2), 43.0 (CH_2), 36.7 (CH), 22.0 (CH_3).

R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.31.

Benzyl cyclohexanecarboxylate (3ai)



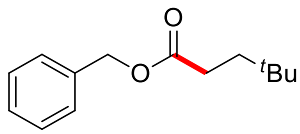
$C_{14}H_{18}O_2$, 218.29 g mol^{-1}

Compound **3ai** was prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and cyclohexene (**2i**, 0.46 ml, 4.5 mmol). The reaction was carried out at 150 °C under otherwise standard conditions. The product was purified by column chromatography and obtained as colorless oil (1.05 mmol, **35%**). The spectral data are in agreement with the literature.[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 5.12 (s, 2H), 2.37 (tt, *J* = 11.3, 3.6 Hz, 1H), 2.08 – 1.86 (m, 2H), 1.82 – 1.73 (m, 2H), 1.69 – 1.60 (m, 1H), 1.56 – 1.40 (m, 2H), 1.38 – 1.18 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 175.9 (C), 136.4 (C), 128.6 (CH), 128.1 (CH), 128.0 (CH), 66.0 (CH_2), 43.3 (CH), 29.1 (CH_2), 25.8 (CH_2), 25.5 (CH_2).

R*f* (SiO_2, *n*-heptane/EtOAc 9:1) 0.42.

Benzyl 4,4-dimethylpentanoate (3aj)



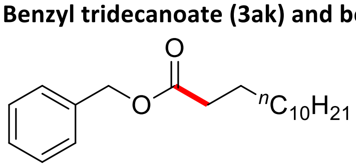
$C_{14}H_{20}O_2$, 220.31 g mol^{-1}

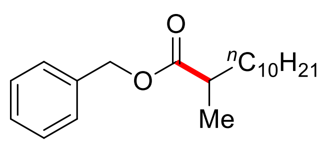
Compound **3aj** was prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and 3,3-dimethyl-1-butene (**2j**, 0.58 ml, 4.5 mmol). The reaction was carried out at 150 °C under otherwise standard conditions. The product was purified by column chromatography and obtained as colorless oil (0.31 mmol, **11%**). The spectral data are in agreement with the literature.[12]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.12 (s, 2H), 2.39 – 2.29 (m, 2H), 1.65 – 1.53 (m, 2H), 0.90 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4 (C), 136.2 (C), 128.7 (CH), 128.4 (CH), 128.3 (CH), 66.3 (CH_2), 38.7 (CH_2), 30.3, (CH_2) 30.2 (C), 29.1 (CH_3).

R*f* (SiO_2, *n*-heptane/EtOAc 9:1) 0.47.

Benzyl tridecanoate (3ak) and benzyl 2-methyldodecanoate (3'ak)





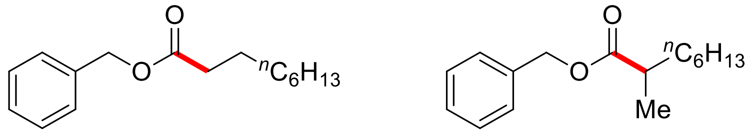
$C_{20}H_{32}O_2$, 304.47 g mol^{-1}

Compounds **3ak** and **3'ak** were prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and 1-dodecene (**2k**, 1.00 ml, 4.5 mmol). The reaction was carried out at 150 °C under otherwise standard conditions. The mixture was purified by column chromatography and obtained as colorless oil (0.50 mmol, **17%**, 76:24). The spectral data are in agreement with the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) **3ak** 7.41 – 7.28 (m, 5H), 5.12 (s, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.64 (p, *J* = 7.4 Hz, 2H), 1.28 – 1.24 (m, 18H), 0.88 (t, *J* = 6.7 Hz, 3H); **3'ak** δ 7.41 – 7.28 (m, 5H), 5.12 (s, 2H), 2.48 (h, *J* = 6.9 Hz, 1H), 1.69 – 1.59 (m, 2H), 1.28 – 1.24 (m, 16H), 1.16 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H).

R*f* (SiO_2, *n*-heptane/EtOAc 9:1) 0.54.

Benzyl nonanoate (3al) and benzyl 2-methyloctanoate (3'al)



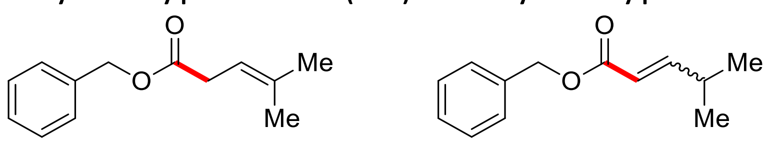
$C_{16}H_{24}O_2$, 248.36 g mol^{-1}

Compounds **3al** and **3'al** were prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and either 1-octene (**2l**, 0.70 ml, 4.5 mmol) or 2-octene (**2'l**, 0.70 ml, 4.5 mmol). The reactions were carried out at 150 °C and 65 h reaction time under otherwise standard conditions. The product mixture was purified by column chromatography and obtained as colorless oil in **44%** (1.33 mmol, 70:30) yield from **2l** and **40%** (1.21 mmol, 67:33) yield from **2'l**, respectively. The spectral data are in agreement with the literature.[13,14]

^{1}H NMR (300 MHz, $CDCl_3$) **3al** δ 7.44 – 7.27 (m, 5H), 5.13 (s, 2H), 2.37 (t, *J* = 7.5 Hz, 2H), 1.66 (p, *J* = 7.5 Hz, 2H), 1.37 – 1.22 (m, 10H), 0.90 (t, *J* = 6.8 Hz, 3H); **3'al** δ 7.44 – 7.27 (m, 5H), 5.13 (s, 2H), 2.51 (q, *J* = 7.0 Hz, 1H), 1.37 – 1.22 (m, 10H), 1.18 (d, *J* = 7.0 Hz, 3H), 0.93 – 0.86 (m, 3H).

R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.48 – 0.49.

Benzyl 4-methylpent-3-enoate (3am) and benzyl 4-methylpent-2-enoate (3'am)



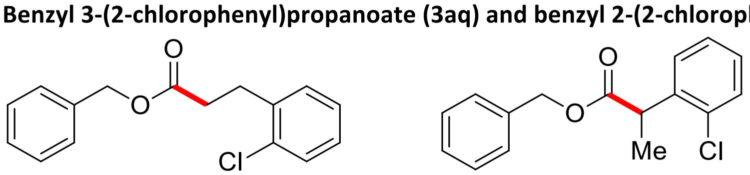
$C_{13}H_{16}O_2$, 204.26 g mol^{-1}

Compounds **3am** and **3'am** were prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and isoprene (**2m**, 0.45 ml, 4.5 mmol) following the general procedure. The product mixture was purified by column chromatography and obtained as colorless oil (2.20 mmol, **73%**, 82:18). The spectral data are in agreement with the literature.[15,16]

^{1}H NMR (300 MHz, $CDCl_3$) **3am** δ 7.41 – 7.29 (m, 5H), 5.36 (m, 1H), 5.14 (s, 2H), 3.13 – 3.08 (m, 2H), 1.79 – 1.75 (m, 3H), 1.66 – 1.64 (m, 3H); **3'am** δ 7.46 – 7.28 (m, 5H), 7.03 (dd, *J* = 15.7, 6.7 Hz, 1H), 5.85 (dd, *J* = 15.7, 1.5 Hz, 1H), 5.20 (s, 2H), 2.53 – 2.42 (m, 1H), 1.08 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) **3am** δ 172.3 (C), 136.1 (C), 135.7 (C), 128.6 (CH), 128.2 (CH), 115.8 (CH), 66.4 (CH_2), 33.9 (CH_2), 25.7 (CH_3), 18.1 (CH_3); **3'am** δ 166.9 (C), 156.2 (CH), 136.3 (C), 128.6 (CH), 128.3 (CH), 128.2 (CH) 118.4 (CH), 66.1 (CH_2), 31.1 (CH), 21.3 (CH_3).

R_f (SiO_2, *n*-heptane/EtOAc 9:1) 0.42.

Benzyl 3-(2-chlorophenyl)propanoate (3aq) and benzyl 2-(2-chlorophenyl)propanoate (3'aq)



$C_{16}H_{15}ClO_2$, 274.74 g mol^{-1}

Compounds **3aq** and **3'aq** were prepared from benzyl formate (**1a**, 0.38 ml, 3.0 mmol) and 2-chlorostyrene (**2q**, 0.58 ml, 4.5 mmol) following the general procedure. The product mixture was purified by column chromatography and obtained as colorless oil (0.51 mmol, **17%**, 91:9). High polymerization rate of the remaining styrene derivative has been observed when applying the crude product mixture onto the column.

^{1}H NMR (300 MHz, $CDCl_3$) **3aq** δ 7.42 – 7.27 (m, 6H), 7.25 – 7.12 (m, 3H), 5.13 (s, 2H), 3.10 (t, *J* = 7.7 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H); **3'aq** δ 7.42 – 7.27 (m, 6H), 7.25 – 7.12 (m, 3H), 5.17 (d, *J* = 12.5 Hz, 1H), 5.12 (d, *J* = 12.1 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) **3aq** δ 172.6 (C), 138.1 (C), 136.0 (C), 134.1 (C), 130.6 (CH), 129.7 (CH), 128.7 (CH), 128.4 (CH), 128.0 (CH), 127.0 (CH), 66.5 (CH_2), 34.1 (CH_2), 29.1 (CH_2). The signals of **3'aq** could not be determined due to its low concentration.

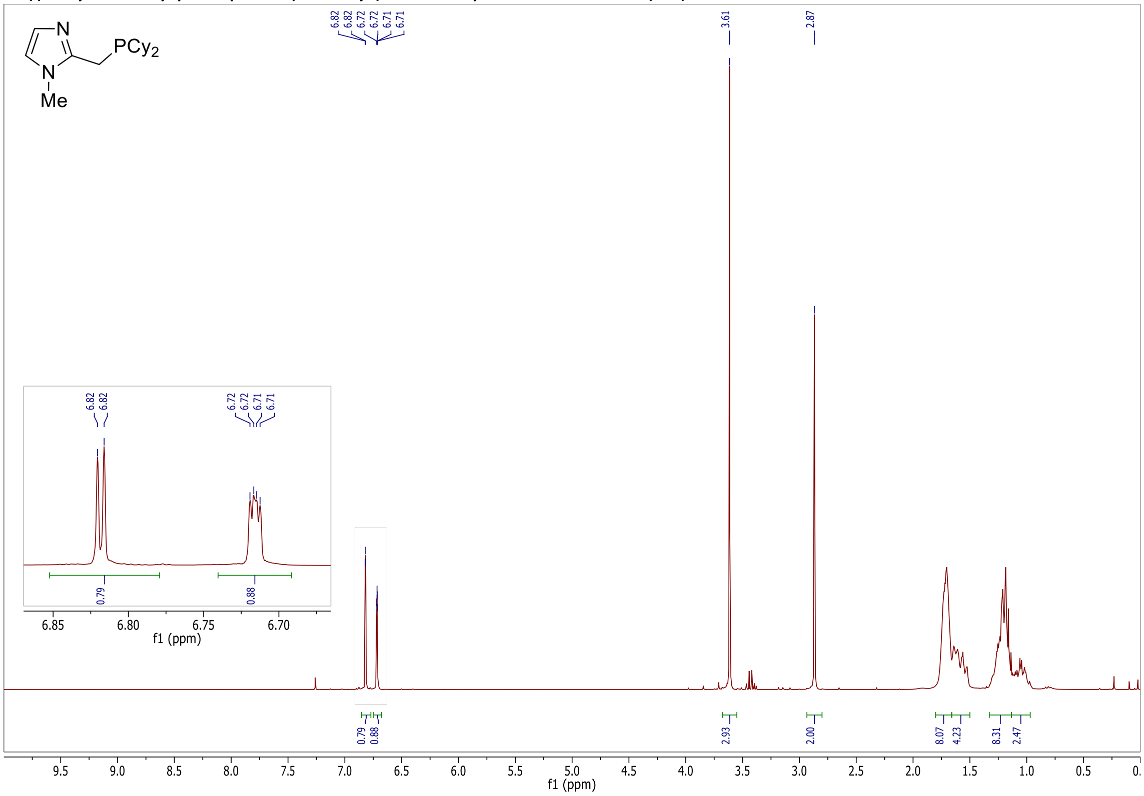
R_f (SiO_2, *n*-heptane/EtOAc 4:1) 0.47.

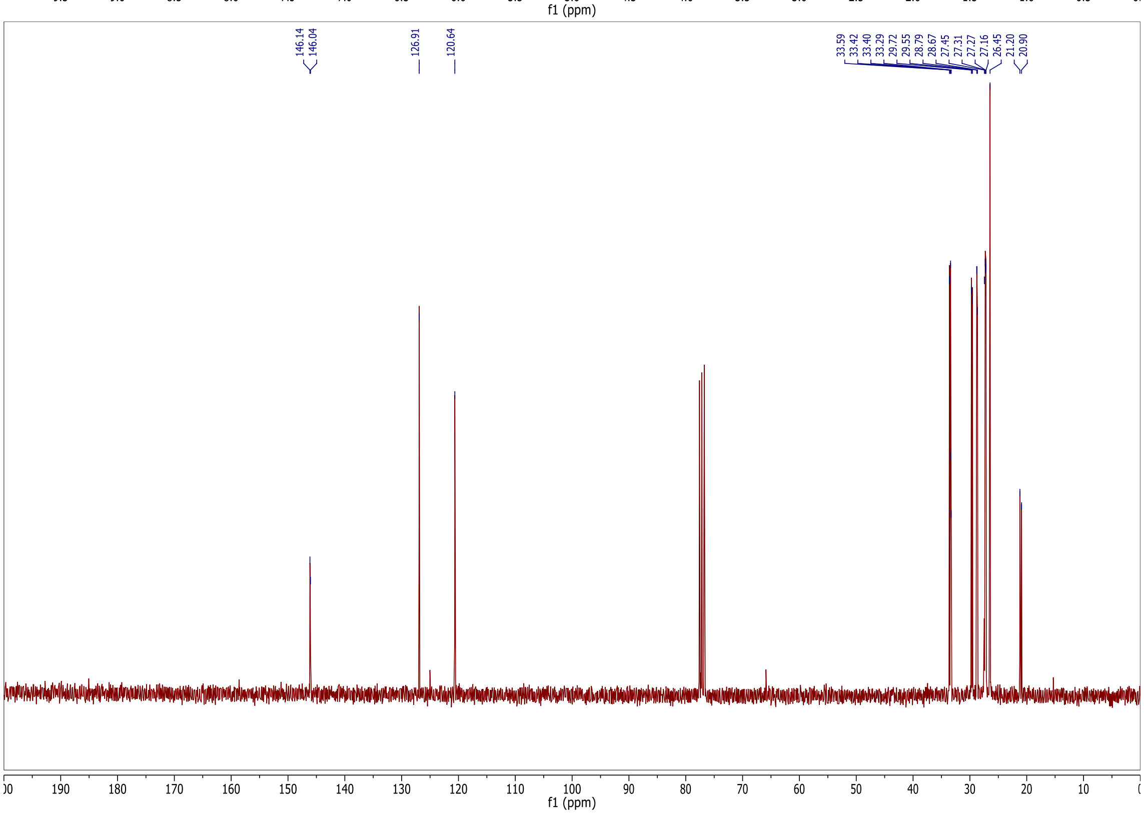
IR (ATR) λ^{-1} 3065 (w), 3033 (w), 2943 (w), 1732 (vs), 1572 (w), 1498 (w), 1475 (m), 1455 (m), 1444 (m), 1381 (w), 1354 (w), 1294 (m), 1151 (vs), 1121 (m), 1080 (w), 1052 (s), 1002 (m), 910 (w), 825 (w), 748 (vs), 695 (vs), 675 (s), 574 (m), 499 (w), 458 (m).

MS (GC-MS, EI) **3aq** m/z (%) 274 (0.3) [M^+], 239 (8), 214 (35), 141 (35), 139 (9), 125 (14), 103 (19), 91 (100), 77 (24), 65 (12); **3'aq** m/z (%) 274 (2) [M^+], 239 (17), 201 (4), 141 (31), 139, (95), 103 (37), 91 (100), 77 (28), 65 (14).
HR-MS (EI) m/z calcd. for $C_{16}H_{15}ClO_2$ 274.07551; found 274.07592.

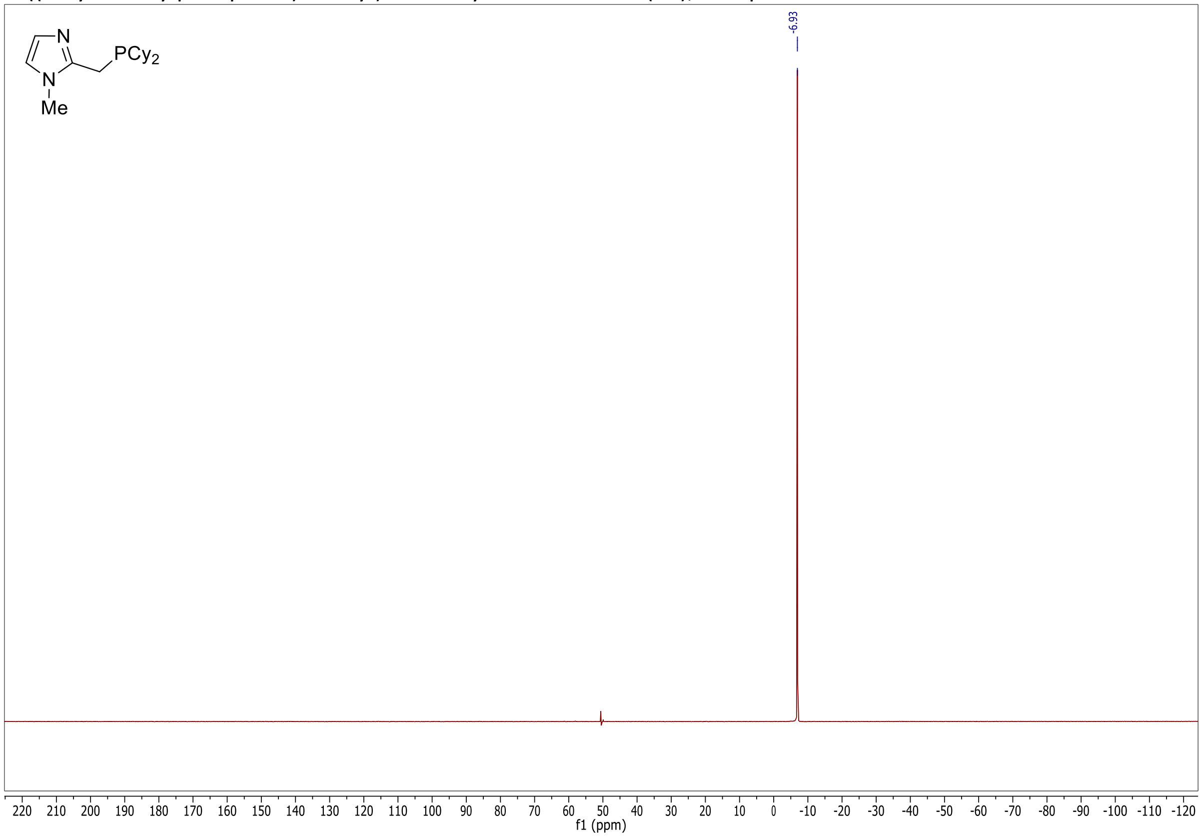
E. NMR Spectra

2-((Dicyclohexylphosphino)methyl)-1-methyl-1*H*-imidazole (**4a**)

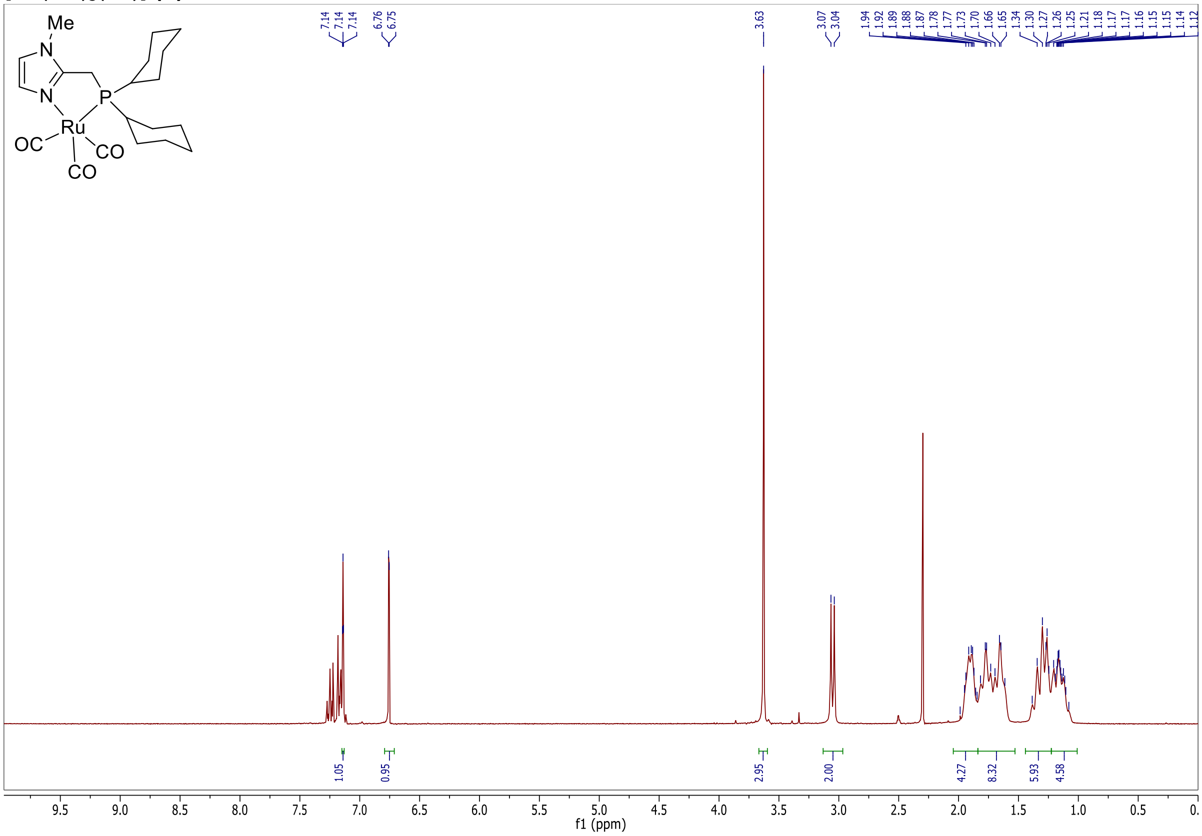




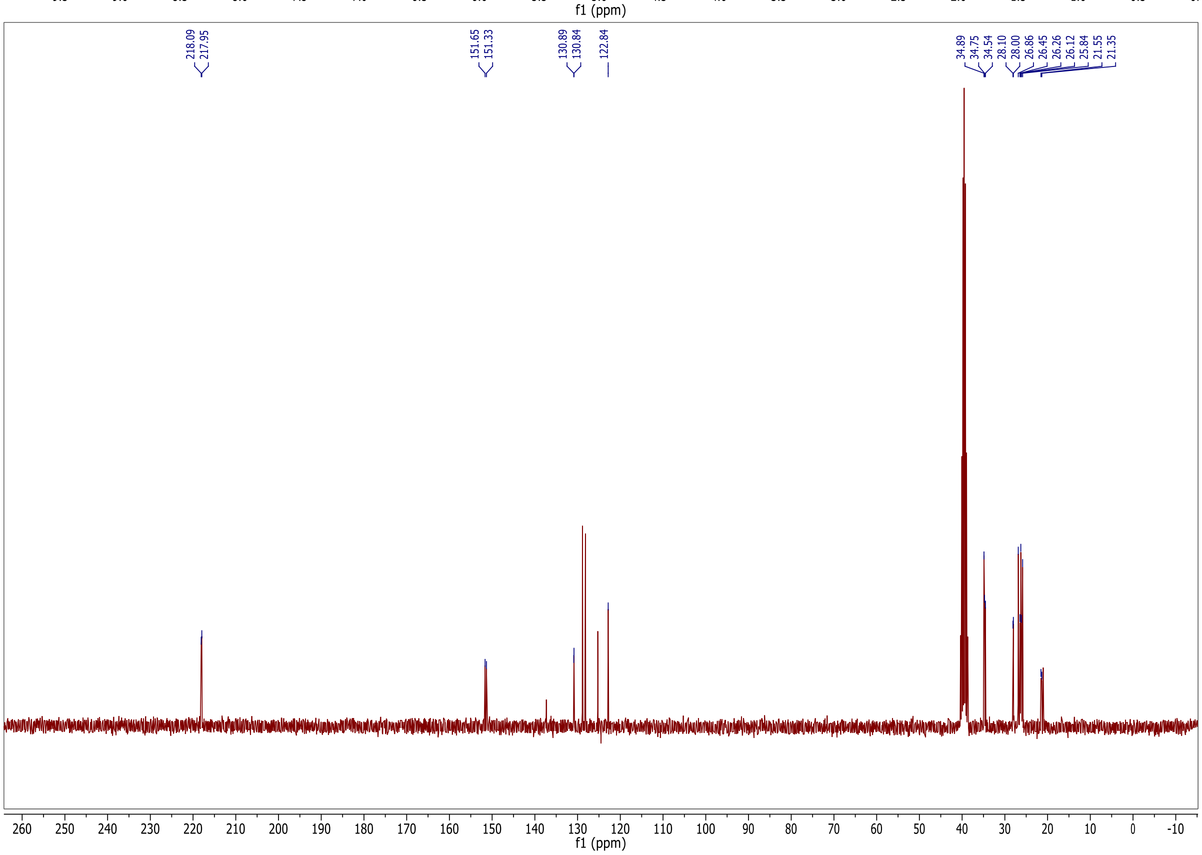
2-((Dicyclohexylphosphino)methyl)-1-methyl-1*H*-imidazole (**4a**), ^{31}P spectrum



[Ru(CO)$_3$(4a)] **(6)**

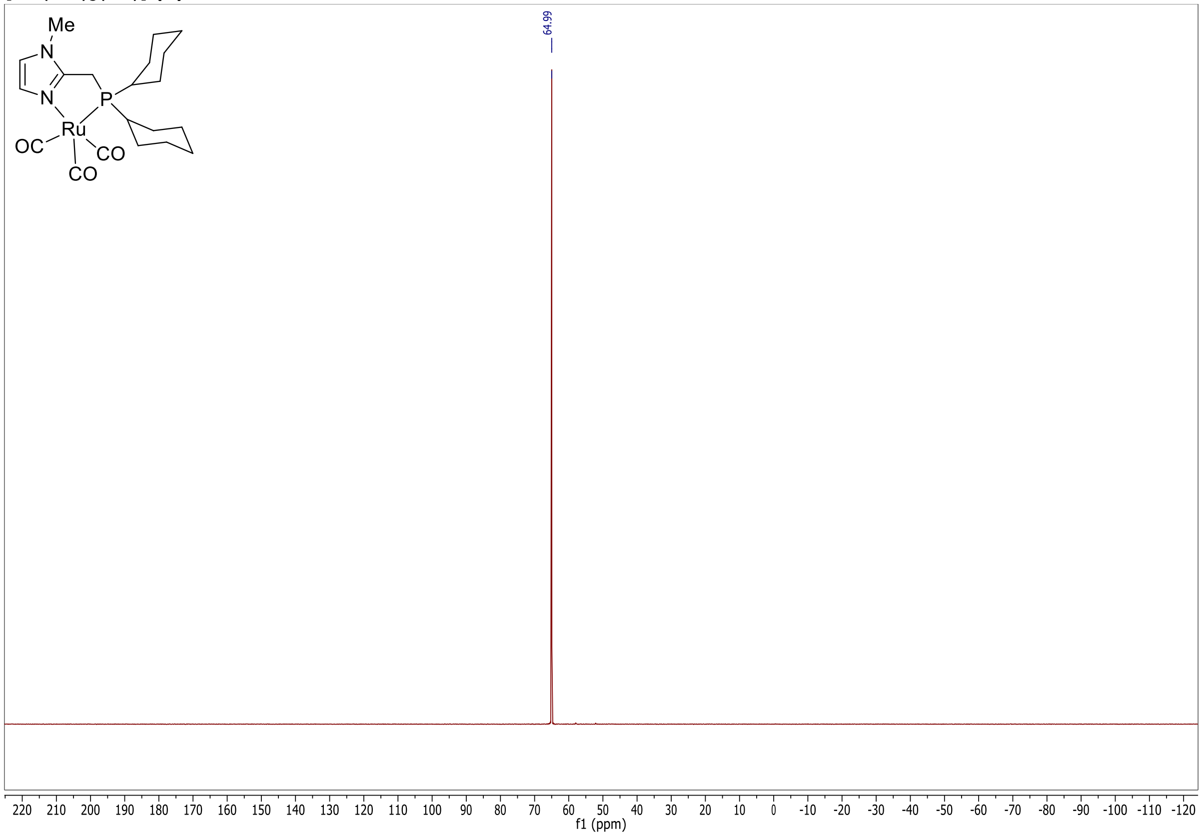


Me
N
N
P
Ru
OC
CO
CO
7.14 7.14 7.14 6.76 6.75
3.63
3.07 3.04
1.94 1.92 1.89 1.88 1.87 1.78 1.77 1.73 1.70 1.66 1.65 1.34 1.30 1.27 1.26 1.25 1.21 1.18 1.17 1.17 1.16 1.15 1.15 1.14 1.12
1.05 0.95 2.95 2.00 4.27 8.32 5.93 4.58
f1 (ppm)

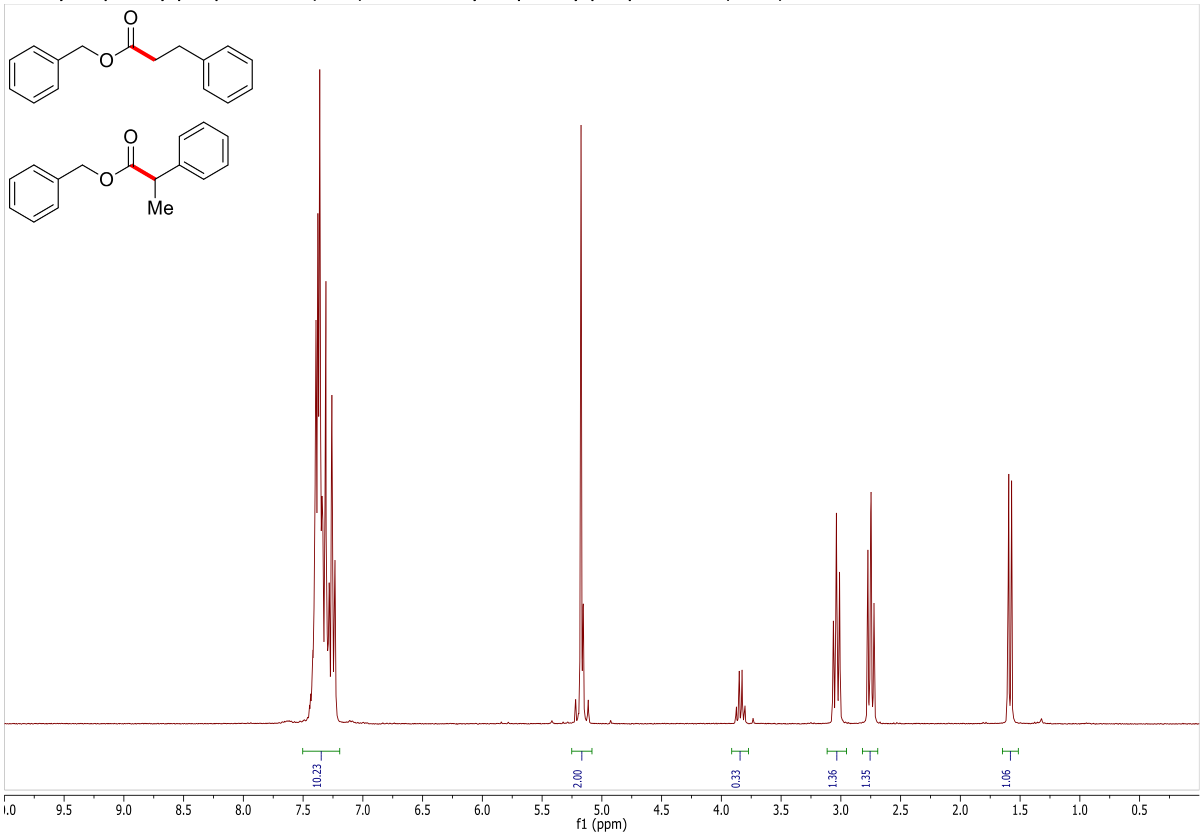


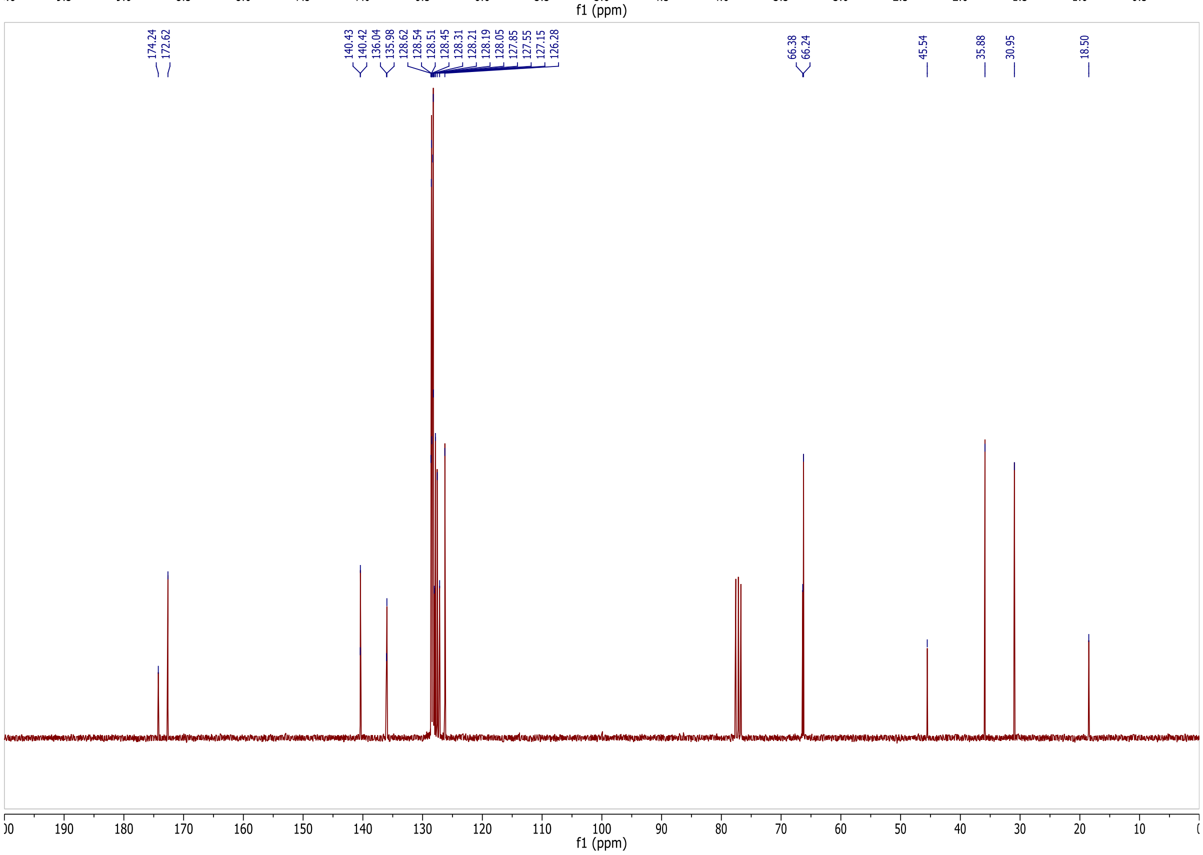
218.09 217.95
151.65 151.33
130.89 130.84
122.84
34.89 34.75 34.54 28.10 28.00 26.86 26.45 26.26 26.12 25.84 21.55 21.35
f1 (ppm)

[Ru(CO)$_3$(4a)] **(6)**

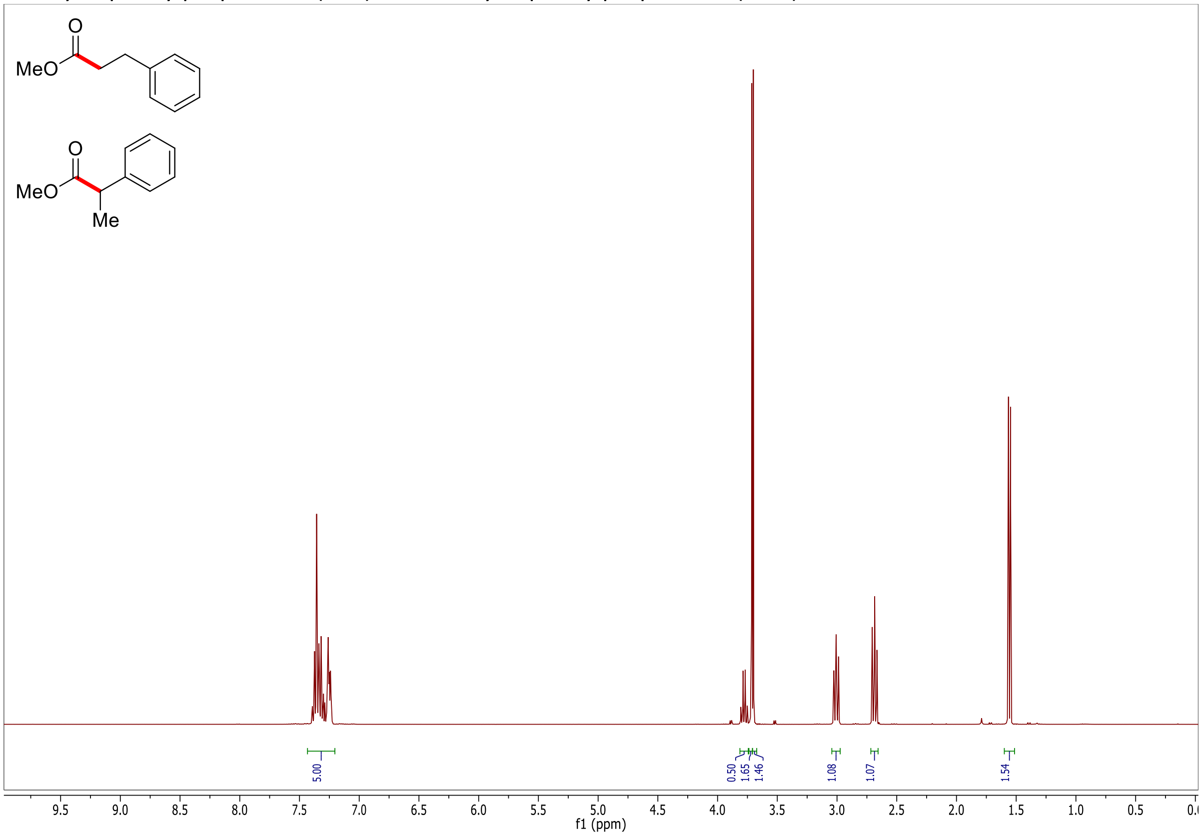

Me
N
N
Ru
P
OC
CO
CO
64.99
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

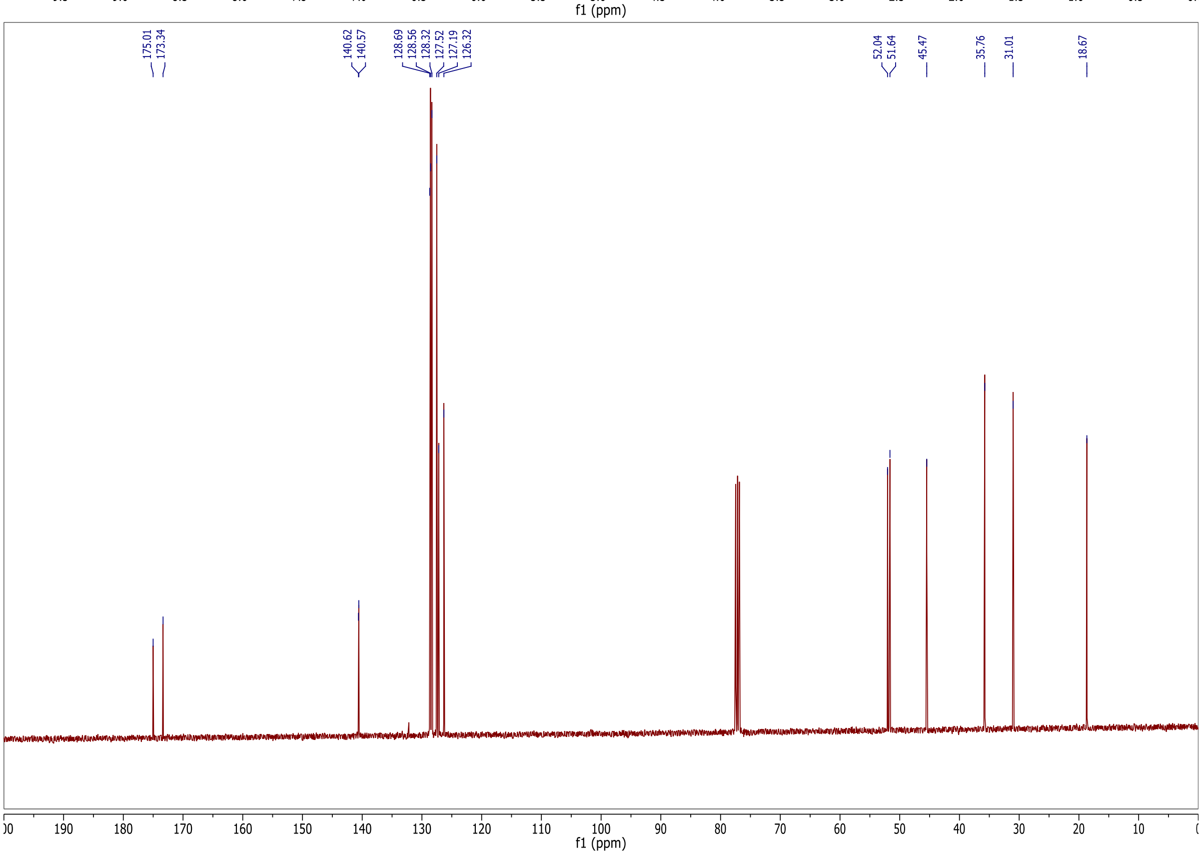
Benzyl 3-phenylpropanoate (**3aa**) and benzyl 2-phenylpropanoate (**3’aa**)



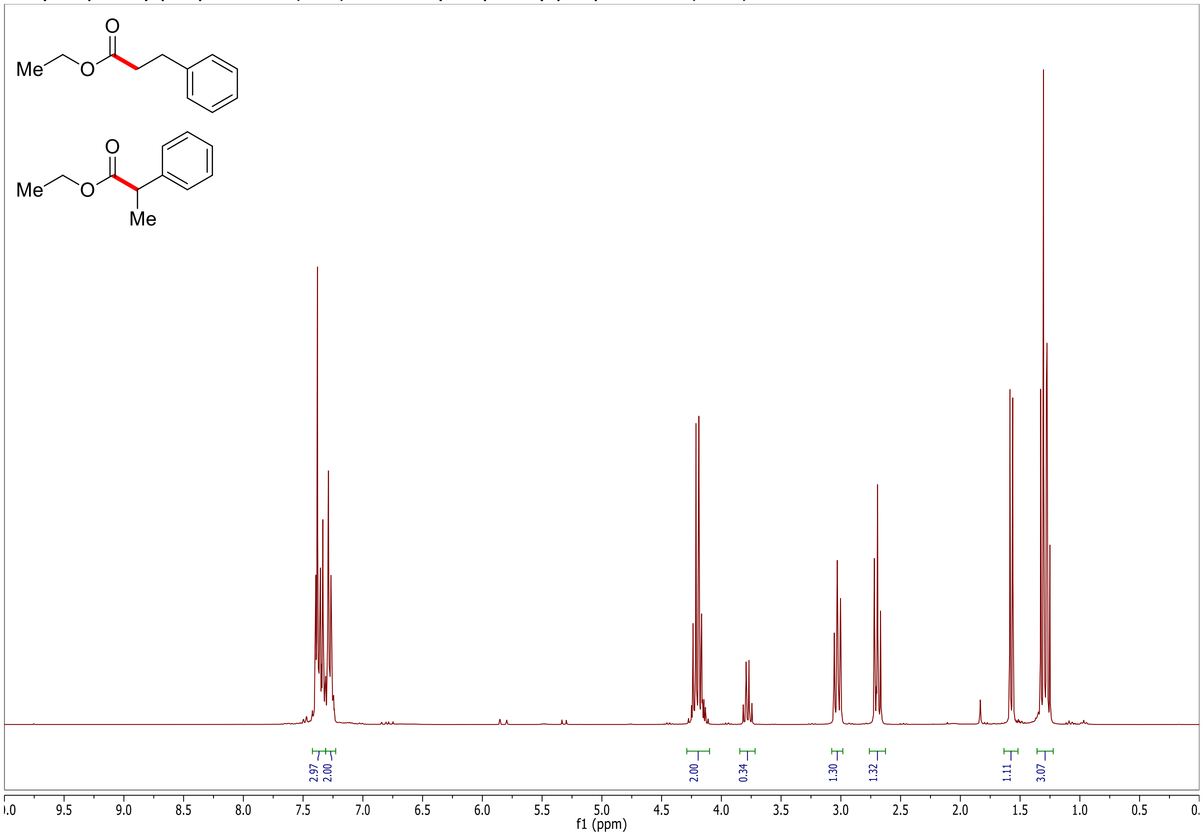


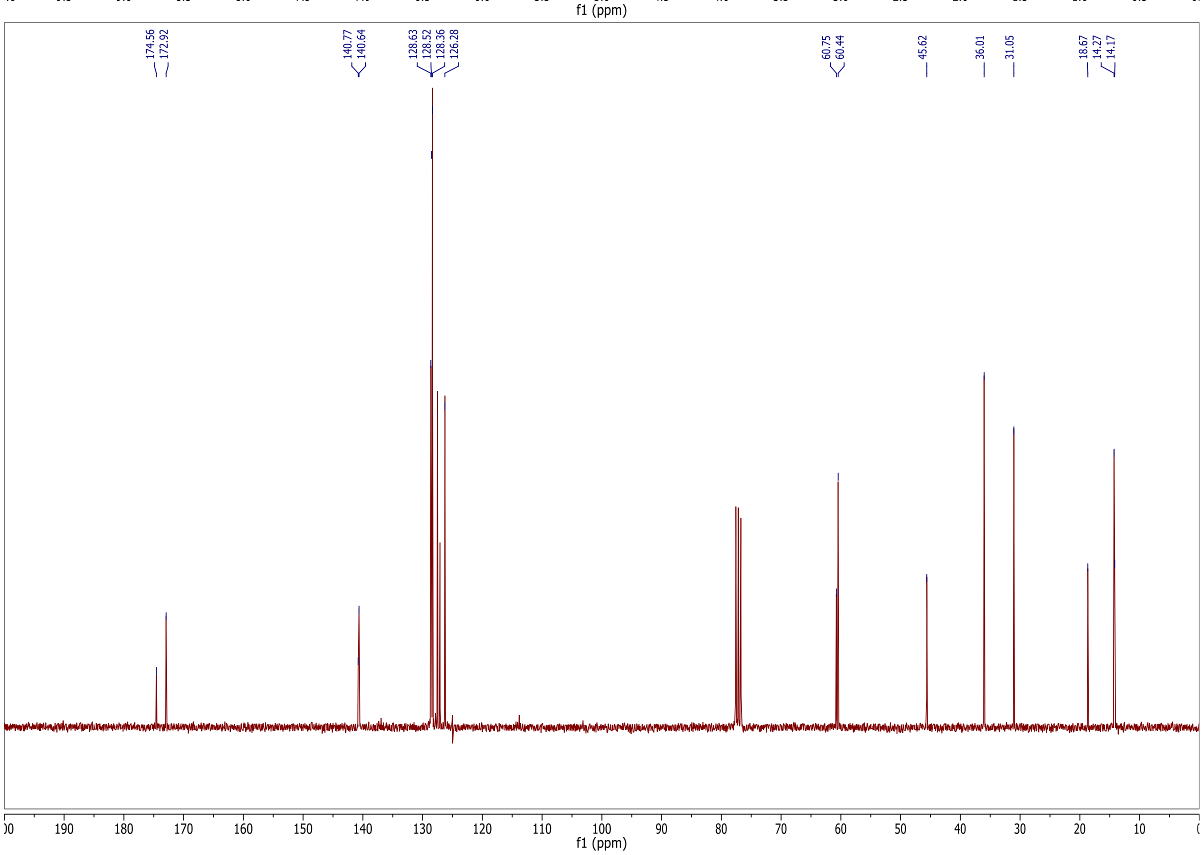
Methyl 3-phenylpropanoate (**3ba**) and methyl 2-phenylpropanoate (**3’ba**)



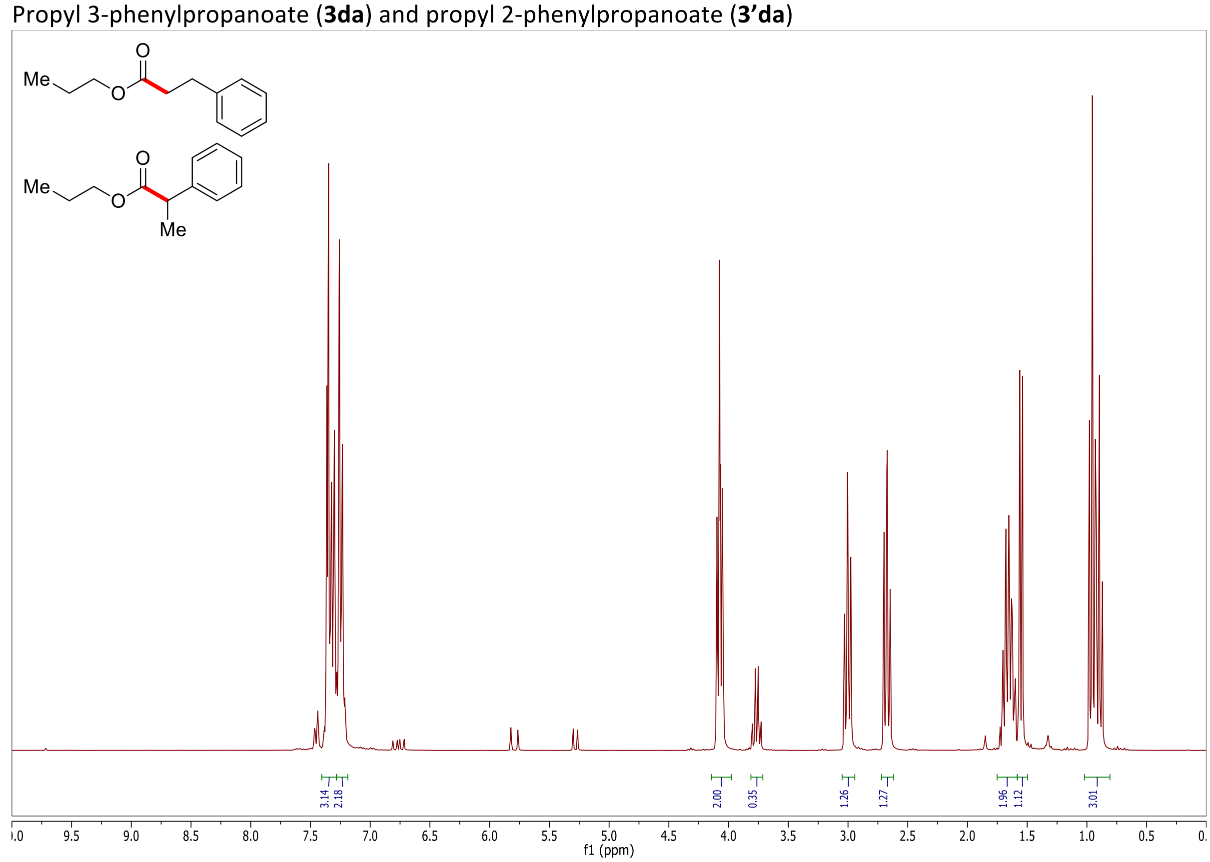


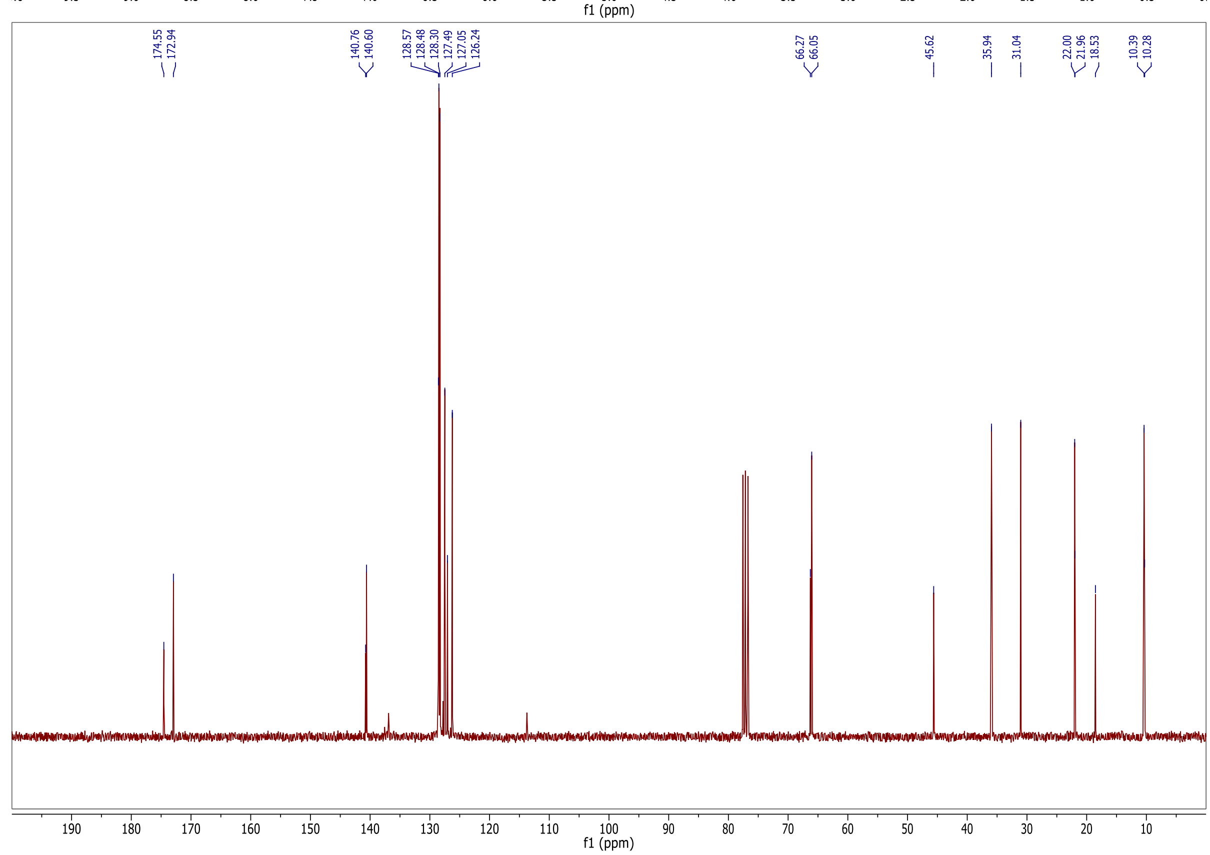
Ethyl 3-phenylpropanoate (**3ca**) and ethyl 2-phenylpropanoate (**3'ca**)



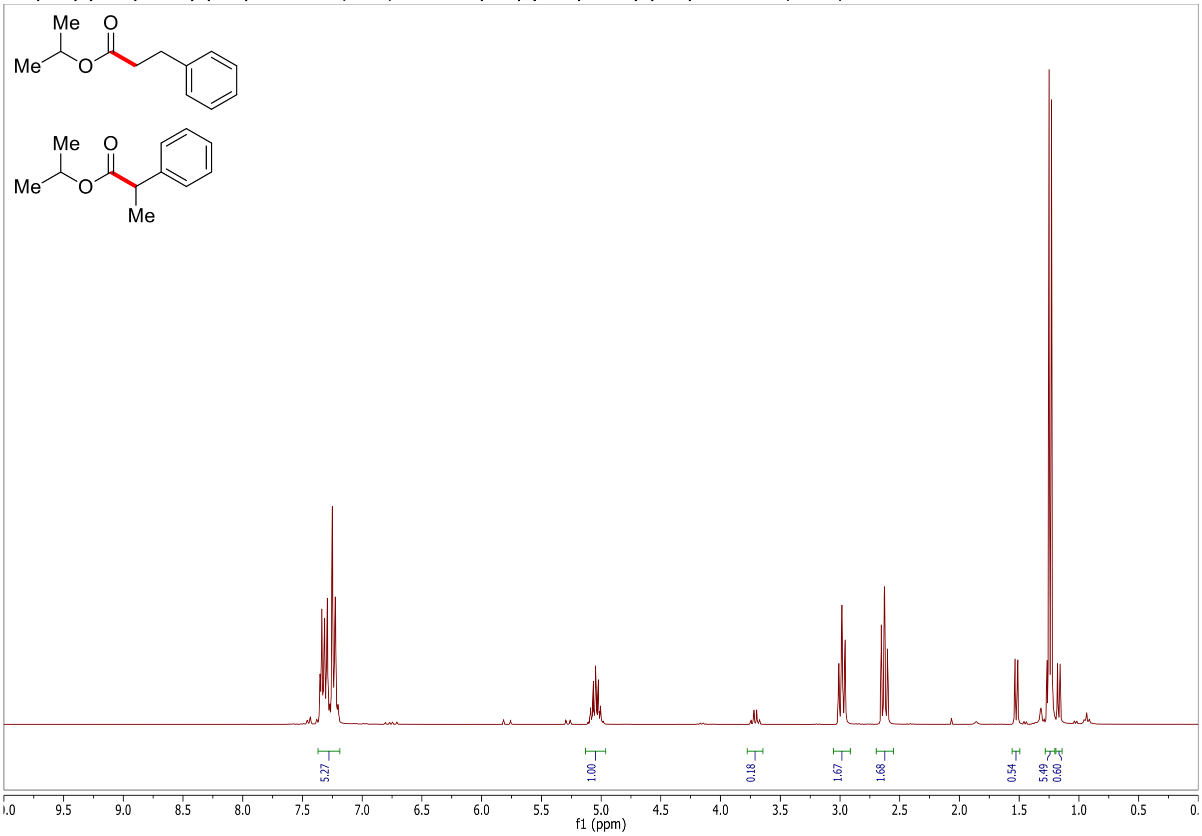


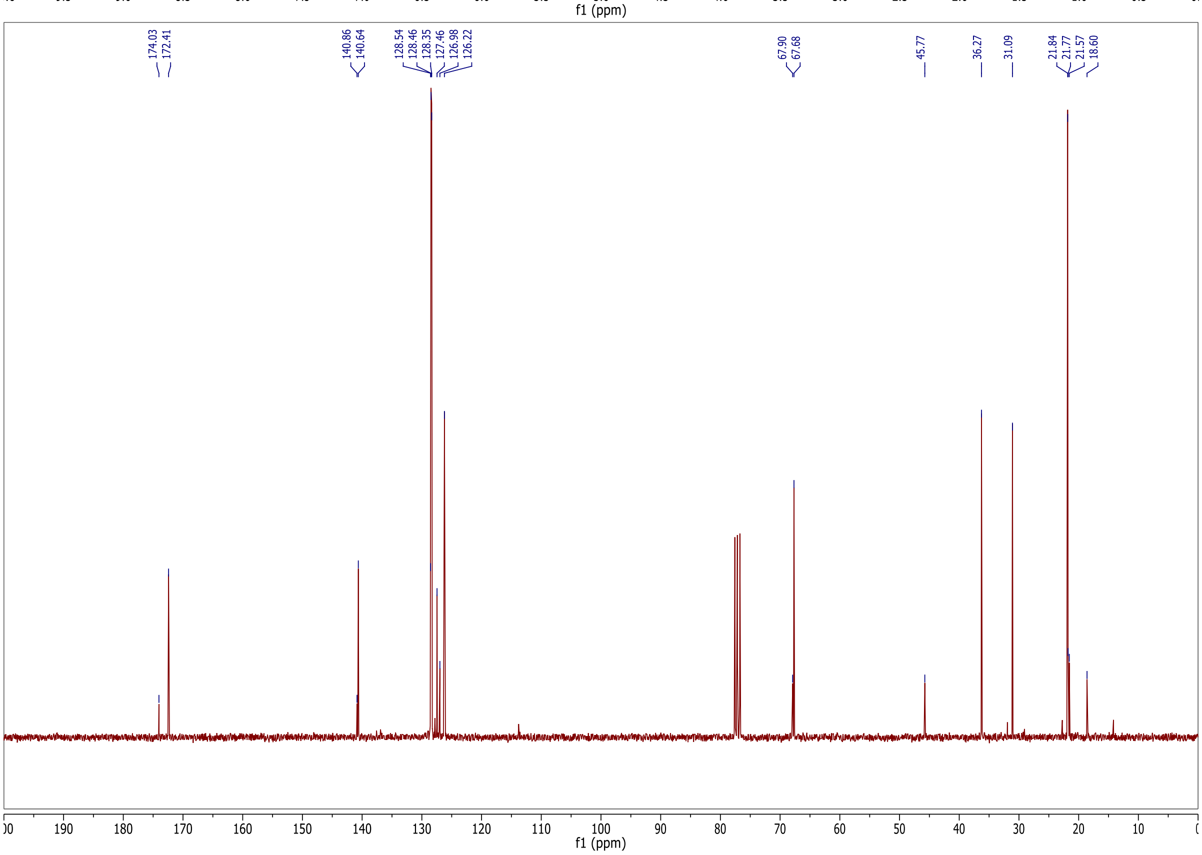
Propyl 3-phenylpropanoate (**3da**) and propyl 2-phenylpropanoate (**3'da**)



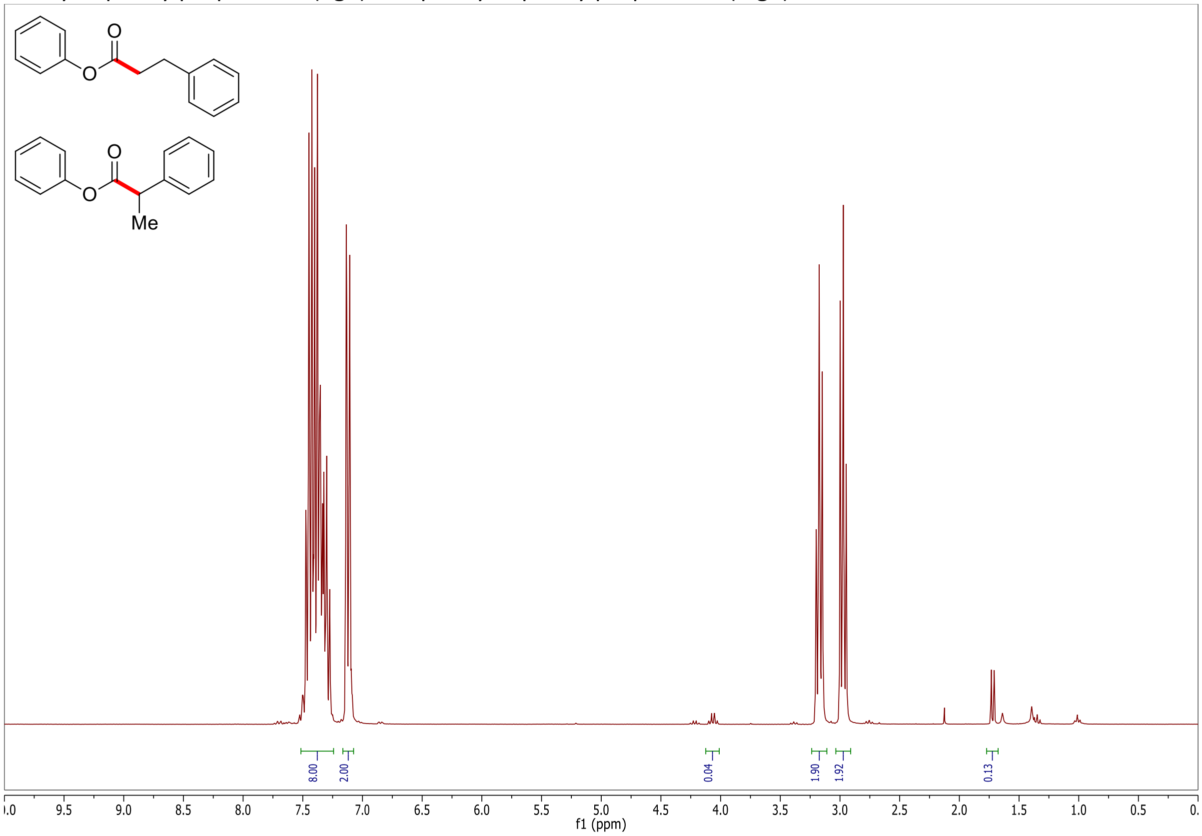


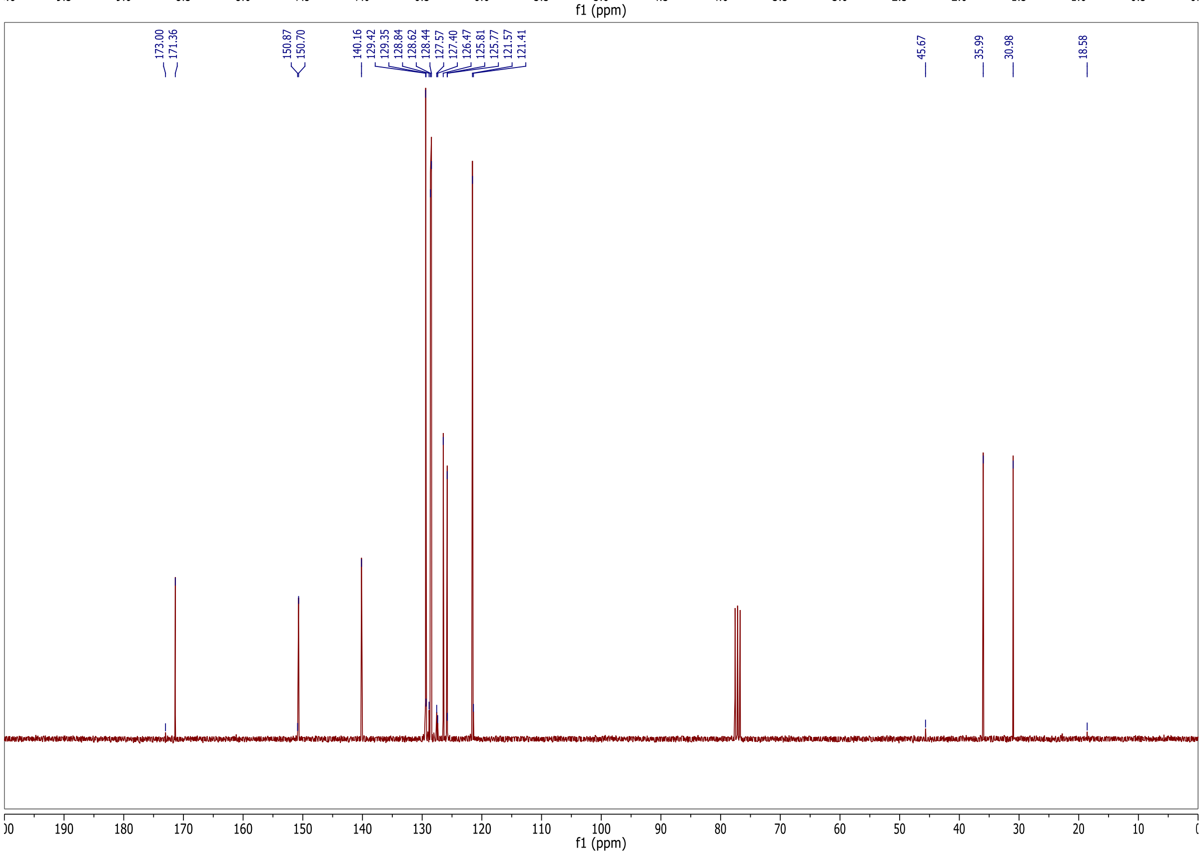
Isopropyl 3-phenylpropanoate (**3ea**) and isopropyl 2-phenylpropanoate (**3’ea**)



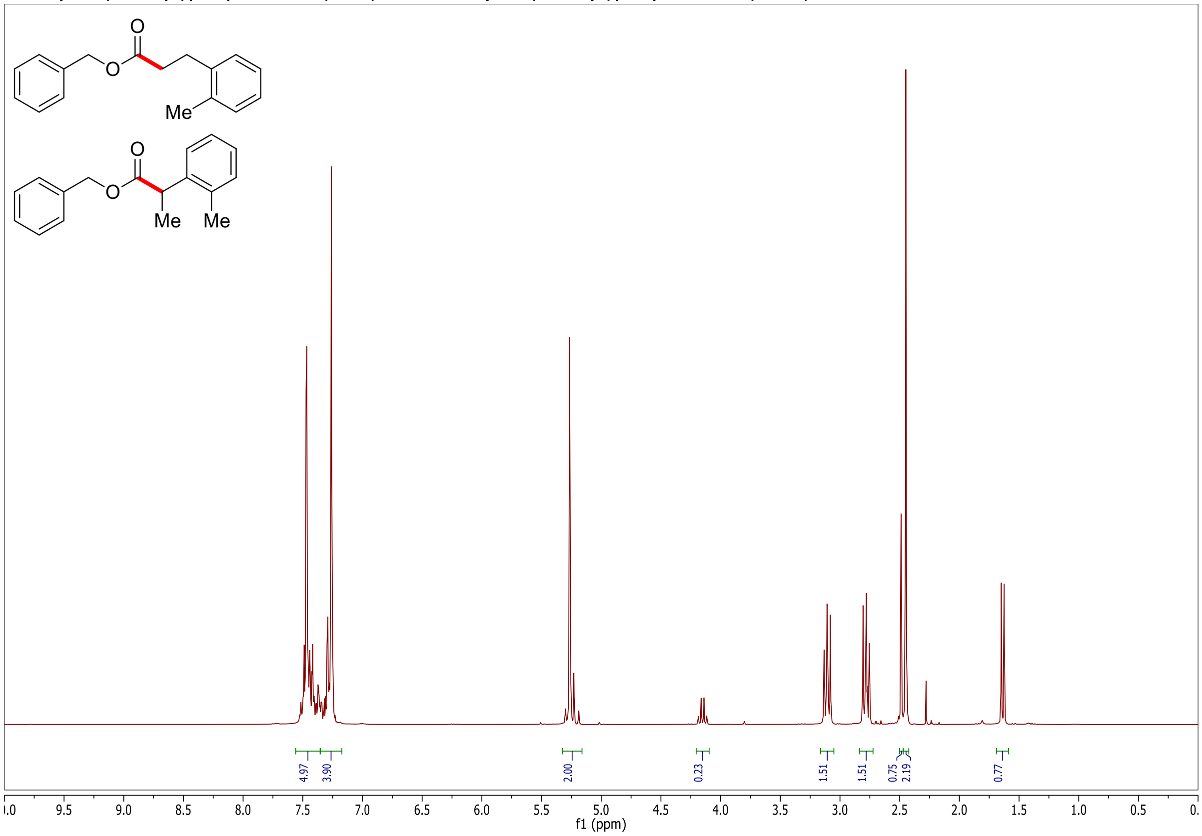


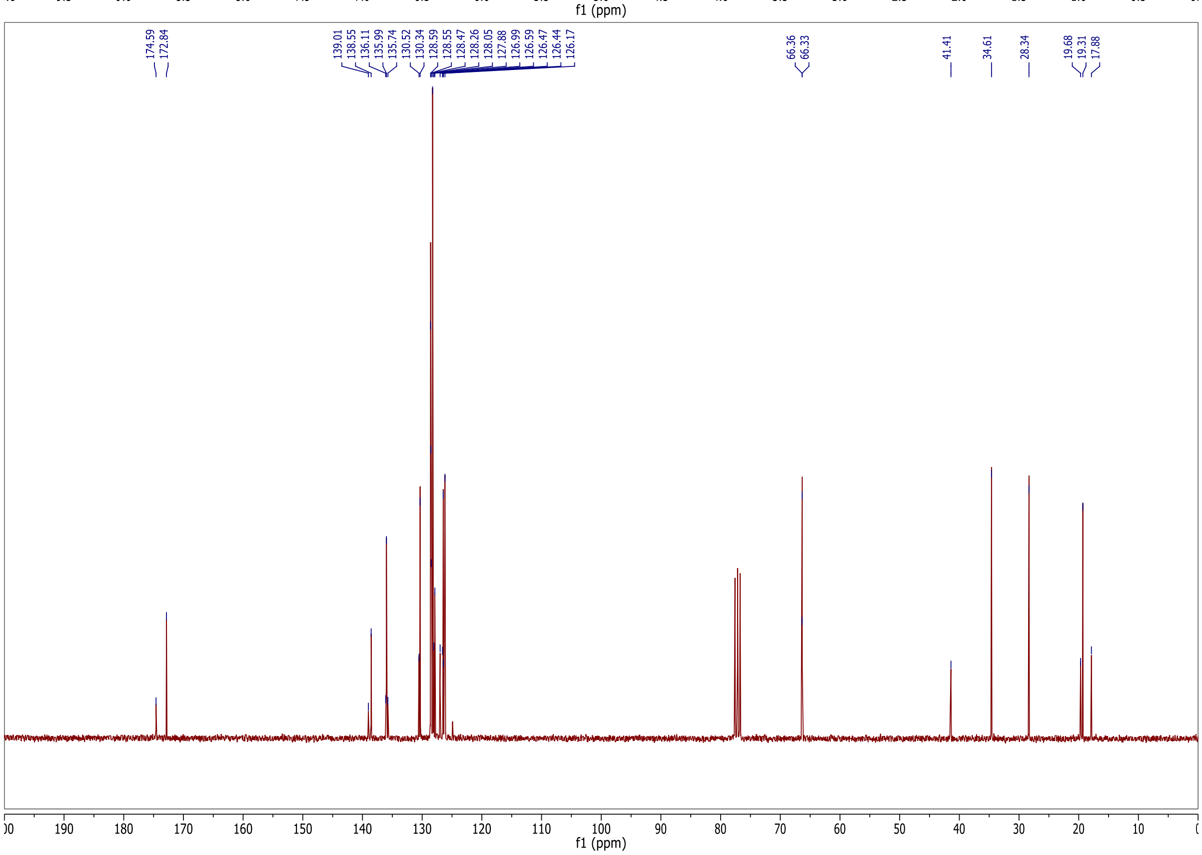
Phenyl 3-phenylpropanoate (**3ga**) and phenyl 2-phenylpropanoate (**3’ga**)



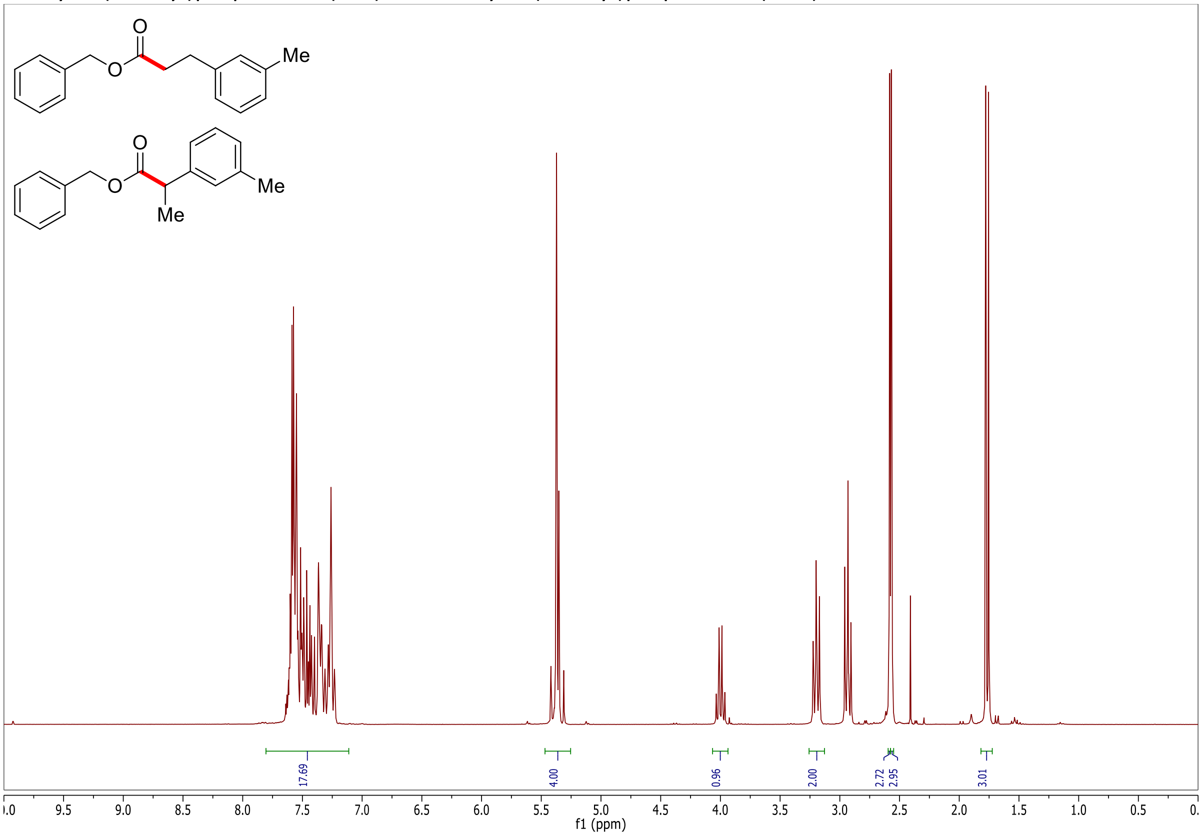


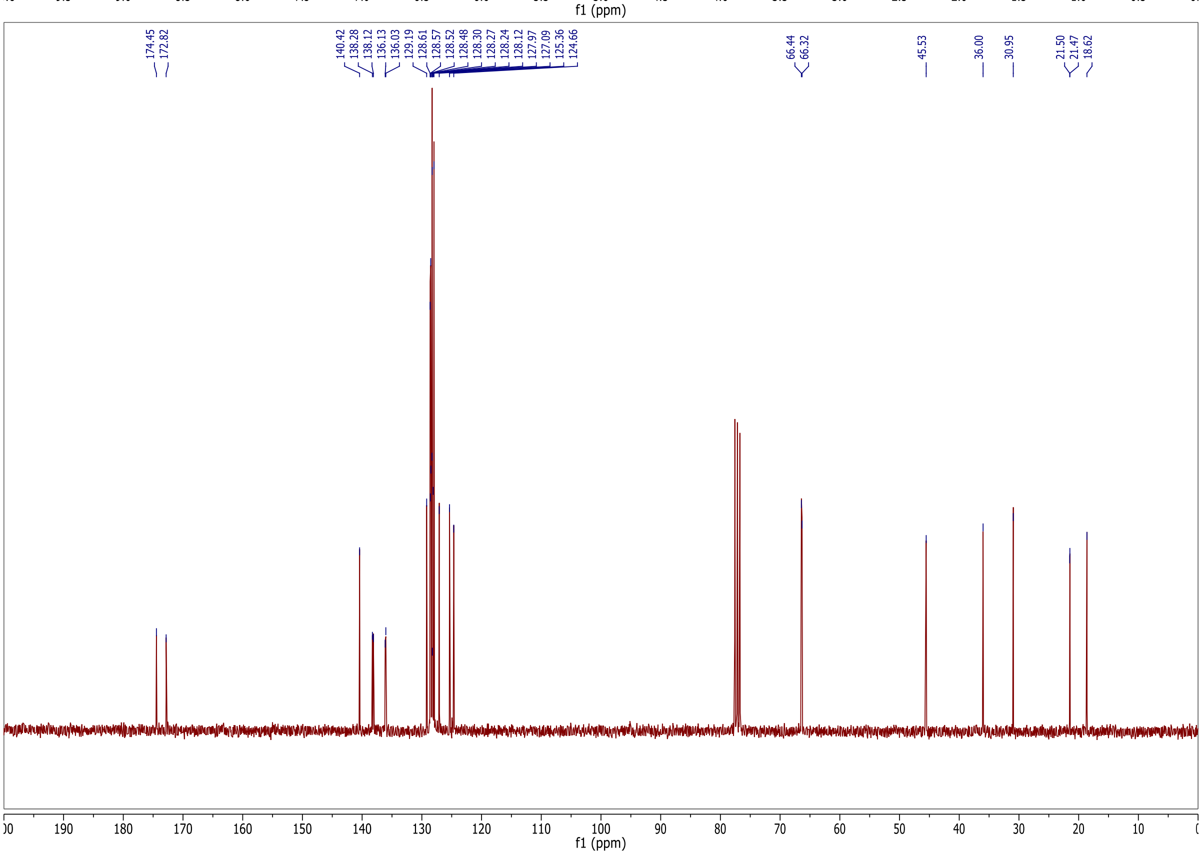
Benzyl 3-(*o*-tolyl)propanoate (**3ab**) and benzyl 2-(*o*-tolyl)propanoate (**3'ab**)



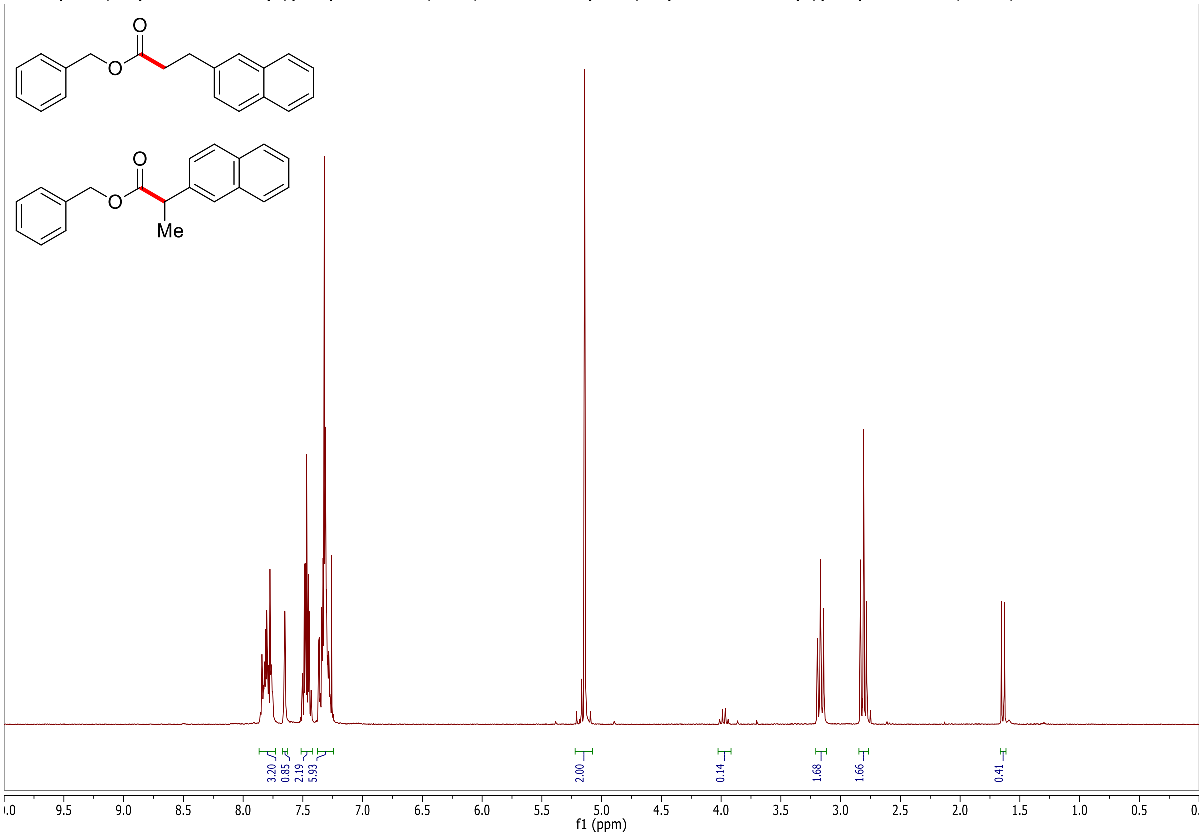


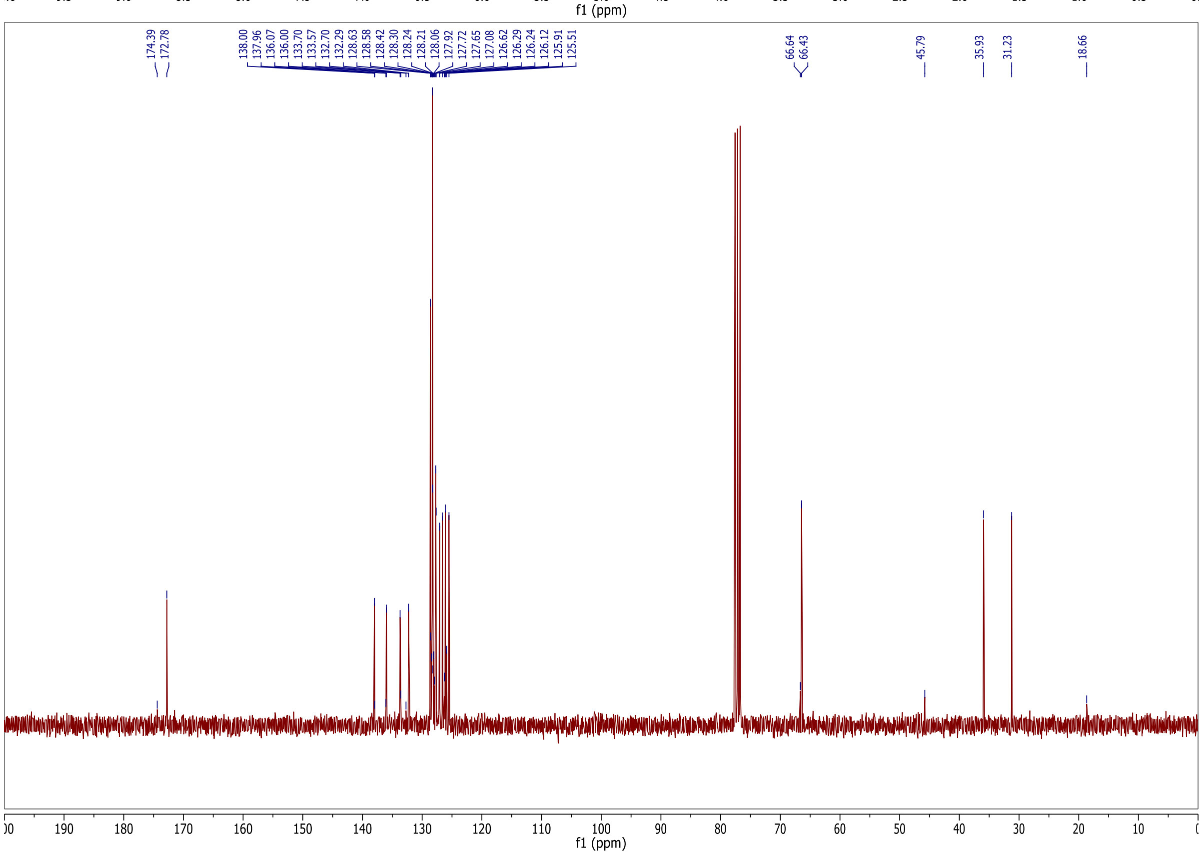
Benzyl 3-(*m*-tolyl)propanoate (**3ac**) and benzyl 2-(*m*-tolyl)propanoate (**3’ac**)



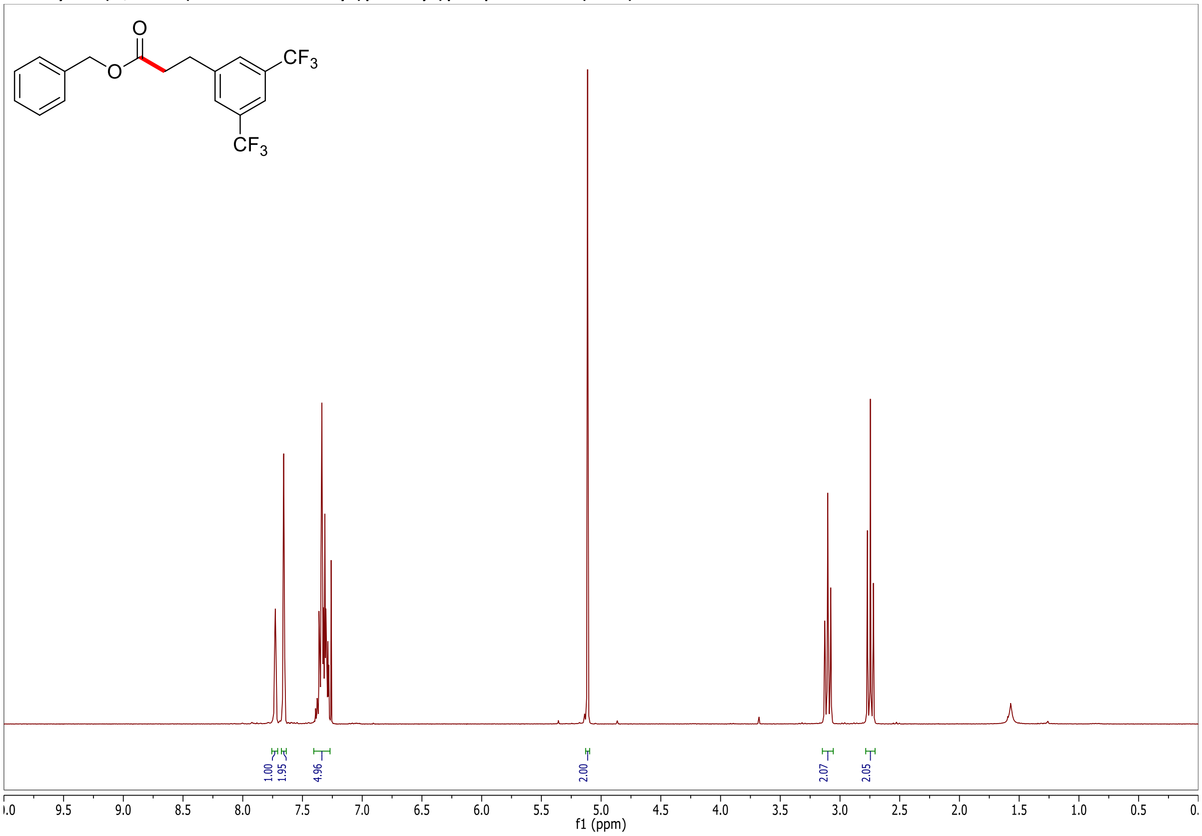


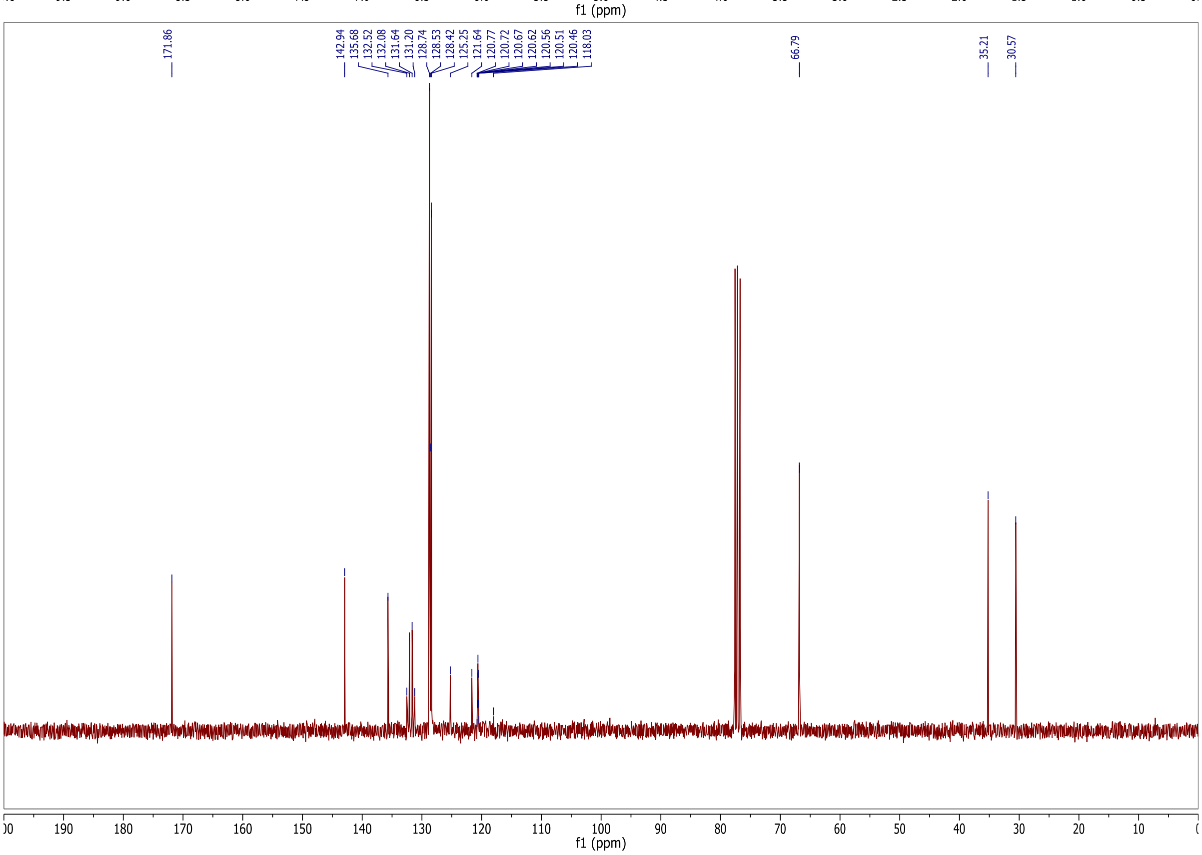
Benzyl 3-(naphthalen-2-yl)propanoate (**3ad**) and benzyl 2-(naphthalen-2-yl)propanoate (**3'ad**)



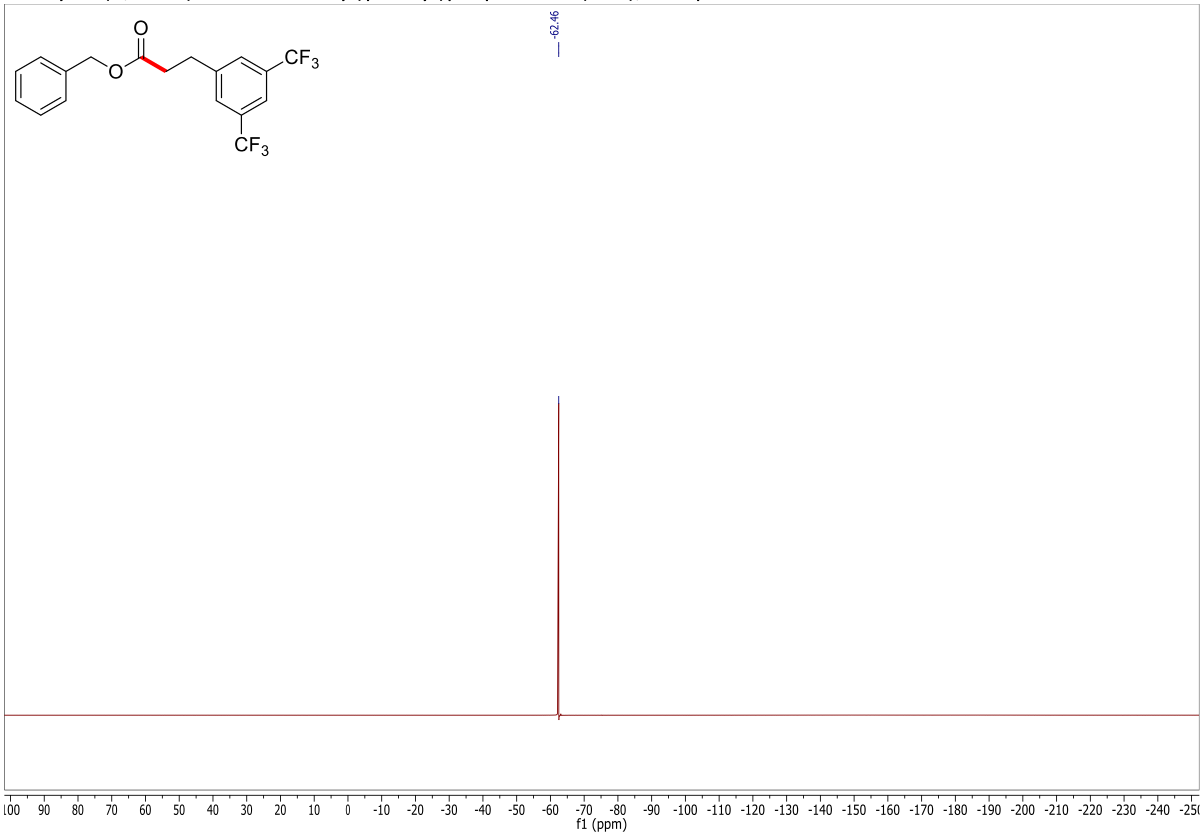


Benzyl 3-(3,5-bis(trifluoromethyl)phenyl)propanoate (**3ae**)

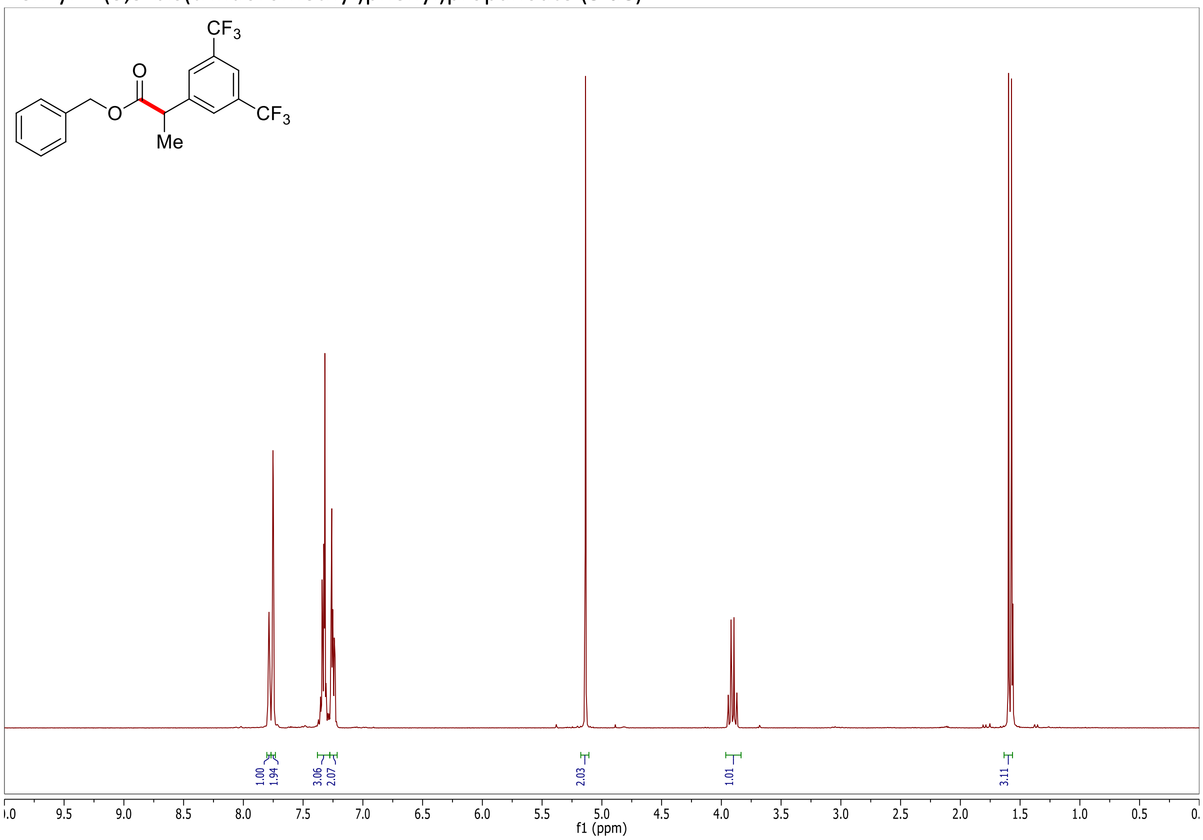


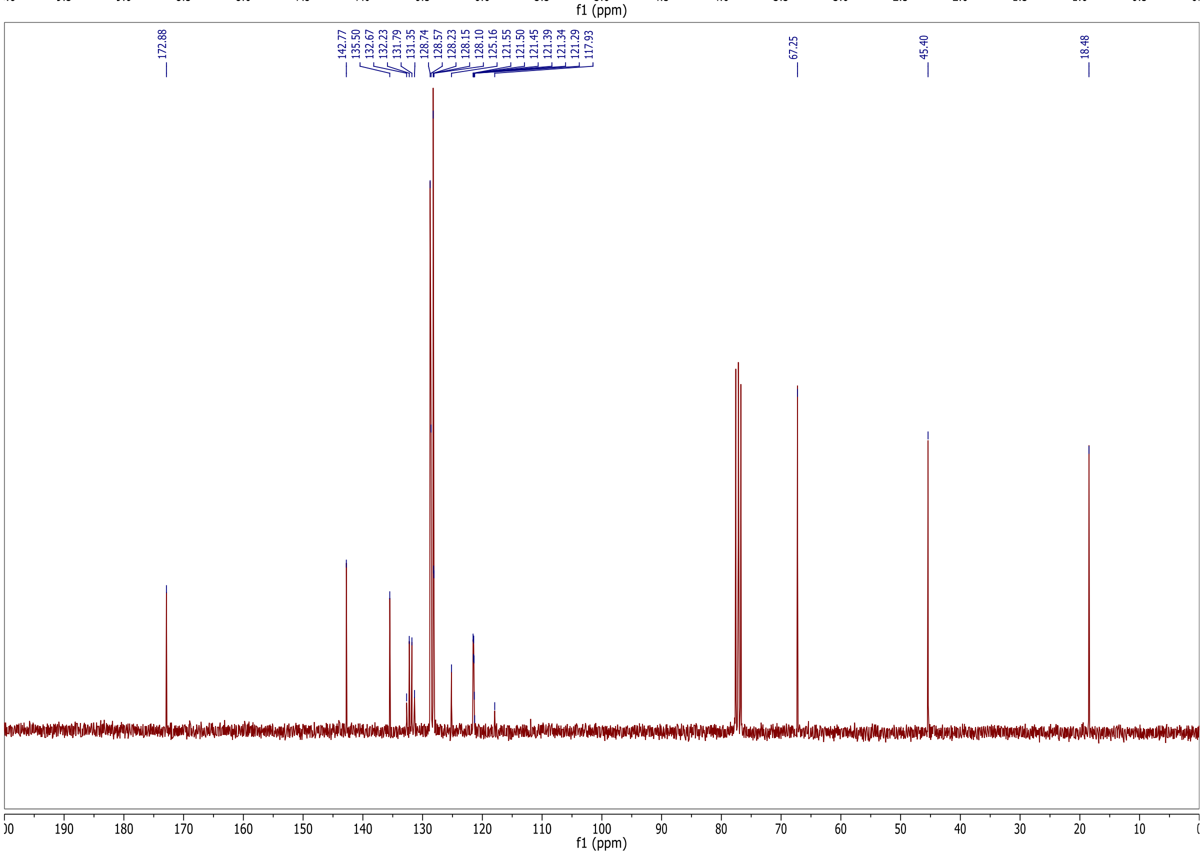


Benzyl 3-(3,5-bis(trifluoromethyl)phenyl)propanoate (**3ae**), ^{19}F spectrum

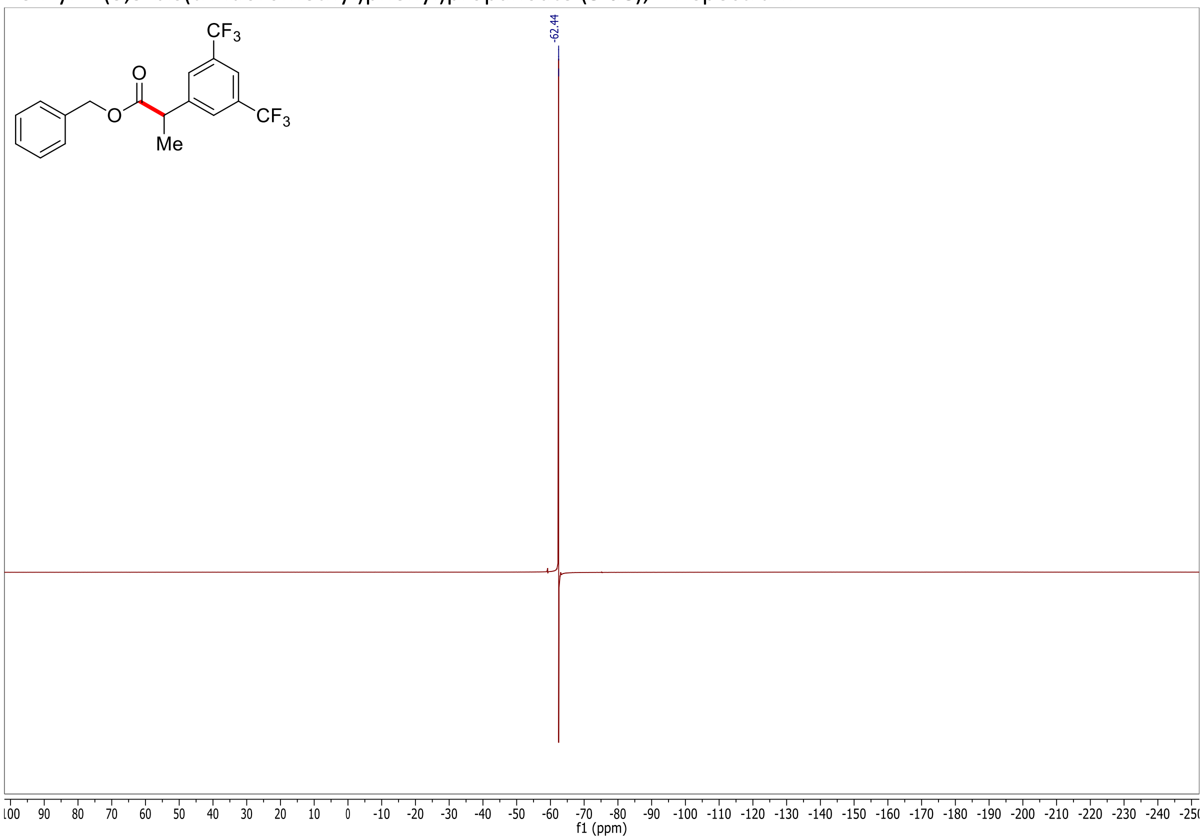


Benzyl 2-(3,5-bis(trifluoromethyl)phenyl)propanoate (**3’ae**)

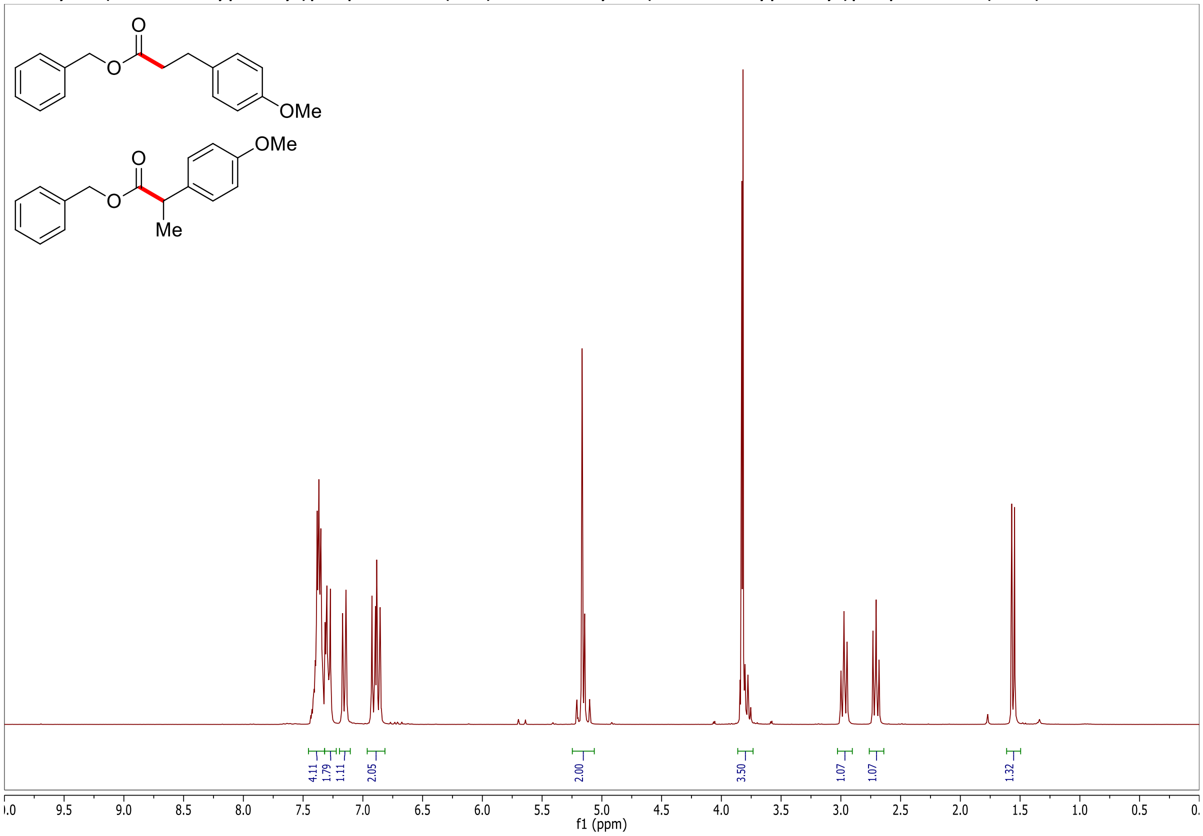


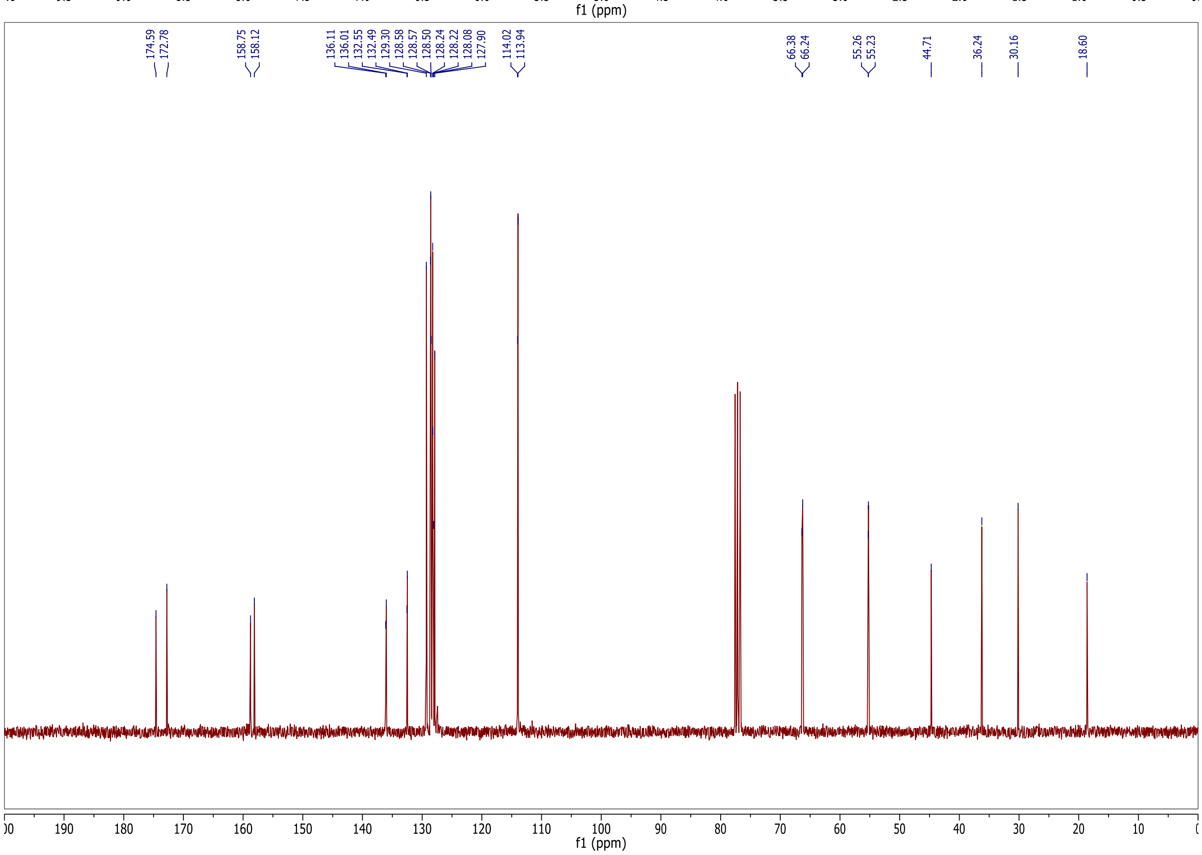


Benzyl 2-(3,5-bis(trifluoromethyl)phenyl)propanoate (**3’ae**), ^{19}F spectrum

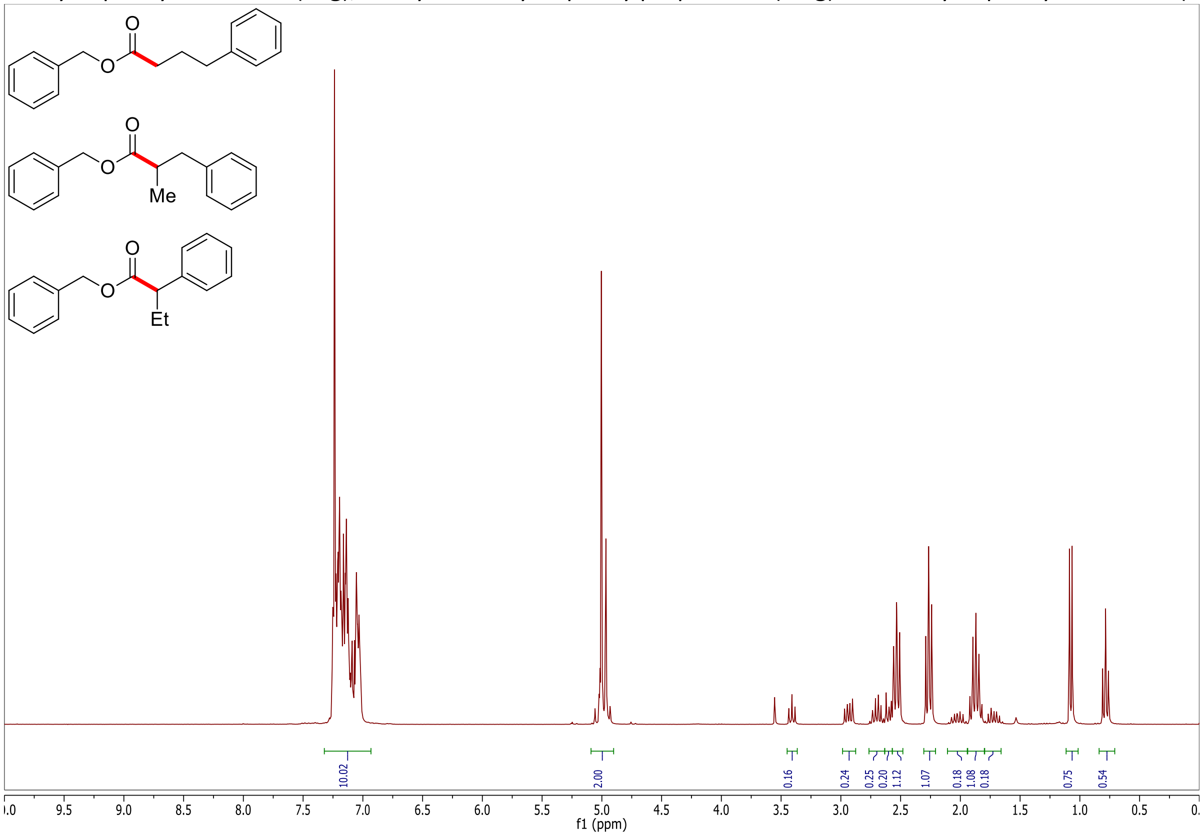


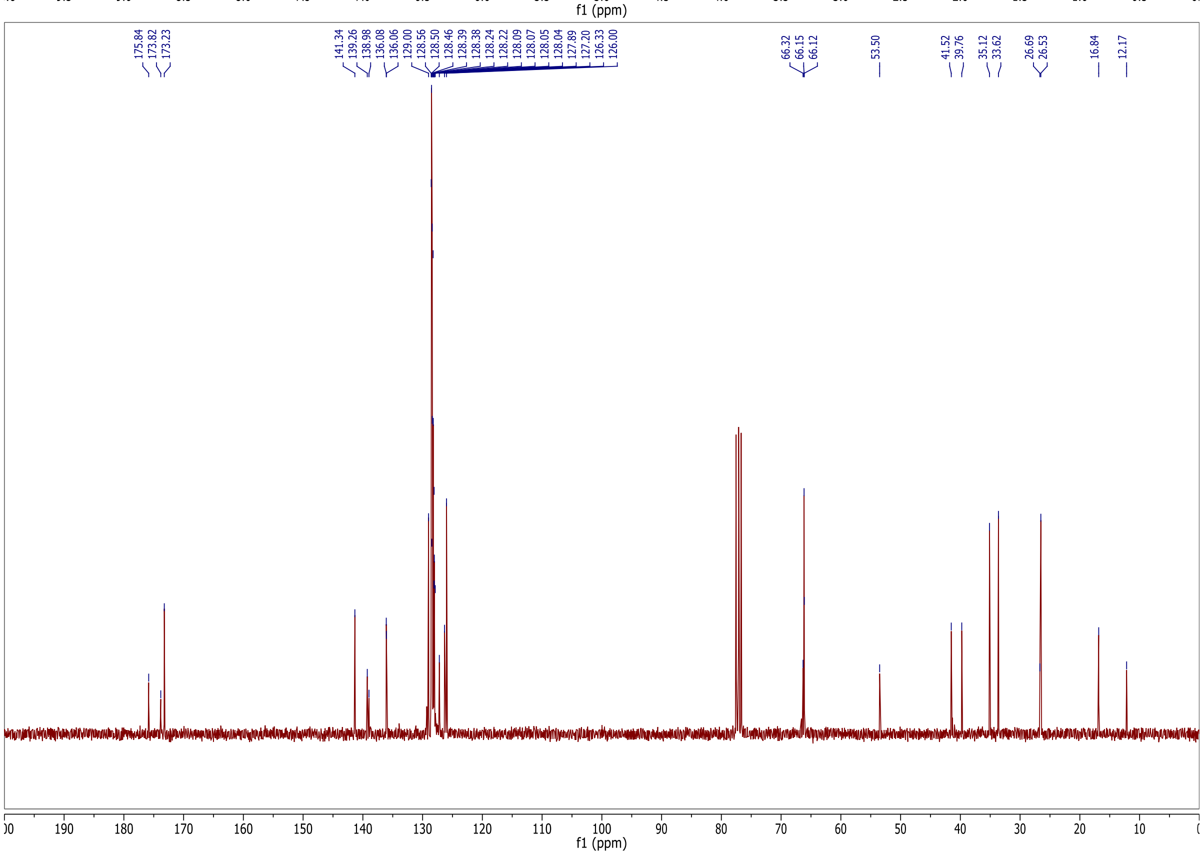
Benzyl 3-(4-methoxyphenyl)propanoate (**3af**) and benzyl 2-(4-methoxyphenyl)propanoate (**3’af**)



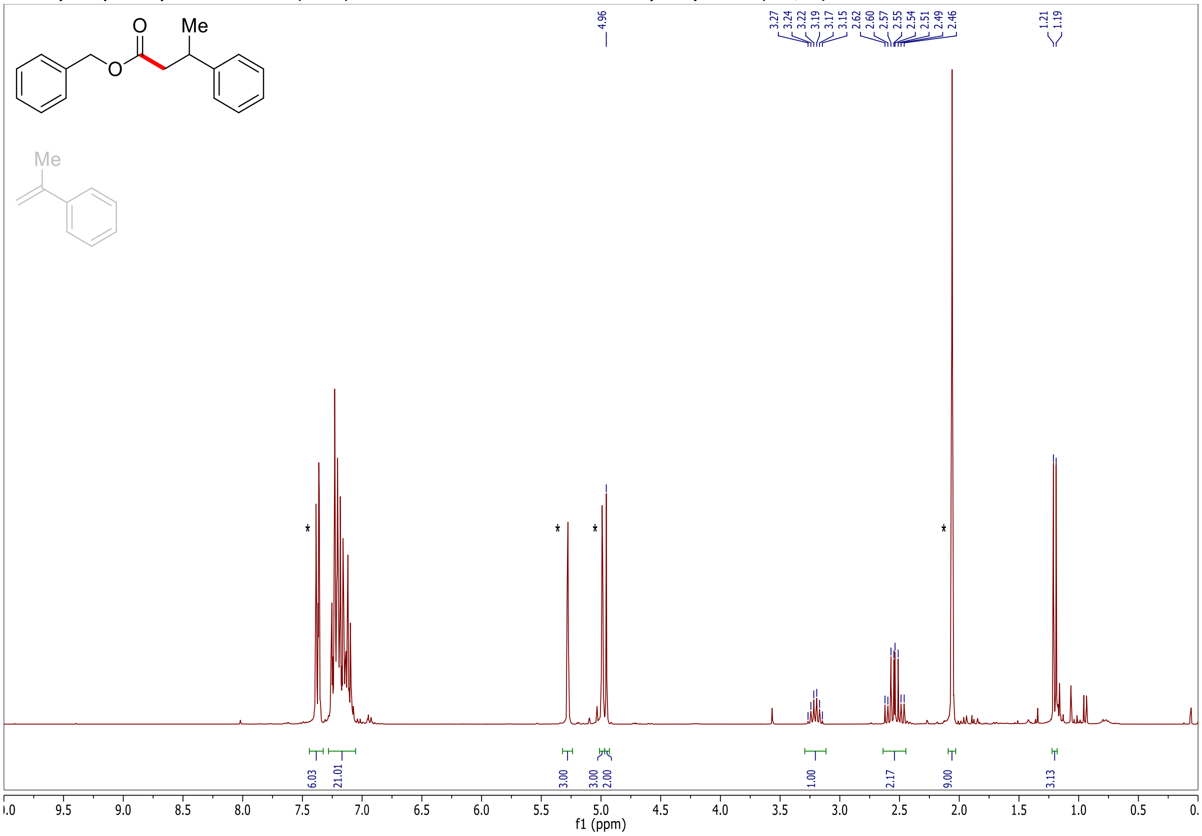


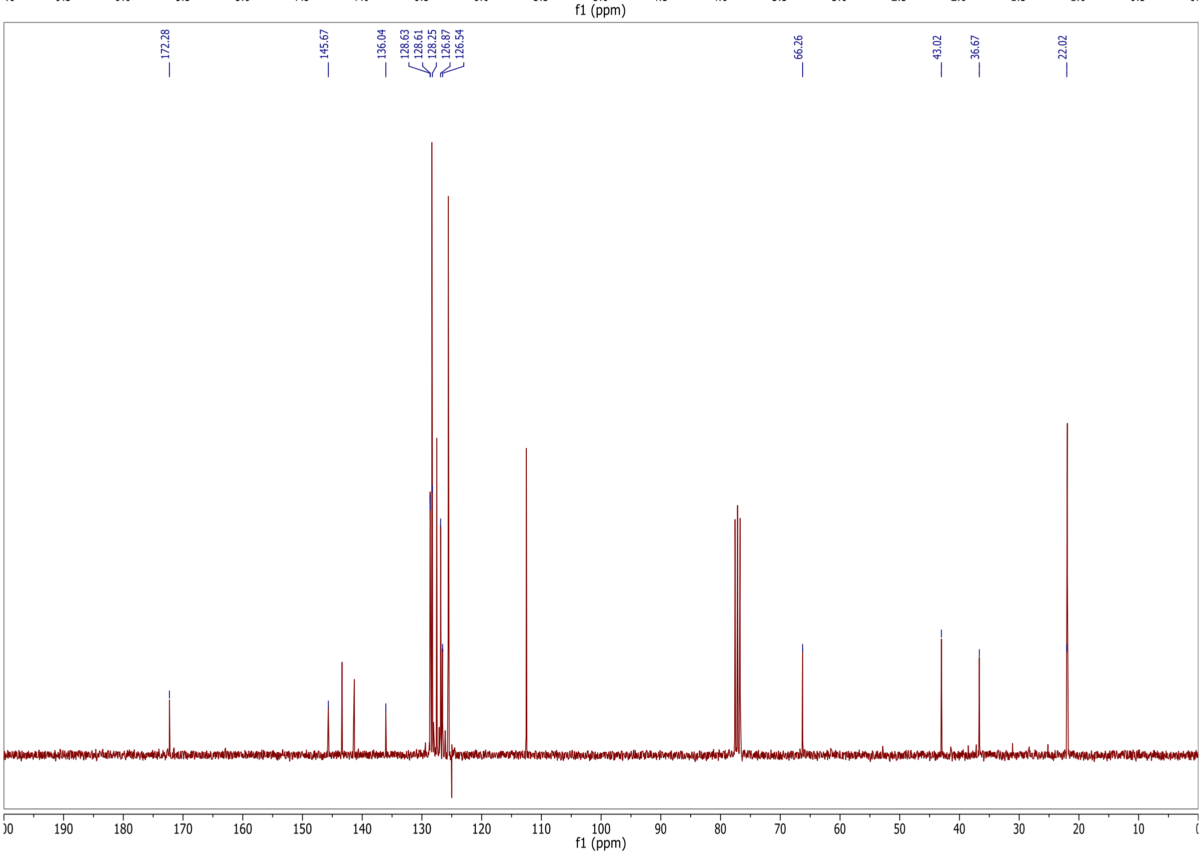
Benzyl 4-phenylbutanoate (**3ag**), benzyl 2-methyl-3-phenylpropanoate (**3’ag**) and benzyl 2-phenylbutanoate (**3’’ag**)



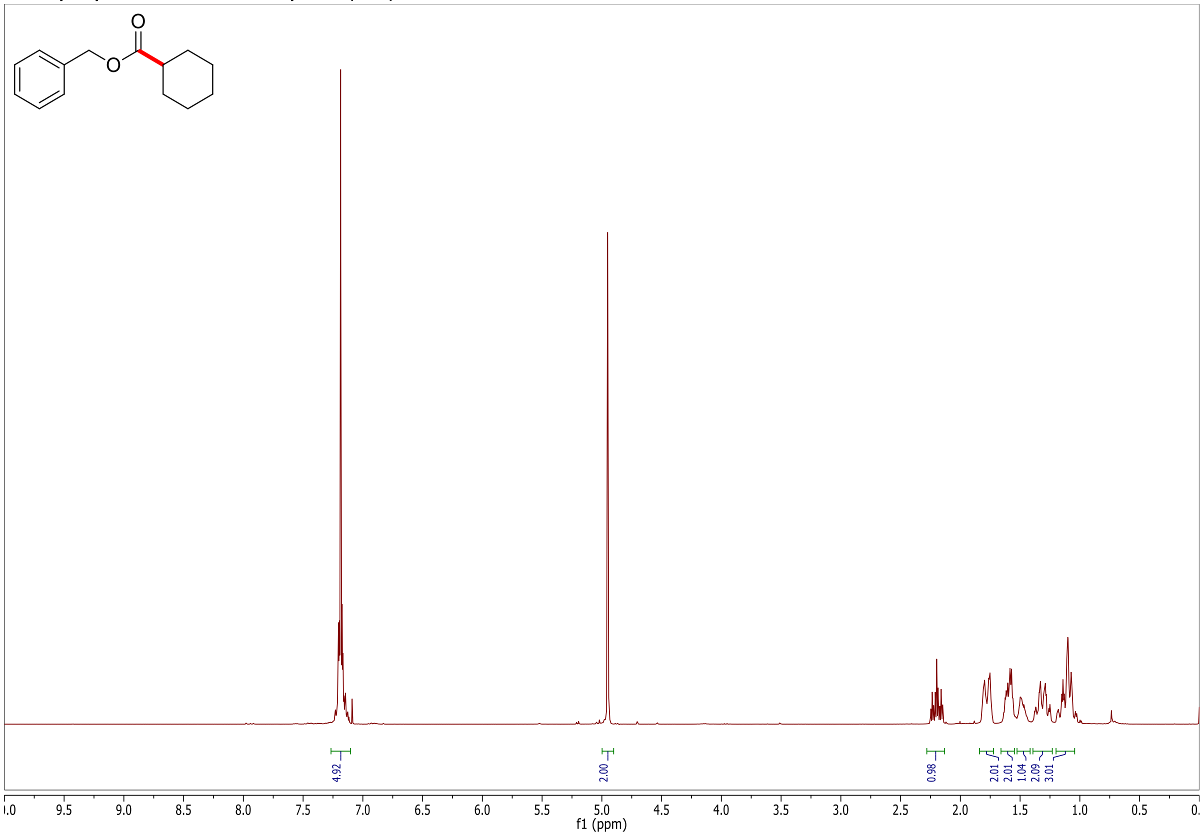


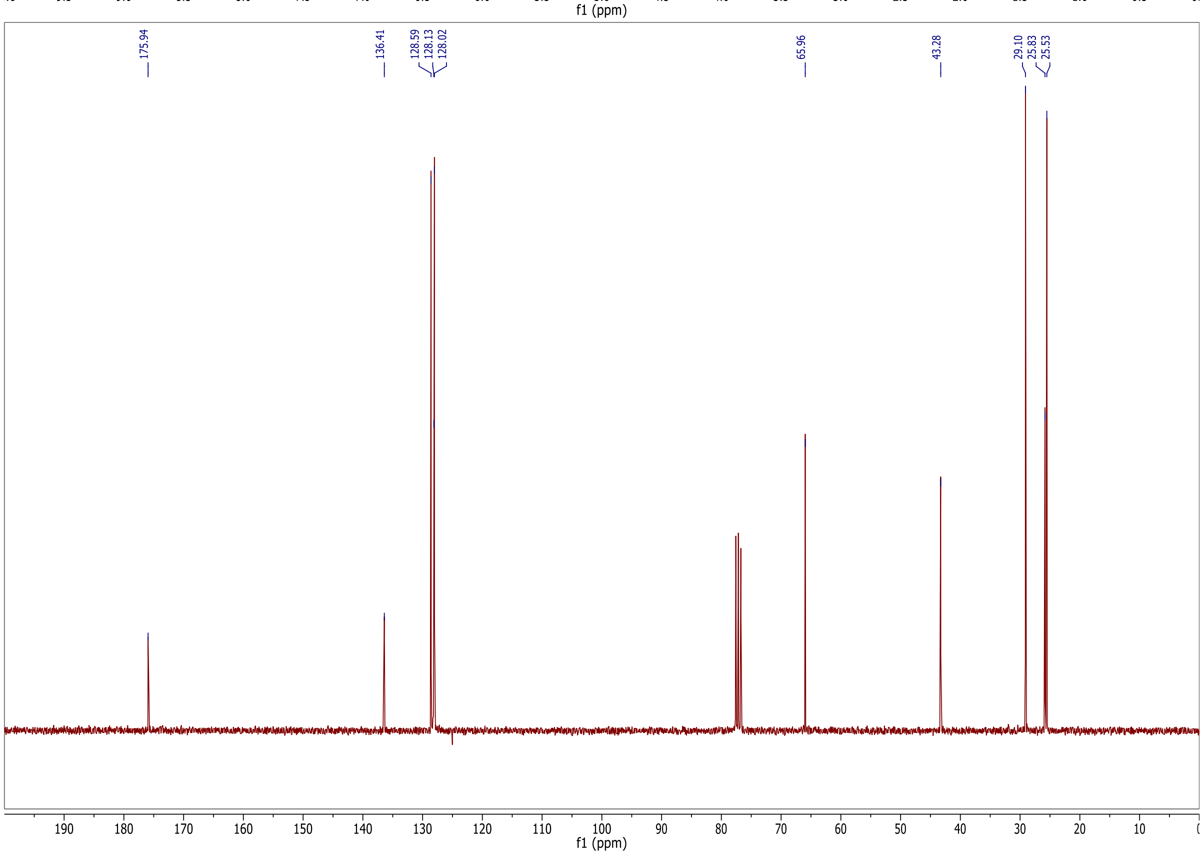
Benzyl 3-phenylbutanoate (**3ah**) in 1:3 mixture with a-methyl styrene (**2h, ***)



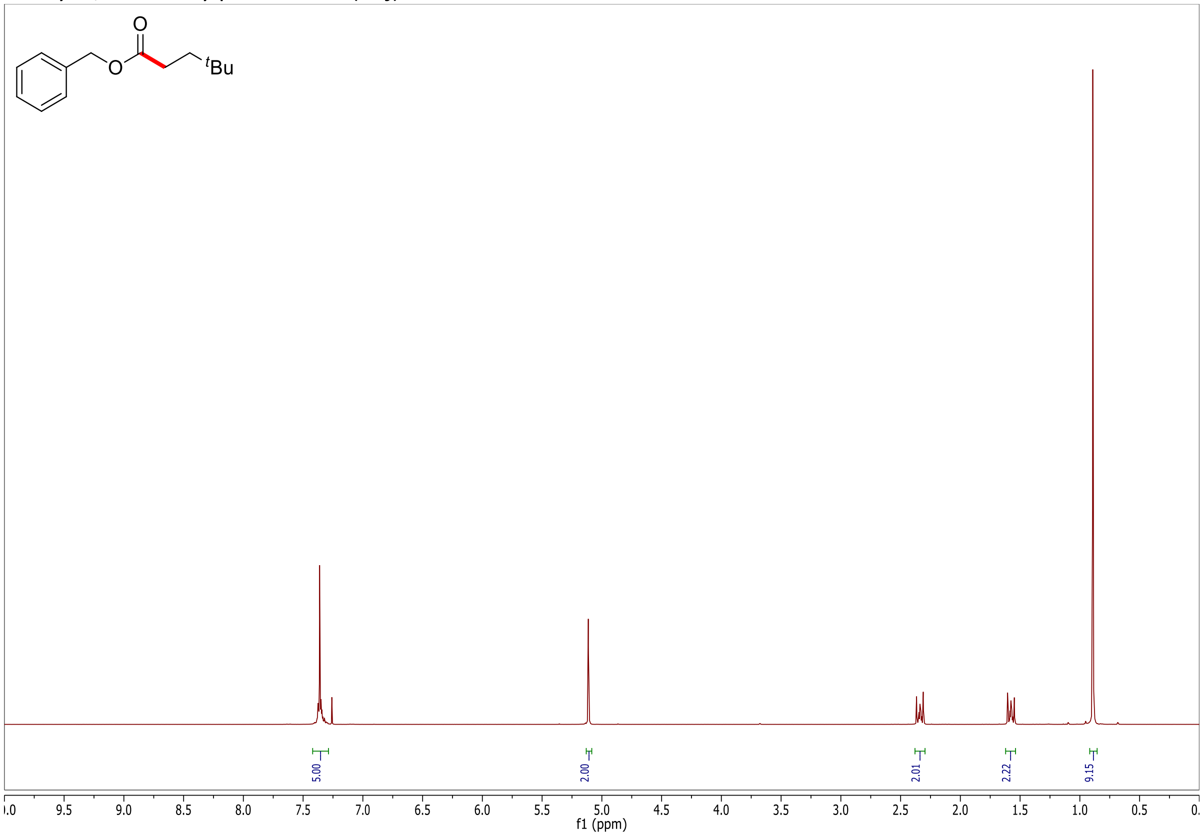


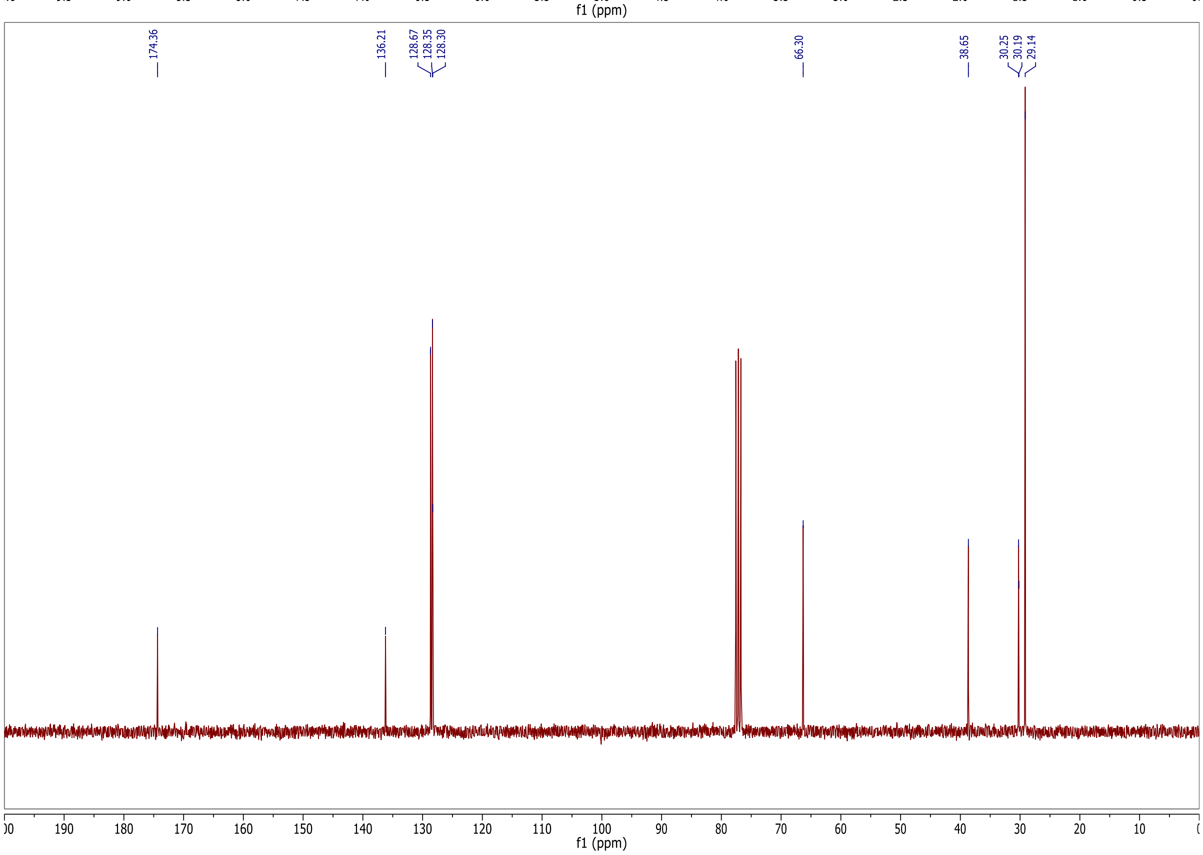
Benzyl cyclohexanecarboxylate (**3ai**)



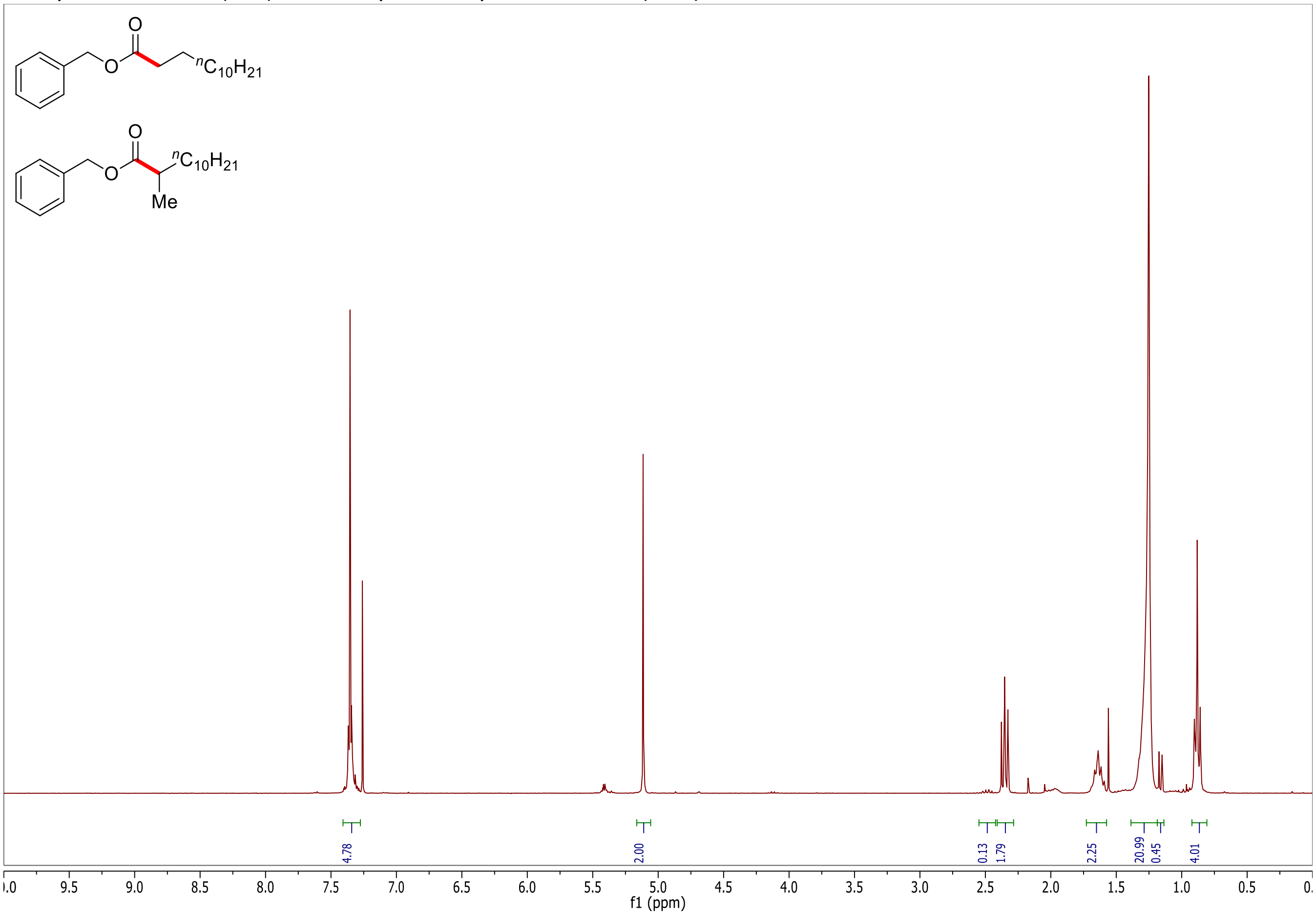


Benzyl 4,4-dimethylpentanoate (**3aj**)

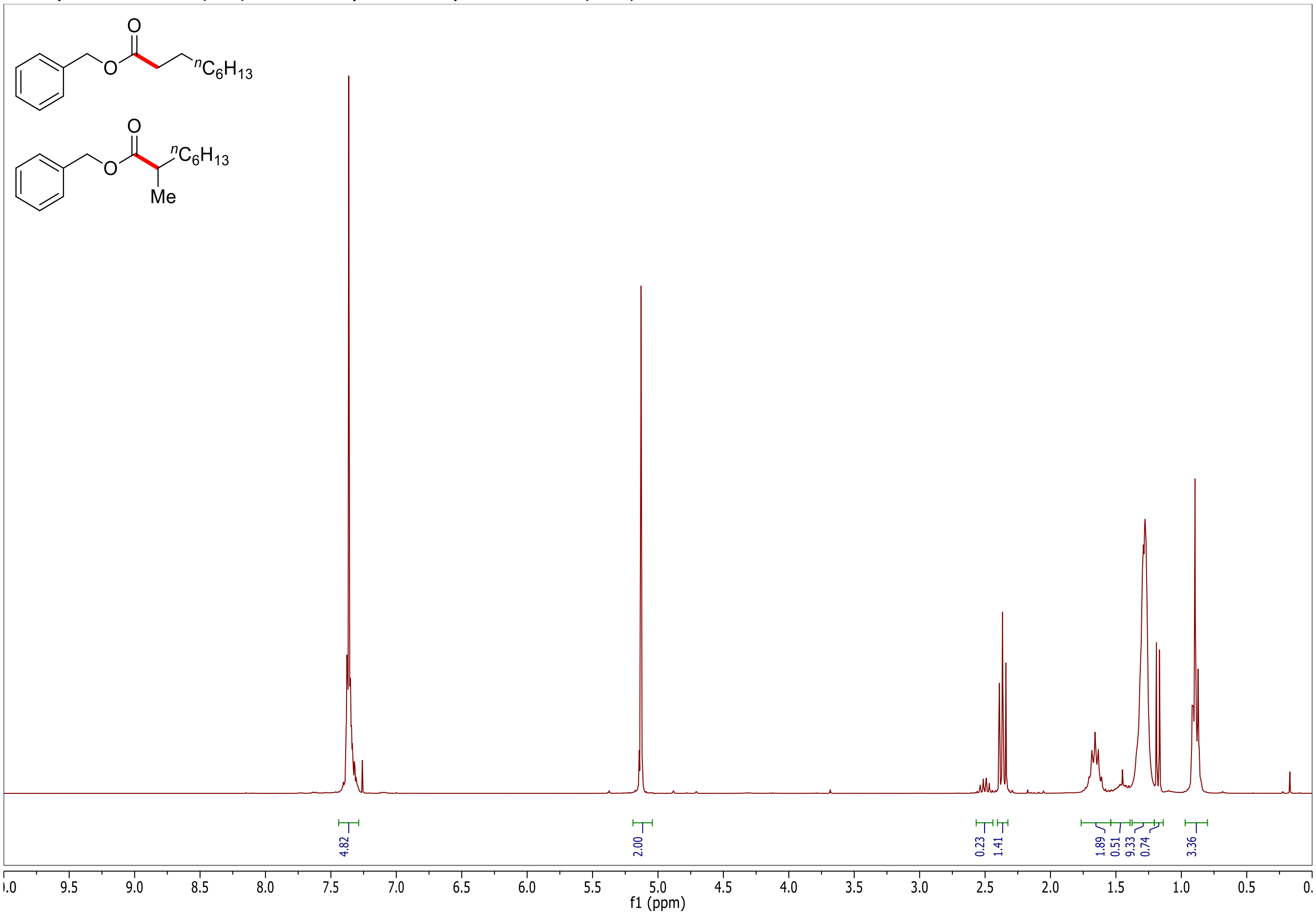




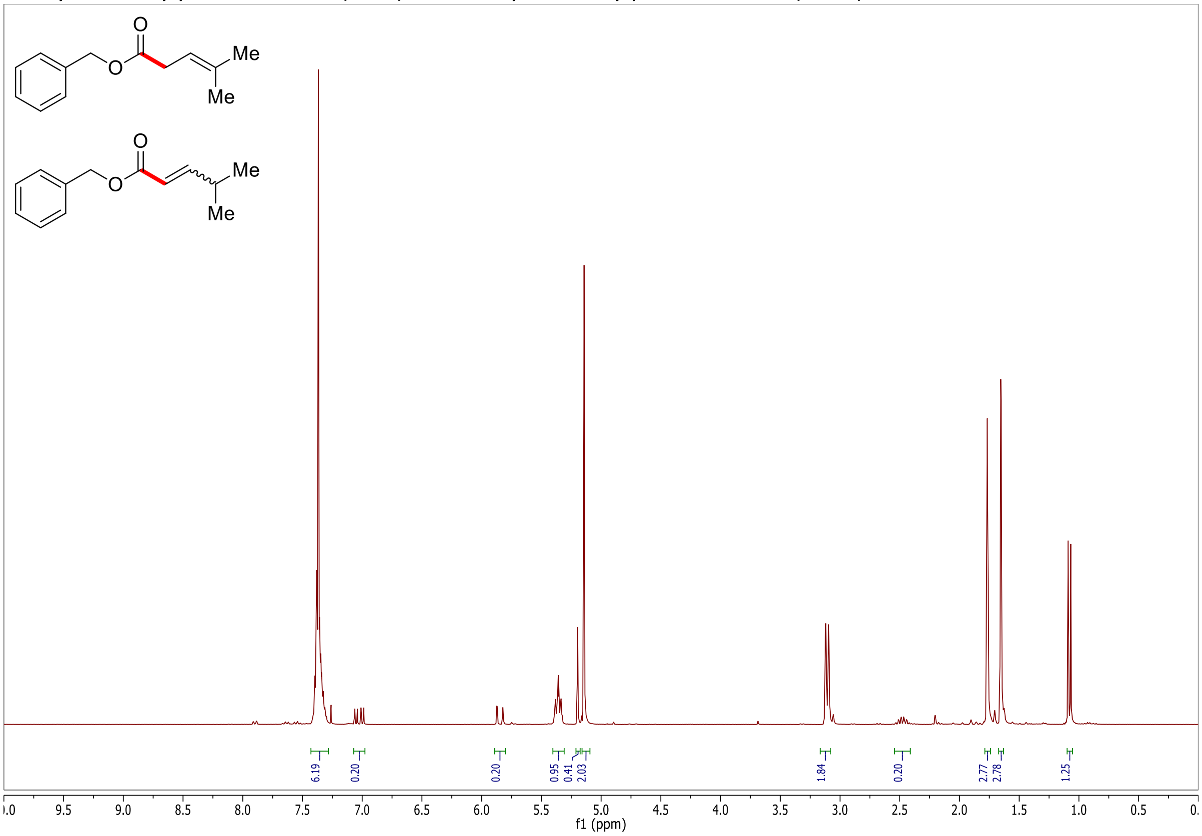
Benzyl tridecanoate (**3ak**) and benzyl 2-methyldodecanoate (**3’ak**)

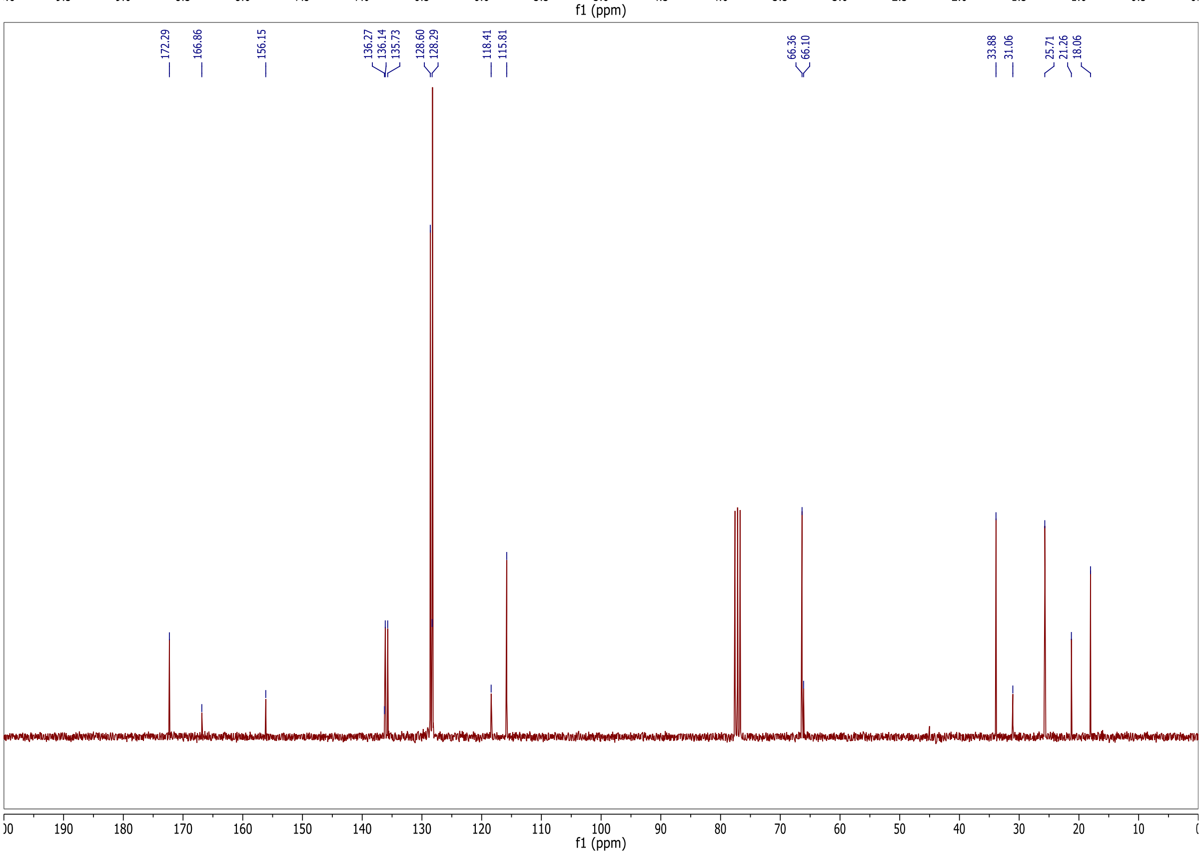


Benzyl nonanoate (**3al**) and benzyl 2-methyloctanoate (**3'al**)

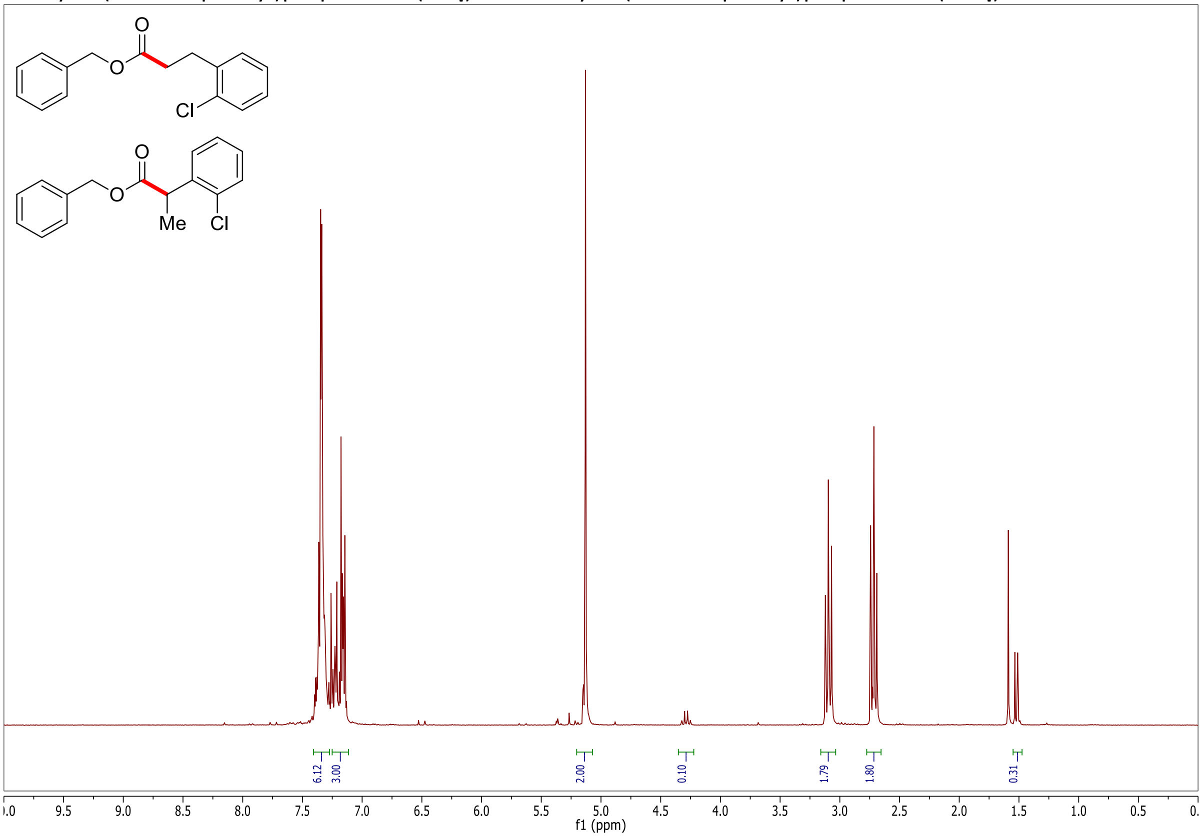


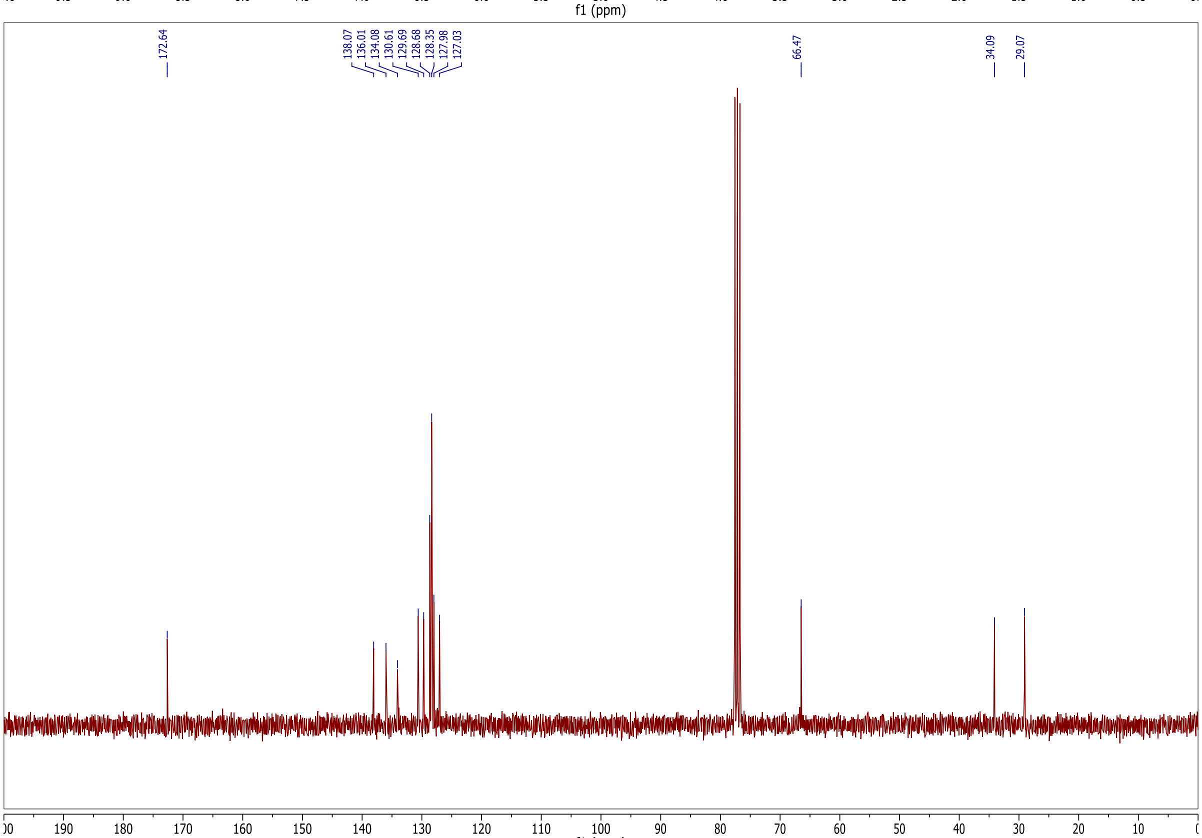
Benzyl 4-methylpent-3-enoate (**3am**) and benzyl 4-methylpent-2-enoate (**3'am**)





Benzyl 3-(2-chlorophenyl)propanoate (**3aq**) and benzyl 2-(2-chlorophenyl)propanoate (**3'aq**)





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